

Synthese ausgedehnter π -konjugierter Organoborane

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“Knowing how contented, free, and joyful is life in the realms of science, one fervently wishes that many would enter their portals.”

“... I have endeavoured to incite in the reader a spirit of inquiry, which, unsatisfied with speculative reasonings alone, should subject every idea to experiment, excite the habit of stubborn work, necessitate a knowledge of the past, and a search for fresh threads to complete the bridge over the bottomless unknown. Experience proves that it is possible by this means to avoid two equally pernicious extremes, the Utopian – a visionary contemplation which proceeds from a current of thought only – and the realistic stagnation which is content with bare facts. In sciences like chemistry, which treat of ideas as well as of the substances of nature, experience demonstrates at every step that the work of the past has availed much, and that without it it would be impossible to advance ‘into the ocean of the unknown.’ We are compelled to value their history, to cast aside classical illusions, and to engage in a work which not only gives mental satisfaction but is also practically useful.”

Dimitrij Ivanovič Mendeleev

The Principles of Chemistry
(5th Edition, Preface of Volume 1)

Translated from the Russian (5th Edition) by George Kamensky
Longmans, Green and Co., London, 1891

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Inhaltsverzeichnis

1.	Einleitung und Zielsetzung	1
1.1	Borhaltige, π -konjugierte Verbindungen: Materialwissenschaftlicher Hintergrund der Forschung	1
1.1.1	Polyzyklische aromatische Kohlenwasserstoffe (PAKs)	1
1.1.2	Einbau von Elementen der Hauptgruppen III bis VI in PAKs	2
1.1.3	Synthese polyzyklischer aromatischer Kohlenwasserstoffe	3
1.1.4	PAKs in der organischen Elektronik	5
1.1.5	Organische Leuchtdioden	6
1.1.6	Organoborane: Reaktivität und chemische Eigenschaften	7
1.2	Triarylborane in der Fachliteratur	10
1.2.1	Synthese und Eigenschaften der Triarylborane	10
1.2.2	Zu Beginn des Forschungsprojekts bekannte borhaltige PAKs (bis 2013)	16
1.2.3	Abgrenzung zur eigenen Masterarbeit	17
1.2.4	Neuere Entwicklungen (seit 2013)	19
1.2.5	Überblick und Kommentar	21
1.3	Zielsetzung	22
2.	Übersicht der Experimente und Ergebnisse	24
2.1	Synthesemethoden zum Aufbau borhaltiger PAKs	24
2.1.1	<i>Peterson</i> -Olefinierung	24
2.1.2	Stilben-Typ Photozyklisierungen	28
2.1.3	Ruthenium-katalysierte Benzanellierungen	29
2.1.4	Silizium/Bor-Austausch	30
2.2	Sterische Abschirmung im Vergleich zu struktureller Stabilisierung	32
2.3	Neue borhaltige PAKs: Variation der Grundstrukturen	37
2.4	Neue borhaltige PAKs: Variation der Substituenten	38
2.5	Neue borhaltige PAKs: Variation von Heteroatomen im Molekülgerüst	41
2.6	Chemische Modifikationen und molekulare Sensorik	45
2.7	TADF-fähige Arylborane	50
3.	Zusammenfassung	53
4.	Literaturverzeichnis	56
5.	Anhang	64

5.1	Ausgewählte Veröffentlichungen	64
5.1.1	Eigene Anteile an den ausgewählten Veröffentlichungen	64
5.1.2	Boron-Containing Polycyclic Aromatic Hydrocarbons: Facile Synthesis of Stable, Redox-Active Luminophores	65
5.1.3	Ru-Catalyzed Benzannulation Leads to Luminescent Boron-Containing Polycyclic Aromatic Hydrocarbons	144
5.1.4	En Route to Stimuli-Responsive Boron-, Nitrogen-, and Sulfur-Doped Polycyclic Aromatic Hydrocarbons	184
5.1.5	Steric Shielding vs Structural Constraint in a Boron-Containing Polycyclic Aromatic Hydrocarbon	256
5.2	Lebenslauf	295
5.3	Publikationsliste	296
5.4	Erklärung über frühere Promotionsverfahren und Versicherung	297

Φ_{PL}	Quantenausbeute der Photolumineszenz
$\lambda_{\text{Em/Abs}}$	Wellenlänge des Emissions/Absorptionsmaximums
CV	Cyclovoltammetrie
DBA	9,10-Dihydro-9,10-diboraanthracen
DDQ	2,3-Dichlor-5,6-dicyano-1,4-benzodion
$E_{1/2}$	Halbstufenpotential
FcH	Ferrocen
HOMO	<i>Highest Occupied Molecular Orbital</i>
ISC	<i>Intersystem Crossing</i>
LUMO	<i>Lowest Unoccupied Molecular Orbital</i>
MALDI	<i>Matrix Assisted Laser Desorption Ionisation</i>
<i>m</i> CPBA	<i>meta</i> -Chlorperbenzoesäure
Mes	Mesityl (2,4,6-Trimethylphenyl)
NMR	<i>Nuclear Magnetic Resonance</i>
OFET	<i>Organic Field Effect Transistor</i>
OLED	<i>Organic Light Emitting Diode</i>
ORTEP	<i>Oak Ridge Thermal Ellipsoid Plot</i>
PAK	Polyzyklischer Aromatischer Kohlenwasserstoff
PPO	Propylenoxid
RT	Raumtemperatur
TADF	<i>Thermally Activated Delayed Fluorescence</i>
TBAF	Tetra- <i>n</i> -butylammoniumfluorid
(TD-)DFT	<i>(Time-Dependent) Density Functional Theory</i>
THF	Tetrahydrofuran

1. Einleitung und Zielsetzung

1.1 Borhaltige, π -konjugierte Verbindungen: Materialwissenschaftlicher Hintergrund der Forschung

Die ersten Kapitel sollen eine Einführung in die grundlegenden Begriffe und Stoffklassen bieten, die für diese Arbeit relevant sind. Sie beschreiben π -konjugierte Verbindungen im Hinblick auf Möglichkeiten zur Veränderung der elektronischen Eigenschaften und der Anwendungen im Bereich der organischen Elektronik. Anhand ausgewählter Beispiele werden die chemischen und elektronischen Eigenschaften von Organoboranen betrachtet. Als Ergänzung zu diesem Basiswissen wird auf hilfreiche Fachliteratur verwiesen, die zur Vertiefung der Thematik dienen kann.

1.1.1 Polyzyklische aromatische Kohlenwasserstoffe (PAKs)

Verbindungen mit mehreren anellierten Sechsringen aus sp^2 -hybridisierten Kohlenstoffatomen bezeichnet man als „polyzyklische aromatische Kohlenwasserstoffe“ (PAK). Typische Eigenschaften dieser Stoffklasse sind eine hohe chemische Beständigkeit, geringe Löslichkeit (vor allem in nicht-aromatischen Lösungsmitteln) und Fluoreszenz. Aufgrund eines delokalisierten Systems von $4n + 2$ π -Elektronen sind die meisten PAKs thermodynamisch sehr stabil (Regel nach *E. Hückel*), allerdings gibt es Unterschiede in Abhängigkeit von ihrer Größe und Form:¹ Größere PAKs haben grundsätzlich eine höhere Reaktivität und einen geringeren Abstand zwischen der energetischen Lage ihrer Grenzorbitale. Aber selbst Verbindungen mit der gleichen Summenformel unterscheiden sich je nach Anordnung der sechsgliedrigen Ringe. Eine praktische Hilfe zur Vorhersage der Stabilität und elektronischen Struktur bietet die Sextett-Regel nach *E. Clar*.² Demnach sind PAKs stabiler, bei denen sich mehr Sextette aus π -Elektronen (dargestellt als Kreis innerhalb eines sechsgliedrigen Rings, Abbildung 1) zeichnen lassen.

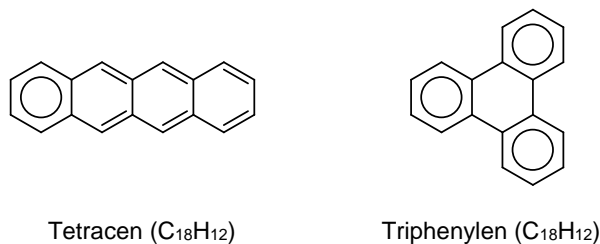


Abbildung 1: Die PAKs Tetracen (ein Elektronensextett) und Triphenylen (drei Elektronensextette) haben die gleiche Summenformel, unterscheiden sich aber in ihrer Stabilität.

Die Systeme aus delokalisierten π -Elektronen bestimmen die charakteristischen Eigenschaften der PAKs: Vielen Reaktionen, die synthetisch zur Modifikation dieser Verbindungen genutzt werden können, liegt eine Wechselwirkung der π -Elektronen mit *Lewis*-Säuren zugrunde. Auch die geringe Löslichkeit von Vertretern dieser Stoffklasse ist auf eine anziehende Wechselwirkung der π -Elektronen (in diesem Fall zwischen benachbarten Molekülen im Festkörper) zurückzuführen. Außerdem sind PAKs aufgrund ihres π -Systems Chromophore und wechselwirken mit Licht. Sie besitzen energetisch niedrig liegende elektronische Übergänge, die ihre Absorptions- und Emissionseigenschaften bestimmen, und entscheidend durch die Größe und Form der Moleküle beeinflusst werden.³ Elektronisch angeregte aromatische Moleküle geben ihre Energie häufig in Form von Licht wieder ab. Untersuchungen der Absorption, Fluoreszenz und Phosphoreszenz können wesentliche Erkenntnisse zur elektronischen Struktur von PAKs liefern.

1.1.2 Einbau von Elementen der Hauptgruppen III bis VI in PAKs

In PAKs sind die p-Orbitale der Kohlenstoffatome in das π -Elektronensystem eingebunden, während die sp^2 -Hybridorbitale das σ -Gerüst ausbilden. Die Kohlenstoffatome an der Peripherie des Moleküls tragen nur mit zweien ihrer drei sp^2 -Hybridorbitale zu dem σ -Gerüst bei, das verbleibende Hybridorbital bildet üblicherweise eine Bindung mit einem Wasserstoffatom. Dieses Wasserstoffatom kann jedoch auch durch ein anderes Atom oder eine Gruppe von Atomen substituiert werden. Im Vergleich zum Wasserstoffatom verändern Substituenten die Eigenschaften eines PAKs. Die Elektronendichte des aromatischen Moleküls wird über das σ -Gerüst in Abhängigkeit von der Elektronegativität des Substituenten verändert (induktiver Effekt). Wenn der Substituent ein p-Orbital (bzw. π -Gruppenorbital) aufweist, dessen räumliche Ausrichtung eine Wechselwirkung ermöglicht, übt er auch einen Einfluss auf das π -Elektronensystem des PAKs aus (mesomerer Effekt). Dabei wird oft neben der Elektronendichte auch die Gestalt und energetische Lage einzelner Molekülorbitale entscheidend beeinflusst.

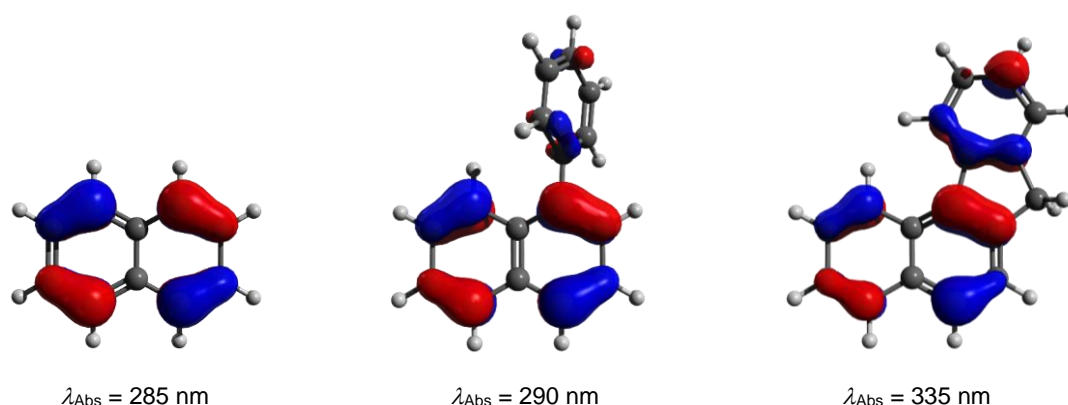


Abbildung 2: Plots der HOMOs⁴ (Iso-Wert $0.05 a_0^{-3/2}$) und experimentell bestimmte Absorptionsmaxima von Naphthalin,⁵ 1-Phenylnaphthalin⁶ und Benzo[c]fluoren⁷.

Schon bei der Betrachtung der einfachen Beispiele in Abbildung 2 wird deutlich, dass es oft nicht ohne weiteres möglich ist, den Einfluss einzelner Faktoren auf die elektronischen Strukturen der PAKs zu bestimmen. Die im Vergleich zu 1-Phenyl-naphthalin bathochrom verschobene Absorptionswellenlänge von Benzo[*c*]fluoren kann sowohl der Planarisierung (erhöhte π -Konjugation) als auch der Einführung des Alkylsubstituenten (positiver induktiver Effekt) zugeschrieben werden. Welchen Beitrag die einzelnen Faktoren jeweils liefern lässt sich nur schwer quantifizieren. Um Erkenntnisse über Struktur-Eigenschafts-Beziehungen zu gewinnen ist es daher hilfreich, möglichst ähnliche Moleküle miteinander zu vergleichen.

Die Substitution peripherer Wasserstoffatome bietet eine Möglichkeit zur Modifikation von PAKs. Eine weitere Möglichkeit besteht im Austausch von Kohlenstoffatomen des Molekülgerüsts gegen andere Atome. Hierzu eignen sich vorrangig die Elemente Bor, Stickstoff, Sauerstoff, Phosphor und Schwefel, deren im Vergleich zu Kohlenstoff ähnliche Elektronegativitäten und kovalente Bindungsradien⁸ die Ausbildung stabiler C–Heteroatom-Bindungen in einem PAK-Gerüst ermöglichen. Von den genannten Elementen besitzt Bor als einziges weniger Elektronen als Kohlenstoff und lässt sich als π -Elektronenakzeptor einsetzen.⁹ Im Gegensatz zu Bor können Stickstoff und Sauerstoff aufgrund ihrer freien Elektronenpaare einen +M Effekt ausüben und somit die Elektronendichte im π -Elektronensystem erhöhen. Die homologen Elemente der dritten Periode, Phosphor und Schwefel, lassen sich darüber hinaus noch oxidieren, was zu Phosphanoxiden, Sulfoxiden und Sulfonen mit einer hohen Gruppenelektronegativität führt.^{10,11} In zwei kürzlich erschienenen Übersichtsartikeln beschreiben *A. Narita et al.* und *M. Stepień et al.* die Synthesen und Eigenschaften zahlreicher PAKs mit Heteroatomen.^{12,13}

1.1.3 Synthese polyzyklischer aromatischer Kohlenwasserstoffe

Einige PAKs kommen natürlicherweise in Erdöl und Kohle vor oder entstehen bei der unvollständigen Verbrennung von organischem Material.¹⁴ Grundlegende Arbeiten zur gezielten Herstellung von PAKs wurden von *R. Scholl*, *E. Clar* und *M. Zander* veröffentlicht.¹⁵⁻¹⁷ Im Zuge neuer Entwicklungen auf dem Gebiet der organischen Elektronik wurde diesem Forschungsgebiet wachsende Aufmerksamkeit zuteil.¹⁸ Für die effiziente Synthese ausgedehnter, π -konjugierter Verbindungen werden Reaktionen zur Knüpfung von C–C-Einfach- und C=C-Doppelbindungen benötigt, die ausgehend von möglichst einfachen Substraten ohne funktionelle Gruppen durchführbar sind; einige Beispiele sind in Abbildung 3 dargestellt. Eine gute Übersicht über nützliche Methoden bietet ein Artikel von *X. Feng et al.*¹⁹

1. Einleitung und Zielsetzung

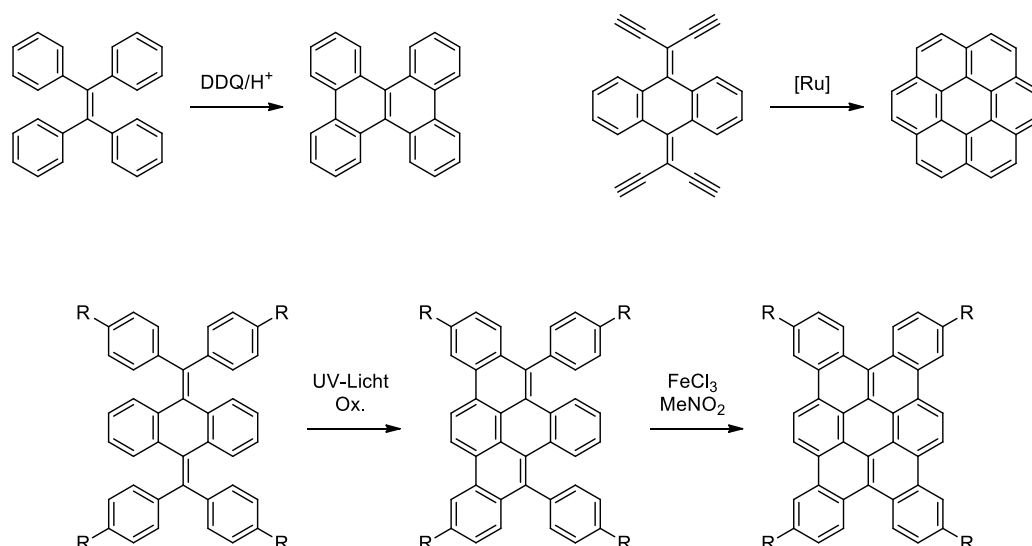


Abbildung 3: Einige Beispiele für C-C-Kupplungsreaktionen zum Aufbau von PAKs. [Ru] = $(\text{Ph}_3\text{P})\text{Ru}(p\text{-Cymol})\text{Cl}_2$.²⁰⁻²²

Die Substrate der in Abbildung 3 dargestellten Reaktionen enthalten vierfach substituierte C=C-Doppelbindungen. Die Synthese solcher Moleküle birgt große Herausforderungen. Für symmetrische Alkene kann in einfachen Fällen eine *McMurry*-Kupplung eingesetzt werden,^{21,23} die stattdessen jedoch manchmal unerwünschte tetrasubstituierte Alkane liefert.^{24,25} Eine aufwändige, aber häufig erfolgreiche Methode baut die zentrale Doppelbindung durch eine Diaza-Thion-Kupplung auf.^{24,26} Dabei wird ein Diarylthioke-ton mit einem Diaryldiazomethan zur Reaktion gebracht um ein Tetraarylthiiran zu bilden (Abbildung 4, oben). Das Schwefelatom wird anschließend durch Zugabe von Triphenylphosphan entfernt um die zentrale C=C-Doppelbindung zu generieren. Des Weiteren lässt sich die *Peterson*-Olefinierung zu diesem Zweck einsetzen: Bei dieser Variante reagieren ein α -Silylcarbanion und ein Keton unter Abspaltung eines Silanolats zu einem Alken.^{27,28}

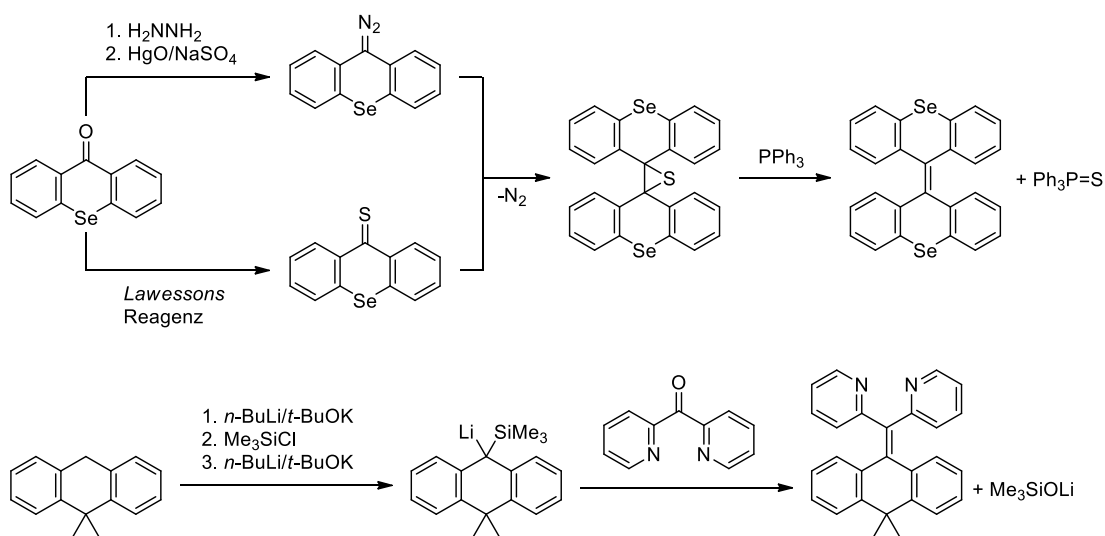


Abbildung 4: Beispiele für die Synthese tetrasubstituierter Alkene mittels Diazo-Thion-Kupplung (oben) und *Peterson*-Olefinierung (unten).^{24,28}

1.1.4 PAKs in der organischen Elektronik

Die klassische Elektronik basiert hauptsächlich auf dem anorganischen Halbmetall Silizium. Im Gegensatz zu Metallen (elektrische Leitfähigkeit etwa 10^4 bis $10^6 \Omega^{-1} \text{ cm}^{-1}$) besitzen Halbmetalle eine geringere elektrische Leitfähigkeit von etwa 10^{-6} bis $10 \Omega^{-1} \text{ cm}^{-1}$.²⁹ In der quantenmechanischen Betrachtung werden Halbmetalle durch eine Bandlücke charakterisiert, die sich aus der Energiedifferenz zwischen dem Valenzband und dem Leitungsband ergibt. Für die elektrische Leitung ist es notwendig, Elektronen vom Valenzband in das Leitungsband zu befördern. Bei einer kleinen Bandlücke von unter ca. 1.6 eV ist dies thermisch möglich. Halbmetalle mit einer Bandlücke zwischen 1.6 und 3.1 eV absorbieren sichtbares Licht. Dadurch werden Elektronen energetisch in das Leitungsband angehoben, weshalb man diese Halbmetalle auch Photohalbleiter nennt.²⁹ Die Leitfähigkeit von Halbmetallen lässt sich auch durch Anlegen einer Spannung beeinflussen. Dieses Prinzip kann zur Konstruktion von Transistoren genutzt werden und bildet die Grundlage der modernen Halbleiterelektronik.³⁰

Die Energiedifferenz zwischen den Grenzorbitalen π -konjugierter Moleküle liegt häufig zwischen 1 und 4 eV. Daraus ergeben sich Ähnlichkeiten zwischen den Festkörpereigenschaften von Halbmetallen einerseits und PAKs andererseits. Ein Übersichtsartikel von *H. Sirringhaus* aus dem Jahr 2014 beschreibt die Fortschritte in der Entwicklung von Feldeffekt-Transistoren, die aus organischen Halbleitermaterialien bestehen (auch OFET genannt).³¹ Grundlegende Erkenntnisse über die Mechanismen des Ladungstransports in organischen Materialien führten zu einer Verbesserung ihrer Halbleitereigenschaften und machen organische Transistoren zu einer realistischen Option für viele elektronische Anwendungen. Dabei steht nicht die Verdrängung von siliziumbasierten Halbleitern in bestehenden Anwendungen im Vordergrund, sondern vielmehr die Realisierung neuartiger Schaltelemente. Klassische Halbleiter sind starre Feststoffe, für deren Verarbeitung aufwändige Verfahren eingesetzt werden müssen. Organische Halbleiterschichten sind prinzipiell flexibler und lassen sich teilweise mittels Drucktechniken fertigen.³² Ein besonders prominentes Anwendungsbeispiel sind organische Leuchtdioden (*organic light emitting diodes*, OLEDs).³³ Welche Anforderungen organische Moleküle für eine Anwendung in der Halbleiterelektronik erfüllen müssen wird im folgenden Kapitel am Beispiel einer OLED näher beschrieben.

1.1.5 Organische Leuchtdioden

Die Lichtquellen, die heutzutage hauptsächlich Verwendung finden, sind entweder Punktlichtquellen (z.B. klassische LEDs) oder längliche Leuchtkörper (z.B. Leuchtstoffröhren). Mit organischen Leuchtdioden ist es erstmals möglich, flächenförmige Lichtquellen herzustellen. Eine OLED besteht aus organischen Halbleiterschichten, die sich zwischen zwei Elektroden befinden. Beim Anlegen einer Spannung werden Elektronen von der Kathode auf das organische Halbleitermaterial übertragen. Nahe der Anode gibt das organische Material Elektronen ab, sodass Elektronenlöcher zurückbleiben. Die unterschiedlichen Ladungsträger wandern entlang des elektrischen Feldes aufeinander zu und treffen sich in der Emissionsschicht (Abbildung 5). Die Rekombination von Elektronen und Löchern erzeugt angeregte Zustände (Exzitone), deren Energie von geeigneten Farbstoffmolekülen in sichtbares Licht umgewandelt werden kann (Elektrolumineszenz).

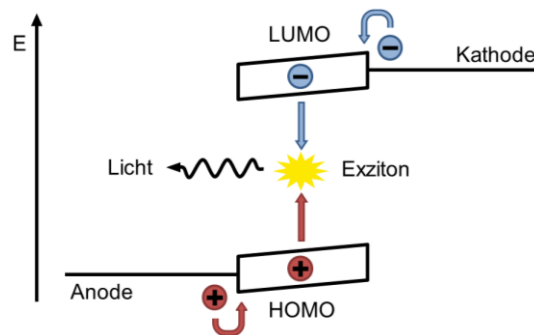


Abbildung 5: Vereinfachtes Energieniveau-Schema einer OLED.

Mindestens eine der beiden Elektroden muss aus einem lichtdurchlässigen Material bestehen; indem beide Elektroden transparent gestaltet werden, lassen sich mit OLEDs transparente Bildschirme realisieren. Durch Verwendung unterschiedlicher Lumineszenzfarbstoffe und eine Strukturierung der Emissionsschicht können OLED-Bildschirme hergestellt werden, die sich im Vergleich zu Flüssigkristallbildschirmen durch eine gute Farbwiedergabe und geringen Stromverbrauch auszeichnen. Es wird erwartet, dass der Marktanteil von OLED-Bildschirmen ab 2016 stark zunimmt.³⁴ Damit dürfte auch die Nachfrage nach geeigneten Lumineszenzfarbstoffen steigen. Für die Farben Rot und Grün werden üblicherweise Übergangsmetallkomplexe mit Schweratomen wie Iridium oder Platin verwendet, die nicht nur die erzeugten Singulett-Exzitonen, sondern auch die Triplett-Exzitonen mittels Phosphoreszenz in Licht umwandeln können.³⁵ Dies ist für die Energieeffizienz der OLED von entscheidender Bedeutung, da bei der Rekombination von Elektronen und Elektronenlöchern Singulett- und Triplett-Exzitonen im Verhältnis von 1:3 entstehen. Problematisch wird es bei der Erzeugung des energiereicheren blauen Lichts. Die hohe Energie der angeregten Zustände führt häufig zu chemischen Reaktionen, die den Farbstoff zerstören.³⁶ Phosphoreszierende metallorganische Komplexe sind besonders anfällig für diese Art der Zersetzung. Daher werden für die Farbe Blau häufig fluoreszierende Moleküle verwendet, obwohl dann der Großteil der Triplett-Exzitonen nicht in Licht umgewandelt werden kann. Die Optimierung der elektrochemischen Stabilität blauer Lumineszenzfarbstoffe ist aus diesen Gründen aktuell Gegenstand der Forschung.^{37,38}

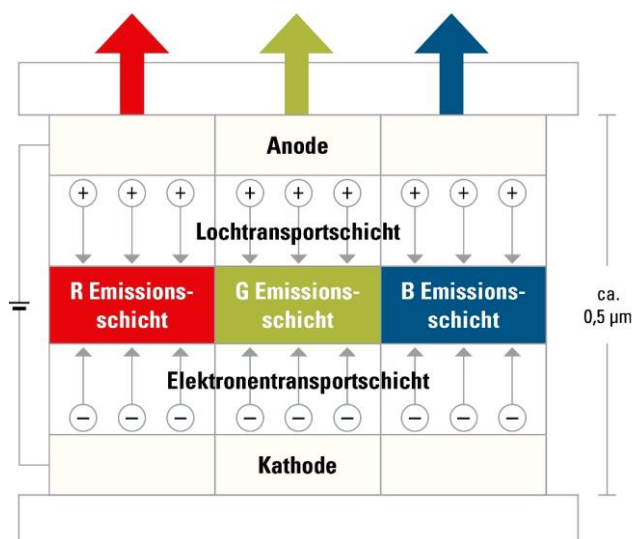


Abbildung 6: Schematische Darstellung einer OLED. Die Abbildung wurde unverändert aus *Forschung Frankfurt 2/2015* entnommen.³⁹

Für die Produktion eines OLED-Bildschirms können verschiedene Techniken zur Abscheidung der organischen Schichten (Ladungstransportschichten und Emissionsschicht, Abbildung 6) eingesetzt werden. Gängig ist das Abscheiden aus der Gasphase, das zur Strukturierung der Emitterschicht mit einer entsprechenden Maske kombiniert werden kann, die Teile des Substrats abdeckt.³⁴ Dadurch geht jedoch ein großer Anteil der eingesetzten Materialien verloren. Moleküle, die sich in organischen Lösungsmitteln lösen lassen, eignen sich grundsätzlich auch für einfachere und gleichzeitig sparsamere Verfahren.⁴⁰ Die Löslichkeit der Lumineszenzfarbstoffe ist daher eine wichtige Eigenschaft im Hinblick auf ihre Verwendung in OLEDs.

1.1.6 Organoborane: Reaktivität und chemische Eigenschaften

Bor ist das fünfte Element des Periodensystems. Es zeigt aufgrund seiner elektronenarmen Natur eine ungewöhnliche chemische Reaktivität und beeinflusst die optoelektronischen Eigenschaften von Materialien auf besondere Weise.⁴¹ In der Halbleiterindustrie wird es zur p-Dotierung von Silizium verwendet.²⁹ Die chemische Reaktivität von Boranen wird durch ihr leeres p-Orbital bestimmt, das senkrecht zur Ebene der drei Substituenten ausgerichtet ist (Abbildung 7). Mit *Lewis*-Basen bilden sich leicht Addukte, wodurch die chemischen und elektronischen Eigenschaften des Borans stark verändert werden.

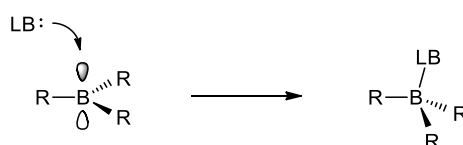


Abbildung 7: Adduktbildung zwischen einer *Lewis*-Base (LB) und einem dreifach koordinierten Boran.

Durch die Adduktbildung werden die Bindungen zu den drei Substituenten (R) geschwächt. Diesen Effekt macht man sich bei der *Suzuki-Miyaura*-Reaktion zu Nutze: Durch Zugabe eines Alkoholats wird ein dreifach koordiniertes Boran in ein vierfach koordiniertes Borat überführt. Anschließend kann ein (ungesättigter) organischer Substituent auf das Metallzentrum eines geeigneten Katalysators übertragen werden (Abbildung 8). In der organischen Chemie werden Borane daher häufig für Kreuzkupplungsreaktionen eingesetzt. Bedeutende Entwicklungen auf diesem Gebiet wurden im Jahr 2010 mit dem Nobelpreis für Chemie gewürdigt.⁴²

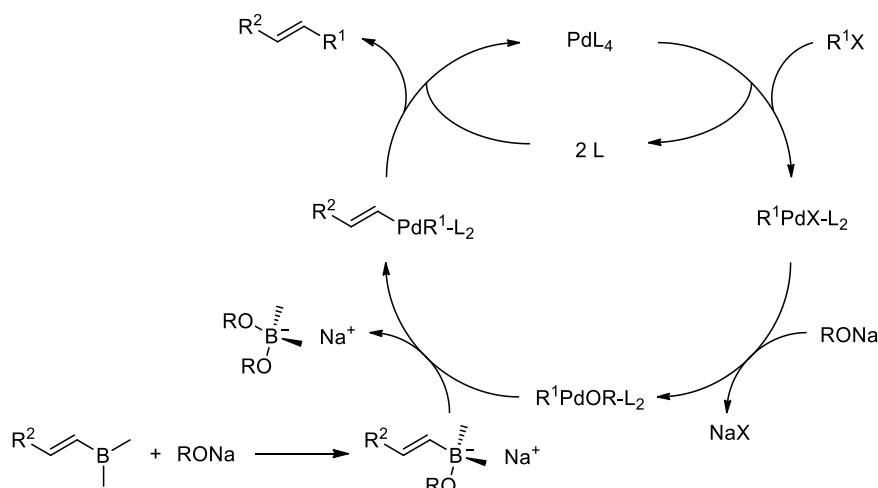


Abbildung 8: Katalysezyklus für die Kupplungsreaktion von Alkenylboranen mit Alkenylhalogeniden (R¹X).⁴²

Die Änderung der Koordinationszahl von Drei zu Vier führt meist zu einer hypsochromen Verschiebung der Absorptionswellenlängen von Boranen mit ungesättigten Substituenten und kann mittels UV-vis Spektroskopie detektiert werden. Auf Basis dieses Effekts wurden chemische Sensoren entwickelt, die zur Bestimmung der Konzentration bestimmter *Lewis*-Basen eingesetzt werden können.⁴³ Borane zeigen eine besonders starke Affinität zu Fluorid-Ionen. Der große Unterschied zwischen den Assoziationskonstanten von Boranen mit Fluorid- im Vergleich zu Chlorid-Ionen (ca. Faktor 500)⁴⁴ verhindert, dass andere Halogenide den Nachweis stören. Durch Optimierung der molekularen Strukturen wurden Borane entwickelt, die in wässriger Lösung entweder selektiv Fluorid- oder Cyanid-Ionen binden.⁴⁵

Während die Adduktbildung in vielen Fällen noch reversibel ist, neigen manche Borane zu irreversiblen Zersetzungsreaktionen. Bei Kontakt mit protischen Verbindungen, wie z. B. Wasser, kann es zur Protonierung kommen.⁴⁶ Dies ist insbesondere für die Anwendung von borhaltigen, π -konjugierten Verbindungen in optoelektronischen Materialien problematisch. Um die Bildung von Addukten zu erschweren und eine Zersetzung von Arylboranen zu vermeiden eignen sich drei Designstrategien.

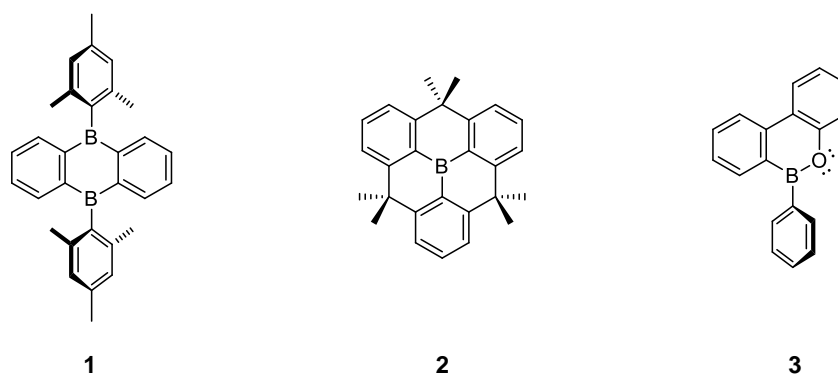


Abbildung 9: Beispiele für Triarylborane, die sich an Luft nicht zersetzen.⁴⁷⁻⁵⁰

Die in Abbildung 9 dargestellten Arylborane sind aus den folgenden Gründen gegenüber Wasser inert: In **1** schirmen sterisch anspruchsvolle Mesitylsubstituenten die Boratome ab.^{47,48} Diese Form der kinetischen Stabilisierung wird häufig zum Schutz reaktiver (Bor-)Zentren verwendet. In **2** ist das Boratom in ein steifes Gerüst eingebaut, welches eine trigonal-planare Konfiguration unterstützt. Die drei Arylsubstituenten sind durch Methylenbrücken miteinander verbunden, sodass ein Chelat-Effekt zum Tragen kommt. In **3** wird die Elektronendichte am Boratom durch die freien Elektronenpaare des benachbarten Sauerstoffatoms erhöht. Dadurch ist die Lewis-Acidität des Borans reduziert und eine Adduktbildung wird energetisch ungünstiger. Die mit einer Stabilisierung durch Elektronendonoren einhergehenden Veränderungen der elektronischen Eigenschaften sind jedoch häufig nicht erwünscht. Beispielsweise verhalten sich PAKs mit BN-Substruktur oftmals ähnlich zu den entsprechenden undotierten Kohlenwasserstoffen.

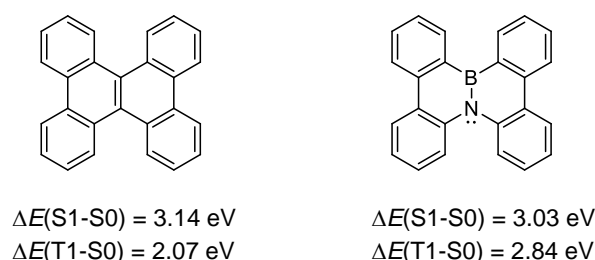


Abbildung 10: Dibenzo[*g,p*]chrysen (links) und ein BN-substituierter PAK mit derselben Anzahl an π -Elektronen (rechts).⁵¹

Abbildung 10 zeigt die Ähnlichkeiten und Unterschiede zwischen Dibenzo[*g,p*]chrysen und dessen Derivat mit einer zentralen B–N-Bindung (an Stelle der C=C-Bindung) in Bezug auf die elektronisch angeregten Zustände. Die Energieniveaus der ersten angeregten Singulett-Zustände (S1) und die Ionisationspotentiale der beiden Verbindungen unterscheiden sich kaum.⁵¹ Deutlich unterschiedlich sind jedoch die Energieniveaus der ersten angeregten Triplett-Zustände (T1). Verbindungen mit hohem Triplett-Energieniveau sind als Hostsubstanzen für OLEDs von Bedeutung.^{51,52}

1.2 Triarylborane in der Fachliteratur

Die folgenden Kapitel sollen einen Überblick über den Stand der Forschung zu Beginn dieser Doktorarbeit bieten und erklären, weshalb borhaltige PAKs als Forschungsobjekt gewählt wurden. Besondere Vertreter dieser Stoffklasse werden vorgestellt, um die Forschungsergebnisse in ihren wissenschaftlichen Kontext einordnen zu können. In einem gesonderten Abschnitt werden neuere Entwicklungen betrachtet, die zeitgleich mit der Bearbeitung dieses Projekts publiziert wurden und die Aktualität und Relevanz der Forschung an Arylboranen illustrieren.

1.2.1 Synthese und Eigenschaften der Triarylborane

Die Mehrzahl der in der Fachliteratur beschriebenen Triarylborane entsprechen der Formel Aryl-BMes₂. Die beiden Mesitylsubstituenten bieten ausreichend Schutz gegenüber Hydrolyse, sodass keine sterisch anspruchsvollen Gruppen in der *ortho*-Position des (dritten) Arylsubstituenten mehr benötigt werden. Verbindungen dieses Typs lassen sich besonders leicht durch Substitution eines Halogenatoms (Mes₂B-X) oder Alkoholates (Mes₂B-OR) mit einem Organometallreagenz (z. B. Ar-Li, Ar-MgCl) herstellen. In Triarylboranen wirkt das Boratom als Elektronenakzeptor. Im Unterschied zu anderen Akzeptorgruppen (z. B. -NO₂, -CN und -SO₂R) ist der elektronenziehende Effekt aber auf das π -System beschränkt, da Bor eine niedrigere Elektronegativität als Kohlenstoff besitzt. Aufgrund dieser Eigenschaften wurden zahlreiche Triarylborane des Typs Aryl-BMes₂ hergestellt und untersucht.⁵³ Arylborane lassen sich vergleichsweise leicht reduzieren und die entstehenden Anionen sind relativ stabil; einige außergewöhnliche Beispiele sind in Abbildung 11 dargestellt.

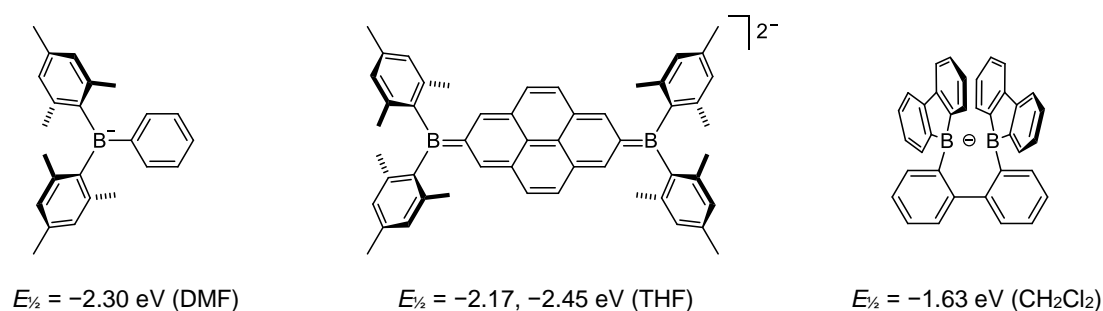


Abbildung 11: Drei Beispiele für reduzierte Triarylborane und ihre mittels Cyclovoltammetrie bestimmten Halbstufenpotentiale (gegen FcH/FcH⁺).⁵⁴⁻⁵⁶

Die starke Elektronenaffinität der Arylborane und die außergewöhnliche Stabilität der gebildeten Anionen ist eine gute Voraussetzung für ihre Anwendung als elektronenleitende Materialien in der organischen Elektronik.^{57,58} Im Gegensatz zu organischen Elektronenlochleitern sind entsprechende Elektronenleiter

noch vergleichsweise wenig erforscht.⁵⁹ Dies lässt sich darauf zurückführen, dass elektronenreiche Arylamine sehr einfach zu synthetisieren sind und daher zur bedeutendsten Klasse der Lochleiter-Substanzen wurden. Arylborane sind zwar das naheliegende elektronenarme Gegenstück, ihre Empfindlichkeit gegenüber Feuchtigkeit und die Notwendigkeit, das Moleküldesign entsprechend anzupassen (siehe Kapitel 1.1.6), haben ihre Entwicklung jedoch verzögert. Stattdessen wird häufig die metallorganische Verbindung Aluminium-tris(8-hydroxychinolin) (Alq3, Abbildung 12) eingesetzt. Aufgrund seines kationischen Metallzentrums ist dieser Komplex ein guter Elektronenakzeptor, allerdings lässt sich seine Elektronenaffinität kaum noch für die geplante Anwendung optimieren. Die Veränderung der 8-Hydroxychinolinliganden durch Substitution hat praktisch keinen Einfluss auf das Reduktionspotential Alq3-artiger Komplexe.⁶⁰ Im Gegensatz dazu bieten Arylborane die Möglichkeit, ihr Reduktionspotential in Abhängigkeit von der Struktur und dem Substitutionsmuster über einen weiten Bereich einzustellen (vgl. Abbildung 11). In ersten Studien zur Verwendung von Arylboranen als Elektronenleiter in OLEDs wurden bereits Verbindungen identifiziert, die sich ähnlich gut eignen wie Alq3.^{61,62}

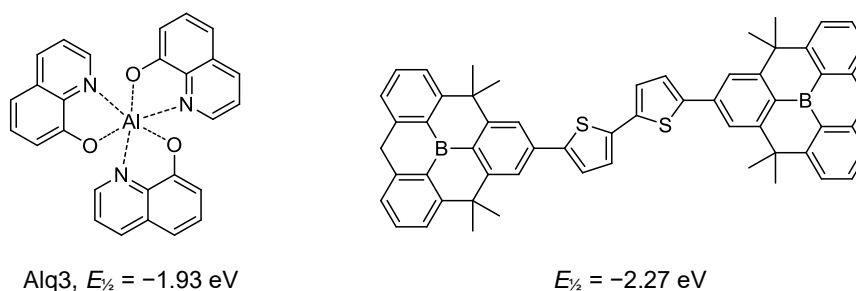


Abbildung 12: Zwei Beispiele für Verbindungen, die sich als Elektronenleiter für OLEDs eignen. Die Halbstufenpotentiale wurden mittels Cyclovoltammetrie in CH_2Cl_2 gemessen (gegen FcH/FcH^+).^{60,61}

Die Kombination von Amin- und Boran-Untereinheiten im selben Molekül führt zu dipolaren Verbindungen, die häufig intensiv fluoreszieren und deren Fluoreszenzfarbe stark von der Polarität ihrer Umgebung abhängt. Als Folge ihres dipolaren Charakters gehen sie im angeregten Zustand einen intermolekularen Ladungstransfer ein.⁶³ Die stark polarisierte Ladungsverteilung im angeregten Zustand wird in Lösungsmitteln mit hohem Dipolmoment besonders gut stabilisiert, sodass sich die Energie der Fluoreszenz verringert und die Emissionsfarbe in Richtung Rot verschoben wird.⁶⁴ Dieses Phänomen nennt man (positive) Solvatochromie. Des Weiteren zeichnen sich Arylboran-Amin-Verbindungen durch ihre hohe elektrochemische Stabilität aus. Mittels Cyclovoltammetrie ist häufig sowohl eine reversible Oxidation als auch eine reversible Reduktion zu beobachten.⁶⁵ Für eine Anwendung als Emitter-Materialien in OLEDs ist dies ein großer Vorteil, weil dort sowohl Elektronen als auch Elektronenlöcher transportiert werden müssen, ohne dass die Ladungsträger eine Zersetzung der Moleküle induzieren. Beispiele für solche Verbindungen sind in Abbildung 13 dargestellt und wurden teilweise bereits in OLEDs getestet.^{63,65}

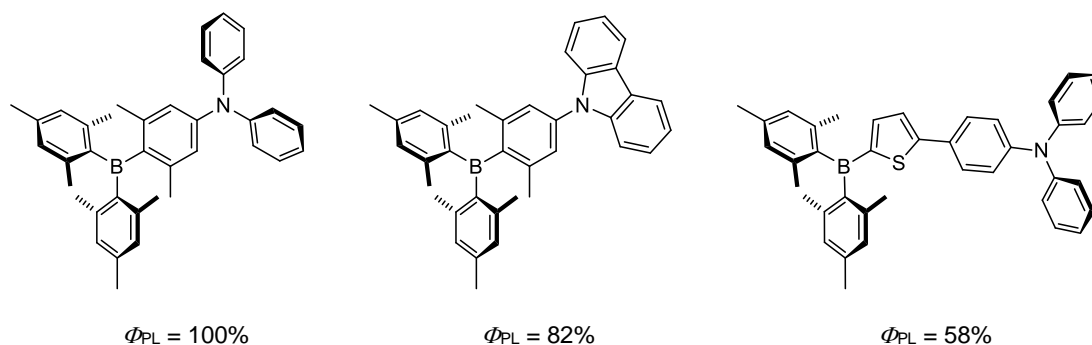


Abbildung 13: Beispiele für Moleküle mit hohen Lumineszenzquantenausbeuten (Φ_{PL} , gemessen in THF), die jeweils aus einer Arylboran- und einer Arylamin-Untereinheit zusammengesetzt sind.^{63,65}

Um die strukturelle Vielfalt an verfügbaren Arylboran-Bausteinen zu erweitern und die π -Konjugation zu beeinflussen, wurden Borane untersucht, bei denen zwei oder drei der Substituenten miteinander verbunden sind. Eine starre Brücke führt zu einer koplanaren Ausrichtung der verbrückten Arylgruppen und maximaler Wechselwirkung ihrer π -Elektronensysteme mit dem p-Orbital am Boratom.⁶⁶ Wenn zwei Arylsubstituenten verbrückt sind, ist der dritte Substituent entscheidend für die Stabilität der Verbindung (Abbildung 14).

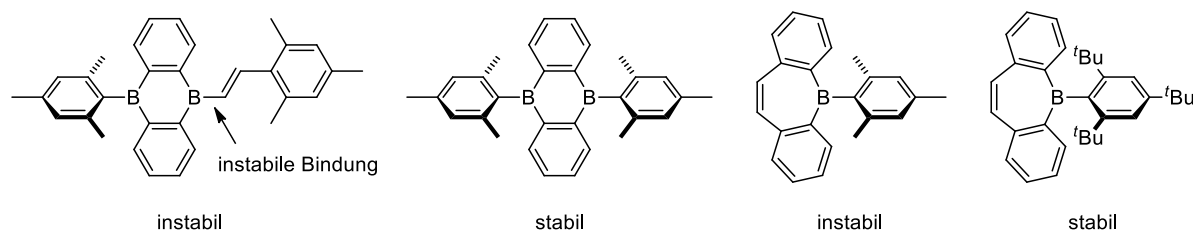


Abbildung 14: Borane mit zwei koplanaren Arylsubstituenten und ihre Reaktivitäten gegenüber Wasser.^{47,67-69}

Durch zusätzliche Brücken zum dritten Arylsubstituenten lassen sich Borane auch ohne sterische Abschirmung des *Lewis*-sauen Zentrums stabilisieren (siehe Kapitel 1.1.6). Zur Herstellung verbrückter Moleküle werden häufig Transmetallierungsreaktionen genutzt. Als synthetische Vorläufer bieten sich Methylsilane und -stannane an, da diese einerseits unter Normalbedingungen stabil und gut lagerbar sind, auf der anderen Seite jedoch mit BBr_3 bereitwillig eine Austauschreaktion eingehen (Abbildung 15).

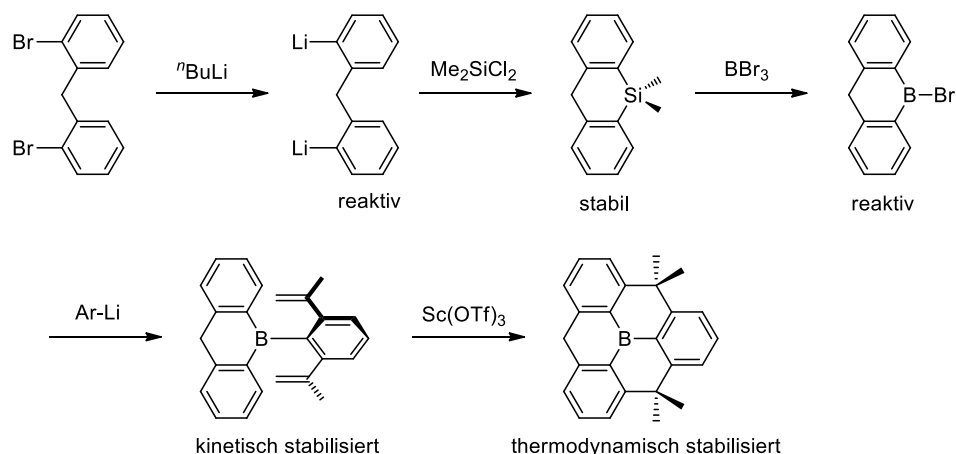


Abbildung 15: Verfahren zur Synthese dreifach verbrückter Arylborane.⁴⁹ Die als reaktiv gekennzeichneten Zwischenprodukte zersetzen sich bei Kontakt mit Luft.

In der Fachliteratur finden sich nur wenige Beispiele für verbrückte Arylborane mit mehr als einem Boratom, die am besten untersuchten Vertreter dieser Stoffklasse leiten sich vom 9,10-Dihydro-9,10-diboraanthracen (DBA) ab. Für die Herstellung dieser Verbindungen wurden drei unterschiedliche Syntheserouten publiziert, die alle auf ähnliche Reaktionstypen zurückgreifen (Abbildung 16).^{47,67,70}

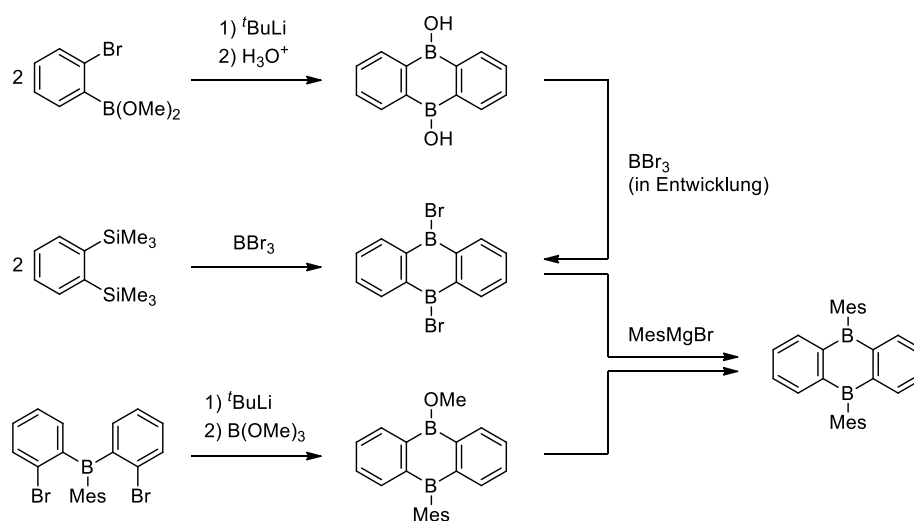


Abbildung 16: Unterschiedliche Syntheserouten zu 9,10-Dihydro-9,10-diboraanthracen.^{47,67,70}

Die ungewöhnliche elektronische Struktur von 9,10-Dihydro-9,10-diboraanthracen macht sie zu einem vielseitigen Forschungsobjekt. Die beiden gegenüberliegenden Bor-Zentren können zusammen als ditope *Lewis*-Säuren wirken.⁷¹ *H. A. Wegner et al.* testeten DBAs als Katalysatoren für verschiedene chemische Transformationen,⁷² darunter *Diels-Alder*-Reaktionen (Abbildung 17),⁷³ die Reduktion von Kohlenstoffdioxid,⁷⁴ und die Freisetzung von Diwasserstoff aus Amminboran.⁷⁵ Mit einem dianionischen DBA-Derivat gelang die homolytische Spaltung von Diwasserstoff, eine Reaktion mit hoher Aktivierungsbarriere für die in der präparativen Chemie üblicherweise schwermetallhaltige Katalysatoren eingesetzt werden.⁷⁶

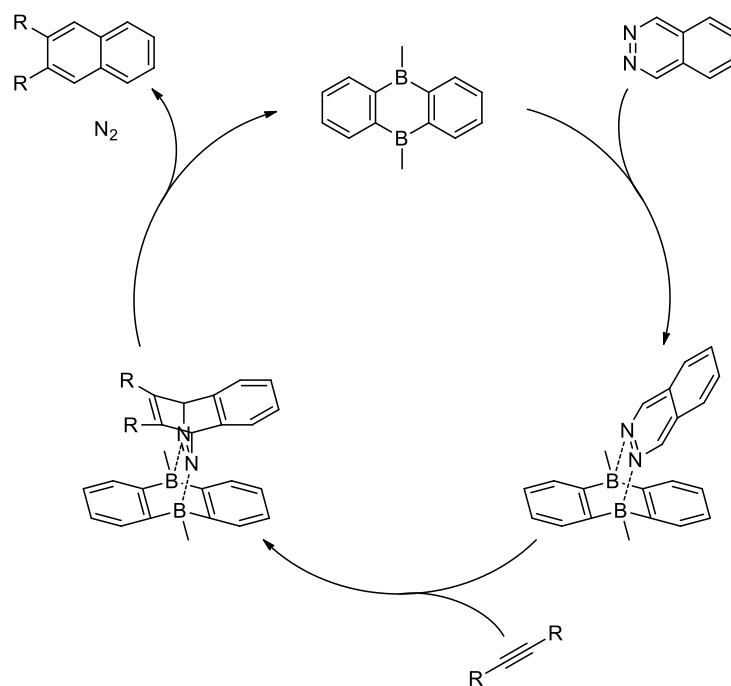


Abbildung 17: Verwendung von 9,10-Dimethyl-9,10-dihydro-9,10-diboraanthracen als *Lewis*-saurer Katalysator für die *Diels-Alder*-Reaktion von 1,2-Diazinen.⁷³

Die in den Abbildungen 14-17 dargestellten Organoborane besitzen eher kleine π -Elektronensysteme, daher liegen ihre Absorptions- und Emissionswellenlängen im UV-Bereich. Die Lumineszenzquantenausbeuten sind mit maximal 36% (im Falle des oberen Borepin-Derivats in Abbildung 18) gering. Analog zu den zuvor beschriebenen BMe_2 -Verbindungen werden durch Einführung von π -Donorsubstituenten die Fluoreszenzwellenlängen deutlich bathochrom verschoben.

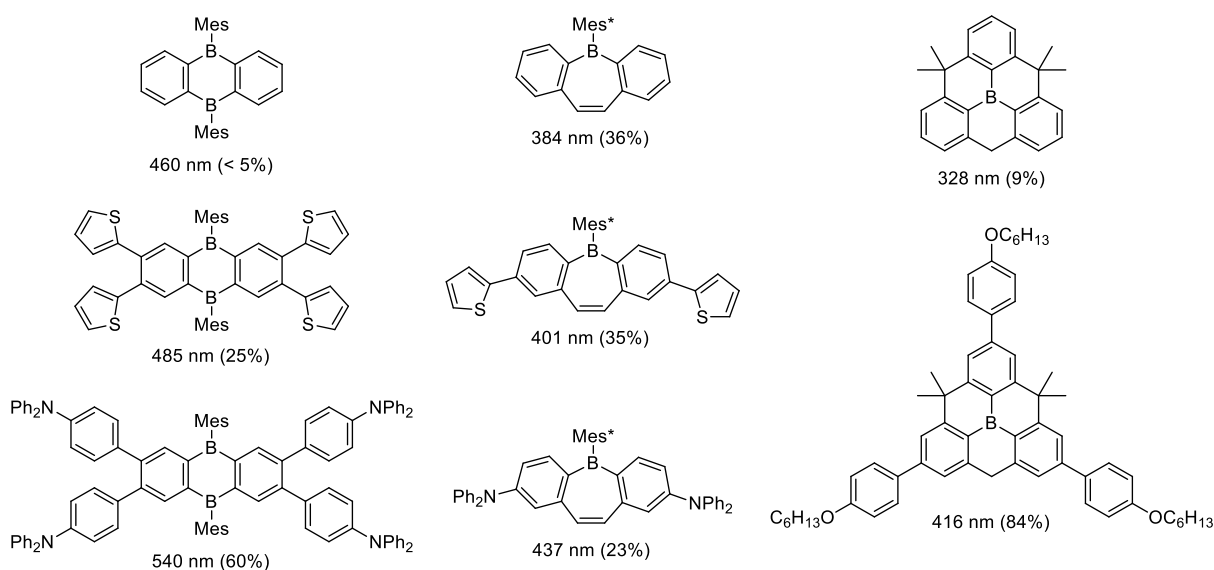


Abbildung 18: Beispiele für verbrückte Arylborane mit und ohne π -Donorsubstituenten. Die Emissionsmaxima und Lumineszenzquantenausbeuten wurden in C_6H_6 (linke Spalte)^{48,77}, CHCl_3 (mittlere Spalte)⁷⁸ und 3-Methylpentan (rechte Spalte)⁷⁹ gemessen. $\text{Mes}^* = 2,4,6$ -Tri-*tert*-butylphenyl.

In den bislang beschriebenen verbrückten Triarylboranen tragen die Boratome ausschließlich Aryl-substituenten, darüber hinaus finden sich in der Literatur auch viele (verbrückte) Thierylborane und einige Pyrrolyl- und Furanylborane.⁸⁰⁻⁸² Die zusätzlichen Heteroatome S, N und O wirken in diesen Verbindungen als π -Elektronendonoren und beeinflussen die chemischen und optoelektronischen Eigenschaften stark. Dieser Einfluss ist abhängig von der Position der Heteroatome in der π -konjugierten Struktur. Abbildung 19 zeigt ein Dibenzoborepin im Vergleich zu zwei isomeren Thiophen-Derivaten. Die Energiedifferenz zwischen den jeweiligen HOMOs und LUMOs der Moleküle wird durch den Einbau der Schwefelatome drastisch verringert, was u.a. an den rotverschobenen Absorptionswellenlängen zu erkennen ist.^{68,82}

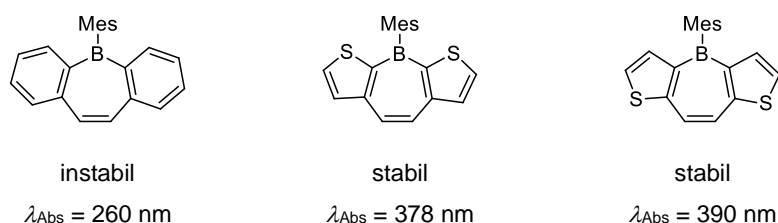


Abbildung 19: Drei mesitylgeschützte Borepin-Derivate und ihre Reaktivitäten gegenüber Wasser sowie ihre Absorptionswellenlängen.^{68,82}

Wenn zwei Phenylsubstituenten eines Arylborans über ein weiteres Heteroatom verbrückt sind, lässt sich die resultierende Molekülstruktur als ein Derivat von 9,10-Dihydroanthracen beschreiben. Zu diesem Strukturtyp finden sich zahlreiche Beispiele in der Literatur (Abbildung 20). Der Einbau eines weiteren Boratoms führt zu den 9,10-Dihydro-9,10-diboraanthracenen, die trotz ihres besonders elektronenarmen Charakters durch Mesitylsubstituenten ausreichend gegen Hydrolyse geschützt sind.^{47,48} Zusätzliche Stabilisierung bieten Donoratome wie zum Beispiel Sauerstoff oder Stickstoff.

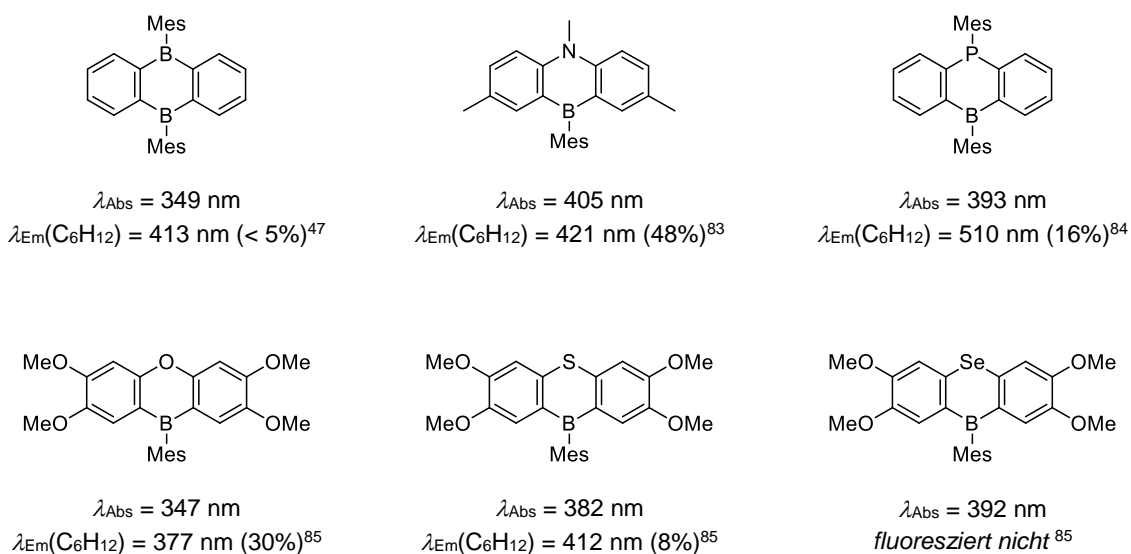


Abbildung 20: Derivate von 9,10-Dihydroanthracen mit Heteroatomen in den Brückenpositionen (Prozentzahlen geben Φ_{PL} an).

Die Auswahl des stabilisierenden Substituenten ist nicht auf Mesityl und 2,4,6-Tri-*tert*-butylphenyl beschränkt. 9-Anthracenylsubstituenten bieten ebenfalls einen gewissen Schutz, entsprechende 9,10-Dihydro-9,10-diboraanthracenene sind allerdings nicht uneingeschränkt stabil gegenüber Wasser.^{77,86}

1.2.2 Zu Beginn des Forschungsprojekts bekannte borhaltige PAKs (bis 2013)

Die Synthese verbrückter Triarylborane ist relativ aufwändig, da die elektronenarme Natur und hohe Reaktivität des Borzentrums in Bezug auf die Synthesepaltung besondere Herausforderungen in sich birgt. Wesentliche Fortschritte auf dem Gebiet der borhaltigen PAKs wurden erst in den Jahren seit 2008 veröffentlicht. In Abbildung 21 sind die wichtigsten, bis zum Beginn dieser Doktorarbeit bekannten, Moleküle dargestellt.

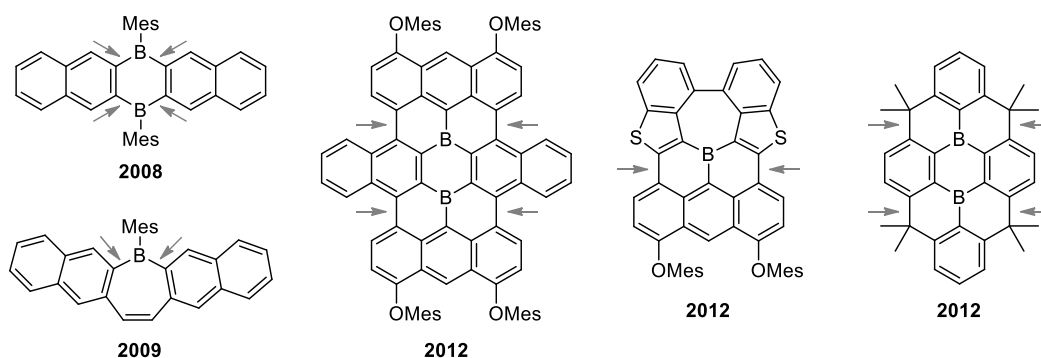


Abbildung 21: Borhaltige PAKs mit Veröffentlichungsdatum vor dem Jahr 2013. Die mit Pfeilen markierten Bindungen wurden jeweils im letzten Schritt der PAK-Synthesesequenz geknüpft.^{49,68,87-89}

Bei der Synthese ausgedehnter PAKs ist das Knüpfen neuer C–C-Bindungen zum Aufbau des planaren Gerüsts von zentraler Bedeutung. Die wichtigsten zur Synthese reiner C,H-PAKs verwendeten Reaktionstypen sind in einem Übersichtsartikel von *K. Müllen et al.* beschrieben.⁹⁰ Elektronenreiche Substrukturen lassen sich mit starken *Lewis*-Säuren zu ausgedehnten PAKs verbinden. Diese oxidative Zyklodehydrogenierung wird auch als *Scholl*-Reaktion bezeichnet, für kleine und elektronenarme Substrukturen ist diese Methode allerdings ungeeignet.^{91,92} Mit π -Donorsubstituenten ausgestattete Ringsysteme werden unter den entsprechenden Reaktionsbedingungen bevorzugt in der *para*-Position verbunden.⁹² Diese Strategie wurde bereits erfolgreich zur Synthese von borhaltigen PAKs genutzt: Die markierten Bindungen der mittleren Moleküle in Abbildung 21 wurden durch *Scholl*-Reaktionen geknüpft.^{88,89} Das rechte Molekül wurde durch eine *Friedel-Crafts*-artige Reaktion mit Scandium(III)triflat hergestellt (siehe auch Abbildung 15).⁴⁹

1.2.3 Abgrenzung zur eigenen Masterarbeit

In der dieser Dissertation vorangegangenen Masterarbeit wurde eine Syntheseroute zu einem borhaltigen PAK entwickelt.²⁵ Die dabei gewonnenen Erkenntnisse hatten großen Einfluss auf unsere späteren Arbeiten und werden aus diesem Grund im folgenden Abschnitt detailliert beschrieben. Als Ausgangsverbindung wurde ein 9-Sila-9,10-dihydroanthracen verwendet und durch Oxidation, bzw. Metallierung mit den geeigneten funktionellen Gruppen ausgestattet um eine *Peterson-Olefinierung*^{93,94} durchzuführen. Dabei entsteht ein Molekül mit Stilben-artigen Substrukturen (**6**, Abbildung 22), dass sich anschließend mit UV-Licht in Gegenwart eines Oxidationsmittels in die planare Verbindung **7** überführen lässt.

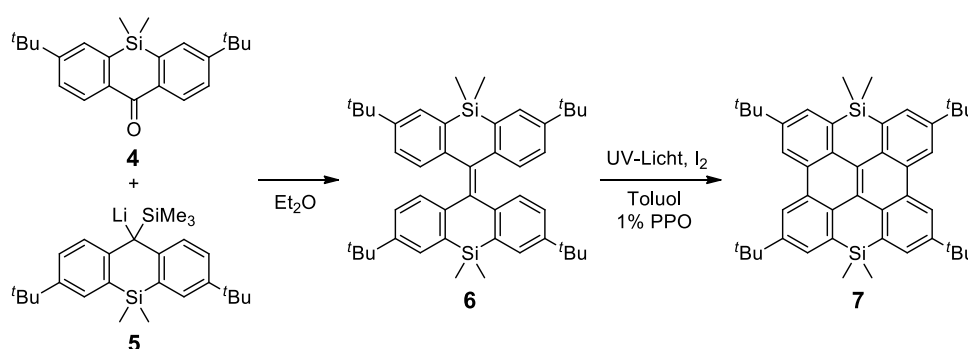


Abbildung 22: Ausschnitt aus der Synthese eines 7,14-Dihydro-7,14-diborabisanthens.²⁵ Propylenoxid (PPO) dient bei der Photozyklisierung als H⁺-Fänger.

Die Photozyklisierung von Stilben und verwandten Molekülen ist ausführlich in einem Übersichtsartikel von *F. B. Mallory* und *C. W. Mallory* beschrieben.⁹⁵ Neben der Photozyklisierung wurden auch *Scholl*-artige Reaktionsbedingungen für die Zyklodehydrogenierung von **6** getestet, diese führten allerdings nur zu Zersetzungsprodukten. Die Photozyklisierung ist im Vergleich zu *Scholl*-Reaktionen eine milde Methode, da neben UV-Licht nur ein schwaches Oxidationsmittel (I₂ oder O₂) eingesetzt wird. Durch Zugabe eines Epoxids kann die bei der Reaktion mit Iod entstehende starke Säure Iodwasserstoff neutralisiert werden.

In reinem BBr₃ (Überschuss) können die beiden SiMe₂-Gruppen von **7** gegen eine BBr-Einheit ausgetauscht werden (Abbildung 23).²⁵ In diesem speziellen Fall erfordert die Austauschreaktion allerdings drastische Bedingungen und wurde bei 200 °C durchgeführt. Nach Einführung von Mesitylschutzgruppen, Säulenchromatographie und Umkristallisation betrug die Ausbeute an **9** lediglich 29% relativ zu **7**. Der Grund für die Schwierigkeiten bei dieser Umsetzung konnte in der Masterarbeit nicht aufgeklärt werden.

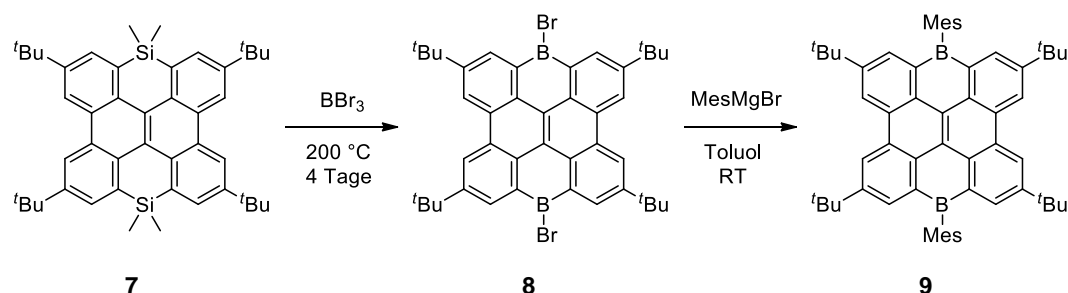


Abbildung 23: Synthese des 7,14-Dihydro-7,14-diborabisanthens **9**.

Der Vergleich mit reinen C,H-PAKs offenbart deutliche Unterschiede in Bezug auf die optoelektronischen Eigenschaften (Abbildung 24). Dibenzo[*g,p*]chrysen absorbiert und emittiert UV-Licht. Die Einführung der BMes-Brücken in den Fjord-Regionen von Dibenzo[*g,p*]chrysen verwandelt das Molekül in den mit hoher Quantenausbeute blau fluoreszierenden Farbstoff **9**. 7,14-Dimesitylbisanthen besitzt mit seinen zwei zusätzlichen π -Elektronen ein ausgedehnteres konjugiertes System und absorbiert im roten Bereich des sichtbaren Spektrums.

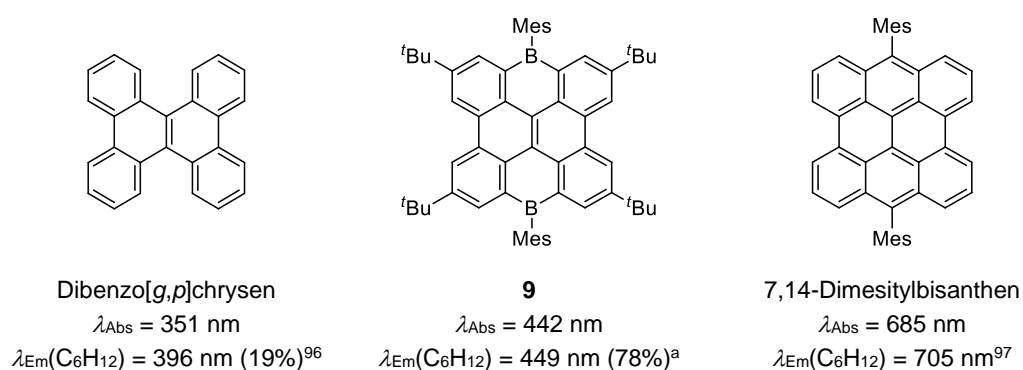


Abbildung 24: Absorptions- und Fluoreszenzeigenschaften von Dibenzo[*g,p*]chrysen (links), dem 7,14-Dihydro-7,14-diborabisanthen **9** (Mitte) und 7,14-Dimesitylbisanthen (rechts, Φ_{PL} nicht bekannt).

Alle drei in Abbildung 24 dargestellten Verbindungen wurden mittels Cyclovoltammetrie untersucht.^{25,96,97} Bei Dibenzo[*g,p*]chrysen wurden keine reversiblen Redoxvorgänge beobachtet. Die beiden anderen Moleküle sind elektrochemisch sehr stabil und können sowohl reversibel oxidiert als auch reversibel reduziert werden.

^a Die Fluoreszenzquantenausbeute konnte in der Masterarbeit nicht zuverlässig bestimmt werden, der hier aufgeführte Wert wurde im Rahmen der Doktorarbeit gemessen.

1.2.4 Neuere Entwicklungen (seit 2013)

In den Jahren seit 2013 wurden große Fortschritte auf dem Gebiet der optoelektronischen Materialien im Allgemeinen und der borhaltigen PAKs im Speziellen erzielt. Beispielsweise zeichnet sich das Triarylboran **11** in Abbildung 25 durch eine hohe Lumineszenzquantenausbeute aus ($\Phi_{\text{PL}} = 81\%$)⁹⁸ und kann auf zwei unterschiedlichen Syntheserouten hergestellt werden.^{98,99}

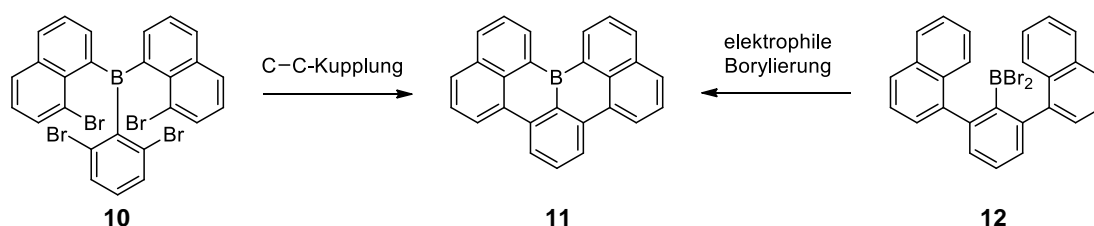


Abbildung 25: Zwei unterschiedliche Syntheserouten führen zum selben borhaltigen PAK **11**.

Die Durchführung von C-C-Kupplungsreaktionen an borhaltigen Molekülen ist eine große Herausforderung, da viele Methoden gleichzeitig zur Spaltung der B-C-Bindungen führen (vgl. Kapitel 1.1.6). Die Transformation in Abbildung 25 (links) wurde durch eine *Yamamoto*-Reaktion erreicht.⁹⁸ Weitere Kupplungsreaktionen, die B-C-Bindungen relativ gut tolerieren, sind die *Stille*-Reaktion^{48,100,101} und die *Sonogashira*-Reaktion¹⁰²⁻¹⁰⁴.

Die direkte elektrophile Borylierung von aromatischen Kohlenwasserstoffen durch Halogenborane wurde bereits 1959 erstmals entdeckt; in einem Übersichtsartikel beschreibt *M. J. Ingleson* die historische Entwicklung, Herausforderungen und Möglichkeiten dieser Methode.¹⁰⁵ Seit 2014 wurden mehrere Beispiele für die Anwendung der elektrophilen Borylierung zur Synthese borhaltiger PAKs veröffentlicht (vgl. rechter Syntheseweg zu **11** in Abbildung 25).^{51,99,106} Die Zugabe einer sterisch anspruchsvollen Base (z. B. *i*-Pr₂NEt) hat sich als vorteilhaft für die Ausbeute dieser Reaktionen erwiesen (Abbildung 26). Zum einen kann eine Base durch Komplexierung des Borans die Eliminierung eines Halogenids und damit die Bildung reaktiver Boreniumionen fördern, zum anderen kann der freigesetzte Halogenwasserstoff von der Base gebunden und damit die Rückreaktion durch Protodeborierung verhindert werden. Einige der auf diese Weise hergestellten Arylborane wurden sogar bereits auf ihre Eignung als Hostmaterialien in den Emitterschichten von OLEDs getestet und als besonders haltbar eingestuft.¹⁰⁶

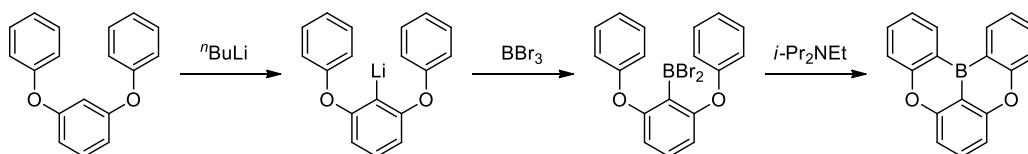


Abbildung 26: Synthese eines borhaltigen PAKs mittels *ortho*-dirigierter Lithiierung, Li/B Austausch und elektrophiler Borylierung. Die Gesamtausbeute der dargestellten Synthesesequenz beträgt 62%.¹⁰⁶

Im Jahr 2015 sind mehrere Veröffentlichungen erschienen, die Arylborane beschreiben, welche mittels verzögerter Fluoreszenz die Energie angeregter Triplett-Zustände in Licht umwandeln können (*thermally activated delayed fluorescence*, TADF).¹⁰⁷⁻¹⁰⁹ Dieses Phänomen wurde erstmals bei Zinn(IV)-Porphyrinkomplexen beobachtet.¹¹⁰ Moleküle mit sehr kleiner Energiedifferenz zwischen dem ersten angeregten Singulett- und dem ersten angeregten Triplett-Zustand ($\Delta E(S_1-T_1) < 0.2$ eV) können demnach bei Raumtemperatur zwischen den beiden Zuständen wechseln. Dieser Effekt ermöglicht es, in entsprechenden OLEDs sowohl die Energie der Singulett-, als auch der Triplett-Exzitonen in Fluoreszenzlicht umzuwandeln (Abbildung 27). Im Gegensatz zu schwermetallhaltigen phosphoreszierenden Emittern geht dabei keine Energie durch Umwandlung der Exzitonen in energiearme Triplett-Zustände verloren und es ist leichter, energiereiches blaues Licht zu erzeugen.

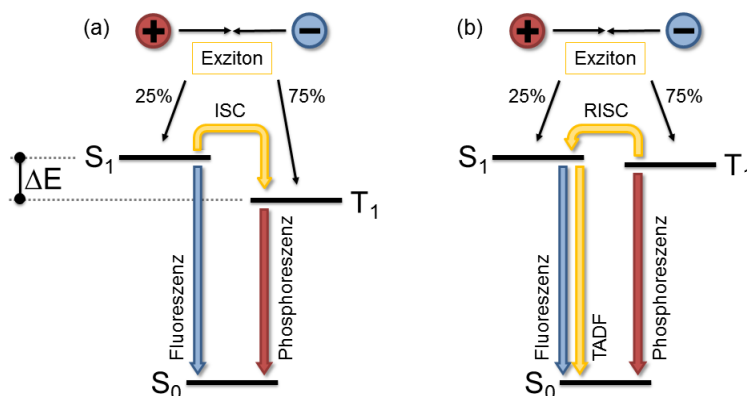


Abbildung 27: Prozesse nach elektrischer Bildung von Triplett- und Singulett-Exzitonen und deren Übergang in den elektronischen Grundzustand in konventionellen fluoreszierenden oder phosphoreszierenden Emittern (a), bzw. in TADF-Emittern (b). (R)ISC = (*reverse*) intersystem crossing.

In einem Übersichtsartikel aus dem Jahr 2014 bezeichnet *C. Adachi* TADF-fähige organische Farbstoffe daher als „Elektrolumineszenz-Materialien der dritten Generation“ und beschreibt ihre Vorteile gegenüber phosphoreszierenden Emittern, sowie die wichtigen Prinzipien zum Design neuer TADF-fähiger Verbindungen.¹¹¹ Demnach eignen sich besonders organische Moleküle, die aus einer elektronenreichen und einer elektronenarmen Untereinheit zusammengesetzt sind. Für die elektronenarme Substruktur sind Triarylborane geeignet. Die beiden angeregten Zustände S_1 und T_1 weisen ein ähnliches Energieniveau auf, wenn die π -Konjugation zwischen den beiden Untereinheiten gering ist. Eine zu geringe π -Konjugation hat jedoch wiederum eine geringe Fluoreszenzquantenausbeute zur Folge. In vielen Molekülen, die sich als besonders geeignet herausgestellt haben, sind die Donor- und Akzeptor-Substrukturen über sp^2 -hybridisierte Atome verbunden, deren p-Orbitale in einem Winkel von etwa 90° zueinander stehen (Abbildung 28). Diese Anordnung scheint die π -Konjugation weit genug einzuschränken um die Energieniveaus von S_1 und T_1 anzugleichen und gleichzeitig noch den Übergang in den Grundzustand mittels Fluoreszenz zuzulassen.

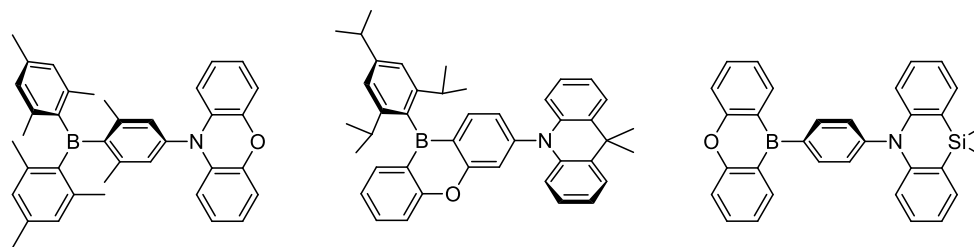


Abbildung 28: Beispiele für B,N-haltige Donor-Akzeptor-Verbindungen, die sich als TADF-Emitter in OLEDs eignen.^{107,108,112}

Es spricht vieles dafür, dass sich organische, TADF-fähige Moleküle in Zukunft als Emitter in OLEDs etablieren werden: i) Die zu ihrer Herstellung benötigten Rohstoffe sind sehr günstig im Vergleich zu den (Edel-)Metallen, die für phosphoreszierende Emitter benötigt werden. ii) Die Eigenschaften organischer Moleküle lassen sich relativ einfach durch Veränderung ihrer chemischen Struktur (z. B. mittels Substitution) optimieren; bei Metallkomplexen ist dies nur eingeschränkt möglich (vgl. die Beschreibung von Alq3 in Kapitel 1.1.6). iii) Aufgrund der guten Löslichkeit vieler organischer Verbindungen können einfache Produktionsverfahren angewendet werden. Vor diesem Hintergrund wird die Bedeutung von (borhaltigen) π -konjugierten Verbindungen für die organische Elektronik in Zukunft weiter zunehmen.

1.2.5 Überblick und Kommentar

Die steigende Anzahl an Publikationen im Zusammenhang mit borhaltigen π -konjugierten Molekülen zeigt, dass sich dieses Forschungsgebiet rasant weiterentwickelt. Es gibt viele Arylborane, die besondere Eigenschaften, wie z. B. eine hohe Lumineszenzquantenausbeute, aufweisen. Bei den meisten publizierten borhaltigen PAKs handelt es sich um Einzelbeispiele, die jeweils durch eine aufwändige und speziell optimierte Synthesesequenz hergestellt wurden und sich in ihren Molekülstrukturen stark voneinander unterscheiden. Dies erschwert es, die Eigenschaften dieser Moleküle mit ihren strukturellen Merkmalen in Verbindung zu bringen. Während die Fachliteratur bereits seit vielen Jahren eine große Zahl an Vertretern der Stoffklasse Aryl-BMes₂ enthält, sind Organoborane mit verbrückten Arylsubstituenten eher eine jüngere Entwicklung. Die Anwendung in OLED-Materialien ist aktuell ein wichtiges Forschungsgebiet, in dem Organoborane aufgrund ihres elektronenarmen Charakters und ihrer hohen Stabilität nach elektrochemischer Reduktion eine bedeutende Rolle einnehmen können.

1.3 Zielsetzung

Für die organische Elektronik werden spezielle Materialien zum Transport von Elektronen oder Elektronenlöchern in den Halbleiterbauelementen benötigt. Die Eigenschaften kohlenstoffbasierter Verbindungen lassen sich durch den Einbau von Heteroatomen (z. B. Bor, Stickstoff, Schwefel) modifizieren und damit für unterschiedliche Anwendungen anpassen. Elektronenreiche Materialien, die sich als Lochleiter eignen, sind gut erforscht und kommerziell erhältlich.¹¹³ Über Verbindungen, die sich als Elektronenleiter einsetzen lassen, ist wesentlich weniger bekannt.⁵⁹ Für diesen Zweck müssen Moleküle entwickelt werden, die eine hohe Elektronenaffinität aufweisen und reversibel elektrochemisch reduzierbar sind.⁵⁷ Die Integration des Elements Bor in organische Verbindungen eröffnet die Möglichkeit, ihnen diese Attribute zu verleihen.⁹ Gleichzeitig birgt sie das Risiko, dass die labilen B–C-Bindungen bei Kontakt mit Feuchtigkeit gespalten werden und aus diesem Grund die Haltbarkeit des Materials sinkt. Der Abbau durch Hydrolyse lässt sich mittels sterischer Abschirmung der Borzentren verhindern.⁵³ Darüber hinaus wurden Triarylborane durch eine Verbrückung von zwei Arylsubstituenten über ein elektronenreiches Heteroatom stabilisiert, allerdings sank dadurch ihre Elektronenaffinität deutlich.⁸³⁻⁸⁵ Ziel dieser Arbeit war es daher, Triarylborane herzustellen, in denen zwei Arylsubstituenten über sp^2 -hybridisierte Kohlenstoffatome miteinander verbunden und auf diese Weise in ein ausgedehntes π -konjugiertes Elektronensystem eingebunden sind (Abbildung 29).

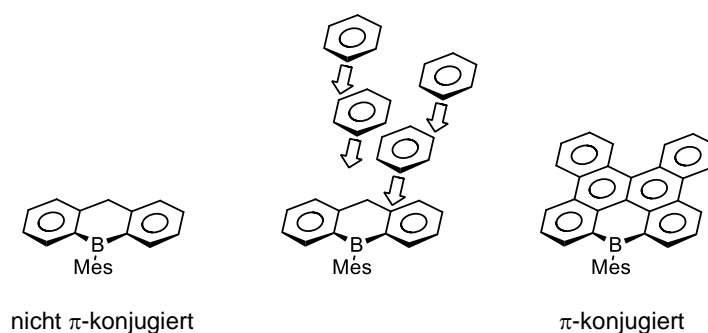


Abbildung 29: Erweiterung des konjugierten π -Elektronensystems durch Anellierung sechsgliedriger Ringe.

Zunächst musste ein synthetischer Zugang zu dieser speziellen Stoffklasse gefunden werden. Die in der vorangegangenen Masterarbeit²⁵ zur Synthese eines Diborabisanthens angewendeten Reaktionen sollten zu einem Repertoire an geeigneten Methoden weiterentwickelt werden, welches eine größere Vielfalt an borhaltigen polyzyklischen aromatischen Kohlenwasserstoffen (PAKs) erschließt. Von speziellem Interesse war die Frage, wie sich die Größe des π -konjugierten Elektronensystems auf die molekularen Eigenschaften auswirkt und ob die Anellierung von Benzolringen an verbrückte Triarylborane in diesem Zusammenhang Vorteile mit sich bringt. Außerdem wurde eine Möglichkeit zur gezielten Justierung der optoelektronischen Eigenschaften (beispielsweise durch Substitution peripherer Wasserstoffatome) gesucht, um diese Verbindungen für die angestrebte Anwendung zu optimieren.

Dieses Projekt wurde auch von der Hoffnung geleitet, durch die Synthese und Untersuchung neuer borhaltiger PAKs einen tieferen Einblick in deren elektronische Strukturen zu gewinnen. Insbesondere wurden Erkenntnisse darüber gesucht, wie sich die Planarisierung der Arylsubstituenten in Triarylboranen auswirkt und ob die dadurch resultierende Ausrichtung der π -Elektronensysteme mit dem borzentrierten p-Orbital eine π -Konjugation zwischen den Substituenten ermöglicht.

Diese Fragen sind relevant für das gezielte Design von Arylboranen zur Anwendung in der organischen Elektronik. Entsprechende Antworten könnten den Weg für die Verbreitung borhaltiger PAKs auf diesem Gebiet bereiten und einen wichtigen Beitrag zur Weiterentwicklung organischer Halbleitermaterialien liefern.

2. Übersicht der Experimente und Ergebnisse

2.1 Synthesemethoden zum Aufbau borhaltiger PAKs

Die literaturbekannte Verbindung 9,9-Dimethyl-9,10-dihydro-9-silaanthracen (**14a**, Abbildung 30) eignet sich hervorragend als Startmaterial zur Synthese silizium- und borhaltiger PAKs. Nach einer von *S. Yamaguchi et al.* publizierten Vorschrift lässt sie sich in einer Ausbeute von 56% aus Bis(2-bromphenyl)methan und Me_2SiCl_2 über eine Li/Br-Austauschreaktion darstellen.⁴⁹ Eine Steigerung der Ausbeute auf 80% wurde im Rahmen der vorliegenden Arbeit durch eine niedrigere Reaktionstemperatur und die anschließende Zugabe einer NaHCO_3 -Pufferlösung erreicht. Das entsprechende Molekül mit zwei *tert*-Butyl-Substituenten in den Positionen 2 und 7 (**14**, Abbildung 30) ist synthetisch noch einfacher und kostengünstiger zugänglich.^{25,114} Durch Zugabe von BBr_3 ist bei beiden Verbindungen ein Austausch des Siliziumatoms in Position 9 gegen Bor möglich (**13/13a**). Aber auch die Position 10 eignet sich zur weiteren Derivatisierung: Sie lässt sich mit starken Basen (z. B. *n*-Butyllithium) deprotonieren und anschließend mit Me_3SiCl silylieren (**15/15a**).²⁵ Außerdem ist eine Oxidation zum Keton mit CrO_3 in Essigsäure möglich (**4/4a**).^{25,115}

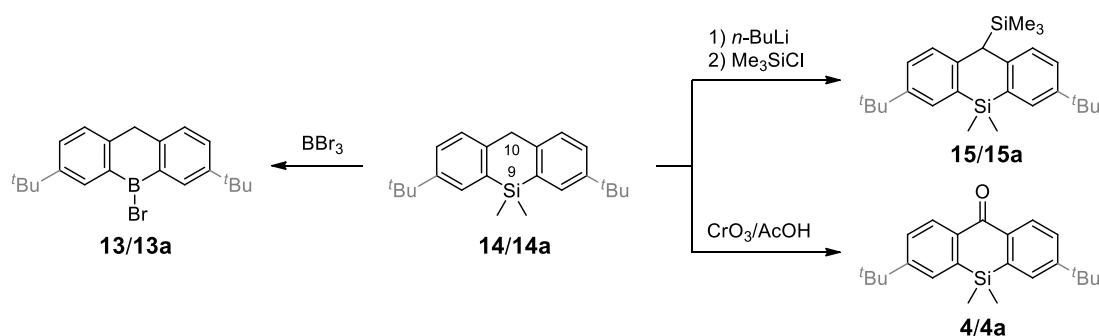


Abbildung 30: Grundlegende Möglichkeiten zur Derivatisierung von **14/14a** (mit und ohne *t*-Bu-Substituenten erfolgreich durchgeführte Reaktionen).²⁵

2.1.1 Peterson-Olefinierung

Die *Peterson*-Reaktion lässt sich zur Olefinierung benzylicher Positionen einsetzen. Um die Anwendungsbreite der Methode auszuloten, wurde **15** zunächst lithiiert und das resultierende Nucleophil **5** mit einer Vielzahl unterschiedlicher Carbonylverbindungen umgesetzt. Ausgewählte Beispiele **16-21** sind in Abbildung 31 aufgeführt. In fast allen Fällen bildete sich das jeweils gewünschte olefinische Produkt. Eine Ausnahme stellte *N*-Ethylacridin-9-on dar, dessen Carbonylfunktion aufgrund des vom Stickstoffatom ausgehenden positiven mesomeren Effekts gegenüber Nucleophilen relativ reaktionsträge ist. Die

Umsetzung mit Xanthen-9-on war dagegen erfolgreich und lieferte ein sterisch belastetes, tetra-substituiertes Olefin (auch bistrizyklisches Alken genannt).¹¹⁶ Es gibt nur wenige Synthesemethoden, mit denen solche Alkene hergestellt werden können.

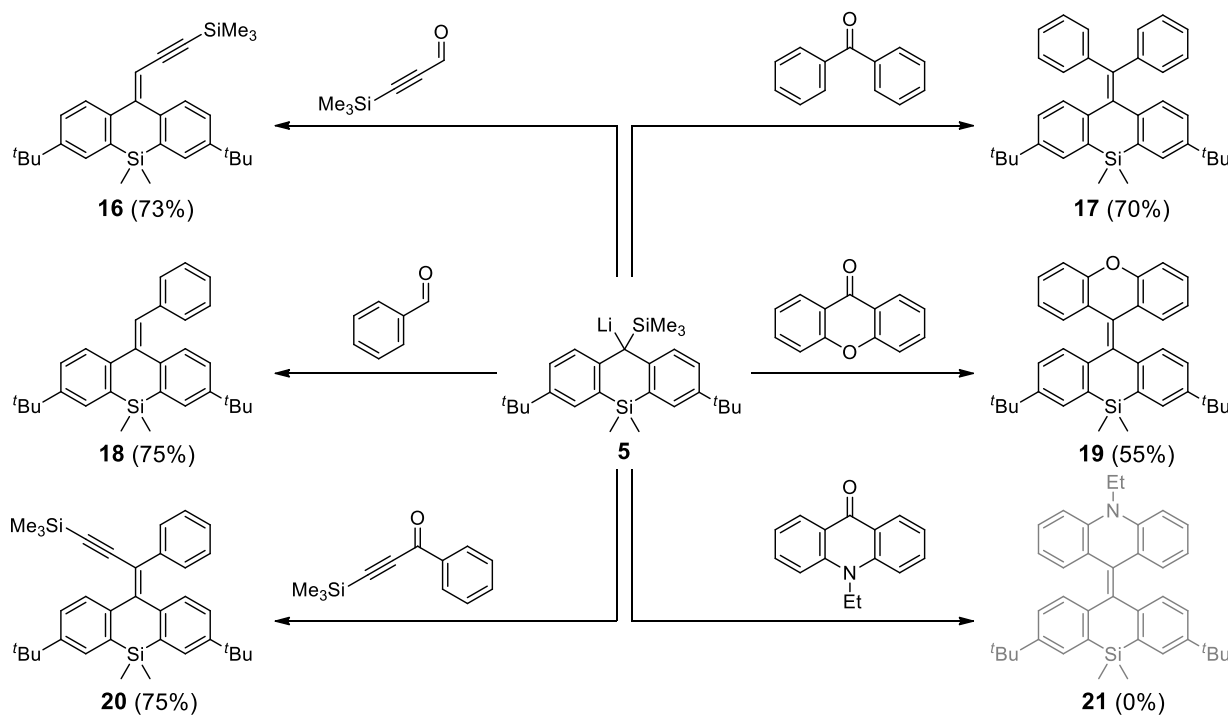


Abbildung 31: Peterson-Reaktionen von **5** mit ausgewählten Aldehyden und Ketonen.

In bistrizyklischen Alkenen weisen die *peri*-Wasserstoffatome der zwei Untereinheiten auf beiden Seiten der zentralen Doppelbindung aufeinander zu, außerdem würden in einer planaren Struktur die Abstände gegenüberliegender *peri*-Kohlenstoffatome die Summe der *van-der-Waals*-Radien drastisch unterschreiten. Aufgrund dieser Strukturmerkmale werden solche Verbindungen auch als sterisch überfrachtet bezeichnet und nehmen meistens eine *anti*-gefaltete Konformation ein (Abbildung 32).¹¹⁷ Außerdem ist eine *cis/trans*-Isomerisierung solcher Olefine nur noch schwer möglich. Dies haben *B. Feringa et al.* durch die Bestimmung der Energiebarriere dieser Isomerisierung in unsymmetrischen Derivaten mit anderen Heteroatomen in den verbrückenden Positionen (z. B. S/S oder N/N an Stelle von O/Si, Abbildung 32) gezeigt.¹¹⁶ Die hohe sterische Belastung begründet die Schwierigkeiten, die mit der Synthese solcher Moleküle verbunden sind.

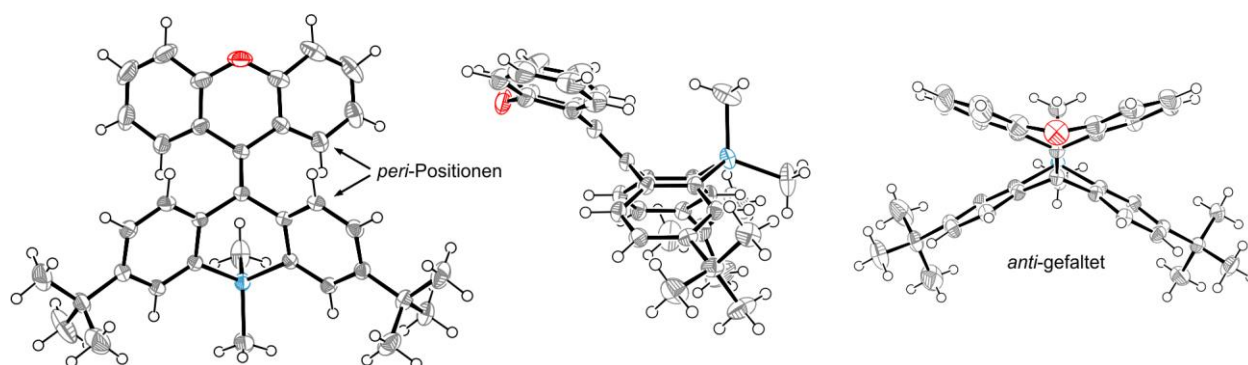


Abbildung 32: Frontal- und Seitenansichten der Molekülstruktur des bistrizyklischen Alkens **19** im Festkörper (ORTEPs; Rot = Sauerstoff, Blau = Silizium). Die Aufenthaltswahrscheinlichkeit der thermischen Ellipsoide beträgt 50%.

Da die meisten vom Silazyklus **15** ausgehenden *Peterson*-Olefinierungen erfolgreich verlaufen waren, stellte sich die Frage, ob auch ein borhaltiges Startmaterial für diese Reaktionen geeignet wäre. Dabei ist zu beachten, dass der negative mesomere Effekt des Boratoms im 9,10-Dihydro-9-boraanthracen **22** eine Deprotonierung der Benzylposition erleichtern, die Nucleophilie des gebildeten Carbanions hingegen dämpfen sollte.

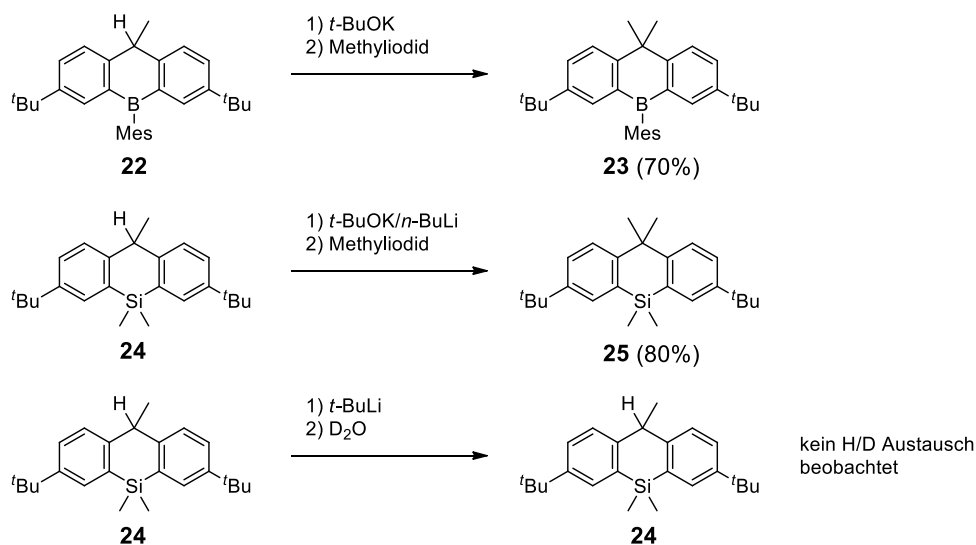


Abbildung 33: Experimente zur Deprotonierung von 9,10-Dihydro-9-(sila/bora)anthracenen.¹¹⁸

In Abbildung 33 sind Testreaktionen zur Deprotonierung der Benzylpositionen von **22** und **24** dargestellt. Im Fall der borhaltigen Verbindung (oben) reicht die relativ schwache Base Kalium-*tert*-butanolat zur Abstraktion eines Protons aus, wie die Abfangreaktion mit Methyljodid belegt, die **23** in Ausbeuten von 70% liefert. Aus der analogen siliziumhaltigen Verbindung **24** lässt sich erst mit der *Schlosser*-Base das entsprechende Anion erzeugen, welches ebenfalls mit Methyljodid zur Reaktion gebracht wurde (**25**, 80%). Eine Deprotonierung von **24** durch Lithiumorganyle wurde nicht beobachtet, die Zugabe von D₂O zu der Reaktionsmischung führte nicht zu dem erwarteten H/D-Austausch in der Benzylposition. Eine Erklärung

für diese Befunde liefert die relative Stabilität der jeweiligen Anionen. Im Fall der borhaltigen Verbindung kann die negative Ladung über die sp^2 -hybridisierten Atome des mittleren Rings delokalisiert werden, sodass ein *Hückel*-aromatischer, sechsgliedriger Ring ausgebildet wird (Abbildung 34).

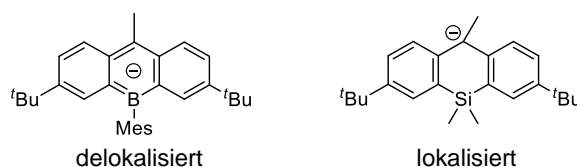


Abbildung 34: Anionen, die durch Deprotonierung von **22** bzw. **24** erzeugt wurden.

Im Einklang mit dieser Interpretation wurde im Fall der borhaltigen Verbindung als Startmaterial für *Peterson*-Reaktionen auch eine geringere Reaktivität im Vergleich zu **5** festgestellt (Abbildung 35): Mit **29** als Nucleophil und Xanthen-9-on oder *N*-Ethylacridin-9-on als Elektrophile wurde keine Umsetzung beobachtet. Thioxanthen-9-on ist dagegen elektrophil genug, um die Olefinierungsreaktion mit **29** einzugehen.

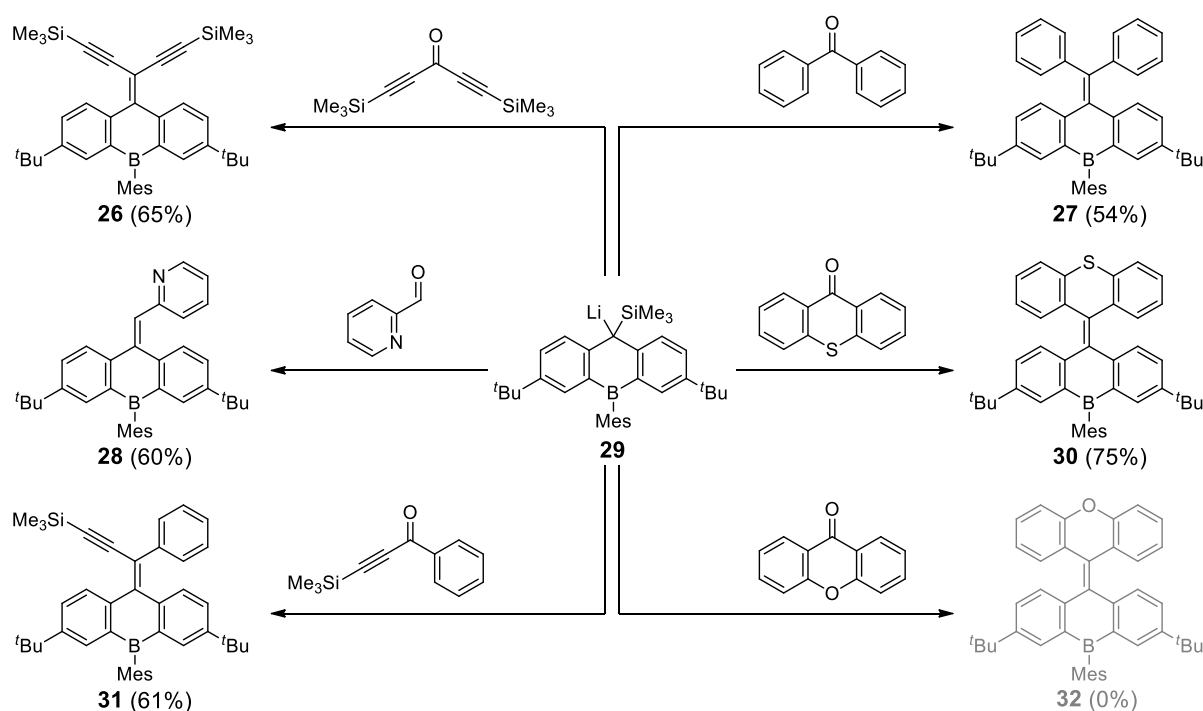


Abbildung 35: *Peterson*-Reaktionen von **29** mit ausgewählten Aldehyden und Ketonen.

Der Vergleich zwischen den Abbildungen 31 und 35 zeigt, dass sich auch das borhaltige Startmaterial **29** gut für *Peterson*-Olefinierungen einsetzen lässt. Diese Reaktionen lieferten jedoch etwas geringere Ausbeuten im Vergleich zu jenen, die von dem Silazyklus **5** ausgingen. Die Gründe hierfür liegen in der geringeren Nucleophilie von **29** und dessen höherer Neigung zu Nebenreaktionen.

2.1.2 Stilben-Typ Photozyklisierungen

Viele der in Kapitel 2.1.1 vorgestellten Alkene enthalten eine Stilben-Substruktur, die sich photochemisch cyclisieren lässt.⁹⁵ Um diese Reaktion durchzuführen, wurden verdünnte Lösungen der Substrate in Cyclohexan oder Toluol mit einer starken UV-Lichtquelle bestrahlt. Einer bekannten Literaturvorschrift folgend wurde unter Luftausschluss gearbeitet und als Oxidationsmittel Iod zugegeben, um oxidative Nebenreaktionen mit Sauerstoff auszuschließen.¹¹⁹ Ein weiterer Vorteil der Verwendung von Iod besteht darin, dass der Reaktionsfortschritt an der Entfärbung der violetten Lösung abgeschätzt werden kann. Abbildung 36 gewährt eine Übersicht über Photozyklisierungen an Arylsilanen und -boranen, die nach dieser Methode erfolgten.

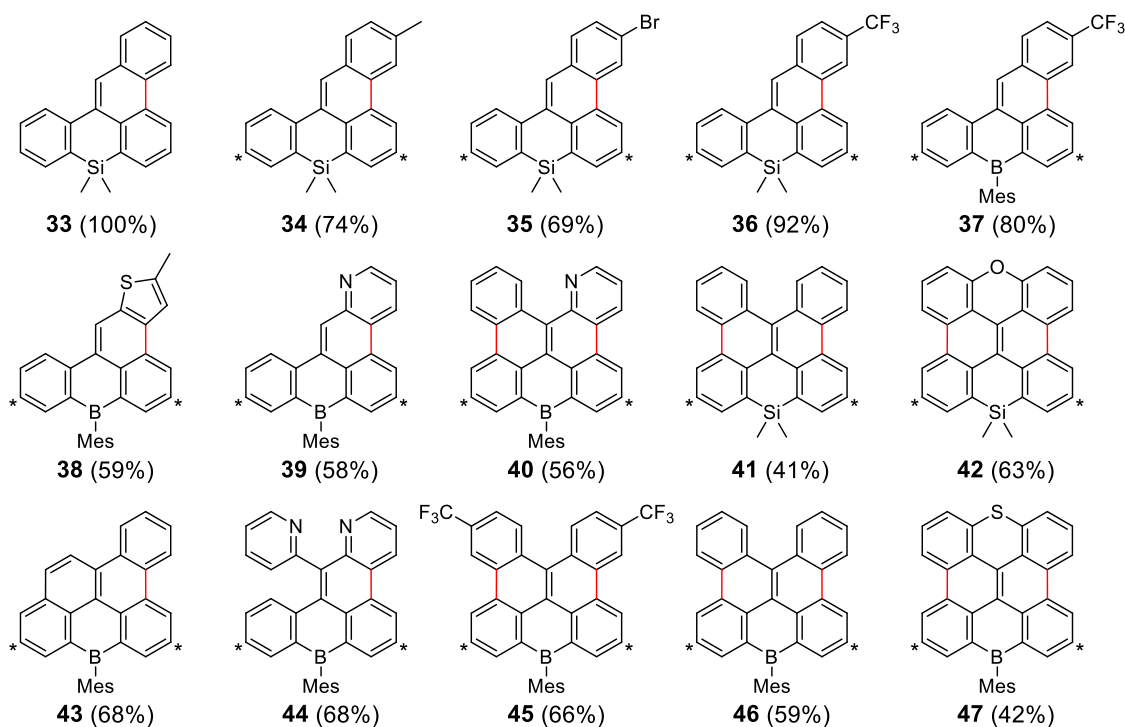


Abbildung 36: Durch Photozyklisierung hergestellte Arylsilane und -borane. Die Prozentzahlen stellen isolierte Ausbeuten dar und beziehen sich jeweils nur auf die Zyklisierungsreaktion. Mit Sternchen markierte Kohlenstoffatome tragen *tert*-Butylgruppen.

Im präparativen Maßstab erfolgten diese Reaktionen in einem Photoreaktor mit 800 mL Fassungsvermögen, in welchen eine wassergekühlte Quecksilberdampflampe mit 150 W Leistung eingetaucht wurde. Die maximal verwendbare Stoffmenge ist auf ca. 3 mmol beschränkt, da mit konzentrierteren Lösungen die benötigte Reaktionszeit unverhältnismäßig stark ansteigt. Manche Zyklisierungsreaktionen benötigten viele Stunden, bis ein annähernd quantitativer Umsatz erzielt wurde. Besonders langsam verlief die Photozyklisierung der bromhaltigen Verbindung **35** (Abbildung 36). In solchen Fällen verblieb auch nach achtstündiger Belichtung noch unzyklisiertes Startmaterial in der Lösung, wodurch die isolierten Ausbeuten der Zyklisierungsprodukte geringer ausfielen. Mit den borhaltigen Arylboranen kam es

manchmal zu störenden Nebenreaktionen: Wasserstoffatome in der *meta*-Position des Mesitylsubstituenten wurden teilweise durch Iod substituiert. Der Anteil an substituiertem Nebenprodukt variierte stark zwischen kaum nachweisbaren Spuren und bis zu 25% im Fall der Synthese von **47**. Diese Verunreinigungen erforderten eine aufwändige Aufarbeitungsprozedur mit einem Iod-Lithium-Austausch als Schlüsselschritt, die letztendlich aber in jedem Fall reines Produkt lieferte. Nur wenige Zyklisierungsreaktionen verliefen nicht erfolgreich. Die Substrate, die sich unter den Reaktionsbedingungen als inert erwiesen haben, sind in Abbildung 37 dargestellt.

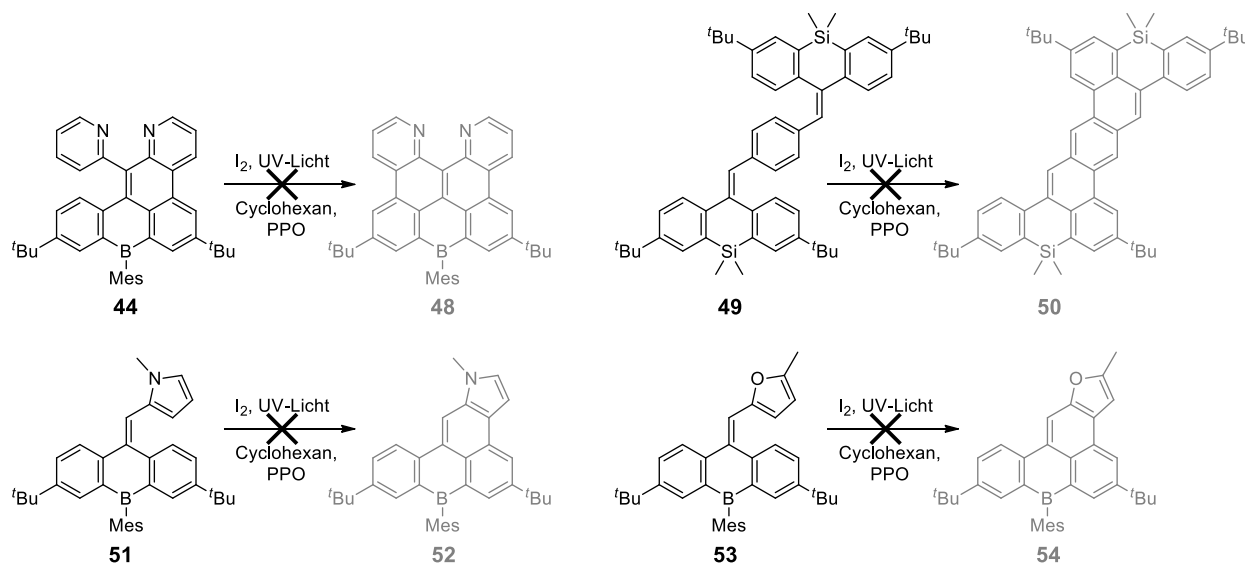


Abbildung 37: Zur Photozyklisierung ungeeignete Substrate.¹²⁰

Eine Photozyklisierung von **44** würde dazu führen, dass sich die freien Elektronenpaare der Stickstoffatome in **48** nahekommen. Einerseits wäre ein solches Molekül als Ligand oder Protonenfänger¹²¹ sehr interessant, andererseits ist eine solche Ausrichtung der Elektronenpaare energetisch ungünstig und scheint der Grund dafür zu sein, dass die Zyklierung von **44** unter den getesteten Bedingungen nicht stattfindet. Auch die Verbindungen **49**, **51** und **53** waren nach acht Stunden Reaktionszeit noch weitgehend unverändert. *C. J. Timmons* und *W. Carruthers* haben bereits beschrieben, dass Furan- und Pyrrol-Substrukturen in der Photozyklisierungsreaktion Probleme bereiten.^{122,123}

2.1.3 Ruthenium-katalysierte Benzanellierungen

Die im vorangegangenen Kapitel beschriebene Photozyklisierung erwies sich als ausgesprochen gut geeignet, um sechsgliedrige aromatische Ringe in das π -konjugierte Elektronensystem der Moleküle einzubauen. Solche C₆-Bausteine vergrößern die Molekülgerüste deutlich. Um auch kleinere C₂-Bausteine angliedern zu können, wurde auf eine Reaktion zurückgegriffen, welche die Anellierung von Alkin-Substrukturen ermöglicht (Abbildung 38), und mit einer großen Vielfalt an Substraten und Katalysatoren

2. Übersicht der Experimente und Ergebnisse

durchführbar ist.^{124,125} Der Komplex $(\text{Ph}_3\text{P})\text{Ru}(p\text{-Cymol})\text{Cl}_2$ wurde als Katalysator gewählt, da er sich einerseits in vielen Beispielen als geeignet herausgestellt hat und -andererseits relativ leicht herzustellen ist.^{124,126}

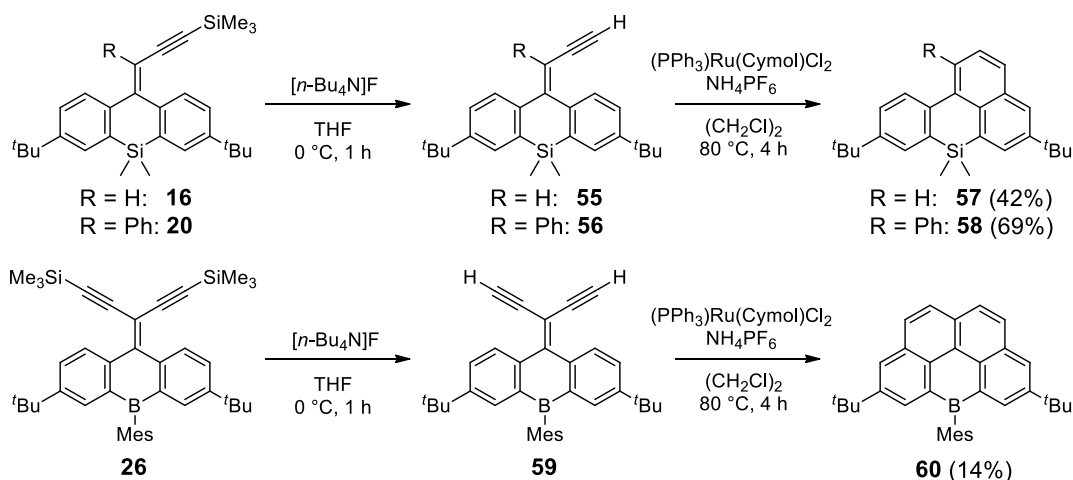


Abbildung 38: Ru(II)-katalysierte Anellierung über terminale En-ine an Arylsilanen und einem Arylboran.

Ein Nachteil dieser Methode ist, dass sie terminale (ungeschützte) Alkine als Substrate benötigt. Diese sind sehr reaktiv und gehen leicht Nebenreaktionen ein.²⁰ Besonders schwierig war die zweifache Alkin-Anellierung über **59**, da sich dieses Substrat als thermolabil erwies und schon bei Raumtemperatur nach kurzer Zeit braun färbte. Des Weiteren verläuft die C–C-Bindungsknüpfung dieser Ru(II)-katalysierten Reaktion nach dem Mechanismus der elektrophilen aromatischen Substitution, welcher elektronenreiche Substrate bevorzugt.¹²⁵ Trotz dieser Schwierigkeiten konnte das Boran **60** in einer Ausbeute von 14% isoliert werden. Dieses Ergebnis ist bemerkenswert, da viele Übergangsmetall-katalysierte Reaktionen nicht an Mesitylboranen durchgeführt werden können, ohne dass B–C-Bindungen gespalten werden. Die zweifache Alkin-Anellierung an dem elektronenarmen Arylboran **59** ist daher ein außergewöhnliches Beispiel für den erfolgreichen Übergangsmetall-katalysierten Aufbau eines borhaltigen PAK-Gerüsts.

2.1.4 Silizium/Bor-Austausch

Der Austausch von Trimethylsilyl-Gruppen an Aromaten gegen Dibromboryl-Substituenten mittels BBr_3 ist eine Reaktion, die bei Raumtemperatur rasch und selektiv abläuft. Ein analoger Austausch fand an dem ausgedehnteren Bisanthen-Derivat **7** (Abbildung 39) bei Raumtemperatur hingegen nicht statt; in diesem Fall musste die Temperatur auf 200 °C erhöht werden.²⁵ Um diesen experimentellen Befund näher zu beleuchten, wurde eine Reihe von Versuchen mit unterschiedlichen Diaryldimethylsilanen durchgeführt.

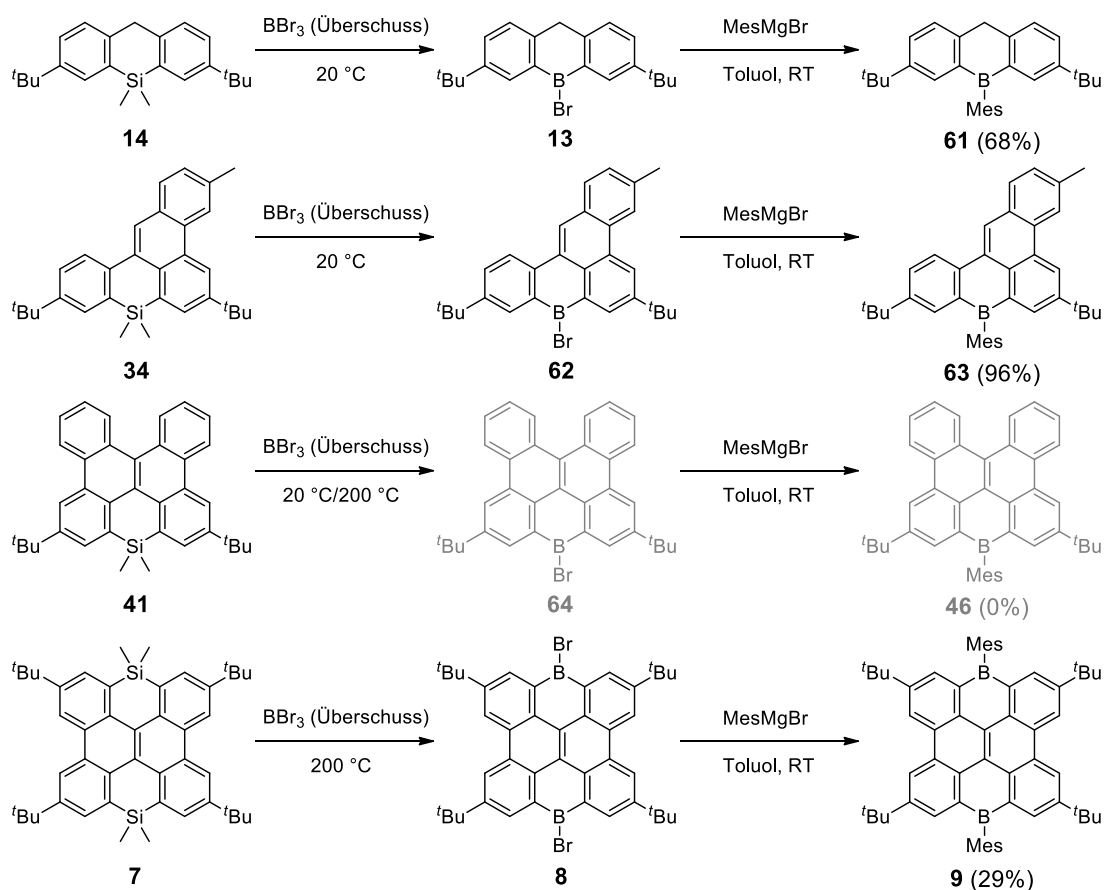


Abbildung 39: Experimente zum Silizium/Bor-Austausch in reinem BBr_3 .

Wenn ein großer Überschuss an BBr_3 zu den Diarylsilanen gegeben wird (ohne ein weiteres Lösungsmittel), entsteht eine homogene Lösung. Um die Menge an eingesetztem BBr_3 zu minimieren, wurden die Reaktionen im präparativen Maßstab meistens mit weniger BBr_3 in einer Suspension durchgeführt und über einen längeren Zeitraum leicht erwärmt. Anschließend wurde überschüssiges BBr_3 abkondensiert. Die gebildeten BBr -Spezies lassen sich durch Zugabe von Mesitylgrignard in stabile Triarylborane überführen. Bei geeigneten Substraten (z. B. **34**) und sorgfältiger Durchführung können mit dieser Prozedur hervorragende Ausbeuten erzielt werden. Im Fall von **61** ist die isolierte Ausbeute deutlich geringer, da die Verbindung eine reaktive Benzylposition aufweist und Nebenreaktionen eingeht. Weder in **41** noch in **7** können die SiMe_2 -Gruppen bei Raumtemperatur ausgetauscht werden. Die Ursache liegt wahrscheinlich in der rigiden Molekülstruktur dieser Verbindungen. Bei der Si/B-Austauschreaktion werden die C–Si-Bindungen sukzessive gelöst. In einem derartigen Zwischenprodukt wäre der linke Arylsubstituent in **34** nur über eine C–C-Bindung mit der Phenanthren-Substruktur verbunden und daher frei drehbar. Es ist plausibel, dass **7** aufgrund seines unflexibleren Molekülgerüsts die Austauschreaktion erst bei höherer Temperatur eingeht. Erhitzen von **41** in BBr_3 führt zur Zersetzung des Moleküls, daher konnte das Boran **46** nicht auf diesem Syntheseweg hergestellt werden. Problematisch ist die Si/B-Austauschreaktion auch bei Verbindungen, die elektronenreiche Atome der Hauptgruppen V und VI enthalten. Über eine alternative Route ausgehend von **61** konnten **46** und Borane mit Donoratomen dennoch synthetisiert werden (vgl. Abbildung 36).

2.2 Sterische Abschirmung im Vergleich zu struktureller Stabilisierung

Um die Boratome in Triarylboranen vor Hydrolyse zu schützen und gleichzeitig ihren elektronenarmen Charakter zu bewahren, kommen grundsätzlich zwei unterschiedliche Strategien in Betracht: Sterische Abschirmung oder Stabilisierung durch Einbettung in ein starres Molekülgerüst (siehe Kapitel 1.1.6). In dem letzteren Fall sind alle drei Arylsubstituenten koplanar, wodurch ihre π -Elektronensysteme bestmöglich mit dem leeren p-Orbital des Boratoms wechselwirken können. Die Auswirkungen dieser Ausrichtung auf die Eigenschaften des Triarylborans erforschten *S. Yamaguchi et al.* durch den Vergleich von **2** mit Trimesitylboran (Abbildung 40).

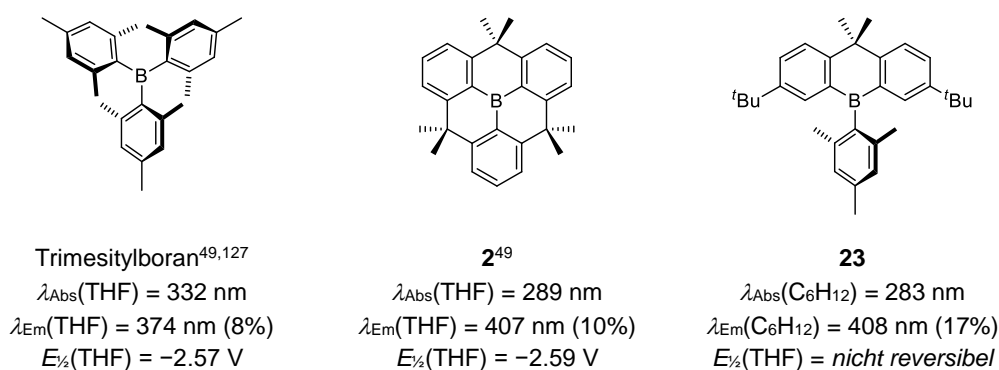


Abbildung 40: Drei strukturell unterschiedliche Triarylborane. Verbindung **23** wurde in der vorliegenden Arbeit erstmalig dargestellt (Prozentzahlen geben Φ_{PL} an, Halbstufenpotentiale $E_{1/2}$ wurden gegen FcH/FcH⁺ gemessen).

Die Absorptions- und Emissionswellenlängen weisen auf Unterschiede zwischen den elektronischen Strukturen von **2** und dem propellerförmigen Trimesitylboran hin, die sich nach einer DFT-Analyse von *Jin et al.* durch Abweichungen in Gestalt und energetischer Lage der HOMOs erklären lassen.¹²⁸ Im Rahmen der vorliegenden Arbeit sollten planare, strukturell stabilisierte Triarylborane mit Molekülen wie **23** verglichen werden, in welchen einer der Arylsubstituenten zur sterischen Abschirmung orthogonal zum übrigen Molekülgerüst angeordnet ist. Neben der Verbindung **23**, die wie **2** nur eine geringe Lumineszenzquantenausbeute aufweist, wurden zu diesem Zweck die beiden Triarylborane **66** und **68** dargestellt (Abbildung 41).

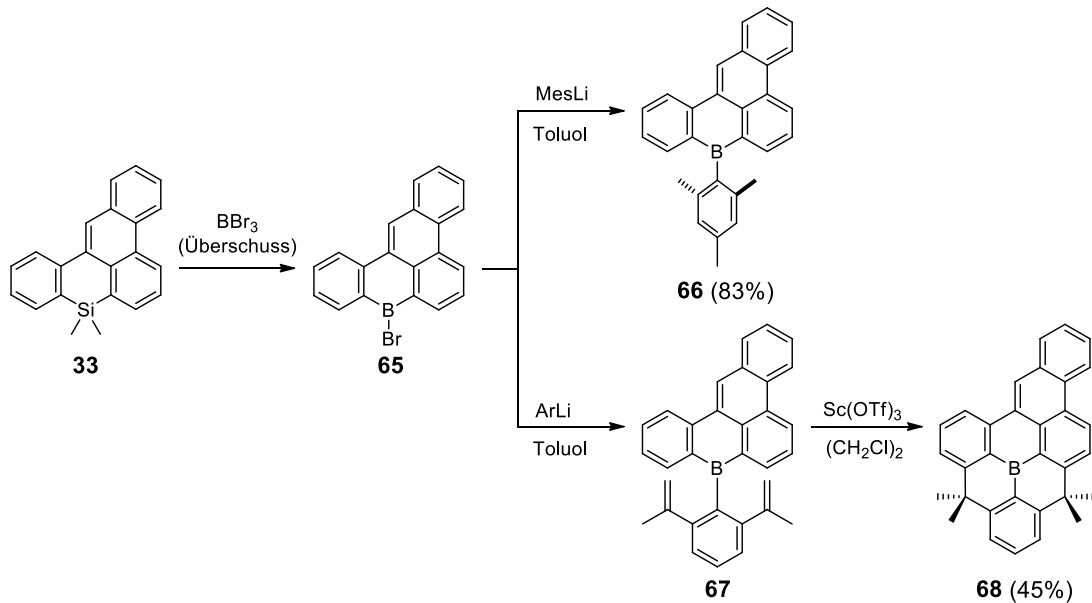


Abbildung 41: Synthese des strukturell stabilisierten Triarylborans **68** und der vergleichbaren mesitylgeschützten Verbindung **66**. Die Ausbeuten beziehen sich jeweils auf alle Synthesestufen ab **33**. Ar = 2,6-Di(prop-1-en-2-yl)phenyl.

Überraschenderweise wurde gefunden, dass sich die wesentlichen Moleküleigenschaften von **66** und **68** kaum unterscheiden. Beide Verbindungen sind stabil an Luft, sowie bei Kontakt mit Wasser oder organischen Säuren. Die Maxima ihrer UV/vis-Absorptionsspektren sind fast identisch (beide: $\lambda_{\text{Abs}} = 400 \text{ nm}$, Abbildung 42). Auch die Fluoreszenzeigenschaften von **66** und **68** unterscheiden sich kaum. Sie emittieren blaues Licht mit hohen Fluoreszenzquantenausbeuten (**66**: $\lambda_{\text{Em}} = 411 \text{ nm}$, $\Phi_{\text{PL}} = 85\%$; **68**: $\lambda_{\text{Em}} = 408 \text{ nm}$, $\Phi_{\text{PL}} = 89\%$). Geringe Unterschiede ließen sich mittels Cyclovoltammetrie feststellen: **66** zeigt sowohl in CH_2Cl_2 als auch in THF eine reversible Redoxwelle (CH_2Cl_2 : $E_{1/2} = -2.04 \text{ V}$, THF: $E_{1/2} = -2.05 \text{ V}$). Für **68** kann nur in THF ein Halbstufenpotential bestimmt werden, der Redoxvorgang in CH_2Cl_2 verläuft nicht reversibel. Außerdem ist das planarisierte Molekül mit $E_{1/2} = -2.14 \text{ V}$ etwas schwerer zu reduzieren, was vermutlich auf den positiven induktiven Effekt der Alkylbrücken zurückzuführen ist.

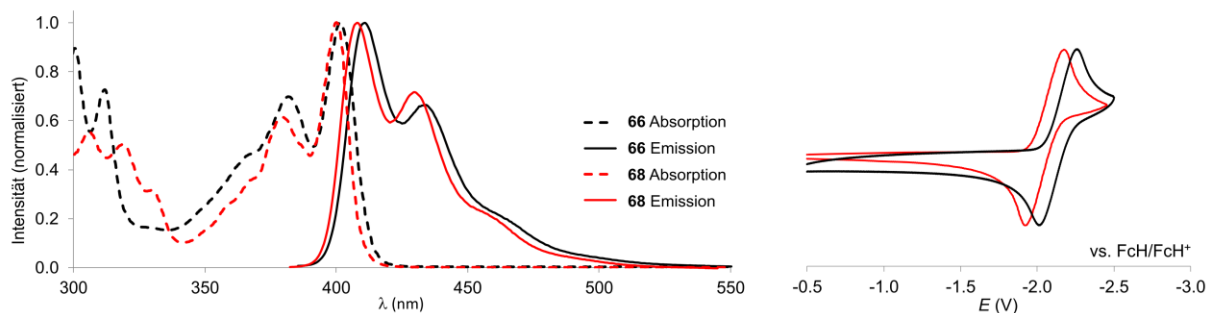


Abbildung 42: UV/vis-Absorptions- und Emissionsspektren (links) sowie Cyclovoltammogramme (rechts) von **66** (schwarz) und **68** (rot).

Die Kristallstrukturanalysen von **66** und **68** zeigen erhebliche Unterschiede in den B–C-Bindungslängen (Abbildung 43). Die Bindung zu dem exozyklischen, orthogonalen Mesitylsubstituenten in **66** ist deutlich länger als die endozyklischen B–C-Bindungen in **66** und **68**. Dies ist ein Hinweis auf bindende Wechselwirkungen zwischen den π -Elektronensystemen der koplanaren Arylsubstituenten und dem p-Orbital des jeweiligen Boratoms und steht im Einklang mit theoretischen Untersuchungen.¹²⁸

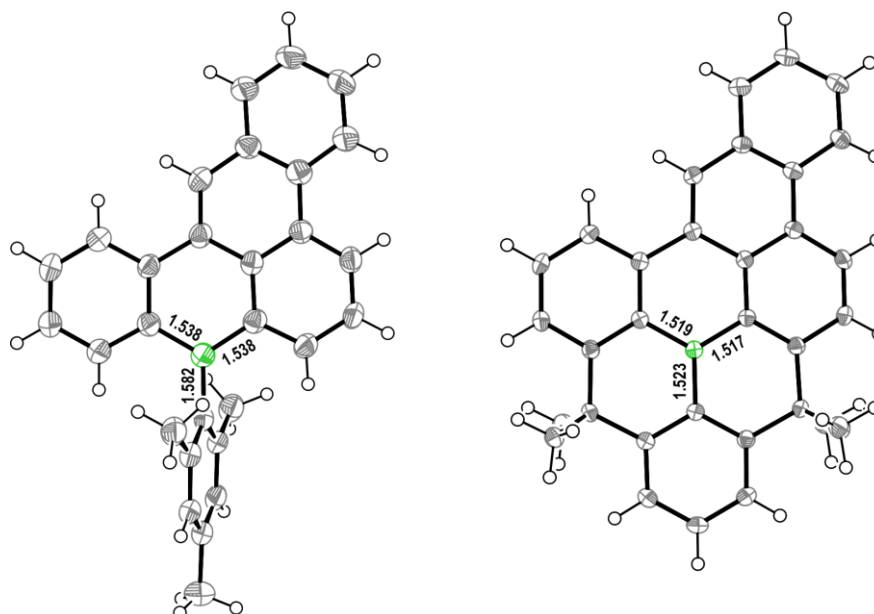


Abbildung 43: ORTEP-Darstellungen der Molekülstrukturen von **66** (links) und **68** (rechts) im Festkörper. Die C–B-Bindungslängen sind in Ångstrom angegeben. **66** kristallisiert mit zwei kristallographisch unabhängigen Molekülen in der asymmetrischen Einheit; die C–B-Bindungslängen wurden in diesem Fall gemittelt. Die Aufenthaltswahrscheinlichkeit der thermischen Ellipsoide beträgt 50%.

Als Maß für die *Lewis*-Aciditäten der beiden Triarylborane wurden ihre Fluorid-Affinitäten experimentell bestimmt. In THF wurden in beiden Fällen Assoziationskonstanten von mehr als 10^6 M^{-1} gemessen (Abbildung 44). In CHCl_3 sind die entsprechenden Werte aufgrund von Wechselwirkungen der Fluorid-Ionen mit dem Lösungsmittel deutlich geringer, sodass der Unterschied zwischen den beiden Molekülen **66** und **68** quantifiziert werden konnte (Abbildung 45).

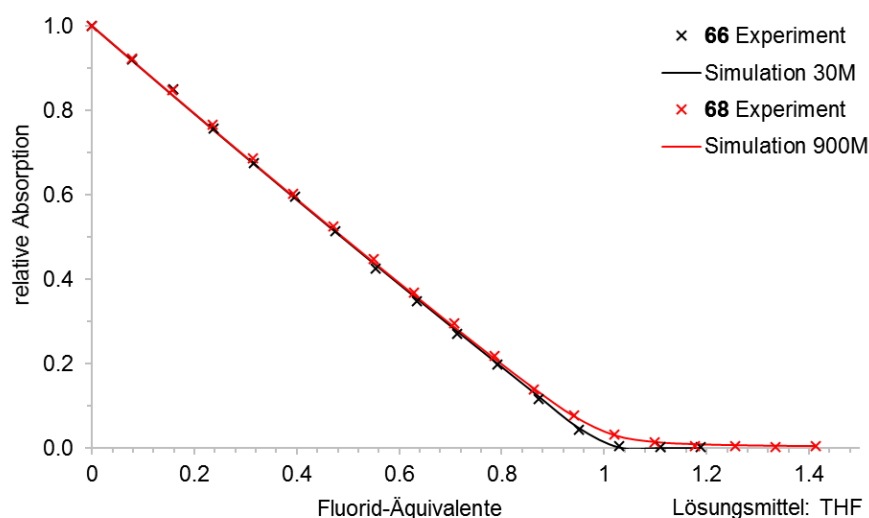


Abbildung 44: Titrationsen von **66** (schwarz) und **68** (rot) mit TBAF in THF. Die Kreuze markieren experimentell erhaltene Werte, die durchgezogenen Linien entsprechen Simulationen für $K_a = 30 \cdot 10^6 \text{ M}^{-1}$ (schwarz) und $K_a = 900 \cdot 10^6 \text{ M}^{-1}$ (rot).

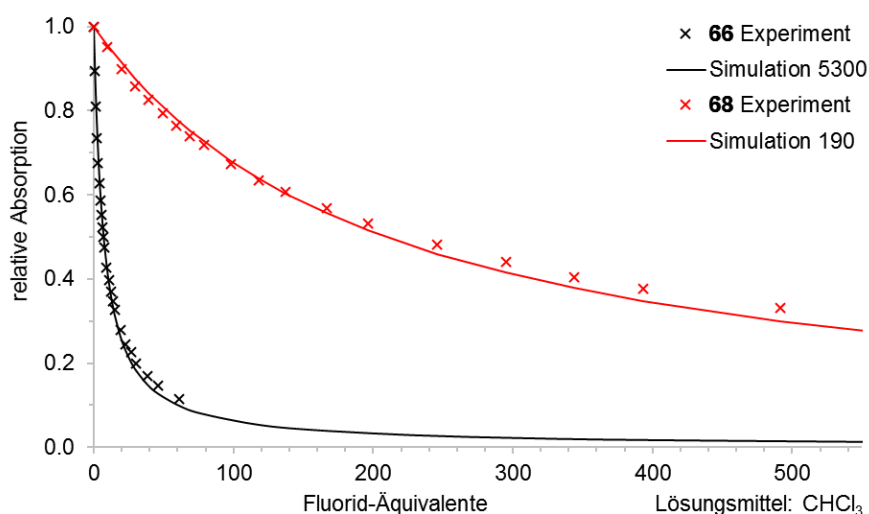


Abbildung 45: Titrationsen von **66** (schwarz) und **68** (rot) mit TBAF in CHCl_3 . Die Kreuze markieren experimentell erhaltene Werte, die durchgezogenen Linien entsprechen Simulationen für $K_a = 5300 \text{ M}^{-1}$ (schwarz) und $K_a = 190 \text{ M}^{-1}$ (rot).

Das Mesitylboran **66** weist eine 28-fach höhere Assoziationskonstante als **68** auf. Dieses Ergebnis korreliert mit der höheren Elektronenaffinität von **66** (siehe CV-Messungen in Abbildung 42). Ein Zusammenhang zwischen der Fluorid-Affinität und dem LUMO-Energieniveau wurde bereits in vielen Fällen festgestellt.¹²⁹ Inwiefern die Planarisierung einen Einfluss auf die Lewis-Acidität (gegenüber Fluorid) ausübt, kann durch die Untersuchung von lediglich zwei Verbindungen noch nicht abgeleitet werden.

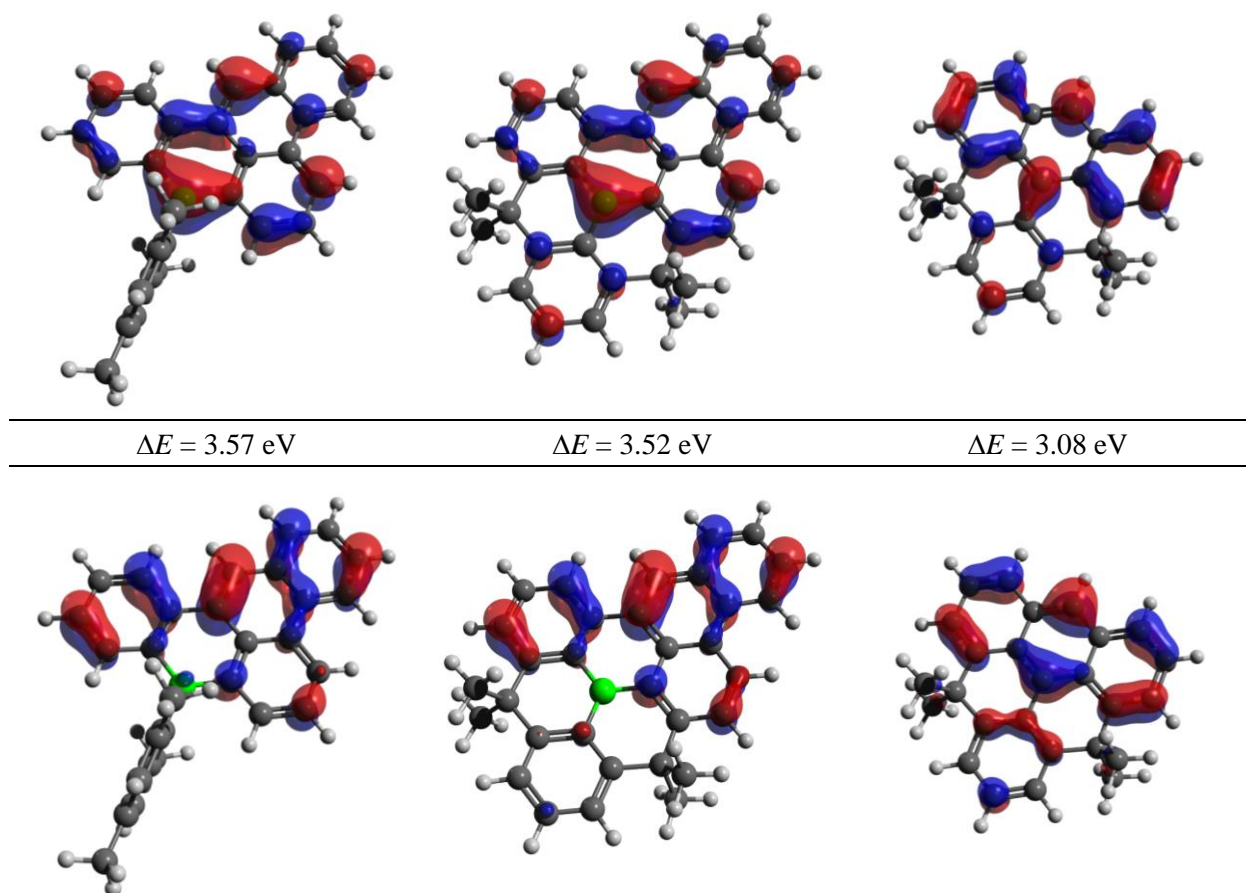


Abbildung 46: Plots der HOMOs (unten) und LUMOs (oben, Iso-Wert = $0.04 a_0^{-3/2}$) von **66** (links), **68** (Mitte) und einem planarisierten Phenylanthracen (rechts).⁴

Der Grund für die nahezu identischen Eigenschaften des Mesitylborans **66** und des planarisierten Borans **68** liegt in der überraschend großen Ähnlichkeit ihrer elektronischen Strukturen. In Abbildung 46 sind die Grenzorbitale der beiden Verbindungen im Vergleich zu einem Phenylanthracen-Derivat dargestellt. Im Fall des Anthracens trägt der planarisierte Phenylsubstituent deutlich zum HOMO bei. In **68** ist dagegen kaum ein Orbitalbeitrag der Atome des planarisierten Phenylsubstituenten zu erkennen. Die Gestalt der Grenzorbitale ist nahezu identisch zu jenen der Verbindung **66**, in welcher der Mesitylsubstituent aufgrund einer Verdrillung um ca. 90° nicht mit dem PAK-Gerüst π -konjugiert ist. Die Betrachtung der experimentellen und theoretischen Ergebnisse zu **66** und **68** legt den Schluss nahe, dass eine π -Konjugation zwischen den drei Arylsubstituenten eines ladungsneutralen Triarylborans über das leere p-Orbital des Boratoms nicht möglich ist, selbst wenn durch Planarisierung eine optimale Orbitalwechselwirkung ermöglicht wird. Da die Synthese von Mesitylboranen im Vergleich zu planarisierten Boranen im Allgemeinen einfacher, kostengünstiger und in höherer Ausbeute möglich ist, wurde das MesB(Ar)₂-Strukturmotiv für die folgenden Untersuchungen bevorzugt.

2.3 Neue borhaltige PAKs: Variation der Grundstrukturen

Die in den vorangegangenen Kapiteln beschriebenen Synthesemethoden lassen sich in modularer Weise miteinander kombinieren, um eine Vielzahl untereinander verwandter borhaltiger PAKs darzustellen. Dadurch wurde es erstmalig möglich, in nachfolgenden Untersuchungen den Einfluss der Größe und Form des jeweiligen π -konjugierten Elektronensystems auf die molekularen Eigenschaften der Triarylborane zu beleuchten. Dazu wurde eine Reihe von sechs Boranen mit systematisch variiert Grundstruktur synthetisiert (Abbildung 47). Die Anzahl π -konjugierter, sp^2 -hybridisierter Kohlenstoffatome in diesen Verbindungen variiert zwischen sechs (**23**) und 26 (**46**).

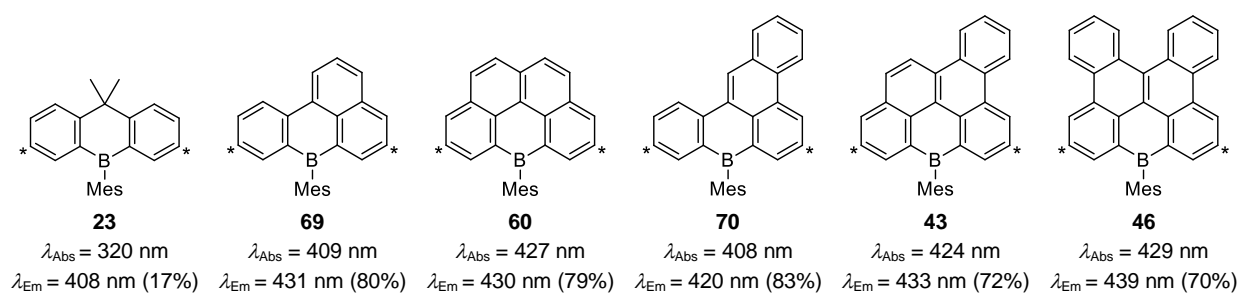


Abbildung 47: Arylborane mit unterschiedlich großen π -Elektronensystemen. Mit Sternchen markierte Kohlenstoffatome tragen *tert*-Butylgruppen. Die UV/vis- und Fluoreszenzmessungen wurden in Cyclohexan durchgeführt (Prozentzahlen geben Φ_{PL} an).

Auf den ersten Blick wird deutlich, dass das kleinste Molekül (**23**) sich deutlich von den übrigen Verbindungen in dieser Reihe unterscheidet. Für die optische Anregung von **23** wird relativ energiereiches UV-Licht benötigt und die Lumineszenzquantenausbeute ist vergleichsweise niedrig. In diesen Eigenschaften ähnelt **23** stark den verwandten Verbindungen Trimesitylboran (in Cyclohexan: $\lambda_{Abs} = 330$ nm, $\Phi_{PL} = 11\%$)^{130,131} und dem von *S. Yamaguchi et al.* beschriebenen, vollständig planaren Triarylboran **2** (in THF: $\lambda_{Abs} = 320$ nm, $\Phi_{PL} = 10\%$). Alle übrigen Arylborane der Reihe (Abbildung 47) unterscheiden sich von **23** dadurch, dass jeweils zwei der drei Arylsubstituenten des Boratoms Teil eines gemeinsamen PAK-Gefüges sind und daher in π -Konjugation miteinander stehen. Die spektroskopischen Messungen zeigten, dass dieses Strukturmotiv generell mit einer Absorptionsbande bei $\lambda_{Abs} = 420 \pm 10$ nm und einer intensiven blauen Lumineszenz mit hoher Quantenausbeute einhergeht. Trotz unterschiedlich großer π -Elektronensysteme sind die optoelektronischen Eigenschaften dieser konjugierten Arylborane überraschend ähnlich. Die Anellierung zusätzlicher C_6 -Ringe in der Peripherie hat keine großen Auswirkungen (vgl. **69**→**70** oder **60**→**43/46**). Ein merklicher Unterschied besteht jedoch zwischen den Arylboranen, in denen das Boratom in ein 1-Phenyl-naphthalin-Gerüst eingefasst ist (**69/70**: $\lambda_{Abs} = 408/409$ nm) und jenen, in denen vier anellierte sechsgliedrige Ringe das jeweilige Boratom umgeben (**60/43/46**: $\lambda_{Abs} = 424/427/429$ nm). In den letztgenannten Fällen ist die Absorptionswellenlänge im Durchschnitt 18 nm größer, was sich durch eine bessere π -Konjugation zwischen den verbrückten Arylsubstituenten dieser Borane erklären lässt.

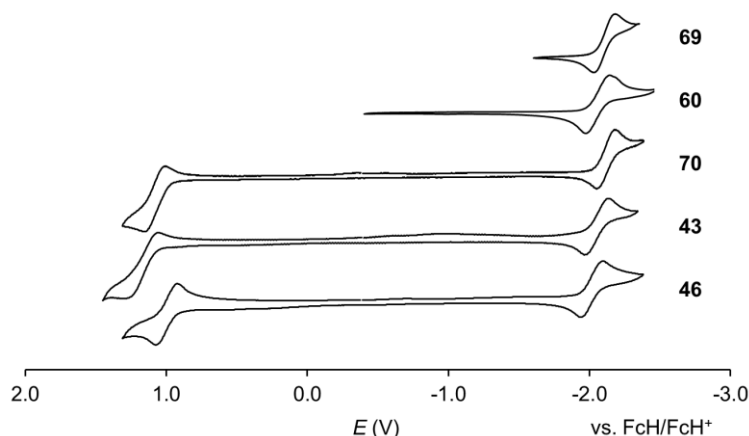


Abbildung 48: Cyclovoltammogramme von **43**, **46**, **60**, **69** und **70**, gemessen in CH_2Cl_2 .

Im Gegensatz zu den optischen Eigenschaften hängt die elektrochemische Stabilität der Triarylborane entscheidend von der Größe des individuellen π -Elektronensystems ab. Mittels Cyclovoltammetrie lassen sich die Verbindungen elektrochemisch reduzieren oder oxidieren und die Stabilitäten der gebildeten Moleküle beurteilen. Wenn die geladenen Spezies keine chemischen Reaktionen eingehen, werden anschließend durch den umgekehrten Prozess die neutralen Moleküle unbeschadet zurückerhalten. Mit dieser Methode erwies sich das kleine Arylboran **23** als instabil, es konnte weder in CH_2Cl_2 noch in THF ein reversibler Oxidations- oder Reduktionsprozess beobachtet werden. Bei allen anderen Arylboranen der Reihe ist jeweils eine reversible Reduktion möglich, die Halbstufenpotentiale dieser Redoxvorgänge liegen in einem engen Bereich zwischen -2.11 und -2.01 V (gemessen in CH_2Cl_2 gegen FcH/FcH^+ , Abbildung 48). Im oxidativen Bereich wurden bei **69** und **60** keine interpretierbaren Redoxprozesse beobachtet. Im Gegensatz dazu verliefen die Oxidationen von **70** und **46** reversibel (**43**: teilweise reversibel). Demnach weisen die Arylborane mit größerem π -Elektronensystem eine höhere elektrochemische Stabilität auf. In diesen Verbindungen können elektrische Ladungen besser delokalisiert werden, wodurch ihre Neigung zu Zersetzungsreaktionen abnimmt.

Aus der Reihe der Arylborane in Abbildung 47 sticht **70** heraus, da es neben einer hohen elektrochemischen Stabilität auch die höchste Lumineszenzquantenausbeute aller Triarylborane dieser Serie aufweist. Darüber hinaus lassen sich Verbindungen dieses Strukturtyps in nur vier Reaktionsschritten und mit einer Ausbeute von etwa 30-50% aus dem gemeinsamen Vorläufer **14** herstellen, die meisten anderen Borane in Abbildung 47 wurden in deutlich geringerer Ausbeute erhalten.

2.4 Neue borhaltige PAKs: Variation der Substituenten

Durch Verwendung von *para*-Brombenzaldehyd als Elektrophil in der *Peterson*-Olefinierung kann sehr leicht ein halogensubstituiertes Derivat von **70** hergestellt werden (Abbildung 49). Die Synthese erfolgte analog zu **70** und in guter Ausbeute, allerdings benötigte die Photozyklisierung in diesem Fall eine ungewöhnlich lange Reaktionszeit von etwa 14 h.

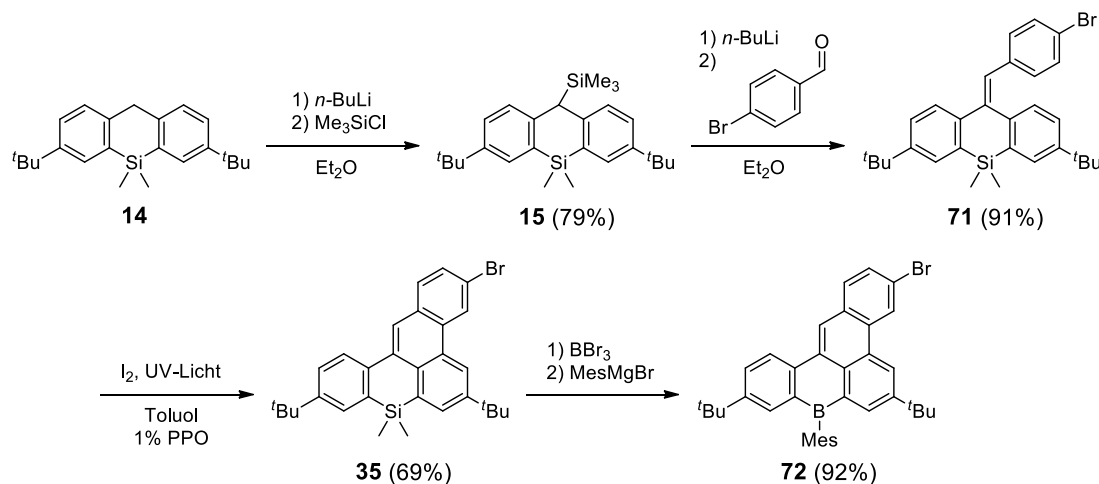


Abbildung 49: Synthese des bromsubstituierten Arylborans **72** (Gesamtausbeute **14**→**72**: 46%).

Arylbromide sind synthetisch vielseitig verwendbar und eignen sich als Substrate für diverse C–C-Kupplungsreaktionen. Im Falle von **72** bestand eine Herausforderung allerdings darin, Reaktionsbedingungen zu finden, unter denen die gewünschte Kupplungsreaktion abläuft, ohne dass gleichzeitig die B–C-Bindungen gespalten werden. In der Fachliteratur finden sich nicht viele Beispiele für Kreuzkupplungsreaktionen an Mesitylboranen. *Negishi*-,^{132,133} *Sonogashira*-^{103,104} und *Stille*-Reaktionen^{48,100,134} kommen ohne starke Basen aus und eignen sich daher vergleichsweise gut für diesen Zweck.

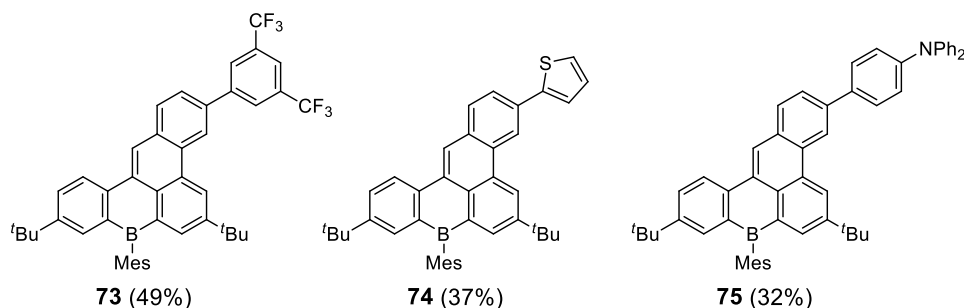


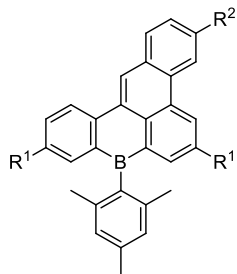
Abbildung 50: Produkte der (*t*-Bu₃P)₂Pd-katalysierten Reaktionen von **72** mit Aryltri(*n*-butyl)stannanen.

An **72** wurden drei *Stille*-Reaktionen mit unterschiedlichen Arylstannanen in sauerstofffreiem Toluol durchgeführt (Abbildung 50). Die isolierten Ausbeuten waren mit 32–49% nicht besonders hoch. Obwohl das Stannan jeweils im Überschuss eingesetzt wurde (1.5 bis 2.5 Äquivalente), verblieb nach Reaktionszeiten von bis zu 48 Stunden bei einer Temperatur von 90 °C immer noch **72** in der Mischung und musste anschließend mittels Säulenchromatographie abgetrennt werden. Die B–C-Bindungen blieben unter diesen Reaktionsbedingungen intakt. Durch die Wahl eines anderen Katalysators oder Lösungsmittels könnte es daher möglich sein, die Ausbeuten noch zu steigern.

Um die Einflüsse unterschiedlicher Substituenten auf die optoelektronischen Eigenschaften von **70** zu untersuchen, wurden zusätzlich zu **73–75** weitere Derivate von **70** mit und ohne Alkylsubstituenten, sowie ein Derivat mit CF₃-Gruppe (analog zu **72**) synthetisiert. Die Ergebnisse sind in Tabelle 1 dargestellt:

Tabelle 1: Optoelektronische Daten eines π -konjugierten Triarylborans mit ausgewählten Substituenten.

R^1	R^2	λ_{Abs} (nm)	λ_{Em} (nm)	Φ_{PL} (%)	$E_{1/2}$ (V)
H	H	400	410	85	-2.04
<i>t</i> -Bu	H	408	420	83	-2.11, 1.09
<i>t</i> -Bu	Me	416	428	88	-2.17, 0.99
<i>t</i> -Bu	CF ₃	401	412	79	-2.01
<i>t</i> -Bu	2-Thienyl	429	447	73	-2.09
<i>t</i> -Bu	4-C ₆ H ₄ NPh ₂	433	471	92	-2.17, 0.48, 0.94
<i>t</i> -Bu	3,5-(CF ₃) ₂ C ₆ H ₃	413	428	89	-2.05, 1.11



UV/vis-Absorptionen und -Emissionen wurden in Cyclohexan gemessen, Nebenmaxima der Schwingungsfeinstrukturen sind hier nicht aufgeführt. Die CV-Messungen wurden in CH₂Cl₂ durchgeführt, die Potentiale sind relativ zu $E_{1/2}(\text{FcH}/\text{FcH}^+)$ angegeben.

Alle Verbindungen des in Tabelle 1 dargestellten Strukturtyps weisen im kathodischen Bereich ihres Cyclovoltammogramms einen reversiblen Redoxvorgang auf, demnach sind die gebildeten Radikalanionen grundsätzlich stabil. Die elektronenreichen Vertreter der Reihe zeigen zusätzlich einen (oder sogar zwei) reversible Redoxvorgänge im anodischen Bereich. Des Weiteren sind die Lumineszenzquantenausbeuten dieser Derivate durchweg sehr hoch. Durch verschiedene Substituenten an der mit R^2 markierten Position lassen sich die Absorptionswellenlängen im Bereich von 401 bis 433 nm variieren. Wie erwartet führen Akzeptorsubstituenten zu einer hypsochromen Verschiebung, während Donorsubstituenten eine bathochrome Verschiebung zur Folge haben. Der elektronenreichste unter den getesteten Substituenten ist die Triphenylamin-Gruppe, die in Verbindung mit dem elektronenarmen Triarylboran ein Molekül mit ausgeprägt dipolarem Charakter bildet. Bei optischer Anregung dieses Moleküls wird intramolekular Ladungsdichte von der Amin-Untereinheit in Richtung Boratom verschoben. Dieser Ladungstransfer macht sich durch eine starke Abhängigkeit der Fluoreszenzwellenlänge von der Polarität der Umgebung, bzw. des Lösungsmittels, bemerkbar (Solvatochromie, Abbildung 51).

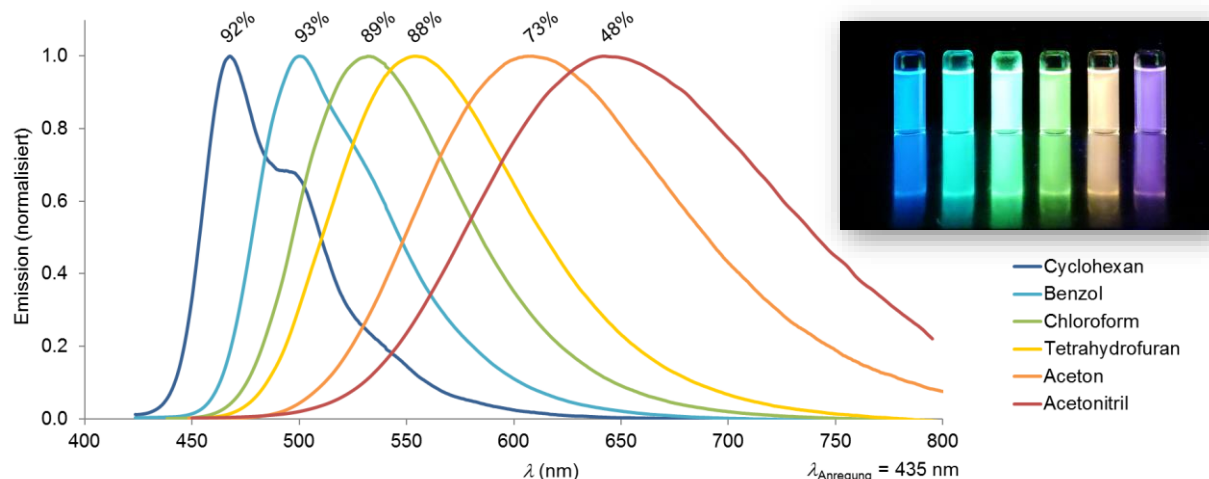


Abbildung 51: Emissionsspektren des dipolaren, aminsubstituierten Arylborans **75** in verschiedenen Lösungsmitteln. Die Prozentzahlen an den Graphen beziehen sich auf die jeweilige Lumineszenzquantenausbeute.

2.5 Neue borhaltige PAKs: Variation von Heteroatomen im Molekülgerüst

Die Anwesenheit der Triphenylamin-Gruppe in **75** beeinflusst die Eigenschaften des borhaltigen Arylborans stark. In Erweiterung dieses Ansatzes wurden zudem borhaltige PAKs mit weiteren Heteroatomen (\neq B) im Molekülgerüst synthetisiert. Pyridin ist ein Heteroaromat mit elektronenarmem π -Elektronensystem,¹²⁷ dessen freies Elektronenpaar am Stickstoffatom als *Lewis*-Base wirken kann. Durch Verwendung von Bis(2-pyridyl)methanon in einer *Peterson*-Olefinierung mit **76** und anschließende Reaktion mit PdCl_2 in CH_3CN konnte der Chelat-Komplex **78** synthetisiert werden (Abbildung 52).

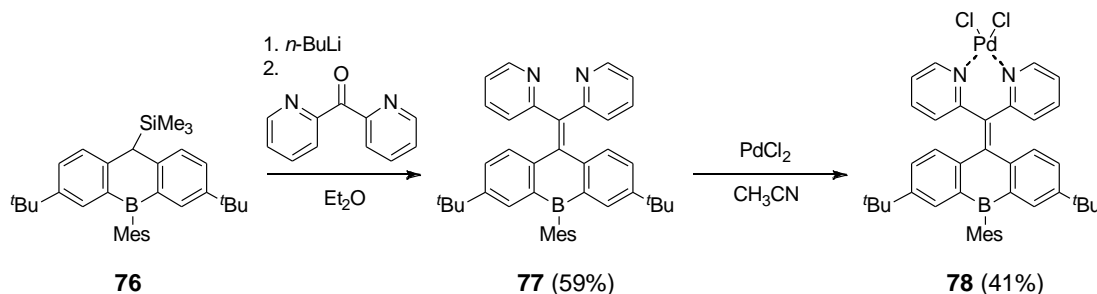


Abbildung 52: Synthese eines Pd(II)-Chelatkomplexes, die Ausbeuten beziehen sich jeweils auf den letzten Reaktionsschritt.

Vergleichbare Verbindungen (ohne Boratome) sind bereits von *B. Feringa et al.* beschrieben,²⁸ daher wurden im Rahmen der vorliegenden Arbeit keine weiteren Versuche zur Synthese und Charakterisierung solcher Komplexe durchgeführt. Bei der Photozyklisierung von **77** erwiesen sich die freien Elektronenpaare der Stickstoffatome als hinderlich: Wie schon in Kapitel 2.1.2 erwähnt, wurde nur ein Pyridin-Ring in das planare Molekülgerüst eingebaut (**44**); die Planarisierung der zweiten Pyridin-Substruktur ist mutmaßlich aufgrund der Abstoßung der freien Elektronenpaare nicht möglich. Das analoge benzenellierte Molekül **46** (Abbildung 53) konnte zwar zweifach zyklisiert werden, weist aber aufgrund der gegenseitigen Repulsion von zwei Wasserstoffatomen in der Fjord-Region eine verzerrte Struktur auf. Durch Kombination eines Benzolrings einerseits und eines Pyridinrings andererseits ist die zweifache Zyklisierung ebenfalls möglich. Dabei bildet sich eine vollständig planare Struktur (**40**), die in der Fjord-Region eine C–H···N-Wasserstoffbrückenbindung aufweist. Die ¹H-NMR-Resonanz des entsprechenden Wasserstoffatoms erfährt durch die Nähe zu dem freien Elektronenpaar eine starke Tieffeld-Verschiebung ($\delta = 10.12$ ppm).

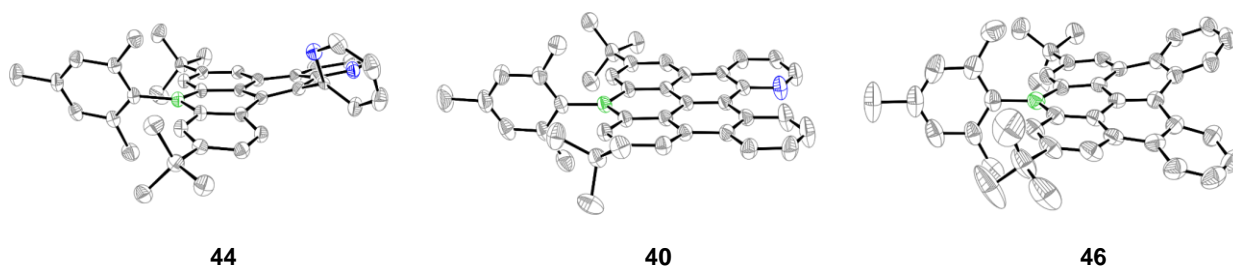


Abbildung 53: ORTEP-Darstellungen der Molekülstrukturen von **44**, **40** und **46** im Festkörper. Die Aufenthaltswahrscheinlichkeit der thermischen Ellipsoide beträgt 50%.

Durch den Einbau von Pyridinringen konnten Arylboran-Derivate von **70** und **46** hergestellt werden, in denen formal ein Kohlenstoffatom des Grundgerüsts gegen Stickstoff ersetzt ist. Als Folge sind die Absorptions- und Emissionswellenlängen dieser Verbindungen hypsochrom verschoben und eine elektrochemische Reduktion ist leichter möglich (Abbildung 54). In dieser Hinsicht ist der durch einmaligen C/N-Austausch erzielte Effekt mit der Substitution eines peripheren Wasserstoffatoms gegen CF_3 quantitativ vergleichbar (vgl. **37/39**). Die Löslichkeit der Pyridin-anellierten PAKs in polaren Lösungsmitteln (z. B. Methanol) ist deutlich höher als die der unsubstituierten/ CF_3 -substituierten Derivate.

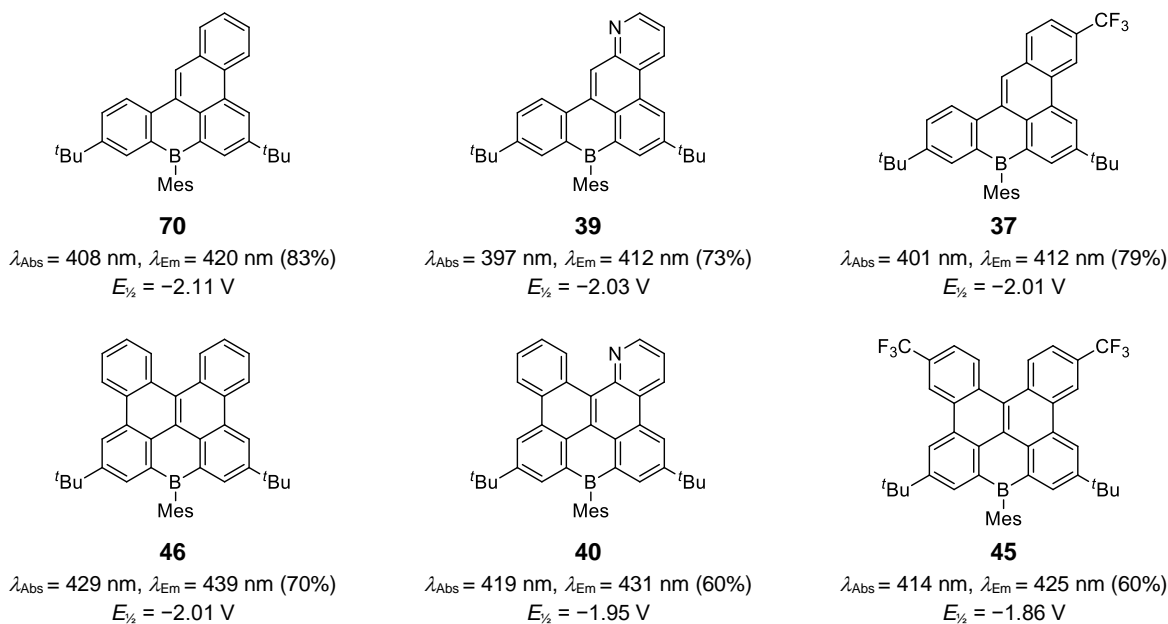


Abbildung 54: Pyridin-anellierte Triarylborane **39/40** und ausgewählte Vergleichssysteme. Die UV/vis-Absorption und -Emission wurden in Cyclohexan gemessen (Prozentzahlen geben Φ_{PL} an). Die CV-Messungen wurden in CH_2Cl_2 durchgeführt, die Halbstufenpotentiale sind relativ zu $E_{1/2}(\text{FcH}/\text{FcH}^+)$ angegeben.

Ergänzend zum Einbau elektronenarmer Pyridinringe wurde auch versucht, die elektronenreichen fünfgliedrigen Heterozyklen¹²⁷ Furan, Pyrrol und Thiophen in π -konjugierte Triarylborane zu integrieren. *C. J. Timmons* und *W. Carruthers* haben bereits beschrieben, dass sich Thiophen gut als Substruktur für die Photozyklisierungsreaktion einsetzen lässt, Furan und Pyrrol dagegen Probleme bereiten.^{122,123} In der Tat ließ sich auf diesem Weg nur der B,S-haltige PAK **80** herstellen, die Verbindungen **53** und **51** zeigten keine Veränderung unter den Reaktionsbedingungen der Photozyklisierung (Abbildung 55). Verbindung **79** wurde mit einer Methylgruppe ausgestattet, um Nebenreaktionen in der α -Position der Thiophen-Substruktur zu verhindern.

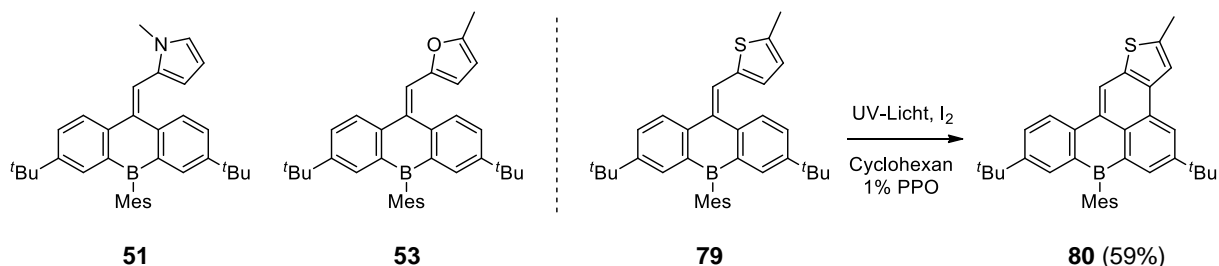


Abbildung 55: Versuche zur Photozyklisierung mit fünfgliedrigen Heterocyclen. Nur **79** ließ sich erfolgreich unter den üblichen Reaktionsbedingungen umsetzen.

2. Übersicht der Experimente und Ergebnisse

Mit dem Ziel, B,O-, B,N- und B,S-haltige Bisanthen-Derivate zu synthetisieren, wurden Xanthen-9-on, *N*-Ethylacridin-9-on, Bis(5-methylthiophen-2-yl)methanon und Thioxanthen-9-on für *Peterson*-Olefinierungen mit **29** eingesetzt (Abbildung 56). Nur Thioxanthen-9-on erwies sich als elektrophil genug um diese Reaktion einzugehen. Nach anschließender Photozyklisierung wurde die dipolare Verbindung **47** erhalten.

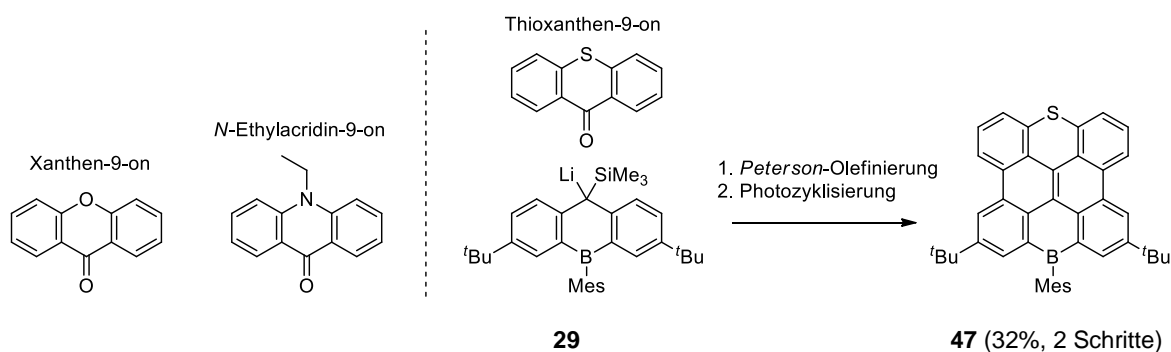


Abbildung 56: Versuche zur *Peterson*-Olefinierung mit verschiedenen donorhaltigen Ketonen. Xanthen-9-on und *N*-Ethylacridin-9-on reagierten nicht mit **29**.

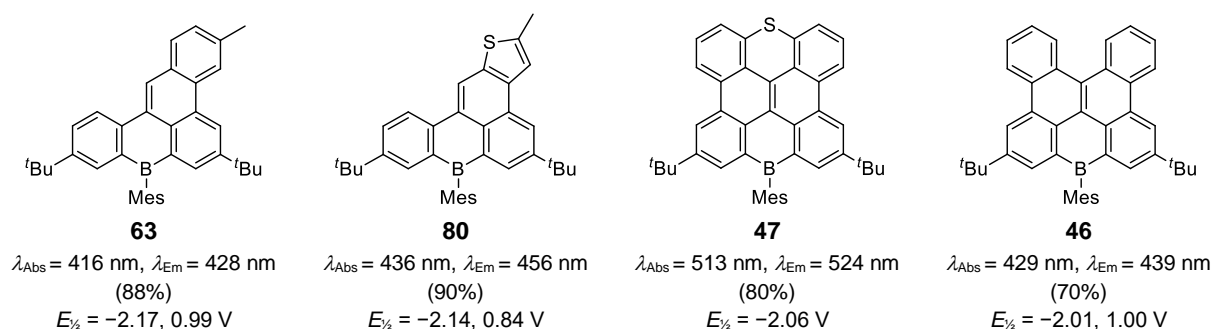


Abbildung 57: B,S-haltige PAKs **80/47** und Vergleichssysteme ohne Schwefelatome. Die UV/vis-Absorption und -Emission wurden in Cyclohexan gemessen (Prozentzahlen geben Φ_{PL} an). Die CV-Messungen wurden in CH_2Cl_2 durchgeführt, die Halbstufenpotentiale sind relativ zu $E_{1/2}(\text{FcH}/\text{FcH}^+)$ angegeben.

Das S-haltige Arylboran **80** ist im CV-Experiment deutlich leichter zu oxidieren als **63**, was auf eine Erhöhung des HOMO-Energieniveaus durch den Einbau des Donoratoms schließen lässt (Abbildung 57). Des Weiteren sind die Absorptions- und Emissionsbanden von **80** im Vergleich zu **63** um ca. 20-30 nm rotverschoben. Noch deutlich stärker macht sich die Einführung der Schwefelbrücke in der Fjord-Region von **46** bemerkbar: Sie führt zu einer bathochromen Verschiebung der Absorptions- und Emissionsbanden um rund 85 nm. Außerdem zeigt **47** eine deutliche positive Solvatochromie (Abbildung 58, oben). Die Fluoreszenzfarbe ändert sich von Grün in Cyclohexan zu Orange in Aceton, was auf einen dipolaren Charakter des angeregten Zustands schließen lässt. Demnach ist der dipolare Charakter von **47** ausgeprägter als der von **80** (Abbildung 58, unten). In beiden Fällen sind die Lumineszenzquantenausbeuten hoch, die Schwefelatome haben in dieser Hinsicht keinen negativen Einfluss.

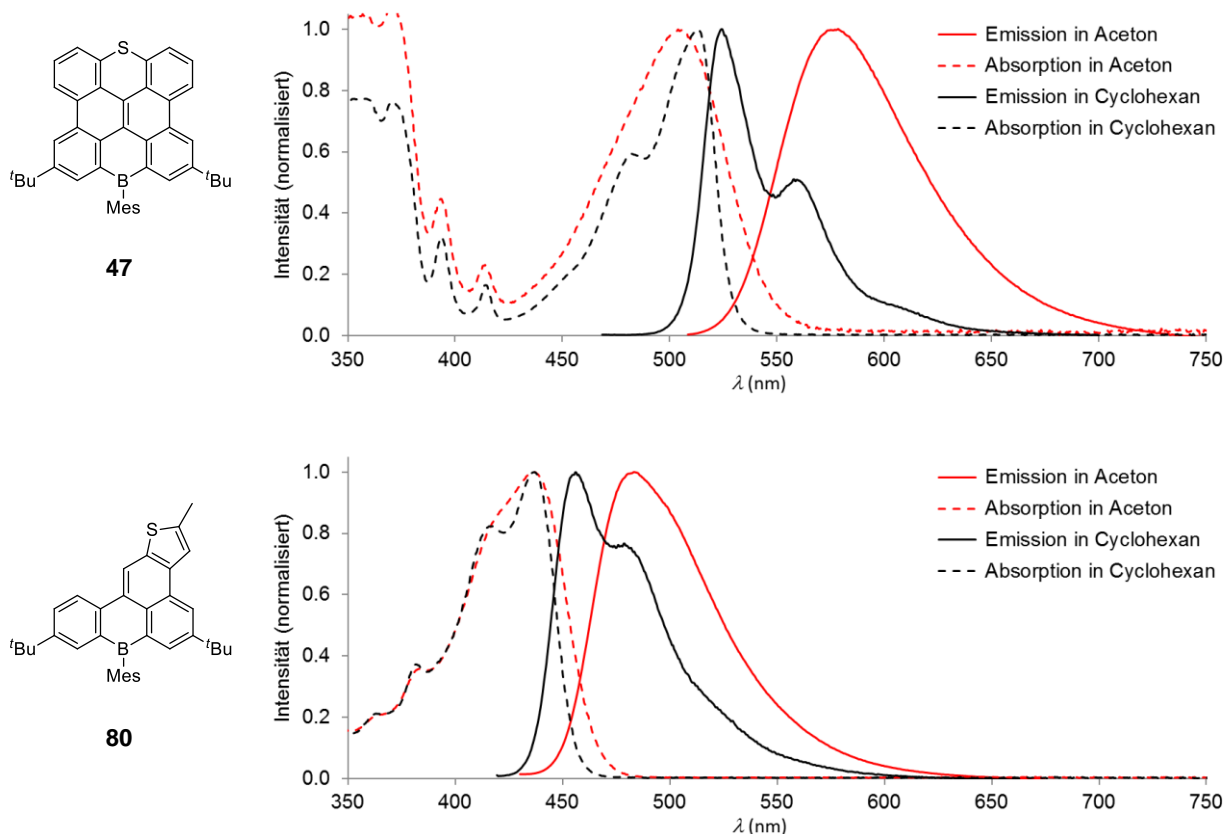


Abbildung 58: Absorptions- und Emissionsspektren der B,S-haltigen PAKs **47** und **80** in Aceton und Cyclohexan.

2.6 Chemische Modifikationen und molekulare Sensorik

In der molekularen Sensorik nutzt man Moleküle, die ihre Absorptions- und/oder Emissionseigenschaften in Abhängigkeit von ihrer chemischen Umgebung ändern, als sogenannte Indikatoren. Ein einfaches und allseits bekanntes Beispiel ist Lackmus, dessen Farbe in wässriger Lösung je nach pH-Wert zwischen Rot (sauer) und Blau (alkalisch) wechselt. Der pH-Wert, eine nicht sichtbare Eigenschaft der wässrigen Lösung, wird durch Zugabe dieses Indikators angezeigt. Eine ähnliche Farbänderung zeigen manche Arylborane bei Komplexierung durch Fluorid-Ionen (siehe Kapitel 2.2).

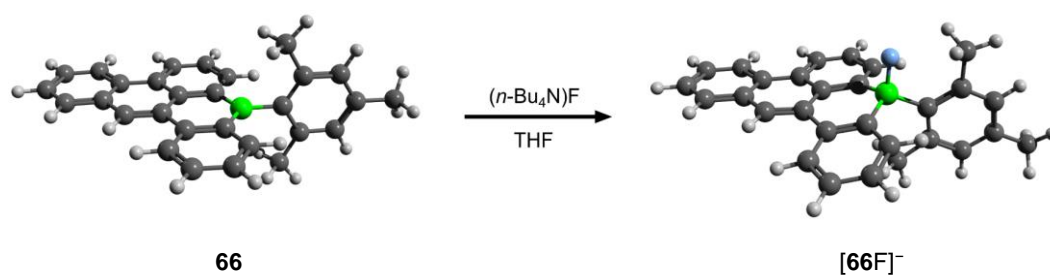


Abbildung 59: Berechnete Molekülstrukturen von **66** und des Fluorid-Addukts $[\text{66F}]^-$.⁴

Abbildung 59 zeigt die Veränderung der Molekülstruktur des neutralen Triarylborans **66** bei Anlagerung von Fluorid. Das Boratom wechselt durch die Adduktbildung seine Koordinationszahl (3→4) und Hybridisierung ($sp^2 \rightarrow sp^3$). Im Rahmen dieser Arbeit wurde spektroskopisch untersucht, wie sich die optischen Eigenschaften des Borans dadurch ändern. Sowohl die Absorptions- als auch die Emissionsbanden erfahren durch die Komplexbildung eine hypsochrome Verschiebung (Abbildung 60).

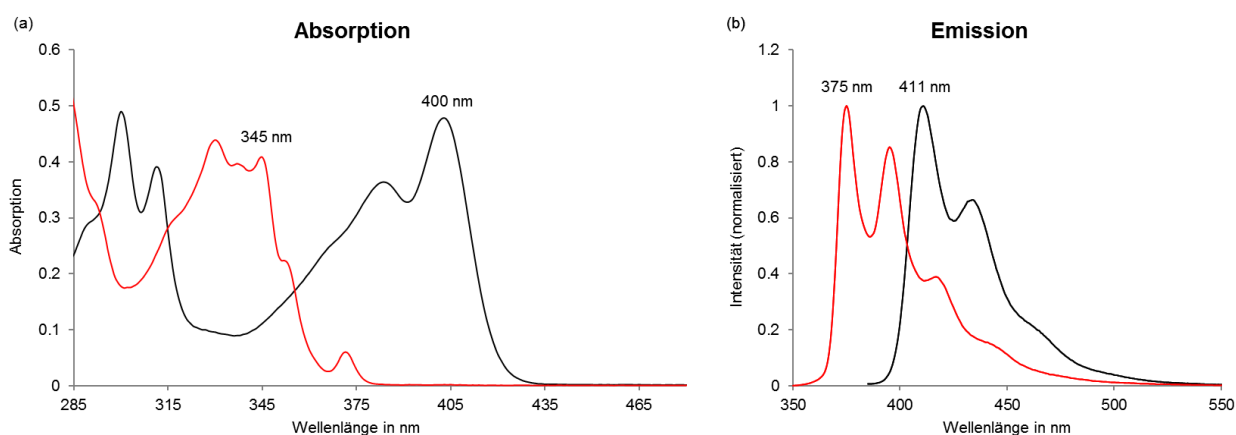


Abbildung 60: Optische Spektren von **66** (schwarz) und $[\text{66F}]^-$ (rot): (a) Absorption in THF, (b) Emission in Cyclohexan (**66**) bzw. THF ($[\text{66F}]^-$).

Arylborane können nicht nur die Gegenwart von Fluorid-Ionen anzeigen, sondern auch durch die Aufnahme von Elektronen ihre optischen Eigenschaften verändern. Die Farbänderung des Diborabisanthens **9** durch elektrochemische Reduktion wurde in einem Coulometrie-UV/vis-Kombinationsexperiment untersucht. Um eine Reoxidation der reduzierten Spezies durch Luftsauerstoff zu vermeiden, wurde dieser Versuch in einer mit Argon gefüllten Glovebox durchgeführt (Abbildung 61).

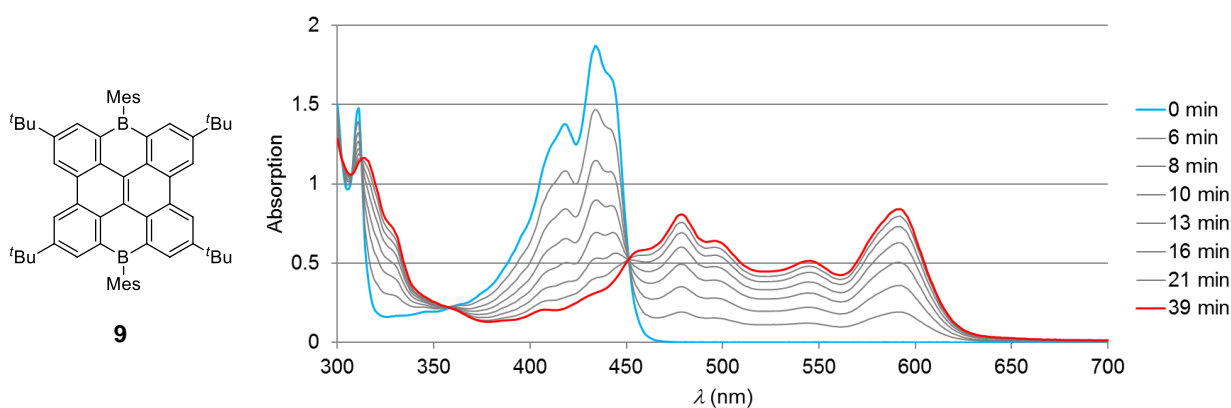


Abbildung 61: UV/vis-spektroelektrochemische Messung an **9** in THF bei $E_A = -1.96$ V.

Nach etwa 39 min bei einem angelegten Potential von $E_A = -1.96$ V lagen alle Moleküle in der THF-Lösung einfach reduziert vor ($9 \rightarrow [9]^\bullet-$) und das Spektrum veränderte sich nicht weiter. Zu diesem Zeitpunkt waren ca. 1.1 Elektronen pro Molekül auf die Lösung übertragen worden. An den isosbestischen Punkten im UV/vis-Spektrum (z. B. bei 450 nm) ist zu erkennen, dass es sich um eine Reaktion ohne Zwischen- oder Nebenprodukte handelt. Die langwelligste Absorptionsbande des Anions $[9]^\bullet-$ ist im Vergleich zu jener der Neutralverbindung um ca. 150 nm rotverschoben, die Farbe der Elektrolyselösung änderte sich entsprechend von hellgelb-grün zu violett. Durch Erhöhung des elektrischen Potentials der Arbeitselektrode (E_A) wurde noch eine zweite Reduktion durchgeführt (Abbildung 62).

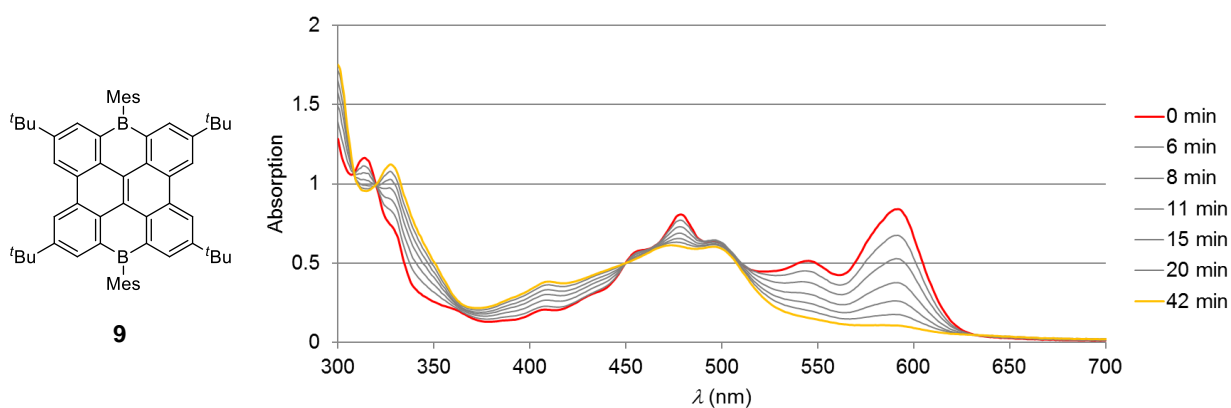


Abbildung 62: UV/vis-spektroelektrochemische an $[9]^\bullet-$ in THF bei $E_A = -2.21$ V.

Nach etwa 42 min Elektrolyse bei einem angelegten Potential von $E_A = -2.21$ V waren etwa 0.9 Elektronen pro Molekül auf die Lösung übertragen worden und das Spektrum veränderte sich nicht mehr. Die Reaktion $[9]^\bullet- \rightarrow [9]^{2-}$ war zu diesem Zeitpunkt wahrscheinlich abgeschlossen. Die langwellige Absorptionsbande bei 593 nm hatte stark an Intensität verloren und die Lösung war orange gefärbt. Anschließend wurde das Potential der Arbeitselektrode auf 0 V eingestellt, um die Anionen wieder zu oxidieren. Die Absorptionsspektren der Lösung waren vor und nach dem Experiment identisch, woraus sich schließen

2. Übersicht der Experimente und Ergebnisse

lässt, dass die Anionen $[9]^-$ und $[9]^{2-}$ elektrochemisch äußerst stabil sind und in THF-Lösungen keine Zersetzungsreaktionen eingehen. Aufgrund der quantitativen Reversibilität der Redoxvorgänge und der drastischen Farbänderung von hellgelb-grün zu violett bzw. orange eignet sich **9** als Redoxindikator.

Die Cyclovoltammogramme der B,S-haltigen PAKs **80** und **47** lassen darauf schließen, dass sie sich ebenfalls reversibel reduzieren lassen (Abbildungen 63 und 64). Zusätzlich zu der (elektro)chemischen Reduktion und der Adduktbildung mit Fluorid-Ionen bietet sich bei diesen Verbindungen noch eine dritte Möglichkeit, um die optoelektronischen Eigenschaften zu beeinflussen: Die Schwefelbrücken können zu stark elektronenziehenden Sulfoxid- bzw. Sulfongruppen oxidiert werden. Überraschenderweise wirken sich diese Transformationen auf die optoelektronischen Eigenschaften von **80** und **47** unterschiedlich stark aus.

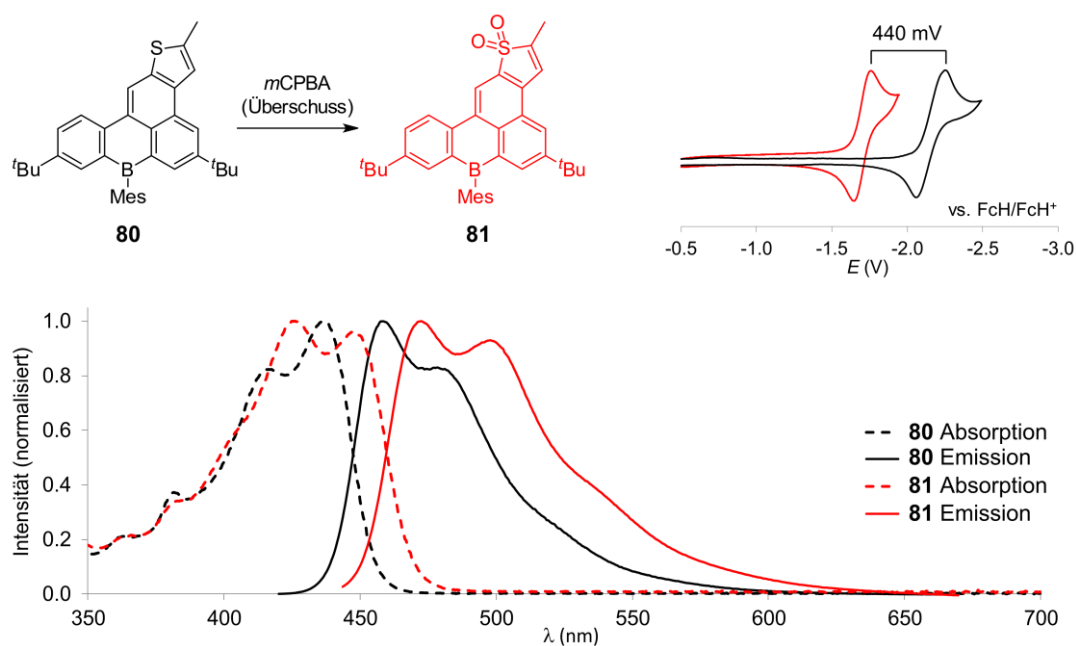


Abbildung 63: Auswirkungen der Oxidation von **80** mit *meta*-Chlorperbenzoesäure (*m*CPBA) auf die optoelektronischen Eigenschaften des PAKs.

Die Verbindung **80** reagiert mit zwei Äquivalenten *meta*-Chlorperbenzoesäure (*m*CPBA) zu dem Sulfoxid **81** (Abbildung 63). Das Sulfoxid-Zwischenprodukt wurde nicht isoliert, da es nur in einer Mischung mit **80** und **81** entsteht. Durch die Oxidation des Schwefelatoms steigt die Elektronenaffinität des PAKs stark an, was an der Verschiebung des Halbstufenpotentials von $E_{1/2} = -2.14$ nach -1.70 V im CV-Experiment zu erkennen ist. Auf die Absorptions- und Emissionseigenschaften hat die Oxidation eher geringen Einfluss; die Lumineszenzquantenausbeute von **81** ist mit $\Phi_{\text{PL}} = 94\%$ immer noch sehr hoch.

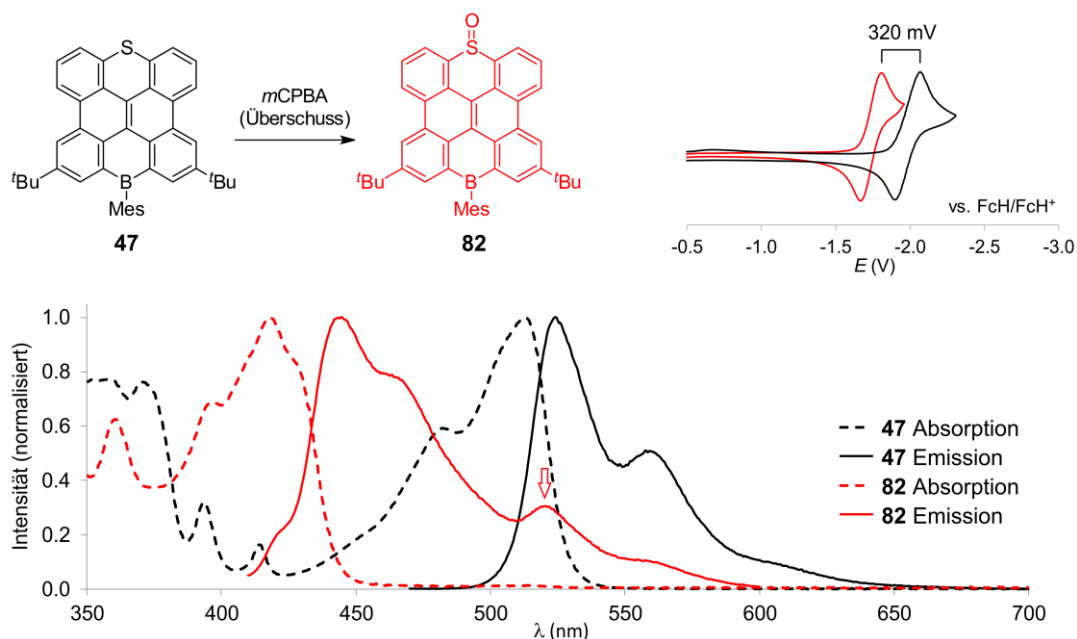


Abbildung 64: Auswirkungen der Oxidation von **47** mit *meta*-Chlorperbenzoesäure (*m*CPBA) auf die optoelektronischen Eigenschaften des PAKs. In stark verdünnten Lösungen von **82** fand die Rückreaktion zu **47** statt, wie an der markierten Emissionsbande zu erkennen ist.

Erstaunlicherweise reagiert **47** selbst mit einem Überschuss an *m*CPBA nur zu dem Sulfoxid **82** und nicht zum entsprechenden Sulfon (siehe Abbildungen 64 und 65). Durch Oxidation lässt sich daher die Elektronenaffinität von **47** nicht ganz so stark beeinflussen wie die von **80**. Die Auswirkungen der Sulfoxidbildung auf die Absorptions- und Emissionseigenschaften von **47** sind jedoch drastisch: Die Fluoreszenzwellenlänge wird durch die Oxidation von $\lambda_{\text{Em}} = 524$ nach 445 nm hypsochrom verschoben, außerdem zeigt das Sulfoxid **82** im Gegensatz zu **47** praktisch keine Solvatochromie. In Bezug auf Elektronenaffinität und Fluoreszenzwellenlänge ähnelt **82** dem 7,14-Dihydro-7,14-diborabisanthen **9**, welches ebenfalls zwei Akzeptorgruppen enthält ($E_{1/2}^{\text{Red1}}$: -1.85 (**9**), -1.74 V (**82**); λ_{Em} : 449 (**9**), 445 nm (**82**)). Die Lumineszenzquantenausbeute von **82** beträgt allerdings weniger als 20%, eine genaue Bestimmung wird dadurch erschwert, dass in stark verdünnten Lösungen ein messbarer Anteil der intensiv fluoreszierenden Verbindung **47** zurückgebildet wird. Dies deutet darauf hin, dass die Oxidation von **47** im Prinzip reversibel ist. Mit dem Auge ist die Reaktion zwischen **47** und dem Peroxid an einem Farbumschlag von Orange nach Hellgelb zu erkennen.

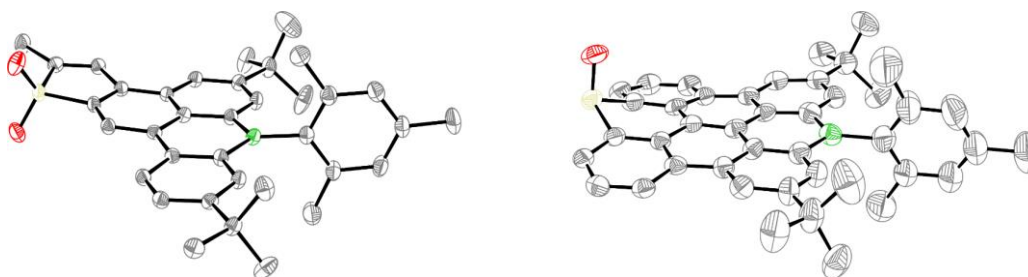


Abbildung 65: ORTEP-Darstellungen der Molekülstrukturen des Sulfons **81** und des Sulfoxids **82** im Festkörper. Die Aufenthaltswahrscheinlichkeit der thermischen Ellipsoide beträgt 50%

2.7 TADF-fähige Arylborane

Dipolare Moleküle, bei denen die π -Konjugation zwischen der Donor- und der Akzeptorsubstruktur eingeschränkt ist, zeigen in manchen Fällen thermisch angeregte, verzögerte Fluoreszenz (engl. *thermally activated delayed fluorescence*, TADF). Dieses Phänomen und seine Bedeutung für die organische Elektronik sind in Kapitel 1.2.4 näher beschrieben. Durch computergestützte (TD-)DFT-Rechnungen lässt sich abschätzen, ob ein entworfenes Molekül TADF zeigen könnte.¹⁰⁸ Es wurden die zwei Verbindungen **83** und **83a** entworfen, die sich als blaue TADF-Emitter zu eignen scheinen, da sie gemäß der Ergebnisse von (TD-)DFT-Rechnungen sowohl räumlich getrennte Grenzorbitale als auch nahezu energiegeliche S_1 - und T_1 -Anregungsenergien aufweisen (Abbildung 66). Sie unterscheiden sich lediglich durch die Dimethylmethylen-Brücke, die in **83** die zwei Phenylsubstituenten des Triarylamins miteinander verbindet und in einer koplanaren Anordnung fixiert. In der Folge ist das HOMO auf dieser Substruktur lokalisiert, während es sich im unteren Molekül auf die Arylbrücke zwischen dem Stickstoff- und dem Boratom ausdehnt. Die räumliche Trennung der Grenzorbitale ist ein Merkmal von TADF-Emittern, das die entscheidenden Eigenschaften ($\Delta E(S_1-T_1)$ und Fluoreszenzquantenausbeute) maßgeblich beeinflusst.¹⁰⁸ Da eine genaue Vorhersage der Moleküleigenschaften nur schwer möglich ist, sollten beide Zielstrukturen experimentell untersucht werden.

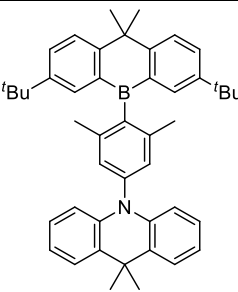
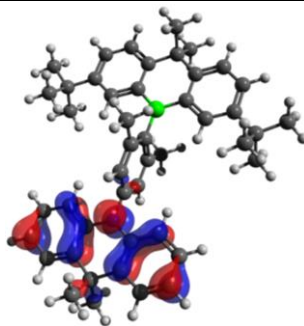
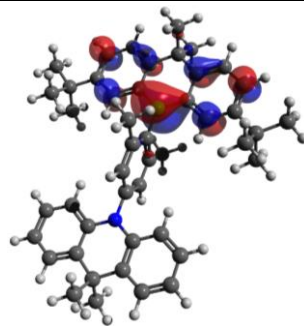
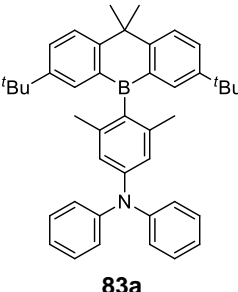
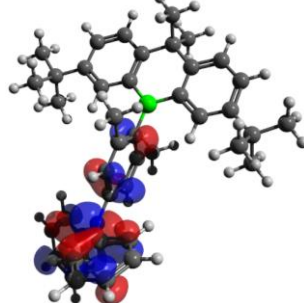
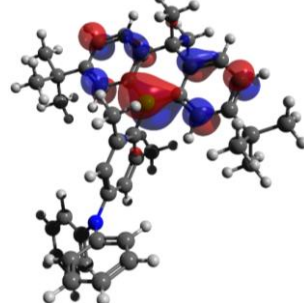
Molekülstruktur	HOMO	LUMO	$\Delta E(S_1-T_1)$
 83			0.002 eV
 83a			0.016 eV

Abbildung 66: Ergebnisse von (TD-)DFT-Rechnungen zur Analyse möglicher TADF-Emitter.⁴

Es wurde eine Syntheseroute ausgearbeitet, über die sich **83** und **83a** möglichst einfach herstellen lassen. Da schon eine einzelne Methylgruppe in Position 10 von 9,10-Dihydro-9-boraanthracen-Derivaten ausreichend Schutz gegen Nebenreaktionen an der Benzylposition bietet, wurde das in Abbildung 67 dargestellte Silan **24** als Startmaterial gewählt, welches bereitwillig eine Si/B-Austauschreaktion mit BBr_3 eingeht.¹¹⁸ Die Verbindungen **87/87a** sollten durch Deprotonierung und Reaktion mit Methyljodid in **83/83a** überführt werden.

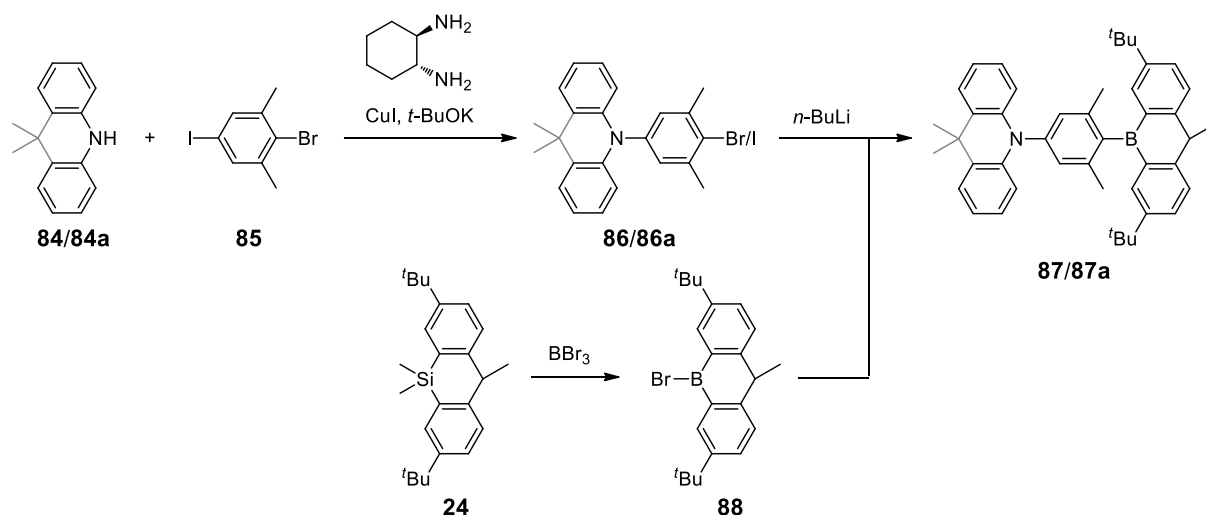


Abbildung 67: Schema zur Synthese zweier dipolarer B,N-Verbindungen (mit und ohne die graue Dimethylmethylenbrücke).

Das jeweilige Amin **84** oder **84a** wurde in Anlehnung an eine Literaturvorschrift für strukturell verwandte Triarylamine⁶³ durch eine *Ullmann*-Kupplung mit der Arylbrücke verbunden. Gleichzeitig dazu fand in einer Art aromatischer *Finkelstein*-Reaktion¹³⁵ bei einem Teil der Moleküle der Austausch von Brom gegen Iod statt, was jedoch für den folgenden Halogen/Lithium Austausch ohne Bedeutung war. Die lithiierten Verbindungen wurden anschließend jeweils zu einer Lösung des Bromborans **88** in Toluol gegeben, wobei in beiden Fällen blau fluoreszierende Lösungen entstanden. Leider zersetzten sich die Produkte **87** und **87a** bei Kontakt mit Luft. Als Schwachstelle wurde die exozyklische B–C-Bindung identifiziert, da entsprechende Fragmente säulenchromatographisch isoliert und mittels $^1\text{H-NMR}$ -Spektroskopie analysiert werden konnten. Bislang wurde keine geeignete Methode gefunden, um die reinen B,N-Verbindungen zu isolieren. Im $^1\text{H-NMR}$ -Spektrum (Abbildung 68) des Rohprodukts der Synthese von **87** sind jedoch die erwarteten Resonanzen erkennbar. Auch das Ergebnis der Massenspektrometrie zeigt eindeutig, dass das Zielmolekül gebildet wurde (Abbildung 69).

2. Übersicht der Experimente und Ergebnisse

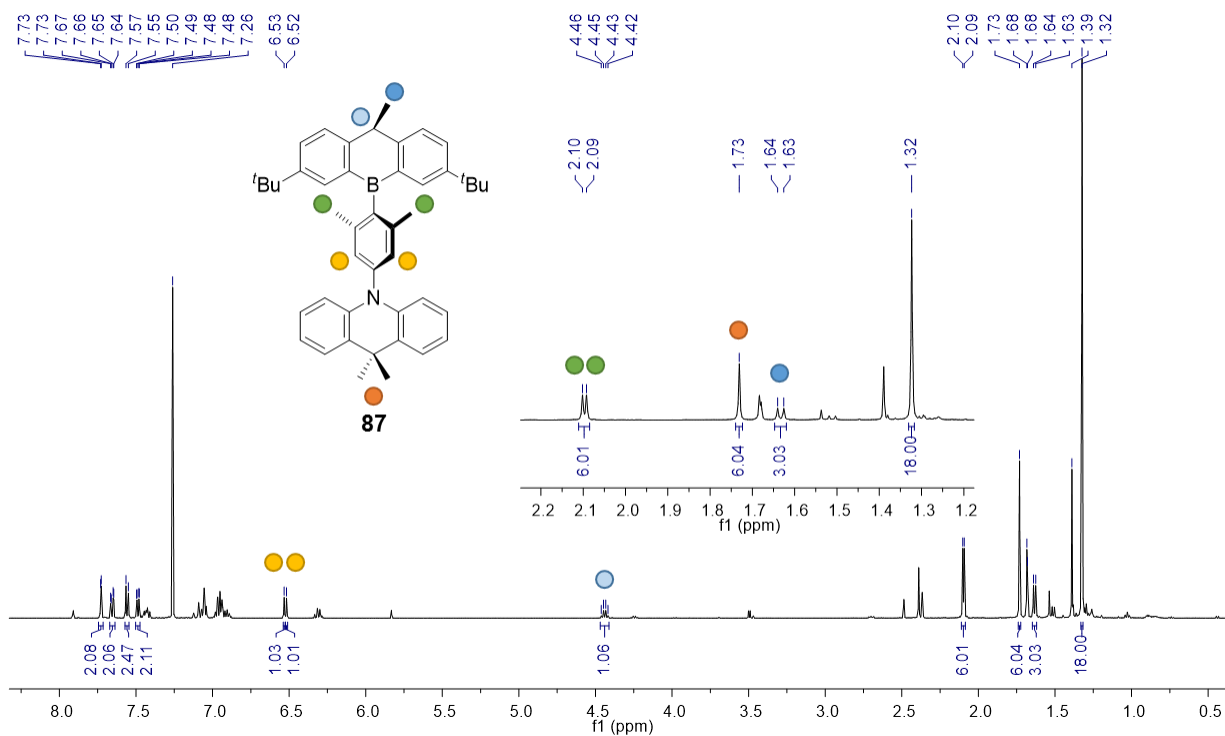


Abbildung 68: ^1H -NMR-Spektrum des Rohprodukts der Synthese von **87**. Aufgrund von Verunreinigungen konnten nicht alle aromatischen Resonanzen zugeordnet werden.

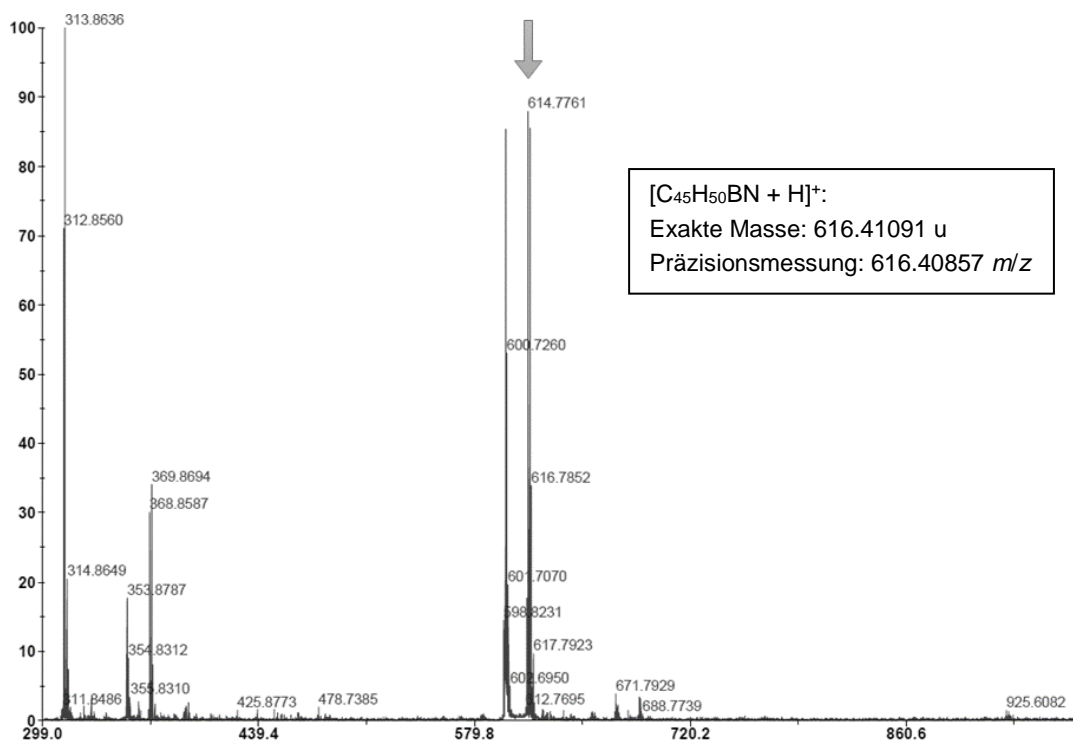


Abbildung 69: MALDI-Massenspektrum des Rohprodukts der Synthese von **87**. Die Masse des markierten Peaks wurde durch eine Präzisionsmessung exakt bestimmt.

3. Zusammenfassung

In der organischen Elektronik werden Moleküle mit konjugierten π -Elektronensystemen als Halbleiter und Lichtemitter eingesetzt. Für die Fabrikation fortschrittlicher elektronischer Bauelemente, wie z. B. organischer Leuchtdioden, werden Materialien mit besonderen optoelektronischen Eigenschaften benötigt. Die Stoffklasse der Arylamine ist für den Transport positiver Ladungen etabliert, da die exozyklischen Stickstoffatome Elektronenlöcher mesomer zu stabilisieren vermögen. Komplementär dazu sind auch Materialien für den Transport negativer Ladungen in der organischen Elektronik unverzichtbar. Zu diesem Zweck sollten borhaltige Verbindungen ideal geeignet sein, da das Element Bor weniger Valenzelektronen als Kohlenstoff besitzt und Arylborane daher im Vergleich zu den entsprechenden Kohlenwasserstoffen eine geringere Elektronendichte aufweisen. Als Halbleitermaterialien sind Arylborane jedoch nicht so weit verbreitet wie Arylamine, da die Instabilität vieler Vertreter gegenüber Luft und Feuchtigkeit sowie der Mangel an effizienten Synthesemethoden ihre Anwendung verzögert haben. Um geeignete organische Elektronenleiter bereitzustellen, ist die Entwicklung stabiler, π -konjugierter Borane erstrebenswert. Ansatzpunkte für diese Arbeit waren Erkenntnisse aus der vorangegangenen Masterarbeit, sowie Beispiele für hydrolysestabile Arylborane, welche in der jüngeren Vergangenheit von *M. Wagner et al.* und *S. Yamaguchi et al.* veröffentlicht wurden.

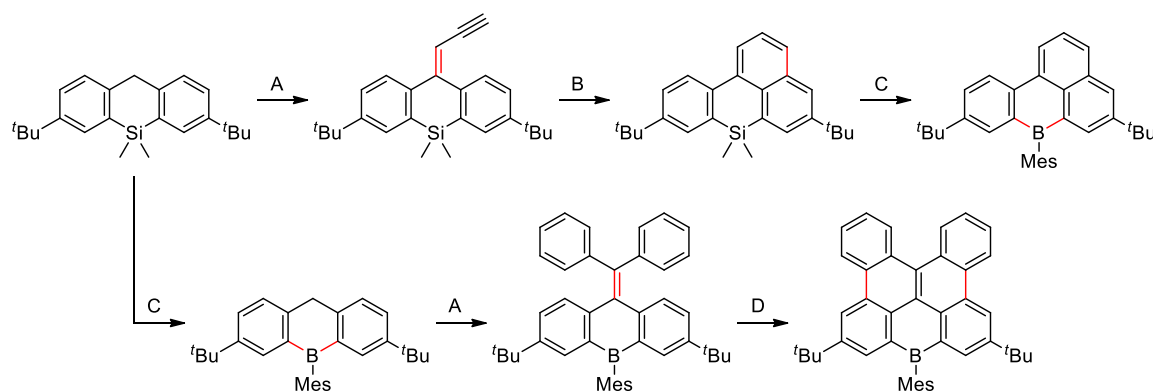


Abbildung 70: Beispiele für die Synthese borhaltiger PAKs (Schlüsselschritte: A: *Peterson*-Olefinierung, B: Ru-katalysierte Benzanellierung, C: Si/B-Austausch, D: Photozyklisierung; die durch die jeweilige Reaktion neu geknüpften Bindungen sind rot markiert).

Im Rahmen der vorliegenden Arbeit gelang die Entwicklung einer modularen Synthesestrategie, die einen vielseitigen Zugang zur Stoffklasse der borhaltigen polyzyklischen aromatischen Kohlenwasserstoffe (PAKs) ermöglicht (Abbildungen 70,71): Ausgehend von einem gut verfügbaren siliziumhaltigen Startmaterial und diversen, zum Großteil kommerziell erhältlichen, Carbonylverbindungen wurden mehr als zwanzig verschiedene Triarylborane dargestellt. Dabei wurde eine Auswahl spezieller Reaktionstypen nach den jeweiligen Erfordernissen in geeigneter Weise miteinander kombiniert. Zu diesen gehörte die *Peterson*-Olefinierung zum Aufbau drei- und vierfach substituierter Alkene, die Photozyklisierung der resultierenden Stilben-artigen Verbindungen, eine Ru(II)-katalysierte Reaktion zur Benzanellierung und der Silizium/Bor-

3. Zusammenfassung

Austausch mittels BBr_3 . An wichtigen Zwischenprodukten wurden Reaktivitätsstudien durchgeführt, um die Anwendungsmöglichkeiten und Einschränkungen dieser Synthesestrategie zu ergründen.

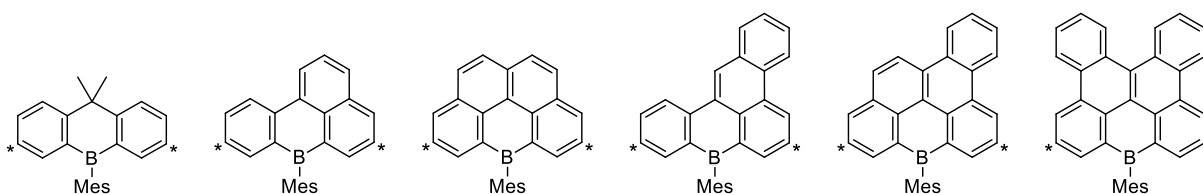


Abbildung 71: Arylborane mit unterschiedlich großem π -Elektronensystem. Mit Sternchen markierte Kohlenstoffatome tragen *tert*-Butylgruppen.

Um die Stabilität der Produkte gegenüber Luft und Feuchtigkeit zu gewährleisten, wurden die reaktiven Borzentren in bewährter Weise durch Einführung eines sterisch anspruchsvollen Mesitylsubstituenten kinetisch abgeschirmt. Die überwiegende Zahl der synthetisierten borhaltigen PAKs erwies sich als absolut unempfindlich gegenüber Wasser und konnte mit den gängigen Methoden der organischen Chemie (z. B. Säulenchromatographie an Kieselgel) gereinigt werden. Als Alternative zur sterischen Abschirmung wurde der Einbau des Boratoms in ein starres Molekülgerüst an einem Ausführungsbeispiel verwirklicht (Abbildung 72). Diese zweite Möglichkeit der Stabilisierung stellte sich in Bezug auf die Eigenschaften des Produkts als vergleichbar heraus, erforderte aber einen größeren synthetischen Aufwand und lieferte eine geringere Ausbeute über die gesamte Reaktionssequenz.

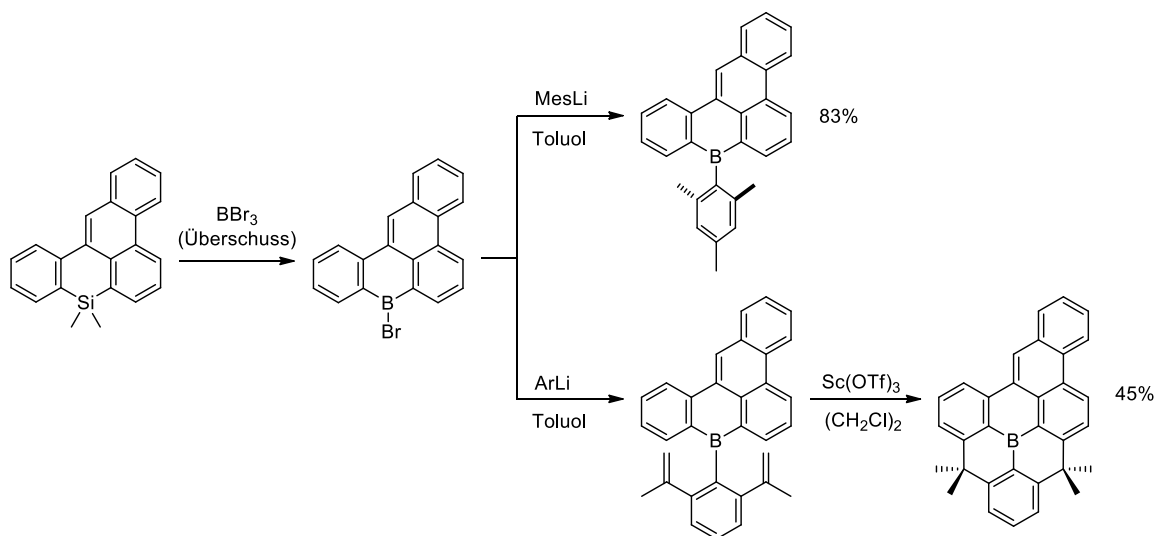


Abbildung 72: Synthese eines strukturell stabilisierten Triarylborans (unten) und einer vergleichbaren, mesitylgeschützten Verbindung (oben).

Die in dieser Arbeit dargestellten borhaltigen PAKs wurden mittels Röntgenkristallographie umfassend strukturell charakterisiert. Die intensiv genutzten Methoden Cyclovoltammetrie, UV/vis- und Fluoreszenzspektroskopie gewährten zusätzlich einen detaillierten Einblick in ihre elektronischen Strukturen. Die Synthese und systematische Variation der Moleküle führten zu neuen Erkenntnissen über grundlegende Struktur-Eigenschafts-Beziehungen. Insbesondere zeigten diese Vergleiche, dass in ladungsneutralen

Triarylboranen keine Delokalisation der π -Elektronen über das leere p-Orbital eines Boratoms stattfindet. Von entscheidender Bedeutung für die elektronische Struktur borhaltiger PAKs ist das Gerüst aus sp^2 -hybridisierten Kohlenstoffatomen: Wenn mindestens zwei der Arylsubstituenten am Boratom zu einem gemeinsamen Gefüge verbrückt sind, zeigen diese Verbindungen elektronische Übergänge im sichtbaren Bereich des elektromagnetischen Spektrums und in den meisten Fällen auch eine intensive Fluoreszenz. Des Weiteren besitzen diese borhaltigen PAKs eine hohe Elektronenaffinität und lassen sich elektrochemisch reversibel reduzieren. Damit erfüllen sie bedeutende Kriterien für eine mögliche Anwendung als Elektronenleiter. Von den Molekülen mit ausgedehntem π -Elektronensystem ließen sich manche zusätzlich reversibel oxidieren und zeichnen sich daher durch eine außergewöhnlich hohe elektrochemische Stabilität aus. An Arylboranen, deren Farbe sich durch externe Stimuli verändern lässt, wurden grundlegende Untersuchungen im Kontext der molekularen Sensorik durchgeführt. Einige der synthetisierten Verbindungen ändern ihr Absorptions- und Emissionsspektrum bei Kontakt mit Fluorid-Ionen, bei Oxidation integrierter Schwefelatome durch ein Carbonsäureperoxid (siehe Abbildung 73), bei elektrochemischer Reduktion oder in Abhängigkeit der Polarität ihrer Umgebung.

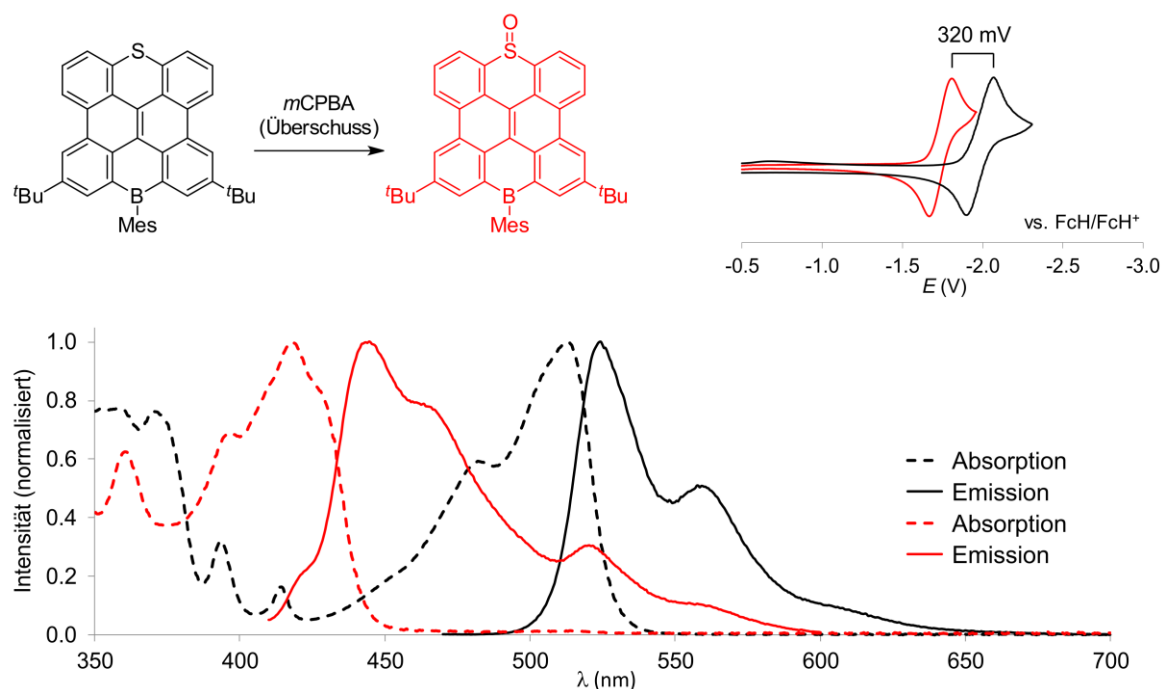


Abbildung 73: Beispiel für ein PAK, das unter geeigneten Reaktionsbedingungen seine Farbe ändert (*m*CPBA = *meta*-Chlorperbenzoesäure).

Die Ergebnisse dieser Arbeit wurden in vier Fachartikeln beschrieben und veröffentlicht (siehe Anhang). Sie können zu einem besseren Verständnis der elektronischen Eigenschaften borhaltiger PAKs beitragen und die Entwicklung neuer Halbleitermaterialien auf der Basis dieser Stoffklasse erleichtern.

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- 118 **Synthese von 2,7-Di-*tert*-butyl-9,9,10-trimethyl-9,10-dihydro-9-silaanthracen (24)**: In einem 100 mL Zweihalskolben wurde 2,7-Di-*tert*-butyl-9,9-dimethyl-9,10-dihydro-9-silaanthracen (4.15 g, 12.3 mmol) in Et₂O (60 mL) gelöst. Bei 0 °C wurde eine Lösung von *n*-BuLi (1.55 M, 8.75 mL, 13.6 mmol) zugegeben. Die rote Lösung wurde für 1 h zum Rückfluss erhitzt. Bei 0 °C wurde MeI (0.92 mL, 15 mmol) zugegeben und für 1 h bei Raumtemperatur gerührt. Es wurde eine wässrige NH₃-Lösung (25 gew%, 25 mL) zugegeben und für 1 h bei Raumtemperatur gerührt. Nach Zugabe von H₂O (50 mL) wurden die Phasen getrennt und die wässrige Phase mit Et₂O (2 × 40 mL) extrahiert. Die vereinten organischen Phasen wurden mit H₂O (2 × 50 mL) sowie ges. wässriger NaCl-Lösung (30 mL) gewaschen und mit MgSO₄ getrocknet. Das Lösungsmittel wurde unter vermindertem Druck entfernt und der Rückstand aus siedendem EtOH umkristallisiert. Ausbeute: 3.43 g (79%) farblose Kristalle. ¹H-NMR (500.2 MHz, CDCl₃): δ 7.60 (d, ⁴J_{H,H} = 2.2 Hz, 2H; H-4,5), 7.36 (dd, ³J_{H,H} = 8.1 Hz, ⁴J_{H,H} = 2.2 Hz, 2H; H-3,6), 7.26 (d, ³J_{H,H} = 8.1 Hz, 2H; H-1,8), 4.16 (q, ³J_{H,H} = 7.4 Hz, 1H; H-10), 1.49 (d, ³J_{H,H} = 7.4 Hz, 3H; CH₃ an C-10), 1.34 (s, 18H; *t*-Bu), 0.56 (s, 3H; CH₃ an Si), 0.47 ppm (s, 3H; CH₃ at Si). ¹³C{¹H}-NMR (125.8 MHz, CDCl₃): δ 149.2, 147.8, 133.8, 130.3 (C-4,5), 127.7 (C-1,8), 126.6 (C-3,6), 46.3 (C-10), 34.6 (*t*-Bu-C), 31.6 (*t*-Bu-CH₃), 30.7 (CH₃ at C-10), 1.6 (CH₃ at Si), -2.4 ppm (CH₃ an Si). ²⁹Si^{INEPT}-NMR (99.4 MHz, CDCl₃): δ -19.7 ppm. EA berechnet für C₂₄H₃₄Si: C 82.22, H 9.77; gefunden: C 81.96, H 9.91.

Synthese von 2,7-Di-*tert*-butyl-9-mesityl-10-methyl-9,10-dihydro-9-boraanthracen (22): In einem Schlenk-Kolben wurde 2,7-Di-*tert*-butyl-9,9,10-trimethyl-9,10-dihydro-9-silaanthracen (380 mg, 1.08 mmol) mit BBr₃ (0.8 mL, Überschuss) versetzt. Die entstandene Suspension wurde für 16 h bei Raumtemperatur gerührt. Überschüssiges BBr₃ wurde abkondensiert und der gelbe Rückstand für 2 h im Ölpumpenvakuum getrocknet. Es wurde Toluol (20 mL) zugegeben und die Lösung für 1 h bei 25 torr gerührt. Eine Lösung von MesMgBr (0.80 M, 2.0 mL, 1.6 mmol) wurde bei Raumtemperatur zugegeben. Nach dem Rühren für 1 h wurde ges. wässrige NaHCO₃-Lösung (30 mL), H₂O (30 mL) und Et₂O (40 mL) zugegeben. Die Phasen wurden getrennt und die wässrige Phase mit Et₂O (2 × 20 mL) extrahiert. Die vereinten organischen Phasen wurden mit H₂O (2 × 50 mL) sowie ges. wässriger NaCl-Lösung (30 mL) gewaschen und mit MgSO₄ getrocknet. Das Lösungsmittel wurde unter vermindertem Druck entfernt und der Rückstand durch eine Filtersäule (10 cm Kieselgel, *d* = 2 cm, Eluent Cyclohexan) gereinigt. Das Eluat wurde auf ein Volumen von 10 mL eingengt und gefriergetrocknet. Ausbeute: 315 mg (69%) farbloser Feststoff. ¹H-NMR (500.2 MHz, CDCl₃): δ 7.64 (d, ⁴J_{H,H} = 2.3 Hz, 2H; H-4,5), 7.59 (dd, ³J_{H,H} = 8.1 Hz, ⁴J_{H,H} = 2.3 Hz, 2H; H-3,6), 7.50 (d, ³J_{H,H} = 8.1 Hz, 2H; H-1,8), 6.92 (s, 1H; Mes-CH-*m*), 6.87 (s, 1H; Mes-CH-*m*), 4.38 (q, ³J_{H,H} = 7.3 Hz, 1H; H-10), 2.40 (s, 3H; Mes-CH₃-*p*), 2.01 (s, 3H; Mes-CH₃-*o*), 1.99 (s, 3H; Mes-CH₃-*o*), 1.59 (d, ³J_{H,H} = 7.3 Hz, 3H; CH₃ an C-10), 1.25 ppm (s, 18H; *t*-Bu). ¹³C{¹H}-NMR (125.8 MHz, CDCl₃): δ 151.2, 148.0, 140.2, 138.0, 137.8, 136.1, 135.6, 134.4 (C-4,5), 129.9 (C-3,6), 127.5 (C-1,8), 126.8 (Mes-CH-*m*), 126.7 (Mes-CH-*m*), 42.6 (C-10), 34.4 (Mes-CH₃-*p*), 31.4 (CH₃ an C-10), 31.4 (*t*-Bu-CH₃), 26.9, 22.8 (Mes-CH₃-*o*), 22.7 (Mes-CH₃-*o*), 21.4 ppm. ¹¹B-NMR (160.5 MHz, CDCl₃): δ 67 ppm (*h*₂ ≈ 1500 Hz). EA berechnet für C₃₁H₃₉B: C 88.14, H 9.31; gefunden: C 87.15, H 9.17.

Synthese von 2,7-Di-*tert*-butyl-9,9,10,10-tetramethyl-9,10-dihydro-9-silaanthracen (25): In einem Schlenk-Kolben wurde *t*-BuOK (670 mg, 6.0 mmol) und 2,7-Di-*tert*-butyl-9,9,10-trimethyl-9,10-dihydro-9-silaanthracen (1.5 g, 4.3 mmol) in THF (30 mL) gelöst. Bei -78 °C wurde eine *t*-BuLi-Lösung (1.55 M, 3.9 mL, 6.0 mmol) zugegeben, wobei sich die Lösung rot färbte. Nach dem Rühren für 1 h wurde bei -78 °C MeI (0.43 mL,

6.9 mmol) zugegeben. Die Lösung entfärbte sich. Nach dem Rühren für 1 h wurde das Kühlbad entfernt und eine wässrige NH_3 -Lösung (25 gew%, 5 mL) zugegeben. Es wurde für 1 h bei Raumtemperatur gerührt, dann H_2O (50 mL) zugegeben. Die Phasen wurden getrennt und die wässrige Phase mit Et_2O (2×50 mL) extrahiert. Die vereinten organischen Phasen wurden mit H_2O (2×100 mL) sowie ges. wässriger NaCl -Lösung (30 mL) gewaschen und mit MgSO_4 getrocknet. Das Lösungsmittel wurde unter vermindertem Druck entfernt und der Rückstand mittels Säulenchromatographie (10 cm Kieselgel, $d = 3$ cm, Eluent Cyclohexan, $R_f = 0.65$) gereinigt. Ausbeute: 1.25 g (80%) farbloser Feststoff. Das Produkt lässt sich auch aus EtOH umkristallisieren. $^1\text{H-NMR}$ (500.2 MHz, CDCl_3): δ 7.61 (d, $^4J_{\text{H,H}} = 2.4$ Hz, 2H; H-4,5), 7.56 (d, $^3J_{\text{H,H}} = 8.5$ Hz, 2H; H-1,8), 7.37 (dd, $^3J_{\text{H,H}} = 8.5$ Hz, $^4J_{\text{H,H}} = 2.4$ Hz, 2H; H-3,6), 1.73 (s, 6H; CH_3 an C-10), 1.34 (s, 18H; *t*-Bu), 0.53 ppm (s, 6H; SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz, CDCl_3): δ 152.9, 147.3, 134.9, 130.8 (C-4,5), 126.3 (C-3,6), 124.4 (C-1,8), 42.3, 34.4, 34.0 (CH_3 an C-10), 31.5 (*t*-Bu- CH_3), 0.33 ppm (SiMe_2). $^{29}\text{Si}^{\text{INEPT}}$ -NMR (99.4 MHz, CDCl_3): δ -20.0 ppm. EA berechnet für $\text{C}_{25}\text{H}_{36}\text{Si}$: C 82.35, H 9.95; gefunden: C 82.31, H 10.16.

Synthese von 2,7-Di-*tert*-butyl-9-mesityl-10,10-dimethyl-9,10-dihydro-9-boraanthracen (23): *Bemerkung:* Ein Si/B-Austausch an 2,7-Di-*tert*-butyl-9,9,10,10-tetramethyl-9,10-dihydro-9-silaanthracen mit BBr_3 (50 °C, 16 h) war nicht erfolgreich, es wurde nur Bis(4-*tert*-butylphenyl)dimethylmethan isoliert. *Stattdessen:* In einem Schlenk-Kolben wurde *t*-BuOK (45 mg, 0.40 mmol) in THF (8 mL) gelöst. Bei -78 °C wurde 2,7-Di-*tert*-butyl-9-mesityl-10-methyl-9,10-dihydro-9-boraanthracen zugegeben und die orangefarbige Lösung für 45 min gerührt. Es wurde MeI (28 μL , 0.45 mmol) zugegeben und die Temperatur langsam erhöht (10 °C h^{-1}). Nach 2 h wurde das Kältebad entfernt, ges. wässrige NaHCO_3 -Lösung (10 mL), H_2O (20 mL) und Et_2O (30 mL) zugegeben. Die Phasen wurden getrennt und die wässrige Phase mit Et_2O (30 mL) extrahiert. Die vereinten organischen Phasen wurden mit ges. wässriger NaCl -Lösung (2×30 mL) gewaschen und mit MgSO_4 getrocknet. Das Lösungsmittel wurde unter vermindertem Druck entfernt und der Rückstand durch eine Filtersäule (5 cm Kieselgel, $d = 2$ cm, Eluent Cyclohexan) gereinigt. Ausbeute: 87 mg (70%) hellgelber Feststoff. $^1\text{H-NMR}$ (500.2 MHz, CDCl_3): δ 7.72 (m, 2H), 7.66-7.64 (m, 4H), 6.88 (s, 2H; Mes-CH-*m*), 2.39 (s, 3H; Mes- CH_3 -*p*), 1.97 (s, 6H; Mes- CH_3 -*o*), 1.77 (s, 6H; CH_3 an C-10), 1.25 ppm (s, 18H; *t*-Bu). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz, CDCl_3): δ 154.7 (C-4a,10a), 147.7 (C-2,7), 140.6 (Mes-C-*i*), 138.2 (Mes-C-*o*), 136.2 (Mes-C-*p*), 134.9 (C-8a,9a), 134.8, 130.5, 126.9 (Mes-CH-*m*), 126.3, 41.8 (C-10), 34.4 (*t*-Bu-C), 34.2 (CH_3 at C-10), 31.4 (*t*-Bu- CH_3), 23.0 (Mes- CH_3 -*o*), 21.5 ppm (Mes- CH_3 -*p*). $^{11}\text{B-NMR}$ (160.5 MHz, CDCl_3): δ 66 ppm ($h_{1/2} \approx 1500$ Hz). EA berechnet für $\text{C}_{32}\text{H}_{41}\text{B}$: C 88.06, H 9.47; gefunden: C 88.19, H 9.46. UV/vis (Cyclohexan): 283 (34600), 308 nm (8800 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$). Fluoreszenz (Cyclohexan, $\lambda_{\text{Ex}} = 283$ nm, 25 °C): 408 nm ($\Phi_{\text{PL}} = 17\%$).

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- 120 **Synthese von 1,4-Bis((2,7-di-*tert*-butyl-9,9-dimethyl-9,10-dihydro-9-silaanthracen-10-yliden)methyl)-benzol (49):** In einem Zweihalskolben mit Rückflusskühler wurde 2,7-Di-*tert*-butyl-9,9-dimethyl-10-(trimethyl)silyl-9,10-dihydro-9-silaanthracen (1.00 g, 2.45 mmol) in Et_2O (20 mL) gelöst. Es wurde eine *n*-BuLi-Lösung (1.54 M, 1.6 mL, 2.5 mmol) zugegeben und die rote Lösung für 1 h zum Rückfluss erhitzt. Es wurde Terephthalaldehyd (164 mg, 1.22 mmol) zugegeben und für 1 h zum Rückfluss erhitzt. Es wurde ges. wässrige NaHCO_3 -Lösung (30 mL), H_2O (30 mL) und Et_2O (30 mL) zugegeben. Die Phasen wurden getrennt und die wässrige Phase mit Et_2O (50 mL) extrahiert. Die vereinten organischen Phasen wurden mit H_2O (2×60 mL) sowie ges. wässriger NaCl -Lösung (30 mL) gewaschen und mit MgSO_4 getrocknet. Das Lösungsmittel wurde unter vermindertem Druck entfernt, der Rückstand in *i*-PrOH suspendiert (Ultraschallbad), durch Filtration isoliert und getrocknet. Ausbeute: 0.83 g (88%) hellgelb-grüner Feststoff. $^1\text{H-NMR}$ (500.2 MHz, CDCl_3): δ 7.62-7.60 (s, 4H), 7.58 (d, $^4J_{\text{H,H}} = 2.0$ Hz, 2H), 7.41 (dd, $^3J_{\text{H,H}} = 8.2$ Hz, $^4J_{\text{H,H}} = 1.9$ Hz, 2H), 7.28 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 2H), 7.14 (dd, $^3J_{\text{H,H}} = 8.2$ Hz, $^4J_{\text{H,H}} = 1.8$ Hz, 2H), 7.04 (s, 4H), 6.80 (s, 2H), 1.34 (s, 18H), 1.31 (s, 18H), 0.51 ppm (br, 12H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz, CDCl_3): δ 149.0, 148.5, 146.9, 141.6, 136.3, 136.3, 134.7, 129.3, 129.3, 129.2, 128.8, 126.6, 125.7, 125.0, 34.7, 34.7, 31.6, 31.6, -3.2 ppm. $^{29}\text{Si}^{\text{INEPT}}$ -NMR (99.4 MHz, CDCl_3): δ -17.6 ppm. EA berechnet für $\text{C}_{54}\text{H}_{66}\text{Si}_2$: C 84.09, H 8.63; gefunden: C 83.66, H 8.62.

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5. Anhang

5.1 Ausgewählte Veröffentlichungen

5.1.1 Eigene Anteile an den ausgewählten Veröffentlichungen

- I) *Boron-Containing Polycyclic Aromatic Hydrocarbons: Facile Synthesis of Stable, Redox-Active Luminophores* (von Valentin M. Hertz, Michael Bolte, Hans-Wolfram Lerner und Matthias Wagner):

Sämtliche präparativen Arbeiten, NMR-, UV/vis- und Fluoreszenzspektroskopie, Cyclovoltammetrie, Coulometrie.

- II) *Ru-Catalyzed Benzannulation Leads to Luminescent Boron-Containing Polycyclic Aromatic Hydrocarbons* (von Valentin M. Hertz, Hans-Wolfram Lerner und Matthias Wagner):

Sämtliche präparativen Arbeiten, NMR-, UV/vis- und Fluoreszenzspektroskopie, Cyclovoltammetrie.

- III) *En Route to Stimuli-Responsive Boron-, Nitrogen-, and Sulfur-Doped Polycyclic Aromatic Hydrocarbons* (von Valentin M. Hertz, Julian G. Massoth, Michael Bolte, Hans-Wolfram Lerner und Matthias Wagner):

Großteil der präparativen Arbeiten, NMR-, UV/vis- und Fluoreszenzspektroskopie, Cyclovoltammetrie.

- IV) *Steric Shielding vs Structural Constraint in a Boron-Containing Polycyclic Aromatic Hydrocarbon* (von Valentin M. Hertz, Naoki Ando, Masato Hirai, Michael Bolte, Hans-Wolfram Lerner, Shigehiro Yamaguchi und Matthias Wagner):

Sämtliche präparativen Arbeiten, NMR-, UV/vis- und Fluoreszenzspektroskopie, Cyclovoltammetrie, Fluorid-Titrationen.

5.1.2 Boron-Containing Polycyclic Aromatic Hydrocarbons: Facile Synthesis of Stable, Redox-Active Luminophores

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Supporting Information

Boron-Containing Polycyclic Aromatic Hydrocarbons: Facile Synthesis of Stable, Redox-Active Luminophores**

*Valentin M. Hertz, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner**

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Table of contents:

1. General experimental procedures	S2
2. Nomenclature	S3
3. Additional remarks	S4
4. Syntheses, purification methods and analytical data	S5
5. Plots of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra	S25
6. UV/Vis absorption and emission spectra	S49
7. Plots of cyclic voltammograms	S53
8. Spectroelectrochemistry on 12	S57
9. X-ray crystal structure analyses	S58
10. References	S72

1. General experimental procedures

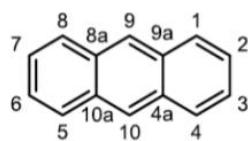
If not stated otherwise, all reactions and manipulations were carried out under an atmosphere of dry nitrogen using Schlenk techniques or in an inert-atmosphere glovebox. C₆H₆, toluene, Et₂O, and THF were distilled from Na/benzophenone prior to use. CH₂Cl₂, Me₃SiCl, and Me₂SiCl₂ were distilled from CaH₂. BBr₃ was stored over Hg. The starting material, bis(4-*tert*-butylphenyl)methane, was either prepared from diphenylmethane by Friedel-Crafts alkylation^[S1] or purchased from Alfa Aesar (99 %). Bis(2-bromo-4-*tert*-butylphenyl)methane (**S2**) was synthesized according to literature procedures.^[S1]

NMR spectra were recorded at 300 K using the following spectrometers: Bruker DPX-250, AM-250, Avance-300, Avance-400, or Avance-500. Chemical shift values are referenced to (residual) solvent signals (¹H/¹³C{¹H}; CDCl₃: δ = 7.26/77.16 ppm, C₆D₆: δ = 7.16/128.06 ppm) or external BF₃·Et₂O (¹¹B{¹H}; 0.00 ppm), Si(CH₃)₄ (²⁹Si INEPT: 0.00 ppm), and CFCl₃ (¹⁹F: 0.00 ppm). Abbreviations: s = singlet, d = doublet, t = triplet, vt = virtual triplet, q = quartet, quint = quintet, m = multiplet, br. = broad, n.o. = not observed, n.r. = multiplet expected in the ¹H NMR spectrum but not resolved, Th = 2-thienyl. Resonances of carbon atoms attached to boron atoms were typically broadened and sometimes not observed due to the quadrupolar relaxation of boron. Boron resonances of triarylborane compounds were typically very broad (*h*_{1/2} > 1500 Hz) and only observed in highly concentrated samples.

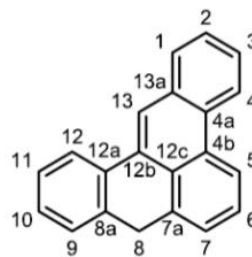
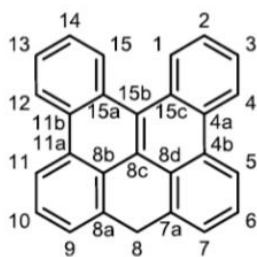
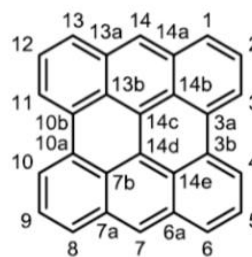
For photochemical reactions, a medium pressure Hg vapor lamp was used (Heraeus Noblelight; TQ 150, 150 W). UV/Vis absorption spectra were recorded at room temperature using a Varian Cary 50 Scan UV/Vis spectrophotometer. Photoluminescence (PL) spectra were recorded at room temperature using a Jasco FP-8300 spectrofluorometer equipped with a calibrated Jasco ILF-835 100 mm diameter integrating sphere and analyzed using the Jasco FWQE-880 software. For PL quantum yield (QY) measurements each sample was carefully degassed with argon using an injection needle and a septum-capped cuvette. Under these conditions, the QY of the fluorescence standard 9,10-diphenylanthracene was determined as 96 % (lit.: 97 %)^[S2]. For all QY measurements, at least three samples of different concentrations were used (range between 10⁻⁵ and 10⁻⁷ mol L⁻¹). Due to self-absorption, slightly lower QYs were observed at higher concentrations. This effect was corrected by applying a method reported by Bardeen *et al.*, which improved QYs slightly (4 % at most).^[S3] Cyclic voltammetry (CV) measurements were performed in a glovebox at room temperature in a one-chamber, three-electrode cell using an EG&G Princeton Applied Research 263A potentiostat. A platinum disk electrode (2.00 mm diameter) was used as the working electrode with a platinum wire counter electrode and a silver wire reference electrode, which was coated with AgCl by immersion into HCl/HNO₃ (3:1). Prior to measurements, the solvent (CH₂Cl₂) was dried as described above and additionally degassed with argon. [*n*Bu₄N][PF₆] was employed as the supporting electrolyte (0.1 mol L⁻¹). All potential values were referenced against the FcH/FcH⁺ redox couple (FcH = ferrocene; *E*_{1/2} = 0 V). Scan rates were varied between 100 and 400 mV s⁻¹. High-resolution mass spectra were measured in positive mode using a Thermo Fisher Scientific MALDI LTQ Orbitrap XL and 2,5-dihydroxybenzoic acid as the matrix. Exact masses were calculated based on the predominant combination of natural isotopes. Combustion analyses were performed by the microanalytical laboratory of the Goethe-University Frankfurt.

2. Nomenclature

Assignment of NMR signals: The same numbering schemes as for the all-carbon compounds (see below) were employed for their 9-silicon- or 9-boron-doped congeners.



anthracene

*8H*-benzo[*gh*]tetraphene*8H*-benzo[*gh*]naphtho[1,2,3,4-*pqr*]tetraphenephenanthro[1,10,9,8-*opqra*]perylene

For reasons of simplification, we will refer to phenanthro[1,10,9,8-*opqra*]perylene as bisanthene, which is also a common name for this molecule.

3. Additional remarks

3.1 General synthesis strategy

All synthesis sequences are based on the same key transformations, i.e., a Peterson olefination,^[S4] a photocyclization,^[S5] and an Si-B exchange^[S6] reaction (cf. Schemes 2, 3 in the main paper). After an evaluation of several methods for the olefination of ketone **3** (among them the McMurry reaction,^[S7] the Wittig reaction,^[S7] and diazo-thione coupling^[S8]), the Peterson olefination turned out to be the method of choice, because it furnished the challenging, sterically encumbered olefin **10** in 54% yield. The strategy for the subsequent dehydrogenative C–C-coupling steps has to account for the heteroatom bridges. The Scholl reaction,^[S9] and related methods such as DDQ/H⁺,^[S10] tend to fail not only for electron-poor, boron-doped species, but also for acid-sensitive, silicon-containing intermediates. The twofold stilbene-type photocyclization of **10** to **11**, however, greatly benefits from the heteroatom bridges, as they assist in the appropriate preorganization of the *peri*-hydrogen atoms. Parent dibenzo[*g,p*]chrysene, which lacks the bridging elements, cannot be obtained through photocyclization of tetraphenylethene.^[S10a]

Overcrowded bistricyclic enes, such as **10** (Scheme 3), are forced to adopt strained, distorted conformations. Proton NMR spectroscopy provides a useful diagnostic tool to elucidate the character of the out-of-plane deformation^[S10b], which is a critical issue. The *peri*-hydrogen atoms on both sides of the central double bond of **10** are comparatively well shielded (6.65 ppm), thereby indicating the *anti*-folded solid-state conformation to persist also in solution.

3.2 Comparison of **12** with bisanthene, bisanthenequinone and dibenzo[*g,p*]chrysene

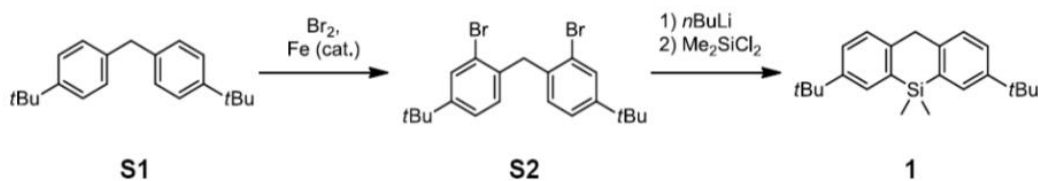
Table S1: UV/Vis absorption and emission maxima of **12** and related compounds.

compound	solvent	λ_{abs} (nm)	λ_{em} (nm)
bisanthene ^a	C ₆ H ₆	685	705
7,14-bisanthenequinone ^b	H ₂ SO ₄	605	632
7,14-bisanthenequinone ^b	CH ₂ Cl ₂	442	469
7,14-diborabisanthene (12) ^c	C ₆ H ₁₂	442	449
dibenzo[<i>g,p</i>]chrysene ^[S11]	CH ₂ Cl ₂	351	395

^a7,14-dimesitylbisanthene^[S12]; ^b2,3,9,10-Tetrahexyl-7,14-bisanthenequinone^[S13];

^c7,14-dimesityl-7,14-dihydro-7,14-diborabisanthene

4. Syntheses, purification methods and analytical data



Synthesis of 1: The following synthesis protocol is adapted from a protocol developed by S. Yamaguchi *et al.* for the synthesis of 9,9-dimethyl-9,10-dihydro-9-silaanthracene.^[S14]

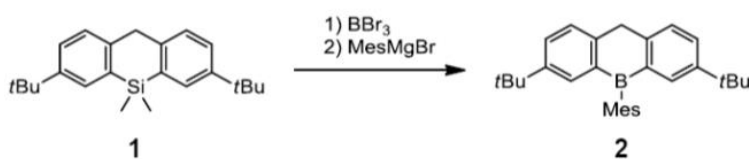
S2 (12.42 g, 28.34 mmol) was placed in a 500 mL 3-necked round-bottom flask equipped with a condenser and two dropping funnels and dissolved in Et₂O (200 mL). A solution of *n*BuLi in *n*-hexane (1.51 M; 40.0 mL, 60.4 mmol) was added dropwise while stirring at 0 °C. After the addition was complete, the mixture was heated to reflux temperature for 1 h. A solution of Me₂SiCl₂ (4.80 mL, 5.14 g, 39.8 mmol) in Et₂O (10 mL) was added dropwise while stirring at 0 °C, whereupon a colorless precipitate formed. The slurry was heated to reflux temperature for 30 min, allowed to cool to room temperature again, and was quenched by adding a saturated aqueous NaHCO₃ solution (50 mL) and H₂O (50 mL). The aqueous layer was separated and extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with H₂O (2 × 100 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (5 cm silica gel, *n*-hexane:EtOAc = 10:1). After removal of the solvent, the product was obtained as a pale yellow oil (9.85 g, 103%), which still contained minor impurities, but was already suitable for subsequent reactions. Compound **1** can be obtained as a colorless, analytically pure crystalline solid from concentrated solutions in *n*-hexane.

¹H NMR (400.1 MHz, CDCl₃): δ 7.62 (d, ⁴J(H,H) = 2.1 Hz, 2H; H-1,8), 7.34 (dd, ³J(H,H) = 8.0 Hz, ⁴J(H,H) = 2.1 Hz, 2H; H-3,6), 7.26 (d, ³J(H,H) = 8.0 Hz, 2H; H-4,5), 4.07 (s, 2H, H-10), 1.34 (s, 18H; *t*Bu-CH₃), 0.50 (s, 6H; SiMe₂)

¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 148.2 (C-2,7), 143.4 (C-4a,10a), 135.5 (C-8a,9a), 129.8 (C-1,8), 127.7 (C-4,5), 126.3 (C-3,6), 40.6 (C-10), 34.6 (*t*Bu-C), 31.6 (*t*Bu-CH₃), -2.7 (SiMe₂)

²⁹Si NMR (79.5 MHz, CDCl₃): δ -18.1

EA (%): Calculated for C₂₃H₃₂Si [336.59]: C 82.07, H 9.58; found: C 82.26, H 9.14



Synthesis of 2: Compound **1** (4.00 g, 11.9 mmol) was placed in a thoroughly flame-dried Schlenk tube equipped with a dropping funnel and dissolved in neat BBr₃ (3 mL, added through the tap of the Schlenk tube via a syringe while maintaining positive nitrogen pressure); room temperature was maintained by means of a water bath. The mixture was stirred for 16 h before excess BBr₃ was removed from the red solution under reduced pressure to obtain a dark solid. Toluene (20 mL) was added and the resulting suspension was stirred at 25 torr for 1 h to remove residual BBr₃ (the volume of the solution decreases only slightly). The dropping funnel was charged with

a solution of MesMgBr in THF (0.87 M; 16.4 mL, 14.3 mmol), which was added dropwise at room temperature over a period of 30 min. The color of the mixture changed from red to yellow. After stirring for 1 h, the reaction mixture was quenched with MeOH (3 mL) and all volatiles were removed under reduced pressure. The orange residue was parted between H₂O and cyclohexane, the organic layer was separated, and the solvent was evaporated *in vacuo*. Colored impurities were removed by column chromatography (8 cm silica gel, cyclohexane). The colorless eluate was concentrated to a volume of 20 mL and freeze-dried to obtain the solid product, which contained only trace amounts of mesitylene. Yield: 3.31 g (8.10 mmol, 68%) The product is not long-term stable and turns orange when stored under ambient atmosphere.

¹H NMR (500.2 MHz, CDCl₃): δ 7.71 (n.r., 2H; H-1,8), 7.63 (dd, ³J(H,H) = 8.1 Hz, ⁴J(H,H) = n.r. 2H; H-3,6), 7.51 (d, ³J(H,H) = 8.1 Hz, 2H; H-4,5), 6.90 (s, 2H; Mes-CH), 4.49 (s, 2H; H-10), 2.41 (s, 3H; Mes-CH₃-*p*), 1.98 (s, 6H; Mes-CH₃-*o*), 1.27 (s, 18H; *t*Bu-CH₃)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 148.2, 145.0, 140.2, 138.2, 136.6, 136.3, 134.6 (C-1,8), 129.9 (C-3,6), 127.8 (C-4,5), 126.9 (Mes-CH), 37.5 (C-10), 34.5 (*t*Bu-C), 31.5 (*t*Bu-CH₃), 23.0 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

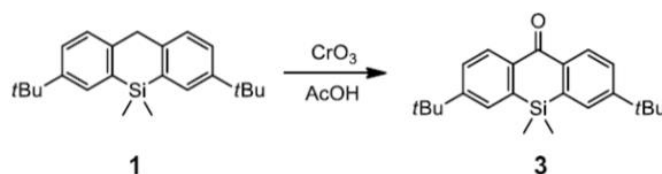
¹¹B NMR (160.5 MHz, CDCl₃): δ 66 (*h*_{1/2} ≈ 1500 Hz)

EA (%): Calculated for C₃₀H₃₇B [408.43]: C 88.22, H 9.13; found: C 87.91, H 9.12

HRMS: Calculated *m/z* for C₃₀H₃₆B: 407.29099, found: 407.29021

UV/Vis (cyclohexane): λ_{max} (ε) = 324 (7000), 282 nm (30000)

Fluorescence (cyclohexane, λ_{Ex} = 280 nm): λ_{max} = 395 nm; Φ_{PL} = <10%



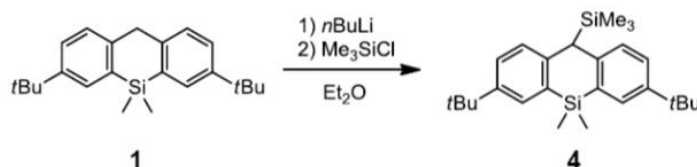
Synthesis of 3: CrO₃ (4.4 g, 44 mmol) was added to a solution of **1** (13.58 g, 40.35 mmol) in glacial acetic acid (100 mL) under ambient atmosphere (1-necked round-bottom flask, condenser). The stirred reaction mixture was heated to 70 °C for 1 h, cooled, and poured into a stirred mixture of *n*-hexane (100 mL) and H₂O (200 mL). The aqueous layer was separated and extracted with *n*-hexane (2 × 100 mL). The combined organic layers were washed with H₂O (2 × 150 mL), dried over Na₂SO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure to obtain the crude product as a brown oil. Yield: 12.8 g (36.5 mmol, 90 %) Colored impurities can be removed by column chromatography (silica gel, *n*-hexane:EtOAc 25:1, TLC: *R*_f = 0.4); recrystallization of **3** from *n*-hexane yields colorless single crystals. Yield: The yields of analytically pure **3** varied from batch to batch between 30-50%.

¹H NMR (400.1 MHz, CDCl₃): δ 8.39 (d, ³J(H,H) = 8.4 Hz, 2H; H-4,5), 7.67 (d, ⁴J(H,H) = 2.0 Hz, 2H; H-1,8), 7.61 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 2.0 Hz, 2H; H-3,6), 1.40 (s, 18H; *t*Bu-CH₃), 0.52 (s, 6H; SiMe₂)

¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 187.6 (C-10), 154.9 (C-2,7), 139.0 (C-8a,9a), 138.8 (C-4a,10a), 129.7 (C-1,8 or 4,5), 129.6 (C-1,8 or 4,5), 127.5 (C-3,6), 35.2 (*t*Bu-C), 31.3 (*t*Bu-CH₃), -1.1 (SiMe₂)

²⁹Si NMR (59.6 MHz, CDCl₃): δ -23.7

EA (%): Calculated for C₂₃H₃₀OSi [350.57]: C 78.80, H 8.63; found: C 78.68, H 8.78



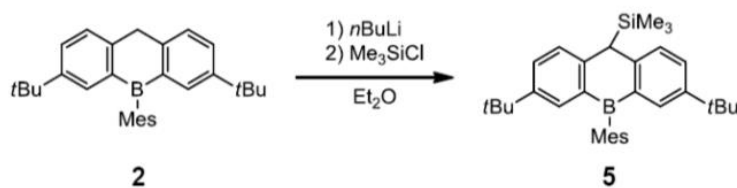
Synthesis of 4: Compound **1** (2.01 g, 5.97 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (40 mL). A solution of *n*BuLi in *n*-hexane (1.6 M; 4.1 mL, 6.6 mmol) was added via a syringe at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 1 h, whereupon it turned red. The mixture was cooled to 0 °C, Me₃SiCl (1.0 mL, 0.86 g, 7.9 mmol) was added dropwise while stirring, and the resulting mixture was heated to reflux temperature for 1.5 h. The suspension obtained was allowed to cool to room temperature and quenched by adding a saturated aqueous NaHCO₃ solution (40 mL). The transparent layers were separated and the aqueous layer was extracted with Et₂O (2 × 30 mL). The combined organic layers were washed with H₂O (2 × 50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. Colored impurities were removed by column chromatography (10 cm silica gel, *n*-hexane, TLC: R_f = 0.4). The product was obtained as a colorless oil which crystallized on standing. Yield: 1.93 g (4.72 mmol, 79%).

¹H NMR (400.1 MHz, CDCl₃): δ 7.53 (d, ⁴J(H,H) = 2.1 Hz, 2H; H-1,8), 7.28 (dd, ³J(H,H) = 8.2 Hz, ⁴J(H,H) = 2.1 Hz, 2H; H-3,6), 7.01 (d, ³J(H,H) = 8.2 Hz, 2H; H-4,5), 3.90 (s, 1H; H-10), 1.33 (s, 18H; *t*Bu-CH₃), 0.46 (s, 3H; SiMe₂), 0.42 (s, 3H; SiMe₂), -0.15 (s, 9H; SiMe₃)

¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 146.4 (C-2,7), 144.8 (C-4a,10a), 131.7 (C-8a,9a), 130.4 (C-1,8), 127.8 (C-4,5), 125.8 (C-3,6), 46.2 (C-10), 34.4 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 0.7 (SiMe₂), 0.6 (SiMe₂), -1.4 (SiMe₃)

²⁹Si NMR (59.6 MHz, CDCl₃): δ 5.1 (SiMe₃), -19.5 (SiMe₂)

EA (%): Calculated for C₂₆H₄₀Si₂ [408.77]: C 76.40, H 9.86; found: C 77.18, H 9.89



Synthesis of 5: Compound **2** (3.25 g, 7.96 mmol) was placed in a 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (50 mL). *n*BuLi in *n*-hexane (1.56 M; 6.6 mL, 10 mmol) was added via a syringe at 0 °C. The mixture, which immediately turned red, was warmed to room temperature and stirred for 30 min. Me₃SiCl (1.5 mL, 1.3 g, 12 mmol) was added via a syringe and the reaction mixture was heated to reflux temperature for 5.5 h, whereupon the red color faded. After quenching with a saturated aqueous NaHCO₃ solution (50 mL), the aqueous layer was separated and extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with H₂O (50 mL) and brine (50 mL), dried over MgSO₄, and filtered. All volatiles were

removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (8 cm silica gel, cyclohexane). The colorless eluate was concentrated to a volume of 30 mL and freeze-dried to obtain the solid product. Yield: 3.51 g (7.30 mmol, 92%).

¹H NMR (500.2 MHz, CDCl₃): δ 7.68 (n.r., 2H; H-1,8), 7.51 (dd, ³J(H,H) = 8.2 Hz, ⁴J(H,H) = n.r., 2H; H-3,6), 7.33 (d, ³J(H,H) = 8.2, 2H; H-4,5), 6.90 (s, 1H; Mes-CH), 6.88 (s, 1H; Mes-CH), 4.39 (s, 1H; H-10), 2.40 (s, 3H; Mes-CH₃-*p*), 2.11 (s, 3H; Mes-CH₃-*o*), 1.81 (s, 3H; Mes-CH₃-*o*), 1.24 (s, 18H; *t*Bu-CH₃), -0.15 (s, 9 H; SiMe₃)

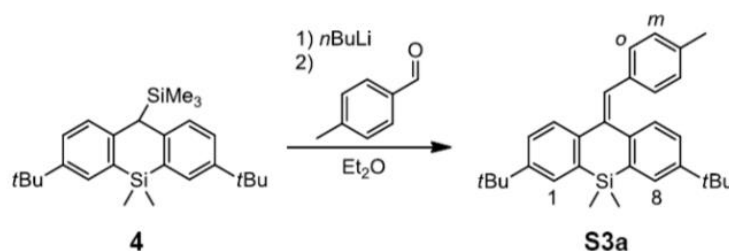
¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 148.7 (C-4a,10a), 146.5 (C-2,7), 140.7 (Mes-C-*i*), 139.1 (Mes-C-*o*), 138.1 (Mes-C-*o*), 136.3 (C-8a,9a), 136.0 (Mes-C-*p*), 134.7 (C-1,8), 128.6 (C-3,6), 127.3 (C-4,5), 127.0 (Mes-CH-*m*), 126.8 (Mes-CH-*m*), 47.0 (C-10), 34.4 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 23.7 (Mes-CH₃-*o*), 23.0 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*), -1.7 (SiMe₃)

¹¹B NMR (160.5 MHz, CDCl₃): δ 65 (*h*_{1/2} \approx 1500 Hz)

²⁹Si NMR (99.5 MHz, CDCl₃): δ 7.5

EA (%): Calculated for C₃₃H₄₅BSi [480.61]: C 82.47, H 9.44; found: C 82.70, H 9.62

HRMS: Calculated *m/z* for C₃₃H₄₄BSi: 479.33059, found: 479.32982



Synthesis of S3a: Compound **4** (1.00 g, 2.45 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (20 mL). *n*BuLi in *n*-hexane (1.61 M; 1.52 mL, 2.45 mmol) was added at room temperature. After the addition was complete, the reaction mixture was heated to reflux temperature for 1.5 h, whereupon its color changed to red. A solution of 4-methylbenzaldehyde (0.32 mL, 0.33 g, 2.7 mmol) in Et₂O (5 mL) was added at 0 °C via a syringe, whereupon the red color faded. After the addition was complete, the mixture was heated to reflux temperature for 30 min. A saturated aqueous NaHCO₃ solution (30 mL) was added, followed by H₂O (50 mL), and Et₂O (20 mL). The aqueous layer was separated and extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with H₂O (50 mL) and brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (10 cm silica gel, cyclohexane, TLC: R_f = 0.28). The solvent was removed under reduced pressure to obtain the product as a colorless solid (co-evaporation with EtOH (10 mL) is recommended). Yield: 1.02 g (2.32 mmol, 95 %). If traces of starting materials are still present in the sample, it can be purified further by sonication in cold MeOH; single crystals were grown from hot MeOH.

¹H NMR (500.2 MHz, CDCl₃): δ 7.64 (d, ³J(H,H) = 8.1 Hz, 1H; H-4), 7.63 (d, ⁴J(H,H) = 2.2 Hz, 1H; H-8), 7.59 (d, ⁴J(H,H) = 2.2 Hz, 1H; H-1), 7.43 (dd, ³J(H,H) = 8.1 Hz, ⁴J(H,H) = 2.2 Hz, 1H; H-3), 7.21 (d, ³J(H,H) = 8.2 Hz, 1H; H-5), 7.11 (dd, ³J(H,H) = 8.2 Hz, ⁴J(H,H) = 2.2 Hz, 1H; H-6), 7.09 (d, ³J(H,H) = 8.0 Hz, 2H; Tol-H-*o*), 7.00 (d, ³J(H,H) = 8.0 Hz, 2H; Tol-H-*m*), 6.84 (s, 1H;

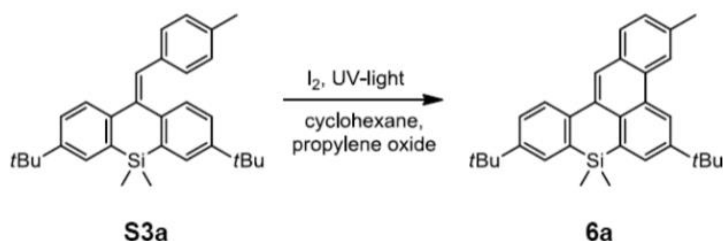
TolCH=), 2.30 (s, 3H; Tol-CH₃), 1.35 (s, 9H; *t*Bu-CH₃), 1.31 (s, 9H; *t*Bu-CH₃), 0.53 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 148.9 (C-7), 148.5 (C-2), 146.9 (C-4a), 141.7 (C-10a), 141.2 (C-10), 136.4 (Tol-C-*p*), 136.3 (C-8a), 135.1 (Tol-C-*i*), 134.8 (C-9a), 129.6 (Tol-C-*o*), 129.3 (TolCH=), 129.2 (C-5), 129.2 (C-8), 128.8 (Tol-C-*m*), 128.8 (C-1), 126.6 (C-3), 125.7 (C-6), 124.9 (C-4), 34.7 (*t*Bu-C), 34.7 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 31.5 (*t*Bu-CH₃), 21.4 (Tol-CH₃), -3.2 (SiMe₂)

²⁹Si NMR (99.4 MHz, CDCl₃): δ -17.6

EA (%): Calculated for C₃₁H₃₈Si [438.72]: C 84.87, H 8.73; found: C 85.09, H 8.95

HRMS: Calculated for C₃₁H₃₈Si: 438.27373, found: 438.27392



Synthesis of 6a: A solution of **S3a** (0.610 g, 1.39 mmol) in cyclohexane (700 mL) was prepared in a 1 L flask equipped with a water-cooled quartz immersion well containing a medium pressure Hg lamp. Propylene oxide (20 mL) was added and the solution was purged with Ar for 15 min using a cannula. The solution was irradiated for 5 h during which time neat I₂ (0.53 g, 2.1 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I₂ and the eluate was evaporated to dryness under reduced pressure. The residue was purified by column chromatography (7 cm silica gel, cyclohexane:EtOAc = 50:1) to obtain the product as a colorless solid (co-evaporation with EtOH is recommended). To remove traces of residual starting material, the product was suspended in EtOH (5 mL), sonicated, cooled to 8 °C, isolated by filtration while still cold, and washed with cold EtOH (3 mL). Yield: 0.450 g (1.03 mmol, 74 %).

¹H NMR (500.2 MHz, CDCl₃): δ 8.80 (d, ⁴J(H,H) = 2.0 Hz, 1H; H-5 or 7), 8.46 (n.r., 1H; H-4), 8.42 (s, 1H; H-13), 8.17 (d, ³J(H,H) = 8.6 Hz, 1H; H-12), 7.96 (d, ⁴J(H,H) = 2.0 Hz, 1H; H-5 or 7), 7.86 (d, ³J(H,H) = 8.0 Hz, 1H; H-1), 7.73 (d, ⁴J(H,H) = 2.3 Hz, 1H; H-9), 7.57 (dd, ³J(H,H) = 8.6 Hz, ⁴J(H,H) = 2.3 Hz, 1H; H-11), 7.42 (dd, ³J(H,H) = 8.0 Hz, ⁴J(H,H) = n.r., 1H; H-2), 2.65 (s, 3H; CH₃), 1.55 (s, 9H; *t*Bu-CH₃), 1.42 (s, 9H; *t*Bu-CH₃), 0.51 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.1 (C-10), 147.6 (C-6), 140.6 (C-12a), 136.4 (C-3), 134.1 (C-8a), 133.3 (C-7a), 132.2 (C-12c), 131.9 (C-12b), 131.1 (C-4a), 130.7 (C-5 or 7), 130.3 (C-13a), 130.2 (C-9), 130.0 (C-4b), 129.1 (C-1), 128.5 (C-2), 127.4 (C-11), 126.5 (C-12), 125.1 (C-13), 122.2 (C-4), 120.5 (C-5 or 7), 35.1 (*t*Bu-C), 34.6 (*t*Bu-C), 31.7 (*t*Bu-CH₃), 31.5 (*t*Bu-CH₃), 22.4 (CH₃), 0.0 (SiMe₂)

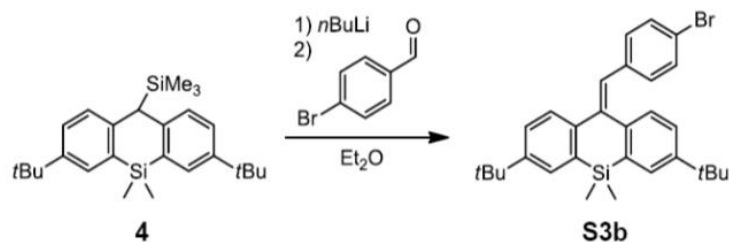
²⁹Si NMR (99.4 MHz, CDCl₃): δ -20.6

EA (%): Calculated for C₃₁H₃₆Si [436.70]: C 85.26, H 8.31; found: C 85.24, H 8.25

HRMS: Calculated for C₃₁H₃₆Si: 436.25808, found: 436.25800

UV/Vis (cyclohexane): λ_{max} (ε) = 339 (21000), 329 nm (24000)

Fluorescence (cyclohexane, λ_{Ex} = 330 nm): λ_{max} = 417, 396, 377 nm; Φ_{PL} = 35%



Synthesis of S3b: Compound **4** (1.25 g, 3.06 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (22 mL). *n*BuLi in *n*-hexane (1.63 M; 1.88 mL, 3.06 mmol) was added at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 1.5 h, whereupon its color changed to red. A solution of 4-bromobenzaldehyde (0.567 g, 3.06 mmol) in Et₂O (8 mL) was added at 0 °C via a syringe, whereupon the red color faded. After the addition was complete, the mixture was heated to reflux temperature for 30 min. A saturated aqueous NaHCO₃ solution (30 mL) was added, followed by H₂O (50 mL) and Et₂O (20 mL). The aqueous layer was separated and extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with H₂O (50 mL) and brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (10 cm silica gel, cyclohexane:EtOAc = 25:1, TLC: R_f = 0.84). The solvent was removed under reduced pressure to obtain the product as a colorless solid (co-evaporation with is EtOH recommended). If traces of starting materials are still present in the sample, it can be purified further by sonication in cold MeOH. Yield: 1.40 g (2.78 mmol, 91 %).

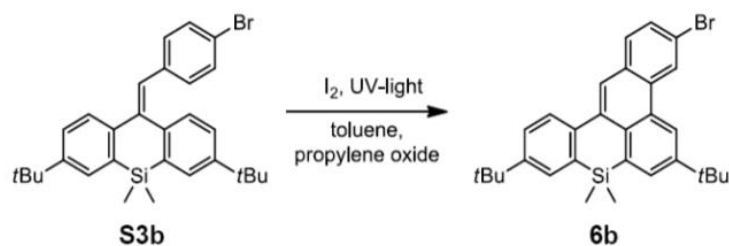
¹H NMR (500.2 MHz, CDCl₃): δ 7.64-7.61 (m, 3H; H-1 and 4 and 8), 7.44 (dd, ³J(H,H) = 8.2 Hz, ⁴J(H,H) = 2.2 Hz, 1H; H-3), 7.31 (d, ³J(H,H) = 8.5 Hz, 2H; Ar-H-*m*), 7.14 (d, ³J(H,H) = 8.2 Hz, 1H; H-5), 7.12 (dd, ³J(H,H) = 8.2 Hz, ⁴J(H,H) = 1.9 Hz 1H; H-6), 7.05 (d, ³J(H,H) = 8.5 Hz, 2H; Ar-H-*o*), 6.79 (s, 1H; ArCH=), 1.36 (s, 9H; *t*Bu-CH₃), 1.32 (s, 9H; *t*Bu-CH₃), 0.54 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.3 (C-2 or 7), 148.9 (C-2 or 7), 146.4 (C-4a), 142.7 (C-10), 141.1 (C-10a), 137.1 (Ar-C-*i*), 136.4 (C-8a), 134.7 (C-9a), 131.3 (Ar-C-*o* and *m*), 129.4 (C-8), 129.2 (C-5), 128.9 (C-1), 128.0 (ArCH=), 126.7 (C-3), 125.9 (C-6), 124.9 (C-4), 120.4 (Ar-C-*p*), 34.7 (*t*Bu-C), 34.7 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 31.5 (*t*Bu-CH₃), -3.1 (SiMe₂)

²⁹Si-NMR (99.4 MHz, CDCl₃): δ -17.6

EA (%): Calculated for C₃₀H₃₅BrSi [503.59]: C 71.55, H 7.01; found: C 71.69, H 7.08

HRMS: Calculated for C₃₀H₃₅BrSi: 504.16702, found: 504.16666



Synthesis of 6b: A solution of **S3b** (0.50 g, 0.99 mmol) in toluene (700 mL) was prepared in a 1 L flask equipped with a water-cooled quartz immersion well containing a medium pressure Hg

lamp. Propylene oxide (10 mL) was added and the solution was purged with Ar for 15 min using a cannula. The solution was irradiated for 20 h during which time neat I₂ (1.13 g, 4.45 mmol) was added in several portions. A saturated aqueous Na₂SO₃ solution (100 mL) was added and stirred for 30 min. The organic layer was separated, washed with H₂O (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The brown residue was purified by column chromatography (7 cm silica gel, cyclohexane:EtOAc = 50:1) to obtain a colorless solid (approx. 0.50 g), which still contained minor amounts of the starting material (approx. 10 %). The solid was suspended in MeOH (10 mL), sonicated, cooled to 8 °C, isolated by filtration, washed with cold MeOH (2 × 5 mL), and dried *in vacuo* to obtain pure **6b**. Yield: 0.34 g (0.68 mmol, 69%).

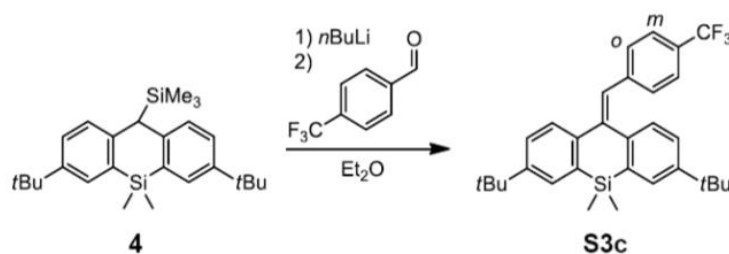
¹H NMR (500.2 MHz, CDCl₃): δ 8.80 (d, ⁴J(H,H) = 1.2 Hz, 1H; H-4), 8.69 (d, ⁴J(H,H) = 2.0 Hz, 1H; H-5 or 7), 8.39 (s, 1H; H-13), 8.15 (d, ³J(H,H) = 8.6 Hz, 1H; H-12), 8.01 (d, ⁴J(H,H) = 2.0 Hz, 1H; H-5 or 7), 7.82 (d, ³J(H,H) = 8.5 Hz, 1H; H-1), 7.74 (d, ⁴J(H,H) = 2.3 Hz, 1H; H-9), 7.67 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 1.8 Hz, 1H; H-2), 7.58 (dd, ³J(H,H) = 8.6 Hz, ⁴J(H,H) = 2.3 Hz, 1H; H-11), 1.55 (s, 9H; *t*Bu-CH₃), 1.43 (s, 9H; *t*Bu-CH₃), 0.52 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.7 (C-6 or 10), 148.3 (C-6 or 10), 140.1 (C-12a), 134.4 (C-7a or 8a), 133.7 (C-7a or 8a), 133.4 (C-12b), 132.5 (C-4a), 132.2 (C-12c), 131.5 (C-5 or 7), 130.9 (C-13a), 130.7 (C-1), 130.3 (C-9), 129.9 (C-2), 129.3 (C-4b), 127.5 (C-11), 126.7 (C-12), 125.3 (C-4), 124.4 (C-13), 120.9 (C-3), 120.5 (C-5 or 7), 35.2 (*t*Bu-C), 34.7 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 31.4 (*t*Bu-CH₃), -0.1 (SiMe₂)

²⁹Si NMR (99.4 MHz, CDCl₃): δ -20.5

EA (%): Calculated for C₃₀H₃₃BrSi [501.57]: C 71.84, H 6.63; found: C 71.97, H 6.65

HRMS: Calculated for C₃₀H₃₃SiBr: 502.15137, found: 502.15120



Synthesis of S3c: Compound **4** (0.975 g, 2.39 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (220 mL). *n*BuLi in *n*-hexane (1.60 M; 1.5 mL, 2.4 mmol) was added at room temperature. After the addition was complete, the reaction mixture was heated to reflux temperature for 1 h, whereupon its color changed to red. Neat 4-(trifluoromethyl)benzaldehyde (0.33 mL, 0.42 g, 2.4 mmol) was added at 0 °C via a syringe, whereupon the red color faded. After the addition was complete, the mixture was heated to reflux temperature for 30 min. A saturated aqueous NaHCO₃ solution (20 mL) was added, followed by H₂O (20 mL) and Et₂O (20 mL). The aqueous layer was separated and extracted with Et₂O (2 × 50 mL). The combined organic layers were dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by short-column chromatography (5 cm silica gel, cyclohexane, TLC: R_f = 0.44). The solvent was removed under reduced pressure and the colorless residue was suspended in 50 mL MeOH, cooled to 8 °C,

isolated by filtration while still cold, and washed with cold MeOH (10 mL) to obtain **S3c** as a colorless powder. Yield: 0.820 g (1.66 mmol, 70 %).

¹H NMR (400.1 MHz, C₆D₆): δ 7.81 (d, ⁴J(H,H) = 2.1 Hz, 1H; H-1 or 8), 7.76 (d, ⁴J(H,H) = 2.1 Hz, 1H; H-1 or 8), 7.65 (d, ³J(H,H) = 8.2 Hz, 1H; H-4 or 5), 7.43 (dd, ³J(H,H) = 8.2 Hz, ⁴J(H,H) = 2.1 Hz, 1H; H-3 or 6), 7.26 (d, ³J(H,H) = 8.2 Hz, 1H; H-4 or 5), 7.13 (m, 4H; C₆H₄), 6.97 (dd, ³J(H,H) = 8.2 Hz, ⁴J(H,H) = 2.1 Hz, 1H; H-3 or 6), 6.83 (s, 1H; ArCH=), 1.34 (s, 9H; *t*Bu-CH₃), 1.24 (s, 9H; *t*Bu-CH₃), 0.53 (s, 6H; SiMe₂)

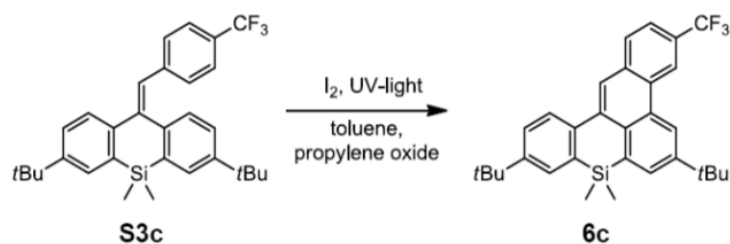
¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.6, 149.1, 146.2, 144.1, 141.9, 140.8, 136.4, 134.7 (8 × C_{quart}), 129.8 (Ar-C-*o*), 129.5, 129.2, 128.9, 128.3 (q, ²J(H,F) = 32.3 Hz; Ar-C-*p*), 127.7 (ArCH=), 126.7, 125.9, 125.0 (q, ³J(H,F) = 3.7 Hz; Ar-C-*m*), 124.9, 124.4 (q, ¹J(H,F) = 271.8 Hz; CF₃), 34.8 (*t*Bu-C), 34.7 (*t*Bu-C), 31.5(*t*Bu-CH₃), 31.5 (*t*Bu-CH₃), -3.2 (SiMe₂, only located in the HSQC spectrum)

¹⁹F NMR (470.6 MHz, CDCl₃): δ -62.4

²⁹Si-NMR (99.4 MHz, CDCl₃): δ -17.5

EA (%): Calculated for C₃₁H₃₅F₃Si [492.69]: C 75.57, H 7.16; found: C 75.76, H 7.18

HRMS: Calculated for C₃₁H₃₅F₃Si: 492.24546, found: 492.24442



Synthesis of 6c: A solution of **S3c** (0.525 g, 1.07 mmol) in toluene (700 mL) was prepared in a 1 L flask equipped with a water-cooled quartz immersion well containing a medium pressure Hg lamp. Propylene oxide (10 mL) was added and the solution was purged with Ar for 15 min using a cannula. The solution was irradiated for 27 h during which time neat I₂ (1.62 g, 6.39 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (5 cm; activity grade I) to remove residual I₂ and the eluate was evaporated to dryness under reduced pressure. The residue was suspended in MeOH (20 mL), sonicated, cooled to 8 °C, isolated by filtration while still cold, and washed with cold MeOH (5 mL) to obtain **6c** as a colorless powder. Yield: 0.484 g (0.986 mmol, 92 %).

¹H NMR (500.2 MHz, CDCl₃): δ 8.93 (n.r., 1H; H-4), 8.79 (d, ⁴J(H,H) = n.r., 1H; H-5), 8.47 (s, 1H; H-13), 8.18 (d, ³J(H,H) = 8.6 Hz, 1H; H-12), 8.06 (d, ³J(H,H) = 8.3 Hz, 1H; H-1), 8.04 (d, ⁴J(H,H) = 1.9 Hz, 1H; H-7), 7.78 (dd, ³J(H,H) = 8.3 Hz, ⁴J(H,H) = n.r. Hz, 1H; H-2), 7.76 (d, ⁴J(H,H) = 2.2 Hz, 1H; H-9), 7.60 (dd, ³J(H,H) = 8.6 Hz, ⁴J(H,H) = 2.2 Hz, 1H; H-11), 1.56 (s, 9H; *t*Bu-CH₃), 1.43 (s, 9H; *t*Bu-CH₃), 0.53 (s, 6H; SiMe₂)

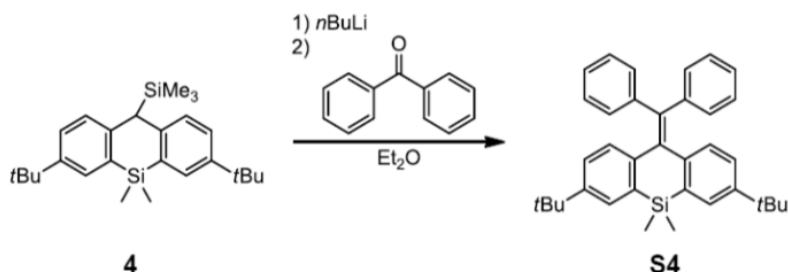
¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 150.1 (C-6 or 10), 148.7 (C-6 or 10), 139.9, 135.2, 134.7, 134.2, 134.2, 134.0, 132.3, 131.6 (C-7), 130.4 (C-9), 130.2, 129.9 (C-1), 128.0 (q, ²J(H,F) = 31.9 Hz; C-3), 127.6 (C-11), 126.9 (C-12), 124.9 (q, ¹J(H,F) = 272.1 Hz; CF₃), 124.2 (C-13), 122.6 (q, ³J(H,F) = 3.3 Hz; C-2), 120.4 (C-5), 119.9 (q, ³J(H,F) = 4.3 Hz; C-4), 35.2 (*t*Bu-C), 34.7 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 31.4 (*t*Bu-CH₃), -0.1 (SiMe₂)

^{19}F NMR (470.6 MHz, CDCl_3): δ -61.6

^{29}Si -NMR (99.4 MHz, CDCl_3): δ -20.4

EA (%): Calculated for $\text{C}_{31}\text{H}_{33}\text{F}_3\text{Si}$ [490.67]: C 75.88, H 6.78; found: C 75.81, H 6.83

HRMS: Calculated for $\text{C}_{31}\text{H}_{33}\text{F}_3\text{Si}$: 490.22981, found: 490.22926



Synthesis of S4: Compound **4** (1.82 g, 4.45 mmol) was placed in a 2-necked round-bottom flask equipped with a condenser and dissolved in Et_2O (30 mL). $n\text{BuLi}$ in n -hexane (1.61 M; 2.9 mL, 4.7 mmol) was added at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 1 h, whereupon its color changed to red. A solution of benzophenone (0.890 g, 4.88 mmol) in Et_2O (5 mL) was added at 0 °C via a syringe, and a change of color from red to blue was noticed. After the addition was complete, the mixture was heated to reflux temperature for 1 h. A saturated aqueous NaHCO_3 solution (30 mL) was added, the aqueous layer was separated, and extracted with Et_2O (2×30 mL). The combined organic layers were washed with H_2O (2×50 mL), dried over MgSO_4 , and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (20 cm silica gel, n -hexane: EtOAc = 50:1 to 20:1, TLC: R_f (20:1) = 0.77) to obtain a colorless solid (2.33 g), which still contained traces of benzophenone. The product was suspended in MeOH (20 mL), sonicated, cooled to 5 °C, isolated by filtration while still cold, and washed with cold MeOH (2×5 mL) to obtain pure **S4**. Yield: 1.58 g (3.15 mmol, 70%). Single crystals were grown from hot MeOH.

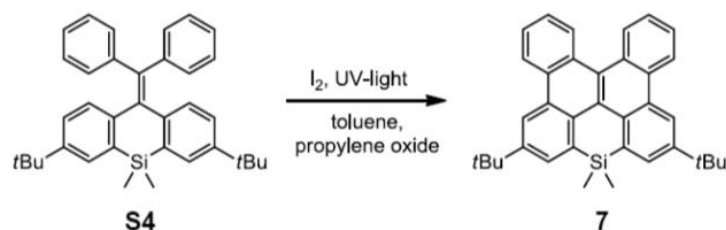
^1H NMR (500.2 MHz, CDCl_3): δ 7.52 (d, $^4J(\text{H,H})$ = 2.1 Hz, 2H; H-1,8), 7.24-7.22 (m, 4H; Ph-CH-*o*), 7.16-7.13 (m, 4H; Ph-CH-*m*), 7.09-7.05 (m, 2H; Ph-CH-*p*), 7.00 (d, $^3J(\text{H,H})$ = 8.2 Hz, 2H; H-4,5), 6.94 (dd, $^3J(\text{H,H})$ = 8.2 Hz, $^4J(\text{H,H})$ = 2.1 Hz, 2H; H-3,6), 1.23 (s, 18H; *t*Bu- CH_3), 0.68 (br, 3H; SiMe_2), 0.64 (br, 3H; SiMe_2)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 147.7 (C-2,7), 144.3 (C-4a,10a), 143.0 (Ph-C-*i*), 140.2 (C-10), 140.1 ($\text{Ph}_2\text{C}=\text{C}$), 136.4 (C-8a,9a), 129.8 (Ph-CH-*o*), 129.4 (C-4,5), 128.5 (C-1,8), 127.8 (Ph-CH-*m*), 126.1 (Ph-CH-*p*), 125.1 (C-3,6), 34.5 (*t*Bu-C), 31.5 (*t*Bu- CH_3), -1.3 (SiMe_2), -5.4 (SiMe_2)

^{29}Si NMR (99.4 MHz, CDCl_3): δ -17.2

EA (%): Calculated for $\text{C}_{36}\text{H}_{40}\text{Si}$ [500.79]: C 86.34, H 8.05; found: C 87.24, H 8.18

HRMS: Calculated m/z for $\text{C}_{36}\text{H}_{40}\text{Si}$: 500.28938, found: 500.28797



Synthesis of 7: A solution of **S4** (1.56 g, 3.12 mmol) in toluene (700 mL) was prepared in a 1 L flask equipped with a water-cooled quartz immersion well containing a medium pressure Hg lamp. Propylene oxide (20 mL) was added and the solution was purged with Ar for 15 min using a cannula. The solution was irradiated for 5 h during which time neat I₂ (1.6 g, 6.3 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I₂, and the eluate was evaporated to dryness under reduced pressure. Column chromatography of the crude product (25 cm silica gel, *n*-hexane:EtOAc = 100:3, TLC: *R_f* = 0.50) yielded several fractions. Fractions with only minor impurities (determined by TLC) were combined and evaporated to obtain a pale yellow solid (0.81 g). The solid was dissolved in C₆H₆ (2 mL) and layered with MeOH (20 mL). After several days, **7** was collected in single-crystalline form. Yield: 0.64 g (1.3 mmol, 41 %)

¹H NMR (500.2 MHz, CDCl₃): δ 8.80 (d, ⁴*J*(H,H) = 2.2 Hz, 2H; H-5,11 or 7,9), 8.68 (d, ³*J*(H,H) = 8.1 Hz, 2H; H-1,15 or 4,12), 8.60 (dd, ³*J*(H,H) = 8.2 Hz, ⁴*J*(H,H) = n.r., 2H; H-1,15 or 4,12), 8.05 (d, ⁴*J*(H,H) = 2.2 Hz, 2H; H-5,11 or 7,9), 7.66 (m, 2H; H-2,14 or 3,13), 7.55 (m, 2H; H-2,14 or 3,13), 1.57 (s, 18H; *t*Bu-CH₃), 0.58 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 148.3 (C-6,10), 133.6 (C-7a,8a), 131.9, 131.8, 131.7 (C-5,11 or 7,9), 130.3 (C-1,15 or 4,12), 130.1, 129.9, 126.6, 126.5 (C-2,14 or 3,13), 125.6 (C-2,14 or 3,13), 123.4 (C-1,15 or 4,12), 121.2 (C-5,11 or 7,9), 35.1 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 1.3 (SiMe₂), one carbon resonance not observed

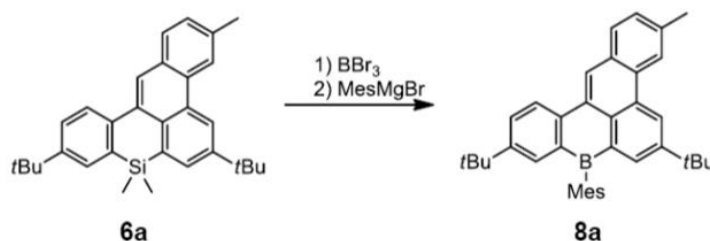
²⁹Si NMR (99.4 MHz, CDCl₃): δ -21.4

EA (%): Calculated for C₃₆H₃₆Si [496.76] × C₆H₆ [78.11]: C 87.75, H 7.36; found: C 87.59, H 7.73; the amount of C₆H₆ present in the sample was independently confirmed by ¹H NMR spectroscopy and X-ray crystallography

HRMS: Calculated *m/z* for C₃₆H₃₆Si: 496.25808, found: 496.25836

UV/Vis (cyclohexane): λ_{max} (ε) = 360 (16000), 344 (18000)

Fluorescence (cyclohexane, λ_{Ex} = 345 nm): λ_{max} = 407, 395 nm; Φ_{PL} = 20%



Synthesis of 8a: Compound **6a** (0.105 g, 0.240 mmol) was placed in a thoroughly flame-dried Schlenk tube equipped with a dropping funnel and dissolved in neat BBr₃ (2.5 mL; added through

the tap of the Schlenk tube using a syringe while maintaining positive nitrogen pressure); room temperature was maintained by means of a water bath. The mixture was stirred for 16 h at 50 °C before excess BBr₃ was removed under reduced pressure to obtain a dark solid. Toluene (20 mL) was added and the resulting suspension was stirred at 25 torr for 1 h to remove residual BBr₃ (the volume of the solution decreases only slightly). The dropping funnel was charged with a solution of MesMgBr in THF (0.87 M; 0.60 mL, 0.52 mmol), which was added dropwise at 0 °C. The solution, which already showed blue fluorescence, was stirred for 1 h at room temperature. MeOH (5 mL) was added and the mixture was evaporated to dryness under reduced pressure. The solid residue was extracted with *n*-hexane (20 mL). The solvent was removed from the extract under reduced pressure to obtain the product as a yellow solid with only minor impurities. Yield: 0.12 g (0.23 mmol, 96%). Single crystals used for X-ray analysis and photophysical investigations were grown by layering a solution of **8a** in C₆H₆ (50 mg mL⁻¹) with MeOH.

¹H NMR (500.2 MHz, CDCl₃): δ 9.10 (d, ⁴J(H,H) = 2.1 Hz, 1H; H-5), 8.93 (s, 1H; H-13), 8.62 (d, ³J(H,H) = 8.5 Hz, 1H; H-12), 8.58 (n.r., 1H; H-4), 8.25 (d, ⁴J(H,H) = 2.1 Hz, 1H; H-7), 8.01 (d, ³J(H,H) = 8.1 Hz, 1H; H-1), 7.86 (d, ⁴J(H,H) = 2.3 Hz, 1H; H-9), 7.82 (dd, ³J(H,H) = 8.5 Hz, ⁴J(H,H) = 2.3 Hz, 1H; H-11), 7.51 (dd, ³J(H,H) = 8.1 Hz, ⁴J(H,H) = n.r., 1H; H-2), 6.95 (s, 2H; Mes-CH-*m*), 2.71 (s, 3H; CH₃), 2.44 (s, 3H; Mes-CH₃-*p*), 2.01 (s, 6H; Mes-CH₃-*o*), 1.47 (s, 9H; *t*Bu-CH₃ at C-6), 1.33 (s, 9H; *t*Bu-CH₃ at C-10)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 149.6 (C-10), 148.5 (C-6), 140.5 (Mes-C-*i*), 139.6 (C-12a), 138.8 (Mes-C-*o*), 138.4 (C-7), 137.5 (C-3), 136.5 (C-8a) 136.4 (Mes-C-*p*), 135.0 (C-9), 135.0 (C-7a), 131.4 (C-4a), 130.6 (C-11), 130.2 (C-12c), 130.1 (C-13a), 129.8 (C-1), 129.8 (C-12b), 129.4 (C-4b), 128.6 (C-2), 127.0 (Mes-CH-*m*), 126.2 (C-13), 125.2 (C-5), 123.4 (C-12), 122.3 (C-4), 35.2 (*t*Bu-C at C-6), 34.6 (*t*Bu-C at C-10), 31.6 (*t*Bu-CH₃ at C-6), 31.4 (*t*Bu-CH₃ at C-10), 23.4 (Mes-CH₃-*o*), 22.6 (CH₃), 21.5 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 65 (*h*_{1/2} ≈ 1500 Hz)

EA (%): Calculated for C₃₈H₄₁B [508.54]: C 89.75, H 8.13; found: C 89.91, H 7.95

HRMS: Calculated for C₃₈H₄₁B: 508.33024, found: 508.33017

UV/Vis (cyclohexane): λ_{max} (ε) = 416 (30000), 395 nm (18000)

Fluorescence (cyclohexane, λ_{ex} = 375 nm, 25 °C): λ_{max} = 450, 428 nm; Φ_{PL} = 88%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 400 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = 0.99, -2.17 V



Synthesis of 8b: Compound **6b** (0.102 g, 0.203 mmol) was placed in a thoroughly flame-dried Schlenk tube equipped with a dropping funnel and suspended in neat BBr₃ (1 mL; added through the tap of the Schlenk tube using a syringe while maintaining positive nitrogen pressure); room temperature was maintained by means of a water bath. The mixture was stirred for 16 h at 50 °C before excess BBr₃ was removed under reduced pressure to obtain a dark solid. Toluene (20 mL) was added and the suspension was stirred at 25 torr for 1 h to remove residual BBr₃ (the volume

of the solution decreases only slightly). The dropping funnel was charged with a solution of MesMgBr in THF (0.87 M; 0.5 ml, 0.4 mmol), which was added dropwise at 0 °C. The solution was stirred for 30 min at room temperature. MeOH (4 mL) was added and the mixture was evaporated to dryness under reduced pressure. The solid residue was extracted with *n*-hexane (20 mL). The solvent was removed from the extract under reduced pressure, the yellow residue (0.133 g) was dissolved in C₆H₆ (2.5 mL), and layered with MeOH (15 mL). After the vessel had been stored for several days at 8 °C, yellow crystals of **8b** were collected and dried *in vacuo*. Yield: 0.107 g (0.187 mmol, 92%).

¹H NMR (500.2 MHz, CDCl₃): δ 8.98 (d, ⁴J(H,H) = 2.1 Hz, 1H; H-5), 8.92 (n.r., 1H; H-4), 8.88 (s, 1H; H-13), 8.59 (d, ³J(H,H) = 8.6 Hz, 1H; H-12), 8.27 (d, ⁴J(H,H) = 2.1 Hz, 1H; H-7), 7.96 (d, ³J(H,H) = 8.5 Hz, 1H; H-1), 7.87 (d, ⁴J(H,H) = 2.3 Hz, 1H; H-9), 7.83 (dd, ³J(H,H) = 8.5 Hz, ⁴J(H,H) = 2.4 Hz, 1H; H-11), 7.75 (dd, ³J(H,H) = 8.5 Hz, ⁴J(H,H) = 1.8 Hz, 1H; H-2), 6.95 (s, 2H; Mes-CH-*m*), 2.44 (s, 3H; Mes-CH₃-*p*), 2.01 (s, 6H; Mes-CH₃-*o*), 1.46 (s, 9H; *t*Bu-CH₃ at C-6), 1.33 (s, 9H; *t*Bu-CH₃ at C-10)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 150.2 (C-10), 149.3 (C-6), 140.1 (Mes-C-*i*), 139.2 (C-7), 139.1 (C-12a), 138.7 (Mes-C-*o*), 136.6 (Mes-C-*p*), 136.6 (C-8a; only located in the HMBC spectrum), 135.2 (C-9), 135.0 (C-7a), 132.6 (C-4a), 131.3 (C-1), 131.2 (C-12b), 130.8 (C-11), 130.6 (C-13a), 130.3 (C-12c), 130.0 (C-2), 128.6 (C-4b), 127.1 (Mes-CH-*m*), 125.5 (C-4), 125.4 (C-13), 125.2 (C-5), 123.6 (C-12), 121.8 (C-3), 35.3 (*t*Bu-C at C-6), 34.7 (*t*Bu-C at C-10), 31.6 (*t*Bu-CH₃ at C-6), 31.4 (*t*Bu-CH₃ at C-10), 23.4 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

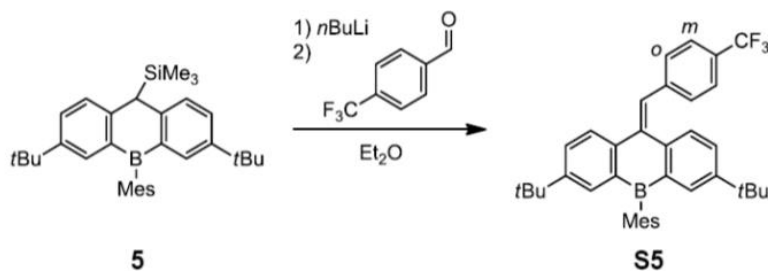
¹¹B{¹H}-NMR (160.5 MHz, CDCl₃): δ 66 (h_{1/2} ≈ 1500 Hz)

EA (%): Calculated for C₃₇H₃₈BBr [573.41]: C 77.50, H 6.68; found: C 77.82, H 6.79

HRMS: Calculated for C₃₇H₃₈BBr: 574.22364, found: 574.22207

UV/Vis (cyclohexane): λ_{max} = 411, 390 nm

Fluorescence (cyclohexane, λ_{Ex} = 265 nm): λ_{max} = 446, 426 nm; Φ_{PL} = <10%



Synthesis of S5: Compound **5** (0.80 g, 1.7 mmol) was placed in a 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (15 mL). *n*BuLi in *n*-hexane (1.54 M; 1.1 mL, 1.7 mmol) was added while stirring at room temperature. The reaction mixture was heated to reflux temperature for 30 min, whereupon its color changed to orange. Neat 4-(trifluoromethyl)benzaldehyde (0.24 mL, 0.31 g, 1.8 mmol) was added dropwise while stirring at 0 °C. After the addition was complete, the solution was heated to reflux temperature for 1.5 h, allowed to cool to room temperature again and quenched with a saturated aqueous NaHCO₃ solution (30 mL). The aqueous layer was separated and extracted with Et₂O (30 mL). The combined organic layers were washed with H₂O (50 mL) and brine (30 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. Column

chromatography (25 cm silica gel, cyclohexane) of the crude product (0.9 g) yielded several fractions. Only fractions containing pure **S5** (investigated by TLC) were combined ($R_f = 0.33$ in cyclohexane). After removal of the solvent, **S5** was obtained as a yellow powder. Yield: 0.24 g (0.43 mmol, 25%).

^1H NMR (500.2 MHz, CDCl_3): δ 7.97 (d, $^3J(\text{H,H}) = 8.3$ Hz, 1H; H-4 or 5), 7.66 (d, $^4J(\text{H,H}) = 2.2$ Hz, 1H; H-1 or 8), 7.64 (d, $^4J(\text{H,H}) = 2.2$ Hz, 1H; H-1 or 8), 7.61 (dd, $^3J(\text{H,H}) = 8.3$ Hz, $^4J(\text{H,H}) = 2.2$ Hz, 1H; H-3 or 6), 7.53 (d, $^3J(\text{H,H}) = 8.2$ Hz, 2H; Ar-H-*m*), 7.42 (d, $^3J(\text{H,H}) = 8.2$ Hz, 2H; Ar-H-*o*), 7.40 (d, $^3J(\text{H,H}) = 8.3$ Hz, 1H; H-4 or 5), 7.37 (s, 1H; ArCH=), 7.20 (dd, $^3J(\text{H,H}) = 8.3$ Hz, $^4J(\text{H,H}) = 2.2$ Hz, 1H; H-3 or 6), 6.92 (s, 2H; Mes-CH-*m*), 2.41 (s, 3H; Mes-CH₃-*p*), 2.06 (s, 6H; Mes-CH₃-*o*), 1.27 (s, 9H; *t*Bu-CH₃), 1.22 (s, 9H; *t*Bu-CH₃)

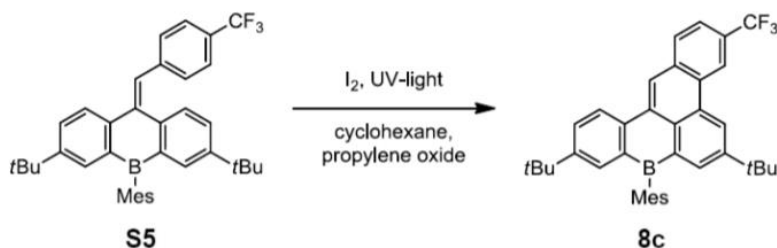
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 150.5, 149.9, 144.8, 142.7, 141.0, 139.7 (br.; CB), 139.5, 138.2 (br.; CB), 138.0, 136.6, 135.9 (br.; CB), 134.2 (C-1 or 8), 134.0 (C-1 or 8), 130.0 (Ar-C-*o*), 130.0 (C-3 or 6), 129.5 (C-4 or 5), 129.1 (ArCH=), 128.8 (q, $^2J(\text{C,F}) = 32.7$ Hz; Ar-C-*p*), 128.2 (C-3 or 6), 127.1 (Mes-CH-*m*), 125.4 (q, $^3J(\text{C,F}) = 3.6$ Hz; Ar-C-*m*), 123.3 (C-4 or 5), 34.7 (*t*Bu-C), 34.6 (*t*Bu-C), 31.4 (*t*Bu-CH₃), 31.3 (*t*Bu-CH₃), 22.9 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*), one carbon resonance (CF₃) not observed; resonances marked in red or blue belong to the same six-membered ring

^{11}B NMR (160.5 MHz, C_6D_6): δ 67 ($h_{1/2} \approx 1500$ Hz)

^{19}F NMR (470.6 MHz, CDCl_3): δ -62.4

EA (%): Calculated for $\text{C}_{38}\text{H}_{40}\text{BF}_3$ [564.53]: C 80.85, H 7.14; found: C 80.25, H 7.35

HRMS: Calculated for $\text{C}_{38}\text{H}_{41}\text{BF}_3$: 565.32545, found: 565.32338.



Synthesis of **8c:** A solution of **S5** (145 mg, 257 μmol) in cyclohexane (700 mL) was prepared in a 1 L flask equipped with a water-cooled quartz immersion well containing a medium pressure Hg lamp. Propylene oxide (5 mL) was added and the solution was purged with Ar for 15 min using a cannula. The solution was irradiated and neat I_2 (103 mg, 406 μmol) was added in several portions over a period of 1.5 h. After 2 h, the I_2 was completely consumed and the lamp was switched off. After the solvent had been removed under reduced pressure, the solid residue was purified by column chromatography (5 cm silica gel, cyclohexane: $\text{CH}_2\text{Cl}_2 = 25:1$) to obtain the yellow product. Yield: 115 mg (204 μmol , 80%). Single crystals were grown by layering MeOH onto a solution of **8c** in C_6H_6 (25 mg mL^{-1}) and storing the vessel at 8 $^\circ\text{C}$.

^1H NMR (500.2 MHz, C_6D_6): δ 9.16 (n.r., 1H; H-4), 9.01 (d, $^4J(\text{H,H}) = 2.1$ Hz, 1H; H-5), 8.78 (s, 1H; H-13), 8.62 (d, $^4J(\text{H,H}) = 2.1$ Hz, 1H; H-7), 8.50 (d, $^3J(\text{H,H}) = 8.6$ Hz, 1H; H-12), 8.29 (d, $^4J(\text{H,H}) = 2.4$ Hz, 1H; H-9), 7.78 (dd, $^3J(\text{H,H}) = 8.6$ Hz, $^4J(\text{H,H}) = 2.4$ Hz, 1H; H-11), 7.70 (d, $^3J(\text{H,H}) = 8.4$ Hz, 1H; H-1), 7.65 (dd, $^3J(\text{H,H}) = 8.4$ Hz, $^4J(\text{H,H}) = \text{n.r.}$, 1H; H-2), 7.04 (s, 2H; Mes-

CH-m), 2.32 (s, 3H; Mes-CH_{3-p}), 2.19 (s, 6H; Mes-CH_{3-o}), 1.26 (s, 9H; *t*Bu-CH₃ at C-10), 1.21 (s, 9H; *t*Bu-CH₃ at C-6)

¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ 151.0 (C-10), 150.0 (C-6), 140.6 (br.; Mes-C-*i*), 139.7 (C-7), 139.5 (C-12a), 138.9 (Mes-C-*o*), 137.4 (br.; C-8a), 137.3 (Mes-C-*p*), 135.6 (br.; C-7a), 135.5 (C-9), 134.2 (C-13a), 133.4 (C-12b), 131.3 (C-11), 131.0 (C-4a or 12c), 130.9 (C-4a or 12c), 130.9 (C-1), 130.1 (C-4b), 129.0 (q, ²J(C,F) = 32.0 Hz; C-3), 127.8 (Mes-CH-*m*), 125.5 (q, ¹J(C,F) = 272.2 Hz; CF₃), 125.5 (C-5), 125.4 (C-13), 124.6 (C-12), 122.7 (q, ³J(C,F) = 3.1 Hz; C-2), 120.2 (q, ³J(C,F) = 4.2 Hz; C-4), 35.0 (*t*Bu-C at C-6), 34.7 (*t*Bu-C at C-10), 31.3 (*t*Bu-CH₃ at C-10), 31.2 (*t*Bu-CH₃ at C-6), 23.5 (Mes-CH_{3-*o*}), 21.5 (Mes-CH_{3-*p*})

¹¹B NMR (160.5 MHz, C₆D₆): δ 67 (*h*_{1/2} ≈ 1500 Hz)

¹⁹F NMR (470.6 MHz, C₆D₆): δ -61.5

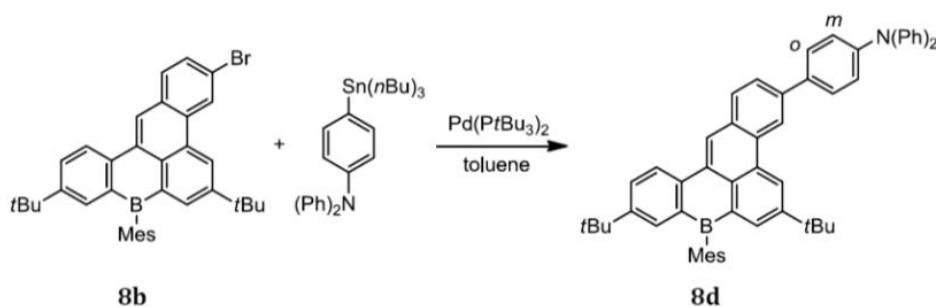
EA (%): Calculated for C₃₈H₃₈BF₃ [562.51]: C 81.14, H 6.81; found: C 80.82, H 6.81

HRMS: Calculated for C₃₈H₃₈BF₃: 562.30197, found: 562.30097

UV/Vis (cyclohexane): λ_{max} (ε) = 401 (30000), 381 nm (21000)

Fluorescence (cyclohexane, λ_{ex} = 370 nm, 25 °C): λ_{max} = 434, 412 nm; Φ_{PL} = 79%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆], 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = -2.01 V



Synthesis of 8d: Compound **8b** (44 mg, 77 μmol) and 4-(*n*Bu)₃Sn(C₆H₄)NPh₂ (0.104 g, 0.194 mmol) were placed in a small Schlenk tube. Toluene (1.5 mL) was added and the solution was degassed with N₂ for 5 min. Pd(PtBu₃)₂ (2 mg, 4 μmol) was added and the stirred mixture was heated to 100 °C (oil-bath temperature) for 48 h. After the mixture had cooled to room temperature again, the solvent was removed under reduced pressure and the residue was purified by column chromatography (25 cm silica gel). The first fraction was eluted with cyclohexane:toluene = 10:1 and contained starting material (TLC: R_f = 0.58 with cyclohexane:EtOAc 25:1), the second, highly colored fraction was eluted with cyclohexane:EtOAc = 10:1 and contained **8d** (TLC: R_f = 0.42 with cyclohexane:EtOAc 10:1). The solvent was removed from the second fraction under reduced pressure to obtain a yellow solid (35 mg; according to ¹H NMR spectroscopy, the material still contained approximately 10% of **8b**). Recrystallization from *n*-hexane afforded analytically pure **8d**, which was used for X-ray analysis and the photophysical characterization of **8d**.

¹H NMR (500.2 MHz, CDCl₃): δ 9.17 (d, ⁴J(H,H) = 1.9 Hz, 1H; H-5 or 7), 8.96 (s, 1H; H-13), 8.95 (n.r., 1H; H-4), 8.64 (d, ³J(H,H) = 8.6 Hz, 1H; H-12), 8.26 (d, ⁴J(H,H) = 1.9 Hz, 1H; H-5 or 7), 8.15 (d, ³J(H,H) = 8.3 Hz, 1H; H-1), 7.90 (dd, ³J(H,H) = 8.3 Hz, ⁴J(H,H) = n.r., 1H; H-2), 7.87 (d, ⁴J(H,H) = 2.3 Hz, 1H; H-9), 7.83 (dd, ³J(H,H) = 8.6 Hz, ⁴J(H,H) = 2.3 Hz, 1H; H-11), 7.73 (d, ³J(H,H) = 8.5 Hz, 2H; C₆H₄-CH-*o*), 7.31 (vt, 4H; Ph-CH-*m*), 7.26 (d, ³J(H,H) = 8.5 Hz, 2H; C₆H₄-

CH-m), 7.20 (d, $^3J(\text{H,H}) = 8.2$ Hz, 4H; Ph-*CH-o*), 7.08 (t, $^3J(\text{H,H}) = 7.3$ Hz, 2H; Ph-*CH-p*), 6.95 (s, 2H; Mes-*CH-m*), 2.44 (s, 3H; Mes- CH_3 -*p*), 2.01 (s, 6H; Mes- CH_3 -*o*), 1.46 (s, 9H; *t*Bu- CH_3 at C-6), 1.33 (s, 9H; *t*Bu- CH_3 at C-10)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 149.8 (C-10), 148.8 (C-6), 147.8 (Ph-C-*i*), 147.7 (C_6H_4 -CN), 140.4 (br.; Mes-C-*i*), 139.7 (C-3), 139.5, 138.7 (Mes-C-*o*), 138.6 (C-5 or 7), 136.5 (br.; C-8a), 136.5 (Mes-C-*p*), 135.4 (C_6H_4 -CC), 135.0 (br.; C-7a), 135.0 (C-9), 131.6, 131.0, 130.7 (C-11), 130.5 (C-12b), 130.4, 130.4 (C-1), 129.7, 129.5 (Ph-*CH-m*), 128.4 (C_6H_4 -*CH-o*), 127.0 (Mes-*CH-m*), 126.0 (C-13), 126.0 (C-2), 125.2 (C-5 or 7), 124.8 (Ph-*CH-o*), 124.0 (C_6H_4 -*CH-m*), 123.6 (C-12), 123.3 (Ph-*CH-p*), 120.3 (C-4), 35.3 (*t*Bu-C at C-6), 34.7 (*t*Bu-C at C-10), 31.6 (*t*Bu- CH_3 at C-6), 31.4 (*t*Bu- CH_3 at C-10), 23.4 (Mes- CH_3 -*o*), 21.5 (Mes- CH_3 -*p*)

EA (%): Calculated for $\text{C}_{55}\text{H}_{52}\text{BN}$ [737.82]: C 89.53, H 7.10, N 1.90; found: C 90.00, H 7.27, N 1.46

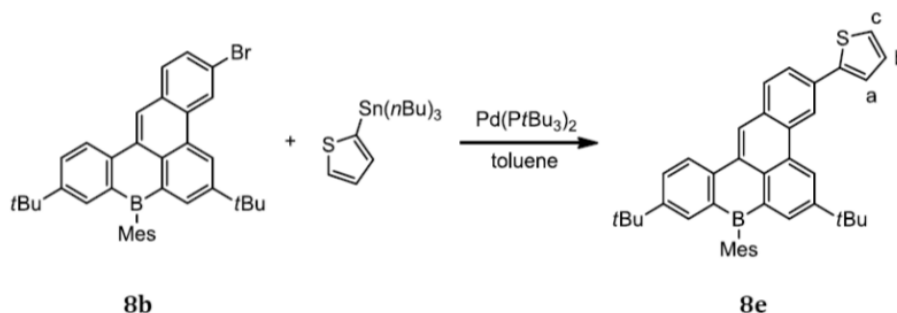
HRMS: Calculated for $\text{C}_{55}\text{H}_{52}\text{BN}$: 737.41964, found: 737.41916

UV/Vis (cyclohexane): λ_{max} (ϵ) = 391 (22000), 433 nm (40000)

Fluorescence (cyclohexane, $\lambda_{\text{ex}} = 415$ nm): λ_{max} = 498, 471 nm; $\Phi_{\text{PL}} = 92$ %

Fluorescence (other solvents, $\lambda_{\text{ex}} = 435$ nm): λ_{max} (Φ_{PL}) = C_6H_6 : 501 nm (93%), CHCl_3 : 534 nm (89%), THF: 555 nm (88%), acetone: 609 nm (73%), CH_3CN : 646 nm (48%)

Cyclic voltammetry (CH_2Cl_2 , [*n*Bu $_4$ N][PF $_6$] 0.1 M, 400 mV s $^{-1}$, vs. FcH/FcH $^+$): $E_{1/2} = 0.94, 0.48, -2.10$ V



Synthesis of 8e: Compound **8b** (40 mg, 70 μmol) and 2-(*n*Bu) $_3$ Sn($\text{C}_4\text{H}_3\text{S}$) (0.044 g, 0.118 mmol) were placed in a small Schlenk tube. Toluene (1.0 mL) was added and the solution was degassed with N_2 for 5 min. Pd(*Pt*Bu $_3$) $_2$ (2 mg, 4 μmol) was added and the stirred mixture was heated to 90 $^\circ\text{C}$ (oil-bath temperature) for 4 h. After the intensely green mixture had cooled to room temperature again, the solvent was removed under reduced pressure and the residue was purified by column chromatography (30 cm silica gel, cyclohexane:toluene = 25:1). The first colored fraction contained pure **8e**, which was obtained as a yellow solid after removal of the solvent. Yield: 26 mg (45 μmol , 64%).

^1H -NMR (500.2 MHz, CDCl_3): δ 9.14 (d, $^4J(\text{H,H}) = 2.0$ Hz, 1H; H-5 or 7), 9.00 (n.r., 1 H; H-4), 8.93 (s, 1 H; H-13), 8.62 (d, $^3J(\text{H,H}) = 8.6$ Hz, 1H; H-12), 8.27 (d, $^4J(\text{H,H}) = 2.1$ Hz, 1H; H-5 or 7), 8.11 (d, $^3J(\text{H,H}) = 8.3$ Hz, 1H; H-1), 7.93 (dd, $^3J(\text{H,H}) = 8.3$ Hz, $^4J(\text{H,H}) = 1.6$ Hz, 1H; H-2), 7.88 (d, $^4J(\text{H,H}) = 2.4$ Hz, 1H; H-9), 7.83 (dd, $^3J(\text{H,H}) = 8.6$ Hz, $^4J(\text{H,H}) = 2.4$ Hz, 1H; H-11), 7.58 (dd, $^3J(\text{H,H}) = 3.6$ Hz, $^4J(\text{H,H}) = 1.0$ Hz, 1H; Th-H-a or c), 7.41 (dd, $^3J(\text{H,H}) = 5.0$ Hz, $^4J(\text{H,H}) = 1.0$ Hz, 1H; Th-H-a or c), 7.21 (dd, $^3J(\text{H,H}) = 5.0$ Hz, $^3J(\text{H,H}) = 3.6$ Hz, 1H; Th-H-b), 6.96 (s, 2H; Mes-*CH-m*), 2.44 (s, 3H; Mes- CH_3 -*p*), 2.02 (s, 6H; Mes- CH_3 -*o*), 1.48 (s, 9H; *t*Bu- CH_3), 1.34 (s, 9H; *t*Bu- CH_3)

$^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz, CDCl_3): δ 149.9 (C-6 or 10), 148.9 (C-6 or 10), 145.0, 140.3 (br.; Mes-C-*i*), 139.3, 138.8 (C-5 or 7), 138.7, 136.6 (br.), 136.5, 135.1 (C-9), 133.4, 131.6, 131.4, 130.8, 130.7 (C-11), 130.5 (C-1), 129.5, 128.5 (Th-C-*b*), 127.0 (Mes-CH-*m*), 125.8 (C-13), 125.6 (Th-C-*a* or *c*), 125.1 (C-5 or 7), 125.1 (C-2), 124.0 (Th-C-*a* or *c*), 123.6 (C-12), 119.6 (C-4), 35.2 (*t*Bu-C), 34.7 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 31.4 (*t*Bu-CH₃), 23.4 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*), two carbon resonances not observed

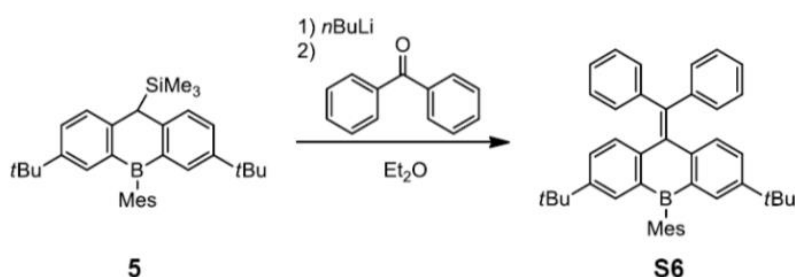
EA (%): Calculated for C₄₁H₄₁BS [576.64]: C 85.40, H 7.17, S 5.56; found: C 85.36, H 7.08, S 5.64

HRMS: Calculated for C₄₁H₄₁BS: 576.30236, found: 576.30165

UV/Vis (cyclohexane): λ_{max} (ϵ) = 429 (32000), 411 (shoulder, 23000), 389 nm (18000)

Fluorescence (cyclohexane, λ_{ex} = 400 nm): λ_{max} = 473, 447 nm; Φ_{PL} = 73%

Cyclic voltammetry (CH_2Cl_2 , [*n*Bu₄N][PF₆] 0.1 M, 400 mV s⁻¹, vs. FcH/FcH⁺): $E_{1/2}$ = -2.09 V



Synthesis of S6: Compound **5** (0.525 g, 1.09 mmol) was placed in a 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (15 mL). *n*BuLi in *n*-hexane (1.56 M; 0.70 mL, 1.1 mmol) was added at room temperature while stirring and the reaction mixture was heated to reflux temperature for 30 min, whereupon its color changed to orange. After cooling to 0 °C, benzophenone (0.200 g, 1.10 mmol) was added. The mixture was heated to reflux temperature for 2 h and then allowed to cool to room temperature before adding a saturated aqueous NaHCO₃ solution (20 mL). The aqueous layer was separated and extracted with Et₂O (40 mL). The combined organic layers were washed with H₂O (50 mL) and brine (40 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product (0.64 g) was purified by column chromatography (25 cm silica gel, cyclohexane:EtOAc = 50:1, TLC: R_f = 0.45). After evaporation of the solvent, the product was suspended in MeOH (10 mL), sonicated, isolated by filtration, washed with MeOH (5 mL), and dried in vacuo (colorless powder). Yield: 0.336 g (0.587 mmol, 54%).

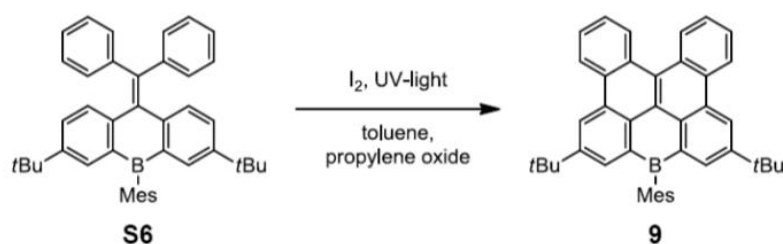
^1H NMR (500.2 MHz, CDCl_3): δ 7.54 (d, $^4J(\text{H,H})$ = 2.2 Hz, 2H; H-1,8), 7.25-7.19 (m, 8H; Ph-CH-*o,m*), 7.14 (m, 2H; Ph-CH-*p*), 7.11 (d, $^3J(\text{H,H})$ = 8.3 Hz, 2H; H-4,5), 7.00 (dd, $^3J(\text{H,H})$ = 8.3 Hz, $^4J(\text{H,H})$ = 2.2 Hz, 2H; H-3,6), 6.95 (s, 2H; Mes-CH-*m*), 2.41 (s, 3H; Mes-CH₃-*p*), 2.17 (s, 6H; Mes-CH₃-*o*), 1.16 (s, 18H; *t*Bu-CH₃)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 148.6 (C-2,7), 144.2, 143.4, 142.6, 140.3 (br., Mes-C-*i*), 138.6 (br., C-8a,9a), 138.5, 137.7, 136.4, 132.6 (C-1,8), 129.8 (Ph-CH-*o*), 129.3 (C-4,5), 128.2 (Ph-CH-*m*), 127.5 (C-3,6), 127.0 (Mes-CH-*m*), 126.4 (m, 2H; Ph-CH-*p*), 34.4 (*t*Bu-C), 31.3 (*t*Bu-CH₃), 22.7 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

^{11}B NMR (160.5 MHz, C₆D₆): δ 69 ($h_{1/2}$ \approx 1500 Hz)

EA (%): Calculated for C₄₃H₄₅B [572.63]: C 90.19, H 7.92; found: C 90.09, H 7.94

HRMS: Calculated for C₄₃H₄₅B: 572.36162, found: 572.36100



Synthesis of 9: A solution of **S6** (0.165 g, 0.288 mmol) in toluene (700 mL) was prepared in a 1 L flask equipped with a water-cooled quartz immersion well containing a medium pressure Hg lamp. Propylene oxide (20 mL) was added and the solution was purged with Ar for 15 min. using a cannula. The solution was irradiated and neat I₂ (0.190 g, 0.749 mmol) was added in several portions over a period of 1.5 h. After 4 h, the lamp was switched off and the reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I₂. All volatiles were removed under reduced pressure. The residue was suspended in MeOH (20 mL), sonicated, isolated by filtration, washed with MeOH (5 mL), and dried in vacuo to obtain the product as a yellow powder. Yield: 0.103 g (0.181 mmol, 63%). The sample still contained a side product (3-4% by NMR). This side product turned out to be compound **9^I**, iodinated at the *m*-position of the mesityl ring (**9^I**). Single crystals for X-ray analysis were grown by layering a solution of **9** (100 mg) in C₆H₆ (3 mL) with MeOH (14 mL). We found that **9^I** crystallizes more readily than **9**. As a consequence, the first crystals of **9** harvested contained a higher proportion of cocrystallized **9^I** than subsequent crops (in order to identify the side product, an X-ray analysis of the mixed crystal **9/9^I** was performed on a specimen obtained at the first stage of the fractional crystallization process (cf. Table S2) in addition to ¹H NMR spectroscopy). To remove **9^I** on a preparative scale, we recommend treating the mixture **9/9^I** with *t*BuLi in *n*-hexane/Et₂O at -78 °C, quench the product of the I/Li-exchange reaction with an aqueous NaHCO₃ solution, and purify the product by column chromatography. Single crystals of pure **9** were grown by the same method described for the mixture **9/9^I** (cf. Figure S67, Table S2, and main paper).

¹H NMR (500.2 MHz, CDCl₃): δ 9.16 (d, ⁴*J*(H,H) = 2.1 Hz, 2H; H-5,11 or 7,9), 8.92 (m, 4H; H-1,4,12,15), 8.34 (d, ⁴*J*(H,H) = 2.1 Hz, 2H; H-5,11 or 7,9), 7.78 (vt, 2H; H-2,14 or 3,13), 7.68 (vt, 2H; H-2,14 or 3,13), 6.98 (s, 2H; Mes-CH-*m*), 2.46 (s, 3H, Mes-CH₃-*p*), 2.03 (s, 6H; Mes-CH₃-*o*), 1.50 (s, 18H; *t*Bu-CH₃)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.1 (C-6,10), 140.4 (br., Mes-C-*i*), 138.9 (Mes-C-*o*), 138.1 (C-5,11 or 7,9), 136.4 (Mes-C-*p*), 135.4 (br., C-7a,8a), 131.8, 130.7, 130.1 (C-1,15 or 4,12), 130.1 (C-8b,8d), 129.6, 129.0, 126.9 (C-2,14 or 3,13), 126.9 (Mes-CH-*m*), 125.7 (C-2,14 or 3,13), 125.1, 125.0 (C-5,11 or 7,9), 123.3 (C-1,15 or 4,12), 35.1 (*t*Bu-C), 31.5 (*t*Bu-CH₃), 23.6 (Mes-C-*o*), 21.5 (Mes-C-*p*)

¹¹B NMR (160.5 MHz, CDCl₃): δ 65 (*h*_{1/2} ≈ 1500 Hz)

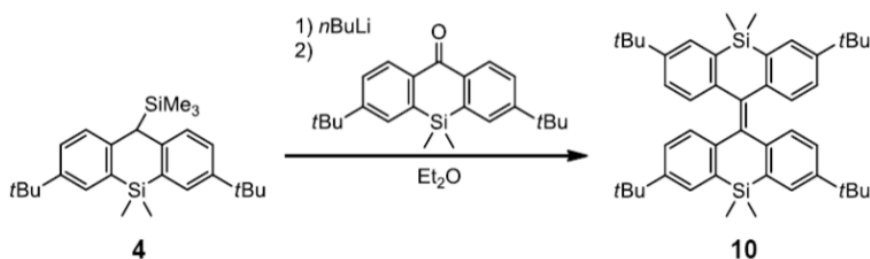
EA (%): Calculated for C₄₃H₄₁B [568.60]: C 90.83, H 7.27; found: C 90.13, H 7.32

HRMS: Calculated for C₄₃H₄₁B: 568.33032, found: 568.32910

UV/Vis (cyclohexane): λ_{max} (ε) = 429 (22000), 407 nm (14000)

Fluorescence (cyclohexane, λ_{Ex} = 400 nm): 465, 439 nm; Φ_{PL} = 70%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = 1.00, -2.01 V



Synthesis of 10: Compound **4** (1.00 g, 2.45 mmol) was placed in a 2-necked round-bottom flask and dissolved in THF (25 mL). *n*BuLi in *n*-hexane (1.6 M; 1.5 mL, 2.4 mmol) was added while stirring at $-78\text{ }^{\circ}\text{C}$. The solution was allowed to warm to room temperature, whereupon its color changed to red. The reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$ again and a solution of **3** (0.847 g, 2.42 mmol) in THF (ca. 3 mL) was added while stirring via a syringe. The mixture was warmed to room temperature, stirred for 16 h, and quenched with MeOH (1 mL), whereupon its dark blue color faded and a colorless precipitate formed. The mixture was evaporated to dryness under reduced pressure, redissolved in a minimum amount of CH_2Cl_2 , and purified by short-column chromatography (5 cm silica gel, CH_2Cl_2). The solvent was removed from the eluate under reduced pressure, the solid residue was suspended in *n*-hexane (10 mL), sonicated, isolated by filtration, washed with *n*-hexane ($2 \times 10\text{ mL}$), and dried in vacuo (colorless powder). Yield: 0.879 g (1.31 mmol, 54%). Slow evaporation of a CH_2Cl_2 solution gave X-ray quality crystals.

^1H NMR (400.1 MHz, CDCl_3): δ 7.55 (d, $^4J(\text{H,H}) = 2.1\text{ Hz}$, 4H; H-1,1',8,8'), 6.90 (dd, $^3J(\text{H,H}) = 8.2\text{ Hz}$, $^4J(\text{H,H}) = 2.1\text{ Hz}$, 4H; H-3,3',6,6'), 6.65 (d, $^3J(\text{H,H}) = 8.2\text{ Hz}$, 4H; H-4,4',5,5'), 1.26 (s, 36H; *t*Bu- CH_3), 0.72 (s, 6H; SiMe_2), 0.64 (s, 6H; SiMe_2)

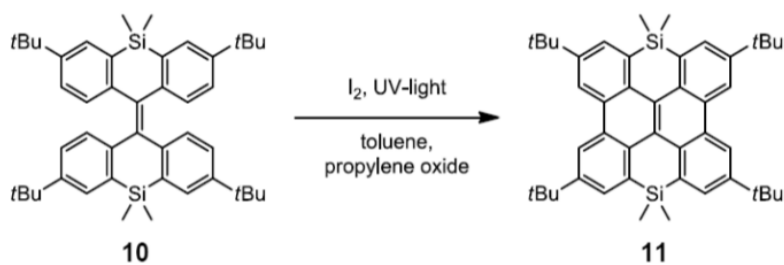
$^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ 147.7 (C-2,2',7,7'), 144.9 (C-4a,4a',10a,10a'), 138.0 (C-10,10'), 137.2 (C-8a,8a',9a,9a'), 129.5 (C-4,4',5,5'), 128.2 (C-1,1',8,8'), 125.0 (C-3,3',6,6'), 34.6 (*t*Bu-C), 31.5 (*t*Bu- CH_3), -1.6 (SiMe_2), -5.6 (SiMe_2)

^{29}Si NMR (59.6 MHz, CDCl_3): δ -17.1

EA (%): Calculated for $\text{C}_{46}\text{H}_{60}\text{Si}_2$ [669.14]: C 82.57, H 9.04; found: C 83.02, H 8.97

HRMS: Calculated for $\text{C}_{46}\text{H}_{60}\text{Si}_2$: 668.42281, found: 668.42208

UV/Vis (CHCl_3): $\lambda_{\text{max}} (\epsilon) = 319\text{ nm}$ (20000)



Synthesis of 11: A solution of **10** (0.833 g, 1.24 mmol) in toluene (700 mL) was prepared in a 1 L flask equipped with a water-cooled quartz immersion well containing a medium pressure Hg lamp. Propylene oxide (20 mL) was added and the solution was purged with Ar for 15 min using a cannula. The solution was irradiated for 3 h during which time neat I_2 (0.650 g, 2.56 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm;

activity grade I) to remove residual I₂, and the eluate was evaporated to dryness under reduced pressure. The brown residue was suspended in *n*-hexane (12 mL) and sonicated. Cold (8 °C) MeOH (50 mL) was added, whereupon a precipitate formed, which was isolated by filtration, washed with cold MeOH (2 × 20 mL), and dried in vacuo (colorless powder). Yield: 0.588 g (0.884 mmol, 71%). **11** can be crystallized by layering a concentrated solution in C₆H₆ with MeOH.

¹H NMR (500.2 MHz, CDCl₃): δ 8.80 (d, ⁴J(H,H) = 2.0 Hz, 4H; H-3,4,10,11), 8.02 (d, ⁴J(H,H) = 2.0 Hz, 4H; H-1,6,8,13), 1.56 (s, 36H; *t*Bu-CH₃), 0.57 (s, 12H; SiMe₂)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 147.8 (C-2,5,9,12), 134.3 (C-6a,7a,13a,14a), 132.2 (C-7b,13b,14b,14e), 130.9 (C-3a,3b,10a,10b), 130.2 (C-1,6,8,13), 127.6 (C-14c,14d), 120.6 (C-3,4,10,11), 35.0 (*t*Bu-C), 31.5 (*t*Bu-CH₃), -0.8 (SiMe₂)

²⁹Si NMR (99.4 MHz, CDCl₃): δ -19.9

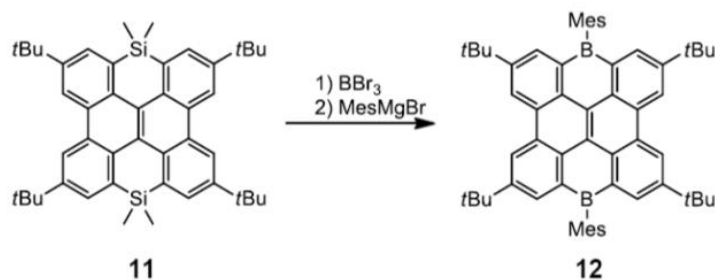
EA (%): Calculated for C₄₆H₅₆Si₂ [665.11]: C 83.07, H 8.49, found: C 83.31, H 8.49

HRMS: Calculated for C₄₆H₅₆Si₂: 664.39151, found: 664.39115

UV/Vis (cyclohexane): λ_{max} (ε) = 384 (4000), 361 (18000), 347 nm (18000)

Fluorescence (cyclohexane, λ_{Ex} = 345 nm): λ_{max} = 408, 390 nm; Φ_{PL} = 35%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = 0.81 V



Synthesis of 12: Compound **11** (0.300 g, 0.451 mmol) was placed in an ampule and dissolved in BBr₃ (0.8 mL, 2 g, 8 mmol). The ampule was vacuum sealed and heated to 200 °C for 4 d. Afterwards it was opened at room temperature and the dark reaction mixture was transferred to a thoroughly flame-dried round-bottom Schlenk tube equipped with a dropping funnel. Excess BBr₃ was removed under reduced pressure at 60 °C and the solid residue was dissolved in toluene (20 mL). A solution of MesMgBr in THF (0.87 M, 1.6 mL, 1.4 mmol) was placed in the dropping funnel and added while stirring at 0 °C. Stirring was continued at room temperature for 16 h before the reaction solution was poured into a stirred mixture of saturated aqueous NaHCO₃ (100 mL) and toluene (30 mL). The aqueous layer was separated and extracted with toluene (2 × 50 mL). The combined organic layers were washed with H₂O (50 mL), dried over MgSO₄, filtered, and all volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (15 cm silica gel, *n*-hexane:EtOAc = 25:1). The first colored fraction contained the product, which was further purified by recrystallization from *n*-hexane to obtain a yellow solid of **12** × C₆H₁₂ (the amount of *n*-hexane present in the sample was determined by ¹H NMR spectroscopy; the solvent remained in the sample even after prolonged storage under vacuum). Yield of **12** × C₆H₁₄: 0.116 g (0.130 mmol, 29%). Alternatively, crystals of **12** × 2C₆H₆ can be grown by layering a concentrated solution of **12** in C₆H₆ (10 mg mL⁻¹) with MeOH.

¹H NMR (500.2 MHz, CDCl₃): δ 9.40 (d, ⁴J(H,H) = 2.0 Hz, 4H; H-3,4,10,11), 8.46 (d, ⁴J(H,H) = 2.0 Hz, 4H; H-1,6,8,13), 7.02 (s, 4H; Mes-CH-*m*), 2.49 (s, 6H; Mes-CH₃-*p*), 2.09 (s, 12H; Mes-CH₃-*o*), 1.55 (s, 36H; *t*Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 149.1 (C-2,5,9,12), 140.8 (Mes-C-*i*), 139.0 (Mes-C-*o*), 138.5 (C-1,6,8,13), 136.5 (Mes-C-*p*), 136.3 (C-6a,7a,13a,14a), 130.5 (C-7b,13b,14b,14e), 129.9 (C-3a,3b,10a,10b), 128.3 (C-14c,14d), 127.1 (Mes-CH-*m*), 125.3 (C-3,4,10,11), 35.3 (*t*Bu-C), 31.6 (*t*Bu-CH₃), 23.8 (Mes-CH₃-*o*), 21.6 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 66 (h_{1/2} ≈ 1500 Hz)

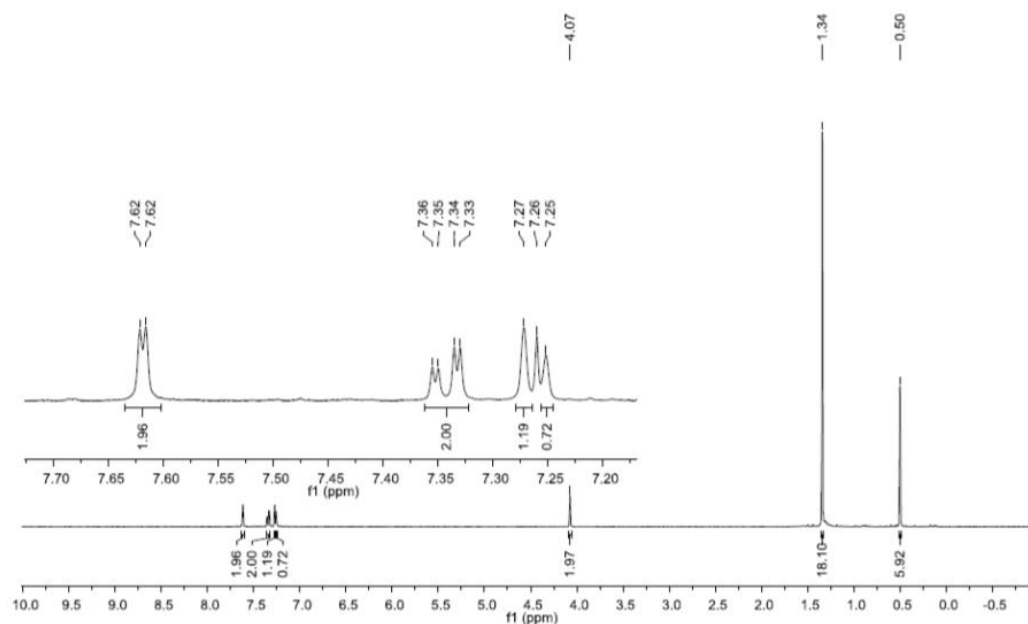
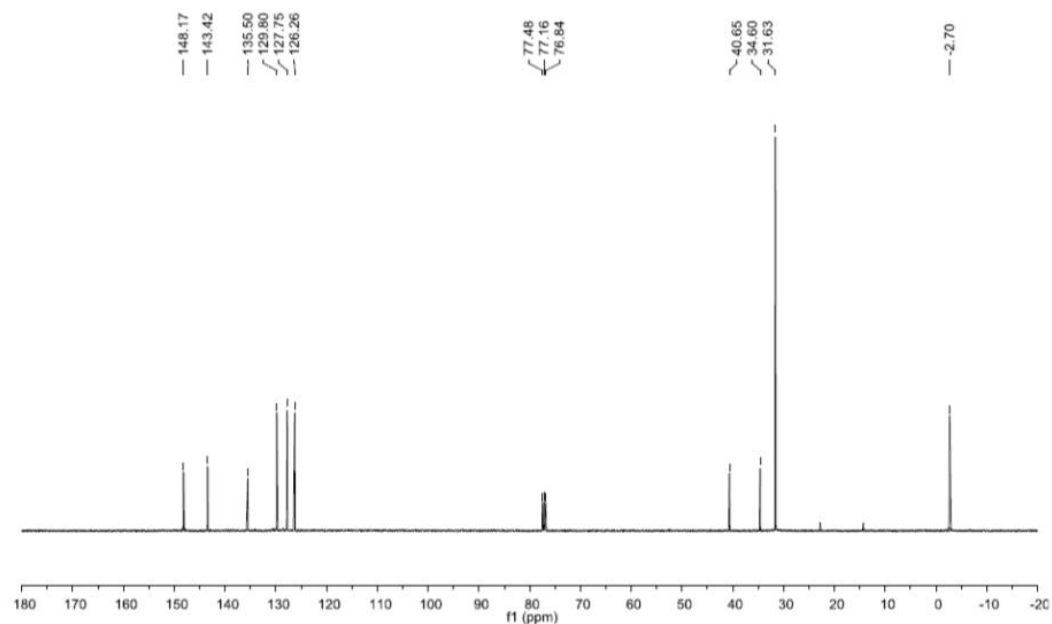
EA (%): Calculated for C₆₀H₆₆B₂ [808.79] × 2C₆H₆ [78.11]: C 89.61, H 8.15; found: C 89.10, H 8.14; the amount of C₆H₆ present in the sample was independently confirmed by ¹H NMR spectroscopy and X-ray crystallography

HRMS: Calculated for C₆₀H₆₆B₂: 808.53451, found: 808.53687

UV/Vis (cyclohexane): λ_{max} (ε) = 442 (34000), 432 (42000), 418 nm (31000)

Fluorescence (cyclohexane, λ_{ex} = 400 nm): λ_{max} = 475, 449 nm; Φ_{PL} = 78%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = 1.09, -1.85, -2.14 V

5. Plots of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectraFigure S1: ^1H NMR spectrum of **1** (CDCl_3 , 400.1 MHz).Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** (CDCl_3 , 100.6 MHz).

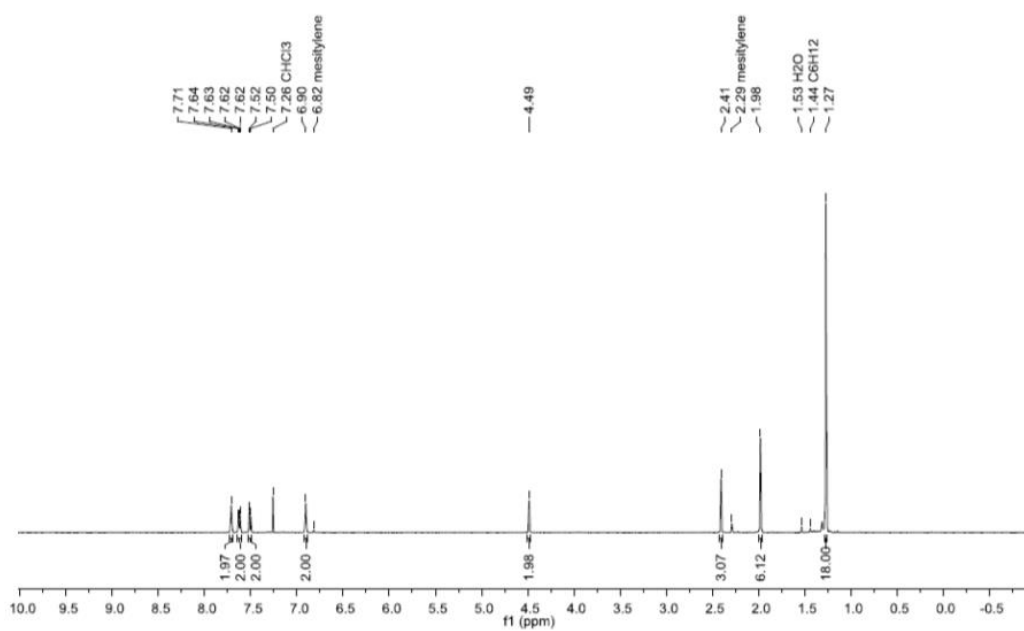


Figure S3: ¹H NMR spectrum of **2** (CDCl₃, 500.2 MHz).

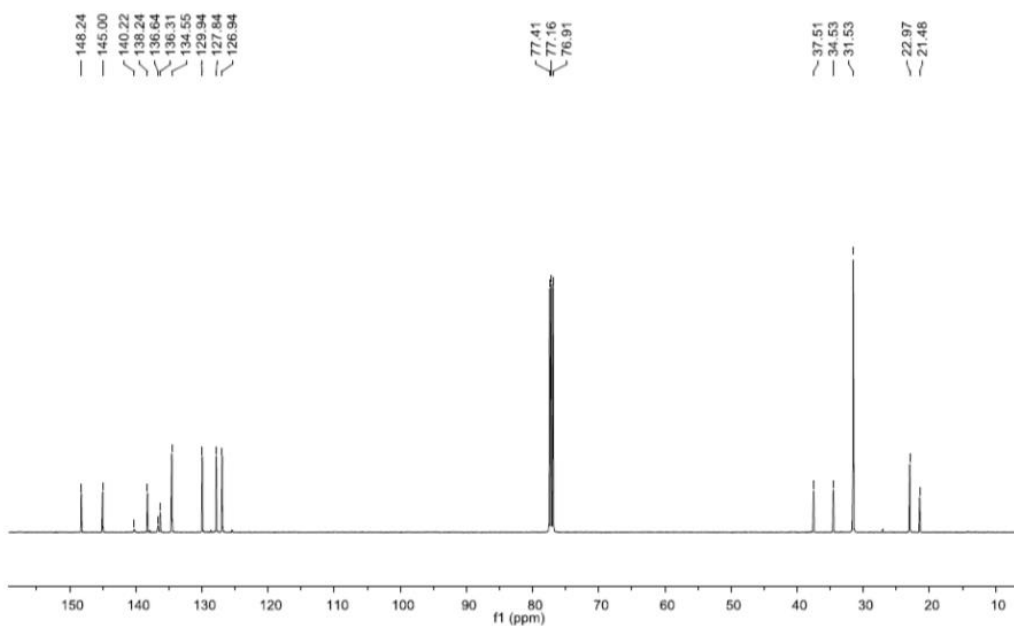


Figure S4: ¹³C{¹H} NMR spectrum of **2** (CDCl₃, 125.8 MHz).

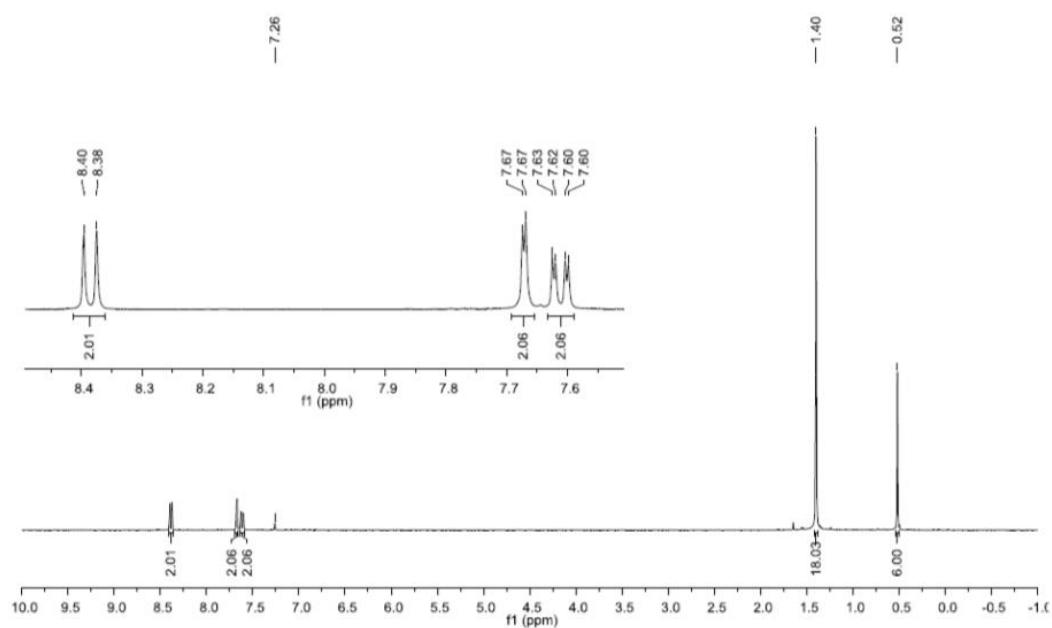


Figure S5: ^1H NMR spectrum of **3** (CDCl_3 , 400.1 MHz).

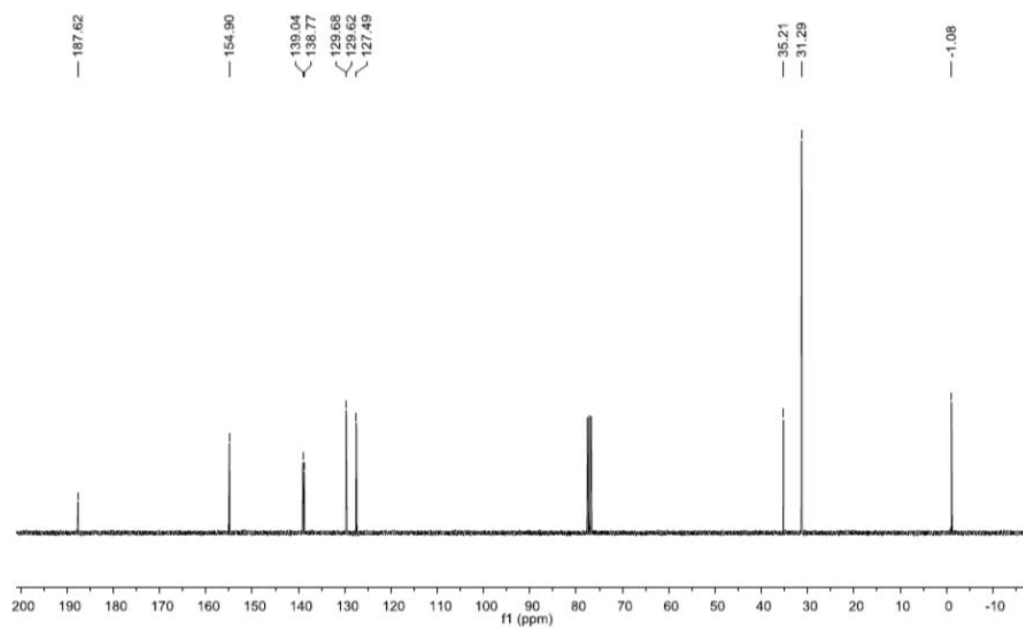


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** (CDCl_3 , 75.4 MHz).

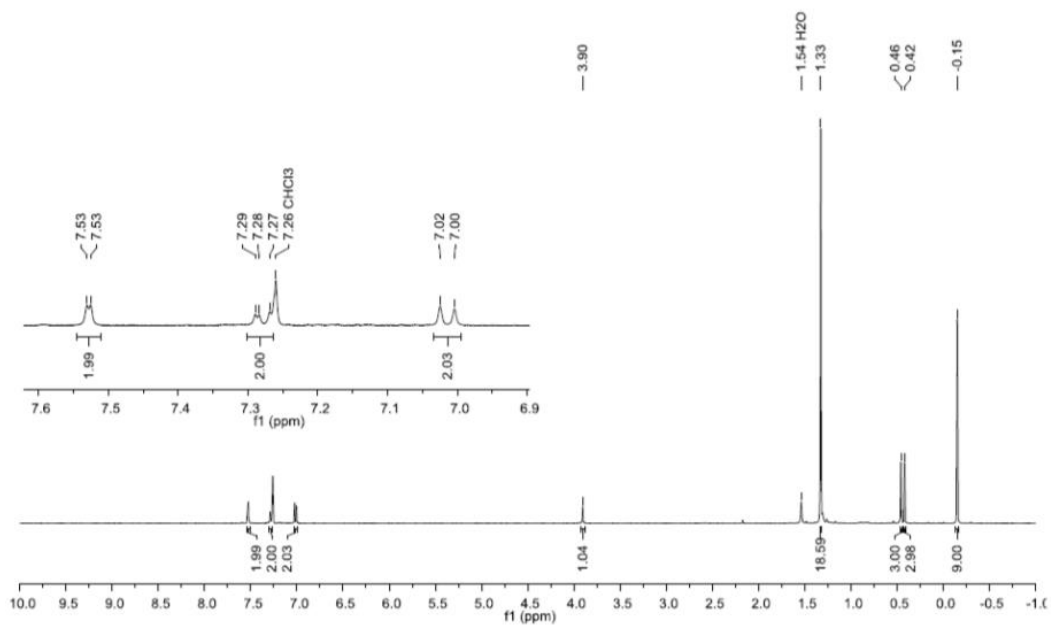


Figure S7: ^1H NMR spectrum of **4** (CDCl_3 , 400.1 MHz).

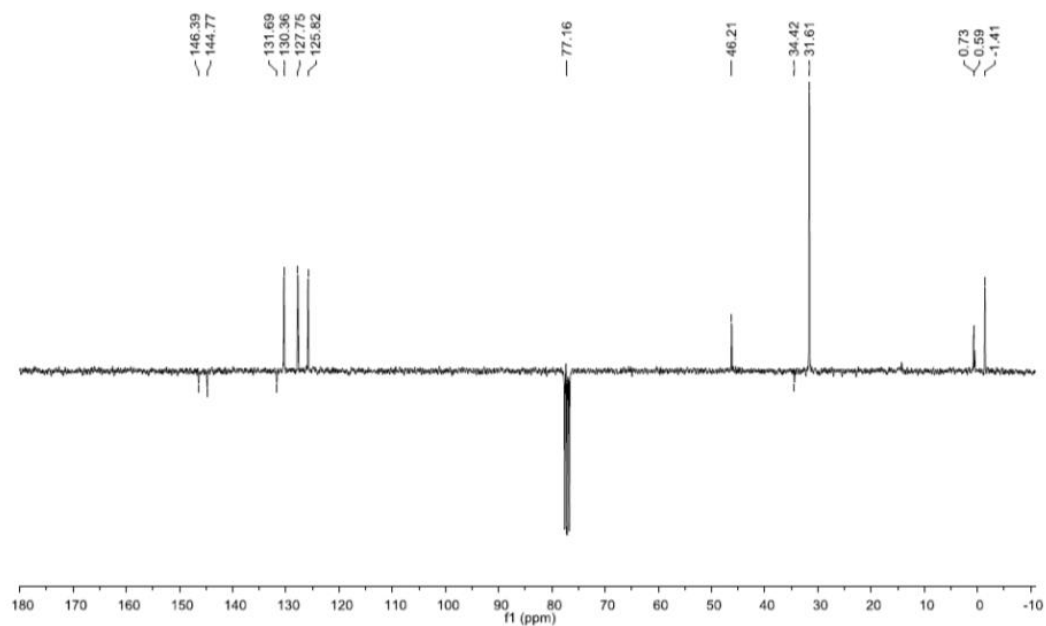


Figure S8: $^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR spectrum of **4** (CDCl_3 , 75.4 MHz).

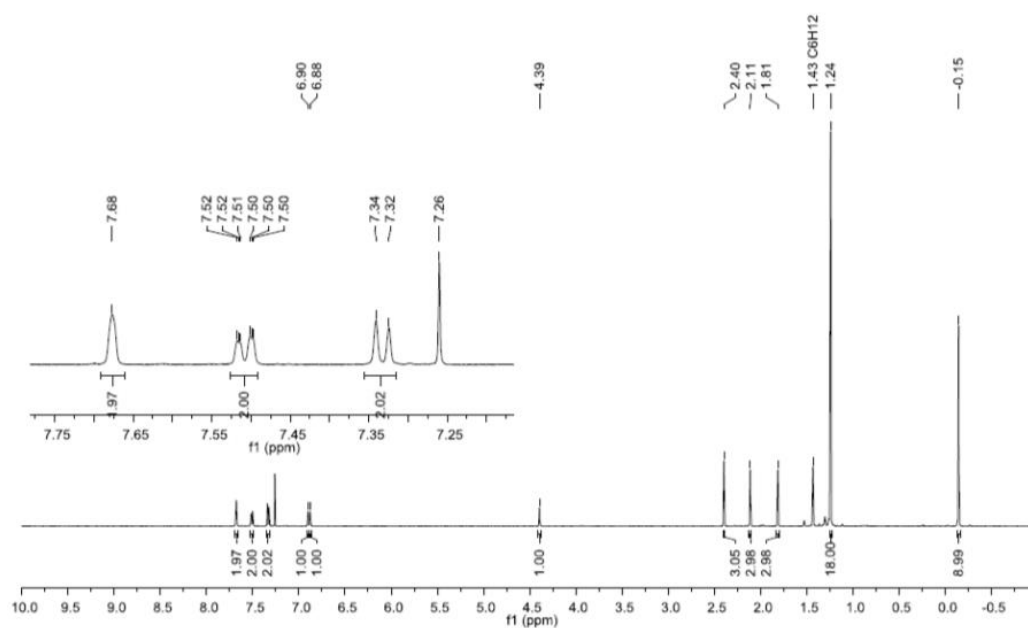


Figure S9: ^1H NMR spectrum of **5** (CDCl_3 , 500.2 MHz).

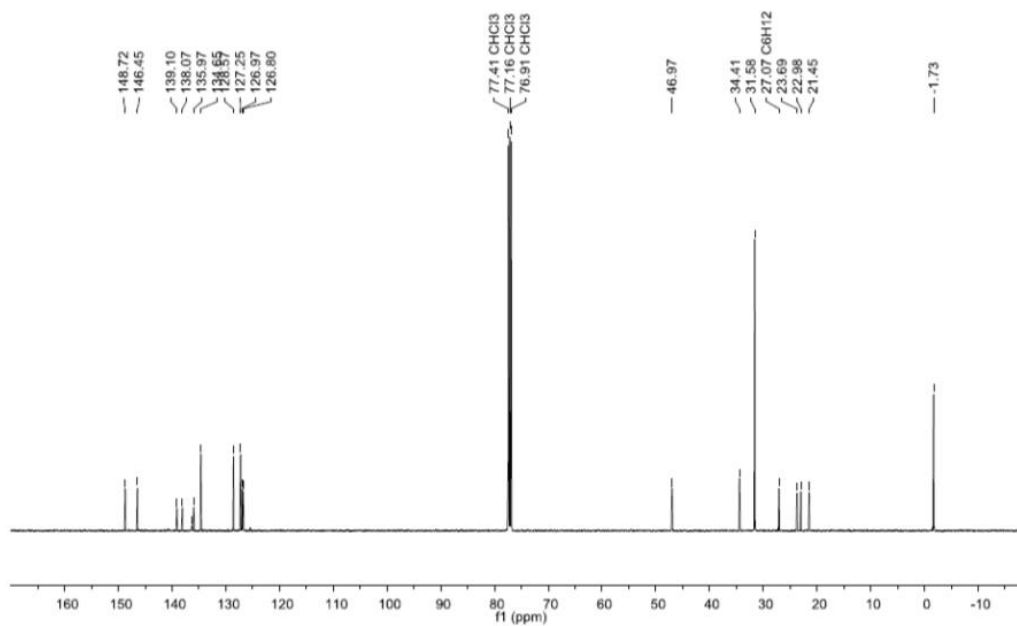


Figure S10: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** (CDCl_3 , 125.8 MHz).

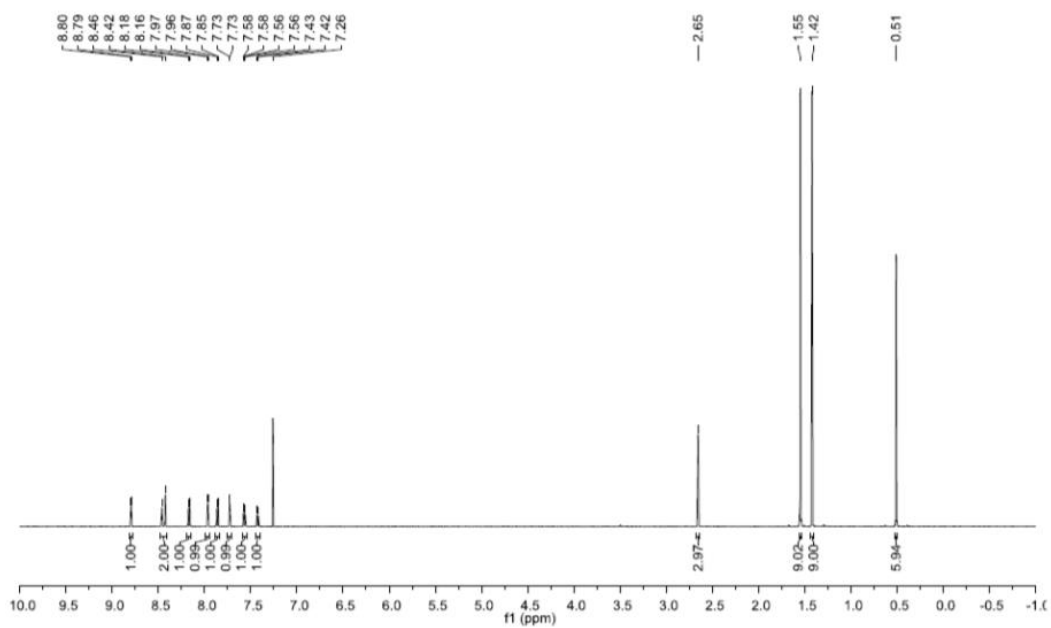


Figure S11: ^1H NMR spectrum of **6a** (CDCl_3 , 500.2 MHz).

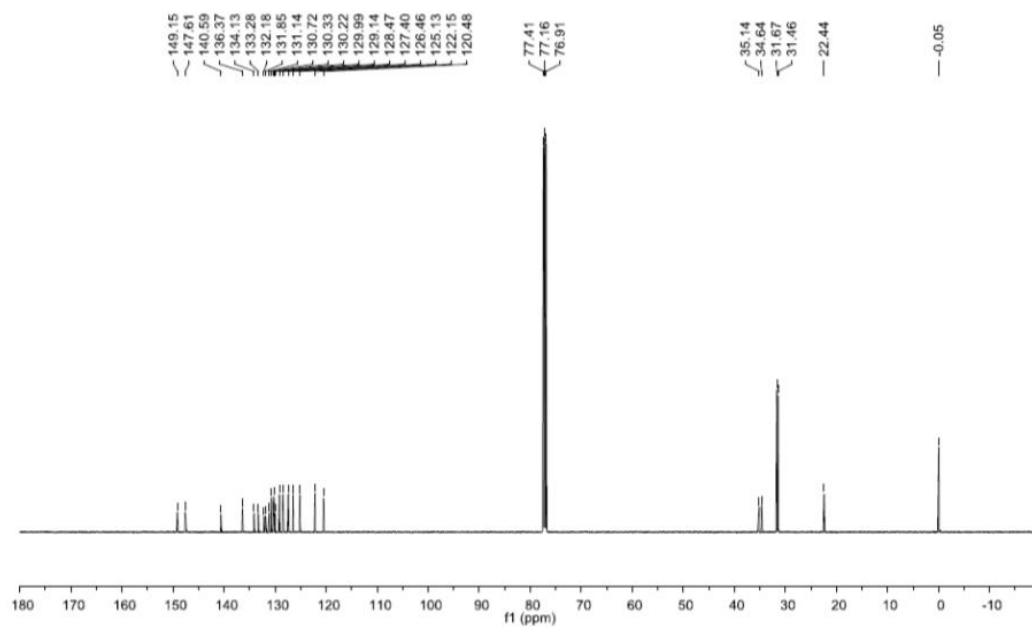


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6a** (CDCl_3 , 125.8 MHz).

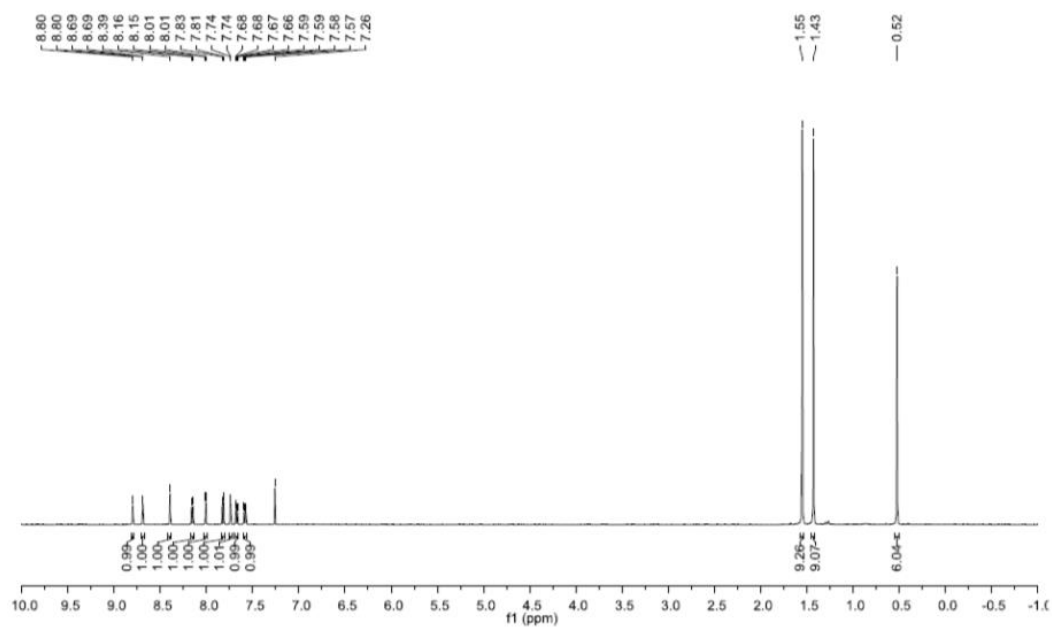


Figure S13: ¹H NMR spectrum of **6b** (CDCl₃, 500.2 MHz).

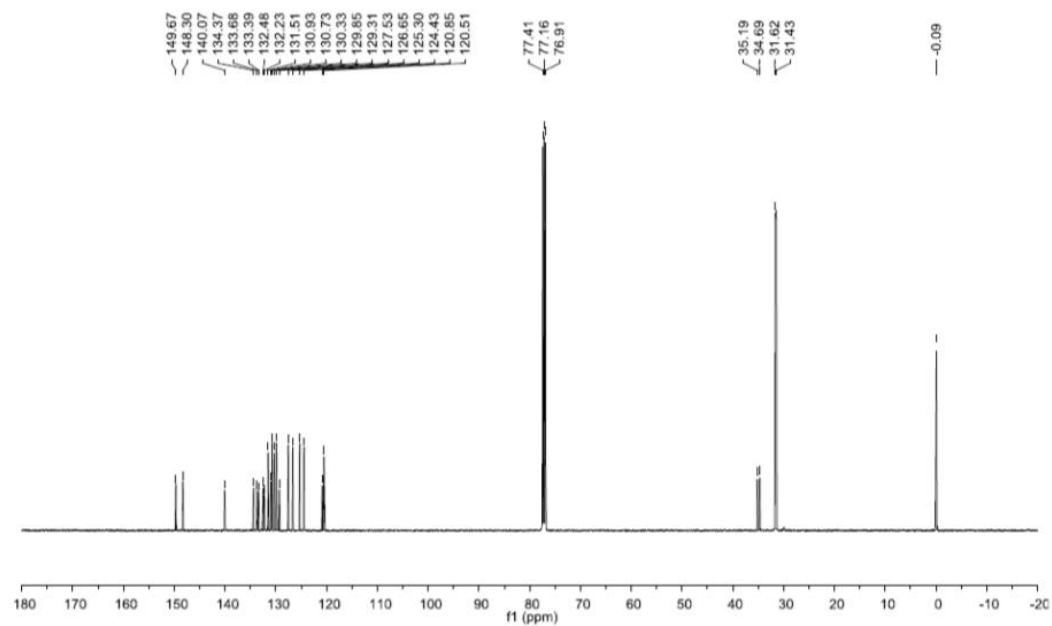


Figure S14: ¹³C{¹H} NMR spectrum of **6b** (CDCl₃, 125.8 MHz).

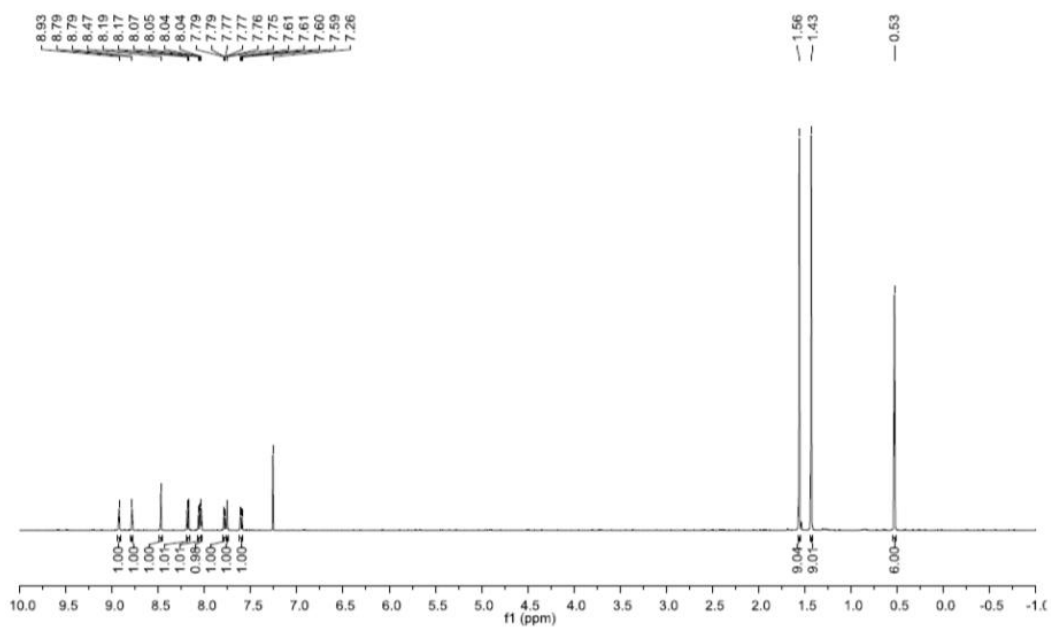


Figure S15: ^1H NMR spectrum of **6c** (CDCl_3 , 500.2 MHz).

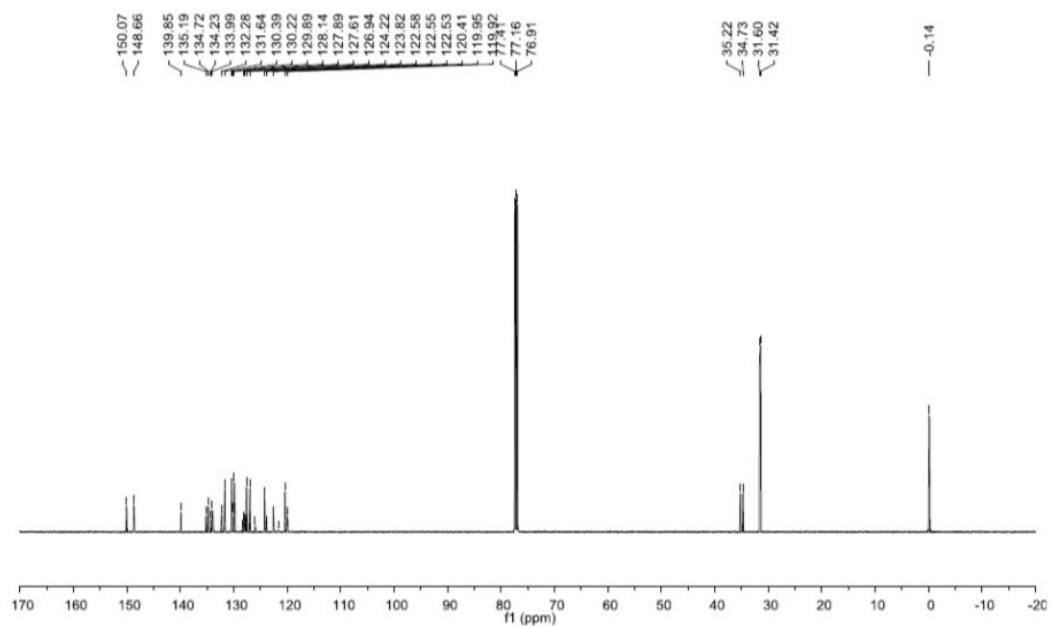


Figure S16: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6c** (CDCl_3 , 125.8 MHz).

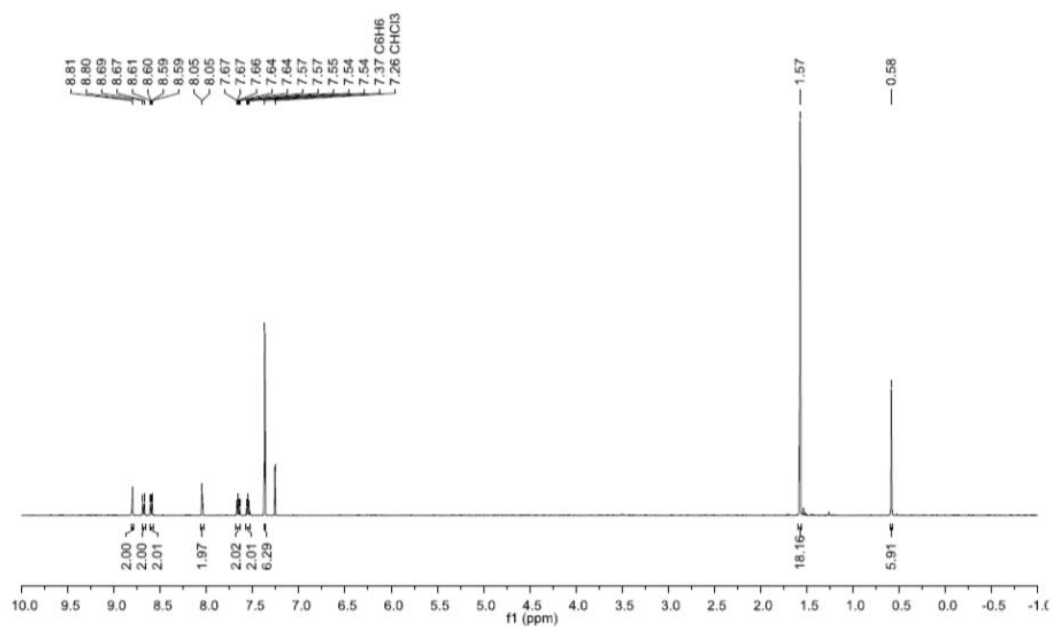


Figure S17: ^1H NMR spectrum of **7** (CDCl_3 , 500.2 MHz).

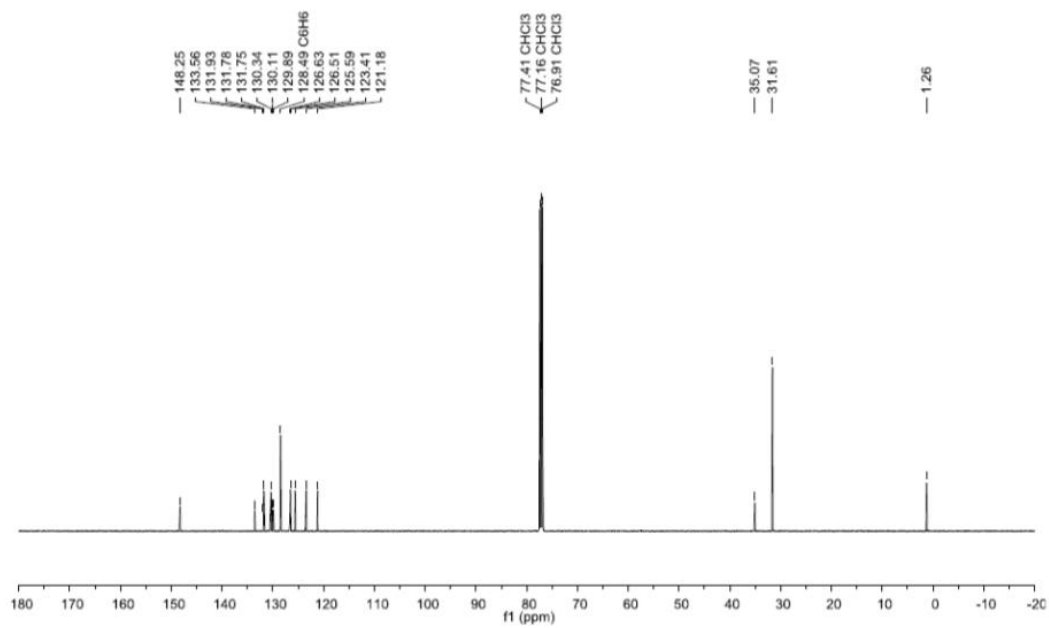


Figure S18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** (CDCl_3 , 125.8 MHz).

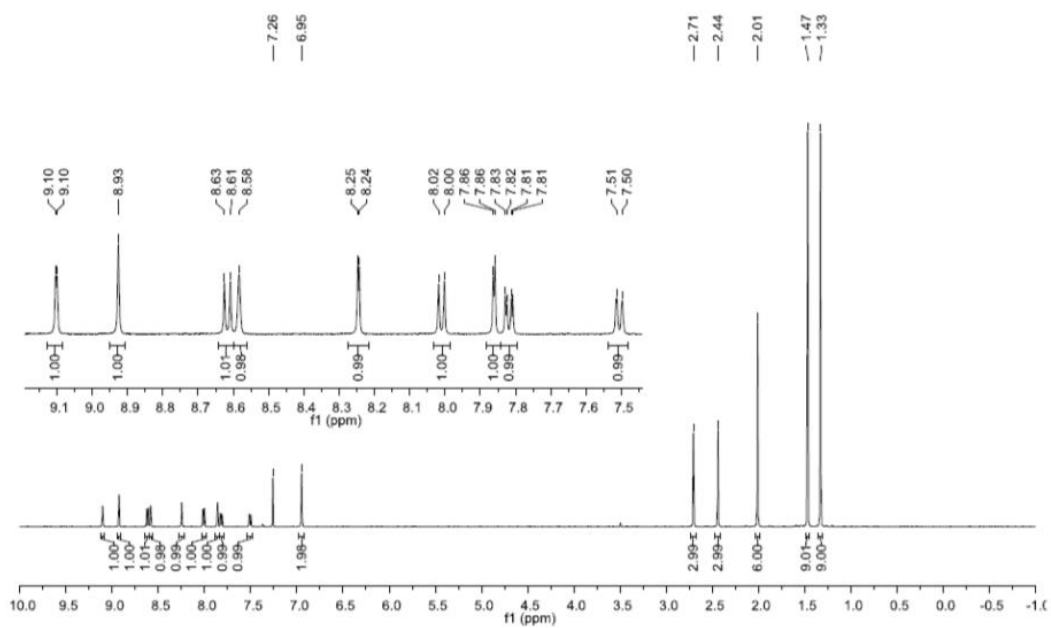


Figure S19: ^1H NMR spectrum of **8a** (CDCl_3 , 500.2 MHz).

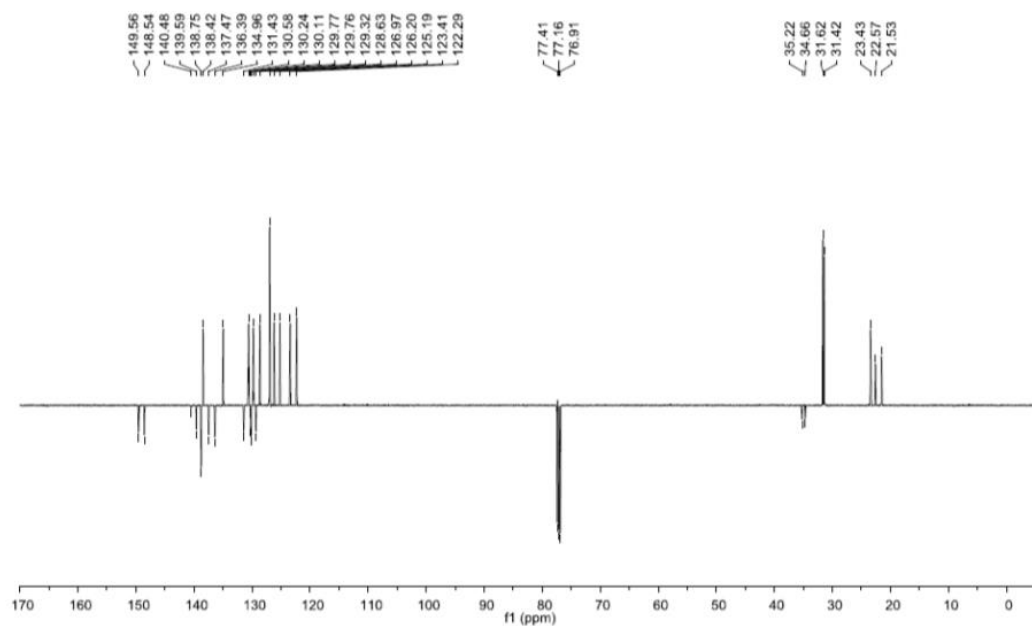


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR spectrum of **8a** (CDCl_3 , 125.8 MHz).

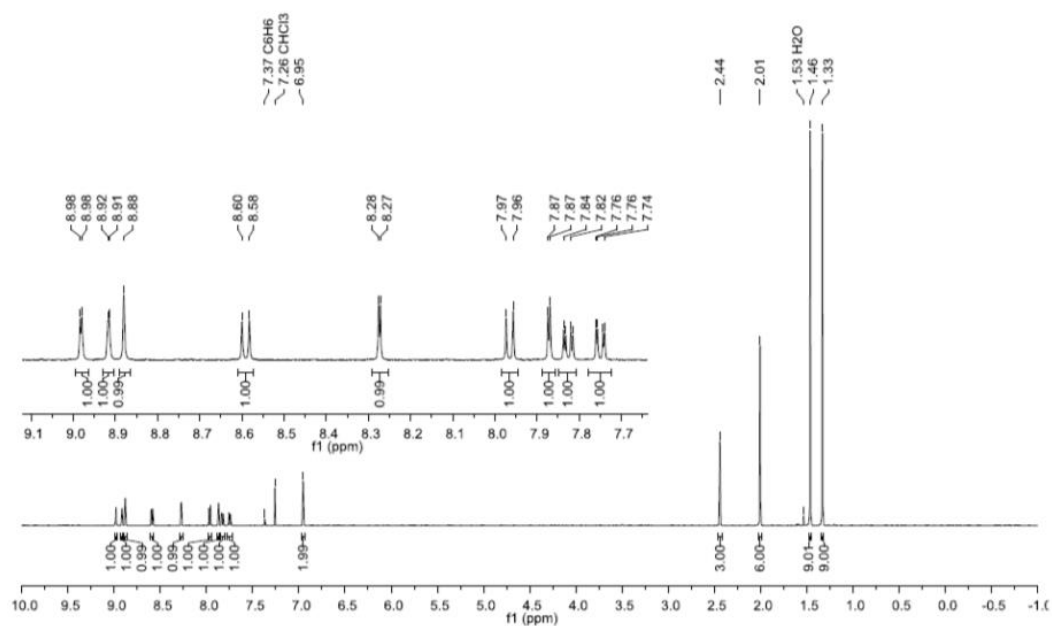


Figure S21: ^1H NMR spectrum of **8b** (CDCl_3 , 500.2 MHz).

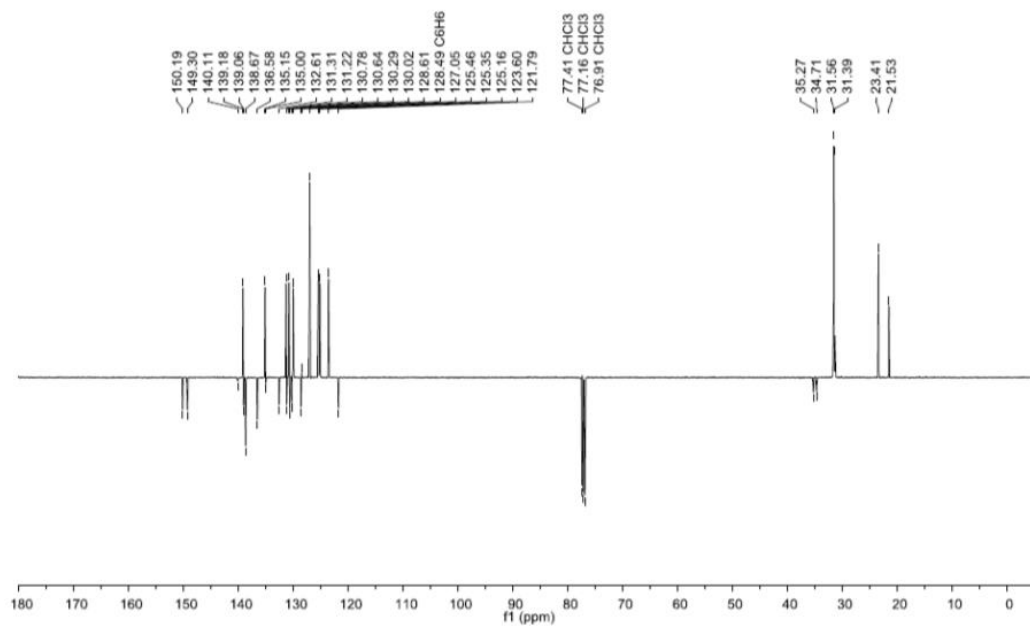


Figure S22: $^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR spectrum of **8b** (CDCl_3 , 125.8 MHz).

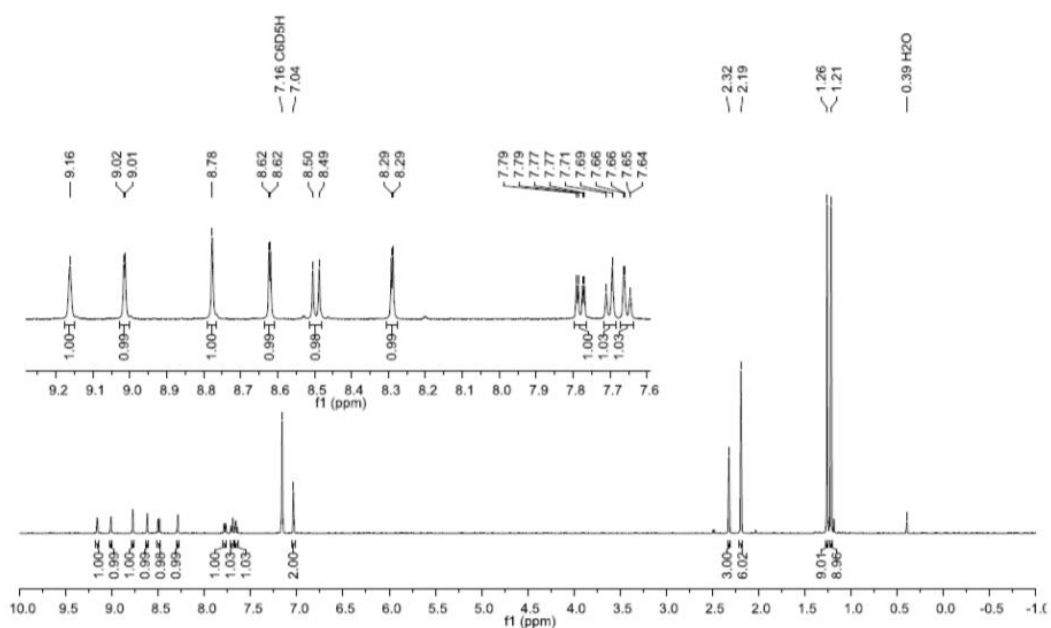


Figure S23: ^1H NMR spectrum of **8c** (C_6D_6 , 500.2 MHz).

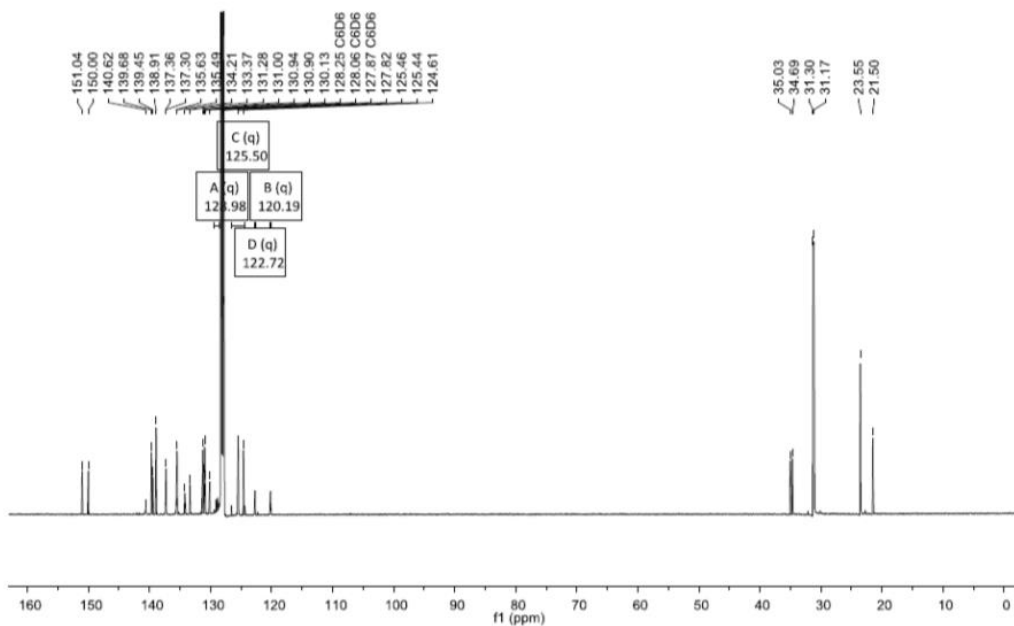


Figure S24: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8c** (C_6D_6 , 125.8 MHz), peaks belonging to the quartets A, B, C and D are not picked individually.

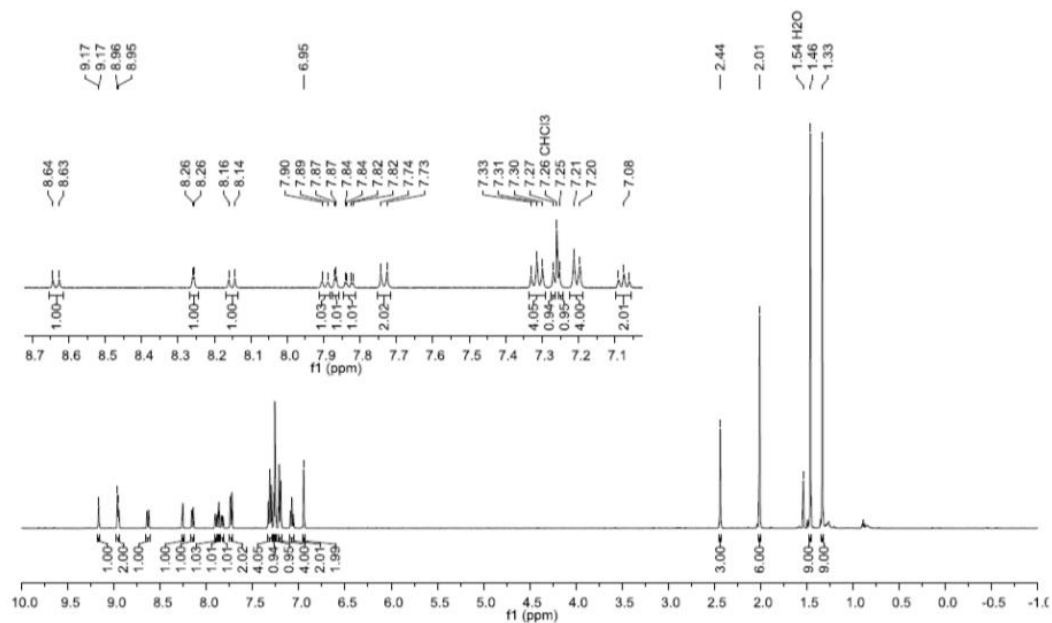


Figure S25: ¹H NMR spectrum of **8d** (CDCl₃, 500.2 MHz).

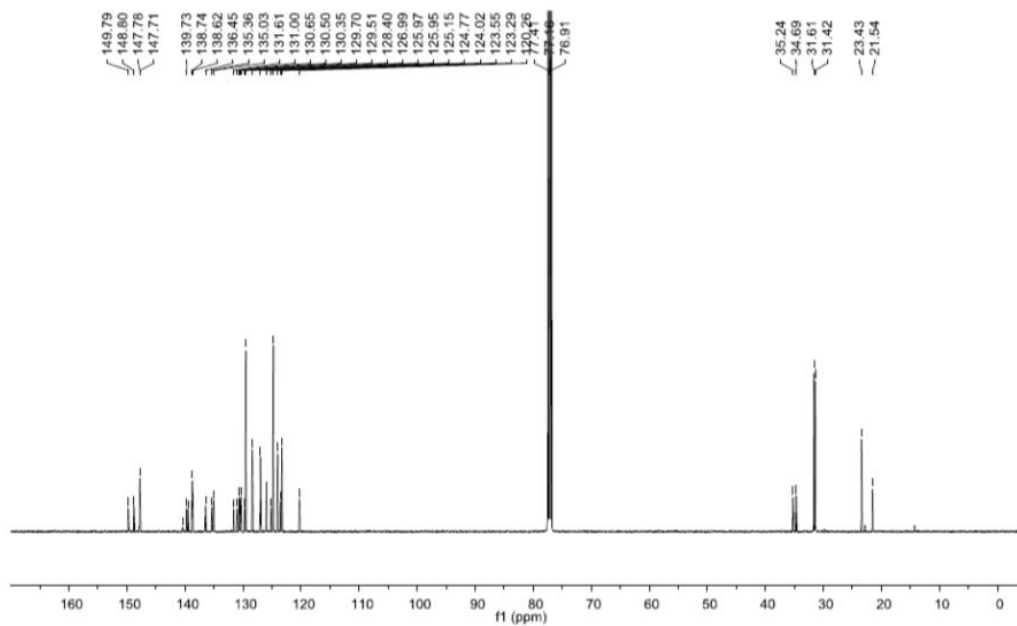


Figure S26: ¹³C{¹H} NMR spectrum of **8d** (CDCl₃, 125.8 MHz).

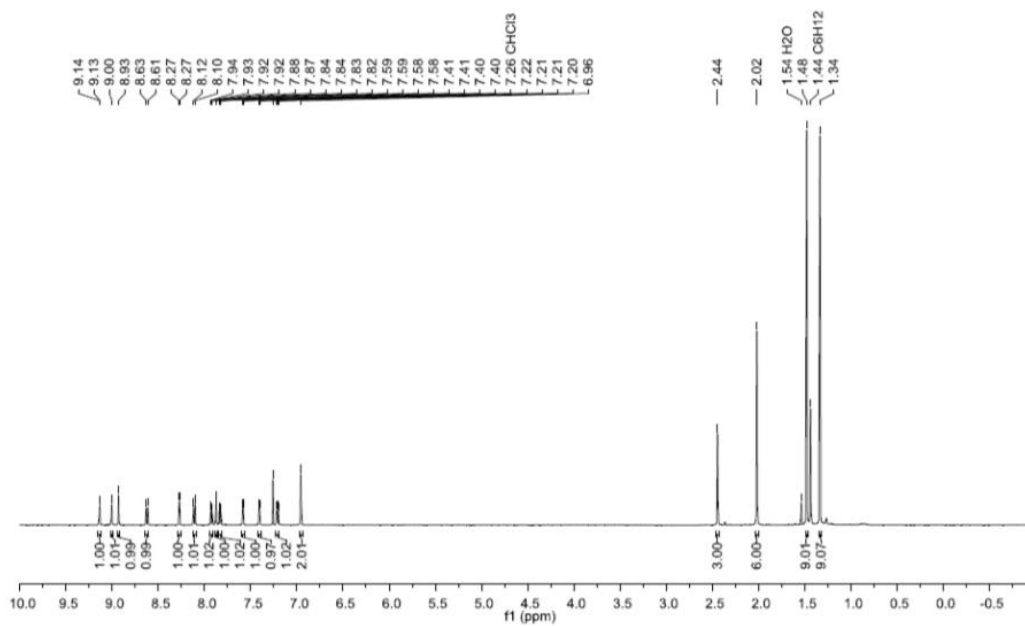


Figure S27: ^1H NMR spectrum of **8e** (CDCl_3 , 500.2 MHz).

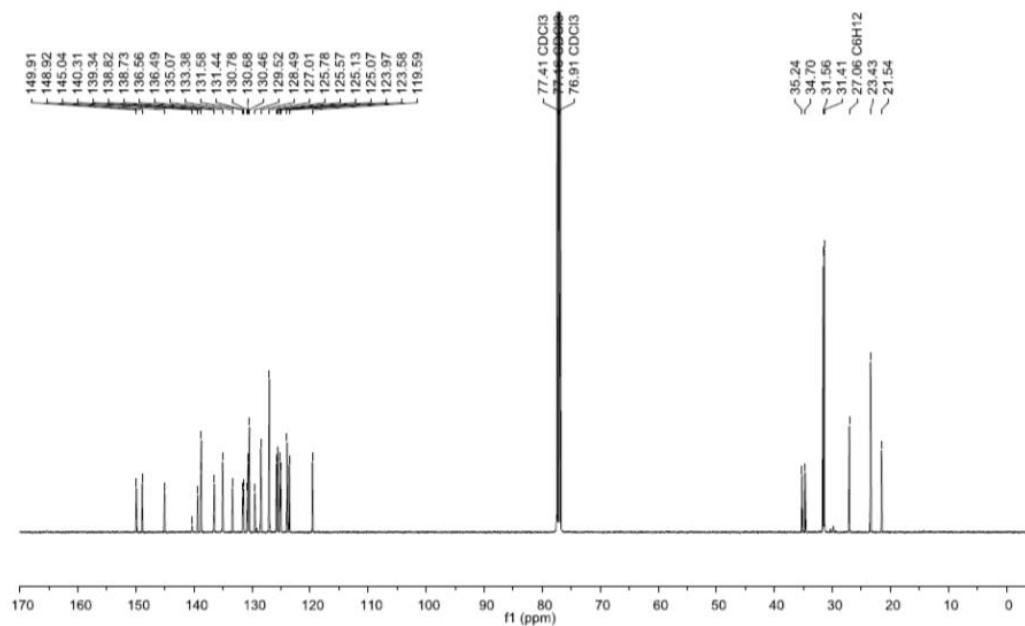
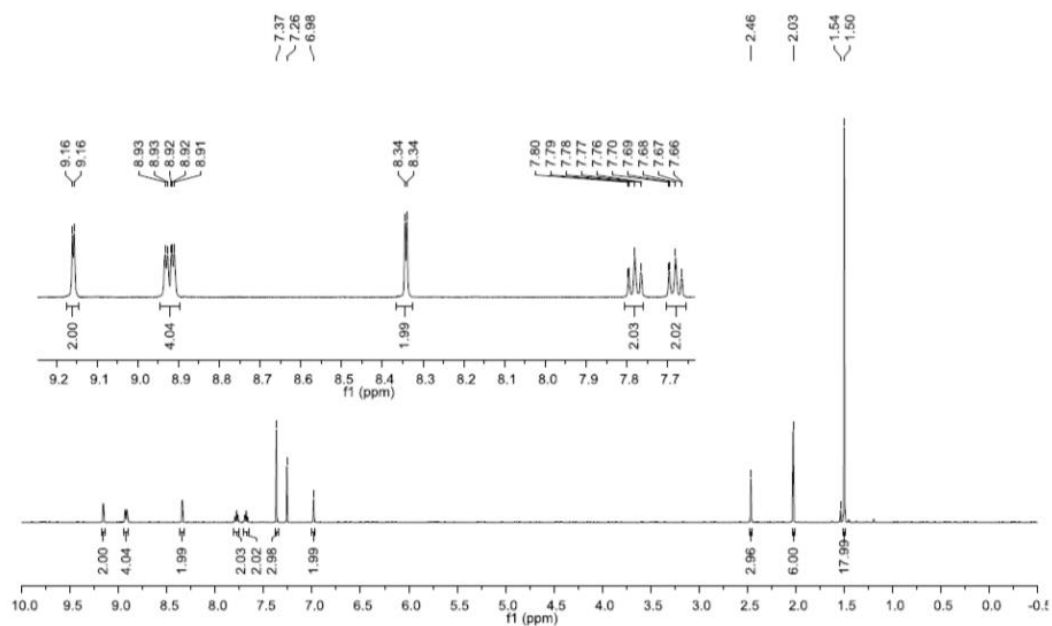
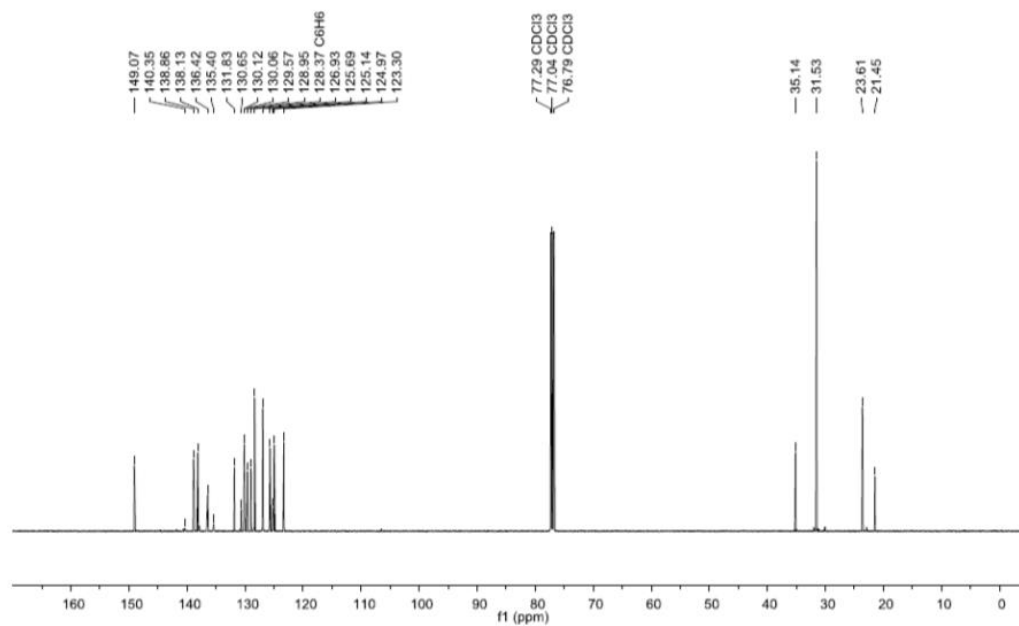


Figure S28: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8e** (CDCl_3 , 125.8 MHz).

Figure S29: ^1H NMR spectrum of **9** (CDCl_3 , 500.2 MHz).Figure S30: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** (CDCl_3 , 125.8 MHz).

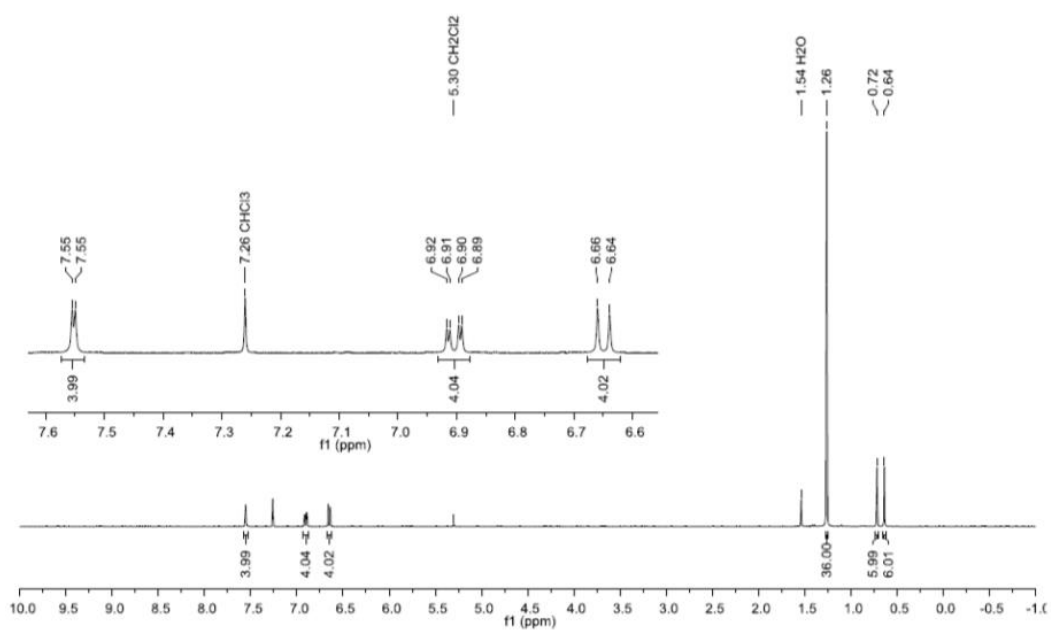


Figure S31: ^1H NMR spectrum of **10** (CDCl_3 , 400.1 MHz).

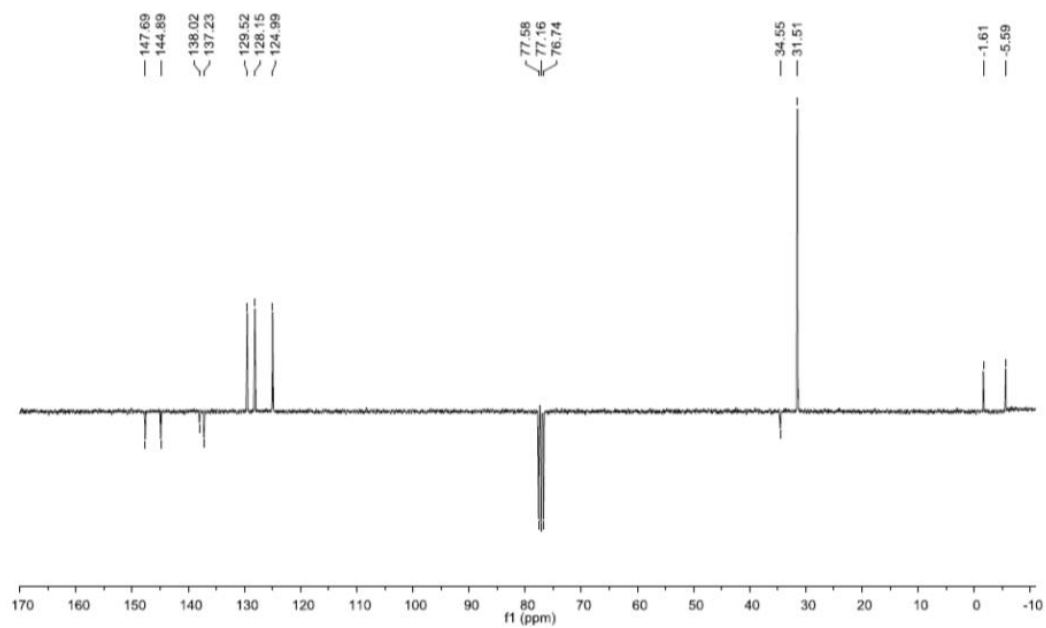


Figure S32: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10** (CDCl_3 , 75.4 MHz).

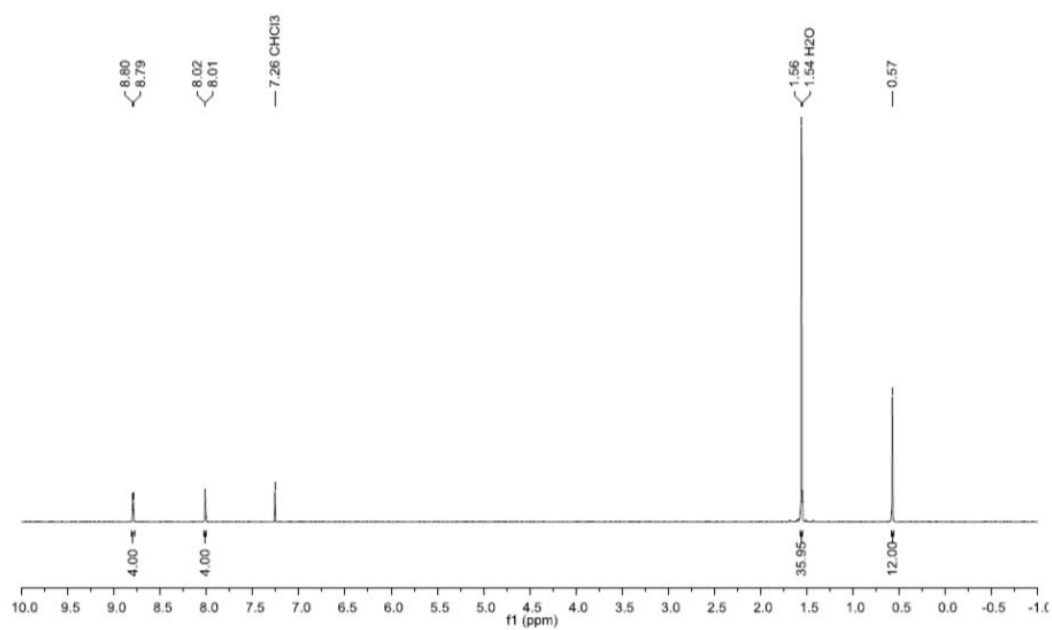


Figure S33: ¹H NMR spectrum of **11** (CDCl₃, 500.2 MHz).

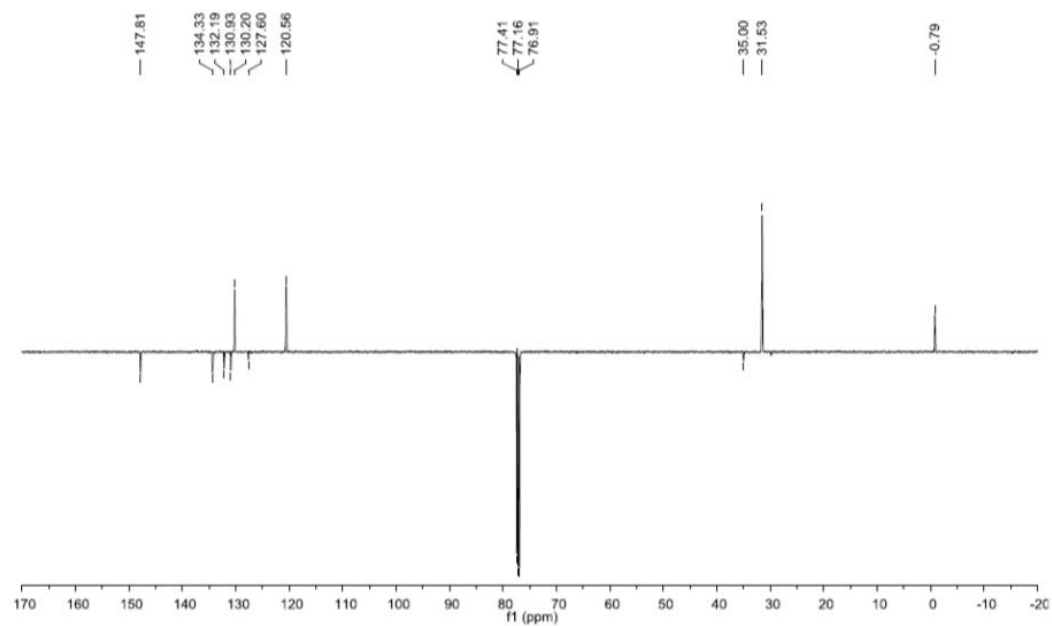


Figure S34: ¹³C{¹H}-DEPT NMR spectrum of **11** (CDCl₃, 125.8 MHz).

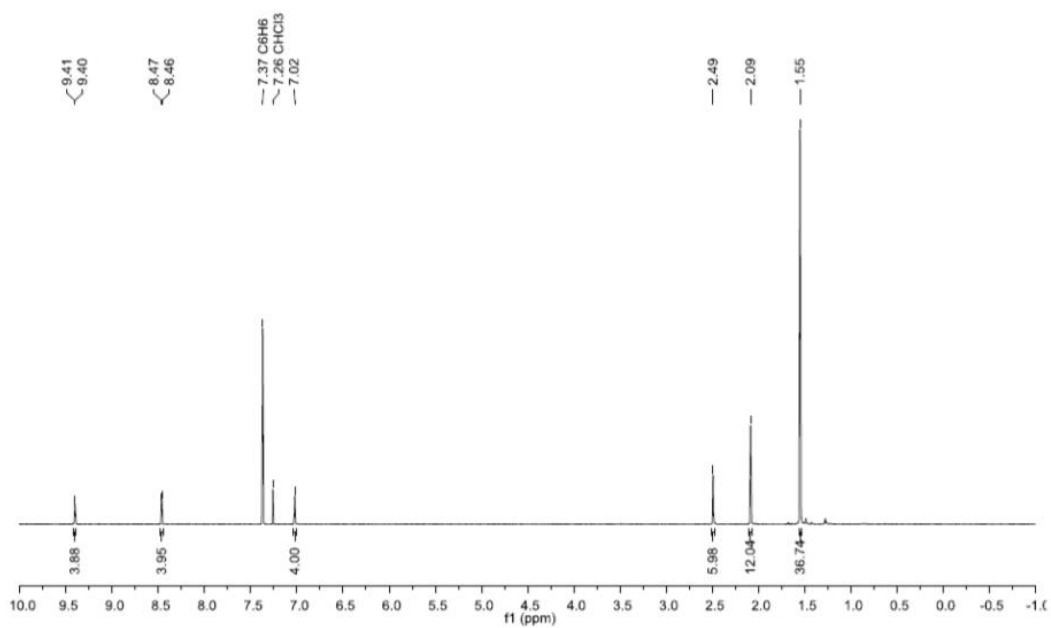


Figure S35: ^1H NMR spectrum of **12** (CDCl_3 , 500.2 MHz).

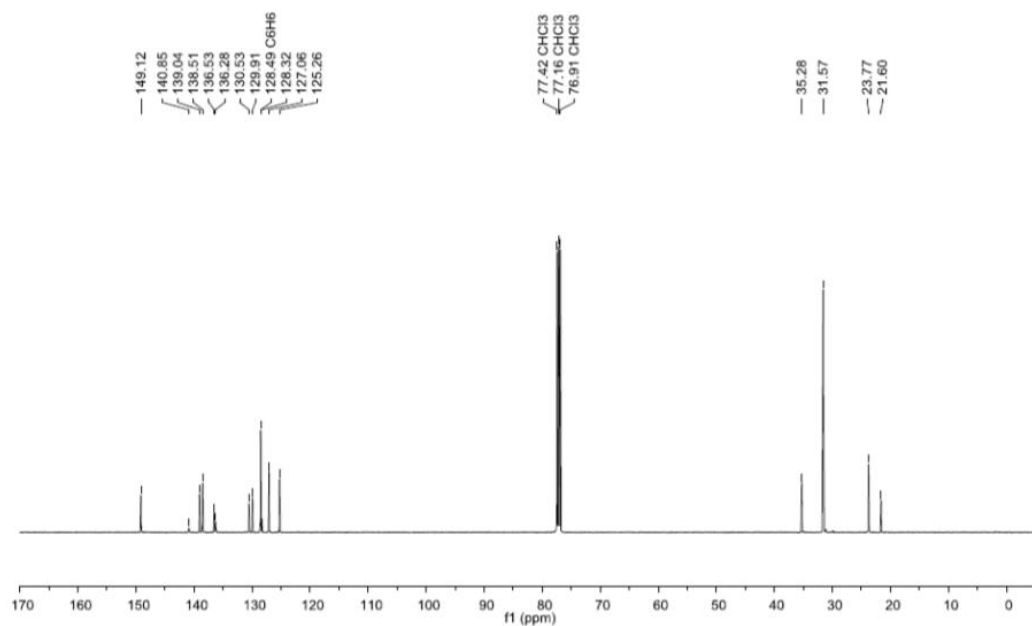


Figure S36: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **12** (CDCl_3 , 125.8 MHz).

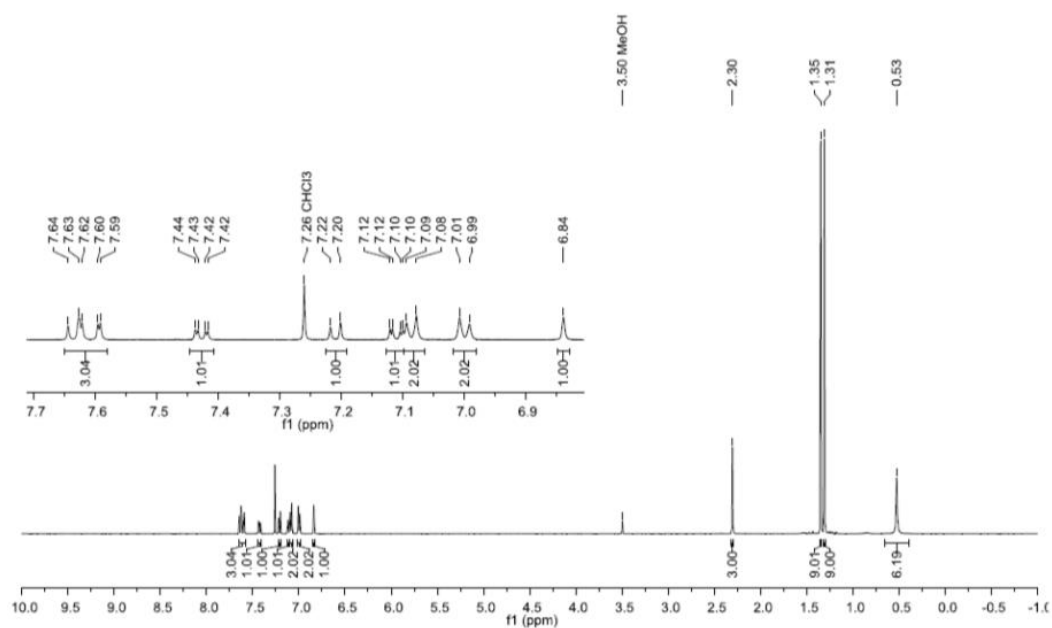


Figure S37: ^1H NMR spectrum of S3a (CDCl_3 , 500.2 MHz).

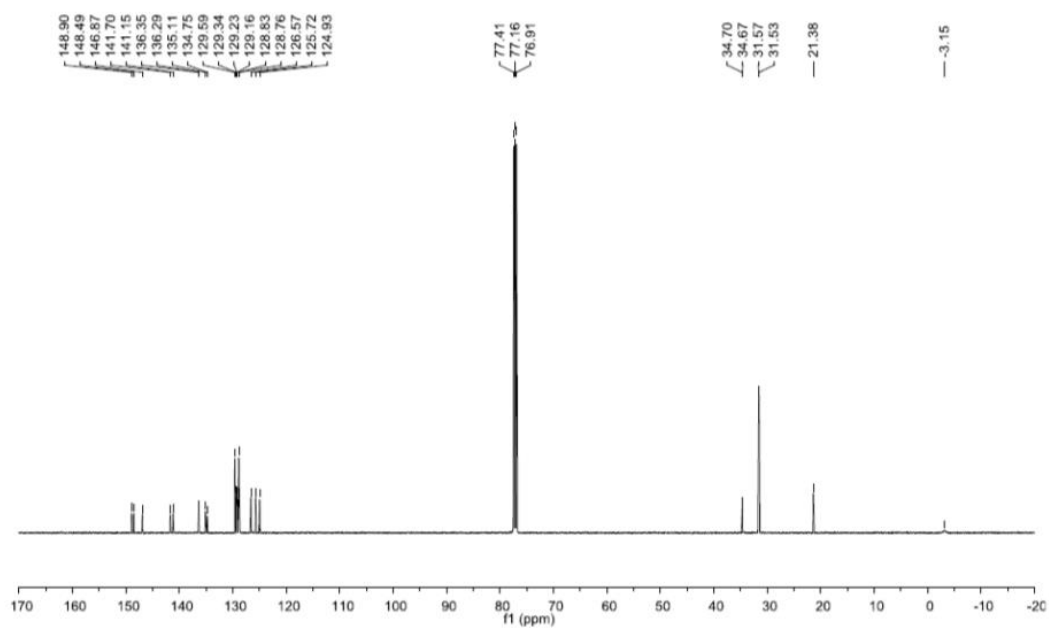


Figure S38: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of S3a (CDCl_3 , 125.8 MHz).

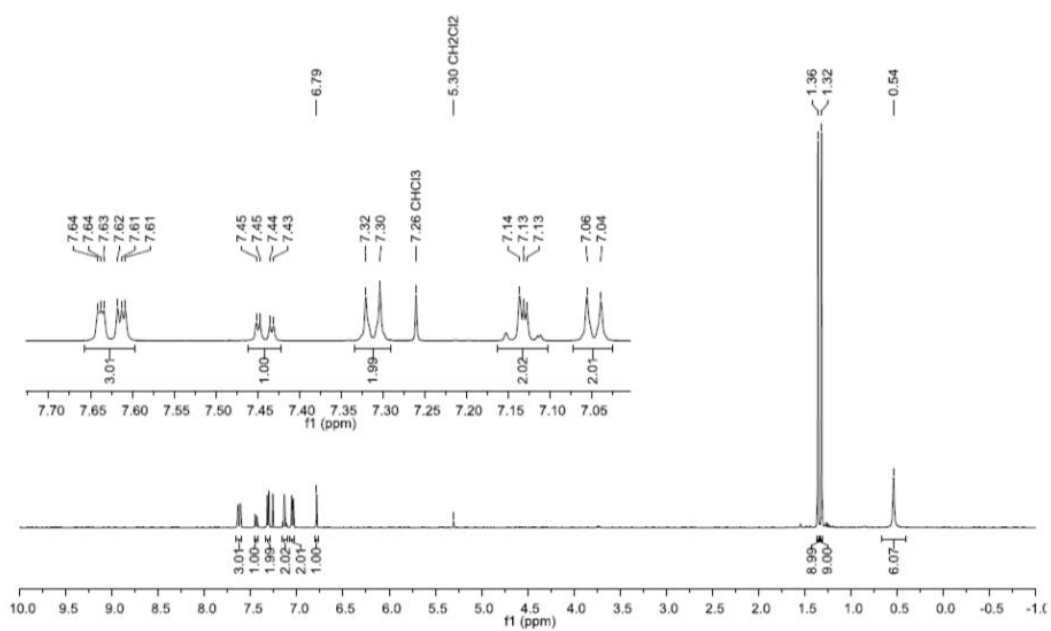


Figure S39: ^1H NMR spectrum of **S3b** (CDCl_3 , 500.2 MHz).

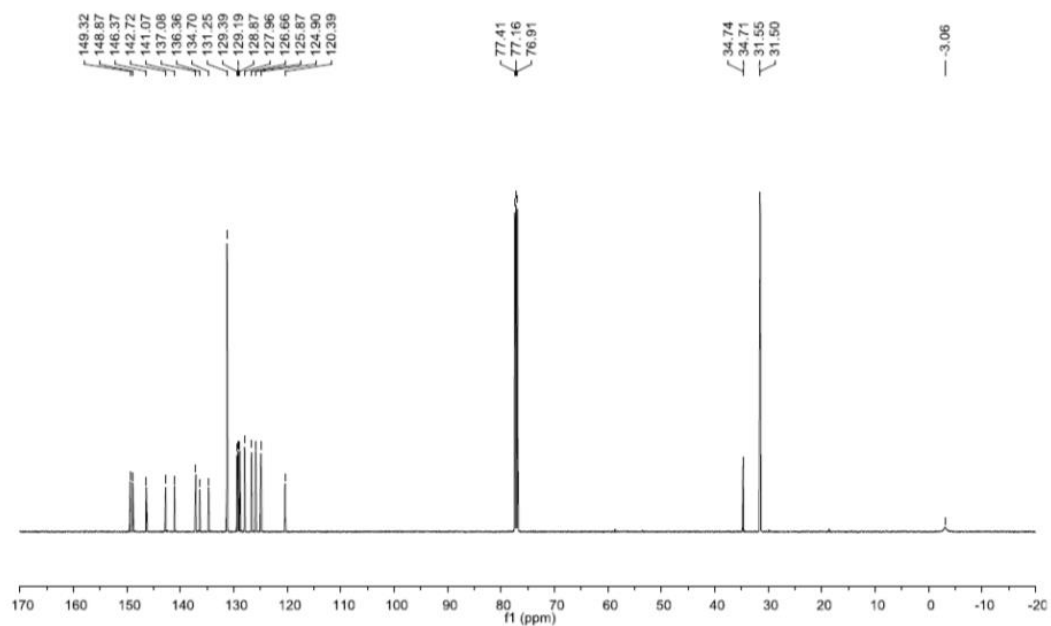


Figure S40: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S3b** (CDCl_3 , 125.8 MHz).

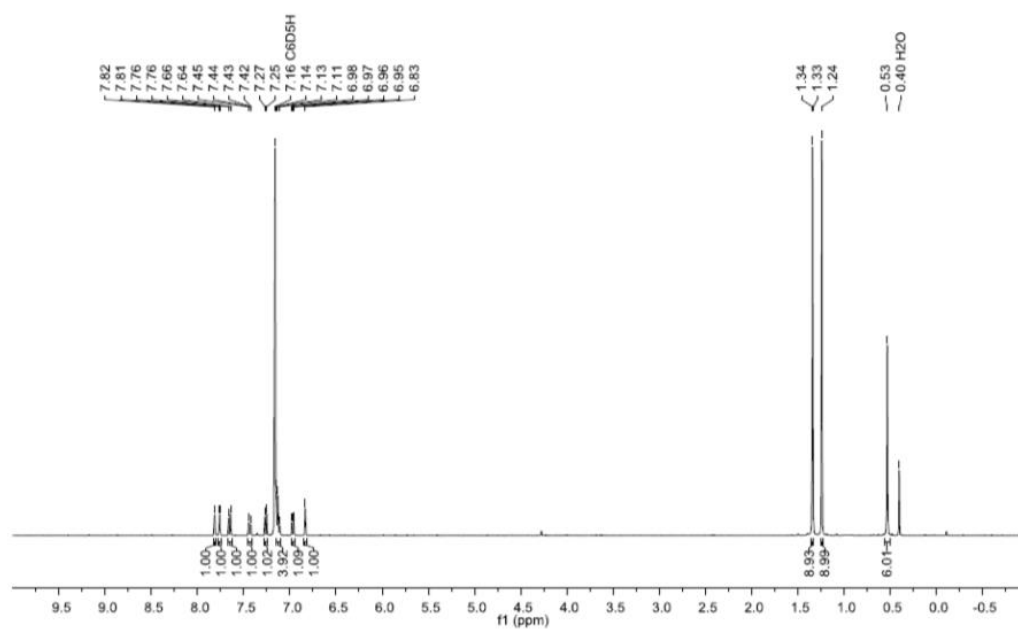


Figure S41: ¹H NMR spectrum of **S3c** (C₆D₆, 400.1 MHz).

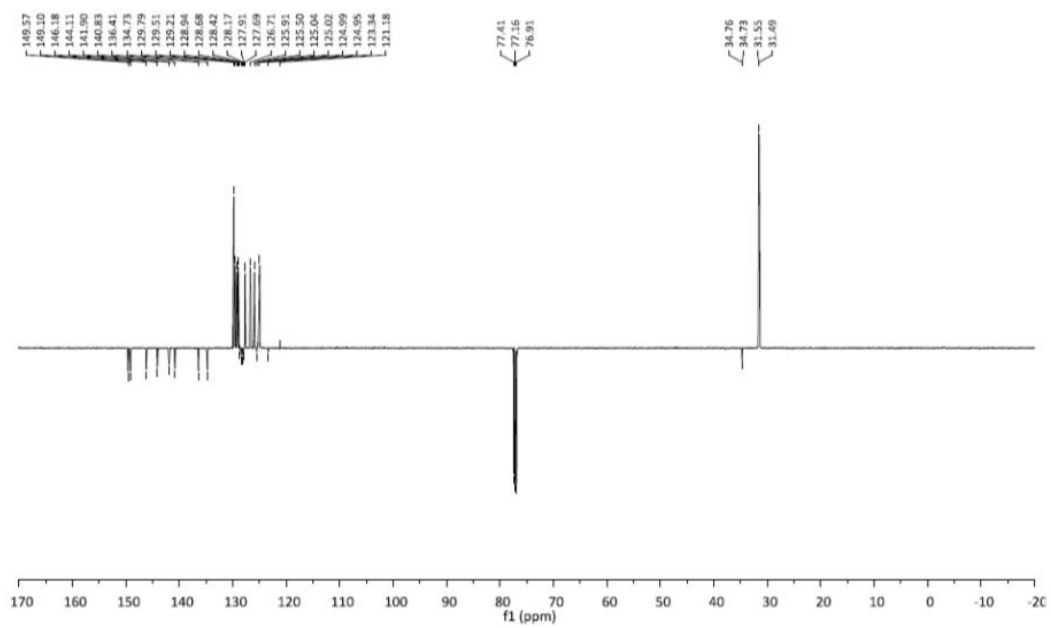


Figure S42: ¹³C{¹H}-DEPT NMR spectrum of **S3c** (CDCl₃, 125.8 MHz).

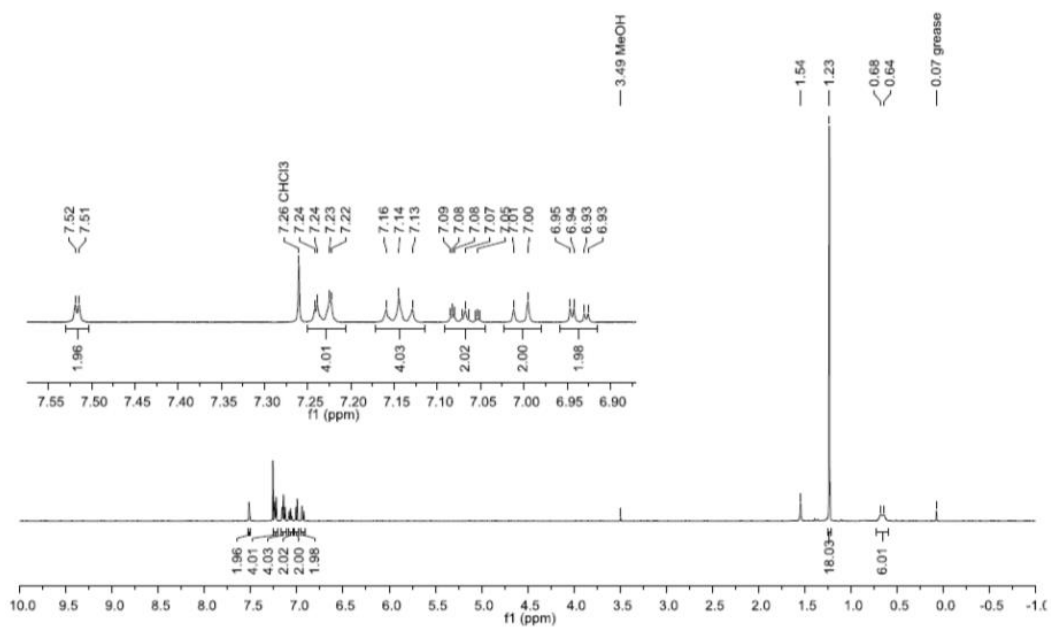


Figure S43: ^1H NMR spectrum of S4 (CDCl_3 , 500.2 MHz).

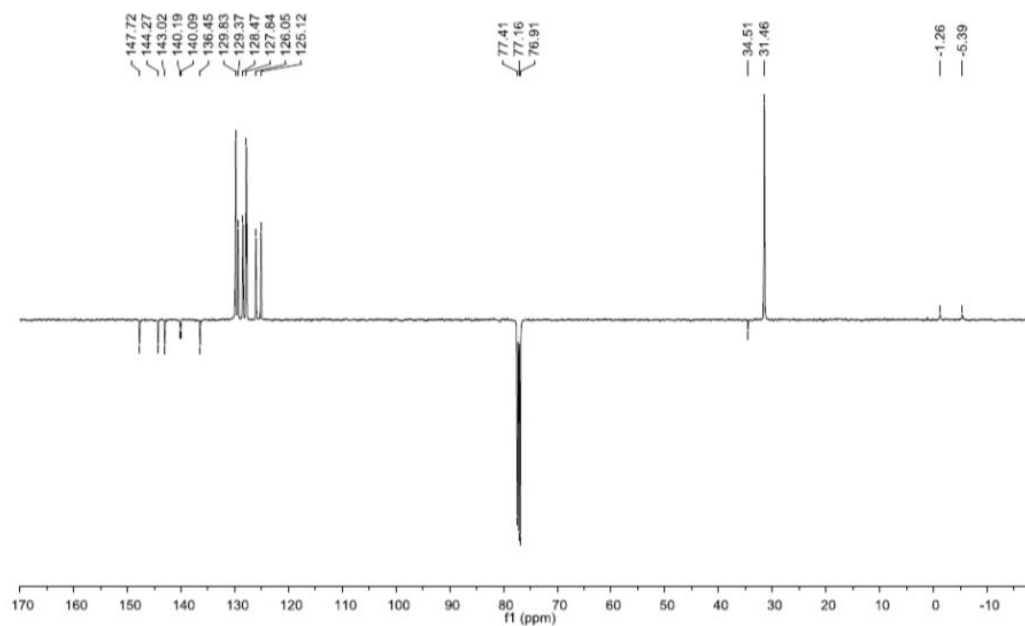


Figure S44: $^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR spectrum of S4 (CDCl_3 , 125.8 MHz).

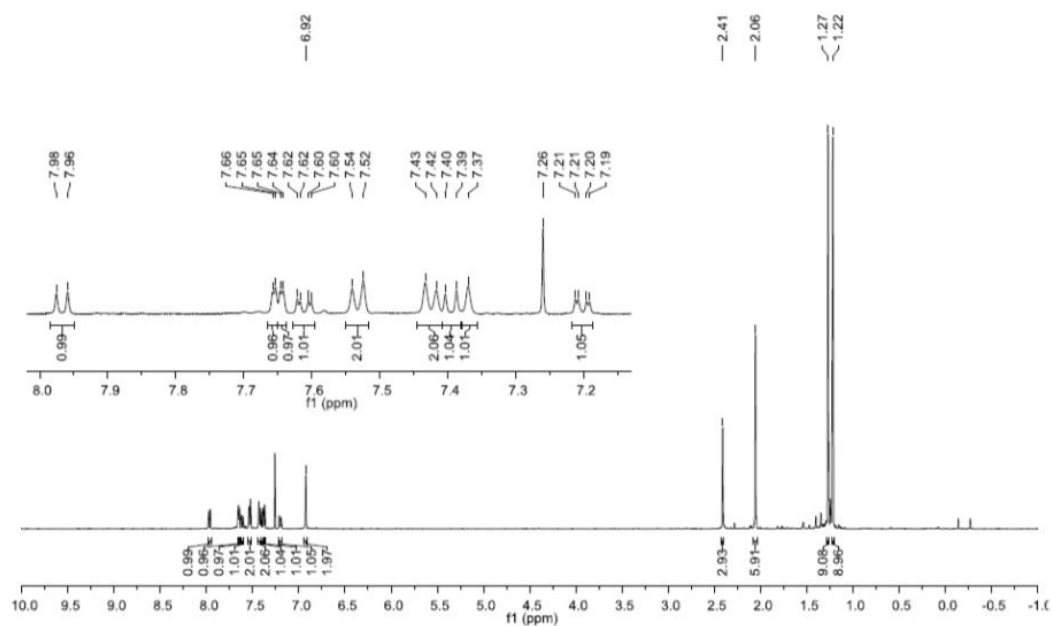


Figure S45: ^1H NMR spectrum of **S5** (CDCl_3 , 500.2 MHz).

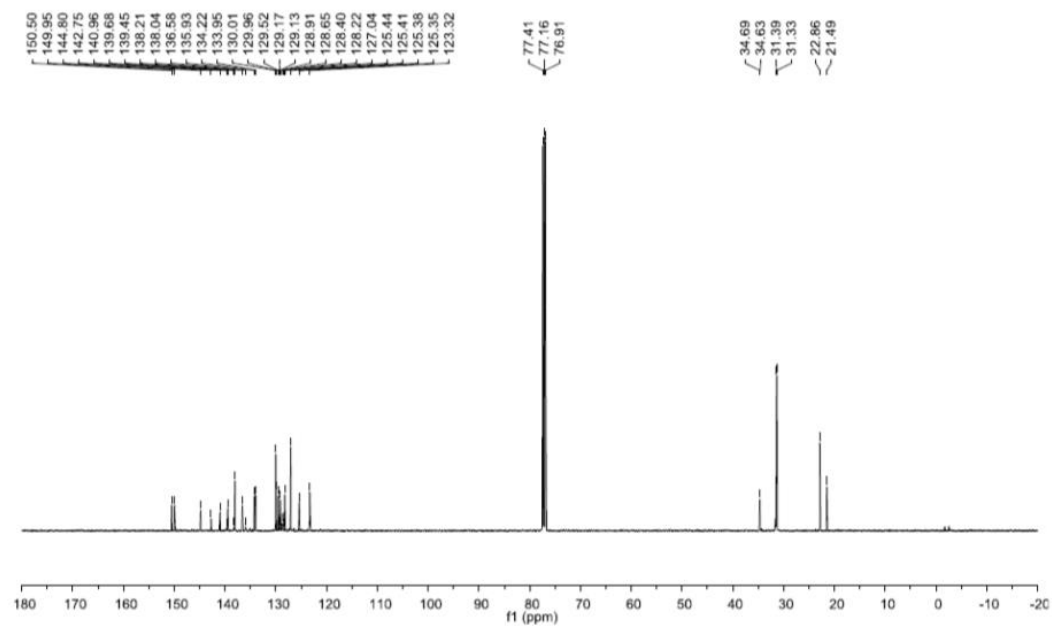


Figure S46: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S5** (CDCl_3 , 125.8 MHz).

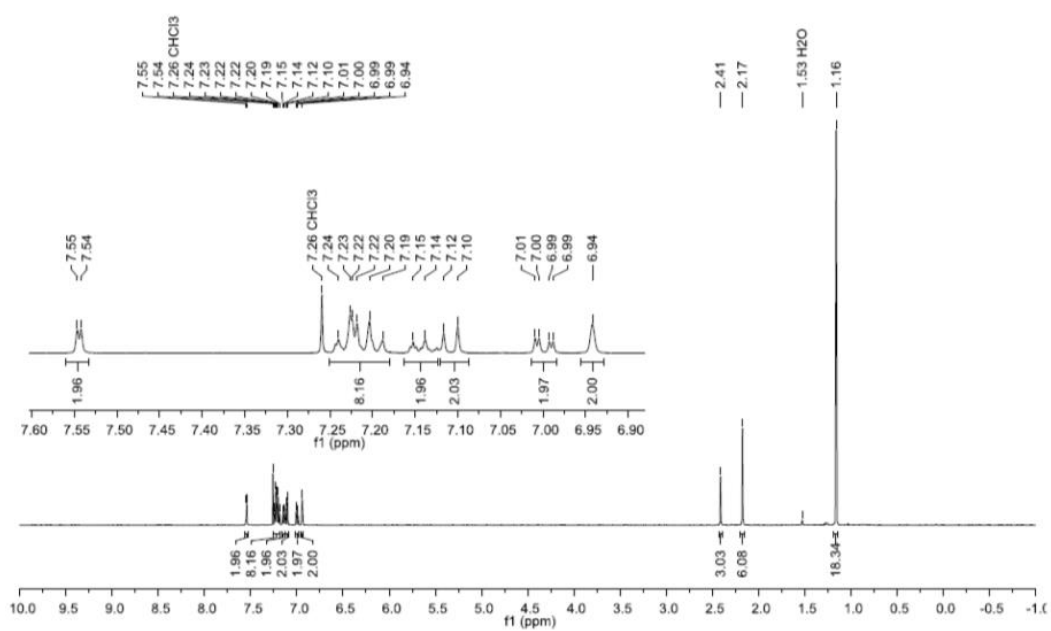


Figure S47: ^1H NMR spectrum of S6 (CDCl_3 , 500.2 MHz).

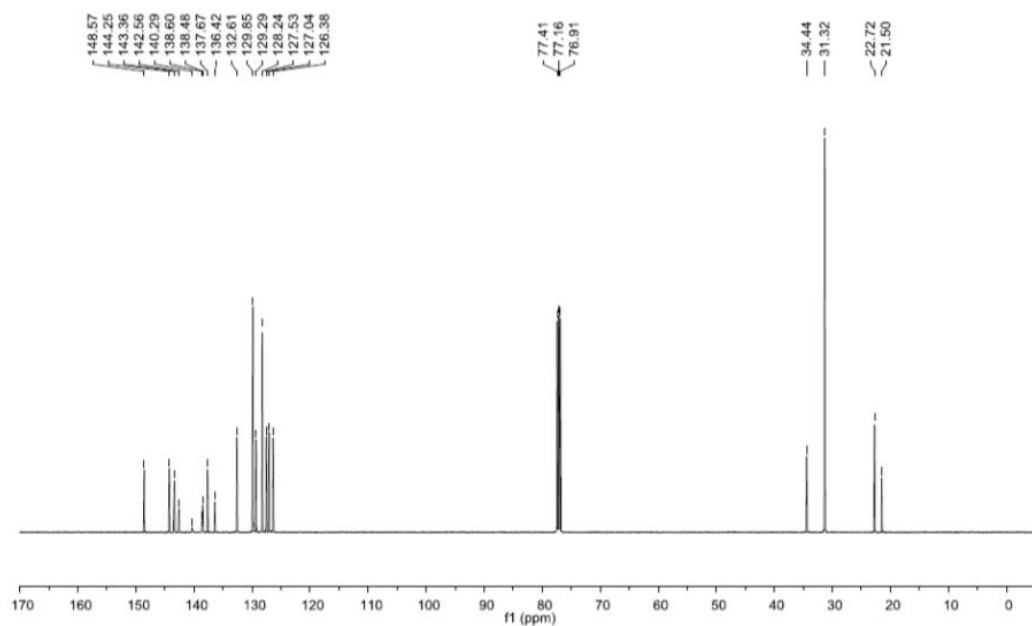
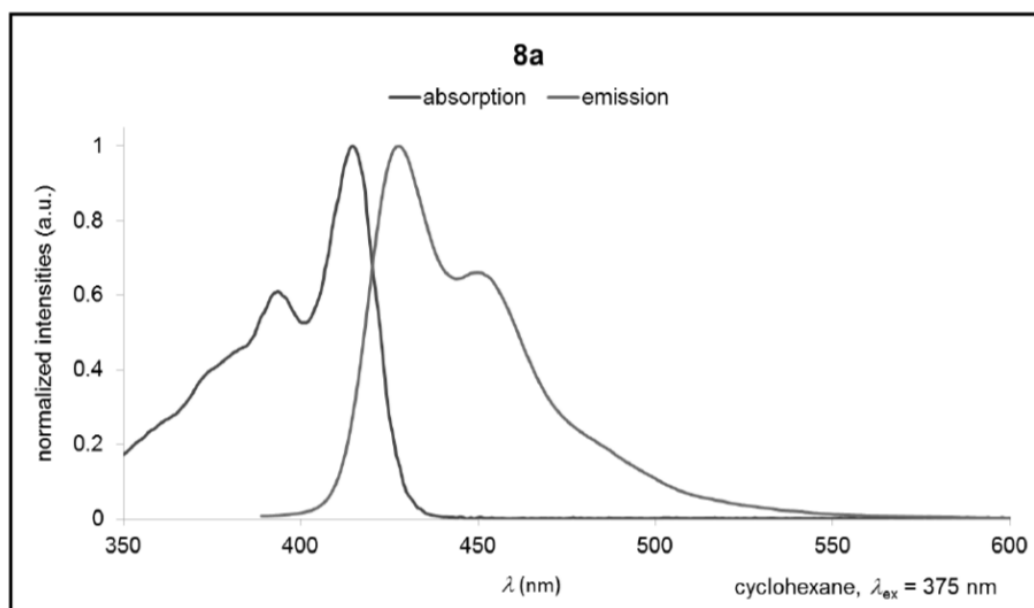
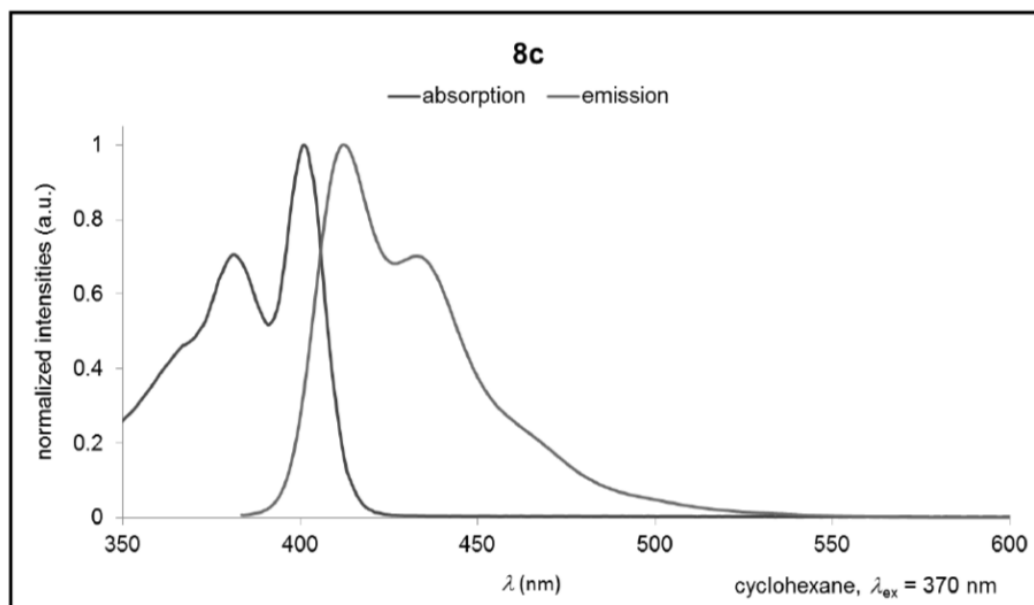


Figure S48: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of S6 (CDCl_3 , 125.8 MHz).

6. UV/Vis absorption and emission spectra

Figure S49: Normalized UV/Vis absorption and emission spectrum of **8a**.Figure S50: Normalized UV/Vis absorption and emission spectrum of **8c**.

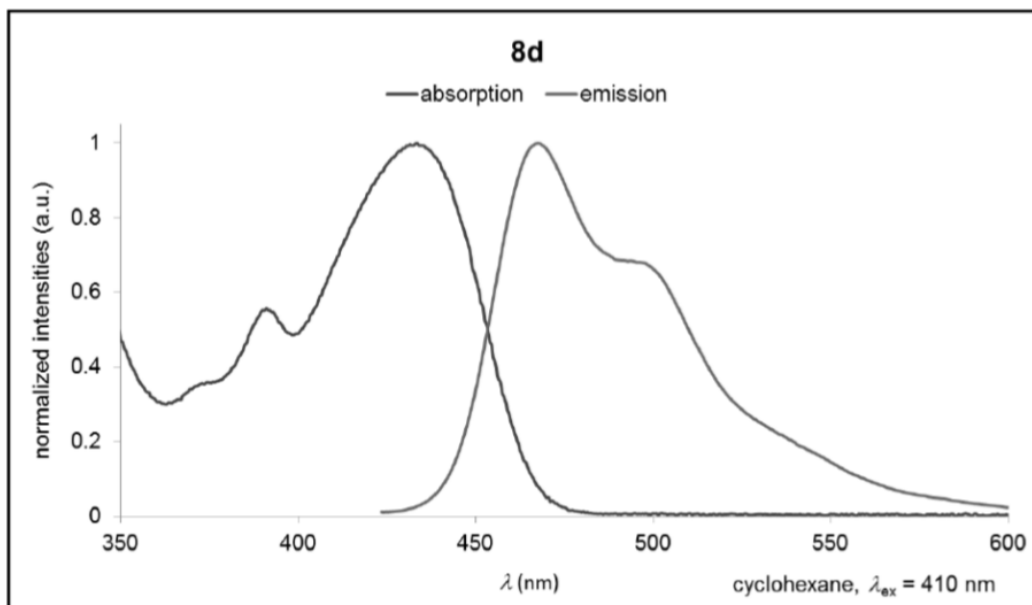


Figure S51: Normalized UV/Vis absorption and emission spectrum of **8d**.

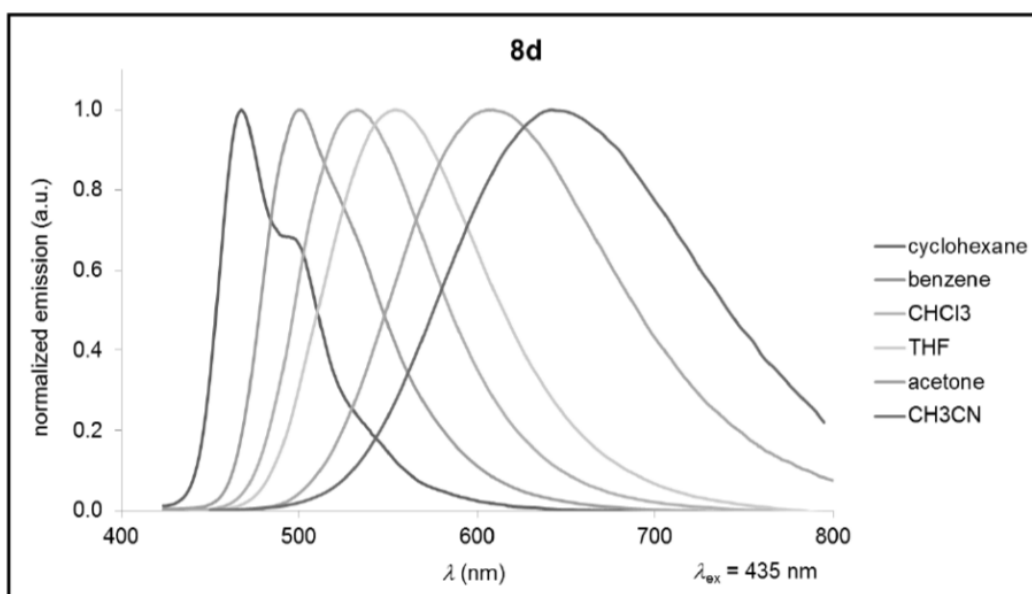


Figure S52: Normalized emission spectra of **8d** in various solvents.

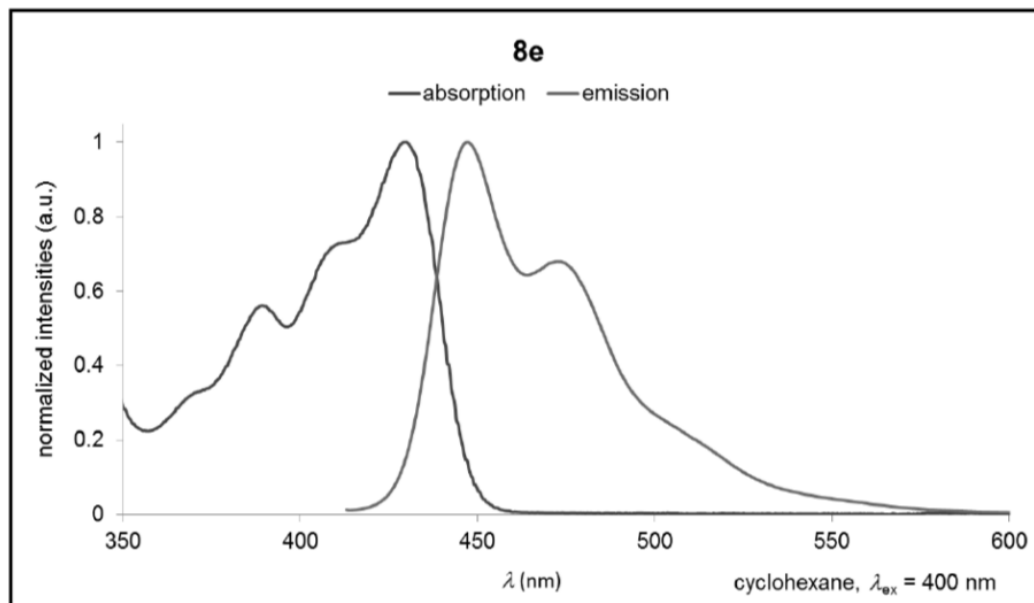


Figure S53: Normalized UV/Vis absorption and emission spectrum of **8e**.

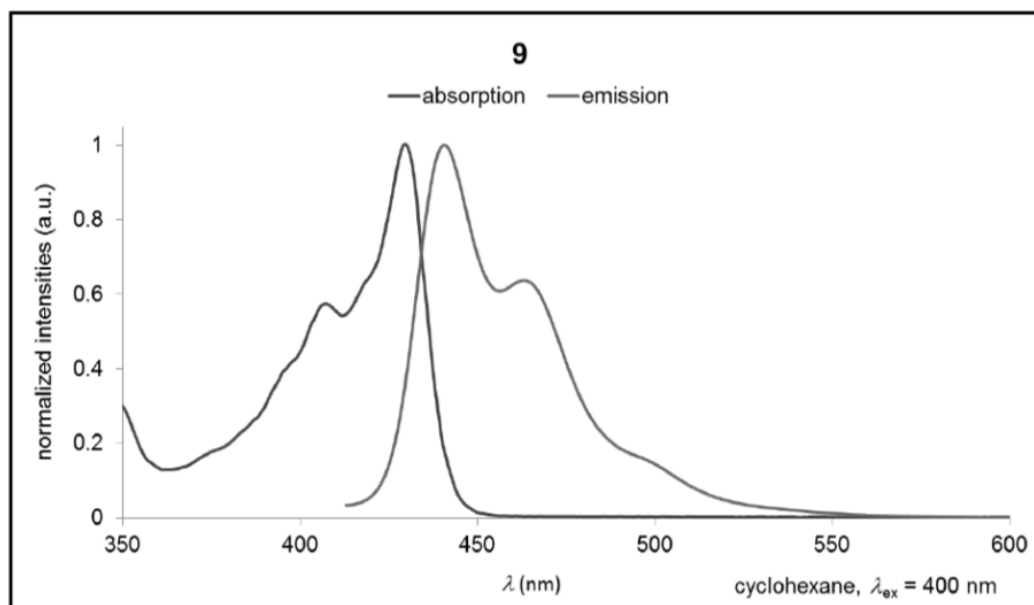


Figure S54: Normalized UV/Vis absorption and emission spectrum of **9**.

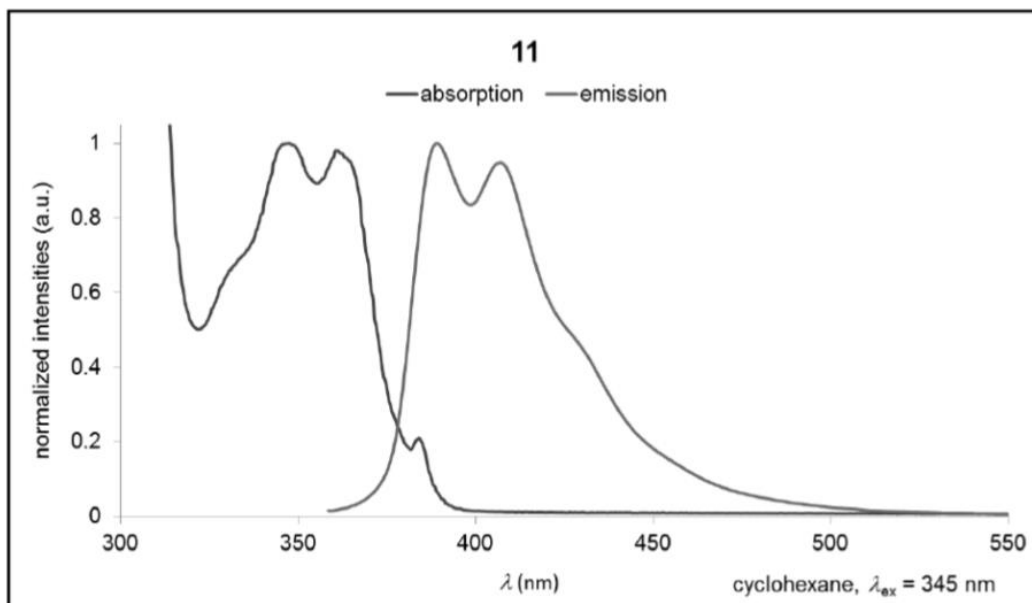


Figure S55: Normalized UV/Vis absorption and emission spectrum of **11**.

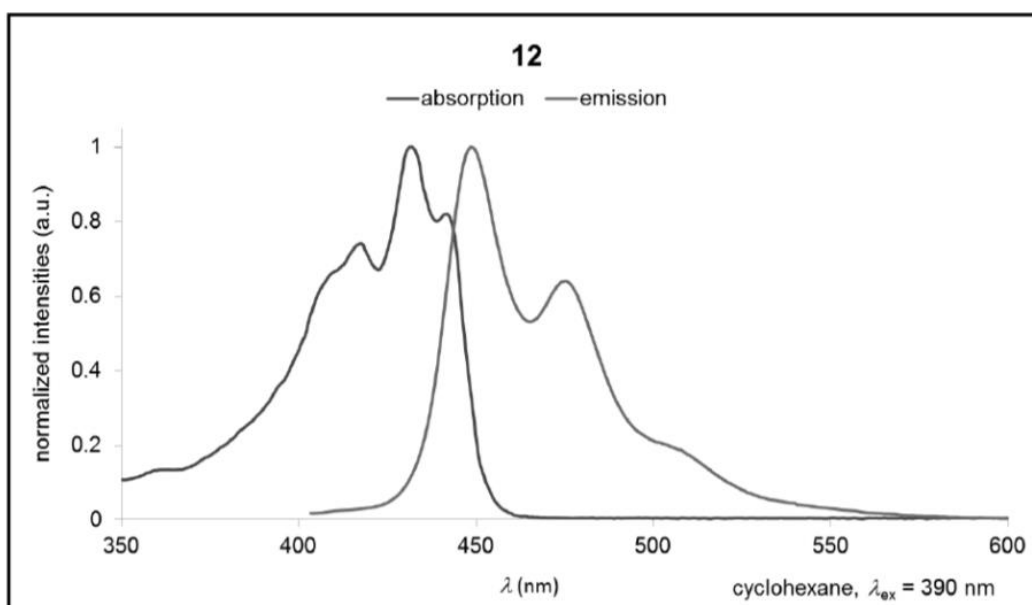


Figure S56: Normalized UV/Vis absorption and emission spectrum of **12**.

7. Plots of cyclic voltammograms

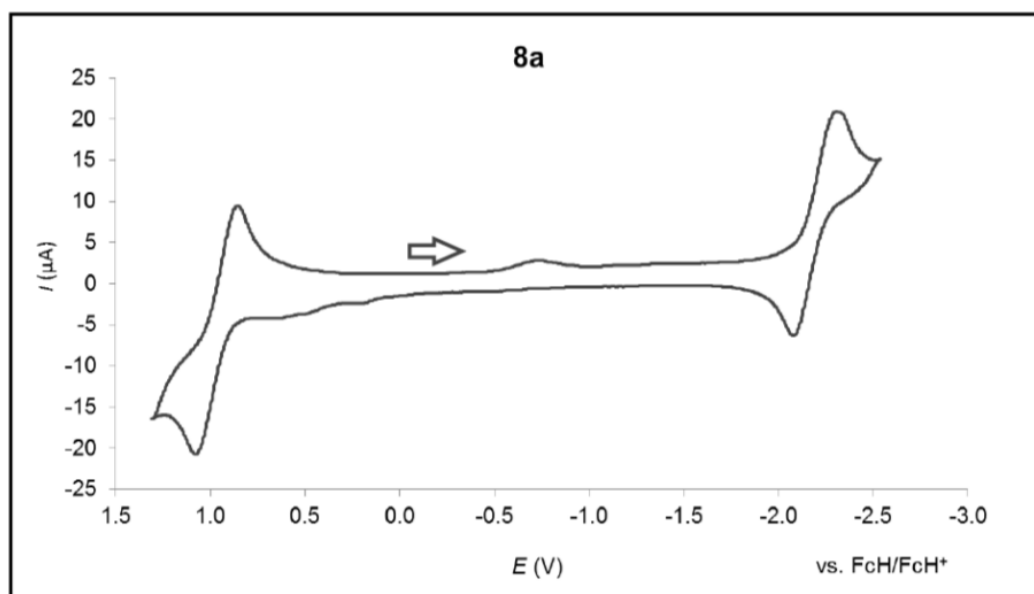


Figure S57: Cyclic voltammogram of **8a** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 400 mV s^{-1}).

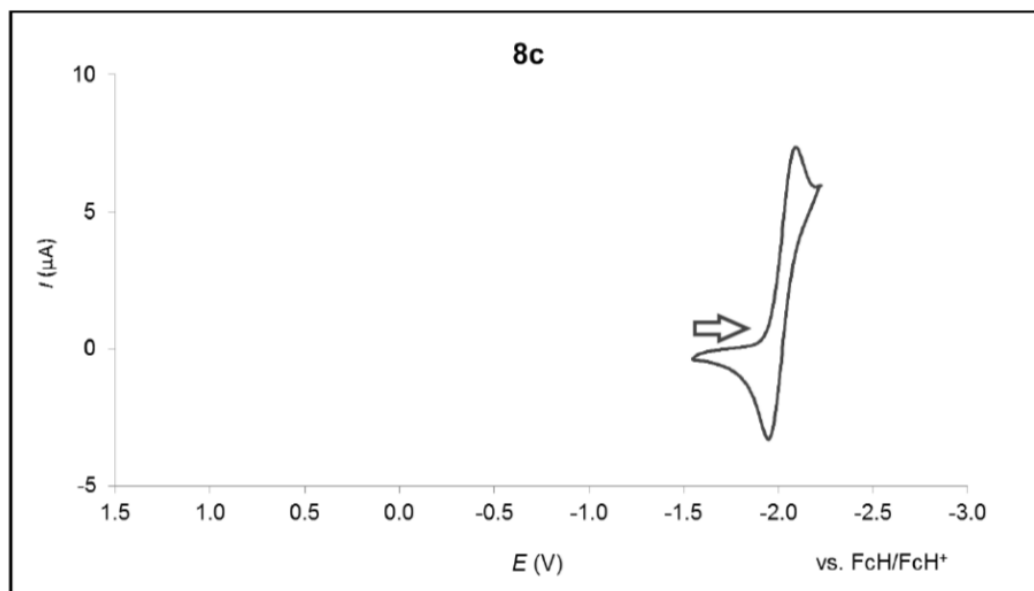


Figure S58: Cyclic voltammogram of **8c** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

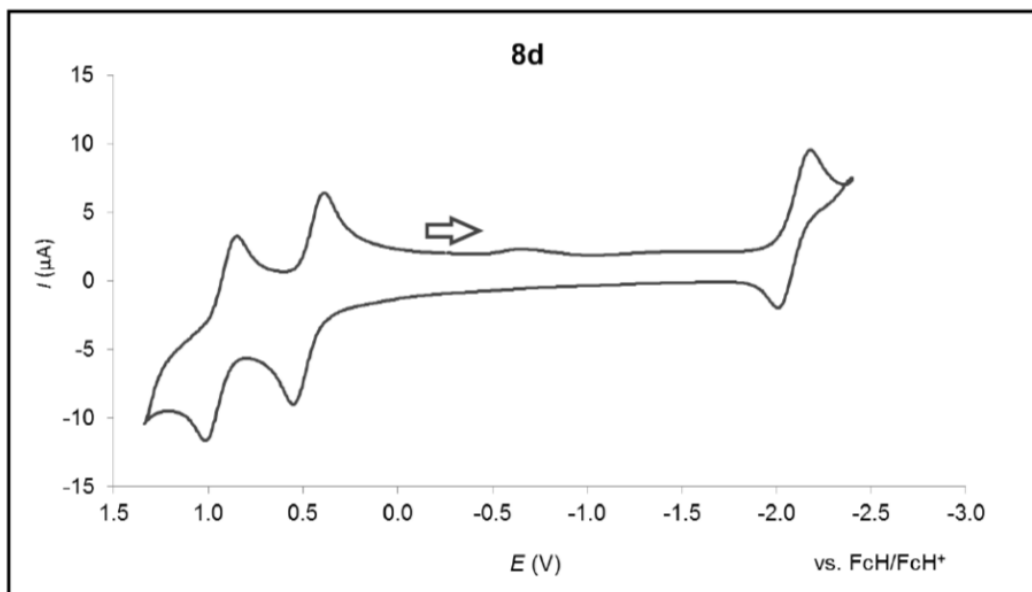


Figure S59: Cyclic voltammogram of **8d** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 400 mV s^{-1}).

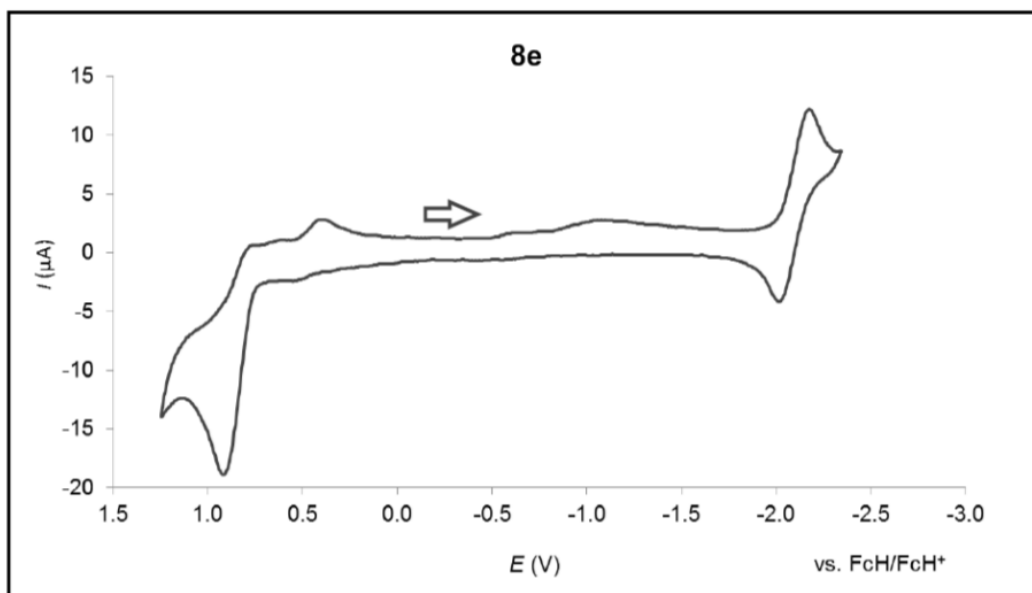


Figure S60: Cyclic voltammogram of **8e** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 400 mV s^{-1}).

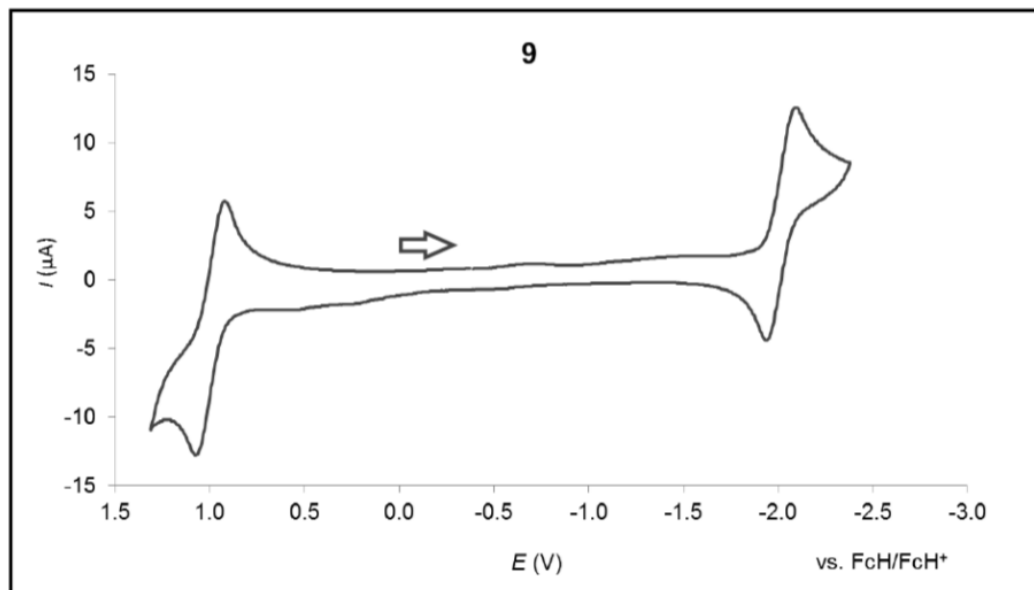


Figure S61: Cyclic voltammogram of **9** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

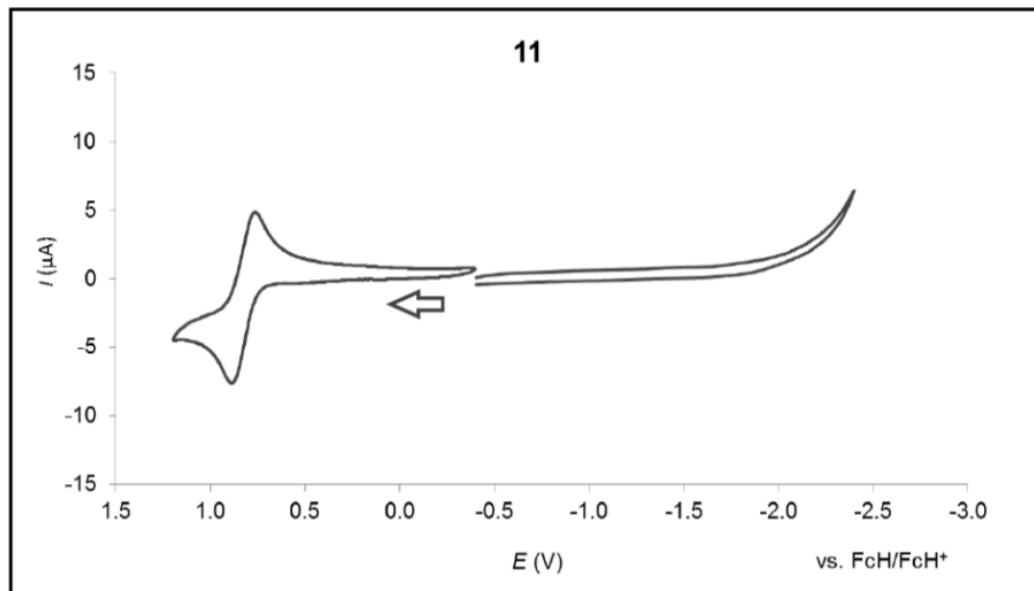


Figure S62: Cyclic voltammograms of **11** in CH_2Cl_2 (anodic and cathodic scan; room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

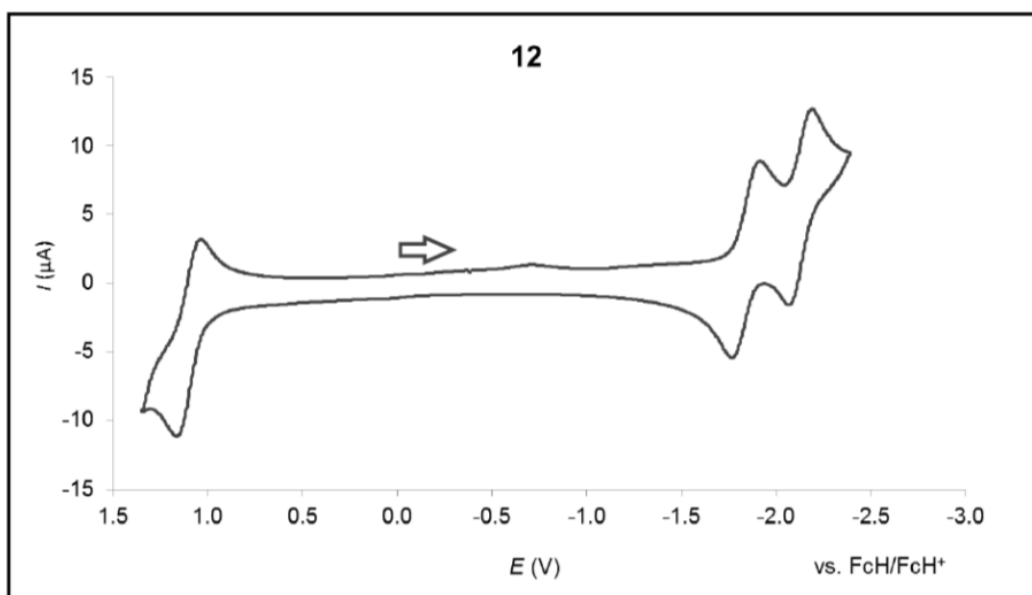


Figure S63: Cyclic voltammogram of **12** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

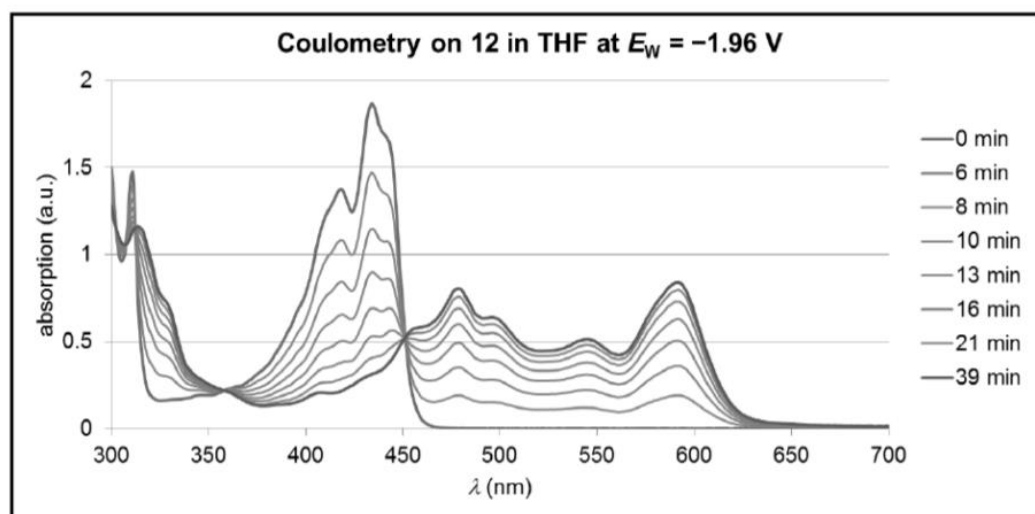
8. Spectroelectrochemistry on **12**

Figure S64: UV/Vis absorption spectra were recorded during controlled potential electrolysis of **12** at a Pt-net electrode. (2.1 μmol in 60 mL THF, room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), reduction of **12** to $[\mathbf{12}]^{\bullet-}$ at $E_w = -1.96$ V vs. FcH/FcH⁺, charge transferred: 232 mC).

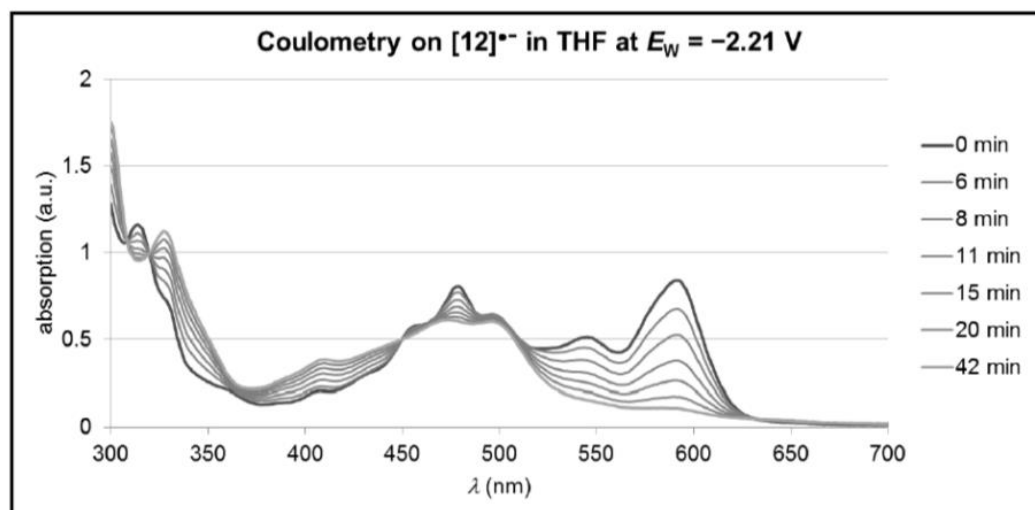


Figure S65: UV/Vis absorption spectra were recorded during controlled potential electrolysis of **12** at a Pt-net electrode. (2.1 μmol in 60 mL THF, room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), reduction of $[\mathbf{12}]^{\bullet-}$ to $[\mathbf{12}]^{2-}$ at $E_w = -2.21$ V vs. FcH/FcH⁺, charge transferred: 186 mC).

9. X-ray crystal structure analyses

Data for all structures were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and were scaled using the frame scaling procedure in the *X-AREA*^[S15] program system. The structure was solved by direct methods using the program *SHELXS*^[S16] and refined against F^2 with full-matrix least-squares techniques using the program *SHELXL-97*.^[S16]

In CCDC 1037642 (**8a**), one *t*Bu group is disordered over two positions with a site occupation factor of 0.519(5) for the major occupied site.

In CCDC 1037644 (**12**), one *t*Bu group is disordered over two positions with a site occupation factor of 0.51(1) for the major occupied site. The disordered atoms were isotropically refined.

In CCDC 1037645 (**1**), one *t*Bu group is disordered over two positions with a site occupation factor of 0.723(5) for the major occupied site. The disordered atoms were isotropically refined. Bond lengths and angles of the two disordered moieties were restrained to be equal.

In CCDC 1037646 (**3**), the two *t*Bu groups of one of the three molecules in the asymmetric unit are disordered over two positions with site occupation factors of 0.51(1) and 0.536(6) for the major occupied sites. The disordered atoms were isotropically refined.

In CCDC 1037647 (**S3a**), one *t*Bu group is disordered over two positions with a site occupation factor of 0.65(1) for the major occupied site. The disordered atoms were isotropically refined. The absolute structure was determined: Flack-x-parameter -0.13(7).

In CCDC 1037648 (**S4**), one phenyl group is disordered over two positions with a site occupation factor of 0.50(2) for the major occupied site. The absolute structure was determined: Flack-x-parameter 0.05(6).

The crystal of CCDC 1037652 (**8d**) was a very small, weakly diffracting needle, and the size of the asymmetric unit was very large. As a result, the figures of merit are rather high.

In CCDC 1037653 (**10**), two *t*Bu groups are disordered over two positions with site occupation factors of 0.65(1) and 0.59(2) for the major occupied sites. The disordered atoms were isotropically refined. Bond lengths and angles of the two disordered moieties were restrained to be equal. The crystal was a non-merohedral twin with a fractional contribution of 0.090(4) for the minor domain.

In CCDC 1037654 (**11**), one *t*Bu group is disordered over two positions with a site occupation factor of 0.646(9) for the major occupied site. The disordered atoms were isotropically refined. Bond lengths and angles of the two disordered moieties were restrained to be equal.

CCDC files 1037642, 1037644-1037654, 1052209, and 1052210 contain the supplementary crystallographic data for this paper and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

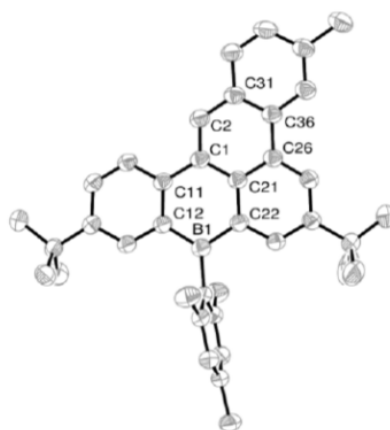


Figure S66: Molecular structure of **8a** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. One of the *t*Bu substituents was disordered and refined over two positions, only the major conformation is shown. Selected bond lengths [Å], bond angles (°), and dihedral angle (°): B1–C12 = 1.530(2), B1–C22 = 1.544(2), C1–C2 = 1.363(2), C1–C11 = 1.487(2), C1–C21 = 1.445(2), C12–B1–C22 = 116.9(1), C11–C1–C21 = 121.4(1), C₆(11)//C₆(21) = 6.9(1). C₆(X): Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **8a**.

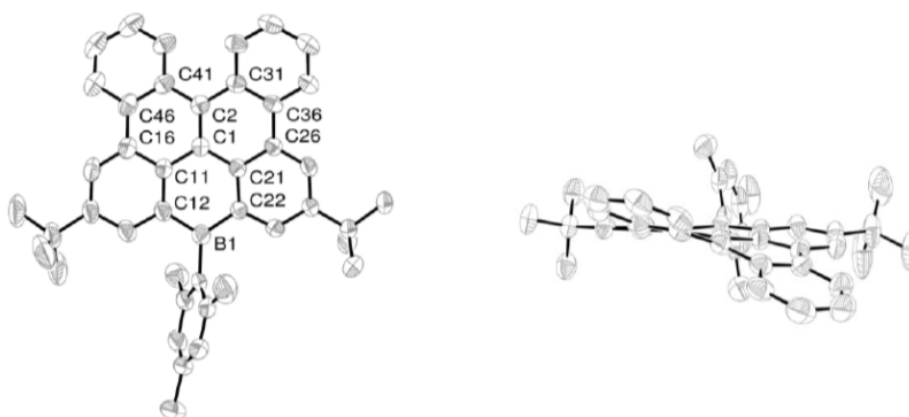


Figure S67: Molecular structure of **9** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles (°), and dihedral angles (°): B1–C12 = 1.538(3), B1–C22 = 1.535(3), C1–C2 = 1.390(3), C1–C11 = 1.452(3), C1–C21 = 1.450(3), C12–B1–C22 = 115.9(2), C11–C1–C21 = 120.1(2), C₆(11)//C₆(21) = 12.9(1), C₆(31)//C₆(41) = 37.5(1). C₆(X): Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **9**.

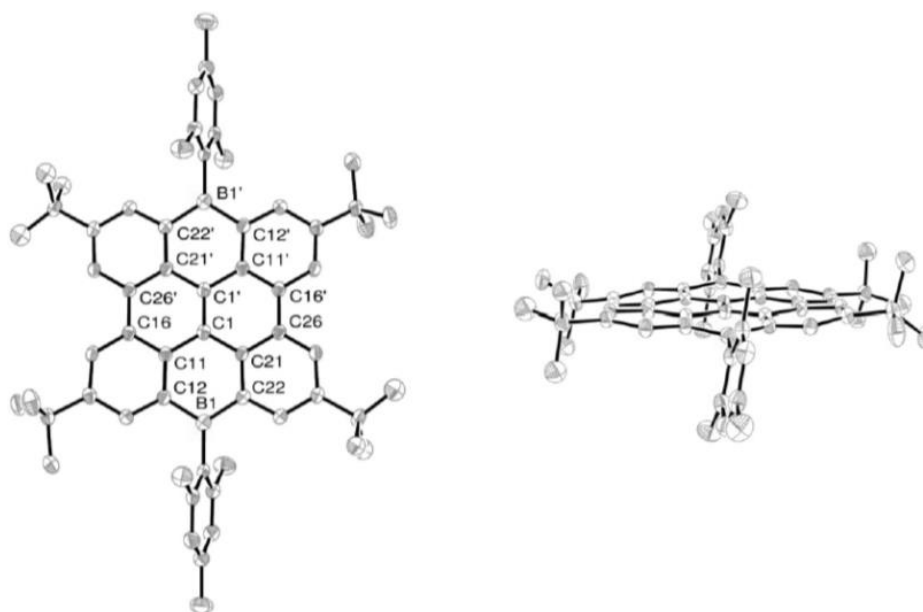


Figure S68: Molecular structure of **12** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and cocrystallized C_6H_6 are omitted for clarity. One of the *t*Bu substituents was disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [\AA], bond angles ($^\circ$), and dihedral angle ($^\circ$): B1–C12 = 1.546(3), B1–C22 = 1.546(3), C1–C1' = 1.404(4), C1–C11 = 1.468(3), C1–C21 = 1.461(3), C12–B1–C22 = 116.2(2), C11–C1–C21 = 120.6(2), $C_6(11)/C_6(21)$ = 10.4(1). $C_6(X)$: Six-membered ring containing C(X). Symmetry operation used to generate equivalent atoms: $-x+1, -y+1, -z+1$. X-ray crystallography confirms the identity of the compound as **12**.

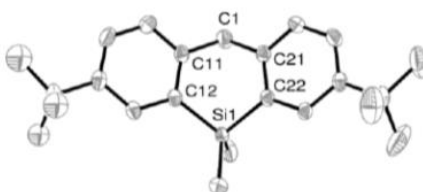


Figure S69: Molecular structure of **1** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. One of the *t*Bu substituents was disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [\AA], bond angles ($^\circ$), and dihedral angle ($^\circ$): Si1–C12 = 1.866(2), Si1–C22 = 1.868(2), C1–C11 = 1.518(3), C1–C21 = 1.513(3), C12–Si1–C22 = 101.3(1), C11–C1–C21 = 115.2(2), $C_6(11)/C_6(21)$ = 44.5(1). $C_6(X)$: Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **1**.

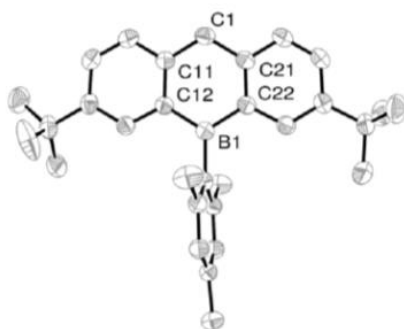


Figure S70: Molecular structure of **2** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Only one of two molecules in the asymmetric unit is shown, bond lengths and angles do not vary significantly between the molecules. Selected bond lengths [Å], bond angles (°), and dihedral angle (°): B1–C12 = 1.548(2), B1–C22 = 1.553(2), C1–C11 = 1.503(2), C1–C21 = 1.496(2), C12–B1–C22 = 116.8(1), C11–C1–C21 = 117.5(1), C₆(11)//C₆(21) = 13.6(1). C₆(X): Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **2**.

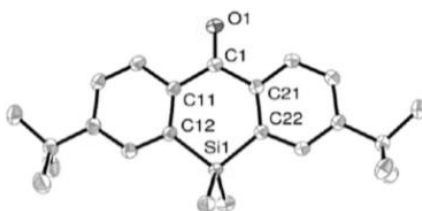


Figure S71: Molecular structure of **3** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Only one of three molecules in the asymmetric unit is shown, bond lengths and angles do not vary significantly between the molecules. Selected bond lengths [Å], bond angles (°), and dihedral angle (°): Si1–C12 = 1.861(2), Si1–C22 = 1.856(2), O1–C1 = 1.222(2), C1–C11 = 1.503(2), C1–C21 = 1.501(2), O1–C1–C11 = 118.5(2), O1–C1–C21 = 118.7(2), C12–Si1–C22 = 104.5(1), C11–C1–C21 = 122.8(2), C₆(11)//C₆(21) = 7.1(1). C₆(X): Six-membered ring containing C(X) X-ray crystallography confirms the identity of the compound as **3**.

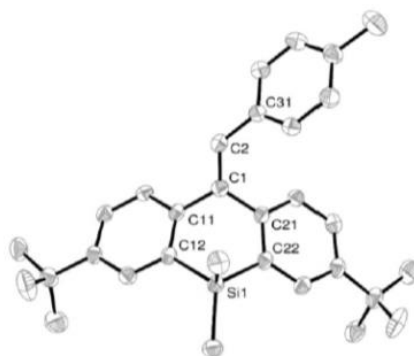


Figure S72: Molecular structure of **S3a** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Only one of two molecules in the asymmetric unit is shown, the following bond lengths and angles are given for both molecules: **S3a** (**S3a***). Selected bond lengths [Å], bond angles (°), torsion angle (°), and dihedral angle (°): Si1–C12 = 1.866(3) (1.878(3)), Si1–C22 = 1.861(3) (1.863(4)), C1–C2 = 1.345(5) (1.341(5)), C1–C11 = 1.505(5) (1.496(5)), C1–C21 = 1.490(5) (1.495(5)), C12–Si1–C22 = 100.7(2) (100.4(1)), C11–C1–C21 = 117.3(3) (115.4(3)), C21–C1–C2–C31 = –7.9(6) (–4.4(6)), C₆(11)//C₆(21) = 45.1(1) (51.9(1)). C₆(X): Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **S3a**.

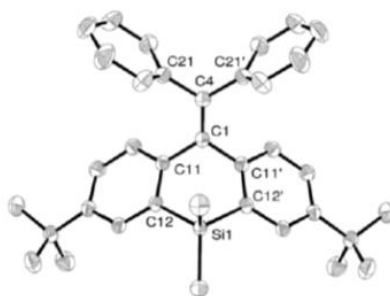


Figure S73: Molecular structure of **S4** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. One of the phenyl substituents was disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [Å], bond angles (°), and dihedral angle (°): Si1–C12 = 1.872(2), C1–C11 = 1.499(2), C1–C4 = 1.337(4), C12–Si1–C12' = 100.1(1), C11–C1–C11' = 115.0(2), C₆(11)//C₆(11') = 52.0(1). C₆(X): Six-membered ring containing C(X). Symmetry operation used to generate equivalent atoms: –x+1, y, z. X-ray crystallography confirms the identity of the compound as **S4**.

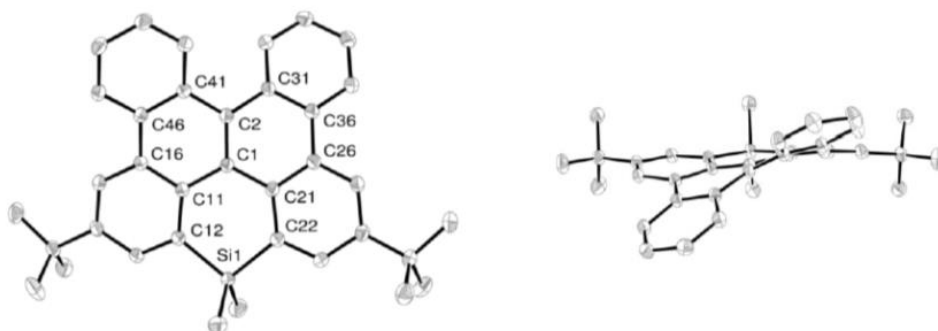


Figure S74: Molecular structure of **7** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and cocrystallized C_6H_6 are omitted for clarity. Selected bond lengths [\AA], bond angles ($^\circ$), and dihedral angles ($^\circ$): $Si1-C12 = 1.856(1)$, $Si1-C22 = 1.857(1)$, $C1-C2 = 1.394(2)$, $C1-C11 = 1.475(2)$, $C1-C21 = 1.472(2)$, $C12-Si1-C22 = 103.1(1)$, $C11-C1-C21 = 124.1(1)$, $C_6(11)//C_6(21) = 17.0(1)$, $C_6(31)//C_6(41) = 44.5(1)$. $C_6(X)$: Six-membered ring containing $C(X)$. X-ray crystallography confirms the identity of the compound as **7**.

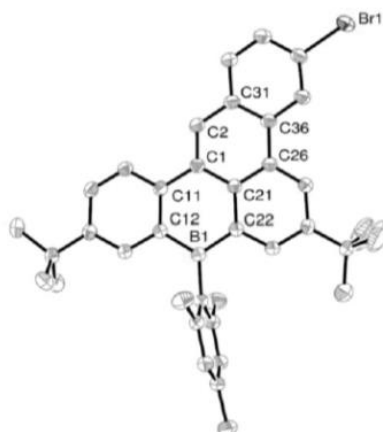


Figure S75: Molecular structure of **8b** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [\AA], bond angles ($^\circ$), and dihedral angle ($^\circ$): $B1-C12 = 1.538(3)$, $B1-C22 = 1.542(3)$, $C1-C2 = 1.367(3)$, $C1-C11 = 1.480(3)$, $C1-C21 = 1.449(3)$, $C12-B1-C22 = 116.9(2)$, $C11-C1-C21 = 120.9(2)$, $C_6(11)//C_6(21) = 6.8(1)$. $C_6(X)$: Six-membered ring containing $C(X)$. X-ray crystallography confirms the identity of the compound as **8b**.

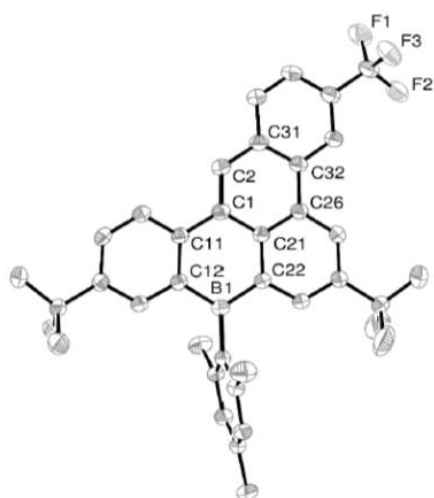


Figure S76: Molecular structure of **8c** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles (°), and dihedral angle (°): B1–C12 = 1.537(3), B1–C22 = 1.541(3), C1–C2 = 1.366(3), C1–C11 = 1.482(3), C1–C21 = 1.450(3), C12–B1–C22 = 116.8(2), C11–C1–C21 = 121.1(2), C₆(11)//C₆(21) = 6.2(1). C₆(X): Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **8c**.

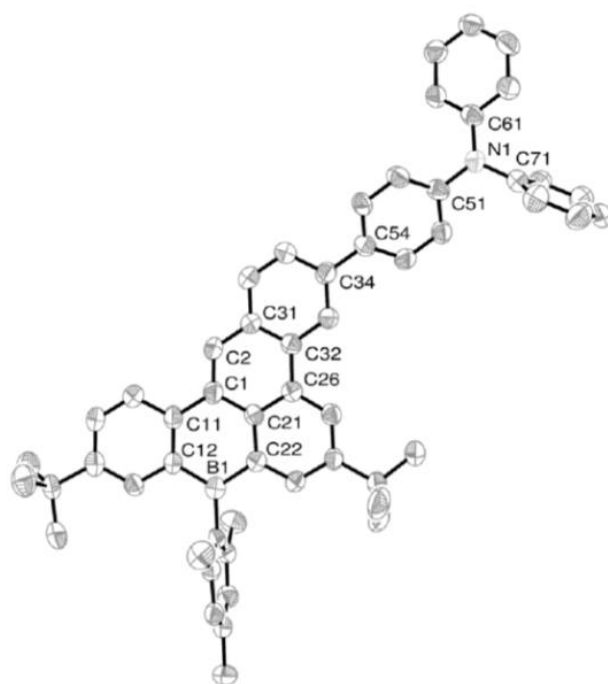


Figure S77: Molecular structure of **8d** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond

angles ($^{\circ}$), and dihedral angles ($^{\circ}$): B1–C12 = 1.546(8), B1–C22 = 1.561(8), C1–C2 = 1.356(7), C1–C11 = 1.475(7), C1–C21 = 1.448(7), C34–C54 = 1.490(7), N1–C51 = 1.428(7), N1–C61 = 1.419(6), N1–C71 = 1.446(7), C12–B1–C22 = 116.1(5), C11–C1–C21 = 120.5(5), C₆(11)//C₆(21) = 9.3(3), C₆(31)//C₆(51) = 25.4(2). C₆(X): Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **8d**.

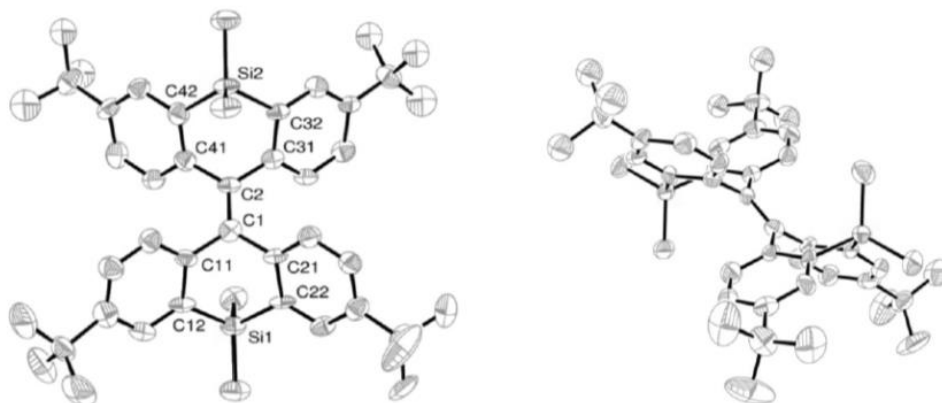


Figure S78: Molecular structure of **10** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Two of the *t*Bu substituents were disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [Å], bond angles ($^{\circ}$), and dihedral angles ($^{\circ}$): Si1–C12 = 1.877(7), Si1–C22 = 1.886(7), Si2–C32 = 1.875(7), Si2–C42 = 1.858(7), C1–C2 = 1.367(8), C1–C11 = 1.500(9), C1–C21 = 1.502(10), C2–C31 = 1.481(9), C2–C41 = 1.484(10), C12–Si1–C22 = 98.7(3), C32–Si2–C42 = 99.5(3), C11–C1–C21 = 114.2(6), C31–C2–C41 = 116.2(6), C₆(11)//C₆(21) = 58.7(2), C₆(31)//C₆(41) = 59.5(2). C₆(X): Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **10**.

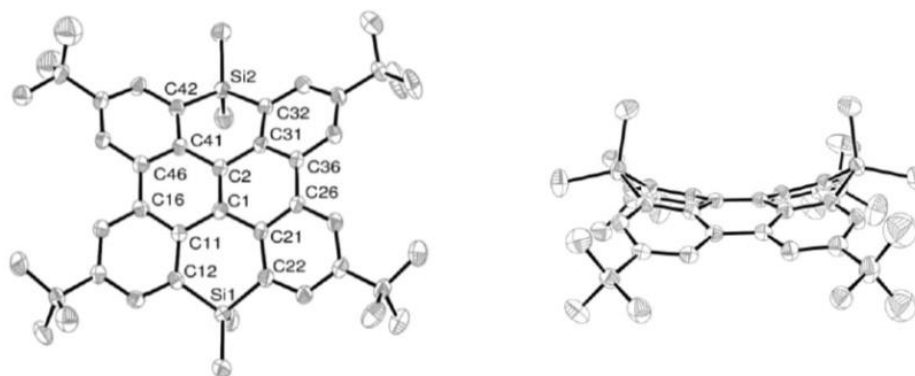


Figure S79: Molecular structure of **11** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. One of the *t*Bu substituents was disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [Å], bond angles (°), and dihedral angles (°): Si1–C12 = 1.839(4), Si1–C22 = 1.851(4), Si2–C32 = 1.848(4), Si2–C42 = 1.851(3), C1–C2 = 1.395(5), C1–C11 = 1.482(4), C1–C21 = 1.472(5), C2–C31 = 1.479(4), C2–C41 = 1.466(5), C12–Si1–C22 = 99.9(2), C32–Si2–C42 = 100.2(2), C11–C1–C21 = 120.6(3), C31–C2–C41 = 121.3(3), C₆(11)//C₆(21) = 37.4(2), C₆(31)//C₆(41) = 34.0(2). C₆(X): Six-membered ring containing C(X). X-ray crystallography confirms the identity of the compound as **11**.

Table S2: Selected crystallographic data for **8a**, **9**, and a mixed crystal of **9/9I**.

compound	8a	9	9/9I
CCDC	1037642	1052209	1052009
formula	C ₃₈ H ₄₁ B	C ₄₃ H ₄₁ B	C ₄₃ H _{40.94} BI _{0.06}
<i>M_r</i>	508.52	568.57	576.43
<i>T</i> (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	21.9899(16)	20.2549(14)	20.2891(8)
<i>b</i> (Å)	14.9737(8)	7.2340(5)	7.2182(4)
<i>c</i> (Å)	9.2690(6)	22.7365(13)	22.7875(9)
α (°)	90	90	90
β (°)	96.663(5)	94.902(5)	94.953(3)
γ (°)	90	90	90
<i>V</i> (Å ³)	3031.4(3)	3319.3(4)	3324.8(3)
<i>Z</i>	4	4	4
<i>D_{calcd}</i> (g cm ⁻³)	1.114	1.138	1.152
F(000)	1096	1216	1229
μ (mm ⁻¹)	0.062	0.063	0.121
crystal size (mm)	0.32 × 0.26 × 0.11	0.29 × 0.12 × 0.06	0.52 × 0.24 × 0.13
reflections collected	14413	36127	50416
independent reflections	5380	5866	7169
<i>R_{int}</i>	0.0322	0.0863	0.0963
data/restraints/parameters	5380/0/384	5866/0/400	7169/0/411
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0443, 0.1034	0.0562, 0.1182	0.0645, 0.1620
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0719, 0.1127	0.1000, 0.1341	0.0824, 0.1722
Goodnes-of-fit on <i>F</i> ²	0.942	0.973	1.091
Largest diff peak and hole (e Å ⁻³)	0.138, -0.143	0.194, -0.208	0.553, -0.282

Table S3: Selected crystallographic data for **12**, **1**, and **2**.

compound	12	1	2
CCDC	1037644	1037645	1052210
formula	C ₆₀ H ₆₆ B ₂ × 2 C ₆ H ₆	C ₂₃ H ₃₂ Si	C ₃₀ H ₃₇ B
<i>M_r</i>	964.96	336.57	408.40
<i>T</i> (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	MoKα, 0.71073	MoKα, 0.71073	MoKα, 0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.3000(14)	17.0023(10)	13.7277(6)
<i>b</i> (Å)	11.2763(11)	9.8067(4)	25.8699(8)
<i>c</i> (Å)	23.422(3)	12.9821(8)	15.8788(6)
α (°)	90	90	90
β (°)	101.903(10)	104.047(5)	113.000(3)
γ (°)	90	90	90
<i>V</i> (Å ³)	2920.3(6)	2099.9(2)	5190.8(4)
<i>Z</i>	2	4	8
<i>D</i> _{calcd} (g cm ⁻³)	1.097	1.065	1.045
F(000)	1040	736	1776
μ (mm ⁻¹)	0.061	0.113	0.058
crystal size (mm)	0.38 × 0.23 × 0.22	0.20 × 0.10 × 0.10	0.54 × 0.31 × 0.27
reflections collected	23856	25659	62424
independent reflections	5486	4030	10111
<i>R</i> _{int}	0.0986	0.0572	0.0734
data/restraints/parameters	5486/0/335	4030/12/215	10111/0/565
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0624, 0.1630	0.0660, 0.1658	0.0459, 0.1192
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0984, 0.1776	0.0735, 0.1709	0.0626, 0.1262
Goodnes-of-fit on <i>F</i> ²	1.050	1.033	1.060
Largest diff peak and hole (e Å ⁻³)	0.480, -0.343	0.781, -0.550	0.229, -0.192

Table S4: Selected crystallographic data for **3**, **S3a**, and **S4**.

compound	3	S3a	S4
CCDC	1037646	1037647	1037648
formula	C ₂₃ H ₃₀ OSi	C ₃₁ H ₃₈ Si	C ₃₆ H ₄₀ Si
<i>M</i> _r	350.56	438.70	500.77
<i>T</i> (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
crystal system	Triclinic	Orthorhombic	Orthorhombic
space group	<i>P</i> -1	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> mc2 ₁
<i>a</i> (Å)	13.0836(7)	10.9279(4)	24.630(5)
<i>b</i> (Å)	16.4963(8)	20.8100(9)	10.890(2)
<i>c</i> (Å)	17.2956(9)	23.7306(9)	11.319(2)
α (°)	64.623(4)	90	90
β (°)	70.425(4)	90	90
γ (°)	80.842(4)	90	90
<i>V</i> (Å ³)	3177.3(3)	5396.6(4)	3035.9(11)
<i>Z</i>	6	8	4
<i>D</i> _{calcd} (g cm ⁻³)	1.099	1.080	1.096
F(000)	1140	1904	1080
μ (mm ⁻¹)	0.118	0.102	0.099
crystal size (mm)	0.25 × 0.20 × 0.20	0.36 × 0.19 × 0.03	0.42 × 0.37 × 0.22
reflections collected	48698	49619	8954
independent reflections	12212	9497	2640
<i>R</i> _{int}	0.0560	0.0950	0.0434
data/restraints/parameters	12212/0/672	947/0/577	2640/1/212
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0538, 0.1382	0.0459, 0.1063	0.0285, 0.0763
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0638, 0.1443	0.0550, 0.1097	0.0294, 0.0767
Goodnes-of-fit on <i>F</i> ²	1.025	0.990	1.079
Largest diff peak and hole (e Å ⁻³)	0.850, -0.449	0.355, -0.276	0.161, -0.162

Table S5: Selected crystallographic data for **7**, **8b**, and **8c**.

compound	7	8b	8c
CCDC	1037649	1037650	1037651
formula	C ₃₆ H ₃₆ Si × C ₆ H ₆	C ₃₇ H ₃₈ BBr	C ₃₈ H ₃₈ BF ₃
<i>M</i> _r	574.84	573.39	562.49
<i>T</i> (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	MoKα, 0.71073	MoKα, 0.71073	MoKα, 0.71073
crystal system	Triclinic	Monoclinic	Monoclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	9.9401(7)	22.2228(7)	22.4969(13)
<i>b</i> (Å)	12.1075(7)	15.0783(6)	15.0020(7)
<i>c</i> (Å)	14.4834(9)	9.0678(3)	9.2457(5)
α (°)	73.959(5)	90	90
β (°)	73.909(5)	96.255(3)	94.176(5)
γ (°)	80.607(5)	90	90
<i>V</i> (Å ³)	1602.48(19)	3020.37(18)	3112.1(3)
<i>Z</i>	2	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.191	1.261	1.201
F(000)	616	1200	1192
μ (mm ⁻¹)	0.102	1.385	0.080
crystal size (mm)	0.50 × 0.48 × 0.10	0.32 × 0.26 × 0.11	0.38 × 0.31 × 0.10
reflections collected	29473	60643	41709
independent reflections	7354	7973	6351
<i>R</i> _{int}	0.0562	0.0804	0.1009
data/restraints/parameters	7354/0/388	7973/0/355	6351/0/382
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0408, 0.1066	0.0537, 0.1369	0.0638, 0.1737
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0485, 0.1106	0.0586, 0.1406	0.0822, 0.1877
Goodnes-of-fit on <i>F</i> ²	1.032	1.068	0.927
Largest diff peak and hole (e Å ⁻³)	0.368, -0.283	1.162, -0.692	0.709, -0.335

Table S6: Selected crystallographic data for **8d**, **10** and **11**.

compound	8d	10	11
CCDC	1037652	1037653	1037654
formula	C ₅₅ H ₅₂ BN	C ₄₆ H ₆₀ Si ₂	C ₄₆ H ₅₆ Si ₂
<i>M</i> _r	737.78	669.12	665.08
<i>T</i> (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
crystal system	Orthorhombic	Monoclinic	Monoclinic
space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>C2/c</i>
<i>a</i> (Å)	23.9816(15)	13.2019(14)	38.275(5)
<i>b</i> (Å)	10.3018(7)	11.5767(11)	10.7131(8)
<i>c</i> (Å)	34.582(3)	28.580(4)	27.398(3)
α (°)	90	90	90
β (°)	90	101.282(10)	133.030(7)
γ (°)	90	90	90
<i>V</i> (Å ³)	8543.6(11)	4283.6(9)	8212.3(17)
<i>Z</i>	8	4	8
<i>D</i> _{calcd} (g cm ⁻³)	1.147	1.038	1.076
F(000)	3152	1456	2880
μ (mm ⁻¹)	0.065	0.111	0.115
crystal size (mm)	0.13 × 0.03 × 0.02	0.19 × 0.16 × 0.05	0.24 × 0.12 × 0.02
reflections collected	75659	7565	30722
independent reflections	7539	7565	7738
<i>R</i> _{int}	0.2719	0.1631	0.1290
data/restraints/parameters	7539/0/535	7565/30/430	7738/18/431
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.1013, 0.1518	0.1042, 0.2242	0.0752, 0.1507
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.2189, 0.1981	0.2211, 0.2743	0.1407, 0.1762
Goodnes-of-fit on <i>F</i> ²	1.019	0.979	0.998
Largest diff peak and hole (e Å ⁻³)	0.213, -0.220	0.817, -0.372	0.639, -0.399

10. References

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5.1.3 Ru-Catalyzed Benzannulation Leads to Luminescent Boron-Containing Polycyclic Aromatic Hydrocarbons

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Ru-catalyzed benzannulation leads to luminescent boron-containing polycyclic aromatic hydrocarbons

Supporting Information

Valentin M. Hertz, Hans-Wolfram Lerner, and Matthias Wagner

Table of contents:

1. General experimental procedures	S2
2. Nomenclature	S3
3. Syntheses, purification methods and analytical data	S4
4. Plots of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra	S16
5. UV/Vis absorption and emission spectra	S30
6. Plots of cyclic voltammograms	S32
7. References	S35

1. General experimental procedures

If not stated otherwise, all reactions and manipulations were carried out under an atmosphere of dry nitrogen using Schlenk techniques. C₆H₆, toluene, Et₂O, and THF were distilled from Na/benzophenone prior to use. CH₂Cl₂, Me₃SiCl, and Me₂SiCl₂ were distilled from CaH₂. BBr₃ was stored over Hg to remove traces of HBr and Br₂. The starting materials **6/10**,^{S1} 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-one^{S2,S3}, and 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-one^{S4}, as well as the catalyst (PPh₃)Ru(cymene)Cl₂^{S5} were synthesized according to previously reported procedures. 3-Trimethylsilylpropynal (97%; *Alfa Aesar*) and di- μ -chlorobis(*p*-cymene)chlororuthenium(II) (98%; *Acros Organics*) are commercially available and were used as received.

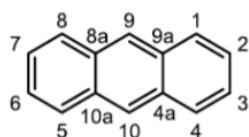
NMR spectra were recorded at 300 K using an Avance-400 or Avance-500 spectrometer. Chemical shift values are referenced to (residual) solvent signals (¹H/¹³C{¹H}; CDCl₃: δ = 7.26/77.16 ppm) or external BF₃·Et₂O (¹¹B{¹H}: 0.00 ppm) and Si(CH₃)₄ (²⁹Si INEPT: 0.00 ppm). Abbreviations: s = singlet, d = doublet, t = triplet, vt = virtual triplet, q = quartet, quint = quintet, m = multiplet, br. = broad, n.o. = not observed, n.r. = multiplet expected in the ¹H NMR spectrum but not resolved. Resonances of carbon atoms attached to boron atoms were typically broadened and sometimes not observed due to the quadrupolar relaxation of boron. Boron resonances of triarylborane compounds are typically very broad ($h_{1/2}$ > 1500 Hz) and were observed only in highly concentrated samples. Resonance assignments were aided by ¹H,¹³C COSY, ¹H,¹³C HSQC, and in some cases ¹H,¹³C HMBC and ¹H,¹³C ROESY NMR spectra.

The microwave-heated reactions were carried out in a *Biotage Initiator+* synthesizer using sealed reaction vessels; the temperature was monitored by an infrared sensor. For photochemical reactions, a medium-pressure Hg vapor lamp was used (*Heraeus Noblelight*; TQ 150, 150 W). UV/Vis absorption spectra were recorded at room temperature using a *Varian Cary 50 Scan* UV/Vis spectrophotometer. Photoluminescence (PL) spectra were recorded at room temperature using a *Jasco FP-8300* spectrofluorometer equipped with a calibrated *Jasco ILF-835* 100 mm diameter integrating sphere and analyzed using the *Jasco FWQE-880* software. For PL quantum yield (Φ_{PL}) measurements each sample was carefully degassed with argon using an injection needle and a septum-capped cuvette. Under these conditions, Φ_{PL} of the fluorescence standard 9,10-diphenylanthracene was determined as 96% (lit.: 97%)^{S6,S7}. For all measurements of Φ_{PL} , at least three samples of different concentrations were used (range between 10⁻⁵ and 10⁻⁷ mol L⁻¹). Due to self-absorption, slightly lower Φ_{PL} values were observed at higher concentrations. This effect was corrected by applying a method reported by *Bardeen et al.*, which slightly improved the Φ_{PL} values (4% at most).^{S8} Cyclic voltammetry (CV) measurements were performed in an inert-atmosphere glovebox at room temperature using a one-chamber, three-electrode cell and an *EG&G Princeton Applied Research 263A* potentiostat. A platinum disk electrode (2.00 mm diameter) was used as the working electrode with a platinum wire counter electrode and a silver wire reference electrode, which was coated with AgCl by immersion into HCl/HNO₃ (3:1). Prior to measurements, the solvent (CH₂Cl₂) was dried as described above and additionally degassed with argon. [*n*-Bu₄N][PF₆] was employed as the supporting electrolyte (0.1 mol L⁻¹). All potential values were referenced against the FcH/FcH⁺ redox couple (FcH = ferrocene; $E_{1/2}$ = 0 V). Scan rates were varied between 100 and 400 mV s⁻¹. High-resolution mass spectra were measured in positive mode using a *Thermo Fisher Scientific MALDI LTQ Orbitrap XL* and 2,5-dihydroxybenzoic acid or α -cyano-4-hydroxycinnamic acid as the matrix. Exact masses were calculated based on the

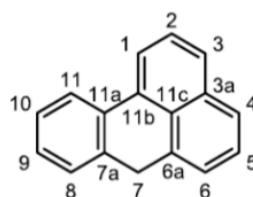
predominant combination of natural isotopes. Combustion analyses were performed by the microanalytical laboratory of the *Goethe-University Frankfurt*.

2. Nomenclature

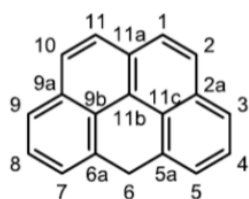
Assignment of NMR signals: The same numbering schemes as for the all-carbon compounds (see below) were employed for their silicon- or boron-containing congeners.



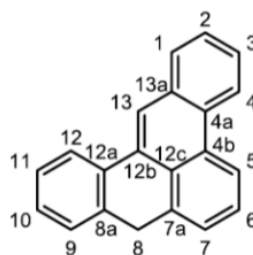
anthracene



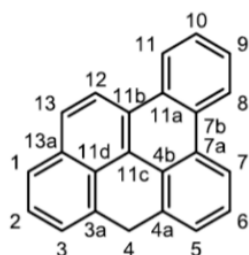
7H-benzo[de]anthracene



6H-benzo[cd]pyrene

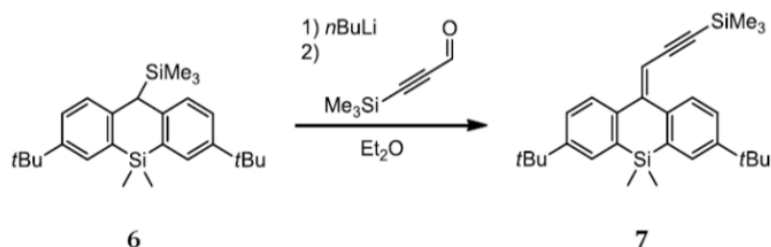


8H-benzo[gh]tetraphene



4H-dibenzo[gh,pqr]tetraphene

3. Syntheses, purification methods and analytical data



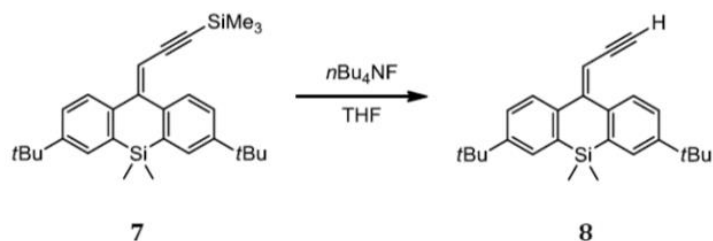
2,7-Di-*tert*-butyl-10-(3-trimethylsilyl-prop-2-yn-1-ylidene)-9,9-dimethyl-9,10-dihydro-9-silaanthracene (7): Compound 6 (0.777 g, 1.90 mmol) was placed in a 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (20 mL). *n*-BuLi in *n*-hexane (1.56 M; 1.2 mL, 1.9 mmol) was added via a syringe at room temperature. The mixture was heated to reflux temperature for 1 h, whereupon it turned red. After cooling the mixture to room temperature, a solution of 3-trimethylsilylpropynal (0.24 g, 1.9 mmol) in Et₂O (1 mL) was added slowly via syringe. After the addition was complete, the mixture was heated to reflux temperature for 1.5 h. A saturated aqueous NaHCO₃ solution (40 mL) and Et₂O (30 mL) were added. The aqueous layer was separated and extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with H₂O (50 mL) and brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (20 cm silica gel, cyclohexane, *R_f* = 0.23). The product was freeze-dried with cyclohexane (5 mL) to obtain a colorless solid. Yield: 616 mg (73%).

¹H NMR (500.2 MHz, CDCl₃): δ 8.14 (d, ³*J*_{H,H} = 8.3 Hz, 1H; H-4 or 5), 7.63 (d, ⁴*J*_{H,H} = 2.1 Hz, 1H; H-1 or 8), 7.58 (d, ⁴*J*_{H,H} = 2.0 Hz, 1H; H-1 or 8), 7.46 (d, ³*J*_{H,H} = 8.2 Hz, 1H; H-4 or 5), 7.41-7.38 (m, 2H; H-3 and 6), 6.03 (s, 1H; CH=), 1.35 (s, 9H; *t*-Bu-CH₃), 1.33 (s, 9H; *t*-Bu-CH₃), 0.47 (s, 6H; SiMe₂), 0.20 (s, 9H, SiMe₃)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 151.4, 149.7, 149.7, 144.1, 140.4, 135.2, 134.7, 129.0 (C-1 or 8), 129.0 (C-1 or 8), 128.8 (C-4 or 5), 126.8 (C-3 or 6), 125.7 (C-4 or 5), 125.5 (C-3 or 6), 107.9 (CH=), 105.2 (C≡C), 100.2 (C≡C), 34.8 (*t*-Bu-C), 34.7 (*t*-Bu-C), 31.5 (*t*-Bu-CH₃), 0.0 (SiMe₃), -2.4 (SiMe₂)

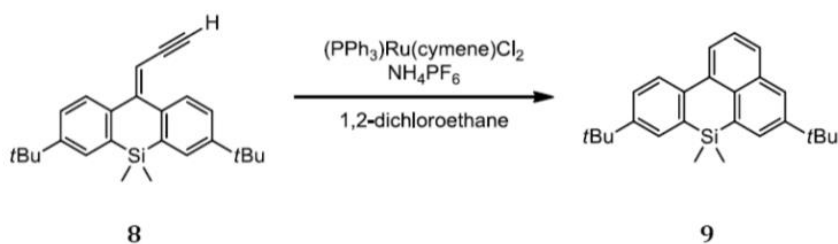
²⁹Si NMR (99.5 MHz, CDCl₃): δ -18.2, -18.4

EA (%): Calculated for C₂₉H₄₀Si₂ [444.80]: C 78.31, H 9.06; found: C 78.41, H 9.15



2,7-Di-tert-butyl-10-(prop-2-yn-1-ylidene)-9,9-dimethyl-9,10-dihydro-9-silaanthracene (8): Compound **7** (0.25 g, 0.56 mmol) was placed in a round bottom flask and dissolved in THF (10 mL). A solution of *n*-Bu₄NF in THF (1.0 M; 0.67 mL, 0.67 mmol) was added via syringe at 0 °C. After stirring for 1 h, the solvent was removed under reduced pressure and the residue was purified by short-column chromatography (5 cm silica gel, cyclohexane:EtOAc = 25:1). The obtained product was analyzed by ¹H NMR spectroscopy and, even though it still contained some residual cyclohexane, immediately used for subsequent reactions. Yield: 0.22 g (quant.).

¹H NMR (400.1 MHz, CDCl₃): δ 8.06 (d, ³J_{H,H} = 8.3 Hz, 1H; H-4 or 5), 7.63 (d, ⁴J_{H,H} = 2.0 Hz, 1H; H-1 or 8), 7.59 (d, ⁴J_{H,H} = 1.9 Hz, 1H; H-1 or 8), 7.46 (d, ³J_{H,H} = 8.2 Hz, 1H; H-4 or 5), 7.43-7.39 (m, 2H; H-3 and 6), 5.99 (d, ³J_{H,H} = 2.5 Hz, 1H; CH=), 3.13 (d, ³J_{H,H} = 2.5 Hz, 1H; C≡CH), 1.35 (s, 9H; *t*-Bu-CH₃), 1.33 (s, 9H; *t*-Bu-CH₃), 0.47 (s, 6H; SiMe₂)



5,9-Di-tert-butyl-7,7-dimethyl-7H-7-silabenzodeanthracene (9): Compound **8** (210 mg, 0.56 mmol), (PPh₃)₃Ru(cymene)Cl₂ (48 mg, 0.085 mmol), and NH₄PF₆ (28 mg, 0.17 mmol) were placed in a microwave vial and dissolved in 1,2-dichloroethane (11 mL). The vial was sealed with a septum and the solution was degassed with argon for 5 min. The mixture was heated to 75 °C for 3 h in a microwave reactor. The solvent was removed under reduced pressure and the residue was purified by column chromatography (15 cm silica gel, cyclohexane, *R_f* = 0.33). Yield: 90 mg (43%).

¹H NMR (500.2 MHz, CDCl₃): δ 8.23 (d, ³J_{H,H} = 7.2 Hz, 1H; H-1), 8.11 (d, ³J_{H,H} = 8.7 Hz, 1H; H-11), 7.89 (d, ⁴J_{H,H} = 2.2 Hz, 1H; H-4 or 6), 7.83 (d, ⁴J_{H,H} = 2.2 Hz, 1H; H-4 or 6), 7.79 (d, ³J_{H,H} = 7.6 Hz, 1H; H-3), 7.70 (d, ⁴J_{H,H} = 2.3 Hz, 1H; H-8), 7.54 (dd, ³J_{H,H} = 8.7 Hz, ⁴J_{H,H} = 2.3 Hz, 1H; H-10), 7.52 (vt, 1H; H-2), 1.46 (s, 9H, *t*-Bu-CH₃), 1.40 (s, 9H, *t*-Bu-CH₃), 0.49 (s, 6H, SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.2, 147.2, 140.1, 134.3, 134.2, 134.0, 133.0, 132.4, 131.7 (C-4 or 6), 130.6 (C-8), 129.3 (C-3), 127.4 (C-10), 126.0 (C-11), 126.0 (C-2), 125.9 (C-4 or 6), 123.8 (C-1), 34.7 (*t*-Bu-C), 34.6 (*t*-Bu-C), 31.4 (*t*-Bu-CH₃), 31.3 (*t*-Bu-CH₃), 0.3 (SiMe₂)

²⁹Si NMR (99.5 MHz, CDCl₃): δ -21.3

EA (%): Calculated for C₂₆H₃₂Si [372.62]: C 83.81, H 8.66; found: C 83.76, H 8.68

HRMS: Calculated for C₂₆H₃₂Si: 372.22678, found: 372.22779



5,9-Di-*tert*-butyl-7-mesityl-7H-7-borabenzodeanthracene (1): Compound **9** (75 mg, 0.20 mmol) was placed in a flame-dried Schlenk tube and dissolved in neat BBr₃ (0.4 mL, added through the tap of the Schlenk tube via a syringe while maintaining positive nitrogen pressure); room temperature was maintained by means of a water bath. The mixture was stirred for 16 h. Excess BBr₃ was removed from the red reaction mixture under reduced pressure to obtain an orange solid. Toluene (5 mL) was added and the resulting orange solution was stirred at 25 torr for 30 min to remove traces of residual BBr₃ (the volume of the solution decreased only slightly). A solution of MesMgBr in THF (0.87 M; 0.35 mL, 0.30 mmol) was added at room temperature via syringe. After stirring for 1 h, the reaction mixture was quenched with *i*-PrOH (0.3 mL) and all volatiles were removed under reduced pressure. The crude product was purified by short column chromatography (5 cm silica gel, cyclohexane) to obtain **1** as a yellow solid. Yield: 75 mg (84%). Crystals were grown by layering a solution of **1** (70 mg) in CH₂Cl₂ (1 mL) with CH₃CN (5 mL).

¹H NMR (500.2 MHz, CDCl₃): δ 8.65 (d, ³*J*_{H,H} = 7.4 Hz, 1H; H-1), 8.50 (d, ³*J*_{H,H} = 8.5 Hz, 1H; H-11), 8.24 (d, ⁴*J*_{H,H} = 2.2 Hz, 1H; H-6), 8.18 (d, ⁴*J*_{H,H} = 2.2 Hz, 1H; H-4), 8.00 (d, ³*J*_{H,H} = 7.9 Hz, 1H; H-3), 7.86 (d, ⁴*J*_{H,H} = 2.4 Hz, 1H; H-8), 7.79 (dd, ³*J*_{H,H} = 8.5 Hz, ⁴*J*_{H,H} = 2.4 Hz, 1H; H-10), 7.72 (vt, ³*J*_{H,H} = 7.8 Hz, 1H; H-2), 6.94 (s, 2H; Mes-CH-*m*), 2.43 (s, 3H; Mes-CH₃-*p*), 1.99 (s, 6H; Mes-CH₃-*o*), 1.39 (s, 9H; *t*-Bu-CH₃ at C-5), 1.31 (s, 9H; *t*-Bu-CH₃ at C-9)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.6 (C-9), 148.6 (C-5), 140.8 (C-6), 140.2 (Mes-C-*i*), 139.4 (C-11a), 138.8 (Mes-C-*o*), 136.7 (C-7a), 136.4 (Mes-C-*p*), 135.3 (C-8), 134.7 (C-6a), 133.1 (C-3a), 132.1 (C-11b), 131.2 (C-4), 130.6 (C-10), 129.9 (C-3), 129.9 (C-11c), 127.0 (Mes-CH-*m*), 126.1 (C-2), 124.4 (C-1), 123.4 (C-11), 34.9 (*t*-Bu-C at C-5), 34.7 (*t*-Bu-C at C-9), 31.4 (*t*-Bu-CH₃ at C-9), 31.3 (*t*-Bu-CH₃ at C-5), 23.5 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

¹¹B NMR (160.5 MHz, CDCl₃): δ 65 (*h*_{1/2} \approx 1500 Hz)

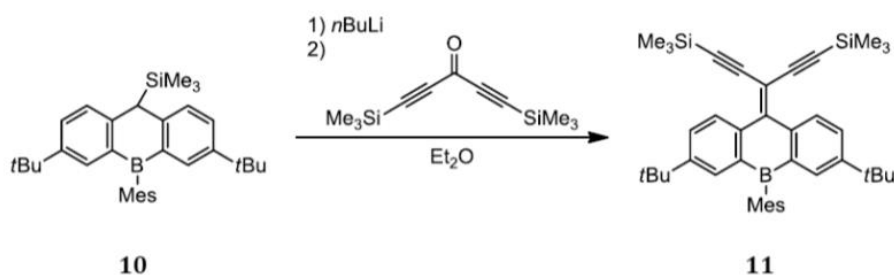
EA (%): Calculated for C₃₃H₃₇B [444.46]: C 89.18, H 8.39; found: C 89.38, H 8.30

HRMS: Calculated for C₃₃H₃₇B: 444.29886, found: 444.29763

UV/Vis (cyclohexane): λ_{\max} (ϵ) = 409 (11000), 395 nm (13000)

Photoluminescence (cyclohexane, λ_{Ex} = 390 nm): 450, 431 nm; Φ_{PL} = 80%

Cyclic voltammetry (CH₂Cl₂, [*n*-Bu₄N][PF₆] 0.1 M, 400 mV s⁻¹, vs. FcH/FcH⁺): $E_{1/2} = -2.11$ V



2,7-Di-*tert*-butyl-10-(1,5-bis(trimethylsilyl)penta-1,4-diyne-3-ylidene)-9-mesityl-9,10-dihydro-9-boraanthracene (11): Compound **10** (0.405 g, 0.843 mmol) was placed in a 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (20 mL). *n*-BuLi in *n*-hexane (1.50 M; 0.56 mL, 0.84 mmol) was added via a syringe at room temperature. The mixture was heated to reflux temperature for 20 min, whereupon it turned red. The mixture was cooled to 0 °C and 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-one (0.187 g, 0.843 mmol) was added, whereupon the color changed to brown. The solution was heated to reflux temperature for 1 h. A saturated aqueous NaHCO₃ solution (20 mL), H₂O (30 mL), and Et₂O (30 mL) were added. The aqueous layer was separated and extracted with Et₂O (30 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by short-column chromatography (10 cm silica gel, cyclohexane:EtOAc = 100:1, *R_f* = 0.17). All fractions containing **11** (determined by TLC) were combined and the solvent was removed under reduced pressure. The product was suspended in MeOH (10 mL), sonicated, isolated by filtration, washed with MeOH (5 mL), and dried in vacuo to furnish a yellow powder. Yield: 0.336 g (65%).

¹H NMR (500.2 MHz, CDCl₃): δ 8.44 (d, ³*J*_{H,H} = 8.3 Hz, 2H; H-4,5), 7.58 (d, ⁴*J*_{H,H} = 2.3, 2H; H-1,8), 7.45 (d, ³*J*_{H,H} = 8.3 Hz, ⁴*J*_{H,H} = 2.3 Hz, 2H; H-3,6), 6.89 (s, 2H; Mes-*CH-m*), 2.39 (s, 3H; Mes-*CH_{3-p}*), 2.01 (s, 6H; Mes-*CH_{3-o}*), 1.24 (s, 18H; *t*-Bu-CH₃), 0.23 (s, 18H; SiMe₃)

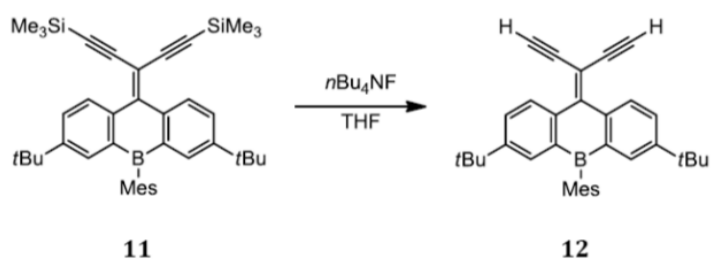
¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 153.0, 151.0, 141.4, 139.3, 138.2, 137.5, 136.5, 133.9 (C-1,8), 128.7 (C-4,5), 128.1 (C-3,6), 127.0 (Mes-*CH-m*), 105.0, 102.0, 100.6, 34.7 (*t*-Bu-C), 31.3 (*t*-Bu-CH₃), 23.0 (Mes-*CH_{3-o}*), 21.5 (Mes-*CH_{3-p}*), -0.2 (SiMe₃)

¹¹B NMR (160.5 MHz, CDCl₃): not observed

²⁹Si NMR (99.4 MHz, CDCl₃): δ -17.3

EA (%): Calculated for C₄₁H₅₃BSi₂ [612.84]: C 80.35, H 8.72; found: C 80.35, H 8.83

HRMS: Calculated for C₄₁H₅₃BSi₂: 612.37810, found: 612.37588



2,7-Di-*tert*-butyl-10-(penta-1,4-diyne-3-ylidene)-9-mesityl-9,10-dihydro-9-boraanthracene (12): Compound **11** (0.40 g, 0.65 mmol) was placed in a Schlenk flask and dissolved in THF (10 mL). The solution was cooled to 0 °C and *n*-Bu₄NF in THF (1.0 M; 1.4 mL, 1.4 mmol) was added via syringe. After stirring at 0 °C for 1 h, cyclohexane (20 mL) was added at room temperature, the mixture was passed over a short silica pad, and the pad was further eluted with cyclohexane: EtOAc = 25:1. The solvent was evaporated from the eluate using a rotary evaporator ($T \leq 35$ °C). The residue was purified by column chromatography (15 cm silica gel, cyclohexane: EtOAc = 50:1) to remove residual organosilane contaminants. Compound **12** (0.23 g, 75%) was pure by ¹H-NMR and used immediately in the subsequent reaction. *Note:* This compound is not long-term stable and turns brown if stored at ambient conditions.

¹H NMR (400.1 MHz, CDCl₃): δ 8.40 (d, ³*J*_{H,H} = 8.3 Hz, 2H; H-4,5), 7.61 (s, ⁴*J*_{H,H} = 2.3 Hz, 2H; H-1,8), 7.50 (dd, ³*J*_{H,H} = 8.3 Hz, ⁴*J*_{H,H} = 2.3 Hz, 1H; H-3,6), 6.90 (s, 2H; Mes-CH-*m*), 3.31 (s, 2H; C≡CH), 2.39 (s, 3H; Mes-CH₃-*p*), 2.02 (s, 6H, Mes-CH₃-*o*), 1.24 (s, 18H; *t*-Bu-CH₃)



4,8-Di-*tert*-butyl-6-mesityl-6H-6-borabenz[cd]pyrene (2): Compound **12** (0.20 g, 0.43 mmol), (PPh₃)Ru(cymene)Cl₂ (72 mg, 0.13 mmol), and NH₄PF₆ (35 mg, 0.21 mmol) were placed in a microwave vial and dissolved in 1,2-dichloroethane (16 mL). The vial was sealed with a septum and the solution was degassed with argon for 5 min. The mixture was heated to 80 °C for 4 h in a microwave reactor. The solvent was removed under reduced pressure. The residue was purified by column chromatography (15 cm silica gel, cyclohexane, *R_f* = 0.10) and freeze-dried with cyclohexane (3 mL) to obtain **2** as a yellow solid. Yield: 39 mg (19%).

¹H NMR (500.2 MHz, CDCl₃): δ 8.43 (n.r., 2H; H-5,7), 8.36 (n.r., 2H, H-3,9), 8.16 (d, ³*J*_{H,H} = 8.5 Hz, 2H; H-2,10), 8.10 (d, ³*J*_{H,H} = 8.5 Hz, 2H, H-1,11), 6.99 (s, 2H; Mes-CH-*m*), 2.47 (s, 3H; Mes-CH₃-*p*), 2.03 (s, 6H, Mes-CH₃-*o*), 1.46 (s, 18H; *t*-Bu-CH₃)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 148.7 (C-4,8), 140.3 (Mes-C-*i*), 139.4 (C-5,7), 139.2 (Mes-C-*o*), 136.5 (Mes-C-*p*), 135.4 (C-5a,6a), 132.8 (C-11a), 131.2 (C-2a,9a), 131.1 (C-3,9), 130.2 (C-

9b,11c), 128.7 (C-2,10), 127.1 (C-1,11), 127.0 (Mes-CH-*m*), 126.1 (C-11b), 35.0 (*t*-Bu-C), 31.6 (*t*-Bu-CH₃), 24.0 (Mes-CH₃-*o*), 21.6 (Mes-CH₃-*p*)

¹¹B NMR (160.5 MHz, CDCl₃): δ 64

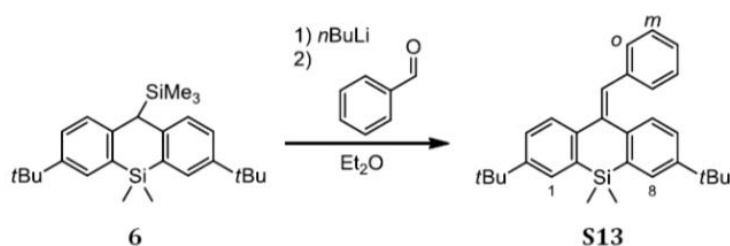
EA (%): Calculated for C₃₅H₃₇B [468.48]: C 89.73, H 7.96; found: C 89.81, H 7.63

HRMS: Calculated for C₃₅H₃₇B: 468.29889, found: 468.29777

UV/Vis (cyclohexane): λ_{max} (ε) = 427 (13000), 404 (11000), 392 (11300), 303 nm (32600)

Photoluminescence (cyclohexane, λ_{Ex} = 392 nm): 486, 456, 430 nm; Φ_{PL} = 79%

Cyclic voltammetry (CH₂Cl₂, [*n*-Bu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = -2.06 V



2,7-Di-tert-butyl-9,9-dimethyl-10-(benzylidene)-9,10-dihydro-9-silaanthracene (S13):

Compound **6** (0.50 g, 1.22 mmol) was placed in a 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (20 mL). *n*-BuLi in *n*-hexane (1.56 M; 0.78 mL, 1.22 mmol) was added at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 1 h, whereupon its color changed to red. Benzaldehyde (0.15 mL, 0.16 g, 1.5 mmol) was added at 0 °C via a syringe, whereupon the red color vanished. The mixture was heated to reflux temperature for 30 min. After cooling to room temperature, a saturated aqueous NaHCO₃ solution (30 mL) was added. The aqueous layer was separated and extracted with Et₂O (2 × 20 mL). The combined organic layers were washed with H₂O (30 mL) and brine (30 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (12 cm silica gel, cyclohexane, R_f = 0.32). Only fractions containing exclusively **S13** (determined by TLC) were combined. The solvent was removed under reduced pressure to obtain the product as a colorless solid (co-evaporation with EtOH (10 mL) is recommended). Yield: 0.39 g (75 %).

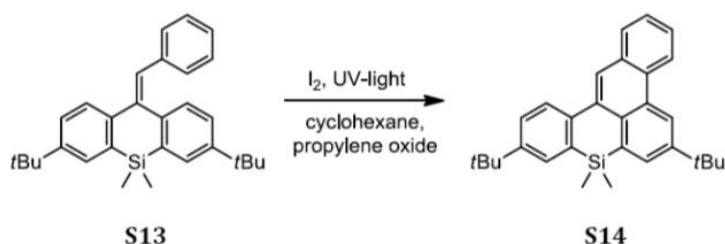
¹H NMR (500.2 MHz, CDCl₃): δ 7.65 (d, ³J_{H,H} = 8.2 Hz, 1H; H-4), 7.62 (n.r., 1H; H-8), 7.60 (n.r., 1H; H-1), 7.43 (br. d, ³J_{H,H} = 8.1 Hz, 1H; H-3), 7.21-7.12 (m, 6H; H-5, Ph-H), 7.09 (br. d, ³J_{H,H} = 8.2 Hz, 1H; H-6), 6.88 (s, 1H; CH=), 1.35 (s, 9H; *t*-Bu-CH₃), 1.30 (s, 9H; *t*-Bu-CH₃), 0.53 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.0, 148.6, 146.7, 141.9, 141.5, 138.2, 136.3, 134.8, 129.7 (Ph-C-*o*), 129.3 (CH=), 129.3 (C-5), 129.2 (C-8), 128.8 (C-1), 128.1 (Ph-C-*m*), 126.6 (C-3), 126.6 (Ph-C-*p*), 125.7 (C-6), 125.0 (C-4), 34.7 (*t*-Bu-C), 34.7 (*t*-Bu-C), 31.6 (*t*-Bu-CH₃), 31.5 (*t*-Bu-CH₃), -3.0 (SiMe₂)

²⁹Si NMR (99.4 MHz, CDCl₃): δ -17.6

EA (%): Calculated for C₃₀H₃₆Si [424.69]: C 84.84, H 8.54; found: C 84.86 H 7.98

HRMS: Calculated for C₃₀H₃₆Si: 424.25808, found: 424.25735



6,10-Di-*tert*-butyl-8,8-dimethyl-8H-8-silabenzog[h]tetraphene (S14): A solution of **S13** (0.33 g, 0.78 mmol) in cyclohexane (800 mL) was prepared in a 1 L photoreactor, equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (5 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 7.5 h during which time neat I₂ (0.29 g, 1.2 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I₂ and the eluate was evaporated to dryness under reduced pressure. The residue was suspended in MeOH (10 mL), sonicated, cooled to 8 °C, isolated by filtration while still cold, and washed with cold MeOH (10 mL). The colorless solid was dried for 5 h in an oil-pump vacuum, but still contained ca. 4 mol% MeOH (determined by ¹H NMR spectroscopy). Yield: 0.23 g (70 %).

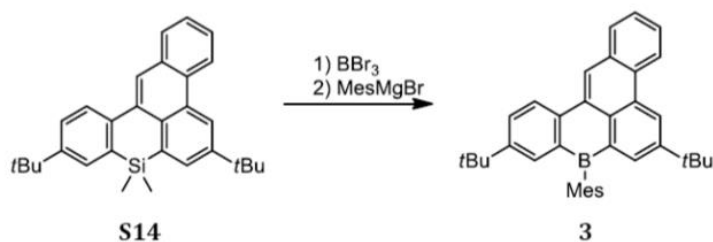
¹H NMR (500.2 MHz, CDCl₃): δ 8.84 (d, ⁴J_{H,H} = 2.1 Hz, 1H; H-5), 8.72 (br. d, ³J_{H,H} = 8.1 Hz, 1H; H-4), 8.47 (s, 1H; H-13), 8.20 (d, ³J_{H,H} = 8.6 Hz, 1H; H-12), 8.00 (d, ⁴J_{H,H} = 2.1 Hz, 1H; H-7), 7.98 (dd, ³J_{H,H} = 7.8 Hz, ⁴J_{H,H} = 1.3 Hz 1H; H-1), 7.76 (d, ⁴J_{H,H} = 2.3 Hz, 1H; H-9), 7.64 (m, 1H; H-3), 7.62-7.58 (m, 2H; H-2 and 11), 1.56 (s, 9H; *t*-Bu-CH₃), 1.44 (s, 9H; *t*-Bu-CH₃), 0.53 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 149.4 (C-6 or 10), 147.9 (C-6 or 10), 140.5, 134.3, 133.4, 132.8, 132.4, 132.0, 131.1, 130.8 (C-7), 130.3, 130.3 (C-9), 129.2 (C-1), 127.5 (C-11), 126.7 (C-2), 126.6 (C-3), 126.6 (C-12), 125.2 (C-13), 122.5 (C-4), 120.5 (C-5), 35.1 (*t*-Bu-C), 34.7 (*t*-Bu-C), 31.6 (*t*-Bu-CH₃), 31.5 (*t*-Bu-CH₃), -0.1 (SiMe₂)

²⁹Si NMR (99.4 MHz, CDCl₃): δ -20.6

EA (%): Calculated for C₃₀H₃₄Si [422.68]: C 85.25, H 8.11; found: C 83.93, H 8.12

HRMS: Calculated for C₃₀H₃₄Si: 422.24243, found: 422.24178



6,10-Di-*tert*-butyl-8-mesityl-8H-8-borabenzog[h]tetraphene (3): Compound **S14** (0.100 g, 0.237 mmol) was placed in a flame-dried Schlenk tube and dissolved in neat BBr₃ (0.4 mL; added through the tap of the Schlenk tube using a syringe while maintaining positive nitrogen pressure); room temperature was maintained by means of a water bath. The mixture was stirred for 16 h at room temperature. Excess BBr₃ was removed under reduced pressure to obtain a yellow solid. Toluene (15 mL) was added and the resulting suspension was stirred at 25 torr for 1 h to remove traces of residual BBr₃ (the volume of the solution decreases only slightly). MesMgBr in THF (0.87

M; 0.40 mL, 0.35 mmol) was added at room temperature. The solution, which already showed blue fluorescence, was stirred for 1 h. A saturated aqueous NaHCO₃ solution (30 mL) and Et₂O (20 mL) were added. The aqueous layer was separated and extracted with Et₂O (2 × 20 mL). The combined organic layers were washed with brine (2 × 40 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (15 cm silica gel, cyclohexane:toluene 20:1, *R_f* = 0.29). After co-evaporation with MeOH, **3** was obtained as a pale yellow solid. Yield: 88 mg (75%).

¹H NMR (500.2 MHz, CDCl₃): δ 9.13 (d, ⁴*J*_{H,H} = 2.1 Hz, 1H; H-5), 8.96 (s, 1H; H-13), 8.83 (d, ³*J*_{H,H} = 8.2 Hz, 1H; H-4), 8.64 (d, ³*J*_{H,H} = 8.5 Hz, 1H; H-12), 8.26 (d, ⁴*J*_{H,H} = 2.1 Hz, 1H; H-7), 8.12 (d, ³*J*_{H,H} = 7.2 Hz, 1H; H-1), 7.87 (d, ⁴*J*_{H,H} = 2.3 Hz, 1H; H-9), 7.83 (dd, ³*J*_{H,H} = 8.5 Hz, ⁴*J*_{H,H} = 2.3 Hz, 1H; H-11), 7.74 (m, 1H; H-3), 7.67 (m, 1H; H-2), 6.95 (s, 2H; Mes-CH-*m*), 2.44 (s, 3H; Mes-CH₃-*p*), 2.01 (s, 6H; Mes-CH₃-*o*), 1.46 (s, 9H; *t*-Bu-CH₃ at C-6), 1.34 (s, 9H; *t*-Bu-CH₃ at C-10)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 149.8 (C-10), 148.8 (C-6), 140.4 (Mes-C-*i*), 139.4 (C-12a), 138.7 (Mes-C-*o*), 138.5 (C-7), 136.6 (C-8a), 136.5 (Mes-C-*p*), 135.0 (C-9), 135.0 (C-7a), 132.1 (C-13a), 131.3 (C-4a), 130.7 (C-12b), 130.7 (C-11), 130.1 (C-12c), 129.9 (C-1), 129.6 (C-4b), 127.5 (C-3), 127.0 (Mes-CH-*m*), 126.8 (C-2), 126.2 (C-13), 125.2 (C-5), 123.6 (C-12), 122.6 (C-4), 35.2 (*t*-Bu-C at C-6), 34.7 (*t*-Bu-C at C-10), 31.6 (*t*-Bu-CH₃ at C-6), 31.4 (*t*-Bu-CH₃ at C-10), 23.4 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 65 (*h*_{1/2} ≈ 1500 Hz)

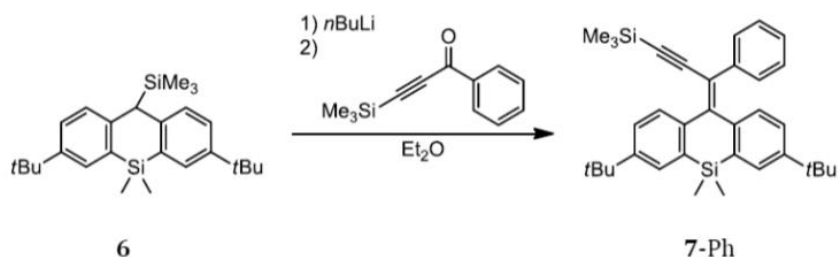
EA (%): Calculated for C₃₇H₃₉B [494.52]: C 89.86, H 7.95; found: C 89.77, H 8.10

HRMS: Calculated for C₃₇H₃₉B: 494.31393, found: 494.31299

UV/Vis (cyclohexane): λ_{max} (ε) = 408 (28800), 388 (19000), 317 (21500), 304 nm (24700)

Photoluminescence (cyclohexane, λ_{ex} = 380 nm, 25 °C): λ_{max} = 443, 420 nm; Φ_{PL} = 83 %

Cyclic voltammetry (CH₂Cl₂, [*n*-Bu₄N][PF₆] 0.1 M, 100 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = 1.09, -2.11 V



2,7-Di-*tert*-butyl-10-(3-trimethylsilyl-1-phenylprop-2-yn-1-ylidene)-9,9-dimethyl-9,10-dihydro-9-silaanthracene (7-Ph): Compound **6** (2.42 g, 5.92 mmol) was placed in a 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (50 mL). *n*-BuLi in *n*-hexane (1.53 M; 3.9 mL, 5.9 mmol) was added via a syringe at room temperature. The mixture was heated to reflux temperature for 1 h, whereupon it turned red. After cooling to room temperature, neat 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-one (1.26 g, 6.22 mmol) was added slowly via syringe. After the addition was complete, the mixture was stirred for 20 h. A saturated aqueous NaHCO₃ solution (40 mL), H₂O (40 mL), and Et₂O (40 mL) were added. The aqueous layer was separated and extracted with Et₂O (50 mL). The combined organic layers were washed with brine (2 × 50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (20 cm silica gel,

cyclohexane:CHCl₃ = 4:1). The product was freeze-dried with cyclohexane (20 mL) to obtain a colorless solid. Yield: 2.30 g (75%).

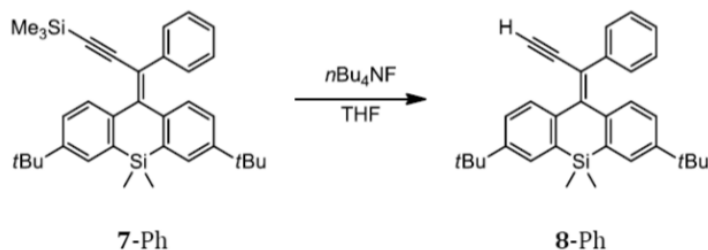
¹H NMR (500.2 MHz, CDCl₃): δ 8.10 (d, ³J_{H,H} = 8.2 Hz, 1H; H-4 or 5), 7.62 (d, ⁴J_{H,H} = 2.1 Hz, 1H; H-1 or 8), 7.55 (d, ⁴J_{H,H} = 2.1 Hz, 1H; H-1 or 8), 7.37 (d, ³J_{H,H} = 8.2 Hz, ⁴J_{H,H} = 2.1 Hz, 1H; H-3 or 6), 7.21 (m, 2H; Ph-CH-*o*), 7.15 (m, 3H, Ph-CH-*m,p*), 6.92 (dd, ³J_{H,H} = 8.2 Hz, ⁴J_{H,H} = 2.1 Hz, 1H; H-3 or 6), 6.73 (d, ³J_{H,H} = 8.2 Hz, 1H; H-4 or 5), 1.35 (s, 9H; *t*-Bu-CH₃), 1.24 (s, 9H; *t*-Bu-CH₃), 0.68 (s, 3H; SiMe₂), 0.48 (s, 3H; SiMe₂), 0.15 (s, 9H, SiMe₃)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 148.8, 148.7, 147.4, 143.7, 142.8, 139.8, 136.8, 136.2, 130.5 (Ph-CH-*o*), 129.6 (C-4 or 5), 128.8 (C-4 or 5), 128.8 (C-1 or 8), 128.5 (C-1 or 8), 127.7 (Ph-CH-*m*), 126.8 (Ph-CH-*p*), 125.3 (C-3 or 6), 125.0 (C-3 or 6), 120.9, 107.4 (C≡C), 99.9 (C≡C), 34.8 (*t*-Bu-C), 34.6 (*t*-Bu-C), 31.5(*t*-Bu-CH₃), 31.4 (*t*-Bu-CH₃), -0.1 (SiMe₃), -1.0 (SiMe₂), -5.4 (SiMe₂)

²⁹Si NMR (99.5 MHz, CDCl₃): δ -17.2, -18.1

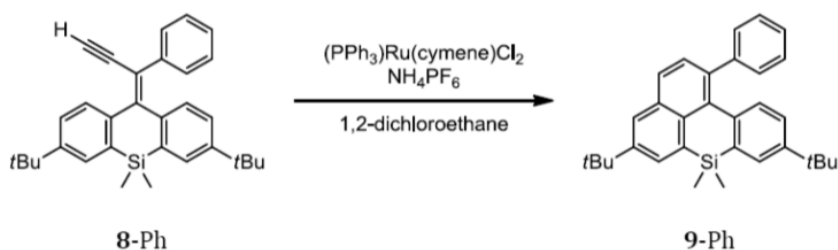
EA (%): Calculated for C₃₅H₄₄Si₂ [520.89]: C 80.70, H 8.51; found: C 80.64, H 8.63

HRMS: Calculated for C₃₅H₄₄Si₂: 520.29761, found: 520.29648



2,7-Di-*tert*-butyl-10-(1-phenylprop-2-yn-1-ylidene)-9,9-dimethyl-9,10-dihydro-9-silaanthracene (8-Ph): Compound 7-Ph (1.03 g, 1.98 mmol) was placed in a round-bottom flask and dissolved in THF (30 mL). A solution of *n*-Bu₄NF in THF (1.0 M; 2.5 mL, 2.5 mmol) was added via syringe at 0 °C. After stirring for 1 h, the solvent was removed under reduced pressure and the residue was purified by short-column chromatography (10 cm silica gel, cyclohexane:EtOAc = 25:1). The obtained product was characterized by ¹H NMR spectroscopy and immediately used for subsequent reactions. Yield: 0.865 g (quant.).

¹H NMR (250.1 MHz, CDCl₃): δ 8.06 (d, ³J_{H,H} = 8.2 Hz, 1H; H-4 or 5), 7.63 (d, ⁴J_{H,H} = 2.1 Hz, 1H; H-1 or 8), 7.56 (d, ⁴J_{H,H} = 2.1 Hz, 1H; H-1 or 8), 7.40 (dd, ³J_{H,H} = 8.2 Hz, ⁴J_{H,H} = 2.2 Hz, 1H; H-3 or 6), 7.22-7.15 (m, 5H; Ph-CH-*o, m, p*), 6.93 (dd, ³J_{H,H} = 8.2 Hz, ⁴J_{H,H} = 2.2 Hz, 1H; H-3 or 6), 6.74 (d, ³J_{H,H} = 8.2 Hz, 1H; H-4 or 5), 3.15 (s, 1H; C≡CH), 1.35 (s, 9H; *t*-Bu-CH₃), 1.24 (s, 9H; *t*-Bu-CH₃), 0.69 (s, 3H; SiMe₂), 0.48 (s, 3H, SiMe₂)



5,9-Di-tert-butyl-7,7-dimethyl-1-phenyl-7H-7-silabenzodeanthracene (9-Ph):

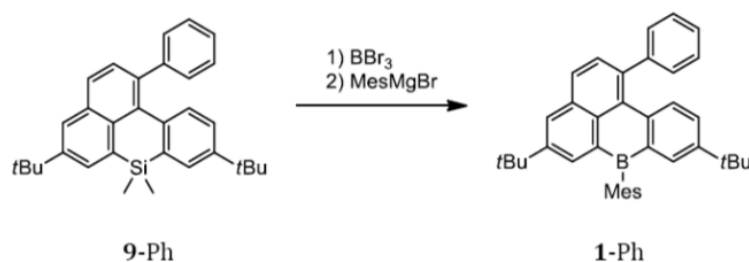
(PPh₃)Ru(cymene)Cl₂ (107 mg, 0.189 mmol) and NH₄PF₆ (62 mg, 0.38 mmol) were placed in a 2-necked round-bottom flask equipped with a condenser and a dropping funnel and suspended in 1,2-dichloroethane (20 mL). The dropping funnel was charged with a solution of **8-Ph** (850 mg, 1.89 mmol) in 1,2-dichloroethane (10 mL). The flask was gently heated (oil-bath temperature: 75 °C) and the solution of **8-Ph** was added slowly over a period of 1 h. After the addition was complete, the mixture was heated to reflux temperature for 1 h. The solvent was removed under reduced pressure and the brown solid residue was purified by column chromatography (25 cm silica gel, cyclohexane:CHCl₃ = 15:1, R_f = 0.25); **9-Ph** was obtained as a colorless solid. Yield: 615 mg (72%). Crystals were grown by layering a solution of **9-Ph** (50 mg) in CH₂Cl₂ (0.5 mL) with CH₃CN (3 mL) and storing the mixture at 8 °C for 3 d.

¹H NMR (500.2 MHz, CDCl₃): δ 7.87 (d, ⁴J_{H,H} = 2.1 Hz, 1H; H-4 or 6), 7.81-7.79 (m, 2H; H-4 or 6, H-2 or 3), 7.64 (d, ⁴J_{H,H} = 2.3 Hz, 1H; H-8), 7.61 (d, ³J_{H,H} = 8.3 Hz, 1H; H-2 or 3), 7.45 (d, ³J_{H,H} = 7.3 Hz, 2H; Ph-CH-*o*), 7.32 (vt, 2H; Ph-CH-*m*), 7.25 (t, ³J_{H,H} = 7.5 Hz, 1H; Ph-CH-*p*), 7.03 (d, ³J_{H,H} = 8.5 Hz, 1H; H-11), 6.92 (d, ³J_{H,H} = 8.6 Hz, ⁴J_{H,H} = 2.3 Hz, 1H; H-10), 1.45 (s, 9H; *t*-Bu-CH₃), 1.28 (s, 9H; *t*-Bu-CH₃), 0.53 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 148.0, 147.3, 145.2, 140.6, 139.0, 135.5, 134.3 (C-11), 134.0, 134.0, 133.4, 132.7, 130.9 (Ph-CH-*o*), 130.7 (C-4 or 6), 130.2 (C-2 or 3), 129.3 (C-8), 128.6 (Ph-CH-*m*), 128.4 (C-2 or 3), 126.4 (Ph-CH-*p*), 125.5 (C-10), 124.8 (C-4 or 6), 34.7 (*t*-Bu-C), 34.5 (*t*-Bu-C), 31.4 (*t*-Bu-CH₃ at C-5 and 9), -1.6 (SiMe₂)

²⁹Si NMR (99.5 MHz, CDCl₃): δ -19.6

EA (%): Calculated for C₃₂H₃₆Si [448.71]: C 85.65, H 8.09; found: C 85.45, H 8.33



5,9-Di-tert-butyl-7-mesityl-1-phenyl-7H-7-borabenzodeanthracene (1-Ph): Compound **9-Ph** (0.32 g, 713 μmol) was placed in a flame-dried Schlenk tube and dissolved in neat BBr₃ (0.9 mL, added through the tap of the Schlenk tube via a syringe while maintaining positive nitrogen pressure); room temperature was maintained by means of a water bath. The mixture was stirred for 16 h. Excess BBr₃ was removed from the red reaction mixture under reduced

pressure to obtain a yellow solid. Toluene (5 mL) was added and the resulting orange solution was stirred at 25 torr for 30 min to remove traces of residual BBr_3 (the volume of the solution decreased only slightly). A solution of MesMgBr in THF (0.87 M; 0.90 mL, 0.78 mmol) was added at room temperature via syringe. After stirring for 1 h, the reaction mixture was quenched with *i*-PrOH (0.5 mL) and all volatiles were removed under reduced pressure. The crude product was purified by short-column chromatography (5 cm silica gel, cyclohexane) to obtain **1-Ph** as a yellow solid. Yield: 0.36 g (97%). Single crystals were grown by layering a solution of **1-Ph** (0.36 g) in CH_2Cl_2 (2.5 mL) with CH_3CN (10 mL) and storing the vessel at 8 °C. The first crop, harvested after 5 d, gave 0.22 g of analytically pure **1-Ph**.

^1H NMR (500.2 MHz, CDCl_3): δ 8.21 (d, $^4J_{\text{H,H}} = 2.3$ Hz, 1H; H-6), 8.14 (d, $^4J_{\text{H,H}} = 2.3$ Hz, 1H; H-4), 7.97 (d, $^3J_{\text{H,H}} = 8.3$ Hz, 1H; H-3), 7.79 (d, $^4J_{\text{H,H}} = 2.4$ Hz, 1H; H-8), 7.63 (d, $^3J_{\text{H,H}} = 8.3$ Hz, 1H; H-2), 7.52 (m, 2H; Ph-CH-*o*), 7.48-7.45 (m, 3H; Ph-CH-*m*, H-11), 7.41 (tt, $^3J_{\text{H,H}} = 7.3$ Hz, $^4J_{\text{H,H}} = 2.0$ Hz, 1H; Ph-CH-*p*), 7.17 (dd, $^3J_{\text{H,H}} = 8.7$ Hz, $^4J_{\text{H,H}} = 2.5$ Hz, 1H; H-10), 6.94 (s, 2H; Mes-CH-*m*), 2.43 (s, 3H; Mes-CH₃-*p*), 2.02 (s, 6H; Mes-CH₃-*o*), 1.38 (s, 9H, *t*-Bu-CH₃ at C-5), 1.21 (s, 9H, *t*-Bu-CH₃ at C-9)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 148.6 (C-9), 148.3 (C-5), 145.9 (Ph-C-*i*), 141.5 (C-1), 140.6 (C-6), 140.3 (Mes-C-*i*), 139.9 (C-11a), 138.8 (Mes-C-*o*), 138.7 (C-7a), 136.3 (Mes-C-*p*), 134.9 (C-6a), 134.6 (C-8), 132.2 (C-11b), 131.4 (C-11c), 131.2 (C-2), 131.2 (C-11), 131.0 (C-3a), 130.8 (C-4), 130.0 (Ph-CH-*o*), 129.1 (Ph-CH-*m*), 128.9 (C-3), 128.6 (C-10), 127.1 (Ph-CH-*p*), 126.9 (Mes-CH-*m*), 34.8 (*t*-Bu-C at C-5), 34.5 (*t*-Bu-C at C-9), 31.3 (*t*-Bu-CH₃ at C-5 and 9), 23.5 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

^{11}B NMR (160.5 MHz, CDCl_3): δ 64 ($h_{\nu} \approx 1500$ Hz)

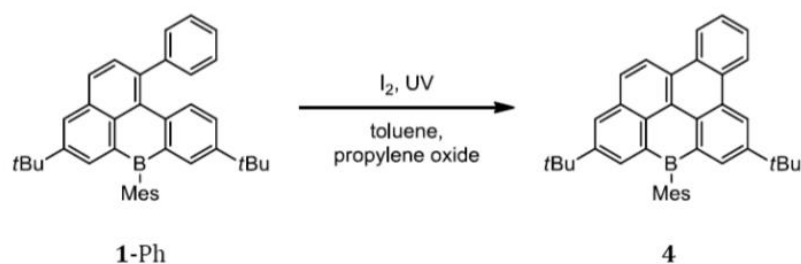
EA (%): Calculated for $\text{C}_{39}\text{H}_{41}\text{B}$ [520.55]: C 89.98, H 7.94; found: C 90.02, H 7.88

HRMS: Calculated for $\text{C}_{39}\text{H}_{41}\text{B}$: 520.33026, found: 520.32847

UV/Vis (cyclohexane): λ_{max} (ϵ) = 406 nm (14400)

Photoluminescence (cyclohexane, $\lambda_{\text{Ex}} = 395$ nm): 470 nm; $\Phi_{\text{PL}} = 91\%$

Cyclic voltammetry (CH_2Cl_2 , [*n*-Bu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): $E_{1/2} = -2.15$ V



2,6-Di-*tert*-butyl-4-mesityl-4H-4-boradibenzo[*gh,pqr*]tetraphene (4): A solution of **1-Ph** (0.26 g, 0.50 mmol) in toluene (700 mL) was prepared in a 1 L photoreactor equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (10 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 8 h, during which time neat I_2 (0.19 g, 0.75 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I_2 . All volatiles were evaporated under reduced pressure to obtain a yellow solid

(0.26 g), which contained a side product, i.e., **4** iodinated at the *m*-position of the mesityl ring (ca. 4%). By applying the following procedure, this impurity was transformed into **4**: All of the crude product was placed in a round-bottom Schlenk flask and dissolved in Et₂O (20 mL). A solution of *t*-BuLi (1.7 M; 0.2 mL, 0.34 mmol) in *n*-hexane was added at -78 °C and the mixture, which immediately adopted a purple color, was stirred for 20 min. *i*-PrOH (0.5 mL) and a saturated aqueous solution of NaHCO₃ (20 mL) were added at -78 °C. The partly solid mixture was warmed to room temperature, whereupon it liquefied again. After the color of the mixture had changed to pale yellow, the aqueous phase was separated and washed with Et₂O (2 × 30 mL). The combined organic layers were extracted with H₂O (30 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure (0.27 g of crude product). Further purification was achieved by column chromatography (30 cm silica gel, cyclohexane:CHCl₃ = 10:1, *R_f* = 0.48). The eluate was evaporated to dryness, the residue was dissolved in CH₂Cl₂ (3 mL) and layered with CH₃CN (30 mL). Analytically pure **4** was obtained as a yellow microcrystalline solid after the vessel had been stored for 3 d at 8 °C. Yield: 0.18 g (68%).

¹H NMR (500.2 MHz, CDCl₃): δ 9.21 (d, ⁴*J*_{H,H} = 2.1 Hz, 1H; H-7), 8.98-8.94 (m, 3H; H-8, 11, 12), 8.43 (d, ⁴*J*_{H,H} = 2.3 Hz, 1H; H-3), 8.38 (d, ⁴*J*_{H,H} = 2.1 Hz, 1H; H-5), 8.36 (d, ⁴*J*_{H,H} = 2.2 Hz, 1H; H-1), 8.29 (d, ³*J*_{H,H} = 8.9 Hz, 1H; H-13), 7.81 (m, 2H; H-9, 10), 7.00 (s, 2H; Mes-*CH-m*), 2.47 (s, 3H; Mes-*CH_{3-p}*), 2.04 (s, 6H; Mes-*CH_{3-o}*), 1.50 (s, 9H, *t*-Bu-*CH₃*), 1.46 (s, 9H, *t*-Bu-*CH₃*)

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 148.8 (C-2), 148.8 (C-6), 140.5 (Mes-C-*i*), 140.1 (C-3), 139.1 (Mes-C-*o*), 138.2 (C-5), 136.5 (Mes-C-*p*), 136.0 (C-4a), 135.5 (C-3a), 131.6, 131.3 (C-1), 130.9, 130.6, 130.5, 130.4, 130.2, 129.4 (C-13), 128.8, 127.5 (C-9 or 10), 127.1 (C-9 or 10), 127.0 (Mes-*CH-m*), 125.6, 125.3 (C-7), 124.4 (C-8 or 11), 123.5 (C-8 or 11), 121.7 (C-12), 35.2 (*t*-Bu-C), 35.0 (*t*-Bu-C), 31.7 (*t*-Bu-*CH₃*), 31.5 (*t*-Bu-*CH₃*), 23.9 (Mes-*CH_{3-o}*), 21.6 (Mes-*CH_{3-p}*)

¹¹B NMR (160.5 MHz, CDCl₃): δ 65

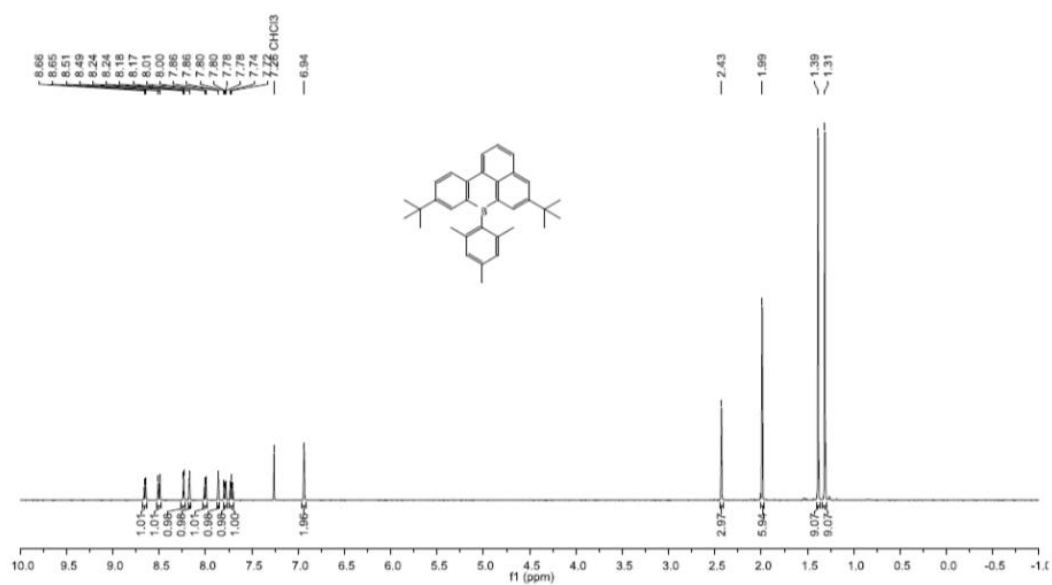
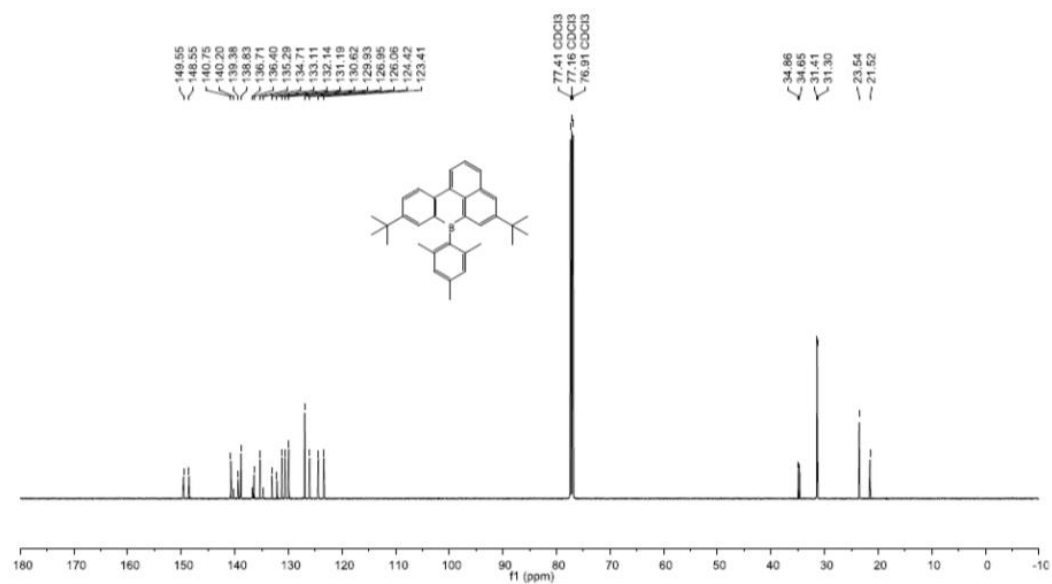
EA (%): Calculated for C₃₉H₃₉B [518.54]: C 90.33, H 7.58; found: C 89.37, H 7.62

HRMS: Calculated for C₃₉H₃₉B: 518.31461, found: 518.31346

UV/Vis (cyclohexane): λ_{max} (ε) = 424 (14500), 404 (18800), 395 nm (17200)

Photoluminescence (cyclohexane, λ_{ex} = 390 nm): 457, 433 nm; Φ_{PL} = 72%

Cyclic voltammetry (CH₂Cl₂, [*n*-Bu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): *E*_½ = ~1.18 (not completely reversible), -2.05 V

4. Plots of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectraFigure S1: ^1H NMR spectrum of **1** (CDCl_3 , 500.2 MHz).Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** (CDCl_3 , 125.8 MHz).

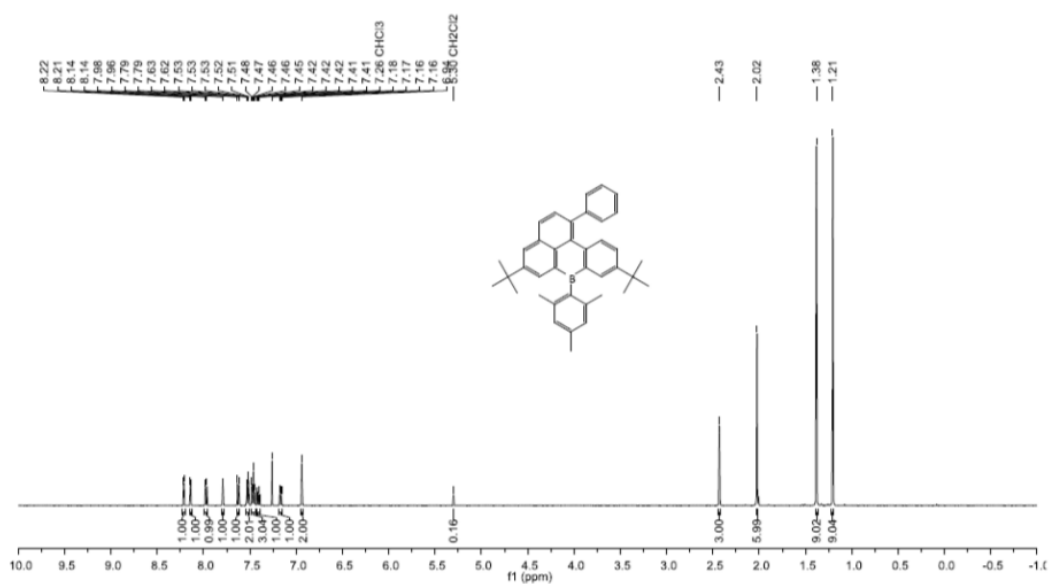


Figure S3: ^1H NMR spectrum of **1-Ph** (CDCl_3 , 500.2 MHz).

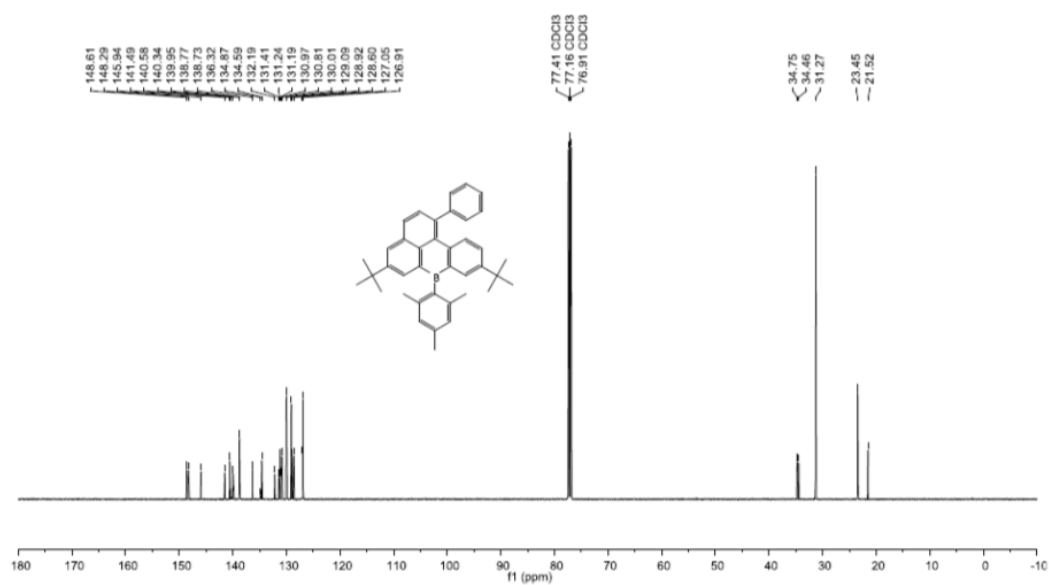
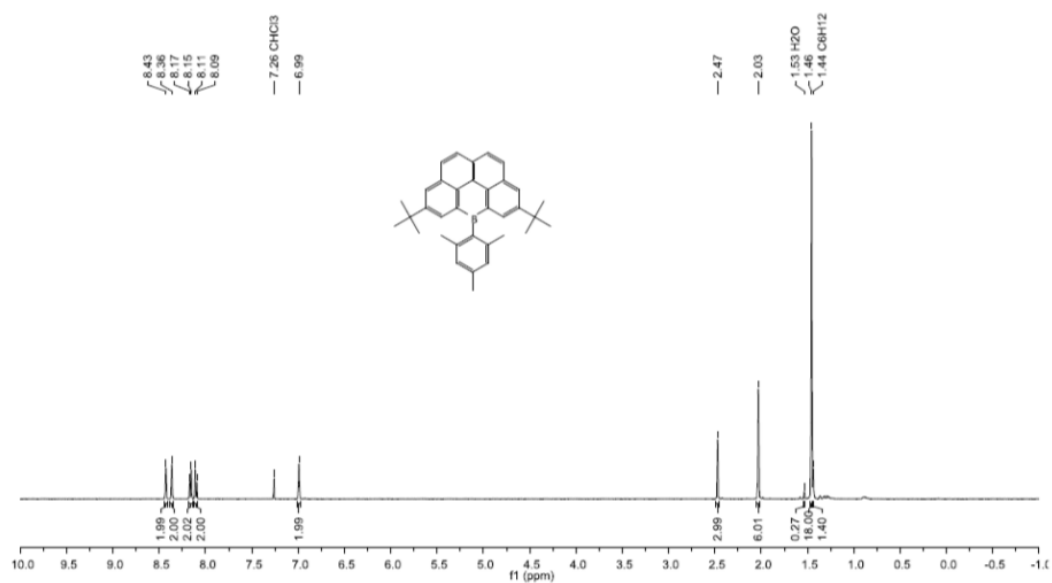
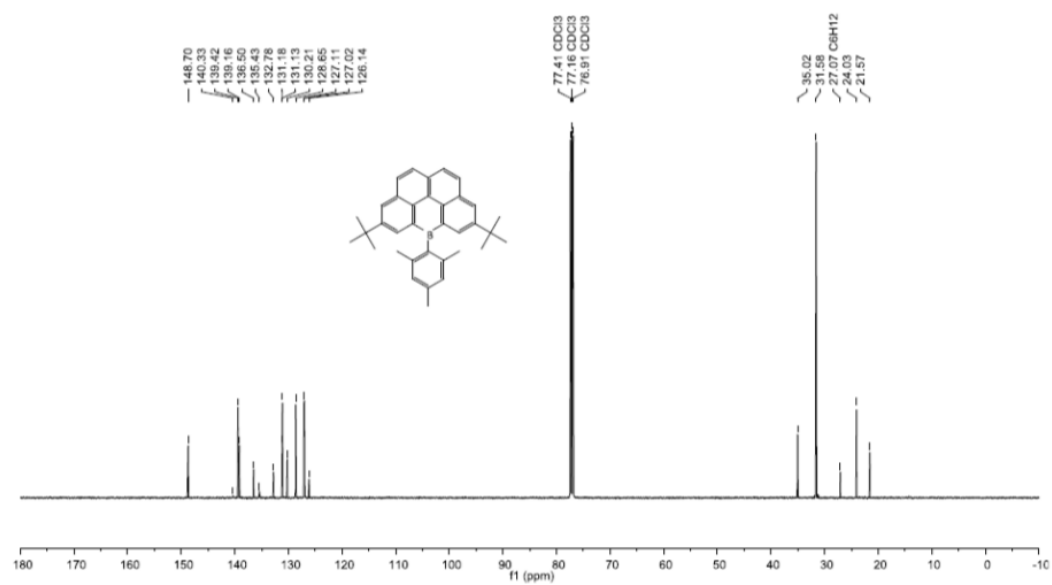


Figure S4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1-Ph** (CDCl_3 , 125.8 MHz).

Figure S5: ^1H NMR spectrum of 2 (CDCl_3 , 500.2 MHz).Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2 (CDCl_3 , 125.8 MHz).

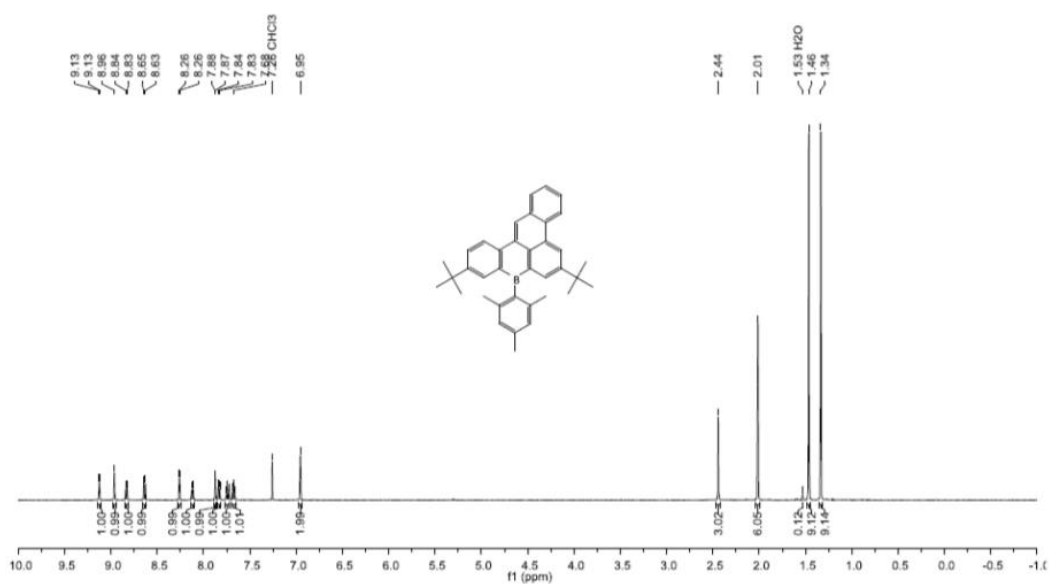


Figure S7: ^1H NMR spectrum of 3 (CDCl_3 , 500.2 MHz).

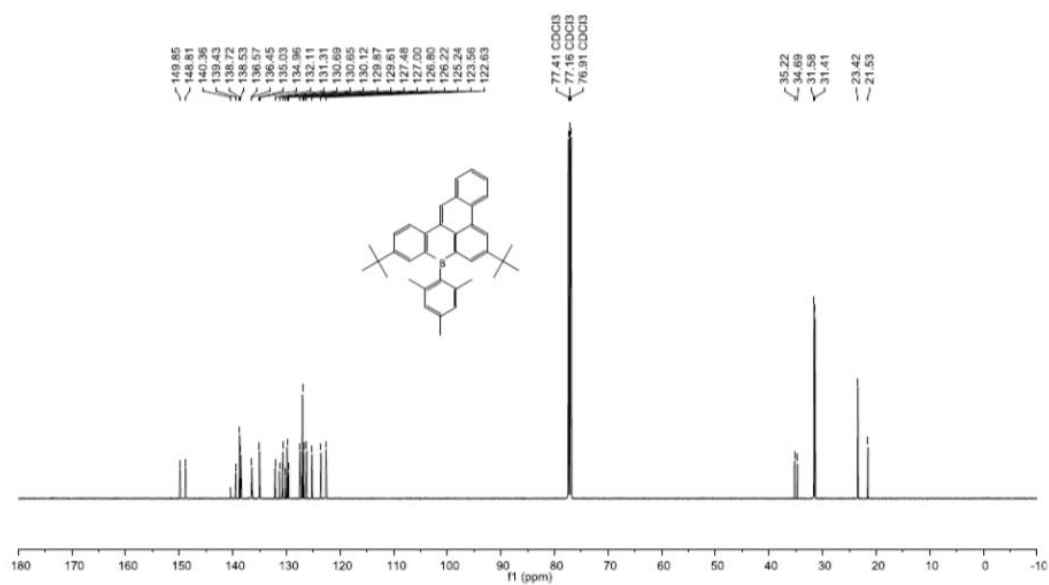


Figure S8: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3 (CDCl_3 , 125.8 MHz).

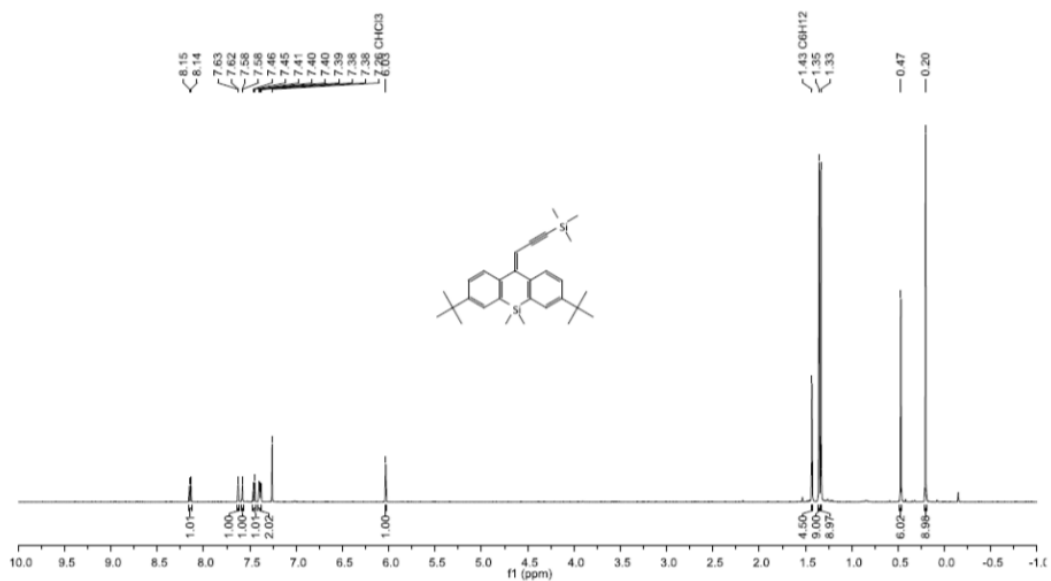


Figure S11: ^1H NMR spectrum of 7 (CDCl_3 , 500.2 MHz).

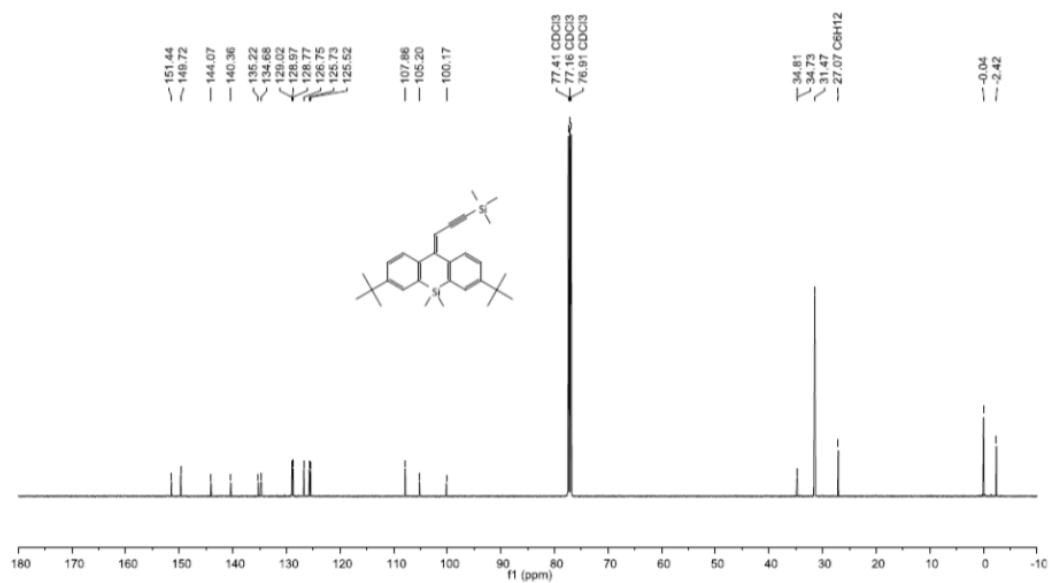
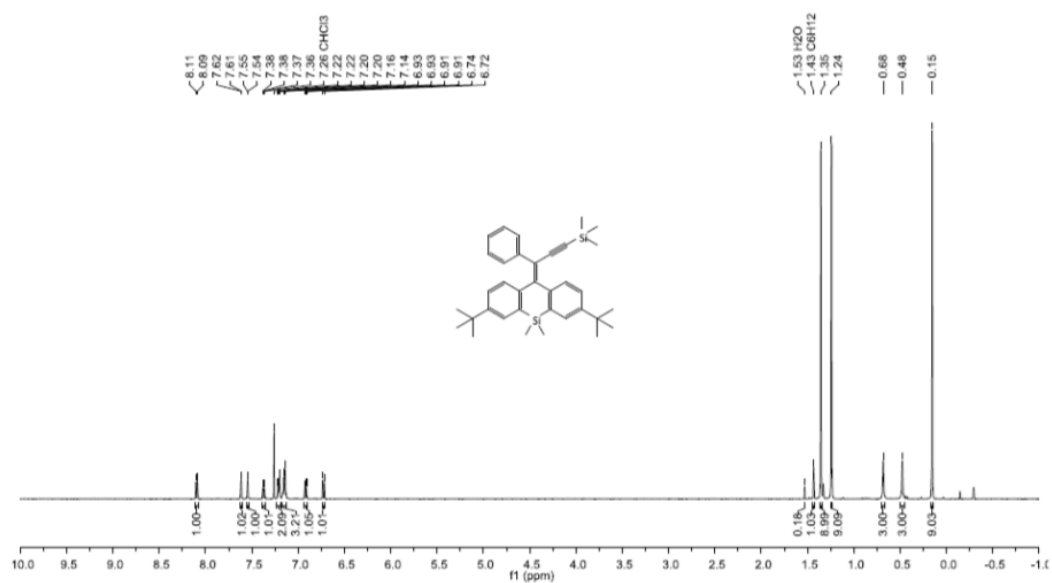
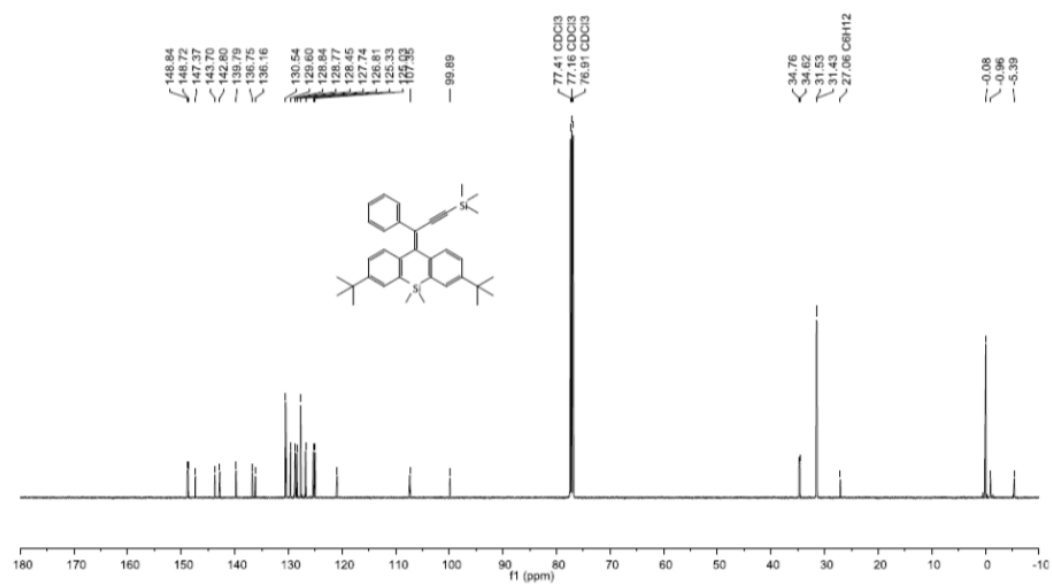


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 7 (CDCl_3 , 125.8 MHz).

Figure S13: ^1H NMR spectrum of 7-Ph (CDCl_3 , 500.2 MHz).Figure S14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 7-Ph (CDCl_3 , 125.8 MHz).

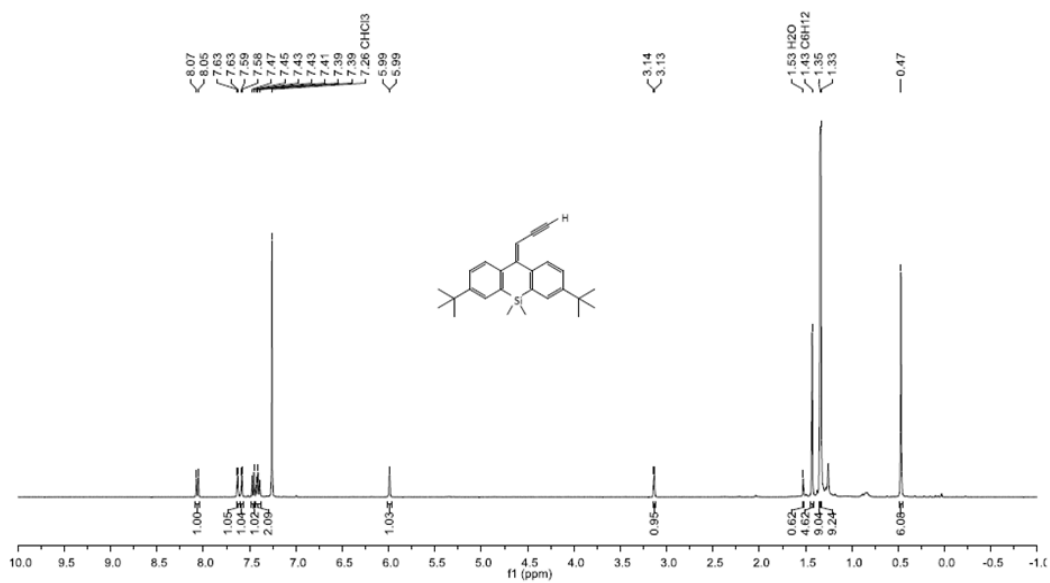


Figure S15: ^1H NMR spectrum of **8** (CDCl_3 , 400.1 MHz).

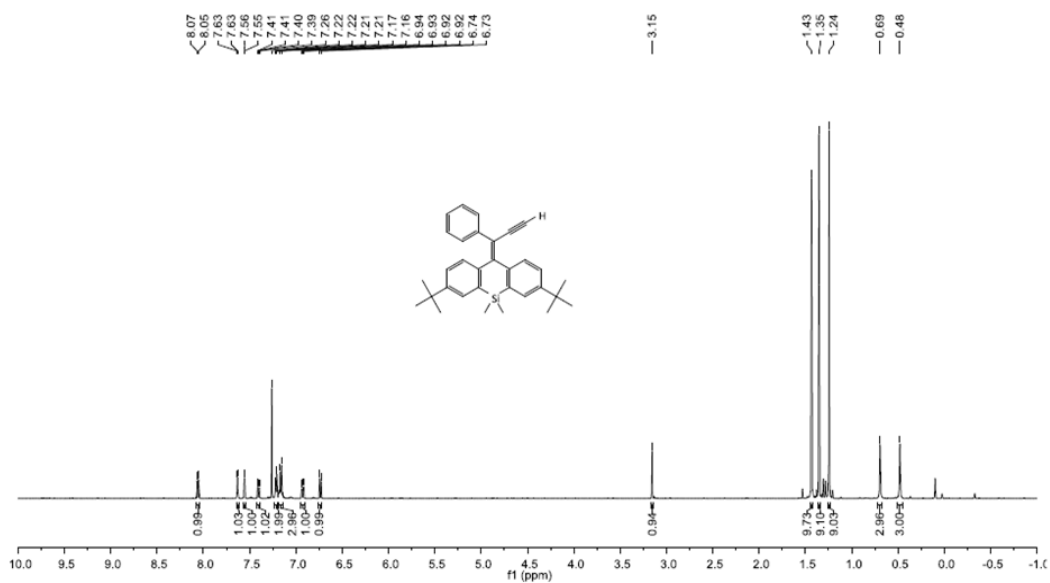


Figure S16: ^1H NMR spectrum of **8-Ph** (CDCl_3 , 500.1 MHz).

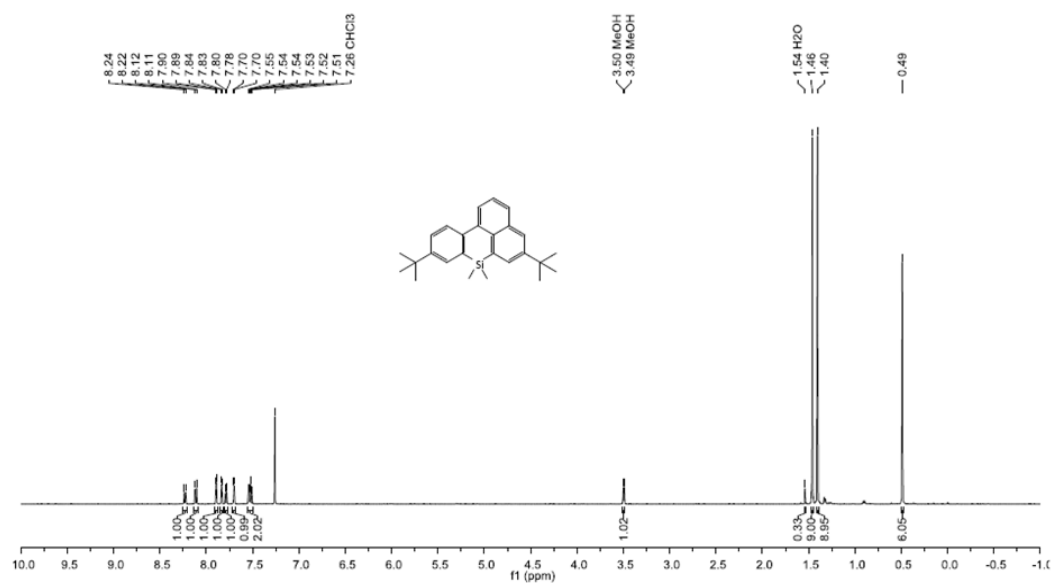


Figure S17: ^1H NMR spectrum of **9** (CDCl_3 , 500.2 MHz).

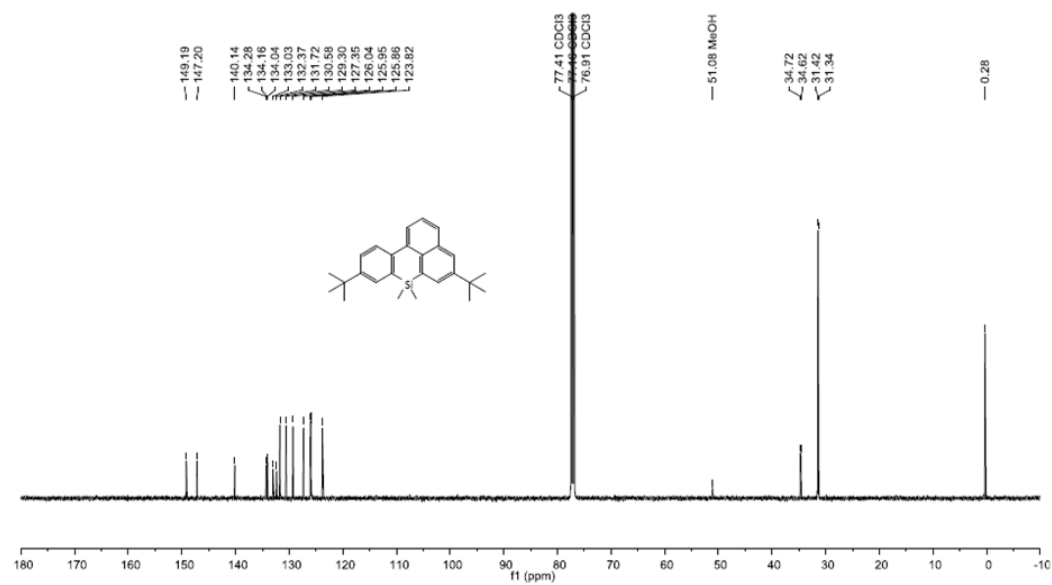


Figure S18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** (CDCl_3 , 125.8 MHz).

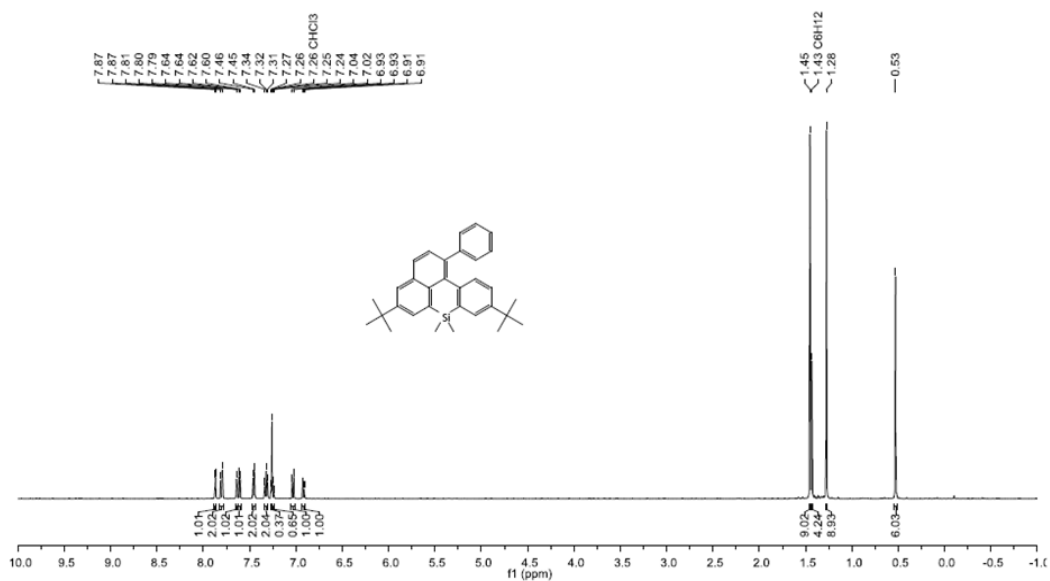


Figure S19: ^1H NMR spectrum of 9-Ph (CDCl_3 , 500.2 MHz).

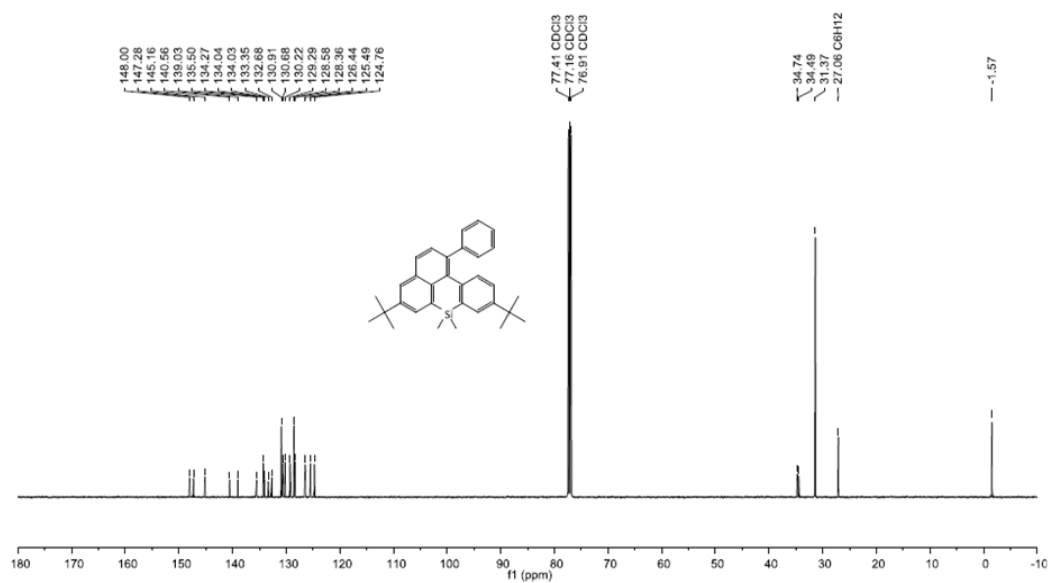
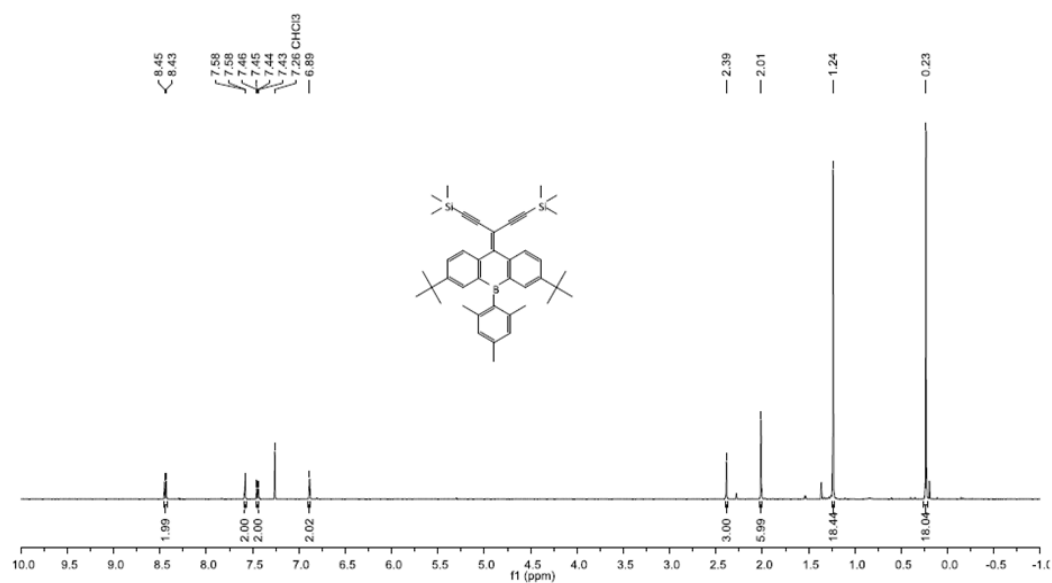
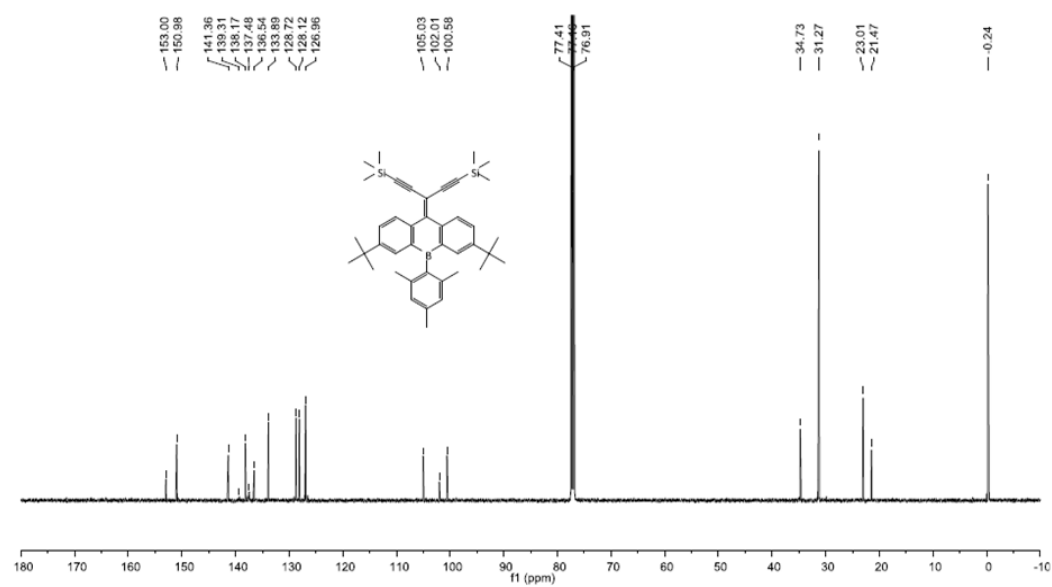


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 9-Ph (CDCl_3 , 125.8 MHz).

Figure S21: ¹H NMR spectrum of **11** (CDCl₃, 500.2 MHz).Figure S22: ¹³C{¹H} NMR spectrum of **11** (CDCl₃, 125.8 MHz).

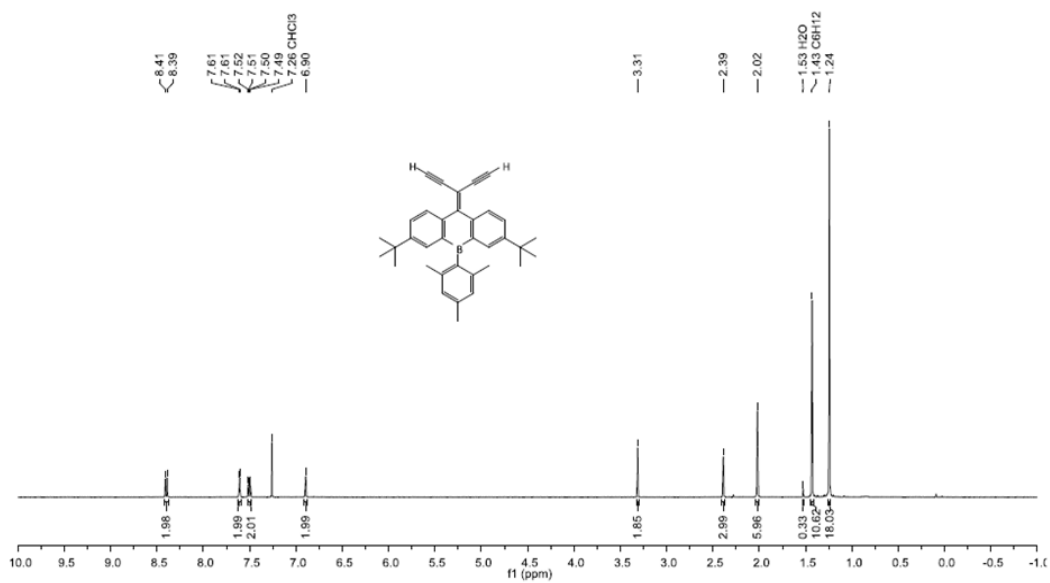


Figure S23: ¹H NMR spectrum of **12** (CDCl₃, 400.1 MHz).

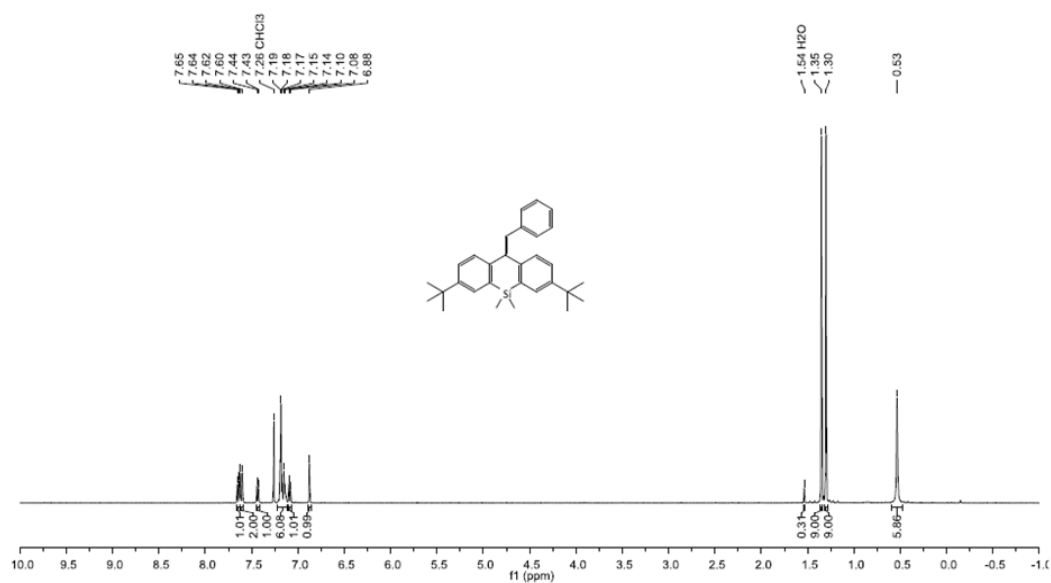


Figure S24: ^1H NMR spectrum of **S13** (CDCl_3 , 500.2 MHz).

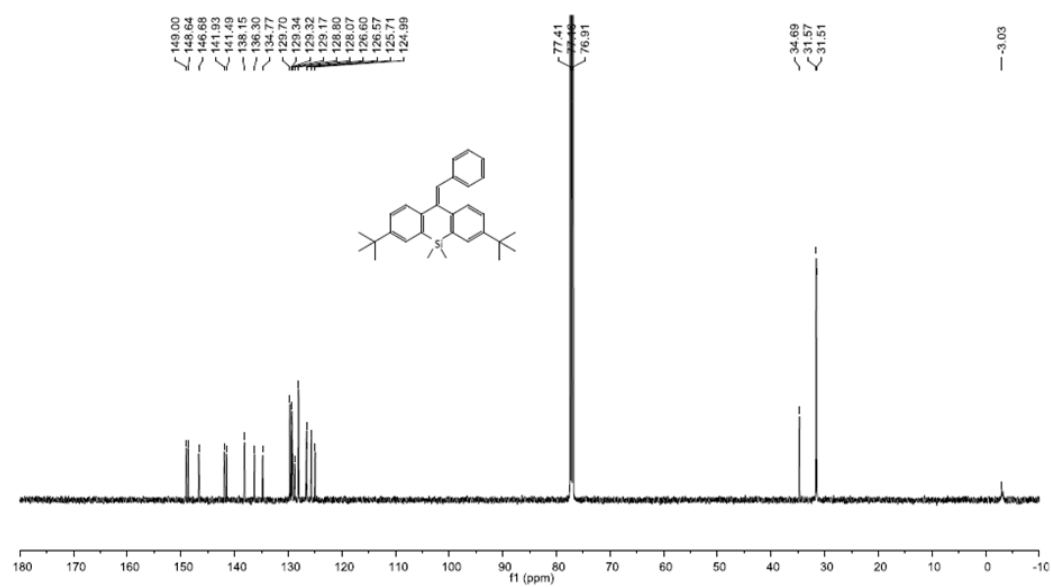


Figure S25: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **S13** (CDCl_3 , 125.8 MHz).

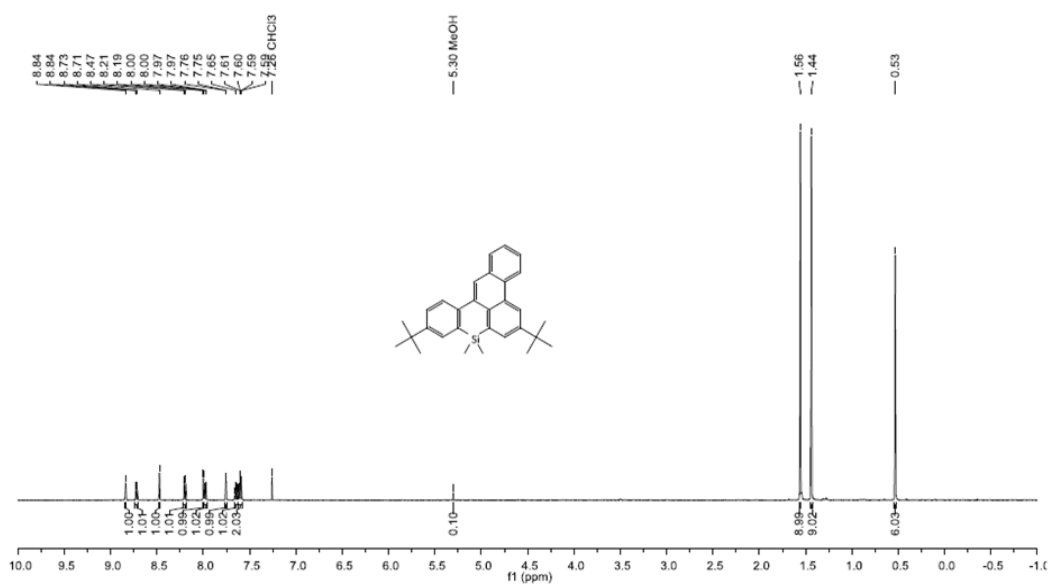


Figure S26: ¹H NMR spectrum of S14 (CDCl₃, 500.2 MHz).

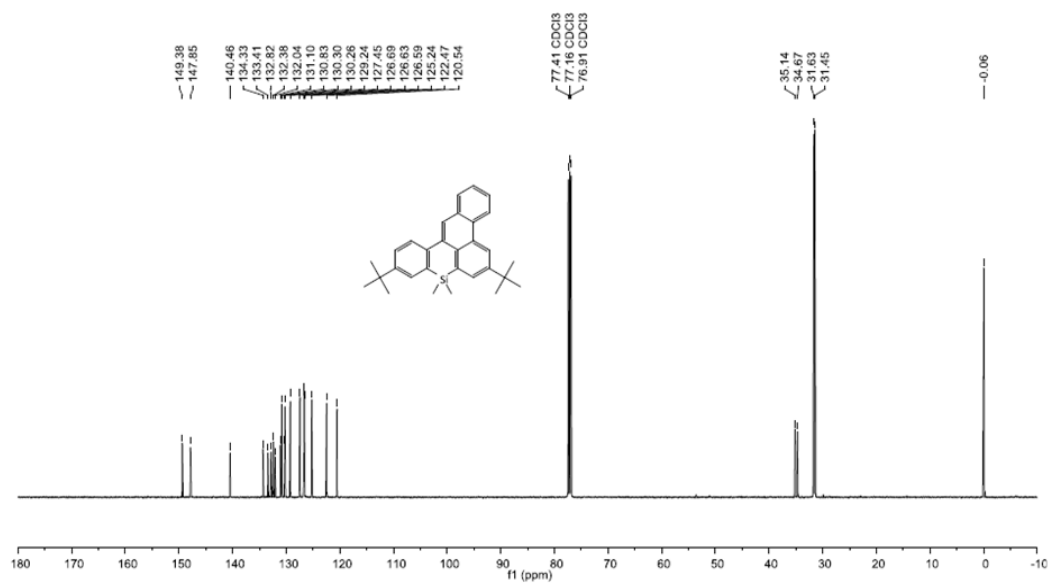
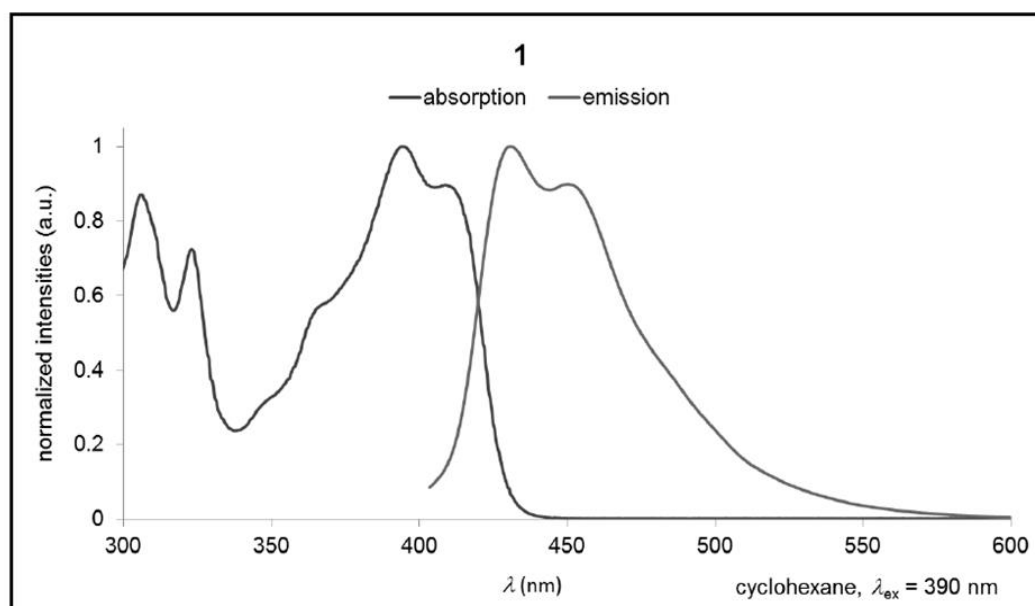
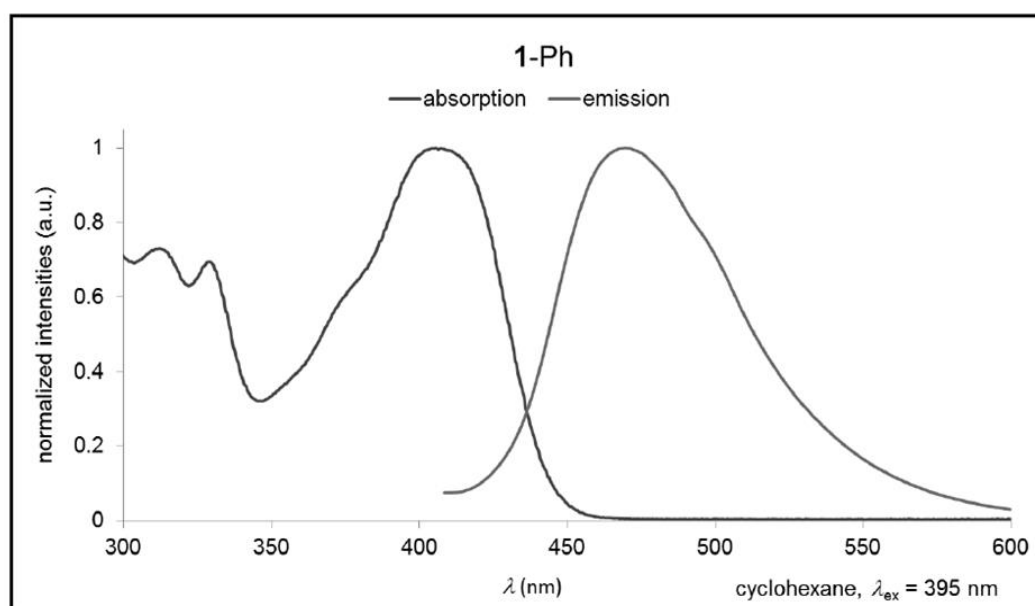


Figure S27: ¹³C{¹H} NMR spectrum of S14 (CDCl₃, 125.8 MHz).

5. UV/Vis absorption and emission spectra

Figure S28: Normalized UV/Vis absorption and emission spectrum of **1**.Figure S29: Normalized UV/Vis absorption and emission spectrum of **1-Ph**.

For a normalized UV/Vis absorption and emission spectrum of **2** see main paper.

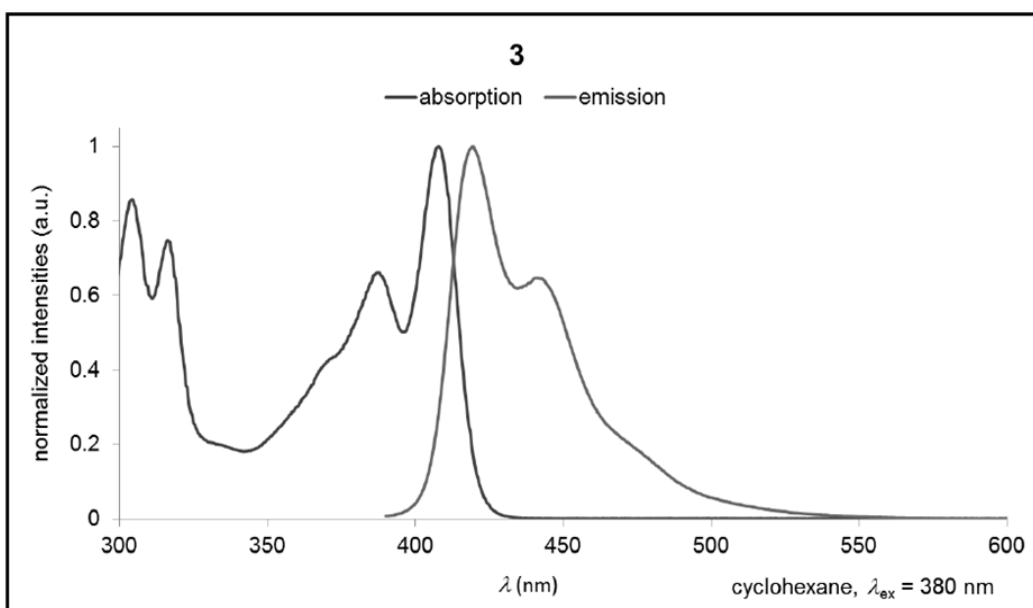


Figure S30: Normalized UV/Vis absorption and emission spectrum of 3.

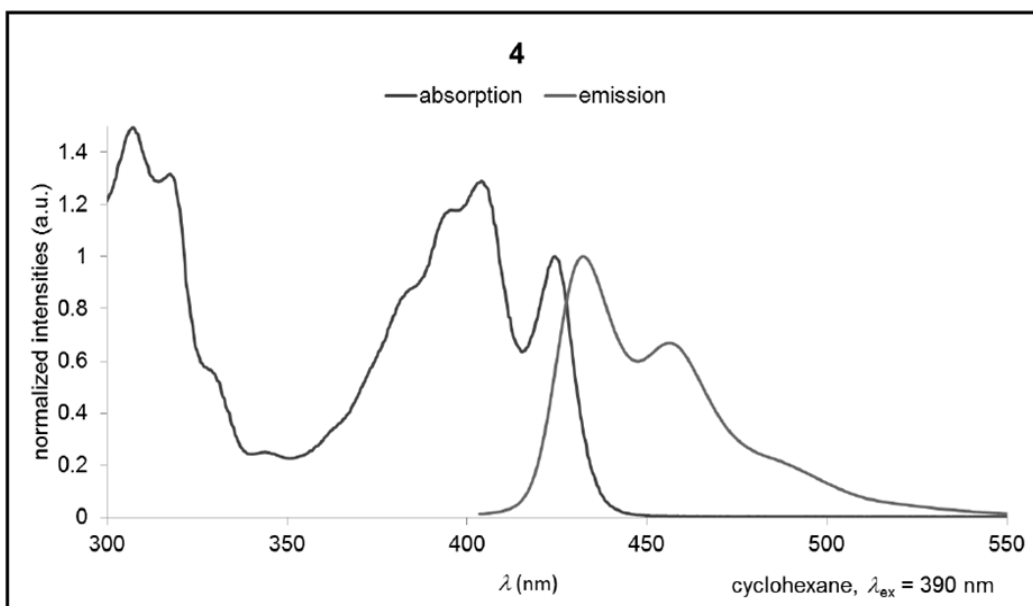


Figure S31: Normalized UV/Vis absorption and emission spectrum of 4.

6. Plots of cyclic voltammograms

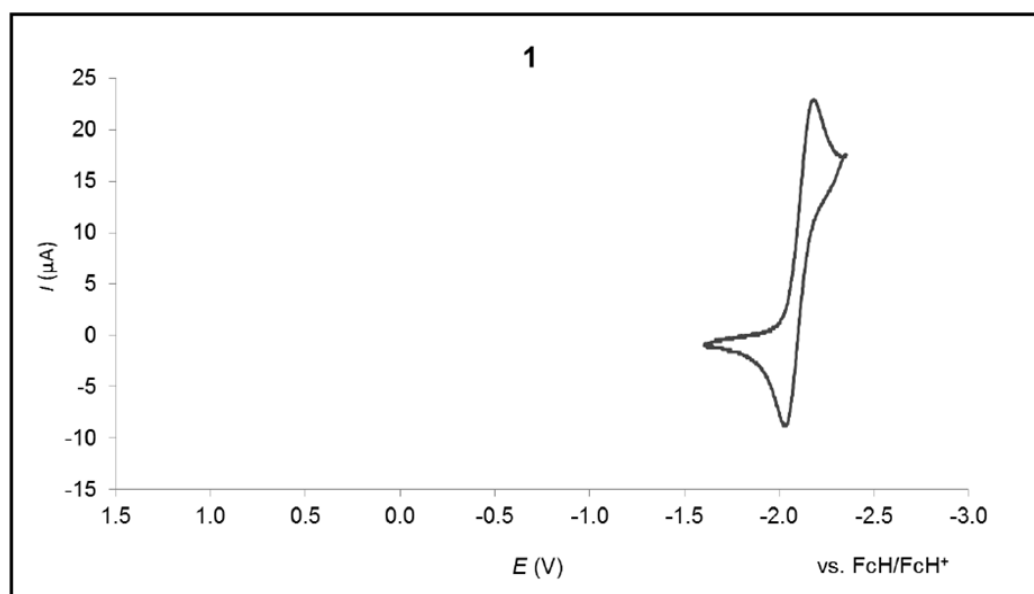


Figure S32: Cyclic voltammogram of **1** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 400 mV s^{-1}).

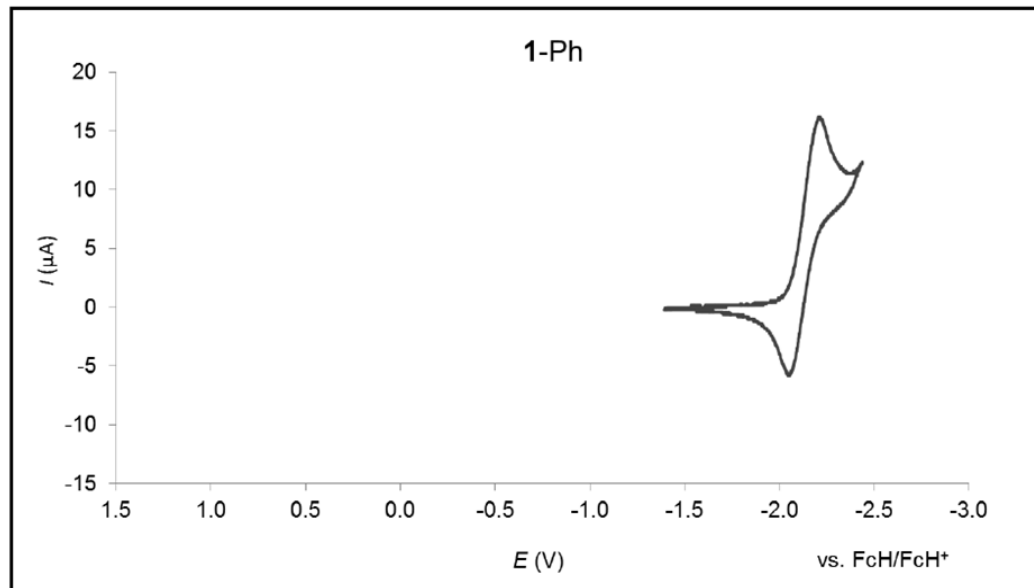


Figure S33: Cyclic voltammogram of **1-Ph** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

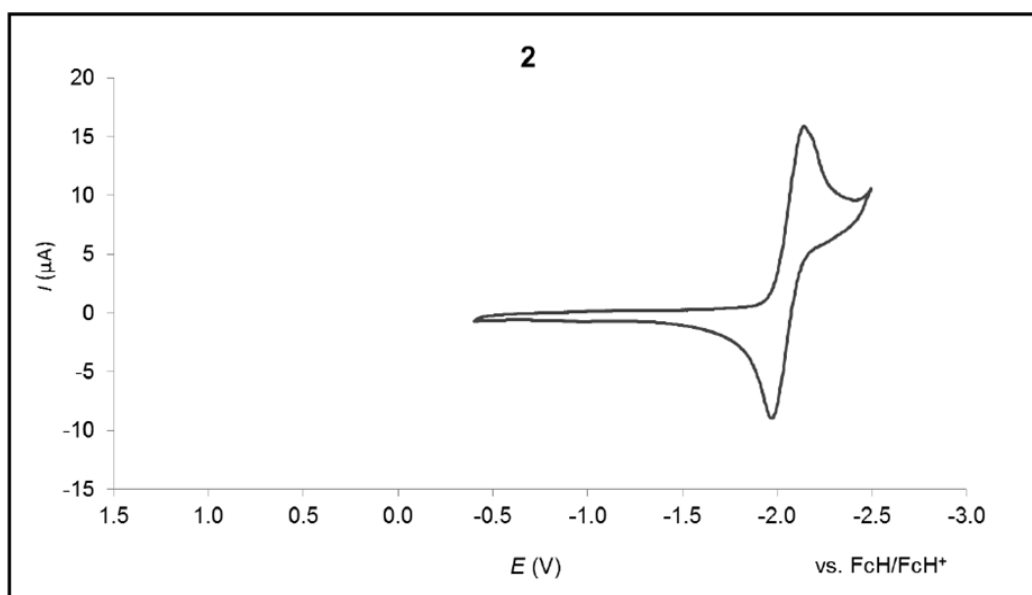


Figure S34: Cyclic voltammogram of **2** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

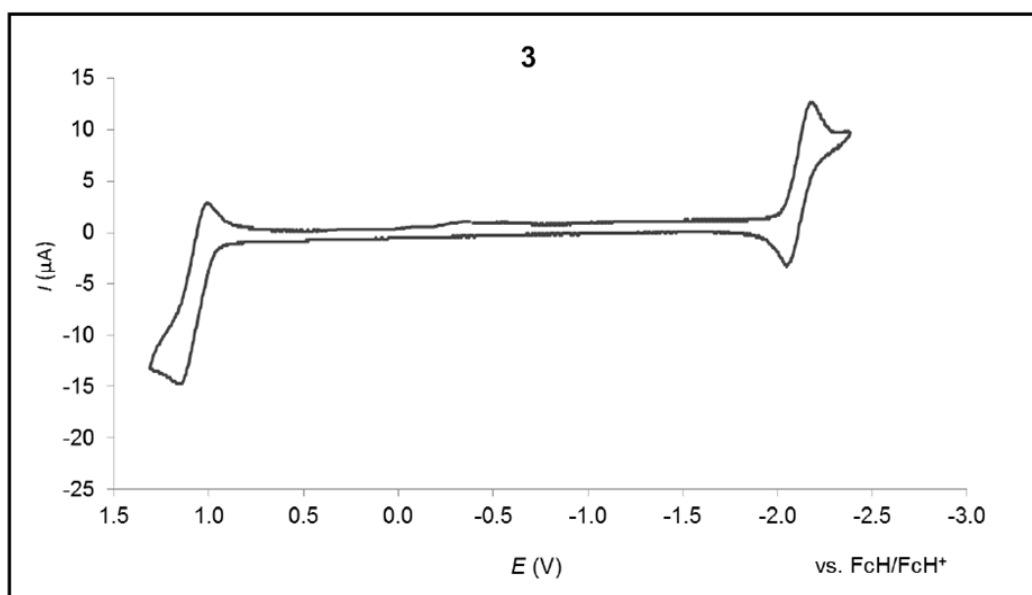


Figure S35: Cyclic voltammogram of **3** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 100 mV s^{-1}).

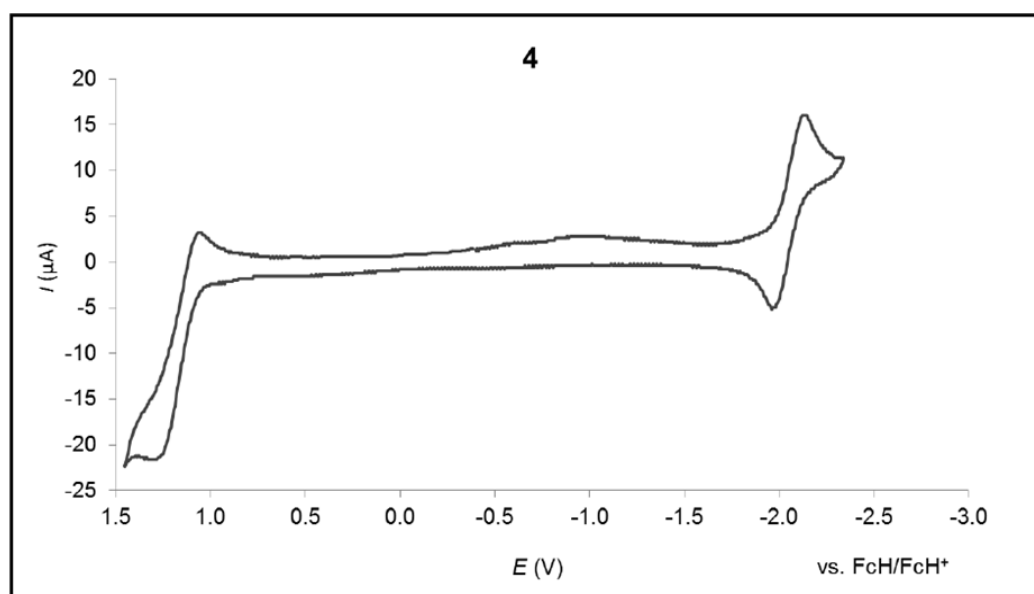


Figure S36: Cyclic voltammogram of **4** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

7. References

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5.1.4 En Route to Stimuli-Responsive Boron-, Nitrogen-, and Sulfur-Doped Polycyclic Aromatic Hydrocarbons

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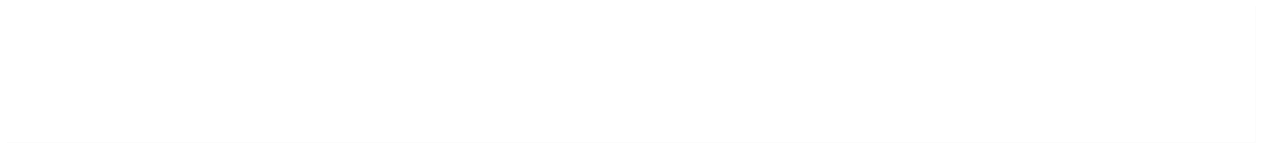






Table of contents:

1. General experimental procedures	S2
2. Nomenclature	S3
3. Additional remarks	S4
4. Syntheses, purification methods and analytical data	S8
5. Plots of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra	S24
6. UV/Vis absorption and emission spectra	S42
7. Plots of cyclic voltammograms	S47
8. X-ray crystal structure analyses	S52
9. References	S63

1. General experimental procedures

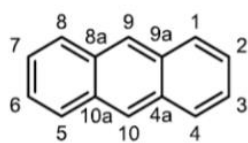
If not stated otherwise, all reactions and manipulations were carried out under an atmosphere of dry nitrogen using Schlenk techniques. C₆H₆, toluene, Et₂O, and THF were distilled from Na/benzophenone prior to use. CH₂Cl₂, Me₃SiCl, and Me₂SiCl₂ were distilled from CaH₂. BBr₃ was stored over Hg to remove traces of HBr and Br₂. The starting materials **1**^[S1], **2**^[S1], **S3**^[S1], and 1-(tri-*n*-butylstannyl)-3,5-bis(trifluoromethyl)benzene^[S2] were synthesized according to previously reported procedures. The procedures applied for the preparation of **S5**^[S3] and **S6**^[S4] differ from the literature protocols and are therefore described in detail.

NMR spectra were recorded at 300 K using a DPX-250, Avance-400, or Avance-500 spectrometer. Chemical shift values are referenced to (residual) solvent signals (¹H/¹³C{¹H}); CDCl₃: δ = 7.26/77.16 ppm, C₆D₆: δ = 7.16/128.08 ppm) or external BF₃·Et₂O (¹¹B{¹H}: 0.00 ppm) and Si(CH₃)₄ (²⁹Si INEPT: 0.00 ppm). Abbreviations: s = singlet, d = doublet, t = triplet, vt = virtual triplet, q = quartet, m = multiplet, br. = broad, n.o. = not observed, n.r. = multiplet expected in the ¹H NMR spectrum but not resolved. Resonances of carbon atoms attached to boron atoms were typically broadened and sometimes not observed due to the quadrupolar relaxation of boron. Boron resonances of triarylborane compounds are typically very broad (*h*_ν > 1500 Hz) and were observed only in highly concentrated samples. Resonance assignments were aided by ¹H-¹³C COSY, ¹H-¹³C HSQC, and in some cases ¹H-¹³C HMBC and ¹H-¹H ROESY NMR spectra.

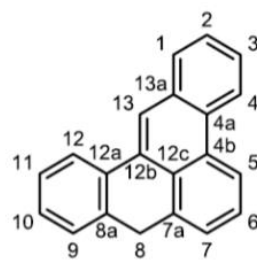
For photochemical reactions, a medium-pressure Hg vapor lamp was used (*Heraeus Noblelight*; TQ 150, 150 W). UV/Vis absorption spectra were recorded at room temperature using a *Varian Cary 50 Scan* UV/Vis spectrophotometer. Photoluminescence (PL) spectra were recorded at room temperature using a *Jasco FP-8300* spectrofluorometer equipped with a calibrated *Jasco ILF-835* 100 mm diameter integrating sphere and analyzed using the *Jasco FWQE-880* software. For PL quantum yield (Φ_{PL}) measurements, each sample was carefully degassed with argon using an injection needle and a septum-capped cuvette. Under these conditions, Φ_{PL} of the fluorescence standard 9,10-diphenylanthracene was determined as 96% (lit.: 97%)^[S5,S6]. For all measurements of Φ_{PL} , at least three samples of different concentrations were used (range between 10⁻⁵ and 10⁻⁷ mol L⁻¹). Due to self-absorption, slightly lower Φ_{PL} values were observed at higher concentrations. This effect was corrected by applying a method reported by *Bardeen et al.*, which slightly improved the Φ_{PL} values (4% at most).^[S7] Cyclic voltammetry (CV) measurements were performed in an inert-atmosphere glovebox at room temperature using a one-chamber, three-electrode cell and an *EG&G Princeton Applied Research 263A* potentiostat. A platinum disk electrode (2.00 mm diameter) was used as the working electrode with a platinum wire counter electrode and a silver wire reference electrode, which was coated with AgCl by immersion into HCl/HNO₃ (3:1). Prior to measurements, the solvent (CH₂Cl₂) was dried as described above and additionally degassed with argon. [*n*-Bu₄N][PF₆] was employed as the supporting electrolyte (0.1 mol L⁻¹). All potential values were referenced against the FcH/FcH⁺ redox couple (FcH = ferrocene; *E*_{1/2} = 0 V). Scan rates were varied between 100 and 400 mV s⁻¹. High-resolution mass spectra were measured in positive mode using a *Thermo Fisher Scientific MALDI LTQ Orbitrap XL* and 2,5-dihydroxybenzoic acid or α-cyano-4-hydroxycinnamic acid as the matrix. Exact masses were calculated based on the predominant combination of natural isotopes. Combustion analyses were performed by the microanalytical laboratory of the *Goethe-University Frankfurt*.

2. Nomenclature

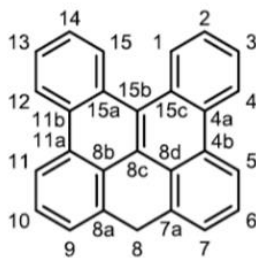
Assignment of NMR signals: The same numbering schemes as for the all-carbon compounds (see below) were employed for their silicon- or boron-doped congeners.



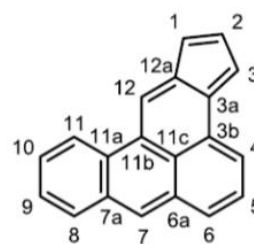
anthracene



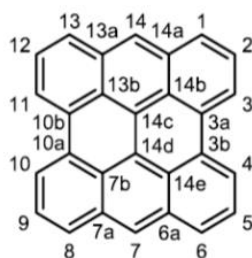
8*H*-benzo[*gh*]tetraphene



8*H*-benzo[*gh*]naphtho[1,2,3,4-*pqr*]tetraphene



indeno[4,5,6-*de*]anthracene



phenanthro[1,10,9,8-*opqra*]perylene

For simplicity reasons, we will refer to phenanthro[1,10,9,8-*opqra*]perylene as bisanthene, which is also a common name for this molecule. In the cases of anthracene-type boranes, boron occupies the position 9.

3. Additional remarks

3.1 Conformations of sterically overcrowded alkenes

Bistricyclic aromatic olefins generally feature distorted molecular structures.^[S8] The distortion is caused by the central rings on each side of the olefinic double bond, which prevent rotational motion of the aryl substituents (cf. **10**, upper half vs. lower half; Figure S1). This leads to steric repulsion between the *peri*-H atoms in compounds such as **13** and **S11**. The latter molecules are therefore referred to as overcrowded alkenes.

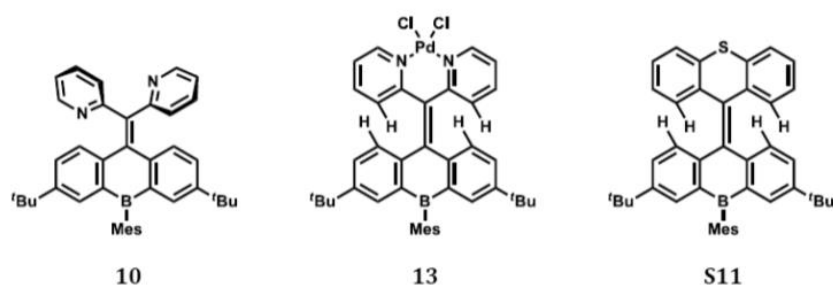


Figure S1: Selected examples of alkenes with conformationally flexible substituents (pyridine groups in **10**) as opposed to overcrowded molecular structures (**13**, **S11**).

On the one hand, the synthesis of tetrasubstituted, sterically encumbered olefins is challenging, on the other hand, the rigid conformation induced by the bridging elements (i.e., B, S, and Pd; Figure S1) preorganizes the molecular structures for subsequent dehydrogenative C–C coupling reactions. Such preorganization tends to increase the reaction rates in stilbene-type photocyclizations.^[S1] Given that only one pyridyl substituent of **10** is incorporated into the planar molecular framework under photocyclization conditions, we decided to transform **10** into the bistricyclic **13** by introduction of a bridging element and to compare the resulting molecular structure with the overcrowded alkene **S11** (which undergoes twofold C–C photocyclization). X-ray crystal structure analysis shows a close match between the solid state structures of **13** (green) and **S11** (black; Figure S2).

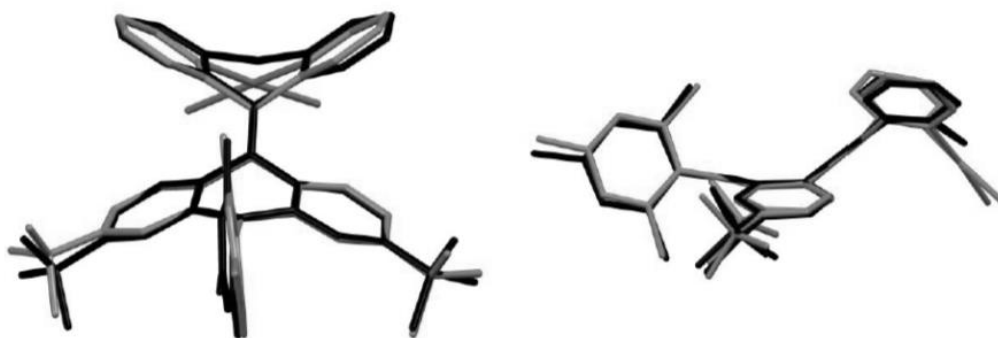


Figure S2: Overlay of the molecular structures of **13** (green) and **S11** (black), as determined by X-ray crystal structure analysis (see chapter 8 for further crystallographic details).

3.2 Syntheses of sulfoxides and sulfones

Oxidation of **8** and **9** with varying amounts of *meta*-chloroperbenzoic acid (*m*CPBA) at room temperature showed a propensity of **8** to give the sulfone **17** and of **9** to give the sulfoxide **16**: According to *in situ* ¹H NMR spectroscopy, the reaction of **8** with one equivalent of *m*CPBA yielded a four-component mixture consisting of benzoic acid, residual **8**, the sulfone **17**, and its corresponding sulfoxide. Upon addition of a second equivalent of *m*CPBA, the resonances assignable to **8** and the sulfoxide vanished. The oxidation of **9**, however, stopped at the stage of the sulfoxide **16**, even when two equivalents of *m*CPBA were used. Both products, **17** and **16**, tend to decompose in the presence of excess *m*CPBA.

The behavior of **8** versus **9** could be specific to these two compounds, or it could be related to the different electronic structures of (benzo)thiophene derivatives (cf. **8**) versus electron-poor diarylsulfides (cf. **9**). To obtain further insight into this matter, we treated benzo[*b*]thiophene on the one hand and 9*H*-thioxanthen-9-one on the other with one equivalent of *m*CPBA (CDCl₃, room temperature). The resulting product mixtures were investigated with respect to the ratios of sulfoxide to sulfone products (see ¹H NMR spectra in Figures S3 and S4). Under the conditions applied, 9*H*-thioxanthen-9-one was mainly converted to its sulfoxide (71%). In contrast, oxidation of benzo[*b*]thiophene gave only 41% of benzo[*b*]thiophene-1-oxide (once *m*CPBA was completely consumed, all product ratios remained stationary).

In conclusion, the behavior of **8** and **9** under oxidizing conditions is qualitatively reflected by their organic model systems benzo[*b*]thiophene and 9*H*-thioxanthen-9-one, respectively. These observations conform with the literature, because thiophene derivatives are known to proceed rapidly from the sulfoxide to the sulfone stage.^[S9]

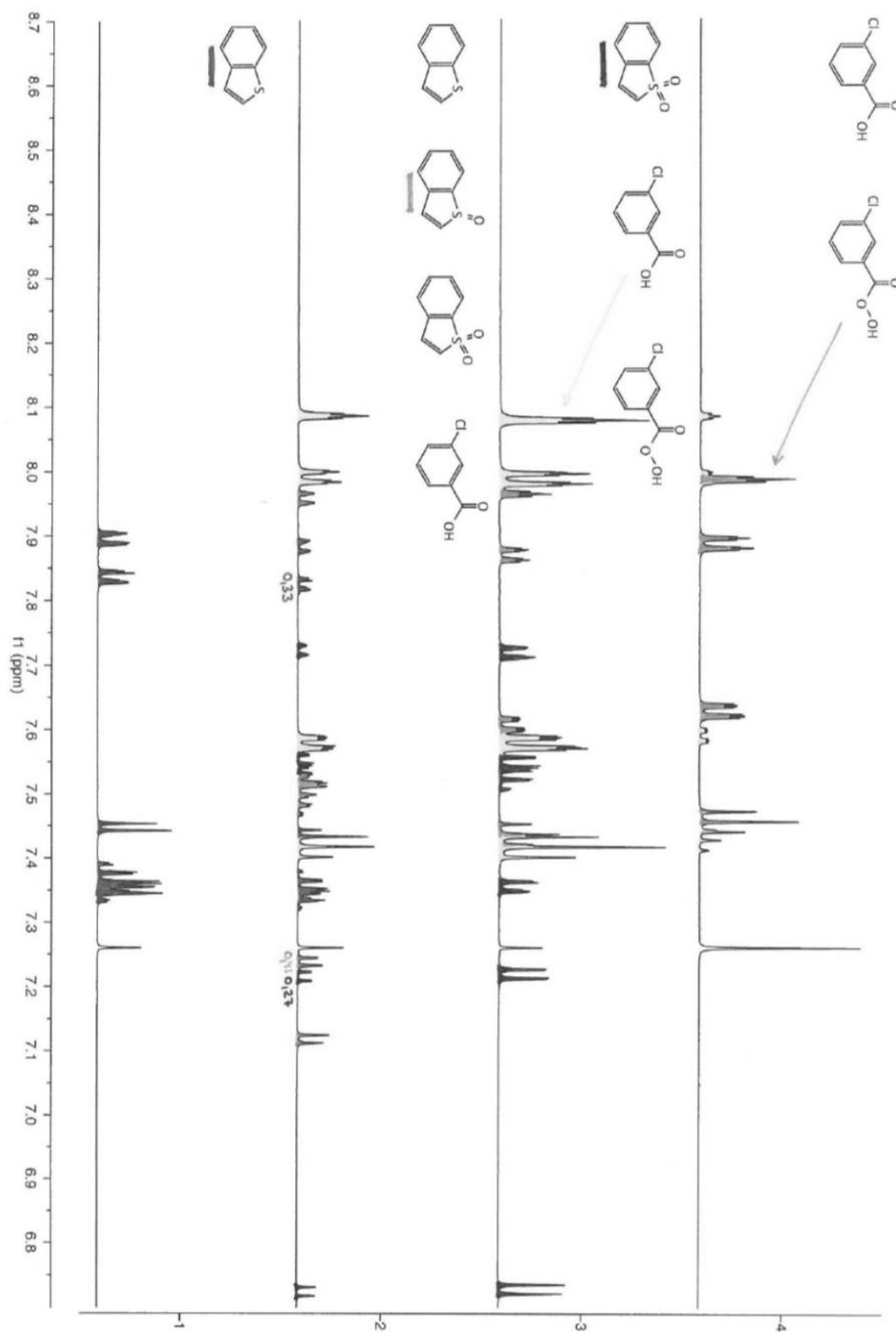


Figure S3: ¹H NMR spectra (500.2 MHz, CDCl₃) of benzo[*b*]thiophene (1), benzo[*b*]thiophene + 1 eq. mCPBA (2), benzo[*b*]thiophene + 3 eq. mCPBA (3), and mCPBA (4, as purchased).

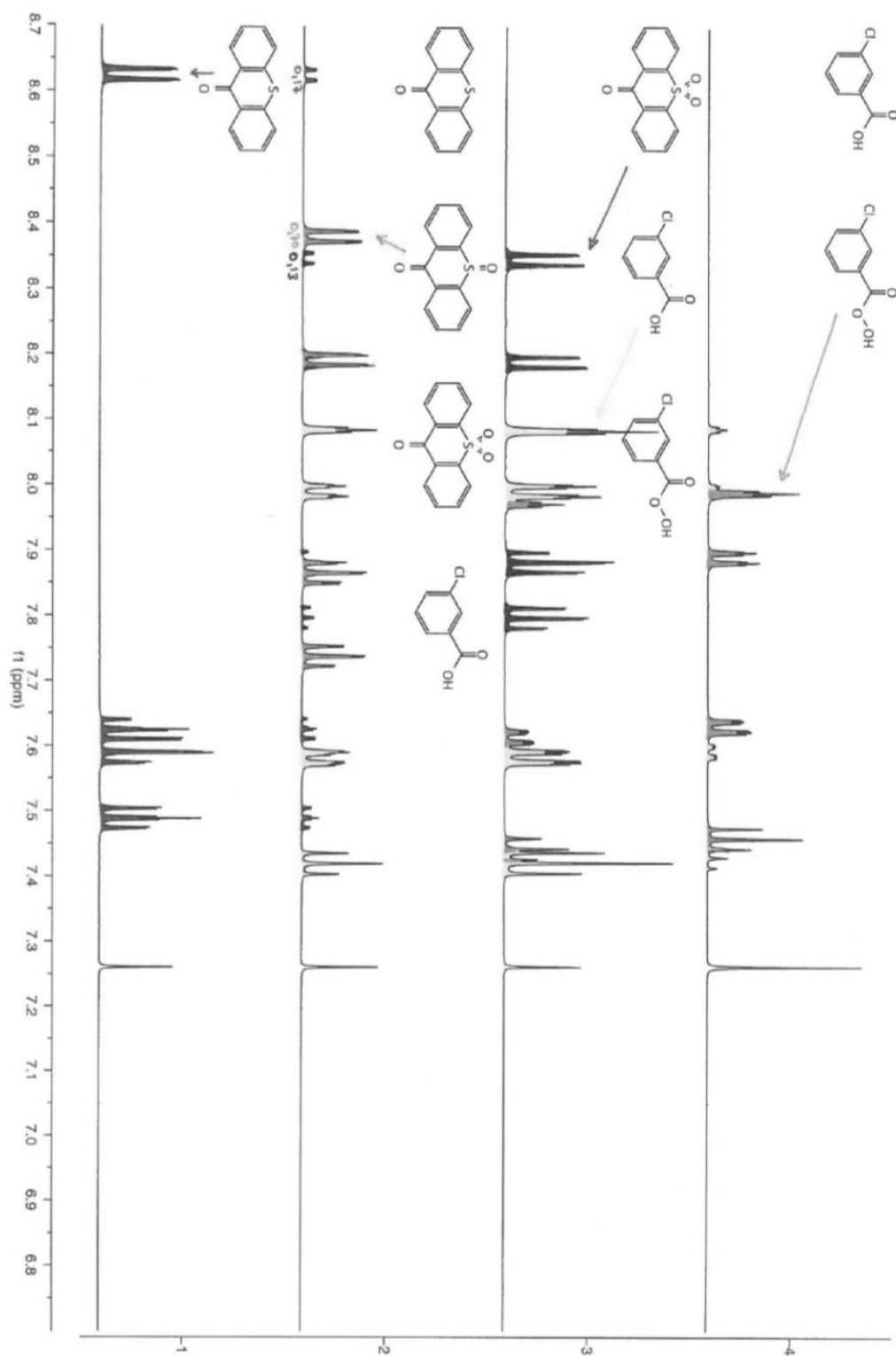
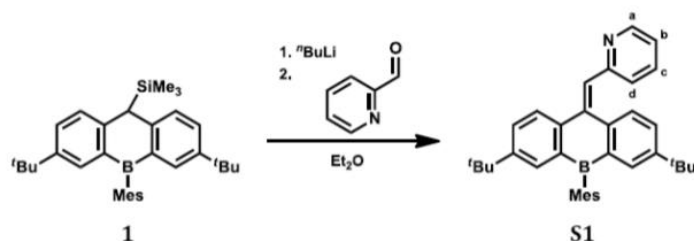


Figure S4: ¹H NMR (500.2 MHz, CDCl₃) spectra of 9H-thioxanthen-9-one (1), 9H-thioxanthen-9-one + 1 eq. mCPBA (2), 9H-thioxanthen-9-one + 3 eq. mCPBA (3), and mCPBA (4, as purchased).

4. Syntheses, purification methods and analytical data



Synthesis of S1: Compound **1** (500 mg, 1.04 mmol) was placed in a 50 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (15 mL). *n*-BuLi in *n*-hexane (1.56 M; 0.70 mL, 1.09 mmol) was added with stirring via a syringe at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 30 min, whereupon its color changed to red. Neat pyridine-2-aldehyde (0.11 mL, 0.12 g, 1.14 mmol) was added at 0 °C via a syringe, whereupon the red color darkened. The mixture was heated to reflux temperature for 30 min. After cooling to room temperature, a saturated aqueous NaHCO₃ solution (20 mL) was added. The aqueous layer was separated and extracted with Et₂O (2 × 30 mL). The combined organic layers were washed with water (50 mL) and brine (20 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (15 cm silica gel, cyclohexane:EtOAc = 5:1, *R_f* = 0.35). After removal of the solvent, **S1** was obtained as a yellow solid. Yield: 310 mg (60%).

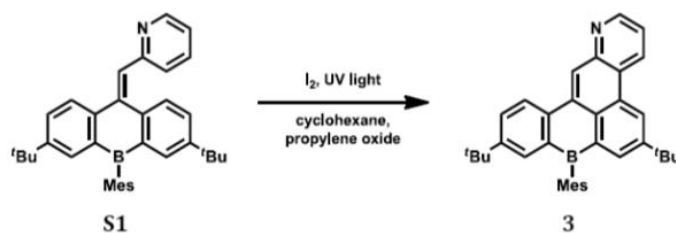
¹H NMR (500.2 MHz, CDCl₃): δ 8.70 (m, 1H; Py-H-a), 8.06 (d, ³*J*_{HH} = 8.2 Hz, 1H; H-4 or 5), 7.64 (m, 2H; H-1,8), 7.61 (dd, ³*J*_{HH} = 8.2 Hz, ⁴*J*_{HH} = 2.3 Hz, 1H; H-3 or 6), 7.46 (ddd, ³*J*_{HH} = 7.8 Hz, ³*J*_{HH} = 7.8 Hz, ⁴*J*_{HH} = 1.8 Hz, 1H; Py-H-c), 7.43 (s, 1H; ArCH=), 7.39 (d, ³*J*_{HH} = 8.3 Hz, 1H; H-4 or 5), 7.17 (dd, ³*J*_{HH} = 8.3 Hz, ⁴*J*_{HH} = 2.3 Hz, 1H; H-3 or 6), 7.15 (d, ³*J*_{HH} = 7.8 Hz, 1H; Py-H-d), 7.13 (m, 1H; Py-H-b), 6.92 (s, 2H, Mes-CH-*m*), 2.40 (s, 3H; Mes-CH₃-*p*), 2.05 (s, 6H; Mes-CH₃-*o*), 1.26 (s, 9H; *t*-Bu-CH₃), 1.20 (s, 9H; *t*-Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 158.4, 150.6, 150.0, 149.9 (Py-C-a), 144.7, 141.7, 139.7, 138.1, 136.5, 135.8 (Py-C-c), 134.2 (C-1 or 8), 133.9 (C-1 or 8), 130.4 (PyCH=), 130.1 (C-3 or 6), 129.5 (C-4 or 5), 128.1 (C-3 or 6), 127.0 (Mes-CH-*m*), 125.6 (Py-C-d), 123.6 (C-4 or 5), 121.6 (Py-C-b), 34.7 (*t*-Bu-C), 34.6 (*t*-Bu-C), 31.4 (*t*-Bu-CH₃), 31.3 (*t*-Bu-CH₃), 22.9 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*), n.o. (C-B)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): n.o.

EA (%): Calculated for C₃₆H₄₀BN [497.52]: C 86.91, H 8.10, N 2.82; found: C 86.84, H 8.48, N 2.42

HRMS: Calculated for C₃₆H₄₀BN: 498.33328, found: 498.33238



Synthesis of 3: A solution of **S1** (0.174 g, 0.350 mmol) in cyclohexane (800 mL) was prepared in a 1 L photoreactor, equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (5 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 5 h during which time neat I₂ (0.13 g, 0.51 mmol) was added in several portions. A brown, turbid mixture was obtained and the solvent was evaporated under reduced pressure. The crude product was dissolved in *n*-hexane (30 mL) and filtered to remove insoluble side products. The filtrate was

evaporated to dryness, suspended in MeOH (10 mL), sonicated, cooled to 8 °C, collected by filtration while still cold, and washed with cold MeOH (5 mL) to obtain a yellow solid. Yield: 0.100 g (58%). Single crystals were grown by layering a solution of **3** (50 mg) in C₆H₆ (0.5 mL) with MeOH (3 mL) and storing the vessel at 8 °C for 3 d. Traces of MeOH remained in the product even after drying in an oil-pump vacuum for 8 h.

¹H NMR (500.2 MHz, CDCl₃): δ 9.21 (s, 1H; H-13), 9.10 (br. d, ³J_{HH} = 8.3 Hz, 1H; H-4), 9.06 (dd, ³J_{HH} = 4.3 Hz, ⁴J_{HH} = 1.5 Hz, 1H; H-2), 9.02 (d, ³J_{HH} = 2.1 Hz, 1H; H-5), 8.70 (d, ³J_{HH} = 8.2 Hz, 1H; H-12), 8.29 (d, ⁴J_{HH} = 2.1 Hz, 1H; H-7), 7.88-7.85 (m, 2H; H-9 and 11), 7.64 (dd, ³J_{HH} = 8.3 Hz, ³J_{HH} = 4.3 Hz, 1H; H-3), 6.95 (s, 2H; Mes-CH-*m*), 2.44 (s, 3H; Mes-CH₃-*p*), 2.01 (s, 6H; Mes-CH₃-*o*), 1.46 (s, 9H; *t*-Bu-CH₃ at C-6), 1.33 (s, 9H; *t*-Bu-CH₃ at C-10)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 150.8 (C-10), 150.3 (C-2), 149.6 (C-6), 148.4 (C-13a), 134.0 (Mes-C-*i*), 139.2 (C-7), 138.9 (C-12a), 138.7 (Mes-C-*o*), 136.8 (C-8a), 136.7 (Mes-C-*p*), 135.2 (C-9), 135.1 (C-7a), 134.6 (C-12b), 131.1 (C-11), 130.6 (C-4), 129.9 (C-12c), 129.0 (C-4b), 127.1 (Mes-CH-*m*), 126.8 (C-13), 126.4 (C-4a), 124.9 (C-5), 124.3 (C-12), 121.9 (C-3), 35.3 (*t*-Bu-C at C-6), 34.8 (*t*-Bu-C at C-6), 31.5 (*t*-Bu-CH₃ at C-6), 31.4(*t*-Bu-CH₃ at C-10), 23.4 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 66 (*h*_ν ≈ 1500 Hz)

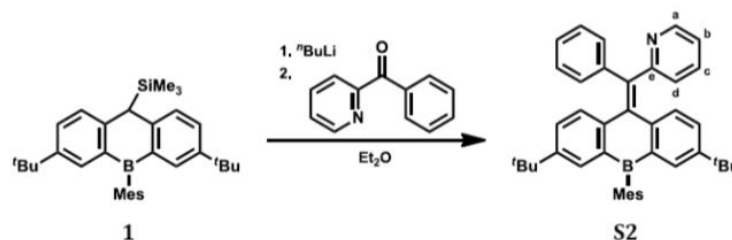
EA (%): Calculated for C₃₆H₃₈BN [495.50]: C 87.26, H 7.73, N 2.83; found: C 86.42, H 7.76, N 2.76

HRMS: Calculated for C₃₆H₃₈BN: 496.31763, found: 496.31749

UV/Vis (cyclohexane): λ_{max} (ε) = 378 (12500), 397 nm (14400 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, λ_{ex} = 370 nm, 25 °C): λ_{max} = 412, 432 nm; Φ_{PL} = 73%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = -2.03 V



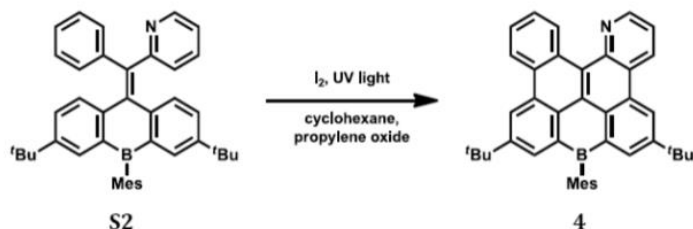
Synthesis of S2: Compound **1** (500 mg, 1.04 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (30 mL). *n*-BuLi in *n*-hexane (1.56 M; 0.67 mL, 1.04 mmol) was added with stirring via a syringe at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 30 min, whereupon its color changed to red. Neat phenyl(pyridine-2-yl)methanone (0.210 g, 1.14 mmol) was added at 0 °C, whereupon the color changed to blue. The mixture was heated to reflux temperature for 1 h. After cooling to room temperature, a saturated aqueous NaHCO₃ solution (30 mL) was added. The aqueous layer was separated and extracted with Et₂O (30 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (15 cm silica gel, cyclohexane:EtOAc = 15:1, R_f = 0.24). Only fractions containing exclusively **S2** (determined by TLC) were combined. After freeze-drying with cyclohexane (10 mL), the product (480 mg) still contained residual cyclohexane (approx. 0.5 equivalents according to ¹H NMR spectroscopy). Estimated yield: 75%.

¹H NMR (500.2 MHz, CDCl₃): δ 8.76 (br. d, ³J_{HH} = 4.9 Hz, 1H; Py-H-a), 7.56 (dd, ³J_{HH} = 5.5 Hz, ⁴J_{HH} = 2.1 Hz, 2H), 7.41 (m, 2H), 7.36 (ddd, ³J_{HH} = 7.7 Hz, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.7 Hz, 1H), 7.21-7.18 (m, 2H), 7.16-7.13 (m, 2H), 7.09 (m, 1H), 7.04 (dd, ³J_{HH} = 8.3 Hz, ⁴J_{HH} = 2.3 Hz, 1H), 6.99 (dd, ³J_{HH} = 8.3 Hz, ⁴J_{HH} = 2.2 Hz, 1H), 6.97-6.95 (m, 3H), 6.73 (d, ³J_{HH} = 7.8 Hz, 1H), 2.42 (s, 3H; Mes-CH₃-*p*), 2.18 (s, 6H; Mes-CH₃-*o*), 1.17 (s, 9H; *t*-Bu-CH₃), 1.16 (s, 9H; *t*-Bu-CH₃)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 162.3 (C-e), 149.0 (C-a), 149.0, 143.2, 142.8, 142.0, 140.8, 140.1 (Mes-C-i), 139.5, 138.7, 138.4, 137.6 (Mes-C-o), 136.7, 136.5 (Mes-C-p), 132.9, 132.7, 130.3, 129.8, 128.6, 128.1, 127.7, 127.5, 127.1 (Mes-CH-m), 126.7, 124.9, 121.5, 34.5 (*t*-Bu-C), 34.5 (*t*-Bu-C), 31.3 (*t*-Bu- CH_3), 31.3 (*t*-Bu- CH_3), 22.7 (Mes- CH_3 -o), 21.5 (Mes- CH_3 -p)

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.5 MHz, CDCl_3): δ 68 ($h_{1/2} \approx 1500$ Hz)

EA (%): Calculated for $\text{C}_{42}\text{H}_{44}\text{BN}$ [573.62]: C 87.94, H 7.73, N 2.44; found: C 87.76, H 8.13, N 2.06



Synthesis of 4: A solution of **S2** (0.230 g, 0.401 mmol) in cyclohexane (800 mL) was prepared in a 1 L photoreactor, equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (10 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 5 h during which time neat I_2 (0.25 g, 0.98 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I_2 and the eluate was evaporated to dryness under reduced pressure. The yellow solid (190 mg) contained a side product, which was identified as **4** iodinated at one *m*-position of the mesityl ring (ca. 15%). This impurity was removed by applying the following procedure: The crude product was placed in a round-bottom Schlenk flask and dissolved in THF (20 mL). A solution of *t*-BuLi (1.7 M; 0.2 mL, 0.34 mmol) in *n*-hexane was added at -78 °C. The mixture, which immediately adopted a red color, was stirred for 1 h at this temperature. *i*-PrOH (0.5 mL) was added at -78 °C and the dark solution was stirred for 10 min. A saturated aqueous solution of NaHCO_3 (10 mL), H_2O (10 mL), and Et_2O (40 mL) were added. The partly solid mixture was warmed to room temperature, whereupon it liquefied again. After stirring for 30 min, the red-colored organic layer was separated, washed with brine (40 mL), dried over MgSO_4 , and filtered. All volatiles were removed from the filtrate under reduced pressure. Further purification was achieved by column chromatography (30 cm silica gel, cyclohexane:EtOAc = 15:1, R_f = 0.33) to afford a yellow solid. Yield: 0.129 mg (56%). Single crystals were grown by layering a solution of **4** in CHCl_3 (15 mg mL^{-1}) with CH_3CN and storing the vessel at 8 °C for 3 d.

^1H NMR (500.2 MHz, CDCl_3): δ 10.12 (m, 1H; H-15), 9.25-9.23 (m, 2H; H-4 and 5 or 11), 9.20 (dd, $^3J_{\text{HH}} = 4.2$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, 1H; H-2), 9.10 (d, $^4J_{\text{HH}} = 2.1$ Hz, 1H; H-5 or 11), 8.95 (m, 1H; H-12), 8.41 (d, $^4J_{\text{HH}} = 2.1$ Hz, 1H; H-7 or 9), 8.38 (d, $^4J_{\text{HH}} = 2.1$ Hz, 1H; H-7 or 9), 7.83-7.78 (m, 2H; H-13,14), 7.73 (dd, $^3J_{\text{HH}} = 8.26$ Hz, $^3J_{\text{HH}} = 4.2$ Hz, 1H; H-3), 7.00 (s, 2H; Mes-CH-m), 2.47 (s, 3H; Mes- CH_3 -p), 2.04 (s, 6H; Mes- CH_3 -o), 1.51 (s, 9H; *t*-Bu- CH_3), 1.50 (s, 9H; *t*-Bu- CH_3)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 149.8 (C-6 or 10), 149.4 (C-6 or 10), 148.0 (C-2), 147.3 (C-15c), 140.3 (Mes-C-i), 139.1 (C-7 or 9), 139.0 (Mes-C-o), 138.4 (C-7 or 9), 136.7 (Mes-C-p), 135.8 (C-7a), 135.8 (C-8a), 132.3 (C-15), 132.0, 131.1 (C-4), 130.2, 130.1, 129.9, 129.8, 129.5, 128.2, 128.1, 127.4 (C-13), 127.1 (Mes-CH-m), 126.6, 126.4 (C-14), 125.5 (C-5 or 11), 124.8 (C-5 or 11), 122.7 (C-12), 121.6 (C-3), 35.3 (*t*-Bu-C), 35.3 (*t*-Bu-C), 31.6 (*t*-Bu- CH_3), 31.6 (*t*-Bu- CH_3), 23.7 (Mes- CH_3 -o), 21.6 (Mes- CH_3 -p)

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.5 MHz, CDCl_3): δ 65 ($h_{1/2} \approx 1500$ Hz)

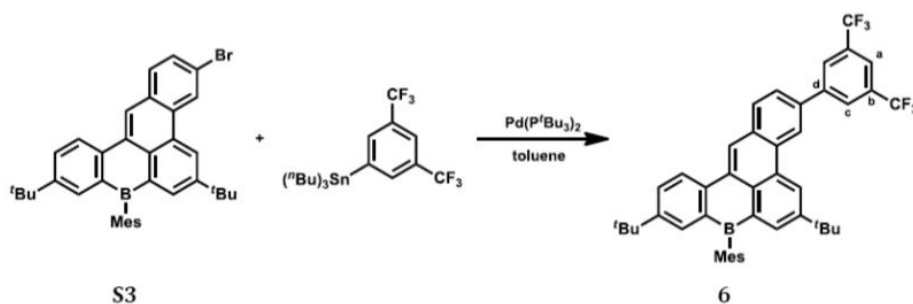
EA (%): Calculated for $\text{C}_{42}\text{H}_{40}\text{BN}$ [569.58]: C 88.56, H 7.08, N 2.46; found: C 88.26, H 7.10, N 2.18

HRMS: Calculated for $\text{C}_{42}\text{H}_{40}\text{BN}$: 570.33266, found: 570.33194

UV/Vis (cyclohexane): λ_{max} (ϵ) = 352 (11500), 399 (18800), 419 nm (28400 $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$)

Fluorescence (cyclohexane, $\lambda_{\text{ex}} = 390$ nm, 25 °C): $\lambda_{\text{max}} = 431, 454$ nm; $\Phi_{\text{PL}} = 60\%$

Cyclic voltammetry (CH_2Cl_2 , [*n*Bu₄N][PF₆] 0.1 M, 100 mV s^{-1} , vs. FcH/FcH⁺): $E_{1/2} = -1.95$ V



Synthesis of 6: Compound **S3** (60 mg, 100 μ mol), 1-(tri-*n*-butylstannyl)-3,5-bis(trifluoromethyl)benzene (80 mg, 158 μ mol), and (*t*-Bu₃P)₂Pd were placed in a small Schlenk tube. Toluene (1.5 mL) was added and the solution was degassed with Ar for 5 min using a cannula. The solution was heated in an oil bath at 100 °C for 40 h. After the mixture had cooled to room temperature again, the solvent was removed under reduced pressure and the residue was purified by column chromatography (25 cm silica gel). The first fraction was eluted with cyclohexane and contained residual **S3**. The highly fluorescent second fraction was eluted with cyclohexane:EtOAc = 25:1 and contained **6** (*R*_f = 0.39). The solvent was removed from the second fraction under reduced pressure to obtain a yellow-green solid. Yield: 36 mg (49%)

¹H NMR (500.2 MHz, CDCl₃): δ 9.14 (n.r., 1H; H-5), 8.99 (s, 1H; H-13), 8.94 (n.r., 1H; H-4), 8.65 (d, ³*J*_{H,H} = 8.5 Hz, 1H; H-12), 8.30 (n.r., 1H; H-7), 8.25 (d, ³*J*_{H,H} = 8.0 Hz, 1H; H-1), 8.24 (n.r., 2H; H-c), 7.96 (n.r., 1H; H-a), 7.89 (n.r., 1H; H-9), 7.88 (dd, ³*J*_{H,H} = 8.0 Hz, ⁴*J*_{H,H} = 1.6 Hz, 1H; H-2), 7.85 (dd, ³*J*_{H,H} = 8.5 Hz, ⁴*J*_{H,H} = 2.1 Hz, 1H; H-11), 6.96 (s, 2H; Mes-CH-*m*), 2.45 (s, 3H; Mes-CH₃-*p*), 2.02 (s, 6H; Mes-CH₃-*o*), 1.48 (s, 9H; *t*-Bu-CH₃), 1.34 (s, 9H; *t*-Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 150.3 (C-10), 149.4 (C-6), 144.0 (C-13a), 140.1 (Mes-C-*i*), 139.1 (C-7), 139.1 (C-12a), 138.7 (Mes-C-*o*), 137.2 (C-3), 136.7 (C-8a), 136.6 (Mes-C-*p*), 135.2 (C-9), 135.2 (C-7a), 132.5 (q, ²*J*_{C,F} = 33.2 Hz; C-b) 132.1 (C-d), 131.8 (C-12b), 131.6 (C-4a), 131.0 (C-1), 130.8 (C-11), 130.5 (C-12c), 129.5 (C-4b), 127.9 (C-c), 127.1 (Mes-CH-*m*), 125.9 (C-2), 125.4 (C-13), 124.9 (C-5), 123.7 (C-12), 123.6 (q, ¹*J*_{C,F} = 272.8 Hz; CF₃), 121.5 (C-4), 121.3 (m, C-a), 35.3 (*t*-Bu-C at C-6), 34.7 (*t*-Bu-C at C-10), 31.6 (*t*-Bu-CH₃ at C-6), 31.4 (*t*-Bu-CH₃ at C-10), 23.4 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 65 (*h*₂ ≈ 1500 Hz)

¹⁹F NMR (470.6 MHz, CDCl₃): δ -62.7 (s)

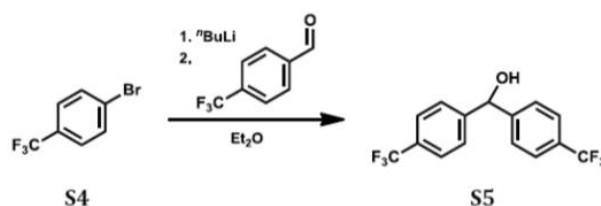
EA (%): Calculated for C₄₅H₄₁BF₆ [706.61]: C 76.49, H 5.85; found: C 76.08, H 6.11

HRMS: Calculated for C₄₅H₄₁BF₆: 706.32077, found: 706.32059

UV/Vis (cyclohexane): λ _{max} (ϵ) = 391 (25200), 413 nm (38200 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, λ _{ex} = 370 nm, 25 °C): λ _{max} = 428, 451 nm; Φ _{PL} = 89%

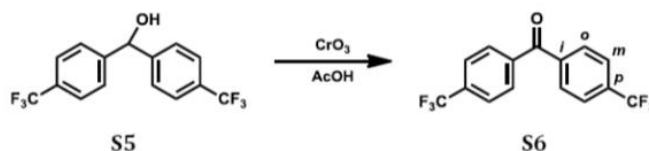
Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): *E*_{1/2} = -2.05, 1.11 V



Synthesis of S5: Compound **S4** (6.79 mL, 11.0 g, 48.9 mmol) was placed in a 250 mL Schlenk flask equipped with a dropping funnel and dissolved in Et₂O (100 mL). The solution was cooled to -78 °C and *n*-BuLi in *n*-hexane (1.56 M; 31.5 mL, 49.1 mmol) was added dropwise over 10 min. The solution turned orange and was stirred for 1 h at this temperature. A solution of 4-(trifluoromethyl)benzaldehyde (6.6 mL, 8.5 g, 49 mmol) in Et₂O (10 mL) was added dropwise at -78 °C over a period of 10 min. The reaction mixture turned red

and was stirred for 3 h before it was allowed to warm to room temperature. A saturated aqueous NaHCO₃ solution (150 mL) was added. The aqueous layer was separated and extracted with Et₂O (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The product was obtained as a colorless solid and sufficiently pure for subsequent oxidation to S5. Yield: 15.7 g (quantitative)

¹H NMR (400.1 MHz, CDCl₃): δ 7.62 (d, ³J_{HH} = 8.2 Hz, 4H), 7.50 (d, ³J_{HH} = 8.2 Hz, 4H), 5.95 (d, ³J_{HH} = 3.3 Hz, 1H), 2.34 (d, ³J_{HH} = 3.3 Hz, 1H)

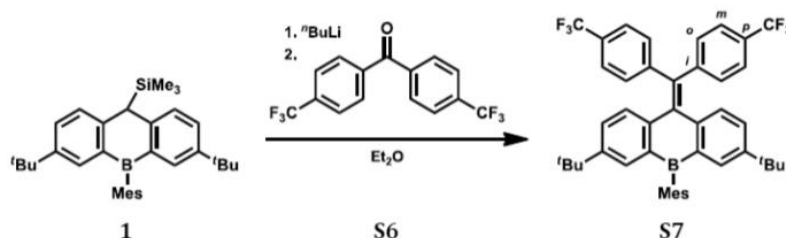


Synthesis of S6: A solution of S5 (5.00 g, 15.6 mmol) in glacial acetic acid (20 mL) was prepared under ambient atmosphere in a 100 ml round-bottom flask equipped with a condenser. Freshly powdered CrO₃ (1.7 g, 17 mmol) was added at room temperature and the resulting dark colored mixture was heated with stirring at 70 °C. After 2 h, TLC indicated complete conversion (cyclohexane:EtOAc = 10:1, R_f = 0.54). The mixture was diluted with H₂O (150 mL) and extracted with *n*-hexane (3 × 75 mL). The combined colorless extracts were washed with several portions of aqueous NaOH (2 M) until the washings remained basic, dried over MgSO₄, and filtered. The solvent was removed under reduced pressure to afford S6 as a colorless solid, which was pure by ¹H NMR (yield: 4.70 g; 95%). The product was nevertheless purified further by recrystallization from *n*-hexane prior to the subsequent reaction.

¹H NMR (250.1 MHz, CDCl₃): δ 7.88 (d, ³J_{HH} = 8.2 Hz, 4H), 7.75 (d, ³J_{HH} = 8.2 Hz, 4H)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 194.5 (C=O), 139.9 (Ar-C-*i*), 134.5 (q, ²J_{CF} = 32.8 Hz; Ar-C-*p*), 130.4 (Ar-C-*o*), 125.8 (q, ³J_{CF} = 3.7 Hz; Ar-C-*m*), 123.7 (q, ¹J_{CF} = 272.8 Hz; CF₃)

¹⁹F NMR (470.6 MHz, CDCl₃): δ -63.1 (s)



Synthesis of S7: Compound 1 (500 mg, 1.04 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (40 mL). *n*-BuLi in *n*-hexane (1.56 M; 0.68 mL, 1.06 mmol) was added with stirring via a syringe at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 30 min, whereupon its color changed to red. Neat S6 (364 mg, 1.14 mmol) was added at 0 °C. The mixture was again heated to reflux temperature for 1 h. After cooling to room temperature, a saturated aqueous NaHCO₃ solution (50 mL) was added. The aqueous layer was separated and extracted with Et₂O (2 × 40 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was suspended in methanol (30 mL), sonicated, collected by filtration and dried in vacuo to obtain S7 as a yellow powder. Yield: 549 mg (74%)

¹H NMR (500.2 MHz, CDCl₃): δ 7.57 (d, ⁴J_{HH} = 1.6 Hz, 2H; H-1,8), 7.49 (d, ³J_{HH} = 8.1 Hz, 2H; Ar-CH-*m*), 7.34 (d, ³J_{HH} = 8.1 Hz, 2H; Ar-CH-*o*), 7.05-7.00 (m, 4H; H-3,4,5,6), 6.95 (s, 2H; Mes-CH-*m*), 2.42 (s, 3H; Mes-CH₃-*p*), 2.16 (s, 6H; Mes-CH₃-*o*), 1.17 (s, 18H; *t*-Bu-CH₃)

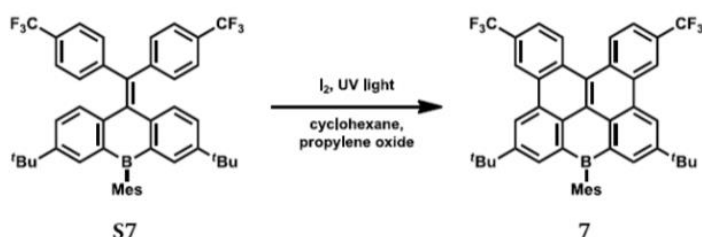
¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 149.6 (C-2,7), 147.1 (Ar-C-*i*), 142.4 (C-4a,10a), 140.8 (C-10), 139.7 (Mes-C-*i*), 139.0 (Ar₂C=), 138.6 (C-8a,9a), 137.5 (Mes-C-*o*), 136.7 (Mes-C-*p*), 133.2 (C-1,8), 130.3 (Ar-C-*o*), 129.1 (C-4,5), 128.9 (q, ²J_{HF} = 32.5 Hz; Ar-C-*p*) 127.9 (C-3,6), 127.2 (Mes-CH-*m*), 125.5 (q, ³J_{HF} = 3.7 Hz; Ar-C-*m*), 124.2 (q, ¹J_{HF} = 272.0 Hz; CF₃), 34.5 (*t*-Bu-C), 31.3 (*t*-Bu-CH₃), 22.7 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): n.o.

¹⁹F NMR (470.6 MHz, CDCl₃): δ -63.1 (s)

EA (%): Calculated for C₄₅H₄₃BF₆ [708.62]: C 76.27, H 6.12; found: C 76.05, H 5.89

HRMS: Calculated for C₄₅H₄₃BF₆: 708.33642, found: 708.33589



Synthesis of 7: A solution of **S7** (0.500 g, 0.706 mmol) in cyclohexane (800 mL) was prepared in a 1 L photoreactor, equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (10 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 6 h during which time neat I₂ (0.43 g, 1.7 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I₂ and the eluate was evaporated to dryness under reduced pressure. The yellow solid (0.464 g) contained a side product, which was identified as **7** iodinated at one *m*-position of the mesityl ring (ca. 25%). This impurity was removed by applying the following procedure: The crude product was placed in a round-bottom Schlenk flask and dissolved in THF (40 mL). A solution of *t*-BuLi (1.7 M; 0.20 mL, 0.34 mmol) in *n*-hexane was added at -78 °C and the mixture, which immediately adopted a violet color, was stirred for 20 min. *i*-PrOH (1 mL) was added at -78 °C and the dark solution was stirred for 10 min. A saturated aqueous solution of NaHCO₃ (20 mL), H₂O (20 mL) and Et₂O (20 mL) were added. The partly solid mixture was warmed to room temperature, whereupon it liquefied again. After the color of the mixture had changed to yellow, the aqueous phase was separated and extracted with Et₂O (20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. Further purification was achieved by column chromatography (8 cm silica gel, cyclohexane, *R_f* = 0.17) to afford a yellow solid. Yield: 0.327 g (66%)

¹H NMR (500.2 MHz, CDCl₃): δ 9.13 (m, 4H; H-4,5,11,12), 8.93 (d, ³J_{HH} = 8.7 Hz, 2H; H-1,15), 8.42 (d, ⁴J_{HH} = 2.1 Hz, 2H; H-7,9), 7.89 (dd, ³J_{HH} = 8.7 Hz, ⁴J_{HH} = n.r., 2H; H-2,14), 7.01 (s, 2H; Mes-CH-*m*), 2.47 (s, 3H; Mes-CH₃-*p*), 2.03 (s, 6H; Mes-CH₃-*o*), 1.53 (s, 18H; *t*-Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 150.7 (C-6,10), 139.7 (Mes-C-*i*), 139.4 (C-7,9), 138.9 (Mes-C-*o*), 137.0 (Mes-C-*p*), 135.7 (C-7a,8a), 131.5, 131.4, 130.6 (C-1,15), 130.2 (C-8b,8d), 129.0, 128.9 (q, ²J_{CF} = 32.4 Hz; C-3,13), 128.5, 127.8, 127.2 (Mes-CH-*m*), 125.1 (C-5,11), 124.6 (q, ¹J_{CF} = 272.3 Hz; CF₃), 122.0 (q, ³J_{CF} = 3.3 Hz; C-2,14), 121.0 (q, ³J_{CF} = 4.2 Hz; C-4,12), 35.4 (*t*-Bu-C), 31.6 (*t*-Bu-CH₃), 23.7 (Mes-CH₃-*o*), 21.6 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 65 (*h*_ν ≈ 1500 Hz)

¹⁹F NMR (470.6 MHz, CDCl₃): δ -61.9 (s)

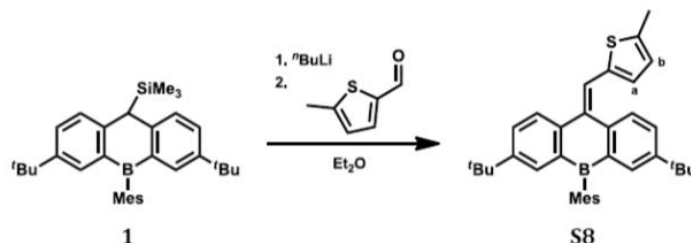
EA (%): Calculated for C₄₅H₃₉BF₆ [704.59]: C 76.71, H 5.58; found: C 76.64, H 5.57

HRMS: Calculated for $C_{45}H_{39}BF_6$: 704.30512, found: 704.30450

UV/Vis (cyclohexane): λ_{max} (ϵ) = 331 (20800), 348 (10600), 392 (20500), 414 nm (36000 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, λ_{ex} = 390 nm, 25 °C): λ_{max} = 425, 448 nm; Φ_{PL} = 60%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 400 mV s⁻¹, vs. FcH/FcH⁺): $E_{1/2}$ = -1.86 V



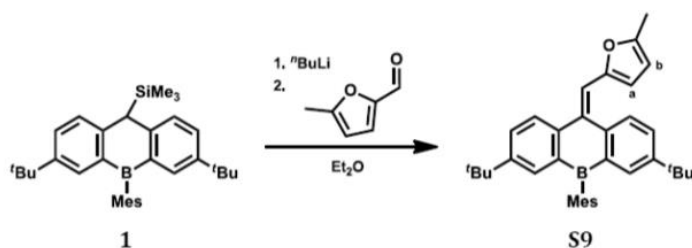
Synthesis of S8: Compound **1** (500 mg, 1.04 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (20 mL). *n*-BuLi in *n*-hexane (1.56 M; 0.67 mL, 1.04 mmol) was added with stirring via a syringe at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 30 min, whereupon its color changed to red. Neat 5-methylthiophene-2-aldehyde (0.12 mL, 0.13 g, 1.1 mmol) was added at 0 °C via a syringe, whereupon the red color of the lithiated **1** vanished. The mixture was heated to reflux temperature for 1 h. After cooling to room temperature, a saturated aqueous NaHCO₃ solution (30 mL) was added. The aqueous layer was separated and extracted with Et₂O (20 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (15 cm silica gel, cyclohexane:EtOAc = 100:1, R_f = 0.45). Only fractions containing exclusively **S8** (determined by TLC) were combined. The product was freeze-dried with cyclohexane (15 mL) to obtain a yellow solid. Yield: 465 mg (87%).

¹H NMR (500.2 MHz, CDCl₃): δ 8.20 (d, $^3J_{HH}$ = 8.2 Hz, 1H; H-4 or 5), 7.90 (d, $^3J_{HH}$ = 8.3 Hz, 1H; H-4 or 5), 7.64 (d, $^4J_{HH}$ = 2.3 Hz, 1H; H-1 or 8), 7.60 (d, $^4J_{HH}$ = 2.3 Hz, 1H; H-1 or 8), 7.57 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.3 Hz, 1H; H-3 or 6), 7.41 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.3 Hz, 1H; H-3 or 6), 7.29 (s, 1H; ThCH=), 6.99 (d, $^3J_{HH}$ = 3.6 Hz, 1H; Th-CH-a), 6.90 (s, 2H; Mes-CH-*m*), 6.61 (m, 1H; Th-CH-b), 2.45 (n.r., 3H, Th-CH₃), 2.40 (s, 3H; Mes-CH₃-*p*), 2.02 (s, 6H; Mes-CH₃-*o*), 1.26 (s, 9H; *t*-Bu-CH₃), 1.25 (s, 9H; *t*-Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 150.3, 149.0, 145.7, 140.8, 140.1, 139.9, 139.0, 138.2, 138.1, 136.9, 136.4, 135.8, 133.9 (C-1 or 8), 133.6 (C-1 or 8), 130.2 (Th-CH-a), 129.8 (C-3 or 6), 129.0 (C-4 or 5), 128.1 (C-3 or 6), 126.9 (Mes-CH-*m*), 125.5 (Th-CH-b), 124.3 (ThCH=), 122.9 (C-4 or 5), 34.7 (*t*-Bu-C), 34.6 (*t*-Bu-C), 31.4 (*t*-Bu-CH₃), 31.4 (*t*-Bu-CH₃), 22.9 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*), 15.6 (Th-CH₃)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 66 ($h_{1/2} \approx 1500$ Hz)

EA (%): Calculated for C₃₆H₄₁BS [516.59]: C 83.70, H 8.00, S 6.21; found: C 83.56, H 7.97, S 6.51



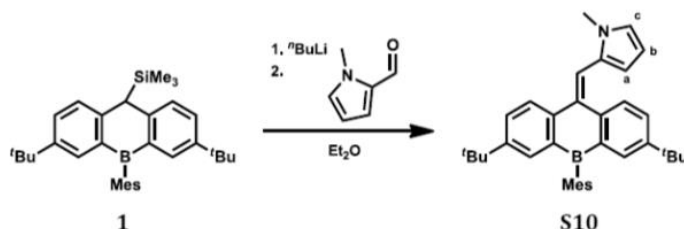
Synthesis of S9: The compound was prepared from **1** (500 mg, 1.04 mmol) and 5-methylfuran-2-aldehyde (0.12 ml, 0.14 mg, 1.3 mmol) analogous to the synthesis of **S8**. The crude product was purified by column chromatography (15 cm silica gel, cyclohexane, $R_f = 0.36$). Only fractions containing exclusively **S9** (determined by TLC) were combined. The solvent was removed under reduced pressure (co-evaporation with MeOH recommended) to obtain a yellow solid. Yield: 445 mg (85%).

$^1\text{H NMR}$ (500.2 MHz, CDCl_3): δ 8.27 (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H; H-4 or 5), 7.91 (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H; H-4 or 5), 7.65 (d, $^4J_{\text{HH}} = 2.3$ Hz, 1H; H-1 or 8), 7.59 (d, $^4J_{\text{HH}} = 2.3$ Hz, 1H; H-1 or 8), 7.56 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 2.3$ Hz, 1H; H-3 or 6), 7.46 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 2.3$ Hz, 1H; H-3 or 6), 7.10 (s, 1H; FuCH=), 6.90 (s, 2H; Mes-CH-*m*), 6.66 (d, $^3J_{\text{HH}} = 3.3$ Hz, 1H; Fu-CH-*a*), 6.02 (m, 1H; Fu-CH-*b*), 2.39 (s, 3H; Mes-CH₃-*p*), 2.33 (n.r., 3H; Fu-CH₃), 2.01 (s, 6H; Mes-CH₃-*o*), 1.27 (s, 9H; *t*-Bu-CH₃), 1.25 (s, 9H; *t*-Bu-CH₃)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 152.8, 151.3, 150.0, 148.9, 145.7, 140.6, 140.0, 138.2, 137.9, 136.3, 135.8, 135.0, 134.0 (C-1 or 8), 133.4 (C-1 or 8), 129.8 (C-3 or 6), 128.8 (C-4 or 5), 127.8 (C-3 or 6), 126.9 (Mes-CH-*m*), 123.1 (C-4 or 5), 118.9 (FuCH=), 113.0 (Fu-CH-*a*), 108.3 (Fu-CH-*b*), 34.7 (*t*-Bu-C), 34.6 (*t*-Bu-C), 31.4 (*t*-Bu-CH₃), 31.4 (*t*-Bu-CH₃), 22.9 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*), 14.0 (Fu-CH₃)

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.5 MHz, CDCl_3): δ 65 ($h_{1/2} \approx 1500$ Hz)

EA (%): Calculated for C₃₆H₄₁BO [500.52]: C 86.39, H 8.26; found: C 86.32, H 8.30



Synthesis of S10: The compound was prepared from **1** (500 mg, 1.04 mmol) and *N*-methylpyrrole-2-aldehyde (0.13 mL, 0.14 mg, 1.3 mmol) analogous to the synthesis of **S8**. The crude product was purified by column chromatography (25 cm silica gel, cyclohexane:EtOAc = 75:1, $R_f = 0.42$). Only fractions containing exclusively **S10** (determined by TLC) were combined. The product was freeze-dried with cyclohexane (10 mL) to obtain an orange solid. Yield: 213 mg (41%).

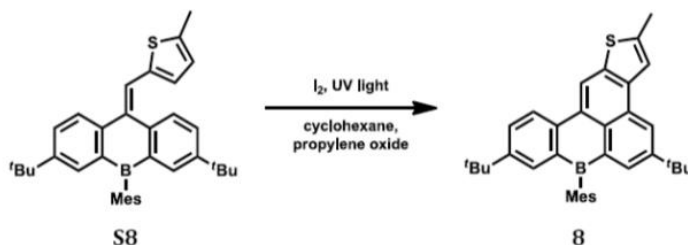
$^1\text{H NMR}$ (500.2 MHz, CDCl_3): δ 7.98 (d, $^3J_{\text{HH}} = 8.3$ Hz, 1H; H-4 or 5), 7.73 (d, $^3J_{\text{HH}} = 8.4$ Hz, 1H; H-4 or 5), 7.64 (d, $^4J_{\text{HH}} = 2.3$ Hz, 1H; H-1 or 8), 7.62 (d, $^4J_{\text{HH}} = 2.3$ Hz, 1H; H-1 or 8), 7.59 (dd, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 2.3$ Hz, 1H; H-3 or 6), 7.34 (dd, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HH}} = 2.3$ Hz, 1H; H-3 or 6), 7.26 (s, 1H; PyrCH=), 6.91 (s, 2H; Mes-CH-*m*), 6.63 (m, 1H; Pyr-CH-*c*), 6.40 (d, $^3J_{\text{HH}} = 3.7$ Hz, 1H; Pyr-CH-*a*), 6.16 (m, 1H; Pyr-CH-*b*), 3.32 (s, 3H; Pyr-CH₃), 2.40 (s, 3H; Mes-CH₃-*p*), 2.02 (s, 6H; Mes-CH₃-*o*), 1.27 (s, 9H; *t*-Bu-CH₃), 1.23 (s, 9H; *t*-Bu-CH₃)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 149.7, 149.0, 145.0, 144.1, 140.1, 138.1, 137.9, 137.4, 136.4, 135.9, 133.9 (C-1 or 8), 133.3 (C-1 or 8), 130.9, 129.8 (C-3 or 6), 128.5 (C-3 or 6), 128.1 (C-4 or 5), 127.0 (Mes-CH-*m*), 123.5 (Pyr-CH-*c*), 123.0 (C-4 or 5), 120.4 (PyrCH=), 110.1 (Pyr-CH-*a*), 108.4 (Pyr-CH-*b*),

34.6 (*t*-Bu-C), 34.6 (*t*-Bu-C), 34.4 (Pyr-CH₃), 31.4 (*t*-Bu-CH₃), 31.4 (*t*-Bu-CH₃), 22.8 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 65 (*h*_{1/2} ≈ 1500 Hz)

EA (%): Calculated for C₃₆H₄₂BN [499.54]: C 86.56, H 8.47, N 2.80; found: C 86.31, H 8.57, N 2.49



Synthesis of 8: A solution of **S8** (0.250 g, 0.483 mmol) in cyclohexane (800 mL) was prepared in a 1 L photoreactor, equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (10 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 11 h during which time neat I₂ (0.20 g, 0.79 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I₂ and the eluate was evaporated to dryness under reduced pressure. The residue was suspended in MeOH (15 mL), sonicated, cooled to 8 °C, isolated by filtration while still cold, and washed with cold MeOH (5 mL). The yellow solid (0.17 g) contained a side product, which was identified as **8** iodinated at one *m*-position of the mesityl ring (ca. 3%). This impurity was removed by applying the following procedure: The crude product was placed in a round-bottom Schlenk flask and dissolved in THF (10 mL). A solution of *t*-BuLi (1.7 M; 0.15 mL, 0.26 mmol) in *n*-hexane was added at -78 °C and the mixture, which immediately adopted a red color, was stirred at this temperature for 1 h. *i*-PrOH (0.5 mL) was added at -78 °C and the solution was stirred for 10 min. A saturated aqueous solution of NaHCO₃ (10 mL), H₂O (10 mL), and Et₂O (40 mL) were added. The partly solid mixture was warmed to room temperature, whereupon it liquefied again. After the color of the mixture had changed to green, the organic layer was separated, washed with brine (40 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. Further purification was achieved by column chromatography (30 cm silica gel, cyclohexane:EtOAc = 50:1, *R*_f = 0.48). Yield: 0.148 g (59%).

¹H NMR (500.2 MHz, CDCl₃): δ 8.97 (s, 1H; H-12), 8.64 (d, ⁴*J*_{HH} = 2.2 Hz, 1H; H-4), 8.51 (d, ³*J*_{HH} = 8.6 Hz, 1H; H-11), 8.23 (d, ⁴*J*_{HH} = 2.2 Hz, 1H; H-6), 7.86 (d, ⁴*J*_{HH} = 2.3 Hz, 1H; H-8), 7.79 (m, 2H; H-3 and 10), 6.94 (s, 2H; Mes-CH-*m*), 2.78 (d, ⁴*J*_{HH} = 0.9 Hz, 3H; CH₃ at C-2), 2.43 (s, 3H; Mes-CH₃-*p*), 2.00 (s, 6H; Mes-CH₃-*o*), 1.42 (s, 9H; *t*-Bu-CH₃ at C-5), 1.32 (s, 9H; *t*-Bu-CH₃ at C-9)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 149.2 (C-9), 148.5 (C-5), 142.7 (C-3b or 12a), 140.4 (Mes-C-*i*), 139.8 (C-11a), 138.8 (Mes-C-*o*), 138.6 (C-6), 138.3 (C-3a), 137.5 (C-3b or 12a), 136.4 (C-7a), 136.4 (Mes-C-*p*), 135.2 (C-8), 135.1 (C-6a), 130.6 (C-10), 128.4 (C-11b), 128.2 (C-2), 128.1 (C-11c), 126.9 (Mes-CH-*m*), 126.5 (C-4), 123.1 (C-11), 120.5 (C-3), 119.3 (C-12), 35.1 (*t*-Bu-C at C-5), 34.6 (*t*-Bu-C at C-9), 31.5 (*t*-Bu-CH₃), 31.4 (*t*-Bu-CH₃), 23.5 (Mes-CH₃-*p*), 21.5 (Mes-CH₃-*o*), 16.7 (CH₃ at C-2)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 64 (*h*_{1/2} ≈ 1500 Hz)

EA (%): Calculated for C₃₆H₃₉BS [514.57]: C 84.03, H 7.64, S 6.23; found: C 83.85, H 7.64, S 6.36

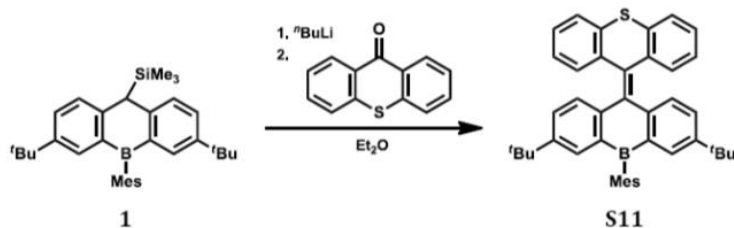
HRMS: Calculated for C₃₆H₃₉BS: 514.28600, found: 514.28509

UV/Vis (cyclohexane): λ_{max} (ε) = 321 (19500), 416 (20300), 436 nm (24600 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, λ_{ex} = 410 nm, 25 °C): λ_{max} = 456, 479 nm; Φ_{PL} = 90%

Fluorescence (acetone, λ_{ex} = 420 nm, 25 °C): λ_{max} = 483 nm; Φ_{PL} = 90%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = 0.84, -2.14 V



Synthesis of S11: Compound **1** (600 mg, 1.25 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (50 mL). *n*-BuLi in *n*-hexane (1.50 M; 0.87 mL, 1.31 mmol) was added with stirring via a syringe at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 30 min, whereupon its color changed to red. Thioxanthone (0.44 g, 2.1 mmol) was added at 0 °C, whereupon the color darkened. The mixture was heated to reflux temperature for 4 h. After cooling to room temperature, a saturated aqueous NaHCO₃ solution (30 mL) was added. The aqueous layer was separated and extracted with Et₂O (30 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (15 cm silica gel, cyclohexane:EtOAc = 100:1, *R_f* = 0.30). Only fractions containing exclusively **S11** (determined by TLC) were combined. The product was dried under an oil-pump vacuum (690 mg), but still contained residual cyclohexane (approx. 1.2 equivalents according to ¹H NMR spectroscopy). Estimated yield: 75%. Analytically pure, yellow crystals were obtained by layering a solution of **S11** in CH₂Cl₂ (150 mg mL⁻¹) with CH₃CN and storing the vessel for 3 d at 8 °C. Solutions of **S11** are prone to photocyclization under ambient conditions.

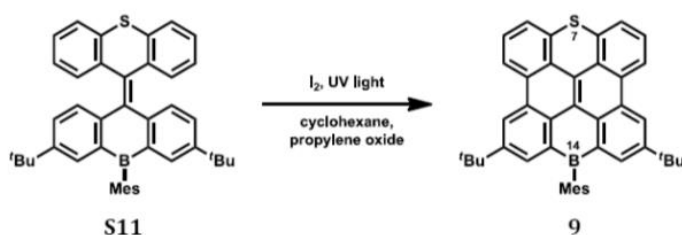
¹H NMR (500.2 MHz, CDCl₃): δ 7.59 (m, 4H), 7.14 (m, 2H), 7.03 (dd, ³*J*_{HH} = 8.2 Hz, ⁴*J*_{HH} = 2.2 Hz, 2H), 7.01 (s, 1H; Mes-CH-*m*), 6.94-6.86 (m, 7H), 2.43 (s, 3H; Mes-CH₃-*p*), 2.27 (s, 3H; Mes-CH₃-*o*), 2.17 (s, 3H; Mes-CH₃-*o*), 1.21 (s, 18H; *t*-Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 149.4 (C-2 and 7), 142.8, 139.9 (Mes-C-*i*), 139.4 (C-8a and 9a), 137.8, 137.7, 137.5, 137.0, 136.6, 136.3, 134.1, 132.5 (CH), 130.7 (CH), 129.5 (CH), 127.6 (CH), 127.2 (CH), 127.2 (Mes-CH-*m*), 127.1 (Mes-CH-*m*), 126.4 (CH), 125.8 (CH), 34.6 (*t*-Bu-C), 31.4 (*t*-Bu-CH₃), 23.1 (Mes-CH₃-*o*), 22.3 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 67 (*h*₂ ≈ 1500 Hz)

EA (%): Calculated for C₄₃H₄₃BS [602.68]: C 85.69, H 7.19, S 5.32; found: C 85.74, H 7.27, S 5.20

HRMS: Calculated for C₄₃H₄₃BS: 602.31804, found: 602.31775



Synthesis of 9: A solution of **S11** (150 mg, 249 μmol) in cyclohexane (800 mL) was prepared in a 1 L photoreactor, equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (10 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 10 h during which time neat I₂ (0.26 g, 1.0 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (3 cm; activity grade I) to remove residual I₂ and the eluate was evaporated to dryness under reduced pressure. The residue was suspended in MeOH (15 mL), sonicated, cooled to 8 °C, collected by filtration while still cold, and washed with cold

MeOH (5 mL). The red solid (95 mg) contained a side product, which was identified as **9** iodinated at one *m*-position of the mesityl ring (ca. 10%). This impurity was removed by applying the following procedure: The crude product was placed in a round-bottom Schlenk flask and dissolved in THF (40 mL). A solution of *t*-BuLi (1.7 M; 0.05 mL, 70 μ mol) in *n*-hexane was added at -78 °C and the mixture, which immediately adopted a dark color, was stirred for 15 min at this temperature. *i*-PrOH (0.5 mL) was added at -78 °C and the dark solution was stirred for 10 min. A saturated aqueous solution of NaHCO₃ (20 mL), H₂O (20 mL) and Et₂O (20 mL) were added. The partly solid mixture was warmed to room temperature, whereupon it liquefied again. After the color of the mixture had changed to fluorescent orange, the aqueous phase was separated and extracted with Et₂O (30 mL). The combined organic layers were washed with brine (40 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. Further purification was achieved by sonification with MeOH (10 mL). The red product was collected by filtration and dried under reduced pressure. Yield: 63 mg (42%). Single crystals were grown by layering a solution of **9** in CH₂Cl₂ (5 mg mL⁻¹) with methanol and storing the vessel at room temperature for 2 d.

¹H NMR (500.2 MHz, CDCl₃): δ 9.00 (d, ⁴*J*_{HH} = 2.2 Hz, 2H; H-3 and 11), 8.54 (d, ³*J*_{HH} = 8.2 Hz, 2H; H-4 and 10), 8.30 (d, ⁴*J*_{HH} = 2.2 Hz, 2H; H-1 and 13), 7.52 (m, 2H; H-5 and 9), 7.36 (d, ³*J*_{HH} = 7.2 Hz, 2H; H-6 and 8), 6.98 (s, 2H; Mes-CH-*m*), 2.46 (s, 3H; Mes-CH₃-*p*), 2.04 (s, 6H; Mes-CH₃-*o*), 1.46 (s, 18H; *t*-Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 148.9 (C-2, 12), 140.6 (Mes-C-*i*), 139.1 (C-1, 13), 138.9 (Mes-C-*o*), 136.6 (Mes-C-*p*), 135.9 (C-13a, 14a), 133.0 (C-3b, 10a), 132.2 (C-6a, 7a), 130.7 (C-13b, 14b), 129.1 (C-3a, 10b), 128.0 (C-14c or 14d), 127.4 (C-5, 9), 127.1 (Mes-CH-*m*), 126.7 (C-7b, 14e), 125.5 (C-3, 11), 123.3 (C-14c or 14d), 122.6 (C-6, 8), 120.2 (C-4, 10), 35.1 (*t*-Bu-C), 31.5 (*t*-Bu-CH₃), 23.7 (Mes-CH₃-*o*), 21.6 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 65 (*h*_{1/2} \approx 1500 Hz)

EA (%): Calculated for C₄₃H₃₉BS [598.65]: C 86.27, H 6.57, S 5.36; found: C 85.75, H 6.22, S 5.28

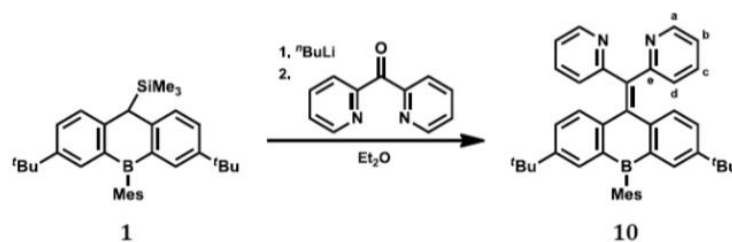
HRMS: Calculated for C₄₃H₃₉BS: 598.28600, found: 598.28525

UV/Vis (cyclohexane): λ_{\max} (ϵ) = 482 (13000), 513 nm (21900 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, λ_{ex} = 460 nm, 25 °C): λ_{\max} = 524, 560 nm; Φ_{PL} = 80%

Fluorescence (acetone, λ_{ex} = 500 nm, 25 °C): λ_{\max} = 579 nm; Φ_{PL} = 76%

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): $E_{1/2} = -2.06$ V



Synthesis of **10:** Compound **1** (500 mg, 1.04 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et₂O (40 mL). *n*-BuLi in *n*-hexane (1.53 M; 0.71 mL, 1.09 mmol) was added with stirring via a syringe at 0 °C. After the addition was complete, the reaction mixture was heated to reflux temperature for 30 min, whereupon its color changed to red. Neat di(pyridine-2-yl)methanone (0.249 g, 1.35 mmol) was added at 0 °C, whereupon the color changed to blue. The mixture was heated to reflux temperature for 2 h. After cooling to room temperature, a saturated aqueous NaHCO₃ solution (40 mL) was added. The aqueous layer was separated and extracted with Et₂O (50 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (15 cm silica gel, cyclohexane:EtOAc = 3:2, *R_f* = 0.45). The solvent was removed and a

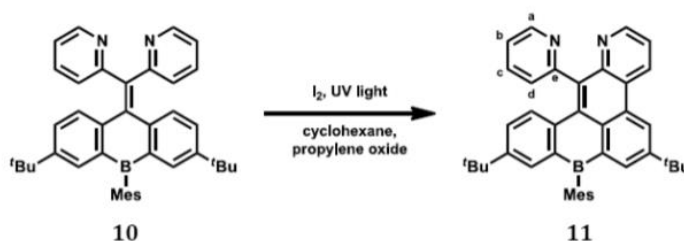
viscous oil was obtained (510 mg). **10** was further purified by sonification with *n*-hexane (7 mL). The solid was collected by filtration and dried in vacuo to afford a colorless powder. Yield: 350 mg (59%).

¹H NMR (500.2 MHz, CDCl₃): δ 8.72 (br. d, ³J_{HH} ≈ 5 Hz, 2H; Py-H-a), 7.56 (d, ⁴J_{HH} = 2.1 Hz, 2H; H-1 and 8), 7.41 (ddd, ³J_{HH} = 7.7 Hz, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.8 Hz, 2H; Py-H-c), 7.08 (m, 2H; Py-H-b), 7.06 (d, ³J_{HH} = 8.3 Hz, 2H; H-4 and 5), 7.02 (dd, ³J_{HH} = 8.3 Hz, ⁴J_{HH} = 2.2 Hz, 2H; H-3 and 6), 6.99 (br. d, ³J_{HH} = 7.7 Hz, 2H; Py-H-d), 6.94 (s, 2H; Mes-CH-*m*), 2.41 (s, 3H; Mes-CH₃-*p*), 2.17 (s, 6H; Mes-CH₃-*o*), 1.16 (s, 18H; *t*-Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 160.5 (Py-C-e), 149.5 (Py-C-a), 149.3, 142.9, 140.9, 140.2, 139.9 (Mes-C-i), 138.3 (C-8a and 9a), 137.7, 136.5, 136.1 (Py-C-c), 133.1 (C-1 and 8), 129.0 (C-4 and 5), 127.8 (C-3 and 6), 127.0 (Mes-CH-*m*), 125.4 (Py-C-d), 121.5 (Py-C-b), 34.5 (*t*-Bu-C), 31.3 (*t*-Bu-CH₃), 22.8 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*).

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 68 (*h*₂ ≈ 1500 Hz)

EA (%): Calculated for C₄₁H₄₃BN₂ [574.60]: C 85.70, H 7.54, N 4.88; found: C 85.59, H 7.69, N 4.55



Synthesis of 11: A solution of **10** (200 mg, 0.348 mmol) in cyclohexane (800 mL) was prepared in a 1 L photoreactor, equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (10 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 9 h during which time neat I₂ (350 mg, 1.4 mmol) was added in several portions. The brown suspension obtained was diluted with EtOAc until all solids were dissolved. The mixture was washed with a solution of Na₂S₂O₅ (30 g) in H₂O (150 mL) to reduce residual I₂. The aqueous layer was separated and extracted with a mixture of cyclohexane and EtOAc (50 mL each). The combined organic layers were dried with MgSO₄, filtered, and evaporated to dryness under reduced pressure. The residue was suspended in MeOH (10 mL), sonicated, cooled to 8 °C, isolated by filtration while still cold, and washed with cold MeOH (5 mL) to afford pure **11** as a yellow solid (95 mg). The filtrate (MeOH extract) was adsorbed on silica gel (ca. 5 g) and purified by column chromatography (20 cm silica gel, EtOAc, *R*_f = 0.30) to obtain additional product (40 mg). Combined yield: 135 mg (68%)

¹H NMR (500.2 MHz, C₆D₆): δ 8.80 (m, 2H; H-5 and Py-H-a), 8.76 (dd, ³J_{HH} = 4.2 Hz, ⁴J_{HH} = 1.6 Hz, 1H; H-2), 8.59-8.56 (m, 2H; H-4 and 7), 8.21 (d, ⁴J_{HH} = 2.4 Hz, 1H; H-9), 7.79 (d, ³J_{HH} = 8.6 Hz, 1H; H-12), 7.45 (d, ³J_{HH} = 7.8 Hz, 1H; Py-H-d), 7.27 (m, 1H; Py-H-c), 7.24 (dd, ³J_{HH} = 8.7 Hz, ⁴J_{HH} = 2.5 Hz, 1H; H-11), 7.02 (s, 2H; Mes-CH-*m*), 6.91 (dd, ³J_{HH} = 8.3 Hz, ³J_{HH} = 4.2 Hz, 1H; H-3), 6.84 (ddd, ³J_{HH} = 7.5 Hz, ³J_{HH} = 4.9 Hz, ⁴J_{HH} = 1.1 Hz, 1H; Py-H-b), 2.31 (s, 3H; Mes-CH₃-*p*), 2.22 (br. s, 6H; Mes-CH₃-*o*), 1.32 (s, 9H; *t*-Bu-CH₃ at C-6), 1.09 (s, 9H, *t*-Bu-CH₃ at C-10)

¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ 162.1 (Py-C-e), 150.0 (Py-C-a), 149.8 (C-10), 149.3 (C-2), 149.2 (C-6), 149.1 (C-13a), 141.4 (C-12a), 141.2 (C-13), 140.8 (Mes-C-i), 139.7 (C-8a), 138.9 (Mes-C-o), 138.8 (C-7), 137.1 (Mes-C-p), 136.0 (C-7a), 135.4 (Py-C-c), 135.1 (C-9), 134.8 (C-12b), 132.3 (C-12), 131.6 (C-12c), 129.8 (C-4), 129.5 (C-11), 128.6 (C-4b), 127.7 (Mes-CH-*m*), 127.5 (Py-C-d), 126.4 (C-4a), 124.9 (C-5), 121.8 (Py-C-b), 121.4 (C-3), 35.0 (*t*-Bu-C at C-6), 34.4 (*t*-Bu-C at C-10), 31.3 (*t*-Bu-CH₃ at C-6), 31.1 (*t*-Bu-CH₃ at C-10), 23.5 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 65 (*h*₂ ≈ 1500 Hz)

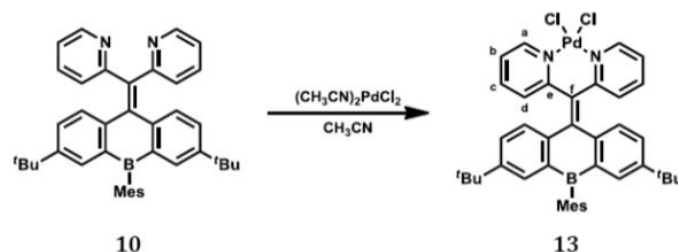
EA (%): Calculated for C₄₁H₄₁BN₂ [572.59]: C 86.00, H 7.22, N 4.89; found: C 85.47, H 6.88, N 4.46

HRMS: Calculated for $C_{41}H_{41}BN_2 + H^+$: 573.34356, found: 573.34235

UV/Vis (cyclohexane): λ_{max} (ϵ) = 311 (20200), 395 nm ($18700 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$)

Fluorescence (cyclohexane, λ_{ex} = 310 nm, 25 °C): not fluorescent

Cyclic voltammetry (CH_2Cl_2 , [nBu_4N][PF_6] 0.1 M, 200 mV s^{-1} , vs. FcH/FcH $^+$): $E_{1/2} = -2.00$ V



Synthesis of 13: $PdCl_2$ (23 mg, 130 μmol) was placed in a 50 mL 2-necked round-bottom flask equipped with a condenser and dissolved in boiling CH_3CN (10 mL). After the resulting orange solution had been cooled to room temperature, **10** (70 mg, 120 μmol) was added. The mixture was heated to reflux temperature for 2 h. The solvent was removed under reduced pressure and $CHCl_3$ (2.5 mL) was added to the solid residue. The resulting solution was separated from small amounts of remaining solid and layered with CH_3CN (10 mL). After the vessel had been stored at 8 °C for 4 d, **13** was collected as single crystals. Yield: 38 mg (41%)

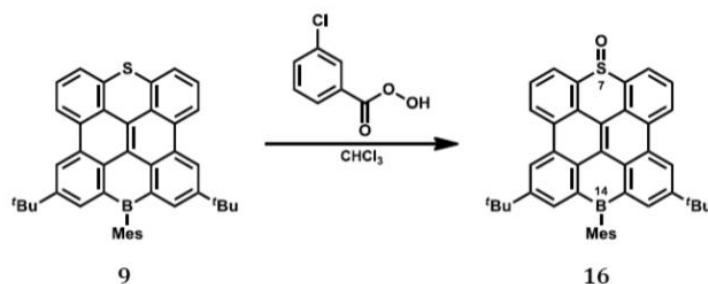
1H NMR (500.2 MHz, $CDCl_3$): δ 9.16 (br. d, $^3J_{HH} = 5.8$ Hz, 2H; Py-H-a), 7.64 (d, $^4J_{HH} = 2.2$ Hz, 2H; H-1,8), 7.56 (ddd, $^3J_{HH} = 7.7$ Hz, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.5$ Hz, 2H; Py-H-c), 7.28 (ddd, $^3J_{HH} = 7.7$ Hz, $^3J_{HH} = 5.8$ Hz, $^4J_{HH} = 1.5$ Hz, 2H; Py-H-b), 7.15 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 2.2$ Hz, 2H; H-3,6), 7.04 (d, $^3J_{HH} = 8.1$ Hz, 2H; H-4,5), 7.02 (br. s, 1H; Mes-CH-*m*), 6.93 (br. s, 1H; Mes-CH-*m*), 6.87 (m, $^3J_{HH} = 7.7$ Hz, 2H; Py-H-d), 2.42 (s, 3H; Mes- CH_3 -*p*), 2.23 (s, 3H; Mes- CH_3 -*o*), 2.13 (s, 3H; Mes- CH_3 -*o*), 1.19 (s, 18H; *t*-Bu- CH_3)

$^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): δ 155.7 (Py-C-e), 153.7 (Py-C-a), 152.0 (C-2,7), 147.0 (C-10), 140.1 (C-4a,10a), 138.7 (Mes-C-*i*), 138.6 (Py-C-c), 138.4 (C-8a,9a), 138.0 (Mes-C-*o*), 137.2 (Mes-C-*p*), 136.8 (Mes-C-*o*), 134.2 (C-1,8), 132.0 (C-f), 129.5 (C-4,5), 128.6 (C-3,6), 127.5 (Mes-CH-*m*), 127.4 (Py-C-d), 127.2 (Mes-CH-*m*), 123.8 (Py-C-b), 34.8 (*t*-Bu-C), 31.2 (*t*-Bu- CH_3), 23.2 (Mes- CH_3 -*o*), 22.5 (Mes- CH_3 -*o*), 21.5 (Mes- CH_3 -*p*)

$^{11}B\{^1H\}$ NMR (160.5 MHz, $CDCl_3$): not observed

EA (%): Calculated for $C_{41}H_{43}BN_2Cl_2Pd$ [751.93]: C 65.49, H 5.76, N 3.73; found: C 65.33, H 5.75, N 3.50

UV/Vis (chloroform): λ_{max} (ϵ) = 269 (34900), 368 nm ($19900 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$)



Synthesis of 16: A solution of *m*-chloroperbenzoic acid in $CHCl_3$ (15 mL ca. 15 mM, ca. 225 μmol) was added dropwise to a solution of **9** (100 mg, 167 μmol) in $CHCl_3$ (20 mL) at room temperature (under ambient atmosphere). After the color had changed from orange to yellow, the reaction solution was washed with a saturated aqueous $NaHCO_3$ solution (2 \times 50 mL) and the combined aqueous layers were extracted with

CHCl₃ (20 mL). The combined organic layers were washed with H₂O (50 mL), dried over MgSO₄, and filtered. All volatiles were removed from the filtrate under reduced pressure to obtain an orange solid. For purification, the crude product was dissolved in CHCl₃ (2 mL) and layered with MeOH (12 mL). After storing the vessel for 4 d at 8 °C, crystalline **16** was collected. Yield: 62 mg (60%)

¹H NMR (500.2 MHz, CDCl₃): δ 9.25-9.24 (m, 4H; H-3,4,10,11), 8.52 (d, ³J_{HH} = 7.1 Hz, 2H; H-6,8), 8.47 (s, ⁴J_{HH} = 2.1 Hz, 2H; H-1,13), 8.06 (m, 2H; H-5,9), 7.03 (s, 1H; Mes-CH-*m*), 7.01 (s, 1H; Mes-CH-*m*), 2.48 (s, 3H; Mes-CH₃-*p*), 2.10 (s, 3H; Mes-CH₃-*o*), 2.02 (s, 3H; Mes-CH₃-*o*), 1.52 (s, 18H, *t*-Bu-CH₃)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 150.4 (C-2,12), 139.9 (Mes-C-*i*), 139.6 (C-1,13), 139.0 (Mes-C-*o*), 138.7 (Mes-C-*o*), 136.9 (Mes-C-*p*), 136.2 (C-13a,14a), 135.4 (C-6a,7a), 131.7 (C-3b,10a), 131.3 (C-6,8), 130.2 (C-13b,14b), 129.3 (C-3a,10b), 128.0 (C-14c or 14d), 127.6 (C-5,9), 127.5 (C-4,10), 127.3 (Mes-CH-*m*), 127.2 (Mes-CH-*m*), 125.6 (C-3,11), 123.2 (C-7b,14e), 122.1 (C-14c or 14d), 35.4 (*t*-Bu-C), 31.5 (*t*-Bu-CH₃), 23.8 (Mes-CH₃-*o*), 23.7 (Mes-CH₃-*o*), 21.6 (Mes-CH₃-*p*)

¹¹B{¹H} NMR (160.5 MHz, CDCl₃): δ 66 (*h*₂ ≈ 1500 Hz)

HRMS: Calculated for C₄₃H₃₉BOS: 614.28092 found: 614.27811 (also detected by mass spectrometry: [M-O]⁺)

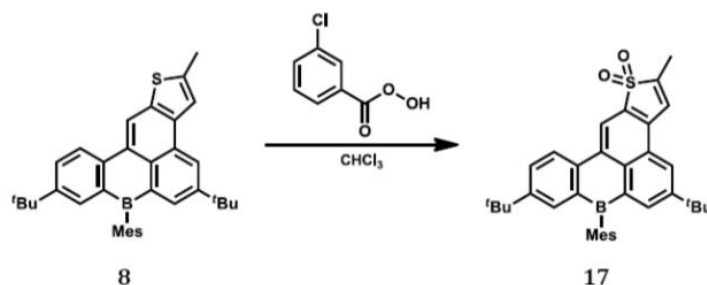
UV/Vis (cyclohexane): λ_{max} (ε) = 361, 397, 419 nm (ε values were not determined because of low solubility in cyclohexane)

UV/Vis (acetone): λ_{max} (ε) = 364 (15600), 397 (24600), 419 nm (29500 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, λ_{ex} = 397 nm, 25 °C): ca. 444 nm; Φ_{PL} < 20% (accurate fluorescence wavelengths and quantum yield could not be determined because of slow deoxygenation to the highly fluorescent **9** during measurements)

Fluorescence (acetone, λ_{ex} = 397 nm, 25 °C): ca. 465 nm; Φ_{PL} < 20% (accurate fluorescence wavelengths and quantum yield could not be determined because of slow deoxygenation to the highly fluorescent **9** during measurements)

Cyclic voltammetry (CH₂Cl₂, [nBu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): E_{1/2} = -1.74 V



Synthesis of 17: A solution of **8** (95.0 mg, 185 μmol) in CHCl₃ (7 mL) was prepared under ambient atmosphere. Neat *m*-chloroperbenzoic acid (91 mg, ca. 70%, 370 μmol) was added and the solution was stirred at room temperature for 0.5 h. The solvent was removed under reduced pressure and the solid residue was purified by column chromatography (35 cm silica gel, cyclohexane:EtOAc = 10:1, R_f = 0.08). All fractions containing **17** were combined and the solvent was removed under reduced pressure. For additional purification, the product was suspended in MeOH (10 mL), sonicated, cooled to 8 °C, collected by filtration and washed with cold MeOH (5 mL). Yield: 32 mg (32 %, yellow powder). Single crystals for X-ray structure analysis were grown by layering a solution of **17** in C₆H₆ (20 mg mL⁻¹) with MeOH and storing the vessel at 8 °C for 4 d.

¹H NMR (500.2 MHz, CDCl₃): δ 8.87 (s, 1H; H-12), 8.46 (d, ³J_{HH} = 8.5 Hz, 1H; H-11), 8.32 (s, 2H; H-4,6), 7.85 (d, ⁴J_{HH} = 2.3 Hz, 1H; H-8), 7.83 (dd, ³J_{HH} = 8.4 Hz, ⁴J_{HH} = 2.3 Hz, 1H; H-10), 7.56 (n.r., 1H; H-3), 6.94 (s, 2H; Mes-CH-*m*), 2.42 (s, 3H; Mes-CH₃-*p*), 2.41 (d, ⁴J_{HH} = 1.6 Hz, 3H; CH₃ at C-2), 1.96 (s, 6H; Mes-CH₃-*o*), 1.39 (s, 9H; *t*-Bu-CH₃ at C-5), 1.31 (s, 9H; *t*-Bu-CH₃ at C-9)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 151.1 (C-9), 150.7 (C-5), 143.3 (C-6), 141.8 (C-2), 139.2 (Mes-C-*i*), 138.7 (Mes-C-*o*), 138.3 (C-11a), 136.9 (Mes-C-*p*), 136.5 (C-7a), 135.7 (C-8), 135.7 (C-6a), 134.3 (C-11b), 133.9 (C-12a), 132.4 (C-11c), 131.5 (C-10), 129.0 (C-3a), 127.2 (Mes-CH-*m*), 127.0 (C-3b), 125.1 (C-4), 124.1 (C-11), 122.8 (C-3), 115.2 (C-12), 35.2 (*t*-Bu-C at C-5), 34.8 (*t*-Bu-C at C-9), 31.3 (*t*-Bu-CH₃ at C-9), 31.1 (*t*-Bu-CH₃ at C-5), 23.5 (Mes-CH₃-*o*), 21.5 (Mes-CH₃-*p*), 9.8 (CH₃ at C-2)

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.5 MHz, CDCl_3): δ 65 ($h_{1/2} \approx 1500$ Hz)

HRMS: Calculated for $\text{C}_{36}\text{H}_{39}\text{BO}_2\text{S}$: 546.27583 found: 546.27444 (also detected by mass spectrometry: $[M+\text{Na}]^+$, $[M-\text{O}]^+$, $[M-2\text{O}]^+$)

UV/Vis (cyclohexane): λ_{max} (ϵ) = 317, 427, 449 nm (ϵ values were not determined because of low solubility in cyclohexane)

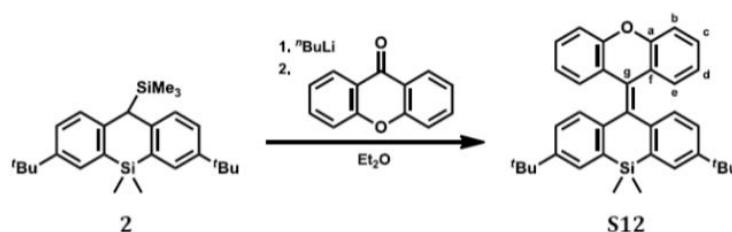
UV/Vis (benzene): λ_{max} (ϵ) = 319 (9700), 430 (16700), 452 nm ($16300 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$)

Fluorescence (cyclohexane, $\lambda_{\text{ex}} = 430$ nm, 25 °C): $\lambda_{\text{max}} = 473, 498$ nm; $\Phi_{\text{PL}} = 94\%$

Fluorescence (benzene, $\lambda_{\text{ex}} = 430$ nm, 25 °C): $\lambda_{\text{max}} = 483, 503$ nm; $\Phi_{\text{PL}} = 92\%$

Fluorescence (acetone, $\lambda_{\text{ex}} = 430$ nm, 25 °C): $\lambda_{\text{max}} = 483, \sim 502$ (shoulder) nm; $\Phi_{\text{PL}} = 93\%$

Cyclic voltammetry (CH_2Cl_2 , $[\text{nBu}_4\text{N}][\text{PF}_6]$ 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): $E_{1/2} = -1.70$ V



Synthesis of S12: Compound **2** (1.21 g, 2.96 mmol) was placed in a 100 mL 2-necked round-bottom flask equipped with a condenser and dissolved in Et_2O (60 mL). *n*-BuLi in *n*-hexane (1.60 M; 1.85 mL, 2.96 mmol) was added with stirring via a syringe at room temperature. After the addition was complete, the reaction mixture was heated to reflux temperature for 1 h, whereupon its color changed to red. Neat xanthone (581 mg, 2.96 mmol) was added at room temperature. The resulting orange-brown mixture was stirred for 48 h. A saturated aqueous NaHCO_3 solution (50 mL) was added to the dark violet mixture, whereupon the color disappeared. The aqueous layer was separated and extracted with Et_2O (50 mL). The combined organic layers were washed with H_2O (50 mL), dried over MgSO_4 , and filtered. All volatiles were removed from the filtrate under reduced pressure. The crude product was purified by short column chromatography (silica gel/cyclohexane) to obtain a solid, which contained ca. 25% residual **2**. The solid was suspended in MeOH (20 mL), sonicated, and cooled to 8 °C. Light yellow **S12** was collected by filtration, washed with MeOH (10 mL) and dried in vacuo. Yield: 0.844 g (55%)

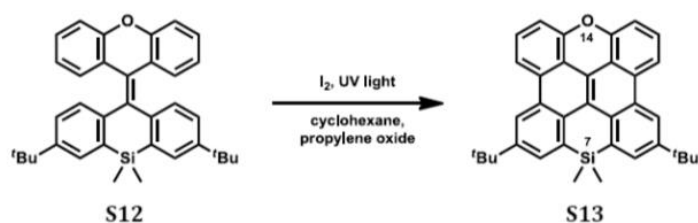
^1H NMR (500.2 MHz, CDCl_3): δ 7.64 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2H; H-1,8), 7.20 (dd, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H; H-b), 7.14 (m, 2H; H-c), 7.07 (dd, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 2.0$ Hz, 2H; H-3,6), 6.97 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H; H-4,5), 6.71 (m, 2H; H-d), 6.65 (dd, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, 2H; H-e), 1.31 (s, 18H; *t*-Bu-CH₃), 0.73 (s, 3H; SiMe₂), 0.56 (s, 3H; SiMe₂)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 155.0 (C-a), 148.6 (C-2,7), 144.6 (C-4a,10a), 138.0 (C-8a,9a), 136.1 (C-10), 129.8 (C-e), 129.2 (C-1,8), 127.8 (C-4,5), 127.8 (C-c), 125.5 (C-3,6), 125.3 (C-f), 123.5 (C-g), 122.1 (C-d), 116.6 (C-b), 34.7 (*t*-Bu-C), 31.6 (*t*-Bu-CH₃), -1.9 (SiMe₂), -5.7 (SiMe₂)

^{29}Si NMR (99.4 MHz, INEPT, CDCl_3): δ -16.4

EA (%): Calculated for $\text{C}_{36}\text{H}_{38}\text{OSi}$ [514.77]: C 84.00, H 7.44; found: C 84.16, H 7.51

HRMS: Calculated for $\text{C}_{36}\text{H}_{38}\text{OSi}$: 514.26864, found: 514.26881



Synthesis of S13: A solution of **S12** (0.800 g, 1.55 mmol) in cyclohexane (800 mL) was prepared in a 1 L photoreactor, equipped with a water-cooled quartz immersion well containing a medium-pressure Hg lamp. Propylene oxide (20 mL) was added and the solution was purged with argon for 15 min using a cannula. The solution was irradiated for 14 h during which time neat I₂ (2.0 g, 7.8 mmol) was added in several portions. The reaction mixture was filtered through neutral alumina (5 cm; activity grade I) to remove residual I₂ and the eluate was evaporated to dryness under reduced pressure. The crude product was suspended in MeOH (20 mL), sonicated, and cooled to 8 °C. The yellow product was collected by filtration, washed with MeOH (10 mL) and dried in vacuo. Yield: 0.50 g (63%). Single crystals were grown by layering a concentrated solution of **S13** in C₆H₆ with MeOH and storing the vessel at 8 °C for 3 d; the compound crystallized together with 0.5 eq. C₆H₆.

¹H NMR (500.2 MHz, CDCl₃): δ 8.78 (d, ⁴J_{H,H} = 2.2 Hz, 2H; H-4,10), 8.29 (d, ³J_{H,H} = 8.2 Hz, 2H; H-3,11), 8.05 (d, ⁴J_{H,H} = 2.2 Hz, 2H; H-6,8), 7.58 (dd, ³J_{H,H} = 8.2 Hz, ³J_{H,H} = 7.8 Hz, 2H; H-2,12), 7.18 (d, ³J_{H,H} = 7.8 Hz, 2H; H-1,13), 1.57 (s, 18H; *t*-Bu-CH₃), 0.61 (s, 6H; SiMe₂)

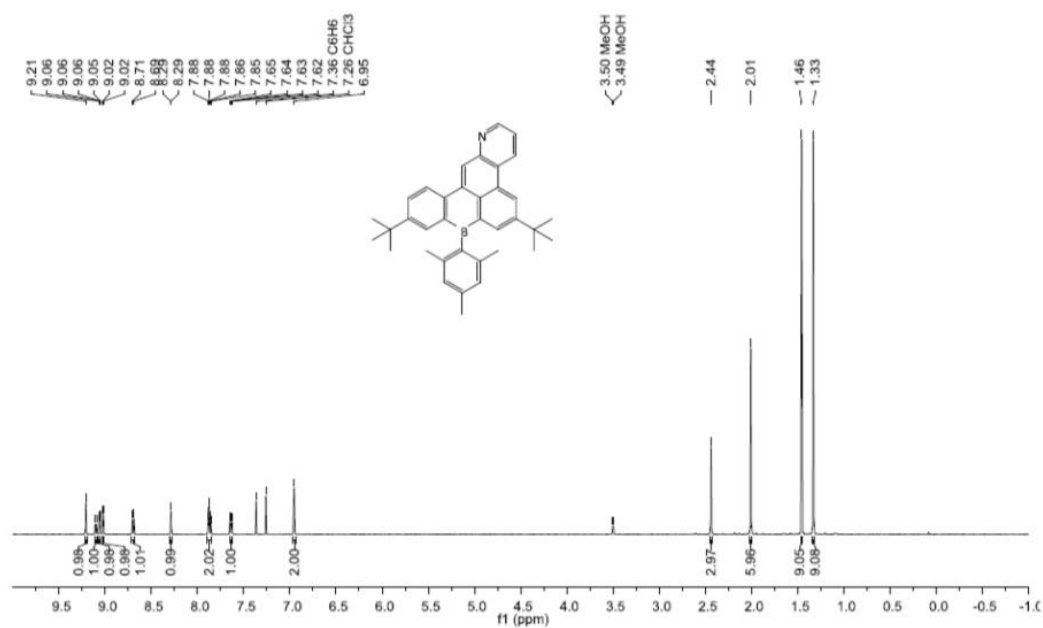
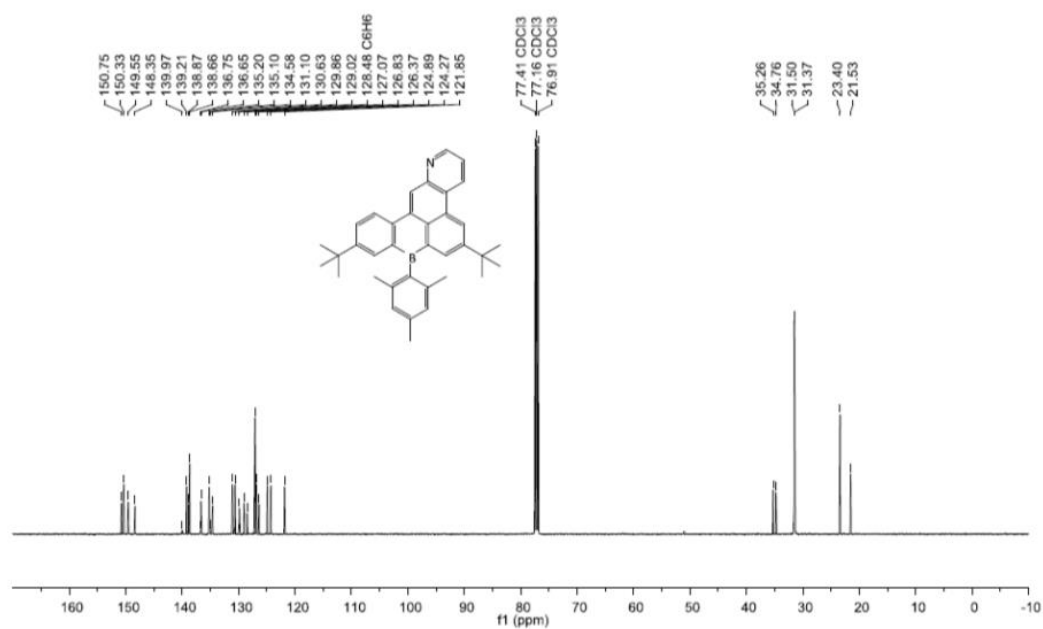
¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 152.1 (C-13a,14a), 147.8 (C-5,9), 133.9 (C-6a,7a), 132.5 (C-7b,14e), 132.3 (C-6,8), 131.9 (C-3a,10b), 129.2 (C-3b,10a), 128.4 (C-2,12), 121.7 (C-4,10), 121.5 (C-14c), 120.7 (C-14d), 118.6 (C-13b,14b), 116.1 (C-3,11), 111.6 (C-1,13), 35.0 (*t*-Bu-C), 31.5 (*t*-Bu-CH₃), 1.3 (SiMe₂)

²⁹Si NMR (99.4 MHz, CDCl₃): δ -20.9

EA (%): Calculated for C₃₆H₃₄O₂Si [510.74]: C 84.66, H 6.71; found: C 84.76, H 6.80

UV/Vis (cyclohexane): λ_{max} (ϵ) = 318 (25600), 385 (16000), 406 nm (27000 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, λ_{ex} = 318 nm, 25 °C): λ_{max} = 410, 434, 461 nm; Φ_{PL} = 60%

5. Plots of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectraFigure S5: ^1H NMR spectrum of 3 (CDCl_3 , 500.2 MHz).Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3 (CDCl_3 , 125.8 MHz).

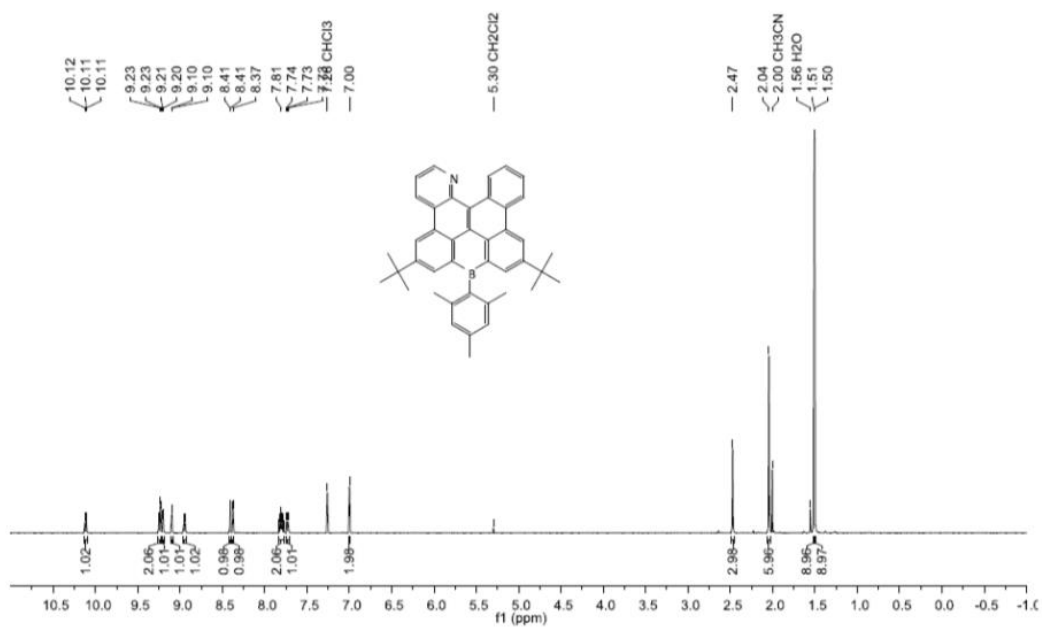


Figure S7: ¹H NMR spectrum of 4 (CDCl₃, 500.2 MHz).

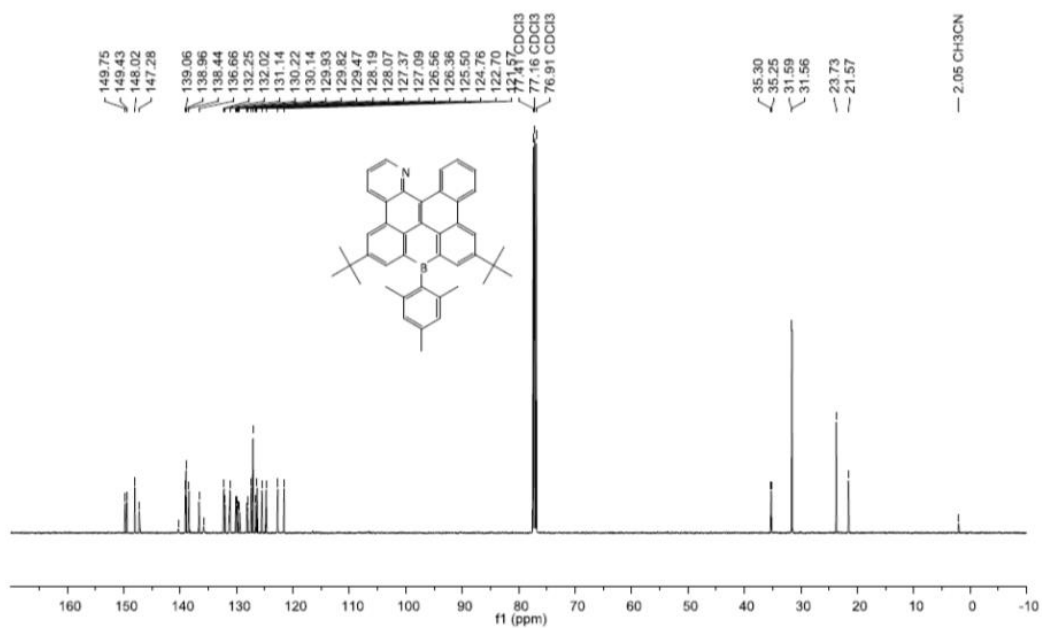


Figure S8: ¹³C{¹H} NMR spectrum of 4 (CDCl₃, 125.8 MHz).

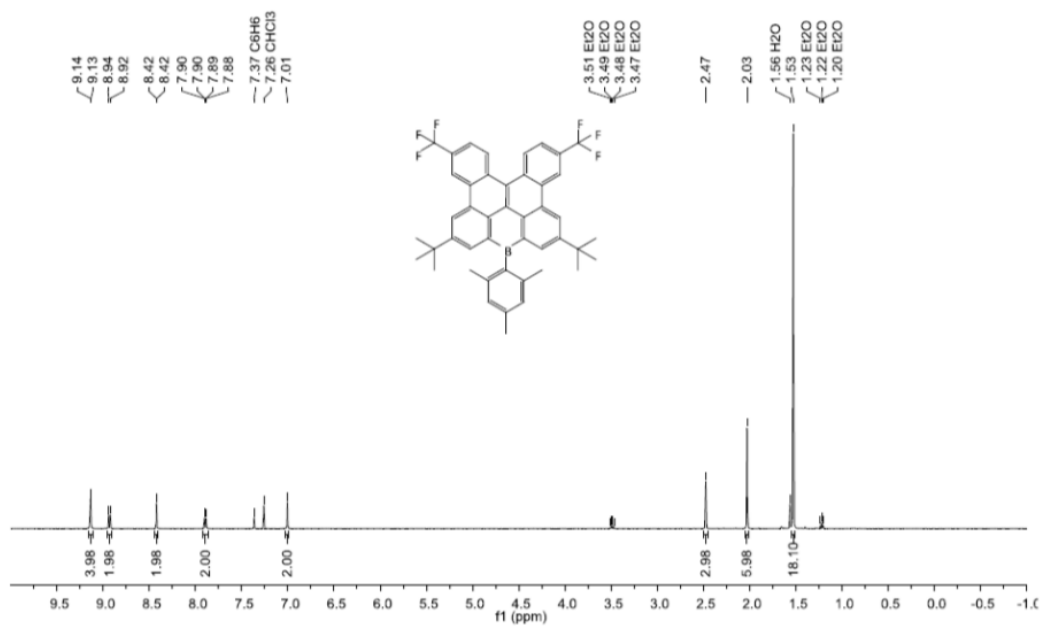


Figure S11: ^1H NMR spectrum of 7 (CDCl_3 , 500.2 MHz).

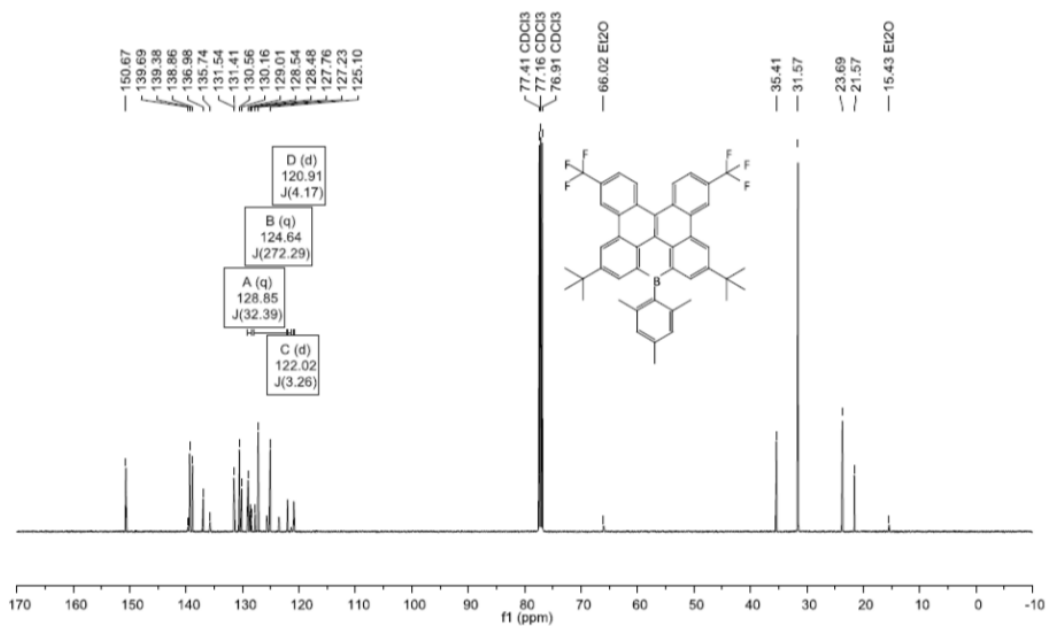


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 7 (CDCl_3 , 125.8 MHz).

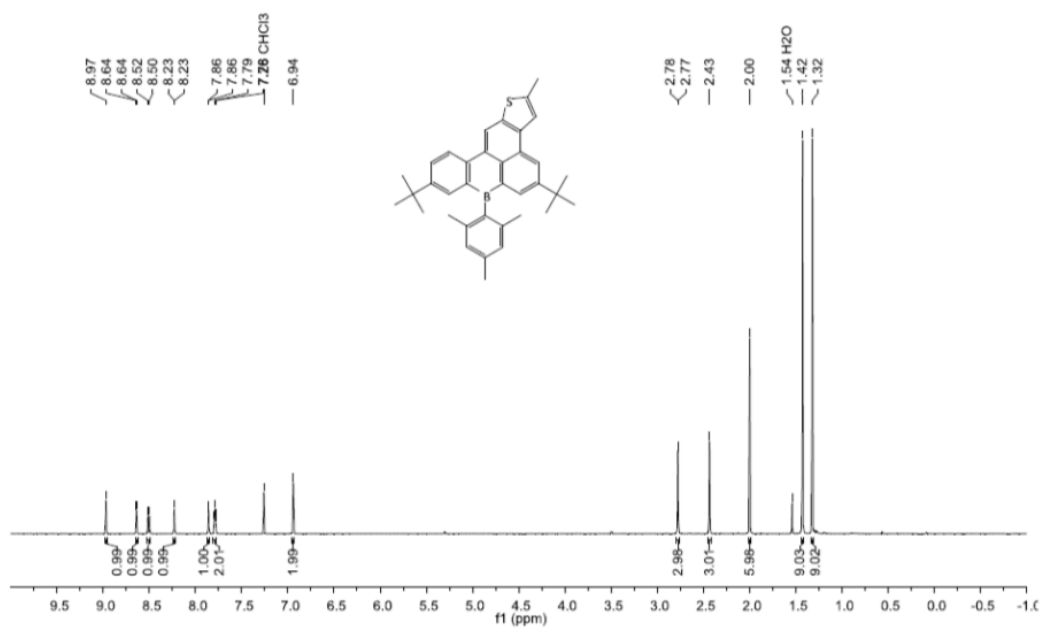


Figure S13: ¹H NMR spectrum of 8 (CDCl₃, 500.2 MHz).

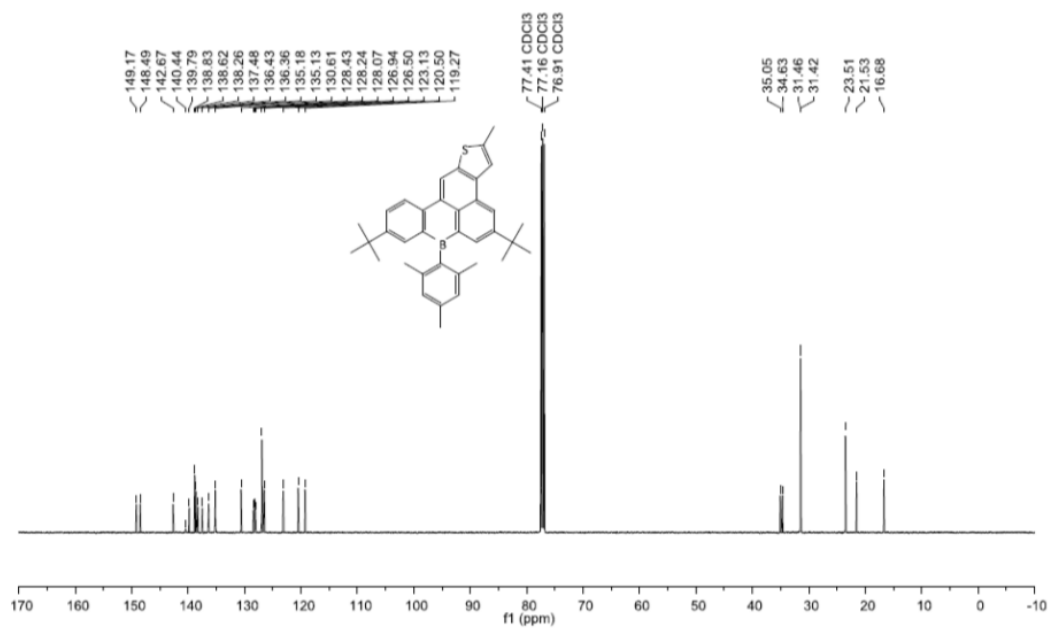


Figure S14: ¹³C{¹H} NMR spectrum of 8 (CDCl₃, 125.8 MHz).

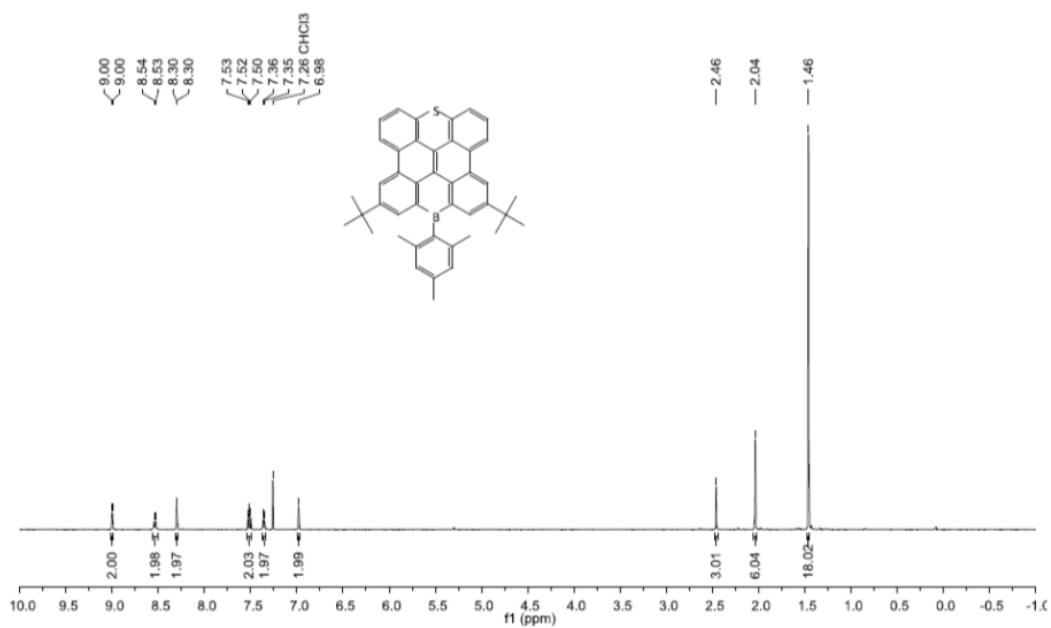


Figure S15: ^1H NMR spectrum of **9** (CDCl_3 , 500.2 MHz).

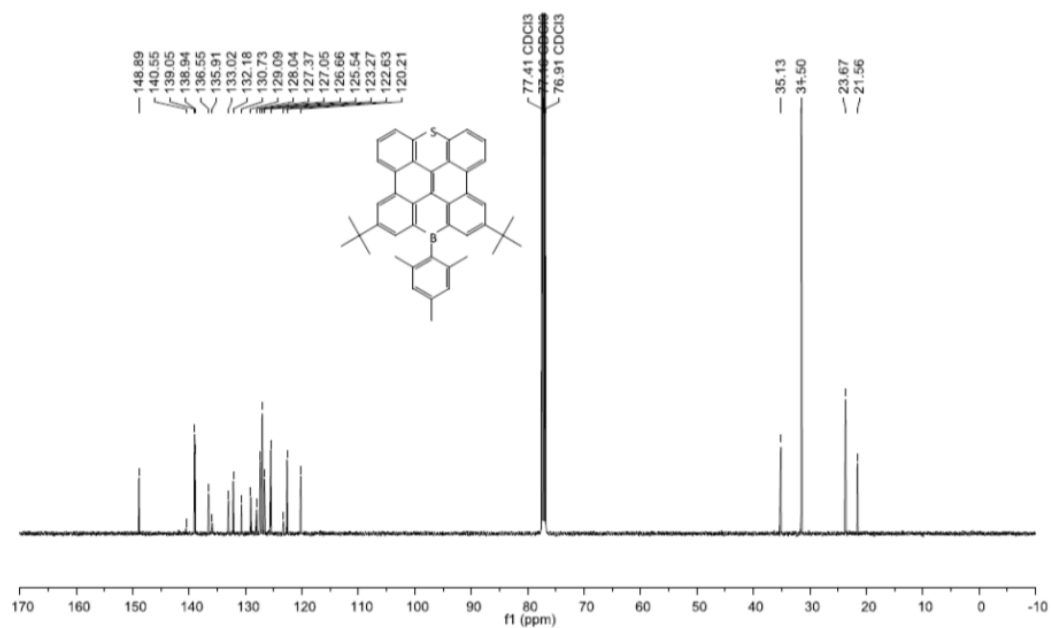


Figure S16: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** (CDCl_3 , 125.8 MHz).

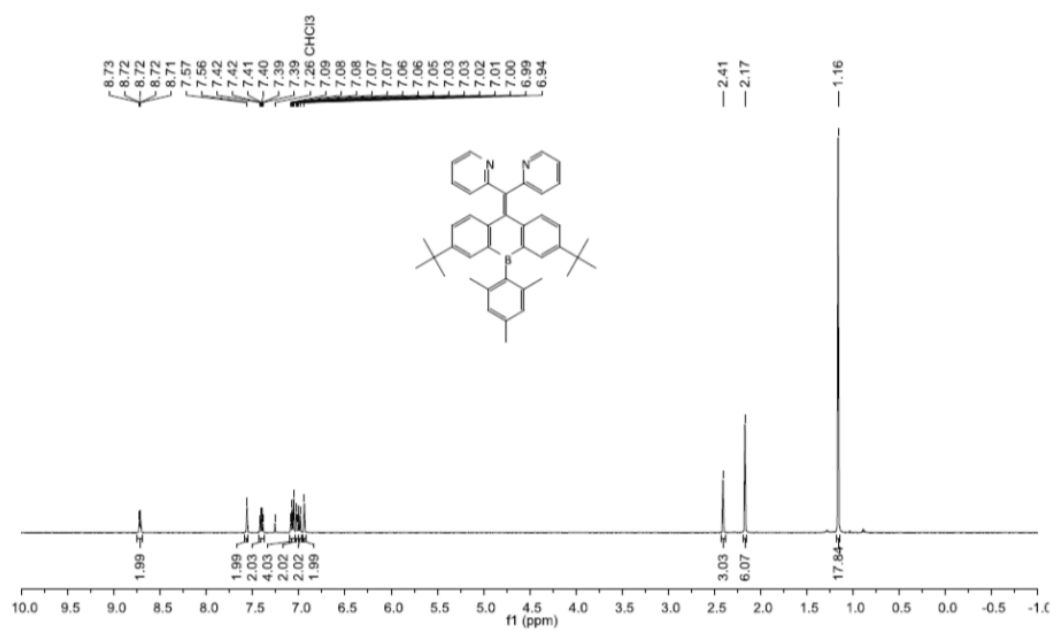


Figure S17: ¹H NMR spectrum of **10** (CDCl₃, 500.2 MHz).

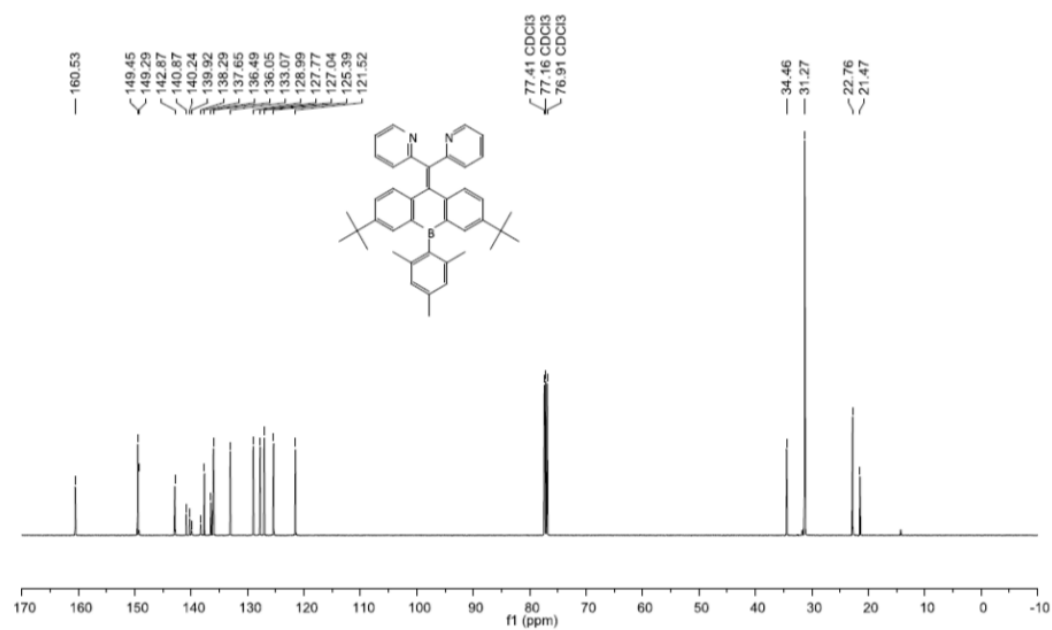


Figure S18: ¹³C{¹H} NMR spectrum of **10** (CDCl₃, 125.8 MHz).

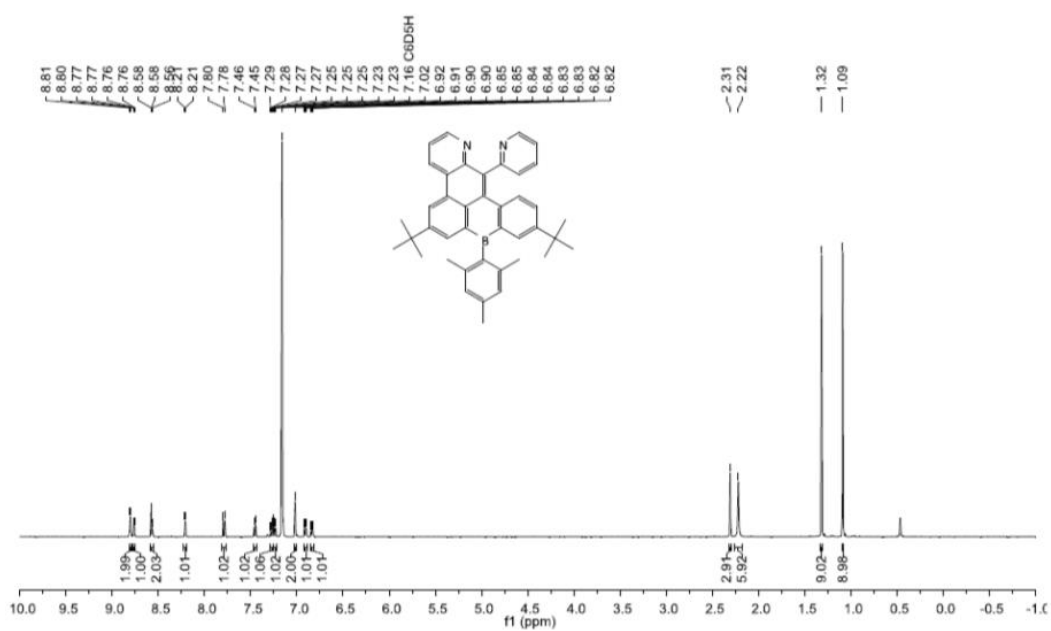


Figure S19: ^1H NMR spectrum of **11** (C_6D_6 , 500.2 MHz).

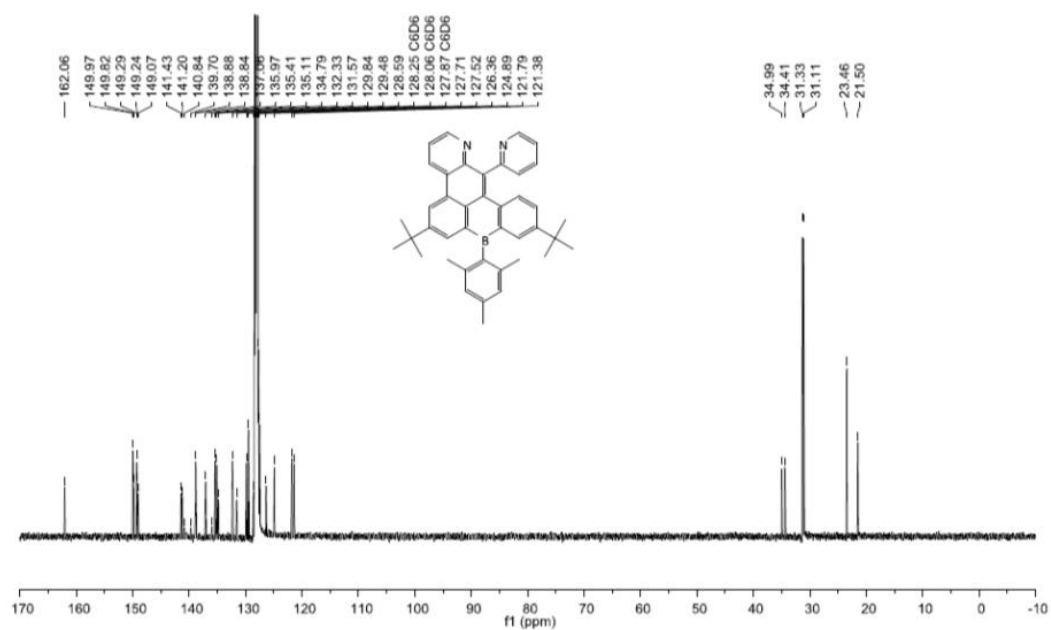


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **11** (C_6D_6 , 125.8 MHz).

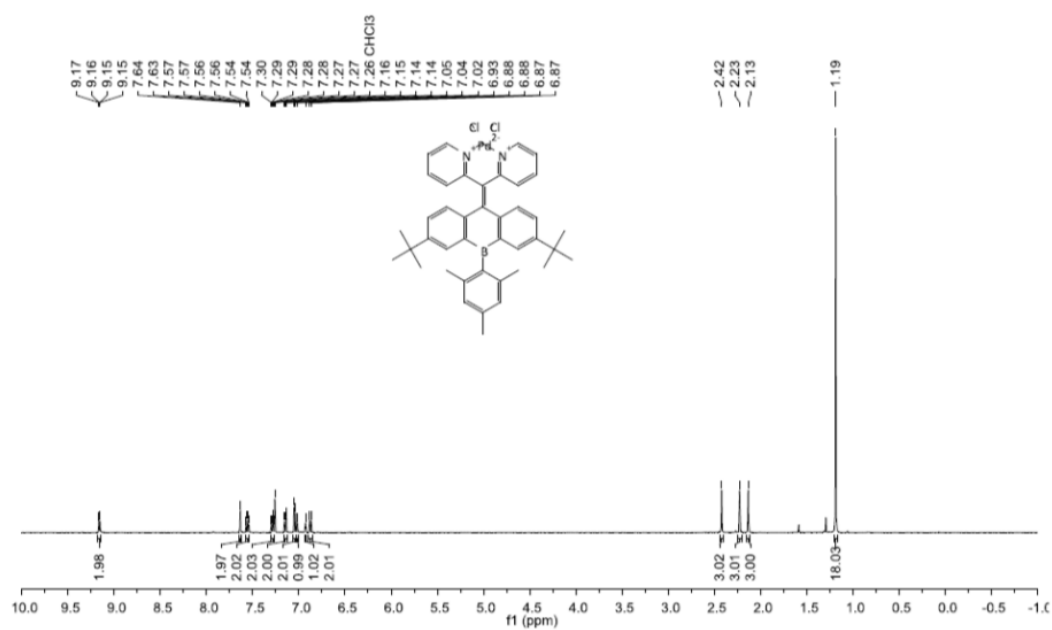


Figure S21: ¹H NMR spectrum of 13 (CDCl₃, 500.2 MHz).

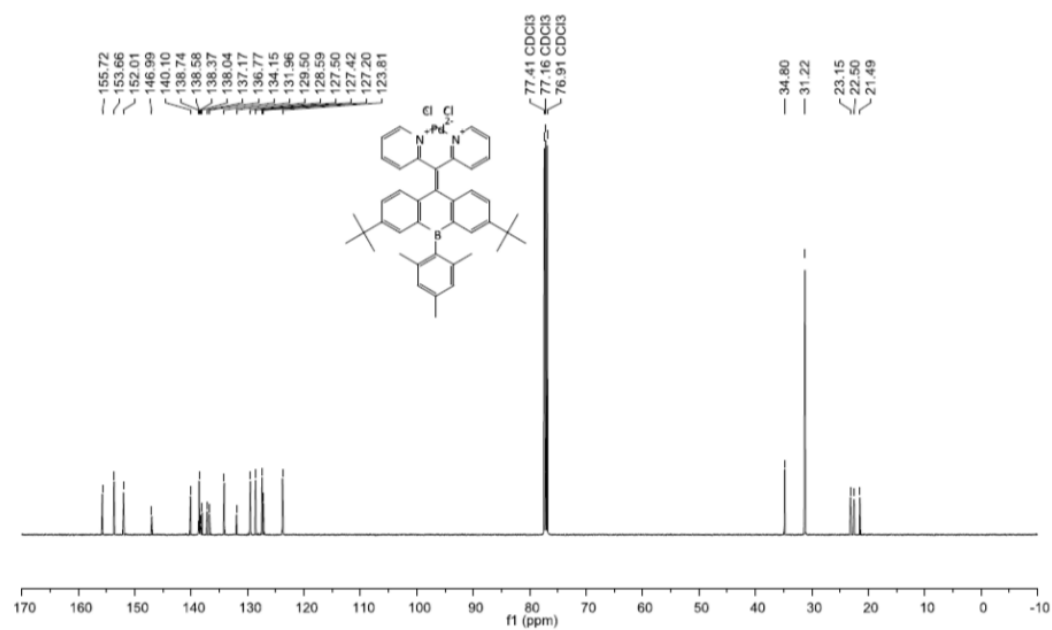


Figure S22: ¹³C{¹H} NMR spectrum of 13 (CDCl₃, 125.8 MHz).

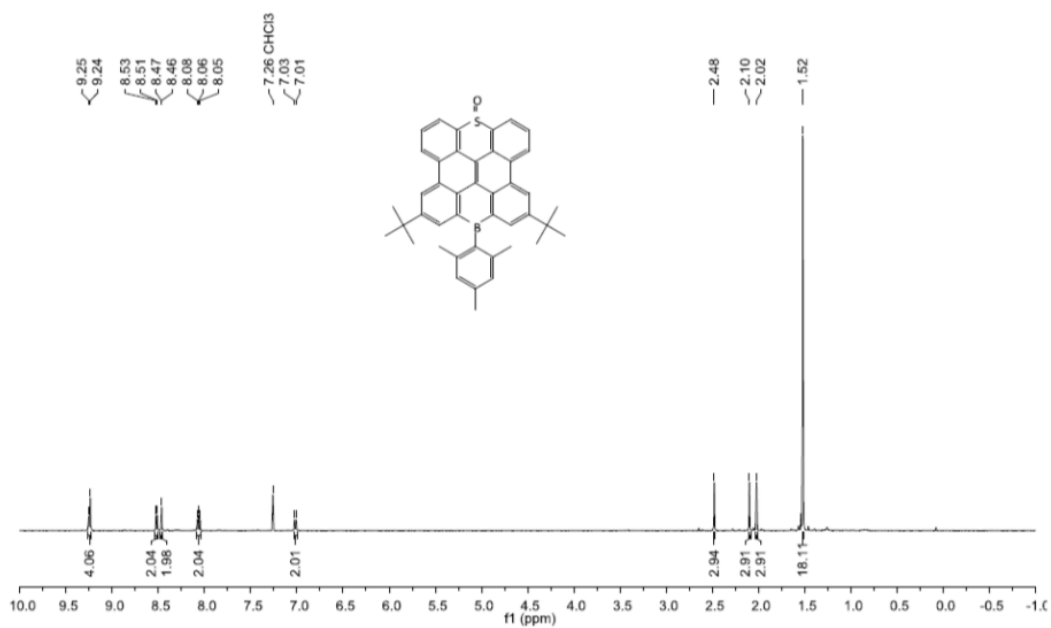


Figure S23: ^1H NMR spectrum of **16** (CDCl_3 , 500.2 MHz).

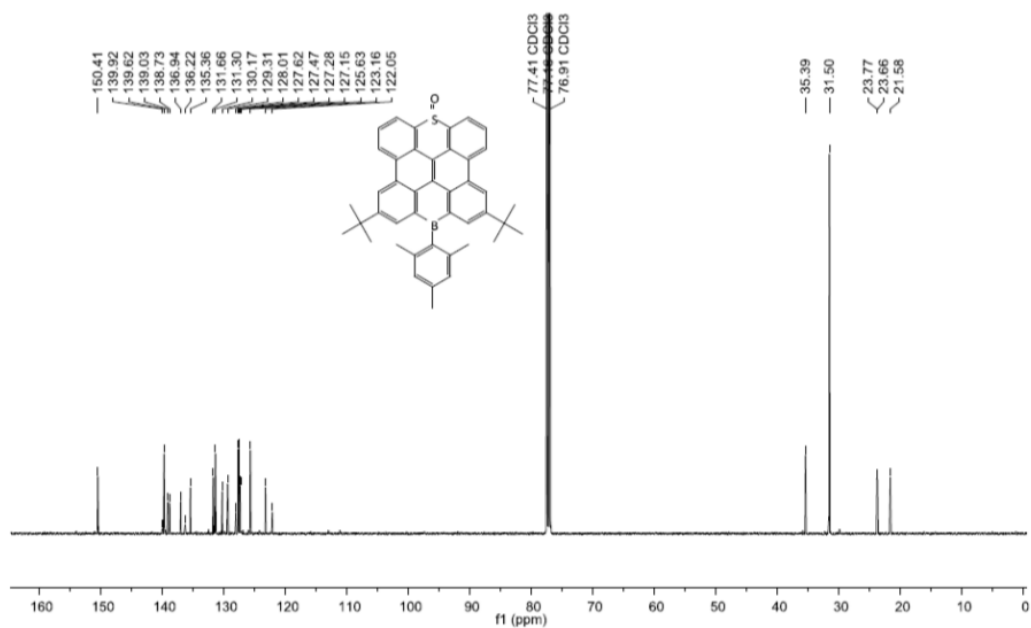


Figure S24: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **16** (CDCl_3 , 125.8 MHz).

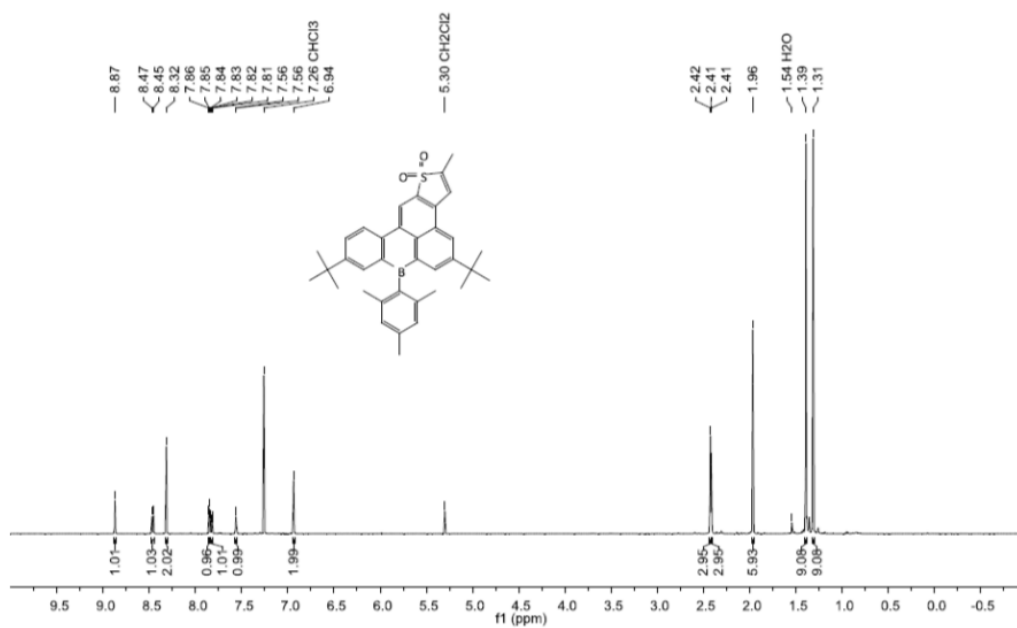


Figure S25: ^1H NMR spectrum of **17** (CDCl_3 , 500.2 MHz).

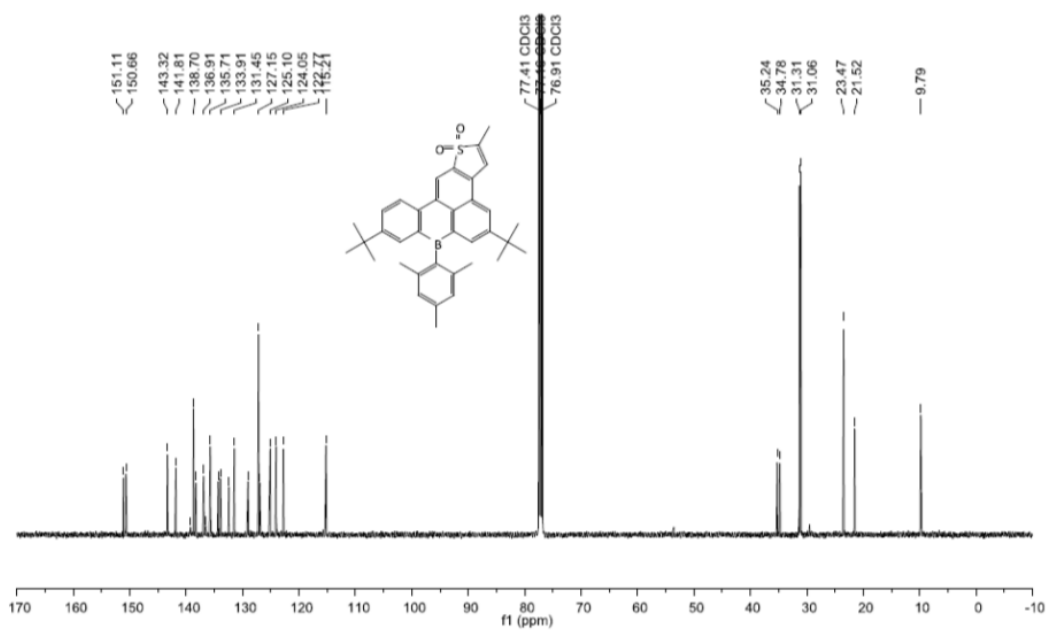


Figure S26: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **17** (CDCl_3 , 125.8 MHz).

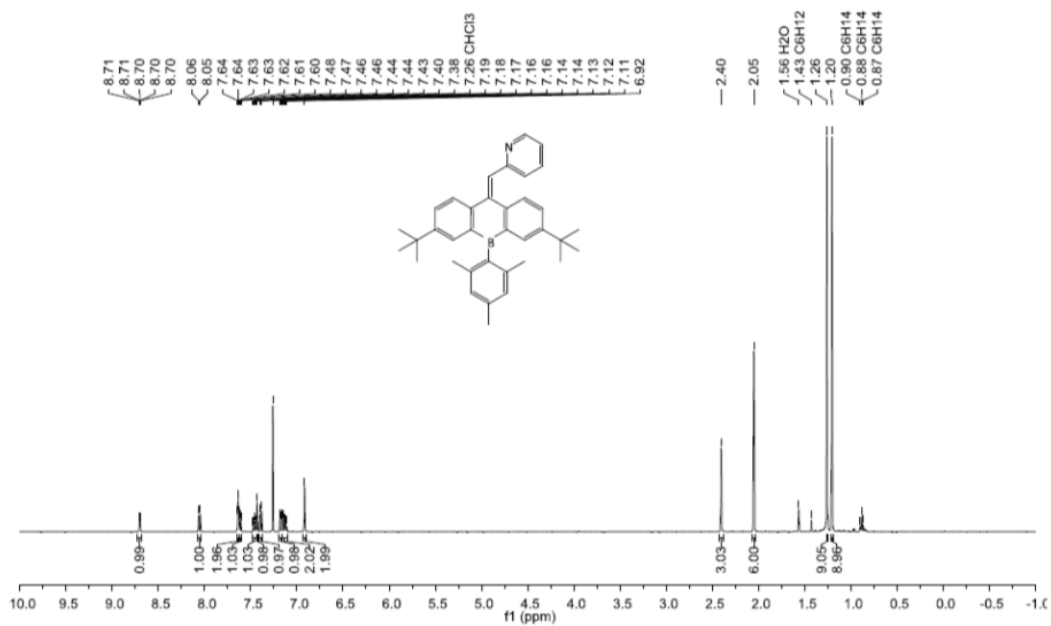


Figure S27: ¹H NMR spectrum of S1 (CDCl₃, 500.2 MHz).

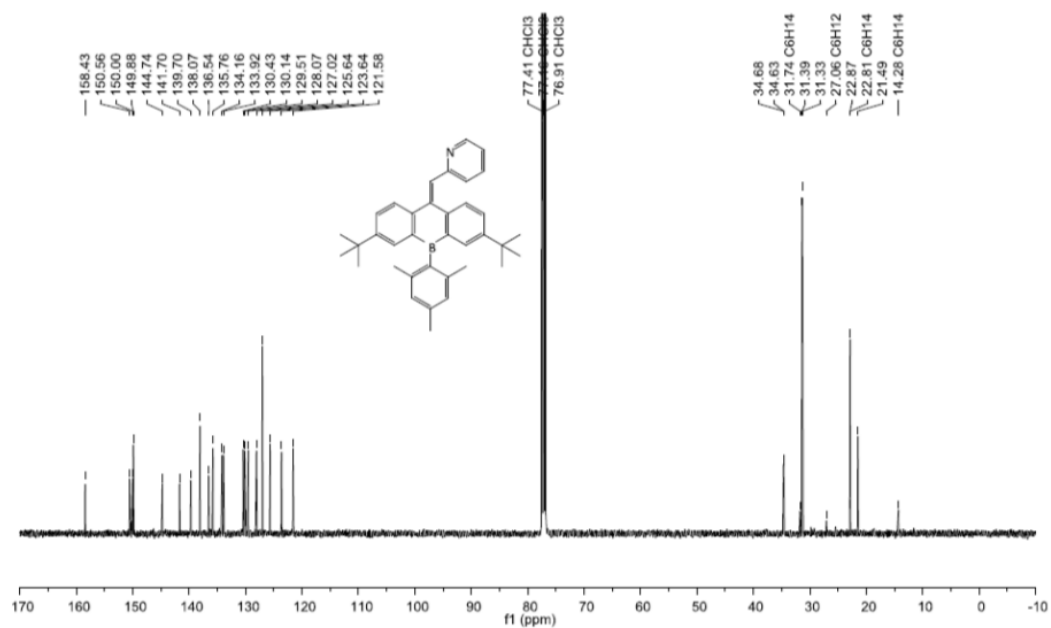
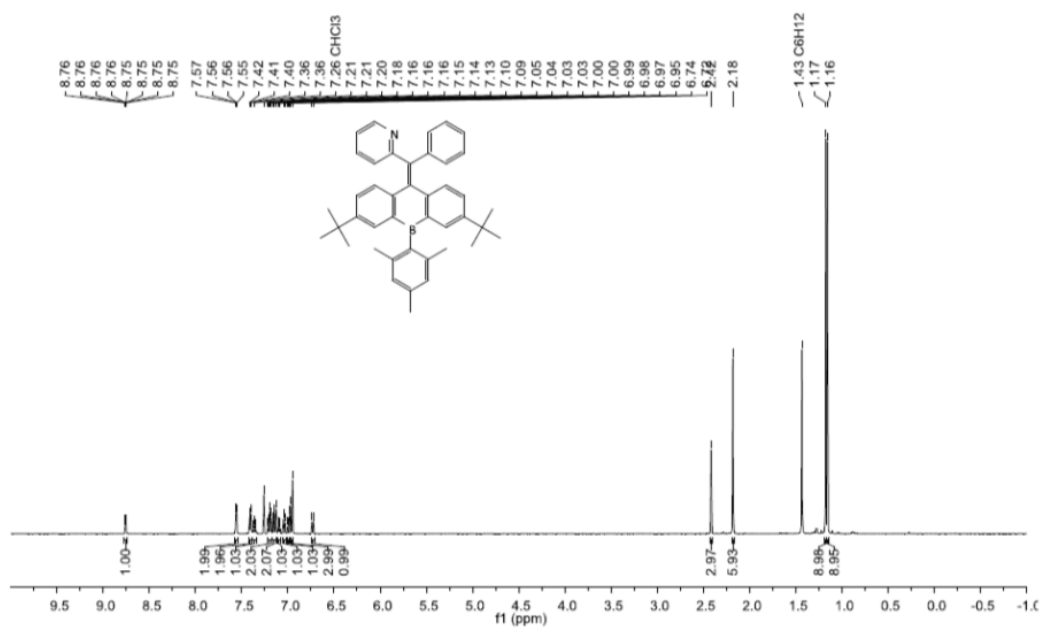
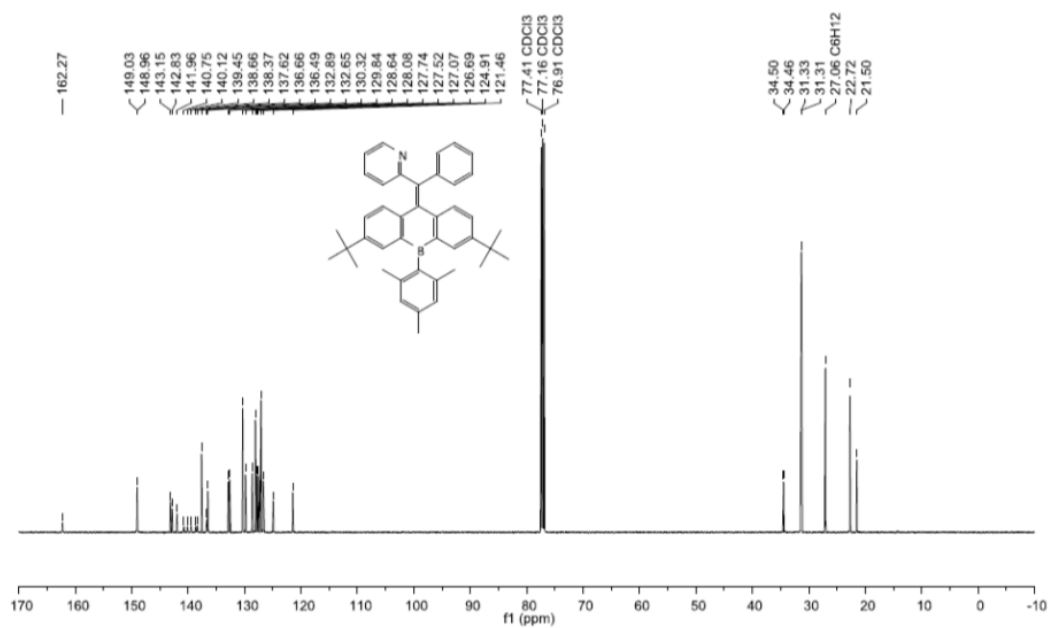


Figure S28: ¹³C{¹H} NMR spectrum of S1 (CDCl₃, 125.8 MHz).

Figure S29: ¹H NMR spectrum of S2 (CDCl₃, 500.2 MHz).Figure S30: ¹³C{¹H} NMR spectrum of S2 (CDCl₃, 125.8 MHz).

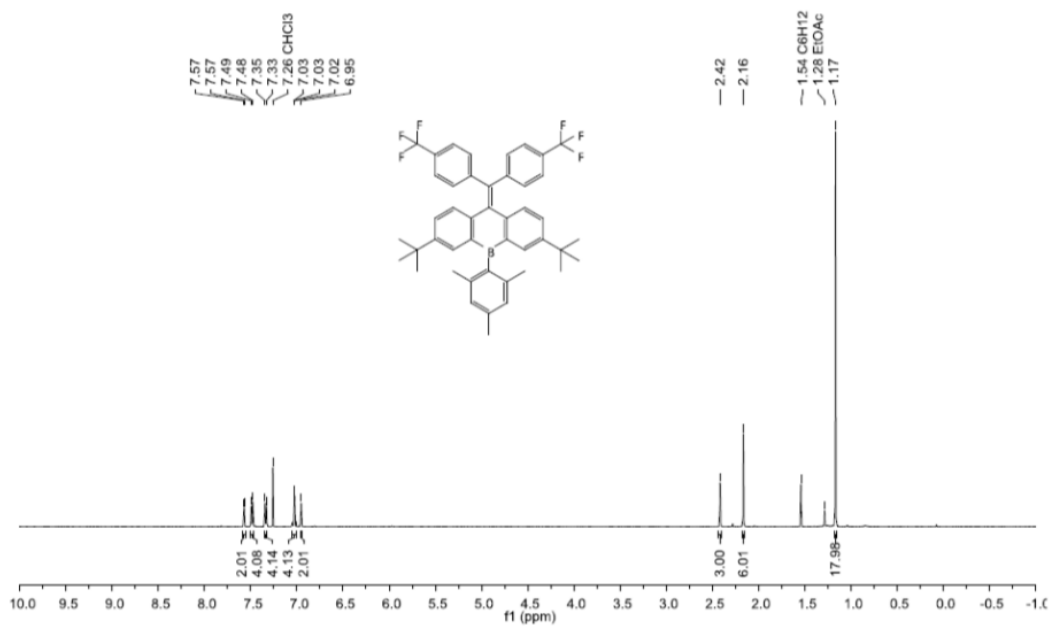


Figure S31: ¹H NMR spectrum of S7 (CDCl₃, 500.2 MHz).

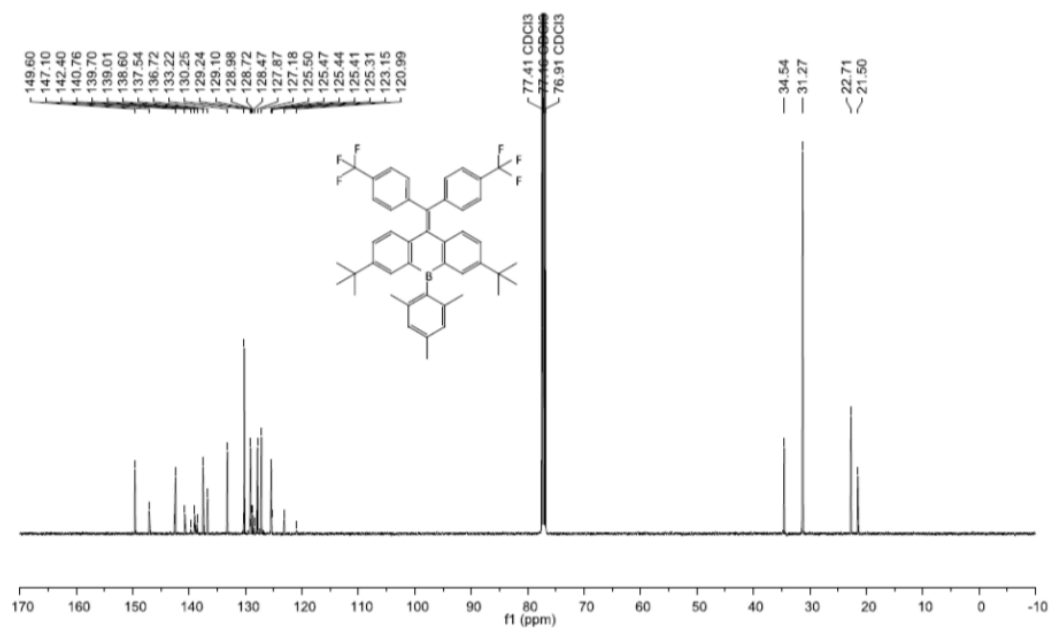


Figure S32: ¹³C{¹H} NMR spectrum of S7 (CDCl₃, 125.8 MHz).

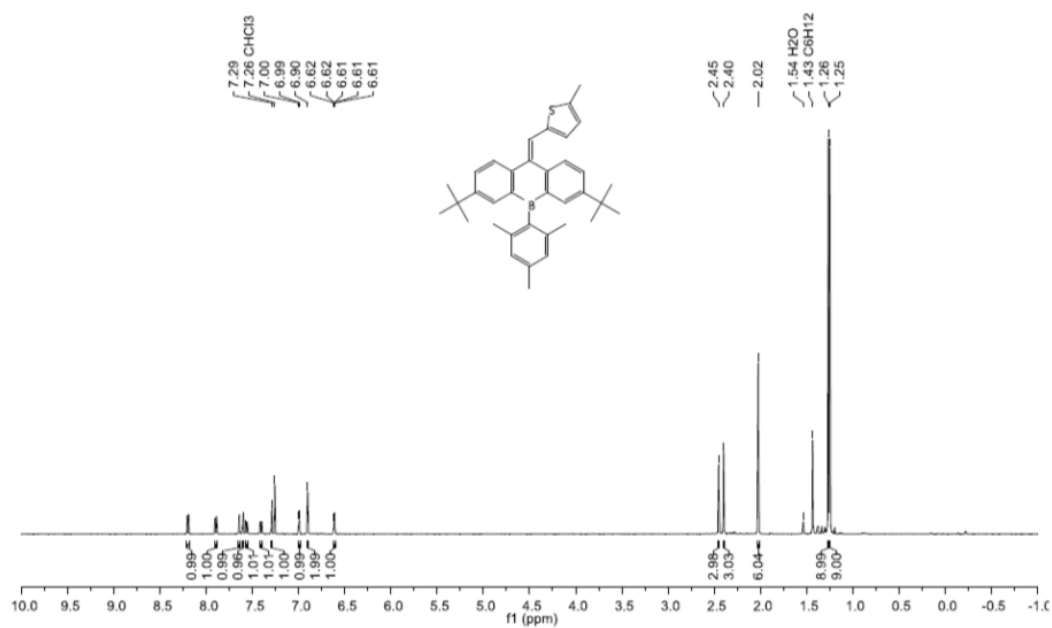


Figure S33: ¹H NMR spectrum of S8 (CDCl₃, 500.2 MHz).

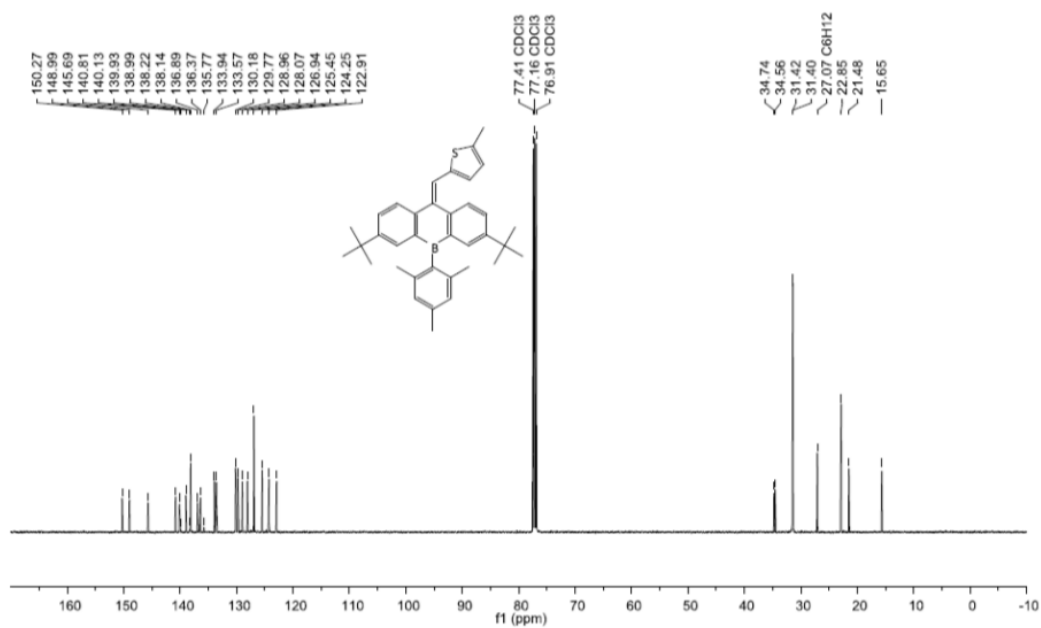


Figure S34: ¹³C{¹H} NMR spectrum of S8 (CDCl₃, 125.8 MHz).

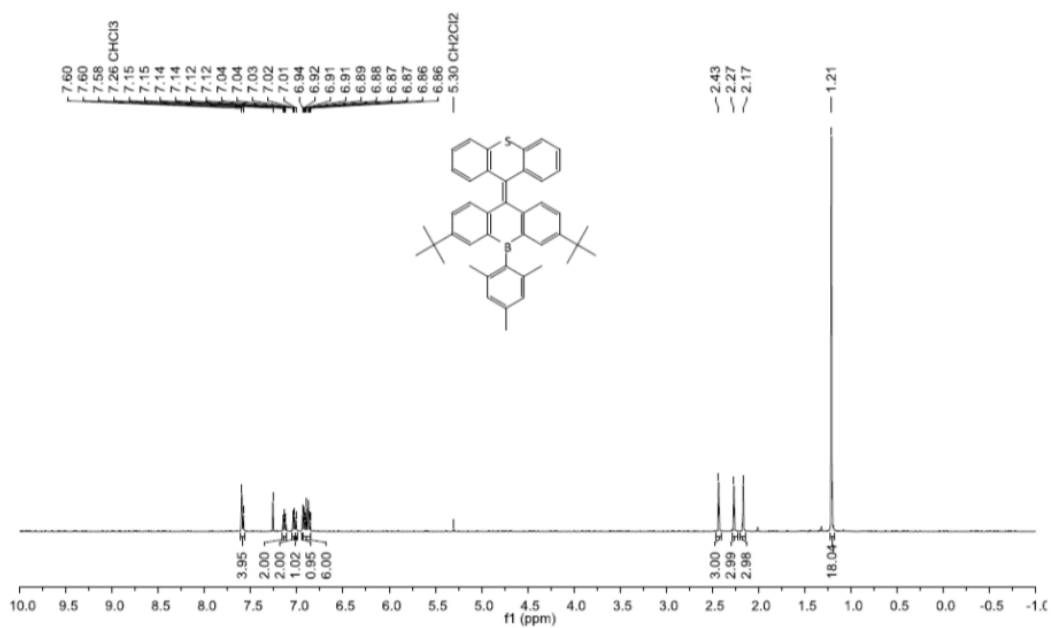


Figure S35: ^1H NMR spectrum of S11 (CDCl_3 , 500.2 MHz).

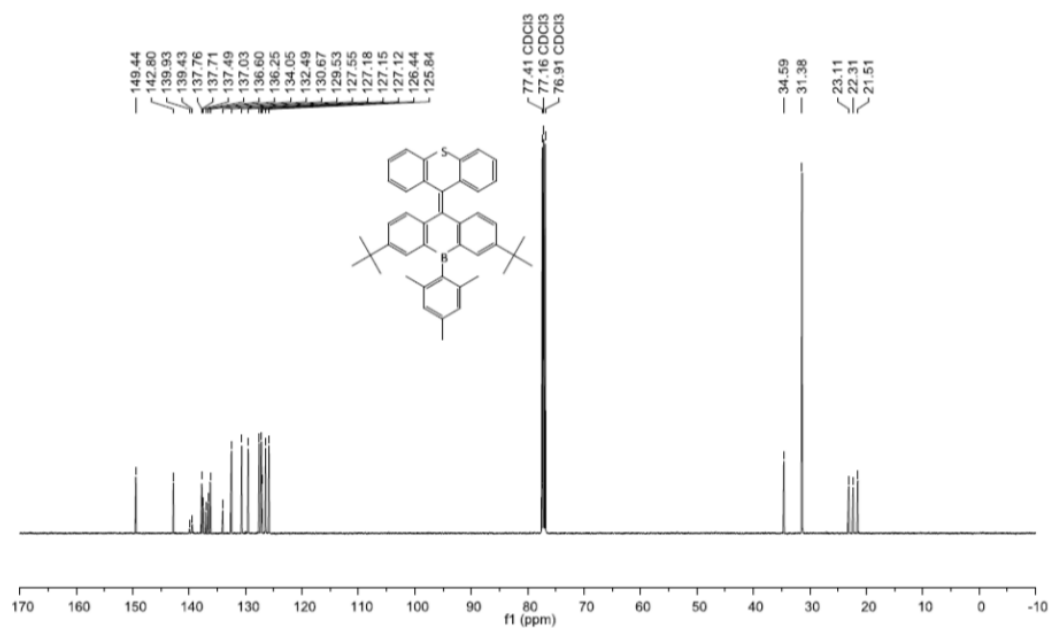
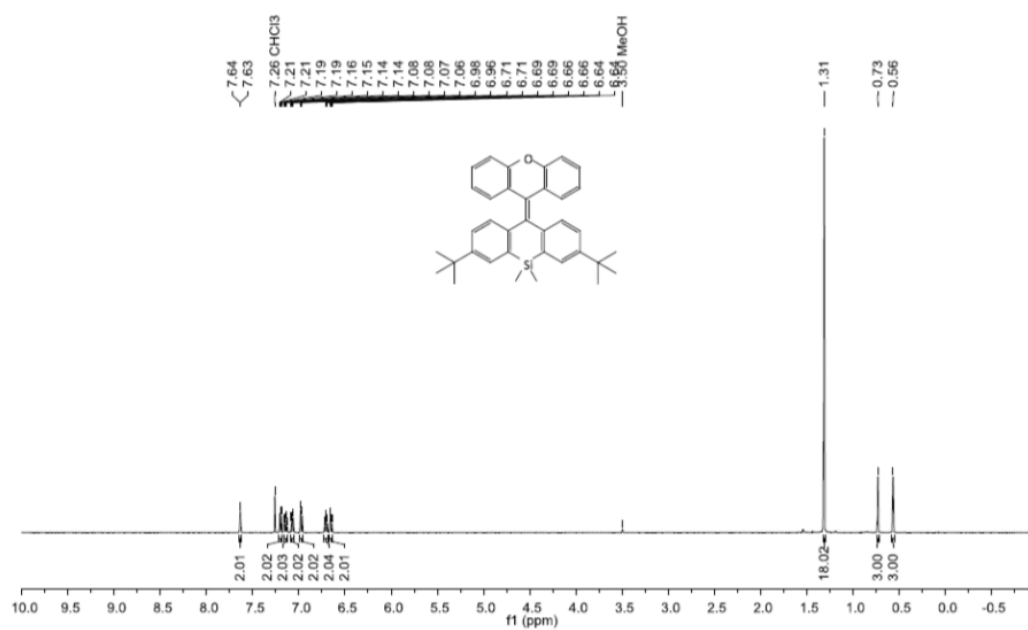
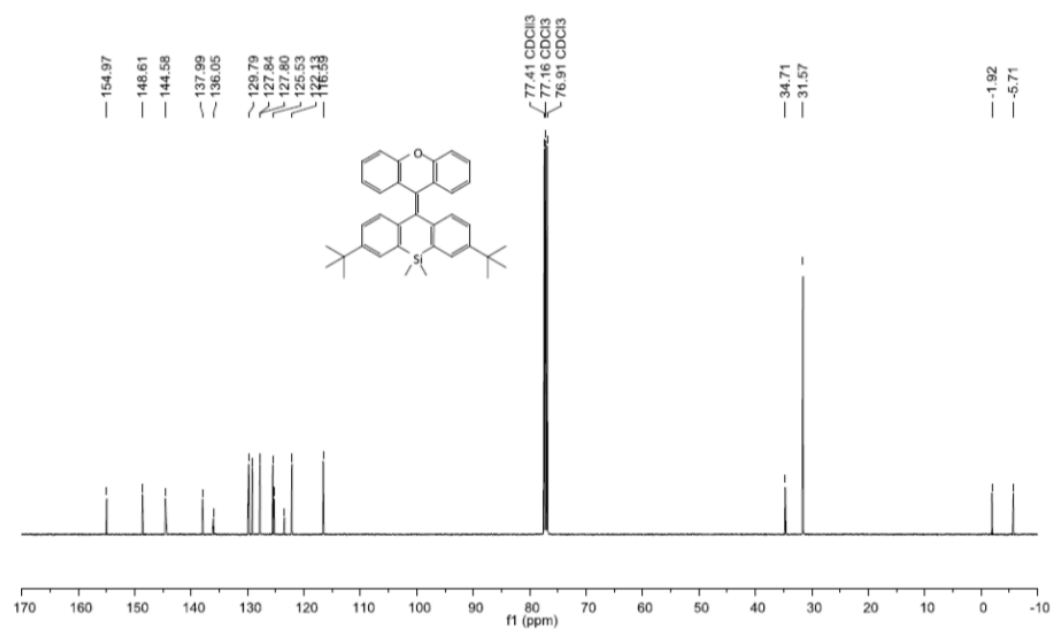


Figure S36: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of S11 (CDCl_3 , 125.8 MHz).

Figure S37: ^1H NMR spectrum of S12 (CDCl_3 , 500.2 MHz).Figure S38: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of S12 (CDCl_3 , 125.8 MHz).

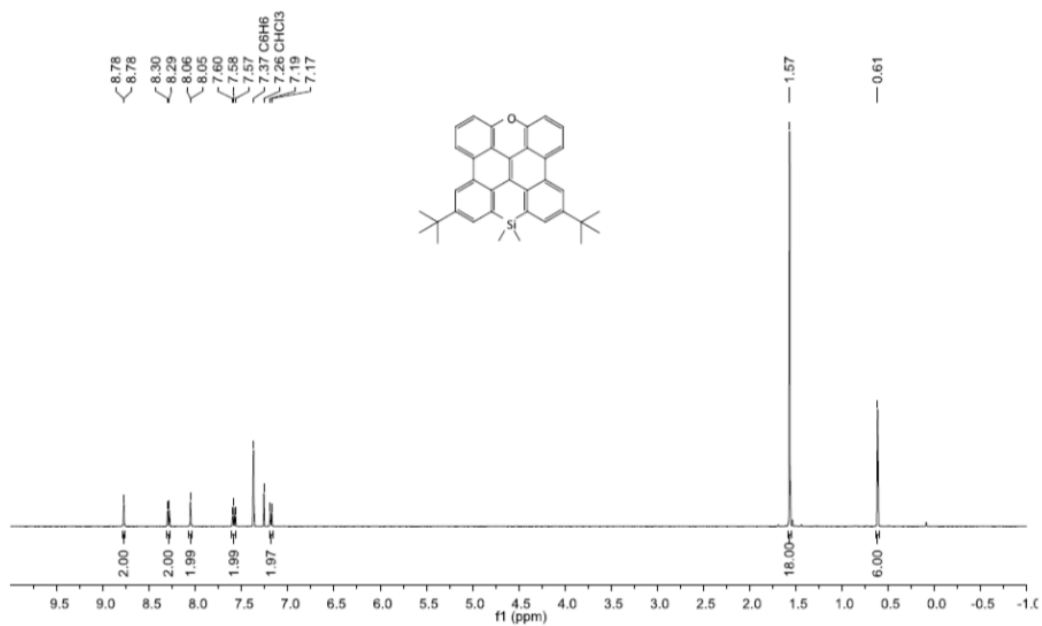


Figure S39: ^1H NMR spectrum of S13 (CDCl_3 , 500.2 MHz).

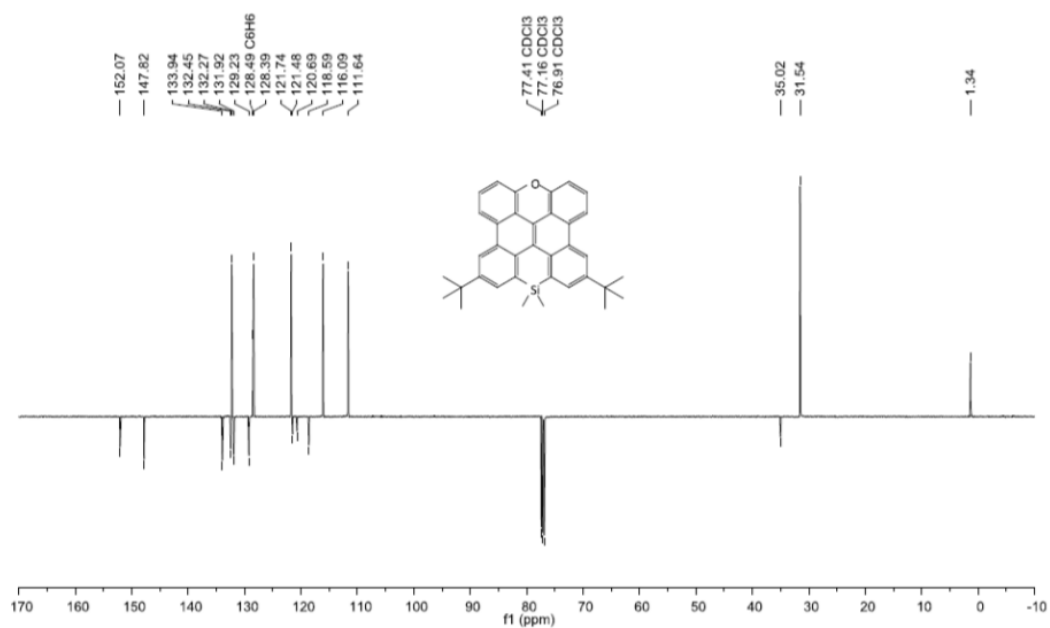


Figure S40: $^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR spectrum of S13 (CDCl_3 , 125.8 MHz).

6. UV/Vis absorption and emission spectra

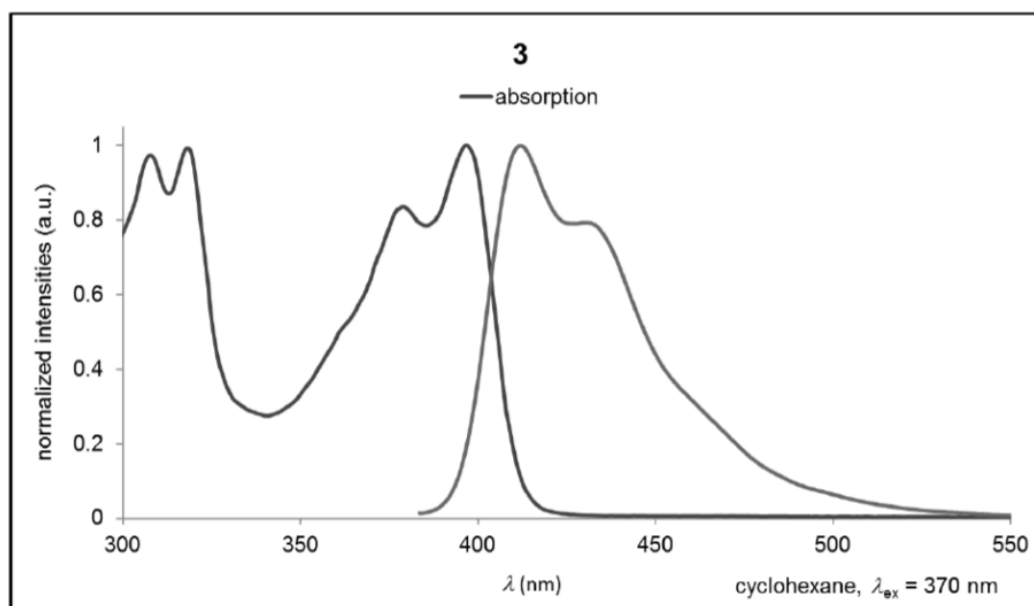


Figure S41: Normalized UV/Vis absorption and emission spectrum of 3.

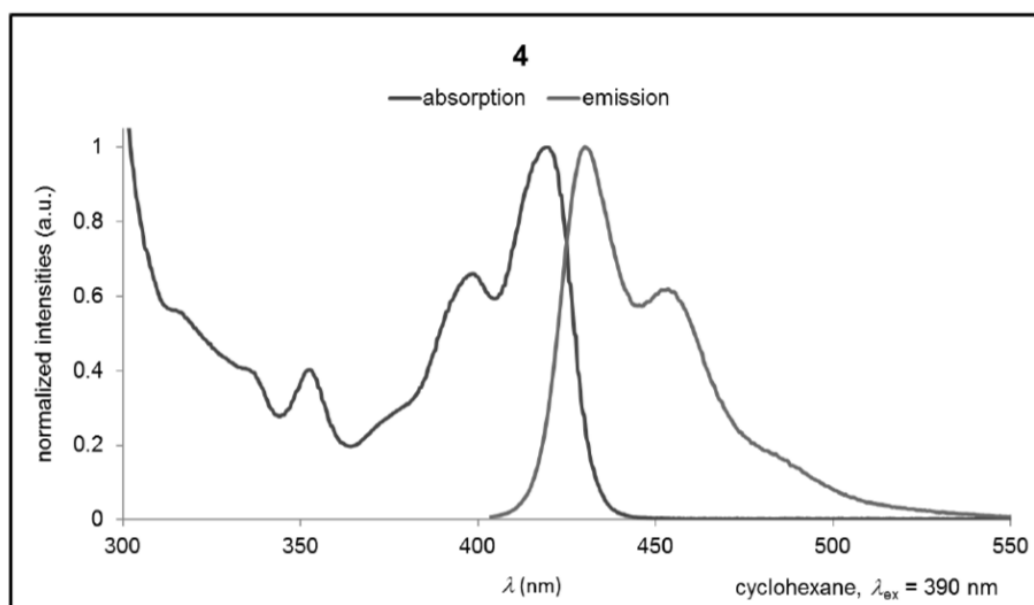


Figure S42: Normalized UV/Vis absorption and emission spectrum of 4.

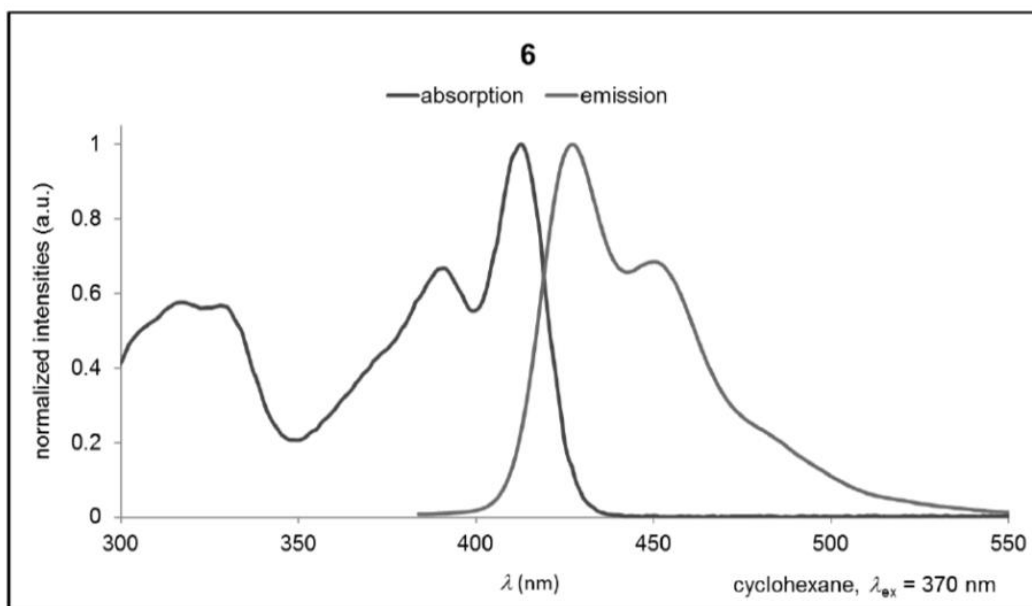


Figure S43: Normalized UV/Vis absorption and emission spectrum of 6.

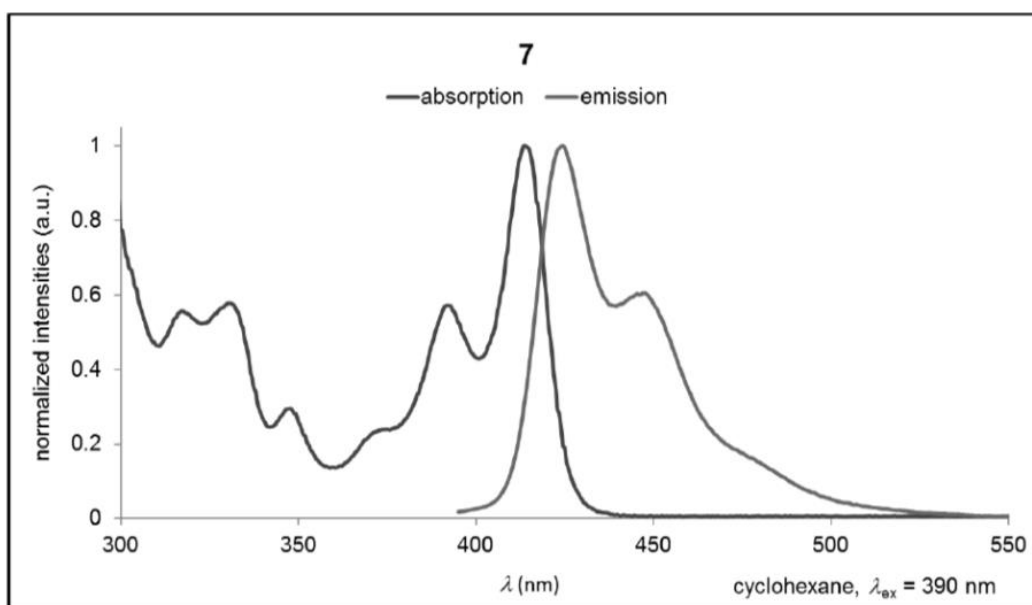


Figure S44: Normalized UV/Vis absorption and emission spectrum of 7.

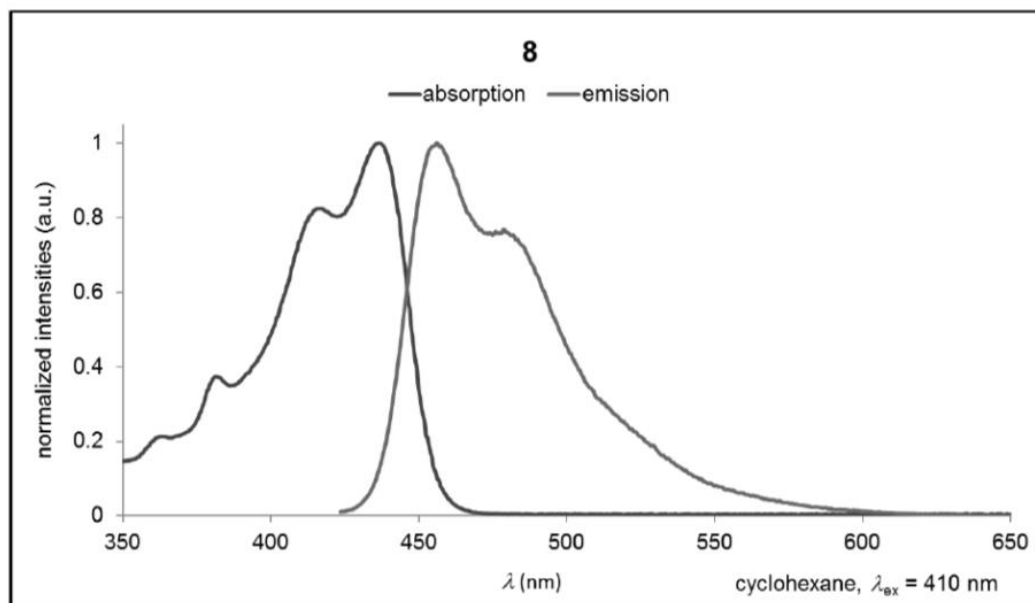


Figure S45: Normalized UV/Vis absorption and emission spectrum of 8.

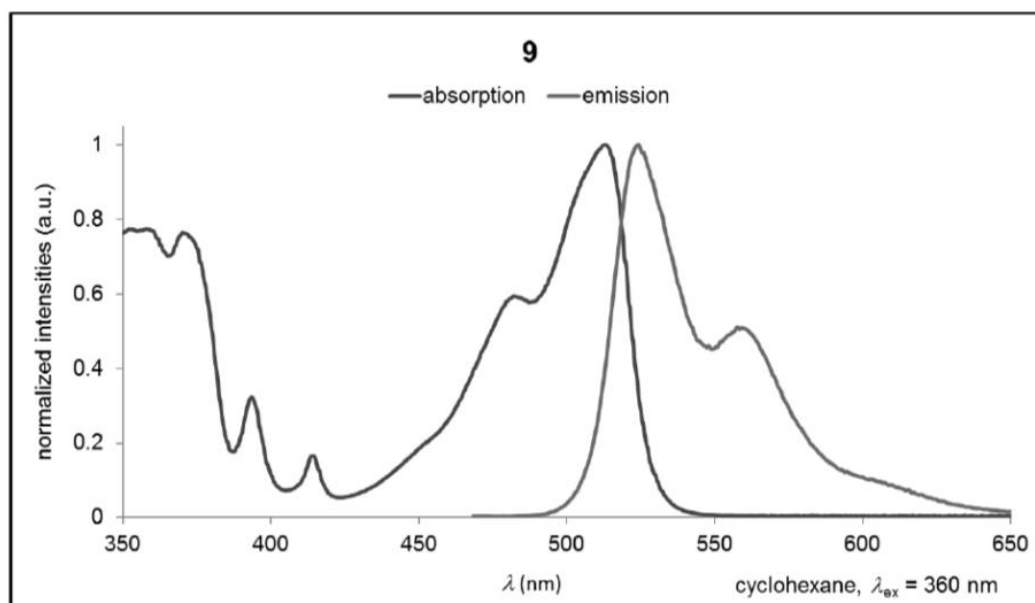


Figure S46: Normalized UV/Vis absorption and emission spectrum of 9.

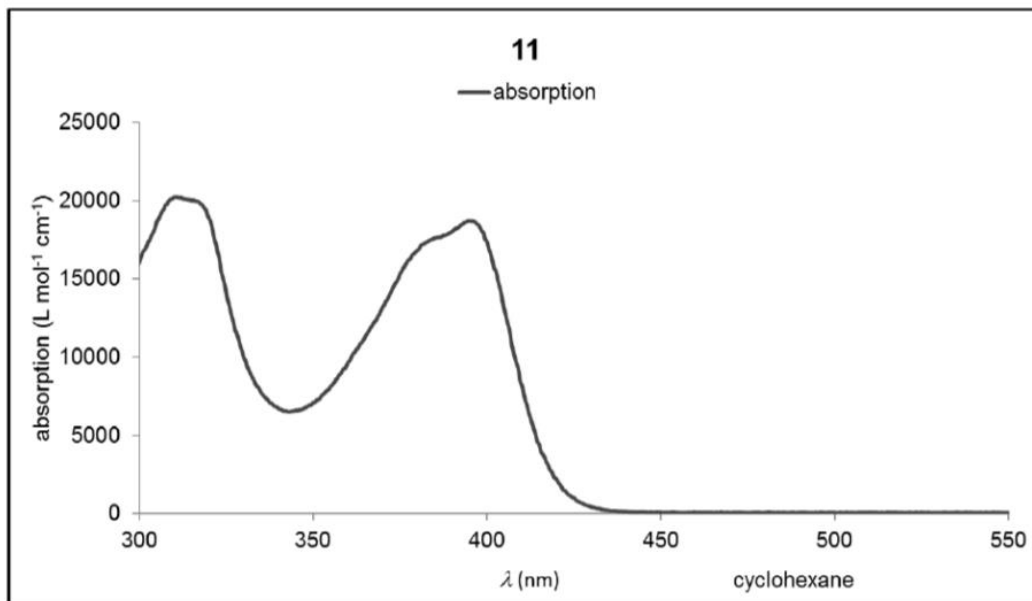


Figure S47: UV/Vis absorption spectrum of **11**. Note: The compound shows no photoluminescence.

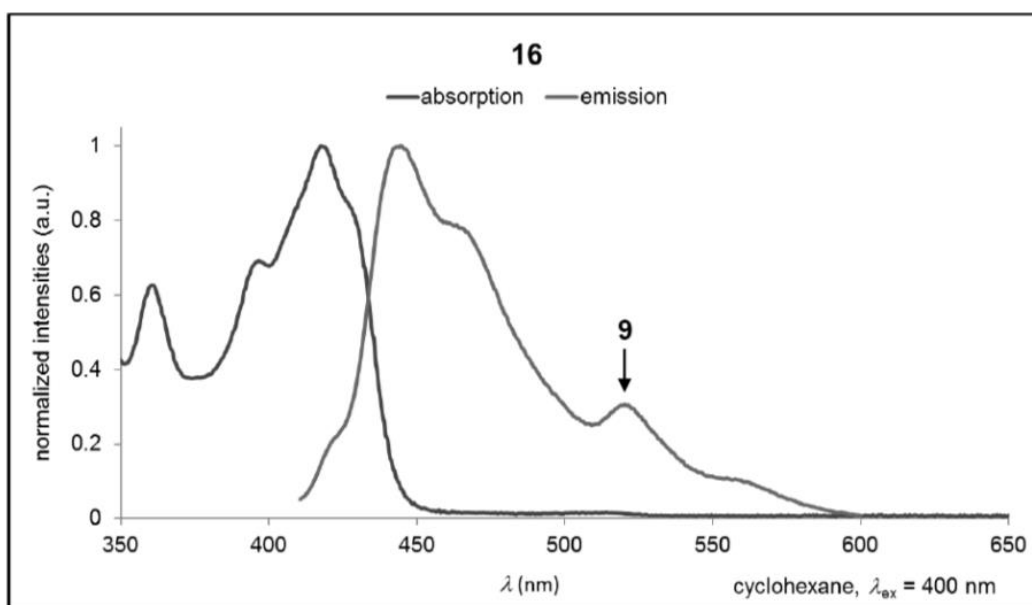


Figure S48: Normalized UV/Vis absorption and emission spectrum of **16**. Note: Compound **16** tends to lose oxygen and to convert back to **9** under the conditions of UV/Vis and PL measurements.

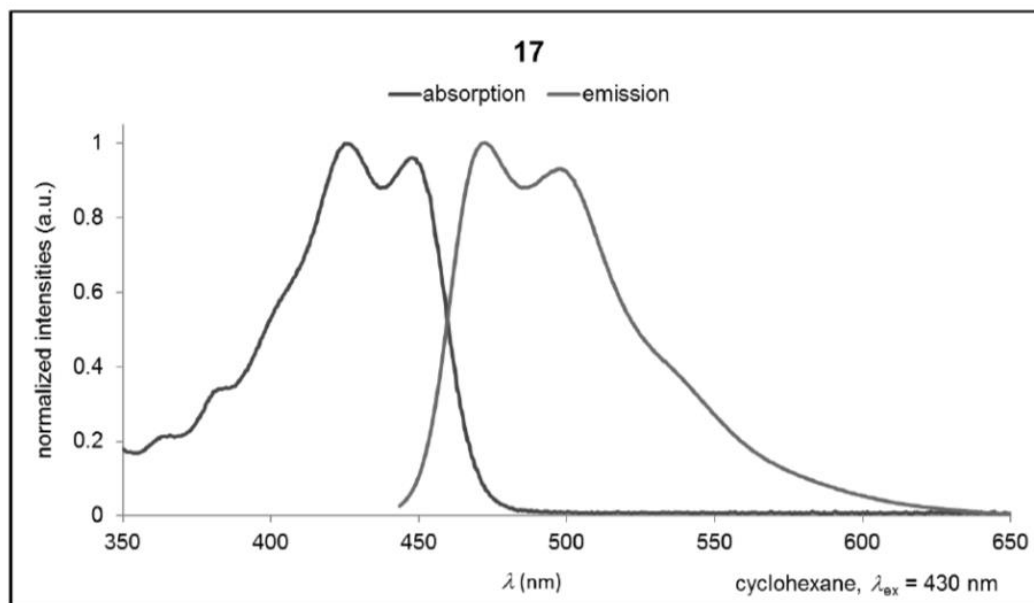


Figure S49: Normalized UV/Vis absorption and emission spectrum of 17.

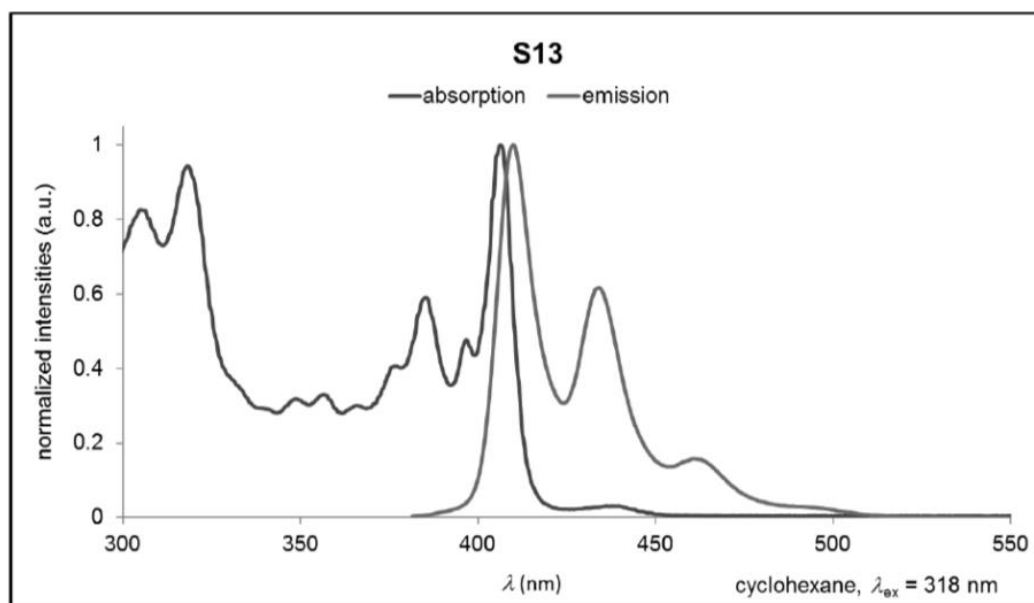


Figure S50: Normalized UV/Vis absorption and emission spectrum of S13.

7. Plots of cyclic voltammograms

Note: Redox events at anodic potential values were only recorded if the corresponding transitions are not entirely ill-defined.

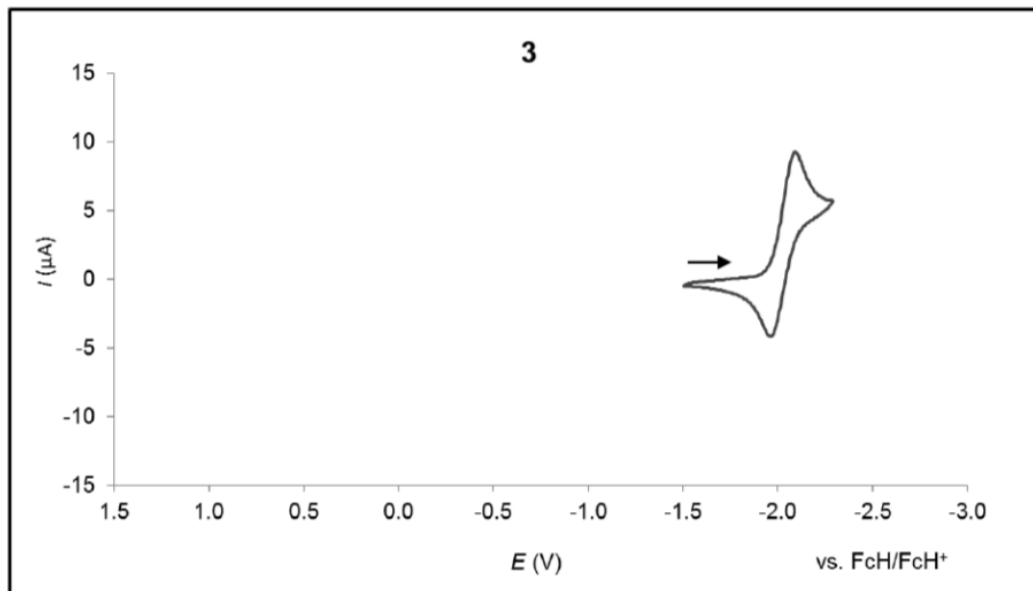


Figure S51: Cyclic voltammogram of **3** in CH₂Cl₂ (room temperature, supporting electrolyte: [nBu₄N][PF₆] (0.1 M), scan rate 200 mV s⁻¹).

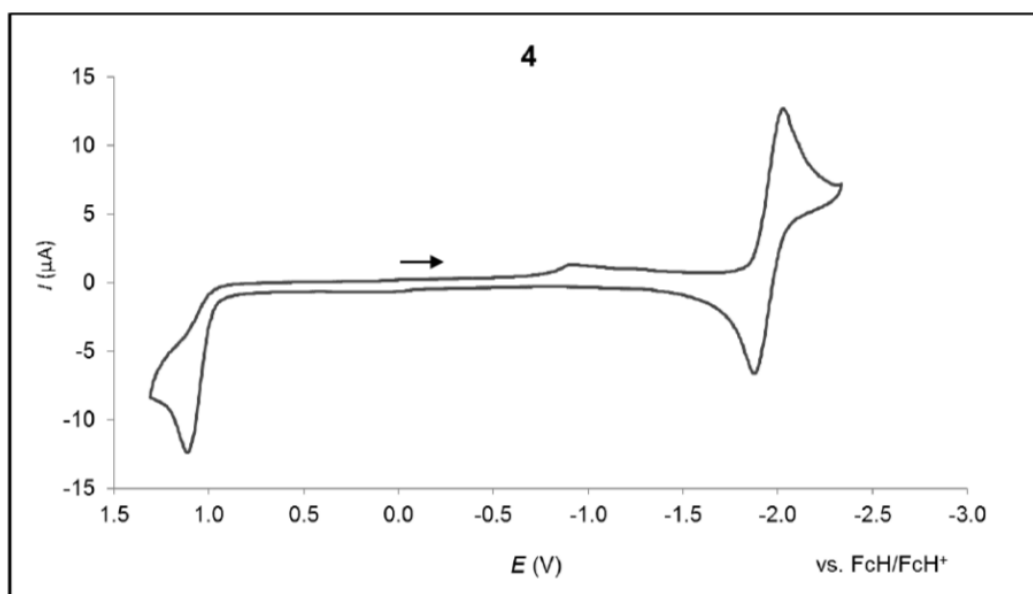


Figure S52: Cyclic voltammogram of **4** in CH₂Cl₂ (room temperature, supporting electrolyte: [nBu₄N][PF₆] (0.1 M), scan rate 100 mV s⁻¹).

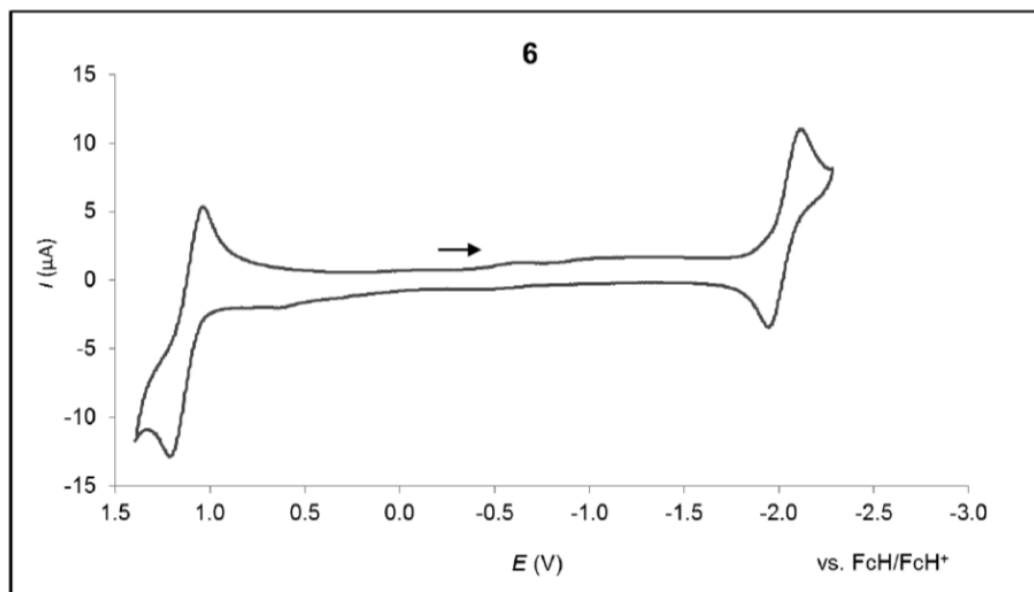


Figure S53: Cyclic voltammogram of **6** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

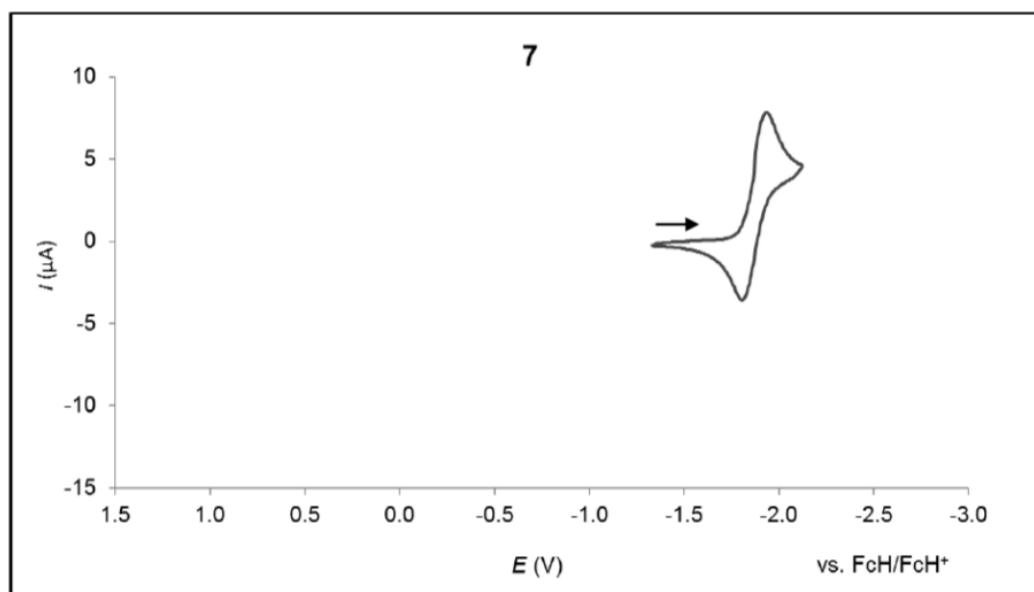


Figure S54: Cyclic voltammogram of **7** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}).

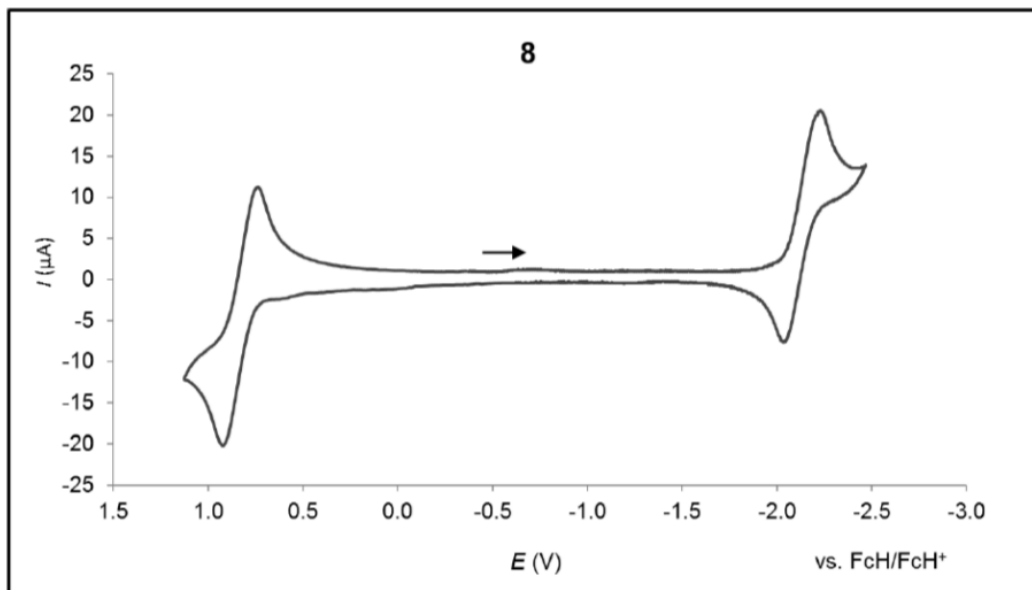


Figure S55: Cyclic voltammogram of **8** in CH₂Cl₂ (room temperature, supporting electrolyte: [nBu₄N][PF₆] (0.1 M), scan rate 200 mV s⁻¹).

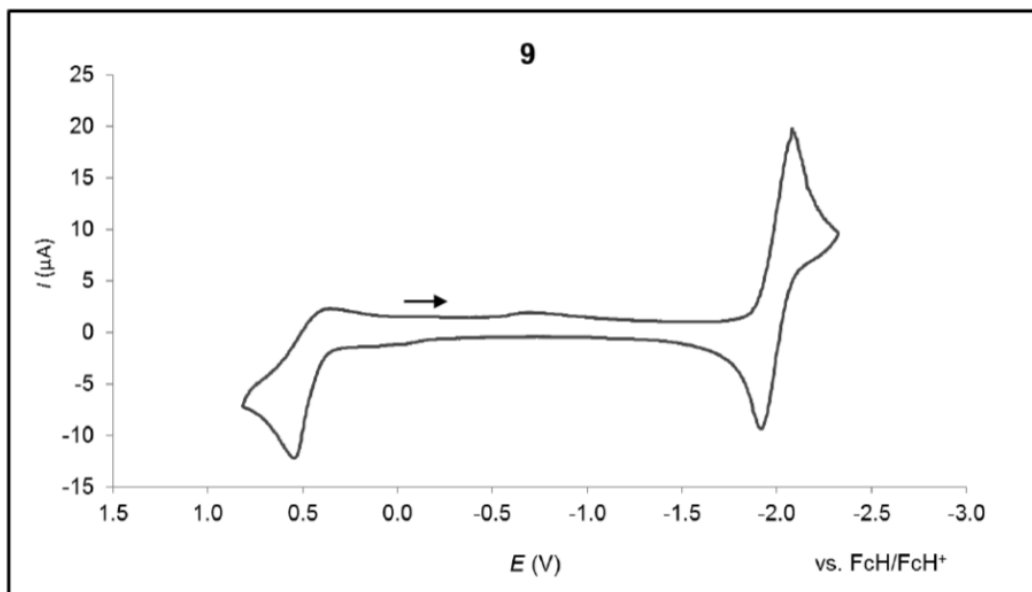
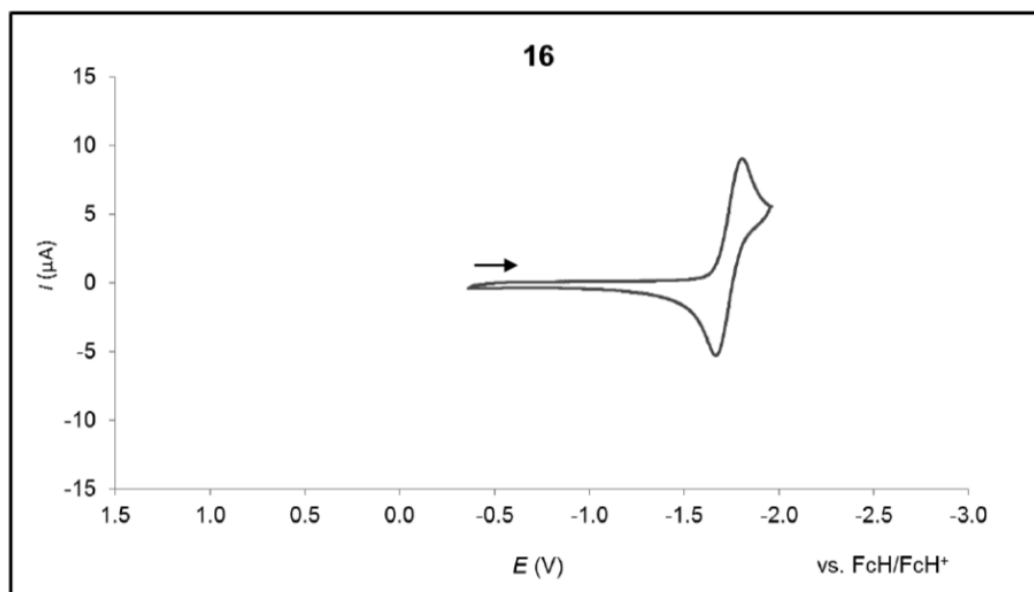
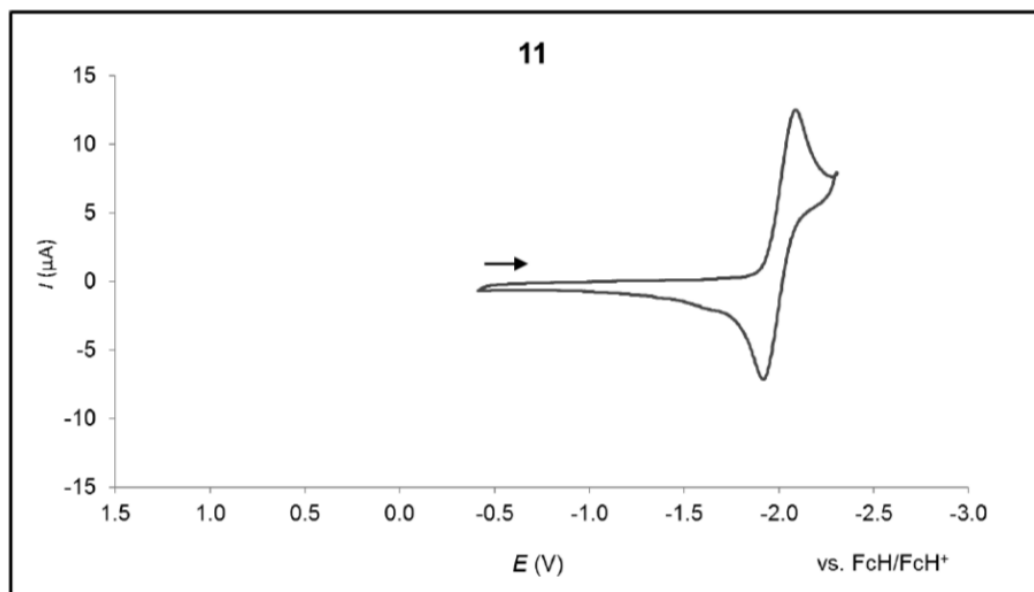


Figure S56: Cyclic voltammogram of **9** in CH₂Cl₂ (room temperature, supporting electrolyte: [nBu₄N][PF₆] (0.1 M), scan rate 200 mV s⁻¹).



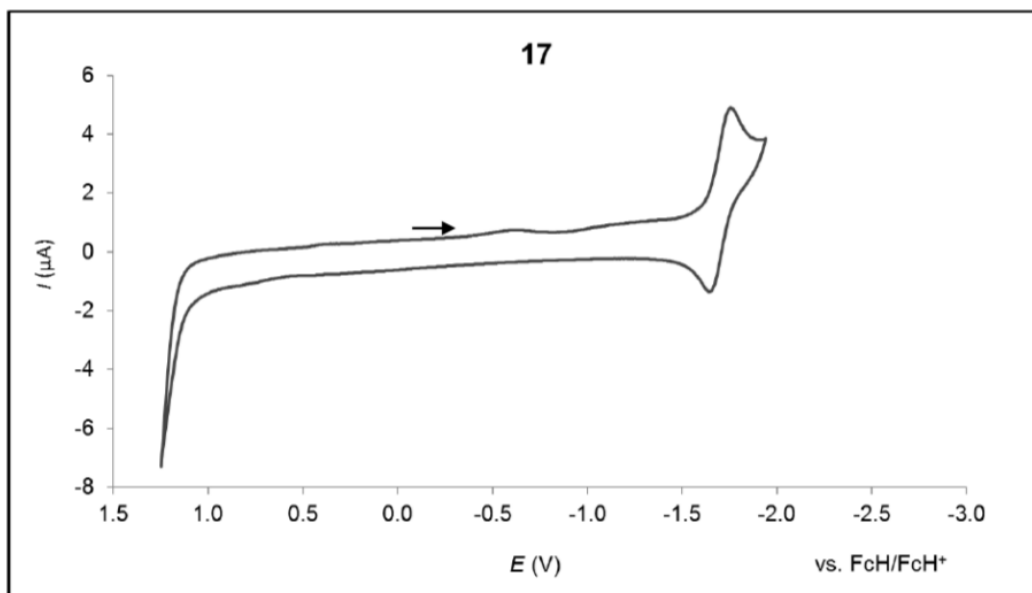


Figure S59: Cyclic voltammogram of **17** in CH_2Cl_2 (room temperature, supporting electrolyte: $[\text{nBu}_4\text{N}][\text{PF}_6]$ (0.1 M), scan rate 200 mV s^{-1}). Note: CH_2Cl_2 decomposes at $E = 1.2 \text{ V}$.

8. X-ray crystal structure analyses

Data for all structures were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and were scaled using the frame scaling procedure in the *X-AREA*^[S10] program system. The structures were solved by direct methods using the program *SHELXS*^[S11] and refined against F^2 with full-matrix least-squares techniques using the program *SHELXL-97*.^[S11]

In 1477502 (**4**), the N/CH atoms are mutually disordered with a site occupation factor of 0.68(2) for the major occupied site. C and N sharing the same site were refined with their coordinates and their displacement parameters constrained to the same values. The displacement parameters of the three acetonitrile atoms were restrained to an isotropic behavior.

In 1477508 (**9**), one *t*-Bu group is disordered over two positions with a site occupation factor of 0.50(2) for the major occupied site. The displacement parameters of the disordered atoms were restrained to an isotropic behavior.

In 1477503 (**11**), the pyridyl ring is disordered over two positions with a site occupation factor of 0.57(2) for the major occupied site.

In 1477504 (**13**), one *t*-Bu group is disordered over two positions with a site occupation factor of 0.70(1) for the major occupied site. The displacement parameters of the disordered atoms were restrained to an isotropic behavior. Bond lengths and angles of the two disordered moieties were restrained to those of the non-disordered *t*-Bu group.

In 1477506 (**16**), the contribution of the disordered solvent has been suppressed using the SQUEEZE option in PLATON.^[S12]

The crystal of 1477505 (**17**) was a racemic twin with a fractional contribution of 0.52(10) of the major domain.

The crystal of 1477509 (**S11**) was a non-merohedral twin with a fractional contribution of 0.663(1) of the major domain. Four atoms of the mesityl ring are disordered over two positions with a site occupation factor of 0.53(4) for the major occupied site.

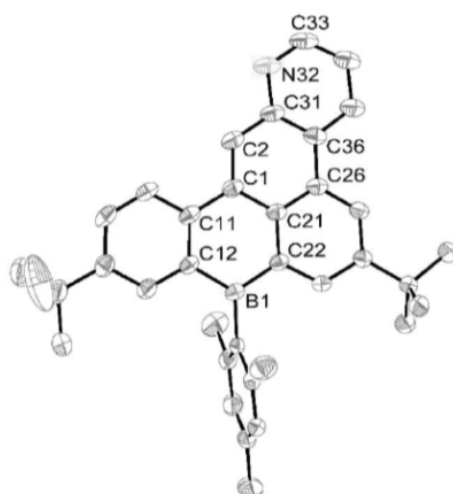


Figure S60 (CCDC 1477501): Molecular structure of **3** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): B1–C12 = 1.552(3), B1–C22 = 1.544(3), C1–C2 = 1.363(3), C26–C36 = 1.454(3), C31–N32 = 1.365(3), N32–C33 = 1.318(3); C12–B1–C22 = 116.9(2), C31–N32–C33 = 116.9(2), C2–C31–N32 = 116.5(2), C36–C31–N32 = 123.2(2); C₆(11)//C₆(21) = 6.3(1). C₆(X): Six-membered ring containing C(X).

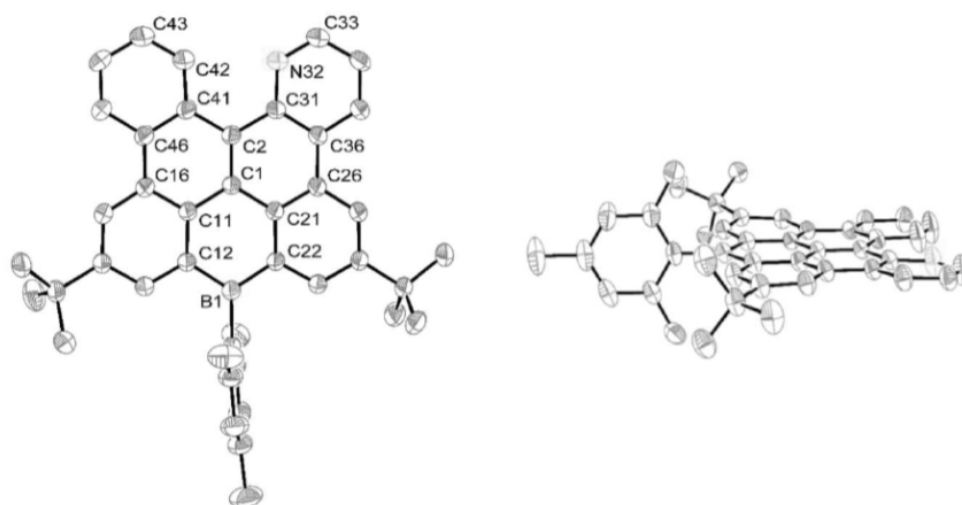


Figure S61 (CCDC 1477502): Molecular structure of **4** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and co-crystallized CH₃CN are omitted for clarity. N32 and C42 were disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [Å] and angles (°): B1–C12 = 1.531(3), B1–C22 = 1.535(3), C1–C2 = 1.407(2), C16–C46 = 1.452(2), C26–C36 = 1.448(2), C31–N32 = 1.375(2), N32–C33 = 1.342(3); C12–B1–C22 = 115.7(2), C31–C2–C41 = 122.3(2); C₆(11)//C₆(21) = 4.7(1), Py(N32)//C₆(41) = 3.7(2). C₆(X): Six-membered ring containing C(X).

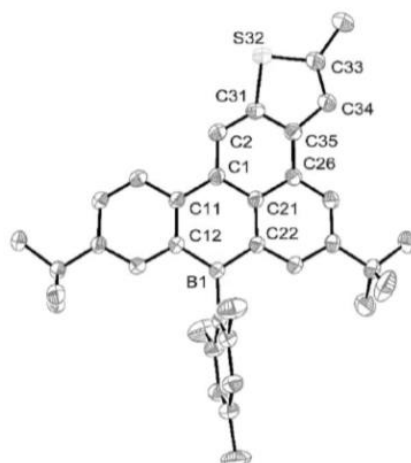


Figure S62 (CCDC 1477507): Molecular structure of **8** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): B1–C12 = 1.540(2), B1–C22 = 1.542(3), C1–C2 = 1.388(3), C31–S32 = 1.743(2), S32–C33 = 1.743(2); C12–B1–C22 = 116.2(2), C31–S32–C33 = 91.8(1); C₆(11)//C₆(21) = 4.2(1). C₆(X): Six-membered ring containing C(X).

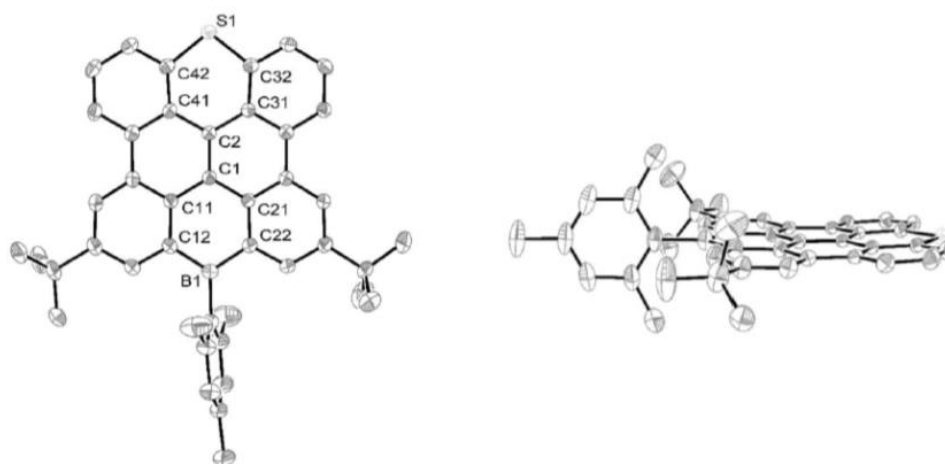


Figure S63 (CCDC 1477508): Molecular structure of **9** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. One of the *t*-Bu substituents was disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [Å] and angles (°): B1–C12 = 1.535(3), B1–C22 = 1.533(3), S1–C32 = 1.736(2), S1–C42 = 1.736(2), C1–C2 = 1.410(2); C12–B1–C22 = 115.8(2), C32–S1–C42 = 103.84(9); C₆(11)//C₆(21) = 1.22(7), C₆(31)//C₆(41) = 1.88(7). C₆(X): Six-membered ring containing C(X).

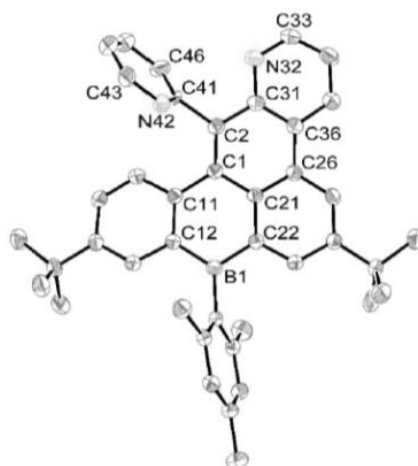


Figure S64 (CCDC 1477503): Molecular structure of **11** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. The 2-pyridyl substituent was disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [Å] and angles (°): B1–C12 = 1.539(3), B1–C22 = 1.550(3), C31–N32 = 1.366(3), N32–C33 = 1.328(3), C41–N42 = 1.34(1), N42–C43 = 1.33(1), C1–C2 = 1.384(3), C2–C31 = 1.447(3), C2–C41 = 1.58(1); C12–B1–C22 = 116.0(2), C31–N32–C33 = 117.5(2); C₆(11)//C₆(21) = 12.3(1), C₆(11)//Py(N42) = 69.8(2), Py(N32)//Py(N42) = 67.1(2)°. C₆(X): Six-membered ring containing C(X).

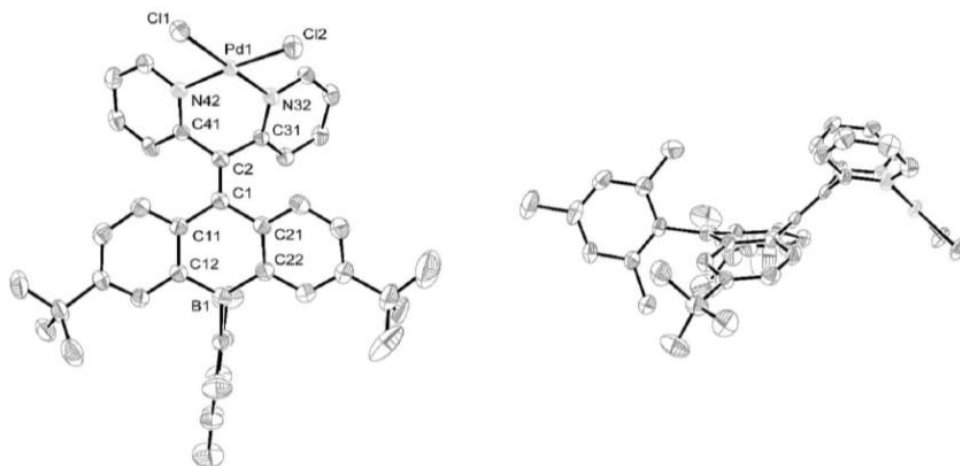


Figure S65 (CCDC 1477504): Molecular structure of **13** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. One of the *t*-Bu substituents was disordered and refined over two positions, only the major occupied conformation is shown. Selected bond lengths [Å] and angles (°): B1–C12 = 1.564(6), B1–C22 = 1.556(6), Pd1–N32 = 2.026(3), Pd1–N42 = 2.037(3), Pd1–Cl1 = 2.303(1), Pd1–Cl2 = 2.282(1), C1–C2 = 1.353(5); C12–B1–C22 = 114.6(3), C31–C2–C41 = 112.2(3), N32–Pd1–N42 = 87.8(1), Cl1–Pd1–N42 = 90.95(8), Cl1–Pd1–Cl2 = 92.24(4), Cl2–Pd1–N32 = 89.08(9); C₆(11)//C₆(21) = 37.9(2), Py(N32)//Py(N42) = 63.4(1). C₆(X): Six-membered ring containing C(X).

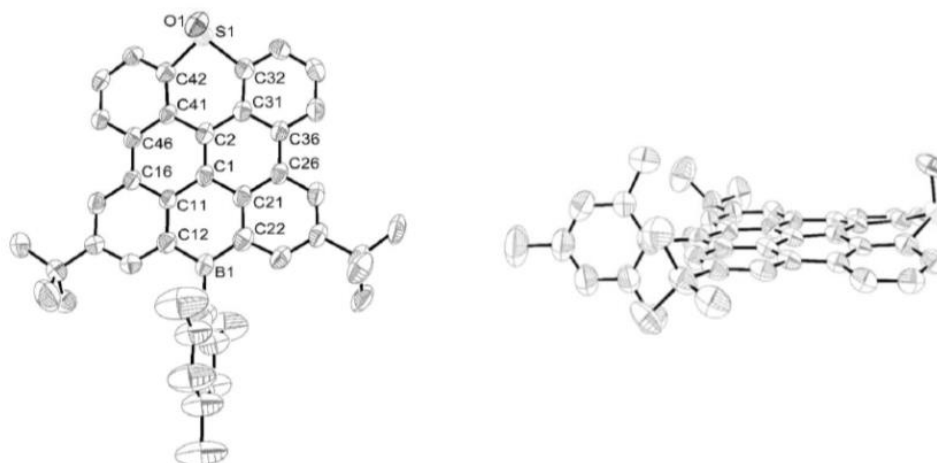


Figure S66 (CCDC 1477506): Molecular structure of **16** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles (°), and dihedral angles (°): B1–C12 = 1.507(7), B1–C22 = 1.512(7), S1–O1 = 1.499(3), S1–C32 = 1.774(4), S1–C42 = 1.772(5), C1–C2 = 1.401(6); C12–B1–C22 = 116.9(4), C32–S1–C42 = 98.0(2), O1–S1–C32 = 105.6(2), O1–S1–C42 = 107.2(2); O1–S1–C32–C31 = 75.6(4), O1–S1–C42–C41 = –75.8(4), C31/C32/C41/C42//C32/S1/C42 = 28.3(3), C₆(11)//C₆(21) = 3.1(2), C₆(31)//C₆(41) = 19.4(2). C₆(X): Six-membered ring containing C(X).

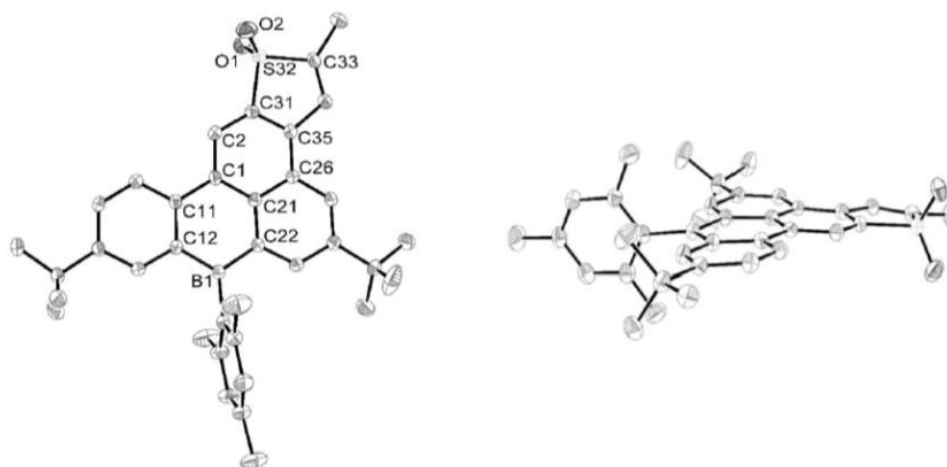


Figure S67 (CCDC 1477505): Molecular structure of **17** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): B1–C12 = 1.543(4), B1–C22 = 1.542(4), C1–C2 = 1.400(4), C31–S32 = 1.772(3), S32–C33 = 1.785(3), S32–O1 = 1.443(3), S32–O2 = 1.441(3); C12–B1–C22 = 116.0(3), C31–S32–C33 = 93.6(1), O1–S32–O2 = 117.5(2); C₆(11)//C₆(21) = 4.7(2), C₆(21)//C₅(31) = 5.8(2). C₆(X): Six-membered ring containing C(X).

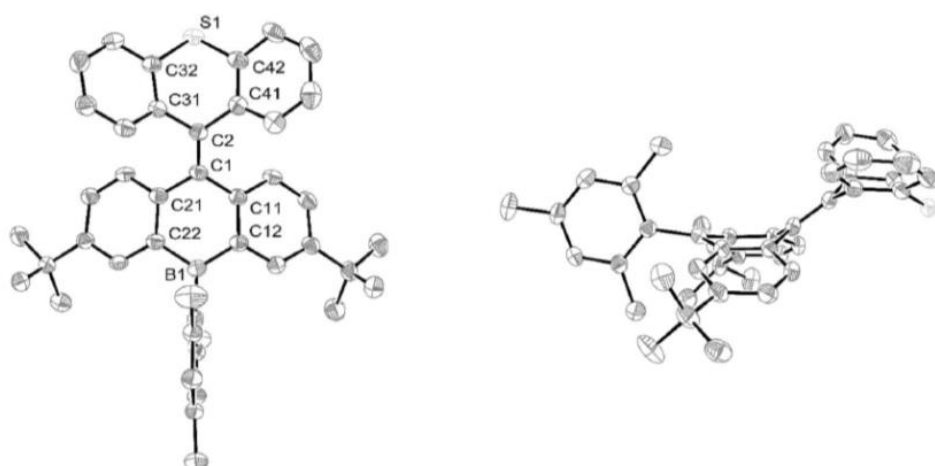


Figure S68 (CCDC 1477509): Molecular structure of **S11** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Only one of two molecules in the asymmetric unit is shown, bond lengths and angles vary slightly between the molecules. Selected bond lengths [Å] and angles (°): B1–C12 = 1.554(6)/1.553(6), B1–C22 = 1.566(6)/1.553(6), C1–C2 = 1.365(5)/1.363(6), S1–C32 = 1.768(4)/1.775(6), S1–C42 = 1.762(5)/1.771(5); C12–B1–C22 = 113.7(3)/114.5(4), C32–S1–C42 = 97.7(2)/96.9(2); C₆(11)//C₆(21) = 44.3(1)/41.6(2), C₆(31)//C₆(41) = 52.2(2)/56.5(2). C₆(X): Six-membered ring containing C(X).

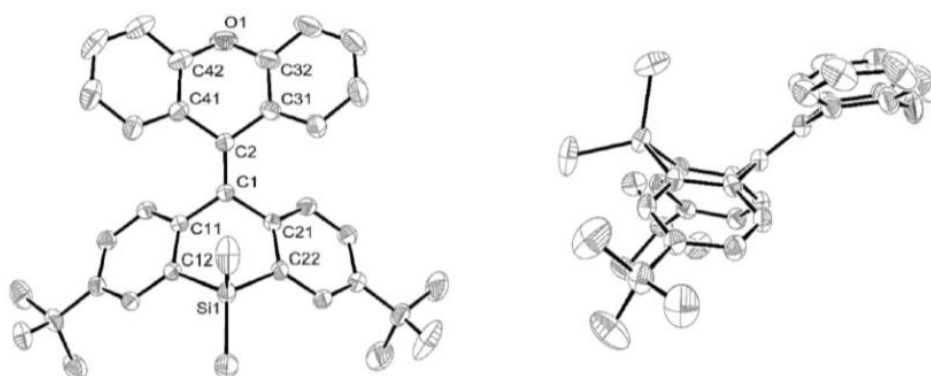


Figure S69 (CCDC 1477510): Molecular structure of **S12** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Only one of two molecules in the asymmetric unit is shown, bond lengths and angles do not vary significantly between the molecules. Selected bond lengths [Å] and angles (°): Si1–C12 = 1.869(2), Si1–C22 = 1.871(2), O1–C32 = 1.381(3), O1–C42 = 1.380(2), C1–C2 = 1.352(2); C12–Si1–C22 = 99.48(7), C11–C1–C21 = 113.2(1), C31–C2–C41 = 110.6(1), C32–O1–C42 = 114.5(1); C₆(11)//C₆(21) = 59.55(6), C₆(31)//C₆(41) = 39.40(8). C₆(X): Six-membered ring containing C(X).

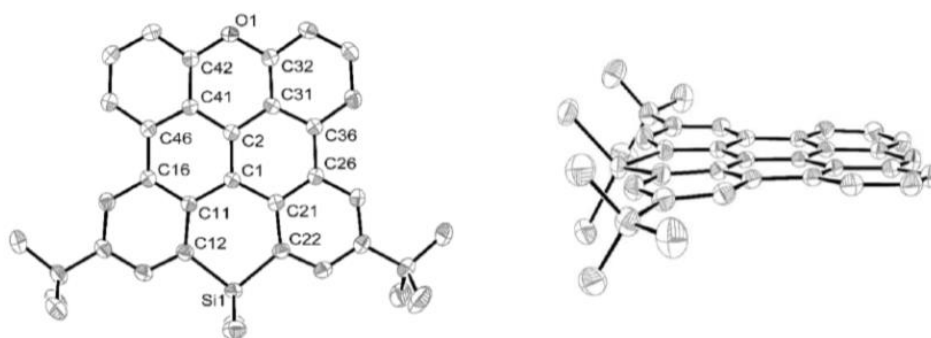


Figure S70 (CCDC 1477511): Molecular structure of **S13** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and co-crystallized benzene are omitted for clarity. Selected bond lengths [Å] and angles (°): Si1–C12 = 1.842(2), Si1–C22 = 1.841(2), O1–C32 = 1.369(2), O1–C42 = 1.370(2), C1–C2 = 1.383(2); C12–Si1–C22 = 103.42(7), C11–C1–C21 = 124.6(1), C31–C2–C41 = 115.8(1), C32–O1–C42 = 119.2(1); C₆(11)//C₆(21) = 3.82(5), C₆(31)//C₆(41) = 4.48(6). C₆(X): Six-membered ring containing C(X).

Table S1: Selected crystallographic data for **3**, **4**, and **8**.

compound	3	4	8
CCDC	1477501	1477502	1477507
formula	C ₃₆ H ₃₈ BN	C ₄₂ H ₄₀ BN × CH ₃ CN	C ₃₆ H ₃₉ BS
<i>M_r</i>	495.48	610.61	514.54
<i>T</i> (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	MoKα, 0.71073	MoKα, 0.71073	MoKα, 0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Cc</i>
<i>a</i> (Å)	9.7729(6)	12.9363(5)	21.9073(6)
<i>b</i> (Å)	17.6806(15)	29.0747(8)	15.1533(5)
<i>c</i> (Å)	16.6120(11)	9.0325(3)	9.9257(3)
α (°)	90	90	90
β (°)	94.038(5)	98.912(3)	110.204(2)
γ (°)	90	90	90
<i>V</i> (Å ³)	2863.3(4)	3356.3(2)	3092.27(17)
<i>Z</i>	4	4	4
<i>D_{calcd}</i> (g cm ⁻³)	1.149	1.208	1.105
F(000)	1064	1304	1104
μ (mm ⁻¹)	0.065	0.069	0.126
crystal size (mm)	0.31 × 0.19 × 0.17	0.38 × 0.24 × 0.18	0.35 × 0.18 × 0.17
reflections collected	36087	59953	39053
independent reflections	5851	8865	8100
<i>R_{int}</i>	0.1012	0.0514	0.0445
data/restraints/parameters	5851/0/346	8865/18/429	8100/2/347
<i>R₁</i> , <i>wR₂</i> (<i>I</i> > 2σ(<i>I</i>))	0.0662, 0.1636	0.0845, 0.2470	0.0436, 0.1139
<i>R₁</i> , <i>wR₂</i> (all data)	0.0967, 0.1801	0.1050, 0.2640	0.0461, 0.1155
Absolute structure parameter	n/a	n/a	0.07(5)
Goodness-of-fit on <i>F</i> ²	1.051	1.067	1.056
Largest diff peak and hole (e Å ⁻³)	0.581, -0.214	0.923, -0.634	0.254, -0.192

Table S2: Selected crystallographic data for **9**, **11**, and **13**.

compound	9	11	13
CCDC	1477508	1477503	1477504
formula	C ₄₃ H ₃₉ BS	C ₄₁ H ₄₁ BN ₂	C ₄₁ H ₄₃ BCl ₂ N ₂ Pd
<i>M_r</i>	598.61	572.57	751.88
<i>T</i> (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
crystal system	triclinic	orthorhombic	monoclinic
space group	<i>P</i> -1	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.2807(4)	11.9943(4)	21.0074(12)
<i>b</i> (Å)	12.6295(8)	18.9554(7)	8.6094(3)
<i>c</i> (Å)	18.0982(11)	27.9545(12)	23.6213(14)
α (°)	100.516(5)	90	90
β (°)	91.288(5)	90	114.733(4)
γ (°)	92.231(5)	90	90
<i>V</i> (Å ³)	1634.23(17)	6355.6(4)	3880.3(4)
<i>Z</i>	2	8	4
<i>D_{calcd}</i> (g cm ⁻³)	1.216	1.197	1.287
F(000)	636	2448	1552
μ (mm ⁻¹)	0.129	0.068	0.645
crystal size (mm)	0.42 × 0.30 × 0.20	0.32 × 0.25 × 0.24	0.23 × 0.11 × 0.02
reflections collected	19367	63997	32119
independent reflections	6907	6855	6834
<i>R_{int}</i>	0.0677	0.0674	0.0593
data/restraints/parameters	6907/36/437	6855/0/452	6834/54/455
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0651, 0.1839	0.0683, 0.1668	0.0432, 0.0811
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0734, 0.1905	0.0846, 0.1761	0.0690, 0.0879
Absolute structure parameter	n/a	n/a	n/a
Goodness-of-fit on <i>F</i> ²	1.024	1.120	0.983
Largest diff peak and hole (<i>e</i> Å ⁻³)	1.138, -0.347	0.396, -0.347	0.863, -0.393

Table S3: Selected crystallographic data for **16**, **17**, and **S11**.

compound	16	17	S11
CCDC	1477506	1477505	1477509
formula	C ₄₃ H ₃₉ BOS	C ₃₆ H ₃₉ BO ₂ S	C ₄₃ H ₄₃ BS
<i>M_r</i>	614.61	546.54	602.64
<i>T</i> (K)	173(2)	173(2)	173(2)
radiation, λ (Å)	MoK α , 0.71073	MoK α , 0.71073	MoK α , 0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P2₁/c</i>	<i>Cc</i>	<i>P2₁/c</i>
<i>a</i> (Å)	19.5678(18)	22.2076(13)	23.415(5)
<i>b</i> (Å)	14.5208(14)	15.3065(8)	13.693(3)
<i>c</i> (Å)	13.2754(11)	9.7742(5)	23.144(5)
α (°)	90	90	90
β (°)	100.584(7)	109.935(4)	106.96(3)
γ (°)	90	90	90
<i>V</i> (Å ³)	3707.9(6)	3123.4(3)	7098(3)
<i>Z</i>	4	4	8
<i>D_{calcd}</i> (g cm ⁻³)	1.101	1.162	1.128
F(000)	1304	1168	2576
μ (mm ⁻¹)	0.118	0.133	0.119
crystal size (mm)	0.21 × 0.16 × 0.02	0.34 × 0.13 × 0.11	0.29 × 0.26 × 0.14
reflections collected	34503	17675	53778
independent reflections	6538	7343	53778
<i>R_{int}</i>	0.1334	0.0527	n/a
data/restraints/parameters	6538/0/418	7343/2/366	53778/0/856
<i>R₁</i> , <i>wR₂</i> (<i>I</i> > 2 σ (<i>I</i>))	0.0907, 0.2031	0.0535, 0.1250	0.0765, 0.1907
<i>R₁</i> , <i>wR₂</i> (all data)	0.1597, 0.2378	0.0629, 0.1295	0.0943, 0.2024
Absolute structure parameter	n/a	0.52(10)	n/a
Goodness-of-fit on <i>F</i> ²	0.970	1.031	1.015
Largest diff peak and hole (<i>e</i> Å ⁻³)	0.519, -0.340	0.306, -0.253	0.342, -0.352

Table S4: Selected crystallographic data for **S12** and **S13**.

compound	S12	S13
CCDC	1477510	1477511
formula	C ₃₆ H ₃₈ OSi	C ₃₆ H ₃₄ OSi × ½ C ₆ H ₆
<i>M_r</i>	514.75	549.77
<i>T</i> (K)	173(2)	173(2)
radiation, λ (Å)	MoKα, 0.71073	MoKα, 0.71073
crystal system	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	9.9683(6)	7.1229(10)
<i>b</i> (Å)	17.2049(9)	14.7972(17)
<i>c</i> (Å)	18.7360(10)	15.6177(19)
α (°)	105.633(4)	65.291(9)
β (°)	102.444(4)	86.006(10)
γ (°)	91.630(4)	87.461(10)
<i>V</i> (Å ³)	3008.9(3)	1491.5(3)
<i>Z</i>	4	2
<i>D_{calcd}</i> (g cm ⁻³)	1.136	1.224
F(000)	1104	586
μ (mm ⁻¹)	0.104	0.109
crystal size (mm)	0.45 × 0.36 × 0.29	0.94 × 0.16 × 0.09
reflections collected	49806	19130
independent reflections	13165	6858
<i>R_{int}</i>	0.0578	0.0691
data/restraints/parameters	13165/0/685	6858/0/370
<i>R₁</i> , <i>wR₂</i> (<i>I</i> > 2σ(<i>I</i>))	0.0524, 0.1361	0.0514, 0.1273
<i>R₁</i> , <i>wR₂</i> (all data)	0.0624, 0.1416	0.0749, 0.1365
Absolute structure parameter	n/a	n/a
Goodness-of-fit on <i>F</i> ²	1.055	1.021
Largest diff peak and hole (<i>e</i> Å ⁻³)	0.529, -0.410	0.298, -0.332

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5.1.5 Steric Shielding vs Structural Constraint in a Boron-Containing Polycyclic Aromatic Hydrocarbon

Erschienen in: Organometallics

ACS Publications

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Steric Shielding vs. Structural Constraint in a Boron-Containing Polycyclic Aromatic Hydrocarbon

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Supporting Information

Table of contents:

1. General experimental procedures	S2
2. Nomenclature	S3
3. Syntheses, purification methods and analytical data	S4
4. Plots of ¹ H and ¹³ C{ ¹ H} NMR spectra	S9
5. UV/Vis absorption and emission spectra	S16
6. Fluoride titration	S18
7. Plots of cyclic voltammograms	S25
8. X-ray crystal structure analyses	S26
9. Computational details and HOMO/LUMO analysis	S28
10. References	S30

1. General experimental procedures

If not stated otherwise, all reactions and manipulations were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Toluene, Et₂O, and THF were distilled from Na/benzophenone prior to use. CH₂Cl₂, Me₃SiCl, and Me₂SiCl₂ were distilled from CaH₂. BBr₃ was stored over Hg to remove traces of HBr and Br₂. Commercially available anhydrous (CH₂Cl)₂ (*Sigma Aldrich*) and Sc(OTf)₃ (*TCI Chemicals*) were used as received; benzaldehyde (*Acros*) was distilled under an atmosphere of dry nitrogen prior to use. 2-Bromo-1,3-di(prop-1-en-2-yl)benzene^{S1}, mesityllithium,^{S2} and **S1**^{S3} were prepared according to literature procedures. The procedure applied for the preparation of **S2** differs from the literature protocol^{S4} and is therefore described in detail.

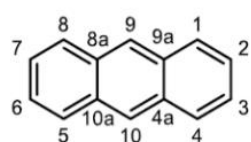
NMR spectra were recorded at 300 K using a *Bruker Avance-500* spectrometer. Chemical shift values are referenced to (residual) solvent signals (¹H/¹³C{¹H}; CDCl₃: δ = 7.26/77.16 ppm) or external BF₃·Et₂O (¹¹B{¹H}: 0.00 ppm) and Si(CH₃)₄ (²⁹Si INEPT: 0.00 ppm). Abbreviations: s = singlet, d = doublet, t = triplet, vt = virtual triplet, m = multiplet, br. = broad, n.r. = multiplet expected in the ¹H NMR spectrum but not resolved. Resonances of carbon atoms attached to boron atoms were typically broadened due to the quadrupolar relaxation of boron. Boron resonances of triarylborane compounds are typically very broad (*h*_ν > 1000 Hz) and were observed only in highly concentrated samples. Resonance assignments were aided by ¹H COSY, ¹H C HSQC, and, if necessary, also ¹H C HMBC spectra.

For photochemical reactions, a medium-pressure Hg vapor lamp was used (*Heraeus Noblelight*; TQ 150, 150 W). UV/Vis absorption spectra were recorded at room temperature using a *Shimadzu UV-3150* or *Varian Cary 50 Scan UV/Vis* spectrophotometer. Photoluminescence (PL) spectra were recorded at room temperature using a *Jasco FP-8300* spectrofluorometer equipped with a calibrated *Jasco ILF-835* 100 mm diameter integrating sphere and analyzed using the *Jasco FWQE-880* software. For PL quantum yield (Φ_{PL}) measurements, each sample was carefully degassed with argon using an injection needle and a septum-capped cuvette. Under these conditions, Φ_{PL} of the fluorescence standard 9,10-diphenylanthracene was determined as 96% (lit.: 97%)^{S5,S6}. For all measurements of Φ_{PL} , at least three samples of different concentrations were used (range between 10⁻⁵ and 10⁻⁷ mol L⁻¹). Due to self-absorption, slightly lower Φ_{PL} values were observed at higher concentrations. This effect was corrected by applying a method reported by *Bardeen et al.*, which slightly improved the Φ_{PL} values (4% at most).^{S7} Cyclic voltammetry (CV) measurements were performed in an inert-atmosphere glovebox at room temperature using a one-chamber, three-electrode cell and an *EG&G Princeton Applied Research 263A* potentiostat. A platinum disk electrode (2.00 mm diameter) was used as the working electrode with a platinum wire counter electrode and a silver wire reference electrode, which was coated with AgCl by immersion into HCl/HNO₃ (3:1). Prior to measurements, the solvent THF was dried with NaK. [*n*-Bu₄N][PF₆] (*Sigma Aldrich*; used as received) was employed as the supporting electrolyte (0.1 mol L⁻¹). All potential values were referenced against the FcH/FcH⁺ redox couple (FcH = ferrocene; *E*_{1/2} = 0 V). High-resolution mass spectra were measured in positive mode using a *Thermo Fisher Scientific MALDI LTQ Orbitrap XL* and 2,5-dihydroxybenzoic acid or α -cyano-4-hydroxycinnamic acid as the matrix. Exact masses were calculated based on the predominant combination of natural isotopes. Combustion analyses were performed by the microanalytical laboratory of the *Goethe-University Frankfurt*.

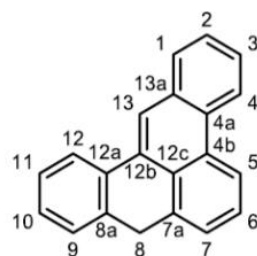
Purity of the Synthesized Compounds. All products were purified by column chromatography on silica gel/aluminum oxide, whereby inorganic, NMR-inactive impurities are reliably removed. Plots of the ¹H and ¹³C NMR spectra and a compilation of assigned resonances of all products are provided in the SI. Correct elemental analyses have been obtained on all solid products.

2. Nomenclature

Assignment of NMR signals: The same numbering schemes as for the all-carbon compounds (see below) were employed for their silicon- or boron-doped congeners.

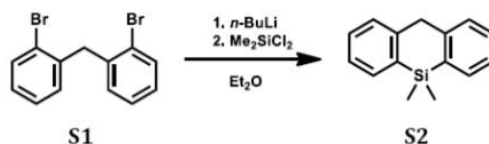


anthracene



8*H*-benzo[*gh*]tetraphene

3. Syntheses, purification methods and analytical data



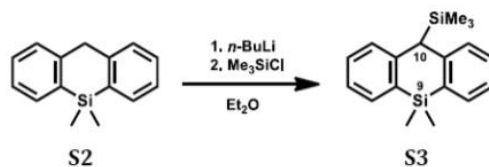
Improved procedure for the preparation of S2: Compound **S1** (8.30 g, 25.5 mmol) was placed in a three-necked round-bottom flask equipped with a condenser and two addition funnels. Et₂O (200 mL) was added and the solution was cooled to 0 °C. *n*-BuLi in *n*-hexane (1.56 M; 34 mL, 53.5 mmol) was added dropwise at 0 °C. After complete addition, the yellow solution was heated to reflux temperature for 40 min. Me₂SiCl₂ (3.7 mL, 31 mmol) in Et₂O (10 mL) was added dropwise at 0 °C, whereupon a colorless precipitate formed. After complete addition, the mixture was stirred at room temperature for 1 h. A saturated aqueous solution of NaHCO₃ (150 mL) was added to the colorless suspension, and the mixture was stirred for 15 min. The aqueous layer was separated and extracted with Et₂O (50 mL). The combined organic layers were washed with H₂O (200 mL) and brine (100 mL), dried with MgSO₄, and filtered. The solvent was removed from the filtrate under reduced pressure. The crude product was purified by short-column chromatography (10 cm silica gel, *d* = 3.5 cm, cyclohexane). All volatiles were removed from the eluate under reduced pressure. A colorless oil was obtained, which solidified upon storage at 0 °C (melting point: 38-39 °C). Yield: 4.59 g (80%). *Caution:* Oxidation of the benzylic position can occur if the product is stored at ambient conditions for a long time.

¹H NMR (500.2 MHz, CDCl₃): δ 7.61-7.59 (m, 2H), 7.35-7.24 (m, 6H), 4.12 (s, 2H; CH₂), 0.47 (s, 6H; SiMe₂)

¹³C{¹H} NMR (125.7 MHz, CDCl₃): δ 146.1, 135.9, 133.2, 129.2, 128.0, 125.8, 41.7, -2.9

²⁹Si-INEPT NMR (99.4 MHz, CDCl₃): δ -18.5

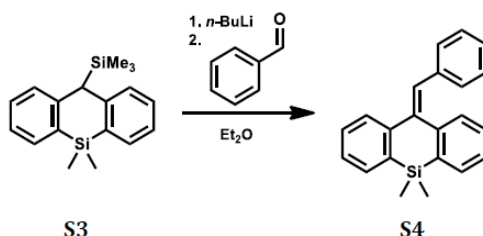
EA (%): Calculated for C₁₅H₁₆Si [224.10]: C 80.30, H 7.19; found: C 80.26, H 7.28



Synthesis of S3: Compound **S2** (3.00 g, 13.4 mmol) was placed in a two-necked round-bottom flask equipped with a condenser. Et₂O (60 mL) was added and the solution was cooled to 0 °C. *n*-BuLi in *n*-hexane (1.56 M; 9.4 mL, 15 mmol) was added via a syringe at 0 °C. The dark red solution was stirred at room temperature for 1 h. Neat Me₃SiCl (2.2 mL, 17 mmol) was added via a syringe at 0 °C, whereupon a colorless precipitate formed. The mixture was stirred at room temperature for 1 h. A saturated aqueous solution of NaHCO₃ (150 mL) was added to the orange suspension, and the mixture was stirred for 15 min. The aqueous layer was separated and extracted with Et₂O (50 mL). The combined organic layers were washed with H₂O (200 mL) and brine (100 mL), dried with MgSO₄, and filtered. The solvent was removed from the filtrate under reduced pressure. The crude product was purified by short-column chromatography (8 cm silica gel, *d* = 3.5 cm, cyclohexane). All volatiles were removed from the eluate under reduced pressure to give **S3** as a pale yellow oil. Yield: 3.49 g (88%).

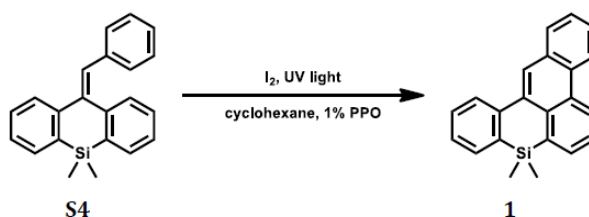
¹H NMR (500.2 MHz, CDCl₃): δ 7.56 (dd, ³J_{HH} = 7.3 Hz, ⁴J_{HH} = 1.5 Hz, 2H; H-1,8), 7.28 (ddd, ³J_{HH} = 7.5 Hz, ³J_{HH} = 7.3 Hz, ⁴J_{HH} = 1.5 Hz, 2H; H-3,6), 7.18 (ddd, ³J_{HH} = 7.8 Hz, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.5 Hz, 2H; H-2,7), 7.10

(dd, $^3J_{\text{H,H}} = 7.8$ Hz, $^4J_{\text{H,H}} = \text{n.r.}$, 2H; H-4,5), 3.98 (s, 1H; H-10), 0.46 (s, 3H; SiMe₂), 0.41 (s, 3H; SiMe₂), -0.15 (s, 9H; SiMe₃)
 $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl₃): δ 147.7 (C-4a,10a), 134.1 (C-1,8), 132.2 (C-8a,9a), 128.7 (C-3,6), 128.0 (C-4,5), 124.3 (C-2,7), 47.5 (C-10), 0.7 (SiMe₂), 0.3 (SiMe₂), -1.5 (SiMe₃)
 ^{29}Si -INEPT NMR (99.4 MHz, CDCl₃): δ 5.8, -19.5
 HRMS (m/z): Calculated for [C₁₈H₂₄Si₂ + H]⁺: 297.14893, found: 297.14905



Synthesis of S4: Compound S3 (5.5 g, 18.6 mmol) was placed in a three-necked round-bottom flask equipped with a condenser and an addition funnel. Et₂O (120 mL) was added and the solution was cooled to 0 °C. *n*-BuLi in *n*-hexane (1.56 M; 13.1 mL, 20.4 mmol) was added via a syringe at 0 °C. The red solution was heated to reflux temperature for 1 h. A solution of benzaldehyde (2.2 mL, 21.3 mmol) in Et₂O (5 mL) was added dropwise at 0 °C, whereupon the color changed to pale yellow. The mixture was stirred at room temperature for 15 min. A saturated, aqueous solution of NaHCO₃ (100 mL) was added. The aqueous layer was separated and extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with H₂O (150 mL) and brine (50 mL), dried with MgSO₄, and filtered. The solvent was removed from the filtrate under reduced pressure. The crude product was purified by column chromatography (15 cm silica gel, *d* = 5 cm, cyclohexane). The solvent was removed under reduced pressure and a colorless, highly viscous oil was obtained. Small amounts of cyclohexane remained in the product even after drying in an oil-pump vacuum for 5 h. Yield: 5.1 g (ca. 85%).

^1H NMR (500.2 MHz, CDCl₃): δ 7.72 (d, $^3J_{\text{H,H}} = 7.7$ Hz, 1H), 7.66-7.64 (m, 1H), 7.60 (dd, $^3J_{\text{H,H}} = 7.2$ Hz, $^4J_{\text{H,H}} = 1.0$ Hz, 1H), 7.43 (ddd, $^3J_{\text{H,H}} = 7.6$ Hz, $^3J_{\text{H,H}} = 7.6$ Hz, $^4J_{\text{H,H}} = 1.4$ Hz, 1H), 7.31 (ddd, $^3J_{\text{H,H}} = 7.4$ Hz, $^3J_{\text{H,H}} = 7.4$ Hz, $^4J_{\text{H,H}} = 1.0$ Hz, 1H), 7.25-7.18 (m, 4H), 7.16-7.13 (m, 3H), 7.10-7.07 (m, 1H), 6.91 (s, 1H; PhCH=), 0.52 (br., 6H; SiMe₂)
 $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl₃): δ 149.2, 144.3, 142.3, 137.8, 136.8, 135.1, 132.8, 132.2, 130.5 (PhCH=), 129.7, 129.7, 129.6, 128.5, 128.2, 126.8, 126.5, 126.2, 125.2, -3.4 (SiMe₂)
 ^{29}Si -INEPT NMR (99.4 MHz, CDCl₃): δ -17.9
 HRMS (m/z): Calculated for [C₂₂H₂₀Si + H]⁺: 313.14070, found: 313.13906



Synthesis of 1: see main text

^1H NMR (500.2 MHz, CDCl₃): δ 8.85 (dd, $^3J_{\text{H,H}} = 8.3$ Hz, $^4J_{\text{H,H}} = 1.1$ Hz, 1H; H-5), 8.69 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 1H; H-4), 8.53 (s, 1H; H-13), 8.22 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 1H; H-12), 7.99 (dd, $^3J_{\text{H,H}} = 7.7$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 1H; H-1), 7.94 (dd, $^3J_{\text{H,H}} = 6.8$ Hz, $^4J_{\text{H,H}} = 1.1$ Hz, 1H; H-7), 7.76 (dd, $^3J_{\text{H,H}} = 7.3$ Hz, $^4J_{\text{H,H}} = 1.5$ Hz, 1H; H-9), 7.74 (dd,

$^3J_{\text{H,H}} = 8.3$ Hz, $^3J_{\text{H,H}} = 6.8$ Hz, 1H; H-6), 7.66 (m, 1H; H-3), 7.62 (m, 1H; H-2), 7.57 (ddd, $^3J_{\text{H,H}} = \text{n.r.}$, $^3J_{\text{H,H}} = \text{n.r.}$, $^4J_{\text{H,H}} = 1.6$ Hz, 1H; H-11), 7.43 (ddd, $^3J_{\text{H,H}} = 7.2$ Hz, $^3J_{\text{H,H}} = 7.2$ Hz, $^4J_{\text{H,H}} = 0.9$ Hz, 1H; H-10), 0.50 (s, 6H; SiMe₂)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl₃): δ 143.1 (C-12a), 134.6 (C-8a), 134.0 (C-12c), 133.7 (C-9), 133.5 (C-7a), 133.0 (C-12b), 132.8 (C-7), 132.0 (C-13a), 131.0 (C-4a), 130.4 (C-4b), 130.0 (C-11), 129.1 (C-1), 127.0 (C-12), 126.9 (C-2 or 3), 126.9 (C-2 or 3), 126.8 (C-10), 126.5 (C-13), 125.7 (C-6), 124.5 (C-5), 122.5 (C-4), -0.5 (SiMe₂)

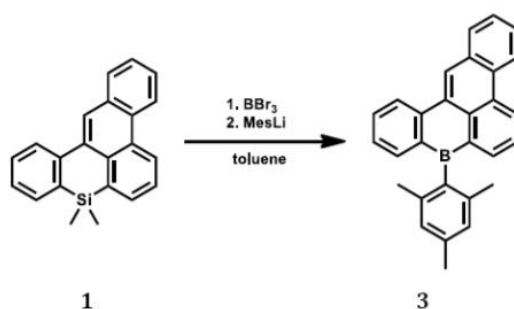
^{29}Si -INEPT NMR (99.4 MHz, CDCl₃): δ -20.6

EA (%): Calculated for C₂₂H₁₈Si [310.46]: C 85.11, H 5.84; found: C 85.19, H 5.89

HRMS (*m/z*): Calculated for [C₂₂H₁₈Si]⁺: 310.11723, found: 310.11712

UV/Vis (cyclohexane): λ_{max} (ϵ) = 226 (41500), 322 (23700), 334 nm (20800 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, $\lambda_{\text{ex}} = 322$ nm, 25 °C): $\lambda_{\text{max}} = 369, 389, 410$ nm; $\Phi_{\text{PL}} = 23\%$



Synthesis of 3: see main text

^1H NMR (500.2 MHz, CDCl₃): δ 9.14 (dd, $^3J_{\text{H,H}} = 8.2$ Hz, $^4J_{\text{H,H}} = 1.1$ Hz, 1H; H-5), 9.07 (s, 1H; H-13), 8.80 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 1H; H-4), 8.73 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 1H; H-12), 8.18 (dd, $^3J_{\text{H,H}} = 6.9$ Hz, $^4J_{\text{H,H}} = 1.1$ Hz, 1H; H-7), 8.14 (d, $^3J_{\text{H,H}} = 7.2$ Hz, 1H; H-1), 7.87 (dd, $^3J_{\text{H,H}} = 7.4$ Hz, $^4J_{\text{H,H}} = 1.4$ Hz, 1H; H-9), 7.83-7.79 (m, 2H; H-6,11), 7.78-7.74 (m, 1H; H-3), 7.72-7.69 (m, 1H; H-2), 7.44 (ddd, $^3J_{\text{H,H}} = 7.4$ Hz, $^3J_{\text{H,H}} = 7.4$ Hz, $^4J_{\text{H,H}} = \text{n.r.}$, 1H; H-10), 6.99 (s, 2H; Mes-CH-*m*), 2.44 (s, 3H; Mes-CH₃-*p*), 2.03 (s, 6H; Mes-CH₃-*o*)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl₃): δ 141.9 (C-12a), 140.5 (Mes-C-*i*), 140.2 (C-7), 138.8 (Mes-C-*o*), 138.4 (C-9), 136.8 (Mes-C-*p*), 136.4 (C-8a), 134.8 (C-7a), 133.4 (C-11), 132.0 (C-12c), 131.7 (C-13a), 131.3 (C-4a), 130.6 (C-12b), 129.8 (C-4b), 129.8 (C-1), 129.5 (C-5), 127.9 (C-3), 127.5 (C-13), 127.3 (C-10), 127.0 (C-2), 126.9 (Mes-CH-*m*), 126.5 (C-6), 123.7 (C-12), 122.6 (C-4), 23.2 (Mes-CH₃-*o*), 21.4 (Mes-CH₃-*p*)

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.5 MHz, CDCl₃): δ 65 ($h_{\frac{1}{2}} \approx 1500$ Hz)

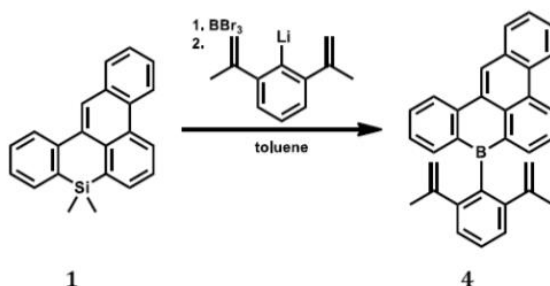
EA (%): Calculated for C₂₉H₂₃B [382.30]: C 91.11, H 6.06; found: C 91.17, H 6.21

HRMS (*m/z*): Calculated for C₂₉H₂₃B: 382.18873, found: 382.18823

UV/Vis (cyclohexane): λ_{max} (ϵ) = 311 (22400), 382 (21500), 400 nm (30900 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, $\lambda_{\text{ex}} = 375$ nm, 25 °C): $\lambda_{\text{max}} = 411, 433$ nm; $\Phi_{\text{PL}} = 85\%$

Cyclic voltammetry ([*n*Bu₄N][PF₆] 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): $E_{\frac{1}{2}} = -2.04$ (CH₂Cl₂)/-2.05 V (THF)



Synthesis of 4: see main text

^1H NMR (500.2 MHz, CDCl_3): δ 9.05 (dd, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = \text{n.r.}$, 1H; H-5), 8.96 (s, 1H; H-13), 8.78 (d, $^3J_{\text{HH}} = 8.1$ Hz, 1H; H-4), 8.64 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H; H-12), 8.15 (dd, $^3J_{\text{HH}} = 7.1$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H; H-7), 8.10 (dd, $^3J_{\text{HH}} = 8.0$ Hz, $^4J_{\text{HH}} = \text{n.r.}$, 1H; H-1), 7.85 (dd, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, 1H; H-9), 7.78 (dd, $^3J_{\text{HH}} = 8.2$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, 1H, H-6), 7.74-7.70 (m, 2H; H-3,11), 7.69-7.66 (m, 1H; H-2), 7.49-7.46 (m, 1H; Ar-CH-*p*), 7.43-7.39 (m, 3H; H-10, Ar-CH-*m*), 4.60-4.58 (m, 2H; =CH₂), 4.53 (s, 2H; =CH₂), 1.93 (s, 6H; CH₃)

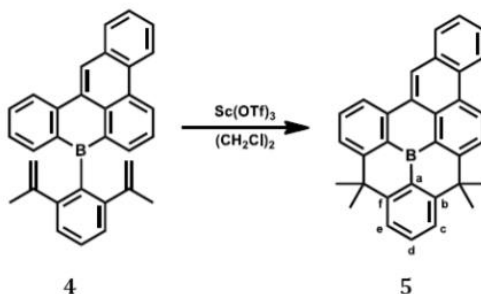
$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 147.6 (C=CH₂), 147.3 (Ar-C-*o*), 140.9 (C-12a), 140.8 (Ar-C-*i*), 139.0 (C-7), 137.8 (C-9), 137.6 (C-8a), 136.1 (C-7a), 132.3 (C-11), 131.9 (C-12c), 131.8 (C-13a), 131.3 (C-4a), 131.0 (C-12b), 129.9 (C-4b), 129.8 (C-1), 128.3 (C-5), 127.7 (C-3), 127.3 (Ar-C-*p*), 127.0 (C-2), 127.0 (C-10), 126.7 (C-13), 126.2 (C-6), 125.5 (Ar-C-*m*), 123.7 (C-12), 122.7 (C-4), 117.8 (C=CH₂), 24.5 (CH₃)

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.5 MHz, CDCl_3): δ 61 ($h_{\frac{1}{2}} \approx 1500$ Hz)

EA (%): Calculated for C₃₂H₂₅B [420.35]: C 91.43, H 5.99; found: C 91.56, H 6.14

UV/Vis (cyclohexane): λ_{max} (ϵ) = 312 (15800), 377 (19100), 396nm (25100 mol⁻¹dm³cm⁻¹)

Fluorescence (cyclohexane, $\lambda_{\text{ex}} = 365$ nm, 25 °C): $\lambda_{\text{max}} = 408, 429$ nm; $\Phi_{\text{PL}} = 70\%$



Synthesis of 5: see main text

^1H NMR (500.2 MHz, CDCl_3): δ 9.15 (dd, $^3J_{\text{HH}} = 8.9$ Hz, 1H; H-5); 9.05 (s, 1H; H-13), 8.80 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H; H-4), 8.59 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H; H-12), 8.20 (d, $^3J_{\text{HH}} = 8.9$ Hz, 1H; H-6), 8.13 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = \text{n.r.}$, 1H; H-1), 7.89 (vt, $^3J_{\text{HH}} = 7.8$ Hz, 1H; H-11), 7.84 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H; H-10), 7.79-7.73 (m, 4H; H-3,c,d,e), 7.70-7.66 (m, 1H; H-2), 1.91 (s, 6H; C(CH₃)₂ at C-7,b), 1.87 (s, 6H; C(CH₃)₂ at C-9,f)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3): δ 157.7 (C-7), 156.7 (C-9), 155.9 (C-f), 155.7 (C-b), 140.8 (C-12a), 132.8 (C-11), 132.6 (C-d), 131.8 (C-13a), 131.8 (C-12c), 131.4 (C-12b), 131.2 (C-8a), 130.8 (C-4a), 129.7 (C-1), 129.5 (C-a), 128.6 (C-7a), 128.5 (C-5), 127.5 (C-4b), 127.4 (C-3), 126.6 (C-2), 126.6 (C-13), 125.6 (C-10), 125.6 (C-6), 124.1 (C-c), 124.1 (C-e), 122.3 (C-4), 120.9 (C-12), 43.2 (C(CH₃)₂ at C-7,b), 42.9 (C(CH₃)₂ at C-9,f), 34.5 (C(CH₃)₂ at C-9,f), 33.6 (C(CH₃)₂ at C-7,b)

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.5 MHz, CDCl_3): δ 45 ($h_{\frac{1}{2}} \approx 1000$ Hz)

EA (%): Calculated for C₃₂H₂₅B [420.35]: C 91.43, H 5.99; found: C 91.13, H 6.24

HRMS (*m/z*): Calculated for C₃₂H₂₅B: 420.20438, found: 420.20395

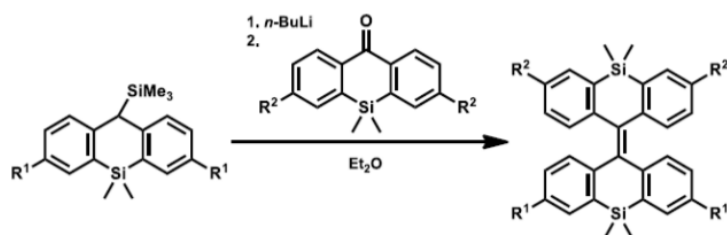
UV/Vis (cyclohexane): $\lambda_{\max} (\epsilon) = 330 (11400), 379 (22300), 400 \text{ nm} (36400 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1})$

Fluorescence (cyclohexane, $\lambda_{\text{ex}} = 370 \text{ nm}, 25 \text{ }^\circ\text{C}$): $\lambda_{\max} = 408, 430 \text{ nm}; \Phi_{\text{PL}} = 89\%$

Cyclic voltammetry (THF, $[\text{nBu}_4\text{N}][\text{PF}_6]$ 0.1 M, 200 mV s⁻¹, vs. FcH/FcH⁺): $E_{1/2} = -2.14 \text{ V}$

Comment on the attempted synthesis of a diborabisanthene stabilized by structural constraint:

We previously described the synthesis of a diborabisanthene derivative featuring a Peterson olefination reaction as a key step:^{S8}



With $R^1 = R^2 = t\text{-Bu}$, this reaction proceeded in 54% yield. Subsequently, a photocyclization, a Si-B exchange reaction, and the incorporation of mesityl substituents for steric protection lead to a stable arylborane. In order to create a planar diborabisanthene stabilized by structural constraint (c.f. synthesis of 5), we aimed to synthesize a silane with $R^1 = R^2 = \text{H}$. In this case however, the olefination reaction was not successful. Following the same procedure as for the synthesis of the *t*-Bu-substituted silane, only the starting materials were recovered after aqueous work-up. The same was true for reactions with $R^1 = t\text{-Bu}, R^2 = \text{H}$ and $R^1 = \text{H}, R^2 = t\text{-Bu}$ (the starting materials were prepared according to literature procedures).^{S8, S9}

4. Plots of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra

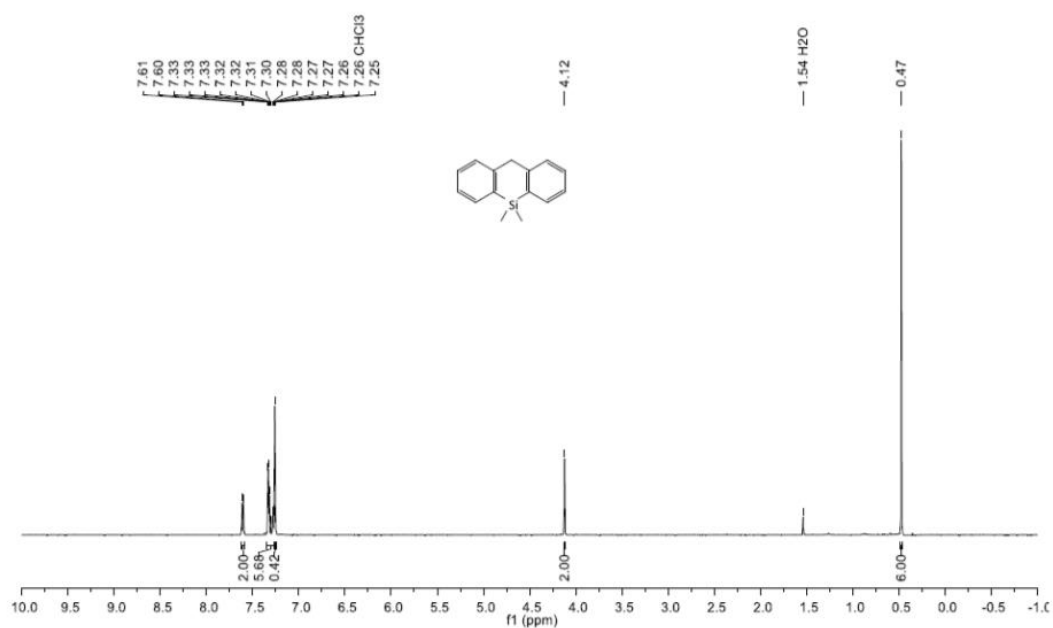


Figure S1: ^1H NMR spectrum of S2 (CDCl_3 , 500.2 MHz).

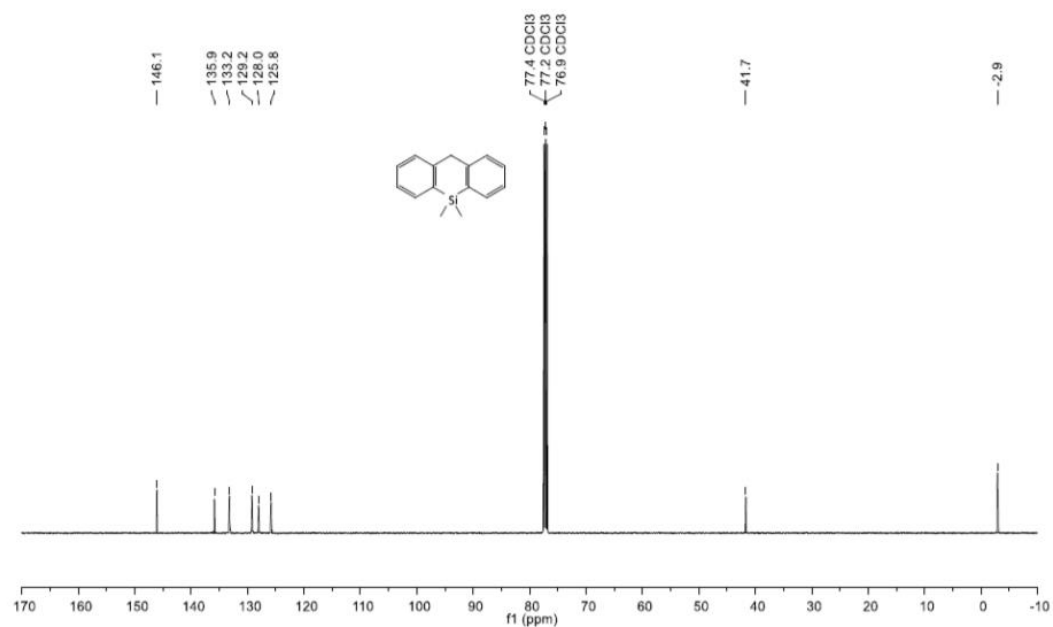


Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of S2 (CDCl_3 , 125.8 MHz).

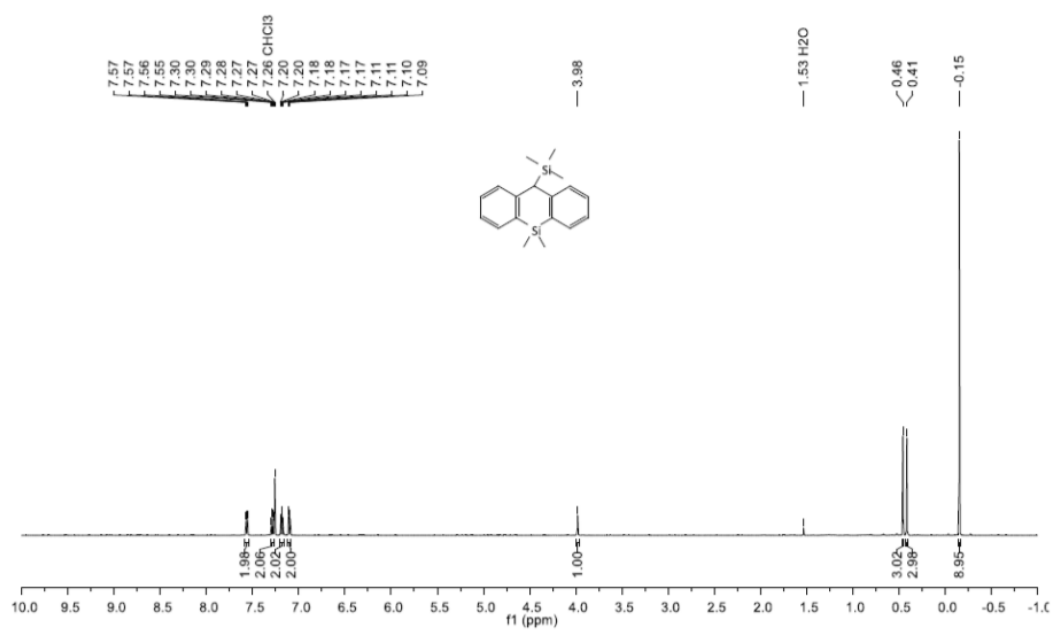


Figure S3: ^1H NMR spectrum of S3 (CDCl_3 , 500.2 MHz).

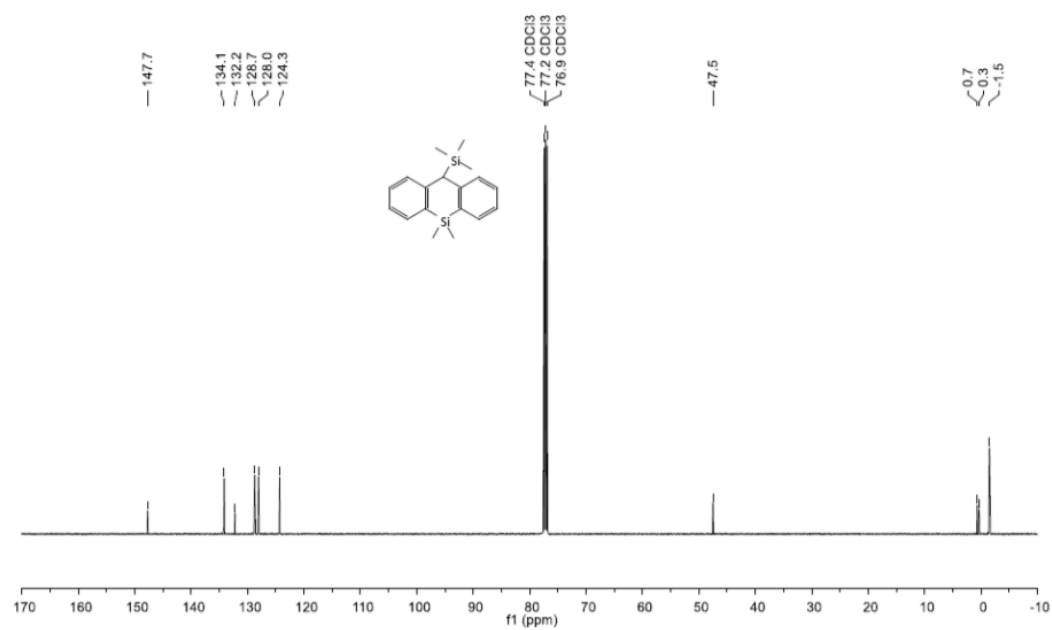


Figure S4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of S3 (CDCl_3 , 125.8 MHz).

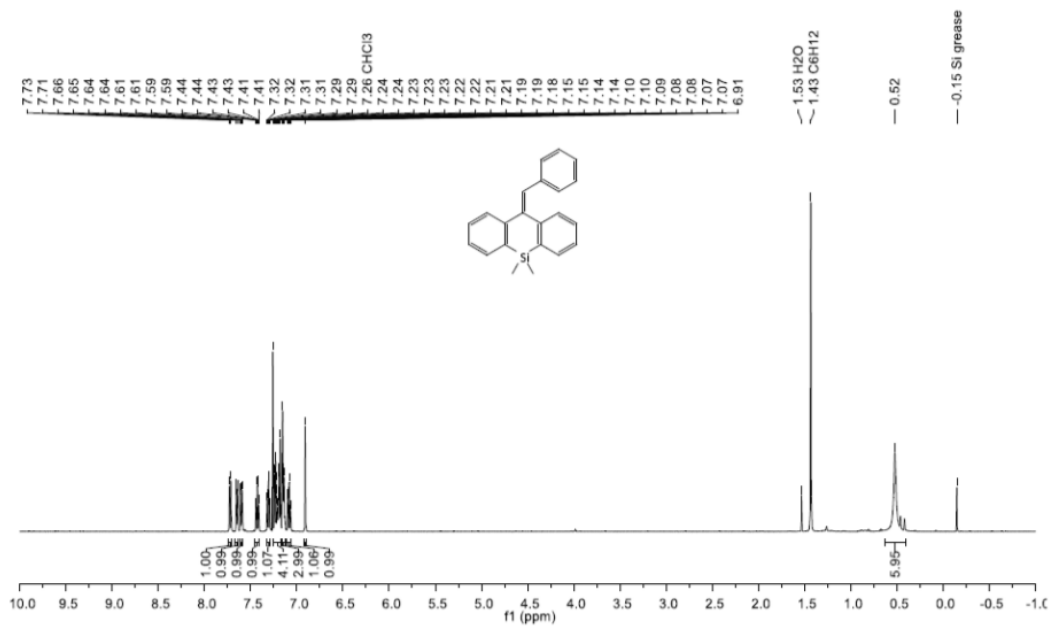


Figure S5: ¹H NMR spectrum of S4 (CDCl₃, 500.2 MHz).

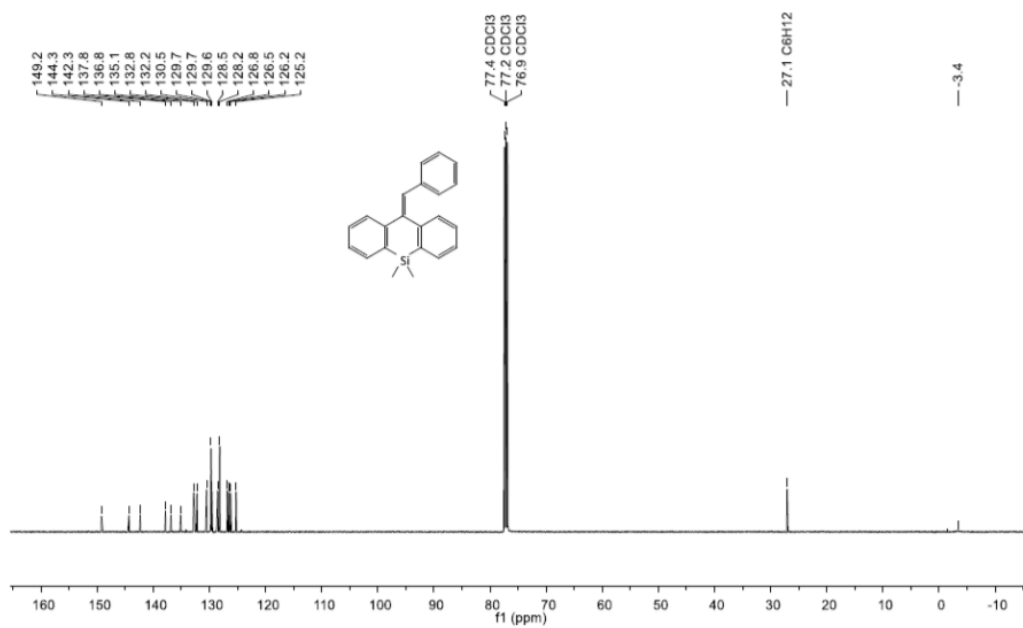


Figure S6: ¹³C{¹H} NMR spectrum of S4 (CDCl₃, 125.8 MHz).

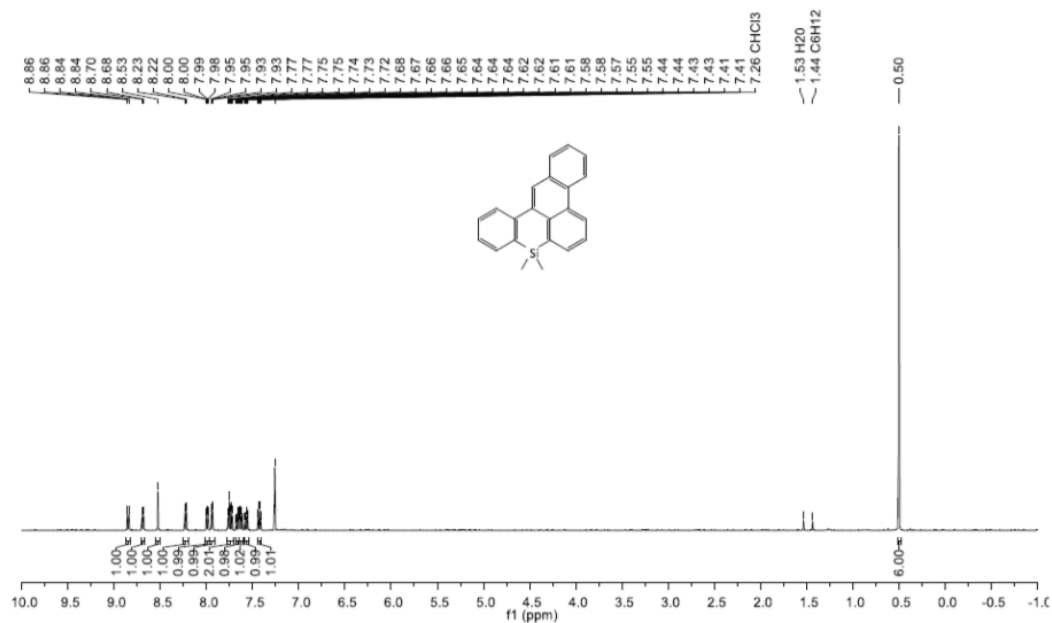


Figure S7: ^1H NMR spectrum of **1** (CDCl_3 , 500.2 MHz).

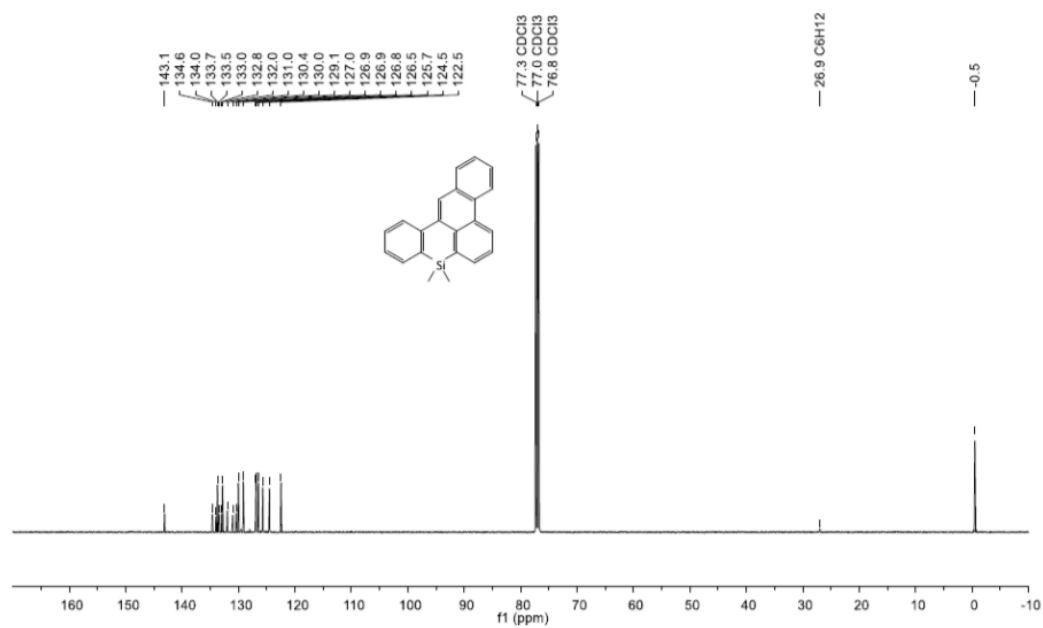


Figure S8: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** (CDCl_3 , 125.8 MHz).

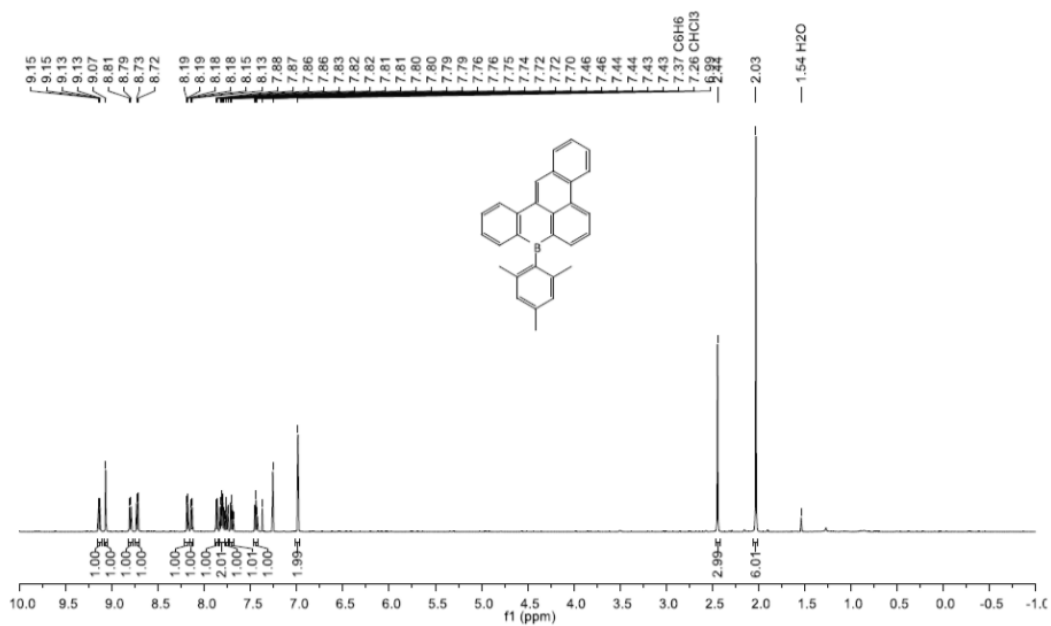


Figure S9: $^1\text{H NMR}$ spectrum of 3 (CDCl_3 , 500.2 MHz).

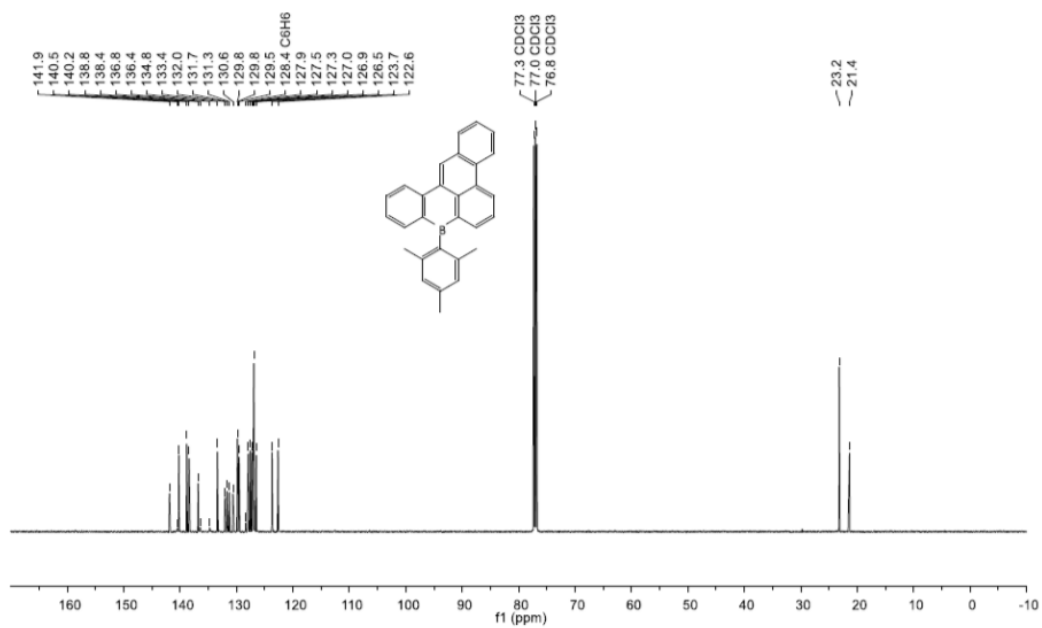


Figure S10: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 3 (CDCl_3 , 125.8 MHz).

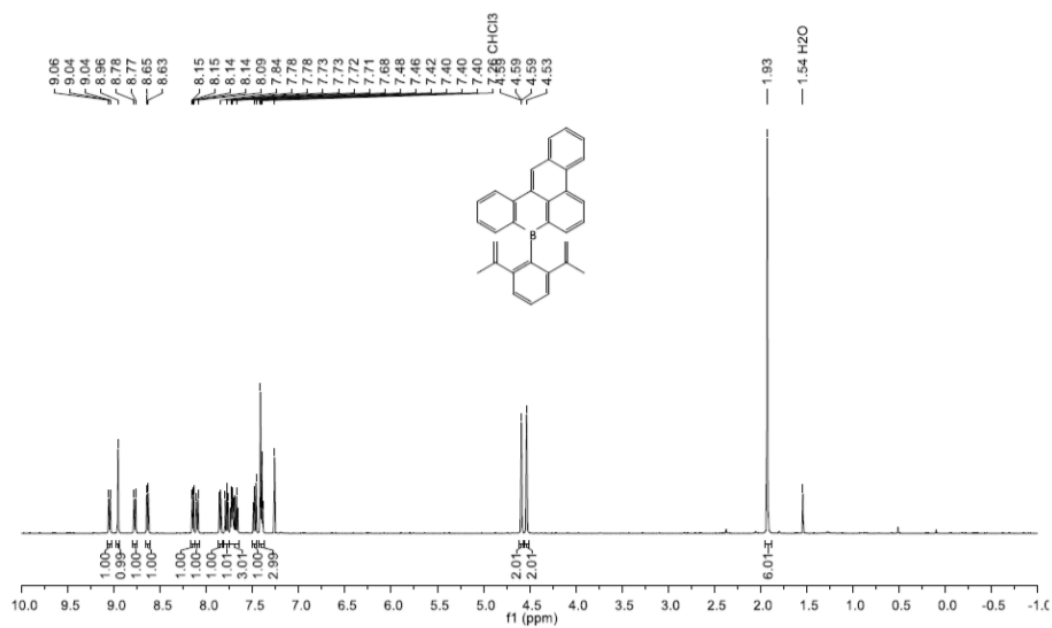


Figure S11: ^1H NMR spectrum of **4** (CDCl_3 , 500.2 MHz).

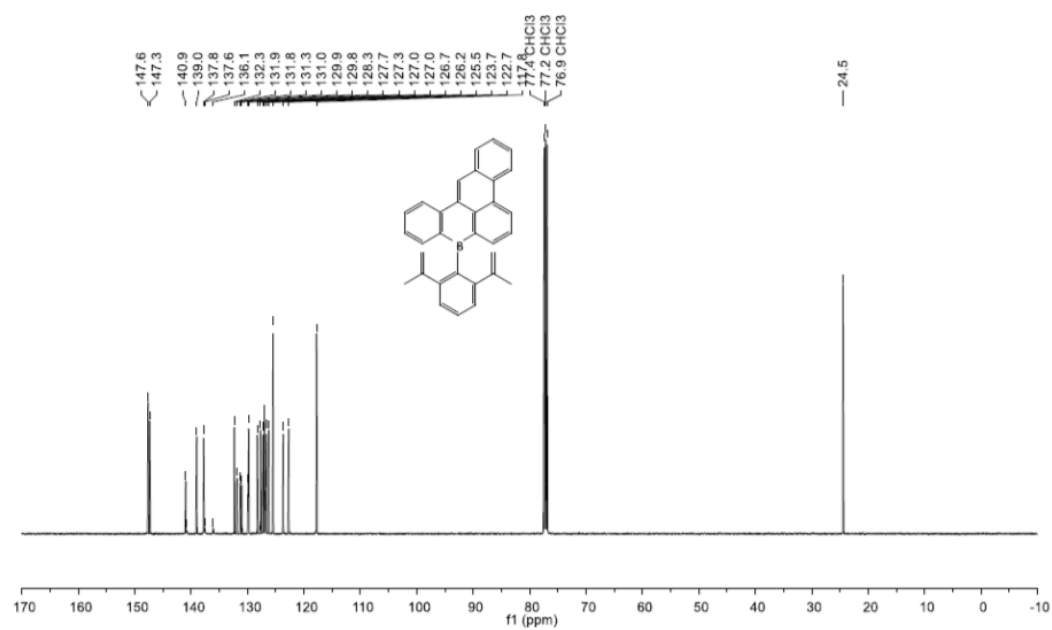


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** (CDCl_3 , 125.8 MHz).

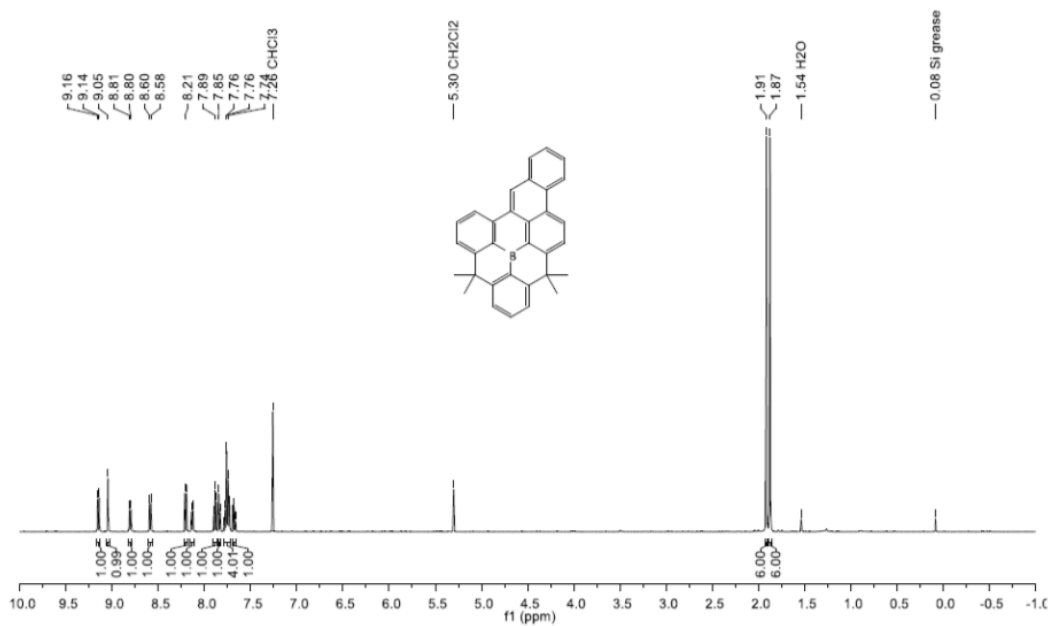


Figure S13: ^1H NMR spectrum of 5 (CDCl_3 , 500.2 MHz).

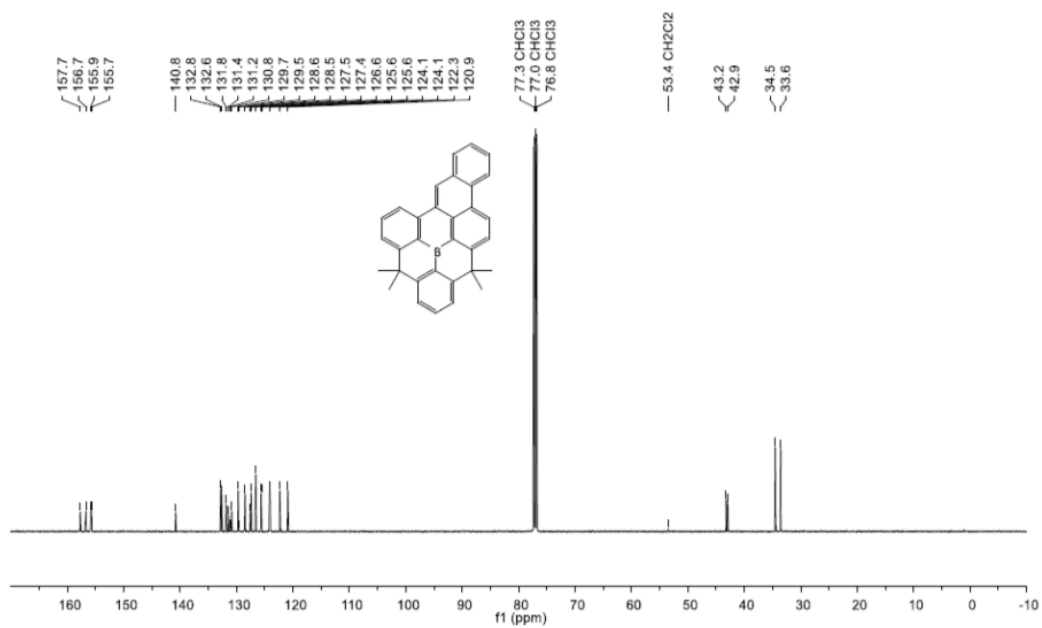


Figure S14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 5 (CDCl_3 , 125.8 MHz).

5. UV/Vis absorption and emission spectra

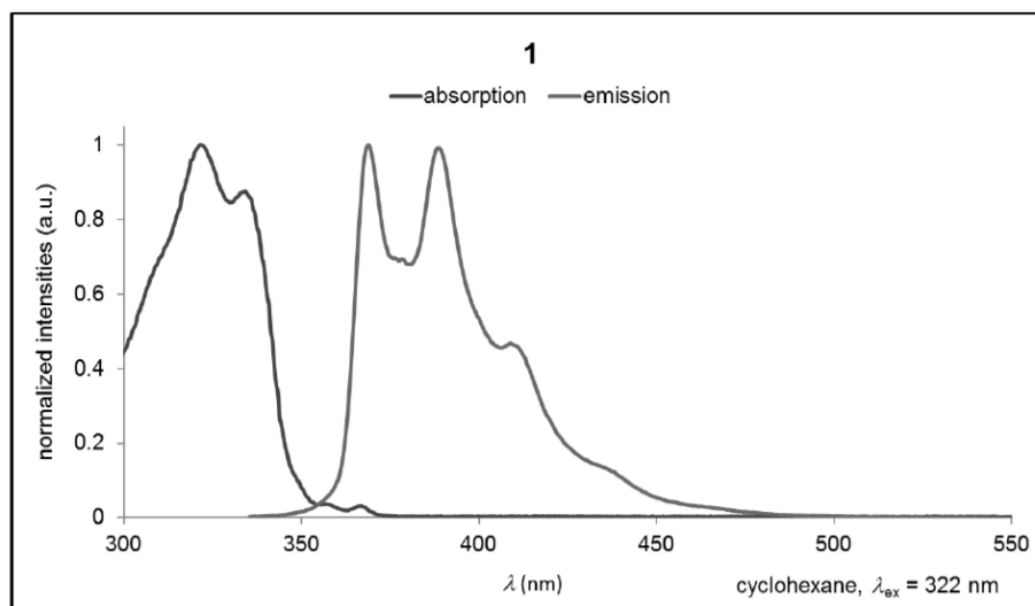


Figure S15: Normalized UV/Vis absorption and emission spectra of 1.

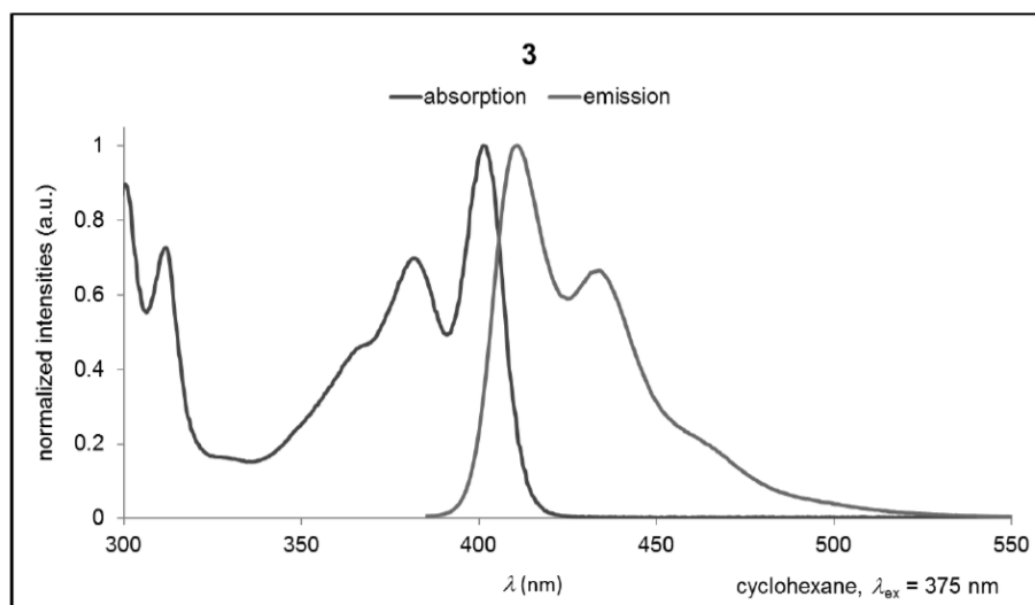


Figure S16: Normalized UV/Vis absorption and emission spectra of 3.

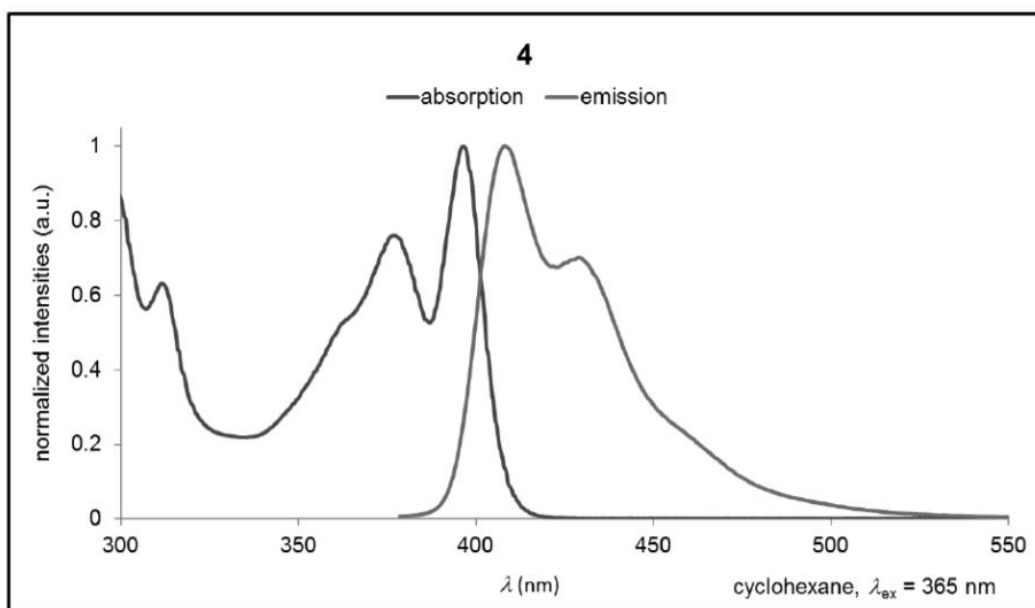


Figure S17: Normalized UV/Vis absorption and emission spectra of 4.

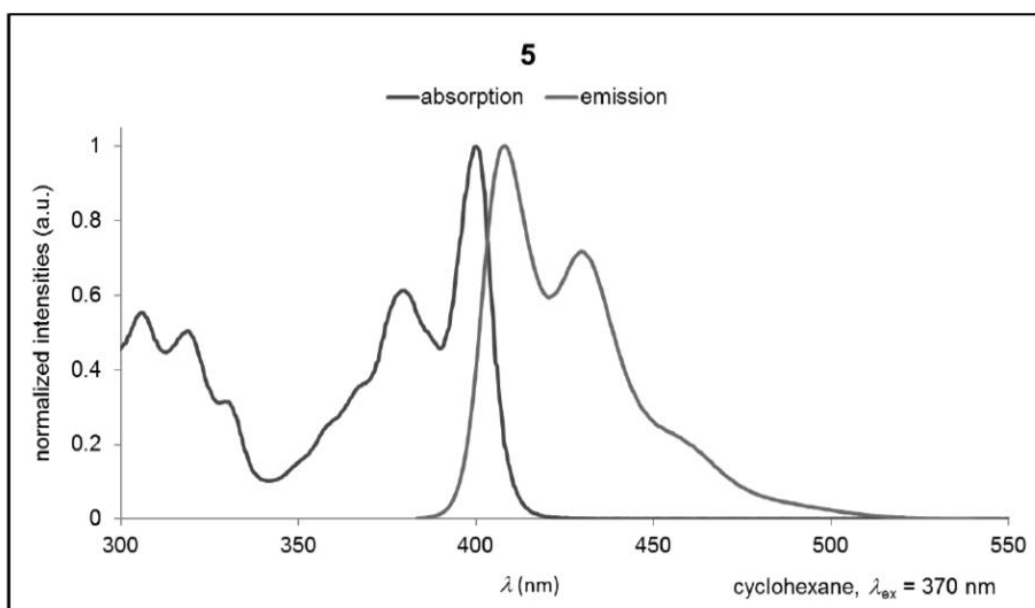
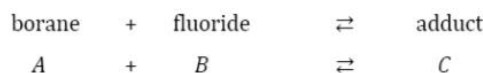


Figure S18: Normalized UV/Vis absorption and emission spectra of 5.

6. Fluoride titration

Experiment: For each fluoride titration experiment, a solution of the arylborane in UV/vis-grade CHCl₃ (0.5% ethanol as stabilizer) or anhydrous THF with an initial absorption at λ_{\max} of approx. 0.6 was placed in a quartz cuvette ($d = 1$ cm). A solution of tetra-*n*-butylammonium fluoride trihydrate (TBAF, *Sigma Aldrich*) was added incrementally using a microsyringe. The absorption was monitored λ_{\max} and a temperature of 25 °C.

Simulation:



$$K_a = \frac{C}{A * B} = \frac{C}{A * (B_t - C)} = \frac{A_t - A}{A * [B_t - (A_t - A)]}$$

Solve for A (equation 1):

$$A = \frac{1}{2} \left[\sqrt{\left(\frac{1}{K_a} - A_t + B_t \right)^2 + \frac{4A_t}{K_a}} - \frac{1}{K_a} + A_t - B_t \right]$$

The total concentration of the borane (A_t) is known and decreases slightly during the experiment as the total volume of the solution increases. The total concentrations of added fluoride (B_t) are also known and increase incrementally during the titration. The association constant (K_a) was estimated by fitting equation 1 to the experimentally determined borane concentrations (A).^{S10}

Data:

3 in THF		5 in THF		3 in CHCl ₃		5 in CHCl ₃	
$V_0 = 2.50$ mL		$V_0 = 2.50$ mL		$V_0 = 3.00$ mL		$V_0 = 3.00$ mL	
$A_0 = 21.2$ μ M		$A_0 = 21.4$ μ M		$A_0 = 28.0$ μ M		$A_0 = 23.4$ μ M	
$C_{\text{TBAF}} = 0.42$ mM		$C_{\text{TBAF}} = 0.42$ mM		$C_{\text{TBAF}} = 6.4$ mM		$C_{\text{TBAF}} = 69$ mM	
V_{TBAF}	<i>Abs</i>	V_{TBAF}	<i>Abs</i>	V_{TBAF}	<i>Abs</i>	V_{TBAF}	<i>Abs</i>
0 μ l	0.47855	0 μ l	0.61658	0 μ l	0.61630	0 μ l	0.68188
10 μ l	0.44100	10 μ l	0.56898	10 μ l	0.55071	10 μ l	0.64829
20 μ l	0.40684	20 μ l	0.52274	20 μ l	0.49935	20 μ l	0.61303
30 μ l	0.36274	30 μ l	0.47218	30 μ l	0.45326	30 μ l	0.58562
40 μ l	0.32353	40 μ l	0.42301	40 μ l	0.41617	40 μ l	0.56274
50 μ l	0.28451	50 μ l	0.37191	50 μ l	0.38756	50 μ l	0.54092
60 μ l	0.24579	60 μ l	0.32381	60 μ l	0.36117	60 μ l	0.52121
70 μ l	0.20397	70 μ l	0.27580	70 μ l	0.34082	70 μ l	0.50441
80 μ l	0.16619	80 μ l	0.22756	80 μ l	0.32272	80 μ l	0.49004
90 μ l	0.12982	90 μ l	0.18291	90 μ l	0.30774	100 μ l	0.45887
100 μ l	0.09499	100 μ l	0.13485	100 μ l	0.29318	120 μ l	0.43295
110 μ l	0.05533	110 μ l	0.08574	120 μ l	0.26367	140 μ l	0.41433
120 μ l	0.02074	120 μ l	0.04729	140 μ l	0.24522	170 μ l	0.38806
130 μ l	0.00218	130 μ l	0.01949	160 μ l	0.22871	200 μ l	0.36313
140 μ l	0.00163	140 μ l	0.00815	180 μ l	0.21385	250 μ l	0.32804
150 μ l	0.00122	150 μ l	0.00319	200 μ l	0.20071	300 μ l	0.30118
		160 μ l	0.00241	250 μ l	0.17125	350 μ l	0.27645
		170 μ l	0.00223	300 μ l	0.15054	400 μ l	0.25667
		180 μ l	0.00278	350 μ l	0.13897	500 μ l	0.22530
				400 μ l	0.12334	600 μ l	0.20316
				500 μ l	0.10421		
				600 μ l	0.09013		

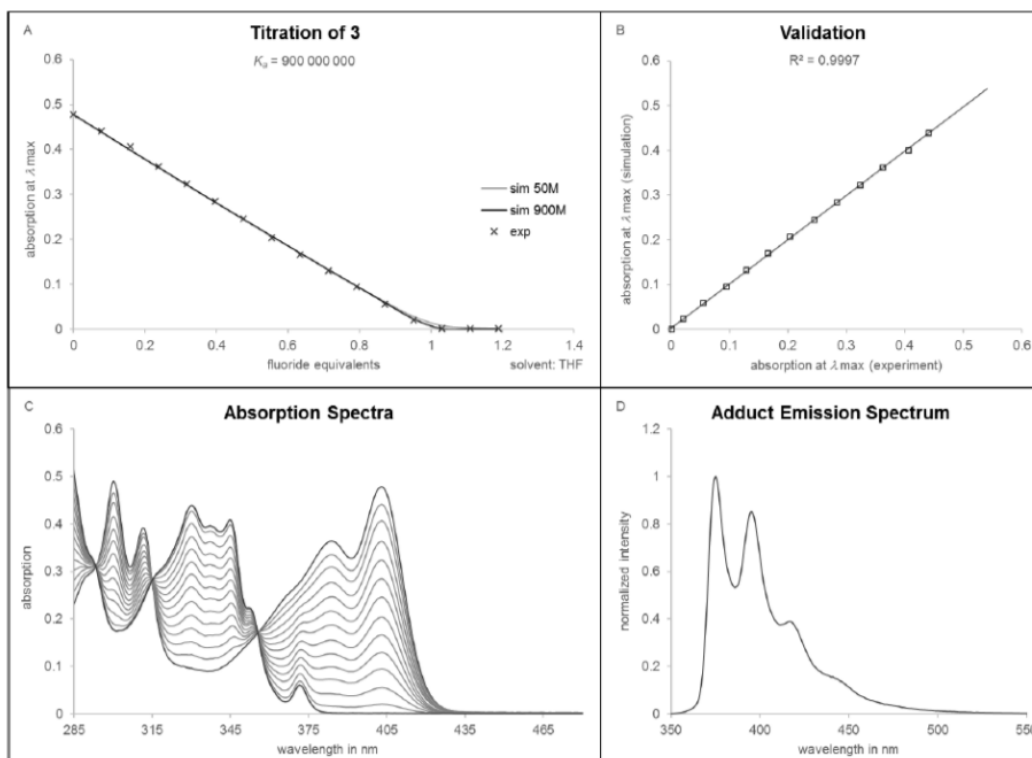


Figure S19: Titration of **3** with TBAF in THF. A: The simulation was fitted with an estimated association constant of $900 \cdot 10^6 \text{ M}^{-1}$ (black line). However, simulation and experiment are in reasonable agreement for all K_a values greater than $50 \cdot 10^6 \text{ M}^{-1}$ (blue line). B: The absorption values simulated for $K_a = 900 \cdot 10^6 \text{ M}^{-1}$ are plotted against the experimental values. C: The absorption spectra corresponding to 0 and 1 equivalents of added TBAF are marked in red. D: The adduct emission spectrum was recorded after addition of 1.2 equivalents of TBAF ($\lambda_{ex} = 330 \text{ nm}$, $\lambda_{max} = 375, 395, 417 \text{ nm}$).

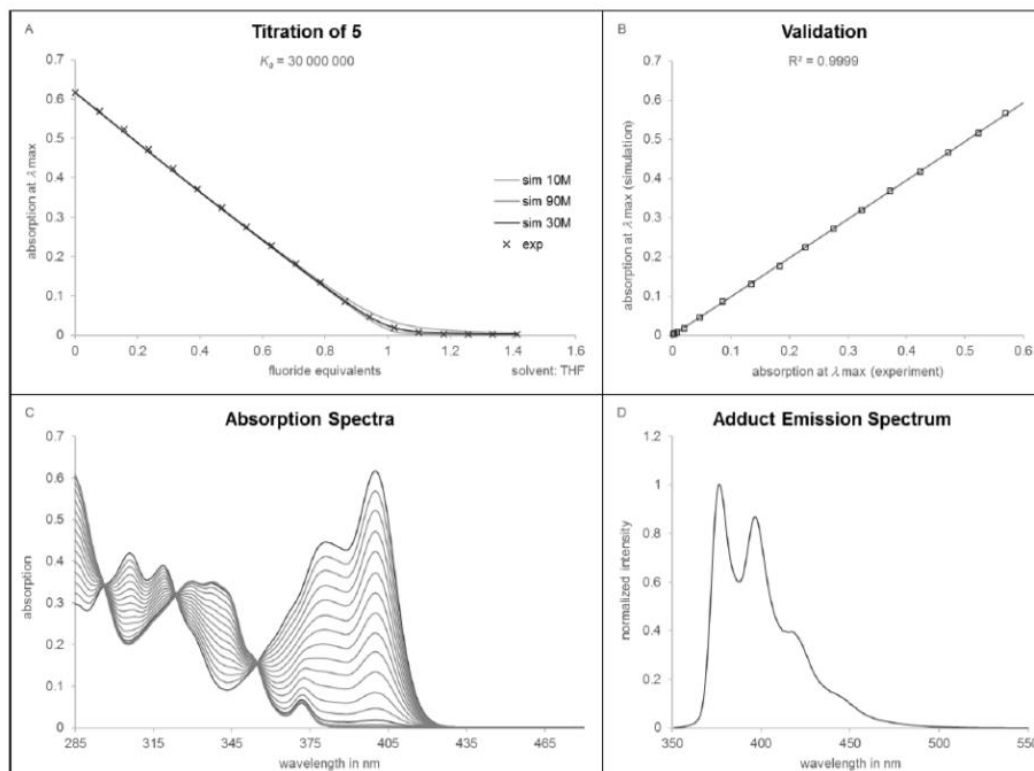


Figure S20: Titration of 5 with TBAF in THF. A: The simulation was fitted with an estimated association constant of $30 \cdot 10^6 \text{ M}^{-1}$ (black line). However, simulation and experiment are in reasonable agreement for all K_a values between $10 \cdot 10^6 \text{ M}^{-1}$ (blue line) and $90 \cdot 10^6 \text{ M}^{-1}$ (orange line). B: The absorption values simulated for $K_a = 30 \cdot 10^6 \text{ M}^{-1}$ are plotted against the experimental values. C: The absorption spectra corresponding to 0 and 1 equivalents of added TBAF are marked in red. D: The adduct emission spectrum was recorded after addition of 1.4 equivalents of TBAF ($\lambda_{\text{ex}} = 330 \text{ nm}$, $\lambda_{\text{max}} = 376, 396, 418 \text{ nm}$).

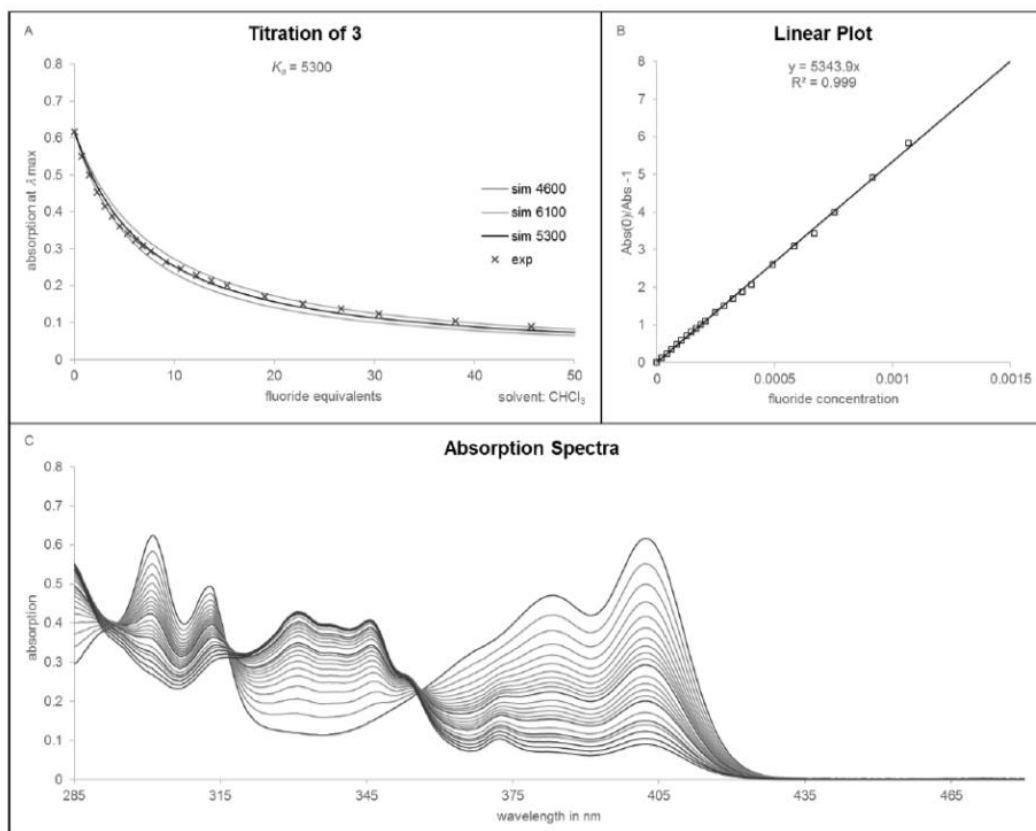


Figure S21: Titration of **3** with TBAF in CHCl_3 . A: The simulation was fitted with an association constant of $K_a = 5300 \text{ M}^{-1}$ (black line). Simulation and experiment are in reasonable agreement for K_a values between 4600 M^{-1} (blue line) and 6100 M^{-1} (orange line). B: Based on two approximations ($B = B_t$ and $V = \text{constant}$), the experimental results can be plotted to give K_a as the slope of a linear fit. C: The amount of TBAF added between any consecutive pair of red-marked absorption spectra is 7.6 equivalents.

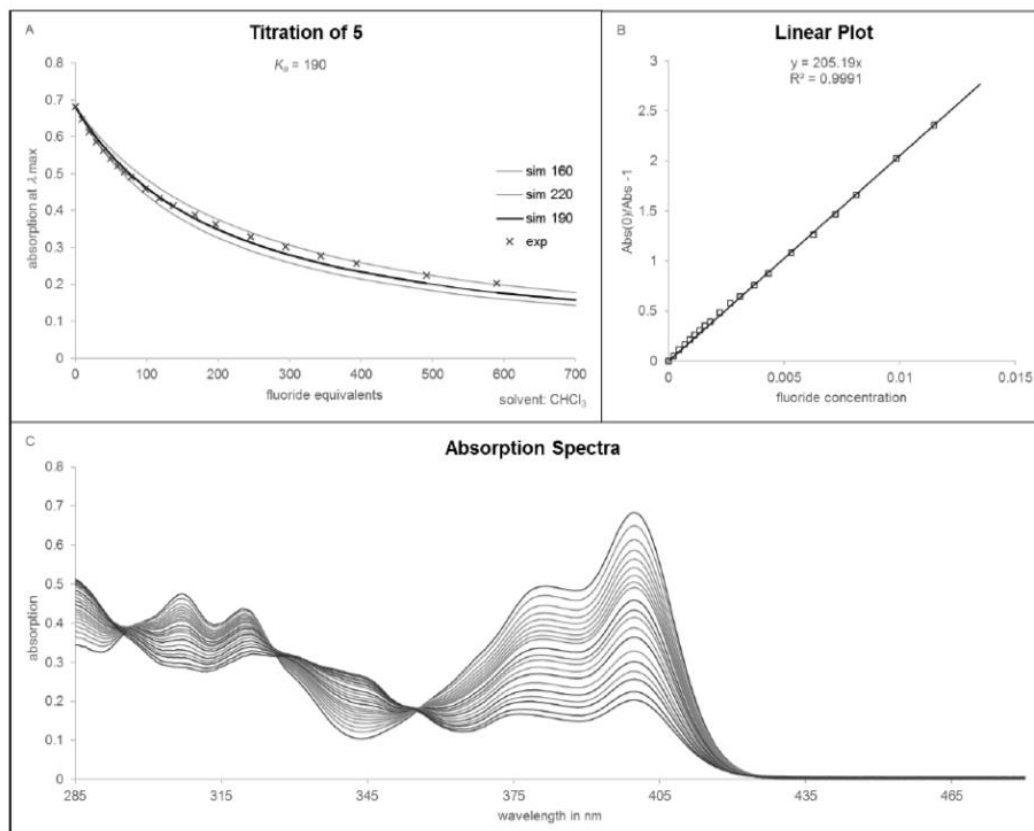


Figure S22: Titration of 5 with TBAF in CHCl_3 . A: The simulation was fitted with an association constant of $K_a = 190 \text{ M}^{-1}$ (black line). Simulation and experiment are in reasonable agreement for K_a values between 160 M^{-1} (blue line) and 220 M^{-1} (orange line). B: Based on two approximations ($B = B_t$ and $V = \text{constant}$), the experimental results can be plotted to give K_a as the slope of a linear fit. C: The amount of TBAF added between any consecutive pair of red-marked absorption spectra is 98 equivalents.

Additional remarks concerning adduct formation

The boranes described herein can also form adducts with Lewis bases other than the fluoride ion. An interaction has been observed with pyridine, although the association constant is apparently very small: even in neat pyridine, the absorption maximum of the free borane **3** is still detectable.

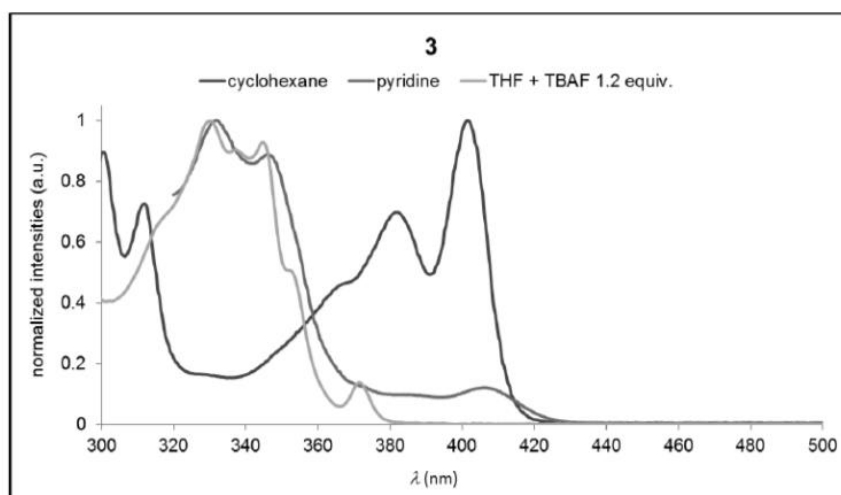


Figure S23: Normalized UV/Vis absorption spectra of **3** in cyclohexane (blue) or pyridine (red) and of $[3F]^-$ in THF (orange).

The planarized borane **5** shows less absorption around 400 nm in pyridine solution, indicating a lower concentration of the free borane **5** compared to **3** in the same donor solvent.

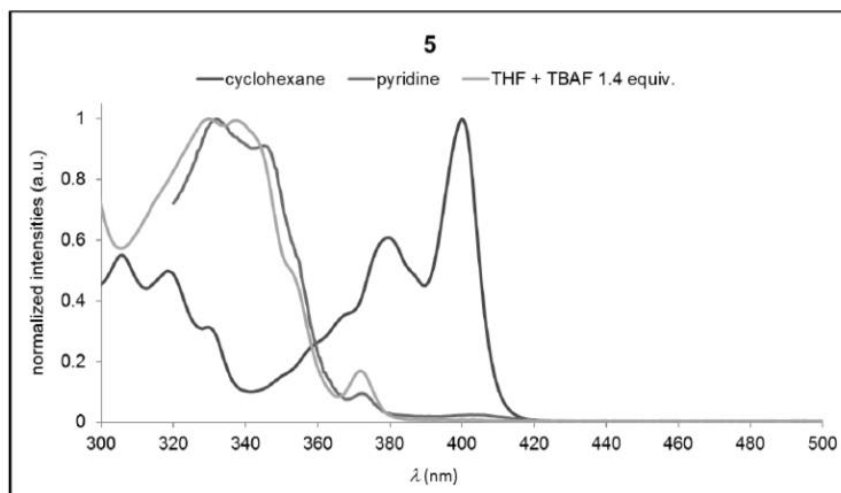


Figure S24: Normalized UV/Vis absorption spectra of **5** in cyclohexane (blue) or pyridine (red) and of $[5F]^-$ in THF (orange).

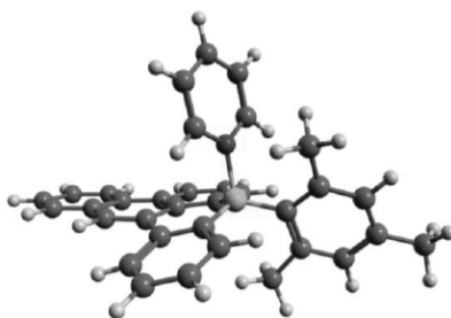


Figure S25: Spatial model of 3-pyridine; the adduct represents a minimum on the potential energy surface (geometry optimized using Gaussian09: B3LYP/6-31G(d)). Although the bulky mesityl substituent causes steric hindrance, pyridine can obviously still attach to the boron atom.

7. Plots of cyclic voltammograms

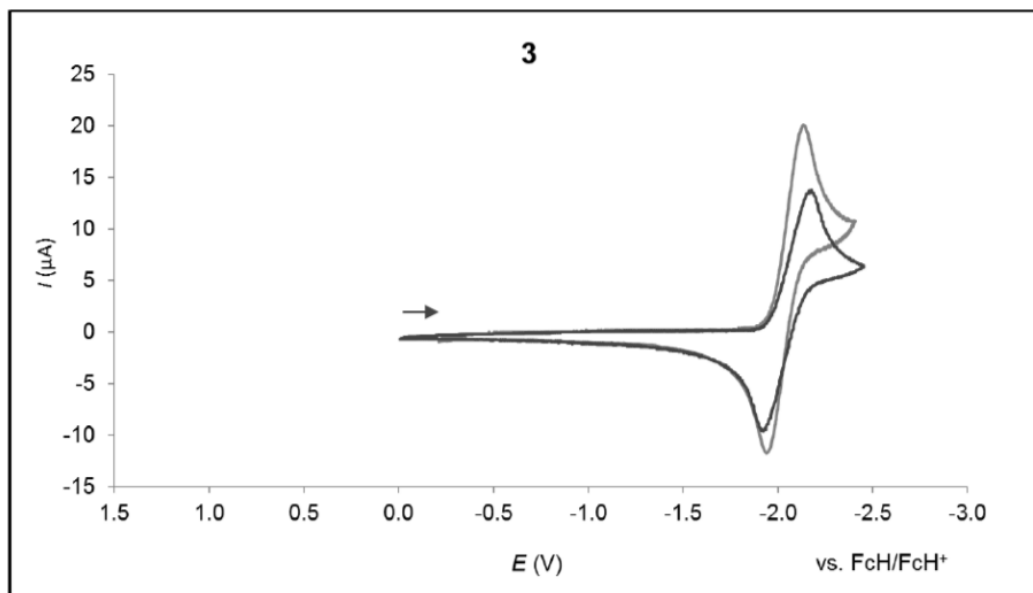


Figure S26: Cyclic voltammogram of **3** in THF (blue) and CH₂Cl₂ (grey; room temperature, supporting electrolyte: [nBu₄N][PF₆] (0.1 M), scan rate: 200 mV s⁻¹).

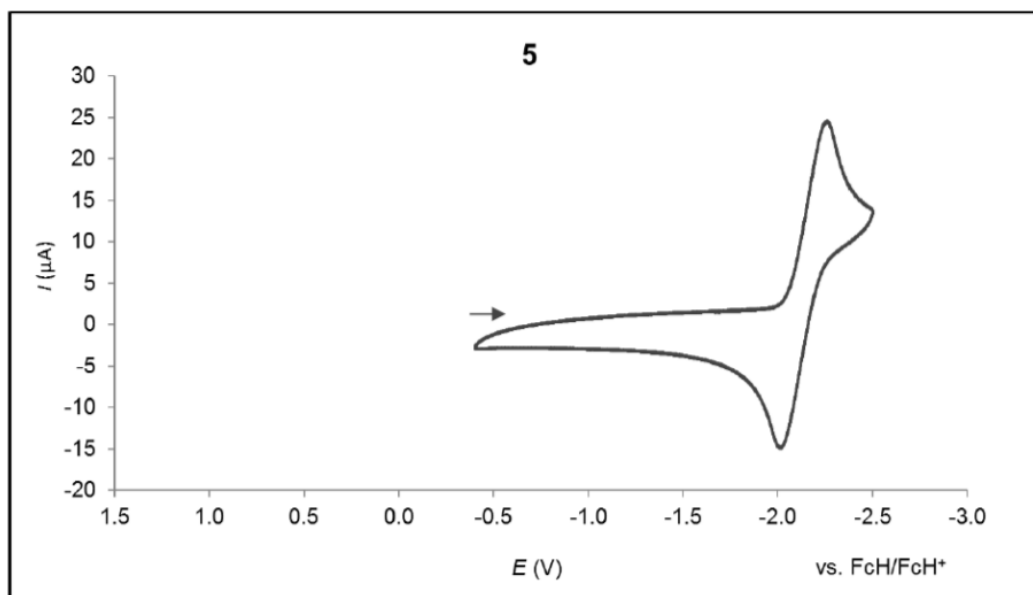


Figure S27: Cyclic voltammogram of **5** in THF (room temperature, supporting electrolyte: [nBu₄N][PF₆] (0.1 M), scan rate: 200 mV s⁻¹).

8. X-ray crystal structure analyses

Data for all structures were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and were scaled using the frame scaling procedure in the *X-Area*^{S11} program system. The structures were solved by direct methods using the program *SHELXS*^{S12} and refined against F^2 with full-matrix least-squares techniques using the program *SHELXL-97*.^{S12}

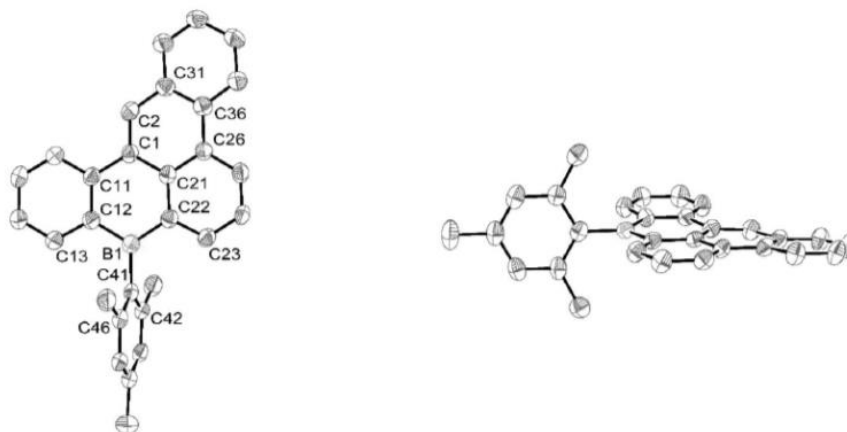


Figure S28 (CCDC 1510163): Molecular structure of **3** in the solid state. The compound crystallizes with two crystallographically independent molecules in the asymmetric unit (**3^A** and **3^B**); the ORTEPs refer to **3^A**. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and angles ($^\circ$) of **3^A/3^B**: B1–C12 = 1.536(6)/1.541(6), B1–C22 = 1.534(5)/1.542(6), B1–C41 = 1.585(6)/1.577(6), C12–C13 = 1.404(5)/1.416(5), C22–C23 = 1.390(5)/1.395(5); C12–B1–C22 = 116.6(3)/117.2(4), C12–B1–C41 = 120.9(3)/120.4(4), C22–B1–C41 = 122.6(3)/122.4(4), C12–B1–C41–C46 = $-74.7(5)/-80.2(5)$, C22–B1–C41–C42 = $-75.6(5)/-84.1(5)$. The crystal was a non-merohedral twin with a fractional contribution of 0.573(2) of the major domain.

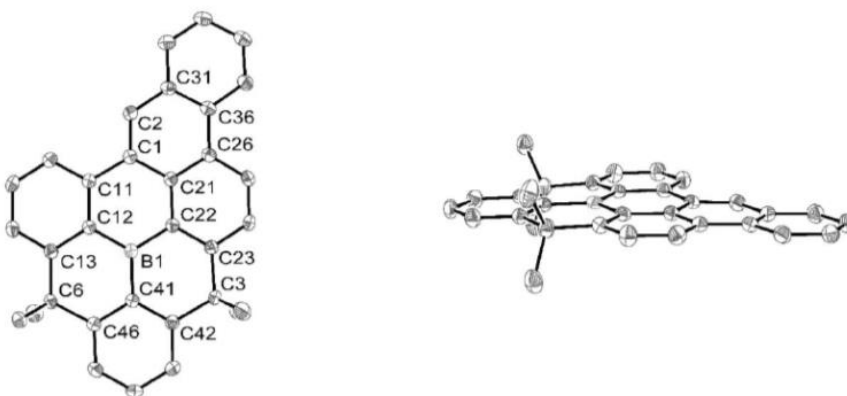


Figure S29 (CCDC 1510164): Molecular structure of **5** in the solid state. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and angles ($^\circ$): B1–C12 = 1.519(2), B1–C22 = 1.517(2), B1–C41 = 1.523(2), C12–C13 = 1.408(2), C22–C23 = 1.394(2); C12–B1–C22 = 119.9(1), C12–B1–C41 = 120.5(1), C22–B1–C41 = 119.6(1), C12–B1–C41–C46 = 1.4(2), C22–B1–C41–C42 = 1.6(2).

Table S1: Selected crystallographic data for **3** and **5**.

compound	3	5
CCDC	1510163	1510164
formula	C ₂₉ H ₂₃ B	C ₃₂ H ₂₅ B
<i>M_r</i>	382.28	420.33
<i>T</i> (K)	173(2)	173(2)
radiation, λ (Å)	MoK α , 0.71073	MoK α , 0.71073
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.8688(5)	14.4275(6)
<i>b</i> (Å)	17.8536(10)	10.0776(3)
<i>c</i> (Å)	29.6812(19)	15.0991(6)
α (°)	90	90
β (°)	97.808(5)	92.965(3)
γ (°)	90	90
<i>V</i> (Å ³)	4131.1(4)	2192.39(14)
<i>Z</i>	8	4
<i>D</i> _{calcd} (g cm ⁻³)	1.229	1.273
F(000)	1616	888
μ (mm ⁻¹)	0.069	0.071
crystal size (mm)	0.25 × 0.19 × 0.11	0.38 × 0.18 × 0.14
reflections collected	22518	52458
independent reflections	7643	5018
<i>R</i> _{int}	0.0725	0.0355
data/restraints/parameters	7643/0/549	5018/0/298
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0737, 0.1578	0.0550, 0.1378
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1062, 0.1758	0.0667, 0.1443
Goodness-of-fit on <i>F</i> ²	1.716	1.127
Largest diff peak and hole (e Å ⁻³)	0.389, -0.418	0.374, -0.186

9. Computational details and HOMO/LUMO analysis

Geometry optimizations and frequency calculations were carried out with the Gaussian 09 software package^{S13} using the B3LYP functional and the 6-31G(d) basis set (Keywords: Opt=Tight Integral(Grid=UltraFineGrid) Freq). The stationary points were characterized as minima (no imaginary frequencies in the vibrational analysis). The graphics were produced with Avogadro 1.1.1 and POV-Ray 3.7.0.

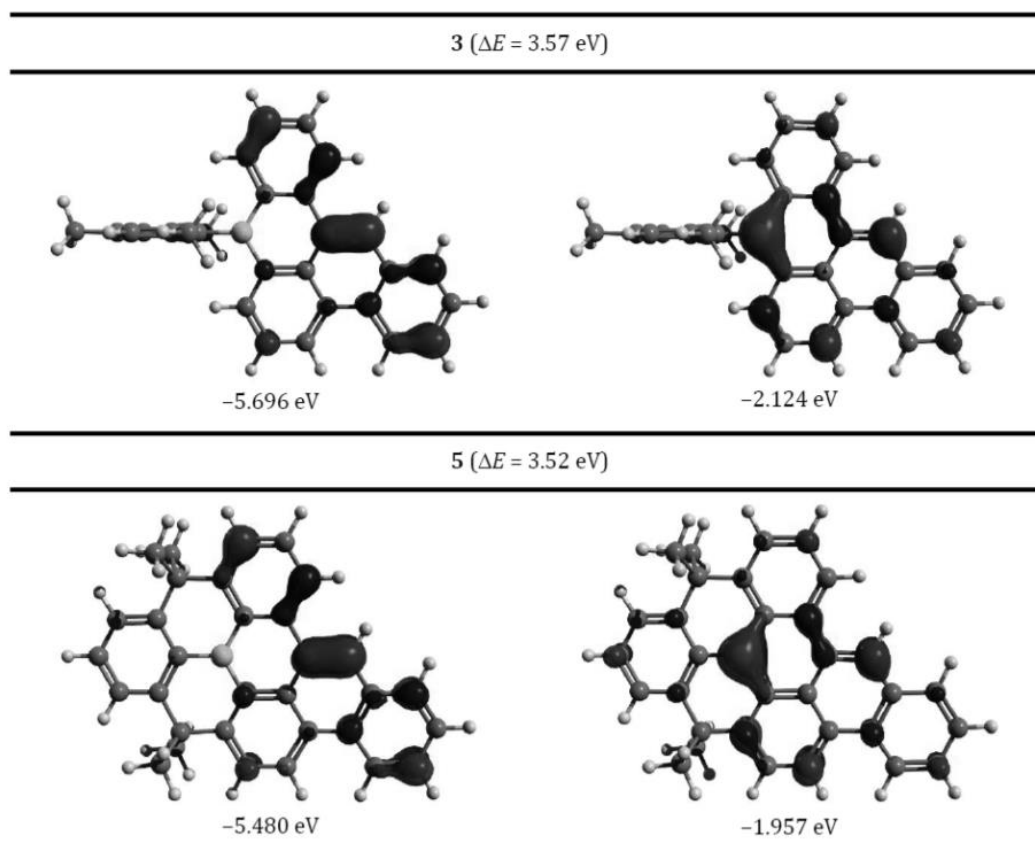
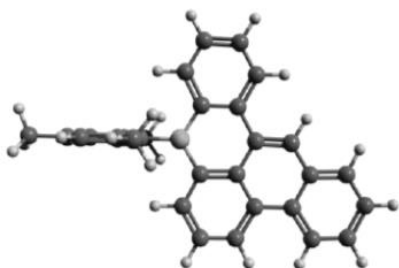


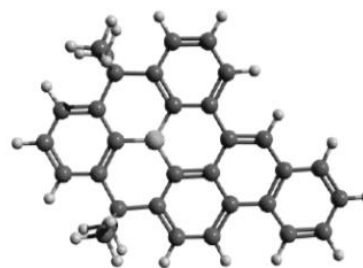
Figure S30: Isosurface plots (isovalue: $0.05 a_0^{-3/2}$) and calculated orbital energy difference for the HOMOs (left) and LUMOs (right).



Total energy: -1143.87937997 Hartree

Atom coordinates:

1	5	0	1.121103	0.185855	0.000001
2	6	0	-1.734246	0.959784	-0.000001
3	6	0	-3.068833	1.292425	0.000005
4	1	0	-3.373967	2.332811	0.000011
5	6	0	-0.688507	2.016985	-0.000003
6	6	0	0.692193	1.670908	0.000002
7	6	0	1.656659	2.701184	0.000004
8	1	0	2.706818	2.421211	0.000009
9	6	0	1.300737	4.042628	-0.000002
10	6	0	-0.057222	4.377166	-0.000011
11	1	0	-0.362305	5.420765	-0.000018
12	6	0	-1.030379	3.384665	-0.000012
13	1	0	-2.067472	3.700007	-0.000021
14	6	0	-1.385568	-0.452768	-0.000004
15	6	0	-0.015207	-0.865485	-0.000005
16	6	0	0.285046	-2.231117	-0.000009
17	1	0	1.328097	-2.535926	-0.000009
18	6	0	-0.721258	-3.201575	-0.000011
19	6	0	-2.046303	-2.805078	-0.000008
20	1	0	-2.814888	-3.570095	-0.000008
21	6	0	-2.419728	-1.441981	-0.000005
22	6	0	-4.126543	0.338597	0.000005
23	6	0	-5.477621	0.765058	0.000011
24	1	0	-5.687247	1.832193	0.000017
25	6	0	-6.509214	-0.150349	0.000010
26	1	0	-7.542447	0.185231	0.000014
27	6	0	-6.212789	-1.527328	0.000001
28	6	0	-4.900340	-1.964514	-0.000004
29	1	0	-4.712438	-3.032411	-0.000011
30	6	0	-3.821086	-1.050110	-0.000002
31	6	0	2.644626	-0.240189	0.000004
32	6	0	3.340914	-0.435605	1.214741
33	6	0	4.687802	-0.813347	1.197151
34	1	0	5.206522	-0.962536	2.143091
35	6	0	5.383082	-1.004861	0.000010
36	6	0	4.687806	-0.813345	-1.197139
37	1	0	5.206530	-0.962532	-2.143078
38	6	0	3.340923	-0.435604	-1.214734
39	6	0	2.636466	-0.242355	2.542199
40	1	0	1.783803	-0.924831	2.650041
41	1	0	2.241129	0.776358	2.643797
42	1	0	3.314113	-0.421535	3.383305
43	6	0	6.846916	-1.381012	0.000001
44	1	0	7.110260	-1.969264	-0.885944
45	1	0	7.110531	-1.968224	0.886551
46	1	0	7.489580	-0.489921	-0.000631
47	6	0	2.636477	-0.242353	-2.542193
48	1	0	3.314127	-0.421519	-3.383299
49	1	0	2.241128	0.776356	-2.643784
50	1	0	1.783821	-0.924838	-2.650040
51	1	0	-7.020404	-2.254298	-0.000001
52	1	0	2.060136	4.819906	0.000000
53	1	0	-0.469773	-4.258734	-0.000013



Total energy: -1259.41545156 Hartree

Atom coordinates:

1	5	0	-0.969799	-0.039270	-0.000001
2	6	0	-2.355885	0.593779	-0.000009
3	6	0	-4.884280	1.750579	-0.000021
4	6	0	-2.474489	2.003288	-0.000013
5	6	0	-3.499209	-0.239252	-0.000015
6	6	0	-4.763250	0.362068	-0.000022
7	6	0	-3.755276	2.567620	-0.000016
8	1	0	-5.667688	-0.239180	-0.000022
9	1	0	-3.891522	3.645157	-0.000014
10	1	0	-5.873366	2.202553	-0.000024
11	6	0	-0.820422	-1.553988	0.000000
12	6	0	-0.535763	-4.316807	0.000038
13	6	0	-1.975687	-2.366429	-0.000002
14	6	0	0.485038	-2.117668	0.000017
15	6	0	0.602234	-3.517155	0.000048
16	6	0	-1.813229	-3.756572	0.000009
17	1	0	1.569650	-4.006554	0.000086
18	1	0	-2.672712	-4.420324	0.000001
19	1	0	-0.426452	-5.398666	0.000055
20	6	0	0.272380	0.842335	0.000014
21	6	0	2.547108	2.440432	0.000025
22	6	0	1.560873	0.224670	0.000014
23	6	0	0.126183	2.234494	0.000016
24	6	0	1.296259	3.023506	0.000026
25	6	0	2.730121	1.038451	0.000017
26	1	0	1.234256	4.107567	0.000030
27	1	0	3.413702	3.093046	0.000031
28	6	0	1.681490	-1.228347	0.000004
29	6	0	2.949398	-1.761896	-0.000024
30	1	0	3.090044	-2.837317	-0.000054
31	6	0	4.141161	-0.980349	-0.000022
32	6	0	4.053302	0.439744	0.000004
33	6	0	5.412427	-1.606011	-0.000040
34	6	0	6.571187	-0.857674	-0.000032
35	1	0	5.458360	-2.692650	-0.000061
36	1	0	7.541244	-1.346948	-0.000044
37	6	0	6.489059	0.548784	-0.000007
38	6	0	5.258454	1.180278	0.000008
39	1	0	7.398452	1.143653	-0.000001
40	1	0	5.231875	2.264576	0.000026
41	6	0	-1.245346	2.936342	0.000003
42	6	0	-3.404655	-1.780684	-0.000011
43	6	0	-1.321915	3.832725	-1.270360
44	1	0	-2.257641	4.399203	-1.296366
45	1	0	-1.271272	3.220250	-2.176676
46	1	0	-0.497549	4.551889	-1.300483
47	6	0	-1.321947	3.832714	1.270372
48	1	0	-2.257677	4.399186	1.296361
49	1	0	-0.497585	4.551883	1.300519
50	1	0	-1.271320	3.220232	2.176684
51	6	0	-4.135424	-2.304875	-1.269959
52	1	0	-5.174520	-1.962920	-1.298326
53	1	0	-4.144742	-3.398800	-1.298642
54	1	0	-3.636037	-1.946614	-2.176343
55	6	0	-4.135429	-2.304865	1.269941
56	1	0	-5.174526	-1.962909	1.298302
57	1	0	-3.636045	-1.946597	2.176323
58	1	0	-4.144746	-3.398790	1.298630

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5.2 Lebenslauf

Die persönlichen Daten wurden aus der digitalen Version entfernt.

5.3 Publikationsliste

Fachartikel

- 06/2015 *Boron-Containing Polycyclic Aromatic Hydrocarbons: Facile Synthesis of Stable, Redox-Active Luminophores*
von V. M. Hertz, M. Bolte, H.-W. Lerner und M. Wagner
erschieden in *Angewandte Chemie Int. Ed.* **2015**, 54, 8800-8804
- 10/2015 *Arylboranverbindung, deren Verfahren zum Herstellen und deren Verwendung*
von M. Wagner, H.-W. Lerner und V. M. Hertz
Patentanmeldung WO2015144133 (A1)
- 10/2015 *Ru-Catalyzed Benzannulation Leads to Luminescent Boron-Containing Polycyclic Aromatic Hydrocarbons*
von V. M. Hertz, H.-W. Lerner und M. Wagner
erschieden in *Organic Letters* **2015**, 17, 5240-5243
- 08/2016 *En Route to Stimuli-Responsive Boron-, Nitrogen- and Sulfur-Doped Polycyclic Aromatic Hydrocarbons*
von V. M. Hertz, J. G. Massoth, M. Bolte, H.-W. Lerner und M. Wagner
erschieden in *Chemistry – A European Journal* **2016**, 22, 13181-13188
- 10/2016 *Steric Shielding vs. Structural Constraint in a Boron-Containing Polycyclic Aromatic Hydrocarbon*
von V. M. Hertz, N. Ando, M. Hirai, M. Bolte, H.-W. Lerner, S. Yamaguchi und M. Wagner
angenommen bei *Organometallics*, DOI: 10.1021/acs.organomet.6b00800

Populärwissenschaftlich

- 12/2015 *Organische Leuchtdioden: Die Tapete als Heimkino*
von M. Wagner und V. M. Hertz
erschieden in *Forschung Frankfurt* **2015**, 2, 30-33

Tagungsbeitrag

- 03/2016 *Modular Synthesis of Luminescent and Benchtop-Stable Boron-Containing PAHs*
Vortrag im Rahmen des 251st National Meeting der American Chemical Society
in San Diego, Kalifornien, USA
Vortragsreihe „Materials, Devices, and Switches“

5.4 Erklärung über frühere Promotionsverfahren und Versicherung

Erklärung

Ich erkläre hiermit, dass ich mich bisher keiner Doktorprüfung unterzogen habe.

Ort, Datum

Unterschrift

Versicherung

Ich erkläre hiermit, dass ich die vorgelegte Dissertation mit dem Titel

Synthese ausgedehnter π -konjugierter Organoborane

selbstständig angefertigt und mich anderer Hilfsmittel als der in ihr angegebenen nicht bedient habe, insbesondere, dass alle Entlehnungen aus anderen Schriften mit Angabe der betreffenden Schrift gekennzeichnet sind.

Ich versichere, die Grundsätze der guten wissenschaftlichen Praxis beachtet und nicht die Hilfe einer kommerziellen Promotionsvermittlung in Anspruch genommen zu haben.

Ort, Datum

Unterschrift