

ADVANCING ORGANIC ELECTRONICS WITH NAPHTHODITHIOPHENE-
BASED MATERIALS

by

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To my mother and father

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To God be all the glory.

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PREFACE

The research presented in this dissertation centers on the design, synthesis, and characterization of functional organic small molecules for applications in organic electronics. Since the first demonstration of an organic electronic device in the 1980s, these materials have evolved from conceptual innovations to integral components of modern optoelectronic technologies. The work herein contributes to advancing the understanding of structure–property relationships that govern molecular performance in such systems. This dissertation focuses on the chemical modification of two isomeric bent naphthodithiophenes (α - and β -NDTs) as versatile scaffolds for the development of photoactive materials. Through the incorporation of electron-donating and electron-withdrawing substituents, the utilization of intramolecular N $\cdots$ S interaction via placement of imine functionalities near fused thiophene moieties, and asymmetric functionalization of NDTs bearing electron deficient aryl ends with imine nucleophiles, these studies demonstrate approaches to tune electronic structures, enhance molecular rigidity, and promote internal charge-transfer characteristics. The outcome ultimately influencing photophysical properties and function. Overall, this dissertation expands the synthetic and conceptual framework for functionalizing heteroarene-based fluorophores and chromophores, and provides new insights into the design of efficient, stable, and tunable materials relevant to the broader fields of organic, inorganic, and materials chemistry.

ABSTRACT

ADVANCING ORGANIC ELECTRONICS WITH NAPHTHODITHIOPHENE-BASED MATERIALS

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Bent naphthodithiophenes (NDTs) represent an emerging class of π -extended heteroaromatic frameworks that exhibit tunable electronic properties, structural rigidity, and photostability, making them promising scaffolds for organic electronic materials. This dissertation investigates the synthesis, structural behavior, and photophysical properties of isomeric bent NDTs and their small molecule derivatives. Chapter one explores the history and development of organic electronic materials to contextualize the design and application of NDT-based chromophores. In chapter two, the photophysical properties of isomeric α - and β -NDT end-capped push-pull fluorophores is evaluated to determine the influence of remote substituents. The **$\alpha(\text{OHex})\text{R}_2$** series was found to exhibit efficient conjugation between aryl end-caps and the NDT core, whereas the **$\beta(\text{Oi-Pent})\text{R}_2$** series showed limited communication unless strong electron-withdrawing substituents are introduced. Chapter three introduces imine-functionalized symmetric α -NDT derivatives with push-pull systems, developed to probe existence intramolecular N $\cdots$ S interactions, poised to enforce rigidity and enhanced photophysical properties. Spectroscopic, crystallographic, and computational analyses

reveal that these interactions stabilize the chromophores while electron-withdrawing groups enhance photophysical responses. In chapter four, asymmetric α -NDT monoimines are synthesized to generate V-shaped donor- π -acceptor systems with enhanced intramolecular charge transfer mechanism (ICT) exhibiting narrow optical bandgaps (2.68–2.72 eV) with broad absorbance and emission spectra. In chapter five, β -NDT diimines with push-pull systems that exhibit shallow conformational landscapes and weak photoluminescence due to torsional flexibility are synthesized. Finally, chapter six summarizes the structure-property relationships identified and outlines future directions for developing NDT-based architectures with improved rigidity and extended conjugation for organic electronic applications.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	iv
PREFACE	v
ABSTRACT	vi
LIST OF TABLES	xxii
LIST OF FIGURES	xxvii
LIST OF ABBREVIATIONS	lviii
CHAPTER ONE: INTRODUCTION TO ORGANIC ELECTRONICS	1
1.0 A historical perspective	1
1.1 Classes of organic materials	3
1.1.1 Small molecules	3
1.1.1.1 Acenes	3
1.1.1.2 Donor-acceptor systems	4
1.1.1.3 Phthalocyanines and porphyrins	5
1.1.2 Conjugated polymers	6
1.1.2.1 Poly(p-phenylene vinylene) (PPV)	7
1.1.2.2 Polythiophenes	8
1.1.2.3 Donor-acceptor copolymers	9
1.1.2.4 Polyaniline and polypyrrole	10
1.1.3 Oligomers	11
1.1.4 Dendrimers	11

TABLE OF CONTENTS-Continued

1.1.5 Hybrid and emerging systems	12
1.2 Conclusion	13
1.3 Kinney laboratory's research with isomeric bent naphthodithiophenes as organic small molecules (α - and β -NDTs)	14
1.4 Dissertation aims	16
1.5 References	17
CHAPTER TWO: BENT NAPHTHODITHIOPHENES: SYNTHESIS AND CHARACTERISATION OF ISOMERIC FLUOROPHORES	32
2.0 Summary	32
2.1 Introduction	33
2.2. Results and discussion	35
2.2.1 Synthesis and structural analysis of $\alpha(\text{OR}')\text{R}_2$ series	35
2.2.2 Photophysical properties of $\alpha(\text{OHex})\text{R}_2$ series	42
2.2.3 Synthesis and structural analysis of $\beta(\text{Oi-Pent})\text{R}_2$ series	44
2.2.4 Photophysical properties of $\beta(\text{Oi-Pent})\text{R}_2$ series	48
2.3 Conclusion	51
2.4 References	52
CHAPTER THREE: INTRAMOLECULAR STABILIZATION OF NAPHTHO[2,1- <i>B</i> :3,4 <i>B'</i>]DITHIOPHENES: SYNTHESIS AND ANALYSIS OF IMINE-BASED CHROMOPHORES	61
3.0 Summary	61

TABLE OF CONTENTS-Continued

3.1 Introduction	62
3.2 Results and discussion	65
3.2.1 Synthesis of $\alpha(\text{CHO})_2$ and $\alpha(\mathbf{1})_2$ series	65
3.2.2 Crystallographic analysis of $\alpha(\mathbf{1})_2$ series	67
3.2.3 Solution state analysis of $\alpha(\mathbf{1})_2$ series	69
3.2.4 Photophysical properties of $\alpha(\mathbf{1})_2$ series	73
3.3 Conclusion	75
3.4 References	76
CHAPTER FOUR: ASYMMETRIC NAPHTHO[2,1- <i>B</i> :3,4- <i>B'</i>]DITHIOPHENES AS π -BRIDGES IN INTRAMOLECULAR PUSH-PULL CHROMOPHORES	86
4.0 Summary	86
4.1 Introduction	87
4.2 Results and discussion	90
4.2.1 Synthesis of $\alpha(\text{PhCF}_3)(\mathbf{1})$ series	90
4.2.2 Solution-state analysis of $\alpha(\text{PhCF}_3)(\mathbf{1})$ series	91
4.2.3 Photophysical properties of $\alpha(\text{PhCF}_3)(\mathbf{1})$ series	94
4.3 Conclusion	96
4.4 References	97

TABLE OF CONTENTS-Continued	
CHAPTER FIVE: BENT NAPHTHO[1,2- <i>B</i> :4,3- <i>B'</i>]DITHIOPHENE	105
CHROMOPHORES: DEPENDANCE OF INTRAMOLECULAR N···S	
STRENGTH ON REMOTE SUBSTITUENTS	
5.0 Summary	105
5.1 Introduction	106
5.2 Results and discussion	108
5.2.1 Synthesis and structural analysis of β(1)₂ series	108
5.2.2 Photophysical properties β(1)₂ series	114
5.3 Conclusion	116
5.4 References	117
CHAPTER SIX: GENERAL CONCLUSIONS AND FUTURE	124
RESEARCH DIRECTIONS	
6.0 General conclusions	124
6.1 Future research directions	125
6.2 Final remarks	127
SUPPLEMENTARY DATA	129
CHAPTER TWO: BENT NAPHTHODITHIOPHENES: SYNTHESIS	130
AND CHARACTERISATION OF ISOMERIC FLUOROPHORES	
2.0 Experimental procedures	130

2.1 Synthesis of a(OHex)R₂ series	131
2.1.1 1,2-dibromo-4,5-dihexyloxybenzene, 1(OHex)	131
2.1.2 1,2-di(3-thienyl)-4,5-dihexyloxybenzene, 2(OHex)	132
2.1.3 5,6-bis(hexyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, a(OHex)	132
2.1.4 2,9-dibromo-5,6-bis(hexyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, a(OHex)Br₂	133
2.1.5 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, a(OHex)Ph₂	133
2.1.6 5,6-bis(hexyloxy)-2,9-di- <i>p</i> -tolynaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, a(OHex)Tol₂	134
2.1.7 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, a(OHex)(PhOMe)₂	135
2.1.8 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, a(OHex)(PhCF₃)₂	136
2.2 Synthesis of a(OMe)R₂ series	136
2.2.1 1,2-dibromo-4,5-dimethoxybenzene, 1(OMe)	136
2.2.2 1,2-di(3-thienyl)-4,5-dimethoxybenzene, 2(OMe)	137
2.2.3 5,6-bis(methoxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, a(OMe)	137
2.2.4 2,9-dibromo-5,6-bis(methoxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, a(OMe)Br₂	138

TABLE OF CONTENTS-Continued

2.2.5 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\text{OMe})\text{Ph}_2$	138
2.2.6 5,6-bis(methoxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\text{OMe})\text{Tol}_2$	139
2.2.7 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\text{OMe})(\text{PhOMe})_2$	140
2.2.8 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\text{OMe})(\text{PhCF}_3)_2$	141
2.3 Synthesis of $\beta(\text{Oi-Pent})\text{R}_2$ series	141
2.3.1 1,2-dibromo-4,5-di-isopentyloxybenzene, $1(\text{Oi-Pent})$	141
2.3.2 1,2-di(2-thienyl)-4,5-di-isopentyloxybenzene, $3(\text{Oi-Pent})$	142
2.3.3 1,2-di(2-(5-bromothieryl)-4,5-di-isopentyloxybenzene, $4(\text{Oi-Pent})$	143
2.3.4 2,5-dibromo-8,9-bis(isopentyloxy)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, $\beta(\text{Oi-Pent})\text{Br}_2$	143
2.3.5 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, $\beta(\text{Oi-Pent})\text{Ph}_2$	144
2.3.6 8,9-bis(isopentyloxy)-2,5-di- <i>p</i> -tolyl naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, $\beta(\text{Oi-Pent})\text{Tol}_2$	145

TABLE OF CONTENTS-Continued

2.3.7 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(<i>Oi</i>-Pent)(PhOMe)₂	146
2.3.8 8,9-bis(isopentyloxy)-2,5-di(4- trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(<i>Oi</i>- Pent)(PhCF₃)₂	146
2.4 NMR spectra	148
2.5 Photophysical properties of α(OHex)R₂ and β(<i>Oi</i>-Pent)R₂	200
2.6 Solution-state analysis	204
2.6.1 Concentration dependent ¹ H NMR analysis	204
2.6.2 Aggregation analysis, α(OHex)Ph₂	205
2.6.3 Aggregation analysis, α(OHex)(PhOMe)₂	206
2.6.4 Aggregation analysis, β(<i>Oi</i>-Pent)Tol₂	207
2.6.5 Aggregation analysis, β(<i>Oi</i>-Pent)(PhOMe)₂	208
2.6.6 Comparison of remote chemical shifts in ¹ H and ¹³ C	209
2.7 Computational analysis	212
2.7.1 <i>α(OMe)R₂</i> ' series models	214
2.7.2 <i>β(OMe)R₂</i> ' series models	215
2.7.3 Experimental vs calculated chemical shift analysis	215
2.7.4 Nucleus independent chemical shift (NICS)-XY scans	220
2.8 Crystallographic analysis	221
2.8.1 α(OMe)Ph₂	221

TABLE OF CONTENTS-Continued

2.8.2 $\alpha(\text{OMe})\text{Tol}_2$	223
2.8.3 $\alpha(\text{OMe})(\text{PhOMe})_2$	225
2.8.4 $\alpha(\text{OMe})(\text{PhCF}_3)_2$	227
2.8.5 $\beta(\text{Oi-Pent})\text{Tol}_2$	228
2.9 References	231
CHAPTER THREE: INTRAMOLECULAR STABILIZATION OF NAPHTHO[2,1- <i>B</i> :3,4- <i>B'</i>]DITHIOPHENES: SYNTHESIS AND ANALYSIS OF IMINE-BASED CHROMOPHORES	240
3.0 Experimental procedures	233
3.1 Synthesis of precursors and $\alpha(\text{CHO})_2$	234
3.1.1 1,2-dibromo-4,5-di-isopentyloxybenzene, 2	234
3.1.2 1,2-di(3-thienyl)-4,5-di-isopentyloxybenzene, 3	235
3.1.3 5,6-bis(isopentyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, α	236
3.1.4 5,6-bis(isopentyloxy)-2,9-di-(formyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\text{CHO})_2$	237
3.2 Synthesis of $\alpha(\textbf{1})_2$ series	237
3.2.1 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl) naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\textbf{1a})_2$	237
3.2.2 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(4- methylphenyl)methaniminyl) naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\textbf{1b})_2$	238

TABLE OF CONTENTS-Continued

3.2.3 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(4-methoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(1c)_2$	239
3.2.4 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(4-trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(1d)_2$	240
3.2.5 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(4-trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(1bb)_2$	242
3.2.6 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(4-trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(1cc)_2$	243
3.2.7 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(4-trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(1dd)_2$	244
3.3 Yield summation, $\alpha(1)_2$ series	245
3.4 NMR spectra	246
3.4.1 Precursors and $\alpha(CHO)_2$	246
3.4.2 $\alpha(1)_2$ series	250
3.4.3 Comparison of remote ^{13}C chemical shifts	278
3.5 Gel Permeation chromatography (GPC) traces for $\alpha(1)_2$ series	279

TABLE OF CONTENTS-Continued

3.6 Photophysical properties $\alpha(1)$ ₂ series	281
3.6.1 <i>p</i> -Aryl series: $\alpha(1a)$ ₂ vs $\alpha(1b-d)$ ₂	282
3.6.2 <i>m</i> -Aryl Series: $\alpha(1a)$ ₂ vs $\alpha(1bb-dd)$ ₂	282
3.7 Computational analysis	283
3.7.1 Experimental vs calculated chemical shift analysis	287
3.8 Crystallographic analysis	290
3.8.1 $\alpha(1b)$ ₂	291
3.8.2 $\alpha(1c)$ ₂	293
3.8.3 $\alpha(1d)$ ₂	295
3.8.4 $\alpha(1cc)$ ₂	297
3.8.5 Attempted crystallization of $\alpha(1a)$ ₂ : partial hydrolysis to $\alpha(1a)(CHO)$	299
3.9 References	300
CHAPTER FOUR: ASYMMETRIC NAPHTHO[2,1- <i>B</i> :3,4- <i>B'</i>]DITHIOPHENES AS π -BRIDGES IN INTRAMOLECULAR PUSH- PULL CHROMOPHORES	303
4.0 Experimental procedures	303
4.1 Synthesis of precursors and $\alpha(PhCF_3)(1)$ series	304
4.1.1 Synthesis of precursors $\alpha(CHO)$, $\alpha(Br)(CHO)$, and $\alpha(PhCF_3)(CHO)$	304

TABLE OF CONTENTS-Continued

4.1.1.1 5,6-bis(isopentyloxy)-2-formylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(CHO)	304
4.1.1.2 5,6-bis(isopentyloxy)-9-bromo-2-formylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(CHO)Br	305
4.1.1.3 5,6-bis(isopentyloxy)-9-(4-trifluoromethylphenyl)-2-formylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(PhCF₃)(CHO)	306
4.1.2 α(PhCF₃)(1) series	307
4.1.2.1 5,6-bis(isopentyloxy)-2-(<i>N</i> -(phenyl)methaniminyl)-9-(trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene (1a)	307
4.1.2.2 5,6-bis(isopentyloxy)-2-(<i>N</i> -(4-methylphenyl)methaniminyl)-9-(trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene (1b)	307
4.1.2.3 5,6-bis(isopentyloxy)-2-(<i>N</i> -(4-methoxyphenyl)methaniminyl)-9-(trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene (1c)	308

TABLE OF CONTENTS-Continued

4.1.2.4 5,6-bis(isopentyloxy)-2-(<i>N</i> -(4-(<i>N,N</i> -dimethylaminophenyl)methaniminyl)-9-(trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>])dithiophene (1d)	309
4.2 NMR Spectra	310
4.2.1 Precursors and α(PhCF₃)(CHO)	310
4.2.2 α(PhCF₃)(1) series	313
4.3 Photophysical properties α(PhCF₃)(1) series	329
4.4 Computational analysis of <i>α(PhCF₃)(1)</i>	330
4.4.1 Experimental vs calculated chemical shift analysis	333
4.6 References	335
CHAPTER FIVE: BENT NAPHTHO[1,2- <i>B</i> :4,3- <i>B'</i>]DITHIOPHENE	336
CHROMOPHORES: DEPENDANCE OF INTRAMOLECULAR N···S	
STRENGTH ON REMOTE SUBSTITUENTS	
5.0 Experimental procedures	336
5.1 Synthesis of β(CHO)₂ and β(1)₂ series	337
5.1.1 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(formyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(CHO)₂	337
5.1.2 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(1a)₂	338

TABLE OF CONTENTS-Continued

5.1.3 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(<i>N</i> -(4-methylphenyl)methaniminyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(1b)₂	339
5.1.4 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(<i>N</i> -(4-methoxyphenyl)methaniminyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(1c)₂	339
5.1.5 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(<i>N</i> -(4-trifluoromethylphenyl)methaniminyl) naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(1d)₂	340
5.1.6 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(<i>N</i> -(4-(<i>N,N</i> -dimethylaminophenyl)methaniminyl) naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(1e)₂	341
5.1.7 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethylphenyl)methaniminyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(1bb)₂	342
5.1.8 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethoxyphenyl)methaniminyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(1cc)₂	343
5.1.9 5,6- <i>bis</i> (isopentyloxy)-2,9-di-(<i>N</i> -(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(1dd)₂	344

TABLE OF CONTENTS-Continued

5.2 Yield summation of $\beta(1)_2$ series	344
5.3 NMR spectra	345
5.3.1 5,6-bis(isopentyloxy)-2,9-di-(formyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, $\beta(\text{CHO})_2$	345
5.3.2 $\beta(1a)_2$ series	347
5.4 Photophysical Properties $\beta(1)_2$ Series	379
5.4.1 <i>p</i> -Aryl Series: $\beta(1a)_2$, $\beta(1c)_2$, and $\beta(1e)_2$	380
5.4.2 $\beta(1a)_2$, $\beta(1b)_2$, and $\beta(1d)_2$	381
5.4.3 <i>m</i> -Aryl Series: $\beta(1a)_2$ vs $\beta(1bb-dd)_2$	381
5.5 Computational Analysis	382
5.5.1 Experimental vs calculated chemical shift analysis	388
5.6 References	393

LIST OF TABLES

Table 1.0	^a UV-visible and emission spectra for α(OHex)R_2 series measured as solutions in dry, degassed THF under inert atmosphere. ^b $E_{g,opt}$ estimated from the tangent of the absorption onset, ($\lambda_{abs,onset}$ = 365 nm)	44
Table 2.0	^a UV-visible and emission spectra for β(Oi-Pent)R_2 series measured as solutions in dry, degassed THF under inert atmosphere. ^b $E_{g,opt}$ estimated from the tangent of the absorption onset, ($\lambda_{abs,onset}$ = 365 nm)	49
Table 3.0	^a UV-visible and emission spectra for β(Oi-Pent)(PhCF₃)₂ series measured as solutions in dry, degassed THF under inert atmosphere. ^b $E_{g,opt}$ estimated from the tangent of the absorption onset, ($\lambda_{abs,onset}$ = 365 nm). ^c Weighed by mole fraction of 1 : 1 solvent mixture	51
Table 4.0	Photophysical metrics of α(1)₂ series: ^a UV-visible and emission spectra were measured as solutions in dry, degassed toluene under inert atmosphere. ^b Highest intensity peak above 315 nm. ^c $E_{g,opt}$ estimated using onset. ^d λ_{ex} = 365 nm	74
Table 5.0	Photophysical metrics of α(PhCF₃)(1) series: ^a UV-visible and emission spectra were measured as solutions in dry, degassed toluene under inert atmosphere. ^b Highest intensity peak above 315 nm. ^c $E_{g,opt}$ estimated using onset. ^d λ_{ex} = 365 nm.	96
Table 6.0	Photophysical metrics of β(1)₂ series. ^a UV-visible and emission spectra were measured as solutions in dry, degassed toluene under inert atmosphere. ^b Highest intensity peak above 315 nm. ^c $E_{g,opt}$ estimated using onset. ^d λ_{ex} = 365 nm.	115
Table A1	¹ H chemical shifts for α(OHex)Ph₂ (50–1 mM, CDCl ₃ , 400 MHz, 298K) used in aggregation analysis.	206
Table A2	¹ H chemical shifts for α(OHex)(PhOMe)₂ (50–1 mM, CDCl ₃ , 400 MHz, 298K) used in aggregation analysis.	207
Table A3	¹ H chemical shifts for β(Oi-Pent)Tol₂ (50–1 mM, CDCl ₃ , 400 MHz, 298K) used in aggregation analysis.	208

LIST OF TABLES

Table A4	¹ H chemical shifts for β(O<i>i</i>-Pent)(PhOMe)₂ (50–1 mM, CDCl ₃ , 400 MHz, 298K) used in aggregation analysis.	209
Table A5	2b resonances and hammett parameters for α(OH<i>ex</i>)R₂ Series	210
Table A6	2b resonances and hammett parameters for α(OMe)R₂ series	211
Table A7	2b resonances and Hammett parameters for β(O<i>i</i>-Pent)R₂ Series	212
Table A8	Computational data for optimized <i>α(OMe)R₂</i> ' models. ZPC = zero-point correction, IF = number of imaginary frequencies	214
Table A9	Computational data for optimized <i>β(OMe)R₂</i> ' models. ZPC = zero-point correction, IF = number of imaginary frequencies	215
Table A10	Crystallographic data and structural refinement parameters, α(OMe)Ph₂	223
Table A11	Crystallographic data and structural refinement parameters, α(OMe)Tol₂	225
Table A12	Crystallographic data and structural refinement parameters, α(OMe)(PhOMe)₂	226
Table A13	Crystallographic data and structural refinement parameters, α(OMe)(PhCF₃)₂	228
Table A14	Crystallographic data and structural refinement parameters, β(O<i>i</i>-Pent)Tol₂	230
Table B1	Summary of isolated yields for the α(1)₂ series employing conditions <i>i</i> , <i>ii</i> , or <i>iii</i> .	245
Table B2	Computational data for optimized <i>α(1<i>a</i>)₂</i> models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2	284

LIST OF TABLES

Table B3	Computational data for optimized $\alpha(1b)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.	284
Table B4	Computational data for optimized $\alpha(1c)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.	285
Table B5	Computational data for optimized $\alpha(1d)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.	285
Table B6	Computational data for optimized $\alpha(1bb)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.	286
Table B7	Computational data for optimized $\alpha(1cc)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.	286
Table B8	Computational data for optimized $\alpha(1dd)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.	287
Table B9	Crystallographic data and structural refinement parameters, $\alpha(1b)_2$	293
Table B10	Crystallographic data and structural refinement parameters, $\alpha(1c)_2$	295
Table B11	Crystallographic data and structural refinement parameters, $\alpha(1d)_2$	297
Table B12	Crystallographic data and structural refinement parameters, $\alpha(1cc)_2$	298

LIST OF TABLES

Table B13	Crystallographic data and structural refinement parameters, $\alpha(1a)(CHO)$	300
Table C1	Computational data for optimized $a(PhCF_3)(1a)$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies.	331
Table C2	Computational data for optimized $a(PhCF_3)(1b)$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies.	331
Table C3	Computational data for optimized $a(PhCF_3)(1c)$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies.	332
Table C4	Computational data for optimized $a(PhCF_3)(1bb)$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies.	333
Table D1	Summary of isolated yields for the $\beta(1)_2$ Series	344
Table D2	Computational data for optimized $\beta(1a)_2$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies. ^d Per number of N $\cdots$ S–C interaction in conformer.	383
Table D3	Computational data for optimized $\beta(1b)_2$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies. ^d Per number of N $\cdots$ S–C interaction in conformer.	383
Table D4	Computational data for optimized $\beta(1c)_2$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies. ^d Per number of N $\cdots$ S–C interaction in conformer.	384

LIST OF TABLES–Continued

Table D5	Computational data for optimized $\beta(1d)_2$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies. ^d Per number of N···S–C interaction in conformer	385
Table D6	Computational data for optimized $\beta(1e)_2$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies. ^d Per number of N···S–C interaction in conformer.	385
Table D7	Computational data for optimized $\beta(1bb)_2$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies. ^d Per number of N···S–C interaction in conformer.	386
Table D8	Computational data for optimized $\beta(1cc)_2$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies. ^d Per number of N···S–C interaction in conformer.	387
Table D9	Computational data for optimized $\beta(1dd)_2$ models. ^a ZPC = zero-point correction, ^b Rel. Energy = relative energetic difference between conformers and conformer-1, ^c IF = number of imaginary frequencies. ^d Per number of N···S–C interaction in conformer.	388

LIST OF FIGURES

Figure 1.1	Structures of example acenes	4
Figure 1.2	Structure of perylene diimide derivative <i>N,N</i> dimethyl-3,4,9,10-Perylenetetracarboxylic diimide (DiMe-PTCDI).	5
Figure 1.3	Structure of copper phthalocyanine	6
Figure 1.4	Poly(<i>p</i> -phenylene vinylene) repeating unit	7
Figure 1.5	Poly(3-hexylthiophene) (P3HT) repeating unit	8
Figure 1.6	Chemical structure of diketopyrrolopyrrole (DPP)	9
Figure 1.7	Chemical structure of polyaniline and polypyrrole	10
Figure 1.8	Structure of α -quaterthiophene	11
Figure 1.9.0	Generation G4 dendrimer with 64 amino groups at the periphery	12
Figure 1.9.1	Polymer-fullerene blends PC _{61/71} BM	13
Figure 1.9.2	a) Generic BDT and NDT cores studied by bauerle; b) representative α - and β -dithienophenazines investigated by hoger; c) bent α - and β -Naphthodithiophene (NDT) building blocks utilized in the kinney laboratory	15
Figure 2.1	Classes of naphthodithiophenes. (a) Isomeric linear and angular naphthodithiophenes. (b) This work: isomeric bent naphthodithiophenes.	33
Figure 2.2	Synthesis of $\alpha(\text{OR}')\text{R}_2$ series. (i) 3-thiophene boronic acid, Pd(PPh ₃) ₂ Cl ₂ , 2 M K ₂ CO ₃ , THF, 80 °C, overnight; (ii) FeCl ₃ , MeNO ₂ , DCM, 0 °C to RT, 1 h; (iii) NBS, CHCl ₃ , RT, 2 d; (iv) R boronic acid, Pd(PPh ₃) ₂ Cl ₂ , 2 M K ₂ CO ₃ , THF, 80 °C, overnight. (Inset): Isolated yields for $\alpha(\text{OHex})\text{R}_2$ and $\alpha(\text{OMe})\text{R}_2$ series.	36
Figure 2.3	Partial ¹ H NMR spectra for the $\alpha(\text{OHex})\text{R}_2$ series with assignment of aromatic resonances (400 MHz, CDCl ₃).	38

LIST OF FIGURES–Continued

Figure 2.4	Computational analysis of $\alpha(\text{Me})\text{R}_2'$ series. (a) Ball-and-stick representations of model compounds $\alpha(\text{OMe})\text{R}_2'$ and their respective experimental vs. calculated NMR plots (^1H is shown in orange, ^{13}C is given in black). (b) Partial NICS _{1.7πZZ} scans for $\alpha(\text{OMe})\text{R}_2'$ with D–B–A path highlighted in orange. (Inset): Enhanced view of the central B ring.	41
Figure 2.5	Photophysical measurements for $\alpha(\text{OHex})\text{R}_2$ series. (a) UV-visible spectra; (b) emission spectra ($\lambda_{\text{ex}} = 365$ nm). All samples were prepared under an inert atmosphere with degassed dry THF.	43
Figure 2.6	Synthesis of $\beta(\text{Oi-Pent})\text{R}_2$ series. (i) 2-Thiophene boronic acid, Pd(PPh ₃) ₂ Cl ₂ , 2 M K ₂ CO ₃ , THF, 80 °C, overnight; (ii) NBS, CHCl ₃ , RT, 2 d; (iii) DDQ, MeSO ₃ H, DCM, 0 °C to RT, 1 h; (iv) R boronic acid, Pd(PPh ₃) ₂ Cl ₂ , 2 M K ₂ CO ₃ , THF, 80 °C, overnight. Inset: isolated yields for $\beta(\text{Oi-Pent})\text{R}_2$ series.	46
Figure 2.7	Partial ^1H NMR spectra for the $\beta(\text{Oi-Pent})\text{R}_2$ series with assignment of aromatic resonances (400 MHz, CDCl ₃).	47
Figure 2.8	Photophysical measurements for $\beta(\text{Oi-Pent})\text{R}_2$ series. (a) UV-visible spectra; (b) emission spectra ($\lambda_{\text{ex}} = 365$ nm). All samples were prepared under inert atmosphere with degassed dry THF.	49
Figure 2.9	Fluorosolvatochromism observed for $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$.	51
Figure 3.1	a) Luminescent α NDTs with phenylene-based end-caps; b) Work from You and co-workers investigating intramolecular chalcogen bonding; c) This work: intramolecular N $\cdots$ S interactions stabilizing α NDT chromophores.	64
Figure 3.2	Top: general depiction of the two <i>E</i> -imine conformations available to α NDTs. Bottom: amines used in this chapter	65
Figure 3.3	Synthesis of $\alpha(\text{1})_2$ series. Conditions: (i) TFA, CHCl ₃ , 4 Å mol. sieves; (ii) Sc(OTf) ₃ , MeCN, CHCl ₃ , 4 Å mol. sieves; (iii) toluene, AcOH, Δ .	66

LIST OF FIGURES–Continued

Figure 3.4	ORTEP diagrams (ellipsoids drawn at 50% probability) of $\alpha(1b)_2$, $\alpha(1c)_2$, $\alpha(1d)_2$, and $\alpha(1cc)_2$. Average select distances (Å): $\alpha(1b)_2$ N $\cdots$ S, 3.00; $\alpha(1c)_2$ N $\cdots$ S, 2.98; $\alpha(1d)_2$ N $\cdots$ S, 2.94; $\alpha(1cc)_2$ N $\cdots$ S, 3.05. Average select bond angles (°): $\alpha(1b)_2$ N–C–C–S, 0.6; $\alpha(1c)_2$ N–C–C–S, -2.5; $\alpha(1d)_2$ N–C–C–S, 4.9; $\alpha(1cc)_2$ N–C–C–S, 1.2. Additional details given in supplementary data section.	68
Figure 3.5	Partial ^1H NMR spectra of the $\alpha(1)_2$ series (400 MHz, CDCl_3). Gold highlighted i resonance covers $\Delta\delta < 0.1$ ppm, grey highlighted 2b resonance covers $\Delta\delta < 0.2$ ppm. Inset: Correlation of ^{13}C imine resonance and Hammett parameter of remote substituent ($R^2 \sim 0.96$).	70
Figure 3.6	Computational analysis of <i>a(1a-d)</i> ₂ series. Top: general representations of two available <i>E</i> conformations. Bottom: Experimental vs calculated ^1H NMR plots reveal strong correlations for conformer-1 (blue) and poor fits for conformer-2 (orange). Gold and grey shaded regions represent the imine (i) and interior thienyl proton (2b). Computational method: PCM(CHCl_3)/ ω B97-XD/cc-pVDZ.	72
Figure 4.1	a)Luminescent phenylene-based end-capped α -NDTs by Adusei and Co-workers. b)Push-pull aryl-substituted diimine α -NDTs rigidified via intramolecular N $\cdots$ S interactions. c) This work: asymmetric functionalized to dynamic imine-based V-shaped α -NDT end-caps	89
Figure 4.2	Synthesis of $\alpha(\text{PhCF}_3)(1)$ Series. (i) deacidified CHCl_3 , , 4Å, aniline or <i>p</i> -substituted anilines, $\text{Sc}(\text{OTf})_3$, MeCN, >16 hrs.	91
Figure 4.3	Partial ^1H NMR spectra for the $\alpha(\text{PhCF}_3)(1)$ series with assignment of aromatic resonances (400 MHz, CDCl_3).	93
Figure 4.4	UV-visible and emission spectra ($\lambda_{\text{ex}} = 365$ nm) of $\alpha(\text{PhCF}_3)(1)$ series. All samples were prepared under inert atmosphere with degassed dry Toluene	96

LIST OF FIGURES–Continued

Figure 5.1	a ⁱ) Oussaid and co-workers work on correlated thiophene–imine orientation with conformational stability in simple 2-iminomethylthiophenes. a ⁱⁱ) <i>E</i> -conformer preferred aryl-substituted diimine α -NDTs rigidified via intramolecular N $\cdots$ S interactions. b) This work: β - naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene (β -NDT) diimines bearing electronically varied aniline end caps	108
Figure 5.2	Partial ¹ H NMR spectra of the β -NDT di-imine series in with the corresponding synthetic scheme presented above. Three derivatives β(1d)₂ , β(1cc)₂ and β(1dd)₂ with electron withdrawing groups display additional minor imine resonances (highlighted), indicative of low-population conformers arising from alternative imine orientations or backbone distortions in solution. All spectra were acquired in CDCl ₃ at ambient temperature at 400 MHz	111
Figure 6.1	Examples of acceptor cyano and di-methoxy groups (a) tunable donor carbazole (b) for future NDT-based donor–acceptor architectures	126
Figure 6.2	Proposed NDT-based macrocycle and metallomacrocycle architectures formed through imine condensation and metal coordination	127
Figure A1	¹ H NMR spectrum of 5,6-bis(hexyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(OHex) (CDCl ₃ , 400 MHz, 298 K)	148
Figure A2	¹³ C{ ¹ H} NMR spectrum of 5,6-bis(hexyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(OHex) (CDCl ₃ , 101 MHz, 298 K)	149
Figure A3	¹ H NMR spectrum of 2,9-dibromo-5,6-bis(hexyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(OHex)Br₂ (CDCl ₃ , 400 MHz, 298 K).	149
Figure A4	¹³ C{ ¹ H} NMR spectrum of 2,9-dibromo-5,6-bis(hexyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(OHex)Br₂ (CDCl ₃ , 101 MHz, 298 K).	150
Figure A5	¹ H NMR spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(OHex)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	150

LIST OF FIGURES—Continued

Figure A6	^1H - ^1H COSY spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	151
Figure A7	^1H - ^{13}C HSQC spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	151
Figure A8	^1H - ^{13}C HMBC spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	152
Figure A9	^1H - ^1H NOESY spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	152
Figure A10	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Ph₂ (CDCl ₃ , 101 MHz, 298 K)	153
Figure A11	5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Ph₂ with assignment of ^1H and ^{13}C resonances	154
Figure A12	^1H NMR spectrum of 5,6-bis(hexyloxy)-2,9-di- <i>p</i> -tolynaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	155
Figure A13	^1H - ^1H COSY spectrum of 5,6-bis(hexyloxy)-2,9-di- <i>p</i> -tolynaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	155
Figure A14	^1H - ^{13}C HSQC spectrum of 5,6-bis(hexyloxy)-2,9-di- <i>p</i> -tolynaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Tol₂ (CDCl ₃ , 400 MHz, 298 K).	156
Figure A15	^1H - ^{13}C HMBC spectrum of 5,6-bis(hexyloxy)-2,9-di- <i>p</i> -tolynaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	156
Figure A16	^1H - ^1H NOESY spectrum of 5,6-bis(hexyloxy)-2,9-di- <i>p</i> -tolynaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	157

LIST OF FIGURES—Continued

Figure A17	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(hexyloxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Tol₂ (CDCl ₃ , 101 MHz, 298 K)	157
Figure A18	5,6-bis(hexyloxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)Tol₂ with assignment of ^1H and ^{13}C resonances	158
Figure A19	^1H NMR spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhOMe)₂ (CDCl ₃ , 400 MHz, 298 K)	159
Figure A20	^1H - ^1H COSY spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhOMe)₂ (CDCl ₃ , 400 MHz, 298 K)	159
Figure A21	^1H - ^{13}C HSQC spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhOMe)₂ (CDCl ₃ , 400 MHz, 298 K)	160
Figure A22	^1H - ^{13}C HMBC spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhOMe)₂ (CDCl ₃ , 400 MHz, 298 K)	160
Figure A23	^1H - ^1H NOESY spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhOMe)₂ (CDCl ₃ , 400 MHz, 298 K)	161
Figure A24	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhOMe)₂ (CDCl ₃ , 101 MHz, 298 K)	161
Figure A25	a(OHex)(PhOMe)₂ with assignment of ^1H and ^{13}C resonances	162
Figure A26	^1H NMR spectrum of 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhCF₃)₂ (CDCl ₃ , 400 MHz, 298 K)	163
Figure A27	^1H - ^{13}C HSQC spectrum of 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhCF₃)₂ (CDCl ₃ , 400 MHz, 298 K)	163

LIST OF FIGURES—Continued

Figure A28	^1H - ^1H NOESY spectrum of 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhCF₃)₂ (CDCl ₃ , 400 MHz, 298 K)	164
Figure A29	5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OHex)(PhCF₃)₂ with assignment of ^1H and ^{13}C resonances. ^{13}C resonances extracted from HSQC	165
Figure A30	^1H NMR spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	166
Figure A31	^1H - ^1H COSY spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	166
Figure A32	^1H - ^{13}C HSQC spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	167
Figure A33	^1H - ^{13}C HMBC spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	167
Figure A34	^1H - ^1H NOESY spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	168
Figure A35	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Ph₂ (CDCl ₃ , 101 MHz, 298 K)	168
Figure A36	5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Ph₂ with assignment of ^1H and ^{13}C resonances.	169
Figure A37	^1H NMR spectrum of 5,6-bis(methoxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	170
Figure A38	^1H - ^1H COSY spectrum of 5,6-bis(methoxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	170

LIST OF FIGURES—Continued

Figure A39	^1H - ^{13}C HSQC spectrum of 5,6-bis(methoxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Tol₂ (CDCl_3 , 400 MHz, 298 K)	171
Figure A40	^1H - ^{13}C HMBC spectrum of 5,6-bis(methoxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Tol₂ (CDCl_3 , 400 MHz, 298 K)	171
Figure A41	^1H - ^1H NOESY spectrum of 5,6-bis(methoxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Tol₂ (CDCl_3 , 400 MHz, 298 K)	172
Figure A42	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(methoxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Tol₂ (CDCl_3 , 101 MHz, 298 K)	172
Figure A43	5,6-bis(methoxy)-2,9-di- <i>p</i> -tolyl naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)Tol₂ with assignment of ^1H and ^{13}C resonances	173
Figure A44	^1H NMR spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)(PhOMe)₂ (CDCl_3 , 400 MHz, 298 K)	174
Figure A45	^1H - ^1H COSY spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)(PhOMe)₂ (CDCl_3 , 400 MHz, 298 K)	174
Figure A46	^1H - ^{13}C HSQC spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)(PhOMe)₂ (CDCl_3 , 400 MHz, 298 K)	175
Figure A47	^1H - ^{13}C HMBC spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)(PhOMe)₂ (CDCl_3 , 400 MHz, 298 K).	175
Figure A48	^1H - ^1H NOESY spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)(PhOMe)₂ (CDCl_3 , 400 MHz, 298 K)	176
Figure A49	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene a(OMe)(PhOMe)₂ (CDCl_3 , 101 MHz, 298 K)	176

LIST OF FIGURES—Continued

Figure A50	$\alpha(\text{OMe})(\text{PhOMe})_2$ with assignment of ^1H and ^{13}C resonances	177
Figure A51	^1H NMR spectrum of 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\text{OMe})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K)	178
Figure A52	^1H - ^1H COSY spectrum of 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\text{OMe})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K)	178
Figure A53	^1H - ^{13}C HSQC spectrum of 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\text{OMe})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K)	179
Figure A54	5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\text{OMe})(\text{PhCF}_3)_2$ with assignment of ^1H and ^{13}C resonances. ^{13}C resonances extracted from HSQC	180
Figure A55	^1H NMR spectrum of 1,2-dibromo-4,5-di-isopentyloxybenzene 1(<i>Oi</i>-Pent) (CDCl_3 , 400 MHz, 298 K)	181
Figure A56	^1H NMR spectrum of 1,2-di(2-thienyl)-4,5-di-isopentyloxybenzene 3(<i>Oi</i>-Pent) (CDCl_3 , 400 MHz, 298 K)	181
Figure A57	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1,2-di(2-thienyl)-4,5-di-isopentyloxybenzene 3(<i>Oi</i>-Pent) (CDCl_3 , 101 MHz, 298 K)	182
Figure A58	^1H NMR spectrum of 1,2-di(2-(5-bromothieryl))-4,5-di-isopentyloxybenzene 4(<i>Oi</i>-Pent) (CDCl_3 , 400 MHz, 298 K)	182
Figure A59	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1,2-di(2-(5-bromothieryl))-4,5-di-isopentyloxybenzene 4(<i>Oi</i>-Pent) (CDCl_3 , 101 MHz, 298 K)	183
Figure A60	^1H NMR spectrum of 2,5-dibromo-8,9-bis(isopentyloxy)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{Oi-Pent})\text{Br}_2$ (CDCl_3 , 400 MHz, 298 K)	183
Figure A61	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2,5-dibromo-8,9-bis(isopentyloxy)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{Oi-Pent})\text{Br}_2$ (CDCl_3 , 101 MHz, 298 K)	184

LIST OF FIGURES—Continued

Figure A62	¹ H NMR spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene β(Oi-Pent)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	184
Figure A63	¹ H- ¹ H COSY spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene β(Oi-Pent)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	185
Figure A64	¹ H- ¹³ C HSQC spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene β(Oi-Pent)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	185
Figure A65	¹ H- ¹³ C HMBC spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene β(Oi-Pent)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	186
Figure A66	¹ H- ¹ H NOESY spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene β(Oi-Pent)Ph₂ (CDCl ₃ , 400 MHz, 298 K)	186
Figure A67	¹³ C{ ¹ H} NMR spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene β(Oi-Pent)Ph₂ (CDCl ₃ , 101 MHz, 298 K)	187
Figure A68	8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene β(Oi-Pent)Ph₂ with assignment of ¹ H and ¹³ C resonances	188
Figure A69	¹ H NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di- <i>p</i> -tolyl naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(Oi-Pent)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	189
Figure A70	¹ H- ¹ H COSY spectrum of 8,9-bis(isopentyloxy)-2,5-di- <i>p</i> -tolyl naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(Oi-Pent)Tol₂ (CDCl ₃ , 400 MHz, 298 K).	189
Figure A71	¹ H- ¹³ C HSQC spectrum of 8,9-bis(isopentyloxy)-2,5-di- <i>p</i> -tolyl naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(Oi-Pent)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	190
Figure A72	¹ H- ¹³ C HMBC spectrum of 8,9-bis(isopentyloxy)-2,5-di- <i>p</i> -tolyl naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, β(Oi-Pent)Tol₂ (CDCl ₃ , 400 MHz, 298 K)	190

LIST OF FIGURES—Continued

Figure A73	^1H - ^1H NOESY spectrum of 8,9-bis(isopentyloxy)-2,5-di- <i>p</i> -tolyl naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, $\beta(\text{O}i\text{-Pent})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K)	191
Figure A74	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di- <i>p</i> -tolyl naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, $\beta(\text{O}i\text{-Pent})\text{Tol}_2$ (CDCl_3 , 101 MHz, 298 K)	191
Figure A75	8,9-bis(isopentyloxy)-2,5-di- <i>p</i> -tolyl naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene, $\beta(\text{O}i\text{-Pent})\text{Tol}_2$ with assignment of ^1H and ^{13}C resonances	192
Figure A76	^1H NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ (CDCl_3 , 400 MHz, 298 K)	193
Figure A77	^1H - ^1H COSY spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ (CDCl_3 , 400 MHz, 298 K)	193
Figure A78	^1H - ^{13}C HSQC spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ (CDCl_3 , 400 MHz, 298 K)	194
Figure A79	^1H - ^{13}C HMBC spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ (CDCl_3 , 400 MHz, 298 K)	194
Figure A80	^1H - ^1H NOESY spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ (CDCl_3 , 400 MHz, 298 K)	195
Figure A81	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ (CDCl_3 , 101 MHz, 298 K)	195
Figure A82	8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ with assignment of ^1H and ^{13}C resonances	196
Figure A83	^1H NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K)	197

LIST OF FIGURES—Continued

Figure A84	^1H - ^1H COSY spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K)	197
Figure A85	^1H - ^{13}C HSQC spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K)	198
Figure A86	^1H - ^{13}C HMBC spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K)	198
Figure A87	^1H - ^1H NOESY spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K)	199
Figure A88	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 101 MHz, 298 K)	199
Figure A89	8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2- <i>b</i> :4,3- <i>b'</i>]dithiophene $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ with assignment of ^1H and ^{13}C resonances	200
Figure A90	Absorbance and emission spectra for $\alpha(\text{OHex})\text{Ph}_2$ and $\beta(\text{O}i\text{-Pent})\text{Ph}_2$ in THF	201
Figure A91	Absorbance and emission spectra for $\alpha(\text{OHex})\text{Tol}_2$ and $\beta(\text{O}i\text{-Pent})\text{Tol}_2$ in THF	202
Figure A92	Absorbance and emission spectra for $\alpha(\text{OHex})(\text{PhOMe})_2$ and $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ in THF	202
Figure A93	Absorbance and emission spectra for $\alpha(\text{OHex})(\text{PhCF}_3)_2$ and $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ in THF	203
Figure A94	Normalised absorbance and emission spectra for $\alpha(\text{OHex})\text{R}_2$ Series in THF	203
Figure A95	Normalised absorbance and emission spectra for $\beta(\text{O}i\text{-Pent})\text{R}_2$ Series in THF	203

LIST OF FIGURES—Continued

Figure A96	Solvatochromism Analysis. Absorbance and emission spectra for $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ in: THF, toluene, DCM, and THF·MeCN (1:1)	204
Figure A97	Plot of absorbance and emission normalized maxima λ vs $E_T(30)$ parameter for $\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$ in THF, toluene, DCM, and THF·MeCN (1:1)	204
Figure A98	Partial ^1H NMR spectra of $\alpha(\text{OHex})\text{Ph}_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K), $K_d = 3.2 \times 10^{-4} \pm 1.6 \times 10^{-4}$ M	205
Figure A99	Partial ^1H NMR spectra of $\alpha(\text{OHex})(\text{PhOMe})_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K), $K_d = 1.2 \pm 0.6$ M	206
Figure A100	Partial ^1H NMR spectra of $\beta(\text{O}i\text{-Pent})\text{Tol}_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K), $K_d = 1.1 \pm 0.6$ M	207
Figure A101	Partial ^1H NMR spectra of $\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K), $K_d = 1.5 \pm 0.8$ M	208
Figure A102	Plot of $\alpha(\text{OHex})\text{R}_2$ ^1H δ (ppm) vs σ	209
Figure A103	Plot of $\alpha(\text{OHex})\text{R}_2$ ^{13}C δ (ppm) vs σ	210
Figure A104	Plot of $\alpha(\text{OMe})\text{R}_2$ ^1H δ (ppm) vs σ	210
Figure A105	Plot of $\alpha(\text{OMe})\text{R}_2$ ^{13}C δ (ppm) vs σ	211
Figure A106	Plot of $\beta(\text{O}i\text{-Pent})\text{R}_2$ ^1H δ (ppm) vs σ	211
Figure A107	Plot of $\beta(\text{O}i\text{-Pent})\text{R}_2$ ^{13}C δ (ppm) vs σ	212
Figure A108	Optimized geometries of <i>a(OMe)R₂'</i> Series	214
Figure A109	Optimized geometries of <i>$\beta(\text{OMe})\text{R}_2'$</i> Series	215
Figure A110	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})\text{Ph}_2$ (experimental) and <i>a(OMe)Ph₂'</i> (calculated)	216
Figure A111	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})\text{Tol}_2$ (experimental) and <i>a(OMe)Tol₂'</i> (calculated)	216

LIST OF FIGURES–Continued

Figure A112	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})(\text{PhOMe})_2$ (experimental) and $\alpha(\text{OMe})(\text{PhOMe})_2'$ (calculated)	216
Figure A113	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})(\text{PhCF}_3)_2$ (experimental) and $\alpha(\text{OMe})(\text{PhCF}_3)_2'$ (calculated)	217
Figure A114	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})\text{Ph}_2$ (experimental) and $\alpha(\text{OMe})\text{Ph}_2'$ (calculated)	217
Figure A115	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})\text{Tot}_2$ (experimental) and $\alpha(\text{OMe})\text{Tot}_2'$ (calculated)	217
Figure A116	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})(\text{PhOMe})_2$ (experimental) and $\alpha(\text{OMe})(\text{PhOMe})_2'$ (calculated)	218
Figure A117	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})(\text{PhCF}_3)_2$ (experimental) and $\alpha(\text{OMe})(\text{PhCF}_3)_2'$ (calculated)	218
Figure A118	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\beta(\text{Oi-Pent})\text{Ph}_2$ (experimental) and $\beta(\text{OMe})\text{Ph}_2'$ (calculated)	218
Figure A119	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\beta(\text{Oi-Pent})\text{Tot}_2$ (experimental) and $\beta(\text{OMe})\text{Tot}_2'$ (calculated)	219
Figure A120	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\beta(\text{Oi-Pent})(\text{PhOMe})_2$ (experimental) and $\beta(\text{OMe})(\text{PhOMe})_2'$ (calculated)	219
Figure A121	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ (experimental) and $\beta(\text{OMe})(\text{PhCF}_3)_2'$ (calculated)	219
Figure A122	NICS $_{1.7\pi\text{ZZ}}$ scans for $\alpha(\text{OMe})R_2'$ Series	220
Figure A123	NICS $_{1.7\pi\text{ZZ}}$ scans for $\beta(\text{OMe})R_2'$ Series	220

LIST OF FIGURES—Continued

Figure A124	ORTEP diagram of $\alpha(\text{OMe})\text{Ph}_2$ (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Select bond lengths (Å) and angles (°): C8–S2, 1.745(1); C5–S2, 1.720(1); C4–S1, 1.727(1); S1–C1, 1.743(1); C24–C23–C8–S2, 19.9(2); S2–C5–C4–S1, -3.4(2); S1–C1–C17–C18, -18.5(2)	222
Figure A125	ORTEP diagram of $\alpha(\text{OMe})\text{Tol}_2$ (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Select bond lengths (Å) and angles (°): C1–S1, 1.745(1); C4–S1, 1.730(1); C5–S2, 1.721(1); C8–S2, 1.748(1); C22–C17–C1–S1, -16.9(2); S1–C4–C5–S2, -0.7(2); S2–C8–C24–C29, 8.3(2)	224
Figure A126	ORTEP diagram of $\alpha(\text{OMe})(\text{PhOMe})_2$ (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Select bond lengths (Å) and angles (°): C5–S2, 1.729(1); C8–S2, 1.747(2); C4–S1, 1.733(2); C1–S1, 1.751(3); C21–C16–C8–S2, 7.7(2); S2–C5–C4–S1, -3.4(2); S1–C1–C9–C10, 1.3(2)	225
Figure A127	ORTEP diagram of $\alpha(\text{OMe})(\text{PhCF}_3)_2$ (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Select bond lengths (Å) and angles (°): C4–S1, 1.731(3); C17–S1, 1.747(3); C5–S2, 1.722(3); C8–S2, 1.742(3); S1–C4–C5–S2, 2.5(4); C22–C1–C17–S1, -6.9(4); S2–C8–C24–C29, 9.5(4)	227
Figure A128	ORTEP diagram of $\beta(\text{Oi-Pent})\text{Tol}_2$ (ellipsoids drawn at 50% probability). Crystallised as a dimer, bottom molecules given as wireframe. Average bond lengths (Å) and angles (°) of the dimers: C1–S1, 1.741; C4–S1, 1.735; C11–S2, 1.736; C14–S2, 1.743; C27–C22–C14–S2, -4.4; C16–C15–C1–S1, -8.2; S2–C8–C24–C29, 9.5(4)	229
Figure B1	Synthetic path to $\alpha(\text{CHO})_2$; details for conditions <i>i</i> , <i>ii</i> , and <i>iii</i> given below with their respective targets	234
Figure B2	^1H NMR spectrum of 1,2-di(3-thienyl)-4,5-di-isopentyloxybenzene 3 (CDCl_3 , 400 MHz, 298 K)	246
Figure B3	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1,2-di(3-thienyl)-4,5-di-isopentyloxybenzene 3 (CDCl_3 , 400 MHz, 298 K)	247
Figure B4	^1H NMR spectrum of 5,6-bis(isopentyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α (CDCl_3 , 400 MHz, 298 K)	247

LIST OF FIGURES—Continued

Figure B5	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α (CDCl_3 , 400 MHz, 298 K)	248
Figure B6	^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-diformylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\text{CHO})_2$ (CDCl_3 , 400 MHz, 298 K)	248
Figure B7	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-diformylnaphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, $\alpha(\text{CHO})_2$ (CDCl_3 , 400 MHz, 298 K)	249
Figure B8	^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	250
Figure B9	^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	251
Figure B10	^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	251
Figure B11	^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	252
Figure B12	^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	252
Figure B13	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	253
Figure B14	5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(phenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\mathbf{1a})_2$ with assignment of ^1H and ^{13}C resonances	254
Figure B15	^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -tolyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene $\alpha(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K)	255

LIST OF FIGURES—Continued

Figure B16	¹ H- ¹ H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -tolyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1b)₂ (CDCl ₃ , 400 MHz, 298 K)	255
Figure B17	¹ H- ¹³ C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -tolyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1b)₂ (CDCl ₃ , 400 MHz, 298 K)	256
Figure B18	¹ H- ¹³ C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -tolyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1b)₂ (CDCl ₃ , 400 MHz, 298 K)	256
Figure B19	¹ H- ¹ H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -tolyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1b)₂ (CDCl ₃ , 400 MHz, 298 K)	257
Figure B20	¹³ C{ ¹ H} NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -tolyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1b)₂ (CDCl ₃ , 400 MHz, 298 K)	257
Figure B21	5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -tolyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1b)₂ with assignment of ¹ H and ¹³ C resonances	258
Figure B22	¹ H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -methoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1c)₂ (CDCl ₃ , 400 MHz, 298 K)	259
Figure B23	¹ H- ¹ H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -methoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1c)₂ (CDCl ₃ , 400 MHz, 298 K)	259
Figure B24	¹ H- ¹³ C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -methoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1c)₂ (CDCl ₃ , 400 MHz, 298 K)	260
Figure B25	¹ H- ¹³ C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -methoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1c)₂ (CDCl ₃ , 400 MHz, 298 K)	260
Figure B26	¹ H- ¹ H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -methoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1c)₂ (CDCl ₃ , 400 MHz, 298 K)	261

LIST OF FIGURES–Continued

Figure B27	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -methoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1c)₂ (CDCl ₃ , 400 MHz, 298 K)	261
Figure B28	5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -methoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1c)₂ with assignment of ^1H and ^{13}C resonances	262
Figure B29	^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1d)₂ (CDCl ₃ , 400 MHz, 298 K)	263
Figure B30	^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1d)₂ (CDCl ₃ , 400 MHz, 298 K)	263
Figure B31	^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1d)₂ (CDCl ₃ , 400 MHz, 298 K)	264
Figure B32	^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1d)₂ (CDCl ₃ , 400 MHz, 298 K)	264
Figure B33	^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1d)₂ (CDCl ₃ , 400 MHz, 298 K)	265
Figure B34	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1d)₂ (CDCl ₃ , 400 MHz, 298 K)	265
Figure B35	5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(<i>p</i> -trifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1d)₂ with assignment of ^1H and ^{13}C resonances. *Additional quartet signals are weak and overlapped with more prominent signals; with reduced line broadening an additional signal at ~122.9 is visible and provides ~273 Hz coupling constant	266

LIST OF FIGURES—Continued

Figure B36	¹ H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, α(1bb)₂ (CDCl ₃ , 400 MHz, 298 K)	267
Figure B37	¹ H- ¹ H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, α(1bb)₂ (CDCl ₃ , 400 MHz, 298 K)	267
Figure B38	¹ H- ¹³ C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, α(1bb)₂ (CDCl ₃ , 400 MHz, 298 K)	268
Figure B39	¹ H- ¹³ C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, α(1bb)₂ (CDCl ₃ , 400 MHz, 298 K)	268
Figure B40	¹ H- ¹ H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, α(1bb)₂ (CDCl ₃ , 400 MHz, 298 K)	269
Figure B41	¹³ C{ ¹ H} NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, α(1bb)₂ (CDCl ₃ , 400 MHz, 298 K)	269
Figure B42	5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene, α(1bb)₂ with assignment of ¹ H and ¹³ C resonances	270
Figure B43	¹ H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1cc)₂ (CDCl ₃ , 400 MHz, 298 K)	271
Figure B44	¹ H- ¹ H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1cc)₂ (CDCl ₃ , 400 MHz, 298 K)	271
Figure B45	¹ H- ¹³ C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1cc)₂ (CDCl ₃ , 400 MHz, 298 K)	272

LIST OF FIGURES—Continued

Figure B46	^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1cc)$_2$ (CDCl_3 , 400 MHz, 298 K)	272
Figure B47	^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1cc)$_2$ (CDCl_3 , 400 MHz, 298 K)	273
Figure B48	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1cc)$_2$ (CDCl_3 , 400 MHz, 298 K)	273
Figure B49	5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1cc)$_2$ with assignment of ^1H and ^{13}C resonances. *Signals are overlapped and resolved by < 0.1 ppm	274
Figure B50	^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-difluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1dd)$_2$ (CDCl_3 , 400 MHz, 298 K)	275
Figure B51	^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-difluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1dd)$_2$ (CDCl_3 , 400 MHz, 298 K)	275
Figure B52	^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-difluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1dd)$_2$ (CDCl_3 , 400 MHz, 298 K)	276
Figure B53	^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-difluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1dd)$_2$ (CDCl_3 , 400 MHz, 298 K)	276
Figure B54	^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-difluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1dd)$_2$ (CDCl_3 , 400 MHz, 298 K)	277
Figure B55	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-difluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1dd)$_2$ (CDCl_3 , 400 MHz, 298 K)	277

LIST OF FIGURES–Continued

Figure B56	5,6-bis(isopentyloxy)-2,9-di-(<i>N</i> -(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[2,1- <i>b</i> :3,4- <i>b'</i>]dithiophene α(1dd)₂ with assignment of ¹ H and ¹³ C resonances	278
Figure B57	Left: Plot of ¹³ C resonances vs σ_p (blue, $R^2 = 0.94$) and σ_m (orange, $R^2 = 0.99$). Right: Plot of 2b ¹³ C resonances vs σ_p (blue, $R^2 = 0.99$) and σ_m (orange, $R^2 = 0.99$)	279
Figure B58	GPC traces of crude reaction mixtures for α(1a–d)₂ series. Each trace shown corresponds to the preferred condensation conditions given in section 1. Highlighted region is the peak of interest	280
Figure B59	GPC traces of crude reaction mixtures for α(1bb–dd)₂ series. Each trace shown corresponds to the preferred condensation conditions given in section 1. Highlighted region is the peak of interest	280
Figure B60	Absorbance and emission spectra for α(1a)₂ and α(1b–d)₂ in toluene	282
Figure B61	Absorbance and emission spectra for α(1a)₂ and α(1bb–dd)₂ in toluene	282
Figure B62	B62. Ball-and-stick representations for optimized conformers of α(1a)₂	283
Figure B63	Ball-and-stick representations for optimized conformers of α(1b)₂	284
Figure B64	Ball-and-stick representations for optimized conformers of α(1c)₂	284
Figure B65	Ball-and-stick representations for optimized conformers of α(1d)₂	285
Figure B66	Ball-and-stick representations for optimized conformers of α(1bb)₂	285
Figure B67	Ball-and-stick representations for optimized conformers of α(1cc)₂	286

LIST OF FIGURES—Continued

Figure B68	Ball-and-stick representations for optimized conformers of $\alpha(1dd)_2$	286
Figure B69	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for a(1a)₂ (experimental) and $a(1a)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.87$; ^{13}C $R^2 = 0.90$) and Conformer 2 is represented in orange (^1H $R^2 = 0.53$; ^{13}C $R^2 = 0.85$)	287
Figure B70	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for a(1b)₂ (experimental) and $a(1b)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.87$; ^{13}C $R^2 = 0.91$) and Conformer 2 is represented in orange (^1H $R^2 = 0.52$; ^{13}C $R^2 = 0.84$)	288
Figure B71	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for a(1c)₂ (experimental) and $a(1c)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.90$; ^{13}C $R^2 = 0.90$) and Conformer 2 is represented in orange (^1H $R^2 = 0.64$; ^{13}C $R^2 = 0.84$)	288
Figure 72	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for a(1d)₂ (experimental) and $a(1d)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.82$; ^{13}C $R^2 = 0.92$) and Conformer 2 is represented in orange (^1H $R^2 = 0.41$; ^{13}C $R^2 = 0.86$)	289
Figure B73	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for a(1bb)₂ (experimental) and $a(1bb)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.91$; ^{13}C $R^2 = 0.89$) and Conformer 2 is represented in orange (^1H $R^2 = 0.67$; ^{13}C $R^2 = 0.84$)	289
Figure B74	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for a(1cc)₂ (experimental) and $a(1cc)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.93$; ^{13}C $R^2 = 0.91$) and Conformer 2 is represented in orange (^1H $R^2 = 0.82$; ^{13}C $R^2 = 0.88$)	290

LIST OF FIGURES—Continued

Figure B75	Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for a(1dd)₂ (experimental) and <i>a(1dd)₂</i> (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.76$; ^{13}C $R^2 = 0.93$) and Conformer 2 is represented in orange (^1H $R^2 = 0.25$; ^{13}C $R^2 = 0.87$)	290
Figure B76	ORTEP diagram of a(1b)₂ (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Select bond lengths (Å), distances (Å), and angles (°): N1 $\cdots$ S1, 3.045(2); N2 $\cdots$ S2, 2.959(2); C5–S1 $\cdots$ N1, 141.69(6); C9–S2 $\cdots$ N2, 143.63(6); N1–C1–C2–S1, 1.0(2); N2–C10–C9–S2, 0.2(2)	292
Figure B77	ORTEP diagram of a(1c)₂ (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Select bond lengths (Å), distances (Å), and angles (°): N1 $\cdots$ S1, 2.967(5); N2 $\cdots$ S2, 2.991(4); C5–S1 $\cdots$ N1, 143.5(2); C6–S2 $\cdots$ N2, 142.9(2); N1–C1–C2–S1, 0.0(7); N2–C10–C9–S2, -5.1(7)	294
Figure B78	ORTEP diagram of a(1d)₂ (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Select bond lengths (Å), distances (Å), and angles (°): N1 $\cdots$ S1, 2.993(7); N2 $\cdots$ S2, 2.898(6); C5–S1 $\cdots$ N1, 142.3(2); C9–S2 $\cdots$ N2, 144.7(2); N1–C1–C2–S1, 2.4(7); N2–C10–C9–S2, 7.4(7)	296
Figure B79	ORTEP diagram of a(1cc)₂ (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Select bond lengths (Å), distances (Å), and angles (°): N1 $\cdots$ S1, 3.071(1); N2 $\cdots$ S2, 3.030(1); C5–S1 $\cdots$ N1, 140.12(4); C6–S2 $\cdots$ N2, 142.44(4); N1–C1–C2–S1, 1.2(1); N2–C10–C9–S2, 1.3(1)	297
Figure B80	ORTEP diagram of a(1a)(CHO) (ellipsoids drawn at 50% probability). Hydrogens have been omitted for clarity. Average select bond lengths (Å), distances (Å), and angles (°): S1 $\cdots$ O1, 3.028; C5–S1 $\cdots$ O1, 141.5; O1–C1–C2–S1, 0.0; S2–C9–C10–N1, 175.9	299
Figure C1	Synthetic path to a(PhCF₃)(CHO)	304
Figure C2	^1H NMR spectrum of a(CHO) (CDCl ₃ , 400 MHz, 298 K)	310

LIST OF FIGURES—Continued

Figure C3	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a(CHO) (CDCl_3 , 400 MHz, 298 K)	311
Figure C4	^1H NMR spectrum of a(Br)(CHO) (CDCl_3 , 400 MHz, 298 K)	311
Figure C5	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a(Br)(CHO) (CDCl_3 , 400 MHz, 298 K)	312
Figure C6	^1H NMR spectrum of a(PhCF₃)(CHO) (CDCl_3 , 400 MHz, 298 K)	312
Figure C7	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a(PhCF₃)(CHO) (CDCl_3 , 400 MHz, 298 K)	313
Figure C8	^1H NMR spectrum of a(PhCF₃)(1a) (CDCl_3 , 400 MHz, 298 K)	313
Figure C9	^1H - ^1H COSY spectrum of a(PhCF₃)(1a) (CDCl_3 , 400 MHz, 298 K)	314
Figure C10	^1H - ^{13}C HSQC spectrum of a(PhCF₃)(1a) (CDCl_3 , 400 MHz, 298 K)	314
Figure C11	^1H - ^{13}C HMBC spectrum of a(PhCF₃)(1a) (CDCl_3 , 400 MHz, 298 K)	315
Figure C12	^1H - ^1H NOESY spectrum of a(PhCF₃)(1a) (CDCl_3 , 400 MHz, 298 K)	315
Figure C13	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a(PhCF₃)(1a) (CDCl_3 , 400 MHz, 298 K)	316
Figure C14	a(PhCF₃)(1a) with assignment of ^1H and ^{13}C resonances	317
Figure C15	^1H NMR spectrum of a(PhCF₃)(1b) (CDCl_3 , 400 MHz, 298 K)	318
Figure C16	^1H - ^1H COSY spectrum of a(PhCF₃)(1b) (CDCl_3 , 400 MHz, 298 K)	318
Figure C17	^1H - ^{13}C HSQC spectrum of a(PhCF₃)(1b) (CDCl_3 , 400 MHz, 298 K)	319

LIST OF FIGURES–Continued

Figure C18	^1H - ^{13}C HMBC spectrum of a(PhCF₃)(1b) (CDCl ₃ , 400 MHz, 298 K)	319
Figure C19	^1H - ^1H NOESY spectrum of a(PhCF₃)(1b) (CDCl ₃ , 400 MHz, 298 K)	320
Figure C20	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a(PhCF₃)(1b) (CDCl ₃ , 400 MHz, 298 K)	320
Figure C21	a(PhCF₃)(1b) with assignment of ^1H and ^{13}C resonances. ^a Signals are weak and unassigned, ^b Signals are overlapped such that exact assignment is no feasible, ^c Resonances obtained from HMBC analysis	321
Figure C22	^1H NMR spectrum of a(PhCF₃)(1c) (CDCl ₃ , 400 MHz, 298 K)	322
Figure C23	^1H - ^1H COSY spectrum of a(PhCF₃)(1c) (CDCl ₃ , 400 MHz, 298 K)	322
Figure C24	^1H - ^{13}C HSQC spectrum of a(PhCF₃)(1c) (CDCl ₃ , 400 MHz, 298 K)	323
Figure C25	^1H - ^{13}C HMBC spectrum of a(PhCF₃)(1c) (CDCl ₃ , 400 MHz, 298 K)	323
Figure C26	^1H - ^1H NOESY spectrum of a(PhCF₃)(1c) (CDCl ₃ , 400 MHz, 298 K)	324
Figure C27	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a(PhCF₃)(1c) (CDCl ₃ , 400 MHz, 298 K)	324
Figure C28	a(PhCF₃)(1c) with assignment of ^1H and ^{13}C resonances	325
Figure C29	^1H NMR spectrum of a(PhCF₃)(1bb) (CDCl ₃ , 400 MHz, 298 K)	326
Figure C30	^1H - ^1H COSY spectrum of a(PhCF₃)(1bb) (CDCl ₃ , 400 MHz, 298 K)	326
Figure C31	^1H - ^{13}C HSQC spectrum of a(PhCF₃)(1bb) (CDCl ₃ , 400 MHz, 298 K)	327

LIST OF FIGURES–Continued

Figure C32	^1H - ^{13}C HMBC spectrum of a(PhCF₃)(1bb) (CDCl ₃ , 400 MHz, 298 K)	327
Figure C33	^1H - ^1H NOESY spectrum of a(PhCF₃)(1bb) (CDCl ₃ , 400 MHz, 298 K)	328
Figure C34	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a(PhCF₃)(1bb) (CDCl ₃ , 400 MHz, 298 K)	328
Figure C35	a(PhCF₃)(1bb) with assignment of ^1H and ^{13}C resonances	329
Figure C36	Absorbance and emission spectra for a(PhCF₃)(1) series in toluene	330
Figure C37	Ball-and-stick representations for optimized conformers of <i>a(PhCF₃)(1a)</i>	331
Figure C38	Ball-and-stick representations for optimized conformers of <i>a(PhCF₃)(1b)</i>	331
Figure C39	Ball-and-stick representations for optimized conformers of <i>a(PhCF₃)(1c)</i>	332
Figure C40	Ball-and-stick representations for optimized conformers of <i>a(PhCF₃)(1d)</i>	332
Figure C41	Comparison of experimental vs calculated ^1H resonances (δ) for a(PhCF₃)(1a) (experimental) and <i>a(PhCF₃)(1a)</i> (calculated). Fits: Conformer-1 (blue, $R^2 = 0.81$), Conformer-2 (orange, $R^2 = 0.53$)	333
Figure C42	Comparison of experimental vs calculated ^1H resonances (δ) for a(PhCF₃)(1b) (experimental) and <i>a(PhCF₃)(1b)</i> (calculated). Fits: Conformer-1 (blue, $R^2 = 0.81$), Conformer-2 (orange, $R^2 = 0.53$)	334
Figure C43	Comparison of experimental vs calculated ^1H resonances (δ) for a(PhCF₃)(1c) (experimental) and <i>a(PhCF₃)(1c)</i> (calculated). Fits: Conformer-1 (blue, $R^2 = 0.83$), Conformer-2 (orange, $R^2 = 0.59$)	334

LIST OF FIGURES—Continued

Figure D1	Synthetic path to $\beta(\text{CHO})_2$ and $\beta(\mathbf{1})_2$	337
Figure D2	^1H NMR spectrum of $\beta(\text{CHO})_2$ (CDCl_3 , 400 MHz, 298 K)	345
Figure D3	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\text{CHO})_2$ (CDCl_3 , 101 MHz, 298 K)	346
Figure D4	^1H NMR spectrum of $\beta(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	347
Figure D5	^1H - ^1H COSY spectrum of $\beta(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	348
Figure D6	^1H - ^{13}C HSQC spectrum of $\beta(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	348
Figure D7	^1H - ^{13}C HMBC spectrum of $\beta(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	349
Figure D8	^1H - ^1H NOESY spectrum of $\beta(\mathbf{1a})_2$ (CDCl_3 , 400 MHz, 298 K)	349
Figure D9	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\mathbf{1a})_2$ (CDCl_3 , 101 MHz, 298 K)	350
Figure D10	$\beta(\mathbf{1a})_2$ with assignment of ^1H and ^{13}C resonances	351
Figure D11	^1H NMR spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K)	352
Figure D12	^1H - ^1H COSY spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K)	352
Figure D13	^1H - ^{13}C HSQC spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K)	353
Figure D14	^1H - ^{13}C HMBC spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K)	353
Figure D15	^1H - ^1H NOESY spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K)	354
Figure D16	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 101 MHz, 298 K)	354
Figure D17	$\beta(\mathbf{1b})_2$ with assignment of ^1H and ^{13}C resonances	355
Figure D18	^1H NMR spectrum of $\beta(\mathbf{1c})_2$ (CDCl_3 , 400 MHz, 298 K)	356
Figure D19	^1H - ^1H COSY spectrum of $\beta(\mathbf{1c})_2$ (CDCl_3 , 400 MHz, 298 K)	356
Figure D20	^1H - ^{13}C HSQC spectrum of $\beta(\mathbf{1c})_2$ (CDCl_3 , 400 MHz, 298 K)	357
Figure D21	^1H - ^{13}C HMBC spectrum of $\beta(\mathbf{1c})_2$ (CDCl_3 , 400 MHz, 298 K)	357

LIST OF FIGURES–Continued

Figure D22	^1H - ^1H NOESY spectrum of $\beta(1\text{c})_2$ (CDCl_3 , 400 MHz, 298 K)	358
Figure D23	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(1\text{c})_2$ (CDCl_3 , 101 MHz, 298 K)	358
Figure D24	$\beta(1\text{c})_2$ with assignment of ^1H and ^{13}C resonances	359
Figure D25	^1H NMR spectrum of $\beta(1\text{d})_2$ (CDCl_3 , 400 MHz, 298 K)	360
Figure D26	^1H - ^1H COSY spectrum of $\beta(1\text{d})_2$ (CDCl_3 , 400 MHz, 298 K)	360
Figure D27	^1H - ^{13}C HSQC spectrum of $\beta(1\text{d})_2$ (CDCl_3 , 400 MHz, 298 K)	361
Figure D28	^1H - ^{13}C HMBC spectrum of $\beta(1\text{d})_2$ (CDCl_3 , 400 MHz, 298 K)	361
Figure D29	^1H - ^1H NOESY spectrum of $\beta(1\text{d})_2$ (CDCl_3 , 400 MHz, 298 K)	362
Figure D30	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(1\text{d})_2$ (CDCl_3 , 101 MHz, 298 K)	362
Figure D31	$\beta(1\text{d})_2$ with assignment of ^1H and ^{13}C resonances. *Signals are weak and not observed at this concentration. A weak signal at 128.3 ppm is likely part of the quartet for the 1d ^{13}C resonance, but the remaining signals are not resolved	363
Figure D32	^1H NMR spectrum of $\beta(1\text{e})_2$ (CDCl_3 , 400 MHz, 298 K)	364
Figure D33	^1H - ^1H COSY spectrum of $\beta(1\text{e})_2$ (CDCl_3 , 400 MHz, 298 K)	364
Figure D34	^1H - ^{13}C HSQC spectrum of $\beta(1\text{e})_2$ (CDCl_3 , 400 MHz, 298 K)	365
Figure D35	^1H - ^{13}C HMBC spectrum of $\beta(1\text{e})_2$ (CDCl_3 , 400 MHz, 298 K)	365
Figure D36	^1H - ^1H NOESY spectrum of $\beta(1\text{e})_2$ (CDCl_3 , 400 MHz, 298 K)	366
Figure D37	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(1\text{e})_2$ (CDCl_3 , 101 MHz, 298 K)	366
Figure D38	$\beta(1\text{e})_2$ with assignment of ^1H and ^{13}C resonances	367
Figure D39	^1H NMR spectrum of $\beta(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K)	368
Figure D40	^1H - ^1H COSY spectrum of $\beta(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K)	368
Figure D41	^1H - ^{13}C HSQC spectrum of $\beta(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K)	369
Figure D42	^1H - ^{13}C HMBC spectrum of $\beta(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K)	369

LIST OF FIGURES–Continued

Figure D43	^1H - ^1H NOESY spectrum of $\beta(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K)	370
Figure D44	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(1\text{bb})_2$ (CDCl_3 , 101 MHz, 298 K)	370
Figure D45	$\beta(1\text{bb})_2$ with assignment of ^1H and ^{13}C resonances	371
Figure D46	^1H NMR spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 400 MHz, 298 K)	372
Figure D47	^1H - ^1H COSY spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 400 MHz, 298 K)	372
Figure D48	^1H - ^{13}C HSQC spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 400 MHz, 298 K)	373
Figure D49	^1H - ^{13}C HMBC spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 400 MHz, 298 K)	373
Figure D50	^1H - ^1H NOESY spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 400 MHz, 298 K)	374
Figure D51	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 101 MHz, 298 K)	374
Figure D52	$\beta(1\text{cc})_2$ with assignment of ^1H and ^{13}C resonances. *Signals are overlapped and resolved by < 0.1 ppm	375
Figure D53	^1H NMR spectrum of $\beta(1\text{dd})_2$ (CDCl_3 , 400 MHz, 298 K)	376
Figure D54	^1H - ^1H COSY spectrum of $\beta(1\text{dd})_2$ (CDCl_3 , 400 MHz, 298 K)	376
Figure D55	^1H - ^{13}C HSQC spectrum of $\beta(1\text{dd})_2$ (CDCl_3 , 400 MHz, 298 K)	377
Figure D56	^1H - ^{13}C HMBC spectrum of $\beta(1\text{dd})_2$ (CDCl_3 , 400 MHz, 298 K)	377
Figure D57	^1H - ^1H NOESY spectrum of $\beta(1\text{dd})_2$ (CDCl_3 , 400 MHz, 298 K)	378
Figure D58	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(1\text{dd})_2$ (CDCl_3 , 101 MHz, 298 K)	378
Figure D59	$\beta(1\text{dd})_2$ with assignment of ^1H and ^{13}C resonances	379
Figure D60	Absorbance and emission spectra for $\beta(1\text{a})_2$, $\beta(1\text{c})_2$, and $\beta(1\text{e})_2$ in toluene	380
Figure D61	Absorbance and emission spectra for $\beta(1\text{a})_2$, $\beta(1\text{b})_2$, and $\beta(1\text{d})_2$ in toluene	381
Figure D62	Absorbance and emission spectra for $\beta(1\text{a})_2$ and $\beta(1\text{bb}-\text{dd})_2$ in toluene	381

LIST OF FIGURES—Continued

Figure D63	Ball-and-stick representations for optimized conformers of $\beta(1a)_2$	382
Figure D64	Ball-and-stick representations for optimized conformers of $\beta(1b)_2$	383
Figure D65	Ball-and-stick representations for optimized conformers of $\beta(1c)_2$	384
Figure D66	Ball-and-stick representations for optimized conformers of $\beta(1d)_2$	384
Figure D67	Ball-and-stick representations for optimized conformers of $\beta(1e)_2$	385
Figure D68	Ball-and-stick representations for optimized conformers of $\beta(1bb)_2$	386
Figure D69	Ball-and-stick representations for optimized conformers of $\beta(1cc)_2$	386
Figure D70	Ball-and-stick representations for optimized conformers of $\beta(1dd)_2$	387
Figure D71	Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1a)_2$ (experimental) and $\beta(1a)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.78$), Conformer-2 (orange, $R^2 = 0.54$), Conformer-4 (black, $R^2 = 0.06$)	389
Figure D72	Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1b)_2$ (experimental) and $\beta(1b)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.75$), Conformer-2 (orange, $R^2 = 0.45$), Conformer-4 (black, $R^2 = 0.15$)	389
Figure D73	Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1c)_2$ (experimental) and $\beta(1c)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.82$), Conformer-2 (orange, $R^2 = 0.60$), Conformer-4 (black, $R^2 = 0.12$)	390

LIST OF FIGURES–Continued

Figure D74	Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1d)_2$ (experimental) and $\beta(1d)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.67$), Conformer-2 (orange, $R^2 = 0.36$), Conformer-4 (black, $R^2 = 0.07$), Conformer-5 (grey, $R^2 = 0.17$)	390
Figure D75	Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1e)_2$ (experimental) and $\beta(1d)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.84$), Conformer-2 (orange, $R^2 = 0.66$), Conformer-4 (black, $R^2 = 0.04$)	391
Figure D76	Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1bb)_2$ (experimental) and $\beta(1bb)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.83$), Conformer-2 (orange, $R^2 = 0.64$), Conformer-4 (black, $R^2 = 0.44$)	391
Figure D77	Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1cc)_2$ (experimental) and $\beta(1cc)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.88$), Conformer-2 (orange, $R^2 = 0.80$), Conformer-4 (black, $R^2 = 0.71$), Conformer-5 (grey, $R^2 = 0.96$)	392
Figure D78	Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1dd)_2$ (experimental) and $\beta(1dd)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.62$), Conformer-2 (orange, $R^2 = 0.25$), Conformer-4 (black, $R^2 = 0.06$), Conformer-5 (grey, $R^2 = 0.70$).	392

LIST OF ABBREVIATIONS

NMR	Nuclear Magnetic Resonance
HRMS	High Resolution Mass Spectroscopy
COSY	Correlation Spectroscopy
HSQC	Heteronuclear Single Quantum Coherence
HMBC	Heteronuclear Multiple Bond Correlation
NOESY	Nuclear Overhauser Effect Spectroscopy
UV-VIS	Ultraviolet-Visible Spectroscopy
GPC	Gel Permeation Chromatography
NDT	Naphthodithiophene
NICS	Nucleus-Independent Chemical Shift
GIAO	Gauge Including Atomic Orbitals
DFT	Density Functional Theory
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
OLED	Organic Light-Emitting Diode

CHAPTER ONE

INTRODUCTION TO ORGANIC ELECTRONICS

1.0 A Historical Perspective

The story of organic electronics began in the mid-20th century with the observation of photoconductivity in crystalline anthracene and other polycyclic aromatic hydrocarbons.¹ Although these results were intriguing, they did not immediately lead to practical applications. Organic compounds for decades were therefore largely considered electrical insulators, useful primarily as plastics or dyes but not as conductors or semiconductors.² This perception was changed in 1977, when Hideki Shirakawa, Alan MacDiarmid, and Alan Heeger demonstrated that polyacetylene could be converted into a material with metallic-like conductivity via doping with iodine.³⁻⁵ Their pioneering work revealed that the π -conjugated backbones of certain polymers could serve as conduits for charge transport, provided that appropriate doping introduced charge carriers. This discovery marked the birth of conducting polymers,^{4,6-8} and the trio was awarded the 2000 Nobel Prize in Chemistry for their contributions. The late 1960s to early 1980s witnessed a surge in research on charge transport in π -conjugated small molecules and polymers. Researchers first demonstrated electroluminescence in organic crystals, showing that organic compounds could convert electrical energy directly into light.^{4,6,9-11} The field accelerated further with the seminal 1987 report by Tang and VanSlyke at Eastman Kodak, who fabricated the first efficient organic light-emitting diode (OLED) using a bilayer of small-molecule materials.^{12,13} Their device exhibited bright, stable emission at low voltages, opening the path toward displays and lighting applications.

The 1990s ushered in polymer-based electronics with the development of poly(phenylene vinylene) (PPV) and its derivatives as polymer light-emitting diodes (PLEDs), highlighting the advantages of solution processing and flexibility.^{14–16} Around the same time, organic photovoltaics (OPVs) and organic field-effect transistors (OFETs) emerged as research frontiers, motivated by the promise of lightweight, flexible, and potentially low-cost alternatives to silicon-based technologies.^{17–19} By the early 2000s, attention turned to bulk heterojunction OPVs, pioneered by blending electron-donor polymers like poly(3-hexylthiophene) (P3HT) with electron-acceptor fullerenes such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM).^{20–22} This architecture enhanced exciton dissociation and charge collection, pushing efficiencies upward. Concurrently, OLED technology matured into commercial reality, with small-molecule and polymer OLED displays entering the consumer market. Today, OLED panels dominate the premium smartphone and television sectors, celebrated for their high contrast, wide viewing angles, and design flexibility.^{23–25} In the last decade, organic electronics has expanded into non-fullerene acceptors (NFAs), narrow-bandgap donor–acceptor polymers, conjugated oligomers and dendrimers, and even organic–inorganic hybrids such as perovskite–organic blends.^{26–29} These advances have elevated OPV efficiencies beyond 19% and enabled organic transistors with mobilities exceeding $10 \text{ cm}^2/\text{V}\cdot\text{s}$.^{30–33} Beyond displays and photovoltaics, organic materials are now deployed in biosensors, bioelectronics, wearable devices, and neuromorphic computing.^{34–38}

1.1 Classes of Organic Materials

Organic materials for electronics can be grouped into five broad categories: small molecules,^{39–42} conjugated polymers,^{14,33,39,43} oligomers,^{27,44} dendrimers,^{45–48} and hybrid/emerging systems.^{49,50} Each category encompasses unique structural features and performance characteristics that dictate their application in devices.

1.1.1 Small Molecules

Small molecules are discrete, π -conjugated compounds with precisely defined structures. Their advantages include synthetic tunability, reproducibility, and the ability to form crystalline domains that facilitate efficient charge transport.^{39,51,52} Small molecules remain indispensable because of their well-defined crystallinity, batch-to-batch reproducibility, and compatibility with vacuum deposition techniques.⁵³ Key subclasses include acenes,⁵⁴ donor–acceptor systems,⁵⁵ phthalocyanines and porphyrins.⁵⁶

1.1.1.1 Acenes (e.g., pentacene, tetracene, anthracene)

Acenes are a class of linearly fused polycyclic aromatic hydrocarbons, typified by anthracene, tetracene, and pentacene, whose extended π -conjugation promotes efficient intermolecular orbital overlap in the solid state.⁵⁴ As the number of fused benzene rings increases, the HOMO–LUMO gap decreases and intermolecular π – π stacking interactions become stronger, leading to enhanced charge transport properties.⁵⁴ Among this family, pentacene has emerged as a benchmark small-molecule semiconductor for organic field-effect transistors (OFETs), routinely exhibiting high hole mobilities under optimized thin-film or single-crystal conditions.^{54,57} The exceptional performance of acenes is

attributed to their rigid, planar molecular structures, and favorable molecular packing motifs that promotes efficient orbital overlap between neighboring molecules.^{54,58} However, higher acenes also suffer from limited environmental stability, as increased conjugation renders them more susceptible to photooxidation and chemical degradation in air.^{49,57} Despite these limitations, acenes remain essential model systems for elucidating structure–property relationships in organic semiconductors and continue to serve as reference materials for evaluating next-generation OFET semiconductors.^{58,59}

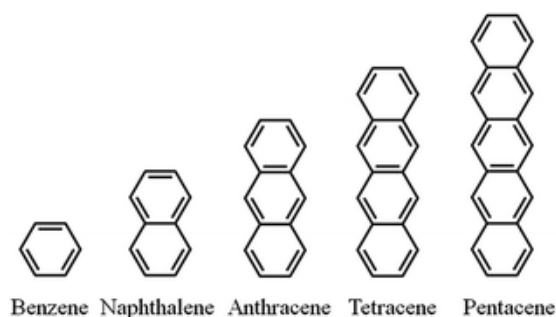


Figure 1.1. Structure of example acenes

1.1.1.2 Donor–acceptor systems

Donor–acceptor (D–A) systems based on perylene diimides (PDIs) and naphthalene diimides (NDIs) represent a prominent class of electron-deficient organic semiconductors widely employed in organic photovoltaics (OPVs).^{55,60} These molecules feature rigid, planar aromatic cores functionalized with imide groups, which impart strong electron affinity, high photochemical stability, and excellent thermal robustness.^{55,61} PDIs and NDIs exhibit deep LUMO energy levels and efficient electron transport, making them particularly attractive as non-fullerene acceptors or n-type components in donor–acceptor heterojunctions.^{55,60} Structural modification through bay-

region substitution or imide-side-chain engineering allows fine tuning of molecular packing, absorption profiles, and energy levels, enabling optimization of charge separation and transport.^{55,61} In OPV devices, PDI- and NDI-based acceptors have demonstrated efficient exciton dissociation and long-term operational stability compared to fullerene derivatives.^{60,62} Consequently, PDIs and NDIs serve not only as high-performance acceptor materials but also as model systems for understanding structure–property relationships in donor–acceptor organic electronics.⁵⁵

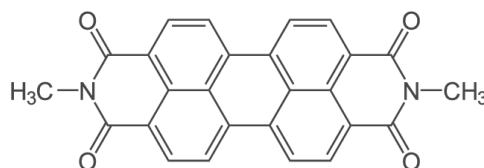


Figure 1.2. Structure of Perylene diimide derivative: *N,N*-dimethyl-3,4,9,10-perylenetetracarboxylic diimide (DiMe-PTCDI).

1.1.1.3 Phthalocyanines and porphyrins

Phthalocyanines and porphyrins are planar, π -conjugated macrocycles featuring central metal-coordination sites, which endow them with rich redox chemistry and tunable electronic properties.^{63,64} Their strong visible and near-infrared absorption, high chemical stability, and efficient charge-transfer characteristics have led to widespread use in organic photovoltaics, particularly as light-harvesting donors and interfacial materials.⁵⁶ Metal coordination within the macrocyclic core enables systematic tuning of energy levels, magnetic behavior, and intermolecular interactions, making these compounds attractive for chemical sensing and molecular spintronics.⁶⁴ In sensor applications, phthalocyanines and porphyrins exhibit selective responses to gases and

biomolecules through metal–analyte coordination and changes in conductivity or optical signatures.⁶⁵ Furthermore, their long spin coherence times and controllable spin states have positioned metalloporphyrins and metallophthalocyanines as promising building blocks for organic spintronic and magnetoresistive devices.⁶⁶ Collectively, these macrocyclic systems serve as versatile model materials bridging organic electronics, coordination chemistry, and functional device applications.^{56,63,64}

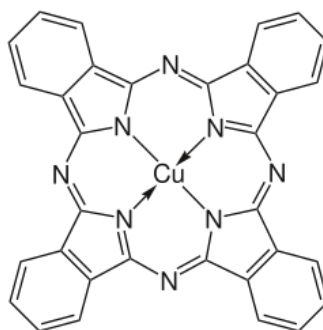


Figure 1.3. Structure of Copper Phthalocyanine

1.1.2 Conjugated Polymers

Conjugated polymers possess delocalized π -electron systems along their backbones, enabling semiconducting or conducting behavior.^{6,67} They combine electronic functionality with the mechanical advantages of plastics, and are especially important because they enable solution processability, making large-area, flexible, and even printable devices possible.²⁴ Important subclasses include poly(p-phenylene vinylene) (PPV),⁴³ polythiophenes,⁶⁸ donor-acceptor co-polymers,²⁷ polyanilines, and polypyrroles.⁶⁹

1.1.2.1 Poly(*p*-phenylene vinylene) (PPV)

Poly(*p*-phenylene vinylene) (PPV) is widely regarded as the archetypal conjugated polymer that established the foundation of polymer light-emitting diodes (PLEDs).⁴³ The landmark demonstration of electroluminescence from PPV in 1990 provided the first clear evidence that solution-processable conjugated polymers could function as efficient emissive semiconductors.^{43,70} PPV is characterized by a rigid π -conjugated backbone, which supports effective intrachain charge transport and radiative recombination of injected charge carriers.^{14,43} A key advantage of PPV lies in its synthetic accessibility via soluble precursor routes, enabling thin-film fabrication through spin coating or printing techniques.⁷⁰ Chemical modification of the PPV backbone and side chains has led to numerous derivatives with tunable bandgaps, improved luminescence efficiencies, and enhanced environmental stability.¹⁴ Despite being surpassed by newer polymer systems, PPV remains a benchmark material for understanding structure–property relationships in conjugated polymers and the fundamental operation of PLEDs.^{14,43}

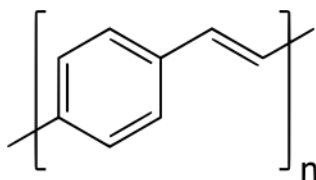


Figure 1.4. Poly(*p*-phenylene vinylene) repeating unit

1.1.2.2 Polythiophenes (e.g., P3HT)

Polythiophenes constitute one of the most extensively studied classes of conjugated polymers in organic electronics, owing to their chemical robustness, synthetic versatility, and favorable charge-transport characteristics.⁷¹ Among them, poly(3-hexylthiophene) (P3HT) has emerged as a prototypical material for both organic photovoltaics (OPVs) and organic field-effect transistors (OFETs).^{22,72} The presence of alkyl side chains promotes solubility and enables self-assembly into semicrystalline domains with strong π - π stacking, which is critical for efficient charge transport.^{71,73} In OPVs, P3HT has been widely employed as an electron-donor polymer in bulk heterojunction architectures, particularly in combination with fullerene acceptors such as PCBM.^{21,22,73} In OFETs, regioregular P3HT films exhibit hole mobilities strongly correlated with molecular ordering, backbone planarity, and processing conditions.⁷² Owing to its tunable electronic properties and well-understood structure-property relationships, P3HT continues to serve as a benchmark system for the development and evaluation of next-generation conjugated polymers.^{21,71}

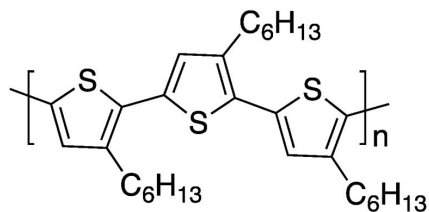


Figure 1.5. Poly(3-hexylthiophene) (P3HT) repeating unit

1.1.2.3 Donor–acceptor copolymers

Donor–acceptor (D–A) copolymers are rationally engineered conjugated polymers composed of alternating electron-rich (donor) and electron-deficient (acceptor) units along the backbone, a design strategy that enables precise control over electronic structure and optoelectronic properties.^{27,74} This push–pull architecture promotes intramolecular charge transfer, resulting in narrowed bandgaps and extended absorption into the visible and near-infrared regions.⁷⁴ Among the most prominent examples, diketopyrrolopyrrole (DPP)-based copolymers have attracted considerable attention due to their strong light absorption, high charge-carrier mobilities, and excellent thermal and photochemical stability.⁷¹ Through molecular engineering of donor strength, acceptor identity, and side-chain architecture, D–A copolymers can be optimized for use in organic photovoltaics (OPVs) and organic field-effect transistors (OFETs).^{74,75} In OPVs, these materials enable efficient photon harvesting and charge separation, contributing to high short-circuit currents and power conversion efficiencies.²² Consequently, donor–acceptor copolymers represent a central materials platform in modern organic electronics and continue to drive performance advances across multiple device technologies.^{71,74}

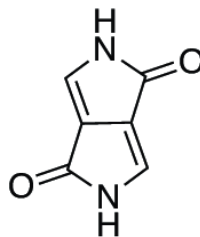


Figure 1.6. Chemical structure of Diketopyrrolopyrrole (DPP)

1.1.2.4 Polyaniline and polypyrrole

Polyaniline (PANI) and polypyrrole (PPy) are among the earliest conducting polymers to be extensively studied, playing a pivotal role in establishing the field of intrinsically conducting polymers.⁷⁶ Their electrical conductivity arises from π -conjugated backbones combined with reversible doping processes, which allow tuning of charge-carrier density through chemical or electrochemical oxidation and reduction.⁶⁷ Polyaniline is particularly notable for its multiple redox states, environmental stability, and low cost, making it attractive for applications in anticorrosion coatings, chemical sensors, and electrochromic devices.^{76,77} Polypyrrole, typically synthesized via electrochemical polymerization, exhibits high conductivity and good mechanical properties, enabling its use in biosensors, actuators, and flexible electronic coatings.⁷⁸ Both polymers have also been widely explored in energy storage technologies, including supercapacitors and battery electrodes, due to their high pseudo-capacitance and fast redox kinetics.^{50,79} Although their charge transport performance is inferior to that of modern semiconducting polymers, PANI and PPy remain important reference materials and continue to find niche applications where robustness, processability, and electrochemical activity are paramount.^{77,78}

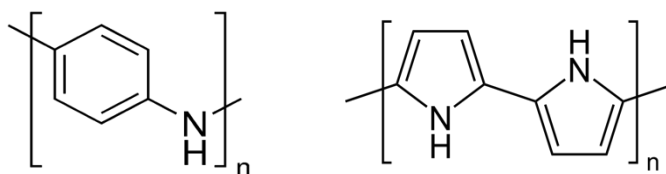


Figure 1.7. Chemical structure of polyaniline and polypyrrole

1.1.3 Oligomers

Oligomers are shape-persistent small molecules and polymers, typically containing 2–20 repeat units of a conjugated backbone.⁸⁰ Unlike the non-uniform dispersity of polymers, oligomers possess well-defined molecular weights and are often crystalline, while still maintaining tunability through length and end-group modification.^{81,82} Oligomers provide a balance between structural precision and device-relevant processability, making them valuable model systems for studying charge transport and exciton dynamics.⁸² Examples include: oligothiophenes (bi-, ter-, quaterthiophenes), which are soluble and easily tuned for specific bandgaps. Oligo(phenylene vinylenes), also offer tunable fluorescence and electroluminescence properties.^{80,81}

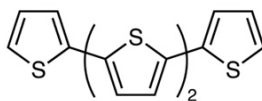


Figure 1.8. Structure of α -Quaterthiophene

1.1.4 Dendrimers

Dendrimers are tree-like, highly branched macromolecules with a central core, repeated branching units, and functional end groups.⁸³ Their 3D architecture differentiates them from linear polymers and oligomers.⁸⁴ Dendrimers offer precise molecular weight and structure due to stepwise synthesis, tunable optoelectronic

properties via functionalization at the periphery or core, and solubility and film-forming capability despite high molecular weight.⁴⁸ Dendrimers bridge molecular and macromolecular design, offering unique opportunities in next-generation organic electronics. Applications include dendrimer OLEDs (PLEDs), where conjugated dendrimers serve as emissive layers,^{84,85} energy harvesting and light-harvesting antennae,⁸⁵ where the branched structure funnels excitons toward a central chromophore, and sensing and biomedical imaging,^{48,86,87} leveraging multivalency for interactions with biological targets.

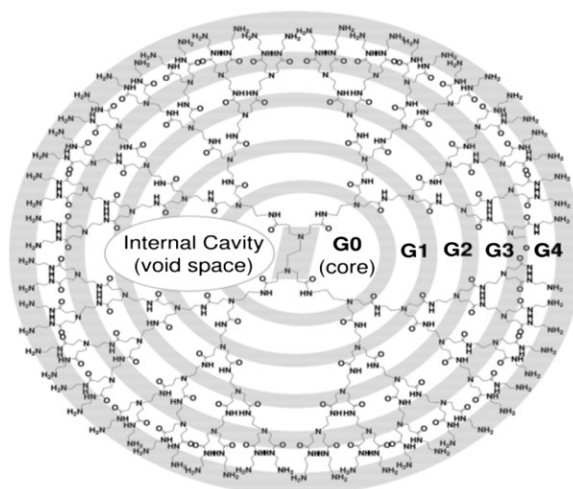


Figure 1.9.0 Generation G4 dendrimer with 64 amino groups at the periphery⁸⁸

1.1.5 Hybrid and Emerging Systems

Hybrid systems combine the strengths of small molecules, conjugated polymers, and inorganic components, enabling materials platforms with complementary optoelectronic and structural advantages.⁸⁹ These materials represent the frontier of organic electronics, combining molecular tunability with device performances that increasingly rival or surpass those of conventional inorganic technologies.^{71,89} Representative examples

include polymer–fullerene blends such as poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM), which established the bulk heterojunction architecture for organic photovoltaics (OPVs).^{21,22} More recently, non-fullerene acceptors (NFAs) such as ITIC and Y6 have emerged as leading materials for high-efficiency OPVs, enabling power conversion efficiencies exceeding 15–19%.³² Organic–inorganic hybrid materials, including metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), further expand the design space by introducing crystallinity, porosity, and modular electronic functionality.^{90,91} In parallel, bio-inspired materials such as indigo, eumelanin, and chlorophyll derivatives are gaining attention as sustainable organic electronic materials that merge biological functionality with semiconductor concepts.^{92,93}

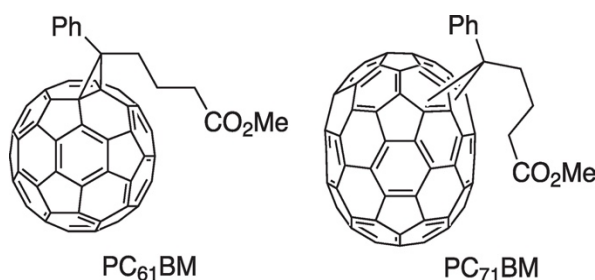


Figure 1.9.1. Polymer-fullerene blends PC_{61/71}BM^{s22,94}

1.2 Conclusion

Organic electronics has grown from scientific curiosity into a global industry. This transformation was made possible by careful design and study of organic materials — small molecules, polymers, oligomers, dendrimers, and hybrid systems. Each class contributes unique advantages in crystallinity, flexibility, tunability, or processability.

Together, they form the materials foundation of devices ranging from OLED displays and solar cells to biosensors and neuromorphic circuits.

1.3 Kinney laboratory's research with isomeric bent naphthodithiophenes as organic small molecules (α - and β -NDTs)

Research in the Kinney Lab is centered on understanding the structure-property relationships of thiophene-based small molecules, specifically isomeric bent naphthodithiophenes in different architectures, and their potential application as functional materials to advance the field of organic electronics.^{95,96} Organic small molecules have proven to be highly tunable and cost effective, with optoelectronic properties conducive for functional materials such as organic field-effect transistors (OFETs),⁹⁷⁻⁹⁹ organic light-emitting diodes (OLEDs),^{100,101} organic solar cells (OSCs),^{102,103} and organic photovoltaics (OPVs).^{103,104} Enhancement of these optoelectronic properties can be accomplished by increasing the planarity of the system through the addition of rigidifying groups (generally fused polyaromatics). This rigidification serves two main purposes: 1) increasing the effective conjugation length and 2) reducing the heavy atom effect of sulfur. By increasing the effective conjugation length of these systems, the resonance contribution can be shifted from the aromatic to the quinoidal species, which is critical in the resultant optoelectronic properties.¹⁰⁵⁻¹⁰⁷

Over the past decade Bäuerle and Höger have investigated dicyanomethylene terminated oligomers of bithiophene derived species for optoelectronic applications.^{101,104,108} Bäuerle has primarily studied benzo- and naphtho[2,1-*b*:3,4-*b'*]dithiophenes (BDTs and NDTs), with both derivatives showing promise as organic

photovoltaics (OPVs) (Figure 1.9.2 a).¹⁰⁴ The Kinney lab's work contrasts well with the work of Höger, who have demonstrated that the two available configurations of the thiophene groups in NDTs display different photophysical properties. By synthesizing the α - and β -isomeric dithieno[2,3-*a*:3',2'-*c*]phenazines (Figure 1.9.2 b)¹⁰¹ his group was able to realize that oligomers of α -isomer composition are fluorescent, while β -isomer-based oligomers are phosphorescent. They attribute these differences in photophysical outcomes to the differences in effective conjugation length between α - and β -isomers.^{101,108}

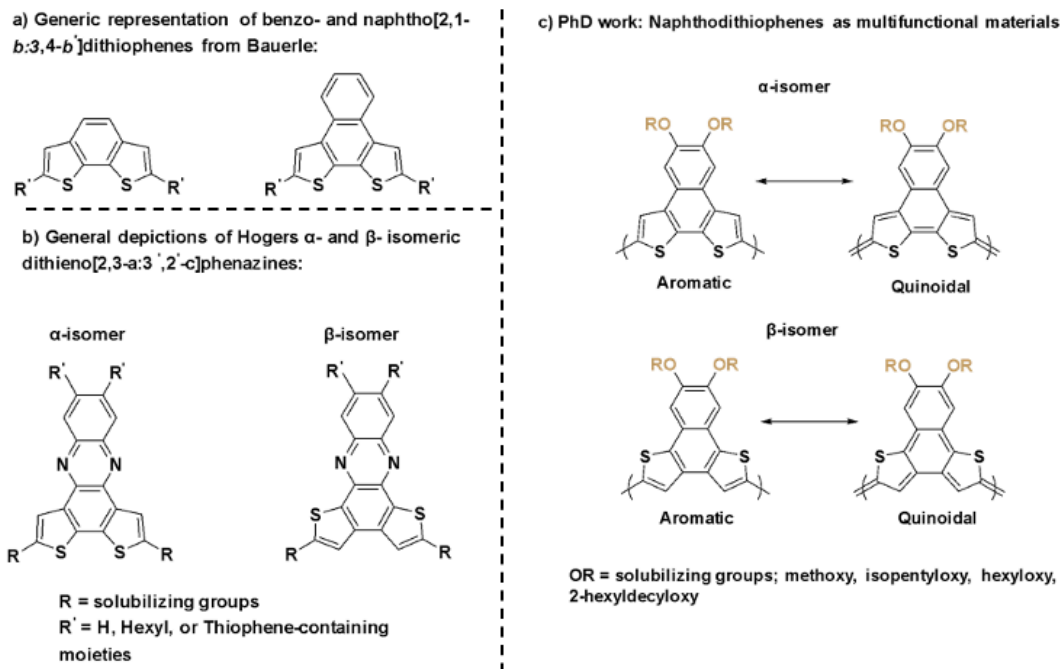


Figure 1.9.2. a) Generic BDT and NDT cores studied by Bäuerle; b) Representative α - and β -dithienophenazines investigated by Höger; c) bent α - and β -Naphthodithiophene (NDT) building blocks utilized in the Kinney Lab.

Collectively this work is part of a shift throughout the organic electronic community to better understand the structure-property relationships of the molecules behind the function, ideally by maximizing the stability of thiophenes quinoidal resonance. This has led researchers to move away from polymeric materials and instead probe small molecules that are solution processable whose properties can directly correlate with their parent structure.^{103,109} Of particular interest are isomeric bent naphthodithiophenes Naphtho[2,1-*b*:3,4-*b'*]dithiophene (α -NDT) and naphtho[1,2-*b*:4,3-*b'*]dithiophene (β -NDT)^{110,111} that allow for extended π -conjugation through the α -positions shown in Figures 1.9.2 c. These isomers are studied in this thesis and represent unique building blocks for π -conjugated materials due to their rigid planar structure and programmable syntheses.^{98,112–114} The isomeric bent naphthodithiophenes are themselves luminescence monomers, thus modification to these core molecules is expected to modulate (or tune) their emission and subsequently their function.^{111,114–116}

1.4 Dissertation Aims

In this doctoral thesis, there are four main research topics of interest demonstrating functionalization of two isomeric bent naphthodithiophenes (α - and β -NDTs) to obtain novel photoactive materials. Aim one explores direct functionalization of isomeric bent naphthodithiophenes (α - and β -NDTs) fashioned with electron donating or withdrawing groups, yielding novel push-pull fluorophores. These end-capped monomers demonstrate efficient modulation of luminescence and allow for analysis of solution-state trends between isomers. Aim two utilizes intramolecular N $\cdots$ S interactions to functionalize and rigidify imine based acyclic α -NDT chromophores. This research direction is made possible through lithiation of the NDT monomers termini, followed by

formyl addition (achieved via metal–carbonyl exchange). In Aim three, the optoelectronic evaluation of a series of functionalized α -NDT chromophores derivatives where the NDT functions as a π bridge in asymmetrical V-shaped donor– π –acceptor (D– π –A) imine systems are explored. The influence of electronic asymmetry on optical absorption, emission, and excited-state behavior are also probed. Lastly, aim four explores intramolecular N $\cdots$ S interaction in novel imine based acyclic β -NDT chromophores. It further explores structurally, the various conformers observed in solution state studies for the synthesized electron withdrawing chromophores experimentally and computationally. Collectively, the four research aims of this thesis are based on the synthesis, characterization, and application of luminescent bent NDT monomers, with the results obtained relevant to the organic, inorganic, materials chemistry, and the organic electronics community.

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CHAPTER TWO

BENT NAPHTHODITHIOPHENES: SYNTHESIS AND CHARACTERISATION OF ISOMERIC FLUOROPHORES

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2.0 Summary

Thiophene-containing heteroarenes are one of the most well-known classes of π -conjugated building blocks for photoactive molecules. Isomeric naphthodithiophenes (NDTs) are at the forefront of this research area due to their straightforward synthesis and derivatization. Notably, NDT geometries that are bent – such as naphtho[2,1-*b*:3,4-*b'*]dithiophene (α -NDT) and naphtho[1,2-*b*:4,3-*b'*]dithiophene (β -NDT) – are seldom employed as photoactive small molecules. This chapter investigates how remote substituents impact the photophysical properties of isomeric α - and β -NDTs. The orientation of the thiophene units plays a critical role in the emission: in the $\alpha(\text{OHex})\text{R}_2$ series conjugation from the end-caps to the NDT core is apparent, while in the $\beta(\text{Oi-Pent})\text{R}_2$ series minimal change is observed unless strong electron acceptors, such as $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$, are employed. This push-pull Acceptor–Donor–Acceptor (A–D–A) fluorophore exhibits positive fluorosolvatochromism that correlates with increasing solvent polarity parameter, $E_T(30)$. In total, these results highlight how remote substituents can modulate the emission of isomeric bent NDTs.

2.1 Introduction

Heteroarenes, polyaromatic hydrocarbons (PAHs) bearing main group elements, are well established as building blocks for π -conjugated functional materials.¹⁻⁴

Thiophene-containing heteroarenes with benzene, naphthalene, or anthracene cores have been thoroughly investigated as electron rich moieties within both small molecule and polymer systems with applications in organic electronics.^{1,5,6} Of the thiophene-based heteroarenes, naphthodithiophenes (NDTs) are of particular interest due to the plethora of isomers available and their straightforward derivatisation.^{7,8} Linear and angular NDTs shown in Figure 2.1 a represent two classes of isomeric NDTs that have found applications throughout organic electronics, most notably as organic field-effect transistors (OFETs),⁹⁻¹¹ organic light-emitting diodes (OLEDs),¹² organic^{13,14} and dye-sensitized¹⁵ solar cells, and more recently as hole-transporting materials (HTMs).^{12,16,17} Due to the orientation of the residual α -positions (2- and 7-positions, labelled in Figure 2.1a), NDT-1 and NDT-2 are considered to be linear rods, while NDT-3 and NDT-4 are described as angular.⁷

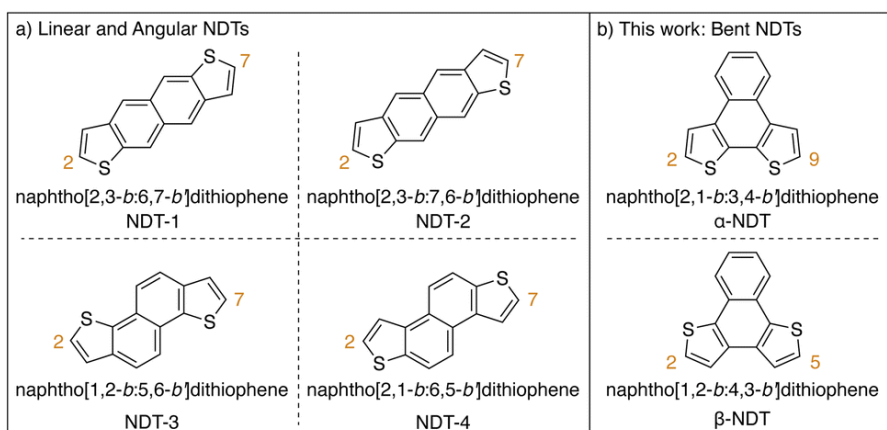


Figure 2.1. Classes of naphthodithiophenes. (a) Isomeric linear and angular naphthodithiophenes. (b) This work: isomeric bent naphthodithiophenes.

Alternatively bent NDTs – such as naphtho[2,1-*b*:3,4-*b'*]dithiophene (α -NDT) and naphtho[1,2-*b*:4,3-*b'*]dithiophene (β -NDT) shown in Figure 2.1 b – are known building blocks in polymeric materials,^{18,19} but are underrepresented as luminescent small molecules.^{16,20} At their core, unfunctionalized α - and β -NDTs are isoelectronic to triphenylene but can be easily fused to other motifs to yield electron deficient cores (e.g. phenazines²¹ or imides^{19,22}). The α -positions of α - and β -NDTs, labelled in Figure 2.1 b, offer a facile means to modulate the emissive properties of the core via peripheral derivatisation (i.e. V-shaped²³ Acceptor–Donor–Acceptor systems). These bent push-pull fluorophores²⁴ are reminiscent of Höger and co-workers isomeric dithienylphenazines (termed α - and β -DTPs), whose systems have inverted electronics (i.e. the electronics are aligned to be Donor–Acceptor–Donor systems). Their series of α - and β -DTPs were shown to have variable conjugation paths based on the isomer employed, ultimately yielding photoactive molecules that are fluorescent (α -DTP) or dual emitters (β -DTP).^{25,26} With this in mind, probing how the peripheral functionalization of α - and β -NDTs impacts the photoactive cores, and ultimately their application as push-pull fluorophores, is of interest. Herein the structure-property relationships in a series of isomeric bent NDTs – naphtho[2,1-*b*:3,4-*b'*]dithiophene (α -NDT) and naphtho[1,2-*b*:4,3-*b'*]dithiophene (β -NDT) – with variable end-caps is investigated. The initial premise of this research effort was to establish if the peripheral **R**-groups are (1) in communication with the NDT core and (2) if there are distinct differences between the isomers. NMR spectroscopy can afford preliminary evidence of communication to the core in the ground state via modulation

of interior resonances far removed from the **R**-groups; while emission spectra are informative of excited state communication. Ultimately, there are clear differences in the photophysical properties between the isomers, with α -NDT being more receptive to all types of peripheral substituents and β -NDT only being responsive to electron-deficient end-caps.

2.2 Results and discussion

2.2.1: Synthesis and structural analysis of $\alpha(\text{OR}')\text{R}_2$ Series

With the goal of having both solution- and solid-state metrics for the $\alpha(\text{OR}')\text{R}_2$ series two monomers with differing solubility are needed. For the solution-state analysis, hexyloxy groups were used to ensure that all α -NDT derivatives are soluble across a range of concentrations, particularly with aggregation being a concern for similar PAH systems.²⁷ To investigate solid-state metrics methoxy groups were used to maximize the chance of growing single crystals for x-ray diffraction. Both $\alpha(\text{OHex})\text{R}_2$ and $\alpha(\text{OMe})\text{R}_2$ can be synthesized via a streamlined bottom-up approach. Figure 2.2 details the synthetic path to the $\alpha(\text{OHex})\text{R}_2$ series beginning with the alkylation of 4,5-dibromocatechol²⁸ with iodohexane to yield solubilized building block **1(OHex)**. Installation of the thiophene units is accomplished via palladium mediated cross-coupling to afford **2(OHex)** in modest yield. Planarisation of **2(OHex)** under typical Scholl oxidation conditions²⁹ affords $\alpha(\text{OHex})$ as an off-white crystalline solid after column purification. Bromination of the open α -positions with NBS yields $\alpha(\text{OHex})\text{Br}_2$, a versatile core molecule for attaching end-caps with variable electronic properties. Commercially available phenyl boronic acid (**R** = **Ph**, $\text{H } \sigma_p = 0.00$) and *para*-functionalized phenyl boronic acid derivatives *p*-tolyl boronic acid (**R** = **Tol**, $\text{Me } \sigma_p = -0.17$), *p*-methoxyphenyl

boronic acid (**R** = **PhOMe**, OMe $\sigma_p = -0.27$), and *p*-(trifluoromethyl)phenyl boronic acid (**R** = **PhCF₃**, CF₃ $\sigma_p = +0.54$) were chosen as end-caps due to their variable electronic properties that are poised to be in resonance with the NDT cores. Due to this arrangement for the **R**-groups Hammett parameters³⁰ for σ_p , which include resonance effects, are more informative than electronically isolated σ_m . Suzuki cross-coupling of the boronic acids proved to be efficient across all derivatives, with modest isolated yields for the $\alpha(\text{OHex})\text{R}_2$ series (Figure 2.2).

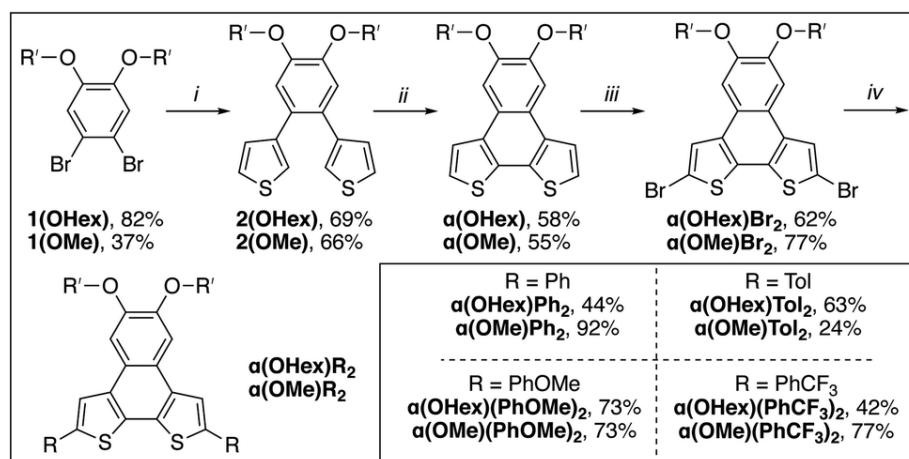


Figure 2.2. Synthesis of $\alpha(\text{OR}')\text{R}_2$ series. (i) 3-thiophene boronic acid, Pd(PPh₃)₂Cl₂, 2 M K₂CO₃, THF, 80 °C, overnight; (ii) FeCl₃, MeNO₂, DCM, 0 °C to RT, 1 h; (iii) NBS, CHCl₃, RT, 2 d; (iv) **R** boronic acid, Pd(PPh₃)₂Cl₂, 2 M K₂CO₃, THF, 80 °C, overnight. (Inset): Isolated yields for $\alpha(\text{OHex})\text{R}_2$ and $\alpha(\text{OMe})\text{R}_2$ series.

The $\alpha(\text{OMe})\text{R}_2$ series follows an identical synthetic path as $\alpha(\text{OHex})\text{R}_2$ (shown in Figure 2.2), with the exception of starting from 4,5-dibromoveratrole.³¹ The solubility of the $\alpha(\text{OMe})\text{R}_2$ series is demonstrably worse than the hexyloxy series, which proved challenging for purification and analysis (Supplementary data section). Due to this poor solubility the $\alpha(\text{OMe})\text{R}_2$ series was used almost explicitly for crystallography. Single

crystals of sufficient quality for X-ray diffraction were grown for each derivative via vapour diffusion of hexanes into saturated solutions of $\alpha(\text{OMe})\text{R}_2$ in THF (see Supplementary data section). Of particular interest are the inter-ring bond lengths, which can detail the level of communication the remote substituents have with the α -NDT core, and the supramolecular organization of the $\alpha(\text{OMe})\text{R}_2$ series. The C–C linkage between the α -NDT core and the appended **R**-groups are expected to display minor elongation due to torsional strain between the ring systems ($\text{C}–\text{C} \approx 1.45 \text{ \AA}$),³² with measurements under this value being indicative of increased conjugation with the α -NDT core. Each $\alpha(\text{OMe})\text{R}_2$ derivative has an inter-ring bond length of $\approx 1.46 \text{ \AA}$, revealing negligible bond elongation with no dependence on the **R**-group. The herringbone arrays formed in the crystallographic packing of the $\alpha(\text{OMe})\text{R}_2$ series reveal that the planar cores of the α -NDTs are arranged into slipped-stacks with arene-arene distances of $\approx 3.5 \text{ \AA}$ (see Supplementary data section for full details).

With these solid-state metrics established, we turned our attention to the solubilized $\alpha(\text{OHex})\text{R}_2$ derivatives for solution-state structural analysis. Specifically of interest are resonances far removed from the **R**-groups that are part of the NDT core, as these signals are expected to shift if there is communication from the end-caps to the core. The NDT cores themselves are electron-rich, therefore **R**-groups that are electron withdrawing are expected to function as intramolecular acceptor–donor–acceptor (A–D–A) systems, while electron-rich groups are expected to yield highly polarized all donor systems. Intramolecular A–D–A species are posited to increase the contribution of the quinoidal resonance, a highly desirable characteristic in photoactive molecules.²³ Key

proton resonances 2b and 3b are highlighted in Figure 2.3 and are matched between each derivative of the $\alpha(\text{OHex})\text{R}_2$ series to ease comparison.

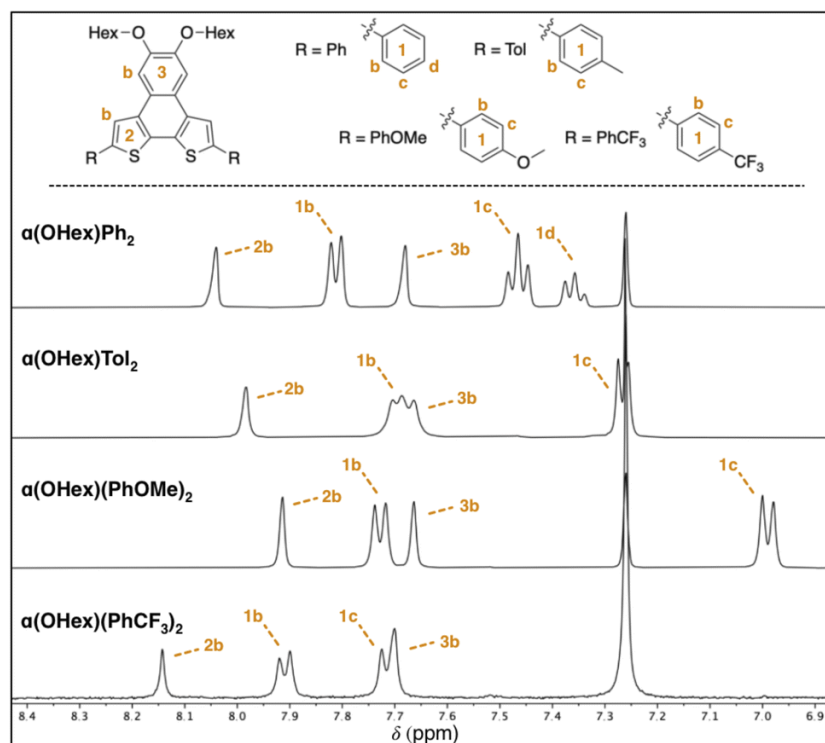


Figure 2.3. Partial ^1H NMR spectra for the $\alpha(\text{OHex})\text{R}_2$ series with assignment of aromatic resonances (400 MHz, CDCl_3). See supplementary data section for full spectra and assignments.

Due to the planar nature of the NDT cores aggregation is likely, thus comparison of NMR spectra at similar dilute concentrations is required. Inspection of the aromatic region of dilute (≤ 10 mM) solutions of each $\alpha(\text{OHex})\text{R}_2$ species reveals slight perturbations of the interior 2b proton ($\Delta\delta \approx 0.20$ ppm, Figure 2.3) and carbon ($\Delta\delta \approx 3$ ppm, see Supplementary data section) resonances. Modulation of the 2b resonances is quite unique: these signals are far removed from the functional group and indicate that there is remote communication to the NDT core upon end-capping. Relative to parent $\alpha(\text{OHex})\text{Ph}_2$ the electron donating groups shift the 2b resonance upfield with

$\alpha(\text{OHex})\text{Tol}_2$ ($\Delta\delta$ -0.06 ppm) and $\alpha(\text{OHex})(\text{PhOMe})_2$ ($\Delta\delta$ -0.13 ppm) both being above the threshold of significance ($\Delta\delta \geq 0.05$ ppm). $\alpha(\text{OHex})(\text{PhCF}_3)_2$ is shifted downfield in comparison ($\Delta\delta$ +0.10 ppm), indicative of a shift towards a higher energy state (with respect to parent $\alpha(\text{OHex})\text{Ph}_2$). Overall, the shift differences observed for the 2b proton resonances are quite small ($\Delta\delta < 0.25$ ppm); thus, inspection of the ^{13}C signals for the 2b resonances could be informative. Indeed, the ^{13}C resonances follow the same trend, wherein $\alpha(\text{OHex})\text{Tol}_2$ ($\Delta\delta$ -0.6 ppm) and $\alpha(\text{OHex})\text{PhOMe}_2$ ($\Delta\delta$ -1.1 ppm) are shifted upfield relative to $\alpha(\text{OHex})\text{Ph}_2$ and $\alpha(\text{OHex})(\text{PhCF}_3)_2$ is shifted downfield ($\Delta\delta$ +1.6 ppm). This trend fits well with σ_p for the **R**-groups for both the observed ^1H and ^{13}C resonances of 2b, while σ_m yields poor fits (see Supplementary data section). To ensure these observations are not artefacts of aggregation, a series of variable concentration solutions were probed for the $\alpha(\text{OHex})\text{R}_2$ series (see Supplementary data section, 50–1 mM in CDCl_3). These data for $\alpha(\text{OHex})\text{Tol}_2$ and $\alpha(\text{OHex})(\text{PhOMe})_2$ suggest that there is minimal propensity to aggregate in CDCl_3 ($\Delta\delta \leq 0.12$ ppm for all resonances), with measured K_d of $\approx 3.2 \times 10^{-4}$ M and ≈ 1.2 M for these two derivatives respectively.^{33,34} To verify the attribution of the small perturbations observed via NMR to the remote **R**-groups, we modelled the NMR spectra of the $\alpha(\text{OHex})\text{R}_2$ series computationally. To simplify simulations and clarify the assignment of NMR features, we replaced the hexyloxy groups with methoxy. To differentiate from the synthesized $\alpha(\text{OMe})\text{R}_2$ series the model series is represented as $\alpha(\text{OMe})\text{R}_2'$. In our ^1H and ^{13}C calculated NMR spectra, we rely on the widely adopted non-relativistic density functional theory (DFT) protocol with gauge including atomic orbitals (GIAO)^{35,36} as implemented in the Gaussian 16 (ref. 37) programme suite. The justification of the non-relativistic approach

comes from the smallness of the heavy atom effect in compounds containing sulfur and lighter elements only.^{38–42} In all DFT calculations, we use a popular global hybrid exchange-correlation functional (XCF) approximation B3LYP^{43,44} widely regarded in the literature as a reliable choice^{45–60} even in light of recent advances.^{47,51,53,61–64} Finally, we choose to work with polarization-consistent basis sets developed by Jensen for rational and systematic reduction of basis-set error specifically in DFT methods.^{65–67} In particular, we use pc-2 (ref. 68) for geometry optimisations and vibrational frequency calculations, and aug-pc-Sseg-2 (ref. 69) for modelling NMR spectra. The latter set belongs to the pc-Sseg-n family of basis sets augmented with additional tight exponents for the description of the electronic density near atomic nuclei and optimized for nuclear magnetic shielding. These sets have been known to markedly outperform other available choices for core-related properties.^{70,71} Due to the poor solubility of **α (OHex)(PhCF₃)₂** – and the entire **α (OMe)**R**₂** series – only experimental resonances extracted from the ¹H–¹³C HSQC spectra were used for comparison to calculated parameters. Comparison of the ¹H and ¹³C isotropic shieldings for the model **α (OMe)**R**₂**' series to the synthesized **α (OHex)**R**₂** (shown in Figure 2.4) and **α (OMe)**R**₂** (see Supplementary data section) series yield quality fits ($r^2 > 0.9$), further indicating that the modulation of the interior chemical shifts is directly related to the remote **R**-groups.

With the model **α (OMe)**R**₂**' series validated, we sought to probe how the **R**-groups impact the aromaticity of the α -NDT core. Nucleus independent chemical shift (NICS)⁷² calculations are a well-known computational means to assess the aromatic (or antiaromatic) character of heteroarene systems.^{73–75} Specifically, NICS-XY scans^{76,77}

wherein the ghost atom is set to 1.7 Å. above the planar α -NDT core were performed to ascertain if there are electronic effects in the core that were not apparent via traditional spectroscopic means. In Figure 2.4b, we detail the results of the NICS-XY scans for the $\alpha(\text{OMe})\text{R}_2'$ series referenced against a model compound without **R**-groups, $\alpha(\text{OMe})'$.

The $\alpha(\text{OMe})\text{R}_2'$ cores are weakly paratropic no matter the **R**-group (NICS_{1.7 π ZZ} values $\approx$ 4–6.5 ppm over the path of the probe); there are minor deviations in the ‘B’ ring that follow the Hammett parameter (σ_p specifically) of the **R**-group (i.e. there is an increase in aromatic character as the R-group becomes more electron deficient).

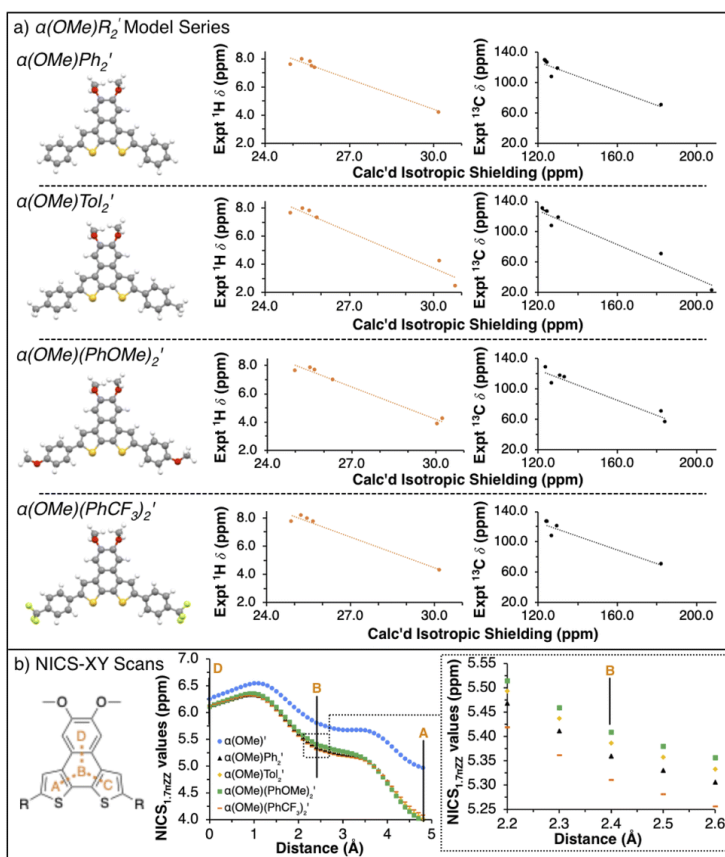


Figure 2.4. Computational analysis of $\alpha(\text{OMe})\text{R}_2'$ series. (a) Ball-and-stick representations of model compounds $\alpha(\text{OMe})\text{R}_2'$ and their respective experimental vs. calculated NMR plots (^1H is shown in orange, ^{13}C is given in black). (b) Partial NICS_{1.7 π ZZ} scans for $\alpha(\text{OMe})\text{R}_2'$ with D–B–A path highlighted in orange. (Inset): Enhanced view of the central B ring.

2.2.2 Photophysical Properties of $\alpha(\text{OHex})\text{R}_2$ Series

Our focus shifted to elucidating the photophysical properties of the $\alpha(\text{OHex})\text{R}_2$ series upon completion of their structural authentication. UV-visible absorption spectra for the $\alpha(\text{OHex})\text{R}_2$ series, shown in Figure 2.5, display defined (despite being broadened) vibronic structure in-line with known α -NDT containing materials.⁷⁸ Table 1 highlights several key metrics of these data, where there is a slight bathochromic shift when progressing from $\alpha(\text{OHex})\text{Ph}_2$ to stronger electron donating groups in $\alpha(\text{OHex})\text{Tol}_2$ and $\alpha(\text{OHex})(\text{PhOMe})_2$ ($\Delta\lambda_{\text{abs,max}} \leq 5\text{nm}$). The lone A–D–A system, $\alpha(\text{OHex})(\text{PhCF}_3)_2$, is quite distinct with a 12 nm bathochromic shift relative to parent $\alpha(\text{OHex})\text{Ph}_2$. The optical band gap ($E_{\text{g,opt}}$) was estimated from the tangent of the absorption onset, with $\alpha(\text{OHex})(\text{PhCF}_3)_2$ having the smallest gap ($E_{\text{g,opt}}$ 2.89 eV). The emission spectra (Figure 2.5 b) have strong, detailed, vibronic structure.

The fine vibronic structure observed in the emission spectra are indicative of enhanced conjugation in the excited state through rigidification of the molecules (as compared to the relatively structure-less absorption spectra). For α -NDT containing molecules this implies stabilization (and an increase in) the quinoidal resonance contribution.⁷⁹ Photoluminescence quantum yield (ϕ_{PL}) measurements were undertaken for each derivative under inert atmosphere in dry THF. $\alpha(\text{OHex})(\text{PhOMe})_2$ provided the highest quantum yield ($\phi_{\text{PL}} = 0.40$) in THF, while $\alpha(\text{OHex})\text{Ph}_2$ ($\phi_{\text{PL}} \approx 0.25$), $\alpha(\text{OHex})\text{Tol}_2$ ($\phi_{\text{PL}} \approx 0.25$), and $\alpha(\text{OHex})(\text{PhCF}_3)_2$ ($\phi_{\text{PL}} \approx 0.24$) are within the error of the technique ($\pm 10\%$). These results are in agreement with known phenylene end-capped α -NDTs $\alpha(\text{PhBu})_2$ ($\phi_{\text{PL}} \approx 0.28$)²⁰ and $\alpha(\text{PhN}(\text{PhOMe})_2)_2$ ($\phi_{\text{PL}} \approx 0.55$).¹⁶ Itami and co-workers posited that these photoactive molecules are suitable hole transporting materials,

which is an application we plan on pursuing in the future with solubilized a-NDTs. It is worth noting that the highly polarized all-donor systems containing anisole-based end-caps provided the highest quantum yields whether directly attached ($\alpha(\text{OHex})(\text{PhOMe})_2$) or connected via an amine linkage ($\alpha(\text{PhN}(\text{PhOMe})_2)_2$).

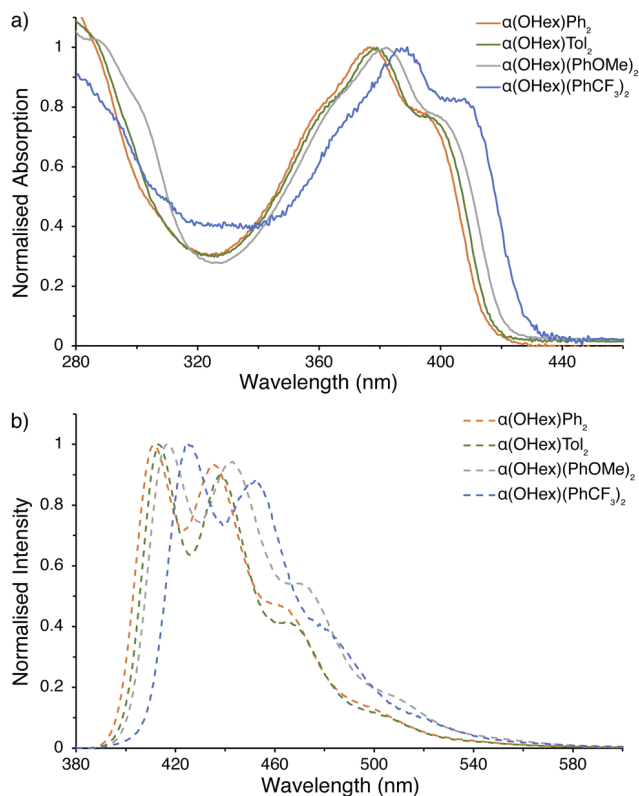


Figure 2.5. Photophysical measurements for $\alpha(\text{OHex})\text{R}_2$ series. (a) UV-visible spectra; (b) emission spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$). All samples were prepared under an inert atmosphere with degassed dry THF.

$\alpha(\text{OR}')\text{R}_2$	ϵ ($\text{M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{abs,max}}$ (nm)	$E_{\text{g,opt}}^b$ (eV)	λ_{em}^c (nm)	Φ_{PL}^c
$\alpha(\text{OHex})\text{Ph}_2$	3.78×10^4	377	2.99	412	0.25
$\alpha(\text{OHex})\text{Tol}_2$	3.67×10^4	379	2.97	416	0.25
$\alpha(\text{OHex})(\text{PhOMe})_2$	3.40×10^4	382	2.94	419	0.40
$\alpha(\text{OHex})(\text{PhCF}_3)_2$	1.18×10^4	389	2.89	427	0.24

Table 1.0. ^aUV-visible and emission spectra for $\alpha(\text{OHex})\text{R}_2$ series measured as solutions in dry, degassed THF under inert atmosphere. ^b $E_{\text{g,opt}}$ estimated from the tangent of the absorption onset, ($\lambda_{\text{abs,onset}} = 365 \text{ nm}$)

2.2.3 Synthesis and structural analysis of $\beta(\text{Oi-Pent})\text{R}_2$ series

The poor solubility of the $\alpha(\text{OHex})\text{R}_2$ series led us to reconfigure the solubilizing groups for the β -NDT series to a short, branched alkoxy group that promotes solubility but still allows for crystallization. Alkylation of 4,5-dibromocatechol with isopentyl bromide efficiently affords **1(Oi-Pent)** as a colorless oil that is converted to **3(Oi-Pent)** via Suzuki cross-coupling with 2-thiophene boronic acid in modest yield on the gram scale (Figure 2.6). This is quite astonishing considering this boronic acid coupling partner is known to undergo moderate proto-deborylation under traditional cross-coupling conditions.⁸⁰ Blocking of the unfunctionalized α -positions of the thienyl groups is required prior to planarization to mitigate polymerization (or rearrangement).^{78,81} With this in mind, bromination⁸² of the residual α -positions of **3(Oi-Pent)** affords **4(Oi-Pent)** in modest yield. In our hands traditional Scholl oxidation conditions were inefficient (yields < 10%) to planarize the brominated species, but organic oxidant and acidic conditions (DDQ, methanesulfonic acid, DCM)^{82,83} proved to be far superior in accessing $\beta(\text{Oi-Pent})\text{Br}_2$ in modest yield (>40% isolated yields on 500 mg scale).

End-capping of **$\beta(\text{Oi-Pent})\text{Br}_2$** with the aryl boronic acid derivatives yields the **$\beta(\text{Oi-Pent})\text{R}_2$** series as off-white to pale yellow solids. Exchanging the solubilizing groups for isopentyloxy resulted in an appreciable improvement in solubility, with all **$\beta(\text{Oi-Pent})\text{R}_2$** being soluble in common organic solvents (e.g. 50 mM in CDCl_3). The central goal of using the isopentyloxy groups is to thread the needle between solubility and the ability to grow single crystals for analysis. After several attempts with all derivatives, single crystals suitable for X-ray diffraction were grown via vapor diffusion of hexanes into a saturated solution of **$\beta(\text{Oi-Pent})\text{Tol}_2$** in THF. The crystal obtained for **$\beta(\text{Oi-Pent})\text{Tol}_2$** is dimeric, wherein the two units are aligned in the same direction with the β -NDT cores offset (i.e. a slip-stacked arene–arene stacking arrangement) with a distance between the dimers of $\approx 3.6 \text{ \AA}$ (see Supplementary data section). The interring C–C bond length for **$\beta(\text{Oi-Pent})\text{Tol}_2$** is $1.46 \text{ \AA}$, nearly identical to the same metrics obtained in the **$\alpha(\text{OMe})\text{R}_2$** series.

However the crystallographic packing of **$\beta(\text{Oi-Pent})\text{Tol}_2$** dimers into columnar stacks is distinct in comparison to the **$\alpha(\text{OMe})\text{R}_2$** series. This difference in crystallographic packing can be brought back to the branch alkoxy solubilizing group of **$\beta(\text{Oi-Pent})\text{Tol}_2$** , which upon crystallization intercalate with adjacent stacks, thus allowing for columnar stacks of the dimers to form.

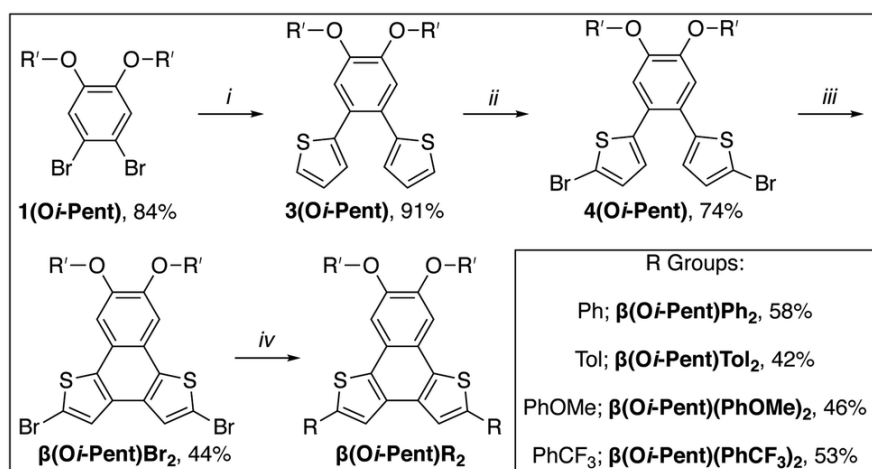


Figure 2.6. Synthesis of **β (Oi-Pent)R₂** series. (i) 2-Thiophene boronic acid, Pd(PPh₃)₂Cl₂, 2 M K₂CO₃, THF, 80 °C, overnight; (ii) NBS, CHCl₃, RT, 2 d; (iii) DDQ, MeSO₃H, DCM, 0 °C to RT, 1 h; (iv) **R** boronic acid, Pd(PPh₃)₂Cl₂, 2 M K₂CO₃, THF, 80 °C, overnight. Inset: isolated yields for **β (Oi-Pent)R₂** series.

The partial aromatic region shown in Figure 2.7 reveals the interior 2b proton resonance (as well as the ¹³C resonance) is responsive to remote functionalization. These perturbations of the 2b proton and carbon resonances are quite similar to those observed in the **α (OHex)R₂** series, with the **β (Oi-Pent)R₂** series having $\Delta\delta \approx 0.2$ ppm for ¹H and $\Delta\delta \approx 2$ ppm for ¹³C. Fitting these chemical shifts to both σ_p and σ_m Hammett parameters reveals a quality correlation to σ_p , albeit not as pure of a fit as with the **α (OHex)R₂** series. Although the **β (Oi-Pent)R₂** derivatives are quite soluble, one concern for the poor fit (r^2 0.7) for the ¹H spectra is aggregation. The orientation of the thiophene rings in the β -NDT isomer give the molecules a pronounced bent shape (the approximate bite angle of the terminal substituents is 110°) in comparison to the α series (bite angle $\approx$ 125°), which may impact their propensity for aggregation.

Solutions of **β (Oi-Pent) Tol₂** and **β (Oi-Pent)(PhOMe)₂** in CDCl₃ were prepared and analyzed across a range of concentrations (50–1 mM, see Supplementary data

section) to probe this concern. Only chemical shifts in which $\Delta\delta \geq 0.05$ ppm were included in the fitting analysis,^{33,34} revealing K_d values of 1.1 M and 1.5 M for $\beta(\text{Oi-Pent})\text{Tol}_2$ and $\beta(\text{Oi-Pent})(\text{PhOMe})_2$, respectively. These values are in-line with the $\alpha(\text{OHex})\text{R}_2$ series, highlighting that the minor geometric differences in the bent NDTs do not impart vastly different aggregation potential.

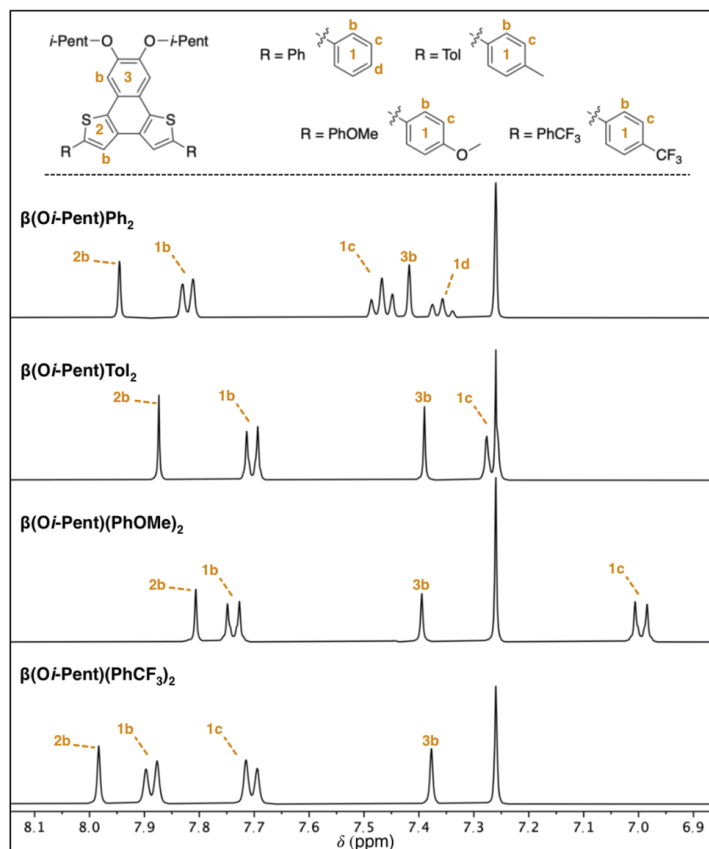


Figure 2.7. Partial ¹H NMR spectra for the $\beta(\text{Oi-Pent})\text{R}_2$ series with assignment of aromatic resonances (400 MHz, CDCl₃). See Supplementary data† for full spectra and complete chemical shift assignments.

Following the same computational methodology as the α -NDT series, model compounds bearing methoxy groups were used to calculate both the NMR spectra and perform NICS-XY scans. The model β -NDT series, $\beta(\text{OMe})\text{R}_2'$, reveals that the experimental ¹H and ¹³C resonances obtained from the ¹H–¹³C HSQC spectra for each

derivative yield quality fits ($r^2 > 0.9$) with the calculated isotropic shielding values (see Supplementary data section). NICS-XY scans across the β -NDT core yields a similar pattern to the $\alpha(OMe)R_2$ series, with the central differences being the NICS_{1.7 π ZZ} values of the 'A' ring ($\beta(OMe)R_2$) are ≈ 0.4 ppm lower than $\alpha(OMe)R_2$). The 'B' ring follows the same trend with σ_p , although the differences between each derivative are minute (Δ NICS_{1.7 π ZZ} values ≈ 0.10 ppm, see Supplementary data).

2.2.4: Photophysical properties of $\beta(Oi-Pent)R_2$ Series

The change in potential conjugation path between the α - and β -isomers opens the possibility of the β -NDT isomer to break the aromaticity of the upper aromatic ring (labelled as ring 3 in Figure 2.7), as is observed in Höger and co-workers β -DTP system.^{25,26} Disrupting this Clar sextet^{84,85} is unlikely, thus conjugation from the R-groups to solely the thiophene units is expected. Figure 2.8 details the UV-visible and emission spectra of the **$\beta(Oi-Pent)R_2$** series, revealing the β -isomer to be quite different than the **$\alpha(OHex)R_2$** series. Critically, there are no discernible differences in the photophysical properties between the **$\beta(Oi-Pent)Ph_2$** , **$\beta(Oi-Pent)Tol_2$** and **$\beta(Oi-Pent)(PhOMe)_2$** derivatives (Table 2). These derivatives have broadened vibronic structure in both the emission and excitation spectra.

In contrast to their α -NDT series counterparts the **$\beta(Oi-Pent)Ph_2$** , **$\beta(Oi-Pent)Tol_2$** and **$\beta(Oi-Pent)(PhOMe)_2$** derivatives have larger band gaps ($E_{g,opt} > 3.10$ eV) and decreased Φ_{PL} , with **$\beta(Oi-Pent)(PhOMe)_2$** having the largest difference between isomers at 20% below **$\alpha(OHex)(PhOMe)_2$** . While there are, to the best of our knowledge, no directly comparable quantum yields in the literature for β -NDTs, this drop in quantum yield has been observed in scrambled bent NDTs (compound 2l, $\Phi_{PL} = 0.03$)²⁰ and with

Miyazaki and co-workers 2,3-naphthalimide-fused benzodithiophenes ($\Phi_{\text{PL}} \approx 0.03$ -
0.09).²²

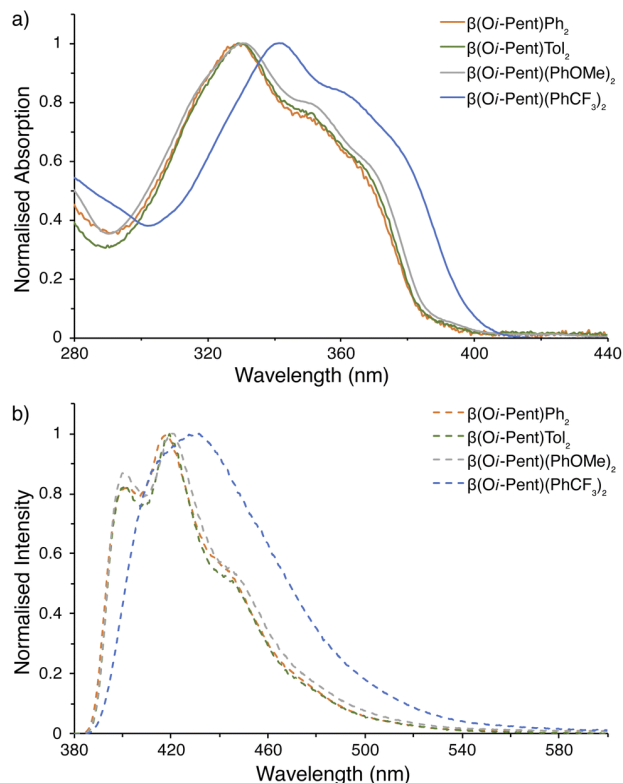


Figure 2.8. Photophysical measurements for **$\beta(\text{Oi-Pent})\text{R}_2$** series. (a) UV-visible spectra; (b) emission spectra ($\lambda_{\text{ex}} = 365$ nm). All samples were prepared under inert atmosphere with degassed dry THF.

$\beta(\text{Oi-Pent})\text{R}_2$	$\varepsilon (\text{M}^{-1}\text{cm}^{-1})$	$\lambda_{\text{abs,max}}$ (nm)	$E_{\text{g,opt}}$ (eV)	λ_{em} (nm)	ϕ_{PL}^c
$\beta(\text{Oi-Pent})\text{Ph}_2$	4.98×10^4	331	3.22	418	0.16
$\beta(\text{Oi-Pent})\text{Tol}_2$	4.31×10^4	330	3.22	420	0.16
$\beta(\text{Oi-Pent})(\text{PhOMe})_2$	6.25×10^4	331	3.21	421	0.20
$\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$	4.40×10^4	342	3.10	432	0.23

Table 2.0. ^aUV-visible and emission spectra for **$\beta(\text{Oi-Pent})\text{R}_2$** series measured as solutions in dry, degassed THF under inert atmosphere. ^b $E_{\text{g,opt}}$ estimated from the tangent of the absorption onset, ($\lambda_{\text{abs,onset}} = 365$ nm)

However, **$\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$** is distinct in this analysis. The UV-visible spectrum is bathochromically shifted ($\lambda_{\text{abs,max}} = 11 \text{ nm}$) in comparison to the rest of the **$\beta(\text{Oi-Pent})\text{R}_2$** series with similar vibronic structure, but the emission spectrum is broadened and ill-defined. This is in stark contrast to the rest of the **$\beta(\text{Oi-Pent})\text{R}_2$** series (and the **$\alpha(\text{OHex})\text{R}_2$** series), where the emission spectra have detailed structure (in THF).

A series of variable polarity solvents was used to elucidate the extent, and type, of solvatochromism. The absorption spectra of **$\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$** display a weak hypsochromic shift ($\Delta\lambda_{\text{abs}} = 4 \text{ nm}$), with a larger (albeit still weak) bathochromic shift ($\Delta\lambda_{\text{em}} = 9 \text{ nm}$) observed in the emission spectra (Figure 2.9). This solvatochromism is well-correlated with the solvent polarity parameter, $E_{\text{T}}(30)$,⁸⁶ with r^2 values of 0.98 and 0.87 for the absorption and emission spectra respectively. It should be noted that $E_{\text{T}}(30)$ values for binary solvent mixtures such as THF-MeCN, used here as the maximum polarity solvent, are quite complex⁸⁷ and the figure used here (based on mole fractions) is an approximation. However, it is apparent that this solvatochromism trend is due to the stabilization of the excited state in polar solvent, which in turn yields a larger Stokes shift as solvent polarity increases (Table 3). The A–D–A alignment of **$\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$** in tandem with the modest Stokes shift ($\approx 10\text{-}20 \text{ nm}$) observed imply that the excited state geometry is quite rigid due to the push-pull of the intramolecular charge transfer.⁸⁸ Photoluminescence quantum yields for each solvent are given in Table 3 for **$\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$** , which are in-line with the positive fluorosolvatochromism observed in Miyazaki and co-workers systems.²²

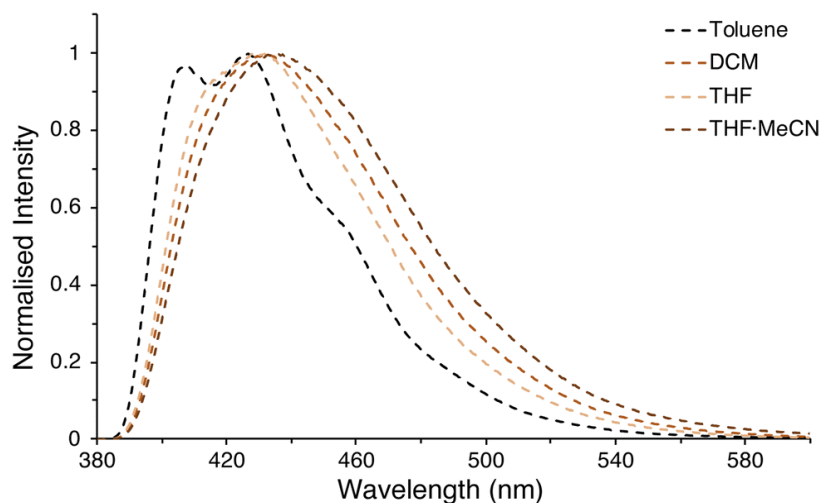


Figure 2.9. Fluoresolvatochromism observed for $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$.

Solvent	$E_T(30)$ (kcal mol ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	$\lambda_{\text{abs,max}}$ (nm)	λ_{em}^b (nm)	Φ_{PL}^b
Tol	33.9	4.37×10^4	343	426	0.18
DCM	40.7	4.68×10^4	340	432	0.17
THF	37.4	4.35×10^4	341	432	0.23
THF·MeCN	42.4 ^c	4.93×10^4	339	435	0.15

Table 3.0. ^aUV-visible and emission spectra for $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ series measured as solutions in dry, degassed THF under inert atmosphere. ^b $E_{\text{g,opt}}$ estimated from the tangent of the absorption onset, ($\lambda_{\text{abs,onset}} = 365$ nm). ^cWeighed by mole fraction of 1:1 solvent mixture.

2.3 Conclusion

In summary, two isomeric sets of bent naphthodithiophenes have been synthesized and characterized as photoactive small molecules. In both the $\alpha(\text{OR}')\text{R}_2$ and $\beta(\text{Oi-Pent})\text{R}_2$ series structural authentication in the solid-state show that the end-caps do not impact inter-ring bond lengths, yet solution-state measurements made via NMR spectroscopy show minor perturbations of interior resonances far removed from the R-

groups. In the $\alpha(\text{OHex})\text{R}_2$ series spectrophotometry measurements detail fine vibronic structure across all derivatives with modest photoluminescence quantum yields ($\Phi_{\text{PL}} \approx 0.24\text{--}0.40$). Alternatively, the $\beta(\text{Oi-Pent})\text{R}_2$ series are far less luminescent due to the limited conjugation path brought on by the orientation of the thiophene moieties.

Attachment of electron donating groups has negligible impact on the properties of the fluorophores, but electron deficient groups have a distinct response to their A–D–A motif. $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ displays positive fluorosolvatochromism and becomes broadened as solvent polarity increases, indicative of increased intramolecular charge transfer character. The photophysical characterisation of these isomeric bent NDTs highlights how these simple fluorophores have unique applications as photoactive small molecules.

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CHAPTER THREE

INTRAMOLECULAR STABILIZATION OF NAPHTHO[2,1-*B*:3,4-*B'*]DITHIOPHENES: SYNTHESIS AND ANALYSIS OF IMINE-BASED CHROMOPHORES

*This chapter is adapted from Adusei, E. B. A.; Ibrahim, S.; Jenneker, K.; Goldsmith, C. D.; Dragoi, D.; Zeller, M.; Kinney, Z. J. Intramolecular Stabilization of Naphtho[2,1-*b*:3,4-*b'*]dithiophenes: Synthesis and Analysis of Imine-Based Chromophores. J. Org. Chem. **2026**, 91, 394–400*

3.0 Summary

The role of non-covalent interactions in stabilizing and organizing complex structures throughout nature is indisputable. Of the various classes of non-covalent interactions those that involve secondary bonding, i.e. attractive interactions between σ -hole and nucleophile, are of interest in the design of materials due to their strength and programmability. This chapter takes the simplistic approach of placing nucleophilic imines in close proximity to fused thiophene moieties within naphtho[2,1-*b*:3,4-*b'*]dithiophene (α NDT) cores, wherein an intramolecular N $\cdots$ S interaction is poised to yield rigid chromophores. These types of N $\cdots$ S interactions have been observed in the solid-state for several decades, but their solution-state analysis remains unexplored, and is absent from the perspective of the photoactive bent naphthodithiophenes. Herein details of how blending $^1\text{H}/^{13}\text{C}$ NMR spectroscopy, X-ray crystallography, and molecular

modelling are used synergistically to describe the strength and impact of intramolecular N $\cdots$ S interactions on imine-functionalized α NDT chromophores, **a(1)**₂ is presented. The remote substituents on the aryl amines employed as condensation partners have minimal structural impact on the N $\cdots$ S; but the photophysical properties of strongly electron deficient (**1d** and **1dd**) or polarizing (**1c** and **1cc**) end-caps are enhanced in comparison to their neutral(**1a**) and weak (**1b** and **1bb**) counterparts. This design strategy, together with the methods employed to characterize and analyze the intramolecular N $\cdots$ S interactions, reveal how NDTs can be incorporated into complex architectures in a programmable manner.

3.1 Introduction

Heteroarenes containing thiophene moieties have been established as viable building blocks throughout organic electronics,^{1,2} with naphthodithiophenes³ finding applications in organic light-emitting diodes (OLEDs),⁴ organic field-effect transistors (OFETs),^{5–7} hole-transporting materials,^{8,9} and as a photoactive material within solar cells.^{10–12} As currently defined there are three isomeric classes of naphthodithiophenes: linear, angular, and bent.^{3,13,14} The bent NDTs are underrepresented as luminescent small molecules,^{8,9,14} presumably due to poor methods to access versatile building blocks that allow for late-stage derivatization^{15,16} and the generally poor emissive properties of thiophenes.¹⁷ Recently our laboratory has explored end-capping the isomeric bent NDTs – naphtho[2,1-*b*:3,4-*b'*]dithiophene (α) and naphtho[1,2-*b*:4,3-*b'*]dithiophene (β) – and probing their photophysical properties.¹⁴ The α series – fashioned with phenyl, *p*-tolyl, *p*-

methoxyphenyl, and *p*-trifluoromethylphenyl end-caps – yielded photoactive molecules strong defined emission ($\Phi \approx 0.20\text{--}0.40$, general depiction in Figure 3.1 a). While insightful this method of end-capping leaves little room for further derivatization or enhancement of their photoactive properties. Therefore, it is of interest to develop methods to access versatile α monomers that can be utilized in a variety of ways (i.e. late-stage derivatization of small molecules, functionalization post-reaction, or incorporation into polymeric systems).

In this regard imines¹⁸ offer several unique advantages: these dynamic linkages are predictable (i.e. the *E* conformer is thermodynamically more favorable than the *Z* conformation) and if placed adjacent to the thiophene cores are known to prefer the cisoid orientation to allow for the imine nitrogen to interact with the interior sulfur δ -hole.^{19,20} Figure 3.1b highlights work from You and co-workers elucidating the conformational landscape of chalcogen bonding^{21,22} between chalcogen bond donors (imines) and various chalcogen bond accepting chalcones (based on sulfur, selenium, and tellurium).²³ Of the four conformers available the most populated configuration is conformer-1, wherein the imine nitrogen is aligned with the chalcogen δ -hole, forming a five membered complex held together via an $\text{N}\cdots\text{S}$ interaction. In light of this finding, we hypothesized that α NDTs equipped with imines could form intramolecular $\text{N}\cdots\text{S}$ contacts, yielding rigidified photoactive molecules.

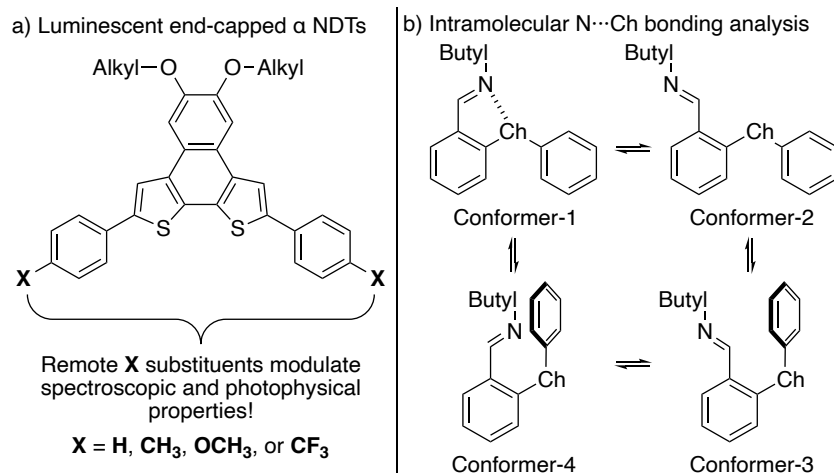


Figure 3.1. a) Luminescent α NDTs with phenylene-based end-caps; b) Work from You and Co-workers investigating intramolecular chalcogen bonding involving imines

Herein we describe the synthesis of α NDTs functionalized with a range of variable electronic amine-based end-caps. Due to the orientation of the imine units and the planar nature of the NDT core there are two potential *E* conformers available (shown in Figure 3.2, top). The remote substituents on the aniline-derived end-caps (Figure 3.2, bottom) are vital in modulating the photophysical properties of the molecules, termed **$\alpha(1)_2$** , and can influence the *E/Z* dynamics of the imine linkage itself. To observe how the remote substituents communicate with the NDT core a multi-tier approach has been taken that blends solution-state properties (NMR, UV-visible, and emission spectroscopy) with crystallographic and computational analysis. In total, the conformational landscape for the synthesized **$\alpha(1)_2$** imine series is quite distinct, with a single orientation being preferred in both the solution- and solid-states.²⁴

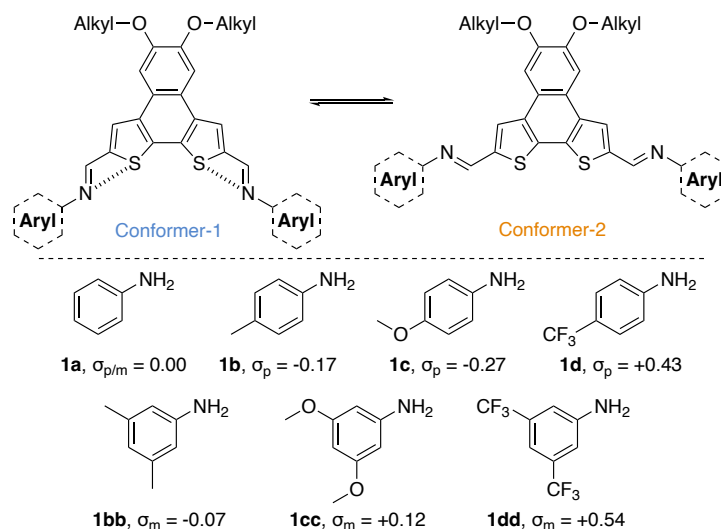


Figure 3.2. Top: general depiction of the two *E*-imine conformations available to α NDTs. Bottom: amines used in this chapter

3.2 Results and discussion

3.2.1 Synthesis of $\alpha(\text{CHO})_2$ and $\alpha(\mathbf{1})_2$ series

Dialdehyde, $\alpha(\text{CHO})_2$ shown in Figure 3.3, can be reached in four steps from 4,5-dibromocatechol²⁵ (four-step yield $\sim 10\%$, full details in Supplementary data (SD) section). Isopentyloxy groups were chosen to balance solution processibility and crystallizability while minimizing solution-state aggregation.²⁶ Due to the vast array of $\text{N}\cdots\text{S}$ interactions observed in the solid-state for benzothienyl-aryl imines^{27–35} the desire to have solid-state metrics for the $\alpha(\mathbf{1})_2$ series to benchmark against their solution-state and computational parameters is critical to the analysis. The synthetic path to solubilized α has been described in the literature (albeit with different solubilizing groups^{14,36–38}), leaving only the addition of formyl groups to the 2,9-positions for optimization. Dialdehyde synthesis was achieved by probing two aldehyde sources – *N,N*-

dimethylformamide (DMF) and 1-formylpiperidine – with dry DMF providing the best conversion of dilithiated **a** to **a(CHO)₂**. With the newly installed *bis*-formyl groups at the 2,9-positions, **a(CHO)₂** is primed to undergo imine condensation with commercially available aniline derivatives (Figure 3.2 bottom): aniline (**1a**), 4-methylaniline (**1b**), 4-methoxyaniline (**1c**), 4-(trifluoromethyl)aniline (**1d**), 3,5-dimethylaniline (**1bb**), 3,5-dimethoxyaniline (**1cc**), and 3,5-*bis*-(trifluoromethyl)aniline (**1dd**). This series of aniline derivatives have a range of electronic properties to modulate the strength of intramolecular N $\cdots$ S interactions or tune the photophysical properties of the di-imine targets.

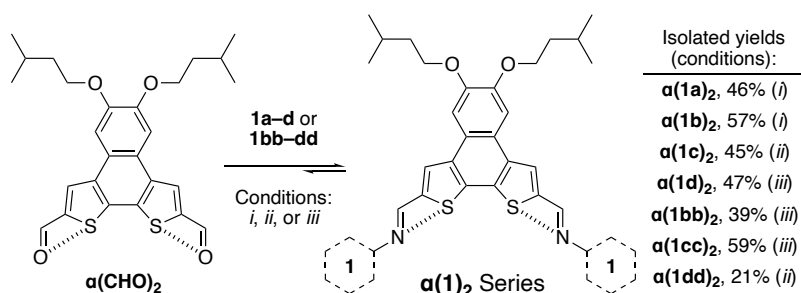


Figure 3.3 Synthesis of **a(1)₂** series. Conditions: (i) TFA, CHCl₃, 4 Å mol. sieves; (ii) Sc(OTf)₃, MeCN, CHCl₃, 4 Å mol. sieves; (iii) toluene, AcOH, Δ.

One of the central benefits of imine condensations are the variety of well-established methodologies available to drive these dynamic reactions forward: (i) acid-catalyzed condensation in the presence of molecular sieves, (ii) scandium-mediated condensation in the presence of molecular sieves,³⁹ and (iii) thermal azeotropic removal of water.¹⁸ In general conditions *ii* proved effective to access the target di-imines **a(1)₂** in modest yields ($\approx$ 33% average for the series, see Table B1). The Sc(OTf)₃ conditions

were particularly efficient at activating the electron deficient aryl amines (**1d** and **1dd**), which did not proceed to any appreciable extent with trifluoroacetic acid (TFA) as catalyst. For cases in which conditions *i* or *ii* yielded poor results (<15% isolated product) thermal conditions (conditions *iii*) were probed to ensure that the best methods were being applied. In the cases of **α (1d)₂**, **α (1bb)₂**, and **α (1cc)₂** the isolated yields for conditions *iii* were elevated to be in-line with the modest yields of the efficient coupling partners **α (1a-c)₂**. Due to the sensitivity of imines to hydrolysis the **α (1)₂** series was purified via gel permeation chromatography (GPC) using toluene as eluent. Representative chromatograms of **α (1)₂** illustrate conversion efficiency and the effectiveness of the purification method, albeit with the caveat that this only accounts for the toluene soluble components of the crude reaction mixtures (see supplementary data).

3.2.2 Crystallographic Analysis of **α (1)₂** series

To verify the presence of the proposed intramolecular N $\cdots$ S interactions we sought to examine the **α (1)₂** series in the solid-state. Due to the poor alignment of the imine lone pair and the σ -hole of the sulfur atom any intramolecular interactions observed would be defined as attractive electrostatic interactions (due to the *cis*-effect)⁴⁰ and not chalcogen bonding (where the N $\cdots$ S–C angle must be close to 180°).²² Vapor diffusion of petroleum ether into solutions of **α (1b)₂** (THF), **α (1c)₂** (DCM), **α (1d)₂** (THF), and **α (1cc)₂** (THF) produced yellow crystals of sufficient quality for single crystal X-ray diffraction. Figure 3.4 portrays ORTEP diagrams for single crystals of **α (1b)₂**, **α (1c)₂**, **α (1d)₂**, and

$\alpha(1cc)_2$ with key atoms labelled (see SI for full details). In each case the intramolecular N $\cdots$ S distance (~ 3 Å) falls within the sum of the van der Waals radii (~ 3.3 Å).

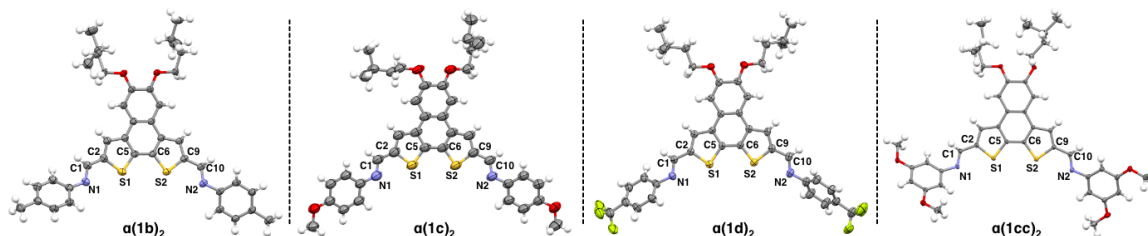


Figure 3.4. ORTEP diagrams (ellipsoids drawn at 50% probability) of **$\alpha(1b)_2$** , **$\alpha(1c)_2$** , **$\alpha(1d)_2$** , and **$\alpha(1cc)_2$** . Average select distances (Å): **$\alpha(1b)_2$** N $\cdots$ S, 3.00; **$\alpha(1c)_2$** N $\cdots$ S, 2.98; **$\alpha(1d)_2$** N $\cdots$ S, 2.94; **$\alpha(1cc)_2$** N $\cdots$ S, 3.05. Average select bond angles ($^\circ$): **$\alpha(1b)_2$** N–C–C–S, 0.6; **$\alpha(1c)_2$** N–C–C–S, -2.5; **$\alpha(1d)_2$** N–C–C–S, 4.9; **$\alpha(1cc)_2$** N–C–C–S, 1.2. Additional details given in supplementary data section.

As anticipated the four-atom arrangement is too compact to allow for quality orbital overlap, with the N $\cdots$ S–C bond angle ($\sim 140^\circ$ in all cases) being mis-aligned for strong contact between imine lone pair and S–C σ -hole. However, the strength of the intramolecular N $\cdots$ S interaction is apparent due to the high degree of planarity of the four-atom arrangement, with the N–C–C–S dihedral being essentially planar ($\pm 5^\circ$). These metrics are comparable to known four-atom benzothienyl-aryl imine crystal structures^{27–35} and their benzothienyl-pyridyl analogues.^{41–44}

Unfortunately, all attempts to crystalize **$\alpha(1a)_2$** proved futile, with hydrolysis byproducts such as **$\alpha(1a)(CHO)$** being isolated instead of the target molecule (see supplementary data section for crystallographic analysis of this particular byproduct). This byproduct is quite unique: the single imine linkage is orientated in the non-intramolecular N $\cdots$ S conformation while the aldehyde is cisoid to the interior sulfur (i.e.

there is an intramolecular O $\cdots$ S contact with a distance of ~ 3 Å). Overall, the **$\alpha(1)_2$** series exhibits modest stability under ambient conditions, with decomposition via hydrolysis being detected for both the *m*-aryl and *p*-aryl derivatives after weeks of storage.

3.2.3 Solution-State Analysis of **$\alpha(1)_2$** series

With the presence of these N $\cdots$ S interactions authenticated in the solid-state we sought to probe their propensity in the solution-state. In solution the imine linkages are proposed to freely rotate between conformer-1 and conformer-2 (Figure 3.5, top), wherein the NMR spectra are expected to correlate to the average conformation. Inspection of the ^1H NMR spectra, shown in Figure 4, reveals that the entire **$\alpha(1)_2$** series have well-resolved signals that are quite uniform in nature, suggesting rapid imine rotation on the NMR timescale. Inspection of resonances **1** and **2b**, which are most impacted by the distribution between the two lowest energy rotamers (conformer-1 and conformer-2), highlight that these molecules are predominately in the same rotamer configuration: the gold highlighted signals of the imine proton have $\Delta\delta < 0.10$ ppm and the grey highlighted signals of the interior thienyl **2b** proton have $\Delta\delta < 0.20$ ppm. Modulation of **2b** of this magnitude is reasonable based on previous results with phenylene end-caps,¹⁴ with concentration effects having minimal impact on the observed δ . This modulation of end-cap communication to the core can also be observed in the imine ^{13}C resonance, which correlates well with the remote substituent Hammett parameter⁴⁵ (Figure 3.5, inset). Aside from these resonances being in similar locations, it

is difficult to surmise which conformation is preferred in solution, thus additional analysis is required to properly assign the dominant solution-state population.

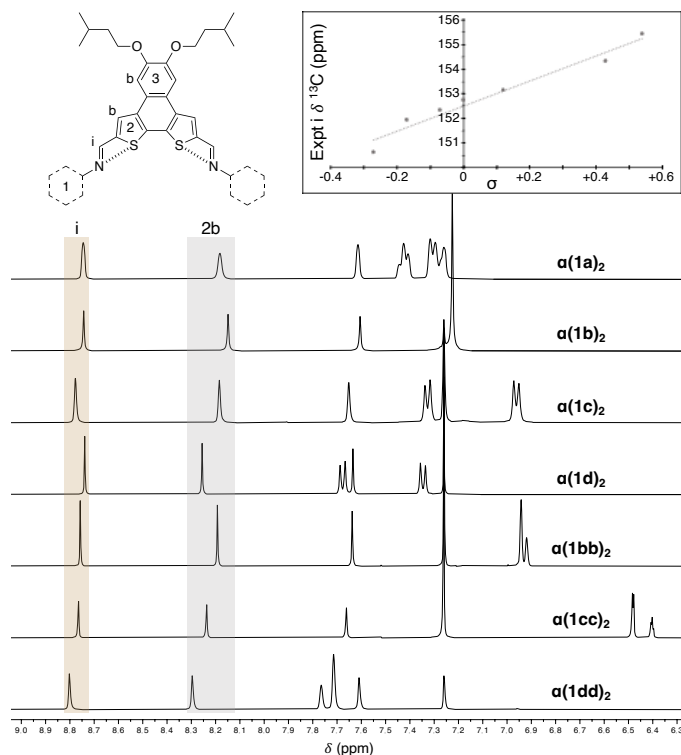


Figure 3.5. Partial ^1H NMR spectra of the $\alpha(\mathbf{1})_2$ series (400 MHz, CDCl_3). Gold highlighted i resonance covers $\Delta\delta < 0.1$ ppm, grey highlighted 2b resonance covers $\Delta\delta < 0.2$ ppm. Inset: Correlation of ^{13}C imine resonance and Hammett parameter of remote substituent ($R^2 \sim 0.96$).

To ascertain which conformation is preferred in solution we explored the $\alpha(\mathbf{1})_2$ series computationally. To reduce variability the isopentyloxy groups were simplified to methoxy groups for the computational analysis – defined as $\alpha(I)_2$ – with the goal of keeping all the aromatic resonances in similar environments. Both conformer-1 and conformer-2 (generic representations of $\alpha(I)_2$ are shown in Figure 3.6, top) were treated under identical conditions in the gas phase to optimize their geometries and perform

vibrational frequency calculations using the dispersion corrected ω B97-XD functional⁴⁶ with a cc-pVDZ basis set,⁴⁷ both of which are well-established for systems of this size and atom composition.⁴⁸ Comparison of the resulting geometries reveals in all cases that conformer-1 is preferred by ~ 3 kcal/mol over conformer-2, with minimal perturbation from the remote substituents on the aryl amines (see supplementary data section tables B 2 – B 8 for full details). The validity of these weak interactions (estimated to be ~ 1.5 kcal mol⁻¹ per N $\cdots$ S based on energetic difference between conformer-1 and conformer-2) was probed by natural bond orbital (NBO)^{49,50} analysis for conformer-1. The lone pair of the imine nitrogen, although mis-aligned for strong interaction with the σ -hole of the S–C bond, was found to be stabilizing by ~ 1 kcal mol⁻¹ for the $\alpha(I)_2$ series with no dependence on the remote substituent (see supplementary data section tables B 2 – B 8 for exact values obtained from NBO analysis of N $\cdots$ S–C interactions). While it is promising that this computational result matches the conformation observed via crystallography, the goal is to understand the propensity of N $\cdots$ S interactions in the solution.

The ¹H and ¹³C spectra for the $\alpha(I)_2$ series were calculated utilizing the Gauge Including Atomic Orbitals (GIAO) protocol^{51,52} as implemented in Gaussian 16 with a polarizable continuum model (PCM)⁵³ to ensure the calculated spectra are corrected for the experimental solvent used (CHCl₃ as solvent, see supplementary data section for additional details).⁵⁴ For comparison of the experimental and computed spectra we focused on the resonances extracted from ¹H-¹³C HSQC spectra, allowing for both the ¹H and ¹³C spectra to be used in the analysis.

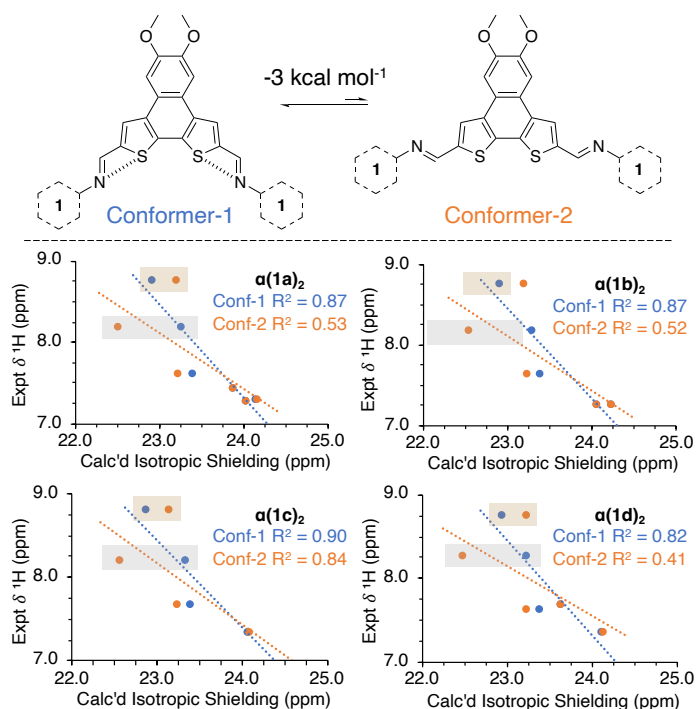


Figure 3.6. Computational analysis of $a(1a-d)_2$ series. Top: general representations of two available E conformations. Bottom: Experimental vs calculated ^1H NMR plots reveal strong correlations for conformer-1 (blue) and poor fits for conformer-2 (orange). Gold and grey shaded regions represent the imine (i) and interior thienyl proton (2b). Computational method: PCM(CHCl_3)/ $\omega\text{B97-XD/cc-pVDZ}$.

The ^1H spectra are vital in this approach: Figure 3.5 reveals that for the p -aryl imine series the calculated chemical shifts of conformer-1 are a quality fit for the observed resonances (average $R^2 \approx 0.86$), while conformer-2 is generally a poor fit (average $R^2 \approx 0.57$). The comparison of experimental ^{13}C resonances and the calculated isotropic shieldings are generally quality fits for all resonances, a feature that was expected based on the carbons being in essentially the same environment in both conformer-1 and conformer-2 (see supplementary data section for full ^1H and ^{13}C computational analysis of both the p -aryl and m -aryl imines). In total, blending the

observed experimental resonances and the calculated isotropic shieldings yields a solution-state preference for the N $\cdots$ S conformer-1 across the **a(1)**₂ series.

3.2.4 Photophysical Properties **a(1)**₂ series

With the authenticated structures in hand our focus shifted to examining the photophysical properties of the **a(1)**₂ series. Imines notoriously diminish the emission of their respective molecules due to energy loss via non-radiative decay pathways.⁵⁵ With these systems displaying intramolecular N $\cdots$ S contacts we hypothesized this may allow for a modest emission response. UV-visible absorption spectra for the **a(1)**₂ series, shown in Figures B60 and B61, have nearly identical vibronic structure that is comparable to previously reported phenylene-based end-caps,^{8,9,14} with the core difference being the n- π^* low energy shoulder being less prominent (i.e. it appears mixed with the λ_{max} attributed to the π - π^* transition). Table 4 details several key metrics obtained throughout the analysis, wherein the λ_{max} and estimated $E_{\text{g,opt}}$ ⁵⁶ reside in a tight range no matter the aryl amine substituent. The emission spectra of the **a(1)**₂ series are quite distinct: **a(1a)**₂, **a(1b)**₂, and **a(1bb)**₂ yield essential no response ($\Phi_{\text{PL}} < 0.1\%$). The other derivatives, whether having an electron donating or withdrawing substituents, **a(1c)**₂, **a(1d)**₂, **a(1cc)**₂, and **a(1dd)**₂ yield emission with modest vibronic structure with weak quantum yields. These emission spectra are substantially overlapped with the absorbance, indicative of an anti-stokes shift. This is reminiscent of the triplet-triplet annihilation anti-stokes shift⁵⁷ observed by Yang and co-workers on BODIPY-based chromophores.⁵⁸ Molecules

displaying this type of emission response, even in low efficiencies, are of interest as bio-imaging agents.⁵⁹

$\alpha(1)_2$	ϵ^a (M ⁻¹ cm ⁻¹)	$\lambda_{\text{abs,max}}^b$ (nm)	$E_{\text{g,opt}}^c$ (eV)	λ_{em}^d (nm)	ϕ_{PL}
$\alpha(1a)_2$	1.02×10^4	417	2.58	—	—
$\alpha(1b)_2$	7.61×10^3	421	2.62	—	—
$\alpha(1c)_2$	1.55×10^3	431	2.56	406	0.4%
$\alpha(1d)_2$	9.42×10^3	420	2.60	468	0.2%
$\alpha(1bb)_2$	4.07×10^3	419	2.62	—	—
$\alpha(1cc)_2$	3.32×10^4	421	2.61	416	0.6%
$\alpha(1dd)_2$	7.40×10^3	426	2.58	440	0.2%

Table 4.0. Photophysical metrics of $\alpha(1)_2$ series: ^aUV-visible and emission spectra were measured as solutions in dry, degassed toluene under inert atmosphere. ^bHighest intensity peak above 315 nm. ^c $E_{\text{g,opt}}$ estimated using 0nset. ^d $\lambda_{\text{ex}} = 365$ nm.

Recently the photoisomerization of imines from *E*-to-*Z* with visible light (405–450 nm) has been studied in detail by Greenfield and co-workers.^{60–62} These imine-systems (aryliminopyrazoles, AIPs) feature electron donating groups *ortho* to the aldehyde coupling partner which assists in stabilizing the *Z* configuration, which then converts thermally to the more stable *E* configuration. Phenylene-thienyl imines have been observed to undergo rapid *E/Z* photoisomerization as well, with the maximum amount of photoconversion to *Z* being 20% after irradiating at 365 nm.⁶³ During the course of analysis under standard conditions the **$\alpha(1)_2$** series does not exhibit ¹H resonances indicative of the *Z* configuration.

However, the **a(1)**₂ series described in this chapter may well undergo *E*-to-*Z* photoisomerization at $\lambda_{\text{ex}} = 365$ nm, therefore we carried out preliminary irradiation experiments followed by prompt ¹H NMR acquisition. Electron deficient end-caps are known to induce photoisomerization in benzylimines,⁶⁴ yet in **a(1dd)**₂ the presence of the *Z* configuration of the imine proton (or any additional signals) was not detected. This result mirrors that of Barik and Skene with imine-linked fluorenes, whose polyaromatic hydrocarbon cores elevate the inversion barrier of photoisomerization such that it is not feasible under these conditions.⁶⁵ The poor emission of imines is often derived from the low rotation barrier about the imine linkage,⁶⁶ which in these systems is likely the reason for the large portion of nonradiative decay (e.g. computational results depict the energetic differences between conformer-1 and conformer-2 to be < 3 kcal/mol, which is far smaller than the photoisomerization inversion barrier).

3.3 Conclusion

This chapter has shown that the **a** NDT building block is a unique building block for photoactive molecules bearing imines. By strategically placing the imines in close proximity to the interior sulfur atoms an attractive electrostatic interaction forms, termed N $\cdots$ S, that rigidifies the **a(1)**₂ series such that their ¹H NMR spectra are representative of a single conformation (conformer-1) in solution. This conformation was also observed in the solid-state for **a(1b)**₂, **a(1c)**₂, **a(1d)**₂, and **a(1cc)**₂ series, with an average N $\cdots$ S distance of 3 Å. The remote substituents of the aryl amines modulate the imine ¹³C resonance, with communication to the thiophene core being weak (internal 2b resonance

of the thienyl moieties is modulated by < 0.20 ppm). Photophysical analysis of the **a(1)**₂ series depict a set of molecules that have modest molar absorptivities ($>10^3$ M⁻¹ cm⁻¹) and poor quantum yields ($<1\%$). These attributes – in combination with the observed anti-stokes shifts in **a(1c)**₂ and **a(1cc)**₂ – depict these chromophores as being useful photoactive materials.

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CHAPTER FOUR

ASYMMETRIC NAPHTHO[2,1-*b*:3,4-*b'*]DITHIOPHENES AS π -BRIDGES IN
INTRAMOLECULAR PUSH-PULL CHROMOPHORES.

4.0 Summary

V-shaped donor– π –acceptor (D– π –A) systems offer a powerful strategy for promoting intramolecular charge transfer (ICT) through geometric asymmetry and directional electronic polarization. Bent naphtho[2,1-*b*:3,4-*b'*]dithiophenes (NDTs) are themselves a V-shaped scaffold due to the inherent angular orientation of the thienyl moieties. However, previous symmetric end-capped and diimine-functionalized derivatives either lacked true donor–acceptor asymmetry or suffered from inefficient emission due to conformational flexibility (this is an imine specific issue). Herein, we report in this chapter the synthesis and photophysical analysis of an asymmetric α -NDT monoimine series, $\alpha(\text{PhCF}_3)(\mathbf{1})$, that realizes a genuine V-shaped D– π –A motif through installation of a trifluoromethyl-substituted aryl acceptor and an aniline-derived imine donor on opposite termini of the bent NDT core. The monoimine derivatives are accessed through a 3-step protocol from a common NDT core. Solution-state NMR spectroscopy reveals well-resolved asymmetry of the aromatic region with chemical shifts reminiscent of end-to-end communication from donor to acceptor. UV–visible absorption spectra show closely related vibronic features and narrow optical bandgaps (2.68–2.72 eV), while emission behavior depends sensitively on donor strength. Stronger aniline donors yield

modest but measurable fluorescence with structured blue emission that closely overlaps the absorption profile, indicative of limited excited-state relaxation within the polarized framework.

4.1 Introduction

V-shaped donor– π –acceptor (D– π –A) small molecules represent a versatile design platform in organic electronics, where angular geometries promote directional intramolecular charge transfer (ICT), enhance dipole moments, and enable tunable photophysical responses.^{1–4} In these systems, molecular shape and electronic asymmetry act cooperatively: the bent π -bridge core enforces spatial separation of donor and acceptor fragments, while maintaining electronic communication necessary for efficient ICT^{5–10} valuable for generating high-performance photoactive materials with vast applications including organic light emitting diodes (OLEDs), nonlinear optical materials, bioimaging agents, and solution-processable organic semiconductors.^{10–13} Our group has long been interested in developing bent NDT-based materials with these characteristics. Initial efforts focused on functionalizing isomeric bent α -NDT core with electron-withdrawing and donating aryl groups at both termini, generating the end-capped NDT derivatives shown in Figure 4.1a.¹⁴ While these systems behave as Acceptor-Donor-Acceptor (A–D–A) motifs and displayed good emission, particularly with derivatives bearing electron-withdrawing substituents (a result of their rigidification of the excited state and suppression of nonradiative decay),^{15,16} they do not constitute true V-shaped A–D–A architectures, and also did not provide room for further

derivatization/optoelectronic tuning of the NDT cores. Next, we synthesized a series of α -NDT diimines (Figure 4.1b) that introduces push–pull aryl-substituted imine functionalities adjacent to the sulfur atoms, enabling intramolecular N $\cdots$ S interactions, favoring the desired conformation. Despite the increased electronic polarization introduced by the diimine groups, the resulting derivatives were poor emitters, functioning primarily as chromophores rather than fluorophores.¹⁷ We attribute this behavior to the imine rotational flexibility that facilitate excited-state relaxation through nonradiative pathways.^{16,18–21} These limitations indicated that the diimine approach, while electronically interesting, was also not suitable for producing true V-shaped donor– π –acceptor (D– π –A) systems that promotes ICT mechanism, as they lack the necessary directional donor–acceptor asymmetry across the bent NDT framework.

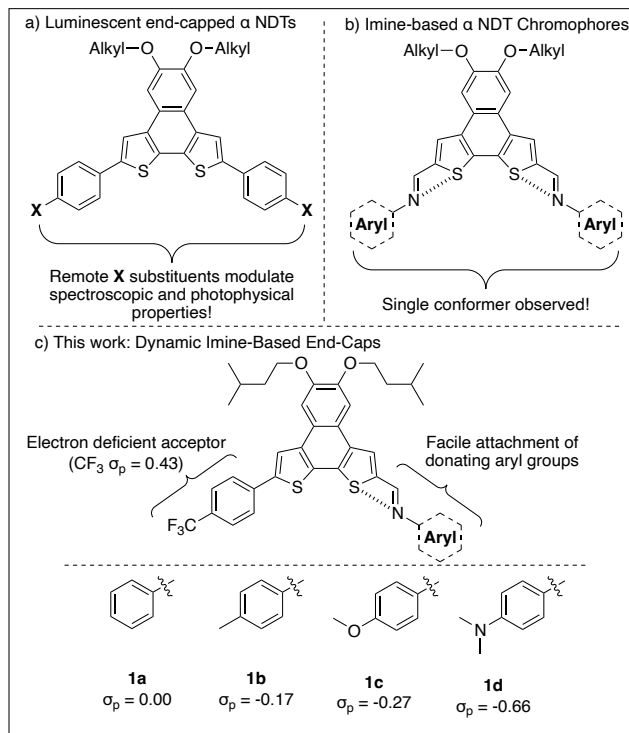


Fig 4.1 a) Luminescent phenylene-based end-capped α -NDTs by Adusei and co-workers. b) Push-pull aryl-substituted diimine α -NDTs rigidified via intramolecular $\text{N} \cdots \text{S}$ interactions. c) This work: asymmetric functionalized to dynamic imine-based V-shaped α -NDT end-caps

To overcome this limitation, we turned our attention to asymmetric functionalization to realize a genuine V-shaped NDT donor–acceptor motif.^{2,22–27} By installing an electron-withdrawing aryl group (*p*-trifluorophenyl, **PhCF₃**) on one terminus of the NDT core (via Suzuki coupling) and an electron-donating aniline-based imine (**1a–d**) on the opposite terminus creates a V-shaped asymmetric system in which the bent α NDT core acts as the bridging π -linker. The resulting systems promise to be capable of enhanced ICT and improved photophysical performance.

Herein, we report in this chapter the synthesis, structural characterization, and photophysical properties of the $\alpha(\text{PhCF}_3)(\mathbf{1a-d})$ asymmetric imine series. Together, these results demonstrate that monoimine functionalization provides an effective route to electronically polarized, emissive NDT-based D–A systems and offer new insight into the interplay between substitution pattern, intramolecular interactions, and excited-state behavior in bent heteroarenes.

4.2 Results and Discussion

4.2.1 Synthesis of $\alpha(\text{PhCF}_3)(\mathbf{1})$ series

Asymmetric functionalization of α NDT can be accomplished via a three-step protocol. Briefly, α is mono lithiated and quenched with dry *N,N*-dimethylformamide (DMF), yielding $\alpha(\text{CHO})$ with a singular formyl group at position 2. Bromination under facile conditions furnishes $\alpha(\text{CHO})\text{Br}$ in moderate yield (see supplementary data section 4.1.1). $\alpha(\text{CHO})\text{Br}$ undergoes Suzuki-miyaura cross-coupling reaction with the commercially available strong electron deficient 4-(trifluoromethyl)phenyl boronic acid to obtain $\alpha(\text{PhCF}_3)(\text{CHO})$ in Fig 4.2. With the already installed formyl group at position 2 on the NDT, $\alpha(\text{PhCF}_3)(\text{CHO})$ is primed to undergo imine condensation^{29–31} to yield $\alpha(\text{PhCF}_3)(\mathbf{1a-c, bb})$ with commercially available aniline derivatives (Figure 4.2, bottom): Aniline (**1a**), 4-methylaniline (**1b**), 4-methoxyaniline (**1c**), and 1,3-dimethylaniline (**1bb**).

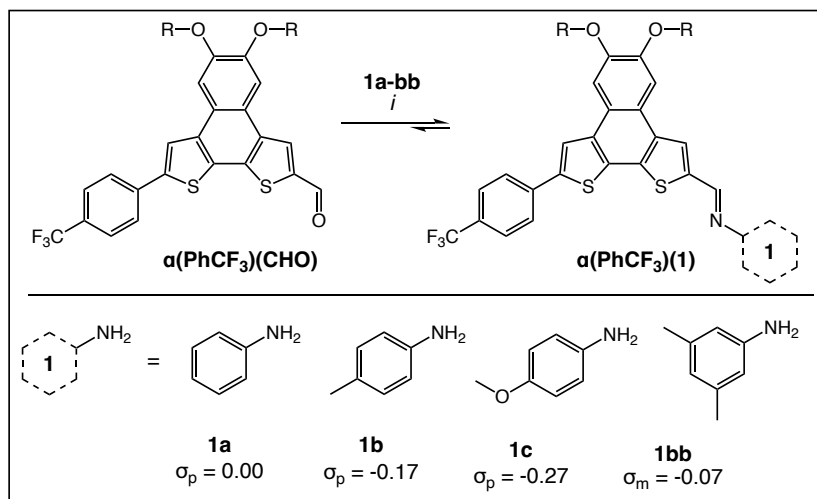


Figure 4.2 Synthesis of $\alpha(\text{PhCF}_3)(\mathbf{1})$ Series. (i) deacidified CHCl_3 , $4\text{\AA}$, Aniline or *p*-substituted anilines, $\text{Sc}(\text{OTf})_3$, MeCN, >16 hrs.

Scandium triflate^{29,31} proved to be an effective catalyst in activating the aryl amines with modest yields recorded for both the asymmetric imine derivatives. All imine products were subjected to purification on the gel permeation chromatography (GPC) using a toluene isocratic elution system.

4.2.2 Solution state analysis of $\alpha(\text{PhCF}_3)(\mathbf{1})$ series

Inspection of the ^1H NMR spectra for the $\alpha(\text{PhCF}_3)(\mathbf{1})$ monoimine series (Figure 4.3) reveals that all derivatives exhibit sharp and well-resolved aromatic resonances, indicating rapid imine rotation on the NMR timescale^{32,33} and that the compounds adopt similar conformations in solution. As expected for an asymmetric NDT scaffold, three protons—*i*, *2b*, and *4b*, offer a reliable measure of substituent-induced electronic changes within the NDT core. Among these, the imine proton *i* shows only a very small dispersion across the series, reflecting modest modulation of the local polarization at the

C=N bond. This behavior is consistent with fast exchange among low-energy conformers, resulting in a single, averaged chemical shift.^{34–36} Protons *2b* and *4b*, located on the interior thienyl NDT ring in different chemical environments, demonstrate how electronic effects from the substituents are communicated through the bent π -system.^{37–39} Although both protons shift systematically across the series, *2b*, situated closer to the CF₃-substituted aryl end cap is more deshielded relative to the *4b*, causing it to resonate downfield. This modest but reproducible modulation mirrors the behavior previously observed for both α -diimine¹⁶ and phenylene end-capped¹⁴ NDT derivatives and is consistent with through-bond transmission of substituent effects from the imine donor toward the CF₃ acceptor terminus.^{40–42}

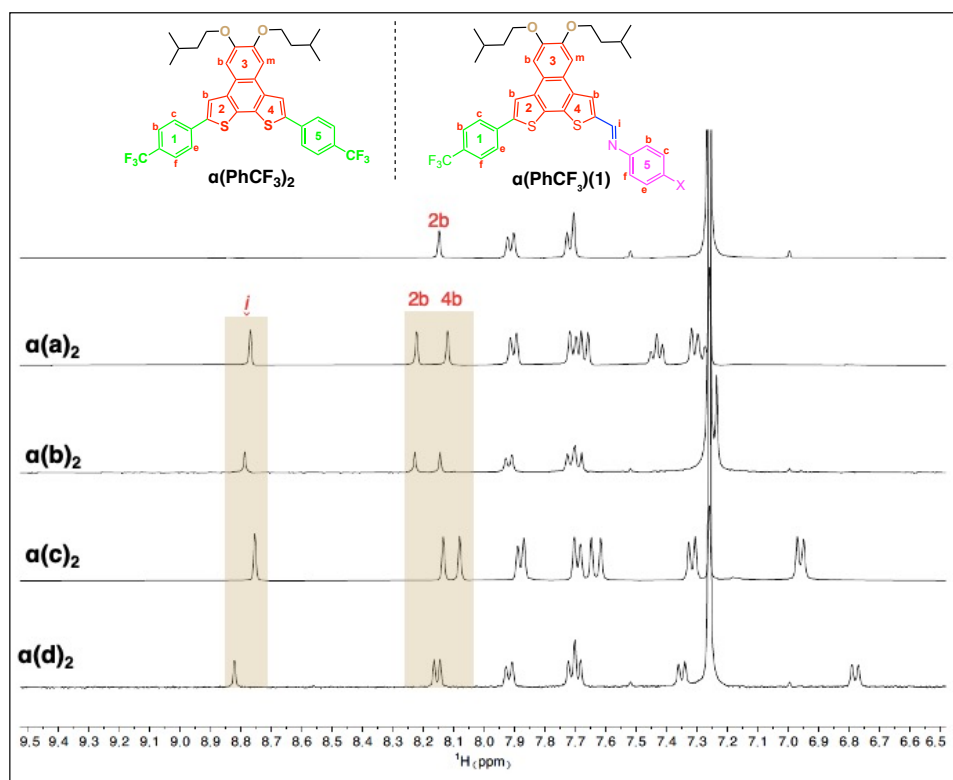


Figure 4.3 Partial ^1H NMR spectra for the $\alpha(\text{PhCF}_3)(\mathbf{1})$ series with assignment of aromatic resonances compared with symmetric endcapped $\alpha(\text{PhCF}_3)_2$ (400 MHz, CDCl_3). Currently include synthesized $\mathbf{1d}$ (*p*-*N,N* Dimethylphenyl derivative). $\mathbf{1bb}$ will be included in publication. See Supplementary data section for full spectra and assignments.

Computational studies were performed to support the structural analysis of the $\alpha(\text{PhCF}_3)(\mathbf{1a-c, bb})$ mono imine series. To reduce computational cost while retaining the electronic features relevant to the NDT core and imine linkages, the isopentyloxy solubilizing groups were simplified to methoxy substituents in all computational models. These truncated structures are hereafter referred to as the $\alpha(\text{PhCF}_3)(\mathbf{1a-c, bb})$ model compounds. Geometry optimizations and harmonic frequency calculations were carried out using Gaussian 16, employing a dispersion corrected functional ($\omega\text{B97X-D}$) and a

well-rounded, albeit limited, basis set from Dunning (cc-pVDZ). This level of theory was selected to provide a balanced description of π -conjugated organic systems while explicitly accounting for dispersion interactions. All optimized structures correspond to true minima, as confirmed by the absence of imaginary frequencies (see supplementary data section figures C37–C40).

The optimized geometries were subsequently used to calculate the NMR spectra to support the experimental spectral assignments. ^1H and ^{13}C NMR isotropic shieldings were computed using the gauge-including atomic orbital (GIAO) method with an implicit chloroform (CHCl_3) solvent model, consistent with prior computational treatments in this work. These calculations were performed at the $\omega\text{B97X-D/cc-pVDZ}$ level of theory in Gaussian 16. Comparison of calculated and experimental chemical shifts indicates that the *E*-conformer featuring an intramolecular $\text{N}\cdots\text{S}$ contact provides the best agreement for the $\alpha(\text{PhCF}_3)(\mathbf{1a-c, bb})$ series (see supplementary data section, figures C41–C43).

4.2.3 Photophysical Properties of $\alpha(\text{PhCF}_3)(\mathbf{1})$ series

The photophysical properties of the $\alpha(\text{PhCF}_3)(\mathbf{1})$ series were examined by steady-state UV–Vis absorption and emission spectroscopy to probe the impact of electronic asymmetry on the excited-state behavior of the NDT core. UV–visible absorption spectra for the $\alpha(\text{PhCF}_3)(\mathbf{1})$ monoimine series (Figure 4.4) display highly similar vibronic structure across all derivatives, closely resembling that observed in previously reported α -diimine NDT systems.⁴³ In contrast to the α -diimine analogues, however, the lower-energy $n\text{--}\pi^*$ shoulder is less distinct in the monoimines and appears merged with the

dominant π – π^* transition. The broad nature of the absorbance spectra is as a result of the increased intramolecular charge transfer mechanism within the series. As summarized in Table 5.0, both the absorption maxima and the estimated optical bandgaps ($E_{g,opt} = 2.68$ – 2.72 eV) fall within a narrow range, indicating that substitution on the aniline ring exerts only modest influence on the ground-state electronic structure.

The emission behavior of this series is more differentiated—the entire series exhibit weak to negligible emission ($\Phi_{PL} < 2.5\%$). In all cases, the emission profiles show substantial overlap with their corresponding absorption spectra, resulting in anti-stokes shifts. Such behavior is reminiscent of chromophores whose rigid excited states undergo minimal structural relaxation, leading to closely aligned absorption and emission bands. Materials with this type of optical response are of growing interest for applications in imaging^{44–47} and sensing,^{48–50} where compact relaxation pathways and blue-shifted emission can be advantageous. The $\alpha(\text{PhCF}_3)(\mathbf{1a-c}, \mathbf{bb})$ scaffolds therefore provide an intriguing platform for further exploration of asymmetric NDT-based fluorophores.

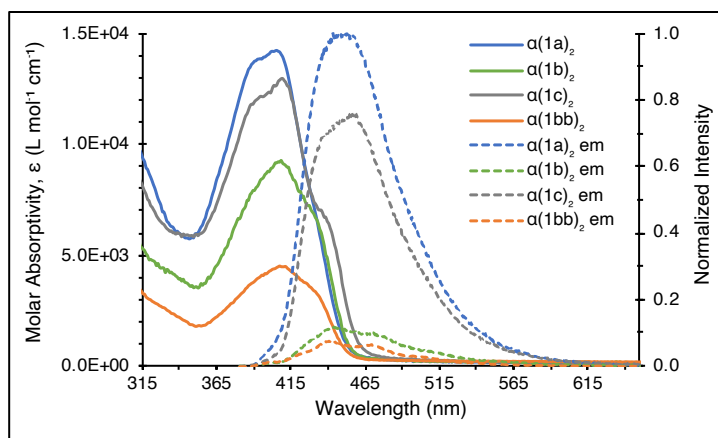


Figure 4.4 UV-visible and emission spectra ($\lambda_{\text{ex}} = 365$ nm) of $\alpha(\text{PhCF}_3)(\mathbf{1})$ series. All samples were prepared under inert atmosphere with degassed dry toluene.

$\alpha(\text{PhCF}_3)(\mathbf{1})$	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{abs,max}}$ (nm)	$E_{\text{g,opt}}$ (eV)	λ_{em} (nm)	Φ_{PL}
$\alpha(\text{PhCF}_3)(\mathbf{1a})$	1.22×10^4	405	2.72	443, 448	2.3%
$\alpha(\text{PhCF}_3)(\mathbf{1b})$	8.83×10^3	408	2.70	447	0.3%
$\alpha(\text{PhCF}_3)(\mathbf{1c})$	1.24×10^4	409	2.68	457	1.9%
$\alpha(\text{PhCF}_3)(\mathbf{1bb})$	4.26×10^3	407	2.70	441	0.6%

Table 5.0 Photophysical metrics of $\alpha(\text{PhCF}_3)(\mathbf{1})$ series: ^aUV-visible and emission spectra were measured as solutions in dry, degassed toluene under inert atmosphere. ^bHighest intensity peak above 315 nm. ^c $E_{\text{g,opt}}$ estimated using Onset. ^d $\lambda_{\text{ex}} = 365$ nm.

4.3 Conclusion

In conclusion, asymmetric monoimine functionalization of the α -NDT scaffold provides an effective strategy for generating true V-shaped donor–acceptor systems. Installation of the CF_3 -aryl acceptor and an aniline-derived imine donor on opposite termini produces monoimines. The monoimines exhibit predictable, substituent-dependent electronic perturbations across the NDT core, as revealed by $^1\text{H}/^{13}\text{C}$ NMR analysis. The resulting $\alpha(\text{PhCF}_3)(\mathbf{1a-c, bb})$ derivatives display tunable absorption and structured blue emission that closely overlaps the absorption profile, reflecting limited

excited-state relaxation within the polarized NDT. These findings demonstrate that asymmetric substitution, rather than symmetric diimine or end-capped architectures, offers a more effective route to electronically polarized NDT chromophores and establishes a foundation for further development of bent heteroarene D- π -A materials.

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CHAPTER FIVE

BENT NAPHTHO[1,2-*B*:4,3-*B'*]DITHIOPHENE CHROMOPHORES: DEPENDANCE OF INTRAMOLECULAR N···S STRENGTH ON REMOTE SUBSTITUENTS

5.0 Summary

Weak non-covalent interactions, including attractive electrostatic interactions, are an effective strategy for controlling the conformational landscape of a chromophore and enhancing the excited-state behavior within the π -conjugated system. In this chapter, we report the synthesis, structural analysis, and photophysical characterization of a series of bent naphtho[2,1-*b*:3,4-*b'*]dithiophene (β -NDT) diimines bearing electronically varied aniline endcaps. The β -diimine derivatives were found to exhibit highly symmetric ^1H NMR spectra, consistent with the presence of one dominant conformational species in solution on the NMR timescale. Density functional theory calculations (ω B97X-D/cc-pVDZ) nevertheless identify several accessible geometries arising from rotation about the C=N bond and thiophene backbone, with the computed energy differences between these conformers being small, in some cases less than 1.0 kcal mol $^{-1}$. This indicates a relatively shallow conformational landscape. UV–visible absorption studies display broad and structured π – π^* transitions ($\lambda_{\text{max}} = 352\text{--}400$ nm). Weak photoluminescence ($\Phi_{\text{PL}} \leq 0.6\%$) was however observed from the emission spectra, reflecting efficient nonradiative decay mediated by imine torsional flexibility.

5.1 Introduction

Imines are among the most versatile π -conjugating linkages in organic materials chemistry as they extend delocalization and provide a synthetically straightforward handle for tuning electronic structure.^{1–3} Through the incorporation of C=N bonds, conjugation length and orbital alignment can be systematically modulated without significant changes in molecular size, making imines valuable design elements in donor–acceptor frameworks, luminescent materials, and charge-transporting systems.^{4–6} Nevertheless, imines often diminish fluorescence efficiency due to torsional relaxation and the accessibility of nonradiative decay channels around the C=N bond.^{7–9} Strategies to suppress these losses, such as rigid aromatic fusion, extended conjugation, and the introduction of noncovalent intramolecular interactions, have therefore been central to enhancing emissive performance in photoactive small molecules and polymeric materials.^{10–12} Among such interactions, heteroatom-assisted contacts, particularly those involving nitrogen and sulfur ($N\cdots S$), are of growing interest for their ability to constrain imine rotation, rigidify π -backbones, and modulate excited-state behavior.^{13–15}

Our earlier work on α -naphtho[1,2-*b*:4,3-*b'*]dithiophene (α -NDT) diimines (Figure 5.1 aⁱⁱ) in chapter three demonstrated that positioning nucleophilic imine nitrogens adjacent to the sulfur atoms of a fused thiophene core promotes intramolecular $N\cdots S$ contacts, generating conformationally biased and π -extended chromophores.¹⁶ This design principle builds upon the seminal observations of Oussaid and co-workers who first correlated thiophene–imine orientation with conformational stability in simple 2-

iminomethylthiophenes.¹⁷ Their work established that imine–thiophene systems preferentially adopt a *trans* (2c-*trans*) arrangement driven by dipolar and hyperconjugative alignment between the nitrogen lone pair and the thiophene π -system, setting a conceptual precedent for modern intramolecular N $\cdots$ S stabilization strategies (Figure 5.1 aⁱ). In the α -NDT framework, these heteroatom-assisted interactions rigidify the backbone, suppressing C=N torsion and leading to a dominant planar conformation that enhances electronic delocalization. The resulting diimines exhibit strong visible absorption yet remain weakly emissive, a behavior linked to facile excited-state relaxation through residual imine flexibility. Building on these insights, the present work in this chapter explores the β -isomeric diimine derivatives based on naphtho[2,1-*b*:3,4-*b'*]dithiophene (β -NDT), (Figure 5.1b) where the reversed annulation attenuates N $\cdots$ S overlap and introduces multiple accessible conformations.^{18–20} This structural inversion provides a stringent test of how geometric constraints modulate secondary bonding and photophysical properties in heteroatom-rich chromophores.

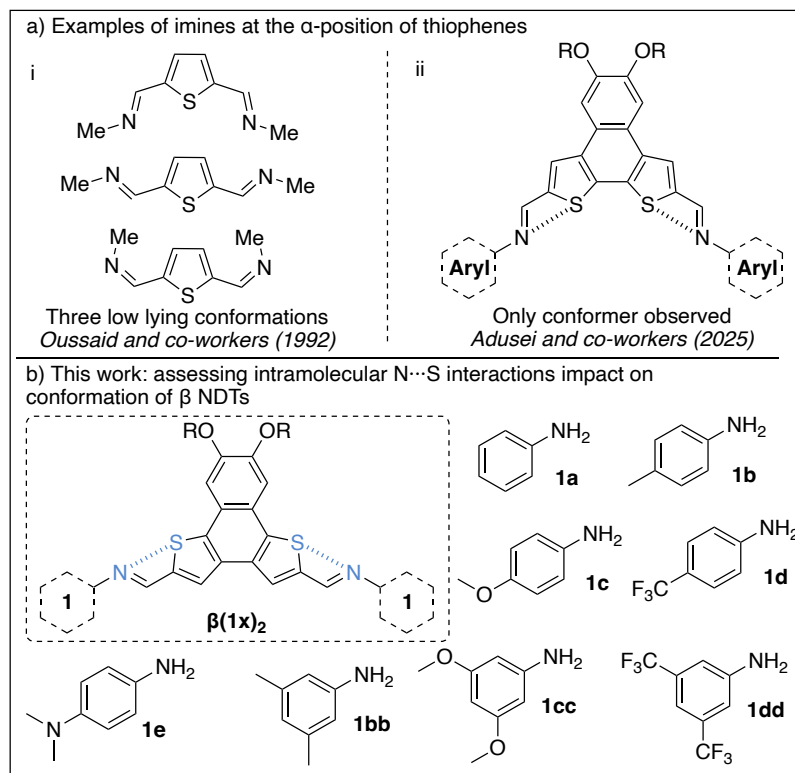


Figure 5.1 aⁱ) Oussaid and co-workers work on correlated thiophene–imine orientation with conformational stability in simple 2-iminomethylthiophenes. aⁱⁱ) *E*-conformer preferred aryl-substituted diimine α -NDTs rigidified via intramolecular N $\cdots$ S interactions. b) This work: naphtho[2,1-*b*:3,4-*b'*]dithiophene (β -NDT) diimines bearing electronically varied aniline end caps.

5.2 Results and discussion

5.2.1 Synthesis and structural analysis of $\beta(1)_2$ series

Synthesis of the naphtho[2,1-*b*:3,4-*b'*]dithiophene *bis*(aldehyde) precursor $\beta(\text{CHO})_2$ commenced with alkylation of 4,5-dibromocatechol using 1-bromo-3-methylbutane to introduce a methylbutyloxy (OMeBu) solubilizing group, which improves both solution-phase processability and solid-state characterization of downstream derivatives.²¹ Subsequent Suzuki–miyaura cross-coupling with 2-

thienylboronic acid furnished the intermediate **3** as a white crystalline solid following column purification. To prevent uncontrolled polymerization during oxidative cyclization^{22,23}, the intermediate **3** was brominated,²⁴ to give the dibrominated precursor **4**. Planarization was achieved using oxidative acidic conditions (DDQ and methanesulfonic acid in dichloromethane),^{24,25} affording $\beta(\text{Br})_2$ as an off-white solid after silica gel purification and trituration in heptane. Directed lithiation at the α -positions of the thiophene rings followed by electrophilic quenching with *N,N*-dimethylformamide (DMF)¹⁶ yielded the dialdehyde $\beta(\text{CHO})_2$ as a yellow solid. Optimization studies indicated that THF was the preferred solvent for the lithiation step and that DMF was superior to 1-formylpiperidine as the formylating agent. As observed in the α -NDT series, trace quantities of the monoaldehyde $\beta(\text{CHO})$ were generated as byproducts but were effectively removed by silica gel chromatography. Installation of aldehyde groups at the α -positions enabled subsequent imine condensation reactions with a panel of commercially available anilines. These included aniline (**1a**), 4-methylaniline (**1b**), 4-methoxyaniline (**1c**), 4-aminobenzotrifluoride (**1d**), 3,5-dimethylaniline (**1bb**), 3,5-dimethoxyaniline (**1cc**), and 3,5-bis(trifluoromethyl)aniline (**1dd**), affording the corresponding β -NDT diimines $\beta(\text{1a-d})_2$ through $\beta(\text{1dd})_2$.

The *para*-substituted β -NDT diimines $\beta(\text{1a-d})_2$ were synthesized via acid-catalyzed condensation of $\beta(\text{CHO})_2$ using scandium triflate²⁶ with the corresponding *para*-substituted anilines. Thermally driven condensation reaction in toluene under Dean–Stark conditions^{16,27} afforded lower yields relative to the scandium triflate approach. The

meta-substituted β -NDT diimines **$\beta(1bb-dd)_2$** were however synthesized by condensation of **$\beta(CHO)_2$** with *meta*-substituted anilines under dehydrative conditions in good yield via reflux in toluene with a dean–stark apparatus to remove water formed. Purification of the crude **$\beta(1a-d)_2$** and **$\beta(1bb-dd)_2$** products was carried out by gel permeation chromatography (GPC) using isocratic elution with toluene. The technique efficiently removed residual starting materials and low molecular weight byproducts while minimizing exposure to moisture and acid, which can compromise product integrity. This demonstrates effective conversion and illustrate the reliability of the purification protocol.

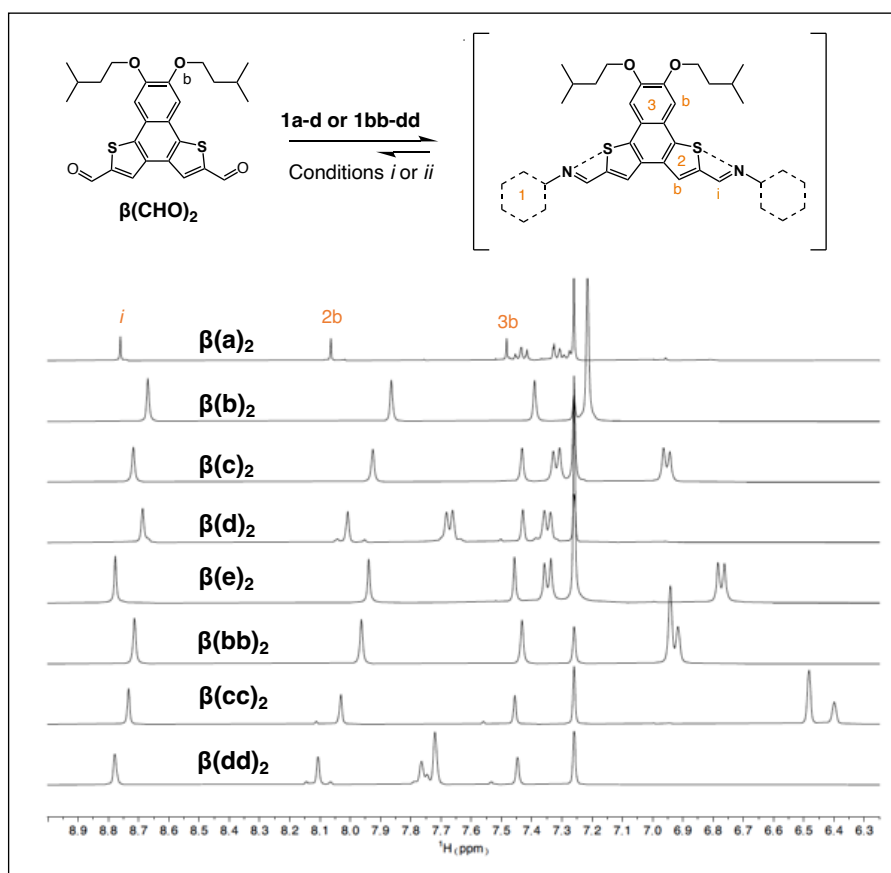


Figure 5.2. Partial ^1H NMR spectra of the β -NDT di-imine series in with the corresponding synthetic scheme presented above. Three derivatives $\beta(1d)_2$, $\beta(1cc)_2$, and $\beta(1dd)_2$ with electron withdrawing groups display additional minor imine resonances (highlighted), indicative of low-population conformers arising from alternative imine orientations or backbone distortions in solution. All spectra were acquired in CDCl_3 at ambient temperature at 400 MHz.

Initial structural insight into the β -diimines, $\beta(1)_2$, was obtained through detailed inspection of their solution-state ^1H NMR spectra (CDCl_3 , 400 MHz). Across all *para*- and *meta*-substituted derivatives, the imine proton ($\text{CH}=\text{N}$) appears as a well-resolved singlet within the δ 8.6–8.8 ppm region, consistent with the formation of a conjugated $\text{C}=\text{N}$ bond.^{28,29} The chemical shift position varies systematically with the electronic

nature of the aryl substituent, reflecting electronic communication across the imine linkage. Particular attention was given to the aromatic protons designated *i* and *2b* on the NDT framework, which are located distal to the condensation site yet remain sensitive to the π -electronic environment. These protons serve as valuable probes of conjugation and intramolecular polarization within the diimine scaffold. In the electron-deficient **β (1d)₂** and **β (1dd)₂** derivatives (bearing *para*- and *meta*-CF₃ substituents), both *i* and *2b* resonances appear downfield-shifted indicating increased π -system polarization and quinoidal character. This effect mirrors that observed in the α -series, where enhanced acceptor strength induced analogous deshielding trends.

Conversely, methyl- and methoxy-substituted derivatives (**β (1b)₂**, **β (1c)₂**, **β (1bb)₂**, **β (1cc)₂**) display upfield shifts consistent with increased aromaticity and donor-enriched D–D–D resonance forms.^{30–33} The pattern of substituent-dependent drift across *i* and *2b* is monotonic, demonstrating efficient through-bond electronic communication between the terminal aniline and the central thiophene–naphthalene core, despite the attenuated conjugation relative to α -NDT analogues.^{34–37} Importantly, minor additional imine resonances observed in some of the spectra, in Figure 5.2, are authentic structural species, not decomposition artifacts. Integration of these small signals suggests the presence of secondary conformers in equilibrium with the major *E* N $\cdots$ S-stabilized geometry in the electron withdrawing β -diimines.^{14,38,39} The occurrence of such conformational heterogeneity is characteristic of thiophene-imine systems with reduced directional N $\cdots$ S overlap, as first documented by Oussaid and co-workers in their foundational study of

thiophenyl-imine conformations¹⁷. Notably, the minor NMR signals diminished over time as the reaction proceeded. Efforts to isolate them proved futile, most likely because they correspond to a transient mixture of conformers, reflecting the reduced stability of the protonated *Z*-imine relative to the *E* form.

The conformational space of **β(1)₂** was explored computationally with Gaussian 16 utilizing the ωB97-XD functional with a cc-pVDZ basis set to accommodate the different light atoms employed.^{40–44} The isopentyloxy solubilizing groups present in the seven di-imine derivatives were simplified to methoxy groups to reduce complexity (See Supplementary data section). Further analysis predicts that the combined population of these minor conformations at 298 K corresponds to 10–15 %, in excellent agreement with the experimental NMR integration of secondary imine resonances.^{45–47} These results support the assignment of the additional small NMR peaks to low-lying conformers rather than decomposition or side products, and the major peaks from N···S calculations to the *E*-conformer (see supplementary data section figures D63–D78 for models and calculations for the conformers).

Despite repeated crystallization trials from a range of nonpolar and mixed solvents, no single-crystal X-ray structures could be obtained for any member of the **β(1)₂** series. All samples consistently produced amorphous precipitates or microcrystalline powders unsuitable for diffraction. This behavior is fully consistent with the presence of multiple low-lying conformers in solution, as inferred from NMR and computational analyses. The coexistence of these conformers likely translates to disordered packing in

the solid state, preventing the formation of a stable, long-range lattice.^{48,49} In the *E*-conformer, the geometry most closely resembling the strongly interacting α -isomer, the N $\cdots$ S distance exceeds 3.0 Å and lacks the directional overlap necessary for robust secondary bonding. As a result, β -NDT diimines lack the structural rigidity required to enforce planarity and ordered aggregation, manifesting instead as flexible, conformationally diverse chromophores. These observations highlight the delicate balance between heteroatom-assisted rigidity and geometric frustration in the design of π -extended imine chromophores.

5.2.2 Photophysical Properties $\beta(1)_2$ series

The $\beta(1)_2$, exhibits optical responses characteristic of moderately conjugated π -systems incorporating flexible C=N linkages.^{50–52} UV–visible spectra (see supplementary data section) show structured absorption bands between 352–400 nm, consistent with π – π^* transitions localized along the NDT–imine backbone. The molar absorptivities are on the order of 10^3 – 10^4 M^{–1} cm^{–1}, indicating respectable oscillator strengths despite the reduced planarity relative to the α -series. Among the derivatives, $\beta(1a)_2$ and $\beta(1c)_2$ display the highest extinction coefficients (1.8×10^4 M^{–1} cm^{–1} and 1.83×10^4 M^{–1} cm^{–1}, respectively), consistent with increased π -delocalization imparted by electron-donating end-caps.^{51,53} The optical band gaps ($E_{g,opt}$) derived from the onset of absorption range narrowly between 2.72 and 2.82 eV, signifying minimal influence of remote substituents on the electronic frontier separation. Emission measurements however reveal poorly emissive behavior, typical of dynamic imine systems prone to torsional and nonradiative

decay. The electron donating derivatives **β(1c)₂** and **β(1cc)₂**, bearing *para*- and *meta*-methoxy substituents, exhibit faint luminescence ($\lambda_{\text{em}} = 435\text{--}448\text{ nm}$; $\Phi_{\text{PL}} < 1\%$). These substituents increase donor strength and rigidify local geometry via enhanced π -resonance, modestly retarding C=N bond rotation. The electron-withdrawing CF₃ derivatives (**β(1d)₂** and **β(1dd)₂**) show negligible emission, paralleling the decreased conjugation and increased charge-transfer character observed in **α(1d)₂**. Overall, the low photoluminescence quantum yields ($\Phi_{\text{PL}} \leq 0.6\%$) indicate efficient internal conversion pathways mediated by imine torsional flexibility, a phenomenon thoroughly characterized by Oussaid and co-workers in thiophenyl-imine systems, where the *trans* conformation remains dominant, but rotation barriers are low ($\Delta E_{\text{rot}} \approx 2\text{--}3\text{ kcal mol}^{-1}$).¹⁷

β(1)₂	ϵ^{a} (M ⁻¹ cm ⁻¹)	$\lambda_{\text{abs,max}}^{\text{b}}$ (nm)	$E_{\text{g,opt}}^{\text{c}}$ (eV)	$\lambda_{\text{em}}^{\text{d}}$ (nm)	Φ_{PL}
β(1a)₂	1.80×10^4	390	2.79	—	—
β(1b)₂	1.95×10^3	395	2.79	—	—
β(1c)₂	1.83×10^4	400	2.75	—	0.4%
β(1d)₂	8.61×10^3	352	2.82	435	0.2%
β(1bb)₂	1.28×10^4	391	2.79	—	—
β(1cc)₂	2.40×10^3	378	2.73	448	0.6%
β(1dd)₂	1.50×10^4	377	2.72	—	0.2%

Table 6.0 Photophysical metrics of **β(1)₂** series. ^aUV-visible and emission spectra were measured as solutions in dry, degassed toluene under inert atmosphere. ^bHighest intensity peak above 315 nm. ^c $E_{\text{g,opt}}$ estimated using Onset. ^d $\lambda_{\text{ex}} = 365\text{ nm}$.

5.3 Conclusion

This work establishes the synthesis and photophysical characterization of a series of β -annulated naphthodithiophene diimines and highlights how annulation topology influences molecular structure and electronic behavior. In contrast to the α -NDT systems examined in chapter four, the β -annulated framework modifies the spatial relationship between the imine nitrogen and thiophene sulfur atoms, attenuating directional $N\cdots S$ interactions. Despite this structural change, the β -diimine derivatives exhibit highly symmetric ^1H NMR spectra, consistent with the presence of a single dominant conformational species in solution. Computational analysis indicates a relatively shallow conformational landscape, with small energetic differences between accessible geometries. Photophysical measurements reveal moderately conjugated chromophores characterized by near-UV absorption and weak photoluminescence across the series. Substituent variation on the terminal aniline units did not result in prominent changes in optical behavior, indicating that the β -annulated scaffold primarily governs the electronic response of these systems.

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CHAPTER SIX

GENERAL CONCLUSIONS AND FUTURE RESEARCH DIRECTIONS

6.0 General Conclusions

This dissertation investigated the design, synthesis, and photophysical characterization of functionalized bent naphthodithiophenes (NDTs) as emerging scaffolds for organic electronic materials. Studies in chapter two demonstrated that direct functionalization of α - and β -NDT cores with electron-donating and electron-withdrawing substituents produces push-pull systems that behave as fluorophores with tunable absorption and emission properties. Variation of these substituents revealed clear band-gap tuning effects, where electron-donating groups increased electron density within the conjugated framework while electron-withdrawing groups promoted intramolecular charge-transfer character, enabling modulation of the optical band gap.

In chapter three, imine functionalities introduced adjacent to the fused thiophene units of the α -NDT framework enabled intramolecular N $\cdots$ S interactions that increased molecular rigidity and conjugation. These derivatives however behaved predominantly as chromophores, displaying strong absorption with poor emission. chapter four further demonstrated that the NDT core can function as an effective π -bridge in donor- π -acceptor architectures, facilitating intramolecular charge transfer and additional band-gap modulation through electronic asymmetry. Consistent with their strong charge-transfer character, the resulting derivatives behaved primarily as chromophores and were generally poor emitters, relative to the fluorophoric systems in chapter two.

Finally, β -NDT diimine derivatives investigated in chapter five exhibited weaker N $\cdots$ S interactions with the possibility of multiple accessible conformations observed especially for the electron withdrawing derivatives in solution, resulting in systems that behaved primarily as chromophores with moderate absorption and weak fluorescence. Overall, these results establish bent NDTs as versatile platforms for tunable π -conjugated materials whose optical properties can be systematically controlled through substituent effects and intramolecular interactions.

6.1 Future Research Directions

While this work establishes a foundational understanding of isomeric bent NDT systems, further investigation could broaden the structural scope and functional potential of these materials. One of such involves expanding the donor–acceptor framework around the NDT core. Incorporating stronger donor groups such as carbazole for instance could enhance intramolecular charge-transfer character and increase fluorescence efficiency (Figure 6.1). Likewise, stronger electron-withdrawing groups such as cyano, dicyanovinyl, or meta methoxy moieties may further extend conjugation and red-shift optical absorption.

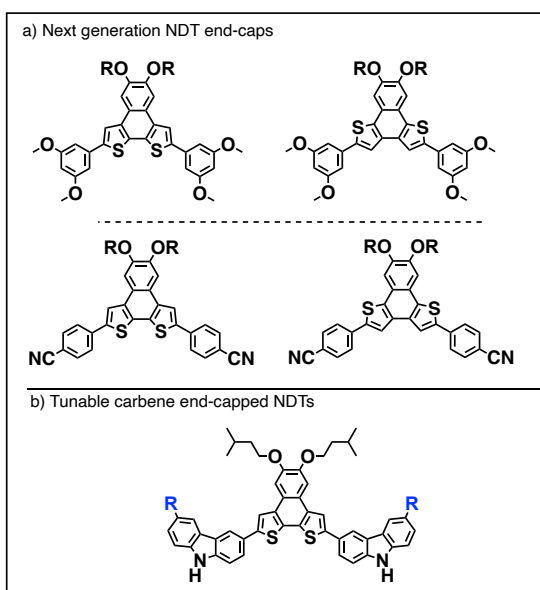


Figure 6.1. Examples of acceptor cyano and dimethoxy groups (a) tunable donor carbazole (b) for future NDT-based donor–acceptor architectures

An additional future direction involves leveraging the imine functionality of the NDT derivatives to construct higher-order architectures such as macrocycles tunable at the diamine linkers utilized. The reversible nature of imine condensation makes these systems attractive building blocks for these dynamic covalent assembly, enabling the formation of extended conjugated networks. Incorporation of metal centers through imine coordination could further yield metallomacrocycles with tunable electronic and photophysical properties (Figure 6.2).

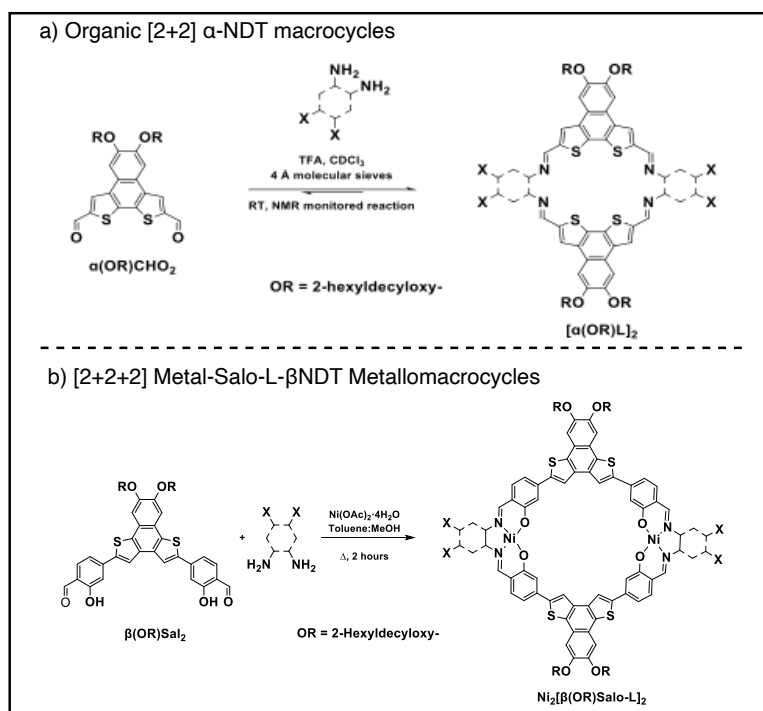


Figure 6.2. Proposed NDT-based macrocycle and metallomacrocyclic architectures formed through imine condensation and metal coordination

Ultimately, the most impactful extension of this research would involve integrating these NDT-based fluorophores and chromophores into functional devices. Thin-film fabrication and device testing could be conducted to evaluate their performance in organic electronic architectures. Even preliminary studies examining charge mobility, electroluminescence, or photovoltaic activity would help determine the practical potential of these materials.

6.2 Final Remarks

Over the course of this doctoral research, bent naphthodithiophenes have emerged as highly versatile building blocks for the design of functional organic molecules. The studies presented in this dissertation demonstrate that careful manipulation of substituent

effects, imine functionality, and intramolecular interactions provides a powerful approach to tuning the electronic structure and optical properties of these systems.

Beyond the specific compounds synthesized in this work, the broader implication is that heteroaromatic frameworks such as NDTs offer significant opportunities for rational molecular design. Continued exploration of these scaffolds, particularly through integration with donor–acceptor architectures and advanced photophysical analysis, will likely yield new materials with improved performance in emerging optoelectronic technologies.

SUPPLEMENTARY DATA

CHAPTER TWO

This supplementary data is adapted from the Supplementary information from
Adusei, Emmanuel B.A.; Casetti, Vincent T.; Goldsmith, Calvin D.; Caswell, Madison;
Alinj, Drecila; Park, Jimin; Zeller, Matthias; Rusakov, Alexander A.; Kinney, Zacharias
J. Bent Naphthodithiophenes: Synthesis and Characterization of Isomeric Fluorophores.*
RSC Advances, 2024, 14, 25120-251229

2.0 Experimental Procedures

Unless otherwise noted, all starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Anhydrous solvents (dichloromethane, hexanes, tetrahydrofuran, toluene) were purified using an Inert PureSolv solvent purification system equipped with an alumina column. NMR spectra were measured on a Bruker Avance III 400 MHz spectrometer, with all samples referenced to the residual solvent signal. High resolution mass spectra were obtained by dissolving samples in dichloromethane/methanol and analysed on a LTQ Orbitrap (ionisation method: APCI+). Absorbance spectra were recorded on a Cary 100Bio spectrophotometer and corrected for solvent background absorbance. Emission spectra were recorded on a Horiba Jobin-Yvon Fluorolog-3 fluorometer. All spectra were recorded at room temperature using 1 cm path length quartz cuvettes with spectrometric grade solvents. Fluorescence quantum yield (ϕ) measurements were performed on solutions prepared under inert atmosphere in a Vacuum Atmosphere Company NexGen glovebox with dry, degassed solvents. Quantum yields were determined by reference to 9,10-diphenylanthracene in cyclohexane ($\phi = 0.91$) which was cross-checked with

quinine bisulfate in 0.5 M H₂SO₄ (aq) ($\phi = 0.54$). Five solutions of varying concentration were prepared for each sample and good fits ($R^2 \geq 0.99$) were obtained in all cases. The absorbance of all sample solutions was kept below 0.10 to avoid the inner-filter effect. Measurements were performed at room temperature with both sample and standard excited at the same wavelength (365 nm).¹ Procedures for **1(OHex)**, **1(OMe)**, **2(OHex)**, **2(OMe)**, **3**, **a(OMe)**, and **a(OMe)Br₂** are given for clarity with appropriate literature references containing spectral identification. All procedures detailed below were carried out multiple times and the yields reported represent the median outcome of an experiment. Common reagent and solvent abbreviations: ethyl acetate (EtOAc), dichloromethane (DCM), tetrahydrofuran (THF), chloroform-*d* (CDCl₃), *N*-bromosuccinimide (NBS), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).

2.1 Synthesis of **a(OHex)R₂** Series

2.1.1 1,2-dibromo-4,5-dihexyloxybenzene, **1(OHex)**

4,5-dibromocatechol (19.0 mmol) was massed into a 250 mL round bottom flask and dissolved in 2-butanone (150 mL). A stir bar was added, followed by K₂CO₃ (57.0 mmol) and a reflux condenser. The reaction flask was flushed with argon for 5 minutes, then iodohexane (34.2 mmol) was added in one portion. The reaction temperature was then raised to 80 °C and allowed to stir for 24 hours. After 24 hours the reaction flask was cooled to RT and poured into H₂O (50 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification via silica gel flash column with Hexanes:EtOAc (99:1) mobile phase afforded 1,2-dibromo-4,5-dihexyloxybenzene (**1(OHex)**) as a colorless oil (R_f 0.56), 5.46 g (82%). Spectral details match literature values.²

2.1.2 1,2-di(3-thienyl)-4,5-dihexyloxybenzene, **2(OHex)**

A 100 mL Schlenk tube was charged with **1(OHex)** (7.23 mmol), 3-thiophene boronic acid (21.8 mmol), Pd(PPh₃)₂Cl₂ (1.13 mmol), and a stir bar added. The reaction flask was then backfilled with argon (x3), after which 40 mL dry THF and 15 mL degassed 2 M K₂CO₃ (aq) were added under positive pressure of argon. The tube was sealed under argon, and the reaction was allowed to stir in an oil bath at 80 °C overnight. After overnight stirring the reaction tube was cooled to RT, poured into H₂O (25 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification via silica gel flash column with Hexanes:DCM (4:1) eluent to afford 1,2-di(3-thienyl)-4,5-dihexyloxybenzene (**2(OHex)**) as a tacky colorless oil (R_f 0.33), 2.20 g (69%). Spectral details match literature values.³

2.1.3 5,6-bis(hexyloxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(OHex)**

A 500 mL Schlenk flask was charged with **2(OHex)** (1.64 mmol) and a stir bar, then was sparged with argon for 10 minutes. After 10 minutes dry DCM (75 mL) was added, and the reaction flask was equipped with a pressure equalising funnel. The reaction flask was then cooled to 0 °C and equilibrated for 15 minutes under argon. FeCl₃ (3.86 mmol) was massed into a beaker and dissolved in MeNO₂ (14 mL), then added to the pressure equalising funnel. The FeCl₃/MeNO₂ solution was added dropwise over five minutes to the reaction flask, after which the ice bath was removed, and the reaction was allowed to come to RT over an hour. The reaction was quenched with MeOH (10x MeNO₂) and concentrated. The crude reaction was resuspended in DCM (50 mL) and H₂O (50 mL), extracted with DCM (2x50 mL), washed with brine (2x50 mL), dried over

anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification via silica gel flash column with Hexanes:DCM (4:1) affords pure ***α*(OHex)** as an off-white solid (*R_f* 0.28), 422 mg (58%): ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 5.4 Hz, 2H), 7.70 (s, 2H), 7.47 (d, *J* = 5.4 Hz, 2H), 4.21 (t, *J* = 6.6 Hz, 4H), 1.99 – 1.88 (m, 4H), 1.56 (dd, *J* = 14.7, 6.8 Hz, 6H), 1.40 (s, 9H), 0.99 – 0.90 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ here; HRMS (APCI+) calcd for C₂₆H₃₃O₂S₂ (M+H)⁺ 441.192199, found 441.19289 (1.56 ppm).

2.1.4 2,9-dibromo-5,6-bis(hexyloxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene, ***α*(OHex)Br₂**

***α*(OHex)** (3.32 mmol) was massed into a 250 mL round bottom flask and dissolved in CHCl₃ (56 mL). A stir bar was added, and the reaction was allowed to stir under argon for 5 minutes, after which NBS (9.10 mmol) was added in portions. The reaction was left to stir for 3 days and quenched in DI water (100 mL), extracted with DCM (2x50 mL), washed with brine (2x50 mL), dried with anhydrous Na₂SO₄, decanted, and concentrated to yield crude product as a pale-yellow solid. Purification via silica gel flash column with Hexanes:DCM (19:1) as mobile phase afforded pure ***α*(OHex)Br₂** as an off-white solid (*R_f* 0.15), 1.23 g (62%): ¹H NMR (400 MHz, CDCl₃) δ 7.82 (s, 2H), 7.50 (s, 2H), 4.17 (t, *J* = 6.6 Hz, 4H), 1.94 (p, *J* = 7.0 Hz, 4H), 1.55 (m, 4H), 1.40 (m, 8H), 0.94 (t, *J* = 6.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ here; HRMS (APCI+) calcd for C₂₆H₃₁Br₂O₂S₂ (M+H)⁺ 597.013220, found 597.01476 (2.57 ppm).

2.1.5 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene, ***α*(OHex)Ph₂**

A 25 mL Schlenk tube was charged with ***α*(OHex)Br₂** (0.539 mmol), phenylboronic acid (1.780 mmol), Pd(PPh₃)₂Cl₂ (0.129 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 5 mL dry THF and 1 mL

degassed 2M K₂CO₃ solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Hexanes:EtOAc (49:1) followed by recrystallisation from hexanes to afford **a(OHex)Ph₂** as a pale yellow solid (R_f 0.22), 204 mg (64%): ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 2H), 7.78 (d, *J* = 7.6 Hz, 4H), 7.59 (s, 2H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.35 (t, *J* = 7.4 Hz, 2H), 4.20 (t, *J* = 6.7 Hz, 4H), 1.96 (p, *J* = 6.9 Hz, 4H), 1.58 (q, *J* = 7.4 Hz, 5H), 1.42 (qd, *J* = 7.1, 4.5 Hz, 8H), 1.00 – 0.91 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 149.0, 141.9, 134.8, 134.5, 129.8, 129.1, 128.0, 126.3, 122.8, 118.2, 106.7, 69.4, 31.8, 29.5, 26.0, 22.8, 14.2; HRMS (APCI+) calcd for C₃₈H₄₁O₂S₂ (M+H)⁺ 593.254799, found 593.25632 (2.56 ppm).

2.1.6 5,6-bis(hexyloxy)-2,9-di-*p*-tolyl naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(OHex)Tol₂**

A 50 mL Schlenk tube was charged with **a(OHex)Br₂** (0.424 mmol), *p*-methylphenylboronic acid (1.101 mmol), Pd(PPh₃)₂Cl₂ (0.115 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 4 mL dry THF and 0.85 mL degassed 2M K₂CO₃ solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Hexanes:Toluene (7:3) followed by recrystallisation from hexanes to afford **a(OHex)Tol₂** as a pale yellow solid (R_f 0.35), 100 mg (38%): ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 2H), 7.67 (d, *J* =

7.7 Hz, 4H), 7.60 (s, 2H), 7.25 (d, $J = 7.6$ Hz, 5H), 4.20 (t, $J = 6.6$ Hz, 4H), 2.42 (s, 6H), 1.96 (p, $J = 6.9$ Hz, 4H), 1.58 (q, $J = 7.3$ Hz, 4H), 1.42 (d, $J = 3.8$ Hz, 4H), 1.01 – 0.92 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.0, 142.1, 138.0, 134.8, 131.8, 129.8, 129.5, 126.2, 122.8, 117.6, 106.8, 69.4, 31.8, 29.5, 26.0, 22.8, 21.4, 14.2; HRMS (APCI+) calcd for $\text{C}_{40}\text{H}_{45}\text{O}_2\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 621.286099, found 621.28751 (2.27 ppm).

2.1.7 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene,

$\alpha(\text{OHex})(\text{PhOMe})_2$

A 50 mL Schlenk tube was charged with **$\alpha(\text{OHex})\text{Br}_2$** (0.512 mmol), *p*-methoxyphenylboronic acid (1.429 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.102 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 5 mL dry THF and 1 mL degassed 2M K_2CO_3 solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H_2O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na_2SO_4 , decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Hexanes:EtOAc (9:1) followed by recrystallisation from hexanes to afford **$\alpha(\text{OHex})(\text{PhOMe})_2$** as a pale yellow solid (R_f 0.49), 98 mg (29%): ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 2H), 7.69 (d, $J = 8.1$ Hz, 4H), 7.60 (s, 2H), 6.97 (d, $J = 8.1$ Hz, 4H), 4.20 (t, $J = 6.6$ Hz, 4H), 3.87 (s, 6H), 2.00 – 1.90 (m, 4H), 1.59 (t, $J = 7.5$ Hz, 5H), 1.42 (s, 9H), 0.96 (d, $J = 7.0$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.7, 148.9, 141.7, 134.7, 127.5, 127.4, 122.8, 117.0, 114.5, 106.8, 69.4, 55.5, 31.8, 29.5, 26.0, 22.8, 14.2; HRMS (APCI+) calcd for $\text{C}_{40}\text{H}_{45}\text{O}_4\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 653.275929, found 653.27712 (1.82 ppm).

2.1.8 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **α (OHex)(PhCF₃)₂**

A 100 mL Schlenk tube was charged with **α (OHex)Br₂** (0.231 mmol), *p*-(trifluoromethyl)phenylboronic acid (0.636 mmol), Pd(PPh₃)₂Cl₂ (0.049 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 4 mL dry THF and 0.50 mL degassed 2M K₂CO₃ solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Hexanes:Toluene (9:1) followed by recrystallisation from toluene to afford **α (OHex)(PhCF₃)₂** as a bright yellow solid (*R*_f 0.19), 70 mg (42%): ¹H NMR (400 MHz, CDCl₃) δ 8.15 (s, 2H), 7.92 (d, *J* = 8.1 Hz, 4H), 7.72 (d, *J* = 7.8 Hz, 6H), 4.25 (t, *J* = 6.6 Hz, 4H), 1.97 (p, *J* = 6.8 Hz, 4H), 1.64 – 1.57 (m, 4H), 1.47 – 1.35 (m, 8H), 0.98 – 0.91 (m, 6H); Due to poor solubility, only ¹³C signals obtained from ¹H–¹³C HSQC were obtained. ¹³C NMR (101 MHz, CDCl₃) δ 126.3, 119.8, 106.6, 69.5, 31.8, 29.2, 25.7, 22.8, 14.1; HRMS (APCI+) calcd for C₄₀H₃₉F₆O₂S₂ (M+H)⁺ 729.229567, found 729.23127 (2.33 ppm).

2.2 Synthesis of **α (OMe)*R*₂** Series

2.2.1 1,2-dibromo-4,5-dimethoxybenzene, **1(OMe)**

Veratrole (39 mmol), AcOH/CHCl₃ (36 mL:36 mL), and stir bar were combined in a 250 mL round bottom flask. The reaction flask was placed under argon for 5 minutes after which NBS (87.60 mmol) was added in portions. After complete addition of NBS

reaction was left under static argon to stir overnight. The reaction was quenched with aqueous Na₂SO₃, extracted with DCM (3x30 mL), washed with brine (2x30 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Recrystallisation from ethanol affords **1(OMe)** as colorless crystals, 6.34 g (37%). Spectral details match literature values.⁴

2.2.2 1,2-di(3-thienyl)-4,5-dimethoxybenzene, **2(OMe)**

A 100 mL Schlenk tube was charged with **1(OMe)** (6.79 mmol), 3-thiophene boronic acid (17.65 mmol), Pd(PPh₃)₂Cl₂ (1.09 mmol), and a stir bar, then was backfilled with argon (3x). Under positive pressure of argon dry THF (27 mL) and degassed 2M K₂CO₃ (14 mL) were added and the tube was sealed. The reaction was placed into an oil bath and stirred at 80 °C overnight. The next day, the reaction was cool to RT and poured into H₂O (25 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved through silica gel flash column with Hexanes:EtOAc (49:1) as mobile phase to afford **2(OMe)** as a colorless oil (R_f 0.xx), 1.36 g (66%). Spectral details match literature values.⁴

2.2.3 5,6-bis(methoxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(OMe)**

A 500 mL round bottom flask was charged with **2(OMe)** (3.40 mmol) and a stir bar, then was sparged with argon for 10 minutes. After 10 minutes dry DCM (136 mL) was added, and the reaction flask was equipped with a pressure equalising funnel. The reaction flask was then cooled to 0 °C and equilibrated for 15 minutes under argon. FeCl₃ (7.92 mmol) was massed into a beaker and dissolved in MeNO₂ (32 mL), then added to the pressure equalising funnel. The FeCl₃/MeNO₂ solution was added dropwise over five

minutes to the reaction flask, after which the ice bath was removed, and the reaction was allowed to come to RT over an hour. The reaction was quenched with MeOH (10x MeNO₂) and concentrated. The crude reaction was resuspended in DCM (50 mL) and H₂O (50 mL), extracted with DCM (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved through silica gel flash column Hexanes:DCM (4:1) to afford pure **a(OMe)** as a pale yellow solid (R_f 0.28), 564 mg (55%). Spectral details match literature values.⁴

2.2.4 2,9-dibromo-5,6-bis(methoxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(OMe)Br₂**

a(OMe) (2.96 mmol) was massed into a 250 mL round bottom flask. A stir bar and CHCl₃ (34 mL) were added, followed by vigorous stirring under argon (5 minutes). After equilibration NBS (7.69 mmol) was added in portions over 5 minutes. Upon complete addition of NBS the reaction was left to stir for 48 hours. After 48 hours the reaction was poured into H₂O (100 mL), extracted with DCM (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product as a yellow solid. Crude product was dissolved in 15 mL CHCl₃ then poured into MeOH (4x volume of CHCl₃), yielding pure **a(OMe)Br₂** as pale-yellow precipitate (1.04 g, 77%). Spectral details match literature values.⁵

2.2.5 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(OMe)Ph₂**

A 25 mL Schlenk tube was charged with **a(OMe)Br₂** (0.549 mmol), phenylboronic acid (1.41 mmol), Pd(PPh₃)₂Cl₂ (0.083 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 4 mL dry THF and 1 mL degassed 2M K₂CO₃ solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled

to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Toluene:EtOAc (49:1) to afford **a(OMe)Ph₂** as a pale yellow solid (*R_f* 0.29), 109 mg (55%). Single crystals suitable for x-ray diffraction were obtained from vapor diffusion of hexanes into a solution of **a(OMe)Ph₂** in THF, yielding yellow crystals. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.56 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 4.09 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.9, 142.1, 134.8, 134.5, 129.9, 129.2, 128.1, 126.3, 122.7, 118.1, 104.7, 77.5, 77.2, 76.8, 56.2; HRMS (APCI+) calcd for C₂₈H₂₁O₄S₂ (M+H)⁺ 453.098299, found 453.09829 (-0.01 ppm).

2.2.6 5,6-bis(methoxy)-2,9-di-*p*-tolyl naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(OMe)Tol₂**

A 25 mL Schlenk tube was charged with **a(OMe)Br₂** (0.557 mmol), *p*-methylphenylboronic acid (1.489 mmol), Pd(PPh₃)₂Cl₂ (0.084 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 4 mL dry THF and 0.85 mL degassed 2M K₂CO₃ solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Toluene:EtOAc (49:1) to afford **a(OMe)Tol₂** as a pale yellow solid (*R_f* 0.32), 170 mg (63%). Single crystals suitable for x-ray diffraction were obtained from vapor diffusion of hexanes into a solution of **a(OMe)Tol₂** in THF, resulting in pale yellow crystals. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 2H), 7.69 (d, *J* = 7.8 Hz, 4H), 7.61 (s, 2H), 7.31 – 7.17 (m, 4H), 4.11 (s,

6H), 2.42 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.9, 142.3, 138.1, 134.7, 131.7, 129.8, 129.7, 126.2, 122.7, 117.5, 104.8, 56.2, 21.4; HRMS (APCI+) calcd for $\text{C}_{30}\text{H}_{25}\text{O}_4\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 481.129599, found 481.13060 (2.08 ppm).

2.2.7 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene,

$\alpha(\text{OMe})(\text{PhOMe})_2$

A 25 mL Schlenk tube was charged with **$\alpha(\text{OMe})\text{Br}_2$** (0.599 mmol), *p*-methoxyphenylboronic acid (1.589 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.118 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 4 mL dry THF and 1.2 mL degassed 2M K_2CO_3 solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H_2O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na_2SO_4 , decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Toluene:EtOAc (49:1) to afford **$\alpha(\text{OMe})(\text{PhOMe})_2$** as a pale yellow solid (R_f 0.16), 123 mg (40%). Vapor diffusion of hexanes into a solution of **$\alpha(\text{OMe})(\text{PhOMe})_2$** in THF resulted in pale yellow crystals suitable for single crystal X-ray diffraction. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 2H), 7.73 (d, J = 8.6 Hz, 4H), 7.63 (s, 2H), 6.99 (d, J = 8.6 Hz, 4H), 4.11 (s, 6H), 3.88 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.8, 148.9, 142.0, 134.7, 129.5, 127.7, 127.3, 122.7, 117.0, 114.6, 104.8, 56.2, 55.6; HRMS (APCI+) calcd for $\text{C}_{30}\text{H}_{25}\text{O}_4\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 513.119429, found 513.12001 (1.13 ppm).

2.2.8 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene,

$\alpha(\text{OMe})(\text{PhCF}_3)_2$

A 25 mL Schlenk tube was charged with **$\alpha(\text{OMe})\text{Br}_2$** (0.531 mmol), *p*-(trifluoromethyl)phenylboronic acid (1.333 mmol), Pd(PPh₃)₂Cl₂ (0.096 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 4 mL dry THF and 0.50 mL degassed 2M K₂CO₃ solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Toluene:EtOAc (49:1) to afford **$\alpha(\text{OMe})(\text{PhCF}_3)_2$** as a bright yellow solid (*R*_f 0.34), 240 mg (77%). Vapor diffusion of toluene into a solution of **$\alpha(\text{OMe})(\text{PhCF}_3)_2$** in THF resulted in yellowish-green crystals suitable for single crystal X-ray diffraction. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 10.8 Hz, 3H), 4.15 (s, 3H); Due to poor solubility, only ¹³C signals obtained from ¹H–¹³C HSQC were obtained. ¹³C NMR (101 MHz, CDCl₃) δ 126.2, 119.4, 104.6, 56.2; HRMS (APCI+) calcd for C₃₀H₁₉F₆O₂S₂ (M+H)⁺ 589.073067, found 589.07387 (1.36 ppm).

2.3 Synthesis of $\beta(\text{Oi-Pent})\text{R}_2$ Series

2.3.1 1,2-dibromo-4,5-di-isopentyloxybenzene, **1(Oi-Pent)**

4,5-dibromocatechol (18.75 mmol) was massed into a 250 mL round bottom flask and dissolved in 2-butanone (100 mL). A stir bar was added, followed by K₂CO₃ (57.89 mmol) and a reflux condenser. Reaction was flushed with argon for 5 minutes, then isopentyl bromide (41.31 mmol) was added in one portion. Reaction temperature was

then raised to 80 °C and allowed to stir for 24 hours. After 24 hours the reaction flask was cooled to RT and poured into H₂O (50 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification via silica gel flash column with Hexanes:EtOAc (99:1) as mobile phase afforded 1,2-dibromo-4,5-di-isopentyloxybenzene (**1(Oi-Pent)**) as a colorless oil (*R*_f 0.53), 6.40 g (84%). Spectral details match literature values.⁶ 7.07 (s, 2H), 3.97 (t, *J* = 6.7 Hz, 4H), 1.83 (dp, *J* = 13.3, 6.9 Hz, 2H), 1.69 (q, *J* = 6.8 Hz, 4H), 0.96 (d, *J* = 6.6 Hz, 6H).

2.3.2 1,2-di(2-thienyl)-4,5-di-isopentyloxybenzene, **3(Oi-Pent)**

A 100 mL Schlenk tube was charged with **1(Oi-Pent)** (6.19 mmol), 2-thiophene boronic acid (18.64 mmol), and Pd(PPh₃)₂Cl₂ (0.95 mmol), and a stir bar added. Under positive pressure of argon dry THF (30 mL) and degassed 2M K₂CO₃ (7.5 mL) were added and the tube was sealed. The reaction was placed into an oil bath and stirred at 80 °C overnight. The next day, the reaction was cool to RT and poured into H₂O (25 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved through silica gel flash column with Hexane:EtOAc (99:1) followed by trituration with cold ethanol to afford 1,2-di(2-thienyl)-4,5-di-isopentyloxybenzene (**3(Oi-Pent)**) as a white solid (*R*_f 0.19), 2.34 g (91%): ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 5.1 Hz, 2H), 7.00 (s, 2H), 6.94 (t, *J* = 4.4 Hz, 2H), 6.84 (d, *J* = 3.5 Hz, 2H), 4.07 (t, *J* = 6.7 Hz, 4H), 1.87 (dt, *J* = 13.2, 6.7 Hz, 2H), 1.74 (q, *J* = 6.7 Hz, 4H), 0.97 (d, *J* = 6.6 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ here; HRMS (APCI+) calcd for C₂₄H₃₁O₂S₂ (M+H)⁺ 415.176549, found 415.17750 (2.29 ppm).

2.3.3 1,2-di(2-(5-bromothieryl)-4,5-di-isopentyloxybenzene, **4(Oi-Pent)**

3(Oi-Pent) (3.56 mmol) was massed into a 100 mL round bottom flask. A stir bar and CHCl_3 (60 mL) were added, followed by vigorous stirring under argon (5 minutes). After equilibration NBS (9.70 mmol) was added in portions over 5 minutes. Upon complete addition of NBS the reaction was left to stir for 3 days. After 3 days the reaction was poured into H_2O (100 mL), extracted with DCM (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na_2SO_4 , decanted, and concentrated to yield crude product as a pale-yellow solid. Purification was achieved through silica gel flash column Hexanes:EtOAc (99:1) followed by recrystallization from ethanol to afford pure 1,2-di(2-(5-bromothieryl)-4,5-di-isopentyloxybenzene (**4(Oi-Pent)**) as an off-white solid (R_f 0.31), 1.50 g (74%): ^1H NMR (400 MHz, CDCl_3) δ = 6.91 (d, J = 3.7 Hz, 4H), 6.64 – 6.60 (m, 2H), 4.05 (t, J = 6.5 Hz, 4H), 1.86 (dt, J = 13.4, 6.7 Hz, 2H), 1.73 (q, J = 6.7 Hz, 4H), 0.97 (dd, J = 6.4, 1.6 Hz, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ here; HRMS (APCI+) calcd for $\text{C}_{24}\text{H}_{29}\text{Br}_2\text{O}_2\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 570.997571, found 570.99892 (2.36 ppm).

2.3.4 2,5-dibromo-8,9-bis(isopentyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene, **β (Oi-Pent)Br₂**

A 100 mL Schlenk tube was charged with **5** (1.10 mmol) and a stir bar, then placed under argon atmosphere. Under positive pressure of argon dry DCM (100 mL) was added, then the reaction was cooled to 0 °C and equilibrated for 10 minutes. After 10 minutes MeSO_3H (11 mL) was added and the reaction was stirred 5 additional minutes. DDQ (1.69 mmol) was added to the reaction in one portion and left to stir for 30 minutes at 0 °C. After 30 minutes the reaction was quenched with an aqueous solution of sodium bicarbonate slowly, and then allowed to come to RT. The reaction mixture poured into a

separatory funnel and was extracted with DCM (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved through silica gel flash column with Hexanes:Toluene (4:1) to afford pure **β(Oi-Pent)Br₂** as an off-white solid (*R_f* 0.58), 269 mg (44%): ¹H NMR (400 MHz, CDCl₃) δ 7.57 (s, 2H), 7.19 (s, 2H), 4.18 (t, *J* = 6.6 Hz, 4H), 1.99 – 1.87 (m, 2H), 1.82 (q, *J* = 6.7 Hz, 4H), 1.03 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ here; HRMS (APCI+) calcd for C₂₄H₂₇Br₂O₂S₂ (M+H)⁺ 568.98121, found 568.98322 (2.28 ppm).

2.3.5 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2-*b*:4,3-*b'*]dithiophene, **β(Oi-Pent)Ph₂**

A 25 mL Schlenk tube was charged with **β(Oi-Pent)Br₂** (0.308 mmol), phenylboronic acid (1.077 mmol), Pd(PPh₃)₂Cl₂ (0.063 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which 5 mL dry THF and 0.6 mL degassed 2M K₂CO₃ solution were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column Hexanes:DCM (9:1) followed by recrystallisation from hexanes to afford **β(Oi-Pent)Ph₂** as an off-white solid (*R_f* 0.30), 102 mg (58%): ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 2H), 7.82 (d, *J* = 7.7 Hz, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.42 (s, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 4.24 (t, *J* = 6.6 Hz, 4H), 1.95 (dq, *J* = 13.2, 6.7 Hz, 2H), 1.85 (q, *J* = 6.7 Hz, 4H), 1.05 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 149.7, 142.6, 134.7, 134.5, 133.0, 129.2, 128.1, 126.4,

121.8, 118.8, 106.2, 67.9, 38.0, 25.5, 22.9; HRMS (APCI+) calcd for C₃₆H₃₇O₂S₂ (M+H)⁺ 565.223499, found 565.22502 (2.69 ppm).

2.3.6 8,9-bis(isopentyloxy)-2,5-di-*p*-tolyl naphtho[1,2-*b*:4,3-*b'*]dithiophene, **β(Oi-Pent)Tol₂**

A 25 mL Schlenk tube was charged with **β(Oi-Pent)Br₂** (0.271 mmol), *p*-methylphenylboronic acid (0.927 mmol), Pd(PPh₃)₂Cl₂ (0.083 mmol) and a stir bar. The reaction tube was backfilled with argon (3x), after which dry THF (5 mL) and degassed 2M K₂CO₃ (0.5 mL) were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column with Hexanes:DCM (9:1) followed by recrystallisation from hexanes to afford **β(Oi-Pent)Tol₂** as an off-white solid (R_f 0.30), 66 mg (41%): ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 2H), 7.70 (d, *J* = 8.1 Hz, 3H), 7.39 (s, 2H), 7.29 – 7.23 (m, 5H), 4.22 (t, *J* = 6.6 Hz, 4H), 2.42 (s, 6H), 1.95 (dq, *J* = 13.2, 6.7 Hz, 2H), 1.85 (q, *J* = 6.7 Hz, 4H), 1.04 (d, *J* = 6.6 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 149.6, 142.7, 138.0, 134.1, 133.0, 131.9, 129.8, 126.2, 121.7, 118.2, 106.2, 67.8, 38.0, 25.5, 22.9, 21.4; HRMS (APCI+) calcd for C₃₈H₄₁O₂S₂ (M+H)⁺ 593.254799, found 593.25583 (1.73 ppm).

2.3.7 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene,

β (*Oi*-Pent)(PhOMe)₂

A 50 mL Schlenk tube was charged with **β (*Oi*-Pent)Br₂** (0.360 mmol), *p*-methoxyphenylboronic acid (0.908 mmol), Pd(PPh₃)₂Cl₂ (0.064 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which dry THF (2.8 mL) and degassed 2M K₂CO₃ (0.7 mL) were added under positive pressure of argon. The reaction tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column with Hexanes:DCM (2:3) followed by recrystallisation from hexanes to afford **β (*Oi*-Pent)(PhOMe)₂** as an off-white solid (R_f 0.50), 104 mg (46%): ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 2H), 7.74 (d, *J* = 8.7 Hz, 3H), 7.39 (s, 2H), 7.00 (d, *J* = 8.8 Hz, 3H), 4.23 (t, *J* = 6.6 Hz, 4H), 3.88 (s, 6H), 1.95 (dt, *J* = 13.2, 6.6 Hz, 2H), 1.84 (q, *J* = 6.7 Hz, 4H), 1.04 (d, *J* = 6.6 Hz, 11H); ¹³C NMR (101 MHz, CDCl₃) δ 159.7, 149.5, 142.5, 133.8, 133.1, 127.6, 127.5, 121.7, 117.7, 114.6, 106.2, 67.8, 55.6, 38.0, 25.5, 22.9; HRMS (APCI+) calcd for C₃₈H₄₁O₄S₂ (M+H)⁺ 625.244629, found 625.24608 (2.32 ppm).

2.3.8 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2-*b*:4,3-

β (*Oi*-Pent)(PhCF₃)₂

A 25 mL Schlenk tube was charged with **β (*Oi*-Pent)Br₂** (0.393 mmol), *p*-(trifluoromethyl)phenylboronic acid (1.146 mmol), Pd(PPh₃)₂Cl₂ (0.070 mmol), and a stir bar. The reaction tube was backfilled with argon (3x), after which dry THF (5 mL) and degassed 2M K₂CO₃ (0.8 mL) were added under positive pressure of argon. The reaction

tube was sealed under argon and stirred in an oil bath at 80 °C overnight. The reaction was cooled to RT, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column with Hexanes:Toluene (9:1) followed by recrystallisation from toluene to afford **β(Oi-Pent)(PhCF₃)₂** as an off-white solid (*R*_f 0.38), 145 mg (53%): ¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 2H), 7.89 (d, *J* = 8.1 Hz, 4H), 7.70 (d, *J* = 8.1 Hz, 4H), 7.38 (s, 2H), 4.22 (t, *J* = 6.6 Hz, 4H), 1.96 (dt, *J* = 13.2, 6.6 Hz, 2H), 1.85 (q, *J* = 6.6 Hz, 4H), 1.05 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 150.0, 140.6, 137.8, 135.3, 132.6, 129.8, 129.5, 126.2, 126.1, 126.0, 122.8, 121.7, 120.0, 105.9, 67.7, 37.8, 25.3, 22.7; HRMS (APCI+) calcd for C₃₈H₃₅F₆O₂S₂ (M+H)⁺ 701.198267, found 701.20016 (2.69 ppm).

2.4 NMR Spectra

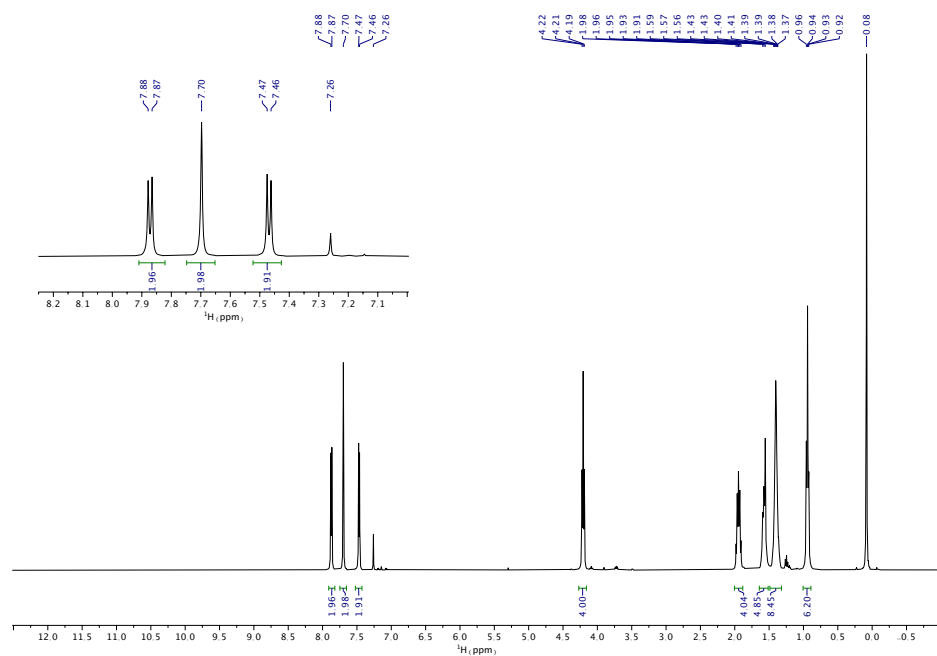


Figure A 1. ^1H NMR spectrum of 5,6-bis(hexyloxy)naphtho[2,1-b:3,4-b']dithiophene $\alpha(\text{OHex})$ (CDCl_3 , 400 MHz, 298 K).

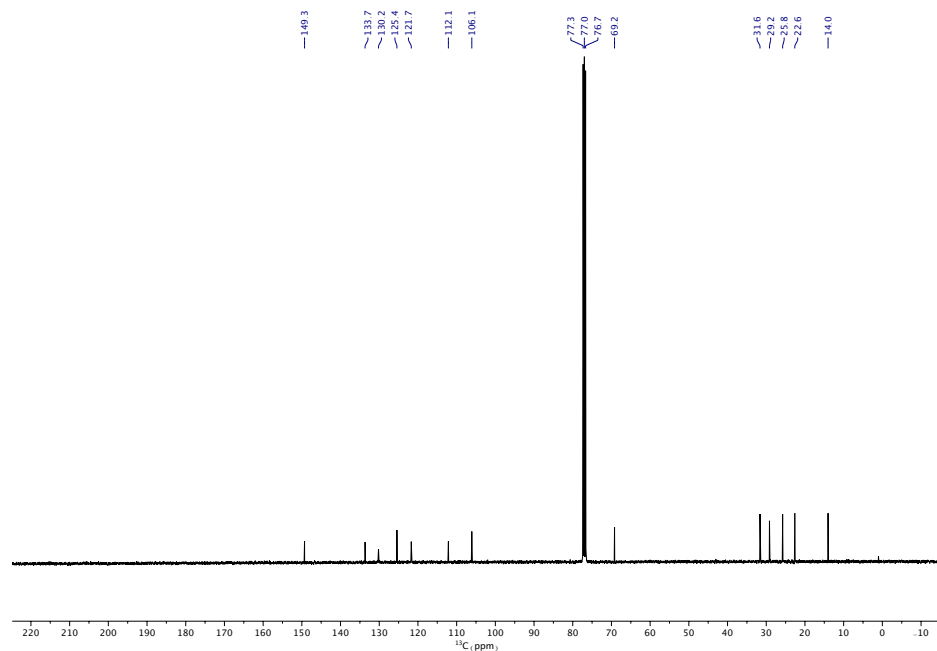


Figure A 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(hexyloxy)naphtho[2,1-b:3,4-b']dithiophene **a(OHEx)** (CDCl_3 , 101 MHz, 298 K).

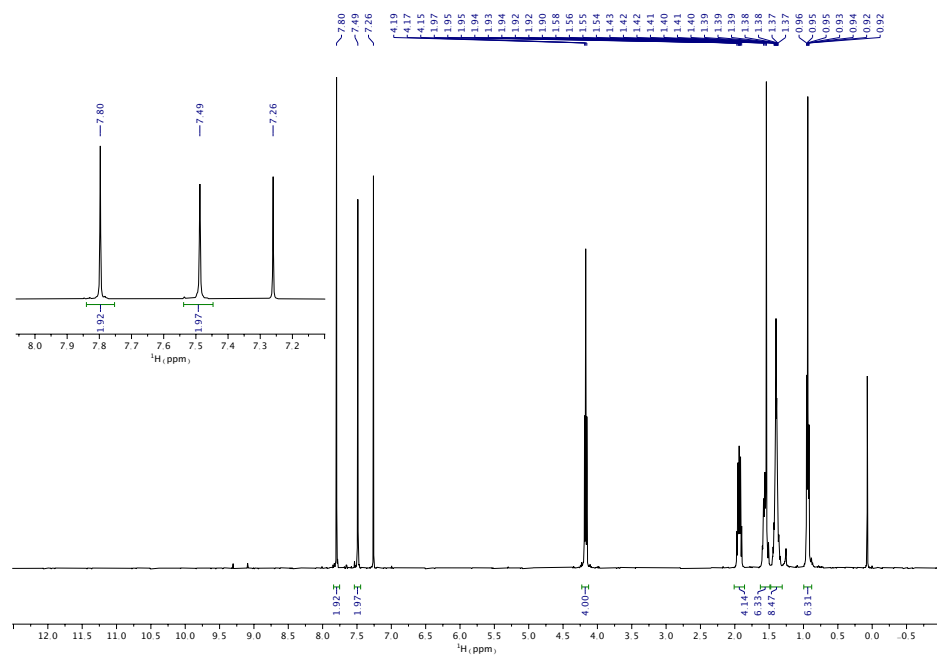


Figure A 3. ^1H NMR spectrum of 2,9-dibromo-5,6-bis(hexyloxy)naphtho[2,1-b:3,4-b']dithiophene **a(OHEx)Br₂** (CDCl_3 , 400 MHz, 298 K).

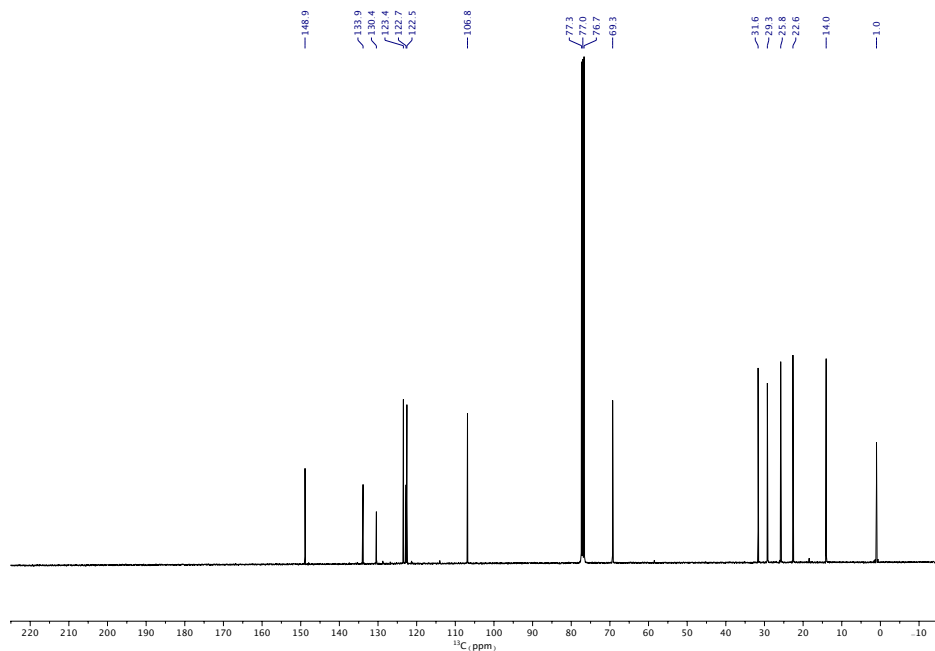


Figure A 4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2,9-dibromo-5,6-bis(hexyloxy)naphtho[2,1-b:3,4-b']dithiophene **a(OHex)Br₂** (CDCl₃, 101 MHz, 298 K).

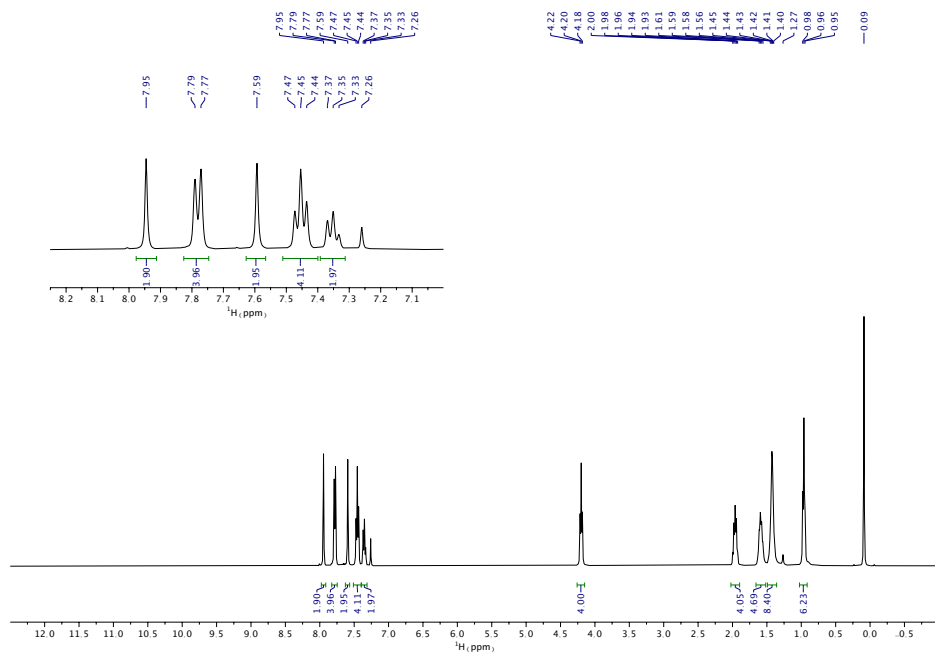


Figure A5. ^1H NMR spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1-b:3,4-b']dithiophene **a(OHex)Ph₂** (CDCl₃, 400 MHz, 298 K)

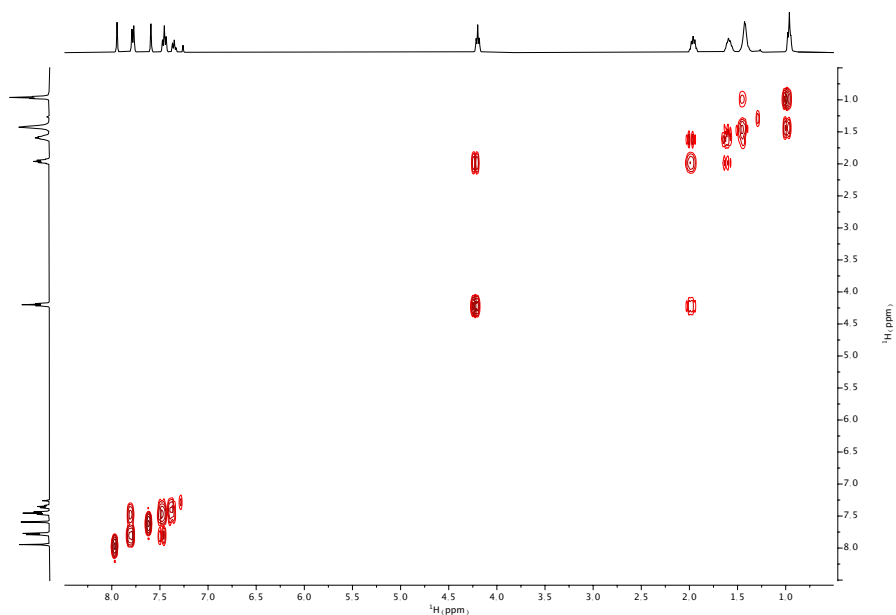


Figure A 6. ^1H - ^1H COSY spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **$\alpha(\text{OHex})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K).

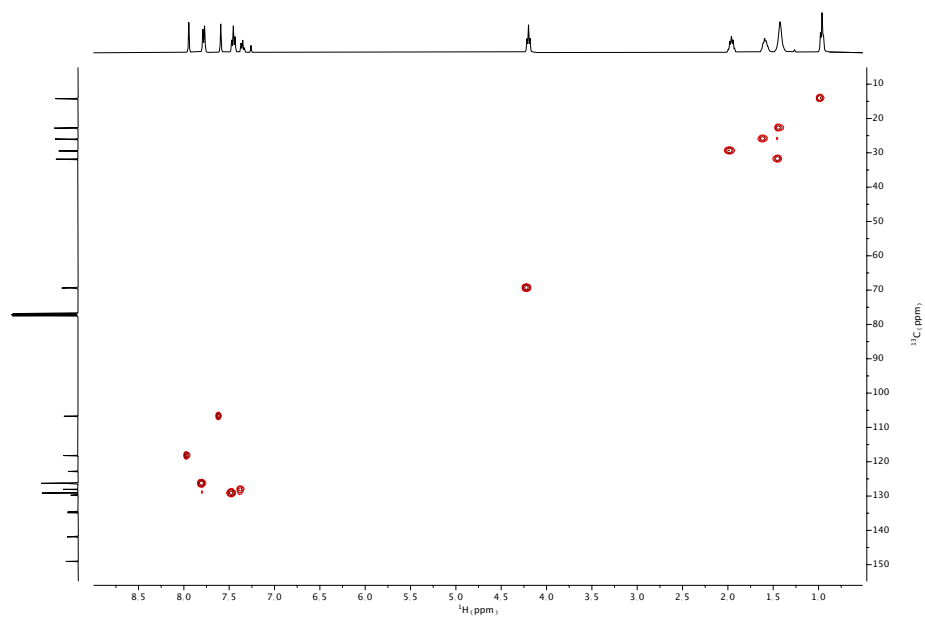


Figure A 7. ^1H - ^{13}C HSQC spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **$\alpha(\text{OHex})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K).

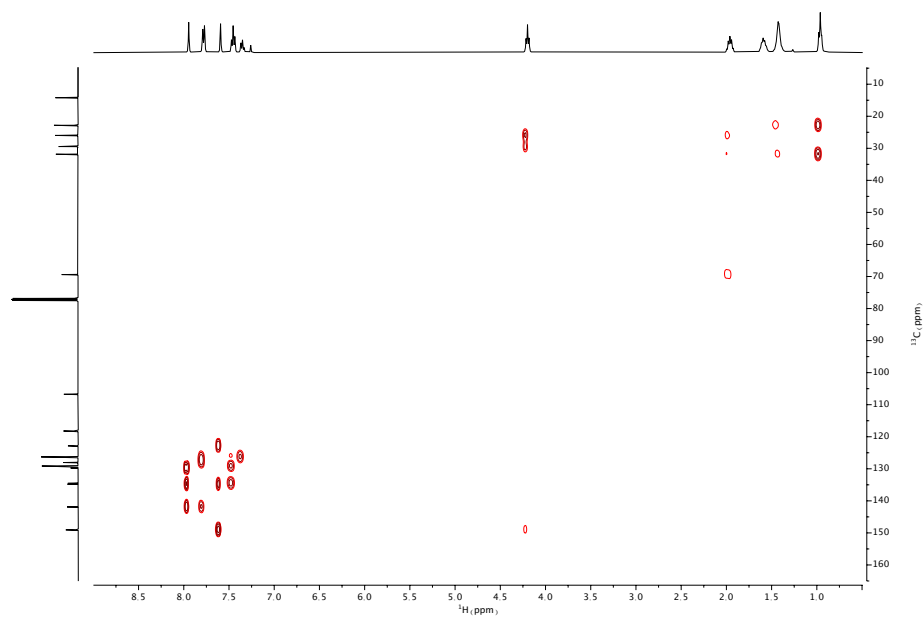


Figure A 8. ^1H - ^{13}C HMBC spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)Ph₂** (CDCl_3 , 400 MHz, 298 K).

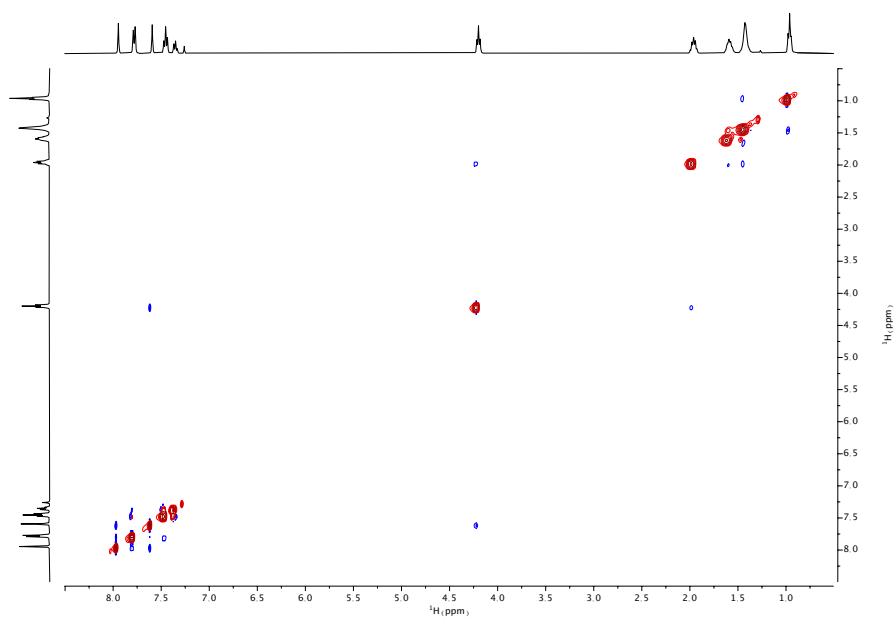


Figure A 9. ^1H - ^1H NOESY spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)Ph₂** (CDCl_3 , 400 MHz, 298 K).

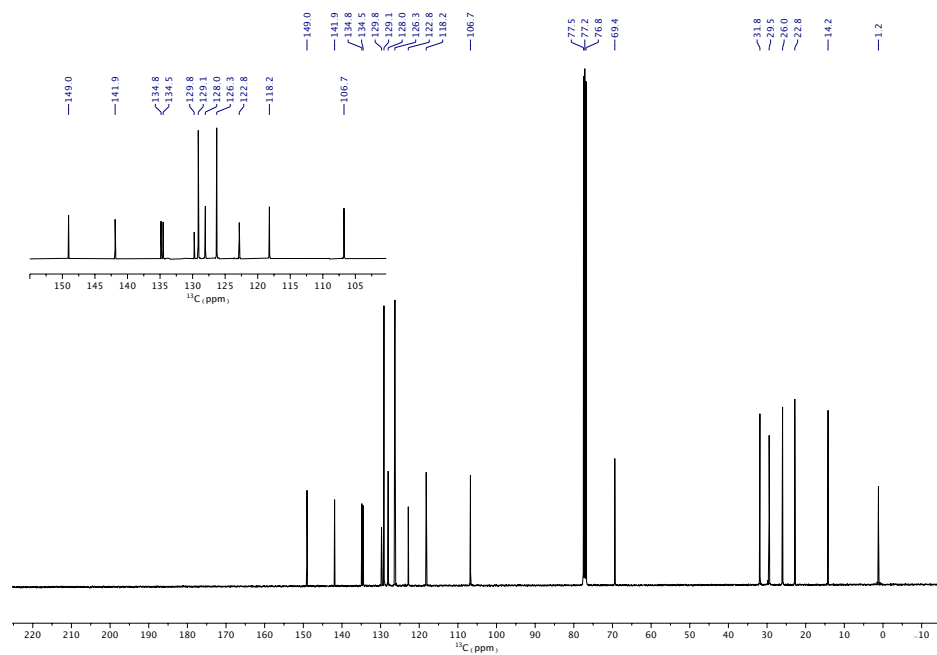
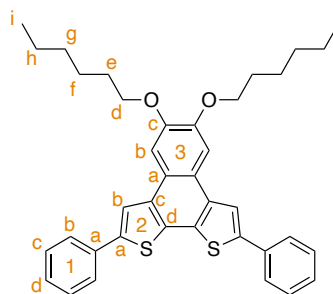


Figure A 10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)Ph₂** (CDCl_3 , 101 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	134.5
1b	7.78	126.3
1c	7.45	129.1
1d	7.35	128.0
2a	-	141.9
2b	7.95	118.2
2c	-	134.9
2d	-	129.8
3a	-	122.8
3b	7.59	106.8
3c	-	149.1
3d	4.20	69.4
3e	1.96	29.5
3f	1.58	26.0
3g	1.42	22.8/31.9
3h	1.42	22.8/31.9
3i	1.00-0.91	14.2

Figure A 11. 5,6-bis(hexyloxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **$\alpha(\text{OHex})\text{Ph}_2$** with assignment of ^1H and ^{13}C resonances.

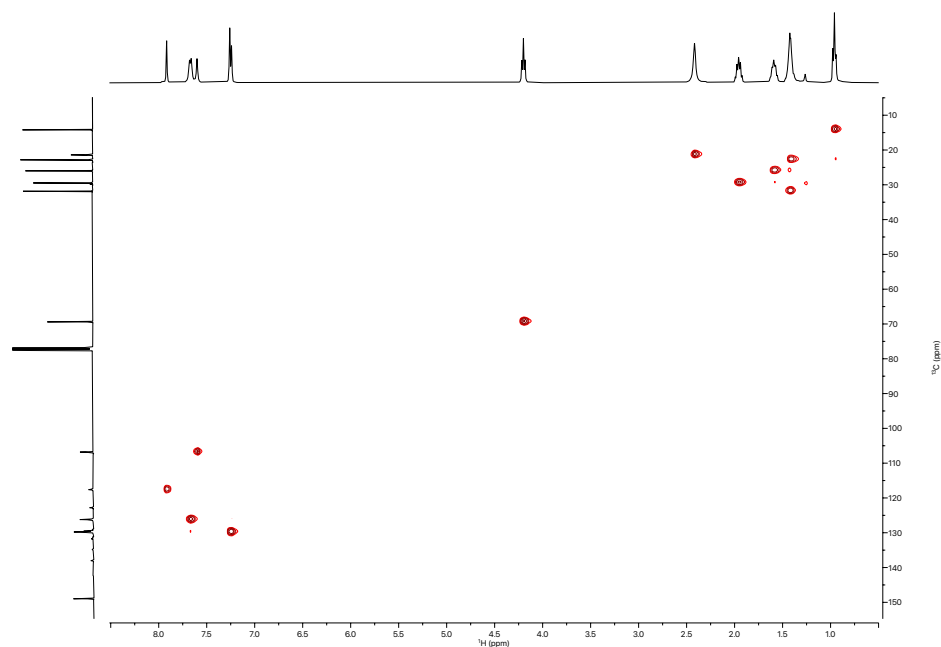


Figure A 14. ^1H - ^{13}C HSQC spectrum of 5,6-bis(hexyloxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OHex})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

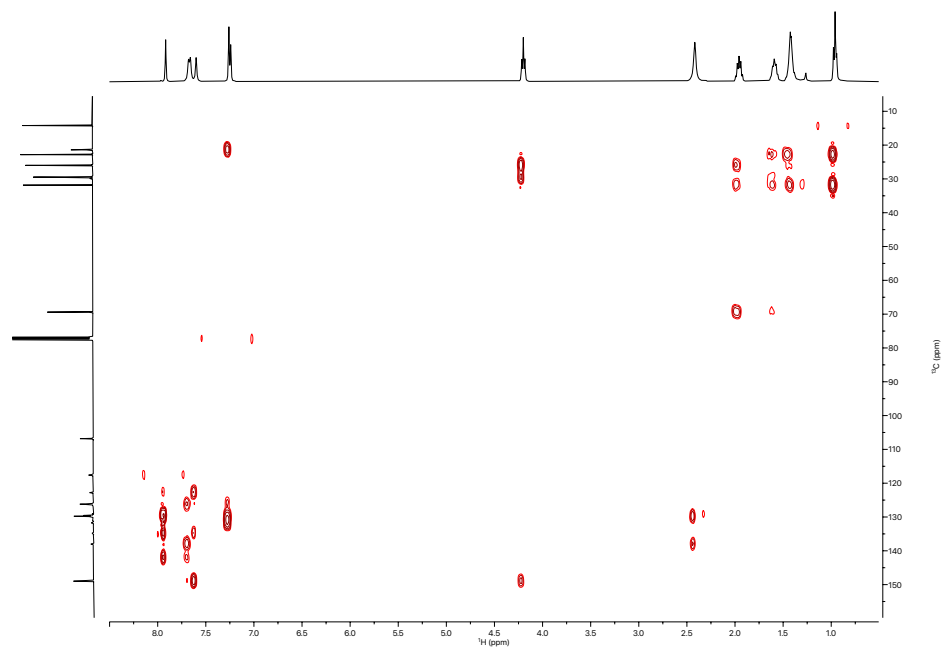


Figure A 15. ^1H - ^{13}C HMBC spectrum of 5,6-bis(hexyloxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OHex})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

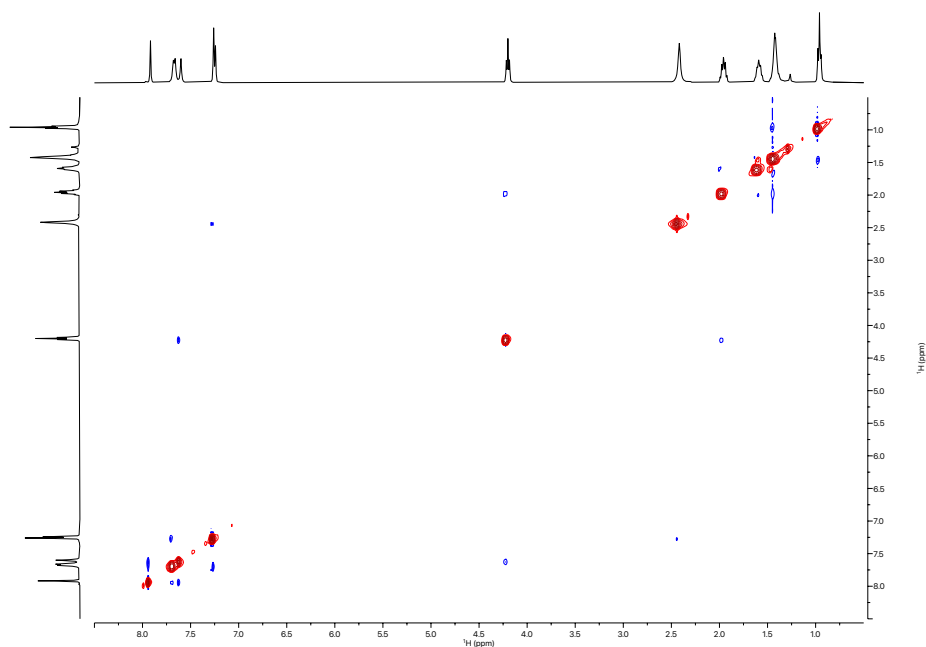


Figure A 16. ^1H - ^1H NOESY spectrum of 5,6-bis(hexyloxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OH})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

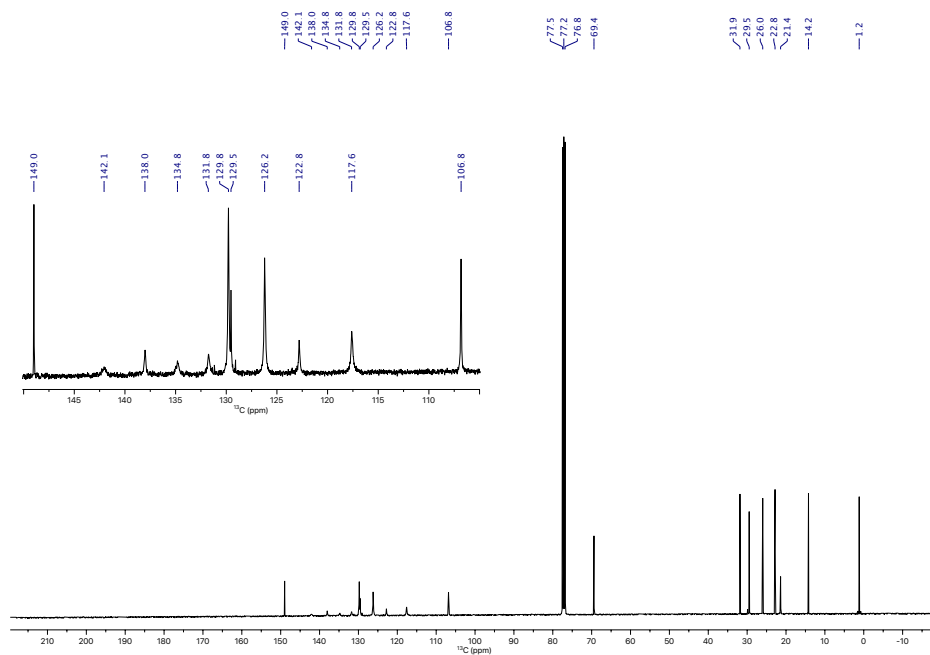
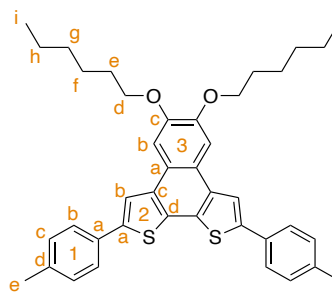


Figure A 17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(hexyloxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OH})\text{Tol}_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	129.5
1b	7.76	126.2
1c	7.25	129.8
1d	-	138.0
1e	2.42	21.4
2a	-	142.1
2b	7.92	117.6
2c	-	134.8
2d	-	131.8
3a	-	122.8
3b	7.60	106.8
3c	-	149.0
3d	4.20	69.4
3e	1.96	29.5
3f	1.58	26.0
3g	1.42	22.8/31.9
3h	1.42	22.8/31.9
3i	1.00–0.92	14.2

Figure A 18. 5,6-bis(hexyloxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)Tol₂** with assignment of ^1H and ^{13}C resonances.

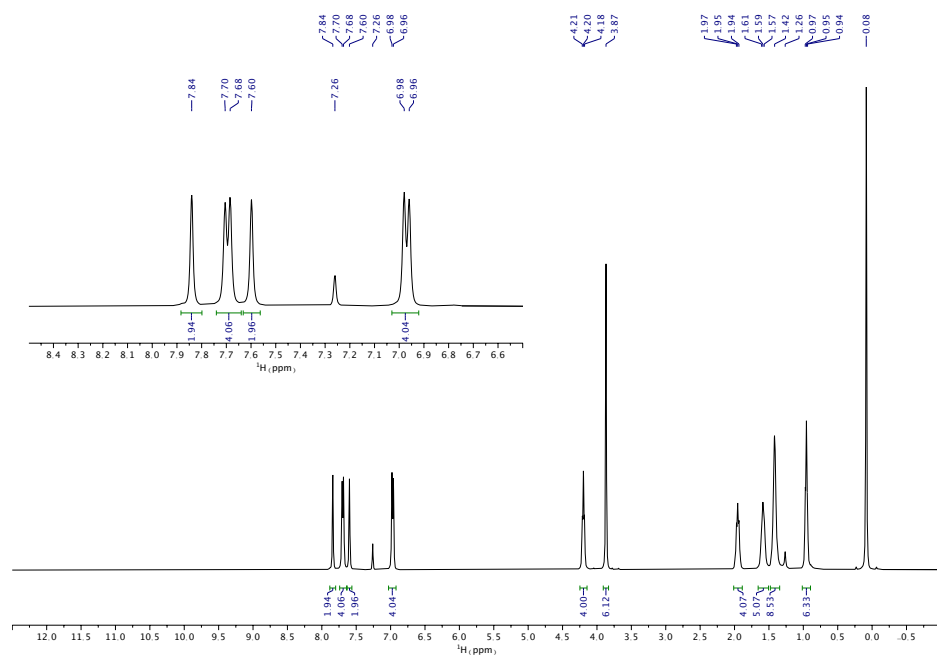


Figure A 19. ^1H NMR spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

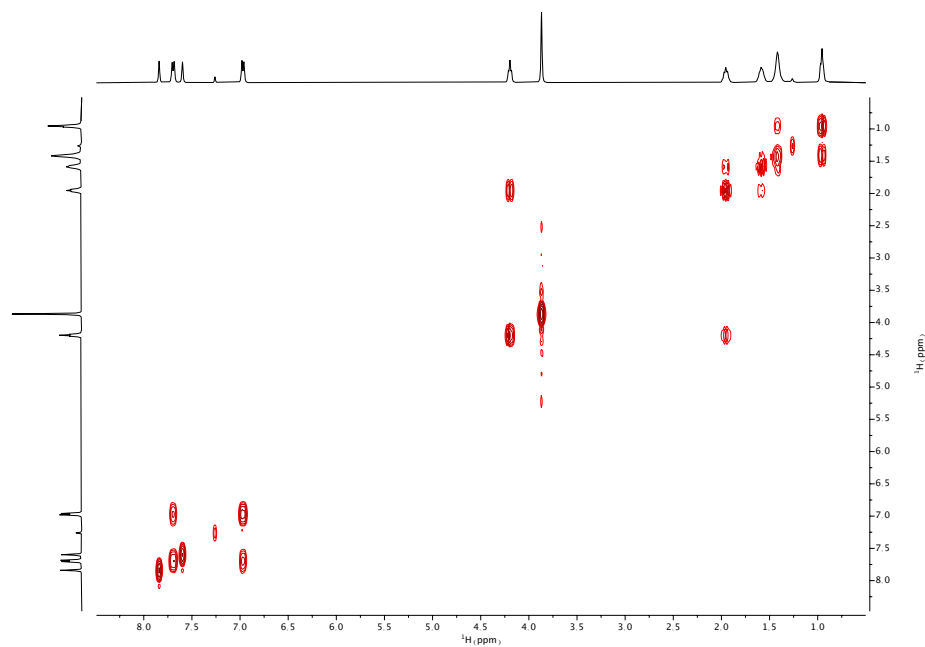


Figure A 20. ^1H - ^1H COSY spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

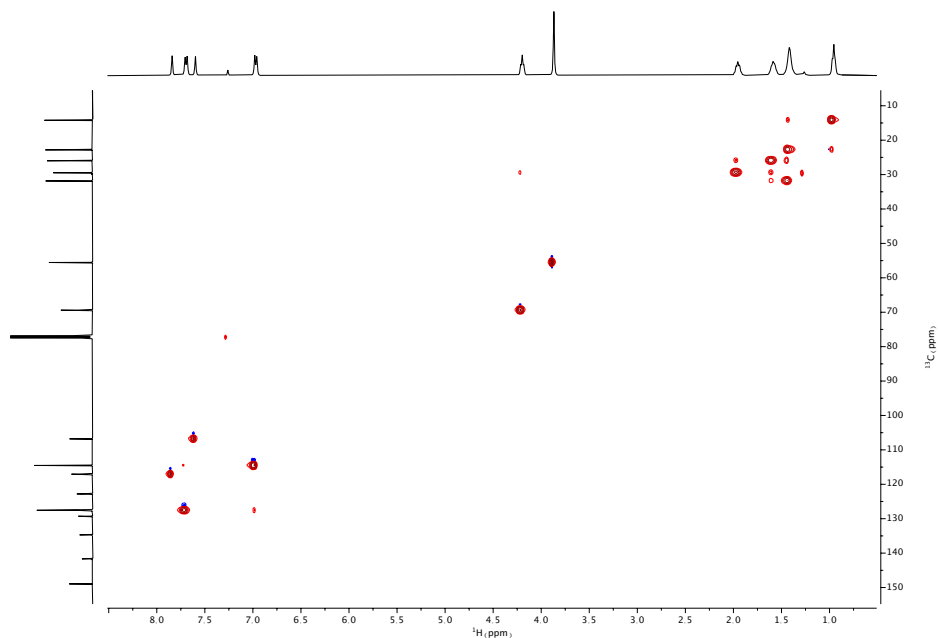


Figure A 21. ^1H - ^{13}C HSQC spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

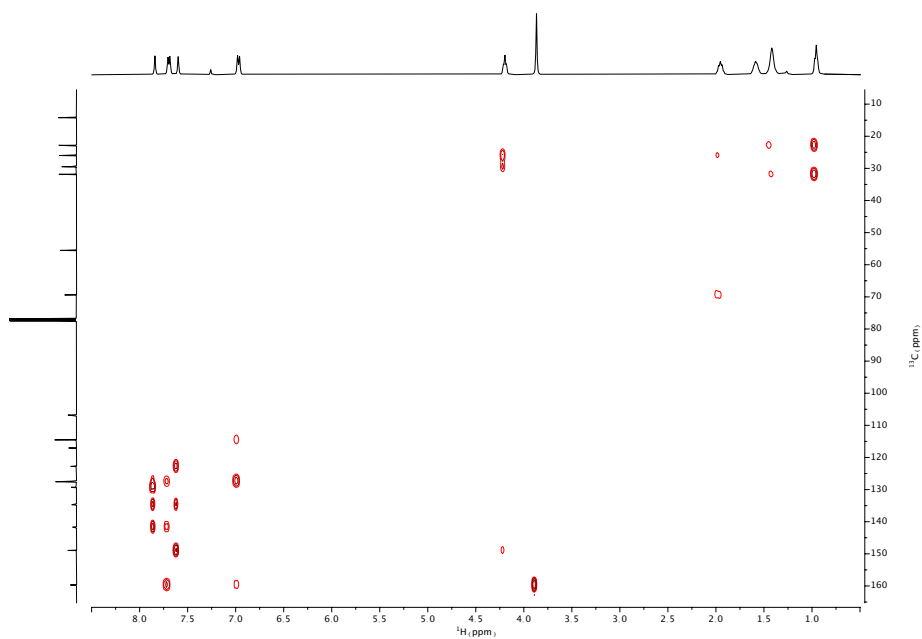


Figure A 22. ^1H - ^{13}C HMBC spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

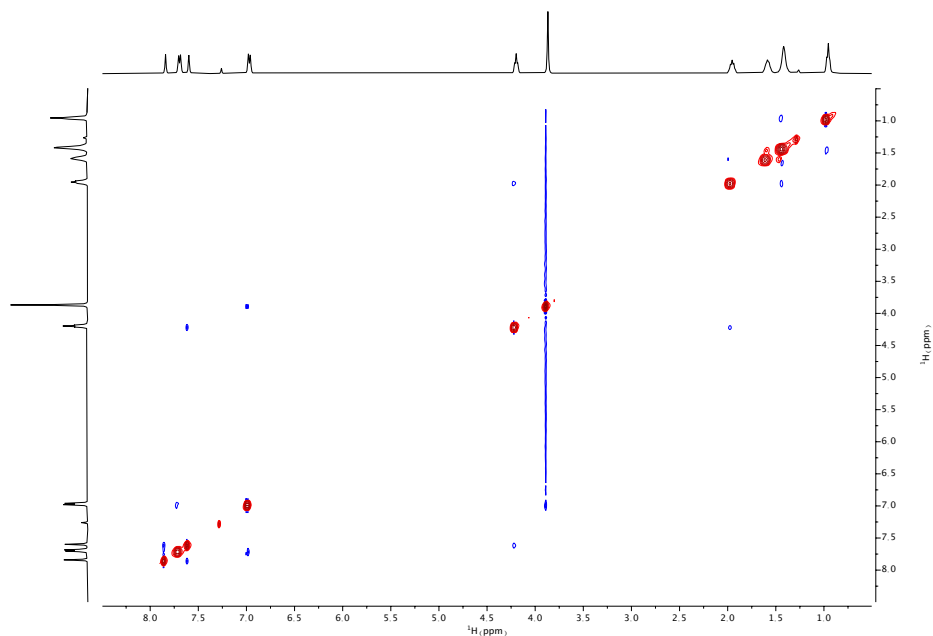


Figure A 23. ^1H - ^1H NOESY spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K)

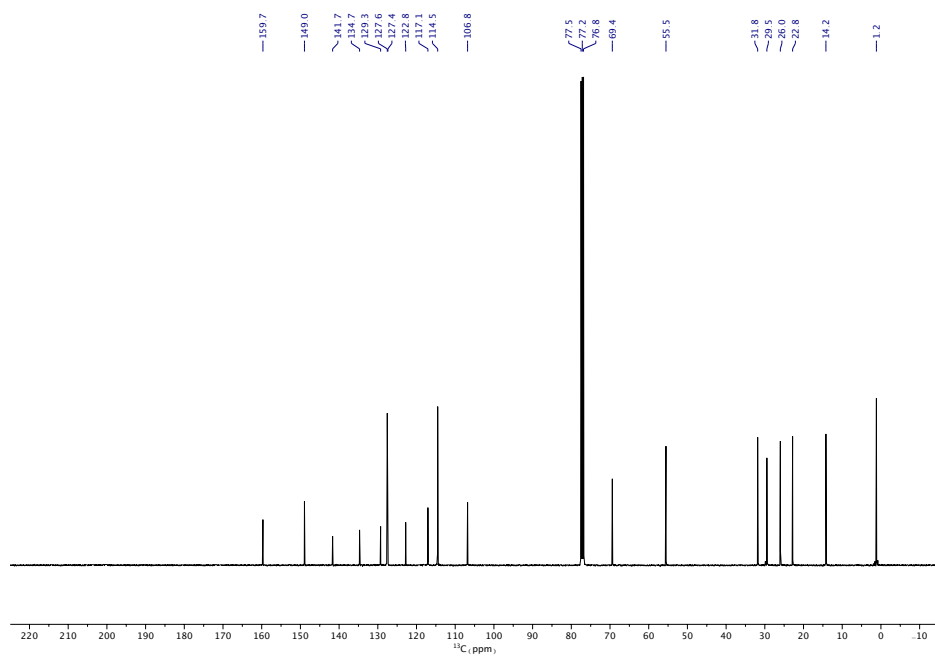
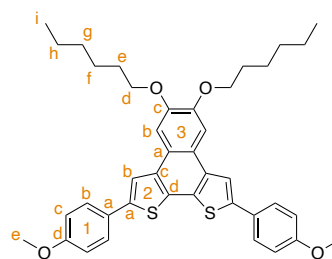


Figure A 24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(hexyloxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhOMe)₂** (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	127.4
1b	7.69	127.6
1c	6.97	114.5
1d	-	159.7
1e	3.87	55.5
2a	-	141.7
2b	7.84	117.1
2c	-	134.7
2d	-	129.3
3a	-	122.8
3b	7.60	106.8
3c	-	149.0
3d	4.20	69.4
3e	2.00–1.90	29.5
3f	1.59	26.0
3g	1.42	22.8/31.9
3h	1.42	22.8/31.9
3i	0.96	14.2

Figure A 25. $\alpha(\text{OHex})(\text{PhOMe})_2$ with assignment of ^1H and ^{13}C resonances.

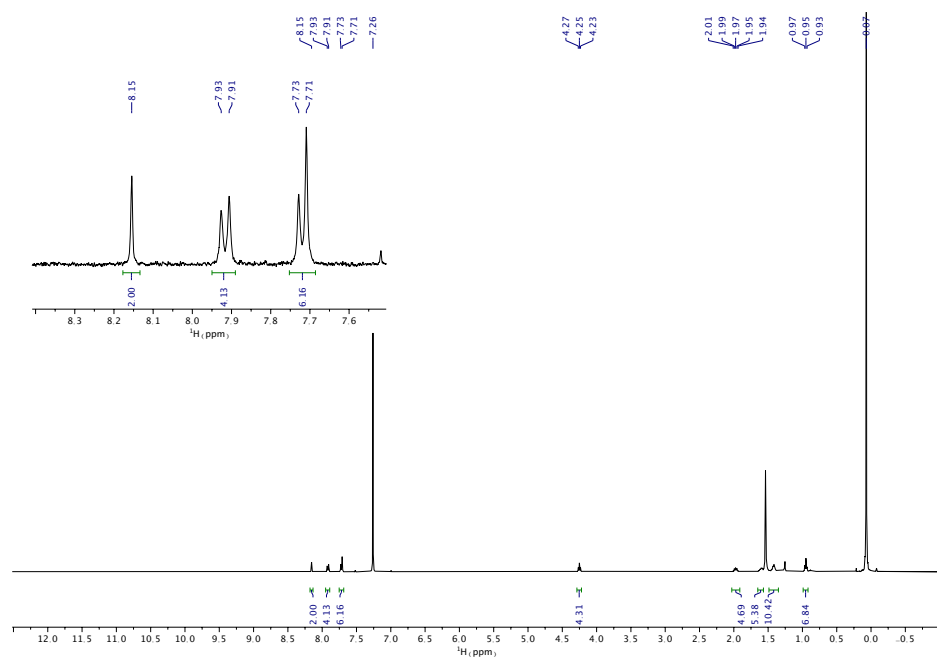


Figure A 26. ^1H NMR spectrum of 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhCF₃)₂** (CDCl₃, 400 MHz, 298 K).

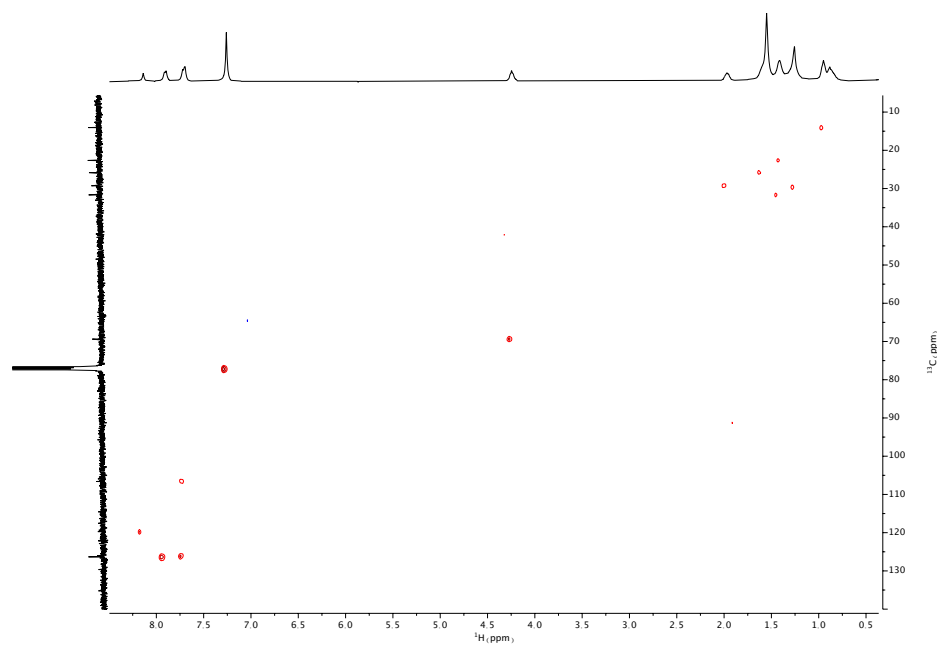


Figure A 27. ^1H - ^{13}C HSQC spectrum of 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhCF₃)₂** (CDCl₃, 400 MHz, 298 K).

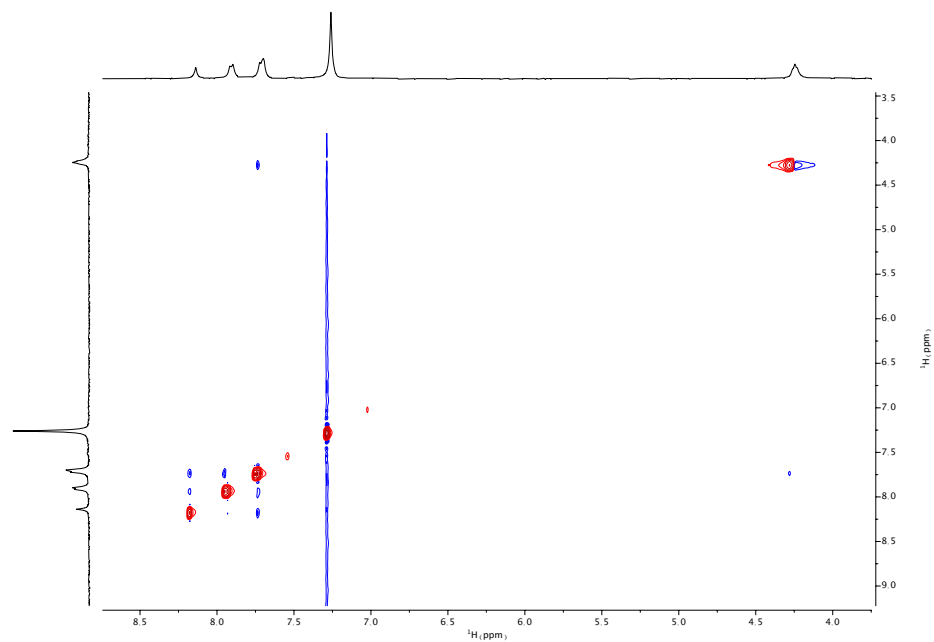
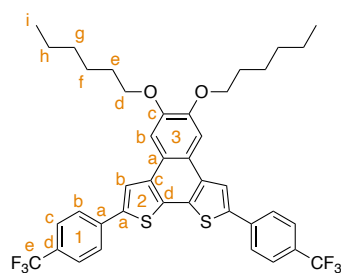


Figure A 28. ^1H - ^1H NOESY spectrum of 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhCF₃)₂** (CDCl₃, 400 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	-
1b	7.92	126.3
1c	7.72	126.3
1d	-	-
1e	-	-
2a	-	-
2b	8.15	119.8
2c	-	-
2d	-	-
3a	-	-
3b	7.71	106.6
3c	-	-
3d	4.25	69.5
3e	1.97	29.2
3f	1.64–1.57	25.7
3g	1.47–1.35	22.8/31.8
3h	1.47–1.35	22.8/31.8
3i	0.98–0.91	14.1

Figure A 29. 5,6-bis(hexyloxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OHex)(PhCF₃)₂** with assignment of ^1H and ^{13}C resonances. ^{13}C resonances extracted from HSQC.

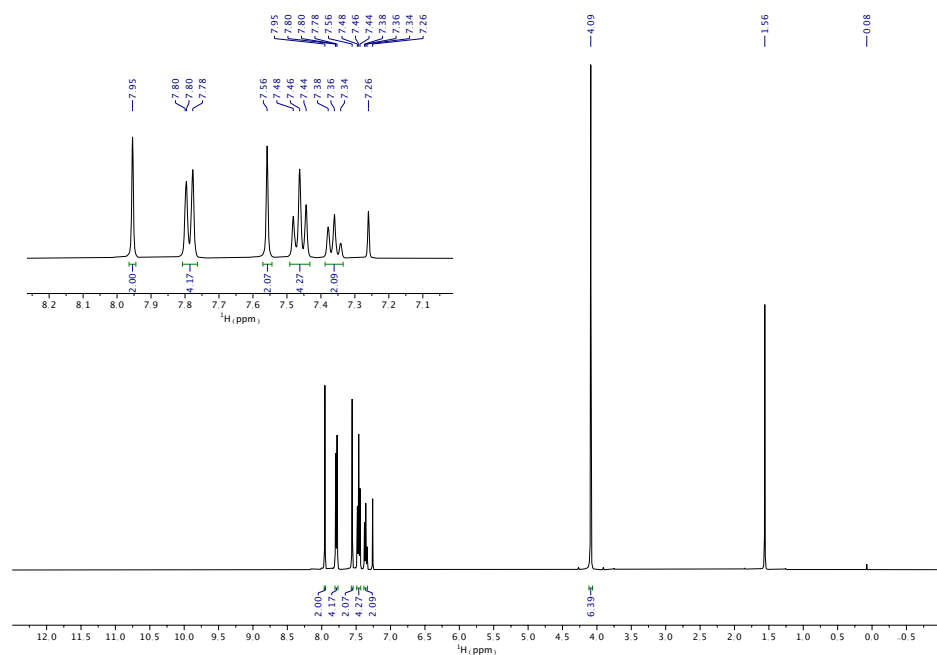


Figure A 30. ^1H NMR spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)Ph₂** (CDCl_3 , 400 MHz, 298 K).

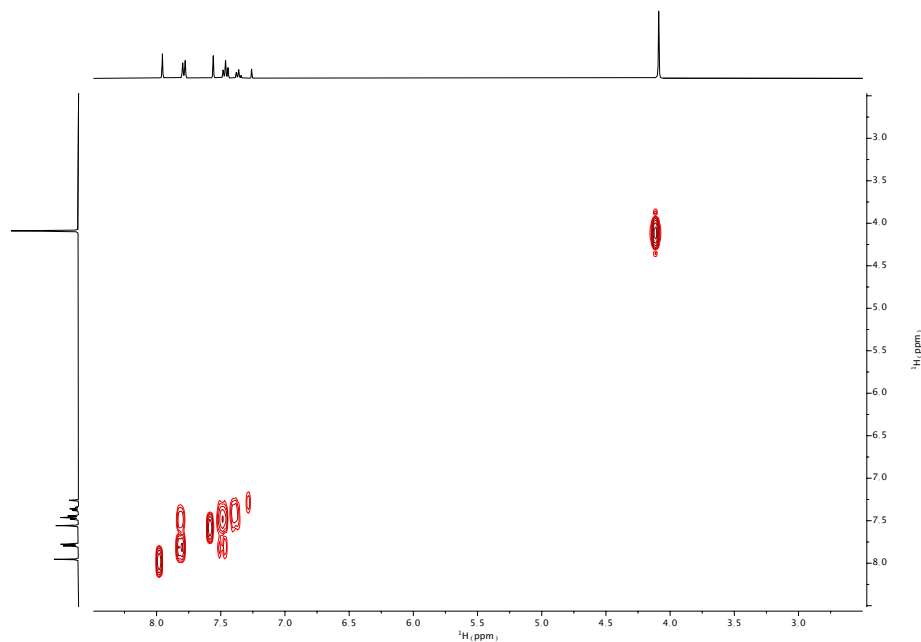


Figure A 31. ^1H - ^1H COSY spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)Ph₂** (CDCl_3 , 400 MHz, 298 K).

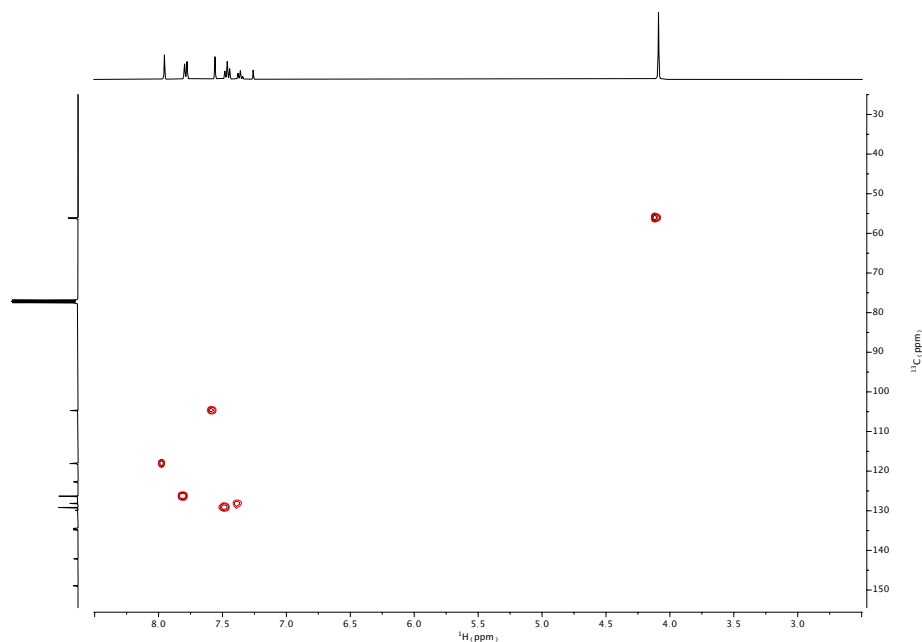


Figure A 32. ^1H - ^{13}C HSQC spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **$\alpha(\text{OMe})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K).

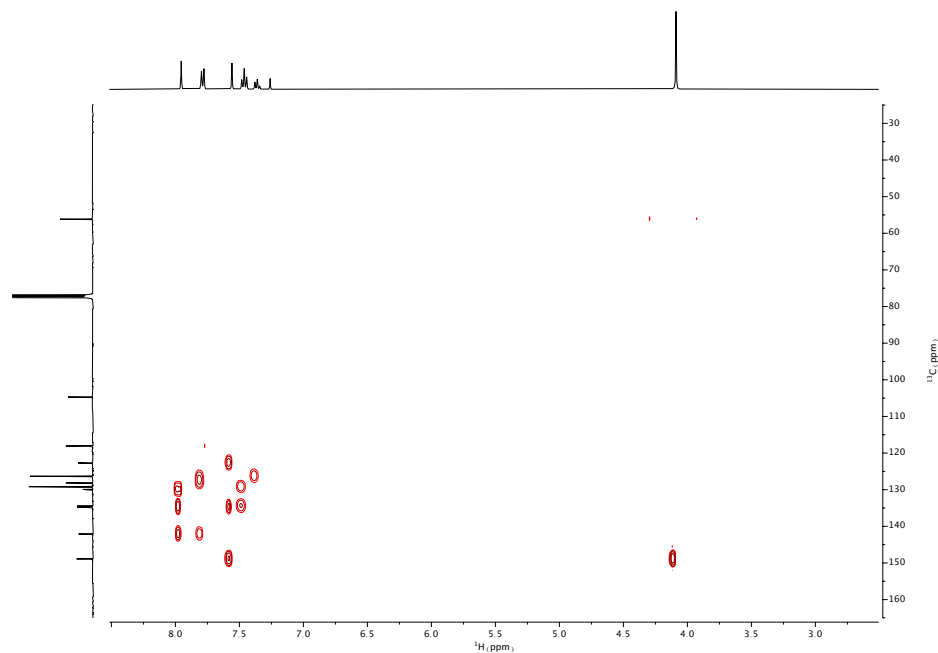


Figure A 33. ^1H - ^{13}C HMBC spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **$\alpha(\text{OMe})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K).

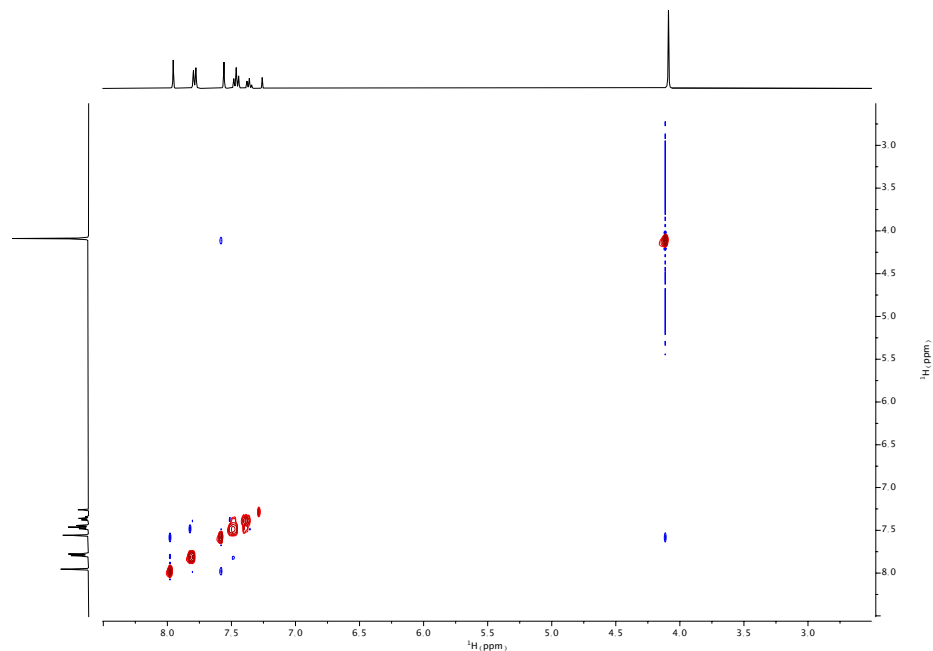


Figure A 34. ^1H - ^1H NOESY spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **$\alpha(\text{OMe})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K).

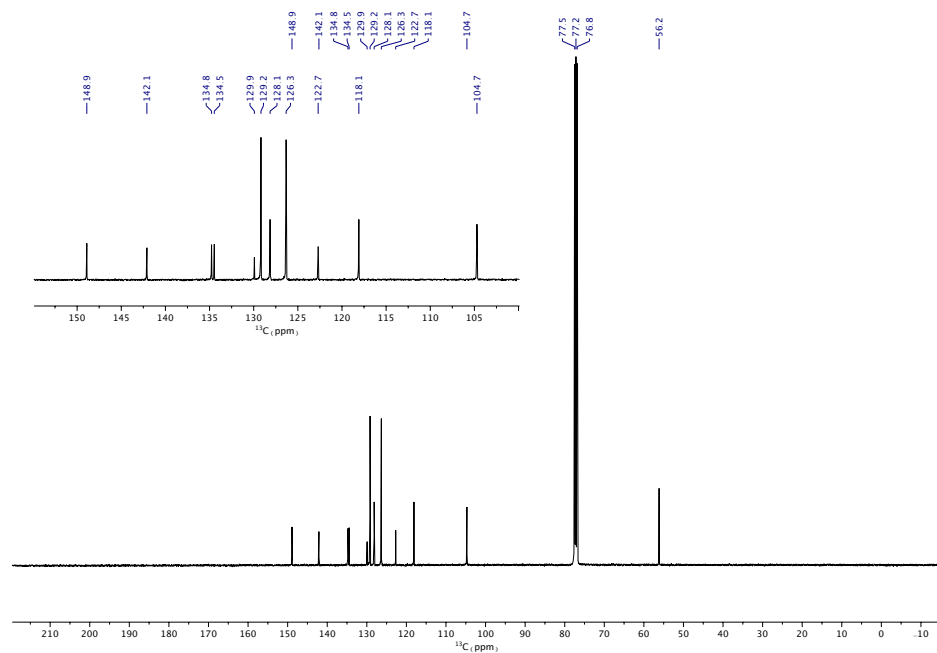
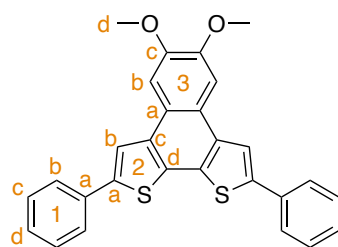


Figure A 35. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **$\alpha(\text{OMe})\text{Ph}_2$** (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	134.5
1b	7.79	126.3
1c	7.46	129.2
1d	7.36	128.1
2a	-	142.1
2b	7.95	118.1
2c	-	134.8
2d	-	129.9
3a	-	122.7
3b	7.56	104.7
3c	-	148.9
3d	4.09	56.2

Figure A 36. 5,6-bis(methoxy)-2,9-diphenylnaphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)Ph₂** with assignment of ^1H and ^{13}C resonances.

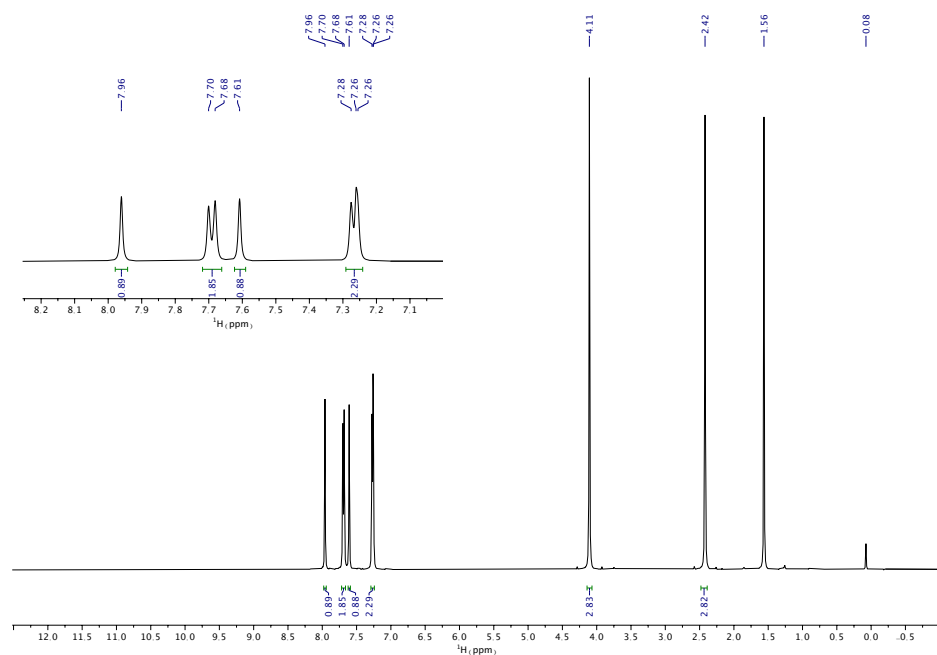


Figure A 37. ^1H NMR spectrum of 5,6-bis(methoxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OMe})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

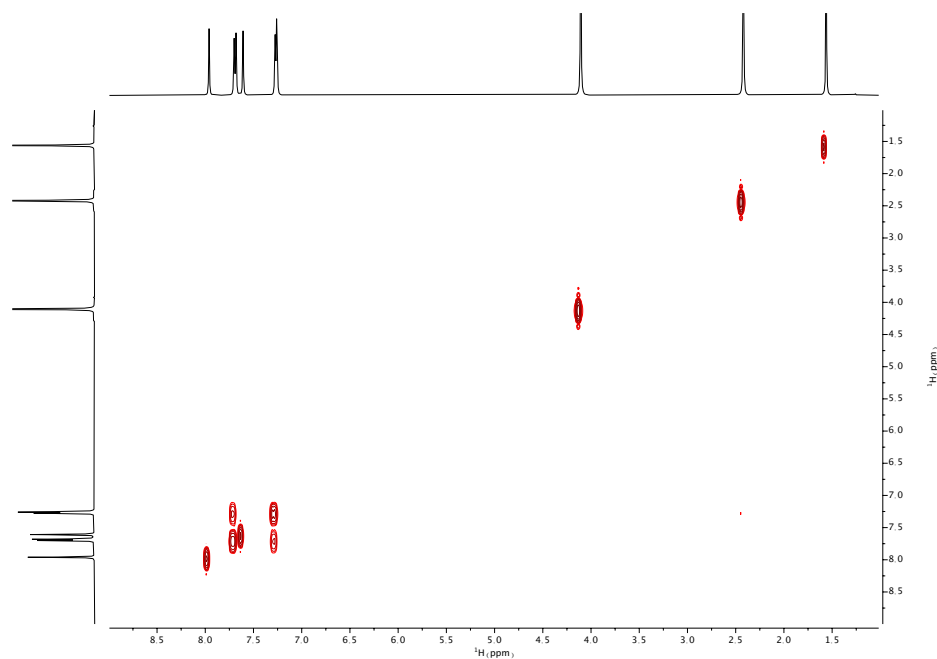


Figure A 38. ^1H - ^1H COSY spectrum of 5,6-bis(methoxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OMe})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

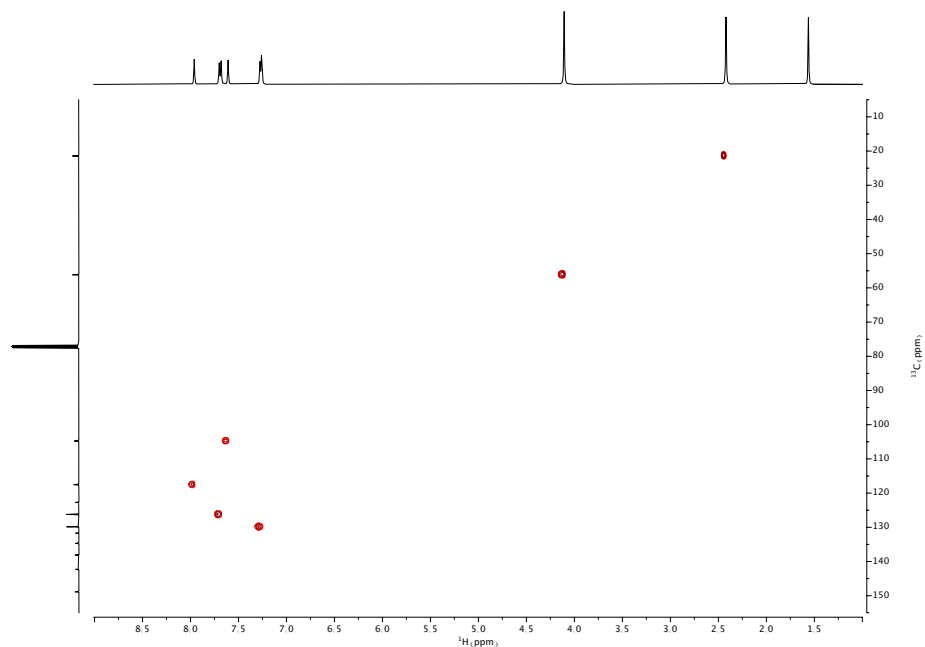


Figure A 39. ^1H - ^{13}C HSQC spectrum of 5,6-bis(methoxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OMe})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

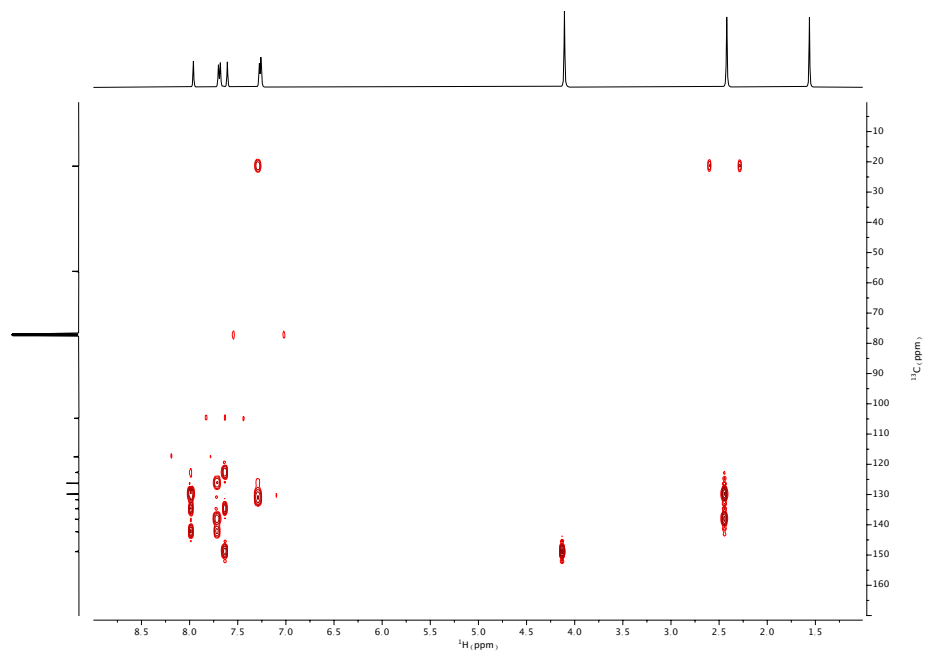


Figure A 40. ^1H - ^{13}C HMBC spectrum of 5,6-bis(methoxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OMe})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

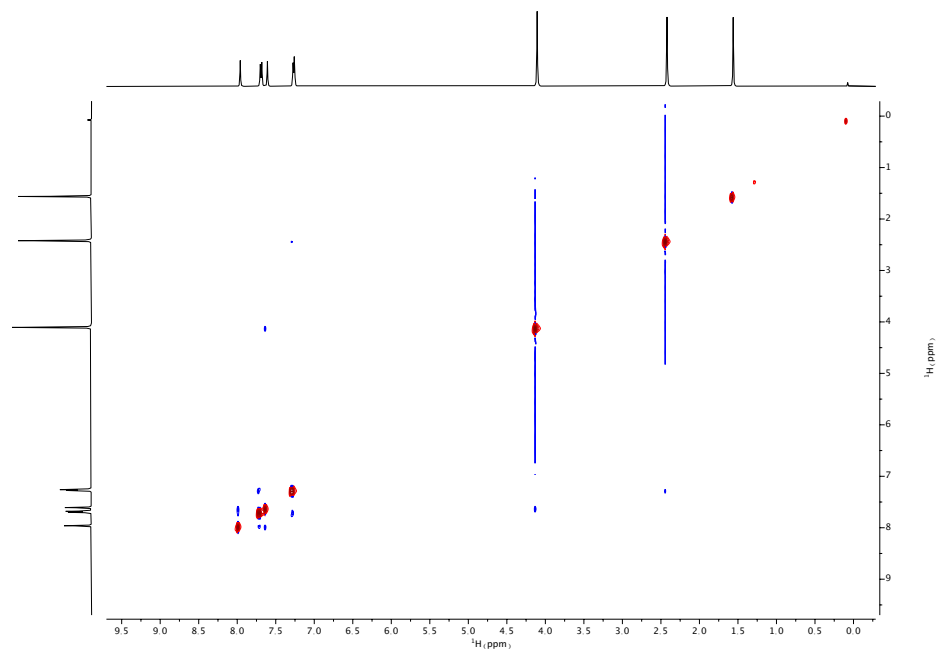


Figure A 41. ^1H - ^1H NOESY spectrum of 5,6-bis(methoxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OMe})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

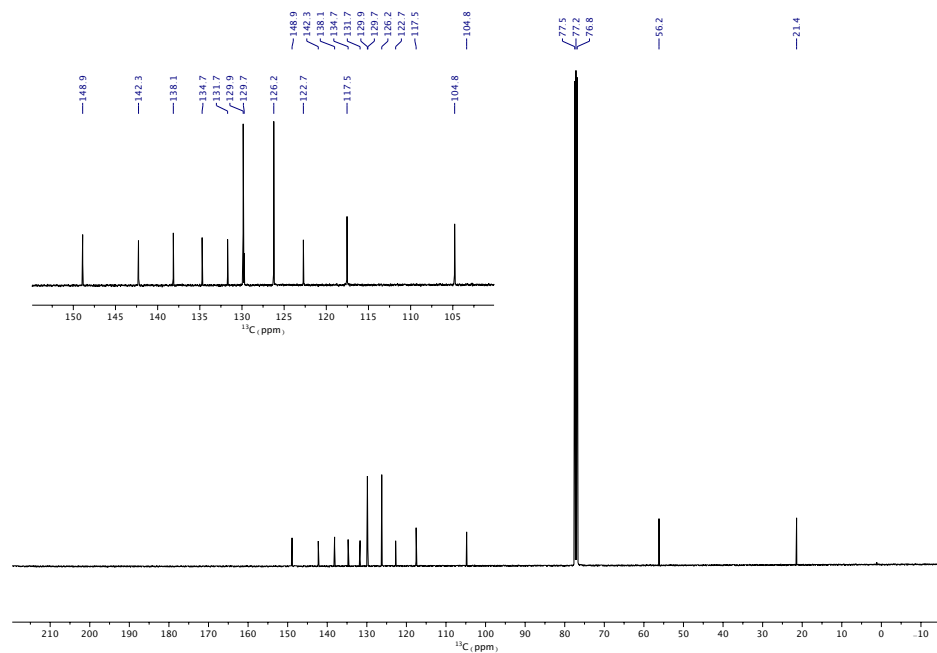
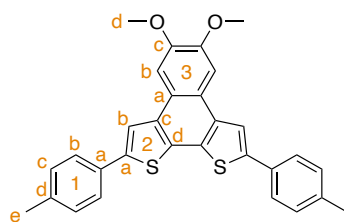


Figure A 42. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(methoxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OMe})\text{Tol}_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	129.7
1b	7.69	126.2
1c	7.31–7.17	129.9
1d	-	138.1
1e	2.42	21.4
2a	-	142.3
2b	7.96	117.5
2c	-	134.7
2d	-	131.7
3a	-	122.7
3b	7.61	104.8
3c	-	148.9
3d	4.11	56.2

Figure A 43. 5,6-bis(methoxy)-2,9-di-*p*-tolynaphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)Tol₂** with assignment of ^1H and ^{13}C resonances.

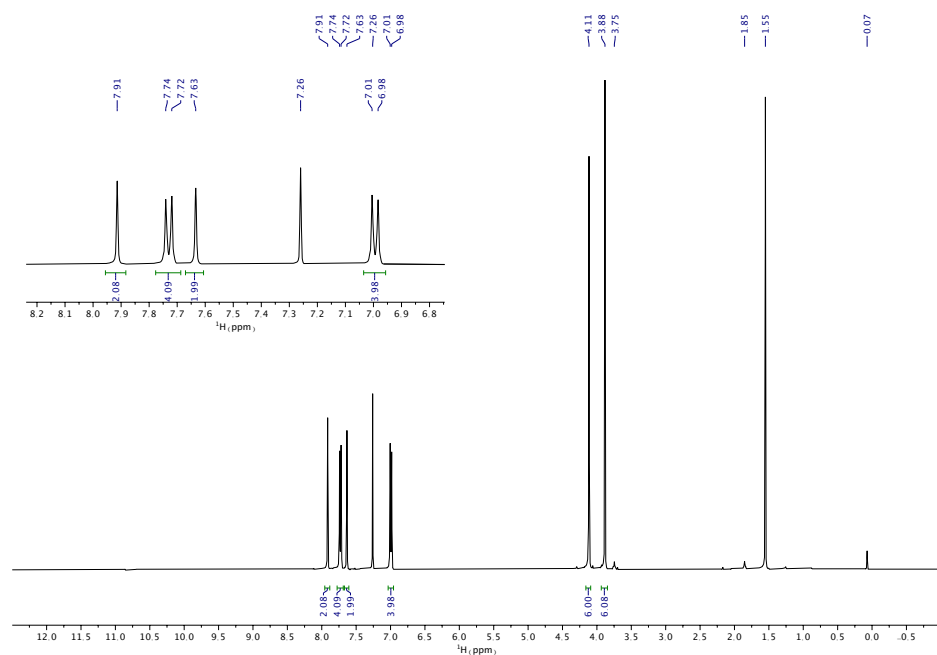


Figure A 44. ^1H NMR spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

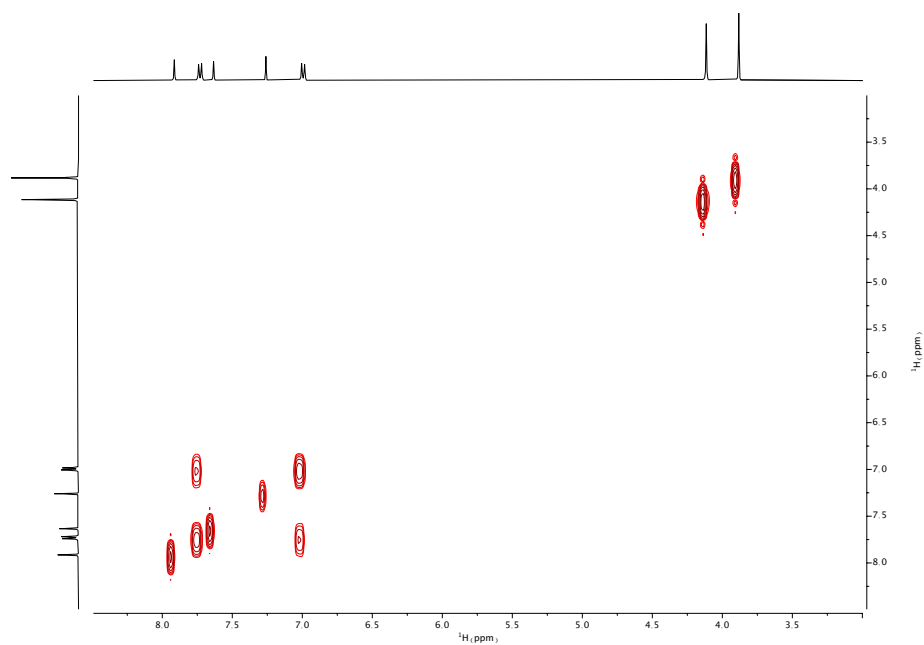


Figure A 45. ^1H - ^1H COSY spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

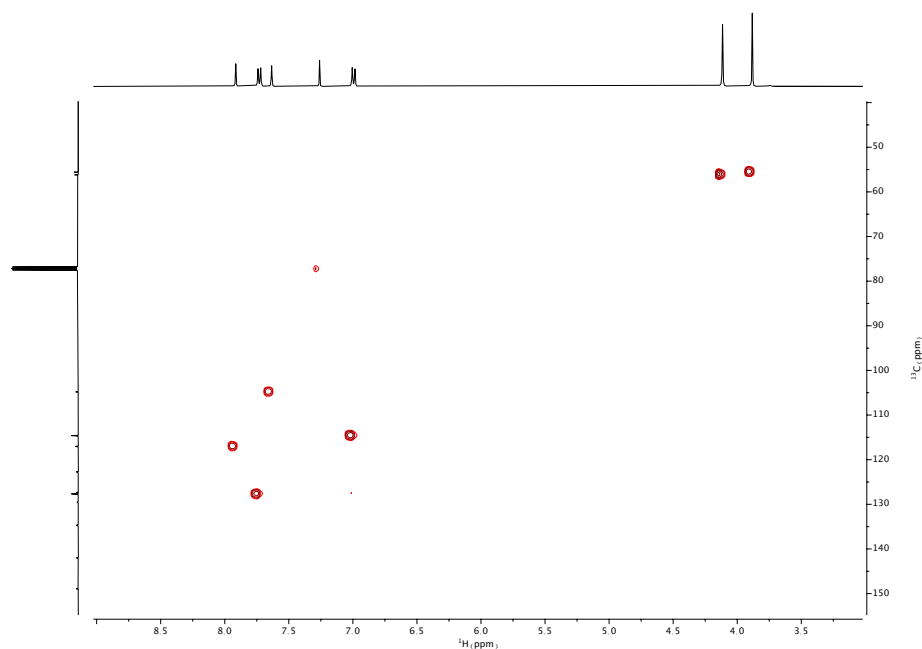


Figure A 46. ^1H - ^{13}C HSQC spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

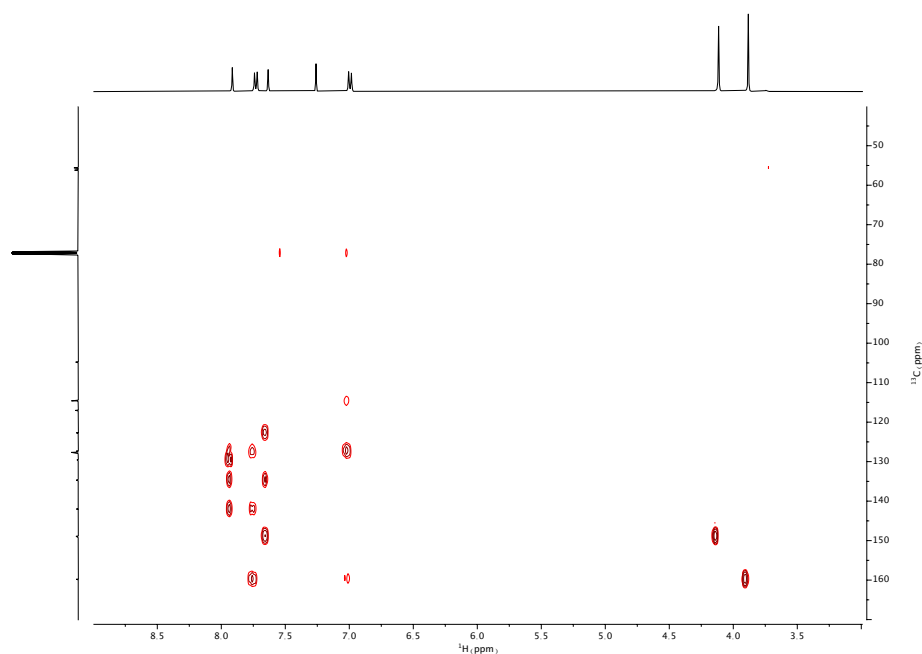


Figure A 47. ^1H - ^{13}C HMBC spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

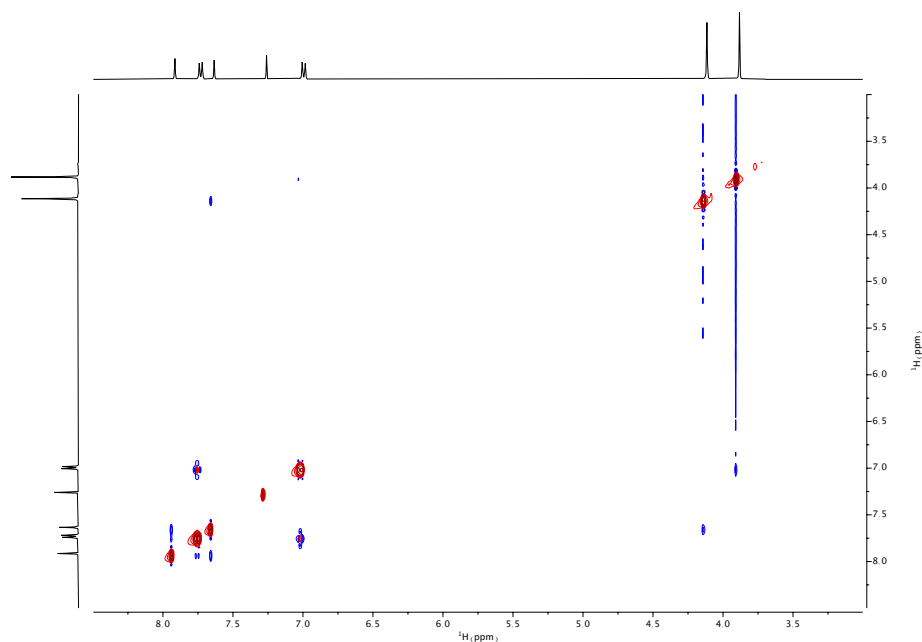


Figure A 48. ^1H - ^1H NOESY spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)(PhOMe)₂** (CDCl_3 , 400 MHz, 298 K).

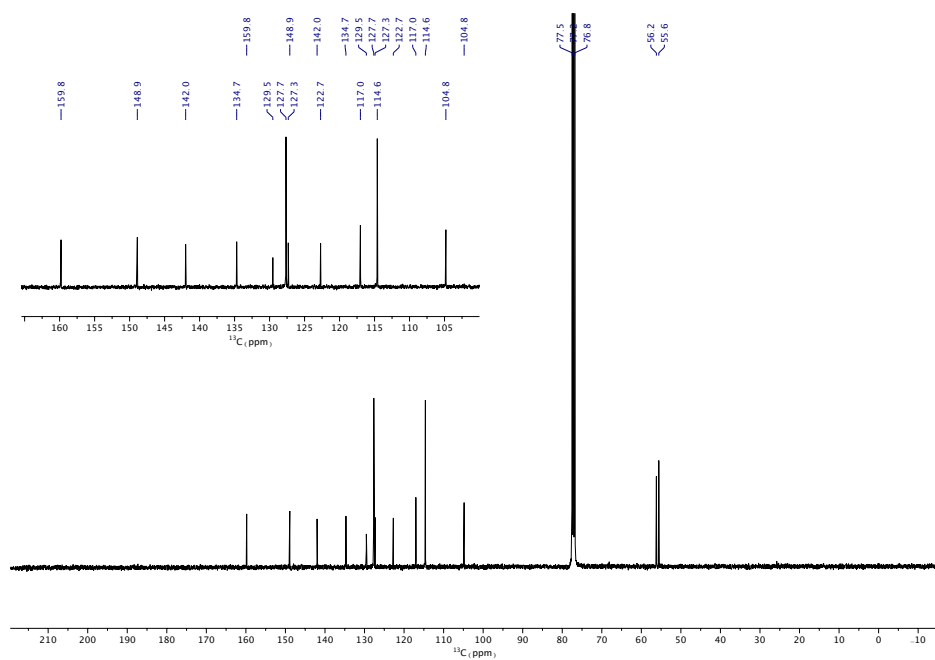
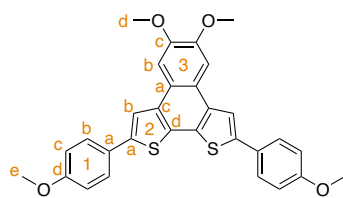


Figure A 49. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(methoxy)-2,9-di(4-methoxyphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)(PhOMe)₂** (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	127.3
1b	7.73	127.7
1c	6.99	114.6
1d	-	159.8
1e	3.88	55.6
2a	-	142.0
2b	7.91	117.0
2c	-	134.7
2d	-	129.5
3a	-	122.7
3b	7.63	104.8
3c	-	148.9
3d	4.11	56.2

Figure A 50. **$\alpha(\text{OMe})(\text{PhOMe})_2$** with assignment of ^1H and ^{13}C resonances.

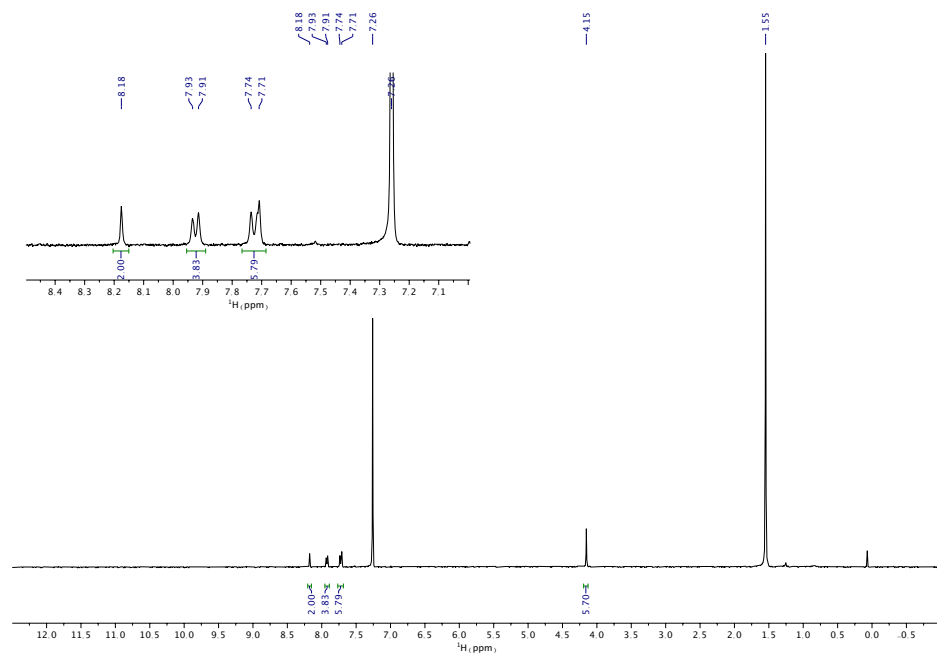


Figure A 51. ^1H NMR spectrum of 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a**(OMe)(PhCF₃)₂ (CDCl₃, 400 MHz, 298 K).

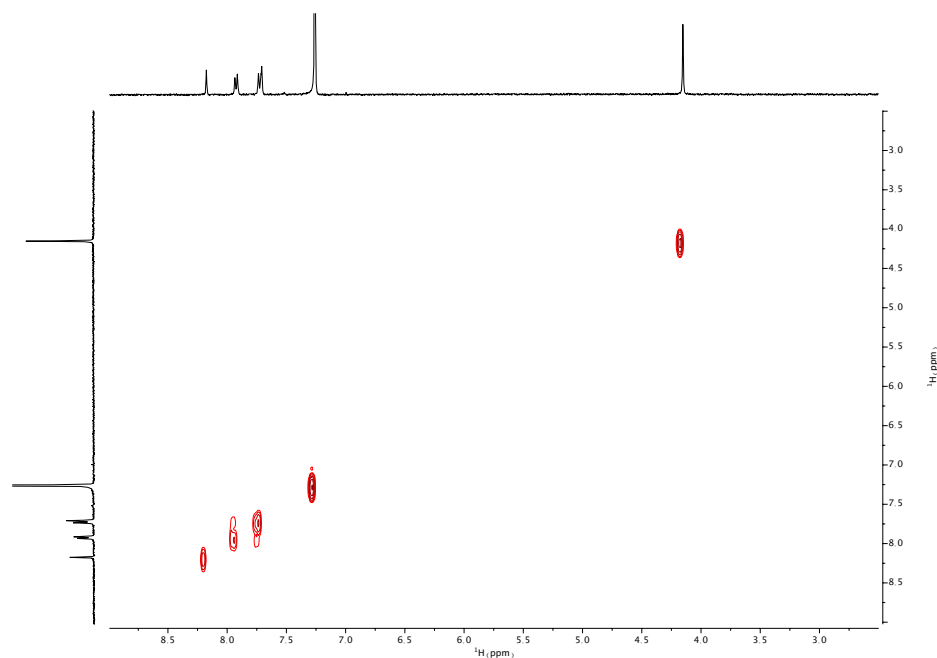


Figure A 52. ^1H - ^1H COSY spectrum of 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a**(OMe)(PhCF₃)₂ (CDCl₃, 400 MHz, 298 K).

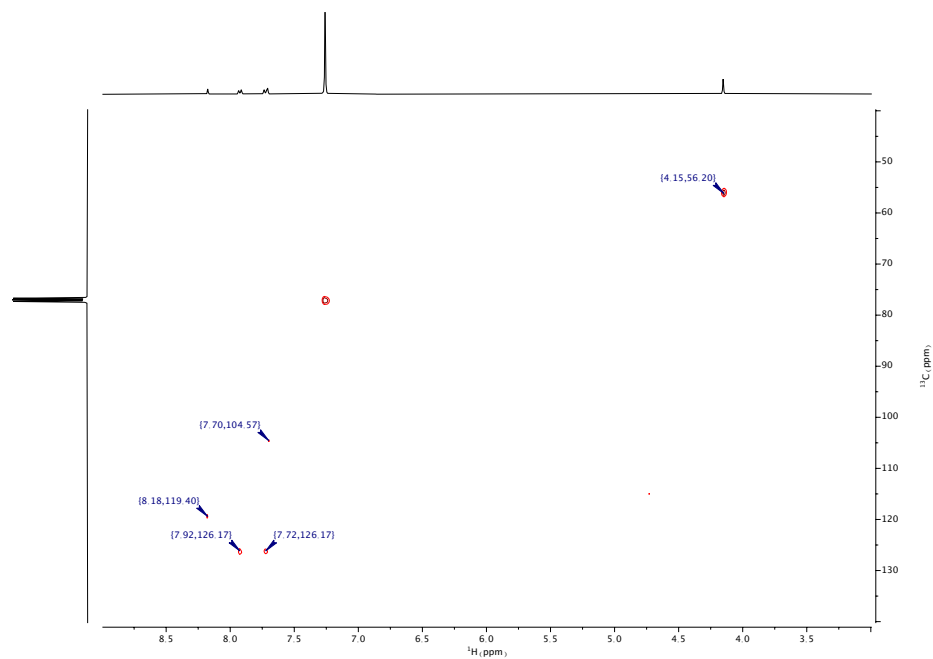
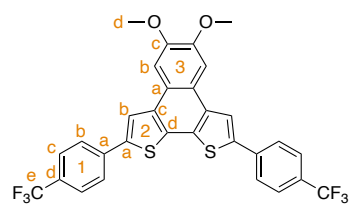


Figure A 53. ^1H - ^{13}C HSQC spectrum of 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(OMe)(PhCF₃)₂** (CDCl_3 , 400 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	-
1b	7.92	126.2
1c	7.72	126.2
1d	-	-
1e	-	-
2a	-	-
2b	8.18	119.4
2c	-	-
2d	-	-
3a	-	-
3b	7.11	104.6
3c	-	-
3d	4.15	56.2

Figure A 54. 5,6-bis(methoxy)-2,9-di(4-trifluoromethylphenyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(\text{OMe})(\text{PhCF}_3)_2$ with assignment of ^1H and ^{13}C resonances. ^{13}C resonances extracted from HSQC.

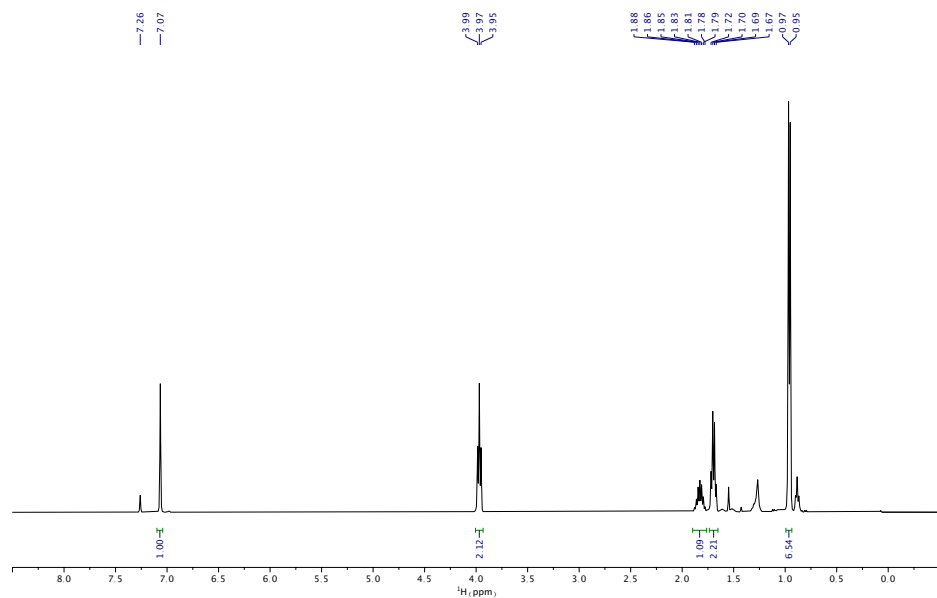


Figure A 55. ¹H NMR spectrum of 1,2-dibromo-4,5-di-isopentyloxybenzene **1(Oi-Pent)** (CDCl₃, 400 MHz, 298 K).

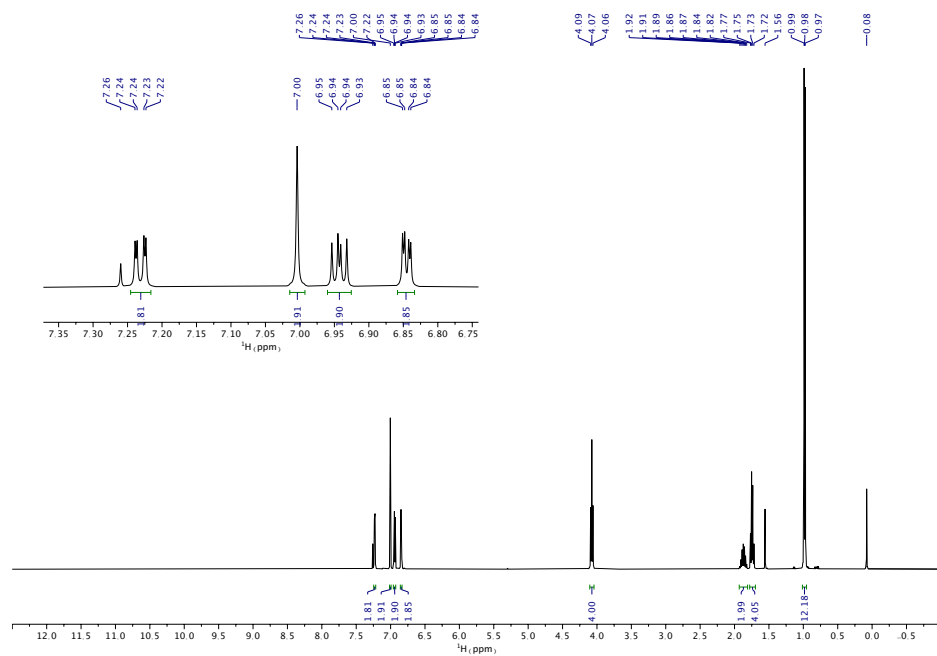


Figure A 56. ¹H NMR spectrum of 1,2-di(2-thienyl)-4,5-di-isopentyloxybenzene **3(Oi-Pent)** (CDCl₃, 400 MHz, 298 K).

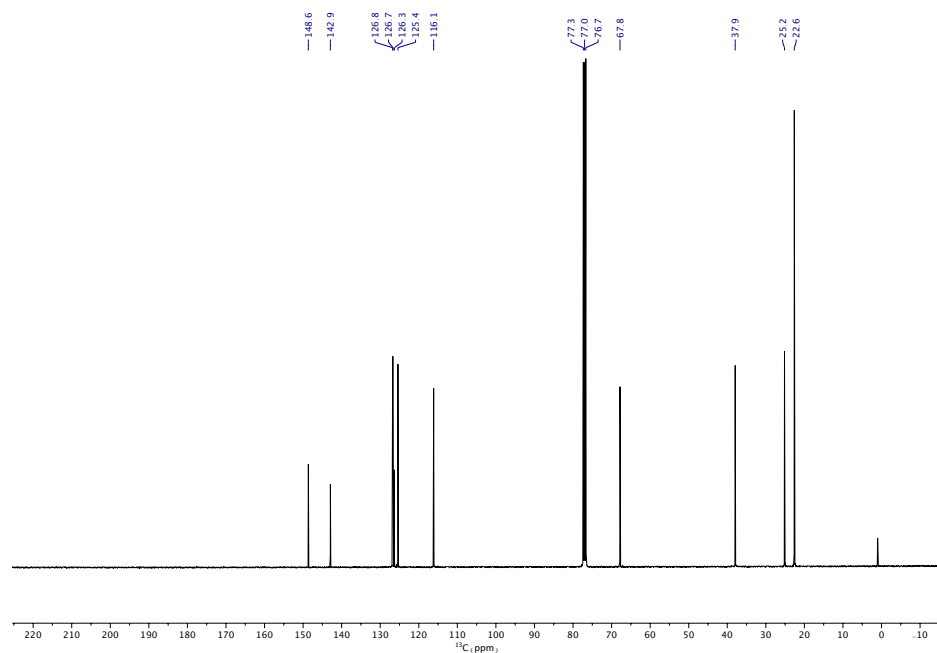


Figure A 57. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1,2-di(2-thienyl)-4,5-di-isopentyloxybenzene **3(Oi-Pent)** (CDCl_3 , 101 MHz, 298 K).

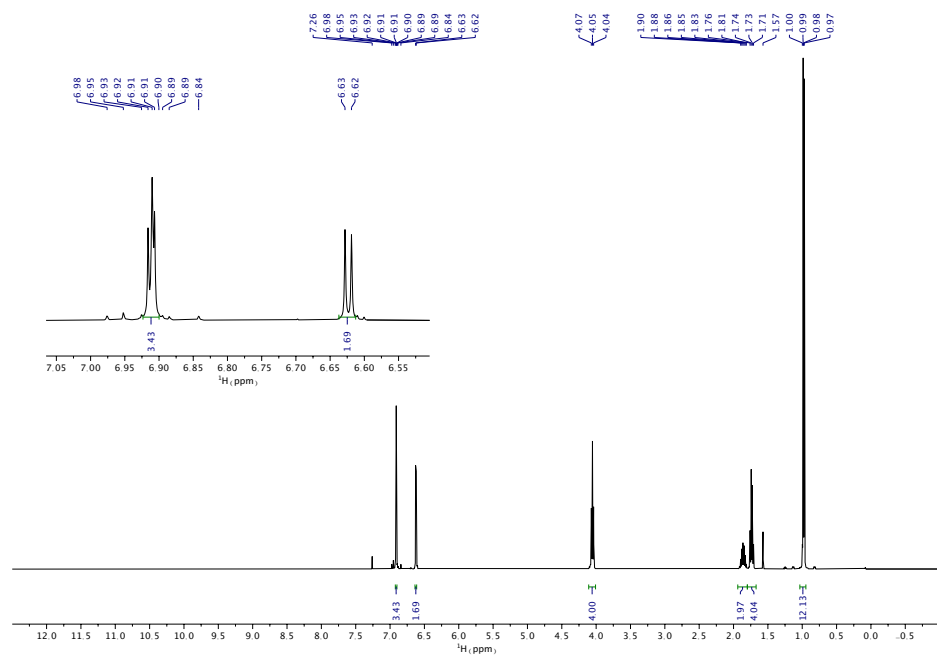


Figure A 58. ^1H NMR spectrum of 1,2-di(2-(5-bromothieryl))-4,5-di-isopentyloxybenzene **4(Oi-Pent)** (CDCl_3 , 400 MHz, 298 K)

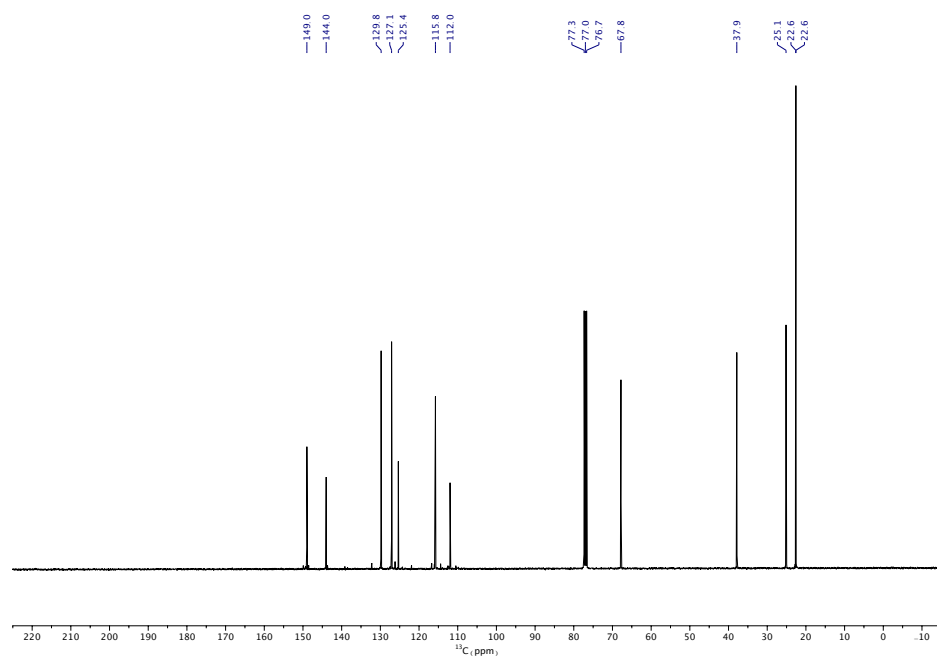


Figure A 59. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1,2-di(2-(5-bromothieryl)-4,5-diisopentyloxybenzene **4(Oi-Pent)** (CDCl_3 , 101 MHz, 298 K).

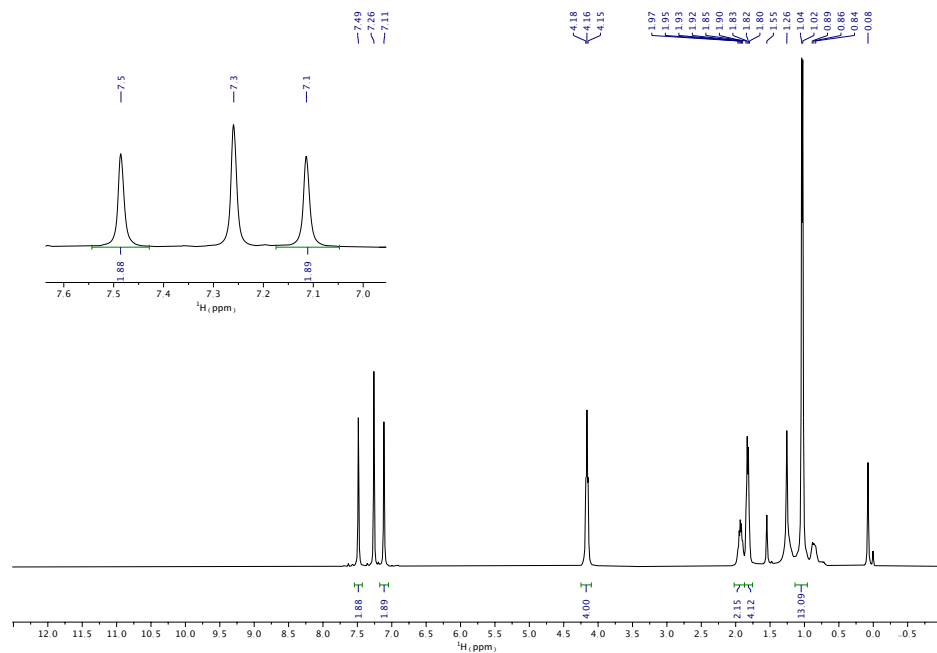


Figure A 60. ^1H NMR spectrum of 2,5-dibromo-8,9-bis(isopentyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})\text{Br}_2$** (CDCl_3 , 400 MHz, 298 K).

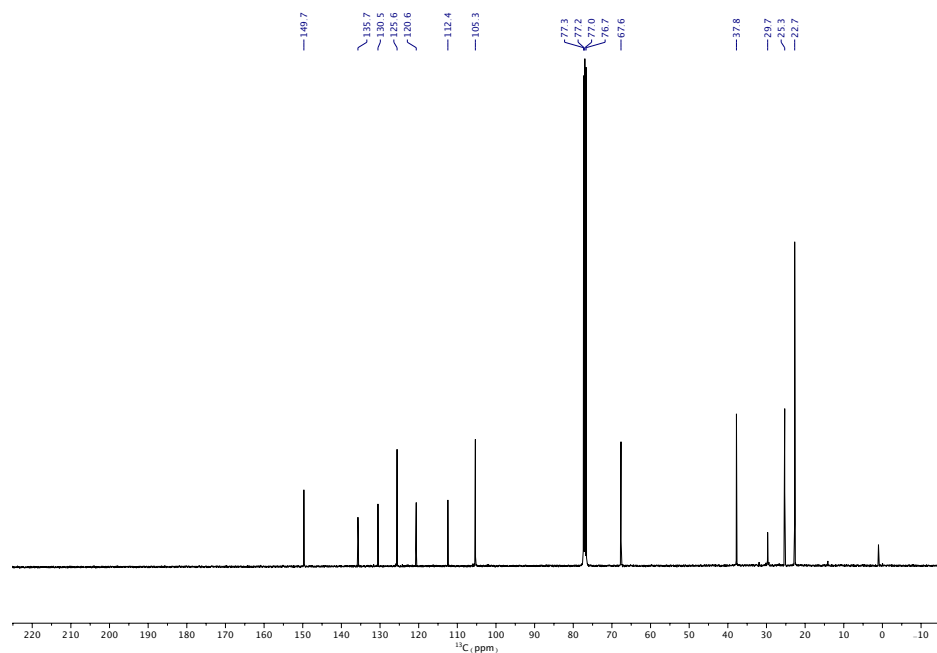


Figure A 61. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2,5-dibromo-8,9-bis(isopentyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene $\beta(\text{Oi-Pent})\text{Br}_2$ (CDCl_3 , 101 MHz, 298 K).

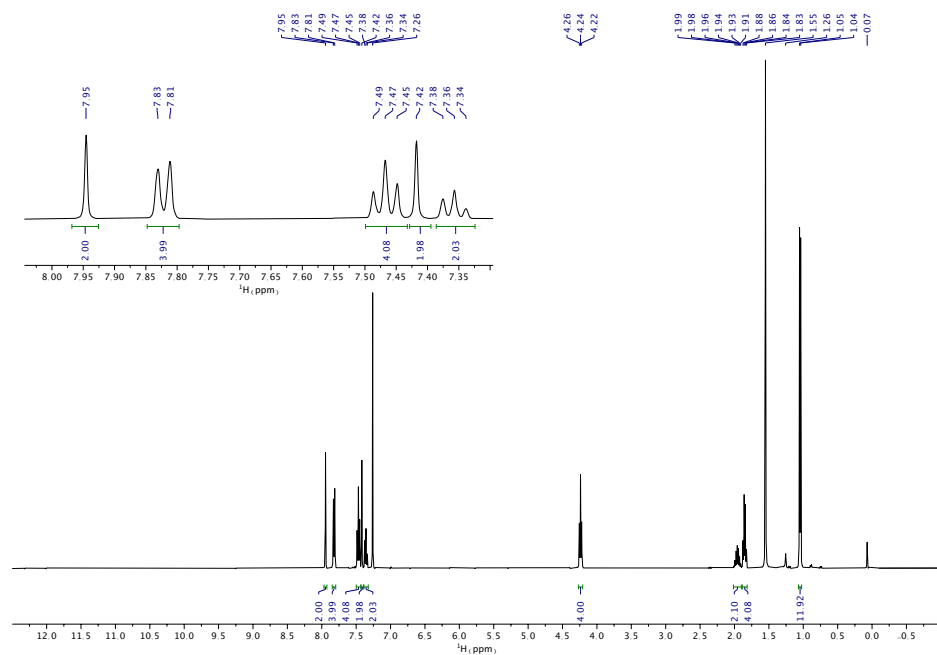


Figure A 62. ^1H NMR spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2-*b*:4,3-*b'*]dithiophene $\beta(\text{Oi-Pent})\text{Ph}_2$ (CDCl_3 , 400 MHz, 298 K).

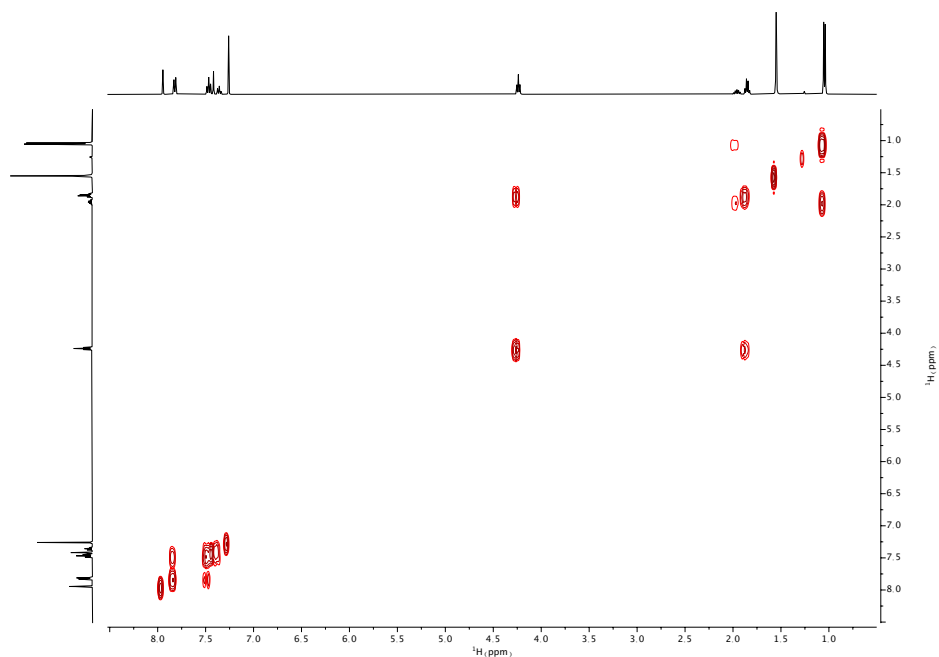


Figure A 63. ^1H - ^1H COSY spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K).

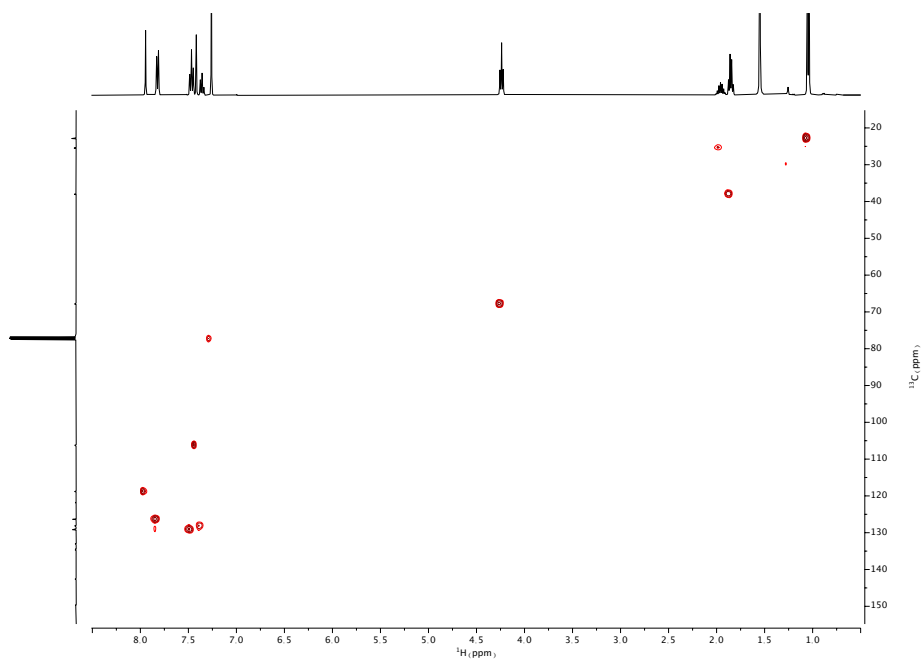


Figure A 64. ^1H - ^{13}C HSQC spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K)

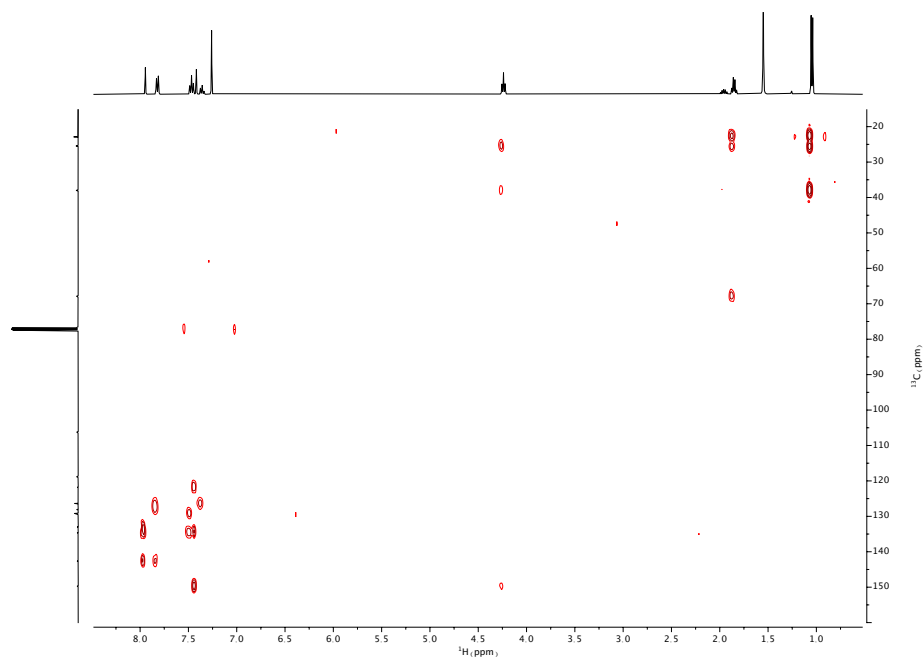


Figure A 65. ^1H - ^{13}C HMBC spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K).

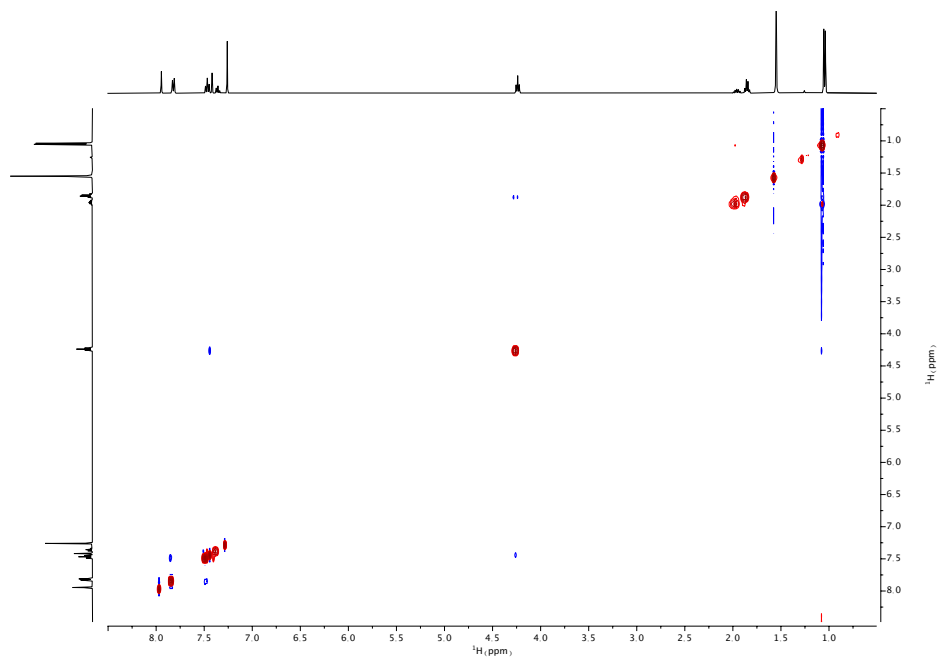


Figure A 66. ^1H - ^1H NOESY spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})\text{Ph}_2$** (CDCl_3 , 400 MHz, 298 K).

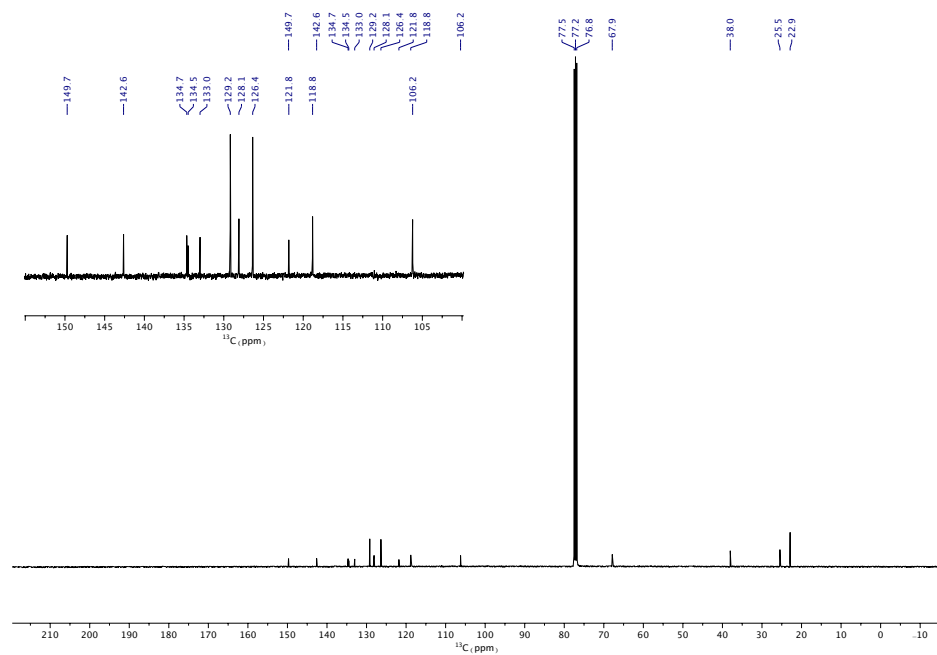
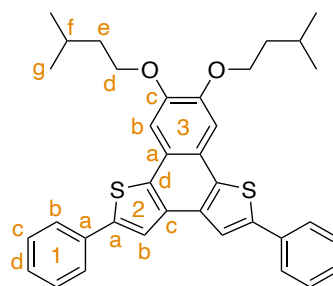


Figure A 67. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})\text{Ph}_2$** (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	133.0
1b	7.82	126.4
1c	7.47	129.2
1d	7.36	128.1
2a	-	142.6
2b	7.95	118.8
2c	-	134.7
2d	-	134.5
3a	-	121.8
3b	7.42	106.2
3c	-	149.7
3d	4.24	67.9
3e	1.85	38.0
3f	1.95	25.5
3g	1.05	22.9

Figure A 68. 8,9-bis(isopentyloxy)-2,5-diphenylnaphtho[1,2-*b*:4,3-*b'*]dithiophene **β (Oi-Pent)Ph₂** with assignment of ^1H and ^{13}C resonances.

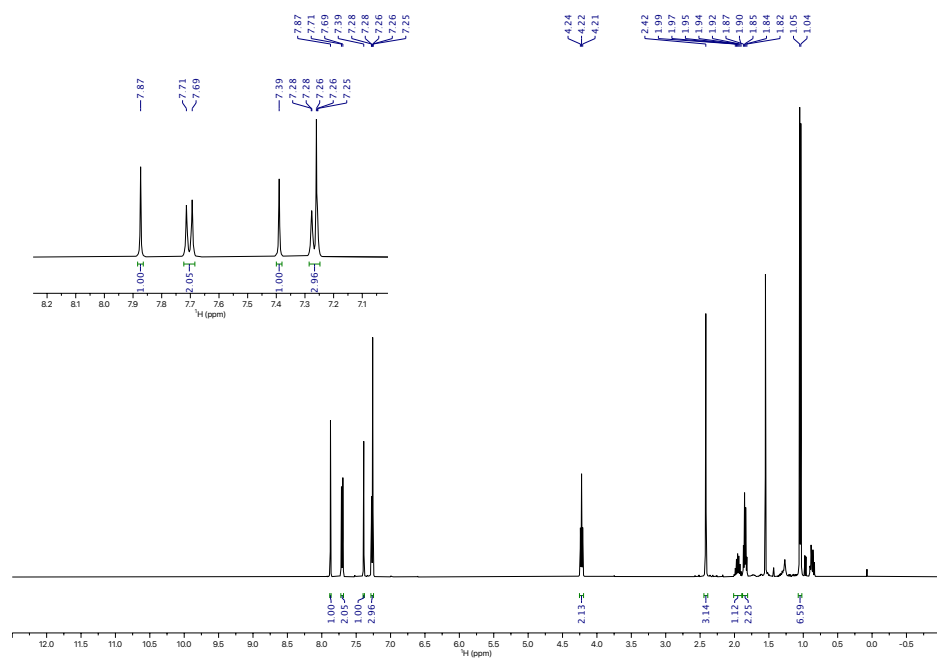


Figure A 69. ^1H NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di-*p*-tolynaphtho[1,2-*b*:4,3-*b'*]dithiophene, $\beta(\text{Oi-Pent})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

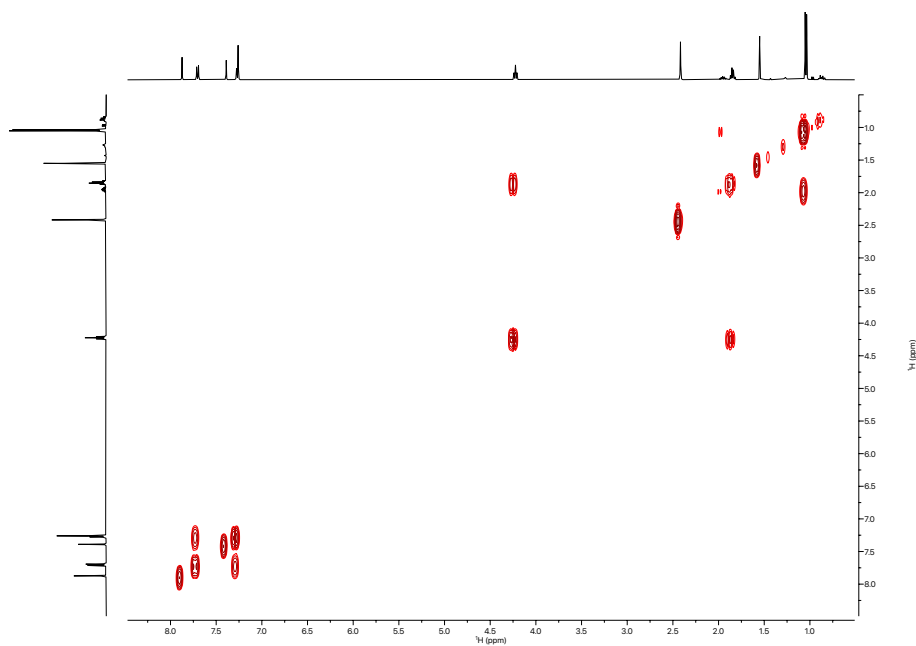


Figure A 70. ^1H - ^1H COSY spectrum of 8,9-bis(isopentyloxy)-2,5-di-*p*-tolynaphtho[1,2-*b*:4,3-*b'*]dithiophene, $\beta(\text{Oi-Pent})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

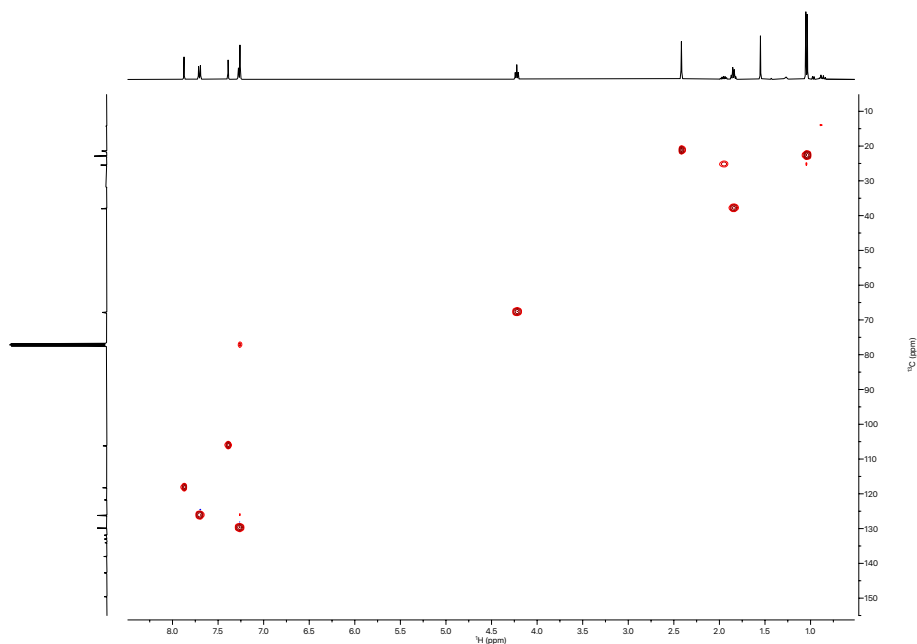


Figure A 71. ^1H - ^{13}C HSQC spectrum of 8,9-bis(isopentyloxy)-2,5-di-*p*-tolynaphtho[1,2-*b*:4,3-*b'*]dithiophene, $\beta(\text{Oi-Pent})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

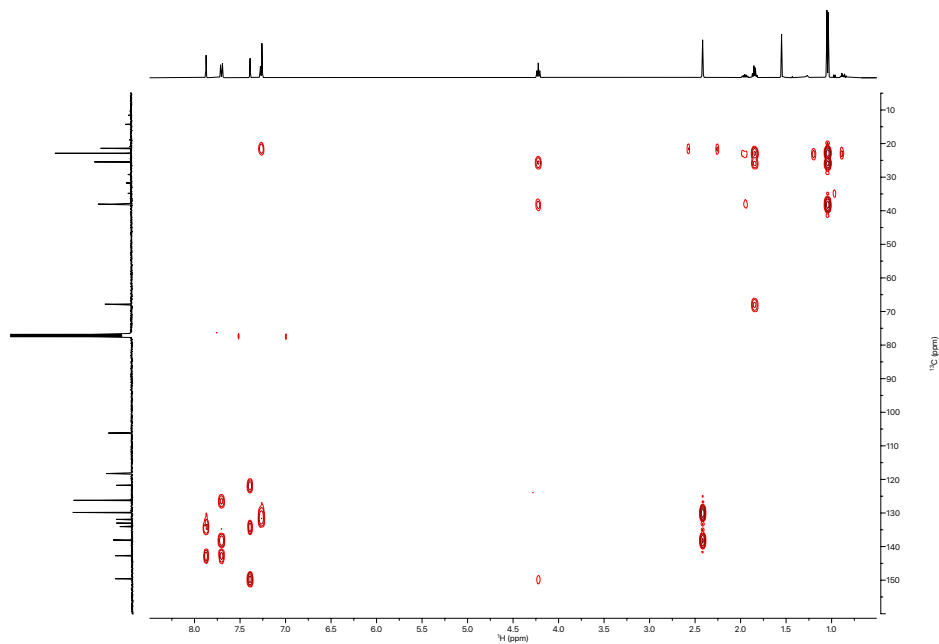


Figure A 72. ^1H - ^{13}C HMBC spectrum of 8,9-bis(isopentyloxy)-2,5-di-*p*-tolynaphtho[1,2-*b*:4,3-*b'*]dithiophene, $\beta(\text{Oi-Pent})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

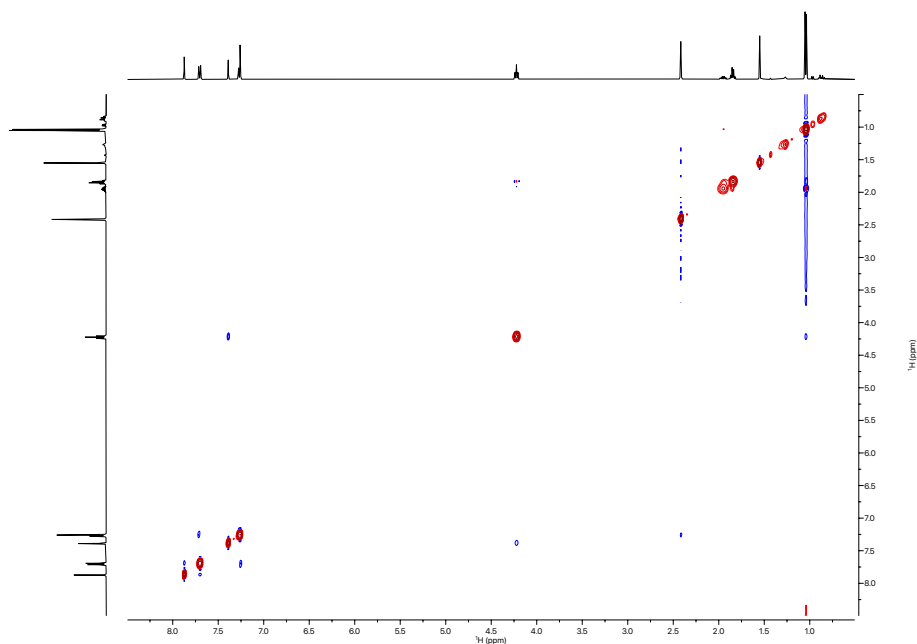


Figure A 73. ^1H - ^1H NOESY spectrum of 8,9-bis(isopentyloxy)-2,5-di-*p*-tolynaphtho[1,2-*b*:4,3-*b'*]dithiophene, $\beta(\text{Oi-Pent})\text{Tol}_2$ (CDCl_3 , 400 MHz, 298 K).

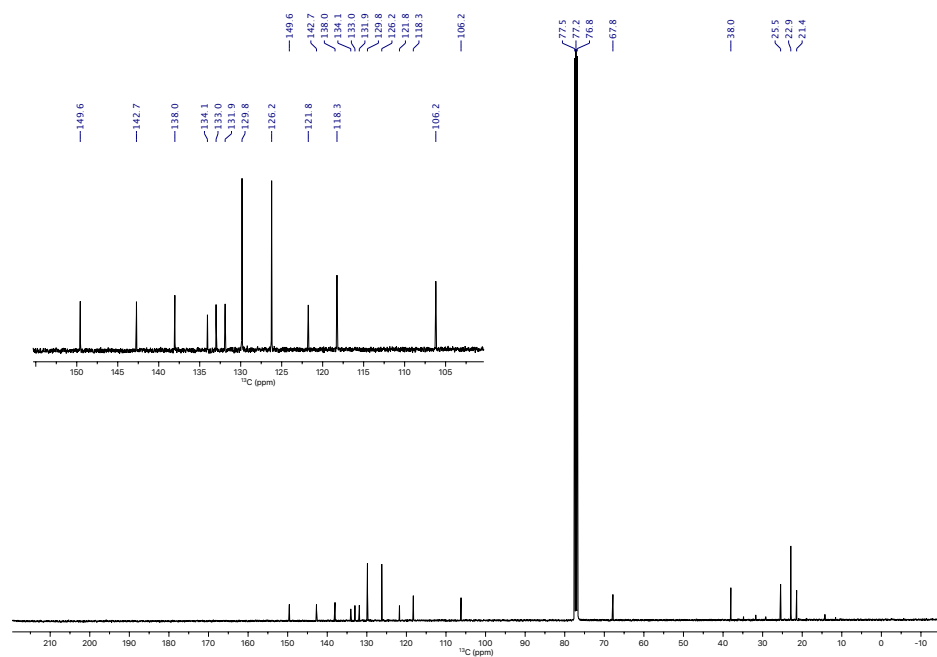
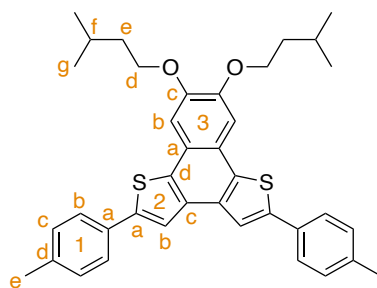


Figure A 74. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di-*p*-tolynaphtho[1,2-*b*:4,3-*b'*]dithiophene, $\beta(\text{Oi-Pent})\text{Tol}_2$ (CDCl_3 , 101 MHz, 298 K)



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	131.9
1b	7.70	126.2
1c	7.29–7.23	129.8
1d	-	138.0
1e	2.42	21.4
2a	-	142.7
2b	7.87	118.3
2c	-	133.0
2d	-	134.1
3a	-	121.8
3b	7.39	106.2
3c	-	149.6
3d	4.22	67.8
3e	1.85	38.0
3f	1.95	25.5
3g	1.04	22.9

Figure A 75. 8,9-bis(isopentyloxy)-2,5-di-*p*-tolynaphtho[1,2-*b*:4,3-*b'*]dithiophene, **β(Oi-Pent)Tol₂** with assignment of ^1H and ^{13}C resonances.

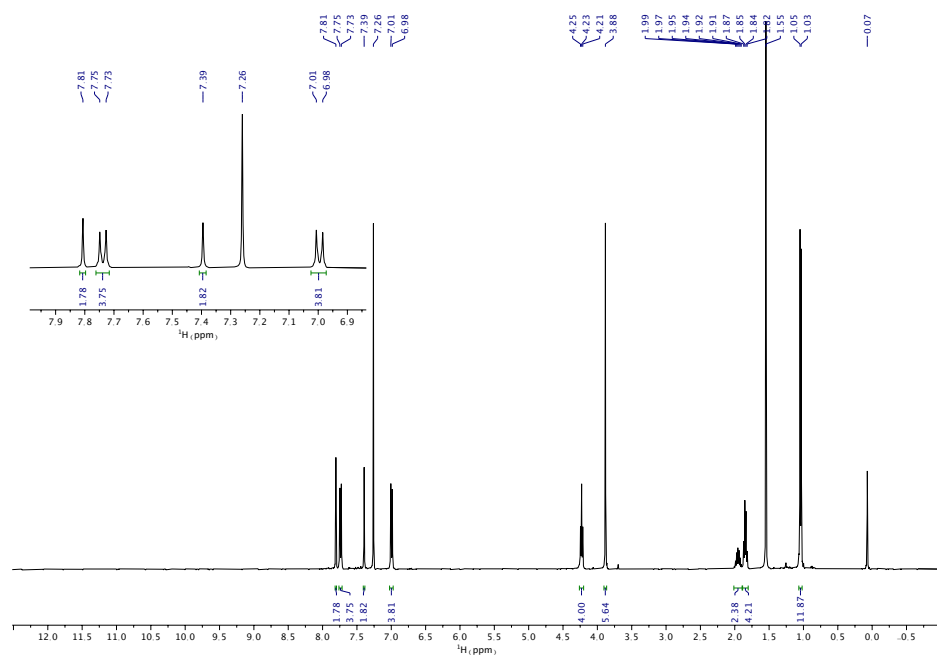


Figure A 76. ^1H NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})(\text{PhOMe})_2$** (CDCl_3 , 400 MHz, 298 K).

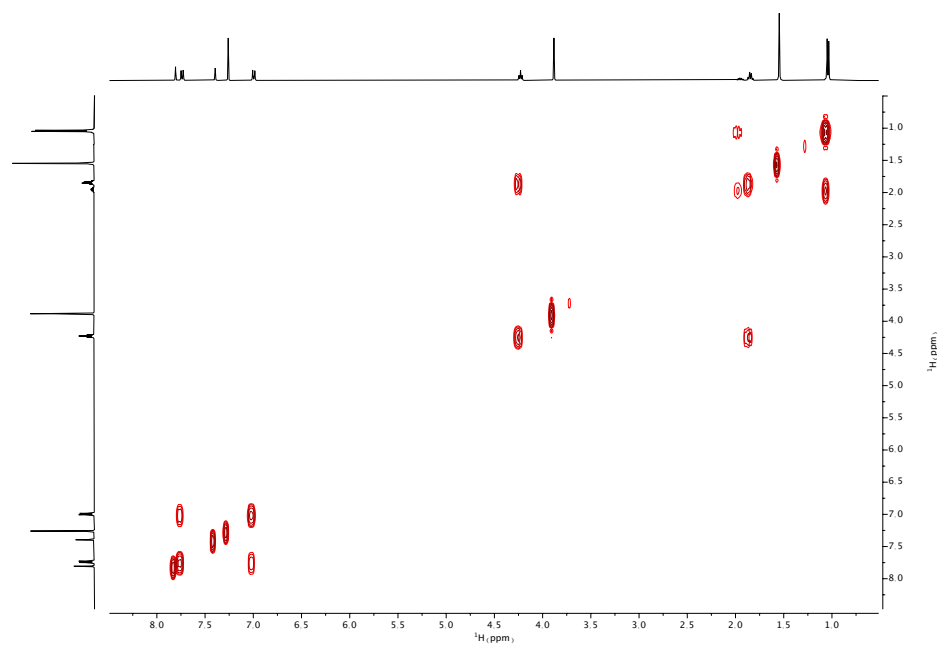


Figure A 77. ^1H - ^1H COSY spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})(\text{PhOMe})_2$** (CDCl_3 , 400 MHz, 298 K).

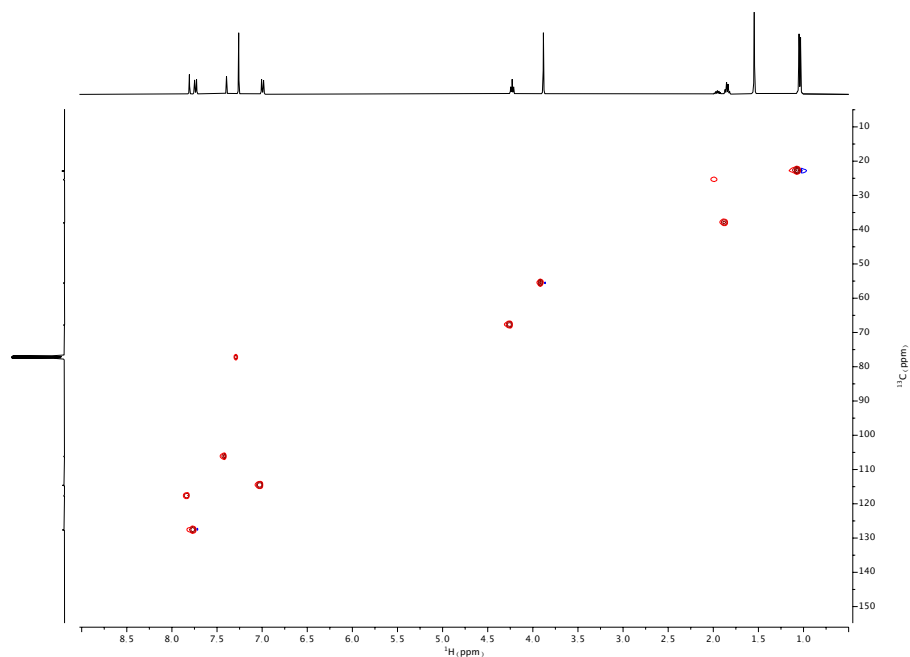


Figure A 78. ^1H - ^{13}C HSQC spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})(\text{PhOMe})_2$** (CDCl_3 , 400 MHz, 298 K).

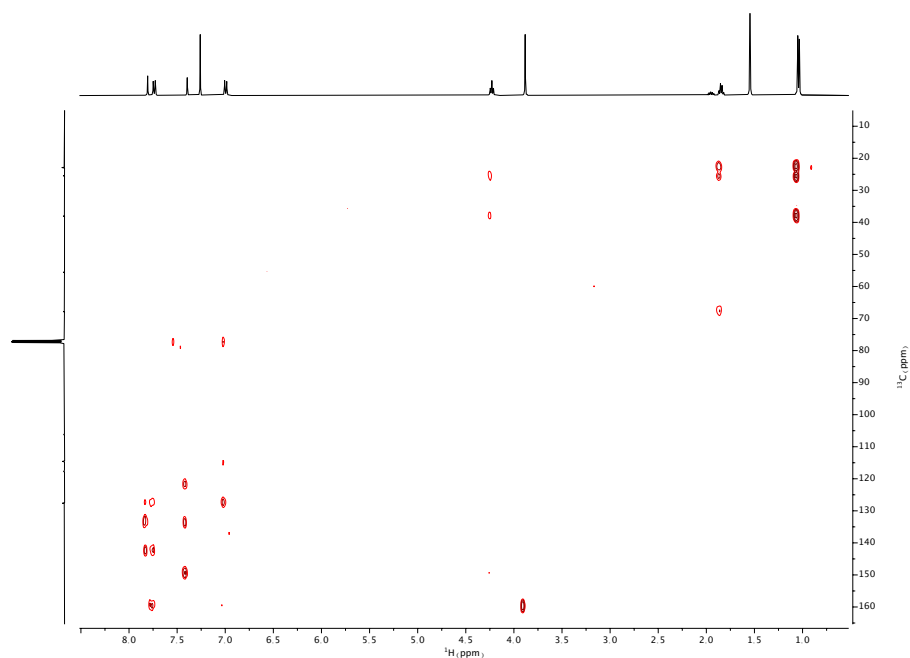


Figure A 79. ^1H - ^{13}C HMBC spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})(\text{PhOMe})_2$** (CDCl_3 , 400 MHz, 298 K).

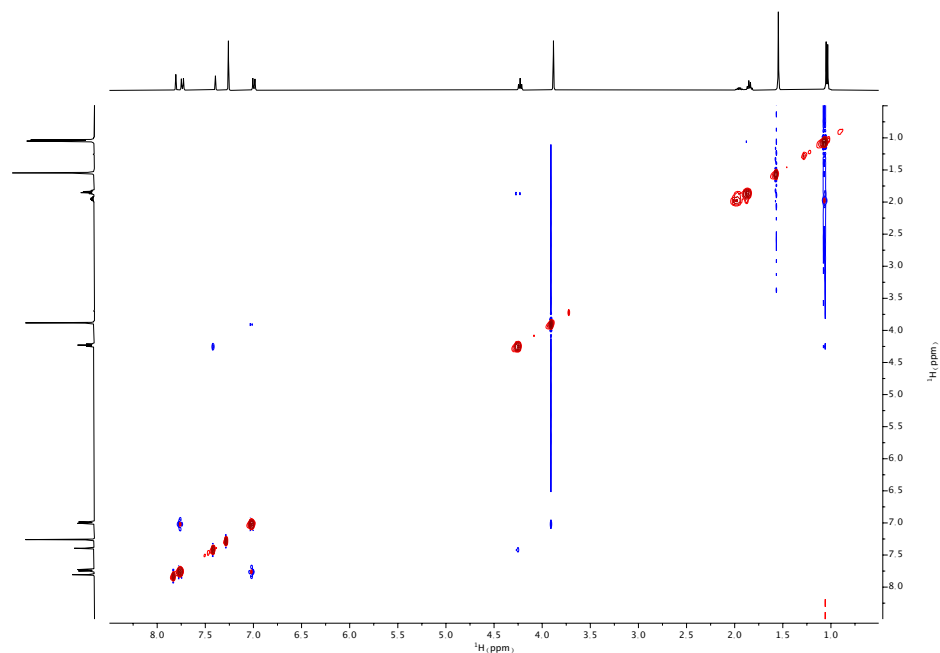


Figure A 80. ^1H - ^1H NOESY spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **β (Oi-Pent)(PhOMe) $_2$** (CDCl_3 , 400 MHz, 298 K).

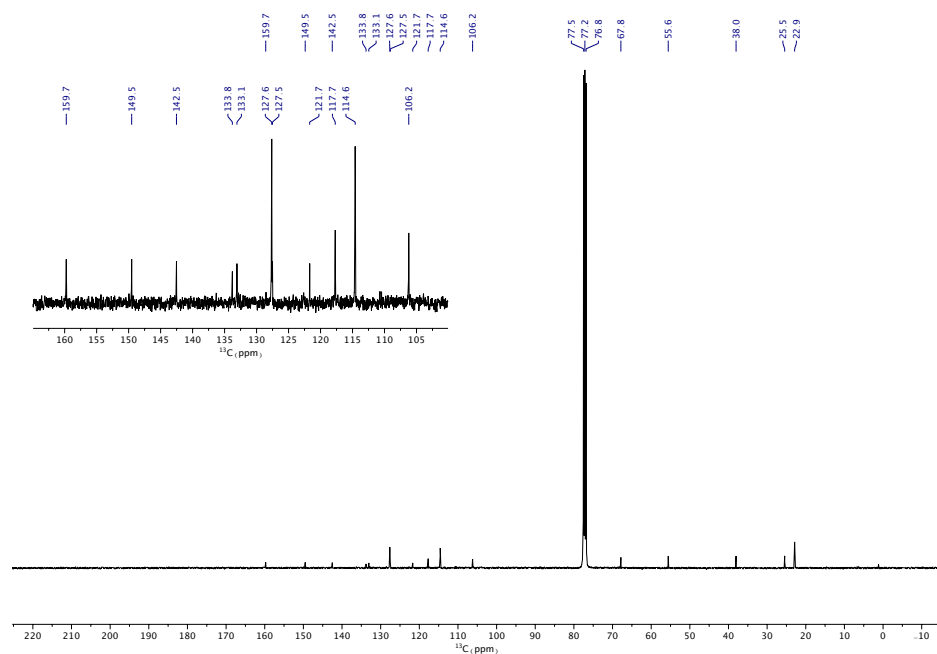
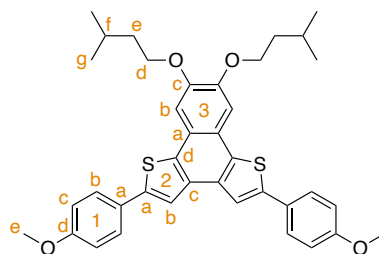


Figure A 81. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **β (Oi-Pent)(PhOMe) $_2$** (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	127.5
1b	7.74	127.6
1c	7.00	114.6
1d	-	159.8
1e	3.88	55.6
2a	-	142.5
2b	7.81	117.7
2c	-	133.1
2d	-	133.8
3a	-	121.7
3b	7.39	106.2
3c	-	149.5
3d	4.23	67.9
3e	1.84	38.0
3f	1.95	25.5
3g	1.04	22.9

Figure A 82. 8,9-bis(isopentyloxy)-2,5-di(4-methoxyphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **β (Oi-Pent)(PhOMe)₂** with assignment of ^1H and ^{13}C resonances.

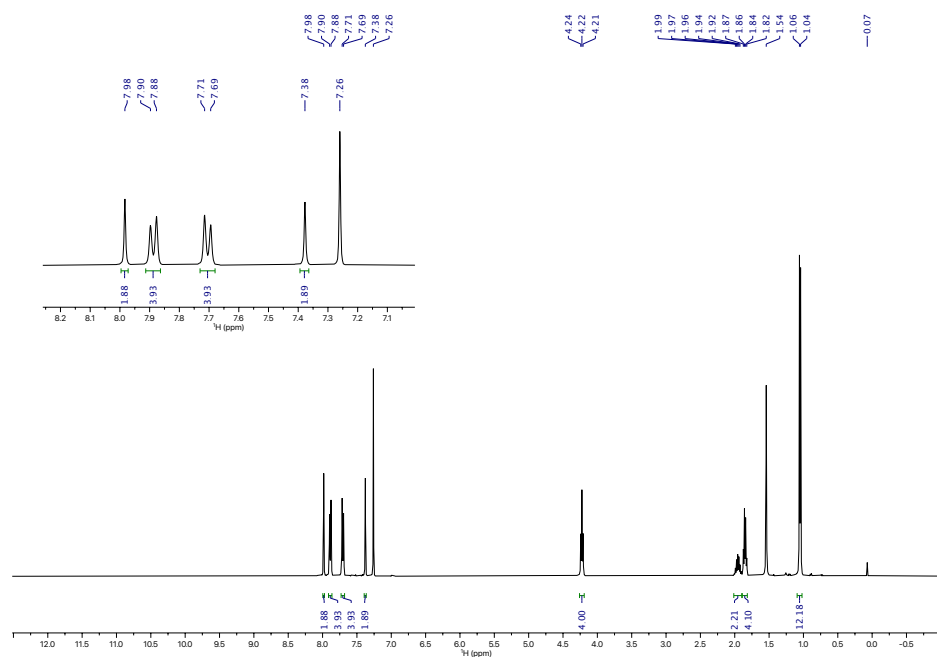


Figure A 83. ^1H NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K).

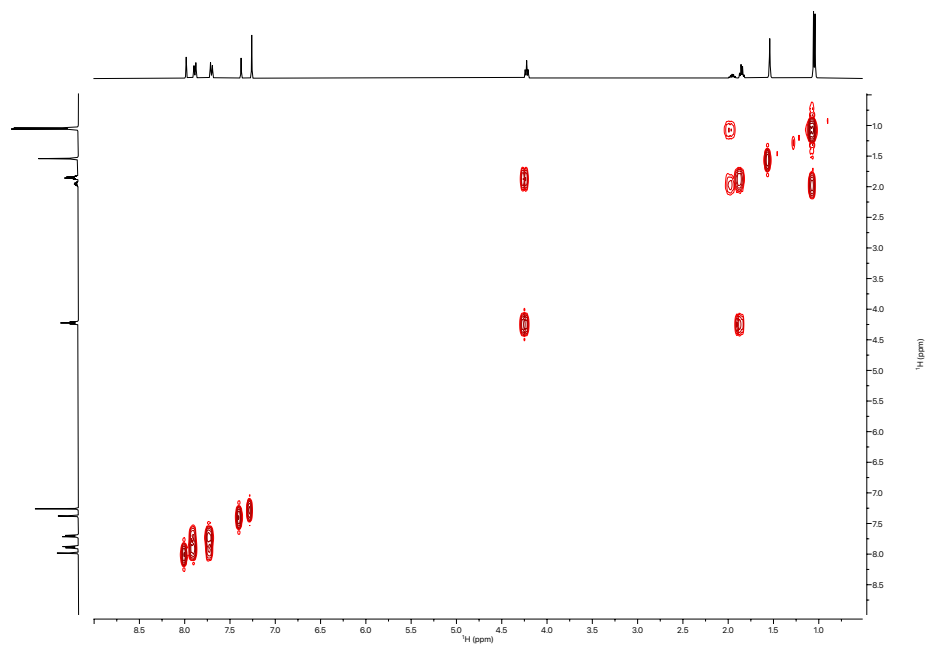


Figure A 84. ^1H - ^1H COSY spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K).

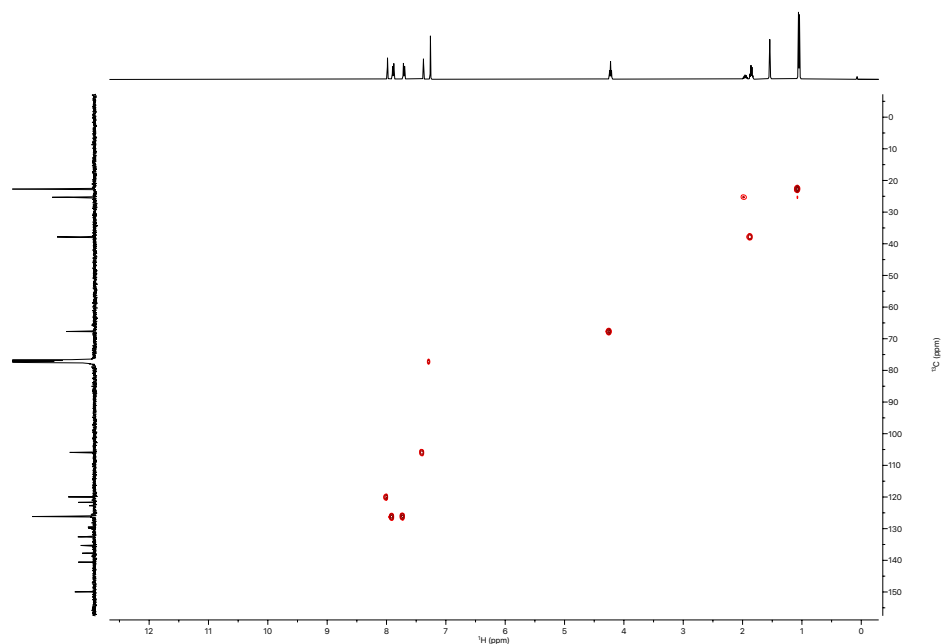


Figure A 85. ^1H - ^{13}C HSQC spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$** (CDCl_3 , 400 MHz, 298 K).

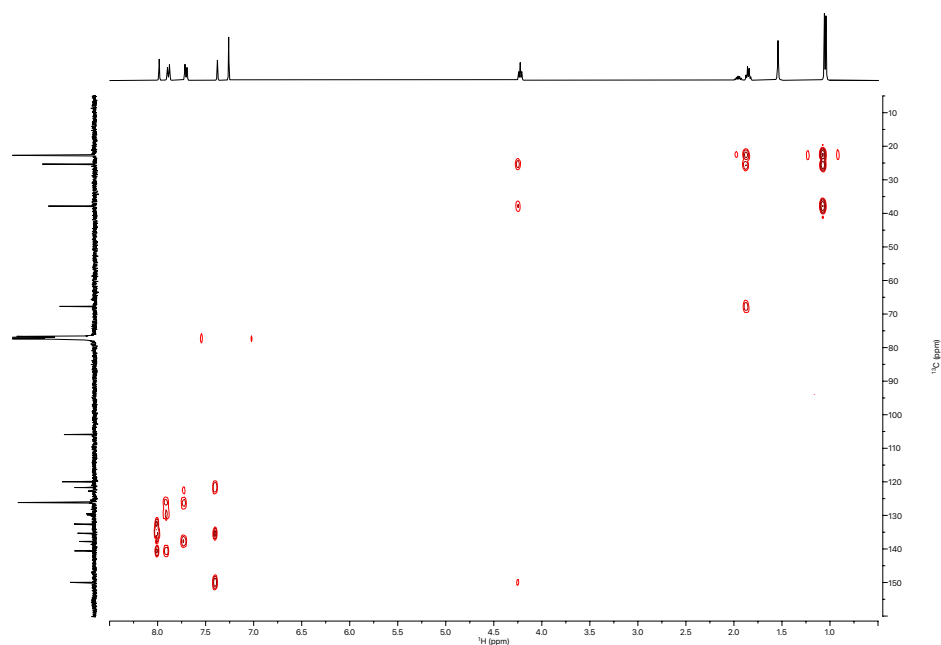


Figure A 86. ^1H - ^{13}C HMBC spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$** (CDCl_3 , 400 MHz, 298 K).

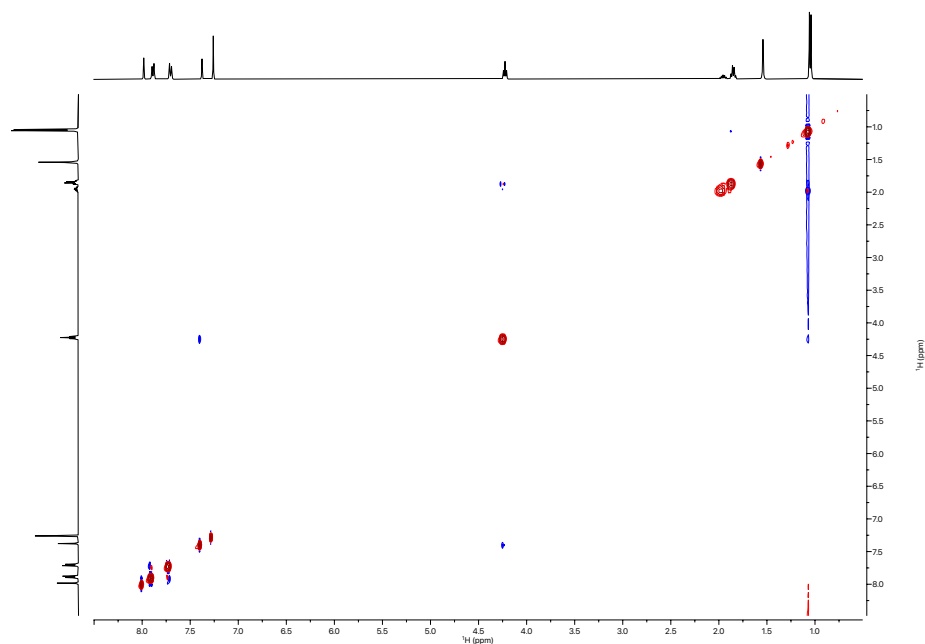


Figure A 87. ^1H - ^1H NOESY spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 400 MHz, 298 K).

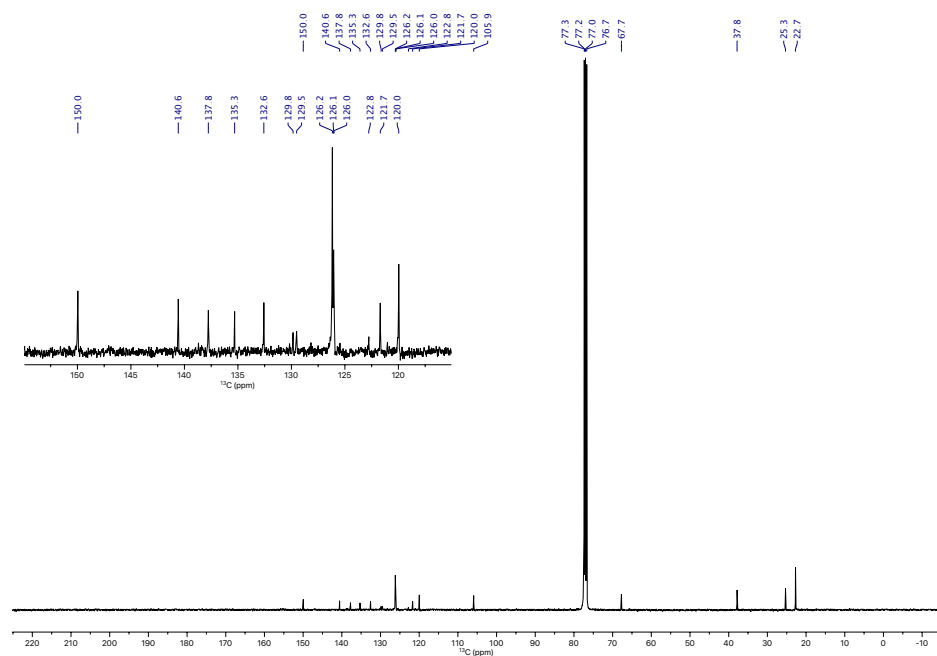
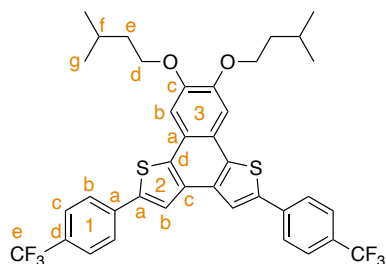


Figure A 88. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	137.8
1b	7.89	126.2
1c	7.70	126.1, J = 3.9 Hz
1d	-	129.7, J = 33.0 Hz
1e	-	121.4, J = 271.7 Hz
2a	-	140.6
2b	7.98	120.0
2c	-	132.6
2d	-	135.3
3a	-	121.7
3b	7.38	105.9
3c	-	150.0
3d	4.22	67.7
3e	1.85	37.8
3f	1.96	25.3
3g	1.05	22.7

Figure A 89. 8,9-bis(isopentyloxy)-2,5-di(4-trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene **$\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$** with assignment of ^1H and ^{13}C resonances.

2.5 Photophysical Properties of **$\alpha(\text{OHex})\text{R}_2$** and **$\beta(\text{Oi-Pent})\text{R}_2$**

Absorbance spectra were collected on an Agilent Cary Bio100 spectrophotometer and corrected for solvent background absorbance and instrument drift. Emission spectra were recorded on a Horiba Jon-Yvon Fluorolog-3 with excitation and emission slit widths set at 2 nm. Both series, **$\alpha(\text{OHex})\text{R}_2$** and **$\beta(\text{Oi-Pent})\text{R}_2$** , were prepared under inert atmosphere, sealed in 1 cm path length quartz cuvettes, and were analyzed at $\lambda_{\text{ex}} = 365$

nm (for emission spectra). Fluorescence quantum yields were determined by reference to 9,10-diphenylanthracene in cyclohexane ($\phi = 0.91$) which was cross-checked with quinine bisulfate in 0.5 M H₂SO₄ (aq) ($\phi = 0.54$). Five solutions of varying concentration were prepared for each sample and good fits ($R^2 \geq 0.99$) were obtained in all cases. The absorbance of all sample solutions was kept below 0.10 to avoid the inner-filter effect. Measurements were performed at room temperature with both sample and standard excited at the same wavelength (365 nm). Plots are given below with UV-visible spectra as solid lines and emission spectra as dashed lines. UV-visible spectra are plotted as either molar absorptivity or normalized absorption (left vertical axis) vs wavelength (horizontal axis). Emission spectra are plotted as normalized intensities (right vertical axis) vs wavelength (horizontal axis).

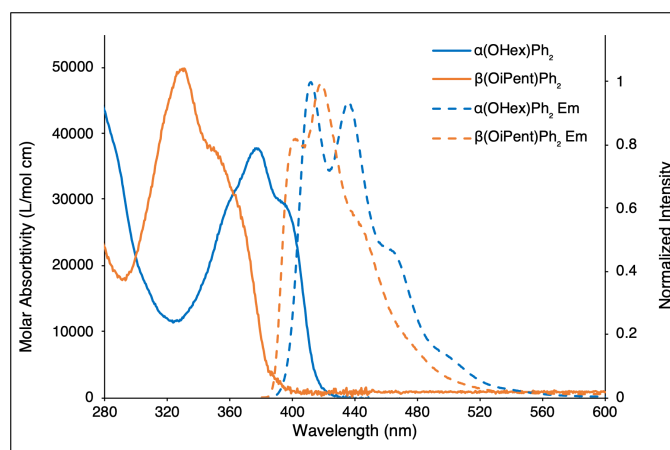


Figure A 90. Absorbance and emission spectra for $\alpha(\text{OHex})\text{Ph}_2$ and $\beta(\text{Oi-Pent})\text{Ph}_2$ in THF.

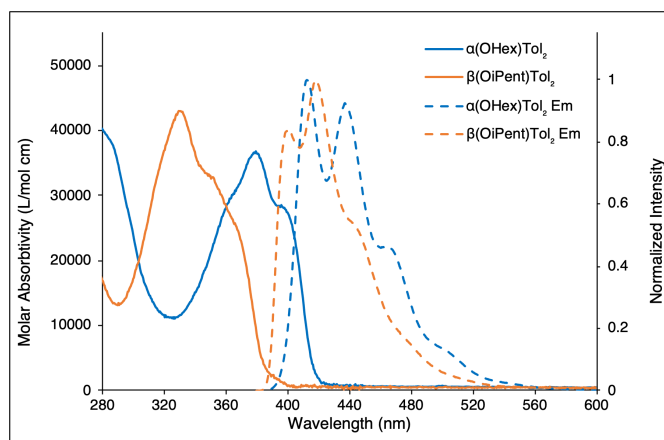


Figure A 91. Absorbance and emission spectra for $\alpha(\text{OHex})\text{Tol}_2$ and $\beta(\text{Oi-Pent})\text{Tol}_2$ in THF.

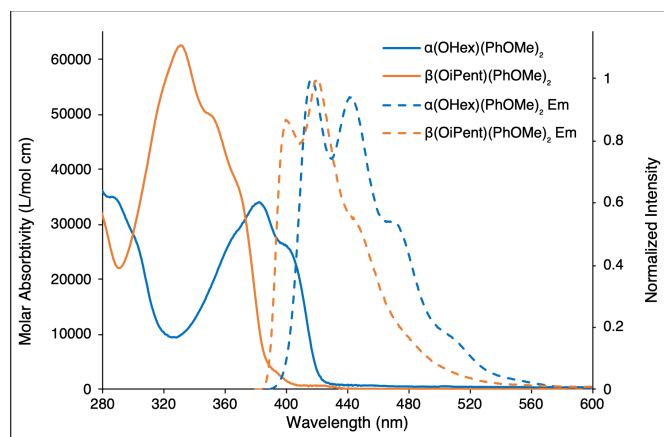


Figure A 92. Absorbance and emission spectra for $\alpha(\text{OHex})(\text{PhOMe})_2$ and $\beta(\text{Oi-Pent})(\text{PhOMe})_2$ in THF.

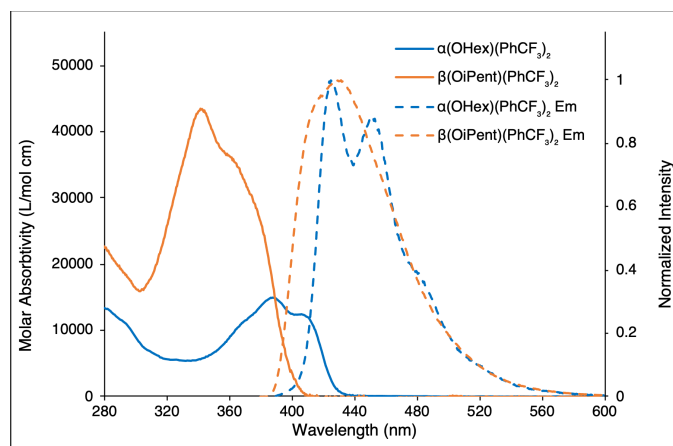


Figure A 93. Absorbance and emission spectra for $\alpha(\text{OHex})(\text{PhCF}_3)_2$ and $\beta(\text{OiPent})(\text{PhCF}_3)_2$ in THF.

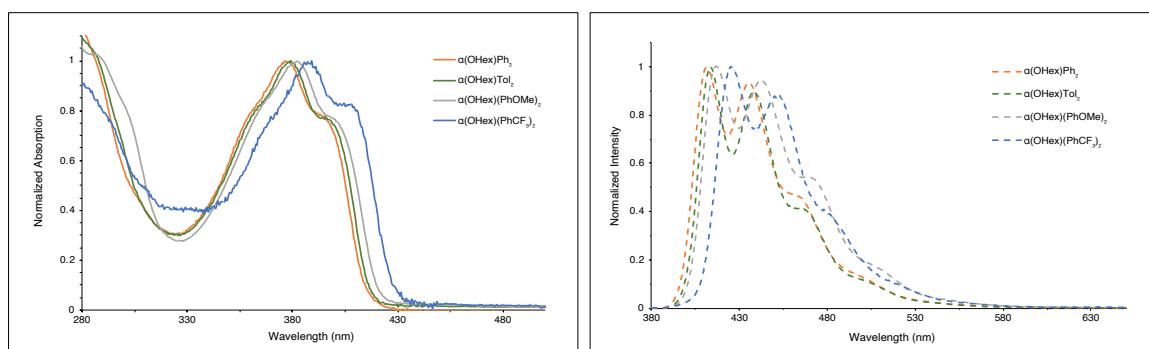


Figure A 94. Normalised absorbance and emission spectra for $\alpha(\text{OHex})\text{R}_2$ Series in THF.

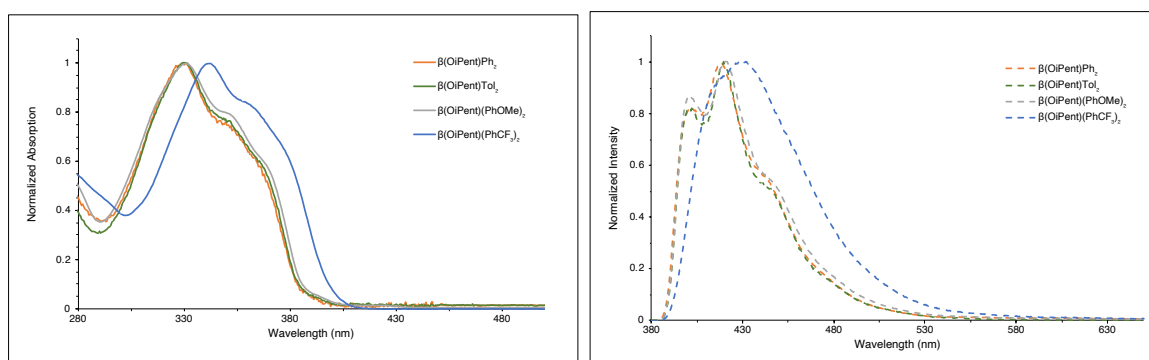


Figure A 95. Normalised absorbance and emission spectra for $\beta(\text{Oi-Pent})\text{R}_2$ Series in THF.

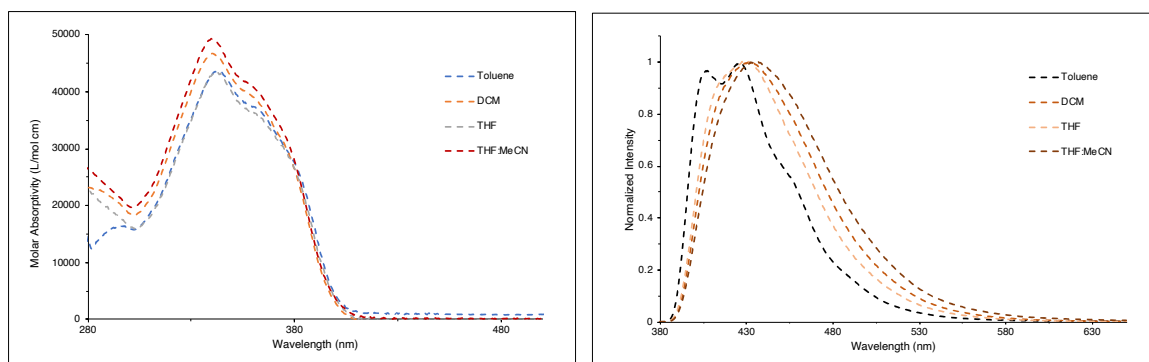


Figure A 96. Solvatochromism Analysis. Absorbance and emission spectra for $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ in: THF, toluene, DCM, and THF·MeCN (1:1).

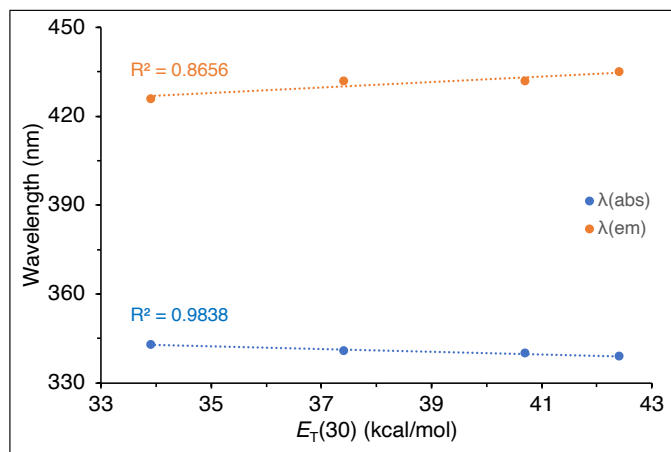


Figure A 97. Plot of absorbance and emission normalized maxima λ vs $E_T(30)$ parameter for $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ in THF, toluene, DCM, and THF·MeCN (1:1).

2.6 Solution-State Analysis

2.6.1 Concentration dependent ^1H NMR analysis

A series of $\alpha(\text{OHex})\text{R}_2$ and $\beta(\text{Oi-Pent})\text{R}_2$ solutions in CDCl_3 were probed via ^1H NMR spectroscopy to determine the extent of solution-state aggregation. Over the concentration range probed (50-1 mM, actual concentrations see Table A 1) only minor ($\Delta\delta$ are observed across aromatic and alkoxy resonances ($\Delta\delta < 0.15$ ppm for all

resonances). Chemical shifts with $\Delta\delta \geq 0.05$ ppm were fit over the concentration range with the NMR aggregation model in Bindfit.⁷

2.6.2 Aggregation Analysis, $\alpha(\text{OHex})\text{Ph}_2$

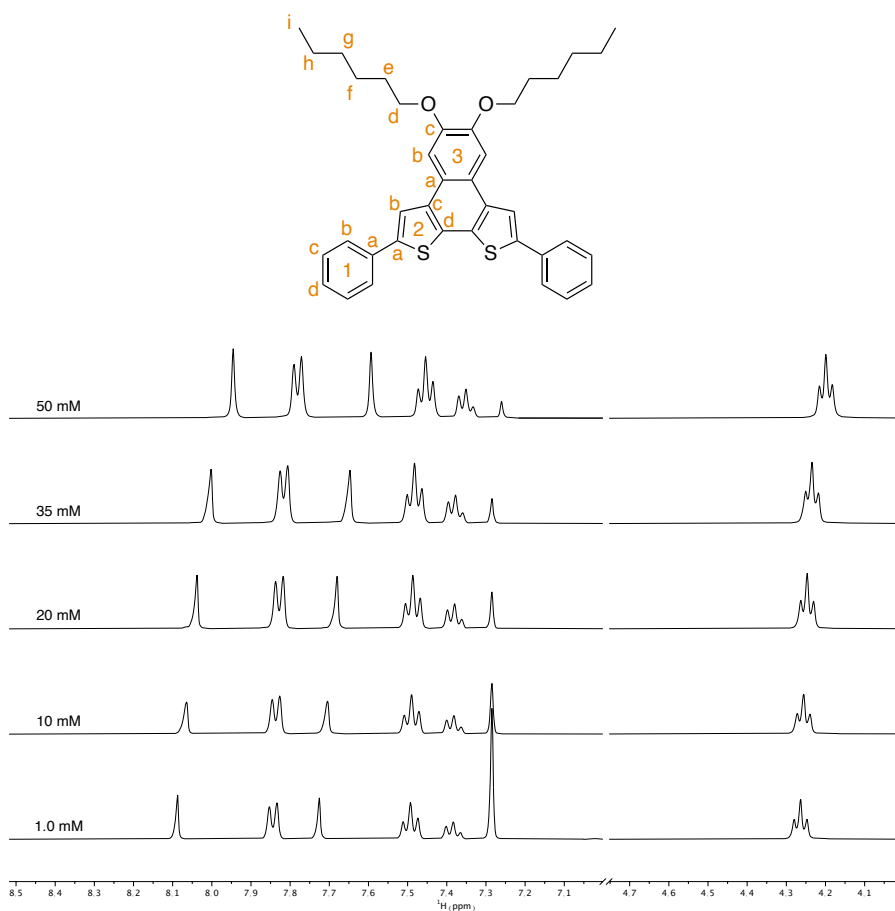


Figure A 98. Partial ^1H NMR spectra of $\alpha(\text{OHex})\text{Ph}_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K), $K_d = 3.2 \times 10^{-4} \pm 1.6 \times 10^{-4}$ M.

Conc. (mM)	1b	1c	1d	2b	3b	3d
50	7.781	7.454	7.351	7.945	7.593	4.119
35	7.792	7.458	7.353	7.977	7.623	4.21
20	7.803	7.462	7.355	8.014	7.657	4.222
10	7.812	7.465	7.357	8.041	7.681	4.232
1.0	7.819	7.468	7.359	8.063	7.701	4.239
$\Delta\delta =$	-	-	-	-	-	-
	0.038	0.014	0.008	0.118	0.108	0.120

Table A 1. ^1H chemical shifts for $\alpha(\text{OHex})\text{Ph}_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K) used in aggregation analysis.

2.6.3 Aggregation Analysis, $\alpha(\text{OHex})(\text{PhOMe})_2$

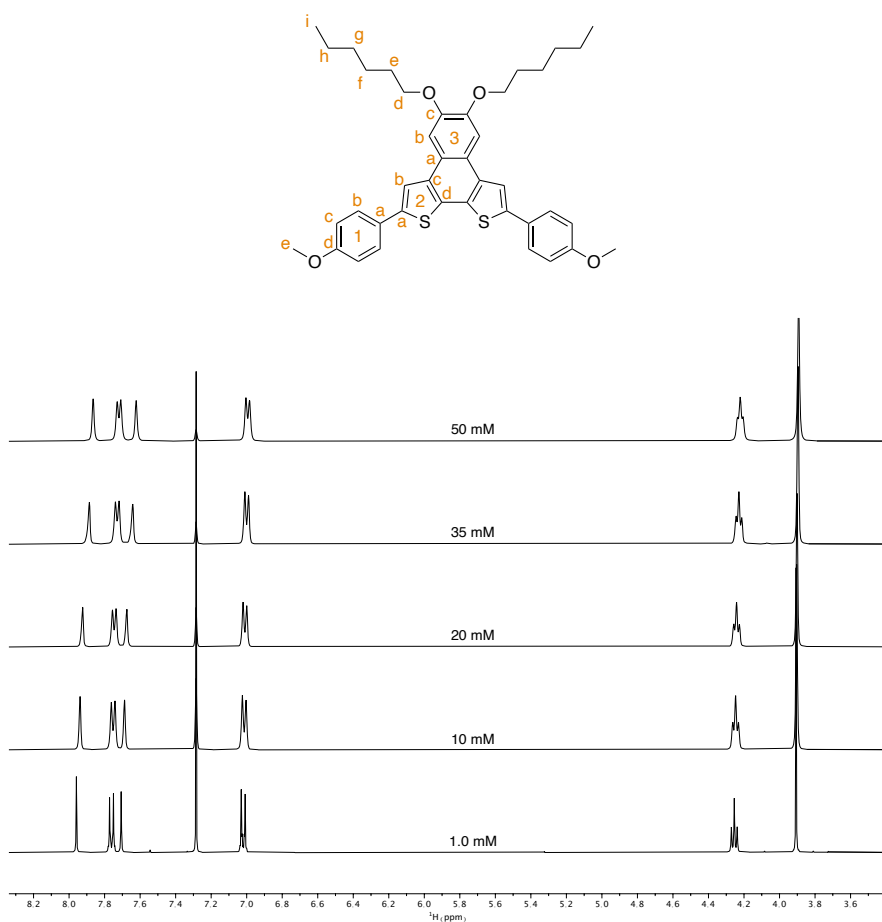


Figure A 99. Partial ^1H NMR spectra of $\alpha(\text{OHex})(\text{PhOMe})_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K), $K_d = 1.2 \pm 0.6 \text{ M}$.

Conc. (mM)	1b	1c	1e	2b	3b	3d
50	7.719	6.994	3.892	7.864	7.622	4.221
35	7.729	7.000	3.896	7.886	7.642	4.229
20	7.745	7.010	3.902	7.924	7.675	4.242
10	7.752	7.011	3.904	7.939	7.688	4.247
1.0	7.761	7.019	3.907	7.959	7.707	4.255
$\Delta\delta =$	-	-	-	-	-	-
	0.042	0.025	0.015	0.095	0.085	0.034

Table A 2. ^1H chemical shifts for $\alpha(\text{OHex})(\text{PhOMe})_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K) used in aggregation analysis.

2.6.4 Aggregation Analysis, $\beta(\text{Oi-Pent})\text{Tol}_2$

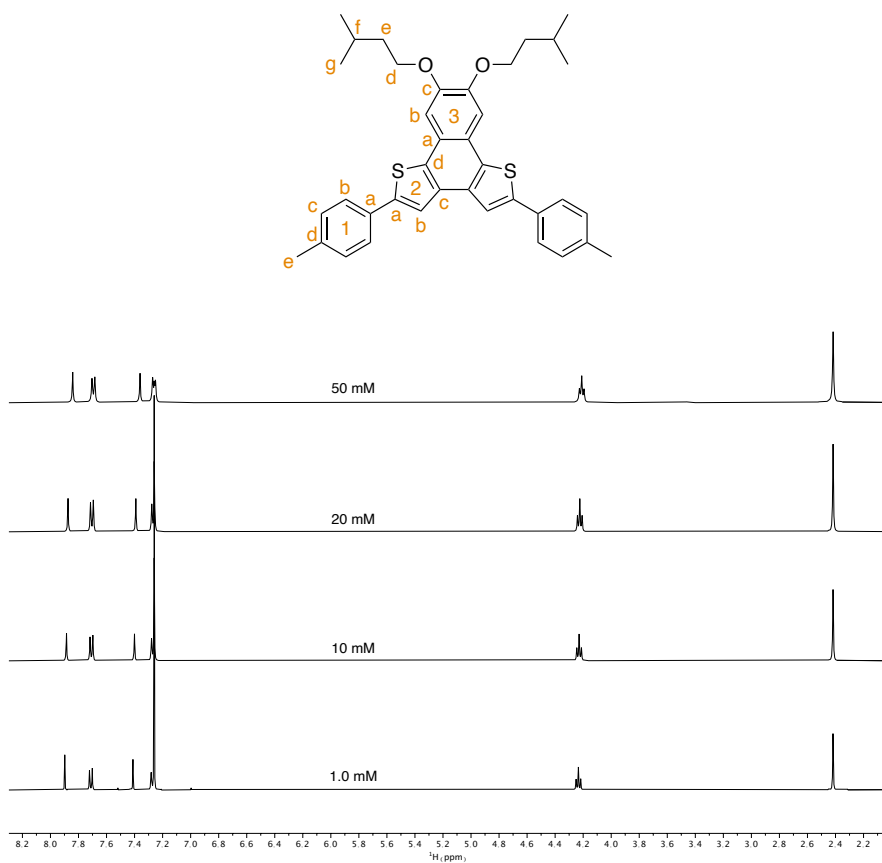


Figure A 100. Partial ^1H NMR spectra of $\beta(\text{Oi-Pent})\text{Tol}_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K), $K_d = 1.1 \pm 0.6$ M.

Conc. (mM)	1b	1c	1e	2b	3b	3d
50	7.694	7.261	2.417	7.841	7.361	4.210
20	7.704	7.269	2.418	7.875	7.391	4.224
10	7.708	7.260	2.418	7.886	7.401	4.229
1.0	7.712	7.260	2.418	7.898	7.412	4.234
$\Delta\delta =$	-	-	-	-	-	-
	0.018	0.001	0.001	0.057	0.051	0.024

Table A 3. ^1H chemical shifts for $\beta(\text{Oi-Pent})\text{Tol}_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K) used in aggregation analysis.

2.6.5 Aggregation Analysis, $\beta(\text{Oi-Pent})(\text{PhOMe})_2$

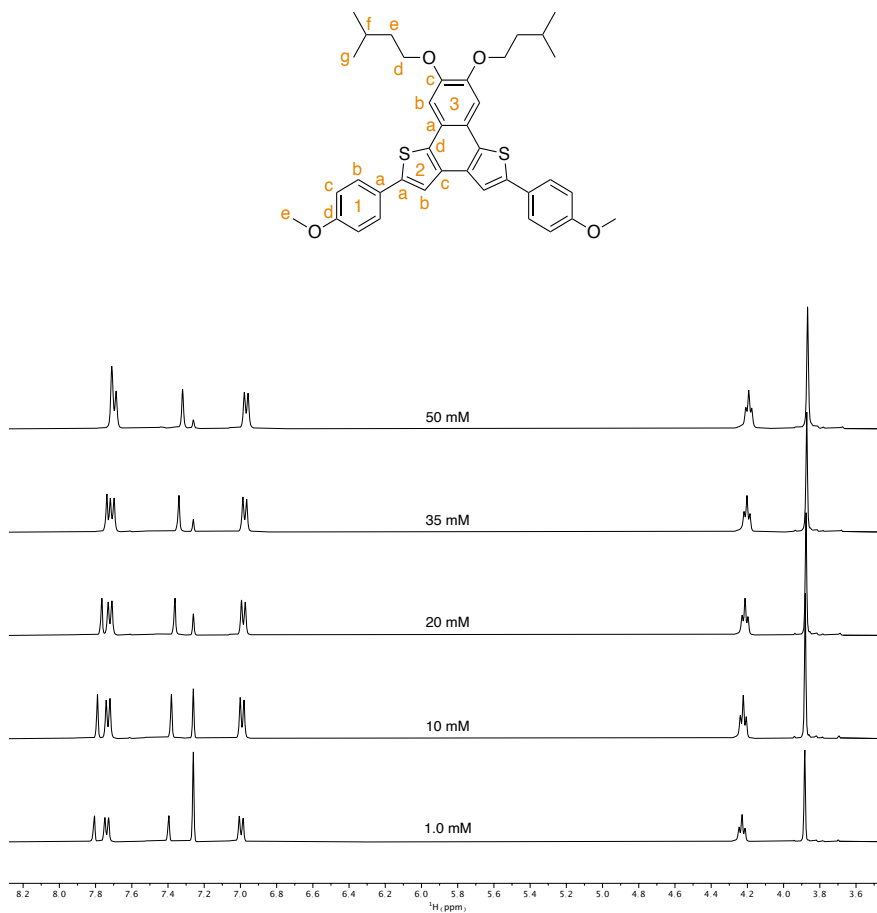


Figure A 101. Partial ^1H NMR spectra of $\beta(\text{Oi-Pent})(\text{PhOMe})_2$ (50–1 mM, CDCl_3 , 400 MHz, 298K), $K_d = 1.5 \pm 0.8$ M.

Conc. (mM)	1b	1c	1d	2b	3b	3d
50	7.702	6.968	3.868	7.710	7.319	4.192
35	7.708	6.976	3.872	7.738	7.340	4.202
20	7.720	6.984	3.876	7.766	7.362	4.213
10	7.731	6.991	3.880	7.790	7.381	4.223
1.0	7.738	6.996	3.883	7.807	7.396	4.230
$\Delta\delta =$	-	-	-	-	-	-
	0.036	0.028	0.015	0.097	0.077	0.038

Table A 4. ^1H chemical shifts for **$\beta(\text{Oi-Pent})(\text{PhOMe})_2$** (50–1 mM, CDCl_3 , 400 MHz, 298K) used in aggregation analysis.

2.6.6 Comparison of remote chemical shifts in ^1H and ^{13}C

The chemical shifts of interior 2b ^1H and ^{13}C shift upfield for electron donating groups and downfield for electron. The Hammett parameters (σ) for both para and meta can be contrasted against these 2b resonances. The fits are presented, wherein σ_{para} provides quality fits (given in blue) while σ_{meta} (shown in orange) yields poor fits.

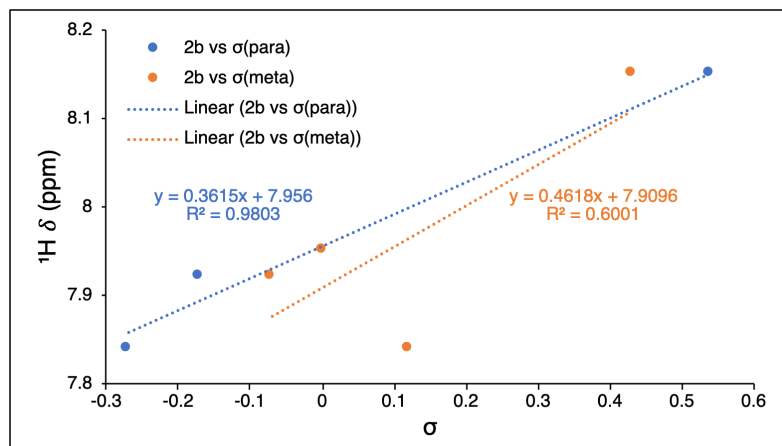


Figure A 102. Plot of **$\alpha(\text{OHex})\text{R}_2$** ^1H δ (ppm) vs σ .

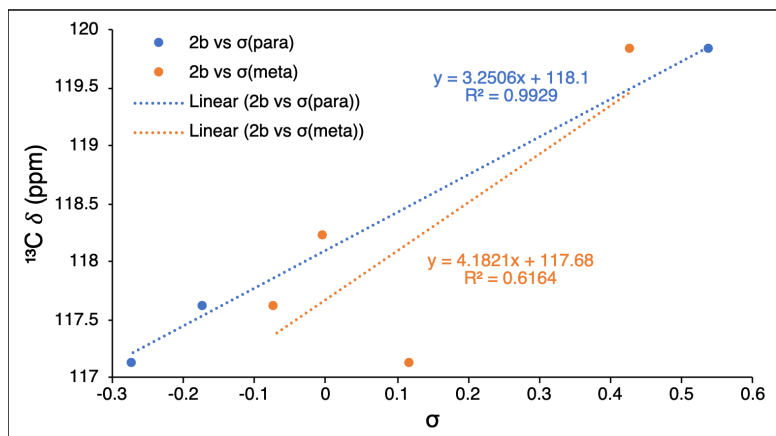


Figure A 103. Plot of $\alpha(\text{OHex})\text{R}_2$ ^{13}C δ (ppm) vs σ .

$\alpha(\text{OHex})\text{R}_2$	2b resonances			
	^1H δ (ppm)	^{13}C δ (ppm)	σ_m	σ_p
$\alpha(\text{OHex})\text{Ph}_2$	7.95	118.2	0.00	0.00
$\alpha(\text{OHex})\text{Tol}_2$	7.92	117.6	-0.07	-0.17
$\alpha(\text{OHex})(\text{PhOMe})_2$	7.84	117.1	0.12	-0.27
$\alpha(\text{OHex})(\text{PhCF}_3)_2$	8.15	119.8	0.43	0.54

Table A 5. 2b resonances and Hammett parameters for $\alpha(\text{OHex})\text{R}_2$ Series.

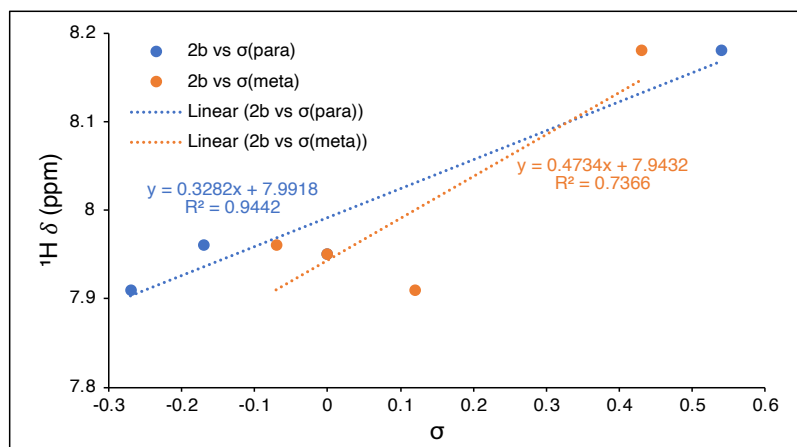


Figure A 104. Plot of $\alpha(\text{OMe})\text{R}_2$ ^1H δ (ppm) vs σ .

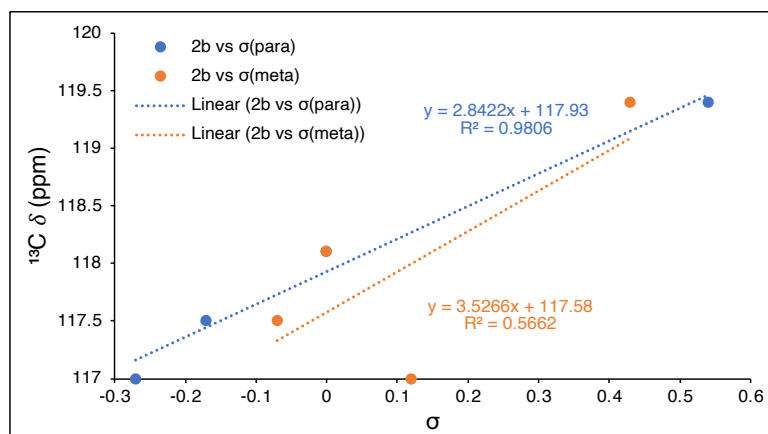


Figure A 105. Plot of $\alpha(\text{OMe})\text{R}_2$ ^{13}C δ (ppm) vs σ .

$\alpha(\text{OHex})\text{R}_2$	2b resonances			
	^1H δ (ppm)	^{13}C δ (ppm)	σ_m	σ_p
$\alpha(\text{OHex})\text{Ph}_2$	7.95	118.1	0.00	0.00
$\alpha(\text{OHex})\text{Tol}_2$	7.96	117.5	-0.07	-0.17
$\alpha(\text{OHex})(\text{PhOMe})_2$	7.91	117.0	0.12	-0.27
$\alpha(\text{OHex})(\text{PhCF}_3)_2$	8.18	119.4	0.43	0.54

Table A 6. 2b resonances and Hammett parameters for $\alpha(\text{OMe})\text{R}_2$ Series.

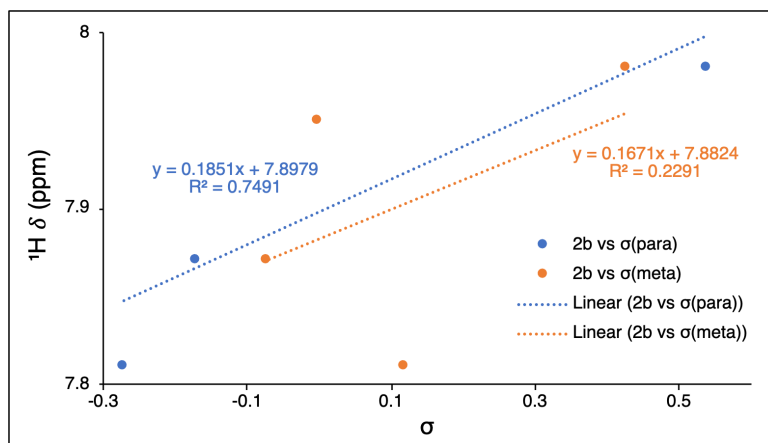


Figure A 106. Plot of $\beta(\text{Oi-Pent})\text{R}_2$ ^1H δ (ppm) vs σ .

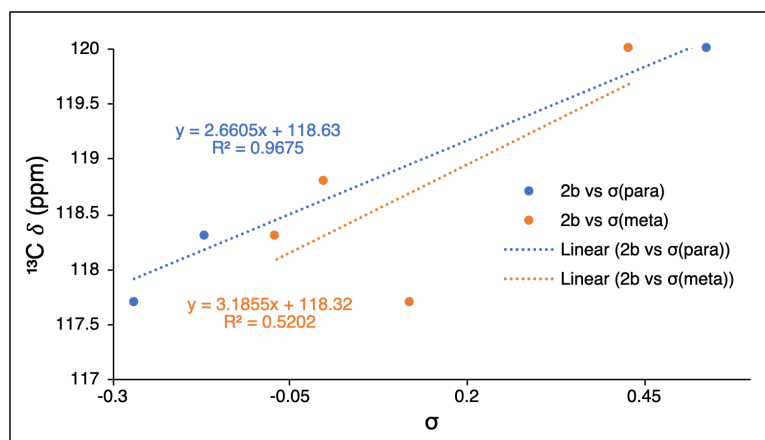


Figure A 107. Plot of $\beta(\text{O}i\text{-Pent})\text{R}_2$ ^{13}C δ (ppm) vs σ .

$\beta(\text{O}i\text{-Pent})\text{R}_2$	2b resonances			
	^1H δ (ppm)	^{13}C δ (ppm)	σ_m	σ_p
$\beta(\text{O}i\text{-Pent})\text{Ph}_2$	7.95	118.8	0.00	0.00
$\beta(\text{O}i\text{-Pent})\text{Tol}_2$	7.87	118.3	-0.07	-0.17
$\beta(\text{O}i\text{-Pent})(\text{PhOMe})_2$	7.81	117.7	0.12	-0.27
$\beta(\text{O}i\text{-Pent})(\text{PhCF}_3)_2$	7.98	120.0	0.43	0.54

Table A 7. 2b resonances and Hammett parameters for $\beta(\text{O}i\text{-Pent})\text{R}_2$ Series.

2.7 Computational Analysis

For the computational analysis, we modeled four different substituents on the α - and β -NDT series along with an unfunctionalized species using non-relativistic density functional theory implemented in Gaussian 16. We use the non-relativistic methods due to the molecule only containing light elements (the heaviest being sulfur). We settled on the widely popular and well-performing global hybrid exchange correlation functional (XCF) B3LYP. The basis sets we used are the polarization-consistent sets developed by the Jensen group, which systematically reduces the basis set error. Each molecule initially underwent a geometry optimization before NMR calculations. The pc-2 basis set used for

geometry optimisation and the B3LYP exchange correlation functional. After geometry optimisation, NICS scans were completed using the Aroma python package with Gaussian 16. The first NICS scan was done to determine the height needed about the plane for the NICS-XY scan. This initial scan was done in the center of each aromatic ring and scanning in 0.1 Å increments along the Z-axis outside of the plane. This was done to find the optimal height to perform an NICS-XY scan where the electrons of the σ -bond are removed and only the π -electron contribution is observed. The height of 1.7 Å was determined to be the optimal height to perform a NICS-XY scan to remove σ -bonding effects, consistent with others. Each scan was performed along the same path for each molecule using the aug-pcSseg-2 basis set and the B3LYP XCF. The aug-pcSseg-2 basis set contains extra tight exponents in the p functions to better describe the behaviour near the nucleus and optimised to the nuclear magnetic shielding constant, while also containing extra diffused functions to create a more complete basis. Overall reducing the basis set error for NMR calculations. Additionally, ^1H and ^{13}C NMR spectra were modeled using the GIAO method using the aug-pcSseg-2 basis set with the B3LYP XCF (the PBE0 XCF was tested as well, with the resultant NMR spectra being insensitive to the XCF employed).

2.7.1 $\alpha(\text{OMe})\text{R}_2'$ Series Models

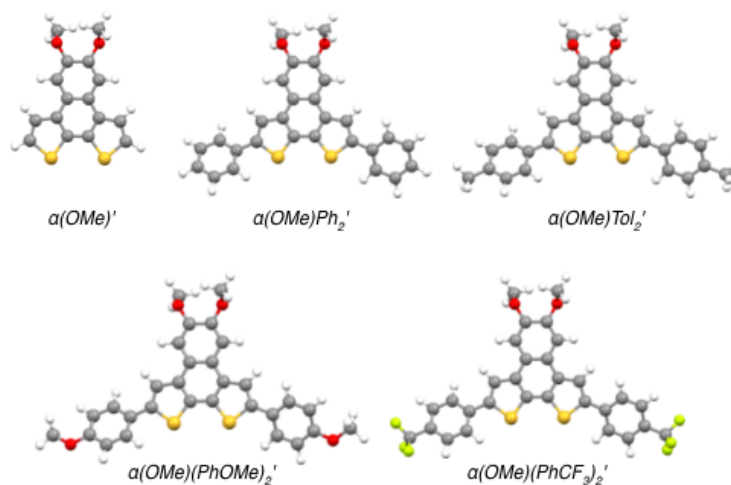


Figure A 108. Optimized geometries of $\alpha(\text{OMe})\text{R}_2'$ Series.

Model Compound	Total Energy		Energy _{Total Energy +}	
	(E _h)	ZPC (E _h)	ZPC (E _h)	IF
$\alpha(\text{OMe})'$	- 1564.12683440	0.237891	-1563.888943	0
$\alpha(\text{OMe})\text{Ph}_2'$	- 2026.42019070	0.399396	-2026.020795	0
$\alpha(\text{OMe})\text{Tol}_2'$	- 2105.08669746	0.453568	-2104.633129	0
$\alpha(\text{OMe})(\text{PhOMe})_2'$	- 2255.56595208	0.463866	-2255.102086	0
$\alpha(\text{OMe})(\text{PhCF}_3)_2'$	- 2700.81348131	0.408085	-2700.405396	0

Table A 8. Computational data for optimized $\alpha(\text{OMe})\text{R}_2'$ models. ZPC = zero-point correction, IF = number of imaginary frequencies.

2.7.2 $\beta(OMe)R_2'$ Series Models

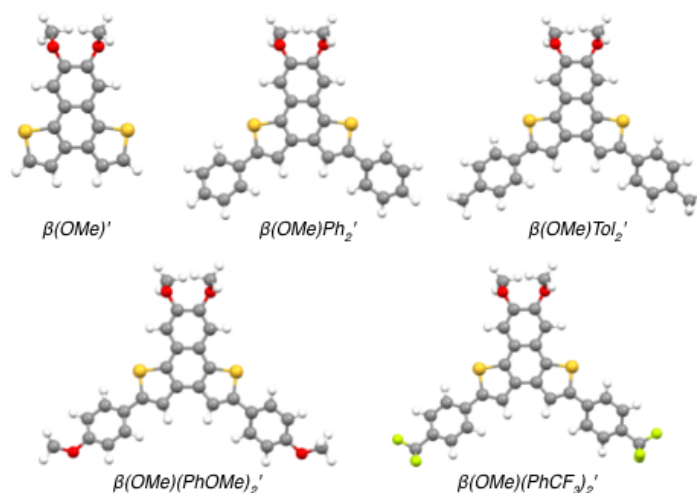


Figure A 109. Optimized geometries of $\beta(OMe)R_2'$ Series.

Model Compound	Total Energy (E _h)	ZPC (E _h)	Energy _{Total Energy + ZPC} (E _h)	IF
$\beta(OMe)'$	-	0.237883	-1563.890222	0
$\beta(OMe)Ph_2'$	-	0.399338	-2026.021850	0
$\beta(OMe)Tol_2'$	-	0.453518	-2255.113722	0
$\beta(OMe)(PhOMe)_2'$	-	0.463811	-2255.103429	0
$\beta(OMe)(PhCF_3)_2'$	-	0.408029	-2700.406468	0

Table A 9. Computational data for optimized $\beta(OMe)R_2'$ models. ZPC = zero-point correction, IF = number of imaginary frequencies.

2.7.3 Experimental vs Calculated Chemical Shift Analysis

The isotropic shieldings for the model compounds with the alkoxy groups simplified to methoxy groups were computed for both protons and carbons using the GIAO method with the aug-pcSseg-2 basis set and B3LYP XCF in Gaussian 16. The

experimental chemical shifts (ppm) were extracted from ^1H – ^{13}C HSQC. Consistently across all molecules the interior 3b proton and carbon are underestimated.

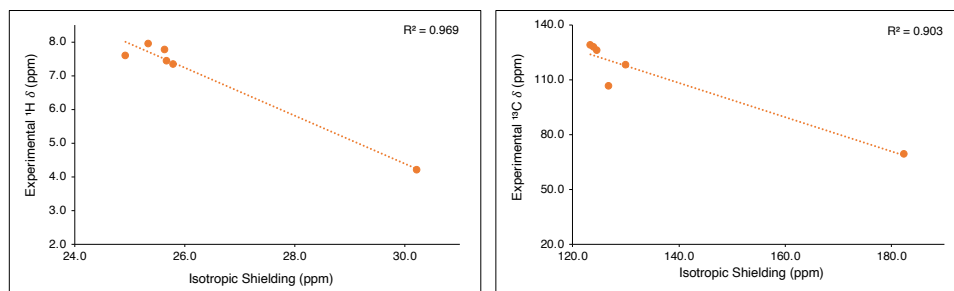


Figure A 110. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})\text{Ph}_2$ (experimental) and $\alpha(\text{OMe})\text{Ph}_2'$ (calculated).

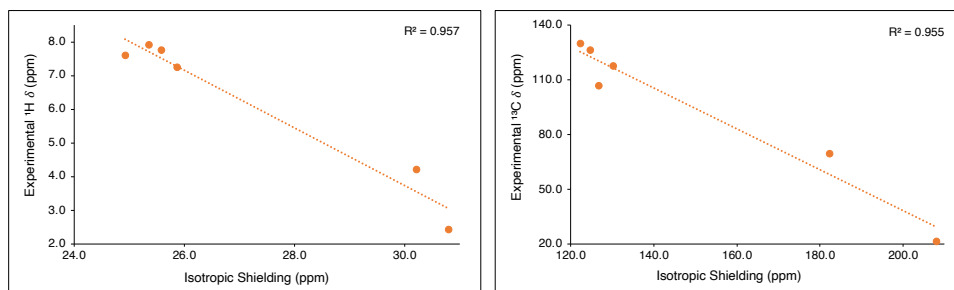


Figure A 111. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})\text{Tol}_2$ (experimental) and $\alpha(\text{OMe})\text{Tol}_2'$ (calculated).

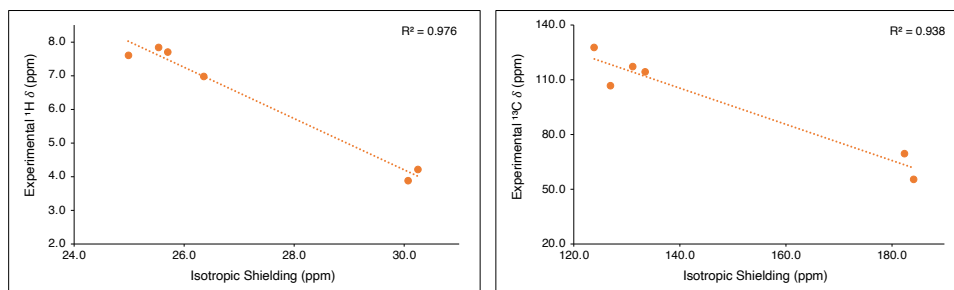


Figure A 112. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})(\text{PhOMe})_2$ (experimental) and $\alpha(\text{OMe})(\text{PhOMe})_2'$ (calculated).

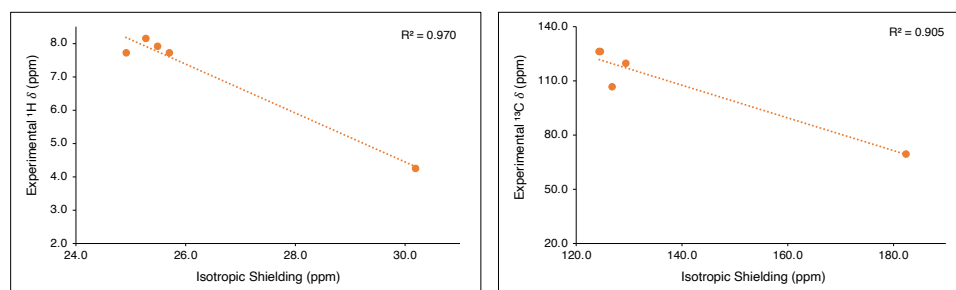


Figure A 113. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})(\text{PhCF}_3)_2$ (experimental) and $\alpha(\text{OMe})(\text{PhCF}_3)_2'$ (calculated).

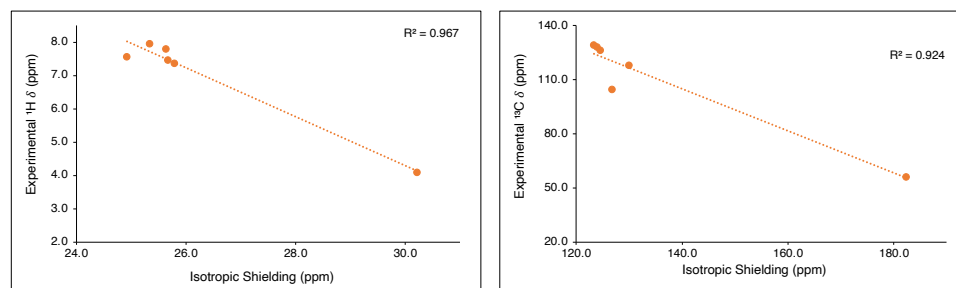


Figure A 114. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})\text{Ph}_2$ (experimental) and $\alpha(\text{OMe})\text{Ph}_2'$ (calculated).

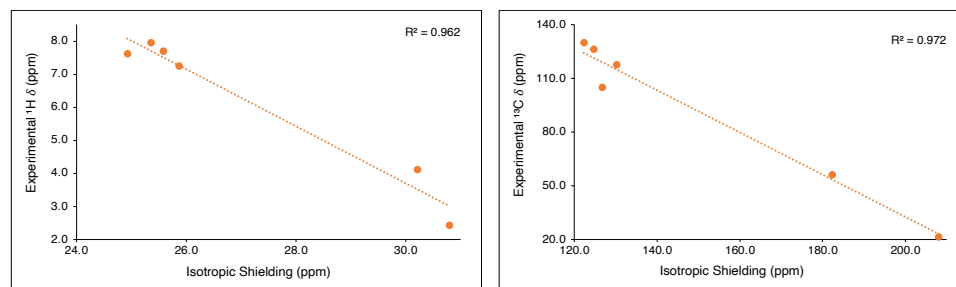


Figure A 115. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})\text{Tol}_2$ (experimental) and $\alpha(\text{OMe})\text{Tol}_2'$ (calculated).

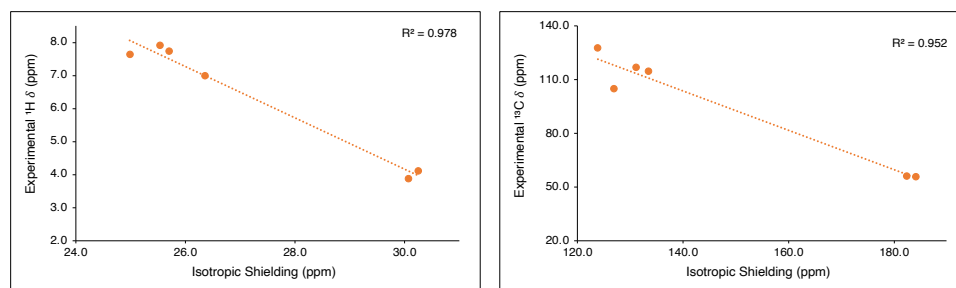


Figure A 116. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})(\text{PhOMe})_2$ (experimental) and $\alpha(\text{OMe})(\text{PhOMe})_2'$ (calculated).

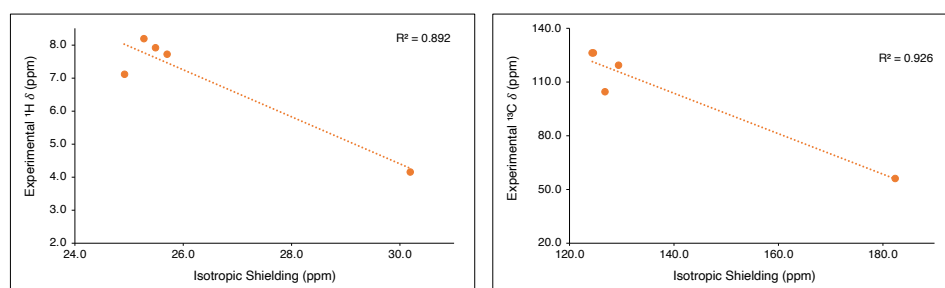


Figure A 117. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\alpha(\text{OHex})(\text{PhCF}_3)_2$ (experimental) and $\alpha(\text{OMe})(\text{PhCF}_3)_2'$ (calculated).

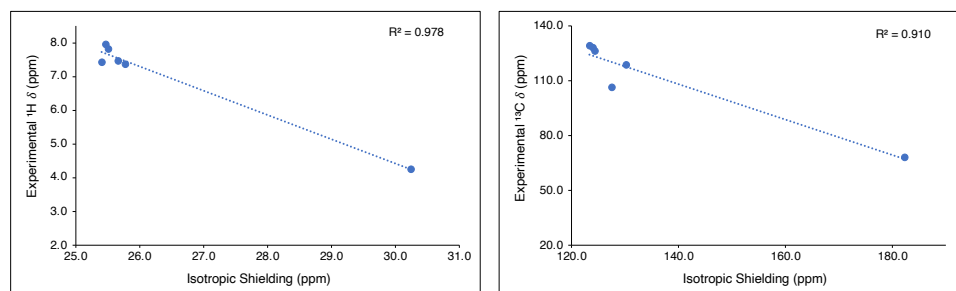


Figure A 118. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\beta(\text{Oi-Pent})\text{Ph}_2$ (experimental) and $\beta(\text{OMe})\text{Ph}_2'$ (calculated).

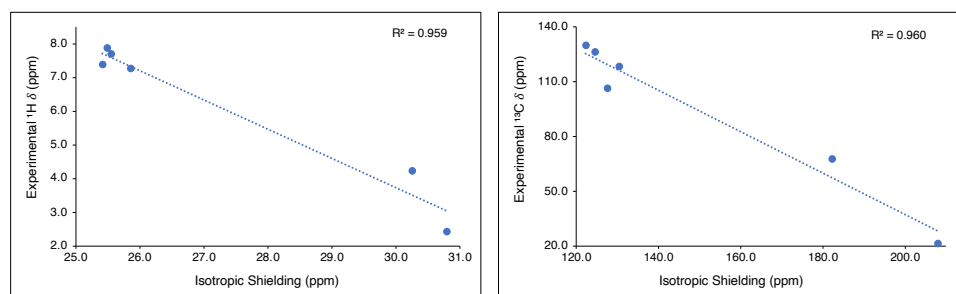


Figure A 119. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\beta(\text{Oi-Pent})\text{Tol}_2$ (experimental) and $\beta(\text{OMe})\text{Tol}_2'$ (calculated).

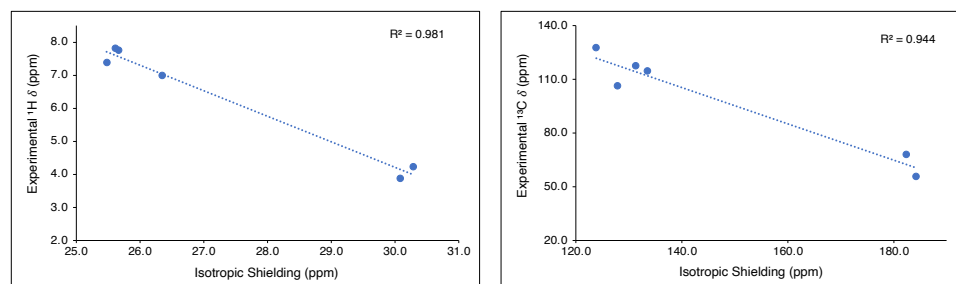


Figure A 120. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\beta(\text{Oi-Pent})(\text{PhOMe})_2$ (experimental) and $\beta(\text{OMe})(\text{PhOMe})_2'$ (calculated).

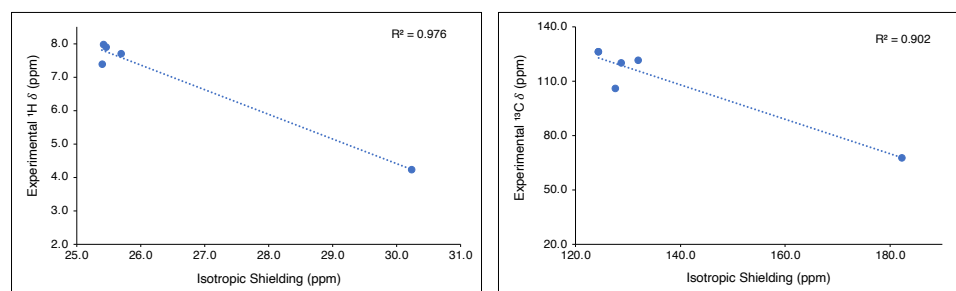


Figure A 121. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $\beta(\text{Oi-Pent})(\text{PhCF}_3)_2$ (experimental) and $\beta(\text{OMe})(\text{PhCF}_3)_2'$ (calculated).

2.7.4 Nucleus Independent Chemical Shift (NICS)-XY Scans

Optimised geometries (given in Figures A108 and A109) were performed using the AROMA package⁸ and referenced against unsubstituted model compounds $\alpha(\text{OMe})'$ and $\beta(\text{OMe})'$.

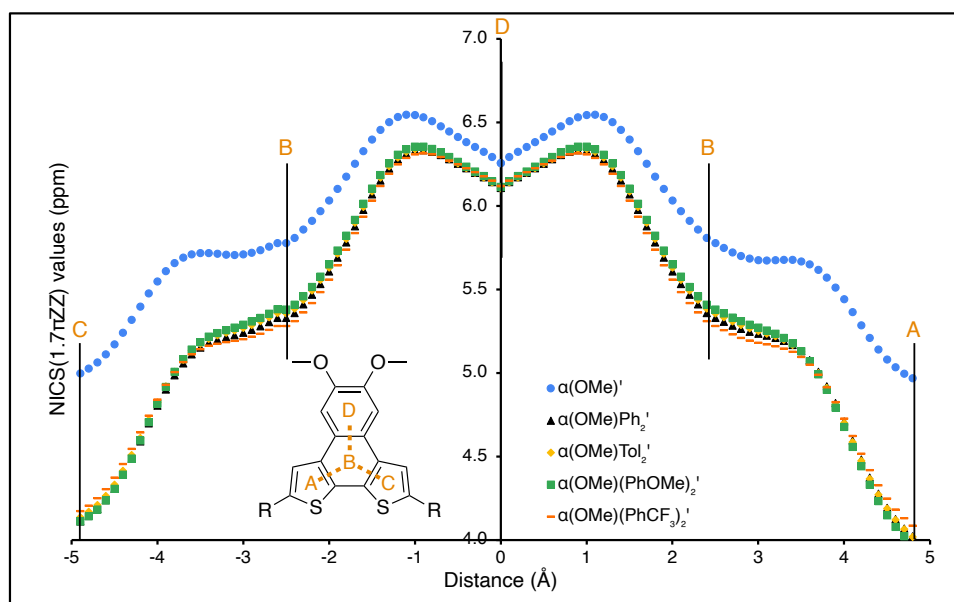


Figure A 122. NICS_{1.7πZZ} scans for $\alpha(\text{OMe})R_2'$ Series.

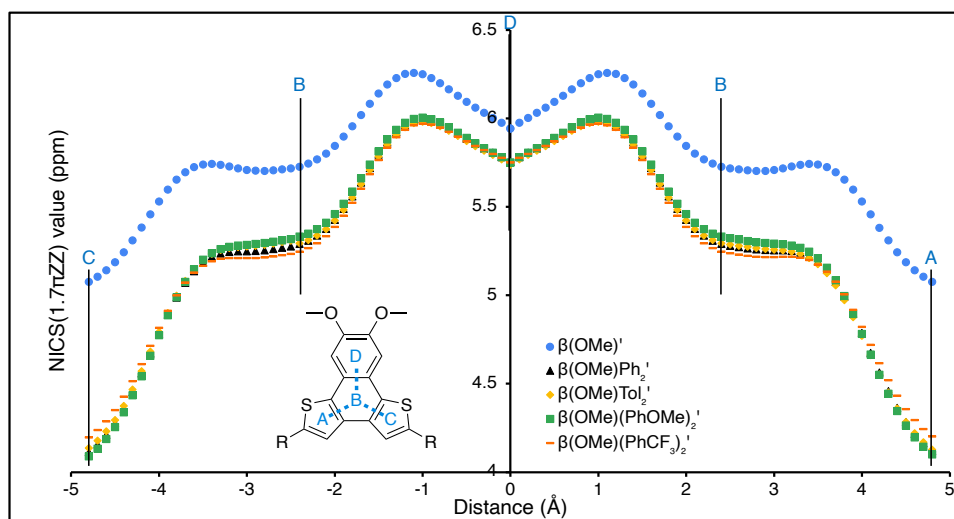


Figure A 123. NICS_{1.7πZZ} scans for $\beta(\text{OMe})R_2'$ Series.

2.8 Crystallographic Analysis

Crystallographic analysis and data for **$\alpha(\text{OMe})\text{Ph}_2$** , **$\alpha(\text{OMe})\text{Tol}_2$** , **$\alpha(\text{OMe})(\text{PhOMe})_2$** , **$\alpha(\text{OMe})(\text{PhCF}_3)_2$** , and **$\beta(\text{O}i\text{-Pent})\text{Tol}_2$** are presented below. Data were collected from a single crystal at 150(2) K on a Bruker AXS D8 Quest three circle diffractometer with a fine focus sealed tube X-ray source using a Triumph curved graphite crystal as monochromator and a PhotonII charge-integrating pixel array (CPAD) detector. The diffractometer was equipped with a low temperature device and used MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.^{9,10} The crystal was solved by dual methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3.^{11,12} All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Tables and general reports were generated with FinalCif and edited accordingly.¹³ Any additional refinement notes are detailed below, all structures have been deposited in the Cambridge Crystallographic Data Centre (CCDC)¹⁴ with their deposition numbers given.

2.8.1 $\alpha(\text{OMe})\text{Ph}_2$

Single crystals of **$\alpha(\text{OMe})\text{Ph}_2$** were obtained through vapor diffusion of hexanes into a saturated solution of **$\alpha(\text{OMe})\text{Ph}_2$** in THF (Figure A 124). One of the phenyl rings is disordered by a twist-rotation. The two disordered moieties were restrained to have

similar geometries as the other not disordered phenyl ring. The ipso-C atom was omitted from the disorder. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.501(3) to 0.499(3). CCDC number: 2361476

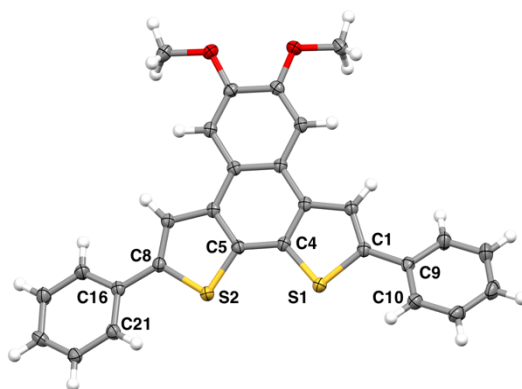


Figure A 124. ORTEP diagram of **$\alpha(\text{OMe})\text{Ph}_2$** (ellipsoids drawn at 50% probability). Select bond lengths (Å) and angles (°): C8–S2, 1.745(1); C5–S2, 1.720(1); C4–S1, 1.727(1); S1–C1, 1.743(1); C24–C23–C8–S2, 19.9(2); S2–C5–C4–S1, -3.4(2); S1–C1–C17–C18, -18.5(2).

	$\alpha(\text{OMe})\text{Ph}_2$
Empirical formula	$\text{C}_{28}\text{H}_{20}\text{O}_2\text{S}_2$
Formula weight	452.56
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	4.8146(4)
b [Å]	20.525(2)
c [Å]	21.556(3)
α [°]	90
β [°]	90.453(5)
γ [°]	90
Volume [Å ³]	2130.1(4)
Z	4
ρ_{calc} [gcm ⁻³]	1.411
μ [mm ⁻¹]	0.275

$F(000)$	944
Crystal size [mm ³]	0.550×0.080×0.070
Crystal color	yellow
Crystal shape	needle
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	4.40 to 66.37 (0.65 Å)
Index ranges	$-6 \leq h \leq 7$ $-31 \leq k \leq 31$ $-32 \leq l \leq 33$
Reflections collected	40142
Independent reflections	7984 $R_{\text{int}} = 0.0684$ $R_{\text{sigma}} = 0.0505$
Completeness to $\theta = 25.242^\circ$	99.7 %
Data / Restraints / Parameters	7984/216/337
Goodness-of-fit on F^2	1.028
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0425$ $wR_2 = 0.0954$
Final R indexes [all data]	$R_1 = 0.0750$ $wR_2 = 0.1081$
Largest peak/hole [eÅ ⁻³]	0.41/-0.38

Table A10. Crystallographic data and structural refinement parameters, **$\alpha(\text{OMe})\text{Ph}_2$** .

2.8.2 $\alpha(\text{OMe})\text{Tol}_2$

Single crystals of **$\alpha(\text{OMe})\text{Tol}_2$** were obtained through vapor diffusion of hexanes into a saturated solution of **$\alpha(\text{OMe})\text{Tol}_2$** in THF (Figure A 125). CCDC number: 2361477

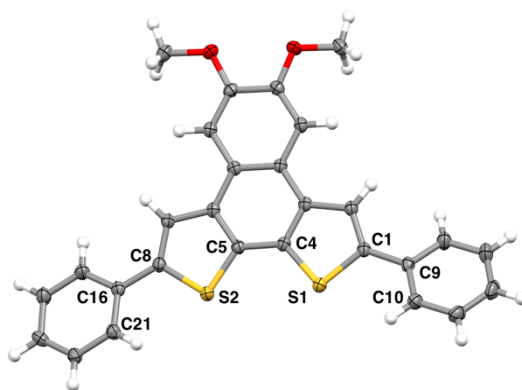


Figure A 125. ORTEP diagram of **$\alpha(\text{OMe})\text{Tol}_2$** (ellipsoids drawn at 50% probability). Select bond lengths (Å) and angles (°): C1–S1, 1.745(1); C4–S1, 1.730(1); C5–S2, 1.721(1); C8–S2, 1.748(1); C22–C17–C1–S1, -16.9(2); S1–C4–C5–S2, -0.7(2); S2–C8–C24–C29, 8.3(2).

	$\alpha(\text{OMe})\text{Tol}_2$
Empirical formula	$\text{C}_{30}\text{H}_{24}\text{O}_2\text{S}_2$
Formula weight	480.61
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$\overline{P}2_1/n$ (14)
a [Å]	13.7285(9)
b [Å]	7.9848(5)
c [Å]	21.6165(14)
α [°]	90
β [°]	100.332(3)
γ [°]	90
Volume [Å ³]	2331.2(3)
Z	4
ρ_{calc} [gcm ⁻³]	1.369
μ [mm ⁻¹]	0.255
$F(000)$	1008
Crystal size [mm ³]	0.450×0.280×0.230
Crystal color	yellow
Crystal shape	rod
Radiation	MoK_α ($\lambda=0.71073$ Å)
2θ range [°]	5.45 to 66.30 (0.65 Å)
Index ranges	$-21 \leq h \leq 20$ $-12 \leq k \leq 12$ $-33 \leq l \leq 32$

Reflections collected	37349
Independent reflections	8895 $R_{\text{int}} = 0.0444$ $R_{\text{sigma}} = 0.0443$
Completeness to $\theta = 25.242^\circ$	99.8 %
Data / Restraints / Parameters	8895/0/311
Goodness-of-fit on F^2	1.024
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0444$ $wR_2 = 0.1049$
Final R indexes [all data]	$R_1 = 0.0719$ $wR_2 = 0.1200$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.39/-0.30

Table A 11. Crystallographic data and structural refinement parameters, **$\alpha(\text{OMe})\text{Tol}_2$** .

2.8.3 $\alpha(\text{OMe})(\text{PhOMe})_2$

Single crystals of **$\alpha(\text{OMe})(\text{PhOMe})_2$** were obtained through vapor diffusion of hexanes into a saturated solution of **$\alpha(\text{OMe})(\text{PhOMe})_2$** in THF. **$\alpha(\text{OMe})(\text{PhOMe})_2$** was obtained as a co-crystal with THF (shown in Figure A 126). CCDC number: 2361478

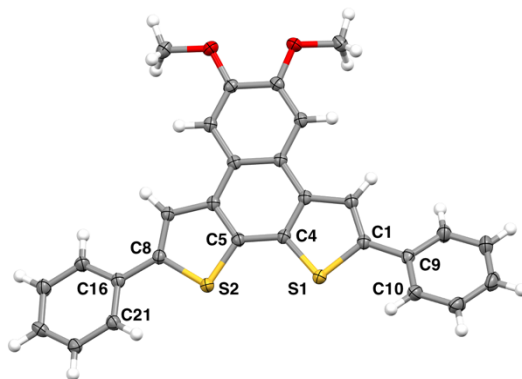


Figure A 126. ORTEP diagram of **$\alpha(\text{OMe})(\text{PhOMe})_2$** (ellipsoids drawn at 50% probability). Select bond lengths ($\text{\AA}$) and angles ($^\circ$): C5–S2, 1.729(1); C8–S2, 1.747(2); C4–S1, 1.733(2); C1–S1, 1.751(3); C21–C16–C8–S2, 7.7(2); S2–C5–C4–S1, -3.4(2); S1–C1–C9–C10, 1.3(2).

	$\alpha(\text{OMe})(\text{PhOMe})_2$
Empirical formula	$\text{C}_{34}\text{H}_{32}\text{O}_5\text{S}_2$
Formula weight	584.72
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$\overline{P}2_1$ (4)
a [Å]	8.7673(7)
b [Å]	6.2302(4)
c [Å]	25.9473(19)
α [°]	90
β [°]	93.533(3)
γ [°]	90
Volume [Å ³]	1414.60(18)
Z	2
ρ_{calc} [gcm ⁻³]	1.373
μ [mm ⁻¹]	0.232
$F(000)$	616
Crystal size [mm ³]	0.350×0.290×0.130
Crystal color	yellow
Crystal shape	plate
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	4.72 to 66.37 (0.65 Å)
Index ranges	$-13 \leq h \leq 13$ $-9 \leq k \leq 9$ $-39 \leq l \leq 39$
Reflections collected	65592
Independent reflections	10845 $R_{\text{int}} = 0.0377$ $R_{\text{sigma}} = 0.0243$
Completeness to $\theta = 25.242^\circ$	99.8 %
Data / Restraints / Parameters	10845/1/374
Goodness-of-fit on F^2	1.049
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0312$ $wR_2 = 0.0858$
Final R indexes [all data]	$R_1 = 0.0333$ $wR_2 = 0.0871$
Largest peak/hole [eÅ ⁻³]	0.34/-0.29
Flack X parameter	0.029(10)

Table A 12. Crystallographic data and structural refinement parameters, **$\alpha(\text{OMe})(\text{PhOMe})_2$** .

2.8.4 $\alpha(\text{OMe})(\text{PhCF}_3)_2$

Single crystals of $\alpha(\text{OMe})(\text{PhCF}_3)_2$ were obtained through vapor diffusion of hexanes into a saturated solution of $\alpha(\text{OMe})(\text{PhCF}_3)_2$ in THF (Figure A 127). CCDC number: 2361479

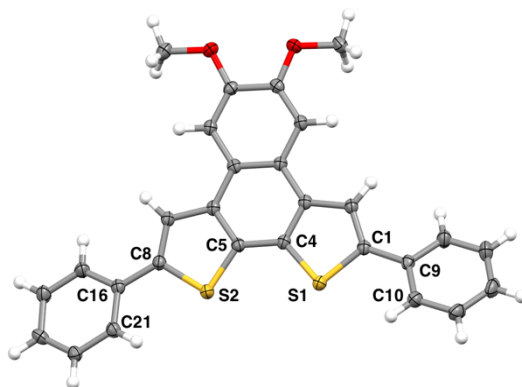


Figure A 127. ORTEP diagram of $\alpha(\text{OMe})(\text{PhCF}_3)_2$ (ellipsoids drawn at 50% probability). Select bond lengths (Å) and angles (°): C4–S1, 1.731(3); C17–S1, 1.747(3); C5–S2, 1.722(3); C8–S2, 1.742(3); S1–C4–C5–S2, 2.5(4); C22–C1–C17–S1, -6.9(4); S2–C8–C24–C29, 9.5(4).

	$\alpha(\text{OMe})(\text{PhCF}_3)_2$
Empirical formula	$\text{C}_{30}\text{H}_{18}\text{F}_6\text{O}_2\text{S}_2$
Formula weight	588.56
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	17.861(5)
b [Å]	8.2438(16)
c [Å]	18.565(4)
α [°]	90
β [°]	111.359(7)
γ [°]	90
Volume [Å ³]	2545.8(10)
Z	4
ρ_{calc} [gcm ⁻³]	1.536
μ [mm ⁻¹]	0.282
$F(000)$	1200

Crystal size [mm ³]	0.310×0.050×0.020
Crystal color	yellow
Crystal shape	needle
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	4.71 to 56.66 (0.75 Å)
Index ranges	-23 ≤ h ≤ 22 -10 ≤ k ≤ 10 -24 ≤ l ≤ 24
Reflections collected	36606
Independent reflections	6296 $R_{\text{int}} = 0.1603$ $R_{\text{sigma}} = 0.0903$
Completeness to $\theta = 25.242^\circ$	100.0 %
Data / Restraints / Parameters	6296/258/437
Goodness-of-fit on F^2	1.008
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0531$ $wR_2 = 0.1137$
Final R indexes [all data]	$R_1 = 0.1142$ $wR_2 = 0.1400$
Largest peak/hole [eÅ ⁻³]	0.42/-0.41

Table A 13. Crystallographic data and structural refinement parameters, **$\alpha(\text{OMe})(\text{PhCF}_3)_2$** .

2.8.5 $\beta(\text{Oi-Pent})\text{Tol}_2$

Single crystals of **$\beta(\text{Oi-Pent})\text{Tol}_2$** were obtained through vapor diffusion of hexanes into a saturated solution of **$\beta(\text{Oi-Pent})\text{Tol}_2$** in THF. **$\beta(\text{Oi-Pent})\text{Tol}_2$** was obtained as a dimer crystal and is shown in Figure A 128 with the rear molecule represented by a wireframe, with the top molecule as thermal ellipsoids. The metrics between the two molecules were averaged and are presented in the figure caption. The structure contains additional 4908 Ångström of solvent accessible voids (ca. 30% of the cell volume).

Fragments could be identified as partially occupied chloroform, disordered with other highly disordered solvate molecules that could not be recognised. The structure factors were instead augmented via reverse Fourier transform methods using the

SQUEEZE routine¹⁵ as implemented in the program Platon. The resultant FAB file containing the structure factor contribution from the electron content of the void space was used in together with the original hkl file in the further refinement. The Squeeze procedure corrected for 948 electrons within the solvent accessible voids. CCDC number: 2361480

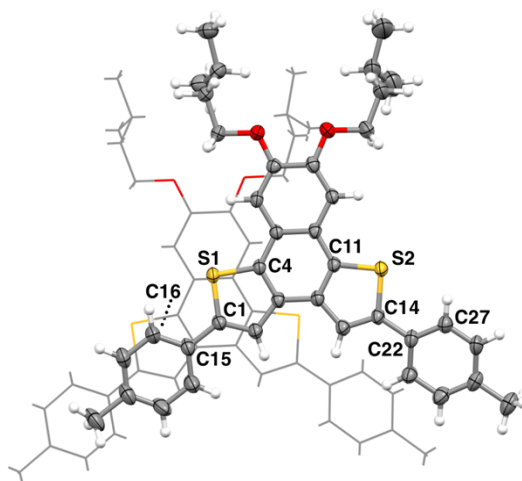


Figure A 128. ORTEP diagram of $\beta(\text{Oi-Pent})\text{Tol}_2$ (ellipsoids drawn at 50% probability). Crystallised as a dimer, bottom molecules given as wireframe. Average bond lengths (Å) and angles (°) of the dimers: C1–S1, 1.741; C4–S1, 1.735; C11–S2, 1.736; C14–S2, 1.743; C27–C22–C14–S2, -4.4; C16–C15–C1–S1, -8.2; S2–C8–C24–C29, 9.5(4).

	$\beta(\text{Oi-Pent})\text{Tol}_2$
Empirical formula	$\text{C}_{38}\text{H}_{40}\text{O}_2\text{S}_2$
Formula weight	592.82
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$\overline{C}2/c$ (15)
a [Å]	41.918(3)
b [Å]	26.6997(19)
c [Å]	15.3487(11)
α [°]	90
β [°]	104.041(2)
γ [°]	90
Volume [Å ³]	16665(2)
Z	16
ρ_{calc} [gcm ⁻³]	0.945
μ [mm ⁻¹]	0.153
$F(000)$	5056
Crystal size [mm ³]	0.320×0.180×0.060
Crystal color	colorless
Crystal shape	blade
Radiation	MoK_α ($\lambda=0.71073$ Å)
2θ range [°]	3.85 to 56.97 (0.75 Å)
Index ranges	$-56 \leq h \leq 46$ $-35 \leq k \leq 35$ $-18 \leq l \leq 20$
Reflections collected	54446
Independent reflections	20701 $R_{\text{int}} = 0.0501$ $R_{\text{sigma}} = 0.0836$
Completeness to $\theta = 25.242^\circ$	99.7 %
Data / Restraints / Parameters	20701/340/857
Goodness-of-fit on F^2	1.031
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0774$ $wR_2 = 0.2225$
Final R indexes [all data]	$R_1 = 0.1257$ $wR_2 = 0.2622$
Largest peak/hole [eÅ ⁻³]	1.06/-0.65

Table A 14. Crystallographic data and structural refinement parameters, **$\beta(\text{Oi-Pent})\text{Tol}_2$** .

2.9 References

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CHAPTER THREE

This supplementary data is adapted from Supplementary information from Adusei, E. B. A.; Ibrahim, S.; Jenneker, K.; Goldsmith, C. D.; Dragoi, D.; Zeller, M.; Kinney, Z. J. Intramolecular Stabilization of Naphtho[2,1-b:3,4-b']dithiophenes: Synthesis and Analysis of Imine-Based Chromophores. J. Org. Chem. 2026, 91, 394–400, with modifications.

3.0 Experimental Procedures

Unless otherwise noted, all starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Anhydrous solvents (dichloromethane, hexanes, tetrahydrofuran, toluene) were purified using an Inert PureSolv solvent purification system equipped with alumina column. 4 Å molecular sieves were activated via vacuum oven (150 °C, > 16 hours) overnight prior to use.

Purification of all di-imine products was accomplished with a Shimadzu Nexera Gel Permeation Chromatography (GPC) equipped with a Shodex organic size exclusion column (100 Å styrogel stationary phase, viable molecular weight range of 400–6000 g/mol) and a toluene mobile phase (flow rate 5 mL/min). NMR spectra were measured on a Bruker Avance III 400 MHz spectrometer, with all samples referenced to the residual solvent signal. High resolution mass spectra were obtained by dissolving samples in dichloromethane/methanol and analyzed on a LTQ Orbitrap (ionization method: APCI+)

Absorbance spectra were recorded on a Cary 100Bio spectrophotometer and corrected for solvent background absorbance. Emission spectra were recorded on a Horiba Jobin-Yvon Fluorolog-3 fluorometer. All spectra were recorded at room temperature using 1 cm path length quartz cuvettes with spectrometric grade solvents.

Fluorescence quantum yield (ϕ) measurements were performed on solutions prepared under inert atmosphere in a Vacuum Atmosphere Company NexGen glovebox with dry, degassed solvents. Quantum yields were determined by reference to 9,10-diphenylanthracene in cyclohexane ($\phi = 0.91$) which was cross-checked with quinine bisulfate in 0.5 M H₂SO₄ (aq) ($\phi = 0.54$). Five solutions of varying concentration were prepared for each sample and good fits ($R^2 \geq 0.99$) were obtained in all cases. The absorbance of all samples was kept below 0.10 to avoid the inner-filter effect, with all measurements of emission being recorded at 365 nm.¹ The procedure for is supplied below for clarity on with reference to the original spectral analysis.^{2,3} All procedures below were carried out multiple times with the yields given representing the median outcome of an experiment. Common solvent and reagent abbreviations: chloroform-*d* (CDCl₃), dichloromethane (DCM), ethyl acetate (EtOAc), tetrahydrofuran (THF), and *N*-bromosuccinimide (NBS).

3.1 Synthesis of precursors and **$\alpha(\text{CHO})_2$**

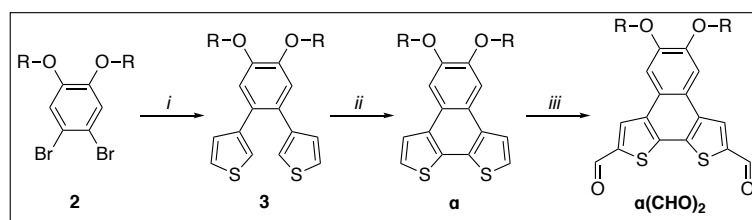


Figure B1. Synthetic path to **$\alpha(\text{CHO})_2$** ; details for conditions *i*, *ii*, and *iii* given below with their respective targets.

3.1.1 1,2-dibromo-4,5-di-isopentyloxybenzene, **2**

4,5-dibromocatechol (18.90 mmol) was massed into a 250 mL round bottom flask and dissolved in 2-butanone (100 mL). A stir bar was added, followed by K₂CO₃ (57.89 mmol) and a reflux condenser. Reaction was flushed with argon for 5 minutes, then 1-

bromo-3-methylbutane (41.31 mmol) was added in one portion. Reaction temperature was then raised to 80 °C and allowed to stir for 24 hours. After 24 hours the reaction flask was cooled to RT and poured into H₂O (50 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification via silica gel flash column with Hexanes:EtOAc (49:1) as mobile phase afforded 1,2-dibromo-4,5-di-isopentyloxybenzene (**2**) as a colorless oil, 6.1899 g (80 %). Spectral details match literature values.^{2,3}

3.1.2 1,2-di(3-thienyl)-4,5-di-isopentyloxybenzene, **3**

A 100 mL Schlenk tube was charged with **2** (7.72 mmol), 3-thiophene boronic acid (23.50 mmol), and Pd(PPh₃)₂Cl₂ (1.19 mmol), and a stir bar added. The reaction flask was then backfilled with argon (x3), after which 40 mL dry THF (30 mL) and 15 mL degassed 2 M K₂CO₃ (30.80 mmol) were added under positive pressure of argon. The tube was sealed under argon, and the reaction was allowed to stir in an oil bath at 80 °C overnight. After overnight stirring the reaction tube was cooled to RT, poured into H₂O (25 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column with Hexanes:EtOAc (49:1) mobile phase, with subsequent recrystallization from afford 1,2-di(3-thienyl)-4,5-di-isopentyloxybenzene (**3**) as a white solid, 1.9476 g (70 %): ¹H NMR (400 MHz, CDCl₃) δ 7.17 (dd, *J* = 4.9, 3.0 Hz, 2H), 7.02 (dd, *J* = 3.0, 1.3 Hz, 2H), 6.97 (s, 2H), 6.78 (dd, *J* = 4.9, 1.3 Hz, 2H), 4.08 (t, *J* = 6.7 Hz, 4H), 1.87 (dq, *J* = 13.3, 6.7 Hz, 2H), 1.75 (q, *J* = 6.7 Hz, 4H), 0.98 (d, *J* = 6.6 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 148.4, 142.0, 129.1, 128.0, 124.5, 122.3,

115.7, 67.9, 38.1, 25.1, 22.6; HRMS (APCI+) calcd for C₂₄H₃₁O₂S₂ (M+H)⁺ 415.1765, found 415.1768.

3.1.3 5,6-bis(isopentyloxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a**

A 500 mL Schlenk flask was charged with **3** (1.06 mmol) and a stir bar, then sparged with argon for 10 minutes. After 10 minutes dry DCM (42 mL) was added, and the reaction flask was equipped with a pressure equalizing funnel. The reaction flask was then cooled to 0 °C and equilibrated for 15 minutes under argon. FeCl₃ (2.23 mmol) was massed into a beaker and dissolved in MeNO₂ (9.0 mL), then added to the pressure equalizing funnel. The FeCl₃/MeNO₂ solution was added dropwise over five minutes to the reaction flask, after which the ice bath was removed, and the reaction was allowed to come to RT over an hour, after which it was quenched with MeOH (10x MeNO₂) and concentrated. The crude reaction was resuspended in DCM (50 mL) and H₂O (50 mL), extracted with DCM (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column with Hexanes:DCM (4:1) to afford pure 5,6-bis(isopentyloxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene (**a**) as an off-white solid, 190 mg (43 %): ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 5.3 Hz, 2H), 7.69 (s, 2H), 7.45 (d, *J* = 5.3 Hz, 2H), 4.25 (t, *J* = 6.6 Hz, 4H), 1.99 (dt, *J* = 13.3, 6.6 Hz, 2H), 1.87 (q, *J* = 6.7 Hz, 4H), 1.07 (d, *J* = 6.6 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 148.8, 133.8, 130.3, 123.3, 122.6, 122.4, 106.7, 67.6, 38.0, 25.2, 22.7; HRMS (APCI+) calcd for or C₂₄H₂₉O₂S₂ (M+H)⁺ 413.1608, found 413.1609.

3.1.4 5,6-bis(isopentyloxy)-2,9-di-(formyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(CHO)₂**

A 100 mL Schlenk flask was massed with **a** (0.58 mmol), a stir bar, dry THF (20mL) and sparged with argon for 15 minutes. The flask was cooled to -78 °C and allowed to equilibrate for 20 minutes. n-Butyllithium (1.22 mmol) was added dropwise to the reaction, and the reaction allowed to stir for 30 minutes. The dry ice bath was covered with a pig mat to minimize exposure to light for the remainder of the reaction. Degassed DMF (5.20 mmol) was added, and reaction allowed to stir under inert atmosphere of argon for 30 minutes. Reaction was cooled to RT for 40 minutes, quenched with 5 mL dilute HCL solution, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification was achieved via recrystallization from toluene to afford 5,6-bis(isopentyloxy)-2,9-di-(formyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene (**a(CHO)₂**) as a yellow solid, 114 mg (42 %): ¹H NMR (400 MHz, CDCl₃) δ 10.09 (s, 2H), 8.23 (s, 2H), 7.32 (s, 2H), 4.19 (t, *J* = 6.6 Hz, 4H), 1.93 (dq, *J* = 13.0, 6.6 Hz, 2H), 1.84 (q, *J* = 6.6 Hz, 4H), 1.05 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 183.4, 151.3, 141.6, 141.2, 131.7, 131.3, 122.6, 105.9, 67.8, 37.6, 25.3, 22.7.; HRMS (APCI+) calcd for C₂₆H₂₉O₄S₂ (M+H)⁺ 469.1507, found 469.1514.

3.2 Synthesis of **a(1)**₂ Series

3.2.1 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl) naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(1a)**₂

Conditions *i*: A 6-dram vial was massed with **a(CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4 Å activated molecular sieves. Aniline (0.11 mmol), and TFA (4.76 x 10⁻³ mmol) were successively added, the vial capped, swirled, and left

undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification via GPC (toluene, 5 mL/min) to yield pure **a(1a)₂** as a yellow solid, 13.6 mg (46 %).

Conditions *ii*: A 6-dram vial was massed with **a(CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. Aniline (0.15 mmol), Sc(OTf)₃ (0.014 mmol) and MeCN (5 % of CHCl₃), were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification via GPC (toluene, 5 mL/min) to yield pure **a(1a)₂** as a yellow solid, 11.7 mg (39 %).

Structural Analysis **a(1a)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 2H), 8.18 (s, 2H), 7.61 (s, 2H), 7.46 – 7.38 (m, 4H), 7.33 – 7.28 (m, 4H), 7.28 – 7.22 (m, 2H), 4.24 (t, *J* = 6.6 Hz, 4H), 1.96 (dp, *J* = 13.1, 6.6 Hz, 2H), 1.85 (q, *J* = 6.6 Hz, 4H), 1.04 (d, *J* = 6.6 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 152.7, 151.0, 149.5, 141.8, 135.3, 132.5, 129.2, 127.3, 126.5, 122.8, 121.2, 106.3, 67.7, 38.0, 25.3, 22.7; HRMS (APCI+) calcd for C₃₈H₃₉N₂O₂S₂ (M+H)⁺ 619.2452, found 619.2440.

3.2.2 5,6-bis(isopentyloxy)-2,9-di-(*N*-(4-methylphenyl)methaniminyl) naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(1b)₂**

Conditions *i*: A 6-dram vial was massed with **a(CHO)₂** (0.04 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. *p*-Toluidine (0.11 mmol), and TFA (4.2 x 10⁻³ mmol) were successively added, the vial capped, swirled, and left undisturbed overnight (> 16 hours). Reaction was transferred into a clean 100 mL RBF containing 1

mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1b)₂** as a yellow solid, 15.6 mg (57 %).

Conditions *ii*: A 6-dram vial was massed with **a(CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. *p*-Toluidine (0.11 mmol), Sc(OTf)₃ (9.55 x 10⁻³ mmol) and MeCN (5 % of CHCl₃), were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1b)₂** as a yellow solid, 13.5 mg (43 %).

Structural Analysis **a(1b)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 2H), 8.15 (s, 2H), 7.61 (s, 2H), 7.23 (s, 8H), 4.23 (t, *J* = 6.6 Hz, 4H), 2.39 (s, 6H), 1.96 (dp, *J* = 13.2, 6.6 Hz, 2H), 1.84 (q, *J* = 6.6 Hz, 4H), 1.04 (d, *J* = 6.6 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 151.9, 149.4, 148.4, 141.9, 136.4, 135.3, 132.4, 129.8, 127.0, 122.8, 121.1, 106.3, 67.7, 38.0, 25.3, 22.7, 21.1; HRMS (APCI+) calcd for C₄₀H₄₃N₂O₂S₂ (M+H)⁺ 647.2765, found 647.2768.

3.2.3 5,6-bis(isopentyloxy)-2,9-di-(*N*-(4-methoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(1c)₂**

Conditions *i*: A 6-dram vial was massed with **a(CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. *p*-Anisidine (0.13 mmol), and TFA (5.6 x 10⁻³ mmol) were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification

was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1c)₂** as a yellow solid, 10.9 mg (30 %).

Conditions *ii*: A 6-dram vial was massed with **a(CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. *p*-Anisidine (0.11 mmol), Sc(OTf)₃ (0.013 mmol) and MeCN (5 % of CHCl₃), were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1c)₂** as a yellow solid, 14.8 mg (45 %).

Structural Analysis **a(1c)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.78 (s, 2H), 8.18 (s, 2H), 7.65 (s, 2H), 7.33 (d, *J* = 8.3 Hz, 4H), 6.96 (d, *J* = 8.6 Hz, 4H), 4.25 (t, *J* = 6.8 Hz, 4H), 3.86 (s, 6H), 2.03 – 1.92 (m, 2H), 1.85 (q, *J* = 6.6 Hz, 4H), 1.04 (d, *J* = 6.4 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 150.6, 149.4, 143.9, 142.1, 135.3, 132.3, 126.6, 122.8, 122.5, 114.5, 106.4, 67.8, 55.5, 38.0, 25.3, 22.7; HRMS (APCI+) calcd for C₄₀H₄₃N₂O₄S₂ (M+H)⁺ 679.2664, found 679.2668.

3.2.4 5,6-bis(isopentyloxy)-2,9-di-(*N*-(4-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(1d)₂**

Conditions *i*: A 6-dram vial was massed with **a(CHO)₂** (0.04 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. 4-Aminobenzotrifluoride (0.09 mmol), and TFA (4.2 μmol) were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product.

Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1d)₂** as a yellow solid, 6 mg (2 %).

Conditions *ii*: A 6-dram vial was massed with **a(CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. 4-Aminobenzotrifluoride (0.15 mmol), Sc(OTf)₃ (0.011 mmol) and MeCN (5 % of CHCl₃), were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1d)₂** as a yellow solid, 15.1 mg (41 %)

Conditions *iii*: A 50 mL RBF was massed with **a(CHO)₂** (0.05 mmol), 4-Aminobenzotrifluoride (0.11 mmol), Toluene (to 10 mM NDT), Acetic acid (4.43 x 10⁻³ mmol), and a stir bar. Reaction was left to stir vigorously for 10 minutes under argon, and heated until reflux with dean-stark trap for >16 hours. Reaction was allowed to cool and transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1d)₂** as a yellow solid, 15.6 mg (47 %)

Structural Analysis **a(1d)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 2H), 8.26 (s, 2H), 7.68 (d, *J* = 8.3 Hz, 4H), 7.63 (s, 2H), 7.35 (d, *J* = 8.1 Hz, 4H), 4.24 (t, *J* = 6.6 Hz, 4H), 1.95 (dq, *J* = 13.1, 6.6 Hz, 2H), 1.85 (q, *J* = 6.7 Hz, 4H), 1.04 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 154.3 (q, *J* = 3.7 Hz), 154.0, 149.7, 141.4, 135.6, 132.9, 128.4, 128.4, 128.1, 125.6, 122.9, 121.3, 106.3, 67.8, 37.9, 25.3, 22.7, 1.0; HRMS (APCI+) calcd for C₄₀H₃₇F₆N₂O₂S₂ (M+H)⁺ 755.2200, found 755.2210.

3.2.5 5,6-bis(isopentyloxy)-2,9-di-(*N*-(4-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **a(1bb)₂**

Conditions *i*: A 6-dram vial was massed with **a(CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. 3,5-Dimethylaniline (0.11 mmol), TFA (4.76 x 10⁻³ mmol) were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1bb)₂** as a yellow solid, 4.1 mg (13 %).

Conditions *ii*: A 50 mL RBF was massed with **a(CHO)₂** (0.05 mmol), 3,5-Dimethylaniline (0.10 mmol), Toluene (to 10 mM NDT), Acetic acid (5.06 x 10⁻³ mmol), and a stir bar. Reaction was left to stir vigorously for 10 minutes under argon, and heated until reflux with dean-stark trap for >16 hours. Reaction was allowed to cool and transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **a(1bb)₂** as a yellow solid, 12.1 mg (39 %)

Structural Analysis **a(1bb)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.76 (s, 2H), 8.19 (s, 2H), 7.64 (s, 2H), 6.94 (s, 4H), 6.92 (s, 2H), 4.24 (t, *J* = 6.6 Hz, 4H), 2.37 (s, 12H), 1.96 (dt, *J* = 13.2, 6.6 Hz, 2H), 1.85 (q, *J* = 6.7 Hz, 4H), 1.04 (d, *J* = 6.5 Hz, 12H).; ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 151.0, 149.4, 141.9, 138.9, 135.3, 132.5, 128.2, 127.1, 122.8, 118.9, 106.3, 67.7, 38.0, 25.3, 22.7, 21.3; HRMS (APCI+) calcd for C₄₂H₄₇N₂O₂S₂ (M+H)⁺ 675.3078, found 675.3087

3.2.6 5,6-bis(isopentyloxy)-2,9-di-(N-(4-trifluoromethylphenyl)methaniminyl)naphtho[2,1-b:3,4-b']dithiophene, **α (1cc)₂**

Conditions *i*: A 6-dram vial was massed with **α (CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. 3,5-Dimethoxyaniline (0.11 mmol), and TFA (4.59 x 10⁻³ mmol) were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **α (1cc)₂** as a yellow solid, 4.8 mg (14 %).

Conditions *ii*: A 6-dram vial was massed with **α (CHO)₂** (0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4Å molecular sieves. 3,5-Dimethoxyaniline (0.12 mmol), Sc(OTf)₃ (0.01 mmol) and MeCN (5 % of CHCl₃), were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **α (1cc)₂** as a yellow solid, 4.7 mg (12 %).

Conditions *iii*: A 50 mL RBF was massed with **α (CHO)₂** (0.05 mmol), 3,5-Dimethoxyaniline (0.11 mmol), Toluene (to 10 mM NDT), Acetic acid (5.06 x 10⁻³ mmol), and a stir bar. Reaction was left to stir vigorously for 10 minutes under argon, and heated until reflux with dean-stark trap for >16 hours. Reaction was allowed to cool and transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **α (1cc)₂** as a yellow solid, 21.3 mg (59 %)

Structural Analysis **$\alpha(1cc)_2$** : ^1H NMR (400 MHz, CDCl_3) δ 8.77 (s, 2H), 8.24 (s, 2H), 7.66 (s, 2H), 6.48 (d, $J = 2.2$ Hz, 4H), 6.40 (t, $J = 2.2$ Hz, 2H), 4.25 (t, $J = 6.6$ Hz, 4H), 3.85 (s, 12H), 1.95 (dq, $J = 13.1, 6.5$ Hz, 2H), 1.85 (q, $J = 6.6$ Hz, 4H), 1.04 (d, $J = 6.6$ Hz, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.3, 153.1, 153.0, 149.5, 141.6, 135.4, 132.7, 127.6, 122.9, 106.3, 99.3, 99.0, 67.7, 55.5, 38.0, 25.3, 22.7; HRMS (APCI+) calcd for $\text{C}_{42}\text{H}_{47}\text{N}_2\text{O}_6\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 739.2875, found 739.2881.

3.2.7 5,6-bis(isopentyloxy)-2,9-di-(*N*-(4-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **$\alpha(1dd)_2$**

Conditions *ii*: A 6-dram vial was massed with **$\alpha(\text{CHO})_2$** (0.05 mmol), deacidified CHCl_3 (to 10 mM NDT), and 4Å molecular sieves. 3,5-Bis(trifluoromethyl)aniline (0.19 mmol), $\text{Sc}(\text{OTf})_3$ (0.01 mmol) and MeCN (5 % of CHCl_3), were successively added, the vial capped, swirled, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **$\alpha(1dd)_2$** as a yellow solid, 8.8 mg (21 %).

Conditions *iii*: A 50 mL RBF was massed with **$\alpha(\text{CHO})_2$** (0.05 mmol), 3,5-Bis(trifluoromethyl)aniline (0.11 mmol), Toluene (to 10 mM NDT), Acetic acid (4.52×10^{-3} mmol), and a stir bar. Reaction was left to stir vigorously for 10 minutes under argon, and heated until reflux with dean-stark trap for >16 hours. Reaction was allowed to cool and transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved via GPC (toluene, 5 mL/min) to yield pure **$\alpha(1dd)_2$** as a yellow solid, 2.5 mg (6 %).

Structural Analysis **$\alpha(1dd)_2$** : ^1H NMR (400 MHz, CDCl_3) δ 8.80 (s, 2H), 8.30 (s, 2H), 7.77 (s, 2H), 7.71 (s, 4H), 7.61 (s, 2H), 4.23 (t, $J = 6.7$ Hz, 4H), 1.94 (dt, $J = 13.3$, 6.7 Hz, 2H), 1.84 (q, $J = 6.7$ Hz, 4H), 1.04 (d, $J = 6.5$ Hz, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.4, 152.2, 149.8, 140.9, 135.7, 133.1, 132.8 (q, $J = 33.6$ Hz), 129.4, 122.3 (q, $J = 273.2$ Hz), 121.4 (d, $J = 3.6$ Hz), 119.6 (t, $J = 3.3$ Hz), 106.1, 67.8, 37.9, 25.3, 22.7; HRMS (APCI+) calcd for $\text{C}_{42}\text{H}_{34}\text{F}_{12}\text{N}_2\text{O}_2\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 891.1948, found 891.1935.

3.3 Yield Summation, **$\alpha(1)_2$** Series

Derivative	Conditions <i>i</i> TFA, CHCl_3 , Mol. Sieves	Conditions <i>ii</i> ScOTf ₃ , MeCN, CHCl_3 , Mol. Sieves	Conditions <i>iii</i> Toluene, Δ
$\alpha(1a)_2$	46%	39%	—
$\alpha(1b)_2$	57%	43%	—
$\alpha(1c)_2$	30%	45%	—
$\alpha(1d)_2$	2%	41%	47%
$\alpha(1bb)_2$	—	33%	39%
$\alpha(1cc)_2$	14%	12%	59%
$\alpha(1dd)_2$	—	21%	6%

Table B 1. Summary of isolated yields for the **$\alpha(1)_2$** series employing conditions *i*, *ii*, or *iii*.

3.4 NMR Spectra

3.4.1 Precursors and $\alpha(\text{CHO})_2$

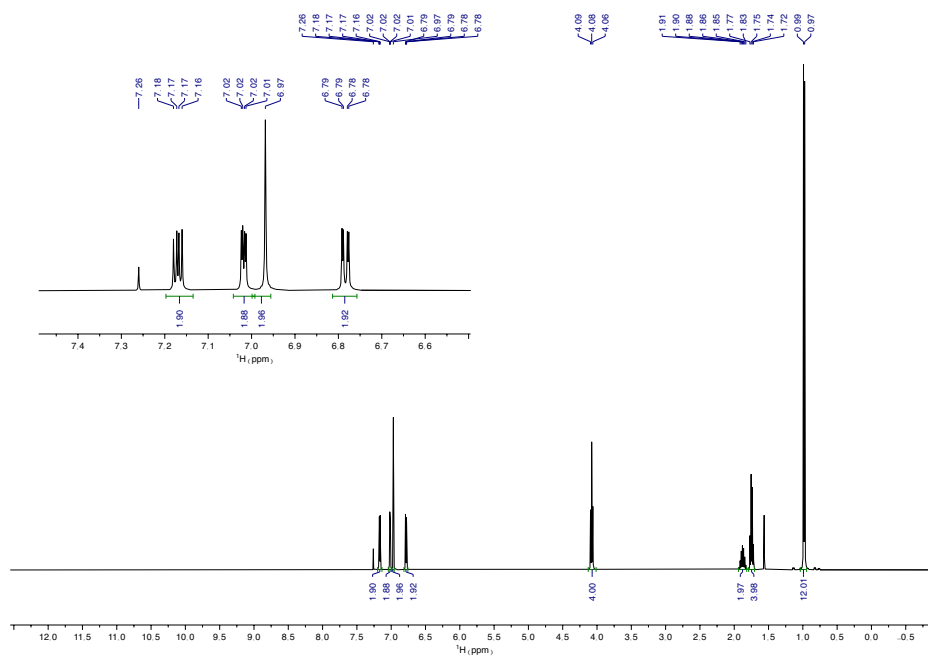


Figure B 2. ^1H NMR spectrum of 1,2-di(3-thienyl)-4,5-di-isopentyloxybenzene **3** (CDCl_3 , 400 MHz, 298 K).

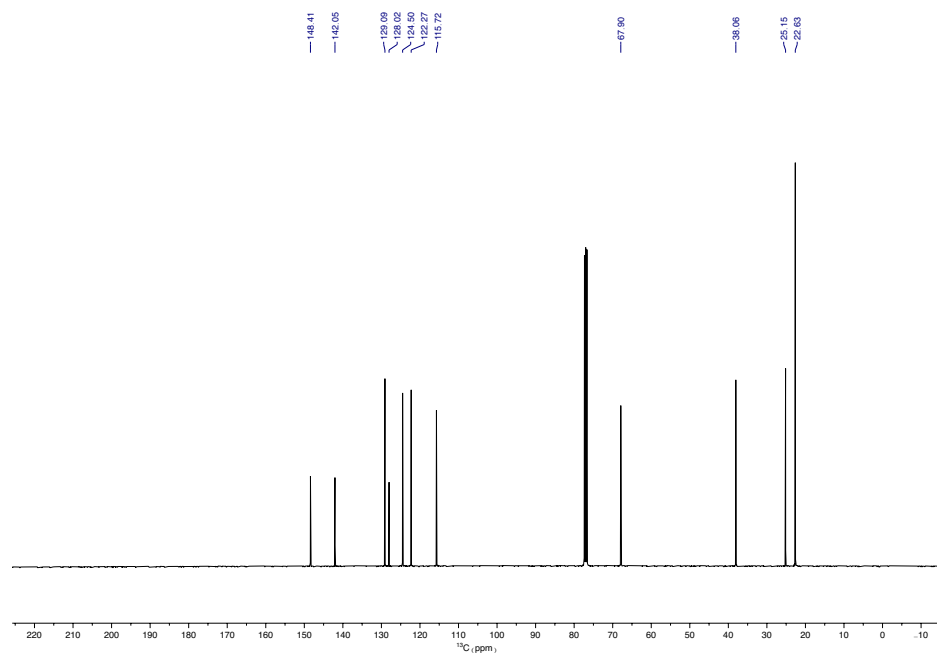


Figure B 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1,2-di(3-thienyl)-4,5-di-isopentyloxybenzene **3** (CDCl_3 , 400 MHz, 298 K).

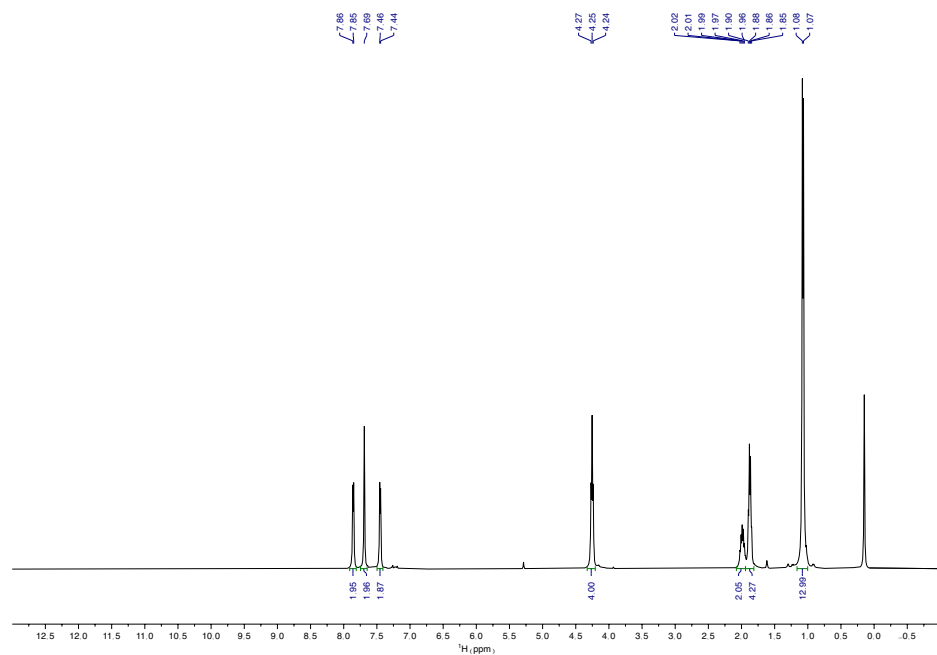


Figure B 4. ^1H NMR spectrum of 5,6-bis(isopentyloxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a** (CDCl_3 , 400 MHz, 298 K).

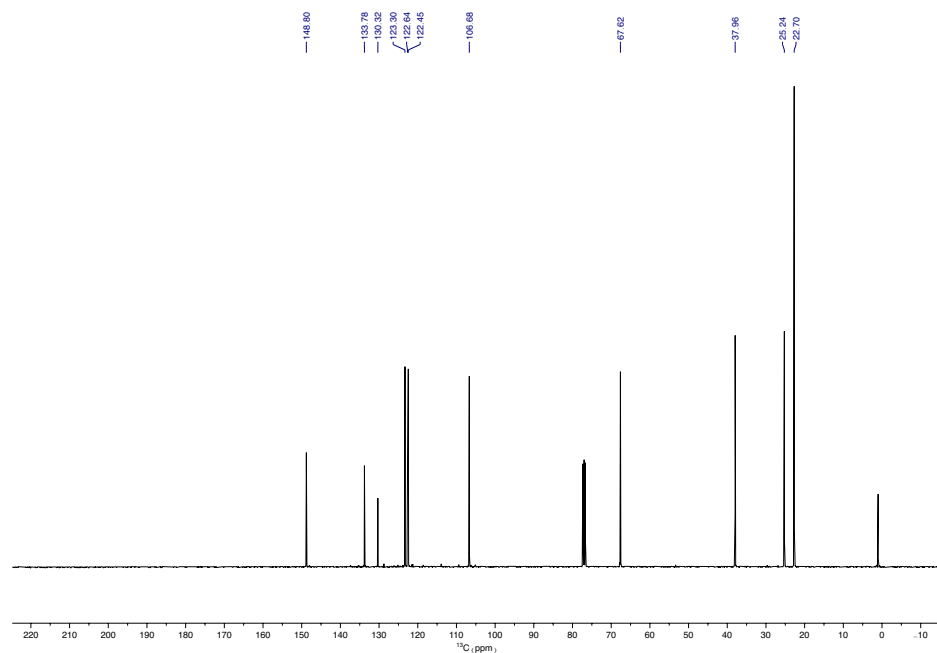


Figure B 5. ¹³C{¹H} NMR spectrum of 5,6-bis(isopentyloxy)naphtho[2,1-*b*:3,4-*b'*]dithiophene **α** (CDCl₃, 400 MHz, 298 K).

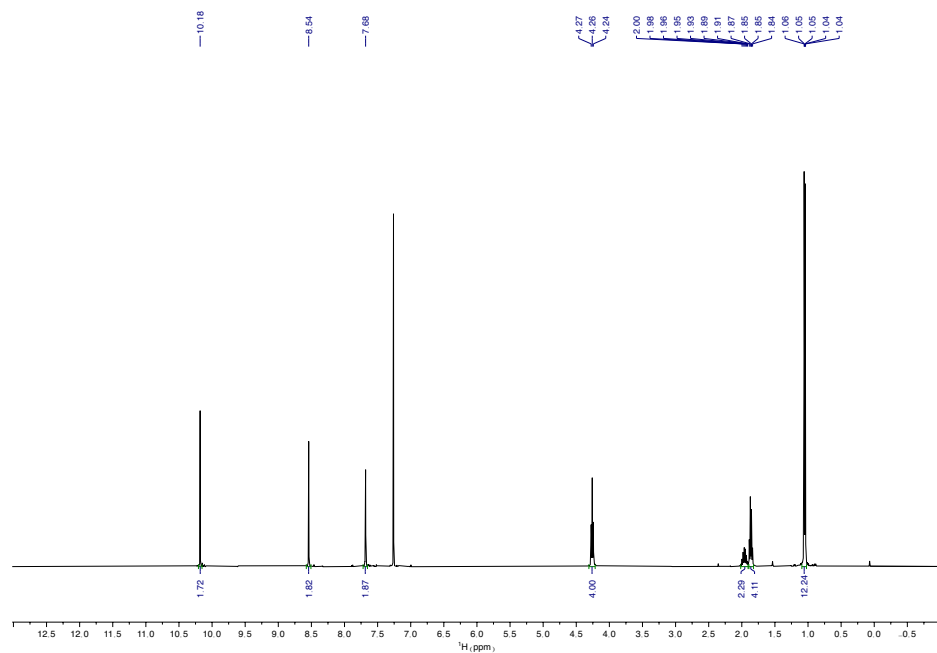


Figure B 6. ¹H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-diformylnaphtho[2,1-*b*:3,4-*b'*]dithiophene, **α**(CHO)₂ (CDCl₃, 400 MHz, 298 K).

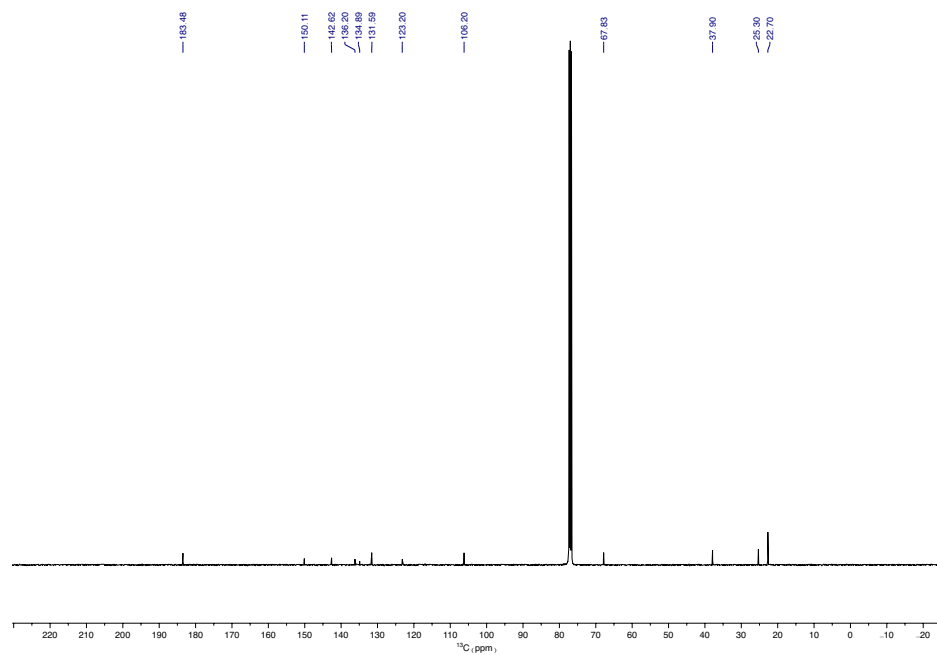


Figure B 7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-diformylnaphtho[2,1-*b*:3,4-*b'*]dithiophene, $\alpha(\text{CHO})_2$ (CDCl_3 , 400 MHz, 298 K).

3.4.2 $\alpha(1)_2$ Series

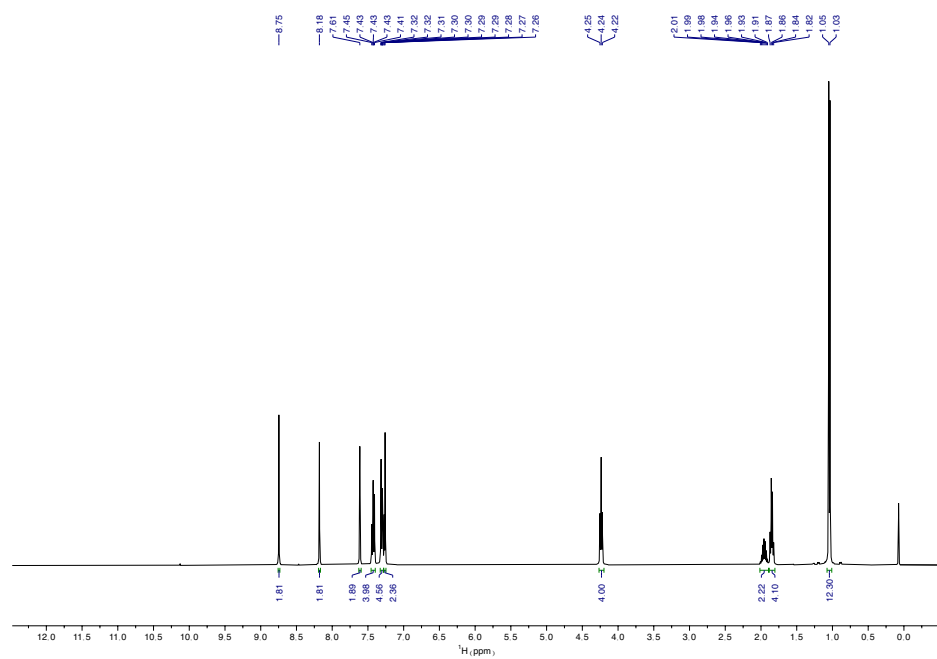


Figure B 8. ¹H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene $\alpha(1a)_2$ (CDCl₃, 400 MHz, 298 K).

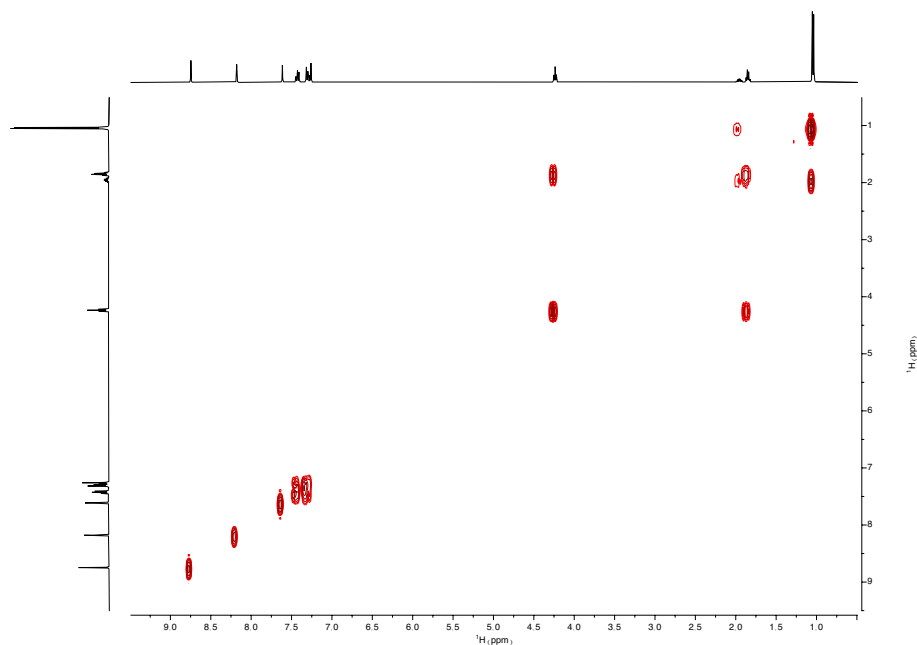


Figure B 9. ^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1a**₂ (CDCl_3 , 400 MHz, 298 K).

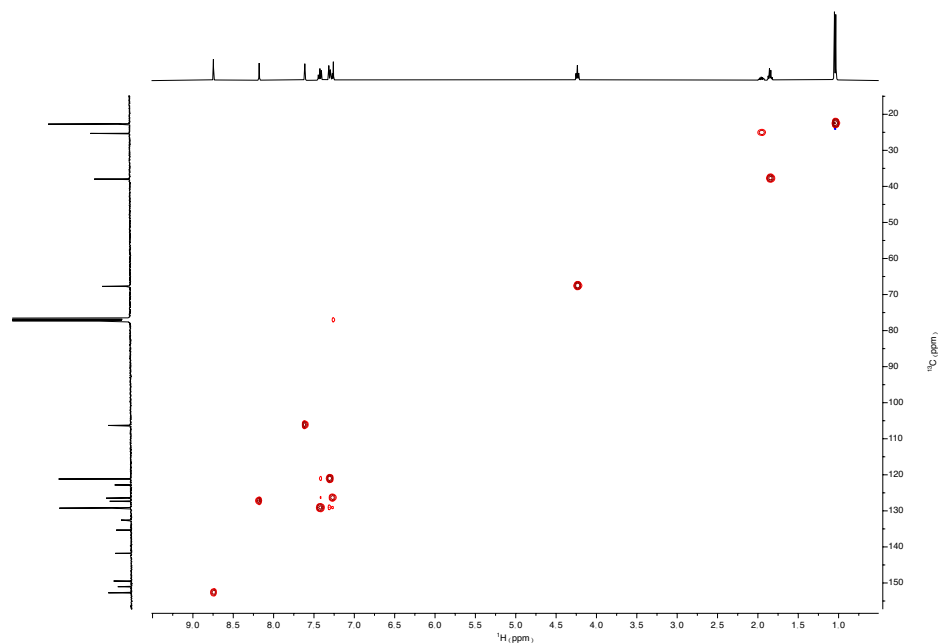


Figure B 10. ^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1a**₂ (CDCl_3 , 400 MHz, 298 K).

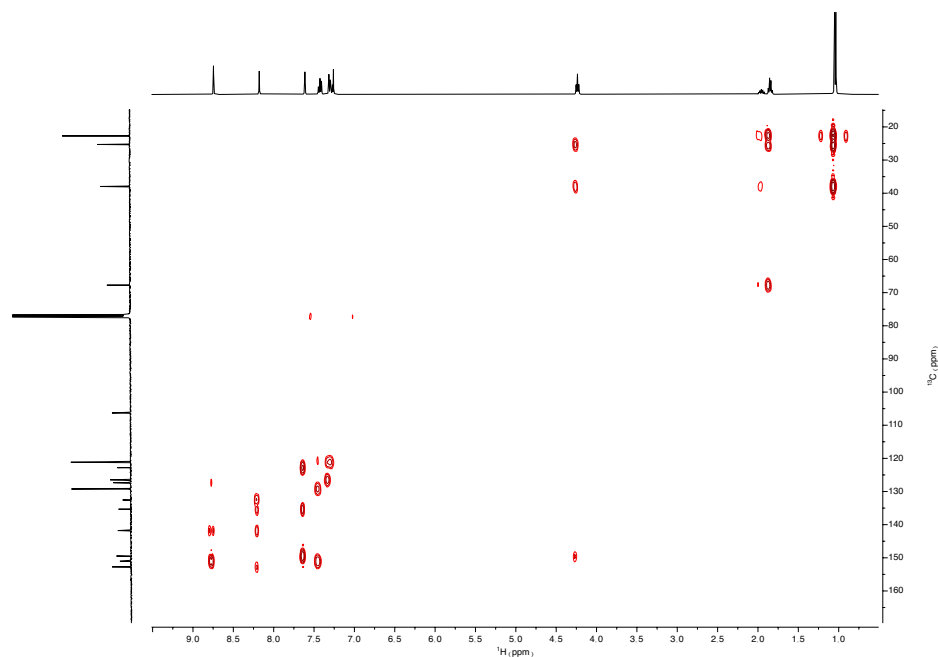


Figure B 11. ^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1a**₂ (CDCl_3 , 400 MHz, 298 K).

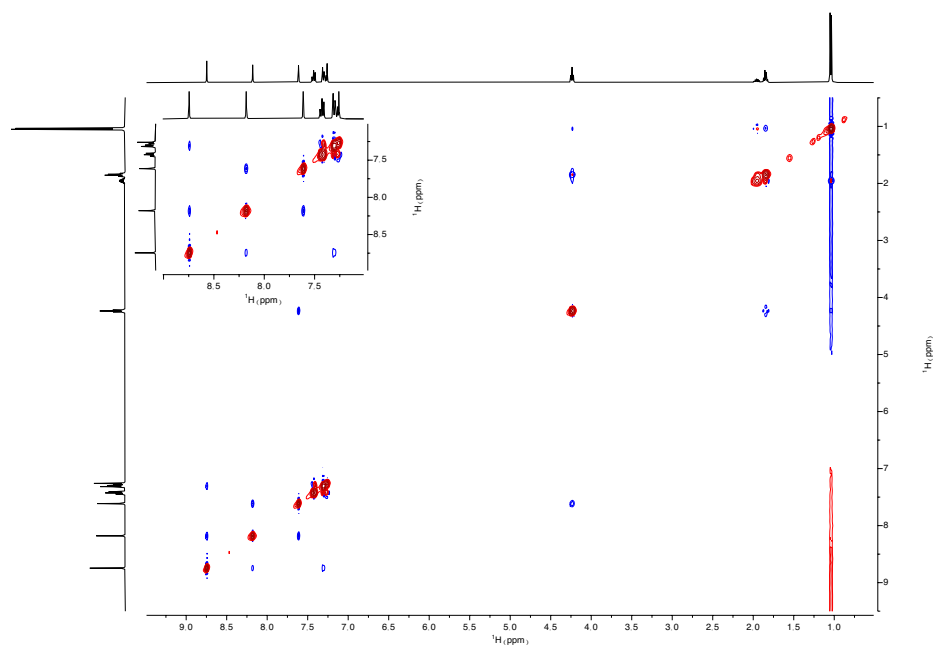


Figure B 12. ^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1a**₂ (CDCl_3 , 400 MHz, 298 K).

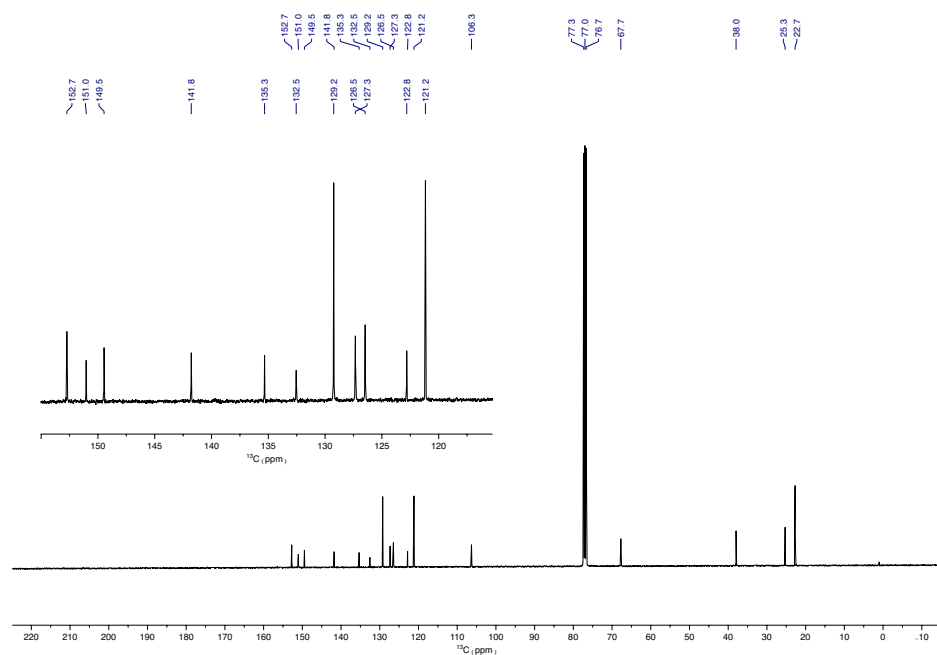
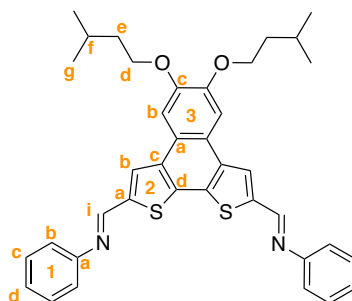


Figure B 13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1a**₂ (CDCl_3 , 400 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	151.0
1b	7.28-7.33	121.2
1c	7.38-7.46	129.2
1d	7.22-7.28	126.5
i	8.75	152.7
2a	-	141.8
2b	8.18	127.3
2c	-	135.3
2d	-	132.5
3a	-	122.8
3b	7.61	106.3
3c	-	149.5
3d	4.24	67.7
3e	1.85	38.0
3f	1.96	25.3
3g	1.04	22.7

Figure B 14. 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1a**)₂ with assignment of ^1H and ^{13}C resonances.

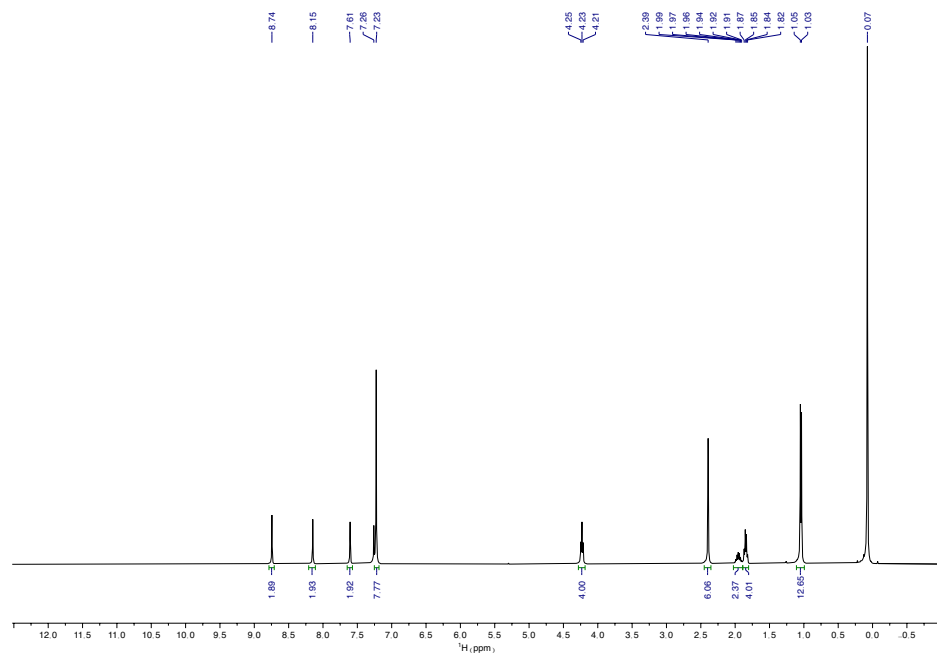


Figure B 15. ^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-tolyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **α (1b) $_2$** (CDCl_3 , 400 MHz, 298 K).

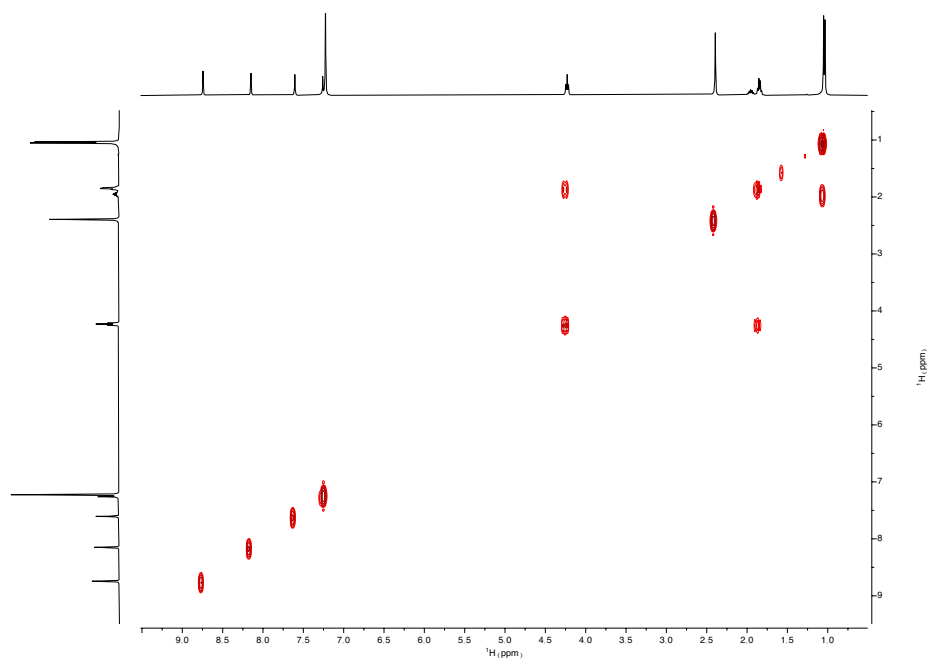


Figure B 16. ^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-tolyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **α (1b) $_2$** (CDCl_3 , 400 MHz, 298 K).

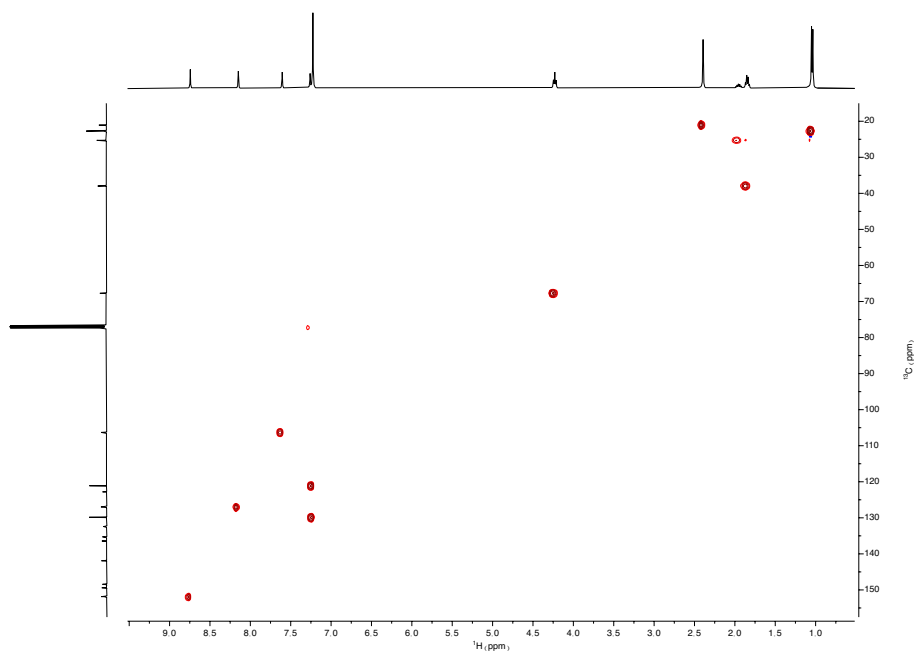


Figure B 17. ^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-tolyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1b**₂ (CDCl_3 , 400 MHz, 298 K).

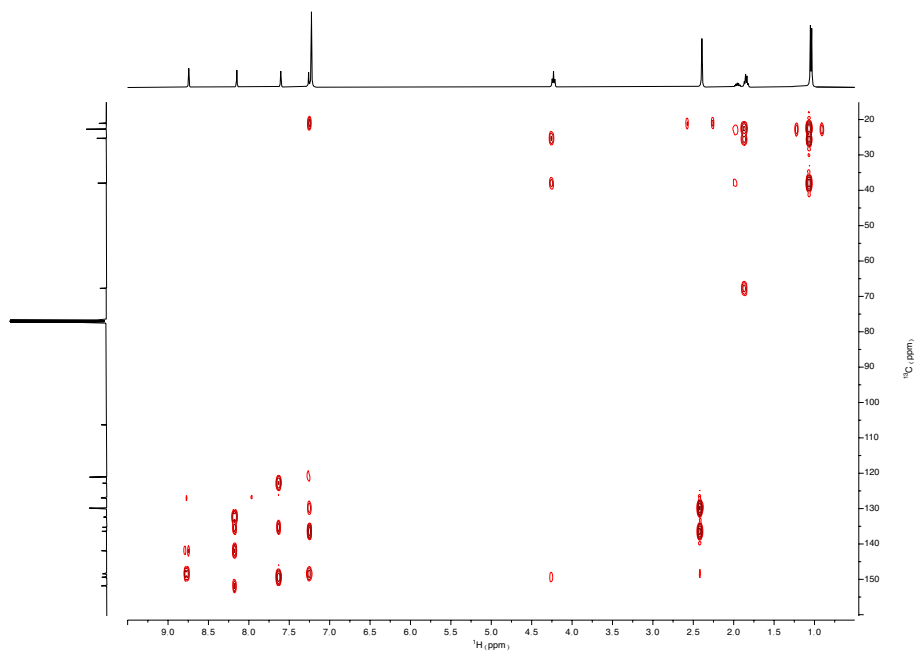


Figure B 18. ^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-tolyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1b**₂ (CDCl_3 , 400 MHz, 298 K).

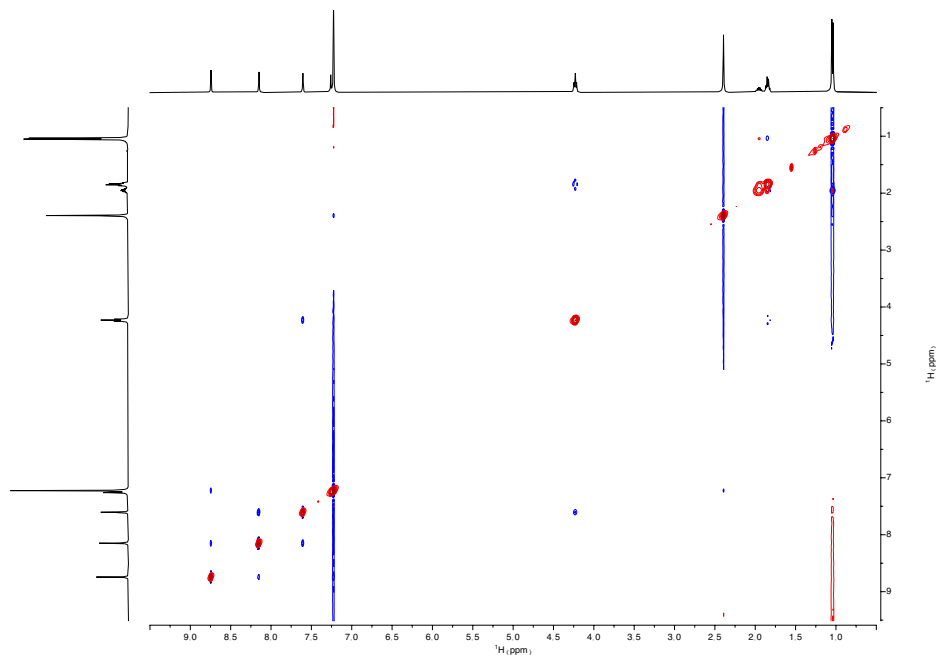


Figure B 19. ^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-tolyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1b**₂ (CDCl_3 , 400 MHz, 298 K).

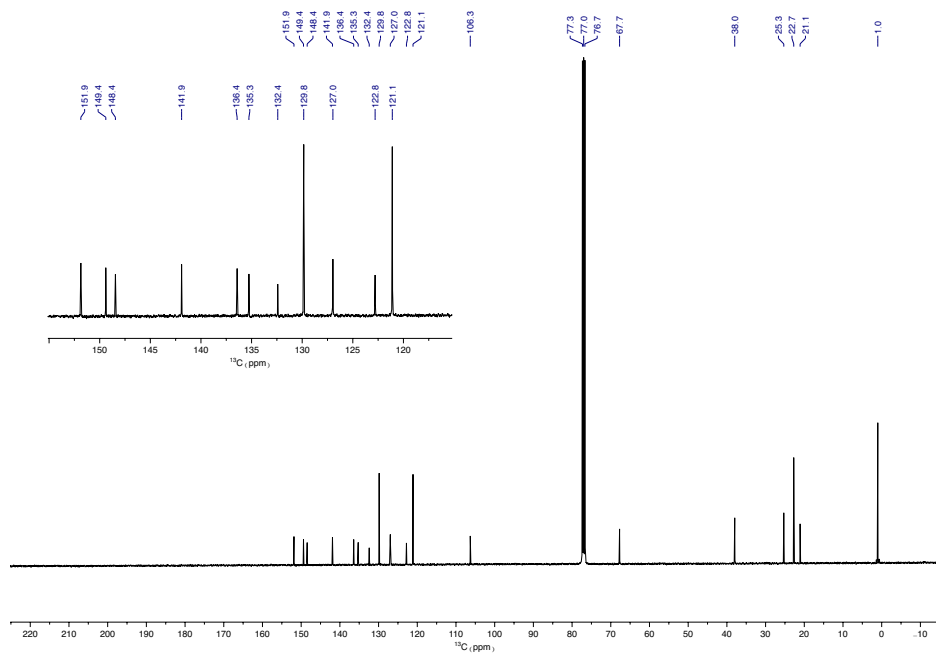
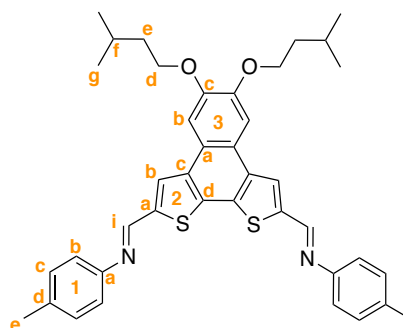


Figure B 20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-tolyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1b**₂ (CDCl_3 , 400 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	148.4
1b	7.23	121.1
1c	7.23	129.8
1d	-	136.4
1e	2.39	21.1
i	8.74	151.9
2a	-	141.9
2b	8.15	127.0
2c	-	135.2
2d	-	132.4
3a	-	122.8
3b	7.61	106.3
3c	-	149.4
3d	4.23	67.7
3e	1.84	37.9
3f	1.96	25.3
3g	1.04	22.7

Figure B 21. 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-tolyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1b** with assignment of ^1H and ^{13}C resonances.

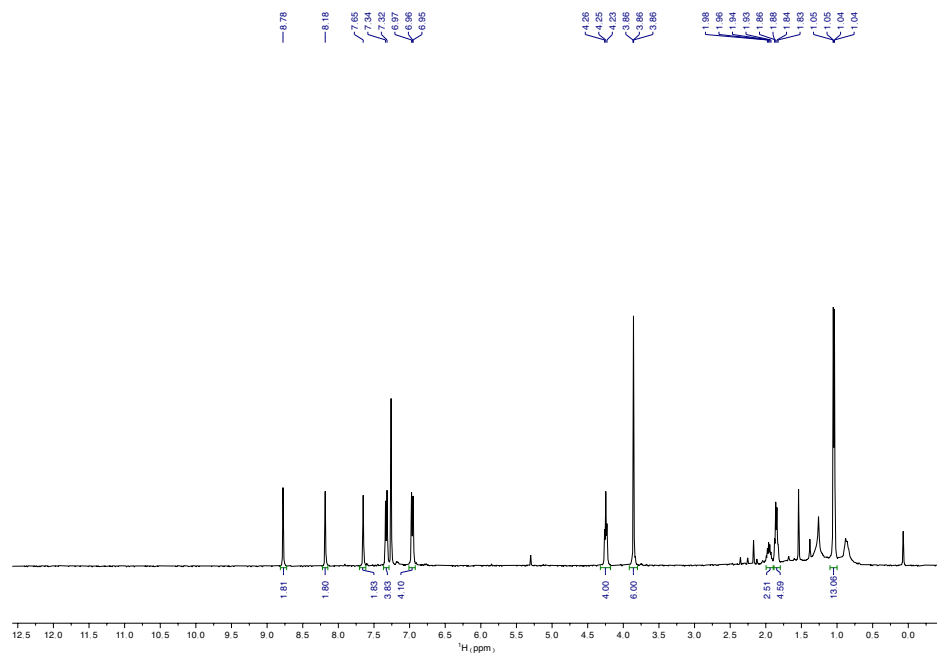


Figure B 22. ^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-methoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(1c)**₂ (CDCl_3 , 400 MHz, 298 K).

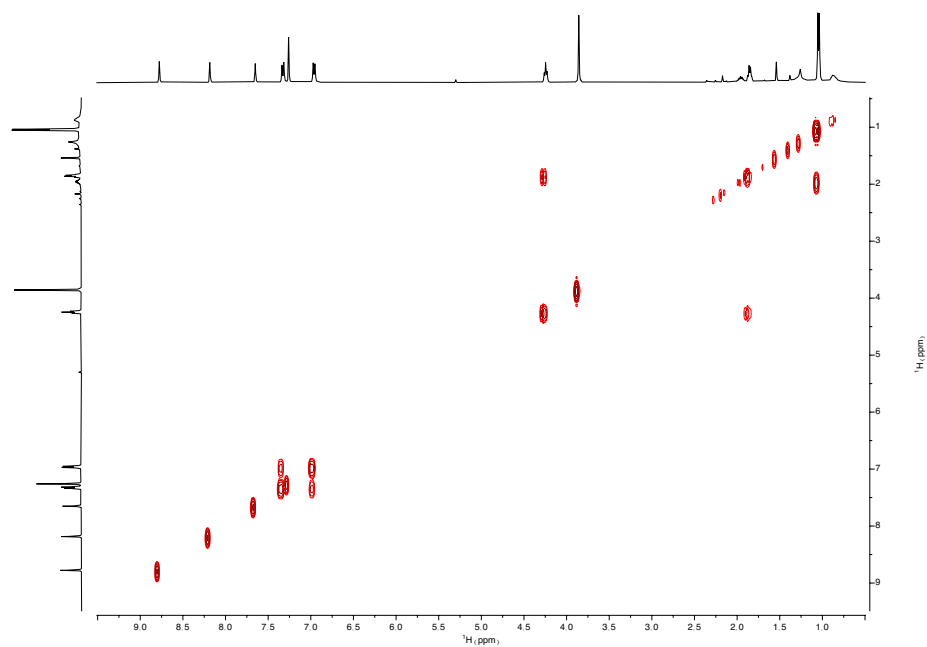


Figure B 23. ^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-methoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(1c)**₂ (CDCl_3 , 400 MHz, 298 K)

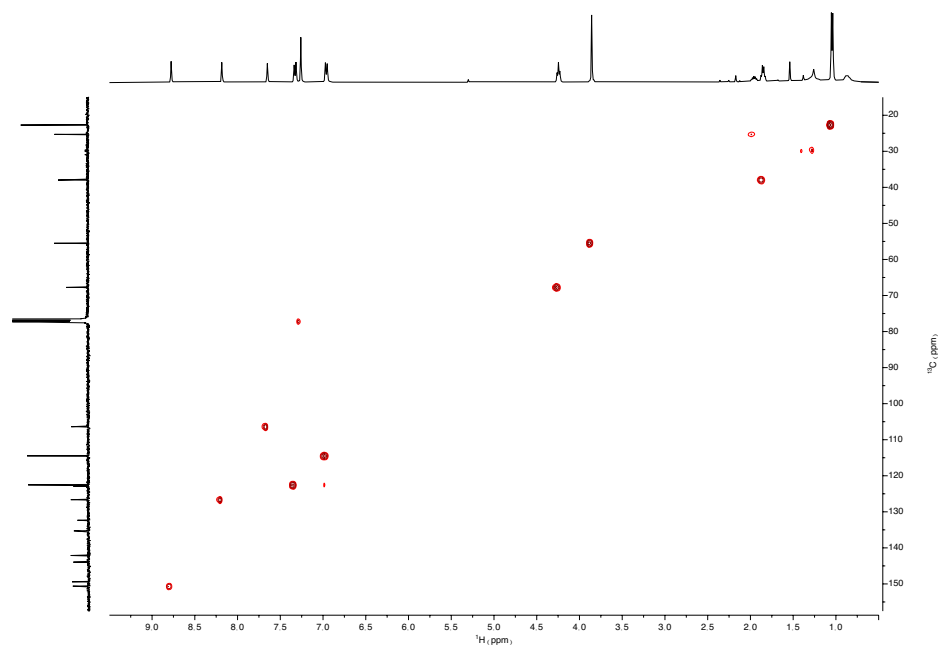


Figure B 24. ^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-methoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(1c)**₂ (CDCl_3 , 400 MHz, 298 K).

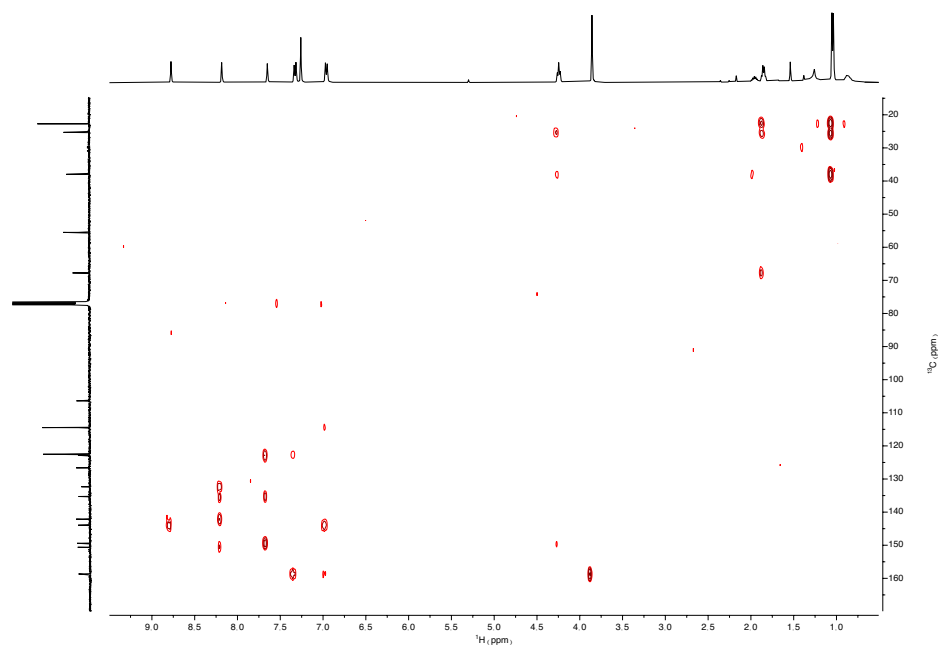


Figure B 25. ^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-methoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(1c)**₂ (CDCl_3 , 400 MHz, 298 K).

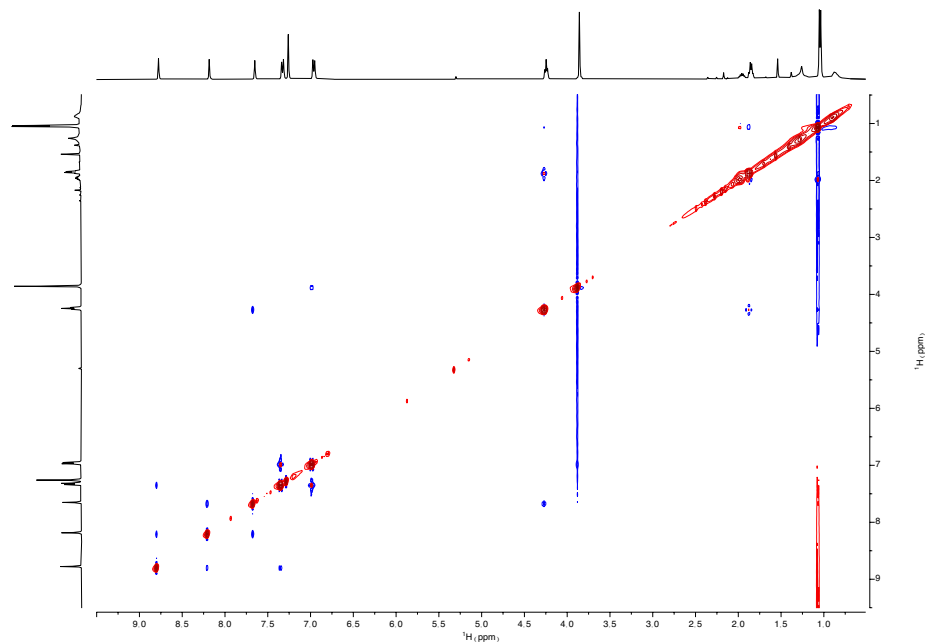


Figure B 26. ^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-methoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1c**₂ (CDCl_3 , 400 MHz, 298 K).

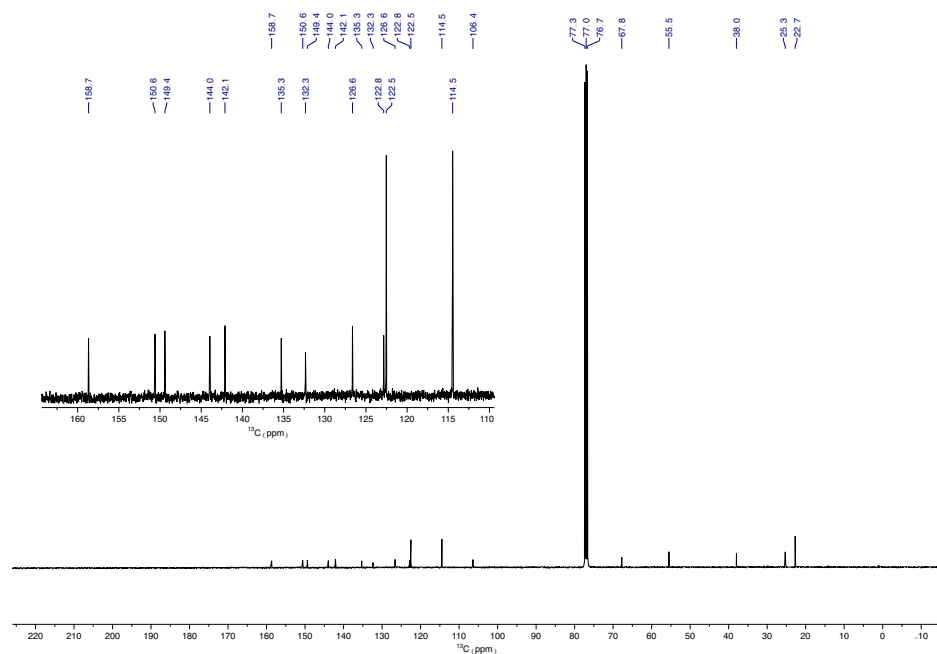
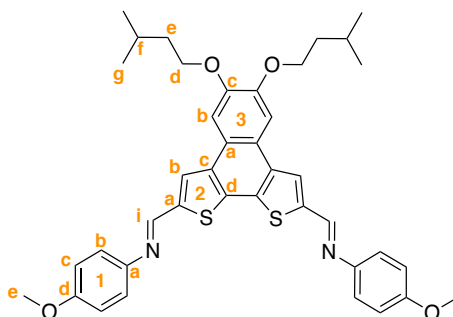


Figure B 27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-methoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1c**₂ (CDCl_3 , 400 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	158.7
1b	7.33	122.5
1c	6.96	114.4
1d	-	158.7
1e	3.86	55.5
i	8.78	150.6
2a	-	142.1
2b	8.18	126.6
2c	-	135.3
2d	-	132.3
3a	-	122.8
3b	7.65	106.4
3c	-	149.4
3d	4.25	67.8
3e	1.85	38.0
3f	2.03-1.92	25.3
3g	1.04	22.7

Figure B 28. 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-methoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **a(1c)₂** with assignment of ^1H and ^{13}C resonances.

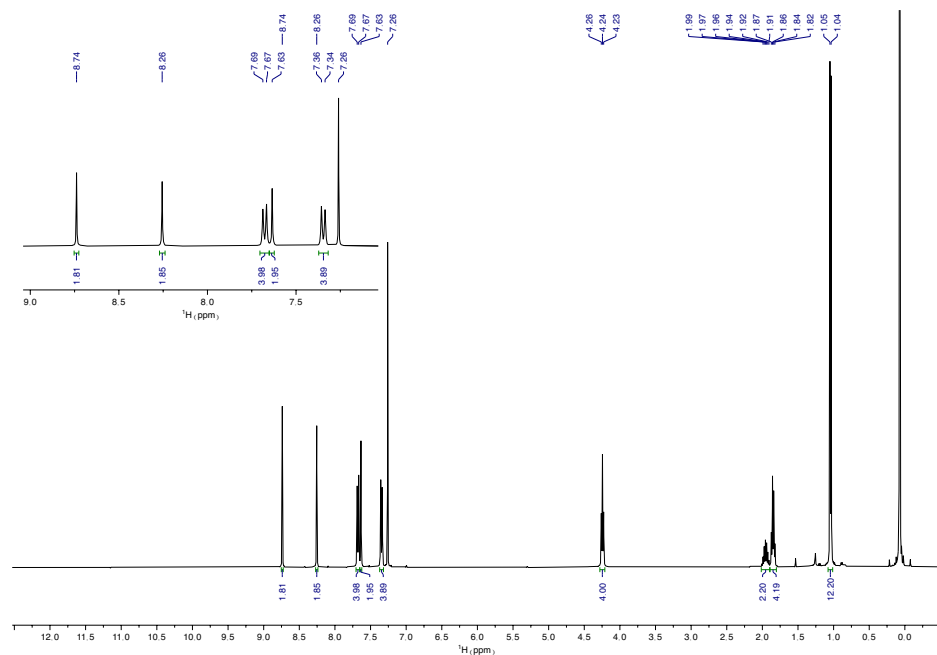


Figure B 29. ¹H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1d** (CDCl₃, 400 MHz, 298 K).

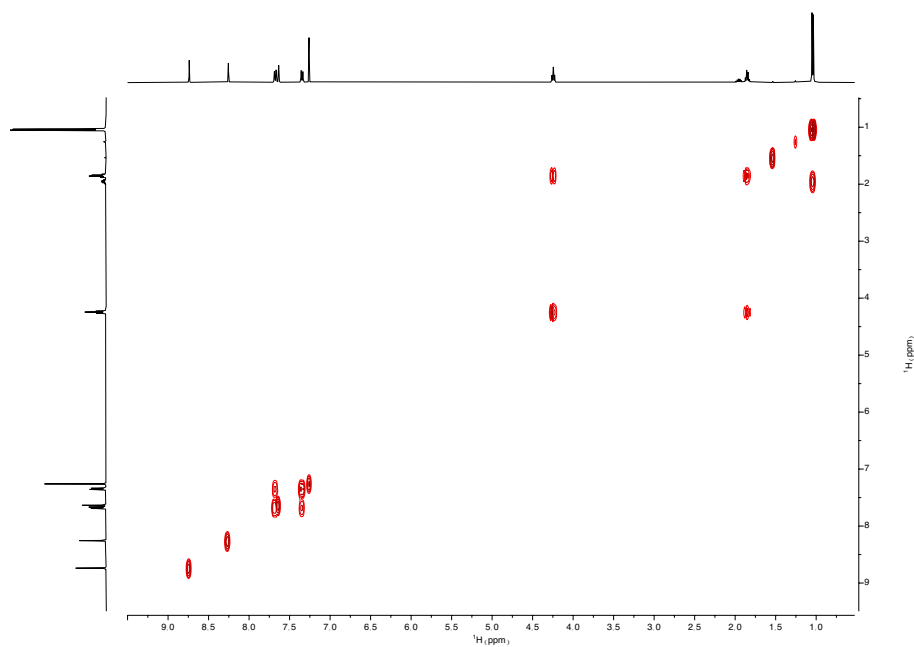


Figure B 30. ¹H-¹H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1d** (CDCl₃, 400 MHz, 298 K).

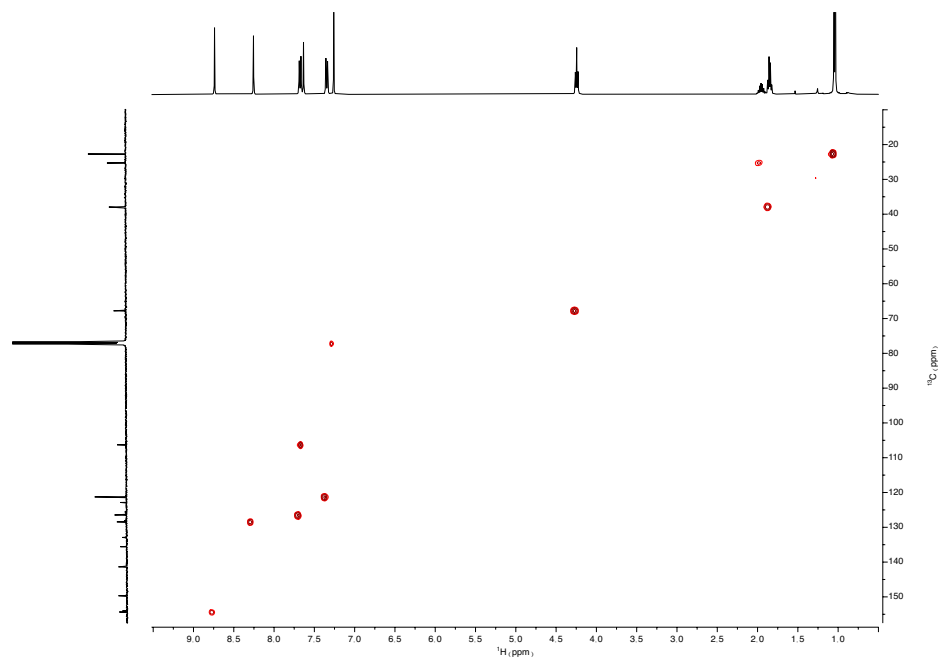


Figure B 31. ^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **α (1d) $_2$** (CDCl_3 , 400 MHz, 298 K).

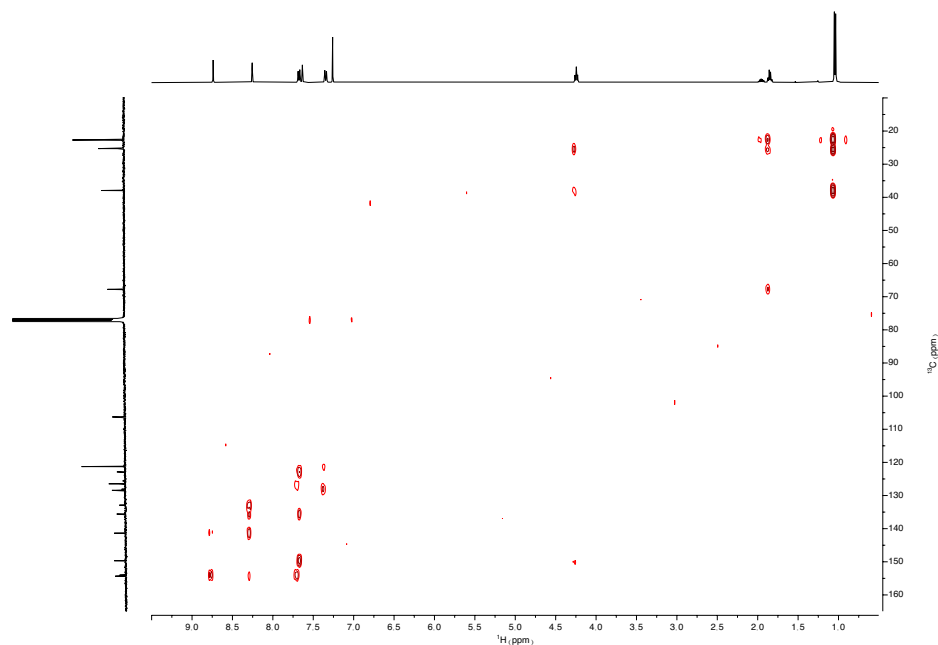


Figure B 32. ^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **α (1d) $_2$** (CDCl_3 , 400 MHz, 298 K).

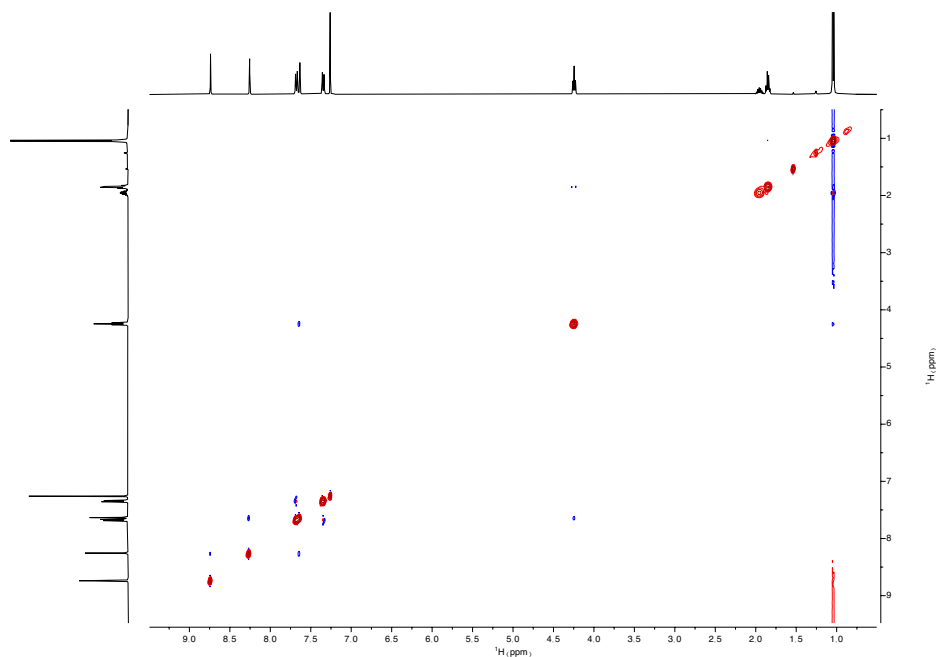


Figure B 33. ^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1d**₂ (CDCl_3 , 400 MHz, 298 K).

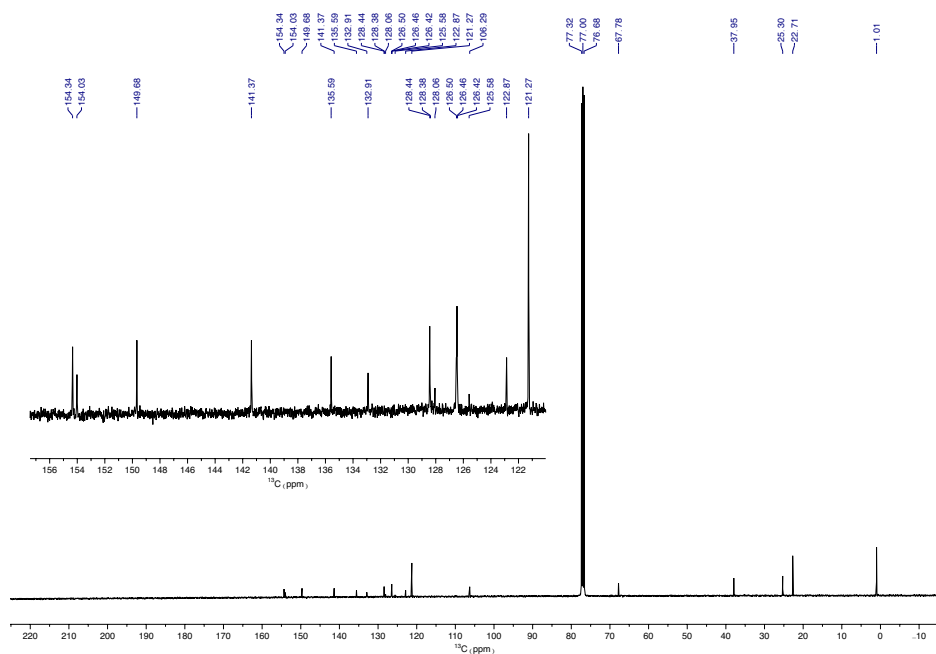
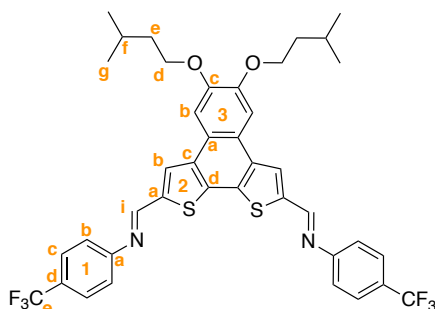


Figure B 34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1d**₂ (CDCl_3 , 400 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	154.0
1b	7.68	125.6
1c	7.35	121.3
1d	-	128.1 (d, J=32 Hz)
1e	-	124.2 (J = 273 Hz)*
i	8.74	154.3
2a	-	141.4
2b	8.26	128.4
2c	-	135.6
2d	-	132.9
3a	-	122.9
3b	7.63	106.3
3c	-	149.7
3d	4.24	67.8
3e	1.85	37.9
3f	1.95	25.3
3g	1.04	22.7

Figure B 35. 5,6-bis(isopentyloxy)-2,9-di-(*N*-(*p*-trifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1d** with assignment of ^1H and ^{13}C resonances. *Additional quartet signals are weak and overlapped with more prominent signals; with reduced line broadening an additional signal at ~122.9 is visible and provides ~273 Hz coupling constant.

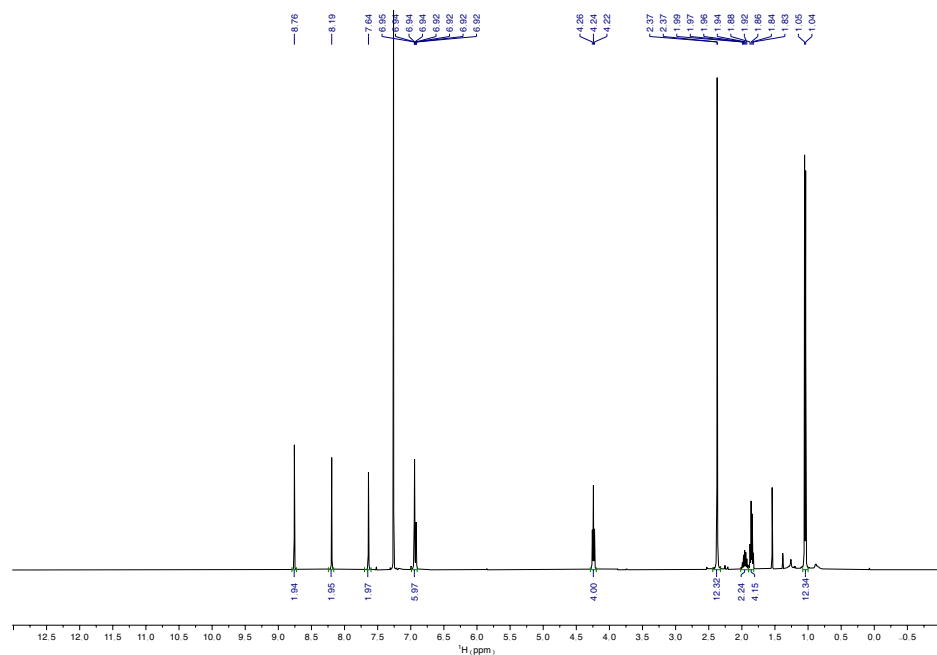


Figure B 36. ^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, $\alpha(\mathbf{1bb})_2$ (CDCl_3 , 400 MHz, 298 K).

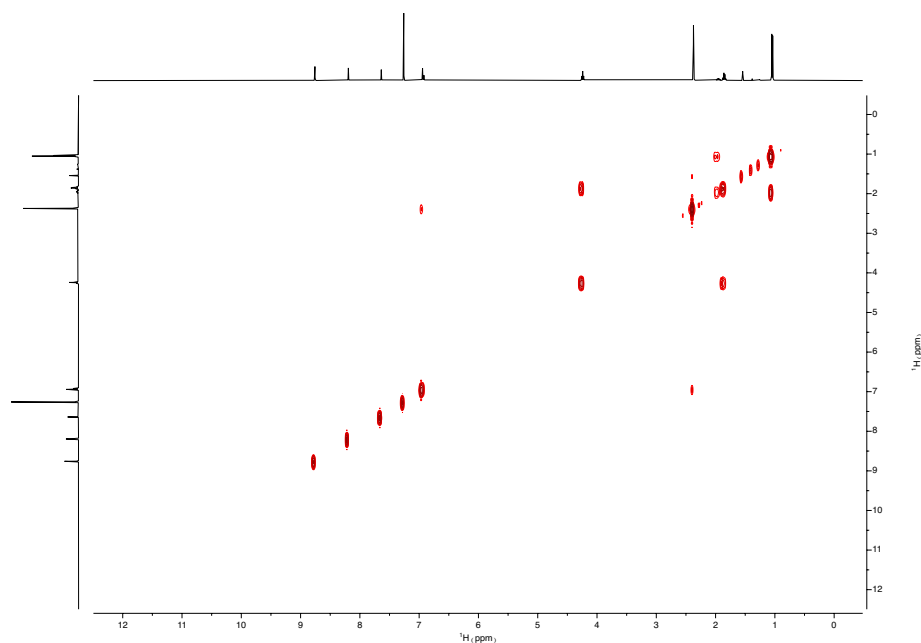


Figure B 37. ^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, $\alpha(\mathbf{1bb})_2$ (CDCl_3 , 400 MHz, 298 K).

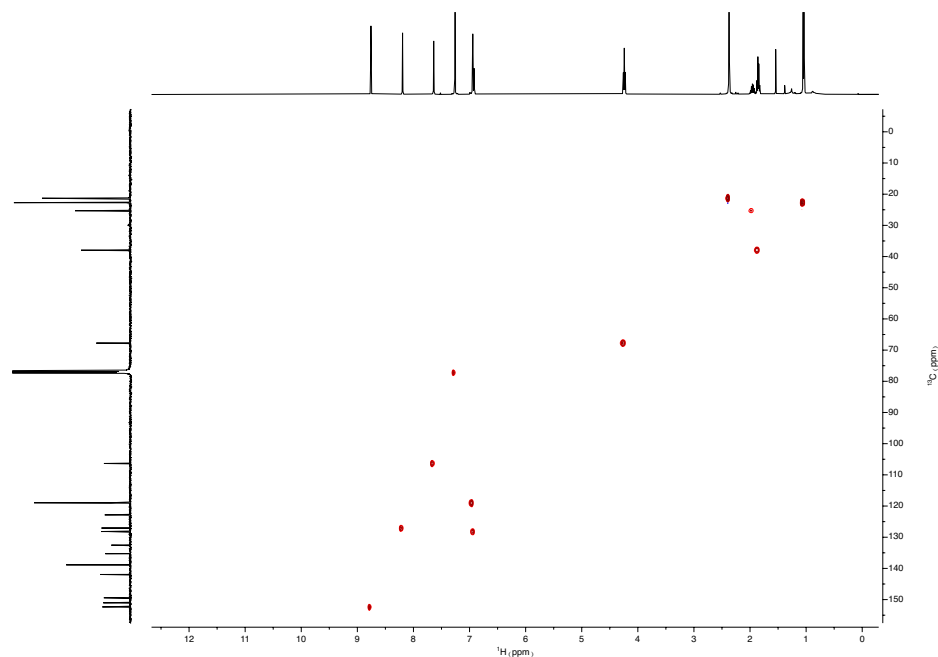


Figure B 38. ^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, ***α*(1bb)₂** (CDCl_3 , 400 MHz, 298 K).

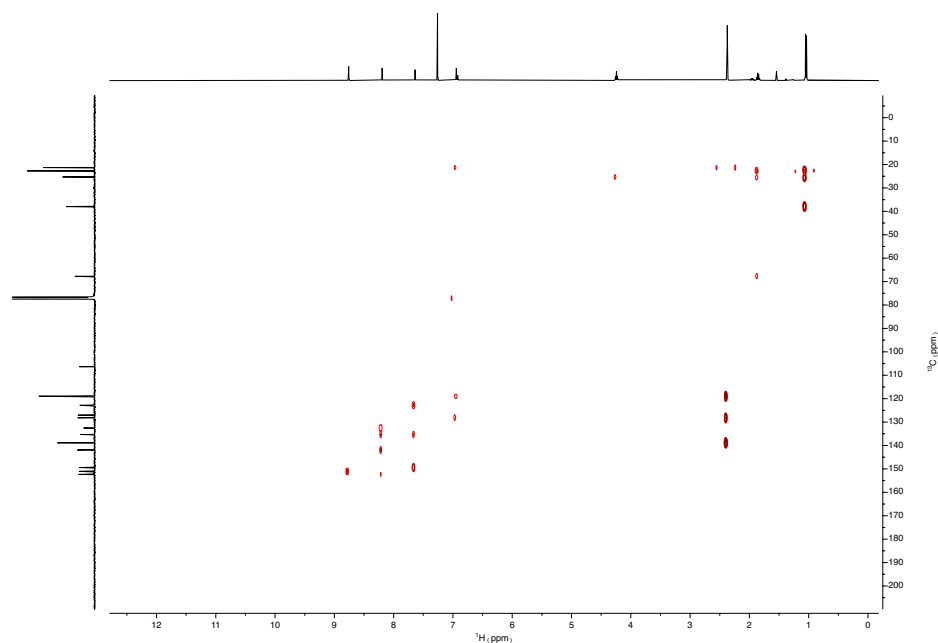


Figure B 39. ^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, ***α*(1bb)₂** (CDCl_3 , 400 MHz, 298 K).

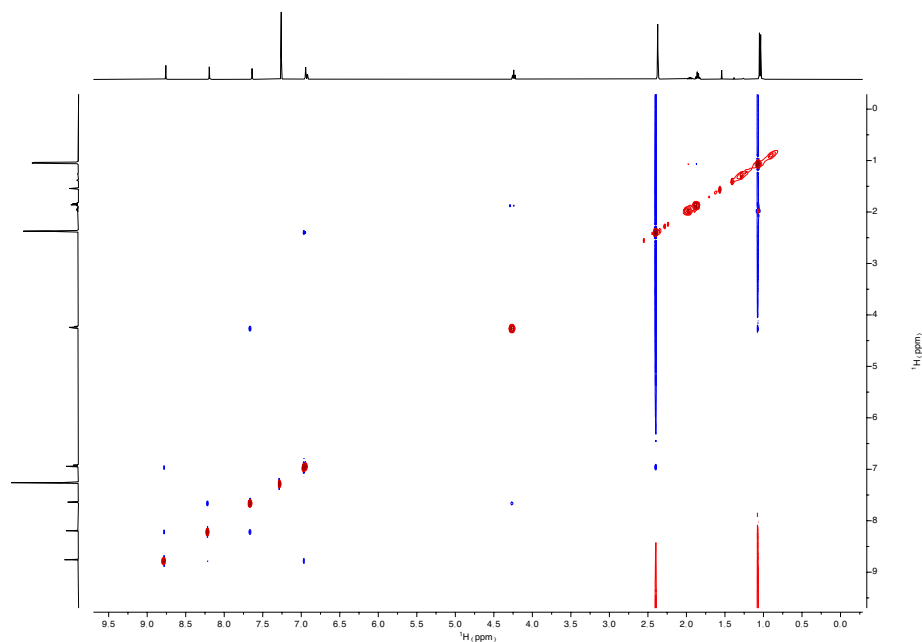


Figure B 40. ^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, $\alpha(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K).

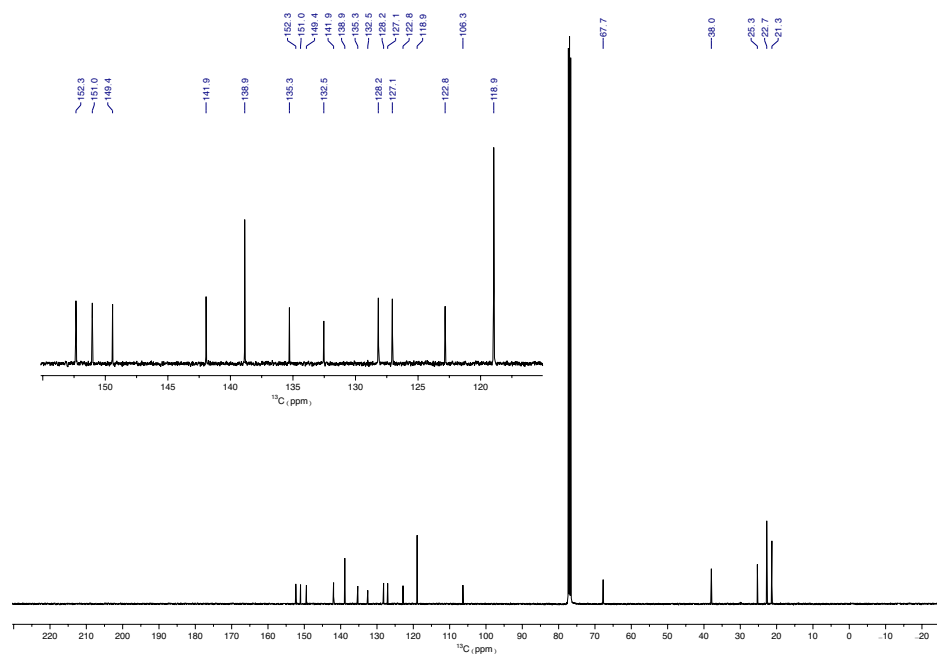
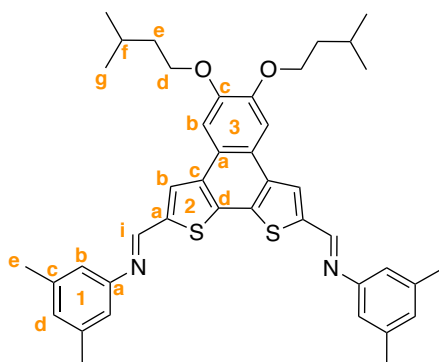


Figure B 41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, $\alpha(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	151.0
1b	6.94	118.9
1c	-	138.9
1d	6.92	128.2
1e	2.37	21.3
i	8.76	152.3
2a	-	141.9
2b	8.19	127.1
2c	-	135.3
2d	-	132.5
3a	-	122.8
3b	7.64	106.4
3c	-	149.4
3d	4.24	67.7
3e	1.85	38.0
3f	1.96	25.3
3g	1.04	22.7

Figure B 42. 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene, **α (1bb) $_2$** with assignment of ^1H and ^{13}C resonances

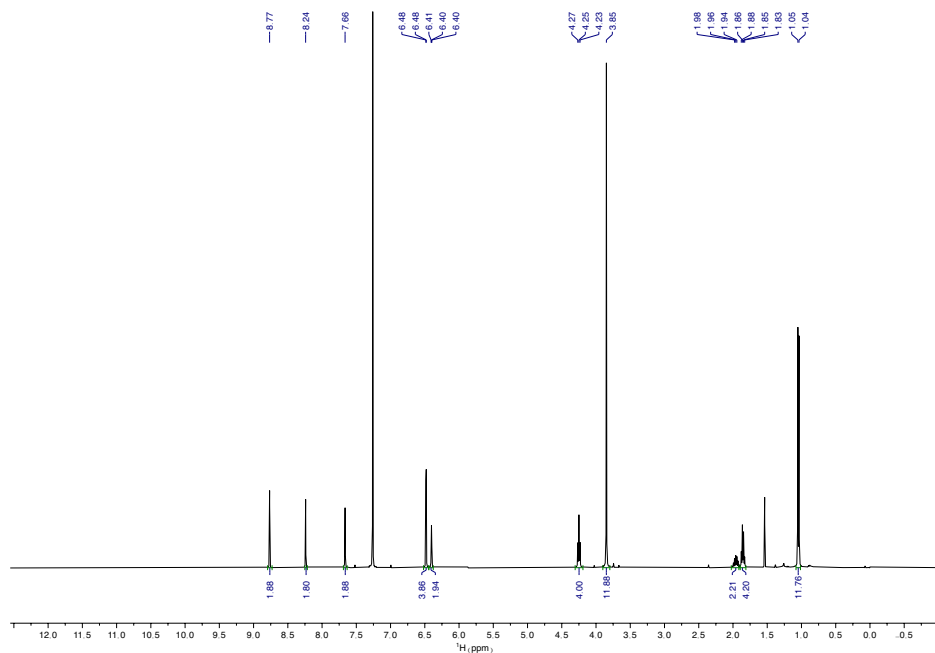


Figure B 43. ^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1cc**₂ (CDCl_3 , 400 MHz, 298 K).

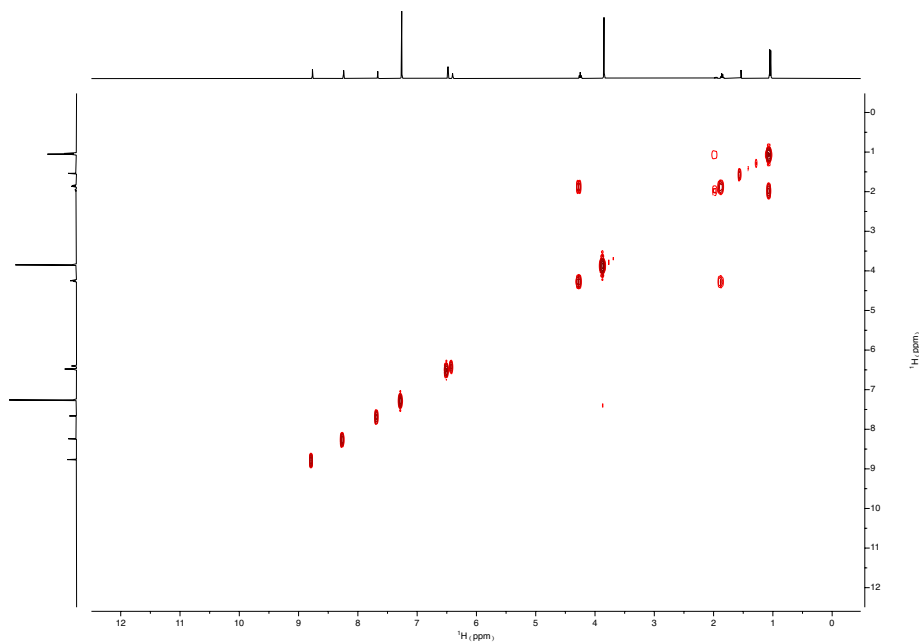


Figure B 44. ^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1cc**₂ (CDCl_3 , 400 MHz, 298 K).

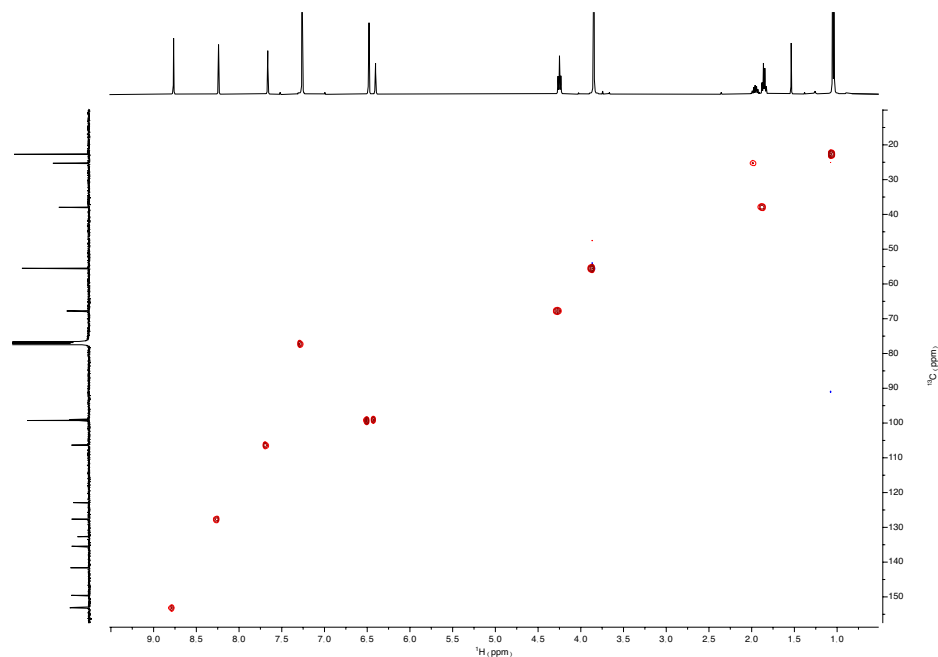


Figure B 45. ^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1cc**₂ (CDCl_3 , 400 MHz, 298 K).

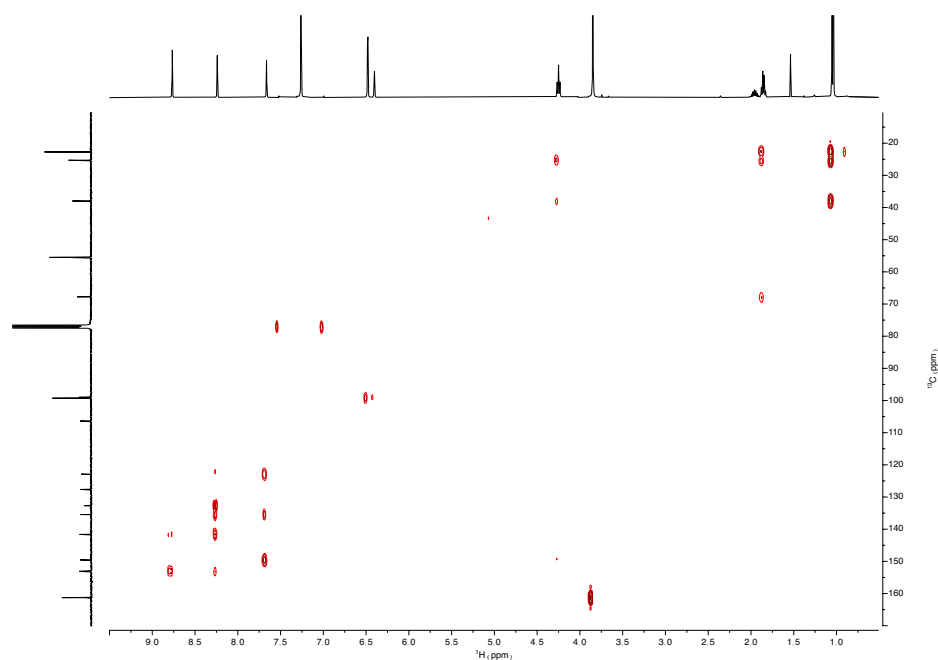


Figure B 46. ^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1cc**₂ (CDCl_3 , 400 MHz, 298 K).

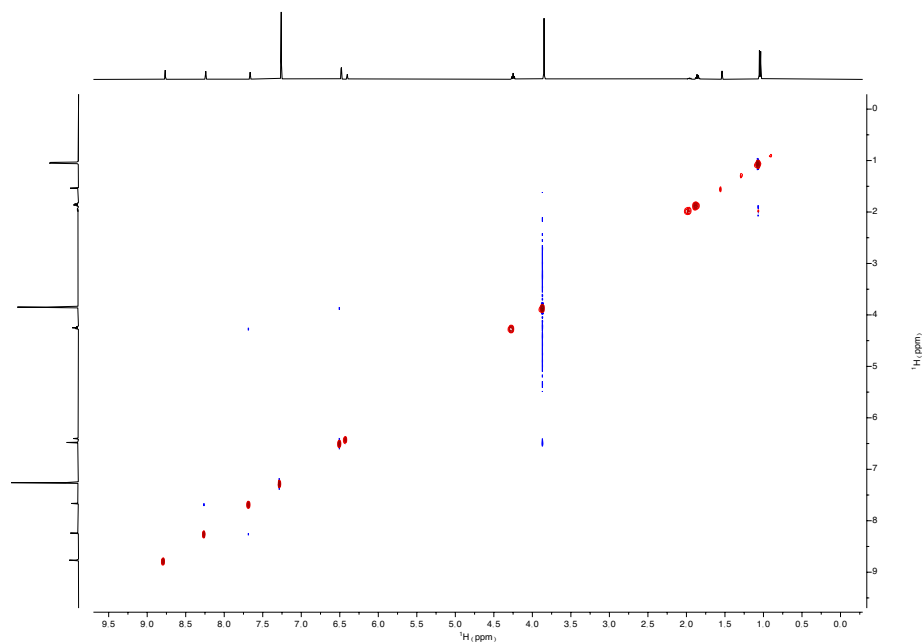


Figure B 47. ^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1cc**₂ (CDCl_3 , 400 MHz, 298 K).

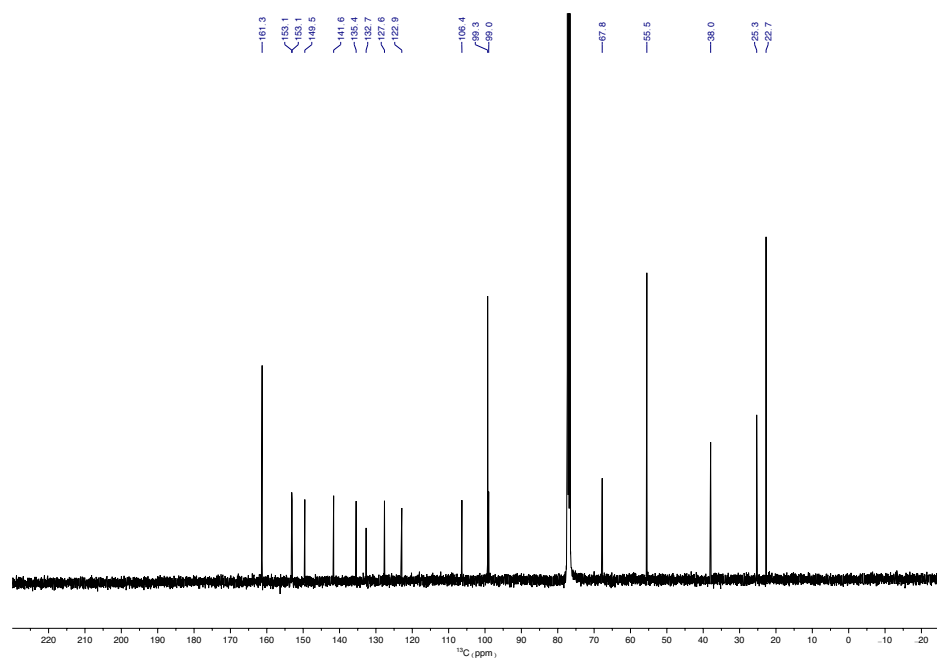
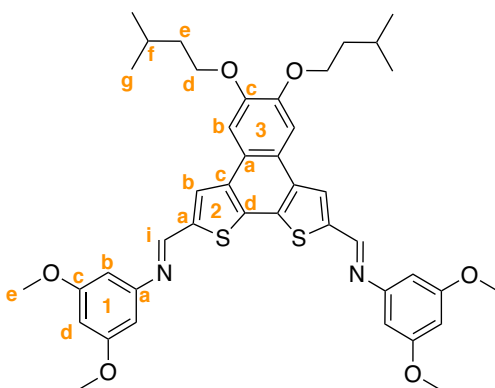


Figure B 48. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1cc**₂ (CDCl_3 , 400 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	153.1*
1b	6.48	99.3
1c	-	161.3
1d	3.85	99.0
1e	6.40	55.5
i	8.77	153.1*
2a	-	141.6
2b	8.24	127.6
2c	-	135.4
2d	-	132.7
3a	-	122.9
3b	7.66	106.4
3c	-	149.5
3d	4.25	67.8
3e	1.85	38.0
3f	1.95	25.3
3g	1.04	22.7

Figure B 49. 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethoxyphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1cc**)₂ with assignment of ^1H and ^{13}C resonances. *Signals are overlapped and resolved by < 0.1 ppm.

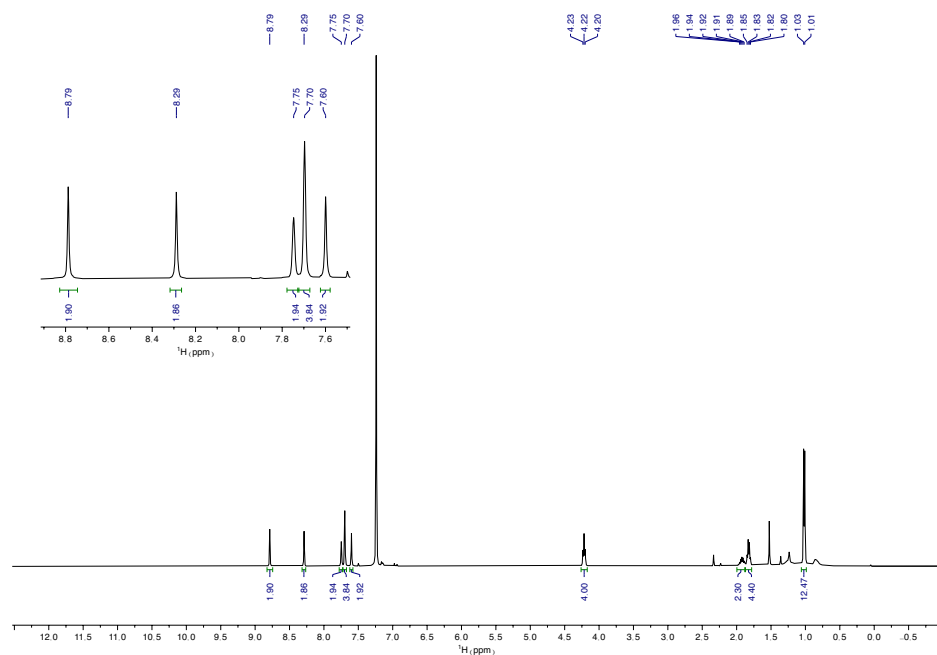


Figure B 50. ^1H NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **α (1dd) $_2$** (CDCl_3 , 400 MHz, 298 K).

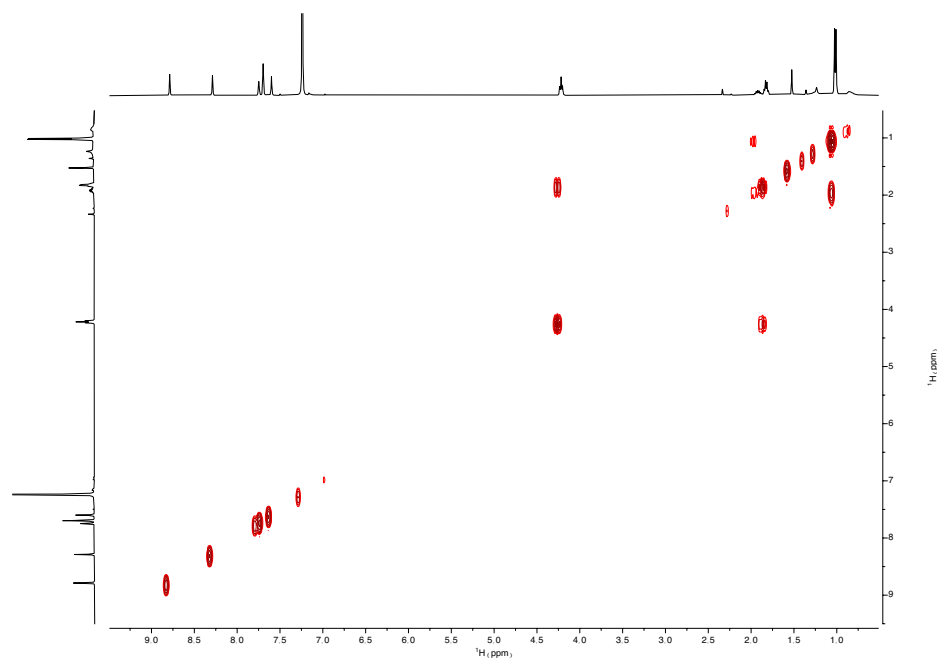


Figure B 51. ^1H - ^1H COSY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **α (1dd) $_2$** (CDCl_3 , 400 MHz, 298 K).

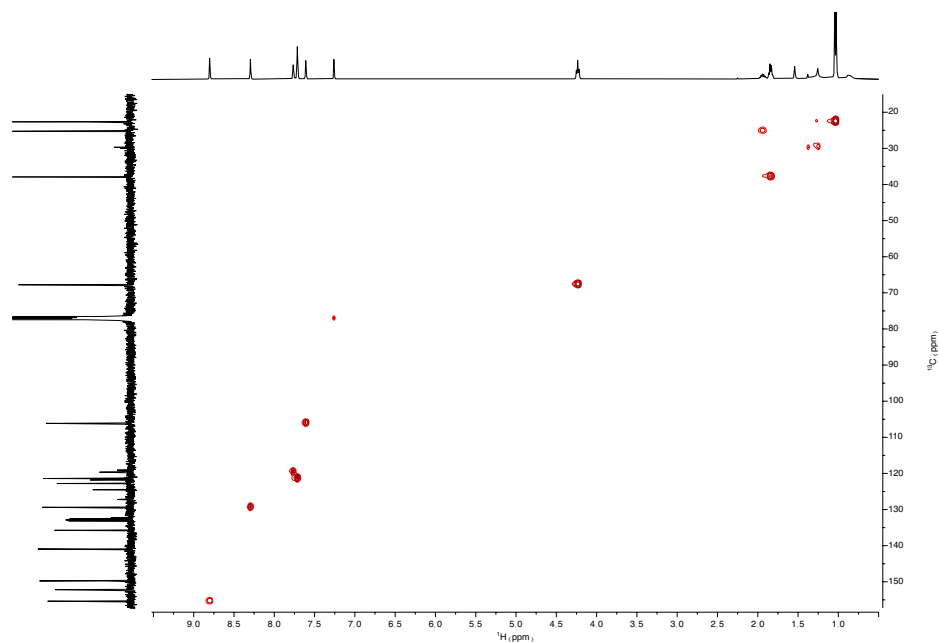


Figure B 52. ^1H - ^{13}C HSQC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1dd**₂ (CDCl_3 , 400 MHz, 298 K).

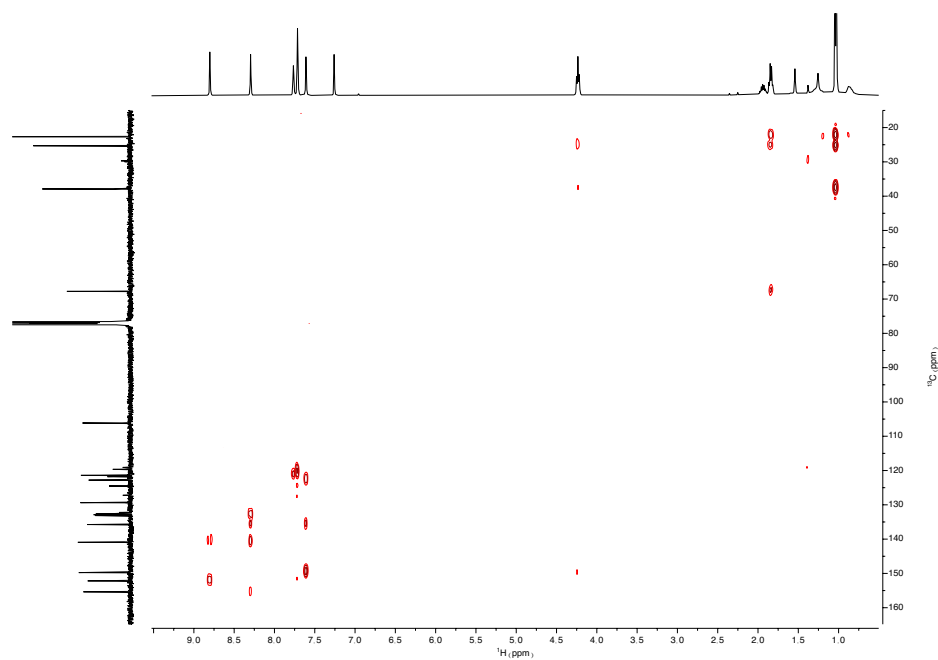


Figure B 53. ^1H - ^{13}C HMBC spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1dd**₂ (CDCl_3 , 400 MHz, 298 K).

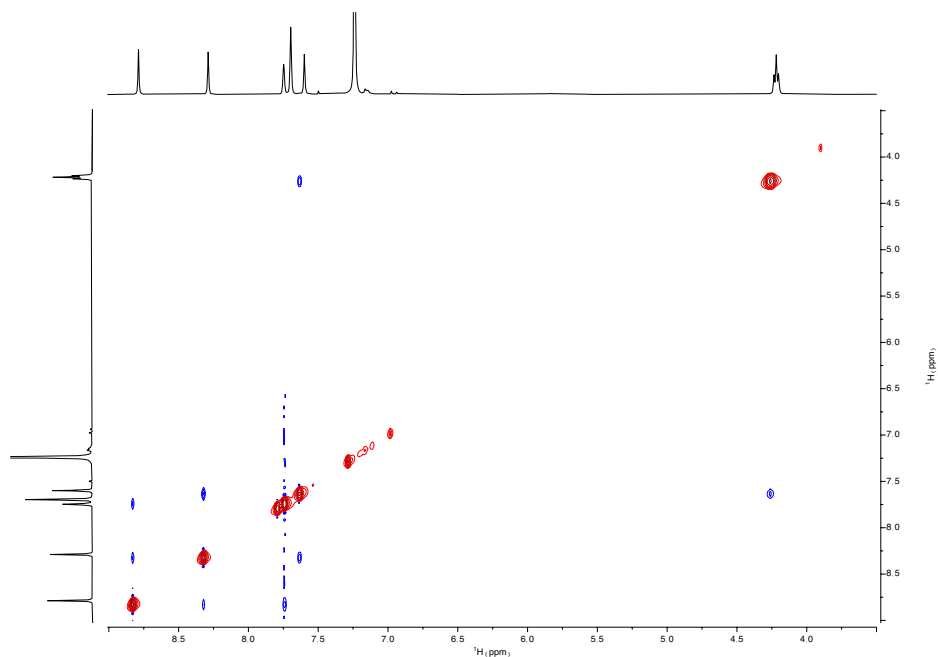


Figure B 54. ^1H - ^1H NOESY spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1dd**₂ (CDCl_3 , 400 MHz, 298 K).

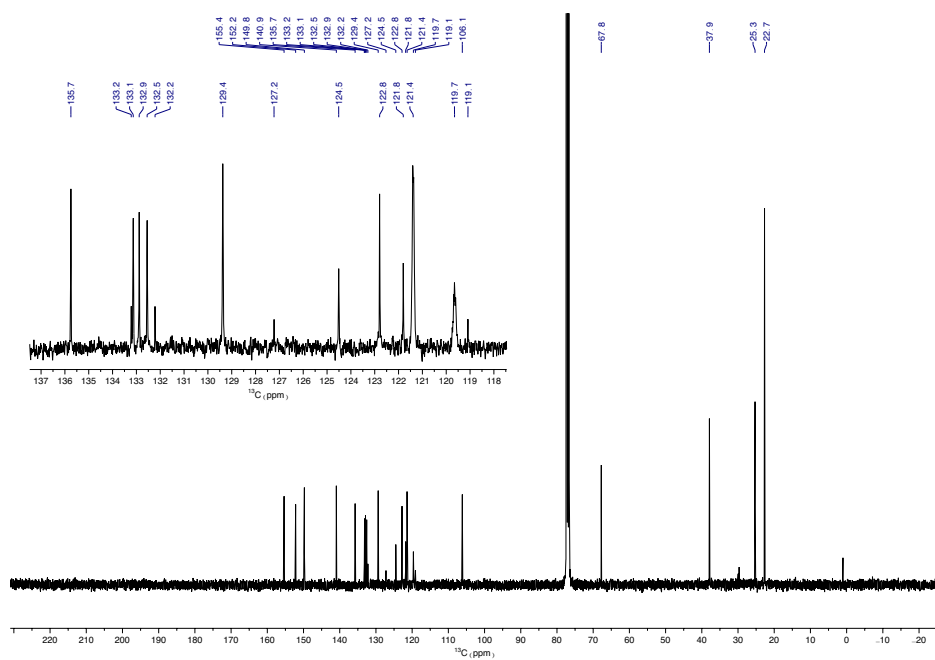
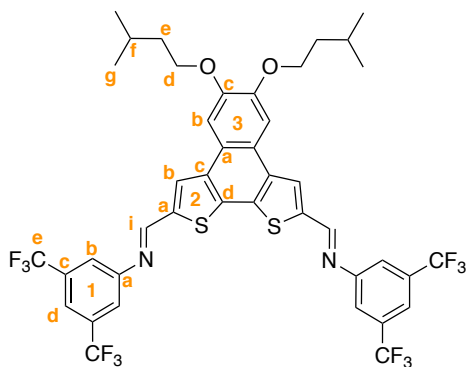


Figure B 55. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **1dd**₂ (CDCl_3 , 400 MHz, 298 K)



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	152.2
1b	7.71	121.4 (d, J = 3.6 Hz)
1c	-	132.9 (q, 33.6 Hz)
1d	7.77	119.7 (t, J = 3.8 Hz)
1e	-	122.4 (q, J = 273.2 Hz)
i	8.80	155.4
2a	-	140.9
2b	8.30	129.4
2c	-	135.7
2d	-	133.1
3a	-	122.8
3b	7.61	106.1
3c	-	149.8
3d	4.23	67.8
3e	1.84	37.9
3f	1.94	25.3
3g	1.04	22.7

Figure B 56. 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-ditrifluoromethylphenyl)methaniminyl)naphtho[2,1-*b*:3,4-*b'*]dithiophene **α (1dd) $_2$** with assignment of ^1H and ^{13}C resonances.

3.4.3 Comparison of remote ^{13}C chemical shifts

The chemical shifts of interior 2b ^1H and ^{13}C shift upfield for electron donating groups and downfield for electron withdrawing substituents. The Hammett parameters (σ) for both *para* and *meta* can be contrasted against these 2b resonances.

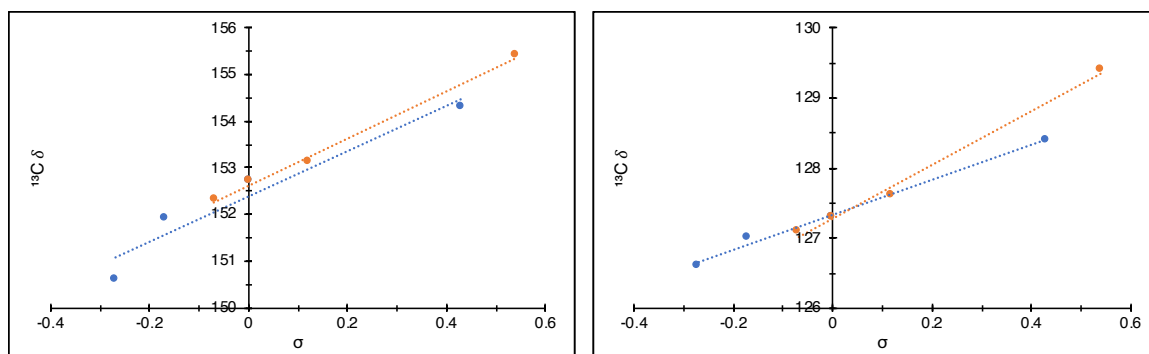


Figure B 57. Left: Plot of i ^{13}C resonances vs σ_p (blue, $R^2 = 0.94$) and σ_m (orange, $R^2 = 0.99$). Right: Plot of 2b ^{13}C resonances vs σ_p (blue, $R^2 = 0.99$) and σ_m (orange, $R^2 = 0.99$).

3.5 Gel Permeation Chromatography (GPC) Traces for **a(1)₂** Series

Purification of all di-imine products was accomplished with a Shimadzu Nexera Gel Permeation Chromatography (GPC) equipped with a Shodex organic size exclusion column (100 Å styrogel stationary phase, viable molecular weight range of 400–6000 g/mol) and a toluene mobile phase (flow rate 5 mL/min). The highlight region in the below chromatograms represents the target compounds. While this method removes any non-toluene soluble components, the chromatograms demonstrate good conversion to the di-imine species with only trace mono-coupled byproducts. The exceptions to these findings are the electron deficient amine end-caps, **1d** and **1dd**, which have elevated levels of partial coupling byproduct.

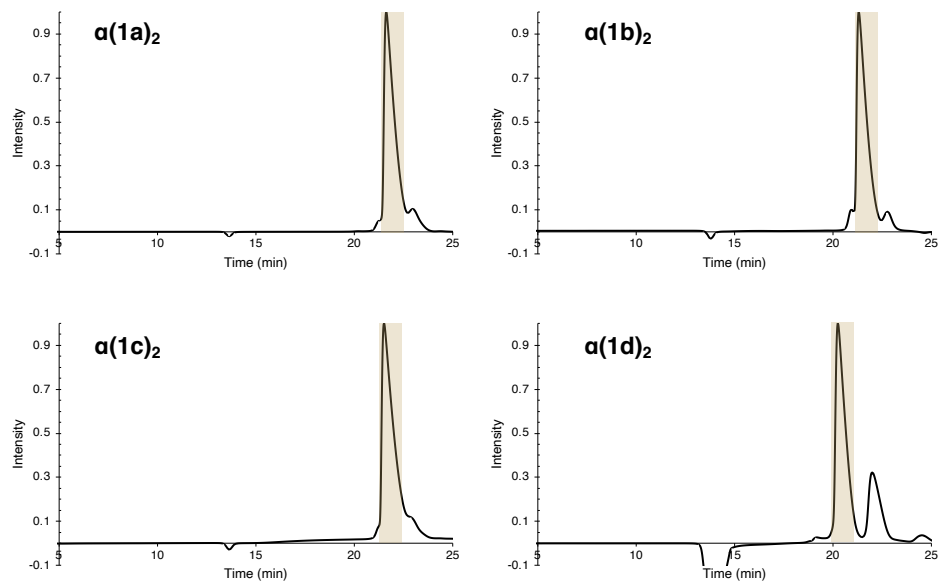


Figure B 58. GPC traces of crude reaction mixtures for $\alpha(1a-d)_2$ series. Each trace shown corresponds to the preferred condensation conditions given in section 1. Highlighted region is the peak of interest.

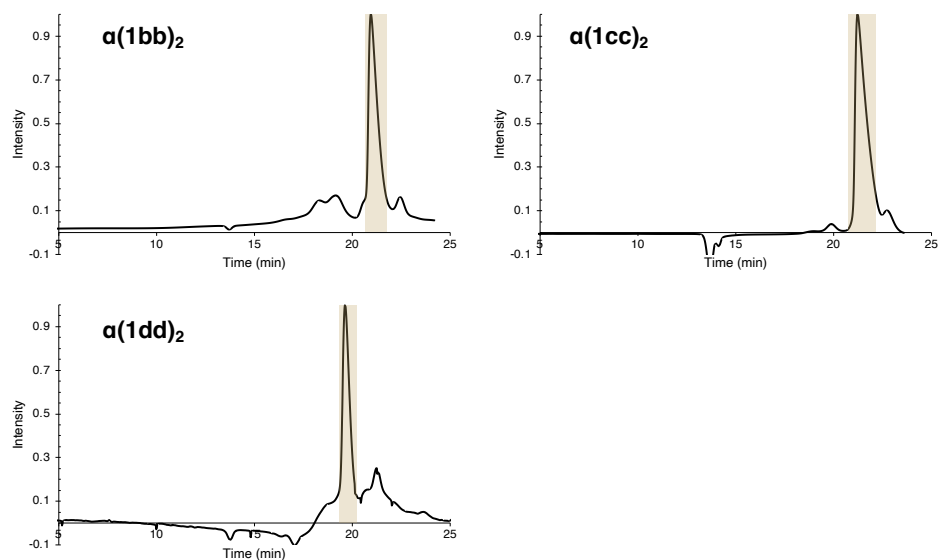


Figure B 59. GPC traces of crude reaction mixtures for $\alpha(1bb-dd)_2$ series. Each trace shown corresponds to the preferred condensation conditions given in section 1. Highlighted region is the peak of interest.

3.6 Photophysical Properties **$\alpha(1)_2$** Series

Absorbance spectra were collected on an Agilent Cary Bio100 spectrophotometer and corrected for solvent background absorbance and instrument drift. Emission spectra were recorded on a Horiba Jon-Yvon Fluorolog-3 with excitation and emission slit widths set at 2 nm. **$\alpha(1a-d)_2$** and **$\alpha(1bb-dd)_2$** , were prepared with degassed, dry, solvents and degassed prior to sealing in 1 cm path length quartz cuvettes. Emission spectra were analyzed at $\lambda_{ex} = 365$ nm. Fluorescence quantum yields were determined for select compounds – **$\alpha(1c)_2$** and **$\alpha(1cc)_2$** – by reference to 9,10-diphenylanthracene in cyclohexane ($\phi = 0.91$) which was cross-checked with quinine bisulfate in 0.5 M H₂SO₄ (aq) ($\phi = 0.54$). Five solutions of varying concentration were prepared for each sample and good fits ($R^2 \geq 0.99$) were obtained in all cases. The absorbance of all sample solutions was kept below 0.10 to avoid the inner-filter effect. Measurements were performed at room temperature with both sample and standard excited at the same wavelength (365 nm).¹ All quantum yields obtained were below 1%, with fits for the remainder of the derivatives proving to be of low quality. Plots are given below with UV-visible spectra as solid lines and emission spectra as dashed lines. UV-visible spectra are plotted as either molar absorptivity or normalized absorption (left vertical axis) vs wavelength (horizontal axis). Emission spectra are plotted as normalized intensities (right vertical axis) vs wavelength (horizontal axis).

3.6.1 *p*-Aryl Series: $\alpha(1a)_2$ vs $\alpha(1b-d)_2$

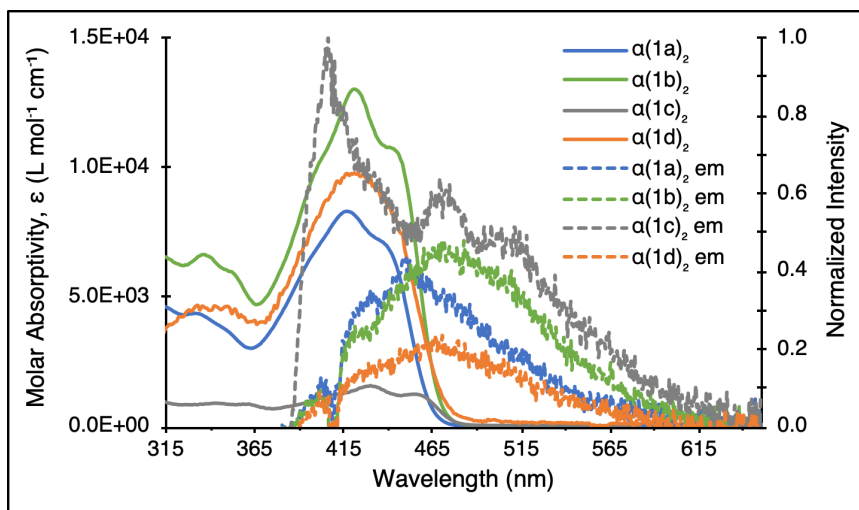


Figure B 60. Absorbance and emission spectra for $\alpha(1a)_2$ and $\alpha(1b-d)_2$ in toluene.

3.6.2 *m*-Aryl Series: $\alpha(1a)_2$ vs $\alpha(1bb-dd)_2$

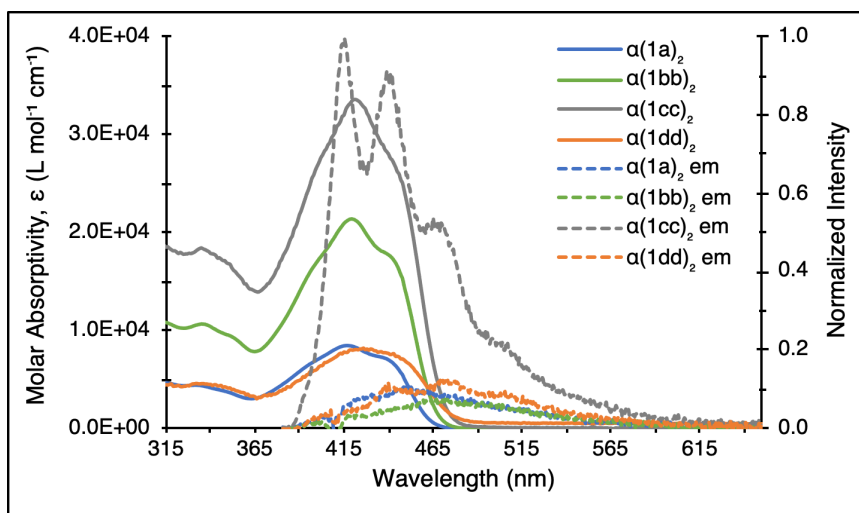


Figure B 61. Absorbance and emission spectra for $\alpha(1a)_2$ and $\alpha(1bb-dd)_2$ in toluene.

3.7 Computational Analysis

For the computational analysis, we modeled the seven di-imine derivatives with methoxy solubilizing groups in place of the isopentoxy groups employed in the experimental work, with the abbreviation for the model compounds being $\alpha(l)_2$. Due to the close proximity of the imine nitrogens to the σ -hole of the interior thiophenes sulfur atoms the formation of attractive non-covalent interactions is plausible (i.e. the cis-effect is likely to be a factor). With that in mind we carried out computations in Gaussian 16, utilizing the ω B97-XD functional with a cc-pVDZ basis set to accommodate the variety of light atoms employed in this work and account for the likelihood of dispersion interactions, to perform geometry optimizations and frequency calculations on the $\alpha(1)_2$ series.⁴ Cartesian coordinates for all output geometries have been included as a separate .txt file for ease.

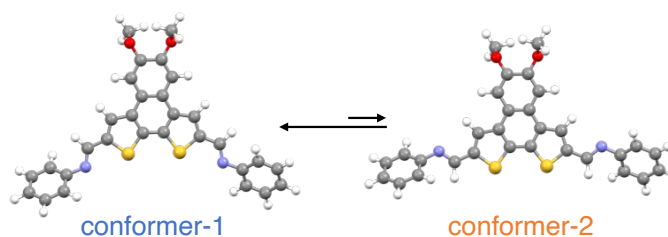


Figure B 62. Ball-and-stick representations for optimized conformers of $\alpha(1a)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S- c} (kcal mol ⁻¹)
$\alpha(1a)_2$ - Conformer 1	-2212.36980437	0.447909	-2211.921895	0.00	0	0.94
$\alpha(1a)_2$ - Conformer 2	-2212.36519223	0.447855	-2211.917337	+2.86	0	–

Table B 2. Computational data for optimized $\alpha(1a)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.

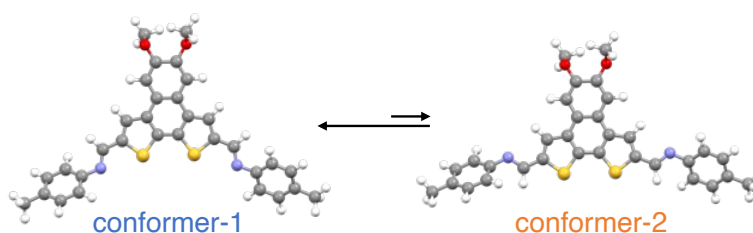


Figure B 63. Ball-and-stick representations for optimized conformers of $\alpha(1b)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S- c} (kcal mol ⁻¹)
$\alpha(1b)_2$ - Conformer 1	-2290.9848472	0.502267	-2290.48258	0.00	0	0.95
$\alpha(1b)_2$ - Conformer 2	-2290.98022711	0.502186	-2290.478041	+2.84	0	–

Table B 3. Computational data for optimized $\alpha(1b)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.

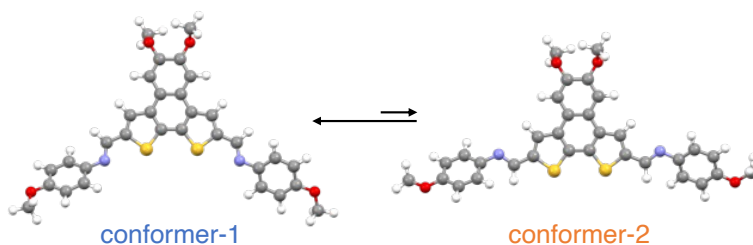


Figure B 64. Ball-and-stick representations for optimized conformers of $\alpha(1c)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S} ^c (kcal mol ⁻¹)
<i>α(1c)₂ - Conformer 1</i>	-2441.35850602	0.513194	-2440.845312	0.00	0	0.99
<i>α(1c)₂ - Conformer 2</i>	-2441.35373844	0.513132	-2440.840606	+2.95	0	–

Table B 4. Computational data for optimized $\alpha(1c)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.

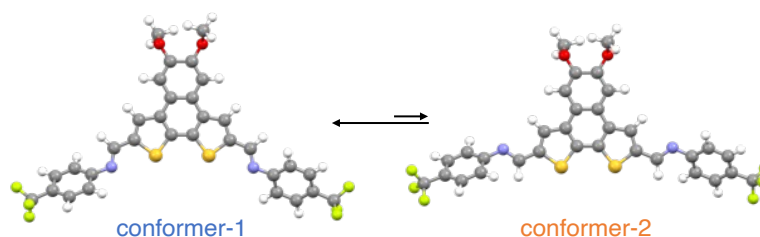


Figure B 65. Ball-and-stick representations for optimized conformers of $\alpha(1d)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S} ^c (kcal mol ⁻¹)
<i>α(1d)₂ - Conformer 1</i>	-2886.32153091	0.457726	-2885.863805	0.00	0	0.90
<i>α(1d)₂ - Conformer 2</i>	-2886.31687113	0.457661	-2885.85921	+2.88	0	–

Table B 5. Computational data for optimized $\alpha(1d)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.

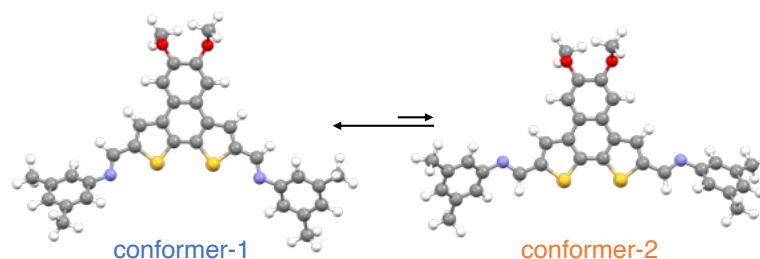


Figure B 66. Ball-and-stick representations for optimized conformers of $\alpha(1bb)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy ^{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S- C} (kcal mol ⁻¹)
<i>α(1bb)₂ – Conformer 1</i>	-2369.60097548	0.556987	-2369.043988	0.00	0	0.94
<i>α(1bb)₂ – Conformer 2</i>	-2369.59643228	0.556775	-2369.039657	+2.72	0	–

Table B 6. Computational data for optimized $\alpha(1bb)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.

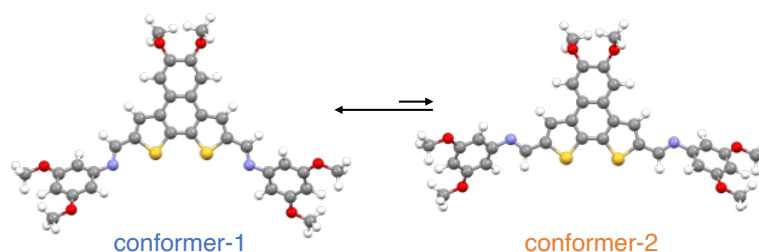


Figure B 67. Ball-and-stick representations for optimized conformers of $\alpha(1cc)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy ^{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S- C} (kcal mol ⁻¹)
<i>α(1cc)₂ – Conformer 1</i>	-2670.3487298	0.578006	-2669.770724	0.00	0	0.94
<i>α(1cc)₂ – Conformer 2</i>	-2670.34426905	0.578046	-2669.766223	+2.82	0	–

Table B 7. Computational data for optimized $\alpha(1cc)_2$ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.

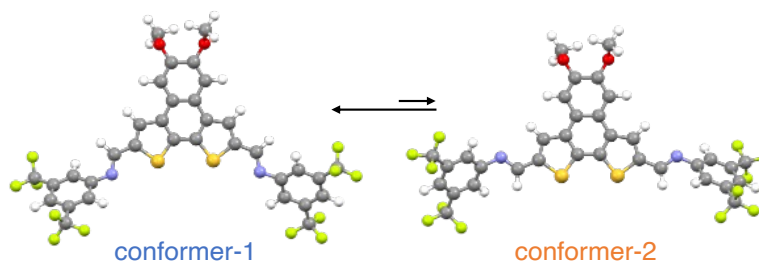


Figure B 68. Ball-and-stick representations for optimized conformers of $\alpha(1dd)_2$.

Model Compound	Total Energy (E _h)	ZPC ^a (E _h)	Energy ^b Total Energy + ZPC (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S} ^c (kcal mol ⁻¹)
<i>α</i> (1 <i>dd</i>) ₂ - Conformer 1	-3560.26816949	0.467056	-3559.801113	0.00	0	0.87
<i>α</i> (1 <i>dd</i>) ₂ - Conformer 2	-3560.26344817	0.467127	-3559.796321	+3.01	0	–

Table B 8. Computational data for optimized *α*(1*dd*)₂ models. ZPC = zero-point correction, IF = number of imaginary frequencies, Rel. Energy = relative energetic difference between conformer-1 vs conformer-2.

3.7.1 Experimental vs Calculated Chemical Shift Analysis

The optimized structures were then used to calculate the ¹H and ¹³C NMR spectra using the GIAO method with implicit solvent (CHCl₃). The isotropic shieldings for the model compounds with the alkoxy groups simplified to methoxy groups were computed for both protons and carbons using the GIAO method with the cc-pVDZ basis set and ωB97-XD functional in Gaussian 16 with implicit solvent (CHCl₃). The experimental chemical shifts (ppm) were extracted from ¹H–¹³C HSQC.

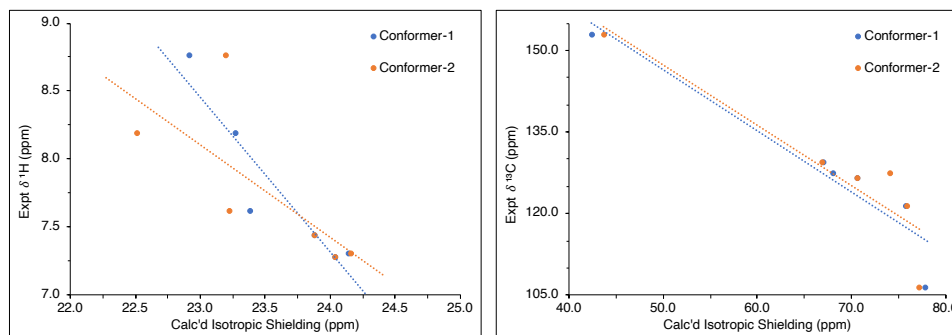


Figure B 69. Comparison of experimental vs calculated ¹H (left) and ¹³C (right) resonances (δ) for *α*(1*a*)₂ (experimental) and *α*(1*a*)₂ (calculated). Conformer 1 is given in blue (¹H R² = 0.87; ¹³C R² = 0.90) and Conformer 2 is represented in orange (¹H R² = 0.53; ¹³C R² = 0.85).

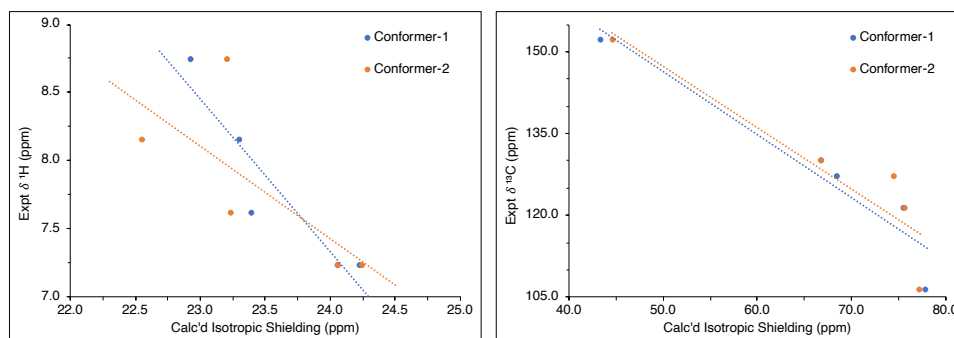


Figure B 70. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $a(1b)_2$ (experimental) and $a(1b)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.87$; ^{13}C $R^2 = 0.91$) and Conformer 2 is represented in orange (^1H $R^2 = 0.52$; ^{13}C $R^2 = 0.84$).

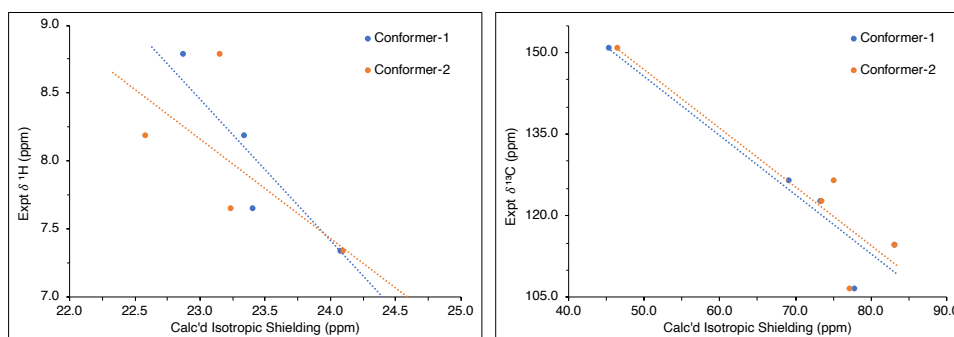


Figure B 71. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $a(1c)_2$ (experimental) and $a(1c)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.90$; ^{13}C $R^2 = 0.90$) and Conformer 2 is represented in orange (^1H $R^2 = 0.64$; ^{13}C $R^2 = 0.84$).

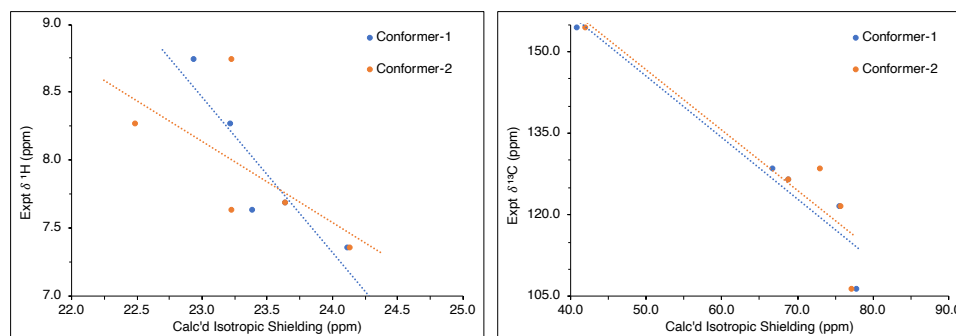


Figure B 72. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $a(1d)_2$ (experimental) and $a(1d)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.82$; ^{13}C $R^2 = 0.92$) and Conformer 2 is represented in orange (^1H $R^2 = 0.41$; ^{13}C $R^2 = 0.86$).

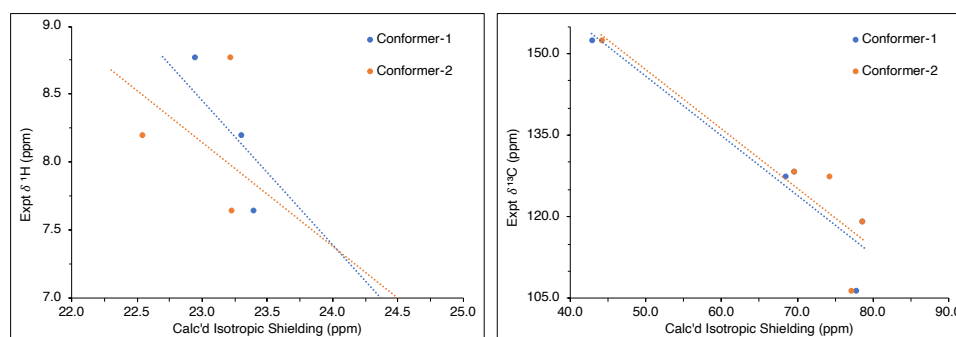


Figure B 73. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $a(1bb)_2$ (experimental) and $a(1bb)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.91$; ^{13}C $R^2 = 0.89$) and Conformer 2 is represented in orange (^1H $R^2 = 0.67$; ^{13}C $R^2 = 0.84$).

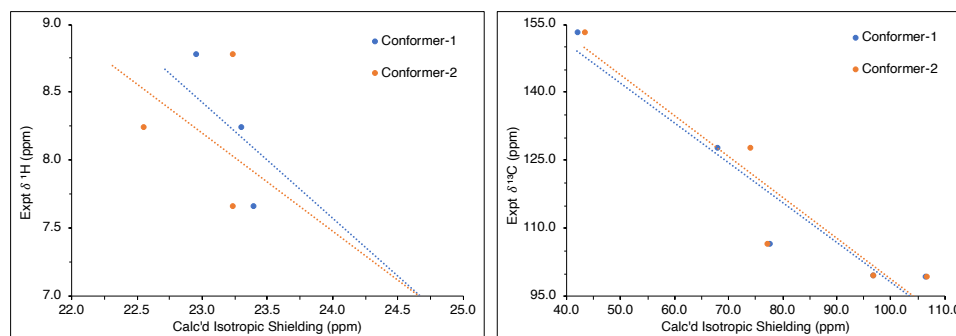


Figure B 74. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $a(1cc)_2$ (experimental) and $a(1cc)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.93$; ^{13}C $R^2 = 0.91$) and Conformer 2 is represented in orange (^1H $R^2 = 0.82$; ^{13}C $R^2 = 0.88$).

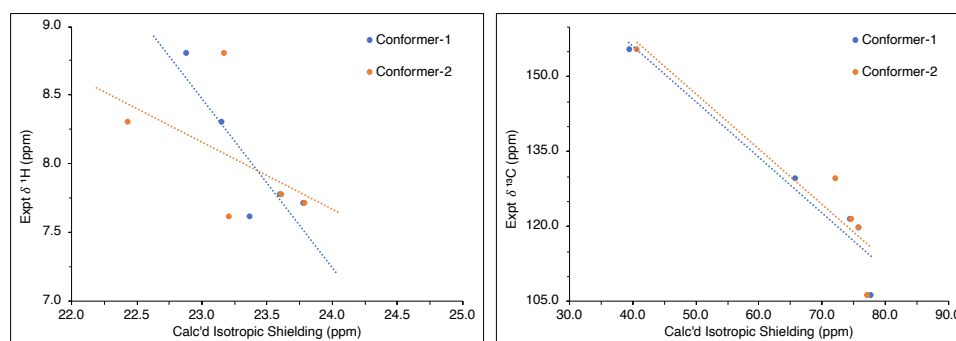


Figure B 75. Comparison of experimental vs calculated ^1H (left) and ^{13}C (right) resonances (δ) for $a(1dd)_2$ (experimental) and $a(1dd)_2$ (calculated). Conformer 1 is given in blue (^1H $R^2 = 0.76$; ^{13}C $R^2 = 0.93$) and Conformer 2 is represented in orange (^1H $R^2 = 0.25$; ^{13}C $R^2 = 0.87$).

3.8 Crystallographic Analysis

Crystallographic analysis and data for **a(1b)₂**, **a(1c)₂**, **a(1d)₂**, **a(1cc)₂**, and **a(1a)(CHO)** are presented below. Data for **a(1b)₂**, **a(1c)₂**, **a(1d)₂**, and **a(1a)(CHO)** were collected from a single crystal at 150(2) K on a Bruker AXS D8 Quest four circle diffractometer with an I-mu-S 3.0 microsource X-ray tube using a HELIOS multilayer Montel optics as monochromator and a PhotonIII_C14 charge-integrating and photon counting pixel array detector. The diffractometer used $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$).

Data for **a(1cc)₂** were collected from a single crystal at 150(2) K on a Bruker AXS D8 Quest three circle diffractometer with a fine focus sealed tube X-ray source using a Triumph curved graphite crystal as monochromator and a PhotonII charge-integrating pixel array (CPAD) detector. The diffractometer used MoK α radiation ($\lambda = 0.71073$ Å). All data were integrated with SAINT V8.40B and a multi-scan absorption correction using SADABS 2016/2 was applied.^{5,6} The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/2.^{7,8} All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. Tables and general reports were generated with FinalCif and edited accordingly.⁹ Any additional refinement notes are detailed below, all structures have been deposited in the Cambridge Crystallographic Data Centre (CCDC)¹⁰ with their deposition numbers given (2477200–2477204).

3.8.1 a(1b)₂

Single crystals of **a(1b)₂** were obtained through vapor diffusion of petroleum ether into a saturated solution of **a(1b)₂** in THF (Figure B 76). The two alkyl substituents were disordered over the two orientations and were restrained to have similar geometries. U_{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.390(19) to 0.610(19) and to 0.709(4) to 0.291(4). The structure contains 191 Å³ of solvent accessible pore areas. Due to the disorder of the solvate molecules (major

components of petroleum ether are pentane, isopentane, 3-methylpentane and *n*-hexane) the structure factors were instead augmented via reverse Fourier transform methods using the SQUEEZE routine¹¹ as implemented in the program Platon. The resultant FAB file containing the structure factor contribution from the electron content of the void space was used in together with the original hkl file in the further refinement. (The FAB file with details of the Squeeze results is appended to the cif file). The Squeeze procedure corrected for 74 electrons within the solvent accessible voids. CCDC number: 2477202

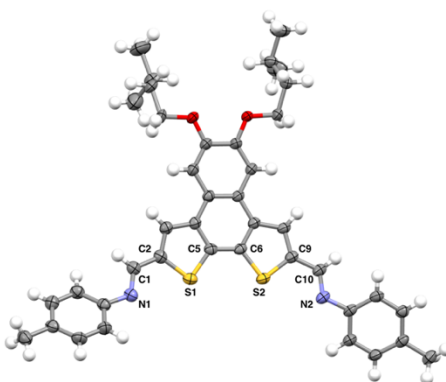


Figure B 76. ORTEP diagram of **a(1b)₂** (ellipsoids drawn at 50% probability). Select bond lengths (Å), distances (Å), and angles (°): N1⋯S1, 3.045(2); N2⋯S2, 2.959(2); C5–S1⋯N1, 141.69(6); C9–S2⋯N2, 143.63(6); N1–C1–C2–S1, 1.0(2); N2–C10–C9–S2, 0.2(2).

	a(1b)₂
Empirical formula	C ₄₀ H ₄₂ N ₂ O ₂ S ₂
Formula weight	646.87
Temperature [K]	150(2)
Crystal system	triclinic
Space group (number)	$\overline{P}1$ (2)
<i>a</i> [Å]	5.1111(2)
<i>b</i> [Å]	17.6434(5)
<i>c</i> [Å]	21.0008(7)
α [°]	87.960(2)
β [°]	83.543(2)
γ [°]	83.451(2)

Volume [$\text{\AA}^3$]	1869.00(11)
<i>Z</i>	2
ρ_{calc} [gcm^{-3}]	1.149
μ [mm^{-1}]	1.554
<i>F</i> (000)	688
Crystal size [mm^3]	0.040×0.050×0.660
Crystal color	yellow
Crystal shape	needle
Radiation	CuK α ($\lambda=1.54178 \text{ \AA}$)
2 θ range [$^\circ$]	4.24 to 160.11 (0.78 $\text{\AA}$)
Index ranges	$-6 \leq h \leq 5$ $-22 \leq k \leq 22$ $-26 \leq l \leq 26$
Reflections collected	34435
Independent reflections	7954 $R_{\text{int}} = 0.0535$ $R_{\text{sigma}} = 0.0424$
Completeness to $\theta = 25.242^\circ$	99.9 %
Data / Restraints / Parameters	7954 / 366 / 535
Absorption correction $T_{\text{min}}/T_{\text{max}}$ (method)	0.5530 / 0.7543 (multi-scan)
Goodness-of-fit on F^2	1.077
Final <i>R</i> indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0441$ $wR_2 = 0.1189$
Final <i>R</i> indexes [all data]	$R_1 = 0.0531$ $wR_2 = 0.1235$
Largest peak/hole [$\text{e\AA}^{-3}$]	0.56/−0.22

Table B 9. Crystallographic data and structural refinement parameters, **a(1b)₂**.

3.8.2 **a(1c)₂**

Single crystals of **a(1c)₂** were obtained through vapor diffusion of petroleum ether into a saturated solution of **a(1c)₂** in THF (Figure B 77). The structure contains additional 943 $\text{\AA}^3$ of solvent accessible pores (~12% of the crystal volume). The residual electron density peaks are not arranged in an interpretable pattern (the antisolvent used was petroleum ether and the content of the voids appears to consist of a highly disordered mixture of various low chain alkanes). The structure factors were instead augmented via reverse Fourier transform methods using the SQUEEZE routine¹¹ as implemented in the

program Platon. The resultant FAB file containing the structure factor contribution from the electron content of the void space was used in together with the original hkl file in the further refinement. (The FAB file with details of the Squeeze results is appended to the cif file). The Squeeze procedure corrected for 240 electrons within the solvent accessible pores. CCDC number: 2477203

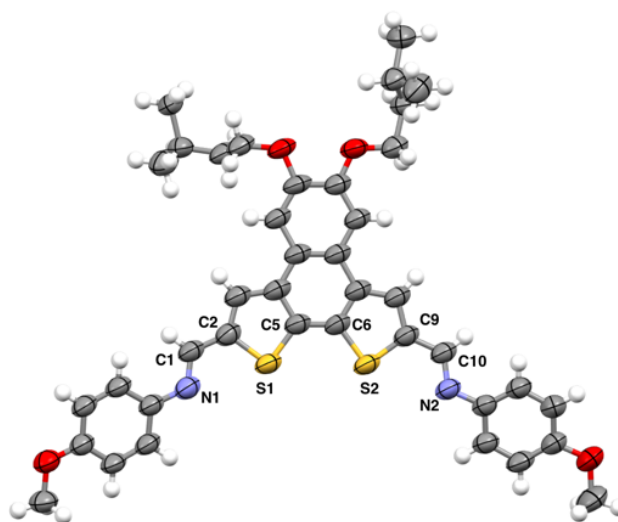


Figure B 77. ORTEP diagram of **a(1c)₂** (ellipsoids drawn at 50% probability). Select bond lengths (Å), distances (Å), and angles (°): N1⋯S1, 2.967(5); N2⋯S2, 2.991(4); C5–S1⋯N1, 143.5(2); C6–S2⋯N2, 142.9(2); N1–C1–C2–S1, 0.0(7); N2–C10–C9–S2, -5.1(7).

	a(1c)₂
Empirical formula	C ₄₀ H ₄₂ N ₂ O ₄ S ₂
Formula weight	678.87
Temperature [K]	150(2)
Crystal system	orthorhombic
Space group (number)	<i>Pbca</i> (61)
<i>a</i> [Å]	20.903(3)
<i>b</i> [Å]	8.026(2)
<i>c</i> [Å]	45.905(10)
α [°]	90
β [°]	90

γ [°]	90
Volume [Å ³]	7701(3)
<i>Z</i>	8
ρ_{calc} [gcm ⁻³]	1.171
μ [mm ⁻¹]	1.571
<i>F</i> (000)	2880
Crystal size [mm ³]	0.030×0.090×0.130
Crystal color	yellow
Crystal shape	needle
Radiation	CuK α (λ =1.54178 Å)
2 θ range [°]	5.72 to 159.97 (0.78 Å)
Index ranges	-26 ≤ <i>h</i> ≤ 19 -9 ≤ <i>k</i> ≤ 9 -57 ≤ <i>l</i> ≤ 57
Reflections collected	49479
Independent reflections	8204 <i>R</i> _{int} = 0.1764 <i>R</i> _{sigma} = 0.1533
Completeness to $\theta = 25.242^\circ$	99.9 %
Data / Restraints / Parameters	8204 / 0 / 440
Absorption correction T _{min} /T _{max} (method)	0.5426 / 0.7543 (multi-scan)
Goodness-of-fit on <i>F</i> ²	0.967
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0840 <i>wR</i> ₂ = 0.2305
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1489 <i>wR</i> ₂ = 0.2911
Largest peak/hole [eÅ ⁻³]	0.34/-0.34
Extinction coefficient	0.00090(16)

Table B 10. Crystallographic data and structural refinement parameters, **a(1c)₂**.

3.8.3 **a(1d)₂**

Single crystals of **a(1d)₂** were obtained through vapor diffusion of petroleum ether into a saturated solution of **a(1d)₂** in dichloromethane (Figure B 78). The structure was refined as a 2-component inversion twin. CCDC number: 2477200

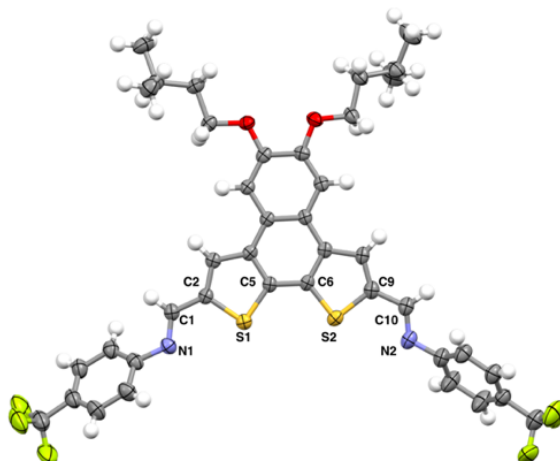


Figure B 78. ORTEP diagram of $\alpha(\mathbf{1d})_2$ (ellipsoids drawn at 50% probability). Select bond lengths (Å), distances (Å), and angles (°): N1 $\cdots$ S1, 2.993(7); N2 $\cdots$ S2, 2.898(6); C5–S1 $\cdots$ N1, 142.3(2); C9–S2 $\cdots$ N2, 144.7(2); N1–C1–C2–S1, 2.4(7); N2–C10–C9–S2, 7.4(7).

	$\alpha(\mathbf{1d})_2$
Empirical formula	C ₄₀ H ₃₆ F ₆ N ₂ O ₂ S ₂
Formula weight	754.83
Temperature [K]	150(2)
Crystal system	trigonal
Space group (number)	$P3_2$ (145)
<i>a</i> [Å]	17.665(2)
<i>b</i> [Å]	17.665(2)
<i>c</i> [Å]	10.1037(11)
α [°]	90
β [°]	90
γ [°]	120
Volume [Å ³]	2730.4(8)
<i>Z</i>	3
ρ_{calc} [gcm ^{−3}]	1.377
μ [mm ^{−1}]	1.923
<i>F</i> (000)	1176
Crystal size [mm ³]	0.030×0.040×0.230
Crystal color	yellow
Crystal shape	needle
Radiation	CuK α (λ =1.54178 Å)
2 θ range [°]	5.78 to 160.51 (0.78 Å)

Index ranges	$-20 \leq h \leq 22$ $-22 \leq k \leq 22$ $-12 \leq l \leq 9$
Reflections collected	22290
Independent reflections	6762 $R_{\text{int}} = 0.0587$ $R_{\text{sigma}} = 0.0638$
Completeness to $\theta = 25.242^\circ$	99.9 %
Data / Restraints / Parameters	6762 / 1 / 475
Absorption correction $T_{\text{min}}/T_{\text{max}}$ (method)	0.5206 / 0.7543 (multi-scan)
Goodness-of-fit on F^2	1.066
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0522$ $wR_2 = 0.1254$
Final R indexes [all data]	$R_1 = 0.0633$ $wR_2 = 0.1330$
Largest peak/hole [$\text{e}\text{\AA}^{-3}$]	0.37/−0.26
Extinction coefficient	0.0019(3)
Flack X parameter	0.49(3)

Table B 11. Crystallographic data and structural refinement parameters, **a(1d)**₂.

3.8.4 **a(1cc)**₂

Single crystals of **a(1cc)**₂ were obtained through vapor diffusion of petroleum ether into a saturated solution of **a(1cc)**₂ in THF (Figure S77). CCDC number: 2477204

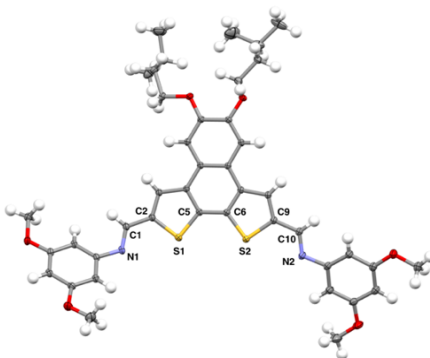


Figure B 79. ORTEP diagram of **a(1cc)**₂ (ellipsoids drawn at 50% probability). Select bond lengths (Å), distances (Å), and angles (°): N1⋯S1, 3.071(1); N2⋯S2, 3.030(1); C5–S1⋯N1, 140.12(4); C6–S2⋯N2, 142.44(4); N1–C1–C2–S1, 1.2(1); N2–C10–C9–S2, 1.3(1).

	$\alpha(1cc)_2$
Empirical formula	$C_{42}H_{46}N_2O_6S_2$
Formula weight	738.93
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	11.082(3)
b [Å]	36.517(9)
c [Å]	9.3470(16)
α [°]	90
β [°]	98.235(14)
γ [°]	90
Volume [Å ³]	3743.7(16)
Z	4
ρ_{calc} [gcm ⁻³]	1.311
μ [mm ⁻¹]	0.193
$F(000)$	1568
Crystal size [mm ³]	0.080×0.130×0.410
Crystal color	yellow
Crystal shape	plate
Radiation	MoK α ($\lambda=0.71073$ Å)
2 θ range [°]	4.46 to 66.30 (0.65 Å)
Index ranges	$-17 \leq h \leq 16$ $-49 \leq k \leq 56$ $-14 \leq l \leq 9$
Reflections collected	65863
Independent reflections	13970 $R_{\text{int}} = 0.0344$ $R_{\text{sigma}} = 0.0248$
Completeness to $\theta = 25.242^\circ$	99.9 %
Data / Restraints / Parameters	13970 / 0 / 477
Absorption correction T _{min} /T _{max} (method)	0.6743 / 0.7465 (multi-scan)
Goodness-of-fit on F^2	1.029
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0352$ $wR_2 = 0.0954$
Final R indexes [all data]	$R_1 = 0.0459$ $wR_2 = 0.1007$
Largest peak/hole [eÅ ⁻³]	0.49/−0.23

Table B 12. Crystallographic data and structural refinement parameters, **$\alpha(1cc)_2$** .

3.8.5 Attempted crystallization of $\alpha(1a)_2$: partial hydrolysis to $\alpha(1a)(CHO)$

Single crystals of $\alpha(1a)(CHO)$ were obtained through vapor diffusion of petroleum ether into a saturated solution of $\alpha(1a)_2$ in chloroform (Figure S78). Over the course of two days crystals formed that were of the partially hydrolyzed $\alpha(1a)(CHO)$. The structure was refined as a 2-component inversion twin. CCDC number: 2477201

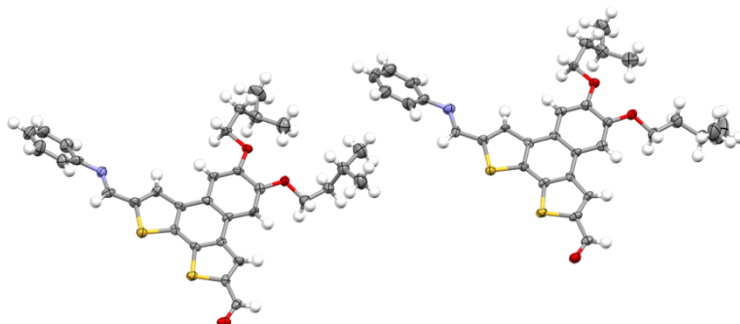


Figure B 80. ORTEP diagram of $\alpha(1a)(CHO)$ (ellipsoids drawn at 50% probability). Average select bond lengths (Å), distances (Å), and angles (°): S1 $\cdots$ O1, 3.028; C5–S1 $\cdots$ O1, 141.5; O1–C1–C2–S1, 0.0; S2–C9–C10–N1, 175.9.

	$\alpha(1a)(CHO)$
Empirical formula	C ₃₂ H ₃₃ NO ₃ S ₂
Formula weight	543.71
Temperature [K]	150(2)
Crystal system	monoclinic
Space group (number)	Pn (7)
<i>a</i> [Å]	5.0375(13)
<i>b</i> [Å]	37.547(7)
<i>c</i> [Å]	14.793(4)
α [°]	90
β [°]	95.803(14)
γ [°]	90
Volume [Å ³]	2783.7(11)
<i>Z</i>	4
ρ_{calc} [gcm ⁻³]	1.297
μ [mm ⁻¹]	2.001
<i>F</i> (000)	1152
Crystal size [mm ³]	0.001×0.050×0.080

Crystal color	green
Crystal shape	flake
Radiation	CuK α ($\lambda=1.54178$ Å)
2 θ range [°]	4.71 to 160.40 (0.78 Å)
Index ranges	$-5 \leq h \leq 5$ $-47 \leq k \leq 46$ $-14 \leq l \leq 18$
Reflections collected	20114
Independent reflections	8745 $R_{\text{int}} = 0.1225$ $R_{\text{sigma}} = 0.1758$
Completeness to $\theta = 25.242^\circ$	98.4 %
Data / Restraints / Parameters	8745 / 2 / 694
Absorption correction T _{min} /T _{max} (method)	0.5806 / 0.7543 (multi-scan)
Goodness-of-fit on F^2	0.981
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0711$ $wR_2 = 0.1430$
Final R indexes [all data]	$R_1 = 0.1700$ $wR_2 = 0.1841$
Largest peak/hole [eÅ ⁻³]	0.37/−0.35
Flack X parameter	0.10(3)

Table B 13. Crystallographic data and structural refinement parameters, **a(1a)(CHO)**.

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CHAPTER FOUR

4.0 Experimental Procedures

Unless otherwise noted, all starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Anhydrous solvents (dichloromethane, hexanes, tetrahydrofuran, toluene) were purified using an Inert PureSolv solvent purification system equipped with an alumina column. 4Å molecular sieves were activated via vacuum oven (150 °C, > 16 hours) overnight prior to use. Purification of all imine products was accomplished with a Shimadzu Nexera Gel Permeation Chromatography (GPC) equipped with a Shodex organic size exclusion column (100 Å styrogel stationary phase, viable molecular weight range of 400–6000 g/mol) and a toluene mobile phase (flow rate 5 mL/min). NMR spectra were measured on a Bruker Avance III 400 MHz spectrometer, with all samples referenced to the residual solvent signal. High resolution mass spectra were obtained by dissolving samples in acetonitrile and analyzed on a Shimadzu LCMS-9050 Q-TOF (ionization method: APCI+). Absorbance spectra were recorded on a Cary 100Bio spectrophotometer and corrected for solvent background absorbance. Emission spectra were recorded on a Horiba Jobin-Yvon Fluorolog-3 fluorometer. All spectra were recorded at room temperature using 1 cm path length quartz cuvettes with spectrometric grade solvents. Fluorescence quantum yield (ϕ) measurements were performed on solutions prepared at room temperature with dry, degassed solvents. Quantum yields were determined by reference to 9,10-diphenylanthracene in cyclohexane ($\phi = 0.91$) which was cross-checked with quinine bisulfate in 0.5 M H₂SO₄ (aq) ($\phi = 0.54$). Five solutions of varying concentration were prepared for each sample and good fits ($R^2 \geq 0.99$) were obtained in

all cases. The absorbance of all samples was kept below 0.10 to avoid the inner-filter effect, with all measurements of emission being recorded at 365 nm.¹ The procedure for 4,5-dibromo-1,2-di(isopentyloxy)benzene has been detailed elsewhere and was followed accordingly.² All procedures below were carried out multiple times with the yields given representing the median outcome of an experiment. Common solvent and reagent abbreviations: chloroform-*d* (CDCl₃), dichloromethane (DCM), ethyl acetate (EtOAc), tetrahydrofuran (THF), and *N*-bromosuccinimide (NBS).

4.1 Synthesis of Precursors and *a*(PhCF₃)(1) Series

4.1.1 Synthesis of precursors *a*(CHO), *a*(Br)(CHO), and *a*(PhCF₃)(CHO)

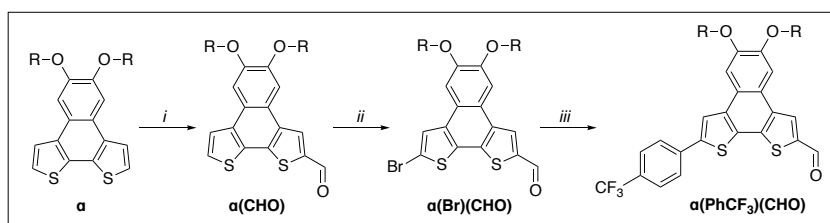


Figure C1. Synthetic path to *a*(PhCF₃)(CHO).

4.1.1.1 5,6-bis(isopentyloxy)-2-formylnaphtho[2,1-*b*:3,4-*b'*]dithiophene *a*(CHO)

A 100 mL Schlenk flask was massed with **a** (0.28 mmol), a stir bar, dry THF (20 mL) and sparged with argon for 15 minutes. The flask was cooled to -78 °C and allowed to equilibrate for 20 minutes. *n*-Butyllithium (0.42 mmol) was added dropwise to the reaction, and the reaction allowed to stir for 30 minutes. The dry ice bath was replaced with a 0 °C bath for 20 minutes. Degassed DMF (1.29 mmol) was added, and reaction allowed to stir under inert atmosphere of argon for 30 minutes. Reaction was cooled to RT, quenched with 5 mL dilute HCl solution, poured into H₂O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄,

decanted, and concentrated to yield crude product. Purification was achieved via silica gel flash column with Toluene:EtOAc (9:1) to afford **α (CHO)** as a yellow solid, 38.3 mg (32 %). ^1H NMR (400 MHz, CDCl_3) δ 10.08 (s, 1H), 8.40 (s, 1H), 7.82 (d, $J = 5.3$ Hz, 1H), 7.61 – 7.57 (m, 3H), 4.22 (t, $J = 6.6$ Hz, 4H), 2.03 – 1.91 (m, 2H), 1.91 – 1.78 (m, 4H), 1.09 – 0.96 (m, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 183.5, 149.5, 149.4, 140.3, 137.0, 135.9, 133.2, 132.2, 130.9, 129.8, 129.7, 128.8, 126.5, 122.9, 122.8, 122.7, 106.7, 106.1, 67.7, 38.0, 37.9, 25.3, 22.7

4.1.1.2 5,6-bis(isopentyloxy)-9-bromo-2-formylnaphtho[2,1-*b*:3,4-*b'*]dithiophene

α (CHO)Br

α (CHO) (0.46 mmol) was massed into a 250 mL round bottom flask and dissolved in CHCl_3 (20 mL). A stir bar was added, and the reaction was allowed to stir under argon for 5 minutes, after which NBS (0.69 mmol) was added in portions. Reaction was left to stir for 3 days and quenched in DI water (100 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried with anhydrous Na_2SO_4 , decanted, and concentrated to yield crude product as a pale-yellow solid. Purification via silica gel flash column with Toluene:EtOAc (99:1) as mobile phase afforded pure **α (CHO)Br** as an off-white solid, 126 mg (53 %): ^1H NMR (400 MHz, CDCl_3) δ 10.13 (s, 1H), 8.49 (s, 1H), 7.83 (s, 1H), 7.64 (s, 1H), 7.50 (s, 1H), 4.29 – 4.14 (m, 4H), 2.02 – 1.92 (m, 2H), 1.91 – 1.77 (m, 4H), 1.09 – 1.00 (m, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 183.5, 149.8, 149.7, 140.7, 136.8, 134.5, 133.3, 132.0, 130.7, 125.7, 123.2, 121.8, 115.2, 106.3, 105.9, 67.7, 67.7, 37.9, 37.9, 25.3, 22.7.

4.1.1.3 5,6-bis(isopentyloxy)-9-(4-trifluoromethylphenyl)-2-formylnaphtho[2,1-*b*:3,4-*b'*]dithiophene ***a*(PhCF₃)(CHO)**

A 100 mL Schlenk tube was charged with ***a*(CHO)Br** (0.27 mmol), 4-(Trifluoromethyl)phenylboronic acid (0.36 mmol), and Pd(PPh₃)₂Cl₂ (0.05 mmol), and a stir bar added. The reaction tube was then backfilled with argon (x3), after which dry THF (4 mL) and 0.60 mL degassed 2 M K₂CO₃ (165.85 mmol) were added under positive pressure of argon. The tube was sealed under argon, and the reaction was allowed to stir in an oil bath at 80 °C overnight. After overnight stirring the reaction tube was cooled to RT, poured into H₂O (25 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na₂SO₄, decanted, and concentrated to yield crude product. Purification via silica gel flash column with Toluene:EtOAc (9:1) mobile phase, with subsequent recrystallization from ethanol afforded ***a*(PhCF₃)(CHO)** as a yellowish solid, 39 mg (25 %): ¹H NMR (400 MHz, CDCl₃) δ 10.16 (s, 1H), 8.54 (s, 1H), 8.13 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.69 (s, 1H), 7.68 (s, 1H), 4.30 – 4.23 (m, 4H), 2.02 – 1.91 (m, 2H), 1.91 – 1.82 (m, 4H), 1.09 – 1.00 (m, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 183.5, 149.8, 149.7, 142.9, 140.9, 137.8, 137.2, 135.4, 133.8, 132.2, 129.9, 126.6, 126.2, 123.3, 122.7, 119.7, 106.6, 106.2, 67.8, 67.8, 38.0, 29.7, 25.3, 22.7; HRMS (APCI+) calcd for C₃₂H₃₂F₃O₃S₂ (M+H)⁺ 585.174498, found 585.174439

4.1.2 $\alpha(\text{PhCF}_3)(1)$ series

4.1.2.1 5,6-bis(isopentyloxy)-2-(*N*-(phenyl)methaniminyl)-9-(trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene (**1a**)

A 6-dram vial was massed with $\alpha(\text{CHO})\text{PhCF}_3$ (0.04 mmol), deacidified CHCl_3 (to 10 mM NDT), and 4 activated molecular sieves. Aniline (0.05 mmol), $\text{Sc}(\text{OTf})_3$ (0.01 mmol) and MeCN (5 % of CHCl_3), were successively added, the vial capped, swirled, and left undisturbed for overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved on an isocratic GPC with toluene (5 mL/min) to yield desired fraction further concentrated and dried on the high vac to yield the pure product as a greenish-yellowish solid, 7.5 mg (32 %): ^1H NMR (400 MHz, CDCl_3) δ 8.77 (s, 1H), 8.22 (s, 1H), 8.12 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.68 (s, 1H), 7.66 (s, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.26 (m, 1H), 4.26 (m, 4H), 1.97 (m, 2H), 1.86 (m, 4H), 1.05 (m, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.8, 151.1, 149.5, 149.4, 141.5, 140.9, 137.5, 136.3, 134.2, 132.5, 130.4, 129.3, 127.5, 126.4, 126.1, 126.0, 125.4, 123.0, 122.7, 121.1, 119.6, 106.6, 106.3, 67.8, 67.7, 38.0, 38.0, 29.7, 25.3, 22.7; HRMS (APCI+) calcd for $\text{C}_{38}\text{H}_{37}\text{F}_3\text{NO}_2\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 660.221782, found 660.222317

4.1.2.2 5,6-bis(isopentyloxy)-2-(*N*-(4-methylphenyl)methaniminyl)-9-(trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene (**1b**)

A 6-dram vial was massed with $\alpha(\text{CHO})\text{PhCF}_3$ (0.03 mmol), deacidified CHCl_3 (to 10 mM NDT), and 4 activated molecular sieves. *p*-Toluidine (0.03 mmol), $\text{Sc}(\text{OTf})_3$ (0.01 mmol) and MeCN (5 % of CHCl_3), were successively added, the vial capped,

swirled, and left undisturbed for overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved on an isocratic GPC with toluene (5mL/min) to yield desired fraction further concentrated and dried on the high vac to yield the pure product as a greenish-yellowish solid, 8.1 mg (46 %): ¹H NMR (400 MHz, CDCl₃) δ 8.78 (s, 1H), 8.22 (s, 1H), 8.14 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.69 (s, 1H), 7.67 (s, 1H), 7.23 (s, 4H), 4.27 (t, *J* = 7.0 Hz, 4H), 4.24 (t, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 2.03 – 1.90 (m, 2H), 1.89 – 1.82 (m, 4H), 1.08 – 1.01 (m, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 151.9, 149.5, 149.3, 148.5, 141.2, 136.4, 134.3, 132.3, 129.9, 127.1, 126.4, 126.0, 123.0, 122.7, 121.1, 119.7, 106.6, 106.3, 67.8, 67.7, 38.0, 25.3, 22.7, 21.1; HRMS (APCI⁺) calcd for C₃₉H₃₉F₃NO₂S₂ (M+H)⁺ 674.237432, found 674.238042

4.1.2.3 5,6-bis(isopentyloxy)-2-(*N*-(4-methoxyphenyl)methaniminyl)-9-(trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene (**1c**)

A 6-dram vial was massed with **a**(CHO)PhCF₃ (0.03 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4 activated molecular sieves. *p*-Anisidine (0.05 mmol), Sc(OTf)₃ (0.01 mmol) and MeCN (5 % of CHCl₃), were successively added, the vial capped, swirled, and left undisturbed for overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved on an isocratic GPC with toluene (5mL/min) to yield desired fraction further concentrated and dried on the high vac to yield the pure product as a greenish-yellowish solid, 10.5 mg (49 %): ¹H NMR (400 MHz, CDCl₃) δ 8.75 (d, *J* = 1.6 Hz, 1H), 8.13 (s, 1H), 8.08 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.65 (s, 1H), 7.62 (s, 1H), 7.32 (dd, *J* = 8.7, 1.5 Hz, 2H), 6.96 (d, *J* = 8.2 Hz,

2H), 4.25 (m, 4H), 3.86 (d, $J = 1.4$ Hz, 3H), 1.97 (m, 2H), 1.91 – 1.81 (m, 4H), 1.05 (m, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 150.6, 149.4, 149.3, 143.9, 141.3, 141.2, 137.5, 136.1, 134.3, 132.0, 130.4, 130.0, 129.7, 126.7, 126.3, 126.0, 126.0, 125.4, 122.9, 122.7, 122.6, 122.5, 119.6, 114.5, 106.5, 106.3, 67.8, 67.7, 55.5, 38.0, 38.0, 25.3, 25.3, 22.7; HRMS (APCI+) calcd for $\text{C}_{39}\text{H}_{39}\text{F}_3\text{NO}_3\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 690.232347, found 690.232581

4.1.2.4 5,6-bis(isopentyloxy)-2-(*N*-(3,5-dimethylphenyl)methaniminyl)-9-(trifluoromethylphenyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene (**1bb**)

A 6-dram vial was massed with **a(CHO)PhCF₃** (0.01 mmol), deacidified CHCl_3 (to 10 mM NDT), and 4 activated molecular sieves. 3,5-Dimethylaniline (0.018 mmol), $\text{Sc}(\text{OTf})_3$ (0.008 mmol) and MeCN (5 % of CHCl_3), were successively added, the vial capped, swirled, and left undisturbed for overnight (>16 hours). Reaction was transferred into a clean 100 mL RBF containing 1 mL Triethylamine to quench and concentrated to yield the crude product. Purification was achieved on an isocratic GPC with toluene (5mL/min) to yield desired fraction further concentrated and dried on the high vac to yield the pure product as a yellowish solid, mg (85 %): Full spectroscopic characterization is currently in progress and will be included prior to publication soon.

4.2 NMR Spectra

4.2.1 Precursors and $\alpha(\text{PhCF}_3)(\text{CHO})$

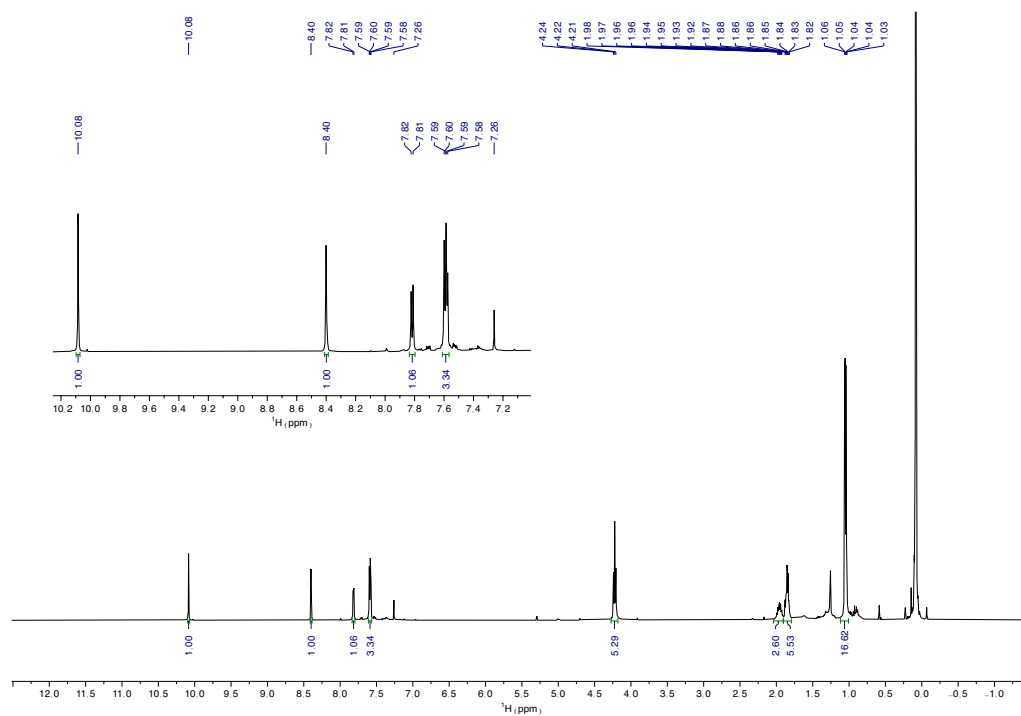


Figure C 2. ^1H NMR spectrum of $\alpha(\text{CHO})$ (CDCl_3 , 400 MHz, 298 K).

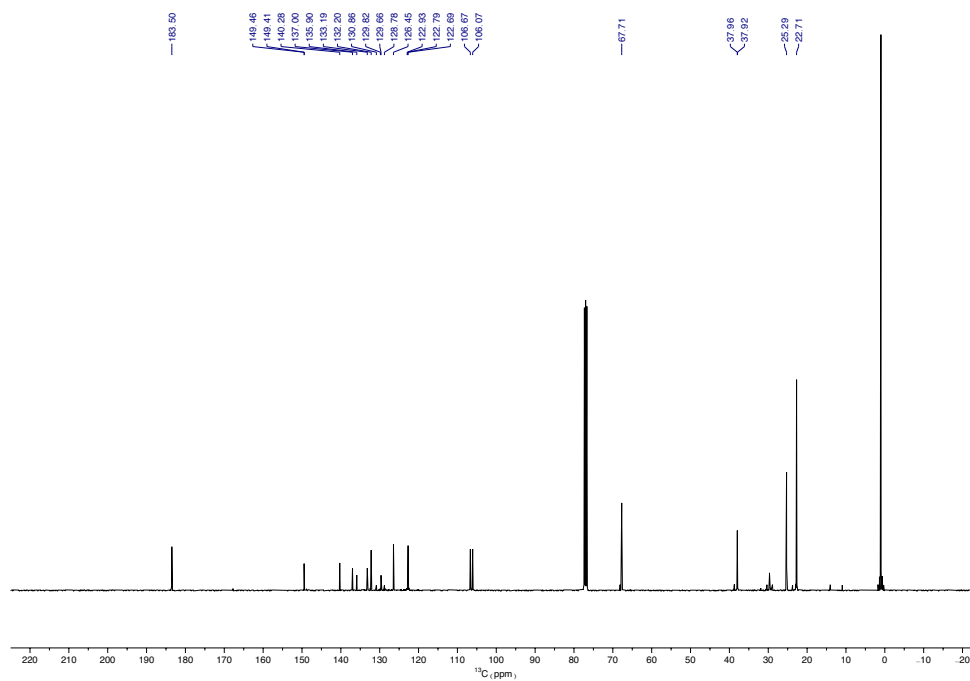


Figure C 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a(CHO)** (CDCl_3 , 400 MHz, 298 K).

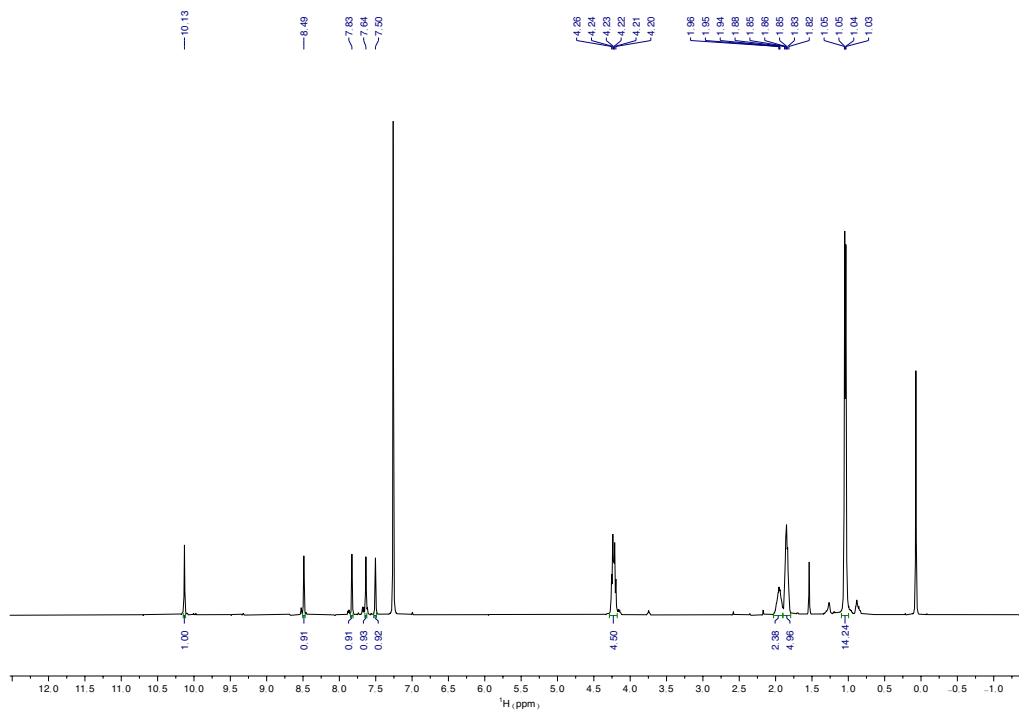


Figure C 4. ^1H NMR spectrum of **a(Br)(CHO)** (CDCl_3 , 400 MHz, 298 K).

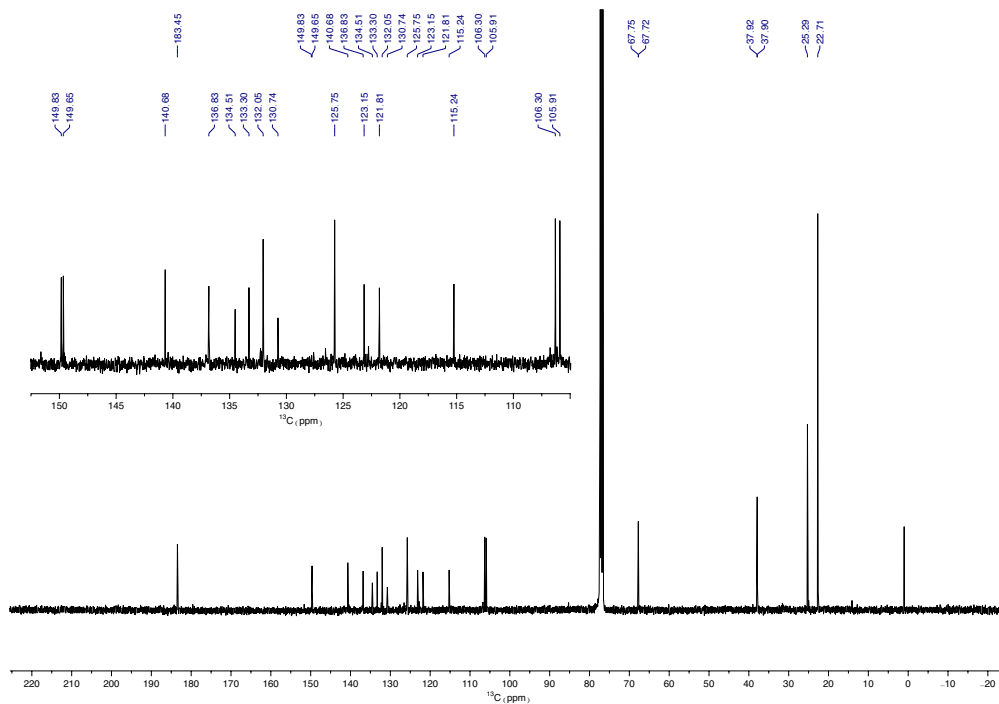


Figure C 5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a(Br)(CHO)** (CDCl_3 , 400 MHz, 298 K).

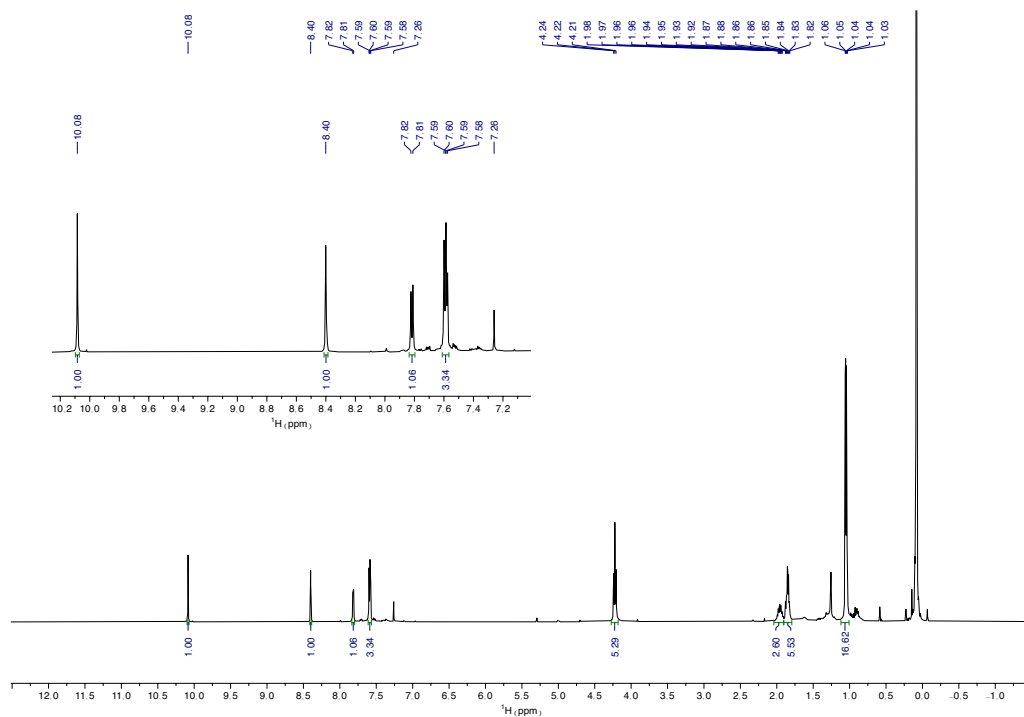


Figure C 6. ^1H NMR spectrum of **a(PhCF₃)(CHO)** (CDCl_3 , 400 MHz, 298 K).

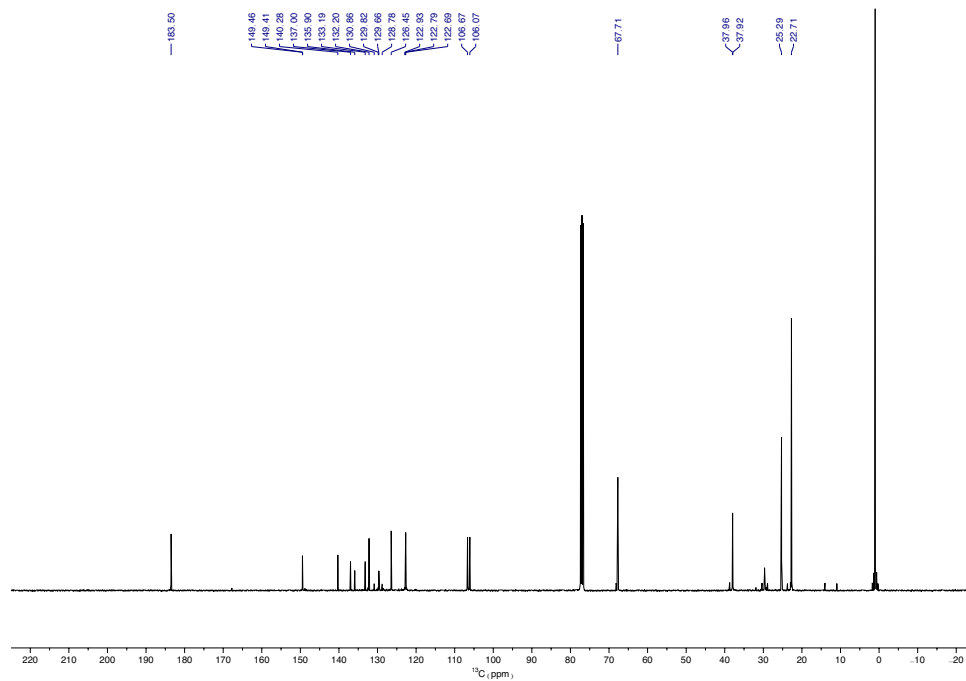


Figure C 7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\alpha(\text{PhCF}_3)(\text{CHO})$ (CDCl_3 , 400 MHz, 298 K).

4.2.2 $\alpha(\text{PhCF}_3)(1)$ Series

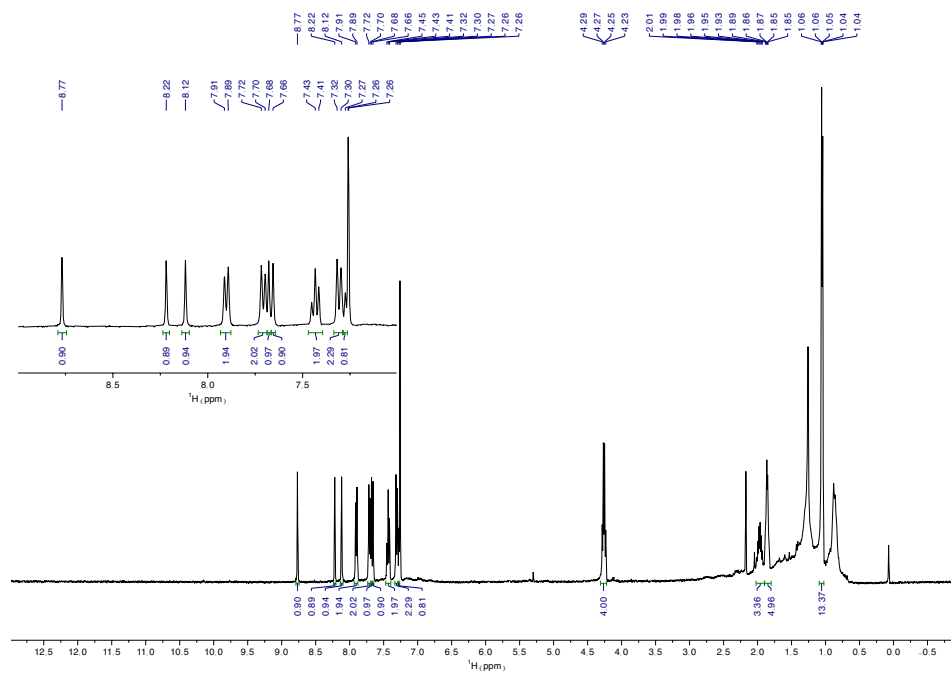


Figure C 8. ^1H NMR spectrum of $\alpha(\text{PhCF}_3)(1\text{a})$ (CDCl_3 , 400 MHz, 298 K).

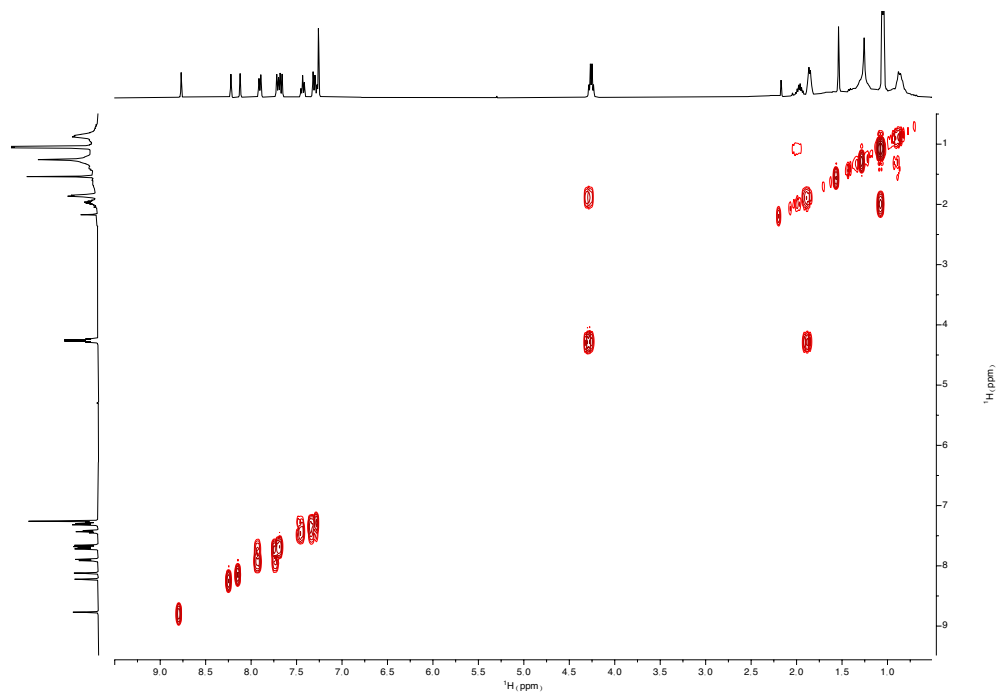


Figure C 9. ^1H - ^1H COSY spectrum of **a(PhCF₃)(1a)** (CDCl₃, 400 MHz, 298 K).

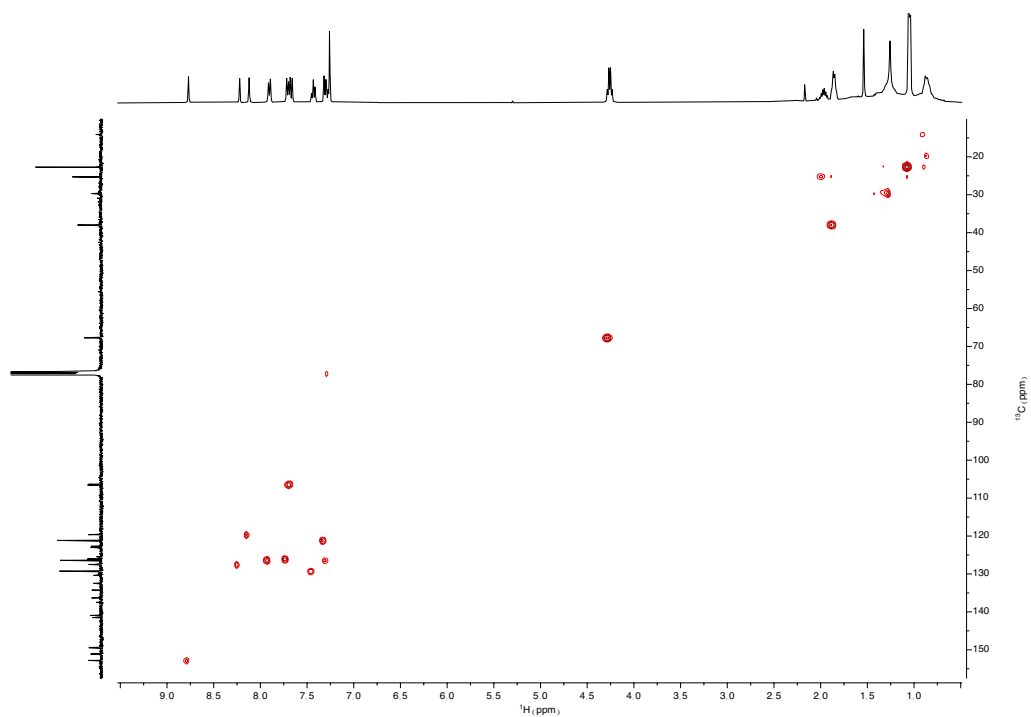


Figure C 10. ^1H - ^{13}C HSQC spectrum of **a(PhCF₃)(1a)** (CDCl₃, 400 MHz, 298 K).

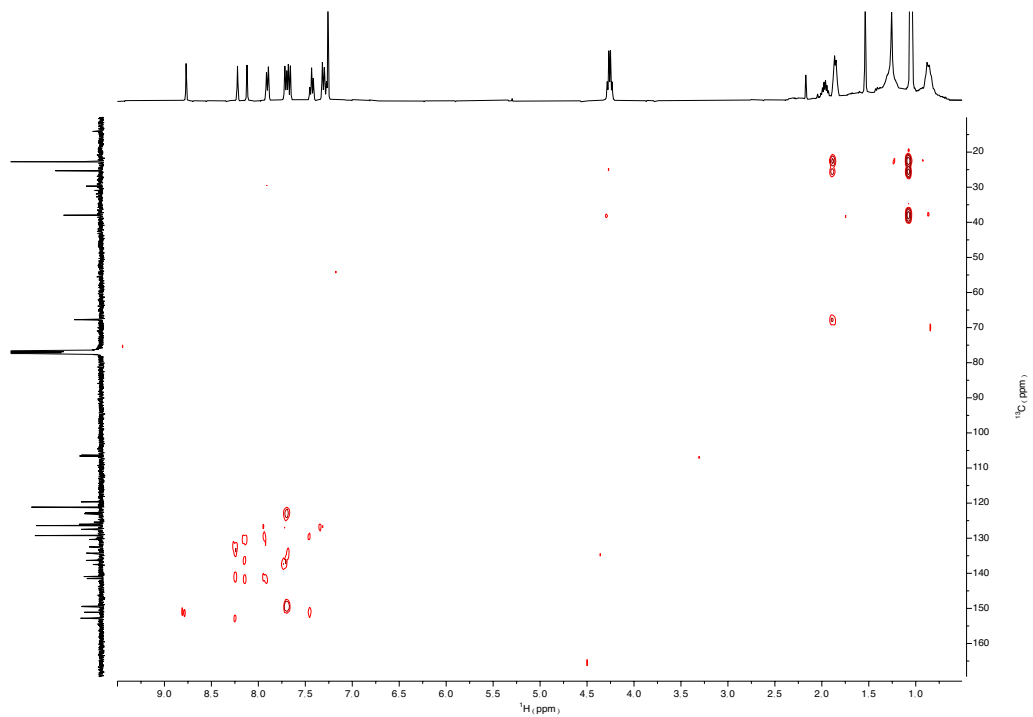


Figure C 11. ^1H - ^{13}C HMBC spectrum of **a(PhCF₃)(1a)** (CDCl_3 , 400 MHz, 298 K).

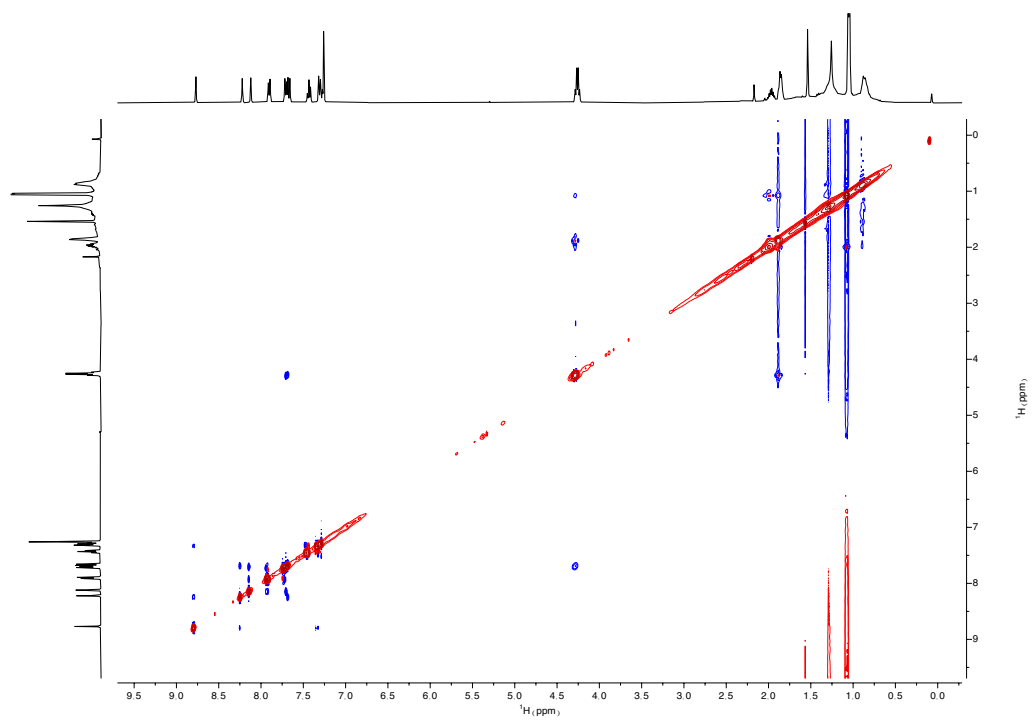


Figure C 12. ^1H - ^1H NOESY spectrum of **a(PhCF₃)(1a)** (CDCl_3 , 400 MHz, 298 K).

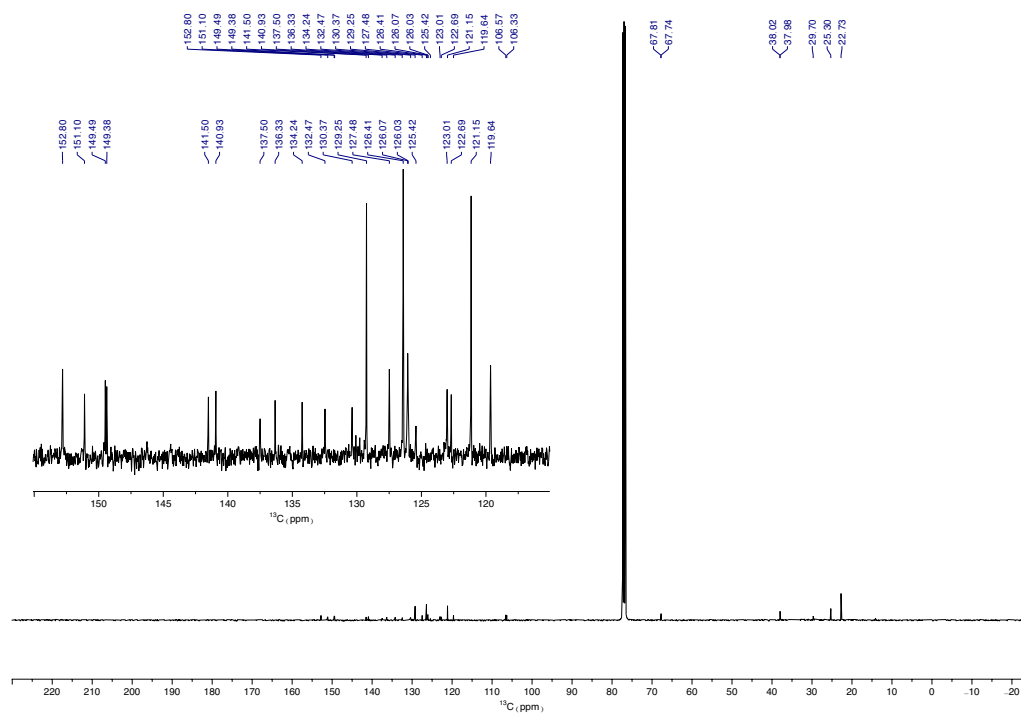
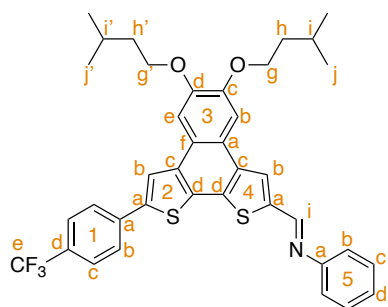


Figure C 13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a(PhCF₃)(1a)** (CDCl_3 , 400 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	137.5
1b	7.90	126.4
1c	7.71	126.1 (q, J = 4.0 Hz)
1d	-	129.9 ^a
1e	-	125.4 ^b
2a	-	141.5
2b	8.12	119.6
2c	-	134.2
2d	-	130.4
3a	-	123.0
3b	7.66	106.6 ^c
3c	-	149.5 ^c
3d	-	149.4 ^c
3e	7.68	106.3 ^c
3f	-	122.7
3g/g'	4.26	67.8/67.7
3h/h'	1.86	38.0/38.0
3i/i'	1.97	25.3
3j/j'	1.05	22.7
4a	-	140.9
4b	8.22	127.5
4c	-	136.3
4d	-	132.5
i	8.77	152.8
5a	-	151.1
5b	7.31	121.2
5c	7.43	129.3
5d	7.26	126.4

Figure C 14. **$\alpha(\text{PhCF}_3)(1\text{a})$** with assignment of ^1H and ^{13}C resonances.

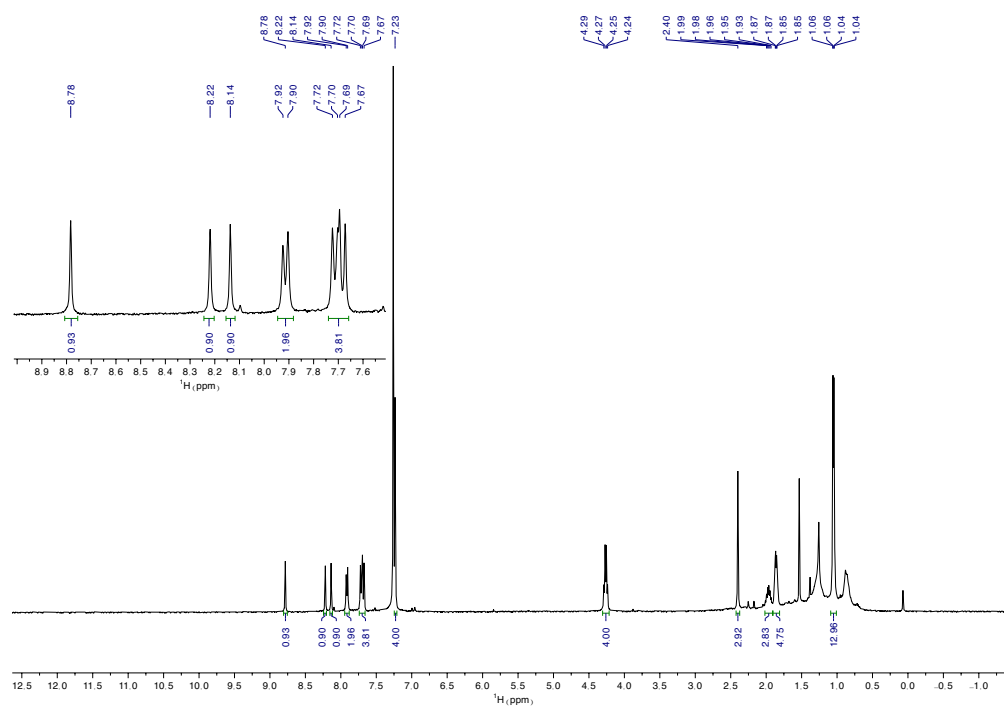


Figure C 15. ^1H NMR spectrum of $\alpha(\text{PhCF}_3)(\mathbf{1b})$ (CDCl_3 , 400 MHz, 298 K).

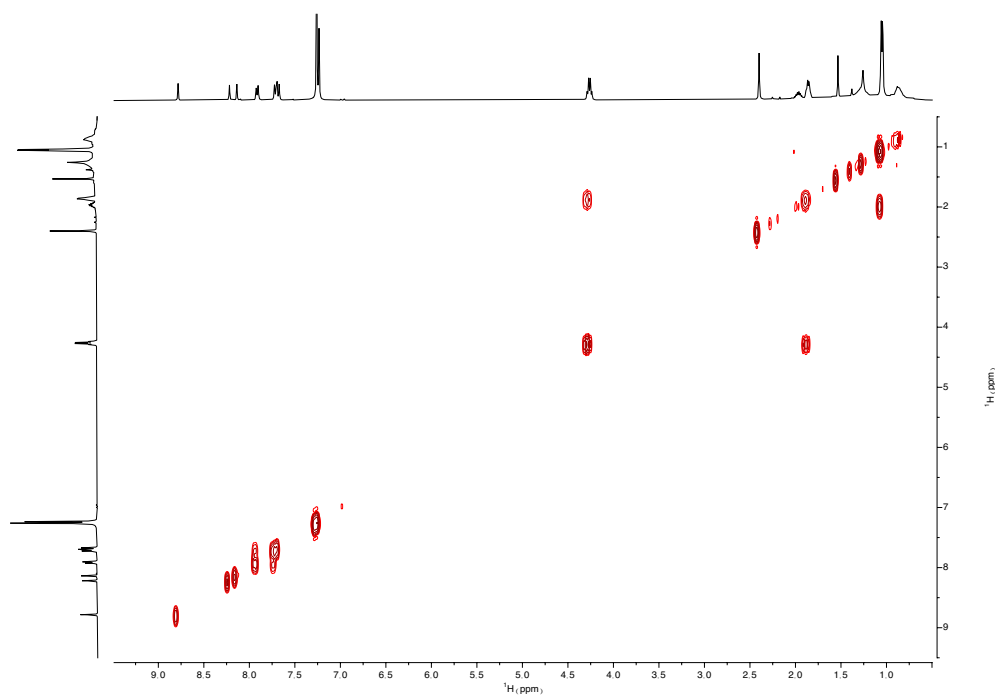


Figure C 16. ^1H - ^1H COSY spectrum of $\alpha(\text{PhCF}_3)(\mathbf{1b})$ (CDCl_3 , 400 MHz, 298 K).

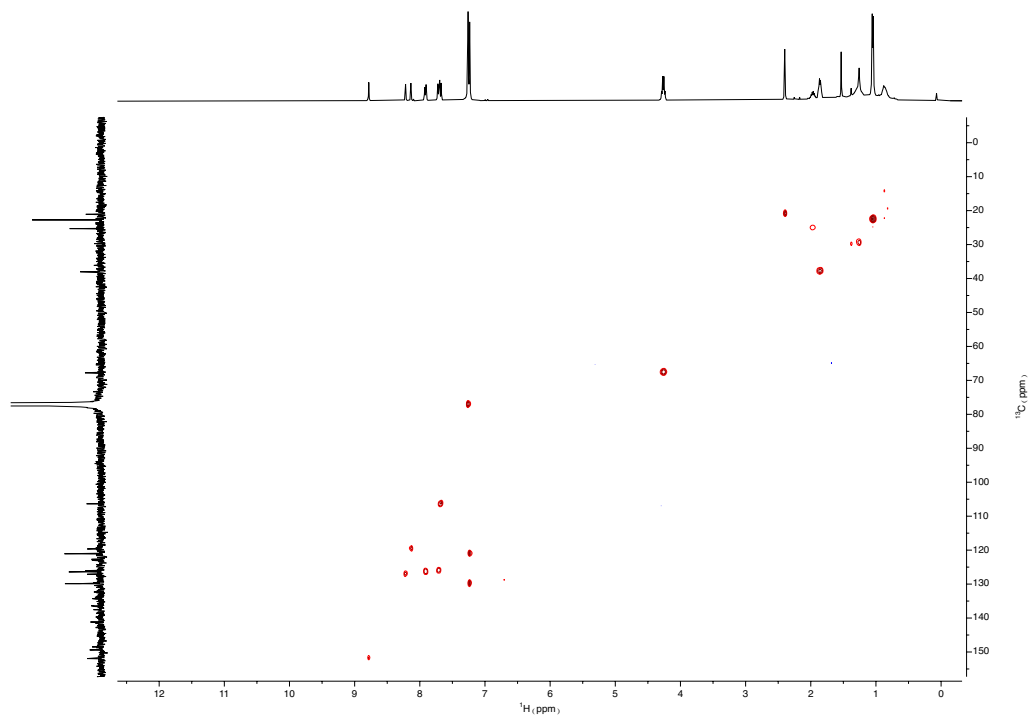


Figure C 17. ^1H - ^{13}C HSQC spectrum of **a(PhCF₃)(1b)** (CDCl_3 , 400 MHz, 298 K).

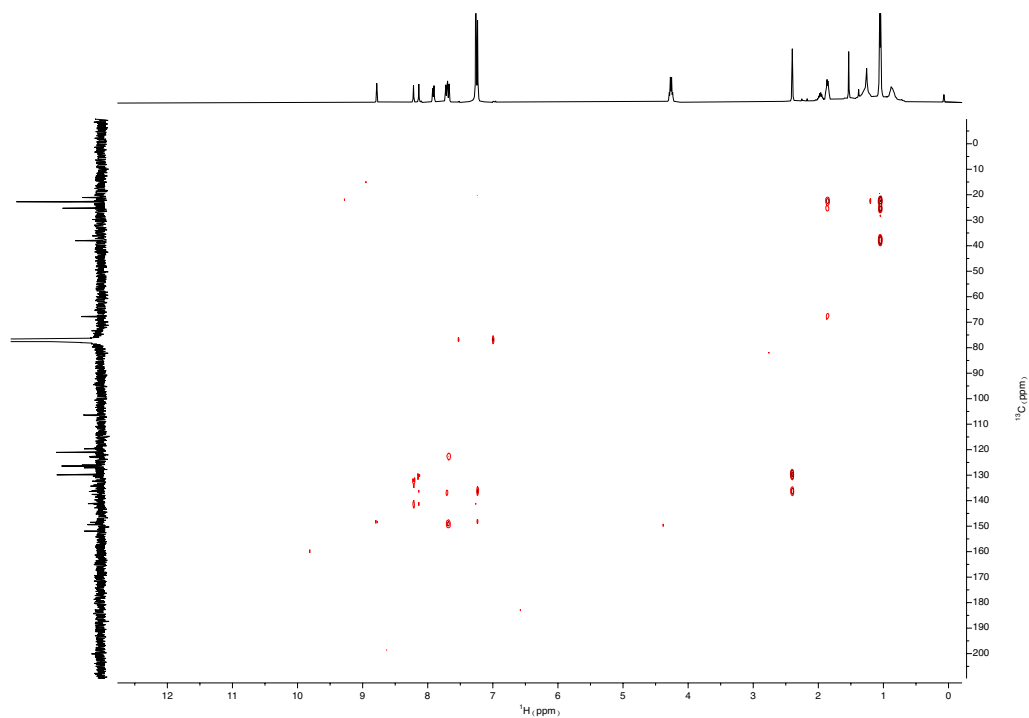


Figure C 18. ^1H - ^{13}C HMBC spectrum of **a(PhCF₃)(1b)** (CDCl_3 , 400 MHz, 298 K).

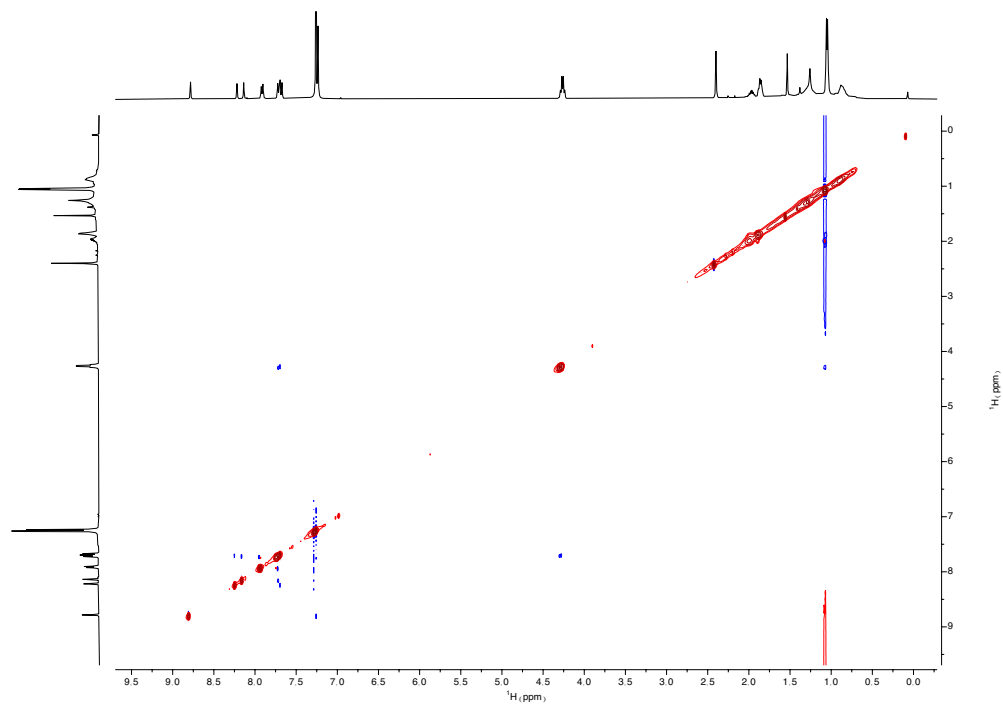


Figure C 19. ^1H - ^1H NOESY spectrum of **a(PhCF₃)(1b)** (CDCl_3 , 400 MHz, 298 K).

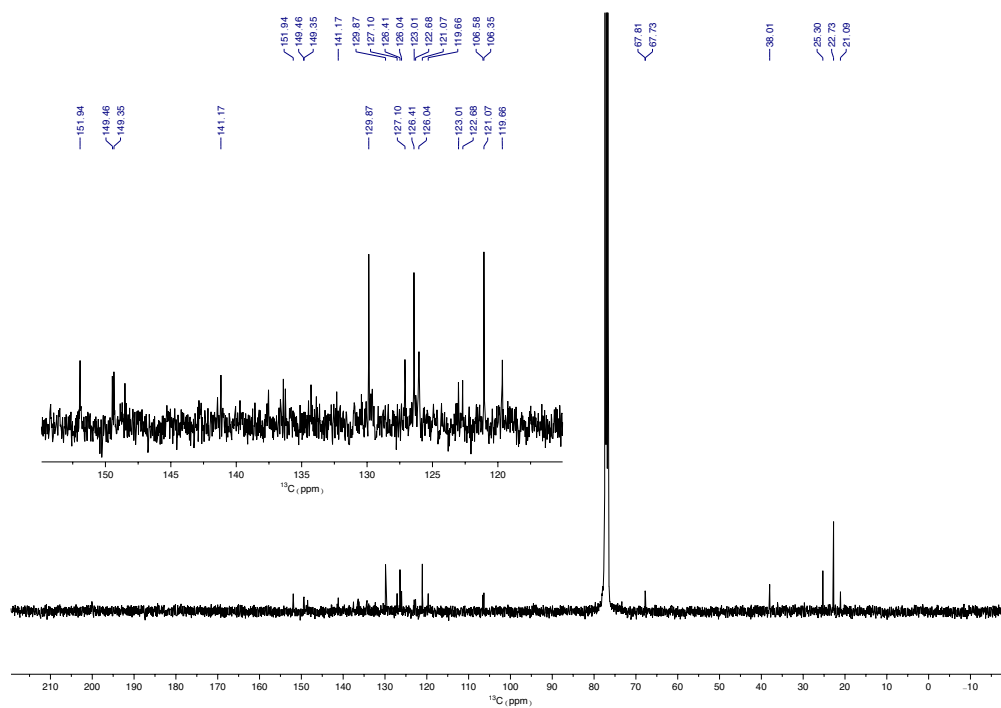
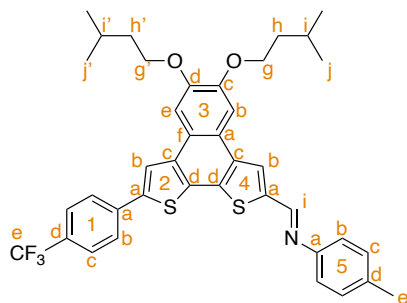


Figure C 20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a(PhCF₃)(1b)** (CDCl_3 , 400 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	— ^a
1b	7.91	126.4
1c	7.71	126.0
1d	-	— ^a
1e	-	— ^a
2a	-	— ^a
2b	8.14	119.7
2c	-	— ^a
2d	-	— ^a
3a	-	123.0 ^{b,c}
3b	7.67	106.6 ^b
3c	-	149.5 ^b
3d	-	149.4 ^b
3e	7.69	106.4 ^b
3f	-	122.7 ^{b,c}
3g/g'	4.27/4.24	67.8/67.7
3h/h'	1.86	38.0
3i/i'	1.96	25.3
3j/j'	1.05	22.7
4a	-	141.2 ^c
4b	8.22	127.1
4c	-	— ^a
4d	-	— ^a
i	8.78	151.9
5a	-	148.5 ^c
5b	7.23	121.1
5c	7.23	129.9
5d	-	136.3 ^c
5e	2.40	21.1

Figure C 21. **$\alpha(\text{PhCF}_3)(\mathbf{1b})$** with assignment of ^1H and ^{13}C resonances. ^aSignals are weak and unassigned, ^bSignals are overlapped such that exact assignment is no feasible, ^cResonances obtained from HMBC analysis.

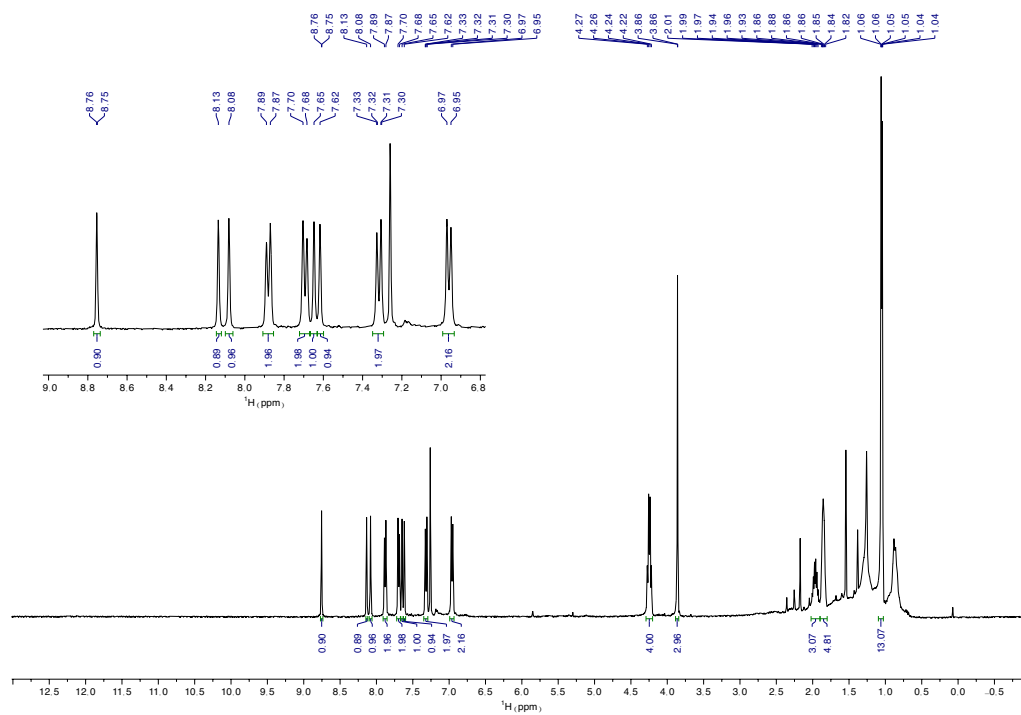


Figure C 22. ¹H NMR spectrum of **a(PhCF₃)(1c)** (CDCl₃, 400 MHz, 298 K).

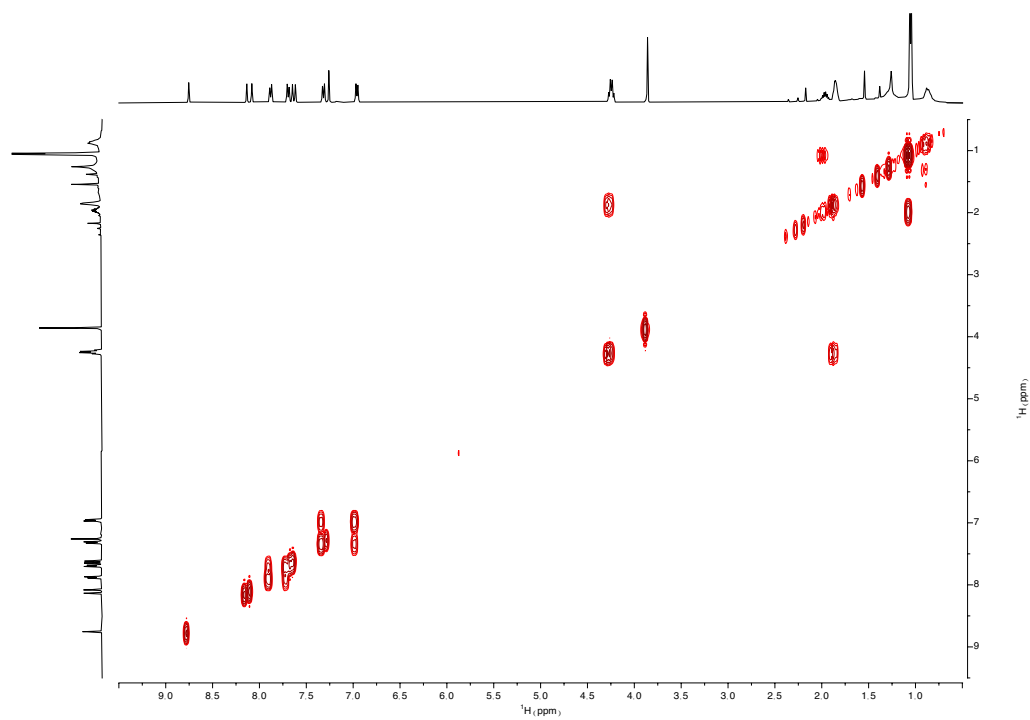


Figure C 23. ¹H-¹H COSY spectrum of **a(PhCF₃)(1c)** (CDCl₃, 400 MHz, 298 K).

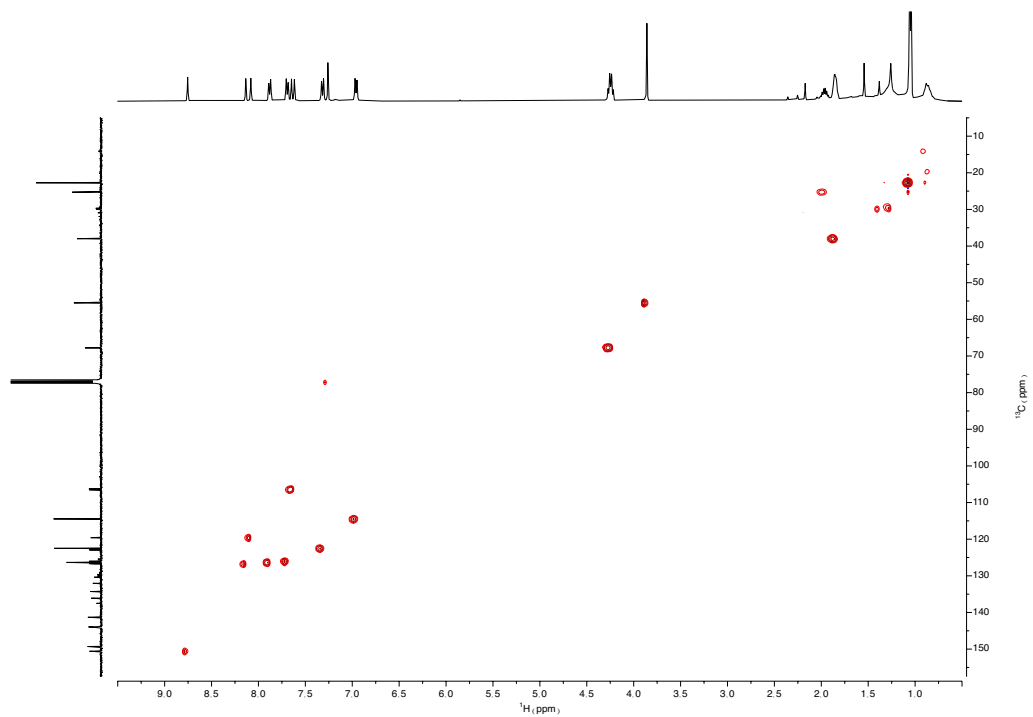


Figure C 24. ^1H - ^{13}C HSQC spectrum of **a(PhCF₃)(1c)** (CDCl_3 , 400 MHz, 298 K).

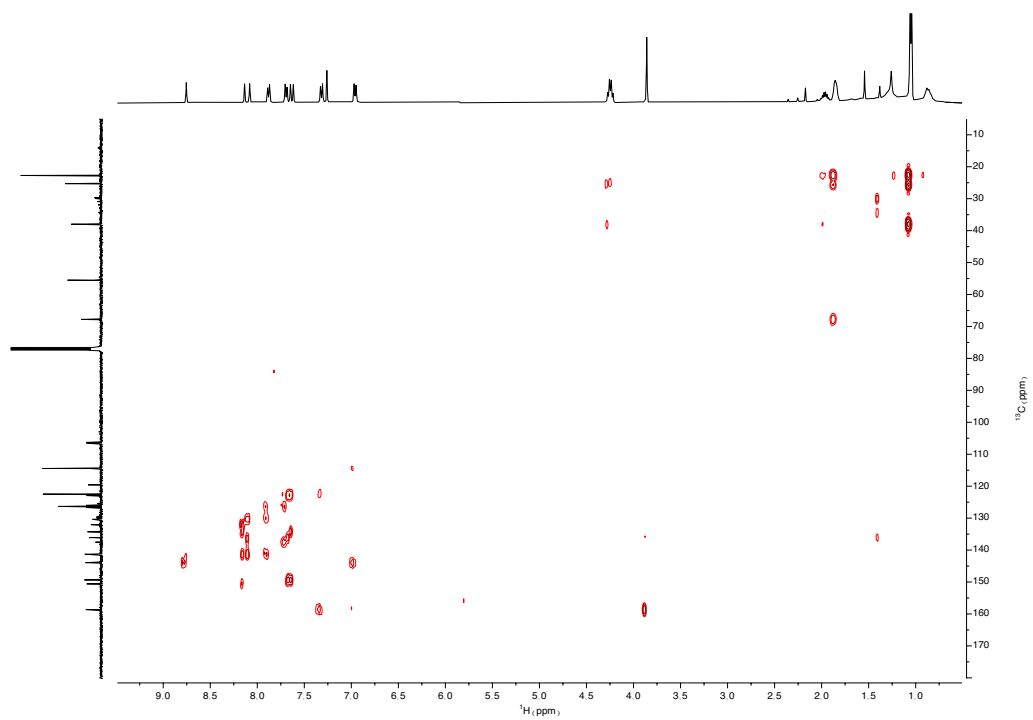


Figure C 25. ^1H - ^{13}C HMBC spectrum of **a(PhCF₃)(1c)** (CDCl_3 , 400 MHz, 298 K).

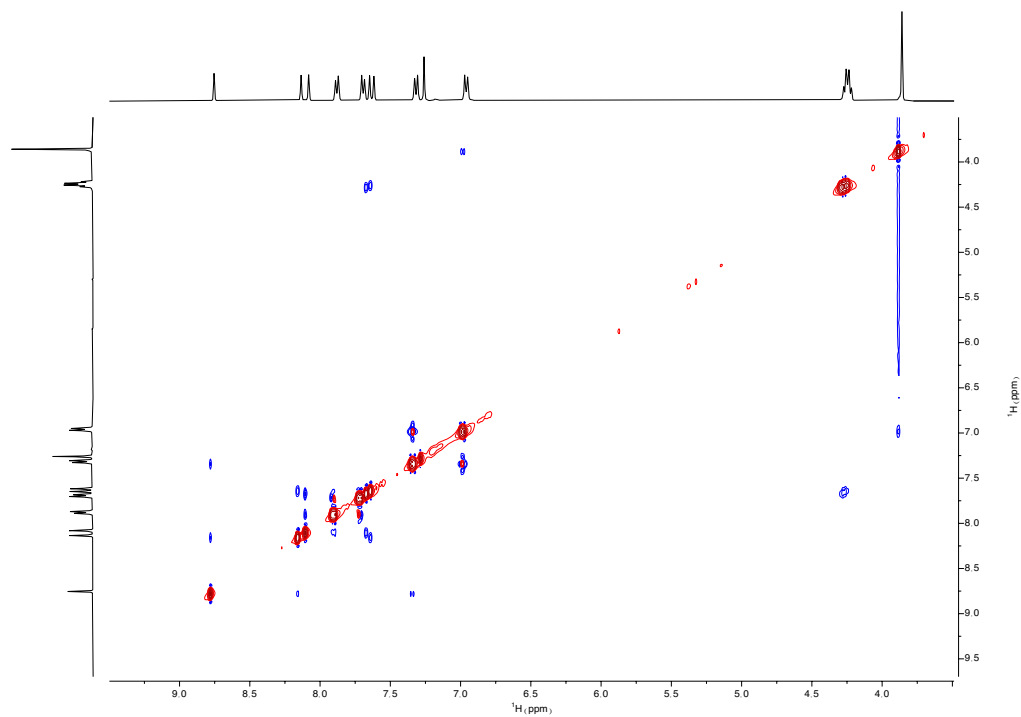


Figure C 26. ^1H - ^1H NOESY spectrum of **a(PhCF₃)(1c)** (CDCl_3 , 400 MHz, 298 K).

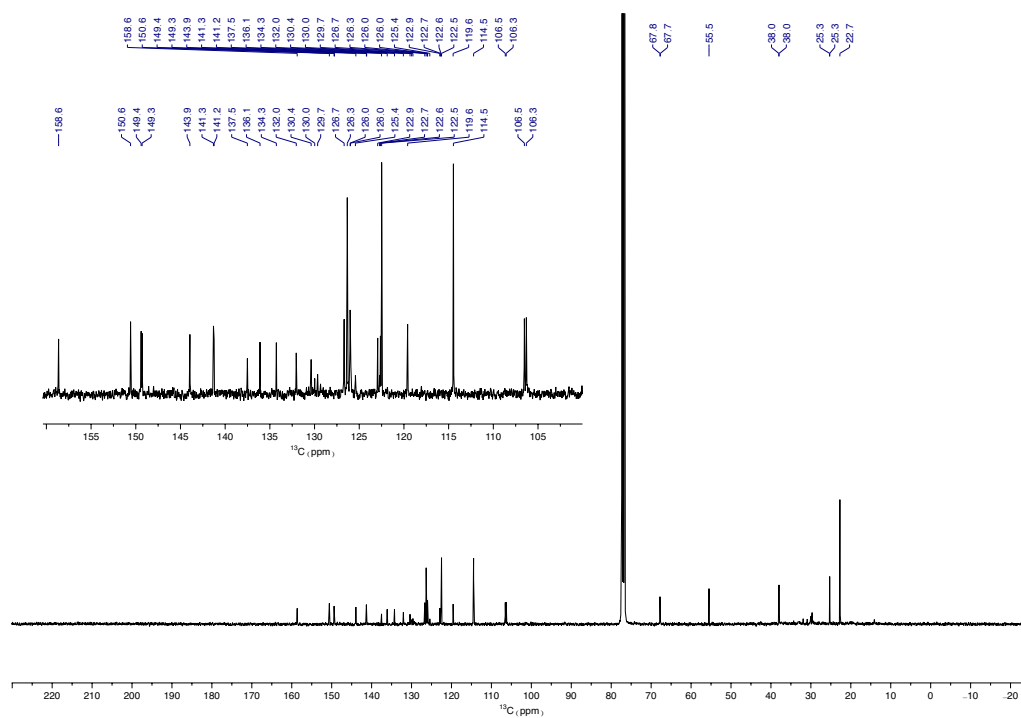
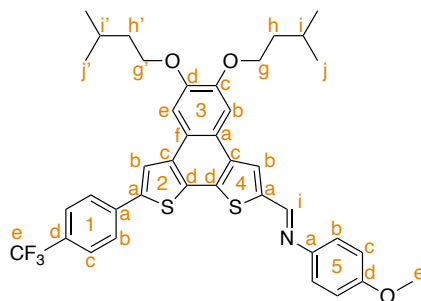


Figure C 27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **a(PhCF₃)(1c)** (CDCl_3 , 400 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	137.5
1b	7.88	126.3
1c	7.69	126.0 (q, J = 3.7 Hz)
1d	-	129.8 (q, J = 32.7 Hz) ^a
1e	-	125.4 (q, J = 271.8 Hz) ^b
2a	-	141.2
2b	8.08	119.6
2c	-	136.1
2d	-	130.4
3a	-	122.9
3b	7.62	106.3 ^c
3c	-	149.4 ^c
3d	-	149.3 ^c
3e	7.65	106.5 ^c
3f	-	122.6
3g/g'	4.25	67.8/67.7
3h/h'	1.86	38.0/38.0
3i/i'	1.97	25.3/25.3
3j/j'	1.05	22.7
4a	-	141.3
4b	8.13	126.7
4c	-	134.3
4d	-	132.0
i	8.75	150.6
5a	-	143.9
5b	7.32	126.3
5c	6.96	114.5
5d	-	158.6
5e	3.86	55.5

Figure C 28. **$\alpha(\text{PhCF}_3)(1\text{c})$** with assignment of ^1H and ^{13}C resonances.

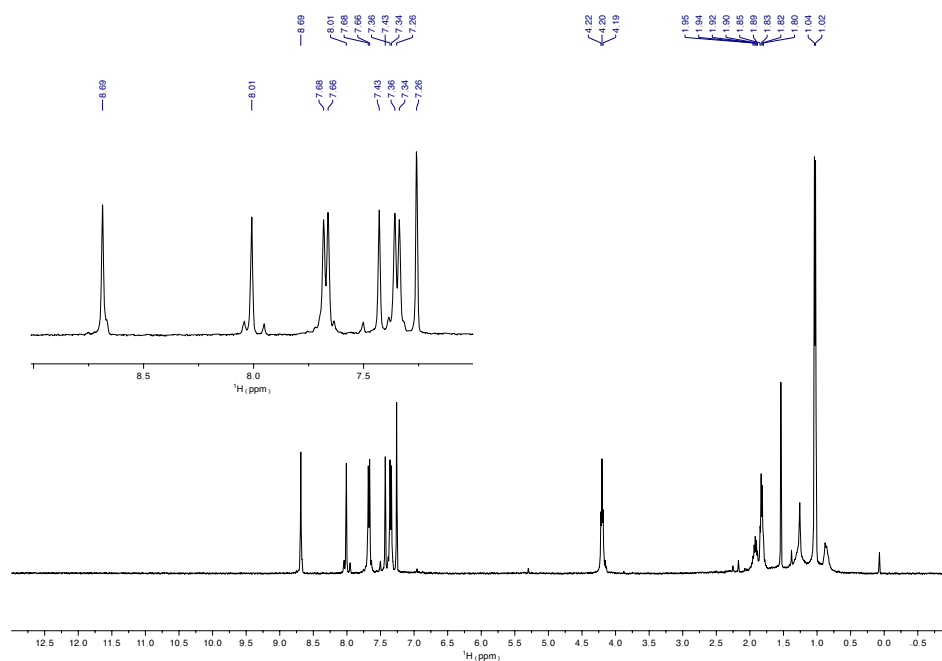


Figure C29. ¹H NMR spectrum of **a(PhCF₃)(1bb)** (CDCl₃, 400 MHz, 298 K).

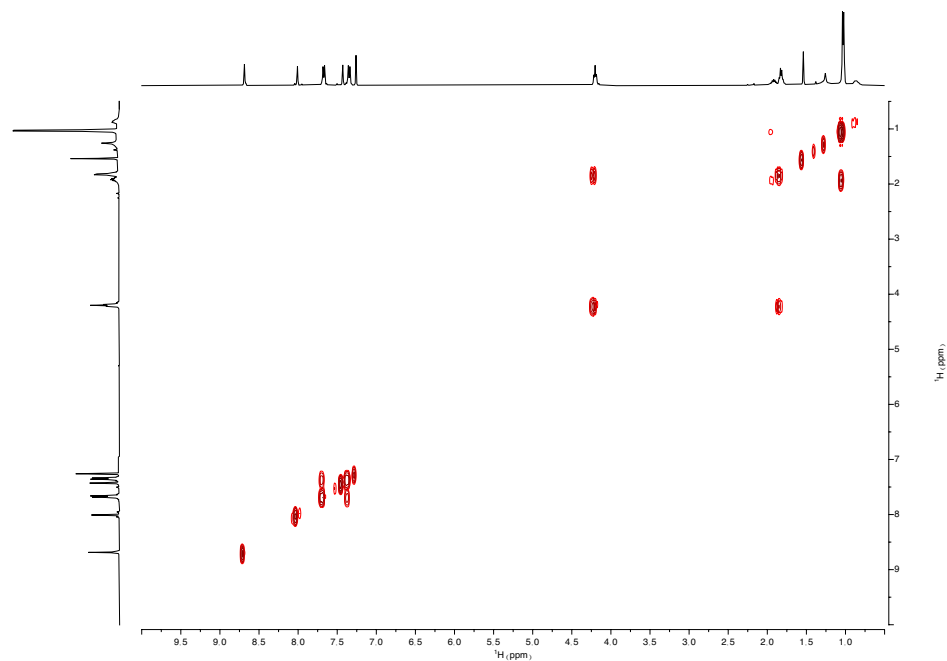


Figure C30. ¹H-¹H COSY spectrum of **a(PhCF₃)(1bb)** (CDCl₃, 400 MHz, 298 K).

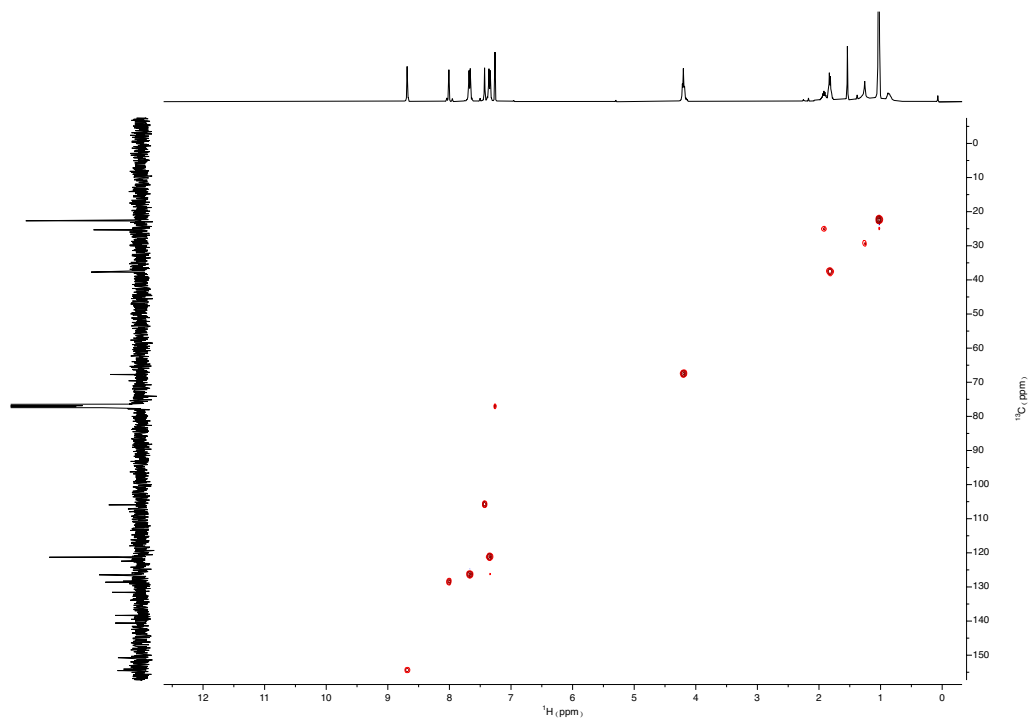


Figure C31. ^1H - ^{13}C HSQC spectrum of **a(PhCF₃)(1bb)** (CDCl_3 , 400 MHz, 298 K).

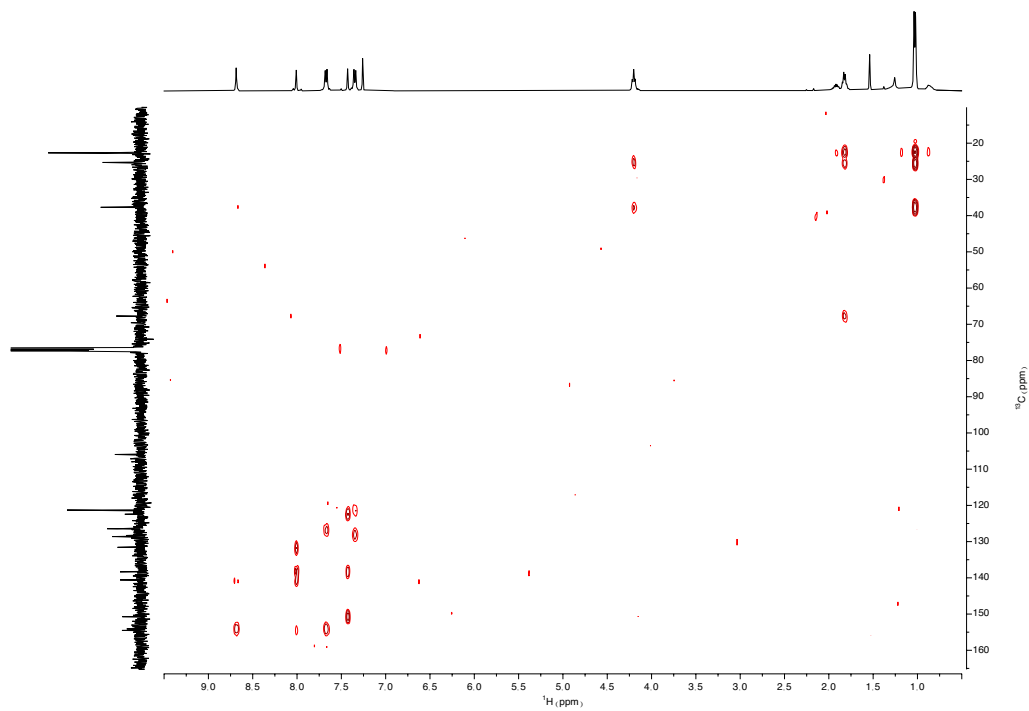


Figure C32. ^1H - ^{13}C HMBC spectrum of **a(PhCF₃)(1bb)** (CDCl_3 , 400 MHz, 298 K).

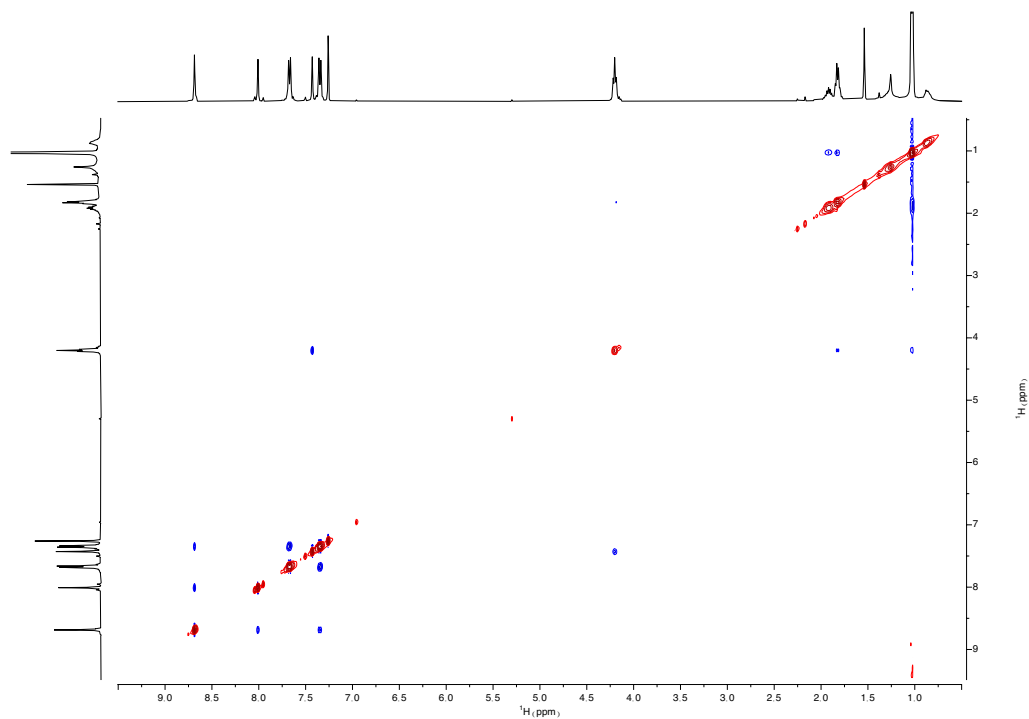


Figure C33. ^1H - ^1H NOESY spectrum of $\alpha(\text{PhCF}_3)(\mathbf{1bb})$ (CDCl_3 , 400 MHz, 298 K).

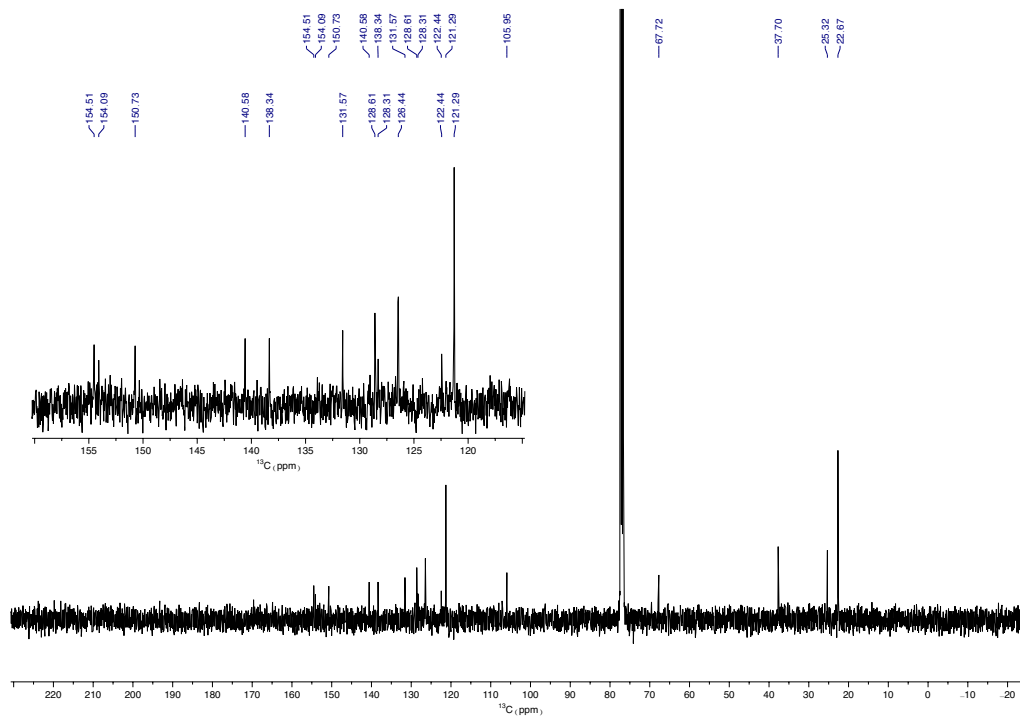
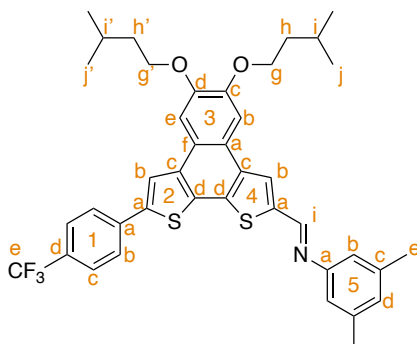


Figure C34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\alpha(\text{PhCF}_3)(\mathbf{1bb})$ (CDCl_3 , 400 MHz, 298 K).



Assignment of ^1H and ^{13}C resonances for **$\alpha(\text{PhCF}_3)(1\text{bb})$** is currently in progress and will be included soon in publication

Figure C35. **$\alpha(\text{PhCF}_3)(1\text{bb})$** with assignment of ^1H and ^{13}C resonances.

4.3 Photophysical Properties **$\alpha(\text{PhCF}_3)(1)$** Series

Absorbance spectra were collected on an Agilent Cary Bio100 spectrophotometer and corrected for solvent background absorbance and instrument drift. Emission spectra were recorded on a Horiba Jon-Yvon Fluorolog-3 with excitation and emission slit widths set at 2 nm. **$\alpha(\text{PhCF}_3)(1)$** series were prepared with degassed, dry, solvents and degassed prior to sealing in 1 cm path length quartz cuvettes. Emission spectra were analyzed at $\lambda_{\text{ex}} = 365$ nm. Fluorescence quantum yields were determined by reference to 9,10-diphenylanthracene in cyclohexane ($\phi = 0.91$) which was cross-checked with quinine bisulfate in 0.5 M H_2SO_4 (aq) ($\phi = 0.54$). Five solutions of varying concentration were prepared for each sample and good fits ($R^2 \geq 0.99$) were obtained in all cases. The absorbance of all sample solutions was kept below 0.10 to avoid the inner-filter effect. Measurements were performed at room temperature with both sample and standard excited at the same wavelength (365 nm).¹ All quantum yields obtained were below 1%, which is apparent when normalizing the emission spectra relative to concentration (see below). Plots are given below with UV-visible spectra as solid lines and emission spectra

as dashed lines. UV-visible spectra are plotted as molar absorptivity (left vertical axis) vs wavelength (horizontal axis). Emission spectra are plotted as normalized intensities (intensities were corrected for concentration and then normalized relative to most emissive sample, $\alpha(\text{PhCF}_3)(1\text{a})$; right vertical axis) vs wavelength (horizontal axis).

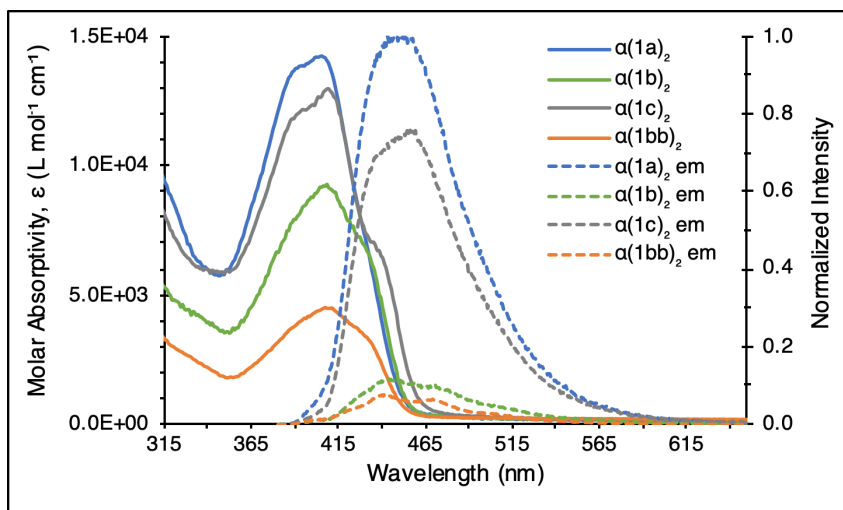


Figure C 36. Absorbance and emission spectra for $\alpha(\text{PhCF}_3)(1)$ series in toluene.

4.4 Computational Analysis of $\alpha(\text{PhCF}_3)(1)$

For the computational analysis the isopentyloxy solubilizing groups of the seven di-imine derivatives were simplified to methoxy groups, with the model compounds being identified as $\alpha(\text{PhCF}_3)(1)$. Computations were ran in Gaussian 16 utilizing the ω B97-XD functional with a cc-pVDZ basis set to accommodate the variety of light atoms employed in this work and account for the likelihood of dispersion interactions, to perform geometry optimizations and frequency calculations on the $\alpha(\text{PhCF}_3)(1)$ series.³ Cartesian coordinates for all output geometries have been included as a separate .txt file for ease.

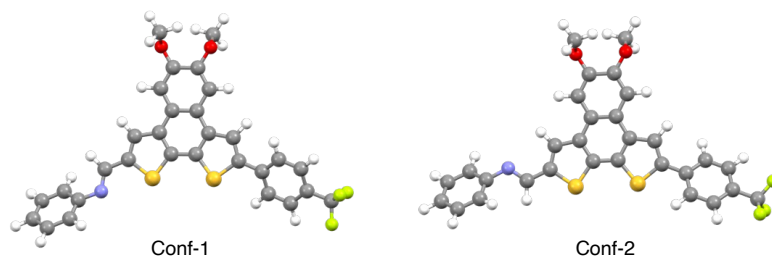


Figure C 37. Ball-and-stick representations for optimized conformers of $a(PhCF_3)(1a)$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S- C^d} (kcal mol ⁻¹)
$a(PhCF_3)(1a)$ Conformer 1	-2455.926828	0.430979	-2455.495850	0.0	0	0.95
$a(PhCF_3)(1a)$ Conformer 2	-2455.924367	0.430998	-2455.493370	+1.56	0	—

Table C 1. Computational data for optimized $a(PhCF_3)(1a)$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies.

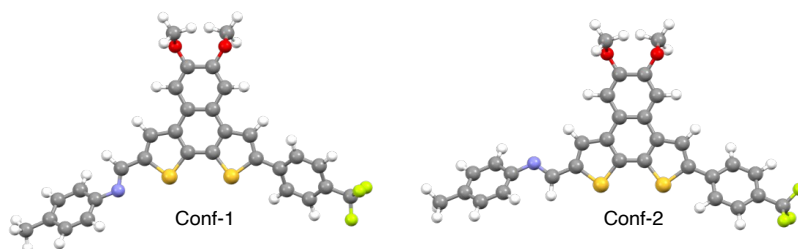


Figure C 38. Ball-and-stick representations for optimized conformers of $a(PhCF_3)(1b)$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S- C^d} (kcal mol ⁻¹)
$a(PhCF_3)(1b)$ Conformer 1	-2495.23433155	0.458168	-2494.776164	0.00	0	0.96
$a(PhCF_3)(1b)$ Conformer 2	-2495.23187542	0.45817	-2494.773705	+1.54	0	—

Table C 2. Computational data for optimized $a(PhCF_3)(1b)$ models ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies.

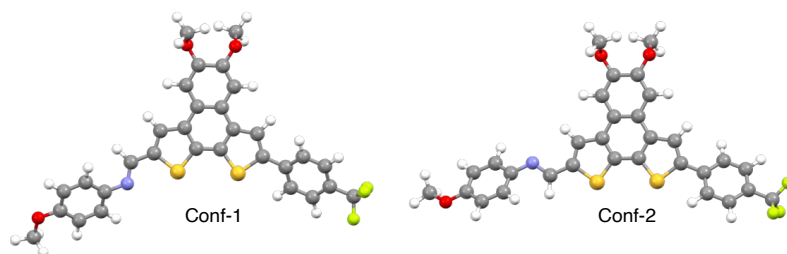


Figure C 39. Ball-and-stick representations for optimized conformers of $a(PhCF_3)(1c)$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S- C^d} (kcal mol ⁻¹)
<i>a(PhCF₃)(1c)</i> <i>Conformer 1</i>	-2570.42115918	0.463631	-2569.957528	0.00	0	0.99
<i>a(PhCF₃)(1c)</i> <i>Conformer 2</i>	-2570.41865987	0.463534	-2569.955126	+1.51	0	—

Table C 3. Computational data for optimized $a(PhCF_3)(1c)$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies.

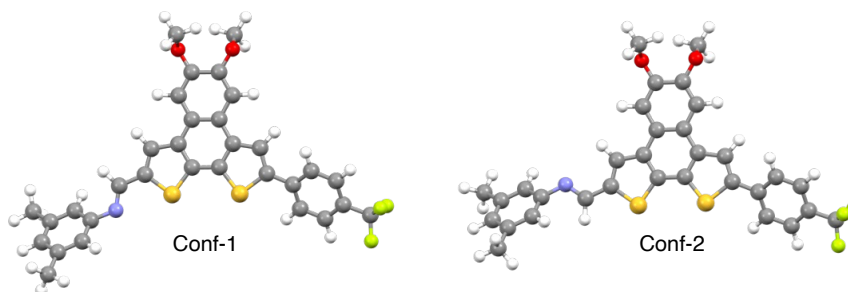


Figure C40. Ball-and-stick representations for optimized conformers of $a(PhCF_3)(1bb)$.

Model Compound	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S- C^d} (kcal mol ⁻¹)
<i>a</i> (PhCF ₃)(1 <i>bb</i>) Conformer 1	-2534.54240949	0.485311	-2534.057098	0.00	0	0.96
<i>a</i> (PhCF ₃)(1 <i>bb</i>) Conformer 2	-2534.54000687	0.485298	-2534.054709	+1.50	0	—

Table C4. Computational data for optimized *a*(PhCF₃)(1*bb*) models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies.

4.4.1 Experimental vs Calculated Chemical Shift Analysis

The optimized structures were used to calculate the ¹H NMR spectra using the GIAO method with implicit solvent (CHCl₃). The isotropic shieldings for the model compounds with the alkoxy groups simplified to methoxy groups were computed for both protons and carbons using the GIAO method with the cc-pVDZ basis set and ωB97-XD functional in Gaussian 16 with implicit solvent (CHCl₃).

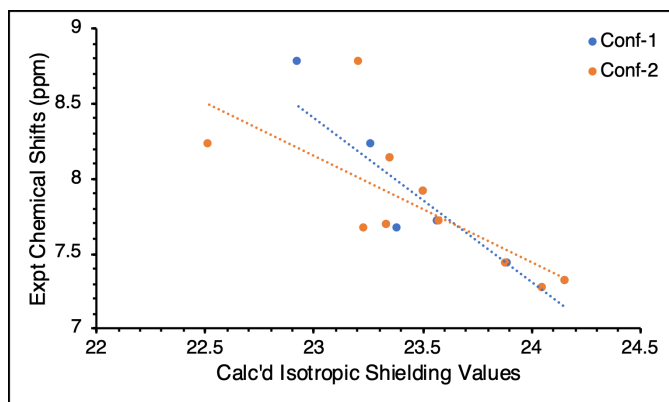


Figure C 41. Comparison of experimental vs calculated ¹H resonances (δ) for ***a*(PhCF₃)(1*a*)** (experimental) and *a*(PhCF₃)(1*a*) (calculated). Fits: Conformer-1 (blue, R² = 0.81), Conformer-2 (orange, R² = 0.53).

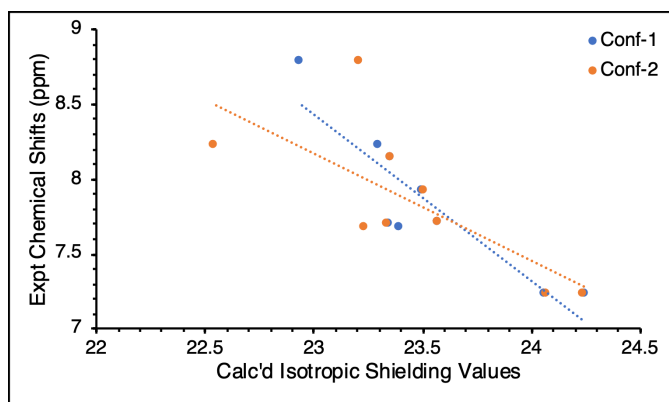


Figure C 42. Comparison of experimental vs calculated ^1H resonances (δ) for **a(PhCF₃)(1b)** (experimental) and *a(PhCF₃)(1b)* (calculated). Fits: Conformer-1 (blue, $R^2 = 0.81$), Conformer-2 (orange, $R^2 = 0.53$).

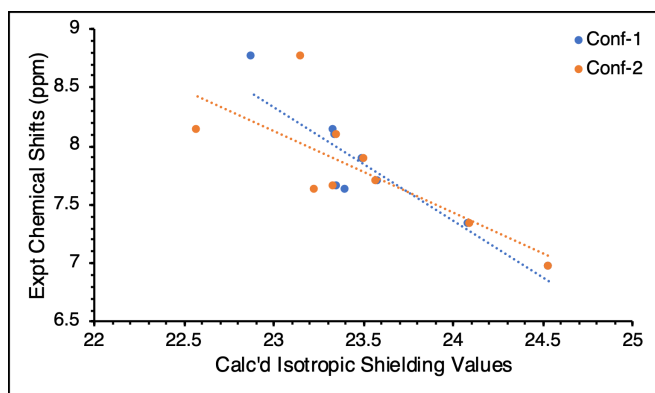


Figure C 43. Comparison of experimental vs calculated ^1H resonances (δ) for **a(PhCF₃)(1c)** (experimental) and *a(PhCF₃)(1c)* (calculated). Fits: Conformer-1 (blue, $R^2 = 0.83$), Conformer-2 (orange, $R^2 = 0.59$).

4.5 References

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- (2) Adusei, E. B. A.; Casetti, V. T.; Goldsmith, C. D.; Caswell, M.; Alinj, D.; Park, J.; Zeller, M.; Rusakov, A. A.; Kinney, Z. J. Bent Naphthodithiophenes: Synthesis and Characterization of Isomeric Fluorophores. *RSC Adv.* 2024, **14**, 25120–25129.
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CHAPTER FIVE

5.0 Experimental Procedures

Unless otherwise noted, all starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Anhydrous solvents (dichloromethane, hexanes, tetrahydrofuran, toluene) were purified using an Inert PureSolv solvent purification system equipped with an alumina column. 4 Å molecular sieves were activated via vacuum oven (150 °C, > 16 hours) overnight prior to use. Purification of all di-imine products was accomplished with a Shimadzu Nexera Gel Permeation Chromatography (GPC) equipped with a Shodex organic size exclusion column (100 Å styrogel stationary phase, viable molecular weight range of 400–6000 g/mol) and a toluene mobile phase (flow rate 5 mL/min). NMR spectra were measured on a Bruker Avance III 400 MHz spectrometer, with all samples referenced to the residual solvent signal. High resolution mass spectra were obtained by dissolving samples in acetonitrile and analyzed on a Shimadzu LCMS-9050 Q-TOF (ionization method: APCI+). Melting point was measured with a Stuart SMP10 melting point apparatus for **β(CHO)₂**. The procedure for **β(Br)₂** and its precursors has been detailed elsewhere.² All procedures below were carried out multiple times with the yields given representing the median outcome of an experiment. Common solvent and reagent abbreviations: chloroform-*d* (CDCl₃), dichloromethane (DCM), ethyl acetate (EtOAc), tetrahydrofuran (THF), and *N*-bromosuccinimide (NBS).

5.1 Synthesis of $\beta(\text{CHO})_2$ and $\beta(1)_2$ series

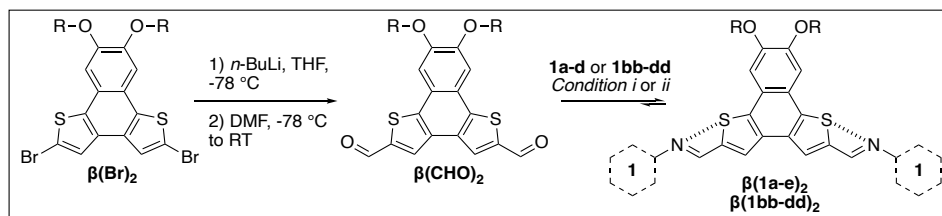


Figure D 1. Synthetic path to $\beta(\text{CHO})_2$ and $\beta(1)_2$.

5.1.1 5,6-bis(isopentyloxy)-2,9-di-(formyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene,

$\beta(\text{CHO})_2$

A 100 mL Schlenk flask was charged with $\beta(\text{Br})_2$ (0.373 g, 0.65 mmol), a stir bar, dry THF (20 mL) and sparged with argon for 15 minutes. The flask was cooled to $-78\text{ }^\circ\text{C}$ and allowed to equilibrate for 20 minutes. *n*-Butyllithium (0.94 mL, 1.2 mmol) was added dropwise to the reaction, and the reaction allowed to stir for 30 minutes. The dry ice bath was shielded from light for the remainder of the reaction. Degassed DMF (0.60 mL, 7.8 mmol) was added, and reaction allowed to stir under inert atmosphere of argon for 30 minutes. Reaction was cooled to RT for 40 minutes, quenched with 5 mL dilute HCl solution, poured into H_2O (15 mL), extracted with EtOAc (2x50 mL), washed with brine (2x50 mL), dried over anhydrous Na_2SO_4 , decanted, and concentrated. The crude product was purified by silica gel column with Toluene:EtOAc (9:1) as eluent followed by recrystallization from toluene to give 5,6-bis(isopentyloxy)-2,9-di-(formyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene ($\beta(\text{CHO})_2$) as a yellow solid, 145 mg (47%): mp $210\text{ }^\circ\text{C}$ (decomposition); ^1H NMR (400 MHz, CDCl_3) δ 10.09 (s, 2H), 8.23 (s, 2H), 7.32 (s, 2H), 4.19 (t, $J = 6.6\text{ Hz}$, 4H), 1.93 (dq, $J = 13.0, 6.6\text{ Hz}$, 2H), 1.84 (q, $J = 6.6\text{ Hz}$, 4H), 1.05 (d, $J = 6.5\text{ Hz}$, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 183.4, 151.3, 141.6,

141.2, 131.7, 131.3, 122.6, 105.9, 67.8, 37.6, 25.3, 22.7; HRMS (APCI+) calcd for C₂₆H₂₉O₄S₂ (M+H)⁺ 469.1507, found 469.1501.

5.1.2 5,6-bis(isopentyloxy)-2,9-di-(*N*-(phenyl)methaniminyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene, **β(1a)₂**

Conditions *i*: A 6-dram vial was massed with **β(CHO)₂** (22.1 mg, 0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4 Å molecular sieves. Aniline (0.014 mL, 0.15 mmol), Sc(OTf)₃ (6 mg, 0.01 mmol) and MeCN (5 % of CHCl₃) were added. The reaction vial was capped, inverted several times to mix, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **β(1a)₂** was isolated by GPC as a yellow solid, 5.0 mg (16%).

Conditions *ii*: A 50 mL round bottom flask was massed with **β(CHO)₂** (21.4 mg, 0.05 mmol), aniline (0.014 mL, 0.15 mmol), Toluene (to 10 mM NDT), Acetic acid (0.018 mL, 4.8 μmol), and a stir bar. Reaction was left to stir vigorously for 10 minutes under argon, and heated until reflux with dean-stark trap for >16 hours. Reaction was cooled and transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **β(1a)₂** was isolated by GPC as a yellow solid, 3.6 mg (13%).

Analysis **β(1a)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 2H), 8.05 (s, 2H), 7.48 (s, 2H), 7.43 (t, *J* = 7.6 Hz, 4H), 7.32 (d, *J* = 7.9 Hz, 4H), 7.28 (t, *J* = 8.1 Hz, 2H), 4.22 (t, *J* = 6.6 Hz, 2H), 1.93 (dt, *J* = 13.2, 6.7 Hz, 2H), 1.84 (q, *J* = 6.6 Hz, 4H), 1.04 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 153.0, 151.1, 150.5, 141.3, 137.7, 131.8, 129.2,

127.7, 126.4, 122.5, 121.1, 106.0, 67.7, 37.7, 25.3, 22.7; HRMS (APCI+) calcd for $C_{38}H_{39}N_2O_2S_2$ (M+H)⁺ 619.2452, found 619.2449.

5.1.3 5,6-bis(isopentyloxy)-2,9-di-(N-(4-methylphenyl)methaniminyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene, **β(1b)₂**

Conditions *i*: A 6-dram vial was massed with **β(CHO)₂** (20.4 mg, 0.04 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4 Å molecular sieves. *p*-Toluidine (10.6 mg, 0.10 mmol), Sc(OTf)₃ (6.4 mg, 0.01 mmol) and MeCN (5 % of CHCl₃) were added. The reaction vial was capped, inverted several times to mix, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **β(1b)₂** was isolated by GPC as a yellow solid, 5.2 mg (18%).

Analysis **β(1b)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 2H), 7.86 (s, 2H), 7.39 (s, 2H), 7.22 (s, 8H), 4.17 (t, *J* = 6.8 Hz, 4H), 2.39 (s, 6H), 1.91 (dt, *J* = 13.2, 6.6 Hz, 2H), 1.81 (q, *J* = 6.8 Hz, 4H), 1.03 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 152.0, 150.3, 148.5, 141.3, 137.3, 136.3, 131.7, 129.8, 127.3, 122.3, 121.1, 105.9, 67.6, 37.7, 25.3, 22.7, 21.1; HRMS (APCI+) calcd for $C_{40}H_{43}N_2O_2S_2$ (M+H)⁺ 647.2765, found 647.2758.

5.1.4 5,6-bis(isopentyloxy)-2,9-di-(N-(4-methoxyphenyl)methaniminyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene, **β(1c)₂**

Conditions *i*: A 6-dram vial was massed with **β(CHO)₂** (19.0 mg, 0.04 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4 Å molecular sieves. *p*-Anisidine (12.2 mg, 0.10 mmol), Sc(OTf)₃ (5.6 mg, 0.01 mmol) and MeCN (5 % of CHCl₃) were added. The reaction vial was capped, inverted several times to mix, and left undisturbed overnight

(>16 hours). Reaction was transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **$\beta(1c)_2$** was isolated by GPC as a yellow solid, 5.7 mg (21%).

Analysis **$\beta(1c)_2$** : ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 2H), 7.93 (s, 2H), 7.43 (s, 2H), 7.32 (d, $J = 8.4$ Hz, 4H), 6.95 (d, $J = 8.3$ Hz, 4H), 4.19 (t, $J = 6.7$ Hz, 4H), 3.85 (s, 6H), 1.91 (dq, $J = 13.0, 6.6$ Hz, 2H), 1.83 (q, $J = 6.8$ Hz, 4H), 1.03 (d, $J = 6.5$ Hz, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 150.9, 150.3, 144.0, 141.5, 137.2, 131.8, 126.9, 122.5, 122.4, 114.4, 106.0, 67.7, 55.5, 37.7, 25.3, 22.7; HRMS (APCI+) calcd for $\text{C}_{40}\text{H}_{43}\text{N}_2\text{O}_4\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 679.2664, found 679.2656.

5.1.5 5,6-bis(isopentyloxy)-2,9-di-(*N*-(4-trifluoromethylphenyl)methaniminyl)
naphtho[1,2-*b*:4,3-*b'*]dithiophene, **$\beta(1d)_2$**

Conditions *i*: A 6-dram vial was massed with **$\beta(\text{CHO})_2$** (22.0 mg, 0.05 mmol), deacidified CHCl_3 (to 10 mM NDT), and 4 Å molecular sieves. *p*-Aminobenzotrifluoride (0.020 mL, 0.16 mmol), $\text{Sc}(\text{OTf})_3$ (4.3 mg, 0.009 mmol) and MeCN (5 % of CHCl_3) were added. The reaction vial was capped, inverted several times to mix, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **$\beta(1d)_2$** was isolated by GPC as a yellow solid, 14.5 mg (41%).

Conditions *ii*: A 50 mL round bottom flask was massed with **$\beta(\text{CHO})_2$** (22.7 mg, 0.05 mmol), *p*-aminobenzotrifluoride (0.014 mL, 0.11 mmol), Toluene (to 10 mM NDT), Acetic acid (0.018 mL, 4.8 μmol), and a stir bar. Reaction was left to stir vigorously for 10 minutes under argon, and heated until reflux with dean-stark trap for >16 hours. Reaction was cooled and transferred into a clean 100 mL round bottom flask containing 1

mL triethylamine and concentrated to yield the crude product. **$\beta(1d)_2$** was isolated by GPC as a yellow solid, 2.0 mg (5%).

Analysis **$\beta(1d)_2$** : ^1H NMR (400 MHz, CDCl_3) δ 8.69 (s, 2H), 8.01 (s, 2H), 7.67 (d, $J = 8.2$ Hz, 4H), 7.43 (s, 2H), 7.35 (d, $J = 8.3$ Hz, 4H), 4.20 (t, $J = 6.5$ Hz, 4H), 1.92 (dt, $J = 13.1, 6.8$ Hz, 2H), 1.82 (q, $J = 6.9$ Hz, 4H), 1.03 (d, $J = 6.3$ Hz, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.5, 150.7, 140.6, 138.3, 131.6, 128.6, 128.3, 126.5, 122.4, 121.3, 67.7, 37.7, 25.3, 22.7; HRMS (APCI+) calcd for $\text{C}_{38}\text{H}_{39}\text{F}_6\text{N}_2\text{O}_2\text{S}_2$ ($\text{M}+\text{H}$) $^+$ 755.2200, found 755.2201.

5.1.6 5,6-bis(isopentyloxy)-2,9-di-(*N*-(4-(*N,N*-dimethylaminophenyl)methaniminyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene, **$\beta(1e)_2$**

Conditions *i*: A 6-dram vial was massed with **$\beta(\text{CHO})_2$** (18.9 mg, 0.04 mmol), deacidified CHCl_3 (to 10 mM NDT), and 4 Å molecular sieves. *N,N*-dimethyl-*p*-phenylenediamine (11.5 mg, 0.09 mmol), $\text{Sc}(\text{OTf})_3$ (4.5 mg, 0.01 mmol) and MeCN (5 % of CHCl_3) were added. The reaction vial was capped, inverted several times to mix, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **$\beta(1e)_2$** was isolated by GPC as a yellow solid, 9.9 mg (37%).

Analysis **$\beta(1e)_2$** : ^1H NMR (400 MHz, CDCl_3) δ 8.78 (s, 2H), 7.94 (s, 2H), 7.46 (s, 2H), 7.35 (d, $J = 8.5$ Hz, 4H), 6.77 (d, $J = 8.5$ Hz, 4H), 4.20 (t, $J = 6.7$ Hz, 4H), 3.01 (s, 12H), 1.93 (dt, $J = 13.2, 6.7$ Hz, 2H), 1.84 (q, $J = 6.7$ Hz, 4H), 1.03 (d, $J = 6.6$ Hz, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.2, 149.7, 148.4, 142.2, 140.0, 136.7, 132.0, 126.0, 122.6, 122.3, 112.7, 106.0, 67.7, 40.7, 37.7, 25.3, 22.7.

5.1.7 5,6-bis(isopentyloxy)-2,9-di-(*N*-(3,5-dimethylphenyl)methaniminyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene, **β (1bb)₂**

Conditions *i*: A 6-dram vial was massed with **β (CHO)₂** (19.5 mg, 0.04 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4 Å molecular sieves. 3,5-dimethylaniline (0.014 mL, 0.11 mmol), Sc(OTf)₃ (6.0 mg, 0.01 mmol) and MeCN (5 % of CHCl₃) were added. The reaction vial was capped, inverted several times to mix, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **β (1bb)₂** was isolated by GPC as a yellow solid, 5.5 mg (20%).

Conditions *ii*: A 50 mL round bottom flask was massed with **β (CHO)₂** (23.6 mg, 0.05 mmol), 3,5-dimethylaniline (0.020 mL, 0.16 mmol), Toluene (to 10 mM NDT), Acetic acid (0.020 mL, 5.3 µmol), and a stir bar. Reaction was left to stir vigorously for 10 minutes under argon, and heated until reflux with dean-stark trap for >16 hours. Reaction was allowed to cool and transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **β (1bb)₂** was isolated by GPC as a yellow solid, 11.6 mg (34%)

Analysis **β (1bb)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.71 (s, 2H), 7.96 (s, 2H), 7.43 (s, 2H), 6.94 (s, 4H), 6.92 (s, 2H), 4.19 (t, *J* = 6.7 Hz, 4H), 2.37 (s, 12H), 1.92 (dt, *J* = 13.1, 6.5 Hz, 2H), 1.83 (q, *J* = 6.7 Hz, 4H), 1.03 (d, *J* = 6.4 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 152.5, 151.0, 150.4, 141.3, 138.8, 137.5, 131.7, 128.1, 127.4, 122.4, 118.9, 105.9, 67.6, 37.7, 25.3, 22.7, 21.3; HRMS (APCI+) calcd for C₄₂H₄₇N₂O₂S₂ (M+H)⁺ 675.3078, found 675.3079.

5.1.8 5,6-bis(isopentyloxy)-2,9-di-(N-(3,5-dimethoxyphenyl)methaniminyl)naphtho[1,2-
b:4,3-b']dithiophene, **β (1cc)₂**

Conditions *i*: A 6-dram vial was massed with **β (CHO)₂** (26.0 mg, 0.06 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4 Å molecular sieves. 3,5-dimethoxyaniline (21.3 mg, 0.14 mmol), Sc(OTf)₃ (5.8 mg, 0.01 mmol) and MeCN (5 % of CHCl₃) were added. The reaction vial was capped, inverted several times to mix, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **β (1cc)₂** was isolated by GPC as a yellow solid, 4.9 mg (12%).

Conditions *ii*: A 50 mL round bottom flask was massed with **β (CHO)₂** (21.8 mg, 0.05 mmol), 3,5-dimethoxyaniline (17.5 mg, 0.11 mmol), Toluene (to 10 mM NDT), Acetic acid (0.020 mL, 5.3 µmol), and a stir bar. Reaction was left to stir vigorously for 10 minutes under argon, and heated until reflux with dean-stark trap for >16 hours. Reaction was allowed to cool and transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **β (1cc)₂** was isolated by GPC as a yellow solid, 9.8 mg (28%)

Analysis **β (1cc)₂**: ¹H NMR (400 MHz, CDCl₃) δ 8.73 (s, 2H), 8.03 (s, 2H), 7.46 (s, 2H), 6.48 (d, *J* = 2.2 Hz, 4H), 6.40 (t, *J* = 2.2 Hz, 2H), 4.20 (t, *J* = 6.7 Hz, 4H), 3.85 (s, 12H), 1.92 (dq, *J* = 12.8, 6.5 Hz, 2H), 1.84 (q, *J* = 6.8 Hz, 4H), 1.03 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 161.3, 153.3, 153.2, 150.5, 141.0, 137.8, 131.7, 127.9, 122.4, 106.0, 99.3, 98.8, 67.7, 55.5, 37.7, 25.3, 22.7; HRMS (APCI+) calcd for C₄₂H₄₇N₂O₆S₂ (M+H)⁺ 739.2875, found 739.2865.

5.1.9 5,6-bis(isopentyloxy)-2,9-di-(N-(3,5-ditrifluoromethylphenyl)methaniminylnaphtho[1,2-b:4,3-b']dithiophene, **$\beta(1dd)_2$**

Conditions *i*: A 6-dram vial was massed with **$\beta(CHO)_2$** (23.1 mg, 0.05 mmol), deacidified CHCl₃ (to 10 mM NDT), and 4 Å molecular sieves. 3,5-bis(trifluoromethyl)aniline (0.020 mL, 0.13 mmol), Sc(OTf)₃ (5.0 mg, 0.01 mmol) and MeCN (5 % of CHCl₃) were added. The reaction vial was capped, inverted several times to mix, and left undisturbed overnight (>16 hours). Reaction was transferred into a clean 100 mL round bottom flask containing 1 mL triethylamine and concentrated to yield the crude product. **$\beta(1dd)_2$** was isolated by GPC as a yellow solid, 16.8 mg (38%).

Analysis **$\beta(1dd)_2$** : ¹H NMR (400 MHz, CDCl₃) δ 8.80 (s, 2H), 8.30 (s, 2H), 7.77 (s, 2H), 7.71 (s, 4H), 7.61 (s, 2H), 4.23 (t, *J* = 6.7 Hz, 4H), 1.94 (dt, *J* = 13.3, 6.7 Hz, 2H), 1.84 (q, *J* = 6.7 Hz, 4H), 1.04 (d, *J* = 6.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 155.4, 152.2, 149.8, 140.9, 135.7, 133.1, 132.8 (q, *J* = 33.6 Hz), 129.4, 122.3 (q, *J* = 273.2 Hz), 121.4 (d, *J* = 3.6 Hz), 119.6 (t, *J* = 3.3 Hz), 106.1, 67.8, 37.9, 25.3, 22.7; HRMS (APCI+) calcd for C₄₂H₃₅F₁₂N₂O₂S₂ (M+H)⁺ 891.1948, found 891.1954.

5.2 Yield Summation of **$\beta(1)_2$** Series

Derivative	Conditions <i>i</i> ScOTf ₃ , MeCN, CHCl ₃ , Mol. Sieves	Conditions <i>ii</i> Tol, AcOH, Δ
$\beta(1a)_2$	16%	13%
$\beta(1b)_2$	18%	—
$\beta(1c)_2$	21%	—
$\beta(1d)_2$	41%	5%
$\beta(1e)_2$	37%	—
$\beta(1bb)_2$	20%	34%
$\beta(1cc)_2$	12%	28%
$\beta(1dd)_2$	38%	—

Table D 1. Summary of isolated yields for the **$\beta(1)_2$** Series

5.3 NMR Spectra

5.3.1 5,6-bis(isopentyloxy)-2,9-di-(formyl)naphtho[1,2-*b*:4,3-*b'*]dithiophene, **$\beta(\text{CHO})_2$**

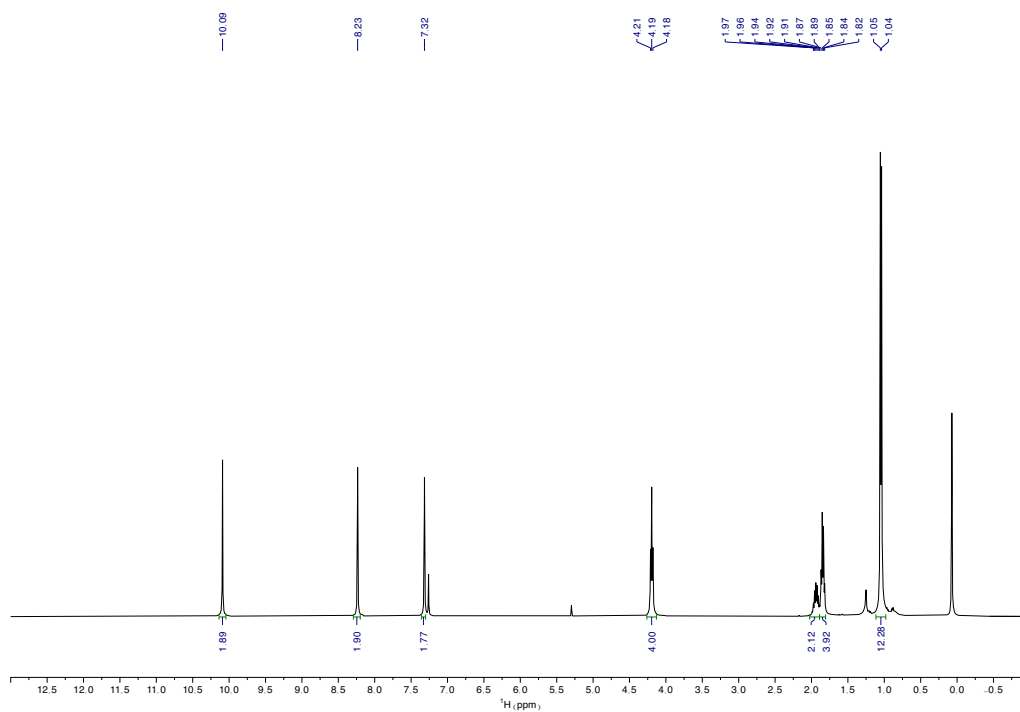


Figure D 2. ^1H NMR spectrum of **$\beta(\text{CHO})_2$** (CDCl_3 , 400 MHz, 298 K).

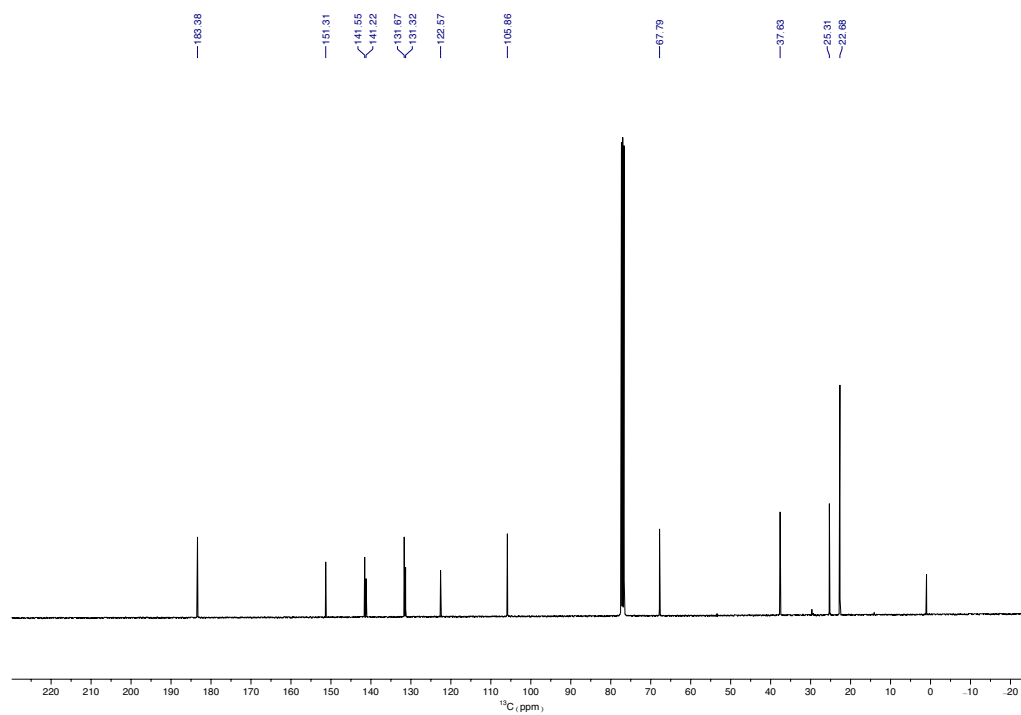


Figure D 3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\text{CHO})_2$ (CDCl_3 , 101 MHz, 298 K).

5.3.2 $\beta(1a)_2$ Series

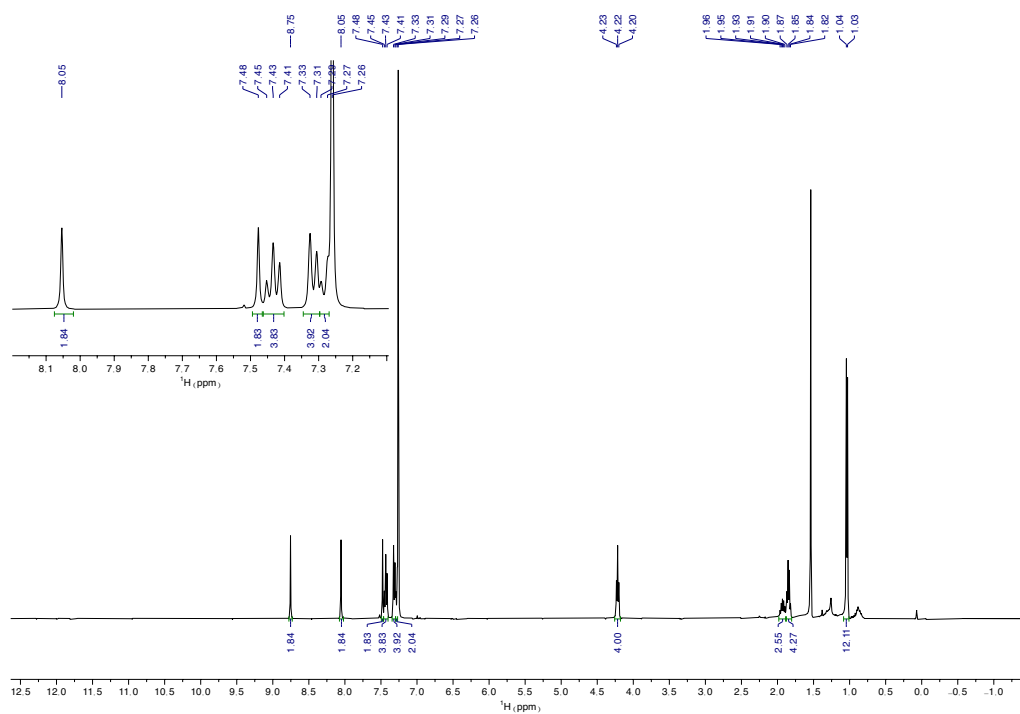


Figure D 4. ^1H NMR spectrum of $\beta(1a)_2$ (CDCl_3 , 400 MHz, 298 K).

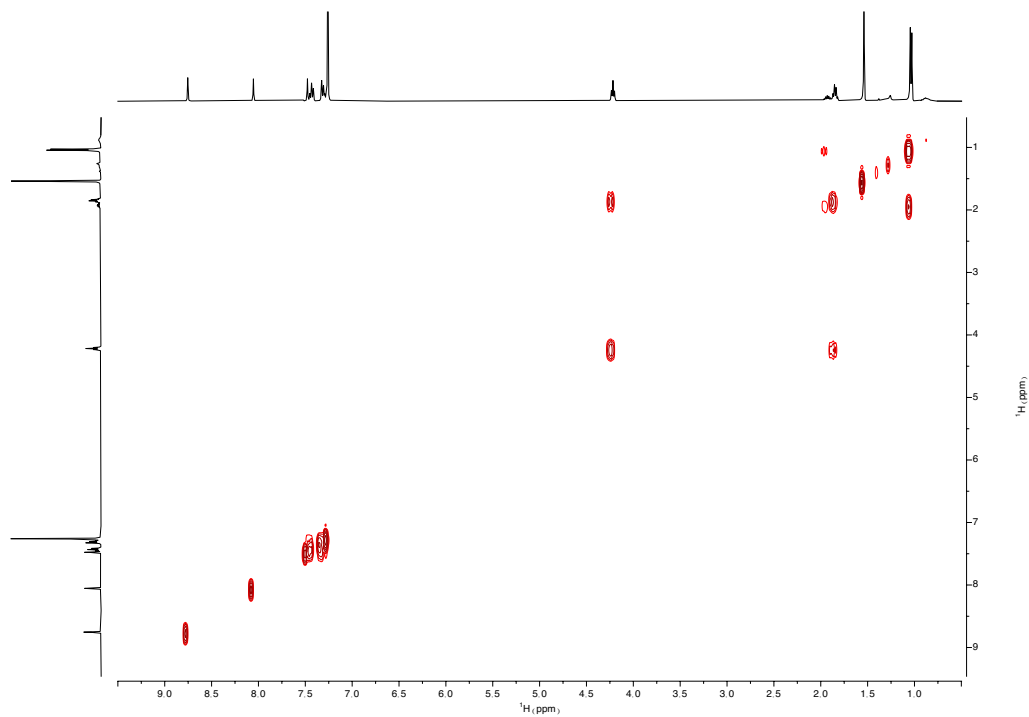


Figure D 5. ^1H - ^1H COSY spectrum of $\beta(1a)_2$ (CDCl_3 , 400 MHz, 298 K).

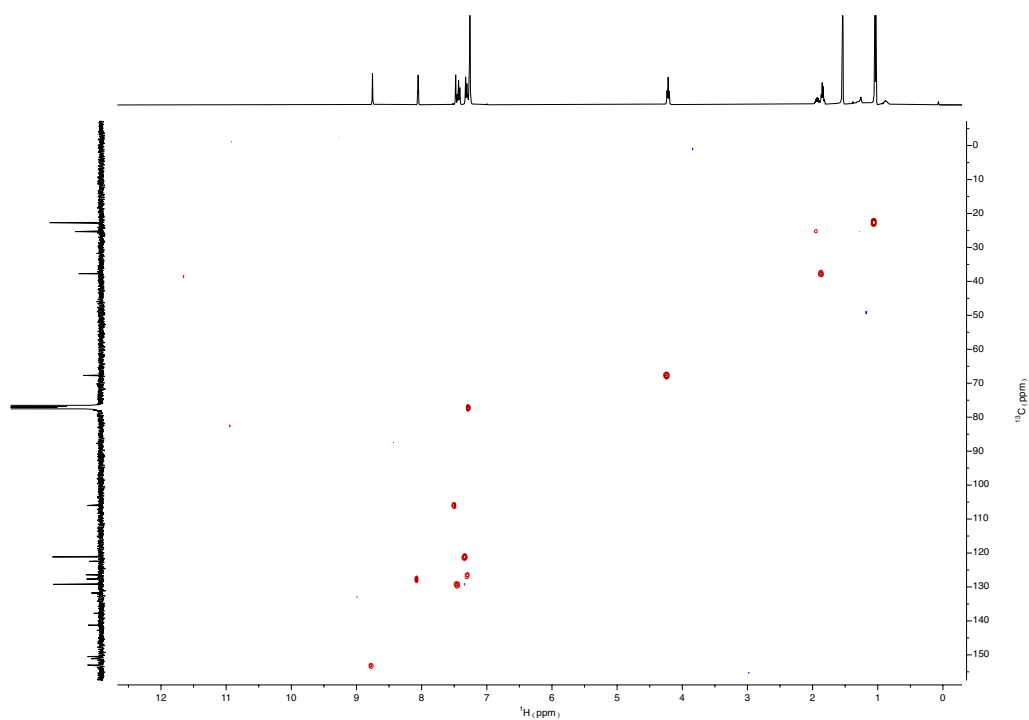


Figure D 6. ^1H - ^{13}C HSQC spectrum of $\beta(1a)_2$ (CDCl_3 , 400 MHz, 298 K).

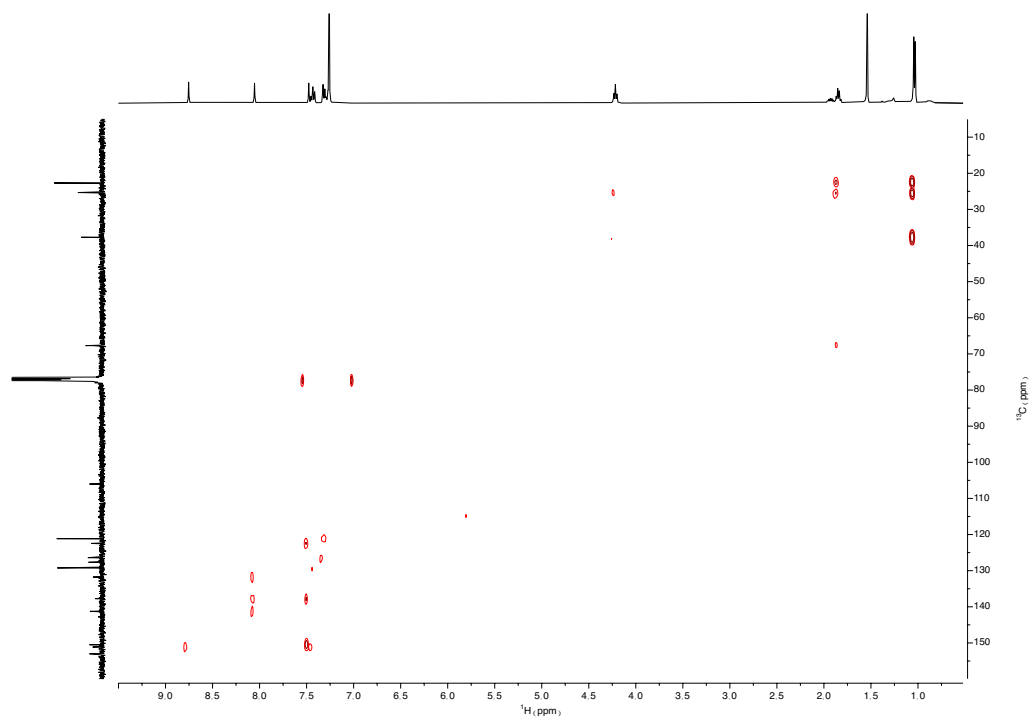


Figure D 7. ^1H - ^{13}C HMBC spectrum of $\beta(1\text{a})_2$ (CDCl_3 , 400 MHz, 298 K).

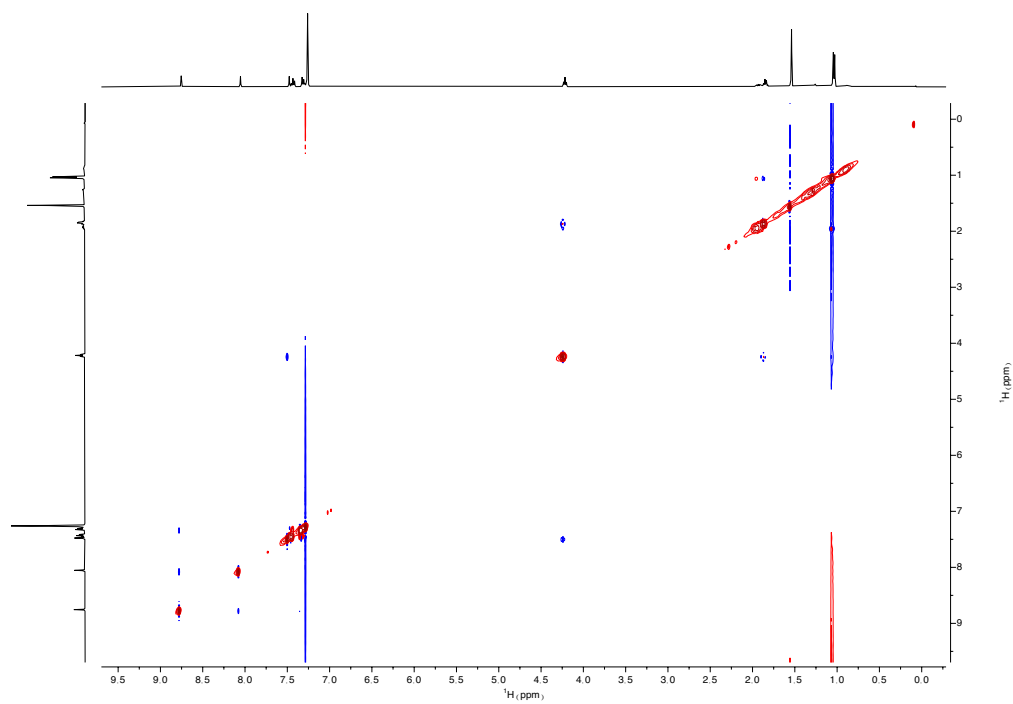


Figure D 8. ^1H - ^1H NOESY spectrum of $\beta(1\text{a})_2$ (CDCl_3 , 400 MHz, 298 K).

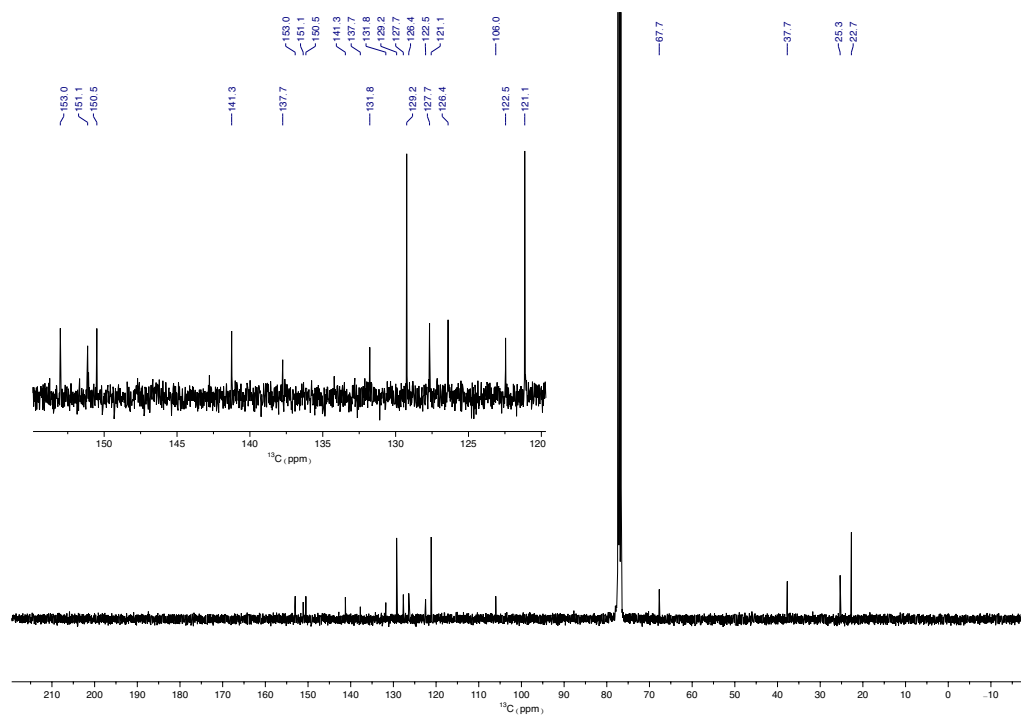
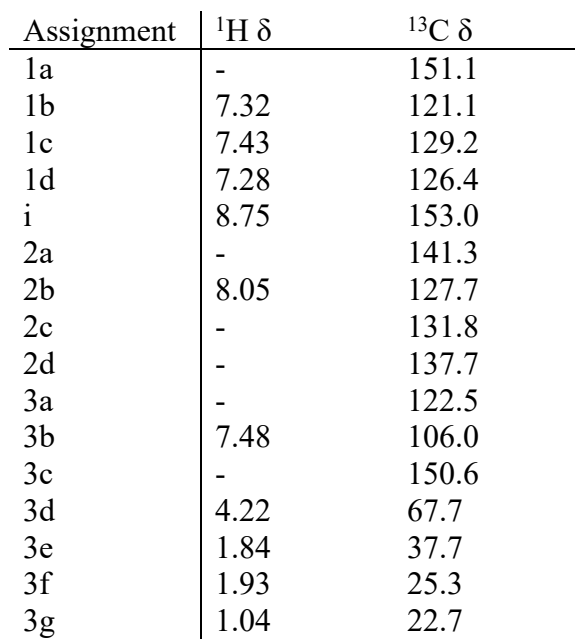


Figure D 9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(1a)_2$ (CDCl_3 , 101 MHz, 298 K).



351

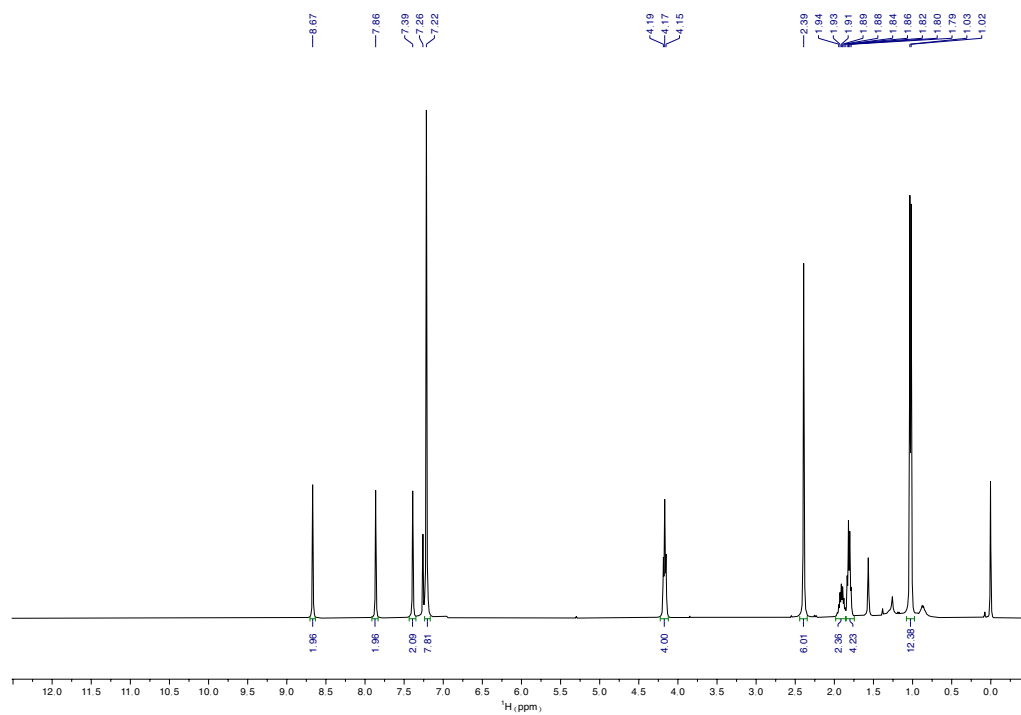


Figure D 11. ¹H NMR spectrum of $\beta(1b)_2$ (CDCl₃, 400 MHz, 298 K).

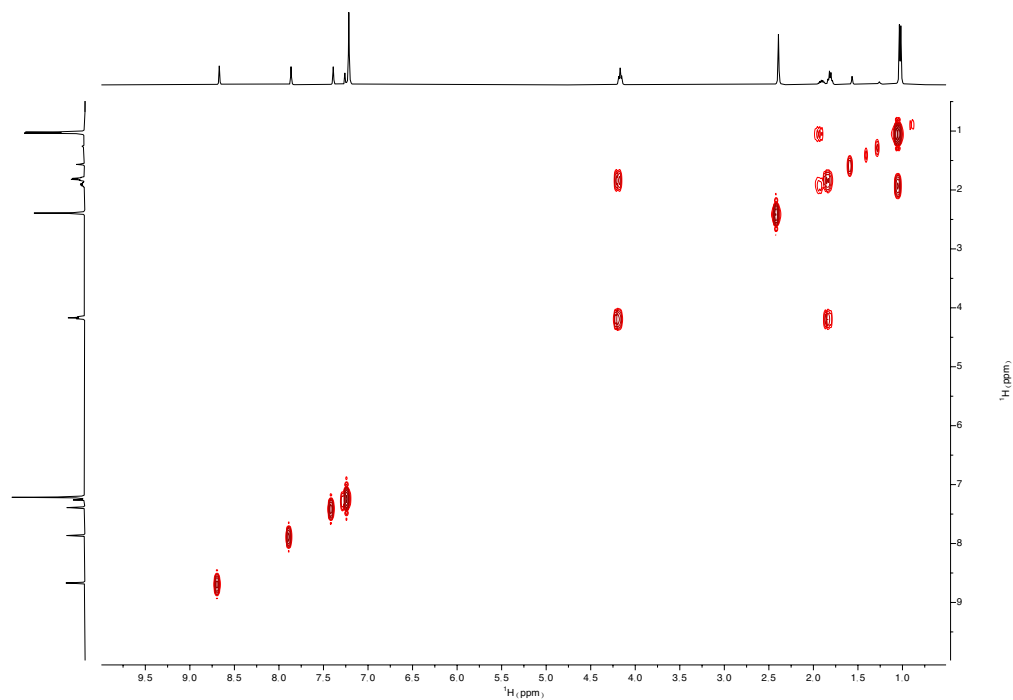


Figure D 12. ¹H-¹H COSY spectrum of $\beta(1b)_2$ (CDCl₃, 400 MHz, 298 K).

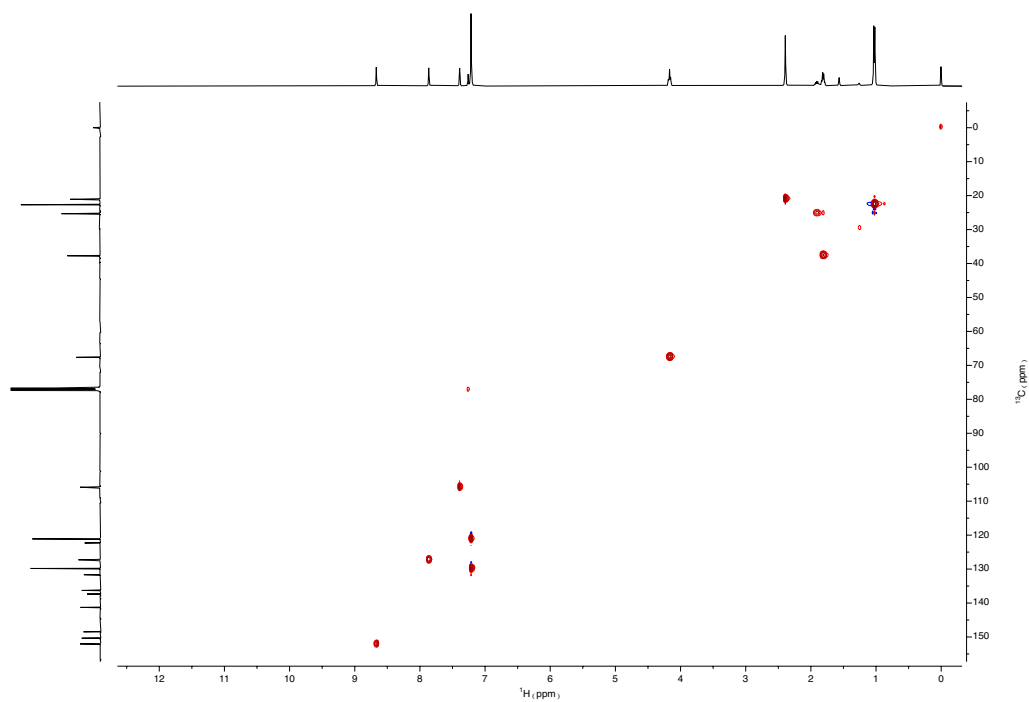


Figure D 13. ^1H - ^{13}C HSQC spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K).

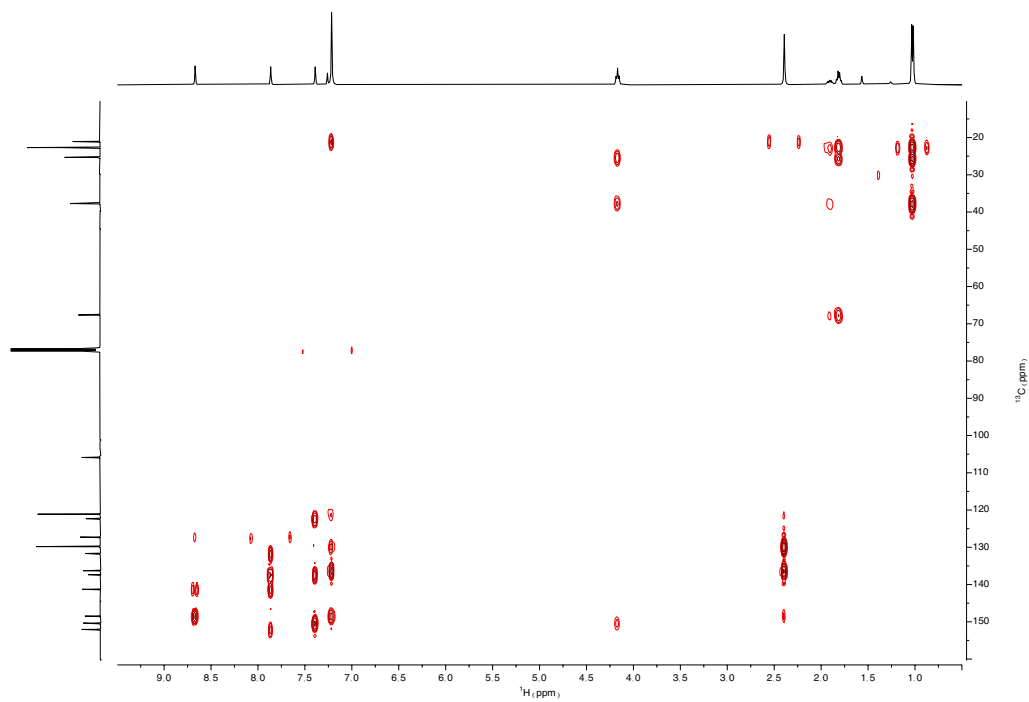


Figure D 14. ^1H - ^{13}C HMBC spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K).

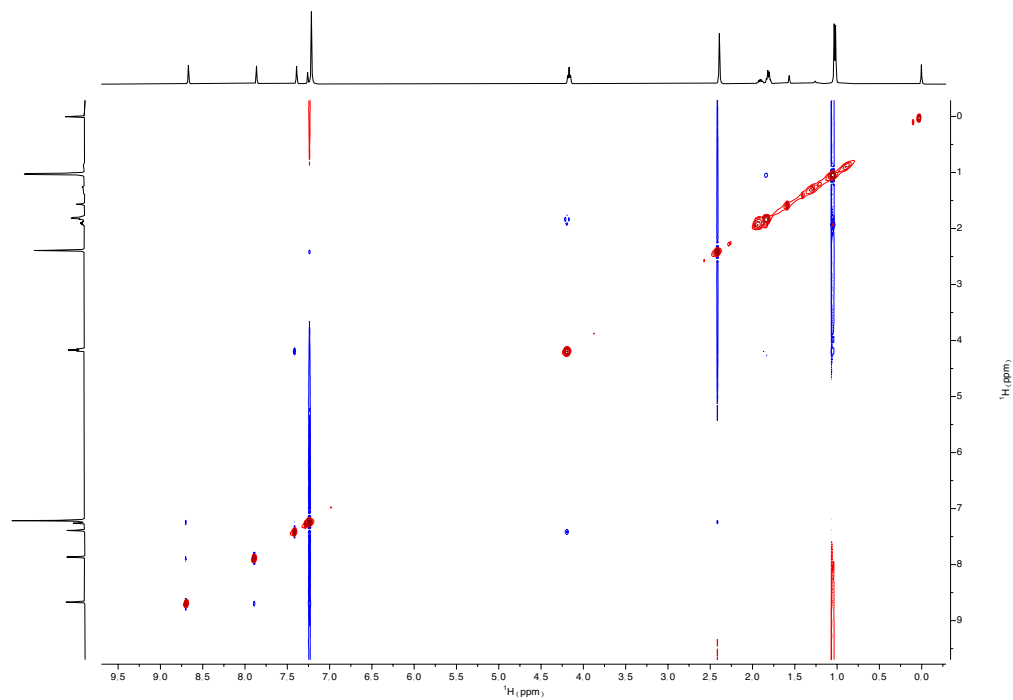


Figure D 15. ^1H - ^1H NOESY spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 400 MHz, 298 K).

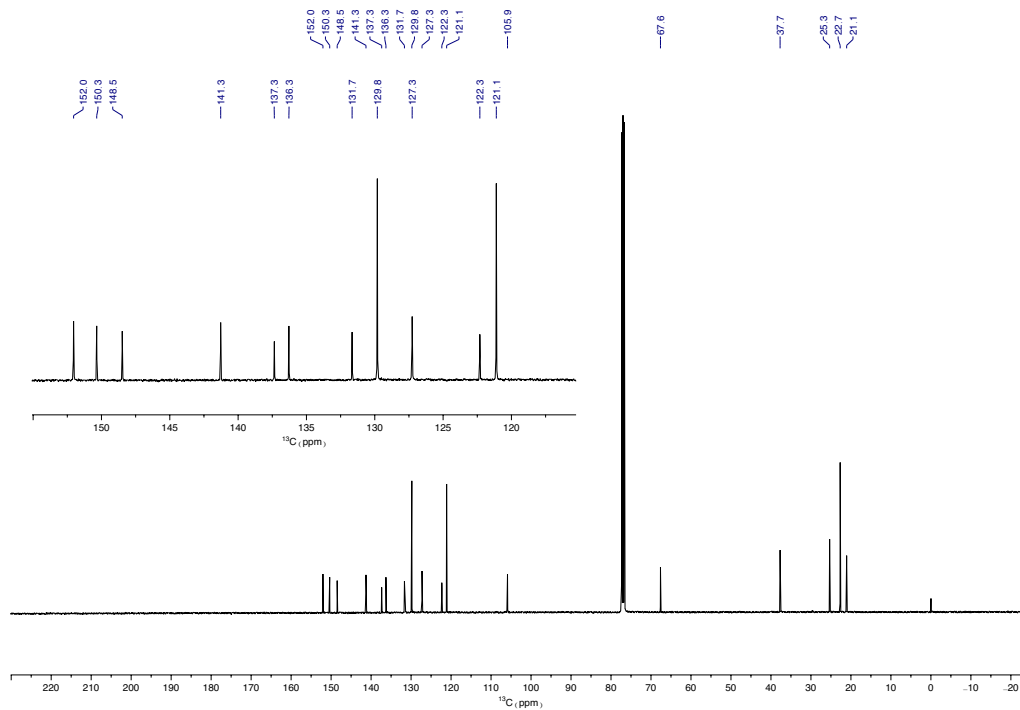
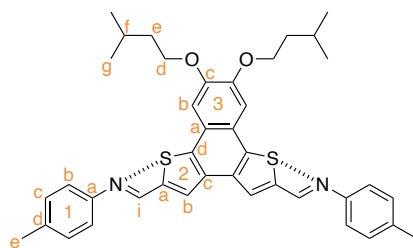


Figure D 16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\mathbf{1b})_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	148.5
1b	7.22	121.1
1c	7.22	129.8
1d	-	136.3
1e	2.39	21.1
i	8.67	152.0
2a	-	141.3
2b	7.86	127.3
2c	-	131.7
2d	-	137.3
3a	-	122.3
3b	7.39	105.9
3c	-	150.3
3d	4.17	67.6
3e	1.81	37.7
3f	1.91	25.3
3g	1.03	22.7

Figure D 17. **$\beta(1b)_2$** with assignment of ^1H and ^{13}C resonances.

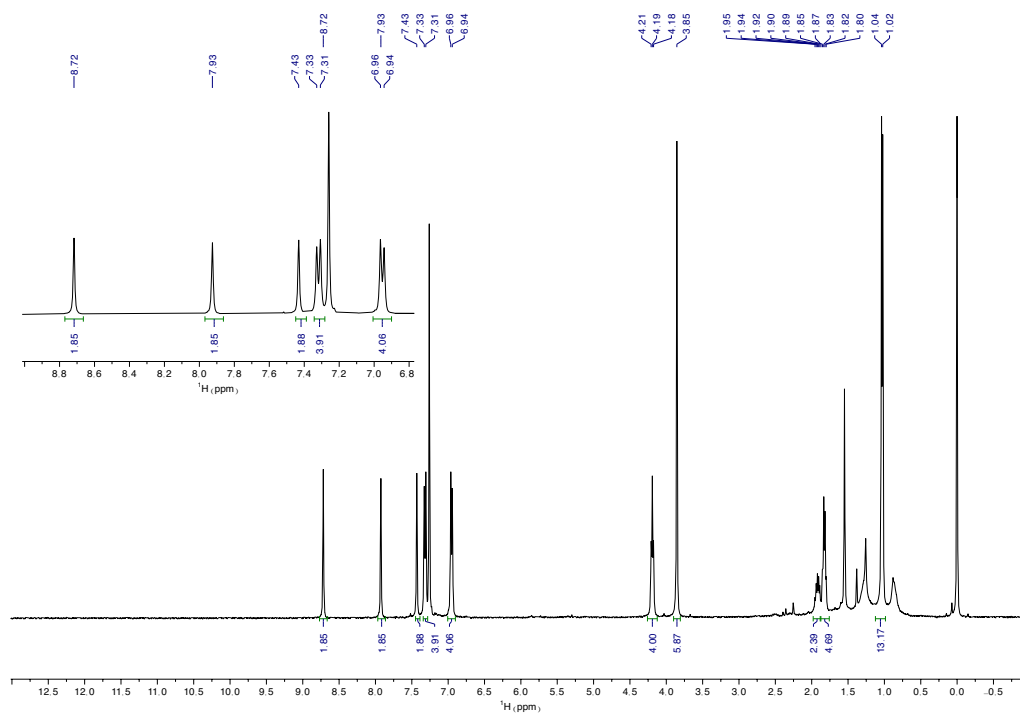


Figure D 18. ¹H NMR spectrum of $\beta(1c)_2$ (CDCl₃, 400 MHz, 298 K).

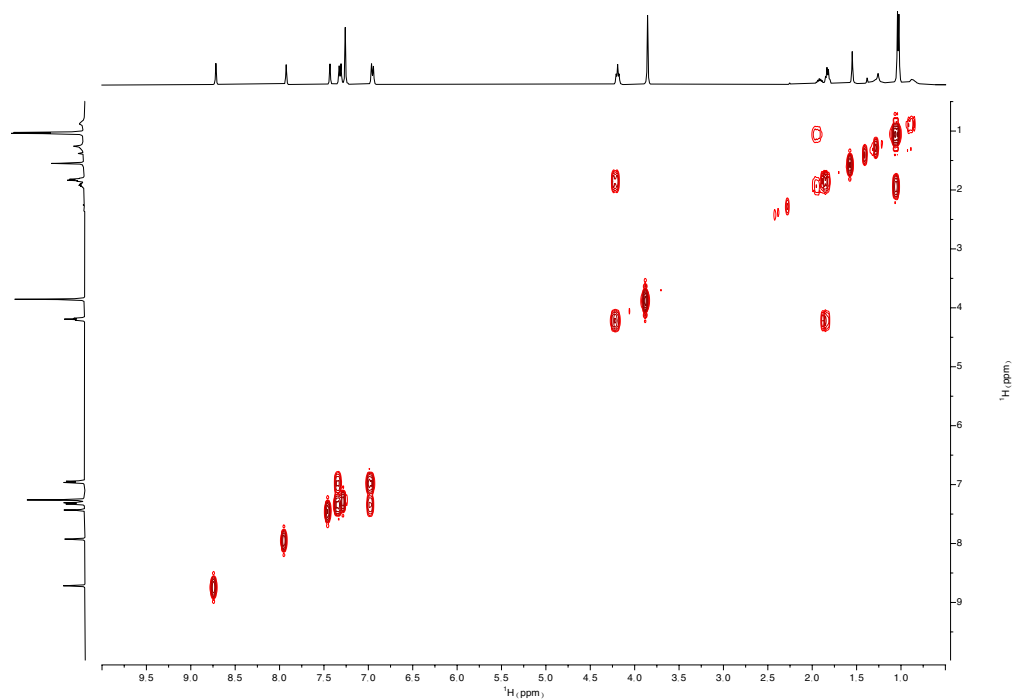


Figure D 19. ¹H-¹H COSY spectrum of $\beta(1c)_2$ (CDCl₃, 400 MHz, 298 K).

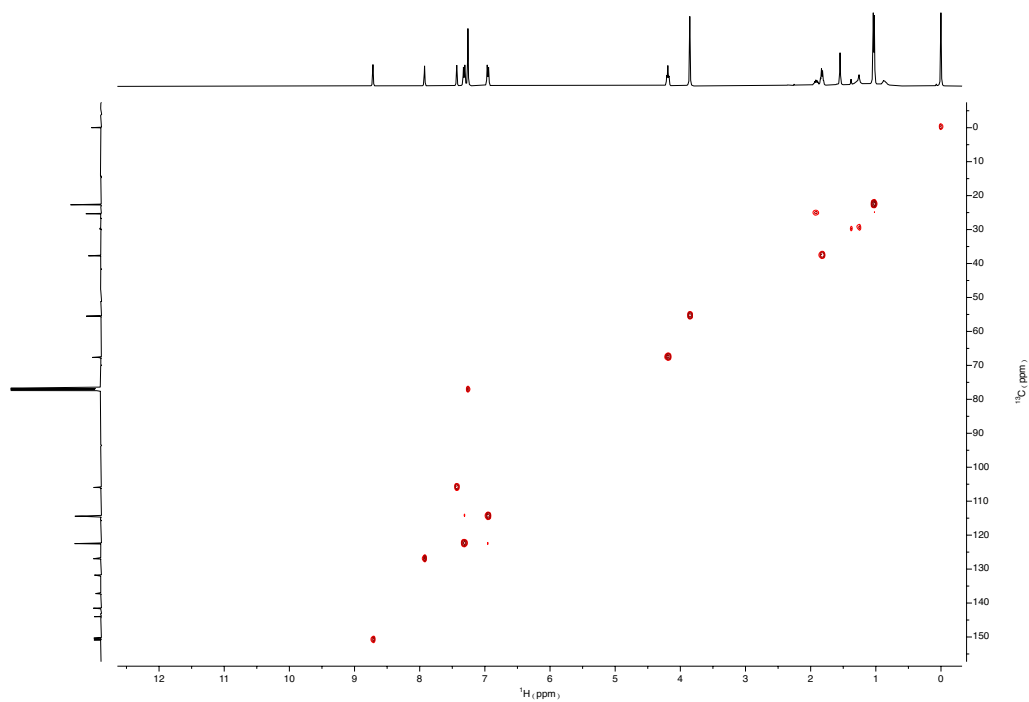


Figure D 20. ^1H - ^{13}C HSQC spectrum of $\beta(1\text{c})_2$ (CDCl_3 , 400 MHz, 298 K).

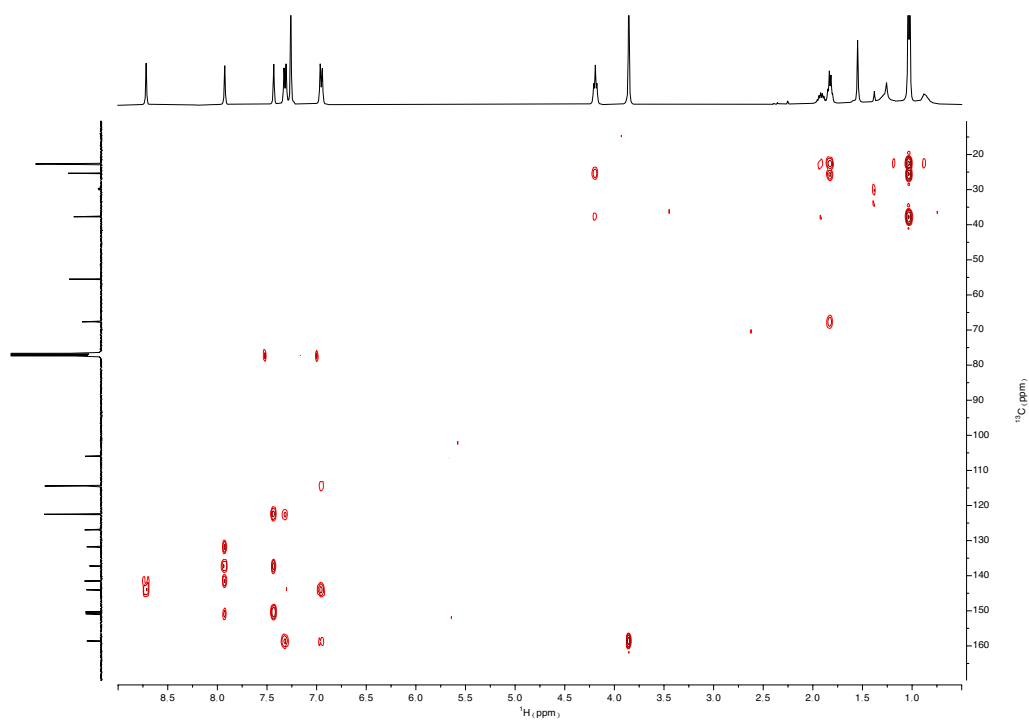


Figure D 21. ^1H - ^{13}C HMBC spectrum of $\beta(1\text{c})_2$ (CDCl_3 , 400 MHz, 298 K).

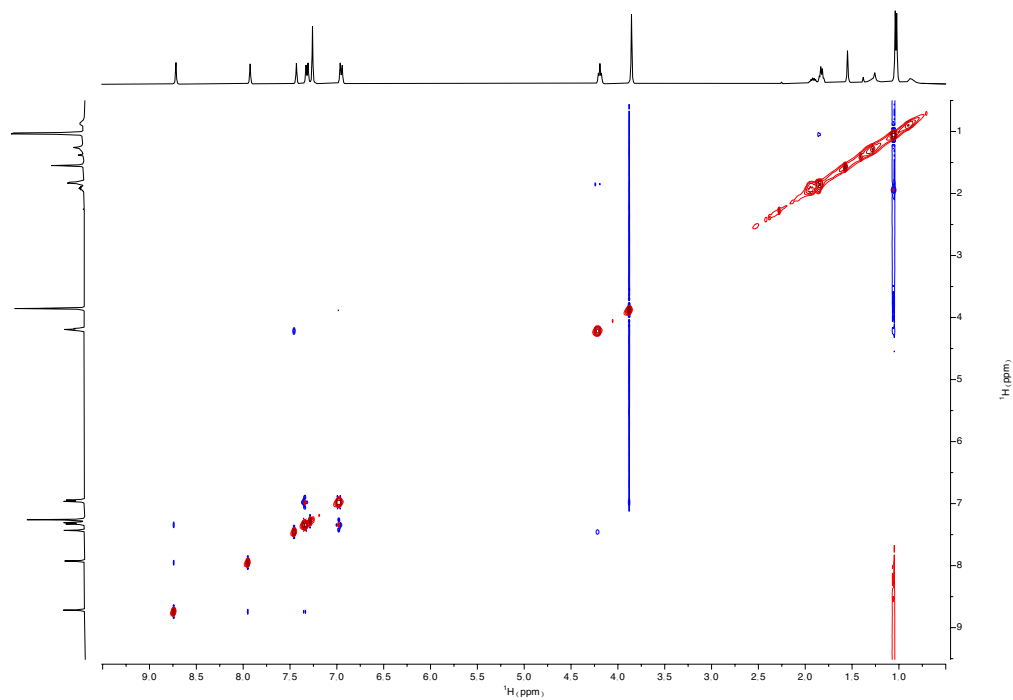


Figure D 22. ^1H - ^1H NOESY spectrum of $\beta(\mathbf{1c})_2$ (CDCl_3 , 400 MHz, 298 K).

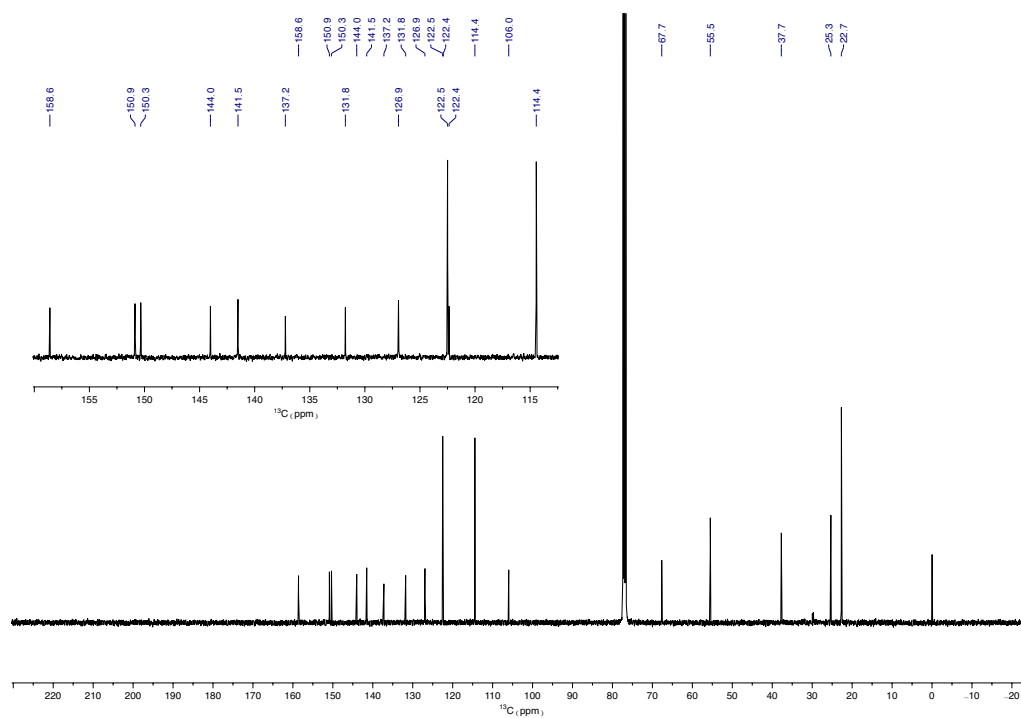
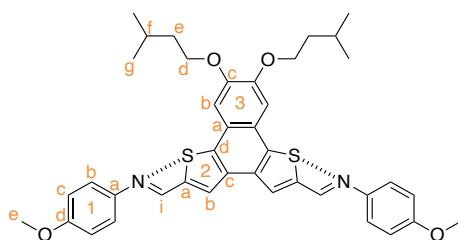


Figure D 23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\mathbf{1c})_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	144.0
1b	7.32	122.5
1c	6.95	114.4
1d	-	158.6
1e	3.85	55.5
i	8.72	150.9
2a	-	141.5
2b	7.93	126.9
2c	-	131.8
2d	-	137.2
3a	-	122.4
3b	7.43	106.0
3c	-	150.3
3d	4.19	67.7
3e	1.83	37.7
3f	1.91	25.3
3g	1.03	22.7

Figure D 24. $\beta(1\text{c})_2$ with assignment of ^1H and ^{13}C resonances.

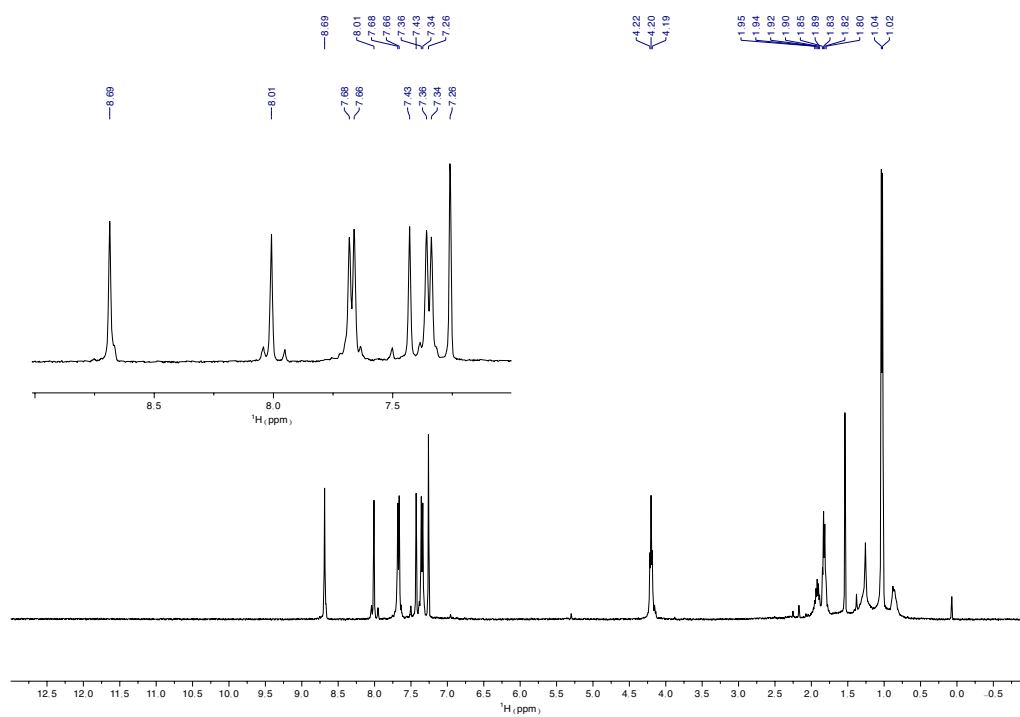


Figure D 25. ^1H NMR spectrum of $\beta(\mathbf{1d})_2$ (CDCl_3 , 400 MHz, 298 K).

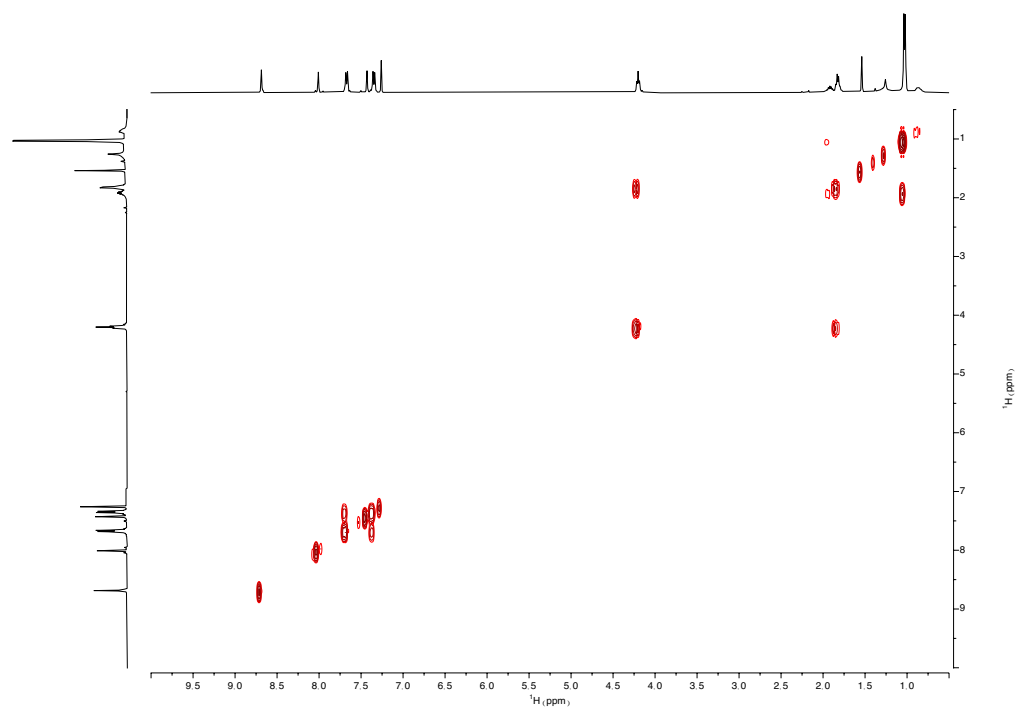


Figure D 26. ^1H - ^1H COSY spectrum of $\beta(\mathbf{1d})_2$ (CDCl_3 , 400 MHz, 298 K).

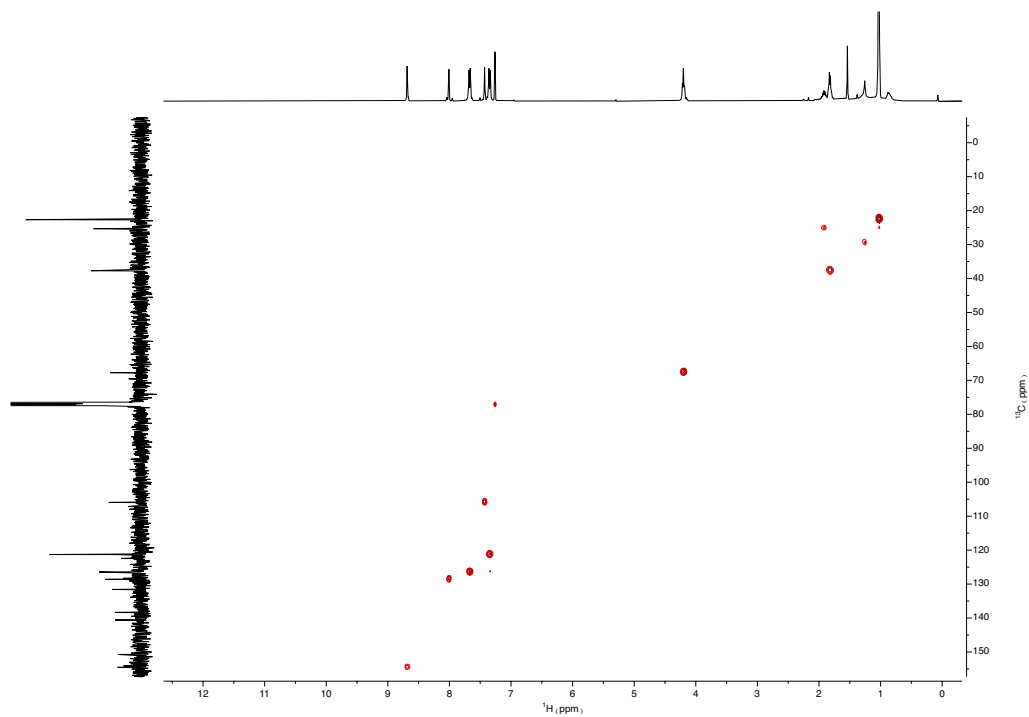


Figure D 27. ^1H - ^{13}C HSQC spectrum of $\beta(1\text{d})_2$ (CDCl_3 , 400 MHz, 298 K).

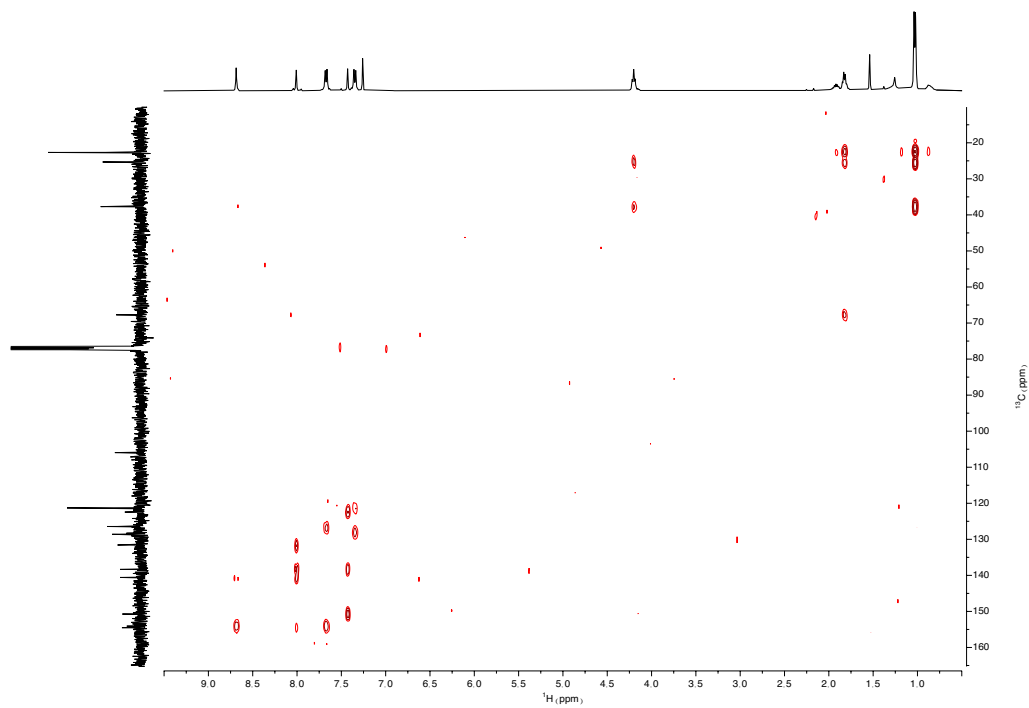


Figure D 28. ^1H - ^{13}C HMBC spectrum of $\beta(1\text{d})_2$ (CDCl_3 , 400 MHz, 298 K).

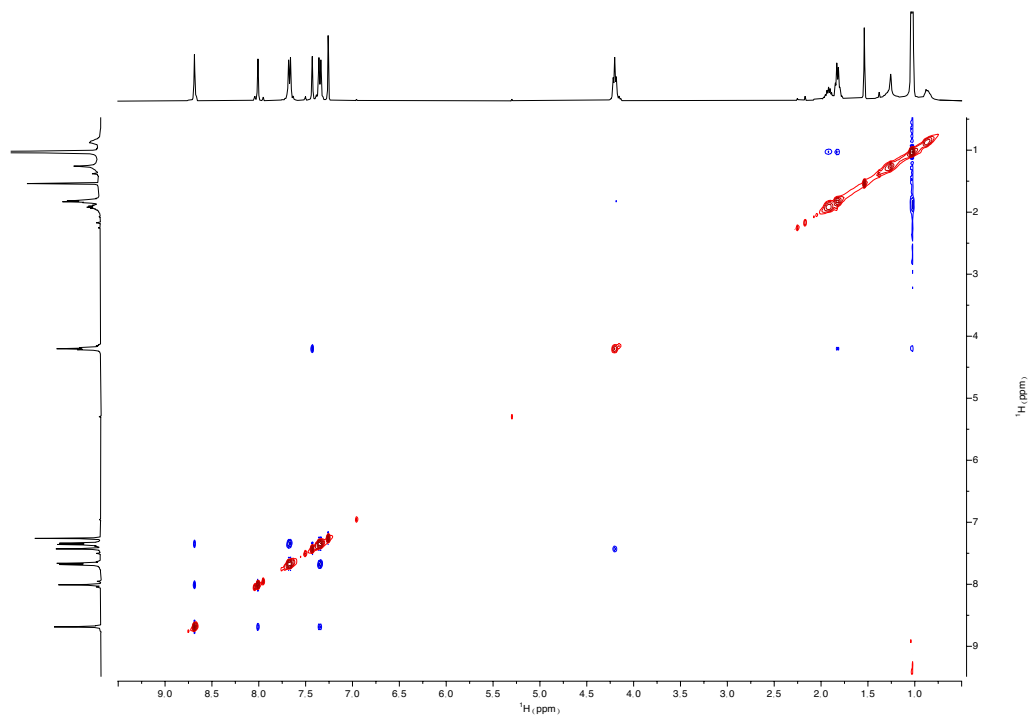


Figure D 29. ^1H - ^1H NOESY spectrum of $\beta(\mathbf{1d})_2$ (CDCl_3 , 400 MHz, 298 K).

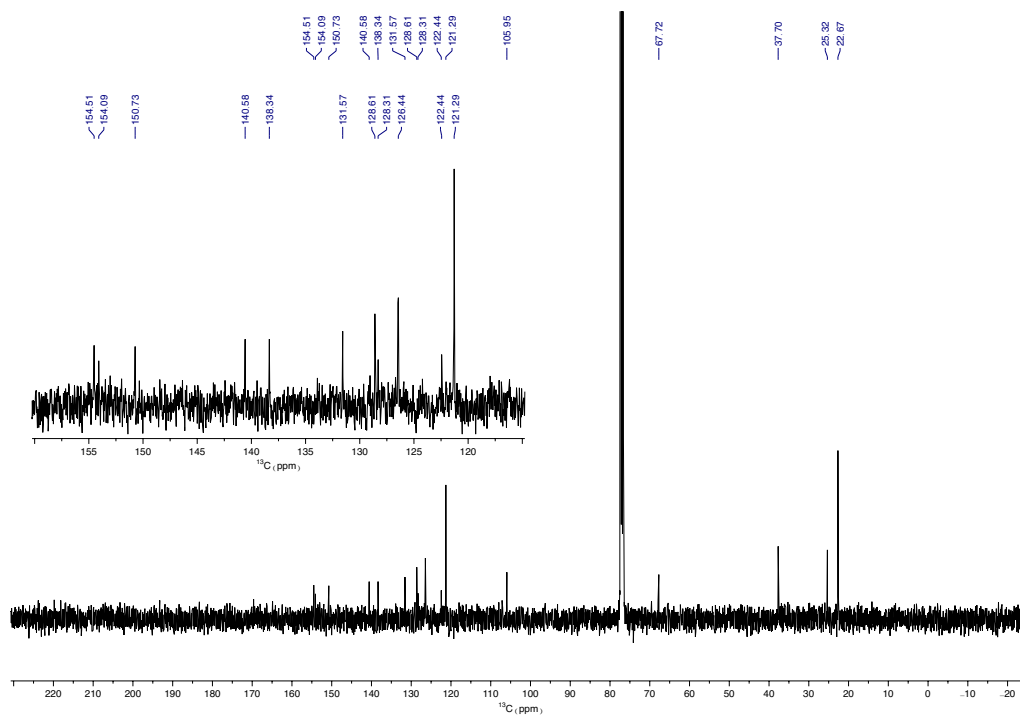
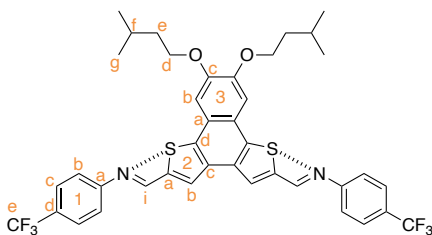


Figure D 30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\mathbf{1d})_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	154.1
1b	7.35	121.3
1c	7.67	126.5
1d	-	*
1e	-	*
i	8.69	154.5
2a	-	140.6
2b	8.01	128.6
2c	-	131.6
2d	-	138.3
3a	-	122.4
3b	7.43	105.9
3c	-	150.7
3d	4.20	67.7
3e	1.82	37.7
3f	1.92	25.3
3g	1.03	22.7

Figure D 31. **$\beta(1d)_2$** with assignment of ^1H and ^{13}C resonances. *Signals are weak and not observed at this concentration. A weak signal at 128.3 ppm is likely part of the quartet for the 1d ^{13}C resonance, but the remaining signals are not resolved.

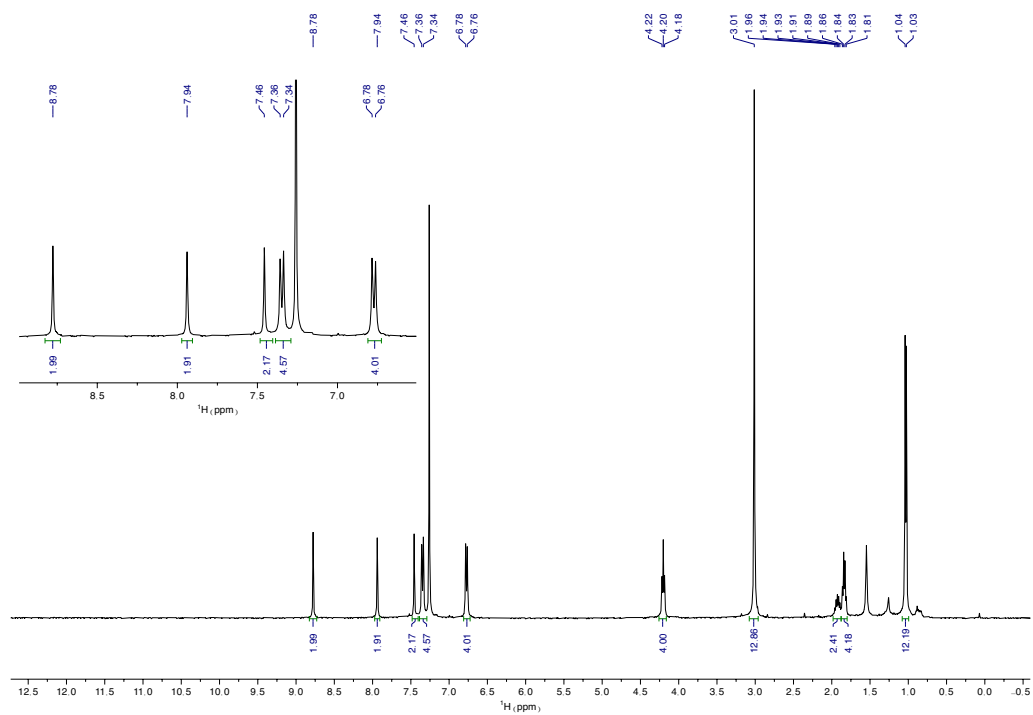


Figure D 32. ¹H NMR spectrum of $\beta(1e)_2$ (CDCl₃, 400 MHz, 298 K).

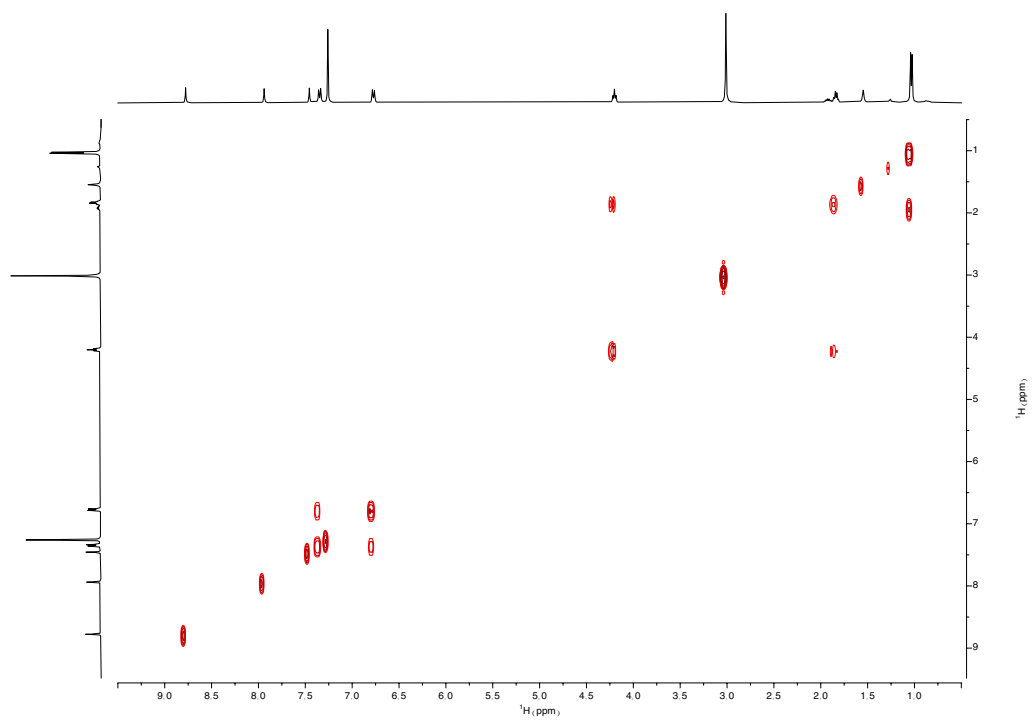


Figure D 33. ¹H-¹H COSY spectrum of $\beta(1e)_2$ (CDCl₃, 400 MHz, 298 K).

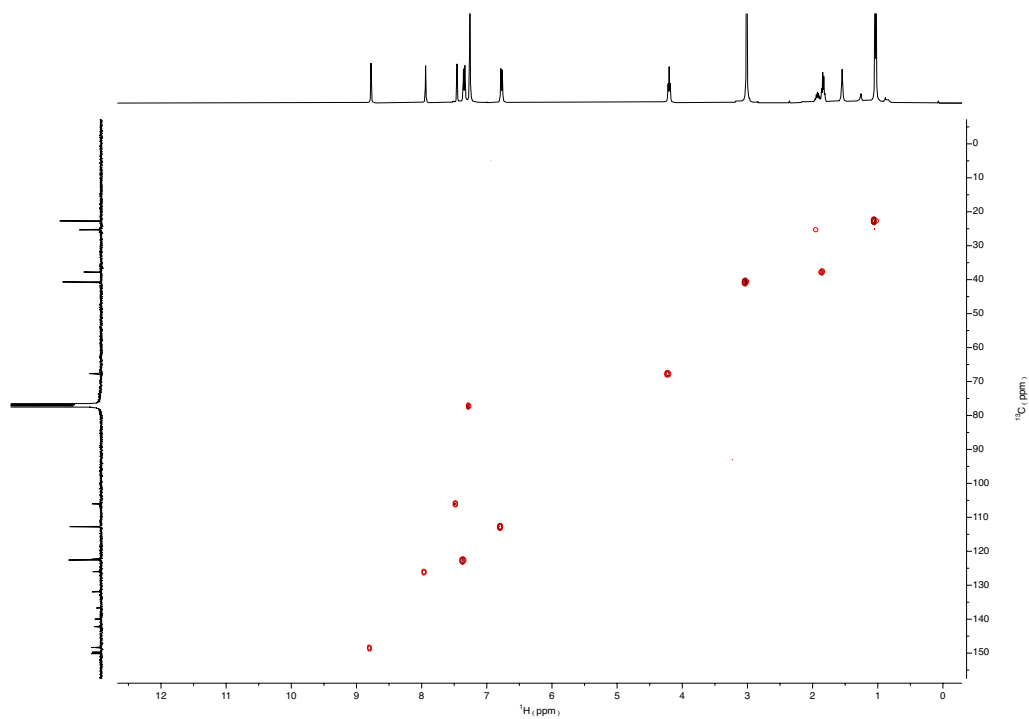


Figure D 34. ^1H - ^{13}C HSQC spectrum of **$\beta(1e)_2$** (CDCl_3 , 400 MHz, 298 K).

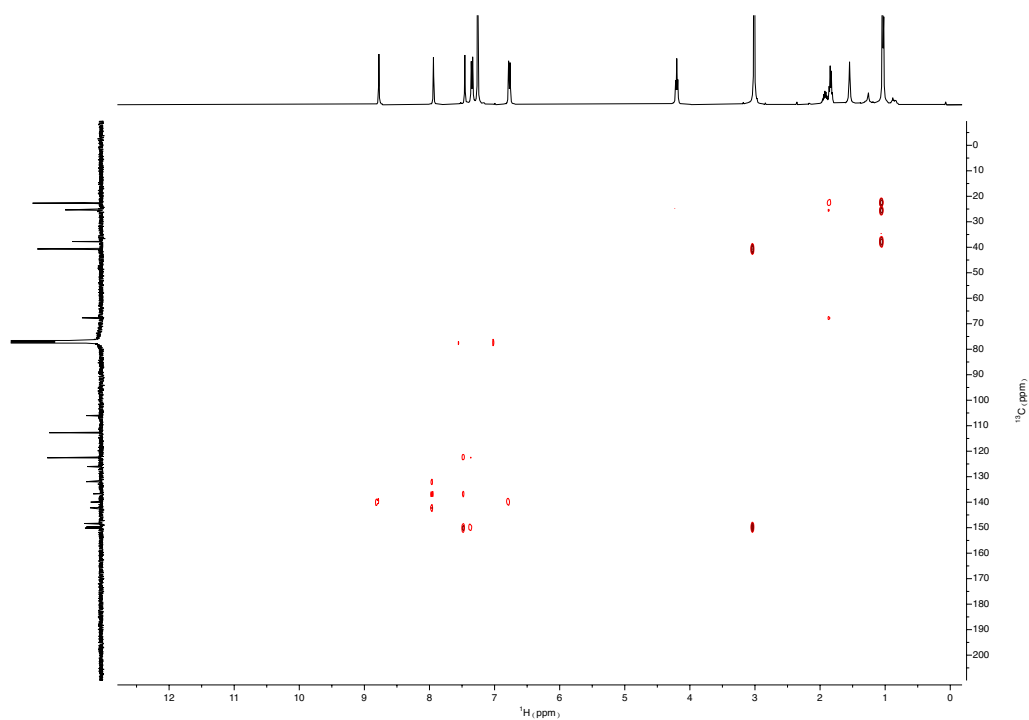


Figure D 35. ^1H - ^{13}C HMBC spectrum of **$\beta(1e)_2$** (CDCl_3 , 400 MHz, 298 K).

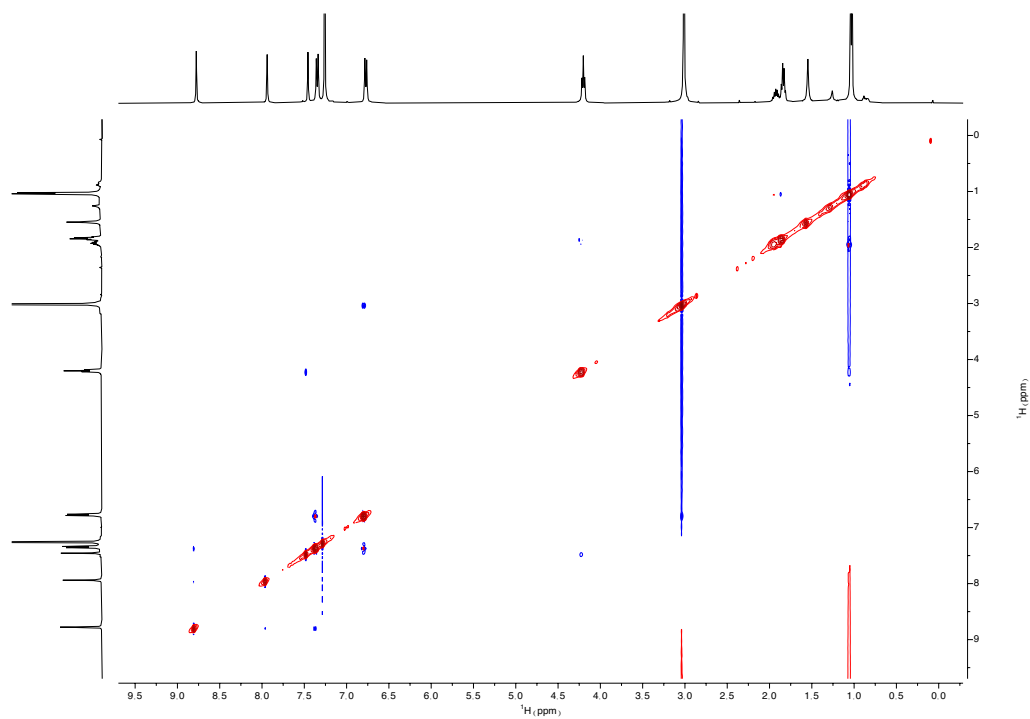


Figure D 36. ^1H - ^1H NOESY spectrum of $\beta(\mathbf{1e})_2$ (CDCl_3 , 400 MHz, 298 K).

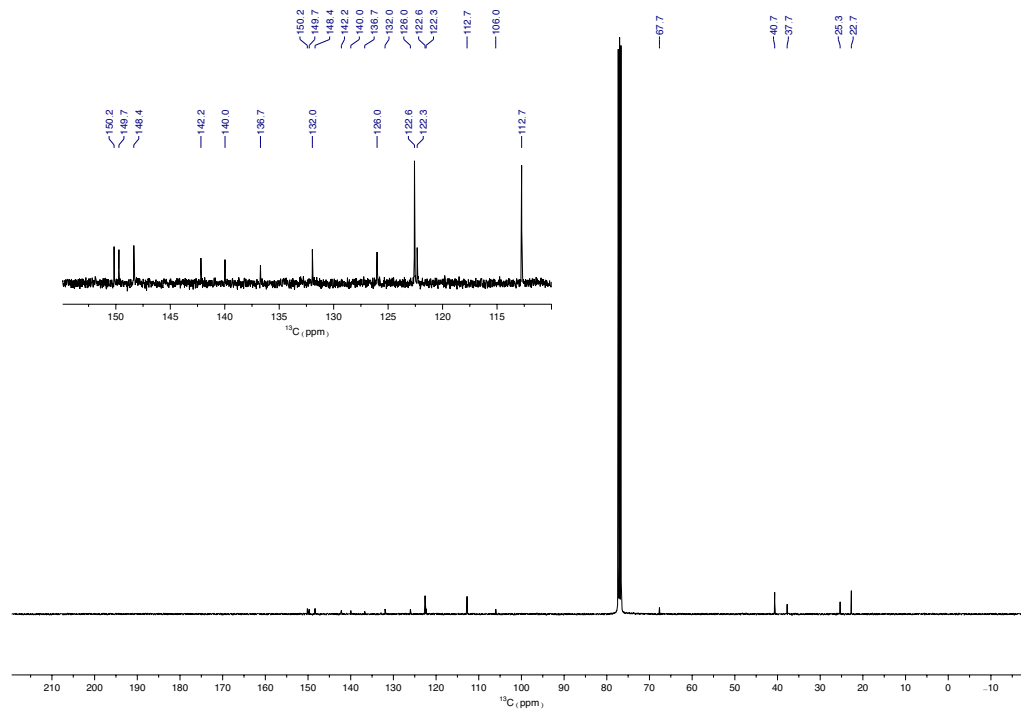
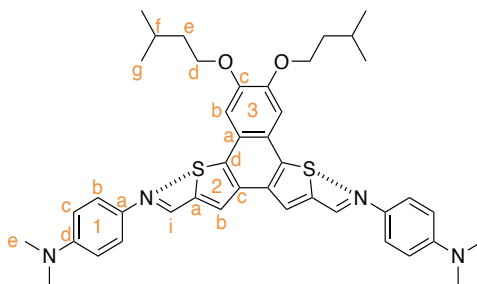


Figure D 37. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\mathbf{1e})_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	$^1\text{H } \delta$	$^{13}\text{C } \delta$
1a	-	140.0
1b	7.35	122.6
1c	6.77	112.7
1d	-	149.7
1e	3.01	40.7
i	8.78	148.4
2a	-	142.2
2b	7.94	126.0
2c	-	132.0
2d	-	136.7
3a	-	122.3
3b	7.46	106.0
3c	-	150.2
3d	4.20	67.7
3e	1.84	37.7
3f	1.93	25.3
3g	1.03	22.7

Figure D 38. $\beta(1e)_2$ with assignment of ^1H and ^{13}C resonances.

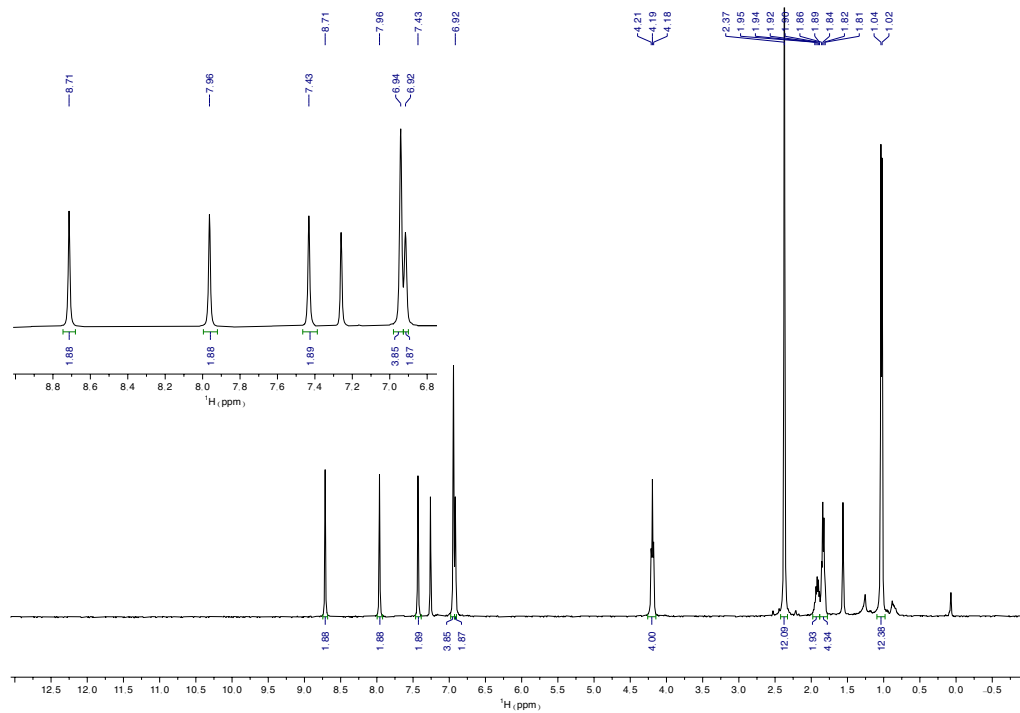


Figure D 39. ¹H NMR spectrum of $\beta(1bb)_2$ (CDCl₃, 400 MHz, 298 K).

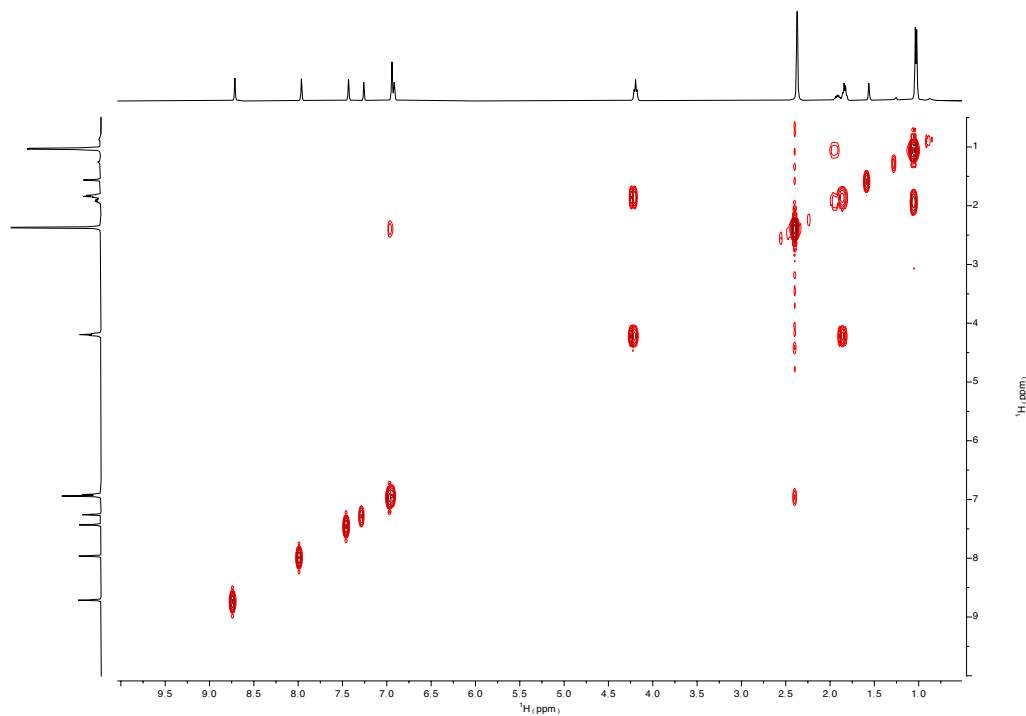


Figure D 40. ¹H-¹H COSY spectrum of $\beta(1bb)_2$ (CDCl₃, 400 MHz, 298 K).

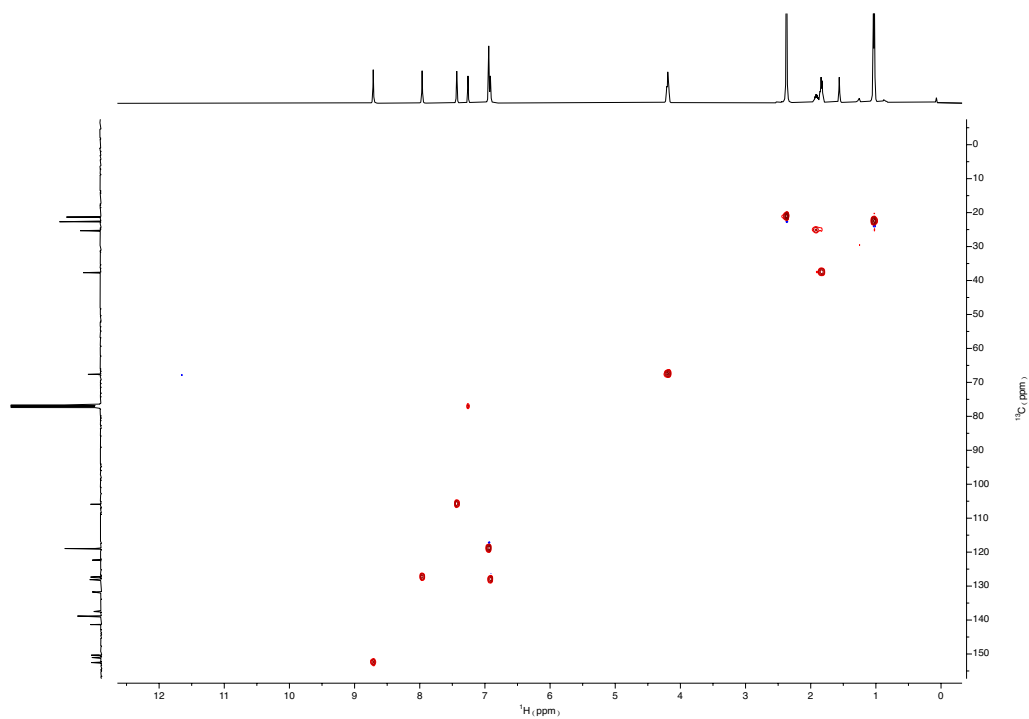


Figure D 41. ^1H - ^{13}C HSQC spectrum of $\beta(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K).

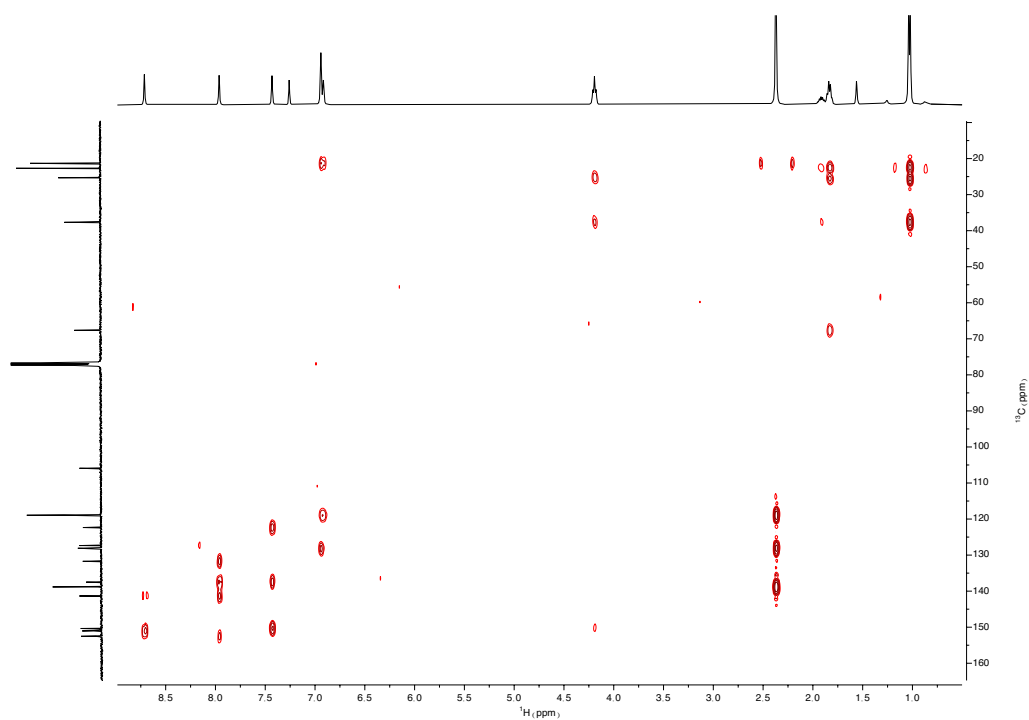


Figure D 42. ^1H - ^{13}C HMBC spectrum of $\beta(1\text{bb})_2$ (CDCl_3 , 400 MHz, 298 K).

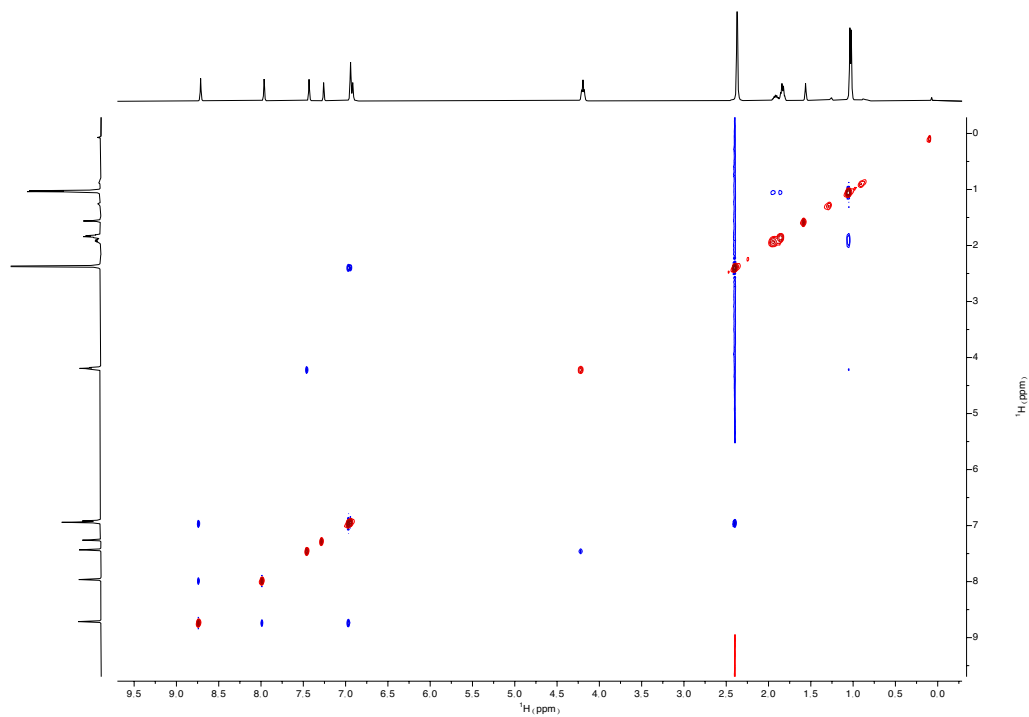


Figure D 43. ^1H - ^1H NOESY spectrum of $\beta(\mathbf{1bb})_2$ (CDCl_3 , 400 MHz, 298 K).

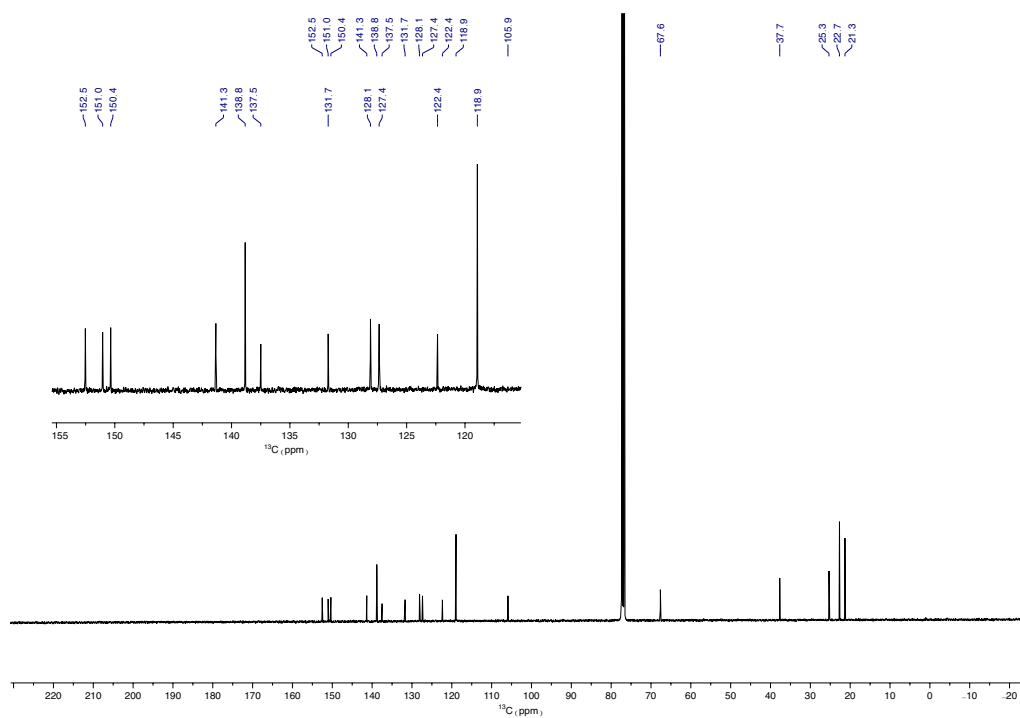
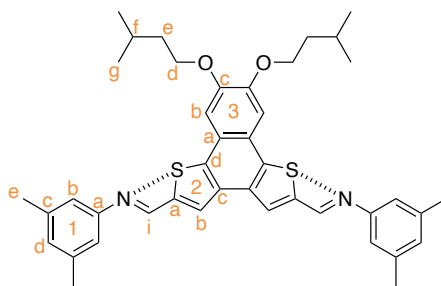


Figure D 44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\mathbf{1bb})_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	¹ H δ	¹³ C δ
1a	-	151.0
1b	6.94	118.9
1c	-	138.8
1d	6.92	128.1
1e	2.37	21.3
i	8.71	152.5
2a	-	141.3
2b	7.96	127.4
2c	-	131.7
2d	-	137.5
3a	-	122.4
3b	7.43	105.9
3c	-	150.4
3d	4.19	67.6
3e	1.83	37.7
3f	1.92	25.3
3g	1.03	22.7

Figure D 45. **β(1bb)₂** with assignment of ¹H and ¹³C resonances

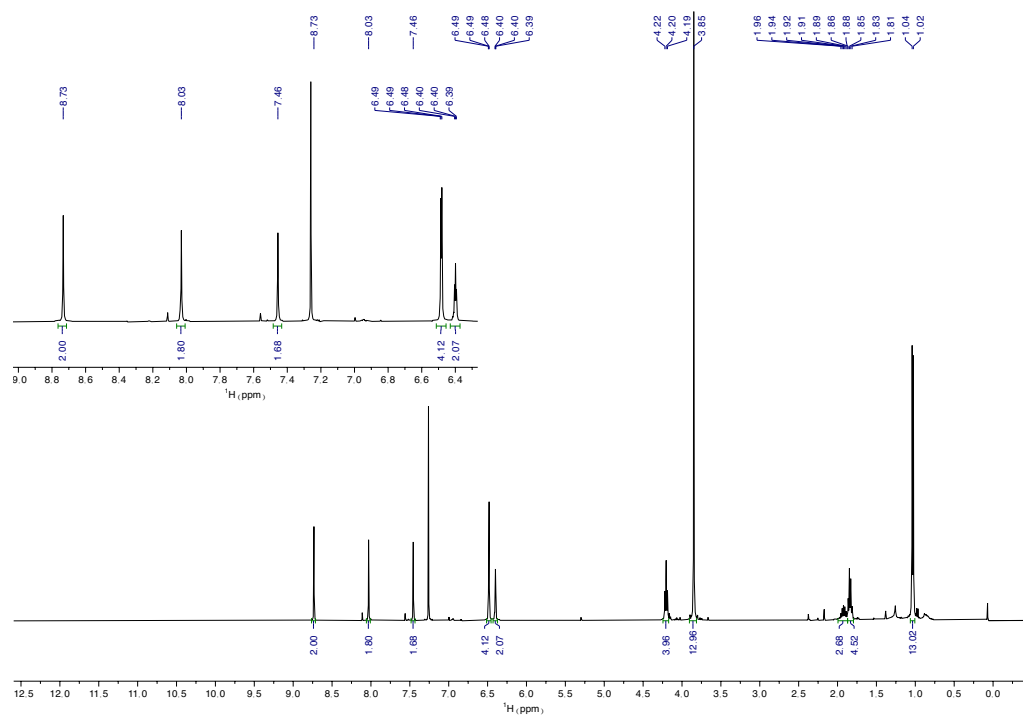


Figure D 46. ¹H NMR spectrum of $\beta(1cc)_2$ (CDCl₃, 400 MHz, 298 K).

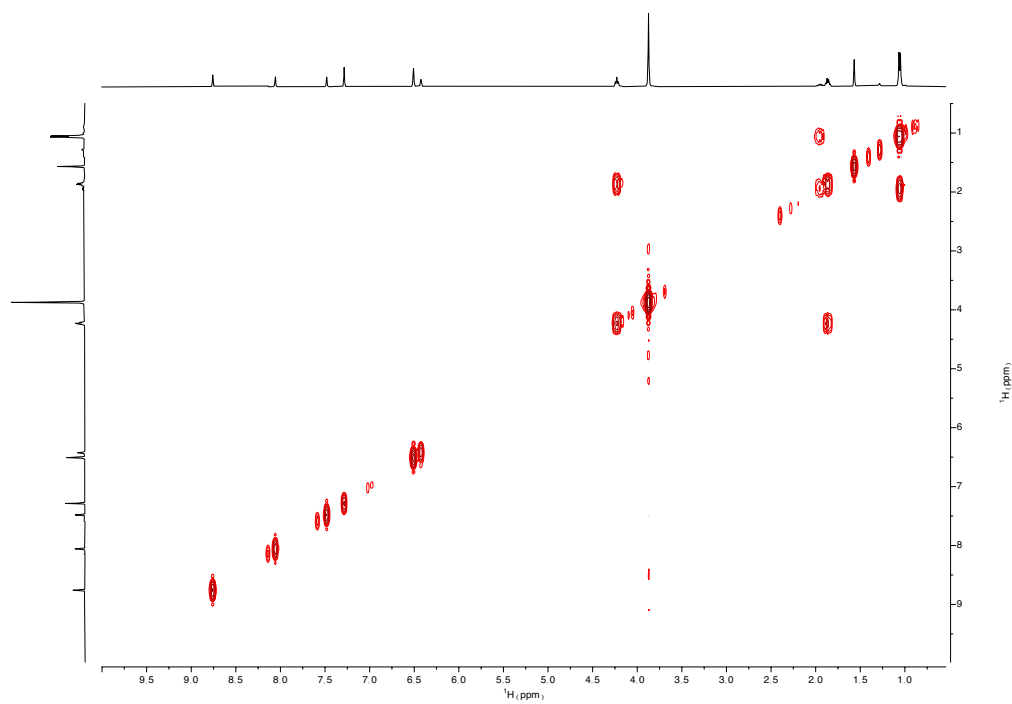


Figure D 47. ¹H-¹H COSY spectrum of $\beta(1cc)_2$ (CDCl₃, 400 MHz, 298 K).

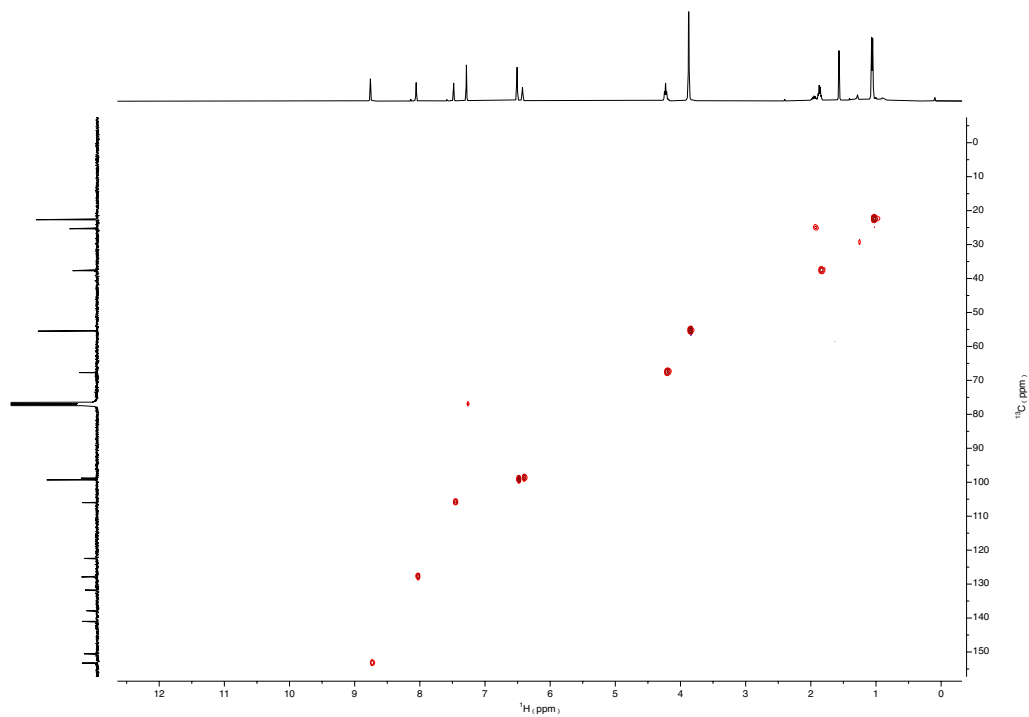


Figure D 48. ^1H - ^{13}C HSQC spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 400 MHz, 298 K).

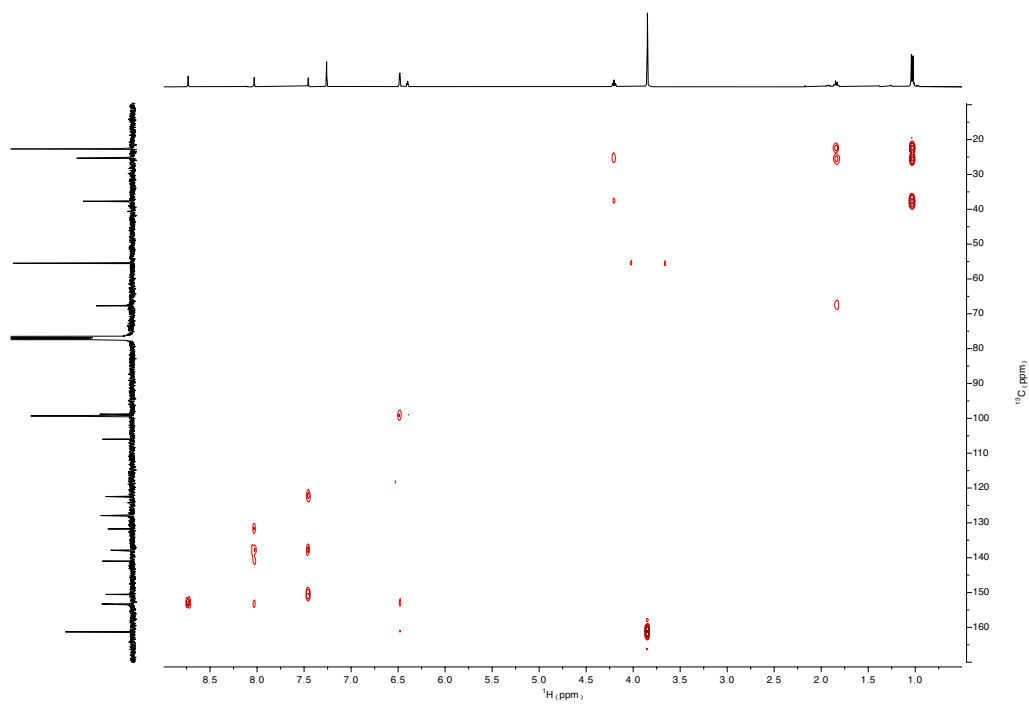


Figure D 49. ^1H - ^{13}C HMBC spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 400 MHz, 298 K).

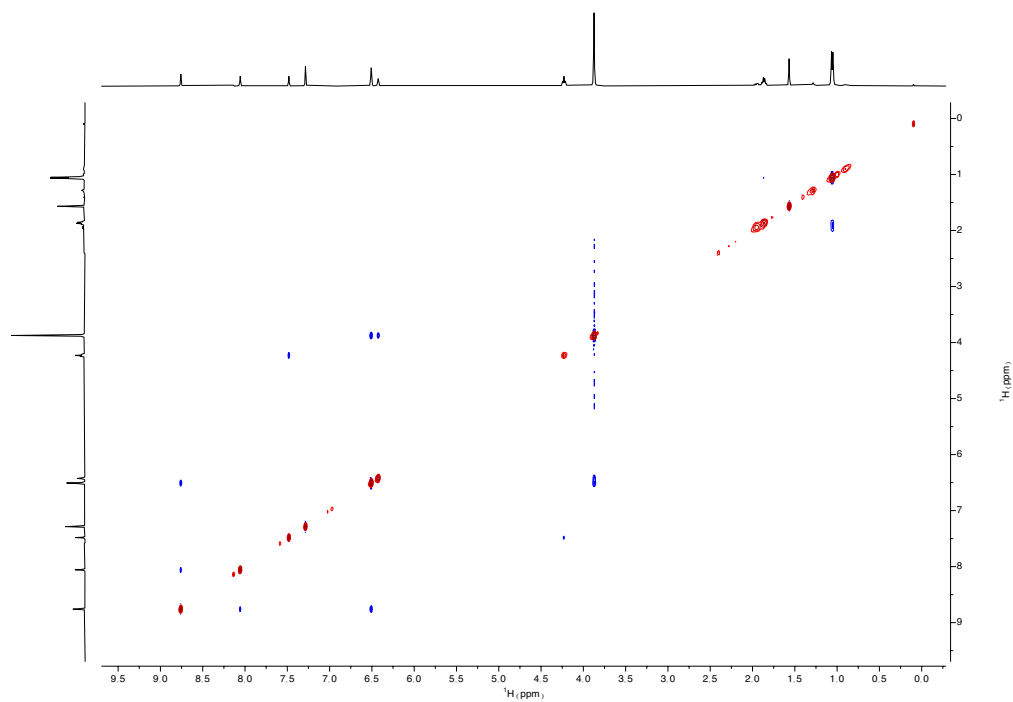


Figure D 50. ^1H - ^1H NOESY spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 400 MHz, 298 K).

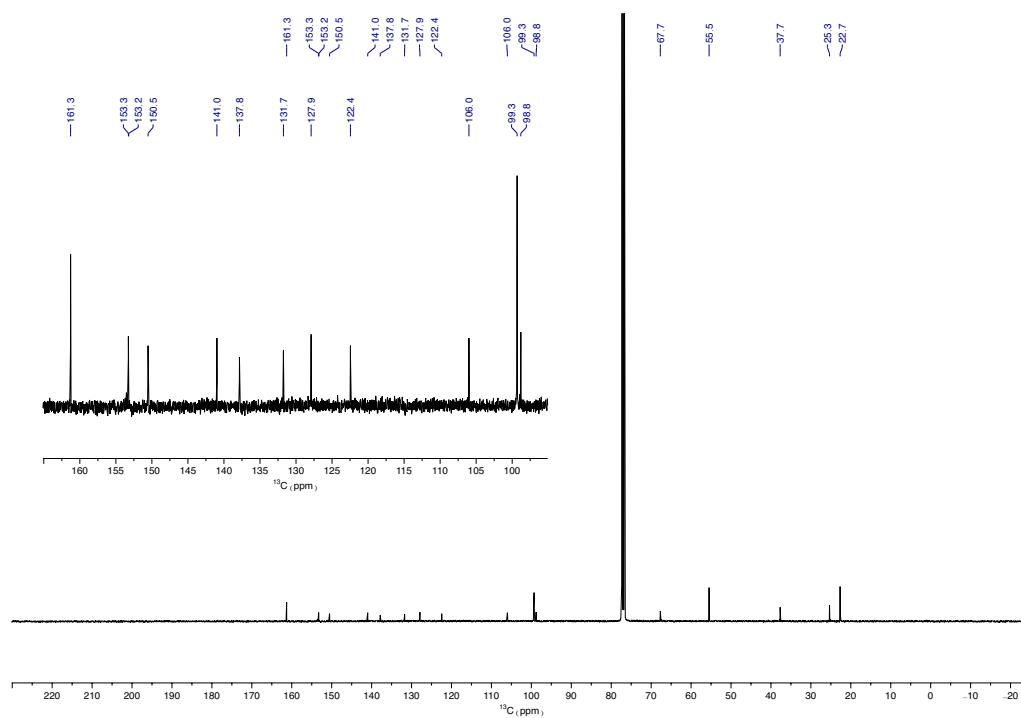
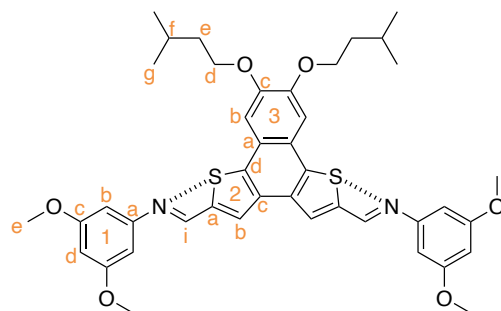


Figure D 51. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(1\text{cc})_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	153.2*
1b	6.48	99.3
1c	-	161.3
1d	3.85	98.8
1e	6.40	55.5
i	8.73	153.3*
2a	-	141.0
2b	8.03	127.9
2c	-	131.7
2d	-	137.8
3a	-	122.4
3b	7.46	106.0
3c	-	150.5
3d	4.20	67.7
3e	1.84	37.7
3f	1.92	25.3
3g	1.03	22.7

Figure D 52. **$\beta(1\text{cc})_2$** with assignment of ^1H and ^{13}C resonances. *Signals are overlapped and resolved by < 0.1 ppm.

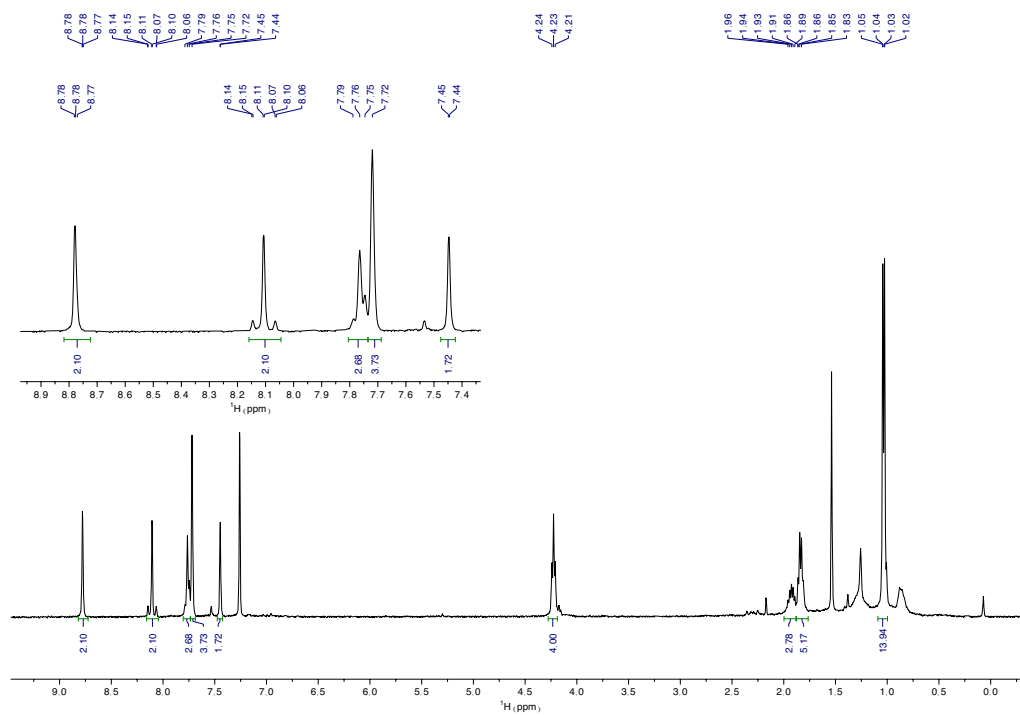


Figure D 53. ¹H NMR spectrum of $\beta(1dd)_2$ (CDCl₃, 400 MHz, 298 K).

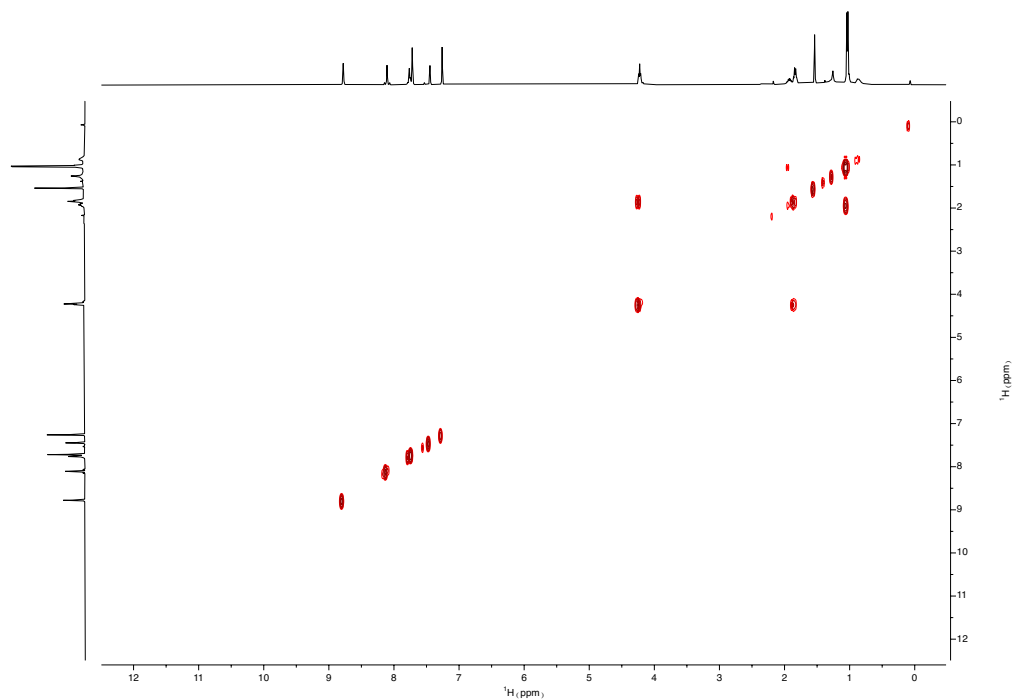


Figure D 54. ¹H-¹H COSY spectrum of $\beta(1dd)_2$ (CDCl₃, 400 MHz, 298 K).

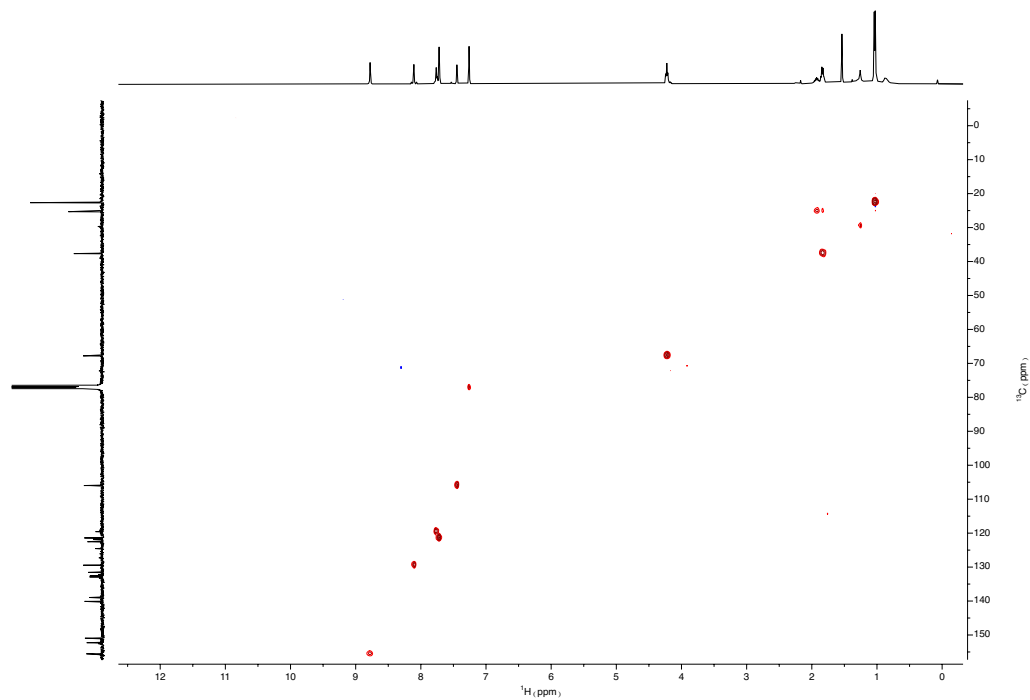


Figure D 55. ^1H - ^{13}C HSQC spectrum of $\beta(1\text{dd})_2$ (CDCl_3 , 400 MHz, 298 K).

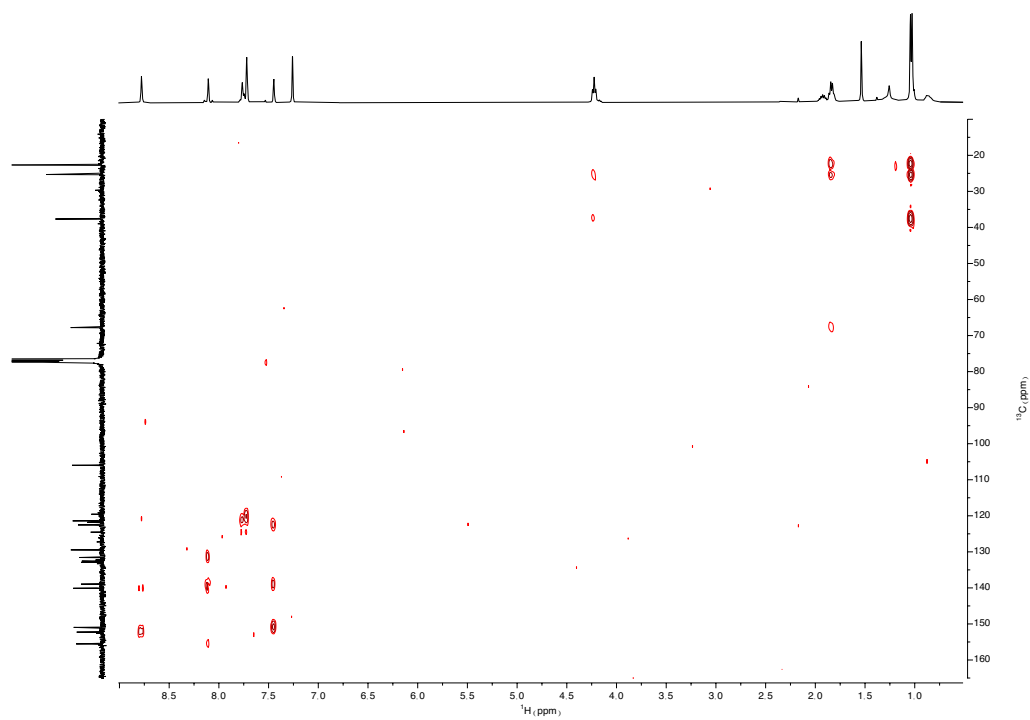


Figure D 56. ^1H - ^{13}C HMBC spectrum of $\beta(1\text{dd})_2$ (CDCl_3 , 400 MHz, 298 K).

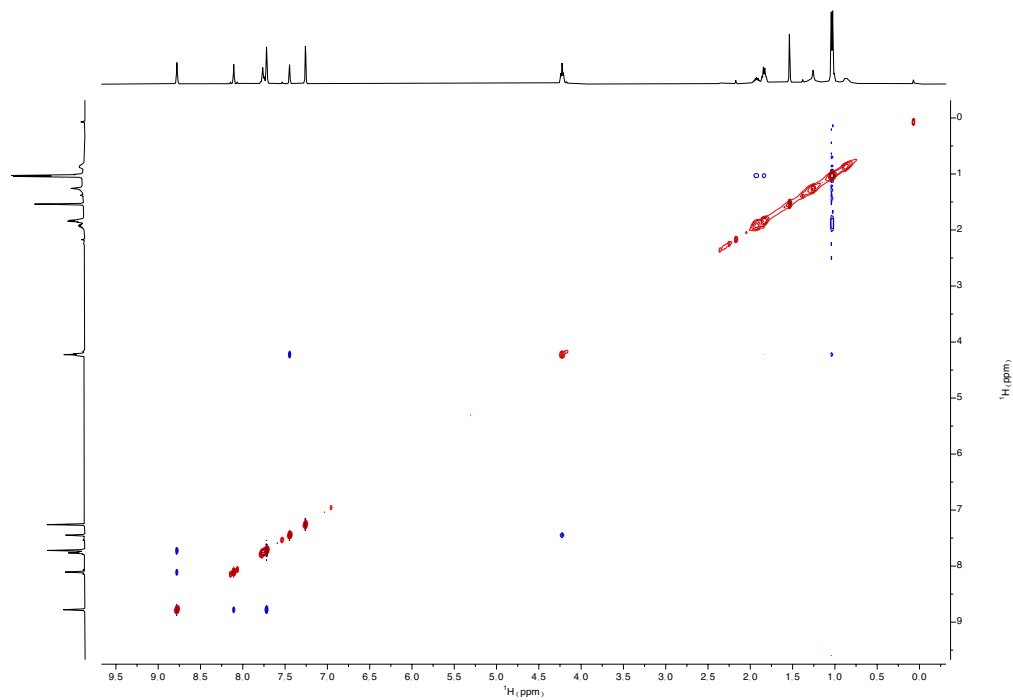


Figure D 57. ^1H - ^1H NOESY spectrum of $\beta(\mathbf{1dd})_2$ (CDCl_3 , 400 MHz, 298 K).

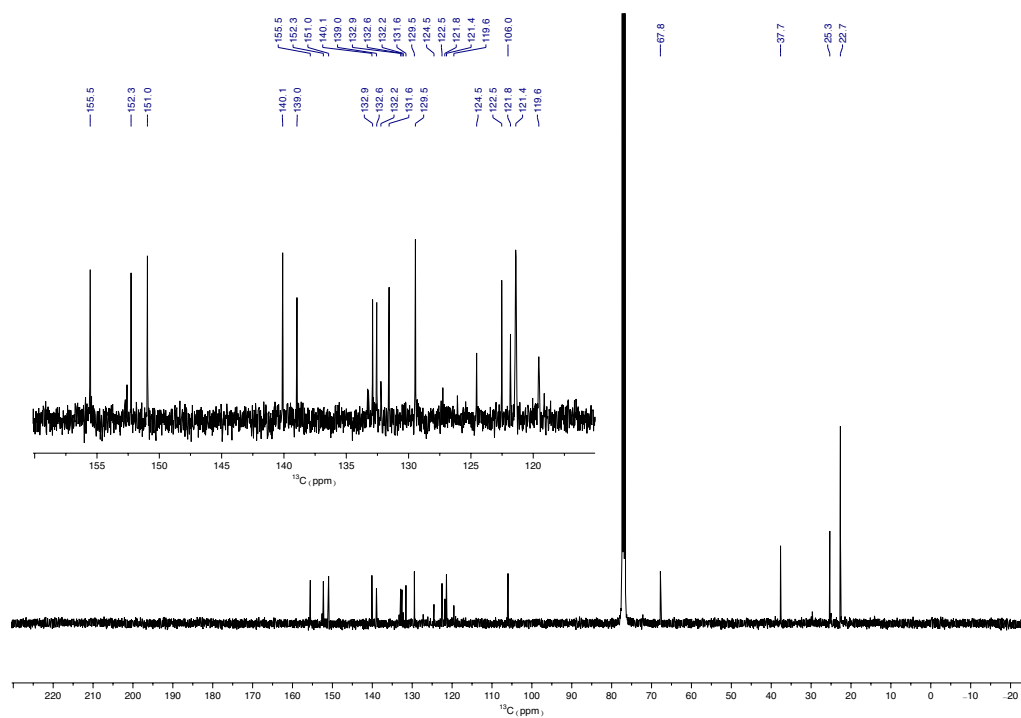
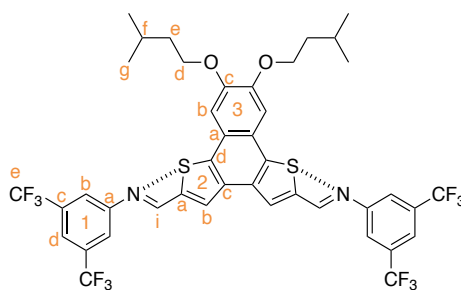


Figure D 58. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\beta(\mathbf{1dd})_2$ (CDCl_3 , 101 MHz, 298 K).



Assignment	^1H δ	^{13}C δ
1a	-	152.3
1b	7.72	121.4
1c	-	132.7 (q, 34.3 Hz)
1d	7.76	119.6
1e	-	123.4 (q, $J = 272.9$ Hz)
i	8.78	155.5
2a	-	140.1
2b	8.11	129.5
2c	-	135.6
2d	-	139.0
3a	-	122.5
3b	7.45	106.0
3c	-	151.0
3d	4.23	67.8
3e	1.85	37.7
3f	1.93	25.3
3g	1.03	22.7

Figure D 59. $\beta(1\text{dd})_2$ with assignment of ^1H and ^{13}C resonances.

5.4 Photophysical Properties $\beta(1)_2$ Series

Absorbance spectra were collected on an Agilent Cary Bio100 spectrophotometer and corrected for solvent background absorbance and instrument drift. Emission spectra were recorded on a Horiba Jon-Yvon Fluorolog-3 with excitation and emission slit widths set at 2 nm. $\beta(1\text{a-e})_2$ and $\beta(1\text{bb-dd})_2$, were prepared with degassed, dry, solvents and degassed prior to sealing in 1 cm path length quartz cuvettes. Emission spectra were analyzed at $\lambda_{\text{ex}} = 365$ nm. Fluorescence quantum yield for $\beta(1\text{d})_2$ was determined by

reference to 9,10-diphenylanthracene in cyclohexane ($\phi = 0.91$) which was cross-checked with quinine bisulfate in 0.5 M H₂SO₄ (aq) ($\phi = 0.54$). Five solutions of varying concentration were prepared for each sample and good fits ($R^2 \geq 0.99$) were obtained in all cases. The absorbance of all sample solutions was kept below 0.10 to avoid the inner-filter effect. Measurements were performed at room temperature with both sample and standard excited at the same wavelength (365 nm).¹ Quantum yields were attempted for all $\beta(1a-e)_2$ and $\beta(1bb-dd)_2$ with efficiencies well below were below 1%, which is apparent when normalizing the emission spectra relative to concentration (see below). Plots are given below with UV-visible spectra as solid lines and emission spectra as dashed lines. UV-visible spectra are plotted as molar absorptivity (left vertical axis) vs wavelength (horizontal axis). Emission spectra are plotted as normalized intensities (intensities were corrected for concentration and then normalized relative to most emissive sample, $\beta(1d)_2$; right vertical axis) vs wavelength (horizontal axis). $\beta(1a)_2$ is shown in all spectra to provide a consistent reference (given in blue).

5.4.1 *p*-Aryl Series: $\beta(1a)_2$, $\beta(1c)_2$, and $\beta(1e)_2$

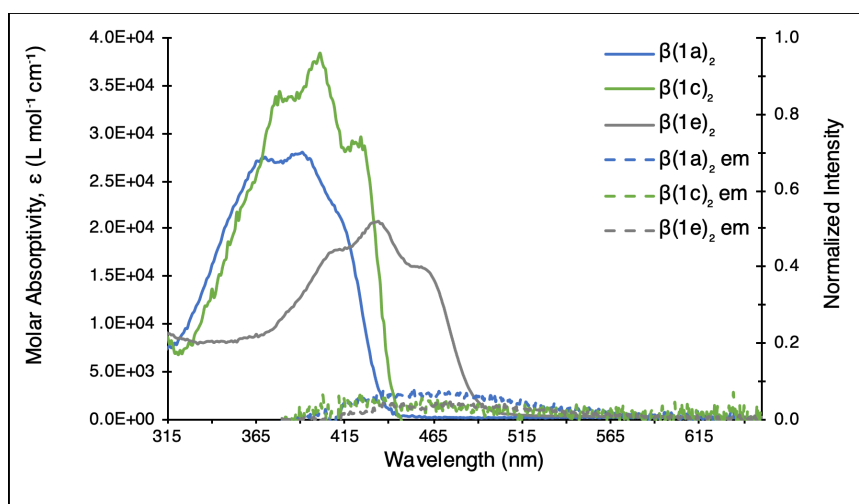


Figure D 60. Absorbance and emission spectra for $\beta(1a)_2$, $\beta(1c)_2$, and $\beta(1e)_2$ in toluene.

5.4.2 *p*-Aryl Series: $\beta(1a)_2$, $\beta(1b)_2$, and $\beta(1d)_2$

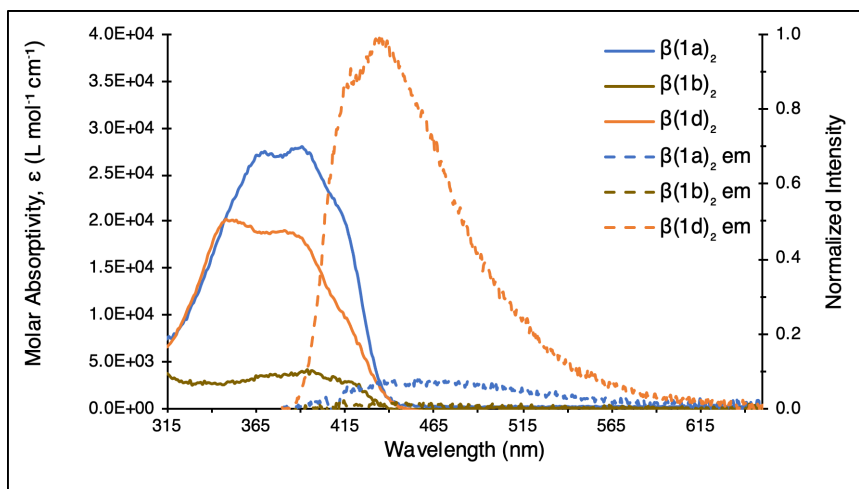


Figure D 61. Absorbance and emission spectra for $\beta(1a)_2$, $\beta(1b)_2$, and $\beta(1d)_2$ in toluene.

5.4.3 *m*-Aryl Series: $\beta(1a)_2$ vs $\beta(1bb-dd)_2$

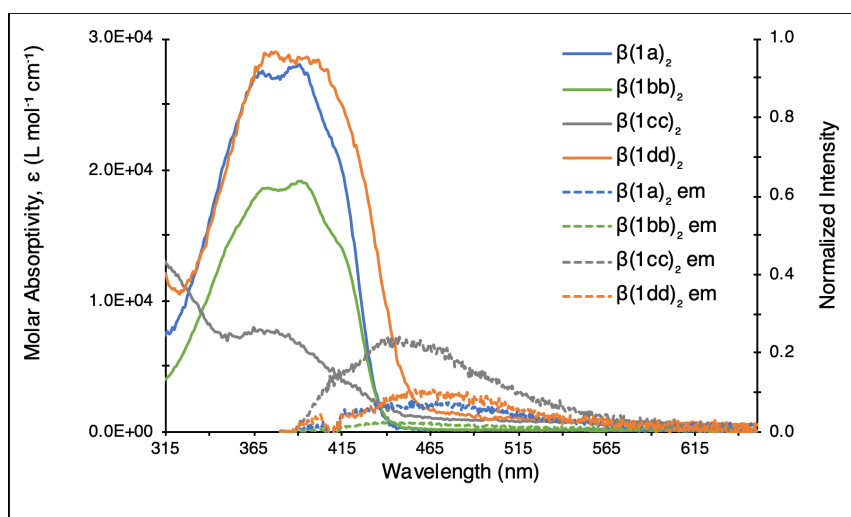


Figure D 62. Absorbance and emission spectra for $\beta(1a)_2$ and $\beta(1bb-dd)_2$ in toluene.

5.5 Computational Analysis

For the computational analysis the isopentyloxy solubilizing groups of the seven di-imine derivatives were simplified to methoxy groups, with the model compounds being identified as $\beta(1)_2$. Computations were ran in Gaussian 16 utilizing the ω B97-XD functional with a cc-pVDZ basis set to accommodate the variety of light atoms employed in this work and account for the likelihood of dispersion interactions, to perform geometry optimizations and frequency calculations on the $\beta(1)_2$ series.³ An additional conformation, conformer-5, was probed for $\beta(1d)_2$, $\beta(1cc)_2$, and $\beta(1dd)_2$ to confirm if conformer-4 is the most likely *Z/Z* configuration and verify that this C_2 species is not major NMR population. Natural Bond Orbital (NBO) analysis was carried out to further valid the strength of the $N\cdots S-C$ interaction. The values obtained for single interactions are given in the tables below and correlate to approximately half of the relative energy difference between conformer-1 (two $N\cdots S-C$ interactions) and conformer-2 (no $N\cdots S-C$ interactions).

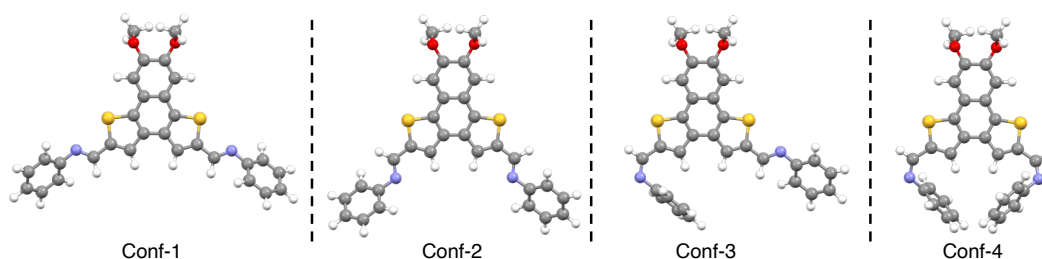


Figure D 63. Ball-and-stick representations for optimized conformers of $\beta(1a)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S-} C ^d (kcal mol ⁻¹)
$\beta(1a)_2$ - Conformer 1	-2212.37070263	0.447600	-2211.923103	0.0	0	1.78
$\beta(1a)_2$ - Conformer 2	-2212.36604316	0.447528	-2211.918515	+2.8	0	—
$\beta(1a)_2$ - Conformer 3	-2212.36573049	0.448014	-2211.917716	+3.4	0	0.89
$\beta(1a)_2$ - Conformer 4	-2212.36078054	0.448299	-2211.912482	+6.7	0	—

Table D 2. Computational data for optimized $\beta(1a)_2$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies. ^dPer number of N...S—C interaction in conformer.

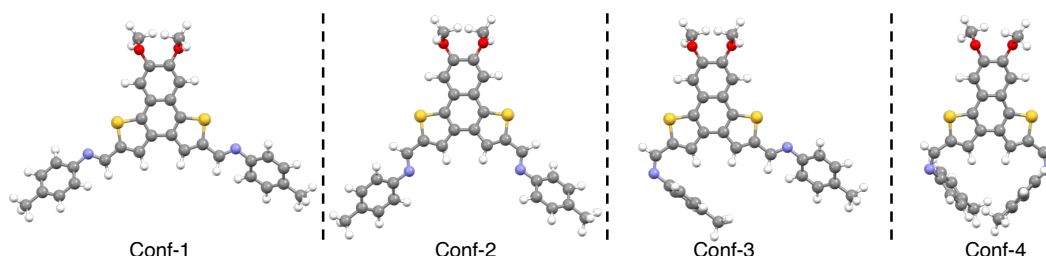


Figure D 64. Ball-and-stick representations for optimized conformers of $\beta(1b)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S-} C ^d (kcal mol ⁻¹)
$\beta(1b)_2$ - Conformer 1	-2290.98570449	0.502096	-2290.483608	0.0	0	1.80
$\beta(1b)_2$ - Conformer 2	-2290.98104653	0.502181	-2290.478866	+3.0	0	—
$\beta(1b)_2$ - Conformer 3	-2290.98060927	0.502908	-2290.477701	+3.7	0	0.89
$\beta(1b)_2$ - Conformer 4	-2290.97771816	0.503715	-2290.474003	+6.0	0	—

Table D 3. Computational data for optimized $\beta(1b)_2$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies. ^dPer number of N...S—C interaction in conformer.

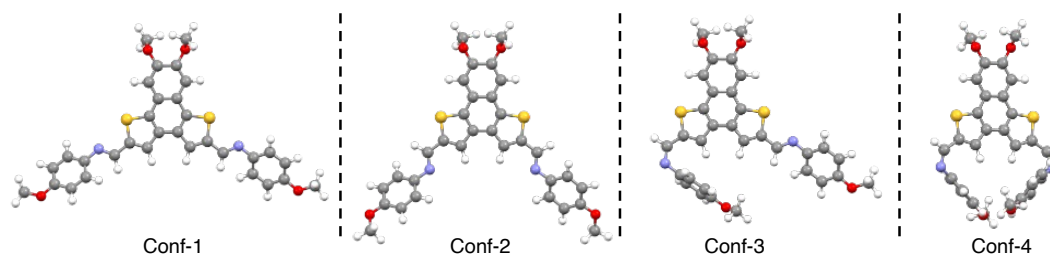


Figure D 65. Ball-and-stick representations for optimized conformers of $\beta(1c)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S-C} ^d (kcal mol ⁻¹)
$\beta(1c)_2$ - Conformer 1	-2441.35927452	0.513058	-2440.846217	0.0	0	1.86
$\beta(1c)_2$ - Conformer 2	-2441.35456707	0.512912	-2440.841655	+2.9	0	—
$\beta(1c)_2$ - Conformer 3	-2441.35357537	0.513564	-2440.840011	+3.9	0	0.91
$\beta(1c)_2$ - Conformer 4	-2441.35336939	0.514289	-2440.839080	+4.5	0	—

Table D 4. Computational data for optimized $\beta(1c)_2$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies. ^dPer number of N...S—C interaction in conformer.

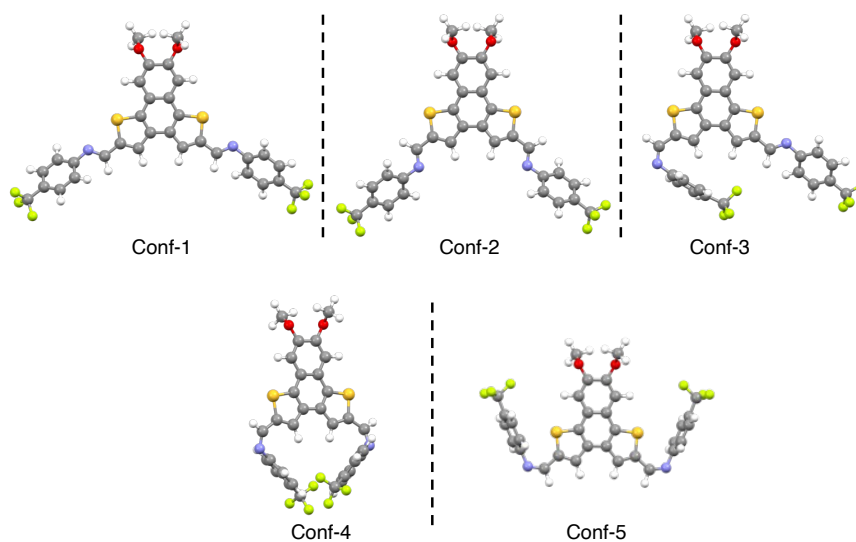


Figure D 66. Ball-and-stick representations for optimized conformers of $\beta(1d)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S-} C ^d (kcal mol ⁻¹)
$\beta(1d)_2$ - Conformer 1	-2886.32245606	0.457615	-2885.864841	0.00	0	1.70
$\beta(1d)_2$ - Conformer 2	-2886.31789857	0.457459	-2885.860440	+2.8	0	—
$\beta(1d)_2$ - Conformer 3	-2886.32115575	0.458205	-2885.862951	+1.2	0	0.83
$\beta(1d)_2$ - Conformer 4	-2886.32189441	0.458633	-2885.863261	+1.0	0	—
$\beta(1d)_2$ - Conformer 5	-2886.31406027	0.458006	-2885.856054	+5.5	0	—

Table D 5. Computational data for optimized $\beta(1d)_2$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies. ^dPer number of N...S-C interaction in conformer.

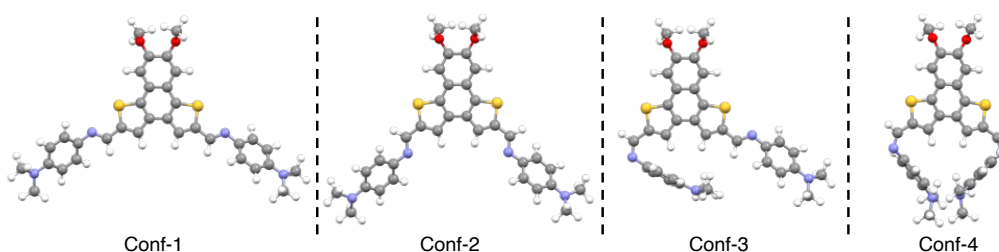


Figure D 67. Ball-and-stick representations for optimized conformers of $\beta(1e)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S-} C ^d (kcal mol ⁻¹)
$\beta(1e)_2$ - Conformer 1	-2480.23928666	0.593608	-2479.645679	0.0	0	1.92
$\beta(1e)_2$ - Conformer 2	-2480.23456027	0.593686	-2479.640874	+3.0	0	—
$\beta(1e)_2$ - Conformer 3	-2480.23376987	0.594165	-2479.639605	+3.8	0	0.84
$\beta(1e)_2$ - Conformer 4	-2480.23450797	0.595137	-2479.639371	+4.0	0	—

Table D 6. Computational data for optimized $\beta(1e)_2$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies. ^dPer number of N...S-C interaction in conformer.

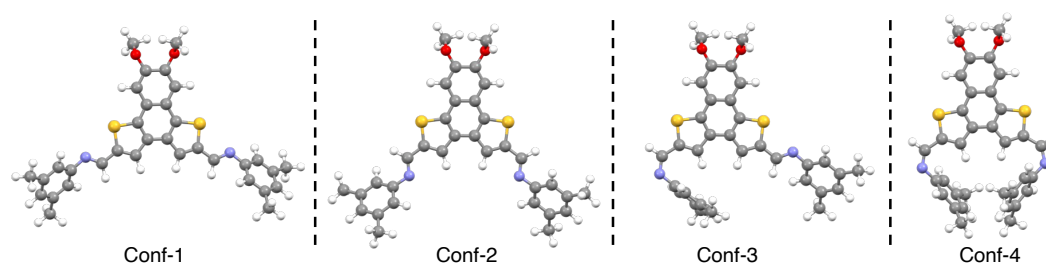


Figure D 68. Ball-and-stick representations for optimized conformers of $\beta(1bb)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S-C} ^d (kcal mol ⁻¹)
$\beta(1bb)_2$ - Conformer 1	-2369.60186206	0.556678	-2369.045184	0.0	0	1.78
$\beta(1bb)_2$ - Conformer 2	-2369.59721371	0.556684	-2369.040530	+2.9	0	–
$\beta(1bb)_2$ - Conformer 3	-2369.59753921	0.557012	-2369.040527	+2.9	0	0.89
$\beta(1bb)_2$ - Conformer 4	-2369.59557098	0.558805	-2369.036766	+5.3	0	–

Table D 7. Computational data for optimized $\beta(1bb)_2$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies. ^dPer number of N...S–C interaction in conformer.

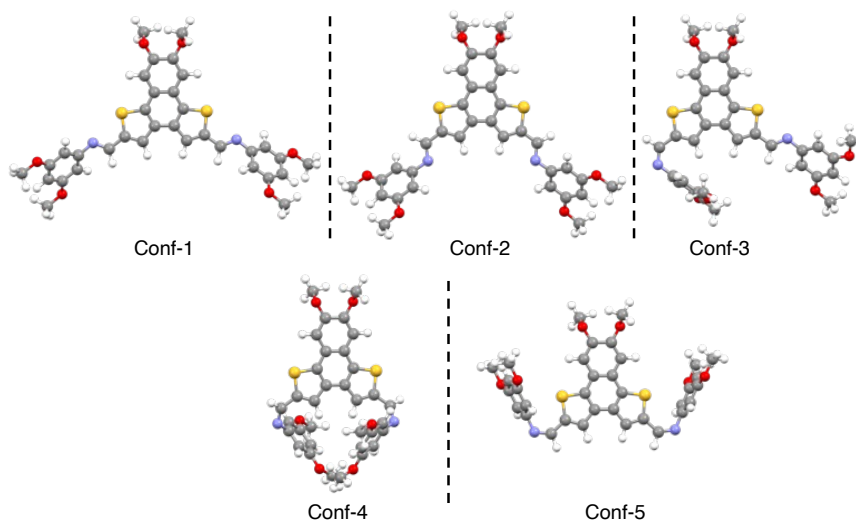


Figure D 69. Ball-and-stick representations for optimized conformers of $\beta(1cc)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy _{Total Energy + ZPC} (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N...S-C} ^d (kcal mol ⁻¹)
$\beta(1cc)_2$ - Conformer 1	-2670.34972278	0.57836	-2669.771363	0.0	0	1.78
$\beta(1cc)_2$ - Conformer 2	-2670.344958	0.578098	-2669.766860	+2.8	0	—
$\beta(1cc)_2$ - Conformer 3	-2670.34887025	0.578967	-2669.769903	+0.9	0	0.88
$\beta(1cc)_2$ - Conformer 4	-2670.34316747	0.57973	-2669.763437	+5.0	0	—
$\beta(1cc)_2$ - Conformer 5	-2670.34040946	0.578768	-2669.761641	+6.1	0	—
$\beta(1cc)_2$ - Conformer 6	-2670.34510449	0.578431	-2669.766673	+2.9	0	—

Table D 8. Computational data for optimized $\beta(1cc)_2$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies. ^dPer number of N...S-C interaction in conformer.

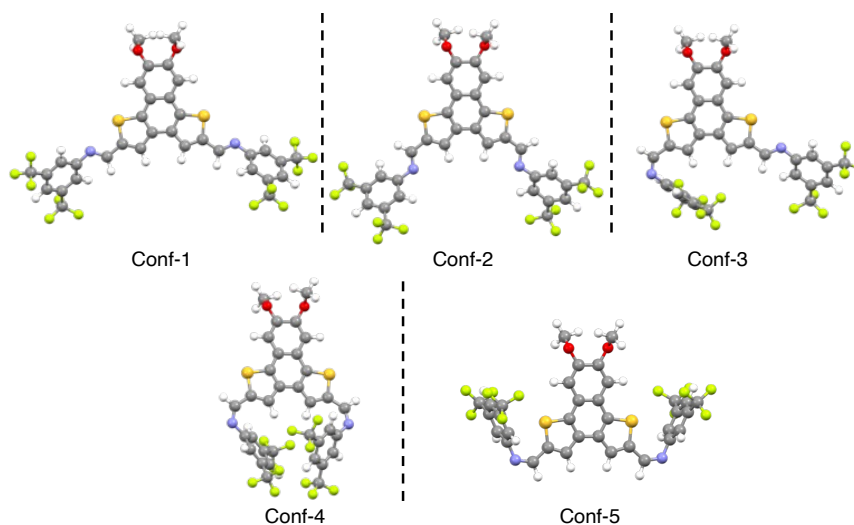


Figure D 70. Ball-and-stick representations for optimized conformers of $\beta(1dd)_2$.

<i>Model Compound</i>	Total Energy (E _h)	ZPC ^a (E _h)	Energy ^{Total Energy} + ZPC (E _h)	Rel. Energy ^b (kcal mol ⁻¹)	IF ^c	NBO _{N··S-C} ^d (kcal mol ⁻¹)
<i>β(1dd)₂ - Conformer 1</i>	- 3560.269141 98	0.4668 08	-3559.802334	0.0	0	1.64
<i>β(1dd)₂ - Conformer 2</i>	- 3560.264553 24	0.4666 93	-3559.797860	+2.8	0	—
<i>β(1dd)₂ - Conformer 3</i>	- 3560.265488 42	0.4675 68	-3559.797920	+2.8	0	0.82
<i>β(1dd)₂ - Conformer 4</i>	- 3560.268759 41	0.4683 76	-3559.800383	+1.2	0	—
<i>β(1dd)₂ - Conformer 5</i>	- 3560.261091 51	0.4674 74	-3559.793618	+5.5	0	—

Table D 9. Computational data for optimized $\beta(1dd)_2$ models. ^aZPC = zero-point correction, ^bRel. Energy = relative energetic difference between conformers and conformer-1, ^cIF = number of imaginary frequencies. ^dPer number of N···S–C interaction in conformer.

5.5.1 Experimental vs Calculated Chemical Shift Analysis

The symmetric optimized structures were used to calculate the ¹H NMR spectra using the GIAO method with implicit solvent (CHCl₃). The isotropic shieldings for the model compounds with the alkoxy groups simplified to methoxy groups were computed for both protons and carbons using the GIAO method with the cc-pVDZ basis set and ωB97-XD functional in Gaussian 16 with implicit solvent (CHCl₃). The experimental chemical shifts (ppm) were extracted for the most populated conformer in solution (i.e. in cases where minor signals are present, they have been assigned to conformer-3 due to their reduced symmetry) and compared to the three potential C₂ symmetric conformations (conf-1, conf-2, conf-4, and in specific cases conf-5).

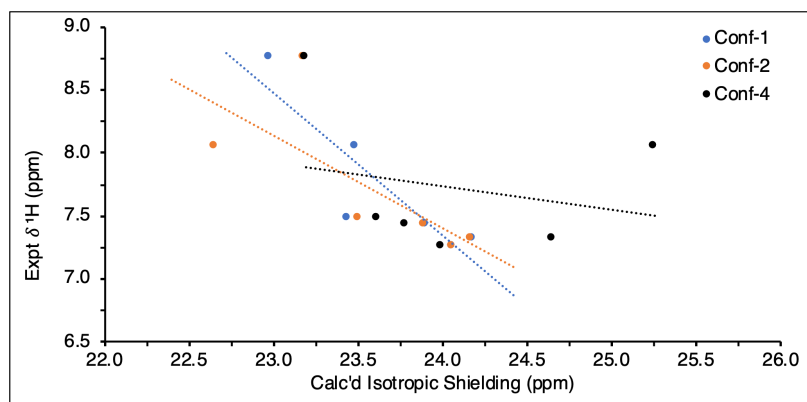


Figure D 71. Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1a)_2$ (experimental) and $\beta(1a)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.78$), Conformer-2 (orange, $R^2 = 0.54$), Conformer-4 (black, $R^2 = 0.06$).

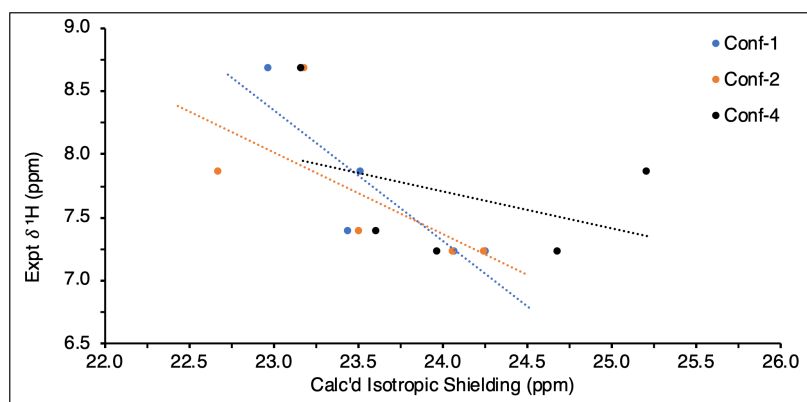


Figure D 72. Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1b)_2$ (experimental) and $\beta(1b)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.75$), Conformer-2 (orange, $R^2 = 0.45$), Conformer-4 (black, $R^2 = 0.15$).

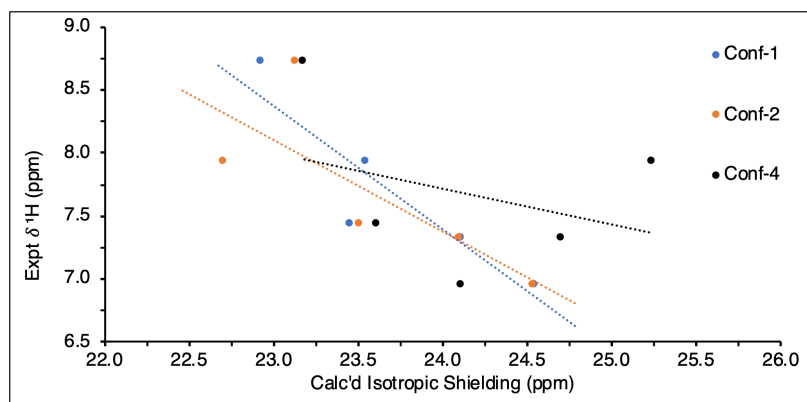


Figure D 73. Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1c)_2$ (experimental) and $\beta(1c)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.82$), Conformer-2 (orange, $R^2 = 0.60$), Conformer-4 (black, $R^2 = 0.12$).

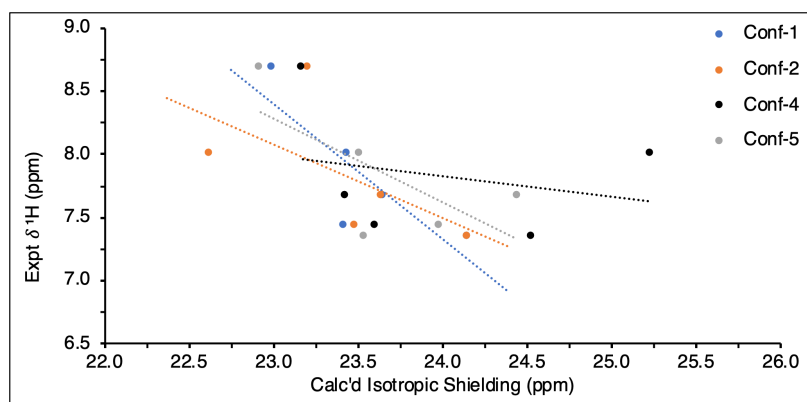


Figure D 74. Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1d)_2$ (experimental) and $\beta(1d)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.67$), Conformer-2 (orange, $R^2 = 0.36$), Conformer-4 (black, $R^2 = 0.07$), Conformer-5 (grey, $R^2 = 0.17$).

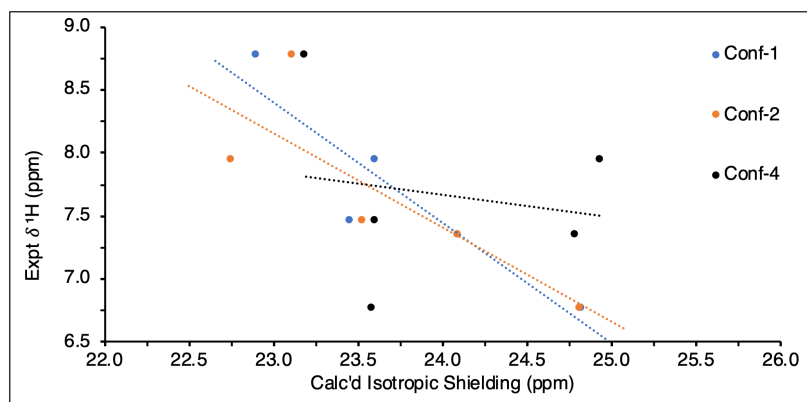


Figure D 75. Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1e)_2$ (experimental) and $\beta(1d)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.84$), Conformer-2 (orange, $R^2 = 0.66$), Conformer-4 (black, $R^2 = 0.04$).

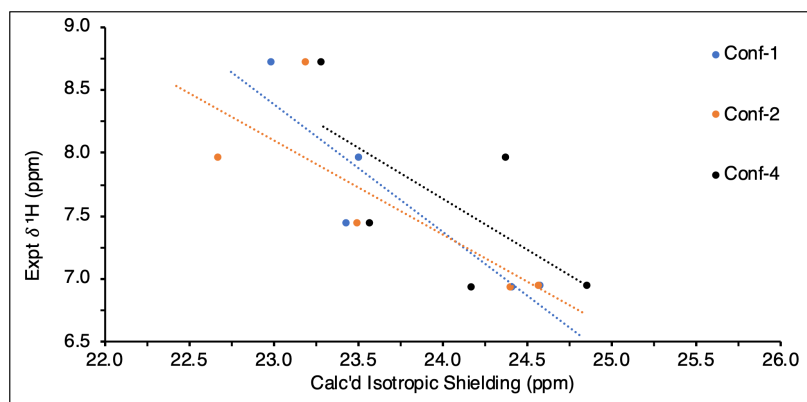


Figure D 76. Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1bb)_2$ (experimental) and $\beta(1bb)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.83$), Conformer-2 (orange, $R^2 = 0.64$), Conformer-4 (black, $R^2 = 0.44$).

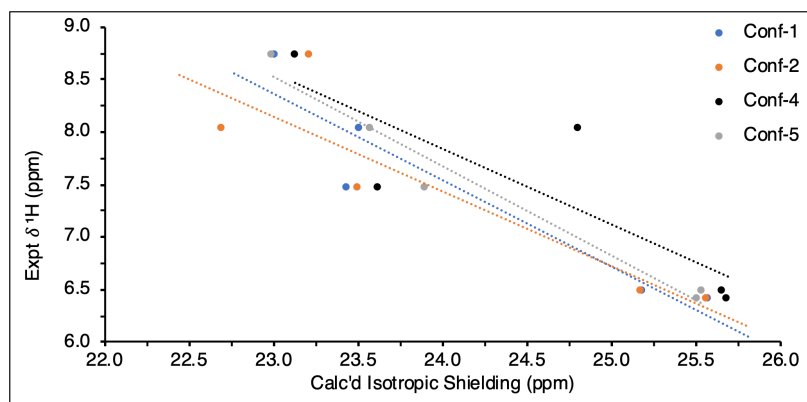


Figure D 77. Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1cc)_2$ (experimental) and $\beta(1cc)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.88$), Conformer-2 (orange, $R^2 = 0.80$), Conformer-4 (black, $R^2 = 0.71$), Conformer-5 (grey, $R^2 = 0.96$).

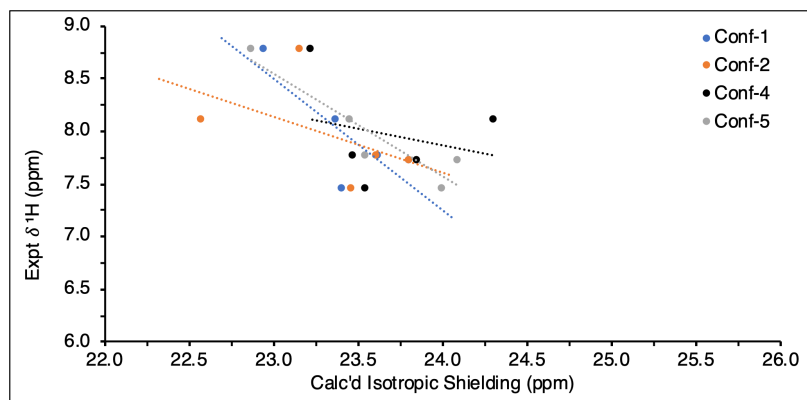


Figure D 78. Comparison of experimental vs calculated ^1H resonances (δ) for $\beta(1dd)_2$ (experimental) and $\beta(1dd)_2$ (calculated). C_2 symmetric conformations: Conformer-1 (blue, $R^2 = 0.62$), Conformer-2 (orange, $R^2 = 0.25$), Conformer-4 (black, $R^2 = 0.06$), Conformer-5 (grey, $R^2 = 0.70$).

5.6 References

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