SYNTHESIS OF INDENO[1,2-*B*]FLUORENES AND THE INCORPORATION OF BODIPY FLUOROPHORES INTO TETRAKIS(ARYLETHYNYL)BENZENES

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Highly conjugated, carbon rich molecules are of great interest due to their unique optoelectronic properties. These molecules are now recognized as suitable materials for advanced materials applications such as light-emitting diodes, photovoltaics, and thin film transistors. Of particular interest is the indenofluorene (IF) scaffold, a 6-5-6-5-6-fused ring system that holds a striking topological similarity to pentacene, a very successful electron donating organic semiconductor. Also of interest is another class of compounds referred to as tetrakis(arylethynyl)benzenes, TAEBs, which are cruciform-shaped molecules that possess numerous pathways for electronic and photonic transfer and are amenable to a host of substitution patterns.

Chapter I examines the history of the IF scaffold and its development over the last century through the use of literature examples relating to both its synthesis and potential use as an emerging class of electron accepting materials. Chapter II introduces the feasibility of stable, fully conjugated IFs. Two examples of 5,6,11,12-tetraethynyl-indeno[1,2-*b*]fluorenes are synthesized where their structural and optoelectronic properties are explored. Chapter III further explores the IF scaffold and outlines the

synthesis of a series of 6,12-diethynylindeno[1,2-*b*]fluorenes in conjunction with detailed computational, structural, and photophysical studies. Chapter IV discusses the synthesis and characterization of a series of 6,12-diarylindeno[1,2-*b*]fluorenes and examines their structural and optoelectronic properties. Chapter V describes a series of donor/acceptor-functionalized TAEBs that incorporate the 4,4-difluoro-4-bora-3a,4a,-diaza-s-indacene moiety, better known as BODIPY, as the acceptor unit. Additionally, two TAEB molecules and three structurally related bis(arylethynyl)benzene (BAEB) isomers where only acceptors are used to evaluate the effectiveness of the donor group are synthesized.

This dissertation includes both previously published and unpublished co-authored material.

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For my loving wife, Stacey, and daughter, Natalie.

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CHAPTER I

INDENOFLUORENES AND INDENOFLUORENEDIONES: SYNTHESIS AND EMERGING APPLICATIONS AS N-TYPE SEMICONDUCTORS

Introduction

This chapter was co-authored by Michael M. Haley, who provided guidance and editorial assistance. This work is in progress towards publication in *Physical Organic Chemistry*.

Polycyclic aromatic hydrocarbons (PAHs) have been the subject of great interest for over a century and constitute a significant cornerstone to the advancement of organic chemistry in the nineteenth and twentieth centuries.[1] Initially discovered in the resins of fossil fuels, PAHs have been observed in a myriad of environments that range from natural mineral deposits to meteor rocks.[2] Isolation of PAH-rich tars and ashes has not only contributed to modern purification and separation techniques commonly used today but has also brought forth fundamental concepts such as aromaticity, a topic that remains to be a dominant source of discussion in the current literature. Furthermore, efforts in understanding the reactivity of PAHs have resulted in the elucidation of many novel reaction mechanisms and catalytic pathways which represent the foundation of modern physical organic chemistry.

In the last quarter century, PAH research has made a remarkable return to the literature spotlight as compound accessibility has been made easier with the advent of modern instrumentation and synthetic methods.[3] One motivation for this resurgence lies

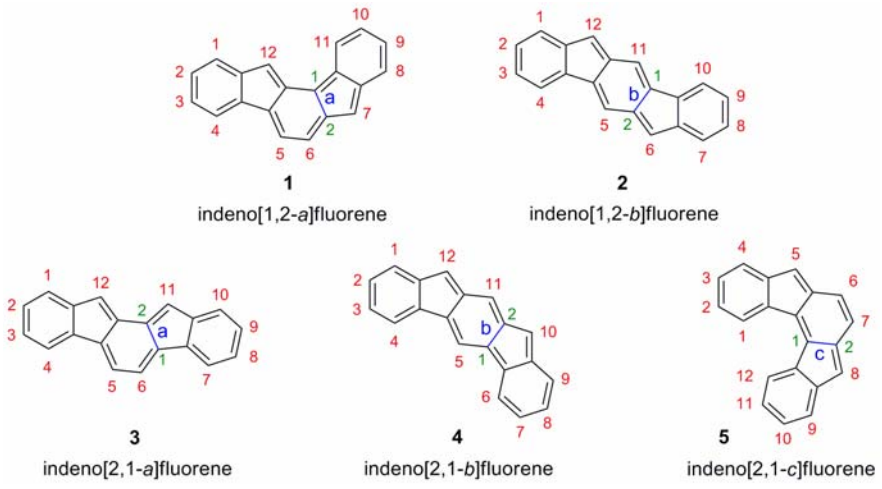
with the unique optoelectronic properties that PAHs possess due to their inherently high levels of π-conjugation and delocalization. These attributes make PAHs promising candidates for a variety of materials applications such as organic light-emitting diodes (OLEDs), field-effect transistors (OFETs), and photovoltaics (OPVs).[4] Such impetus has led to the development and expansion of various PAH classes, such as fullerenes[5] and higher order acenes,[6] that were found to exhibit high electron (n-type) and hole (p-type) mobilities, respectively. Nontraditional PAH structures that consist of five-membered rings such as buckybowls[7] and dibenzopentalenes[8] are making a rapid appearance as well.

This review focuses on the pentacyclic indenofluorenes (IFs), another reemerging class of aromatic compounds, where the B and D rings each contain a five-membered ring. First synthesized in the late 19th century by Gabriel,[9] IF derivatives were a sporadic topic in the literature for roughly seventy years[10] until the pioneering work by Deuschel[11] and Chardonnens[12] in the 1950's devised a general strategy for their synthesis. However, at that time, modern spectroscopic and structural identification techniques were rare in the scientific community; thus, IFs were not typically characterized beyond their melting points and elemental analyses. As such, outside their initial syntheses, IF development languished for nearly over quarter century. Following the excitement and possibility of PAHs as viable organic materials, interest in the IF scaffold resumed a decade ago. Since then, IFs have been recognized as a potential candidate for stable emissive materials by Rault-Berthelot[13] and just recently have begun to be considered as an n-type material.[14]

The IF family is comprised of five structural isomers which can be difficult to discern as multiple naming and numbering strategies as well as graphical presentations

have been employed over the last century to describe their shape and structure (Figure 1). In an effort to maintain topological consistency, and thus prevent confusion, this review will keep the fluorenyl component in a fixed position. Current nomenclature uses a bracketed set of numbers and a letter to distinguish one isomer from another where the set of numbers refer to the orientation of how the indene group faces the fluorene and the letter corresponds to the edge of the indene/fluorene ring fusion. Both '1,2' isomers exhibit an *anti* relationship between the B and D rings, while the three remaining '2,1' isomers exhibit a *syn* relationship. The IF scaffold exhibits a variety of symmetries: the [1,2-*a*] isomer is asymmetrical, the [1,2-*b*] isomer exhibits rotational symmetry, and the [2,1-*a*], [2,1-*b*], and [2,1-*c*] isomers possess a mirror plane. As such, each isomer has its own unique ring topology, which, in turn, has structural and electronic consequences.

Figure 1. IF isomers and their nomenclature.

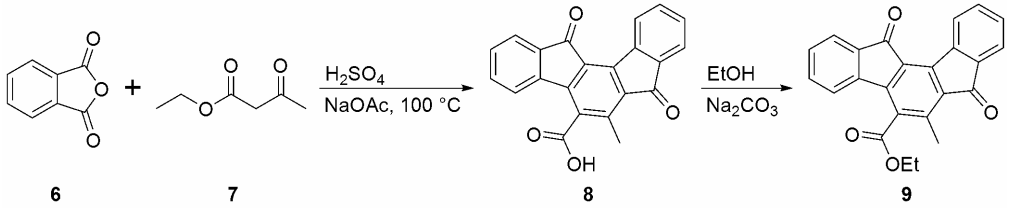


This review will outline the five IF isomers and discuss both conjugated and cross-conjugated forms of each isomer. We will describe the synthetic procedures used to obtain each form as well as describe the available structural and optoelectronic properties. IFs possessing sp^3-hybridization as part of the five-membered rings, while a critical area of research in the realm of emissive materials, will not be discussed here. Instead, the authors wish to direct the reader to the work performed by Rault-Berthelot[13] and others[15] for specific details.

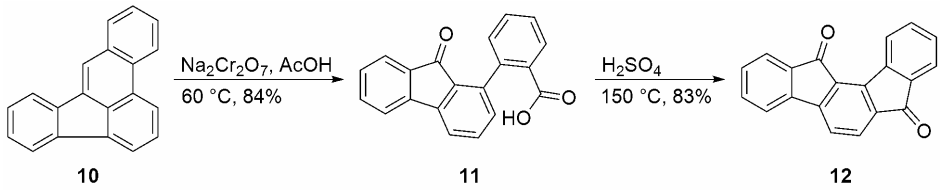
Indeno[1,2-*a*]fluorenes

Diones. The first reported synthesis of the IF scaffold in the literature dates to 1893 when Gabriel condensed two equivalents of phthalic anhydride (**6**) with ethyl acetoacetonate (**7**) to form carboxylic acid **8** and later ethyl ester **9** (Scheme 1).[9] The next account of an [1,2-*a*] IF dione dates to 1955 where Chardonnens and coworkers isolated the parent dione **12** through oxidative cleavage of benzo[*e*]acephenanthrylene (**10**) using sodium dichromate to generate 2-fluorenonyl-benzoic acid **11** followed by ring closure using concentrated sulfuric acid (Scheme 2).[16, 17]

Scheme 1. Synthesis of Gabriel's [1,2-*a*] IF dione **9**.



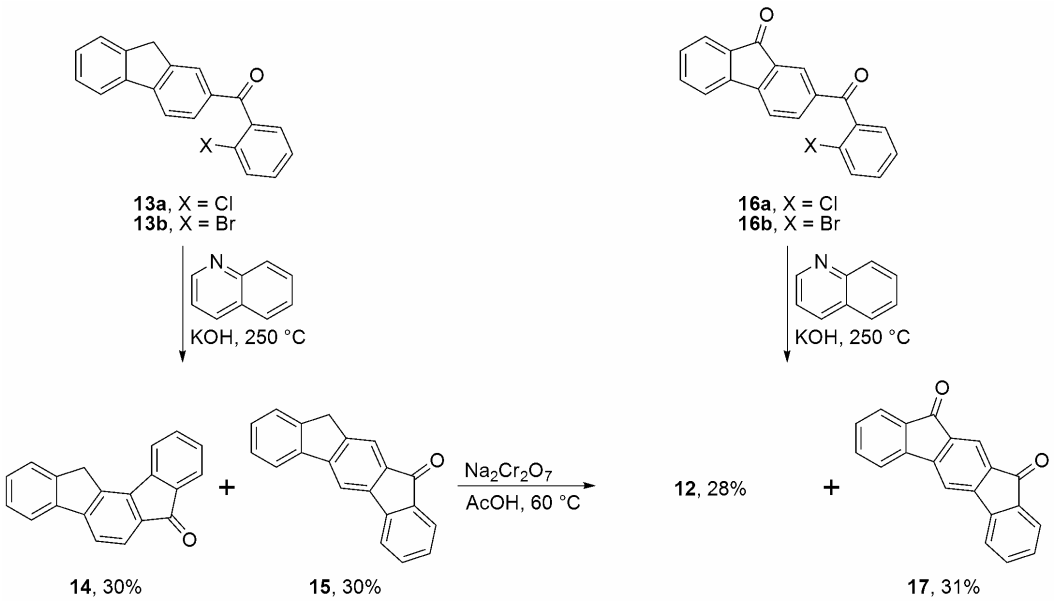
Scheme 2. Syntheses of parent [1,2-*a*] IF dione **12**.



Chardonnens and coworkers later devise a more general pathway to **12** by condensing either 2-chloro- or 2-bromophenyl indenyl ketone (**13a** or **13b**, respectively) with quinoline and sodium hydroxide in a stainless steel autoclave at 250 °C to give 7-keto-12-hydroindeno[1,2-*a*]fluorenone (**14**) in 30% yield (Scheme 3).[18] Incidentally, 9-keto-12-hydroindeno[2,1-*b*]fluoreneone (**15**), also formed in equal yield as addition could occur at either the 6- or 8-positions of the fluorene unit. Addition of either 2-chloro- or 2-bromophenyl indenonyl ketone (**16a** and **16b**, respectively) under similar conditions afforded both parent **12** and parent [2,1-*b*] IF dione (**17**) in 28% and 31% yield, respectively. Furthermore, oxidation of **14** and **15** using sodium dichromate at elevated temperatures led to the expected diones **12** and **17**. Despite the formation of two discrete condensation products, both **14** and **15** as well as **12** and **17** can be and isolated separately

either through soxhlet extraction or by selective crystallization. Both techniques take advantage of the key topological differences that the [1,2-*a*] and [2,1-*b*] structures possess; namely, the [2,1-*b*] isomer is more solublized than the [1,2-*a*] isomer due to the fact that the *syn* arrangement of the ketones exerts a greater dipole moment and is thus more amenable to dissolution in polar solvents.

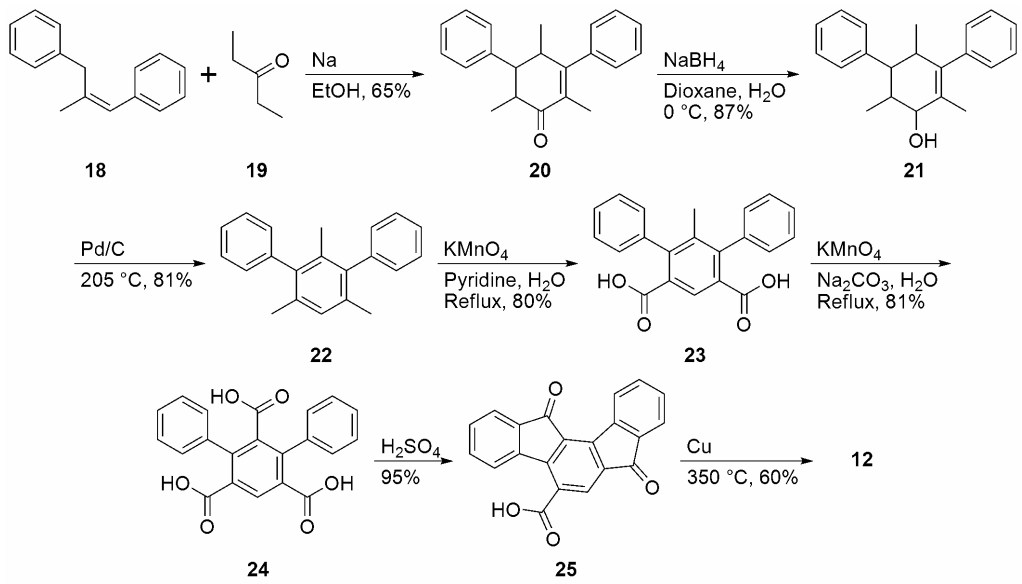
Scheme 3. Asymmetric synthesis of **12** and [2,1-*b*] IF dione **17**.



This general synthetic route has been exhaustively investigated and applied to a multitude of indeno[1,2-*a*]fluorene diones of both symmetrical and asymmetrical nature.[17] In most cases, a mixture of [1,2-*a*] and [2,1-*b*] species were formed during the cyclization stage, although in some instances the [1,2-*a*] isomer was the exclusive product. One such example involves tricarboxylic acid precursor **24**, so that the acylation step forms in the correct configuration regardless of direction (Scheme 4).[19] To achieve

this, *cis*-1,3-diphenylpropene (**18**) was reacted with 3-pentanone (**19**) to yield cyclohexenone **20**. Reduction with sodium borohydride afforded cyclohexanol **21** followed by reaction with palladium on carbon to form 1,3,5-trimethyl-2,4-diphenylbenzene **22**. Oxidation with potassium permanganate, first using pyridine as the base, and then again using sodium carbonate provided **24**. Cyclization in concentrated sulfuric acid afforded 5-carboxyindeno[1,2-*a*]fluorene dione **25** in near quantitative yield. Subsequent decarboxylation using elemental copper at 350 °C gave parent **12** as the sole product.

Scheme 4. Synthesis of **12** using a tricarboxy-terphenyl precursor **24**.

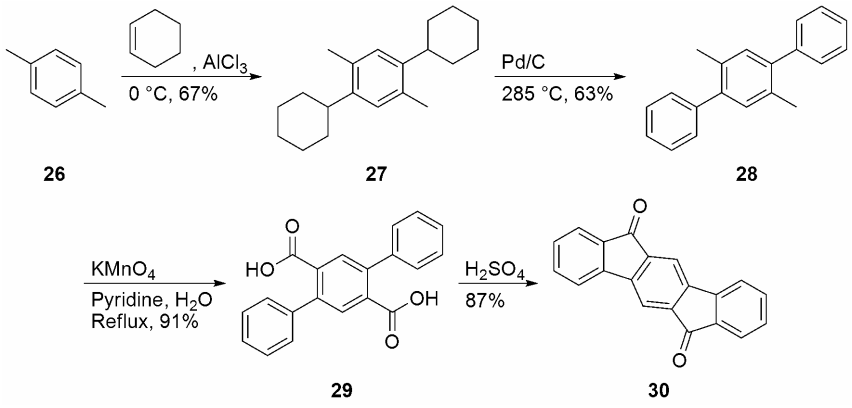


Indeno[1,2-*b*]fluorenes

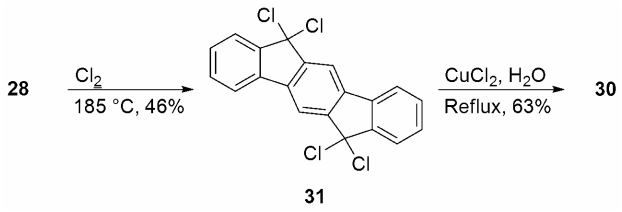
Diones. The first account of the [1,2-*b*] IF skeleton dates to 1951 where Deuschel was able to alkylate *p*-xylene (**26**) with two equivalents of cyclohexene to give tricycle

27. Treatment with palladium on carbon afforded 1,4-dimethyl-2,5-diphenylbenzene (**28**) (Scheme 5).[11b] Oxidation of the methyls using potassium permanganate and pyridine generated diacid **29**. Subsequent cyclization using concentrated sulfuric acid gave the parent indeno[1,2-*b*]fluorene-6,12-dione (**30)** in 87% yield. Alternatively, passing a stream of chlorine gas in a neat solution of **28** at 185 °C afforded **31** in 46% yield (Scheme 6). A refluxing aqueous solution of $CuCl_2$ oxidized **31** to the parent dione **30**.

Scheme 5. Synthesis of parent [1,2-*b*] IF dione **30**.



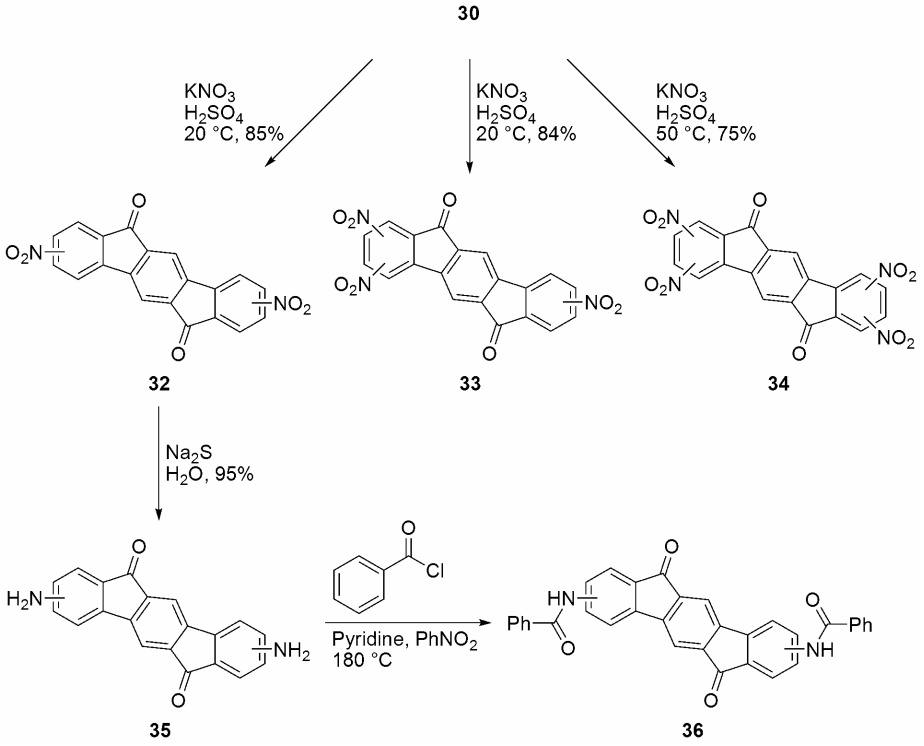
Scheme 6. Chlorination/oxidation route to **30**.



Continued work by Deuschel determined that **30** was amenable to nitration using potassium nitrate in concentrated sulfuric acid at 20 °C (Scheme 7).[20] By variation of the

amount of nitrate used, [1,2-*a*] IF diones can be nitrated either two (**32**), three (**33**), or four (**34**) times. Reduction of dinitro **32** with aqueous sodium sulfide afforded diamino dione **35** in 95% yield which, in turn, was amenable to amidation in a pyridine/nitromethane solution at 180 °C to give **36**. While the sites of nitration for **30** were most likely on the peripheral rings, no specific information about their exact positions was provided.

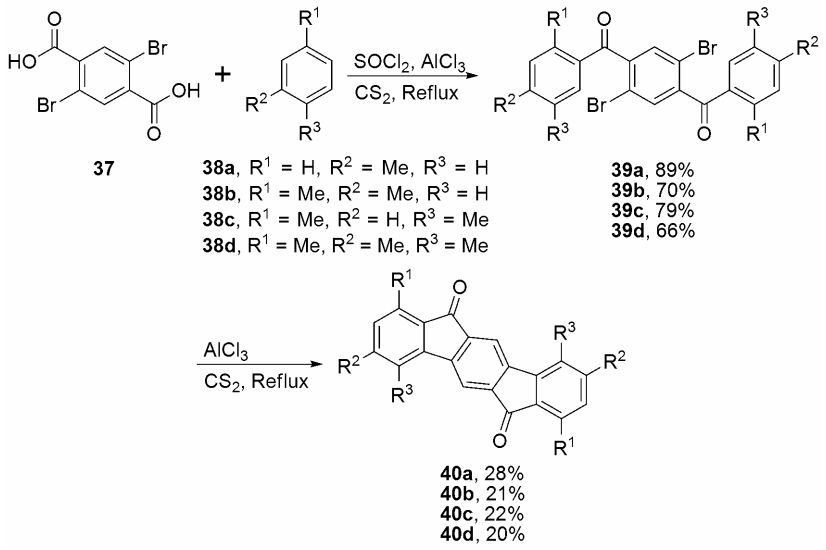
Scheme 7. Nitration, reduction, and amidation of **30**.



Chardonnens and coworkers also synthesized a number of substituted [1,2-*b*] diones, which were typically made in the same fashion as the [1,2-*a*] diones mentioned earlier (Scheme 3).[21] For example, treatment of 2,5-dibromoterephthalic acid (**37**) with

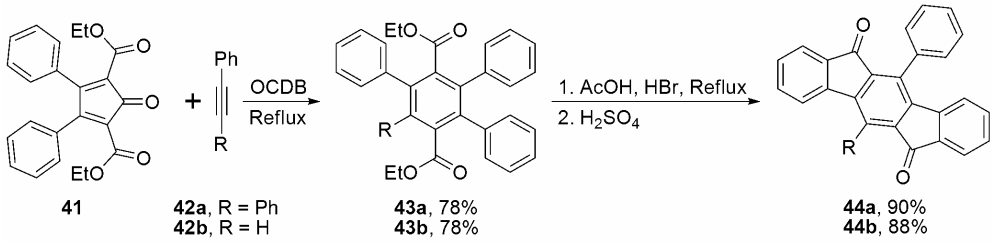
thionyl chloride and subsequent Friedel-Crafts acylation with **38a-d** provided diones **39a-d** (Scheme 8). Alkylation as before at elevated temperatures furnished diones **40a-d** in 20-28% yield. This technique has also been successfully applied to asymmetric 1,3,4-trisubstituted diones as well as 2,3,8,9-tetrasubstituted diones.[18]

Scheme 8. Synthesis of 1,3,4,7,9,10-substituted diones **40a-d**.



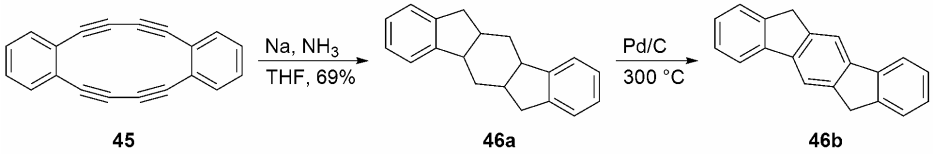
Diels-Alder methods can also be used to generate [1,2-*b*] IF diones. Wang found that the [4+2] cycloaddition of cyclopentadienone **41** with either diphenylacetylene **42a** or phenylacetylene **42b** followed by cheletropic eleimination of CO afforded diesters **43a-b** (Scheme 9).[22] Ester hydrolysis and subsequent cyclization furnished 5,11-diphenyl and 5-phenyl [1,2-*b*] IF diones **44a-b** in 90 and 88% yield, respectively. A noted consequence of this alternative pathway was the suppressed formation of the corresponding [2,1-*c*] IF diones.

Scheme 9. Synthesis of IF diones **44a-b**.

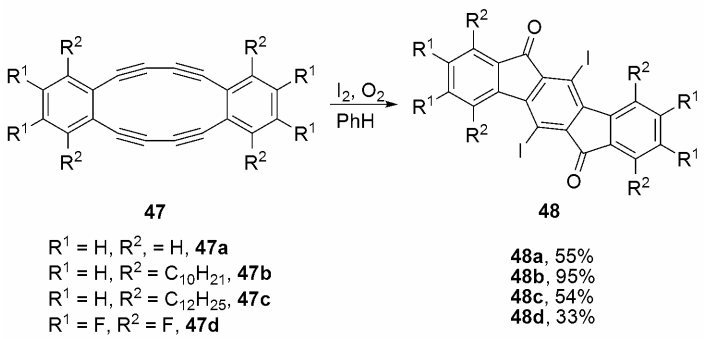


Access to the [1,2-*b*] IF core was also discovered through collapse of the dehydrobenzoannulene (DBA) scaffold. First described by Eglinton and coworkers in 1960 (Scheme 10), [12]DBA **45** underwent a transannular cyclization when reacted with elemental sodium in liquid ammonia to provide 4b,5,5a,6,10b,11,11a,12-octahydro-indeno[1,2-*b*]fluorene (**46a)** as a mixture of two isomers in 69% yield.[23] Further treatment with palladium on carbon afforded the parent 6,12-dihydroindeno[1,2-*b*]fluorene **46b**. Later, encouraged by the potential semiconducting properties polyacetylenes could offer, Swager[24] (and later Komatsu[25]) reacted **47a-d** and derivatives with iodine under aerobic conditions to give 5,11-diiodoindeno[1,2-*b*]fluorene diones **48a-d** in 33% to 95% yield (Scheme 11).

Scheme 10. Na/NH_3-induced transannular cyclization of **45**.

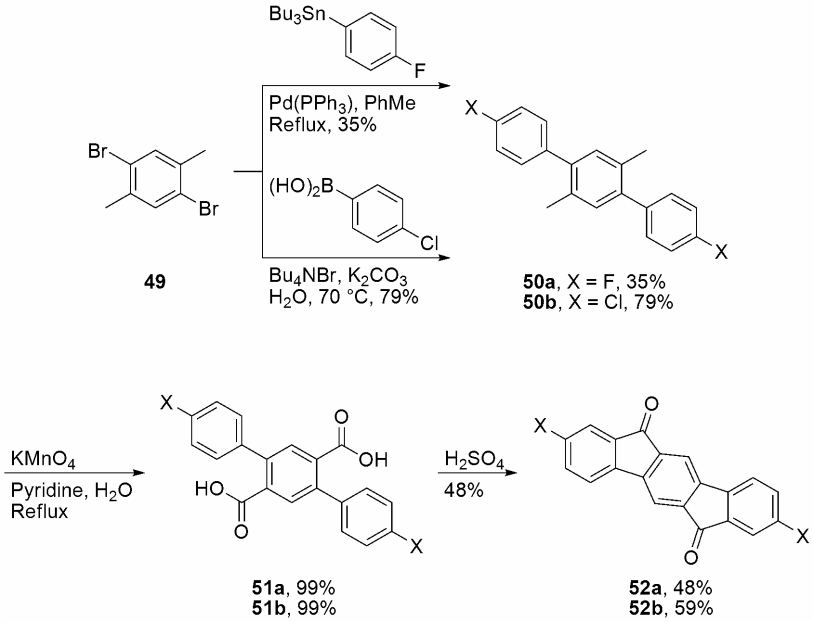


Scheme 11. Aerobic iodine-induced transannular cyclization of **48a-d**.

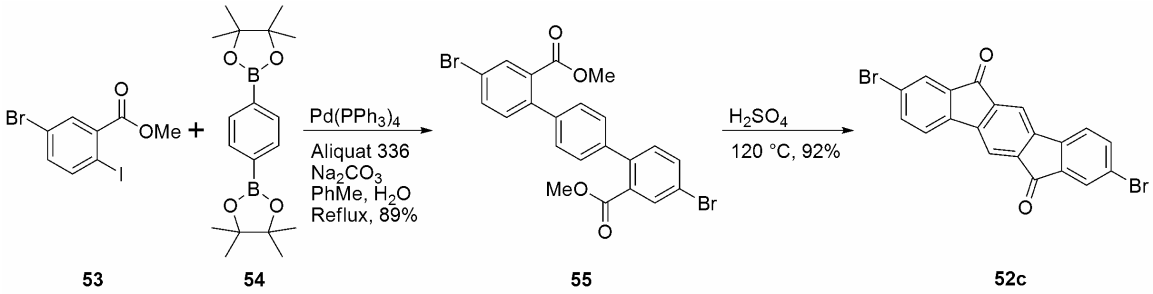


Yamashita found that 2,8-dihalo IF diones could be readily synthesized through Pd-catalyzed cross-coupling.[26] Difluoro and dichloro terphenyls (**50a** and **50b**) were formed via either Stille or Suzuki cross-coupling conditions from 2,5-dibromo-*p*-xylene **49** (Scheme 12). Oxidation with potassium permanganate generated diacids **51a-b** and further cyclization afforded **52a-b** in moderate yield. Marks showed that 2,8-dibromoindeno[1,2-*b*]fluorene dione **52c** could be made through a slightly different manner (Scheme 13).[26] Suzuki cross-coupling of methyl 5-bromo-2-iodobenzoate (**53**) with 1,4-dibenzenediboronic acid dipinacol ester (**54**) afforded diester **55**; subsequent hydrolysis and cyclization using concentrated sulfuric acid gave **52c**.

Scheme 12. Preparation of 2,8-dihalo IF diones **52a-b**.



Scheme 13. Preparation of 2,8-dibromo IF dione **52c**.



The extent of halogenation had a dramatic effect on the solid state ordering as perfluoro **48d** exhibited one-dimensional columnar stacking while difluoro **52a**, demonstrated face-to-face π-stacking (Figure 2, Table 1).[25,26] Despite these subtle

structural differences, close contact distances for **48d** and **52a** were found to be 3.31 Å and 3.30 Å, respectively.

Figure 2. Solid state packing of **48d** (left) and **52a** (right).

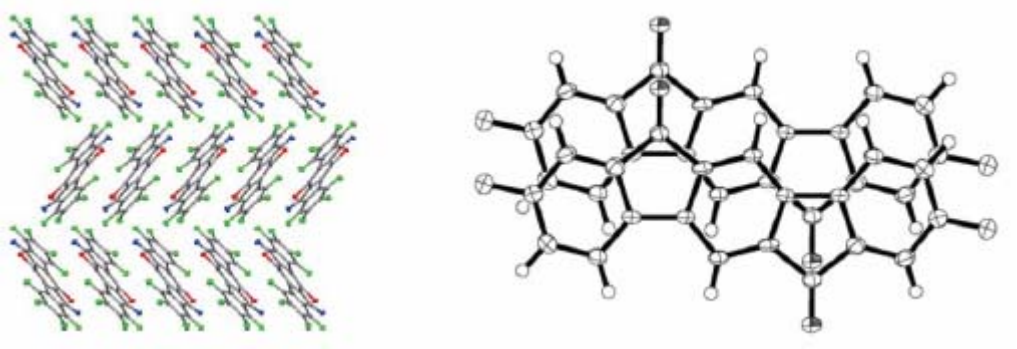
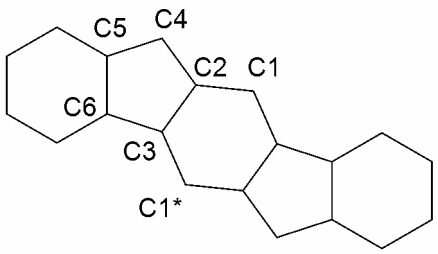


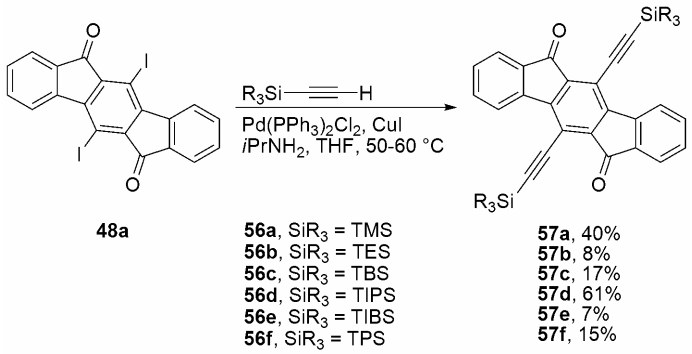
Table 1. Experimental bond lengths of [1,2-*b*] IF diones **48d**, **52a**, **57c**, olefin **74e**, and fully conjugated IFs **82a** and **85a**,**b**,**h**.



Entry	C1–C2	C2–C3	C3–C1*	C2–C4	C4–C5	C5–C6	C3–C6
48d	1.391	1.407	1.396	1.505	1.478	1.405	1.511
52a	1.405	1.387	1.406	1.492	1.505	1.395	1.469
57c	1.394	1.406	1.409	1.506	1.484	1.401	1.479
74e	1.400	1.417	1.404	1.466	1.474	1.418	1.474
82a	1.438	1.457	1.374	1.390	1.470	1.412	1.470
83a	1.424	1.456	1.354	1.382	1.472	1.410	1.481
85b	1.435	1.453	1.350	1.383	1.473	1.402	1.478
85h	1.417	1.453	1.355	1.386	1.473	1.402	1.463

Taking advantage of the fortuitous halogenation on the 5 and 11 positions, Haley and coworkers appeneded a variety of silylacetylenes **56a-f** on **48a** under typical Sonogashira cross-coupling conditions to afford 5,11-diethynylindeno[1,2-*b*]fluorene diones **57a-f** in 7-61% yield (Scheme 14).[27] While little variance in optoelectronic properties exists between **57a-f**, cyclic voltammetry data shows their ability to reversibly accept two electrons (Table 2). The half-wave potential for the first reduction occurs at ca. -0.80 V for **57a-f**, which is less negative than that of parent **30** (-1.19 V) due to the electron withdrawing silylacetylenes but more negative compared to halogenated IF diones **52a-c** (-0.7 V to -0.57 V) and **48d** (-0.45 V). Another advantage of silylacetylene incorporation was a significant increase in solubility as **30**, **48a-d**, and **52a-c** all demonstrated minimal solubility.

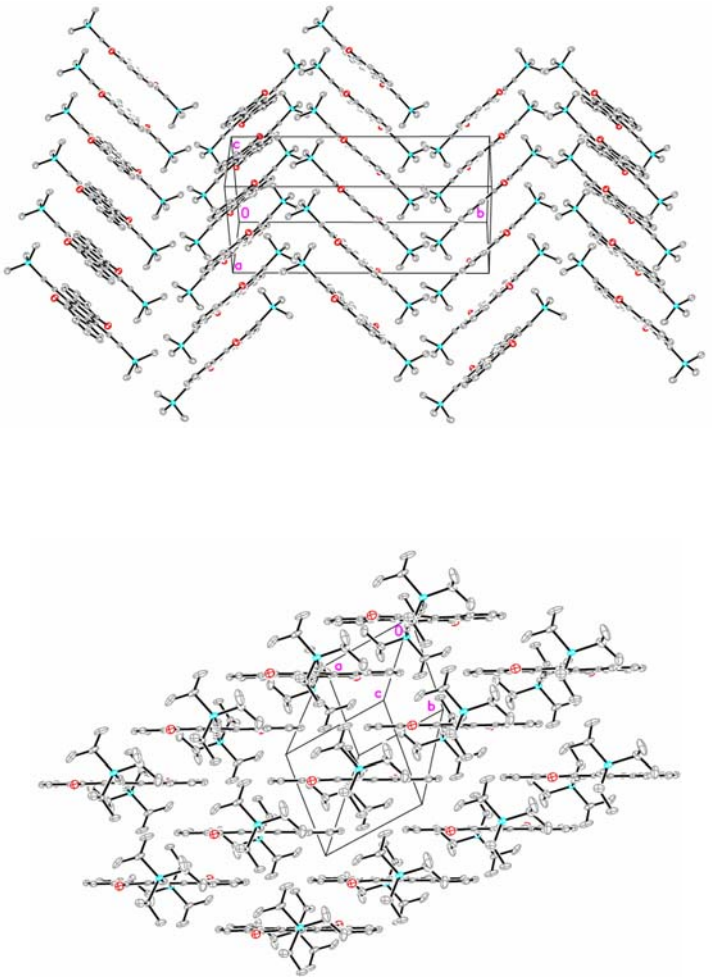
Scheme 14. 5,11-Diethynyl IF diones **57a-f**.

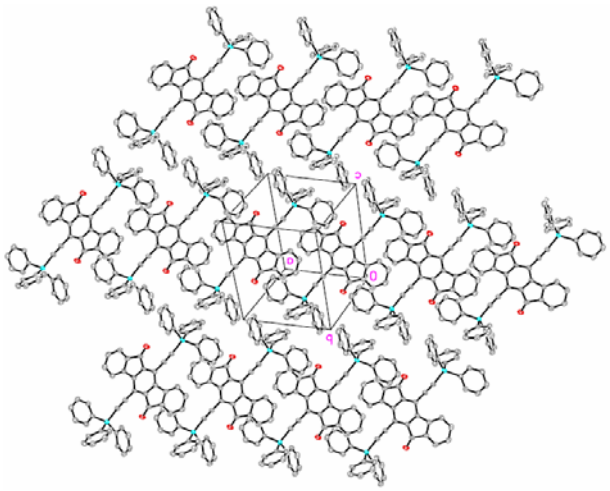


Silyl substitution on the acetyelene, however, had a significant effect on the solid state ordering of **57a-f** as three separate packing motifs were observed (Figure 2). TMS-capped acetylene **57a** was found to exhibit herring bone, while the larger TPS-capped

acetylene **57f** exhibited one-dimensional columns without π-π interactions. In accordance with Anthony's observations,[28] TIPS-capped **57d** exhibited a most favorable columnar stacking in two dimensions, also known as brick-and-mortar stacking, which maximized intermolecular π-π interactions. This was clearly seen by comparison of the close-contact distances of **57a**, **57d**, and **57f**, which were 3.50 Å, 3.40 Å, and 3.77 Å, respectively.

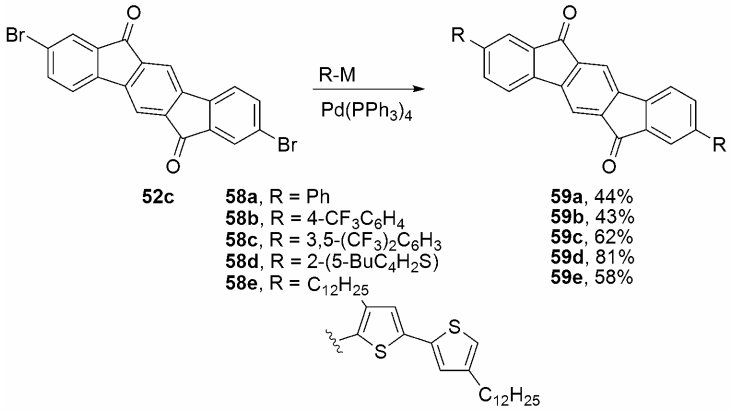
Figure 3. Solid state packing of **57a** (top), **57d**, middle, and **57f** (bottom).





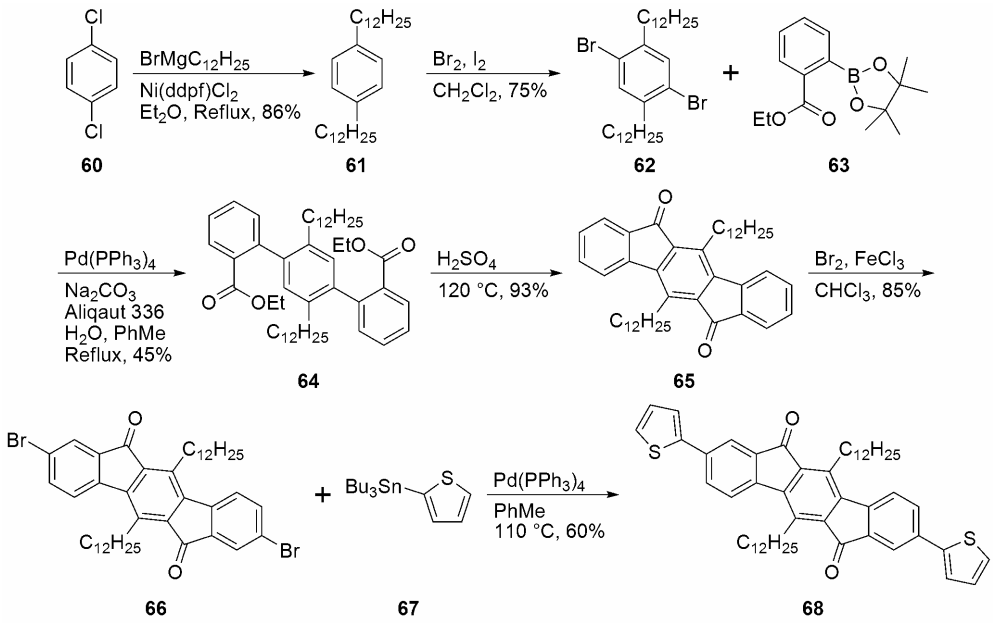
Despite its highly insoluble nature, Marks and Haley found dibromo **52c** an extremely useful precursor for a variety arylated diones as such species can further provide access to a larger variance of electronic donating/accepting parameters (Scheme 15).[14] Reaction of **52c** with aryls **58a-e** in either Suzuki or Stille cross-coupling conditions furnished **59a-e** in 35% to 81% yield.

Scheme 15. Cross-coupling of 2,8-dibromo IF diones **59a-e**.



For materials testing, Marks installed long alkyl groups onto the IF dione core as another method to combat dione insolubility (Scheme 16).[14] Kumada cross-coupling of 1,4-dichlorobenzene (**60**) with didodecylmagnesium bromide formed 1,4-didodecylbenzene (**61**). Bromination of **61** yielded 2,5-dibromo-1,4-didodecylbenzene (**62**), which was reacted with boronic acid **63** under Suzuki cross-coupling conditions to afford terphenyl **64**. Cyclization with concentrated sulfuric acid at elevated temperatures gave 5,11-didodecylindeno[1,2-*b*]fluorene **65** in 93% yield. Unlike parent **30**, **65** was directly brominated on the 2 and 8-positions to cleanly generate **66**, which upon further cross-coupling with 2-tributylstannylthiophene **67** under standard Stille conditions afforded **68**.

Scheme 16. Formation of 2,8-dithiophene-5,11-didodecyl IF dione **68**.



Like **57a-f**, cyclic voltammetry data for **59d-e**, **65**, and **68** showed that these molecules readily accept electrons at low voltages (Table 2). Thiophene substitution results in a slight shift of reduction potentials to more negative values with respect to non-thiophene derivative **65**, in addition to a small decrease in bad gap. Substitution on the central 5 and 11-positions also seemed to have a slight influence of on reduction potentials as **59d** exhibited a reduction potential (-0.74 V) that was less negative than the corresponding 5,11-didodecyl derivative **68** (-0.90 V).

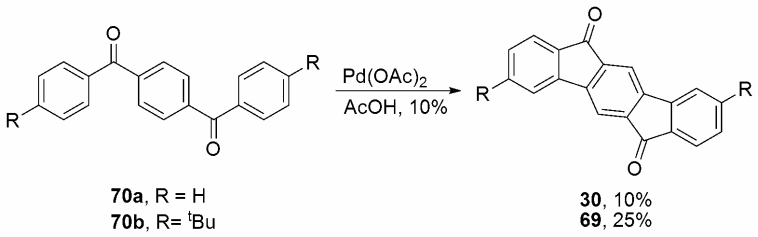
Table 2. Optoelectronic data for 5,11-diethynyl IF diones **57a-f**, **59d-e**, **65**, and **68**.

	Electrochemical				Optical		
Entry	E_{red}^{1} (V)	E_{red}^{2} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	λ_{max} (nm)	E_{gap} (eV)	λ_{em} (nm)
57a	−0.80	−1.21	−6.26	−3.89	310, 330, 498, 522	2.37	571
57b	−0.79	−1.23	−6.28	−3.90	311, 332, 498, 522	2.38	569
57c	−0.81	−1.25	−6.23	−3.87	312, 331, 498, 526	2.36	571
57d	−0.82	−1.24	−6.23	−3.87	313, 333, 500, 525	2.36	568
57e	−0.84	−1.26	−6.22	−3.85	314, 333, 498, 524	2.37	567
57f	−0.78	−1.18	−6.29	−3.90	312, 333, 496, 520	2.39	570
59d	-0.74	–	-5.75	-3.70	377, 525	2.05	619
59e	-0.85	–	-5.53	-3.59	394, 540	1.94	670
65	-0.77	–	-5.95	-3.67	368, 484	2.28	590
68	-0.90	–	-5.54	-3.54	374, 537	2.02	623

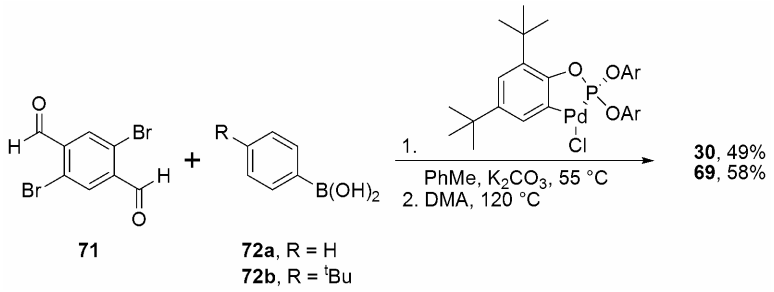
The most recent method towards the synthesis and functionalization of [1,2-*b*] IF diones also involves palladium catalysis. The first example was performed by Kistenmacher and coworkers in 1989 where they showed that that parent **30** and 2,8-di-*t*-butyl[1,2-b]IF diones, **69**, could be formed when precursors **70a-b** were reacted with palladium acetate in acetic acid (Scheme 17).[29] Similarly, developments by Hu and

coworkers regarding one-pot fluorenone syntheses found that the reaction of dialdehyde **71** with two equivalents phenyl and 4-*t*-butylphenyl boronic acids, **72a**, and **72b**, respectively, in the presence of a custom palladacycle formed diones **30** and **69** in 49% and 55% yield, respectively (Scheme 18).[30]

Scheme 17. $Pd(OAc)_2$-mediated cyclization of **51a-b**.



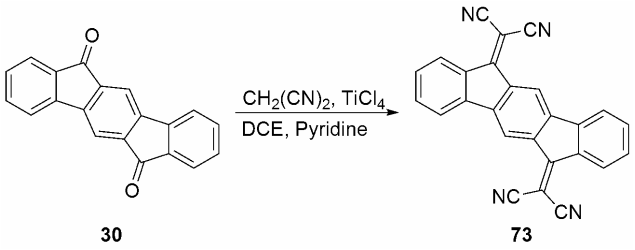
Scheme 18. Pd-catalyzed preparation of IF diones **30**, **69**.



Olefins. While not yet as ubiquitous as the above-mentioned diones, olefination at the 6 and 12-positions on the [1,2-*b*] scaffold has recently gained interest due to the increased use of the electron accepting dicyanovinylene moiety. This technique was initially described by Gompper in 1987 where dione **30** was reacted with two equivalents

of malononitrile in the presence of titanium tetrachloride to form olefin **73** (Scheme 19).[31] Although no yield nor information on its characterization were given, the authors suggested that **73** possessed low reduction potentials.

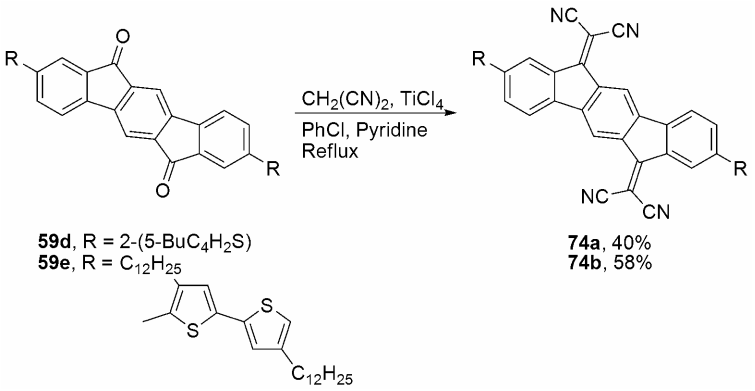
Scheme 19. Preparation of [1,2-*b*] IF olefin **73**.



In 2008, Marks expanded the scope of synthesizing IF olefins. Diones **59d-e** and **65** were converted to their corresponding exocyclic olefins **74a-c** using the same method described above (Schemes 20-21).[14] Olefin **74d** was synthesized through Stille cross-coupling of stannane **67** with olefin **74e** which derived from dione **66** (Scheme 21).[14] Due to the highly electron deficient dicyanovinylene moiety, **74a-d** showed consistent stabilization of their HOMO and LUMO levels compared to **59d-e**, **65**, and **68** by approximately 0.15 eV, and 0.60 eV, respectively, as well as a lowered energy gap of approximately 0.50 eV (Table 3). Furthermore, **74a-d** exhibited an approximate +0.6 V shift with respect to **59d-e**, **65**, and **68** in reduction potentials, reaffirming Gompper's initial expectations that appending electron withdrawing groups significantly increased the electron accepting propensity of the IF core. Solid state analysis of **74e** detailed that the IF core maintains the bond lengths of three aromatic benzene rings. Interestingly, the

exocyclic dicyanovinylene groups contorted the IF core by 13° pointing opposite of the central alkyl chains (Figure 4).

Scheme 20. Preparation of IF olefins **74a-b**.



Scheme 21. Preparation of IF olefins **74c-d**.

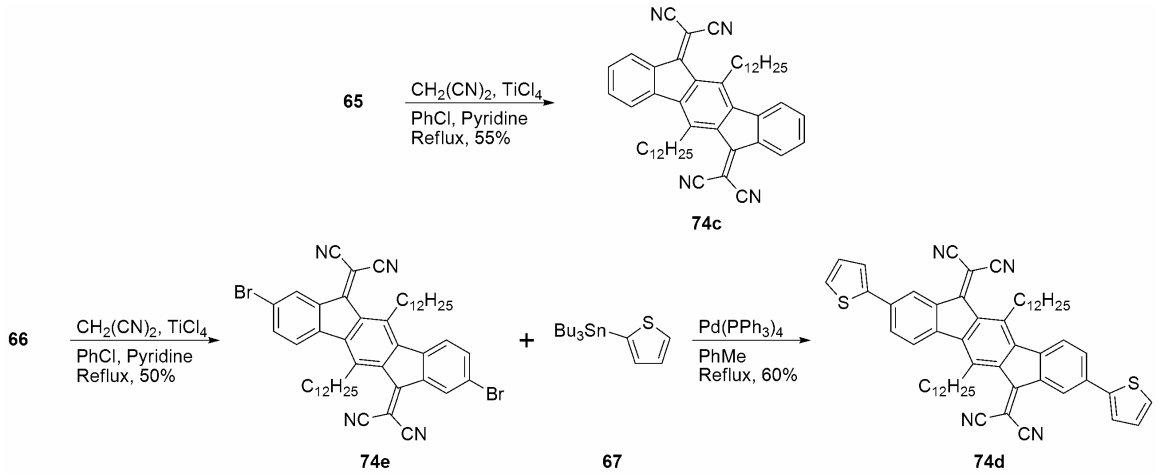


Figure 4. X-ray single crystal structure of **74e**.

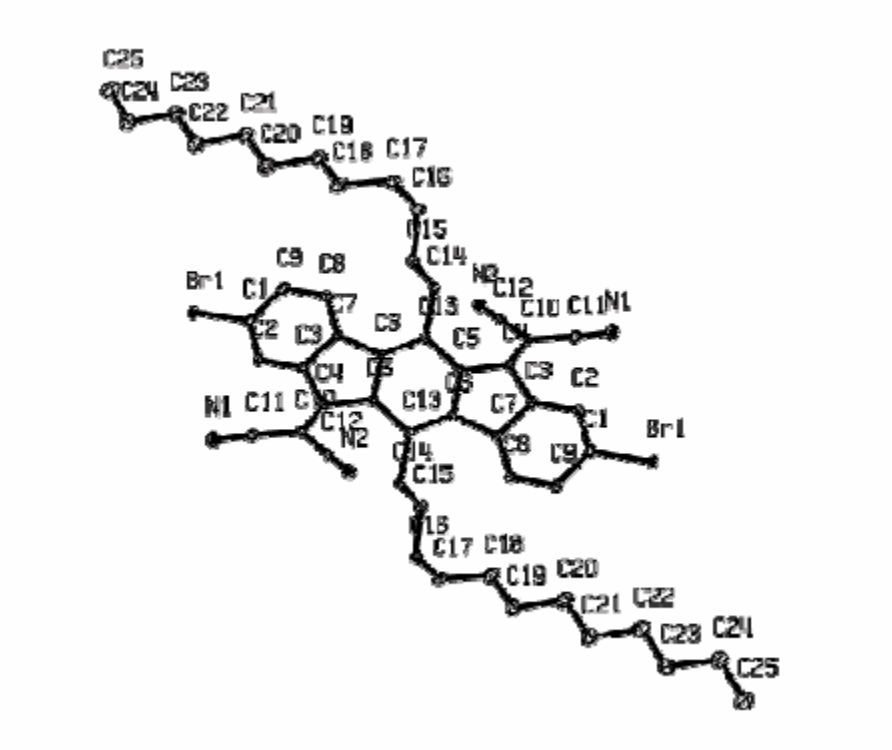
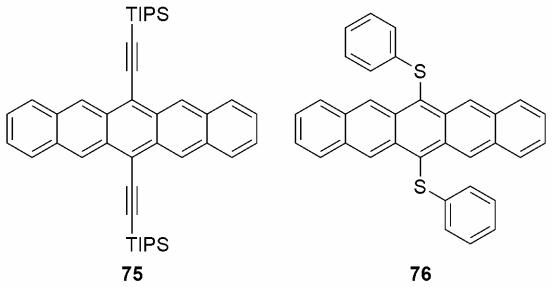


Table 3. Optoelectronic data for olefins **74a-d**.

	Electrochemical			Optical		
Entry	E_{red}^{1} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	λ_{max} (nm)	E_{gap} (eV)	λ_{em} (nm)
74a	-0.12	-5.84	-4.32	418, 653	1.52	780
74b	-0.20	-5.64	-4.20	410, 711	1.44	785
74c	-0.14	-6.16	-4.30	426, 579	1.83	762
74d	-0.24	-5.74	-4.20	430, 661	1.54	770

Full Conjugation. Interest in pentacene over the last decade has risen because of its ability to act as a suitable electron donating organic semiconductor due to its low band gap energy of 1.81 eV. However, pentacenes are susceptible to oxidative and photolytic degradation where the driving force for degradation is the formation of two smaller, more aromatic naphthalene units. Works by Anthony[6,32] and Miller,[33] among others,[34] have shown that while ethynylogation or appending heteroatoms to acenes (e.g., **75** and **76**, respectively) results in a marked increase in stability, their half lives in solution still remain relatively short (Figure 4). Furthermore, acenes larger than pentacene typically exhibit fleeting stability in aerobic conditions.[35]

Figure 5. Ethynylated and heteroatom substituted pentacenes **75** and **76**.

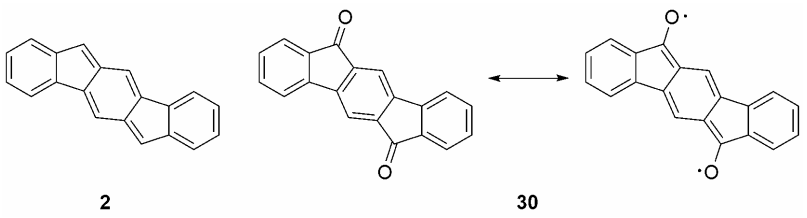


75 **76**

First mentioned by Deuschel as a possible resonance structure of dione **30**, a fully conjugated indeno[1,2-*b*] fluorene **2**, (Figure 5), might serve as a suitable analogue of pentacene due to its topological similarities and π-conjugation path length.[20] Furthermore, **2** does not possess any *s*-*cis* diene linkages in its structure, meaning that it should be less susceptible to the deleterious degradation pathways that pentacenes succumb to; however, until recently, there has been skepticism to the existence of such a species for a

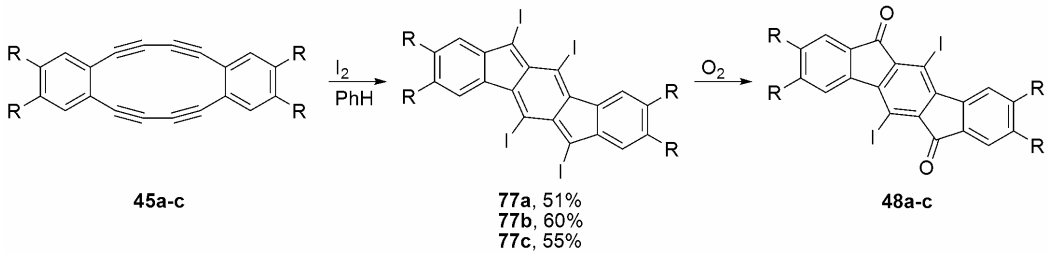
number of reasons: (1) the formation of **2** should be energetically costly due to the necessary disruption of the aromaticity of the central benzene ring; (2) the product **2** would possess 20 π-electrons resulting in the formation of an unfavorable antiaromatic species; and (3) the central rings of **2** would also host a *p*-xylylene (*p*-quinodimethane) core, a notoriously reactive moiety that cannot typically be isolated due to its tendency to oligomerize/polymerize.

Figure 6. Fully conjugated indeno[1,2-*b*]fluorene **2** and resonance structures of **30**.



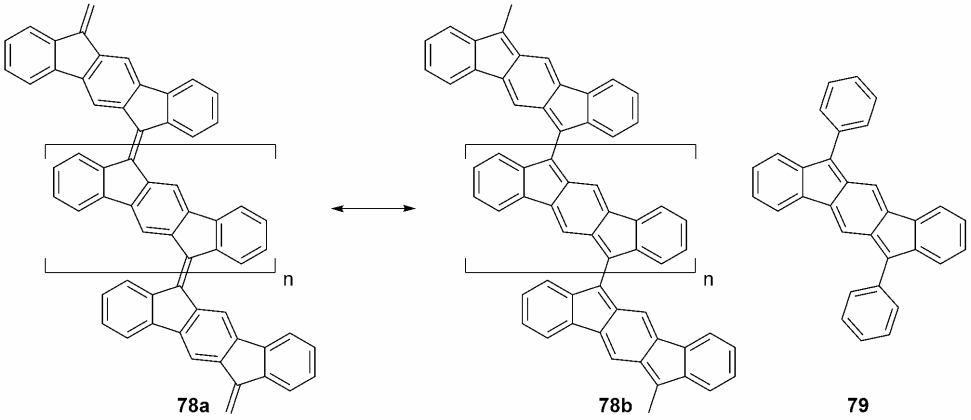
As previously mentioned, Swager and coworkers were able to obtain diones **48a-c** through the iodine-induced transannular cyclization of **45a-c** in aerobic conditions (Scheme 22).[24] However, under anaerobic conditions, another class of products formed that possessed only two aromatic signals in the ^{1}H NMR spectrum that were shifted up-field from **48a-c**. Furthermore, they found that exposure to air converted these compounds into **48a-c** in near quantitative yield. Swager deduced the air-sensitive intermediates to be fully conjugated 5,6,11,12-tetraiodoindeno[1,2-*b*]fluorenes **77a-c** through the basis that the up-field chemical shifts were due to their antiaromatic nature and that the UV-Vis spectrum of **77a** exhibited low energy absorptions of 534 and 571 nm, nearly 250 nm bathochromically shifted from **48a** due to its fully conjugated state.

Scheme 22. Preparation of fully conjugated indeno[1,2-*b*]fluorenes **77a-c**.



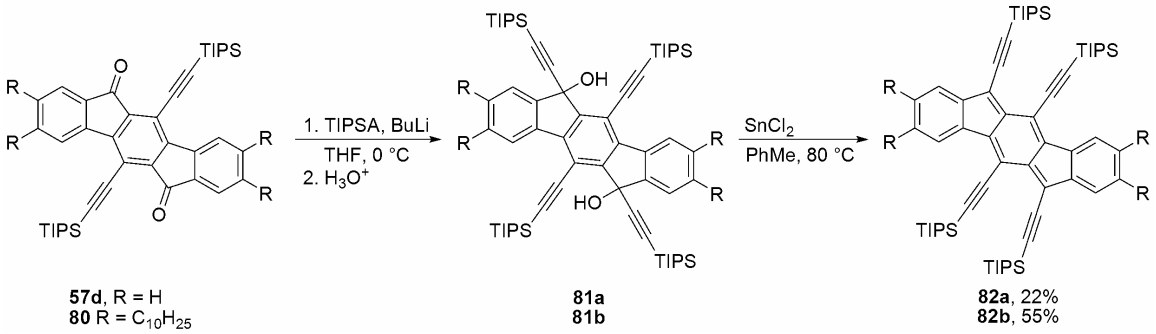
Studies by Scherf and coworkers in 1996 on the design and structural properties of indeno[1,2-*b*]fluorene polymers (**78a**) came to a similar conclusion.[36] Their argument, based on structurally related 9,9'-bisfluorenes, was that in order to reduce steric hinderance between subunits, the bridging olefinic carbons could lengthen and hence reduce the overall double bond character (**78b**, Figure 6).[37] A consequence to such a bond lengthening would be an overall decrease in band gap energy and geometric distortions. Another consequence would be an overall change of the bond structure of the subunit itself. As a model system for **78b**, IF **79b** was prepared and reported to exhibit a UV-Vis λ_{max} of 543 nm; however, neither the synthetic scheme, NMR spectroscopic parameters, nor any information on its stability were given.

Figure 7. Poly(indeno[1,2-*b*]fluorene) **78** and model subunit **79**.



Applying the same rationale that Anthony used for stabilizing pentacenes, work by Haley et al. considered the synthesis of 5,6,11,12-tetrakis[(triisopropylsilyl)ethynyl]indeno[1,2-*b*]fluorenes **82a-b** using the tetraiodo framework **77a-b** that Swager had already investigated.[38] Unfortunately, direct Sonogashira cross-coupling of (triisopropylsilyl)acetylene (TIPSA) with **77a-b** did not yield the corresponding fully conjugated compounds **82a-b**. However, ethynylation of diones **57d** and **80** with TIPSA to diols **81a-b** and subsequent reduction using anhydrous tin(II) chloride at elevated temperatures, a common technique used in acene synthesis, afforded **82a-b** in 22% and 55% yield, respectively, over two steps (Scheme 23). As in **77a-c**, **82a-b** exhibit up-field aromatic chemicals shifts with respect to **57d** and **80**, an indicator of their fully conjugated state.

Scheme 23. Synthesis of fully conjugated 5,6,11,12-tetraethynyl IFs **82a-b**.



The absorption spectra of **82a-b** showed three low-energy transitions in a pattern with λ_{max} values of 594 and 614 nm, respectively, roughly 25 and 45 nm bathochromically shifted with respect to **77a** due to the increased conjugation the four ethynyl groups provide. In comparison to **75**, whose λ_{max} value is 644 nm, **82a-b** were hypsochromcially shifted by 50 and 30 nm, a consequence of having two fewer π-electrons in the antiaromatic core. Unlike **75** though, **82a-b** are non-emissive, a common trait of antiaromatic molecules.

Like the previously mentioned IF diones **46a-f**, **59d-e**, **65**, and **68**, cyclic voltammetry data of **82a** showed first and second reduction potentials of -0.62 V and -1.16 V, respectively, while decyl IF **82b** exhibited potentials of -0.73 and -1.29 V, respectively (Table 4). Additionally, **82a-b** do exhibit oxidation potentials between 1.10 and 1.30 V, although this process is irreversible. Despite the lack of electron withdrawing diones, the first reduction potentials of **82a-b** meet or surpass the vales of **57a-f**, **59d-e**, **65**, and **68** due to the fact that a two-fold reduction of the fully conjugated indeno[1,2-

b]core is extremely favorable as the dianion product would exhibit a 22 π-electron species where every ring was aromatic.

Table 4. Optoelectronic data for fully conjugated IFs **82**, **85a-e**, and **88a-e**.

	Electrochemical					Optical	
Entry	E_{red} (V)	E_{ox} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	λ_{max} (nm)	E_{gap} (eV)
82a	-0.62, -1.16	1.23	-5.92	-4.07	1.85	594	1.98
85a	-0.69, -1.20	1.20	-5.88	-4.00	1.88	568	2.12
85b	-0.60, -1.07	1.33	-6.01	-4.08	1.93	561	2.15
85c	-0.59, -1.07	1.35	-6.03	-4.09	1.94	567	2.13
85d	-0.60, -1.10	1.32	-6.01	-4.09	1.92	567	2.13
85e	-0.69, -1.27	1.16	-5.84	-3.99	1.85	569	2.11
85f	-0.66, -1.20	1.21	-5.90	-4.03	1.87	570	2.10
85g	-0.62, -1.11	1.25	-5.93	-4.06	1.87	572	2.11
85h	-0.52, -1.00	1.35	-6.03	-4.16	1.87	570	2.11
85i	-0.62, -1.16	-	-	-	-	577	2.08
88a	-0.96, -1.49	1.01, 1.31, 1.51	-5.68	-3.72	1.96	544	2.17
88b	-1.12, -1.73	1.10, 1.59	-5.78	-3.56	2.22	516	2.29
88c	-0.84, -1.12	1.41, 1.54, 2.06	-3.85	-5.91	2.06	545	2.16
88d	-0.68, -1.17	1.49, 1.66	-6.17	-4.00	2.17	533	2.20
88e	-1.01, -1.53	0.81, 1.07	-5.50	-3.68	1.82	558	2.05

X-ray analysis of **82a** concluded that there was indeed long and short bond alternation throughout the central portion of IF core, which agrees with Scherf's initial hypothesis regarding the internal bond structure of polymer **78** and model compound **79** (Figure 7). Interestingly, the peripheral benzene rings remain homogenized in length, indicating that **82a** represented a stable example of a molecule containing a *p*-xylylene core, similar to Thiele's and Chichibabin's hydrocarbons.[39] Examination of the crystal packing indicated that **82a** exhibited an expanded herringbone pattern often found with

unsubstituted pentacenes (Figure 8).[40] The most likely cause for this undesirable packing motif was the steric bulk of the four interdigitated (triisopropylsilyl)ethynyl groups.

Figure 8. X-ray single crystal structure of **82a**.

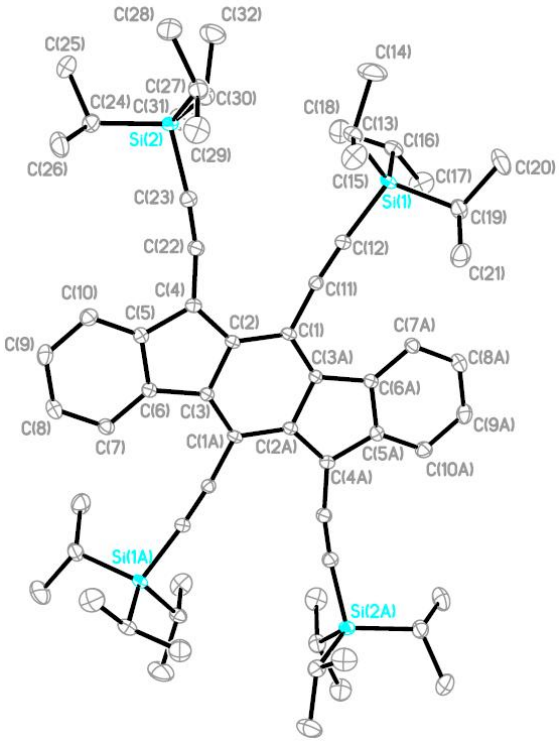
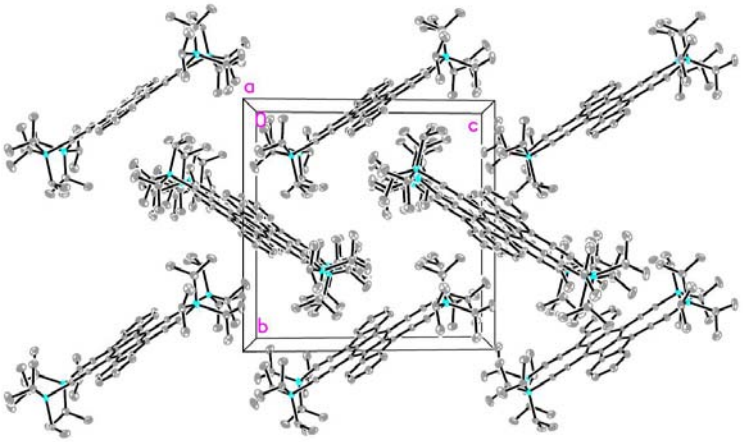
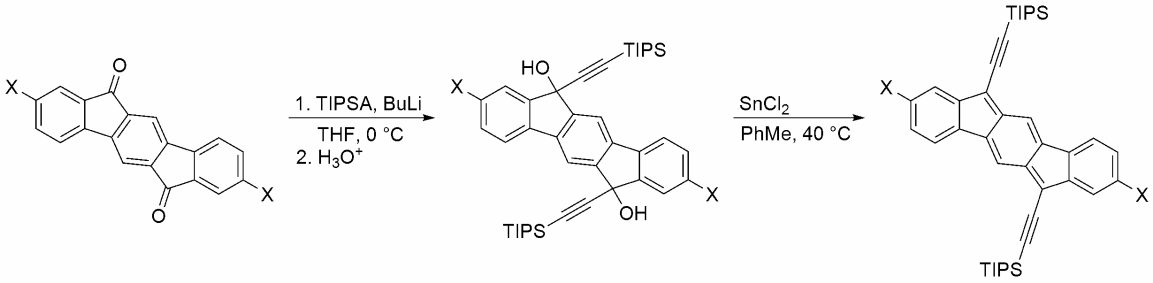


Figure 9. Solid state packing of **82a**.



In continuing the investigation of fully conjugated indeno[1,2-*b*]fluorenes, Haley et al. employed computational studies to determine the effect ethynylation has on the IF core.[41] In comparison to the desilylated analogue of **82a**, ethynylation on the 5 and 11-positions had only a minor influence as their removal changed the HOMO and LUMO energies by +0.02 eV and -0.10 eV, respectively. Functionalization of the favorable 6,12-diethynyl IF scaffold with withdrawing groups on the 2 and 8-positions further lowered the calculated HOMO and LUMO energies to levels that approach those in the fullerene PCBM.[4,42] Ethynylation of **30**, **52a-c**, **58a-d**, and **83** using the lithiate of TIPSA generated diol racemate **85a-i** where further reduction using anhydrous tin(II) chloride afforded **85a-i** in 31-81% yield over two steps (Scheme 24).

Scheme 24. Synthesis of 6,12-Diethynyl IFs **85a-i**.



30, X = H
52a, X = F
52b, X = Cl
52c, X = Br
84, X = Me
58a, X = Ph
58b, X = 4-$CF_3C_6H_4$
58c,X = 3,5-$(CF_3)_2C_6H_3$
58d, X = 2-(5-BuC_4H_2S)

84a-i

85a, 71%
85b, 31%
85c, 35%
85d, 47%
85e, 60%
85f, 44%
85g, 43%
85h, 62%
85i, 81%

Like **82a-b**, the absorption spectra of **85a-i** showed three low energy transitions with a λ_{max} between 561 and 577 nm that correspond to a band gap of 2.08 − 2.15 eV (Table 4). Cyclic voltammetry measurements exhibited first reduction potentials between -0.70 and -0.50 V and second reduction potentials between -1.20 and -1.00 V, correlating to LUMO energies that range between -4.00 V and -4.10 V. Explanation for the lack of HOMO and LUMO energy level variation was due to low orbital density on the 2 and 8-positions where only inductive effects could be invoked.

While removal of ethynyl groups on the 5 and 11-positions did reduce steric hinderance, substitution had a significant impact on the crystal morphology of **85**. Parent **85a** packed without any π-interactions (Figure 9) where the closest intermolecular distance was an edge to face contact of 3.85 Å. On the other hand, 3,5-$(CF_3)_2$-Ph **85h** exhibited one-dimensional columnar stacks with an intermolecular distance of 3.40 Å (Figure 10).

Figure 10. Solid state packing of **86a**.

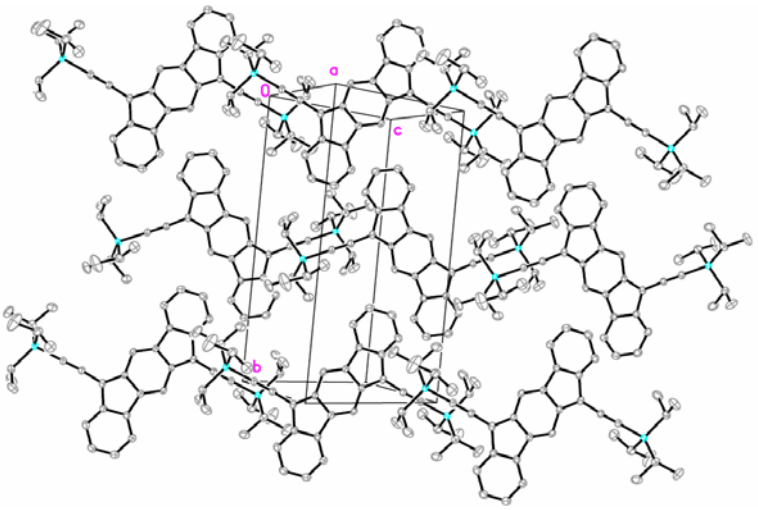
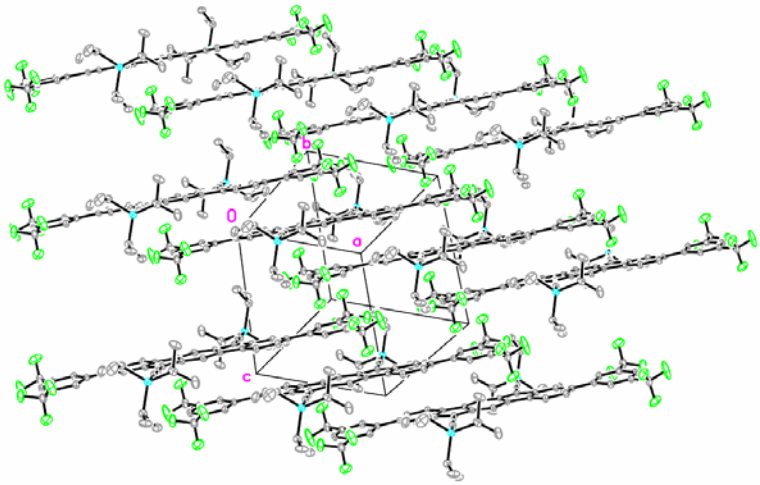


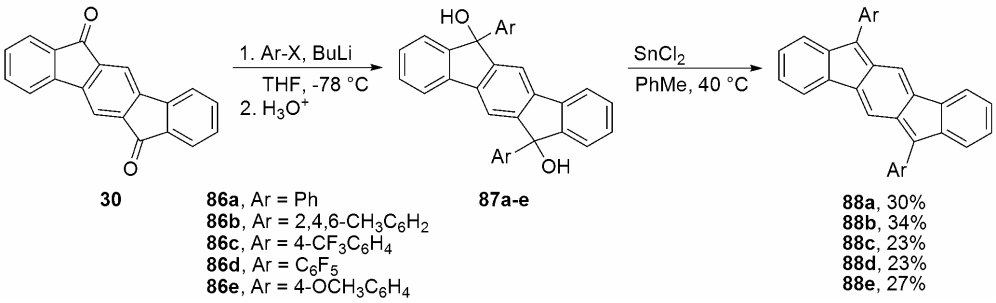
Figure 11. Solid state packing of **86h**.



The next series of fully conjugated indeno[1,2-*b*]fluorenes synthesized by Haley was 6,12-diarylindeno[1,2-*b*]fluorenes (Scheme 25).[43] Similar to **85a-i**, lithium halogen exchange with the appropriate aryl halide **86a-e** and reaction with **30** afforded racemic

87a-e. Reduction using anhydrous tin(II) chloride at elevated temperatures provided **88a-e** in 23% to 37% yield. However, electron withdrawing **87d** would not reduce until an aliquot of trifluoroacetic acid was added.

Scheme 25. Synthesis of 6,12-diaryl IFs **88a-e**.

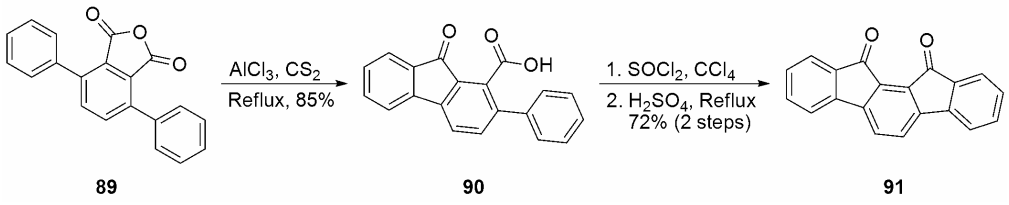


The absorption spectra for **88a-e** displayed a greater variation in λ_{max} values than **85a-i** due to the higher amount of orbital density found on the 6 and 12-positions of the IF core. Cyclic voltammetry data for **89a-e** possessed both reversible reduction and oxidation peaks, a trait not seen before with fully conjugated indeno[1,2-*b*]fluorenes (Table 4). This is chiefly observed with 6,12-diphenylindeno[1,2-*b*]fluorene **88a** that it exhibited two reduction peaks and three oxidation peaks. The reduction and oxidation values for **88a-e** corresponded to HOMO and LUMO energies that range between -5.5 and -5.8 eV and -3.6 and -4.0 eV, respectively. Coincidentally, **88e** displayed reduction and oxidation potentials within 0.03 V that of **75**.

Indeno[2,1-*a*]fluorenes

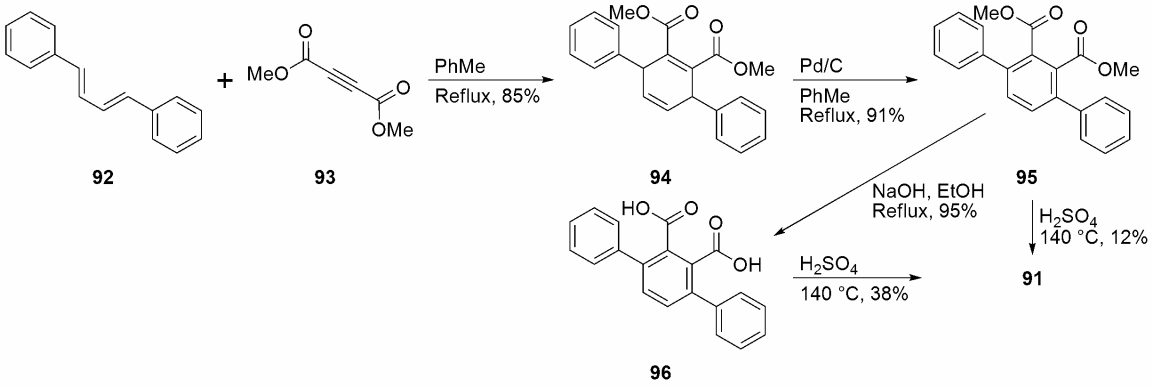
Diones. The first account of the indeno[2,1-*a*]fluorene core in the literature dates to 1939 where Weizmann was investigating polycyclic structures and their potential carcinogenic properties.[10g] Intramolecular Friedel-Crafts acylation of 3,6-diphenylphthalic anhydride (**89**) in refluxing carbon disulfide afforded fluorenone carboxylic acid **90** (Scheme 26). Acid chloride formation of **90** and subsequent cyclization in concentrated sulfuric acid generated the parent indeno[2,1-*a*]fluorene dione **91** in 5% yield with respect to **89**. This was reaffirmed by Deuschel in 1951 where **91** is obtained in 72% under the same conditions.[11b]

Scheme 26. Preparation of parent indeno[2,1-*a*]fluorene dione **91**.



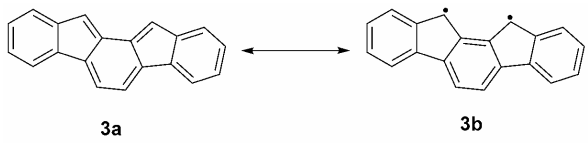
Recent work by Rault-Berthelot and coworkers considered an alternative pathway to **91**. (Scheme 27).[10f] Diels-Alder cyclization with *trans*,*trans*-1,4-diphenyl-1,3-butadiene **92** and DMAD **93** resulted in cyclohexadiene **94** where oxidation with palladium on carbon afforded terphenyl **95**. Direct cyclizaton of **95** using concentrated sulfuric acid does give **91**, but only in 12% yield. Instead, saponification of **95** to diacid **96** followed by cyclization forms **91** in a more modest 38%.

Scheme 27. Diels-Alder approach to the preparation of **91**.



Full Conjugation. Like **2**, the indeno[2,1-*a*]fluorene isomer also supports full conjugation, illustrated by **3**, where an *o*-xylylene core (*o*-quinodimethane) is present in the structure (Figure 11). As such, interest in this structure lies in the inherent nature of the *o*-xylylene core to exist as a stable open shell configuration (**3b**).

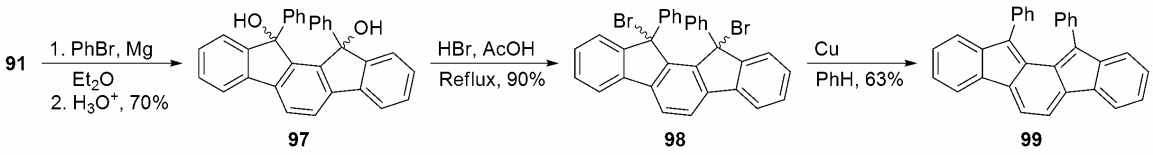
Figure 12. Resonance structures of **3**.



Work on **3** originated in 1957 when LeBerre and coworkers reacted phenylmagnesium bromide with **91** to form diol **97** (Scheme 28).[44] Refluxing in a hydrobromic acid/acetic acid solution resulted in dibromide **98** where reduction using elemental copper afforded 11,12-diphenylindeno[2,1-*a*]fluorene **99** in 63% yield. While

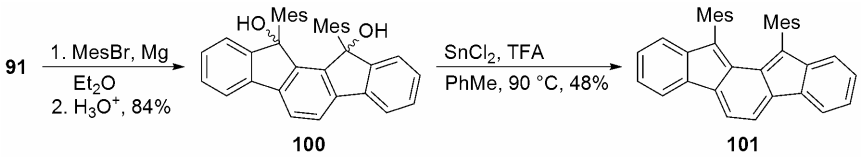
99 readily degraded in aerobic conditions, solutions under an inert atmosphere were said to be stable but no information regarding time were given. However, due to these air-sensitive issues as well as the limitations of the time, no further work on its structural or electronic properties were explored.

Scheme 28. Preparation of fully conjugated 11,12-diphenylindeno[2,1-*a*]flluorene **99**.



Recent work by Tobe examined the synthesis of 11,12-dimesitylindeno[2,1-*a*]fluorene **100** which was also derived from **91** (Scheme 29).[45] After reaction of **91** with mesityl gringard, diol **100** was reduced with anhydrous tin(II) chloride in the presence of trifluoroacetic acid at elevated temperatures in toluene to afford **101** in 48% yield. Fortunately, **101** was stable on the order of weeks in air, attributed to the bulky mesityl groups to adequately protect the sensitive 11 and 12-positions.

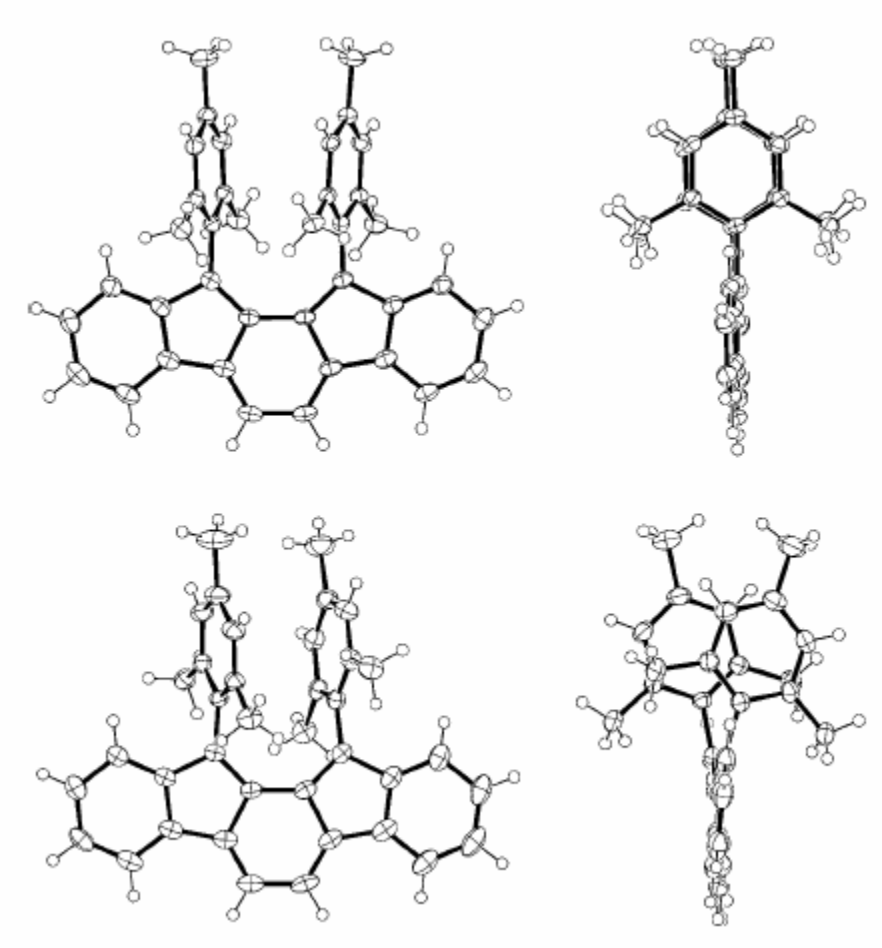
Scheme 29. Preparation of fully conjugated 11,12-dimesitylindeno[2,1-*a*]fluorene **101**.



The absorption spectra of **101** showed three distinct transitions in the 480 to 540 nm domain (λ_{max}: 537 nm) as well as a low energy tail at 730 nm, affording a 1.70 eV band gap energy. As with the previous mentioned fully conjugated [1,2-*b*] IFs, no fluorescence was observed for **101**. Cyclic voltammetry data showed that **101** exhibited both a reversible oxidation and reduction at -1.51 and 0.59 V, respectively.

X-ray single crystals of **101** clearly showed the indeno[2,1-*a*]fluorene scaffold (Figure 12). Interestingly, two independent molecules of **101** were found where the mesityl groups are either in an eclipsed or staggered fashion (top and bottom, respectively), exhibiting a torsion angle of 1.7° and 15.2°, respectively. Examination of the internal bond lengths of **101** revealed the expected alternating long (1.431 and 1.480 Å) and short (1.359 and 1.391 Å) motif, similar to **82a**.

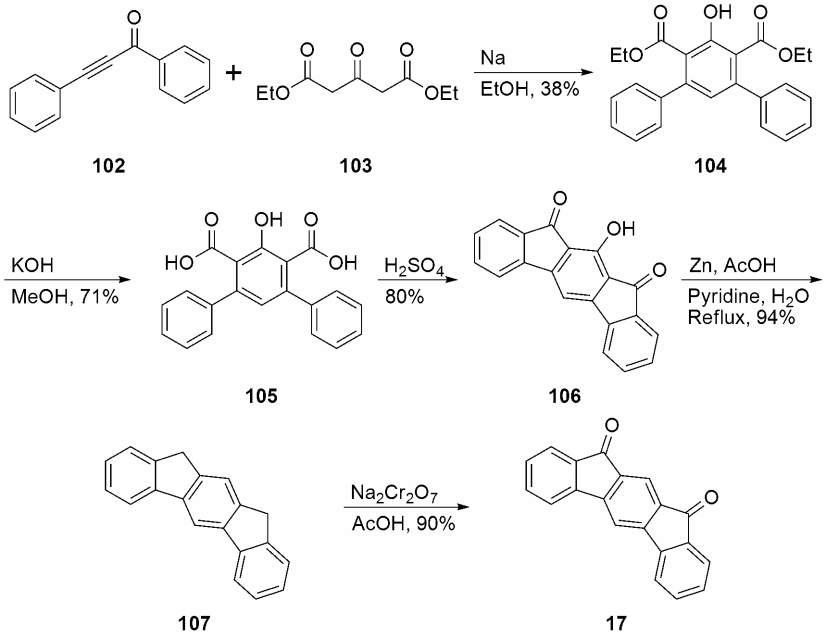
Figure 13. Eclipsed (top) and staggered (bottom) crystal morphs of **101**.



Indeno[2,1-*b*]fluorenes

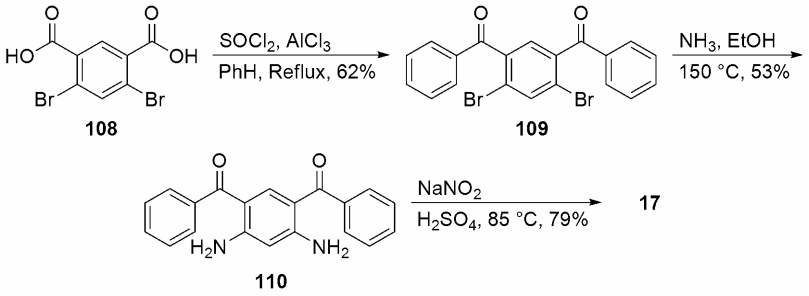
Diones. The first account of 10,12-indeno[2,1-*b*]fluorene IF dione **17** dates to 1951 where Deuschel condensed phenylbenzoylacetylene **102** with ketodiester **103** to afford terphenyl diester **104** (Scheme 30).[11b] Saponification of **104** to **105** and subsequent ring closure yielded 11-hydroxy [2,1-*b*] dione **106**. Reduction using zinc metal provided 10,12-dihydroindeno[2,1-*b*]fluorene **107** and oxidation with sodium dichromate gave **17**.

Scheme 30. Original preparation of parent indeno[2,1-*b*]fluorene dione **17**.



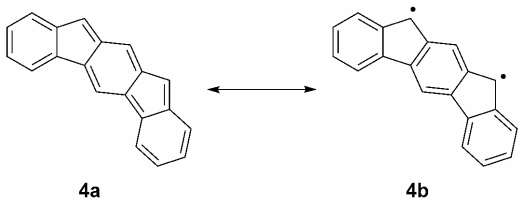
Work by Chardonnens and coworkers in 1955 proposed an alternative pathway to **17** where 4,6-dibromoisophthalic acid **108** was converted to the acid chloride and subsequently underwent a two-fold Friedel-Crafts acylation with benzene to afford dibromodione **109** (Scheme 31).[12a] Aryl amination of **109** yielded **110** where a subsequent Sandmeyer-mediated cyclization gave **17** in 79% yield. The synthesis of substituted indeno[2,1-*b*]fluorenes has also been explored. As discussed earlier, the [2,1-*b*] isomer was often formed in equal amounts of the corresponding [1,2-*a*] isomer in a multitude of cyclizations performed by Chardonnens and coworkers (Scheme 3).[18]

Scheme 31. Chardonnen's synthesis to **17**.



Full Conjugation. Full conjugation for the indeno[2,1-*b*]fluorene isomer is also possible (**4**, Figure 13). However, due to ring positioning, formation of the requisite xylylene core in **4** requires the disruption of two benzene rings rather than one needed for the [1,2-*b*] and [2,1-*a*] isomers. As such, **4** displays an asymmetrical arrangement of the π-system where the D and E-rings both possess *s-cis* diene linkages. Like the above mentioned fully conjugated [2,1-*a*] **3**, interest for **4** lies in its ability to stable biradical character (**4b**).

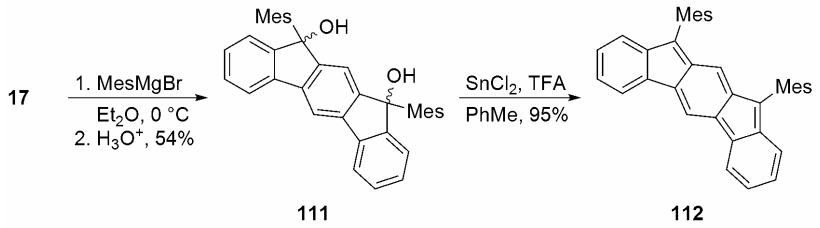
Figure 14. Resonance structures of **4**.



Currently, only one example of a fully conjugated indeno[2,1-*b*]fluorene is known and its existence at this time remains unofficial.[46] It was recently synthesized by Tobe

and coworkers in a near identical manner in which **101** was made; IF dione **17** was reacted with two equivalents of mesitylmagnesium bromide to form racemate diol **111** where further reaction with tin(II) chloride in the presence of trifluoroacetic acid yielded 10,12-dimesitylindeno[2,1-*b*]fluorene **112** (Scheme 32). Little is known about this molecule in terms of optoelectronic properties as well as relative stability. Due to the presence of the two *s*-*cis* diene linkages, however, **112** is presumably less stable than its [1,2-*b*] and [1,2-*a*] counterparts.

Scheme 32. Preparation of fully conjugated IF **112**.

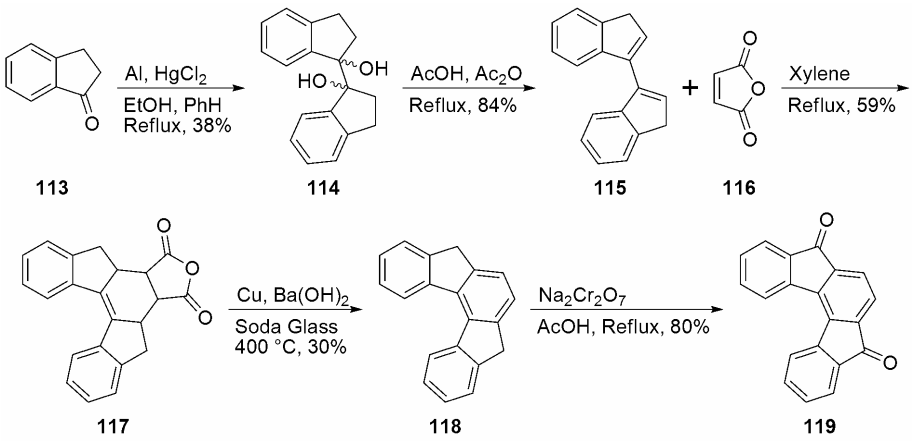


Indeno[2,1-*c*]fluorenes

Diones. The first account of the [2,1-*c*] IF dione in the literature occurred in 1961 where work by Ginsburg and coworkers investigated the Diels-Alder chemistry regarding bi(cyclopentenes) and bi(cycloheptenes) (Scheme 33).[47] They found that reaction of indanone **113** in the presence of an aluminum amalgam resulted in pinacol **114** which further eliminated to form 3,3'-biindenyl **115** by means of refluxing acetic acid and acetic anhydride. Cyclization of **115** with maleic anhydride **116** afforded anhydride **117**. Decarboxylation of **117** using elemental copper, barium hydroxide, and soda glass at 400

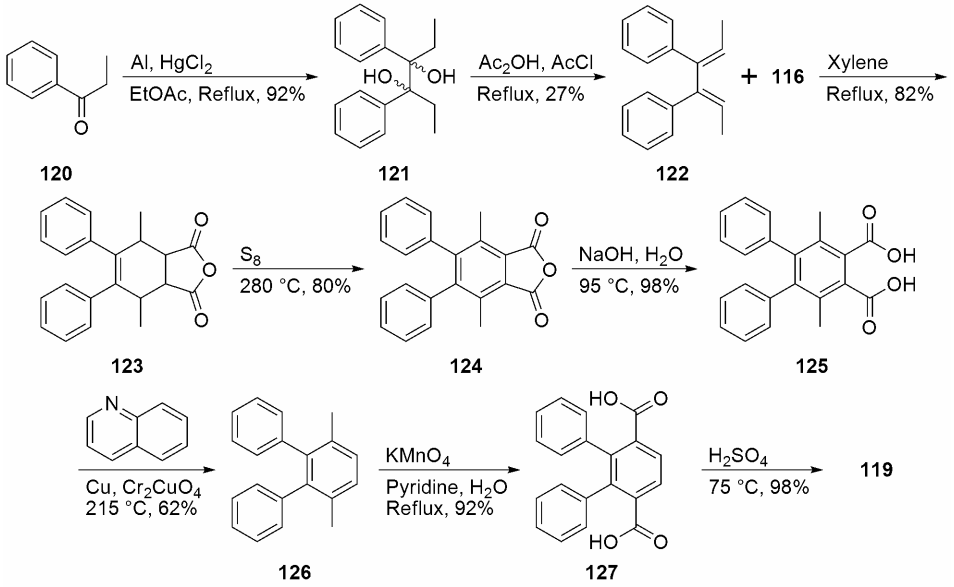
°C generated 5,8-dihydroindeno[2,1-*c*]fluorene **118**. Oxidation of **118** with sodium dichromate in refluxing acetic acid afforded dione **119**.

Scheme 33. Preparation of parent [1,2-*c*] IF dione **119**.



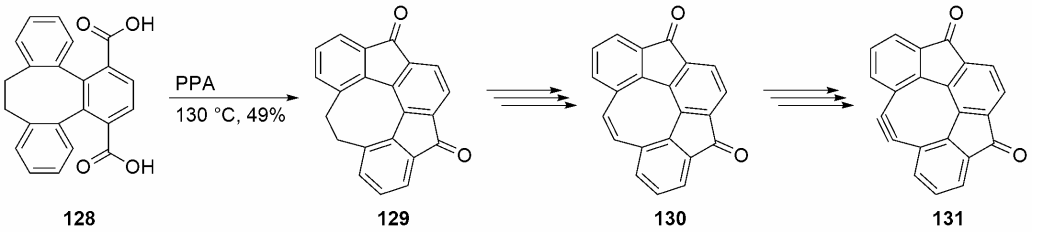
An alternative route to **119** was devised by Chardonnens and coworkers in 1966 where propiophenone **120** is converted to pinacol **121** through an aluminum amalgam in refluxing ethyl acetate (Scheme 34).[48] Double elimination of **121** using acetyl chloride in refluxing acetic anhydride afforded diene **122** which is cyclized with **116** to give anhdyride **123**. Aromatization of the central ring using elemental sulfur at 280 °C formed terphenyl anhydride **124**. Saponification to **125** and subsequent decarboxylation using the Lazier catalyst at 215 °C yielded 3,6-dimethyl-1,2-diphenyl benzene (**126**). Oxidation via potassium permanganate in a refluxing solution of water and pyridine formed diacid **127** and further cyclization using concentrated sulfuric acid at elevated temperatures gave **119**.

Scheme 34. Alternate synthesis to **119**.



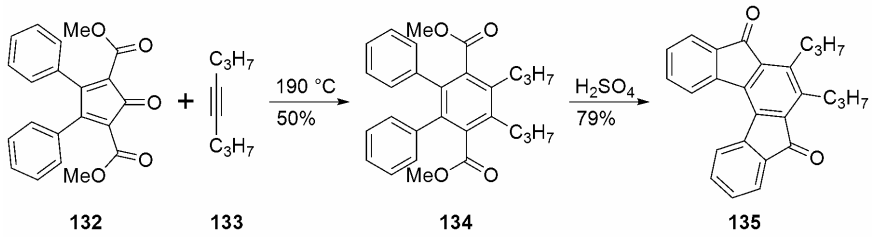
The few examples of substituted [2,1-*c*] IF diones in the literature are limited to the 1, 6, 7, and 12-positions. For example, work by Wong and coworkers on the investigation of planarized cyclooctatetraenes cyclized diacid **128**, with polyphosphoric acid at elevated temperatures to form dione **129** where the 1 and 12-positions are tethered together with an ethane bridge.[49] A combination of bromination and elimination reactions with **129** resulted in an unsaturation to ethene- and ethyne-bridged IFs **130** and **131**, respectively.

Scheme 35. Preparation of fused [2,1-*c*] IF dione **129**.



Substitution on the 6 and 7-positions of the [2,1-*c*] core was obtained by Wang where cyclopentadienone **132** was reacted with 4-octyne **133** in a [4+2] Diels-Alder reaction to form terphenyl diester **134**.[50] Cyclization with concentrated sulfuric acid gave 6,7-dipropyl indeno[2,1-*c*]fluorene dione **135** in 79% yield. Recall that these results are in contrast to the observations found in Scheme 12 where use of either a phenyl acetylene or diphenyl acetylene resulted in the corresponding [1,2-*b*] isomer in high yield.[22]

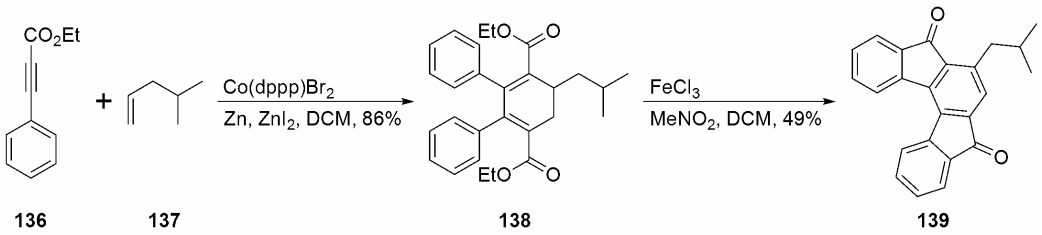
Scheme 36. Preparation of 6,7,-dipropyl [2,1-*c*] IF dione **135**.



Isobutyl [2,1-*c*] IF dione **139** was isolated by Hilt and coworkers that performed a cobalt-mediated [2+2+2] cyclization with two equivalents of ethyl 3-phenyl propiolate **136** and 4-methylpentene **137** that gave terphenyl diester **138** in 86% yield.[51] Reaction of

138 with an excess of iron(III) chloride cyclized and aromatized the central ring to afford **139**.

Scheme 37. Preparation of 6-isobutyl [2,1-*c*] IF dione **139**.



Conclusions

Like many PAHs, IFs are experiencing a considerable reemergence into the current literature due to their interesting optoelectronic and photophysical properties. While recent attention has mostly pertained to the [1,2-*b*] isomer, it is reasonable expectation that similar studies will be performed on the remaining isomers as they too hold great potential. Fully conjugated IFs also are of great interest due to their electron accepting abilities and potential ambipolar behaviors.

Bridge to Chapter II

After examination of the literature, it was determined that fully conjugated indeno[1,2-*b*]fluorenes (IFs) might prove useful as suitable acene analogues due to their topological similarities that IFs and pentacenes share. Chapter II describes the synthesis of the first stable examples of fully conjugated IFs, provides a detailed structure analysis of the IF core, and conveys their optoelectronic properties.

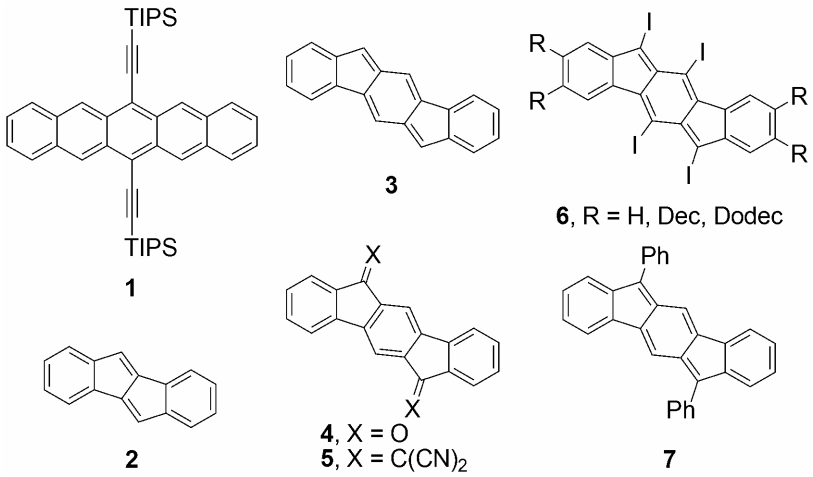
CHAPTER II

INDENO[1,2-*B*]FLUORENES: FULLY CONJUGATED ANTIAROMATIC ANALOGUES OF PENTACENE

Introduction

This chapter was co-authored by Bradley D. Rose, who performed synthetic experiments under my supervision, Sean P. McClintock, who performed computational studies, Lev N. Zakharov, who performed single crystal X-ray crystallographic analyses, and Michael M. Haley, who provided guidance and editorial assistance. This work has been published in *Angewandte Chemie, International Edition* (**2011**, *50*, 1127-1130).

Conjugated hydrocarbons with extended polycyclic frameworks have fascinated chemists for more than a century.[1] Originally studied because of interest in the fundamental, intrinsic properties associated with such aesthetically appealing structures, more recent investigations have focused on utilization of these π-electron-rich compounds as materials in optical and electronic device applications.[2] Acenes such as pentacene and its derivatives (e.g., **1**)[3] have received the bulk of the renewed attention,[1c,d] but they unfortunately are prone toward oxidative degradation;[4] hence, there is demand for alternative, acene-like topologies. While incorporation of heteroatoms is one possibility,[5] very recent studies by the groups of Saito, Kawase, and Tilley have reported improved syntheses of derivatives of dibenzopentalene (**2**), in which two five-membered rings have replaced the more traditional six-membered rings, as potential acene analogues.[6]



The indeno[1,2-*b*]fluorene skeleton (**3**), a 6-5-6-5-6 fused ring system also known as dibenzo[a,g]-*s*-indacene,[7] is an attractive structural motif in this regard. A fully conjugated indenofluorene (IF) should possess some remarkable characteristics: (i) Compounds like **3** have two fewer carbons than pentacene and thus two fewer π-electrons, making **3** formally anti-aromatic (20 π-electrons). (ii) Such molecules host a *para*-xylylene (*p*-quinodimethane) core, a reactive moiety that typically cannot be isolated because of its tendency to oligomerize/polymerize.[8] (iii) The bonding picture of **3** should be interesting as the IF core can be viewed several possible ways (e.g., a [20]annulene, a dibenzo-fused [12]annulene). (iv) IFs do not possess any internal *s-cis* diene linkages, which could make them more resistant to the cycloaddition pathways that degrade acenes.

Although a number of molecules incorporate the indenofluorene core, nearly all bear substituents on positions 5 and 11 that either result in cross-conjugation (ketones **4**, olefins **5**)[9] or disrupt conjugation altogether (disubstitution, spiro-fusion).[10] Examples of fully conjugated species are extremely rare, as only four compounds have been reported

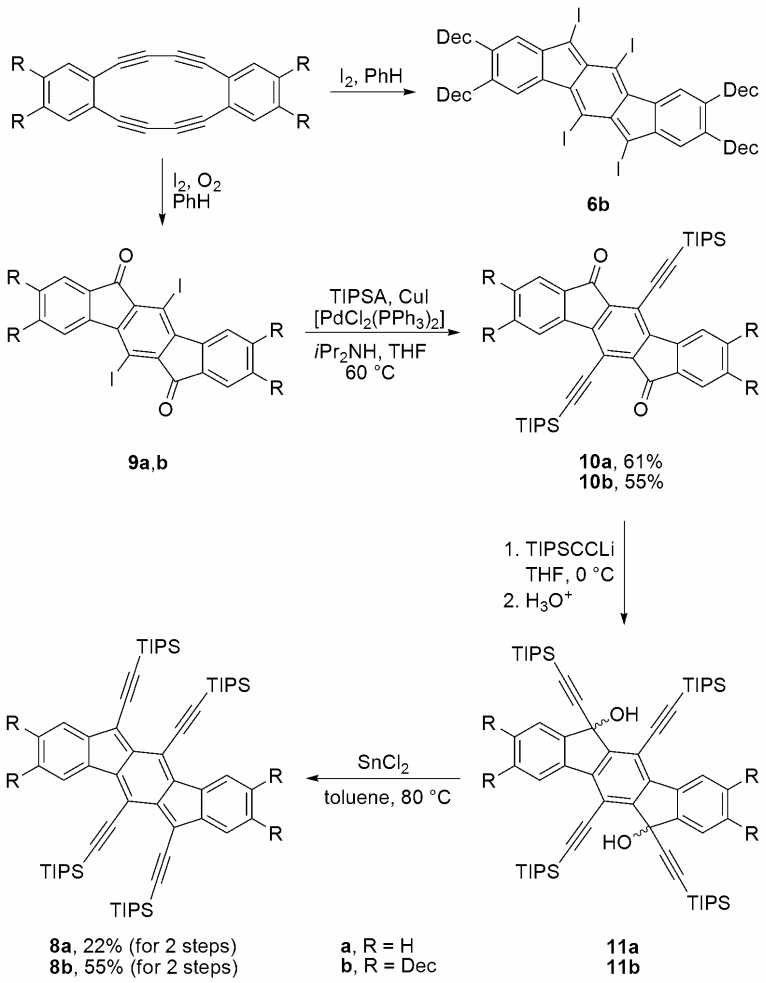
to date. In 1994 Swager et al. prepared and characterized tetraiodides **6** but these rapidly oxidized to the corresponding diones upon exposure to air.[11] Very little is known about IF **7** prepared by Scherf as the synthesis has not been disclosed; the only spectroscopic feature mentioned is a UV-vis λ_{max} absorption of 543 nm.[12] Recently Kubo and co-workers prepared naphthalene-fused IFs. These molecules exhibited singlet biradical behavior, however, meaning that the dominant resonance structure has a benzene unit as the central six-membered ring; thus, the molecules cannot be considered fully delocalized.[13] In this communication, we disclose the synthesis of stable indenofluorenes **8a–b**. We also report the X-ray crystal structure of **8a**, which unambiguously confirms the planar, fully conjugated state and provides a rare glimpse into the *p*-xylylene core. Also discussed are the optoelectronic profiles of **8a–b**, as well as a cursory examination of their stability to photooxidative conditions in comparison to **1**.

Results and Discussion

Synthesis. Initial attempts to access the tetraethynylated derivatives via Sonogashira cross-coupling of **6b** (prepared as previously described from the corresponding dehydrobenzo[12]annulene, Scheme 1),[11] with either phenylacetylene or (triisopropylsilyl)acetylene (TIPSA) proved to be problematic, affording complex mixtures of products. Instead, the syntheses of IFs **8a-b** introduced the alkynes in a stepwise manner. Starting with known diiododiones **9a-b,** again prepared from the dehydrobenzo[12]annulene,[11] cross-coupling with TIPSA afforded diynes **10a-b**. Addition of the lithiated acetylide of TIPSA and subsequent reduction of the intermediate diols **11a-b** overnight using $SnCl_2$ in toluene at 80 °C provided **8a-b** in modest overall

yield. While red in the solid state, solutions of IFs **8a-b** exhibit a brilliant blue-purple color.

Scheme 1. Synthesis of **8a-b**.



Computational and Solid State Studies. Single crystals of **8a** suitable for x-ray diffraction were obtained by slow evaporation of a solution in hexanes. The molecular structure (Figure 1) reveals that the fused ring system is essentially planar (deviation rms

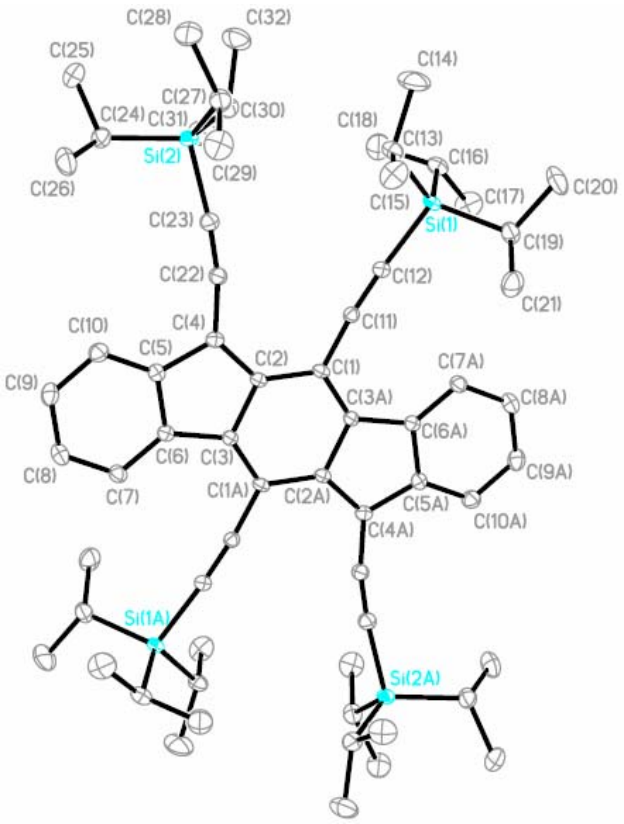
= 0.013 Å). * The bulky TIPS-capped acetylenes are bent away from one another by 4-11° and are also bent out the plane of the 20-carbon core by 3.5-4.0°. Our initial hypothesis regarding bond lengths consisted of two possibilities: (1) the overall anti-aromaticity of the molecule would dominate, resulting in alternating long and short bonds throughout the entire ring system, i.e., a [20]annulene; or (2) the benzene rings would stay fully delocalized and the *p*-xylylene unit would possess long and short bond lengths as typical for non-aromatic single and double bonds, i.e., a dibenzo[12]annulene.

Examination of the C–C bond lengths (Table 1) indicates that indeed there are alternating long (1.438(3) and 1.457(3) Å for C1–C2 and C2–C3, respectively) and short (1.374(3) and 1.390(3) Å for C1–C3A and C2–C4, respectively) bonds in the central *p*-xylylene core but the peripheral benzene bond lengths are relatively homogenized (1.392-1.412 Å). Interestingly, this bonding situation closely resembles the x-ray data analyses of Thiele's and Chichibabin's hydrocarbons, two previously reported molecules containing crystallographically determined *p*-xylylene cores.[14]

To shed additional light, NICS(1) calculations for the desilylated analogue of **8a** afforded NICS values for the peripheral, five-membered, and central rings to be –7.12, 1.84, and 0.02, respectively. The B3LYP/6-311+G**-optimized geometry of desilylated **8a** (Table 1) using Gaussian 03[15] provided bond lengths of 1.444, 1.457, and 1.379 Å for C1-C2, C2-C3, and C1-C3A, respectively, and 1.393 to 1.418 Å for bond lengths of the

* X-ray data for **8a**: $C_{64}H_{92}Si_4$, M = 973.74, 0.26 x 0.12 x 0.05 mm, T = 173(2) K, monoclinic, space group $P2_1/c$, a = 13.579(2) Å, b = 15.042(2) Å, c = 15.054(2) Å, β = 97.502(3)°, V = 3048.6(8) Å^3, Z = 2, Z' = 0.5, D_c = 1.061 Mg/m^3, μ = 0.133 mm^{-1}, F(000) = 1064, $2\theta_{max}$ = 50.00°, 29004 reflections, 5357 independent reflections [R_{int} = 0.0554], R1 = 0.0453, wR2 = 0.1092 and GOF = 1.103 for 4217 reflections (491 parameters) with $I>2\sigma(I)$, R1 = 0.0651, wR2 = 0.1273 and GOF = 1.103 for all 5357 reflections, max/min residual electron density +0.338/–0.274 eÅ^3. CCDC-787154 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure 1. Molecular structure of indenofluorene **8a**; ellipsoids drawn at 30% probability level.



peripheral arene rings, values which nearly coincide with the crystallographic data. Lower level semi-empirical calculations by Kataoka and Toyota also confirm these findings.[16] Such good agreement between the experimental and computational data suggests that neither hypothesis is correct. Instead, **8a** should be considered a fully conjugated 20 π-electron hydrocarbon with fused *s-trans* 1,3-diene linkages across both the top and bottom portions of the carbon skeleton. The 1,4-diphenyl-1,3-butadiene bonding picture is also consistent in solution, as the ^{3}J values of the arene protons are within a narrow range of 7.44-7.55 Hz. As initially described by Günther[17] and used

extensively by Mitchell,[18] one can utilize these coupling constants to determine the bond alternance parameter, *Q*, which equals the ratio of the bond orders of the benzene C7-C8 and C8-C9 bonds (as shown in Figure 1) and thus reveals the nature of the ring current in the fused ring. As such, we obtain a *Q* value of 1.01, which is indicative of a nonaromatic fused ring, analogous to the NICS results.

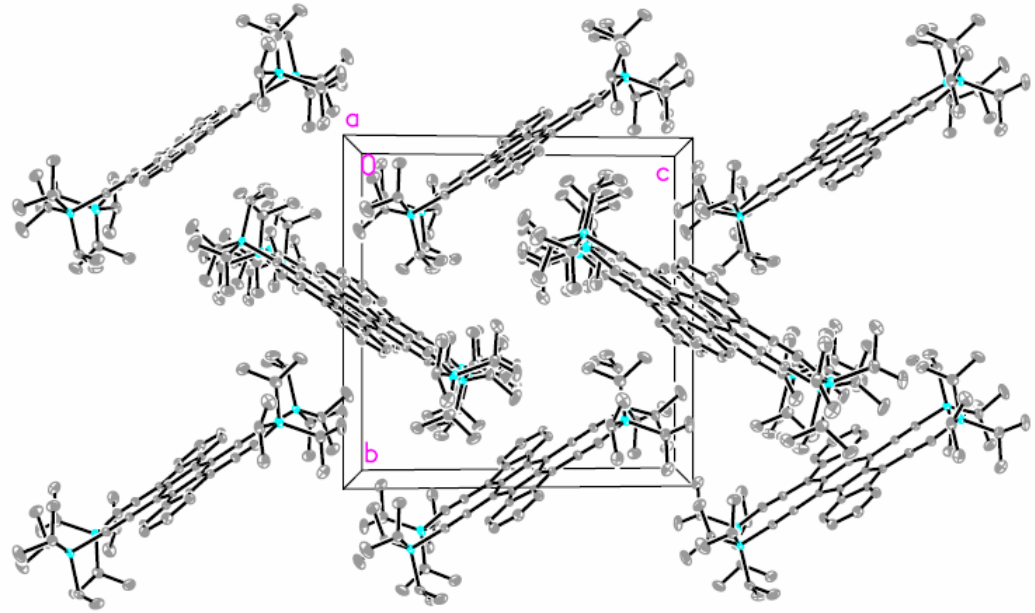
Table 1. Experimental and calculated bond lengths of indenofluorene **8a** and a structurally related *p*-xylylene molecule.

Bond	X-Ray	DFT Calcs[a]	SCF MO Calcs[b]	Thiele's Hydrocarbon[c,d]
C1-C3A	1.374(3)	1.379	1.365	1.346
C1-C2	1.438(3)	1.444	1.457	1.449
C2-C3	1.457(3)	1.457	1.462	1.449
C2-C4	1.390(3)	1.396	1.371	1.381
C3-C6	1.470(3)	1.466	1.470	[e]
C4-C5	1.470(3)	1.463	1.456	1.482
C5-C6	1.412(3)	1.417	1.411	[e]
Benzene (avg)	1.389(3)	1.398	1.402	[e]

[a]Performed using Gaussian 03 at the B3LYP/6-311+G** level of theory. [b]Ref. 16. [c]Ref. 14a. [d]A more descriptive name is 3,6-bis(diphenylmethylene)-1,4-cyclohexadiene. [e]Not applicable.

The crystal packing of **8a** (Figure 2) loosely resembles the herringbone pattern often found in unsubstituted acenes such as pentacene. The presence of four interdigitated TIPS groups per indenofluorene expands this basic motif, yet the packing is sufficiently tight that no solvent molecules co-crystallize with **8a**. The major contacts in the unit cell are between the TIPS groups and the central IF ring with an average distance of 3.93 Å.

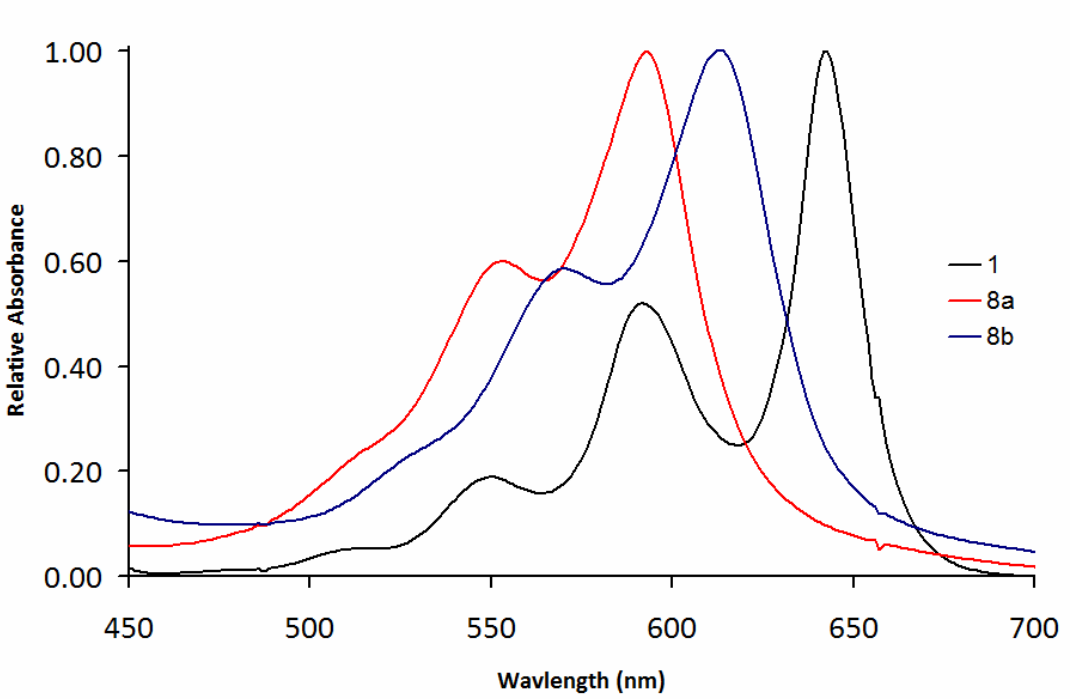
Figure 2. Crystal packing of **8a**.



Electronic Spectra. The optoelectronic spectra of **8a-b** are shown along with pentacene **1** in Figure 3. Similar to **1**, IFs **8a** and **8b** exhibit three low energy absorptions (λ_{max}: 594 and 614 nm, respectively) but are blue-shifted ca. 50 and 30 nm, respectively, compared to **1**. These optical data correspond to estimated HOMO-LUMO gaps of 1.98 and 1.91 eV for **8a** and **8b**, respectively, compared to 1.85 eV for **1**,[*] which agree quite well with the B3LYP/6-311+G**-calculated gap of 1.97 eV for the desilylated analog of **8a**. Unlike **1**, both **8a** and **8b** are non-emissive, which is usually the case with [4*n*] π-electron systems.

[*] The optical HOMO–LUMO gap of **8a** and **8b** were determined as the intersection of the x-axis and a tangent line that passes through the inflection point of their lowest energy absorption.

Figure 3. Electronic absorption spectra of **1**, **8a**, and **8b** in $CHCl_3$.



Stability The relative stabilities of **8a** and **8b** were also briefly examined. Initial testing via UV-vis spectroscopy was performed under similar conditions as reported by Miller et al. but no degradation was observed in the traditional time frame used for their pentacene studies (< 12 h).[4c] Instead, samples of **8a** and **8b** were allowed to stand in loosely capped volumetric flasks under air in the light, and periodic ^{1}H NMR measurements were made. While it was found that samples of **8a** and **8b** were stable on the order of a few weeks, the molecules eventually did degrade over the course of 2-3 months.

Conclusions

In summary, we have demonstrated the feasibility of fully conjugated, formally anti-aromatic indenofluorenes. Through x-ray crystallography, we have also captured a rare glimpse of the *p*-xylylene core and confirmed the structure of **8a** with comparison to the other known molecules that contain this moiety. Examination of the optoelectronic properties of IFs **8a** and **8b** unambiguously confirm that a clear comparison of fully conjugated indenofluorenes to pentacenes can be made with potentially superior stabilities. Future work will consist of exploring more efficient methodologies to generate the conjugated indenofluorene core along with investigating a larger variety of substitution motifs to better improve packing in the solid state as well as to provide a greater opportunity for detailed study of structure-property-relationships.

Experimental

General Methods. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using either a Varian Inova 300 (^{1}H: 299.93 MHz, ^{13}C: 75.42 MHz) or 500 (^{1}H: 500.11 MHz, ^{13}C: 125.75 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm relative to the residual chloroform (^{1}H: 7.27 ppm, ^{13}C: 77.23 ppm) reference. Coupling constants are expressed in hertz. IR spectra were recorded using a Nicolet Magna FTIR 550 spectrometer. UV-Vis spectra were recorded on an HP 8453 UV-Vis spectrometer. Fluorescence spectra and were recorded on a Horiba Jobin Yvon Fluoromax-4 spectrofluorimeter. High resolution mass spectra were recorded on a Applied Biosystems 4000 Qtrap mass spectrometer. THF was distilled over Na/benzophenone under N_2.

Unless otherwise stated, all reagents were purchased and used as received. Compounds **9a** and **9b** were prepared according to reference 11.

Bis(TIPSA)Indenofluorenyldione 10a. Dione **9a** (0.150 g, 0.233 mmol), $Pd(PPh_3)Cl_2$ (0.009 g, 0.014 mmol), CuI (0.005 g, 0.028 mmol) in THF (30 mL) and DIPA (30 mL) was degassed with Ar for 50 min. TIPSA (0.21 mL, .932 mmol) was added to the mixture and the resulting solution was covered with Al foil and stirred overnight at 60 °C. Upon completion, the mixture was evaporated to dryness. The crude material was chromatographed over basic alumina (9:1 hexanes/CH_2Cl_2) to give **10a** (0.091 g, 61%) as a red crystalline solid. ^{1}H NMR ($CDCl_3$): δ 8.72 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 7.0 Hz, 2H), 7.51 (dt, *J* = 7.6, 1.2 Hz), 7.38 (dt, *J* = 7.5, 0.7 Hz, 2H), 1.36-1.26 (m, 42H); ^{13}C NMR ($CDCl_3$): δ 190.06, 146.44, 142.06, 138.47, 134.44, 133.78, 129.60, 124.09, 123.49, 114.02, 106.78, 100.37, 18.65, 11.42; IR (NaCl): *v* 2942, 2865, 1721, 1605, 1465, 1432, 1282, 1268, 1181, 928, 882, 764, 718, 680, 658 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ε): 312 (4.39), 327 (4.42), 343 (4.61), 519 (2.82) nm; Em. ($CHCl_3$) λ_{max}: 602 nm; HRMS (MALDI) for $C_{42}H_{51}O_2Si_2$ [M+1]: calcd 643.3428, found 643.3447.

Decyl-Bis(TIPSA)Indenofluorenyldione 10b. Dione **9b** (0.146 g, 0.133 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 0.005 mmol), and CuI (2 mg, 0.002 mmol) in THF (20 mL) and DIPA (20 mL) was degassed with Ar for 45 min. TIPSA (0.12 mL, 0.532 mmol) was added to the mixture and the resulting solution was covered with Al foil and stirred overnight at 60 °C. Upon completion, the mixture was evaporated to dryness and the crude product dissolved in 3:10 hexanes/CH_2Cl_2 and then passed through a pad of silica to remove insoluble material. The filtrate was evaporated to dryness and the crude product chromatographed on silica (1:9 hexanes/CH_2Cl_2) to give **10b** (0.088 g, 55%) as a

red/orange solid. ^{1}H NMR ($CDCl_3$): δ 8.24 (s, 2H), 7.43 (s, 2H), 2.56-2.52 (m, 8H), 1.57-1.53 (m, 8H), 1.37-1.23 (m, 98H), 0.91-0.85 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 190.34, 148.54, 146.37, 142.24, 139.91, 139.07, 132.11, 125.01, 124.56, 113.49, 150.60, 100.68, 34.22, 32.62, 32.17, 31.88, 31.01, 30.24, 29.66, 29.61, 29.55, 29.50, 29.31, 22.67, 18.78, 14.09, 11.46; IR (NaCl): *v* 2924, 2854, 1716, 1609, 1466, 1445, 1285, 1160, 1069, 997, 898, 882, 794, 678, 662, 619 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ε): 313 (4.47), 333 (4.33), 500 (3.08) nm; Em. ($CHCl_3$) λ_{max}: 565 nm; HRMS (MALDI) for $C_{82}H_{131}O_2Si_2$ [M+1]: calcd 1203.9688, found 1205.1110

Tetrakis(TIPSA)Indenofluorene 8a. TIPSA (0.104 mL, 0.466 mmol) in THF (5 mL) was degassed with Ar for 15 min and subsequently cooled to 0 °C. BuLi (0.300 mL, 0.466 mmol) was added and the mixture was stirred for 15 min at 0 °C. In a separate flask, dione **10a** (0.075 g, 0.117 mmol) in THF (10 mL) was degassed with Ar for 15 minutes, and then also cooled to 0 °C. The lithiate solution was cannulated into the flask containing **10a** and stirred for 2 h at 0 °C. Upon completion, the solution was diluted with ether (20 mL) and water (20 mL), and washed with brine (20 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated to dryness. The crude diol **11a** was then redissolved in toluene (15 mL) and anhydrous $SnCl_2$ (0.088 g, 0.466 mmol) was added. The resulting mixture was stirred overnight at 80 °C. Upon completion, the mixture was evaporated to dryness and chromatographed over neutral alumina (hexanes) to give **8a** (0.024 g, 21%) as a violet crystalline solid. ^{1}H NMR ($CDCl_3$): δ 8.35 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.3 Hz, 2H), 7.14 (t, J = 7.3 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 1.29-1.19 (m, 84H); ^{13}C NMR ($CDCl_3$): δ 144.68, 141.78, 135.83, 135.55, 128.43, 127.82, 125.52, 123.99, 116.41, 114.61, 106.58, 104.03, 102.70, 18.95, 18.92, 12.32,

12.10; IR (NaCl): *ν* 2943, 2889, 2865, 1521, 1462, 1378, 1366, 1334, 1301, 1150, 1110, 1074, 1016, 996, 953, 882, 869, 759, 754 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ε): 553 (3.69), 593 (3.91) nm; HRMS (MALDI) for $C_{64}H_{93}Si_4$ [$M+Na^+$]: calcd 995.6174, found 995.6144

Decyl-Tetrakis(TIPSA)Indenofluorene 8b. TIPSA (0.056 mL, 0.249 mmol) in THF (5 mL) was degassed with Ar for 15 min and subsequently cooled to 0 °C. BuLi (0.16 mL, 0.249 mmol) was added and the mixture was stirred for 15 min at 0 °C. In a separate flask, dione **10b** (0.075 g, 0.062 mmol) in THF (10 mL) was degassed with Ar for 15 min, and then also cooled to 0 °C. The lithiate solution was cannulated into the flask containing **10a** and the resulting mixture was stirred for 2 h at 0 °C. Upon completion, the solution was diluted with ether (20 mL) and water (20 mL), and washed with brine (20 mL). The organic layer was dried ($MgSO_4$) filtered, and evaporated to dryness. The crude diol **11b** was then redissolved in toluene (15 mL) and anhydrous $SnCl_2$ (0.045 g, 0.249 mmol) was added. The resulting mixture was stirred overnight at 80 °C. Upon completion, the mixture was evaporated to dryness and chromatographed over neutral alumina (hexanes) to give **8b** (0.052 g, 55%) as a blue crystalline solid. ^1H NMR ($CDCl_3$): δ 7.96 (s, 2H), 7.15 (s, 2H), 2.56-2.52 (m, 8H), 1.57-1.53 (m, 8H), 1.37-1.20 (m, 148H), 0.91-0.85 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 143.29, 147.74, 141.58, 141.16, 135.90, 134.01, 125.31, 125.14, 123.24, 115.80, 113.55, 105.47, 14.82, 103.11, 34.08, 33.08, 32.15, 30.57, 29.90, 29.59, 22.93, 19.31, 19.22, 14.34, 12.65, 12.49; IR (NaCl): *ν* 2924, 2863, 1524, 1463, 1689, 1338, 1166, 1189, 1075, 1017, 997, 918, 864 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ε): 570 (3.82), 613 (4.05) nm; HRMS (MALDI) for $C_{104}H_{173}Si_4$ [M+1]: calcd 1534.2609, found 1534.4403

Computational Methods. All computations were calculated using the Gaussian 03[16] suite of programs at the B3LYP/6-31G* or B3LYP/6-31G+** level of theory. All stationary points were confirmed by harmonic frequency analysis and checked for stability for triplet and SCF convergence. The energies of the stationary points were determined, including zero point energies, at the same level of theory. NICS calculations were carried out using standard GIAO methods with Bq atoms (NICS probes) 1.0 Å above the geometric center of the ring.

Bridge to Chapter III

Given the satisfying results of isolating and investigating stable examples of indeno[1,2-*b*]fluorenes, their current synthetic route is problematic due to the low yields and intolerance to functionalization. Therefore, finding an alternate pathway to gain access to the IF core is of great importance. Fortunately, computational studies suggested that functionalization on the 5 and 11-positions on the central arene is not a critical parameter in obtaining low HOMO and LUMO energy levels. As such, Chapter III describes access to 6,12-diethynyl IFs through a three-step Suzuki / Friedel-Crafts route. Given the versatility of this route, nine IF derivatives are synthesized where the 2 and 8-positions are amenable to functionalization. Furthermore, this chapter also describes the electrochemistry of fully conjugated IFs and the realization that IFs may prove to be more suitable pentacene compliments rather than replacements.

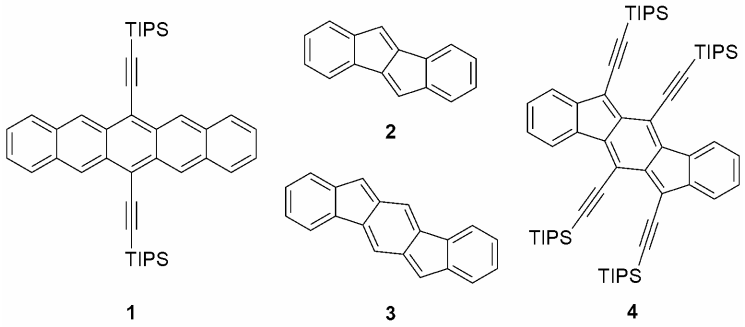
CHAPTER III

SYNTHESIS, CRYSTAL STRUCTURE, & PHOTOPHYSICAL PROPERTIES OF ELECTRON-ACCEPTING 6,12-DIETHYNYLINDENO[1,2-*B*]FLUORENES

Introduction

This chapter was co-authored by Aaron G. Fix, who assisted with synthetic experiments, Bradley D. Rose, who performed computational studies, Christopher D. Weber, who performed electrochemical experiments, Shunpei Nobusue and Chelsea E. Stockwell, who also assisted with synthetic experiments under my supervision, Lev N. Zakharov, who performed single crystal X-ray analyses, as well as Mark C. Lonergan, and Michael M. Haley, who provided guidance and editorial assistance. This work has been accepted to *Angewandte Chemie, International Edition*.

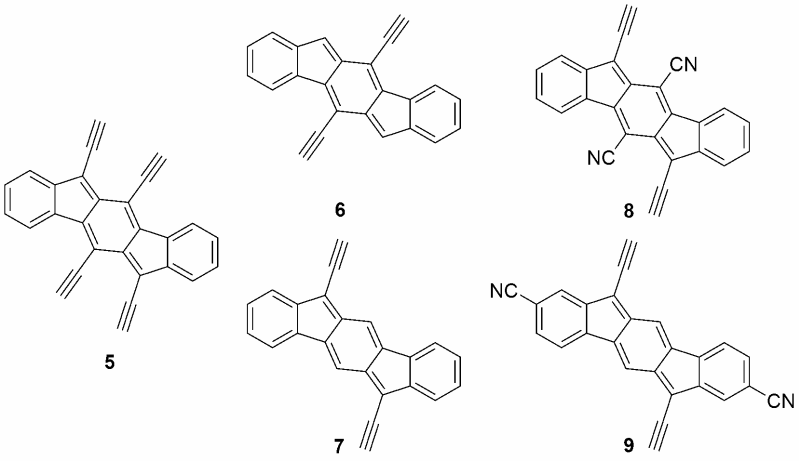
Polycyclic hydrocarbons that possess extended π-conjugation are of significant interest because of their potential use in optical and electronic device applications such as organic light emitting devices, field-effect transistors and solar cells.[1] While a majority of studies have focused on acenes such as pentacene and its derivatives (e.g., **1**),[2] these systems are susceptible to oxidative and photolytic degradation;[3] thus, there is a need for alternative, acene-like molecules. One avenue in this search has explored compounds containing five-membered rings, rather than the more traditional six-membered rings. Prime examples of such molecules are dibenzopentalene (**2**) and derivatives, where the groups of Saito, Kawase, and Tilley have recently described improved methods for their construction.[4]



Another attractive topology is the indeno[1,2-*b*]fluorene (IF) skeleton (e.g., **3**), an acene analogue where the B and D rings each contain one fewer carbon atom, thus making the 20 π–electron molecule formally anti-aromatic. While the pentacyclic IF core is common in the literature, nearly all examples bear substituents on the 6 and 12 positions, resulting in either cross-conjugation (e.g., ketones, exocyclic olefins)[5] or disrupted conjugation (e.g., disubstitution, spiro-fusion).[6] Of the four fully conjugated IFs known prior to 2011, three are rapidly oxidized by trace oxygen[7] and the other is poorly characterized.[8]

Very recently we reported the synthesis of tetraalkynylated indeno[1,2-*b*]fluorenes (e.g., **4**).[9] The compounds exhibited similar UV-Vis absorption profiles and slightly larger HOMO/LUMO energy gaps compared to **1** while maintaining potentially superior solution stabilities; however, the packing of **4** in the solid state resembled an expanded herringbone pattern, a motif often found in unsubstituted acenes. Since the steric bulk of the four interdigitated (triisopropylsilyl)ethynyl groups was the most likely cause for inhibiting a desirable "brick and mortar" π-stacking, we sought to examine additional IF derivatives.

Figure 1. Calculated ethynylindenofluorene derivatives.



As a guide for experimental studies, we performed DFT calculations (B3LYP/6-311+G**)* on a variety of substituted IFs. Our initial task was to determine the effect ethynylogation of **3** has on the HOMO (–5.53 eV) and LUMO energy levels (–3.03 eV) and energy gap (2.50 eV) of the IF core (Figure 1, Table 1). Inclusion of the four ethynyl units in **5** significantly lowers the LUMO by ca. 0.5 eV while the HOMO level remains unchanged, affording a gap energy of 1.97 eV. Inclusion of only two acetylenes on positions 5 and 11 (e.g., **6**) raises both the HOMO and LUMO (–5.62 and –3.24 eV, respectively) compared to **5** (–5.53 and –3.56 eV), affording a net gap increase of 0.41 eV. If the two alkynes are located on positions 6 and 12, as in **7**, the HOMO level (–5.51 eV) is on par with **5** and the LUMO is elevated slightly (–3.46 eV), thus increasing the gap by only 0.08 eV. Similar to acenes,[2] these results illustrate that judicious positioning of the alkyne moieties will significantly affect electronic and photophysical properties.

* All calculations were performed using Gaussian 09, Revision A.02. Frisch, M. J. et al. Gaussian, Inc., Wallingford, CT, 2009.

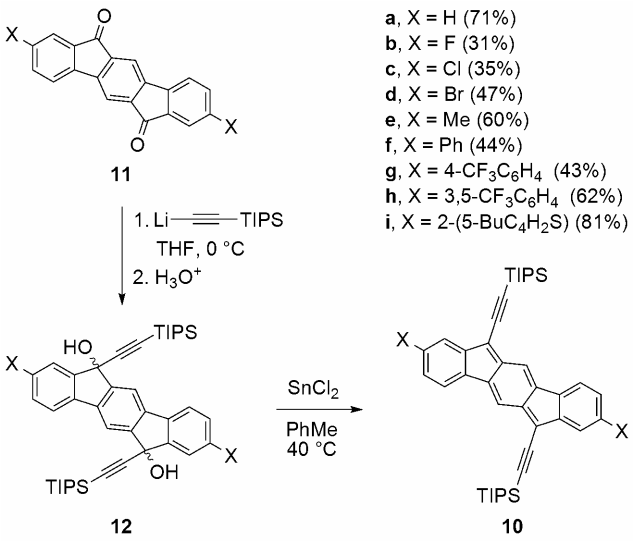
Functionalization of the favorable 6,12-diethynylIF scaffold with electron withdrawing groups further lowers the calculated HOMO and LUMO energies. For instance, dicyano-functionalized scaffolds **8** and **9** exhibit calculated HOMO energies of –6.00 and –6.19 eV, respectively, and LUMO energies of –4.07 and –4.14 eV, respectively. Such molecules may prove to be suitable n-type organic semiconductors, as these energy levels and gaps closely resemble those of ubiquitous electron acceptor PCBM[10] (–6.2 and –3.95 eV).[11] Encouraged by these initial computational studies, we targeted a number of 6,12-diethynylindeno[1,2-*b*]fluorenes for synthesis and study. We disclose herein the preparation of IFs **10a**–**i** along with their respective optical, electrochemical and computational data. We also report the X-ray structures of **10b** and **10h**, highlighting the effects that substitution on the IF core has on crystal packing.

Results and Discussion

Synthesis. Since the transannular cyclization route previously used to synthesize the IF core was low yielding, intolerant of facile substitution, and difficult to scale up,[7,9,12] we sought a more efficient pathway. Fortunately, dione **11a** is readily synthesized on multi-gram scale via the three-step Suzuki / Friedel-Crafts route devised by Merlet et al.[13] Addition of lithiated (triisopropylsilyl)acetylene afforded crude diol **12a** (Scheme 1); subsequent reduction using $SnCl_2$ in toluene at 40 °C provided a deep magenta solution, from which IF **10a** was isolated in very good yield. This methodology could be extended to a number of 2,8-disubstituted IFs starting from the respective diones, either known (**11b**–**d**[14]) or easily synthesized (**11e**–**i**; see Supporting Information); thus, IFs **10b**–**i** were

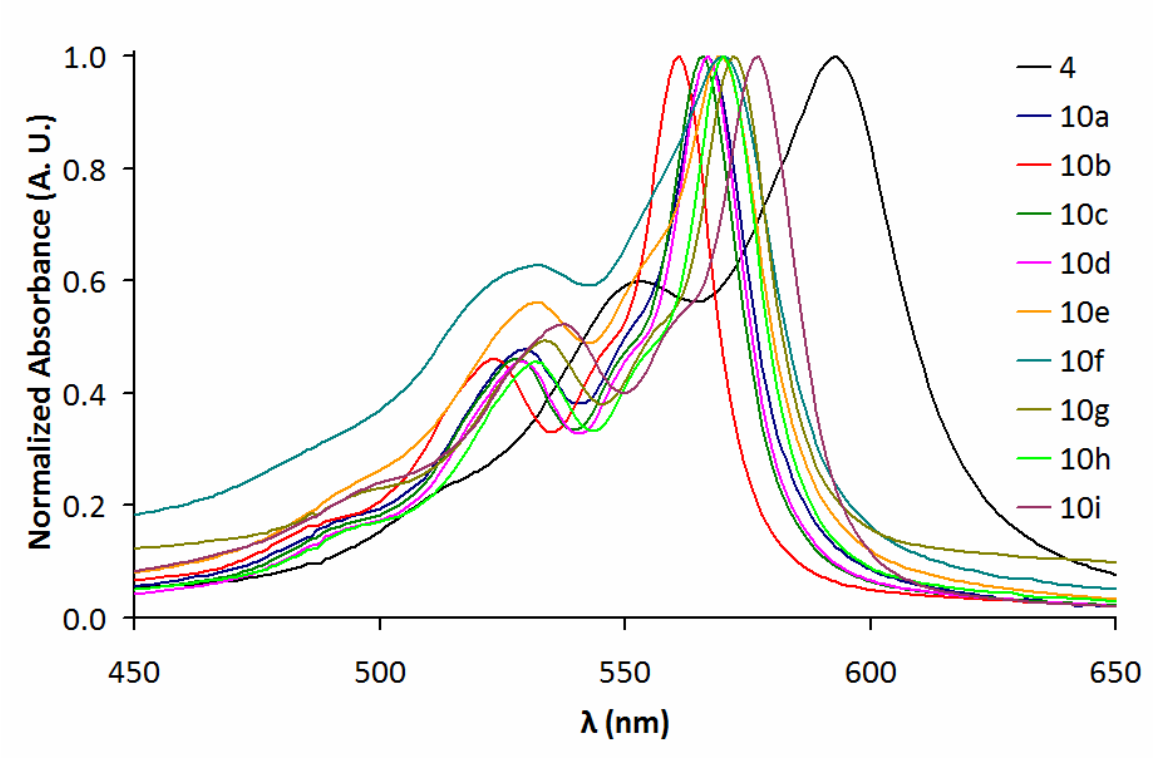
prepared via the same two-step process and isolated in moderate to very good yields after recrystallization (Scheme 1).

Scheme 1. Synthesis of diethynylIFs **10a-i**.



Electronic Absorption Spectra. The absorption spectra of **4** and **10a-i** are shown in Figure 2. Similar to **4**, IF **10a** exhibits three low- energy absorptions (λ_{max} 567 nm), but these are blue-shifted ca. 25-30 nm compared to **4**. This can be attributed to removal of the two acetylenes at the 5 and 11 positions in **10a**. Interestingly, variation of the substituents bound to the IF core at the 2 and 8 positions has only modest effect on the absorption profiles: fluoro IF **10b** has the lowest λ_{max} value of 561 nm, whereas the λ_{max} of thienyl IF **10i** is at 577 nm. The optical data correspond to a relatively narrow 2.08–2.15 eV range for the HOMO-LUMO energy gaps of **10a**–**i**. As observed with **4**, **10a**–**i** are non-emissive, as is usually the case with [4*n*] π–electron systems.

Figure 2. Electronic absorption spectra for IFs **4** and **10a-i**.



Electrochemical Studies. Figure 3 depicts the experimental cyclic voltammetry (CV) data for **4** and **10a**,**b**,**h** (see Supporting Information for **10c**–**g**). In solution, the IFdiyne scaffold shows quasi-reversible behavior, accepting up to two electrons. The first reduction half-wave potential at ca. –0.5 to –0.7 V (vs. SCE) for **10a**–**h** is 0.2–0.3 V less negative than the recently reported diynyl IF-diones.[12] These data suggest that IFs have comparable or greater electron affinities to that of PCBM. Substitution of electron withdrawing groups on the IF core shifts the reduction half-wave potentials to less negative values. This is chiefly observed with parent **10a**, fluoro **10b**, and 3,5-$(CF_3)_2C_6H_3$ **10h**, which possess first reduction half-wave potentials of –0.69, –0.60, and –0.52 V,

Table 1. Computational, electrochemical, and optical data for indenofluorenes

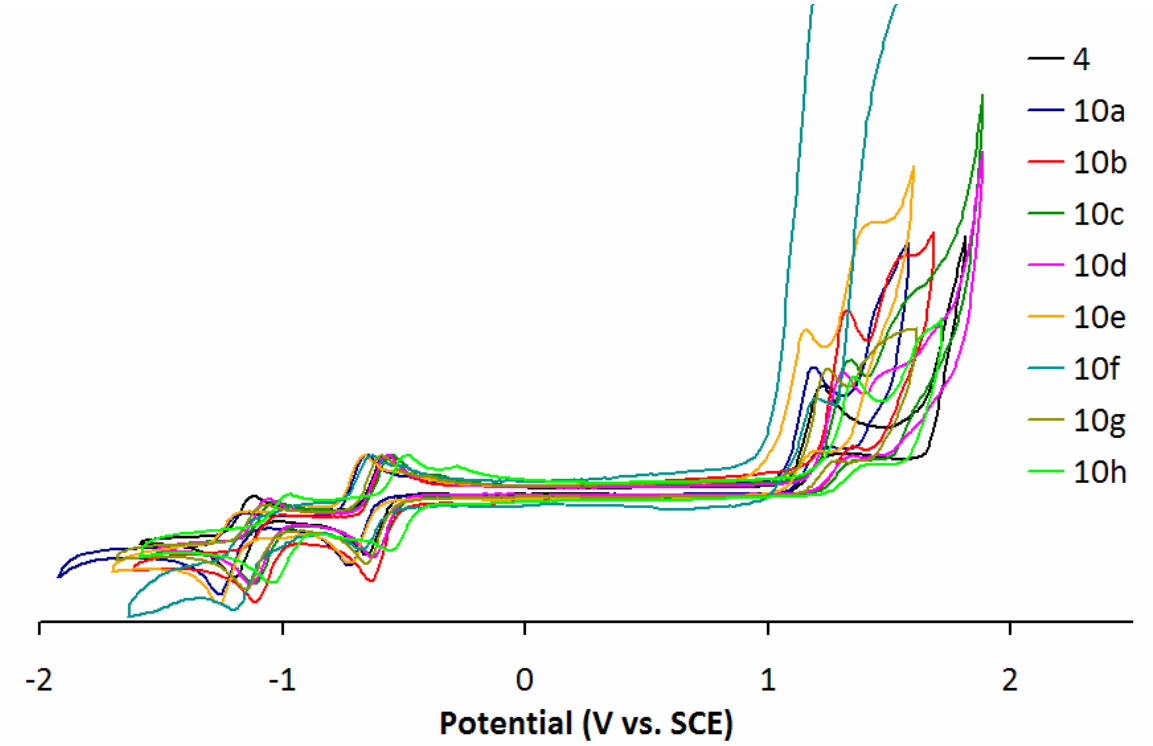
	computational[a]			electrochemical[b]					optical	
compd	E_{HOMO}	E_{LUMO}	E_{Gap}	$E(A^+/A)$	$E(A/A, A/A^{2-})$	E_{HOMO}	E_{LUMO}	E_{Gap}	λ_{max}[c]	E_{Gap}[d]
3	–5.53	–3.03	2.50	—	—	—	—	—	—	—
4/5[e]	–5.53	–3.36	1.97	1.23	–0.62, –1.16	–5.92	–4.07	1.85	594	1.98
6	–5.62	–3.24	2.38	—	—	—	—	—	—	—
7	–5.51	–3.46	2.05	—	—	—	—	—	—	—
8	–6.00	–4.07	1.93	—	—	—	—	—	—	—
9	–6.19	–4.14	2.05	—	—	—	—	—	—	—
10a	–5.51	–3.46	2.05	1.20	–0.69, –1.20	–5.88	–4.00	1.88	568	2.12
10b	–5.79	–3.70	2.09	1.33	–0.60, –1.07	–6.01	–4.08	1.93	561	2.15
10c	–5.82	–3.74	2.08	1.35	–0.59, –1.07	–6.03	–4.09	1.94	567	2.13
10d	–5.83	–3.75	2.08	1.32	–0.60, –1.10	–6.01	–4.09	1.92	567	2.13
10e	–5.43	–3.36	2.07	1.16	–0.69, –1.27[f]	–5.84	–3.99	1.85	569	2.11
10f	–5.53	–3.47	2.06	1.21	–0.66, –1.20[f]	–5.90	–4.03	1.87	570	2.10
10g	–5.81	–3.75	2.06	1.25	–0.62, –1.11	–5.93	–4.06	1.87	572	2.11
10h	–5.97	–3.91	2.06	1.35	–0.52, –1.00	–6.03	–4.16	1.87	570	2.11
10i	–5.89[g]	–3.83[g]	2.06[g]	—[h]	—[h]	—[h]	—[h]	—[h]	577	2.08
PCBM[i]	—	—	—	1.54	–0.71, –1.12	–6.2	–3.95	2.35	—	—

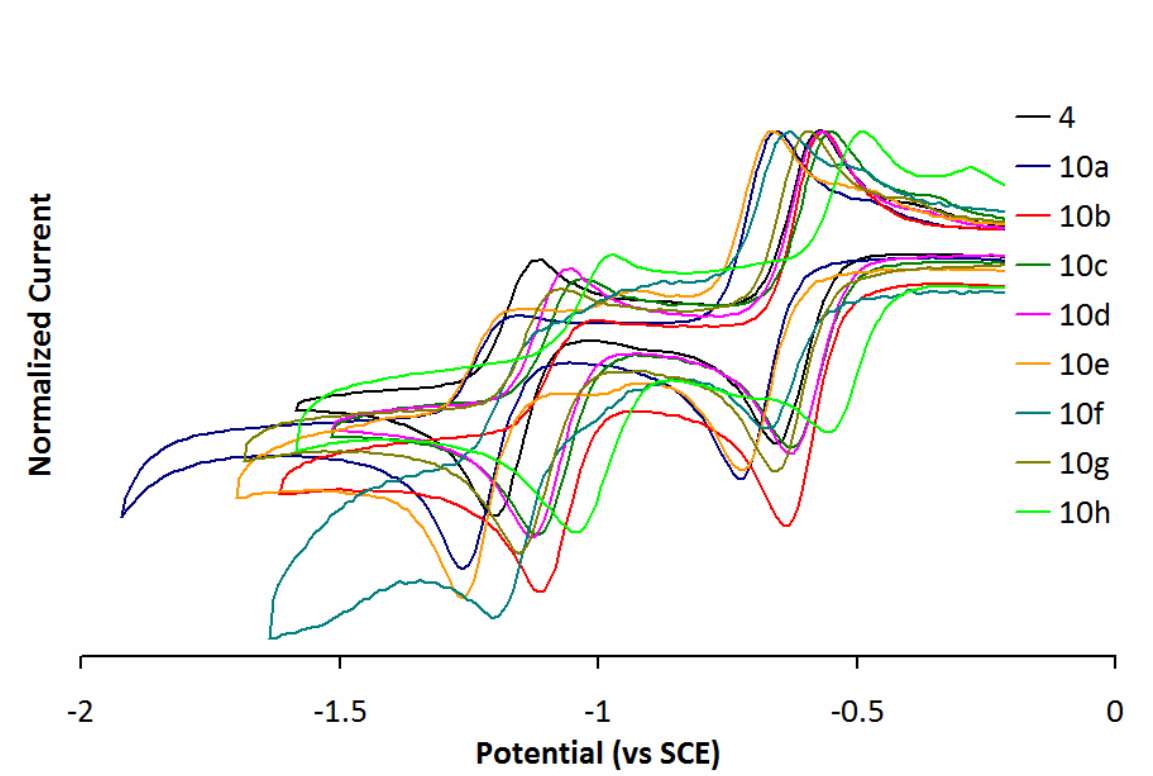
[a]Calculations performed at the B3LYP/6-311+G** level of theory; energies in eV. For computational efficiency, the TIPS groups of **10a-i** were replaced by H atoms. [b]CV recorded using 1–5 mM of analyte in 0.1 M Bu_4NOTf/CH_2Cl_2 using a scan rate of 50 mV/s. The working electrode was a glassy carbon electrode with a Pt coil counter electrode and Ag wire pseudo reference. Values reported as the half-wave potential (vs. SCE) using the Fc^+/Fc couple (0.46 V) as an internal standard. HOMO and LUMO energy levels were approximated using SCE = –4.2 eV vs. vacuum; see reference 5b. Reduction potentials in V; energies in eV. [c]Spectra obtained in $CHCl_3$; wavelength in nm. [d]The optical HOMO–LUMO gap was determined as the intersection of the x-axis and a tangent line that passes through the inflection point of the lowest energy absorption; energies in eV. [e]Experimental data for **4**; computational data for **5**. [f]The second reduction wave was irreversible; the potential of the peak anodic current is reported. [g]Me group in place of Bu to simplify calculations. [h]Unable to obtain. [i]Converted from reference 11.

respectively. This trend is pronounced even further where **10a**, **10b**, and **10h** exhibit second reduction half-wave potentials of –1.20, –1.07, and –1.00 V, respectively. Unlike the IF-diones,[13] **10a**–**h** also exhibit an irreversible oxidation around1.2–1.3 V. The above mentioned trend also holds true for peak potentials for oxidation of the IF scaffold; substitution of increasing electron withdrawing groups shifts the potential to more positive values as demonstrated by **10a**, **10b**, and **10h**, which exhibit peak potentials of 1.20, 1.33, and 1.35 V, respectively. This behavior is justified by examining the products of reduction or oxidation: a two-electron reduction of the IF core results in a 22 π–electron species where every ring is aromatic, i.e., three benzenes and two Cp anions. Hence, an increase in electron withdrawing capability would better stabilize the dianion. Conversely, the formation of oxidative products, especially the 18 π–electron dication, would be destabilized by electron-withdrawing groups. The sole exception to the above mentioned behavior is **10i**, which exhibits an irreversible reduction and polymerizes under oxidative conditions.

Interestingly, while the electrochemically determined energy gaps are somewhat lower (1.85–1.94 eV) than the optical and computational values, all three data sets exhibit a < 0.1 eV range of values, whether substituted with electron-rich or electron-poor groups. Examination of the calculated HOMO-LUMO plots for **10a** (Figure 4) reveals that the 2- and 8-positions possess little orbital density, and hence exhibit virtually no overlap. Therefore, perturbing the electronic nature of the IF scaffold from these positions can be performed only through weak inductive effects.

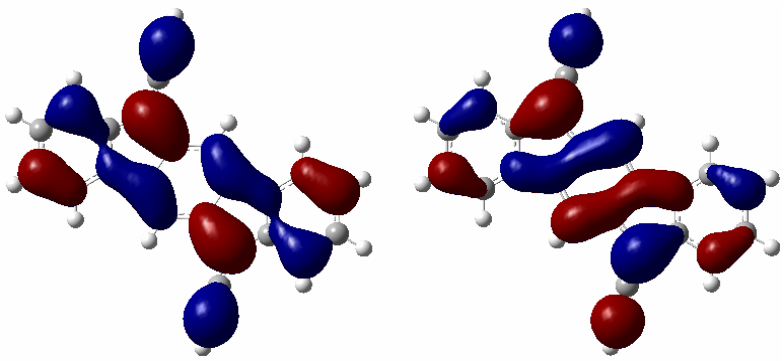
Figure 3. Cyclic voltammetry of IFs **4** and **10a-h**; voltammogram currents are normalized to the E_{pa} (A/A^{-}) peak.





Solid State Studies. Single crystals of **10b** and **10h** suitable for X-ray diffraction were obtained from CH_2Cl_2/CH_3CN and $CHCl_3$, respectively (Figure 5). Similar to **4**, the molecular structures of **10b** and **10h** show that the fused ring system is essentially planar (within 0.017 and 0.042 Å, respectively); however, unlike **4**, the TIPS-capped acetylenes in both species are nearly linear (179°) and planar (0.5° deviation) with the 20-carbon-

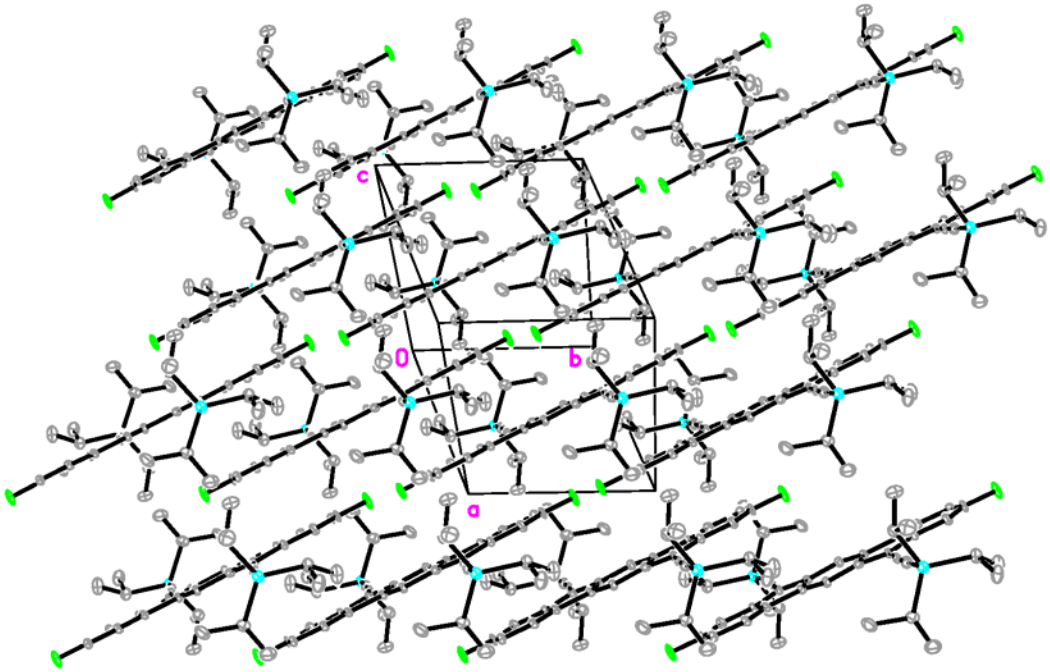
Figure 4. Calculated HOMO (left) and LUMO (right) plots of **10a**.

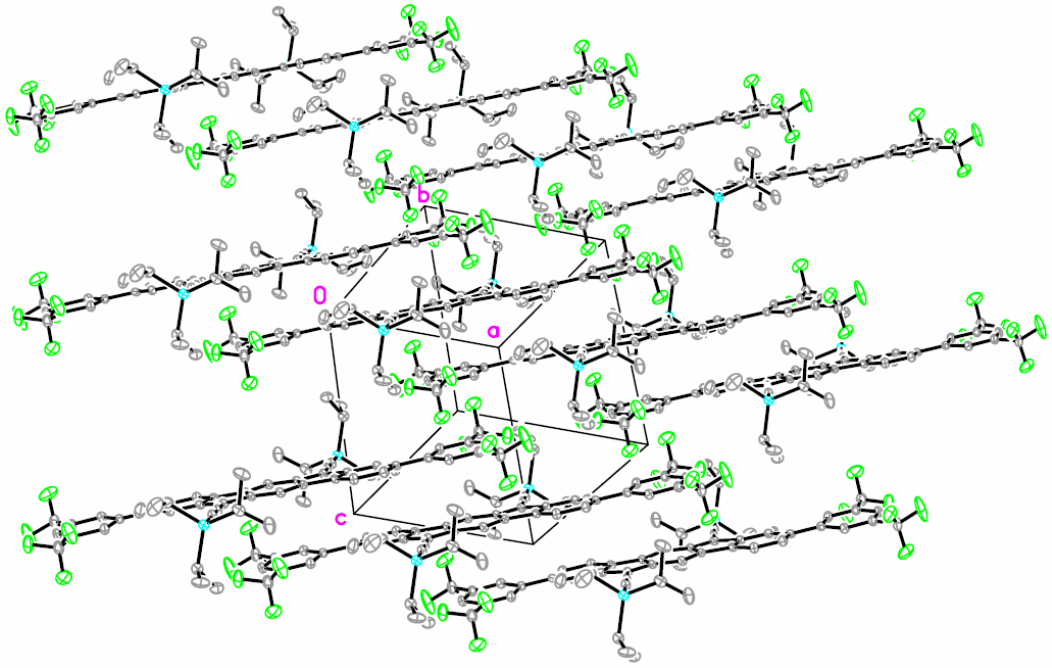


atom core, which is due to the fact that these lack the steric congestion that **4** possesses. Furthermore, the C–C bonds in the central six-membered ring are slightly compressed (0.02 Å) compared to **4**. In the crystal lattice IFs **10b** and **10h** are organized as 1-D π-stacks with close C•••C contacts of 3.43 and 3.40 Å, respectively. The 1-D π-stacks in **10b** form a layer with a shift between two nearest π-stacks. Such an arrangement avoids strong π-interactions between the π-stacks in the layers, but some of C•••C contacts between 1-D π-stacks are in the range 3.14–3.50 Å, indicating that weak interactions between 1-D π-stacks in **10b** are possible. On the other hand, the 1-D π-stacks in the crystal of **10h** are isolated without specific interactions between them. Additionally, the

peripheral 3,5-$(CF_3)_2C_6H_3$ groups for **10h** are nearly coplanar with the IF core, exhibiting a slight 5.5° twist, which is much less than the 35-45° torsion angle typically seen in most biphenyls.[15] This unexpected co- planarity is likely due to the enhanced overlap the phenyl rings provide as they lay directly above and below the central arene of the neighboring molecules as well as the interdigitation of two electron deficient $–CF_3$ groups with electron rich alkynes (3.50 Å intermolecular distance).

Figure 5. Crystal packing of diethynylIFs **10b** (top) and **10h** (bottom); ellipsoids drawn at the 30% probability level.





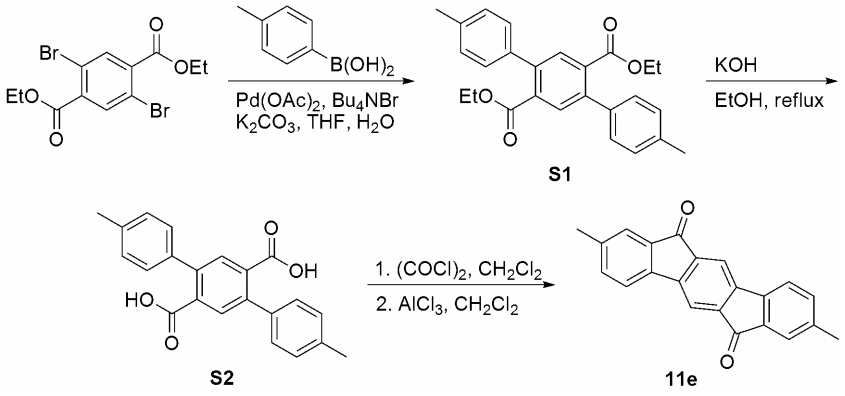
Conclusions

In summary, we have demonstrated a facile approach to a family of fully conjugated indeno[1,2-*b*]fluorenes. The optical and electrochemical data support the computational findings of low-lying HOMO and LUMO energy levels for **10a-i**. These values are similar to PCBM and other mainstream n-type semiconductors, suggesting that IFs could be potential compliments to the usually p-type acenes. Through X-ray crystallography, **10b** and **10h** were shown to pack in dimeric π-stacks in the solid-state, which further improves their credibility for materials applications. Future work will consist of employing **10a-i** in realistic device settings to test their performance as n-type semiconductors, as well as exploring further derivatization of the indeno-[1,2-b]fluorene scaffold.

Experimental

General Comments. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or DMSO-d^6 using either a Varian Inova 500 (^{1}H: 500.11 MHz, ^{13}C: 125.75 MHz) or 600 (^{1}H: 599.98 MHz, ^{13}C: 150.87 MHz) NMR spectrometer. Chemical shifts (δ) are expressed in ppm relative to the residual $CHCl_3$ (^{1}H: 7.27 ppm, ^{13}C: 77.23 ppm), CH_2Cl_2 (^{1}H: 5.32 ppm, ^{13}C: 54.00 ppm), or DMSO (^{1}H: 2.50 ppm, ^{13}C: 39.51 ppm) reference. Coupling constants are expressed in hertz. UV-Vis spectra were recorded on an HP 8453 UV-Vis spectrometer. High resolution mass spectra were recorded on a JEOL MS-Route mass spectrometer. CH_2Cl_2, THF, and toluene were distilled from their appropriate drying agents under N_2. Unless otherwise stated, all reagents were purchased and used as received. Diones **11a**–**d** were synthesized according to previously described procedures.[14,15]

Scheme 2. Preparation of **11e**.



Diester S1. A mixture of 1,4-dibromoterephthalic acid (1.55 g, 4.08 mmol), 4-methylphenylboronic acid (2.22 g, 16.3 mmol), $Pd(OAc)_2$ (0.010 g, 0.03 mmol), and

Bu_4NBr (2.63 g, 8.16 mmol) in toluene (20 mL) was degassed with Ar for 20 min. In a separate flask, a solution of K_2CO_3 (2.82 g, 20.4 mmol) in H_2O (20 mL) was also degassed with Ar for 20 min. The carbonate solution was then cannulated into the terephthalic acid solution and heated at 70 °C for 18 h. After cooling, the mixture was extracted in toluene and the organic layer was washed with H_2O until the washings were colorless. The organic layer was then dried ($MgSO_4$), filtered, and evaporated to dryness to give **S1** (1.55 g, 94%) as a colorless solid. ^{1}H NMR ($CDCl_3$): δ 7.79 (s, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.15 (q, *J* = 7.5 Hz, 4H), 2.42 (s, 6H), 1.07 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 168.3, 141.1, 137.6, 137.4, 133.7, 131.2, 129.1, 128.5, 61.5, 21.4, 14.0; HRMS (ESI) for $C_{26}H_{27}O_4$ [M^++1]: calcd 403.1909, found 403.1902.

Diacid S2. To a solution of **S1** (0.700 g, 1.74 mmol) in anhydrous EtOH (40 mL) was added KOH (1.5 g, 37.40 mmol) dissolved in H_2O (20 mL). The resulting mixture was stirred at reflux overnight. After cooling, the EtOH was evaporated to dryness. Concentrated HCl was added until no more precipitation occurred. The precipitate was then heated to dryness at 120 °C to afford **S2** (0.58 g, 95%) as a colorless solid. ^{1}H NMR (DMSO-d_6): δ 13.06 (s, 2H), 7.63 (s, 2H), 7.30 (d, *J* = 8.0 Hz, 4H), 7.25 (d, *J* = 8.0 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (DMSO-d_6): δ 169.2, 139.2, 136.9, 136.7, 134.3, 130.8, 129.0, 128.2, 20.8; HRMS (ESI) for $C_{22}H_{18}O_4$ [M^+]: calcd 346.3759, found 346.3705.

Dione 11e. To a solution of **S2** (0.58 g, 1.66 mmol) in CH_2Cl_2 (40 mL) was added oxalyl chloride (2.25 mL, 26.6 mmol). To this was added anhydrous DMF (1.0 mL) dropwise at room temperature and the resultant mixture was stirred overnight. The mixture was evaporated to dryness to yield the crude acid chloride as a yellow solid. This material was redissolved in CH_2Cl_2 (30 mL) and the solution was degassed with Ar for

20 min. The solution was cooled to 0 °C and then $AlCl_3$ (1.0 g, 7.47 mmol) was added. The mixture was stirred at 0 °C for 15 min, then warmed to room temperature for 2 h. The reaction was quenched by pouring into an ice-cold 10% HCl solution (50 mL). The resultant precipitate was collected by filtration and dried to yield **11e** (0.36 g, 68%) as a magenta solid. ^{1}H NMR ($CDCl_3$): δ 7.74 (s, 2H), 7.51 (s, 2H), 7.44 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz), 2.41 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 193.5, 146.0, 141.3, 140.0, 139.6, 136.0, 134.5, 125.5, 120.6, 115.8, 21.6; HRMS (ESI) for $C_{22}H_{14}O_2$ [M^+]: calcd 310.0994, found 310.0986.

Dione 11f. A mixture of dione **11d** (0.25 g, 0.57 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol), phenylboronic acid (0.15 g, 1.25 mmol) and Aliquat 336 (0.1 mL) in toluene (40 mL) was degassed with Ar for 2 h. In a separate flask, a solution of K_2CO_3 (0.39 g, 2.82 mmol) in H_2O (10 mL) was also degassed with Ar for 2 h. The carbonate solution was cannulated into the bromodione solution and refluxed for 48 h. After evaporating the mixture to dryness, the crude material was placed on a fine frit and rinsed with H_2O (2 x 50 mL) and acetone (2 x 50 mL) until the washings were colorless, giving **11f** (0.20 g, 48%) as an insoluble pink solid. Mp: > 300 °C; HRMS (ESI) for $C_{32}H_{18}O_2$ [M^+]: calcd 434.1307, found 434.1314.

Dione 11g. A mixture of **11d** (0.25 g, 0.57 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol), *p*-trifluoromethylphenylboronic acid (0.24 g, 1.25 mmol) and Aliquat 336 (0.1 mL) in toluene (40 mL) was degassed with Ar for 2 h. In a separate flask, a solution of K_2CO_3 (0.39 g, 2.82 mmol) in H_2O (10 mL) was also degassed with Ar for 2 h. The carbonate solution was cannulated into the bromodione solution and refluxed for 96 h. After evaporating the mixture to dryness, the crude material was placed a fine frit and rinsed

with H_2O (2 x 50 mL) and acetone (2 x 50 mL) until the washings were colorless, affording **11g** (0.165 g, 51%) as an insoluble pink solid. Mp: > 300 °C; HRMS (ESI) for $C_{34}H_{16}F_6O_2$ [M^+]: calcd 570.1054, found 570.1068.

Dione 11h. A mixture of **11d** (0.13 g, 0.30 mmol) and $Pd(PPh_3)_4$ (0.040 g, 0.04 mmol) in toluene (25 mL) was degassed with Ar for 20 min. In a separate flask, a solution of 3,5-bis(trifluoromethyl)phenyltributylstannane (0.377 g, 0.71 mmol) in toluene (25 mL) was also degassed with Ar for 20 min. The solution containing the stannane was then transferred by cannula into the first flask and the mixture was refluxed overnight. After evaporating the mixture to dryness, the crude material was collected over a fine frit and washed with hexanes and then CH_2Cl_2 to obtain **11h** (0.168 g, 80%) as a poorly soluble red solid. ^{1}H NMR ($CDCl_3$): δ 8.05 (s, 4H), 7.96 (s, 2H), 7.94 (s, 2H), 7.91 (s, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 2H); HRMS (ESI) $C_{36}H_{14}O_2F_{12}$ [M^+]: calcd 706.0802, found 706.0783.

Dione 11i. A mixture of **11d** (0.22 g, 0.50 mmol) and $Pd(PPh_3)_4$ (0.040 g, 0.04 mmol) in toluene (25 mL) was degassed with Ar for 20 min. In a separate flask, a solution of 2-butyl-5-tributylstannylthiophene (0.52 g, 1.2 mmol) in toluene (25 mL) was also degassed for 20 min. The solution containing the stannane was then transferred by cannula into the first flask and the mixture was refluxed overnight. After evaporating the mixture to dryness, the crude material was placed on a plug of celite and rinsed with CH_3CN until the washings were colorless, and then extracted with $CHCl_3$ and evaporated to dryness. The mixture was then suspended in pentane and the precipitate was collected to obtain **11i** (0.168 g, 60%) as a dark violet solid. ^{1}H NMR ($CDCl_3$): δ 7.87 (s, 2H), 7.78 (s, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 3.6 Hz, 2H), 6.78

(d, J = 3.6 Hz, 2H), 2.85 (t, J = 7.2 Hz, 4H), 1.71 (m, 4H), 1.44 (m. 4H), 0.97 (t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 192.7, 147.0, 145.6, 141.5, 140.1, 139.6, 136.6, 134.7, 131.6, 125.4, 123.7, 121.2, 121.0, 115.9, 33.7, 30.0, 22.2, 13.8; HRMS (ESI) $C_{36}H_{30}O_2S_2$ [M^+]: calcd 558.1687, found 558.1673.

General Procedure for 10a-i. (Triisopropylsilyl)acetylene (TIPSA) was dissolved in THF (10 mL), degassed with Ar for 10 min, and cooled to 0 °C. BuLi was added and the mixture stirred at 0 °C for 20 min. In a separate flask, **11a-i** was dissolved in THF (15 mL), and also degassed with Ar for 10 min, and cooled to 0 °C. The lithiate was transferred by cannula to the cold solution containing **11a-i** and then warmed to room temperature for 2 h. The reaction was quenched with 10% HCl soln (30 mL) and extracted in Et_2O (50 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated to dryness. The crude diol was then redissolved in dry toluene (15 mL) and degassed with Ar for 10 min. $SnCl_2$ was added to the mixture and warmed to 40 °C for 2 h. The resulting magenta solution was then filtered and the filtrate was subsequently evaporated to dryness. Recrystallization of the crude material from CH_3CN/CH_2Cl_2 gave the corresponding IF derivative.

IF 10a. TIPSA (1.42 mL, 6.36 mmol), BuLi (3.3 mL, 5.30 mmol), **11a** (0.300 g, 1.06 mmol) and $SnCl_2$ (0.80 g, 4.24 mmol) were reacted according to the general procedure to afford **10a** (0.459 g, 71%) as magenta crystals. ^{1}H NMR ($CDCl_3$): δ 7.36-7.33 (m, 2H), 7.26 (s, 2H), 7.26-7.23 (m, 2H), 7.13-7.07 (m, 4H), 1.21-1.19 (br s, 42H); ^{13}C NMR ($CDCl_3$): δ 143.6, 140.9, 139.3, 137.6, 128.5, 128.2, 126.7, 122.5, 120.5, 119.1, 110.1, 102.1, 19.0, 11.6; UV-vis ($CHCl_3$) λ_{max} (log ε): 491 sh (3.89), 529 (4.37), 568 (4.70) nm; HRMS (ESI) for $C_{42}H_{52}Si_2$ [M^+]: calcd 612.3608, found 612.3623.

IF 10b. TIPSA (1.02 mL, 4.58 mmol), BuLi (2.4 mL, 3.82 mmol), **11b** (0.243 g, 0.76 mmol), and $SnCl_2$ (0.58 g, 3.06 mmol) were reacted according to the general procedure to afford **10b** (0.155 g, 31%) as magenta needles. ^{1}H NMR (CD_2Cl_2): δ 7.31 (dd, *J* = 8.4, 4.8 Hz, 2H), 7.19 (s, 2H), 6.87 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.78 (ddd, *J* = 8.4, 4.8, 2.4 Hz, 2H), 1.24-1.19 (br s, 42H); ^{13}C NMR (CD_2Cl_2): δ 164.1 (d, *J* = 245.6 Hz), 145.8 (d, *J* = 8.6 Hz), 142.2, 139.1, 133.8, 126.7, 122.1 (d, *J* = 9.6 Hz), 119.2, 115.1 (d, *J* = 24.0 Hz), 111.7, 110.0 (d, *J* = 24.0 Hz), 101.6, 19.1, 11.9; UV-vis ($CHCl_3$) λ_{max} (log ε): 485 sh (3.78), 523 (4.26), 561 (4.61) nm; HRMS (ESI) for $C_{42}H_{50}F_2Si_2$ [M^+]: calcd 648.3419, found 648.3422.

IF 10c. TIPSA (0.19 mL, 0.84 mmol), BuLi (0.44 mL, 0.70 mmol), **11c** (0.050 g, 0.14 mmol), and $SnCl_2$ (0.106 g, 0.56 mmol) were reacted according to the general procedure to afford **10c** (0.033 g, 35%) as magenta crystal. ^{1}H NMR (CD_2Cl_2): δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.27 (s, 2H), 7.21 (d, *J* = 2.1 Hz, 2H), 7.10 (dd, *J* = 8.1, 2.1 Hz, 2H), 1.21-1.18 (br s, 42H); ^{13}C NMR (CD_2Cl_2): δ 145.3, 141.8, 139.0, 136.2, 134.7, 128.5, 126.8 122.9, 121.9, 119.7, 112.3, 101.5, 19.1, 11.9; UV-vis ($CHCl_3$) λ_{max} (log ε): 485 sh (3.72), 528 (4.32), 567 (4.66) nm; HRMS (ESI) for $C_{42}H_{50}Cl_2Si_2$ [M+1]: calcd 681.2906, found 681.2887.

IF 10d. TIPSA (0.43 mL, 1.16 mmol), BuLi (0.60 mL, 0.97 mmol), **11d** (0.085 g, 0.19 mmol), and $SnCl_2$ (0.15 g, 0.77 mmol) were reacted according to the general procedure to afford **10d** (0.069 g, 47%) as magenta crystals. ^{1}H NMR (CD_2Cl_2): δ 7.37 (s, 2H), 7.28 (s, 2H), 7.25 (s, 4H), 1.21-1.17 (br s, 42H); ^{13}C NMR (CD_2Cl_2): δ 145.5, 141.6, 139.1, 136.6, 131.4, 126.7, 125.8, 122.7, 122.3, 119.8, 112.4, 101.5, 19.1, 11.9;

UV-vis ($CHCl_3$) λ_{max} (log ε): 486 sh (3.99), 529 (4.52), 567 (4.86) nm; HRMS (ESI) for $C_{42}H_{50}Br_2Si_2$ [M^+]: calcd 768.1818, found 768.1791.

IF 10e. TIPSA (0.17 mL, 0.76 mmol), BuLi (0.40 mL, 0.63 mmol), **11e** (0.070 g, 0.13 mmol), and $SnCl_2$ (0.096 g, 0.50 mmol) were reacted according to the general procedure to afford **10e** (0.050g, 60%) as a magenta crystals. ^{1}H NMR (CD_2Cl_2): δ 7.23 (d, *J* = 7.5 Hz, 2H), 7.18 (s, 2H), 7.04 (s, 2H), 6.90 (d, *J* = 7.5 Hz, 2H), 2.30 (s, 6H), 1.21-1.18 (br s, 42H); ^{13}C NMR (CD_2Cl_2): δ 144.1, 141.6, 139.6, 139.1, 135.3, 129.4, 126.8, 123.5, 120.7, 118.7, 110.4, 102.3, 19.1, 11.9; UV-vis ($CHCl_3$) λ_{max} (log ε): 491 sh (4.02), 531 (4.47), 569 (4.79) nm; HRMS (ESI) for $C_{44}H_{56}Si_2$ [M^+]: calcd 640.3921, found 640.3924.

IF 10f. TIPSA (0.12 mL, 0.55 mmol), BuLi (0.29 mL, 0.46 mmol), **11f** (0.040 g, 0.09 mmol), and $SnCl_2$ (0.070 g, 0.50 mmol) were reacted according to the general procedure to afford **10f** (0.030 g, 44%) as a magenta crystals. ^{1}H NMR (CD_2Cl_2): δ 7.62 (d, *J* = 7.2 Hz, 4H), 7.52 (s, 2H), 7.46 (t, *J* = 7.2 Hz, 6H), 7.37 (d, *J* = 7.2 Hz, 4H), 7.35 (s, 2H) 1.21-1.17 (br s, 42H); ^{13}C NMR (CD_2Cl_2): δ 144.7, 142.0, 141.7, 141.3, 139.4, 136.9, 129.4, 128.1, 127.6, 127.2 (2), 121.5, 121.4, 119.6, 111.4, 102.2, 19.1, 12.0; UV-vis ($CHCl_3$) λ_{max} (log ε): 484 sh (2.93), 534 (3.93), 570 (4.26) nm; HRMS (ESI) for $C_{54}H_{60}Si_2$ [M^+]: calcd 764.4234, found 764.4234.

IF 10g. TIPSA (0.15 mL, 0.68 mmol), BuLi (0.36 mL, 0.57 mmol), **11g** (0.065 g, 0.11 mmol), and $SnCl_2$ (0.087 g, 0.46 mmol) were reacted according to the general procedure to afford **10g** (0.043 g, 43%) as a magenta crystals. ^{1}H NMR (CD_2Cl_2): δ 7.73 (*AB*m, *J* = 8.4 Hz, 8H), 7.53 (s, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.39 (s, 2H), 1.21-1.17 (br s, 42H); ^{13}C NMR (CD_2Cl_2): δ 145.0, 144.7, 141.6, 140.4,

139.3, 137.7, 129.8 (q, J = 32.4 Hz), 127.8, 127.6, 127.3, 126.3, 126.2, 121.6, 121.5, 120.0, 111.9, 102.1, 19.1, 12.0; UV-vis ($CHCl_3$) λ_{max} (log ε): 486 sh (3.95), 534 (4.47), 572 (4.80) nm; HRMS (ESI) $C_{56}H_{58}F_6Si_2$ [M^+]: calcd 900.3981, found 900.4050.

IF 10h. TIPSA (0.12 mL, 0.55 mmol), BuLi (0.29 mL, 0.46 mmol), **11h** (0.065 g, 0.09 mmol), and $SnCl_2$ (0.070 g, 0.37 mmol) were reacted according to the general procedure to afford **10h** (0.058 g, 62%) as a magenta needles. ^{1}H NMR ($CDCl_3$): δ 8.02 (s, 4H), 7.85 (s, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.51 (s, 2H), 7.37 (dd, J = 7.8, 1.2 Hz, 2H), 7.36 (s, 2H), 1.25-1.19 (br s, 42H); ^{13}C NMR ($CDCl_3$): δ 144.9. 143.0. 140.9. 132.4 (q, J = 33.1 Hz), 127.0, 126.8, 124.6 (q, J = 272.8 Hz), 121.4, 121.2, 120.0, 111.9, 101.7, 19.0. 11.6; UV-vis ($CHCl_3$) λ_{max} (log ε): 493 sh (3.79), 532 (4.08), 570 (4.35) nm; HRMS (ESI) $C_{58}H_{56}F_{12}Si_2$ [M^+]: calcd 1036.3729, found 1036.3695.

IF 10i. TIPSA (0.30 mL, 1.36 mmol), BuLi (0.87 mL, 1.13 mmol), **11i** (0.128 g, 0.23 mmol), and $SnCl_2$ (0.171 g, 0.90 mmol) were reacted according to the general procedure to afford **10i** (0.165 g, 81%) as a magenta solid. ^{1}H NMR (CD_2Cl_2): δ 7.44 (s, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 3.3 Hz, 2H), 6.76 (d, J = 3.3 Hz, 2H), 2.83 (t, J = 7.5 Hz, 4H), 1.69 (pent, J = 7.5 Hz, 4H), 1.42 (sext, J = 7.5 Hz, 4H), 1.24-1.19 (br s, 42H), 0.96 (t, J = 7.5 Hz, 6H); ^{13}C NMR (CD_2Cl_2): δ 146.5, 144.7, 141.9, 141.7, 139.6, 136.2, 135.5, 126.8, 125.7, 125.4, 123.2, 121.3, 119.5, 119.2, 111.2, 102.2, 34.3, 30.4, 22.7, 19.1, 14.2, 12.0; UV-vis ($CHCl_3$) λ_{max} (log ε): 498 sh (3.95), 537 (4.24), 577 (4.47) nm; HRMS (ESI) $C_{58}H72S_2Si_2$ [M^+]: calcd 888.4614, found 888.4594.

Bridge to Chapter IV

Given the success of synthesizing a series of 6,12-diethynyl IFs, the inability to effectively influence the HOMO and LUMO energy levels from the 2 and 8-positions was disappointing. Therefore, a logical next step in IF synthesis involves moving beyond the traditional silylacetylenes and instead using a functional group that could provide greater influence. Chapter IV discusses the transition to 6,12-diaryl IFs where donor and acceptor groups are tethered at the *para* position of the arene and their optoelectronic properties are surveyed.

CHAPTER IV

SYNTHESIS, CHARACTERIZATION, & PHOTOPHYSICAL PROPERTIES OF AMBIPOLAR 6,12-DIARYLINDENO[1,2-*B*]FLUORENES

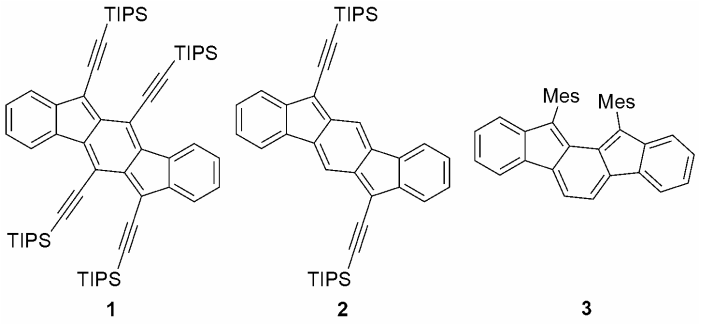
Introduction

This chapter was co-authored by Bradley D. Rose, who performed computational studies and assisted with synthetic experiments, Aaron G. Fix, who also assisted with synthetic experiments, Christopher D. Weber, who performed electrochemical experiments, and Michael M. Haley, who provided guidance and editorial assistance. This work is in progress towards publication in *Organic Letters*.

Conjugated polycyclic hydrocarbons have been the subject of intense research over the last decade for their potential use in a variety of materials applications such as organic light-emitting diodes, thin film transistors, and solar cells.[1] Of particular interest to our laboratory is the indeno[1,2-*b*]fluorene skeleton (IF, **1**, **2**, Figure 1), a 6-5-6-5-6 fused ring system, which in its fully conjugated state, closely resembles pentacene.[2] As IFs possess two less carbon atoms, and hence two fewer π-electrons than pentacenes, they are considered to be formally anti-aromatic molecules.[3] Furthermore, **1** and **2** host a *p*-xylylene unit at their core, a highly reactive moiety that is known to oligomerize/polymerize. Nonetheless, IFs do not possess any *s-cis* diene linkages, meaning that they are less susceptible to the cycloaddition reactions that acenes readily succumb to.[4] In addition to our studies, Tobe and Shimizu recently synthesized and

characterized 11,12-dimesitylindeno[2,1-*a*]fluorene (**3**), an isomerically related species that possesses the equally rare *o*-xylylene moiety.[5]

Figure 1. Fully conjugated indenofluorenes (**1**-**3**).



Recently, we reported the synthesis of a series of 6,12-diethynylindeno[1,2-*b*]fluorenes (**2**).[6] These compounds exhibited similar UV-Vis profiles to **1** with slightly larger HOMO/LUMO gaps. Analogous to our reported diynyl IF diones,[7] **2** accepted two electrons in a quasi-reversible manner, exhibiting LUMO energy levels comparable to or greater than that of the ubiquitous electron acceptor, PCBM.[8] Furthermore, solid state structures of several derivatives of **2** exhibited one-dimensional π-stacks with intermolecular distances as little as 3.40 Å, an improvement over the expanded herringbone motif exhibited by **1**. However, functionalization on the 2 and 8-positions had only a modest effect on the HOMO and LUMO energy levels as minimal orbital density was found to reside on those positions.

In an effort to further expand the versatility of the IF scaffold, we considered other substitution motifs beyond the previously used (triisopropylsilyl)ethynyl moiety. Arylation on the 6 and 12-positions presents a logical next step as arenes functionalized

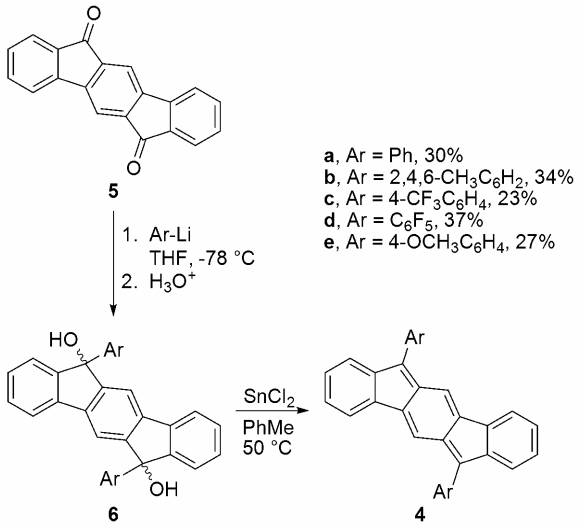
with either donor or acceptor groups might provide a more diverse range of optoelectronic properties. The synthesis of arylated IFs also fulfills a historic purpose in that one of the original IFs exhibiting full conjugation, 6,12-diphenyl IF **4a**, was solely characterized by a UV-Vis absorption λ_{max} of 543 nm.[9] Here, we disclose the synthesis of IFs **4a-e**, along with their respective optical, electrochemical, and computational data.

Results and Discussion.

Synthesis. The same strategy used to synthesize **2** through dione **5** can be readily applied to **4a-e**.[10] Addition of lithiated iodobenzene gave crude diol **6a** and subsequent reduction using $SnCl_2$ in toluene at 50 °C afforded a magenta solution, from which **4a** was obtained in moderate yield (Scheme 1). This reaction scheme was then extended to a variety of 6,12-diaryl IFs (**4b-e**) using the same two-step procedure, which were isolated in modest yields after recrystallization. Strongly electron deficient arenes such as **6d** would not reduce under these conditions nor at elevated temperatures as high as 80 °C; instead, it was found that **6d** required the addition of trifluoroacetic acid (0.50 mL) for the reduction to occur. This observation is in agreement with respect to the synthesis of **3**.

Electronic Absorption Spectra. The absorption spectra of **2** and **4a-e** are shown in Figure 2 and compiled in Table 1. Like **2**, **4a** exhibits three low-energy absorptions (λ_{max} 544 nm) but these are hypsochromically shifted by approximately 50 and 25 nm with respect to **1** and **2**. This can be attributed to the exchange of acetylene groups with aryl groups, a consequence also observed with substituted pentacenes.[11] Variation of the aryl substituents on the 6 and 12-positions has a notable impact on the absorption

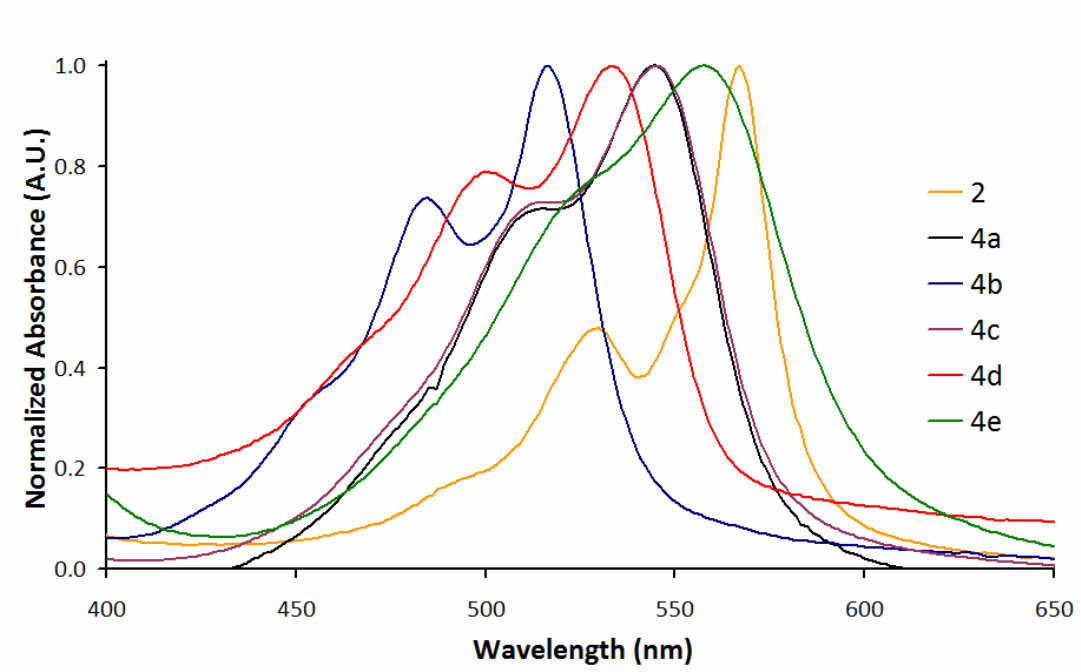
Scheme 1. Synthesis of 6,12-bis(aryl)IFs **4a-e**.



profiles: methoxyphenyl **4e** exhibits a λ_{max} value of 558 nm while pentafluorophenyl **4d** exhibits a λ_{max} value of 533 nm. Interestingly, mesityl **4b** exhibits a λ_{max} value of 516 nm, which is due to the *ortho*- bound methyl groups enforcing the mesityl and IF portions in a fixed orthogonal relationship. As such, no communication of the π-systems exists in this instance, which effectively reduces the conjugation path length. The line shape of **4a-e** agrees with this assessement as **4b** exhibits sharper and narrower transitions compared to **4a** and **4c-e**. As observed before with **1** and **2**, **4a-e** are non emissive, a typical trait with [4n] π-electron species.

Electrochemical Studies. Cyclic voltammetry data of **4a-e** are displayed in Figure 3 and compiled in Table 1. In solution, the diaryl IF scaffold exhibits quasireversible behavior which can accept up to two electrons. The first reduction half-wave potentials for **4a-e** range from –0.65 to –1.15 V (vs. SCE), which are more negative than **2**. Electron withdrawing groups shift the reduction potential to more positive values

Figure 2. Electronic absorption spectra for IFs **2** and **4a-e**.



while electron donating groups shift to more negative values, as such groups work to respectively stabilize and destabilize the resulting anionic species. This trend holds true for the second reduction potentials as well which range from –1.15 to –1.75 V. With the exception of **4d**, **4a-e** all display reversible oxidation half-wave potentials as well, an unexpected trait based on our previous observations with **1** and **2**. The first oxidation potentials for **4a-e** range from 0.80 to 1.50 V, which is a slightly larger variation found for the corresponding first reduction potentials. With respect to electron withdrawing and donating groups, the converse trend holds true; withdrawing groups destabilize the resulting cationic species while donor groups provide the opposite effect. This trend is also maintained for the second oxidation potentials for **4a-e** which range from 1.07 to 1.66 V. Interestingly, parent **4a** exhibits a third oxidation half-wave potential at 1.51 V,

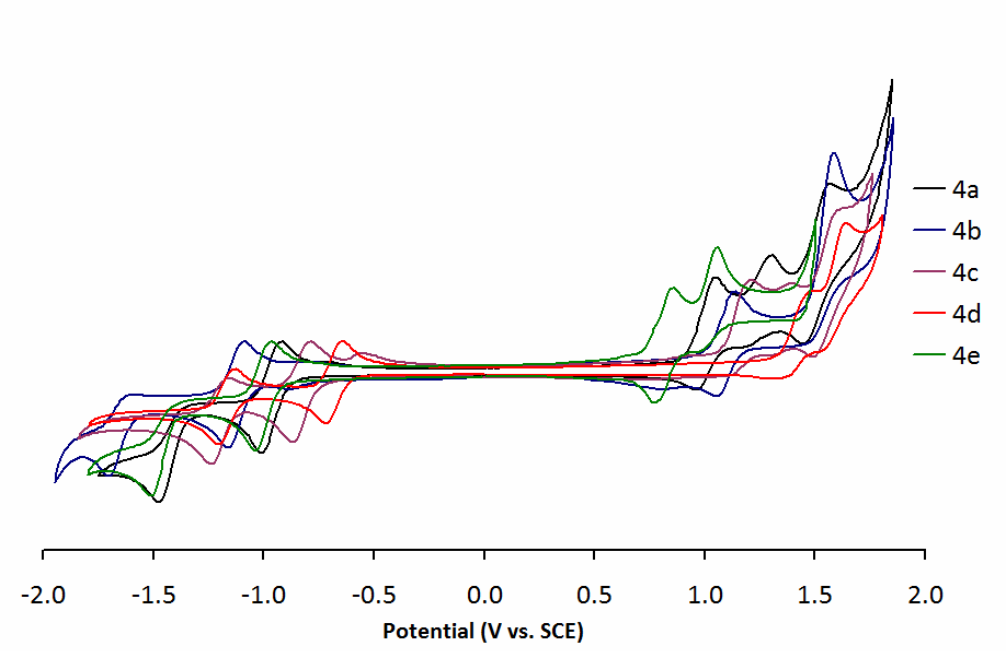
Table 1. Computational, electrochemical, and optical data for indenofluorenes **4a-e**.

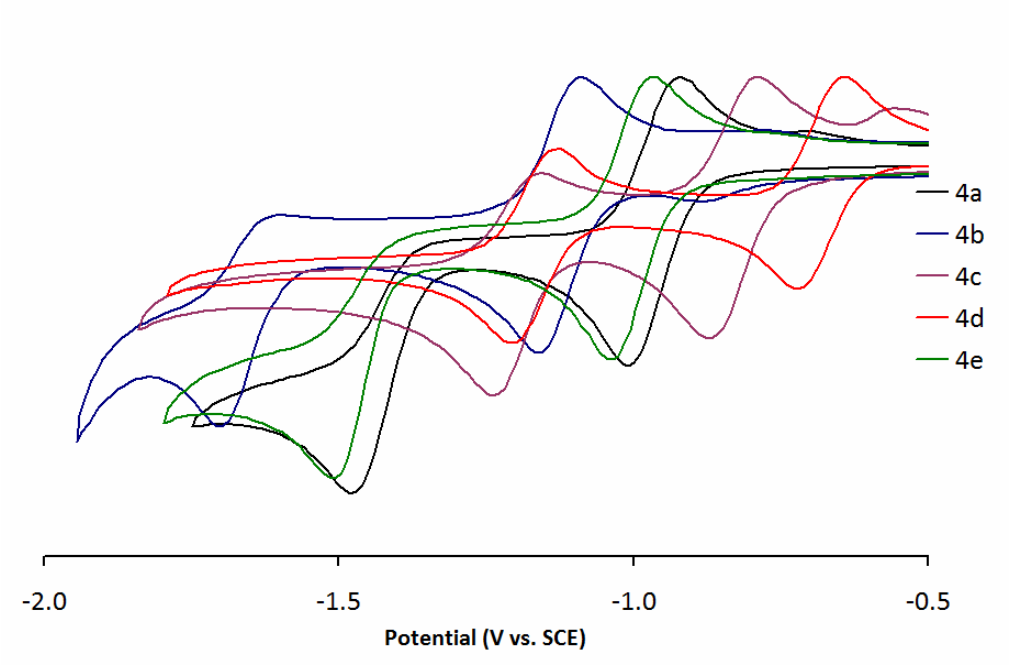
Compd	Computational[a]			Electrochemical[b]					Optical	
	E_{HOMO}	E_{LUMO}	E_{Gap}	E (A^+/A, A^{2+}/A^+, A^{3+}/A^{2+})	E (A/A^-, A^-/A^{2-})	E_{HOMO}	E_{LUMO}	E_{Gap}	λ_{max}[c]	E_{Gap}[d]
2	–5.51	–3.46	2.05	1.20	–0.69, –1.20	–5.88	–4.00	1.88	568	2.12
4a	–5.21	–3.07	2.18	1.01, 1.31[f], 1.51	–0.96, –1.49[g]	–5.68	–3.72	1.96	544	2.17
4b	–5.43	–2.92	2.51	1.10, 1.59[f]	–1.12, –1.73[g]	–5.78	–3.56	2.22	516	2.29
4c	–5.65	–3.49	2.16	1.41, 1.54, 2.06	-0.84, -1.12	-3.85	-5.91	2.06	545	2.16
4d	–5.92	–3.71	2.21	1.49[f], 1.66[f]	–0.68, –1.17	–6.17	–4.00	2.17	533	2.20
4e	–5.00	–2.90	2.10	0.81, 1.07[f]	–1.01, –1.53[g]	–5.50	–3.68	1.82	558	2.05

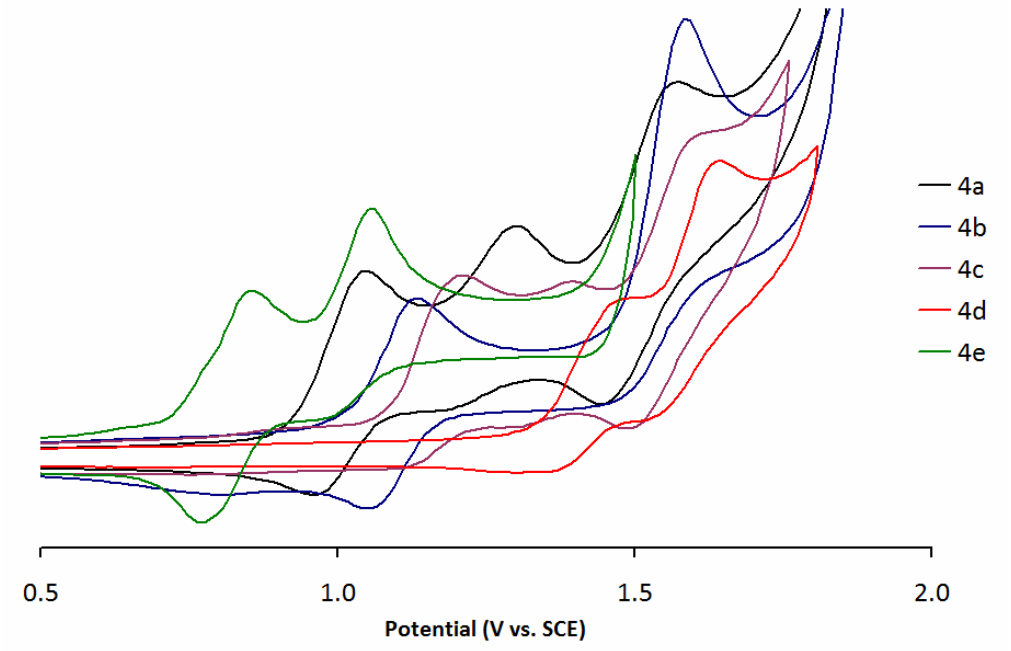
[a] Calculations performed at the B3LYP/6-311+G** level of theory; energies in eV. For computational efficiency, the TIPS groups of **10a-i** were replaced by H atoms. [b] CV recorded using 1–5 mM of analyte in 0.1 M Bu_4NOTf/CH_2Cl_2 using a scan rate of 50 mV/s. The working electrode was a glassy carbon electrode with a Pt coil counter electrode and Ag wire pseudo reference. Values reported as the half-wave potential (vs. SCE) using the Fc^+/Fc couple (0.46 V) as an internal standard. HOMO and LUMO energy levels were approximated using SCE = –4.2 eV vs. vacuum; see reference 8c. Potentials in V; energies in eV. [c] Spectra obtained in $CHCl_3$; wavelength in nm. [d] The optical HOMO–LUMO gap was determined as the intersection of the x-axis and a tangent line that passes through the inflection point of the lowest energy absorption; energies in eV. [f] The oxidation wave was irreversible; the potential of the peak anodic current is reported. [g] The reduction wave was irreversible; the potential of the peak anodic current is reported.

which has not been observed with the IF electronic parameters than **1** and **2** as both the reduction and oxidation potentials widely vary. As such **4a-e** exhibit HOMO and LUMO energy levels within a 0.7 and 0.4 eV range, far beyond the 0.15 eV range demonstrated by **2**. This behavior is chiefly observed with **4e** which displays first oxidation and reduction half-wave potentials of –1.01 and 0.81 V, respectively, which closely mirrors TIPS pentacene whose values are –1.05 and 0.79 V respectively.

Figure 3. Cyclic voltammetry of IFs **4a-e**; voltammogram currents are normalized to the E_{pa} (A/A^{-}) peak.




4a
4b
4c
4d
4e
-2.0
-1.5
-1.0
-0.5
Potential (V vs. SCE)


4a
4b
4c
4d
4e
0.5
1.0
1.5
2.0
Potential (V vs. SCE)

Conclusions

In summary, we have further demonstrated the utility of the fully conjugated indeno[1,2-*b*]fluorene scaffold. Through the use of functionalized phenyl groups, the electronic properties of IF derivatives can be tuned to a large degree. As such, aryl IFs can act as efficient electron acceptors, donors, or both. Current efforts are devoted to obtaining solid state information on **4a-e** to gain information about both intermolecular packing and the single crystal itself.

Experimental

General Comments. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 using either a Varian Inova 500 (^{1}H: 500.11 MHz, ^{13}C: 125.75 MHz) or 600 (^{1}H: 599.98 MHz, ^{13}C: 150.87 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm relative to the residual chloroform (^{1}H: 7.27 ppm, ^{13}C: 77.23 ppm) or CH_2Cl_2 (^{1}H: 5.32 ppm, ^{13}C: 54.00 ppm) reference. Coupling constants are expressed in hertz. UV-Vis spectra were recorded on an HP 8453 UV-Vis spectrometer. THF, toluene, acetonitrile were distilled from their appropriate drying agents under N_2. Unless otherwise stated, all reagents were purchased and used as received. Dione **5** was synthesized according to previously described procedures.

General Procedure for 4a-e. The corresponding aryl halide was dissolved in THF (10 mL), degassed with Ar for 10 min, and cooled to -78 °C. Once cold, BuLi was added the mixture stirred at -78 °C for 20 min. In a separate flask, **5**, was dissolved in THF (30 mL), and also degassed with Ar for 10 min, and cooled to -78 °C. Once cold, the lithiate was transferred by cannula to the solution containing **5** and warmed to room

temperature for 2 h. The reaction mixture was quenched with 10% HCl (30 mL) and extracted in Et_2O (50 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. The crude diol was then redissolved in dry toluene (40 mL) and degassed with Ar for 10 min. $SnCl_2$ was added to the mixture and warmed to 50 °C for 4 h. Trifluoroacetic acid (0.50 mL) was added to **4d**. The solution was then filtered and the filtrate was subsequently evaporated to dryness, redissolved in a minimal amount of acetonitrile, filtered once more, and the solid collected to afford the appropriate IF derivative.

Phenyl IF 4a. Following the general procedure, iodobenzene (0.43 g, 2.12 mmol), BuLi (1.1 mL, 1.77 mmol), **5** (0.10 g, 0.35 mmol), and $SnCl_2$ (0.27 g, 1.42 mmol) were reacted. The solution was then filtered and the filtrate was subsequently evaporated to dryness, redissolved in a minimal amount of acetonitrile, filtered once more, and the solid collected to afford **4a** (0.042 g, 30%) as a magenta solid. ^{1}H NMR ($CDCl_3$): δ 7.64 (d, J = 7.8 Hz, 4H), 7.57 (t, J = 7.8 Hz, 4H), 7.48 (t, J = 7.2 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 7.38 (s, 2H), 7.28 (d, J = 7.2 Hz, 2H), 7.07 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 144.5. 143.5. 139.8. 138.4. 134.4. 133.9. 129.4. 129.1. 128.7. 127.9. 127.5. 122.5. 120.6. 119.7; UV-vis ($CHCl_3$) λ_{max} (log ε): 472 (sh) (3.63), 515 (4.11), 544 (4.25) nm.

Mesityl IF 4b. Following the general procedure, 2-bromomesitylene (0.42 g, 2.12 mmol), BuLi (1.1 mL, 1.77 mmol), **5** (0.10 g, 0.35 mmol), and $SnCl_2$ (0.27 g, 1.42 mmol) were reacted. The solution was then filtered and the filtrate was subsequently evaporated to dryness, redissolved in a minimal amount of acetonitrile, filtered once more, and the solid collected to afford **4b** (0.058 g, 34%) as a red solid. ^{1}H NMR ($CDCl_3$): δ 7.31 (d, J = 7.2 Hz, 2H), 7.03 (s, 4H), 7.00 (t, J = 7.2 Hz, 2H), 6.95 (t, J = 7.2 Hz, 2H), 6.86 (s,

2H), 6.68 (d, 2H), 2.40 (s, 6H), 2.19 (s, 12H); ^{13}C NMR ($CDCl_3$): δ 145.5, 144.4, 139.3, 137.9, 137.7, 137.4, 135.0, 130.2, 128.4, 128.0, 127.2, 122.1, 120.5, 119.2, 21.4, 20.6; UV-vis ($CHCl_3$) λ_{max} (log ε): 455 (4.14), 484 (4.47), 517 (4.60) nm.

4-CF_3-Phenyl IF 4c. Following the general procedure, 4-bromobenzyltrifluoride (0.48 g, 2.12 mmol), BuLi (1.1 mL, 1.77 mmol), **5** (0.10 g, 0.35 mmol), and $SnCl_2$ (0.27 g, 1.42 mmol) were reacted. The solution was then filtered and the filtrate was subsequently evaporated to dryness, redissolved in a minimal amount of acetonitrile, filtered once more, and the solid collected to afford **4c** (0.044 g, 23%) as a magenta solid. ^{1}H NMR (CD_2Cl_2): δ 7.83 (d, 4H), 7.76 (d, 4H), 7.43 (m, 2H), 7.34 (s, 2H), 7.22 (m, 2H), 7.10 (m, 4H); UV-vis ($CHCl_3$) λ_{max}: 473 (sh), 512, 545 nm.

1,2,3,4,5-F-Phenyl IF 4d. Following the general procedure, pentafluoroiodobenzene (0.36 g, 2.12 mmol), BuLi (1.1 mL, 1.77 mmol), **5** (0.10 g, 0.35 mmol), and $SnCl_2$ (0.27 g, 1.42 mmol) were reacted. Trifluoroacetic acid (0.50 mL) was added. The solution was then filtered and the filtrate was subsequently evaporated to dryness, redissolved in a minimal amount of acetonitrile, filtered once more, and the solid collected to afford **4d** (0.076 g, 37%) as a red solid. ^{1}H NMR (CDCl3): δ 7.35 (d, J = 7.2 Hz, 2H), 7.09 (t, J = 7.2 Hz, 2H), 7.05 (t, J = 7.2 Hz, 2H), 6.90 (s, 2H), 6.85 (d, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 145.5, 143.5, 142.5, 140.7, 139.3, 137.4, 137.2, 131.3, 129.3, 128.9, 128.6, 128.4, 125.5, 122.6, 121.2, 119.6; UV-vis ($CHCl_3$) λ_{max} (log ε): 464 (sh) (3.84), 500 (4.11), 533 (4.21) nm.

4-OMe-Phenyl IF 4e. Following the general procedure, 4-bromoanisole (0.50 g, 2.12 mmol), BuLi (1.1 mL, 1.77 mmol), **5** (0.10 g, 0.35 mmol), and $SnCl_2$ (0.27 g, 1.42 mmol) were reacted. The solution was then filtered and the filtrate was subsequently

evaporated to dryness, redissolved in a minimal amount of acetonitrile, filtered once more, and the solid collected to afford **4e** (0.044 g, 27%) as a magenta solid. ^{1}H NMR ($CDCl_3$): δ 7.60 (d, *J* = 7.8 Hz, 4H), 7.44 (m, 2H), 7.40 (s, 2H), 7.29 (m, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.07 (m, 4H), 3.93 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 160.1, 143.5, 139.4, 138.5, 133.4, 130.7, 127.7, 127.3, 127.1, 122.4, 120.5, 119.4, 114.6 (2 C), 55.6; UV-vis ($CHCl_3$) λ_{max} (log ε): 475 (sh) (4.02), 524 (4.26), 558 (4.65) nm.

Bridge to Chapter V

This upcoming chapter involves work unrelated to the previous chapters. Instead, this chapter will discuss tetrakis(arylethynyl)benzenes (TAEBs), cruciform-shaped molecules that possess numerous pathways for electronic and photonic transfer. When functionalized with donor and acceptor groups, the band gap energy of the TAEB scaffold can be tuned with a high degree. Specifically, this chapter will discussthe 4,4,difluoro-4-bora-3a,4a,-diaza-*s*-indacene moiety, also known as BODIPY, as the acceptor group. Six donor/acceptor TAEBs, two all-acceptor TAEBs, and three structurally related bis(arylethynyl)benzenes (BAEBs) will be synthesized and their optoelectronic properties discussed. Due to the significant optoelectronics of the BODIPY core itself, these species exhibit properties previously unseen in TAEBs such as a complete absence of solvatochromism as well as increased quantum yields.

CHAPTER V

INCORPORATING BODIPY FLUOROPHORES INTO TETRAKIS(ARYLETHYNYL)BENZENES

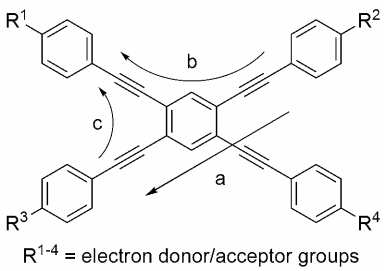
Introduction

This chapter was co-authored by Brian S. Young, who performed the computational studies, and Michael M. Haley, who provided guidance and editorial assistance. The work has been published in the *Journal of Organic Chemistry* (**2011**, *76*, 4043-4051).

Highly conjugated, carbon rich molecules are of great interest due to their unique optoelectronic properties.[1] These molecules are now recognized as suitable materials for advanced applications such as light emitting diodes, photovoltaics, and thin film transistors.[2] Over the last several years, we have described detailed structure-property relationship studies on donor/acceptor-functionalized tetrakis(arylethynyl)benzenes (TAEBs).[3] These cruciform-shaped molecules possess multiple pathways for electronic and photonic transfer and are amenable to a host of substitution patterns (Figure 1). We and others[4] have shown that the band gap of these molecules can be tuned with a high degree of sensitivity with judicious choice of the nature and substitution motif of the donor and acceptor units, thereby enhancing their optical and nonlinear optical (NLO) properties. Additionally, these molecules have aptly demonstrated their ability to act as ionic sensors through dynamic shifting of their emission spectra through stepwise

intramolecular charge-transfer, as evidence of fine control over their HOMO and LUMO energy levels.[5]

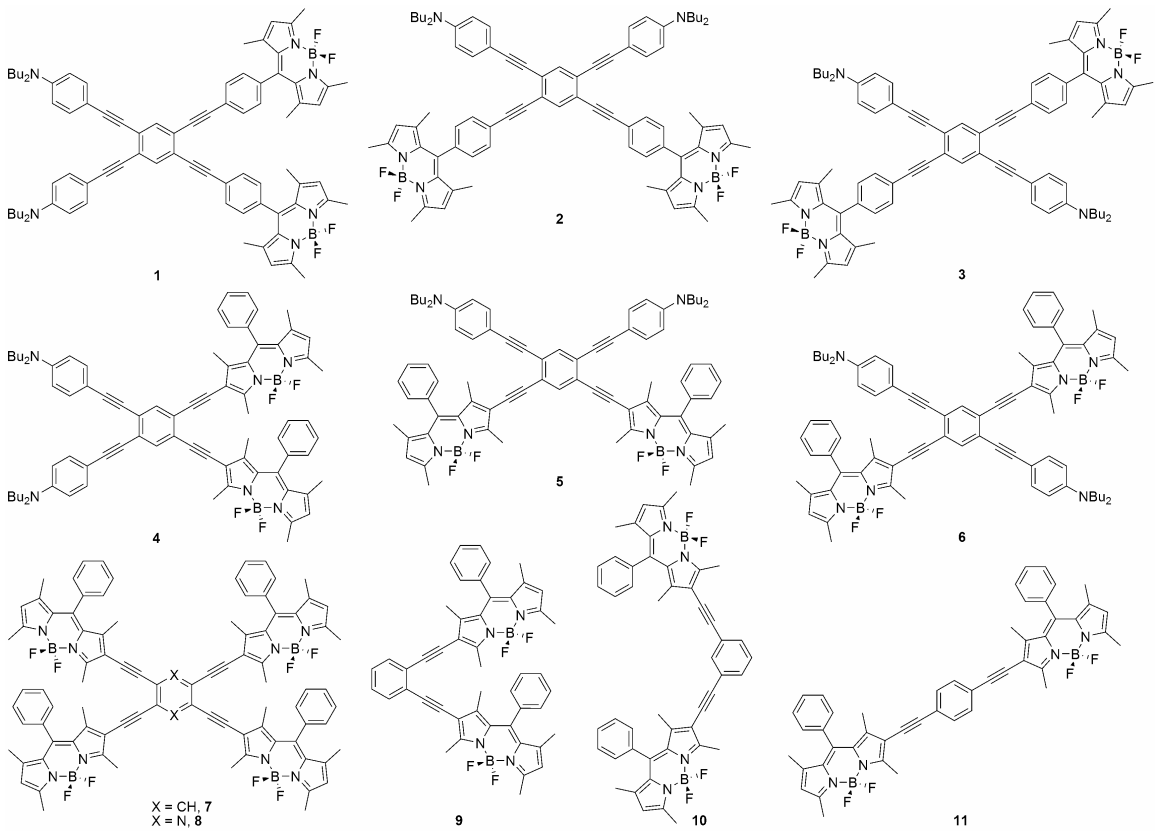
Figure 1. Conjugated pathways present in TAEB compounds. Pathways 'a' and 'c' represent linear and bent conjugation pathways, respectively, while path 'b' represents cross conjugation.



To further explore the potential of the TAEB system, we sought out a stronger acceptor in an effort to increase charge transfer, as seen by a stronger net dipole, and therefore to exhibit a larger bathochromic shifts into the red region. To meet this criteria, we employed the 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene core, better known as BODIPY, as our acceptor unit. The BODIPY moiety has garnered a significant amount of attention due to its strong UV-absorbing and emitting capabilities, high quantum yields, and general insensitivity to various chemical environments such as solution pH and solvent polarity.[6] Not surprisingly, BODIPYs are also pursued for a myriad of optoelectronic applications[7] in their own right, as well as molecular and ionic sensors and as stains for biological markers or dyes.[8] Very recently, ethynylated BODIPYs were successfully fused together to form dimeric and trimeric annulenes[9] that were determined

to possess antiaromatic properties (24 and 36 π-electrons, respectively), which represents another intriguing area of research to us.[10] Here, we report the synthesis of six structurally isomeric donor/acceptor-functionalized TAEBs (**1**–**6**, Figure 2). For control purposes, two additional TAEBs (**7**–**8**) and three structurally related bis(arylethynyl)benzene (BAEBs, **9**–**11**) containing only acceptors were also prepared. The electronic absorption and emission spectra as well as computational studies of each series were also examined for structure-property relationships.

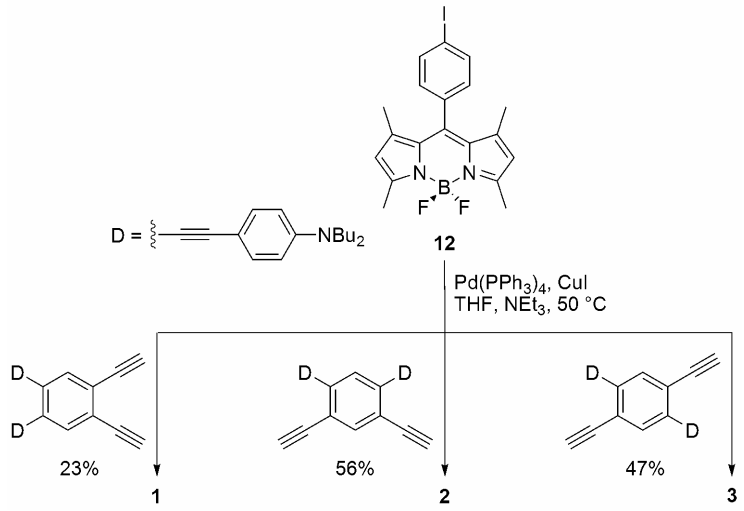
Figure 2. Target donor/acceptor-functionalized TAEBs **1**–**6**, all-acceptor TAEBs **7**–**8** and BAEBs **9**–**11**.



Results and Discussion

Synthesis. The general synthetic strategy for TAEBs **1**–**8** and BAEBs **9**–**11** relies heavily on successive Sonogashira cross-coupling reactions. Donor and acceptor fragments are attached to a central tetrahalobenzene ring in a stepwise fashion that takes advantage of the reactivity differences toward aryl bromides and iodides in the catalytic cycle.[11] Specifically, cross-coupling of known iodide **12**[12] to the terminal alkynes of our previously reported bis(donor)-substituted precursors[3c] afforded TAEBs **1**–**3** as bright orange/red solids in low to moderate yield (Scheme 1).

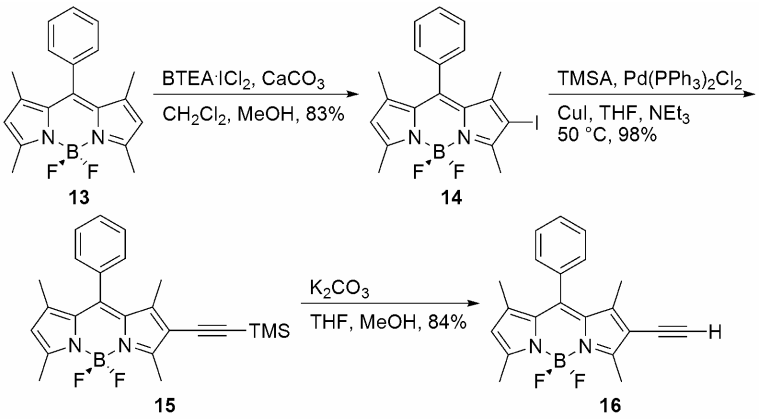
Scheme 1. Synthesis of TAEBs **1**-**3**.



To investigate isomeric TAEBs **4**–**8**, iodination of known precursor **13**[12b] furnished iodoBODIPY **14** (Scheme 2). Cross-coupling with (trimethylsilyl)acetylene (TMSA) provided silyl-protected **15** in high yield and subsequent desilylation afforded ethynylBODIPY **16**. It is worth noting that the deprotection step should proceed no

longer than 15 min as the B–F bonds undergo metathesis with the excess methoxide to produce undesirable MeO-functionalized BODIPYs.[13] Despite this potential pitfall, **16** can be cleanly and efficiently synthesized in excellent overall yield.

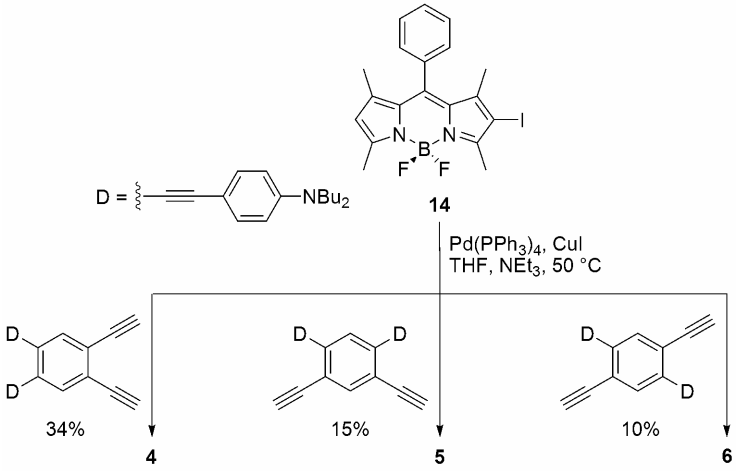
Scheme 2. Synthesis of BODIPY precursor **16**.



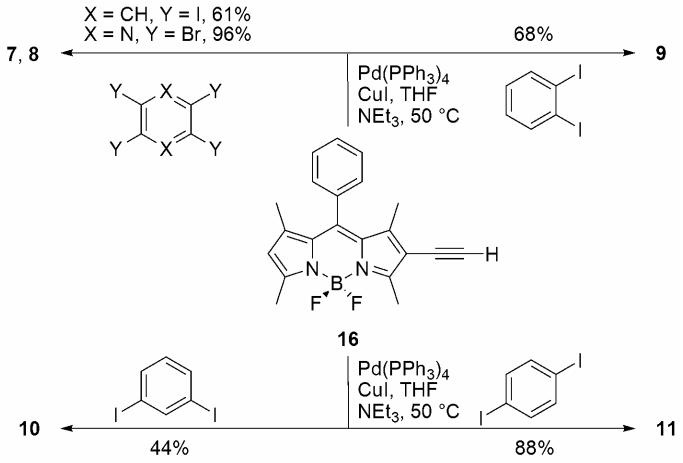
Cross-coupling of **16** to the appropriate bis(donor)-substituted precursors[3c] afforded TAEBs **4**–**6** as bright red solids in low to modest yield (Scheme 3). We explored alternate routes (e.g., cross-coupling **16** with the appropriate bis(donor)dibromoarenes)[3c] and methods (e.g., Negishi-modified Sonogashira reaction),[14] but these variations worked no better.

Fortunately, no such problems for the synthesis of **7**–**8** were encountered. Specifically, cross-coupling ethynylBODIPY **16** with tetraiodobenzene or tetrabromopyrazine afforded all-acceptor TAEBs **7** and **8**, respectively (Scheme 4). Similarly, **16** was cross-coupled with 1,2-, 1,3- and 1,4-diiodobenzene to form related BAEBs **9**–**11**, respectively.

Scheme 3. Synthesis of TAEBs **4-6**.



Scheme 4. Synthesis of TAEBs **7**–**8** and BAEBs **9**–**11**.

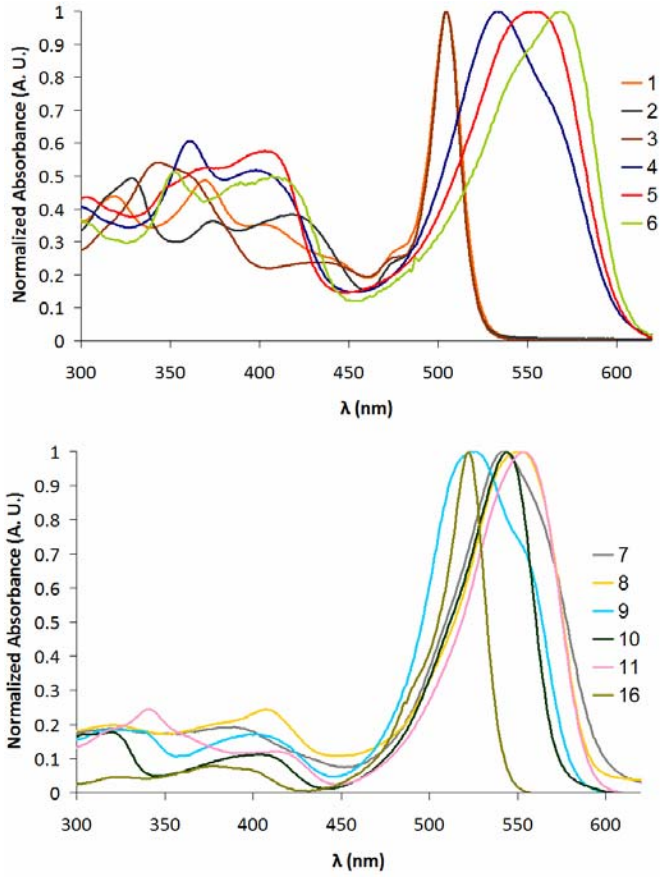


Electronic Absorption Spectra. The absorption spectra of **1**–**11** and **16** in toluene are shown in Figure 3; the data for both toluene and $CHCl_3$ are given in Table 1. All illustrate the characteristic pattern of two broad absorptions between 300 and 500 nm with extinction coefficients between 15,000 and 60,000 M^{-1} cm^{-1}, typical for

intramolecular charge transfer bands in phenylacetylene scaffolds.[3] As seen with our previous systems[3c,d], **1**–**11** follow the established trend for the longest λ_{max} in the high-energy region where the trend is *ortho* < *meta* < *para* with the *para* isomers exhibiting the most red-shifted charge transfer band. For example, **1**–**3** display high-energy absorptions of 404, 423, and 443 nm, respectively, which are on par with TAEBs containing $–NO_2$ and $–CF_3$ groups. Isomers **4**–**6**, however, exhibit absorptions of 400, 402, and 412 nm, respectively, which are a considerably narrower range; similar absorptions are seen for **9**–**11** (398, 399, and 408 nm, respectively). Such behavior can be explained as a function of their attachment to the BODIPY core: while **1**–**3** are bound to the phenyl group on the *meso* position, **4**–**6** and **9**–**11** are bound directly to the electron-rich pyrrole. All-acceptors **7**–**8** and ethynylBODIPY **16** exhibit muted absorptions in this region due to either the lack of donor functionality (**7**–**8**) or conjugation altogether (**16**). However, **1**–**6** and **9**–**11** also possess an intense low-energy absorption, a trait not seen before in the TAEB scaffold. This low-energy absorption, attributable to the BODIPY acceptor unit, appears at ~505 nm for **1**–**3**, regardless of substitution pattern, presumably due to the fact that the acceptor unit is orthogonal to the π-system. A similar *ortho* < *meta* < *para* trend for the longest λ_{max} in the low-energy region with the *para* isomers exhibiting the most red-shifted absorption is observed for **4**–**6** and **9**–**11**. Isomers **4**–**6**, where the donor-functionalized phenylacetylene is directly linked to the BODIPY core, exhibit broad absorptions between 530 and 570 nm. Attachment of the acetylene to the acceptor unit does not induce the aforementioned rotational restrictions; therefore, full conjugation throughout the TAEB is permitted.[7h] Hence, placement of the phenylacetylene scaffold can have profound effects on the optical band gap as the lowest

energy transition of **6** is 64 nm bathochromically shifted from **3** in toluene. All-acceptor **7** exhibits an absorption at 540 nm, which can be explained through similar means as **4**–**6**. Structurally related pyrazine **8** exhibits a similar shift at 541 nm, suggesting that variation of the central arene plays a minimal role in charge transfer. BAEBs **9**–**11** exhibit absorptions between 525 and 550 nm, which are hypsochromically shifted by 5–20 nm from **4**–**6**, rationalized from the lack of donor groups on the central arene. An approximate ratio exists between the extinction coefficients of the high and low-energy regions: for **1**–**6**, the ratio is 1:2 while for **9**–**11**, the ratio is 1:4. This can be rationalized by the simple comparison that **1**–**6** have twice the number of phenylacetylene groups bound to the central core than **9**–**11**. Also, the extinction coefficient for the low-energy absorption appears to be directly proportional to the number of acceptor groups present. For example, **1**–**6** and **9**–**11**, which have two acceptor groups, have low-energy extinction coefficients between 80,000 and 130,000 M^{-1} cm^{-1}, while **7** and **8** have approximate extinction coefficients of 210,000 and 250,000 M^{-1} cm^{-1}, respectively. No significant solvatochromic effects were observed for **1**–**11**, as the absorption spectra differed within 5 nm when compared to $CHCl_3$ and toluene solutions.

Figure 3. Electronic absorption spectra of (a) **1**–**6** and (b) **7**–**11**, **16** in toluene (PhMe); all spectra recorded at 10 μM concentration.



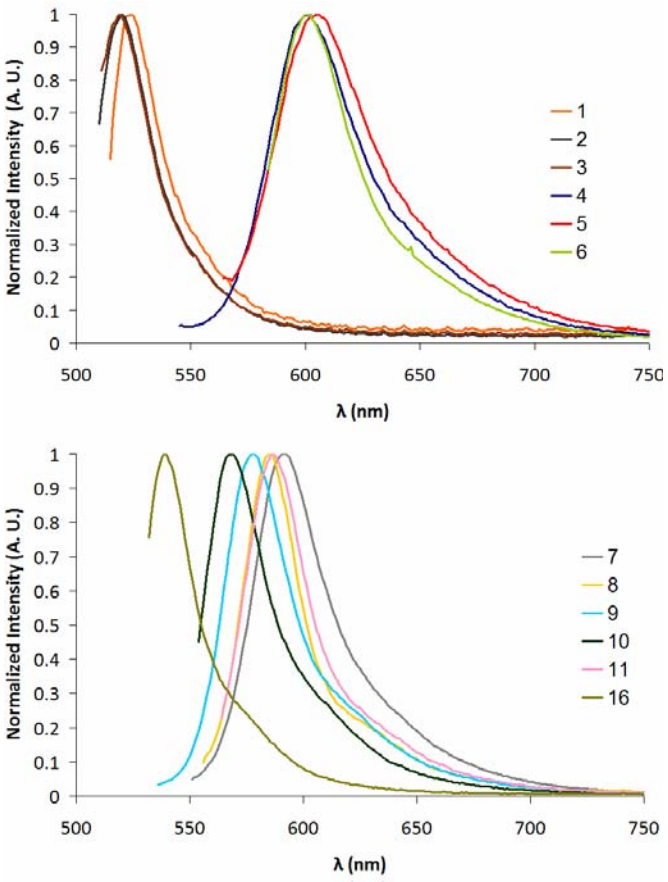
Electronic Emission Spectra. The emission spectra for **1**–**11** and **16** in toluene are shown in Figure 4; the data for both toluene and $CHCl_3$ are given in Table 1. Perhaps the most striking feature is the lack of fluorescence solvatochromism: the largest deviation in emission λ_{max} is 4 nm in the entire series. While this phenomenon is regularly observed (with shifts as large as 65 nm) in the TAEB/BAEB architecture, it is

Table 1. Absorption and emission data for TAEBs **1**–**8**, BAEBs **9**–**11**, and ethynylBODIPY **16**

Entry	Solvent	λ_{abs} (nm) High-Energy	λ_{abs} (nm) Low-Energy	log(ε)[a]	λ_{em} (nm)	Φ_f (%)[b]	Stokes Shift[c] (nm)	Stokes Shift[c] (cm^{-1})	Stokes Shift[d] (nm)	Stokes Shift[d] (cm^{-1})
1	$CHCl_3$	404	502	5.07	520	4	116	5500	18	690
	PhMe	407	505	5.30	524	20	117	5500	19	720
2	$CHCl_3$	423	503	4.92	518	4	95	4300	15	580
	PhMe	418	505	5.06	520	15	102	4700	15	570
3	$CHCl_3$	443	503	5.19	520	8	77	3300	17	640
	PhMe	438	505	5.06	520	15	82	3600	15	570
4	$CHCl_3$	400	533	4.91	606	< 0.1	206	8500	73	2260
	PhMe	398	533	4.96	603	44	205	8500	70	2180
5	$CHCl_3$	402	553	4.96	608	< 0.1	206	8400	55	1640
	PhMe	403	553	4.92	606	19	203	8300	53	1580
6	$CHCl_3$	412	564	4.77	602	< 0.1	190	7700	38	1120
	PhMe	407	569	4.22	601	19	194	7900	32	940
7	$CHCl_3$	–[e]	540	5.33	590	54	–[e]	–[e]	50	1570
	PhMe	–[e]	542	4.66	591	74	–[e]	–[e]	49	1530
8	$CHCl_3$	–[e]	541	5.40	579	38	–[e]	–[e]	38	1210
	PhMe	–[e]	541	5.25	579	42	–[e]	–[e]	38	1210
9	$CHCl_3$	398	525	4.99	575	62	177	7700	50	1660
	PhMe	398	526	4.87	578	81	180	7800	52	1710
10	$CHCl_3$	399	542	5.04	569	78	170	7500	27	880
	PhMe	403	544	5.08	567	78	164	7200	23	750
11	$CHCl_3$	408	551	5.06	586	60	178	7400	35	1080
	PhMe	414	551	4.96	586	60	172	7100	35	1080
16	$CHCl_3$	–[e]	520	4.85	537	74	–[e]	–[e]	17	610
	PhMe	–[e]	522	4.89	539	72	–[e]	–[e]	17	600

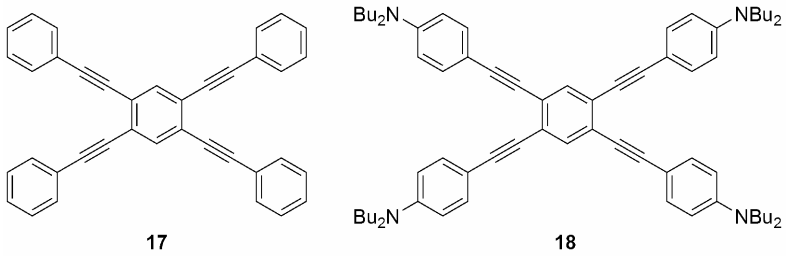
[a]Determined from the low-energy absorption. [b]Quantum yields measured against an internal integrating sphere.[15] [c]Shifts determined as the difference between λ_{em} and high-energy λ_{abs}. [d]Shifts determined as the difference between λ_{em} and low-energy λ_{abs}. [e]Not applicable.

Figure 4. Emission spectra of (a) **1**–**6** and (b) **7**–**11**, **16** in toluene (PhMe); all spectra recorded at 10 μM concentration.



completely absent in **1**–**11**, as is well-known for BODIPY molecules.[6] Positioning of the acceptor groups around the central arene also has little effect on the emission wavelengths: **1**–**3** all exhibit transitions near 520 nm regardless of substitution motif. Although this lack of differentiation is not unusual, typically seen by a 8–20 nm range between isomers where the difference increases in non-polar solvents, **1**–**3** exhibit remarkably narrow difference of 2 nm. This trend is also observed with **4**–**6**, which exhibit emissions near 605 nm with a slightly larger deviation of 6 nm between isomers.

The attachment point of the acceptor group, however, has a significant effect. As can be seen between **1**–**3** and **4**–**6**, the largest difference is observed between **2** and **5**, which possess emissions at 518 and 608 nm, respectively, where **5** demonstrates a 90 nm bathochromic shift from **2**. This behavior correlates well with anthracene/BODIPY systems developed by Burgess et al. where similar shifts were observed between like-systems.[7h] The emission for all-acceptors **7**–**8** were found at 590 and 579 nm, respectively, demonstrating that direct substitution of the two donors with an additional two acceptors results in a modest hypsochromic shift; however, **7**–**8** show a significant bathochromic shift compared to previously synthesized parent and tetra-donor TAEBs **17**–**18**,[3b] which suggests that an all-acceptor system may well outperform an all-donor one. Interestingly though, **9**–**11** emit between 570 and 590 nm, despite the lack of additional conjugation that **7**–**8** possess. Despite this, **9**–**11** follow the trend of *meta* < *ortho* < *para* with the *para* isomer having the longest emission λ_{max}. Due to the fact that the emissions of **1**–**3** and **4**–**6** are within a narrow region, it is difficult to discern whether each series follows this trend; however, in terms of Stokes shifts, both **1**–**6** and **9**–**11** follow the previously established trend of *para* < *meta* < *ortho*, where the *ortho* isomer possess the largest dipole moment and hence the largest shift.



17 **18**

The fluorescence quantum yields were measured against an internal integrating sphere and the values reported in both $CHCl_3$ and toluene in Table 1.[15] In each instance, the Φ_f values were lower in $CHCl_3$ than in toluene. This holds specifically true for **4**–**6** where Φ_f values were nearly nonexistent in $CHCl_3$ while in toluene, Φ_f values were as high as 0.81 for **9**. In toluene, the general isomer trend was *para* < *meta* < *ortho*, the exact opposite found for pyridyl-functionalized systems. Furthermore, the CF_3-functionalized species afforded yet another order, suggesting that no broad generalizations for fluorescence quantum yields can be made for TAEBs/BAEBs.

Molecular Orbital Plots. Representative molecular orbital plots of the *ortho*-substituted systems **1'**, **4'**, and **9** along with all-acceptor **7** are shown in Figure 5, with the corresponding plots for **2'**–**3'**, **5'**–**6'**, **8**, and **10**–**11** in the Supporting Information. Structures **1'**–**6'** are simplified by the replacement of NBu_2 groups with NMe_2 and all calculations are done on the B3LYP/6-31G* level of theory.[16] As seen with our previously synthesized TAEBs,[3c] the FMO plots of **1'** and **4'** indicate that the majority of density of the highest occupied molecular orbital (HOMO) resides on the donor end of the molecule, while the majority of density of the lowest unoccupied molecular orbital (LUMO) resides on the acceptor, indicative of charge-transfer processes. However, the LUMO density is found on the acceptor unit, which is situated orthogonally from the remainder of the phenylacetylene scaffold, thereby eliminating any possible overlap. Such behavior justifies the nearly identical emission profiles of **1**–**3** in Figure 4, which closely resemble **12**.[12a] The remaining compounds avoid this orthogonality issue. By attaching the acetylenes directly to one of the pyrrole units of the acceptor core, this leads

Figure 5. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **1'**.

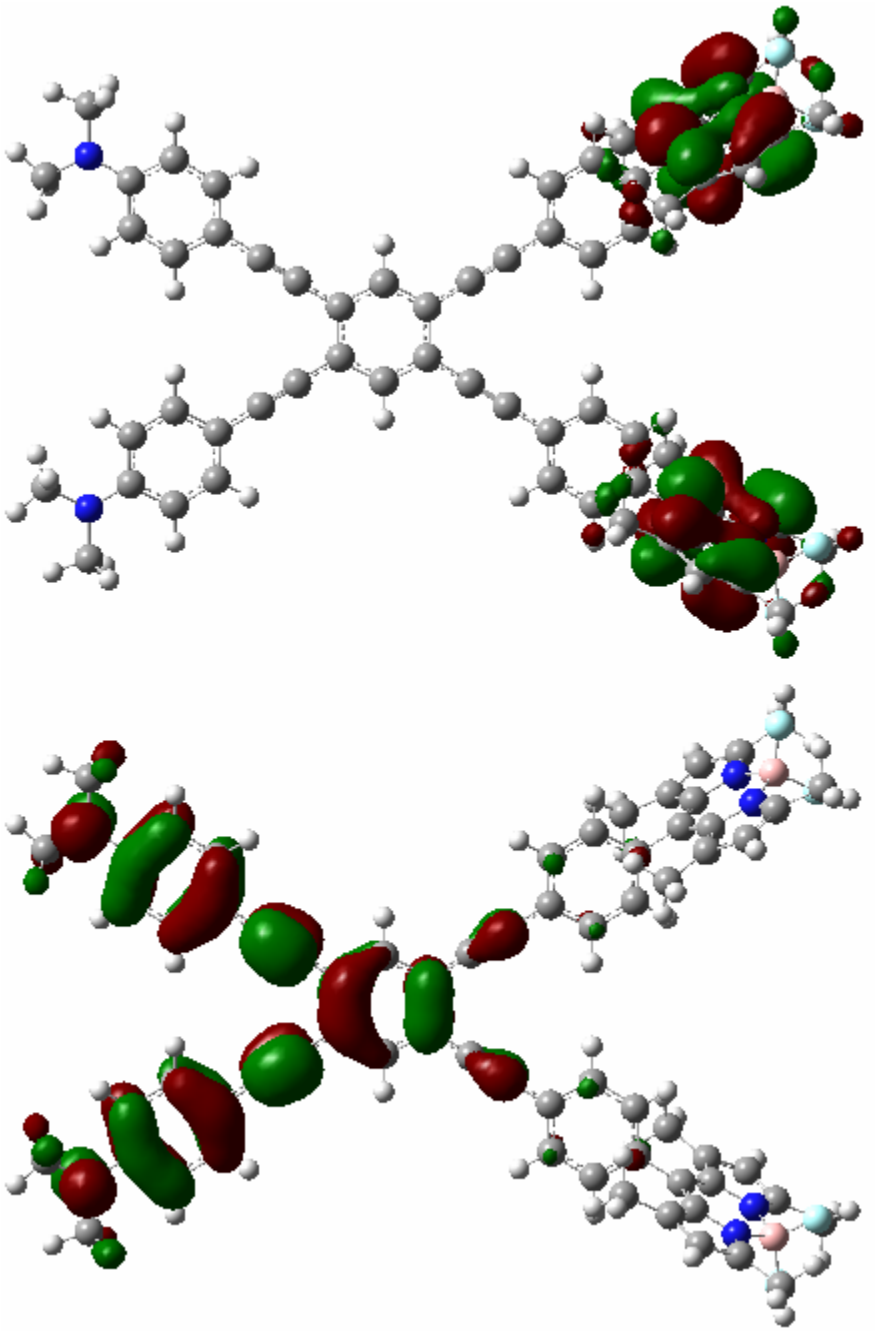


Figure 6. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **2'**

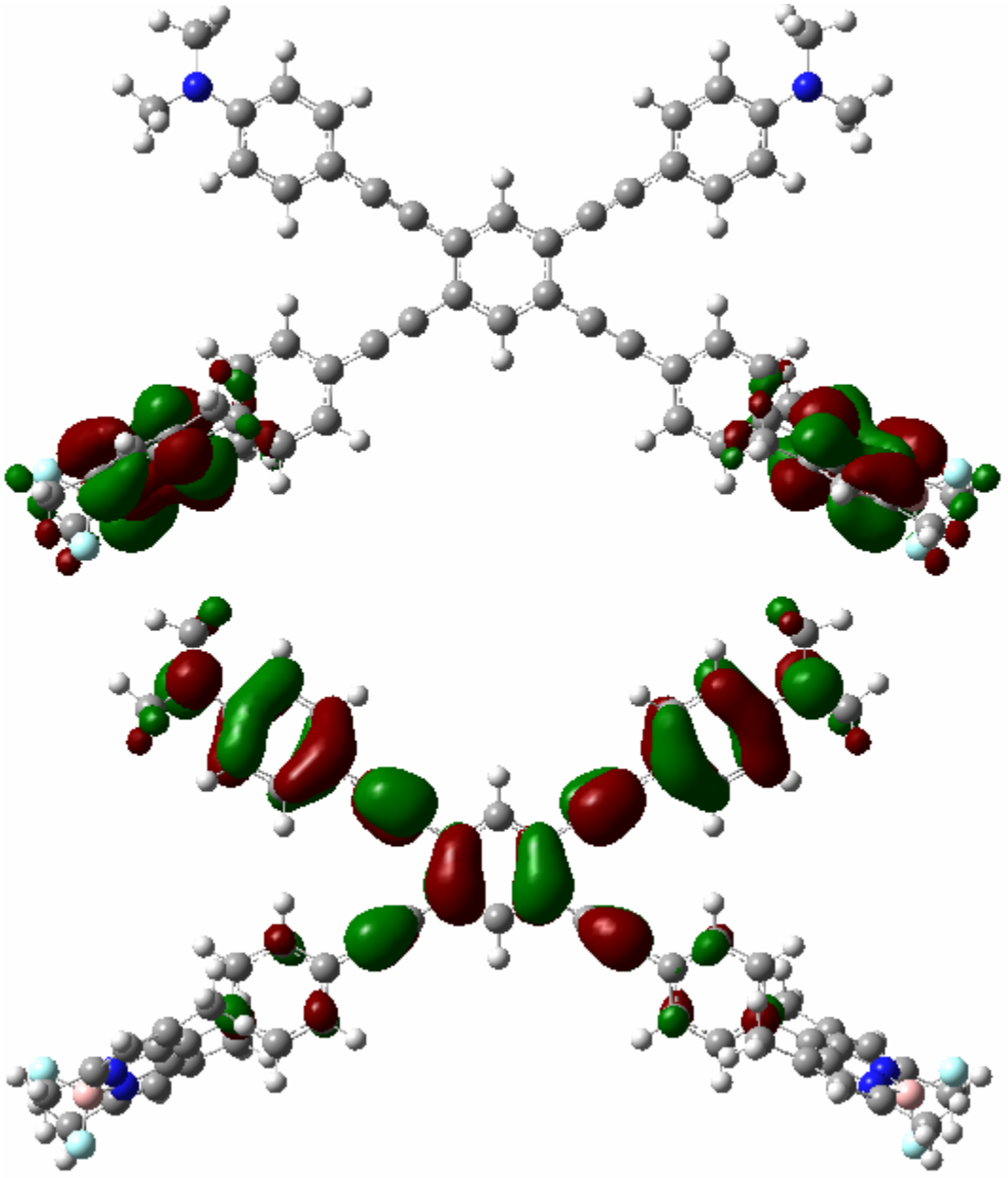


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Figure 7. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **3'**.

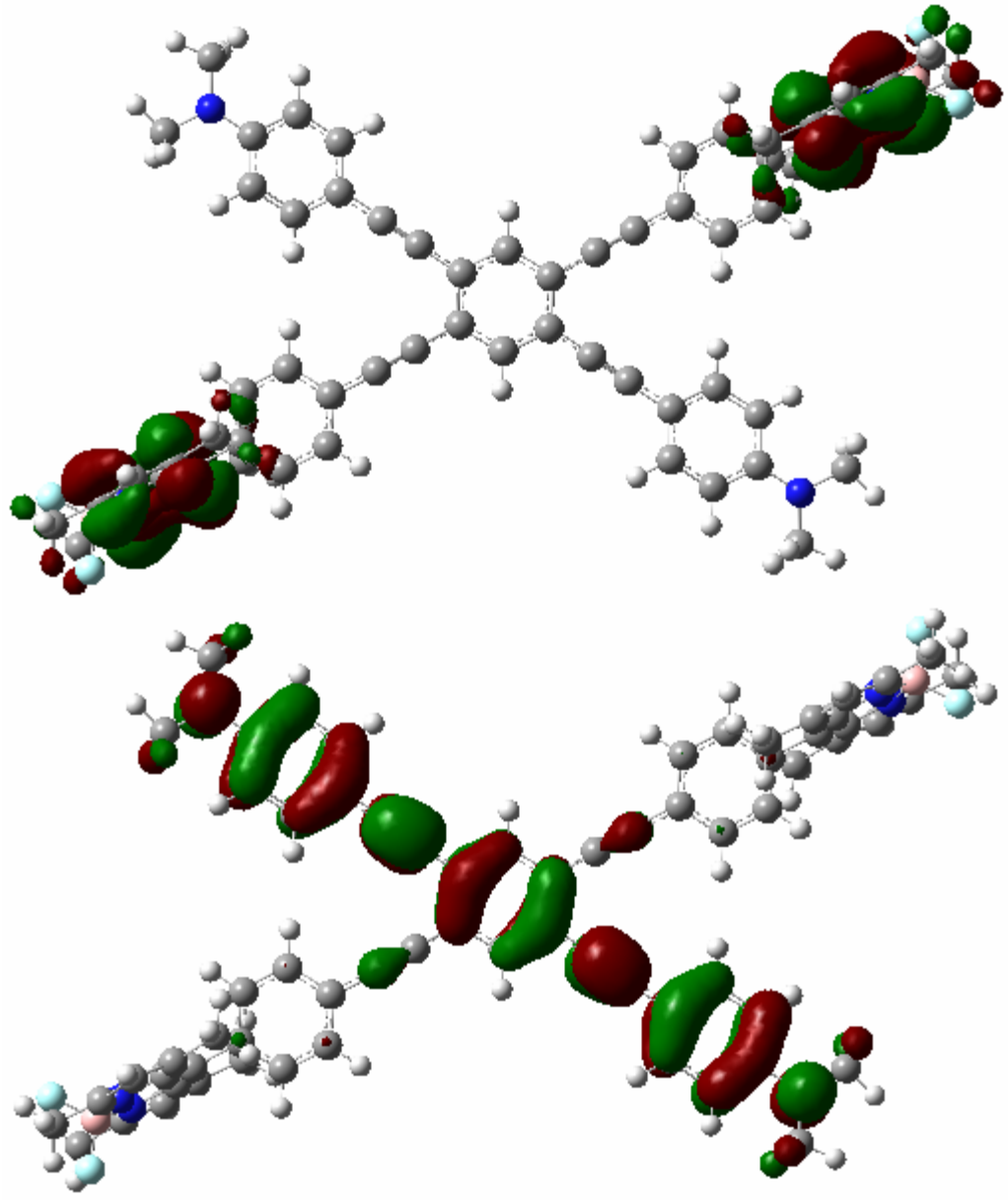


Figure 8. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **4'**.

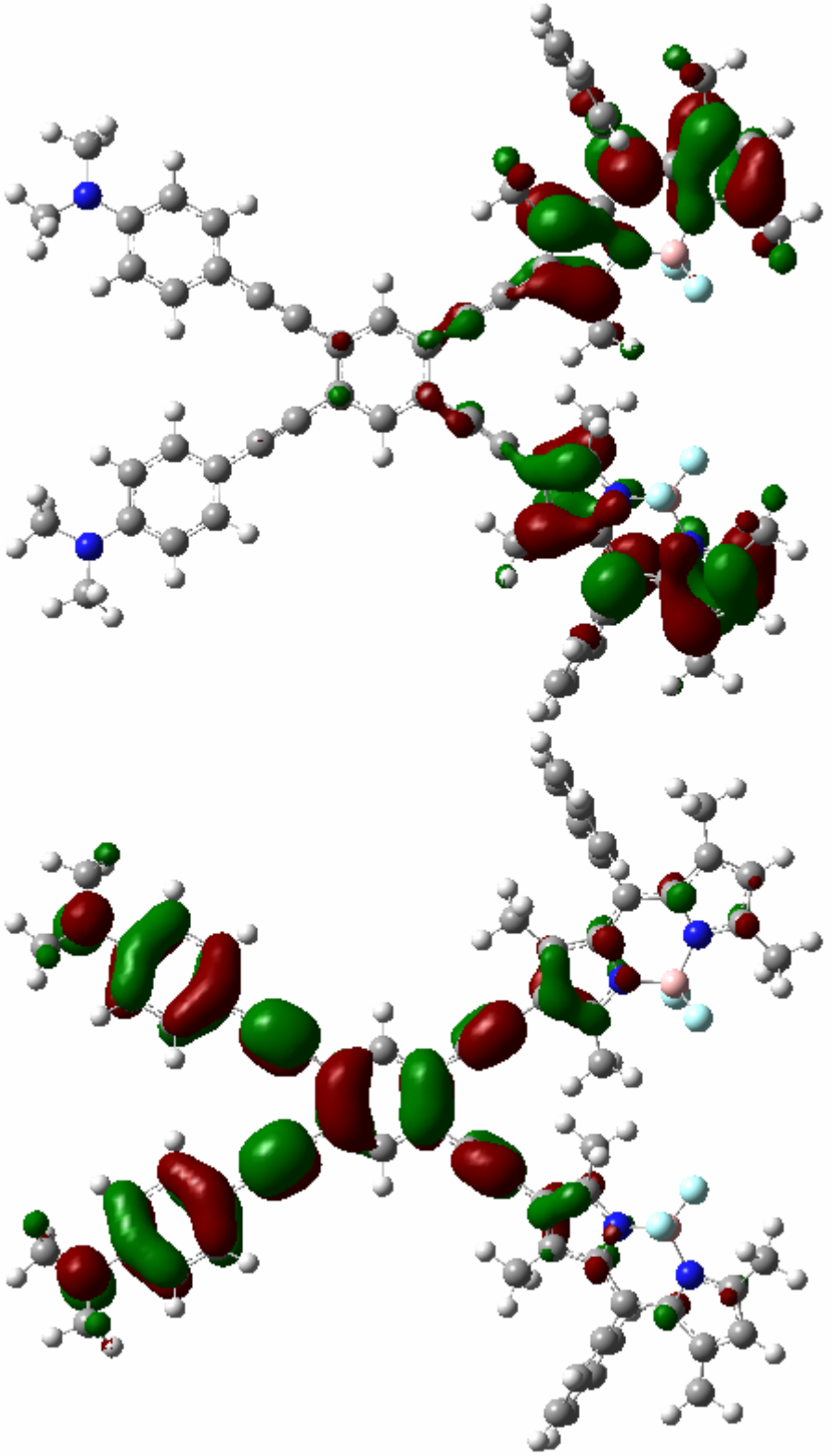


Figure 9. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **5'**.

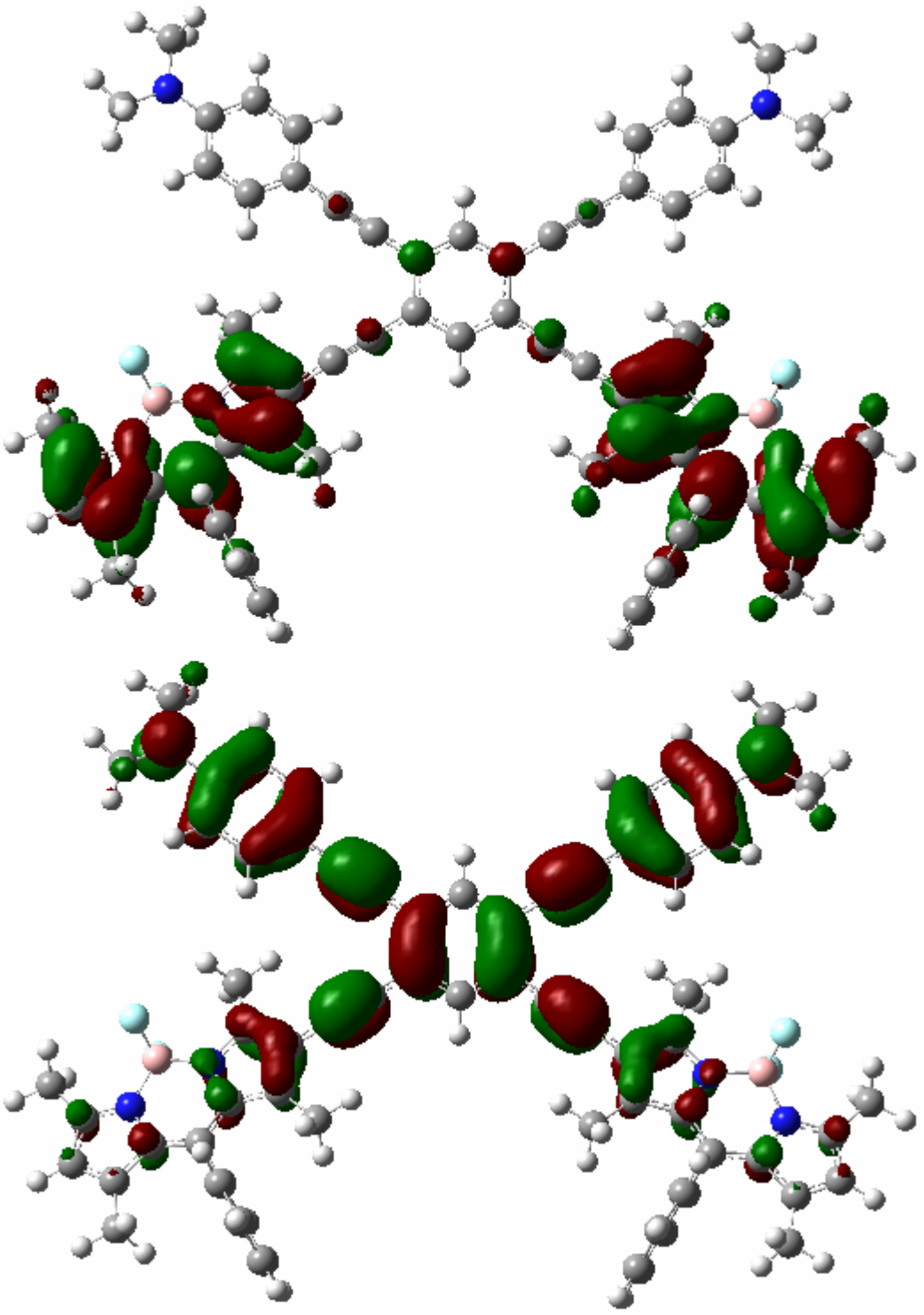


Figure 10. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **6'**.

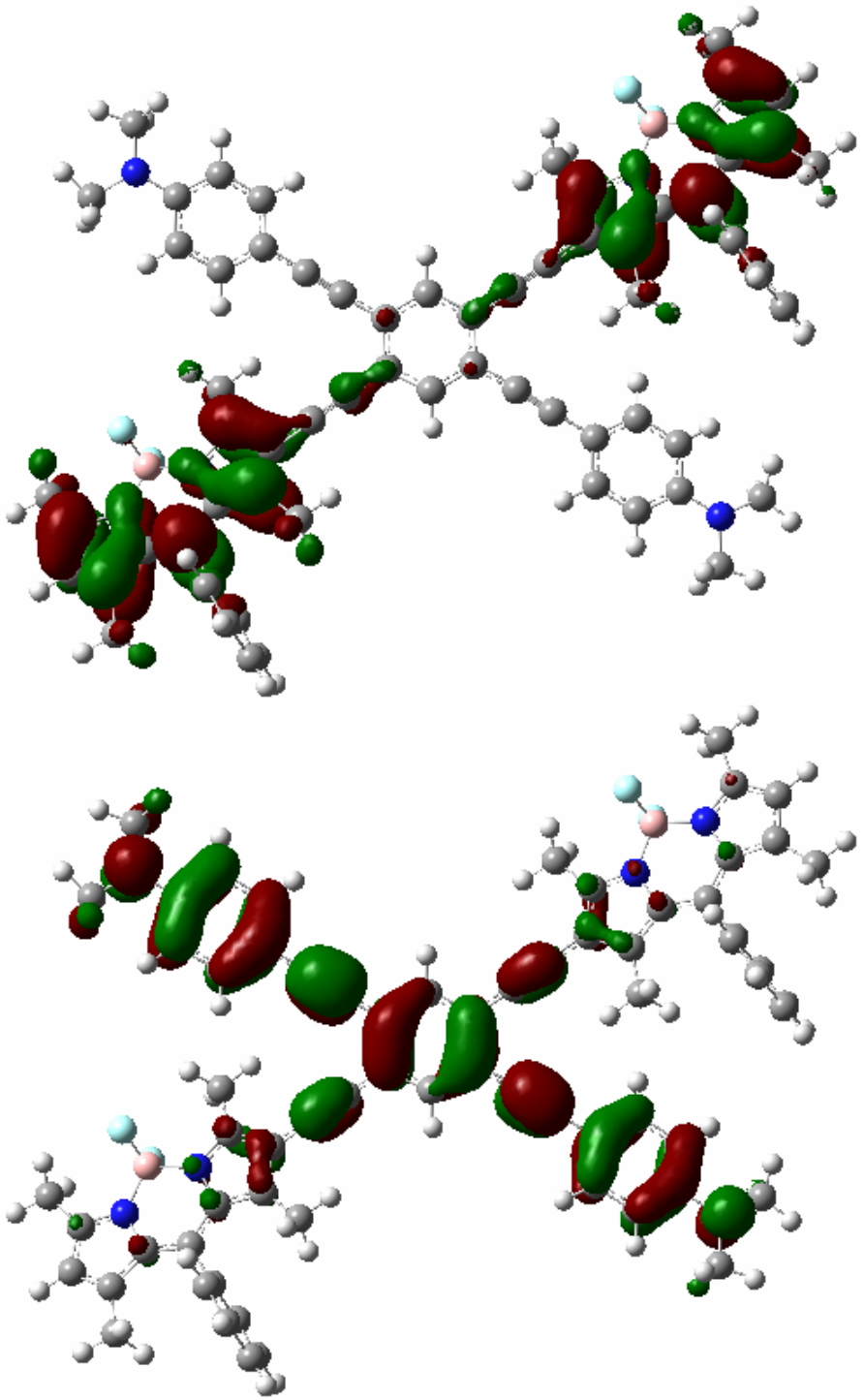


Figure 11. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **7**.

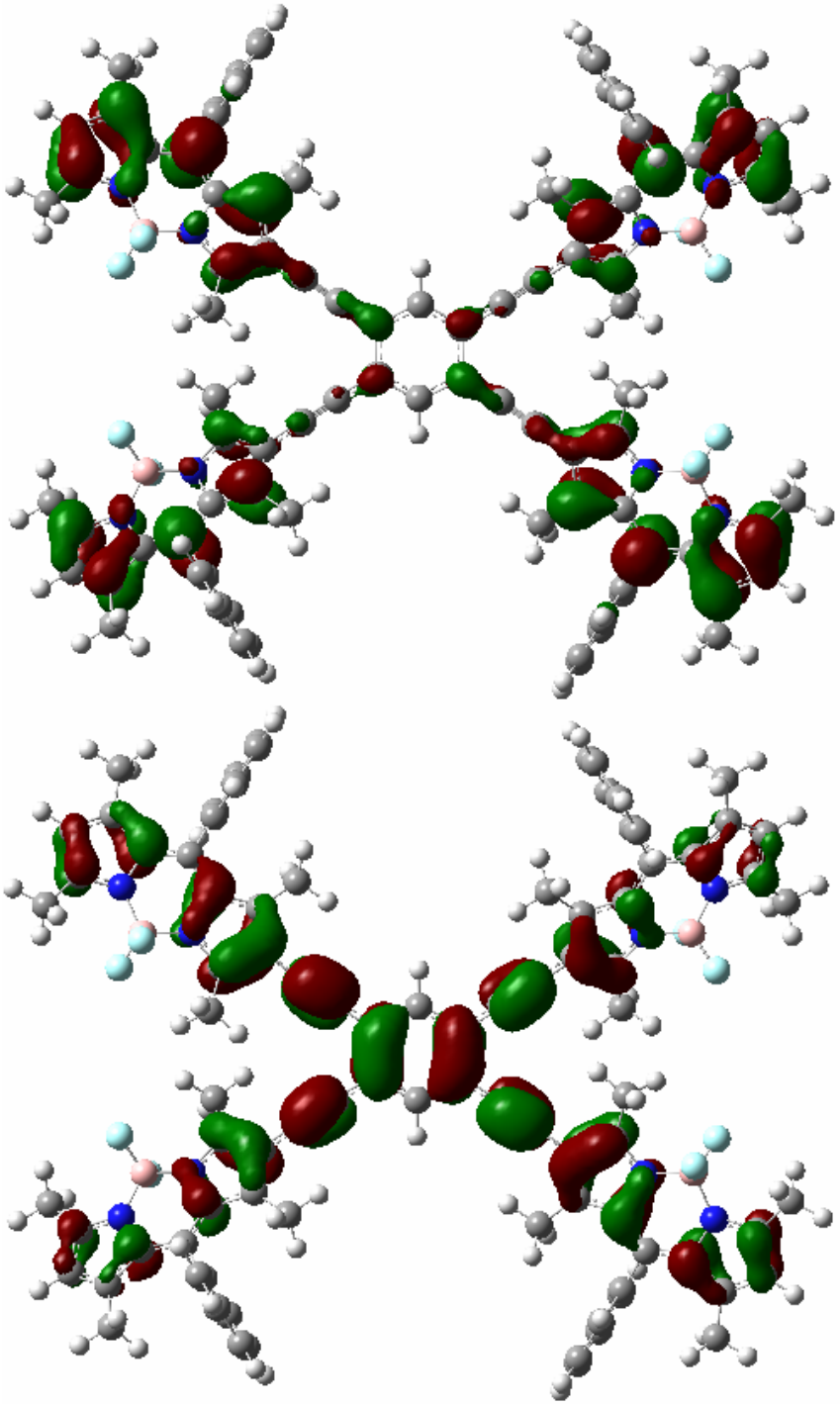


Figure 12. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **8**.

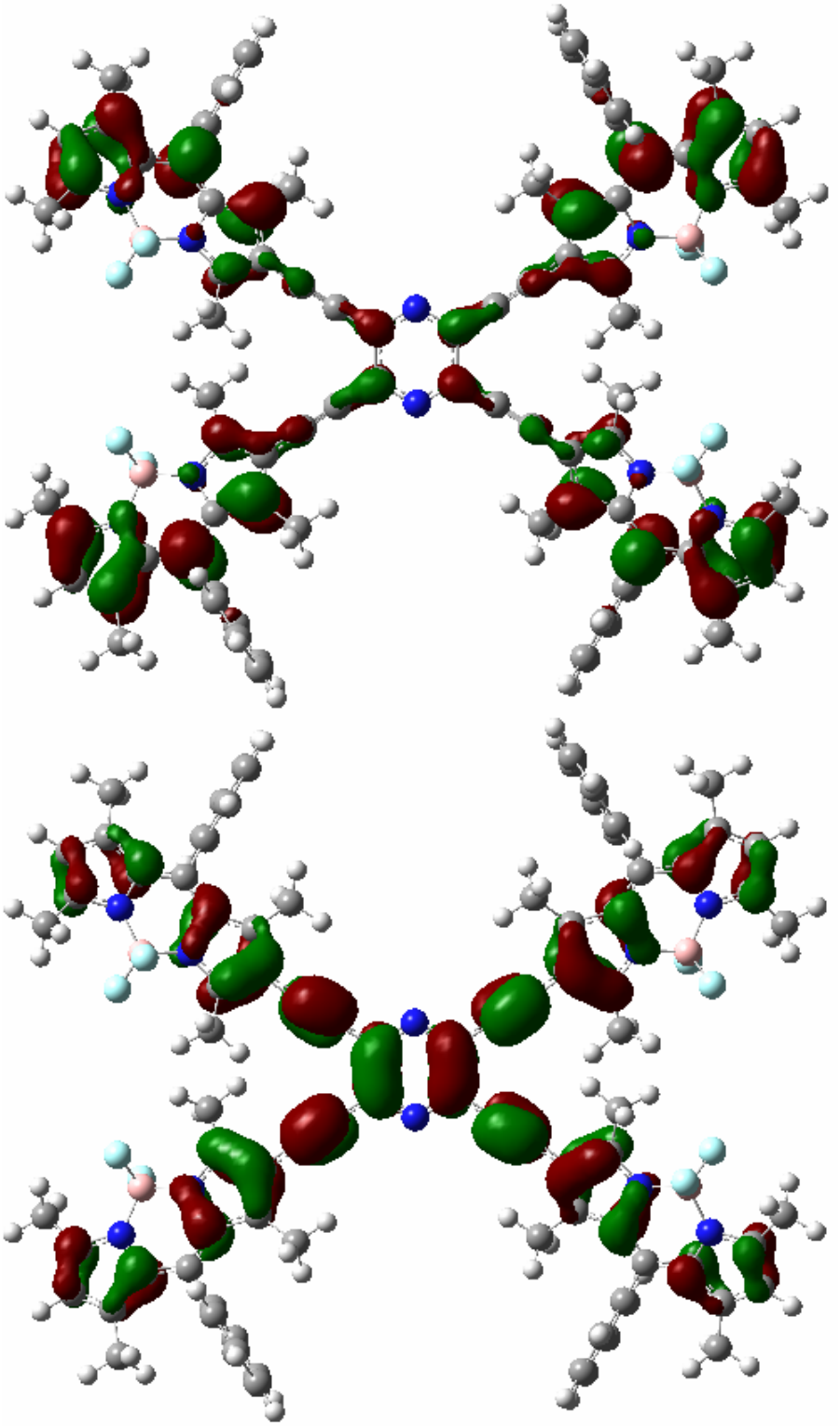


Figure 13. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **9**.

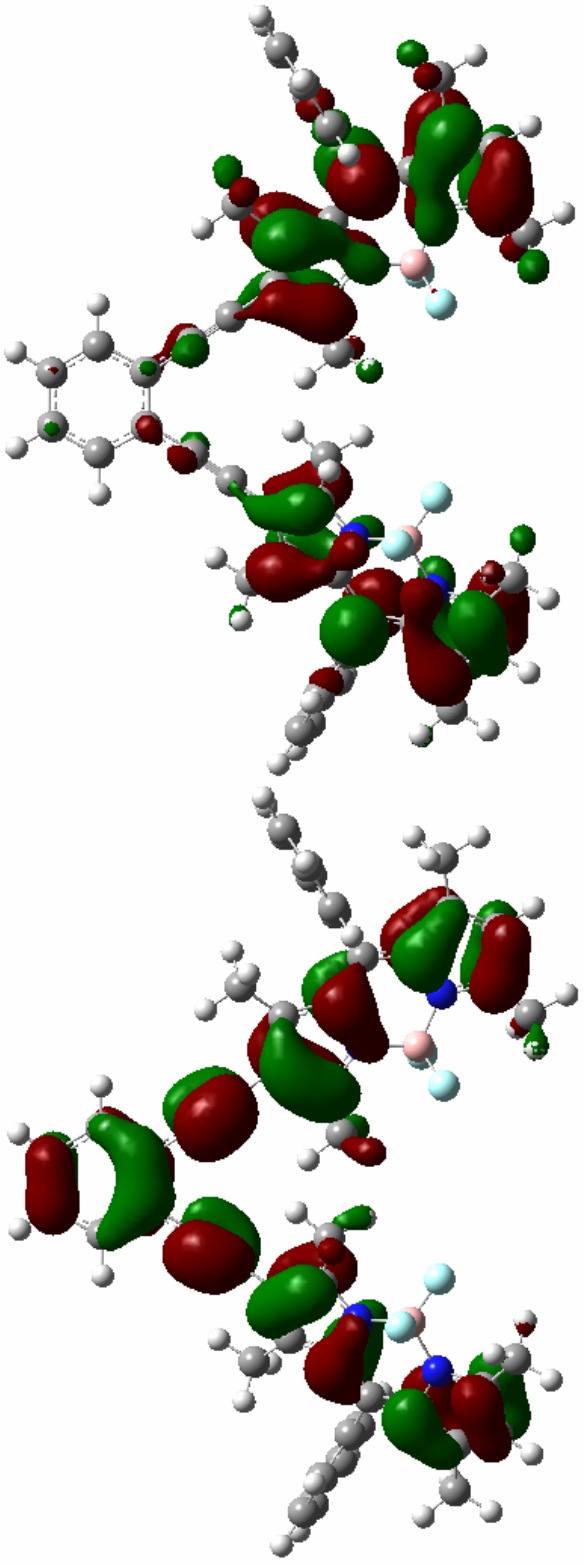


Figure 14. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **10**.

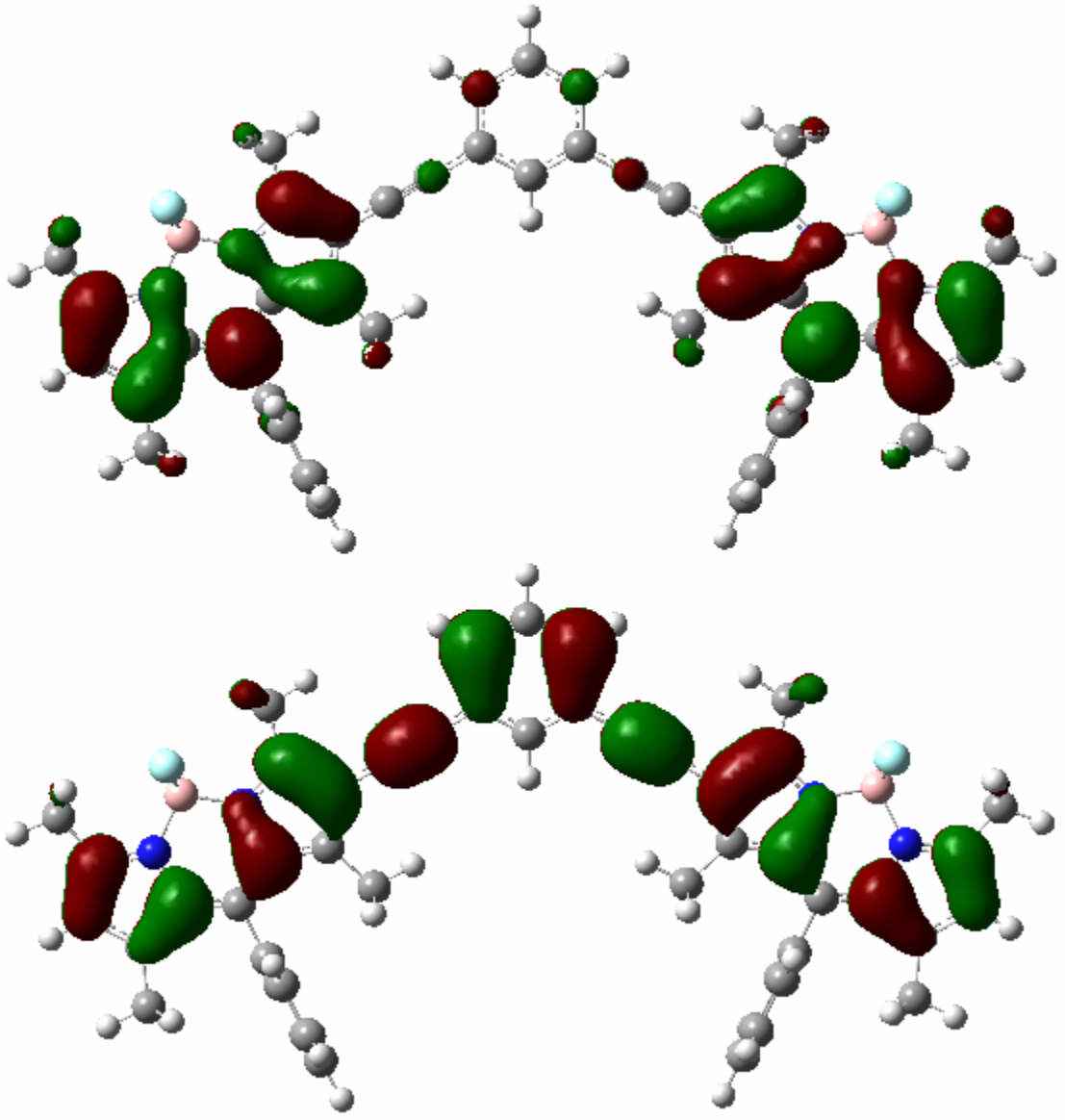
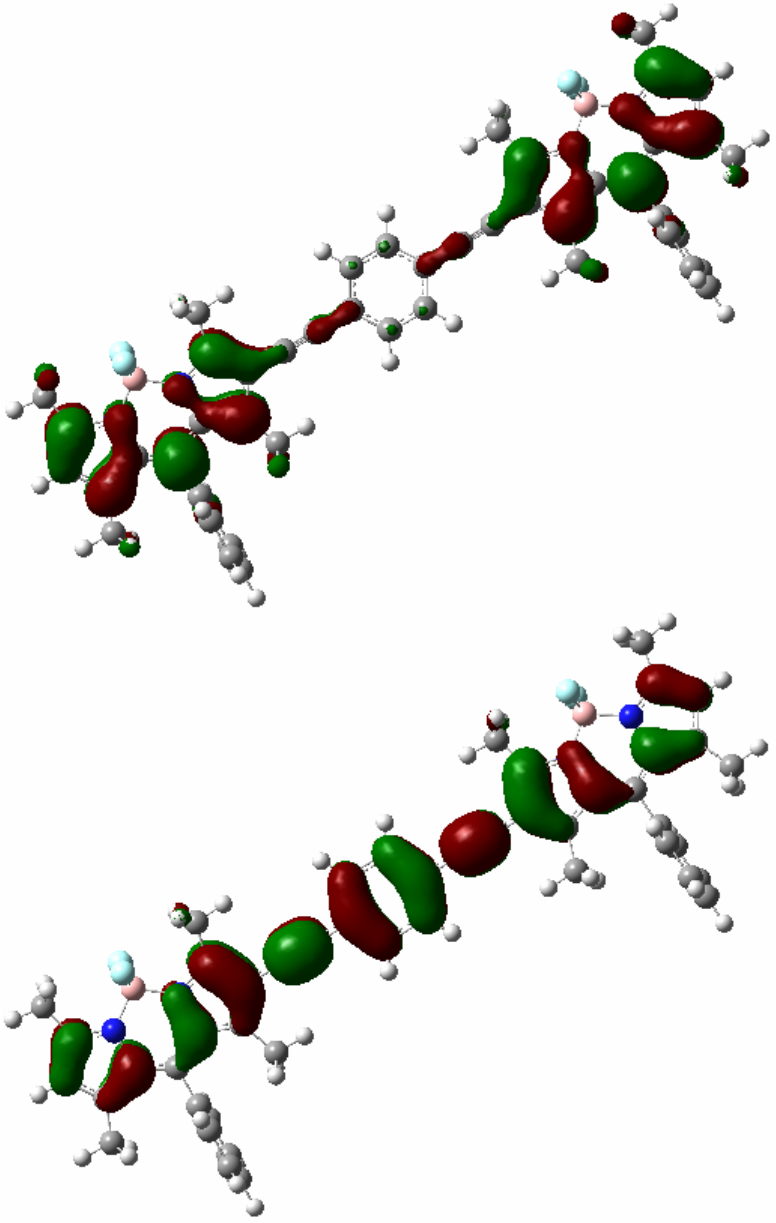


Figure 15. HOMO (bottom) and LUMO (top) maps (B3LYP/6-31G*) of **11**.



essentially to co-planarity of the aromatic groups within TAEBs/BAEBs **4**–**11** as illustrated in the calculations as well as an X-ray structure for **8** (see Supporting Information). Therefore, **4**–**6** exhibit significantly red-shifted emission wavelengths with respect to **1**–**3**, i.e., **4**–**6** maintain good intramolecular charge transfer while in full-conjugation with the phenylacetylene scaffold. Like **1'**–**6'**, the majority of LUMO density for **7**–**11** resides on the acceptor unit; however, the HOMO density for **7** and **9** extends throughout the entire molecule. As such, there is considerable overlap between their respective HOMO and LUMOs which give rise to π–π* transitions, similarly observed with **17**–**18**.[3b] The emission wavelengths of **7**–**11** confirm this assessment as their transitions are hypsochromically shifted as much as 40 nm with respect to **4**–**6**.

Conclusions

Donor/acceptor-functionalized TAEBs **1**–**6** as well as TAEBs **7**–**8** and structurally related BAEBs **9**–**11** containing only acceptors were synthesized and characterized. As such, these molecules displayed an array of intriguing optical properties that can be fine-tuned via small isomeric and structural variations. This especially holds true through comparison of **1**–**3** and **4**–**6**. All-acceptors **7**–**8** and related **9**–**11** also demonstrate the necessity for strong donors to ensure efficient charge transfer pathways. Despite the duality-imposed nature of **1**–**6** and **9**–**11**, all were shown to follow the previously-established trends with respect to absorption and emission. However, the BODIPY acceptor was found to have a remarkable impact on the overall phenylacetylene scaffold such as its inability to exhibit any form of solvatochromism, a trend most often found in these systems. Furthermore, in some instances, despite the tendency to quench in polar

solvents, the BODIPY unit was able to enhance the quantum yields to levels not yet seen with the TAEB molecules.

Experimental

General Comments. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 using either a Varian Inova 300 (^{1}H: 299.93 MHz, ^{13}C: 75.42 MHz) or 500 MHz (^{1}H: 500.11 MHz, ^{13}C: 125.75 MHz) NMR spectrometer. Chemical shifts (δ) are expressed in ppm relative to the residual chloroform (^{1}H: 7.27 ppm, ^{13}C: 77.2 ppm) or dichloromethane (^{1}H: 5.32 ppm, ^{13}C: 54.0 ppm) reference. Coupling constants are expressed in hertz. IR spectra were recorded using a Nicolet Magna FTIR 550 spectrometer. UV-Vis spectra were recorded on an HP 8453 UV-Vis spectrometer. Fluorescence spectra and quantum yields were recorded on a a Horiba Jobin Yvon Fluoromax-4 spectrofluorimeter spectrofluorimeter. High resolution mass spectra were recorded on a Waters Micromass MALDI Q-ToF Mass Spectrometer. THF and CH_2Cl_2 were distilled from their appropriate drying agents under N_2. Unless otherwise stated, all reagents were purchased and used as received. Donor-functionalized phenylacetylenes as well as BODIPYs **12-13** were prepared by the respective previously reported methods.[3c,12]

IodoBODIPY 14. TetramethylBODIPY **13** (0.400 g, 1.23 mmol) and $CaCO_3$ (0.185 g, 1.85 mmol) were added to CH_2Cl_2 (100 mL), and MeOH (20 mL). $BTEA{\cdot}ICl_2$ (0.480 g, 1.23 mmol) was then added and the mixture was stirred at rt for 1 h. After completion, the solution was evaporated to dryness. The crude material was chromatographed over silica gel (7:3 hexanes/CH_2Cl_2) to give **14** (0.460 g, 83%) as a red

crystalline solid. ^{1}H NMR (CD_2Cl_2): δ 7.53–7.51 (m, 3H), 7.29–7.27, (m, 2H), 6.09 (s, 1H), 2.60 (s, 3H), 2.54 (s, 3H), 1.40 (s, 6H); ^{13}C NMR (CD_2Cl_2): δ 158.5, 154.7, 146.1, 143.8, 142.4, 135.3, 132.5, 131.4, 129.9, 129.8, 128.5, 123.9, 122.9, 84.5, 17.0, 16.1, 15.1, 14.9; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2306, 1540, 1421, 1305 cm^{-1}; UV-Vis ($CHCl_3$) λ_{max} (log ε): 518 (4.93) nm; Em. ($CHCl_3$) λ_{max}: 537 nm; HRMS (MALDI) for $C_{19}H_{18}BF_2IN_2$ [M^+]: calcd 450.0576, found 450.0559.

(Trimethylsilylethynyl)BODIPY 15. IodoBODIPY **14** (0.358 g, 0.795 mmol), $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.024 mmol), and CuI (0.009 g, 0.048 mmol) were dissolved in THF (30 mL) and Et_3N (30 mL). The mixture was degassed with Ar for 45 min. TMSA (0.44 mL, 3.18 mmol) was added to the solution and the resulting mixture was stirred overnight at 50 °C. Upon completion, the mixture was evaporated to dryness and the crude product was dissolved in CH_2Cl_2 and then passed through a pad of silica to remove insoluble material. The filtrate was evaporated to dryness and the crude product was chromatographed on silica (1:1 hexanes/CH_2Cl_2) to give **15** (0.325 g, 98%) as a red crystalline solid. ^{1}H NMR (CD_2Cl_2): δ 7.52–7.50 (m, 3H), 7.28–7.26 (m, 2H), 6.06 (s, 1H), 2.62 (s, 3H), 2.54 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 158.5, 156.9, 145.7, 143.8, 143.1, 135.2, 133.2, 130.6, 129.9, 129.8, 128.5, 122.8, 115.8, 101.5, 98.2, 15.1, 14.9, 13. 8, 13.5, 0.5; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2305, 2149, 1541, 1422, 1313 cm^{-1}; UV-Vis ($CHCl_3$) λ_{max} (log ε): 529 (4.74) nm; Em. ($CHCl_3$) λ_{max}: 547; HRMS (MALDI) for $C_{24}H_{27}BF_2N_2Si$ [M^+]: calcd 420.2005, found 420.1991.

EthynylBODIPY 16. (Trimethylsilylethynyl)BODIPY **15** (0.460 g, 1.09 mmol) and K_2CO_3 (1.51 g, 10.9 mmol) were dissolved in THF (30 mL) and MeOH (30 mL) and

then stirred for 15 min. The product mixture was evaporated to dryness, and the crude product was dissolved in CH_2Cl_2 and then passed through a pad of silica to remove excess K_2CO_3. The filtrate was evaporated to dryness and the crude product was chromatographed on silica (1:1 hexanes/CH_2Cl_2) to give **16** (0.292 g, 84%) as a red crystalline solid. ^{1}H NMR (CD_2Cl_2): δ 7.53–7.50 (m, 3H), 7.28–7.26 (m, 2H), 6.08 (s, 1H), 3.37 (s, 1H), 2.62 (s, 3H), 2.55 (s, 3H), 1.47 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (CD_2Cl_2): δ 158.9, 156.6, 146.0, 144.0, 143.1, 135.0, 133.2, 130.3, 129.9, 129.8, 128.4, 122.9, 114.3, 84.0, 76.8, 15.1, 14.9, 13.6, 13.3; IR (NaCl, CH_2Cl_2) ν: 3052, 2987, 2152, 2062, 1485, 1464, 1382 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 522 (4.89) nm; Em. (toluene) λ_{max}: 539 nm; HRMS (MALDI) for $C_{21}H_{19}BF_2N_2$ [M^+]: calcd 348.1609, found 348.1623.

General Procedure for TAEB/BAEB Synthesis. BODIPY **12** or **14** was dissolved in THF (20 mL) and degassed with Ar for 45 min. In a separate flask, the appropriate diethynylarene, $Pd(PPh_3)_4$, and CuI were dissolved in THF (25 mL) and Et_3N (25 mL) and also degassed with Ar for 45 min. The solution containing **12** or **14** was then transferred by cannula into the second flask and the mixture was heated at 60 °C for 18–48 h. After cooling, the mixture was evaporated to dryness and the crude product was dissolved in CH_2Cl_2 and then passed through a pad of silica to remove insoluble material. The filtrate was evaporated to dryness and subsequently chromatographed on silica (1:1 CH_2Cl_2/hexanes) to afford the appropriate TAEB/BAEB derivative.

***ortho*-D/A-TAEB 1**. Following the general procedure, **12** (0.101 g, 0.224 mmol), 1,2-diethynyl-4,5-bis[(4'-*N*,*N*-dibutylaminophenyl)ethynyl]benzene[3c] (0.060 g, 0.102 mmol), $Pd(PPh_3)_4$ (0.007 g, 0.006 mmol), and CuI (0.007 g, 0.012 mmol) were reacted

for 48 h. Chromatography on silica (1:1 CH_2Cl_2/hexanes) gave **1** (0.030 g, 23%) as a red/orange solid. ^{1}H NMR ($CDCl_3$): δ 7.74 (s, 2H), 7.70 (d, J = 8.7 Hz, 4H), 7.44 (d, J = 8.7 Hz, 4H), 7.30 (d, J = 8.7 Hz, 4H), 6.61 (d, J = 8.7 Hz, 4H), 6.00 (s, 4H), 3.32 (t, J = 7.2 Hz, 8H), 2.56 (s, 12H), 1.62–1.56 (m, 8H), 1.44 (s, 12H), 1.42–1.36 (m, 8H), 0.98 (t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 156.0, 148.5, 143.1, 140.8, 135.5, 134.7, 133.4, 132.5, 131.4, 128.5, 126.6, 124.2, 123.7, 121.7, 111.4, 108.6, 98.1, 94.0, 89.6, 86.2, 50.9, 29.6, 20.5, 14.8, 14.2; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2305, 2194, 1605, 1547, 1523, 1513, 1471, 1307, 1270 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 505 (5.30) nm; Em. (toluene) λ_{max}: 524 nm; HRMS (MALDI) for $C_{80}H_{82}B_2F_4N_6$ [M^+]: calcd 1224.6723, found 1224.6744.

***meta*-D/A-TAEB 2**. Following the general procedure, **12** (0.101 g, 0.224 mmol), 1,5-diethynyl-2,4-bis[(4'-*N*,*N*-dibutylaminophenyl)ethynyl]benzene[3c] (0.060 g, 0.102 mmol), $Pd(PPh_3)_4$ (0.007 g, 0.006 mmol), and CuI (0.007 g, 0.012 mmol) were reacted for 48 h. Chromatography on silica (1:1 CH_2Cl_2/hexanes) gave **2** (0.030 g, 23%) as a red/orange solid. ^{1}H NMR ($CDCl_3$): δ 7.75-7.72 (m, 6H), 7.40 (d, J = 8.7 Hz, 4H), 7.32 (d, J = 8.7 Hz, 4H), 6.57 (d, J = 8.7 Hz, 4H), 6.01 (s, 4H), 3.30 (t, J = 7.2 Hz, 8H), 2.58 (s, 12H), 1.62-1.56 (m, 8H), 1.48 (s, 12H), 1.42-1.34 (m, 8H), 0.96 (t, J = 7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$): δ 156.0, 148.7, 143.3, 141.1, 135.4, 135.0, 134.3, 133.4, 132.7, 131.5, 128.5, 127.3, 124.5, 123.2, 121.6, 111.4, 108.4, 98.3, 94.1, 89.9, 86.1, 51.0, 29.6, 20.6, 14.9, 14.2; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2194, 1606, 1547, 1523, 1469, 1404, 1370, 1307, 1270 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 505 (5.06) nm; Em. (toluene) λ_{max}: 520 nm; HRMS (MALDI) for $C_{80}H_{82}B_2F_4N_6$ [M^+]: calcd 1224.6723, found 1224.6741.

***para*-D/A-TEAB 3**. Following the general procedure, **12** (0.101 g, 0.224 mmol), 1,4-diethynyl-2,5-bis[(4'-*N*,*N*-dibutylaminophenyl)ethynyl]benzene[3c] (0.060 g, 0.102

mmol), $Pd(PPh_3)_4$ (0.007 g, 0.006 mmol), and CuI (0.007 g, 0.012 mmol) were reacted for 48 h. Chromatography on silica (1:1 CH_2Cl_2/hexanes) gave **3** (0.030 g, 23%) as a red/orange solid. ^{1}H NMR ($CDCl_3$): δ 7.74 (d, *J* = 8.7 Hz, 4H), 7.73 (s, 2H), 7.40 (d, *J* = 8.7 Hz, 4H), 7.32 (d, *J* = 8.7 Hz, 4H), 6.57 (d, *J* = 8.7 Hz, 4H), 6.01 (s, 4H), 3.30 (t, *J* = 7.2 Hz, 8H), 2.58 (s, 12H), 1.62-1.56 (m, 8H), 1.48 (s, 12H), 1.42-1.34 (m, 8H), 0.96 (t, *J* = 7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$): δ 155.9, 148.6, 143.3, 141.1, 135.4, 134.6, 133.3, 132.7, 131.4, 128.5, 125.8, 124.6, 124.4, 121.6, 111.4, 108.4, 97.8, 94.3, 89.8, 86.0, 50.9, 29.6, 20.5, 14.9, 14.2; IR (NaCl, CH_2Cl_2) ν: 3055, 2958, 2305, 2196, 1604, 1547, 1523, 1471, 1422, 1370, 1307 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 505 (5.06) nm; Em. (toluene) λ_{max}: 520 nm; HRMS (MALDI) for $C_{80}H_{82}B_2F_4N_6$ [M^+]: calcd 1224.6723, found 1224.6767.

***ortho*-D/A-TAEB 4**. Following the general procedure, **14** (0.050 g, 0.145 mmol), 1,2-diethynyl-4,5-bis[(4'-*N*,*N*-dibutylaminophenyl)ethynyl]benzene[3c] (0.050 g, 0.072 mmol), $Pd(PPh_3)_4$ (0.006 g, 0.004 mmol), and CuI (0.002 g, 0.008 mmol) were reacted for 48 h. Chromatography on silica (4:1 toluene/ cyclohexane) gave **4** (0.031 g, 34%) as a red solid. ^{1}H NMR ($CDCl_3$): δ 7.58 (s, 2H), 7.50-7.48 (m, 6H), 7.40 (d, *J* = 8.7 Hz, 4H), 7.29 (m, 4H), 6.57 (d, *J* = 8.7 Hz, 4H), 6.05 (s, 2H), 3.29 (t, *J* = 7.2 Hz, 8H), 2.63 (s, 6H), 2.61 (s, 6H), 1.60-1.56 (m, 8H), 1.42 (s, 6H), 1.40 (s, 6H), 1.40-1.36 (m, 8H), 1.04 (t, *J* = 7.2 Hz, 12 H); ^{13}C NMR (CD_2Cl_2): δ 158.9, 156.9, 149.1, 145.8, 143.3, 143.0, 135.1, 134.8, 133.6, 129.9, 129.8, 129.8, 129.7, 128.5, 125.9, 124.5, 122.8, 111.8, 111.7, 108.6, 97.8, 94.9, 88.0, 86.5, 30.28, 29.9, 20.7, 15.1, 14.9, 14.5, 14.3, 13.9, 13.5; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2360, 2149, 1539, 1521, 1313, 1193 cm^{-1}; UV-Vis

(toluene) λ_{max} (log ε): 533 (4.91) nm; Em. (toluene) λ_{max}: 603 nm; HRMS (MALDI) for $C_{80}H_{82}B_2F_4N_6$ [M^+]: calcd 1224.6723, found 1224.6704.

***meta*-D/A-TEAB 5**. Following the general procedure, **14** (0.050 g, 0.145 mmol), 1,5-diethynyl-2,4-bis[(4'-*N*,*N*-dibutylaminophenyl)ethynyl]benzene[3c] (0.050 g, 0.072 mmol), $Pd(PPh_3)_4$ (0.006 g, 0.004 mmol), and CuI (0.002 g, 0.008 mmol) were reacted for 48 h. Chromatography on silica (4:1 toluene/ cyclohexane) gave **5** (0.013 g, 15%) as a red solid. ^{1}H NMR (CD_2Cl_2): δ 7.61 (s, 1H), 7.54 (s, 1H), 7.52-7.50 (m, 6H), 7.36-7.32 (m, 4H), 7.26 (d, *J* = 8.7 Hz, 4H), 6.55 (d, *J* = 8.7 Hz, 4H), 6.09 (s, 2H), 3.31 (t, *J* = 7.2 Hz, 8H), 2.68 (s, 6H), 2.55 (s, 6H), 1.63-1.56 (m, 8H), 1.53 (s, 6H), 1.42 (s, 6H), 1.39 (q, *J* = 6.5 Hz, 8H), 0.98 (t, *J* = 7.2 Hz, 12H); ^{13}C NMR (CD_2Cl_2): δ 158.5, 156.9, 148.9, 145.7, 143.5, 142.9, 135.3, 135.1, 134.8, 133.6, 129.8, 129.7, 128.5, 125.6, 124.1, 122.7, 111.6, 108.3, 97.6, 95.1, 88.0, 86.3, 51.2, 29.8, 20.9, 15.1, 14.9, 14.3, 14.0, 13.7; IR (NaCl, CH_2Cl_2) ν: 3054, 2960, 2198, 1539, 1520, 1264 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 553 (4.92) nm; Em. (toluene) λ_{max}: 606 nm; HRMS (MALDI) for $C_{80}H_{82}B_2F_4N_6$ [M^+]: calcd 1224.6723, found 1224.6696.

***para*-D/A-TAEB 6**. Following the general procedure, **14** (0.050 g, 0.145 mmol), 1,4-diethynyl-2,5-bis[(4'-*N*,*N*-dibutylaminophenyl)ethynyl]benzene[3c] (0.050 g, 0.072 mmol), $Pd(PPh_3)_4$ (0.006 g, 0.004 mmol), and CuI (0.002 g, 0.008 mmol) were reacted for 48 h. Chromatography on silica (4:1 toluene/ cyclohexane) gave **6** (0.009 g, 10%) as a red solid. ^{1}H NMR (CD_2Cl_2): δ 7.59 (s, 2H), 7.53-7.50 (m, 6H), 7.36-7.32 (m, 4H), 7.26 (d, *J* = 8.7 Hz, 4H), 6.56 (d, *J* = 8.7 Hz, 4H), 6.09 (s, 2H), 3.31 (t, *J* = 7.5 Hz), 2.69 (s, 6H), 2.55 (s, 6H), 1.63-1.56 (m, 8H), 1.54 (s, 6H), 1.42 (s, 6H), 1.39 (q, *J* = 6.5 Hz, 8H), 0.99 (t, *J* = 7.2 Hz); ^{13}C NMR (CD_2Cl_2) δ 158.5, 156.8, 149.0, 145.8, 142.9, 135.1, 133.6,

129.8, 129.7, 129.5, 128.5, 127.3, 126.5, 124.8, 122.8, 114.3, 111.7, 110.5, 110.57, 110.55, 108.3, 97.4, 95.2, 88.2, 86.2, 51.2, 30.3, 29.5, 20.9, 4.9, 14.5, 14.4, 14.3, 13.7; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2929, 2359, 1270 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 569 (4.77) nm; Em. (toluene) λ_{max}: 601 nm; HRMS (MALDI) for $C_{80}H_{82}B_2F_4N_6$ [M^+]: calcd 1224.6723, found 1224.6743.

tetra-A-TAEB 7. Following the general procedure, **16** (0.177 g, 0.508 mmol), 1,2,4,5-tetraiodobenzene (0.074 g, 0.127 mmol), $Pd(PPh_3)_4$ (0.017 g, 0.015 mmol), and CuI (0.006 g, 0.030 mmol) were reacted for 18 h. Chromatography on silica (4:1 $CHCl_3$/toluene) gave **7** (0.066 g, 61%) as a red solid. ^{1}H NMR ($CDCl_3$): δ 7.53-7.49 (m, 14H), 7.29-7.27 (m, 8H), 6.07 (s, 4H), 2.62 (s, 24H), 1.43 (s, 12H), 1.39 (s, 12H); ^{13}C NMR ($CDCl_3$): δ 158.1, 156.7, 145.1, 143.1, 142.4, 135.0, 134.8, 132.8, 130.5, 129.5, 129.4, 128.0, 124.9, 122.4, 115.0, 94.3, 88.2, 15.0, 14.8, 13.8, 13.4; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2305, 2203, 1541, 1421, 1270 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 542 (5.33) nm; Em. (toluene) λ_{max}: 591 nm; HRMS (MALDI) for $C_{90}H_{74}B_4F_8N_8$ [M^+]: calcd 1462.6281, found 1462.6247.

Pyrazine TAEB 8. Following the general procedure, **16** (0.133 g, 0.382 mmol), 1,2,4,5-tetrabromopyrazine (0.038 g, 0.096 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.011 mmol), and CuI (0.005 g, 0.023 mmol) were reacted for 18 h. Chromatography on silica (4:1 $CHCl_3$/toluene) gave **8** (0.131 g, 93%) as a red solid. ^{1}H NMR ($CDCl_3$): δ 7.49-7.45 (m, 12H), 7.29-7.25 (m, 8H), 6.09 (s, 4H), 2.62 (s, 24H), 1.43 (s, 12H), 1.39 (s, 12H); ^{13}C NMR ($CDCl_3$): δ 159.1, 157.0, 145.7, 143.6, 142.6, 138.7, 134.6, 133.2, 130.3, 129.5, 128.0, 122.9, 113.7, 93.0, 91.1, 15.1, 14.8, 13.9, 13.4; IR (NaCl, CH_2Cl_2) ν: 3055, 2927, 2195, 1557, 1547, 1536, 1404, 1309, 1270 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 541

(5.40) nm; Em. (toluene) λ_{max}: 579 nm; HRMS (MALDI) for $C_{88}H_{72}B_4F_8N_{10}$ [M^+]: calcd 1464.6186, found 1464.6172.

***ortho*-BAEB 9**. Following the general procedure, **16** (0.090 g, 0.259 mmol), 1,2-diiodobenzene (0.043 g, 0.129 mmol), $Pd(PPh_3)_4$ (0.007 g, 0.008 mmol), and CuI (0.002 g, 0.016 mmol) were reacted for 18 h. Chromatography on silica (7:3 CH_2Cl_2/hexanes) gave **9** (0.044 g, 44%) as a violet solid. ^{1}H NMR (CD_2Cl_2): δ 7.53-7.47 (m, 8H), 7.31-7.26 (m, 6H), 6.09 (s, 2H), 2.56 (s, 12H), 1.43 (s, 6H), 1.39 (s, 6H); ^{13}C NMR (CD_2Cl_2): δ 158.4, 156.6, 145.7, 143.2, 142.9, 135.0, 133.1, 132.2, 130.7, 129.8, 129.7, 128.4, 128.3, 126.0, 122.7, 115.3, 95.1, 86.6, 15.1, 14.9, 13.8, 13.4; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2305, 2203, 1541, 1421, 1270 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 526 (4.87) nm; Em. (toluene) λ_{max}: 578 nm; HRMS (MALDI) for $C_{48}H_{40}B_2F_4N_4$ [M^+]: calcd 770.3375, found 770.3397.

***meta*-BAEB 10**. Following the general procedure, **16** (0.090 g, 0.259 mmol), 1,3-diiodobenzene (0.043 g, 0.129 mmol), $Pd(PPh_3)_4$ (0.009 g, 0.008 mmol), and CuI (0.003 g, 0.016 mmol) were reacted for 18 h. Chromatography on silica (3:2 CH_2Cl_2/hexanes) gave **10** (0.068 g, 68%) as a violet solid. ^{1}H NMR (CD_2Cl_2): δ 7.55-7.52 (m, 7H), 7.40-7.37 (m, 2H), 7.32-7.30 (m, 4H), 7.29-7.26 (m, 1H), 6.08 (s, 2H), 2.66 (s, 6H), 2.55 (s, 6H), 1.51 (s, 6H), 1.42 (s, 6H); ^{13}C NMR (CD_2Cl_2): δ 158.6, 156.6, 145.9, 143.3, 143.0, 135.1, 133.2, 131.1, 130.7, 129.9, 129.8, 129.1, 128.5, 128.4, 124.5, 122.8, 115.2, 94.6, 83.2, 15.1. 14.9. 13.8. 13.5; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2305, 2203, 1541, 1421, 1270 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 544 (5.08) nm; Em. (toluene) λ_{max}: 567 nm; HRMS (MALDI) for $C_{48}H_{40}B_2F_4N_4$ [M^+]: calcd 770.3375, found 770.3347.

***para*-TEAB 11**. Following the general procedure, **16** (0.070 g, 0.201 mmol), 1,4-diiodobenzene (0.033 g, 0.100 mmol), $Pd(PPh_3)_4$ (0.007 g, 0.006 mmol), and CuI (0.002 g, 0.012 mmol) were reacted for 18 h. Chromatography on silica (1:1 CH_2Cl_2/hexanes) gave **11** (0.068 g, 88%) as a violet solid. ^{1}H NMR (CD_2Cl_2): δ 7.53-7.49 (m, 6H), 7.41 (s, 4H), 7.32-7.30 (m, 4H), 6.09 (s, 2H), 2.65 (s, 6H), 2.55 (s, 6H), 1.51 (s, 6H), 1.42 (s, 6H); ^{13}C NMR (CD_2Cl_2): δ 158.6, 156.6, 145.9, 143.2, 143.0, 135.1, 133.2, 131.6, 130.9, 129.9, 129.8, 128.5, 123.6, 122.8, 115.3, 96.2, 84.5, 15.1, 14.9, 13.8, 13.5; IR (NaCl, CH_2Cl_2) ν: 3054, 2987, 2305, 2203, 1541, 1421, 1270 cm^{-1}; UV-Vis (toluene) λ_{max} (log ε): 554 (4.96) nm; Em. (toluene) λ_{max}: 586 nm; HRMS (MALDI) for $C_{48}H_{40}B_2F_4N_4$ [M^+]: calcd 770.3375, found 770.3336.

APPENDIX A

EXPERIMENTAL DETAILS FOR CHAPTER II

Cartesian Coordinates of Stationary Points[1]

8a

Low level structure:

B3LYP/6-31G* = -1073.93299802 au
B3LYP/6-31G* Zero Point Corrected Energy = -1073.645987 au
NIMAG = 0

C	-5.52204900	0.71581600	-0.00001000
C	-4.87506000	1.95600800	-0.00001900
C	-3.47675500	2.04488500	-0.00002100
C	-2.72747100	0.86937300	-0.00001300
C	-3.39127500	-0.38460000	-0.00000400
C	-4.78123900	-0.46952400	-0.00000300
C	-1.28611700	0.59470600	-0.00001000
C	-1.12066500	-0.85401700	-0.00000700
C	-2.38515800	-1.44833300	0.00000600
C	-0.19786300	1.44659700	-0.00000700
C	1.12066600	0.85401600	-0.00000800
C	1.28611800	-0.59470600	-0.00000900
C	0.19786400	-1.44659800	-0.00001000
C	2.38515900	1.44833300	-0.00000700
C	3.39127600	0.38460000	-0.00000100
C	2.72747200	-0.86937300	-0.00000300
C	4.78124000	0.46952300	0.00000500
C	5.52204900	-0.71581600	0.00000800
C	4.87506100	-1.95600800	0.00000500
C	3.47675500	-2.04488500	0.00000000
C	-2.74815500	-2.81007100	0.00001600
C	0.35436100	-2.86250900	-0.00002100
C	-0.35435900	2.86250900	-0.00000900
C	2.74815300	2.81007100	-0.00001100

[1] Bold number refers to the molecule in Chapter II

C	-3.17928300	-3.94409900	0.00007400
C	0.49175300	-4.06482200	-0.00003000
C	-0.49175200	4.06482100	0.00006500
C	3.17927600	3.94410100	0.00001100
H	-6.60777900	0.67312400	-0.00000800
H	-5.46478700	2.86876400	-0.00002600
H	-2.99083000	3.01264200	-0.00002800
H	-5.27137200	-1.43894900	0.00000700
H	5.27137300	1.43894900	0.00000600
H	6.60778000	-0.67312500	0.00001200
H	5.46478700	-2.86876500	0.00000800
H	2.99083000	-3.01264300	-0.00000100
H	-3.51066400	-4.95758400	0.00007900
H	0.58298100	-5.12736600	-0.00006100
H	-0.58297900	5.12736600	0.00008900
H	3.51065200	4.95758800	-0.00000700

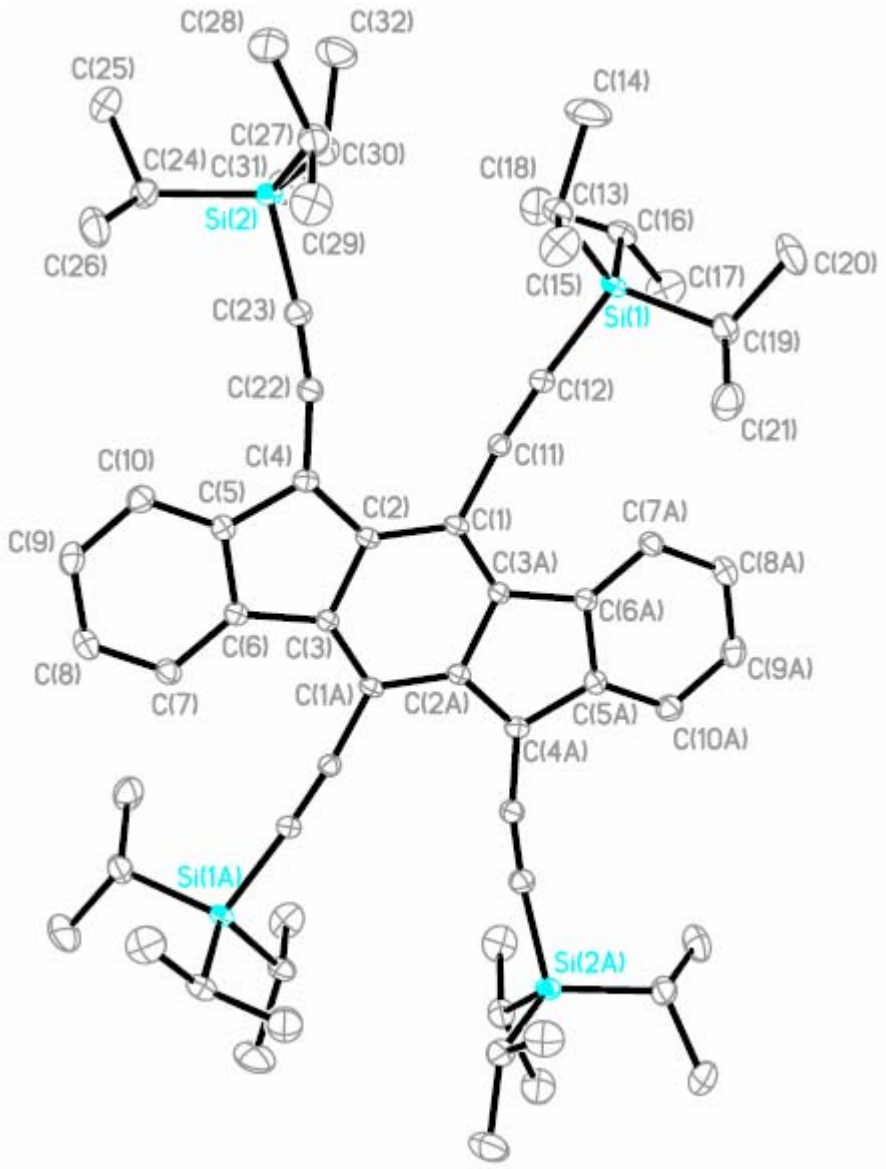
High level structure

B3LYP/6-311+G** = -1074.19272033au
B3LYP/6-311+G** Zero Point Corrected Energy = -1073.906991 au
NIMAG = 0

C	-5.51700900	-0.71349300	0.00001800
C	-4.87185000	-1.95176200	0.00001900
C	-3.47499200	-2.04073000	0.00001400
C	-2.72587400	-0.86739100	0.00000800
C	-3.38838200	0.38533300	0.00000800
C	-4.77653700	0.47044700	0.00001300
C	-1.28477100	-0.59393500	0.00000300
C	-1.11972200	0.85435100	0.00000200
C	-2.38162600	1.44819500	0.00000100
C	-0.19913900	-1.44448100	-0.00000500
C	1.11972200	-0.85435100	0.00000000
C	1.28477100	0.59393500	0.00000100
C	0.19913900	1.44448100	0.00000300
C	2.38162500	-1.44819500	0.00000400
C	3.38838200	-0.38533300	0.00000400
C	2.72587400	0.86739100	0.00000100
C	4.77653700	-0.47044700	0.00000600
C	5.51700900	0.71349300	0.00000600
C	4.87185000	1.95176200	0.00000300
C	3.47499200	2.04073000	0.00000000
C	-2.74495100	2.80707000	-0.00000200

C	0.35764700	2.85735700	0.00000300
C	-0.35764700	-2.85735700	-0.00001200
C	2.74495100	-2.80707000	0.00001200
C	-3.17431100	3.93602300	-0.00004700
C	0.49160300	4.05443500	0.00000300
C	-0.49160300	-4.05443500	-0.00006900
C	3.17431100	-3.93602300	-0.00000200
H	-6.60021600	-0.67096600	0.00002200
H	-5.46086900	-2.86198100	0.00002400
H	-2.99320800	-3.00776500	0.00001500
H	-5.26830900	1.43636600	0.00001200
H	5.26830900	-1.43636600	0.00000900
H	6.60021600	0.67096500	0.00000800
H	5.46086900	2.86198100	0.00000200
H	2.99320800	3.00776500	-0.00000200
H	-3.51387500	4.94289600	-0.00001800
H	0.59117300	5.11240900	0.00000200
H	-0.59117400	-5.11240900	-0.00009800
H	3.51387600	-4.94289500	0.00004900

Crystallographic Data for 8a



Solid State Packing of 8a

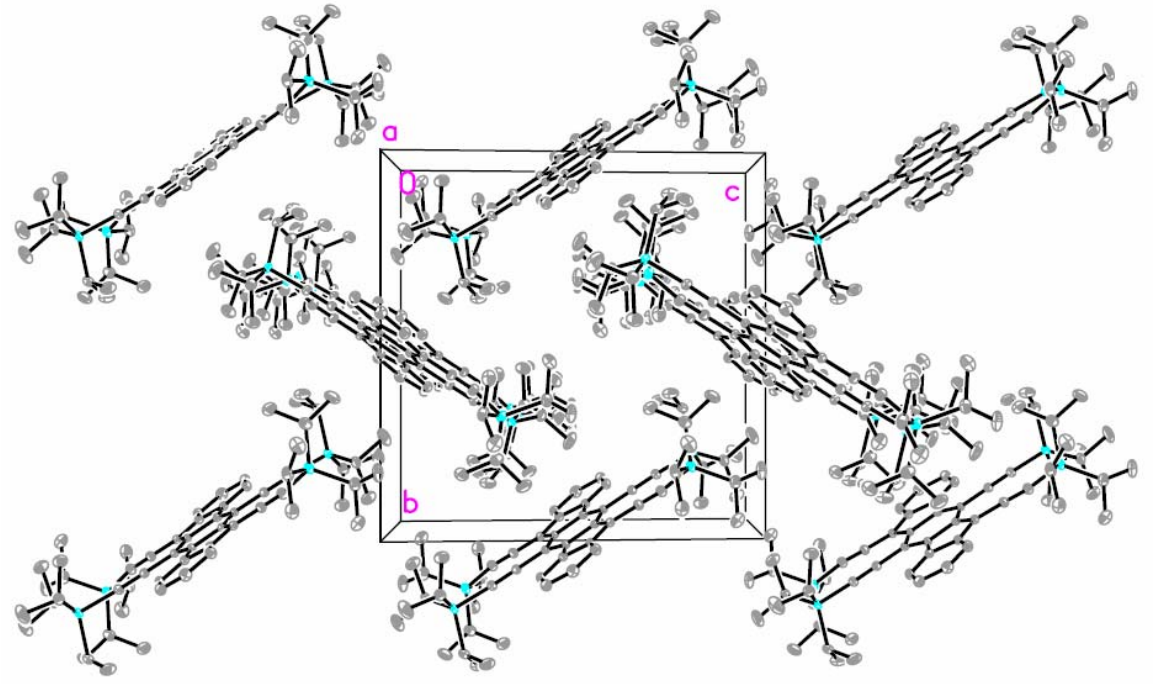


Table 1. Crystal data and structure refinement for **8a**.

Identification code	mh45	
Empirical formula	C64 H92 Si4	
Formula weight	973.74	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.579(2) Å	α = 90°.
	b = 15.042(2) Å	β = 97.502(3)°.
	c = 15.054(2) Å	γ = 90°.
Volume	3048.6(8) $Å^3$	
Z	2	
Density (calculated)	1.061 Mg/m^3	
Absorption coefficient	0.133 mm^{-1}	
F(000)	1064	
Crystal size	0.26 x 0.12 x 0.05 mm^3	
Theta range for data collection	1.51 to 25.00°.	
Index ranges	-16<=h<=16, -17<=k<=17, -17<=l<=17	
Reflections collected	29004	
Independent reflections	5357 [R(int) = 0.0554]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9934 and 0.9661	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5357 / 0 / 491	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1092	
R indices (all data)	R1 = 0.0651, wR2 = 0.1273	
Largest diff. peak and hole	0.338 and -0.274 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	4629(1)	7916(1)	8278(1)	25(1)
Si(2)	8653(1)	8162(1)	8091(1)	28(1)
C(1)	4978(2)	9456(1)	5795(1)	20(1)
C(2)	5891(2)	9808(1)	5555(1)	19(1)
C(3)	5885(2)	10356(1)	4757(1)	20(1)
C(4)	6867(2)	9714(1)	5958(1)	23(1)
C(5)	7512(2)	10218(1)	5429(1)	23(1)
C(6)	6918(2)	10614(1)	4694(1)	22(1)
C(7)	7358(2)	11142(2)	4107(1)	27(1)
C(8)	8382(2)	11264(2)	4253(2)	33(1)
C(9)	8960(2)	10858(2)	4959(2)	35(1)
C(10)	8532(2)	10330(2)	5559(2)	31(1)
C(11)	4954(2)	8934(1)	6589(1)	22(1)
C(12)	4853(2)	8512(1)	7251(1)	25(1)
C(13)	5774(2)	8115(2)	9100(2)	32(1)
C(14)	5926(3)	7442(3)	9871(2)	67(1)
C(15)	5865(2)	9063(2)	9450(2)	51(1)
C(16)	4459(2)	6703(2)	7993(2)	34(1)
C(17)	3515(2)	6516(2)	7346(2)	54(1)
C(18)	5356(2)	6297(2)	7639(3)	53(1)
C(19)	3434(2)	8371(2)	8606(2)	35(1)
C(20)	3218(3)	8013(3)	9509(3)	74(1)
C(21)	3316(2)	9375(2)	8559(2)	47(1)
C(22)	7289(2)	9230(1)	6721(1)	26(1)
C(23)	7802(2)	8850(2)	7323(2)	30(1)
C(24)	9883(2)	8256(2)	7641(2)	37(1)
C(25)	10632(2)	7517(2)	7955(2)	56(1)
C(26)	10349(2)	9176(2)	7793(2)	50(1)
C(27)	8673(2)	8584(2)	9273(2)	37(1)
C(28)	9570(2)	8250(3)	9913(2)	55(1)

C(29)	8579(3)	9594(2)	9342(2)	55(1)
C(30)	8087(2)	7020(2)	7950(2)	38(1)
C(31)	8129(3)	6641(2)	7019(2)	53(1)
C(32)	8422(3)	6334(2)	8668(2)	58(1)

Table 3. Bond lengths [Å] and angles [°] for **8a**.

Si(1)-C(12)	1.846(2)
Si(1)-C(13)	1.881(2)
Si(1)-C(16)	1.881(2)
Si(1)-C(19)	1.885(2)
Si(2)-C(23)	1.843(2)
Si(2)-C(30)	1.882(3)
Si(2)-C(27)	1.886(2)
Si(2)-C(24)	1.887(2)
C(1)-C(3)#1	1.374(3)
C(1)-C(11)	1.434(3)
C(1)-C(2)	1.438(3)
C(2)-C(4)	1.390(3)
C(2)-C(3)	1.457(3)
C(3)-C(1)#1	1.374(3)
C(3)-C(6)	1.470(3)
C(4)-C(22)	1.416(3)
C(4)-C(5)	1.470(3)
C(5)-C(10)	1.384(3)
C(5)-C(6)	1.412(3)
C(6)-C(7)	1.382(3)
C(7)-C(8)	1.391(3)
C(7)-H(7)	0.96(2)
C(8)-C(9)	1.379(3)
C(8)-H(8)	0.97(3)
C(9)-C(10)	1.386(3)
C(9)-H(9)	0.90(2)
C(10)-H(10)	0.96(2)
C(11)-C(12)	1.205(3)
C(13)-C(15)	1.519(3)
C(13)-C(14)	1.535(4)
C(13)-H(13)	0.96(2)
C(14)-H(14A)	1.07(4)
C(14)-H(14B)	1.00(3)
C(14)-H(14C)	1.01(4)

C(15)-H(15A)	1.01(4)
C(15)-H(15B)	0.95(3)
C(15)-H(15C)	1.02(3)
C(16)-C(18)	1.520(4)
C(16)-C(17)	1.531(4)
C(16)-H(16)	0.95(2)
C(17)-H(17A)	1.03(3)
C(17)-H(17B)	0.95(3)
C(17)-H(17C)	0.96(3)
C(18)-H(18A)	0.99(3)
C(18)-H(18B)	0.97(3)
C(18)-H(18C)	0.98(3)
C(19)-C(21)	1.519(4)
C(19)-C(20)	1.525(4)
C(19)-H(19)	0.94(3)
C(20)-H(20A)	0.95(3)
C(20)-H(20B)	0.93(4)
C(20)-H(20C)	1.02(3)
C(21)-H(21A)	1.00(3)
C(21)-H(21B)	1.03(3)
C(21)-H(21C)	0.97(4)
C(22)-C(23)	1.212(3)
C(24)-C(26)	1.526(4)
C(24)-C(25)	1.539(4)
C(24)-H(24)	0.99(3)
C(25)-H(25A)	0.98(3)
C(25)-H(25B)	1.04(3)
C(25)-H(25C)	1.01(3)
C(26)-H(26A)	1.03(3)
C(26)-H(26B)	1.00(3)
C(26)-H(26C)	0.95(3)
C(27)-C(29)	1.529(4)
C(27)-C(28)	1.536(4)
C(27)-H(27)	0.95(2)
C(28)-H(28A)	0.98(3)
C(28)-H(28B)	1.03(4)

C(28)-H(28C)	1.02(3)
C(29)-H(29A)	0.96(3)
C(29)-H(29B)	1.04(4)
C(29)-H(29C)	0.96(3)
C(30)-C(32)	1.521(4)
C(30)-C(31)	1.521(4)
C(30)-H(30)	0.92(3)
C(31)-H(31A)	0.96(3)
C(31)-H(31B)	1.02(4)
C(31)-H(31C)	1.03(3)
C(32)-H(32A)	1.02(3)
C(32)-H(32B)	0.94(3)
C(32)-H(32C)	0.98(3)
C(12)-Si(1)-C(13)	105.10(10)
C(12)-Si(1)-C(16)	107.94(10)
C(13)-Si(1)-C(16)	111.75(11)
C(12)-Si(1)-C(19)	106.55(10)
C(13)-Si(1)-C(19)	115.83(12)
C(16)-Si(1)-C(19)	109.18(11)
C(23)-Si(2)-C(30)	103.15(11)
C(23)-Si(2)-C(27)	109.47(11)
C(30)-Si(2)-C(27)	111.65(12)
C(23)-Si(2)-C(24)	104.15(10)
C(30)-Si(2)-C(24)	113.32(12)
C(27)-Si(2)-C(24)	114.15(12)
C(3)#1-C(1)-C(11)	120.45(18)
C(3)#1-C(1)-C(2)	117.89(17)
C(11)-C(1)-C(2)	121.66(17)
C(4)-C(2)-C(1)	131.11(18)
C(4)-C(2)-C(3)	108.66(17)
C(1)-C(2)-C(3)	120.23(17)
C(1)#1-C(3)-C(2)	121.88(18)
C(1)#1-C(3)-C(6)	130.69(18)
C(2)-C(3)-C(6)	107.42(16)
C(2)-C(4)-C(22)	131.88(19)
C(2)-C(4)-C(5)	108.22(17)

C(22)-C(4)-C(5)	119.87(18)
C(10)-C(5)-C(6)	121.22(19)
C(10)-C(5)-C(4)	130.00(19)
C(6)-C(5)-C(4)	108.77(17)
C(7)-C(6)-C(5)	119.51(19)
C(7)-C(6)-C(3)	133.56(19)
C(5)-C(6)-C(3)	106.91(17)
C(6)-C(7)-C(8)	118.8(2)
C(6)-C(7)-H(7)	122.6(13)
C(8)-C(7)-H(7)	118.4(13)
C(9)-C(8)-C(7)	121.3(2)
C(9)-C(8)-H(8)	121.1(15)
C(7)-C(8)-H(8)	117.6(14)
C(8)-C(9)-C(10)	120.7(2)
C(8)-C(9)-H(9)	119.8(15)
C(10)-C(9)-H(9)	119.5(15)
C(5)-C(10)-C(9)	118.3(2)
C(5)-C(10)-H(10)	119.3(13)
C(9)-C(10)-H(10)	122.3(13)
C(12)-C(11)-C(1)	174.7(2)
C(11)-C(12)-Si(1)	176.09(19)
C(15)-C(13)-C(14)	111.1(3)
C(15)-C(13)-Si(1)	113.62(18)
C(14)-C(13)-Si(1)	114.22(19)
C(15)-C(13)-H(13)	108.1(13)
C(14)-C(13)-H(13)	105.7(13)
Si(1)-C(13)-H(13)	103.4(13)
C(13)-C(14)-H(14A)	109(2)
C(13)-C(14)-H(14B)	108.6(18)
H(14A)-C(14)-H(14B)	110(3)
C(13)-C(14)-H(14C)	107(2)
H(14A)-C(14)-H(14C)	115(3)
H(14B)-C(14)-H(14C)	107(3)
C(13)-C(15)-H(15A)	111.6(19)
C(13)-C(15)-H(15B)	109.2(17)
H(15A)-C(15)-H(15B)	110(2)

C(13)-C(15)-H(15C)	110.1(17)
H(15A)-C(15)-H(15C)	111(2)
H(15B)-C(15)-H(15C)	105(2)
C(18)-C(16)-C(17)	110.2(3)
C(18)-C(16)-Si(1)	112.98(18)
C(17)-C(16)-Si(1)	113.01(19)
C(18)-C(16)-H(16)	107.5(14)
C(17)-C(16)-H(16)	107.2(14)
Si(1)-C(16)-H(16)	105.5(14)
C(16)-C(17)-H(17A)	109.9(18)
C(16)-C(17)-H(17B)	110.6(17)
H(17A)-C(17)-H(17B)	104(2)
C(16)-C(17)-H(17C)	111.4(18)
H(17A)-C(17)-H(17C)	112(3)
H(17B)-C(17)-H(17C)	109(2)
C(16)-C(18)-H(18A)	107.8(17)
C(16)-C(18)-H(18B)	111.4(18)
H(18A)-C(18)-H(18B)	107(2)
C(16)-C(18)-H(18C)	113.4(16)
H(18A)-C(18)-H(18C)	109(2)
H(18B)-C(18)-H(18C)	108(2)
C(21)-C(19)-C(20)	111.2(3)
C(21)-C(19)-Si(1)	116.00(18)
C(20)-C(19)-Si(1)	112.2(2)
C(21)-C(19)-H(19)	107.9(16)
C(20)-C(19)-H(19)	106.2(16)
Si(1)-C(19)-H(19)	102.5(16)
C(19)-C(20)-H(20A)	109(2)
C(19)-C(20)-H(20B)	113(3)
H(20A)-C(20)-H(20B)	111(3)
C(19)-C(20)-H(20C)	111.2(18)
H(20A)-C(20)-H(20C)	104(3)
H(20B)-C(20)-H(20C)	107(3)
C(19)-C(21)-H(21A)	112.4(18)
C(19)-C(21)-H(21B)	110.9(14)
H(21A)-C(21)-H(21B)	106(2)

C(19)-C(21)-H(21C)	111(2)
H(21A)-C(21)-H(21C)	111(3)
H(21B)-C(21)-H(21C)	106(2)
C(23)-C(22)-C(4)	168.9(2)
C(22)-C(23)-Si(2)	170.6(2)
C(26)-C(24)-C(25)	111.3(2)
C(26)-C(24)-Si(2)	112.55(19)
C(25)-C(24)-Si(2)	114.54(19)
C(26)-C(24)-H(24)	110.0(14)
C(25)-C(24)-H(24)	104.7(14)
Si(2)-C(24)-H(24)	103.0(15)
C(24)-C(25)-H(25A)	111.8(18)
C(24)-C(25)-H(25B)	107.7(18)
H(25A)-C(25)-H(25B)	109(3)
C(24)-C(25)-H(25C)	113.4(18)
H(25A)-C(25)-H(25C)	106(3)
H(25B)-C(25)-H(25C)	109(3)
C(24)-C(26)-H(26A)	113.2(15)
C(24)-C(26)-H(26B)	111.5(16)
H(26A)-C(26)-H(26B)	100(2)
C(24)-C(26)-H(26C)	111.9(18)
H(26A)-C(26)-H(26C)	109(2)
H(26B)-C(26)-H(26C)	111(2)
C(29)-C(27)-C(28)	110.4(3)
C(29)-C(27)-Si(2)	114.04(19)
C(28)-C(27)-Si(2)	113.2(2)
C(29)-C(27)-H(27)	108.5(14)
C(28)-C(27)-H(27)	107.5(14)
Si(2)-C(27)-H(27)	102.6(14)
C(27)-C(28)-H(28A)	110.3(19)
C(27)-C(28)-H(28B)	110.6(19)
H(28A)-C(28)-H(28B)	111(3)
C(27)-C(28)-H(28C)	110.6(16)
H(28A)-C(28)-H(28C)	106(2)
H(28B)-C(28)-H(28C)	108(3)
C(27)-C(29)-H(29A)	116.0(17)

C(27)-C(29)-H(29B)	107.7(19)
H(29A)-C(29)-H(29B)	104(3)
C(27)-C(29)-H(29C)	109.3(18)
H(29A)-C(29)-H(29C)	109(2)
H(29B)-C(29)-H(29C)	110(3)
C(32)-C(30)-C(31)	110.9(3)
C(32)-C(30)-Si(2)	117.3(2)
C(31)-C(30)-Si(2)	112.45(19)
C(32)-C(30)-H(30)	107.1(16)
C(31)-C(30)-H(30)	108.8(16)
Si(2)-C(30)-H(30)	99.2(15)
C(30)-C(31)-H(31A)	113(2)
C(30)-C(31)-H(31B)	109.8(19)
H(31A)-C(31)-H(31B)	107(3)
C(30)-C(31)-H(31C)	108.2(17)
H(31A)-C(31)-H(31C)	112(3)
H(31B)-C(31)-H(31C)	107(3)
C(30)-C(32)-H(32A)	108.0(18)
C(30)-C(32)-H(32B)	111.0(18)
H(32A)-C(32)-H(32B)	113(3)
C(30)-C(32)-H(32C)	108(2)
H(32A)-C(32)-H(32C)	107(3)
H(32B)-C(32)-H(32C)	110(3)

Symmetry transformations used to generate equivalent atoms.

#1 -x+1,-y+2,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **8a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	31(1)	23(1)	20(1)	6(1)	5(1)	-1(1)
Si(2)	26(1)	32(1)	24(1)	7(1)	-2(1)	1(1)
C(1)	29(1)	16(1)	16(1)	1(1)	5(1)	2(1)
C(2)	26(1)	15(1)	17(1)	-1(1)	4(1)	2(1)
C(3)	24(1)	18(1)	19(1)	-1(1)	5(1)	2(1)
C(4)	27(1)	21(1)	20(1)	-1(1)	2(1)	1(1)
C(5)	26(1)	22(1)	22(1)	-3(1)	5(1)	-1(1)
C(6)	26(1)	21(1)	20(1)	-1(1)	4(1)	1(1)
C(7)	29(1)	29(1)	22(1)	2(1)	4(1)	-1(1)
C(8)	35(1)	35(1)	31(1)	1(1)	10(1)	-8(1)
C(9)	24(1)	42(2)	40(1)	-3(1)	4(1)	-7(1)
C(10)	29(1)	34(1)	30(1)	2(1)	0(1)	-1(1)
C(11)	22(1)	22(1)	23(1)	0(1)	3(1)	1(1)
C(12)	26(1)	24(1)	25(1)	3(1)	3(1)	1(1)
C(13)	37(1)	33(1)	24(1)	5(1)	3(1)	-1(1)
C(14)	69(2)	81(3)	45(2)	30(2)	-18(2)	-13(2)
C(15)	47(2)	47(2)	56(2)	-16(2)	-4(2)	-4(1)
C(16)	43(2)	26(1)	35(1)	6(1)	7(1)	-4(1)
C(17)	56(2)	38(2)	64(2)	-11(2)	-6(2)	-9(1)
C(18)	56(2)	30(2)	76(2)	-3(2)	19(2)	1(1)
C(19)	35(1)	35(1)	36(1)	2(1)	12(1)	-4(1)
C(20)	78(3)	87(3)	68(3)	29(2)	50(2)	15(2)
C(21)	44(2)	40(2)	61(2)	-6(2)	16(2)	7(1)
C(22)	26(1)	26(1)	26(1)	2(1)	2(1)	-1(1)
C(23)	27(1)	31(1)	30(1)	4(1)	1(1)	-1(1)
C(24)	27(1)	51(2)	32(1)	6(1)	1(1)	-2(1)
C(25)	33(2)	72(2)	64(2)	13(2)	9(2)	12(2)
C(26)	41(2)	65(2)	46(2)	1(2)	10(1)	-19(2)
C(27)	33(1)	48(2)	29(1)	-1(1)	2(1)	-5(1)
C(28)	50(2)	87(3)	26(2)	3(2)	-6(1)	1(2)
C(29)	61(2)	56(2)	49(2)	-15(2)	6(2)	-2(2)

C(30)	32(1)	36(1)	44(2)	6(1)	4(1)	1(1)
C(31)	63(2)	43(2)	51(2)	-9(2)	-1(2)	-6(2)
C(32)	70(2)	41(2)	62(2)	18(2)	3(2)	-7(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **8a**.

	x	y	z	U(eq)
H(7)	6980(16)	11464(15)	3625(15)	32(6)
H(8)	8675(18)	11649(16)	3842(16)	43(7)
H(9)	9619(18)	10945(14)	5039(15)	31(6)
H(10)	8919(16)	10029(15)	6045(15)	31(6)
H(13)	6308(16)	8011(14)	8749(15)	28(6)
H(14A)	5950(30)	6790(30)	9600(30)	118(15)
H(14B)	6570(20)	7570(20)	10250(20)	69(9)
H(14C)	5380(30)	7550(20)	10260(20)	87(12)
H(15A)	5320(30)	9210(20)	9810(20)	87(11)
H(15B)	5850(20)	9462(19)	8958(19)	56(9)
H(15C)	6540(20)	9160(20)	9820(20)	70(9)
H(16)	4387(17)	6416(16)	8542(17)	39(7)
H(17A)	2900(30)	6680(20)	7640(20)	79(10)
H(17B)	3440(20)	5900(20)	7234(18)	57(8)
H(17C)	3520(20)	6820(20)	6780(20)	69(10)
H(18A)	5460(20)	6620(20)	7080(20)	62(9)
H(18B)	5240(20)	5680(20)	7475(19)	73(9)
H(18C)	5960(20)	6330(17)	8063(18)	51(8)
H(19)	2953(19)	8120(17)	8173(17)	47(8)
H(20A)	3680(20)	8260(20)	9970(20)	71(12)
H(20B)	3220(30)	7390(30)	9540(30)	110(15)
H(20C)	2540(30)	8220(20)	9650(20)	75(10)
H(21A)	3380(20)	9620(20)	7950(20)	74(10)
H(21B)	2620(20)	9562(17)	8693(16)	51(7)
H(21C)	3780(30)	9660(20)	9010(20)	88(11)
H(24)	9702(18)	8148(16)	6992(18)	45(7)
H(25A)	11240(30)	7560(20)	7660(20)	74(10)
H(25B)	10830(20)	7590(20)	8640(20)	77(10)
H(25C)	10360(20)	6900(20)	7830(20)	78(11)
H(26A)	9850(20)	9684(19)	7634(17)	54(8)

H(26B)	10550(20)	9298(18)	8450(20)	64(9)
H(26C)	10900(20)	9253(19)	7469(19)	64(9)
H(27)	8095(18)	8319(15)	9454(15)	36(7)
H(28A)	9530(20)	8460(20)	10520(20)	83(10)
H(28B)	9610(20)	7570(20)	9900(20)	88(12)
H(28C)	10210(20)	8495(18)	9732(18)	60(8)
H(29A)	8040(20)	9859(18)	8963(19)	54(8)
H(29B)	9210(30)	9880(20)	9130(20)	91(11)
H(29C)	8540(20)	9755(19)	9960(20)	65(9)
H(30)	7440(20)	7162(16)	8005(16)	46(7)
H(31A)	7730(20)	6120(20)	6910(20)	80(10)
H(31B)	8840(30)	6470(20)	6950(20)	92(12)
H(31C)	7920(20)	7130(20)	6560(20)	72(10)
H(32A)	9160(30)	6210(20)	8650(20)	77(10)
H(32B)	8030(20)	5820(20)	8589(19)	66(9)
H(32C)	8360(20)	6600(20)	9250(20)	80(11)

Table 6. Torsion angles [°] for **8a**.

C(3)#1-C(1)-C(2)-C(4)	-178.1(2)
C(11)-C(1)-C(2)-C(4)	2.8(3)
C(3)#1-C(1)-C(2)-C(3)	0.9(3)
C(11)-C(1)-C(2)-C(3)	-178.24(17)
C(4)-C(2)-C(3)-C(1)#1	178.29(18)
C(1)-C(2)-C(3)-C(1)#1	-0.9(3)
C(4)-C(2)-C(3)-C(6)	-1.0(2)
C(1)-C(2)-C(3)-C(6)	179.82(17)
C(1)-C(2)-C(4)-C(22)	1.7(4)
C(3)-C(2)-C(4)-C(22)	-177.4(2)
C(1)-C(2)-C(4)-C(5)	179.97(19)
C(3)-C(2)-C(4)-C(5)	0.9(2)
C(2)-C(4)-C(5)-C(10)	179.9(2)
C(22)-C(4)-C(5)-C(10)	-1.6(3)
C(2)-C(4)-C(5)-C(6)	-0.5(2)
C(22)-C(4)-C(5)-C(6)	178.06(18)
C(10)-C(5)-C(6)-C(7)	-1.8(3)
C(4)-C(5)-C(6)-C(7)	178.50(18)
C(10)-C(5)-C(6)-C(3)	179.52(19)
C(4)-C(5)-C(6)-C(3)	-0.2(2)
C(1)#1-C(3)-C(6)-C(7)	3.1(4)
C(2)-C(3)-C(6)-C(7)	-177.7(2)
C(1)#1-C(3)-C(6)-C(5)	-178.5(2)
C(2)-C(3)-C(6)-C(5)	0.7(2)
C(5)-C(6)-C(7)-C(8)	0.6(3)
C(3)-C(6)-C(7)-C(8)	178.8(2)
C(6)-C(7)-C(8)-C(9)	1.0(3)
C(7)-C(8)-C(9)-C(10)	-1.4(4)
C(6)-C(5)-C(10)-C(9)	1.4(3)
C(4)-C(5)-C(10)-C(9)	-179.0(2)
C(8)-C(9)-C(10)-C(5)	0.1(4)
C(3)#1-C(1)-C(11)-C(12)	-18(2)
C(2)-C(1)-C(11)-C(12)	161(2)
C(1)-C(11)-C(12)-Si(1)	-29(5)

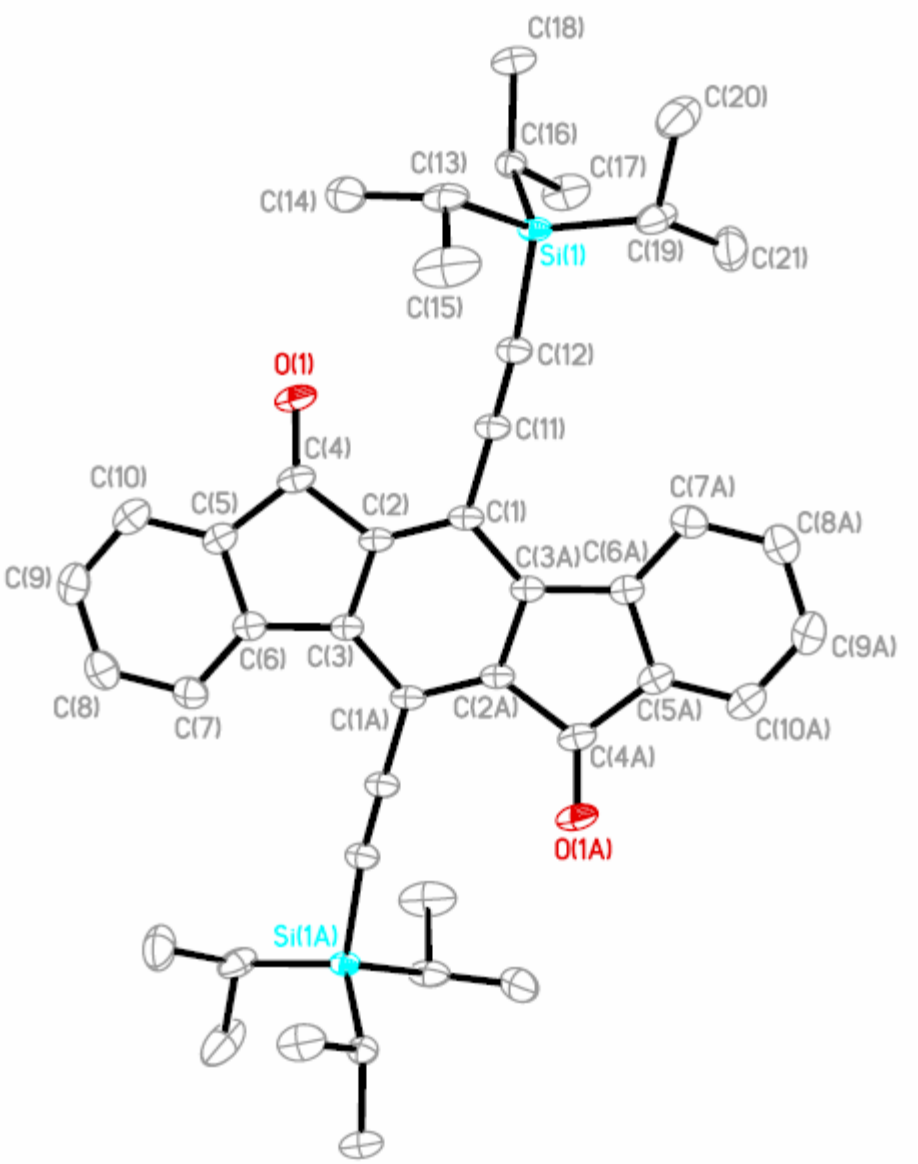
C(13)-Si(1)-C(12)-C(11)	-114(3)
C(16)-Si(1)-C(12)-C(11)	127(3)
C(19)-Si(1)-C(12)-C(11)	10(3)
C(12)-Si(1)-C(13)-C(15)	71.3(2)
C(16)-Si(1)-C(13)-C(15)	-171.9(2)
C(19)-Si(1)-C(13)-C(15)	-46.0(2)
C(12)-Si(1)-C(13)-C(14)	-159.9(2)
C(16)-Si(1)-C(13)-C(14)	-43.1(3)
C(19)-Si(1)-C(13)-C(14)	82.8(3)
C(12)-Si(1)-C(16)-C(18)	59.4(2)
C(13)-Si(1)-C(16)-C(18)	-55.7(2)
C(19)-Si(1)-C(16)-C(18)	174.8(2)
C(12)-Si(1)-C(16)-C(17)	-66.6(2)
C(13)-Si(1)-C(16)-C(17)	178.3(2)
C(19)-Si(1)-C(16)-C(17)	48.8(2)
C(12)-Si(1)-C(19)-C(21)	-44.1(2)
C(13)-Si(1)-C(19)-C(21)	72.3(2)
C(16)-Si(1)-C(19)-C(21)	-160.5(2)
C(12)-Si(1)-C(19)-C(20)	-173.4(3)
C(13)-Si(1)-C(19)-C(20)	-56.9(3)
C(16)-Si(1)-C(19)-C(20)	70.3(3)
C(2)-C(4)-C(22)-C(23)	169.0(11)
C(5)-C(4)-C(22)-C(23)	-9.1(12)
C(4)-C(22)-C(23)-Si(2)	-59(2)
C(30)-Si(2)-C(23)-C(22)	-66.2(12)
C(27)-Si(2)-C(23)-C(22)	174.8(12)
C(24)-Si(2)-C(23)-C(22)	52.3(12)
C(23)-Si(2)-C(24)-C(26)	70.8(2)
C(30)-Si(2)-C(24)-C(26)	-177.85(19)
C(27)-Si(2)-C(24)-C(26)	-48.5(2)
C(23)-Si(2)-C(24)-C(25)	-160.7(2)
C(30)-Si(2)-C(24)-C(25)	-49.3(2)
C(27)-Si(2)-C(24)-C(25)	80.0(2)
C(23)-Si(2)-C(27)-C(29)	-35.3(2)
C(30)-Si(2)-C(27)-C(29)	-148.9(2)
C(24)-Si(2)-C(27)-C(29)	80.9(2)

C(23)-Si(2)-C(27)-C(28)	-162.8(2)
C(30)-Si(2)-C(27)-C(28)	83.7(2)
C(24)-Si(2)-C(27)-C(28)	-46.5(2)
C(23)-Si(2)-C(30)-C(32)	-163.1(2)
C(27)-Si(2)-C(30)-C(32)	-45.6(3)
C(24)-Si(2)-C(30)-C(32)	84.9(3)
C(23)-Si(2)-C(30)-C(31)	66.6(2)
C(27)-Si(2)-C(30)-C(31)	-176.0(2)
C(24)-Si(2)-C(30)-C(31)	-45.4(2)

Symmetry transformations used to generate equivalent atoms.

#1 -x+1,-y+2,-z+1

Crystallographic Data for 10a



Solid State Packing of 10a

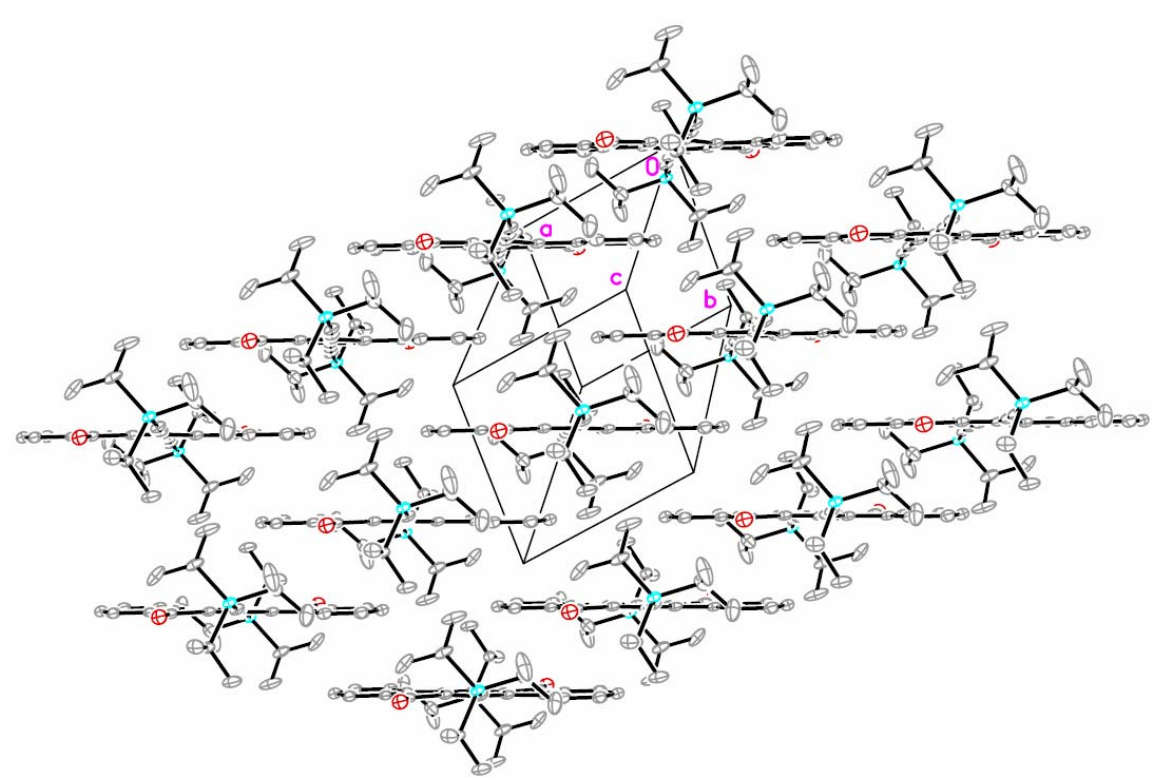


Table 7. Crystal data and structure refinement for **10a**.

Identification code	mh47	
Empirical formula	C42 H50 O2 Si2	
Formula weight	643.00	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.419(3) Å	α = 87.087(6)°.
	b = 7.535(3) Å	β = 82.826(6)°.
	c = 16.904(6) Å	γ = 79.380(6)°.
Volume	921.1(6) $Å^3$	
Z	1	
Density (calculated)	1.159 Mg/m^3	
Absorption coefficient	0.130 mm^{-1}	
F(000)	346	
Crystal size	0.45 x 0.18 x 0.02 mm^3	
Theta range for data collection	1.21 to 27.00°.	
Index ranges	-9<=h<=9, -9<=k<=9, -21<=l<=21	
Reflections collected	9034	
Independent reflections	3973 [R(int) = 0.0273]	
Completeness to theta = 27.00°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9974 and 0.9437	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3973 / 0 / 308	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0553, wR2 = 0.1412	
R indices (all data)	R1 = 0.0744, wR2 = 0.1587	
Largest diff. peak and hole	0.425 and -0.252 $e.Å^{-3}$	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **10a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	7735(1)	7821(1)	6844(1)	29(1)
O(1)	2427(3)	7832(2)	8441(1)	49(1)
C(1)	5716(3)	5500(3)	9204(1)	30(1)
C(2)	3890(3)	6100(3)	9520(1)	29(1)
C(3)	3164(3)	5646(3)	10297(1)	30(1)
C(4)	2346(4)	7236(3)	9123(1)	36(1)
C(5)	706(3)	7434(3)	9733(1)	35(1)
C(6)	1193(3)	6496(3)	10434(1)	32(1)
C(7)	-116(4)	6495(3)	11092(2)	41(1)
C(8)	-1899(4)	7438(4)	11032(2)	48(1)
C(9)	-2362(4)	8348(3)	10337(2)	48(1)
C(10)	-1067(4)	8363(3)	9676(2)	45(1)
C(11)	6422(3)	6104(3)	8428(1)	33(1)
C(12)	7019(3)	6687(3)	7793(1)	35(1)
C(13)	6761(5)	10295(3)	6960(1)	49(1)
C(14)	4654(5)	10711(4)	6990(2)	67(1)
C(15)	7330(9)	11031(4)	7697(2)	85(2)
C(16)	6604(3)	6893(3)	6064(1)	32(1)
C(17)	7079(6)	4849(4)	5994(2)	59(1)
C(18)	6850(5)	7820(4)	5246(2)	50(1)
C(19)	10317(4)	7466(4)	6692(2)	49(1)
C(20)	11041(5)	8546(8)	5965(3)	97(2)
C(21)	11290(5)	5518(5)	6657(3)	73(1)

Table 9. Bond lengths [Å] and angles [°] for **10a**.

Si(1)-C(12)	1.844(2)
Si(1)-C(19)	1.871(3)
Si(1)-C(16)	1.875(2)
Si(1)-C(13)	1.882(2)
O(1)-C(4)	1.214(3)
C(1)-C(2)	1.394(3)
C(1)-C(3)#1	1.409(3)
C(1)-C(11)	1.433(3)
C(2)-C(3)	1.406(3)
C(2)-C(4)	1.506(3)
C(3)-C(1)#1	1.409(3)
C(3)-C(6)	1.479(3)
C(4)-C(5)	1.484(3)
C(5)-C(10)	1.383(4)
C(5)-C(6)	1.401(3)
C(6)-C(7)	1.383(3)
C(7)-C(8)	1.394(4)
C(7)-H(7)	0.96(3)
C(8)-C(9)	1.379(4)
C(8)-H(8)	0.96(3)
C(9)-C(10)	1.380(4)
C(9)-H(9)	0.91(3)
C(10)-H(10)	0.91(3)
C(11)-C(12)	1.204(3)
C(13)-C(15)	1.525(4)
C(13)-C(14)	1.532(5)
C(13)-H(13)	1.02(3)
C(14)-H(14A)	0.95(4)
C(14)-H(14B)	1.02(3)
C(14)-H(14C)	0.96(4)
C(15)-H(15A)	0.92(4)
C(15)-H(15B)	0.99(4)
C(15)-H(15C)	1.05(3)
C(16)-C(17)	1.523(3)

C(16)-C(18)	1.523(3)
C(16)-H(16)	0.97(3)
C(17)-H(17A)	0.99(4)
C(17)-H(17B)	0.95(4)
C(17)-H(17C)	0.99(4)
C(18)-H(18A)	0.98(3)
C(18)-H(18B)	0.99(4)
C(18)-H(18C)	1.04(3)
C(19)-C(21)	1.513(5)
C(19)-C(20)	1.535(4)
C(19)-H(18)	0.99(3)
C(20)-H(20A)	1.01(5)
C(20)-H(20B)	0.93(5)
C(20)-H(20C)	0.97(5)
C(21)-H(21A)	1.03(6)
C(21)-H(21B)	0.94(4)
C(21)-H(21C)	0.98(4)
C(12)-Si(1)-C(19)	108.32(11)
C(12)-Si(1)-C(16)	105.93(10)
C(19)-Si(1)-C(16)	116.23(13)
C(12)-Si(1)-C(13)	106.35(11)
C(19)-Si(1)-C(13)	109.87(14)
C(16)-Si(1)-C(13)	109.61(11)
C(2)-C(1)-C(3)#1	116.33(18)
C(2)-C(1)-C(11)	121.19(19)
C(3)#1-C(1)-C(11)	122.4(2)
C(1)-C(2)-C(3)	123.44(19)
C(1)-C(2)-C(4)	128.82(19)
C(3)-C(2)-C(4)	107.7(2)
C(2)-C(3)-C(1)#1	120.2(2)
C(2)-C(3)-C(6)	109.20(18)
C(1)#1-C(3)-C(6)	130.56(19)
O(1)-C(4)-C(5)	127.4(2)
O(1)-C(4)-C(2)	126.9(2)
C(5)-C(4)-C(2)	105.61(18)
C(10)-C(5)-C(6)	121.7(2)

C(10)-C(5)-C(4)	129.1(2)
C(6)-C(5)-C(4)	109.2(2)
C(7)-C(6)-C(5)	119.7(2)
C(7)-C(6)-C(3)	132.0(2)
C(5)-C(6)-C(3)	108.30(19)
C(6)-C(7)-C(8)	118.3(2)
C(6)-C(7)-H(7)	120.4(17)
C(8)-C(7)-H(7)	121.3(17)
C(9)-C(8)-C(7)	121.4(3)
C(9)-C(8)-H(8)	119.8(18)
C(7)-C(8)-H(8)	118.7(18)
C(8)-C(9)-C(10)	120.9(3)
C(8)-C(9)-H(9)	120.0(19)
C(10)-C(9)-H(9)	119.1(19)
C(9)-C(10)-C(5)	118.0(3)
C(9)-C(10)-H(10)	121.2(19)
C(5)-C(10)-H(10)	120.8(19)
C(12)-C(11)-C(1)	176.9(2)
C(11)-C(12)-Si(1)	173.3(2)
C(15)-C(13)-C(14)	109.5(3)
C(15)-C(13)-Si(1)	111.8(2)
C(14)-C(13)-Si(1)	112.7(2)
C(15)-C(13)-H(13)	107.2(16)
C(14)-C(13)-H(13)	110.1(16)
Si(1)-C(13)-H(13)	105.4(16)
C(13)-C(14)-H(14A)	113(2)
C(13)-C(14)-H(14B)	112.8(16)
H(14A)-C(14)-H(14B)	105(3)
C(13)-C(14)-H(14C)	111(2)
H(14A)-C(14)-H(14C)	104(3)
H(14B)-C(14)-H(14C)	110(3)
C(13)-C(15)-H(15A)	110(2)
C(13)-C(15)-H(15B)	110(2)
H(15A)-C(15)-H(15B)	107(3)
C(13)-C(15)-H(15C)	101.9(17)
H(15A)-C(15)-H(15C)	104(3)

H(15B)-C(15)-H(15C)	123(3)
C(17)-C(16)-C(18)	110.5(2)
C(17)-C(16)-Si(1)	114.69(18)
C(18)-C(16)-Si(1)	114.09(17)
C(17)-C(16)-H(16)	108.4(17)
C(18)-C(16)-H(16)	105.8(17)
Si(1)-C(16)-H(16)	102.5(16)
C(16)-C(17)-H(17A)	110(2)
C(16)-C(17)-H(17B)	113(2)
H(17A)-C(17)-H(17B)	106(3)
C(16)-C(17)-H(17C)	110(2)
H(17A)-C(17)-H(17C)	109(3)
H(17B)-C(17)-H(17C)	110(3)
C(16)-C(18)-H(18A)	106.5(17)
C(16)-C(18)-H(18B)	111.0(19)
H(18A)-C(18)-H(18B)	108(3)
C(16)-C(18)-H(18C)	111.4(17)
H(18A)-C(18)-H(18C)	109(2)
H(18B)-C(18)-H(18C)	111(3)
C(21)-C(19)-C(20)	110.1(3)
C(21)-C(19)-Si(1)	115.5(2)
C(20)-C(19)-Si(1)	112.1(2)
C(21)-C(19)-H(18)	105.7(19)
C(20)-C(19)-H(18)	108.6(19)
Si(1)-C(19)-H(18)	104.2(19)
C(19)-C(20)-H(20A)	114(3)
C(19)-C(20)-H(20B)	107(3)
H(20A)-C(20)-H(20B)	105(4)
C(19)-C(20)-H(20C)	114(2)
H(20A)-C(20)-H(20C)	104(4)
H(20B)-C(20)-H(20C)	112(4)
C(19)-C(21)-H(21A)	107(3)
C(19)-C(21)-H(21B)	116(2)
H(21A)-C(21)-H(21B)	100(4)
C(19)-C(21)-H(21C)	114(2)
H(21A)-C(21)-H(21C)	108(4)

H(21B)-C(21)-H(21C) 109(3)

Symmetry transformations used to generate equivalent atoms.

#1 -x+1,-y+1,-z+2

Table 10. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **10a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	44(1)	19(1)	23(1)	3(1)	-3(1)	-7(1)
O(1)	71(1)	43(1)	32(1)	11(1)	-18(1)	-9(1)
C(1)	52(1)	19(1)	22(1)	0(1)	-6(1)	-13(1)
C(2)	49(1)	20(1)	23(1)	1(1)	-7(1)	-12(1)
C(3)	47(1)	19(1)	26(1)	-1(1)	-6(1)	-11(1)
C(4)	59(2)	22(1)	31(1)	2(1)	-15(1)	-11(1)
C(5)	50(1)	21(1)	37(1)	-4(1)	-14(1)	-9(1)
C(6)	48(1)	19(1)	31(1)	-4(1)	-8(1)	-10(1)
C(7)	54(2)	33(1)	36(1)	-8(1)	-4(1)	-10(1)
C(8)	51(2)	42(1)	52(2)	-17(1)	-2(1)	-11(1)
C(9)	47(2)	34(1)	66(2)	-15(1)	-15(1)	-3(1)
C(10)	60(2)	28(1)	51(2)	-4(1)	-23(1)	-7(1)
C(11)	53(1)	21(1)	25(1)	0(1)	-4(1)	-9(1)
C(12)	56(1)	21(1)	28(1)	0(1)	-3(1)	-5(1)
C(13)	95(2)	20(1)	31(1)	4(1)	-7(1)	-6(1)
C(14)	99(3)	34(2)	48(2)	4(1)	11(2)	23(2)
C(15)	176(5)	28(2)	56(2)	-6(1)	-29(3)	-21(2)
C(16)	38(1)	26(1)	32(1)	2(1)	-4(1)	-7(1)
C(17)	100(3)	29(1)	54(2)	-4(1)	-23(2)	-18(2)
C(18)	74(2)	47(2)	33(1)	7(1)	-19(1)	-18(2)
C(19)	51(2)	52(2)	49(2)	22(1)	-19(1)	-21(1)
C(20)	41(2)	128(4)	120(4)	87(3)	-17(2)	-30(2)
C(21)	44(2)	71(2)	92(3)	25(2)	9(2)	2(2)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **10a**.

	x	y	z	U(eq)
H(7)	200(40)	5840(40)	11574(17)	54(8)
H(8)	-2820(40)	7410(40)	11478(18)	59(9)
H(9)	-3530(40)	8960(40)	10312(17)	56(8)
H(10)	-1380(40)	8940(40)	9210(18)	59(8)
H(13)	7350(40)	10930(40)	6475(17)	54(8)
H(14A)	4150(50)	11960(50)	7060(20)	80(10)
H(14B)	4010(40)	10050(40)	7449(18)	56(8)
H(14C)	4270(50)	10450(50)	6490(20)	82(11)
H(15A)	6900(50)	12260(60)	7720(20)	84(11)
H(15B)	6760(50)	10470(50)	8180(20)	82(11)
H(15C)	8760(40)	10910(40)	7550(18)	54(10)
H(16)	5300(40)	7220(40)	6257(16)	51(8)
H(17A)	6890(50)	4260(50)	6530(20)	93(12)
H(17B)	8330(50)	4440(50)	5800(20)	74(11)
H(17C)	6260(50)	4450(50)	5640(20)	79(10)
H(18)	10650(50)	7940(40)	7180(20)	70(9)
H(18A)	8150(40)	7440(40)	5031(17)	55(8)
H(18B)	6600(50)	9160(50)	5290(20)	75(10)
H(18C)	6020(40)	7420(40)	4861(19)	70(9)
H(20A)	10630(80)	8250(70)	5440(30)	140(20)
H(20B)	10530(70)	9760(70)	6050(30)	120(18)
H(20C)	12370(60)	8350(50)	5870(20)	101(13)
H(21A)	11130(80)	5040(80)	6120(30)	150(20)
H(21B)	10750(50)	4690(50)	7000(20)	71(10)
H(21C)	12620(60)	5340(60)	6700(20)	102(13)

Table 12. Torsion angles [°] for **10a**.

C(3)#1-C(1)-C(2)-C(3)	1.3(3)
C(11)-C(1)-C(2)-C(3)	-175.57(18)
C(3)#1-C(1)-C(2)-C(4)	-176.18(18)
C(11)-C(1)-C(2)-C(4)	6.9(3)
C(1)-C(2)-C(3)-C(1)#1	-1.4(3)
C(4)-C(2)-C(3)-C(1)#1	176.59(17)
C(1)-C(2)-C(3)-C(6)	-179.61(17)
C(4)-C(2)-C(3)-C(6)	-1.6(2)
C(1)-C(2)-C(4)-O(1)	0.4(3)
C(3)-C(2)-C(4)-O(1)	-177.4(2)
C(1)-C(2)-C(4)-C(5)	179.14(19)
C(3)-C(2)-C(4)-C(5)	1.3(2)
O(1)-C(4)-C(5)-C(10)	-1.8(4)
C(2)-C(4)-C(5)-C(10)	179.5(2)
O(1)-C(4)-C(5)-C(6)	178.3(2)
C(2)-C(4)-C(5)-C(6)	-0.5(2)
C(10)-C(5)-C(6)-C(7)	-0.3(3)
C(4)-C(5)-C(6)-C(7)	179.65(18)
C(10)-C(5)-C(6)-C(3)	179.57(19)
C(4)-C(5)-C(6)-C(3)	-0.5(2)
C(2)-C(3)-C(6)-C(7)	-178.8(2)
C(1)#1-C(3)-C(6)-C(7)	3.2(4)
C(2)-C(3)-C(6)-C(5)	1.4(2)
C(1)#1-C(3)-C(6)-C(5)	-176.6(2)
C(5)-C(6)-C(7)-C(8)	0.1(3)
C(3)-C(6)-C(7)-C(8)	-179.7(2)
C(6)-C(7)-C(8)-C(9)	0.2(3)
C(7)-C(8)-C(9)-C(10)	-0.4(4)
C(8)-C(9)-C(10)-C(5)	0.2(4)
C(6)-C(5)-C(10)-C(9)	0.1(3)
C(4)-C(5)-C(10)-C(9)	-179.8(2)
C(2)-C(1)-C(11)-C(12)	77(5)
C(3)#1-C(1)-C(11)-C(12)	-100(5)
C(1)-C(11)-C(12)-Si(1)	-47(6)

C(19)-Si(1)-C(12)-C(11)	134.5(19)
C(16)-Si(1)-C(12)-C(11)	-100.2(19)
C(13)-Si(1)-C(12)-C(11)	16.4(19)
C(12)-Si(1)-C(13)-C(15)	54.2(3)
C(19)-Si(1)-C(13)-C(15)	-62.9(3)
C(16)-Si(1)-C(13)-C(15)	168.3(3)
C(12)-Si(1)-C(13)-C(14)	-69.6(2)
C(19)-Si(1)-C(13)-C(14)	173.40(19)
C(16)-Si(1)-C(13)-C(14)	44.5(2)
C(12)-Si(1)-C(16)-C(17)	-57.6(2)
C(19)-Si(1)-C(16)-C(17)	62.7(2)
C(13)-Si(1)-C(16)-C(17)	-172.0(2)
C(12)-Si(1)-C(16)-C(18)	173.48(19)
C(19)-Si(1)-C(16)-C(18)	-66.2(2)
C(13)-Si(1)-C(16)-C(18)	59.1(2)
C(12)-Si(1)-C(19)-C(21)	59.4(3)
C(16)-Si(1)-C(19)-C(21)	-59.6(3)
C(13)-Si(1)-C(19)-C(21)	175.2(3)
C(12)-Si(1)-C(19)-C(20)	-173.4(3)
C(16)-Si(1)-C(19)-C(20)	67.6(4)
C(13)-Si(1)-C(19)-C(20)	-57.6(4)

Symmetry transformations used to generate equivalent atoms.
#1 -x+1,-y+1,-z+2

APPENDIX B

EXPERIMENTAL DETAILS FOR CHAPTER III

Cartesian Coordinates of Stationary Points[2]

3

B3LYP/6-311+G(d,p) = -769.528249572 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -769.277775 au
NIMAG = 0

C	1.25931700	-0.64211300	0.00000000
C	1.25931700	0.71732400	0.00000000
H	2.18189100	1.28945100	0.00000000
C	-0.00267200	1.40140300	0.00000000
C	-1.25931700	0.64211300	0.00000000
C	-1.25931700	-0.71732400	0.00000000
H	-2.18189100	-1.28945100	0.00000000
C	0.00267200	-1.40140300	0.00000000
C	-0.29567400	2.74437400	0.00000000
H	0.42526200	3.55209000	0.00000000
C	-1.73846900	2.91843300	0.00000000
C	-2.34414300	1.62975800	0.00000000
C	2.34414300	-1.62975800	0.00000000
C	0.29567400	-2.74437400	0.00000000
H	-0.42526200	-3.55209000	0.00000000
C	1.73846900	-2.91843300	0.00000000
C	-3.72614400	1.50568100	0.00000000
H	-4.20091700	0.53030000	0.00000000
C	-2.52666500	4.06825900	0.00000000
H	-2.07204500	5.05314600	0.00000000
C	3.72614400	-1.50568100	0.00000000
H	4.20091700	-0.53030000	0.00000000
C	2.52666500	-4.06825900	0.00000000
H	2.07204500	-5.05314600	0.00000000
C	4.51008100	-2.66616600	0.00000000
H	5.59089000	-2.58165100	0.00000000
C	3.91720000	-3.93142900	0.00000000
H	4.54408100	-4.81593100	0.00000000

[2] Bold number refers to the molecule in Chapter III

C	-3.91720000	3.93142900	0.00000000
H	-4.54408100	4.81593100	0.00000000
C	-4.51008100	2.66616600	0.00000000
H	-5.59089000	2.58165100	0.00000000

5

B3LYP/6-311+G(d,p) = -1074.19271902 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -1073.907008 au
NIMAG = 0

C	1.24716100	-0.66907400	0.00000000
C	1.27355500	0.70984700	0.00000000
C	0.00894300	1.40840100	0.00000000
C	-1.24716100	0.66907400	0.00000000
C	-1.27355500	-0.70984700	0.00000000
C	-0.00894300	-1.40840100	0.00000000
C	-0.27598100	2.77375200	0.00000000
C	-1.73048700	2.93847600	0.00000000
C	-2.33262100	1.65562400	0.00000000
C	2.33262100	-1.65562400	0.00000000
C	0.27598100	-2.77375200	0.00000000
C	1.73048700	-2.93847600	0.00000000
C	-3.72053700	1.54818400	0.00000000
H	-4.20297400	0.58146700	0.00000000
C	-2.49761300	4.09866900	0.00000000
H	-2.02175900	5.07253400	0.00000000
C	3.72053700	-1.54818400	0.00000000
H	4.20297400	-0.58146700	0.00000000
C	2.49761300	-4.09866900	0.00000000
H	2.02175900	-5.07253400	0.00000000
C	4.48965800	-2.71759400	0.00000000
H	5.57108700	-2.64060500	0.00000000
C	3.88867100	-3.97790400	0.00000000
H	4.50644800	-4.86868100	0.00000000
C	-3.88867100	3.97790400	0.00000000
H	-4.50644800	4.86868100	0.00000000
C	-4.48965800	2.71759400	0.00000000
H	-5.57108700	2.64060500	0.00000000
C	-2.49761300	-1.43291600	0.00000000
C	-0.59089700	-3.88138000	0.00000000
C	-1.23545500	-4.90272900	0.00000000
H	-1.83594400	-5.77930400	0.00000000
C	-3.53392300	-2.04668900	0.00000000
H	-4.43888100	-2.60359200	0.00000000
C	2.49761300	1.43291600	0.00000000

C	0.59089700	3.88138000	0.00000000
C	1.23545500	4.90272900	0.00000000
H	1.83594400	5.77930400	0.00000000
C	3.53392300	2.04668900	0.00000000
H	4.43888100	2.60359200	0.00000000

6

B3LYP/6-311+G(d,p) = -921.859763721 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -921.591516 au
NIMAG = 0

C	-5.53348600	0.53189500	0.00000100
C	-5.18890500	-0.82075600	-0.00000100
C	-3.84708600	-1.22481400	0.00000200
C	-2.85444700	-0.25279300	0.00001100
C	-3.20695700	1.12734000	0.00001300
C	-4.54328300	1.51867700	0.00000600
C	-1.38854000	-0.32022100	0.00002800
C	-0.90826400	1.06388800	-0.00001100
C	-1.98660400	1.91219500	0.00002500
C	-0.50829600	-1.37268800	0.00004400
C	0.90826400	-1.06388800	0.00001100
C	1.38854000	0.32022100	-0.00002800
C	0.50829600	1.37268800	-0.00004400
C	1.98660400	-1.91219500	-0.00002500
C	3.20695700	-1.12734000	-0.00001300
C	2.85444700	0.25279300	-0.00001100
C	4.54328300	-1.51867700	-0.00000600
C	5.53348600	-0.53189500	-0.00000100
C	5.18890500	0.82075600	0.00000100
C	3.84708600	1.22481400	-0.00000200
H	-6.57880800	0.81937400	-0.00000100
H	-5.97047500	-1.57203400	-0.00000400
H	-3.59548300	-2.27707200	0.00000400
H	-4.81327800	2.56918200	0.00000900
H	4.81327800	-2.56918200	-0.00000900
H	6.57880800	-0.81937400	0.00000100
H	5.97047500	1.57203400	0.00000400
H	3.59548300	2.27707200	-0.00000400
H	-1.93789000	2.99259200	0.00002500
H	1.93789000	-2.99259200	-0.00002500
C	0.91471200	2.73587900	-0.00003900
C	1.21191300	3.90422200	-0.00003200
H	1.48808500	4.93057700	-0.00002700
C	-0.91471200	-2.73587900	0.00003900

C	-1.21191300	-3.90422200	0.00003200
H	-1.48808500	-4.93057700	0.00002700

7

B3LYP/6-311+G(d,p) = -921.872407785 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -921.603982 au
NIMAG = 0

C	5.48740700	0.82525800	0.00027100
C	4.81585500	2.05071600	0.00012800
C	3.41716400	2.10382900	-0.00009400
C	2.70151800	0.91395300	-0.00021900
C	3.38654200	-0.32891200	-0.00009400
C	4.77736000	-0.37801600	0.00019900
C	1.26436100	0.62433800	-0.00039300
C	1.12261900	-0.82668400	0.00007700
C	2.38988400	-1.40382000	-0.00048900
C	0.16846000	1.43627700	-0.00054300
C	-1.12261900	0.82668400	-0.00012500
C	-1.26436100	-0.62433800	0.00035900
C	-0.16846000	-1.43627700	0.00052200
C	-2.38988400	1.40382000	0.00036800
C	-3.38654200	0.32891200	0.00012200
C	-2.70151800	-0.91395300	0.00020000
C	-4.77736000	0.37801600	-0.00006900
C	-5.48740700	-0.82525800	-0.00011000
C	-4.81585500	-2.05071700	-0.00001900
C	-3.41716400	-2.10382900	0.00011600
H	6.57129300	0.80876100	0.00042200
H	5.38569000	2.97295700	0.00020100
H	2.90918200	3.06209000	-0.00017000
H	5.29689500	-1.32956700	0.00024700
H	-5.29689500	1.32956700	-0.00010300
H	-6.57129300	-0.80876100	-0.00020100
H	-5.38569000	-2.97295700	-0.00005400
H	-2.90918200	-3.06209000	0.00018100
H	0.25298700	2.51771900	-0.00061000
H	-0.25298700	-2.51771900	0.00059200
C	-2.68896800	2.77814900	0.00025800
C	-2.96541300	3.95441800	0.00015800
H	-3.20558600	4.98965200	0.00007000
C	2.68896800	-2.77814900	-0.00038900
C	2.96541300	-3.95441800	-0.00029400
H	3.20558500	-4.98965200	-0.00021100

8

B3LYP/6-311+G(d,p) = -1106.39276308 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -1106.127270 au
NIMAG = 0

C	-5.51854600	0.52465800	0.00000500
C	-4.90996900	1.79274200	0.00002000
C	-3.52116400	1.91484400	0.00002200
C	-2.74221400	0.76392200	0.00001000
C	-3.35886500	-0.51559600	-0.00000400
C	-4.74001300	-0.64527500	-0.00000800
C	-2.30738100	-1.53625000	-0.00001200
C	-1.07492900	-0.88861300	0.00000000
C	0.24654400	-1.42635800	0.00000500
C	1.29475000	-0.55277200	0.00000400
C	1.07492900	0.88861300	-0.00000100
C	-1.29475000	0.55277100	0.00000400
C	-0.24654400	1.42635800	0.00000300
C	2.74221400	-0.76392200	0.00001000
C	2.30738100	1.53625000	-0.00001200
C	3.35886500	0.51559600	-0.00000400
C	3.52116400	-1.91484400	0.00002200
C	4.74001300	0.64527500	-0.00000600
C	5.51854600	-0.52465800	0.00000700
C	4.90996900	-1.79274200	0.00002100
C	2.53539700	2.92305200	-0.00002200
H	2.94685300	5.15653600	-0.00004000
C	2.75489600	4.11077500	-0.00003000
C	-2.53539700	-2.92305200	-0.00002200
H	-2.94685400	-5.15653600	-0.00004000
C	-2.75489600	-4.11077500	-0.00003100
H	-3.06825700	2.89956100	0.00003300
H	-5.21396800	-1.61912300	-0.00001800
H	3.06825700	-2.89956100	0.00003200
H	5.21396800	1.61912300	-0.00001600
H	-5.53459300	2.67718600	0.00002800
H	5.53459300	-2.67718600	0.00003000
H	-0.39082000	2.50127300	0.00000600
H	0.39082000	-2.50127300	0.00001000
C	6.94567400	-0.42639900	0.00000600
C	-6.94567400	0.42639900	0.00000300
N	8.09890000	-0.34783800	0.00000000
N	-8.09890000	0.34783800	0.00000500

9

B3LYP/6-311+G(d,p) = -1106.40483212 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -1106.139345 au
NIMAG = 0

C	-5.51854600	0.52465800	0.00000500
C	-4.90996900	1.79274200	0.00002000
C	-3.52116400	1.91484400	0.00002200
C	-2.74221400	0.76392200	0.00001000
C	-3.35886500	-0.51559600	-0.00000400
C	-4.74001300	-0.64527500	-0.00000800
C	-2.30738100	-1.53625000	-0.00001200
C	-1.07492900	-0.88861300	0.00000000
C	0.24654400	-1.42635800	0.00000500
C	1.29475000	-0.55277200	0.00000400
C	1.07492900	0.88861300	-0.00000100
C	-1.29475000	0.55277100	0.00000400
C	-0.24654400	1.42635800	0.00000300
C	2.74221400	-0.76392200	0.00001000
C	2.30738100	1.53625000	-0.00001200
C	3.35886500	0.51559600	-0.00000400
C	3.52116400	-1.91484400	0.00002200
C	4.74001300	0.64527500	-0.00000600
C	5.51854600	-0.52465800	0.00000700
C	4.90996900	-1.79274200	0.00002100
C	2.53539700	2.92305200	-0.00002200
H	2.94685300	5.15653600	-0.00004000
C	2.75489600	4.11077500	-0.00003000
C	-2.53539700	-2.92305200	-0.00002200
H	-2.94685400	-5.15653600	-0.00004000
C	-2.75489600	-4.11077500	-0.00003100
H	-3.06825700	2.89956100	0.00003300
H	-5.21396800	-1.61912300	-0.00001800
H	3.06825700	-2.89956100	0.00003200
H	5.21396800	1.61912300	-0.00001600
H	-5.53459300	2.67718600	0.00002800
H	5.53459300	-2.67718600	0.00003000
H	-0.39082000	2.50127300	0.00000600
H	0.39082000	-2.50127300	0.00001000
C	6.94567400	-0.42639900	0.00000600
C	-6.94567400	0.42639900	0.00000300
N	8.09890000	-0.34783800	0.00000000
N	-8.09890000	0.34783800	0.00000500

10a

B3LYP/6-311+G(d,p) = -921.872420748 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -921.603989 au
NIMAG = 0

C	1.25433100	-0.64426500	0.00000000
C	1.25433100	0.71963200	0.00000000
C	-0.00400700	1.39403700	0.00000000
C	-1.25433100	0.64426500	0.00000000
C	-1.25433100	-0.71963200	0.00000000
C	0.00400700	-1.39403700	0.00000000
C	-0.29460400	2.75588600	0.00000000
C	-1.75147600	2.91699600	0.00000000
C	-2.34253400	1.62673200	0.00000000
C	2.34253400	-1.62673200	0.00000000
C	0.29460400	-2.75588600	0.00000000
C	1.75147600	-2.91699600	0.00000000
C	-3.72462200	1.49366600	0.00000000
H	-4.19225500	0.51512200	0.00000000
C	-2.53977000	4.06397200	0.00000000
H	-2.08440400	5.04783000	0.00000000
C	3.72462200	-1.49366600	0.00000000
H	4.19225500	-0.51512200	0.00000000
C	2.53977000	-4.06397200	0.00000000
H	2.08440400	-5.04783000	0.00000000
C	4.51432800	-2.64932900	0.00000000
H	5.59458000	-2.55841900	0.00000000
C	3.92923600	-3.91837000	0.00000000
H	4.56116800	-4.79913400	0.00000000
C	-3.92923600	3.91837000	0.00000000
H	-4.56116800	4.79913400	0.00000000
C	-4.51432800	2.64932900	0.00000000
H	-5.59458000	2.55841900	0.00000000
C	-0.63187100	-3.81409700	0.00000000
C	-1.41250800	-4.73631100	0.00000000
H	-2.10189800	-5.54505700	0.00000000
C	0.63187100	3.81409700	0.00000000
C	1.41250800	4.73631100	0.00000000
H	2.10189800	5.54505700	0.00000000
H	2.17350700	1.29560600	0.00000000
H	-2.17350700	-1.29560600	0.00000000

10b

B3LYP/6-311+G(d,p) = -1120.40853210 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -1120.156787 au
NIMAG = 0

H	2.09675500	5.06268700	0.00000000
C	2.52759500	4.06920100	0.00000000
C	3.72494000	1.49809900	0.00000000
C	1.74951300	2.91596700	0.00000000
C	3.90613400	3.89648200	0.00000000
C	4.51919500	2.64981900	0.00000000
C	2.34260800	1.62735500	0.00000000
H	5.60023500	2.59134600	0.00000000
H	4.19730700	0.52233700	0.00000000
C	0.29177200	2.75450200	0.00000000
C	1.25541000	0.64400600	0.00000000
C	0.00401700	1.39333800	0.00000000
C	-1.25541000	0.71900000	0.00000000
C	-1.25541000	-0.64400600	0.00000000
C	1.25541000	-0.71900000	0.00000000
C	-0.00401700	-1.39333800	0.00000000
C	-0.29177200	-2.75450200	0.00000000
C	-2.34260800	-1.62735500	0.00000000
C	-1.74951300	-2.91596700	0.00000000
C	-3.72494000	-1.49809900	0.00000000
H	-4.19730700	-0.52233700	0.00000000
C	-4.51919500	-2.64981900	0.00000000
H	-5.60023500	-2.59134600	0.00000000
C	-3.90613400	-3.89648200	0.00000000
C	-2.52759500	-4.06920100	0.00000000
H	-2.09675500	-5.06268700	0.00000000
C	-0.63242500	3.81423400	0.00000000
H	-2.09444800	5.55201400	0.00000000
C	-1.40884000	4.73977900	0.00000000
C	0.63242500	-3.81423400	0.00000000
H	2.09444800	-5.55201400	0.00000000
C	1.40884000	-4.73977900	0.00000000
F	-4.69317200	-5.00100100	0.00000000
F	4.69317200	5.00100100	0.00000000
H	2.17376700	-1.29611700	0.00000000
H	-2.17376700	1.29611700	0.00000000

10c

B3LYP/6-311+G(d,p) = -1841.11692468 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -1840.867873 au
NIMAG = 0

H	2.08413400	5.05274800	0.00000000
C	2.53029900	4.06636500	0.00000000
C	3.72420200	1.49761300	0.00000000
C	1.75115800	2.91437400	0.00000000
C	3.91567300	3.90747500	0.00000000
C	4.51770500	2.64927100	0.00000000
C	2.34208700	1.62522600	0.00000000
H	5.59725900	2.57251400	0.00000000
H	4.19900600	0.52289500	0.00000000
C	0.29331900	2.75530200	0.00000000
C	1.25487000	0.64326200	0.00000000
C	0.00438500	1.39376400	0.00000000
C	-1.25487000	0.72031600	0.00000000
C	-1.25487000	-0.64326200	0.00000000
C	1.25487000	-0.72031600	0.00000000
C	-0.00438500	-1.39376400	0.00000000
C	-0.29331900	-2.75530200	0.00000000
C	-2.34208700	-1.62522600	0.00000000
C	-1.75115800	-2.91437400	0.00000000
C	-3.72420200	-1.49761300	0.00000000
H	-4.19900600	-0.52289500	0.00000000
C	-4.51770500	-2.64927100	0.00000000
H	-5.59725900	-2.57251400	0.00000000
C	-3.91567300	-3.90747500	0.00000000
C	-2.53029900	-4.06636500	0.00000000
H	-2.08413400	-5.05274800	0.00000000
C	-0.63009600	3.81550000	0.00000000
H	-2.09156200	5.55384000	0.00000000
C	-1.40648200	4.74111600	0.00000000
C	0.63009600	-3.81550000	0.00000000
H	2.09156200	-5.55384000	0.00000000
C	1.40648200	-4.74111600	0.00000000
Cl	4.93589900	5.34058000	0.00000000
Cl	-4.93589900	-5.34058000	0.00000000
H	2.17327500	-1.29731400	0.00000000
H	-2.17327500	1.29731400	0.00000000

10d

B3LYP/6-311+G(d,p) = -6068.95626833 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -6068.708503 au
NIMAG = 0

H	2.07962600	5.05085600	0.00000000
C	2.53024700	4.06667200	0.00000000
C	3.72400300	1.49740200	0.00000000
C	1.75112700	2.91413600	0.00000000
C	3.91588800	3.90769600	0.00000000
C	4.51807100	2.64933700	0.00000000
C	2.34197600	1.62498700	0.00000000
H	5.59705900	2.56746000	0.00000000
H	4.19918000	0.52282300	0.00000000
C	0.29325800	2.75524900	0.00000000
C	1.25473900	0.64320900	0.00000000
C	0.00438800	1.39374600	0.00000000
C	-1.25473900	0.72039400	0.00000000
C	-1.25473900	-0.64320900	0.00000000
C	1.25473900	-0.72039400	0.00000000
C	-0.00438800	-1.39374600	0.00000000
C	-0.29325800	-2.75524900	0.00000000
C	-2.34197600	-1.62498700	0.00000000
C	-1.75112700	-2.91413600	0.00000000
C	-3.72400300	-1.49740200	0.00000000
H	-4.19918000	-0.52282300	0.00000000
C	-4.51807100	-2.64933700	0.00000000
H	-5.59705900	-2.56746000	0.00000000
C	-3.91588800	-3.90769600	0.00000000
C	-2.53024700	-4.06667200	0.00000000
H	-2.07962600	-5.05085600	0.00000000
C	-0.63024500	3.81535300	0.00000000
H	-2.09174100	5.55363900	0.00000000
C	-1.40674600	4.74084500	0.00000000
C	0.63024500	-3.81535300	0.00000000
H	2.09174100	-5.55363900	0.00000000
C	1.40674600	-4.74084500	0.00000000
Br	5.02727100	5.46957500	0.00000000
Br	-5.02727100	-5.46957500	0.00000000
H	2.17318500	-1.29726000	0.00000000
H	-2.17318500	1.29726000	0.00000000

10e

B3LYP/6-311+G(d,p) = -1000.52708199 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -1000.204539 au
NIMAG = 0

C	5.54303900	0.58013000	-0.00387500
C	4.90732300	1.82869500	-0.00852900
C	3.51259600	1.94916100	-0.00618000
C	2.73814400	0.79879300	-0.00075300
C	3.37049700	-0.47061600	0.00018600
C	4.75564000	-0.58143200	-0.00224100
C	2.32818500	-1.50293800	-0.00098800
C	1.08685800	-0.87295200	-0.00141200
C	-0.22899100	-1.42819600	-0.00175700
C	-1.29016700	-0.57177500	-0.00183400
C	-1.08685800	0.87295300	-0.00146300
C	1.29016800	0.57177600	-0.00148400
C	0.22899100	1.42819700	-0.00145600
C	-2.73814400	-0.79879300	-0.00142100
C	-2.32818500	1.50293800	-0.00116300
C	-3.37049700	0.47061600	-0.00037400
C	-3.51259400	-1.94916000	-0.00720400
C	-4.75564000	0.58143200	-0.00304700
C	-5.54303800	-0.58013100	-0.00504300
C	-4.90732000	-1.82869400	-0.00979900
C	-2.56827100	2.88889600	-0.00120700
H	-2.98904500	5.12065500	-0.00139900
C	-2.79444900	4.07595200	-0.00132100
C	2.56827100	-2.88889600	-0.00123600
H	2.98904500	-5.12065400	-0.00175100
C	2.79444900	-4.07595100	-0.00152200
H	3.05574800	2.93293300	-0.01187200
H	5.22522900	-1.55996800	-0.00447300
H	-3.05574400	-2.93293100	-0.01298600
H	-5.22522900	1.55996800	-0.00519100
H	5.51436100	2.72802500	-0.01597500
H	-5.51435700	-2.72802300	-0.01752400
H	0.35822300	2.50520900	-0.00140300
H	-0.35822300	-2.50520900	-0.00192100
C	-7.04948600	-0.47990000	0.02115500
H	-7.41102100	-0.25317200	1.03020300
H	-7.40723300	0.31550900	-0.63794500
H	-7.51684400	-1.41540900	-0.29322500
C	7.04948100	0.47989700	0.02260900
H	7.41082100	0.25312400	1.03171800

H	7.40735700	-0.31548200	-0.63645700
H	7.51690100	1.41542000	-0.29163700

10f

B3LYP/6-311+G(d,p) = -1384.09525467 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -1383.666212 au
NIMAG = 0

C	-1.06025200	-0.90539000	-0.02450100
C	-1.30609800	0.53277000	-0.02465300
C	-0.27102500	1.42121600	-0.02486400
H	-0.43262800	2.49380900	-0.02429400
C	1.06028600	0.90553200	-0.02413100
C	0.27106200	-1.42107200	-0.02523700
H	0.43266300	-2.49366500	-0.02496700
C	1.30613100	-0.53262600	-0.02466200
C	2.28245200	1.57206400	-0.02082300
C	3.35399400	0.57027100	-0.02127000
C	2.75884000	-0.71675800	-0.02088400
C	4.73426800	0.72386700	-0.01070500
H	5.17253300	1.71494300	0.01541200
C	5.55718800	-0.41616400	-0.00006600
C	3.56711200	-1.84516900	-0.01240900
H	3.13883600	-2.84158700	-0.02163500
C	4.95522000	-1.68673700	-0.00256400
H	5.58631400	-2.56758300	-0.02142200
C	-2.28241100	-1.57193300	-0.02159300
C	-3.35395600	-0.57014100	-0.02190200
C	-2.75880000	0.71689200	-0.02101700
C	-4.73421300	-0.72379700	-0.01167500
H	-5.17234900	-1.71493800	0.01412700
C	-5.55723300	0.41617500	-0.00089100
C	-4.95525000	1.68675400	-0.00286800
C	-3.56714800	1.84524800	-0.01235700
H	-3.13895400	2.84170500	-0.02118100
H	-5.58629100	2.56763400	-0.02165700
C	7.03569700	-0.27958600	0.01521300
C	7.83036900	-1.12351500	0.80609600
C	7.67743100	0.69896200	-0.75911100
C	9.21650000	-0.99389900	0.82204100
H	7.35589700	-1.87002100	1.43304600
C	9.06356500	0.82883500	-0.74347700
H	7.08670700	1.34683400	-1.39678900
C	9.83982900	-0.01698300	0.04726100
H	9.80983600	-1.65094800	1.44834900

H	9.53849900	1.58637200	-1.35711900
H	10.91910200	0.08428200	0.05974400
C	-7.03571100	0.27951400	0.01395300
C	-7.83081700	1.12375000	0.80409100
C	-7.67711500	-0.69945800	-0.76013200
C	-9.21694200	0.99403500	0.81954600
H	-7.35673200	1.87058900	1.43092900
C	-9.06323400	-0.82946200	-0.74496400
H	-7.08616700	-1.34757000	-1.39735600
C	-9.83990600	0.01667700	0.04503000
H	-9.81055100	1.65138200	1.44528400
H	-9.53783400	-1.58736200	-1.35841800
H	-10.91917400	-0.08467400	0.05713400
C	2.48225000	2.96416000	-0.01877000
C	2.67409800	4.15714700	-0.01691600
H	2.83916900	5.20700100	-0.01410400
C	-2.48219900	-2.96403100	-0.01998300
C	-2.67397800	-4.15703000	-0.01887300
H	-2.83889500	-5.20691000	-0.01666800

10g

Energy = -2058.39491825 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -2057.957187 au
NIMAG = 0

C	1.06949000	-0.89159500	-0.07263500
C	1.29987300	0.54333600	0.05366000
C	0.25611100	1.41873100	0.12467600
H	0.40668100	2.48879900	0.21836600
C	-1.06948900	0.89159700	0.07263500
C	-0.25611000	-1.41872800	-0.12467600
H	-0.40668100	-2.48879700	-0.21836600
C	-1.29987200	-0.54333300	-0.05366000
C	-2.29826100	1.54388100	0.12450100
C	-3.35838200	0.53521000	0.02871700
C	-2.75026200	-0.74165600	-0.07681100
C	-4.73994200	0.67393500	0.03742600
H	-5.18851700	1.65502900	0.14342200
C	-5.54883600	-0.47184000	-0.05741400
C	-3.54584300	-1.87517900	-0.17298400
H	-3.10675100	-2.86247900	-0.26486800
C	-4.93531400	-1.73252300	-0.16143700
H	-5.55598300	-2.61514900	-0.26220000
C	2.29826100	-1.54387900	-0.12450100
C	3.35838200	-0.53520800	-0.02871700

C	2.75026300	0.74165900	0.07681100
C	4.73994200	-0.67393300	-0.03742600
H	5.18851700	-1.65502700	-0.14342000
C	5.54883700	0.47184200	0.05741300
C	4.93531500	1.73252600	0.16143500
C	3.54584400	1.87518200	0.17298200
H	3.10675200	2.86248100	0.26486600
H	5.55598300	2.61515100	0.26219700
C	7.02759500	0.34984800	0.04922900
C	7.82613800	1.26836400	-0.64837000
C	7.66802700	-0.68971000	0.74135300
C	9.21139000	1.15427000	-0.65777300
H	7.35740700	2.06764600	-1.21000100
C	9.05210300	-0.80986800	0.73643700
H	7.07725900	-1.39661800	1.31165800
C	9.82893900	0.11458100	0.03720600
H	9.81046800	1.87052100	-1.20604600
H	9.52837900	-1.61055900	1.28872200
C	-7.02759500	-0.34984700	-0.04922900
C	-7.82613800	-1.26836500	0.64836700
C	-7.66802700	0.68971200	-0.74135100
C	-9.21138900	-1.15427200	0.65776900
H	-7.35740700	-2.06764800	1.20999600
C	-9.05210400	0.80987000	-0.73643500
H	-7.07726000	1.39662300	-1.31165400
C	-9.82893900	-0.11458200	-0.03720800
H	-9.81046700	-1.87052600	1.20604000
H	-9.52838000	1.61056100	-1.28871800
C	-11.32191600	0.04731300	0.01301500
C	11.32191500	-0.04731700	-0.01301500
F	-11.81913100	0.57422100	-1.12991200
F	-11.96080100	-1.12620900	0.22142200
F	-11.70764600	0.87875100	1.01696500
F	11.96080300	1.12619700	-0.22145800
F	11.81913200	-0.57419200	1.12992800
F	11.70764200	-0.87878700	-1.01694000
C	-2.51407400	2.92797400	0.24684400
C	-2.72074900	4.11368800	0.35224700
C	2.51407400	-2.92797200	-0.24684300
C	2.72074900	-4.11368600	-0.35224500
H	-2.89851400	5.15738800	0.44667700
H	2.89851400	-5.15738600	-0.44667500

10h

B3LYP/6-311+G(d,p) = -2732.68844834 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -2732.29452301 au
NIMAG = 0

C	1.05696200	0.90952900	-0.01569400
C	1.30666000	-0.52745800	-0.01682000
C	0.27570900	-1.42076300	-0.01688400
H	0.44128600	-2.49266200	-0.01709500
C	-1.05696200	-0.90956500	-0.01601900
C	-0.27570800	1.42072700	-0.01650100
H	-0.44128500	2.49262700	-0.01642300
C	-1.30665900	0.52742300	-0.01675400
C	-2.27651300	-1.58109500	-0.01440700
C	-3.34982500	-0.58225400	-0.01714000
C	-2.75934500	0.70738000	-0.01584200
C	-4.72935700	-0.74014700	-0.01277200
H	-5.16299100	-1.73340000	0.01261300
C	-5.55139500	0.39953900	-0.00597300
C	-3.56941100	1.83466800	-0.01124300
H	-3.14398300	2.83195100	-0.02017800
C	-4.95648800	1.67319700	-0.00573400
H	-5.58810600	2.55358200	-0.02867700
C	2.27651100	1.58106000	-0.01381200
C	3.34982400	0.58222200	-0.01675900
C	2.75934700	-0.70741400	-0.01586600
C	4.72935500	0.74011700	-0.01226200
H	5.16298500	1.73336500	0.01343100
C	5.55139700	-0.39956800	-0.00574100
C	4.95649300	-1.67322700	-0.00590100
C	3.56941600	-1.83470000	-0.01154000
H	3.14399300	-2.83198200	-0.02078800
H	5.58811400	-2.55360500	-0.02906200
C	-7.02889900	0.26052300	0.00034600
C	-7.82957200	1.11690500	0.76889500
C	-7.66241900	-0.72961100	-0.76033200
C	-9.21516800	0.98797600	0.76798200
H	-7.36623100	1.87702000	1.38468600
C	-9.04991700	-0.85736300	-0.75084400
H	-7.07050200	-1.39329000	-1.37811400
C	-9.83975900	-0.00013900	0.00938800
H	-10.91659600	-0.09935600	0.01117200
C	7.02889900	-0.26054000	0.00069100
C	7.82955100	-1.11713400	0.76902700
C	7.66243900	0.72982400	-0.75967000

C	9.21514500	-0.98818300	0.76821400
H	7.36619500	-1.87743600	1.38457600
C	9.04993400	0.85759800	-0.75007800
H	7.07054100	1.39367400	-1.37728700
C	9.83975500	0.00016500	0.00993900
H	10.91659100	0.09939900	0.01180200
C	-2.47500000	-2.97292500	-0.01271700
C	-2.66840400	-4.16542900	-0.01185500
H	-2.83511800	-5.21535600	-0.01076800
C	2.47499700	2.97289000	-0.01171000
C	2.66839900	4.16539400	-0.01049400
H	2.83511200	5.21532100	-0.00909400
C	-10.04790600	1.88143200	1.65104700
C	-9.69720400	-1.89720300	-1.62921300
C	10.04786300	-1.88188100	1.65105200
C	9.69724400	1.89771400	-1.62810400
F	8.98606700	3.04783500	-1.65635600
F	9.79853100	1.47455200	-2.91252100
F	10.94495000	2.20787100	-1.21913900
F	11.27103200	-2.11466500	1.12836900
F	9.46314200	-3.08301300	1.85541300
F	10.24518000	-1.33204800	2.87495300
F	-10.94494100	-2.20744600	-1.22041300
F	-8.98605600	-3.04733500	-1.65776400
F	-9.79840200	-1.47365800	-2.91351100
F	-11.27108700	2.11430800	1.12843500
F	-10.24519100	1.33129400	2.87481600
F	-9.46321800	3.08253200	1.85569600

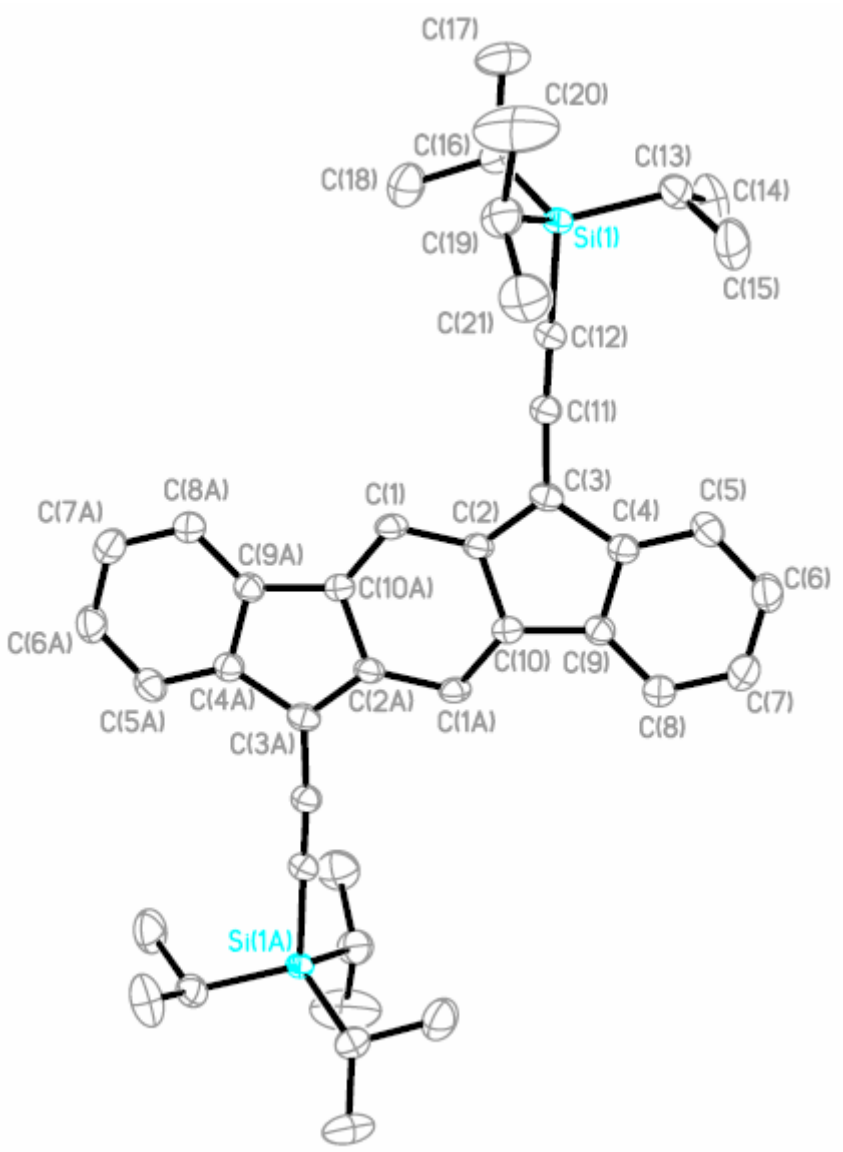
10i

B3LYP/6-311+G(d,p) = -2104.28054316 au
B3LYP/6-311+G(d,p) Zero Point Corrected Energy = -2103.863829 au
NIMAG = 0

C	-1.09939900	0.85354200	-0.08315400
C	-1.28118500	-0.59118700	0.01945600
C	-0.20723200	-1.42860000	0.10050000
H	-0.32041500	-2.50469800	0.17651900
C	1.09939900	-0.85354200	0.08315400
C	0.20723200	1.42860000	-0.10050100
H	0.32041500	2.50469800	-0.17651900
C	1.28118500	0.59118700	-0.01945700
C	2.34934800	-1.46160000	0.15215600
C	3.37505000	-0.41398400	0.09293700
C	2.72282100	0.84078400	-0.00907000

C	4.75902500	-0.50496500	0.13470600
H	5.23786500	-1.47197500	0.23971700
C	5.53250900	0.66961500	0.06503000
C	3.48174100	2.00195300	-0.07905800
H	3.01022300	2.97446100	-0.17006300
C	4.87359000	1.90945200	-0.04958900
H	5.46460600	2.81302000	-0.13771100
C	-2.34934800	1.46160000	-0.15215700
C	-3.37505000	0.41398400	-0.09293800
C	-2.72282100	-0.84078400	0.00907000
C	-4.75902500	0.50496500	-0.13470600
H	-5.23786500	1.47197500	-0.23971700
C	-5.53250900	-0.66961500	-0.06503000
C	-4.87359000	-1.90945200	0.04958900
C	-3.48174100	-2.00195300	0.07905700
H	-3.01022400	-2.97446100	0.17006300
H	-5.46460600	-2.81302000	0.13771100
C	6.99685800	0.62053000	0.11843000
C	7.87322800	1.57123100	0.57951000
S	7.89019400	-0.77717600	-0.45790000
C	9.24072700	1.18872300	0.47925600
H	7.54755000	2.50993100	1.00839500
C	9.42904400	-0.05536100	-0.05714700
H	10.06309100	1.81398500	0.80488600
C	-6.99685800	-0.62053000	-0.11843000
C	-7.87322800	-1.57123100	-0.57951000
S	-7.89019400	0.77717600	0.45790000
C	-9.24072700	-1.18872300	-0.47925600
H	-7.54755000	-2.50993000	-1.00839500
C	-9.42904400	0.05536100	0.05714800
H	-10.06309200	-1.81398500	-0.80488600
C	2.61174000	-2.83899800	0.25964200
C	2.85868000	-4.01810700	0.35258200
H	3.07339300	-5.05570500	0.43435700
C	-2.61174000	2.83899800	-0.25964200
C	-2.85868000	4.01810700	-0.35258200
H	-3.07339300	5.05570500	-0.43435700
C	-10.71568300	0.77999000	0.30926100
H	-10.76844900	1.72206400	-0.24505600
H	-11.55565000	0.15769700	-0.00658100
H	-10.85143900	1.01366200	1.36973000
C	10.71568300	-0.77999000	-0.30926000
H	11.55565000	-0.15769700	0.00658100
H	10.76845000	-1.72206400	0.24505800
H	10.85143900	-1.01366300	-1.36972900

Crystallographic Data for 10a



Solid State Packing of 10a

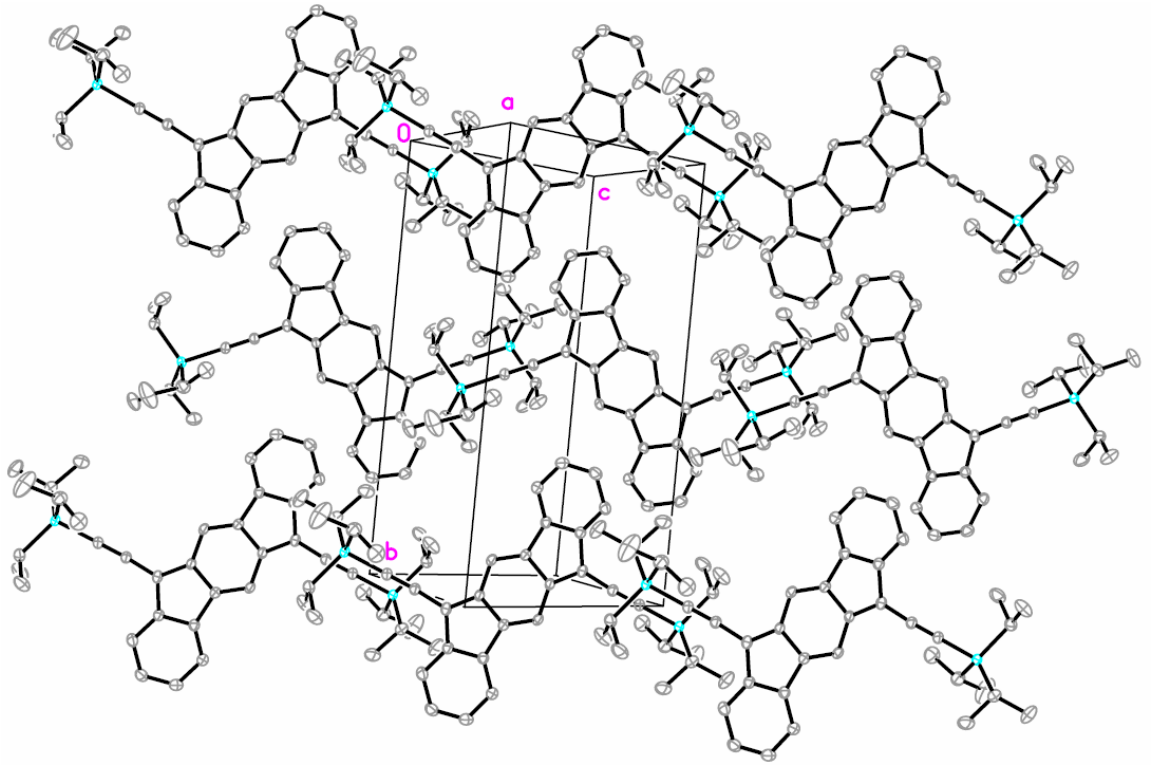


Table 1. Crystal data and structure refinement for **10a**.

Identification code	mh61	
Empirical formula	C42 H52 Si2	
Formula weight	613.02	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.393(3) Å	α = 90°.
	b = 16.693(4) Å	β = 119.083(4)°.
	c = 11.163(2) Å	γ = 90°.
Volume	1855.4(7) $Å^3$	
Z	2	
Density (calculated)	1.097 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	664	
Crystal size	0.20 x 0.06 x 0.03 mm^3	
Theta range for data collection	2.05 to 24.99°.	
Index ranges	-13<=h<=13, -19<=k<=19, -13<=l<=13	
Reflections collected	17344	
Independent reflections	3245 [R(int) = 0.0492]	
Completeness to theta = 24.99°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9963 and 0.9759	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3245 / 0 / 199	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R1 = 0.0824, wR2 = 0.1955	
R indices (all data)	R1 = 0.0970, wR2 = 0.2037	
Largest diff. peak and hole	0.494 and -0.305 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **10a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	1151(1)	5572(1)	3215(1)	27(1)
C(1)	4321(4)	5631(2)	9017(4)	29(1)
C(2)	4230(4)	4814(2)	8614(4)	28(1)
C(3)	3561(4)	4463(3)	7333(4)	31(1)
C(4)	3820(4)	3594(2)	7482(4)	31(1)
C(5)	3409(5)	2994(3)	6513(4)	38(1)
C(6)	3842(5)	2220(3)	6953(5)	44(1)
C(7)	4662(5)	2051(3)	8317(5)	46(1)
C(8)	5066(5)	2652(3)	9299(5)	38(1)
C(9)	4658(4)	3425(2)	8884(4)	30(1)
C(10)	4938(4)	4195(2)	9633(4)	29(1)
C(11)	2759(4)	4849(2)	6068(4)	31(1)
C(12)	2078(4)	5136(3)	4946(4)	34(1)
C(13)	371(5)	4717(3)	2000(5)	42(1)
C(14)	-614(6)	4274(4)	2305(6)	66(2)
C(15)	1396(6)	4138(3)	1988(6)	62(2)
C(16)	-156(5)	6266(3)	3195(5)	39(1)
C(17)	-1080(6)	6628(4)	1787(6)	63(2)
C(18)	434(6)	6912(3)	4272(6)	59(2)
C(19)	2488(5)	6137(3)	2997(5)	49(1)
C(20)	2037(7)	6403(6)	1564(8)	109(3)
C(21)	3813(5)	5702(4)	3566(6)	63(2)

Table 3. Bond lengths [Å] and angles [°] for **10a**.

Si(1)-C(12)	1.843(4)
Si(1)-C(13)	1.870(5)
Si(1)-C(16)	1.878(5)
Si(1)-C(19)	1.905(5)
C(1)-C(10)#1	1.354(6)
C(1)-C(2)	1.424(6)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.382(6)
C(2)-C(10)	1.456(5)
C(3)-C(11)	1.411(6)
C(3)-C(4)	1.472(6)
C(4)-C(5)	1.379(6)
C(4)-C(9)	1.410(6)
C(5)-C(6)	1.384(6)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.374(7)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.389(6)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.373(6)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.481(6)
C(10)-C(1)#1	1.354(6)
C(11)-C(12)	1.206(6)
C(13)-C(14)	1.515(7)
C(13)-C(15)	1.520(7)
C(13)-H(13A)	1.0000
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(18)	1.508(7)

C(16)-C(17)	1.528(6)
C(16)-H(16A)	1.0000
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(20)	1.490(8)
C(19)-C(21)	1.510(7)
C(19)-H(19A)	1.0000
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(12)-Si(1)-C(13)	106.7(2)
C(12)-Si(1)-C(16)	107.7(2)
C(13)-Si(1)-C(16)	111.6(2)
C(12)-Si(1)-C(19)	104.1(2)
C(13)-Si(1)-C(19)	114.4(2)
C(16)-Si(1)-C(19)	111.8(2)
C(10)#1-C(1)-C(2)	117.9(4)
C(10)#1-C(1)-H(1A)	121.0
C(2)-C(1)-H(1A)	121.0
C(3)-C(2)-C(1)	130.7(4)
C(3)-C(2)-C(10)	109.0(4)
C(1)-C(2)-C(10)	120.3(3)
C(2)-C(3)-C(11)	127.2(4)
C(2)-C(3)-C(4)	108.7(3)
C(11)-C(3)-C(4)	124.0(4)
C(5)-C(4)-C(9)	120.9(4)
C(5)-C(4)-C(3)	130.9(4)
C(9)-C(4)-C(3)	108.2(3)
C(4)-C(5)-C(6)	118.3(4)

C(4)-C(5)-H(5A)	120.9
C(6)-C(5)-H(5A)	120.9
C(7)-C(6)-C(5)	121.2(4)
C(7)-C(6)-H(6A)	119.4
C(5)-C(6)-H(6A)	119.4
C(6)-C(7)-C(8)	120.8(4)
C(6)-C(7)-H(7A)	119.6
C(8)-C(7)-H(7A)	119.6
C(9)-C(8)-C(7)	119.0(4)
C(9)-C(8)-H(8A)	120.5
C(7)-C(8)-H(8A)	120.5
C(8)-C(9)-C(4)	119.9(4)
C(8)-C(9)-C(10)	132.9(4)
C(4)-C(9)-C(10)	107.2(3)
C(1)#1-C(10)-C(2)	121.7(4)
C(1)#1-C(10)-C(9)	131.5(4)
C(2)-C(10)-C(9)	106.8(3)
C(12)-C(11)-C(3)	175.8(5)
C(11)-C(12)-Si(1)	175.6(4)
C(14)-C(13)-C(15)	110.4(4)
C(14)-C(13)-Si(1)	110.6(3)
C(15)-C(13)-Si(1)	113.3(3)
C(14)-C(13)-H(13A)	107.4
C(15)-C(13)-H(13A)	107.4
Si(1)-C(13)-H(13A)	107.4
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5
C(18)-C(16)-C(17)	110.8(4)
C(18)-C(16)-Si(1)	112.8(3)
C(17)-C(16)-Si(1)	113.7(3)
C(18)-C(16)-H(16A)	106.3
C(17)-C(16)-H(16A)	106.3
Si(1)-C(16)-H(16A)	106.3
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20)-C(19)-C(21)	110.3(5)
C(20)-C(19)-Si(1)	113.9(4)
C(21)-C(19)-Si(1)	114.0(4)
C(20)-C(19)-H(19A)	106.0
C(21)-C(19)-H(19A)	106.0
Si(1)-C(19)-H(19A)	106.0
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5

H(21B)-C(21)-H(21C) 109.5

Symmetry transformations used to generate equivalent atoms.
#1 -x+1,-y+1,-z+2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **10a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	30(1)	28(1)	20(1)	3(1)	9(1)	1(1)
C(1)	32(2)	32(2)	23(2)	7(2)	12(2)	6(2)
C(2)	26(2)	31(2)	22(2)	3(2)	8(2)	2(2)
C(3)	30(2)	38(2)	23(2)	3(2)	13(2)	1(2)
C(4)	31(2)	32(2)	28(2)	2(2)	13(2)	0(2)
C(5)	40(2)	42(3)	30(2)	-4(2)	15(2)	-5(2)
C(6)	52(3)	37(3)	41(3)	-8(2)	22(2)	-4(2)
C(7)	56(3)	31(2)	46(3)	1(2)	22(2)	3(2)
C(8)	42(3)	35(2)	32(2)	2(2)	14(2)	2(2)
C(9)	30(2)	32(2)	27(2)	1(2)	14(2)	-1(2)
C(10)	27(2)	30(2)	28(2)	4(2)	12(2)	2(2)
C(11)	32(2)	32(2)	26(2)	0(2)	12(2)	3(2)
C(12)	34(2)	34(2)	26(2)	-1(2)	9(2)	2(2)
C(13)	48(3)	40(3)	30(2)	-2(2)	14(2)	-4(2)
C(14)	69(4)	65(4)	73(4)	-29(3)	41(3)	-30(3)
C(15)	67(4)	54(3)	65(4)	-23(3)	33(3)	-5(3)
C(16)	41(3)	38(2)	39(3)	6(2)	20(2)	4(2)
C(17)	56(3)	81(4)	52(3)	23(3)	26(3)	35(3)
C(18)	71(4)	44(3)	64(4)	-6(3)	34(3)	9(3)
C(19)	43(3)	46(3)	56(3)	6(2)	22(2)	-4(2)
C(20)	67(4)	165(8)	104(6)	79(6)	47(4)	6(5)
C(21)	48(3)	72(4)	72(4)	2(3)	31(3)	-2(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **10a**.

	x	y	z	U(eq)
H(1A)	3875	6040	8359	35
H(5A)	2843	3108	5569	45
H(6A)	3568	1799	6300	52
H(7A)	4955	1517	8592	55
H(8A)	5616	2531	10243	45
H(13A)	-149	4947	1057	50
H(14A)	-1012	3828	1660	99
H(14B)	-1324	4642	2210	99
H(14C)	-142	4065	3244	99
H(15A)	928	3705	1334	92
H(15B)	1940	3912	2906	92
H(15C)	1980	4424	1714	92
H(16A)	-741	5932	3435	47
H(17A)	-1734	6982	1848	95
H(17B)	-1554	6198	1130	95
H(17C)	-544	6936	1478	95
H(18A)	-288	7256	4217	89
H(18B)	1067	7235	4118	89
H(18C)	906	6665	5182	89
H(19A)	2672	6638	3551	59
H(20A)	2771	6688	1527	164
H(20B)	1262	6761	1262	164
H(20C)	1782	5934	960	164
H(21A)	4449	6027	3419	94
H(21B)	3679	5186	3099	94
H(21C)	4173	5612	4551	94

Table 6. Torsion angles [°] for **10a**.

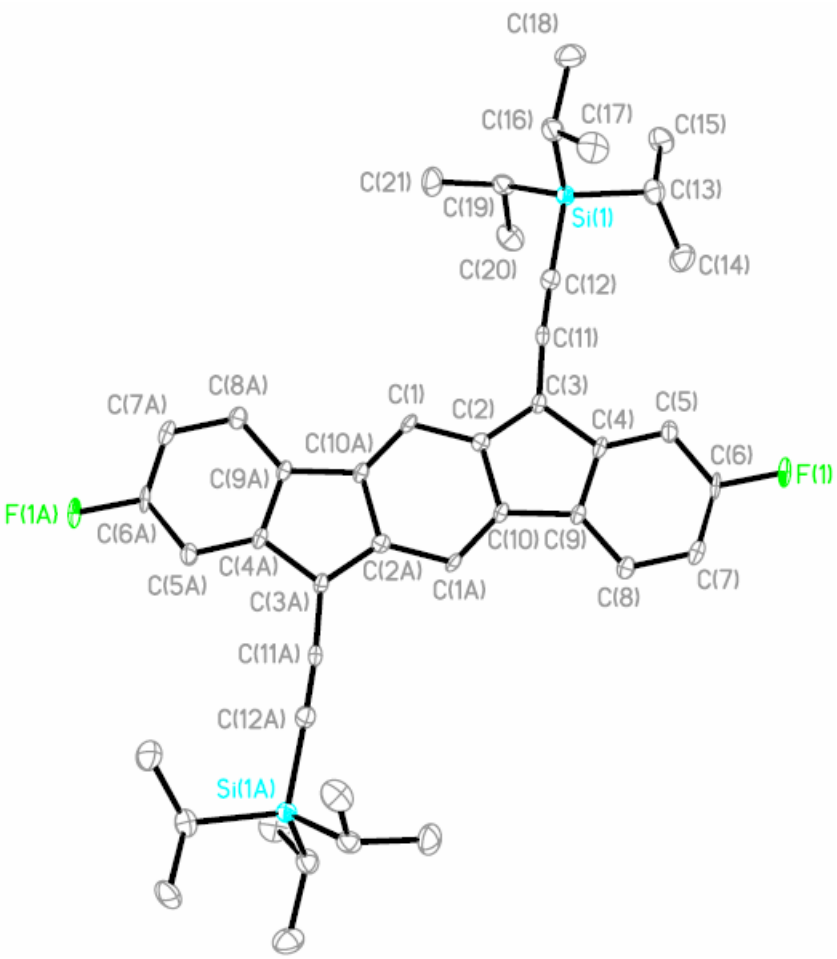
C(10)#1-C(1)-C(2)-C(3)	-179.9(4)
C(10)#1-C(1)-C(2)-C(10)	-1.0(6)
C(1)-C(2)-C(3)-C(11)	-0.9(7)
C(10)-C(2)-C(3)-C(11)	-179.8(4)
C(1)-C(2)-C(3)-C(4)	178.7(4)
C(10)-C(2)-C(3)-C(4)	-0.2(5)
C(2)-C(3)-C(4)-C(5)	-178.3(4)
C(11)-C(3)-C(4)-C(5)	1.3(7)
C(2)-C(3)-C(4)-C(9)	0.3(5)
C(11)-C(3)-C(4)-C(9)	179.9(4)
C(9)-C(4)-C(5)-C(6)	-0.1(6)
C(3)-C(4)-C(5)-C(6)	178.3(4)
C(4)-C(5)-C(6)-C(7)	0.0(7)
C(5)-C(6)-C(7)-C(8)	0.8(8)
C(6)-C(7)-C(8)-C(9)	-1.4(7)
C(7)-C(8)-C(9)-C(4)	1.2(7)
C(7)-C(8)-C(9)-C(10)	-177.4(4)
C(5)-C(4)-C(9)-C(8)	-0.4(6)
C(3)-C(4)-C(9)-C(8)	-179.2(4)
C(5)-C(4)-C(9)-C(10)	178.5(4)
C(3)-C(4)-C(9)-C(10)	-0.2(5)
C(3)-C(2)-C(10)-C(1)#1	-179.8(4)
C(1)-C(2)-C(10)-C(1)#1	1.1(7)
C(3)-C(2)-C(10)-C(9)	0.1(5)
C(1)-C(2)-C(10)-C(9)	-179.0(4)
C(8)-C(9)-C(10)-C(1)#1	-1.2(8)
C(4)-C(9)-C(10)-C(1)#1	-180.0(4)
C(8)-C(9)-C(10)-C(2)	178.9(5)
C(4)-C(9)-C(10)-C(2)	0.1(4)
C(2)-C(3)-C(11)-C(12)	166(6)
C(4)-C(3)-C(11)-C(12)	-13(7)
C(3)-C(11)-C(12)-Si(1)	-69(9)
C(13)-Si(1)-C(12)-C(11)	93(5)
C(16)-Si(1)-C(12)-C(11)	-147(5)

C(19)-Si(1)-C(12)-C(11)	-29(5)
C(12)-Si(1)-C(13)-C(14)	62.1(4)
C(16)-Si(1)-C(13)-C(14)	-55.3(4)
C(19)-Si(1)-C(13)-C(14)	176.6(4)
C(12)-Si(1)-C(13)-C(15)	-62.5(4)
C(16)-Si(1)-C(13)-C(15)	-179.8(4)
C(19)-Si(1)-C(13)-C(15)	52.0(4)
C(12)-Si(1)-C(16)-C(18)	57.0(4)
C(13)-Si(1)-C(16)-C(18)	173.8(3)
C(19)-Si(1)-C(16)-C(18)	-56.7(4)
C(12)-Si(1)-C(16)-C(17)	-175.7(4)
C(13)-Si(1)-C(16)-C(17)	-59.0(4)
C(19)-Si(1)-C(16)-C(17)	70.6(4)
C(12)-Si(1)-C(19)-C(20)	168.0(5)
C(13)-Si(1)-C(19)-C(20)	52.0(6)
C(16)-Si(1)-C(19)-C(20)	-76.1(6)
C(12)-Si(1)-C(19)-C(21)	40.2(5)
C(13)-Si(1)-C(19)-C(21)	-75.8(5)
C(16)-Si(1)-C(19)-C(21)	156.1(4)

Symmetry transformations used to generate equivalent atoms.

#1 -x+1,-y+1,-z+2

Crystallographic Data for 10b



Solid State Packing of 10b

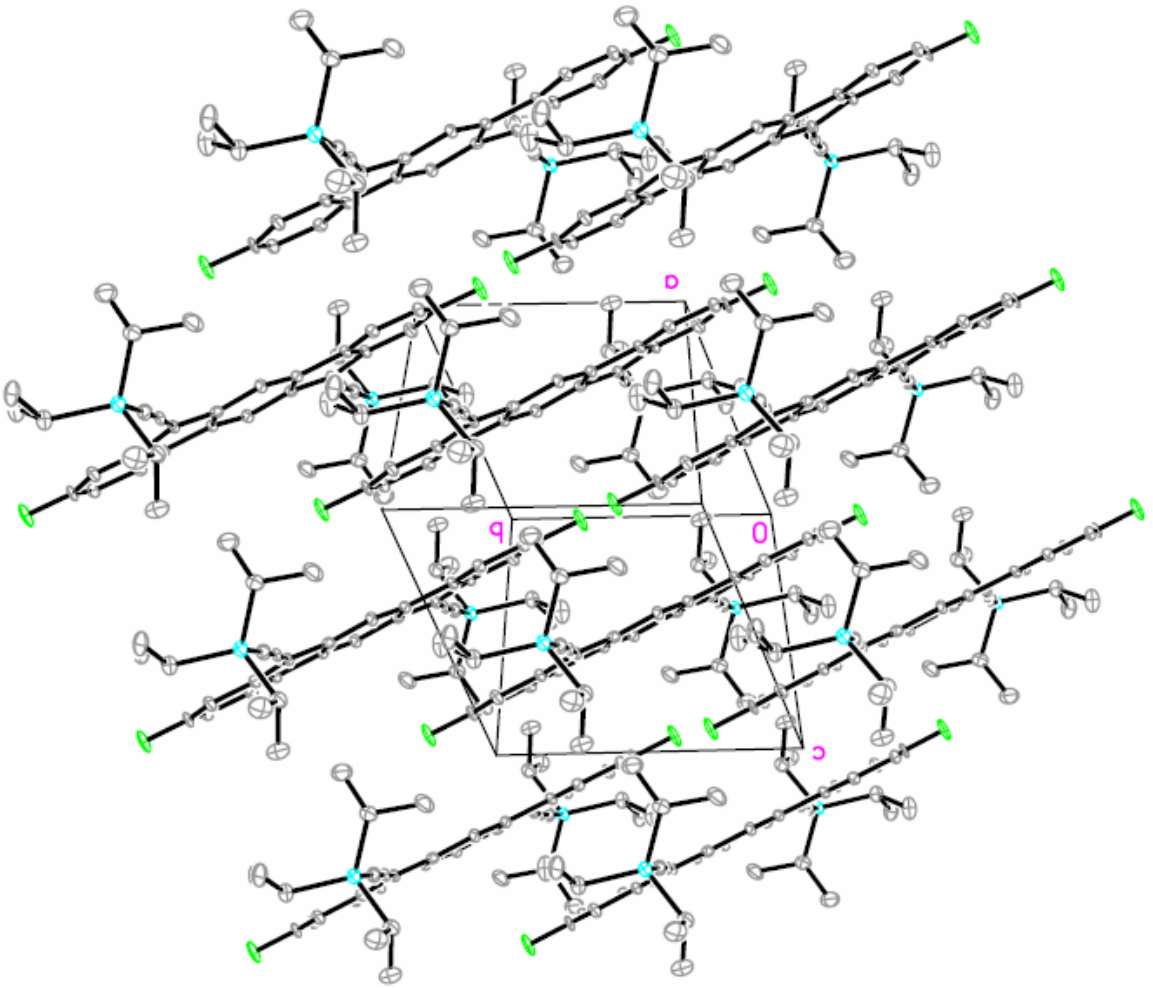


Table 7. Crystal data and structure refinement for **10b**.

Identification code	mh66	
Empirical formula	C42 H50 F2 Si2	
Formula weight	649.00	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.585(3) Å	α = 86.918(5)°.
	b = 7.910(3) Å	β = 84.113(6)°.
	c = 16.802(6) Å	γ = 68.699(5)°.
Volume	934.2(5) $Å^3$	
Z	1	
Density (calculated)	1.154 Mg/m^3	
Absorption coefficient	0.132 mm^{-1}	
F(000)	348	
Crystal size	0.23 x 0.19 x 0.03 mm^3	
Theta range for data collection	1.22 to 25.00°.	
Index ranges	-9<=h<=9, -9<=k<=9, -19<=l<=19	
Reflections collected	8788	
Independent reflections	3278 [R(int) = 0.0669]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9960 and 0.9702	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3278 / 0 / 208	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0714, wR2 = 0.1545	
R indices (all data)	R1 = 0.1165, wR2 = 0.1818	
Largest diff. peak and hole	0.539 and -0.319 $e.Å^{-3}$	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **10b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	7221(2)	2459(2)	1702(1)	25(1)
F(1)	13811(4)	-3997(3)	4097(1)	47(1)
C(1)	8832(5)	5809(4)	4353(2)	20(1)
C(2)	9904(5)	3899(5)	4398(2)	20(1)
C(3)	10045(5)	2527(5)	3891(2)	20(1)
C(4)	11352(5)	813(5)	4214(2)	21(1)
C(5)	11970(5)	-922(5)	3913(2)	27(1)
C(6)	13178(5)	-2268(5)	4372(2)	29(1)
C(7)	13733(5)	-1982(5)	5084(2)	27(1)
C(8)	13115(5)	-225(5)	5375(2)	25(1)
C(9)	11943(5)	1166(5)	4930(2)	20(1)
C(10)	11053(5)	3141(5)	5062(2)	19(1)
C(11)	9099(5)	2633(5)	3197(2)	21(1)
C(12)	8331(5)	2596(5)	2609(2)	27(1)
C(13)	7649(6)	-5(6)	1525(3)	38(1)
C(14)	7811(8)	-1208(6)	2279(3)	55(1)
C(15)	6164(7)	-216(6)	1014(3)	47(1)
C(16)	8464(6)	3378(6)	858(2)	36(1)
C(17)	10621(6)	2549(7)	859(3)	52(1)
C(18)	7851(7)	3200(7)	36(2)	51(1)
C(19)	4625(5)	3894(6)	1860(2)	32(1)
C(20)	3631(7)	3247(7)	2581(3)	50(1)
C(21)	4310(6)	5898(6)	1926(3)	46(1)

Table 9. Bond lengths [Å] and angles [°] for **10b**.

Si(1)-C(12)	1.841(4)
Si(1)-C(19)	1.881(4)
Si(1)-C(16)	1.882(4)
Si(1)-C(13)	1.891(4)
F(1)-C(6)	1.364(4)
C(1)-C(10)#1	1.350(5)
C(1)-C(2)	1.435(5)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.383(5)
C(2)-C(10)	1.453(4)
C(3)-C(11)	1.413(5)
C(3)-C(4)	1.473(5)
C(4)-C(5)	1.385(5)
C(4)-C(9)	1.402(5)
C(5)-C(6)	1.384(5)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.364(5)
C(7)-C(8)	1.394(5)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.377(5)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.478(5)
C(10)-C(1)#1	1.350(5)
C(11)-C(12)	1.204(5)
C(13)-C(14)	1.530(6)
C(13)-C(15)	1.545(5)
C(13)-H(13A)	1.0000
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.526(6)

C(16)-C(18)	1.532(5)
C(16)-H(16A)	1.0000
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(21)	1.524(6)
C(19)-C(20)	1.525(6)
C(19)-H(19A)	1.0000
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(12)-Si(1)-C(19)	107.73(17)
C(12)-Si(1)-C(16)	105.95(17)
C(19)-Si(1)-C(16)	111.57(19)
C(12)-Si(1)-C(13)	108.60(18)
C(19)-Si(1)-C(13)	112.81(19)
C(16)-Si(1)-C(13)	109.88(19)
C(10)#1-C(1)-C(2)	117.8(3)
C(10)#1-C(1)-H(1A)	121.1
C(2)-C(1)-H(1A)	121.1
C(3)-C(2)-C(1)	130.1(3)
C(3)-C(2)-C(10)	109.6(3)
C(1)-C(2)-C(10)	120.3(3)
C(2)-C(3)-C(11)	128.8(3)
C(2)-C(3)-C(4)	107.7(3)
C(11)-C(3)-C(4)	123.4(3)
C(5)-C(4)-C(9)	121.7(3)
C(5)-C(4)-C(3)	129.4(3)
C(9)-C(4)-C(3)	108.8(3)
C(6)-C(5)-C(4)	115.4(3)

C(6)-C(5)-H(5A)	122.3
C(4)-C(5)-H(5A)	122.3
F(1)-C(6)-C(7)	118.4(3)
F(1)-C(6)-C(5)	117.2(3)
C(7)-C(6)-C(5)	124.4(3)
C(6)-C(7)-C(8)	119.4(3)
C(6)-C(7)-H(7A)	120.3
C(8)-C(7)-H(7A)	120.3
C(9)-C(8)-C(7)	118.3(3)
C(9)-C(8)-H(8A)	120.9
C(7)-C(8)-H(8A)	120.9
C(8)-C(9)-C(4)	120.7(3)
C(8)-C(9)-C(10)	132.0(3)
C(4)-C(9)-C(10)	107.3(3)
C(1)#1-C(10)-C(2)	121.9(3)
C(1)#1-C(10)-C(9)	131.7(3)
C(2)-C(10)-C(9)	106.4(3)
C(12)-C(11)-C(3)	175.5(4)
C(11)-C(12)-Si(1)	178.0(3)
C(14)-C(13)-C(15)	110.1(4)
C(14)-C(13)-Si(1)	115.4(3)
C(15)-C(13)-Si(1)	111.9(3)
C(14)-C(13)-H(13A)	106.3
C(15)-C(13)-H(13A)	106.3
Si(1)-C(13)-H(13A)	106.3
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(18)	110.7(4)
C(17)-C(16)-Si(1)	112.2(3)
C(18)-C(16)-Si(1)	113.3(3)
C(17)-C(16)-H(16A)	106.8
C(18)-C(16)-H(16A)	106.8
Si(1)-C(16)-H(16A)	106.8
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(21)-C(19)-C(20)	110.8(3)
C(21)-C(19)-Si(1)	111.8(3)
C(20)-C(19)-Si(1)	112.1(3)
C(21)-C(19)-H(19A)	107.3
C(20)-C(19)-H(19A)	107.3
Si(1)-C(19)-H(19A)	107.3
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5

H(21B)-C(21)-H(21C) 109.5

Symmetry transformations used to generate equivalent atoms.
#1 -x+2,-y+1,-z+1

Table 10. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **10b**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	25(1)	24(1)	27(1)	-2(1)	-6(1)	-8(1)
F(1)	61(2)	10(1)	57(2)	-7(1)	-8(1)	4(1)
C(1)	16(2)	14(2)	26(2)	6(2)	-8(2)	-1(2)
C(2)	14(2)	21(2)	24(2)	1(2)	-3(1)	-7(2)
C(3)	16(2)	13(2)	27(2)	0(2)	-3(2)	-3(2)
C(4)	18(2)	12(2)	29(2)	3(2)	0(2)	-1(2)
C(5)	26(2)	18(2)	31(2)	-4(2)	-2(2)	-2(2)
C(6)	28(2)	6(2)	46(2)	-4(2)	0(2)	2(2)
C(7)	23(2)	15(2)	39(2)	5(2)	-1(2)	-2(2)
C(8)	19(2)	20(2)	31(2)	0(2)	-2(2)	-5(2)
C(9)	16(2)	14(2)	27(2)	1(2)	-2(2)	-1(2)
C(10)	14(2)	14(2)	28(2)	2(2)	-3(1)	-2(2)
C(11)	22(2)	11(2)	27(2)	-2(2)	1(2)	-4(2)
C(12)	28(2)	23(2)	31(2)	1(2)	-4(2)	-9(2)
C(13)	43(3)	30(2)	44(3)	-5(2)	-2(2)	-16(2)
C(14)	73(4)	35(3)	61(3)	6(2)	-21(3)	-23(3)
C(15)	65(3)	41(3)	48(3)	-8(2)	-13(2)	-32(3)
C(16)	37(3)	33(3)	34(2)	-5(2)	2(2)	-11(2)
C(17)	38(3)	65(4)	54(3)	-2(3)	8(2)	-22(3)
C(18)	55(3)	59(3)	35(3)	9(2)	-2(2)	-16(3)
C(19)	26(2)	37(3)	31(2)	-5(2)	-7(2)	-9(2)
C(20)	42(3)	59(3)	48(3)	-11(2)	7(2)	-22(3)
C(21)	34(3)	34(3)	61(3)	-7(2)	-5(2)	1(2)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **10b**.

	x	y	z	U(eq)
H(1A)	8066	6319	3924	24
H(5A)	11591	-1171	3424	32
H(7A)	14535	-2972	5379	33
H(8A)	13492	7	5867	29
H(13A)	8903	-500	1201	46
H(14A)	8035	-2454	2128	82
H(14B)	6629	-747	2629	82
H(14C)	8873	-1194	2562	82
H(15A)	6437	-1508	934	70
H(15B)	6223	393	493	70
H(15C)	4892	333	1289	70
H(16A)	8090	4706	951	43
H(17A)	11209	3065	412	79
H(17B)	11042	1231	801	79
H(17C)	10996	2818	1364	79
H(18A)	8541	3703	-377	77
H(18B)	6482	3867	27	77
H(18C)	8137	1916	-69	77
H(19A)	4019	3765	1376	38
H(20A)	2286	4028	2641	74
H(20B)	4228	3304	3065	74
H(20C)	3740	1993	2502	74
H(21A)	2945	6600	2008	69
H(21B)	4841	6318	1432	69
H(21C)	4942	6066	2379	69

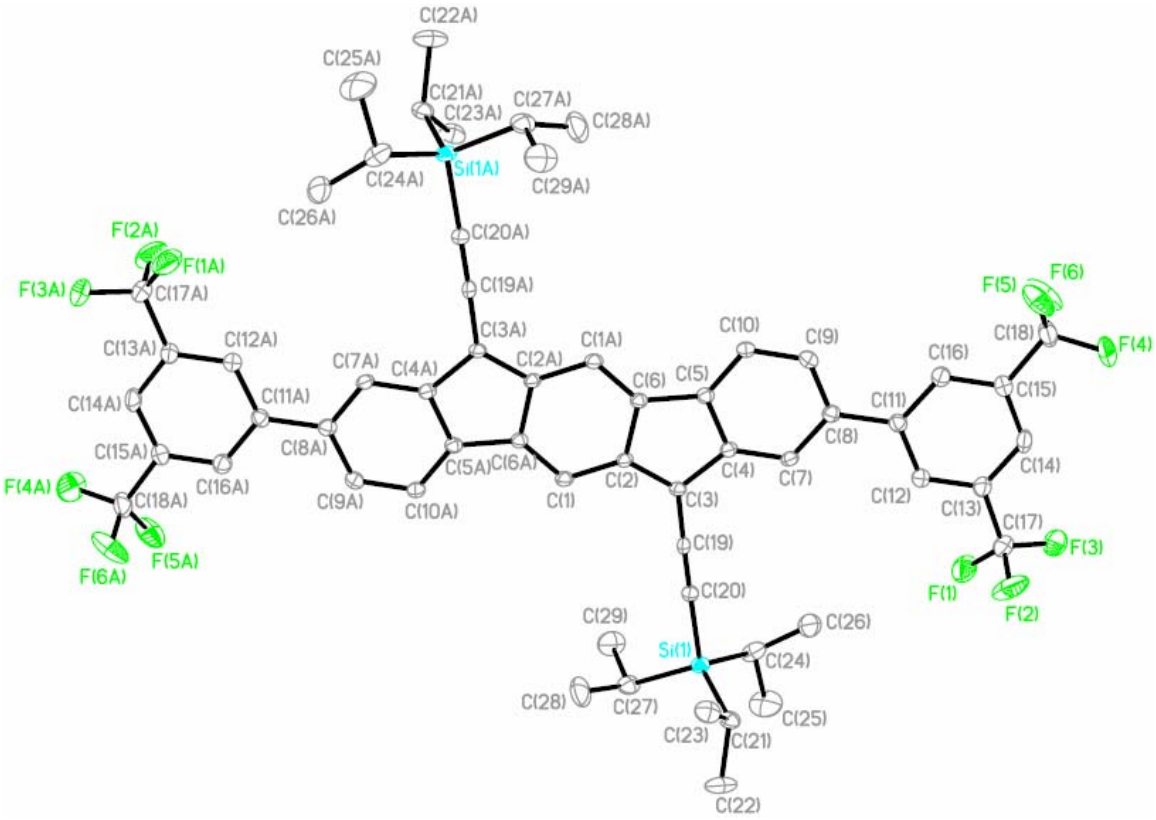
Table 12. Torsion angles [°] for **10b**.

C(10)#1-C(1)-C(2)-C(3)	179.8(4)
C(10)#1-C(1)-C(2)-C(10)	0.6(5)
C(1)-C(2)-C(3)-C(11)	-2.6(6)
C(10)-C(2)-C(3)-C(11)	176.6(3)
C(1)-C(2)-C(3)-C(4)	179.6(3)
C(10)-C(2)-C(3)-C(4)	-1.2(4)
C(2)-C(3)-C(4)-C(5)	-178.7(4)
C(11)-C(3)-C(4)-C(5)	3.3(6)
C(2)-C(3)-C(4)-C(9)	1.8(4)
C(11)-C(3)-C(4)-C(9)	-176.1(3)
C(9)-C(4)-C(5)-C(6)	0.9(5)
C(3)-C(4)-C(5)-C(6)	-178.5(4)
C(4)-C(5)-C(6)-F(1)	179.7(3)
C(4)-C(5)-C(6)-C(7)	1.3(6)
F(1)-C(6)-C(7)-C(8)	179.6(3)
C(5)-C(6)-C(7)-C(8)	-2.0(6)
C(6)-C(7)-C(8)-C(9)	0.5(5)
C(7)-C(8)-C(9)-C(4)	1.6(5)
C(7)-C(8)-C(9)-C(10)	-179.9(3)
C(5)-C(4)-C(9)-C(8)	-2.3(5)
C(3)-C(4)-C(9)-C(8)	177.2(3)
C(5)-C(4)-C(9)-C(10)	178.8(3)
C(3)-C(4)-C(9)-C(10)	-1.6(4)
C(3)-C(2)-C(10)-C(1)#1	-180.0(3)
C(1)-C(2)-C(10)-C(1)#1	-0.7(6)
C(3)-C(2)-C(10)-C(9)	0.2(4)
C(1)-C(2)-C(10)-C(9)	179.5(3)
C(8)-C(9)-C(10)-C(1)#1	2.5(7)
C(4)-C(9)-C(10)-C(1)#1	-178.9(4)
C(8)-C(9)-C(10)-C(2)	-177.8(4)
C(4)-C(9)-C(10)-C(2)	0.9(4)
C(2)-C(3)-C(11)-C(12)	-165(5)
C(4)-C(3)-C(11)-C(12)	12(5)
C(3)-C(11)-C(12)-Si(1)	-30(14)

C(19)-Si(1)-C(12)-C(11)	153(10)
C(16)-Si(1)-C(12)-C(11)	-88(10)
C(13)-Si(1)-C(12)-C(11)	30(10)
C(12)-Si(1)-C(13)-C(14)	30.1(4)
C(19)-Si(1)-C(13)-C(14)	-89.2(4)
C(16)-Si(1)-C(13)-C(14)	145.6(3)
C(12)-Si(1)-C(13)-C(15)	157.0(3)
C(19)-Si(1)-C(13)-C(15)	37.7(4)
C(16)-Si(1)-C(13)-C(15)	-87.5(3)
C(12)-Si(1)-C(16)-C(17)	48.2(3)
C(19)-Si(1)-C(16)-C(17)	165.2(3)
C(13)-Si(1)-C(16)-C(17)	-68.9(3)
C(12)-Si(1)-C(16)-C(18)	174.4(3)
C(19)-Si(1)-C(16)-C(18)	-68.6(3)
C(13)-Si(1)-C(16)-C(18)	57.3(4)
C(12)-Si(1)-C(19)-C(21)	65.3(3)
C(16)-Si(1)-C(19)-C(21)	-50.6(3)
C(13)-Si(1)-C(19)-C(21)	-174.8(3)
C(12)-Si(1)-C(19)-C(20)	-59.8(3)
C(16)-Si(1)-C(19)-C(20)	-175.7(3)
C(13)-Si(1)-C(19)-C(20)	60.0(3)

Symmetry transformations used to generate equivalent atoms.
#1 -x+2,-y+1,-z+1

Crystallographic Data for 10h



Solid State Packing of 10h

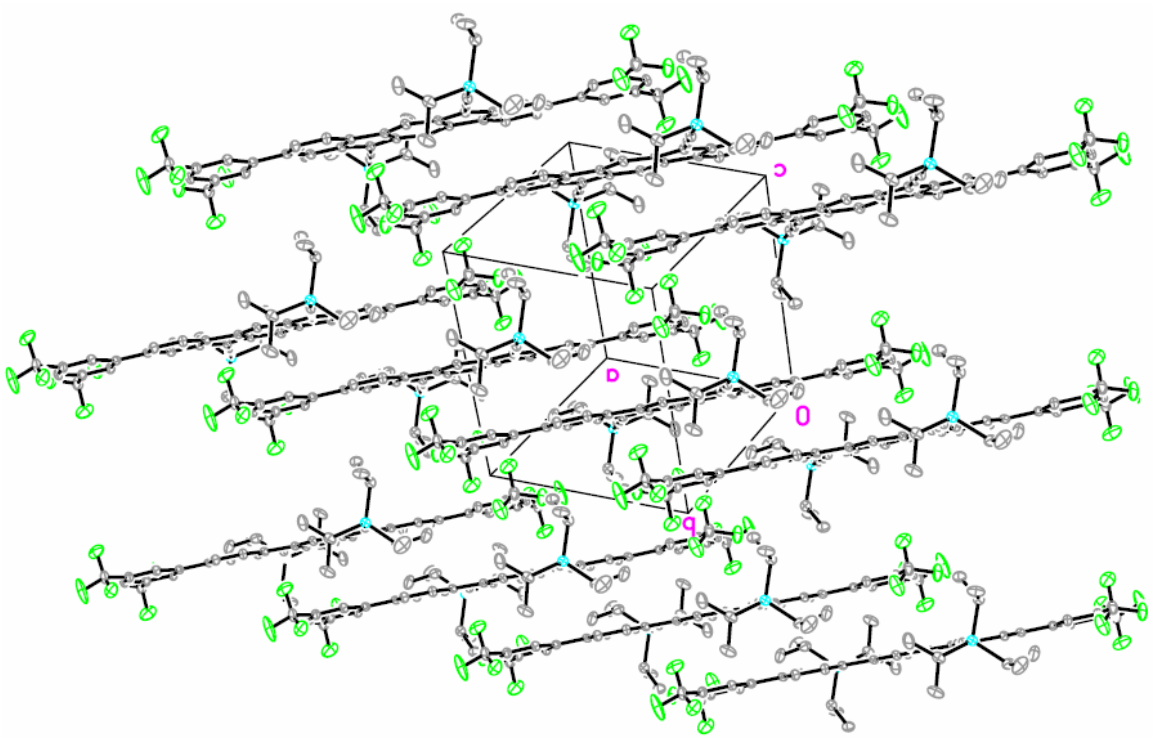


Table 13. Crystal data and structure refinement for **10h**.

Identification code	mh69	
Empirical formula	C58 H56 F12 Si2	
Formula weight	1037.21	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.268(2) Å	α = 80.996(4)°.
	b = 11.807(3) Å	β = 79.842(4)°.
	c = 12.531(3) Å	γ = 76.792(4)°.
Volume	1304.4(5) $Å^3$	
Z	1	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.149 mm^{-1}	
F(000)	540	
Crystal size	0.37 x 0.05 x 0.02 mm^3	
Theta range for data collection	1.66 to 25.00°.	
Index ranges	-11<=h<=11, -14<=k<=14, -14<=l<=14	
Reflections collected	12578	
Independent reflections	4559 [R(int) = 0.0558]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9970 and 0.9470	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4559 / 0 / 437	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1127	
R indices (all data)	R1 = 0.1017, wR2 = 0.1311	
Largest diff. peak and hole	0.330 and -0.263 $e.Å^{-3}$	

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **10h**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	4838(1)	2869(1)	8632(1)	28(1)
F(1)	-90(3)	-70(2)	8357(2)	85(1)
F(2)	252(3)	-1662(3)	9416(2)	89(1)
F(3)	-1541(2)	-1256(2)	8481(2)	69(1)
F(4)	-47(3)	-4596(3)	6425(2)	124(1)
F(5)	2166(3)	-5068(2)	5656(2)	71(1)
F(6)	644(3)	-3786(2)	4849(2)	83(1)
C(1)	9741(3)	938(3)	5660(2)	26(1)
C(2)	8642(3)	274(2)	5673(2)	22(1)
C(3)	7204(3)	372(2)	6245(2)	23(1)
C(4)	6534(3)	-541(2)	5966(2)	23(1)
C(5)	7589(3)	-1169(2)	5209(2)	24(1)
C(6)	8935(3)	-673(2)	5000(2)	22(1)
C(7)	5145(3)	-803(3)	6330(2)	25(1)
C(8)	4767(3)	-1733(2)	5950(2)	26(1)
C(9)	5828(4)	-2364(3)	5204(3)	31(1)
C(10)	7223(3)	-2092(3)	4825(2)	28(1)
C(11)	3284(3)	-2057(3)	6352(2)	27(1)
C(12)	2274(3)	-1510(3)	7173(3)	33(1)
C(13)	896(3)	-1810(3)	7549(3)	34(1)
C(14)	486(4)	-2678(3)	7123(3)	36(1)
C(15)	1471(3)	-3239(3)	6316(3)	33(1)
C(16)	2842(4)	-2927(3)	5927(3)	32(1)
C(17)	-125(4)	-1204(4)	8446(3)	48(1)
C(18)	1047(4)	-4155(3)	5815(3)	46(1)
C(19)	6474(3)	1181(3)	6990(2)	25(1)
C(20)	5824(3)	1864(3)	7632(2)	29(1)
C(21)	4794(4)	2016(3)	10025(3)	34(1)
C(22)	4486(6)	2799(4)	10952(3)	54(1)
C(23)	6154(5)	1027(3)	10179(4)	45(1)

C(24)	2900(4)	3414(3)	8270(3)	45(1)
C(25)	1901(6)	4303(6)	8996(5)	80(2)
C(26)	2124(5)	2416(5)	8230(4)	62(1)
C(27)	5884(4)	4088(3)	8442(3)	40(1)
C(28)	7494(5)	3669(4)	8640(5)	65(1)
C(29)	5790(7)	4822(4)	7326(4)	64(1)

Table 15. Bond lengths [Å] and angles [°] for **10h**.

Si(1)-C(20)	1.839(3)
Si(1)-C(21)	1.874(3)
Si(1)-C(24)	1.874(4)
Si(1)-C(27)	1.875(3)
F(1)-C(17)	1.334(4)
F(2)-C(17)	1.324(4)
F(3)-C(17)	1.321(4)
F(4)-C(18)	1.314(4)
F(5)-C(18)	1.327(4)
F(6)-C(18)	1.309(4)
C(1)-C(6)#1	1.355(4)
C(1)-C(2)	1.417(4)
C(1)-H(1)	0.95(3)
C(2)-C(3)	1.386(4)
C(2)-C(6)	1.453(4)
C(3)-C(19)	1.416(4)
C(3)-C(4)	1.473(4)
C(4)-C(7)	1.376(4)
C(4)-C(5)	1.402(4)
C(5)-C(10)	1.387(4)
C(5)-C(6)	1.463(4)
C(6)-C(1)#1	1.355(4)
C(7)-C(8)	1.398(4)
C(7)-H(7)	0.95(3)
C(8)-C(9)	1.398(4)
C(8)-C(11)	1.491(4)
C(9)-C(10)	1.388(4)
C(9)-H(9)	0.92(3)
C(10)-H(10)	0.97(3)
C(11)-C(12)	1.394(4)
C(11)-C(16)	1.396(4)
C(12)-C(13)	1.386(4)
C(12)-H(12)	0.98(3)
C(13)-C(14)	1.379(4)

C(13)-C(17)	1.495(4)
C(14)-C(15)	1.379(4)
C(14)-H(14)	0.94(3)
C(15)-C(16)	1.387(4)
C(15)-C(18)	1.488(4)
C(16)-H(16)	0.94(3)
C(19)-C(20)	1.212(4)
C(21)-C(23)	1.527(5)
C(21)-C(22)	1.544(5)
C(21)-H(21)	0.86(2)
C(22)-H(22A)	1.03(4)
C(22)-H(22B)	0.97(3)
C(22)-H(22C)	0.97(4)
C(23)-H(23A)	0.99(3)
C(23)-H(23B)	0.96(3)
C(23)-H(23C)	0.99(3)
C(24)-C(26)	1.526(6)
C(24)-C(25)	1.531(6)
C(24)-H(24)	0.90(3)
C(25)-H(25A)	0.98(4)
C(25)-H(25B)	0.95(4)
C(25)-H(25C)	1.05(4)
C(26)-H(26A)	1.00(4)
C(26)-H(26B)	0.93(4)
C(26)-H(26C)	0.98(4)
C(27)-C(28)	1.513(6)
C(27)-C(29)	1.531(5)
C(27)-H(27)	0.94(3)
C(28)-H(28A)	1.05(5)
C(28)-H(28B)	0.97(4)
C(28)-H(28C)	0.91(4)
C(29)-H(29A)	0.93(5)
C(29)-H(29B)	0.95(4)
C(29)-H(29C)	0.99(4)
C(20)-Si(1)-C(21)	107.99(14)
C(20)-Si(1)-C(24)	105.72(15)

C(21)-Si(1)-C(24)	111.06(17)
C(20)-Si(1)-C(27)	106.49(15)
C(21)-Si(1)-C(27)	113.66(16)
C(24)-Si(1)-C(27)	111.43(18)
C(6)#1-C(1)-C(2)	118.4(3)
C(6)#1-C(1)-H(1)	123.2(16)
C(2)-C(1)-H(1)	118.5(16)
C(3)-C(2)-C(1)	130.3(3)
C(3)-C(2)-C(6)	109.0(2)
C(1)-C(2)-C(6)	120.7(2)
C(2)-C(3)-C(19)	127.4(3)
C(2)-C(3)-C(4)	108.3(2)
C(19)-C(3)-C(4)	124.3(3)
C(7)-C(4)-C(5)	122.1(3)
C(7)-C(4)-C(3)	130.1(3)
C(5)-C(4)-C(3)	107.8(2)
C(10)-C(5)-C(4)	118.9(3)
C(10)-C(5)-C(6)	132.9(3)
C(4)-C(5)-C(6)	108.3(2)
C(1)#1-C(6)-C(2)	121.0(3)
C(1)#1-C(6)-C(5)	132.4(3)
C(2)-C(6)-C(5)	106.6(2)
C(4)-C(7)-C(8)	119.5(3)
C(4)-C(7)-H(7)	121.1(16)
C(8)-C(7)-H(7)	119.4(16)
C(7)-C(8)-C(9)	118.1(3)
C(7)-C(8)-C(11)	120.7(3)
C(9)-C(8)-C(11)	121.2(3)
C(10)-C(9)-C(8)	122.5(3)
C(10)-C(9)-H(9)	118.9(19)
C(8)-C(9)-H(9)	118.6(19)
C(5)-C(10)-C(9)	118.9(3)
C(5)-C(10)-H(10)	120.1(15)
C(9)-C(10)-H(10)	121.0(15)
C(12)-C(11)-C(16)	116.7(3)
C(12)-C(11)-C(8)	121.7(3)

C(16)-C(11)-C(8)	121.6(3)
C(13)-C(12)-C(11)	121.9(3)
C(13)-C(12)-H(12)	116.0(17)
C(11)-C(12)-H(12)	122.1(17)
C(14)-C(13)-C(12)	120.5(3)
C(14)-C(13)-C(17)	120.3(3)
C(12)-C(13)-C(17)	119.2(3)
C(13)-C(14)-C(15)	118.7(3)
C(13)-C(14)-H(14)	118.4(17)
C(15)-C(14)-H(14)	122.8(17)
C(14)-C(15)-C(16)	120.9(3)
C(14)-C(15)-C(18)	120.2(3)
C(16)-C(15)-C(18)	118.9(3)
C(15)-C(16)-C(11)	121.3(3)
C(15)-C(16)-H(16)	118.3(19)
C(11)-C(16)-H(16)	120.2(19)
F(3)-C(17)-F(2)	106.9(3)
F(3)-C(17)-F(1)	106.3(3)
F(2)-C(17)-F(1)	105.8(3)
F(3)-C(17)-C(13)	113.0(3)
F(2)-C(17)-C(13)	111.7(3)
F(1)-C(17)-C(13)	112.6(3)
F(6)-C(18)-F(4)	107.4(3)
F(6)-C(18)-F(5)	104.6(3)
F(4)-C(18)-F(5)	105.1(3)
F(6)-C(18)-C(15)	113.5(3)
F(4)-C(18)-C(15)	112.9(3)
F(5)-C(18)-C(15)	112.7(3)
C(20)-C(19)-C(3)	178.7(3)
C(19)-C(20)-Si(1)	178.7(3)
C(23)-C(21)-C(22)	110.1(3)
C(23)-C(21)-Si(1)	115.2(3)
C(22)-C(21)-Si(1)	113.2(3)
C(23)-C(21)-H(21)	104.8(18)
C(22)-C(21)-H(21)	109.7(18)
Si(1)-C(21)-H(21)	103.2(17)

C(21)-C(22)-H(22A)	107(2)
C(21)-C(22)-H(22B)	112(2)
H(22A)-C(22)-H(22B)	105(3)
C(21)-C(22)-H(22C)	111(2)
H(22A)-C(22)-H(22C)	109(3)
H(22B)-C(22)-H(22C)	113(3)
C(21)-C(23)-H(23A)	108.8(18)
C(21)-C(23)-H(23B)	110.3(19)
H(23A)-C(23)-H(23B)	113(3)
C(21)-C(23)-H(23C)	111.7(19)
H(23A)-C(23)-H(23C)	107(3)
H(23B)-C(23)-H(23C)	107(3)
C(26)-C(24)-C(25)	110.6(4)
C(26)-C(24)-Si(1)	112.3(3)
C(25)-C(24)-Si(1)	113.9(3)
C(26)-C(24)-H(24)	108.0(19)
C(25)-C(24)-H(24)	108(2)
Si(1)-C(24)-H(24)	103.9(19)
C(24)-C(25)-H(25A)	110(3)
C(24)-C(25)-H(25B)	110(2)
H(25A)-C(25)-H(25B)	113(4)
C(24)-C(25)-H(25C)	108(2)
H(25A)-C(25)-H(25C)	110(4)
H(25B)-C(25)-H(25C)	105(3)
C(24)-C(26)-H(26A)	115(3)
C(24)-C(26)-H(26B)	108(2)
H(26A)-C(26)-H(26B)	108(3)
C(24)-C(26)-H(26C)	109(3)
H(26A)-C(26)-H(26C)	107(4)
H(26B)-C(26)-H(26C)	109(3)
C(28)-C(27)-C(29)	111.0(4)
C(28)-C(27)-Si(1)	113.1(3)
C(29)-C(27)-Si(1)	112.0(3)
C(28)-C(27)-H(27)	104.8(19)
C(29)-C(27)-H(27)	107(2)
Si(1)-C(27)-H(27)	108.8(19)

C(27)-C(28)-H(28A)	115(2)
C(27)-C(28)-H(28B)	110(2)
H(28A)-C(28)-H(28B)	110(3)
C(27)-C(28)-H(28C)	112(3)
H(28A)-C(28)-H(28C)	104(4)
H(28B)-C(28)-H(28C)	105(3)
C(27)-C(29)-H(29A)	111(3)
C(27)-C(29)-H(29B)	109(2)
H(29A)-C(29)-H(29B)	109(4)
C(27)-C(29)-H(29C)	109(2)
H(29A)-C(29)-H(29C)	109(4)
H(29B)-C(29)-H(29C)	110(3)

Symmetry transformations used to generate equivalent atoms.

#1 -x+2,-y,-z+1

Table 16. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **10h**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	32(1)	25(1)	27(1)	-9(1)	1(1)	-3(1)
F(1)	83(2)	77(2)	98(2)	-52(2)	45(2)	-36(1)
F(2)	65(2)	158(3)	33(1)	-17(2)	1(1)	-4(2)
F(3)	32(1)	103(2)	76(2)	-36(1)	12(1)	-19(1)
F(4)	131(3)	142(3)	134(3)	-83(2)	63(2)	-117(2)
F(5)	79(2)	36(1)	109(2)	-24(1)	-40(2)	-6(1)
F(6)	122(2)	46(1)	102(2)	-15(1)	-75(2)	-13(1)
C(1)	32(2)	23(2)	23(2)	-7(1)	1(1)	-8(1)
C(2)	27(2)	19(2)	20(2)	-5(1)	2(1)	-6(1)
C(3)	27(2)	22(2)	22(2)	-8(1)	0(1)	-5(1)
C(4)	27(2)	22(2)	21(2)	-4(1)	0(1)	-5(1)
C(5)	28(2)	21(2)	22(2)	-3(1)	-2(1)	-6(1)
C(6)	26(2)	19(2)	21(2)	-4(1)	-2(1)	-5(1)
C(7)	27(2)	27(2)	21(2)	-7(1)	2(1)	-5(1)
C(8)	31(2)	24(2)	22(2)	-1(1)	-3(1)	-7(1)
C(9)	34(2)	28(2)	34(2)	-11(2)	-3(2)	-10(2)
C(10)	28(2)	28(2)	30(2)	-13(2)	2(2)	-5(2)
C(11)	30(2)	27(2)	27(2)	-2(1)	-6(1)	-8(1)
C(12)	29(2)	39(2)	32(2)	-10(2)	-1(2)	-10(2)
C(13)	29(2)	43(2)	33(2)	-5(2)	-2(2)	-12(2)
C(14)	30(2)	43(2)	38(2)	3(2)	-1(2)	-20(2)
C(15)	32(2)	32(2)	37(2)	-4(2)	-6(2)	-11(2)
C(16)	31(2)	32(2)	32(2)	-4(2)	-2(2)	-8(2)
C(17)	36(2)	68(3)	41(2)	-15(2)	6(2)	-18(2)
C(18)	39(2)	44(2)	62(3)	-9(2)	-5(2)	-20(2)
C(19)	23(2)	27(2)	29(2)	-5(1)	2(1)	-13(1)
C(20)	29(2)	29(2)	30(2)	-12(2)	3(1)	-9(1)
C(21)	41(2)	29(2)	35(2)	-12(2)	-3(2)	-8(2)
C(22)	96(4)	38(2)	25(2)	-9(2)	-6(2)	-5(3)
C(23)	58(3)	34(2)	43(3)	-5(2)	-12(2)	-6(2)
C(24)	41(2)	54(3)	31(2)	-5(2)	0(2)	3(2)

C(25)	51(3)	87(4)	89(4)	-38(4)	-10(3)	29(3)
C(26)	36(3)	99(4)	54(3)	-21(3)	-5(2)	-16(3)
C(27)	56(3)	26(2)	39(2)	-10(2)	1(2)	-11(2)
C(28)	59(3)	52(3)	92(4)	-15(3)	-6(3)	-31(3)
C(29)	98(4)	41(3)	51(3)	4(2)	-2(3)	-25(3)

Table 17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **10h**.

	x	y	z	U(eq)
H(1)	9510(30)	1550(20)	6110(20)	26(8)
H(7)	4430(30)	-360(20)	6830(20)	25(8)
H(9)	5600(30)	-2990(30)	4970(20)	40(9)
H(10)	7940(30)	-2540(20)	4310(20)	22(7)
H(12)	2510(30)	-910(30)	7530(20)	37(9)
H(14)	-450(30)	-2870(20)	7400(20)	31(8)
H(16)	3450(30)	-3290(30)	5330(20)	41(10)
H(21)	4070(30)	1670(20)	10070(20)	14(8)
H(22A)	5420(40)	3150(30)	10910(30)	71(13)
H(22B)	4400(40)	2340(30)	11670(30)	59(11)
H(22C)	3630(40)	3430(40)	10860(30)	74(14)
H(23A)	6320(30)	530(30)	9580(30)	46(10)
H(23B)	6010(30)	600(30)	10890(30)	37(9)
H(23C)	7080(40)	1330(30)	10120(30)	52(11)
H(24)	3050(30)	3790(30)	7590(20)	35(9)
H(25A)	1720(50)	3940(40)	9750(40)	93(18)
H(25B)	1000(50)	4650(30)	8700(30)	70(13)
H(25C)	2460(40)	4990(30)	8960(30)	65(13)
H(26A)	2670(50)	1840(40)	7720(40)	100(16)
H(26B)	1190(40)	2740(30)	8010(30)	60(12)
H(26C)	1980(50)	1980(40)	8960(40)	89(16)
H(27)	5440(30)	4600(30)	8970(30)	46(10)
H(28A)	7640(50)	3190(40)	9410(40)	104(18)
H(28B)	8000(40)	4330(30)	8520(30)	60(11)
H(28C)	8030(40)	3170(40)	8160(30)	71(15)
H(29A)	4800(60)	5130(40)	7230(40)	100(20)
H(29B)	6240(40)	4340(30)	6770(30)	63(13)
H(29C)	6320(40)	5470(40)	7280(30)	73(13)

Table 18. Torsion angles [°] for **10h**.

C(6)#1-C(1)-C(2)-C(3)	-178.5(3)
C(6)#1-C(1)-C(2)-C(6)	0.5(5)
C(1)-C(2)-C(3)-C(19)	-0.8(5)
C(6)-C(2)-C(3)-C(19)	-179.9(3)
C(1)-C(2)-C(3)-C(4)	-179.8(3)
C(6)-C(2)-C(3)-C(4)	1.1(3)
C(2)-C(3)-C(4)-C(7)	179.3(3)
C(19)-C(3)-C(4)-C(7)	0.3(5)
C(2)-C(3)-C(4)-C(5)	-0.8(3)
C(19)-C(3)-C(4)-C(5)	-179.8(3)
C(7)-C(4)-C(5)-C(10)	-0.7(4)
C(3)-C(4)-C(5)-C(10)	179.4(3)
C(7)-C(4)-C(5)-C(6)	-179.9(3)
C(3)-C(4)-C(5)-C(6)	0.2(3)
C(3)-C(2)-C(6)-C(1)#1	178.7(3)
C(1)-C(2)-C(6)-C(1)#1	-0.5(5)
C(3)-C(2)-C(6)-C(5)	-1.0(3)
C(1)-C(2)-C(6)-C(5)	179.8(3)
C(10)-C(5)-C(6)-C(1)#1	1.9(6)
C(4)-C(5)-C(6)-C(1)#1	-179.1(3)
C(10)-C(5)-C(6)-C(2)	-178.6(3)
C(4)-C(5)-C(6)-C(2)	0.5(3)
C(5)-C(4)-C(7)-C(8)	0.9(4)
C(3)-C(4)-C(7)-C(8)	-179.2(3)
C(4)-C(7)-C(8)-C(9)	-0.2(4)
C(4)-C(7)-C(8)-C(11)	178.4(3)
C(7)-C(8)-C(9)-C(10)	-0.6(5)
C(11)-C(8)-C(9)-C(10)	-179.3(3)
C(4)-C(5)-C(10)-C(9)	-0.1(4)
C(6)-C(5)-C(10)-C(9)	178.8(3)
C(8)-C(9)-C(10)-C(5)	0.8(5)
C(7)-C(8)-C(11)-C(12)	-4.9(4)
C(9)-C(8)-C(11)-C(12)	173.7(3)
C(7)-C(8)-C(11)-C(16)	175.4(3)

C(9)-C(8)-C(11)-C(16)	-6.0(4)
C(16)-C(11)-C(12)-C(13)	-0.2(5)
C(8)-C(11)-C(12)-C(13)	-179.9(3)
C(11)-C(12)-C(13)-C(14)	0.7(5)
C(11)-C(12)-C(13)-C(17)	178.9(3)
C(12)-C(13)-C(14)-C(15)	-0.2(5)
C(17)-C(13)-C(14)-C(15)	-178.3(3)
C(13)-C(14)-C(15)-C(16)	-0.8(5)
C(13)-C(14)-C(15)-C(18)	-178.1(3)
C(14)-C(15)-C(16)-C(11)	1.4(5)
C(18)-C(15)-C(16)-C(11)	178.7(3)
C(12)-C(11)-C(16)-C(15)	-0.8(5)
C(8)-C(11)-C(16)-C(15)	178.9(3)
C(14)-C(13)-C(17)-F(3)	-23.3(5)
C(12)-C(13)-C(17)-F(3)	158.4(3)
C(14)-C(13)-C(17)-F(2)	97.3(4)
C(12)-C(13)-C(17)-F(2)	-80.9(4)
C(14)-C(13)-C(17)-F(1)	-143.8(3)
C(12)-C(13)-C(17)-F(1)	38.0(5)
C(14)-C(15)-C(18)-F(6)	102.5(4)
C(16)-C(15)-C(18)-F(6)	-74.9(4)
C(14)-C(15)-C(18)-F(4)	-20.0(5)
C(16)-C(15)-C(18)-F(4)	162.6(3)
C(14)-C(15)-C(18)-F(5)	-138.8(3)
C(16)-C(15)-C(18)-F(5)	43.8(5)
C(2)-C(3)-C(19)-C(20)	-177(100)
C(4)-C(3)-C(19)-C(20)	1(14)
C(3)-C(19)-C(20)-Si(1)	64(21)
C(21)-Si(1)-C(20)-C(19)	8(11)
C(24)-Si(1)-C(20)-C(19)	-111(11)
C(27)-Si(1)-C(20)-C(19)	130(11)
C(20)-Si(1)-C(21)-C(23)	33.0(3)
C(24)-Si(1)-C(21)-C(23)	148.5(3)
C(27)-Si(1)-C(21)-C(23)	-84.9(3)
C(20)-Si(1)-C(21)-C(22)	160.9(3)
C(24)-Si(1)-C(21)-C(22)	-83.6(3)

C(27)-Si(1)-C(21)-C(22)	43.0(4)
C(20)-Si(1)-C(24)-C(26)	55.0(3)
C(21)-Si(1)-C(24)-C(26)	-61.9(3)
C(27)-Si(1)-C(24)-C(26)	170.3(3)
C(20)-Si(1)-C(24)-C(25)	-178.3(4)
C(21)-Si(1)-C(24)-C(25)	64.8(4)
C(27)-Si(1)-C(24)-C(25)	-63.0(4)
C(20)-Si(1)-C(27)-C(28)	-60.7(3)
C(21)-Si(1)-C(27)-C(28)	58.1(4)
C(24)-Si(1)-C(27)-C(28)	-175.5(3)
C(20)-Si(1)-C(27)-C(29)	65.7(4)
C(21)-Si(1)-C(27)-C(29)	-175.5(3)
C(24)-Si(1)-C(27)-C(29)	-49.1(4)

Symmetry transformations used to generate equivalent atoms.

#1 -x+2,-y,-z+1

APPENDIX C

EXPERIMENTAL DETAILS FOR CHAPTER IV

Cartesian Coordinates of Stationary Points[3]

4a

B3LYP/6-31G* = -1231.75589385 au

C	0.66924700	-1.23657100	0.00187400
C	-0.69584700	-1.26498200	0.00053200
C	-1.40986600	-0.02307300	0.03292100
C	-0.66937700	1.23672200	0.00182000
C	0.69571600	1.26513400	0.00049500
C	1.40974500	0.02322800	0.03296600
C	-2.77688800	0.24531600	0.01174800
C	-2.94860500	1.70227300	-0.03285200
C	-1.66182100	2.31148200	-0.03853400
C	1.66168000	-2.31133900	-0.03848200
C	2.77676300	-0.24517500	0.01181000
C	2.94846400	-1.70214100	-0.03283800
C	-1.53481000	3.69599800	-0.05807300
H	-0.55428500	4.16585300	-0.06187100
C	-4.09765500	2.49727700	-0.02047300
H	-5.08525900	2.04764800	0.01838900
C	1.53466400	-3.69585600	-0.05802000
H	0.55413800	-4.16570700	-0.06178400
C	4.09751600	-2.49714000	-0.02051500
H	5.08512300	-2.04751200	0.01831300
C	2.69289100	-4.48308900	-0.06838400
H	2.60626100	-5.56612300	-0.08689000
C	3.95940700	-3.88868100	-0.04495000
H	4.84731300	-4.51516900	-0.03976200
C	-3.95955100	3.88881800	-0.04490400
H	-4.84745800	4.51530400	-0.03967400
C	-2.69303800	4.48323000	-0.06839100
H	-2.60641000	5.56626400	-0.08689900
H	-1.24093200	-2.20398900	-0.04195500
H	1.24078800	2.20414200	-0.04205900

[3] Bold number refers to the molecule in Chapter IV

C	-3.86705900	-0.73726300	0.02796600
C	-4.97066400	-0.60813800	-0.83837800
C	-3.83895600	-1.83803100	0.90667000
C	-5.99760900	-1.54955600	-0.83330200
C	-4.86967600	-2.77575000	0.91253900
C	-5.95276700	-2.63701800	0.04207900
C	3.86704300	0.73728700	0.02797500
C	4.97059300	0.60792000	-0.83840800
C	3.83923100	1.83804700	0.90670100
C	5.99775000	1.54910700	-0.83337400
C	4.87016600	2.77552900	0.91252900
C	5.95318500	2.63657200	0.04201700
H	-6.83334000	-1.43649100	-1.51890300
H	-6.75661800	-3.36808900	0.04800900
H	-4.83133400	-3.61188800	1.60585700
H	-5.00086400	0.22001200	-1.53984000
H	-3.01606100	-1.93299600	1.60872400
H	5.00056500	-0.22023400	-1.53987500
H	3.01642900	1.93316900	1.60883900
H	4.83205100	3.61165800	1.60587100
H	6.75720000	3.36746300	0.04792400
H	6.83342900	1.43585500	-1.51900700

4b

B3LYP/6-31G* = -1467.71169861 au

C	-0.42602800	1.34688300	-0.00900300
C	0.91832800	1.12088400	-0.01010200
C	1.38434800	-0.23671700	-0.00500800
C	0.42603000	-1.34687000	-0.00898900
C	-0.91832700	-1.12087100	-0.01004800
C	-1.38434600	0.23672900	-0.00497100
C	2.67436000	-0.73927900	-0.00720800
C	2.58793400	-2.20175300	-0.01247700
C	1.21550900	-2.58120000	-0.01316800
C	-1.21551000	2.58121200	-0.01318100
C	-2.67435900	0.73929000	-0.00713800
C	-2.58793500	2.20176300	-0.01243700
C	0.85945600	-3.92490100	-0.01268300
H	-0.18515500	-4.22681400	-0.01239900
C	3.59059700	-3.17286700	-0.00692200
H	4.63845700	-2.88420400	0.00022500
C	-0.85946000	3.92491400	-0.01273600
H	0.18515100	4.22682800	-0.01249200

C	-3.59059800	3.17287600	-0.00687100
H	-4.63845800	2.88421100	0.00031700
C	-1.87198300	4.89439400	-0.01164100
H	-1.60479500	5.94771200	-0.01206400
C	-3.22109600	4.52243500	-0.00828100
H	-3.99011200	5.29025000	-0.00517000
C	3.22109200	-4.52242600	-0.00829200
H	3.99010700	-5.29024200	-0.00519000
C	1.87197800	-4.89438300	-0.01160100
H	1.60478900	-5.94770100	-0.01199300
H	1.63913600	1.93542400	-0.01727700
H	-1.63913700	-1.93541000	-0.01717200
C	3.93966900	0.03843600	0.00118900
C	4.65247800	0.23965600	-1.20137500
C	4.43846400	0.56904800	1.21117500
C	5.84584100	0.96757000	-1.17079000
C	5.63723600	1.28896300	1.19423500
C	6.35881500	1.49824900	0.01590200
H	6.38669400	1.12646000	-2.10195900
H	6.01766900	1.69493700	2.12983600
C	-3.93966400	-0.03843300	0.00127500
C	-4.65244900	-0.23966100	-1.20131000
C	-4.43848100	-0.56905800	1.21124400
C	-5.84580000	-0.96758600	-1.17076000
C	-5.63724100	-1.28900300	1.19426400
C	-6.35879200	-1.49828600	0.01591900
H	-6.38662500	-1.12648300	-2.10194300
H	-6.01767800	-1.69500600	2.12985000
C	4.13090100	-0.29871000	-2.51506900
H	4.03103900	-1.39017600	-2.49495200
H	3.13752000	0.10345700	-2.74663800
H	4.80214500	-0.03635700	-3.33862300
C	3.70242700	0.36524000	2.51723400
H	2.73406700	0.87935600	2.52311700
H	3.49638000	-0.69538600	2.70170400
H	4.28946600	0.74765700	3.35798200
C	7.66781100	2.25314000	0.02927900
H	8.51481600	1.57894800	0.21528800
H	7.85389900	2.75019900	-0.92880300
H	7.68305600	3.01563600	0.81552300
C	-4.13084300	0.29871800	-2.51498700
H	-4.03115900	1.39020400	-2.49491500
H	-3.13737600	-0.10329500	-2.74644700
H	-4.80197400	0.03621900	-3.33858500
C	-3.70256000	-0.36519600	2.51736200
H	-2.73378800	-0.87851900	2.52302900

H	-3.49738800	0.69553200	2.70224500
H	-4.28928000	-0.74839500	3.35797800
C	-7.66777200	-2.25320700	0.02924800
H	-8.51482800	-1.57899000	0.21492700
H	-7.85367200	-2.75051000	-0.92874600
H	-7.68314100	-3.01550700	0.81567800

4c

B3LYP/6-31G* = -1906.05420662 au

C	-1.39583000	-0.17496300	0.01897600
C	-0.92697800	1.10711700	0.01754300
C	0.48977900	1.32137500	0.04988400
C	1.39583000	0.17496300	0.01897600
C	0.92697800	-1.10711700	0.01754300
C	-0.48977900	-1.32137500	0.04988400
C	1.23763600	2.49651200	0.02600600
C	2.65800900	2.12934000	-0.01871800
C	2.75786500	0.70963200	-0.02210300
C	-2.75786500	-0.70963200	-0.02210300
C	-1.23763600	-2.49651200	0.02600600
C	-2.65800900	-2.12934000	-0.01871800
C	4.00120500	0.08810700	-0.04131200
H	4.08353500	-0.99596200	-0.04377000
C	3.81548900	2.91171700	-0.00842300
H	3.75677300	3.99534200	0.02893400
C	-4.00120500	-0.08810700	-0.04131200
H	-4.08353500	0.99596200	-0.04377000
C	-3.81548900	-2.91171700	-0.00842300
H	-3.75677300	-3.99534200	0.02893400
C	-5.15535000	-0.88161000	-0.05347000
H	-6.13274000	-0.40745500	-0.07172100
C	-5.06189300	-2.27723500	-0.03227700
H	-5.96792900	-2.87687400	-0.02848500
C	5.06189300	2.27723500	-0.03227700
H	5.96792900	2.87687400	-0.02848500
C	5.15535000	0.88161000	-0.05347000
H	6.13274000	0.40745500	-0.07172100
H	-1.60530200	1.95474900	-0.02551400
H	1.60530200	-1.95474900	-0.02551400
C	0.71578900	3.86766600	0.03470700
C	1.23763600	4.84673900	-0.83388500
C	-0.32117100	4.24465500	0.91033200
C	0.73317100	6.14278700	-0.83834200

H	2.02531400	4.57650400	-1.52973000
C	-0.82497200	5.54145800	0.90988500
H	-0.70748300	3.51927800	1.61918800
C	-0.30080500	6.49544200	0.03378000
H	1.14235500	6.88323300	-1.51803700
H	-1.61345300	5.81897900	1.60171500
C	-0.71578900	-3.86766600	0.03470700
C	-1.23763600	-4.84673900	-0.83388500
C	0.32117100	-4.24465500	0.91033200
C	-0.73317100	-6.14278700	-0.83834200
H	-2.02531400	-4.57650400	-1.52973000
C	0.82497200	-5.54145800	0.90988500
H	0.70748300	-3.51927800	1.61918800
C	0.30080500	-6.49544200	0.03378000
H	-1.14235500	-6.88323300	-1.51803700
H	1.61345300	-5.81897900	1.60171500
C	0.88361300	-7.88106100	-0.01205700
C	-0.88361300	7.88106100	-0.01205700
F	-1.40586100	8.24855200	1.17918100
F	-1.88225000	7.97267000	-0.92241100
F	0.04170100	8.80538700	-0.35407400
F	-0.04170100	-8.80538700	-0.35407400
F	1.40586100	-8.24855200	1.17918100
F	1.88225000	-7.97267000	-0.92241100

4d

B3LYP/6-31G* = -2224.36026153 au

C	-0.36372000	1.36066400	0.00998000
C	0.96890800	1.07295100	0.00740100
C	1.37335200	-0.30238800	0.01821800
C	0.36359600	-1.36041500	0.00983900
C	-0.96903100	-1.07270200	0.00753600
C	-1.37347600	0.30264100	0.01850800
C	2.63430300	-0.88376100	-0.00910100
C	2.47310700	-2.34178700	-0.02502200
C	1.08220300	-2.63644800	-0.00894800
C	-1.08232300	2.63669400	-0.00857300
C	-2.63444900	0.88401900	-0.00859000
C	-2.47323900	2.34206100	-0.02441500
C	0.63928600	-3.95356800	0.00414000
H	-0.42256200	-4.18562100	0.02035200
C	3.40998600	-3.37602200	-0.01749900
H	4.47505700	-3.16780800	-0.02127000

C	-0.63935300	3.95379700	0.00462700
H	0.42250800	4.18579900	0.02066700
C	-3.41006800	3.37634800	-0.01646400
H	-4.47514600	3.16820800	-0.02001000
C	-1.58637900	4.98612000	0.00307200
H	-1.25322400	6.02013400	0.01229900
C	-2.95516000	4.69875100	-0.00452900
H	-3.67544100	5.51201000	-0.00067300
C	2.95513000	-4.69844600	-0.00567700
H	3.67543400	-5.51168600	-0.00213700
C	1.58635800	-4.98585600	0.00221000
H	1.25324000	-6.01988200	0.01134500
H	1.71401800	1.86251200	-0.00511800
H	-1.71413400	-1.86226600	-0.00486200
C	3.92368600	-0.17682400	-0.00705500
C	4.92959200	-0.47056600	-0.94175600
C	4.22645800	0.81956000	0.93514600
C	6.16020300	0.17843600	-0.94309600
C	5.44838400	1.48545100	0.94892100
C	6.42152500	1.16324700	0.00645800
C	-3.92376200	0.17697300	-0.00626400
C	-4.93013400	0.47077100	-0.94045400
C	-4.22595400	-0.81981600	0.93571400
C	-6.16062300	-0.17846600	-0.94145800
C	-5.44774300	-1.48594100	0.94981300
C	-6.42136400	-1.16361900	0.00789300
F	-7.59633700	-1.79649800	0.01337000
F	-5.69633800	-2.42353900	1.87082900
F	-3.33164200	-1.15145600	1.87871700
F	-7.08611200	0.12639700	-1.85755900
F	-4.71479400	1.39304700	-1.88981600
F	3.33260000	1.15102400	1.87863700
F	5.69757400	2.42270500	1.87012600
F	7.59662100	1.79590300	0.01163200
F	7.08526800	-0.12633500	-1.85965600
F	4.71365500	-1.39264200	-1.89117300

4e

B3LYP/6-31G* = -1460.86961595 au

C	0.44031000	1.33396700	0.03363100
C	1.39733000	0.35896600	0.03265200
C	0.98408400	-1.01169800	0.06706000
C	-0.44031000	-1.33396700	0.03363100

C	-1.39733000	-0.35896600	0.03265200
C	-0.98408400	1.01169800	0.06706000
C	1.72640300	-2.19295300	0.04820100
C	0.78008100	-3.31442900	0.00093900
C	-0.54475100	-2.79243000	-0.00925200
C	0.54475100	2.79243000	-0.00925200
C	-1.72640300	2.19295300	0.04820100
C	-0.78008100	3.31442900	0.00093900
C	-1.64206900	-3.64669400	-0.03117300
H	-2.65525400	-3.25206000	-0.03766500
C	0.98408400	-4.69697800	0.01852000
H	1.98680900	-5.11060800	0.06658300
C	1.64206900	3.64669400	-0.03117300
H	2.65525400	3.25206000	-0.03766500
C	-0.98408400	4.69697800	0.01852000
H	-1.98680900	5.11060800	0.06658300
C	1.42522600	5.02994800	-0.03909000
H	2.27482600	5.70723700	-0.05960000
C	0.12545900	5.54771500	-0.00885600
H	-0.02439800	6.62407200	0.00030900
C	-0.12545900	-5.54771500	-0.00885600
H	0.02439800	-6.62407200	0.00030900
C	-1.42522600	-5.02994800	-0.03909000
H	-2.27482600	-5.70723700	-0.05960000
H	2.45409700	0.60784000	-0.01297100
H	-2.45409700	-0.60784000	-0.01297100
C	3.18572300	-2.31533300	0.07607900
C	3.86134500	-3.22891700	-0.75162900
C	3.97254200	-1.51523800	0.93403700
C	5.25166700	-3.33932100	-0.74490100
H	3.29101900	-3.84291400	-1.44185100
C	5.35457600	-1.61887600	0.95506400
H	3.48077300	-0.82819000	1.61579100
C	6.00876100	-2.53105100	0.11242600
H	5.72977300	-4.04745800	-1.41226400
H	5.95414300	-1.01152700	1.62604600
C	-3.18572300	2.31533300	0.07607900
C	-3.86134500	3.22891700	-0.75162900
C	-3.97254200	1.51523800	0.93403700
C	-5.25166700	3.33932100	-0.74490100
H	-3.29101900	3.84291400	-1.44185100
C	-5.35457600	1.61887600	0.95506400
H	-3.48077300	0.82819000	1.61579100
C	-6.00876100	2.53105100	0.11242600
H	-5.72977300	4.04745800	-1.41226400
H	-5.95414300	1.01152700	1.62604600

O	7.36824500	-2.55546500	0.20657900
O	-7.36824500	2.55546500	0.20657900
C	-8.08453700	3.46363400	-0.61603900
H	-7.92167500	3.25693700	-1.68196000
H	-9.13908500	3.31518500	-0.37713100
H	-7.80742300	4.50463200	-0.40395000
C	8.08453700	-3.46363400	-0.61603900
H	7.92167500	-3.25693700	-1.68196000
H	9.13908500	-3.31518500	-0.37713100
H	7.80742300	-4.50463200	-0.40395000

APPENDIX D

EXPERIMENTAL DETAILS FOR CHAPTER V

Cartesian Coordinates of Stationary Points[4]

1'

B3LYP/6-31G* = -3403.96398297 au
B3LYP/6-31G* Zero Point Corrected Energy = -3402.865410 au
NIMAG = 0

C	-5.04425800	0.71203300	0.06940300
C	-5.04425500	-0.71199400	-0.07072400
C	-3.81486200	-1.38438900	-0.13991600
C	-2.58838700	-0.71089800	-0.07076600
C	-2.58839000	0.71098000	0.06915100
C	-3.81486900	1.38444900	0.13842600
C	-6.25724600	1.44314800	0.12470600
C	-6.25724100	-1.44312700	-0.12580000
C	-1.37233600	-1.44259200	-0.11969700
C	-1.37234700	1.44268700	0.11805300
C	-7.29314800	2.08323400	0.15848700
C	-7.29315500	-2.08320700	-0.15931400
C	-0.33687700	2.08121900	0.14383300
C	-0.33685100	-2.08110300	-0.14539000
C	-8.51026700	2.81282300	0.18846500
C	0.88453200	2.81076800	0.15279400
C	-8.51029400	-2.81277300	-0.18895100
C	0.88457700	-2.81062000	-0.15413000
C	-9.72753400	-2.21574200	0.19750400
C	-10.91982400	-2.92228600	0.17607100
C	-10.96336800	-4.27430400	-0.24440200
C	-9.73785000	-4.87591000	-0.62175500
C	-8.55020100	-4.16174000	-0.59468200
C	-8.55008100	4.16165200	0.59467600
C	-9.73769800	4.87585600	0.62213800
C	-10.96326800	4.27442600	0.24465100
C	-10.91984200	2.92252300	-0.17621700
C	-9.72757400	2.21595500	-0.19803400

[4] Bold number refers to the molecule in Chapter V

C	2.08387600	2.20569400	-0.27609200
C	3.27679200	2.92132200	-0.27785700
C	3.31216000	4.25777400	0.14532100
C	2.12245200	4.86214500	0.57531700
C	0.92521900	4.15323200	0.58047600
C	2.08398300	-2.20522800	0.27414300
C	3.27690000	-2.92084700	0.27624200
C	3.31220700	-4.25762100	-0.14594200
C	2.12244400	-4.86230000	-0.57534000
C	0.92521600	-4.15337900	-0.58088100
C	4.59481600	5.02470300	0.12777600
C	4.59484500	-5.02456600	-0.12786500
C	5.43248100	4.99711900	1.25495100
N	6.64330100	5.69997400	1.25195000
B	7.20059800	6.56160300	0.07997500
N	6.14264200	6.47723200	-1.06021600
C	4.94271800	5.75709700	-1.01953300
C	5.43278800	-4.99739400	-1.25484700
N	6.64360000	-5.70026700	-1.25130900
B	7.20047900	-6.56167100	-0.07897000
N	6.14226400	-6.47684700	1.06094600
C	4.94239800	-5.75664900	1.01974500
C	5.30702500	-4.34727000	-2.52901300
C	6.45029300	-4.68440500	-3.24349400
C	7.25490200	-5.51529800	-2.43691300
C	6.24097200	-7.08531000	2.25822500
C	5.10134400	-6.77256800	3.02737200
C	4.27512200	-5.94401100	2.27757800
C	6.24171200	7.08600800	-2.25730900
C	5.10224200	6.77359800	-3.02682000
C	4.27574600	5.94492400	-2.27745700
C	5.30650600	4.34637200	2.52878100
C	6.44968000	4.68311400	3.24359500
C	7.25443300	5.51438200	2.43754100
C	7.40740200	7.94153100	-2.63282100
C	2.96362300	5.39699700	-2.75743300
C	4.20333300	3.47424600	3.05310400
C	8.57592900	6.12762600	2.76792500
C	2.96296200	-5.39577100	2.75709300
C	7.40643300	-7.94093200	2.63422300
C	4.20394100	-3.47540000	-3.05395100
C	8.57622300	-6.12908400	-2.76698600
F	8.41729300	6.04265200	-0.35847200
F	7.35449900	7.88400300	0.49142600
F	8.41713200	-6.04275300	0.35971000
F	7.35433400	-7.88416700	-0.49004400

N	-12.15456200	-4.97681100	-0.28874000
C	-12.14281000	-6.39969000	-0.58345800
C	-13.36279400	-4.38190600	0.25676200
N	-12.15435800	4.97700100	0.28917000
C	-13.36299600	4.38190900	-0.25517900
C	-12.14274700	6.39949300	0.58566200
H	-3.81514100	-2.46419400	-0.24044700
H	-3.81515500	2.46425400	0.23896500
H	-9.72459600	-1.18223500	0.53141700
H	-11.82532800	-2.41866600	0.49252100
H	-9.71096100	-5.91207000	-0.93668000
H	-7.62726100	-4.65143500	-0.89094500
H	-7.62709500	4.65119700	0.89104400
H	-9.71076800	5.91189200	0.93747300
H	-11.82542500	2.41903200	-0.49265200
H	-9.72471500	1.18254700	-0.53225400
H	2.06338700	1.17479900	-0.61611900
H	4.19272700	2.44428800	-0.61579200
H	2.13832500	5.89736700	0.90502900
H	0.00926100	4.63073800	0.91421500
H	2.06353500	-1.17409500	0.61344600
H	4.19288300	-2.44356700	0.61370000
H	2.13826000	-5.89776500	-0.90428900
H	0.00921600	-4.63112600	-0.91416300
H	6.69319800	-4.36865300	-4.25020200
H	4.91252000	-7.12447000	4.03370800
H	4.91367000	7.12585200	-4.03308100
H	6.69241800	4.36688000	4.25019200
H	7.49986400	8.78934800	-1.94544200
H	8.34034500	7.37322200	-2.55735200
H	7.29461400	8.31675400	-3.65316400
H	2.12511600	5.72005900	-2.13119800
H	2.94758400	4.30186100	-2.76197900
H	2.77270700	5.74093600	-3.77875500
H	4.43211000	3.16754300	4.07852900
H	3.23660700	3.98877100	3.06282500
H	4.06982700	2.56759000	2.45303200
H	8.88662000	5.84878500	3.77804000
H	8.52183900	7.21899300	2.69476200
H	9.33947700	5.80271900	2.05315000
H	2.94656100	-4.30064500	2.76003400
H	2.77238700	-5.73830800	3.77894900
H	2.12440400	-5.72003400	2.13153000
H	8.33957900	-7.37309800	2.55782800
H	7.29382300	-8.31508200	3.65498000
H	7.49829200	-8.78951400	1.94769400

H	4.43274100	-3.16946000	-4.07959800
H	4.07053100	-2.56829800	-2.45453500
H	3.23716500	-3.98984100	-3.06329000
H	9.33911200	-5.80678200	-2.05036800
H	8.52090100	-7.22060100	-2.69666500
H	8.88853800	-5.84814600	-3.77602000
H	-13.16935400	-6.77001300	-0.59971200
H	-11.70393300	-6.59603300	-1.56956300
H	-11.57904300	-6.98194000	0.16190300
H	-14.19474300	-5.07565900	0.12382000
H	-13.61872000	-3.45227100	-0.26702100
H	-13.27369800	-4.15381000	1.33021300
H	-14.19471400	5.07597900	-0.12248400
H	-13.27441700	4.15294300	-1.32847300
H	-13.61892100	3.45271500	0.26943800
H	-13.16926500	6.76989000	0.60157100
H	-11.57841900	6.98254400	-0.15862700
H	-11.70452300	6.59470800	1.57230700

2'

B3LYP/6-31G* = -3403.96482629 au
B3LYP/6-31G* Zero Point Corrected Energy = -3402.866463 au
NIMAG = 0

C	1.22799700	2.82989700	-0.03932100
C	1.22632600	1.39969900	-0.02674300
C	0.00000700	0.72217600	-0.00002200
C	-1.22630700	1.39970700	0.02670100
C	-1.22796800	2.82990600	0.03928600
C	0.00001700	3.50605200	-0.00001600
C	2.44115700	3.56131500	-0.09676300
C	2.44461500	0.67121800	-0.02693800
C	-2.44460200	0.67123500	0.02689900
C	-2.44112400	3.56133000	0.09673500
C	3.47666600	4.19969000	-0.16312500
C	3.49112400	0.05063600	-0.00897500
C	-3.47663600	4.19970100	0.16310400
C	-3.49111500	0.05066000	0.00893800
C	4.69289400	4.92680000	-0.24668900
C	-4.69288600	4.92677000	0.24668900
C	4.73683300	-0.63506600	0.02844900
C	-4.73682300	-0.63504200	-0.02847900
C	5.92681500	0.06777900	0.31013100
C	7.14817500	-0.59631600	0.35036700

C	7.22273000	-1.97624000	0.11170700
C	6.04198100	-2.67881200	-0.16732800
C	4.81561400	-2.02216800	-0.20835700
C	4.75441700	6.29842200	0.07135500
C	5.94202400	7.00842400	-0.00891400
C	7.14602600	6.38034200	-0.41288800
C	7.07994300	5.00485400	-0.74645600
C	5.88784100	4.30334700	-0.66042000
C	-5.88780400	4.30327500	0.66044100
C	-7.07993000	5.00473800	0.74649900
C	-7.14606800	6.38022400	0.41293100
C	-5.94209600	7.00834800	0.00893400
C	-4.75446500	6.29838900	-0.07135600
C	-4.81560200	-2.02214600	0.20831900
C	-6.04196800	-2.67879100	0.16729700
C	-7.22272000	-1.97621700	-0.11172200
C	-7.14816900	-0.59629100	-0.35037100
C	-5.92680900	0.06780400	-0.31014200
C	8.53957800	-2.68135700	0.15773900
C	-8.53956900	-2.68133400	-0.15774600
C	-9.00550500	-3.19325900	-1.37976900
N	-10.24287500	-3.84515100	-1.44616700
B	-11.21708200	-4.08653000	-0.25510600
N	-10.53308000	-3.46282000	0.99746400
C	-9.29355400	-2.81226600	1.02067900
C	-8.43787800	-3.19417900	-2.69890600
C	-9.35924300	-3.84614000	-3.50963200
C	-10.45864600	-4.23512100	-2.71685600
C	-11.04910000	-3.45522800	2.24146200
C	-10.15207100	-2.79554300	3.10634100
C	-9.04816700	-2.38385900	2.36880200
C	-7.87333900	-1.64462800	2.93948800
C	-12.37085700	-4.06887400	2.57076100
C	-7.13106000	-2.63362200	-3.17879500
C	-11.69629700	-4.95724000	-3.13936100
C	9.00550000	-3.19329900	1.37976000
N	10.24286700	-3.84519500	1.44616200
B	11.21706300	-4.08660700	0.25509800
N	10.53310100	-3.46283000	-0.99746100
C	9.29357800	-2.81227000	-1.02067900
C	8.43787200	-3.19421100	2.69889700
C	9.35923200	-3.84617500	3.50962600
C	10.45863300	-4.23516600	2.71685200
C	11.04914400	-3.45520200	-2.24144800
C	10.15213600	-2.79548500	-3.10632400
C	9.04822000	-2.38381900	-2.36879300

C	7.87341600	-1.64454400	-2.93947200
C	12.37090300	-4.06884600	-2.57074200
C	7.13106600	-2.63362800	3.17878700
C	11.69627700	-4.95729600	3.13935900
F	11.40817200	-5.45421400	0.06396400
F	12.43428400	-3.45402400	0.49886100
F	-12.43426800	-3.45387100	-0.49885300
F	-11.40827000	-5.45412900	-0.06399800
N	-8.33687600	7.07902400	0.47574400
C	-8.34615400	8.51508900	0.25313000
C	-9.52162900	6.44135900	1.02514800
N	8.33681200	7.07918300	-0.47567700
C	9.52158800	6.44156700	-1.02508900
C	8.34603200	8.51525100	-0.25307800
H	0.00000300	-0.36246200	-0.00002300
H	0.00002100	4.59040200	-0.00001200
H	5.87662700	1.13488900	0.50328400
H	8.05705900	-0.04322400	0.57120300
H	6.08823500	-3.74855000	-0.35238200
H	3.90711100	-2.57540400	-0.42512700
H	3.84882300	6.80853900	0.38604000
H	5.93287000	8.06189300	0.24336100
H	7.96705300	4.47962700	-1.07938100
H	5.86702400	3.25151300	-0.93042500
H	-5.86694400	3.25144100	0.93044600
H	-7.96701400	4.47948000	1.07944300
H	-5.93298500	8.06181700	-0.24334300
H	-3.84889500	6.80853900	-0.38605800
H	-3.90709600	-2.57538200	0.42507600
H	-6.08821900	-3.74853000	0.35234300
H	-8.05705600	-0.04319900	-0.57119500
H	-5.87662400	1.13491600	-0.50328600
H	-9.26013900	-4.03138800	-4.57174200
H	-10.30756200	-2.64194700	4.16678000
H	-8.03359400	-1.46653200	4.00746200
H	-6.93808900	-2.20374000	2.82838700
H	-7.71728300	-0.67475500	2.45517600
H	-12.38406300	-5.12649800	2.28760100
H	-12.57935900	-3.97848500	3.63988700
H	-13.17340700	-3.58247400	2.00564000
H	-7.01187200	-2.83967700	-4.24707000
H	-6.27473100	-3.06952100	-2.65337800
H	-7.06706400	-1.54946000	-3.03629600
H	-11.64461100	-5.21909200	-4.19925700
H	-11.83013900	-5.86797200	-2.54673900
H	-12.58207100	-4.33638500	-2.96551700

H	9.26012500	-4.03142100	4.57173600
H	10.30764700	-2.64185900	-4.16675500
H	8.03361700	-1.46655700	-4.00747200
H	7.71748200	-0.67461000	-2.45523700
H	6.93812300	-2.20355800	-2.82825500
H	12.38412400	-5.12645900	-2.28754100
H	13.17345800	-3.58241500	-2.00565300
H	12.57938900	-3.97849600	-3.63987500
H	7.01181200	-2.83980300	4.24703200
H	7.06715700	-1.54944200	3.03642200
H	6.27473200	-3.06939700	2.65327500
H	11.83014200	-5.86799900	2.54669700
H	12.58205300	-4.33642700	2.96557200
H	11.64456100	-5.21920000	4.19924000
H	-9.37209400	8.88065400	0.32099800
H	-7.73792200	9.06003500	0.99133000
H	-7.96952400	8.76435500	-0.74694300
H	-10.35921100	7.13904200	0.97523600
H	-9.38865700	6.13974200	2.07539500
H	-9.79705700	5.54943100	0.44826500
H	10.35914500	7.13928100	-0.97517100
H	9.79705000	5.54964500	-0.44821400
H	9.38862600	6.13995500	-2.07533900
H	7.73780600	9.06017000	-0.99130400
H	9.37196200	8.88085100	-0.32091100
H	7.96935900	8.76451200	0.74697900

3'

B3LYP/6-31G* = -3403.96460682 au
B3LYP/6-31G* Zero Point Corrected Energy = -3402.866010 au
NIMAG = 0

C	-0.82879700	1.15774100	-0.07312400
C	-1.40799900	-0.14344900	0.05135300
C	-0.56905700	-1.26345700	0.12394500
C	0.82861000	-1.15726200	0.07245700
C	1.40781400	0.14393200	-0.05203000
C	0.56887400	1.26393600	-0.12463600
C	-1.63603600	2.32159800	-0.13226300
C	-2.81748600	-0.31285300	0.08256200
C	1.63586900	-2.32110600	0.13162500
C	2.81730500	0.31331200	-0.08320700
C	-2.31764100	3.33056000	-0.17153300
C	-4.02407400	-0.46849200	0.09319300

C	4.02390200	0.46888300	-0.09375400
C	2.31753400	-3.33001900	0.17108900
C	-3.12573800	4.49698300	-0.21219900
C	5.43761000	0.62711700	-0.08920000
C	-5.43776000	-0.62691300	0.08878700
C	3.12577100	-4.49634600	0.21186600
C	-6.27672500	0.43773300	-0.29980200
C	-7.65907400	0.28145100	-0.31086500
C	-8.24622400	-0.93533700	0.06456200
C	-7.41532600	-1.99590600	0.45283400
C	-6.03189500	-1.84839600	0.46514700
C	-2.60813300	5.73595800	-0.64052100
C	-3.39713300	6.87458200	-0.68623500
C	-4.75825400	6.83949000	-0.29509700
C	-5.27878200	5.59270800	0.13141900
C	-4.48160800	4.45966800	0.17205900
C	6.27635400	-0.43752900	0.29988000
C	7.65872300	-0.28143800	0.31113900
C	8.24611400	0.93513400	-0.06460800
C	7.41543600	1.99569000	-0.45339100
C	6.03198400	1.84838600	-0.46586400
C	2.60838000	-5.73530000	0.64049500
C	3.39752900	-6.87381600	0.68631800
C	4.75859400	-6.83863900	0.29497200
C	5.27891800	-5.59185500	-0.13180700
C	4.48159100	-4.45892500	-0.17255900
C	-9.73126900	-1.10210800	0.04603300
C	9.73117700	1.10171300	-0.04589300
C	-10.47299600	-0.81894000	1.20509300
N	-11.86436200	-0.97511000	1.20890700
B	-12.73650100	-1.45327500	0.01023500
N	-11.75010600	-1.70739700	-1.16824400
C	-10.36023100	-1.54245400	-1.13016100
C	-10.07971500	-0.35898400	2.50702100
C	-11.25270700	-0.25711600	3.24567900
C	-12.33383600	-0.64116100	2.42622600
C	-12.10145000	-2.13509400	-2.39579700
C	-10.94181100	-2.25880900	-3.18841900
C	-9.84109500	-1.89539200	-2.42182700
C	-8.42412500	-1.89701400	-2.91622100
C	-13.51884500	-2.41301100	-2.77702000
C	-8.71287900	-0.03307200	3.03440300
C	-13.78591500	-0.69594300	2.77345400
C	10.36008300	1.54176500	1.13044300
N	11.74998300	1.70639600	1.16873400
B	12.73645700	1.45236300	-0.00968300

N	11.86436000	0.97477300	-1.20861000
C	10.47298700	0.81868000	-1.20493600
C	9.84083200	1.89475600	2.42204800
C	10.94152200	2.25788400	3.18882300
C	12.10124600	2.13396400	2.39636700
C	12.33391700	0.64098300	-2.42593800
C	11.25283600	0.25712900	-3.24554200
C	10.07979000	0.35892200	-2.50695800
C	8.71298500	0.03317300	-3.03451800
C	13.78603100	0.69571200	-2.77303500
C	8.42378300	1.89675200	2.91621000
C	13.51863900	2.41163200	2.77777500
F	-13.39847300	-2.63402000	0.34145800
F	-13.65302200	-0.46273400	-0.33859500
F	13.39877100	2.63304000	-0.34046600
F	13.65269300	0.46148400	0.33895900
N	-5.54474200	7.97581400	-0.32278000
C	-6.96551300	7.88001800	-0.03437300
C	-5.01474000	9.20936800	-0.87834100
N	5.54520400	-7.97487400	0.32273600
C	5.01554100	-9.20826400	0.87897700
C	6.96585600	-7.87903600	0.03381000
H	-1.01557600	-2.24768200	0.21334600
H	1.01539000	2.24816300	-0.21404500
H	-5.82938200	1.38038000	-0.59970600
H	-8.29391900	1.10877900	-0.61616300
H	-7.86043000	-2.94316600	0.74470900
H	-5.39692600	-2.67582000	0.76608700
H	-1.56805700	5.79586100	-0.94717400
H	-2.95098500	7.79992100	-1.03003100
H	-6.31511500	5.50815100	0.43558900
H	-4.90657100	3.52029300	0.51384500
H	5.82882500	-1.38001700	0.60000400
H	8.29339400	-1.10875400	0.61683400
H	7.86073000	2.94278200	-0.74551900
H	5.39718500	2.67580700	-0.76717100
H	1.56835200	-5.79527600	0.94729600
H	2.95153800	-7.79914500	1.03033800
H	6.31522500	-5.50719800	-0.43603500
H	4.90639700	-3.51955100	-0.51454300
H	-11.33474700	0.06215200	4.27696200
H	-10.92438500	-2.58455300	-4.22078300
H	-8.39539500	-2.25496600	-3.95009300
H	-7.77555700	-2.54434400	-2.31664100
H	-7.97588700	-0.89766800	-2.89407200
H	-14.13414100	-1.51667000	-2.64571400

H	-13.94646700	-3.18489600	-2.12826900
H	-13.57869600	-2.74289500	-3.81727200
H	-8.78920800	0.30293000	4.07327700
H	-8.22434500	0.76024500	2.45860400
H	-8.04044000	-0.89730800	3.00914500
H	-14.36378300	-0.03849500	2.11514000
H	-14.17743500	-1.70830900	2.62814700
H	-13.94345400	-0.39417800	3.81209700
H	10.92401800	2.58355500	4.22121000
H	11.33494700	-0.06199500	-4.27686400
H	8.78949700	-0.30362500	-4.07312000
H	8.22390800	-0.75947900	-2.45827900
H	8.04092500	0.89773900	-3.01013800
H	13.94361800	0.39423400	-3.81175300
H	14.17765200	1.70798900	-2.62739100
H	14.36377300	0.03800200	-2.11487000
H	7.77550500	2.54428500	2.31652700
H	8.39497900	2.25470100	3.95008100
H	7.97525700	0.89754200	2.89396500
H	14.13400400	1.51548000	2.64555800
H	13.94615400	3.18420100	2.12976000
H	13.57851900	2.74052900	3.81834000
H	-7.49520800	7.22604000	-0.74381500
H	-7.41063800	8.87472400	-0.09198700
H	-7.14188800	7.49487000	0.97815400
H	-5.77139300	9.99177700	-0.79954900
H	-4.12815700	9.54619900	-0.32596400
H	-4.73626300	9.10731100	-1.93837600
H	5.77234100	-9.99055600	0.80044500
H	4.12893000	-9.54554500	0.32691500
H	4.73722300	-9.10574100	1.93900800
H	7.41094900	-8.87379100	0.09085200
H	7.49590800	-7.22533400	0.74325300
H	7.14180100	-7.49354800	-0.97865200

4'

B3LYP/6-31G* = -3403.97008022 au
B3LYP/6-31G* Zero Point Corrected Energy = -3402.871676 au
NIMAG = 0

C	-3.93163900	-0.71984900	0.04371800
C	-3.94479200	0.70812000	-0.03244500
C	-2.72225300	1.39347800	-0.07006500
C	-1.48692700	0.73060700	-0.02672100

C	-1.47409100	-0.69398200	0.07204200
C	-2.69611500	-1.38060400	0.09845400
C	-5.13741700	-1.46683200	0.06252400
C	-5.16660100	1.42811400	-0.06429300
C	-0.28302500	1.48061300	-0.09326400
C	-0.25794600	-1.42525200	0.15262700
C	-6.16374500	-2.12257700	0.06864100
C	-6.21272300	2.05158100	-0.07852000
C	0.75162400	-2.10029700	0.25223600
C	0.72666900	2.15720200	-0.18129300
C	-7.36852700	-2.87455600	0.07069300
C	1.91742100	-2.89036200	0.37394500
C	-7.44620800	2.75529000	-0.08560500
C	1.89708700	2.93947000	-0.29330600
C	-8.65145200	2.11351200	0.26409500
C	-9.86066800	2.79183600	0.26396700
C	-9.93438600	4.15891000	-0.09760400
C	-8.72121400	4.80556000	-0.43599400
C	-7.51620900	4.11931100	-0.43105700
C	-7.39021200	-4.22623100	0.46784100
C	-8.56565300	-4.96152200	0.47592200
C	-9.79413600	-4.38375300	0.07384300
C	-9.77260700	-3.02356100	-0.31901700
C	-8.59229500	-2.29565500	-0.32158400
C	3.07557600	-2.53859000	1.12777900
N	3.97472900	-3.52734100	1.03249600
C	3.45201200	-4.54862300	0.22452700
C	2.14614200	-4.15601200	-0.19550100
C	3.15128500	2.47377600	-0.78835500
N	4.03159500	3.48295900	-0.76280100
C	3.40142400	4.63133100	-0.25882700
C	2.04650000	4.29815800	0.03904800
B	5.51433100	3.38631100	-1.24514500
N	6.14087900	4.79043800	-0.99740100
C	5.47648000	5.91183100	-0.48592900
C	4.12269600	5.83191500	-0.12479300
B	5.36842900	-3.53734600	1.73768200
N	6.05247100	-4.87350100	1.32097100
C	5.49947000	-5.86309500	0.49922000
C	4.21321300	-5.70259800	-0.03800900
C	7.28339200	-5.26339800	1.70083300
C	7.56210000	-6.52369900	1.13108000
C	6.46549000	-6.92014500	0.37632700
C	7.41842800	5.12502200	-1.25796200
C	7.61617600	6.48028100	-0.91944900
C	6.41994200	6.99456400	-0.43562900

C	3.43374200	7.04397700	0.41577900
C	0.94576600	5.14962100	0.59420400
C	3.48397300	1.10741600	-1.28422000
C	8.40870600	4.15549000	-1.81528000
C	6.22945600	8.40845000	0.02946900
C	3.30172200	-1.29963000	1.92635200
C	1.15772300	-4.87391600	-1.06284200
C	3.64157900	-6.77637700	-0.90769000
C	6.38235000	-8.20806900	-0.38912500
C	8.15423400	-4.43185700	2.58449700
C	3.41408200	7.29299900	1.79465300
C	2.76808500	8.42306800	2.29863400
C	2.13576500	9.31520000	1.43047500
C	2.15224200	9.07320900	0.05550200
C	2.79810600	7.94380600	-0.45022100
C	3.82833700	-6.73865100	-2.29594300
C	3.29447300	-7.74118400	-3.10732700
C	2.56852200	-8.79025300	-2.54006100
C	2.37889200	-8.83365300	-1.15747200
C	2.91290500	-7.83250200	-0.34448000
F	6.12918900	-2.45740000	1.30309300
F	5.19961700	-3.49811300	3.11934700
F	6.19214800	2.42438400	-0.50387600
F	5.55001900	3.08066200	-2.60273100
N	-10.96672900	-5.12163000	0.05903600
C	-12.23147500	-4.45673800	-0.20248600
C	-10.98358900	-6.45466400	0.63664100
N	-11.14463800	4.83368000	-0.12512100
C	-11.16085000	6.27181500	-0.33178100
C	-12.33429800	4.19458800	0.41084600
H	-2.73269900	2.47581500	-0.13844200
H	-2.68570300	-2.46288500	0.16753600
H	-8.62583600	1.06651200	0.55178700
H	-10.75542000	2.25242800	0.55078000
H	-8.71650000	5.85530400	-0.70369500
H	-6.60330600	4.64393700	-0.69718700
H	-6.46402400	-4.69885900	0.78125200
H	-8.52630600	-5.99505800	0.79831800
H	-10.68593900	-2.52832800	-0.62634200
H	-8.60630800	-1.25624800	-0.63643600
H	8.48163000	-7.07911800	1.26602900
H	8.54987100	7.01852100	-1.02305900
H	1.18508300	5.53374000	1.59165700
H	0.03041200	4.55597100	0.66908300
H	0.74018100	6.02052600	-0.03694700
H	2.62628900	0.44199000	-1.16536600

H	4.34470800	0.70320100	-0.74196200
H	3.76977600	1.14681000	-2.34134400
H	8.04692500	3.73926000	-2.76139600
H	8.54570300	3.31008800	-1.13252600
H	9.37219900	4.64417300	-1.98086400
H	5.90597700	8.46079200	1.07437600
H	5.47325200	8.93924900	-0.55881500
H	7.17303300	8.95572000	-0.06071400
H	2.45242200	-0.62135200	1.82045000
H	4.21837700	-0.79730100	1.60123700
H	3.43852100	-1.54957700	2.98425900
H	0.88706900	-5.85371200	-0.65562000
H	0.24726600	-4.27430600	-1.14885000
H	1.54647800	-5.04891400	-2.07181900
H	7.31322400	-8.77024700	-0.26520400
H	6.22652500	-8.04300100	-1.46054100
H	5.55671200	-8.84119800	-0.04701100
H	7.63248700	-4.18947700	3.51596000
H	9.08279500	-4.95992900	2.81558700
H	8.39296500	-3.47813800	2.10133100
H	3.90504500	6.59741400	2.46993600
H	2.75868900	8.60493600	3.36993300
H	1.63224400	10.19417400	1.82346900
H	1.66156100	9.76310900	-0.62581200
H	2.80998300	7.75429100	-1.52019600
H	4.39196000	-5.92084300	-2.73683700
H	3.44547700	-7.70089100	-4.18268500
H	2.15209700	-9.56966800	-3.17224900
H	1.81436400	-9.64702700	-0.70953300
H	2.76548600	-7.86543700	0.73165600
H	-13.03332700	-5.19739700	-0.19401200
H	-12.46871000	-3.68445600	0.54631000
H	-12.23099300	-3.98093700	-1.19094100
H	-10.28328800	-7.12037200	0.11700000
H	-11.98349000	-6.87889100	0.52851400
H	-10.72320900	-6.45623000	1.70672900
H	-10.70578700	6.53657100	-1.29391000
H	-12.19584400	6.61826000	-0.35089000
H	-10.62789000	6.82235500	0.45962800
H	-13.18530600	4.86806600	0.29383200
H	-12.23775400	3.94422700	1.47912600
H	-12.56623800	3.27091600	-0.13361100

5'

B3LYP/6-31G* = -3403.97167389 au
B3LYP/6-31G* Zero Point Corrected Energy = -3402.872834 au
NIMAG = 0

C	-1.24232100	2.84677300	0.03613000
C	-1.24172100	1.41940200	-0.03871400
C	-0.01353800	0.74407600	-0.06980000
C	1.21521900	1.41772700	-0.03345100
C	1.21742400	2.84509000	0.04364000
C	-0.01196900	3.51961300	0.06915700
C	-2.45193300	3.58610300	0.09844700
C	-2.45324000	0.68142200	-0.09742100
C	2.42688000	0.67976800	-0.09054100
C	2.42881700	3.58045700	0.11728100
C	-3.46780700	4.25394000	0.18060100
C	-3.47640900	0.02360600	-0.16690700
C	3.44915800	4.23972900	0.21202800
C	3.45243900	0.02584000	-0.16130700
C	-4.65488400	5.02768700	0.28141700
C	4.64513300	4.99679600	0.33270600
C	4.65234200	-0.71394600	-0.24839500
C	-4.66277300	6.40159500	-0.03200500
C	-5.81886700	7.16063300	0.06394000
C	-7.04324200	6.58158400	0.47821800
C	-7.03041700	5.20464700	0.80927500
C	-5.86946000	4.45391700	0.70884200
C	4.68212200	6.36873200	0.01332200
C	5.84934000	7.10838600	0.12672800
C	7.05257000	6.51397100	0.57921300
C	7.01536300	5.13391300	0.89507000
C	5.84375600	4.40269400	0.77713000
C	-4.67218300	-0.72315900	-0.25032600
C	-4.87197600	-2.06062200	0.13453800
C	-6.24189800	-2.35185500	-0.14122200
N	-6.83160100	-1.19877900	-0.68256600
C	-5.91136000	-0.22808300	-0.75512200
C	5.88503100	-0.21281100	-0.76320200
N	6.81206400	-1.17718000	-0.69259300
C	6.23335400	-2.33187500	-0.14283700
C	4.86336500	-2.04837000	0.14071500
C	-7.00623000	-3.51867400	0.03659900
C	-8.36522600	-3.55938800	-0.31424800
N	-8.99202900	-2.42960900	-0.85398900
B	-8.32168100	-1.05102200	-1.12489200
B	8.29885900	-1.02090600	-1.14285900
N	8.97962400	-2.39424600	-0.87165500

C	8.36333400	-3.52631700	-0.32469700
C	7.00630600	-3.49304100	0.03456900
C	-9.34402100	-4.60759000	-0.23537300
C	-10.52336600	-4.06610100	-0.73231700
C	-10.28089800	-2.72812500	-1.10565000
C	10.26868500	-2.68550500	-1.13081500
C	10.52181500	-4.02088100	-0.75542300
C	9.34904900	-4.56825200	-0.24938500
C	-3.80146900	-2.93235600	0.71647800
C	-6.35803000	-4.73991300	0.60653700
C	-9.20103100	-6.01473500	0.26605900
C	-11.23880300	-1.74207100	-1.69037000
C	-6.19020100	1.12959100	-1.30418200
C	6.15134100	1.14443700	-1.31964400
C	3.80238800	-2.92461800	0.73322100
C	6.36981900	-4.71642300	0.61307700
C	9.21794800	-5.97506900	0.25624300
C	11.21666200	-1.69526300	-1.72458300
C	-6.35035900	-4.95960000	1.99041200
C	-5.74294400	-6.09891900	2.52092100
C	-5.13814800	-7.03000400	1.67432200
C	-5.14293200	-6.81739800	0.29437800
C	-5.74964500	-5.67847600	-0.23768800
C	6.37568400	-4.93288100	1.99746400
C	5.77981200	-6.07454900	2.53596600
C	5.17324100	-7.01127200	1.69688400
C	5.16445400	-6.80183600	0.31647600
C	5.75946100	-5.66048500	-0.22354900
F	-8.38589200	-0.74559800	-2.48094400
F	-8.94344600	-0.06099500	-0.36725500
F	8.91788000	-0.02471900	-0.39108200
F	8.35451000	-0.71889000	-2.50012400
N	8.21568400	7.25218700	0.71500500
C	8.26062900	8.62194600	0.23318500
C	9.46490700	6.57616400	1.02336400
N	-8.20526300	7.32942300	0.55196200
C	-9.40797000	6.73994900	1.11544200
C	-8.15117100	8.76762200	0.35544000
H	-0.01414900	-0.33849800	-0.13655600
H	-0.01147500	4.60209400	0.13424700
H	-3.74035500	6.87442600	-0.35613400
H	-5.76844600	8.21344700	-0.18647500
H	-7.93447600	4.71476100	1.15014300
H	-5.89146100	3.40137100	0.97350400
H	3.77585700	6.85403100	-0.33691900
H	5.82424200	8.15776400	-0.14143300

H	7.90912100	4.62530100	1.23566400
H	5.84616000	3.34791900	1.03374500
H	-11.47425100	-4.57586400	-0.82281700
H	11.47520200	-4.52504400	-0.85079000
H	-4.05787700	-3.28440600	1.72142900
H	-3.62028800	-3.82440000	0.10759400
H	-2.86831500	-2.36582800	0.78118500
H	-10.15922900	-6.53625000	0.17729200
H	-8.45364600	-6.58196700	-0.29881500
H	-8.89239500	-6.05054300	1.31625800
H	-10.87763000	-1.38455800	-2.66045300
H	-11.32793800	-0.86185600	-1.04458200
H	-12.22505300	-2.19556500	-1.81784500
H	-6.48323000	1.06098300	-2.35769500
H	-7.02978900	1.59234900	-0.77564000
H	-5.30538800	1.76318300	-1.21507600
H	6.44298800	1.07281100	-2.37331200
H	5.26148300	1.77104900	-1.23162600
H	6.98769200	1.61742500	-0.79499600
H	4.07013600	-3.27544300	1.73559500
H	3.61921400	-3.81756400	0.12618500
H	2.86737500	-2.36223100	0.80671200
H	8.46891300	-6.54755100	-0.30108900
H	8.91842200	-6.01036900	1.30909400
H	10.17817200	-6.49161900	0.16051300
H	12.20535300	-2.14246700	-1.85535100
H	10.84799000	-1.34431200	-2.69424500
H	11.30306400	-0.81176300	-1.08292800
H	-6.82018000	-4.23387200	2.64881000
H	-5.74228900	-6.25771200	3.59592800
H	-4.66515400	-7.91647700	2.08786300
H	-4.67367900	-7.53776300	-0.37028600
H	-5.75232500	-5.51170900	-1.31148000
H	6.84706400	-4.20286700	2.64998600
H	5.78958900	-6.23079200	3.61130000
H	4.70935000	-7.89963600	2.11663200
H	4.69368400	-7.52656800	-0.34234100
H	5.75158500	-5.49617400	-1.29769400
H	9.24377900	9.04429400	0.44851300
H	8.08429900	8.69645300	-0.85139600
H	7.51399000	9.24485400	0.74120100
H	9.40291400	6.04891300	1.98339900
H	9.75221500	5.84479800	0.25221800
H	10.26183800	7.31753300	1.10455800
H	-9.28030600	6.44232800	2.16789200
H	-10.22065200	7.46670400	1.06308600

H	-9.71750400	5.85358700	0.54803200
H	-7.51475300	9.27253100	1.09887100
H	-7.76918800	9.01777700	-0.64240800
H	-9.15942600	9.17779700	0.43562600

6'

B3LYP/6-31G* = -3403.97112859 au
B3LYP/6-31G* Zero Point Corrected Energy = -3402.872380 au
NIMAG = 0

C	-0.91046000	1.46815200	-0.02660400
C	-1.44239700	0.14326600	-0.09704800
C	-0.55715100	-0.94022900	-0.17954200
C	0.83527200	-0.77413300	-0.20708900
C	1.36742000	0.55043700	-0.14132800
C	0.48214500	1.63419200	-0.05556700
C	-1.75540100	2.60127200	0.09222800
C	-2.84365100	-0.08786600	-0.10515500
C	1.67664700	-1.91165600	-0.32118900
C	2.76816000	0.78328100	-0.14455400
C	-2.45144000	3.59285500	0.22312400
C	-4.04122100	-0.30877000	-0.13947700
C	3.96477500	1.01142600	-0.12603900
C	2.35727900	-2.91425600	-0.44671700
C	-3.26878000	4.74292000	0.38485400
C	5.35443200	1.26110900	-0.09636500
C	-5.43318100	-0.54314400	-0.19180000
C	3.14811400	-4.08441500	-0.60344400
C	-2.75827400	6.04049200	0.18078200
C	-3.55404100	7.16519200	0.33502200
C	-4.91454100	7.05397300	0.71283300
C	-5.42778400	5.74918400	0.91270200
C	-4.62404700	4.63084100	0.75612700
C	2.64753900	-5.35621300	-0.26075700
C	3.40982200	-6.50350900	-0.41992000
C	4.72886600	-6.44169900	-0.93035700
C	5.22525400	-5.16520400	-1.28856900
C	4.45606400	-4.02291600	-1.12409400
C	-6.12710200	-1.67600800	0.26840400
C	-7.50596600	-1.43755000	-0.01367300
N	-7.61275200	-0.18204900	-0.63252700
C	-6.39159900	0.35699100	-0.74533100
C	5.98142600	2.47007600	-0.51898800
N	7.30547200	2.35847800	-0.34964100

C	7.59498400	1.09278300	0.18449200
C	6.36419900	0.38883700	0.34911200
C	-8.65720200	-2.21181900	0.21602000
C	-9.92944000	-1.75502100	-0.16331300
N	-10.07886000	-0.50814000	-0.78255300
B	-8.93521800	0.49508800	-1.11191700
B	8.34776700	3.46440700	-0.70824800
N	9.74194800	2.88045800	-0.33620700
C	9.98814700	1.61184300	0.20259600
C	8.92612600	0.72999100	0.45787400
C	-11.23408600	-2.34464600	-0.04563700
C	-12.11840900	-1.42734800	-0.60001000
C	-11.38443900	-0.30855900	-1.04511900
C	10.91556300	3.52332900	-0.48518900
C	11.95857900	2.68287900	-0.04388000
C	11.40685200	1.48406400	0.39067000
C	-11.63733300	-3.66670600	0.53875200
C	-11.89417100	0.92995600	-1.70677500
C	-8.52387800	-3.54797900	0.87418100
C	-5.46695100	-2.85421400	0.91706700
C	-6.13264400	1.68253700	-1.37714100
C	5.32581400	3.68792900	-1.07669800
C	6.10296800	-0.98530100	0.88547700
C	9.21659700	-0.62046900	1.03041100
C	12.19974500	0.33291500	0.93634500
C	11.01156000	4.90793600	-1.03735700
C	-8.32359500	-4.70131200	0.10401700
C	-8.20066400	-5.94818900	0.71942200
C	-8.27674200	-6.05499200	2.10940300
C	-8.47615400	-4.90952800	2.88252100
C	-8.59912200	-3.66188400	2.26874400
C	9.46774500	-1.71006800	0.18586300
C	9.74353600	-2.96917400	0.72150400
C	9.77054500	-3.15252600	2.10526800
C	9.52010600	-2.07123000	2.95206500
C	9.24444300	-0.81136100	2.41823400
F	-9.13423100	1.68781000	-0.42040100
F	-8.88083000	0.72520200	-2.48320200
F	8.09787900	4.61335800	0.03708600
F	8.29349700	3.74130300	-2.07147100
N	5.50396500	-7.58311100	-1.06708700
C	6.77405000	-7.50778800	-1.76833400
C	4.89812200	-8.88882600	-0.86767700
N	-5.70855100	8.17421100	0.88673700
C	-7.13640700	8.01726900	1.10861700
C	-5.19445000	9.48477200	0.52810900

H	-0.96336800	-1.94398700	-0.24025300
H	0.88834600	2.63797600	0.00407600
H	-1.71880800	6.15925100	-0.11057000
H	-3.11289000	8.13853000	0.15698600
H	-6.46416900	5.60487000	1.19306600
H	-5.04504300	3.64454500	0.92435900
H	1.63921300	-5.43722800	0.13441400
H	2.97244900	-7.45617700	-0.14663200
H	6.22066900	-5.06169300	-1.70344300
H	4.86295700	-3.05876200	-1.41309900
H	-13.19191600	-1.54126800	-0.68248700
H	13.01019800	2.94029900	-0.04757400
H	-12.72300200	-3.78539600	0.46636500
H	-11.16990500	-4.50931800	0.01804500
H	-11.35646300	-3.75637400	1.59344700
H	-11.62934700	1.81602200	-1.11993500
H	-12.98030000	0.88477000	-1.82016800
H	-11.43318000	1.05663400	-2.69209900
H	-4.38937100	-2.67784100	0.97754900
H	-5.84206700	-3.03103100	1.93063100
H	-5.63146200	-3.77964700	0.35470800
H	-6.44158300	1.66963600	-2.42818600
H	-5.07105800	1.93045600	-1.31422200
H	-6.72206600	2.46426600	-0.88703900
H	4.24165400	3.55765200	-1.09104900
H	5.68211000	3.88100600	-2.09442000
H	5.58329300	4.56857200	-0.47934900
H	6.43633200	-1.09068600	1.92375900
H	6.62172700	-1.76023300	0.31123600
H	5.03034300	-1.19445200	0.84870000
H	13.26508100	0.58397600	0.93056600
H	11.91627900	0.08583000	1.96505700
H	12.06377300	-0.57985900	0.34678000
H	12.05486300	5.22969000	-1.08740500
H	10.44694600	5.60971100	-0.41421700
H	10.57066900	4.95284800	-2.03874300
H	-8.26351800	-4.61721400	-0.97772300
H	-8.04487600	-6.83549800	0.11173700
H	-8.18036400	-7.02574500	2.58783400
H	-8.53528200	-4.98531300	3.96492900
H	-8.75354000	-2.76989700	2.86990900
H	9.44655100	-1.56671400	-0.89115400
H	9.93702700	-3.80662900	0.05645800
H	9.98414300	-4.13304200	2.52177400
H	9.53754000	-2.20710200	4.03002700
H	9.04827000	0.03015600	3.07717000

H	7.24721400	-8.49145900	-1.75651200
H	7.45650600	-6.80653000	-1.27267700
H	6.66425700	-7.19087700	-2.81762700
H	4.08197800	-9.09304200	-1.57875600
H	5.66097900	-9.65960800	-0.99257000
H	4.49443700	-8.98473200	0.14754100
H	-7.33515200	7.44621900	2.02408000
H	-7.64042500	7.50643900	0.27372200
H	-7.58952500	9.00289900	1.22913100
H	-4.94356900	9.56426900	-0.54128900
H	-5.94846800	10.23964800	0.75833000
H	-4.29424400	9.72859400	1.10584900

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B3LYP/6-31G* = -4810.96496931 au
B3LYP/6-31G* Zero Point Corrected Energy = -4809.524255 au
NIMAG = 0

C	1.21929200	-0.73147400	-0.03028000
C	1.23881000	0.69633200	-0.04302300
C	0.01979100	1.38859300	-0.03650900
C	-1.21940700	0.73149000	-0.03022000
C	-1.23892800	-0.69631600	-0.04299300
C	-0.01990700	-1.38857800	-0.03653600
C	2.41756200	-1.49227200	-0.00605400
C	2.45843500	1.42515600	-0.06888400
C	-2.41768500	1.49227300	-0.00594800
C	-2.45855600	-1.42513700	-0.06882900
C	3.41944200	-2.18459900	0.03874400
C	3.47297300	2.09828300	-0.11796000
C	-3.47305200	-2.09832900	-0.11791000
C	-3.41958300	2.18457300	0.03886800
C	-4.64485300	-2.88597000	-0.17874900
C	-4.57948700	2.98785700	0.09480700
C	-5.81707600	-2.56209200	-0.92247300
N	-6.71866300	-3.53999900	-0.76136000
C	-6.18380200	-4.52584400	0.08164600
C	-4.86728600	-4.12309600	0.45395700
C	-5.83843700	2.57790400	0.62429400
N	-6.70546800	3.59360800	0.52038600
C	-6.06137700	4.69133200	-0.07078500
C	-4.71139600	4.31960700	-0.34094700
B	-8.18701900	3.55506600	1.01468100
N	-8.79647400	4.94315300	0.65667900

C	-8.11991600	6.01116700	0.05416000
C	-6.76841000	5.88705000	-0.29949200
B	-8.12911500	-3.57141700	-1.43180400
N	-8.81192100	-4.88087000	-0.93599500
C	-8.24489200	-5.83674300	-0.08380300
C	-6.94621300	-5.66146800	0.41536300
C	-10.05347600	-5.27901500	-1.26848200
C	-10.32597900	-6.51102600	-0.63618000
C	-9.21428800	-6.88105700	0.10891800
C	-10.06994400	5.31183100	0.88751000
C	-10.25383200	6.63633100	0.43627400
C	-9.05299100	7.09578000	-0.08816300
C	-6.06369100	7.04473600	-0.93134800
C	-3.59953500	5.11083000	-0.95960000
C	-6.18864400	1.25984600	1.22702300
C	-11.06954200	4.40325300	1.52483100
C	-8.84901800	8.46150600	-0.67486500
C	-6.05608000	-1.35976600	-1.77165000
C	-3.86309200	-4.80536400	1.33222800
C	-6.35990100	-6.69769000	1.31993300
C	-9.11906200	-8.13454900	0.92803300
C	-10.93919000	-4.48435700	-2.17094100
C	-6.02386100	7.17801000	-2.32563300
C	-5.36410700	8.25917200	-2.91255000
C	-4.73760000	9.21676300	-2.11270000
C	-4.77361600	9.08966600	-0.72272400
C	-5.43383700	8.00984900	-0.13409900
C	-6.51770400	-6.59841200	2.70868200
C	-5.96934200	-7.56619000	3.55206500
C	-5.25812700	-8.64165900	3.01641500
C	-5.09752200	-8.74632100	1.63341300
C	-5.64581300	-7.77992600	0.78851300
F	-8.87011100	-2.46552200	-1.02957200
F	-7.99490000	-3.59879600	-2.81731300
F	-8.22006200	3.35902600	2.39211500
F	-8.88034600	2.54584300	0.35474300
C	10.25378400	-6.63615700	0.43679800
C	10.06973700	-5.31175800	0.88826300
N	8.79630700	-4.94308300	0.65721100
C	8.11993200	-6.01100000	0.05431300
C	9.05308500	-7.09554500	-0.08801700
B	8.18671000	-3.55509700	1.01536300
N	6.70529100	-3.59358200	0.52067000
C	6.06137200	-4.69122000	-0.07084500
C	6.76850600	-5.88686300	-0.29963600
C	5.83819800	-2.57793000	0.62457700

C	4.57937600	-2.98783600	0.09474500
C	4.71143800	-4.31949600	-0.34124100
C	11.06913600	-4.40328600	1.52604500
C	8.84929700	-8.46117000	-0.67502000
C	6.06398500	-7.04444200	-0.93190700
C	3.59975000	-5.11063900	-0.96030600
C	6.18823100	-1.25996100	1.22760300
C	5.43412500	-8.00983900	-0.13499900
C	4.77410000	-9.08956800	-0.72400300
C	4.73828000	-9.21629200	-2.11401800
C	5.36479000	-8.25841700	-2.91352600
C	6.02435000	-7.17734400	-2.32622900
F	8.21939600	-3.35936700	2.39285000
F	8.88017000	-2.54570200	0.35583100
C	4.64479900	2.88588600	-0.17880300
C	5.81704800	2.56190300	-0.92244900
N	6.71865100	3.53980600	-0.76138300
C	6.18378900	4.52572700	0.08153300
C	4.86725200	4.12303900	0.45383200
B	8.12913500	3.57111500	-1.43175300
N	8.81195000	4.88061200	-0.93605600
C	8.24490400	5.83657600	-0.08397700
C	6.94621200	5.66136800	0.41517100
C	10.05353000	5.27869300	-1.26851900
C	10.32603100	6.51076200	-0.63632500
C	9.21431500	6.88089000	0.10868300
C	6.05606500	1.35948600	-1.77149300
C	3.86304800	4.80538600	1.33203000
C	6.35989800	6.69766600	1.31965400
C	9.11907800	8.13445700	0.92768200
C	10.93926800	4.48392600	-2.17085900
C	5.64583900	7.77986700	0.78811900
C	5.09755100	8.74635200	1.63291900
C	5.25812900	8.64181300	3.01593400
C	5.96931300	7.56638000	3.55169600
C	6.51767200	6.59851400	2.70841300
F	8.87008600	2.46525400	-1.02935400
F	7.99499900	3.59834200	-2.81727300
H	0.03586500	2.47294000	-0.03732400
H	-0.03597900	-2.47292400	-0.03736800
H	-11.25199000	-7.06495300	-0.72437400
H	-11.18221300	7.19041900	0.49310700
H	-3.39720900	6.03685000	-0.41151300
H	-2.68638200	4.50913800	-0.96691100
H	-3.82392300	5.39892200	-1.99242900
H	-5.34217900	0.57350800	1.15631800

H	-7.05911600	0.82824500	0.72293600
H	-6.46665500	1.38659300	2.27929400
H	-12.03455500	4.90589100	1.62739600
H	-11.19660700	3.49384800	0.92819800
H	-10.72183600	4.08379900	2.51314300
H	-8.08375200	9.03277200	-0.13877400
H	-9.78591100	9.02539400	-0.62915100
H	-8.53066000	8.41787100	-1.72190600
H	-6.25552100	-1.65962000	-2.80608600
H	-6.94201800	-0.81728900	-1.42572600
H	-5.18755400	-0.69827600	-1.74442000
H	-4.22857100	-4.92796600	2.35750300
H	-3.60816200	-5.80579800	0.96738100
H	-2.94710300	-4.20904100	1.36779500
H	-10.05513400	-8.69639300	0.85118000
H	-8.93635100	-7.92370200	1.98705900
H	-8.30471800	-8.78638500	0.59408400
H	-11.89567300	-4.99275100	-2.31597000
H	-11.11822200	-3.48825900	-1.75262900
H	-10.45802200	-4.33398400	-3.14321900
H	-6.51064900	6.43167300	-2.94762200
H	-5.33965300	8.35174600	-3.99496100
H	-4.22355500	10.05755300	-2.57026600
H	-4.28754300	9.83110800	-0.09431100
H	-5.46127900	7.90962800	0.94758800
H	-7.07024100	-5.76028500	3.12470700
H	-6.09780200	-7.47832900	4.62750000
H	-4.83082800	-9.39413100	3.67347800
H	-4.54492500	-9.58074700	1.21001100
H	-5.52105300	-7.86058300	-0.28797700
H	11.18217300	-7.19022000	0.49374600
H	10.72121800	-4.08417200	2.51439400
H	12.03417400	-4.90587000	1.62863900
H	11.19622800	-3.49368400	0.92972100
H	8.53115400	-8.41735400	-1.72211700
H	9.78620600	-9.02502400	-0.62921700
H	8.08394500	-9.03257100	-0.13919400
H	2.68652800	-4.50905000	-0.96753900
H	3.82431000	-5.39834400	-1.99320800
H	3.39746200	-6.03687100	-0.41256900
H	5.34169500	-0.57370000	1.15700000
H	7.05867400	-0.82814900	0.72364300
H	6.46621900	-1.38690300	2.27985500
H	5.46142600	-7.90991100	0.94671800
H	4.28802400	-9.83123400	-0.09585500
H	4.22438400	-10.05701300	-2.57188000

H	5.34049100	-8.35070100	-3.99596500
H	6.51114300	-6.43078800	-2.94795300
H	11.25206000	7.06465700	-0.72453100
H	6.94200400	0.81705600	-1.42549800
H	5.18754400	0.69799100	-1.74419100
H	6.25551200	1.65922400	-2.80596100
H	4.22854400	4.92815700	2.35727800
H	3.60806500	5.80575900	0.96704500
H	2.94708400	4.20903000	1.36769600
H	10.05515500	8.69628900	0.85080100
H	8.93634500	7.92370200	1.98672300
H	8.30474400	8.78626800	0.59366200
H	11.89576000	4.99229600	-2.31591500
H	11.11828300	3.48787200	-1.75243100
H	10.45812500	4.33344700	-3.14313300
H	5.52110600	7.86043000	-0.28838100
H	4.54498100	9.58075100	1.20942900
H	4.83083600	9.39435300	3.67292300
H	6.09775400	7.47861600	4.62714000
H	7.07018900	5.76041700	3.12452600

8

B3LYP/6-31G* = -4843.02969218 au
B3LYP/6-31G* Zero Point Corrected Energy = -4841.614190 au
NIMAG = 0

C	1.15653200	-0.70620800	0.08392900
C	1.14604300	0.72344300	0.03511100
N	-0.01076500	1.40398600	0.05953400
C	-1.15651900	0.70619800	0.08389600
C	-1.14602800	-0.72346500	0.03510500
N	0.01077400	-1.40400000	0.05956500
C	2.37226800	-1.43809400	0.16589600
C	2.34944600	1.47330800	-0.05092500
C	-2.37226100	1.43807300	0.16584600
C	-2.34943800	-1.47332100	-0.05092800
C	3.39397900	-2.09367200	0.26759700
C	3.36091700	2.14369000	-0.15948000
C	-3.36090800	-2.14369900	-0.15951900
C	-3.39398500	2.09363200	0.26752800
C	-4.51487500	-2.94448700	-0.28401600
C	-4.56186000	2.87726800	0.37953300
C	-5.76539800	-2.51634600	-0.81731200
N	-6.62539600	-3.54240100	-0.78255500

C	-5.98353800	-4.66469700	-0.23537000
C	-4.64254800	-4.29972700	0.07891100
C	-5.76560700	2.48031100	1.03119700
N	-6.65497300	3.47812500	0.94387500
C	-6.08004800	4.54914400	0.24186800
C	-4.74973700	4.18302700	-0.11419000
B	-8.09077200	3.44837700	1.55884200
N	-8.74808300	4.80977700	1.18299200
C	-8.14404500	5.84761400	0.46180300
C	-6.82565600	5.72041200	0.00310500
B	-8.09720300	-3.48942100	-1.30367300
N	-8.70393400	-4.89645600	-1.02265500
C	-8.02957900	-5.98997900	-0.46421500
C	-6.68608900	-5.87607100	-0.08120000
C	-9.97089800	-5.26010000	-1.29135500
C	-10.15338000	-6.60731200	-0.91050900
C	-8.95821400	-7.08605900	-0.39176600
C	-10.00427600	5.17427300	1.49714000
C	-10.25056900	6.46583300	0.98304700
C	-9.10729400	6.90813600	0.33186000
C	-6.20056200	6.84562700	-0.75791100
C	-3.70077200	4.95365800	-0.85624900
C	-6.04203500	1.19580800	1.73676200
C	-10.92987300	4.29241700	2.26903700
C	-8.98055300	8.23602500	-0.35478900
C	-6.11271900	-1.17354400	-1.36491000
C	-3.53349700	-5.11189100	0.67493900
C	-5.98418000	-7.05971200	0.50352600
C	-8.75356000	-8.47883800	0.12696800
C	-10.96716300	-4.32549400	-1.89509800
C	-6.26161700	6.87383300	-2.15747600
C	-5.68222200	7.92656700	-2.86759900
C	-5.03413600	8.95909600	-2.18704100
C	-4.96834400	8.93579600	-0.79254900
C	-5.54964700	7.88530800	-0.08051000
C	-5.96132000	-7.25878500	1.89031200
C	-5.30390500	-8.36390300	2.43347600
C	-4.66231300	-9.27928900	1.59702600
C	-4.68096900	-9.08610700	0.21434300
C	-5.33934900	-7.98269300	-0.33082700
F	-8.81008700	-2.51652700	-0.61101400
F	-8.10538000	-3.22989100	-2.67074500
F	-8.01135400	3.32165600	2.94221200
F	-8.82002000	2.40007300	1.00742100
C	10.25054500	-6.46590900	0.98308900
C	10.00420700	-5.17441000	1.49731500

N	8.74803700	-4.80988300	1.18311300
C	8.14406000	-5.84763600	0.46175200
C	9.10732000	-6.90814400	0.33176800
B	8.09064200	-3.44858400	1.55918600
N	6.65489700	-3.47826000	0.94410300
C	6.08006000	-4.54916500	0.24185200
C	6.82570500	-5.72038800	0.00297400
C	5.76551600	-2.48046100	1.03147900
C	4.56185000	-2.87731600	0.37961100
C	4.74979600	-4.18298900	-0.11431800
C	10.92973700	-4.29264100	2.26939200
C	8.98062800	-8.23595700	-0.35503400
C	6.20068900	-6.84549100	-0.75827400
C	3.70095100	-4.95347700	-0.85669600
C	6.04186900	-1.19606300	1.73726400
C	5.54942900	-7.88511200	-0.08110600
C	4.96819300	-8.93548900	-0.79335900
C	5.03437800	-8.95873000	-2.18783500
C	5.68280200	-7.92626200	-2.86815900
C	6.26214800	-6.87364500	-2.15781900
F	8.01111700	-3.32214700	2.94258000
F	8.81989700	-2.40014100	1.00803800
C	4.51488700	2.94447500	-0.28396300
C	5.76546700	2.51627900	-0.81708100
N	6.62544200	3.54235600	-0.78239400
C	5.98351500	4.66471800	-0.23542400
C	4.64250700	4.29976600	0.07879500
B	8.09728500	3.48933500	-1.30339200
N	8.70400300	4.89638900	-1.02242300
C	8.02957300	5.98998400	-0.46421200
C	6.68603900	5.87612000	-0.08134400
C	9.97099100	5.26000700	-1.29103100
C	10.15341800	6.60727600	-0.91035100
C	8.95819000	7.08608400	-0.39181300
C	6.11286800	1.17339800	-1.36443100
C	3.53339300	5.11198000	0.67464200
C	5.98405800	7.05983200	0.50315400
C	8.75346700	8.47892700	0.12672000
C	10.96734800	4.32532900	-1.89451200
C	5.33923500	7.98266800	-0.33136300
C	4.68079600	9.08614100	0.21361500
C	4.66206900	9.27952600	1.59626900
C	5.30365300	8.36428500	2.43288300
C	5.96113200	7.25911100	1.88991100
F	8.81011400	2.51648900	-0.61061400
F	8.10556700	3.22971600	-2.67044800

H	-11.07736000	-7.16276800	-1.00972600
H	-11.18154200	7.00921700	1.08379900
H	-3.50141400	5.92567500	-0.39417900
H	-2.76894800	4.38163200	-0.86994600
H	-3.99343200	5.15147600	-1.89344100
H	-5.20068700	0.50953900	1.61942900
H	-6.95422600	0.73387800	1.34685500
H	-6.21327200	1.37901000	2.80349400
H	-11.89029000	4.78893000	2.42821700
H	-11.09360300	3.34942400	1.73683500
H	-10.49122400	4.03290700	3.23839300
H	-8.19860600	8.85999500	0.09087400
H	-9.92803300	8.77911400	-0.28334200
H	-8.72924800	8.12966200	-1.41538000
H	-6.35582600	-1.25083500	-2.43066800
H	-7.00332200	-0.77655500	-0.86804400
H	-5.27690300	-0.48273900	-1.23490300
H	-3.76028200	-5.42559500	1.70008100
H	-3.33828400	-6.02419700	0.10262000
H	-2.61656200	-4.51654000	0.69765600
H	-9.69016300	-9.04025300	0.05377400
H	-8.43371300	-8.48676000	1.17421800
H	-7.98842000	-9.02215600	-0.43779400
H	-11.92017100	-4.83431100	-2.06004600
H	-11.12715000	-3.46116300	-1.24183300
H	-10.59610900	-3.93389000	-2.84813700
H	-6.76537200	6.06939500	-2.68657100
H	-5.73673300	7.93826800	-3.95279700
H	-4.58199500	9.77734100	-2.74070500
H	-4.46439000	9.73552700	-0.25654300
H	-5.49932900	7.86631000	1.00481000
H	-6.45929200	-6.54494400	2.54093700
H	-5.29257300	-8.50775900	3.51046700
H	-4.14951200	-10.13841500	2.02063000
H	-4.18240500	-9.79403200	-0.44225600
H	-5.35282300	-7.83091700	-1.40675600
H	11.18151100	-7.00930300	1.08385400
H	10.49100600	-4.03325300	3.23874400
H	11.89014400	-4.78916500	2.42858900
H	11.09350000	-3.34958100	1.73731800
H	8.72979400	-8.12945900	-1.41572600
H	9.92798200	-8.77922100	-0.28323700
H	8.19837800	-8.85982100	0.09024000
H	2.76919500	-4.38134800	-0.87063300
H	3.99388900	-5.15129400	-1.89380900
H	3.50134800	-5.92548600	-0.39471600

H	5.20047900	-0.50982600	1.62005200
H	6.95402800	-0.73400900	1.34742600
H	6.21313100	-1.37943900	2.80396100
H	5.49880400	-7.86615300	1.00420100
H	4.46397900	-9.73517900	-0.25753600
H	4.58227900	-9.77688700	-2.74166500
H	5.73761800	-7.93791600	-3.95334100
H	6.76616800	-6.06925400	-2.68673400
H	11.07740300	7.16272600	-1.00955100
H	7.00333400	0.77643200	-0.86729900
H	5.27699500	0.48264000	-1.23453600
H	6.35624200	1.25054700	-2.43013800
H	3.76005700	5.42572500	1.69979900
H	3.33826800	6.02426200	0.10225800
H	2.61644800	4.51664200	0.69727900
H	9.69002400	9.04040100	0.05337500
H	8.43370600	8.48697800	1.17399800
H	7.98824100	9.02210400	-0.43805600
H	11.92029500	4.83420600	-2.05963000
H	11.12745900	3.46121500	-1.24098700
H	10.59632100	3.93339400	-2.84742400
H	5.35276400	7.83073700	-1.40727000
H	4.18223900	9.79395400	-0.44311000
H	4.14921900	10.13869800	2.01972100
H	5.29226700	8.50829800	3.50985300
H	6.45909900	6.54538400	2.54066400

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B3LYP/6-31G* = -2521.60663907 au
B3LYP/6-31G* Zero Point Corrected Energy = -2520.836245 au
NIMAG = 0

C	-0.57324900	7.40197000	0.21704200
C	0.82332400	7.37864200	0.14239800
C	1.49540300	6.16307200	0.08497700
C	0.79458700	4.94109100	0.10266900
C	-0.62763200	4.96463800	0.19551600
C	-1.28608900	6.20852000	0.24477000
C	1.51161700	3.71717600	0.01079400
C	-1.38821900	3.76353700	0.25251600
C	-2.08552800	2.76808700	0.33602400
C	2.16622600	2.69617300	-0.10500400

C	-2.89519200	1.61400000	0.44341600
C	2.92262100	1.51245300	-0.25296700
C	-2.56721500	0.44744900	1.19421200
N	-3.56828600	-0.43644700	1.08511300
C	-4.57414900	0.10486200	0.27056600
C	-4.15888200	1.40672500	-0.13891400
C	2.42453600	0.27834900	-0.76550900
N	3.41797600	-0.62021600	-0.77815500
C	4.58675700	-0.02214200	-0.28295800
C	4.28428600	1.33105200	0.05119100
B	3.28421800	-2.09118900	-1.28697200
N	4.68143300	-2.74747800	-1.08044900
C	5.82562800	-2.11323900	-0.58047200
C	5.77733200	-0.76721600	-0.18860500
B	-3.60572900	-1.83194600	1.78568300
N	-4.94834100	-2.49389100	1.35468200
C	-5.92211400	-1.92301700	0.52582100
C	-5.73756500	-0.63812500	-0.00542100
C	-5.35963300	-3.72030500	1.72548200
C	-6.61859400	-3.97858900	1.14250600
C	-6.99195500	-2.87365700	0.38878100
C	4.98796900	-4.02413900	-1.37606000
C	6.34744000	-4.25187300	-1.07389200
C	6.89330300	-3.07565800	-0.57693600
C	7.01177700	-0.11142900	0.34273300
C	5.16651600	2.40342400	0.61370000
C	1.04237700	-0.02010000	-1.23931900
C	3.98947500	-4.98627200	-1.93145100
C	8.32162900	-2.91873600	-0.14476900
C	-1.33948900	0.19826300	2.00330600
C	-4.85384500	2.41009800	-1.00802300
C	-6.79422500	-0.04699000	-0.88291200
C	-8.27123100	-2.76835600	-0.38817100
C	-4.54927700	-4.60673300	2.61316100
C	7.29450300	-0.13912500	1.71495200
C	8.44446800	0.47706500	2.21117900
C	9.32339600	1.12590400	1.34171300
C	9.04801300	1.15619200	-0.02673500
C	7.89821700	0.54086800	-0.52464100
C	-6.74154800	-0.22167200	-2.27223200
C	-7.72886500	0.32961600	-3.09063700
C	-8.77706600	1.06149700	-2.52938400
C	-8.83504900	1.23948100	-1.14576600
C	-7.84948300	0.68760000	-0.32570300
F	-2.53357100	-2.60789000	1.35835500
F	-3.57612000	-1.66769600	3.16807100

F	2.32544600	-2.76566100	-0.53955600
F	2.95130300	-2.09482900	-2.63875400
H	2.57853900	6.13737300	0.01652800
H	-2.36946400	6.21736100	0.31366600
H	-7.18818600	-4.89066200	1.26835700
H	6.86695300	-5.19173500	-1.21142200
H	5.58757500	2.12349100	1.58506200
H	4.58480300	3.32015100	0.74492900
H	6.01383800	2.62579900	-0.04362500
H	0.40133100	0.85484700	-1.11260700
H	0.62339400	-0.86764900	-0.68715700
H	1.05783300	-0.31117600	-2.29541400
H	3.54670400	-4.59041500	-2.85137600
H	3.16531400	-5.13660300	-1.22570700
H	4.46147200	-5.94913300	-2.14266500
H	8.40745300	-2.63459700	0.90940100
H	8.84545600	-2.14796600	-0.72007800
H	8.85417400	-3.86476500	-0.28396400
H	-0.64382700	1.03402500	1.90251600
H	-0.85281300	-0.72840200	1.68307600
H	-1.60089300	0.06730900	3.05920900
H	-5.84123500	2.67943900	-0.61909300
H	-4.24819100	3.31865900	-1.06902700
H	-5.00782500	2.03594200	-2.02603800
H	-8.84177600	-3.69660300	-0.28493300
H	-8.09419200	-2.59589800	-1.45500800
H	-8.90151100	-1.94361000	-0.03844800
H	-4.31121100	-4.09354900	3.55051100
H	-5.09122000	-5.53008300	2.83252300
H	-3.59307800	-4.85384000	2.13929300
H	6.60912400	-0.64289300	2.39122900
H	8.65243500	0.44994300	3.27740900
H	10.21814500	1.60576100	1.72861900
H	9.72770100	1.65960000	-0.70900200
H	7.68270700	0.56551000	-1.58947600
H	-5.92470900	-0.79039600	-2.70833500
H	-7.67758400	0.18721900	-4.16669300
H	-9.54471800	1.49127000	-3.16698800
H	-9.64797600	1.80832100	-0.70252500
H	-7.89413000	0.82538500	0.75129100
H	1.38637400	8.30761200	0.12447400
H	-1.10403900	8.34893500	0.25891000

10

B3LYP/6-31G* = -2521.60798242 au
B3LYP/6-31G* Zero Point Corrected Energy = -2520.837821 au
NIMAG = 0

C	-1.21044300	-4.98318500	0.00083300
C	-1.22298700	-3.57279600	0.00066100
C	0.00000500	-2.88003000	0.00057200
C	1.22299500	-3.57280500	0.00064600
C	1.21044000	-4.98319200	0.00081900
C	-0.00000400	-5.67161800	0.00090200
C	-2.45640000	-2.85985600	0.00054600
C	2.45640900	-2.85986800	0.00051500
C	-3.51486100	-2.25739600	0.00039600
C	3.51487000	-2.25740800	0.00035500
C	4.74452200	-1.56144700	0.00016900
C	-4.74451600	-1.56143900	0.00022900
C	-4.93473100	-0.16728400	0.00022500
C	-6.34614200	0.03887900	-0.00002300
N	-6.97017400	-1.21771500	-0.00016500
C	-6.03170500	-2.17370500	-0.00001000
C	6.03171300	-2.17370800	-0.00021300
N	6.97017900	-1.21771500	-0.00034900
C	6.34614300	0.03887800	-0.00005700
C	4.93473200	-0.16729200	0.00027600
C	-7.12221300	1.21341400	-0.00008700
C	-8.52365100	1.15829500	-0.00032000
N	-9.18500400	-0.07649900	-0.00045100
B	-8.50994200	-1.47923800	-0.00029200
B	8.50994900	-1.47923400	-0.00059000
N	9.18500600	-0.07649200	-0.00044900
C	8.52364900	1.15829900	-0.00023000
C	7.12221000	1.21341500	-0.00001500
C	-9.52434400	2.19041600	-0.00039600
C	-10.74832900	1.53454400	-0.00060700
C	-10.51287000	0.14338800	-0.00063900
C	10.51287000	0.14339900	-0.00061100
C	10.74832500	1.53455600	-0.00046500
C	9.52433800	2.19042400	-0.00021900
C	-3.81666200	0.83014400	0.00041700
C	-6.43894900	2.54342900	0.00003100
C	-9.36046500	3.68190600	-0.00028700
C	-11.51411300	-0.96494600	-0.00095200
C	-6.34842100	-3.63103500	-0.00005900
C	6.34843500	-3.63103700	-0.00035500
C	3.81665900	0.83013200	0.00067500
C	6.43894300	2.54342800	0.00019500

C	9.36045400	3.68191300	0.00004900
C	11.51411800	-0.96493000	-0.00105300
C	-6.11509800	3.17425100	-1.20852400
C	-5.47809600	4.41635000	-1.20743800
C	-5.15903000	5.03994100	0.00031700
C	-5.47863700	4.41635700	1.20793000
C	-6.11565200	3.17426100	1.20873000
C	6.11482000	3.17417900	-1.20832600
C	5.47782400	4.41628000	-1.20717200
C	5.15901500	5.03993500	0.00061900
C	5.47888500	4.41641800	1.20819600
C	6.11591300	3.17432900	1.20892800
F	-8.87062000	-2.18333600	1.14506500
F	-8.87046700	-2.18350400	-1.14557300
F	8.87045200	-2.18322600	-1.14605100
F	8.87065100	-2.18360200	1.14458700
H	0.00001100	-1.79539300	0.00042100
H	-0.00000700	-6.75817600	0.00104500
H	-11.72550400	2.00055300	-0.00075500
H	11.72549900	2.00056800	-0.00057400
H	-3.84724600	1.48350200	-0.87805600
H	-3.84732100	1.48324800	0.87908400
H	-2.85912600	0.30194800	0.00038900
H	-10.34476900	4.16048400	-0.00110800
H	-8.81212700	4.03819100	0.87826200
H	-8.81061900	4.03819000	-0.87787400
H	-11.37778600	-1.60552500	0.87680700
H	-11.37871100	-1.60421300	-0.87982700
H	-12.53066700	-0.56374600	-0.00016100
H	-6.94728900	-3.89158000	0.87894400
H	-6.94777600	-3.89141600	-0.87876700
H	-5.42646300	-4.21626600	-0.00033900
H	6.94665200	-3.89178500	0.87903700
H	5.42647900	-4.21627000	-0.00141200
H	6.94844300	-3.89121100	-0.87867300
H	3.84705100	1.48346500	-0.87782300
H	3.84750400	1.48326100	0.87931700
H	2.85912500	0.30193200	0.00086300
H	8.81275800	4.03814900	0.87902600
H	8.80996400	4.03824200	-0.87710800
H	10.34475500	4.16049500	-0.00144200
H	12.53067100	-0.56372700	-0.00010300
H	11.37772200	-1.60568700	0.87656500
H	11.37879300	-1.60402200	-0.88006800
H	-6.36303900	2.68798700	-2.14817400
H	-5.23148400	4.89577200	-2.15092000

H	-4.66336900	6.00682000	0.00042000
H	-5.23245400	4.89578000	2.15152300
H	-6.36402600	2.68800100	2.14826800
H	6.36255800	2.68786200	-2.14800200
H	5.23101000	4.89565000	-2.15062700
H	4.66335000	6.00681300	0.00077700
H	5.23290100	4.89589100	2.15181600
H	6.36449600	2.68812400	2.14843900
H	-2.15238200	-5.52233500	0.00091800
H	2.15237400	-5.52235200	0.00089200

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B3LYP/6-31G* = -2521.60959833 au
B3LYP/6-31G* Zero Point Corrected Energy = -2520.838727 au
NIMAG = 0

C	-0.69316400	-1.73038800	-0.00507600
C	-1.41722800	-0.51861100	-0.00962200
C	-0.69319400	0.69311200	-0.00448600
C	0.69320300	0.69311000	0.00469100
C	1.41723600	-0.51861300	0.00936200
C	0.69317600	-1.73038900	0.00433500
C	-2.83800200	-0.51899400	-0.01937300
C	2.83801300	-0.51899700	0.01913400
C	-4.05683200	-0.52185900	-0.02808200
C	4.05684200	-0.52186600	0.02783000
C	5.46875400	-0.52824700	0.03916700
C	-5.46874100	-0.52823100	-0.03938000
C	-6.32743500	0.58047300	0.08146900
C	-7.65415400	0.06224300	0.01172400
N	-7.57065900	-1.32919200	-0.14970400
C	-6.28149300	-1.69112200	-0.18061300
C	6.28149800	-1.69113700	0.18042300
N	7.57066600	-1.32920900	0.14956200
C	7.65416900	0.06222700	-0.01183200
C	6.32745500	0.58046000	-0.08163400
C	-8.91192300	0.69148300	0.07546600
C	-10.09997000	-0.04759500	-0.02233300
N	-10.05957700	-1.43736100	-0.19284000
B	-8.77598900	-2.31270300	-0.28897400
B	8.77598600	-2.31268900	0.28909500
N	10.05958300	-1.43735600	0.19296500
C	10.09998300	-0.04759200	0.02244000
C	8.91194200	0.69147600	-0.07548400

C	-11.48152500	0.34778400	0.02099200
C	-12.21717500	-0.82070200	-0.12667600
C	-11.32092800	-1.90276100	-0.25615800
C	11.32092900	-1.90275000	0.25638400
C	12.21718400	-0.82069500	0.12691900
C	11.48154100	0.34778500	-0.02082800
C	-12.08058900	1.71293400	0.19096300
C	-11.63844800	-3.35150900	-0.43312700
C	-8.98129600	2.17513800	0.24908500
C	-5.85296800	1.99179500	0.24847800
C	-5.83221800	-3.10377300	-0.34283100
C	5.83221300	-3.10378000	0.34268600
C	5.85298300	1.99178600	-0.24859500
C	8.98130500	2.17513200	-0.24909100
C	12.08061400	1.71293200	-0.19079700
C	11.63843200	-3.35149300	0.43342200
C	-8.99518900	2.74015700	1.53126700
C	-9.06141000	4.12528600	1.69117700
C	-9.11327400	4.95884200	0.57226800
C	-9.09888600	4.40193100	-0.70808700
C	-9.03394500	3.01704100	-0.86978200
C	9.03409900	3.01700700	0.86979100
C	9.09899600	4.40190200	0.70812200
C	9.11321300	4.95884400	-0.57222200
C	9.06121400	4.12531400	-1.69114500
C	8.99501800	2.74018200	-1.53126100
F	-8.72315100	-2.95235700	-1.52416200
F	-8.75225400	-3.24137300	0.74741800
F	8.75237000	-3.24150800	-0.74716000
F	8.72302800	-2.95216100	1.52437600
H	-1.23626100	1.63317700	-0.00832700
H	1.23598300	-2.67053700	0.00744600
H	-13.29671800	-0.90110800	-0.14061900
H	13.29672600	-0.90110000	0.14093300
H	-13.17240600	1.63748100	0.19799100
H	-11.76765900	2.18775800	1.12677200
H	-11.79393000	2.39467400	-0.61690300
H	-11.16792700	-3.73868800	-1.34289600
H	-12.71913200	-3.50295200	-0.49253800
H	-11.23787400	-3.93724300	0.40137700
H	-4.75963800	2.01111600	0.23377900
H	-6.21822600	2.64722200	-0.54910500
H	-6.18907800	2.42994400	1.19448200
H	-6.24285400	-3.72877700	0.45693400
H	-4.74162000	-3.15643200	-0.32543200
H	-6.20288200	-3.51586900	-1.28745300

H	4.74162100	-3.15646900	0.32496800
H	6.20258000	-3.51573200	1.28749100
H	6.24312100	-3.72888500	-0.45685500
H	6.18893700	2.42991500	-1.19466400
H	6.21838900	2.64721700	0.54891600
H	4.75965600	2.01112400	-0.23371700
H	13.17242400	1.63743200	-0.19816600
H	11.76741200	2.18791400	-1.12643000
H	11.79423800	2.39456400	0.61726700
H	12.71911200	-3.50295300	0.49283100
H	11.23782500	-3.93726600	-0.40103700
H	11.16791300	-3.73861500	1.34321900
H	-8.95395500	2.09060600	2.40150100
H	-9.07199400	4.55196400	2.69049100
H	-9.16390200	6.03693300	0.69734300
H	-9.13809300	5.04496200	-1.58319400
H	-9.02281000	2.58263600	-1.86576500
H	9.02309500	2.58257700	1.86576500
H	9.13830600	5.04491500	1.58323800
H	9.16380800	6.03694000	-0.69727400
H	9.07166700	4.55201500	-2.69045100
H	8.95367000	2.09065300	-2.40150500
H	1.23627000	1.63317400	0.00890700
H	-1.23597000	-2.67053600	-0.00855700

Crystallographic Data for 8

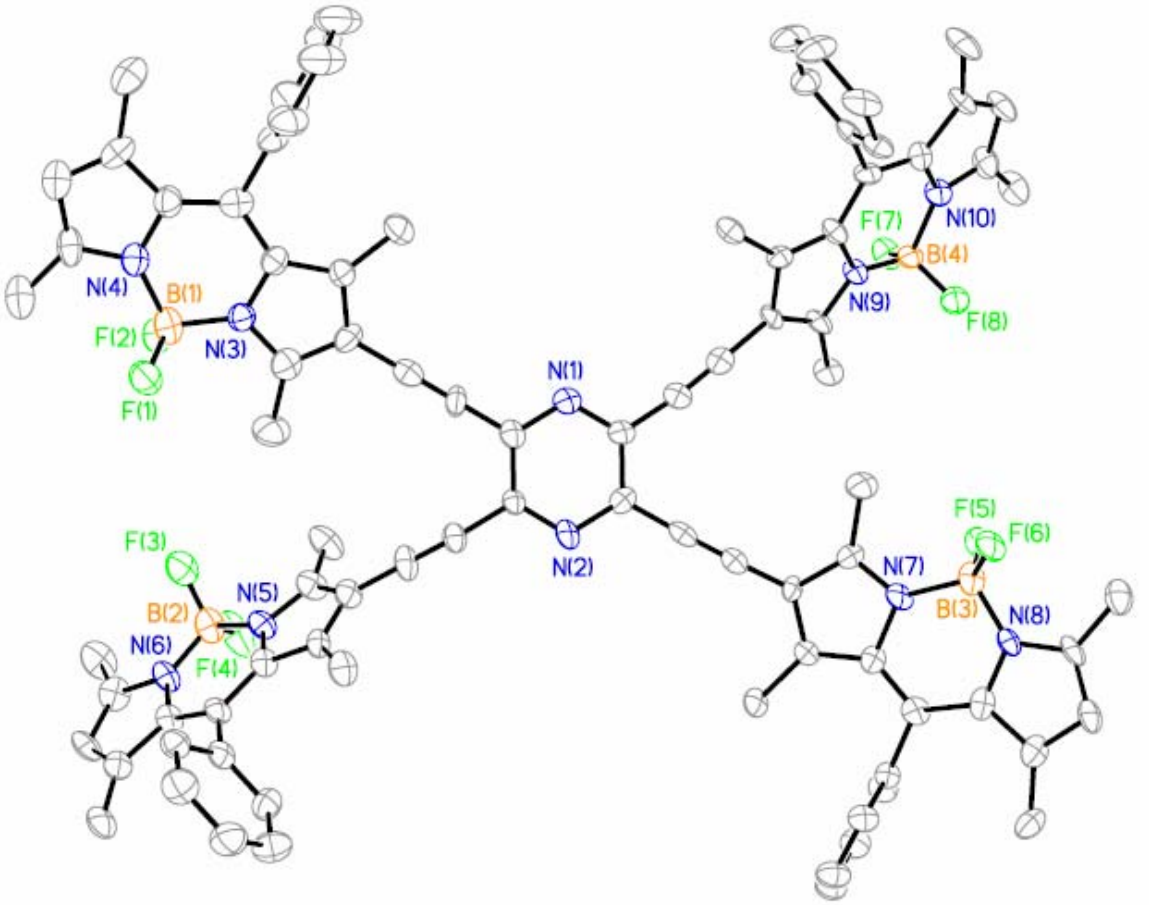

Table 1. Crystal data and structure refinement for **8**.

Identification code	mh67	
Empirical formula	C121 H116 B4 F8 N10	
Formula weight	1905.48	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.922(8) Å	α = 68.929(8)°.
	b = 20.395(14) Å	β = 81.221(9)°.
	c = 25.136(17) Å	γ = 81.589(9)°.
Volume	5138(6) $Å^3$	
Z	2	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	2008	
Crystal size	0.38 x 0.20 x 0.01 mm^3	
Theta range for data collection	0.87 to 24.00°.	
Index ranges	-12<=h<=12, -23<=k<=23, -28<=l<=28	
Reflections collected	37416	
Independent reflections	16057 [R(int) = 0.1200]	
Completeness to theta = 24.00°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9992 and 0.9696	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16057 / 0 / 1117	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0909, wR2 = 0.1953	
R indices (all data)	R1 = 0.2196, wR2 = 0.2193	
Largest diff. peak and hole	0.286 and -0.304 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	-3627(5)	4766(4)	-2766(3)	50(2)
N(2)	-2145(5)	4155(3)	-1842(3)	49(2)
N(3)	-2283(6)	2450(3)	-4349(3)	59(2)
N(4)	-2382(6)	1763(4)	-4977(3)	62(2)
N(5)	2406(5)	1764(4)	-2615(3)	61(2)
N(6)	4114(5)	874(4)	-2692(3)	60(2)
N(7)	-4740(5)	6161(3)	-53(3)	51(2)
N(8)	-5344(5)	6687(3)	710(3)	46(2)
N(9)	-7005(5)	7953(3)	-2799(2)	44(2)
N(10)	-8551(5)	9036(4)	-3077(2)	55(2)
B(1)	-1543(10)	1881(6)	-4567(5)	70(3)
B(2)	3558(9)	1603(7)	-3005(5)	74(3)
B(3)	-5616(8)	6754(6)	108(5)	61(3)
B(4)	-7232(8)	8753(6)	-2859(4)	61(3)
F(1)	-1321(4)	1261(3)	-4106(2)	84(2)
F(2)	-428(4)	2128(2)	-4876(2)	75(1)
F(3)	3170(4)	1668(3)	-3530(2)	89(2)
F(4)	4388(4)	2125(2)	-3117(2)	113(2)
F(5)	-5448(4)	7390(2)	-281(2)	73(1)
F(6)	-6868(3)	6582(2)	158(2)	71(1)
F(7)	-6310(3)	9114(2)	-3256(2)	68(1)
F(8)	-7242(3)	8826(2)	-2334(2)	64(1)
C(1)	-2827(7)	4177(4)	-2726(3)	53(2)
C(2)	-2054(6)	3889(4)	-2261(3)	44(2)
C(3)	-2993(6)	4736(4)	-1875(3)	49(2)
C(4)	-3687(6)	5065(4)	-2364(3)	46(2)
C(5)	-2810(7)	3851(5)	-3128(4)	62(3)
C(6)	-2841(6)	3558(4)	-3452(4)	56(2)
C(7)	-2846(8)	3202(5)	-3863(3)	65(2)
C(8)	-1930(8)	2668(5)	-3945(4)	70(3)

C(9)	-3791(7)	3313(4)	-4215(3)	59(2)
C(10)	-3456(7)	2825(4)	-4503(3)	56(2)
C(11)	-3993(7)	2693(5)	-4933(3)	63(2)
C(12)	-3496(8)	2170(5)	-5160(4)	68(3)
C(13)	-3863(9)	1905(5)	-5556(3)	65(3)
C(14)	-3029(10)	1359(5)	-5602(4)	81(3)
C(15)	-2136(9)	1281(5)	-5235(4)	71(3)
C(16)	-729(7)	2394(5)	-3666(4)	96(3)
C(17)	-4950(7)	3826(4)	-4225(3)	78(3)
C(18)	-5227(9)	3129(5)	-5129(4)	67(2)
C(19)	-6359(9)	2895(5)	-4839(4)	89(3)
C(20)	-7471(10)	3286(7)	-5023(5)	112(4)
C(21)	-7436(12)	3890(8)	-5488(5)	130(5)
C(22)	-6311(13)	4143(6)	-5787(4)	101(3)
C(23)	-5162(10)	3750(5)	-5607(4)	93(3)
C(24)	-5071(7)	2182(5)	-5878(3)	86(3)
C(25)	-1010(8)	756(5)	-5140(4)	95(3)
C(26)	-1125(7)	3283(4)	-2241(3)	55(2)
C(27)	-376(7)	2823(5)	-2262(4)	62(3)
C(28)	597(7)	2294(5)	-2302(4)	60(2)
C(29)	1622(7)	2378(5)	-2735(4)	66(2)
C(30)	760(6)	1587(4)	-1891(3)	50(2)
C(31)	1907(6)	1269(5)	-2091(4)	52(2)
C(32)	2567(7)	600(4)	-1858(4)	56(2)
C(33)	3693(6)	407(5)	-2145(4)	55(2)
C(34)	4546(7)	-234(5)	-1989(4)	62(2)
C(35)	5427(7)	-129(5)	-2456(4)	68(3)
C(36)	5177(7)	523(5)	-2879(4)	71(3)
C(37)	1870(7)	3041(4)	-3242(4)	84(3)
C(38)	-166(6)	1275(4)	-1363(3)	67(2)
C(39)	2038(6)	98(4)	-1294(4)	54(2)
C(40)	1446(8)	-467(4)	-1311(4)	65(2)
C(41)	938(8)	-910(5)	-791(4)	87(3)
C(42)	1021(9)	-824(6)	-265(4)	96(3)
C(43)	1634(9)	-267(6)	-269(5)	92(3)
C(44)	2145(7)	192(5)	-786(4)	70(3)

C(45)	4492(7)	-868(4)	-1452(4)	72(3)
C(46)	5911(7)	877(5)	-3455(4)	102(3)
C(47)	-3169(6)	5025(4)	-1406(3)	45(2)
C(48)	-3409(6)	5242(4)	-1000(4)	44(2)
C(49)	-3695(6)	5501(4)	-564(3)	41(2)
C(50)	-4691(6)	6017(4)	-535(3)	44(2)
C(51)	-3066(6)	5340(4)	-78(3)	41(2)
C(52)	-3723(6)	5727(4)	257(3)	47(2)
C(53)	-3564(6)	5792(4)	782(3)	51(2)
C(54)	-4376(7)	6240(4)	1019(3)	52(2)
C(55)	-4410(7)	6353(5)	1566(3)	60(2)
C(56)	-5365(7)	6872(4)	1553(4)	63(2)
C(57)	-5908(6)	7058(4)	1035(4)	57(2)
C(58)	-5588(6)	6410(4)	-969(3)	68(3)
C(59)	-1869(5)	4826(4)	25(3)	52(2)
C(60)	-2429(6)	5378(4)	1082(3)	43(2)
C(61)	-1365(6)	5748(4)	960(3)	61(2)
C(62)	-250(7)	5384(5)	1201(3)	65(2)
C(63)	-208(7)	4665(5)	1546(3)	64(2)
C(64)	-1294(7)	4296(5)	1653(3)	69(3)
C(65)	-2390(7)	4665(4)	1425(3)	55(2)
C(66)	-3567(7)	5996(4)	2044(3)	71(3)
C(67)	-6951(7)	7607(4)	855(3)	77(3)
C(68)	-4505(7)	5710(5)	-2435(3)	50(2)
C(69)	-5183(7)	6247(4)	-2548(3)	49(2)
C(70)	-6077(6)	6877(4)	-2677(3)	49(2)
C(71)	-5971(6)	7521(4)	-2630(3)	48(2)
C(72)	-7254(6)	6928(4)	-2896(3)	44(2)
C(73)	-7821(6)	7599(4)	-2946(3)	49(2)
C(74)	-9018(6)	7924(4)	-3113(3)	48(2)
C(75)	-9385(7)	8616(4)	-3157(3)	49(2)
C(76)	-10523(6)	9070(4)	-3314(3)	57(2)
C(77)	-10341(7)	9732(5)	-3335(4)	74(3)
C(78)	-9122(8)	9703(5)	-3188(4)	68(3)
C(79)	-4903(6)	7735(4)	-2445(3)	63(2)
C(80)	-7627(6)	6352(4)	-3065(3)	56(2)

C(81)	-9956(6)	7493(4)	-3187(4)	50(2)
C(82)	-10766(6)	7113(4)	-2693(3)	55(2)
C(83)	-11658(6)	6743(4)	-2774(4)	69(3)
C(84)	-11740(7)	6721(5)	-3318(4)	78(3)
C(85)	-10957(7)	7093(5)	-3797(4)	82(3)
C(86)	-10038(7)	7461(4)	-3723(3)	59(2)
C(87)	-11715(6)	8873(4)	-3444(4)	88(3)
C(88)	-8494(7)	10271(4)	-3137(3)	80(3)
C(1S)	-10424(8)	8156(5)	-1687(3)	68(3)
C(2S)	-11682(8)	8285(5)	-1740(4)	88(3)
C(3S)	-12477(9)	7750(6)	-1460(5)	99(4)
C(4S)	-11987(8)	7102(6)	-1133(4)	95(3)
C(5S)	-10692(8)	6963(5)	-1079(4)	81(3)
C(6S)	-9892(7)	7500(5)	-1353(4)	65(2)
C(7S)	-8484(6)	7359(5)	-1295(4)	86(3)
C(8S)	-13821(19)	11141(10)	-1728(10)	159(7)
C(9S)	-13075(17)	11337(8)	-2256(9)	146(6)
C(10S)	-12041(16)	10857(11)	-2338(8)	154(6)
C(11S)	-11738(13)	10250(10)	-1943(9)	138(6)
C(12S)	-12441(16)	10044(9)	-1381(7)	148(6)
C(13S)	-13444(17)	10501(13)	-1309(9)	147(7)
C(14S)	-14209(14)	10317(9)	-752(6)	242(10)

Table 3. Bond lengths [Å] and angles [°] for **8**.

N(1)-C(4)	1.345(8)
N(1)-C(1)	1.361(8)
N(2)-C(2)	1.334(8)
N(2)-C(3)	1.379(8)
N(3)-C(8)	1.368(9)
N(3)-C(10)	1.424(9)
N(3)-B(1)	1.532(11)
N(4)-C(15)	1.337(9)
N(4)-C(12)	1.407(9)
N(4)-B(1)	1.579(12)
N(5)-C(29)	1.373(9)
N(5)-C(31)	1.427(9)
N(5)-B(2)	1.545(10)
N(6)-C(36)	1.384(9)
N(6)-C(33)	1.413(9)
N(6)-B(2)	1.496(12)
N(7)-C(50)	1.337(8)
N(7)-C(52)	1.450(8)
N(7)-B(3)	1.562(11)
N(8)-C(57)	1.332(8)
N(8)-C(54)	1.418(9)
N(8)-B(3)	1.539(11)
N(9)-C(71)	1.348(8)
N(9)-C(73)	1.389(8)
N(9)-B(4)	1.570(11)
N(10)-C(78)	1.360(9)
N(10)-C(75)	1.418(8)
N(10)-B(4)	1.574(10)
B(1)-F(1)	1.395(11)
B(1)-F(2)	1.396(10)
B(2)-F(3)	1.403(12)
B(2)-F(4)	1.423(11)
B(3)-F(5)	1.332(11)
B(3)-F(6)	1.438(8)

B(4)-F(8)	1.377(9)
B(4)-F(7)	1.392(10)
C(1)-C(5)	1.391(10)
C(1)-C(2)	1.443(9)
C(2)-C(26)	1.471(10)
C(3)-C(47)	1.475(10)
C(3)-C(4)	1.442(9)
C(4)-C(68)	1.447(10)
C(5)-C(6)	1.178(10)
C(6)-C(7)	1.462(11)
C(7)-C(8)	1.418(10)
C(7)-C(9)	1.402(10)
C(8)-C(16)	1.520(10)
C(9)-C(10)	1.407(10)
C(9)-C(17)	1.517(9)
C(10)-C(11)	1.425(10)
C(11)-C(12)	1.389(10)
C(11)-C(18)	1.546(11)
C(12)-C(13)	1.418(10)
C(13)-C(14)	1.359(11)
C(13)-C(24)	1.581(10)
C(14)-C(15)	1.398(11)
C(14)-H(14A)	0.9500
C(15)-C(25)	1.496(11)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.391(10)
C(18)-C(23)	1.399(10)
C(19)-C(20)	1.396(12)
C(19)-H(19A)	0.9500
C(20)-C(21)	1.359(13)
C(20)-H(20A)	0.9500

C(21)-C(22)	1.402(13)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.429(12)
C(22)-H(22A)	0.9500
C(23)-H(23A)	0.9500
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.163(9)
C(27)-C(28)	1.419(10)
C(28)-C(30)	1.445(10)
C(28)-C(29)	1.421(9)
C(29)-C(37)	1.513(10)
C(30)-C(31)	1.432(9)
C(30)-C(38)	1.536(9)
C(31)-C(32)	1.410(9)
C(32)-C(33)	1.407(9)
C(32)-C(39)	1.507(10)
C(33)-C(34)	1.455(10)
C(34)-C(35)	1.373(10)
C(34)-C(45)	1.498(10)
C(35)-C(36)	1.392(10)
C(35)-H(35A)	0.9500
C(36)-C(46)	1.525(10)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-C(44)	1.383(10)
C(39)-C(40)	1.416(10)
C(40)-C(41)	1.383(10)

C(40)-H(40A)	0.9500
C(41)-C(42)	1.412(11)
C(41)-H(41A)	0.9500
C(42)-C(43)	1.398(11)
C(42)-H(42A)	0.9500
C(43)-C(44)	1.390(10)
C(43)-H(43A)	0.9500
C(44)-H(44A)	0.9500
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-C(48)	1.231(9)
C(48)-C(49)	1.357(9)
C(49)-C(51)	1.404(8)
C(49)-C(50)	1.413(9)
C(50)-C(58)	1.504(8)
C(51)-C(52)	1.404(9)
C(51)-C(59)	1.545(8)
C(52)-C(53)	1.412(9)
C(53)-C(54)	1.403(9)
C(53)-C(60)	1.530(9)
C(54)-C(55)	1.470(9)
C(55)-C(56)	1.369(9)
C(55)-C(66)	1.526(9)
C(56)-C(57)	1.416(10)
C(56)-H(56A)	0.9500
C(57)-C(67)	1.476(9)
C(58)-H(58A)	0.9800
C(58)-H(58B)	0.9800
C(58)-H(58C)	0.9800
C(59)-H(59A)	0.9800
C(59)-H(59B)	0.9800
C(59)-H(59C)	0.9800

C(60)-C(65)	1.397(9)
C(60)-C(61)	1.413(8)
C(61)-C(62)	1.427(9)
C(61)-H(61A)	0.9500
C(62)-C(63)	1.409(10)
C(62)-H(62A)	0.9500
C(63)-C(64)	1.437(9)
C(63)-H(63A)	0.9500
C(64)-C(65)	1.401(9)
C(64)-H(64A)	0.9500
C(65)-H(65A)	0.9500
C(66)-H(66A)	0.9800
C(66)-H(66B)	0.9800
C(66)-H(66C)	0.9800
C(67)-H(67A)	0.9800
C(67)-H(67B)	0.9800
C(67)-H(67C)	0.9800
C(68)-C(69)	1.198(9)
C(69)-C(70)	1.462(10)
C(70)-C(71)	1.383(9)
C(70)-C(72)	1.451(8)
C(71)-C(79)	1.492(8)
C(72)-C(73)	1.389(9)
C(72)-C(80)	1.508(9)
C(73)-C(74)	1.428(9)
C(74)-C(75)	1.378(9)
C(74)-C(81)	1.514(9)
C(75)-C(76)	1.452(9)
C(76)-C(77)	1.373(10)
C(76)-C(87)	1.531(9)
C(77)-C(78)	1.423(10)
C(77)-H(77A)	0.9500
C(78)-C(88)	1.481(9)
C(79)-H(79A)	0.9800
C(79)-H(79B)	0.9800
C(79)-H(79C)	0.9800

C(80)-H(80A)	0.9800
C(80)-H(80B)	0.9800
C(80)-H(80C)	0.9800
C(81)-C(86)	1.390(9)
C(81)-C(82)	1.449(9)
C(82)-C(83)	1.396(9)
C(82)-H(82A)	0.9500
C(83)-C(84)	1.402(9)
C(83)-H(83A)	0.9500
C(84)-C(85)	1.405(9)
C(84)-H(84A)	0.9500
C(85)-C(86)	1.408(9)
C(85)-H(85A)	0.9500
C(86)-H(86A)	0.9500
C(87)-H(87A)	0.9800
C(87)-H(87B)	0.9800
C(87)-H(87C)	0.9800
C(88)-H(88A)	0.9800
C(88)-H(88B)	0.9800
C(88)-H(88C)	0.9800
C(1S)-C(2S)	1.377(10)
C(1S)-C(6S)	1.396(10)
C(1S)-H(1SA)	0.9500
C(2S)-C(3S)	1.407(11)
C(2S)-H(2SA)	0.9500
C(3S)-C(4S)	1.362(11)
C(3S)-H(3SA)	0.9500
C(4S)-C(5S)	1.419(11)
C(4S)-H(4SA)	0.9500
C(5S)-C(6S)	1.411(10)
C(5S)-H(5SA)	0.9500
C(6S)-C(7S)	1.542(9)
C(7S)-H(7SA)	0.9800
C(7S)-H(7SB)	0.9800
C(7S)-H(7SC)	0.9800
C(8S)-C(13S)	1.40(2)

C(8S)-C(9S)	1.404(17)
C(8S)-H(8SA)	0.9500
C(9S)-C(10S)	1.424(17)
C(9S)-H(9SA)	0.9500
C(10S)-C(11S)	1.314(15)
C(10S)-H(10A)	0.9500
C(11S)-C(12S)	1.449(17)
C(11S)-H(11A)	0.9500
C(12S)-C(13S)	1.364(18)
C(12S)-H(12A)	0.9500
C(13S)-C(14S)	1.469(19)
C(14S)-H(14B)	0.9800
C(14S)-H(14C)	0.9800
C(14S)-H(14D)	0.9800
C(4)-N(1)-C(1)	118.8(6)
C(2)-N(2)-C(3)	117.2(6)
C(8)-N(3)-C(10)	107.7(7)
C(8)-N(3)-B(1)	124.6(8)
C(10)-N(3)-B(1)	127.6(8)
C(15)-N(4)-C(12)	107.5(8)
C(15)-N(4)-B(1)	126.3(9)
C(12)-N(4)-B(1)	126.1(8)
C(29)-N(5)-C(31)	108.2(6)
C(29)-N(5)-B(2)	126.4(8)
C(31)-N(5)-B(2)	125.1(8)
C(36)-N(6)-C(33)	105.7(7)
C(36)-N(6)-B(2)	126.3(8)
C(33)-N(6)-B(2)	128.0(7)
C(50)-N(7)-C(52)	107.2(6)
C(50)-N(7)-B(3)	126.3(7)
C(52)-N(7)-B(3)	126.1(7)
C(57)-N(8)-C(54)	105.5(7)
C(57)-N(8)-B(3)	127.9(7)
C(54)-N(8)-B(3)	126.5(7)
C(71)-N(9)-C(73)	110.3(6)
C(71)-N(9)-B(4)	125.3(6)

C(73)-N(9)-B(4)	124.3(6)
C(78)-N(10)-C(75)	108.1(7)
C(78)-N(10)-B(4)	126.8(7)
C(75)-N(10)-B(4)	125.0(7)
F(1)-B(1)-F(2)	111.0(9)
F(1)-B(1)-N(3)	109.9(8)
F(2)-B(1)-N(3)	109.3(8)
F(1)-B(1)-N(4)	110.9(8)
F(2)-B(1)-N(4)	109.8(8)
N(3)-B(1)-N(4)	105.8(8)
F(3)-B(2)-F(4)	107.5(9)
F(3)-B(2)-N(6)	113.1(9)
F(4)-B(2)-N(6)	112.7(8)
F(3)-B(2)-N(5)	108.3(8)
F(4)-B(2)-N(5)	108.2(8)
N(6)-B(2)-N(5)	106.9(8)
F(5)-B(3)-F(6)	111.7(8)
F(5)-B(3)-N(8)	113.0(7)
F(6)-B(3)-N(8)	107.5(7)
F(5)-B(3)-N(7)	111.5(7)
F(6)-B(3)-N(7)	106.6(7)
N(8)-B(3)-N(7)	106.1(8)
F(8)-B(4)-F(7)	111.3(8)
F(8)-B(4)-N(9)	110.5(7)
F(7)-B(4)-N(9)	108.8(7)
F(8)-B(4)-N(10)	108.9(7)
F(7)-B(4)-N(10)	110.4(7)
N(9)-B(4)-N(10)	106.8(7)
N(1)-C(1)-C(5)	118.5(7)
N(1)-C(1)-C(2)	119.9(7)
C(5)-C(1)-C(2)	121.6(8)
N(2)-C(2)-C(1)	122.3(7)
N(2)-C(2)-C(26)	117.7(7)
C(1)-C(2)-C(26)	119.9(7)
N(2)-C(3)-C(47)	119.0(7)
N(2)-C(3)-C(4)	120.9(7)

C(47)-C(3)-C(4)	120.1(7)
N(1)-C(4)-C(68)	117.2(7)
N(1)-C(4)-C(3)	120.6(7)
C(68)-C(4)-C(3)	122.2(7)
C(6)-C(5)-C(1)	176.9(10)
C(5)-C(6)-C(7)	178.4(9)
C(8)-C(7)-C(9)	109.7(7)
C(8)-C(7)-C(6)	125.2(8)
C(9)-C(7)-C(6)	125.0(8)
N(3)-C(8)-C(7)	107.8(8)
N(3)-C(8)-C(16)	124.5(8)
C(7)-C(8)-C(16)	127.7(9)
C(7)-C(9)-C(10)	105.4(7)
C(7)-C(9)-C(17)	124.5(8)
C(10)-C(9)-C(17)	129.9(8)
C(11)-C(10)-C(9)	133.1(8)
C(11)-C(10)-N(3)	117.4(8)
C(9)-C(10)-N(3)	109.3(7)
C(12)-C(11)-C(10)	123.3(8)
C(12)-C(11)-C(18)	118.8(8)
C(10)-C(11)-C(18)	117.8(8)
C(11)-C(12)-N(4)	119.1(8)
C(11)-C(12)-C(13)	134.9(10)
N(4)-C(12)-C(13)	106.0(8)
C(14)-C(13)-C(12)	109.3(9)
C(14)-C(13)-C(24)	125.0(9)
C(12)-C(13)-C(24)	125.6(9)
C(13)-C(14)-C(15)	106.0(9)
C(13)-C(14)-H(14A)	127.0
C(15)-C(14)-H(14A)	127.0
N(4)-C(15)-C(14)	111.1(9)
N(4)-C(15)-C(25)	122.2(10)
C(14)-C(15)-C(25)	126.6(9)
C(8)-C(16)-H(16A)	109.5
C(8)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5

C(8)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(9)-C(17)-H(17A)	109.5
C(9)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(9)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(19)-C(18)-C(23)	121.9(9)
C(19)-C(18)-C(11)	120.0(9)
C(23)-C(18)-C(11)	118.0(9)
C(18)-C(19)-C(20)	119.8(10)
C(18)-C(19)-H(19A)	120.1
C(20)-C(19)-H(19A)	120.1
C(21)-C(20)-C(19)	119.5(11)
C(21)-C(20)-H(20A)	120.2
C(19)-C(20)-H(20A)	120.2
C(20)-C(21)-C(22)	122.1(12)
C(20)-C(21)-H(21A)	119.0
C(22)-C(21)-H(21A)	119.0
C(21)-C(22)-C(23)	119.3(10)
C(21)-C(22)-H(22A)	120.4
C(23)-C(22)-H(22A)	120.4
C(18)-C(23)-C(22)	117.4(9)
C(18)-C(23)-H(23A)	121.3
C(22)-C(23)-H(23A)	121.3
C(13)-C(24)-H(24A)	109.5
C(13)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(13)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(15)-C(25)-H(25A)	109.5
C(15)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5

C(15)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(27)-C(26)-C(2)	175.7(9)
C(26)-C(27)-C(28)	176.2(9)
C(30)-C(28)-C(29)	107.9(7)
C(30)-C(28)-C(27)	126.0(8)
C(29)-C(28)-C(27)	126.0(8)
N(5)-C(29)-C(28)	109.5(7)
N(5)-C(29)-C(37)	123.9(7)
C(28)-C(29)-C(37)	126.6(8)
C(28)-C(30)-C(31)	105.7(7)
C(28)-C(30)-C(38)	124.5(7)
C(31)-C(30)-C(38)	129.8(8)
C(32)-C(31)-N(5)	119.7(7)
C(32)-C(31)-C(30)	131.6(8)
N(5)-C(31)-C(30)	108.7(7)
C(31)-C(32)-C(33)	120.7(8)
C(31)-C(32)-C(39)	118.4(7)
C(33)-C(32)-C(39)	120.8(8)
N(6)-C(33)-C(32)	119.0(8)
N(6)-C(33)-C(34)	109.9(7)
C(32)-C(33)-C(34)	131.0(9)
C(35)-C(34)-C(33)	103.7(8)
C(35)-C(34)-C(45)	127.2(8)
C(33)-C(34)-C(45)	129.1(8)
C(34)-C(35)-C(36)	111.4(8)
C(34)-C(35)-H(35A)	124.3
C(36)-C(35)-H(35A)	124.3
N(6)-C(36)-C(35)	109.2(8)
N(6)-C(36)-C(46)	120.5(9)
C(35)-C(36)-C(46)	130.2(8)
C(29)-C(37)-H(37A)	109.5
C(29)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(29)-C(37)-H(37C)	109.5

H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(30)-C(38)-H(38A)	109.5
C(30)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(30)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(44)-C(39)-C(40)	122.3(8)
C(44)-C(39)-C(32)	120.4(9)
C(40)-C(39)-C(32)	117.3(8)
C(41)-C(40)-C(39)	116.4(8)
C(41)-C(40)-H(40A)	121.8
C(39)-C(40)-H(40A)	121.8
C(40)-C(41)-C(42)	122.6(10)
C(40)-C(41)-H(41A)	118.7
C(42)-C(41)-H(41A)	118.7
C(41)-C(42)-C(43)	118.9(10)
C(41)-C(42)-H(42A)	120.5
C(43)-C(42)-H(42A)	120.5
C(44)-C(43)-C(42)	119.8(9)
C(44)-C(43)-H(43A)	120.1
C(42)-C(43)-H(43A)	120.1
C(39)-C(44)-C(43)	119.9(9)
C(39)-C(44)-H(44A)	120.1
C(43)-C(44)-H(44A)	120.1
C(34)-C(45)-H(45A)	109.5
C(34)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5
C(34)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(36)-C(46)-H(46A)	109.5
C(36)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(36)-C(46)-H(46C)	109.5

H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(48)-C(47)-C(3)	174.7(7)
C(47)-C(48)-C(49)	178.1(9)
C(48)-C(49)-C(51)	128.2(7)
C(48)-C(49)-C(50)	124.5(7)
C(51)-C(49)-C(50)	107.2(6)
N(7)-C(50)-C(49)	110.6(6)
N(7)-C(50)-C(58)	120.6(7)
C(49)-C(50)-C(58)	128.7(7)
C(52)-C(51)-C(49)	107.5(6)
C(52)-C(51)-C(59)	129.9(7)
C(49)-C(51)-C(59)	122.6(6)
C(51)-C(52)-C(53)	134.5(7)
C(51)-C(52)-N(7)	107.4(6)
C(53)-C(52)-N(7)	118.0(7)
C(54)-C(53)-C(52)	122.3(7)
C(54)-C(53)-C(60)	119.9(7)
C(52)-C(53)-C(60)	117.7(7)
C(53)-C(54)-N(8)	120.1(7)
C(53)-C(54)-C(55)	130.5(8)
N(8)-C(54)-C(55)	109.4(7)
C(56)-C(55)-C(54)	104.3(7)
C(56)-C(55)-C(66)	126.7(8)
C(54)-C(55)-C(66)	129.0(8)
C(55)-C(56)-C(57)	108.8(7)
C(55)-C(56)-H(56A)	125.6
C(57)-C(56)-H(56A)	125.6
N(8)-C(57)-C(56)	112.0(7)
N(8)-C(57)-C(67)	122.5(8)
C(56)-C(57)-C(67)	125.4(8)
C(50)-C(58)-H(58A)	109.5
C(50)-C(58)-H(58B)	109.5
H(58A)-C(58)-H(58B)	109.5
C(50)-C(58)-H(58C)	109.5
H(58A)-C(58)-H(58C)	109.5

H(58B)-C(58)-H(58C)	109.5
C(51)-C(59)-H(59A)	109.5
C(51)-C(59)-H(59B)	109.5
H(59A)-C(59)-H(59B)	109.5
C(51)-C(59)-H(59C)	109.5
H(59A)-C(59)-H(59C)	109.5
H(59B)-C(59)-H(59C)	109.5
C(65)-C(60)-C(61)	120.8(7)
C(65)-C(60)-C(53)	123.4(6)
C(61)-C(60)-C(53)	115.7(7)
C(60)-C(61)-C(62)	119.0(8)
C(60)-C(61)-H(61A)	120.5
C(62)-C(61)-H(61A)	120.5
C(63)-C(62)-C(61)	120.4(7)
C(63)-C(62)-H(62A)	119.8
C(61)-C(62)-H(62A)	119.8
C(62)-C(63)-C(64)	119.6(7)
C(62)-C(63)-H(63A)	120.2
C(64)-C(63)-H(63A)	120.2
C(65)-C(64)-C(63)	119.3(8)
C(65)-C(64)-H(64A)	120.4
C(63)-C(64)-H(64A)	120.4
C(60)-C(65)-C(64)	121.0(7)
C(60)-C(65)-H(65A)	119.5
C(64)-C(65)-H(65A)	119.5
C(55)-C(66)-H(66A)	109.5
C(55)-C(66)-H(66B)	109.5
H(66A)-C(66)-H(66B)	109.5
C(55)-C(66)-H(66C)	109.5
H(66A)-C(66)-H(66C)	109.5
H(66B)-C(66)-H(66C)	109.5
C(57)-C(67)-H(67A)	109.5
C(57)-C(67)-H(67B)	109.5
H(67A)-C(67)-H(67B)	109.5
C(57)-C(67)-H(67C)	109.5
H(67A)-C(67)-H(67C)	109.5

H(67B)-C(67)-H(67C)	109.5
C(69)-C(68)-C(4)	173.6(8)
C(68)-C(69)-C(70)	176.4(7)
C(71)-C(70)-C(72)	107.8(6)
C(71)-C(70)-C(69)	128.2(6)
C(72)-C(70)-C(69)	124.1(7)
N(9)-C(71)-C(70)	108.2(6)
N(9)-C(71)-C(79)	124.1(7)
C(70)-C(71)-C(79)	127.7(7)
C(73)-C(72)-C(70)	105.6(6)
C(73)-C(72)-C(80)	131.5(6)
C(70)-C(72)-C(80)	122.8(7)
N(9)-C(73)-C(72)	108.1(6)
N(9)-C(73)-C(74)	121.9(7)
C(72)-C(73)-C(74)	130.0(7)
C(75)-C(74)-C(73)	120.7(7)
C(75)-C(74)-C(81)	118.6(7)
C(73)-C(74)-C(81)	120.5(7)
C(74)-C(75)-N(10)	120.7(7)
C(74)-C(75)-C(76)	132.3(8)
N(10)-C(75)-C(76)	106.9(7)
C(77)-C(76)-C(75)	107.4(7)
C(77)-C(76)-C(87)	124.9(7)
C(75)-C(76)-C(87)	127.7(8)
C(76)-C(77)-C(78)	108.1(8)
C(76)-C(77)-H(77A)	126.0
C(78)-C(77)-H(77A)	126.0
N(10)-C(78)-C(77)	109.6(7)
N(10)-C(78)-C(88)	121.4(8)
C(77)-C(78)-C(88)	129.0(8)
C(71)-C(79)-H(79A)	109.5
C(71)-C(79)-H(79B)	109.5
H(79A)-C(79)-H(79B)	109.5
C(71)-C(79)-H(79C)	109.5
H(79A)-C(79)-H(79C)	109.5
H(79B)-C(79)-H(79C)	109.5

C(72)-C(80)-H(80A)	109.5
C(72)-C(80)-H(80B)	109.5
H(80A)-C(80)-H(80B)	109.5
C(72)-C(80)-H(80C)	109.5
H(80A)-C(80)-H(80C)	109.5
H(80B)-C(80)-H(80C)	109.5
C(86)-C(81)-C(82)	120.3(7)
C(86)-C(81)-C(74)	120.3(7)
C(82)-C(81)-C(74)	119.4(7)
C(83)-C(82)-C(81)	118.5(7)
C(83)-C(82)-H(82A)	120.8
C(81)-C(82)-H(82A)	120.8
C(84)-C(83)-C(82)	120.7(7)
C(84)-C(83)-H(83A)	119.7
C(82)-C(83)-H(83A)	119.7
C(83)-C(84)-C(85)	120.7(8)
C(83)-C(84)-H(84A)	119.7
C(85)-C(84)-H(84A)	119.7
C(86)-C(85)-C(84)	119.5(8)
C(86)-C(85)-H(85A)	120.2
C(84)-C(85)-H(85A)	120.2
C(81)-C(86)-C(85)	120.2(8)
C(81)-C(86)-H(86A)	119.9
C(85)-C(86)-H(86A)	119.9
C(76)-C(87)-H(87A)	109.5
C(76)-C(87)-H(87B)	109.5
H(87A)-C(87)-H(87B)	109.5
C(76)-C(87)-H(87C)	109.5
H(87A)-C(87)-H(87C)	109.5
H(87B)-C(87)-H(87C)	109.5
C(78)-C(88)-H(88A)	109.5
C(78)-C(88)-H(88B)	109.5
H(88A)-C(88)-H(88B)	109.5
C(78)-C(88)-H(88C)	109.5
H(88A)-C(88)-H(88C)	109.5
H(88B)-C(88)-H(88C)	109.5

C(2S)-C(1S)-C(6S)	121.9(8)
C(2S)-C(1S)-H(1SA)	119.1
C(6S)-C(1S)-H(1SA)	119.1
C(1S)-C(2S)-C(3S)	120.6(9)
C(1S)-C(2S)-H(2SA)	119.7
C(3S)-C(2S)-H(2SA)	119.7
C(4S)-C(3S)-C(2S)	119.0(9)
C(4S)-C(3S)-H(3SA)	120.5
C(2S)-C(3S)-H(3SA)	120.5
C(3S)-C(4S)-C(5S)	120.7(9)
C(3S)-C(4S)-H(4SA)	119.6
C(5S)-C(4S)-H(4SA)	119.6
C(6S)-C(5S)-C(4S)	120.5(9)
C(6S)-C(5S)-H(5SA)	119.7
C(4S)-C(5S)-H(5SA)	119.7
C(1S)-C(6S)-C(5S)	117.2(8)
C(1S)-C(6S)-C(7S)	121.7(8)
C(5S)-C(6S)-C(7S)	121.1(8)
C(6S)-C(7S)-H(7SA)	109.5
C(6S)-C(7S)-H(7SB)	109.5
H(7SA)-C(7S)-H(7SB)	109.5
C(6S)-C(7S)-H(7SC)	109.5
H(7SA)-C(7S)-H(7SC)	109.5
H(7SB)-C(7S)-H(7SC)	109.5
C(13S)-C(8S)-C(9S)	117(2)
C(13S)-C(8S)-H(8SA)	121.5
C(9S)-C(8S)-H(8SA)	121.5
C(8S)-C(9S)-C(10S)	117.9(19)
C(8S)-C(9S)-H(9SA)	121.0
C(10S)-C(9S)-H(9SA)	121.0
C(11S)-C(10S)-C(9S)	123.5(19)
C(11S)-C(10S)-H(10A)	118.2
C(9S)-C(10S)-H(10A)	118.2
C(10S)-C(11S)-C(12S)	120.4(17)
C(10S)-C(11S)-H(11A)	119.8
C(12S)-C(11S)-H(11A)	119.8

C(13S)-C(12S)-C(11S)	115.7(18)
C(13S)-C(12S)-H(12A)	122.2
C(11S)-C(12S)-H(12A)	122.2
C(8S)-C(13S)-C(12S)	125(2)
C(8S)-C(13S)-C(14S)	116(2)
C(12S)-C(13S)-C(14S)	118(2)
C(13S)-C(14S)-H(14B)	109.5
C(13S)-C(14S)-H(14C)	109.5
H(14B)-C(14S)-H(14C)	109.5
C(13S)-C(14S)-H(14D)	109.5
H(14B)-C(14S)-H(14D)	109.5
H(14C)-C(14S)-H(14D)	109.5

Symmetry transformations used to generate equivalent atoms.

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **8**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	25(4)	69(5)	54(5)	-19(4)	4(3)	-14(4)
N(2)	18(3)	57(5)	80(5)	-34(4)	2(3)	-4(3)
N(3)	54(5)	66(5)	57(5)	-25(4)	-4(4)	-3(4)
N(4)	56(5)	63(5)	70(5)	-29(4)	7(4)	-12(4)
N(5)	31(4)	71(5)	77(5)	-26(4)	-3(4)	4(4)
N(6)	25(4)	59(5)	92(6)	-25(5)	0(4)	0(4)
N(7)	16(3)	67(5)	65(5)	-20(4)	-2(3)	-5(3)
N(8)	22(3)	47(4)	70(5)	-24(4)	-3(3)	-3(3)
N(9)	26(3)	41(4)	71(5)	-23(4)	-5(3)	-12(3)
N(10)	38(4)	62(5)	72(5)	-27(4)	-3(3)	-15(4)
B(1)	61(7)	67(9)	71(9)	-24(7)	27(7)	-13(7)
B(2)	39(6)	86(10)	90(10)	-32(8)	22(7)	-7(7)
B(3)	21(5)	85(9)	92(9)	-51(8)	6(5)	-19(6)
B(4)	28(5)	104(10)	48(7)	-29(7)	-3(5)	3(6)
F(1)	87(4)	76(4)	81(4)	-22(3)	-7(3)	4(3)
F(2)	62(3)	76(4)	88(4)	-35(3)	10(3)	-15(3)
F(3)	74(4)	94(4)	80(4)	-21(3)	16(3)	5(3)
F(4)	39(3)	67(4)	209(6)	-30(4)	26(3)	-17(3)
F(5)	64(3)	62(3)	81(4)	-12(3)	1(3)	-6(3)
F(6)	32(2)	96(4)	99(4)	-49(3)	-19(2)	6(2)
F(7)	36(2)	64(3)	97(4)	-22(3)	7(2)	-18(2)
F(8)	55(3)	70(3)	74(3)	-29(3)	-10(2)	-10(2)
C(1)	30(5)	59(6)	74(6)	-29(5)	0(4)	-7(4)
C(2)	28(4)	48(5)	59(6)	-24(5)	-4(4)	-3(4)
C(3)	24(4)	81(7)	50(6)	-30(5)	7(4)	-19(4)
C(4)	21(4)	69(6)	46(5)	-16(5)	2(4)	-11(4)
C(5)	47(5)	74(7)	90(7)	-60(6)	-9(5)	3(5)
C(6)	37(5)	52(6)	73(7)	-11(5)	-7(5)	-10(4)
C(7)	67(6)	79(7)	63(6)	-38(5)	-11(5)	-15(6)
C(8)	63(6)	82(8)	64(7)	-25(6)	6(5)	-12(6)
C(9)	51(5)	66(6)	65(6)	-31(5)	-7(5)	4(5)

C(10)	58(6)	63(6)	48(6)	-20(5)	3(5)	-11(5)
C(11)	52(6)	76(7)	52(6)	-11(5)	4(5)	-20(5)
C(12)	67(7)	71(7)	70(7)	-32(6)	-3(5)	-3(6)
C(13)	79(7)	77(7)	42(6)	-16(5)	5(5)	-42(6)
C(14)	82(8)	75(8)	93(8)	-43(6)	12(6)	-15(6)
C(15)	69(7)	53(7)	96(8)	-37(6)	20(6)	-20(6)
C(16)	55(6)	132(9)	104(8)	-44(7)	-19(6)	3(6)
C(17)	55(6)	84(7)	99(7)	-42(6)	-18(5)	13(5)
C(18)	71(7)	84(8)	50(6)	-26(6)	-8(5)	-11(6)
C(19)	56(6)	123(9)	86(8)	-34(7)	-13(6)	-8(7)
C(20)	86(9)	154(12)	86(9)	-25(8)	-28(7)	-4(9)
C(21)	99(10)	197(16)	83(10)	-39(10)	-41(8)	28(10)
C(22)	136(10)	85(9)	71(8)	-13(6)	-27(8)	7(9)
C(23)	94(8)	89(9)	73(8)	-8(6)	3(6)	-7(7)
C(24)	76(7)	114(8)	86(7)	-52(6)	10(6)	-38(6)
C(25)	86(7)	82(8)	126(9)	-57(7)	17(6)	-13(6)
C(26)	41(5)	59(6)	65(6)	-28(5)	6(4)	-3(5)
C(27)	26(5)	69(7)	103(7)	-50(6)	12(5)	-8(5)
C(28)	37(5)	72(7)	72(7)	-30(6)	-1(5)	-1(5)
C(29)	42(5)	70(7)	74(7)	-13(6)	2(5)	-7(5)
C(30)	35(5)	55(6)	68(6)	-33(5)	-2(4)	-5(4)
C(31)	25(4)	63(6)	71(6)	-28(5)	0(4)	-10(5)
C(32)	35(5)	59(6)	77(7)	-27(5)	-20(5)	7(5)
C(33)	19(4)	67(6)	82(7)	-31(6)	0(4)	-5(5)
C(34)	36(5)	74(7)	81(7)	-34(6)	-12(5)	-1(5)
C(35)	31(5)	59(7)	103(8)	-19(6)	-12(5)	11(5)
C(36)	29(5)	95(8)	90(8)	-37(7)	18(5)	-23(6)
C(37)	40(5)	72(7)	117(8)	-12(6)	5(5)	-4(5)
C(38)	39(5)	77(7)	84(7)	-34(5)	14(5)	-7(5)
C(39)	32(5)	62(6)	61(6)	-21(5)	4(4)	5(4)
C(40)	82(6)	45(6)	61(7)	-8(5)	-12(5)	-9(5)
C(41)	90(7)	83(8)	77(8)	-16(7)	3(6)	-13(6)
C(42)	104(9)	105(10)	67(8)	-23(7)	-8(6)	7(7)
C(43)	84(8)	111(10)	87(9)	-33(7)	-33(6)	-12(7)
C(44)	67(6)	83(8)	66(7)	-35(6)	0(5)	-8(6)
C(45)	42(5)	72(7)	105(8)	-36(6)	-18(5)	15(5)

C(46)	50(6)	113(9)	119(9)	-29(7)	25(6)	-1(6)
C(47)	12(4)	44(5)	68(6)	-6(5)	-3(4)	-8(4)
C(48)	25(4)	39(5)	63(6)	-11(5)	-4(4)	-11(4)
C(49)	19(4)	63(6)	49(5)	-33(5)	6(4)	-7(4)
C(50)	21(4)	73(6)	39(5)	-18(5)	6(4)	-21(4)
C(51)	29(4)	41(5)	50(5)	-11(4)	0(4)	-11(4)
C(52)	26(4)	65(6)	56(6)	-27(5)	4(4)	-17(4)
C(53)	15(4)	71(6)	66(6)	-21(5)	4(4)	-21(4)
C(54)	38(5)	59(6)	64(6)	-28(5)	17(5)	-27(5)
C(55)	36(5)	86(7)	62(6)	-31(5)	16(4)	-26(5)
C(56)	30(5)	74(7)	90(7)	-42(6)	7(5)	-1(5)
C(57)	21(4)	61(6)	95(7)	-37(6)	-9(5)	7(4)
C(58)	32(4)	106(8)	67(6)	-30(5)	-6(4)	-9(5)
C(59)	27(4)	69(6)	63(6)	-29(5)	8(4)	-5(4)
C(60)	25(4)	54(6)	57(5)	-24(4)	-1(4)	-15(4)
C(61)	25(4)	86(7)	78(6)	-32(5)	-4(4)	-17(5)
C(62)	32(5)	90(8)	82(7)	-36(6)	-9(5)	-17(5)
C(63)	39(5)	81(7)	69(6)	-19(5)	-14(4)	-2(5)
C(64)	53(6)	79(7)	60(6)	-5(5)	-9(5)	-11(5)
C(65)	38(5)	66(7)	63(6)	-17(5)	-8(4)	-16(5)
C(66)	62(6)	108(8)	50(6)	-35(5)	2(5)	-21(6)
C(67)	54(6)	88(7)	96(7)	-46(6)	5(5)	-6(5)
C(68)	26(5)	61(6)	64(6)	-19(5)	-3(4)	-14(4)
C(69)	36(5)	58(6)	61(6)	-23(5)	-1(4)	-25(5)
C(70)	22(4)	61(6)	67(6)	-29(5)	-7(4)	9(4)
C(71)	21(4)	45(5)	81(6)	-23(5)	-14(4)	-2(4)
C(72)	33(4)	56(6)	49(5)	-19(4)	-6(4)	-15(4)
C(73)	31(4)	42(5)	67(6)	-14(4)	-3(4)	-2(4)
C(74)	30(4)	64(6)	52(5)	-18(4)	-9(4)	-14(4)
C(75)	44(5)	44(6)	58(6)	-18(4)	6(4)	-10(5)
C(76)	26(5)	55(6)	77(6)	-14(5)	-6(4)	7(4)
C(77)	36(5)	68(7)	117(8)	-33(6)	-13(5)	8(5)
C(78)	64(6)	47(6)	98(7)	-33(5)	-4(5)	-7(5)
C(79)	31(4)	73(6)	98(7)	-38(5)	-15(4)	-19(4)
C(80)	35(4)	58(6)	71(6)	-17(5)	-8(4)	1(4)
C(81)	20(4)	55(6)	65(6)	-15(5)	-1(4)	7(4)

C(82)	27(4)	62(6)	72(6)	-17(5)	-12(4)	-4(4)
C(83)	19(4)	98(7)	76(7)	-8(5)	-3(4)	-23(5)
C(84)	44(5)	137(9)	64(7)	-36(6)	-8(5)	-40(6)
C(85)	61(6)	127(9)	76(7)	-41(6)	-22(5)	-29(6)
C(86)	48(5)	73(6)	61(6)	-25(5)	-7(4)	-13(5)
C(87)	27(5)	92(8)	140(9)	-35(6)	-18(5)	7(5)
C(88)	67(6)	51(6)	131(8)	-37(6)	-12(6)	-14(5)
C(1S)	54(6)	59(7)	78(7)	-11(5)	-7(5)	6(5)
C(2S)	56(6)	94(8)	128(9)	-56(7)	-21(6)	5(6)
C(3S)	46(6)	85(9)	159(11)	-35(8)	-31(7)	12(7)
C(4S)	36(6)	118(10)	145(10)	-62(8)	22(6)	-38(6)
C(5S)	71(7)	62(7)	105(8)	-26(6)	4(6)	-13(6)
C(6S)	45(5)	85(7)	79(7)	-43(6)	3(5)	-25(6)
C(7S)	34(5)	110(8)	124(8)	-50(6)	-21(5)	-4(5)
C(8S)	190(20)	134(16)	190(20)	-87(16)	-35(17)	-60(16)
C(9S)	110(12)	154(16)	220(20)	-107(15)	-51(12)	5(13)
C(10S)	112(14)	131(15)	260(20)	-96(17)	-56(13)	-14(12)
C(11S)	101(12)	126(14)	220(20)	-90(13)	-67(14)	14(12)
C(12S)	83(11)	220(20)	156(16)	-81(14)	-3(11)	-45(14)
C(13S)	88(12)	200(20)	220(20)	-131(19)	-18(14)	-47(14)
C(14S)	204(17)	390(30)	218(18)	-185(19)	47(14)	-150(18)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **8**.

	x	y	z	U(eq)
H(14A)	-3050	1086	-5837	97
H(16A)	-279	2025	-3806	144
H(16B)	-923	2198	-3249	144
H(16C)	-209	2783	-3764	144
H(17A)	-4899	4090	-3973	116
H(17B)	-5687	3564	-4092	116
H(17C)	-5013	4156	-4617	116
H(19A)	-6375	2471	-4516	106
H(20A)	-8247	3132	-4825	135
H(21A)	-8197	4148	-5615	156
H(22A)	-6312	4572	-6105	121
H(23A)	-4384	3904	-5804	111
H(24A)	-5105	1914	-6129	130
H(24B)	-5047	2684	-6109	130
H(24C)	-5810	2121	-5597	130
H(25A)	-540	821	-4864	142
H(25B)	-482	825	-5505	142
H(25C)	-1269	277	-4991	142
H(35A)	6120	-459	-2487	81
H(37A)	2641	2952	-3473	126
H(37B)	1955	3423	-3104	126
H(37C)	1175	3178	-3478	126
H(38A)	-861	1632	-1345	101
H(38B)	255	1129	-1015	101
H(38C)	-483	865	-1391	101
H(40A)	1401	-537	-1661	77
H(41A)	516	-1288	-787	105
H(42A)	666	-1140	85	115
H(43A)	1701	-201	80	110
H(44A)	2567	569	-790	84

H(45A)	5209	-1211	-1474	109
H(45B)	3721	-1084	-1409	109
H(45C)	4511	-725	-1121	109
H(46A)	5478	1340	-3650	152
H(46B)	5982	581	-3693	152
H(46C)	6745	939	-3393	152
H(56A)	-5621	7075	1843	76
H(58A)	-6179	6733	-825	102
H(58B)	-6043	6072	-1037	102
H(58C)	-5128	6680	-1330	102
H(59A)	-1581	4790	386	79
H(59B)	-1221	5002	-292	79
H(59C)	-2044	4358	46	79
H(61A)	-1391	6231	722	73
H(62A)	468	5629	1128	78
H(63A)	535	4425	1707	77
H(64A)	-1269	3807	1875	82
H(65A)	-3119	4426	1506	66
H(66A)	-3831	6183	2356	106
H(66B)	-2704	6092	1892	106
H(66C)	-3623	5486	2188	106
H(67A)	-7149	7635	479	115
H(67B)	-6714	8064	828	115
H(67C)	-7682	7488	1137	115
H(77A)	-10927	10138	-3431	89
H(79A)	-5089	8224	-2455	94
H(79B)	-4151	7697	-2704	94
H(79C)	-4769	7424	-2053	94
H(80A)	-8450	6494	-3203	85
H(80B)	-7657	5915	-2731	85
H(80C)	-7017	6272	-3369	85
H(82A)	-10692	7116	-2322	66
H(83A)	-12215	6503	-2457	83
H(84A)	-12330	6451	-3364	93
H(85A)	-11049	7097	-4168	99
H(86A)	-9471	7687	-4041	71

H(87A)	-12329	9288	-3537	132
H(87B)	-12055	8497	-3108	132
H(87C)	-11525	8707	-3771	132
H(88A)	-7657	10083	-3025	120
H(88B)	-8976	10446	-2845	120
H(88C)	-8434	10658	-3507	120
H(1SA)	-9905	8525	-1885	82
H(2SA)	-12015	8740	-1967	106
H(3SA)	-13343	7839	-1499	118
H(4SA)	-12518	6739	-938	114
H(5SA)	-10361	6505	-857	97
H(7SA)	-8084	7792	-1511	128
H(7SB)	-8121	6985	-1447	128
H(7SC)	-8353	7211	-890	128
H(8SA)	-14547	11429	-1657	190
H(9SA)	-13254	11776	-2550	176
H(10A)	-11543	10983	-2698	184
H(11A)	-11053	9944	-2026	166
H(12A)	-12219	9619	-1082	177
H(14B)	-14887	10691	-761	362
H(14C)	-13692	10265	-450	362
H(14D)	-14559	9871	-672	362

Table 6. Torsion angles [°] for **8**.

C(8)-N(3)-B(1)-F(1)	54.9(11)
C(10)-N(3)-B(1)-F(1)	-122.7(9)
C(8)-N(3)-B(1)-F(2)	-67.2(11)
C(10)-N(3)-B(1)-F(2)	115.2(9)
C(8)-N(3)-B(1)-N(4)	174.6(7)
C(10)-N(3)-B(1)-N(4)	-3.0(11)
C(15)-N(4)-B(1)-F(1)	-56.4(11)
C(12)-N(4)-B(1)-F(1)	126.8(8)
C(15)-N(4)-B(1)-F(2)	66.7(11)
C(12)-N(4)-B(1)-F(2)	-110.1(9)
C(15)-N(4)-B(1)-N(3)	-175.5(7)
C(12)-N(4)-B(1)-N(3)	7.8(11)
C(36)-N(6)-B(2)-F(3)	62.5(11)
C(33)-N(6)-B(2)-F(3)	-118.9(9)
C(36)-N(6)-B(2)-F(4)	-59.7(12)
C(33)-N(6)-B(2)-F(4)	118.9(8)
C(36)-N(6)-B(2)-N(5)	-178.4(7)
C(33)-N(6)-B(2)-N(5)	0.2(12)
C(29)-N(5)-B(2)-F(3)	-58.1(11)
C(31)-N(5)-B(2)-F(3)	115.1(9)
C(29)-N(5)-B(2)-F(4)	58.2(12)
C(31)-N(5)-B(2)-F(4)	-128.6(8)
C(29)-N(5)-B(2)-N(6)	179.8(7)
C(31)-N(5)-B(2)-N(6)	-7.0(12)
C(57)-N(8)-B(3)-F(5)	61.0(10)
C(54)-N(8)-B(3)-F(5)	-114.8(8)
C(57)-N(8)-B(3)-F(6)	-62.7(11)
C(54)-N(8)-B(3)-F(6)	121.5(7)
C(57)-N(8)-B(3)-N(7)	-176.5(7)
C(54)-N(8)-B(3)-N(7)	7.8(10)
C(50)-N(7)-B(3)-F(5)	-58.3(9)
C(52)-N(7)-B(3)-F(5)	113.2(9)
C(50)-N(7)-B(3)-F(6)	63.9(11)
C(52)-N(7)-B(3)-F(6)	-124.6(7)

C(50)-N(7)-B(3)-N(8)	178.2(6)
C(52)-N(7)-B(3)-N(8)	-10.3(10)
C(71)-N(9)-B(4)-F(8)	-62.7(9)
C(73)-N(9)-B(4)-F(8)	121.2(7)
C(71)-N(9)-B(4)-F(7)	59.8(10)
C(73)-N(9)-B(4)-F(7)	-116.3(7)
C(71)-N(9)-B(4)-N(10)	179.1(6)
C(73)-N(9)-B(4)-N(10)	2.9(10)
C(78)-N(10)-B(4)-F(8)	60.7(11)
C(75)-N(10)-B(4)-F(8)	-114.9(8)
C(78)-N(10)-B(4)-F(7)	-61.8(11)
C(75)-N(10)-B(4)-F(7)	122.6(8)
C(78)-N(10)-B(4)-N(9)	180.0(7)
C(75)-N(10)-B(4)-N(9)	4.4(10)
C(4)-N(1)-C(1)-C(5)	177.1(7)
C(4)-N(1)-C(1)-C(2)	-0.7(10)
C(3)-N(2)-C(2)-C(1)	-1.7(10)
C(3)-N(2)-C(2)-C(26)	178.1(6)
N(1)-C(1)-C(2)-N(2)	4.3(11)
C(5)-C(1)-C(2)-N(2)	-173.4(7)
N(1)-C(1)-C(2)-C(26)	-175.5(6)
C(5)-C(1)-C(2)-C(26)	6.8(11)
C(2)-N(2)-C(3)-C(47)	177.0(6)
C(2)-N(2)-C(3)-C(4)	-4.0(9)
C(1)-N(1)-C(4)-C(68)	177.3(6)
C(1)-N(1)-C(4)-C(3)	-5.0(10)
N(2)-C(3)-C(4)-N(1)	7.7(10)
C(47)-C(3)-C(4)-N(1)	-173.4(6)
N(2)-C(3)-C(4)-C(68)	-174.7(6)
C(47)-C(3)-C(4)-C(68)	4.3(10)
N(1)-C(1)-C(5)-C(6)	-86(18)
C(2)-C(1)-C(5)-C(6)	92(18)
C(1)-C(5)-C(6)-C(7)	-169(25)
C(5)-C(6)-C(7)-C(8)	62(35)
C(5)-C(6)-C(7)-C(9)	-121(35)
C(10)-N(3)-C(8)-C(7)	-2.5(9)

B(1)-N(3)-C(8)-C(7)	179.5(8)
C(10)-N(3)-C(8)-C(16)	179.9(7)
B(1)-N(3)-C(8)-C(16)	1.9(13)
C(9)-C(7)-C(8)-N(3)	0.6(10)
C(6)-C(7)-C(8)-N(3)	177.8(7)
C(9)-C(7)-C(8)-C(16)	178.1(8)
C(6)-C(7)-C(8)-C(16)	-4.8(14)
C(8)-C(7)-C(9)-C(10)	1.5(10)
C(6)-C(7)-C(9)-C(10)	-175.6(8)
C(8)-C(7)-C(9)-C(17)	177.6(7)
C(6)-C(7)-C(9)-C(17)	0.5(14)
C(7)-C(9)-C(10)-C(11)	-176.9(8)
C(17)-C(9)-C(10)-C(11)	7.3(15)
C(7)-C(9)-C(10)-N(3)	-3.1(9)
C(17)-C(9)-C(10)-N(3)	-178.9(7)
C(8)-N(3)-C(10)-C(11)	178.5(7)
B(1)-N(3)-C(10)-C(11)	-3.6(12)
C(8)-N(3)-C(10)-C(9)	3.5(9)
B(1)-N(3)-C(10)-C(9)	-178.5(8)
C(9)-C(10)-C(11)-C(12)	-179.7(9)
N(3)-C(10)-C(11)-C(12)	6.8(12)
C(9)-C(10)-C(11)-C(18)	-3.0(13)
N(3)-C(10)-C(11)-C(18)	-176.5(7)
C(10)-C(11)-C(12)-N(4)	-2.5(13)
C(18)-C(11)-C(12)-N(4)	-179.1(7)
C(10)-C(11)-C(12)-C(13)	176.0(9)
C(18)-C(11)-C(12)-C(13)	-0.7(15)
C(15)-N(4)-C(12)-C(11)	177.1(8)
B(1)-N(4)-C(12)-C(11)	-5.7(12)
C(15)-N(4)-C(12)-C(13)	-1.8(9)
B(1)-N(4)-C(12)-C(13)	175.5(7)
C(11)-C(12)-C(13)-C(14)	-177.5(10)
N(4)-C(12)-C(13)-C(14)	1.1(10)
C(11)-C(12)-C(13)-C(24)	0.7(16)
N(4)-C(12)-C(13)-C(24)	179.3(7)
C(12)-C(13)-C(14)-C(15)	-0.1(10)

C(24)-C(13)-C(14)-C(15)	-178.2(7)
C(12)-N(4)-C(15)-C(14)	1.8(10)
B(1)-N(4)-C(15)-C(14)	-175.5(8)
C(12)-N(4)-C(15)-C(25)	179.8(7)
B(1)-N(4)-C(15)-C(25)	2.5(13)
C(13)-C(14)-C(15)-N(4)	-1.1(10)
C(13)-C(14)-C(15)-C(25)	-179.0(8)
C(12)-C(11)-C(18)-C(19)	88.8(10)
C(10)-C(11)-C(18)-C(19)	-88.0(10)
C(12)-C(11)-C(18)-C(23)	-90.0(11)
C(10)-C(11)-C(18)-C(23)	93.2(9)
C(23)-C(18)-C(19)-C(20)	-0.3(15)
C(11)-C(18)-C(19)-C(20)	-179.0(9)
C(18)-C(19)-C(20)-C(21)	0.6(16)
C(19)-C(20)-C(21)-C(22)	-1.2(19)
C(20)-C(21)-C(22)-C(23)	1.4(19)
C(19)-C(18)-C(23)-C(22)	0.5(14)
C(11)-C(18)-C(23)-C(22)	179.2(8)
C(21)-C(22)-C(23)-C(18)	-1.0(15)
N(2)-C(2)-C(26)-C(27)	-142(11)
C(1)-C(2)-C(26)-C(27)	38(11)
C(2)-C(26)-C(27)-C(28)	64(21)
C(26)-C(27)-C(28)-C(30)	140(14)
C(26)-C(27)-C(28)-C(29)	-37(15)
C(31)-N(5)-C(29)-C(28)	-0.8(9)
B(2)-N(5)-C(29)-C(28)	173.4(8)
C(31)-N(5)-C(29)-C(37)	176.9(7)
B(2)-N(5)-C(29)-C(37)	-9.0(13)
C(30)-C(28)-C(29)-N(5)	0.0(9)
C(27)-C(28)-C(29)-N(5)	176.7(7)
C(30)-C(28)-C(29)-C(37)	-177.6(8)
C(27)-C(28)-C(29)-C(37)	-0.9(14)
C(29)-C(28)-C(30)-C(31)	0.7(8)
C(27)-C(28)-C(30)-C(31)	-176.0(7)
C(29)-C(28)-C(30)-C(38)	-178.1(7)
C(27)-C(28)-C(30)-C(38)	5.2(12)

C(29)-N(5)-C(31)-C(32)	-177.4(7)
B(2)-N(5)-C(31)-C(32)	8.4(11)
C(29)-N(5)-C(31)-C(30)	1.2(8)
B(2)-N(5)-C(31)-C(30)	-173.0(8)
C(28)-C(30)-C(31)-C(32)	177.2(7)
C(38)-C(30)-C(31)-C(32)	-4.0(13)
C(28)-C(30)-C(31)-N(5)	-1.2(8)
C(38)-C(30)-C(31)-N(5)	177.6(7)
N(5)-C(31)-C(32)-C(33)	-2.1(10)
C(30)-C(31)-C(32)-C(33)	179.7(7)
N(5)-C(31)-C(32)-C(39)	177.9(7)
C(30)-C(31)-C(32)-C(39)	-0.4(12)
C(36)-N(6)-C(33)-C(32)	-175.8(6)
B(2)-N(6)-C(33)-C(32)	5.3(12)
C(36)-N(6)-C(33)-C(34)	1.9(8)
B(2)-N(6)-C(33)-C(34)	-176.9(8)
C(31)-C(32)-C(33)-N(6)	-4.4(10)
C(39)-C(32)-C(33)-N(6)	175.7(7)
C(31)-C(32)-C(33)-C(34)	178.4(7)
C(39)-C(32)-C(33)-C(34)	-1.5(12)
N(6)-C(33)-C(34)-C(35)	-1.3(8)
C(32)-C(33)-C(34)-C(35)	176.1(8)
N(6)-C(33)-C(34)-C(45)	179.1(7)
C(32)-C(33)-C(34)-C(45)	-3.4(13)
C(33)-C(34)-C(35)-C(36)	0.2(9)
C(45)-C(34)-C(35)-C(36)	179.8(8)
C(33)-N(6)-C(36)-C(35)	-1.8(9)
B(2)-N(6)-C(36)-C(35)	177.1(8)
C(33)-N(6)-C(36)-C(46)	-178.6(7)
B(2)-N(6)-C(36)-C(46)	0.2(12)
C(34)-C(35)-C(36)-N(6)	1.0(10)
C(34)-C(35)-C(36)-C(46)	177.4(8)
C(31)-C(32)-C(39)-C(44)	-76.9(9)
C(33)-C(32)-C(39)-C(44)	103.1(9)
C(31)-C(32)-C(39)-C(40)	103.5(8)
C(33)-C(32)-C(39)-C(40)	-76.5(9)

C(44)-C(39)-C(40)-C(41)	2.1(11)
C(32)-C(39)-C(40)-C(41)	-178.3(7)
C(39)-C(40)-C(41)-C(42)	-1.5(13)
C(40)-C(41)-C(42)-C(43)	0.4(14)
C(41)-C(42)-C(43)-C(44)	0.2(14)
C(40)-C(39)-C(44)-C(43)	-1.6(12)
C(32)-C(39)-C(44)-C(43)	178.8(7)
C(42)-C(43)-C(44)-C(39)	0.4(13)
N(2)-C(3)-C(47)-C(48)	-105(9)
C(4)-C(3)-C(47)-C(48)	76(9)
C(3)-C(47)-C(48)-C(49)	-88(27)
C(47)-C(48)-C(49)-C(51)	-157(23)
C(47)-C(48)-C(49)-C(50)	21(24)
C(52)-N(7)-C(50)-C(49)	0.5(8)
B(3)-N(7)-C(50)-C(49)	173.3(6)
C(52)-N(7)-C(50)-C(58)	-177.0(6)
B(3)-N(7)-C(50)-C(58)	-4.2(10)
C(48)-C(49)-C(50)-N(7)	179.6(7)
C(51)-C(49)-C(50)-N(7)	-2.4(8)
C(48)-C(49)-C(50)-C(58)	-3.1(12)
C(51)-C(49)-C(50)-C(58)	174.8(6)
C(48)-C(49)-C(51)-C(52)	-178.8(7)
C(50)-C(49)-C(51)-C(52)	3.4(8)
C(48)-C(49)-C(51)-C(59)	1.5(11)
C(50)-C(49)-C(51)-C(59)	-176.3(6)
C(49)-C(51)-C(52)-C(53)	-179.8(8)
C(59)-C(51)-C(52)-C(53)	-0.1(13)
C(49)-C(51)-C(52)-N(7)	-3.1(8)
C(59)-C(51)-C(52)-N(7)	176.6(6)
C(50)-N(7)-C(52)-C(51)	1.6(7)
B(3)-N(7)-C(52)-C(51)	-171.2(7)
C(50)-N(7)-C(52)-C(53)	179.0(6)
B(3)-N(7)-C(52)-C(53)	6.2(10)
C(51)-C(52)-C(53)-C(54)	178.8(7)
N(7)-C(52)-C(53)-C(54)	2.4(10)
C(51)-C(52)-C(53)-C(60)	1.3(12)

N(7)-C(52)-C(53)-C(60)	-175.1(6)
C(52)-C(53)-C(54)-N(8)	-4.8(10)
C(60)-C(53)-C(54)-N(8)	172.7(6)
C(52)-C(53)-C(54)-C(55)	176.3(7)
C(60)-C(53)-C(54)-C(55)	-6.2(12)
C(57)-N(8)-C(54)-C(53)	-177.7(7)
B(3)-N(8)-C(54)-C(53)	-1.2(10)
C(57)-N(8)-C(54)-C(55)	1.4(8)
B(3)-N(8)-C(54)-C(55)	177.9(7)
C(53)-C(54)-C(55)-C(56)	177.3(7)
N(8)-C(54)-C(55)-C(56)	-1.7(8)
C(53)-C(54)-C(55)-C(66)	-1.3(13)
N(8)-C(54)-C(55)-C(66)	179.8(7)
C(54)-C(55)-C(56)-C(57)	1.3(8)
C(66)-C(55)-C(56)-C(57)	179.9(7)
C(54)-N(8)-C(57)-C(56)	-0.6(8)
B(3)-N(8)-C(57)-C(56)	-177.0(7)
C(54)-N(8)-C(57)-C(67)	177.8(7)
B(3)-N(8)-C(57)-C(67)	1.3(12)
C(55)-C(56)-C(57)-N(8)	-0.5(9)
C(55)-C(56)-C(57)-C(67)	-178.8(7)
C(54)-C(53)-C(60)-C(65)	100.6(9)
C(52)-C(53)-C(60)-C(65)	-81.9(9)
C(54)-C(53)-C(60)-C(61)	-83.7(8)
C(52)-C(53)-C(60)-C(61)	93.9(8)
C(65)-C(60)-C(61)-C(62)	-0.9(11)
C(53)-C(60)-C(61)-C(62)	-176.8(7)
C(60)-C(61)-C(62)-C(63)	1.1(11)
C(61)-C(62)-C(63)-C(64)	0.3(12)
C(62)-C(63)-C(64)-C(65)	-2.0(12)
C(61)-C(60)-C(65)-C(64)	-0.7(11)
C(53)-C(60)-C(65)-C(64)	174.8(7)
C(63)-C(64)-C(65)-C(60)	2.2(12)
N(1)-C(4)-C(68)-C(69)	-16(7)
C(3)-C(4)-C(68)-C(69)	166(6)
C(4)-C(68)-C(69)-C(70)	87(15)

C(68)-C(69)-C(70)-C(71)	151(13)
C(68)-C(69)-C(70)-C(72)	-31(13)
C(73)-N(9)-C(71)-C(70)	1.5(8)
B(4)-N(9)-C(71)-C(70)	-175.1(7)
C(73)-N(9)-C(71)-C(79)	179.8(6)
B(4)-N(9)-C(71)-C(79)	3.2(11)
C(72)-C(70)-C(71)-N(9)	0.7(8)
C(69)-C(70)-C(71)-N(9)	179.4(7)
C(72)-C(70)-C(71)-C(79)	-177.5(7)
C(69)-C(70)-C(71)-C(79)	1.2(13)
C(71)-C(70)-C(72)-C(73)	-2.5(8)
C(69)-C(70)-C(72)-C(73)	178.7(6)
C(71)-C(70)-C(72)-C(80)	173.1(6)
C(69)-C(70)-C(72)-C(80)	-5.7(11)
C(71)-N(9)-C(73)-C(72)	-3.1(8)
B(4)-N(9)-C(73)-C(72)	173.5(6)
C(71)-N(9)-C(73)-C(74)	176.8(6)
B(4)-N(9)-C(73)-C(74)	-6.5(11)
C(70)-C(72)-C(73)-N(9)	3.4(8)
C(80)-C(72)-C(73)-N(9)	-171.7(7)
C(70)-C(72)-C(73)-C(74)	-176.6(7)
C(80)-C(72)-C(73)-C(74)	8.3(13)
N(9)-C(73)-C(74)-C(75)	2.7(11)
C(72)-C(73)-C(74)-C(75)	-177.4(7)
N(9)-C(73)-C(74)-C(81)	-171.1(6)
C(72)-C(73)-C(74)-C(81)	8.9(12)
C(73)-C(74)-C(75)-N(10)	4.6(11)
C(81)-C(74)-C(75)-N(10)	178.4(6)
C(73)-C(74)-C(75)-C(76)	-179.9(7)
C(81)-C(74)-C(75)-C(76)	-6.1(12)
C(78)-N(10)-C(75)-C(74)	175.4(7)
B(4)-N(10)-C(75)-C(74)	-8.3(11)
C(78)-N(10)-C(75)-C(76)	-1.1(8)
B(4)-N(10)-C(75)-C(76)	175.2(6)
C(74)-C(75)-C(76)-C(77)	-174.8(8)
N(10)-C(75)-C(76)-C(77)	1.2(8)

C(74)-C(75)-C(76)-C(87)	4.2(13)
N(10)-C(75)-C(76)-C(87)	-179.8(7)
C(75)-C(76)-C(77)-C(78)	-0.8(9)
C(87)-C(76)-C(77)-C(78)	-179.8(7)
C(75)-N(10)-C(78)-C(77)	0.7(9)
B(4)-N(10)-C(78)-C(77)	-175.5(7)
C(75)-N(10)-C(78)-C(88)	179.4(7)
B(4)-N(10)-C(78)-C(88)	3.2(12)
C(76)-C(77)-C(78)-N(10)	0.1(10)
C(76)-C(77)-C(78)-C(88)	-178.5(8)
C(75)-C(74)-C(81)-C(86)	92.3(9)
C(73)-C(74)-C(81)-C(86)	-93.9(9)
C(75)-C(74)-C(81)-C(82)	-87.9(8)
C(73)-C(74)-C(81)-C(82)	86.0(8)
C(86)-C(81)-C(82)-C(83)	-2.7(10)
C(74)-C(81)-C(82)-C(83)	177.4(7)
C(81)-C(82)-C(83)-C(84)	2.0(11)
C(82)-C(83)-C(84)-C(85)	-2.5(13)
C(83)-C(84)-C(85)-C(86)	3.5(13)
C(82)-C(81)-C(86)-C(85)	3.8(11)
C(74)-C(81)-C(86)-C(85)	-176.4(7)
C(84)-C(85)-C(86)-C(81)	-4.2(13)
C(6S)-C(1S)-C(2S)-C(3S)	-0.8(14)
C(1S)-C(2S)-C(3S)-C(4S)	0.4(16)
C(2S)-C(3S)-C(4S)-C(5S)	-0.8(16)
C(3S)-C(4S)-C(5S)-C(6S)	1.6(15)
C(2S)-C(1S)-C(6S)-C(5S)	1.5(13)
C(2S)-C(1S)-C(6S)-C(7S)	-179.9(8)
C(4S)-C(5S)-C(6S)-C(1S)	-1.9(13)
C(4S)-C(5S)-C(6S)-C(7S)	179.5(8)
C(13S)-C(8S)-C(9S)-C(10S)	3(2)
C(8S)-C(9S)-C(10S)-C(11S)	-1(2)
C(9S)-C(10S)-C(11S)-C(12S)	-2(2)
C(10S)-C(11S)-C(12S)-C(13S)	3(2)
C(9S)-C(8S)-C(13S)-C(12S)	-2(2)
C(9S)-C(8S)-C(13S)-C(14S)	177.8(11)

C(11S)-C(12S)-C(13S)-C(8S)	-1(2)
C(11S)-C(12S)-C(13S)-C(14S)	179.0(11)

Symmetry transformations used to generate equivalent atoms.

REFERENCES CITED

Chapter I

(1) (a) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH: New York, 1997. (b) Clar, E. *Polycyclic Hydrocarbons*, Academic Press: London, 1964.

(2) Wise, S. A.; Campbell, R. M.; West, W. R.; Lee, M. L.; Bartle, K. D. *Chem. Geol*. **1986**, *54*, 339-357.

(3) (a) *Functional Organic Materials*; Müller, T. J. J., Bunz. U. H. F., Eds.; Wiley-VCH: Weinheim, 2007. (b) *Organic Light Emitting Devices: Synthesis, Properties, and Applications*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006. (c) *Carbon-Rich Compounds: From Molecules to Materials*; Haley, M. M. Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2006.

(4) (a) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876-3892.

(5) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891-4945.

(6) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028-5048. (b) Anthony, J. E. *Angew. Chem. Int. Ed.* **2008**, *47*, 452-483.

(7) Scott, L. T. *Polycyclic Aromat. Cmpd.* **2010**, *30*, 247-259.

(8) Inter alia: (a) Saito, M.; Nakamura, M.; Tajima, T. *Chem. Eur. J.* **2008**, *14*, 6062-6068. (b) Kawase, T.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *Chem Eur. J.* **2009**, *15*, 2653-2661. (c) Zerubba, U. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796-2797. (d) Zhang, H.; Karasawa, T.; Yamada, H.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2009**, *11*, 3076-3079. (e) Saito, M. *Symmetry* **2010**, *2*, 950-969. (f) Zerubba, U. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2010**, *132*, 11012-11014. (g) Kawase, T.; Fujiwara, T.; Kitamura, C.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Shinamura, S.; Mori, H.; Miyazaki, E.; Takimiya, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 7728-7732.

(9) Gabriel, S. *Ber. Dt. Chem. Ges.* **1884**, *17*, 1389-1397.

(10) (a) Errera, G. *Gazz. Chim. Ital.* **1907**, *37*, II, 624. (b) Errera, G. *Gazz. Chim. Ital.* **1908**, *38*, II, 588. (c) Errera, G.; Vaccarino, G. *Gazz. Chim. Ital.* **1909**, *39* I, 1. (d) Marotta, D. *Gazz. Chim. Ital.* **1911**, *41*, II, 59. (e) Radulescu, D.; Georgescu, V. *Bull. Soc. Chim. Fr., 4* **1925**, *37*, 1187. (f) Strauss, F.; Kühnel, R.; Hansel, R. *Ber. Dt. Chem. Ges.* **1933**, *66*, 1847. (g) Weizmann, Ch.; Bergmann, E.; Haskelberg,

L. *J. Chem. Soc.* **1939**, 391. (h) Radulescu, D.; Alexa, M. *Chem. Zentralbl.* **1943**, I, 622.

(11) (a) Deuschel, W. *Helv. Chim. Acta* **1951**, *35*, 168-185. (b) Deuschel, W. *Helv. Chim. Acta* **1951**, *35*, 2403-2416.

(12) (a) Chardonnens, L.; Ritter, R. *Helv. Chim. Acta* **1955**, *38*, 393-396.

(13) (a) Poriel, C.; Liang, J.-J.; Rault-Berthelot, J.; Barrière, F.; Cocherel, N.; Slawin, A. M. Z.; Horhant, D.; Virboul, M.; Alcaraz, G.; Audebrand, N.; Vignau, L.; Huby, N.; Wantz, G.; Hirsch, L. *Chem. Eur. J.* **2007**, *13*, 10055-10069. (b) Cocherel, N.; Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Audbrand, N.; Slawin, A. M. Z.; Vignau, L. *Chem. Eur. J.* **2008**, *14*, 11328-11342. (c) Poriel, C.; Barrière, F.; Thirion, D.; Rault-Berthelot, J. *Chem. Eur. J.* **2009**, *15*, 13304-13307. (d) Thirion, D.; Poriel, C.; Barrière, F.; Métivier, R.; Jeannin, O.; Rault-Berthelot, J. *Org. Lett.* **2009**, *11*, 4794-4797. (e) Cocherel, N.; Poriel, C.; Vignau, L.; Bergamini, J.-F.; Rault-Berthelot, J. *Org. Lett.* **2010**, *12*, 452-455. (f) Thirion, D.; Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Jeannin, O. *Chem. Eur. J.* **2010**, *16*, 13646-13658. (g) Cocherel, N.; Poriel, C.; Vignau, L.; Bergamini, J.-F.; Rault-Berthelot, J. *Org. Lett.* **2011**, *12*, 452-455.

(14) (a) Usta, H.; Facchetti, A.; Marks, T. J. *Org. Lett.* **2008**, *10*, 1385-1388. (b) Usta, H.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 8580-8581. (c) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586-5608.

(15) (a) Vak, D.; Lim, B.; Lee, S.-H.; Kim, D.-Y. *Org. Lett.* **2005**, *7*, 4229-4232. (b) Becker, K.; Lupton, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 6468-6479. (c) Amara, J. P.; Swager, T. M. *Macromolecules* **2006**, *39*, 5753-5759. (d) Preis, E.; Scherf, U. *Macromol. Rapid Commun.* **2006**, *27*, 1105-1109. (e) Laquai, F.; Mishra, A. K.; Müllen, K.; Friend, R. H. *Adv. Func. Mater.* **2008**, *18*, 3265-3275. (f) Sonar, P.; Oldridge, L.; Grimsdale, A. C.; Müllen, K.; Surin, M.; Lazzaroni, R.; Leclère, P.; Pinto, J.; Chua, L.-L.; Sirringhaus, H.; Friend, R. H. *Synthetic Met.* **2010**, *160*, 468-474.

(16) Kruber, O.; Oberkobusch, R. *Chem. Ber.* **1952**, *85*, 433-436.

(17) Chardonnens, L.; Rody, J. *Helv. Chim. Acta* **1959**, *42*, 1328-1331.

(18) (a) Chardonnens, L.; Laroche, B.; Sieber, W. *Helv. Chim. Acta* **1974**, *57*, 585-599. (b) Chardonnens, L.; Häger, J. *Helv. Chim. Acta* **1974**, *57*, 1472-1477. (c) Chardonnens, L.; Bitsch, S.; Häger, J. *Helv. Chim. Acta* **1975**, *58*, 503-507.

(19) Chardonnens, L.; Häger, J. *Helv. Chim. Acta* **1970**, *53*, 843-847.

(20) Friedrich, E.; Deuschel, W. *Chem. Ber.* **1956**, *89*, 2794-2799.

(21) Chardonnens, L.; Salamin, L. *Helv. Chim. Acta* **1968**, *51*, 1096-1103.

(22) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157-2159.

(23) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3615-3625.

(24) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294-1301.

(25) (a) Nishinaga, T.; Nodera, N.; Miyata, Y.; Komtasu, K. *J. Org. Chem.* **2002**, *67*, 6091-6096. (b) Miyata, Y.; Minari, T.; Nemoto, T.; Isoda, S.; Komatsu, K. *Org. Biomol. Chem.* **2007**, *5*, 2592-2598.

(26) Nakagawa, T.; Kumaki, D.; Nishida, J.-I.; Tokito, S.; Yamashita, Y. *Chem. Mater.* **2008**, *20*, 2615-2617.

(27) Rose, B. D.; Chase, D. T.; Weber, C. D.; Zakharov, L. N. Lonergan, M. C.; Haley, M. M. *Org. Lett.* **2011**, *13*, 2106-2109.

(28) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15-18.

(29) (a) Hellwinkel, D.; Kistenmacher, T. *Liebigs Ann. Chem.* **1989**, *10*, 945-949. (b) Scherf, U. *Macromol. Rapid Commun.* **1993**, *14*, 575-579

(30) Liu, T.-P.; Liao, Y.-X. Xing, C.-H.; Hu, Q.-S. *Org. Lett.* **2011**, *13*, 2452-2455.

(31) Wolfgang, F.; Gompper, R. *Tet. Lett.* **1987**, *28*, 3083-3086.

(32) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482-9483. (b) Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028-8029. (c) Purushothaman, B.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2010**, *12*, 2060-2063. (d) Purushothaman, B.; Bruzek, M.; Parkin, S. R.; Miller, A.-F.; Anthony, J. E. *Angew. Chem. Int. Ed.* **2011**, *50*, 7013-7017.

(33) (a) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGreur, N. E.; Miller, G. P. *J. Am. Chem. Soc.* **2008**, *130*, 16274-16286. (b) Kaur, I.; Stein, N. N.; Kopreski, R. P.; Miller, G. P. *J. Am. Chem. Soc.* **2009**, *131*, 3424-3425.

(34) (a) Tverskoy, O.; Rominger, F.; Peters, A.; Himmel-H.-J.; Bunz, U. H. F. *Angew. Chem. Int. Ed.* **2011**, *50*, 3557-3560. (b) Bunz, U. H. F. *Chem. Eur. J.* **2009**, *15*, 6780-6789. (c) Wu, J. I.; Wannere, C. S.; Mo, Y.; Schleyer, P. v. R.; Bunz. U. H. F. *J. Org. Chem.* **2009**, *74*, 4343-4349. (d) Miao, S.; Appleton, A. L.; Berger, N.; Barlow, S.; Marder, S. R.; Hardcastle, K. I.; Bunz, U. H. F. *Chem. Eur. J.* **2009**, *15*, 4990-4993.

(35) (a) Reddy, R.; Bendikov, M. *Chem. Commun.* **2006**, 1179-1181. (b) Vollmer, A.; Weiss, H.; Rentenberger, S.; Salzmann, I.; Rabe, J. P.; Koch, N. *Surf. Sci.* **2006**, *600*, 4004-4007.

(36) (a) Reisch, H.; Wiesler, U.; Scherf, U.; Tuytuylkov, N. *Macromolecules* **1996**, *29*, 8204-8210. (b) Reisch, H.; Ph.D. Thesis, University of Mainz, 1995.

(37) Brunetti, F. Gong, X.; Tong, M.; Heeger, A. J.; Wudl, F. *Angew. Chem. Int. Ed.* **2010**, *49*, 532-536.

(38) Chase, D. T.; Rose, B. D.; McClintock, S. P.; Zakharov, L. N.; Haley, M. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 1127-1130.

(39) Montgomery, L. K.; Huffman, J. C.; Jurczak, E. A.; Grendze, M. P. *J. Am. Chem. Soc.* **1986**, *108*, 6004-6011.

(40) Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399-3412.

(41) Chase, D. T.; Fix, A. G.; Rose, B. D.; Weber, C. D.; Nobusue, S.; Stockwell, C. E.; Zakharov, L. N.; Lonergan, M. C.; Haley, M. M. *Angew. Chem. Int. Ed.* **2011**, *50*, *Accepted*.

(42) Dong, H.; Wang, C.; Hu, W. *Chem. Commun.* **2010**, *46*, 5211-5222.

(43) Chase, D. T.; Rose, B. D.; Fix, A. G.; Weber, C. D.; Lonergan, M. C.; Haley, M. M. Unpublished Results.

(44) LeBerre, A. *Ann. Chim.* **1957**, *2*, 371-425.

(45) Shimizu, A.; Tobe, Y. *Angew. Chem. Int. Ed.* **2011**, *50*, 6906-6910.

(46) Shimizu, A.; Tobe, Y. Unpublished Results

(47) Altman, Y.; Ginsburg, D. *J. Chem. Soc.* **1961**, 1498-1505.

(48) Chardonnens, L.; Chardonnens, H. *Helv. Chim. Acta* **1966**, *49*, 1931-1934.

(49) Wang, X.-M.; Hou, X.-L.; Zhou, Z.-Y.; Mak, T. C. W.; Wong, H. N. C. *J. Org. Chem.* **1993**, *58*, 7498-7506.

(50) Yang, Y.; Peterson, J. L.; Wang, K. K. *J. Org. Chem.* **2003**, *68*, 5832-5837.

(51) Hilt, G.; Paul, A.; Harms, K. *J. Org. Chem.* **2008**, *73*, 5187-5190.

Chapter II

(1) (a) Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives and their Valence Isomers*, CRC Press: Boca Raton, 1987. (b) Hopf, H. *Classics in Hydrocarbon Chemistry*, Wiley-VCH: Weinheim, 2000. (c) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048. (d) Anthony, J. E. *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483.

(2) (a) *Functional Organic Materials*; Müller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, 2007. (b) *Light Emitting Devices: Synthesis, Properties and Applications*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006. (c) *Carbon-Rich Compounds*, Haley, M. M., Tykwinksi, R. R., Eds.; Wiley-VCH: Weinheim, 2006.

(3) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483. (b) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15–18.

(4) (a) Vollmer, a.; Weiss, H.; Rentenberger, S.; Salzmann, I.; Rabe, J. P.; Koch, N. *Surf. Sci.* **2006**, *600*, 4004–4007. (b) Reddy, A. R.; Bendikov, M. *Chem. Commun.* **2006**, 1179–1181. (c) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGruer, N. E.; Miller, G. P. *J. Am. Chem. Soc.* **2008**, *130*, 16274–16286.

(5) Recent examples, inter alia: (a) Miao, Q.; Nguyen, T.-Q.; Someya, T.; Blanchet, G. B.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 10284–10287. (b) Miao, S.; Brombosz, S. M.; Schleyer, P. v. R.; Wu, J. I.; Barlow, S.; Marder, S. R.; Hardcastle, K. I.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2008**, *130*, 7339–7344. (c) Tang, Q.; Liu, J.; Chan, H. S.; Miao, Q. *Chem. Eur. J.* **2009**, *15*, 3965–3969. (d) Bunz, U. H. F. *Chem. Eur. J.* **2009**, *15*, 6780–6789.

(6) Recent examples, inter alia: (a) Saito, M.; Nakamura, M.; Tajima, T.; *Chem. Eur. J.* **2008**, *14*, 6062–6068. (b) Kawase, T.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *Chem. Eur. J.* **2009**, *15*, 2653–2661. (c) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796–2797. (d) Zhang, H.; Karasawa, T.; Yamada, H.; Wakamiya, S.; Yamaguchi, S. *Org. Lett.* **2009**, *11*, 3076–3079. (e) Saito, M. *Symmetry* **2010**, *2*, 950–969. (f) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2010**, *132*, 11012–11014. (g) Kawase, T.; Fujiwara, T.; Kitamura, C.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Shinamura, S.; Mori, H.; Miyazaki, E.; Takimiya, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 7728–7732.

(7) Hafner, K.; Stowasser, B.; Krimmer, H. P.; Fischer, S.; Boehm, M. C.; Lindner, H. J. *Angew. Chem. Int. Ed.* **1986**, *25*, 630–632.

(8) Trahanovsky, W. S.; Lorimor, S. P. *J. Org. Chem.* **2006**, *71*, 1784–1794, and references therein.

(9) (a) Usta, H.; Facchetti, A.; Marks, T. J. *Org. Lett.* **2008**, *10*, 1385–1388. (b) Usta, H.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 8580–8581. (c) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomergolu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586–5608.

(10) *Inter alia*: (a) Poriel, C.; Liang, J.-J.; Rault-Berthelot, J.; Barrière, F.; Cocherel, N.; Slawin, A. M. Z.; Horhant, D.; Virboul, M.; Alcaraz, G.; Audebrand, N.; Vignau, L.; Huby, N.; Wantz, G.; Hirsch, L. **2007**, *13*, 10055–10069. (b) Chen, C.-P.; Chan, S.-H.; Chao, T.-C.; Ting, C.; Ko, B.-T. *J. Am. Chem. Soc.* **2008**, *130*, 12828–12833. (c) Cocherel, N.; Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Audebrand, N.; Slawin, A. M. Z.; Vignau, L. *Chem. Eur. J.* **2008**, *14*, 11328–11342. (d) Zhang, W.; Smith, J.; Hamilton, R.; Heeney, M.; Kirkpatrick, J.; Song, K.; Watkins, S. E.; Anthopoulos, T.; McCulloch, I. *J. Am. Chem. Soc.* **2009**, *131*, 10814–10815. (e) Zhang, W.; Smith, J.; Watkins, S. E.; Gysel, R.; McGehee, M.; Salleo, A.; Kirkpatrick, S.; Ashraf, S.; Anthopoulos, T.; Heeney, M.; McCulloch, I. *J. Am. Chem. Soc.* **2010**, *132*, 11437–11439.

(11) Zhou, Q; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294–1301.

(12) Reisch, H.; Wiesler, U.; Shcerf, U.; Tuytuylkov, N. *Macromolecules* **1996**, *29*, 8204–8210.

(13) Shimizu, A.; Uruichi, M.; Yakushi, K.; Matsuzaki, H.; Okamoto, H.; Nakano, M.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *Angew. Chem. Int. Ed.* **2009**, *48*, 5482–5486.

(14) (a) Montgomery, L. K.; Huffman, J. C.; Jurczak, E. A.; Grendze, M. P. *J. Am. Chem. Soc.* **1986**, *108*, 6004–6011. (b) For a closely related acene-like derivative, see Nishida, J.-I.; Fujiwara, Y.; Yamashita, Y. *Org. Lett.* **2009**, *11*, 1813–1816.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.;

Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., *Gaussian 03*, Revision B.04, Gaussian, Inc., Pittsburgh PA, 2003.

(16) Kataoka, M.; Toyota, A. *J. Chem. Research (S)* **1998**, *5*, 278–279.

(17) Cremer, D.; Günther, H. *Liebigs. Ann. Chem.* **1972**, *763*, 87–108. (b) Günther, H.; Shyoukh, A.; Cremer, D.; Frisch, K. H. *Liebigs. Ann. Chem.* **1978**, 150–164.

(18) (a) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301–1315. (b) Mitchell, R. H.; Zhang, R.; Fan, W.; Berg, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 16251–16254.

Chapter III

(1) (a) *Functional Organic Material,s* Müller, T. J. J.; Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, Germany, 2007. (b) *Organic Light Emitting Devices: Synthesis, Properties and Applications*, Mullen, K.; Scherf, U., Eds.; Wiley-VCH: Weinheim, Germany, 2006. (c) *Carbon-Rich Compounds*, Haley, M. M.; Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, Germany, 2006.

(2) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028-5048. (b) Anthony, J. E. *Angew. Chem. Int. Ed.* **2008**, *47*, 452-483.

(3) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 942-9483. (b) Anthony, J. E.; Eaton, D. L.; Parksin, S. R. *Org. Lett.* **2002**, *4*, 15-18.

(4) Inter alia: (a) Saito, M.; Nakamura, M.; Tajima, T. *Chem.–Eur. J.* **2008**, *14*, 6062–6068. (b) Kawase, T.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T. *Chem.–Eur. J.* **2009**, *15*, 2653–2661. (c) Zerubba, U. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796–2797. (d) Zhang, H.; Karasawa, T.; Yamada, H.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2009**, *11*, 3076–3079. (e) Saito, M. *Symmetry* **2010**, *2*, 950–969. (f) Zerubba, U. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2010**, *132*, 11012–11014. (g) Kawase, T.; Fujiwara, T.; Kitamura, C.; Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Shinamura, S.; Mori, H.; Miyazaki, E.; Takimiya, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 7728–7732.

(5) (a) Usta, H.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 8580–8581. (b) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Deliomergolu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586–5608.

(6) *Inter alia*: (a) Chen, C.-P.; Chan, S.-H.; Chao, T.-C.; Ting, C.; Ko, B.-T. *J. Am. Chem. Soc.* **2008**, *130*, 12828–12833. (b) Cocherel, N.; Poriel, C. Rault-Berthelot,

J.; Barrière, F.; Audebrand, N.; Slawin, A. M. Z.; Vignau, L. *Chem. Eur. J.* **2008**, *14*, 11328–11342. (c) Zhang, W.; Smith, J.; Hamilton, R.; Heeney, M.; Kirkpatrick, J.; Song, K.; Watkins, S. E.; Anthopoulos, T.; McCulloch, I. *J. Am. Chem. Soc.* **2009**, *131*, 10814–10815. (d) Zhang, W.; Smith, J.; Watkins, S. E.; Gysel, R.; McGehee, M.; Salleo, A.; Kirkpatrick, J.; Ashraf, S.; Anthopoulos, T.; Heeney, M.; McCulloch, I. *J. Am. Chem. Soc.* **2010**, *132*, 11437–11439.

(7) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294–1301.

(8) Reisch, H.; Wiesler, U.; Scherf, U.; Tuytuylkov, N. *Macromolecules* **1996**, *29*, 8204–8210.

(9) Chase, D. T.; Rose, B. D.; McClintock, S. P.; Zakharov, L. N.; Haley, M. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 1127–1130.

(10) (a) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876–3892. (b) Dong, H.; Wang, C.; Hu, W. *Chem. Commun.* **2010**, *46*, 5211–5222.

(11) Mikroyannidis, J. A.; Kabanakis, A. N.; Sharma, S. S., Sharma, G. D. *Adv. Funct. Mater.* **2011**, *21*, 746–755.

(12) Rose, B. D.; Chase, D. T.; Weber, C. D.; Zakharov, L. N.; Lonergan, M. C.; Haley, M. M. *Org. Lett.* **2011**, *13*, 2106–2109.

(13) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157–2159.

(14) Nakagawa, T.; Kumaki, D.; Nishida, J.-i.; Tokito, S.; Yamashita, Y. *Chem. Mater.* **2008**, *20,* 2615–2617.

(15) Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 59–76.

Chapter IV

(1) (a) *Functional Organic Material,s* Müller, T. J. J.; Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, Germany, 2007. (b) *Organic Light Emitting Devices: Synthesis, Properties and Applications*, Mullen, K.; Scherf, U., Eds.; Wiley-VCH: Weinheim, Germany, 2006. (c) *Carbon-Rich Compounds*, Haley, M. M.; Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, Germany, 2006.

(2) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028-5048. (b) Anthony, J. E. *Angew. Chem. Int. Ed.* **2008**, *47*, 452-483.

(3) Chase, D. T.; Rose, B. D.; Zakharov, L. N.; Haley, M. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 1227-1230.

(4) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 942-9483. (b) Anthony, J. E.; Eaton, D. L.; Parksin, S. R. *Org. Lett.* **2002**, *4*, 15-18. (c) Kaur, I.; Jazdzyk, M.; Stein, N. N.; Prusevich, P.; Miller, G. P. *J. Am. Chem. Soc.* **2010**, *132*, 1261-1263. (d) Purushothaman, B.; Bruzek, M.; Parkin, S. R.; Anthony, J. E. *Angew. Chem. Int. Ed.* **2011**, *50*, 7013-7017.

(5) Shimizu, A.; Tobe, Y. *Angew. Chem. Int. Ed.* **2011**, *50*, 6906-6910.

(6) Chase, D. T.; Fix, A. G.; Rose, B. D.; Weber, C. D.; Nobusue, S.; Stockwell, C. E.; Zakharov, L. N.; Lonergan, M. C.; Haley, M. M. *Angew. Chem. Int. Ed.* **2011**, *50*, *Accepted*.

(7) Rose, B. D.; Chase, D. T.; Weber, C. D.; Zakharov, L. N.; Haley, M. M. *Org. Lett.* **2011**, *13*, 2106-2109.

(8) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876–3892. (b) Dong, H.; Wang, C.; Hu, W. *Chem. Commun.* **2010**, *46*, 5211-5222. (c) Mikroyannidis, J. A.; Kabanakis, A. N.; Sharma, S. S.; Sharma, G. D. *Adv. Funct. Mater.* **2011**, *21*, 746-755.

(9) Reisch, H.; Wiesler, U.; Scherf, U.; Tuytuylkov, N. *Macromolecules* **1996**, *29*, 8204-8210.

(10) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157-2159.

(11) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGruer, N. E.; Miller, G. P. *J. Am. Chem. Soc.* **2008**, *130*, 16274-16286.

Chapter V

(1) (a) de Meijere, A., Ed. *Top. Curr. Chem*. (Carbon Rich Compounds I); Springer: Berlin, 1998; Vol. 196. (b) de Meijere, A., Ed. *Top. Curr. Chem*. (Carbon Rich Compounds II); Springer: Berlin, 1999; Vol. 201. (c) Diederich, F., Stang, P. J., Tykwinski, R. R., Eds. *Acetylene Chemistry: Chemistry, Biology, and Material Science*; Wiley-VCH: Weinheim, 2005. (d) Haley, M. M., Tykwinski, R. R., Eds. *Carbon-Rich Compounds: From Molecules to Materials*; Wiley-VCH: Weinheim, 2006.

(2) Reviews, inter alia: (a) *Organic Light Emitting Devices: Synthesis, Properties and Applications*; Mullen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006. (b) Chen, J.; Reed, M. A.; Dirk, S. M.; Price, D. W.; Rawlett, A. M.; Tour, J. M.;

Grubisha, D. S.; Bennett, D. W. *In NATO Science Series II: Mathematics, Physics, Chemistry (Molecular Electronics: Bio-Sensors and Bio-Computers)*; Plenum: New York, 2003; Vol. 96, pp 59-195. (c) Domerco, B.; Hreha, R. D.; Zhang, Y.-D.; Haldi, A.; Barlow, S.; Marder, S. R.; Kippelen, B. *J. Poly. Sci. Part B: Poly. Phys*. **2003**, *41*, 2726-2732. (d) Shirota, Y. *J. Mater. Chem*. **2000**, *10*, 1-25. (e) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev*. **1999**, *99*, 1863-1933. (f) Electronic Materials: The Oligomer Approach; Mullen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998. (g) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, 1997.

(3) (a) Miller, J. J.; Marsden, J. A.; Haley, M. M. *Synlett* **2004**, 165–168. (b) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464–2476. (c) Spitler, E. L.; Shirtcliff, L. D.; Haley, M. M. *J. Org. Chem.* **2007**, *72*, 86–96. (d) Spitler, E. L.; Monson, J. M.; Haley, M. M. *J. Org. Chem*. **2008**, *73*, 2211–2223. (e) Samori, S.; Tojo, S.; Fujitsuka, M.; Splitler E. L.; Haley, M. M.; Majima, T. *J. Org. Chem*. **2007**, *72*, 2785–2793. (f) Samori, S.; Tojo, S.; Fujitsuka, M.; Splitler E. L.; Haley, M. M.; Majima, T. *J. Org. Chem*. **2008**, *73*, 3551–3558.

(4) *Inter alia:* (a) Zucchero, A. J.; McGrier, P. A.; Bunz, U. H. F. *Acc. Chem. Res.* **2010**, *43*, 397–408. (b) Kang, H.; Zhu, P.; Yang, Y.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 15974–15975. (c) Wilson, J. N.; Josowicz, M.; Wang, Y.; Bunz, U. H. F. *Chem. Commun.* **2003**, 2962–2963. (d) Wilson, J. N.; Hardcastle, K. I.; Josowicz, M.; Bunz. U. H. F. *Tetrahedron*, **2004**, *60*, 7157–7167.

(5) (a) Huang, J.-H.; Sun, Y.-Y.; Chou, P. T.; Fang, J.-M. *J. Org. Chem.* **2005**, *70*, 5827–5832. (b) Wilson, J. N.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2005**, *127*, 4124–4125. (c) Brombosz, S. M.; Zucchero, A. J.; Phillips, R. L.; Vazquez, D.; Wilson, A.; Bunz, U. H. F. *Org. Lett.* **2007**, *9*, 4519–4522. (d) Tolosa, J.; Zucchero, A. J.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2008**, *130*, 6498–6506.

(6) (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891–4932. (b) Ziessel. R.; Ulrich, G.; Harriman, A. *New. J. Chem.* **2007**, *31*, 496–501. (c) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201.

(7) (a) Harriman, A.; Izzet, G.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 10868–10875. (b) Singh-Rachford, T. N.; Haefele, A.; Ziessel, R.; Castellano, F. N. *J. Am. Chem. Soc.* **2008**, *130*, 16164–16165. (c) Guliyev, R.; Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2009**, *131*, 9007–9013. (d) Harriman, A.; Mallon, L. J.; Elliot, K. J.; Haefele, A.; Ulrich, G.; Ziessel, R. *J. Am. Chem. Soc.* **2009**, *131*, 13375–13386. (e) Golovkova, T. A.; Kozlov, D. V.; Neckers, D. C. *J. Org. Chem.* **2005**, *70*, 5545–5549. (f) Goze, C.; Ulrich, G.; Ziessel, R. *J. Org. Chem.* **2007**, *72*, 313–322. (g) Zrig, S.; Rémy, P.; Andrioletti, B.; Rose, E.; Asselberghs, I.; Clay, K. *J. Org. Chem.* **2008**, *73*, 1563–1566. (h) Wan, C.-W.; Burghart, A.; Chen, J.; Berström, F.; Johansson, L. B.-Å.; Wolford, M. F.; Kim, T. G.; Topp, M. R.;

Hochstrasser, R. M.; Burgess, K. *Chem. Eur. J.* **2003**, *9*, 4430–4441. (i) Yilmaz, M. D.; Bozdemir, O. A.; Akkaya, E. U. *Org. Lett.* **2006**, *8*, 2871–2873. (j) Zhang, X.; Qian, X. *Org. Lett.* **2008**, *10*, 29–32. (k) Buyukcaki, O.; Bozdemir, O. A.; Kolemen, S.; Erbas, S.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 4644–4647. (l) Cakmak, Y.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 85–88.

(8) (a) Atilgan, S.; Ozdemir, T.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 4065–4067. (b) Ekmekci, Z.; Yilmaz, M. D.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 461–464. (c) Yuan, M.; Li, Y.; Li, J.; Li, C.; Liu, X.; Lv, J.; Xu, J.; Liu, H.; Wang, S.; Zhu, D. *Org. Lett.* **2007**, *9*, 2313–2316. (d) Gabe, Y.; Urano, Y.; Kikuchi, K.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 3357–3367. (e) Wu, L.; Loudet, A.; Barhoumi, R.; Burgardt, R. C.; Burgess, K. *J. Am. Chem. Soc.* **2009**, *131*, 9156–9157. (f) Sun, Z.-N.; Wang, H.-L.; Liu, F.-Q.; Chen, Y.; Tam, P. K. H.; Yang, D. *Org. Lett.* **2009**, *11*, 1887–1890. (g) Ziessel, R.; Ulrich, G.; Harriman, A.; Alamiry, M. A. H.; Steart, B.; Retailleau, P. *Chem. Eur. J.* **2009**, *15*, 1359–1369. (h) Namkung, W.; Padmawar, P.; Mills, A. D.; Verkman, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 7794–7795.

(9) Sakida, T.; Yamaguchi, S.; Shinokubo, H.; *Angew. Chem. Int. Ed.* **2011**, *50*, 2280–2283.

(10) Spitler, E. S.; Johnson, C. A.; Haley, M. M. *Chem. Rev.* **2006**, *106*, 5344–5386.

(11) (a) Marsden, J. A.; Haley, M. M. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; pp 317–394. (b) Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; pp 203–230.

(12) (a) Burghart, A.; Kim, H.; Welch, M. B.; Thoreson, L. H.; Reibenspies, J.; Burgess K. *J. Org. Chem.* **1999**, *64*, 7813–7819. (b) Singh-Rachfrod, T. N.; Haefele, A.; Ziessel, R.; Castellano, F. N.; *J. Am. Chem. Soc.* **2008**, *130*, 16164–16165.

(13) (a) Gabe, Y.; Ueno, T.; Urano, Y.; Kojima, H.; Nagano, T. *Anal. Bioanal. Chem.* **2006**, *386*, 621–626. (b) L.; Liu, F.-Q.; Chen, Y.; Tam, P. K. H.; Yang, D. *Org. Lett.* **2009**, *11*, 1887–1890.

(14) (a) King, A. O.; Negishi, E.-I. *J. Org. Chem.* **1978**, *43*, 353–360. (b) Sonoda, M.; Inaba, A.; Itahashi, K.; Tobe, Y. *Org. Lett.* **2001**, *3*, 2419–2421.

(15) Porrès, L.; Holland, A.; Pålsson, L.-O.; Monkman, A. P.; Kemp, C.; Beeby, A. *J. Fluoresc.* **2006**, *16*, 267–272.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.;

Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., *Gaussian 03*, Revision B.04, Gaussian, Inc., Pittsburgh PA, 2003.