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"Golden" Cascade Cyclization to Benzo[*c*]-Phenanthridines

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Abstract: Herein, we describe a gold-catalyzed cascade cyclization of Boc-protected benzylamines bearing two tethered alkyne moieties in a domino reaction initiated by a 6-*endo-dig* cyclization. The reaction was screened intensively, and the scope was explored, resulting in nine new Boc-protected dihydrobenzo[*c*]phenanthridines with yields of up to 98%; even a π-extension and two bidirectional approaches were successful. Furthermore, thermal cleavage of the Boc group and subsequent oxidation gave substituted benzo[*c*]phenanthridines in up to quantitative yields. Two bidirectional approaches under the optimized conditions were successful, and the resulting π-extended molecules were tested as organic semiconductors in organic thin-film transistors.

Introduction

Homogeneous gold catalysis went through an impressive evolution during the last decades.[1] Not only for scientific reasons, but also for applications – for example natural product synthesis[2] or materials science,[3] gold catalysis became a versatile tool in organic chemistry. In 2010, Ohno et al. published a cascade cyclization covering an innovative expansion of Utimoto's indole cyclization.[4] In the following years this methodology was even extended to up to five tethered alkynes, which in some cases even gave access to helically chiral compounds.[5] Due to their ability to create complex molecular structures in only a few steps, cascade reactions became a powerful synthetic strategy in the recent time.[6] While in literature many examples for the cyclization of anilines to indole derivatives are reported (Scheme 1),[7] examples for a corresponding cyclization of benzylamines to six-membered N-heterocycle derivatives are rare[8] and Ohno-like cascade cyclizations of tethered alkynes are completely missing. We envisioned that such a process might deliver benzo[*c*]phenanthridines, which are useful intermediates in organic synthesis and important subunits of various pharmaceutically important alkaloids.[9] In this context, we herein wanted to present our studies on a gold-catalyzed cascade cyclization of benzylamines for the formation of benzo[*c*]phenanthridine derivatives, which strategically complements other synthetic approaches like different palladium-catalyzed variations,[10] light, or *tert*-butoxide-promoted variants.[11,12]

Results and Discussion

Our first approach started with the cyclization of the primary benzylamine **1** as model substrate. To the best of our knowledge only one gold-catalyzed cyclization for a similar substrate was conducted up to now.[13] Interestingly, besides not identified side products, 10% of the already oxidized isoquinoline **2** could be obtained when **1** was treated with 5 mol% of commercially available $IPrAuNTf_2$. But the low yield could not be improved, even when the reaction was conducted under an oxygen atmosphere. The first effort to achieve a cascade cyclization with primary amine **3** only led to an unselective decomposition of the starting material instead of the desired formation of benzo[*c*]phenanthridine **4** (Scheme 2).

Based on these results and preceding work of Takemoto et al., who successfully screened the cyclization of Boc-protected benzylamines to isoquinoline derivatives,[14] benzylamine **3** was protected with a Boc group (= **5a**). This addressed first cyclization step of our sequence (for the mechanism, compare Scheme 5; below), Catalan and co-workers had demonstrated that for similar Boc-protected benzylamine substrates a 6-*endo-dig* cyclization is preferred over a 5-*exo-dig*

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[+] Crystallographic investigation

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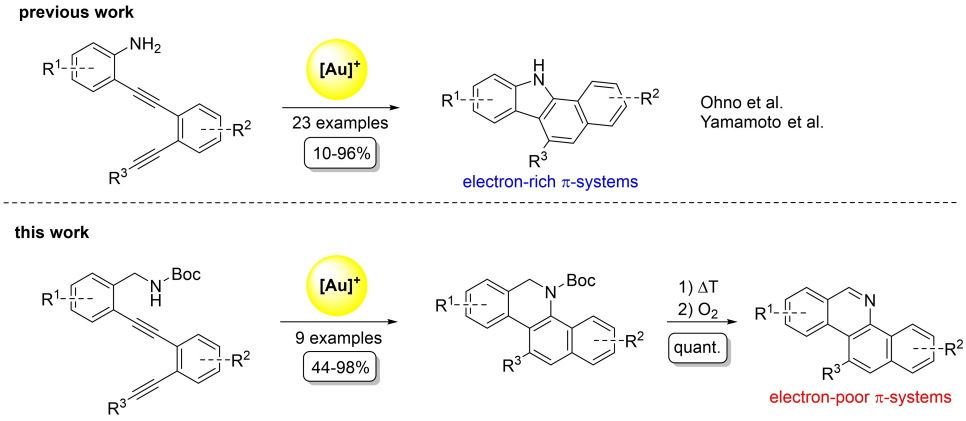
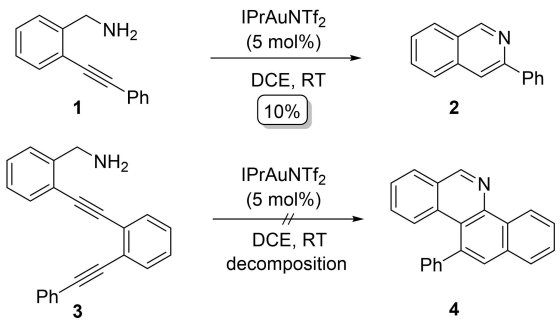


Scheme 1. Comparable previous cascade cyclizations of anilines and our benzylamine approach.

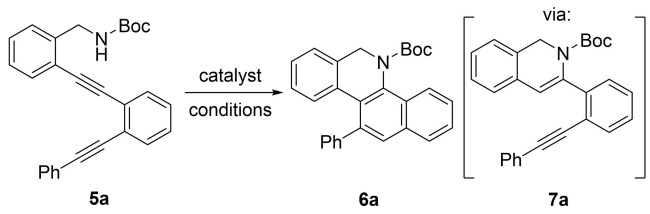


Scheme 2. First evaluations for the synthesis of isoquinoline **2** and benzo[*c*] phenanthridine **4**.

cyclization, the latter is dominating for substrates bearing an electron-withdrawing group (e.g., CF_3) in the benzylic position.[15]

Thus, the Boc-protected diyne **5a** was treated with 5 mol% of $IPrAuNTf_2$, yielding the expected product **6a** in 52% (Scheme 3). Next, we focused on the optimization of this gold-catalyzed step (Scheme 4). With $IPrAuNTf_2$, a 2.5 mol% catalyst loading turned out to be most suitable (for more details see the Supporting Information). Then, $AgSbF_6$, $PtCl_2$ and $Pd(OAc)_2$ were tested, but no product formation was observed with these metal salts (Table 1, entries 1–3). For the screening of the counter anion,[16] IPrAuCl was activated with different silver salts in $CDCl_3$, before the *in situ* formed catalyst was added to the reaction mixture (entries 5–7). SbF_6^- turned out to be the best counter ion. The same procedure was carried out for the screening of the ligand (Figure 1). Besides the sterically more hindered NHC ligand IPr* (9, entry 8), also some phosphane-based ligands were tested (entries 9–12), of which the JohnPhos ligand showed the highest yield. Noticeable is the slightly higher yield for the pre-activated JohnPhosAu(MeCN)SbF_6 complex (entry 13) in comparison to the *in situ* activated catalyst. Interestingly, for some cases also the intermediate **7a** could be observed. Especially for the SPhos ligand (entry 9), the reaction seems to stop at **7a** of the sequence, the observed yield of **7a** was almost ten times higher than the yield of **6a**.

Scheme 3. Gold-catalyzed cascade cyclization of Boc-protected diyne **5a**.



Scheme 4. Screened reaction of diyne **5a** to give **6a** via intermediate **7a**.

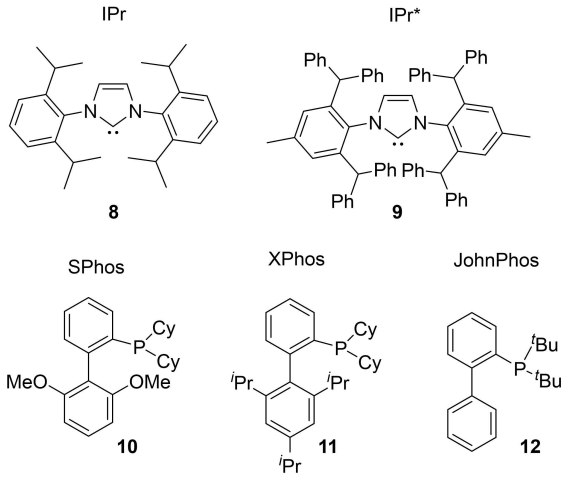


Figure 1. Chemical structure of some of the ligands used for the screening.

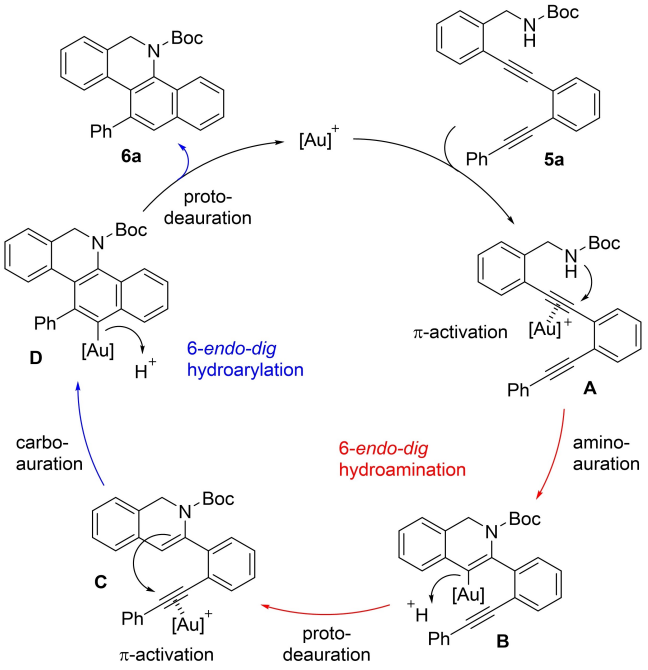
Table 1. Overview of the catalyst systems and conditions for the NMR screening.

	Catalyst	Solvent	*T*	*t* [h]	Conversion	Yield **7a**[a]	Yield **6a**[a]
1	$AgSbF_6$	$CDCl_3$	RT	5	–	–	–
2	$PtCl_2$	$CDCl_3$	RT	5	–	–	–
3	$Pd(OAc)_2$	$CDCl_3$	RT	5	3%	–	–
4	$IPrAuNTf_2$	$CDCl_3$	RT	2	75%	3%	56%
5	$IPrAuCl/AgBF_4$	$CDCl_3$	RT	2	100%	3%	64%
6	$IPrAuCl/AgPF_6$	$CDCl_3$	RT	2	100%	2%	65%
7	$IPrAuCl/AgSbF_6$	$CDCl_3$	RT	2	100%	–	67%
8	$IPr^*AuCl/AgSbF_6$	$CDCl_3$	RT	5	7%	1%	3%
9	$SPhosAuCl/AgSbF_6$	$CDCl_3$	RT	5	27%	19%	2%
10	$PPh3AuCl/AgSbF_6$	$CDCl_3$	RT	5	11%	2%	1%
11	$XPhosAuCl/AgSbF_6$	$CDCl_3$	RT	2	99%	–	86%
12	$JohnPhosAuCl/AgSbF_6$	$CDCl_3$	RT	2	100%	–	87%
13	$JohnPhosAu(MeCN)SbF_6$	$CDCl_3$	RT	2	100%	–	92%
14	$JohnPhosAu(MeCN)SbF_6$	$CDCl_3$	0 °C	1	52%	4%	39%
15	$JohnPhosAu(MeCN)SbF_6$	$CDCl_3$	0 °C	5	94%	29%	51%
16	$JohnPhosAu(MeCN)SbF_6$	$CDCl_3$	50 °C	1	100%	–	94%
17	$JohnPhosAu(MeCN)SbF_6$	CD_2Cl_2	50 °C	1	100%	–	96%
18	$JohnPhosAu(MeCN)SbF_6$	CD_3CN	50 °C	5	76%	26%	40%
19	$JohnPhosAu(MeCN)SbF_6$	C_6D_6	50 °C	5	53%	41%	3%
20	$JohnPhosAu(MeCN)SbF_6$	d_4-DCE	50 °C	1	100%	–	96%

[a] NMR yield.

Next, temperature variations and different solvents were tested. The reaction in deuterated DCM or DCE at 50 °C increased the yields to 96% - in just 1 h reaction time. Surprisingly, the reaction seems to be highly dependent on the solvent. Even after 5 h at 50 °C in deuterated benzene and acetonitrile the conversion is rather low and remarkable amounts of intermediate **7a** could be observed.

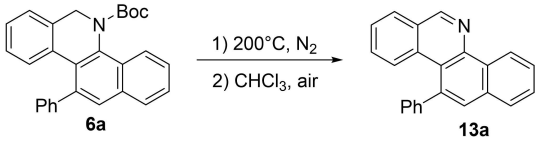
Our mechanistic proposal is shown in Scheme 5. We assume that a similar sequence as published for the indole cascade cyclization from Ohno is operating.[5a] The nucleophilic attack of the Boc-protected secondary amino group to the gold-activated triple bond (**A**) forms the vinyl gold species (**B**), which first undergoes protodeauration, followed by a second nucleophilic attack of the newly formed double bond to the tethered alkyne (**C**). The observation of **7a** in the catalyst screenings and isolation of **7j** (compare Tables 1 and 2) further support this mechanism. Final protodeauration of vinyl gold species **D** furnishes product **6a**.



Scheme 5. Proposed mechanism.

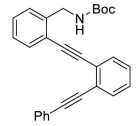
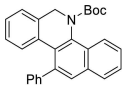
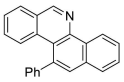
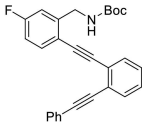
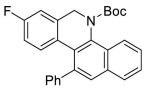
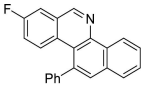
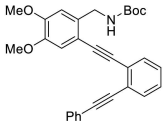
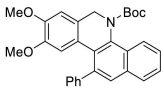
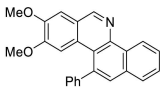
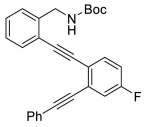
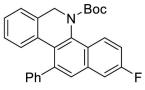
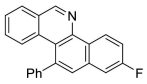
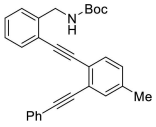
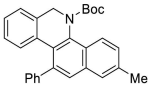
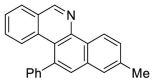
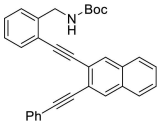
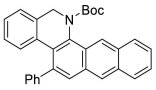
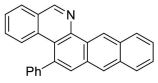
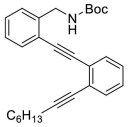
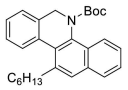
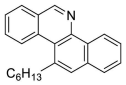
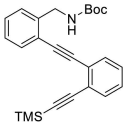
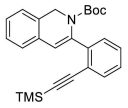
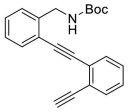
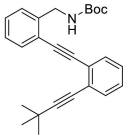
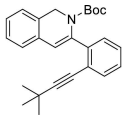
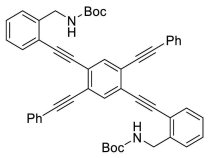
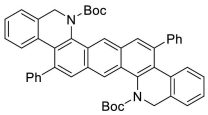
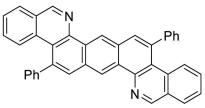
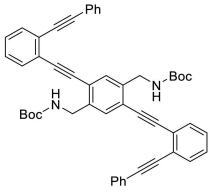
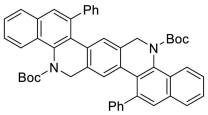
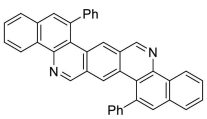
After optimization of the gold-catalyzed step we focused on the cleavage of the Boc protecting group. Besides common ways like acid-mediated deprotection methods,[17] an approach by Cava from 1985,[18] which we had already successfully used for indolocarbazoles[3a] looked promising. This solvent-free thermal deprotection, originally used for pyrrole-based substances, was also effective for our Boc-protected product **6a**. For this step our substrate was heated to 200 °C under a nitrogen atmosphere for about 3 h. In a very efficient way the oxidized benzo[*c*]phenanthridine **13a** was directly obtained by bubbling air through a chloroform solution of the residue after the thermal treatment. The final product was obtained after removing the solvent under reduced pressure without the need of any further purification (Scheme 6).

Even though this procedure already was very simple, we tried to simplify it further by applying a semi-one-pot synthesis of the gold catalysis and the deprotection. In a test reaction first the gold catalysis with **5a** was conducted as described, but



Scheme 6. Conditions for the thermal Boc deprotection and subsequent oxidation to benzo[*c*]phenanthridine **13a**.

Table 2. Overview of all examined structures including yields of the gold catalysis and deprotection/oxidation.

Starting material	Diyne **5a-l**	Cyclization product **6a-l**	Yield	Oxidation product **13a–l**	Yield
5a			**6a** 95%		**13a** quant.
5b			**6b** 90%		**13b** quant.
5c			**6c** 44%[b]		**13c** quant.
5d			**6d** 67%[b]		**13d** quant.
5e			**6e** 96%		**13e** quant.
5f			**6f** 90%		**13f** 39%[c]
5g			**6g** 98%		**13g** quant.
5h			**7h** 76%[d]	–	–
5i		–	–	–	–
5j			**7j** 87%	–	–
5k			**6k** 65%[f]		**13k** 77%
5l			**6l** -[g]		**13l** 33%[h]

[a] Yield for an one-pot approach. [b] Yields were reproduced by a second independent attempt. [c] An additional purification step in form of a short column chromatography was needed. [d] NMR yield. [e] No conversion was observed. [f] Combined yields for two isomers (see the Supporting Information). [g] **6l** was not isolated properly and therefore directly used for the next step. [h] Yield over two steps.

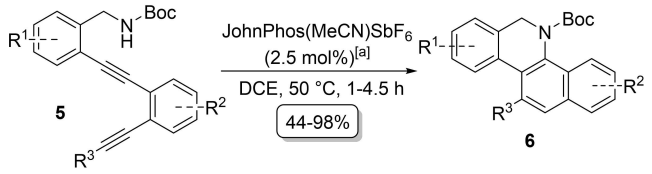
instead of the work up, the crude product was directly used for the thermal deprotection after removing the solvent under reduced pressure. After complete conversion, it was dissolved in chloroform. Then air was bubbled through the solution for the oxidation, followed by flash column chromatography. However, this semi-one-pot variant resulted only in a 74% yield, compared to a 95% combined yield for the two step method.

Once, the gold-catalyzed step and the cleavage of the Boc group were optimized, we explored the scope of this new method (Scheme 7 and Table 2). For synthesizing the corresponding alkyne systems **5**, different synthetic strategies involving sequences of Sonogashira cross couplings, were used (see the Supporting Information for more details). First, we installed an electron-withdrawing (R^1 = F, **5b**) and an electron-donating group (R^1 = two OMe groups, **5c**) in the backbone of the benzyl moiety. For **6b** an isolated yield of 90% was obtained, whereas the yield for the electron-rich **6c** dropped to 44%.

Next, the aryl group connecting the two alkynes was varied. Besides an electron-withdrawing (R^2 = F, **5d**) and an electron-donating group (R^2 = Me, **5e**), also an attempt for a π-extended naphthalene backbone (**5f**) was conducted. In contrast to the upper trend a fluoro substituent at this position (**6d**) led to a drop in yield to 67% while **6e** bearing the slightly electron-donating methyl group furnished the corresponding product in 96% yield. An excellent yield was also obtained for the π-extended **6f** (90%). For this substrate, the thermal treatment for the cleavage of the Boc protecting group was not quantitative, but needed a further purification step. A short column chromatography resulted in 39% yield of **13f**.

Lastly, different substituents on the alkyne moiety were tested (**5g–j**). Substrate **5g**, bearing an alkyl group instead of an aryl substituent, with 98% delivered the highest yield among all substrates investigated here. With sterically hindered substituents like TMS (**5h**) or *tert*-butyl (**5j**) groups, only intermediates **7h** and **7j** were formed which can be explained by the steric repulsion for the second cyclization step. After its isolation, **5j** was again treated with 2.5 mol% gold catalyst in DCE at higher reaction temperatures. But even at 80 or 100 °C, no conversion could be observed. A possible 5-*exo-dig* cyclization was not observed as well. Surprisingly, the terminal alkyne **5i** did not convert at all.

To expand the possibilities of this powerful cascade reaction further, two bidirectional approaches were also established (**5k** and **5l**). Unfortunately, the non-aromatized intermediates of **6k** and **6l** of the bidirectional gold catalysis could not be isolated and characterized properly. This might be due to the fact that different stereoisomers can be formed. The strongly twisted N-heterocycle, in combination with the sterically demanding Boc protecting group could form diastereomers, which is also manifested in the X-ray structure of **6c** (Figure 2, left).[19] Nevertheless, the structure of **6k** showing a "trans"-conformation of the two Boc groups was confirmed by X-ray analysis (Figure 3, left and right top).



Scheme 7. Conditions for the scope of the reaction.[a]For **5c** additional 2.5 mol% catalyst were used.

In order to estimate the rotational barrier of the Boc groups as well as the phenyl rings attached to the aromatic core, relaxed scans were performed on the PBE0-D3/aug-pcseg-1 level of theory as implemented in the TeraChem software package (for more information see the Supporting Information). The barrier for the rotation of the Boc group is 20.7 kcal/mol, whereas a rotational barrier of 12.6 kcal/mol for the phenyl group turned out to be lower. Interestingly, in NMR experiments a coalescence temperature of 318 K between the two structures can be observed.

Due to the mentioned difficulties the products of the gold catalysis were directly used for the next step. The deprotection procedure was similar to the mono directional method, but needed an additional workup in form of column chromatography and subsequent recrystallization (see the Supporting

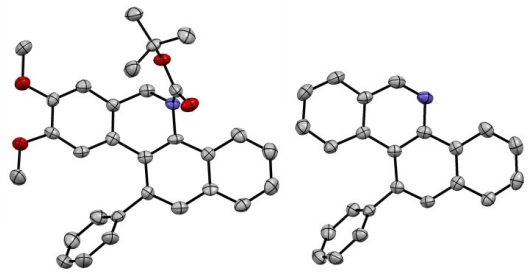


Figure 2. Solid state molecular structures of **6c** (left) and **13a** (right).

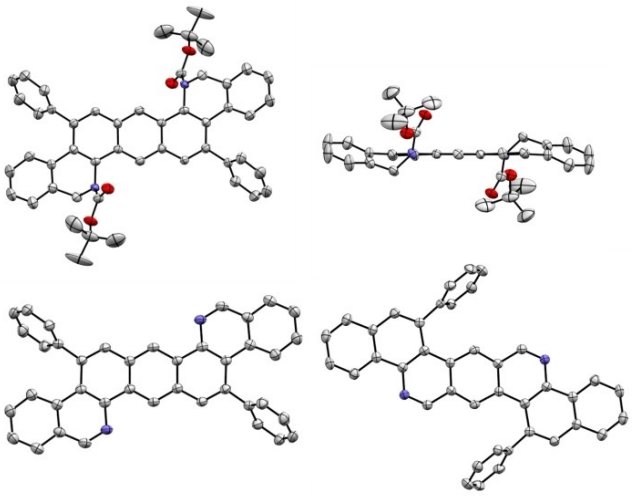


Figure 3. Solid state molecular structures of compounds generated in a bidirectional manner. Top left: **6k**; top right: side view of **6k** (the Ph-substituents are omitted for clarity); bottom left: **13k**; bottom right: **13l**.

Information for more information). This resulted in moderate yields over two steps of 36% (for **13k**) and 27% (for **13l**), respectively. Both structures, **13k** and **13l**, were also confirmed by X-ray crystallography.

Due to the large π-system of both bidirectionally obtained phenanthridines, **13k** and **13l** are potentially interesting as organic semiconductors for materials science. Thus, their optical properties (UV/Vis and fluorescence spectra can be found in the Supporting Information) and their potential charge-transport properties were evaluated. Both molecules are fluorescent and show two local maxima, with **13l** exhibiting a bathochromic shift of about 14 nm. The same trend is observed for the absorption spectra, with an onset of 423 nm for **13k** and 438 nm for **13l**. Using both materials, we attempted the fabrication of thin-film transistors (TFTs) in the inverted staggered (bottom-gate, top-contact) device architecture on heavily doped silicon substrates using different gate dielectrics and by deposition of the organic semiconductors by thermal sublimation in vacuum.[20] However, we were unable to measure any appreciable drain current or field effect with either **13k** or **13l**. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) images (see the Supporting Information) indicate that **13l** did not form a closed (or even percolated) film on any of the substrates, which explains the lack of charge transport. Compound **13k** appears to form a closed film, so the reason for the lack of charge transport remains unclear. The fact that we were not able to fabricate functional transistors by vacuum deposition of **13k** and **13l** does not mean that these materials may not form well-ordered films with good charge-transport properties when processed from solution or produced in the form of single-crystals.

Conclusion

We present a highly effective new cascade cyclization using gold catalysis. It was possible to optimize the gold-catalyzed step from 52 to 96% NMR yield by screening different catalysts and reaction conditions. Overall seven differently substituted Boc-protected dihydrobenzo[*c*]phenanthridines were synthesized and showed the dependence of electron-donating and -withdrawing substituents on different positions of the molecule as well as steric effects. This reaction pattern was then transferred successfully to bidirectional variants enabling the formation of large N-heterocyclic π-systems. It was further possible to thermally cleave the Boc group and to oxidize the cyclization products in a semi-one-pot strategy to furnish benzo[*c*]phenanthridine derivatives. Lastly, two bidirectional approaches successfully led to compounds that were tested as organic semiconductors in thin-film transistors. The presented reaction is an elegant way to synthesize highly substituted six-membered N-heterocycles. This synthetic strategy is especially interesting for materials science, but could also be used for the synthesis of pharmaceutically important alkaloids.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: benzo[*c*]phenanthridines · benzylamines · cascade reactions · homogeneous gold catalysis

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Supporting Information

"Golden" Cascade Cyclization to Benzo[*c*]-Phenanthridines

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ATable 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. ^1H 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 ^1H NMR spectra: s = singlet, bs = broad 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 and fluorine decoupled and interpreted with help of DEPT- and/or 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. 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 the Palladium catalyst was added. After stirring for 10 min at room temperature, the corresponding alkyne and 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: Reductive Amination

According to a slightly modified procedure of Takemoto *et al.*,[2] 1.00 eq of the aldehyde was dissolved in MeCN (and - if needed - DCM for better solubility). 2.00 eq *tert*-butyl carbamate were added and the reaction mixture was cooled down to 0 °C. Subsequently, 2.00 eq triethylsilane and 1.30 eq trifluoracetic acid were added dropwise. The solution was then stirred for 30 min, warmed up to room temperature and stirred overnight. After full conversion was observed by TLC, the reaction mixture was diluted with Et_2O and quenched with an aqueous $NaHCO_3$ solution. The aqueous phase was extracted with Et_2O and the combined organic layer was washed with brine and dried over Sodium sulphate. After filtration, the crude product was adsorbed onto Celite® and purified by flash column chromatography.

GP3: Gold Catalysis

1.00 eq of the corresponding alkyne was dissolved in dichloroethane and 2.5 mol% JohnPhosAu(MeCN)SbF_6 were added. The mixture was stirred at 50 °C until the TLC showed full conversion. The solvent was evaporated under reduced pressure. The resulting crude product was adsorbed onto Celite® and purified by flash column chromatography.

GP4: Cleavage of the Boc-Group

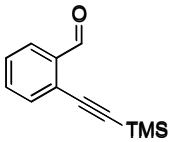
1.00 eq of the corresponding Boc-protected secondary amine was heated up to 200 °C under nitrogen atmosphere for the given time. The conversion was detected via ^1H NMR of the mixture. After full conversion was observed, the residue was dissolved in chloroform and flushed with air for given time. After removing of the solvent, the corresponding benzo[*c*]phenanthridine was obtained as a solid in quantitative yield.

3. Gold Catalysis Screening

For the screening of the gold catalyzed step all test reactions were carried out in an NMR-tube. For the reaction 0.5 mL of a 50 mM stock solution of *tert*-butyl (2-((2-(phenylethynyl)-phenyl)ethynyl)benzyl)carbamate (**5a**) and hexamethylbenzene as internal standard in $CDCl_3$ were used (corresponding to 25.0 µmol of each per reaction). All catalysts were added as salts. Conversion and yields of the intermediate and the expected product were calculated by integration of characteristic signals - namely the benzylic protons - against the internal standard with fixed integrals. To observe the reaction progress, control NMRs were measured after 2 h and 5 h.

4. Experimental Section

2-((Trimethylsilyl)ethynyl)benzaldehyde

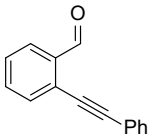


This compound was synthesized in a three step synthesis from *p*-phenylene-diamine according to a previously reported procedure.[3]

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.[3]

2-(Phenylethynyl)benzaldehyde

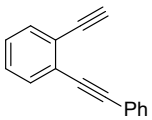


This compound was synthesized in a three step synthesis from *p*-phenylenediamine according to a previously reported procedure.[3]

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, $^3J_{H-H}$ = 7.8 Hz, 1H), 7.56-7.61 (m, 3H), 7.65 (d, $^3J_{H-H}$ = 7.7 Hz, 1H), 7.96 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 10.66 (s, 1H).

Analytics confirm to previously reported data.[3]

1-Ethynyl-2-(phenylethynyl)benzene

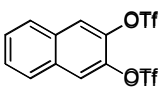


This compound was synthesized in a three step synthesis from *p*-phenylenediamine according to a previously reported procedure.[3]

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.[3]

Naphthalene-2,3-diyl bis(trifluoromethanesulfonate)



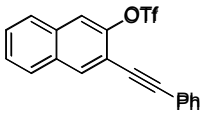
In a baked-out schlenk flask 10.0 eq triethylamine (19.0 g, 26.0 mL, 187 mmol) were added at -78 °C to a solution of 1.00 eq naphthalene-2,3-diol (3.00 g, 18.7 mmol) in 150 mL DCM. The mixture was allowed to warm up to room

temperature and stirred 2 h at this temperature. After re-cooling down to -78 °C 4.50 eq of trifluoromethanesulfonic anhydride (23.8 g, 14.2 mL, 84.3 mmol) were added dropwise. The mixture was again allowed to warm up to room temperature and stirred overnight. After quenching with water, the organic layer was washed with diluted hydrochloric acid and again with water. The aqueous layer was extracted with DCM and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated 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 to PE:EA = 10:1). A colorless solid was obtained (7.10 g, 16.7 mmol, 89%).

R_f: 0.46 (silica gel, PE:EA = 1:2); **^{1}H NMR** ($CDCl_3$, 500.1 MHz): δ[ppm] = 7.67-7.69 (dd, $^3J_{H-H}$ = 6.3 Hz, $^4J_{H-H}$ = 3.2 Hz, 2H), 7.92-7.94 (m, 4H); **^{19}F NMR** ($CDCl_3$, 470.6 MHz): δ[ppm] = -72.9 (s, 6F).

Analytics confirm to previously reported data.[4]

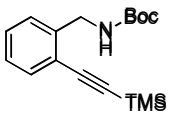
3-(Phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate



According to GP1, 1.10 eq ethynylbenzene (167 mg, 2.73 mmol) and later 2 mol% copper(I) iodide (9.60 mg, 50.4 µmol) were added to a mixture of 1.00 eq naphthalene-2,3-diyl bis(trifluoromethanesulfonate) (1.07 g, 2.52 mmol) and 2 mol% $PdCl_2(PPh_3)_2$ (35.4 mg, 50.4 µmol) in 40 mL solvent. The solution was stirred over night at room temperature and treated according to GP1 (silica gel, PE:EA = 30:1). A beige solid was obtained (884 mg, 2.35 mmol, 93%).

Mp: 107 °C; **R_f**: 0.56 (silica gel, PE:EA = 10:1); **IR** (ATR): ν[cm^{-1}] = 2219, 1602, 1502, 1420, 1249, 1206, 1136, 1054, 958, 921, 891, 875, 816, 749, 725, 687, 608; **^{1}H NMR** ($CDCl_3$, 500.2 MHz): δ[ppm] = 7.39-7.40 (m, 3H), 7.57-7.61 (m, 2H), 7.63-7.65 (m, 2H), 7.77 (s, 1H), 7.85-7.88 (m, 2H), 8.16 (s, 1H); **^{13}C NMR {^{19}F}** ($CDCl_3$, 125.8 MHz): δ[ppm] = 83.2 (s, 1C), 96.0 (s, 1C), 116.3 (s, 1C), 118.9 (s, 1C), 119.8 (d, 1C), 122.5 (s, 1C), 127.9 (d, 1C), 127.9 (d, 1C), 128.1 (d, 1C), 128.3 (d, 1C), 128.6 (d, 2C), 129.2 (d, 1C), 131.9 (d, 2C), 132.1 (s, 1C), 132.7 (s, 1C), 134.2 (d, 1C), 146.7 (s, 1C); **^{19}F NMR** ($CDCl_3$, 470.7 MHz): δ[ppm] = -73.4 (3F); **HRMS** (EI+): $C_{19}H_{11}F_3O_3S^+$, calculated: 376.03755 [M^+], observed: 376.03679 [M^+].

tert-Butyl (2-((trimethylsilyl)ethynyl)benzyl)carbamate



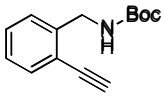
According to GP2 1.00 eq 2-((trimethylsilyl)ethynyl)benzaldehyde (9.42 g, 46.6 mmol) was dissolved in 200 mL MeCN and 5 mL DCM. 2.00 eq *tert*-butyl carbamate (10.9 g, 93.1 mmol) were added and the reaction mixture was cooled down to 0 °C. 2.00 eq triethylsilane (10.8 g, 14.9 mL, 93.1 mmol) and 1.30 eq trifluoroacetic acid (6.90 g, 4.66 mL, 60.5 mmol) were added dropwise. After stirring the solution for 30 min the reaction was warmed up to room temperature, stirred overnight

and treated according to GP2 (silica gel, PE:EA = 20:1). A yellow oil was obtained (13.8 g, 45.4 mmol, 98%).

^{1}H NMR ($CDCl_3$, 300.5 MHz): δ[ppm] = 0.27 (s, 9H), 1.45 (s, 9H), 4.45 (d, $^3J_{H\text{-}H}$ = 5.9 Hz, 2H), 5.10 (s, 1H), 7.18-7.23 (m, 1H), 7.26-7.35 (m, 2H), 7.45 (d, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H).

Analytics confirm to previously reported data.[5]

tert-Butyl (2-ethynylbenzyl)carbamate

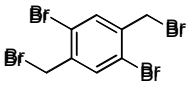


1.00 eq of 2-((trimethylsilyl)ethynyl)benzaldehyde (13.7 g, 45.1 mmol) was dissolved in 300 mL methanol. 2.00 eq K_2CO_3 (12.5 g, 90.4 mmol) were added and the reaction mixture was stirred at room temperature for 3 h. The solution was concentrated under reduced pressure, quenched with water and extracted with DCM. The combined organic layer was dried over sodium sulphate and filtered over a pad of Celite®. The solvent was removed under reduced pressure to obtain a reddish solid (9.81 g, 42.4 mmol, 94%).

^{1}H NMR ($CDCl_3$, 300.5 MHz): δ[ppm] = 1.45 (s, 9H), 3.32 (s, 1H), 4.47 (d, $^3J_{H\text{-}H}$ = 5.8 Hz, 2H), 5.02 (s, 1H), 7.20-7.25 (m, 1H), 7.30-7.38 (m, 2H), 7.48-7.50 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H).

Analytics confirm to previously reported data.[5]

1,4-Dibromo-2,5-bis(bromomethyl)benzene

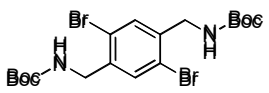


According to a procedure from Chen *et al.*,[6] in baked-out Schlenk flask 1.00 eq 1,4-dibromo-2,5-dimethylbenzene (5.00 g, 18.9 mmol) and 2.20 eq *N*-bromosuccinimide (7.42 g, 41.7 mmol) were dissolved in 110 mL dry benzene. The reaction mixture was stirred at 60 °C for 2 h. 5 mol% azobisisobutyronitrile (156 mg, 947 µmol) were added and the mixture was stirred for 15 h at 80 °C. The solution was quenched with water and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over sodium sulphate and the solvents were evaporated under reduced pressure. The residue was purified by recrystallization in ethanol. The precipitate was filtered and washed with ice-cold ethanol to give a colourless solid (4.88 g, 11.6 mmol, 61%).

R_f: 0.39 (silica gel, PE:EA = 5:1); **^{1}H-NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 4.51 (s, 4H), 7.66 (s, 2H).

Analytics confirm to previously reported data.[6]

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

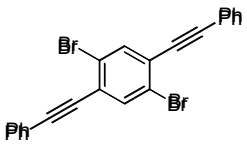


According to a modified procedure from Yaghi *et al.*,[7] 1.00 eq 1,4-dibromo-2,5-bis(bromomethyl)benzene (4.85 g, 11.5 mmol) and 4.00 eq sodium azid (2.99 g, 46.0 mmol) were dissolved in a baked-out Schlenk flask in 100 mL dry dimethylformamide. The reaction mixture was stirred at 65 °C for 15 h and then quenched with 100 mL ethanol. The organic layer was extracted with deionized water and diethylether, dried over sodium sulfate and the solvent was removed under reduced pressure until a volume of 10 mL. The concentrated solution was dissolved with 100 mL dry tetrahydrofuran and the solution was concentrated again up to a volume of 10 mL. This procedure was repeated three times. After the concentrate was dissolved in 100 mL dry tetrahydrofuran and flooded with nitrogen, 2.20 eq triphenylphosphane (6.64 g, 25.3 mmol) were added and the dark red reaction mixture was stirred at 60 °C for 2 h. 8 mL water was then added and the now clear red reaction mixture was stirred at 65 °C for 15 h. After the mixture was cooled down to room temperature, 2.50 eq di-*tert*-butyl dicarbonate (6.27 g, 6.60 mL, 28.8 mmol) were added and the reaction mixture was stirred at room temperature for 8 h. 2.20 eq ethanolamine (1.13 g, 18.5 mmol, 1.12 mL) were added and the mixture was stirred at room temperature for 2 h and 1 h at 50 °C. The solvent was removed under reduced pressure and the residue was dissolved in 110 mL ethylacetate. The organic layer was washed with ionized water and brine, dried over sodium sulfate and the solvent was removed under reduced pressure. The crude solid was purified by column chromatography (silica gel, DCM:EA = 1:1 to DCM). The product was obtained as a light orange solid (3.73 g, 7.55 mmol, 66%).

R_f: 0.27 (silica gel, PE:EA = 5:1); **^{1}H-NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 1.46 (s, 18H), 4.32 (d, $^3J_{H\text{-}H}$= 5.50 Hz, 4H), 4.99 (m, 2H), 7.52 (s, 2H).

Analytics confirm to previously reported data.[7]

((2,5-Dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzene

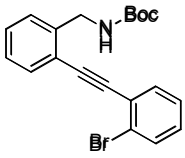


According to GP1, 2.10 eq phenylactelyene (691 mg, 743 µL, 6.77 mmol) and later 2 mol% copper(I) iodide (11.7 mg, 61.5 µmol) were added to a mixture of 1.00 eq 1,4-dibromo-2,5-diiodobenzene (1.50 g, 3.08 mmol) and 2 mol% $PdCl_2(PPh_3)_2$ (43.2 mg, 61.5 µmol) in 30 mL solvent. The solution was stirred for 2 h at room temperature and treated according to GP1 (silica gel, PE). A light yellow solid was obtained (1.24 g, 2.84 mmol, 92%).

R_f: 0.65 (silica gel, PE); **^{1}H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 7.37-7.39 (m, 6H), 7.56-7.60 (m, 4H), 7.79 (s, 2H).

Analytics confirm to previously reported data.[8]

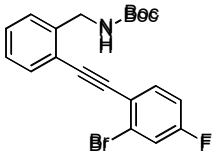
tert-Butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate



According to GP1, 1.00 eq *tert*-butyl (2-ethynylbenzyl)carbamate (5.00 g, 21.6 mmol) and later 2 mol% copper(I) iodide (82.9 mg, 436 µmol) were added to a mixture of 1.00 eq 1-bromo-2-iodo-benzene (6.12 g, 21.6 mmol) and 1 mol% $PdCl_2(PPh_3)_2$ (151 mg, 216 µmol) in 300 mL solvent. The solution was stirred overnight at room temperature and treated according to GP1 (silica gel, PE:EA = 10:1). A yellowish solid was obtained (7.41 g, 19.2 mmol, 89%).

Mp: 76 °C; **R_f**: 0.30 (silica gel, PE:EA = 10:1); **IR** (ATR): ν[cm^{-1}] = 3432, 3350, 3063, 2976, 2930, 2216, 1715, 1506, 1466, 1433, 1391, 1365, 1249, 1167, 1045, 1025, 933, 857, 757, 697, 653; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.43 (s, 9H), 4.60 (d, $^3J_{H-H}$ = 6.2 Hz, 2H), 6.49 (s, 1H), 7.31-7.37 (m, 2H), 7.40-7.47 (m, 3H), 7.59 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.71-7.74 (m, 2H); **^{13}C NMR** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 28.6 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 92.4 (s, 1C), 93.3 (s, 1C), 121.9 (s, 1C), 125.6 (s, 1C), 126.0 (s, 1C), 127.8 (d, 1C), 128.0 (d, 1C), 128.5 (d, 1C), 130.0 (d, 1C), 131.0 (d, 1C), 133.0 (d, 1C), 133.4 (d, 1C), 134.5 (d, 1C), 142.8 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): $C_{20}H_{20}NO_2{}^{79}Br^+$, calculated: 385.06719 [M^+], observed: 385.06570 [M^+].

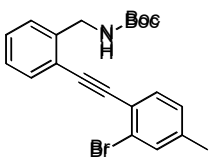
tert-Butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)carbamate



According to GP1, 1.00 eq *tert*-butyl (2-ethynylbenzyl)carbamate (615 mg, 2.66 mmol) and later 2 mol% copper(I) iodide (10.1 mg, 53.2 µmol) were added to a mixture of 1.00 eq 2-bromo-4-fluoro-1-iodobenzene (800 mg, 2.66 mmol) and 2 mol% $PdCl_2(PPh_3)_2$ (37.3 mg, 53.2 µmol) in 40 mL solvent. The solution was stirred for 64 h at room temperature and treated according to GP1 (silica gel, PE:EA = 10:1). A beige solid was obtained (916 mg, 2.27 mmol, 85%).

Mp: 80 °C; **R_f**: 0.28 (silica gel, PE:EA = 10:1); **IR** (ATR): ν[cm^{-1}] = 3355, 3067, 2975, 2894, 1685, 1593, 1538, 1494, 1477, 1390, 1364, 1273, 1253, 1173, 1051, 1032, 959, 938, 892, 861, 832, 796, 759, 705, 642; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.42 (s, 9H), 4.59 (d, $^3J_{H-H}$ = 6.2 Hz, 2H), 6.49 (s, 1H), 7.26-7.34 (m, 2H), 7.40-7.46 (m, 2H), 7.57-7.61 (m, 2H), 7.79 (dd, $^3J_{H-H}$ = 6.0 Hz, $^3J_{H-H}$ = 8.6 Hz, 1H); **^{13}C NMR {^{19}F}** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 28.6 (q, 3C), 43.6 (t, 1C), 79.0 (s, 1C), 92.2 (s, 1C), 92.3 (s, 1C), 116.0 (d, 1C), 120.8 (d, 1C), 121.8 (s, 1C), 122.7 (s, 1C), 126.3 (s, 1C), 127.8 (d, 1C), 128.0 (d, 1C), 130.0 (d, 1C), 133.0 (d, 1C), 135.9 (d, 1C), 142.8 (s, 1C), 156.8 (s, 1C), 162.9 (s, 1C); **^{19}F NMR** ($(CD_3)_2CO$, 470.7 MHz): δ[ppm] = -105.0 (1F); **HRMS** (EI+): $C_{20}H_{19}{}^{79}BrFNO_2{}^+$, calculated: 403.05777 [M^+], observed: 403.05700 [M^+]

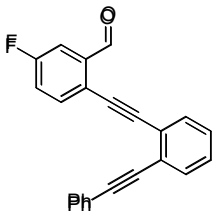
tert-Butyl (2-((2-bromo-4-methylphenyl)ethynyl)benzyl)carbamate



According to GP1, 1.00 eq *tert*-butyl (2-ethynylbenzyl)carbamate (623 mg, 2.69 mmol) and later 2 mol% copper(I) iodide (10.3 mg, 53.9 µmol) were added to a mixture of 1.00 eq 2-bromo-1-iodo-4-methylbenzene (800 mg, 2.69 mmol) and 2 mol% $PdCl_2(PPh_3)_2$ (37.8 mg, 53.9 µmol) in 40 mL solvent. The solution was stirred overnight at room temperature and treated according to GP1 (silica gel, PE:EA = 10:1). A beige solid was obtained (949 mg, 2.37 mmol, 88%).

Mp: 121 °C; **R_f**: 0.37 (silica gel, PE:EA = 10:1); **IR** (ATR): ν[cm^{-1}] = 3359, 2976, 2931, 2216, 1688, 1534, 1497, 1478, 1449, 1390, 1363, 1269, 1250, 1166, 1090, 1049, 1039, 957, 936, 869, 823, 779, 756, 649; **^{1}H NMR** ($(CD_3)_2CO$, 400.3 MHz): δ[ppm] = 1.43 (s, 9H), 2.38 (s, 3H), 4.59 (d, $^3J_{H\text{-}H}$ = 6.0 Hz, 2H), 6.41 (s, 1H), 7.25-7.33 (m, 2H), 7.38-7.45 (m, 2H), 7.56-7.60 (m, 3H); **^{13}C NMR** ($(CD_3)_2CO$, 100.7 MHz): δ[ppm] = 21.1 (q, 1C), 28.7 (q, 3C), 43.7 (t, 1C), 79.0 (s, 1C), 91.7 (s, 1C), 93.5 (s, 1C), 122.2 (s, 1C), 123.0 (s, 1C), 125.5 (s, 1C), 127.8 (d, 1C), 128.0 (d, 1C), 129.3 (d, 1C), 129.8 (d, 1C), 132.9 (d, 1C), 133.8 (d, 1C), 134.2 (d, 1C), 141.8 (s, 1C), 142.7 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): $C_{21}H_{22}BrNO_2^+$, calculated: 399.08284 [M^+], observed: 399.08182 [M^+].

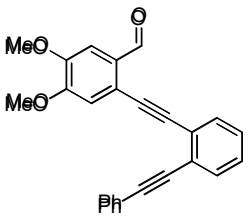
5-Fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde



According to GP1, 1.10 eq 1-ethynyl-2-(phenylethynyl)benzene (1.10 g, 5.42 mmol) and later 2 mol% copper(I) iodide (18.8 mg, 98.5 µmol) were added to a mixture of 1.00 eq 2-bromo-5-fluorobenzaldehyde (1.00 g, 4.93 mmol) and 2 mol% $PdCl_2(PPh_3)_2$ (69.2 mg, 98.5 µmol) in 40 mL solvent. The solution was stirred overnight at room temperature and treated according to GP1 (silica gel, PE:EA = 20:1). A yellow solid was obtained (1.53 g, 4.72 mmol, 96%).

Mp: 81 °C; **R_f**: 0.44 (silica gel, PE:EA = 10:1); **IR** (ATR): ν[cm^{-1}] = 3371, 3063, 2852, 2749, 2216, 1695, 1602, 1495, 1441, 1420, 1390, 1314, 1291, 1266, 1208, 1145, 965, 887, 827, 758, 691, 621; **^{1}H NMR** (CD_2Cl_2, 500.2 MHz): δ[ppm] = 7.31-7.35 (m, 1H), 7.38-7.41 (m, 5H), 7.55-7.56 (m, 2H), 7.59-7.63 (m, 3H), 7.70-7.72 (m, 1H), 10.72 (d, $^4J_{H\text{-}H}$ = 2.4 Hz, 1H); **^{13}C NMR {^{19}F}** (CD_2Cl_2, 125.8 MHz): δ[ppm] = 88.1 (s, 1C), 88.2 (s, 1C), 94.2 (s, 1C), 94.9 (s, 1C), 113.8 (d, 1C), 121.7 (d, 1C), 123.1 (s, 1C), 123.2 (s, 1C), 124.8 (s, 1C), 126.2 (s, 1C), 128.7 (d, 1C), 128.9 (d, 2C), 129.2 (d, 1C), 129.4 (d, 1C), 132.0 (d, 2C), 132.5 (d, 1C), 132.7 (d, 1C), 135.8 (d, 1C), 138.3 (s, 1C), 163.0 (s, 1C), 190.8 (d, 1C); **^{19}F NMR** (CD_2Cl_2, 470.7 MHz): δ[ppm] = -109.5 (1F); **HRMS** (EI+): $C_{23}H_{13}FO^+$, calculated: 324.09449 [M^+], observed: 324.09306 [M^+].

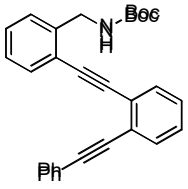
4,5-Dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde



According to GP1, 1.10 eq 1-ethynyl-2-(phenylethynyl)benzene (907 mg, 4.48 mmol) and later 2 mol% copper(I) iodide (15.5 mg, 81.6 µmol) were added to a mixture of 1.00 eq 2-bromo-4,5-dimethoxybenzaldehyde (1.00 g, 4.08 mmol) and 2 mol% $PdCl_2(PPh_3)_2$ (57.0 mg, 81.6 µmol) in 40 mL solvent. The solution was stirred overnight at 50 °C and treated according to GP1 (silica gel, PE:EA = 10:1 to 5:1 to 3:1). An orange solid was obtained (694 mg, 1.89 mmol, 46%).

Mp: 135 °C; **R_f**: 0.36 (silica gel, PE:EA = 3:1); **IR** (ATR): ν[cm^{-1}] = 3002, 2971, 2933, 2831, 2211, 1675, 1587, 1504, 1461, 1444, 1398, 1359, 1304, 1263, 1237, 1219, 1162, 1104, 1080, 1039, 1006, 927, 895, 867, 761, 748, 699, 631; **^{1}H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 3.82 (s, 3H), 3.95 (s, 3H), 7.05 (s, 1H), 7.33-7.36 (m, 5H), 7.42 (s, 1H), 7.56-7.60 (m, 4H), 10.62 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 56.3 (q, 1C), 56.3 (q, 1C), 88.2 (s, 1C), 89.1 (s, 1C), 94.0 (s, 1C), 94.0 (s, 1C), 108.3 (d, 1C), 114.6 (d, 1C), 121.7 (s, 1C), 123.1 (s, 1C), 125.2 (s, 1C), 126.1 (s, 1C), 128.3 (d, 1C), 128.6 (d, 2C), 128.7 (d, 1C), 128.8 (d, 1C), 130.4 (s, 1C), 131.9 (d, 2C), 131.9 (d, 1C), 132.3 (d, 1C), 150.1 (s, 1C), 153.8 (s, 1C), 190.6 (d, 1C); **HRMS** (EI+): $C_{25}H_{18}O_3^+$, calculated: 366.12505 [M^+], observed: 366.12448 [M^+].

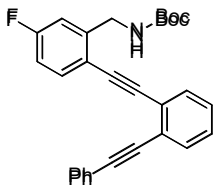
***tert*-Butyl (2-((2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5a**



According to GP1, 1.85 eq ethynylbenzene (167 mg, 1.64 mmol) and later 2 mol% copper(I) iodide (3.40 mg, 17.8 µmol) were added to a mixture of 1.00 eq *tert*-butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate (342 mg, 885 µmol) and 2 mol% $PdCl_2(PPh_3)_2$ (12.5 mg, 17.8 µmol) in 20 mL solvent. The solution was stirred overnight at 50 °C and for further 5 h at 80 °C. 2 mol% $Pd(PPh_3)_4$ (20.5 mg, 17.7 µmol) were added and the reaction mixture was stirred at 80 °C for 64 h and then treated according to GP1 (silica gel, PE:EA = 20:1). An orange solid was obtained (290 mg, 712 µmol, 80%).

Mp: 70 °C; **R_f:** 0.53 (silica gel, PE:EA = 10:1); **IR** (ATR): ν[cm^{-1}] = 3397, 2973, 2876, 1698, 1597, 1512, 1449, 1389, 1362, 1303, 1243, 1164, 1135, 1047, 1024, 947, 916, 884, 864, 803, 754, 689; **^{1}H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 1.43 (s, 9H), 4.64 (d, $^3J_{H-H}$ = 6.2 Hz, 2H), 6.39 (m, 1H), 7.27-7.31 (m, 1H), 7.37-7.47 (m, 7H), 7.58-7.66 (m, 4H), 7.69-7.71 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 28.7 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 88.9 (s, 1C), 92.0 (s, 1C), 93.7 (s, 1C), 94.2 (s, 1C), 122.2 (s, 1C), 123.8 (s, 1C), 126.1 (s, 1C), 126.3 (s, 1C), 127.7 (d, 1C), 127.8 (d, 1C), 129.4 (d, 1C), 129.4 (d, 1C), 129.5 (d, 2C), 129.6 (d, 1C), 129.8 (d, 1C), 132.5 (d, 2C), 133.0 (d, 1C), 133.1 (d, 1C), 133.1 (d, 1C), 142.7 (s, 1C), 156.7 (s, 1C); **HRMS** (ESI+): $C_{20}H_{16}ONa^+$, calculated: 430.1777 [$M+Na^+$], observed: 430.1778 [$M+Na^+$].

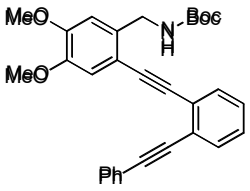
tert-Butyl (5-fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5b



According to GP2, 1.00 eq of the corresponding aldehyde (1.51 g, 4.65 mmol) was dissolved in 50 mL MeCN and 5 mL DCM. 2.00 eq *tert*-butyl carbamate (1.09 g, 9.29 mmol) were added and the reaction mixture was cooled down to 0 °C. 2.00 eq triethylsilane (1.09 g, 1.50 mL, 9.39 mmol) and 1.40 eq trifluoroacetic acid (740 mg, 500 µL, 6.49 mmol) were added dropwise. After stirring the solution for 30 min the formed precipitate was filtrated and washed with cold MeCN. A beige solid was obtained (690 mg, 1.62 mmol, 35%).

Mp: 114 °C; **R_f**: 0.29 (silica gel, PE:EA = 10:1); **IR** (ATR): ν[cm^{-1}] = 3369, 3067, 2971, 2210, 1682, 1605, 1581, 1527, 1494, 1431, 1388, 1363, 1301, 1273, 1250, 1212, 1166, 1080, 1045, 962, 930, 875, 814, 784, 753, 691; **^{1}H NMR** ($CDCl_3$, 500.2 MHz): δ[ppm] = 1.41 (s, 9H), 4.52 (d, $^3J_{H-H}$ = 5.8 Hz, 2H), 5.03 (m, 1H), 6.94 (d, $^3J_{H-H}$ = 8.3 Hz, 1H), 7.10 (d, $^3J_{H-H}$ = 9.1 Hz, 1H), 7.34-7.36 (m, 5H), 7.51-7.59 (m, 5H); **^{13}C NMR {^{19}F}** ($CDCl_3$, 125.8 MHz): δ[ppm] = 28.5 (q, 3C), 43.2 (t, 1C), 79.7 (s, 1C), 88.3 (s, 1C), 90.3 (s, 1C), 92.8 (s, 1C), 93.5 (s, 1C), 114.5 (d, 1C), 115.1 (d, 1C), 117.9 (s, 1C), 123.1 (s, 1C), 125.4 (s, 1C), 125.6 (s, 1C), 128.3 (d, 1C), 128.4 (d, 1C), 128.6 (d, 2C), 128.8 (d, 1C), 131.8 (d, 2C), 132.1 (d, 1C), 132.3 (d, 1C), 134.2 (d, 1C), 144.1 (s, 1C), 155.9 (s, 1C), 162.9 (s, 1C); **^{19}F NMR** ($CDCl_3$, 470.7 MHz): δ[ppm] = -109.7 (1F); **HRMS** (ESI (+)): $C_{28}H_{24}FNO_2Na^+$, calculated: 448.1683 [M^++Na], observed: 448.1685 [M^++Na].

tert-Butyl (4,5-dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5c

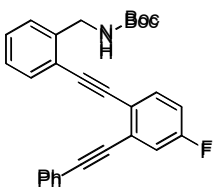


According to GP2, 1.00 eq of the corresponding aldehyde (675 mg, 1.84 mmol) was dissolved in 150 mL MeCN and 12 mL DCM. 2.00 eq *tert*-butyl carbamate (432 mg, 3.69 mmol) were added and the reaction mixture was cooled down to 0 °C. 2.00 eq triethylsilane (430 mg, 590 µL, 3.69 mmol) and 1.27 eq trifluoroacetic acid (266 mg, 180 µL, 2.34 mmol) were added dropwise. After stirring the solution for 30 min the reaction was warmed up to room temperature and stirred overnight. Additional 0.50 eq *tert*-butyl carbamate (108 mg, 921 µmol), 0.51 eq triethylsilane (109 mg, 150 µL, 940 µmol) and 0.35 eq trifluoroacetic acid (74.0 mg, 50.0 µL, 649 µmol) were added. After stirring overnight at 50 °C, the mixture was treated according to GP2 (silica gel, PE:EA = 5:1 to 3:1 to 1:1). An orange solid was obtained (307 mg, 656 µmol, 36%).

Mp: 123 °C; **R_f**: 0.22 (silica gel, PE:EA = 3:1); **IR** (ATR): ν[cm^{-1}] = 3368, 2992, 2970, 2932, 2831, 2208, 1686, 1607, 1514, 1494, 1464, 1428, 1391, 1365, 1348, 1283, 1243, 1210, 1173, 1101, 1079, 1039, 996, 934, 865, 756, 737, 691, 637; **^{1}H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 1.41 (s, 9H), 3.77 (s, 3H), 3.89 (s, 3H), 4.48 (d, $^3J_{H-H}$ = 5.9 Hz, 2H), 5.04 (m, 1H), 6.93 (s, 1H), 7.01 (s, 1H), 7.29-7.35 (m, 5H), 7.55-7.58 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 28.5 (q, 3C), 43.2 (t, 1C), 56.0 (q, 1C), 56.1 (q, 1C), 79.4 (s, 1C), 88.5 (s, 1C), 91.6 (s, 1C), 91.8 (s, 1C), 93.5 (s, 1C), 111.7 (d, 1C), 114.1 (s, 1C), 114.7 (d, 1C), 123.3 (s, 1C), 125.5 (s, 1C), 126.0 (s, 1C), 128.1 (d, 1C), 128.3 (d, 1C), 128.5 (d, 2C), 128.7 (d, 1C), 131.8 (d, 3C), 132.2 (d, 1C), 134.9 (s, 1C), 148.0 (s,

1C), 149.9 (s, 1C), 156.1 (s, 1C); **HRMS** (EI+): $C_{30}H_{29}NO_4^+$, calculated: 467.20911 [M^+], observed: 467.20974 [M^+].

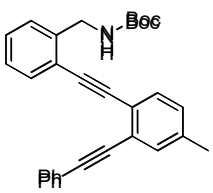
tert-Butyl (2-((4-fluoro-2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5d



According to GP1, 2.00 eq of ethynylbenzene (253 mg, 272 µL 2.47 mmol) and later 3 mol% copper(I) iodide (7.40 mg, 38.8 µmol) were added to a mixture of 1.00 eq *tert*-butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)-carbamate (500 mg, 1.24 mmol) and 4 mol% $Pd(PPh_3)_4$ (57.2 mg, 49.5 µmol) in 40 mL solvent. The solution was stirred overnight at 80 °C and treated according to GP1 (silica gel, PE:EA = 10:1). A brown solid was obtained (521 mg, 1.22 mmol, 99%).

Mp: 95-98 °C; **R_f**: 0.44 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 2973, 2873, 1687, 1598, 1500, 1390, 1363, 1244, 1197, 1163, 1046, 956, 862, 827, 755, 689; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.42 (s, 9H), 4.59 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 2H), 6.46 (m, 1H) 7.25-7.31 (m, 2H), 7.38-7.46 (m, 6H), 7.58 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H), 7.62-7.64 (m, 2H), 7.76 (dd, $^3J_{H\text{-}H}$ = 5.9 Hz, $^3J_{H\text{-}H}$ = 8.7 Hz, 1H); **^{13}C NMR {^{19}F}** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 28.6 (q, 3C), 43.5 (t, 1C), 78.9 (s, 1C), 87.7 (s, 1C), 91.7 (s, 1C), 92.7 (s, 1C), 95.3 (s, 1C), 117.1 (d, 1C), 119.5 (d, 1C), 122.0 (s, 1C), 122.8 (s, 1C), 123.2 (s, 1C), 127.7 (d, 1C), 127.7 (d, 1C), 128.1 (s, 1C), 129.6 (d, 2C), 129.8 (d, 1C), 130.0 (d, 1C), 132.6 (d, 2C), 132.9 (d, 1C), 135.3 (d, 1C), 142.7 (s, 1C), 156.7 (s, 1C), 162.8 (s, 1C); **^{19}F NMR** ($(CD_3)_2CO$, 470.7 MHz): δ[ppm] = -112.2 (1F); **HRMS** (EI+): $C_{28}H_{24}FNO_2^+$, calculated: 425.17856 [M^+], observed: 425.17791 [M^+].

tert-Butyl (2-((4-methyl-2-(phenylethynyl)phenyl)ethynyl)benzyl)carbamate, 5e

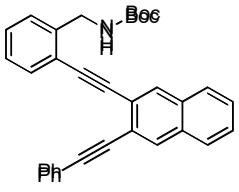


According to GP1, 2.00 eq of ethynylbenzene (255 mg, 274 µL, 2.50 mmol) and later 3 mol% copper(I) iodide (7.60 mg, 40.0 µmol) were added to a mixture of 1.00 eq *tert*-butyl (2-((2-bromo-4-methylphenyl)ethynyl)benzyl)-carbamate (500 mg, 1.24 mmol) and 4 mol% $Pd(PPh_3)_4$ (57.7 mg, 50.0 µmol) in 40 mL solvent. The solution was stirred for 40 h at 80 °C and additional 0.50 eq of ethynylbenzene (63.8 mg, 68.6 µL, 625 µmol) and 2 mol% $Pd(PPh_3)_4$ (28.9 mg, 25.0 µmol) were added. After stirring overnight at 80 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 20:1). A brown solid was obtained (428 mg, 1.02 mmol, 81%).

Mp: 101-104 °C; **R_f**: 0.48 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3376, 2983, 2924, 1682, 1525, 1497, 1443, 1392, 1364, 1305, 1274, 1170, 1138, 1021, 919, 874, 823, 751, 691, 617; **^{1}H NMR** ($(CD_3)_2CO$, 300.2 MHz): δ[ppm] = 1.42 (s, 9H), 2.39 (s, 3H), 4.59 (d, $^3J_{H\text{-}H}$ = 6.2 Hz, 2H), 6.38 (m, 1H), 7.26-7.31 (m, 2H), 7.35-7.43 (m, 5H), 7.47 (s, 1H), 7.55-7.62 (m, 4H); **^{13}C NMR** ($(CD_3)_2CO$, 75.5 MHz): δ[ppm] = 21.2 (q, 1C), 28.7 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 89.1 (s, 1C), 91.3 (s, 1C), 93.8 (s, 1C), 93.9 (s, 1C), 122.4 (s, 1C), 123.4 (s, 1C), 123.9 (s, 1C), 126.0 (s, 1C), 127.7 (d, 2C), 129.5 (d, 2C), 129.6 (d, 2C), 130.3 (d, 1C), 132.5 (d, 2C), 132.9 (d, 1C),

133.1 (d, 1C), 133.5 (d, 1C), 139.8 (s, 1C), 142.7 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): $C_{29}H_{27}NO_2^+$, calculated: 421.20363 [M^+], observed: 421.20217 [M^+].

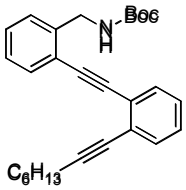
tert-Butyl (2-((3-(phenylethynyl)naphthalen-2-yl)ethynyl)benzyl)carbamate, 5f



According to GP1, 1.20 eq *tert*-butyl (2-ethynylbenzyl)carbamate (553 mg, 2.39 mmol) and later 2 mol% copper(I) iodide (7.60 mg, 39.9 µmol) were added to a mixture of 1.00 eq 3-(phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate (750 mg, 1.99 mmol) and 2 mol% $PdCl_2(PPh_3)_2$ (31.7 mg, 45.2 µmol) in 40 mL solvent. The solution was stirred overnight at room temperature and additional 0.40 eq *tert*-butyl (2-ethynylbenzyl)carbamate (184 mg, 797 µmol) were added. After stirring for 64 h at 50 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 10:1). A beige solid was obtained (627 mg, 1.37 mmol, 69%).

Mp: 119 °C; **R_f**: 0.43 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3362, 2970, 1678, 1510, 1494, 1364, 1247, 1168, 1126, 1047, 1025, 953, 895, 756, 748, 693; **^{1}H NMR** ($(CD_3)_2CO$, 400.3 MHz): δ[ppm] = 1.43 (s, 9H), 4.65 (d, $^3J_{H-H}$ = 5.9 Hz, 2H), 6.41 (m, 1H), 7.31 (dt, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H), 7.39-7.46 (m, 5H), 7.58-7.66 (m, 5H) 7.96-7.98 (m, 2H), 8.23 (s, 1H), 8.30 (s, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 100.7 MHz): δ[ppm] = 28.7 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 89.1 (s, 1C), 91.4 (s, 1C), 93.7 (s, 1C), 94.0 (s, 1C), 122.3 (s, 1C), 122.7 (s, 1C), 122.9 (s, 1C), 123.9 (s, 1C), 127.8 (d, 1C), 127.8 (d, 1C), 128.6 (d, 2C), 128.6 (d, 2C), 129.6 (d, 2C), 129.6 (d, 1C), 129.8 (d, 1C), 132.5 (d, 2C), 133.1 (d, 1C), 133.1 (d, 1C), 133.2 (d, 1C), 133.5 (s, 1C), 133.5 (s, 1C), 142.8 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): $C_{32}H_{27}NO_2^+$, calculated: 457.20363 [M^+], observed: 457.20254 [M^+].

tert-Butyl (2-((2-(oct-1-yn-1-yl)phenyl)ethynyl)benzyl)carbamate, 5g

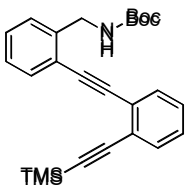


According to GP1, 1.80 eq oct-1-yne (254 mg, 340 µL, 2.30 mmol) and later 2 mol% copper(I) iodide (4.93 mg, 25.9 µmol) were added to a mixture of 1.00 eq *tert*-butyl (2-((2-bromophenyl)ethynyl)-benzyl)carbamate (500 mg, 1.29 mmol) and 2 mol% $Pd(PPh_3)_4$ (29.9 mg, 25.9 µmol) in 20 mL solvent. The solution was stirred over night at 60 °C and additional 4 mol% $Pd(PPh_3)_4$ (59.8 mg, 51.6 µmol) were added. After stirring for 88 h at 80 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 20:1). A green solid was obtained (407 mg, 979 µmol, 76%).

Mp: 47 °C; **R_f**: 0.62 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3432, 3357, 3061, 2957, 2931, 2858, 2227, 1956, 1925, 1717, 1504, 1453, 1391, 1366, 1250, 1171, 1048, 950, 933, 858, 758; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 0.85-0.88 (m, 3H), 1.28-1.31 (m, 4H), 1.44 (s, 9H), 1.47-1.52 (m, 2H), 1.61-1.66 (m, 2H), 2.54 (t, $^3J_{H-H}$ = 7.1 Hz, 2H), 4.64 (d, $^3J_{H-H}$ = 6.2 Hz, 2H), 6.52 (m, 1H), 7.28-7.32 (m, 1H), 7.34-7.37 (m, 2H), 7.38-7.45 (m, 2H), 7.46-7.49 (m, 1H), 7.55 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 7.60-7.62 (m, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 14.3 (q, 1C),

20.0 (t, 1C), 23.2 (t, 1C), 28.6 (q, 3C), 29.4 (t, 1C), 29.6 (t, 1C), 32.1 (t, 1C), 43.6 (t, 1C), 79.0 (s, 1C), 80.2 (s, 1C), 91.2 (s, 1C), 94.1 (s, 1C), 95.8 (s, 1C), 122.2 (s, 1C), 126.1 (s, 1C), 127.2 (s, 1C), 127.4 (d, 1C), 127.6 (d, 1C), 128.5 (d, 1C), 129.3 (d, 1C), 129.7 (d, 1C), 132.8 (d, 1C), 132.9 (d, 1C), 133.0 (d, 1C), 142.8 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): $C_{28}H_{33}NO_2^+$, calculated: 415.25058 [M^+], observed: 415.248884 [M^+].

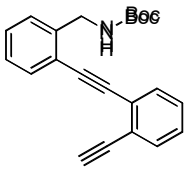
tert-Butyl (2-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzyl)carbamate, 5h



According to GP1, 2.00 eq ethynyltrimethylsilane (255 mg, 360 µL, 2.60 mmol) and later 4 mol% copper(I) iodide (9.90 mg, 51.8 µmol) were added to a mixture of 1.00 eq *tert*-butyl (2-((2-bromophenyl)ethynyl)benzyl)-carbamate (500 mg, 1.29 mmol) and 4 mol% $Pd(PPh_3)_4$ (59.8 mg, 51.8 µmol) in 30 mL solvent. The solution was stirred overnight at 60 °C and additional 0.50 eq ethynyltrimethylsilane (63.6 mg, 90.0 µL, 647 µmol) were added and the reaction mixture was stirred at 80 °C overnight. Again, 0.50 eq ethynyltrimethylsilane (63.6 mg, 90.0 µL, 647 µmol) and 2 mol% $Pd(PPh_3)_4$ (30.0 mg, 25.9 µmol) were added. After stirring for 88 h at 70 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 20:1). A beige solid was obtained (279 mg, 692 µmol, 53%).

Mp: 107 °C; **R_f**: 0.57 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3365, 3053, 3001, 2975, 2152, 1682, 1530, 1491, 1365, 1292, 1247, 1211, 1165, 1049, 953, 871, 841, 755, 646; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 0.27 (s, 9H), 1.43 (s, 9H), 4.61 (d, $^3J_{H-H}$ = 6.2 Hz, 2H), 6.52 (m, 1H), 7.32 (t, $^3J_{H-H}$ = 7.2 Hz, 1H), 7.38-7.46 (m, 4H), 7.55-7.59 (m, 2H), 7.67 (d, $^3J_{H-H}$ = 7.8 Hz, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 0.0 (q, 3C), 28.6 (q, 3C), 43.5 (t, 1C), 78.9 (s, 1C), 91.8 (s, 1C), 93.6 (s, 1C), 99.2 (s, 1C), 104.4 (s, 1C), 122.1 (s, 1C), 126.0 (s, 1C), 126.4 (s, 1C), 127.7 (d, 1C), 127.8 (d, 1C), 129.3 (d, 1C), 129.6 (d, 1C), 129.8 (d, 1C), 133.1 (d, 1C), 133.1 (d, 1C), 133.5 (d, 1C), 142.7 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): $C_{25}H_{29}NO_2Si^+$, calculated: 403.19621 [M^+], observed: 403.19458 [M^+].

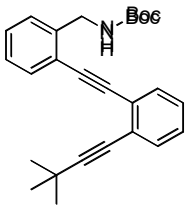
tert-Butyl (2-((2-ethynylphenyl)ethynyl)benzyl)carbamate, 5i



1.00 eq of *tert*-butyl (2-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzyl)-carbamate (204 mg, 505 µmol) was dissolved in 20 mL methanol and 3 mL DCM. 2.00 eq K_2CO_3 (140 mg, 1.01 mmol) were added and the reaction mixture was stirred at room temperature for 3 h until TLC showed full conversion. 20 mL DCM and 20 mL deionized water were added. The aqueous phase was extracted with DCM and the combined organic layer was dried over sodium sulphate. The solution was filtrated and the solvent was removed under reduced pressure. The crude product was adsorbed onto Celite® and purified by flash column chromatography (silica gel, PE:EA = 30:1 to 20:1). A yellowish oil was obtained (55.6 mg, 168 µmol, 33%).

R_f: 0.50 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3102, 3068, 2934, 2841, 1718, 1670, 1612, 1507, 1446, 1383, 1355, 1335, 1303, 1228, 1190, 1160, 1104, 1065, 1042, 953, 853, 700, 632; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.43 (s, 9H), 3.98 (s, 1H), 4.61 (d, $^3J_{H-H}$ = 6.1 Hz, 2H), 6.41 (m, 1H), 7.31 (dt, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 1.2 Hz, 1H), 7.38-7.48 (m, 4H), 7.56-7.61 (m, 2H), 7.65-7.68 (m, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 100.7 MHz): δ[ppm] = 28.6 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 82.9 (s, 1C), 83.6 (d, 1C), 91.8 (s, 1C), 93.3 (s, 1C), 122.1 (s, 1C), 125.3 (s, 1C), 126.8 (s, 1C), 127.7 (d, 1C), 127.8 (d, 1C), 129.3 (d, 1C), 129.7 (d, 1C), 129.7 (d, 1C), 132.8 (d, 1C), 133.0 (d, 1C), 133.3 (d, 1C), 142.6 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): $C_{22}H_{21}NO_2^+$, calculated: 331.15668 [M^+], observed: 331.15584 [M^+].

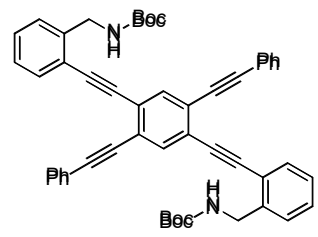
tert-Butyl (2-((2-(3,3-dimethylbut-1-yn-1-yl)phenyl)ethynyl)benzyl)carbamate, 5j



According to GP1, 2.00 eq 3,3-dimethylbut-1-yne (213 mg, 320 µL, 2.59 mmol) and later 4 mol% copper(I) iodide (9.90 mg, 51.8 µmol) were added to a mixture of 1.00 eq *tert*-butyl (2-((2-bromophenyl)ethynyl)benzyl)-carbamate (500 mg, 1.29 mmol) and 4 mol% $Pd(PPh_3)_4$ (59.8 mg, 51.8 µmol) in 30 mL solvent. The solution was stirred for 40 h at 60 °C and additional 1.00 eq 3,3-dimethylbut-1-yne (106 mg, 160 µL, 1.29 mmol) and 2 mol% $Pd(PPh_3)_4$ (30.0 mg, 25.9 µmol) were added. After stirring for 88 h at 70 °C, the mixture was treated according to GP1 (silica gel, PE:EA = 20:1). A colorless solid was obtained (226 mg, 584 µmol, 45%).

Mp: 95 °C; **R_f**: 0.56 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3433, 3346, 3062, 2970, 2929, 2868, 2237, 1703, 1492, 1453, 1391, 1365, 1249, 1169, 1048, 933, 857, 757; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.35 (s, 9H), 1.43 (s, 9H), 4.61 (d, $^3J_{H-H}$ = 6.2 Hz, 2H), 6.53 (m, 1H), 7.31 (t, $^3J_{H-H}$ = 7.3 Hz, 1H), 7.34-7.47 (m, 5H), 7.57 (d, $^3J_{H-H}$ = 7.7 Hz, 1H), 7.63-7.64 (m, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 28.6 (q, 3C), 28.8 (s, 1C), 31.3 (q, 3C), 43.6 (t, 1C), 78.9 (s, 1C), 78.9 (s, 1C), 91.1 (s, 1C), 94.1 (s, 1C), 103.5 (s, 1C), 122.3 (s, 1C), 125.9 (s, 1C), 126.9 (s, 1C), 127.6 (d, 1C), 127.7 (d, 1C), 128.5 (d, 1C), 129.2 (d, 1C), 129.6 (d, 1C), 132.9 (d, 1C), 133.1 (d, 1C), 133.1 (d, 1C), 142.6 (s, 1C), 156.8 (s, 1C); **HRMS** (EI+): $C_{26}H_{29}NO_2^+$, calculated: 387.21928 [M^+], observed: 387.21937 [M^+].

Di-*tert*-butyl ((((2,5-bis(phenylethynyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2,1-phenylene))bis(methylene))dicarbamate, 5k

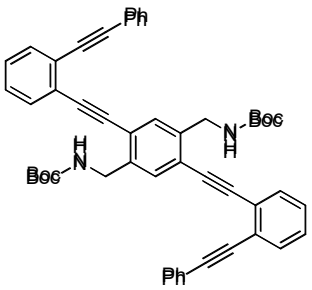


According to GP1, 2.40 eq *tert*-butyl (2-ethynylbenzyl)carbamate (763 mg, 3.30 mmol) and later 4 mol% copper(I) iodide (10.4 mg, 55.0 µmol) were added to a mixture of 1.00 eq ((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzene (600 mg, 1.38 mmol) and 4 mol% $PdCl_2(PPh_3)_2$ (38.6 mg, 55.0 µmol) in 36 mL solvent. After stirring for 15 h at 65 °C, the solvent was 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 of EA. The precipitate was filtered and dried under vacuum. A colourless solid was obtained (881 mg, 1.20 mmol, 87%).

Mp: 184-186 °C; **R_f**: 0.4 (silica gel, PE:EA = 1:2); **IR** (ATR): ν[cm^{-1}] = 3367, 2981, 2205, 1685, 1525, 1502, 1365, 1272, 1251, 1168, 930, 752, 690; **^{1}H NMR** (CD_2Cl_2, 400.3 MHz): δ[ppm] = 1.41 (s, 18H), 4.54 (d, $^3J_{H-H}$= 6.2 Hz, 4H), 5.08 (m, 2H), 7.27-7.31 (m, 2H), 7.35-7.43 (m, 10H), 7.57-7.62 (m, 6H), 7.84 (s, 2H); **^{13}C NMR** (CD_2Cl_2, 100.7 MHz): δ[ppm] = 28.5 (q, 6C), 43.7 (t, 2C), 79.6 (s, 2C), 87.6 (s, 2C), 92.4 (s, 2C), 93.6 (s, 2C), 95.9 s, 2C), 121.9 (s, 2C), 123.0 (s, 2C), 125.5 (s, 2C), 125.6 (s, 2C), 127.6 (d, 2C), 128.2 (d, 2C), 129.0 (d, 4C), 129.4 (d, 2C), 129.7 (d, 2C), 132.2 (d, 4C), 132.9 (d, 2C), 136.0 (d, 2C), 141.9 (s, 2C), 156.1 (s, 2C);; **HRMS** (ESI+) $C_{50}H_{44}N_2NaO_4^+$, calculated: 759.3193 [M+Na^+], observed: 739.3202 [M+Na^+], **UV/VIS** (DCM, 8.00 µg/mL): λ[nm] (logε) = 300 (4.88), 317 (5.12), 352 (4.71), 368 (4.67), 379 (4.44); **Fluorescence** (DCM): λ_{Anr}= 370 nm, λ_{Max}= 393 nm; **Quantum yield**: Φ = 65%.

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

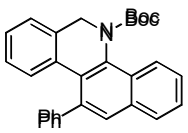


According to GP1, 2.40 eq 1-ethynyl-2-(phenylethynyl)benzene (785 mg, 3.88 mmol) and later 5 mol% copper(I) iodide (15.4 mg, 80.9 µmol) were added to a mixture of 1.00 eq di-*tert*-butyl ((2,5-dibromo-1,4-phenylene)bis(methylene))dicarbamate (800 mg, 1.62 mmol) and 10 mol% $Pd(PPh_3)_4$ (187 mg, 161 µmol) in 42 mL solvent. After stirring for 15 h at 65 °C, the solvent was 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 of EA. The precipitate was filtered and dried under vacuum. A beige solid was obtained (430 mg, 584 µmol, 36%).

Mp: 200 °C; **R_f**: 0.22 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3372, 3057, 2982, 2965, 1693, 1527, 1388, 1270, 1166, 942, 752; **^{1}H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 1.38 (s, 18H), 4.47 (d, $^3J_{H-H}$= 5.1 Hz, 4H), 5.03 (m, 2H), 7.33-7.36 (m, 12H), 7.54-7.60 (m, 8H); **^{13}C NMR** ($CDCl_3$, 100.6 MHz): δ[ppm] = 28.5 (q, 6C), 43.1 (t, 2C), 79.5 (s, 2C), 88.3 (s, 2C), 91.2 (s, 2C), 93.7 (s, 2C), 94.8 (s, 2C), 122.6 (s, 2C), 123.1 (s, 2C), 125.4 (s, 2C), 125.8 (s, 2C), 128.3 (d, 2C), 128.6 (d, 2C), 128.6 (d, 4C), 128.8 (d, 2C), 131.9 (d, 4C), 132.1 (d, 2C), 132.3 (d, 2C), 132.4 (d, 2C), 140.1 (s, 2C), 155.8 (s, 2C); **HRMS** (ESI+): $C_{50}H_{48}N_3O_4^+$, calculated: 754.3639 [M+NH_4^+], observed: 754.3668 [M+NH_4^+]; **UV/VIS** (DCM, 9.20 µg/mL): λ [nm] (logε) = 242 (4.58), 285 (4.67), 348 (4.53), 367 (4.45); **Fluorescence (DCM):** λ_{Anr}= 350 nm λ_{Max}= 384 nm; **Quantum yield:** Φ = 74%.

Gold catalysis

***tert*-Butyl 11-phenylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate, 6a**

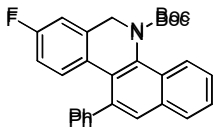


According to GP3, 1.00 eq of *tert*-butyl (2-((2-(phenylethynyl)phenyl)ethynyl)-benzyl) carbamate (1.30 g, 3.19 mmol) was dissolved in 70 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF_6 (61.6 mg, 79.8 µmol) were added and the reaction mixture was stirred at 50 °C for 1.5 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1 to 10:1). A yellow solid was obtained (1.23 g, 3.03 mmol, 95%).

Mp: 74 °C; **R_f**: 0.73 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3057, 2976, 2930, 1702, 1560, 1493, 1480, 1446, 1389, 1366, 1343, 1308, 1245, 1228, 1151, 1131, 1094, 1030, 993, 957, 897, 856, 828, 760, 738, 701, 634; **^{1}H NMR** ($(CD_3)_2CO$, 400.3 MHz): δ[ppm] = 1.25 (s, 9H), 4.29 (d, $^2J_{H\text{-}H}$ = 14.6 Hz, 1H), 5.38 (d, $^2J_{H\text{-}H}$ = 14.6 Hz, 1H), 6.88-6.94 (m, 2H), 7.20 (dt, $^3J_{H\text{-}H}$ = 7.1 Hz, $^4J_{H\text{-}H}$ = 1.6 Hz, 1H), 7.38-7.43 (m, 6H), 7.53-7.60 (m, 2H), 7.79 (s, 1H), 7.93-7.96 (m, 1H), 8.04 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 150.9 MHz): δ[ppm] = 28.1 (q, 3C), 49.3 (t, 1C), 81.3 (s, 1C), 126.4 (d, 2C), 126.6 (d, 1C), 127.1 (d, 1C), 127.5 (d, 1C), 127.9 (d, 1C), 127.9 (d, 1C), 128.8 (d, 1C), 129.3 (s, 1C), 129.4 (d, 1C), 129.6 (d, 1C), 129.8 (d, 1C), 130.3 (s, 1C), 132.5 (s, 1C), 134.0 (s, 1C), 137.9 (s, 1C), 138.3 (s, 1C), 143.3 (s, 1C), 154.3 (s, 1C); **HRMS** (EI+): $C_{28}H_{25}NO_2^+$, calculated: 407.18798 [M^+], observed: 407.18848 [M^+].

Four carbons (1s, 3d) were not detectable (very broad signals between 129-130 ppm).

***tert*-Butyl 8-fluoro-11-phenylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate, 6b**



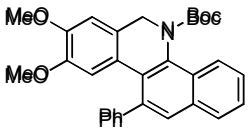
According to GP3, 1.00 eq of *tert*-butyl (5-fluoro-2-((2-(phenylethynyl)-phenyl)ethynyl)-benzyl)-carbamate (250 mg, 588 µmol) was dissolved in 25 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF_6 (11.3 mg, 14.7 µmol) were added and the reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). An orange solid was obtained (225 mg, 529 µmol, 90%).

Mp: 103 °C; **R_f**: 0.48 (silica gel, PE:EA = 10:1); **IR** (ATR): ν[cm^{-1}] = 2978, 1703, 1562, 1488, 1386, 1367, 1342, 1305, 1272, 1238, 1150, 1124, 1030, 997, 960, 890, 858, 829, 792, 769, 701, 650; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.25 (s, 9H), 4.31 (d, $^2J_{H\text{-}H}$ = 14.8 Hz, 1H), 5.40 (d, $^2J_{H\text{-}H}$ = 14.8 Hz, 1H), 6.71 (dt, $^3J_{H\text{-}H}$ = 8.8 Hz, $^4J_{H\text{-}H}$ = 2.8 Hz, 1H), 6.88 (dd, $^3J_{H\text{-}H}$ = 5.7 Hz, $^3J_{H\text{-}H}$ = 8.8 Hz, 1H), 7.27 (dd, $^3J_{H\text{-}H}$ = 8.8 Hz, $^4J_{H\text{-}H}$ = 2.6 Hz, 1H), 7.39-7.40 (m, 3H), 7.54-7.61 (m, 2H), 7.80 (s, 1H), 7.95 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H), 8.03 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 1H); **^{13}C NMR {^{19}F}** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] =28.1 (q, 3C), 49.2 (t, 1C), 81.5 (s, 1C), 113.2 (d, 1C), 113.8 (d, 1C), 126.3 (d, 1C), 126.7 (d, 1C), 127.5 (d, 1C), 128.0 (d, 1C), 128.8 (d, 1C), 129.0 (s, 1C), 129.3 (s, 1C), 129.4 (s, 1C), 129.7 (d, 1C), 130.3 (s, 1C), 131.7 (d, 1C), 133.9 (s, 1C), 138.1 (s, 1C), 140.6 (s, 1C), 143.0 (s, 1C), 154.3 (s, 1C), 162.4 (s, 1C); **^{19}F NMR** ($(CD_3)_2CO$, 470.7 MHz): δ[ppm] = -116.3 (1F); **HRMS** (EI+): $C_{28}H_{24}FNO_2^+$, calculated: 425.17856 [M^+], observed: 425.17749 [M^+].

Two hydrogens were not detectable. (very broad aromatic signal).

Four carbon signals (4d) were not detectable(very broad signals between 129-130 ppm).

tert-Butyl 8,9-dimethoxy-11-phenylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate, 6c



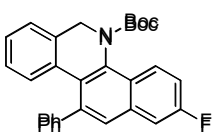
According to GP3, 1.00 eq of *tert*-butyl (4,5-dimethoxy-2-((2-(phenylethynyl)phenyl) ethynyl)-benzyl)carbamate (275 mg, 588 µmol) was dissolved in 25 mL DCE with 2.5 mol% JohnPhosAu(MeCN)SbF_6 (11.4 mg, 14.7 µmol). The reaction mixture was stirred for 4.5 h at 50 °C and further 2.5 mol% JohnPhosAu(MeCN)SbF_6 (11.4 mg, 14.7 µmol) were added. After stirring at 50 °C for one hour, the mixture was treated as described in GP3 (silica gel, PE:EA = 10:1). A yellow solid was obtained (122 mg, 260 µmol, 44%).

Mp: 197 °C; **R_f**: 0.31 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 2977, 2936, 2835, 1691, 1607, 1516, 1489, 1449, 1366, 1327, 1279, 1250, 1223, 1161, 1140, 1100, 1053, 1038, 1025, 1004, 950, 884, 856, 838, 792, 758, 701, 671, 615; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.23 (s, 9H), 3.14 (s, 3H), 3.85 (s, 3H), 4.21 (d, $^2J_{H-H}$ = 14.6 Hz, 1H), 5.32 (d, $^2J_{H-H}$ = 12.2 Hz, 1H), 6.45 (s, 1H), 7.03 (s, 1H), 7.38-7.57 (m, 6H), 7.76 (s, 1H), 7.92 (d, $^3J_{H-H}$ = 8.1 Hz, 1H), 8.01 (d, $^3J_{H-H}$ = 8.3 Hz, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 28.1 (q, 3C), 48.3 (t, 1C), 55.0 (q, 1C), 56.0 (q, 1C), 81.2 (s, 1C), 109.7 (d, 1C), 113.8 (d, 1C), 124.7 (s, 1C), 126.3 (d, 1C), 126.5 (d, 1C), 127.0 (d, 1C), 127.9 (d, 1C), 128.8 (d, 1C), 129.3 (d, 1C), 129.5 (s, 1C), 130.8 (s, 1C), 133.5 (s, 1C), 138.1 (s, 1C), 143.8 (s, 1C), 148.1 (s, 1C), 149.4 (s, 1C), 154.4 (s, 1C); **HRMS** (EI+): $C_{30}H_{29}NO_4^+$, calculated: 467.20911 [M^+], observed: 467.20845 [M^+].

One hydrogen was not detectable (very broad aromatic signal).

Six carbons (2s, 4d) were not detectable (very broad signals between 129-130 ppm).

tert-Butyl 2-fluoro-11-phenylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate, 6d



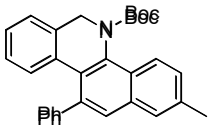
According to GP3, 1.00 eq of *tert*-butyl (2-((4-fluoro-2-(phenylethynyl)-phenyl)ethynyl)-benzyl)carbamate (250 mg, 588 µmol) was dissolved in 25 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF_6 (11.3 mg, 14.7 µmol) were added. The reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). A yellow solid was obtained (167 mg, 392 µmol, 67%).

Mp: 101 °C; **R_f**: 0.65 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 2977, 2930, 1701, 1631, 1561, 1481, 1450, 1392, 1367, 1338, 1291, 1242, 1224, 1151, 1127, 1029, 994, 954, 894, 856, 833, 776, 754, 735, 701, 628; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.25 (s, 9H), 4.30 (d, $^2J_{H-H}$ = 14.6 Hz, 1H), 5.37 (d, $^2J_{H-H}$ = 14.5 Hz, 1H), 6.87 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 6.92 (t, $^3J_{H-H}$ = 7.8 Hz, 1H), 7.21 (t, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.39-7.44 (m, 7H), 7.67 (dd, $^3J_{H-H}$ = 9.9 Hz, $^4J_{H-H}$ = 2.6 Hz, 1H), 7.79 (s, 1H), 8.10 (dd, $^3J_{H-H}$ = 9.3 Hz, $^3J_{H-H}$ = 5.8 Hz, 1H); **^{13}C NMR {^{19}F}** ($(CD_3)_2CO$, 125.8 MHz):

δ[ppm] = 28.1 (q, 3C), 49.3 (t, 1C), 81.6 (s, 1C), 111.6 (d, 1C), 116.7 (d, 1C), 126.4 (d, 1C), 126.5 (s, 1C), 127.1 (d, 1C), 127.9 (d, 1C), 128.1 (d, 1C), 129.0 (d, 1C), 129.4 (s, 1C), 129.6 (d, 1C), 129.7 (d, 1C), 130.2 (s, 1C), 132.3 (s, 1C), 134.9 (s, 1C), 137.7 (s, 1C), 139.7 (s, 1C), 143.0 (s, 1C), 162.0 (s, 1C); **^{19}F NMR** ($(CD_3)_2CO$, 470.7 MHz): δ[ppm] = -115.7 (1F); **HRMS** (EI+): $C_{28}H_{24}FNO_2^+$, calculated: 425.17856 [M^+], observed: 425.17711 [M^+].

Five carbons (1s, 4d) were not detectable (very broad signals between 129-130 ppm).

tert-Butyl 2-methyl-11-phenylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate, 6e



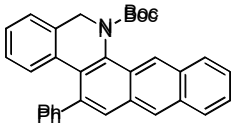
According to GP3, 1.00 eq of *tert*-butyl (2-((4-methyl-2-(phenylethynyl)-phenyl)-ethynyl)benzyl)carbamate (248 mg, 588 µmol) was dissolved in 25 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF_6 (11.4 mg, 14.8 µmol) were added. The reaction mixture was stirred at 50 °C for 1 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). A yellow solid was obtained (237 mg, 564 µmol, 96%).

Mp: 105 °C; **R_f**: 0.66 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 2974, 2927, 2869, 1700, 1629, 1595, 1481, 1450, 1389, 1366, 1340, 1298, 1265, 1245, 1220, 1154, 1133, 1029, 993, 895, 858, 832, 774, 752, 736, 701, 652, 627; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.25 (s, 9H), 2.52 (s, 3H), 4.27 (d, $^2J_{H\text{-}H}$ = 14.6 Hz, 1H), 5.36 (d, $^2J_{H\text{-}H}$ = 13.4 Hz, 1H), 6.85-6.92 (m, 2H), 7.19 (dt, $^3J_{H\text{-}H}$ = 7.4 Hz, $^4J_{H\text{-}H}$ = 1.0 Hz, 1H), 7.37-7.44 (m, 6H), 7.68 (s, 1H), 7.71 (s, 1H), 7.93 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 21.6 (q, 1C), 28.1 (q, 3C), 49.3 (t, 1C), 81.3 (s, 1C), 126.1 (s, 1C), 126.3 (d, 2C), 127.0 (d, 1C), 127.5 (s, 1C), 127.7 (d, 2C), 127.9 (d, 1C), 128.8 (d, 1C), 129.1 (d, 1C), 129.3 (d, 1C), 129.7 (d, 1C), 130.3 (s, 1C), 132.7 (s, 1C), 134.3 (s, 1C), 137.2 (s, 1C), 137.7 (s, 1C), 138.3 (s, 1C), 143.4 (s, 1C), 154.3 (s, 1C); **HRMS** (EI+): $C_{29}H_{27}NO_2^+$, calculated: 421.20363 [M^+], observed: 421.20293 [M^+].

One hydrogen was not detectable. (very broad aromatic signal).

Three carbons (3d) were not detectable.

tert-Butyl 5-phenylnaphtho[2,3-*c*]phenanthridine-13(14*H*)-carboxylate, 6f



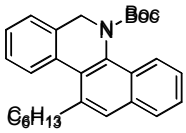
According to GP3, 1.00 eq of *tert*-butyl (2-((3-(phenylethynyl)naphthalen-2-yl)ethynyl)-benzyl)carbamate (269 mg, 588 µmol) was dissolved in 25 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF_6 (11.4 mg, 14.7 µmol) were added and the reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 15:1). A yellow solid was obtained (242 mg, 529 µmol, 90%).

Mp: 144 °C; **R_f**: 0.60 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3055, 2975, 1702, 1436, 1366, 1336, 1242, 1153, 956, 895, 859, 741, 701; **^{1}H NMR** ($(CD_3)_2CO$, 300.2 MHz): δ[ppm] = 1.20 (s, 9H), 4.38 (d, $^2J_{H\text{-}H}$ = 14.7 Hz, 1H), 5.47 (d, $^2J_{H\text{-}H}$ = 14.7 Hz, 1H), 6.87-6.97 (m, 2H), 7.22 (dt,

$^{3}J_{H\text{-}H}$ = 7.1 Hz, $^{4}J_{H\text{-}H}$ = 1.6 Hz, 1H), 7.33-7.47 (m, 6H), 7.50-7.57 (m, 2H), 7.97 (s, 1H), 8.07-8.10 (m, 1H), 8.14-8.17 (m, 1H), 8.57 (s, 1H), 8.66 (s, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 75.5 MHz): δ[ppm] = 28.1 (q, 3C), 49.6 (t, 1C), 81.4 (s, 1C), 125.4 (d, 1C), 126.4 (d, 1C), 126.8 (d, 1C), 126.9 (d, 1C), 127.1 (d, 1C), 127.2 (d, 1C), 127.6 (s, 1C), 128.0 (d, 2C), 128.9 (d, 1C), 129.4 (d, 2C), 129.7 (d, 1C), 129.8 (d, 1C), 129.8 (d, 1C), 130.3 (d, 1C), 132.1 (s, 1C), 132.6 (s, 1C), 132.6 (s, 1C), 133.2 (s, 1C), 137.7 (s, 1C), 138.0 (s, 1C), 143.3 (s, 1C), 154.4 (s, 1C); **HRMS** (EI+): $C_{32}H_{27}NO_2^+$, calculated: 457.20363 [M^+], observed: 457.20531 [M^+].

Three carbons (2s, 1d) were not detectable.

tert-Butyl 11-hexylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate, 6g

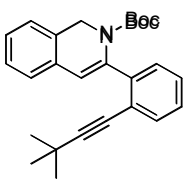


According to GP3, 1.00 eq of *tert*-butyl (2-((2-(oct-1-yn-1-yl)phenyl)ethynyl)-benzyl)-carbamate (244 mg, 587 µmol) was dissolved in 25 mL 1,2-dichloro-ethane. 2.5 mol% JohnPhosAu(MeCN)SbF_6 (11.4 mg, 14.8 µmol) were added. The reaction mixture was stirred at 50 °C for 1 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). A yellow solid was obtained (239 mg, 576 µmol, 98%).

Mp: 118 °C; **R_f**: 0.71 (silica gel, PE:EA = 1:5); **IR** (ATR): ν[cm^{-1}] = 2960, 2926, 2852, 1692, 1560, 1435, 1390, 1365, 1337, 1293, 1245, 1150, 1132, 1093, 929, 858, 765, 621; **^{1}H NMR** ($(CD_3)_2CO$, 400.3 MHz): δ[ppm] = 0.84-0.87 (m, 3H), 1.23 (s, 9H), 1.28-1.30 (m, 4H), 1.37-1.39 (m, 2H), 1.66-1.79 (m, 2H), 3.08-3.12 (m, 1H), 3.23-3.27 (m, 1H), 4.04 (d, $^{2}J_{H\text{-}H}$ = 14.8 Hz, 1H), 5.29 (d, $^{2}J_{H\text{-}H}$ = 14.7 Hz, 1H), 7.37 (dt, $^{3}J_{H\text{-}H}$ = 7.4 Hz, $^{4}J_{H\text{-}H}$ = 1.0 Hz, 1H), 7.44 (dt, $^{3}J_{H\text{-}H}$ = 7.5 Hz, $^{4}J_{H\text{-}H}$ = 1.3 Hz, 1H), 7.46-7.50 (m, 3H), 7.81 (s, 1H), 7.84-7.86 (m, 1H), 7.93-7.98 (m, 2H); **^{13}C NMR** ($(CD_3)_2CO$, 100.7 MHz): δ[ppm] = 14.3 (q, 1C), 23.2 (t, 1C), 28.2 (q, 3C), 30.0 (t, 1C), 32.0 (t, 1C), 32.3 (t, 1C), 35.4 (t, 1C), 49.5 (t, 1C), 81.1 (s, 1C), 125.9 (d, 1C), 126.1 (d, 1C), 126.7 (d, 1C), 127.1 (d, 1C), 128.0 (d, 1C), 128.1 (d, 1C), 128.1 (d, 1C), 128.4 (d, 2C), 128.7 (s, 1C), 133.3 (s, 1C), 134.2 (s, 1C), 137.5 (s, 1C), 138.0 (s, 1C), 138.8 (s, 1C), 154.4 (s, 1C); **HRMS** (EI+): $C_{28}H_{33}NO_2^+$, calculated: 415.25058 [M^+], observed: 415.24943 [M^+].

One carbon (1s) was not detectable.

tert-butyl 3-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)isoquinoline-2(1H)-carboxylate, 7j

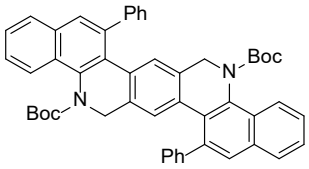


According to GP3, 1.00 eq of *tert*-butyl (2-((2-(3,3-dimethylbut-1-yn-1-yl)-phenyl)-ethynyl)benzyl)carbamate (182 mg, 470 µmol) was dissolved in 20 mL DCE. 2.5 mol% JohnPhosAu(MeCN)SbF_6 (9.10 mg, 11.7 µmol) were added. The reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and treated as described in GP3 (silica gel, PE:EA = 20:1). A colorless solid was obtained (159 mg, 411 µmol, 87%).

Mp: 124 °C; **R_f**: 0.67 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 2971, 2927, 2864, 2239, 1697, 1612, 1474, 1446, 1365, 1312, 1234, 1157, 1129, 987, 941, 866, 828, 791, 761, 744, 726, 630,

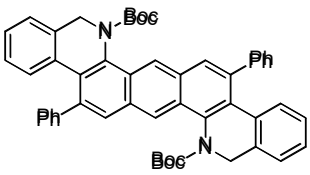
612; **^{1}H NMR** ($(CD_3)_2CO$, 500.2 MHz): δ[ppm] = 1.04 (s, 9H), 1.33 (s, 9H), 4.91 (s, 2H), 6.35 (s, 1H), 7.23-7.32 (m, 5H), 7.35 (dt, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H), 7.42 (dd, $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H), 7.49 (dd, $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.4 Hz, 1H); **^{13}C NMR** ($(CD_3)_2CO$, 125.8 MHz): δ[ppm] = 27.8 (q, 3C), 28.7 (s, 1C), 31.5 (q, 3C), 47.6 (t, 1C), 78.6 (s, 1C), 80.6 (s, 1C), 102.7 (s, 1C), 116.7 (d, 1C), 122.9 (s, 1C), 125.8 (d, 1C), 125.9 (d, 1C), 128.1 (d, 1C), 128.2 (d, 1C), 128.4 (d, 1C), 128.6 (d, 1C), 128.7 (d, 1C), 132.8 (s, 1C), 133.6 (s, 1C), 133.6 (d, 1C), 141.0 (s, 1C), 142.1 (s, 1C), 152.5 (s, 1C); **HRMS** (EI+): $C_{26}H_{29}NO_2^+$, calculated: 387.21928 [M^+], observed: 387.22032 [M^+].

Di-*tert*-butyl 8,17-diphenyl-6,15-dihydrobenzo[*c*]benzo[7,8]quinolino[4,3-*j*]phenanthridine-5,14-dicarboxylate, 6k



According to GP3, 1.00 eq **5k** (400 mg, 543 µmol) was dissolved in 50 mL DCE. 5 mol% JohnPhosAu(MeCN)SbF_6 (21.0 mg, 27.1 µmol) were added and the reaction mixture was stirred at 50 °C for 5 h. The solvent was 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 directly used for the next step.

Di-*tert*-butyl 5,14-diphenyl-9,18-dihydrobenzo[1,2-*c*:4,5-*c'*]diphenanthridine-8,17-dicarboxylate, 6l



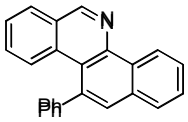
According to GP3, 1.00 eq **5l** (800 mg, 1.09 mmol) was dissolved in 150 mL DCE. 5 mol% JohnPhosAu(MeCN)SbF_6 (41.9 mg, 54.3 µmol) were added and the reaction mixture was stirred at 50 °C for 2 h. The solvent was removed under reduced pressure and the residue was adsorbed onto Celite®. The crude product 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 of EA and PE. The precipitate was filtered and dried under vacuum. The title compound was obtained as a greenish solid in two isomers (523 mg, 710 µmol, 65%, major:minor isomer = 2:1).

^{1}H-NMR ($CDCl_3$, 600.2 MHz): δ[ppm] = 1.21 (bs, 18H), 4.36 (d, $^2J_{H-H}$= 14.5 Hz, 2H), 5.43 (m, 2H), 6.86-6.96 (m, 4H), 7.17-7.21 (m, 2H), 7.23-7.75 (m, 12H), 7.88 (s, 2H)[a], 7.90 (s, 2H)[b], 8.56 (s, 2H)[a], 8.59 (s, 2H)[b]

[a] major isomer, [b] minor isomer

Boc cleavage and Oxidation

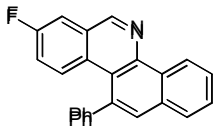
11-Phenylbenzo[*c*]phenanthridine, 13a



According to GP4, 1.00 eq of *tert*-butyl 11-phenylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate (500 mg, 1.23 mmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (3 h air treatment) and the title compound was obtained as a brownish solid in quantitative yield (375 mg, 1.23 mmol).

Mp: 169 °C; **R_f**: 0.22 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3066, 3026, 1954, 1935, 1615, 1586, 1520, 1494, 1471, 1437, 1372, 1284, 1251, 1217, 1077, 1030, 977, 960, 933, 919, 899, 860, 815, 762, 706, 655, 608; **^{1}H NMR** ($CDCl_3$, 400.3 MHz): δ[ppm] = 7.34-7.39 (m, 1H), 7.48-7.53 (m, 5H), 7.56-7.60 (m, 1H), 7.64 (d, $^3J_{H-H}$ = 8.7 Hz, 1H), 7.69-7.73 (m, 1H), 7.76-7.80 (m, 1H), 7.88 (s, 1H), 7.94 (d, $^3J_{H-H}$ = 7.9 Hz, 1H), 8.10 (dd, $^3J_{H-H}$ = 7.9 Hz, $^4J_{H-H}$ = 0.9 Hz, 1H), 9.46 (d, $^3J_{H-H}$ = 8.2 Hz, 1H), 9.50 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100.7 MHz): δ[ppm] = 120.5 (s, 1C), 125.2 (d, 1C), 126.8 (d, 1C), 127.1 (d, 1C), 127.2 (d, 1C), 127.5 (d, 1C), 127.6 (d, 1C), 128.0 (d, 1C), 128.0 (s, 1C), 128.7 (d, 1C), 129.1 (d, 2C), 129.3 (d, 2C), 129.5 (d, 1C), 130.9 (d, 1C), 131.6 (s, 1C), 132.4 (s, 1C), 133.3 (s, 1C), 137.6 (s, 1C), 142.8 (s, 1C), 144.5 (s, 1C), 152.6 (d, 1C); **HRMS** (EI+): $C_{23}H_{15}N^+$, calculated: 305.11990 [M^+], observed: 305.11910 [M^+].

8-Fluoro-11-phenylbenzo[*c*]phenanthridine, 13b

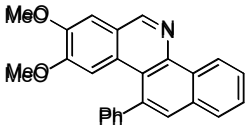


According to GP4, 1.00 eq of *tert*-butyl 8-fluoro-11-phenylbenzo[*c*]-phenanthridine-5(6*H*)-carboxylate (100 mg, 235 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (3 h air treatment) and the title compound was obtained as a brownish solid in quantitative yield (76.0 mg, 235 µmol).

Mp: 166 °C; **R_f**: 0.31 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3057, 1950, 1904, 1868, 1619, 1587, 1571, 1523, 1493, 1463, 1443, 1412, 1357, 1279, 1223, 1149, 1136, 1073, 1024, 968, 953, 936, 899, 865, 834, 801, 765, 746, 714, 695, 665, 651; **^{1}H NMR** ($CDCl_3$, 500.2 MHz): δ[ppm] = 7.10-7.14 (m, 1H), 7.46-7.54 (m, 5H), 7.64 (dd, $^3J_{H-H}$ = 9.5 Hz, $^3J_{H-H}$ = 5.1 Hz, 1H), 7.70-7-73 (m, 2H), 7.77-7.81 (m, 1H), 7.89 (s, 1H), 7.95 (d, $^3J_{H-H}$ = 7.9 Hz, 1H), 9.42-9.45 (m, 2H); **^{13}C NMR {^{19}F}** ($CDCl_3$, 125.8 MHz): δ[ppm] = 112.2 (d, 1C), 119.1 (d, 1C), 120.4 (s, 1C), 125.0 (d, 1C), 127.4 (d, 1C), 127.6 (d, 1C), 127.8 (d, 1C), 128.1 (d, 1C), 129.2 (d, 2C), 129.3 (d, 2C), 129.9 (d, 1C), 130.1 (s, 1C), 131.4 (d, 1C), 132.3 (s, 1C), 137.1 (s, 1C), 144.1 (s, 1C), 151.4 (d, 1C), 160.6 (s, 1C); **^{19}F NMR** ($CDCl_3$, 470.7 MHz): δ[ppm] = -113.2 (1F); **HRMS** (EI+): $C_{23}H_{14}FN^+$, calculated: 323.11048 [M^+], observed: 323.11068 [M^+].

Three carbons (3s) were not detectable.

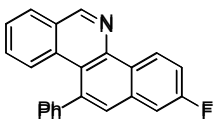
8,9-Dimethoxy-11-phenylbenzo[*c*]phenanthridine, 13c



According to GP4, 1.00 eq of *tert*-butyl 8,9-dimethoxy-11-phenylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate (50.0 mg, 107 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 4 h. The reaction was treated according to GP4 (1 h air treatment) and the title compound was obtained as a yellow solid in quantitative yield (39.1 mg, 107 µmol).

Mp: 185 °C; **R_f**: 0.65 (silica gel, PE:EA = 1:1); **IR** (ATR): ν[cm^{-1}] = 3162, 3060, 2994, 2958, 2932, 1617, 1588, 1518, 1480, 1462, 1422, 1392, 1296, 1275, 1261, 1225, 1200, 1188, 1155, 1074, 1050, 1027, 993, 944, 927, 909, 891, 854, 834, 800, 771, 757, 732, 711, 700, 684, 646, 626, 616; **^{1}H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 3.31 (s, 3H), 4.01 (s, 3H), 7.11 (s, 1H), 7.29 (s, 1H), 7.41-7.54 (m, 5H), 7.64-7.70 (m, 1H), 7.73-7.78 (m, 2H), 7.90 (d, $^3J_{H-H}$ = 7.8 Hz, 1H), 9.27 (s, 1H), 9.41 (d, $^3J_{H-H}$ = 8.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 75.6 MHz): δ[ppm] = 55.0 (q, 1C), 56.0 (q, 1C), 106.9 (d, 1C), 107.6 (d, 1C), 119.8 (s, 1C), 123.8 (s, 1C), 124.9 (d, 1C), 126.9 (d, 1C), 127.4 (d, 1C), 127.4 (d, 1C), 127.6 (d, 1C), 128.9 (s, 1C), 129.1 (d, 2C), 129.6 (d, 2C), 130.1 (d, 1C), 131.9 (s, 1C), 131.9 (s, 1C), 137.1 (s, 1C), 142.2 (s, 1C), 144.9 (s, 1C), 149.2 (s, 1C), 150.4 (d, 1C), 151.0 (s, 1C); **HRMS** (EI+): $C_{25}H_{19}NO_2^+$, calculated: 365.14103 [M^+], observed: 365.14029 [M^+].

2-Fluoro-11-phenylbenzo[*c*]phenanthridine, 13d

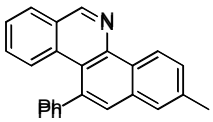


According to GP4, 1.00 eq of *tert*-butyl 2-fluoro-11-phenylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate (100 mg, 235 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (2 h air treatment) and the title compound was obtained as a brownish solid in quantitative yield (76.0 mg, 235 µmol).

Mp: 166 °C; **R_f**: 0.26 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3060, 1920, 1858, 1624, 1575, 1522, 1493, 1468, 1447, 1427, 1376, 1352, 1301, 1279, 1246, 1213, 1147, 1121, 1074, 1028, 968, 927, 895, 848, 834, 803, 780, 756, 701, 656; **^{1}H NMR** ($CDCl_3$, 500.2 MHz): δ[ppm] = 7.36-7.39 (m, 1H), 7.46-7.56 (m, 7H), 7.57-7.61 (m, 2H), 7.80 (s, 1H), 8.10 (d, $^3J_{H-H}$ = 8.0 Hz, 1H), 9.46-9.48 (m, 2H); **^{13}C NMR {^{19}F}** ($CDCl_3$, 125.8 MHz): δ[ppm] = 111.1 (d, 1C), 116.7 (d, 1C), 119.9 (s, 1C), 126.9 (d, 1C), 127.1 (d, 1C), 127.8 (d, 1C), 128.1 (d, 1C), 128.3 (s, 1C), 128.9 (d, 1C), 129.1 (d, 2C), 129.2 (d, 2C), 129.8 (d, 1C), 130.1 (d, 1C), 133.2 (s, 1C), 133.5 (s, 1C), 139.0 (s, 1C), 142.5 (s, 1C), 144.0 (s, 1C), 152.8 (d, 1C), 162.5 (s, 1C); **^{19}F NMR** ($CDCl_3$, 470.7 MHz): δ[ppm] = -113.0 (1F); **HRMS** (EI+): $C_{23}H_{14}FN^+$, calculated: 323.11048 [M^+], observed: 323.11057 [M^+].

One carbon (1s) was not detectable.

2-Methyl-11-phenylbenzo[*c*]phenanthridine, 13e

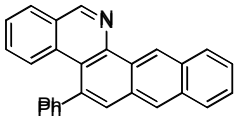


According to GP4, 1.00 eq of *tert*-butyl 2-methyl-11-phenylbenzo[*c*]-phenanthridine-5(6*H*)-carboxylate (150 mg, 356 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 3 h. The reaction was treated according to GP4 (3 h air treatment) and the title compound was obtained as a yellow solid in quantitative yield (114 mg, 356 µmol).

Mp: 195 °C; **R_f**: 0.25 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3058, 3030, 2913, 2854, 1614, 1591, 1523, 1492, 1467, 1443, 1369, 1280, 1250, 1217, 1160, 1135, 1073, 1026, 959, 948, 921, 902, 884, 869, 833, 803, 773, 760, 749, 696, 655, 616; **^{1}H NMR** ($CDCl_3$, 500.2 MHz): δ[ppm] = 2.61 (s, 3H), 7.34-7.38 (m, 1H), 7.47-7.53 (m, 5H), 7.56 (t, $^3J_{H-H}$ = 7.9 Hz, 1H), 7.61 (d, $^3J_{H-H}$ = 8.7 Hz, 2H), 7.71 (s, 1H), 7.80 (s, 1H), 8.09 (d, $^3J_{H-H}$ = 7.9 Hz, 1H), 9.33 (d, $^3J_{H-H}$ = 8.6 Hz, 1H), 9.48 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ[ppm] = 21.9 (q, 1C), 119.9 (s, 1C), 125.0 (d, 1C), 126.6 (d, 1C), 126.8 (d, 1C), 127.1 (d, 1C), 127.5 (d, 1C), 127.8 (s, 1C), 128.8 (d, 1C), 129.1 (d, 2C), 129.3 (d, 2C), 129.3 (d, 1C), 129.5 (s, 1C), 129.5 (d, 1C), 130.7 (d, 1C), 132.6 (s, 1C), 133.4 (s, 1C), 137.6 (s, 1C), 138.0 (s, 1C), 144.5 (s, 1C), 152.4 (d, 1C); **HRMS** (EI+): $C_{24}H_{17}N^+$, calculated: 319.13555 [M^+], observed: 319.13446 [M^+].

One carbon (1s) was not detectable.

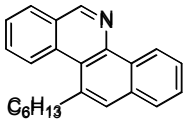
5-Phenylnaphtho[2,3-*c*]phenanthridine, 13f



According to GP4, 1.00 eq of *tert*-butyl 5-phenylnaphtho[2,3-*c*]phen-anthridine-13(14*H*)-carboxylate (150 mg, 328 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 7 h. The reaction was treated according to GP4 (8 h air treatment). Due to significant impurities the residue was dissolved in chloroform and filtrated over silica gel. A yellow solid was obtained (44.9 mg, 126 µmol, 39%).

Mp: 206-208 °C; **R_f**: 0.19 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3051, 3022, 2958, 2924, 2852, 1947, 1810, 1739, 1615, 1600, 1583, 1536, 1492, 1478, 1444, 1392, 1274, 1231, 1193, 1133, 1025, 951, 935, 907, 871, 809, 793, 739, 700, 686, 653, 615; **^{1}H NMR** ($CDCl_3$, 300.5 MHz): δ[ppm] = 7.34-7.39 (m, 1H), 7.51-7.64 (m, 9H), 7.96 (s, 1H), 8.07-8.13 (m, 2H), 8.27-8.30 (m, 1H), 8.45 (s, 1H), 9.54 (s, 1H), 9.98 (s, 1H); **^{13}C NMR** ($CDCl_3$, 150.9 MHz): δ[ppm] = 120.4 (s, 1C), 124.6 (d, 1C), 125.9 (d, 1C), 126.0 (d, 1C), 126.3 (d, 1C), 126.7 (d, 1C), 127.2 (d, 1C), 127.6 (d, 1C), 127.9 (d, 1C), 128.4 (s, 1C), 128.7 (d, 1C), 129.1 (d, 2C), 129.2 (d, 2C), 129.3 (d, 1C), 129.5 (d, 1C), 130.2 (s, 1C), 130.7 (s, 1C), 131.3 (d, 1C), 132.5 (s, 1C), 133.0 (s, 1C), 133.3 (s, 1C), 137.4 (s, 1C), 143.7 (s, 1C), 144.4 (s, 1C), 152.4 (d, 1C); **HRMS** (EI+): $C_{27}H_{17}N^+$, calculated: 355.13555 [M^+], observed: 355.13504 [M^+].

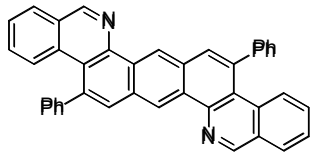
11-Hexylbenzo[*c*]phenanthridine, 13g



According to GP4, 1.00 eq of *tert*-butyl 11-hexylbenzo[*c*]phenanthridine-5(6*H*)-carboxylate (150 mg, 361 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (5.5 h air treatment) and the title compound was obtained as a brown solid in quantitative yield (113.2 mg, 361 µmol).

Mp: 65 °C; **R_f**: 0.28 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3055, 2951, 2929, 2853, 1615, 1592, 1573, 1524, 1463, 1373, 1268, 1218, 1034, 956, 935, 906, 875, 856, 848, 760, 743, 726, 658, 618; **^{1}H NMR** ($CDCl_3$, 500.2 MHz): δ[ppm] = 0.92 (t, $^3J_{H-H}$ = 7.1 Hz, 3H), 1.33-1.41 (m, 4H), 1.53-1.58 (m, 2H), 1.89-1.94 (m, 2H), 3.53 (t, $^3J_{H-H}$ = 7.8 Hz, 2H), 7.66-7.76 (m, 3H), 7.86-7.91 (m, 3H), 8.18 (dd, $^3J_{H-H}$ = 7.9 Hz, $^4J_{H-H}$ = 1.0 Hz, 1H), 8.84 (d, $^3J_{H-H}$ = 8.7 Hz, 1H), 9.40 (d, $^3J_{H-H}$ = 8.1 Hz, 1H), 9.47 (s, 1H); **^{13}C NMR** ($CDCl_3$, 125.8 MHz): δ[ppm] = 14.2 (q, 1C), 22.8 (t, 1C), 29.6 (t, 1C), 30.7 (t, 1C), 31.9 (t, 1C), 38.7 (t, 1C), 121.6 (s, 1C), 125.3 (d, 1C), 126.5 (d, 1C), 126.5 (d, 1C), 126.7 (d, 1C), 126.8 (d, 1C), 127.8 (d, 1C), 127.9 (s, 1C), 129.4 (d, 1C), 130.0 (d, 1C), 130.5 (d, 1C), 131.1 (s, 1C), 132.7 (s, 1C), 133.7 (s, 1C), 137.2 (s, 1C), 143.0 (s, 1C), 151.9 (d, 1C); **HRMS** (EI+): $C_{23}H_{23}N^+$, calculated: 313.18250 [M^+], observed: 313.18132 [M^+].

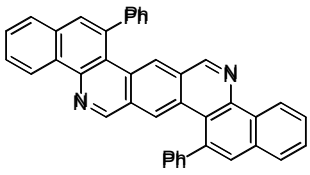
5,14-Diphenylbenzo[1,2-*c*:4,5-*c*']diphenanthridine, 13k



According to GP4, 1.00 eq **6k** (250 mg, 339 µmol) was heated up to 200 °C under nitrogen atmosphere for overall 6 h. The reaction was treated according to GP4 (8 h air treatment). 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 of EA and PE. The precipitate was filtered and dried under vacuum. A yellow solid was obtained (139 mg, 261 µmol, 77%).

Mp: >300°C; **R_f**: 0.36 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3059, 3023, 1837, 1615, 1581, 1539, 1493, 1223, 911, 767, 753; **^{1}H NMR** (d_2-TCE, 400.3 MHz): δ[ppm] = 7.44 (t, $^3J_{H-H}$= 7.5 Hz, 2H), 7.58-7.69 (m, 14H), 8.18 (d, $^3J_{H-H}$= 7.7 Hz, 2H), 8.29 (s, 2H), 9.61 (s, 2H), 10.05 (s, 2H); **^{13}C-NMR** (d_2-TCE, 100.7 MHz): δ[ppm] = 120.7 (s, 2C), 123.9 (d, 2C), 126.8 (d, 2C), 127.0 (d, 2C), 127.5 (d, 2C), 128.0 (s, 2C), 128.5 (d, 2C), 129.0 (d, 4C), 129.0 (d, 4C), 129.4 (d, 2C), 130.9 (s, 2C), 131.0 (s, 2C), 131.7 (d, 2C), 132.9 (s, 2C), 137.5 (s, 2C), 142.7 (s, 2C), 143.8 (s, 2C), 152.4 (d, 2C); **HRMS** (EI+): $C_{40}H_{24}N_2^+$, calculated: 532.1934 [M^+], observed: 532.1927 [M^+]; **UV/VIS** (DCM; 7.00 µg/mL): λ[nm] (logε) = 279 (4.46), 315 (4.92), 333 (4.69), 363 (4.05), 384 (4.12), 405 (4.13); **Fluorescence** (DCM): λ_{Anr} = 405 nm, λ_{Max} = 449 nm, 424 nm; **Quantum yield**: Φ = 26%

8,17-Diphenylbenzo[*c*]benzo[7,8]quinolino[4,3-*j*]phenanthridine, 13l

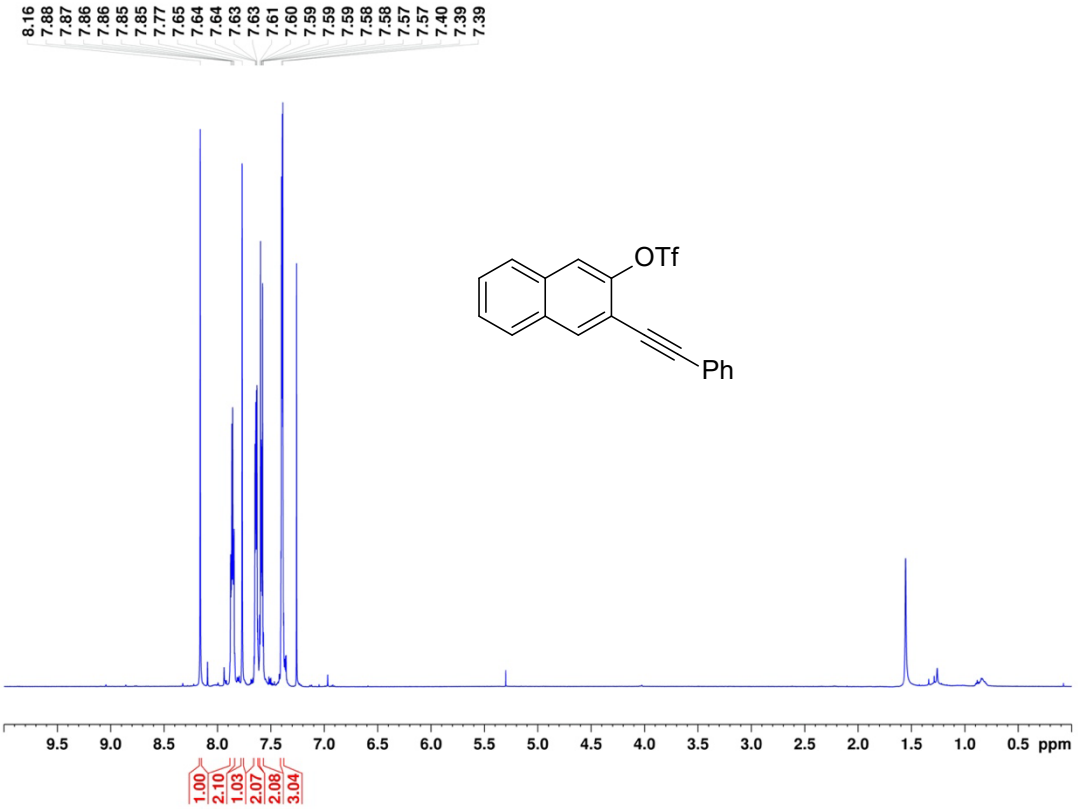


According to GP4, 237 mg of the residue containing **6l** were heated up to 200 °C under nitrogen atmosphere for overall 5 h. The reaction was treated according to GP4 (6 h air treatment). The crude product was filtered through a pad of silica gel (around 10 cm high) to remove major impurities using a mixture of PE and EA and afterwards DCM. Solvents were evaporated and the crude product was precipitated from a hot mixture of EA and PE. The precipitate was filtered and dried under vacuum. A yellow solid was obtained (96.0 mg, 180 µmol, 33% over two steps).

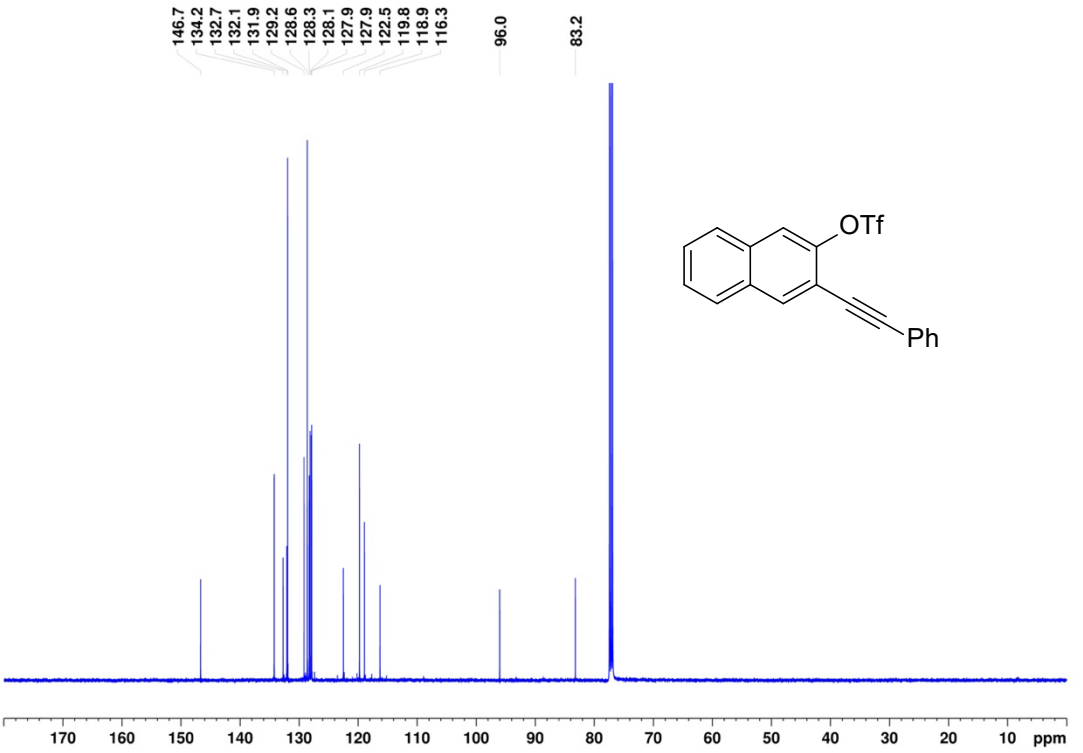
Mp.: >300 °C; **R_f**: 0.59 (silica gel, PE:EA = 5:1); **IR** (ATR): ν[cm^{-1}] = 3043, 1592, 1549, 1495, 1442, 1339, 930, 889, 772, 753; **^{1}H NMR** (d_2-TCE, 500.2 MHz, 373 K): δ[ppm] = 7.64-7.72 (m, 10H), 7.76-7.83 (m, 4H), 8.02-8.03 (m, 4H), 8.27 (s, 2H), 9.08 (s, 2H), 9.48 (d, $^3J_{H-H}$= 8.2 Hz, 2H); **^{13}C NMR** (d_2-TCE, 125.8 MHz, 373 K): δ[ppm] = 119.3 (s, 2C), 125.3 (d, 2C), 126.8 (d, 2C), 127.2 (d, 2C), 127.4 (s, 2C), 127.8 (d, 4C), 128.1 (d, 2C), 129.1 (d, 4C), 129.3 (d, 4C), 129.6 (s, 2C), 130.4 (d, 2C), 131.6 (s, 2C), 132.5 (s, 2C), 137.6 (s, 2C), 143.9 (s, 2C), 154.7 (s, 2C); **HRMS** (EI+): $C_{40}H_{24}N_2^+$, calculated: 532.1934 [M^+], observed: 532.1944 [M^+]; **UV/VIS** (DCM; 5.00 µg/mL): λ[nm] (logε) = 263 (4.70), 291 (4.81), 316 (4.74), 329 (4.81), 335 (4.75), 365 (4.00), 401 (3.91), 425 (3.98); **Fluorescence** (DCM): λ_{Anr} = 425 nm, λ_{Max} = 464 nm, 439 nm; **Quantum yield**: Φ = 27%

One carbon (1s) was not detectable.

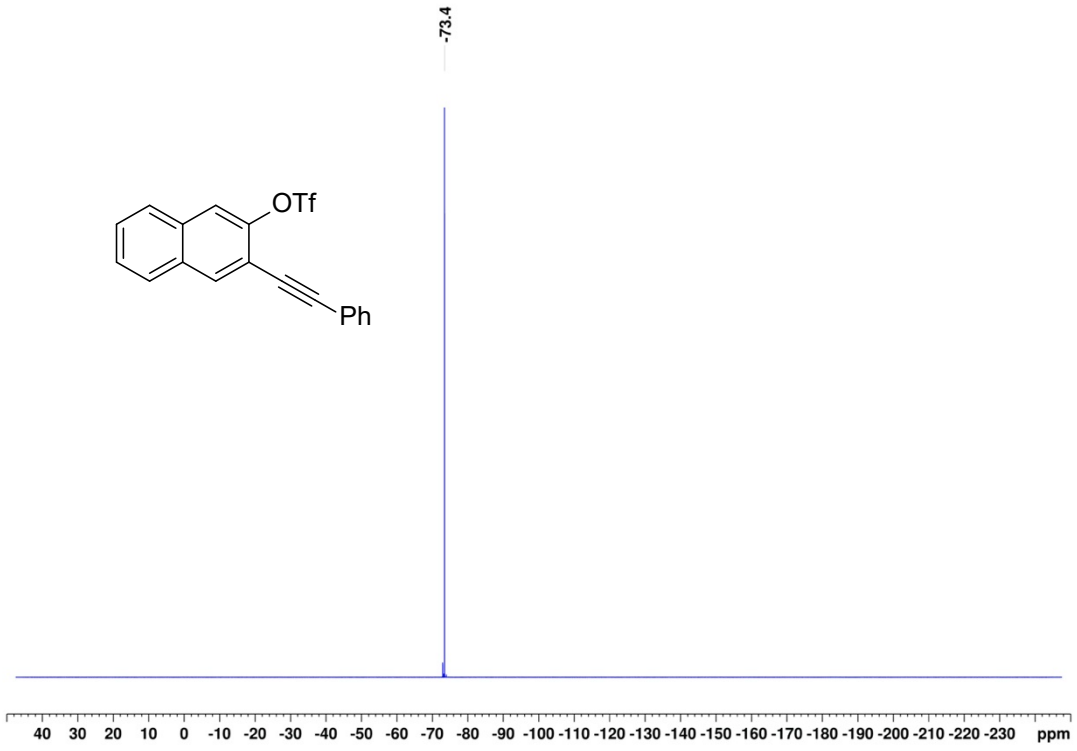
5. NMR Spectra



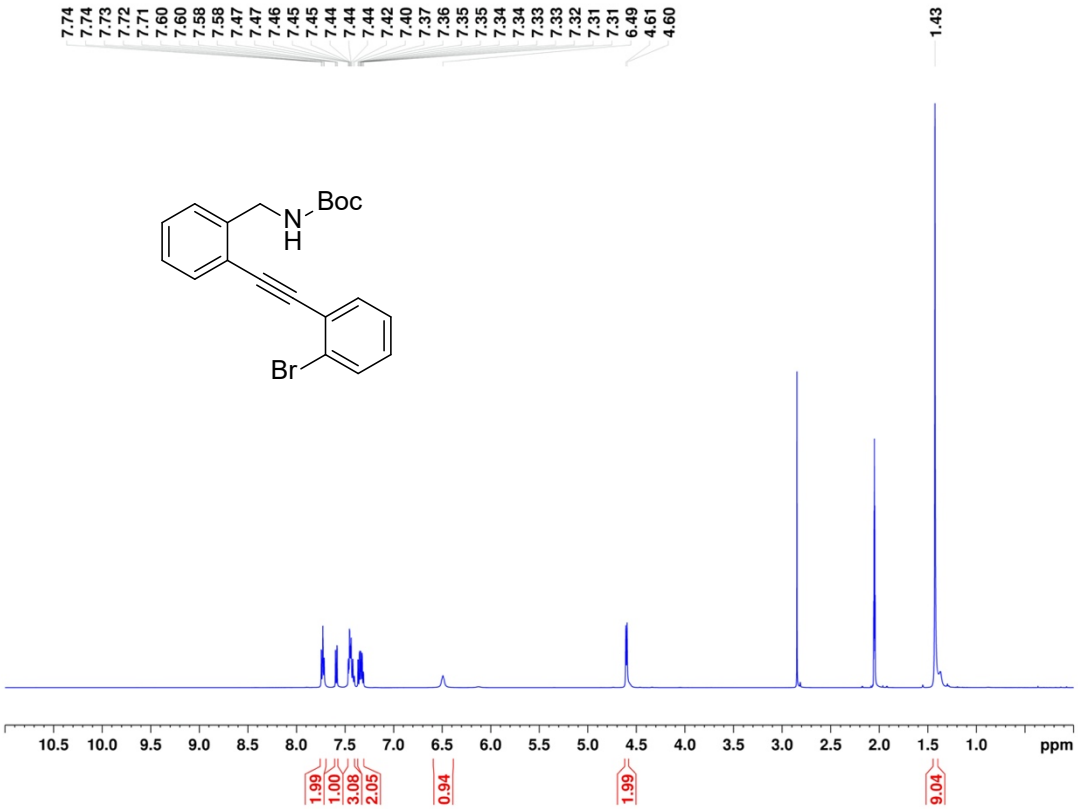
^{1}H NMR spectrum of 3-(Phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate in $CDCl_3$ at 500.2 MHz.



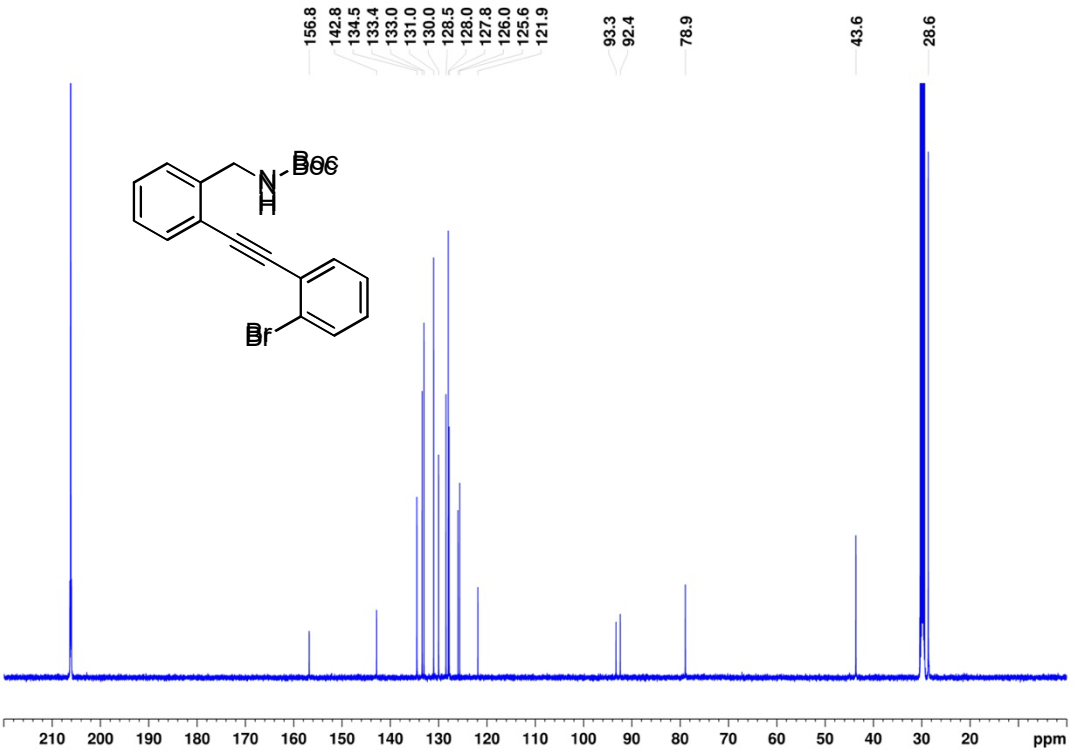
^{13}C NMR {^{19}F} spectrum of 3-(Phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate in $CDCl_3$ at 125.8 MHz.



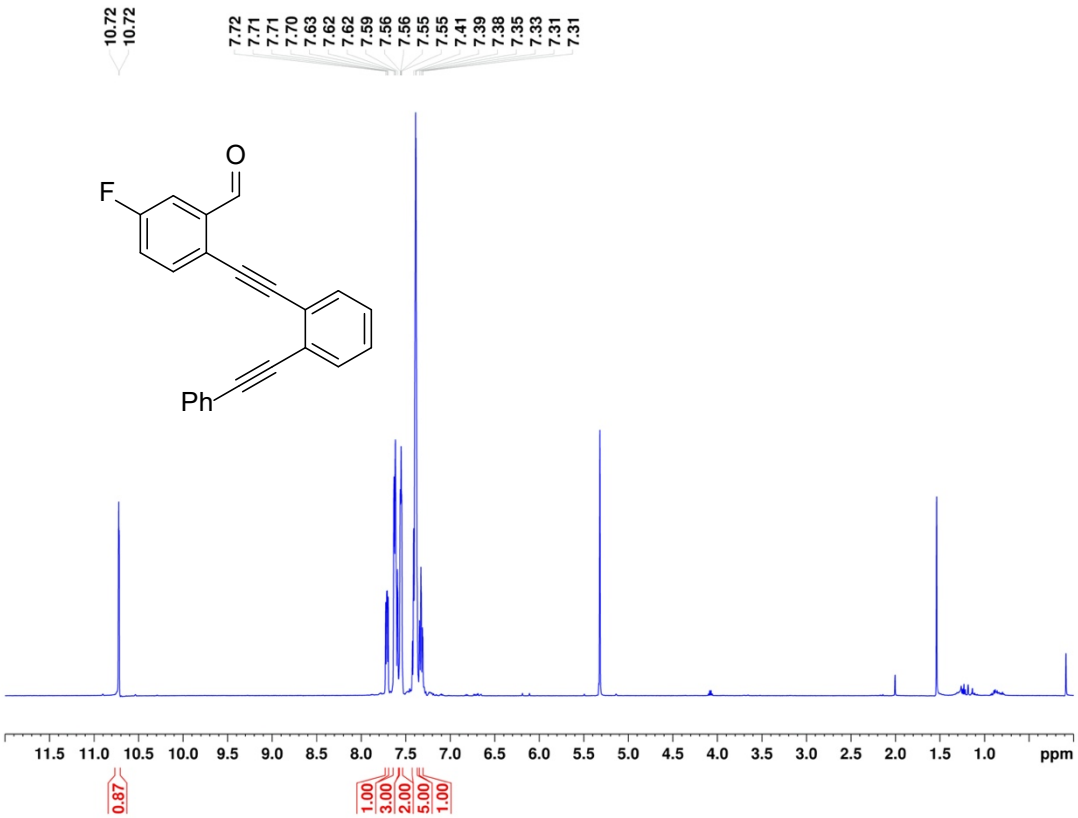
^{19}F NMR spectrum of 3-(Phenylethynyl)naphthalen-2-yl trifluoromethanesulfonate in $CDCl_3$ at 470.7 MHz.



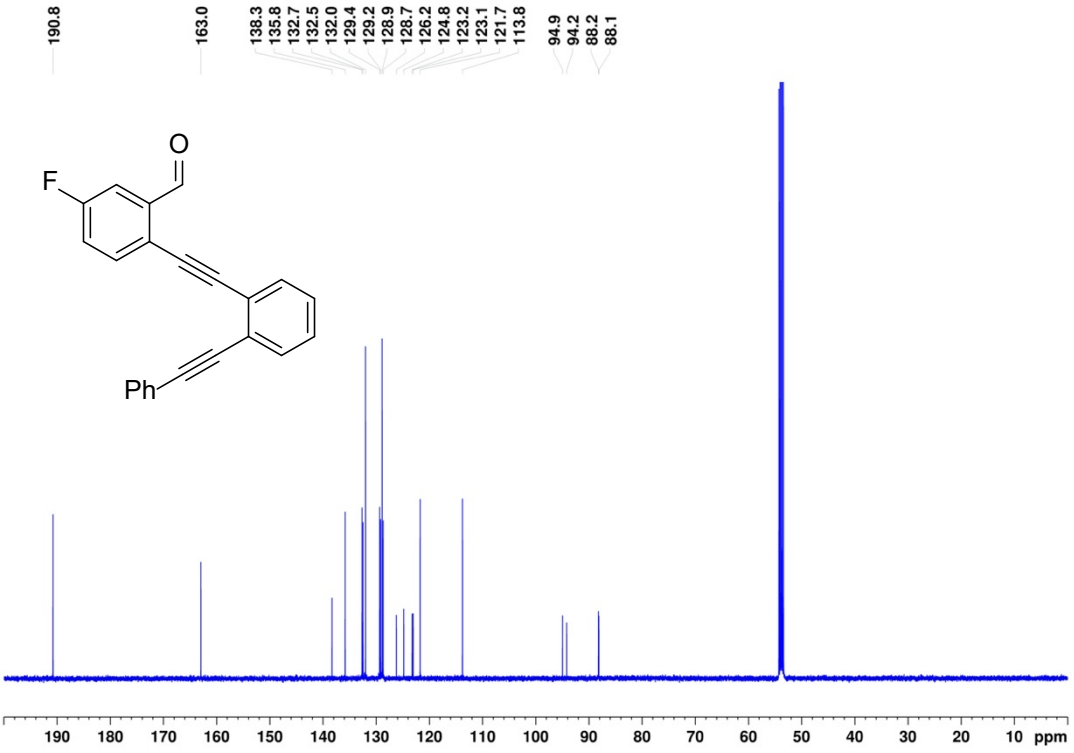
^{1}H NMR spectrum of *tert*-Butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate in $(CD_3)_2CO$ at 500.2 MHz.



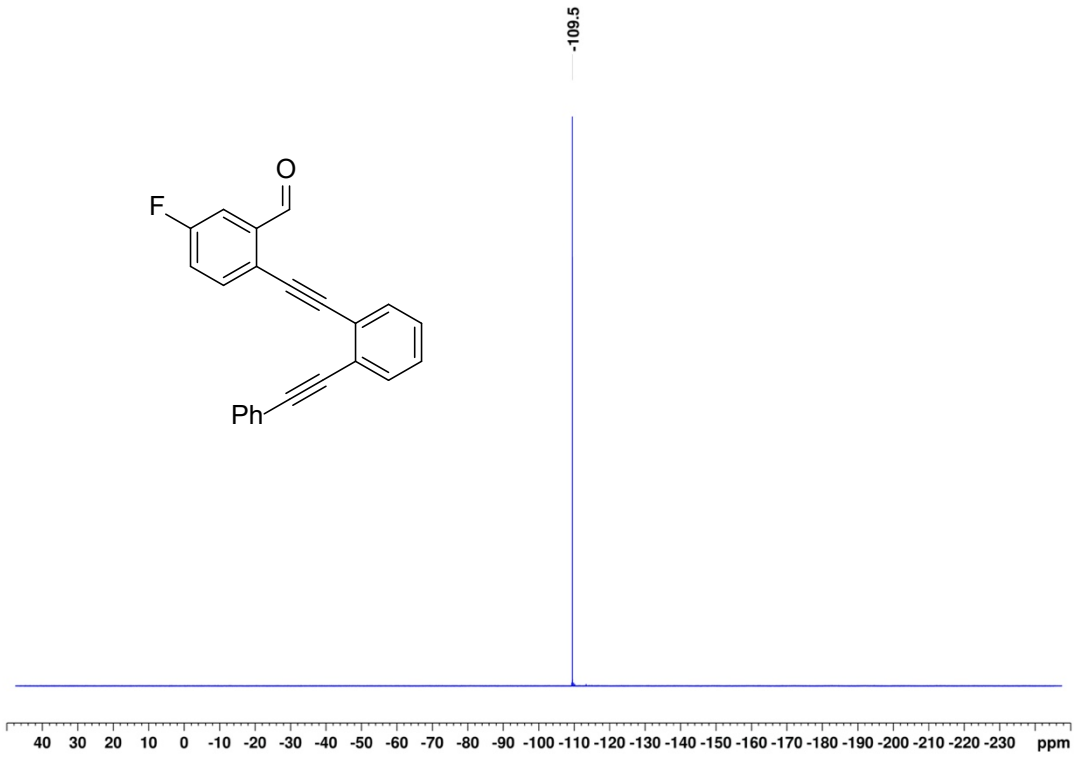
^{13}C NMR spectrum of *tert*-Butyl (2-((2-bromophenyl)ethynyl)benzyl)carbamate in $(CD_3)_2CO$ at 125.8 MHz.



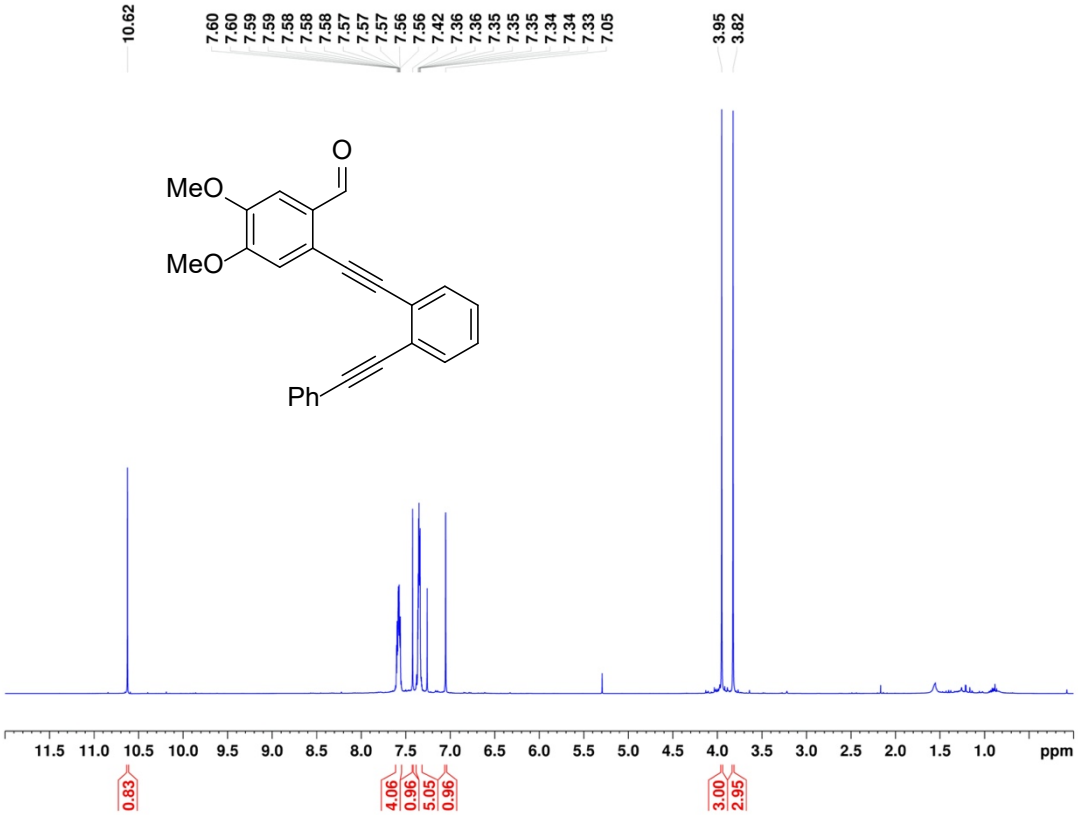
^{1}H NMR spectrum of 5-Fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in CD_2Cl_2 at 500.2 MHz.



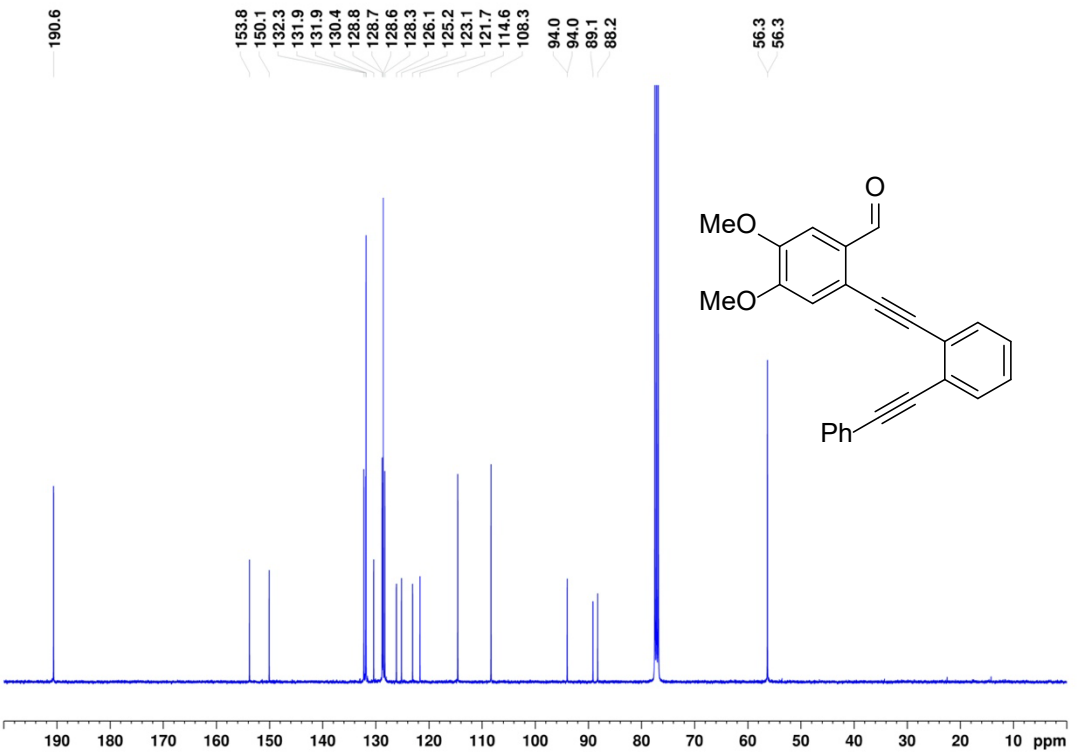
^{13}C NMR {^{19}F} spectrum of 5-Fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in CD_2Cl_2 at 125.8 MHz.



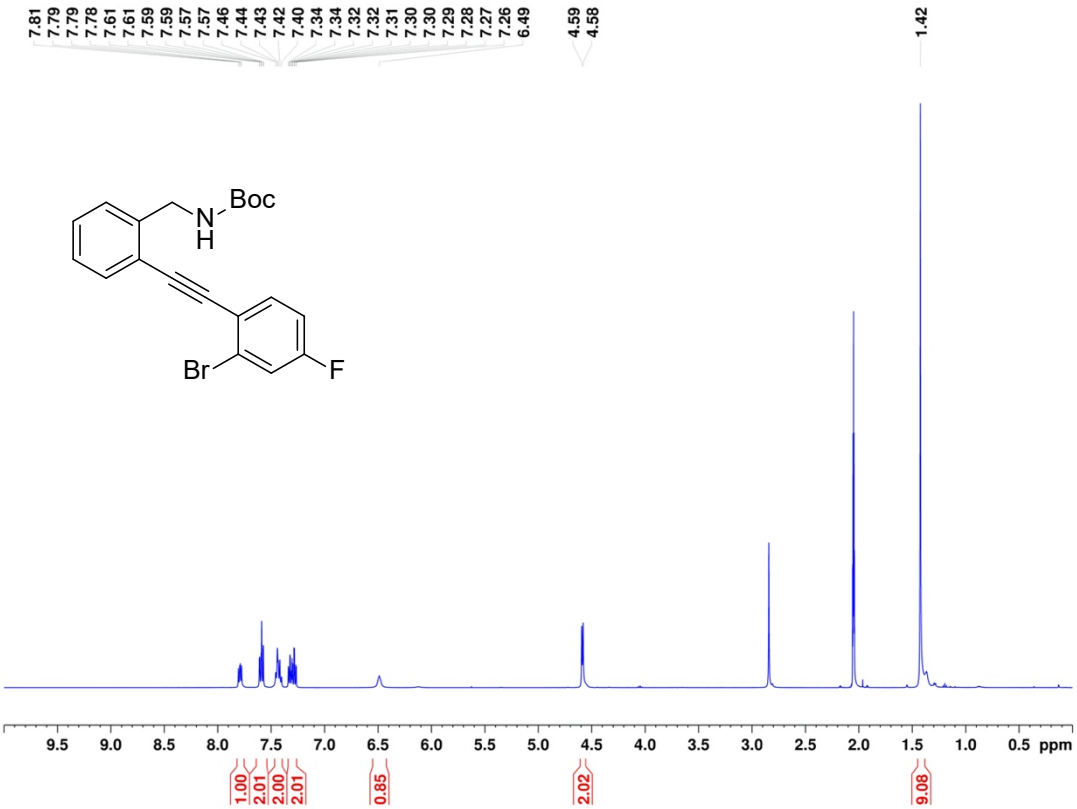
^{19}F NMR spectrum of 5-Fluoro-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in CD_2Cl_2 at 470.7 MHz.



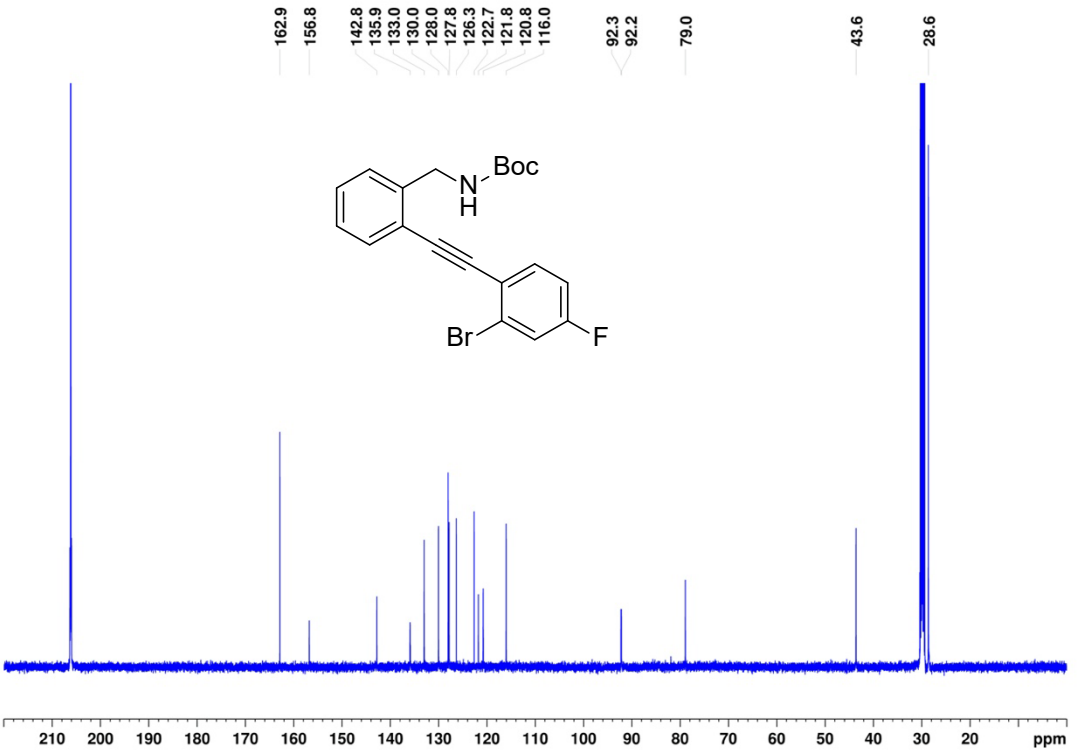
^{1}H NMR spectrum of 4,5-Dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in $CDCl_3$ at 400.3 MHz.



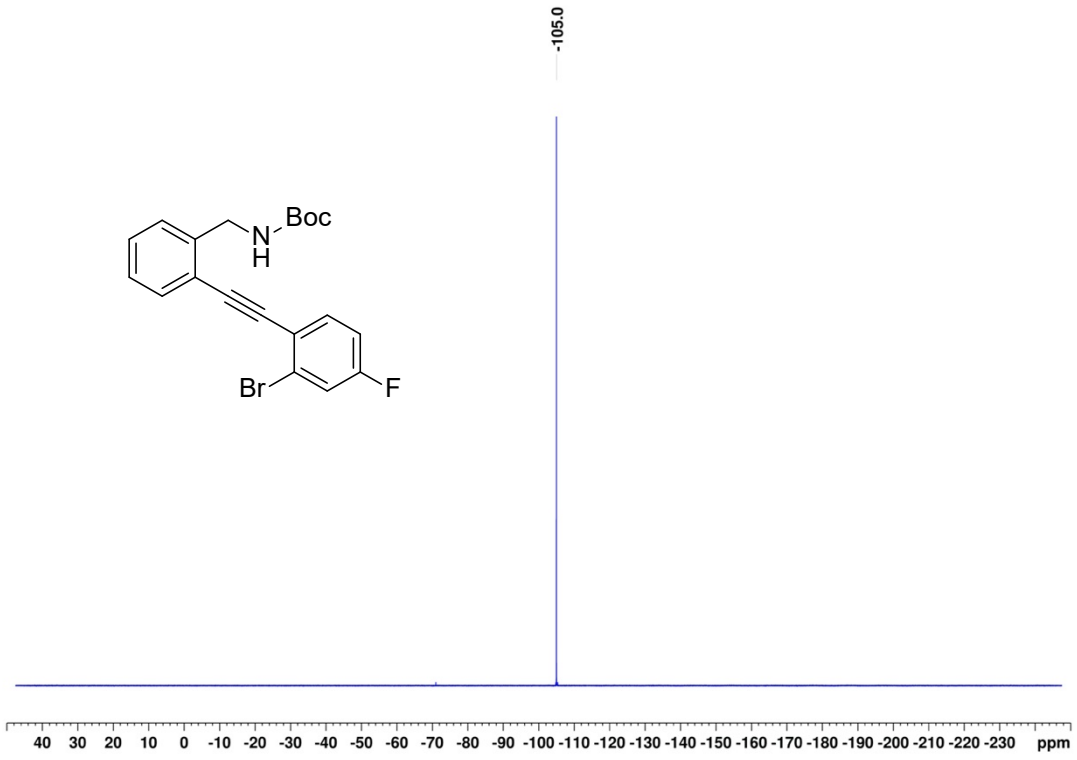
^{13}C NMR spectrum of 4,5-Dimethoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzaldehyde in $CDCl_3$ at 100.7 MHz.



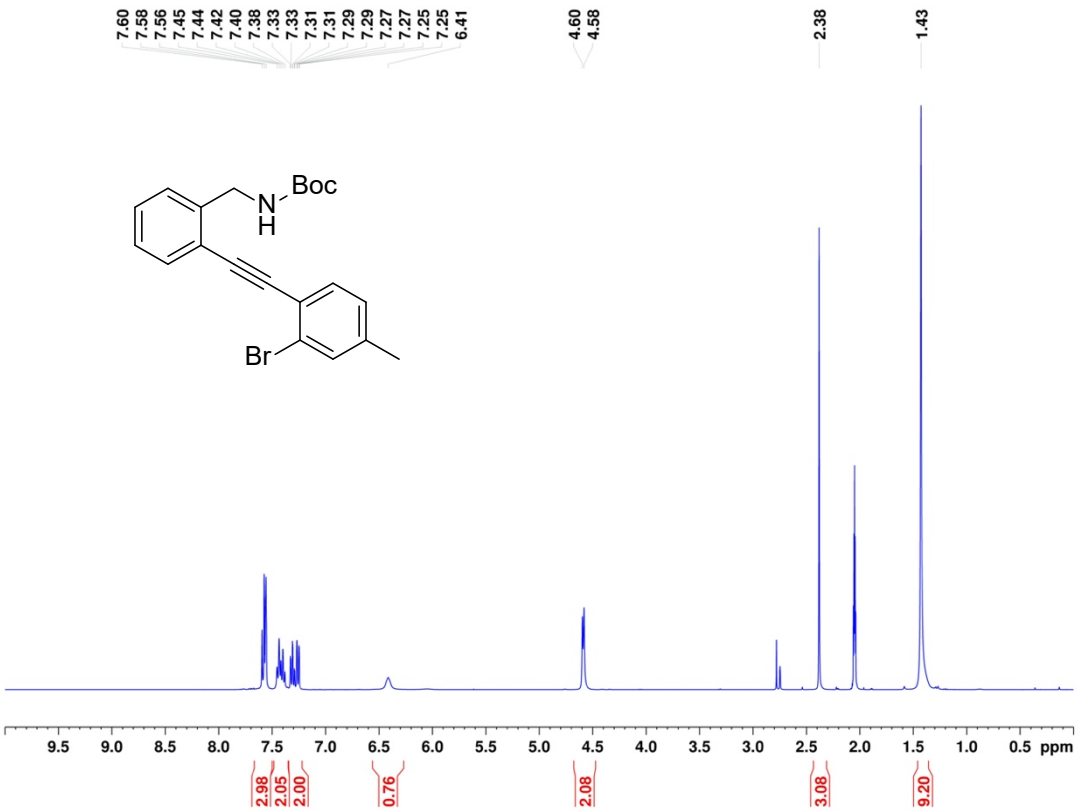
^{1}H NMR spectrum of *tert*-Butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)carbamate in $(CD_3)_2CO$ at 500.2 MHz.



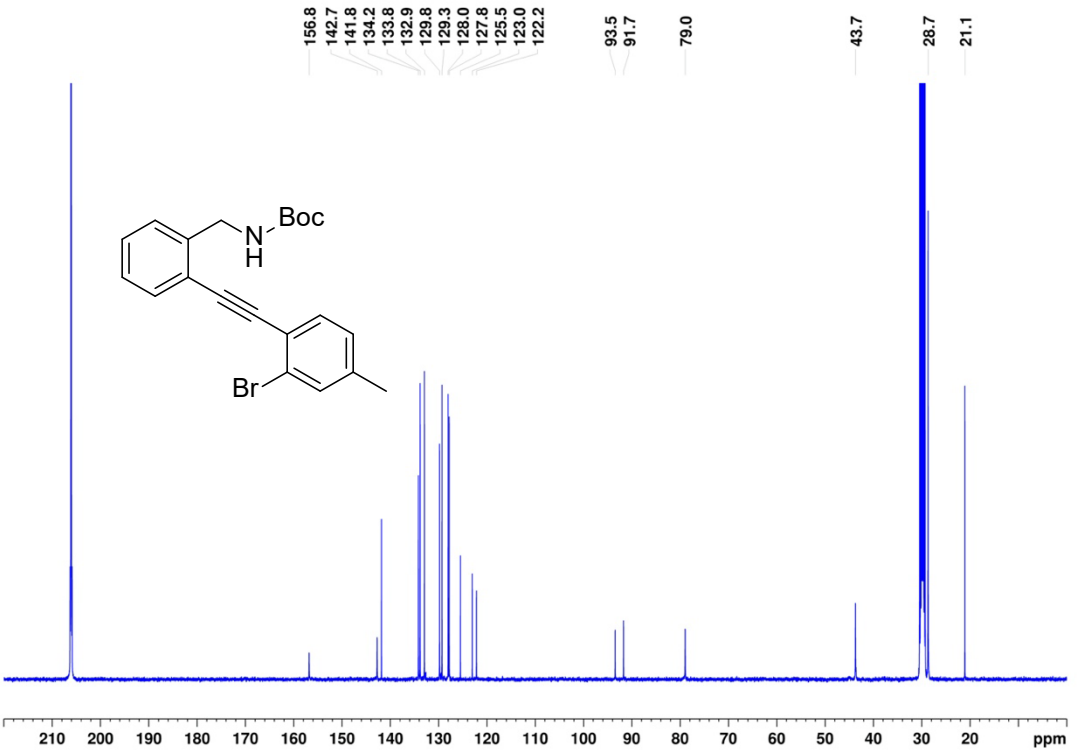
^{13}C NMR {^{19}F} spectrum of *tert*-Butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)carbamate in $(CD_3)_2CO$ at 125.8 MHz.



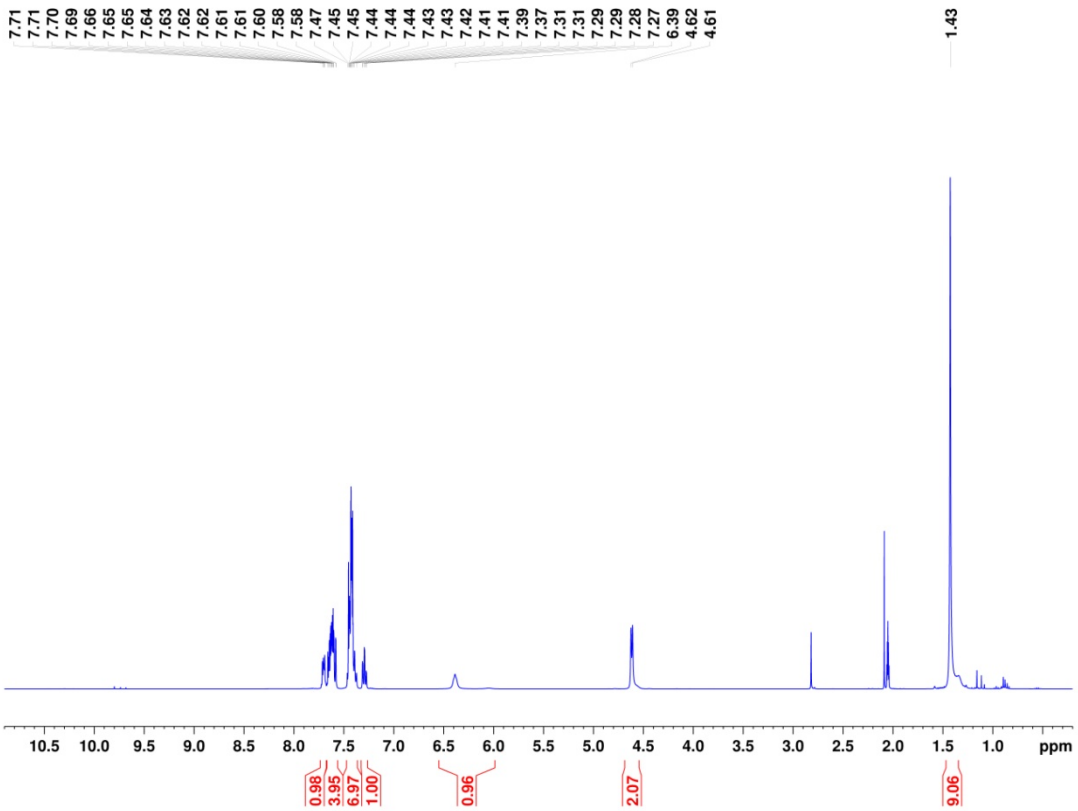
^{19}F NMR spectrum of *tert*-Butyl (2-((2-bromo-4-fluorophenyl)ethynyl)benzyl)carbamate in $(CD_3)_2CO$ at 470.7 MHz.



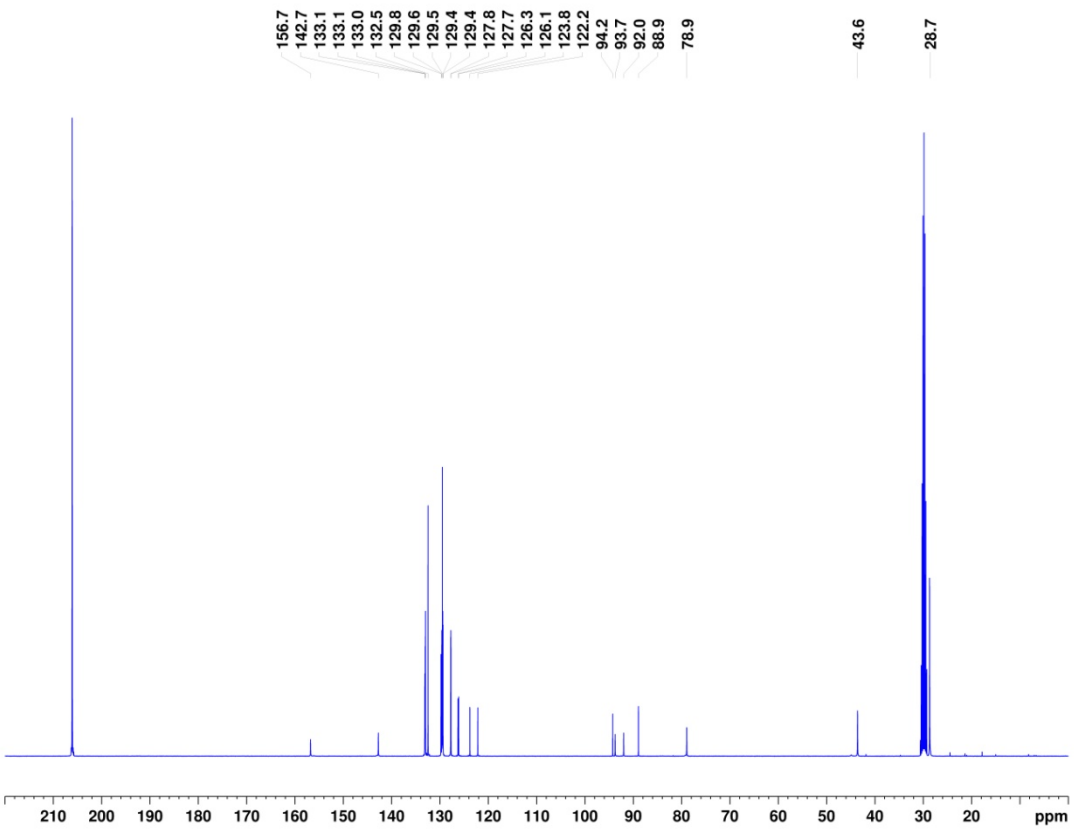
^{1}H NMR spectrum of *tert*-Butyl (2-((2-bromo-4-methylphenyl)ethynyl)benzyl)carbamate in $(CD_3)_2CO$ at 400.3 MHz.



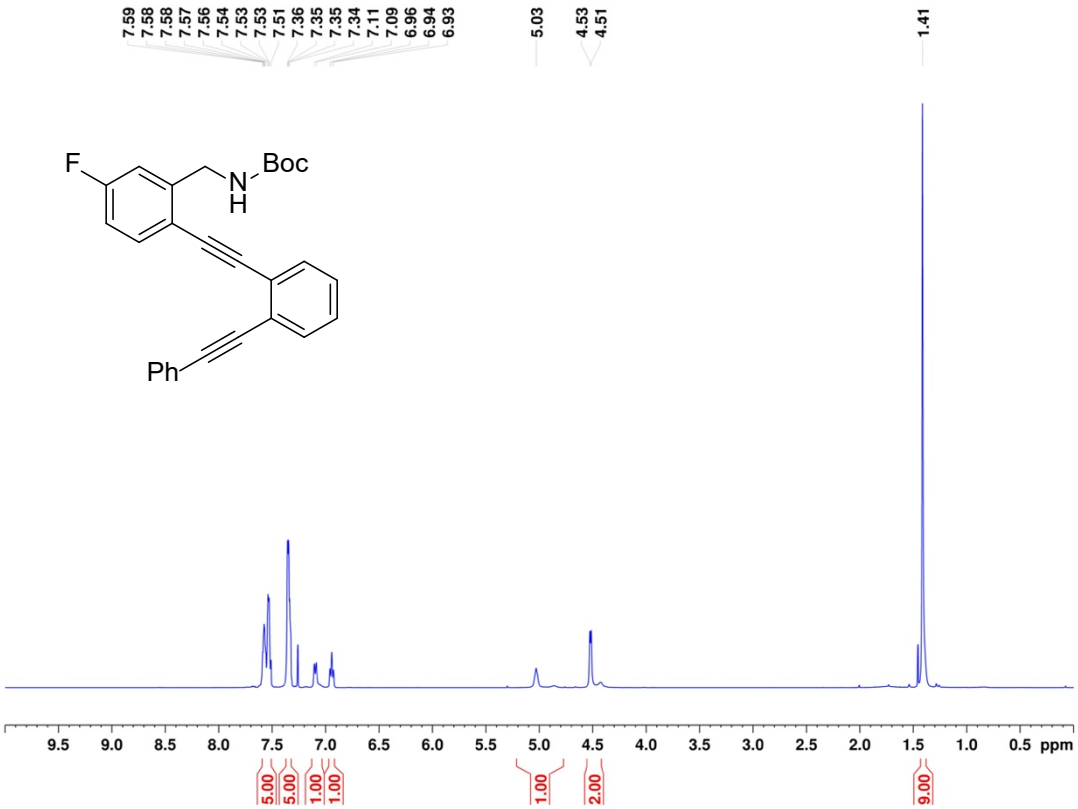
^{13}C NMR spectrum of *tert*-Butyl (2-((2-bromo-4-methylphenyl)ethynyl)benzyl)carbamate in $(CD_3)_2CO$ at 100.7 MHz.



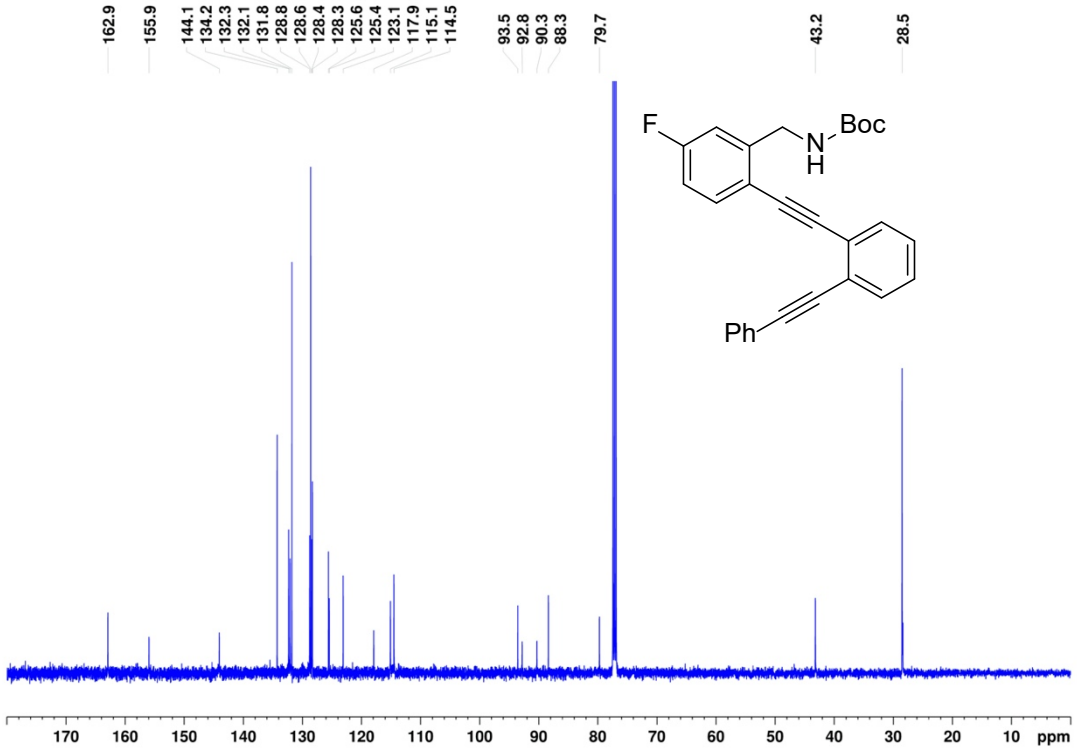
^{1}H NMR spectrum of **5a** in $(CD_3)_2CO$ at 400.3 MHz.



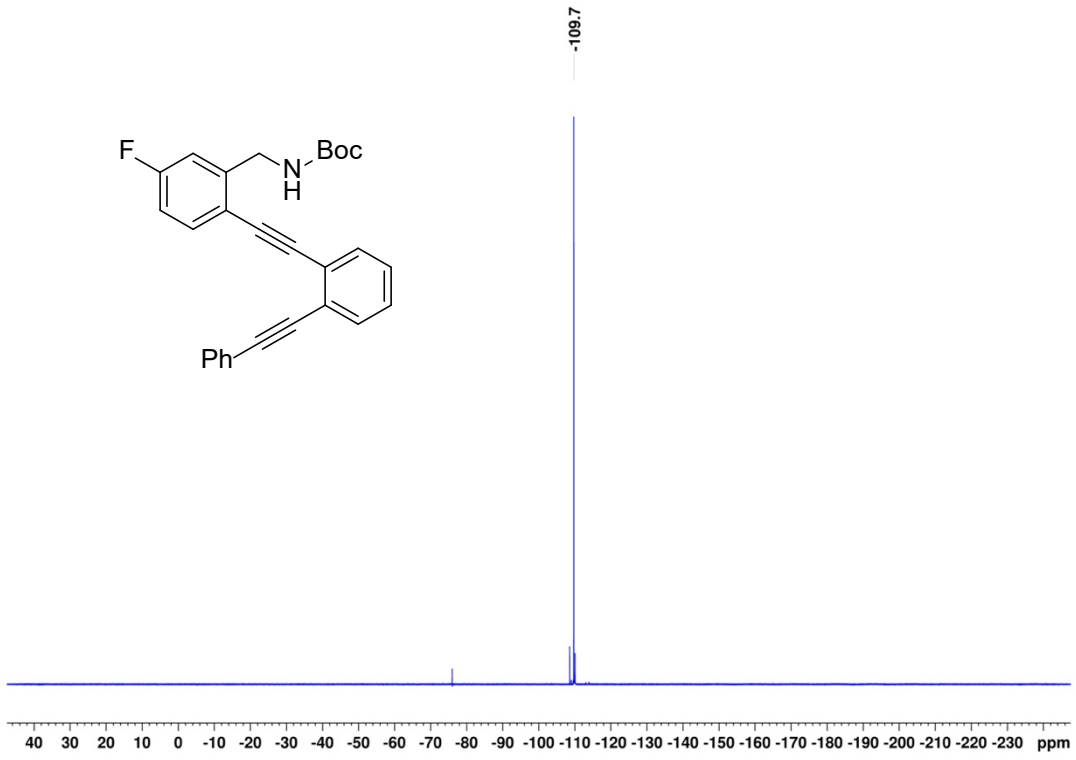
^{13}C NMR spectrum of **5a** in $(CD_3)_2CO$ at 100.7 MHz.



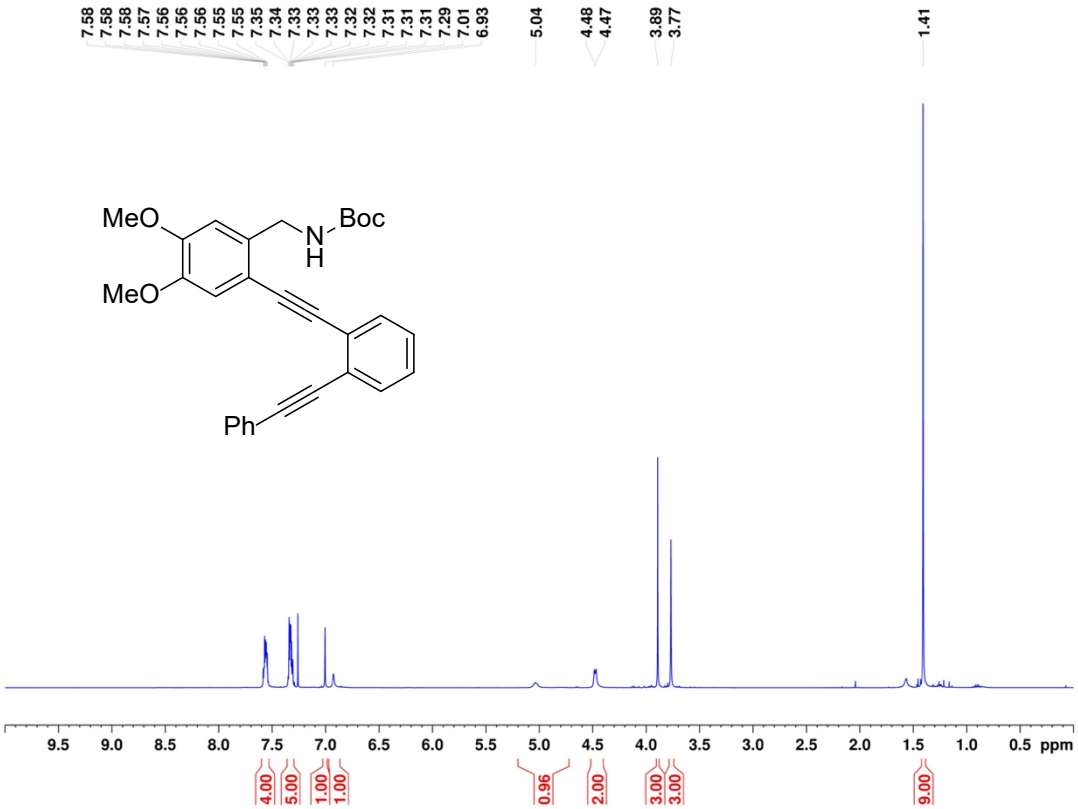
^{1}H NMR spectrum of **5b** in $CDCl_3$ at 500.2 MHz.



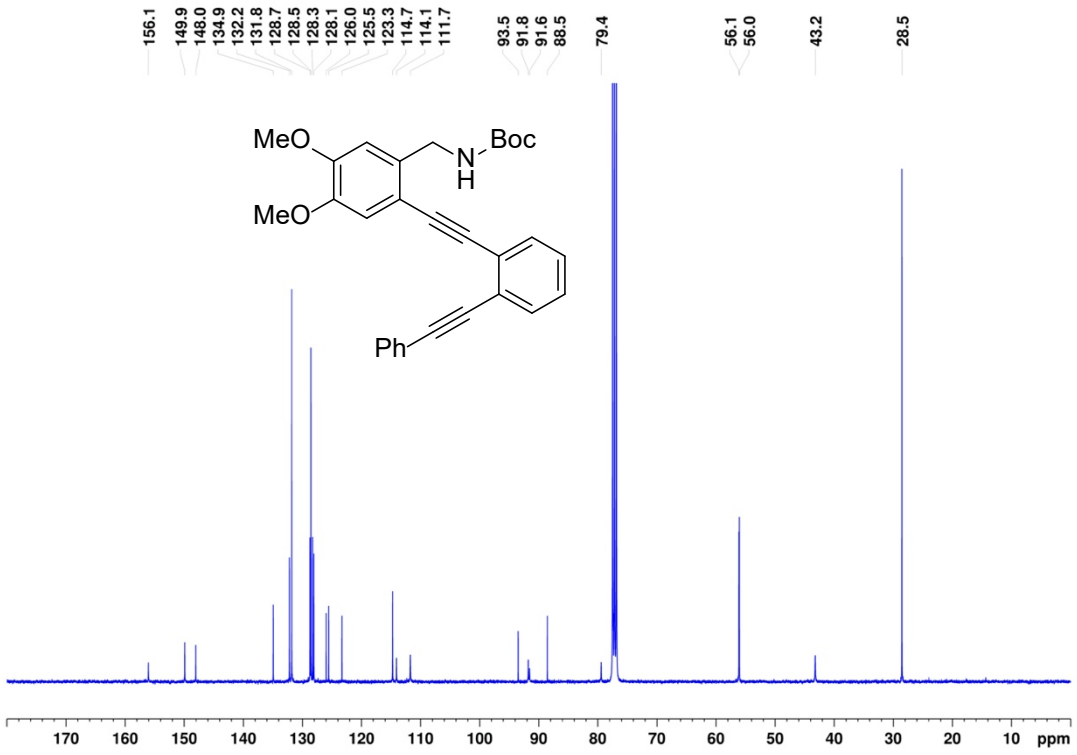
^{13}C NMR {^{19}F} spectrum of **5b** in $CDCl_3$ at 125.8 MHz.



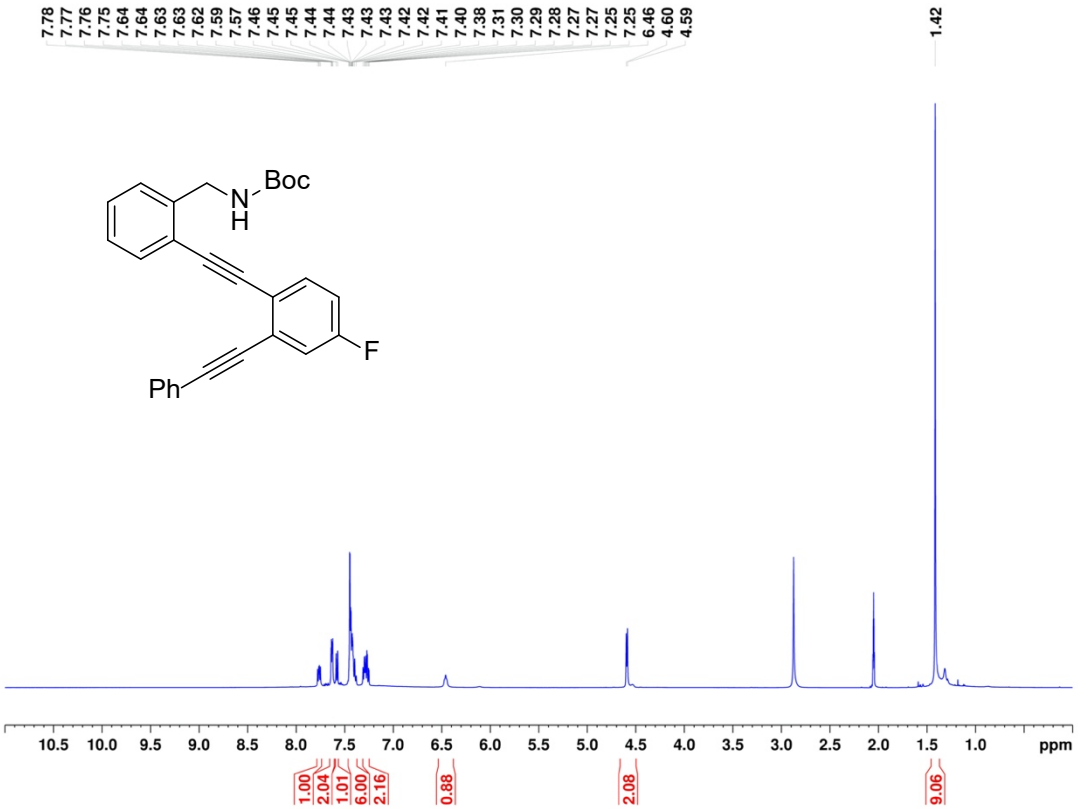
^{19}F NMR spectrum of **5b** in $CDCl_3$ at 470.7 MHz.



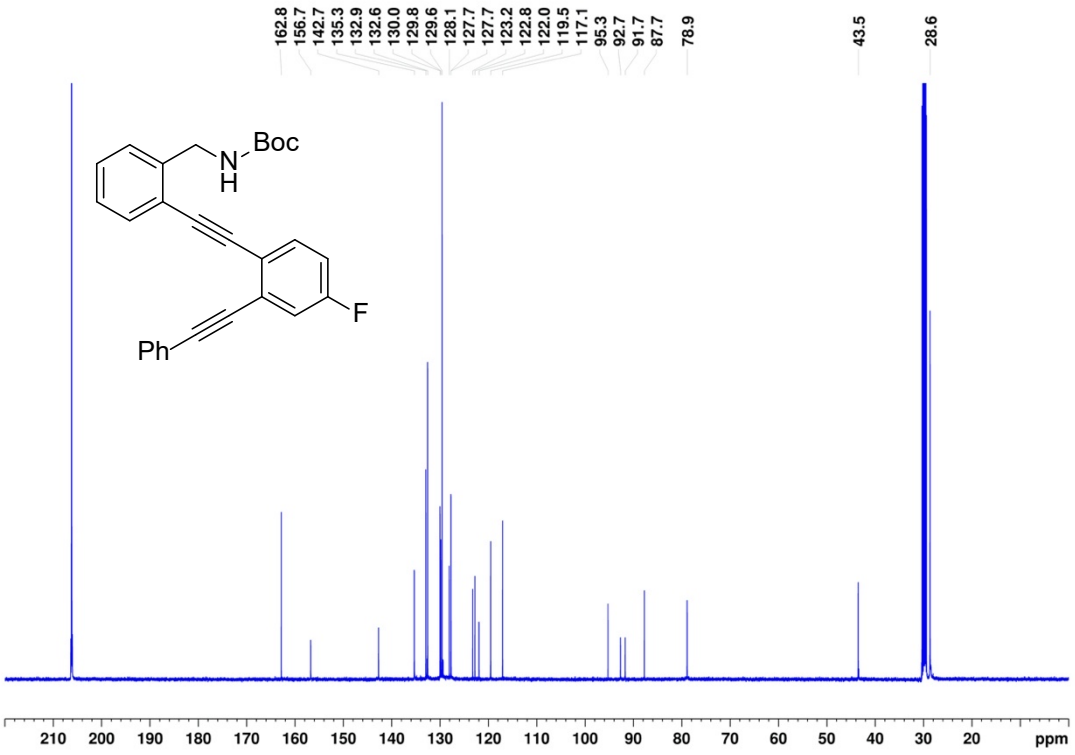
^{1}H NMR spectrum of **5c** in $CDCl_3$ at 400.3 MHz.



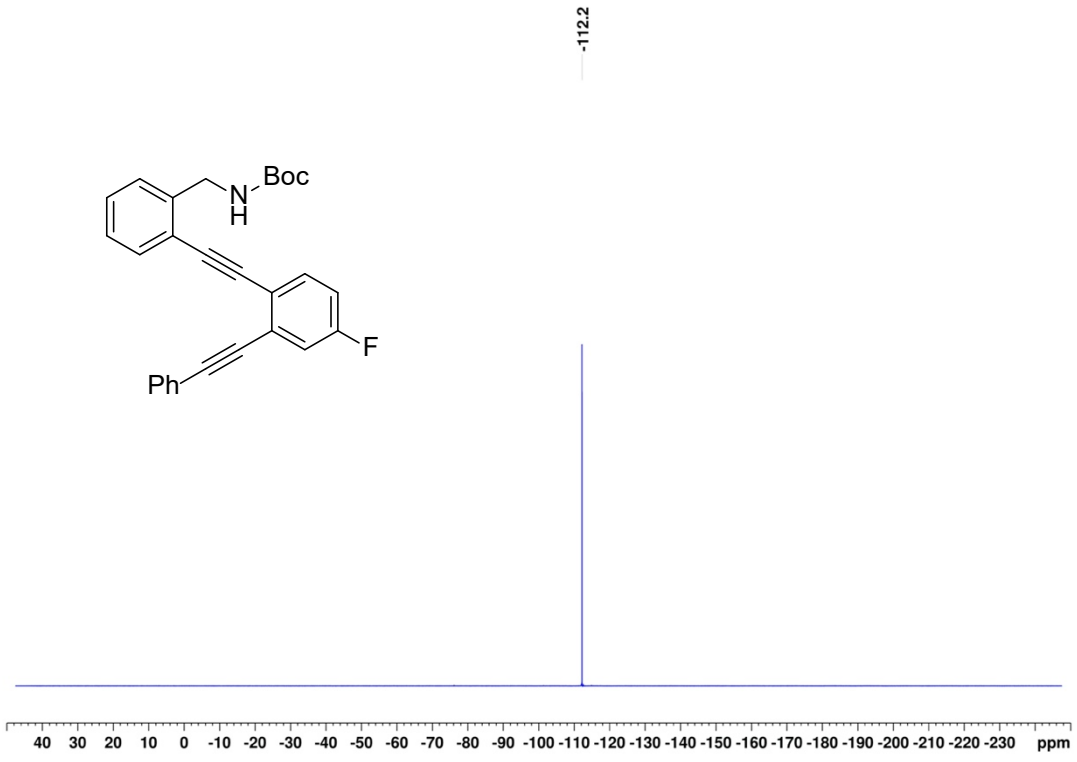
^{13}C NMR spectrum of **5c** in $CDCl_3$ at 100.7 MHz.



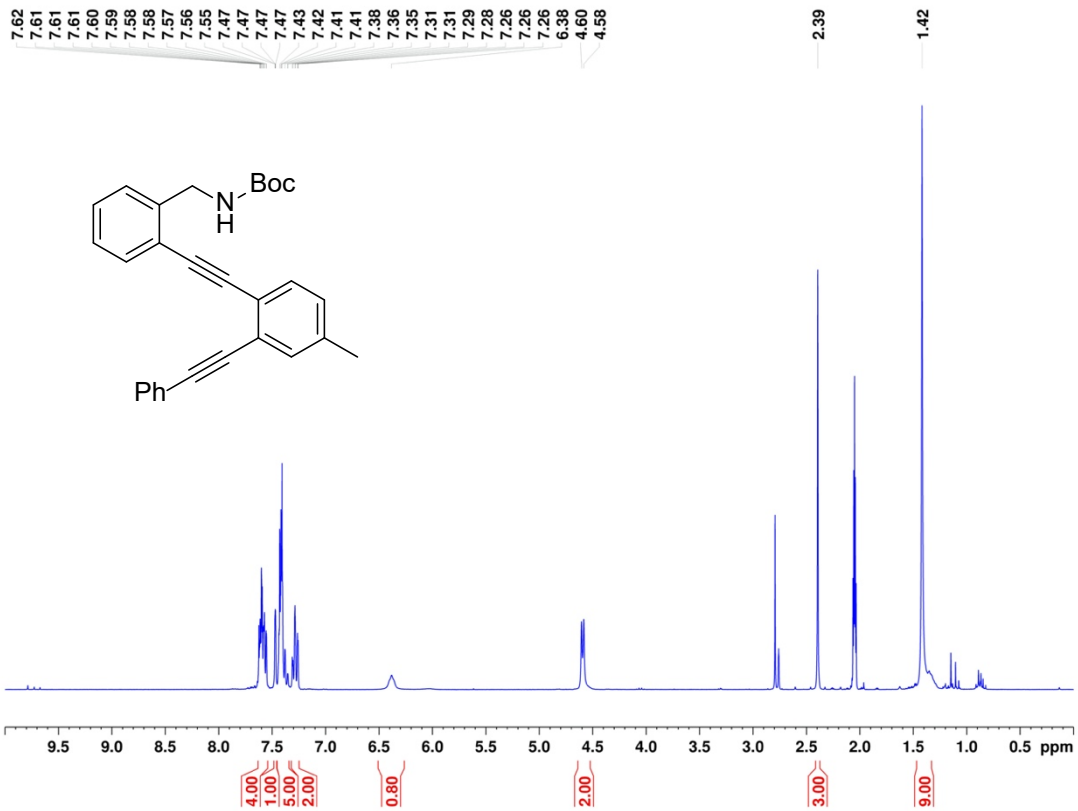
^{1}H NMR spectrum of **5d** in $(CD_3)_2CO$ at 500.2 MHz.



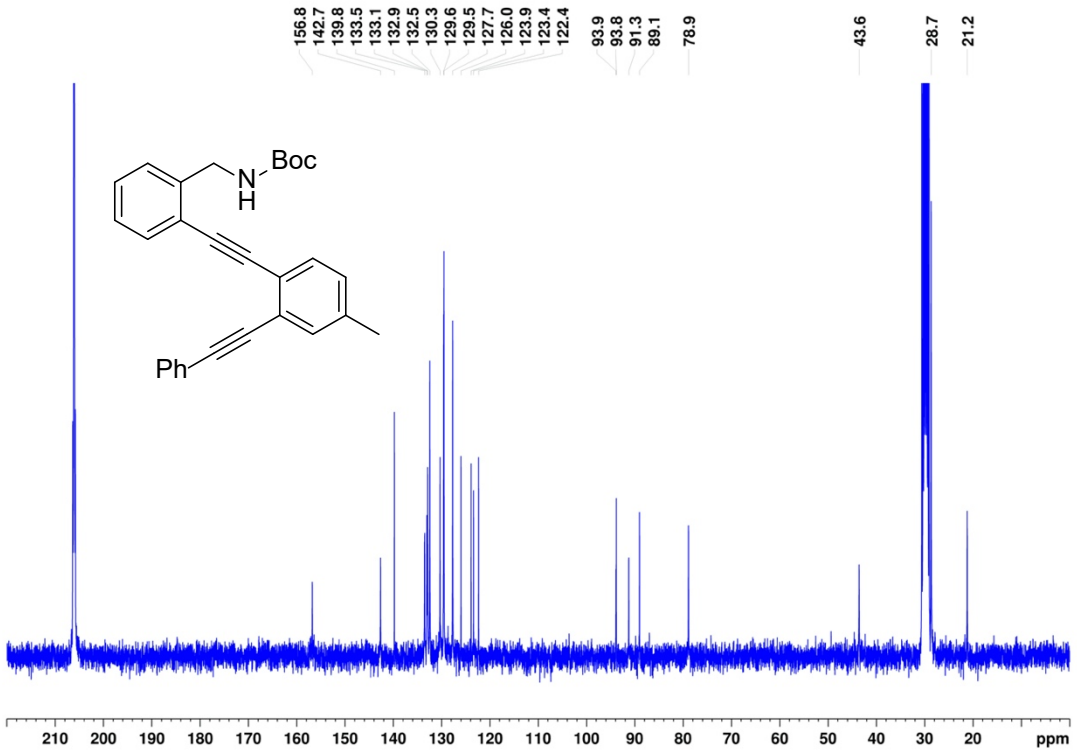
^{13}C NMR {^{19}F} spectrum of **5d** in $(CD_3)_2CO$ at 125.8 MHz.



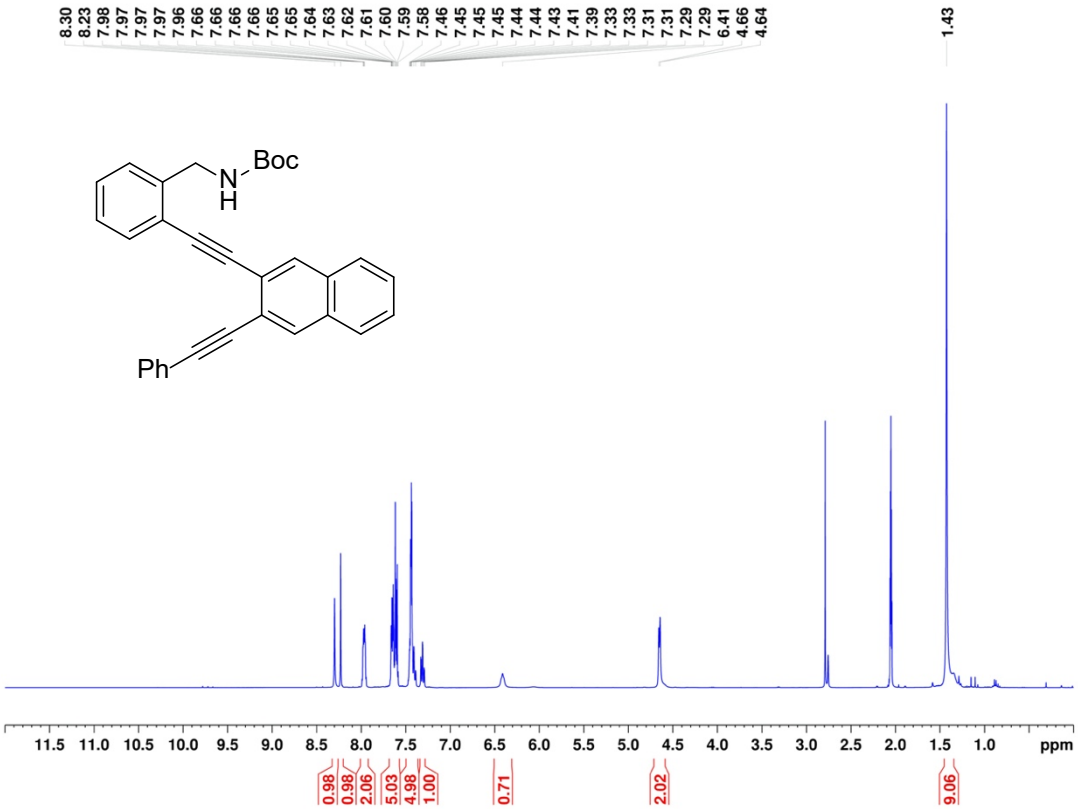
^{19}F NMR spectrum of **5d** in $(CD_3)_2CO$ at 470.7 MHz.



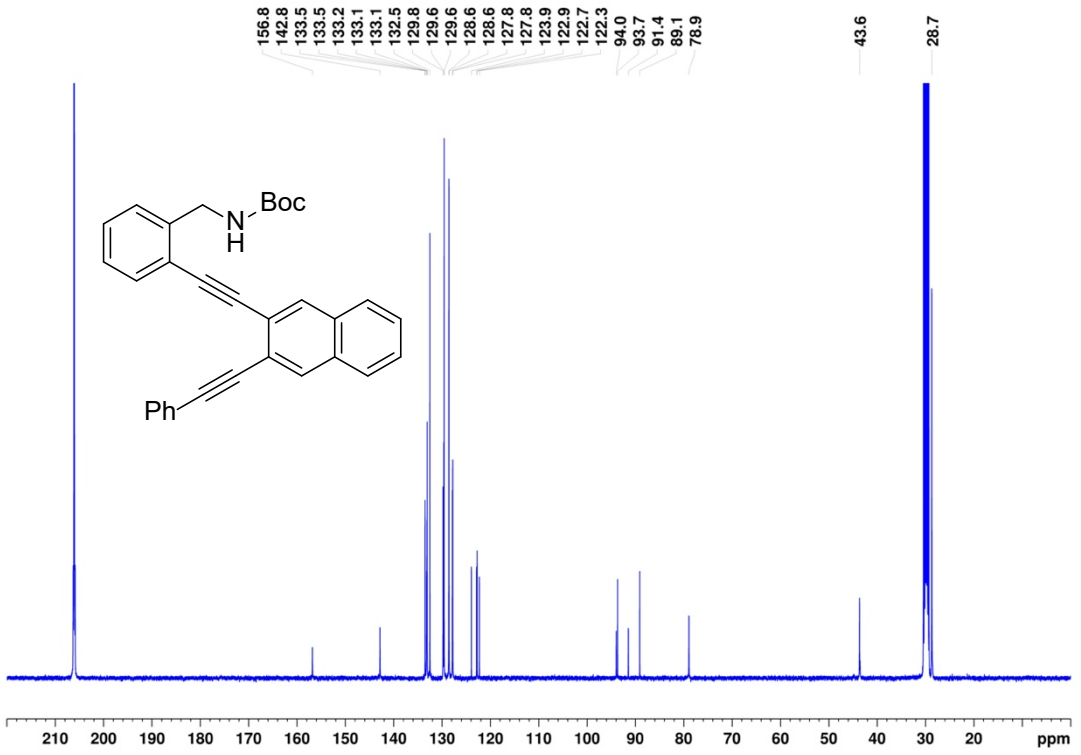
^{1}H NMR spectrum of **5e** in $(CD_3)_2CO$ at 300.2 MHz.



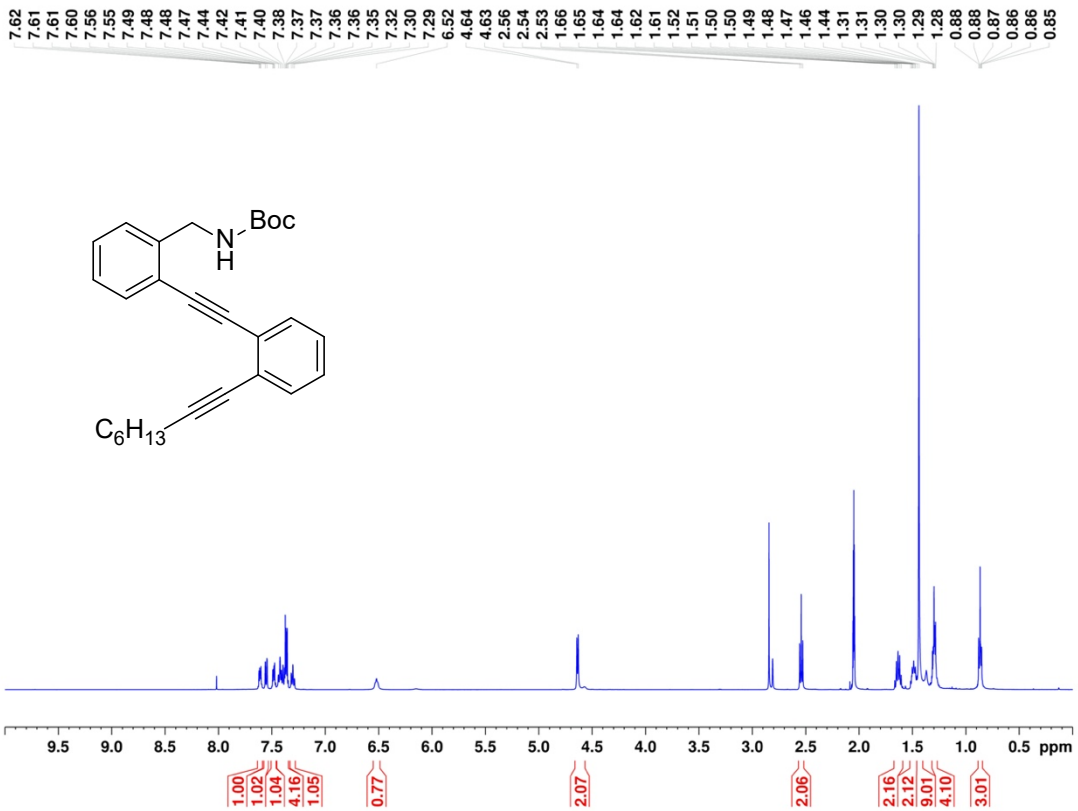
^{13}C NMR spectrum of **5e** in $(CD_3)_2CO$ at 75.5 MHz.



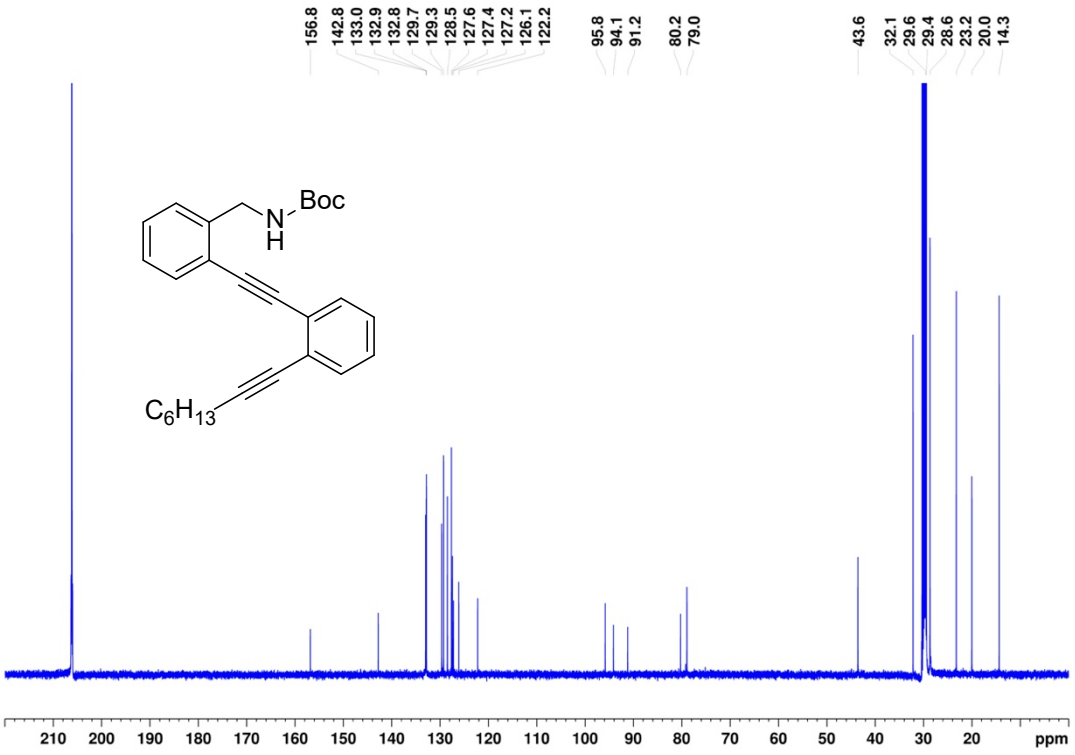
^{1}H NMR spectrum of **5f** in $(CD_3)_2CO$ at 400.3 MHz.



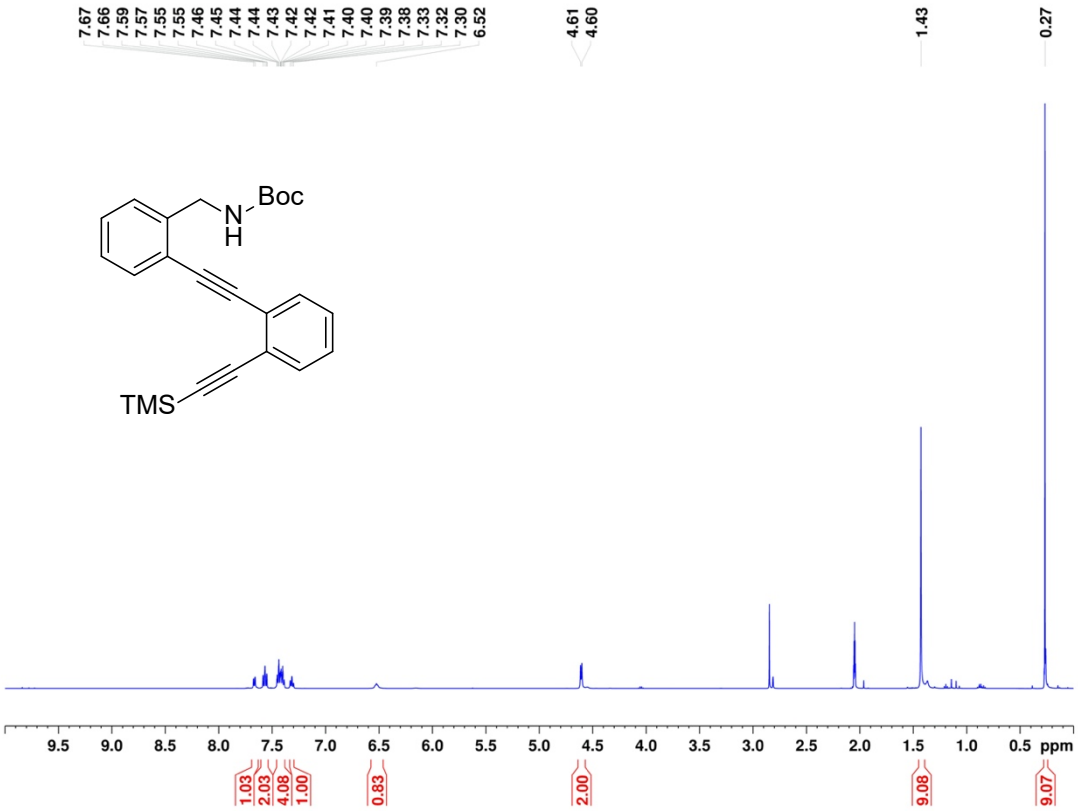
^{13}C NMR spectrum of **5f** in $(CD_3)_2CO$ at 100.7 MHz.



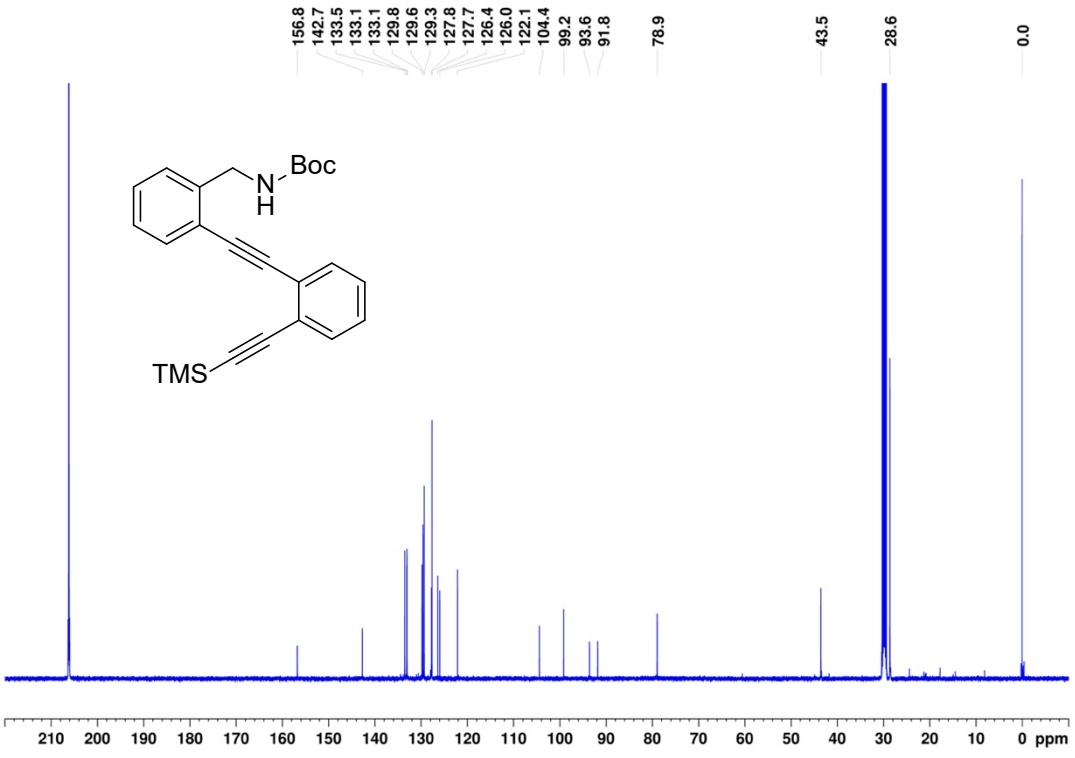
^{1}H NMR spectrum of **5g** in $(CD_3)_2CO$ at 500.2 MHz.



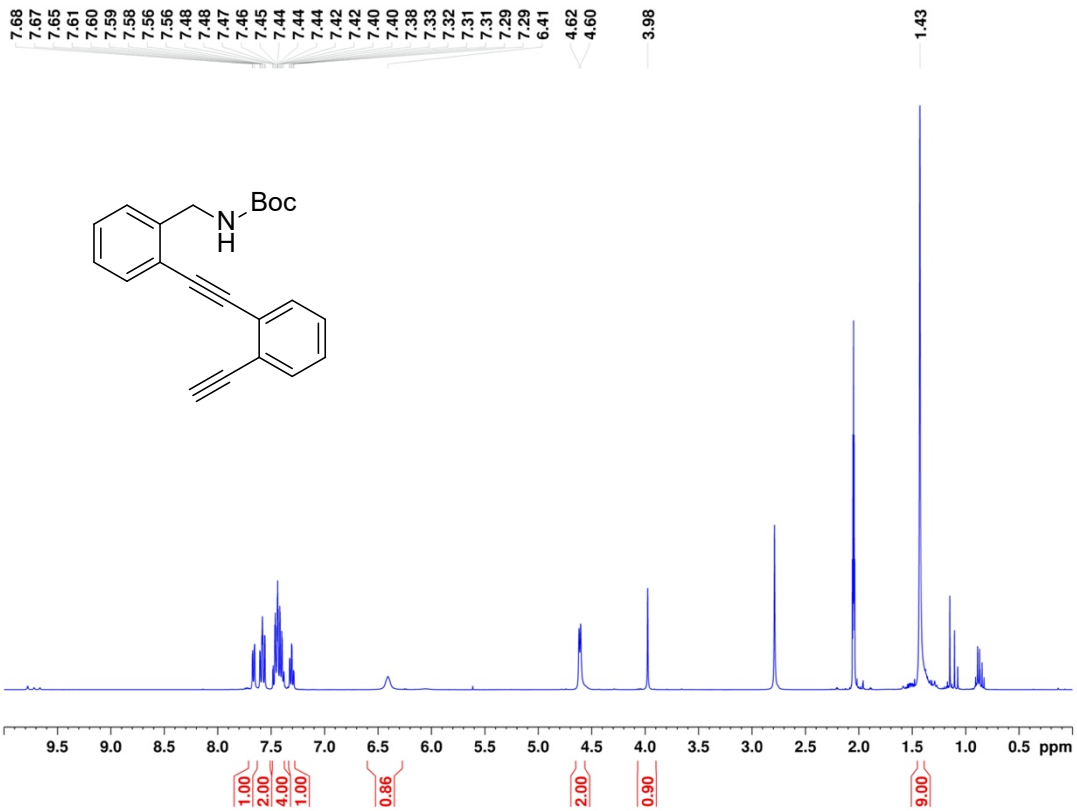
^{13}C NMR spectrum of **5g** in $(CD_3)_2CO$ at 125.8 MHz.



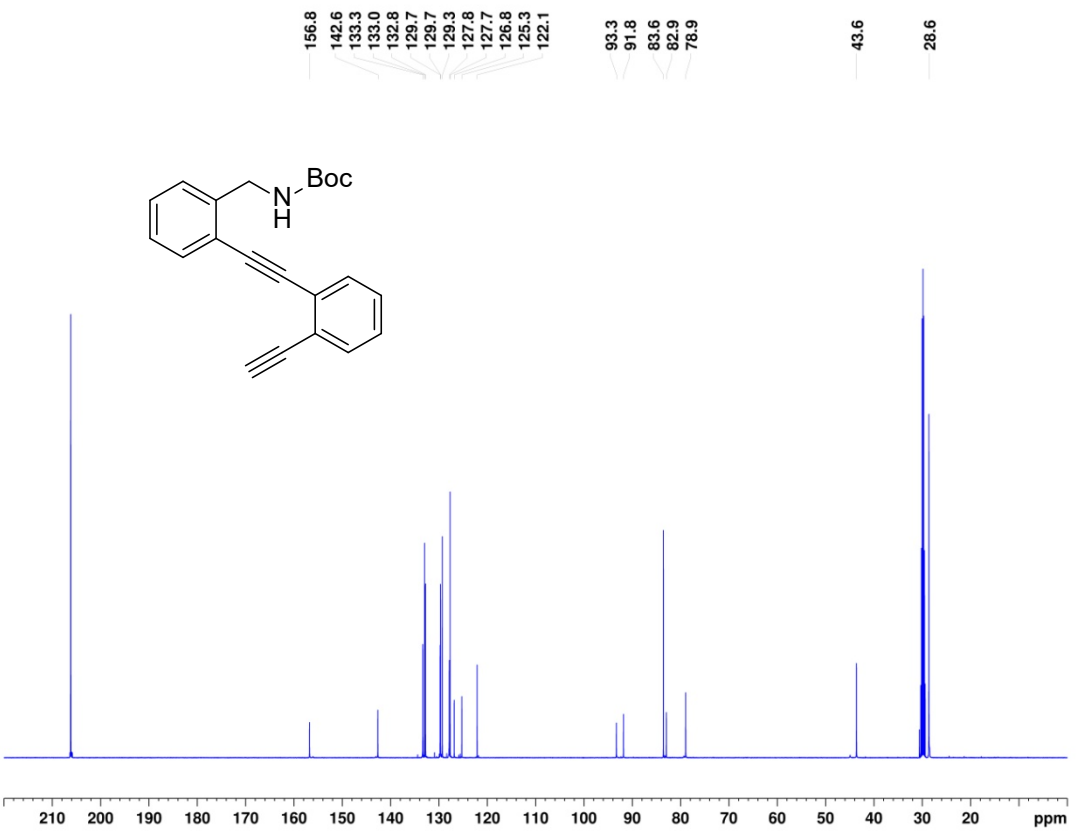
^{1}H NMR spectrum of **5h** in $(CD_3)_2CO$ at 500.2 MHz.



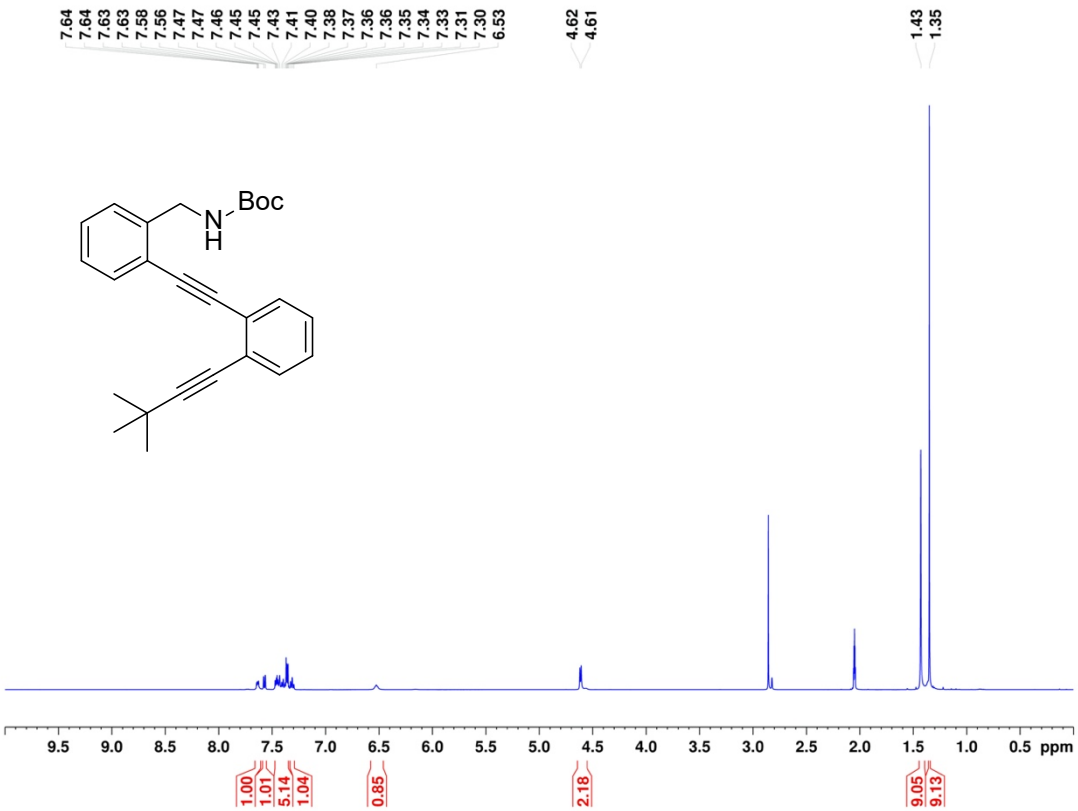
^{13}C NMR spectrum of **5h** in $(CD_3)_2CO$ at 125.8 MHz.



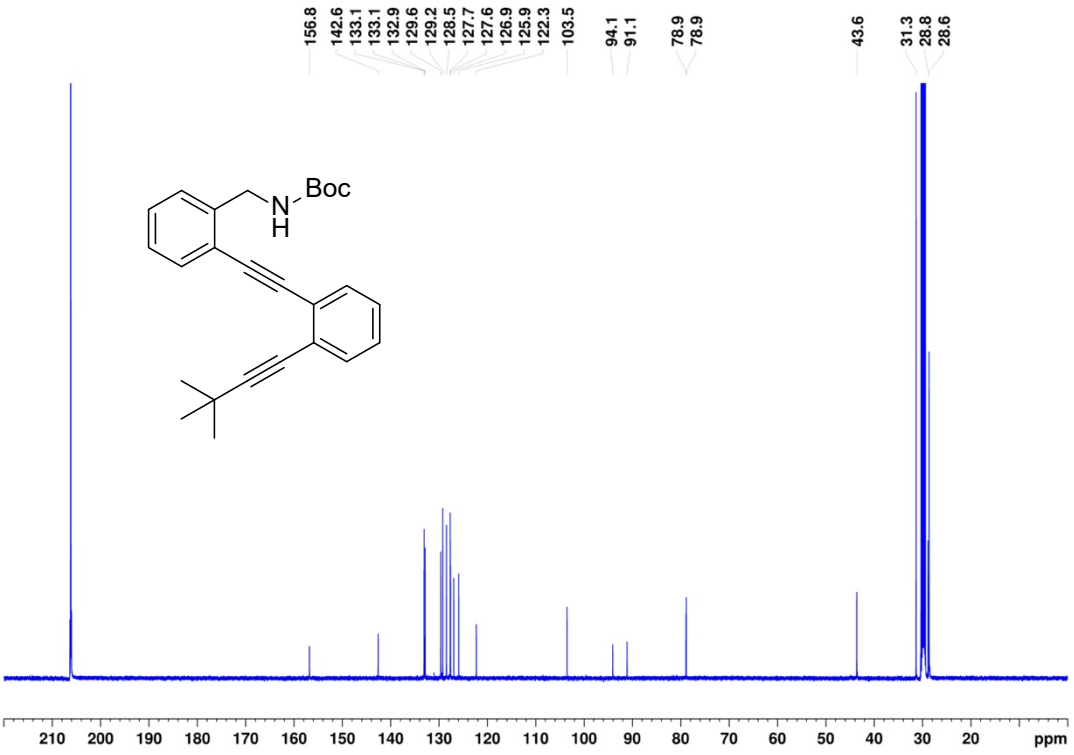
^{1}H NMR spectrum of **5i** in $(CD_3)_2CO$ at 500.2 MHz.



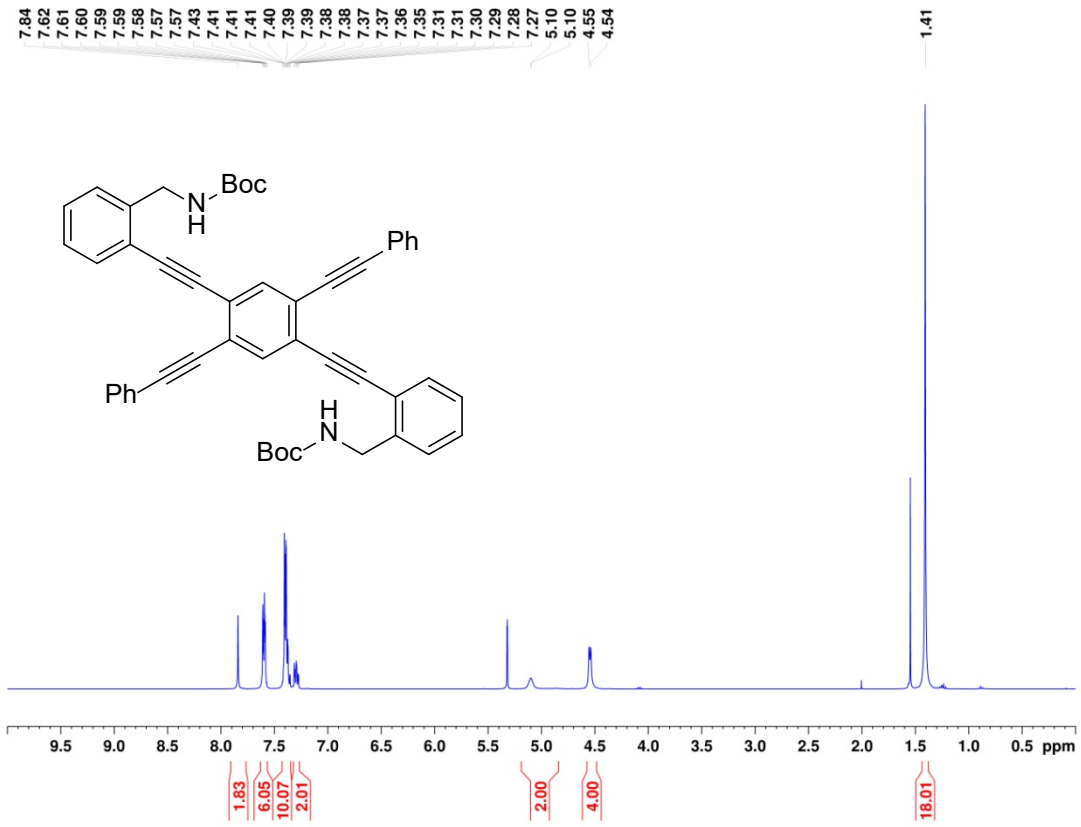
^{13}C NMR spectrum of **5i** in $(CD_3)_2CO$ at 125.8 MHz.



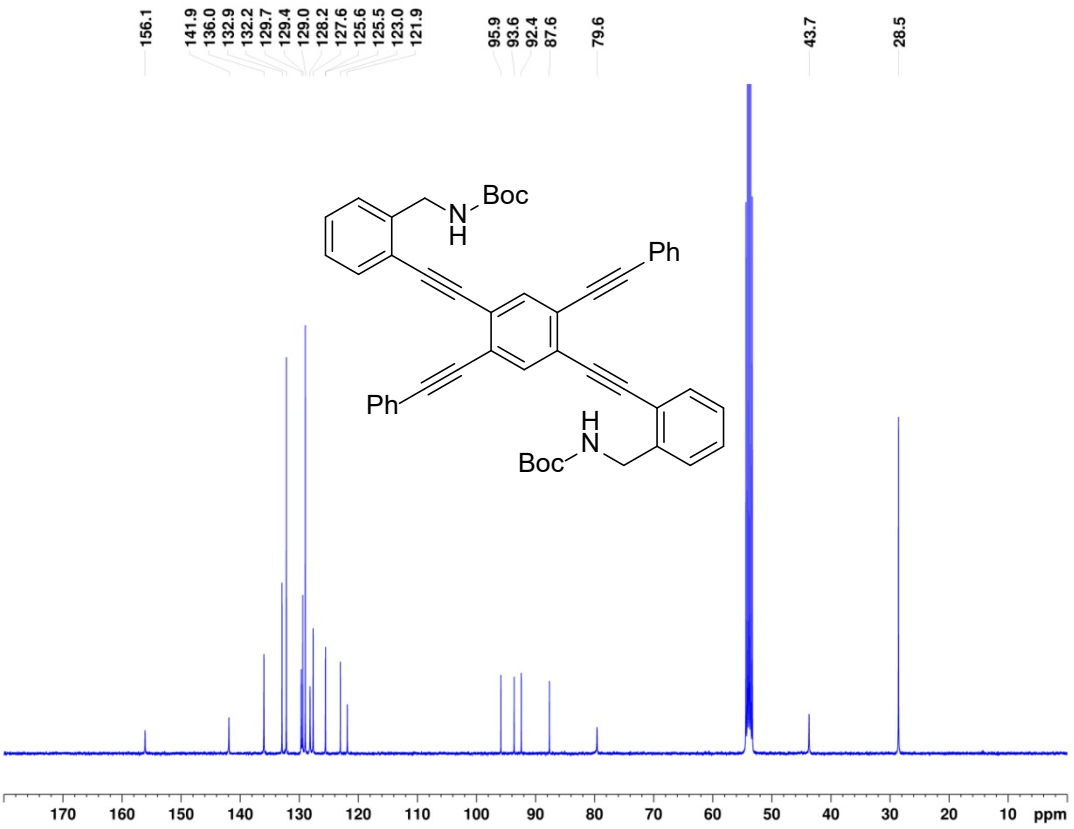
^{1}H NMR spectrum of **5j** in $(CD_3)_2CO$ at 500.2 MHz.



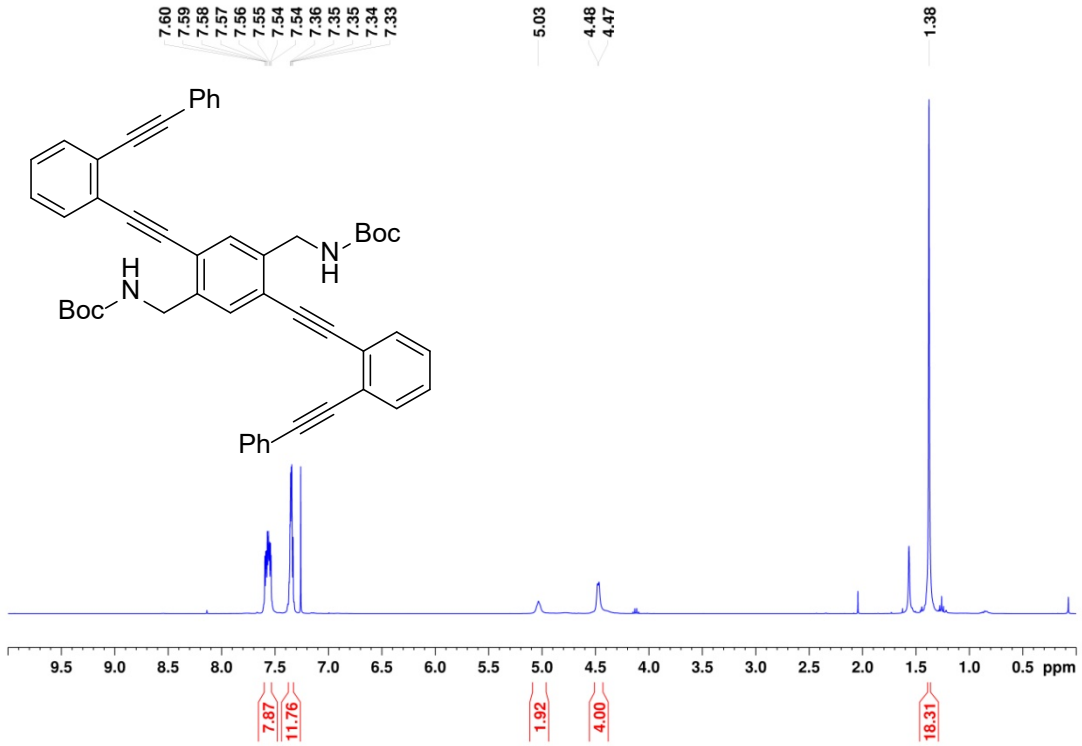
^{13}C NMR spectrum of **5j** in $(CD_3)_2CO$ at 125.8 MHz.



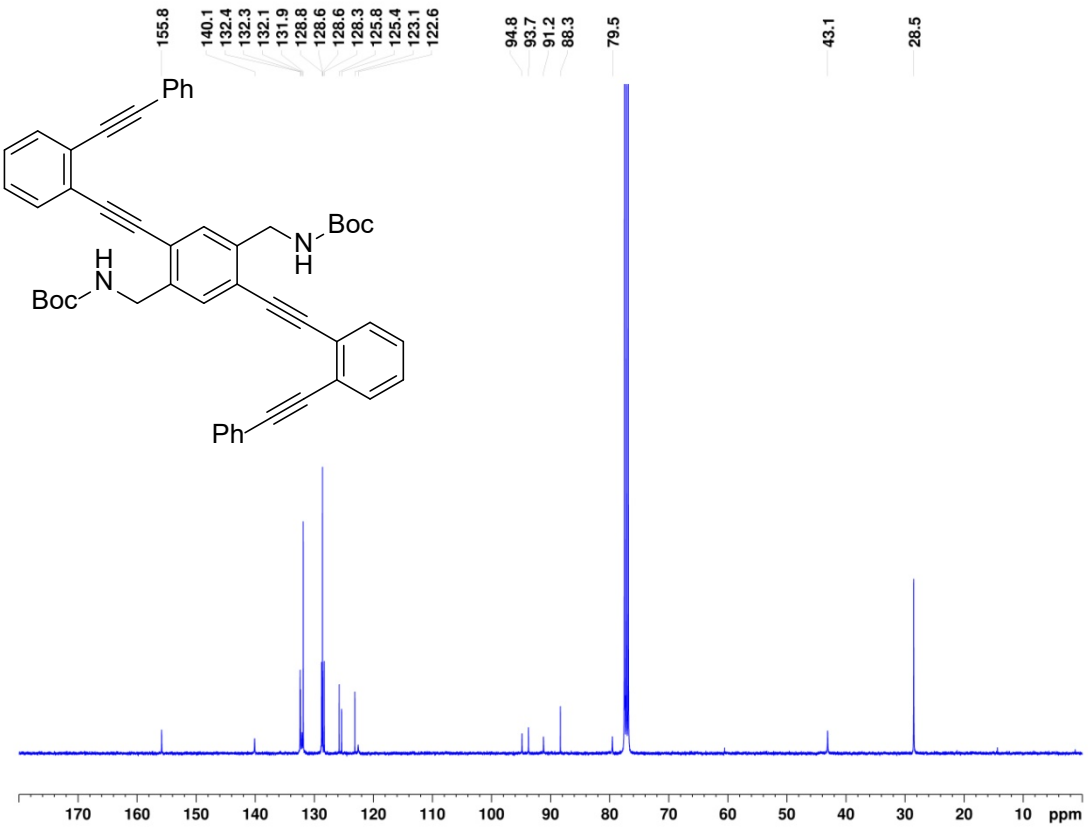
^{1}H NMR spectrum of **5k** in CD_2Cl_2 at 400.3 MHz.



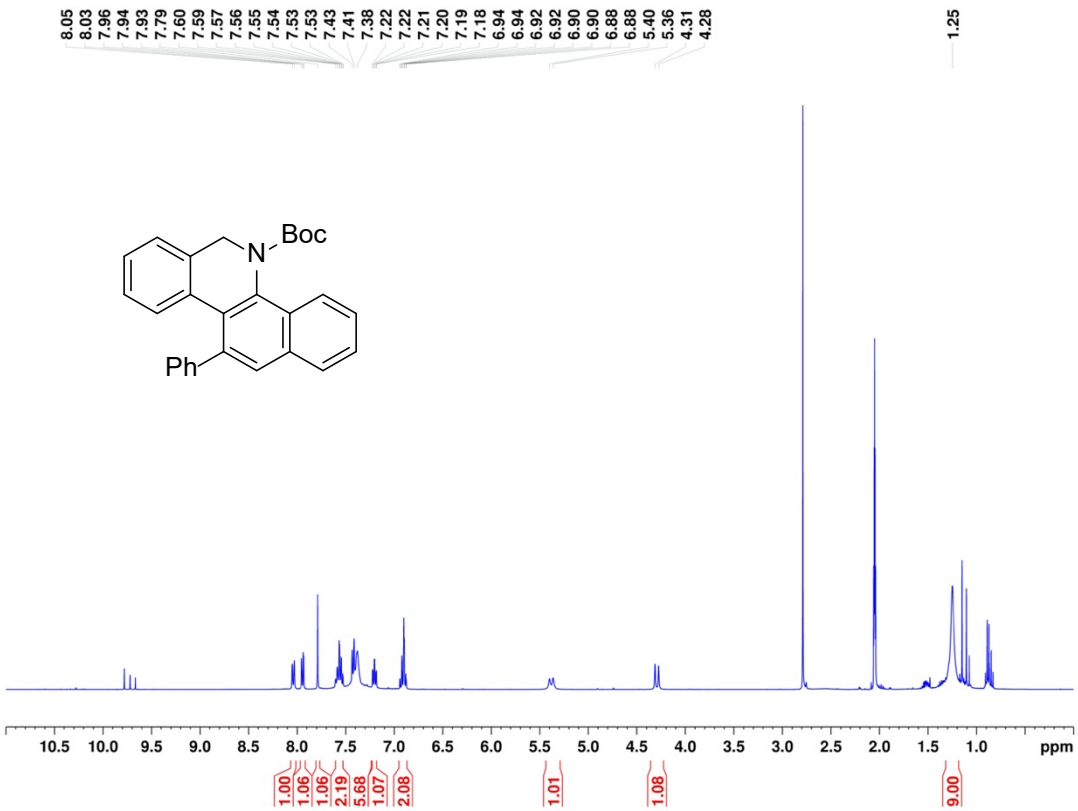
^{13}C NMR spectrum of **5k** in CD_2Cl_2 at 100.7 MHz.



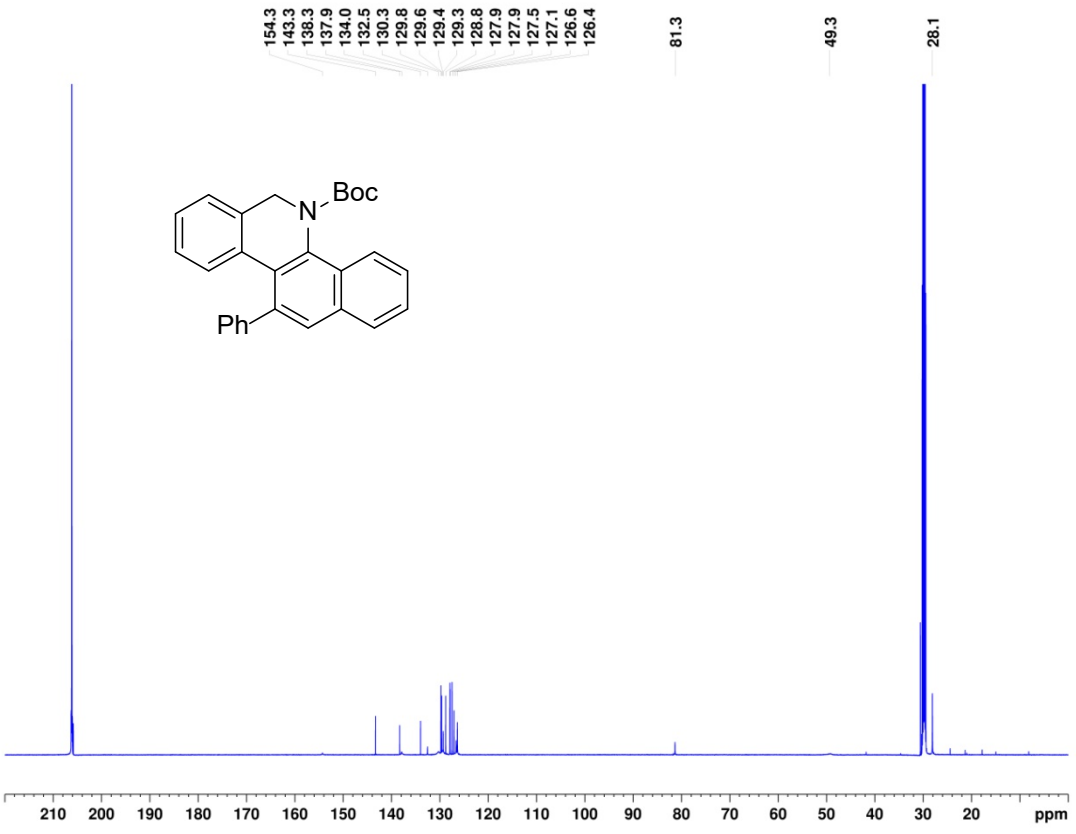
^{1}H NMR spectrum of **5l** in $CDCl_3$ at 400.3 MHz.



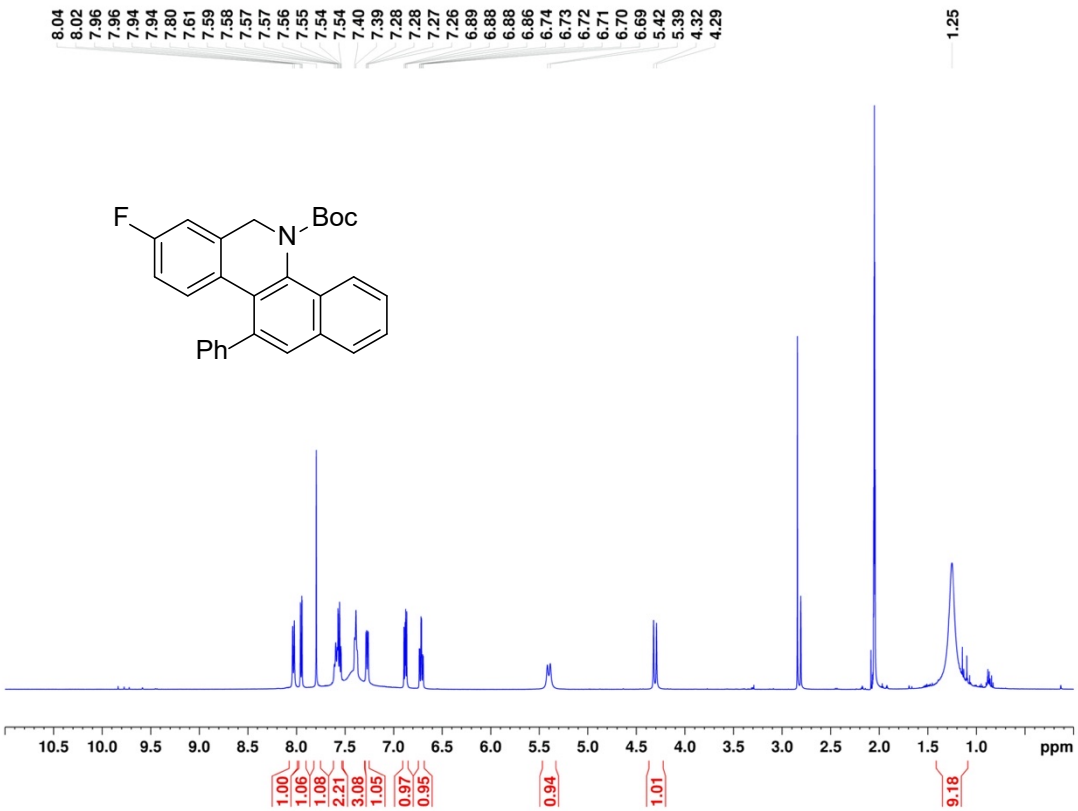
^{13}C NMR spectrum of **5l** in $CDCl_3$ at 100.7 MHz.



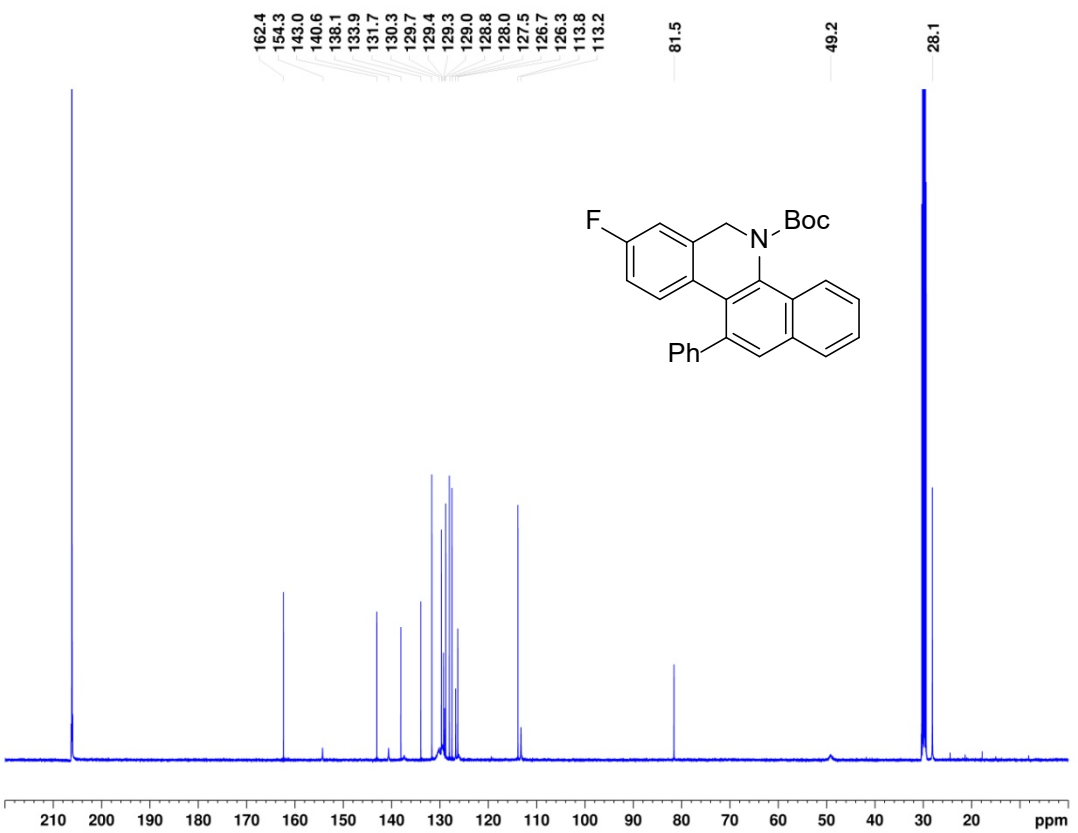
^{1}H NMR spectrum of **6a** in $(CD_3)_2CO$ at 400.3 MHz.



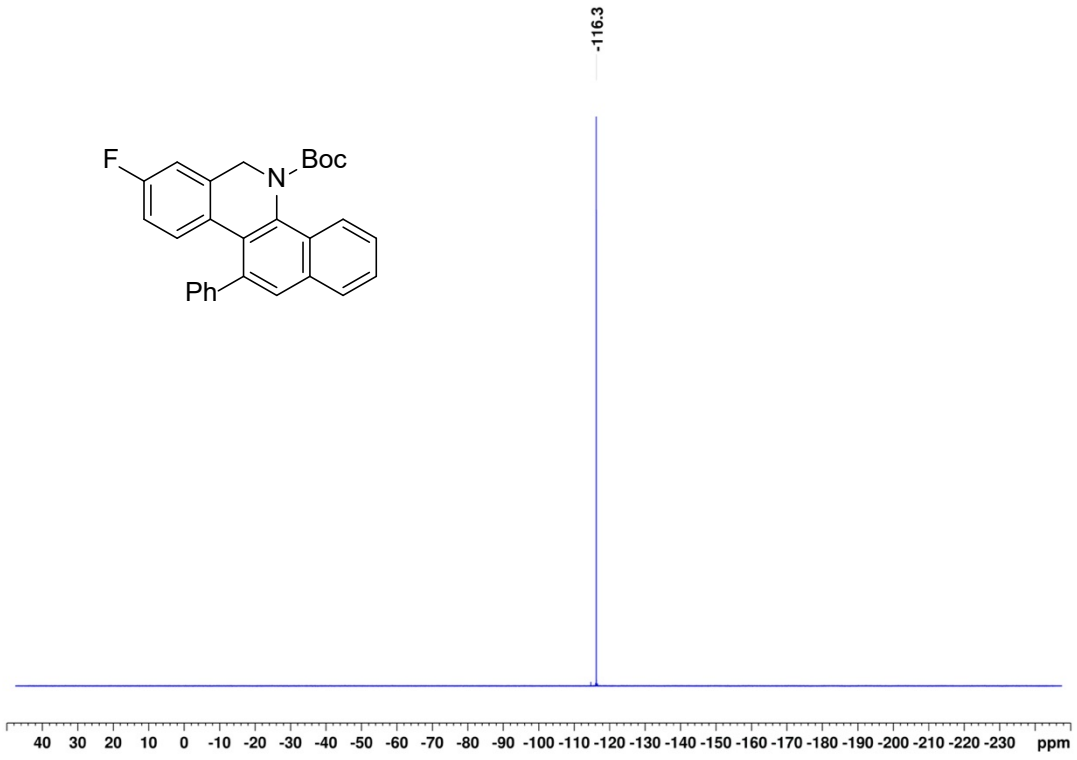
^{13}C NMR spectrum of **6a** in $(CD_3)_2CO$ at 150.9 MHz.



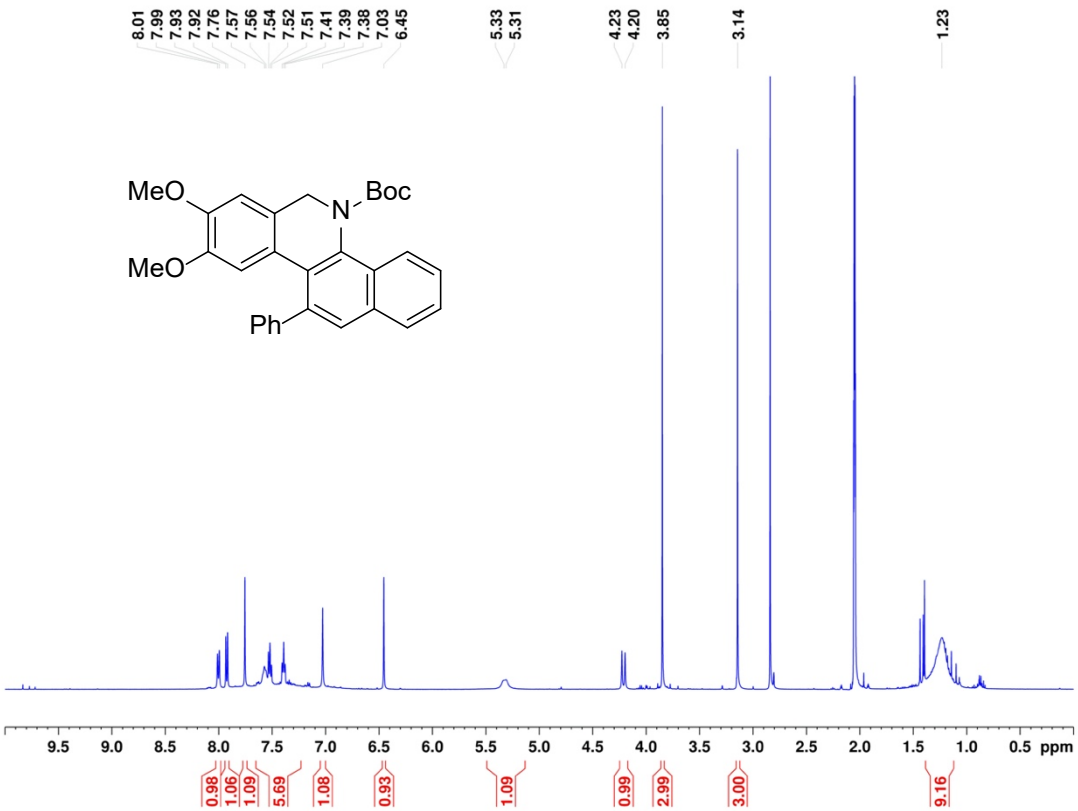
^{1}H NMR spectrum of **6b** in $(CD_3)_2CO$ at 500.2 MHz.



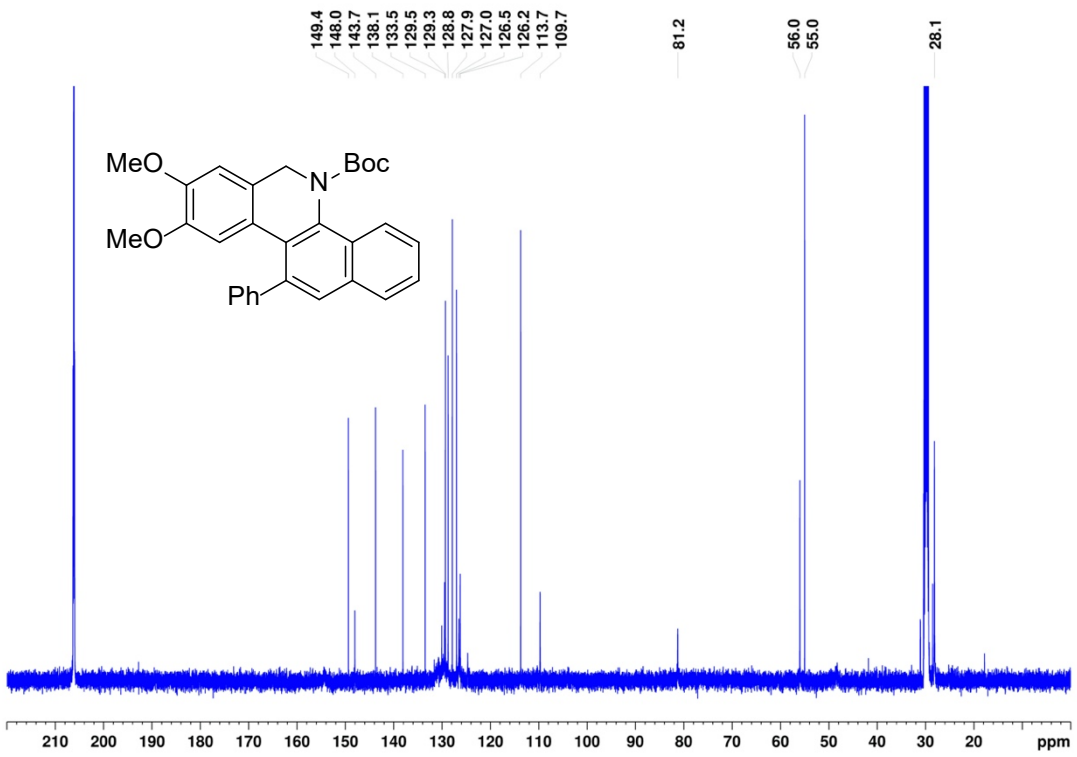
^{13}C NMR spectrum of **6b** in $(CD_3)_2CO$ at 125.8 MHz.



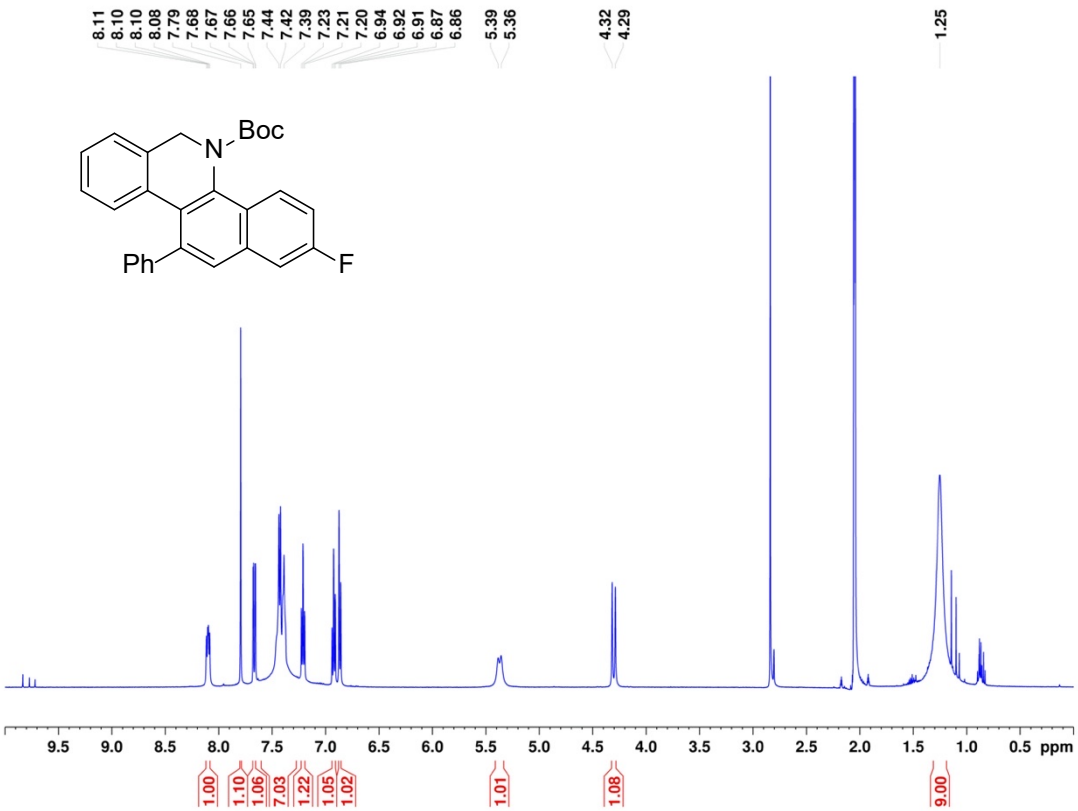
^{19}F NMR spectrum of **6b** in $(CD_3)_2CO$ at 470.7 MHz.



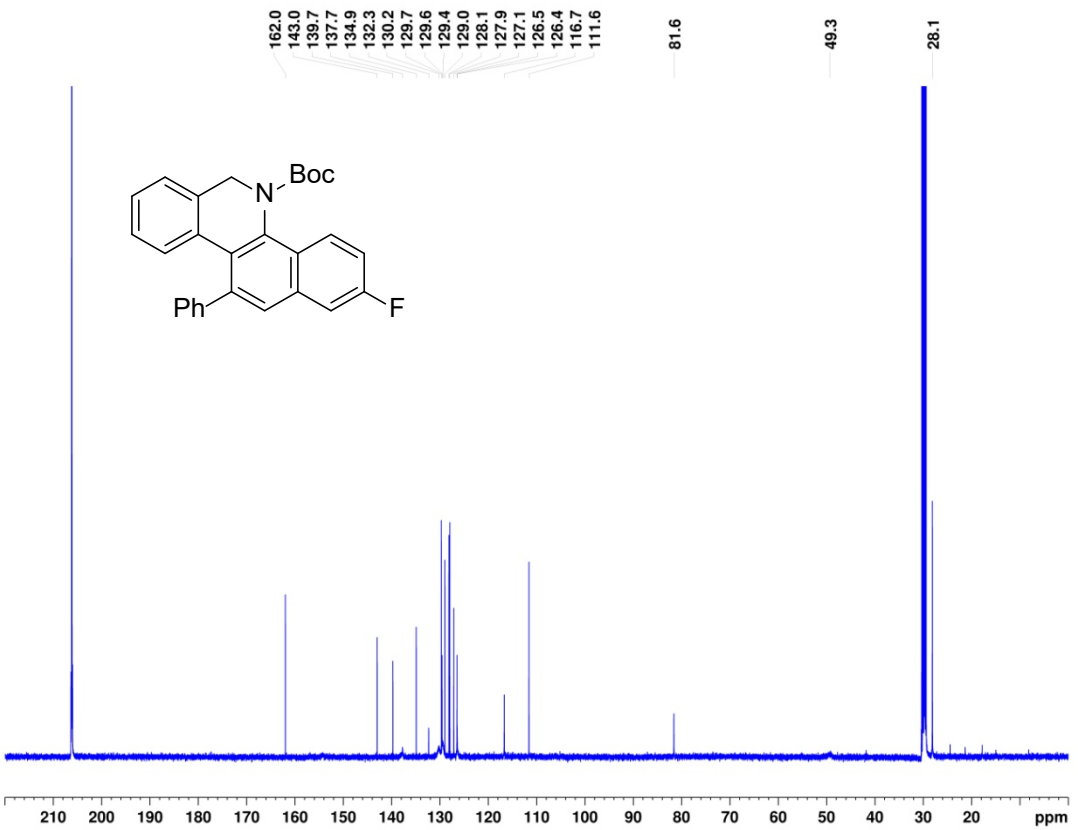
^{1}H NMR spectrum of **6c** in $CDCl_3$ at 500.2 MHz.



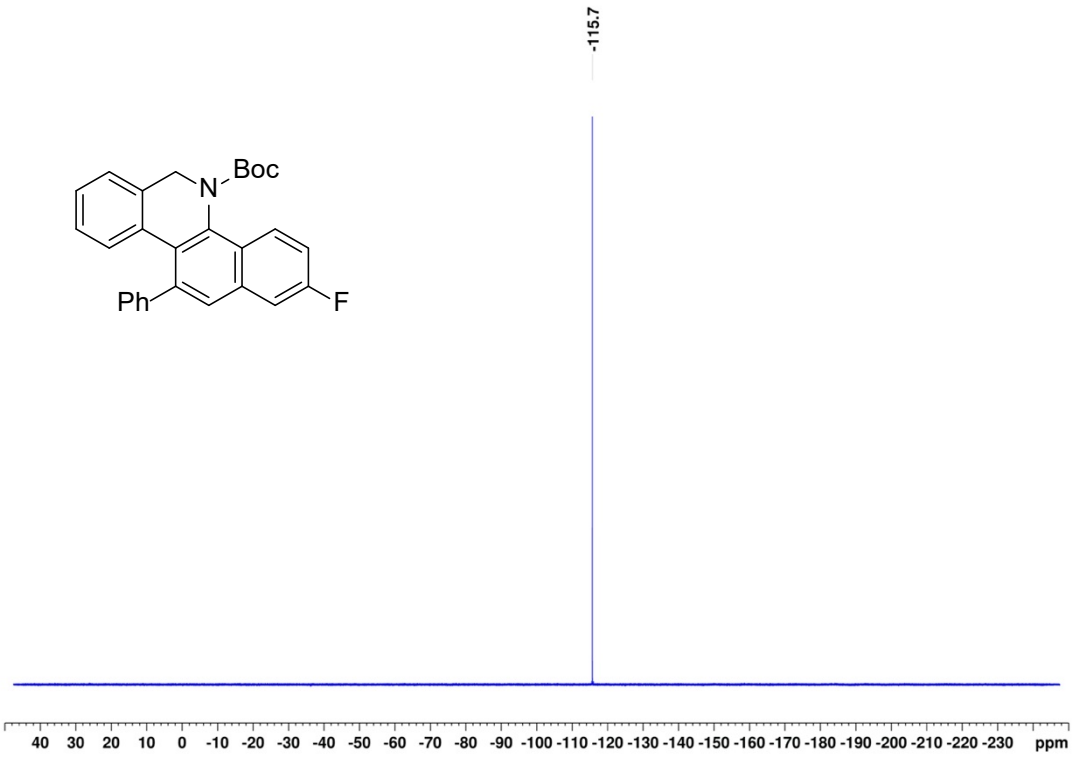
^{13}C NMR spectrum of **6c** in $CDCl_3$ at 125.8 MHz.



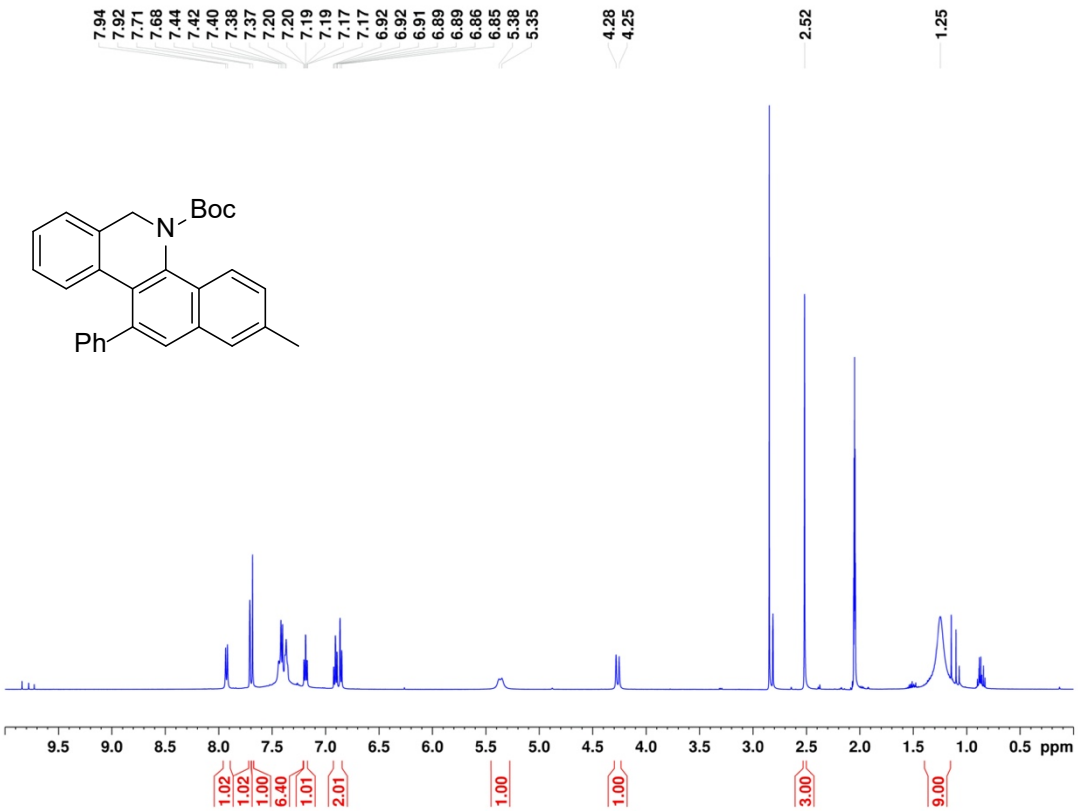
^{1}H NMR spectrum of **6d** in $(CD_3)_2CO$ at 500.2 MHz.



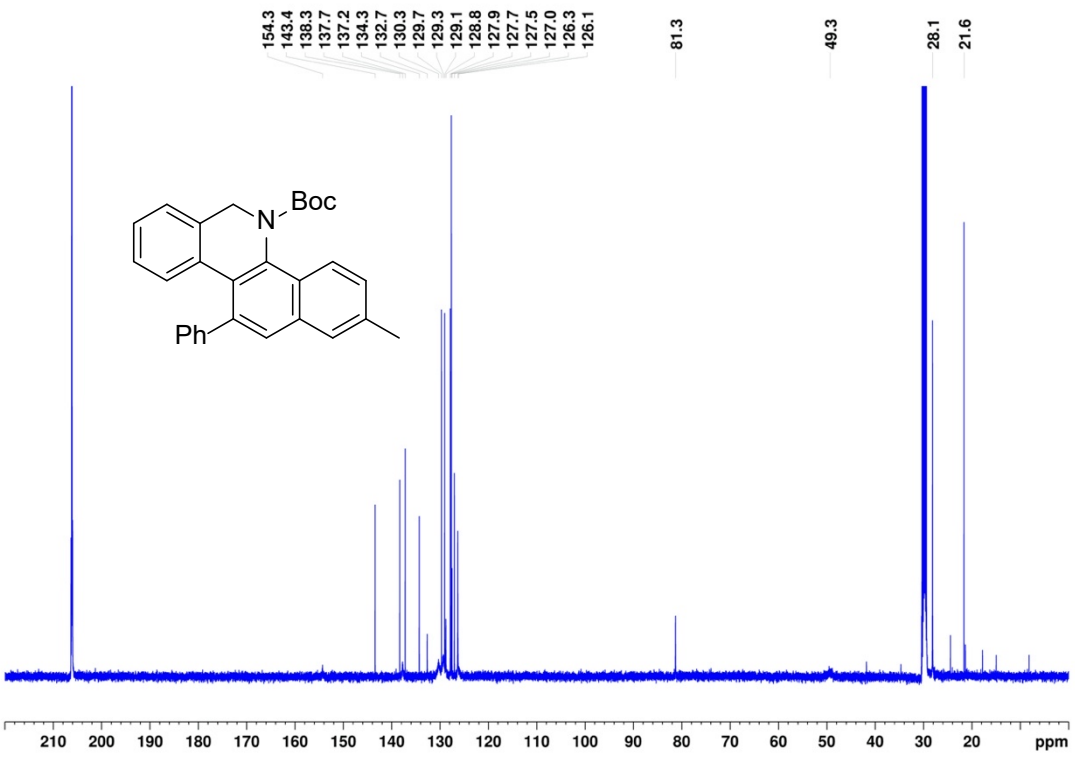
^{13}C NMR spectrum of **6d** in $(CD_3)_2CO$ at 125.8 MHz.



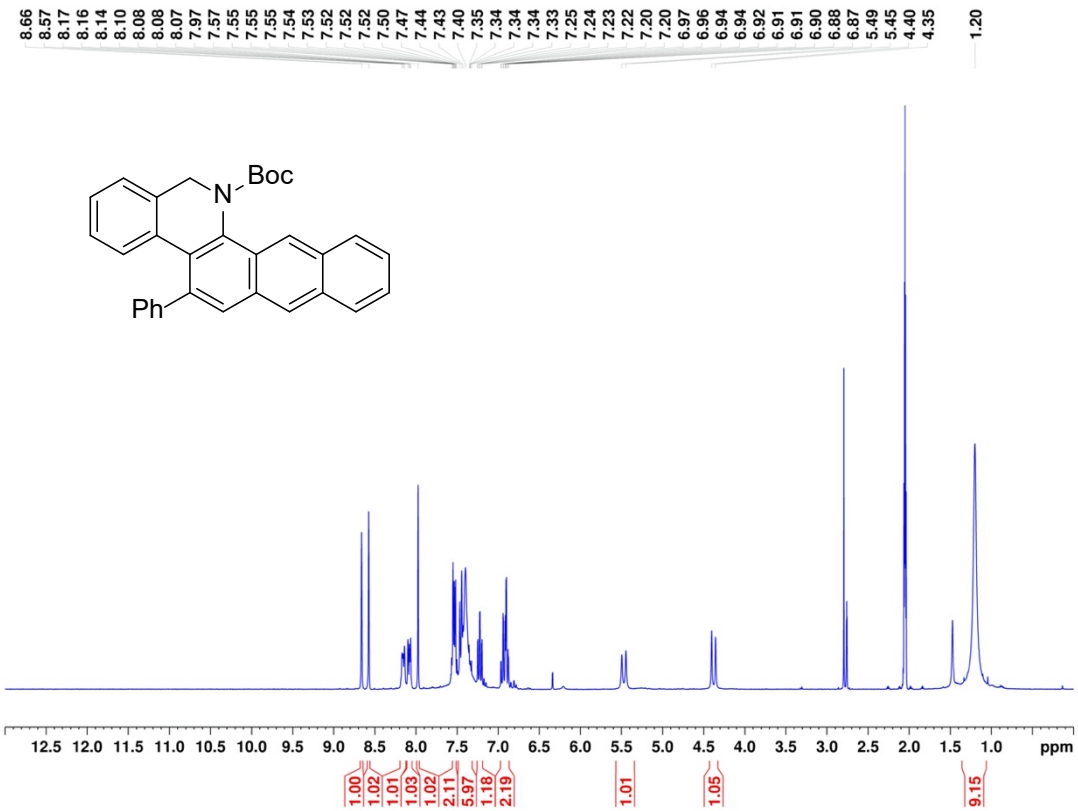
^{19}F NMR spectrum of **6d** in $(CD_3)_2CO$ at 470.7 MHz.



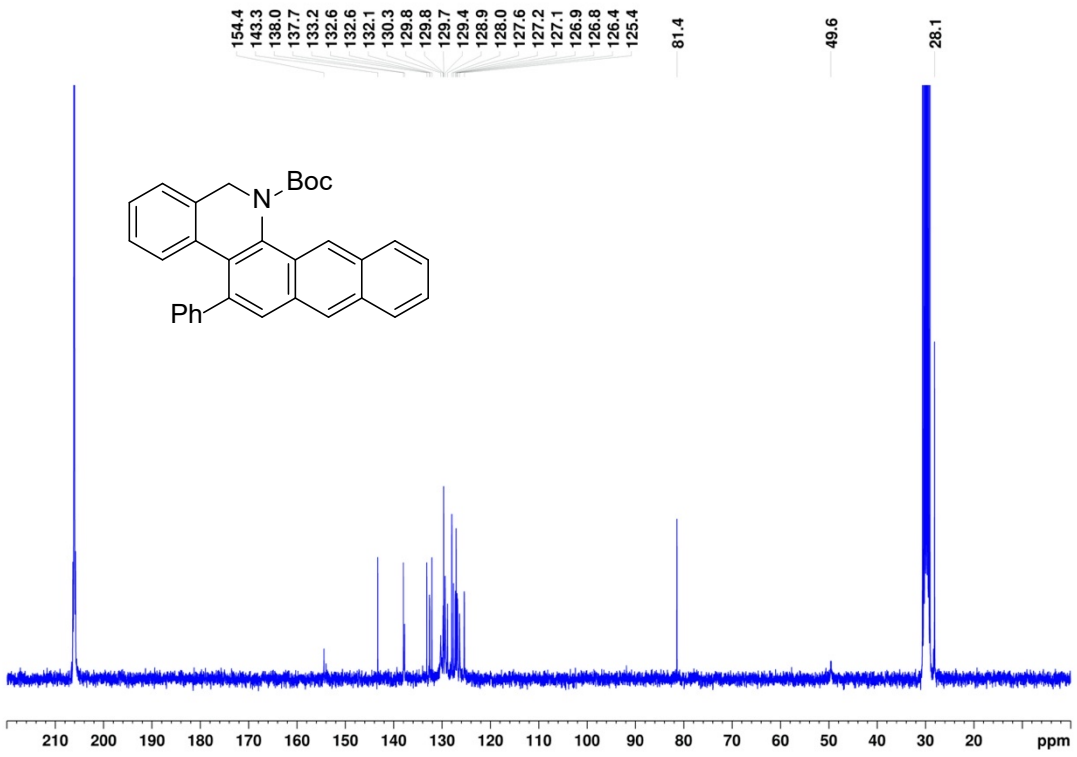
^{1}H NMR spectrum of **6e** in $(CD_3)_2CO$ at 500.2 MHz.



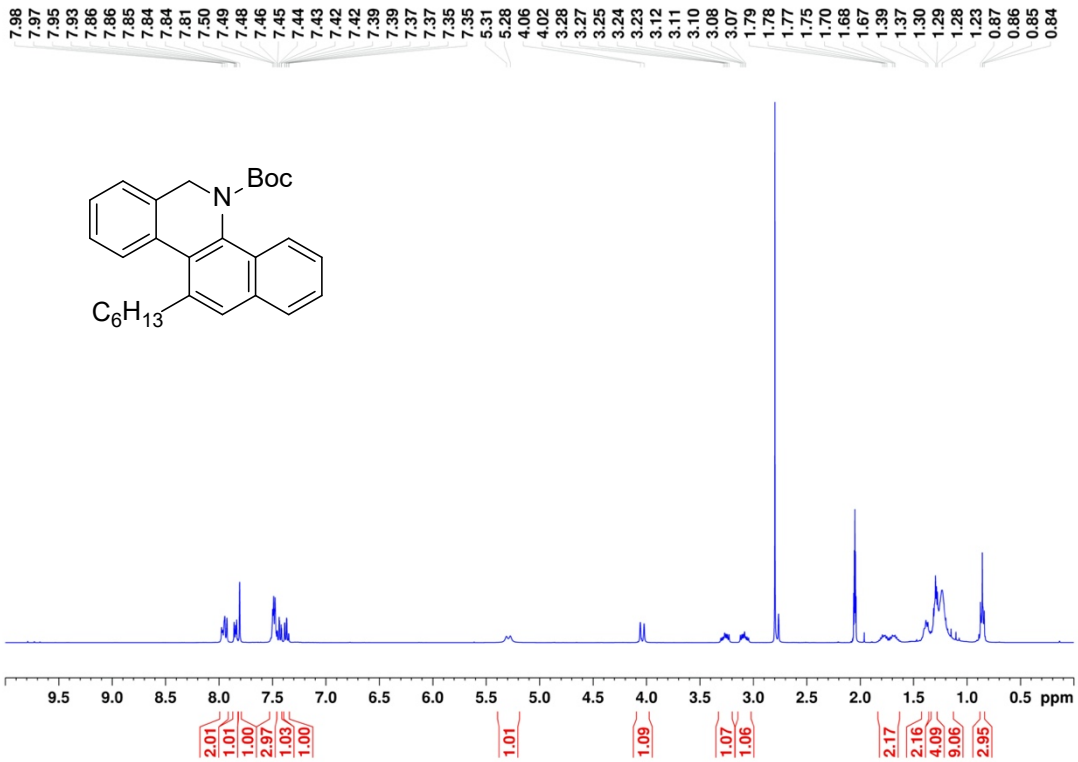
^{13}C NMR spectrum of **6e** in $(CD_3)_2CO$ at 125.8 MHz.



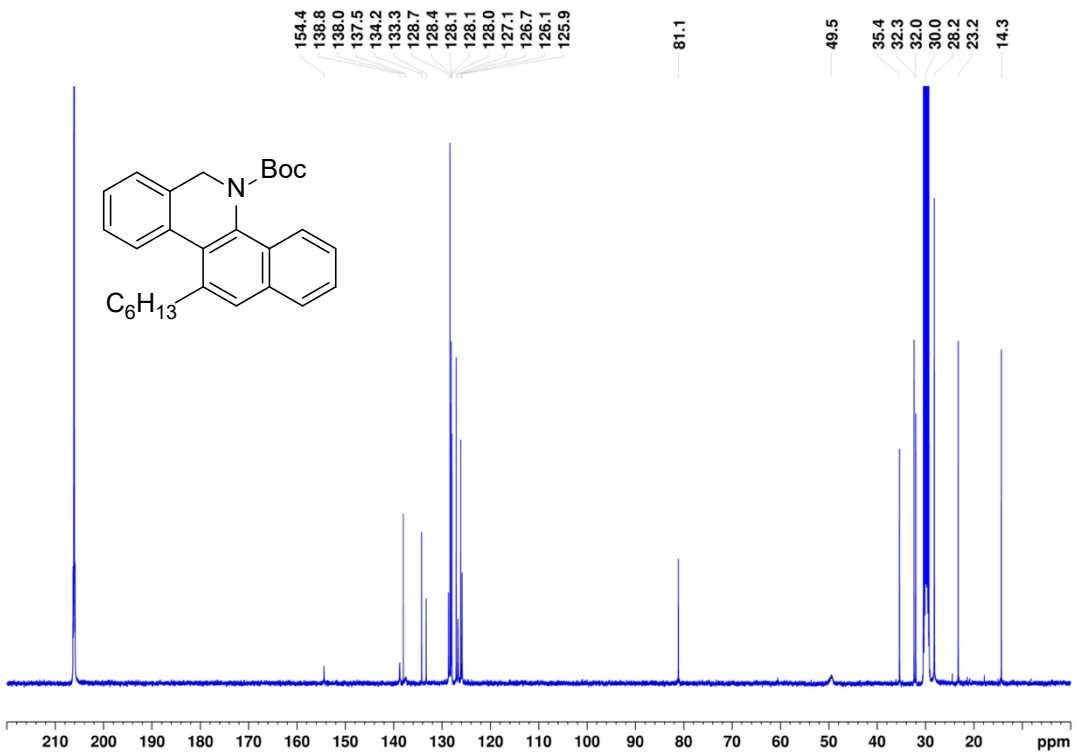
^{1}H NMR spectrum of **6f** in $(CD_3)_2CO$ at 300.2 MHz.



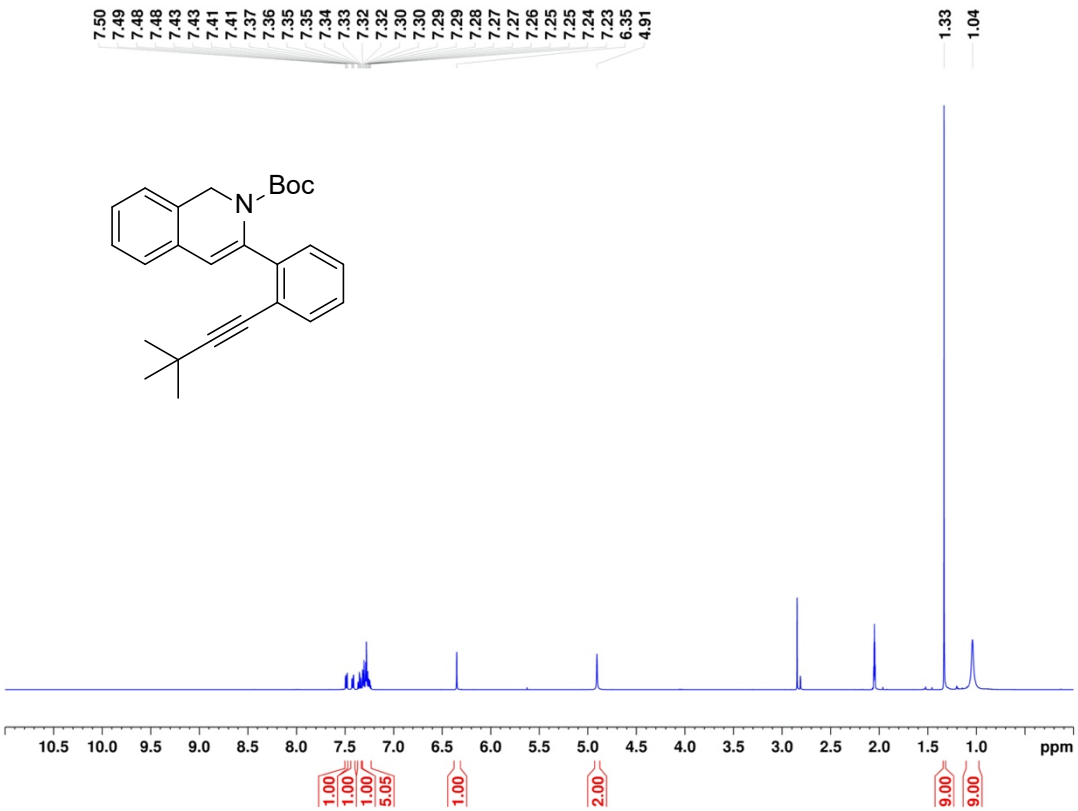
^{13}C NMR spectrum of **6f** in $(CD_3)_2CO$ at 75.5 MHz.



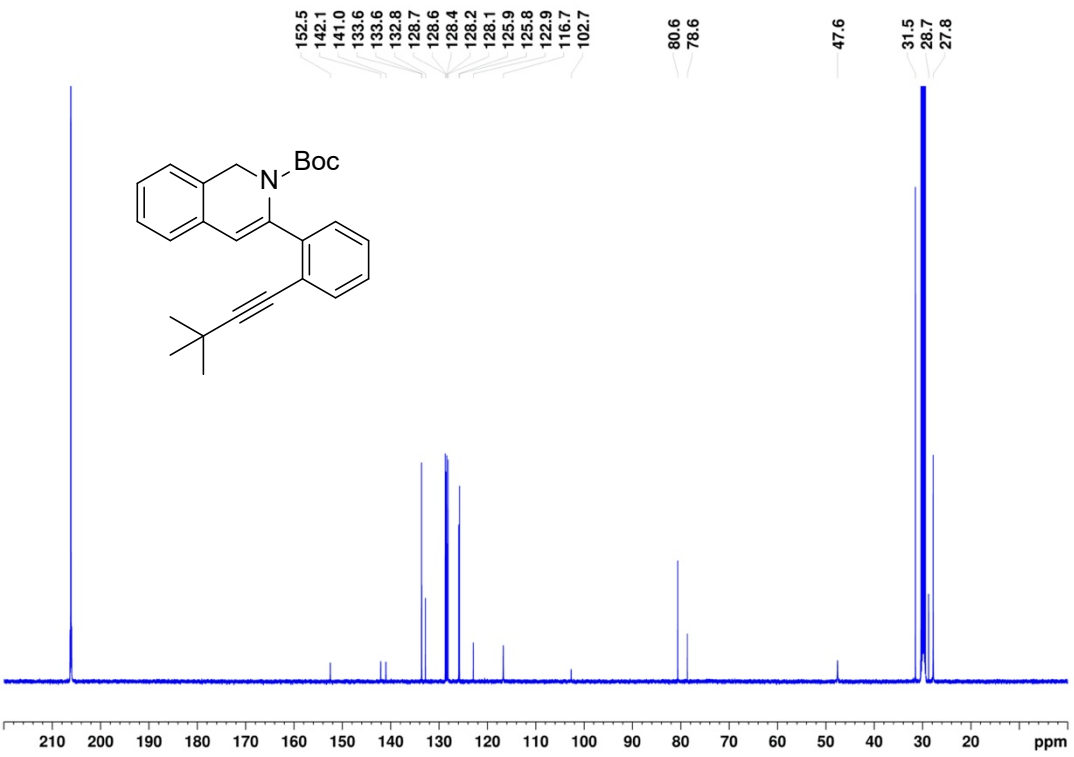
^{1}H NMR spectrum of **6g** in $(CD_3)_2CO$ at 400.3 MHz.



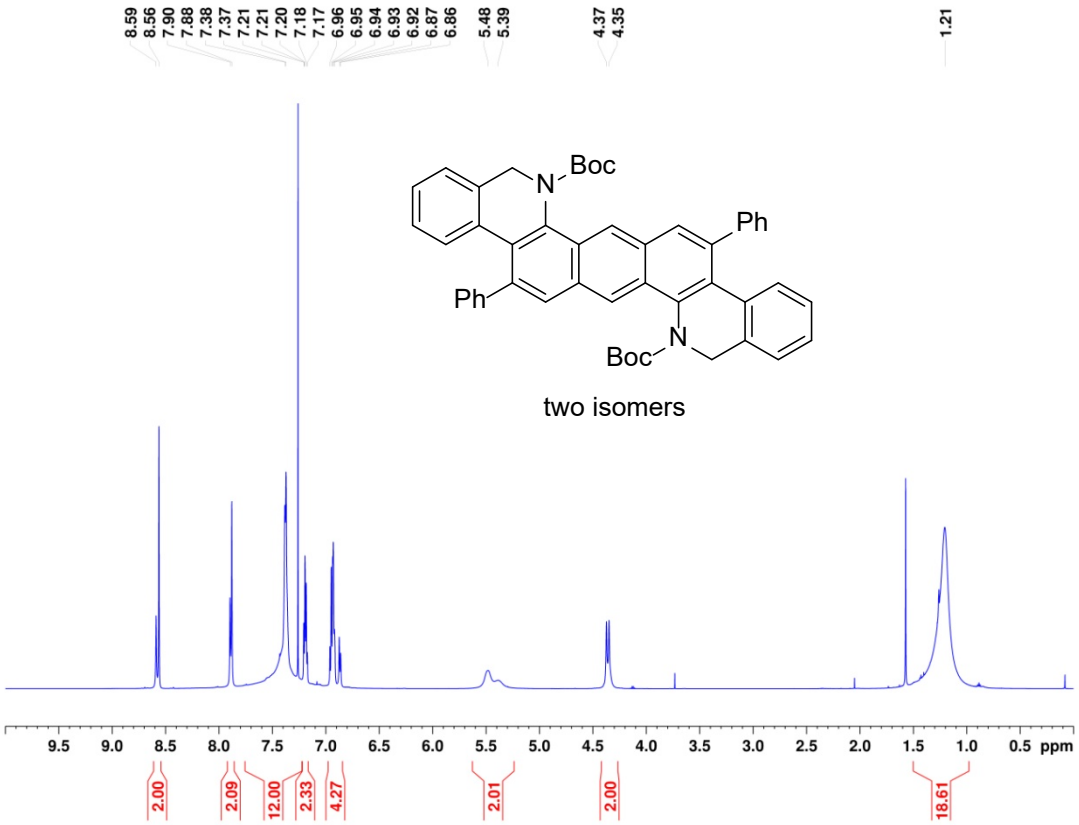
^{13}C NMR spectrum of **6g** in $(CD_3)_2CO$ at 100.7 MHz.



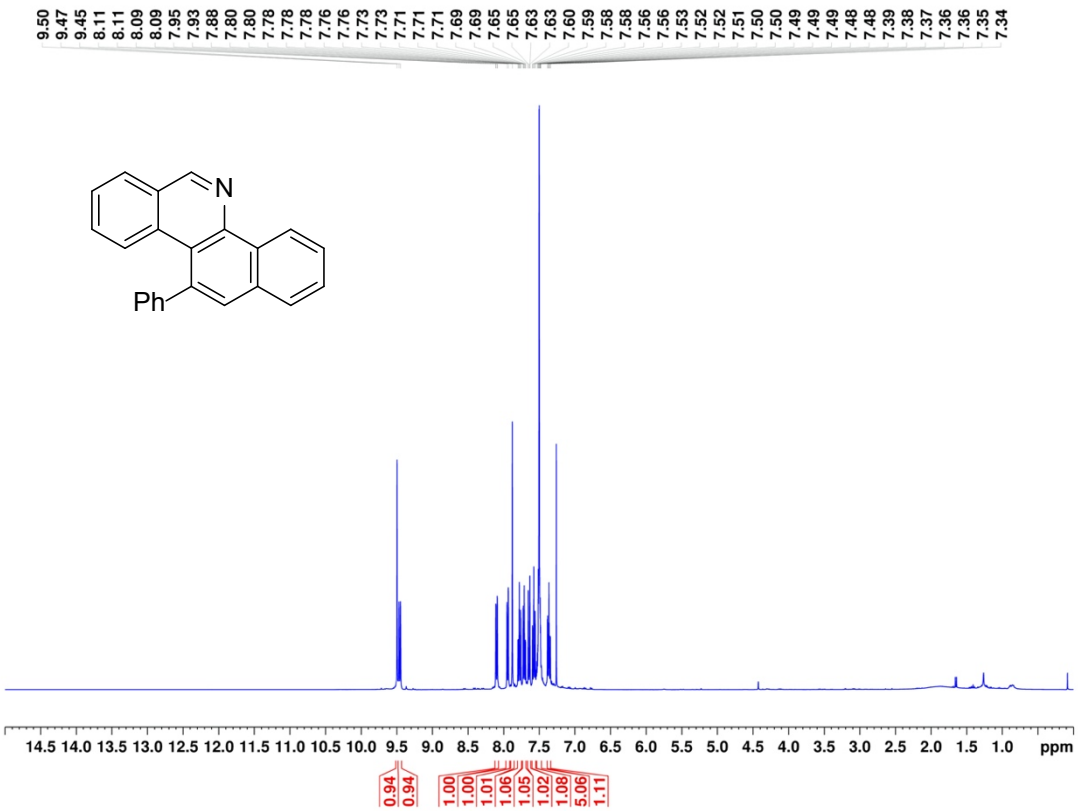
^{1}H NMR spectrum of **7j** in $(CD_3)_2CO$ at 500.2 MHz.



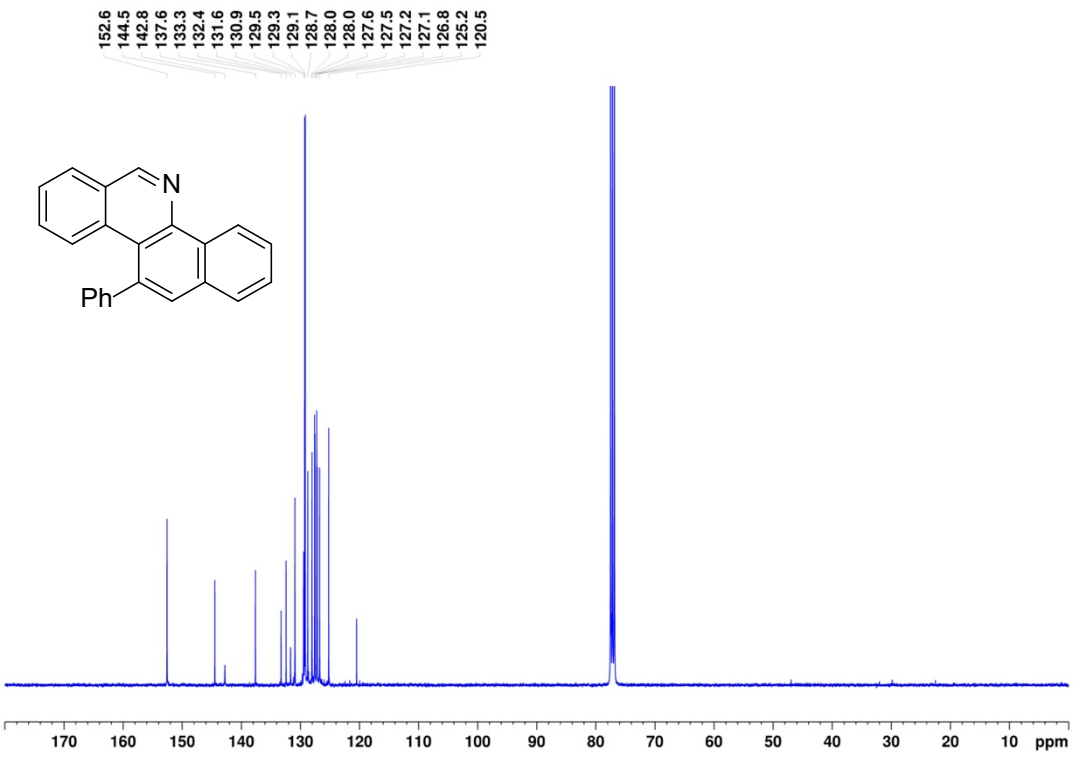
^{13}C NMR spectrum of **7j** in $(CD_3)_2CO$ at 125.8 MHz.



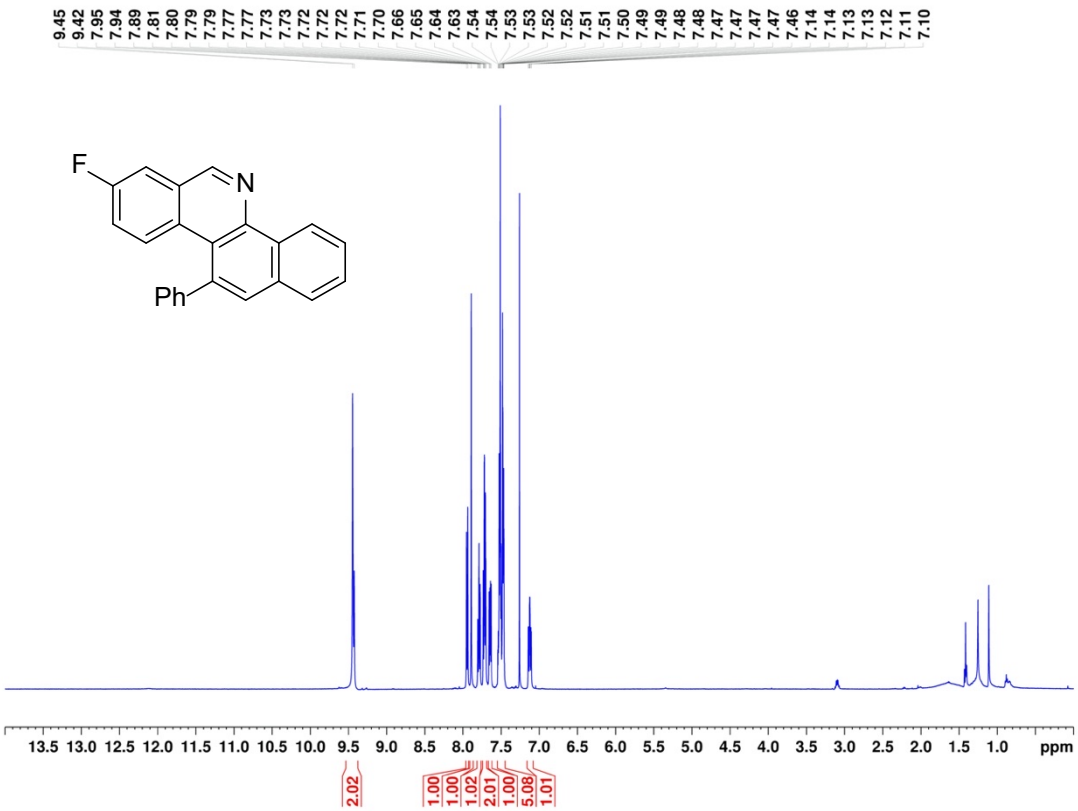
^{1}H NMR spectrum of **6k** in $CDCl_3$ at 600.2 MHz.



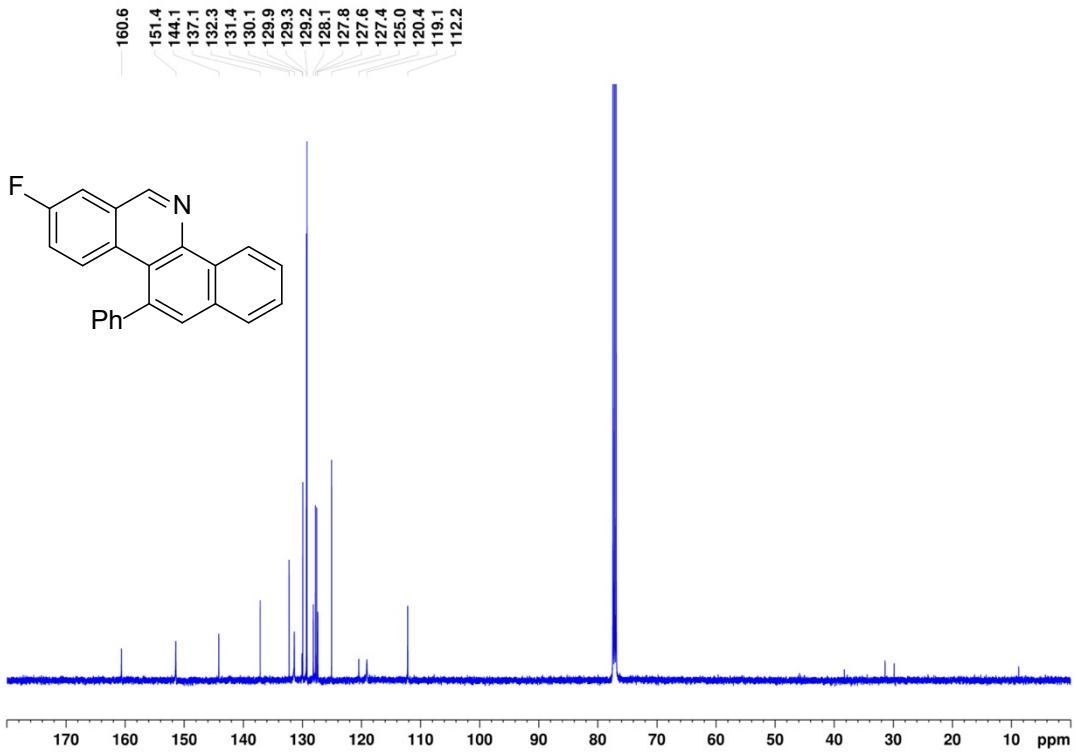
^{1}H NMR spectrum of **13a** in $CDCl_3$ at 400.3 MHz.



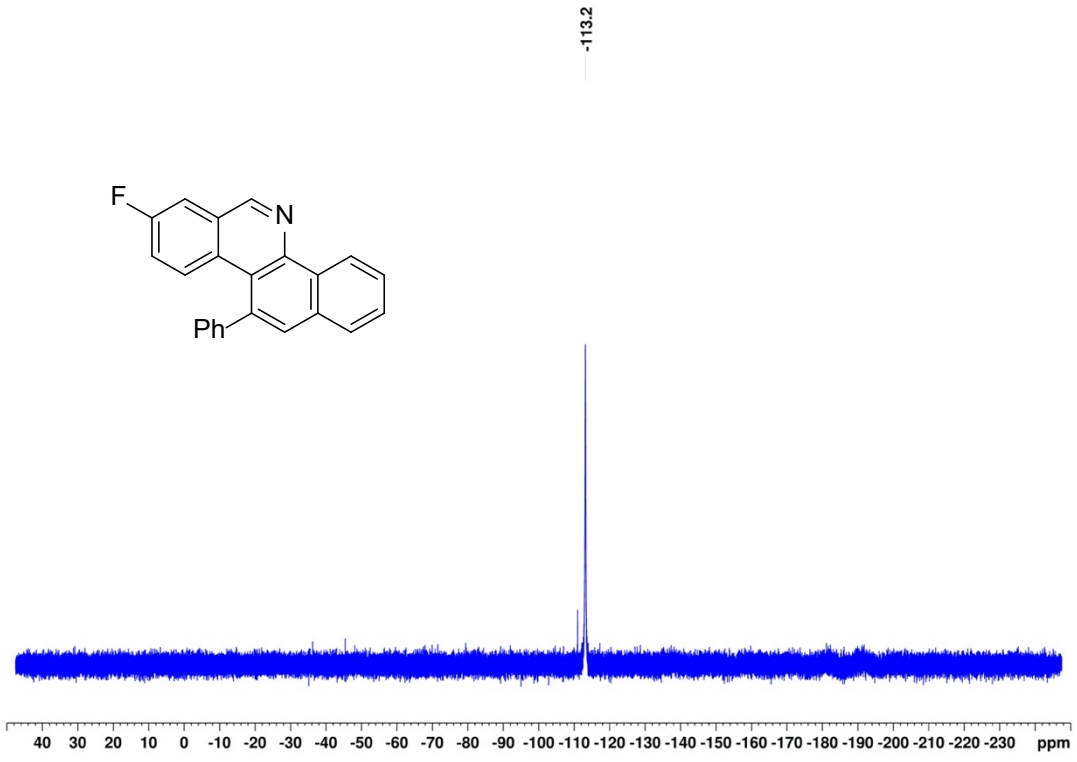
^{13}C NMR spectrum of **13a** in $CDCl_3$ at 100.7 MHz.



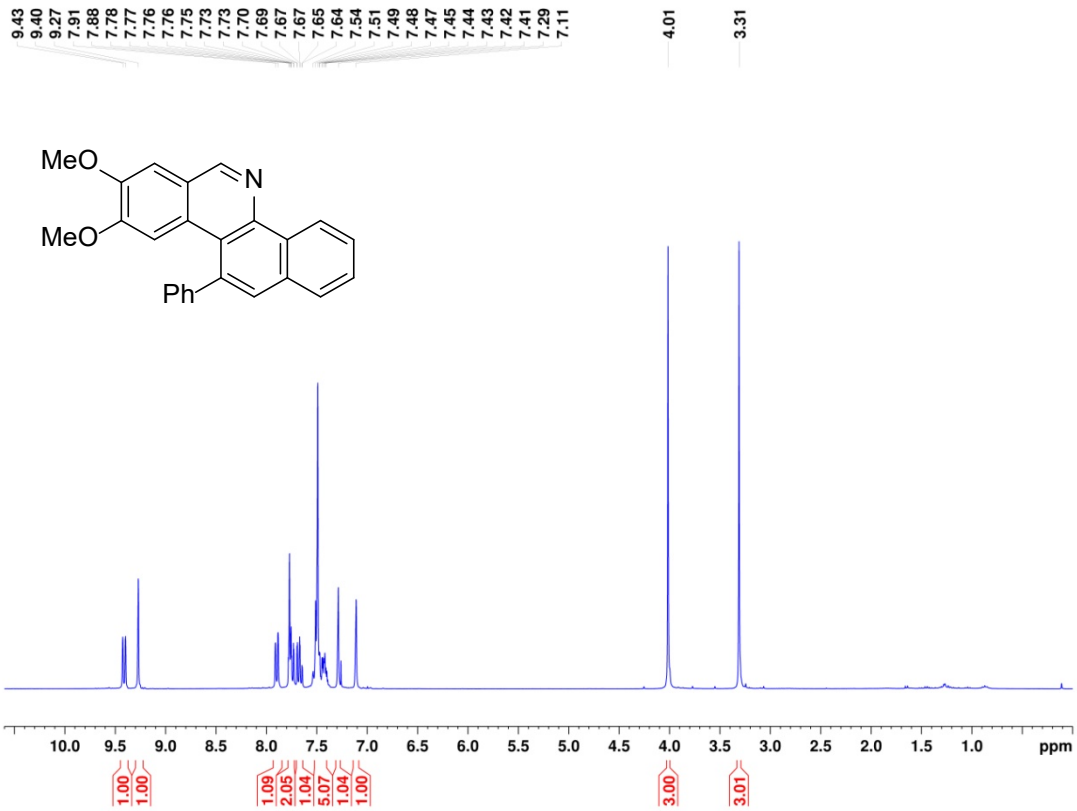
^{1}H NMR spectrum of **13b** in $CDCl_3$ at 500.2 MHz.



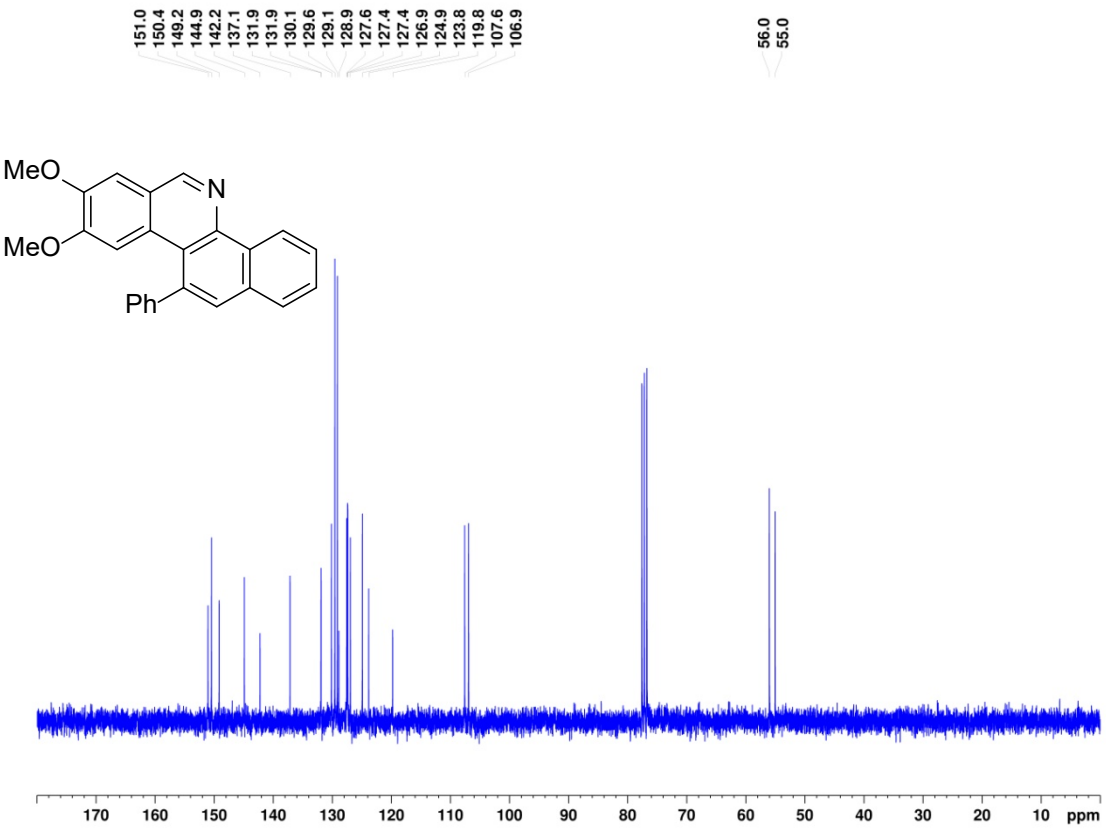
^{13}C NMR spectrum of **13b** in $CDCl_3$ at 125.8 MHz.



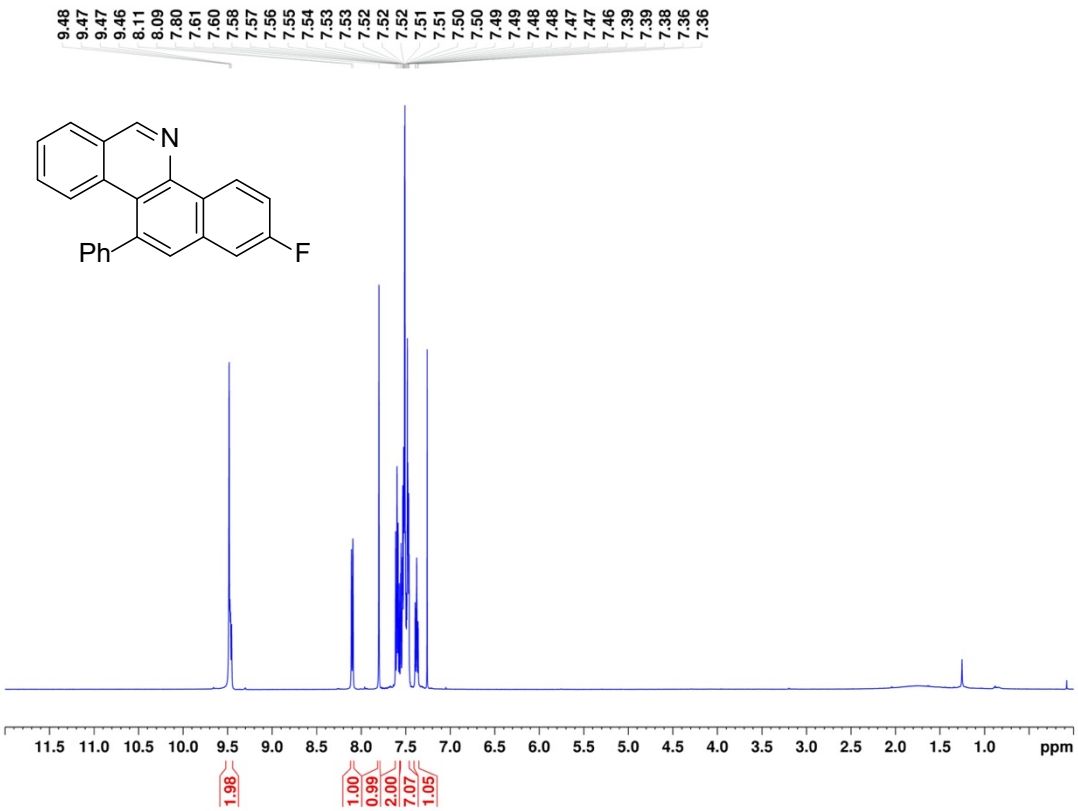
^{19}F NMR spectrum of **13b** in $CDCl_3$ at 470.7 MHz.



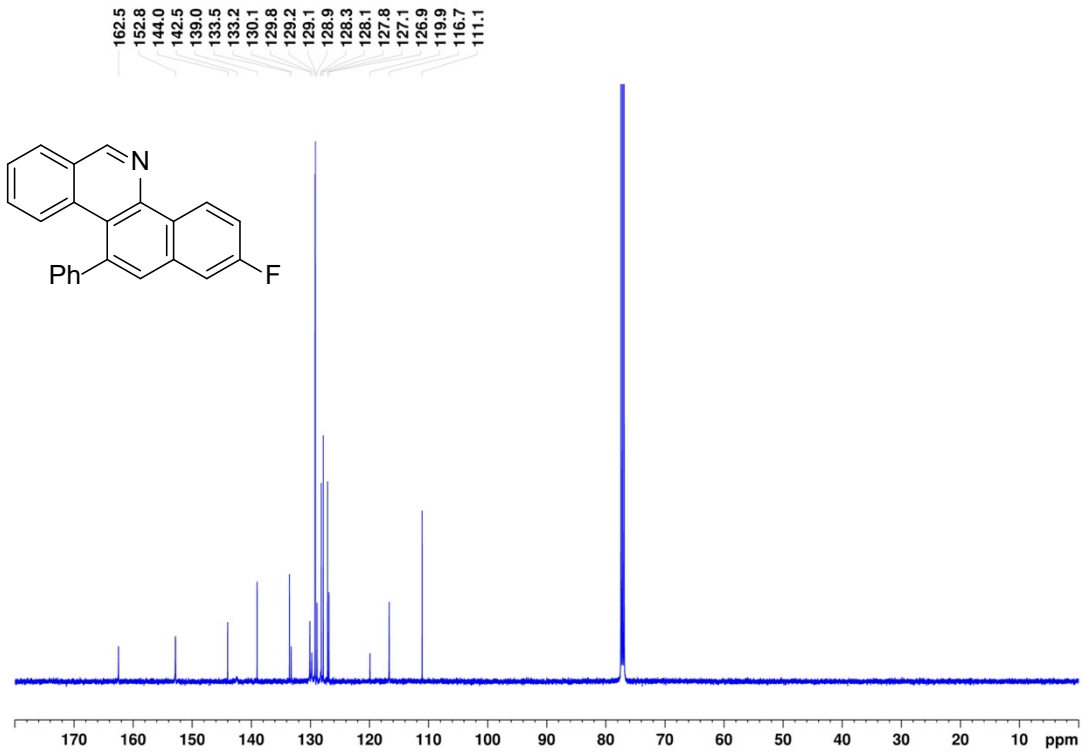
^{1}H NMR spectrum of **13c** in $CDCl_3$ at 300.5 MHz.



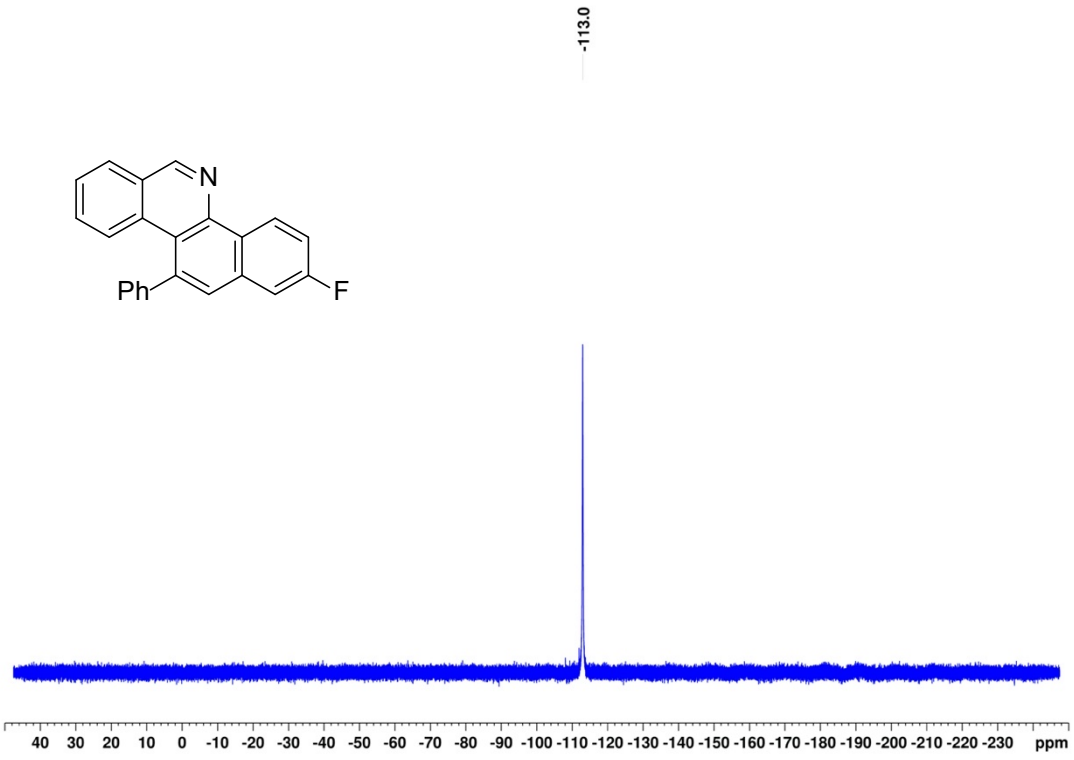
^{13}C NMR spectrum of **13c** in $CDCl_3$ at 75.6 MHz.



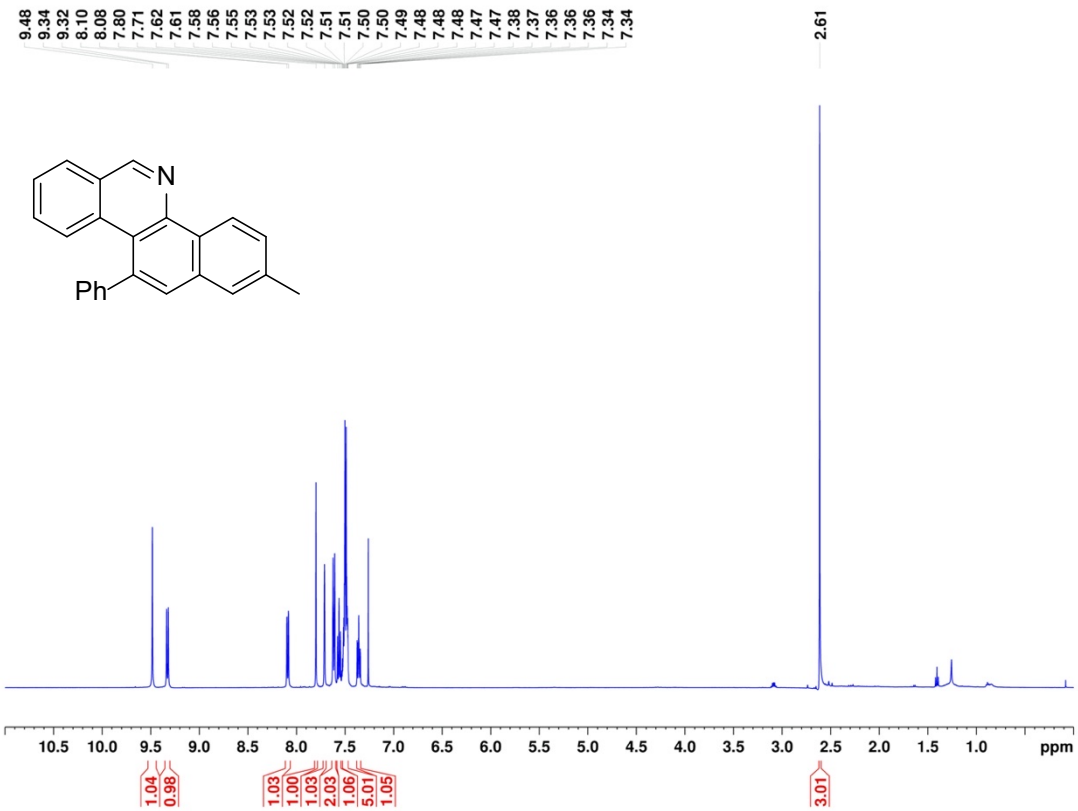
^{1}H NMR spectrum of **13d** in $CDCl_3$ at 500.2 MHz.



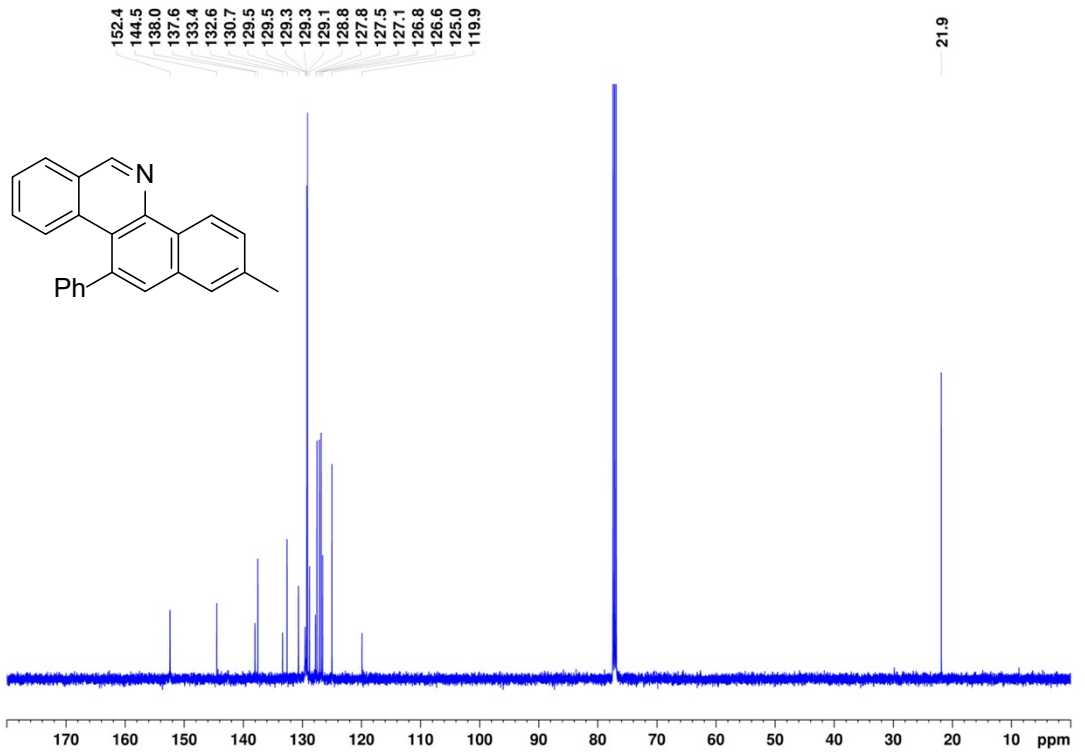
^{13}C NMR spectrum of **13d** in $CDCl_3$ at 125.8 MHz.



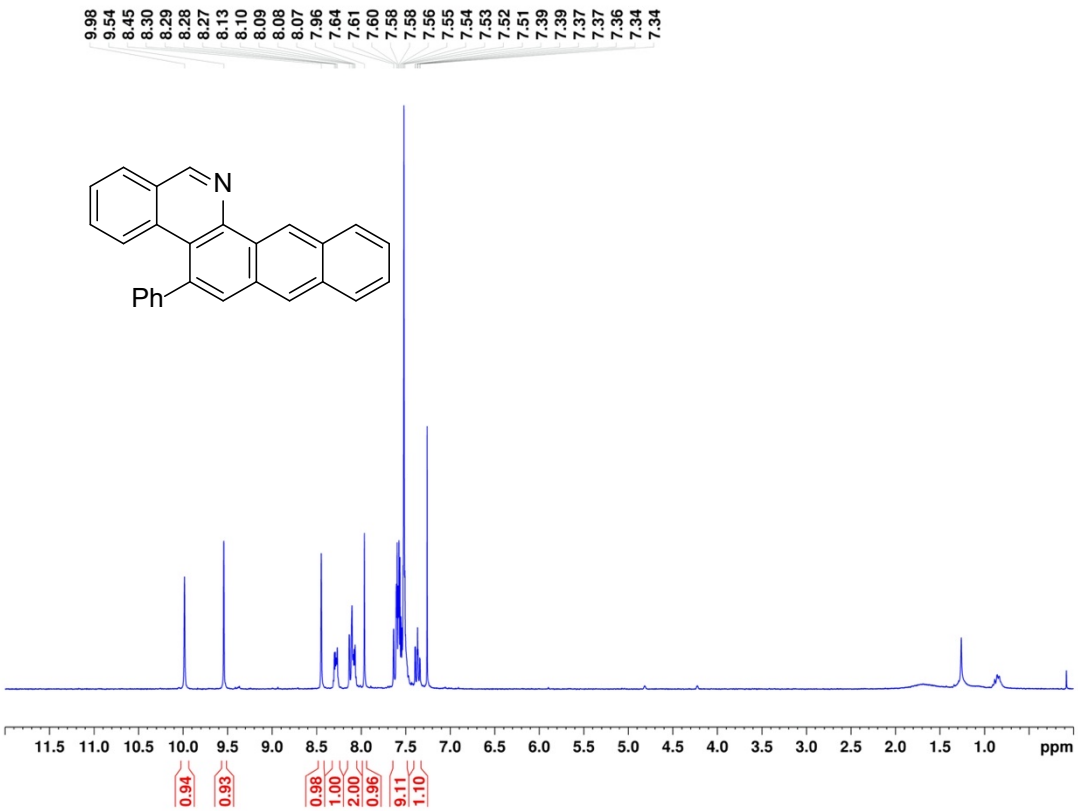
^{19}F NMR spectrum of **13d** in $CDCl_3$ at 470.7 MHz.



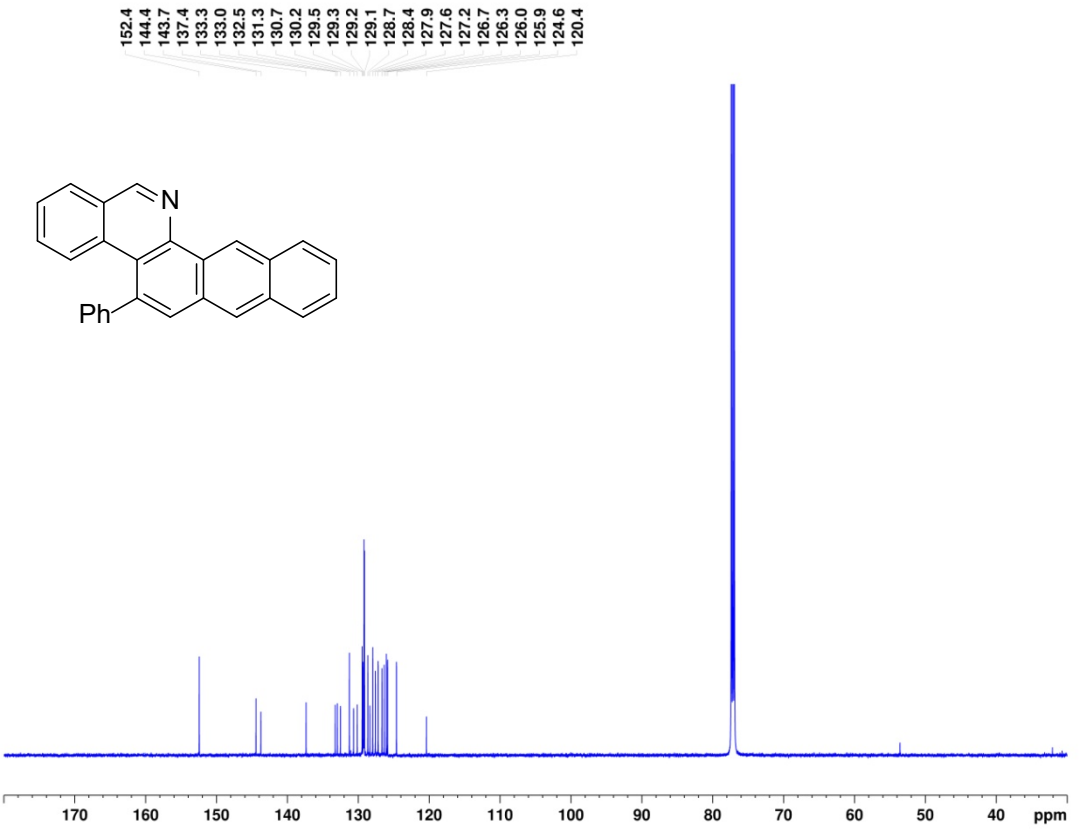
^{1}H NMR spectrum of **13e** in $CDCl_3$ at 500.2 MHz.



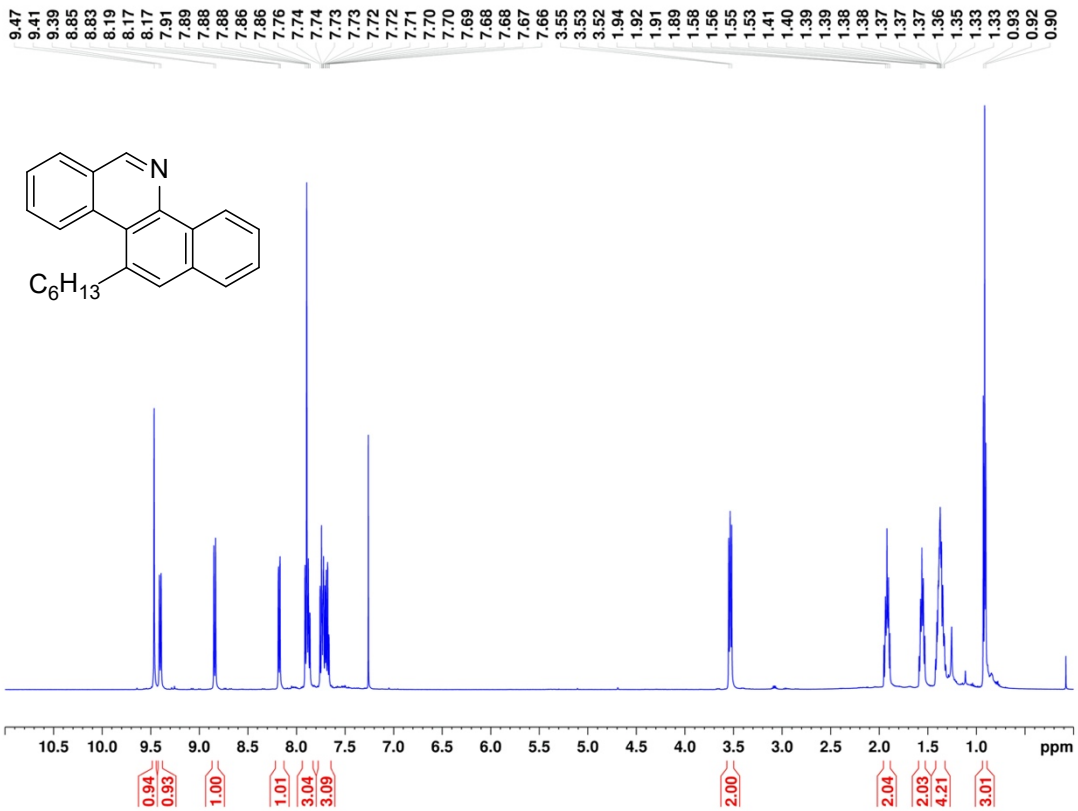
^{13}C NMR spectrum of **13e** in $CDCl_3$ at 125.8 MHz.



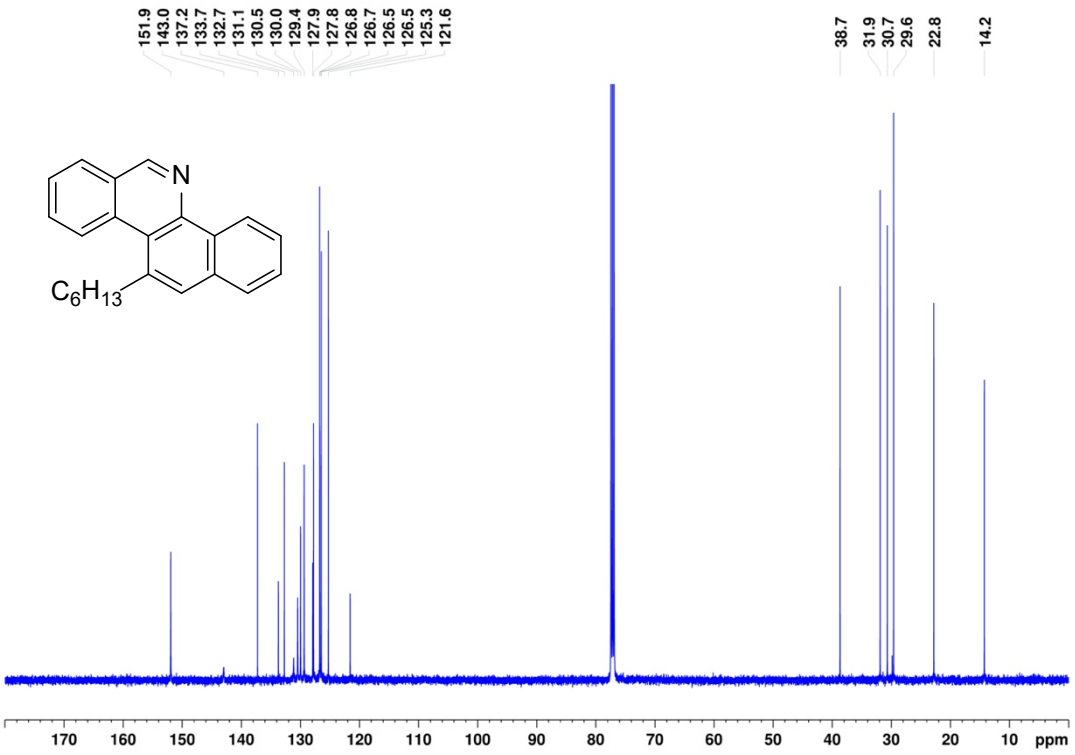
^{1}H NMR spectrum of **13f** in $CDCl_3$ at 300.5 MHz.



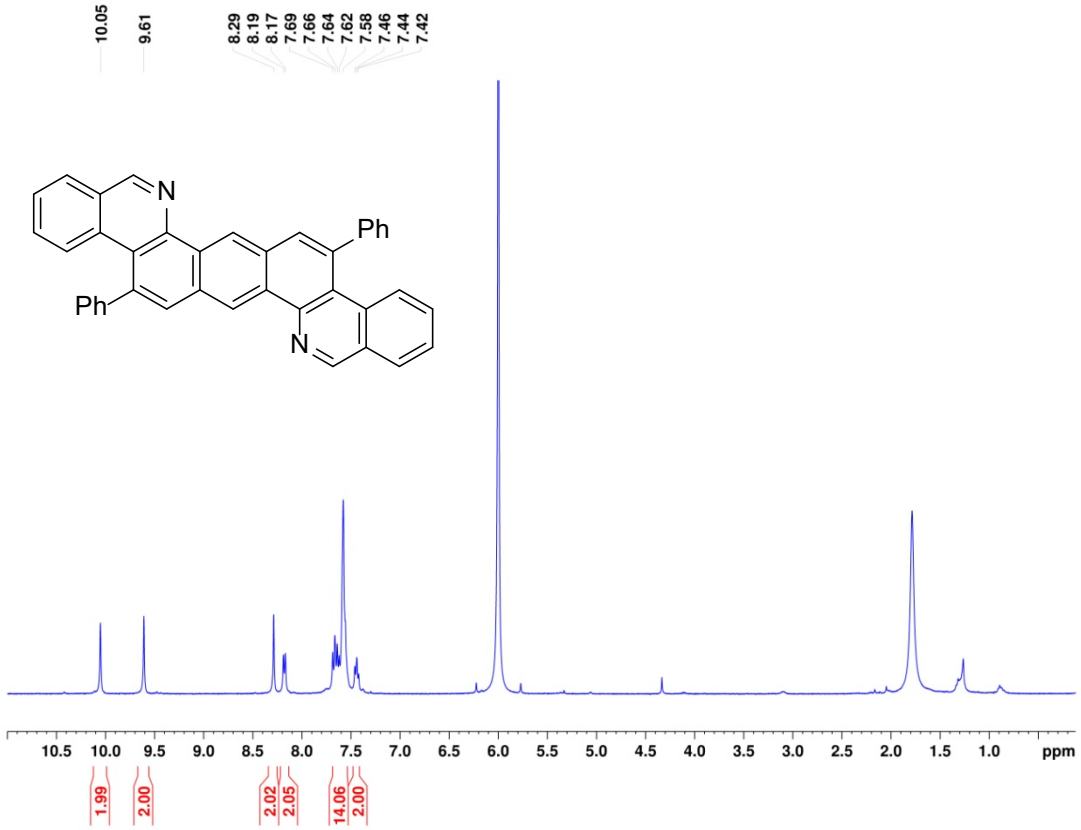
^{13}C NMR spectrum of **13f** in $(CD_3)_2CO$ at 150.9 MHz.



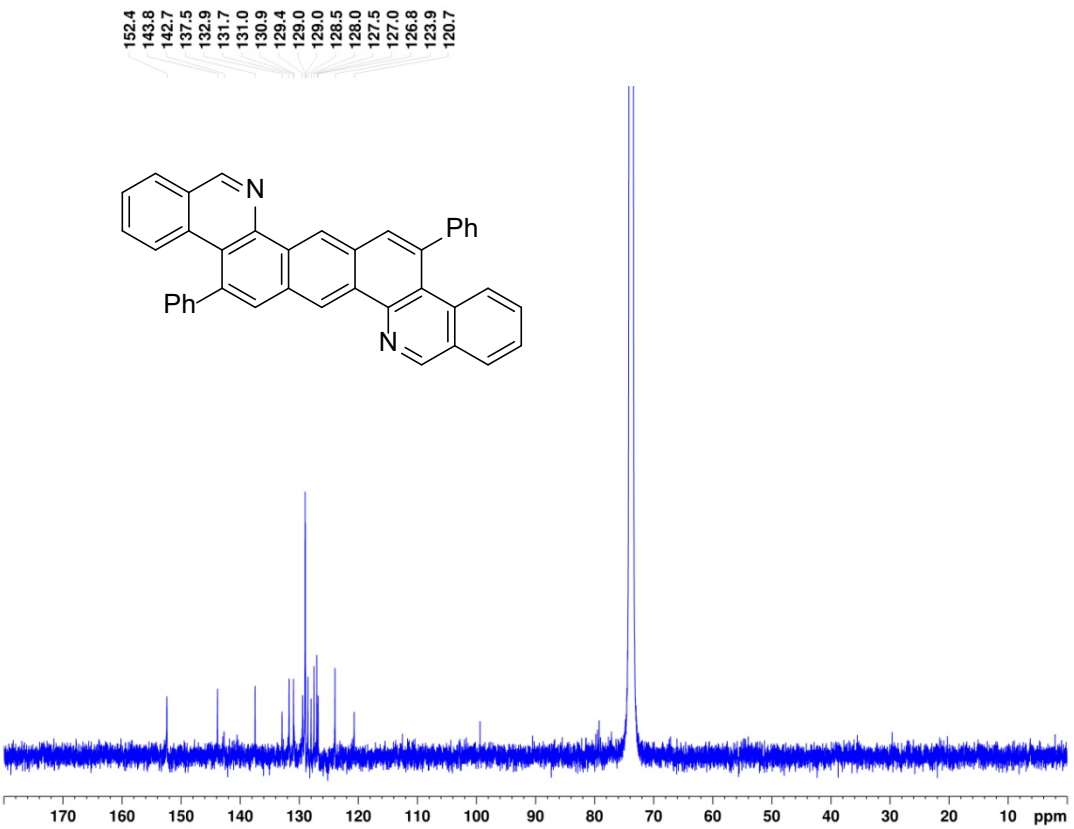
^{1}H NMR spectrum of **13g** in $CDCl_3$ at 500.2 MHz.



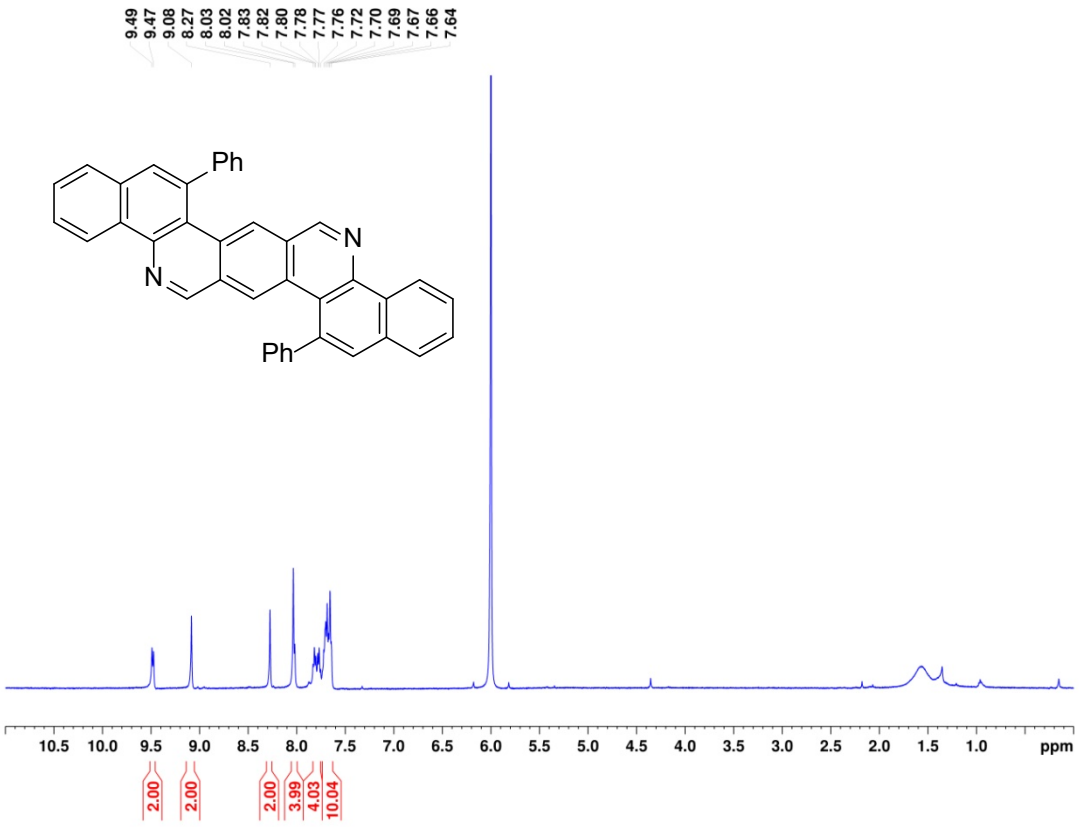
^{13}C NMR spectrum of **13g** in $CDCl_3$ at 125.8 MHz.



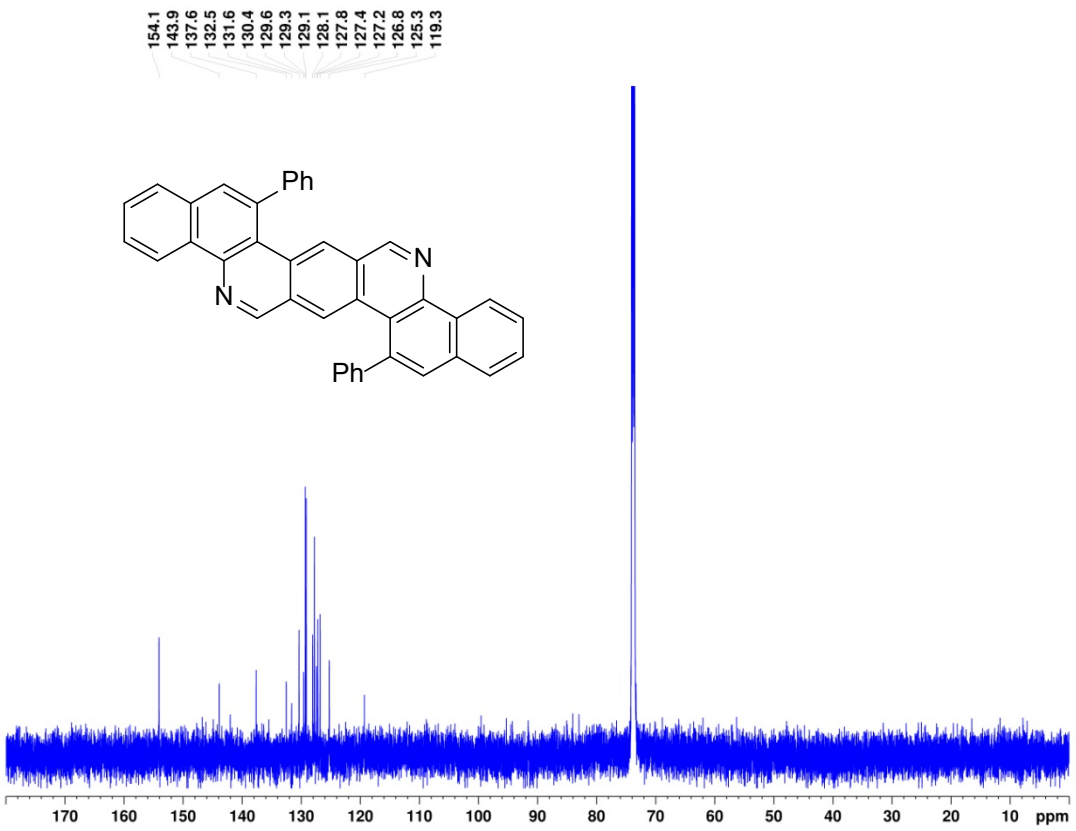
^{1}H NMR spectrum of **13k** in d_2-TCE at 400.3 MHz.



^{13}C NMR spectrum of **13k** in d_2-TCE at 100.7 MHz.



^{1}H NMR spectrum of **13l** in d_2-TCE at 500.2 MHz (373 K).



^{13}C NMR spectrum of **13l** in d_2-TCE at 125.8 MHz (373 K).

6. Absorption and Emission Spectra

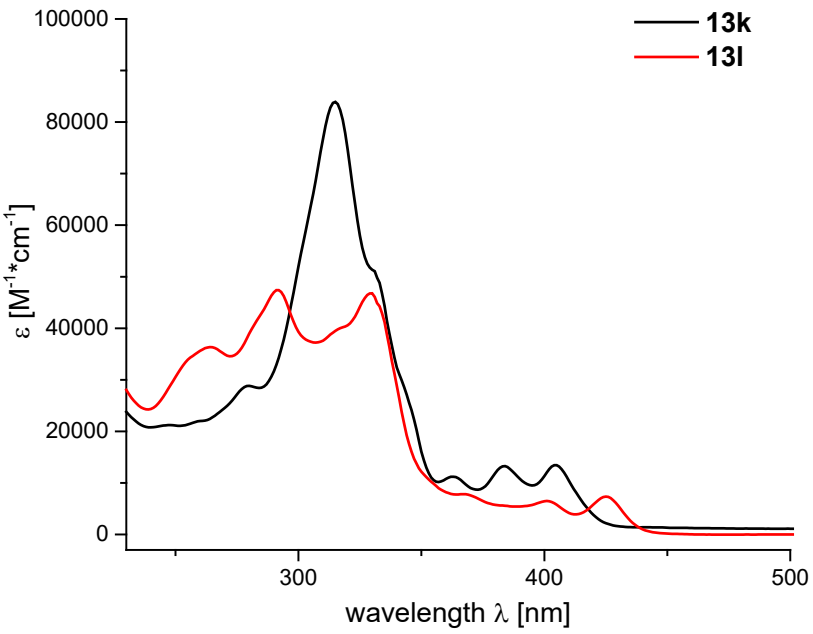


Figure SI1: Absorption spectra of **13k** and **13l** in DCM.

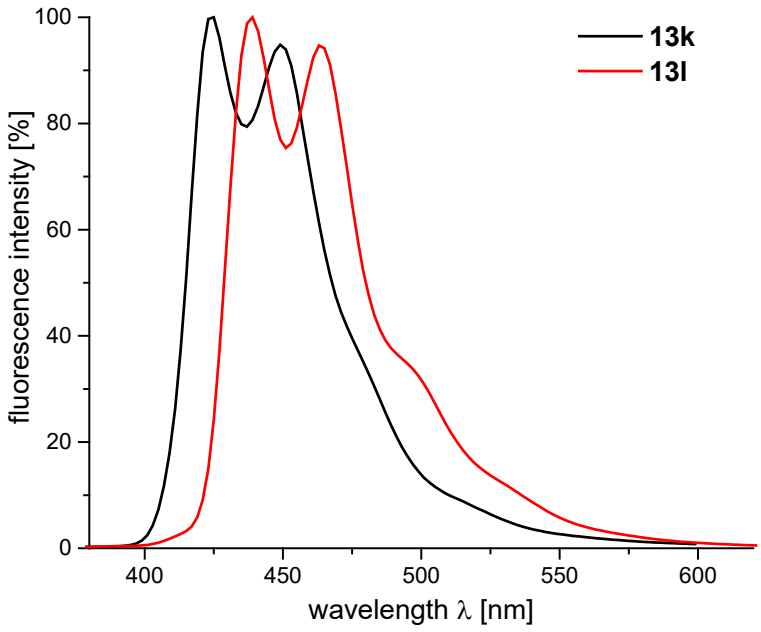


Figure SI2: Emission spectra of **13k** and **13l** in DCM.

7. Calculations and NMR experiments for the rotation barrier

Relaxed scans in steps of 2 degrees were performed on the PBE0-D3/aug-pcseg-1 level of theory using the TeraChem software package.[9,10]

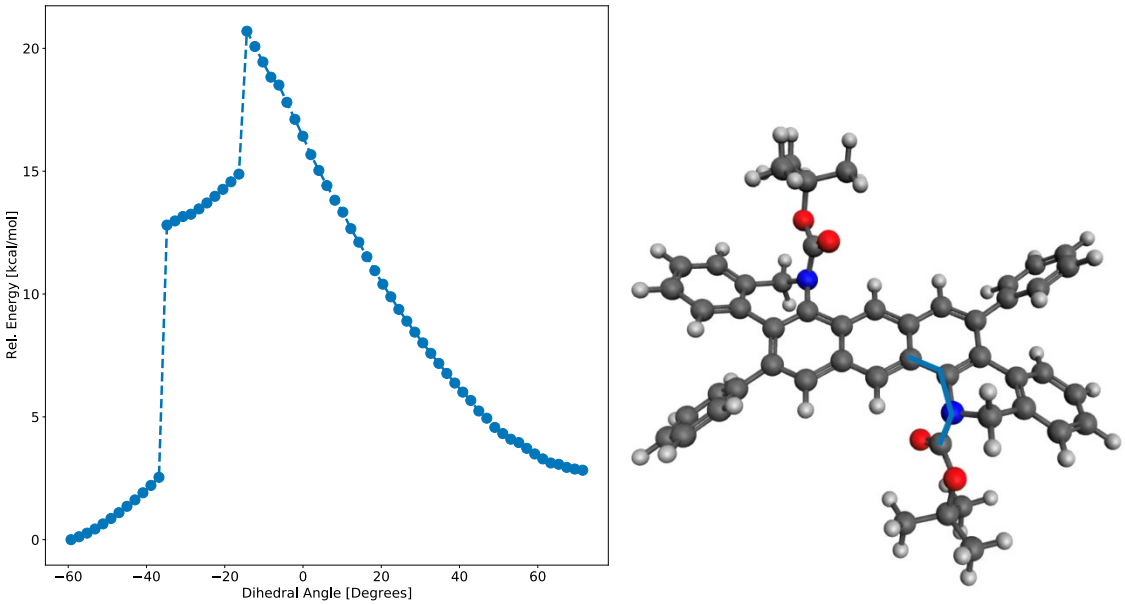


Figure SI3: Relaxed scan (in steps of 2 degrees) of the highlighted dihedral angle involving the boc group.

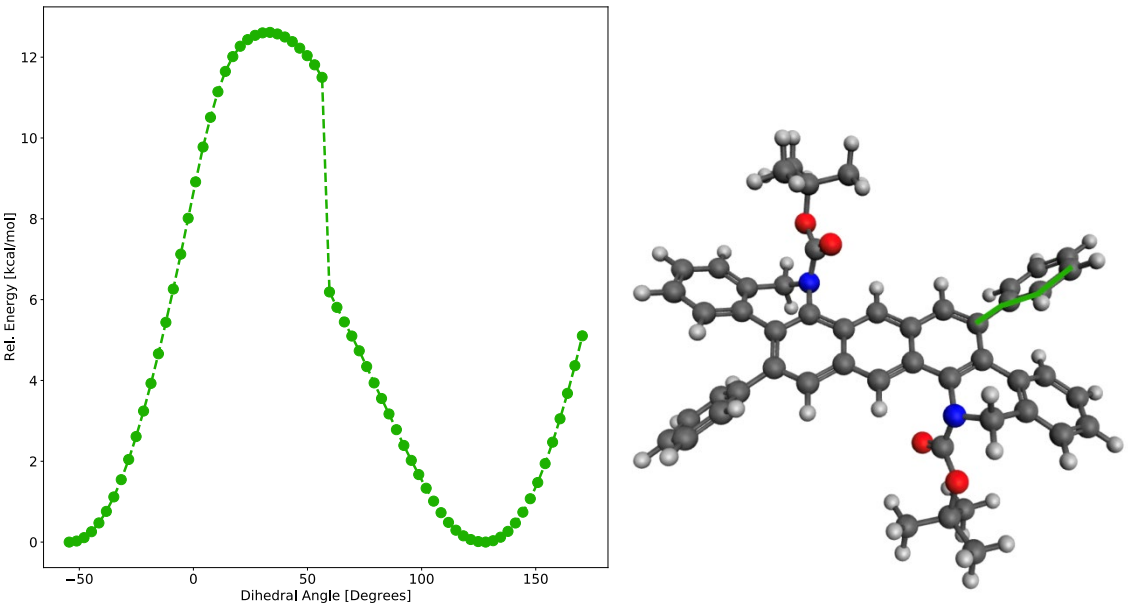
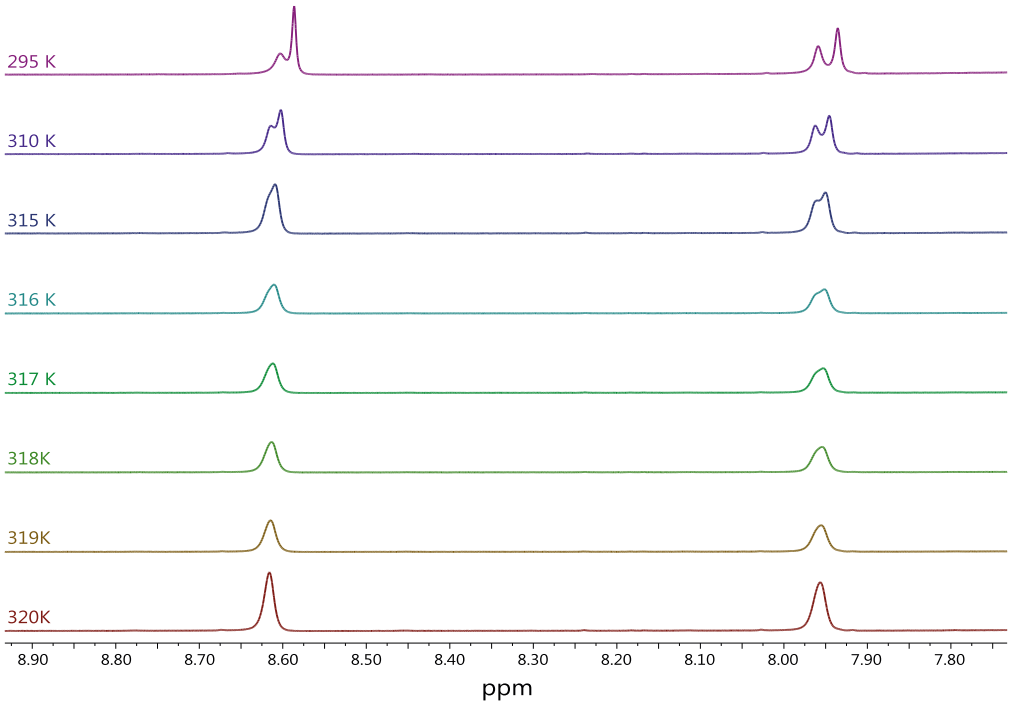
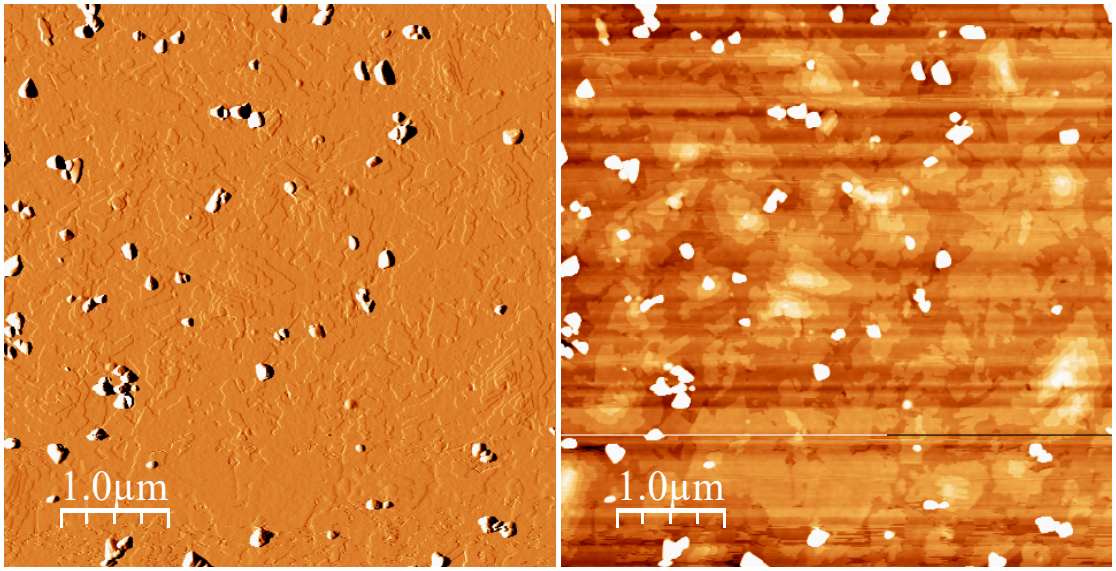


Figure SI4: Relaxed scan (in steps of 2 degrees) of the highlighted dihedral angle involving the phenyl group.

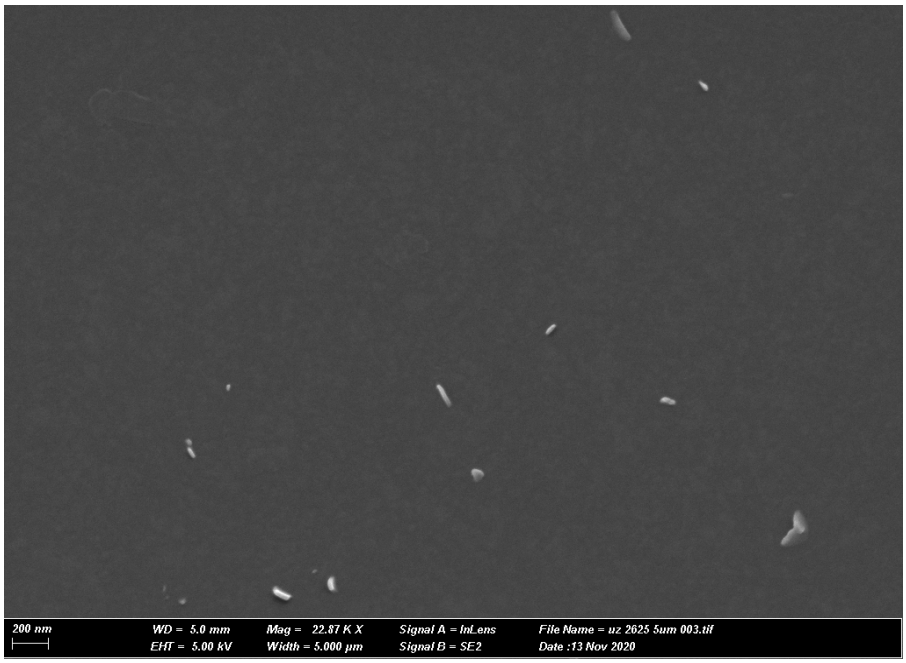


FigureSI5: ^{1}H NMR spectrum of the aromatic region (7.80-8.00 ppm) of **6k** in $CDCl_3$ at different temperatures with a coalescence temperature of 318 K.

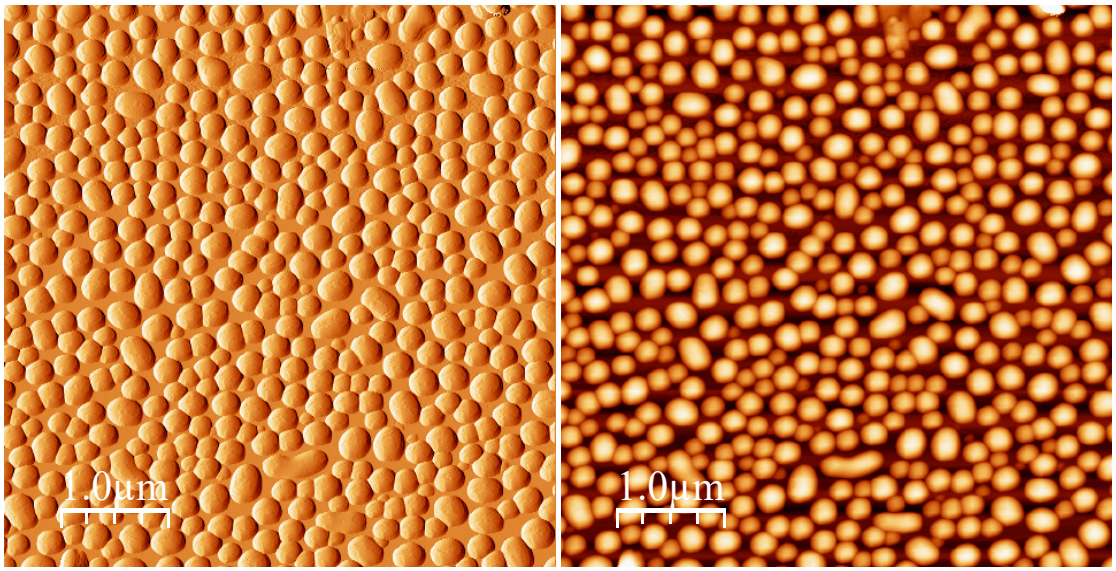
8. AFM/SEM Images



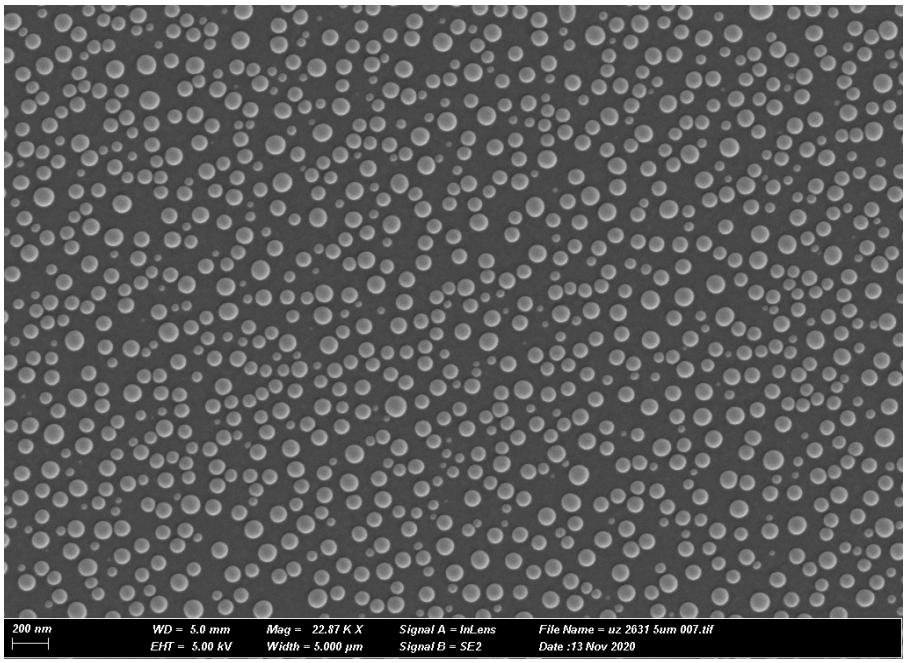
FigureSI6: Atomic force microscopy (AFM) images (left: amplitude, right: topography) of **13k** deposited by thermal sublimation in vacuum onto a silicon substrate coated with thermally grown silicon dioxide, atomic-layer-deposited aluminum oxide and an alkylphosphonic acid self-assembled monolayer.



FigureSI7: Scanning electron microscopy (SEM) image of **13k** deposited by thermal sublimation in vacuum onto a silicon substrate coated with thermally grown silicon dioxide, atomic-layer-deposited aluminum oxide and a fluoroalkylphosphonic acid self-assembled monolayer.



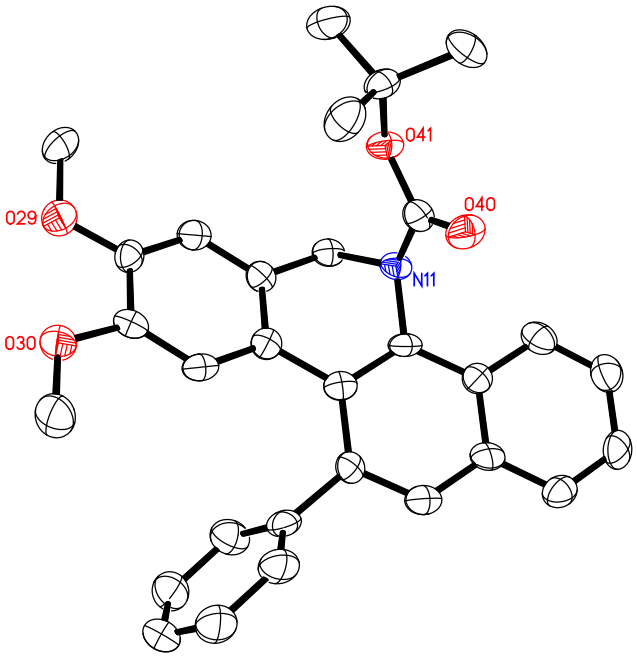
FigureSI8: AFM images (left: amplitude, right: topography) of **13l** deposited by thermal sublimation in vacuum onto a silicon substrate coated with thermally grown silicon dioxide, atomic-layer-deposited aluminum oxide and an alkylphosphonic acid self-assembled monolayer.



FigureSI9: SEM image of **13l** deposited by thermal sublimation in vacuum onto a silicon substrate coated with thermally grown silicon dioxide, atomic-layer-deposited aluminum oxide and a fluoroalkylphosphonic acid self-assembled monolayer.

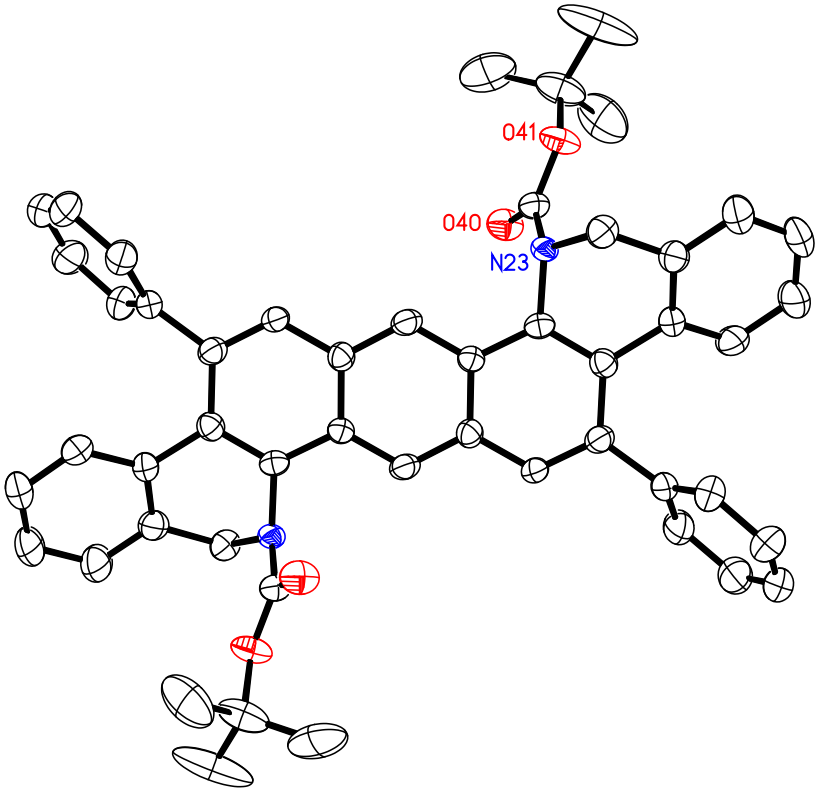
9. X-Ray Crystallography

Table SI1: Crystal data and structure refinement for **6c** (CCDC 2087651).



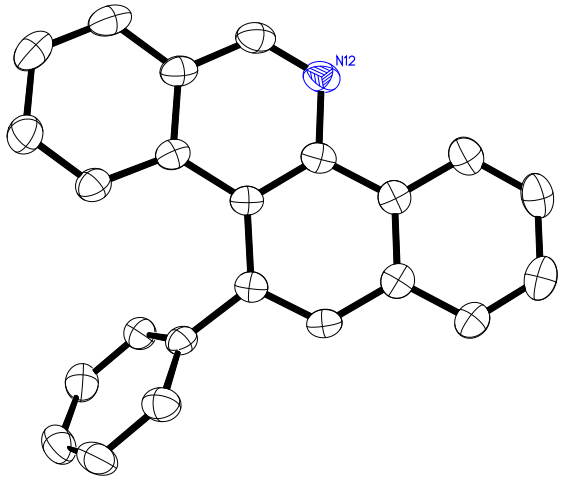
Empirical formula	$C_{30}H_{29}NO_4$	
Formula weight	467.54	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Z	4	
Unit cell dimensions	a =6.0063(6) Å	α = 90 deg.
	b = 19.183(2) Å	β = 90 deg.
	c = 21.328(2) Å	γ = 90 deg.
Volume	2457.3(5) $Å^3$	
Density (calculated)	1.26 g/cm^3	
Absorption coefficient	0.08 mm^{-1}	
Crystal shape	column	
Crystal size	0.127 x 0.040 x 0.026 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.4 to 23.0 deg.	
Index ranges	-6≤h≤6, -21≤k≤21, -23≤l≤23	
Reflections collected	12751	
Independent reflections	3444 (R(int) = 0.1257)	
Observed reflections	2108 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.83	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3444 / 0 / 321	
Goodness-of-fit on F^2	0.98	
Final R indices (I>2sigma(I))	R1 = 0.060, wR2 = 0.113	
Absolute structure parameter	-3.2(10)	
Largest diff. peak and hole	0.18 and -0.29 $eÅ^{-3}$	

Table SI2: Crystal data and structure refinement for **6k** (CCDC 2087652).



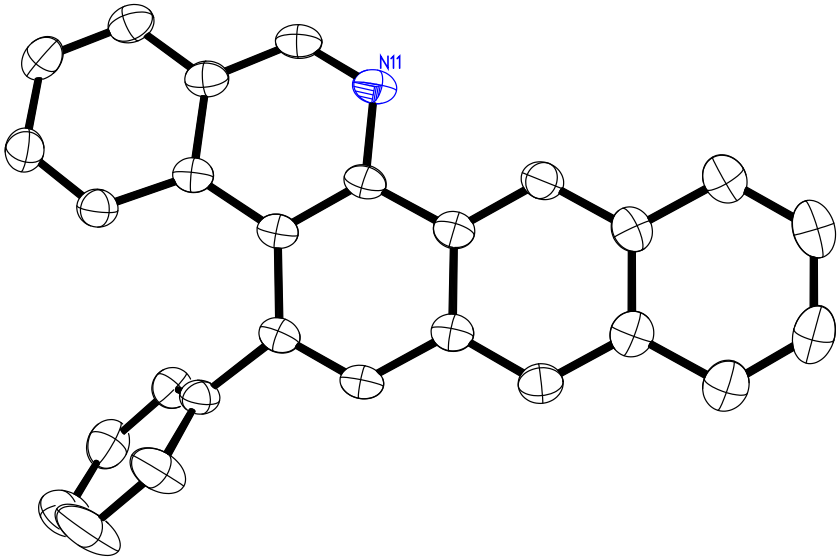
Empirical formula	$C_{50}H_{44}N_2O_4$	
Formula weight	736.87	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	C2/c	
Z	4	
Unit cell dimensions	a = 30.647(3) Å	α = 90 deg.
	b =6.1402(4) Å	β =100.504(6) deg.
	c = 21.8472(16) Å	γ = 90 deg.
Volume	4042.2(5) $Å^3$	
Density (calculated)	1.21 g/cm^3	
Absorption coefficient	0.60 mm^{-1}	
Crystal shape	plate	
Crystal size	0.147 x 0.046 x 0.012 mm^3	
Crystal colour	yellow	
Theta range for data collection	2.9 to 57.9 deg.	
Index ranges	-33≤h≤33, -4≤k≤6, -23≤l≤18	
Reflections collected	9863	
Independent reflections	2779 (R(int) = 0.0979)	
Observed reflections	1409 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.24 and 0.74	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2779 / 0 / 256	
Goodness-of-fit on F^2	1.00	
Final R indices (I>2sigma(I))	R1 = 0.061, wR2 = 0.106	
Largest diff. peak and hole	0.20 and -0.20 $eÅ^{-3}$	

Table SI3: Crystal data and structure refinement for **13a** (CCDC 2087653).



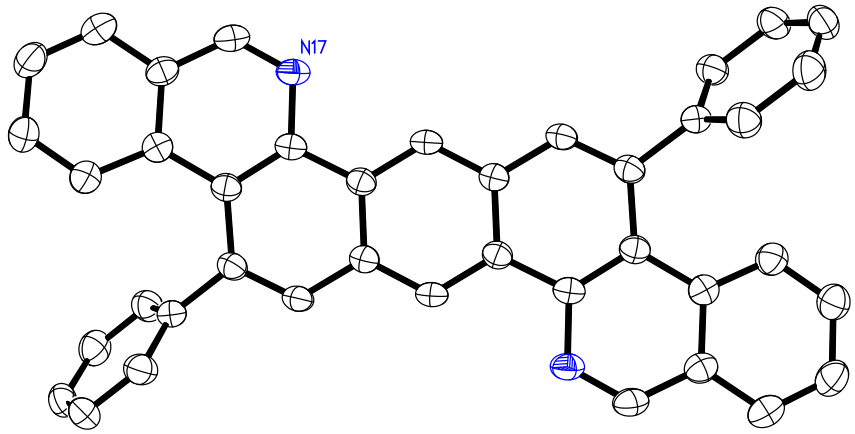
Empirical formula	$C_{23}H_{15}N$	
Formula weight	305.36	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	4	
Unit cell dimensions	a = 11.3680(4) Å	α = 90 deg.
	b = 11.9253(4) Å	β =114.026(2) deg.
	c = 12.3919(4) Å	γ = 90 deg.
Volume	1534.39(9) $Å^3$	
Density (calculated)	1.32 g/cm^3	
Absorption coefficient	0.08 mm^{-1}	
Crystal shape	column	
Crystal size	0.164 x 0.084 x 0.033 mm^3	
Crystal colour	colourless	
Theta range for data collection	2.0 to 25.1 deg.	
Index ranges	-13≤h≤13, -14≤k≤14, -14≤l≤14	
Reflections collected	13987	
Independent reflections	2722 (R(int) = 0.0563)	
Observed reflections	1845 (I > 2σ(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	2722 / 0 / 217	
Goodness-of-fit on F^2	1.04	
Final R indices (I>2sigma(I))	R1 = 0.047, wR2 = 0.108	
Largest diff. peak and hole	0.16 and -0.19 $eÅ^{-3}$	

Table SI4: Crystal data and structure refinement for **13f** (CCDC 2087654).



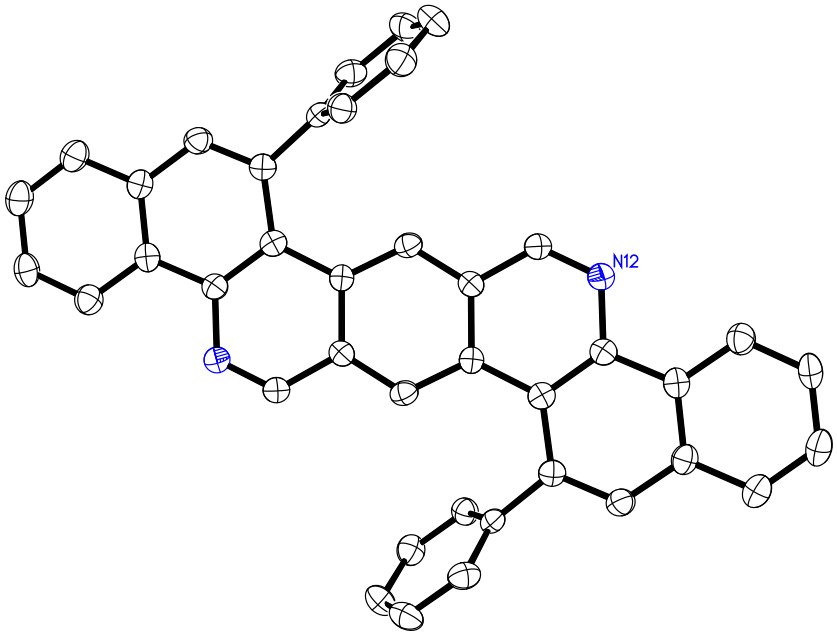
Empirical formula	$C_{27}H_{17}N$	
Formula weight	355.42	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Z	4	
Unit cell dimensions	a =7.8601(4) Å	α = 90 deg.
	b = 10.6012(6) Å	β = 90 deg.
	c = 21.5960(11) Å	γ = 90 deg.
Volume	1799.52(16) $Å^3$	
Density (calculated)	1.31 g/cm^3	
Absorption coefficient	0.08 mm^{-1}	
Crystal shape	plank	
Crystal size	0.311 x 0.172 x 0.076 mm^3	
Crystal colour	brown	
Theta range for data collection	1.9 to 31.5 deg.	
Index ranges	-10≤h≤11, -15≤k≤15, -29≤l≤31	
Reflections collected	15602	
Independent reflections	5844 (R(int) = 0.0342)	
Observed reflections	4030 (I > 2σ(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	5844 / 0 / 253	
Goodness-of-fit on F^2	1.03	
Final R indices (I>2sigma(I))	R1 = 0.058, wR2 = 0.110	
Absolute structure parameter	-1.8(10)	
Largest diff. peak and hole	0.20 and -0.23 $eÅ^{-3}$	

Table SI5: Crystal data and structure refinement for **13k** (CCDC 2087655).



Empirical formula	$C_{40}H_{24}N_2$	
Formula weight	532.61	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	2	
Unit cell dimensions	a =5.9570(4) Å	α = 90 deg.
	b = 20.9412(15) Å	β = 104.072(2) deg.
	c = 10.9419(8) Å	γ = 90 deg.
Volume	1324.01(16) $Å^3$	
Density (calculated)	1.34 g/cm^3	
Absorption coefficient	0.08 mm^{-1}	
Crystal shape	brick	
Crystal size	0.197 x 0.107 x 0.052 mm^3	
Crystal colour	orange	
Theta range for data collection	1.9 to 28.3 deg.	
Index ranges	$-7\leq h\leq 7$, $-26\leq k\leq 26$, $-13\leq l\leq 14$	
Reflections collected	14293	
Independent reflections	3019 (R(int) = 0.0479)	
Observed reflections	1931 ($I > 2\sigma(I)$)	
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	3019 / 0 / 190	
Goodness-of-fit on F^2	1.05	
Final R indices (I>2sigma(I))	R1 = 0.054, wR2 = 0.122	
Largest diff. peak and hole	0.25 and -0.17 $eÅ^{-3}$	

Table SI6: Crystal data and structure refinement for **13l** (CCDC 2087656).



Empirical formula	$C_{40}H_{24}N_2$	
Formula weight	532.61	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	2	
Unit cell dimensions	a = 11.6891(6) Å	α = 90 deg.
	b =7.2017(3) Å	β =104.454(2) deg.
	c = 16.3768(8) Å	γ = 90 deg.
Volume	1334.99(11) $Å^3$	
Density (calculated)	1.33 g/cm^3	
Absorption coefficient	0.08 mm^{-1}	
Crystal shape	brick	
Crystal size	0.090 x 0.055 x 0.028 mm^3	
Crystal colour	brown	
Theta range for data collection	1.8 to 23.1 deg.	
Index ranges	$-12 \le h \le 12$, $-7 \le k \le 7$, $-18 \le l \le 18$	
Reflections collected	9953	
Independent reflections	1864 (R(int) = 0.1302)	
Observed reflections	1291 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.93	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1864 / 0 / 190	
Goodness-of-fit on F^2	1.00	
Final R indices (I>2sigma(I))	R1 = 0.045, wR2 = 0.104	
Largest diff. peak and hole	0.16 and -0.21 $eÅ^{-3}$	

10. References

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