# Gold Catalysis Meets Materials Science – A New Approach to π-Extended Indolocarbazoles

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**Abstract:** Herein we describe a modular, convergent synthesis of substituted benzo[*a*]benzo[6,7]-indolo[2,3-*h*]carbazoles (BBICZs) using a bidirectional gold-catalyzed cyclization reaction as a key step. A building block strategy enabled the easy variation of substituents at different positions of the core structure and a general analysis of substitution effects on the materials properties of the target compounds. All BBICZs were fully characterized and their optical and electronic properties were studied experimentally as well as by computational methods. Organic thin-film transistors based on eight selected derivatives were fabricated by vacuum deposition and charge-carrier mobilities up to 1 $cm^2/Vs$ were measured.

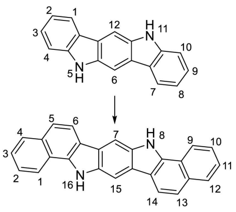
**Keywords:** Materials science; gold catalysis; indolocarbazoles; organic semiconductors; modular synthesis; thin-film transistors

## Introduction

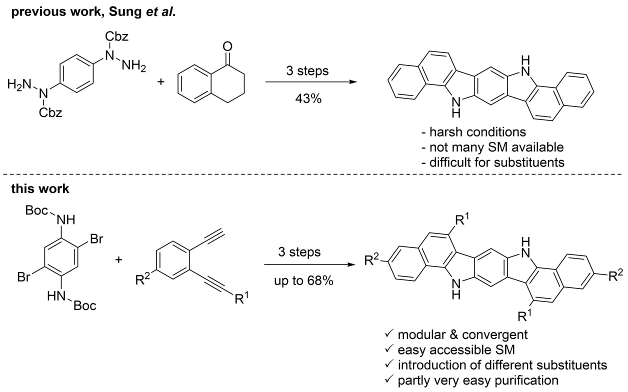
Small-molecule organic semiconductors are of interest for a variety of electronic devices, including organic thin-film transistors (TFTs).[1] Among the large number of molecular motifs that have been explored for the fabrication of organic p-channel TFTs are the indolocarbazoles (ICZs).[2,3] Indolocarbazoles are typically characterized by good solubility in common organic solvents and good air stability, which can be attributed to their low-lying HOMO-energy level. While the performance of the first ICZ-based TFTs was quite disappointing, with a carrier mobility of 0.001 $cm^2$/Vs,[4] the performance of ICZ-based TFTs has been continuously and significantly improved, mainly through strategic substitutions at the various positions of the molecular core. For example, Ong *et al.* introduced a 4-octylphenyl substituent and reported a TFT mobility of 0.14 $cm^2$/Vs.[5] Bao and Leclerc synthesized 3,9-di(*p*-octylbenzene)-5,11-dihydroindolocarbazole and measured a carrier mobility of 0.22 $cm^2$/Vs.[6]

The fact that even small modifications to the molecular structure can have significant effects on the electronic properties was demonstrated by the introduction of chloro-substituents at the 2- and 8-positions of *N*-alkylated ICZs, which led to a carrier mobility of 0.5 $cm^2$/Vs in single-crystal transistors.[7] In 2013, Sung *et al.* reported on the synthesis of 7-ring π-extended indolocarbazoles (Scheme 1), so called benzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazoles (BBICZs), with alkyl substituents ranging in chain length from C5 to C16.[8] The π-extension led to a carrier mobility of 1.5 $cm^2$/Vs for transistors based on a C12-BBICZ single-crystal. C12-BBICZ and its non-alkylated derivative have also been used as a hole-transporting material in perovskite solar cells[9] and as a donor in solution-processed organic semiconductors.[10]

What is currently lacking is a systematic analysis of the effects of the substitution patterns on the material properties of π-extended indolocarbazoles. This is in part due to the fact that the traditional synthesis involves a double Fischer indole reaction of 3,4-dihydronaphthalen-1(2H)-one and Cbz-protected 1,4-dihydrazineylbenzene that is characterized by rather harsh conditions and requires precursors with limited commercial availability (Scheme 2). In order to conduct a deeper study on the effect of substitution manipulations on the electronic properties of BBICZs, as a missing link to the already mentioned current research on ICZs, we envisioned that a modular approach using a gold-catalyzed key step might contribute to a further evolution of this promising substrate class.[11]



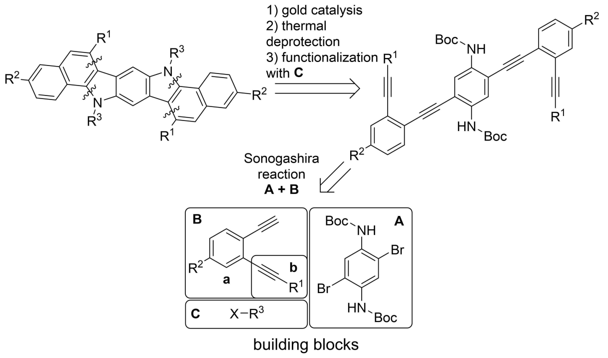
**Scheme 1.** π-Extension of indolocarbazoles.



**Scheme 2.** Previous approach towards BBICZs and our strategy.

## Results and Discussion

In contrast to the established approaches to indolocarbazoles, we reasoned an entirely new approach for the synthesis of BBICZs.[12] Numerous publications during the past decade impressively demonstrated gold catalysis as an effective tool for the formation of extended π-systems.[13] In this context, cascade cyclizations turned out to be especially effective in which polyynes serve as starting materials.[14] As an example, the well-known gold-catalyzed indole synthesis from Utimoto *et al.* served as a first step of a cascade reaction, in which this nucleophilic unit was further transferred to a larger π-system by one or more additional alkyne moieties that react in a nucleophilic cascade towards the extended π-systems.[15] Additionally, bidirectional approaches and cascade cyclizations can be combined, which has already been demonstrated by Yamamoto *et al.* and our group.[16] In the present study, we present a new access to π-extended indolocarbazoles by a gold-catalyzed bidirectional tandem cyclization as crucial step. Tetraynes **1 a–g**, which serve as starting materials for the subsequent gold-catalyzed step, were made accessible by a modular building block principle which opens up a highly variable, convergent synthetic approach towards differently substituted derivatives of the target molecules (Scheme 3).



**Scheme 3.** Building block principle for the BBICZ-synthesis.

The diamine building block **A** was synthesized through a modified literature procedure from Lepoittevin *et al.* in three steps starting from *p*-diaminobenzene in excellent yield (scheme 4).[17] This building block acts as the inner core and is therefore part of all BBICZs.

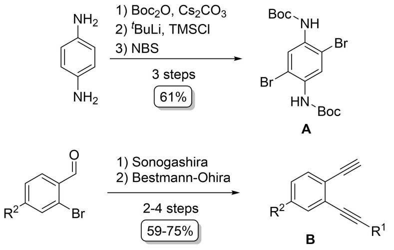
The diyne-building block **B** was derived from different commercially available 2-bromobenzaldehydes (**Ba**) and terminal alkynes (**Bb**). A Sonogashira cross-coupling, followed by a Seyferth-Gilbert homologation with the Bestmann-Ohira reagent or a Corey-Fuchs strategy (for $R^1$ = TMS) delivered this subunit (overall 7 examples). By using the chlorinated 2-bromo-4-chloro-benzaldehyde, it was also possible to introduce a hexyl substituent as an example for an alkyl chain at the $R^2$-position through a Suzuki reaction with hexylboronic acid. Based on the availability of many different alkynes and 2-bromobenzaldehydes in combination with mild reaction conditions, building block **B** turned out to be the most variable one in our strategy. In accordance with already reported procedures, the $R^3$ substituent from building block **C** was introduced by a late stage modification of the *N*-unprotected molecules. Alkyl groups with different chain lengths turned out to be the most suitable units.

By combining the two building blocks **A** and **B** via a bidirectional Sonogashira reaction, tetraynes **1 a**–**g** were achieved in reasonable to excellent yields from 51–88% (scheme 5). Only in the case of **TMS-1 f** ($R^1$ = TMS, $R^2$ = Cl), the yield dropped down to 27%. Owing to their amino-functionality and their moderate solubility, purification of these π-extended alkyne systems was challenging at first, but simple filtration over a short pad of silica gel and subsequent recrystallisation/precipitation from EA or an EA/PE-mixture turned out to be a simple way to furnish the compounds in high purity

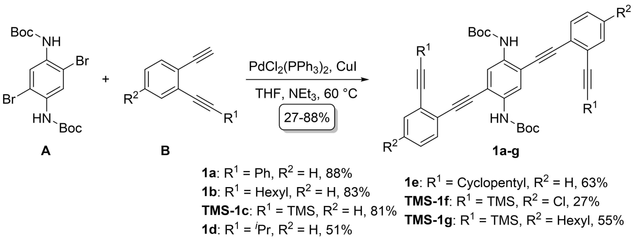
The tetraynes themselves might appear as promising materials as well.[17] Analyzing the optical properties (absorption and emission spectroscopy) of the respective compounds revealed fluorescence quantum yields of up to 68%, indicating potential applicability in organic devices (for absorption and emission spectra see SI). Scheme 6 shows the crucial gold-catalyzed cyclization step of tetraynes **1 a**–**g** to Boc-BBICZs **2 a**–**g**. In general, 5 mol% of the commercially available IPrAuNTf$_2$ served as catalyst in 1,2-dichloroethane at 60 °C over night. Overall, 6 new bonds are formed during the reaction in a single step. Products **2 a**–**g** were either isolated via common flash column chromatography or, for compounds **2 c**–**f** which precipitate due to the formation of the large planar π-system causing low solubility, by simple filtration of the product from the reaction mixture.

It is noteworthy, that it was also possible to synthesize BBICZs with $R^1$ = H (**2 c**) via the cyclization of the corresponding terminal alkynes. These are of particularly interest, because cross-couplings like Sonogashira reaction are once more feasible at this stage of the sequence. To demonstrate this approach, **1 a** was synthesized by a Sonogashira reaction from **1 c** with 2 eq of iodobenzene in 74% yield (scheme 7).

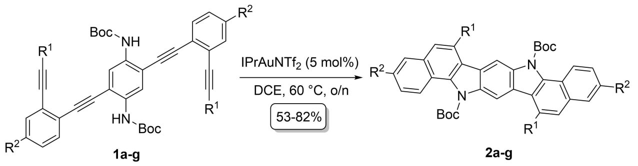
Interestingly, the TMS-protected tetrayne **TMS-1 c** furnished the desilylated BBICZ **2 c** in 29% yield after



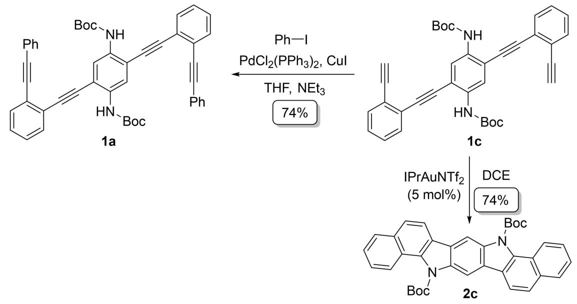
**Scheme 4.** Synthesis of building blocks **A** and **B**.



**Scheme 5.** Combination of building blocks **A** and **B** via a bidirectional Sonogashira reaction. For **1 a** Pd(PPh$_3$)$_4$ was used instead of PdCl$_2$(PPh$_3$)$_2$.



**Scheme 6.** Gold-catalyzed conversion of tetraynes **1 a**–**g**. For **1 a** and **1 b** 10 mol% IPrAuNTf$_2$ were used. For **TMS-1 c**, 29% of deprotected **2 c** was obtained.



**Scheme 7.** Gold-catalyzed conversion of tetrayne **1 c** and further Sonogashira-modification.

the gold-catalyzed step. The reason for this fact can be explained by the isolobal-analogy of LAu$^+$ and a proton combined by the use of non-dry solvents for the gold catalysis.[19,20] To cleave the Boc-protection group, which was introduced for synthetic reasons at the beginning of the synthesis, we applied a modified procedure of Cava and Bergman.[21] This thermal deprotection worked quantitatively under vacuum at temperatures above 200 °C without any solvent. Usually no further purification was needed (scheme 8). Other attempts using more classic deprotection methods like acidic cleavage with TFA or HCl in dioxane resulted in difficult workup or low conversion.

The work by Sung *et al.* already demonstrated a dependence of the product solubility from the length of the alkylchain.[8] In this study, the dodecyl chain gave the best results, hence all synthesized BBICZs were alkylated analogously following Sung's protocol with aqueous NaOH and dodecylbromide in anhydrous DMSO. For **4 a**, **4 b** and **4 e**, THF was used as solvent due to higher solubility of the corresponding starting materials. **3 d**, **3 f** and **3 g** were alkylated using KO$^t$Bu instead of a NaOH solution as base. Following the same strategy it was also possible to introduce a methyl-group (**4 h**). Remarkably, R$^1$ seems to be crucial for the solubility of **3 a–g** as well. For R$^1$ = Ph and $^i$Pr (**3 a**, **3 d**), the products are soluble in common organic solvents such as chloroform or dichloromethane, whereas all other non-alkylated BBICZs were only soluble in THF or DMSO. In contrast, all alkylated BBICZs showed a decent solubility in chloroform and dichloromethane. Overall 15 different BBICZs were synthesized in good to excellent yields (Table 1).

X-Ray structures for BBICZs **3 a**, **3 b**, **3 d** and the alkylated **4 a** and **4 f** were obtained.[22] The solid state molecular structures are in excellent agreement with expected bond lengths and angles.[8] It should be noted that for the non alkylated **3 a–g** in most cases a solvent molecule is part of the determined solid state structure (except for **3 d**). For **3 a** the molecules show π-π-stacking of the naphthyl ends between each other, which leads to one-dimensional chains in direction of the molecule plane (Figure 1). In between there is one solvent molecule (DCM). For **3 b** and **3 d** no π-stacking was observed in the solid state structure. **3 b** forms parallel columns, but one solvent molecule (DMSO) and the alkylchains prevent decent π-stacking. **3 d** also forms columns; however, molecules are strongly laterally shifted against each other so that there is hardly any π-contact. The alkylated **4 a** forms one-dimensional columns perpendicular to the molecular plane with significant π-stacking. **4 f** shows a similar behaviour.

**Table 1.** Yields of gold cyclization and final alkylation.

| Starting material | R$^1$ | R$^2$ | Yield of the gold catalysis | Method of alkylation | Yield of the alkylation |
|---|---|---|---|---|---|
| 1a | Ph | H | 54% | A | 92% |
| 1b | Hexyl | H | 82% | A | 68% |
| TMS-1c | TMS | H | 29%[a] | / | / |
| 1c | H | H | 74% | A<br>B[b] | 77%<br>60%[b] |
| 1d | $^i$Pr | H | 78% | B | 88% |
| 1e | Cyclopentyl | H | 53% | A[c] | 58% |
| 1f | H | Cl | 82% | B | 75% |
| 1 g | H | Hexyl | 73% | B | 85% |

[a] 29% of **2 c** was obtained.

[b] methyl (compound **4h**) by using MeI instead of dodecylbromide.

[c] THF was used due to better solubility.

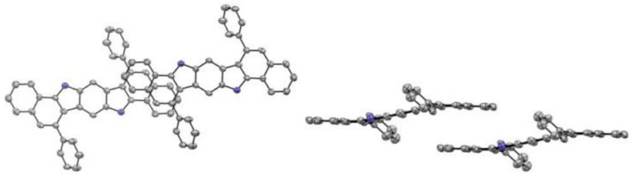
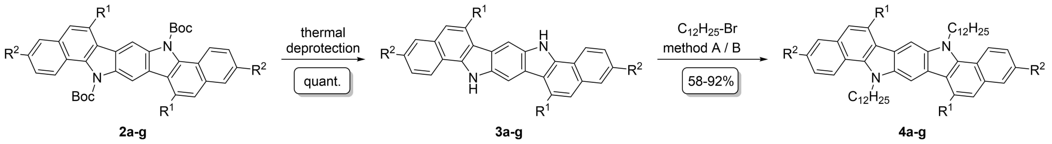


**Figure 1.** X-ray structure with π-π-stacking of the naphthyl ends of **3 a**. Left: top view, right: side view.

Our next efforts concentrated on the evaluation of the optical and redox properties of the obtained BBICZs **3 a–g**, the alkylated BBICZs **4 a–h** and the Boc-protected derivatives (**2**, see Supporting Information). Among themselves, **3 a–g** and **4 a–h** show quite similar absorption spectra with maxima of 395–406 nm and 417–425 nm, respectively (Figure 2). It is striking that while a hexyl substitution at the 3,11-position of derivatives **3 g**/**4 g** leads to the most hypsochromic shift, the same substituents attached to the 6,14-position only have a minor influence on the absorption signal maximum. A similar effect was observed for the fluorescence quantum yields (QY).



**Scheme 8.** Boc-deprotection to the final BBICZs **3 a–g** and alkylation methods to get **4 a–h**. Method A: aqueous NaOH, benzyltriethylammonium chloride (25 mol%), DMSO; method B: KOtBu (4 eq), DMSO.

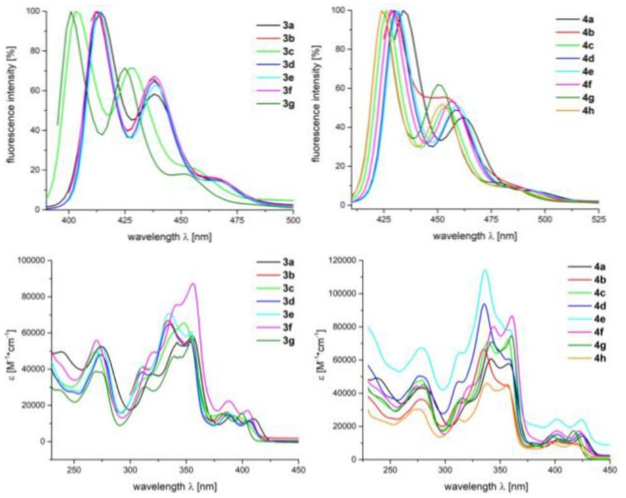


**Figure 2.** Absorption and emission spectra of **3 a**–**g** (left, in THF) and **4 a**–**h** (right, in DCM). All emission spectra were normalized to the maximum emission signal.

All 6,14-substituted BBICZs show similar quantum yields varying between 33–37% for **3 a**–**g** and 24–36% for **4 a**–**h**. However, 3,11-substitution has a notable greater influence. **3 f**/**4 f** with the electron-withdrawing chloro substituent show the lowest QY (15% for **3 f**, 14% for **4 f**), while the hexyl-substituent led to the highest yield with 58% (**3 g**) and 44%, respectively (**4 g**).

Cyclic voltammograms were recorded for all dichloromethane soluble compounds, namely **3 a**, **3 d** and all alkylated **4 a**–**h** (see Supporting Information for more details). All compounds show two reversible oxidation potentials. For **3 a** and **3 d**, the second oxidation potential is almost the same (774 mV vs. 739 mV), but a big difference in the first oxidation potential can be detected (125 mV vs. 317 mV). The alkylated compounds **4 a**–**h** show greater differences between both potentials. **4 f** and **4 a** with an electron-withdrawing chloro, respectively an aryl substituent, have similar and high values for both oxidation states (321–333 mV; 919–934 mV). In contrast the values of the alkyl-substituted (**4 b**, **4 d**, **4 e**, **4 g**) vary much stronger (11–240 mV; 646–981 mV).

In order to get a better understanding of substitution effects on optical and electronic properties, theoretical calculations (computational details see SI) of selected compounds were conducted next, followed by device fabrications of the most notable compounds (Table 2). Calculation of the optical properties using time dependent density functional theory (TDDFT) illuminated the character of the emitting excited state being mainly unchanged and derived from the parent molecule **3 c**. Thus, in the case of **3 c**, a bright π-π* transition (oscillator strength of 0.23) constitutes the first excited singlet state, classified as the typical Ls state of *N*-heteropolycyles,[23] exhibiting a strongly correlated electron-hole pair (exciton) with a pronounced correlation coefficient of 0.56. The excitation

**Table 2.** Overview of quantum yield (QY), photophysical and electrochemical properties of **3 a**–**g** and **4 a**–**h**, including theoretical and device properties of selected BBICZs. $\lambda_{abs,\,max}$ = maximum of the longest absorption wavelength; $\lambda_{em}$ = maximum of the shortest emission wavelength, $E_{g,cal}$ = calculated optical Gap, $IP_{cal}$ = calculated ionization potential, $EA_{cal}$ = calculated electron affinity, $\lambda_{cal}$ = reorganization energy, $FG_{cal}$ = fundamental gap, $\mu^h$ = hole transport mobility.

| Compound | $\lambda_{abs,max}$ [nm] | $\lambda_{em}$ [nm] | $E_{g,opt}$ [eV][a] | QY | Ox-pot. [mV] [b] | $E_{g,cal}$ [eV] | **IP$_{cal}$**/EA$_{cal}$ [eV] | $\lambda_{cal}$ [meV] | **FG$_{cal}$** [eV] | $\mu^h$ [cm$^2$/Vs] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Silicon substrate | PEN substrate |
| 3a | 404 | 414 | 2.99 | 37% | 317/774 | 3.89 | 6.32/0.43 | 100.94 | 5.88 | $3\times10^{-5}$ | No field effect |
| 3b[c] | 405 | 413 | 2.95 | 36% | | 3.93 | 6.36/0.34 | 93.42 | 6.02 | 0.1 | 0.01 |
| 3c | 397 | 403 | 2.99 | 15% | | 3.93 | 6.44/0.37 | 100.52 | 6.07 | 1 | 0.5 |
| 3d | 406 | 413 | 2.98 | 34% | 125/739 | 3.91 | 6.33/0.38 | 96.48 | 5.95 | 0.003 | 0.008 |
| 3e | 406 | 414 | 2.98 | 33% | | | | | | | |
| 3f | 404 | 413 | 2.99 | 24% | | | | | | | |
| 3g[c] | 395 | 400 | 3.06 | 58% | | 3.94 | 6.32/0.29 | 116.23 | 6.03 | 0.1 | 0.05 |
| 4a[c] | 425 | 434 | 2.82 | 36% | 333/934 | 3.78 | 6.11/0.38 | 84.17 | | 0.2 | 0.02 |
| 4b | 423 | 430 | 2.83 | 24% | 11/646 | | | | | | |
| 4c[c] | 420 | 420 | 2.88 | 36% | | | | | | 0.02 | 0.002 |
| 4d[c] | 423 | 425 | 2.83 | 30% | 240/650 | 3.80 | 6.16/0.38 | 96.30 | | No field effect | 0.001 |
| 4e | 424 | 431 | 2.82 | 33% | 195/875 | | | | | | |
| 4f | 422 | 429 | 2.86 | 14% | 321/919 | | | | | | |
| 4 g | 417 | 425 | 2.91 | 44% | 130/981 | | | | | | |
| 4 h | 418 | 425 | 2.87 | 41% | | | | | | | |

[a] from onset of the absorption spectra.
[b] from cyclic voltammographic measurements.
[c] alkyl chains were simplified using a methyl group.

energy (optical gap) for **3 c** of 3.93 eV is in the UV–A region. The effect of alkylation at the carbon skeleton (e.g. for **3 b**) on the photophysical properties is only marginal, except a change in oscillator strength with **3 g** exhibiting an almost twice as large oscillator strength of the first excited singlet state (0.28) compared to **3 b** (0.14). The difference in the coupling of the S1 and S0 states is in line with the experimental findings of an increased quantum yield for the 3,11-substitution pattern in contrast to the 6,14-position. The addition of additional π-systems as substituents, i.e. in **3 a**, results mainly in the reduction of the exciton binding energy (difference between fundamental and optical gap) from 2.15 eV (**3 c**) to 1.99 eV. An alkyl substituent (**3 d**) shows the same trend, but less pronounced, with an exciton binding energy of 2.04 eV. Generally, the alkylation of the amino groups (**4 a** and **4 d**) leads to a decreased exciton binding energy (1.95 eV and 1.98 eV) as well as a smaller optical gap (3.78 eV and 3.80 eV).

The calculations provide an additional puzzle piece to understand structure-property relationships and therefore assist to uncover the potential of deliberate tuning of desired electronic and optical properties. The fundamental gap (single-molecule band gap), being the difference of non-adiabatic (vertical) ionization potential and electron affinity, gives an indication of the energetic barrier of charge transport (creating and eliminating a charge carrier). Therefore, a smaller fundamental gap should have a positive effect on the charge carrier mobility. Furthermore, a decreasing reorganization energy, as defined within Marcus theory (see SI), leads to an acceleration of an electron transfer process. While the fundamental gap turned out to be invariant from the substitution pattern of compounds **3 b** and **3 g** (3,11- vs. 6,14-hexyl substitution), a significant effect on the reorganization energy was calculated. While the 3,11-derivative showed a higher reorganization energy (116.23 meV) compared to **3 c** (100.52 meV), the 6,14-derivative showed a lower one (93.42 meV). The type of substituent on the 6,14-position with either being an alkyl **3 b** or an aryl type substituent **3 a**, influences mainly the electron affinity (0.43 eV for **3 a** and 0.34 eV for **3 b**) leading to a decrease in the fundamental gap in the case of **3 a** (5.88 eV). The difference in reorganization energy is relatively marginal in comparison with **3 b** exhibiting a slightly smaller reorganization energy (93.42 meV) compared to **3 a** (100.94 meV). Varying the type of alkyl substituent (**3 b** compared to **3 d**) has insignificant influence on electronic properties indicating the steric load being responsible for varying measured charge carrier mobilities. The most notable change happens in the case of alkylation (methylation) of the amino group, with the **4 a** derivative showing a significantly lower reorganization energy (84.17 meV) compared to its non-alkylated counterpart **3 a** (100.64 meV). In addition, the ionization potential decreases from 6.32 eV to 6.11 eV which consequently leads to a smaller fundamental gap of 5.73 eV. The same trend can be observed for the alkylated substituents (**3 d** compared to **4 d**). However, the steric hindrance due to the bulkiness of the $^{i}$Pr group (**3 d**/**4 d**) should again be the predominant factor in resulting thin film morphologies and subsequently measured mobilities. Consequently, the substitution pattern of **4 a** should have the most positive influence, as both, the fundamental gap as well as the reorganization energy are the lowest calculated and the ability for π-stacking in aggregation should remedy the increased sterics due the aryl substituent.

To investigate the charge-transport properties of BBICZ **3 c** and its alkylated and non-alkylated derivatives **3 a**, **3 b**, **3 d**, **3 g**, **4 a**, **4 c** and **4 d**, we fabricated TFTs in the inverted staggered (bottom-gate, top-contact) device architecture on heavily doped silicon substrates[24] and on flexible polyethylene naphthalate (PEN) substrates[25] (Figure 3). The organic semiconductors were deposited by thermal sublimation in vacuum (for more details see the Supporting Information). All TFTs operate as p-channel transistors. The best TFT performance was obtained for the parent compound BBICZ **3 c**, which showed effective charge-carrier mobilities of 1 cm$^2$/Vs in TFTs fabricated on a silicon substrate and 0.5 cm$^2$/Vs in TFTs fabricated on flexible PEN (Scheme 9). These mobilities are larger compared to the literature value of 0.21 cm$^2$/Vs reported previously for this compound.[10e] In contrast to the theoretical calculations, which predict carrier mobilities larger than that of **3 c** for some of the derivatives, our measurements of TFTs based on **3 a**,

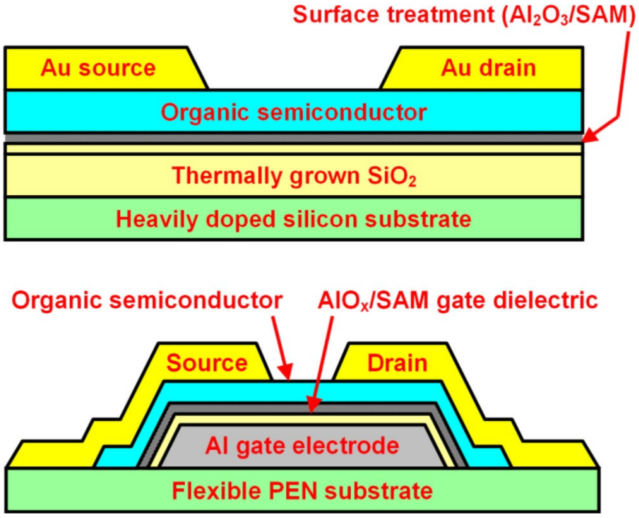
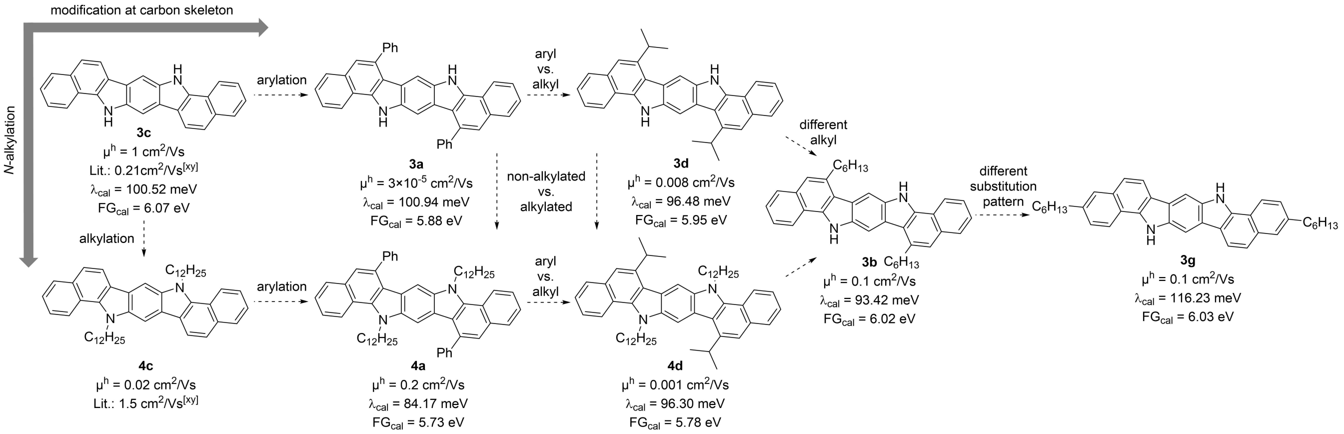


**Figure 3.** Top: Schematic cross-section of organic TFTs fabricated on silicon substrates. Bottom: Schematic cross-section of organic TFTs fabricated on polyethylene naphthalate (PEN) substrates.



**Scheme 9.** Overview of BBICZs used for fabrication of TFTs.

**3b**, **3d**, **3g**, **4a**, **4c** and **4d** all yielded mobilities smaller than that of **3c**. For example, hexyl substitution at the carbon skeleton led to a mobility of 0.1 cm$^2$/Vs, regardless of the position of the substituents (**3b** and **3g**). Especially for **3g** we expected a higher value, based on previous results on similarly substituted DNTTs (dinaphtho[2,3-*b*:2,3‘-*f*]thieno[3,2-*b*]thiophenes).[26] However, the morphology of the vacuum-deposited semiconductor films and thus the obtained carrier mobilities are dependent on the fabrication process, which might be improved further.

Phenyl (**3a**) or isopropyl (**3d**) substitution at the 6,14-positions of the *N*-unsubstituted compounds produced mobilities below 0.01 cm$^2$/Vs. Interestingly, a phenyl substitution at the 6,14-positions in combination with a dodecyl substitution at the nitrogen atoms (**4a**) led to carrier mobilities of 0.2 cm$^2$/Vs on silicon and 0.02 cm$^2$/Vs on flexible PEN substrates. The fact that these mobilities are larger than those of the *N*-unalkylated counterparts (**3a** and **3d**) is consistent with the theoretical predictions which indicate a beneficial effect of *N*-alkylation. In contrast, this effect was not observed for the isopropyl derivate (**4d**), which completely falls out of the series with a carrier mobility of just 0.001 cm$^2$/Vs on PEN and without yielding a field effect on a silicon substrate.

For the previously reported **4c** we measured a mobility of 0.02 cm$^2$/Vs, which is substantially smaller compared to the value of 1.5 cm$^2$/Vs reported by Sung *et al.* for a transistor based on solution-grown single-crystals of this compound.[8] These results serve as a reminder that the specific crystal packing for which theory may predict a large carrier mobility is not always identical to the crystal packing obtained in thin films, especially when these are prepared by vacuum deposition, which typically provides less control over the crystallization process than some solution-based deposition methods. In other words, while vacuum deposition can yield high mobilities for molecules with a simple rod-like shape (such as **3c**), it is often less suitable for molecules with sterically demanding substituents, which means that some of the BBICZ derivatives presented here might perform better if processed using an optimized solution-based protocol. Nevertheless, the fact that we measured carrier mobilities between 0.1 and 1 cm$^2$/Vs for four different compounds (**3b**, **3c**, **3g**, **4a**) confirms that BBICZ is indeed an interesting molecular motif for future device-fabrication efforts.

## Conclusion

We present a new highly modular, bidirectional synthetic strategy to π-extended indolocarbazoles via a variable building block principle. The starting materials for this route are easily accessible by well-known procedures. Bidirectional Sonogashira cross-coupling, followed by gold catalysis as a key step and a final quantitative thermal deprotection, provides access to BBICZs in very good yields. In total, 13 new BBICZ derivatives were synthesized, and their optical, electronic and redox properties were studied. The solid-state structures of some of the compounds were also obtained. Based on these BBICZs, we analyzed a number of potentially useful structure-property relationships. The effects of different substitution patterns on the electronic properties of the molecules were studied theoretically and by fabricating TFTs, in which we measured carrier mobilities up to 1 cm$^2$/Vs. The measurements confirmed some of the trends predicted by the theoretical calculations regarding the effect of certain substitution patterns on the charge-carrier mobility, such as the beneficial effect of *N*-alkylation. In general, however, we measured smaller carrier mobilities in the substituted BBICZs compared to the unsubstituted parent compound **3c**, which is partly in contradiction to the results of the theoretical analysis. This might be due to the fact that certain substitution patterns make it difficult, if not impossible, to obtain a favorable thin-film morphology by vacuum deposition. Such compounds may provide better performance when processed into single-crystals or from solution, much like TIPS pentacene for which the best mobilities obtained by solution processing are significantly larger than the best mobilities obtained by vacuum deposition. More importantly, the modular synthetic approach presented here will greatly accelerate the rapid screening of this class of compounds for materials science. Further screenings of this class of compounds is ongoing in our laboratories.

## Experimental Section

### General Procedure for the Gold Catalysis

1.00 eq of the corresponding alkyne was dissolved in DCE. 5 mol% $IPrAuNTf_2$ were added and the mixture was stirred at given temperature for the given time until TLC showed full conversion. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography.

### General Procedure for the thermal Boc deprotection

In a flask with vacuum-connection the Boc-protected BBICZ was heated up to 200–220 °C on a vacuum of $5*10^{-3}$ mbar for 3–5 h. The progress of the reaction could be determined by colour change and meantime decrease of the applied vacuum.

### Di-tert-butyl 6,14-diphenylbenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate (2 a):

According to the general procedure, 1.00 eq of the corresponding tetrayne (100 mg, 141 µmol) was dissolved in 20 mL DCE and 10 mol% $IPrAuNTf_2$ (12.2 mg, 14.1 µmol) were added to the solution. After stirring over 3 d at 60 °C, the mixture was treated according to general procedure (silica gel, PE:EA = 50:1). A beige solid was obtained (54.0 mg, 76.2 µmol, 54%).

Mp.: decomp. >192 °C; $R_f$: 0.27 (silica gel, PE:EA = 10:1); IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3056, 2979, 2932, 1731, 1495, 1438, 1392, 1368, 1339, 1286, 1254, 1144, 1122, 1065, 878, 852, 832, 784, 864, 742, 698, 643, 617; $^1H$ NMR ($CD_2Cl_2$, 600.2 MHz): δ [ppm] = 1.49 (s, 18H), 7.52–7.57 (m, 4H), 7.62–7.64 (m, 6H), 7.67 (s, 2H), 7.72–7.74 (m, 4H), 7.97 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H), 8.18–8.19 (m, 4H); $^{13}C$ NMR ($CD_2Cl_2$, 150.9 MHz): δ[ppm] = 28.0 (q, 6 C), 84.8 (s, 2 C), 107.8 (d, 2 C), 122.1 (s, 2 C), 123.0 (s, 2 C), 125.2 (d, 2 C), 125.4 (d, 2 C), 125.5 (s, 2 C), 126.1 (d, 2 C), 126.5 (d, 2 C), 128.5 (d, 2 C), 129.0 (d, 2 C), 129.2 (d, 4 C), 129.7 (d, 4 C), 133.3 (s, 2 C), 135.8 (s, 2 C), 136.9 (s, 2 C), 137.7 (s, 2 C), 140.8 (s, 2 C), 152.0 (s, 2 C); HRMS (MALDI+): $C_{48}H_{40}N_2O_4^+$, calculated: 708.2983 [M$^+$], observed: 708.2983 [M$^+$]; UV/VIS (DCM, 2.20 µg/mL): λ[nm] (logε) = 238 (4.87), 272 (4.79), 298 (4.71), 335 (4.74), 348 (4.79), 365 (4.62), 380 (4.43); Fluorescence (DCM): $\lambda_{Anr}$ = 380 nm, $\lambda_{max}$ = 394 nm; Quantum yield: Φ = 52.5%.

### 6,14-Diphenyl-8,16-dihydrobenzo[*a*]benzo[6,7]-indolo[2,3-*h*]carbazole 3 a:

According to the general procedure, the Boc-protected BBICZ (137 mg, 193 µmol) was heated up to 200 °C for 4 h. The deprotected BBICZ was obtained as yellow solid in quantitave yields (98.2 mg, 193 µmol).

Mp.: >300 °C; IR (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3429, 3052, 3027, 1566, 1520, 1493, 1452, 1398, 1370, 1343, 1309, 1280, 1225, 1152, 1103, 1072, 1027, 935, 911, 838, 782, 766, 740, 701, 670, 615; $^1H$ NMR ($CD_2Cl_2$, 600.2 MHz): δ[ppm] = 7.49 (s, 2H), 7.55–7.57 (m, 4H), 7.60–7.63 (m, 4H), 7.65–7.67 (m, 4H), 7.77–7.79 (m, 4H), 8.01 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H), 8.16 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H), 8.88 (s, 2H); $^{13}C$ NMR ($CD_2Cl_2$, 150.9 MHz): δ[ppm] = 102.7 (d, 2 C), 116.4 (s, 2 C), 120.5 (s, 2 C), 120.6 (d, 2 C), 120.9 (d, 2 C), 123.2 (s, 2 C), 125.8 (d, 2 C), 126.1 (d, 2 C), 128.0 (d, 2 C), 128.9 (d, 4 C), 129.1 (d, 2 C), 129.8 (d, 4 C), 132.5 (s, 2 C), 135.1 (s, 2 C), 136.9 (s, 2 C), 137.2 (s, 2 C), 141.8 (s, 2 C); HRMS (DART+): $C_{38}H_{25}N_2^+$, calculated: 509.2012 [M$^+$ + H], observed: 509.2005 [M$^+$ + H]; UV/VIS (THF, 6.10 µg/mL): λ[nm] (logε) = 238 (4.69), 274 (4.72), 320 (4.57), 342 (4.74), 355 (4.77), 391 (4.16), 410 (4.10); Fluorescence (DCM): $\lambda_{Anr}$ = 400 nm, $\lambda_{max}$ = 414 nm, 439 nm, 464 nm; Quantum yield: Φ = 36.8%.

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# Supporting information

# Gold Catalysis Meets Materials Science – A New Approach to π-Extended Indolocarbazoles

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## Table of Contents

## 1. General Information

All employed chemicals were purchased from commercial suppliers (ABCR, TCI, Carbolution, Acros, Alfa Aesar, Chempur, Merck and Sigma Aldrich). Anhydrous solvents were dispensed from the solvent purification system MB SPS 800. THF and $NEt_3$ for Sonogashira cross couplings were degassed using freeze pump techniques. Deuterated solvents were bought from Euriso Top or Sigma Aldrich. Melting points were measured in open glass capillaries on a Stuart SMP10 melting point apparatus and have not been corrected. $R_f$-values were determined by aluminium sheets coated with silica gel produced by Merck (TLC Silica gel 60 F254). Visualization of substances proceeded either by employing a colouring reagent (vanillin, ninhydrin) or exposing the TLC-plate to ultraviolet light (254 and 366 nm). Infrared spectra were recorded on a FT IR spectrometer (Bruker LUMOS) with a Germanium ATR-crystal. The solvent or matrix is denoted in brackets. For the most significant bands the wave number ($cm^{-1}$) is given. NMR spectra were, if not mentioned otherwise, recorded at room temperature at the chemistry department of Heidelberg University under the direction of Dr. J. Graf on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) and Bruker Avance III 600 (600 MHz). Chemical shifts are given in ppm and coupling constants in Hz. $^{1}H$ and $^{13}C$ spectra were calibrated in relation to deuterated solvents according to Fulmer *et al.*[1]. The following abbreviations were used to describe the observed multiplicities: for $^{1}H$ NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of a doublet, dt = doublet of triplet; for $^{13}C$ NMR spectra: s = quaternary carbon, d = CH carbon, t = $CH_2$ carbon and q = $CH_3$ carbon. $^{13}C$ NMR spectra are proton decoupled and interpreted with help of DEPT- and 2D spectra. All spectra were integrated and processed using the TopSpin 3.5 software. Mass spectra and high-resolution mass spectra (HR/MS) were recorded at the chemical department of Heidelberg University under the direction of Dr. J. Gross. EI spectra were measured on a JEOL JMS 700 spectrometer, ESI spectra on a Bruker ApexQe hybrid 9.4 T FT-ICR (also for MALDI spectra) or a Finnigan LCQ spectrometer. GC/MS spectra were measured on an Agilent 7890A gas chromatograph, coupled with an Agilent 5975C mass selective detector. An OPTIMA 5 cross-linked methyl silicone capillary column (30 Mesh, 0.25 mm, 0.25 µm) was employed. Nitrogen served as carrier gas. UV-Vis spectra were recorded on a Jasco UV-VIS V-670. Fluorescence spectra were recorded on a Jasco FT6500. X-Ray structures were measured on a Stoe Stadivari or Bruker Smart APEX II instrument. All data were processed using the Mercury 3.8 software. CV-spectra were measured on a VERSASTAT3-200 potentiostat, using a platinum working electrode, a silver reference electrode and a platinum/titanium counter electrode. Measurements were carried out in a 0.1 M tetrabutlyammonium hexafluorophosphate solution in anhydrous and degassed DCM. Ferrocene/ferrocenium was used as internal standard. For flash column chromatography silica gel of Sigma-Aldrich (silica gel, pore size 60 Å, 230-400 mesh particle size, particle size 40-63 µm) was used as stationary phase. As eluents different mixtures of petroleum ether (PE) and ethyl acetate (EA) or DCM were used.

If not mentioned differently, all reactions were carried out at normal laboratory conditions.

## 2. General Procedures

### GP1: Sonogashira cross coupling

A Schlenk flask was evacuated and backfilled with nitrogen for three times. 1.00 eq of the aryl halide was dissolved in a degassed 1:1 solution of THF and $NEt_3$ and 1-5 mol% of $PdCl_2(PPh_3)_2$ were added. After stirring for 10 min at room temperature, 1.10-2.00 eq of the corresponding alkyne and 1-5 mol% copper(I)-iodide were added. The mixture was stirred at the given temperature for the given time until full conversion. The progress of the reaction was controlled by GC/MS and/or TLC. After the reaction was finished, solvents were removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was purified using flash column chromatography.

### GP2: Sonogashira cross coupling with diynes

A Schlenk flask was evacuated and backfilled with nitrogen for three times. 1.00 eq of the aryl halide was dissolved in a degassed 1:1 solution of THF and $NEt_3$ and 5 mol% of $PdCl_2(PPh_3)_2$ were added. After stirring for 10 min at room temperature, 2.20-3.00 eq of the corresponding diyne and 5 mol% copper(I)-iodide were added. The mixture was stirred at the given temperature for the given time until TLC showed full conversion (fluorescent blue spot). After the reaction was finished, solvents were removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was filtered through a pad of silica gel (around 10 cm high) to remove major impurities using a mixture of PE and EA and afterwards DCM. Solvents were evaporated and the crude product was precipitated from a hot mixture with EA. The precipitate was filtered and dried under vacuum.

### GP3: General procedure for Seyferth-Gilbert homologation with the Bestmann-Ohira reagent

In a baked-out Schlenk flask 1.00 eq of the aldehyde was dissolved under nitrogen atmosphere in anhydrous methanol and (if necessary) DCM. 2.00-3.00 eq of $Cs_2CO_3$/$K_2CO_3$ and later 1.20-2.00 eq of the Bestmann-Ohira reagent were added to the solution. After full conversion was observed by TLC, the mixture was quenched with water and extracted with DCM. The organic layers were combined and dried over magnesium sulphate or sodium sulphate. The solvent was removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was purified by flash column chromatography.

### GP4: Cleavage of the TMS-protecting group

1.00 eq of the TMS-protected alkyne was dissolved in methanol and (if necessary) DCM. 1.50-3.00 eq of $K_2CO_3$ were added and the mixture was stirred at room temperature for the given time. After TLC showed full conversion, the solvent was reduced to half of the volume. The remaining suspension was quenched with water and extracted with DCM. The organic layers were combined and dried over magnesium sulphate or sodium sulphate. The solvent was removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product was purified by flash column chromatography.

### GP5: Gold catalysis

1.00 eq of the corresponding alkyne was dissolved in DCE. 5 mol% $IPrAuNTf_2$ were added and the mixture was stirred at given temperature for the given time until TLC showed full conversion. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography.

GP6: Cleavage of the Boc-protecting group

In a flask with vacuum-connection the Boc-protected BBICZ was heated up to 200-220 °C on a vacuum of $5*10^{-3}$ mbar for 3-5 h. The progress of the reaction could be determined by colour change and meantime decrease of the applied vacuum.

GP7: General procedure for alkylation of BBICZs **3a-g**

Method A

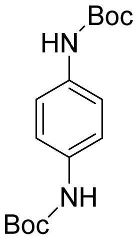
According to a slightly modified procedure of Sung *et al.*[2] 25 mol% benzyltriethylammonium chloride were added to a solution of 1.00 eq of the BBICZ in THF or DMSO. 20.0-40.0 eq 1-bromododecane and later a 50% aqueous NaOH solution were added. The mixture was first stirred for 2 h at room temperature and then heated up to 60 °C until TLC showed full conversion. The mixture was poured into a beaker of methanol. The precipitate was filtered off and washed successively with water and methanol. The residue was dried under vacuum.

Method B

In a baked-out Schlenk flask, 1.00 eq of the BBICZ was dissolved in anhydrous THF or DMSO under nitrogen atmosphere. 2.00-4.00 eq KO$^t$Bu and later 20.0-40.0 eq 1-bromododecane were added. The mixture was then stirred at the given temperature for the given time until TLC showed full conversion. The mixture was poured into a beaker of methanol. The precipitate was filtered off and washed successively with water and methanol. The residue was dried under vacuum.

## 3. Experimental Section

### Di-*tert*-butyl 1,4-phenylenedicarbamate



In a baked-out Schlenk flask 1.00 eq *p*-phenylenediamine (485 mg, 4.48 mmol) was dissolved in 20 mL anhydrous THF. 3.00 eq of $Cs_2CO_3$ (4.38 g, 13.5 mmol) were added and the solution was stirred for 30 min at room temperature. 2.50 eq of di-*tert*-butyl dicarbonate (2.45 g, 11.2 mmol) were added and the mixture was stirred over night at 70 °C. The reaction was quenched with water and extracted with EA. The combined organic layers were dried over sodium sulphate. The solvents were removed under reduced pressure and the residue was recrystallized from acetone. A colourless solid was obtained (1.25 g, 4.05 mmol, 90%).

**R$_f$**: 0.34 (silica gel, PE:EA = 5:1); **$^1$H NMR** ($d_6$-DMSO, 300.5 MHz): δ[ppm] = 1.45 (s, 18H), 7.29 (s, 4H), 9.14 (s, 2H).

Analytics confirm to previously reported data.[3]

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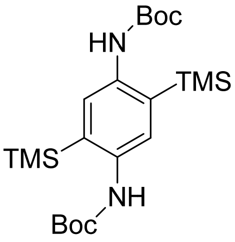
### Di-*tert*-butyl (2,5-bis(trimethylsilyl)-1,4-phenylene)dicarbamate



According to a slightly modified procedure of Lepoittevin *et al.*[3] 1.00 eq of di-*tert*-butyl 1,4-phenylenedicarbamate (3.50 g, 11.4 mmol) was dissolved in each 20 mL THF and $Et_2O$ in a baked-out flask. The mixture was cooled down to -45 °C and 6.00 eq of *tert*-butyllithium (1.7 M solution in pentane, 40.1 mL, 68.1 mmol) were added dropwise. After stirring the yellow solution for 4 h at this temperature, 7.00 eq trimethylsilyl chloride (10.2 mL, 79.5 mmol) were added dropwise at -55°C. The reaction was stirred over night at room temperature and the mixture was quenched with 20 mL of a 10% HCl solution and diluted with water. The aqueous phase was extracted with ethyl acetate and the combined organic layers were dried over magnesium sulphate. The solvent was removed under reduced pressure and the residue was dissolved in DCM and adsorbed onto Celite®. The crude product was purified by flash column chromatography (silica gel, PE:EA, 20:1). A colourless solid was obtained (3.82 g, 8.44 mmol, 74%).

**R$_f$**: 0.68 (silica gel, PE:EA = 5:1); **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.33 (s, 18H), 1.50 (s, 18H), 6.21 (s, 2H), 7.60 (s, 2H).

Analytics confirm to previously reported data.[3]

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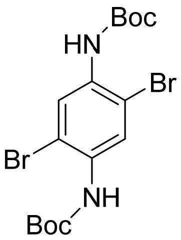
### Di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate



According to a slightly modified procedure of Lepoittevin *et al.*[3] 2.00 eq of recrystallized NBS (2.44 g, 13.7 mmol) were added to a solution of 1.00 eq di-*tert*-butyl (2,5-bis(trimethylsilyl)-1,4-phenylene)dicarbamate (3.10 g, 6.85 mmol) in 40 mL DCM. The mixture was stirred for 4 h at room temperature and then quenched with water. The aqueous phase was extracted with DCM and the combined organic layers were dried over magnesium sulphate. The solvent was removed under reduced pressure and the crude product was recrystallized in ethyl acetate. A colourless, crystalline solid was obtained (2.93 g, 6.29 mmol, 92%).

**$R_f$**: 0.69 (silica gel, PE:EA = 5:1); **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 1.53 (s, 18H), 6.87 (s, 2H), 8.38 (s, 2H).

Analytics confirm to previously reported data.[3]

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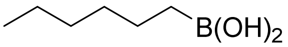
### Hexylboronic acid



According to a procedure of Prati *et al.*[4] in a baked-out Schlenk flask, 1.00 eq of trimethyl borate (3.59 g, 3.85 mL, 34.5 mmol) was dissolved in 25 mL anhydrous diethyl ether and cooled down to -78 °C. 1.00 eq hexylmagnesium chloride (2M solution in THF, 17.3 mL, 34.5 mmol) was added dropwise, as well as further 20 mL of THF. The mixture was stirred for 1 h at this temperature, before it was warmed up to room temperature and stirred over night. The mixture was diluted with 30 mL diethyl ether, quenched with 30 mL of a 10% $H_2SO_4$ solution and stirred at room temperature for 2 h until the white sediment was dissolved. The phases were separated, the aqueous layer was extracted with diethyl ether and the combined organic layers were washed with water and brine and dried over anhydrous magnesium sulphate. The solvent was evaporated under reduced pressure, to obtain the product as acolourless, highly viscous oil (3.80 g, 29.3 mmol, 85%).

**$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.84-0.94 (m, 5H), 1.28-1.46 (m, 8H).

Analytics confirm to previously reported data.[4]

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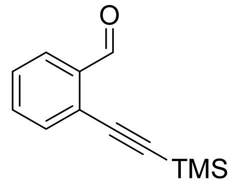
### 2-((Trimethylsilyl)ethynyl)benzaldehyde



According to GP1 1.80 eq trimethylsilylacetylene (4.53 g, 6.39 mL, 46.1 mmol) and later 2 mol% copper(I) iodide (97.6 mg, 512 µmol) were added to a mixture of 1.00 eq 2-bromobenzaldehyde (4.74 g, 3.00 mL, 25.6 mmol) and 2 mol% $PdCl_2(PPh_3)_2$ (360 mg, 512 µmol) in 200 mL solvent. The solution was stirred over night at room temperature and treated according GP1 (silica gel, PE:EA = 50:1 → 30:1). A beige solid was obtained (5.63 g, 27.8 mmol, 90%).

**R$_f$**: 0.60 (silica gel, PE:EA = 10:1); **$^1$H NMR** ($CD_2Cl_2$, 500.1 MHz): δ[ppm] = 0.29 (s, 9H), 7.44-7.47 (m, 1H), 7.54-7.59 (m, 2H), 7.88 (d, $^3J_{H-H}$ = 7.7 Hz, 1H), 10.54 (s, 1H).

Analytics confirm to previously reported data.[5]

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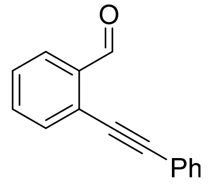
**2-(Phenylethynyl)benzaldehyde**



According to GP1, 1.30 eq ethynylbenzene (3.59 g, 3.86 mL, 35.1 mmol) and later 1 mol% copper(I) iodide (51.5 mg, 270 µmol) were added to a mixture of 1.00 eq 2-bromobenzaldehyde (5.00 g, 27.0 mmol) and 1 mol% $PdCl_2(PPh_3)_2$ (190 mg, 270 µmol). The solution was stirred for 2 h at room temperature and then treated according GP1 (silica gel, PE → PE:EA = 100:1). A light beige solid was obtained (5.09 g, 24.7 mmol, 92%).

**R$_f$**: 0.67 (silica gel, PE:EA = 5:1); **$^1$H NMR** ($CDCl_3$, 500.1 MHz): δ[ppm] = 7.38-7.40 (m, 3H), 7.46 (t, $^3J_{H-H}$ = 7.80 Hz, 1H), 7.56-7.61 (m, 3H), 7.65 (d, $^3J_{H-H}$ = 7.70 Hz, 1H), 7.96 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 10.66 (s, 1H).

Analytics confirm to previously reported data.[6]

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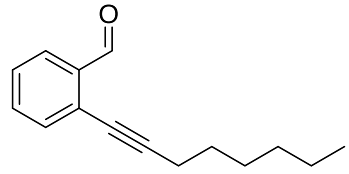
**2-(Oct-1-yn-1-yl)benzaldehyde**

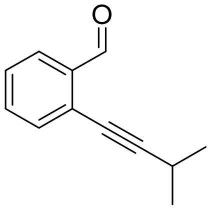


According to GP1, 1.20 eq oct-1-yne (2.27 g, 3.04 mL, 20.6 mmol) and later 5 mol% copper(I) iodide (163 mg, 857 µmol) were added to a mixture of 1.00 eq 2-bromobenzaldehyde (3.17 g, 17.1 mmol) and 5 mol% $PdCl_2(PPh_3)_2$ (601 mg, 857 µmol). The solution was stirred over night at room temperature and treated according to GP1 (silica gel, PE:EA = 50:1). A light yellow oil was obtained (2.86 g, 13.3 mmol, 78%).

**R*f***: 0.69 (silica gel, PE:EA = 5:1); **$^1$H NMR** (CDCl$_3$, 300.5 MHz): δ[ppm] = 0.89-0.93 (m, 3H), 1.30-1.35 (m, 4H), 1.42-1.51 (m, 2H), 1.59-1.69 (m, 2H), 2.48 (t, $^3J_{H-H}$ = 7.0 Hz, 2H), 7.35-7.40 (m, 1H), 7.50-7.52 (m, 2H), 7.89 (d, $^3J_{H-H}$ = 7.7 Hz, 1H), 10.54 (d, $^4J_{H-H}$ = 0.7 Hz, 1H).

Analytics confirm to previously reported data.[7]

### 2-(3-Methylbut-1-yn-1-yl)benzaldehyde

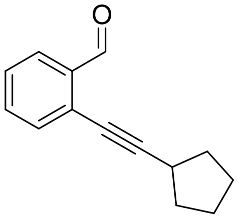


According to GP1, 1.50 eq 3-methylbut-1-yne (2.67 g, 4.01 mL, 39.2 mmol) and later 1 mol% copper(I) iodide (49.8 mg, 261 µmol) were added to a mixture of 1.00 eq 2-bromobenzaldehyde (4.83 g, 26.1 mmol) and 1 mol% PdCl$_2$(PPh$_3$)$_2$ (183 mg, 261 µmol). The solution was stirred over night at room temperature and treated according to GP1 (silica gel, PE → PE:EA = 50:1). A beige solid was obtained (4.11 g, 23.9 mmol, 91%).

**R*f***: 0.62 (silica gel, PE:EA = 10:1); **$^1$H NMR** (CDCl$_3$, 300.5 MHz): δ[ppm] = 1.30 (d, $^3J_{H-H}$ = 6.9 Hz, 6H), 2.85 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H) 7.35-7.40 (m, 1H), 7.48-7.54 (m, 2H), 7.87-7.89 (m, 1H), 10.54 (d, $^4J_{H-H}$ = 0.6 Hz, 1H).

Analytics confirm to previously reported data.[8]

### 2-(Cyclopentylethynyl)benzaldehyde



According to GP1, 1.20 eq ethynylcyclopentane (1.22 g, 13.0 mmol) and later 1 mol% copper(I) iodide (103 mg, 540 µmol) were added to a mixture of 1.00 eq 2-bromobenzaldehyde (2.00 g, 10.8 mmol) and 1 mol% PdCl$_2$(PPh$_3$)$_2$ (379 mg, 540 µmol). The solution was stirred over night at room temperature and treated according to GP1 (silica gel, PE:EA = 100:1). A beige solid was obtained (1.60 g, 8.07 mmol, 75%).

**R*f***: 0.22 (silica gel, PE:EA = 100:1); **$^1$H NMR** (CDCl$_3$, 500.1 MHz): δ[ppm] = 1.61-1.81 (m, 6H), 1.99-2.04 (m, 1H), 2.86-2.92 (m, 1H), 7.35-7.38 (m, 1H), 7.47-7.52 (m, 2H), 7.86-7.87 (m, 1H), 10.53 (s, 1H).

Analytics confirm to previously reported data.[9]

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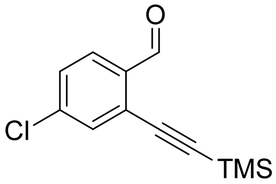
**4-Chloro-2-((trimethylsilyl)ethynyl)benzaldehyde**



According to GP1, 1.20 eq trimethylsilylacetylene (2.69 g, 3.86 mL, 27.3 mmol) and later 1 mol% copper(I) iodide (43.4 mg, 228 µmol) were added to a solution of 1.00 eq 2-bromo-4-chlorobenzaldehyde (5.00 g, 22.8 mmol) and 1 mol% $PdCl_2(PPh_3)_2$ (160 mg, 228 µmol) in a degassed 1:1 mixture of THF and triethylamine (30 mL each). The solution was stirred over night at room temperature and treated according to GP1 (silica gel, PE:EA = 100:1 to 50:1). A yellow oil was obtained (5.25 g, 22.2 mmol, 97%).

**R*f***: 0.79 (silica gel, PE:EA = 5:1); **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.28 (s, 9H), 7.40 (dd, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 2.0 Hz, 1H), 7.56 (d, $^4J_{H-H}$ = 1.9 Hz, 1H), 7.84 (d, $^3J_{H-H}$ = 8.3 Hz, 1H), 10.47 (s, 1H).

Analytics confirm to previously reported data. [10]

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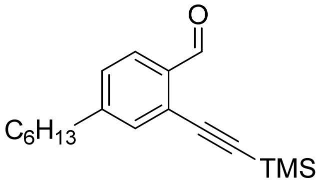
**4-Hexyl-2-((trimethylsilyl)ethynyl)benzaldehyde**



According to a slightly modified procedure of Dichtel *et al.*[11], 1.00 eq 4-chloro-2-((trimethylsilyl)-ethynyl)benzaldehyde (1.80 g, 7.60 mmol), 1.50 eq hexylboronic acid (frozen) (1.48 g, 11.4 mmol), 1.50 eq $K_2CO_3$ (1.58 g, 11.4 mmol), 5 mol% $Pd(OAc)_2$ (85.3 mg, 380 µmol) and 10 mol% SPhos (312 mg, 760 µmol) were dissolved in a degassed mixture of toluene and water (10:1). The mixture was stirred over night at 100 °C and afterwards quenched with 100 mL of a 2 M HCl solution. The phases were separated, the aqueous layer extracted with DCM and the combined organic layers were dried over magnesium sulphate. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (silica gel, PE:EA = 50:1). A yellow oil was obtained (1.91 g, 6.68 mmol, 88%).

**R*f***: 0.30 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3376, 2959, 2931, 2858, 2746, 2153, 1853, 1783, 1694, 1598, 1484, 1466, 1413, 1390, 1251, 1205, 1155, 1104, 946, 859, 814, 761, 723, 701, 650; **$^1$H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 0.28 (s, 9H), 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, 3H), 1.26-1.36 (m, 6H), 1.57-1.66 (m, 2H), 2.63 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 7.24 (dd, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 0.8 Hz, 1H), 7.38 (d, $^4J_{H-H}$ = 1.3 Hz, 1H), 7.82 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 10.50 (d, $^4J_{H-H}$ = 0.8 Hz, 1H). **$^{13}$C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = -0.1 (q, 3C), 14.2 (q, 1C), 22.7 (t, 1C), 29.0 (t, 3C), 31.0 (t, 1C), 31.8 (t, 1C), 36.1 (t, 1C), 100.6

(s, 1C), 101.9 (s, 1C), 126.9 (s, 1C), 127.1 (d, 1C), 129.4 (d, 1C), 133.4 (d, 1C), 134.4 (s, 1C), 149.8 (s, 1C), 191.7 (d, 1C); **HRMS** (EI+): $C_{18}H_{26}OSi^+$, calculated: 286.1747 [$M^+$], observed: 286.1749 [$M^+$].

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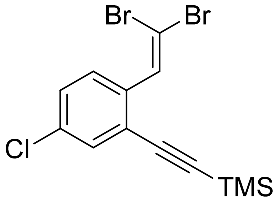
**((5-Chloro-2-(2,2-dibromovinyl)phenyl)ethynyl)trimethylsilane**



In a baked-out Schlenk flask, 2.00 eq $CBr_4$ (8.40 g, 25.3 mmol) were added to a 0 °C cold solution of 4.00 eq $PPh_3$ (13.3 g, 50.7 mmol) in 250 mL anhydrous DCM. The mixture was stirred for 30 min at 0 °C until dissolving was completed. In a second baked-out Schlenk flask, 1.00 eq 4-chloro-2-((trimethylsilyl)ethynyl)benzaldehyde (3.00 g, 12.7 mmol) was dissolved in 50 mL anhydrous DCM. This solution was transferred to the first Schlenk flask *via* a Teflon cannula. The combined reaction mixture was stirred for 30 min at 0 °C and afterwards over night at room temperature. The reaction was quenched with a saturated solution of $NaHCO_3$. The phases were separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over magnesium sulphate and the solvent was removed under reduced pressure. The residue was dissolved in DCM and adsorbed onto Celite®. The crude product was purified by flash column chromatography (silica gel, PE:EA = 100:1). A yellow oil was obtained (3.36 g, 8.55 mmol, 67%).

**$R_f$**: 0.78 (silica gel, PE:EA = 20:1); **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.28 (s, 9H), 7.30 (dd, $^3J_{H\text{-}H}$ = 8.6 Hz, $^4J_{H\text{-}H}$ = 1.9 Hz, 1H), 7.45 (d, $^4J_{H\text{-}H}$ = 1.9 Hz, 1H), 7.68-7.71 (m, 2H).

Analytics confirm to previously reported data. [10]

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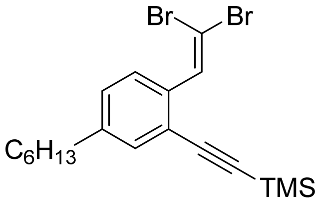
**((5-Hexyl-2-(2,2-dibromovinyl)phenyl)ethynyl)trimethylsilane**



In a baked-out Schlenk flask, 2.00 eq $CBr_4$ (4.40 g, 13.3 mmol) were added to a 0 °C cold solution of 4.00 eq $PPh_3$ (6.96 g, 26.5 mmol) in 100 mL anhydrous DCM. The mixture was stirred for 30 min at 0 °C until dissolving was completed. In a second baked-out Schlenk flask 1.00 eq 4-hexyl-2-((trimethylsilyl)ethynyl)benzaldehyde (1.90 g, 6.63 mmol) was dissolved in 50 mL anhydrous DCM. This solution was transferred to the first Schlenk flask *via* a Teflon cannula. The combined reaction mixture was stirred for 30 min at 0 °C, followed by 3 h at room temperature. The reaction was quenched with a saturated solution of $NaHCO_3$. The phases were separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over magnesium sulphate and the solvent was removed under reduced pressure. The residue was used for the next step without further purification.

**R*f***: 0.88 (silica gel, PE:EA = 5:1); **$^1$H NMR** (CDCl$_3$, 400.3 MHz): δ[ppm] = 0.28 (s, 9H), 0.87-0.90 (m, 3H), 1.25-1.36 (m, 6H), 1.56-1.63 (m, 2H), 2.55 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 7.14 (dd, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.7 Hz, 1H), 7.30 (d, $^4J_{H-H}$ = 1.7 Hz, 1H), 7.69 (d, $^3J_{H-H}$ = 8.1 Hz, 1H), 7.77 (s, 1H).

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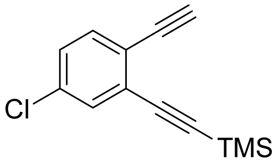
### ((5-Chloro-2-ethynylphenyl)ethynyl)trimethylsilane



In a baked-out flask, 1.00 eq of ((5-chloro-2-(2,2-dibromovinyl)phenyl)ethynyl)trimethylsilane (3.22 g, 8.20 mmol) was dissolved in 100 mL THF and cooled down to 0 °C. 4.00 eq of MeMgBr (3 M in Et$_2$O, 10.9 mL, 32.8 mmol) were added dropwise and the solution was stirred for 15 min at 0 °C. The solution was allowed to warm up to room temperature and stirred over night at this temperature. The reaction was quenched with an ice-cold, saturated solution of NH$_4$Cl. The phases were separated, the aqueous layer was extracted with DCM and the combined organic layers were dried over magnesium sulphate. The solvent was removed under reduced pressure and the crude product filtered through a short plug of silica gel (PE:EA = 10:1). The solvent was again evaporated under reduced pressure to obtain the title compound as a yellow oil (1.89 g, 8.12 mmol, 99%).

**R*f***: 0.71 (silica gel, PE:EA = 20:1); **$^1$H NMR** (CDCl$_3$, 300.5 MHz): δ[ppm] = 0.26 (s, 9H), 3.32 (s, 1H), 7.24 (dd, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 2.0 Hz, 1H), 7.40 (d, $^3J_{H-H}$ = 8.4 Hz, 1H), 7.46 (d, $^4J_{H-H}$ = 1.9 Hz, 1H).

Analytics confirm to previously reported data. [10]

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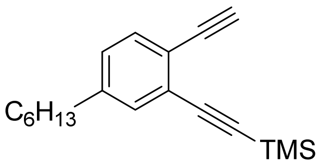
### ((2-Ethynyl-5-hexylphenyl)ethynyl)trimethylsilane



In a baked-out flask, 1.00 eq of crude ((2-(2,2-dibromovinyl)-5-hexylphenyl)ethynyl)trimethylsilane (2.93 g, 6.62 mmol) was dissolved in 100 mL THF and cooled down to 0 °C. 3.00 eq of MeMgBr (3 M in Et$_2$O, 6.62 mL, 19.9 mmol) were added dropwise and the solution was stirred for 30 min at 0 °C. The solution was allowed to warm up to room temperature and was further stirred over night at this temperature. The reaction was then quenched with an ice-cold, saturated solution of NH$_4$Cl. The phases were separated, the aqueous layer was extracted with DCM and the combined organic layers were dried over magnesium sulphate. The solvent was evaporated under reduced pressure and the residue was adsorbed onto Celite®. The crude product was purified by flash column chromatography (silica gel, PE:EA = 50:1). The title compound was obtained as a yellow oil (1.50 g, 5.31 mmol, 80% over two steps).

**R$_f$**: 0.31 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3303, 3027, 2958, 2929, 2857, 2155, 2109, 1602, 1552, 1483, 1467, 1409, 1378, 1249, 1113, 948, 859, 761, 700, 654, 610; **$^1$H NMR** (CDCl$_3$, 400.3 MHz): δ[ppm] = 0.27 (s, 9H), 0.86-0.90 (m, 3H), 1.26-1.32 (m, 6H), 1.54-1.62 (m, 2H), 2.56 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 3.24 (s, 1H), 7.07 (dd, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H), 7.30 (d, $^4J_{H-H}$ = 1.8 Hz, 1H), 7.39 (d, $^3J_{H-H}$ = 8.0 Hz, 1H); **$^{13}$C NMR** (CDCl$_3$, 100.7 MHz): δ[ppm] = 0.1 (q, 3C), 14.2 (q, 1C), 22.7 (t, 1C), 29.0 (t, 1C), 31.1 (t, 1C), 31.8 (t, 1C), 35.8 (t, 1C), 80.4 (d, 1C), 82.3 (s, 1C), 98.5 (s, 1C), 103.6 (s, 1C), 122.5 (s, 1C), 126.1 (s, 1C), 128.7 (d, 1C), 132.2 (d, 1C), 132.5 (d, 1C), 143.8 (s, 1C); **HRMS** (EI+): $C_{19}H_{26}Si$, calculated: 282.17983 [M$^+$], observed: 282.18001 [M$^+$].

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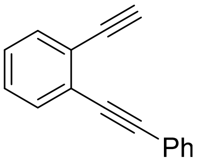
**1-Ethynyl-2-(phenylethynyl)benzene**



According to GP2, 1.00 eq 2-(phenylethynyl)benzaldehyde (2.50 g, 12.1 mmol) was dissolved in 50 mL methanol. 2.00 eq $K_2CO_3$ (1.30 g, 9.41 mmol) and later 1.50 eq of the Bestmann-Ohira reagent (1.36 g, 7.05 mmol) were added. After stirring over night at room temperature, the reaction mixture was treated according to GP2 (silica gel, PE). A colourless oil was obtained (773 mg, 3.82 mmol, 81%).

**R$_f$**: 0.48 (silica gel, PE:EA = 10:1); **$^1$H NMR** (CDCl$_3$, 500.1 MHz): δ[ppm] = 3.38 (s, 1H), 7.28-7.38 (m, 5H), 7.54-7.59 (m, 4H).

Analytics confirm to previously reported data.[7]

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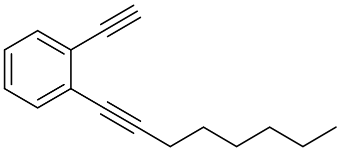
**1-Ethynyl-2-(oct-1-yn-1-yl)benzene**



According to GP2, 1.00 eq 2-(oct-1-yn-1-yl)benzaldehyde (2.76 g, 12.9 mmol) was dissolved in 80 mL methanol. 2.50 eq $Cs_2CO_3$ (10.5 g, 32.2 mmol) and later 1.20 eq of the Bestmann-Ohira reagent (2.97 g, 15.5 mmol) were added. After stirring over night at room temperature, the reaction mixture was treated according to GP2 (silica gel, PE). A colourless oil was obtained (2.04 g, 9.68 mmol, 75%).

**R$_f$**: 0.72 (silica gel, PE:EA = 10:1); **$^1$H NMR** (CDCl$_3$, 300.5 MHz): δ[ppm] = 0.87-0.93 (m, 3H), 1.28-1.35 (m, 4H), 1.48-1.55 (m, 2H), 1.59-1.68 (m, 2H), 2.47 (t, $^3J_{H-H}$ = 7.0 Hz, 2H), 3.26 (s, 1H), 7.18-7.29 (m, 2H), 7.39-7.42 (m, 1H), 7.46-7.49 (m, 1H).

Analytics confirm to previously reported data. [7]

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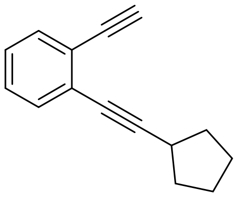
**1-(Cyclopentylethynyl)-2-ethynylbenzene**



According to GP2, 1.00 eq 2-(cyclopentylethynyl)benzaldehyde (3.75 g, 18.9 mmol) was dissolved in 300 mL anhydrous methanol. 3.00 eq $Cs_2CO_3$ (18.5 g, 56.7 mmol) and later 1.30 eq of the Bestmann-Ohira reagent (4.72 g, 24.6 mmol) were added. After stirring over night at room temperature, the reaction mixture was treated according to GP2 (silica gel, PE:EA = 50:1). A orange oil was obtained (2.89 g, 14.9 mmol, 77%).

**$R_f$**: 0.70 (silica gel, PE:EA = 10:1); **$^1$H NMR** ($CDCl_3$, 300.1 MHz): δ[ppm] = 1.58-1.67 (m, 2H), 1.71-1.84 (m, 4H), 1.94-2.04 (m, 2H), 2.85-2.95 (m, 1H), 3.27 (s, 1H), 7.17-7.28 (m, 2H), 7.38-7.41 (m, 1H), 7.45-7.48 (m, 1H).

Analytics confirm to previously reported data. [9]

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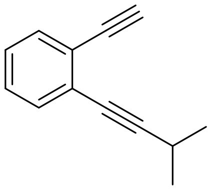
**1-Ethynyl-2-(3-methylbut-1-yn-1-yl)benzene**



According to GP2 1.00 eq 2-(3-methylbut-1-yn-1-yl)benzaldehyde (2.00 g, 11.6 mmol) was dissolved in 100 mL anhydrous methanol. 3.00 eq $K_2CO_3$ (3.00 g, 34.8 mmol) and later 1.20 eq of the Bestmann-Ohira reagent (1.30 g, 15.1 mmol) were added. After stirring over night at room temperature, the reaction mixture was treated according to GP2 (silica gel, PE). A yellow liquid was obtained (1.49 g, 8.86 mmol, 76%).

**$R_f$**: 0.67 (silica gel, PE); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3284, 3061, 2969, 2931, 2869, 2230, 2107, 1928, 1714, 1634, 1592, 1557, 1476, 1462, 1440, 1382, 1363, 1320, 1233, 1160, 1103, 1035, 945, 840, 752, 671, 638; **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 1.28 (s, 3H), 1.30 (s, 3H), 2.83 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 1H), 3.27 (s, 1H), 7.18-7.29 (m, 2H), 7.38-7.41 (m, 1H), 7.46-7.49 (m, 1H); **$^{13}$C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 21.5 (d, 1C), 23.1 (q, 2C), 78.4 (s, 1C), 80.6 (d, 1C), 82.6 (s, 1C), 100.6 (s, 1C), 124.7 (s, 1C), 127.2 (s, 1C), 127.3 (d, 1C), 128.5 (d, 1C), 131.9 (d, 1C), 132.5 (d, 1C); **HR-MS** (EI+): $C_{13}H_{12}^+$, calculated: 168.09335 [M$^+$], observed: 168.09283 [M$^+$].

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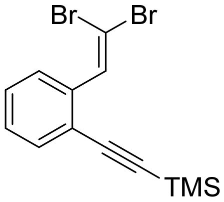
**((2-(2,2-Dibromovinyl)phenyl)ethynyl)trimethylsilane**

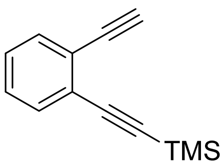


In a baked-out Schlenk flask, 2.00 eq $CBr_4$ (13.8 g, 41.5 mmol) were added to a 0 °C cold solution of 4.00 eq $PPh_3$ (21.8 g, 83.0 mmol) in 250 mL anhydrous DCM. The mixture was stirred for 30 min at 0 °C until dissolving was completed. In a second baked-out Schlenk flask, 1.00 eq 2-((trimethylsilyl)-ethynyl)benzaldehyde (4.20 g, 20.8 mmol) was dissolved in 80 mL anhydrous DCM. This solution was transferred to the first Schlenk flask *via* a Teflon cannula. The combined reaction mixture was stirred for 30 min at 0 °C and then over night at room temperature. The reaction was quenched with a saturated solution of $NaHCO_3$. The phases were separated and the aqueous layer was extracted with DCM. The combined organic layers were dried over magnesium sulphate and the solvent was evaporated under reduced pressure. The residue was dissolved in DCM and adsorbed onto Celite®. The crude product was purified by flash column chromatography (silica gel, PE:EA = 100:1). A yellow oil was obtained (5.83 g, 16.3 mmol, 78%).

**$R_f$**: 0.50 (silica gel, PE); **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.28 (s, 9H), 7.24-7.36 (m, 2H), 7.47 (dd, $^3J_{H\text{-}H}$ = 7.4 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, 1H), 7.75 (m, 1H), 7.78 (s, 1H).

Analytics confirm to previously reported data.[5]

### ((2-Ethynylphenyl)ethynyl)trimethylsilane

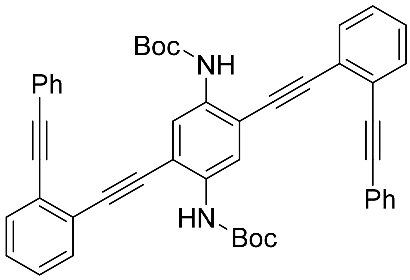


In a baked-out flask, 1.00 eq of ((2-(2,2-dibromovinyl)phenyl)ethynyl)trimethylsilane (1.75 g, 4.89 mmol) was dissolved in 50 mL THF and cooled down to 0 °C. 4.00 eq of MeMgBr (3 M in $Et_2O$, 6.51 mL, 19.5 mmol) were added dropwise and the solution was stirred for 10 min at 0 °C. The solution was allowed to warm up to room temperature and stirred for another 2 h at this temperature. The mixture was quenched with an ice-cold, saturated solution of $NH_4Cl$. The phases were separated, the aqueous layer was extracted with DCM and the combined organic layers were dried over magnesium sulphate. The solvent was evaporated under reduced pressure and the crude product was filtered through a short plug of silica gel (EA as solvent). The solvent was again evaporated under reduced pressure and the title compound was obtained as brown oil (948 mg, 4.78 mmol, 98%).

**$R_f$**: 0.46 (silica gel, PE); **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.27 (s, 9H), 3.30 (s, 1H), 7.25-7.30 (m, 2H), 7.46-7.50 (m, 2H).

Analytics confirm to previously reported data. [5]

**Di-*tert*-butyl (2,5-bis((2-(phenylethynyl)phenyl)ethynyl)-1,4-phenylene)dicarbamate, 1a**

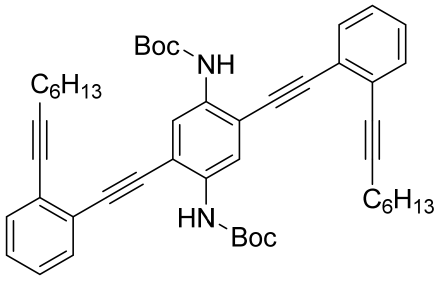


According to GP2, 2.80 eq 1-ethynyl-2-(phenylethynyl)benzene (1.66 g, 8.23 mmol) and later 4 mol% copper(I) iodide (22.4 mg, 118 µmol) were added to a mixture of 1.00 eq di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate (1.37 g, 2.94 mmol) and 4 mol% $Pd(PPh_3)_4$ (136 mg, 118 µmol) in 80 mL solvent. After stirring over night at 60 °C, the solvent was removed under reduced pressure and the residue treated according to GP2. A yellow solid was obtained (1.83 g, 2.58 mmol, 88%).

According to GP1, 1.00 eq di-*tert*-butyl (2,5-bis((2-ethynylphenyl)ethynyl)-1,4-phenylene)dicarbamate (82.0 mg, 147 µmol) and later 5 mol% copper(I) iodide (1.40 mg, 7.37 µmol) were added to a mixture of 3.00 eq iodobenzene (90.2 mg, 49.5 µL, 442 µmol) and 5 mol% $PdCl_2(PPh_3)_2$ (5.17 mg, 7.37 µmol). The solution was stirred for 6 h at 50 °C and then over night at room temperature. The mixture was treated according to GP1 (silica gel, PE:EA = 50:1). A yellow solid was obtained (77.8 mg, 110 µmol, 75%).

**Mp.:** decomp. >202 °C; **R*f***: 0.39 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3406, 3059, 2979, 2930, 1730, 1532, 1445, 1286, 1229, 1148, 1054, 895, 754, 691; **$^1$H NMR** ($CD_2Cl_2$, 600.2 MHz): δ[ppm] = 1.31 (s, 18H), 7.35-7.37 (m, 6H), 7.39-7.41 (m, 4H), 7.54 (s, 2H), 7.58-7.60 (m, 4H), 7.62-7.65 (m, 4H), 8.44 (s, 2H); **$^{13}$C NMR** ($CD_2Cl_2$, 150.9 MHz): δ[ppm] = 28.1 (q, 6C), 80.9 (s, 2C), 88.2 (s, 2C), 88.8 (s, 2C), 94.5 (s, 2C), 96.4 (s, 2C), 112.7 (s, 2C), 120.5 (s, 2C), 123.3 (s, 2C), 125.0 (s, 2C), 126.2 (s, 2C), 128.6 (d, 2C), 128.9 (d, 4C), 129.0 (d, 2C), 129.2 (d, 2C), 132.2 (d, 2C), 132.3 (d, 4C), 132.4 (d, 2C), 134.8 (s, 2C), 152.6 (s, 2C); **HRMS** (ESI+): $C_{46}H_{40}N_2NaO_4^+$, calculated: 731.2880 [M$^+$+Na], observed: 731.2887 [M$^+$+Na]; **UV/VIS** (DCM, 4.40 µg/mL): λ[nm] (logε) = 269 (4.84), 287 (4.85), 315 (4.51), 383 (4.25); **Fluorescence** (DCM): $\lambda_{Anr}$ = 380 nm, $\lambda_{max}$ = 431 nm; **Quantum yield:** Φ = 60.0%.

**Di-*tert*-butyl (2,5-bis((2-(oct-1-yn-1-yl)phenyl)ethynyl)-1,4-phenylene)dicarbamate, 1b**



According to GP2, 3.00 eq 1-ethynyl-2-(oct-1-yn-1-yl)benzene (609 mg, 2.90 mmol) and later 10 mol% copper(I) iodide (18.4 mg, 96.5 µmol) were added to a mixture of 1.00 eq di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate (450 mg, 965 µmol) and 10 mol% $PdCl_2(PPh_3)_2$ (67.8 mg, 96.5 µmol) in

60 mL solvent. After stirring over 3 d at 50 °C, the solvent was removed under reduced pressure and the residue treated according to GP2. A beige solid was obtained (580 mg, 800 µmol, 83%).

**Mp.:** 112-114 °C; **R$_f$**: 0.56 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3392, 2975, 2929, 2858, 2227, 1725, 1532, 1483, 1424, 1283, 1235, 1154, 1055, 903, 855, 756, 685; **$^1$H NMR** ($CD_2Cl_2$, 400.3 MHz): δ[ppm] = 0.82-0.85 (m, 6H), 1.23-1.26 (m, 8H), 1.42-1.45 (m, 4H), 1.53 (s, 18H), 1.59-1.65 (m, 4H), 2.54 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H), 7.29-7.34 (m, 4H), 7.45-7.48 (m, 4H), 7.54-7.56 (m, 2H), 8.33 (s, 2H); **$^{13}$C NMR** ($CD_2Cl_2$, 100.7 MHz): δ[ppm] = 14.2 (q, 2C), 20.0 (t, 2C), 22.9 (t, 2C), 28.4 (q, 6C), 29.1 (t, 2C), 29.1 (t, 2C), 31.8 (t, 2C), 79.4 (s, 2C), 81.1 (s, 2C), 88.2 (s, 2C), 96.2 (s, 2C), 96.6 (s, 2C), 112.8 (s, 2C), 121.0 (d, 2C), 125.0 (s, 2C), 127.2 (d, 2C), 127.8 (d, 2C), 129.0 (s, 2C), 131.9 (d, 2C), 132.2 (d, 2C), 134.6 (s, 2C), 152.8 (s, 2C); **HRMS** (ESI+): $C_{48}H_{56}N_2NaO_4^+$, calculated: 747.42325 [M$^+$+Na], observed: 747.4239 [M$^+$+Na]; **UV/VIS** (DCM, 7.80 µg/mL): λ[nm] (logε) = 262 (4.73), 326 (4.47), 376 (4.33); **Fluorescence** (DCM): $\lambda_{Anr}$ = 376 nm, $\lambda_{max}$ = 421 nm; **Quantum yield:** Φ = 59.0%.

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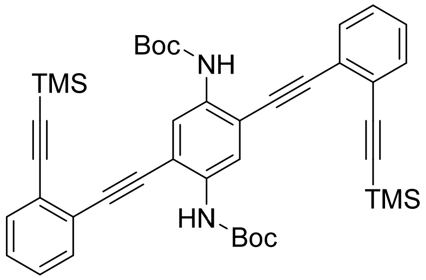
### Di-*tert*-butyl (2,5-bis((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)-1,4-phenylene)dicarbamate, TMS-1c



According to GP2, 3.00 eq ((2-ethynylphenyl)ethynyl)trimethylsilane (758 mg, 3.82 mmol) and later 10 mol% copper(I) iodide (24.3 mg, 127 µmol) were added to a mixture of 1.00 eq di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate (594 mg, 1.27 mmol) and 10 mol% $PdCl_2(PPh_3)_2$ (89.4 mg, 127 µmol) in 70 mL solvent. The solution was stirred for 3 d at 50 °C. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, PE:EA = 40:1 → 20:1). A colourless solid was obtained (727 mg, 1.04 mmol, 81%).

**Mp.:** 184 °C; **R$_f$**: 0.26 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3393, 2960, 2160, 1719, 1530, 1478, 1417, 1247, 1232, 1148, 868, 842, 759; **$^1$H NMR** ($CDCl_3$, 600.2 MHz): δ[ppm] = 0.23 (s, 18H), 1.52 (s, 18H), 7.30-7.34 (m, 6H), 7.50-7.53 (m, 4H), 8.36 (s, 2H); **$^{13}$C NMR** ($CDCl_3$, 150.9 MHz): δ[ppm] = 0.0 (q, 6C), 28.4 (q, 6C), 80.9 (s, 2C), 88.5 (s, 2C), 95.8 (s, 2C), 99.6 (s, 2C), 103.1 (s, 2C), 112.8 (s, 2C), 121.1 (d, 2C), 125.4 (s, 2C), 126.1 (s, 2C), 128.4 (d, 2C), 128.6 (d, 2C), 131.7 (d, 2C), 132.4 (d, 2C), 134.2 (s, 2C), 152.6 (s, 2C); **HRMS** (ESI+): $C_{42}H_{48}N_2NaO_4Si_2^+$, calculated: 723.3045[M$^+$+Na], observed: 723.3056 [M$^+$+Na]; **UV/VIS** (DCM, 1.95 µg/mL): λ[nm] (logε) = 254 (5.14), 264 (4.70), 324 (4.70), 370 (4.94); **Fluorescence** (DCM): $\lambda_{Anr}$ = 370 nm, $\lambda_{max}$ = 428 nm; **Quantum yield:** Φ = 61.1%.

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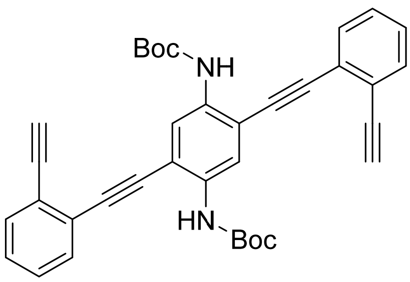
### Di-*tert*-butyl (2,5-bis((2-ethynylphenyl)ethynyl)-1,4-phenylene)dicarbamate, 1c



According to GP4, 3.00 eq of $K_2CO_3$ (1.30 g, 9.41 mmol) were added to a solution of 1.00 eq of the corresponding TMS-protected alkyne (2.20 g, 3.14 mmol) in 500 mL methanol and 500 mL DCM. The mixture was stirred over night at room temperature and treated according to GP4. After evaporation of the solvents, the residue was purified by filtration through a pad of Celite® with DCM. The solvent was evaporated again to obtain a yellow solid (1.66 g, 2.98 µmol, 95%).

**Mp.:** decomp. >190 °C; **R$_f$**: 0.56 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3375, 3312, 2971, 2926, 1726, 1528, 1482, 1418, 1286, 1231, 1143, 1051, 767, 661, 622; **$^1$H NMR** ($CDCl_3$, 600.2 MHz): δ[ppm] = 1.57 (s, 18H), 3.61 (s, 2H), 7.33 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H), 7.38 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H), 7.55 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H), 7.58 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H), 7.63 (s, 2H), 8.44 (s, 2H); **$^{13}$C NMR** ($CDCl_3$, 150.9 MHz): δ[ppm] = 28.6 (q, 6C), 81.2 (s, 2C), 82.4 (s, 2C), 82.8 (d, 2C), 89.2 (s, 2C), 95.9 (s, 2C), 112.5 (s, 2C), 121.0 (d, 2C), 124.3 (s, 2C), 126.0 (s, 2C), 128.5 (d, 2C), 129.0 (d, 2C), 131.7 (d, 2C), 132.3 (d, 2C), 134.4 (s, 2C), 152.8 (s, 2C); **HRMS** (ESI+): $C_{36}H_{32}N_2NaO_4^+$, calculated: 579.2254 [M$^+$+Na], observed: 579.2271 [M$^+$+Na]; **UV/VIS** (DCM, 1.80 µg/mL): λ[nm] (logε) = 262 (4.79), 312 (4.57), 323 (4.67), 335 (4.83), 382 (4.53), 399 (4.44); **Fluorescence** (DCM): $\lambda_{Anr}$ = 380 nm, $\lambda_{max}$ = 423 nm; **Quantum yield:** Φ = 64.9%.

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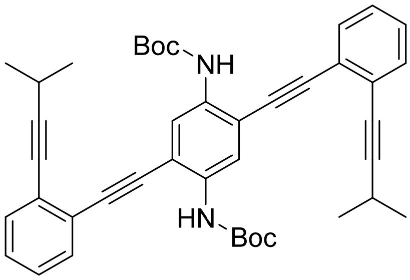
### Di-*tert*-butyl (2,5-bis((2-(3-methylbut-1-yn-1-yl)phenyl)ethynyl)-1,4-phenylene)dicarbamate, 1d



According to GP2, 3.00 eq 1-ethynyl-2-(phenylethynyl)benzene (704 mg, 4.18 mmol) and later 5 mol% copper(I) iodide (13.3 mg, 69.7 µmol) were added to a mixture of 1.00 eq di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate (650 mg, 1.39 mmol) and 5 mol% $PdCl_2(PPh_3)_2$ (48.9 mg, 69.7 µmol) in 60 mL solvent. After stirring over 3 d at 60 °C, the solvent was removed under reduced pressure and the residue treated according to GP2. A light yellow solid was obtained (802 mg, 1.25 mmol, 51%).

**Mp.:** 232 °C; **R$_f$**: 0.72 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3395, 2975, 1720, 1528, 1481, 1420, 1366, 1282, 1233, 1148, 1054, 1028, 896, 857, 763, 737; **$^1$H NMR** ($CD_2Cl_2$, 300.5 MHz): δ[ppm] = 1.28 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H), 1.52 (s, 18H), 2.92 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H), 7.27-7.33 (m, 4H), 7.35 (s, 2H), 7.44-7.49 (m, 2H), 7.52-7.57 (m, 2H), 8.34 (s, 2H); **$^{13}$C NMR** ($CD_2Cl_2$, 150.9 MHz): δ[ppm] = 21.7 (d, 2C), 23.2 (q, 4C), 28.4 (q, 6C), 78.6 (s, 2C), 81.1 (s, 2C), 88.1 (s, 2C), 96.5 (s, 2C), 101.4 (s, 2C), 112.8 (s, 2C), 121.2 (d, 2C), 125.0 (s, 2C), 127.1 (s, 2C), 127.8 (d, 2C), 129.0 (d, 2C), 132.0 (d, 2C), 132.3 (d, 2C), 134.6 (s, 2C), 152.7 (s, 2C); **HRMS** (ESI+): $C_{42}H_{44}N_2NaO_4^+$, calculated: 633.3193 [M$^+$+Na], observed: 633.3205 [M$^+$+Na]; **UV/VIS** (DCM, 4.20 µg/mL): λ[nm] (logε) = 261 (4.61), 322 (4.36), 374 (4.22); **Fluorescence** (DCM): $\lambda_{Anr}$ = 375 nm, $\lambda_{max}$ = 422 nm; **Quantum yield:** Φ = 55.1%.

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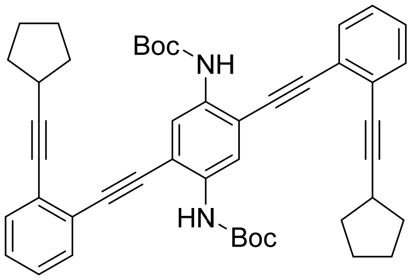
**Di-*tert*-butyl (2,5-bis((2-(cyclopentylethynyl)phenyl)ethynyl)-1,4-phenylene)dicarbamate, 1e**



According to GP2, 2.80 eq 1-(cyclopentylethynyl)-2-ethynylbenzene (429 mg, 2.21 mmol) and later 5 mol% copper(I) iodide (7.52 mg, 39.5 µmol) were added to a mixture of 1.00 eq di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate (368 mg, 789 µmol) and 5 mol% $PdCl_2(PPh_3)_2$ (27.7 mg, 39.5 µmol) in 60 mL solvent. After stirring over night at 60 °C, the solvent was removed under reduced pressure and the residue treated according to GP2. A yellow solid was obtained (343 mg, 495 µmol, 63%).

**Mp.:** 205 °C; **R*f***: 0.72 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3390, 2962, 2871, 1731, 1527, 1483, 1448, 1392, 1367, 1279, 1228, 1147, 1050, 1026, 899, 855, 767, 749; **$^1$H NMR** ($CD_2Cl_2$, 300.5 MHz): δ[ppm] = 1.52 (s, 18H), 1.56-1.63 (m, 4H), 1.67-1.80 (m, 8H), 1.99-2.07 (m, 4H), 2.92-3.02 (m, 2H), 7.28-7.35 (m, 4H), 7.37 (s, 2H), 7.43-7.49 (m, 2H), 7.51-7.57 (m, 2H), 8.34 (s, 2H); **$^{13}$C NMR** ($CD_2Cl_2$, 150.9 MHz): δ[ppm] = 25.5 (t, 4C), 28.4 (q, 6C), 31.3 (d, 2C), 34.3 (t, 4C), 78.9 (s, 2C), 81.1 (s, 2C), 88.1 (s, 2C), 96.6 (s, 2C), 100.3 (s, 2C), 112.8 (s, 2C), 121.0 (d, 2C), 125.0 (s, 2C), 127.3 (s, 2C), 127.7 (d, 2C), 129.0 (d, 2C), 131.9 (d, 2C), 132.2 (d, 2C), 134.6 (s, 2C), 152.7 (s, 2C); **HRMS** (ESI+): $C_{46}H_{48}N_2NaO_4^+$, calculated: 715.3506 [M$^+$+Na], observed: 715.3506 [M$^+$+Na]; **UV/VIS** (DCM, 8.60 µg/mL): λ[nm] (logε) = 262 (4.79), 323 (4.50), 376 (4.37); **Fluorescence** (DCM): $\lambda_{Anr}$ = 375 nm, $\lambda_{max}$ = 422 nm; **Quantum yield:** Φ = 56.3%.

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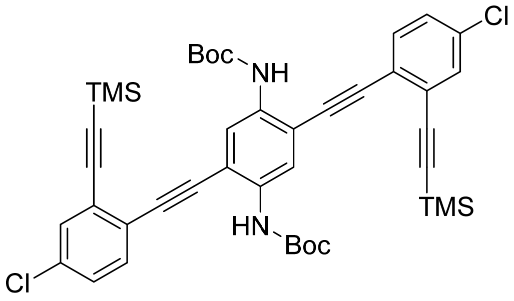
**Di-*tert*-butyl (2,5-bis((4-chloro-2-((trimethylsilyl)ethynyl)phenyl)ethynyl)-1,4-phenylene)dicarbamate, TMS-1f**



According to GP2, 2.80 eq ((5-chloro-2-ethynylphenyl)ethynyl)trimethylsilane (1.54 g, 6.84 mmol) and later 5 mol% copper(I) iodide (23.3 mg, 122 µmol) were added to a mixture of 1.00 eq di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate (1.14 g, 2.44 mmol) and 5 mol% $PdCl_2(PPh_3)_2$ (85.7 mg, 122 µmol) in 140 mL solvent. After stirring over night at room temperature, again 0.40 eq ((5-chloro-2-ethynylphenyl)ethynyl)trimethylsilane (227 mg, 976 µmol) and each 3 mol% copper(I) iodide (14.0 mg, 73.2 µmol) and $Pd(PPh_3)_2Cl_2$ (51.4 mg, 73.2 µmol) were added to the mixture. After stirring for additional 3 d at 60 °C, the solvent was removed under reduced pressure and the residue treated according to GP2. A yellow solid was obtained (513 mg, 666 µmol, 27%).

**Mp.:** 166-168 °C; **R*f***: 0.78 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3406, 2962, 2899, 2162, 1721, 1527, 1486, 1428, 1390, 1365, 1285, 1247, 1228, 1153, 1112, 1083, 1051, 1028, 953, 905, 880, 839, 821, 762, 691, 648; **$^1$H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 0.23 (s, 18H), 1.52 (s, 18H), 7.29 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 2H), 7.31 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 2H), 7.43 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 2H), 7.52 (d, $^4J_{H\text{-}H}$ = 2.1 Hz, 2H), 8.34 (s, 2H); **$^{13}$C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = -0.1 (q, 6C), 28.5 (q, 6C), 81.1 (s, 2C), 89.3 (s, 2C), 94.9 (s, 2C), 101.2 (s, 2C), 101.8 (s, 2C), 112.7 (s, 2C), 121.2 (d, 2C), 123.8 (s, 2C), 127.6 (s, 2C), 128.8 (d, 2C), 132.3 (d, 2C), 132.8 (s, 2C), 134.3 (d, 2C), 134.6 (s, 2C), 152.5 (s, 2C); **HRMS** (ESI+): $C_{42}H_{46}N_2NaO_4Si_2{}^{35}Cl_2^+$, calculated: 791.2265 [$M^+$+Na], observed: 791.2289 [$M^+$+Na]; **UV/VIS** (DCM, 2.46 µg/mL): λ[nm] (logε) = 241 (4.92), 255 (4.94), 266 (4.89), 328 (4.63), 380 (4.49); **Fluorescence** (DCM): $\lambda_{Anr}$ = 330 nm, $\lambda_{max}$ = 436 nm; **Quantum yield:** Φ = 57.8%.

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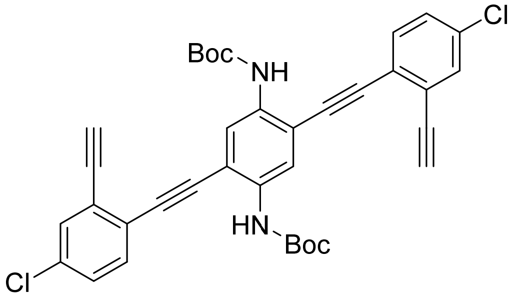
### Di-*tert*-butyl (2,5-bis((4-chloro-2-ethynylphenyl)ethynyl)-1,4-phenylene)dicarbamate, 1f

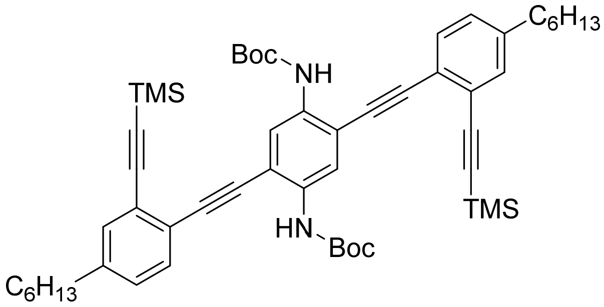


According to GP4, 3.00 eq of $K_2CO_3$ (271 mg, 1.96 mmol) were added to a solution of 1.00 eq of the corresponding TMS-protected alkyne (502 mg, 652 µmol) in 100 mL methanol and 100 mL DCM. The mixture was stirred over night at room temperature and treated according to GP4. After evaporation of the solvents, the crude product was purified by filtration through a pad of Celite® with DCM. The solvent was again evaporated and the residue recrystallized from EA. A yellow solid was obtained (349 mg, 558 µmol, 86%).

**Mp.:** 178 °C (decomp.); **R*f***: 0.14 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3382, 3302, 2978, 2929, 2211, 2114, 1896, 1724, 1587, 1530, 1483, 1421, 1390, 1367, 1281, 1230, 1144, 1111, 1080, 1050, 1026, 898, 877, 843, 821, 767, 734, 651, 642; **$^1$H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 1.56 (s, 18H), 3.64 (s, 2H), 7.34 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 2H), 7.37 (d, $^4J_{H\text{-}H}$ = 2.2 Hz, 2H), 7.49-7.54 (m, 6H), 8.34 (s, 2H); **$^{13}$C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 28.6 (q, 6C), 81.4 (s, 2C), 81.6 (t, 2C), 83.5 (s, 2C), 90.1 (s, 2C), 95.0 (s, 2C), 112.4 (s, 2C), 121.1 (s, 2C), 124.5 (d, 2C), 125.8 (s, 2C), 129.5 (d, 2C), 132.2 (d, 2C), 132.7 (s, 2C), 134.5 (d, 2C), 134.5 (s, 2C), 152.7 (s, 2C); **HRMS** (ESI+): $C_{36}H_{30}N_2NaO_4{}^{35}Cl_2^+$, calculated: 647.1475 [$M^+$+Na], observed: 647.1480 [$M^+$+Na]; **UV/VIS** (DCM, 1.10 µg/mL): λ[nm] (logε) = 249

(4.75), 263 (4.80), 316 (4.68), 327 (4.75), 340 (4.87), 387 (4.63); **Fluorescence** (DCM): $\lambda_{Anr}$ = 340 nm, $\lambda_{max}$ = 432 nm; **Quantum yield**: Φ = 53.6%.

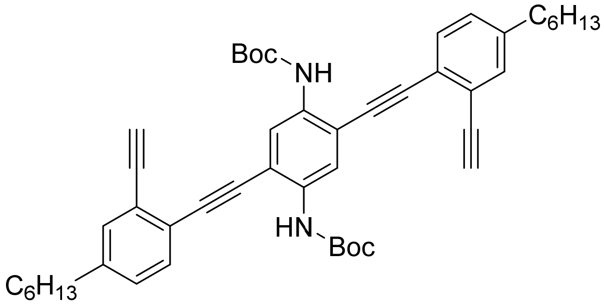
### Di-*tert*-butyl (2,5-bis((4-hexyl-2-((trimethylsilyl)ethynyl)phenyl)ethynyl)-1,4-phenylene)dicarbamate, TMS-1g



According to GP2, 2.80 eq 1-(4-ethynyl-3-((trimethylsilyl)ethynyl)phenyl)hexan-1-one (1.47 g, 5.20 mmol) and later 5 mol% copper(I) iodide (17.7 mg, 93.1 µmol) were added to a mixture of 1.00 eq di-*tert*-butyl (2,5-dibromo-1,4-phenylene)dicarbamate (868 mg, 1.86 mmol) and 5 mol% $PdCl_2(PPh_3)_2$ (65.4 mg, 93.1 µmol) in 150 mL solvent. After stirring over 3 d at 60 °C, the solvent was removed under reduced pressure and the residue treated according to GP2. A colourless solid was obtained (887 mg, 1.02 mmol, 55%).

**Mp.**:135 °C; **$R_f$**: 0.78 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3409, 2959, 2929, 2858, 2149, 1726, 1527, 1492, 1434, 1392, 1366, 1285, 1249, 1231, 1155, 1054, 1029, 941, 899, 882, 840, 762, 735, 699, 655; **$^1$H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 0.23 (s, 18H), 0.89 (t, $^3J_{H-H}$ = 6.8 Hz, 6H), 1.30-1.34 (m, 12H), 1.51 (s, 18H), 1.61 (qi, $^3J_{H-H}$ = 7.6 Hz, 4H), 2.59 (t, $^3J_{H-H}$ = 7.6 Hz, 4H), 7.14 (dd, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.4 Hz, 2H), 7.31 (s, 2H), 7.35 (s, 2H), 7.41 (d, $^3J_{H-H}$ = 7.9 Hz, 2H), 8.33 (s, 2H); **$^{13}$C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 0.1 (q, 6C), 14.2 (q, 2C), 22.7 (t, 2C), 28.5 (q, 6C), 29.1 (t, 2C), 31.2 (t, 2C), 31.8 (t, 2C), 35.8 (t, 2C), 80.8 (s, 2C), 87.8 (s, 2C), 96.0 (s, 2C), 99.0 (s, 2C), 103.5 (s, 2C), 112.8 (s, 2C), 121.0 (s, 2C), 122.7 (s, 2C), 125.8 (s, 2C), 128.8 (s, 2C), 131.7 (s, 2C), 132.4 (s, 2C), 134.2 (s, 2C), 144.0 (s, 2C), 152.6 (s, 2C); **HRMS** (ESI+): $C_{54}H_{72}N_2O_4Si_2^+$, calculated: 868.5025 [M$^+$], observed: 868.5042 [M$^+$]; **UV/VIS** (DCM, 6.00 µg/mL): λ[nm] (logε) = 238 (4.82), 256 (4.86), 265 (4.83), 328 (4.58), 373 (4.48); **Fluorescence** (DCM): $\lambda_{Anr}$ = 330 nm, $\lambda_{max}$ = 423 nm; **Quantum yield**: Φ = 64.0%.

### Di-*tert*-butyl (2,5-bis((2-ethynyl-4-hexylphenyl)ethynyl)-1,4-phenylene)dicarbamate, 1g



According to GP4 3.00, eq of $K_2CO_3$ (418 mg, 3.02 mmol) were added to a solution of 1.00 eq of the corresponding TMS-protected alkyne (876 mg, 1.01 mmol) in 150 mL methanol and 150 mL DCM. The mixture was stirred over night at room temperature and treated according to GP4. After evaporation of the solvents, the residue was purified by filtration through a pad of Celite® with DCM. The solvent was again evaporated and a yellow solid was obtained (703 mg, 970 µmol, 96%).

**Mp.**: 164 °C (decomposition); **$R_f$**: 0.69 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3375, 3306, 2959, 2930, 2857, 1727, 1600, 1528, 1494, 1468, 1421, 1393, 1368, 1279, 1254, 1225, 1145, 1048, 1023, 900, 845, 821, 768, 731, 647, 618; ; **$^1$H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 0.90 (t, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H), 1.30-1.34 (m, 12H), 1.54 (s, 18H), 1.60 (qi, $^3J_{H\text{-}H}$ = 7.4 Hz, 4H), 2.61 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H), 3.57 (s, 2H), 7.19 (dd, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz, 2H), 7.37 (s, 2H), 7.48 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 2H), 7.63 (s, 2H), 8.41 (s, 2H); **$^{13}$C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 14.2 (q, 2C), 22.7 (t, 2C), 28.6 (q, 6C), 29.0 (t, 2C), 31.1 (t, 2C), 31.8 (t, 2C), 35.8 (t, 2C), 81.1 (s, 2C), 81.8 (d, 2C), 83.1 (s, 2C), 88.5 (s, 2C), 96.0 (s, 2C), 112.5 (s, 2C), 120.8 (s, 2C), 123.3 (s, 2C), 124.1 (s, 2C), 129.4 (s, 2C), 131.6 (s, 2C), 132.2 (s, 2C), 134.3 (s, 2C), 143.9 (s, 2C), 152.9 (s, 2C); **HRMS** (ESI+): $C_{48}H_{56}N_2O_4^+$, calculated: 763.3872 [$M^+$], observed: 763.3884 [$M^+$]; **UV/VIS** (DCM, 4.00 µg/mL): λ[nm] (logε) = 262 (4.37), 279 (4.51), 316 (4.27), 327 (4.35), 338 (4.21), 383 (4.15), 395 (3.80); **Fluorescence** (DCM): $\lambda_{Anr}$ = 330 nm, $\lambda_{max}$ = 439 nm, 421 nm; **Quantum yield**: Φ = 68.3%.

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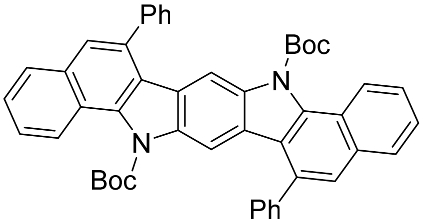
### Di-tert-butyl 6,14-diphenylbenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate, 2a



According to GP5, 1.00 eq of the corresponding tetrayne (100 mg, 141 µmol) was dissolved in 20 mL DCE and 10 mol% $IPrAuNTf_2$ (12.2 mg, 14.1 µmol) were added to the solution. After stirring over 3 d at 60 °C, the mixture was treated according to GP5 (silica gel, PE:EA = 50:1). A beige solid was obtained (54.0 mg, 76.2 µmol, 54%).

**Mp.:** decomp. >192 °C; **$R_f$:** 0.27 (silica gel, PE:EA = 10:1); **IR** (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3056, 2979, 2932, 1731, 1495, 1438, 1392, 1368, 1339, 1286, 1254, 1144, 1122, 1065, 878, 852, 832, 784, 864, 742, 698, 643, 617; **$^1$H NMR** ($CD_2Cl_2$, 600.2 MHz): δ[ppm] = 1.49 (s, 18H), 7.52-7.57 (m, 4H), 7.62-7.64 (m, 6H), 7.67 (s, 2H), 7.72-7.74 (m, 4H), 7.97 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H), 8.18-8.19 (m, 4H); **$^{13}$C NMR** ($CD_2Cl_2$, 150.9 MHz): δ[ppm] = 28.0 (q, 6C), 84.8 (s, 2C), 107.8 (d, 2C), 122.1 (s, 2C), 123.0 (s, 2C), 125.2 (d, 2C), 125.4 (d, 2C), 125.5 (s, 2C), 126.1 (d, 2C), 126.5 (d, 2C), 128.5 (d, 2C), 129.0 (d, 2C), 129.2 (d, 4C), 129.7 (d, 4C), 133.3 (s, 2C), 135.8 (s, 2C), 136.9 (s, 2C), 137.7 (s, 2C), 140.8 (s, 2C), 152.0 (s, 2C); **HRMS** (MALDI+): $C_{48}H_{40}N_2O_4^+$, calculated: 708.2983 [$M^+$], observed: 708.2983 [$M^+$]; **UV/VIS** (DCM, 2.20 µg/mL): λ[nm] (logε) = 238 (4.87), 272 (4.79), 298 (4.71), 335 (4.74), 348 (4.79), 365 (4.62), 380 (4.43); **Fluorescence** (DCM): $\lambda_{Anr}$ = 380 nm, $\lambda_{max}$ = 394 nm; **Quantum yield:** Φ = 52.5%.

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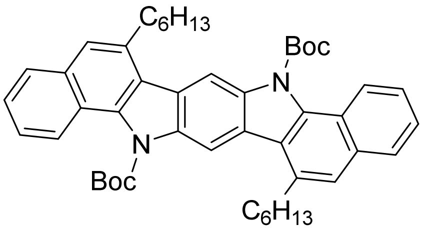
### Di-*tert*-butyl 6,14-dihexylbenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate, 2b



According to GP5, 1.00 eq of the corresponding tetrayne (60.0 mg, 82.7 µmol) was dissolved in 2.5 mL DCE and 10 mol% IPrAuNTf$_2$ (7.16 mg, 8.28 µmol) were added to the solution. After stirring over night at 50 °C, the mixture was treated according to GP5 (silica gel, PE:EA = 20:1). A colourless solid was obtained (49.0 mg, 67.6 µmol, 82%).

**Mp.:** 186 °C; **R$_f$**: 0.63 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 2955, 2928, 2854, 1735, 1434, 1425, 1368, 1279, 1246, 1146, 1118, 1048, 926, 866, 842, 779, 742; **$^1$H NMR** (CD$_2$Cl$_2$, 300.5 MHz): δ[ppm] = 0.93 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 6H), 1.37-1.47 (m, 8H), 1.63-1.71 (m, 22H), 1.96-2.06 (m, 4H), 3.47 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H), 7.48-7.56 (m, 4H), 7.66 (s, 2H), 7.91-7.96 (m, 2H), 8.19-8.24 (m, 2H), 9.04 (s, 2H); **$^{13}$C NMR** (CD$_2$Cl$_2$, 125.8 MHz): δ[ppm] = 14.3 (q, 2C), 23.2 (t, 2C), 28.3 (q, 6C), 29.8 (t, 2C), 30.1 (t, 2C), 32.4 (t, 2C), 34.8 (t, 2C), 84.8 (s, 2C), 108.0 (d, 2C), 122.5 (s, 2C), 123.3 (s, 2C), 124.4 (d, 2C), 124.5 (d, 2C), 125.5 (d, 2C), 125.5 (s, 2C), 125.8 (d, 2C), 128.4 (d, 2C), 133.6 (s, 2C), 136.1 (s, 2C), 136.8 (s, 2C), 138.2 (s, 2C), 152.4 (s, 2C); **HRMS** (MALDI+): $C_{48}H_{56}N_2O_4^+$, calculated: 724.4235 [M$^+$], observed: 724.4235 [M$^+$]; **UV/VIS** (DCM, 2.90 µg/mL): λ[nm] (logε) = 251 (4.72), 273 (4.78), 288 (4.84), 327 (4.76), 344 (4.86), 361 (4.72), 374 (4.42); **Fluorescence** (DCM): λ$_{Anr}$ = 380 nm, λ$_{max}$ = 394 nm, 414 nm; **Quantum yield:** Φ = 43.8%.

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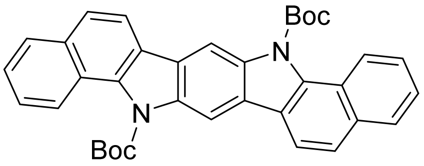
**Di-*tert*-butyl benzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate, 2c**



According to GP5, 1.00 eq of the corresponding tetrayne (49.8 mg, 89.5 µmol) was dissolved in 2.5 mL DCE and 5 mol% IPrAuNTf$_2$ (3.87 mg, 4.47 µmol) were added to the solution. After stirring over night at 50 °C, the precipitate was filtered and washed with ice-cold EA. A yellow solid was obtained (37.0 mg, 66.5 µmol, 74%).

**Mp.:** >300 °C; **R$_f$**: 0.39 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 2984, 1722, 1454, 1367, 1297, 1256, 1145, 1110, 1062, 1042, 1020, 875, 852, 821, 789, 779, 752, 716, 646; **$^1$H NMR** (CD$_2$Cl$_2$, 300.5 MHz): δ[ppm] = 1.79 (s, 18H), 7.51-7.63 (m, 4H), 7.91 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 8.00-8.03 (m, 2H), 8.18 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 8.38 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 8.85 (s, 2H); **$^{13}$C NMR** (CD$_2$Cl$_2$, 150.9 MHz): δ[ppm] = 28.4 (s, 6C), 85.0 (s, 2C), 106.1 (d, 2C), 118.1 (d, 2C), 124.2 (s, 2C), 124.8 (s, 2C), 125.5 (d, 2C), 125.7 (d, 2C), 125.9 (d, 2C), 125.9 (d, 2C), 126.5 (s, 2C), 129.2 (d, 2C), 134.2 (s, 2C), 136.1 (s, 2C), 137.8 (s, 2C), 152.3 (s, 2C); **HRMS** (MALDI+): $C_{36}H_{32}N_2O_4^+$, calculated: 556.2357 [M$^+$], observed: 556.2357 [M$^+$]; **UV/VIS** (DCM, 2.90 µg/mL): λ[nm] (logε) = 246 (4.24), 268 (4.36), 284 (4.24), 329 (4.32), 340 (4.40), 346 (4.40), 356 (4.27), 370 (4.24); **Fluorescence** (DCM): λ$_{Anr}$ = 370 nm, λ$_{max}$ = 378 nm; **Quantum yield:** Φ = 63.5%.

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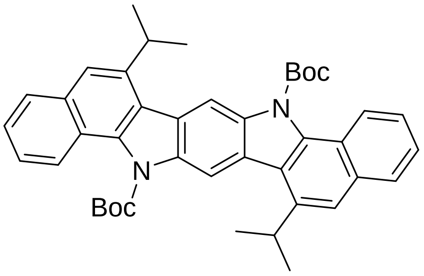
**Di-*tert*-butyl 6,14-diisopropylbenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate, 2d**



According to GP5, 1.00 eq of the corresponding tetrayne (452 mg, 705 µmol) was dissolved in 50 mL DCE at 60 °C and 5 mol% $IPrAuNTf_2$ (30.5 mg, 35.3 µmol) were added to the solution. After stirring over night at 60 °C, the precipitate was filtered and washed with cold DCE. A light beige solid was obtained (351 mg, 548 µmol, 78%).

**Mp.:** >300 °C; **R*f*** 0.70 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 3005, 2968, 2933, 2873, 1726, 1458, 1434, 1368, 1283, 1244, 1216, 1163, 1143, 1117, 1079, 1048, 1027, 975, 944, 927, 875, 858, 841, 782, 765, 741, 664, 625; **$^1$H NMR** ($CD_2Cl_2$, 600.2 MHz): δ[ppm] = 1.64 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12H), 1.76 (s, 18H), 4.20 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 2H), 7.51-7.55 (m, 4H), 7.77 (s, 2H), 7.95-7.99 (m, 2H), 8.15-8.17 (m, 2H), 9.09 (s, 2H); **$^{13}$C NMR** ($CD_2Cl_2$, 150.9 MHz): δ[ppm] = 23.1 (q, 4C), 28.3 (q, 6C), 30.5 (d, 2C), 84.9 (s, 2C), 108.3 (d, 2C), 120.5 (d, 2C), 122.4 (s, 2C), 122.9 (s, 2C), 124.6 (d, 2C), 125.2 (s, 2C), 125.3 (d, 2C), 125.9 (d, 2C), 128.6 (d, 2C), 133.8 (s, 2C), 137.0 (s, 2C), 138.2 (s, 2C), 142.2 (s, 2C), 152.6 (s, 2C); **HR-MS** (ESI+): $C_{42}H_{44}N_2NaO_4^+$, calculated: 663.3193 [$M^+$+Na], observed: 663.3203 [$M^+$+Na]; **UV/VIS** (DCM, 6.60 µg/mL): λ[nm] (logε) = 250 (4.47), 273 (4.65), 288 (4.69), 327 (4.62), 345 (4.74), 360 (4.58), 376 (4.27); **Fluorescence** (DCM): $\lambda_{Anr}$ = 370 nm, $\lambda_{max}$ = 388 nm; **Quantum yield:** Φ = 56.6%.

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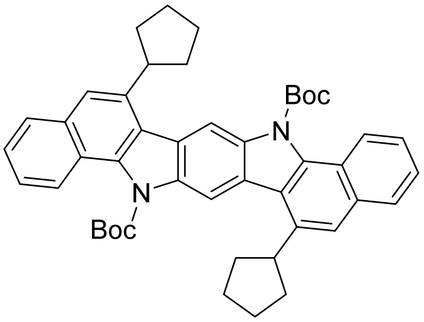
**Di-*tert*-butyl 6,14-dicyclopentylbenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate, 2e**

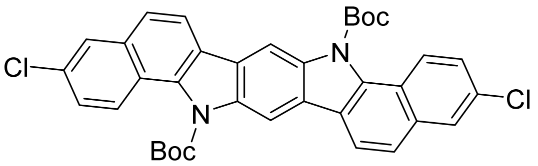


According to GP5, 1.00 eq of the corresponding tetrayne (250 mg, 361 µmol) was dissolved in 10 mL DCE and 5 mol% $IPrAuNTf_2$ (15.6 mg, 18.0 µmol) were added to the solution. After stirring over night at room temperature, the precipitate was filtered and washed with pentane. A slightly yellow solid was obtained (132 mg, 191 µmol, 53%).

**Mp.:** decomposition <230 °C; **R*f***: 0.74 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [$cm^{-1}$] = 2973, 1721, 1459, 1444, 1367, 1282, 1251, 1143, 1125, 1050, 872, 847, 785, 741, 666; **$^1$H NMR** ($CD_2Cl_2$, 300.5 MHz): δ[ppm] = 1.71 (s, 18H), 1.93-2.10 (m, 12H), 2.42-2.49 (m, 4H), 4.31 (quint, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H), 7.49-

7.56 (m, 4H), 7.75 (s, 2H), 7.93-7.97 (m, 2H), 8.16-8.21 (m, 2H), 9.14 (s, 2H); **$^{13}$C NMR** (CD$_2$Cl$_2$, 150.9 MHz): δ[ppm] = 25.4 (t, 4C), 28.2 (q, 6C), 33.1 (t, 4C), 42.7 (d, 2C), 84.8 (s, 2C), 108.3 (d, 2C), 120.8 (d, 2C), 122.4 (s, 2C), 123.5 (s, 2C), 124.5 (d, 2C), 125.4 (d, 2C), 125.5 (s, 2C), 125.8 (d, 2C), 128.6 (d, 2C), 133.6 (s, 2C), 137.0 (s, 2C), 138.2 (s, 2C), 139.8 (s, 2C), 152.6 (s, 2C); **HRMS** (ESI+): $C_{46}H_{48}N_2NaO_4^+$, calculated: 715.3506 [M$^+$+Na], observed: 715.3506 [M$^+$+Na]; **UV/VIS** (DCM, 7.40 µg/mL): λ[nm] (logε) = 250 (4.53), 274 (4.59), 289 (4.65), 330 (4.59), 346 (4.70), 361 (4.55), 375 (4.23); **Fluorescence** (DCM): λ$_{Anr}$ = 375 nm, λ$_{max}$ = 407 nm; **Quantum yield:** Φ = 41.4%.

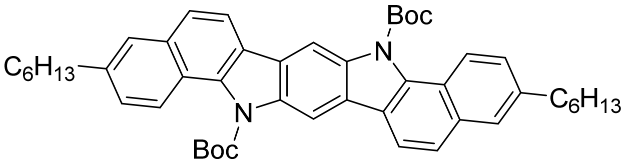
### Di-*tert*-butyl 3,11-dichlorobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate, 2f



According to GP5, 1.00 eq of the corresponding tetrayne (343 mg, 548 µmol) was dissolved in 15 mL DCE and 5 mol% IPrAuNTf$_2$ (23.7 mg, 27.4 µmol) were added to the solution. After stirring for 2 h at 50 °C, the precipitate was filtered and washed with ice-cold EA. A yellowish solid was obtained (281 mg, 449 µmol, 82%).

**Mp.:** >300 °C; **R$_f$**: 0.33 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3124, 3059, 2976, 2932, 1732, 1593, 1566, 1443, 1367, 1290, 1250, 1226, 1143, 1111, 1088, 1043, 1020, 931, 912, 887, 869, 834, 811, 767, 743, 713, 696, 663; **$^1$H NMR** (d$_2$-TCE, 300.5 MHz): δ[ppm] = 1.81 (s, 18H), 7.57 (dd, $^3J_{HH}$ = 9.2 Hz, $^4J_{H-H}$ = 2.2 Hz, 2H), 7.84 (d, $^3J_{H-H}$ = 8.5 Hz, 2H), 8.01 (d, $^4J_{H-H}$ = 2.2 Hz, 2H), 8.17 (d, $^3J_{H-H}$ = 8.5 Hz, 2H), 8.33 (d, $^3J_{H-H}$ = 9.2 Hz, 2H), 8.81 (s, 2H); **$^{13}$C NMR** was not recorded due to its low solubility. **HR-MS** (MALDI+): $C_{36}H_{30}N_2O_4{}^{35}Cl_2$, calculated: 624.1577 [M$^+$], observed: 624.1584 [M$^+$]; **UV/VIS** (DCM, 6.00 µg/mL): λ[nm] (logε) = 250 (4.43), 270 (4.54), 290 (4.38), 333 (4.63), 347 (4.71), 361 (4.60), 371 (4.56); **Fluorescence** (DCM): λ$_{Anr}$ = 370 nm, λ$_{max}$ = 380 nm, 400 nm, 421 nm; **Quantum yield**: Φ = 37.1%;

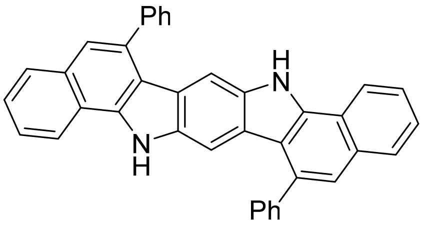
### Di-*tert*-butyl 3,11-dihexylbenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate, 2g



According to GP5, 1.00 eq of the corresponding tetrayne (650 mg, 897 µmol) was dissolved in 60 mL DCE and 5 mol% IPrAuNTf$_2$ (38.8 mg, 44.8 µmol) were added to the solution. After stirring over night at room temperature, the precipitate was filtered and washed with ice-cold EA. A beige solid was obtained (476 mg, 657 µmol, 73%).

**Mp.**: >300 °C; **R$_f$**: 0.71 (silica gel, PE:EA = 5:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 2957, 2927, 2854, 1721, 1599, 1574, 1441, 1369, 1293, 1256, 1224, 1148, 1102, 1045, 1021, 955, 899, 865, 857, 846, 811, 802, 766, 721, 706, 664, 627; **$^1$H NMR** (CDCl$_3$, 400.3 MHz): δ[ppm] = 0.90 (t, $^3J_{H-H}$ = 7.0 Hz, 6H), 1.33-1.37 (m, 8H), 1.39-1.44 (m, 4H), 1.73-1.77 (m, 4H), 1.79 (s, 18H), 2.82 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H), 7.44 (dd, $^3J_{H\text{-}H}$ = 8.8 Hz ,$^4J_{H\text{-}H}$ = 1.7 Hz, 2H), 7.75 (s, 2H), 7.81 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 8.08 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H), 8.30 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H), 8.78 (s, 2H); **$^{13}$C NMR** (CDCl$_3$, 100.7 MHz): δ[ppm] = 14.3 (q, 2C), 22.8 (t, 2C), 28.4 (q, 6C), 29.2 (t, 2C), 31.4 (t, 2C), 31.9 (t, 2C), 36.1 (t, 2C), 84.5 (s, 2C), 105.9 (d, 2C), 117.7 (d, 2C), 122.3 (s, 2C), 124.1 (s, 2C), 125.4 (d, 4C), 126.3 (s, 2C), 126.8 (d, 2C), 127.6 (d, 2C), 134.3 (s, 2C), 136.0 (s, 2C), 137.5 (s, 2C), 140.0 (s, 2C), 152.2 (s, 2C); **HRMS** (MALDI+): $C_{48}H_{56}N_2O_4^+$, calculated: 724.4235 [M$^+$], observed: 724.4243 [M$^+$]; **UV/VIS** (DCM, 1.62 µg/mL): λ[nm] (logε) = 248 (4.81), 271 (4.90), 287 (4.78), 334 (4.89), 349 (4.97), 358 (4.86), 371 (4.90); **Fluorescence** (DCM): $\lambda_{Anr}$ = 330 nm, $\lambda_{max}$ = 422 nm, 399 nm, 378 nm; **Quantum yield**: Φ = 74.8%.

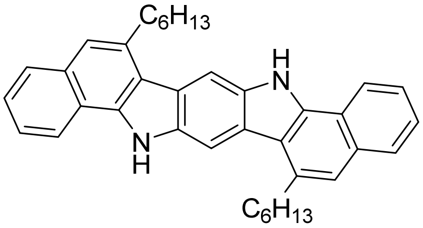
### 6,14-Diphenyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 3a



According to GP6 the Boc-protected BBICZ (137 mg, 193 µmol) was heated up to 200 °C for 4 h. The deprotected BBICZ was obtained as yellow solid in quantitave yields (98.2 mg, 193 µmol).

**Mp.:** >300 °C; **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3429, 3052, 3027, 1566, 1520, 1493, 1452, 1398, 1370, 1343, 1309, 1280, 1225, 1152, 1103, 1072, 1027, 935, 911, 838, 782, 766, 740, 701, 670, 615; **$^1$H NMR** (CD$_2$Cl$_2$, 300.5 MHz): δ[ppm] = 7.49 (s, 2H), 7.53-7.69 (m, 12H), 7.76-7.80 (m, 4H), 7.99-8.02 (m, 2H), 8.16 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H), 8.87 (s, 2H); **$^{13}$C NMR** (CD$_2$Cl$_2$, 150.9 MHz): δ[ppm] = 102.7 (d, 2C), 116.4 (s, 2C), 120.5 (s, 2C), 120.6 (d, 2C), 120.9 (d, 2C), 123.2 (s, 2C), 125.8 (d, 2C), 126.1 (d, 2C), 128.0 (d, 2C), 128.9 (d, 4C), 129.1 (d, 2C), 129.8 (d, 4C), 132.5 (s, 2C), 135.1 (s, 2C), 136.9 (s, 2C), 137.2 (s, 2C), 141.8 (s, 2C); **HRMS** (DART+): $C_{38}H_{25}N_2^+$, calculated: 509.2012 [M$^+$+H], observed: 509.2005 [M$^+$+H]; **UV/VIS** (THF, 6.10 µg/mL): λ[nm] (logε) = 238 (4.69), 274 (4.72), 320 (4.57), 342 (4.74), 355 (4.77), 391 (4.16), 410 (4.10); **Fluorescence** (DCM): $\lambda_{Anr}$ = 400 nm, $\lambda_{max}$ = 414 nm, 439 nm, 464 nm; **Quantum yield:** Φ = 36.8%.

### 6,14-Dihexyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 3b



According to GP6, the Boc-protected BBICZ (675 mg, 931 µmol) was heated up to 220 °C for 5 h. The deprotected BBICZ was obtained as yellow solid in quantitative yield (489 mg, 931 µmol).

**Mp.:** >300 °C; **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3420, 2957, 2922, 2850, 1567, 1520, 1455, 1436, 1412, 1385, 1347, 1282, 1244, 1216, 1086, 944, 919, 896, 863, 834, 748, 730; **$^1$H NMR** ($d_8$-THF, 500.1 MHz): δ[ppm] = 0.93 (t, $^3J_{H-H}$ = 7.1 Hz, 6H), 1.41-1.47 (m, 8H), 1.62-1.67 (m, 4H), 2.00-2.10 (m, 4H), 3.47 (t, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.35 (s, 2H), 7.40-7.51 (m, 4H), 7.88 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 8.31 (s, 2H), 8.35 (t, $^3J_{H-H}$ = 8.0 Hz, 2H), 11.05 (s, 2H); **$^{13}$C NMR** ($d_6$-DMSO, 100.6 MHz, 323 K): δ[ppm] = 13.7 (q, 2C), 21.8 (t, 2C), 28.6 (t, 2C), 29.1 (t, 2C), 31.1 (t, 2C), 34.0 (t, 2C), 101.8 (d, 2C), 115.7 (s, 2C), 117.0 (d, 2C), 119.6 (s, 2C), 121.4 (d, 2C), 121.6 (s, 2C), 124.1 (d, 2C), 125.0 (d, 2C), 127.5 (d, 2C), 131.7 (s, 2C), 135.1 (s, 2C), 136.1 (s, 2C), 136.9 (s, 2C); **HRMS** (ESI+): $C_{38}H_{40}N_2^+$, calculated: 524.3186 [M$^+$], observed: 524.3184 [M$^+$]; **UV/VIS** (THF, 4.30 µg/mL): λ[nm] (logε) = 311 (4.62), 334 (4.83), 353 (4.74), 386 (4.20), 405 (4.09); **Fluorescence** (THF): $\lambda_{Anr}$ = 405 nm, $\lambda_{max}$ = 413, 438 nm; **Quantum yield:** Φ = 36.1%

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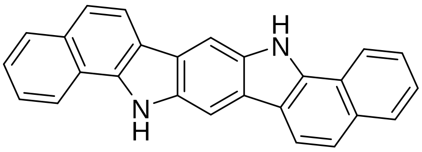
### 8,16-Dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 3c



According to GP6, the Boc-protected BBICZ (500 mg, 898 µmol) was heated up to 220 °C for 4 h. The deprotected BBICZ was obtained as yellowish solid in quantitative yield (320 mg, 898 µmol).

**IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3774, 3430, 3051, 1940, 1887, 1701, 1626, 1565, 1523, 1463, 1452, 1441, 1421, 1385, 1350, 1276, 1246, 1206, 1152, 1093, 1040, 1017, 944, 881, 865, 848, 814, 741, 670; **$^1$H NMR** ($d_6$-DMSO, 300.5 MHz): δ[ppm] = 7.55 (t, $^3J_{H-H}$ = 7.4 Hz, 2H), 7.62-7.67 (m, 4H), 8.05 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 8.32 (s, 2H), 8.37 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 8.57 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 12.02 (s, 2H); **UV/VIS** (THF, 29.2 µg/mL): λ[nm] (logε) = 269 (4.70), 313 (4.54), 340 (4.79), 348 (4.82), 384 (4.19), 397 (4.13); **Fluorescence** (DCM): $\lambda_{Anr}$ = 380 nm, $\lambda_{max}$ = 403 nm; **Quantum yield:** Φ = 15.2%.

Analytics confirm to previously reported data.[2]

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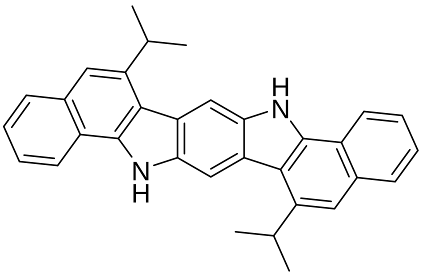
### 6,14-Diisopropyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 3d



According to GP6, the Boc-protected BBICZ (77.7 mg, 121 µmol) was heated up to 220 °C for 5 h. The deprotected BBICZ was obtained as yellow solid in quantitative yield (53.4 mg, 121 µmol).

**Mp.:** >300 °C; **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] =3432, 3060, 2964, 2925, 2873, 1771, 1731, 1682, 1568, 1527, 1456, 1408, 1382, 1350, 1285, 1244, 1218, 1170, 1154, 1081, 1057, 986, 920, 865, 836, 783, 742, 623; **$^1$H NMR** ($CD_2Cl_2$, 300.5 MHz): δ[ppm] = 1.67 (d, $^3J_{H-H}$ = 6.8 Hz, 12H), 4.17 (sept, $^3J_{H-H}$ = 6.8 Hz, 2H), 7.52-

7.62 (m, 6H), 7.99-8.02 (m, 2H), 8.20-8.23 (m, 2H), 8.45 (s, 2H), 9.04 (s, 2H); **$^{13}$C NMR** ($CD_2Cl_2$, 100.7 MHz): δ[ppm] = 22.5 (q, 4C), 30.6 (d, 2C), 103.0 (d, 2C), 114.2 (d, 2C), 116.7 (s, 2C), 119.6 (s, 2C), 120.3 (d, 2C), 122.4 (s, 2C), 124.7 (d, 2C), 125.4 (d, 2C), 128.4 (d, 2C), 132.6 (s, 2C), 135.3 (s, 2C), 136.7 (s, 2C), 143.2 (s, 2C); **HRMS** (DART+): $C_{32}H_{29}N_2^+$, calculated: 441.2325 [M$^+$+H], observed: 441.2323 [M$^+$+H]; **UV/VIS** (THF, 5.28 µg/mL): λ[nm] (logε) = 74 (4.68), 311 (4.58), 335 (4.81), 354 (4.74), 387 (4.17), 406 (4.05); **Fluorescence** (THF): $\lambda_{Anr}$ = 390 nm, $\lambda_{max}$ = 466 nm, 438 nm, 413 nm; **Quantum yield:** Φ = 33.6%.

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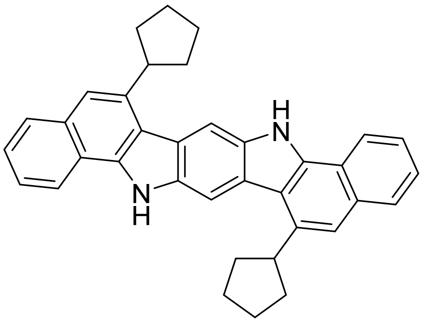
### 6,14-Dicyclopentyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 3e



According to GP6, the Boc-protected BBICZ (50.0 mg, 72.2 µmol) was heated up to 220 °C for 6 h. The deprotected BBICZ was obtained as yellow solid in quantitative yield (35.6 mg, 72.2 µmol).

**Mp.:** >300 °C; **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3461, 3048, 2942, 2869, 1927, 1770, 1654, 1567, 1529, 1455, 1412, 1383, 1284, 1247, 1215, 1161, 1092, 1028, 995, 935, 900, 856, 824, 782, 740; **$^1$H NMR** ($d_6$-DMSO, 400.3 MHz): δ[ppm] = 1.91-1.99 (m, 12H), 2.38-2.46 (m, 4H), 4.16-4.22 (m, 2H), 7.51-7.54 (m, 4H), 7.56-7.60 (m, 2H), 8.00 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 8.40 (s, 2H), 8.49 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 12.08 (s, 2H); **$^{13}$C NMR** ($d_6$-DMSO, 100.7 MHz): δ[ppm] = 24.7 (t, 4C), 32.2 (t, 4C), 42.7 (d, 2C), 102.3 (d, 2C), 113.2 (d, 2C), 116.0 (s, 2C), 119.7 (s, 2C), 121.5 (d, 2C), 121.7 (s, 2C), 124.4 (d, 2C), 125.2 (d, 2C), 128.0 (d, 2C), 131.9 (s, 2C), 135.2 (s, 2C), 136.9 (s, 2C), 139.6 (s, 2C); **HRMS** (DART+): $C_{36}H_{33}N_2^+$, calculated: 493.2638 [M$^+$+H], observed: 493.2637 [M$^+$+H]; **UV/VIS** (THF): λ[nm] (logε, 4.08 µg/mL) =275 (4.71), 312 (4.62), 335 (4.85), 354 (4.78), 388 (4.20), 406 (4.08); **Fluorescence** (THF): $\lambda_{Anr}$ = 390 nm, $\lambda_{max}$ = 466 nm, 439 nm, 414 nm; **Quantum yield:** Φ = 33.4%.

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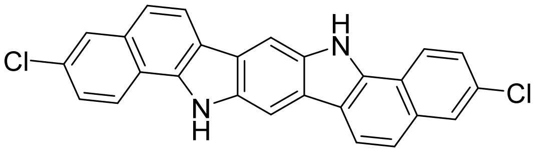
### 3,11-Dichloro-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 3f

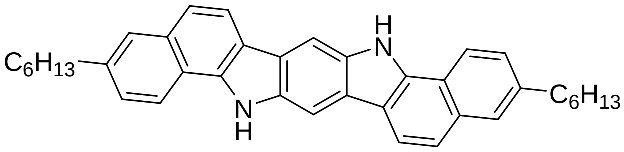


According to GP6, the Boc-protected BBICZ (115 mg, 184 µmol) was heated up to 220 °C for 4 h. The deprotected BBICZ was obtained as yellowish solid in quantitative yield (78.2 mg, 184 µmol).

**Mp.:** >300 °C; **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3430, 1768, 1734, 1625, 1589, 1560, 1522, 1454, 1434, 1397, 1372, 1356, 1287, 1267, 1246, 1148, 1101, 1082, 884, 848, 806, 772, 714, 695; **$^1$H NMR** ($d_6$-DMSO, 600.2 MHz): δ[ppm] = 7.64 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 7.68 (dd, $^3J_{H\text{-}H}$ = 8.8 Hz, $^4J_{H\text{-}H}$ = 2.1 Hz, 2H), 8.17 (d, $^4J_{H\text{-}}$

$_{\text{H}}$ = 2.1 Hz, 2H), 8.36 (s, 2H), 8.46 (d, $^{3}J_{\text{H-H}}$ = 8.5 Hz, 2H), 8.61 (d, $^{3}J_{\text{H-H}}$ = 8.8 Hz, 2H), 12.16 (s, 2H); **$^{13}$C NMR** (d$_6$-DMSO, 150.9 MHz): δ[ppm] = 100.5 (d, 2C), 117.4 (d, 2C), 117.8 (s, 2C), 119.4 (s, 2C), 121.2 (d, 2C), 122.9 (s, 2C), 124.2 (d, 2C), 125.5 (d, 2C), 127.2 (d, 2C), 129.6 (s, 2C), 132.9 (s, 2C), 135.0 (s, 2C), 136.4 (s, 2C); **HRMS** (DART+): $C_{26}H_{15}Cl_2N_2^+$, calculated: 425.0607 [M$^+$+H], observed: 425.0604 [M$^+$+H]; **UV/VIS** (THF, 3.04 µg/mL): λ[nm] (logε) =270 (4.75), 321 (4.69), 342 (4.88), 356 (4.94), 388 (4.35), 404 (4.23); **Fluorescence** (THF): $\lambda_{\text{Anr}}$ = 390 nm, $\lambda_{\text{max}}$ = 467 nm, 438 nm, 413 nm; **Quantum yield:** Φ = 23.5%.

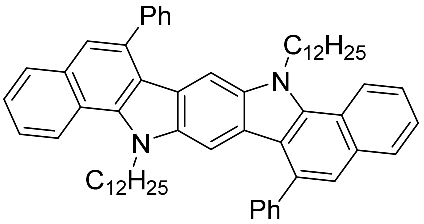
### **3,11-Dihexyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 3g**



According to GP6, the Boc-protected BBICZ (420 mg, 579 µmol) was heated up to 220 °C for 4 h. The deprotected BBICZ was obtained as yellow solid in quantitative yield (304 mg, 579 µmol).

**Mp.:** >300 °C; **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3426, 2959, 2929, 2856, 1737, 1725, 1651, 1573, 1523, 1454, 1438, 1406, 1380, 1291, 1276, 1250, 1228, 1216, 1152, 949, 896, 849, 821, 715, 671, 651; **$^{1}$H NMR** (d$_6$-DMSO, 300.5 MHz): δ[ppm] = 0.87 (t, $^{3}J_{\text{H-H}}$ = 6.9 Hz, 6H), 1.28-1.36 (m, 12H), 1.69-1.76 (m, 4H), 2.81 (t, $^{3}J_{\text{H-H}}$ = 7.6 Hz, 4H), 7.50 (dd, $^{3}J_{\text{H-H}}$ = 8.5 Hz, $^{4}J_{\text{H-H}}$ = 1.4 Hz, 2H), 7.55 (d, $^{3}J_{\text{H-H}}$ = 8.5 Hz, 2H), 7.82 (s, 2H), 8.27 (s, 2H), 8.31 (d, $^{3}J_{\text{H-H}}$ = 8.6 Hz, 2H), 8.47 (d, $^{3}J_{\text{H-H}}$ = 8.5 Hz, 2H), 11.91 (s, 2H); **$^{13}$C NMR** (d$_6$-DMSO, 100.7 MHz): δ[ppm] = 13.7 (q, 2C), 21.8 (t, 2C), 28.6 (t, 2C), 29.1 (t, 2C), 31.1 (t, 2C), 34.0 (t, 2C), 101.8 (d, 2C), 115.7 (s, 2C), 117.0 (d, 2C), 119.6 (d, 2C), 121.4 (s, 2C), 121.6 (d, 2C), 124.1 (s, 2C), 125.0 (d, 2C), 127.5 (d, 2C), 131.7 (s, 2C), 135.1 (s, 2C), 136.1 (s, 2C), 136.9 (s, 2C); **HRMS** (MALDI+): $C_{38}H_{40}N_2^+$, calculated: 524.3186 [M$^+$], observed: 524.3197 [M$^+$]; **UV/VIS** (THF, 3.90 µg/mL): λ[nm] (logε) = 271 (4.59), 313 (4.47), 340 (4.67), 354 (4.75), 382 (4.19), 399 (4.19); **Fluorescence** (DCM): $\lambda_{\text{Anr}}$ = 375 nm, $\lambda_{\text{max}}$ = 450 nm, 425 nm, 400 nm; **Quantum yield**: Φ = 57.8%.

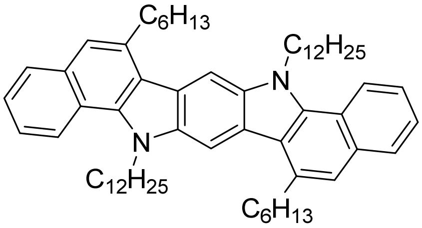
### **8,16-Didodecyl-6,14-diphenyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 4a**



According to GP7A, 25 mol% benzyltriethylammonium chloride (1.12 mg, 4.92 µmol) were added to a solution of 1.00 eq of the corresponding BBICZ (10.0 mg, 19.7 µmol) in 8 mL THF. 20.0 eq 1-bromododecane (94.2 µL, 98.0 mg, 393 µmol) and later 0.5 mL of a 50% aqueous NaOH solution were added. The mixture was first stirred for 2 h at room temperature, then heated up to 60 °C for 3 h and treated according to GP7A. A yellow solid was obtained (15.2 mg, 17.8 µmol, 92%).

**Mp.:** 112-114 °C; **R$_f$**: 0.86 (silica gel, DCM:PE = 2:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3055, 2953, 2919, 2850, 1559, 1525, 1492, 1463, 1430, 1401, 1372, 1350, 1315, 1248, 1229, 1213, 1141, 1029, 936, 908, 862, 843, 834, 782, 766, 736, 719, 702, 681, 618; **$^1$H NMR** (CD$_2$Cl$_2$, 600.2 MHz): δ[ppm] = 0.87-0.89 (m, 6H), 1.29-1.47 (m, 36H), 1.96-1.98 (m, 4H), 4.50 (t, $^3J_{H\text{-}H}$ = 8.1 Hz, 4H), 7.23 (s, 2H), 7.49 (s, 2H), 7.54-7.56 (m, 2H), 7.60-7.66 (m, 8H), 7.71-7.72 (m, 4H), 8.04 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H), 8.51 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H); **$^{13}$C NMR** (CD$_2$Cl$_2$, 150.9 MHz): δ[ppm] = 14.3 (q, 2C), 23.1 (t, 2C), 27.5 (t, 2C), 29.8 (t, 2C), 30.0 (t, 2C), 30.1 (t, 4C), 30.1 (t, 2C), 30.2 (t, 2C), 30.3 (t, 2C), 32.3 (t, 2C), 46.9 (t, 2C), 100.8 (d, 2C), 117.3 (s, 2C), 120.4 (d, 2C), 121.5 (s, 2C), 121.9 (s, 2C), 122.5 (d, 2C), 125.3 (d, 2C), 125.4 (d, 2C), 128.1 (d, 2C), 128.8 (d, 4C), 129.7 (d, 2C), 130.0 (d, 4C), 133.6 (s, 2C), 136.7 (s, 2C), 136.9 (s, 2C), 137.1 (s, 2C), 142.1 (s, 2C); **HRMS** (ESI+): C$_{62}$H$_{72}$N$_2$, calculated: 844.5690 [M$^+$], observed: 844.5692 [M$^+$]; **UV/VIS** (DCM, 3.30 µg/mL): λ[nm] (logε) = 237 (4.69), 279 (4.64), 321 (4.52), 342 (4.79), 358 (4.77), 403 (4.09), 425 (4.16); **Fluorescence** (DCM): λ$_{Anr}$ = 405 nm, λ$_{max}$ = 434, 462 nm; **Quantum yield:** Φ = 36.4%.

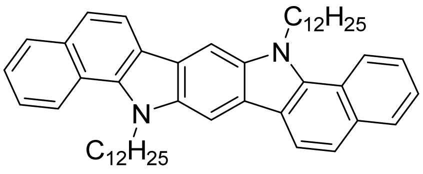
### 8,16-Didodecyl-6,14-dihexyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 4b



According to GP7A, 25 mol% benzyltriethylammonium chloride (1.60 mg, 7.00 µmol) were added to a solution of 1.00 eq of the corresponding BBICZ (14.7 mg, 28.0 µmol) in 4 mL THF. 20.0 eq 1-bromododecane (140 mg, 134 µL, 560 µmol) and later 0.5 mL of a 50% aqueous NaOH solution were added. The mixture was first stirred for 3 h at room temperature, then heated up to 60 °C and treated according to GP7A. A yellow solid was obtained (16.5 mg, 19.2 µmol, 68%).

**Mp.:** decomposition >177 °C; **R$_f$**: 0.64 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 2954, 2921, 2852, 1727, 1648, 1561, 1527, 1467, 1433, 1410, 1355, 1244, 1158, 1063, 870, 840, 826, 782, 740, 664; **$^1$H NMR** (CD$_2$Cl$_2$, 300.5 MHz): δ[ppm] = 0.85-0.88 (m, 6H), 0.95 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 6H), 1.26-1.38 (m, 28H), 1.43-1.49 (m, 8H), 1.62-1.77 (m, 8H), 2.00-2.11 (m, 4H), 2.17-2.27 (m, 4H), 3.51 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H), 4.94 (t, $^3J_{H\text{-}H}$ = 7.9 Hz, 4H), 7.47 (s, 2H), 7.51-7.62 (m, 4H), 7.99-8.02 (2, 2H), 8.33 (s, 2H), 8.57 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 2H); **$^{13}$C NMR** (CD$_2$Cl$_2$, 150.9 MHz): δ[ppm] = 14.3 (q, 2C), 14.4 (q, 2C), 23.1 (t, 2C), 23.2 (t, 2C), 27.8 (t, 2C), 29.7 (t, 2C), 30.0 (t, 2C), 30.0 (t, 4C), 30.1 (t, 2C), 30.1 (t, 2C), 30.3 (t, 2C), 30.4 (t, 4C), 32.3 (t, 2C), 32.4 (t, 2C), 35.7 (t, 2C), 47.0 (t, 2C), 101.0 (d, 2C), 117.9 (s, 2C), 119.6 (d, 2C), 121.1 (s, 2C), 121.8 (s, 2C), 122.5 (d, 2C), 124.7 (s, 2C), 125.1 (d, 2C), 129.0 (d, 2C), 134.0 (s, 2C), 137.0 (s, 2C), 137.2 (s, 2C), 137.6 (s, 2C); **HRMS** (DART+): C$_{62}$H$_{89}$N$_2$$^+$, calculated: 861.7020 [M$^+$+H], observed: 861.7021 [M$^+$+H]; **UV/VIS** (DCM, 13.2 µg/mL): λ[nm] (logε) = 270 (4.56), 278 (4.54), 335 (4.82), 356 (4.65), 399 (4.04), 412 (3.99), 423 (3.95); **Fluorescence** (DCM): λ$_{Anr}$ = 415 nm, λ$_{max}$ = 490 nm, 458 nm, 430 nm; **Quantum yield:** Φ = 23.5%.

### 8,16-Didodecyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 4c

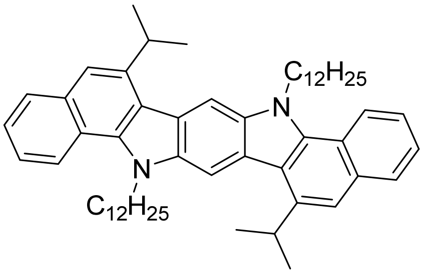


According to GP7A, 25 mol% benzyltriethylammonium chloride (3.32 mg, 14.6 µmol) were added to a solution of 1.00 eq of the corresponding BBICZ (20.8 mg, 58.4 µmol) in 3 mL DMSO. 8.00 eq 1-bromododecane (116 mg, 112 µL, 467 µmol) and later 0.5 mL of a 50% aqueous NaOH solution were added. The mixture was first stirred for 3 h at room temperature, then heated up to 60 °C and treated according to GP7A. A yellow solid was obtained (31.0 mg, 44.7 µmol, 77%).

**IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3045, 2922, 2852, 2359, 1560, 1503, 1464, 1451, 1435, 1416, 1376, 1293, 1256, 1199, 1143, 1114, 1061, 946, 853, 826, 796, 741, 664, 623, 612; **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.85-0.89 (m, 6H), 1.26-1.32 (m, 28H), 1.44-1.48 (m, 4H), 1.60-1.70 (m, 4H), 2.13-2.23 (m, 4H), 4.93 (t, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.52-7.57 (m, 2H), 7.61-7.65 (m, 2H), 7.70 (d, $^3J_{H-H}$ = 8.6 Hz, 2H), 8.07 (d, $^3J_{H-H}$ = 8.1 Hz, 2H), 8.22 (s, 2H), 8.35 (d, $^3J_{H-H}$ = 8.6 Hz, 2H), 8.57 (d, $^3J_{H-H}$ = 8.6 Hz, 2H); **UV/VIS** (DCM, 4.40 µg/mL): λ[nm] (logε) = 279 (4.67), 313 (4.56), 339 (4.85), 357 (4.86), 398 (4.14), 420 (4.18); **Fluorescence** (DCM): $\lambda_{Anr}$ = 420 nm, $\lambda_{max}$ = 454 nm; **Quantum yield:** Φ = 36.3%.

Analytics confirm to previously reported data.[2]

### 8,16-Didodecyl-6,14-diisopropyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 4d



According to GP7B, 4.00 eq KO$^t$Bu (130.5 mg, 1.16 mmol) were added to a solution of 1.00 eq of the corresponding BBICZ (128 mg, 291 µmol) in 10 mL anhydrous DMSO. After stirring for 30 min at room temperature, 40.0 eq of 1-bromododecane (2.90 mg, 2.78 mL, 11.6 mmol) were added. The solution was stirred for 2 h at room temperature and treated according to GP7B. A yellow solid was obtained (198 mg, 255 µmol, 88%).

**Mp.:** 123 °C; **$R_f$**: 0.57 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3049, 2955, 2921, 2852, 1523, 1466, 1435, 1408, 1379, 1364, 1291, 1264, 1248, 1156, 1076, 899, 860, 817, 779, 734, 640, 624; **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.85-0.89 (m, 6H), 1.26-1.34 (m, 28H), 1.47-1.54 (m, 4H), 1.64-1.75 (m, 16H), 2.20-2.30 (m, 4H), 4.27 (quint, $^3J_{H-H}$ = 6.8 Hz, 2H), 4.95 (t, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.51-7.60 (m, 6H), 8.03-8.06 (m, 2H), 8.42 (s, 2H), 8.56 (d, $^3J_{H-H}$ = 8.4 Hz, 2H); **$^{13}$C NMR** ($CDCl_3$, 75.6 MHz): δ[ppm] = 14.3 (q, 2C), 22.8 (t, 2C), 23.0 (q, 2C), 27.6 (t, 2C), 29.5 (t, 2C), 29.7 (t, 2C), 29.8 (t, 4C), 29.8 (t, 2C), 29.8 (t, 2C), 29.8 (t, 2C), 29.8 (t, 2C), 30.2 (t, 2C), 30.7 (d, 2C), 32.1 (t, 2C), 46.7 (t, 2C), 101.3 (d, 2C), 115.0 (d, 2C), 117.5 (s, 2C), 120.8 (s, 2C), 121.2 (s, 2C), 122.2 (d, 2C), 124.5 (d, 2C), 124.8 (d, 2C), 129.3 (d, 2C), 133.8 (s, 2C), 136.8 (s, 2C), 137.5 (s, 2C), 142.9 (s, 2C); **HRMS** (ESI+): $C_{56}H_{76}N_2$, calculated: 799.5901 [M$^+$+Na], observed: 799.5914 [M$^+$+Na]; **UV/VIS** (DCM, 5.00 µg/mL): λ[nm] (logε) = 277

(4.71), 312 (4.67), 336 (4.97), 357 (4.78), 402 (4.18), 423 (4.20); **Fluorescence** (DCM): $\lambda_{Anr}$ = 425 nm, $\lambda_{max}$ = 459 nm; **Quantum yield:** $\Phi$ = 29.7%.

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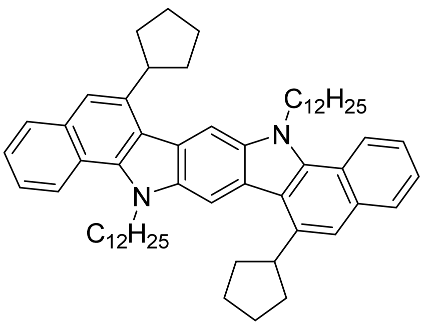
### 6,14-Dicyclopentyl-8,16-didodecyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 4e



According to GP7A, 25 mol% benzyltriethylammonium chloride (4.10 mg, 18.0 µmol) were added to a solution of 1.00 eq of the corresponding BBICZ (35.5 mg, 72.1 µmol) in 8 mL THF. 20.0 eq 1-bromododecane (359 mg, 345 µL, 1.44 mmol) and later 1 mL of a 50% aqueous NaOH solution were added. The mixture was first stirred for 3 h at room temperature, then heated up to 60 °C and treated according to GP7A. A yellow solid was obtained (34.6 mg, 41.7 µmol, 58%).

**Mp.:** 162 °C; **R*f***: 0.58 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3054, 2923, 2854, 1726, 1591, 1561, 1525, 1494, 1469, 1435, 1411, 1365, 1304, 1247, 1159, 1127, 1035, 861, 824, 780, 740, 675, 620; **$^1$H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.85-0.89 (m, 6H), 1.26-1.33 (m, 28H), 1.46-1.51 (m, 4H), 1.65-1.75 (m, 4H), 1.95-2.14 (m, 12H), 2.20-2.30 (m, 4H), 2.46-2.53 (m, 4H), 4.30-4.37 (m, 2H), 4.92 (t, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.50-7.60 (m, 6H), 8.00-8.04 (m, 2H), 8.42 (s, 2H), 8.54 (d, $^3J_{H-H}$ = 8.0 Hz, 2H); **$^{13}$C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 14.2 (q, 2C), 22.8 (t, 2C), 25.1 (t, 4C), 27.7 (t, 2C), 29.5 (t, 2C), 29.8 (t, 4C), 29.8 (t, 2C), 29.8 (t, 2C), 29.8 (t, 2C), 30.3 (t, 2C), 32.1 (t, 2C), 32.7 (t, 4C), 43.4 (q, 2C), 46.9 (t, 2C), 101.2 (d, 2C), 115.4 (d, 2C), 118.1 (s, 2C), 120.8 (s, 2C), 121.6 (s, 2C), 122.1 (d, 2C), 124.5 (d, 2C), 124.8 (d, 2C), 129.2 (d, 2C), 133.7 (s, 2C), 136.8 (s, 2C), 137.5 (s, 2C), 140.0 (s, 2C); **HRMS** (DART+): $C_{60}H_{81}N_2^+$, calculated: 829.6394 [M$^+$+H], observed: 829.6386 [M$^+$+H]; **UV/VIS** (DCM, 6.60 µg/mL): λ[nm] (logε) = 278 (4.83), 314 (4.81), 336 (5.06), 359 (4.90), 402 (4.40), 424 (4.37); **Fluorescence** (DCM): $\lambda_{Anr}$ = 400 nm, $\lambda_{max}$ = 486 nm, 459 nm, 431 nm; **Quantum yield:** $\Phi$ = 33.4%.

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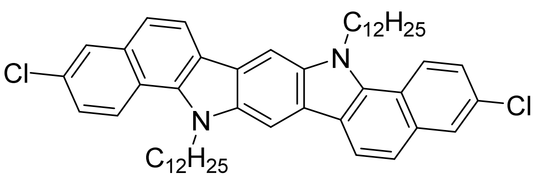
### 3,11-Dichloro-8,16-didodecyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 4f



According to GP7B, 4.00 eq KO$^t$Bu (51.9 mg, 463 µmol) were added to a solution of 1.00 eq of the corresponding BBICZ (49.2 mg, 116 mmol) in 10 mL anhydrous DMSO. After stirring for 30 min at room temperature, 20.0 eq of 1-bromododecane (577 mg, 554 µL, 2.31 mmol) were added. The solution was stirred for 3 h at room temperature and treated according to GP7B. The precipitate was recrystallized from DCM and THF. An orange solid was obtained (66.2 mg, 86.9 mmol, 75%).

**Mp.:** 182-184 °C; **R$_f$**: 0.49 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 2918, 2852, 1758, 1736, 1556, 1501, 1461, 1445, 1376, 1359, 1290, 1251, 1114, 1089, 1059, 870, 808, 789, 765, 719, 622; **$^1$H NMR** (CDCl$_3$, 600.2 MHz): δ[ppm] = 0.87 (t, $^3J_{H-H}$ = 7.0 Hz, 6H), 1.27-1.33 (m, 28H), 1.42-1.47 (m, 4H), 1.57-1.62 (m, 4H), 2.07-2.13 (m, 4H), 4.81 (t, $^3J_{H-H}$ = 7.7 Hz, 4H), 7.54 (dd, $^3J_{H-H}$ = 9.0 Hz, $^4J_{H-H}$ = 1.9 Hz, 2H), 7.59 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 8.02 (d, $^4J_{H-H}$ = 1.9 Hz, 2H), 8.13 (s, 2H), 8.34 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 8.42 (d, $^3J_{H-H}$ = 9.0 Hz, 2H); **$^{13}$C NMR** (CDCl$_3$, 150.9 MHz): δ[ppm] = 14.3 (q, 2C), 22.8 (t, 2C), 27.3 (t, 2C), 29.5 (t, 2C), 29.6 (t, 2C), 29.7 (t, 2C), 29.8 (t, 2C), 29.8 (t, 2C), 29.9 (t, 2C), 29.9 (t, 2C), 32.1 (t, 2C), 46.5 (t, 2C), 98.1 (d, 2C), 118.9 (d, 2C), 119.5 (s, 2C), 120.4 (s, 2C), 120.5 (d, 2C), 122.7 (s, 2C), 123.7 (d, 2C), 125.9 (d, 2C), 128.4 (d, 2C), 130.3 (s, 2C), 134.7 (s, 2C), 135.8 (s, 2C), 137.1 (s, 2C); **HRMS** (DART+): $C_{50}H_{65}N_2^+$, calculated: 693.5142 [M$^+$+H], observed: 693.5141 [M$^+$+H]; **UV/VIS** (DCM, 5.12 µg/mL): λ[nm] (logε) = 274 (4.65); 282 (4.65), 323 (4.65), 344 (4.90), 361 (4.94), 402 (4.24), 422 (4.24) **Fluorescence** (DCM): $\lambda_{Anr}$ = 400 nm, $\lambda_{max}$ = 489 nm, 457 nm, 429 nm; **Quantum yield:** Φ = 13.7%.

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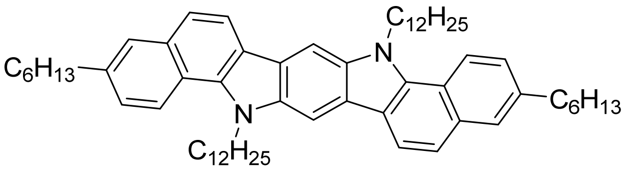
### 8,16-Didodecyl-3,11-dihexyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 4g



According to GP7B, 4.00 eq KO$^t$Bu (25.7 mg, 229 µmol) were added to a solution of 1.00 eq of the corresponding BBICZ (30.0 mg, 57.2 mmol) in 14 mL anhydrous THF. After stirring for 10 min at room temperature, 20.0 eq of 1-bromododecane (285 mg, 274 µL, 1.14 mmol) were added. The solution was stirred for 1 h at room temperature and treated according to GP7B. A beige solid was obtained (42.1 mg, 48.9 mmol, 85%).

**Mp.:** 113-114 °C; **R$_f$**: 0.73 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 2929, 2855, 1734, 1654, 1624, 1568, 1540, 1504, 1465, 1375, 1289, 1155, 1114, 954, 894, 834, 813, 796, 671; **$^1$H NMR** (CDCl$_3$, 600.2 MHz): δ[ppm] = 0.88 (t, $^3J_{H-H}$ = 7.0 Hz, 6H), 0.92 (t, $^3J_{H-H}$ = 7.0 Hz, 6H), 1.26-1.38 (m, 36H), 1.41-1.49 (m, 8H), 1.61-1.65 (m, 4H), 1.77-1.79 (m, 4H), 2.15-2.17 (m, 4H), 2.85 (t, $^3J_{H-H}$ = 7.8 Hz, 4H), 4.88 (t, $^3J_{H-H}$ = 7.9 Hz, 4H), 7.48 (dd, $^3J_{H-H}$ = 8.7 Hz, $^4J_{H-H}$ = 1.5 Hz, 2H), 7.63 (d, $^3J_{H-H}$ = 8.5 Hz, 2H), 7.84 (s, 2H), 8.16 (s, 2H), 8.31 (d, $^3J_{H-H}$ = 8.5 Hz, 2H), 8.47 (d, $^3J_{H-H}$ = 8.7 Hz, 2H); **$^{13}$C NMR** (CDCl$_3$, 150.9 MHz): δ[ppm] = 14.3 (q, 2C), 14.3 (q, 2C), 22.8 (t, 2C), 22.8 (t, 2C), 27.3 (t, 2C), 29.3 (t, 2C), 29.5 (t, 2C), 29.6 (t, 2C), 29.8 (t, 2C), 29.8 (t, 4C), 29.8 (t, 2C), 30.0 (t, 2C), 31.6 (t, 2C), 32.0 (t, 2C), 32.1 (t, 2C), 36.1 (t, 2C), 46.5 (t, 2C), 97.8 (d, 2C), 118.7 (s, 2C), 119.3 (d, 2C), 119.4 (d, 2C), 120.6 (s, 2C), 122.1 (d, 2C), 122.7 (s, 2C), 126.7 (d, 2C), 128.4 (d, 2C), 134.1 (s, 2C), 136.1 (s, 2C), 137.0 (s, 2C), 139.1 (s, 2C); **HRMS** (DART+): $C_{62}H_{88}N_2^+$, calculated: 861.7020 [M$^+$+H], observed: 861.6996 [M$^+$+H]; **UV/VIS** (DCM, 8.20 µg/mL): λ[nm] (logε) = 272 (5.09), 281 (4.82), 315 (4.87), 342 (4.69), 360 (4.47), 397 (4.17), 417 (3.57); **Fluorescence** (DCM): $\lambda_{Anr}$ = 400 nm, $\lambda_{max}$ = 480 nm, 450 nm, 425 nm; **Quantum yield:** Φ = 43.7%.

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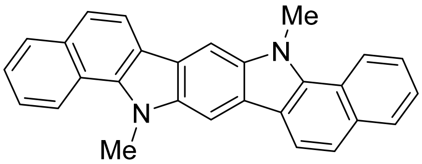
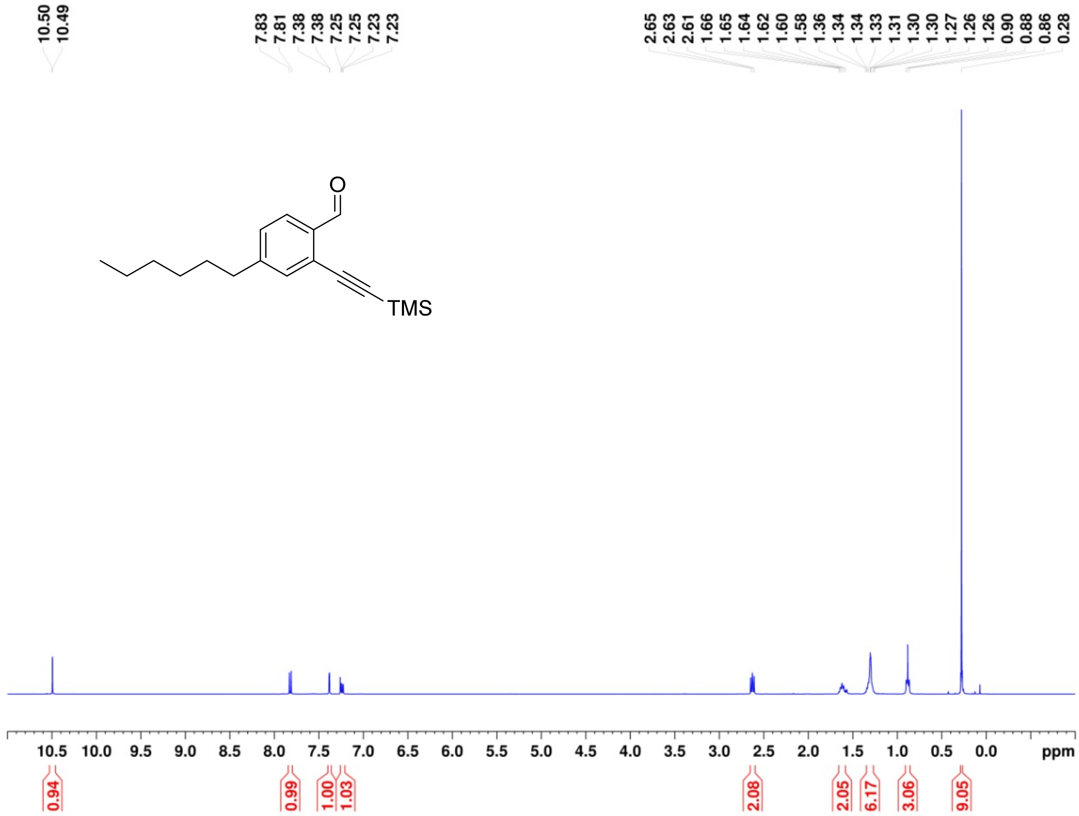
### 8,16-Dimethyl-8,16-dihydrobenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole, 4h



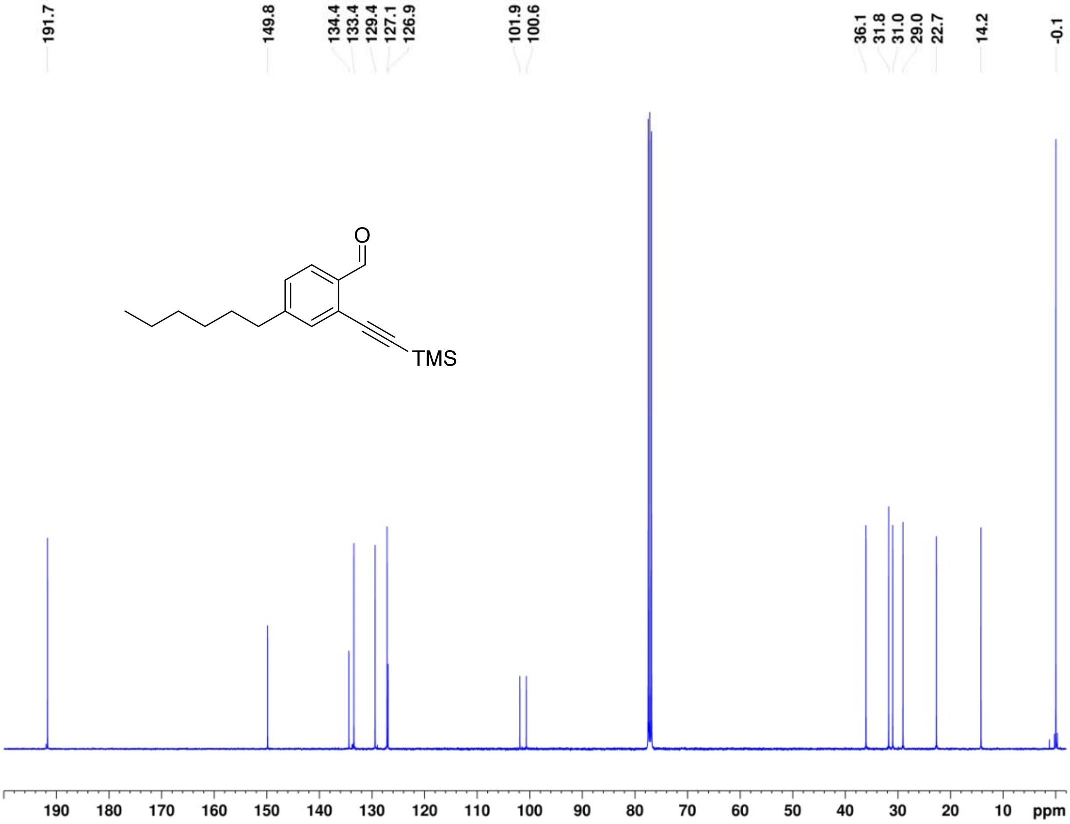
According to GP7B, 4.00 eq KO$^t$Bu (43.5 mg, 387 µmol) were added to a solution of 1.00 eq of the corresponding BBICZ (34.5 mg, 96.8 µmol) in 5 mL anhydrous THF and 1 mL anhydrous DMSO. After stirring for 30 min at room temperature, 20.0 eq of methyliodide (275 mg, 121 µL, 1.94 mmol) were added. The solution was stirred for 1 h at room temperature and treated according to GP7B. A yellow solid was obtained (22.3 mg, 58.0 µmol, 60%).

**Mp.:** >300 °C; **R$_f$**: 0.11 (silica gel, PE:EA = 20:1); **IR** (ATR): $\tilde{\nu}$ [cm$^{-1}$] = 3069, 3046, 2946, 2913, 1928, 1718, 1620, 1594, 1559, 1535, 1504, 1468, 1450, 1423, 1405, 1371, 1296, 1270, 1255, 1231, 1203, 1163, 1133, 1106, 1058, 1020, 875, 847, 820, 791, 770, 735, 666; **$^1$H NMR** (CDCl$_3$, 300.5 MHz): δ[ppm] = 4.57 (s, 6H), 7.52-7.64 (m, 4H), 7.70 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 8.05-8.08 (m, 2H), 8.22 (s, 2H), 8.33 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 8.79 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H); **$^{13}$C NMR** (CDCl$_3$, 100.7 MHz, 323 K): δ[ppm] = 34.7 (q, 2C), 98.2 (d, 2C), 119.2 (d, 2C), 119.3 (s, 2C), 120.0 (d, 2C), 122.4 (d, 2C), 123.0 (s, 2C), 123.0 (s, 2C), 124.7 (d, 2C), 125.2 (d, 2C), 129.6 (d, 2C), 134.1 (s, 2C), 137.3 (s, 2C), 137.9 (s, 2C); **HRMS** (DART+): $C_{28}H_{21}N_2^+$, calculated: 385.1699 [M$^+$+H], observed: 385.1698 [M$^+$+H]; **UV/VIS** (DCM, 3.60 µg/mL): λ[nm] (logε) = 275 (4.48), 311 (4.39), 338 (4.66), 357 (4.65), 397 (3.98), 418 (4.03); **Fluorescence** (DCM): $\lambda_{Anr}$ = 400 nm, $\lambda_{max}$ = 478 nm, 452 nm, 425 nm; **Quantum yield:** Φ = 40.7%.

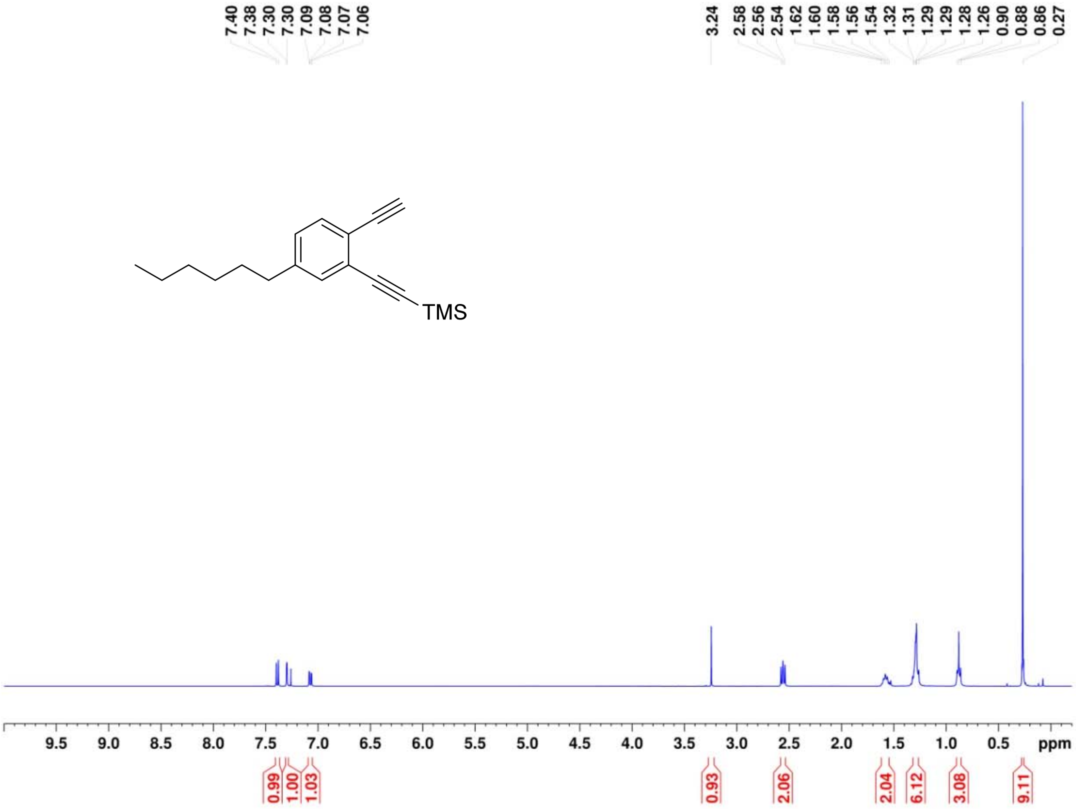
# 4. NMR Spectra



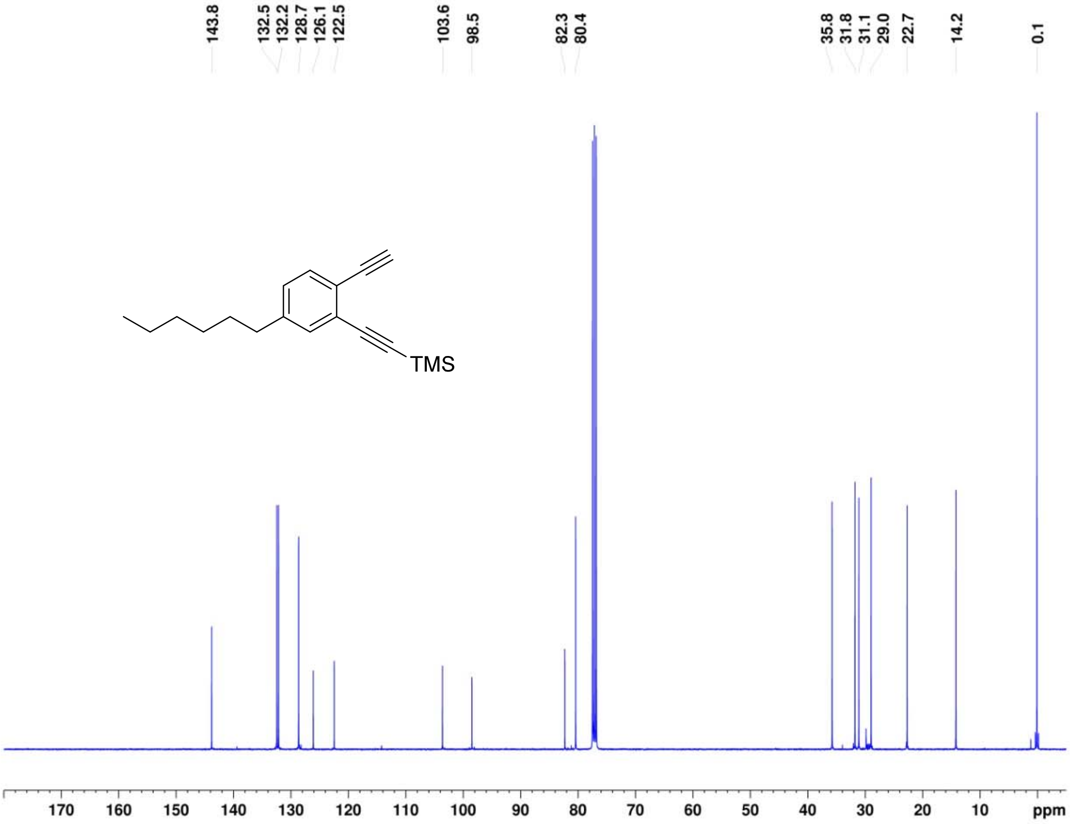
$^{1}$H NMR spectrum of 4-hexyl-2-((trimethylsilyl)ethynyl)benzaldehyde in $CDCl_3$ at 400.3 MHz



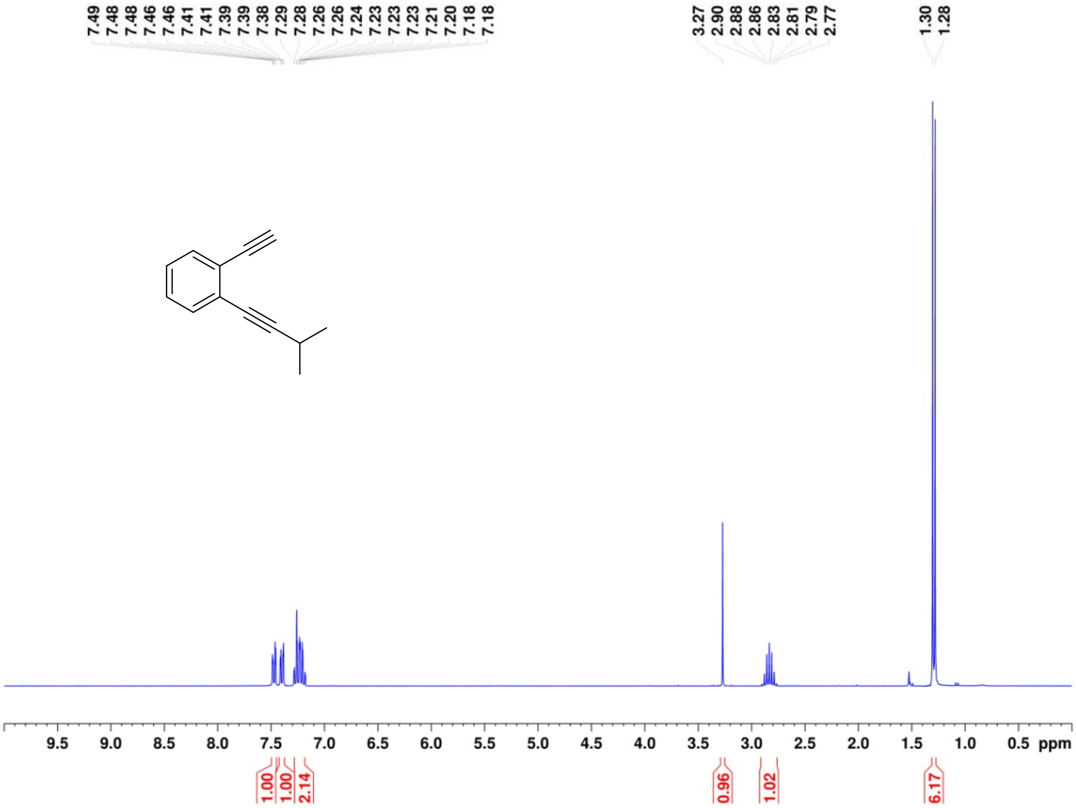
$^{13}$C NMR spectrum of 4-hexyl-2-((trimethylsilyl)ethynyl)benzaldehyde in $CDCl_3$ at 100.7 MHz



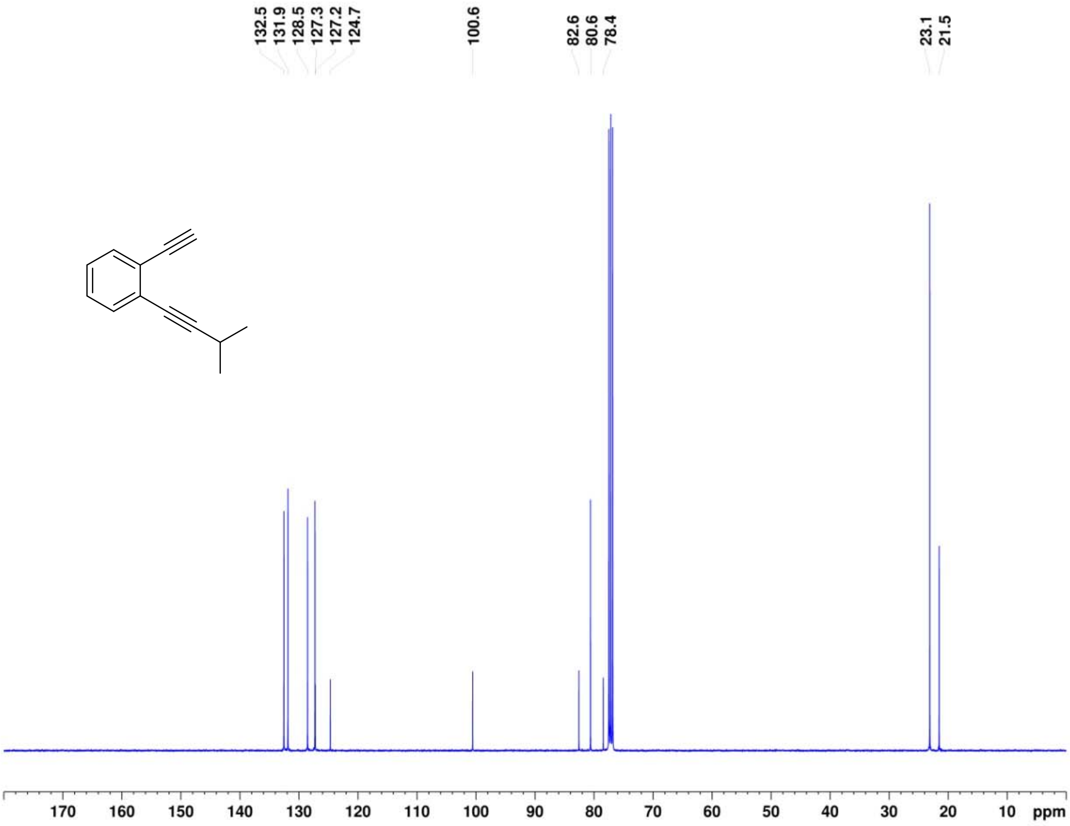
$^1$H NMR spectrum of ((2-ethynyl-5-hexylphenyl)ethynyl)trimethylsilane in CDCl$_3$ at 400.3 MHz



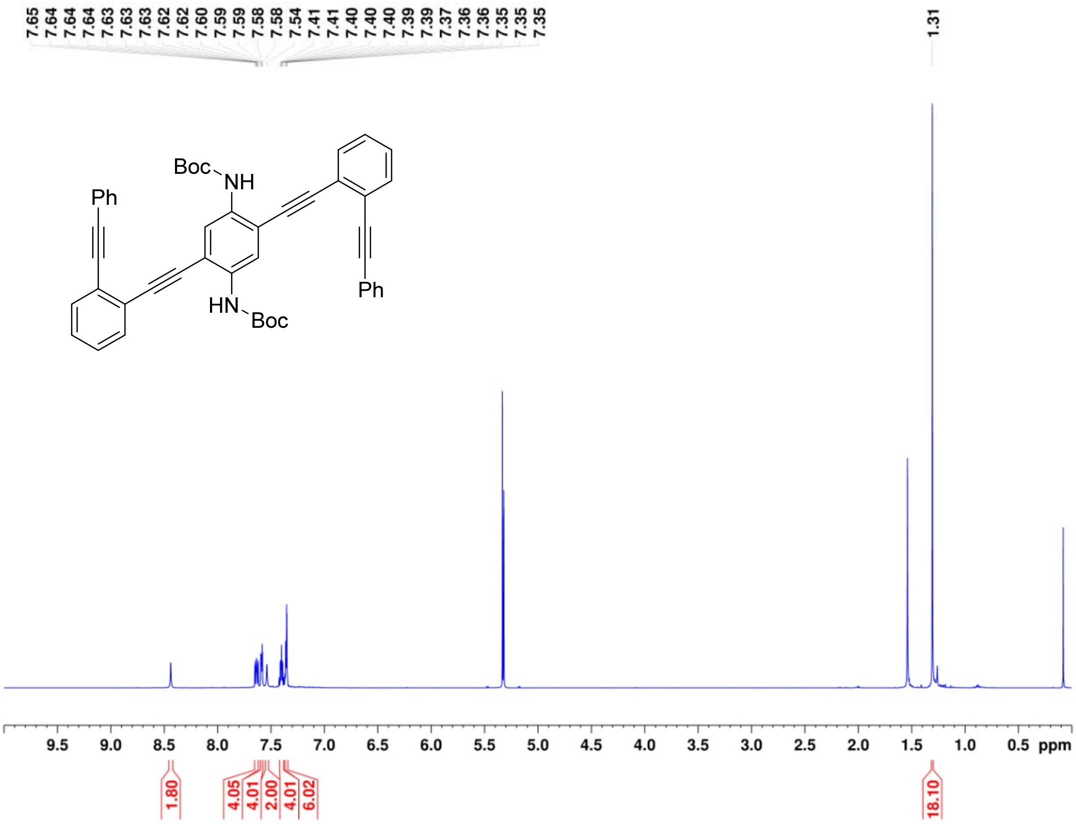
$^{13}$C NMR spectrum of ((2-ethynyl-5-hexylphenyl)ethynyl)trimethylsilane in CDCl$_3$ at 100.7 MHz



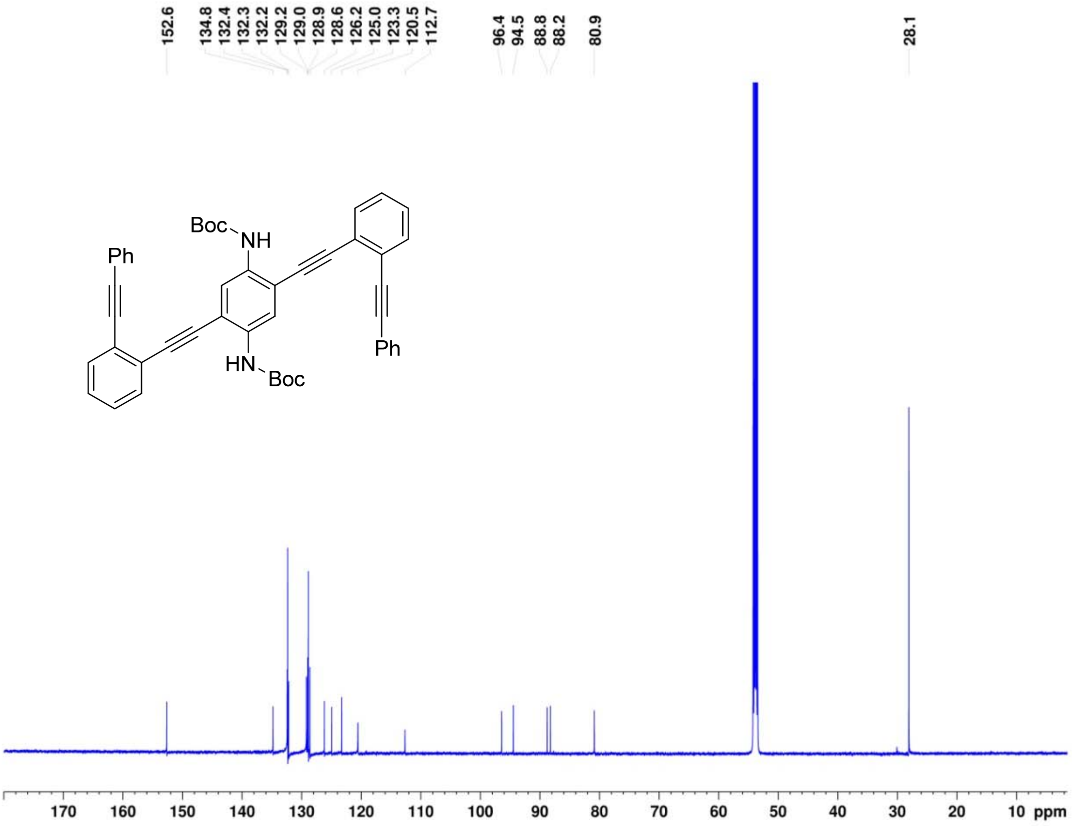
$^1$H NMR spectrum of 1-ethynyl-2-(3-methylbut-1-yn-1-yl)benzene in CDCl$_3$ at 300.5 MHz



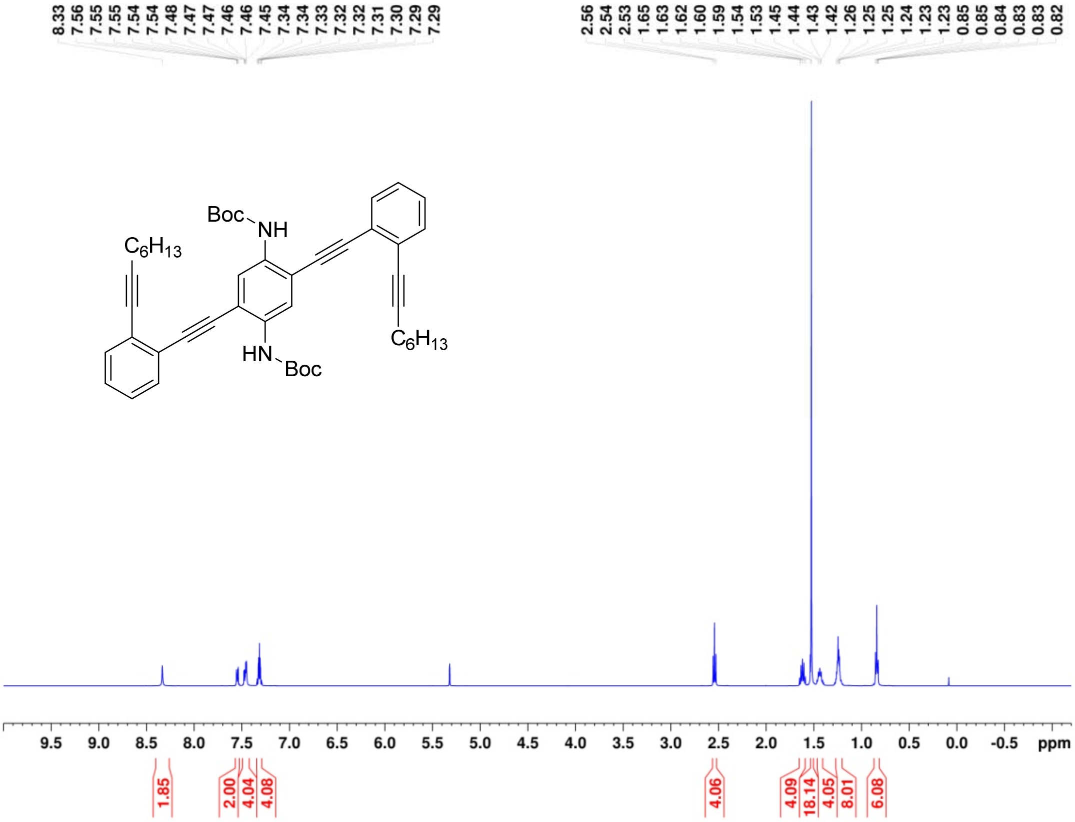
$^{13}$C NMR spectrum of 1-ethynyl-2-(3-methylbut-1-yn-1-yl)benzene in CDCl$_3$ at 100.7 MHz



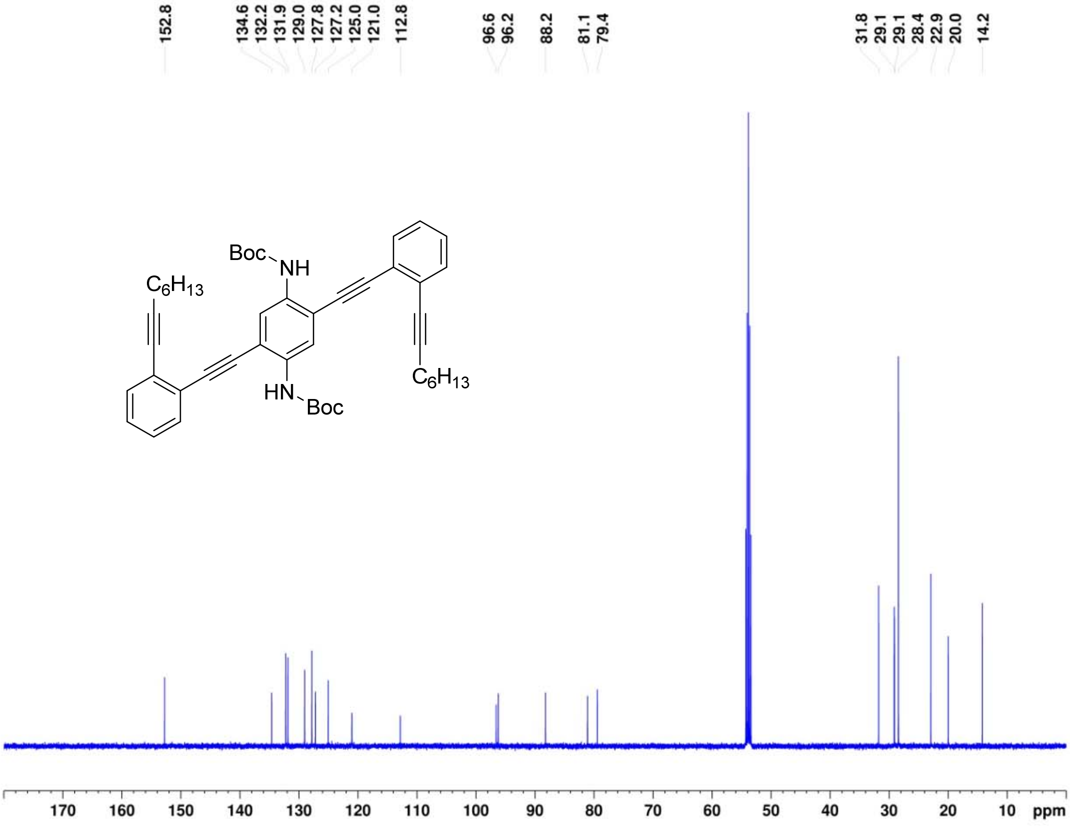
$^1$H NMR spectrum of **1a** in $CD_2Cl_2$ at 600.2 MHz



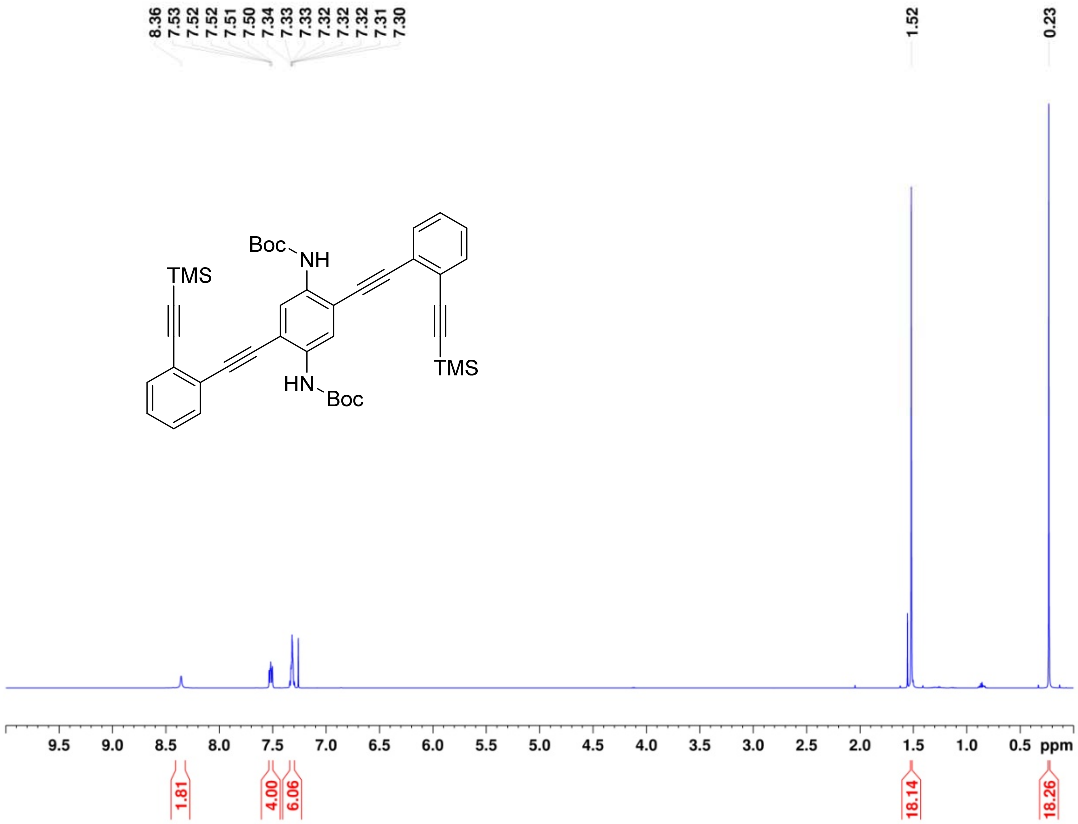
$^{13}$C NMR spectrum of **1a** in $CD_2Cl_2$ at 150.9 MHz



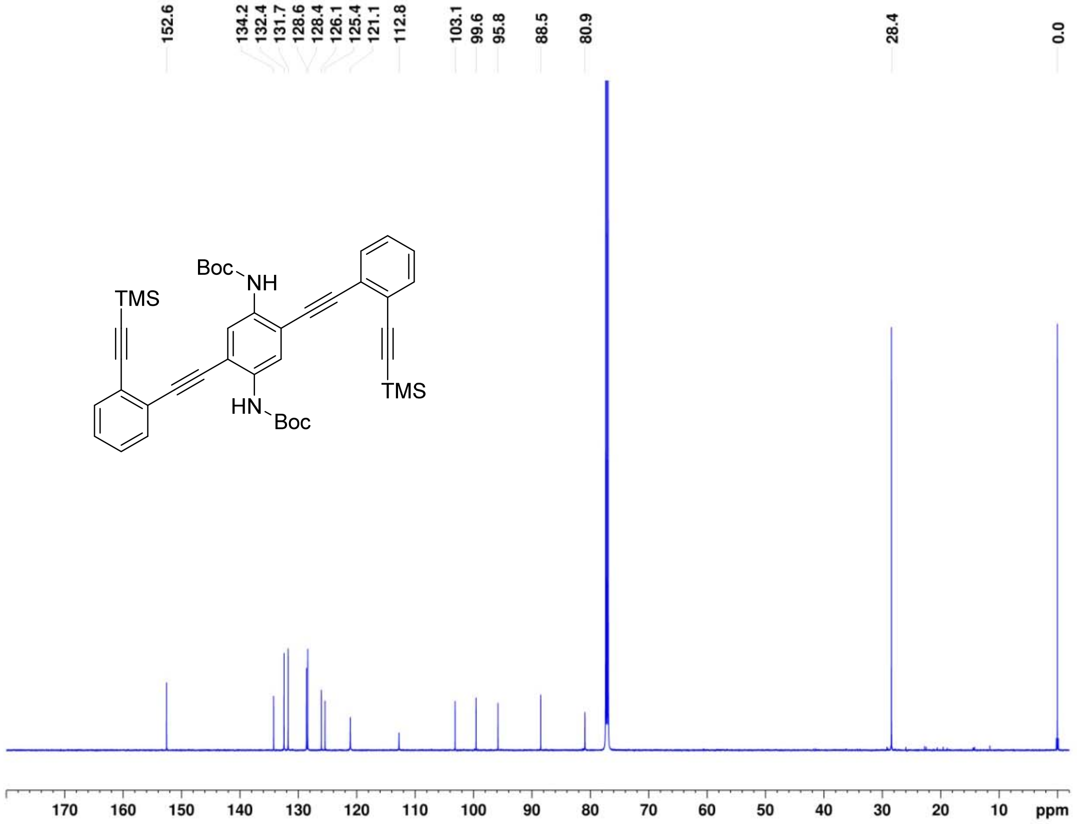
$^1$H NMR spectrum of **1b** in $CD_2Cl_2$ at 400.3 MHz



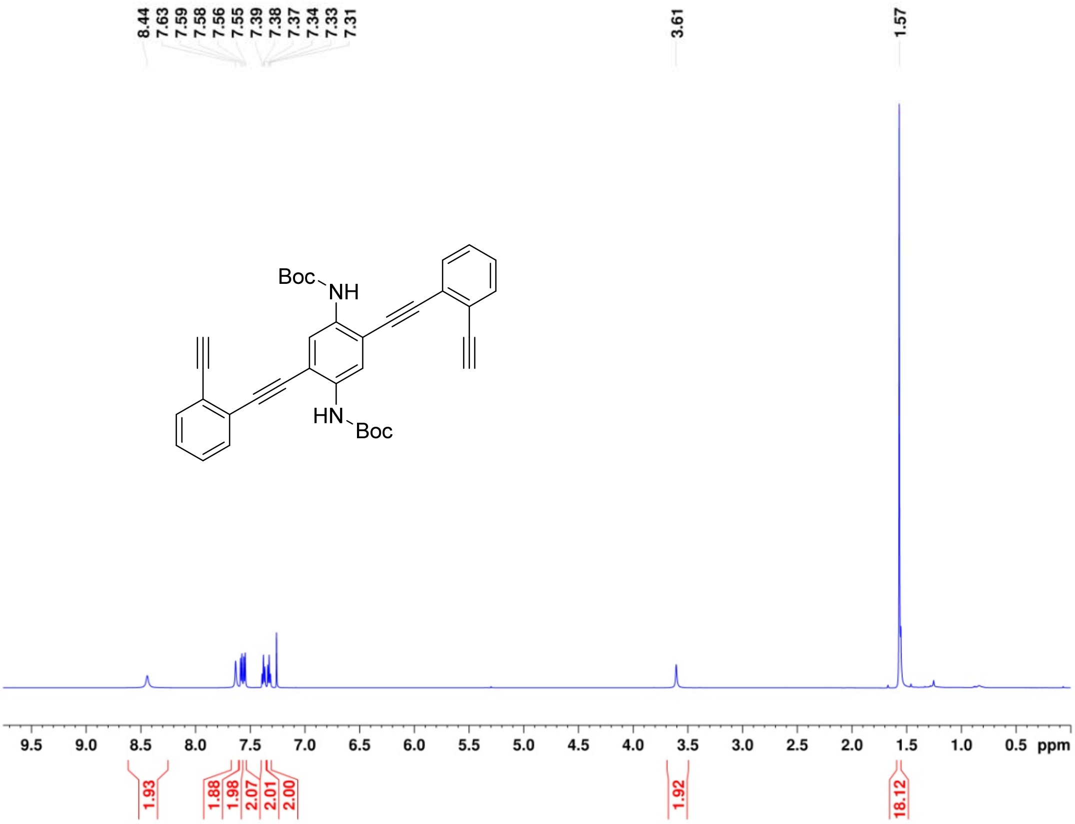
$^{13}$C NMR spectrum of **1b** in $CD_2Cl_2$ at 400.3 MHz in $CD_2Cl_2$ at 100.7 MHz



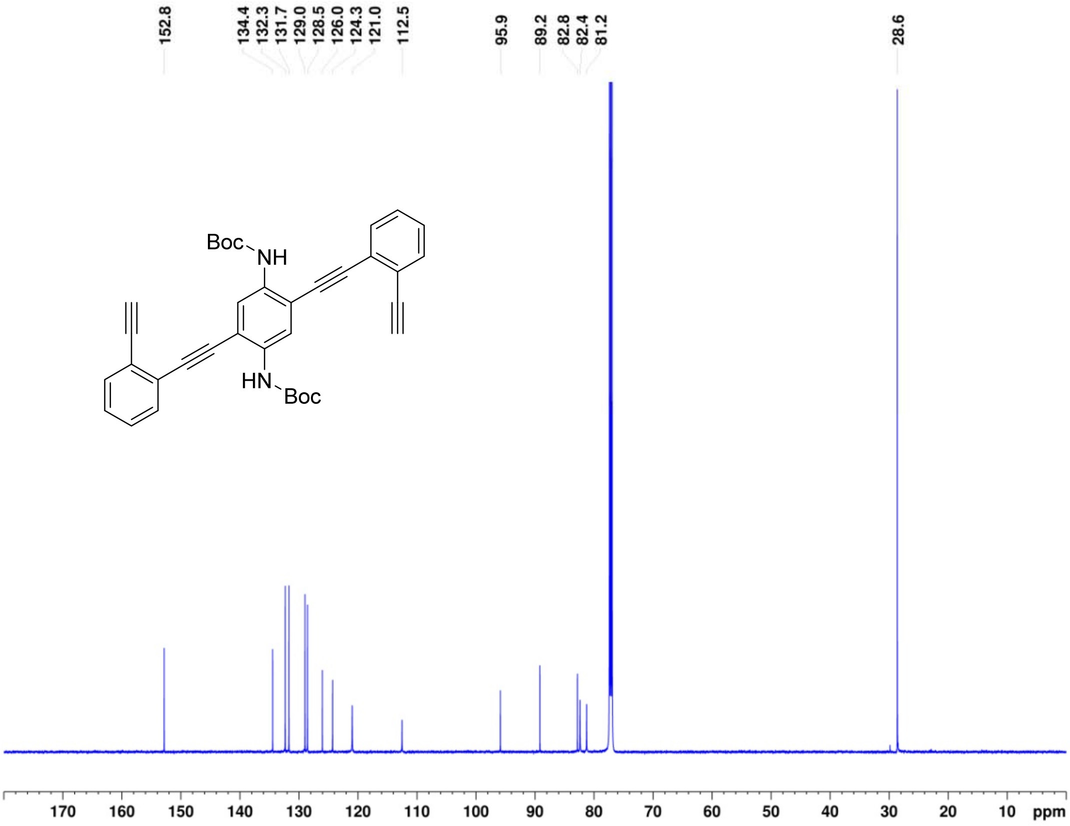
$^{1}$H NMR spectrum of **TMS-1c** in $CDCl_3$ at 600.2 MHz



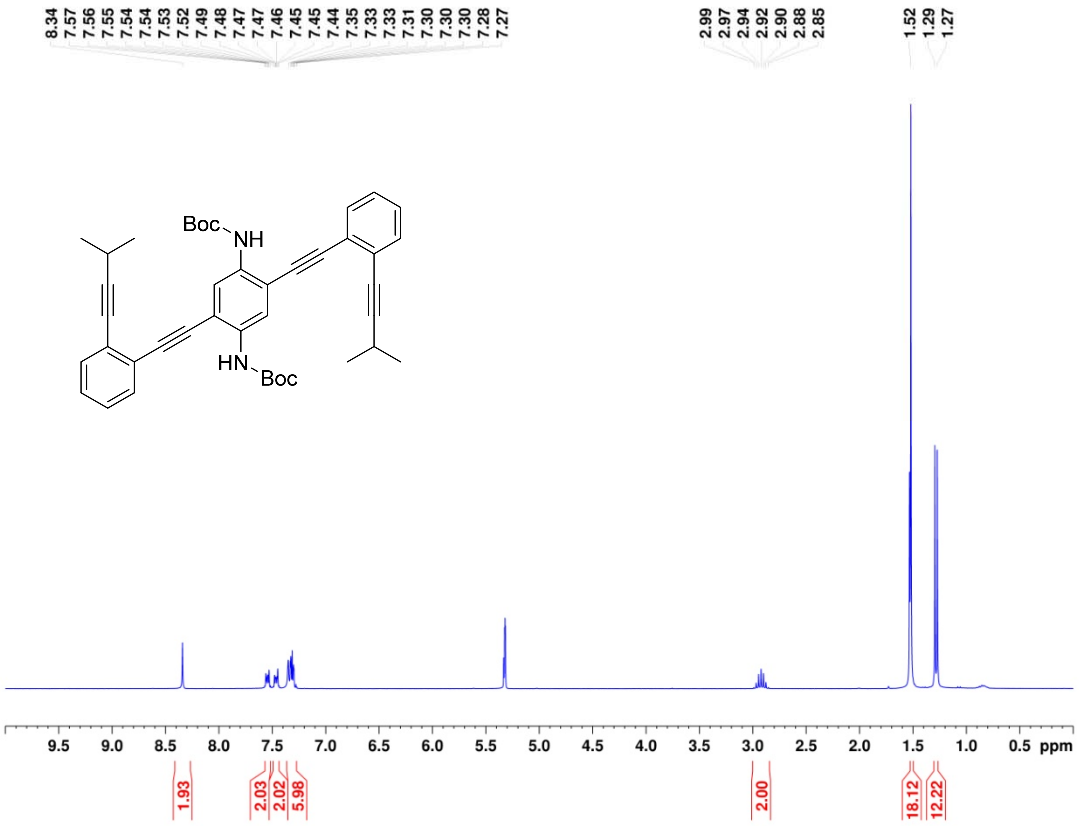
$^{13}$C NMR spectrum of **TMS-1c** in $CDCl_3$ at 150.9 MHz



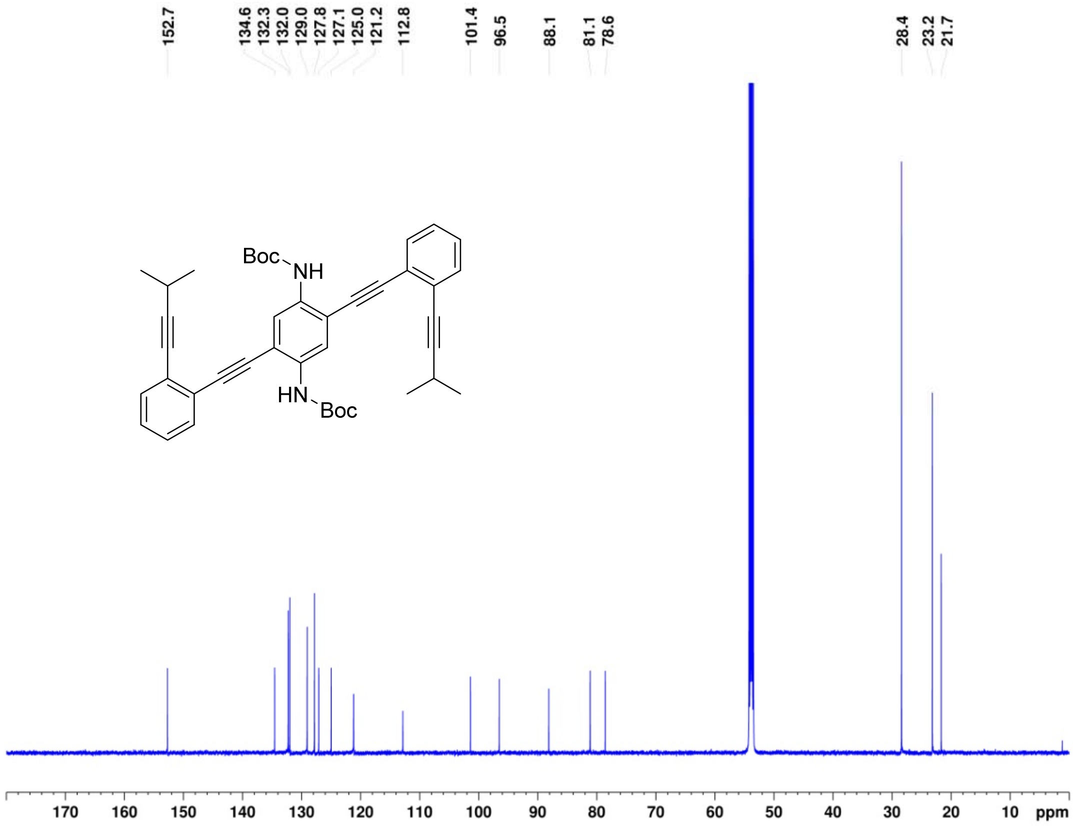
$^1$H NMR spectrum of **1c** in CDCl$_3$ in CDCl$_3$ at 600.2 MHz



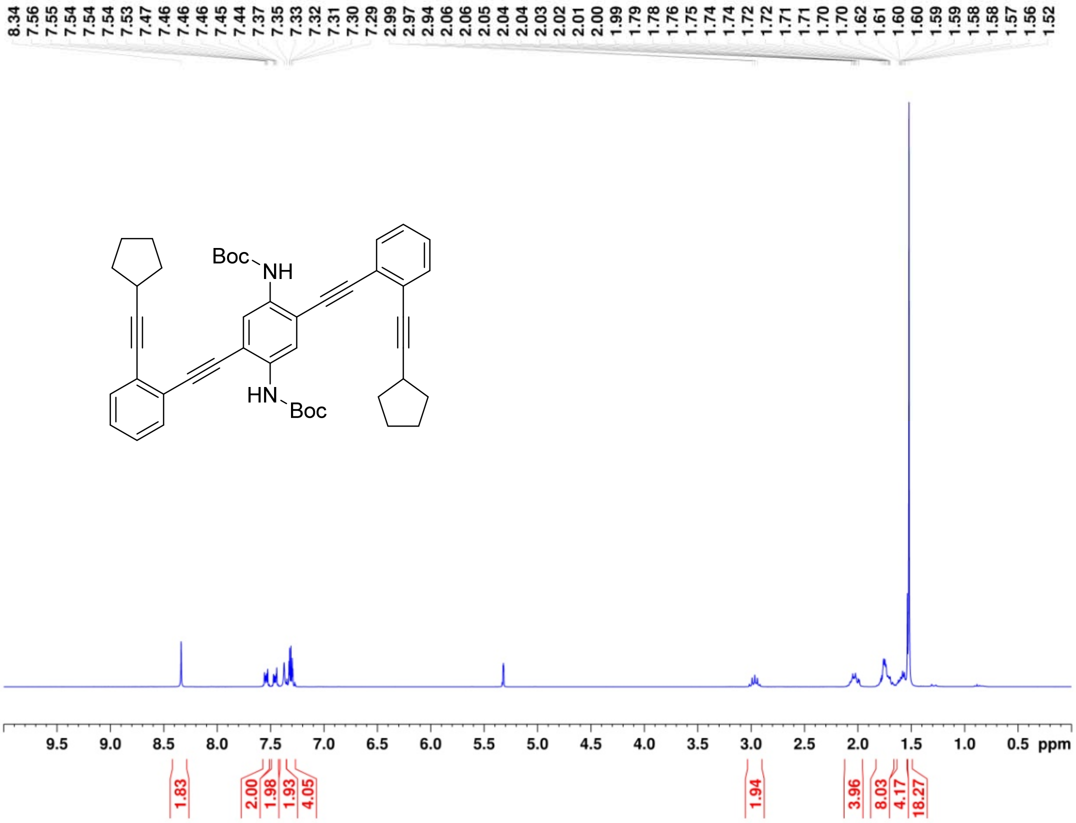
$^{13}$C NMR spectrum of **1c** in CDCl$_3$ at 150.9 MHz



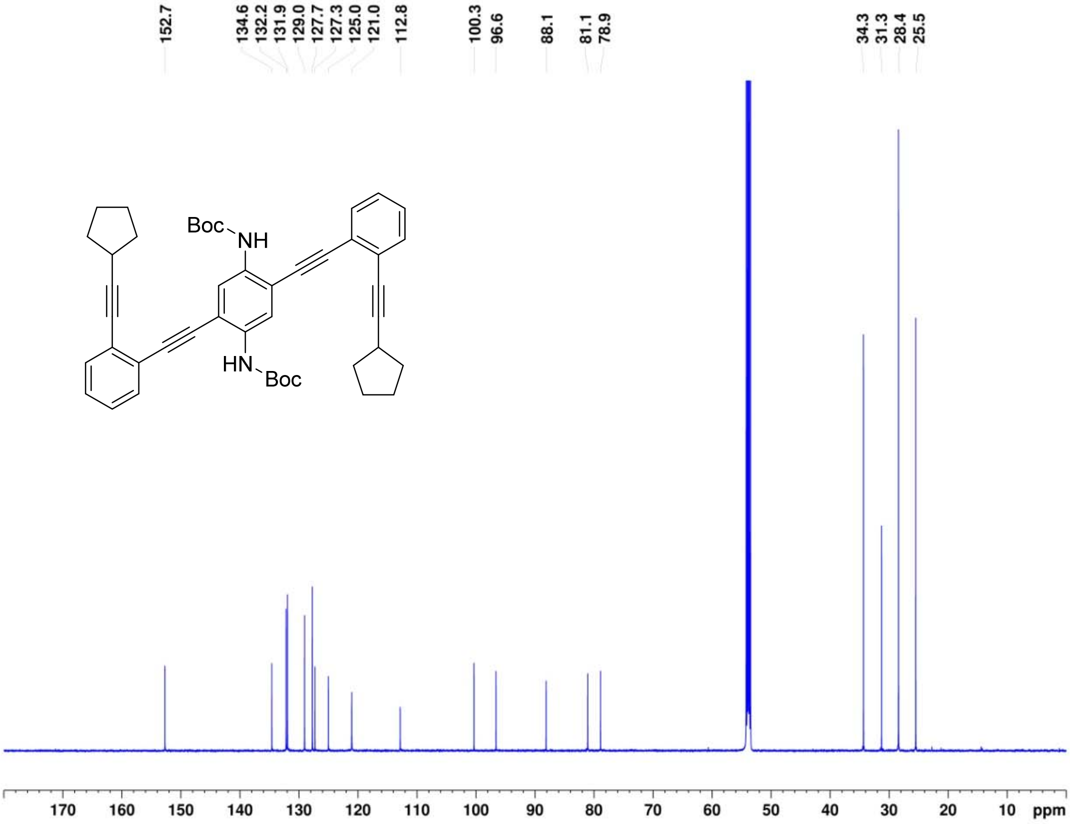
$^1$H NMR spectrum of **1d** in $CD_2Cl_2$ at 300.5 MHz



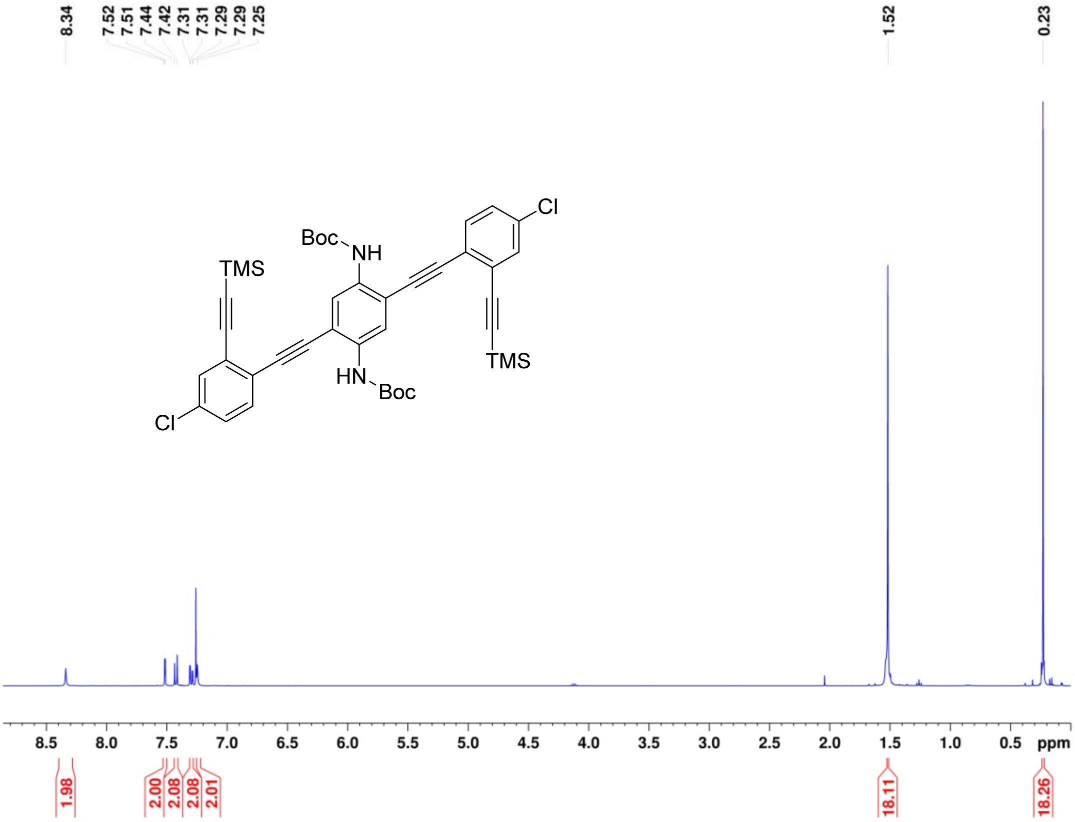
$^{13}$C NMR spectrum of **1d** in $CD_2Cl_2$ at 150.9 MHz



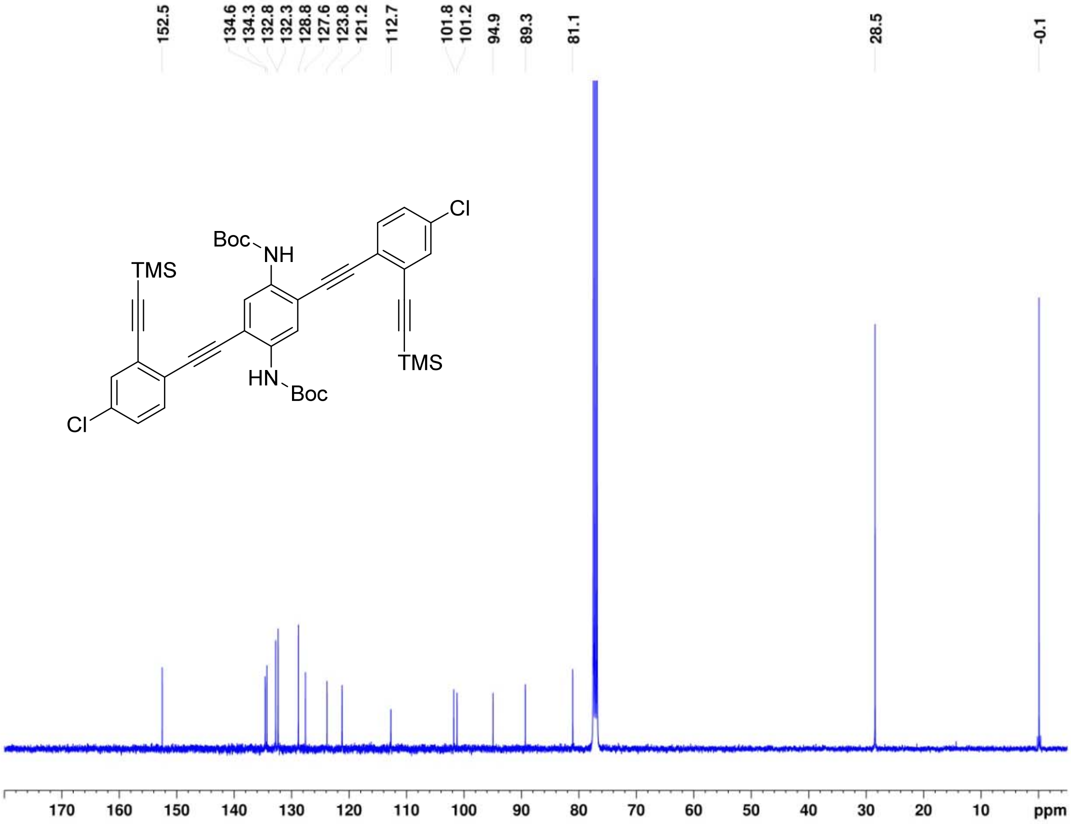
$^{1}$H NMR spectrum of **1e** in $CD_2Cl_2$ at 300.5 MHz



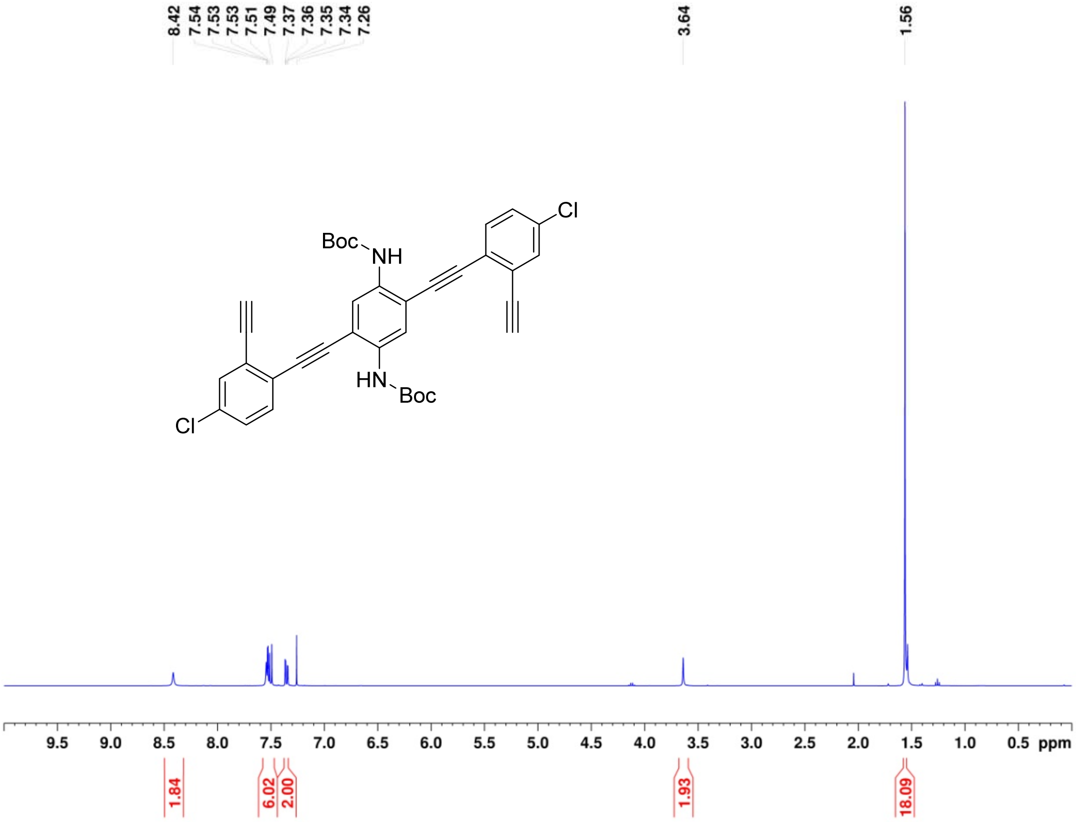
$^{13}$C NMR spectrum of **1e** in $CD_2Cl_2$ at 150.9 MHz



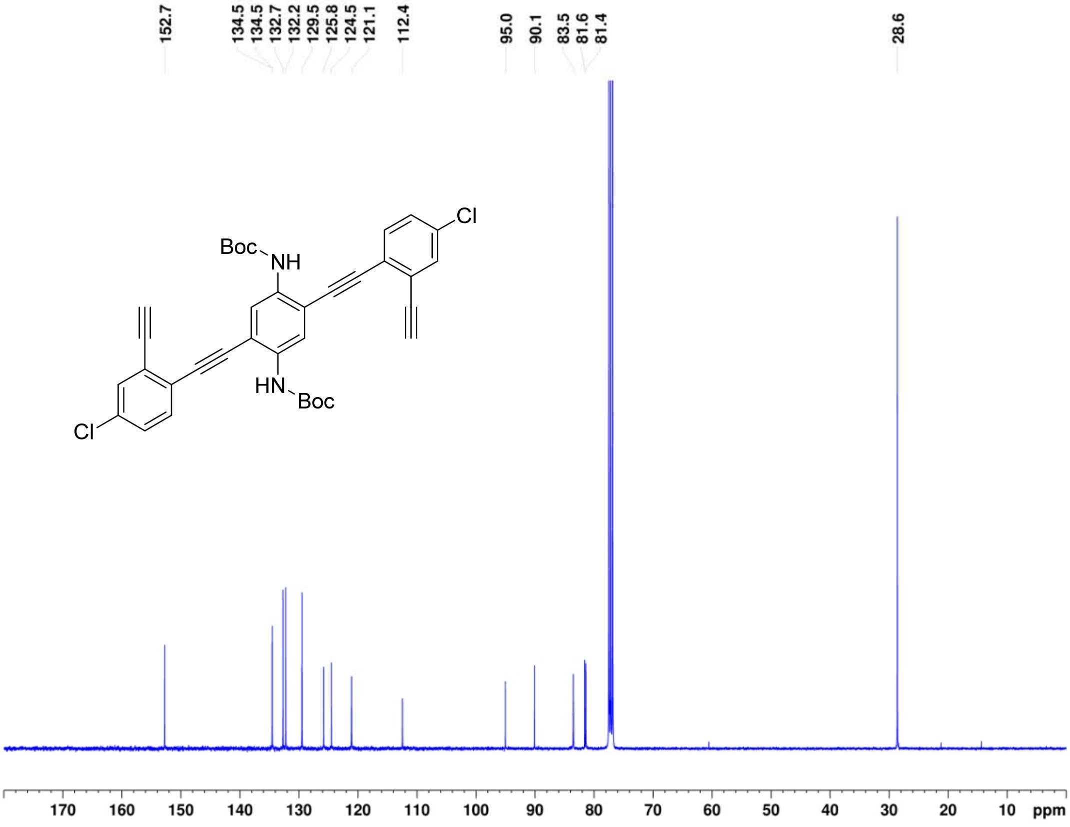
$^{1}$H NMR spectrum of **TMS-1f** in $CDCl_3$ at 400.3 MHz



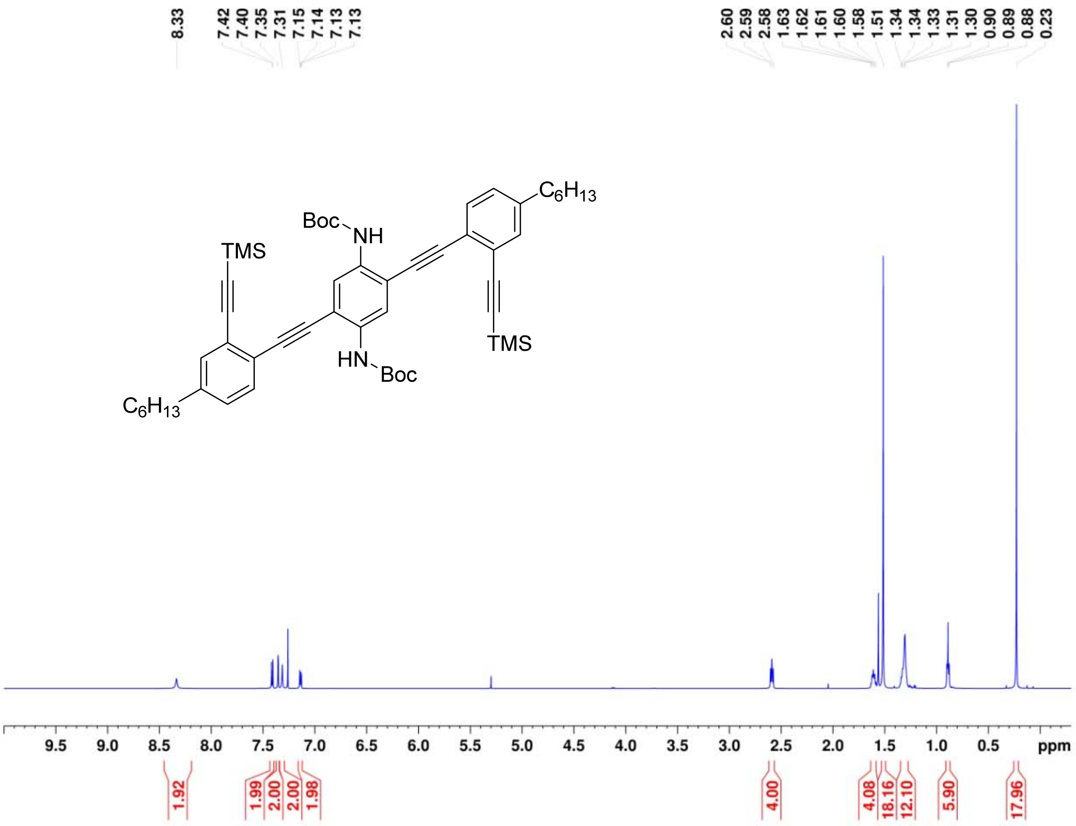
$^{13}$C NMR spectrum of **TMS-1f** in $CDCl_3$ at 100.7 MHz



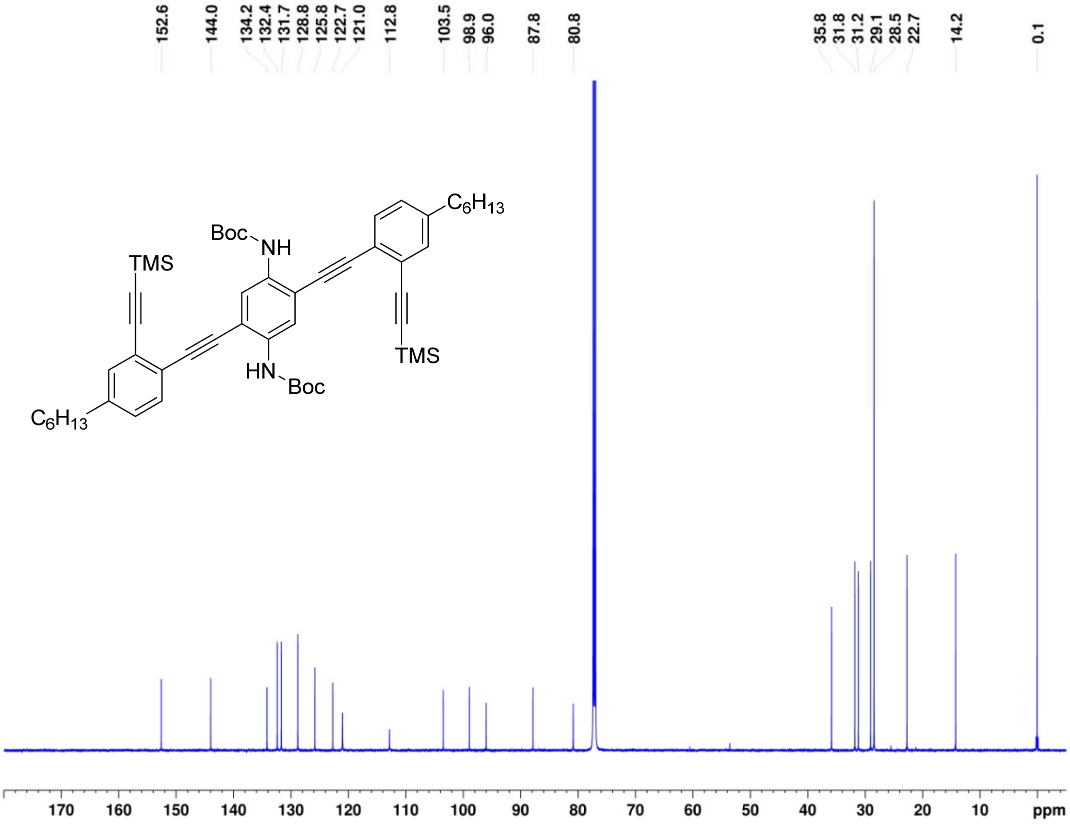
$^{1}$H NMR spectrum of **1f** in $CDCl_3$ at 400.3 MHz



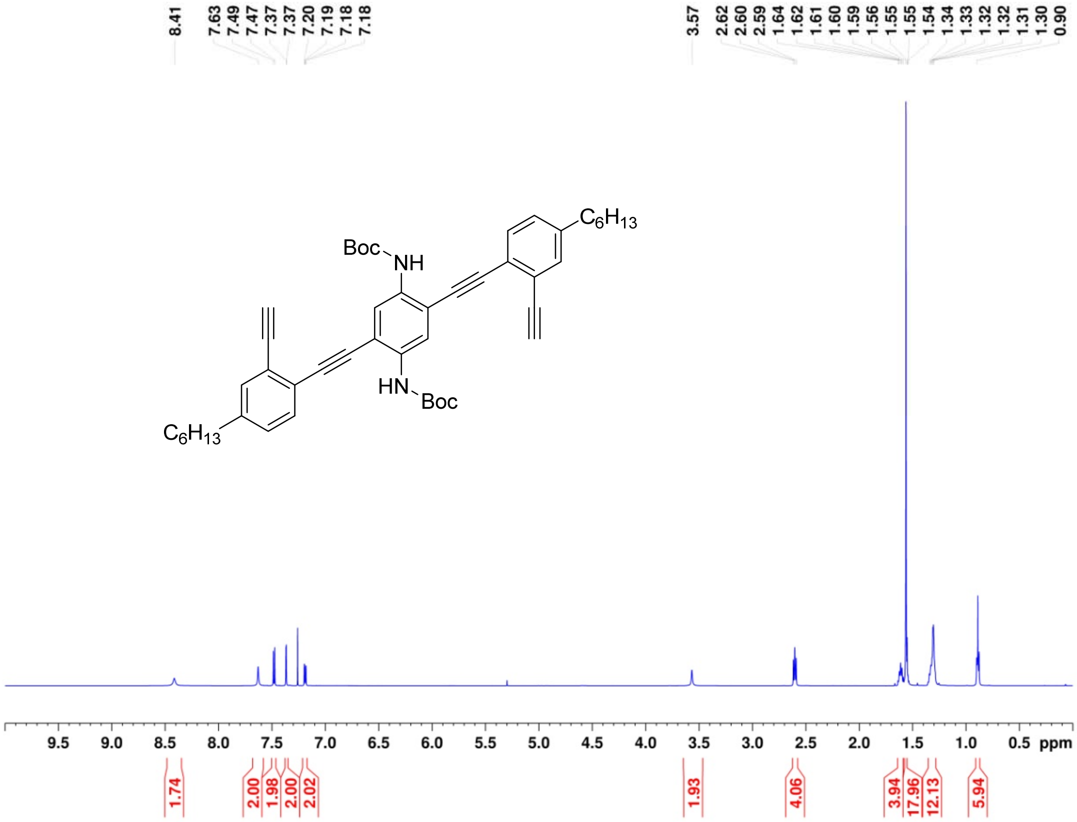
$^{13}$C NMR spectrum of **1f** in $CDCl_3$ at 100.7 MHz



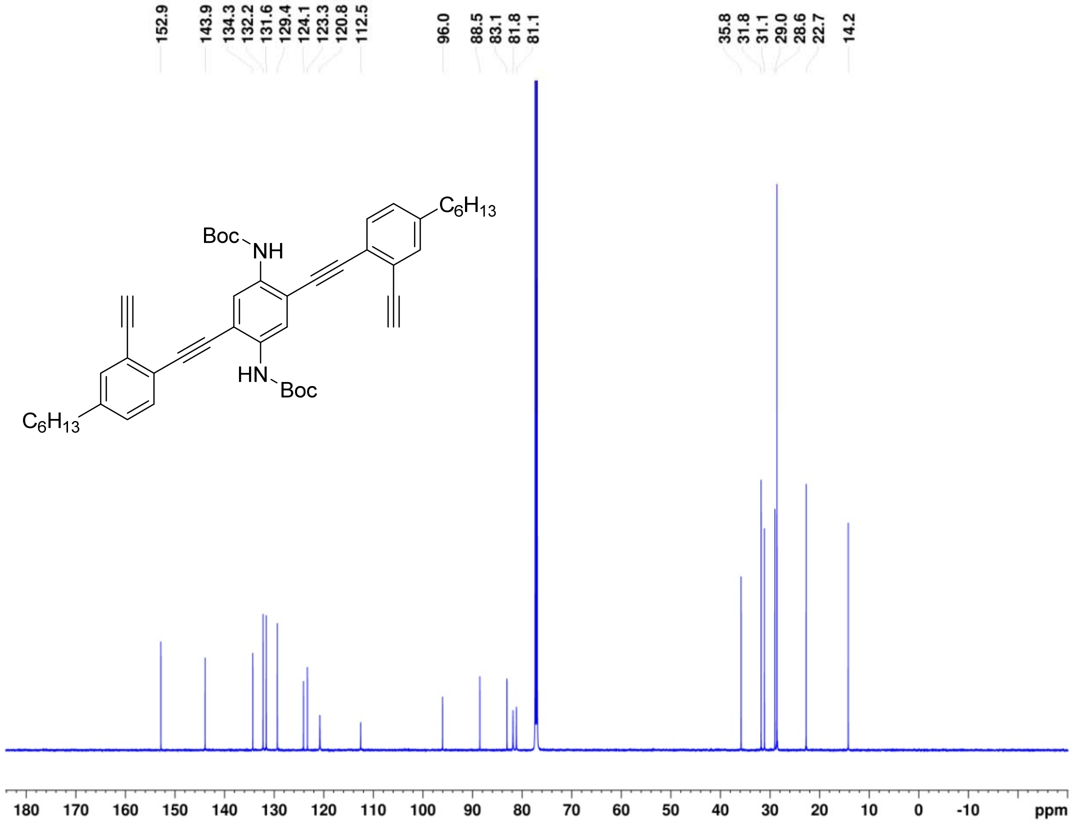
$^1$H NMR spectrum of **TMS-1g** in $CDCl_3$ at 400.3 MHz



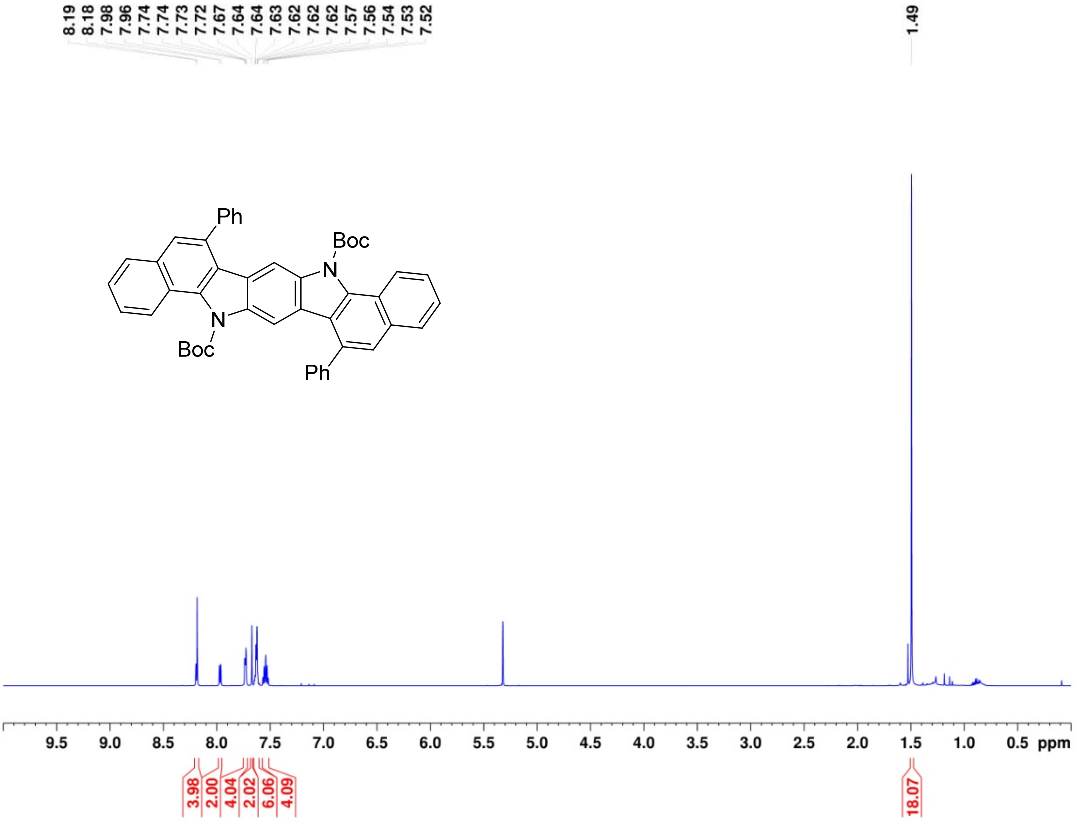
$^{13}$C NMR spectrum of **TMS-1g** in $CDCl_3$ at 100.7 MHz



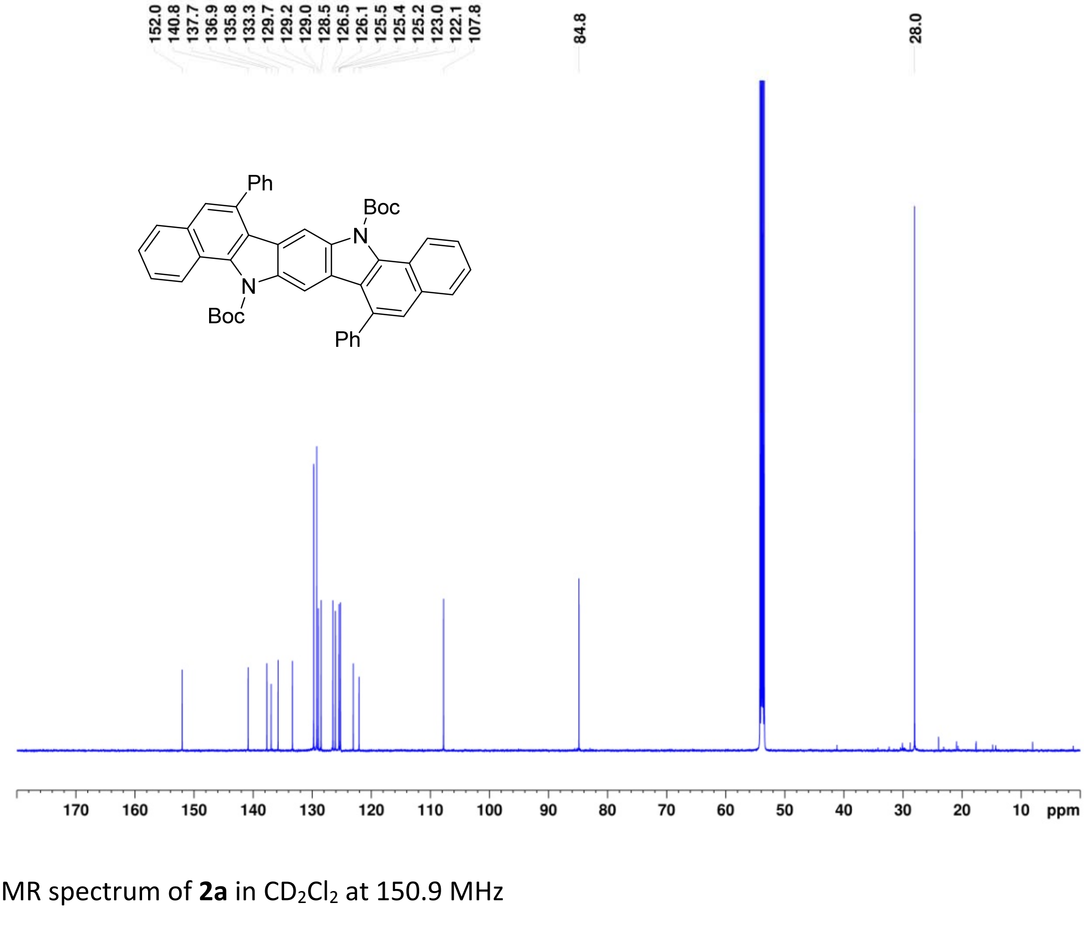
$^1$H NMR spectrum of **1g** in $CDCl_3$ at 400.3 MHz



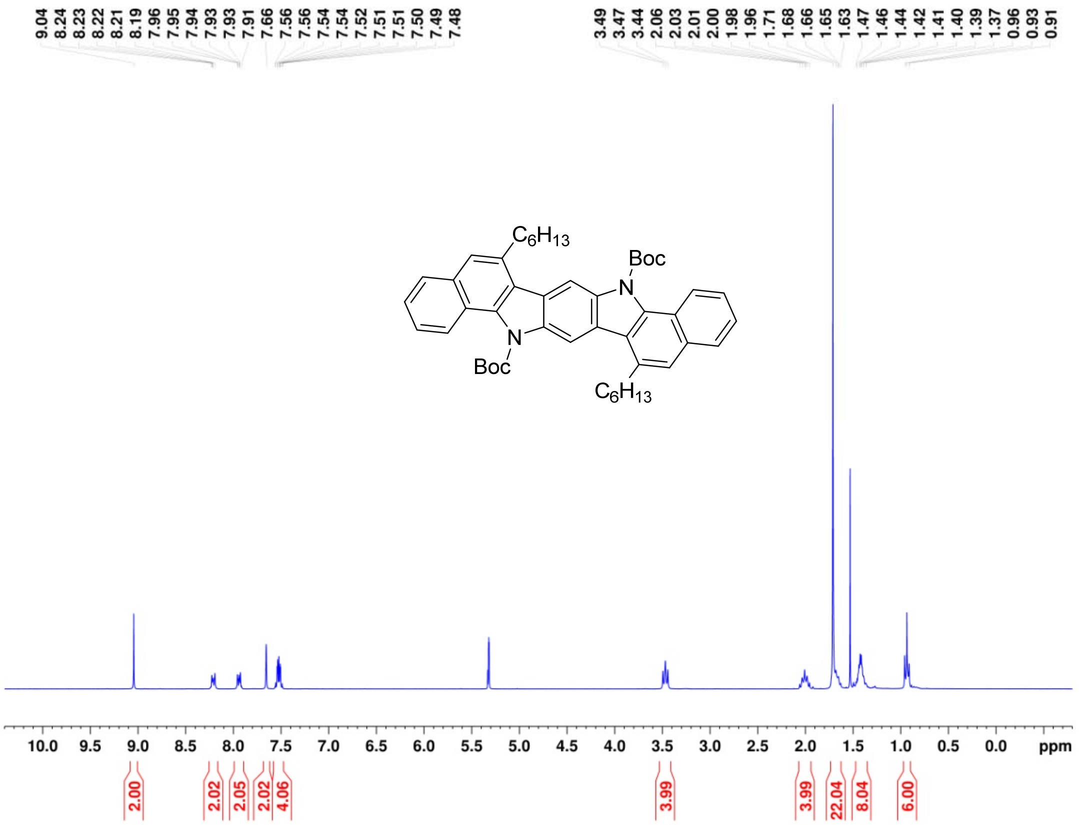
$^{13}$C NMR spectrum of **1g** in $CDCl_3$ at 100.7 MHz



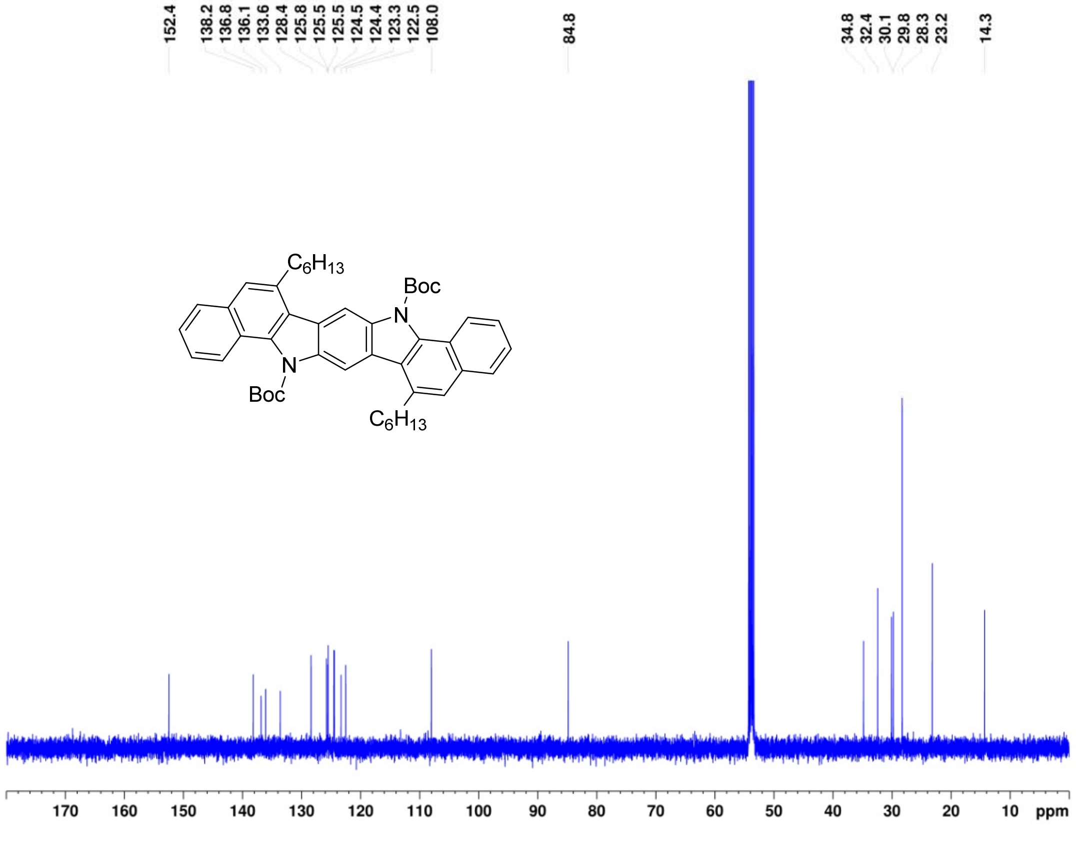
$^{1}$H NMR spectrum of **2a** in $CD_2Cl_2$ at 600.2 MHz



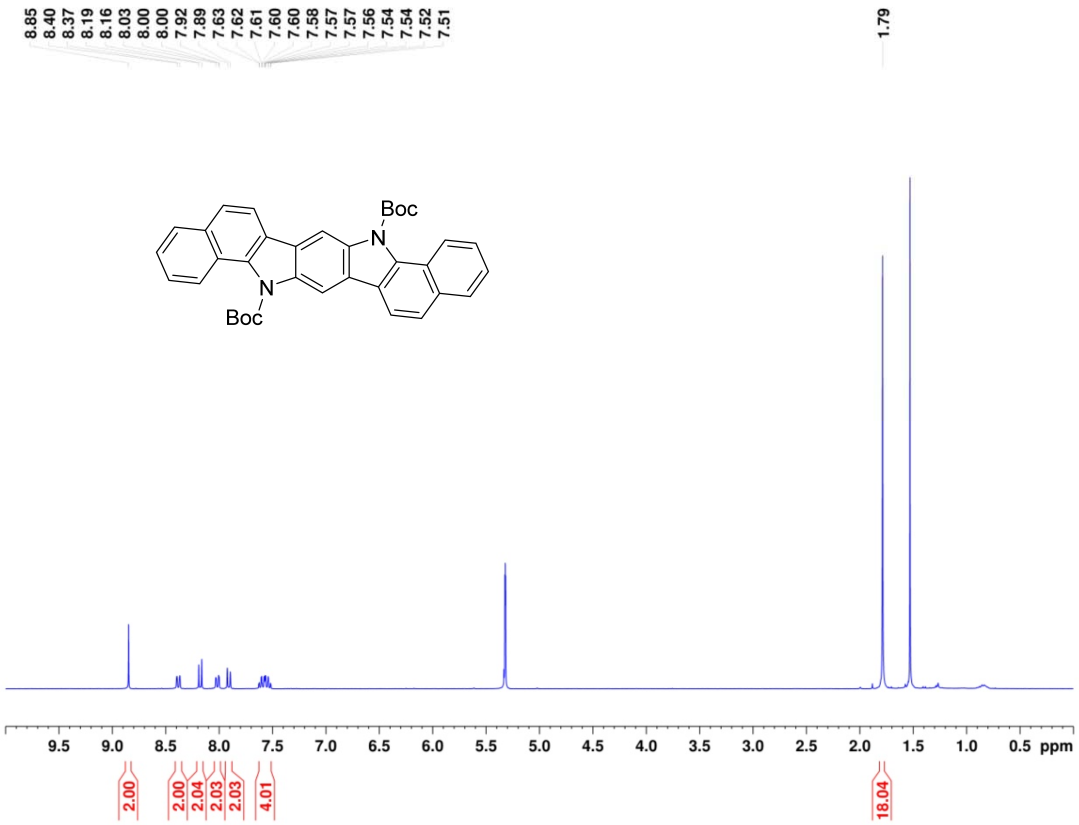
$^{13}$C NMR spectrum of **2a** in $CD_2Cl_2$ at 150.9 MHz



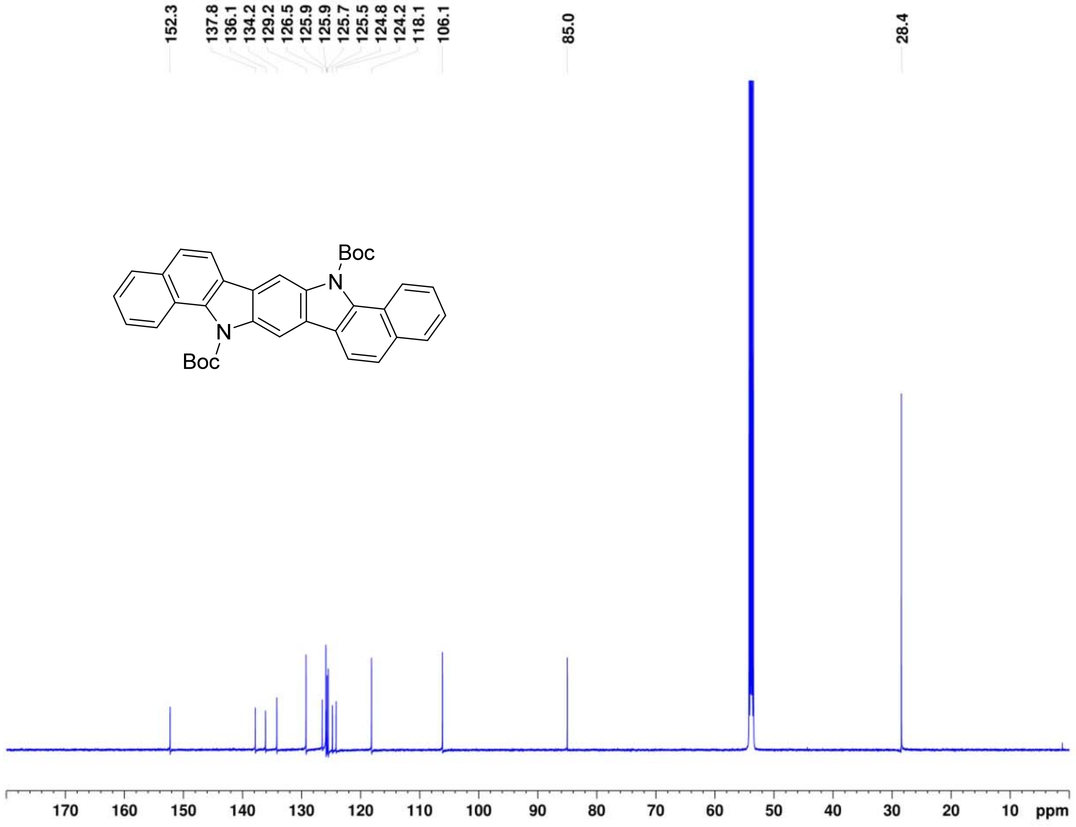
$^{1}$H NMR spectrum of **2b** in $CD_2Cl_2$ at 300.5 MHz



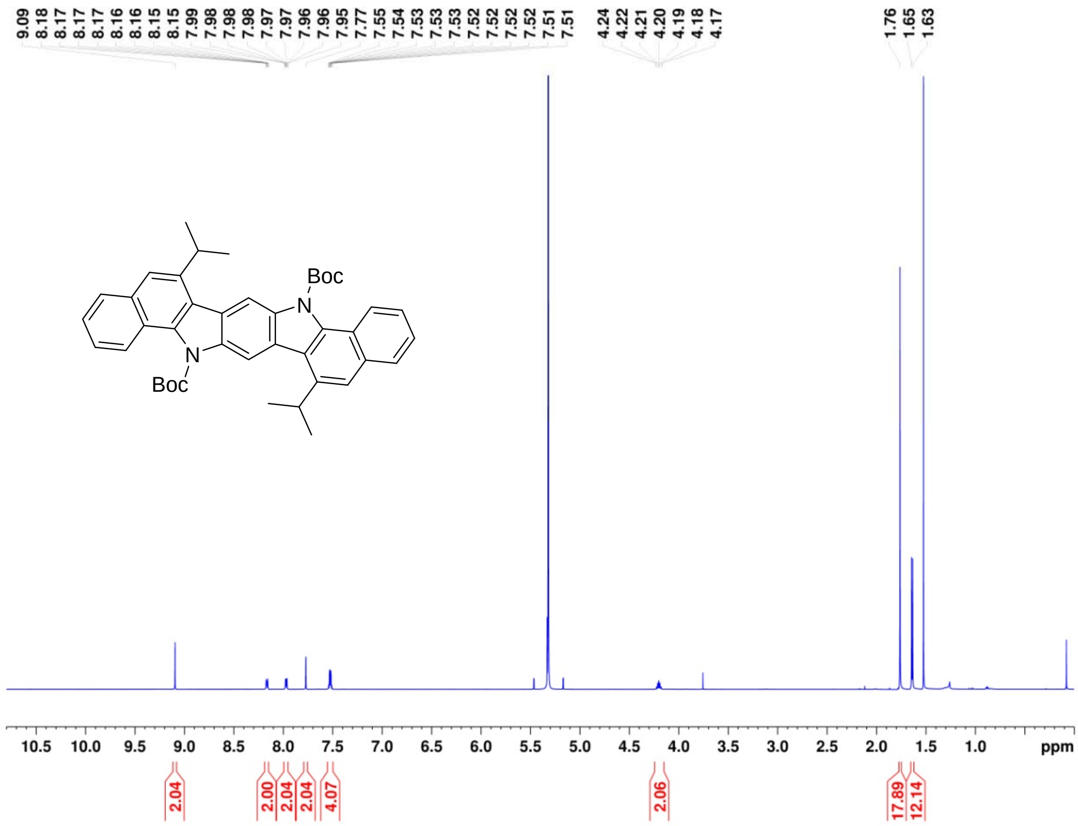
$^{13}$C NMR spectrum of **2b** in $CD_2Cl_2$ at 125.8 MHz



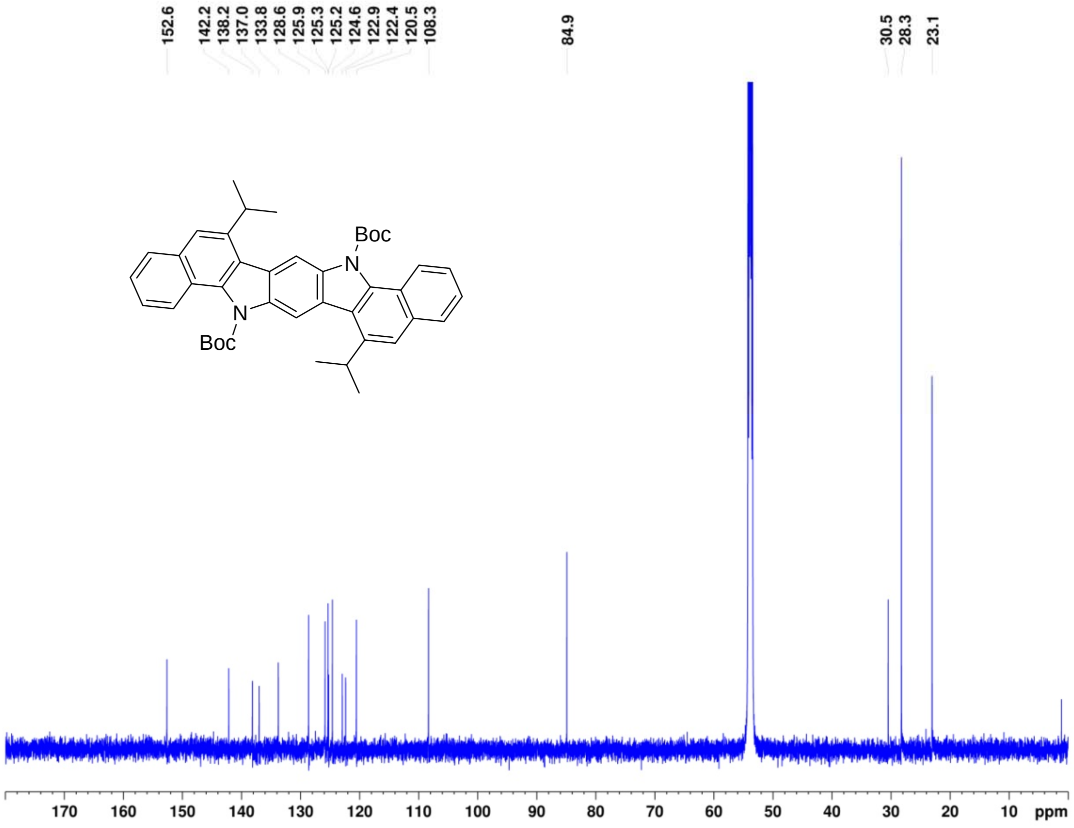
$^1$H NMR spectrum of **2c** in $CD_2Cl_2$ at 300.5 MHz



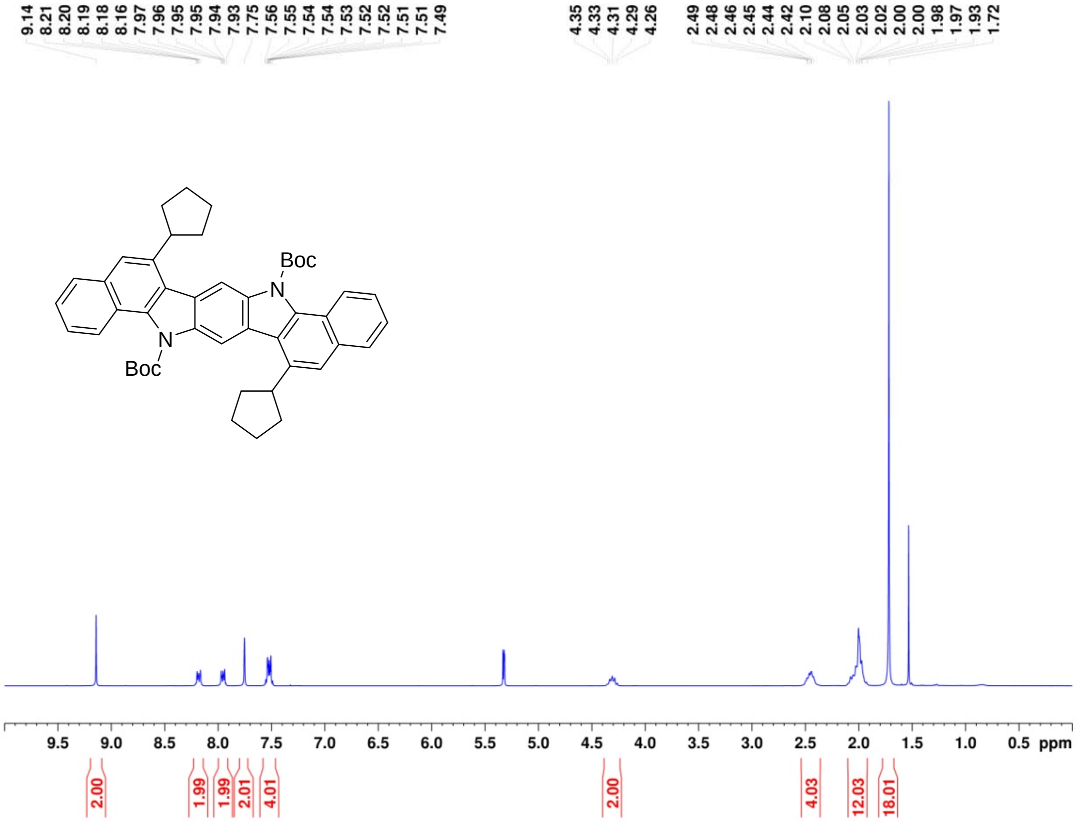
$^{13}$C NMR spectrum of **2c** in $CD_2Cl_2$ at 150.9 MHz



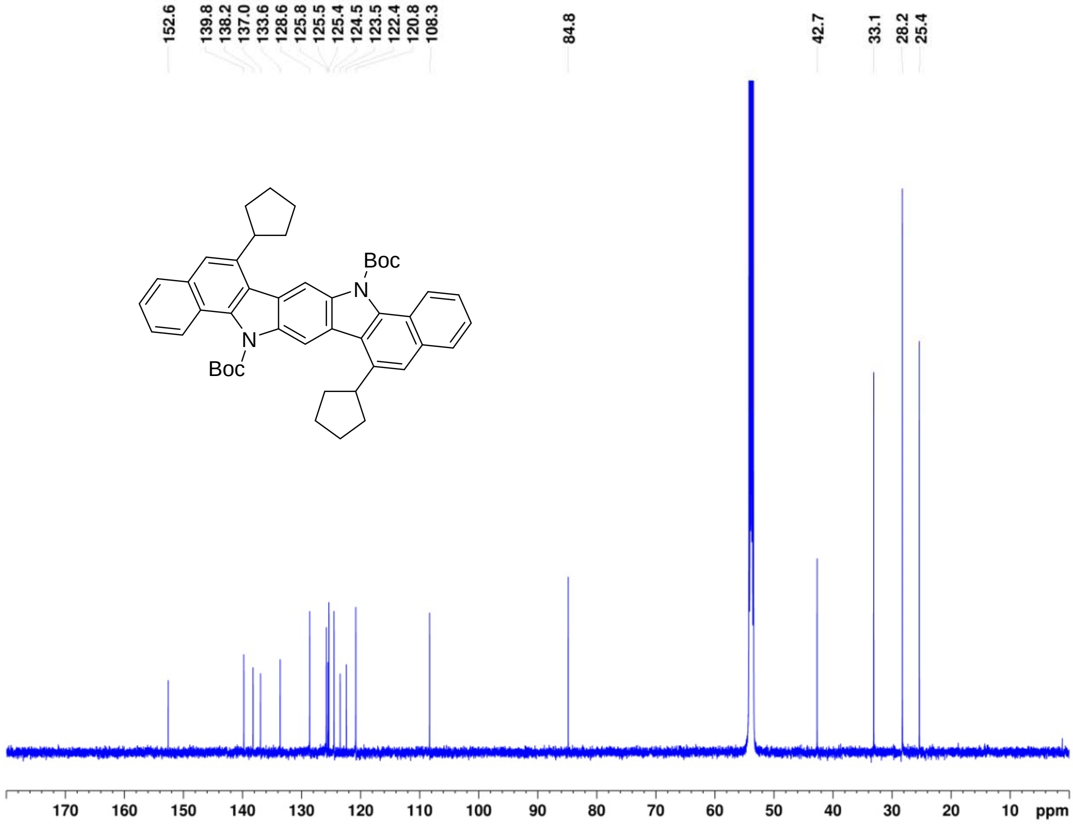
$^1$H NMR spectrum of **2d** in $CD_2Cl_2$ at 600.2 MHz



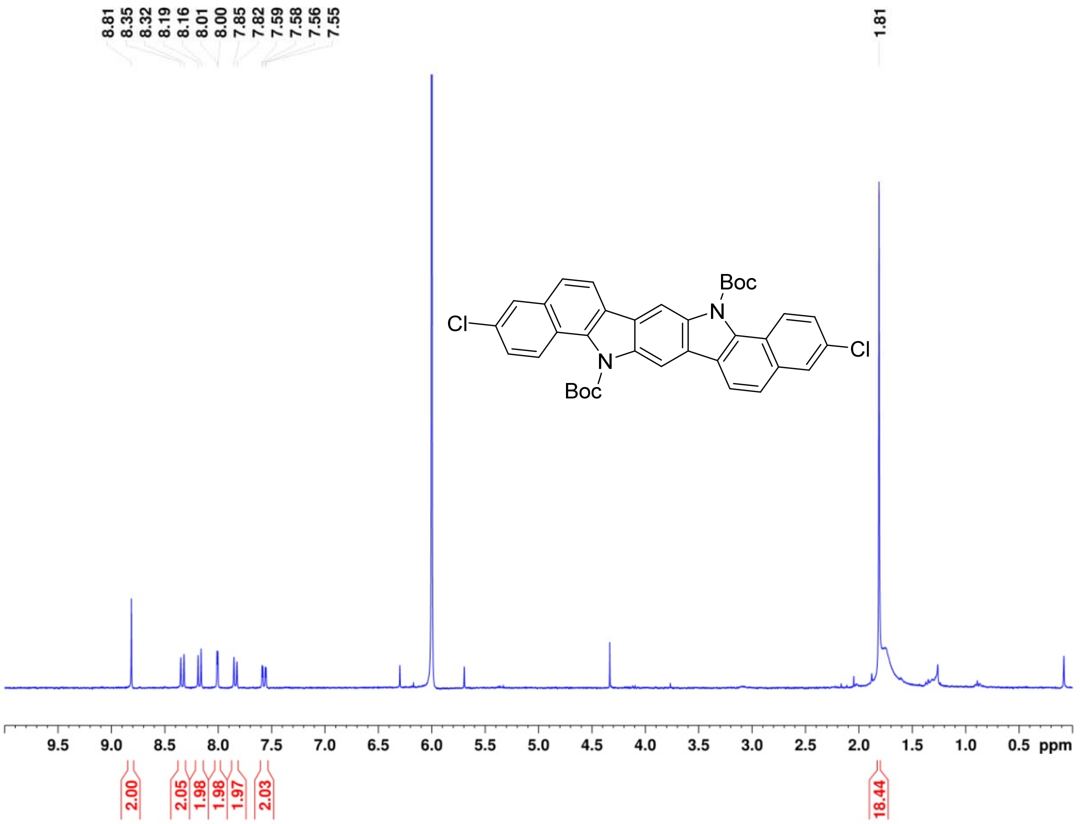
$^{13}$C NMR spectrum of **2d** in $CD_2Cl_2$ at 150.9 MHz



$^1$H NMR spectrum of **2e** in $CD_2Cl_2$ at 300.5 MHz

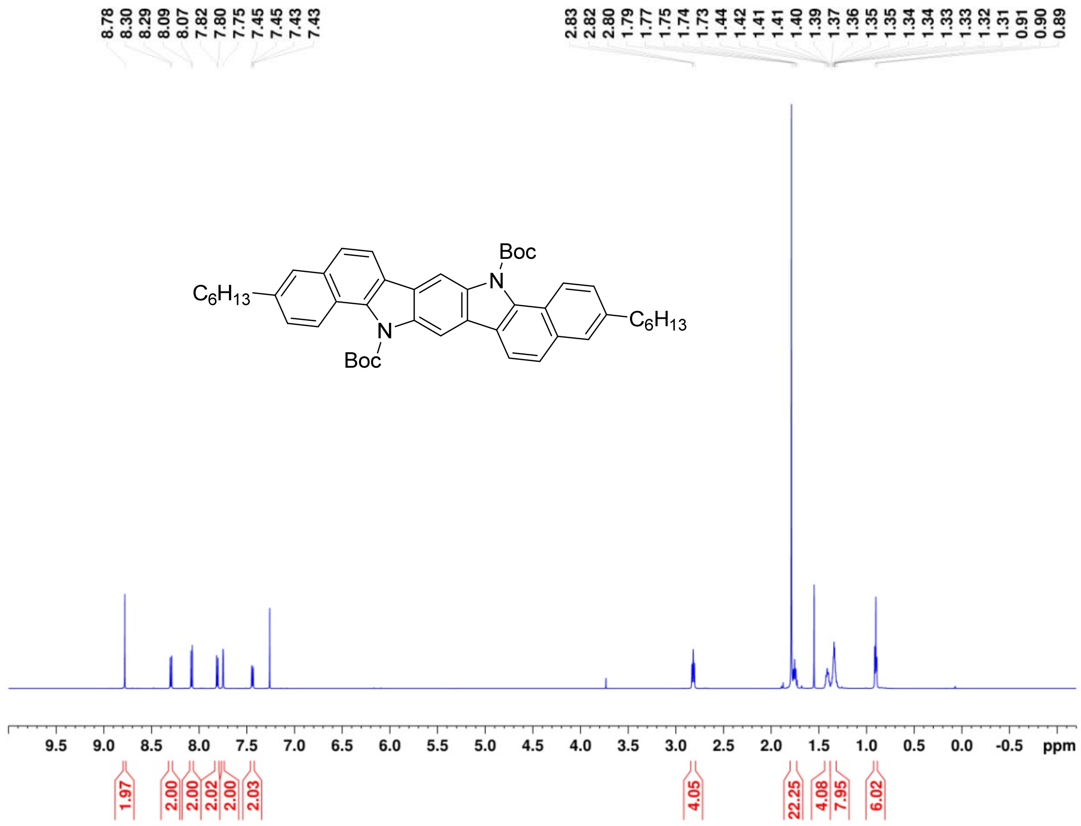


$^{13}$C NMR spectrum of **2e** in $CD_2Cl_2$ at 150.9 MHz

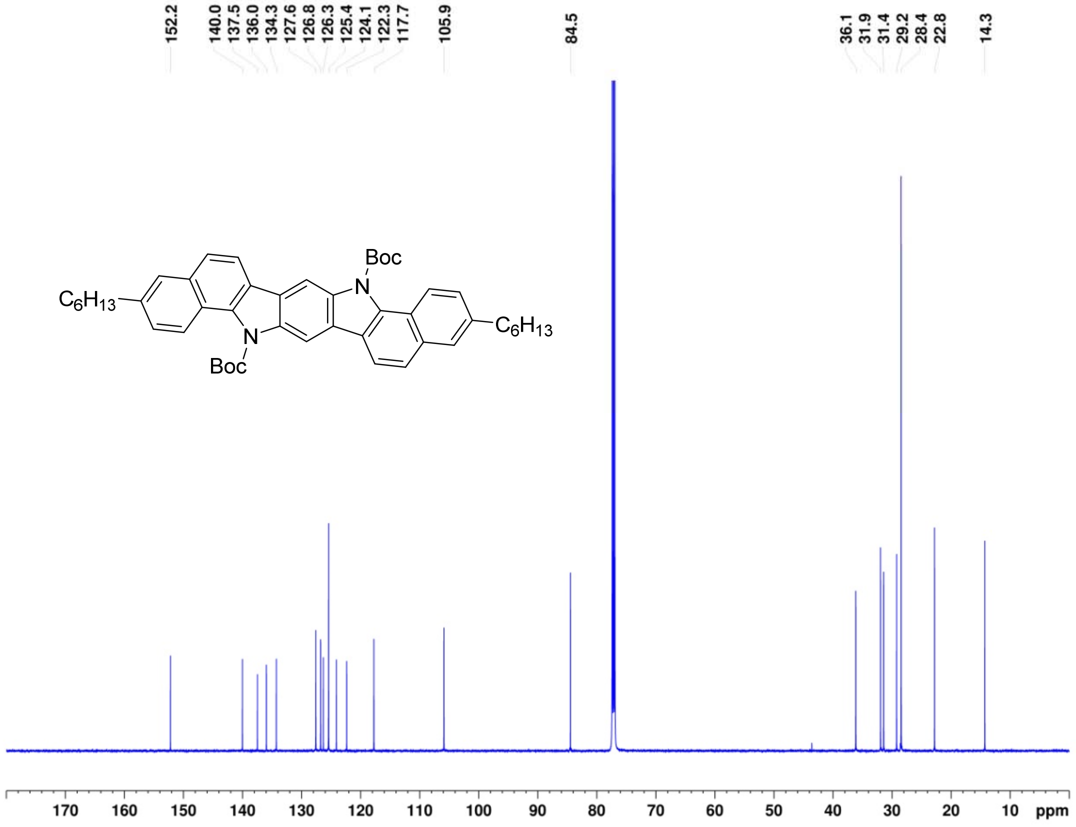


$^{1}$H NMR spectrum of **2f** in $d_2$-TCE at 300.5 MHz

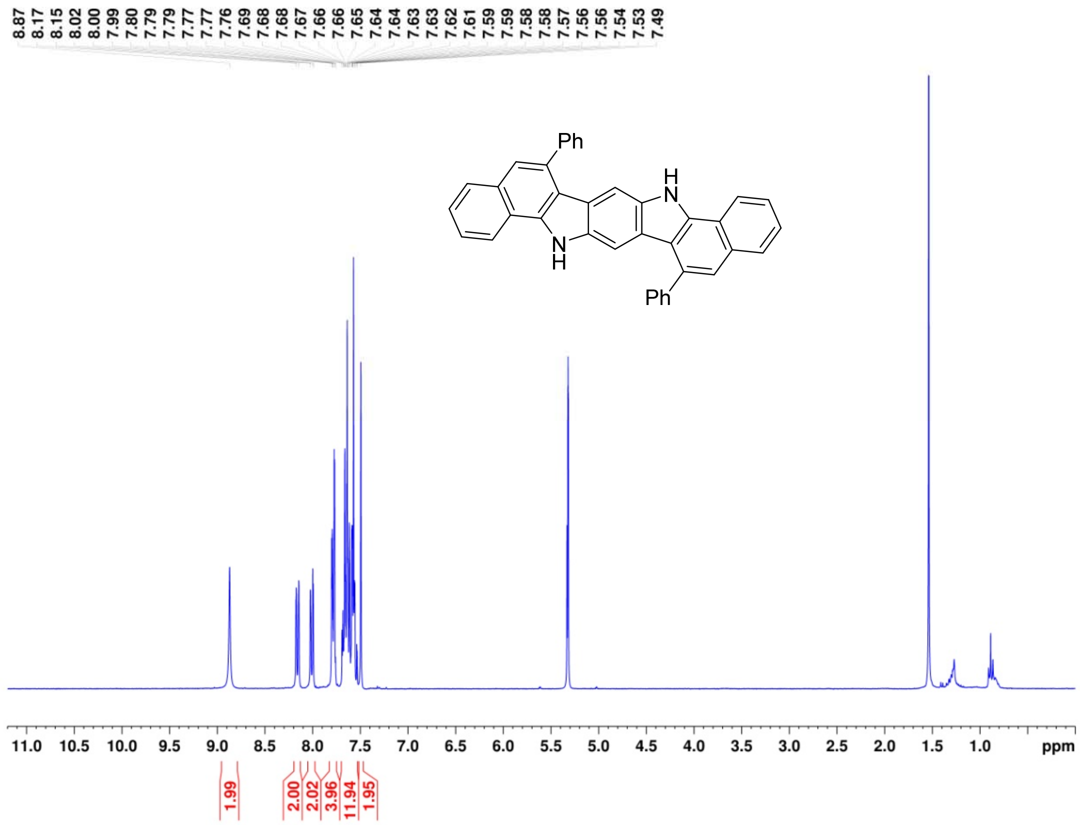
$^{13}$C NMR spectrum was not recorded due to its low solubility.



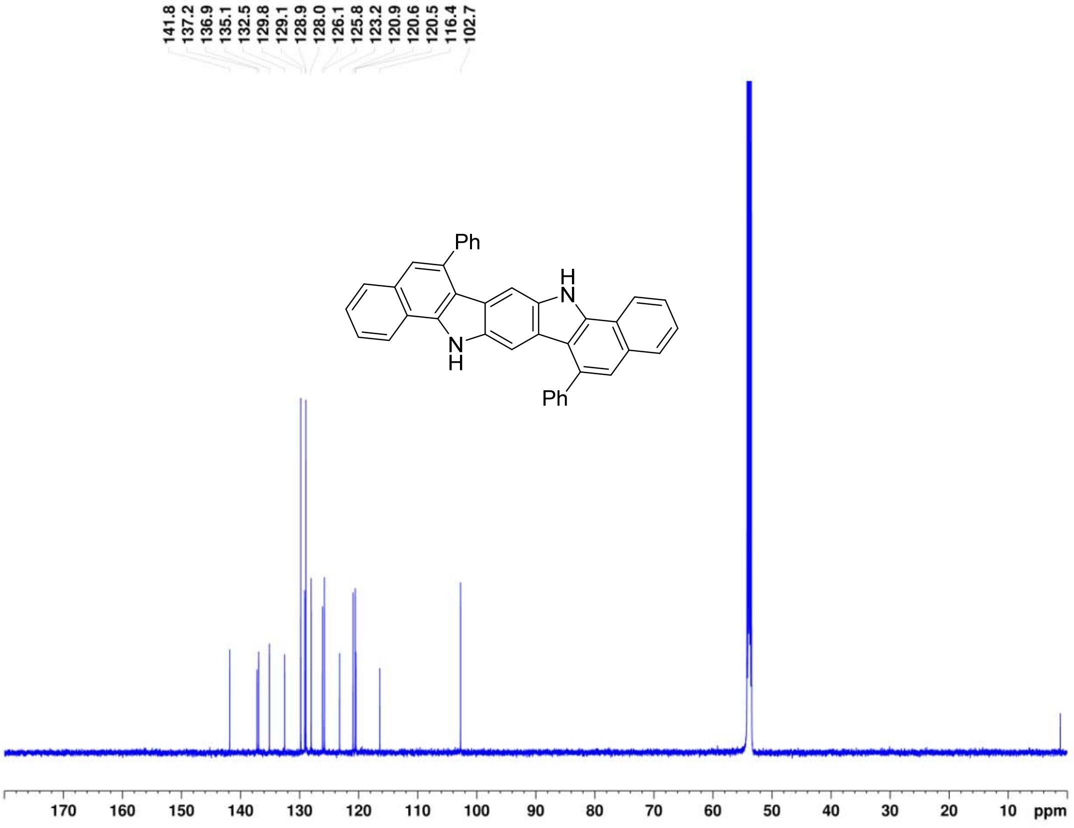
$^1$H NMR spectrum of **2g** in CDCl$_3$ at 400.3 MHz



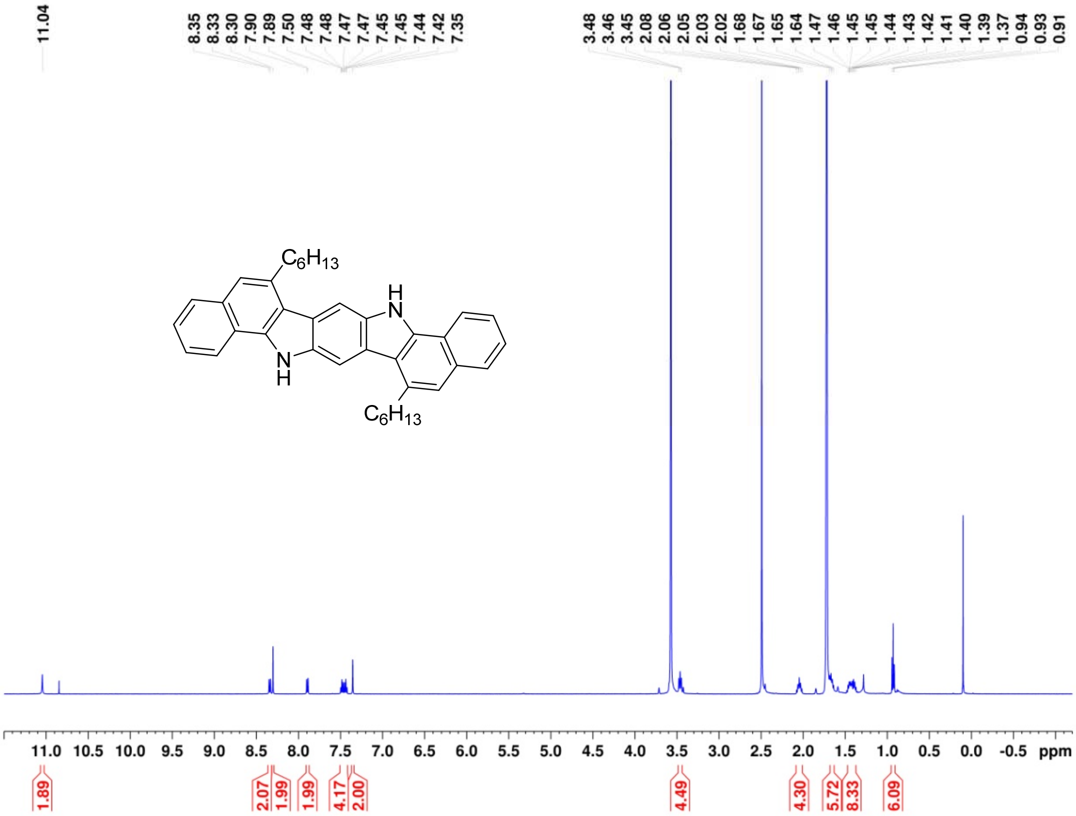
$^{13}$C NMR spectrum of **2g** in CDCl$_3$ at 100.7 MHz



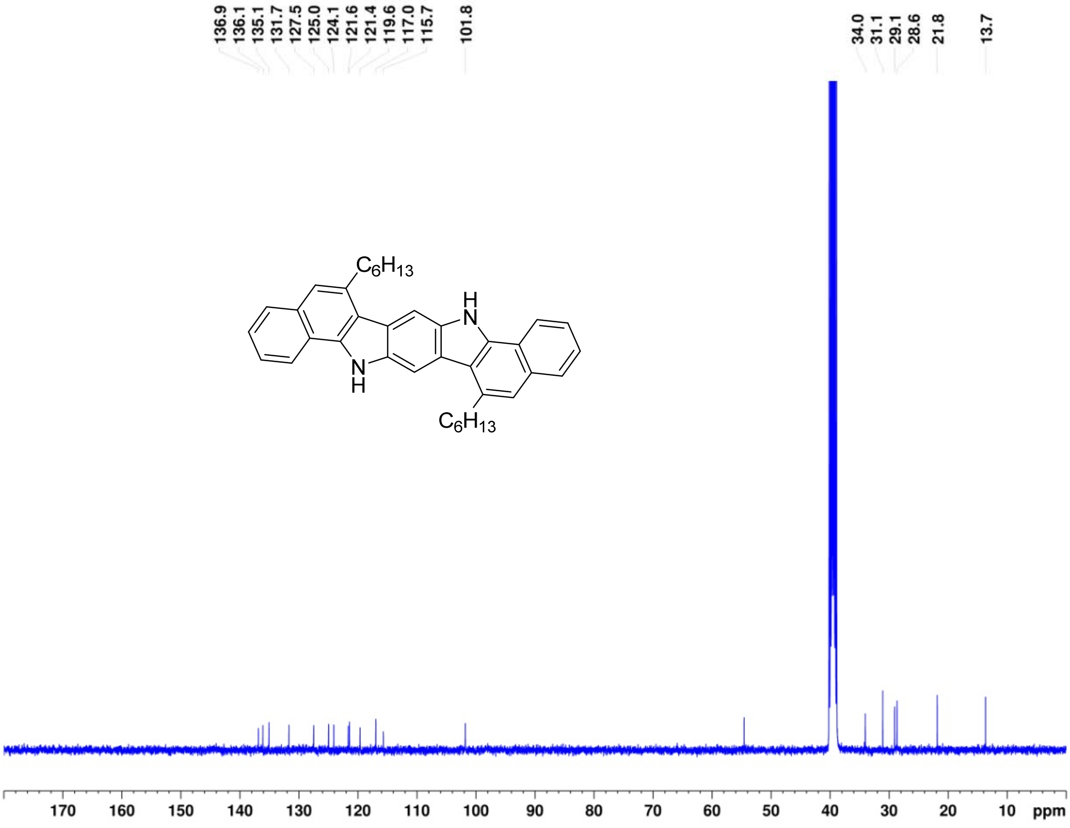
$^1$H NMR spectrum of **3a** in $CD_2Cl_2$ at 300.5 MHz



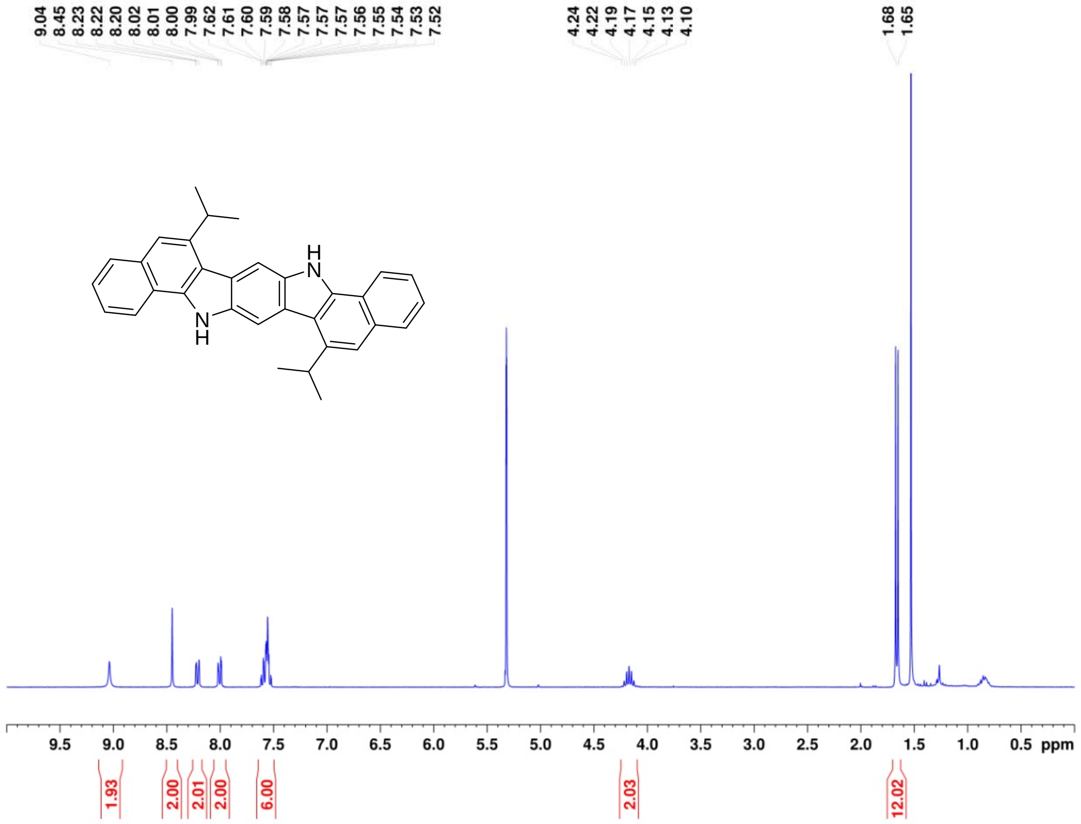
$^{13}$C NMR spectrum of **3a** in $CD_2Cl_2$ at 150.9 MHz



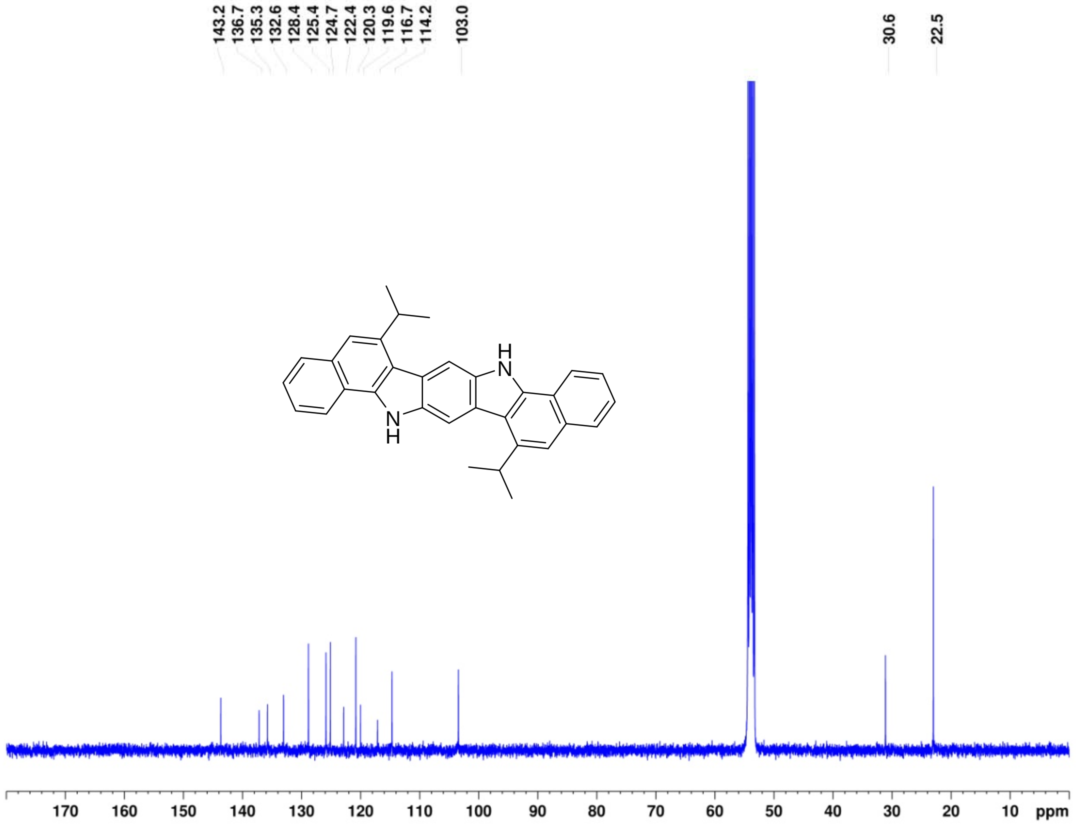
$^1$H NMR spectrum of **3b** in d$_8$-THF at 500.1 MHz



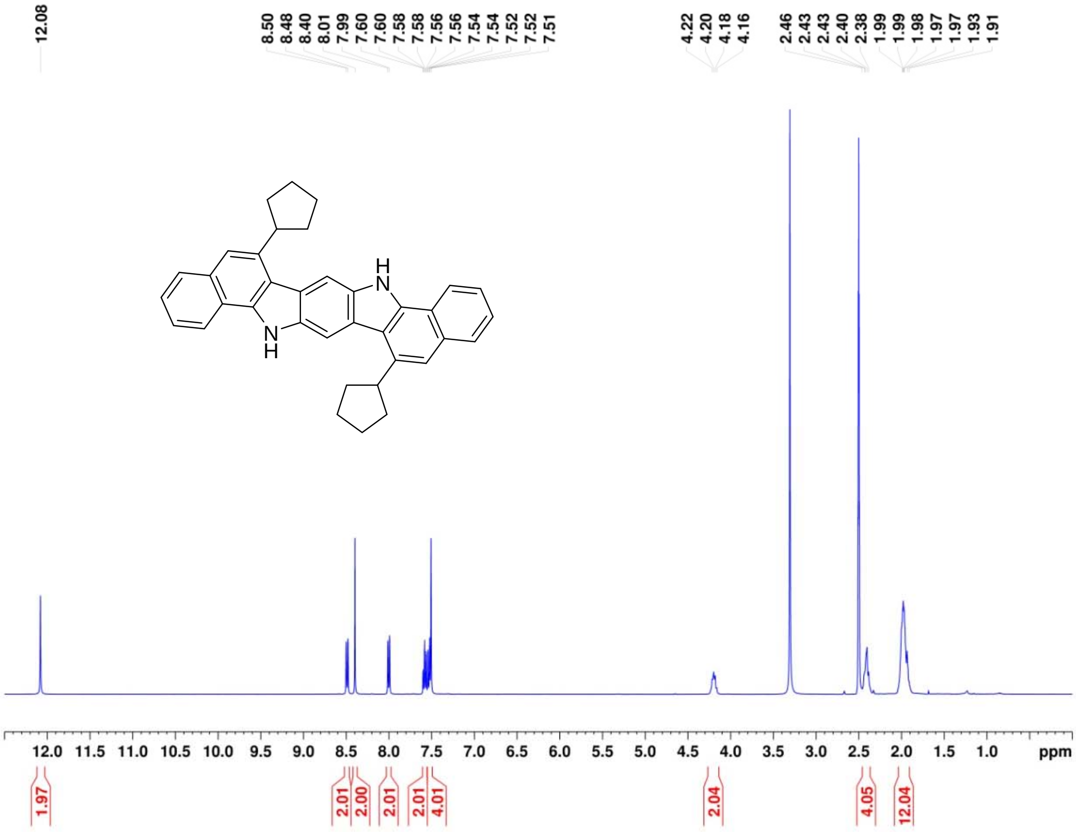
$^{13}$C NMR spectrum of **3b** in d$_6$-DMSO at 100.6 MHz (T = 323 K)



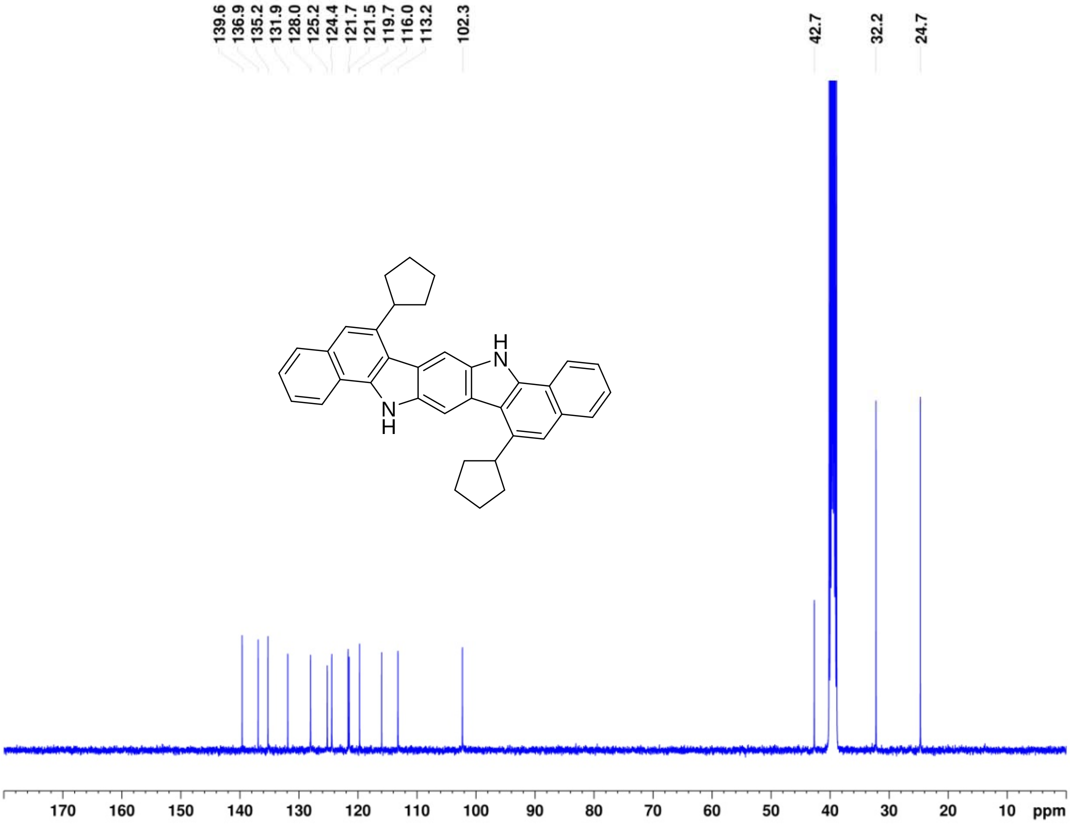
$^1$H NMR spectrum of **3d** in $CD_2Cl_2$ at 300.5 MHz



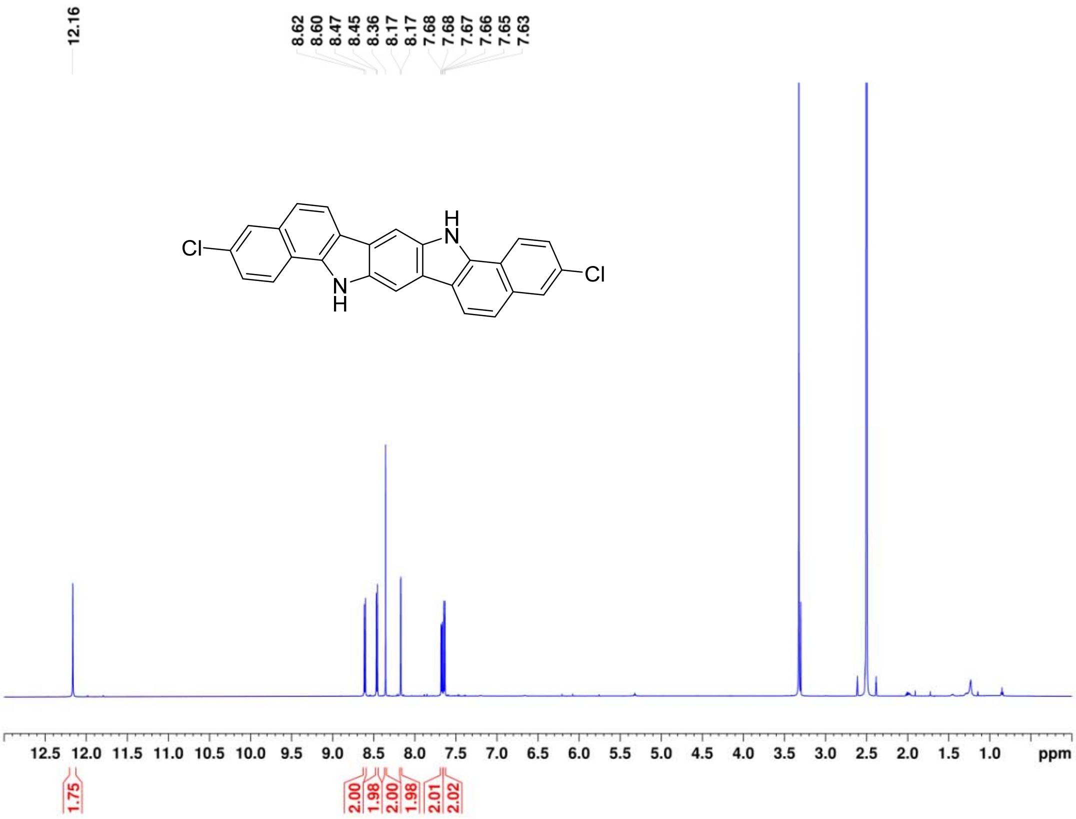
$^{13}$C NMR spectrum of **3d** in $CD_2Cl_2$ at 100.7 MHz



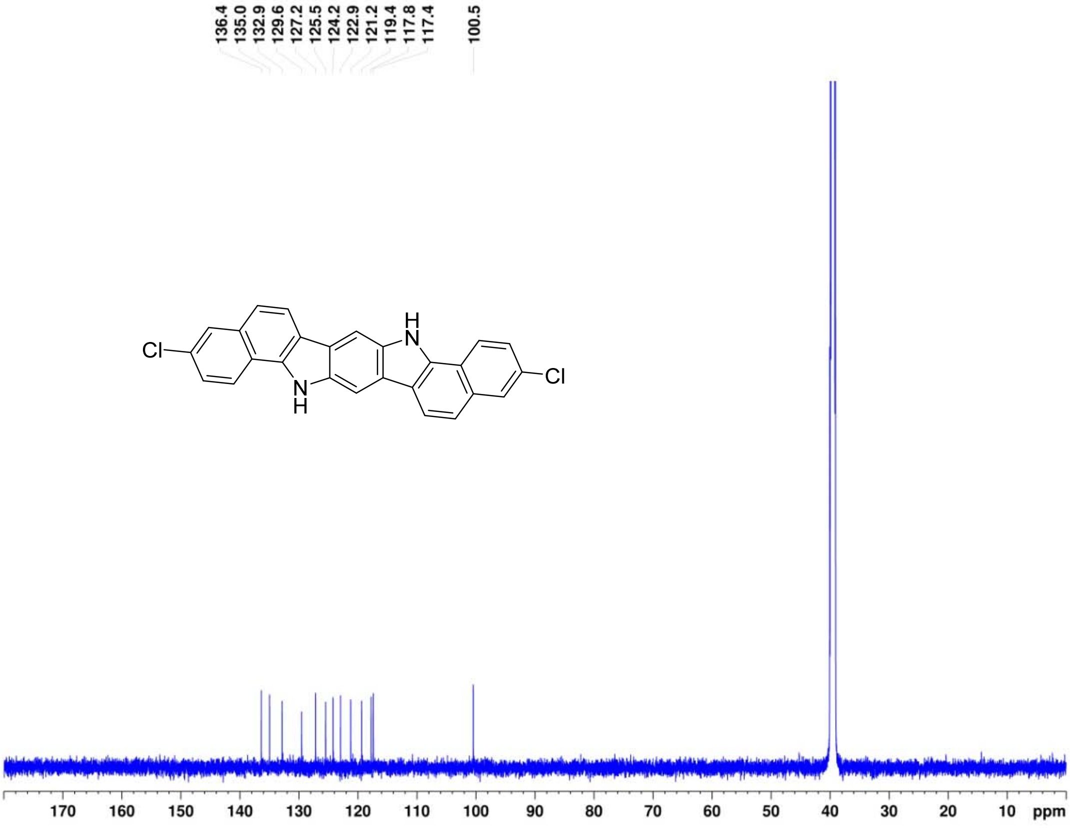
$^{1}H$ NMR spectrum of **3e** in $d_6$-DMSO at 400.3 MHz



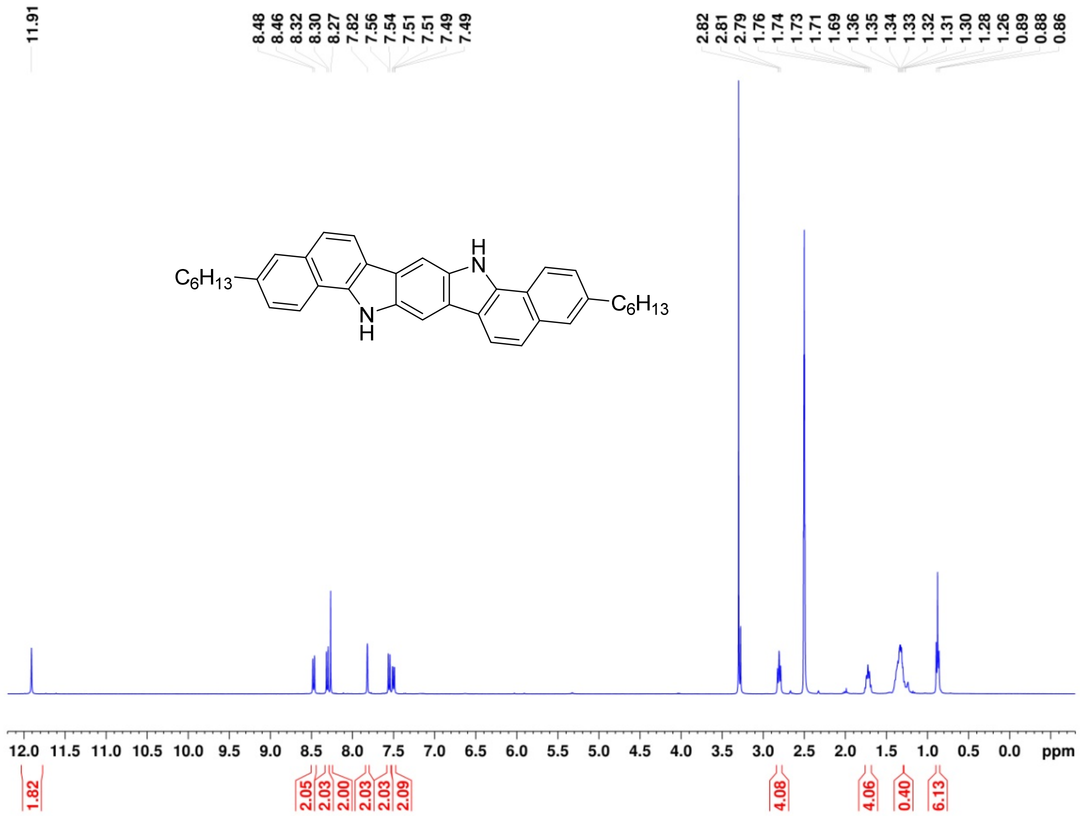
$^{13}C$ NMR spectrum of **3e** in $d_6$-DMSO at 100.7 MHz



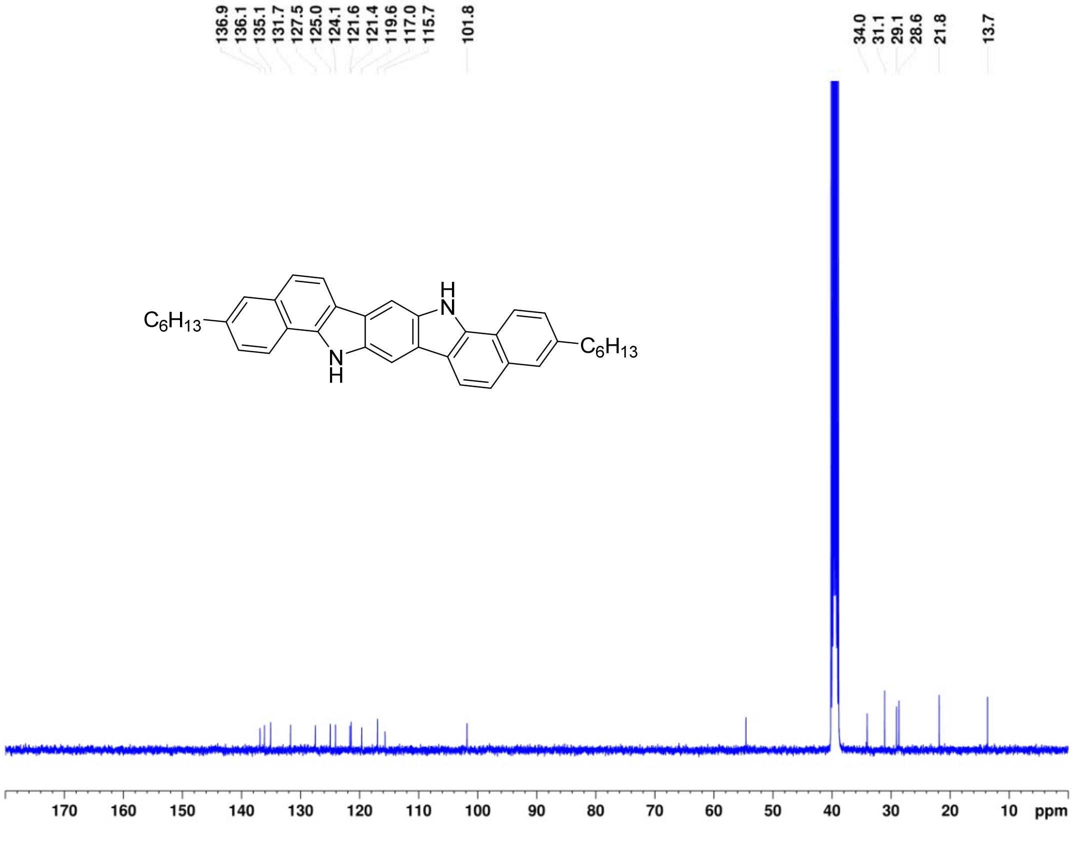
$^{1}H$ NMR spectrum of **3f** in $d_6$-DMSO at 600.2 MHz



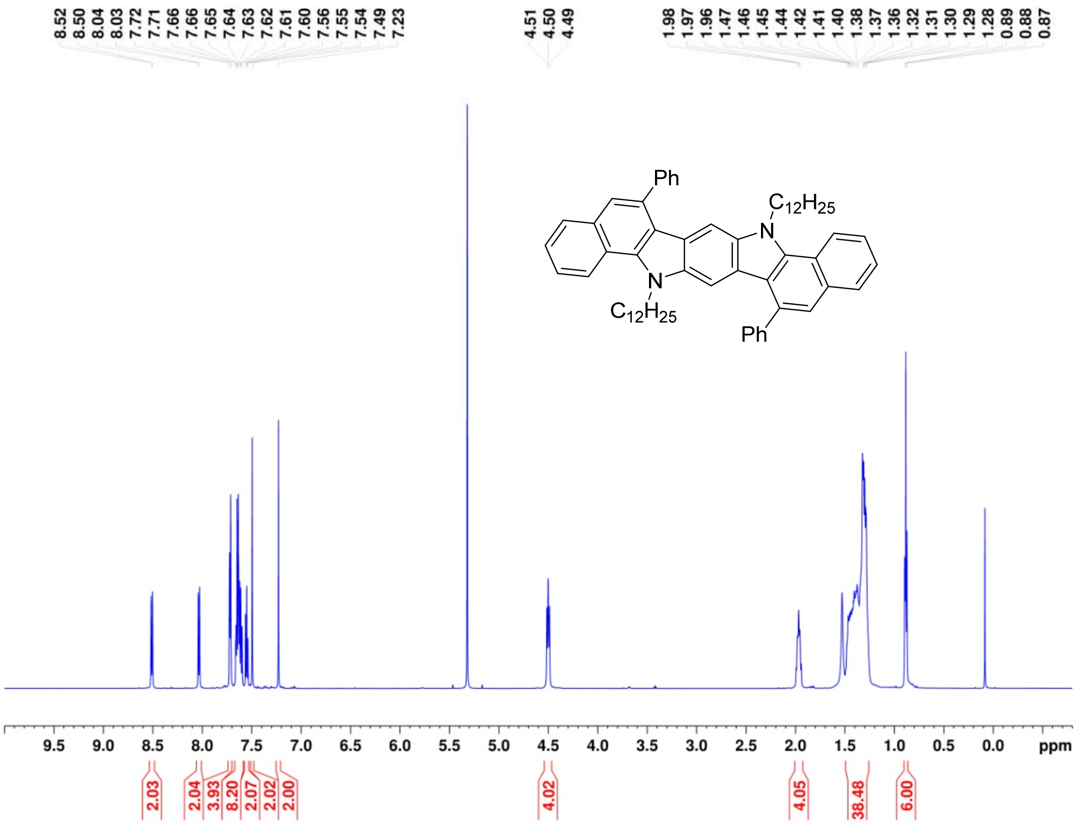
$^{13}C$ NMR spectrum of **3f** in $d_6$-DMSO at 150.9 MHz



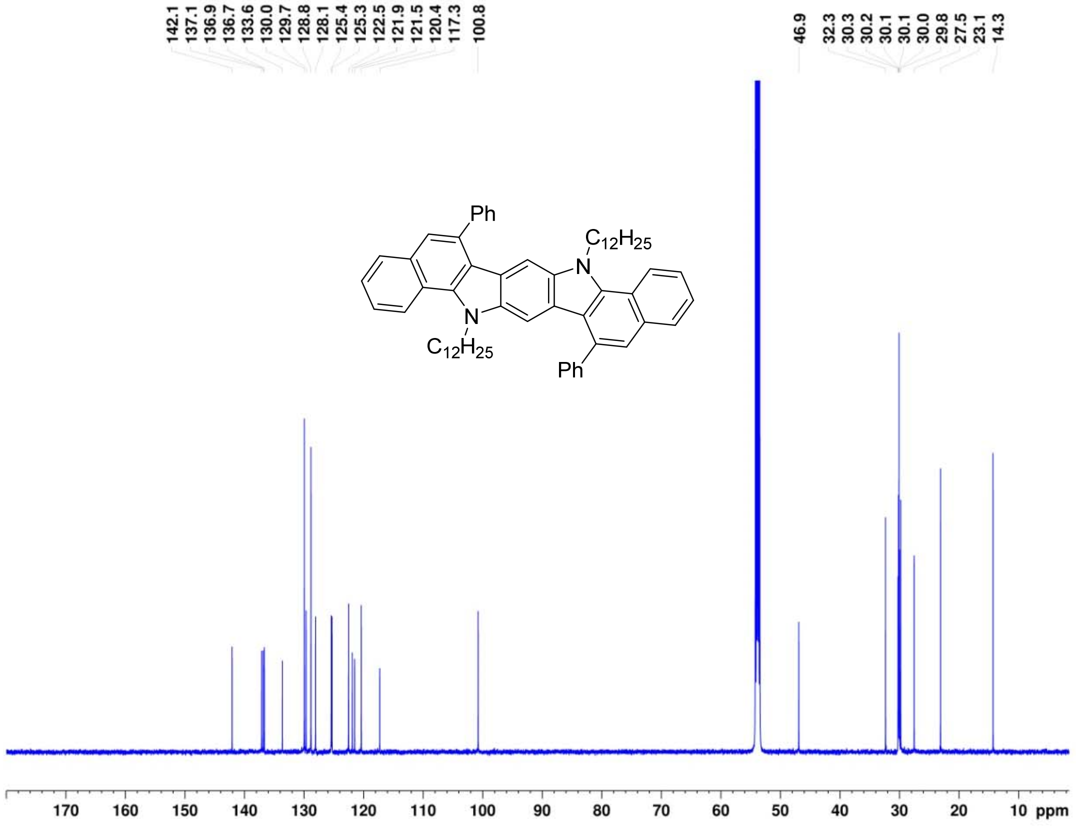
$^1$H NMR spectrum of **3g** in d$_6$-DMSO at 300.5 MHz



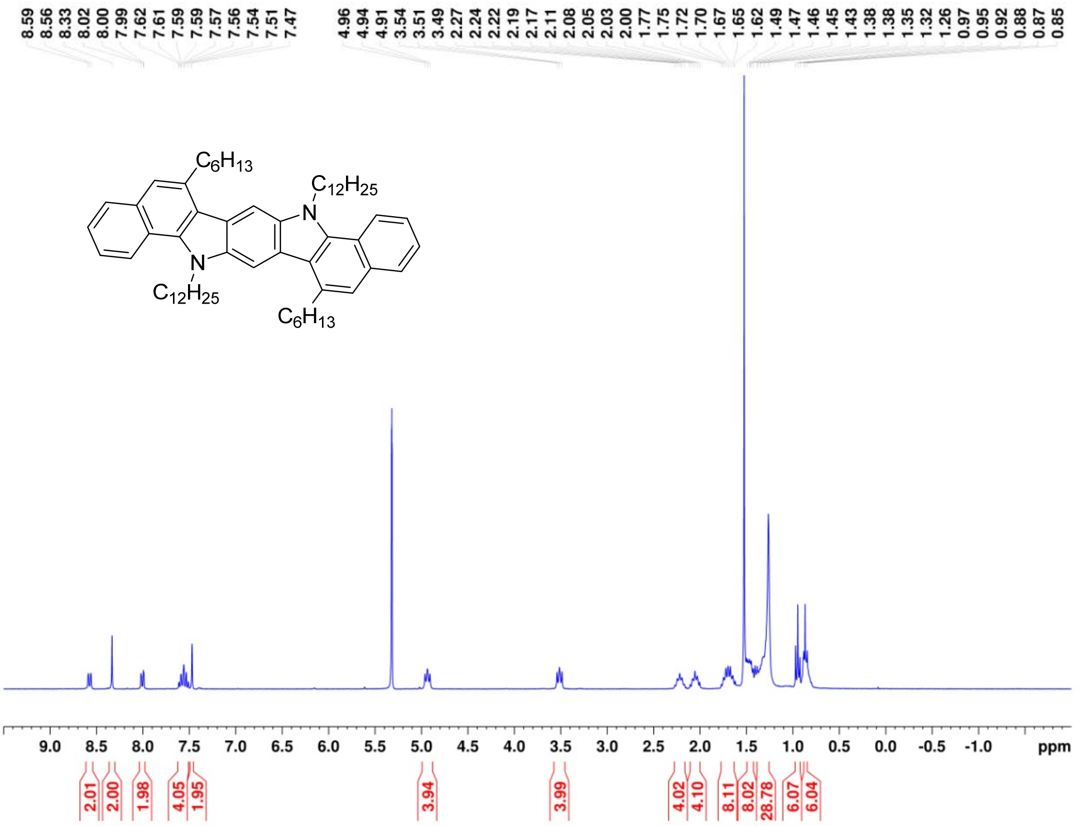
$^{13}$C NMR spectrum of **3g** in d$_6$-DMSO at 100.7 MHz



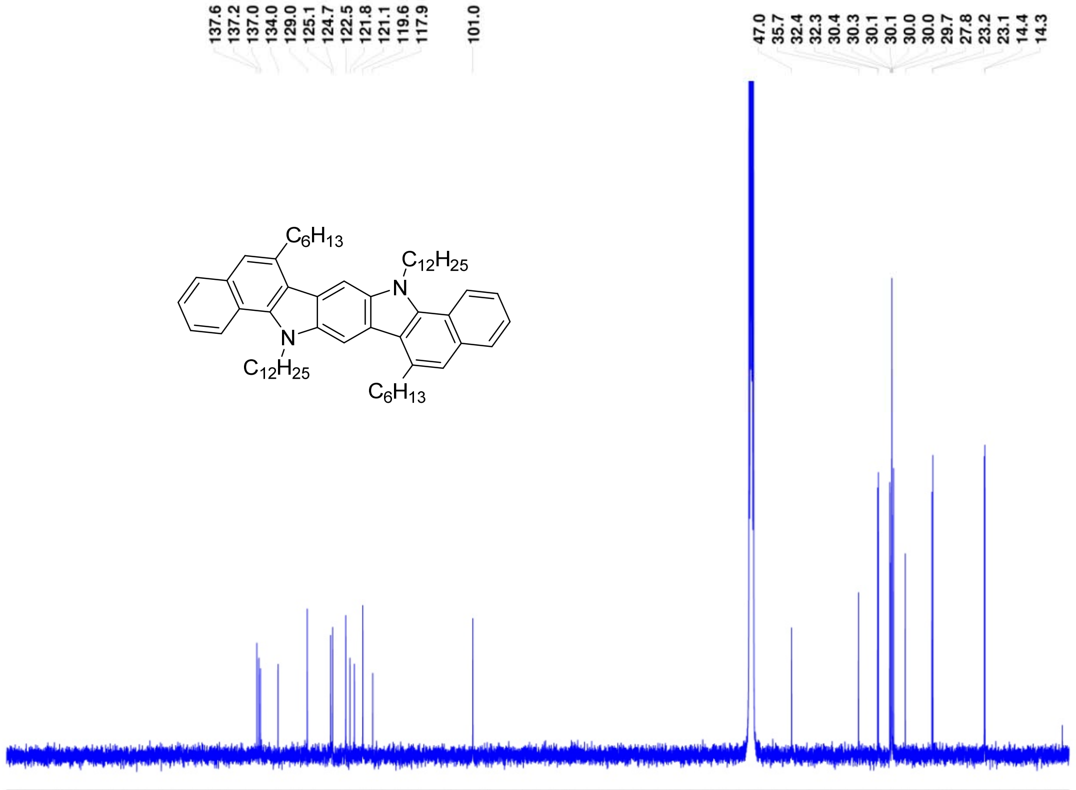
$^1$H NMR spectrum of **4a** in $CD_2Cl_2$ at 600.2 MHz



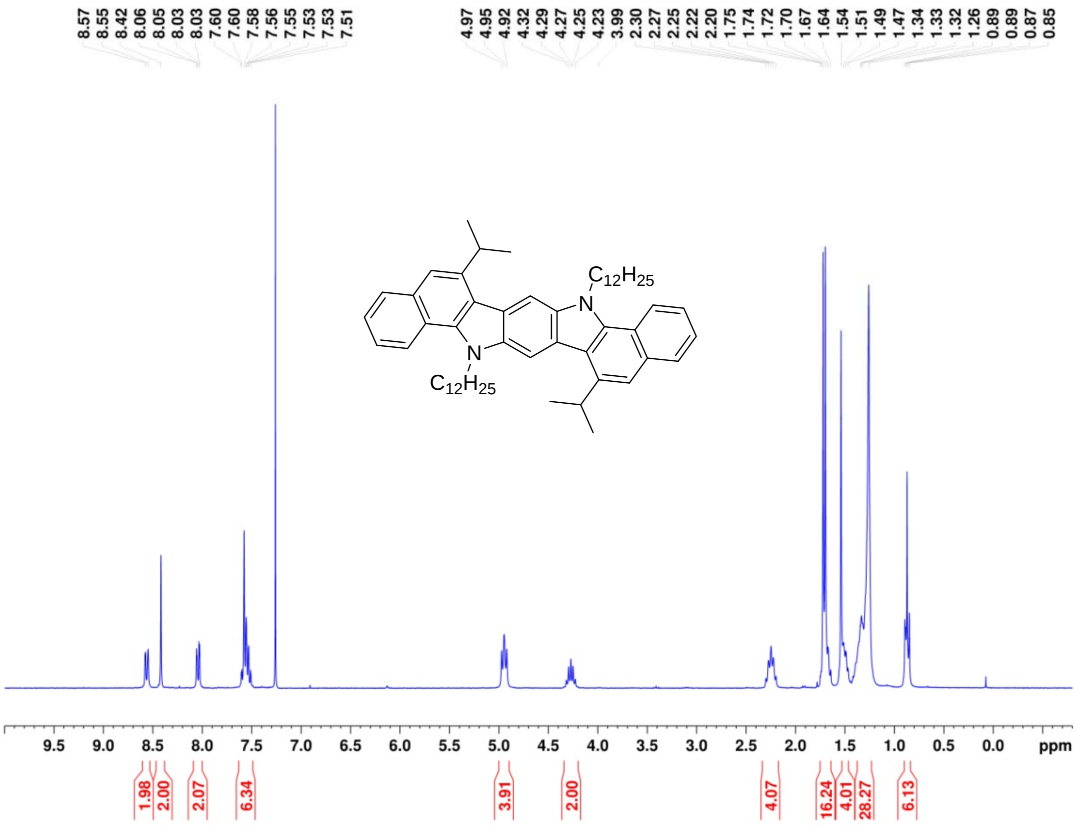
$^{13}$C NMR spectrum of **4a** in $CD_2Cl_2$ at 150.9 MHz



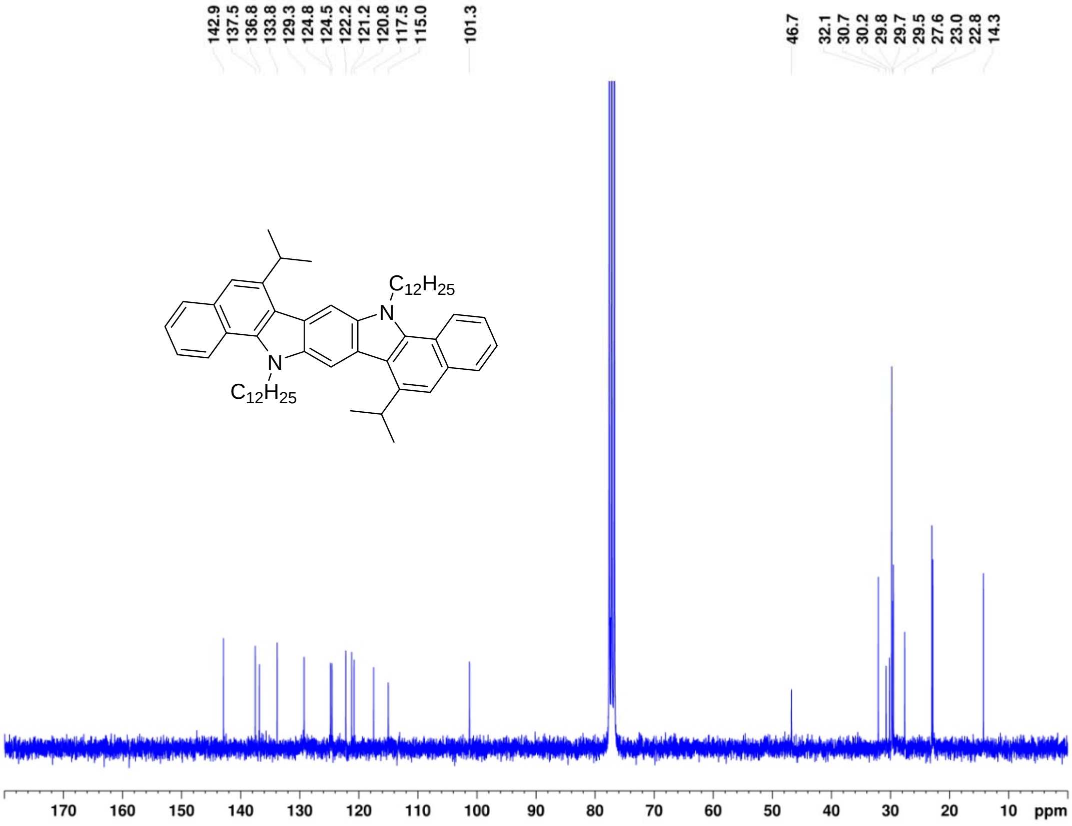
$^1$H NMR spectrum of **4b** in $CD_2Cl_2$ at 300.5 MHz



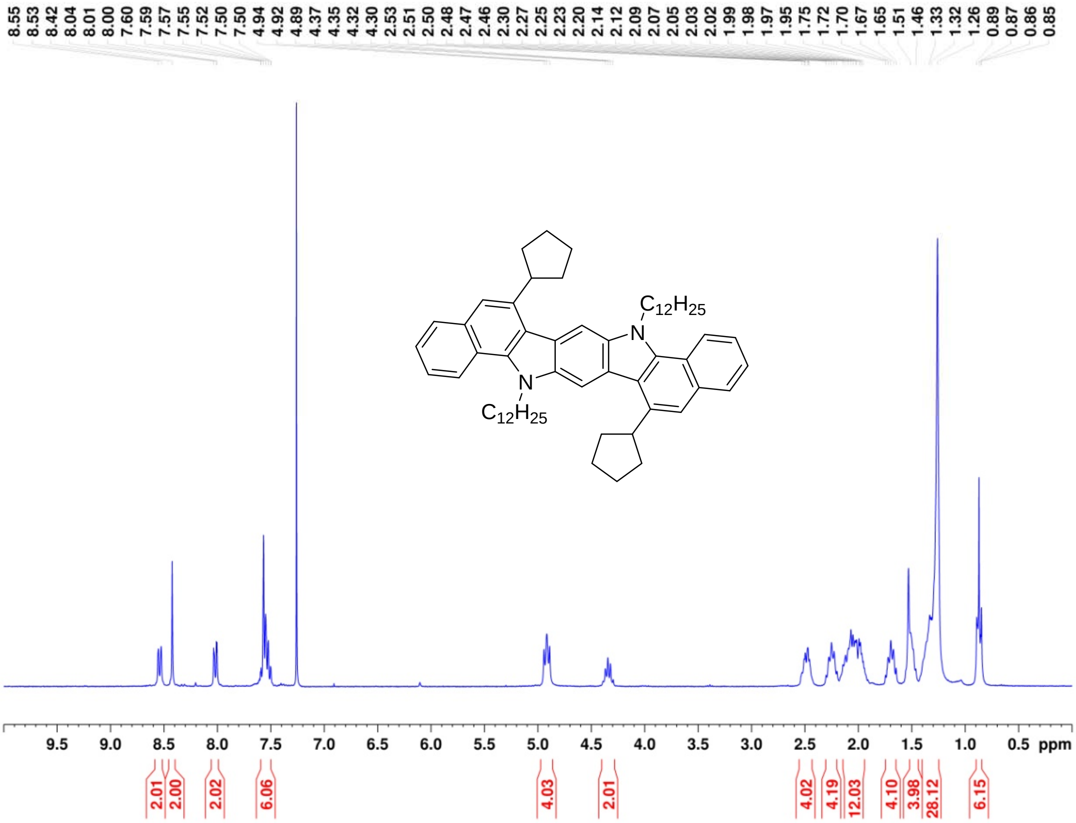
$^{13}$C NMR spectrum of **4b** in $CD_2Cl_2$ at 150.9 MHz



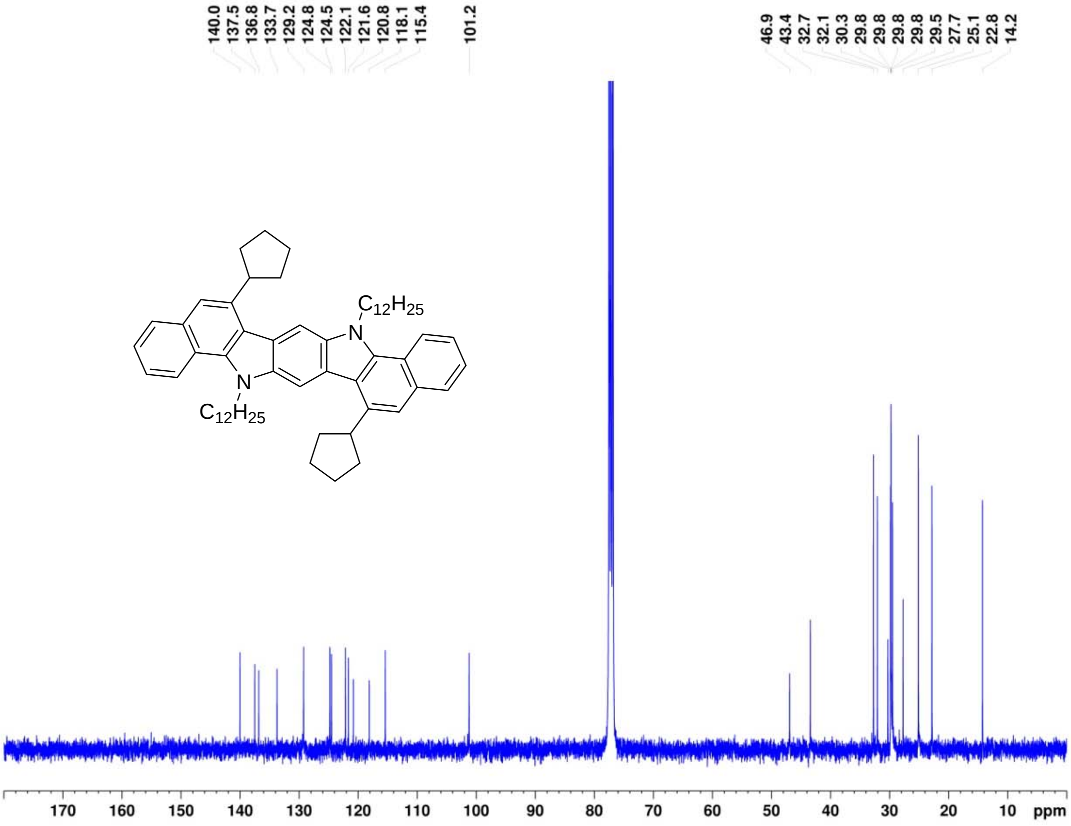
$^{1}$H NMR spectrum of **4d** in $CDCl_3$ at 300.5 MHz



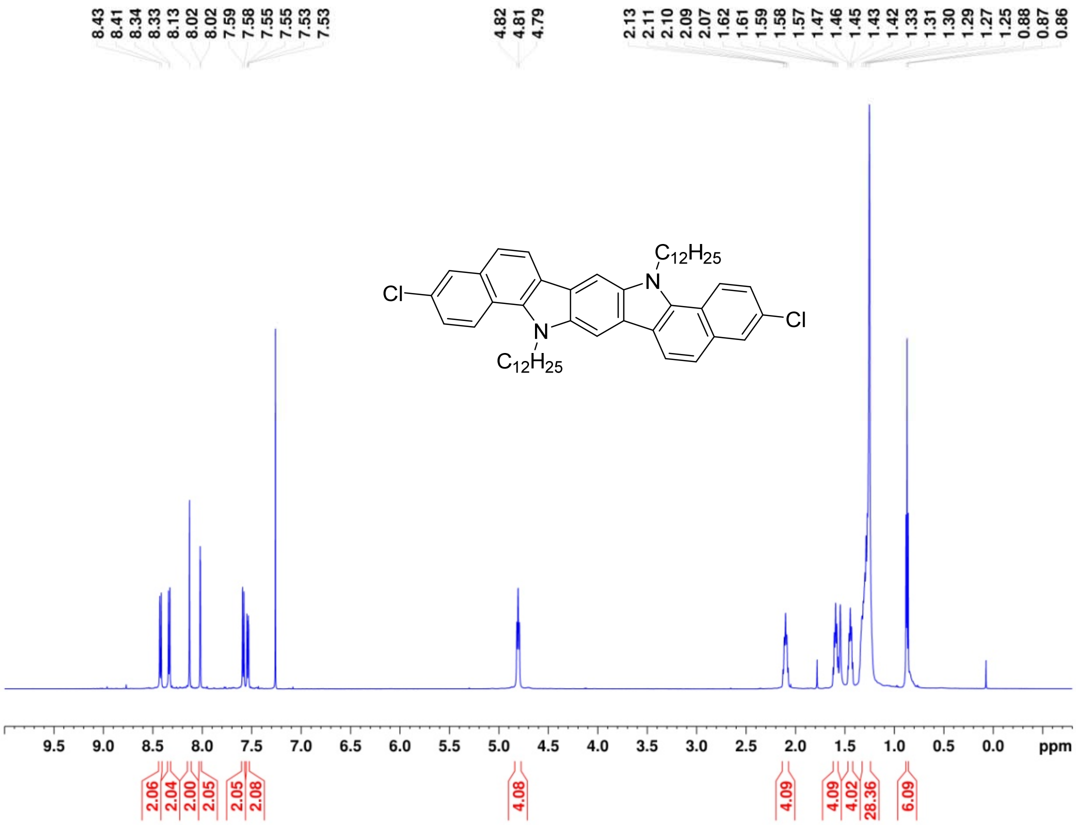
$^{13}$C NMR spectrum of **4d** in $CDCl_3$ at 75.6 MHz



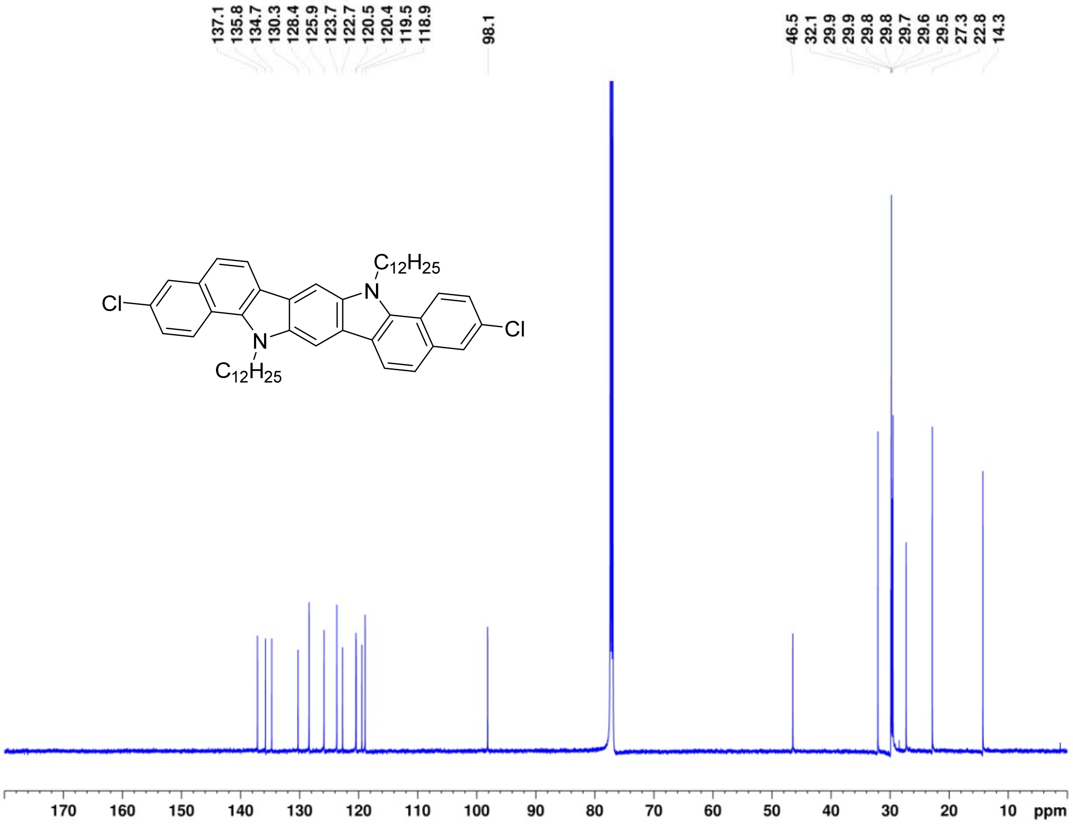
$^1$H NMR spectrum of **4e** in CDCl$_3$ at 300.5 MHz



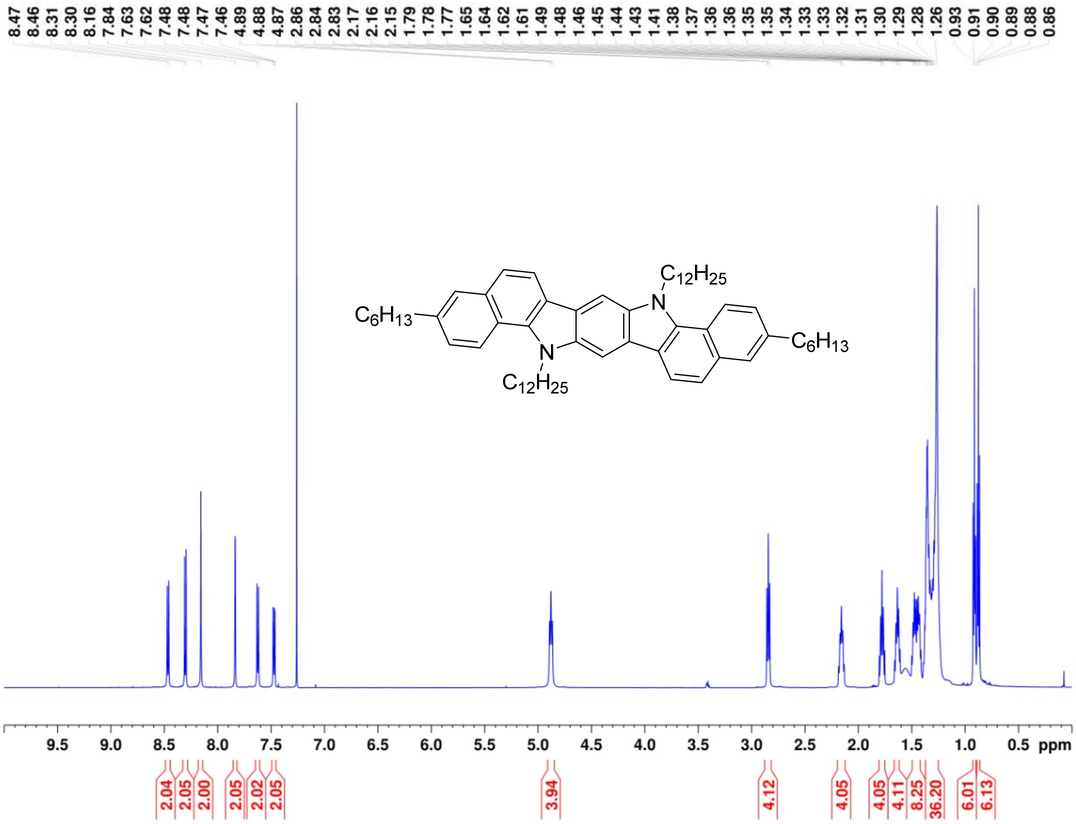
$^{13}$C NMR spectrum of **4e** in CDCl$_3$ at 100.7 MHz



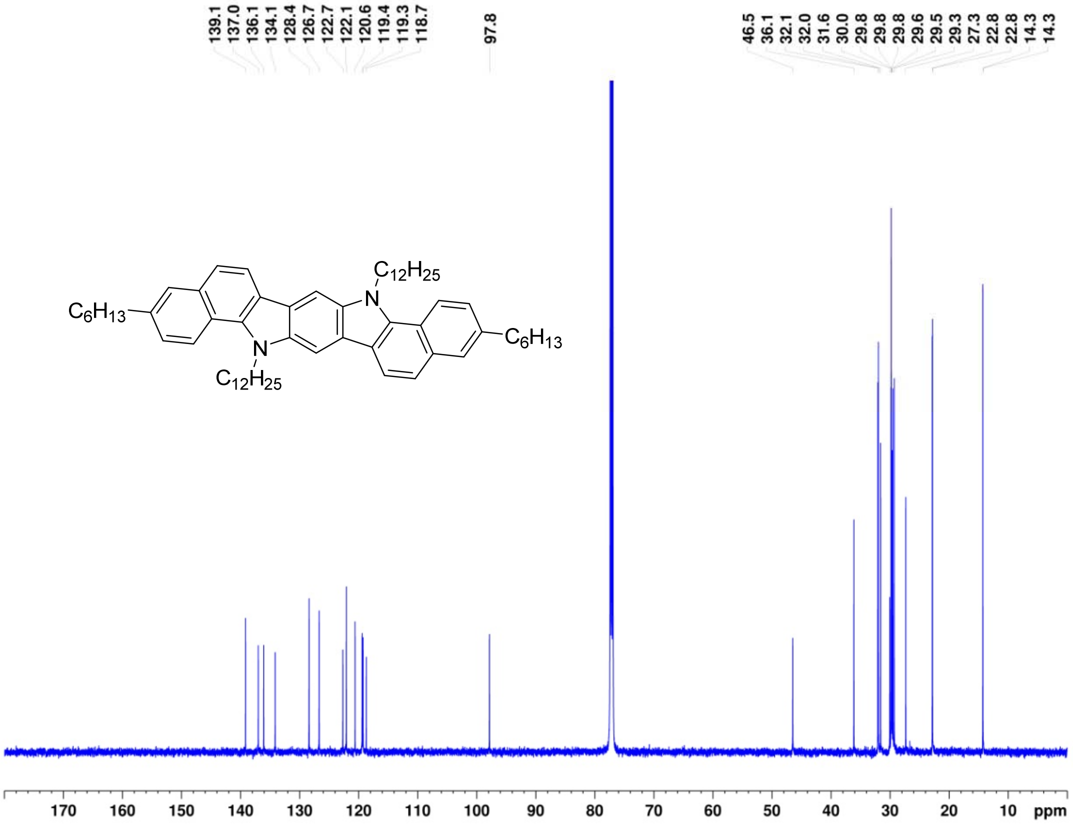
$^{1}$H NMR spectrum of **4f** in $CDCl_3$ at 600.2 MHz



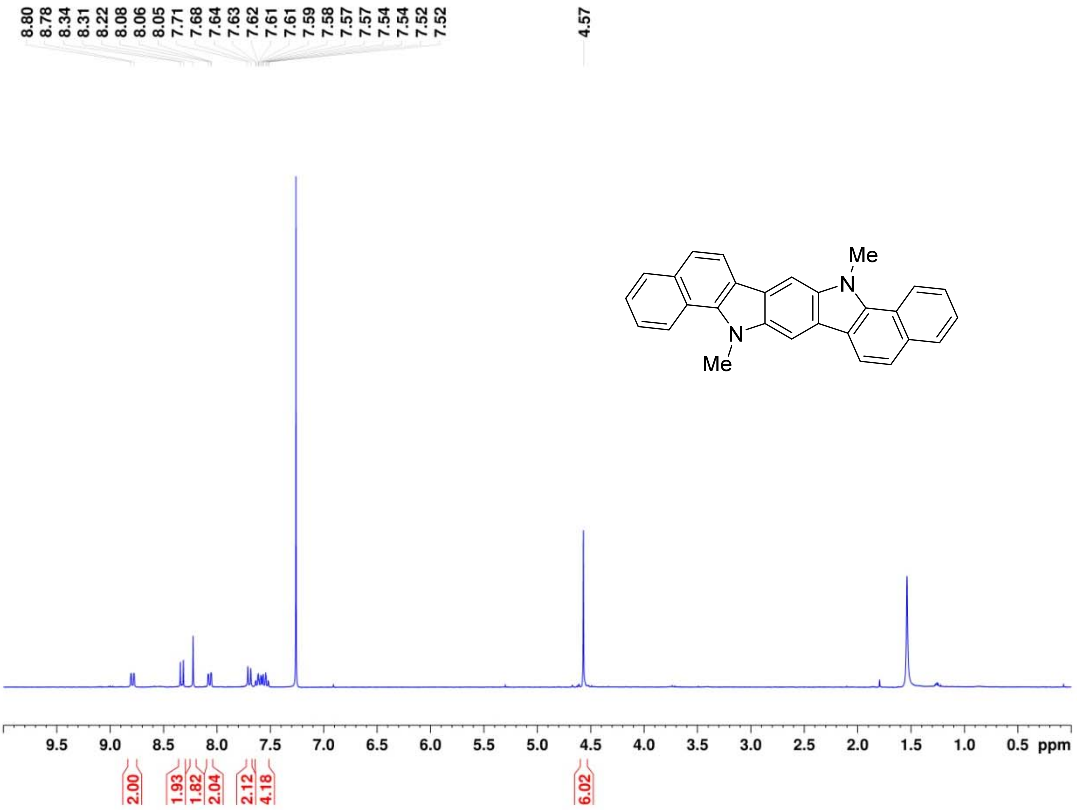
$^{13}$C NMR spectrum of **4f** in $CDCl_3$ at 150.9 MHz



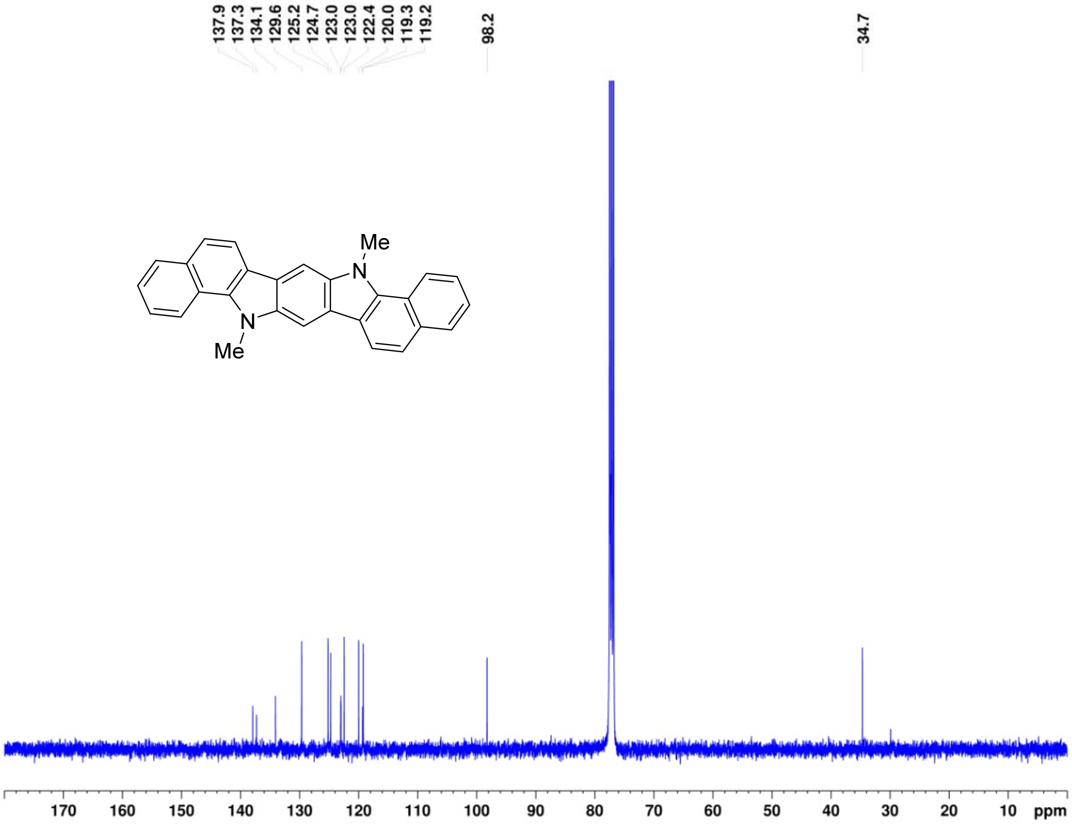
$^1H$ NMR spectrum of **4g** in $CDCl_3$ at 600.2 MHz



$^{13}C$ NMR spectrum of **4g** in $CDCl_3$ at 150.9 MHz



$^{1}$H NMR spectrum of **4h** in CDCl$_3$ at 300.5 MHz



$^{13}$C NMR spectrum of **4h** in CDCl$_3$ at 100.7 MHz (T = 323 K)

## 5. UV/Vis and Fluorescence Spectra

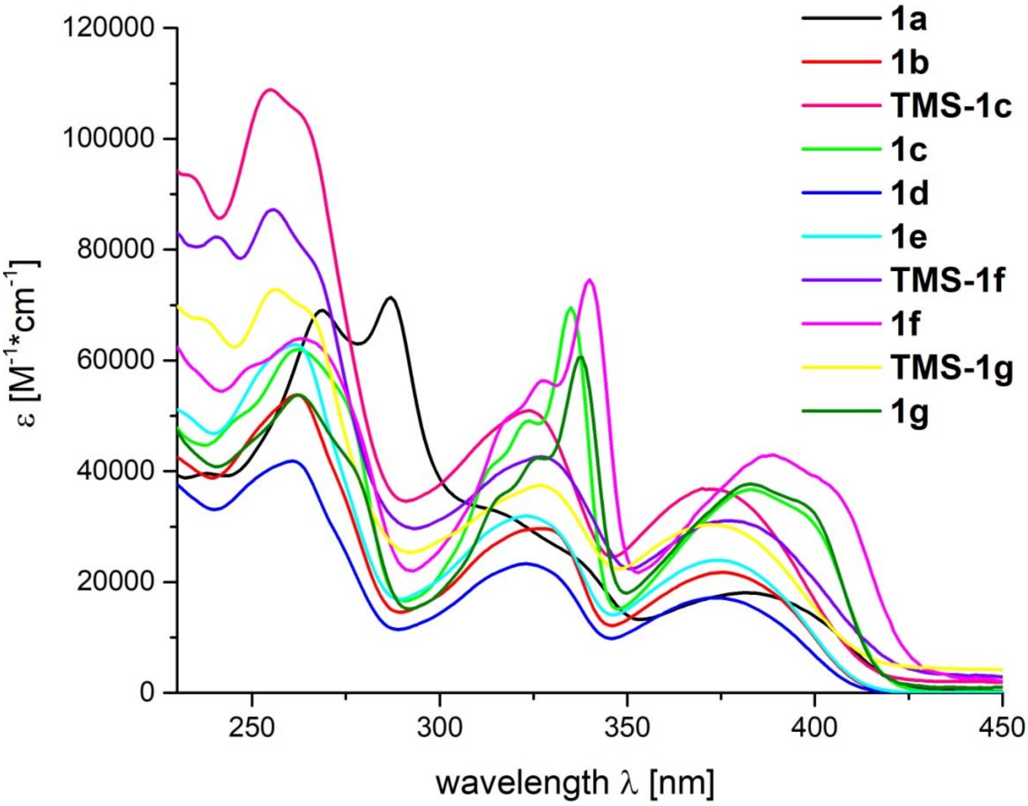


Figure SI1: Absorption spectra of tetraynes **1a-g** in DCM.

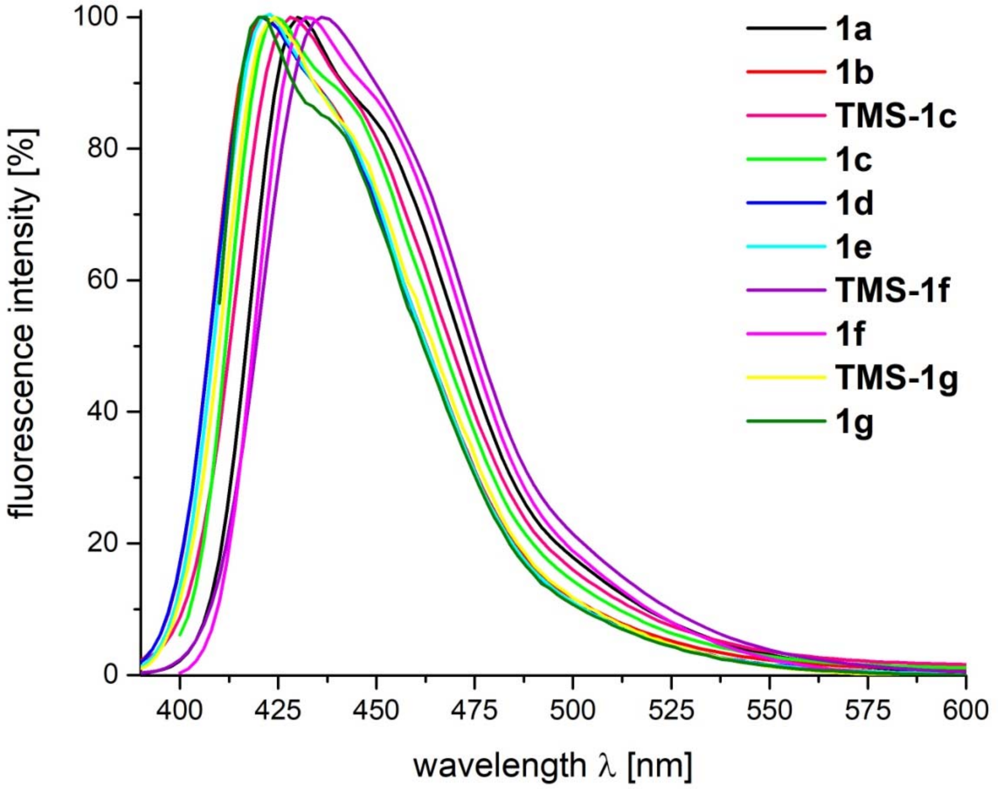


Figure SI2: Emission spectra of tetraynes **1** in DCM.

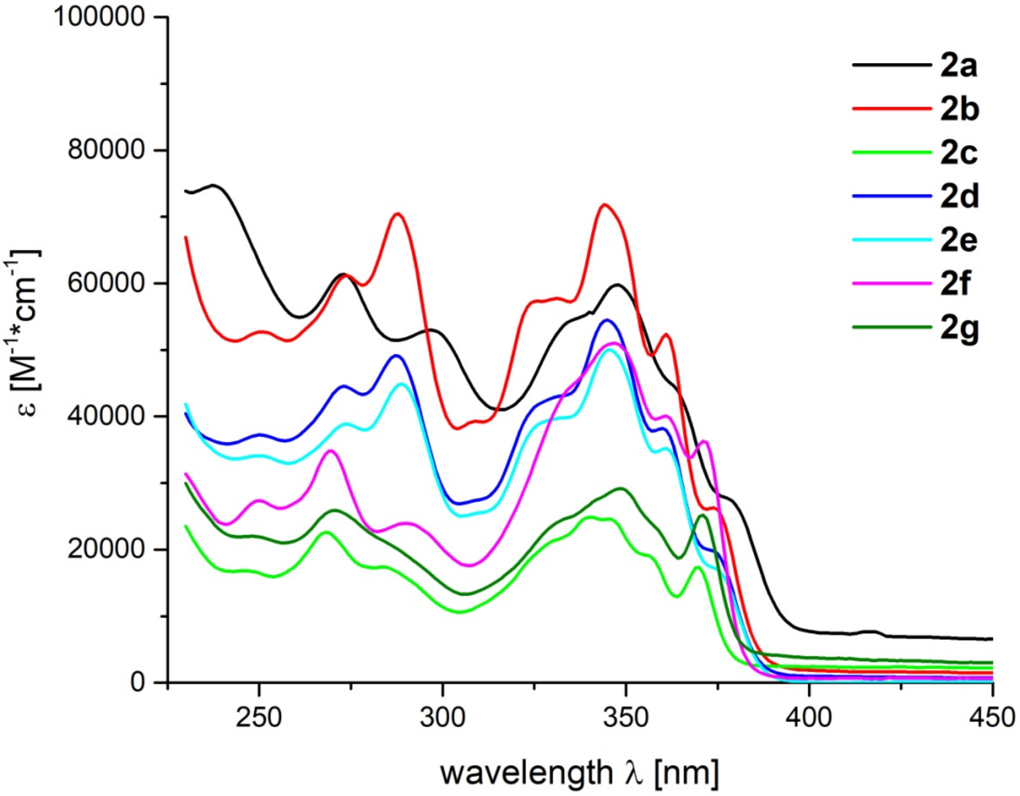


Figure SI3: Absorption spectra of Boc-BBICZs **2a-g** in DCM.

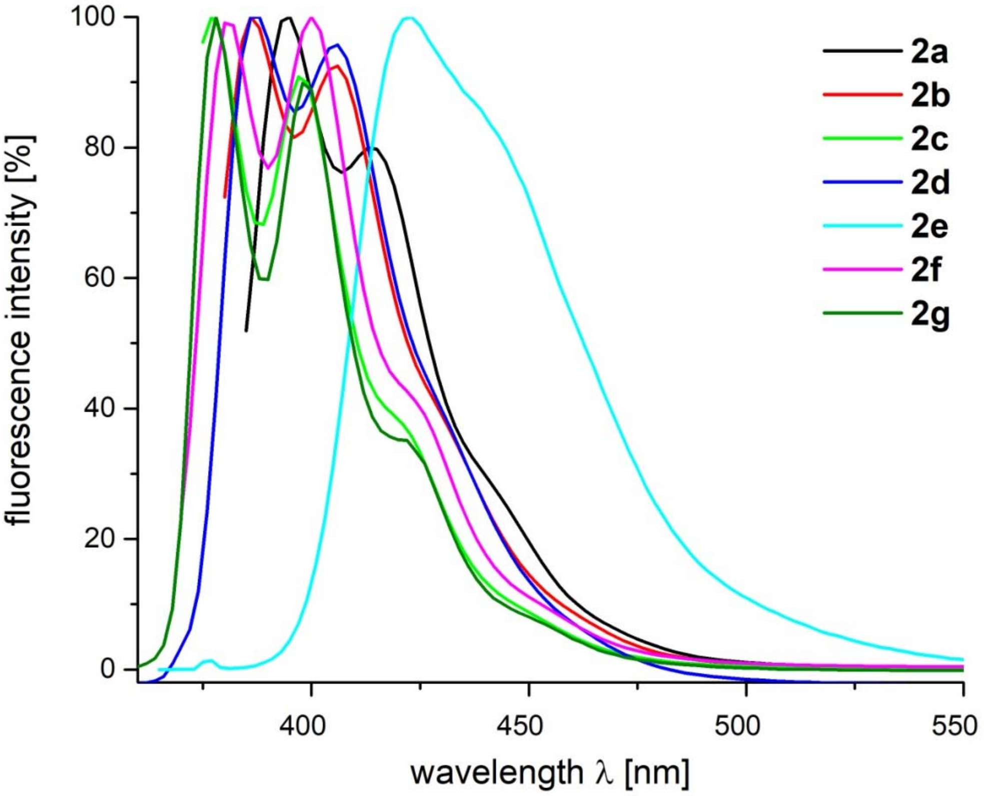


Figure SI4: Emission spectra of Boc-BBICZs **2a-g** in DCM.

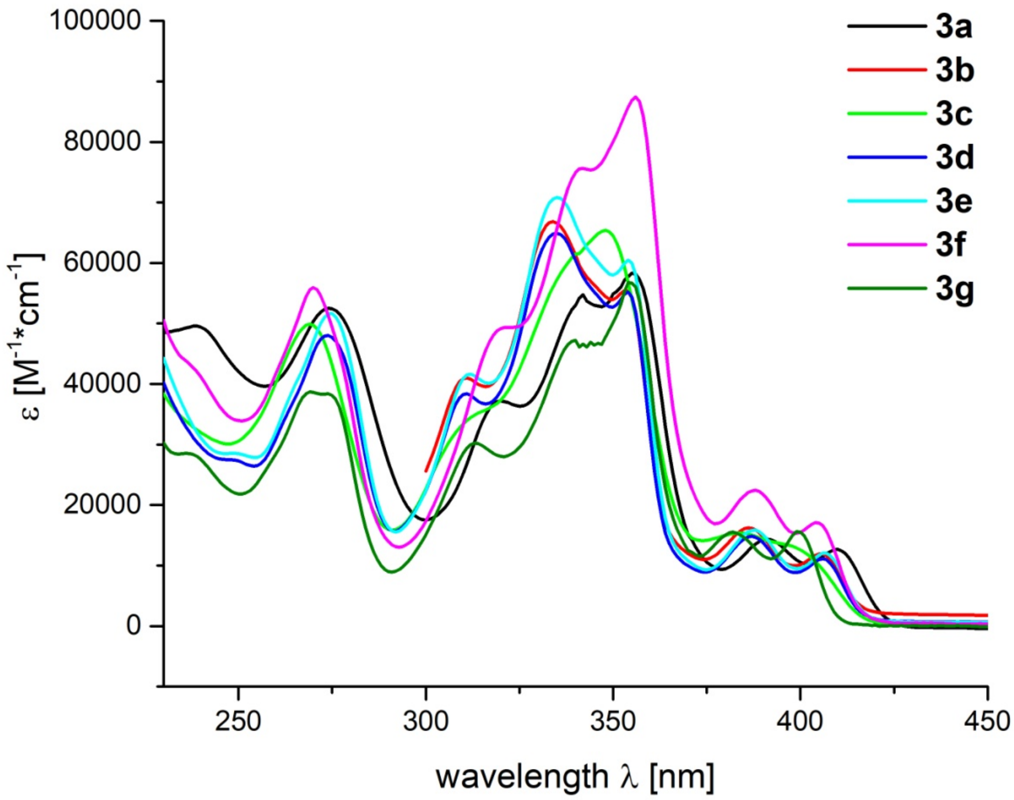


Figure SI5: Absorption spectra of BBICZs **3a-g** in THF.

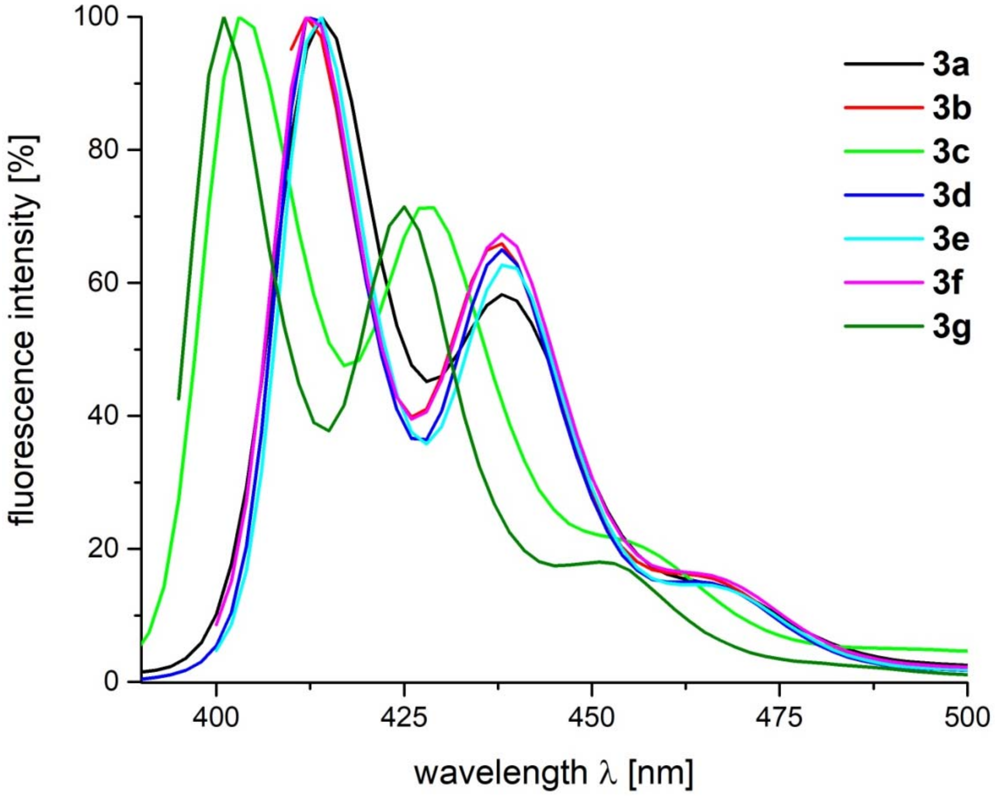


Figure SI6: Emission spectra of BBICZs **3a-g** in THF. **3a**, **3c** and **3g** were recorded in DCM.

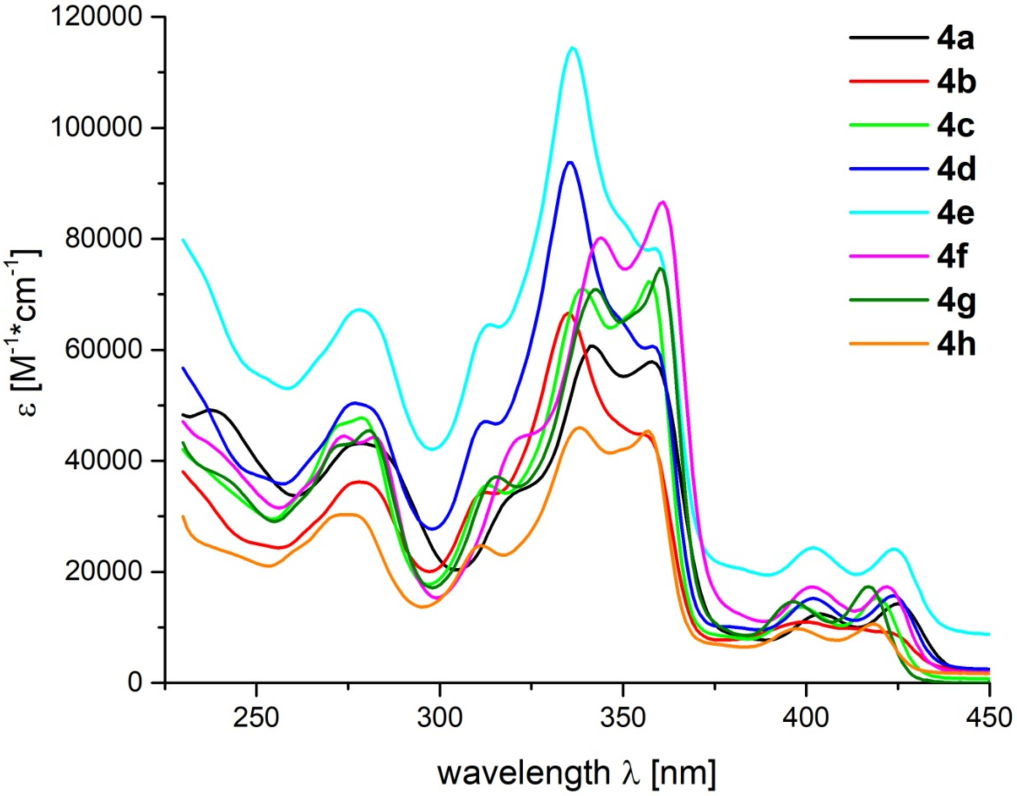


Figure SI7: Absorption spectra of BBICZs **4a-h** in DCM.

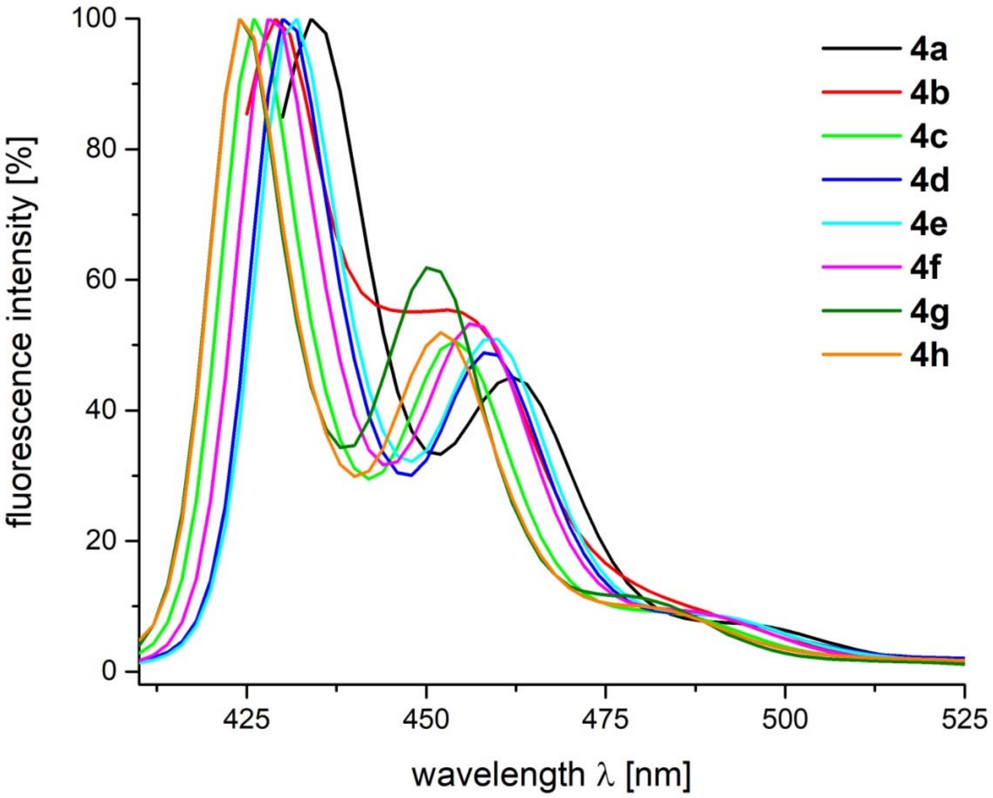
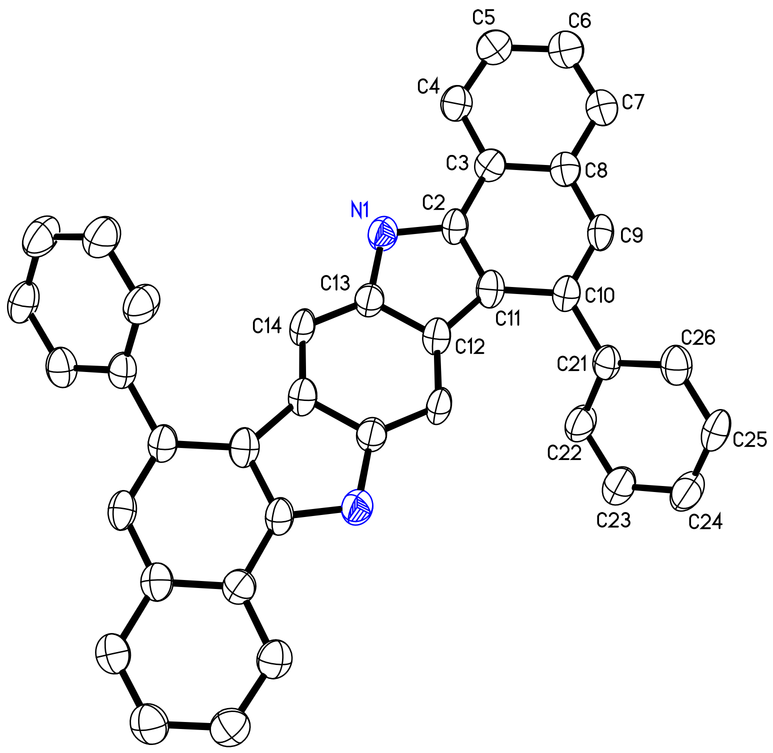


Figure SI8: Emission spectra of BBICZs **4a-h** in DCM.

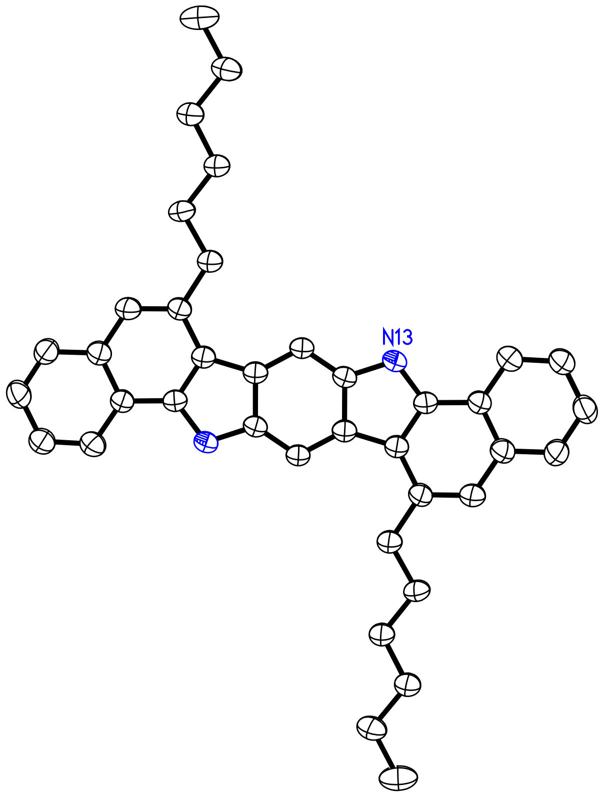
# 6 Crystallographic Data

Table SI1. Crystal data and structure refinement for **3a**. **(CCDC 2026314)**



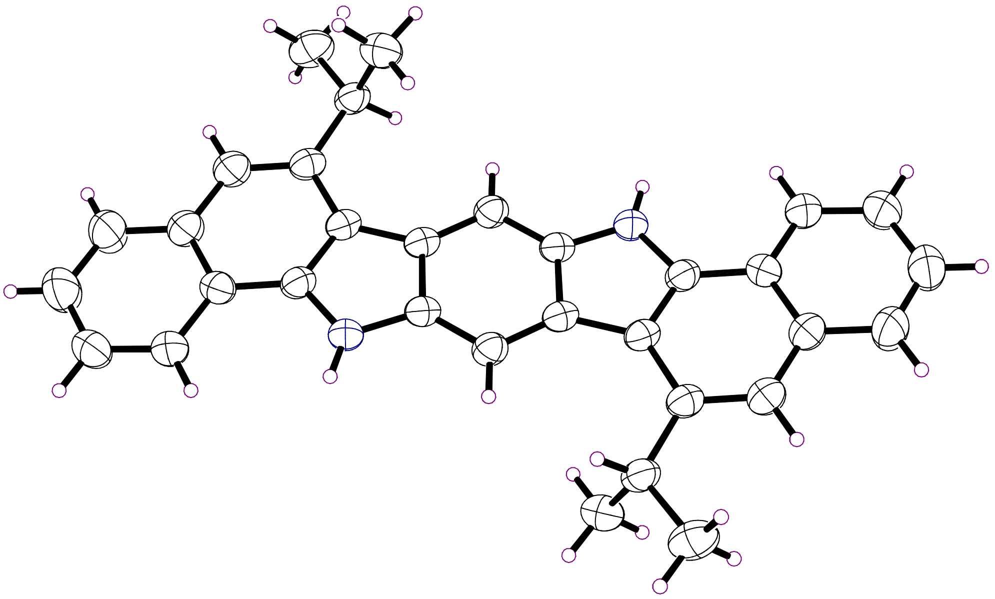
| | | |
|---|---|---|
| Empirical formula | $C_{58}H_{38}Cl_2N_3$ | |
| Formula weight | 847.81 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | triclinic | |
| Space group | $P\bar{1}$ | |
| Z | 2 | |
| Unit cell dimensions | a = 11.2603(17) Å | $\alpha$ =96.806(5) deg. |
| | b = 12.726(2) Å | $\beta$ =93.338(5) deg. |
| | c = 14.659(2) Å | $\gamma$ =91.020(6) deg. |
| Volume | 2081.6(6) Å$^3$ | |
| Density (calculated) | 1.35 g/cm$^3$ | |
| Absorption coefficient | 0.20 mm$^{-1}$ | |
| Crystal shape | octahedron | |
| Crystal size | 0.150 x 0.130 x 0.100 mm$^3$ | |
| Crystal colour | green | |
| Theta range for data collection | 1.8 to 21.0 deg. | |
| Index ranges | $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$ | |
| Reflections collected | 12478 | |
| Independent reflections | 4468 (R(int) = 0.0841) | |
| Observed reflections | 2529 ($I > 2\sigma(I)$) | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.96 and 0.88 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 4468 / 529 / 596 | |
| Goodness-of-fit on $F^2$ | 1.05 | |
| Final R indices (I>2sigma(I)) | R1 = 0.072, wR2 = 0.129 | |
| Largest diff. peak and hole | 0.36 and -0.26 eÅ$^{-3}$ | |

Table SI2. Crystal data and structure refinement for **3b**. **(CCDC 2026317)**



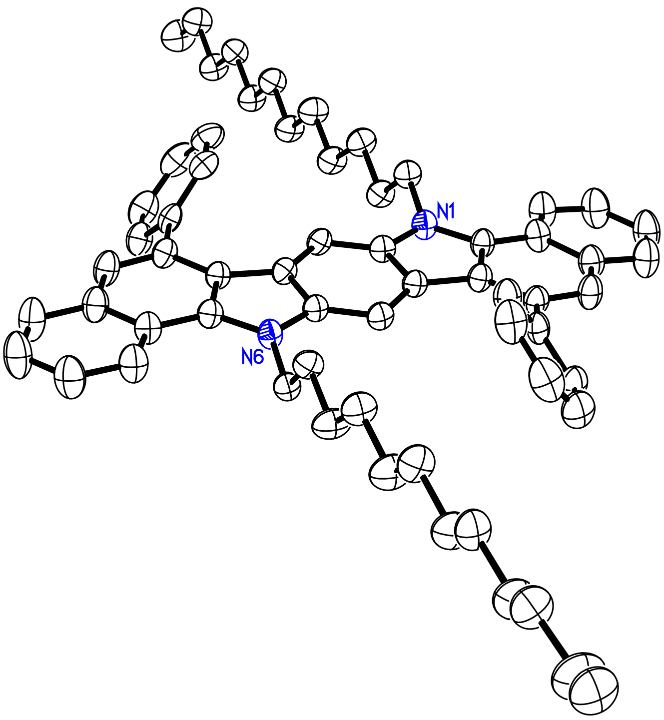
| | | |
|---|---|---|
| Empirical formula | $C_{42}H_{52}N_2O_2S_2$ | |
| Formula weight | 680.97 | |
| Temperature | 240(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | triclinic | |
| Space group | $P\bar{1}$ | |
| Z | 1 | |
| Unit cell dimensions | a =7.1998(12) Å | $\alpha$ =93.092(12) deg. |
| | b =8.8993(13) Å | $\beta$ =94.325(13) deg. |
| | c = 15.782(3) Å | $\gamma$ =112.254(11) deg. |
| Volume | 929.5(3) $Å^3$ | |
| Density (calculated) | 1.22 $g/cm^3$ | |
| Absorption coefficient | 1.58 $mm^{-1}$ | |
| Crystal shape | plate | |
| Crystal size | 0.120 x 0.070 x 0.018 $mm^3$ | |
| Crystal colour | colourless | |
| Theta range for data collection | 2.8 to 68.7 deg. | |
| Index ranges | $-4 \leq h \leq 8$, $-10 \leq k \leq 10$, $-18 \leq l \leq 18$ | |
| Reflections collected | 14786 | |
| Independent reflections | 3345 (R(int) = 0.072) | |
| Observed reflections | 1528 ($I > 2\sigma(I)$) | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.50 and 0.55 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 14786 / 296 / 260 | |
| Goodness-of-fit on $F^2$ | 1.44 | |
| Final R indices (I>2sigma(I)) | R1 = 0.096, wR2 = 0.234 | |
| Largest diff. peak and hole | 0.40 and -0.50 $eÅ^{-3}$ | |

Table SI3. Crystal data and structure refinement for **3d**. **(CCDC 2026316)**



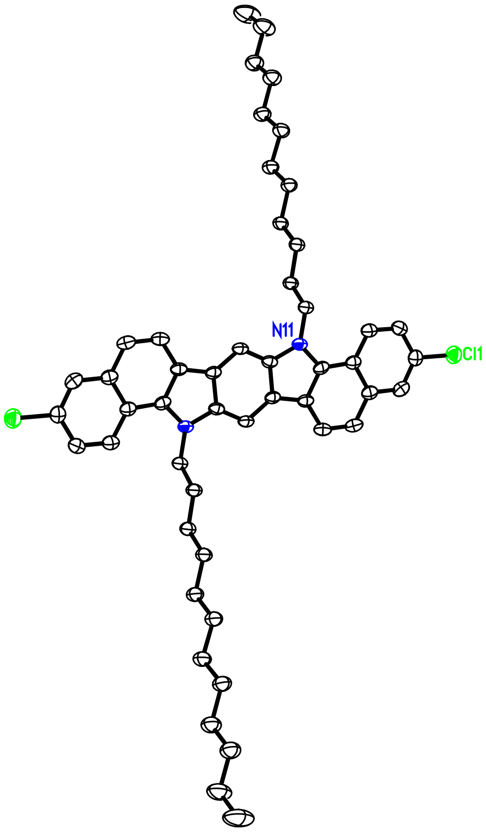
| | | |
|---|---|---|
| Empirical formula | $C_{32}H_{28}N_2$ | |
| Formula weight | 440.56 | |
| Temperature | 299(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Z | 2 | |
| Unit cell dimensions | a = 14.1488(12) Å | $\alpha$ = 90 deg. |
| | b =5.3212(4) Å | $\beta$ =100.246(3) deg. |
| | c = 15.6229(13) Å | $\gamma$ = 90 deg. |
| Volume | 1157.47(16) Å$^3$ | |
| Density (calculated) | 1.26 g/cm$^3$ | |
| Absorption coefficient | 0.07 mm$^{-1}$ | |
| Crystal shape | plate | |
| Crystal size | 0.180 x 0.168 x 0.043 mm$^3$ | |
| Crystal colour | purple | |
| Theta range for data collection | 1.8 to 25.1 deg. | |
| Index ranges | $-16\leq h\leq 16$, $-6\leq k\leq 6$, $-16\leq l\leq 18$ | |
| Reflections collected | 7031 | |
| Independent reflections | 2065 (R(int) = 0.0605) | |
| Observed reflections | 1129 (I > 2\s(I)) | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.96 and 0.85 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data/restraints/parameters | 2065 / 0 / 156 | |
| Goodness-of-fit on F$^2$ | 0.98 | |
| Final R indices (I>2sigma(I)) | R1 = 0.059, wR2 = 0.124 | |
| Largest diff. peak and hole | 0.16 and -0.20 eÅ$^{-3}$ | |

Table SI4. Crystal data and structure refinement for **4a**. **(CCDC 2026315)**



| | | |
|---|---|---|
| Empirical formula | $C_{62}H_{72}N_2$ | |
| Formula weight | 845.21 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group | $P2_1/c$ | |
| Z | 4 | |
| Unit cell dimensions | a =8.9592(4) Å | $\alpha$ = 90 deg. |
| | b = 24.3232(11) Å | $\beta$ =93.0947(12) deg. |
| | c = 22.4162(10) Å | $\gamma$ = 90 deg. |
| Volume | 4877.7(4) Å$^3$ | |
| Density (calculated) | 1.15 g/cm$^3$ | |
| Absorption coefficient | 0.06 mm$^{-1}$ | |
| Crystal shape | needle | |
| Crystal size | 0.380 x 0.070 x 0.040 mm$^3$ | |
| Crystal colour | yellow | |
| Theta range for data collection | 1.2 to 25.1 deg. | |
| Index ranges | $-10\leq h\leq 10$, $-28\leq k\leq 28$, $-26\leq l\leq 23$ | |
| Reflections collected | 31077 | |
| Independent reflections | 8627 (R(int) = 0.0348) | |
| Observed reflections | 5700 ($I > 2\sigma(I)$) | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.96 and 0.90 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data/restraints/parameters | 8627 / 0 / 579 | |
| Goodness-of-fit on F$^2$ | 1.03 | |
| Final R indices (I>2sigma(I)) | R1 = 0.055, wR2 = 0.140 | |
| Largest diff. peak and hole | 0.34 and -0.26 eÅ$^{-3}$ | |

Table SI5. Crystal data and structure refinement for **4f**. **(CCDC 2026318)**



| | | |
|---|---|---|
| Empirical formula | $C_{50}H_{62}Cl_2N_2$ | |
| Formula weight | 761.91 | |
| Temperature | 200(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group | $P2_1/n$ | |
| Z | 2 | |
| Unit cell dimensions | a = 20.0563(6) Å | $\alpha$ = 90 deg. |
| | b =5.2704(1) Å | $\beta$ =104.2280(15) deg. |
| | c = 20.7737(6) Å | $\gamma$ = 90 deg. |
| Volume | 2128.52(10) Å$^3$ | |
| Density (calculated) | 1.19 g/cm$^3$ | |
| Absorption coefficient | 0.19 mm$^{-1}$ | |
| Crystal shape | plank | |
| Crystal size | 0.149 x 0.072 x 0.020 mm$^3$ | |
| Crystal colour | yellow | |
| Theta range for data collection | 1.3 to 25.0 deg. | |
| Index ranges | $-23 \le h \le 23$, $-6 \le k \le 6$, $-24 \le l \le 24$ | |
| Reflections collected | 23711 | |
| Independent reflections | 3759 (R(int) = 0.0607) | |
| Observed reflections | 2569 (I > 2$\sigma$(I)) | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.96 and 0.91 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data/restraints/parameters | 3759 / 0 / 244 | |
| Goodness-of-fit on F$^2$ | 1.03 | |
| Final R indices (I>2sigma(I)) | R1 = 0.045, wR2 = 0.093 | |
| Largest diff. peak and hole | 0.19 and -0.21 eÅ$^{-3}$ | |

## 7. Cyclic Voltammograms

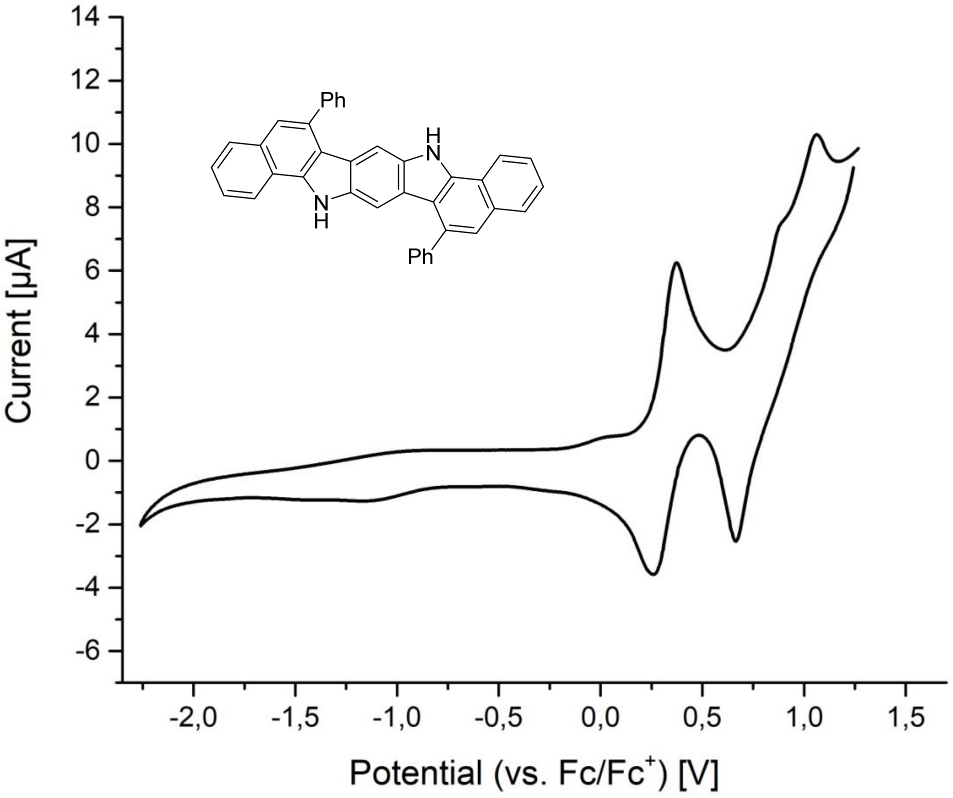


Figure SI9: Cyclic voltamogram of compound **3a** in DCM against ferrocen/ferrocenium (Fc/Fc$^+$).

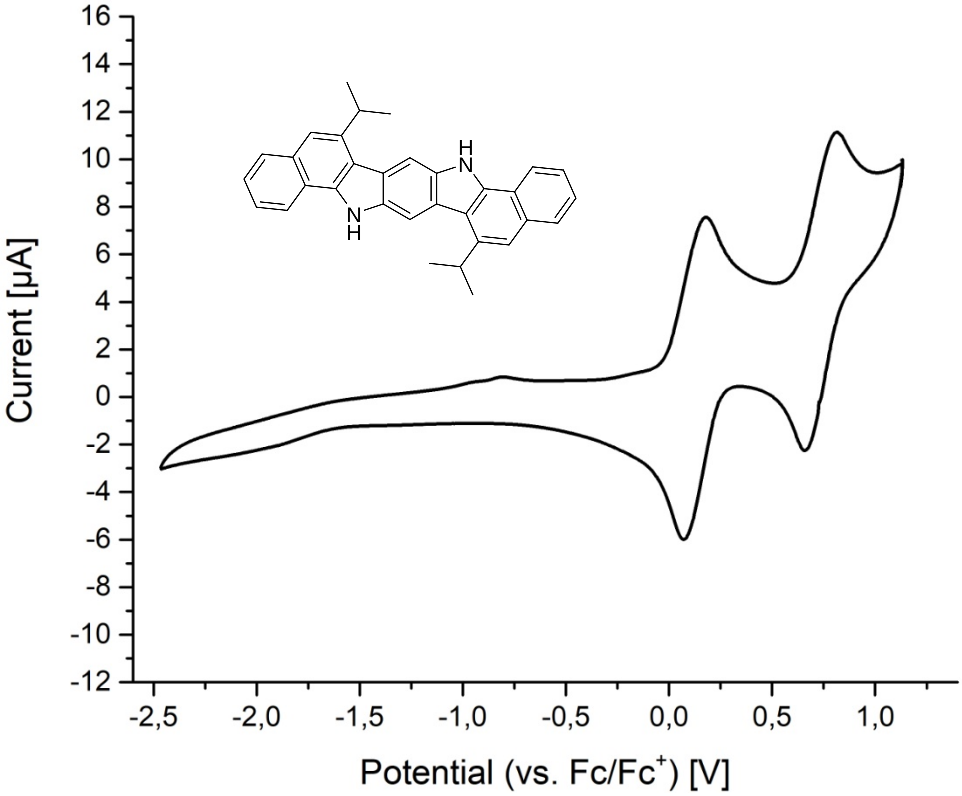


Figure SI10: Cyclic voltamogram of compound **3d** in DCM against ferrocen/ferrocenium (Fc/Fc$^+$).

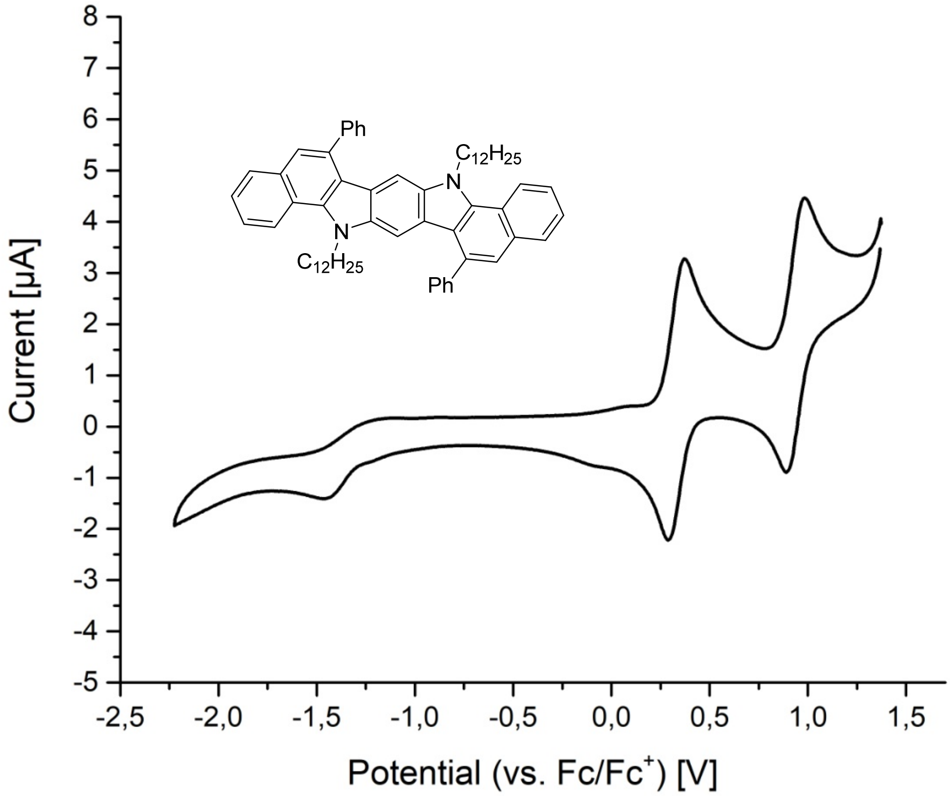


Figure SI11: Cyclic voltamogram of compound **4a** in DCM against ferrocen/ferrocenium (Fc/Fc$^+$). As working electrode a glassy carbon electrode was used.

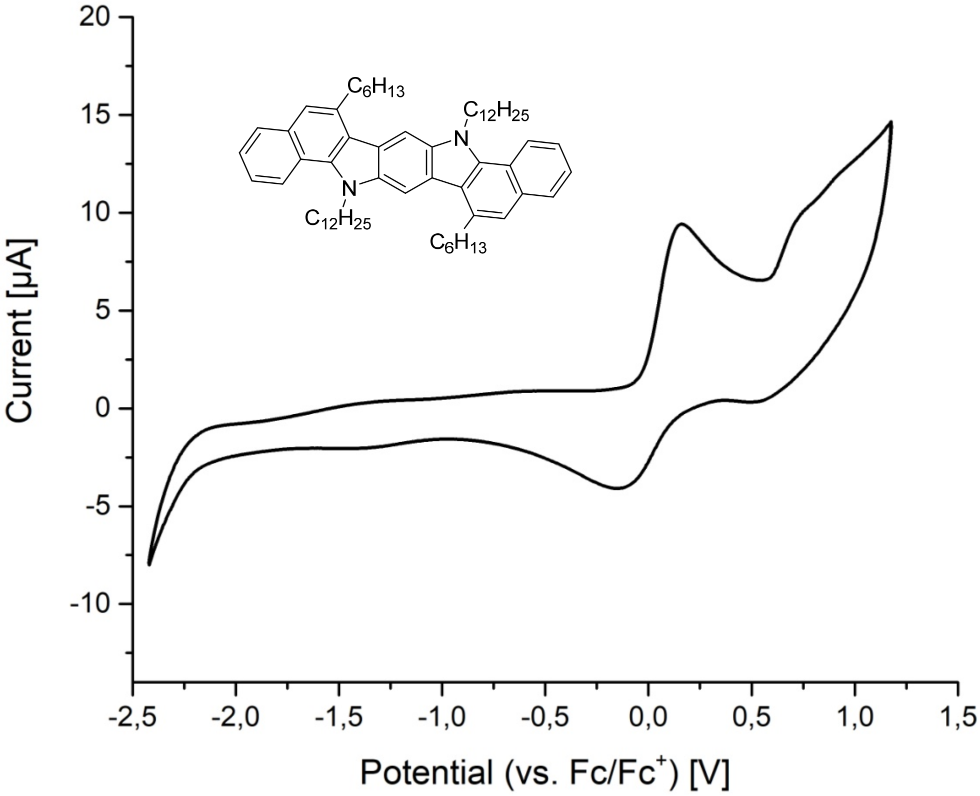


Figure SI12: Cyclic voltamogram of compound **4b** in DCM against ferrocen/ferrocenium (Fc/Fc$^+$).

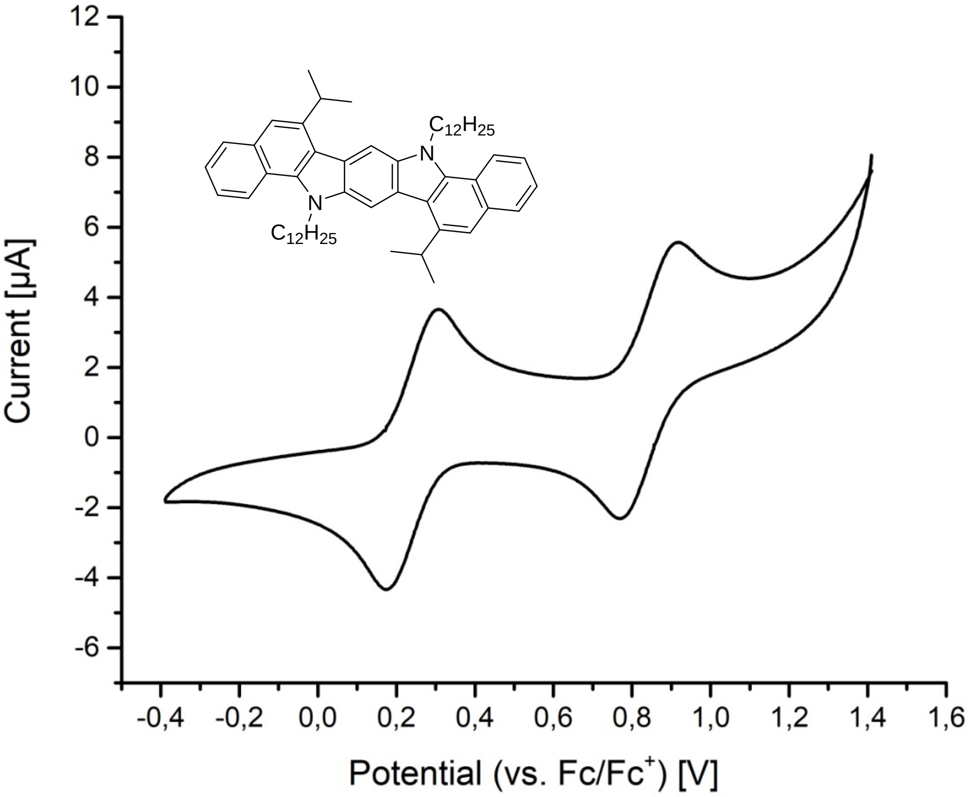


Figure SI13: Cyclic voltamogram of compound **4d** in DCM against ferrocen/ferrocenium (Fc/Fc$^+$).

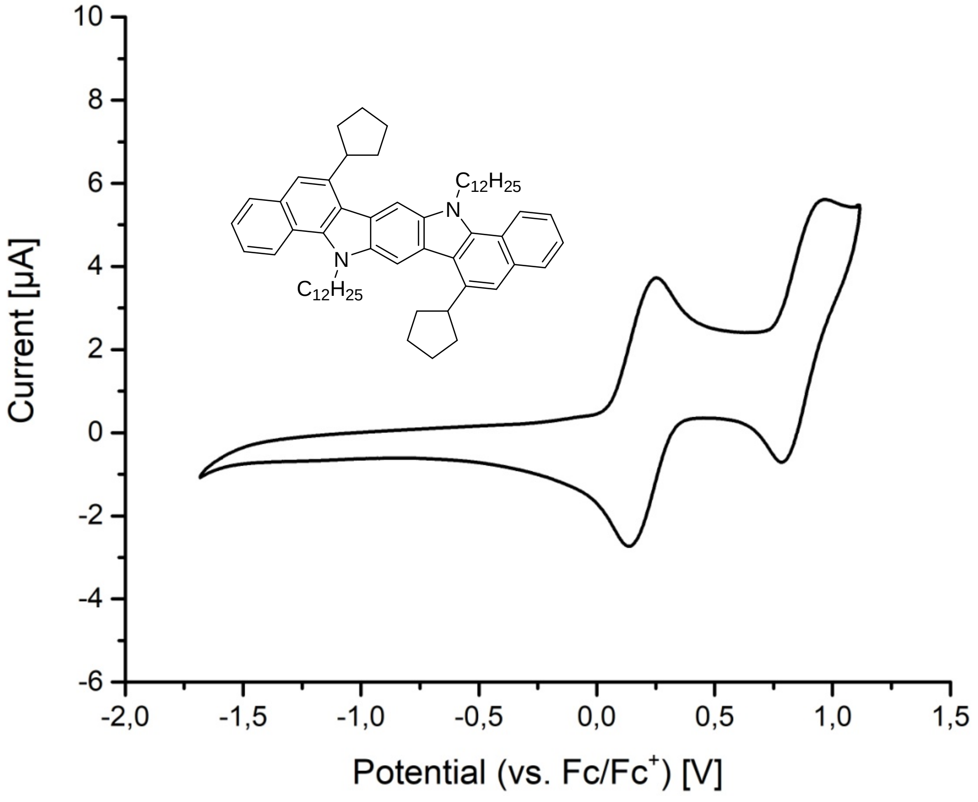


Figure SI14: Cyclic voltamogram of compound **4e** in DCM against ferrocen/ferrocenium (Fc/Fc$^+$).

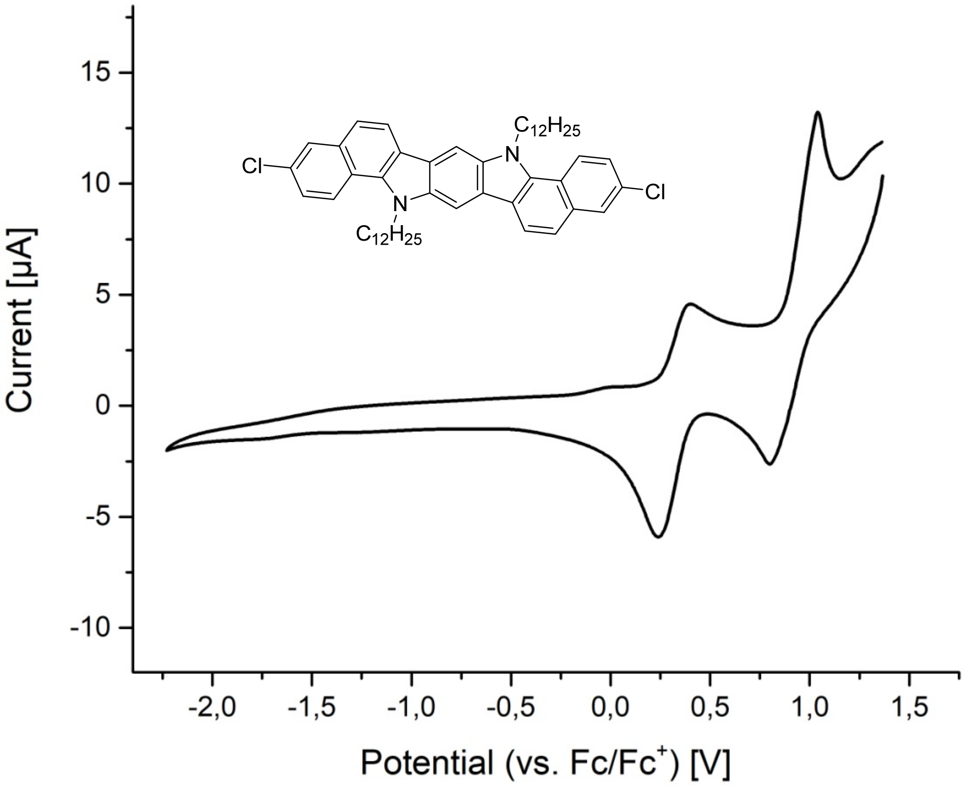


Figure SI15: Cyclic voltamogram of compound **4f** in DCM against ferrocen/ferrocenium (Fc/Fc$^+$).

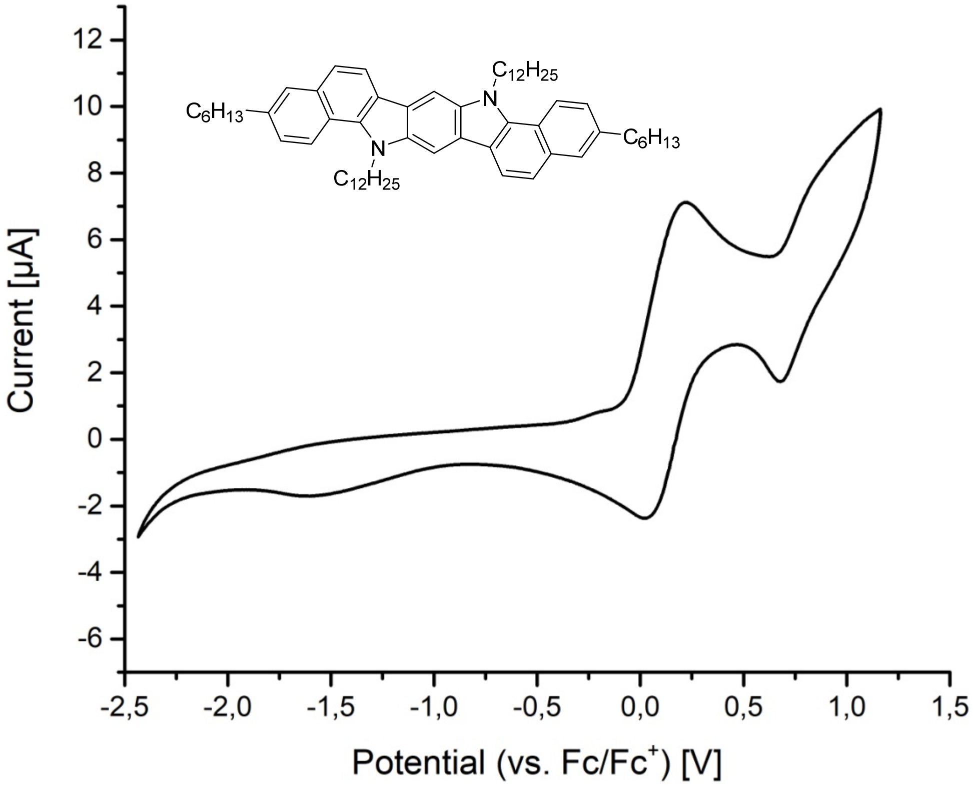


Figure SI16: Cyclic voltamogram of compound **4g** in DCM against ferrocen/ferrocenium (Fc/Fc$^+$).

## 8. Computational Details

Optimizations and subsequent single-point calculations of the structures for both the neutral as well as cationic species were conducted on the PBE0-D3/aug-pc-1 level of theory using the TeraChem[12] software package. Excited state calculations as well as exciton analyses using time dependent density functional theory employing the Tamm-Dancoff approximation on the wB97X-D3/aug-pc-1 level of theory were performed with the Q-Chem[13] software package.

The reorganization energy was calculated using the 4-point approximation:

$$\lambda = \lambda_1 + \lambda_2 = (E^{+}_{(neutral)} - E^{+}_{(cation)}) + (E_{(cation)} - E_{(neutral)})$$

### Optimized Structures

**3a** (neutral)

| | | | |
|---|---|---|---|
| N | 1.0761015982 | 15.3841750457 | 9.3519685868 |
| C | 1.2504229105 | 16.5955181655 | 9.9720274894 |
| C | 1.6903359214 | 16.3795445516 | 11.2848864914 |
| C | 1.9545500882 | 17.4909530043 | 12.1291748673 |
| C | 1.8102506633 | 18.7572982320 | 11.6147402622 |
| H | 2.0023901815 | 19.6175252154 | 12.2534711316 |
| N | 2.6798823208 | 11.7547386725 | 13.1053435371 |
| C | 2.5468264943 | 10.5455281678 | 12.4714422922 |
| C | 2.0156889638 | 10.7549509814 | 11.1909214467 |
| C | 1.8001323915 | 9.6446880428 | 10.3313060062 |
| C | 2.1525552640 | 8.3919835416 | 10.7741349467 |
| H | 1.9847435830 | 7.5324130559 | 10.1277760590 |
| C | 1.4225617933 | 14.3621310324 | 10.2185076323 |
| C | 1.8210159104 | 14.9514969917 | 11.4548100653 |
| C | 2.2672084548 | 14.1364269472 | 12.4968602503 |
| H | 2.6014548328 | 14.5535373998 | 13.4420195349 |
| C | 2.2726877021 | 12.7722503978 | 12.2606418260 |

| | | | |
|---|---|---|---|
| C | 1.8469922719 | 12.1808045675 | 11.0345431730 |
| C | 1.4210002376 | 12.9973743635 | 9.9850623944 |
| H | 1.1129848447 | 12.5820958229 | 9.0303402198 |
| C | 1.0665685352 | 17.8883383776 | 9.4260254430 |
| C | 1.3716332755 | 18.9875661699 | 10.2815099380 |
| C | 1.2108672906 | 20.2950179317 | 9.7698950270 |
| H | 1.4399927538 | 21.1389999657 | 10.4185304522 |
| C | 0.7742529833 | 20.5098665042 | 8.4841048048 |
| H | 0.6580048051 | 21.5253614703 | 8.1117978219 |
| C | 0.4750272916 | 19.4184722786 | 7.6453870613 |
| H | 0.1280954010 | 19.5933696514 | 6.6294025118 |
| C | 0.6192473535 | 18.1327888597 | 8.1104932255 |
| H | 0.3831332172 | 17.2958781766 | 7.4553875980 |
| C | 2.3557619202 | 17.2895245105 | 13.5390187594 |
| C | 1.4894773566 | 16.6503247384 | 14.4310422109 |
| H | 0.5202982604 | 16.3070127306 | 14.0740877239 |
| C | 1.8596053774 | 16.4498250046 | 15.7545782997 |
| H | 1.1720960544 | 15.9564789930 | 16.4389331202 |
| C | 3.1042267405 | 16.8821730571 | 16.2058276391 |
| H | 3.3958538403 | 16.7219295778 | 17.2418557827 |
| C | 3.9704296660 | 17.5232637781 | 15.3265537901 |
| H | 4.9452454175 | 17.8623544216 | 15.6716263338 |
| C | 3.5972359734 | 17.7284043900 | 14.0021624304 |
| H | 4.2784405947 | 18.2165352292 | 13.3080177971 |
| C | 2.8946901322 | 9.2638627192 | 12.9609532118 |
| C | 2.6946138487 | 8.1692841639 | 12.0695395229 |
| C | 3.0357831632 | 6.8730338725 | 12.5167457519 |
| H | 2.8823437922 | 6.0329210872 | 11.8413340018 |

| | | | |
|---|---|---|---|
| C | 3.5503512472 | 6.6644491922 | 13.7743416623 |
| H | 3.8061115127 | 5.6576672542 | 14.0973456843 |
| C | 3.7459165951 | 7.7512053115 | 14.6490348130 |
| H | 4.1514099435 | 7.5810610264 | 15.6439272718 |
| C | 3.4229398984 | 9.0257817933 | 14.2475435436 |
| H | 3.5731868863 | 9.8581950285 | 14.9330088462 |
| C | 1.1992298098 | 9.8174966284 | 8.9904894009 |
| C | -0.0942243759 | 10.3293720477 | 8.8517240435 |
| H | -0.6530058469 | 10.6080295875 | 9.7432543451 |
| C | -0.6638799245 | 10.4774128829 | 7.5934407722 |
| H | -1.6748578349 | 10.8696575766 | 7.5017314738 |
| C | 0.0518760686 | 10.1185100292 | 6.4538512444 |
| H | -0.3943370084 | 10.2354998182 | 5.4683447527 |
| C | 1.3383202442 | 9.6061746601 | 6.5827466373 |
| H | 1.9051033527 | 9.3255486903 | 5.6971473447 |
| C | 1.9068647695 | 9.4547270390 | 7.8430472736 |
| H | 2.9176580471 | 9.0651494141 | 7.9466455483 |
| H | 0.8102538902 | 15.2525986219 | 8.3916560545 |
| H | 3.0756204472 | 11.8952458826 | 14.0185832497 |

**3a** (cation)

| | | | |
|---|---|---|---|
| N | 1.0462631312 | 15.3906764192 | 9.3699626026 |
| C | 1.1964631889 | 16.5908532221 | 9.9841770298 |
| C | 1.6588066788 | 16.3680986313 | 11.3078023927 |
| C | 1.9100964791 | 17.4654991212 | 12.1653295237 |
| C | 1.7277430497 | 18.7305713266 | 11.6574710460 |
| H | 1.9175406969 | 19.5891821290 | 12.2989388133 |

| | | | |
|---|---|---|---|
| N | 2.7097284123 | 11.7559377616 | 13.0878453433 |
| C | 2.5843025658 | 10.5573867854 | 12.4657254846 |
| C | 2.0417172800 | 10.7727781840 | 11.1706711863 |
| C | 1.8266706700 | 9.6756000736 | 10.3027385740 |
| C | 2.1889791521 | 8.4256984600 | 10.7493296856 |
| H | 2.0334814976 | 7.5685989175 | 10.0966928950 |
| C | 1.4089191713 | 14.3648308334 | 10.2265745644 |
| C | 1.8065969239 | 14.9523137512 | 11.4596635377 |
| C | 2.2693649658 | 14.1365037167 | 12.5026305115 |
| H | 2.5961031348 | 14.5590193163 | 13.4488597825 |
| C | 2.2868862024 | 12.7765669718 | 12.2532708867 |
| C | 1.8626568465 | 12.1865668335 | 11.0302878646 |
| C | 1.4179737188 | 13.0041023507 | 9.9807515381 |
| H | 1.1022420312 | 12.5823447911 | 9.0306420413 |
| C | 0.9776054476 | 17.8892313456 | 9.4528087605 |
| C | 1.2685044408 | 18.9742340759 | 10.3262236990 |
| C | 1.0800322445 | 20.2848351103 | 9.8497885987 |
| H | 1.2987244648 | 21.1211090240 | 10.5106193040 |
| C | 0.6239335815 | 20.5148509388 | 8.5675413580 |
| H | 0.4841108462 | 21.5345201614 | 8.2172321379 |
| C | 0.3388718827 | 19.4395238378 | 7.7136821682 |
| H | -0.0212008704 | 19.6271412863 | 6.7052482244 |
| C | 0.5134317352 | 18.1426319393 | 8.1513943855 |
| H | 0.2872678705 | 17.3173701622 | 7.4787196420 |
| C | 2.3482220139 | 17.2339338167 | 13.5603074981 |
| C | 1.4651355607 | 16.6619375230 | 14.4804712352 |
| H | 0.4484509366 | 16.4249894041 | 14.1714485894 |
| C | 1.8781812129 | 16.4025882371 | 15.7813276459 |

|  |  |  |  |
|---|---|---|---|
| H | 1.1798599384 | 15.9693186833 | 16.4942476397 |
| C | 3.1789421724 | 16.7080721862 | 16.1742772404 |
| H | 3.5017671651 | 16.5064041486 | 17.1933047522 |
| C | 4.0598225414 | 17.2837565464 | 15.2648151475 |
| H | 5.0750418200 | 17.5290362717 | 15.5686869753 |
| C | 3.6466908122 | 17.5481047802 | 13.9628336530 |
| H | 4.3378741376 | 17.9887331940 | 13.2470256344 |
| C | 2.9391937847 | 9.2708191748 | 12.9508270773 |
| C | 2.7376146276 | 8.1907334825 | 12.0471488773 |
| C | 3.0792603407 | 6.8924446239 | 12.4686091310 |
| H | 2.9268070250 | 6.0602171262 | 11.7844772052 |
| C | 3.5988180047 | 6.6694761029 | 13.7277131381 |
| H | 3.8569682630 | 5.6593896567 | 14.0360969177 |
| C | 3.7936403014 | 7.7397678565 | 14.6127439337 |
| H | 4.2014722015 | 7.5575463706 | 15.6038361571 |
| C | 3.4672208134 | 9.0245047606 | 14.2291351201 |
| H | 3.6198008872 | 9.8449673364 | 14.9279128924 |
| C | 1.2342071592 | 9.8727598917 | 8.9611015204 |
| C | -0.0879789109 | 10.3073291513 | 8.8325692326 |
| H | -0.6837246970 | 10.4835024348 | 9.7267694455 |
| C | -0.6426634264 | 10.5013461726 | 7.5735030345 |
| H | -1.6776256142 | 10.8242850548 | 7.4832152341 |
| C | 0.1187137956 | 10.2675060806 | 6.4308379521 |
| H | -0.3170974403 | 10.4165246777 | 5.4453900905 |
| C | 1.4334389447 | 9.8309832316 | 6.5527160917 |
| H | 2.0309558498 | 9.6427386109 | 5.6634709787 |
| C | 1.9887150518 | 9.6311788713 | 7.8122984247 |
| H | 3.0197982436 | 9.2967406522 | 7.9095552749 |

| | | | |
|---|---|---|---|
| H | 0.7436093702 | 15.2581483682 | 8.4172237993 |
| H | 3.0836929249 | 11.8946167380 | 14.0141037369 |

**3b** (neutral)

| | | | |
|---|---|---|---|
| N | 2.4211699610 | -1.2863212543 | -0.0000098578 |
| C | 3.3262317678 | -0.2523980366 | -0.0000064815 |
| C | 2.6296422045 | 0.9614868344 | -0.0000064478 |
| C | 3.3467599305 | 2.1782884433 | -0.0000041102 |
| C | 4.7156014188 | 2.1556066155 | 0.0000050301 |
| H | 5.2803133837 | 3.0857737550 | 0.0000110906 |
| N | -2.4250698864 | 1.2564876888 | -0.0000000986 |
| C | -3.3313974126 | 0.2236125379 | 0.0000056412 |
| C | -2.6344447327 | -0.9911517596 | 0.0000032994 |
| C | -3.3521965242 | -2.2062559609 | 0.0000054259 |
| C | -4.7220148019 | -2.1812045912 | 0.0000117175 |
| H | -5.2863887443 | -3.1115016677 | 0.0000107870 |
| C | 1.1329502003 | -0.7787845474 | -0.0000086855 |
| C | 1.2265597869 | 0.6443976360 | -0.0000088547 |
| C | 0.0713257693 | 1.4256589609 | -0.0000085921 |
| H | 0.1201447660 | 2.5121167616 | -0.0000084677 |
| C | -1.1371009826 | 0.7483974184 | -0.0000045822 |
| C | -1.2306947195 | -0.6746535011 | -0.0000030329 |
| C | -0.0756670000 | -1.4560542050 | -0.0000064681 |
| H | -0.1244003321 | -2.5425284962 | -0.0000057732 |
| C | 4.7401853281 | -0.3173968197 | 0.0000003892 |
| C | 5.4392227002 | 0.9264931642 | 0.0000099258 |
| C | 6.8493626384 | 0.9007657544 | 0.0000316009 |

|  |  |  |  |
|---|---|---|---|
| H | 7.3794257633 | 1.8533789283 | 0.0000457453 |
| C | 7.5679127650 | -0.2777497635 | 0.0000379441 |
| C | 6.8550142294 | -1.4963977141 | 0.0000218094 |
| H | 7.4073005760 | -2.4347719743 | 0.0000214283 |
| C | 5.4802025889 | -1.5163686966 | 0.0000070646 |
| H | 4.9625986447 | -2.4742250630 | -0.0000040719 |
| C | -4.7441978901 | 0.2894478950 | 0.0000124435 |
| C | -5.4434907204 | -0.9525740134 | 0.0000139987 |
| C | -6.8565518250 | -0.9252733267 | 0.0000170950 |
| H | -7.3885939084 | -1.8764001463 | 0.0000139948 |
| C | -7.5710179582 | 0.2524173829 | 0.0000249528 |
| C | -6.8557691216 | 1.4736343565 | 0.0000226726 |
| H | -7.4066014749 | 2.4132168520 | 0.0000280980 |
| C | -5.4837174355 | 1.4916136161 | 0.0000164185 |
| H | -4.9639325665 | 2.4482926170 | 0.0000147445 |
| H | 2.6526419808 | -2.2643158521 | 0.0000001803 |
| H | 2.8131300799 | 3.1265488917 | -0.0000039300 |
| H | -2.6555442692 | 2.2346284035 | 0.0000058161 |
| H | -2.8202468478 | -3.1554433694 | 0.0000027640 |
| C | 9.0688727054 | -0.2668207688 | 0.0000766941 |
| C | -9.0695805532 | 0.2658543328 | 0.0000517181 |
| H | -9.4791519159 | -0.7495404894 | -0.0000559449 |
| H | -9.4606102441 | 0.7880125144 | -0.8829699157 |
| H | -9.4605717721 | 0.7878112952 | 0.8832096053 |
| H | 9.4765264160 | -1.2831637064 | -0.0000439638 |
| H | 9.4625298436 | 0.2510889996 | 0.8837023492 |
| H | 9.4625852590 | 0.2513237589 | -0.8833842533 |

**3b** (cation)

| | | | |
|---|---|---|---|
| N | 2.4275969738 | -1.2772809426 | 0.0000121364 |
| C | 3.3231969807 | -0.2593585028 | 0.0000111715 |
| C | 2.6102746765 | 0.9725339397 | 0.0000127050 |
| C | 3.3210736282 | 2.1904243499 | 0.0000102882 |
| C | 4.6889175997 | 2.1576012284 | 0.0000077326 |
| H | 5.2536251804 | 3.0874634986 | 0.0000062369 |
| N | -2.4310881227 | 1.2472698169 | 0.0000201831 |
| C | -3.3273302970 | 0.2288486388 | 0.0000193221 |
| C | -2.6148677220 | -1.0029856124 | 0.0000170258 |
| C | -3.3264494706 | -2.2200818253 | 0.0000160123 |
| C | -4.6946065613 | -2.1855096417 | 0.0000189067 |
| H | -5.2602530755 | -3.1146974188 | 0.0000195099 |
| C | 1.1332294293 | -0.7752393488 | 0.0000135996 |
| C | 1.2248168840 | 0.6465592525 | 0.0000151727 |
| C | 0.0594544320 | 1.4294812962 | 0.0000178801 |
| H | 0.1045732317 | 2.5156330959 | 0.0000195179 |
| C | -1.1375035753 | 0.7448545828 | 0.0000181532 |
| C | -1.2290749592 | -0.6772199517 | 0.0000159922 |
| C | -0.0635584091 | -1.4599891859 | 0.0000140447 |
| H | -0.1086486039 | -2.5461752934 | 0.0000137736 |
| C | 4.7393801188 | -0.3211461652 | 0.0000100295 |
| C | 5.4243048997 | 0.9266972752 | 0.0000079641 |
| C | 6.8261800452 | 0.9219035090 | 0.0000074752 |
| H | 7.3495388783 | 1.8771543782 | 0.0000053707 |
| C | 7.5600221078 | -0.2581738574 | 0.0000108719 |
| C | 6.8608764282 | -1.4785906278 | 0.0000129434 |

| | | | |
|---|---|---|---|
| H | 7.4203304698 | -2.4116303096 | 0.0000130571 |
| C | 5.4821831050 | -1.5126499340 | 0.0000121131 |
| H | 4.9770401996 | -2.4767806981 | 0.0000133401 |
| C | -4.7426405680 | 0.2913158191 | 0.0000187216 |
| C | -5.4279593398 | -0.9544467514 | 0.0000191452 |
| C | -6.8327508666 | -0.9481315762 | 0.0000178967 |
| H | -7.3571406107 | -1.9023779452 | 0.0000190294 |
| C | -7.5628465150 | 0.2304259863 | 0.0000191801 |
| C | -6.8608716119 | 1.4532623496 | 0.0000114661 |
| H | -7.4195645417 | 2.3871995152 | 0.0000099581 |
| C | -5.4851533271 | 1.4857326697 | 0.0000143514 |
| H | -4.9781726369 | 2.4488576644 | 0.0000109684 |
| H | 2.6620169008 | -2.2576649583 | 0.0000013965 |
| H | 2.7914713519 | 3.1394984368 | 0.0000109770 |
| H | -2.6653254077 | 2.2275782077 | 0.0000194646 |
| H | -2.7980110744 | -3.1698112855 | 0.0000141258 |
| C | 9.0561578327 | -0.2259874098 | 0.0000306430 |
| C | -9.0580654559 | 0.2253872241 | 0.0000356308 |
| H | -9.4596283359 | -0.7920910829 | -0.0000483051 |
| H | -9.4492663112 | 0.7472493614 | -0.8823079565 |
| H | -9.4492424379 | 0.7470920256 | 0.8824844317 |
| H | 9.4817223007 | -1.2335601281 | -0.0001154391 |
| H | 9.4355714653 | 0.3031683521 | 0.8828542240 |
| H | 9.4355981844 | 0.3034419729 | -0.8826164364 |

**3c** (neutral)

|  |  |  |  |
|---|---|---|---|
| N | 1.3749182732 | 15.2454798445 | 9.1202233616 |
| C | 1.7449097897 | 16.4794651420 | 9.5981873629 |
| C | 2.2570972748 | 16.3310626222 | 10.8925256701 |
| C | 2.7065831017 | 17.4662658336 | 11.6013897295 |
| C | 2.6355359451 | 18.7002518247 | 11.0122128449 |
| H | 2.9772557495 | 19.5844299422 | 11.5463459491 |
| N | 2.6034374701 | 11.8588851457 | 13.2404223341 |
| C | 2.2334335099 | 10.6248873190 | 12.7624841415 |
| C | 1.7213764964 | 10.7732946798 | 11.4680885201 |
| C | 1.2717875522 | 9.6381058839 | 10.7592615326 |
| C | 1.3426524702 | 8.4041545446 | 11.3485132537 |
| H | 1.0008571527 | 7.5200100206 | 10.8144084837 |
| C | 1.6352981944 | 14.2782443103 | 10.0755767575 |
| C | 2.1951013980 | 14.9300274305 | 11.2139598497 |
| C | 2.5573089021 | 14.1937100774 | 12.3412821971 |
| H | 2.9861818179 | 14.6719996052 | 13.2188070465 |
| C | 2.3433371900 | 12.8260907350 | 12.2849549230 |
| C | 1.7835422274 | 12.1743105038 | 11.1465702297 |
| C | 1.4212351262 | 12.9106512250 | 10.0193018500 |
| H | 0.9922310933 | 12.4323748755 | 9.1418669311 |
| C | 1.6566965536 | 17.7367751685 | 8.9542721048 |
| C | 2.1174937299 | 18.8666480917 | 9.6949751516 |
| C | 2.0443527396 | 20.1386045148 | 9.0846176068 |
| H | 2.3937842539 | 21.0044536818 | 9.6447434655 |
| C | 1.5454085836 | 20.2942791988 | 7.8129675910 |
| H | 1.4993032081 | 21.2839362326 | 7.3638363570 |
| C | 1.0934387708 | 19.1744663503 | 7.0882672232 |
| H | 0.6994899857 | 19.3017762724 | 6.0823821786 |

| | | | |
|---|---|---|---|
| C | 1.1491633094 | 17.9212863083 | 7.6504017001 |
| H | 0.7976343259 | 17.0628538710 | 7.0804049954 |
| C | 2.3215218084 | 9.3675953868 | 13.4064531775 |
| C | 1.8606346121 | 8.2377534257 | 12.6657793336 |
| C | 1.9336799217 | 6.9658078355 | 13.2761684746 |
| H | 1.5842017552 | 6.0999806379 | 12.7160520191 |
| C | 2.4326226322 | 6.8101143542 | 14.5478104982 |
| H | 2.4786593581 | 5.8204674657 | 14.9969711068 |
| C | 2.8846943030 | 7.9299130584 | 15.2724916511 |
| H | 3.2786753388 | 7.8026143398 | 16.2783731911 |
| C | 2.8290643007 | 9.1830865043 | 14.7103252184 |
| H | 3.1806988124 | 10.0415328344 | 15.2802785118 |
| H | 0.9825906055 | 15.0643703494 | 8.2128878665 |
| H | 2.9962488667 | 12.0399342206 | 14.1475813447 |
| H | 3.1065892543 | 17.3588716235 | 12.6075296758 |
| H | 0.8718946638 | 9.7455007517 | 9.7530833642 |

**3c** (cation)

| | | | |
|---|---|---|---|
| N | 1.3787375111 | 15.2503623184 | 9.1248353939 |
| C | 1.7409112393 | 16.4719257140 | 9.5894261415 |
| C | 2.2609550062 | 16.3212141884 | 10.9036333460 |
| C | 2.7091601984 | 17.4537125215 | 11.6106722664 |
| C | 2.6312581386 | 18.6816201072 | 11.0086208006 |
| H | 2.9717030456 | 19.5680534711 | 11.5393480955 |
| N | 2.5995446559 | 11.8539960503 | 13.2359302921 |
| C | 2.2374030444 | 10.6324065909 | 12.7713595059 |

|  |  |  |  |
|---|---|---|---|
| C | 1.7173890856 | 10.7832545643 | 11.4571530203 |
| C | 1.2691750690 | 9.6508333175 | 10.7500002282 |
| C | 1.3470743421 | 8.4228884490 | 11.3519972297 |
| H | 1.0066253659 | 7.5365113525 | 10.8211622584 |
| C | 1.6372527072 | 14.2789048239 | 10.0793551469 |
| C | 2.1960179122 | 14.9306277753 | 11.2148012450 |
| C | 2.5590527123 | 14.1880397228 | 12.3470173515 |
| H | 2.9882800385 | 14.6633370824 | 13.2254842925 |
| C | 2.3411212463 | 12.8255866506 | 12.2815298634 |
| C | 1.7823582925 | 12.1738651799 | 11.1460725449 |
| C | 1.4193081994 | 12.9164629276 | 10.0138599320 |
| H | 0.9900617154 | 12.4412432197 | 9.1353534739 |
| C | 1.6503391742 | 17.7315119841 | 8.9404579357 |
| C | 2.1112255481 | 18.8532285200 | 9.6859543004 |
| C | 2.0434699241 | 20.1255792323 | 9.0913757646 |
| H | 2.3929661405 | 20.9888359093 | 9.6538786664 |
| C | 1.5426991664 | 20.2866737063 | 7.8144772516 |
| H | 1.4983487725 | 21.2784134378 | 7.3712715527 |
| C | 1.0916925237 | 19.1770306368 | 7.0863588075 |
| H | 0.6988252651 | 19.3098562041 | 6.0815231137 |
| C | 1.1449116745 | 17.9151415123 | 7.6424006165 |
| H | 0.7916951331 | 17.0634687699 | 7.0641016409 |
| C | 2.3279573174 | 9.3728034387 | 13.4202811220 |
| C | 1.8670732552 | 8.2511843233 | 12.6746629378 |
| C | 1.9348006692 | 6.9787812872 | 13.2691347676 |
| H | 1.5853047273 | 6.1155923797 | 12.7065155513 |
| C | 2.4355377576 | 6.8175628962 | 14.5460370896 |
| H | 2.4798596732 | 5.8257755428 | 14.9891426911 |

|  |  |  |  |
|---|---|---|---|
| C | 2.8865311423 | 7.9271308624 | 15.2742752625 |
| H | 3.2793668146 | 7.7942200254 | 16.2791121352 |
| C | 2.8333422184 | 9.1890686719 | 14.7183425667 |
| H | 3.1865364283 | 10.0406973944 | 15.2967181575 |
| H | 0.9815842835 | 15.0689165525 | 8.2159300831 |
| H | 2.9967872219 | 12.0353773617 | 14.1448092789 |
| H | 3.1102165628 | 17.3558017416 | 12.6160156270 |
| H | 0.8681442249 | 9.7488315315 | 9.7446436467 |

**3d** (neutral)

|  |  |  |  |
|---|---|---|---|
| C | 4.3819746386 | 2.1194080188 | 7.6317139874 |
| C | 5.2263043977 | 1.7200908504 | 8.6717411567 |
| H | 4.9114426778 | 1.0134093609 | 9.4329417114 |
| C | 6.4988301348 | 2.2656436963 | 8.7019601917 |
| N | 7.5043474440 | 2.0346313708 | 9.6202033220 |
| H | 7.4246474136 | 1.4296854435 | 10.4187769362 |
| C | 8.6082727927 | 2.7811661573 | 9.2951074303 |
| C | 8.3435887596 | 3.5204976383 | 8.1336398397 |
| C | 9.3448193185 | 4.3834217293 | 7.6002500812 |
| C | 10.5422553566 | 4.4656688260 | 8.2669146867 |
| H | 11.3266205405 | 5.1198888870 | 7.8946574612 |
| C | 10.8210177309 | 3.7208280111 | 9.4469538822 |
| C | 12.0634973070 | 3.8218430429 | 10.1116301444 |
| H | 12.8189644315 | 4.4911511362 | 9.7030080289 |
| C | 12.3259656585 | 3.0956274708 | 11.2495130520 |
| H | 13.2904451274 | 3.1893861865 | 11.7438885019 |
| C | 11.3496377443 | 2.2293452295 | 11.7787056896 |

| | | | |
|---|---|---|---|
| H | 11.5618114740 | 1.6563902395 | 12.6786417714 |
| C | 10.1286474868 | 2.1080994597 | 11.1580272749 |
| H | 9.3805529916 | 1.4356945300 | 11.5749161727 |
| C | 9.8395189867 | 2.8437595499 | 9.9894973824 |
| C | 9.0798922708 | 5.1344395818 | 6.3173757001 |
| H | 8.0531683251 | 5.5225507512 | 6.3890340578 |
| C | 9.1465085770 | 4.1695602179 | 5.1291196927 |
| H | 10.1748115185 | 3.8093665036 | 4.9995954274 |
| H | 8.8403759812 | 4.6682153343 | 4.2005654389 |
| H | 8.5048627716 | 3.2951025186 | 5.2804977288 |
| C | 9.9943242822 | 6.3295876810 | 6.0896938026 |
| H | 9.9821255600 | 7.0155764711 | 6.9442141306 |
| H | 9.6722750084 | 6.8850673352 | 5.2014936083 |
| H | 11.0313787031 | 6.0166075525 | 5.9161080598 |
| C | 6.9879444641 | 3.2016653559 | 7.7419857471 |
| C | 6.1436188199 | 3.6009531393 | 6.7019315960 |
| H | 6.4585077822 | 4.3075867319 | 5.9406877532 |
| C | 4.8710891299 | 3.0553920878 | 6.6717239313 |
| N | 3.8656309626 | 3.2862946891 | 5.7533946970 |
| H | 3.9451101132 | 3.8917385949 | 4.9551742083 |
| C | 2.7616378107 | 2.5399109608 | 6.0786016672 |
| C | 3.0263042291 | 1.8006219919 | 7.2400900094 |
| C | 2.0250239362 | 0.9378024968 | 7.7735427935 |
| C | 0.8275433996 | 0.8556557640 | 7.1069569827 |
| H | 0.0431502234 | 0.2015163205 | 7.4792906460 |
| C | 0.5487934592 | 1.6004614134 | 5.9268923656 |
| C | -0.6937267248 | 1.4995457926 | 5.2622758956 |
| H | -1.4492589330 | 0.8303568707 | 5.6709692964 |

| | | | |
|---|---|---|---|
| C | -0.9561621878 | 2.2257191006 | 4.1243558465 |
| H | -1.9206787305 | 2.1320438574 | 3.6300330193 |
| C | 0.0202586465 | 3.0918298664 | 3.5950466382 |
| H | -0.1918617728 | 3.6647343160 | 2.6950643911 |
| C | 1.2412917393 | 3.2129648063 | 4.2156565184 |
| H | 1.9894741782 | 3.8852003176 | 3.7986570574 |
| C | 1.5303704757 | 2.4773715334 | 5.3842463713 |
| C | 2.2899600846 | 0.1867367247 | 9.0563949023 |
| H | 3.3166563946 | -0.2014202662 | 8.9846914096 |
| C | 2.2234254546 | 1.1515418609 | 10.2447213800 |
| H | 1.1950839043 | 1.5115233409 | 10.3744986252 |
| H | 2.5298577412 | 0.6528974606 | 11.1731800912 |
| H | 2.8648705444 | 2.0261289432 | 10.0932615281 |
| C | 1.3754622829 | -1.0083676453 | 9.2840214349 |
| H | 1.3876833652 | -1.6943492183 | 8.4294965637 |
| H | 1.6974227920 | -1.5638722134 | 10.1722340592 |
| H | 0.3384087333 | -0.6953315173 | 9.4575397696 |

**3d** (cation)

| | | | |
|---|---|---|---|
| C | 4.3780772338 | 2.1283131762 | 7.6437828576 |
| C | 5.2244208998 | 1.7395588514 | 8.6930896062 |
| H | 4.9027934682 | 1.0513601985 | 9.4679909916 |
| C | 6.4975435042 | 2.2787630345 | 8.7029821266 |
| N | 7.5061301749 | 2.0588633616 | 9.6223141118 |
| H | 7.4277722799 | 1.4546256161 | 10.4257061341 |
| C | 8.6073478121 | 2.7767128754 | 9.2928199798 |
| C | 8.3410540154 | 3.5111671944 | 8.1046950617 |

| | | | |
|---|---|---|---|
| C | 9.3395080118 | 4.3582132700 | 7.5566181612 |
| C | 10.5378146584 | 4.4286636140 | 8.2299512477 |
| H | 11.3255016647 | 5.0740535143 | 7.8493851844 |
| C | 10.8234909600 | 3.6945720869 | 9.4212029281 |
| C | 12.0705115635 | 3.8017029771 | 10.0637470787 |
| H | 12.8264098686 | 4.4596362002 | 9.6397986753 |
| C | 12.3393459640 | 3.0859764634 | 11.2133420097 |
| H | 13.3090454686 | 3.1804219341 | 11.6957886327 |
| C | 11.3676707897 | 2.2372416858 | 11.7625530975 |
| H | 11.5852576905 | 1.6759074433 | 12.6676912846 |
| C | 10.1339555400 | 2.1132848053 | 11.1559881191 |
| H | 9.3895934979 | 1.4507696175 | 11.5939554701 |
| C | 9.8450847658 | 2.8335834986 | 9.9854385375 |
| C | 9.0843840898 | 5.1075299300 | 6.2717444002 |
| H | 8.0612033030 | 5.5066478054 | 6.3433339963 |
| C | 9.1495125255 | 4.1406167565 | 5.0839532069 |
| H | 10.1763628584 | 3.7793031556 | 4.9518906652 |
| H | 8.8471904197 | 4.6431172153 | 4.1575351576 |
| H | 8.5093134597 | 3.2629683987 | 5.2268436416 |
| C | 10.0088929312 | 6.2961943066 | 6.0499912673 |
| H | 10.0005046369 | 6.9821777492 | 6.9043159471 |
| H | 9.6900051807 | 6.8557320206 | 5.1645161892 |
| H | 11.0428394905 | 5.9772059774 | 5.8710923625 |
| C | 6.9919105154 | 3.1925659582 | 7.7297247569 |
| C | 6.1455668751 | 3.5812737045 | 6.6803721712 |
| H | 6.4672812127 | 4.2694598715 | 5.9055039615 |
| C | 4.8724516333 | 3.0420392488 | 6.6704664264 |
| N | 3.8638345514 | 3.2619705931 | 5.7511680449 |

| | | | |
|---|---|---|---|
| H | 3.9421843579 | 3.8662683610 | 4.9478072218 |
| C | 2.7625404487 | 2.5442808721 | 6.0807858613 |
| C | 3.0288454334 | 1.8098433919 | 7.2689053709 |
| C | 2.0303050103 | 0.9630192502 | 7.8171620631 |
| C | 0.8318918443 | 0.8927670392 | 7.1440041838 |
| H | 0.0441022095 | 0.2476164606 | 7.5247668687 |
| C | 0.5462260841 | 1.6268168786 | 5.9527245646 |
| C | -0.7008947195 | 1.5198702628 | 5.3103677536 |
| H | -1.4569090514 | 0.8621572842 | 5.7344389618 |
| C | -0.9697245703 | 2.2354818641 | 4.1607133405 |
| H | -1.9395191975 | 2.1411508850 | 3.6784627605 |
| C | 0.0020652215 | 3.0839127023 | 3.6112367626 |
| H | -0.2155298842 | 3.6451247838 | 2.7060380131 |
| C | 1.2358783749 | 3.2077094419 | 4.2176407339 |
| H | 1.9802650314 | 3.8700031786 | 3.7793995024 |
| C | 1.5247427964 | 2.4875282911 | 5.3882695916 |
| C | 2.2855300185 | 0.2136871926 | 9.1020019650 |
| H | 3.3086073328 | -0.1856420797 | 9.0302403936 |
| C | 2.2207896398 | 1.1805648975 | 10.2898340178 |
| H | 1.1940044226 | 1.5419445914 | 10.4221946538 |
| H | 2.5233283732 | 0.6779771096 | 11.2161352633 |
| H | 2.8610226198 | 2.0581522390 | 10.1467658078 |
| C | 1.3608431095 | -0.9748222170 | 9.3238991365 |
| H | 1.3690018965 | -1.6608134983 | 8.4695792789 |
| H | 1.6797672197 | -1.5343988186 | 10.2093371137 |
| H | 0.3269822096 | -0.6556489976 | 9.5029436513 |

**3g** (neutral)

| | | | |
|---|---|---|---|
| N | 2.4478604539 | -1.2101281244 | -0.0000075158 |
| C | 3.3325073496 | -0.1607708371 | 0.0001716449 |
| C | 2.6164288288 | 1.0434918880 | 0.0002577513 |
| C | 3.3115311613 | 2.2834539582 | 0.0004523232 |
| C | 4.6843588742 | 2.2520635905 | 0.0006268661 |
| H | 5.2399284642 | 3.1888077959 | 0.0007831861 |
| N | -2.4520588685 | 1.2027003445 | 0.0002560596 |
| C | -3.3366917719 | 0.1533263322 | 0.0001996399 |
| C | -2.6206295312 | -1.0509456151 | 0.0001089910 |
| C | -3.3158046334 | -2.2908760555 | 0.0001007672 |
| C | -4.6886443144 | -2.2594300485 | 0.0001269647 |
| H | -5.2442565696 | -3.1961483689 | 0.0001385673 |
| C | 1.1519598150 | -0.7286998569 | 0.0000525399 |
| C | 1.2161086004 | 0.6970450575 | 0.0001927353 |
| C | 0.0303297057 | 1.4359924700 | 0.0002612465 |
| H | 0.0303558712 | 2.5215316997 | 0.0003681122 |
| C | -1.1561563833 | 0.7212723244 | 0.0002144564 |
| C | -1.2203072326 | -0.7044760301 | 0.0000942947 |
| C | -0.0345183386 | -1.4434120291 | -0.0000276873 |
| H | -0.0345354228 | -2.5289397609 | -0.0001717776 |
| C | 4.7463055382 | -0.2163777610 | 0.0002994376 |
| C | 5.4248118395 | 1.0367469209 | 0.0005703982 |
| C | 6.8376146395 | 1.0286046904 | 0.0007593620 |
| H | 7.3629915543 | 1.9822973905 | 0.0009712099 |
| C | 7.5453135915 | -0.1503296856 | 0.0006887404 |
| C | 6.8668160813 | -1.3845852307 | 0.0004009516 |
| H | 7.4305698441 | -2.3147696575 | 0.0003285009 |

|  |  |  |  |
|---|---|---|---|
| C | 5.4922879326 | -1.4136047554 | 0.0002082606 |
| H | 4.9776196046 | -2.3731468849 | -0.0000322582 |
| C | -4.7504691495 | 0.2089738690 | 0.0002383103 |
| C | -5.4290378940 | -1.0440931037 | 0.0001904082 |
| C | -6.8418441043 | -1.0358832517 | 0.0002413175 |
| H | -7.3673030257 | -1.9895358834 | 0.0002131901 |
| C | -7.5494773154 | 0.1431031669 | 0.0003177238 |
| C | -6.8709421370 | 1.3773285217 | 0.0003526220 |
| H | -7.4345963331 | 2.3075698285 | 0.0004096999 |
| C | -5.4964224945 | 1.4062054719 | 0.0003128197 |
| H | -4.9817119226 | 2.3657333347 | 0.0003376935 |
| H | 2.6980726301 | -2.1834494381 | 0.0001779555 |
| C | 2.5638408738 | 3.5789591796 | 0.0005189934 |
| H | -2.7023118716 | 2.1760128040 | 0.0003888718 |
| C | -2.5682092596 | -3.5864376427 | 0.0000479143 |
| H | 1.9184869290 | 3.6640974682 | 0.8848846740 |
| H | 1.9179045047 | 3.6638715359 | -0.8834373102 |
| H | 3.2524824774 | 4.4291092517 | 0.0001820502 |
| H | 8.6330130486 | -0.1316186791 | 0.0008463482 |
| H | -8.6371812368 | 0.1244513230 | 0.0003555597 |
| H | -3.2568912341 | -4.4365529507 | 0.0004761987 |
| H | -1.9222045365 | -3.6713381397 | 0.8839547314 |
| H | -1.9229104088 | -3.6716564094 | -0.8843555457 |

**3g** (cation)

|  |  |  |  |
|---|---|---|---|
| N | 2.4449942974 | -1.2100100997 | 0.0000551000 |
| C | 3.3294134881 | -0.1825248346 | 0.0004017823 |

| | | | |
|---|---|---|---|
| C | 2.6073151993 | 1.0410816039 | 0.0005404283 |
| C | 3.3005942123 | 2.2759341037 | 0.0004990174 |
| C | 4.6758350815 | 2.2242601691 | 0.0003722386 |
| H | 5.2383843640 | 3.1564678172 | 0.0004563215 |
| N | -2.4491482679 | 1.2026951336 | 0.0003211936 |
| C | -3.3335830402 | 0.1752131534 | 0.0003589837 |
| C | -2.6115514285 | -1.0484439077 | 0.0004649259 |
| C | -3.3047899376 | -2.2833242060 | 0.0003418477 |
| C | -4.6800064492 | -2.2315246960 | 0.0002843332 |
| H | -5.2424681312 | -3.1637886715 | 0.0002197584 |
| C | 1.1480745000 | -0.7279798509 | 0.0010061698 |
| C | 1.2179753928 | 0.6941755557 | 0.0009099046 |
| C | 0.0291883076 | 1.4387921824 | 0.0006291664 |
| H | 0.0316536025 | 2.5241458274 | 0.0002829888 |
| C | -1.1522920554 | 0.7205002581 | 0.0007716952 |
| C | -1.2221987852 | -0.7016559503 | 0.0007707869 |
| C | -0.0334187984 | -1.4463024360 | 0.0006912849 |
| H | -0.0361564647 | -2.5316656892 | 0.0003270011 |
| C | 4.7474854913 | -0.2475345580 | 0.0000031510 |
| C | 5.4198254682 | 1.0046928260 | 0.0001579145 |
| C | 6.8265506885 | 1.0085132801 | -0.0000595679 |
| H | 7.3503351731 | 1.9621532084 | 0.0000546088 |
| C | 7.5384966279 | -0.1744553996 | -0.0004299637 |
| C | 6.8671806371 | -1.4053063285 | -0.0007488546 |
| H | 7.4327400380 | -2.3335955223 | -0.0012054626 |
| C | 5.4874300172 | -1.4410447475 | -0.0005873194 |
| H | 4.9804482327 | -2.4042357679 | -0.0011485790 |
| C | -4.7516688686 | 0.2403070727 | 0.0001628680 |

|  |  |  |  |
|---|---|---|---|
| C | -5.4239613896 | -1.0119437579 | 0.0002230514 |
| C | -6.8306885841 | -1.0158487899 | 0.0001001599 |
| H | -7.3544952343 | -1.9694788878 | 0.0001385921 |
| C | -7.5427061180 | 0.1670646483 | -0.0000558146 |
| C | -6.8713633684 | 1.3978921804 | -0.0001624750 |
| H | -7.4372215751 | 2.3259939452 | -0.0003330770 |
| C | -5.4916087653 | 1.4338199035 | -0.0000761780 |
| H | -4.9847096455 | 2.3970537915 | -0.0002463737 |
| H | 2.6925307075 | -2.1874841904 | 0.0043016784 |
| C | 2.5653563767 | 3.5765545909 | 0.0006961609 |
| H | -2.6966671939 | 2.1801771556 | 0.0016107580 |
| C | -2.5696810143 | -3.5840218847 | 0.0003512299 |
| H | 1.9235779775 | 3.6684922359 | 0.8869241879 |
| H | 1.9247950916 | 3.6694153697 | -0.8863307305 |
| H | 3.2599259469 | 4.4205296780 | 0.0016152733 |
| H | 8.6254473640 | -0.1522400555 | -0.0005612850 |
| H | -8.6296535522 | 0.1448211453 | -0.0001240369 |
| H | -3.2643686612 | -4.4279059886 | -0.0002404928 |
| H | -1.9289792162 | -3.6767620754 | 0.8872932658 |
| H | -1.9280789113 | -3.6762777086 | -0.8859807473 |

**4a** (neutral)

|  |  |  |  |
|---|---|---|---|
| N | 1.9480777816 | -1.9190900783 | 0.1343717580 |
| C | 3.1118438996 | -1.1870551583 | -0.0153687953 |
| C | 2.7756492444 | 0.1738213952 | -0.1414088956 |
| C | 3.7772800470 | 1.1575757466 | -0.3245093820 |

| | | | |
|---|---|---|---|
| C | 5.0836494537 | 0.7545321154 | -0.4178836422 |
| H | 5.8681705263 | 1.4951958110 | -0.5603388490 |
| N | -1.9864058459 | 1.9055787145 | -0.1394554953 |
| C | -3.1501724321 | 1.1735015696 | 0.0100354608 |
| C | -2.8139560005 | -0.1873599173 | 0.1361310286 |
| C | -3.8155814258 | -1.1711863748 | 0.3188779778 |
| C | -5.1219979942 | -0.7682137479 | 0.4118388008 |
| H | -5.9065337433 | -1.5089244550 | 0.5539947315 |
| C | 0.8621251907 | -1.0534203613 | 0.0943388688 |
| C | 1.3425809924 | 0.2730264741 | -0.0839835894 |
| C | 0.4493850901 | 1.3406709005 | -0.1900674392 |
| H | 0.8110435905 | 2.3519052981 | -0.3390042222 |
| C | -0.9004301081 | 1.0399487297 | -0.0992965042 |
| C | -1.3808775766 | -0.2865060292 | 0.0789788965 |
| C | -0.4876921518 | -1.3541515431 | 0.1851015020 |
| H | -0.8493620431 | -2.3653961811 | 0.3339624311 |
| C | 4.4676012207 | -1.6260364511 | -0.0677197922 |
| C | 5.4533566294 | -0.6118020416 | -0.2943663490 |
| C | 6.8139034282 | -0.9859924517 | -0.3736107063 |
| H | 7.5515189958 | -0.2044509448 | -0.5487530375 |
| C | 7.2100303962 | -2.2928712537 | -0.2304262325 |
| H | 8.2634750248 | -2.5564599216 | -0.2947334038 |
| C | 6.2456884044 | -3.2875774251 | 0.0082159866 |
| H | 6.5516174002 | -4.3237983211 | 0.1350152232 |
| C | 4.9120684583 | -2.9612503748 | 0.0879185171 |
| H | 4.2011175291 | -3.7538572533 | 0.2832761477 |
| C | 3.4011406001 | 2.5891816773 | -0.4017549584 |
| C | 3.4149394227 | 3.2679484661 | -1.6205875912 |

| | | | |
|---|---|---|---|
| H | 3.7323288116 | 2.7399240314 | -2.5175071249 |
| C | 3.0011471381 | 4.5944120230 | -1.6947025825 |
| H | 3.0077377246 | 5.1094513722 | -2.6532744617 |
| C | 2.5733967719 | 5.2579548035 | -0.5493925489 |
| H | 2.2474718816 | 6.2946138683 | -0.6075180460 |
| C | 2.5684973353 | 4.5910491286 | 0.6733776428 |
| H | 2.2414430613 | 5.1060077794 | 1.5746141057 |
| C | 2.9787130753 | 3.2654223256 | 0.7459412975 |
| H | 2.9578160290 | 2.7348188825 | 1.6957806462 |
| C | -4.5059684562 | 1.6124163180 | 0.0619808872 |
| C | -5.4917354882 | 0.5981082090 | 0.2882403327 |
| C | -6.8523340491 | 0.9722130784 | 0.3669853950 |
| H | -7.5899687303 | 0.1906202445 | 0.5418241844 |
| C | -7.2484987419 | 2.2790725901 | 0.2237047478 |
| H | -8.3019762071 | 2.5426146005 | 0.2876140093 |
| C | -6.2841331995 | 3.2738503343 | -0.0145420816 |
| H | -6.5900620504 | 4.3100627058 | -0.1414237498 |
| C | -4.9504637282 | 2.9476093776 | -0.0937765163 |
| H | -4.2394891038 | 3.7402673146 | -0.2888541935 |
| C | -3.4393141113 | -2.6027567671 | 0.3961666974 |
| C | -3.0169013023 | -3.2790357457 | -0.7515172304 |
| H | -2.9962345005 | -2.7485193217 | -1.7014093222 |
| C | -2.6063911495 | -4.6045685893 | -0.6788650858 |
| H | -2.2793538203 | -5.1195478469 | -1.5800926365 |
| C | -2.6109719776 | -5.2713275014 | 0.5439815344 |
| H | -2.2848101262 | -6.3079096420 | 0.6021835383 |
| C | -3.0387113033 | -4.6077559384 | 1.6892832099 |
| H | -3.0450598831 | -5.1226962346 | 2.6479114844 |

| | | | |
|---|---|---|---|
| C | -3.4528094854 | -3.2813930645 | 1.6150769755 |
| H | -3.7701797163 | -2.7533317217 | 2.5119858039 |
| C | 1.8065695678 | -3.3494458393 | 0.2197389765 |
| H | 2.2777514617 | -3.8435020126 | -0.6372757387 |
| H | 0.7441052087 | -3.5977871676 | 0.2084699702 |
| C | -1.8449503849 | 3.3359398016 | -0.2247287637 |
| H | -0.7825136359 | 3.5843664089 | -0.2130441966 |
| H | -2.3164863155 | 3.8299303339 | 0.6321252660 |
| H | 2.2374282861 | -3.7433238272 | 1.1479540202 |
| H | -2.2754942996 | 3.7298303212 | -1.1530810008 |

**4a** (cation)

| | | | |
|---|---|---|---|
| N | 1.9606295525 | -1.8853168923 | 0.2811038107 |
| C | 3.1115398782 | -1.1410982066 | 0.3176322887 |
| C | 2.7593777302 | 0.2307612851 | 0.2054000504 |
| C | 3.7399494591 | 1.2451117288 | 0.2095780922 |
| C | 5.0532009024 | 0.8634208073 | 0.3148468803 |
| H | 5.8325289940 | 1.6228141492 | 0.3176510209 |
| N | -1.9974300861 | 1.8707536546 | -0.2866552017 |
| C | -3.1485159388 | 1.1273661091 | -0.3232563893 |
| C | -2.7970596028 | -0.2449598377 | -0.2110433913 |
| C | -3.7784199606 | -1.2587638704 | -0.2154484713 |
| C | -5.0913392067 | -0.8759477583 | -0.3208382656 |
| H | -5.8709873748 | -1.6351387733 | -0.3237928258 |
| C | 0.8679967028 | -1.0408949320 | 0.1413728866 |
| C | 1.3361880894 | 0.2967901791 | 0.0892504658 |
| C | 0.4384828977 | 1.3588650587 | -0.0595622814 |

| | | | |
|---|---|---|---|
| H | 0.7957165301 | 2.3825625352 | -0.1011057495 |
| C | -0.9055306447 | 1.0257328111 | -0.1468881536 |
| C | -1.3738315395 | -0.3117316310 | -0.0947722464 |
| C | -0.4763585714 | -1.3738722226 | 0.0540353682 |
| H | -0.8341523268 | -2.3976515968 | 0.0955882003 |
| C | 4.4756585946 | -1.5553402022 | 0.4304325407 |
| C | 5.4444051013 | -0.5035579670 | 0.4223148462 |
| C | 6.8109816775 | -0.8293411461 | 0.5211044571 |
| H | 7.5381281158 | -0.0199434640 | 0.5130523934 |
| C | 7.2291531385 | -2.1376658935 | 0.6250560234 |
| H | 8.2889148357 | -2.3686729965 | 0.6990073889 |
| C | 6.2812856591 | -3.1682773659 | 0.6350824307 |
| H | 6.6029344445 | -4.2035663267 | 0.7185268560 |
| C | 4.9339266020 | -2.8839616331 | 0.5405458719 |
| H | 4.2369808544 | -3.7114330742 | 0.5528182239 |
| C | 3.3122075551 | 2.6602734774 | 0.0874395599 |
| C | 3.2108262240 | 3.2533766953 | -1.1720503263 |
| H | 3.5181992141 | 2.6936333451 | -2.0530631970 |
| C | 2.7018083228 | 4.5415036736 | -1.3023285112 |
| H | 2.6273280659 | 4.9962563493 | -2.2876585240 |
| C | 2.2889370474 | 5.2451757412 | -0.1745855675 |
| H | 1.8916143000 | 6.2529014001 | -0.2763216985 |
| C | 2.4013941164 | 4.6639562107 | 1.0856079365 |
| H | 2.0933951167 | 5.2157766319 | 1.9710804446 |
| C | 2.9103842579 | 3.3761202511 | 1.2170153061 |
| H | 2.9854401608 | 2.9141482412 | 2.1995699549 |
| C | -4.5124650849 | 1.5427149016 | -0.4361597647 |
| C | -5.4817372054 | 0.4913744859 | -0.4282486163 |

| | | | |
|---|---|---|---|
| C | -6.8480906219 | 0.8177852008 | -0.5271071244 |
| H | -7.5759829507 | 0.0090343776 | -0.5192541381 |
| C | -7.2653935623 | 2.1263430653 | -0.6309152118 |
| H | -8.3248615273 | 2.3582711475 | -0.7049443785 |
| C | -6.3169820159 | 3.1563704371 | -0.6406794159 |
| H | -6.6386968759 | 4.1915591475 | -0.7239982775 |
| C | -4.9697804039 | 2.8717869166 | -0.5461024968 |
| H | -4.2725217337 | 3.6988771150 | -0.5580706731 |
| C | -3.3519638033 | -2.6741652259 | -0.0934667442 |
| C | -2.9503098619 | -3.3901946315 | -1.2229373376 |
| H | -3.0246343778 | -2.9282950042 | -2.2056865577 |
| C | -2.4423362363 | -4.6783457797 | -1.0910743238 |
| H | -2.1343557187 | -5.2303965092 | -1.9766016961 |
| C | -2.3307773240 | -5.2596820919 | 0.1692677682 |
| H | -1.9342375070 | -6.2676491182 | 0.2710584492 |
| C | -2.7434335658 | -4.5557707544 | 1.2969197763 |
| H | -2.6700707297 | -5.0095076787 | 2.2828096737 |
| C | -3.2513841712 | -3.2673869083 | 1.1661455160 |
| H | -3.5585901409 | -2.7073354461 | 2.0473319711 |
| C | 1.8397230962 | -3.3240433097 | 0.3635880741 |
| H | 2.3615752910 | -3.8011611547 | -0.4719290023 |
| H | 0.7848968697 | -3.5951984960 | 0.3137123998 |
| C | -1.8757239616 | 3.3091778417 | -0.3691680517 |
| H | -0.8208998827 | 3.5797253494 | -0.3197272107 |
| H | -2.3969142042 | 3.7867281071 | 0.4665868124 |
| H | 2.2473839553 | -3.6885611057 | 1.3115167298 |
| H | -2.2834633729 | 3.6741102771 | -1.3169197375 |

**4d** (neutral)

| | | | |
|---|---|---|---|
| C | 1.3523006698 | 0.3392534935 | -0.1059921759 |
| C | 0.4016929741 | 1.3634750265 | -0.0892067519 |
| H | 0.6906956301 | 2.4039203714 | -0.1764123965 |
| C | -0.9316925990 | 1.0017965714 | 0.0297912544 |
| N | -2.0396349454 | 1.8327384833 | 0.0795725474 |
| C | -3.1764909543 | 1.0534914388 | 0.1950991492 |
| C | -2.8043355769 | -0.3035567927 | 0.2505877813 |
| C | -3.7855168917 | -1.3186590435 | 0.4301883270 |
| C | -5.0935648614 | -0.9269936062 | 0.5498797981 |
| H | -5.8731966805 | -1.6679468992 | 0.7065500150 |
| C | -5.4989004065 | 0.4303439400 | 0.4512001756 |
| C | -6.8675493162 | 0.7735097975 | 0.5321927001 |
| H | -7.5881895444 | -0.0238823147 | 0.7071667020 |
| C | -7.2928526514 | 2.0705912000 | 0.3812302559 |
| H | -8.3520205397 | 2.3108023196 | 0.4433374124 |
| C | -6.3530027352 | 3.0845072752 | 0.1249797411 |
| H | -6.6849823189 | 4.1090652771 | -0.0279712077 |
| C | -5.0115547311 | 2.7888053104 | 0.0553419867 |
| H | -4.3201049980 | 3.5906156425 | -0.1726592574 |
| C | -4.5388391506 | 1.4670596952 | 0.2390164018 |
| C | -3.3782569460 | -2.7728063655 | 0.4577481760 |
| H | -2.4589658921 | -2.8321078116 | 1.0579137974 |
| C | -3.0614418756 | -3.2534098332 | -0.9613227967 |
| H | -3.9791386881 | -3.2697237131 | -1.5626881810 |
| H | -2.6467105279 | -4.2698158419 | -0.9489798809 |

| | | | |
|---|---|---|---|
| H | -2.3469219223 | -2.5945223098 | -1.4665476558 |
| C | -4.3948794823 | -3.6949015645 | 1.1179947876 |
| H | -4.6601941454 | -3.3495150884 | 2.1235575726 |
| H | -3.9818749107 | -4.7065787904 | 1.2028885236 |
| H | -5.3161126859 | -3.7707351224 | 0.5271123025 |
| C | -1.3671945192 | -0.3491468030 | 0.1337696733 |
| C | -0.4166247603 | -1.3733951139 | 0.1167974195 |
| H | -0.7055651724 | -2.4138790271 | 0.2037881111 |
| C | 0.9167715950 | -1.0117222374 | -0.0021029566 |
| N | 2.0247513157 | -1.8426327554 | -0.0518157481 |
| C | 3.1616350297 | -1.0633153418 | -0.1669797672 |
| C | 2.7894387081 | 0.2937525072 | -0.2224861495 |
| C | 3.7706583289 | 1.3089202529 | -0.4014987969 |
| C | 5.0787742058 | 0.9173201453 | -0.5205330887 |
| H | 5.8584558748 | 1.6583231109 | -0.6766888286 |
| C | 5.4841338799 | -0.4400077601 | -0.4218328124 |
| C | 6.8528282884 | -0.7831126106 | -0.5021539264 |
| H | 7.5735246664 | 0.0143230886 | -0.6766735978 |
| C | 7.2781154976 | -2.0801973612 | -0.3511206225 |
| H | 8.3373141915 | -2.3203655208 | -0.4127208132 |
| C | 6.3381752218 | -3.0941738186 | -0.0954594324 |
| H | 6.6700987316 | -4.1187417193 | 0.0575293189 |
| C | 4.9966856363 | -2.7985290279 | -0.0264485686 |
| H | 4.3051082671 | -3.6003736197 | 0.2011052951 |
| C | 4.5240083271 | -1.4768035137 | -0.2102705881 |
| C | 3.3634082893 | 2.7630417798 | -0.4291803152 |
| H | 2.4445062527 | 2.8223262317 | -1.0299852605 |
| C | 3.0456845605 | 3.2435167618 | 0.9897162137 |

| | | | |
|---|---|---|---|
| H | 3.9629202585 | 3.2591561390 | 1.5918197612 |
| H | 2.6315793273 | 4.2601828705 | 0.9772265320 |
| H | 2.3303653984 | 2.5849197190 | 1.4941981561 |
| C | 4.3804960583 | 3.6851623448 | -1.0887127877 |
| H | 4.6469806691 | 3.3393981476 | -2.0938570041 |
| H | 3.9672902767 | 4.6966750348 | -1.1745477302 |
| H | 5.3010776995 | 3.7615372808 | -0.4968644415 |
| C | -1.9370382700 | 3.2607824592 | 0.2347756382 |
| H | -2.5936592865 | 3.6037191003 | 1.0396310720 |
| H | -0.9113139926 | 3.5116273971 | 0.5144284512 |
| C | 1.9221718959 | -3.2706372825 | -0.2075869447 |
| H | 0.8966770103 | -3.5212703666 | -0.4883353403 |
| H | 2.5795106828 | -3.6133260297 | -1.0119656136 |
| H | -2.1833893803 | 3.7997293299 | -0.6890522680 |
| H | 2.1675990097 | -3.8099106392 | 0.7163195782 |

**4d** (cation)

| | | | |
|---|---|---|---|
| C | 1.3571130894 | 0.3220825151 | -0.0823448531 |
| C | 0.4175290546 | 1.3575033055 | -0.1096478943 |
| H | 0.7278086076 | 2.3911049368 | -0.1990691362 |
| C | -0.9217564670 | 1.0082143045 | -0.0141418969 |
| N | -2.0258130451 | 1.8453209924 | -0.0135015030 |
| C | -3.1672422343 | 1.0964668458 | 0.0958903185 |
| C | -2.8044350138 | -0.2781218619 | 0.1894750230 |
| C | -3.7882806968 | -1.2832372321 | 0.3600807507 |
| C | -5.0955495680 | -0.8665369373 | 0.4305140804 |
| H | -5.8854102565 | -1.5991035074 | 0.5743295242 |

|  |  |  |  |
|---|---|---|---|
| C | -5.4936990928 | 0.4949738603 | 0.3163803610 |
| C | -6.8605742999 | 0.8292698836 | 0.3780127375 |
| H | -7.5840394744 | 0.0302103431 | 0.5270949021 |
| C | -7.2832741719 | 2.1338090860 | 0.2477345211 |
| H | -8.3424764325 | 2.3735687562 | 0.2963644100 |
| C | -6.3402824899 | 3.1480755096 | 0.0441280931 |
| H | -6.6657409766 | 4.1787756221 | -0.0728132030 |
| C | -4.9925729037 | 2.8538427917 | -0.0136720386 |
| H | -4.3041002548 | 3.6700255328 | -0.1849735321 |
| C | -4.5299300438 | 1.5298350459 | 0.1294027783 |
| C | -3.4045640810 | -2.7418017424 | 0.4340439159 |
| H | -2.5081355157 | -2.7980747236 | 1.0696436789 |
| C | -3.0541537250 | -3.2652697398 | -0.9627032732 |
| H | -3.9536280778 | -3.2870739423 | -1.5895221768 |
| H | -2.6598929530 | -4.2872452288 | -0.9077422164 |
| H | -2.3163071604 | -2.6365679773 | -1.4738853558 |
| C | -4.4569879687 | -3.6277167297 | 1.0882545690 |
| H | -4.7513662646 | -3.2487030999 | 2.0731964737 |
| H | -4.0597200864 | -4.6395185475 | 1.2204216861 |
| H | -5.3564009156 | -3.7162597667 | 0.4671597220 |
| C | -1.3720612188 | -0.3317571094 | 0.1111532475 |
| C | -0.4324694593 | -1.3671758545 | 0.1384836549 |
| H | -0.7427238109 | -2.4007920395 | 0.2279261274 |
| C | 0.9068064041 | -1.0178780767 | 0.0429294968 |
| N | 2.0108179362 | -1.8550211139 | 0.0422069553 |
| C | 3.1522546274 | -1.1062075183 | -0.0672306400 |
| C | 2.7894850415 | 0.2683952157 | -0.1607665448 |
| C | 3.7733798774 | 1.2734607922 | -0.3314557606 |

|  |  |  |  |
|---|---|---|---|
| C | 5.0806172826 | 0.8566892396 | -0.4020608393 |
| H | 5.8704954822 | 1.5892288244 | -0.5459525800 |
| C | 5.4787256115 | -0.5048332141 | -0.2879513140 |
| C | 6.8455790985 | -0.8391980395 | -0.3496802383 |
| H | 7.5691161430 | -0.0402071506 | -0.4988348427 |
| C | 7.2682304240 | -2.1437623914 | -0.2193931478 |
| H | 8.3274284865 | -2.3835896063 | -0.2680958680 |
| C | 6.3251898265 | -3.1579791351 | -0.0156818631 |
| H | 6.6505963274 | -4.1887049494 | 0.1012726419 |
| C | 4.9775013619 | -2.8636657738 | 0.0422064761 |
| H | 4.2890222303 | -3.6798398049 | 0.2136050718 |
| C | 4.5149200463 | -1.5396374264 | -0.1008672806 |
| C | 3.3897518080 | 2.7320652888 | -0.4052511691 |
| H | 2.4932318717 | 2.7884807250 | -1.0406986901 |
| C | 3.0395793664 | 3.2554000356 | 0.9916028599 |
| H | 3.9391110100 | 3.2769328141 | 1.6183423719 |
| H | 2.6455180069 | 4.2774581901 | 0.9368545374 |
| H | 2.3016673077 | 2.6267598563 | 1.5027493018 |
| C | 4.4421607794 | 3.6179651608 | -1.0595267753 |
| H | 4.7364292255 | 3.2389738442 | -2.0445116755 |
| H | 4.0449214665 | 4.6297929121 | -1.1916226611 |
| H | 5.3416340263 | 3.7064461787 | -0.4385193710 |
| C | -1.9251753219 | 3.2859397953 | -0.0719567421 |
| H | -2.4381654374 | 3.7368774110 | 0.7824200951 |
| H | -0.8742191221 | 3.5692228772 | -0.0265341617 |
| C | 1.9101289848 | -3.2956384802 | 0.1005575160 |
| H | 0.8591583354 | -3.5788951615 | 0.0551301704 |
| H | 2.4230758279 | -3.7465187514 | -0.7538768093 |

|  |  |  |  |
|---|---|---|---|
| H | -2.3499420582 | 3.6698523413 | -1.0050631477 |
| H | 2.3349206783 | -3.6796487101 | 1.0336117486 |

## 9. Fabrication and Characterization of Organic Thin-Film Transistors

Organic thin-film transistors (TFTs) were fabricated in the inverted staggered (bottom-gate, top-contact) architecture on two different types of substrate: (1) heavily doped silicon wafers, and (2) flexible polyethylene naphthalate (PEN) sheets with a thickness of 125 µm.

For the TFTs on silicon, the substrate also serves as the gate electrode, and the gate dielectric is a combination of a 100 nm-thick film of silicon dioxide (grown by thermal oxidation in dry oxygen), an 8 nm-thick film of aluminum oxide (deposited by atomic layer deposition), and a self-assembled monolayer of either *n*-tetradecylphosphonic acid (Alfa Aesar) or 12,12,13,13,14,14,15,15,16,16,17,-17,18,18,18-pentadecafluorooctadecylphosphonic acid (provided by Matthias Schlörholz). The SAMs were formed by immersing the substrate into a dilute 2-propanol solution of the phosphonic acid, followed by rinsing with pure 2-propanol. These $SiO_2/Al_2O_3$/SAM gate dielectrics have a total thickness of about 110 nm and a unit-area capacitance of about 34 $nF/cm^2$.

For the TFTs on PEN, aluminum gate electrodes with a thickness of 30 nm were deposited onto the PEN by thermal evaporation in vacuum and patterned using a shadow mask. The surface of the aluminum was then briefly exposed to oxygen plasma to form an aluminum-oxide film with a thickness of about 4 nm, followed by the formation of a tetradecyl- or pentadecafluorooctadecylphosphonic acid SAM on the aluminum-oxide surface from solution, as described above. These $AlO_x$/SAM gate dielectrics have a total thickness of about 6 nm and a unit-area capacitance of about 0.7 $\mu F/cm^2$.

For both types of TFT, a 30 nm-thick film of the organic semiconductor was then deposited by thermal sublimation in vacuum ($10^{-6}$ mbar). During the deposition of the organic semiconductor, the substrate was held at an elevated temperature (60 or 80 °C) to promote molecular ordering. Gold source and drain contacts were deposited onto the surface of the organic-semiconductor film by thermal evaporation in vacuum through a shadow mask. The TFTs have a channel length (L) of either 20, 30 or 100 µm and a channel width (W) of either 100 or 200 µm. The current-voltage characteristics of the TFTs were measured in ambient air at room temperature.

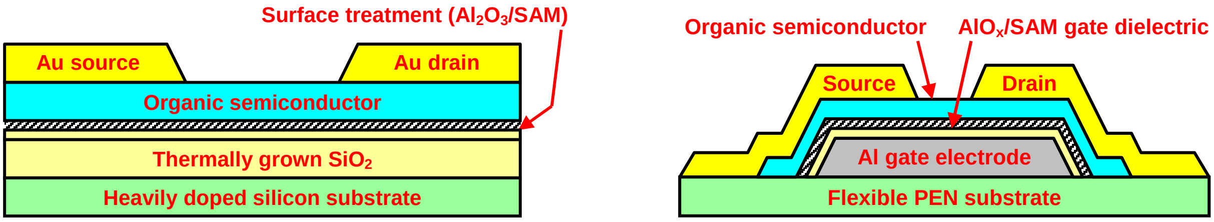


Figure SI17. Left: Schematic cross-section of organic TFTs fabricated on silicon substrates.

Right: Schematic cross-section of organic TFTs fabricated on polyethylene naphthalate (PEN) substrates.

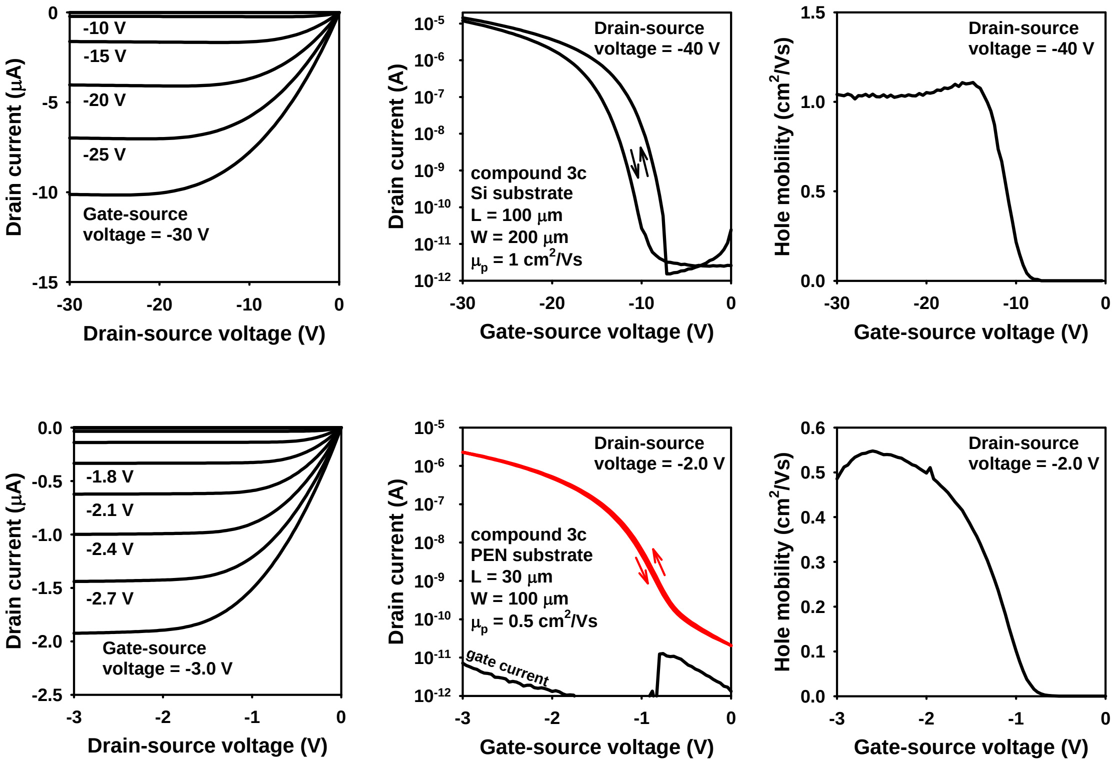


Figure SI18. Current-voltage characteristics of TFTs based on compound **3c**.

Top row: TFT fabricated on a silicon substrate with a $SiO_2/Al_2O_3$/SAM gate dielectric with an *n*-tetradecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 60 °C.

Bottom row: TFT fabricated on a PEN substrate with an $AlO_x$/SAM gate dielectric with an *n*-tetradecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 60 °C.

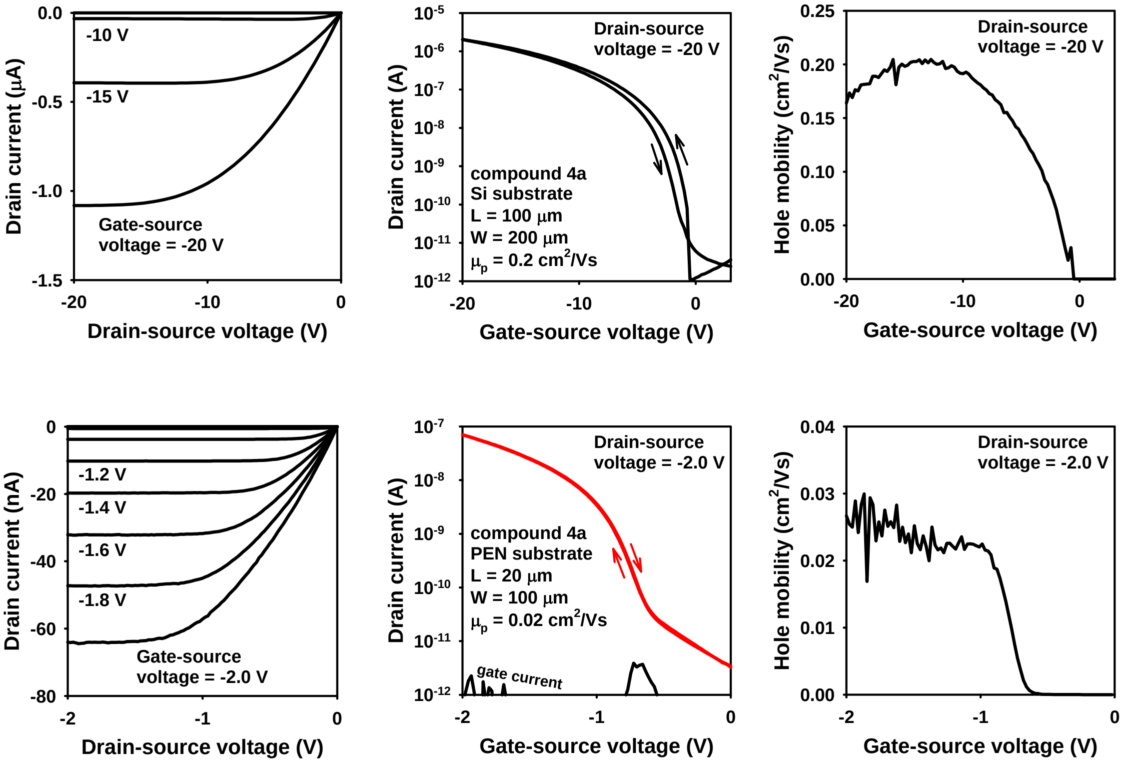


Figure SI19. Current-voltage characteristics of TFTs based on compound **4a**.

Top row: TFT fabricated on a silicon substrate with a $SiO_2/Al_2O_3$/SAM gate dielectric with an *n*-tetradecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 60 °C.

Bottom row: TFT fabricated on a PEN substrate with an $AlO_x$/SAM gate dielectric with an *n*-tetradecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 60 °C.

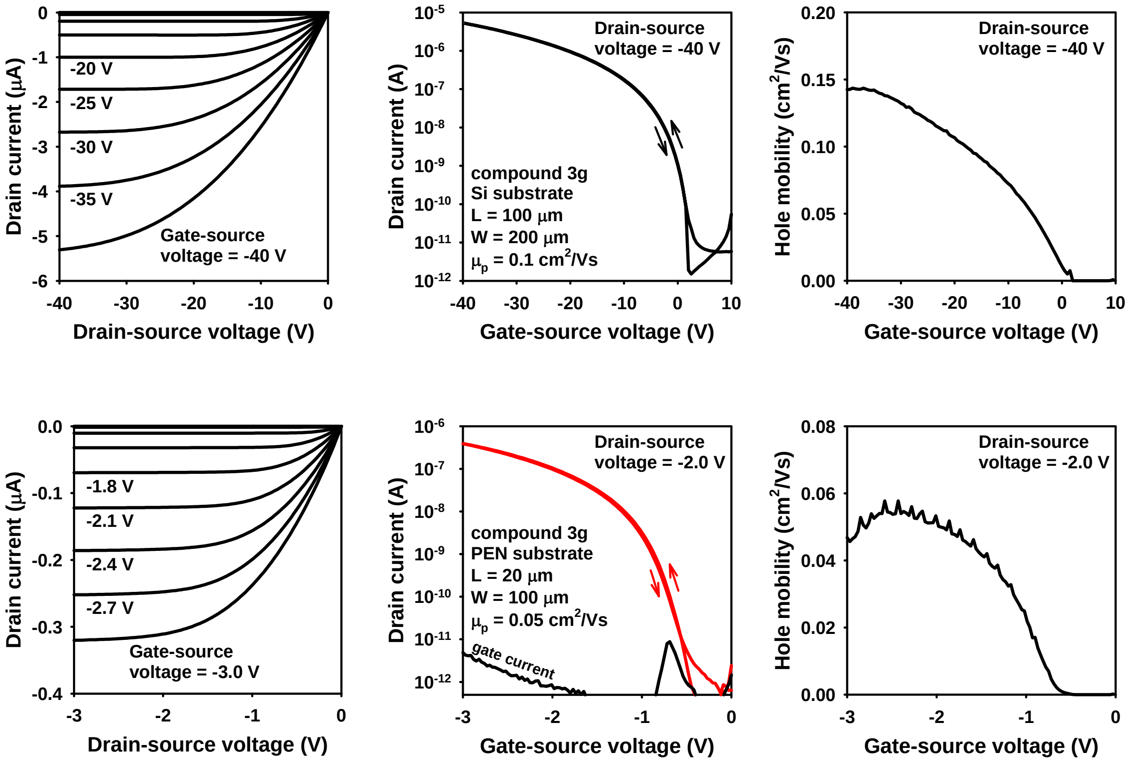


Figure SI20. Current-voltage characteristics of TFTs based on compound **3g**.

Top row: TFT fabricated on a silicon substrate with a $SiO_2/Al_2O_3$/SAM gate dielectric with a pentadecafluorooctadecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 80 °C.

Bottom row: TFT fabricated on a PEN substrate with an $AlO_x$/SAM gate dielectric with an *n*-tetradecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 80 °C.

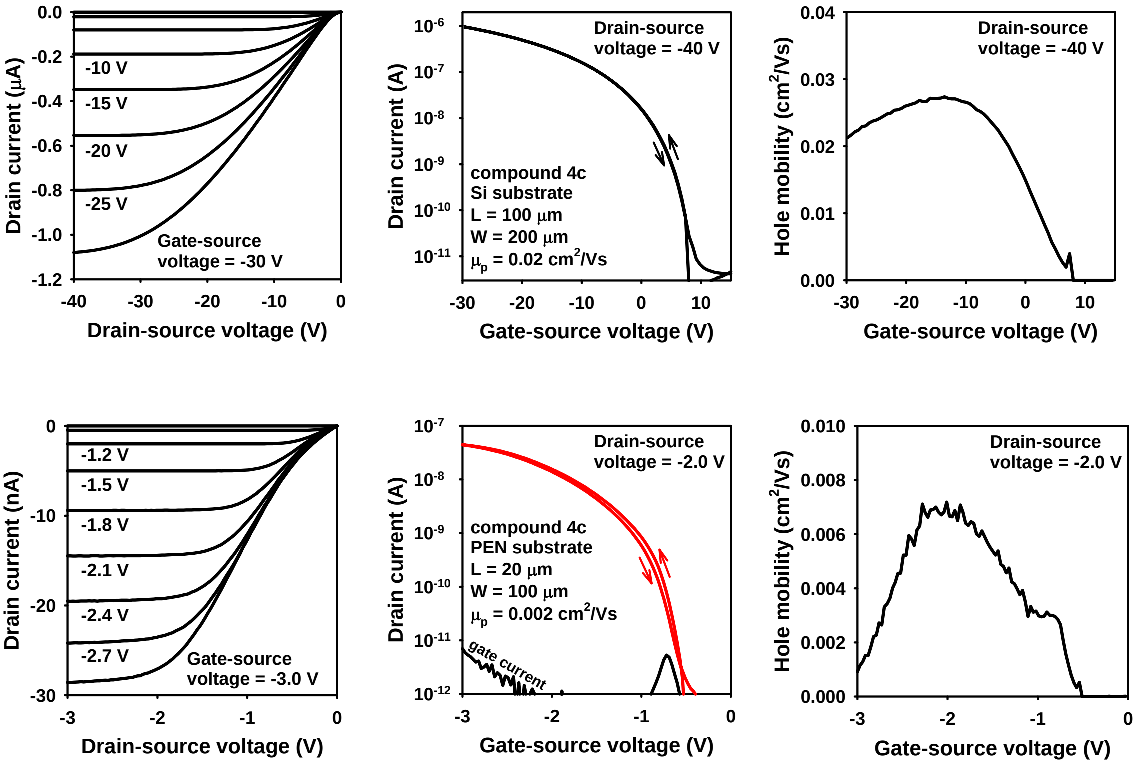


Figure SI21. Current-voltage characteristics of TFTs based on compound **4c**.

Top row: TFT fabricated on a silicon substrate with a $SiO_2/Al_2O_3$/SAM gate dielectric with a pentadecafluorooctadecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 60 °C.

Bottom row: TFT fabricated on a PEN substrate with an $AlO_x$/SAM gate dielectric with an *n*-tetradecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 60 °C.

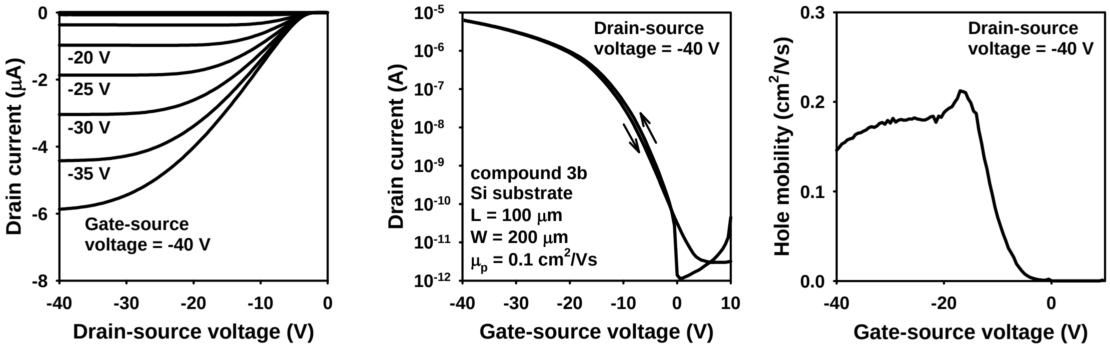


Figure SI22. Current-voltage characteristics of TFTs based on compound **3b**, fabricated on a silicon substrate with a $SiO_2/Al_2O_3$/SAM gate dielectric with a pentadecafluorooctadecylphosphonic acid SAM. During the deposition of the organic-semiconductor layer, the substrate was held at a temperature of 80 °C.

Table SI6. Summary of the charge-carrier field-effect mobilities and on-off current ratios of the organic thin-film transistors.

| **compound** | **Si substrate** | | **PEN substrate** | |
|---|---|---|---|---|
| | carrier mobility (cm$^2$/Vs) | on/off ratio | carrier mobility (cm$^2$/Vs) | on/off ratio |
| **3c** | 1 | $10^6$ | 0.5 | $10^5$ |
| **4a** | 0.2 | $10^6$ | 0.02 | $10^4$ |
| **3g** | 0.1 | $10^6$ | 0.05 | $10^6$ |
| **3b** | 0.1 | $10^6$ | 0.01 | $10^5$ |
| **4c** | 0.02 | $10^5$ | 0.002 | $10^5$ |
| **3d** | $7\times10^{-4}$ | $10^3$ | 0.008 | $10^4$ |
| **3a** | $3\times10^{-5}$ | $10^2$ | no field effect | |
| **4d** | no field effect | | 0.001 | $10^3$ |

# 10. References

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