

# Electrochemical Synthesis of 5-Selenylbenzo[*a*]carbazoles via Cascade Cyclization of Indoles with Diselenides

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## *Supporting Information*

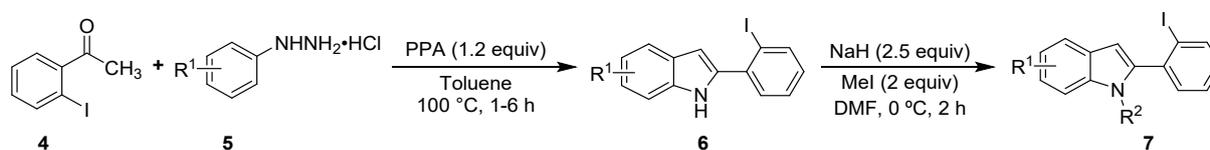
General experimental	S02-S04
General procedures for preparation of starting materials <b>1</b> and <b>2</b>	S05-S06
General procedures of electrochemical reaction	S06-S07
Cyclic voltammograms	S07-S08
Scale up synthesis	S08-S09
Control experiments	S09-S11
Characterization of products	S11-S43
<sup>1</sup> H and <sup>13</sup> C{ <sup>1</sup> H}-NMR spectra all compounds	S44-S90
Crystal structure data	S91-S93
References	S93-S93

## Experimental:

### General methods:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on Bruker Advance 400 (400 MHz) and 600 (600 MHz) spectrometers at 295 K in  $\text{CDCl}_3$ ; chemical shifts ( $\delta$  ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) ( $\delta_{\text{H}} = 0.00$  ppm) or  $\text{CDCl}_3$  ( $\delta_{\text{H}} = 7.26$  ppm).  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on Bruker Advance 400 (101 MHz) spectrometers at RT in  $\text{CDCl}_3$ . Chemical shifts ( $\delta$  ppm) are reported relative to  $\text{CDCl}_3$  [ $\delta = 77.16$  ppm (central line of the triplet)]. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR, the nature of carbons (C, CH,  $\text{CH}_2$ , and  $\text{CH}_3$ ) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for  $\text{CH}_2$ ) and q = quartet (for  $\text{CH}_3$ ). In the  $^1\text{H}$ -NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  CPD, and DEPT spectra. High-resolution mass spectra (HRMS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. Melting points are recorded using the Tempo and Mettler FP1 melting point apparatus in capillary tubes. A single crystal of **3aa** was selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with Olex2. Solve the structure solution program using direct methods and refined with the olex2. refinement package using Gauss–Newton minimization. Electrolysis reactions were conducted using ElectraSyn 2.0 Package supply purchased from IKA Instruments. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether in the boiling range of 60–80 °C was used. Cyclic voltammetry (CV) analysis was performed on the ElectraSyn 2.0 Package, using a glassy carbon electrode as the working electrode, a platinum electrode as a counter electrode and Ag/AgCl electrode as a reference electrode. A cyclic voltammogram was recorded at a 100 mV/s scan rate. The starting materials *o*-iodoacetophenone, phenylhydrazine hydrochloride, phenyl acetylenes, diphenyl diselenide, and  $\text{LiClO}_4$  were purchased from Sigma/TCI/ local sources and used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per gram of crude material).

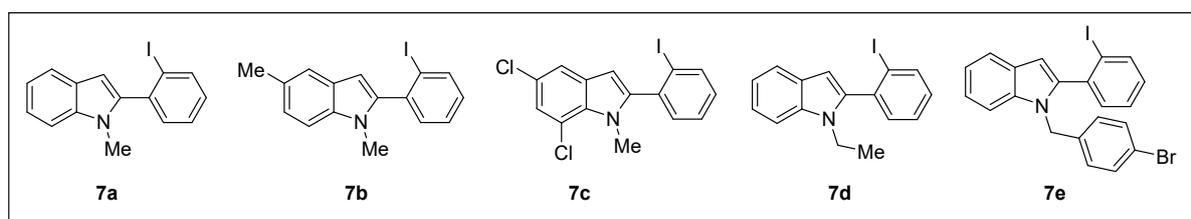
### General Procedure - 1 (GP-1) for the Preparation of 2-(2-Iodophenyl)-1-methyl-1*H*-indole :



Typical procedure is given for the synthesis of 2-(2-iodophenyl)-1*H*-indole (6) add *o*-iodoacetophenone **4** (2 g, 8.13 mmol) and phenylhydrazine hydrochloride (1.41 g, 9.75 mmol) **5** in Toluene (5 mL) at room temperature. To the solution was added polyphosphoric acid (20 g) and the mixture was stirred at 100 °C for 1-6 h. The progress of the reaction was monitored by TLC till the reaction is completed. The mixture was cooled to room temperature, quenched with aqueous NaHCO<sub>3</sub> solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered. Evaporation of the solvent(s) under reduced pressure and resultant crude mixture was carried out with next step.

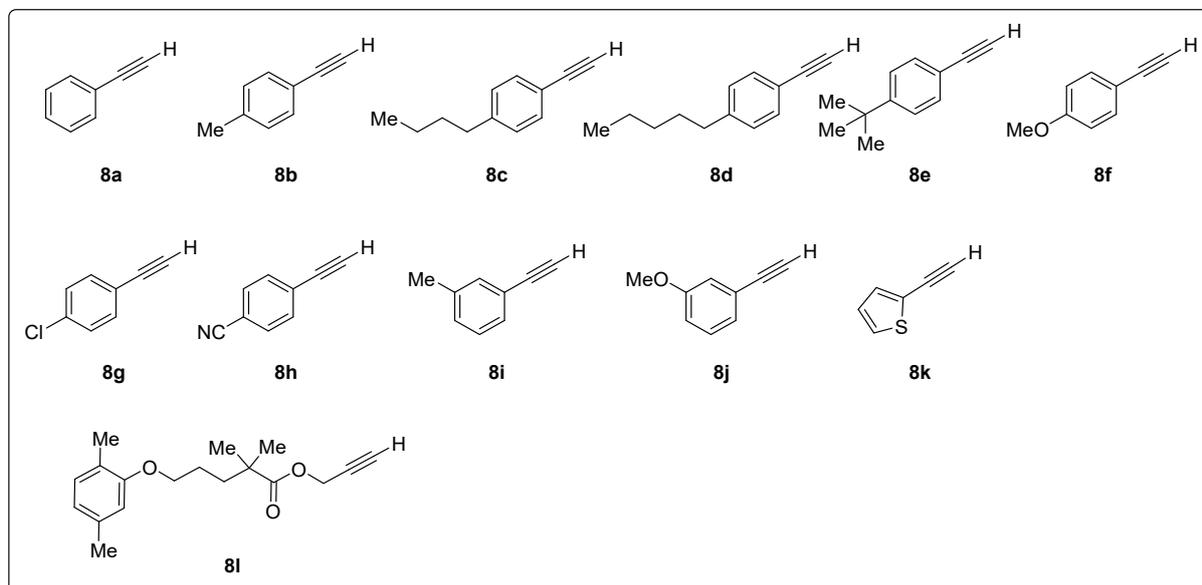
Sodium hydride (156 mg, 2.5 equiv) was added to a solution of 2-(2-iodophenyl)-1*H*-indole **6** (1.65 g, 5.17 mmol) in dry DMF (10 mL) at 0 °C. After stirring for 10 min at 0 °C, iodomethane (0.7 mL, 2 equiv) was added dropwise to the mixture at the same temperature. After stirring for 3 h at room temperature, the mixture was quenched with water and extracted with ethyl acetate. The organic phase was washed with brine, dried over (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), furnished the products as an eluent to give **7** (1.37 g, 80%) as a colourless viscous oil.

The following *N*-Protected-2-(2-Iodophenyl)-1*H*-indole derivatives **7a-7e** (Table-3S) were prepared according to the previous literature reports.<sup>1</sup>



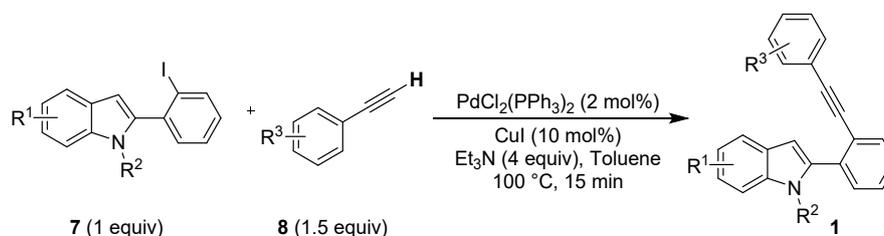
**Table-S1:** *N*-Protected-2-(2-Iodophenyl)-1*H*-indole **7a-7e**.

The following Phenyl acetylenes **8a-8k** (Table-2S) are purchased and used as received. **8l** are prepared by using previous reports.<sup>2</sup>



**Table-S2:** phenyl acetylenes **8a-8l**.

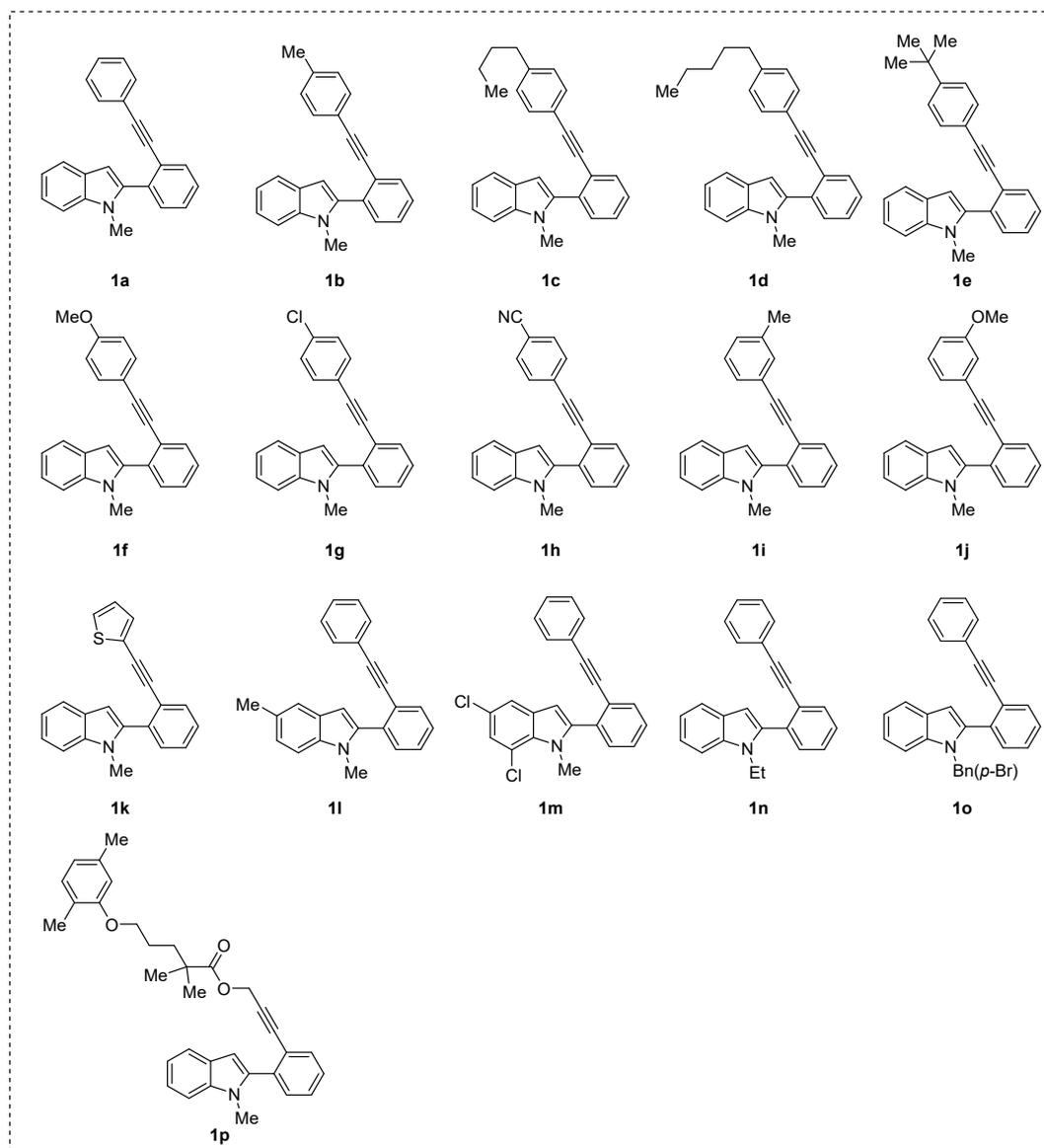
### General Procedure - 2 (GP-2) for the Preparation of 1-methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole (**1**):



In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added **2-(2-iodophenyl)indole 7a-7e** (135–195 mg, 0.4 mmol), phenylacetylenes **8a-8m** (61–296 mg, 0.6 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (2 mol %),  $\text{CuI}$  (10 mol %),  $\text{Et}_3\text{N}$  (404 mg, 4 mmol), and toluene (0.5 mL) at room temperature. The resultant reaction mixture was subjected to an oil bath at  $100\text{ }^\circ\text{C}$  for 10-15 min. The progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous  $\text{NaHCO}_3$  solution and extracted with ethyl acetate ( $3 \times 10\text{ mL}$ ). The organic layers were washed with saturated  $\text{NaCl}$  solution, dried ( $\text{Na}_2\text{SO}_4$ ) and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography

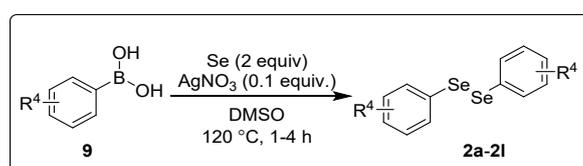
(petroleum ether/ethyl acetate, 98:02), furnished the products **1a-1p** (68–93%) as colourless/brown/dark brown/orange/yellow viscous oil/solid.

The following *N*-substituted 2-(phenylethynylphenyl)-indoles **1a-1p** (Table-S3) are prepared by using the literature reports.<sup>3</sup>



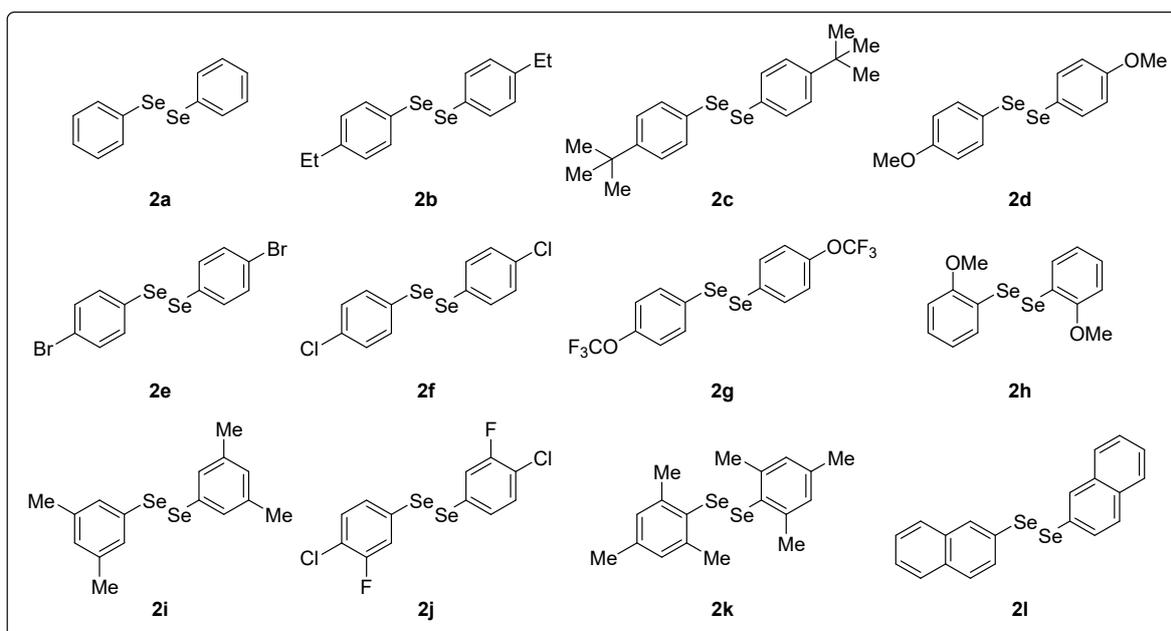
**Table-S3:** *N*-substituted 2-(phenylethynylphenyl)-indoles **1a-1p**.

### General Procedure - 3 (GP-3) for the Preparation of Diaryl Diselenides (**2a-2l**):

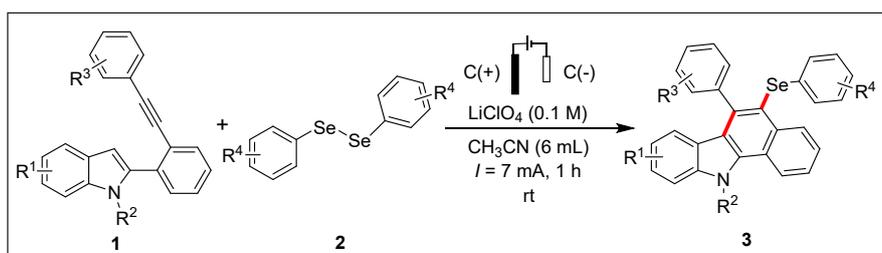


The reaction was carried out in a 25 mL oven-dried round bottom flask equipped with a magnetic stir bar and charged with aryl boronic acid **9** (1.0 equiv), selenium powder (1.0 equiv), AgNO<sub>3</sub> (0.1 equiv), and DMSO (5 mL). The resulting reaction mixture was stirred at 120 °C for 1–4 h. The reaction progress was monitored by TLC. After completion of the reaction, iodine was quenched with hypo solution, and it was worked up with ethyl acetate (3 × 10 mL), and the combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:00–95:05) as the eluent furnished the desired product **2a-2l** (70 to 93%), as yellow liquids or yellow solids (or red solids) (Table S4).

**Table-S4.** The following starting material diaryl diselenide **2a-2l** are prepared by using the literature.<sup>4</sup>



#### General Procedure for the Preparation of 5-selenylbenzo[*a*]carbazole **4** (GP-4):

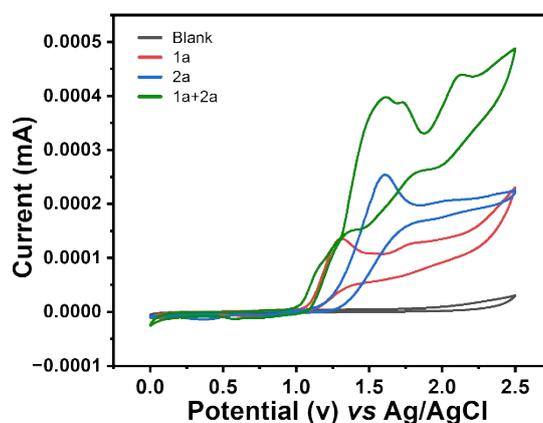


The reaction was carried out with *N*-substituted 2-(phenylethynylphenyl)-indoles **1** (0.25 mmol), diaryl diselenide **2** (0.0125 mmol, 0.5 equiv), LiClO<sub>4</sub> (0.1 M) in 6 mL CH<sub>3</sub>CN

was added to an oven dried ElectraSyn vial (10 mL) with a magnetic stirring bar. The ElectraSyn vial cap equipped with the Graphite as both anode and cathode was inserted into the mixture. The reaction mixture was electrolyzed at ambient temperature under a constant current of 7 mA for 1 h. After electrolysis, the ElectraSyn vial cap was removed, electrodes were rinsed with DCM (2 mL), and the mixture was poured into an aqueous NH<sub>4</sub>Cl solution (40 mL), and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the desired product 11-methyl-6-phenyl-5-(phenylselanyl)-11H-benzo[*a*]carbazole **3** (73-124 mg, 60 to 92% yields) as a brown/orange/red/yellow liquids or solids.

### Cyclic Voltammograms:

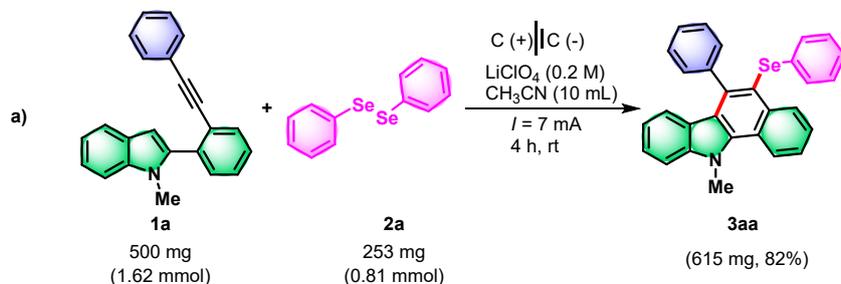
The cyclic voltammetry (CV) studies were carried out to further investigate the reaction mechanism, and Figure 1S shows the cyclic voltammetry (CV) curves with 0.1 M LiClO<sub>4</sub> solution in CH<sub>3</sub>CN as a background. The voltammogram was obtained at a scan rate of 100 mV/s with Pt wire as a counter electrode, Ag/AgCl as a reference electrode, which is submerged in saturated aqueous KCl solution, and Pt disk electrode as a working electrode. Within the scanning window (0 to 2.5 V). An obvious that there is no peak for background (Curve 1). The CV of 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** displayed an oxidation peak at 1.30 V vs Ag/AgCl (curve 2). When testing diphenyl diselenide **2a**, an oxidation peak was seen at 1.61 V vs Ag/AgCl in curve 3. The mixture of 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole (**1a**) and diphenyl diselenide (**2a**) showed two oxidation signals at 1.61 V and 1.74 V vs Ag/AgCl (curve 4), respectively.



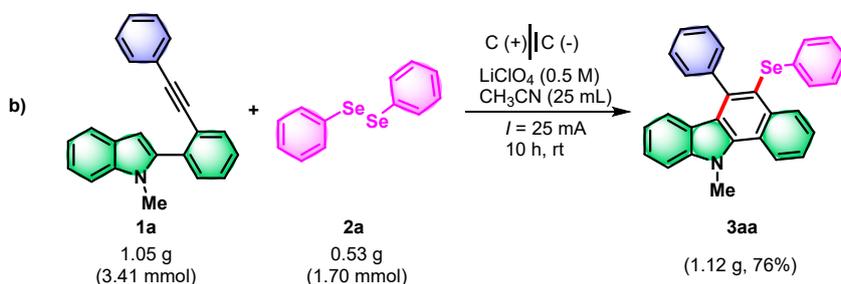
**Figure S1.** Cyclic voltammograms of reactants and their mixtures in 0.1 M LiClO<sub>4</sub> solution in CH<sub>3</sub>CN at room temperature: a) Background; b) 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (0.01

M); c) diphenyl diselenide **2a** (0.01 M); d) 1-methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **1a** (0.01 M) + diphenyl diselenide **2a** (0.01 M); The voltammogram was obtained at a scan rate of 100 mV/s with Pt wire as a counter electrode, Ag/AgCl as a reference electrode, and Pt disk electrode as a working electrode.

**Scheme S1:** Scale-up reactions.



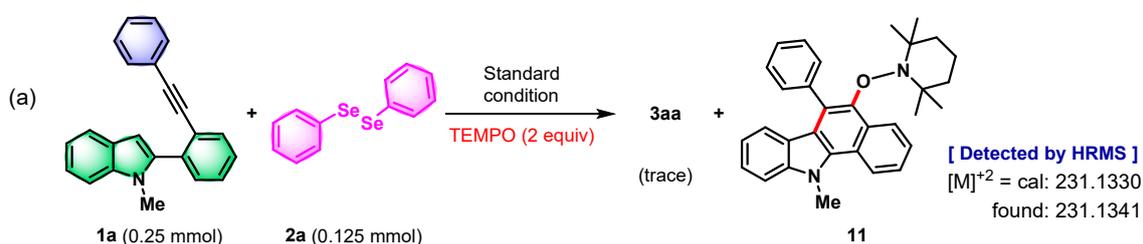
To an oven-dried reaction beaker (100 mL) equipped with a magnetic stirring bar, were added 1-Methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **1a** (500 mg, 1.62 mmol), diaryl diselenide **2a** (253 mg, 0.81 mmol),  $\text{LiClO}_4$  (0.2 M) in 10 mL  $\text{CH}_3\text{CN}$ . The reaction vial equipped with the graphite as an anode and cathode, was inserted into the reaction mixture, and these two electrodes were connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at room temperature under a constant current of 7 mA for 4 h. The reaction was monitored by TLC, and after completion of the reaction, the electrodes were rinsed with DCM (8 mL), and the mixture was poured into an aqueous  $\text{NH}_4\text{Cl}$  solution (100 mL) and 10 extracted with DCM ( $3 \times 30 \text{ mL}$ ). The combined organic layers were washed with brine and dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the desired product **3aa** (615 mg, 82%), as yellow solid.



To an oven-dried reaction beaker (100 mL) equipped with a magnetic stirring bar, were added 1-Methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **1a** (1.05 g, 3.41 mmol), diaryl diselenide **2a** (0.53 g, 1.70 mmol),  $\text{LiClO}_4$  (0.5 M) in 25 mL  $\text{CH}_3\text{CN}$ . The reaction vial equipped with the graphite as an anode and cathode, was inserted into the reaction mixture, and these two

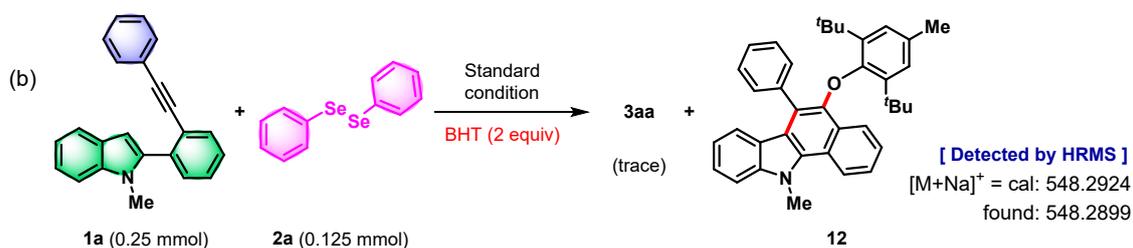
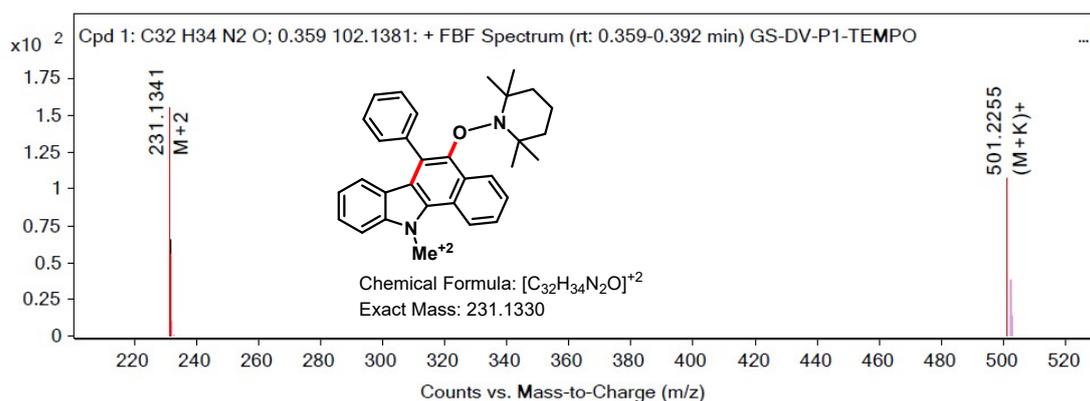
electrodes were connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at room temperature under a constant current of 25 mA for 10 h. The reaction was monitored by TLC, and after completion of the reaction, the electrodes were rinsed with DCM (8 mL), and the mixture was poured into an aqueous NH<sub>4</sub>Cl solution (100 mL) and 10 extracted with DCM (3 × 30 mL). The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the desired product **3aa** (76%), as yellow solid.

**Scheme S2:** Control experiments.



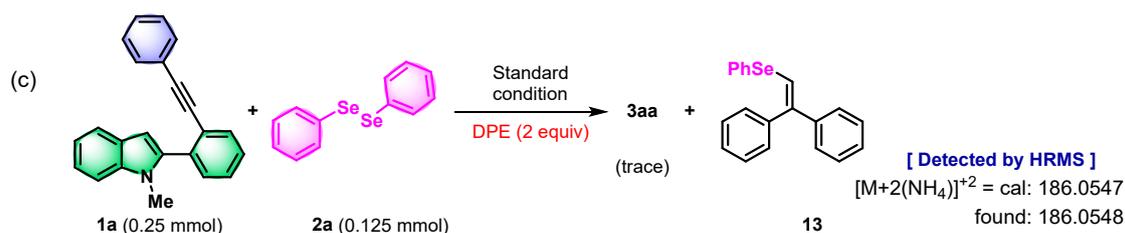
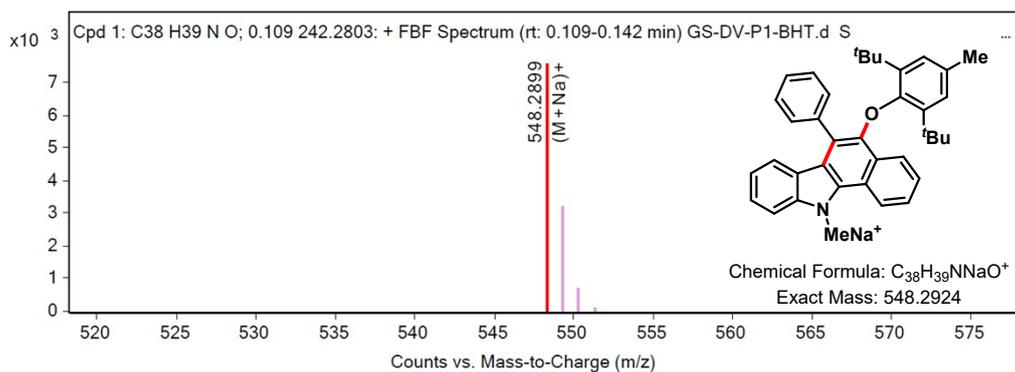
To an oven-dried ElectraSyn 2.0 undivided cell (10 ml) equipped with a magnetic stir bar, were added 1-Methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **1a** (0.25 mmol), diaryl diselenide **2a** (0.0125 mmol, 0.5 equiv), TEMPO (78 mg, 0.5 mmol), and LiClO<sub>4</sub> (0.1 M) in 6 mL CH<sub>3</sub>CN was added to an oven dried ElectraSyn vial (10 mL) with a magnetic stirring bar. The ElectraSyn vial cap equipped with the Graphite as both anode and cathode was inserted into the mixture. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA at room temperature for 1 h. After the completion of the reaction, electrodes were rinsed with DCM (2 mL), and the mixture was poured into an aqueous NH<sub>4</sub>Cl solution (40 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent(s) under reduced pressure. The crude mixture was subjected to mass spectrometric analysis to confirm the formation of 11-methyl-6-phenyl-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-11*H*-benzo[*a*]carbazole **11**.

**HRMS** (ESI) *m/z*:  $[\text{M}]^{+2}$  calcd for  $[\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}]^{+2}$  231.1330; found 231.1341.



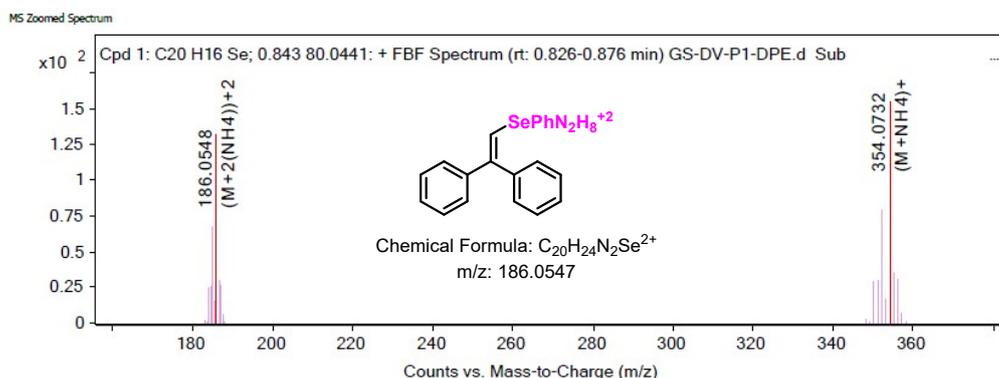
To an oven-dried ElectroSyn 2.0 undivided cell (10 ml) equipped with a magnetic stir bar, were added 1-Methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **1a** (0.25 mmol), diaryl diselenide **2a** (0.0125 mmol, 0.5 equiv), BHT (110 mg, 0.5 mmol), and LiClO<sub>4</sub> (0.1 M) in 6 mL CH<sub>3</sub>CN was added to an oven dried ElectroSyn vial (10 mL) with a magnetic stirring bar. The ElectroSyn vial cap equipped with the Graphite as both anode and cathode was inserted into the mixture. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA at room temperature for 1 h. After the completion of the reaction, electrodes were rinsed with DCM (2 mL), and the mixture was poured into an aqueous NH<sub>4</sub>Cl solution (40 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent(s) under reduced pressure. The crude mixture was subjected to mass spectrometric analysis to confirm the formation of 5-(2,6-di-tert-butyl-4-methylphenoxy)-11-methyl-6-phenyl-11*H*-benzo[*a*]carbazole **12**.

**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for [C<sub>38</sub>H<sub>39</sub>NNaO]<sup>+</sup>548.2924; found 548.2899.

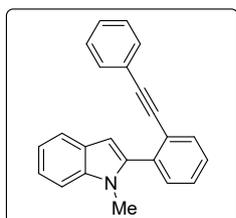


To an oven-dried ElectroSyn 2.0 undivided cell (10 ml) equipped with a magnetic stir bar, were added 1-Methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **1a** (0.25 mmol), diaryl diselenide **2a** (0.0125 mmol, 0.5 equiv), DPE (90 mg, 0.5 mmol), and LiClO<sub>4</sub> (0.1 M) in 6 mL CH<sub>3</sub>CN was added to an oven dried ElectroSyn vial (10 mL) with a magnetic stirring bar. The ElectroSyn vial cap equipped with the Graphite as both anode and cathode was inserted into the mixture. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA at room temperature for 1 h. After the completion of the reaction, electrodes were rinsed with DCM (2 mL), and the mixture was poured into an aqueous NH<sub>4</sub>Cl solution (40 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent(s) under reduced pressure. The crude mixture was subjected to mass spectrometric analysis to confirm the formation of (2,2-diphenylvinyl)(phenyl)selane **13**.

**HRMS (ESI) *m/z***: [M+2(NH<sub>4</sub>)]<sup>+2</sup> calcd for [C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>Se]<sup>+2</sup> 186.0547; found 186.0548.



## Characterization of compounds:



### 1-Methyl-2-(2-(phenylethynyl)phenyl)-1H-indole (**1a**):

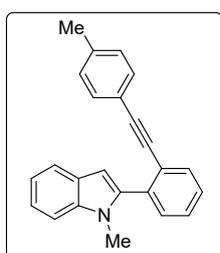
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), phenylacetylene **8a** (62 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1a** (113.12 mg, 92%) as yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8a**) = 0.7, *R<sub>f</sub>*(**1a**) = 0.5 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3055, 2943, 2213, 1717, 1459, 1349, 1010, 751 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 – 7.67 (m, 2H), 7.50 – 7.47 (m, 1H), 7.45 – 7.38 (m, 3H), 7.32 – 7.27 (m, 1H), 7.25 – 7.16 (m, 6H), 6.66 (s, 1H), 3.71 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  139.9, 137.8, 135.2, 132.2, 131.4 (2C), 131.0, 128.2, 128.2 (2C), 128.2, 128.1, 127.9, 123.9, 122.9, 121.6, 120.6, 119.6, 109.4, 102.6, 92.7, 88.5, 31.0 ppm.

**HRMS** (ESI) *m/z*: [M+H<sub>2</sub>O]<sup>+</sup> calcd for [C<sub>23</sub>H<sub>19</sub>NO]<sup>+</sup> 325.1461; found 325.1460.



### 1-Methyl-2-(2-(*p*-tolylethynyl)phenyl)-1H-indole (**1b**):

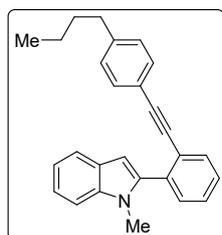
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 1-ethynyl-4-methylbenzene **8b** (69 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1b** (115.71 mg, 90%) as brown viscous oil; [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8b**) = 0.7, *R<sub>f</sub>*(**1b**) = 0.5 UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3045, 2926, 2213, 1909, 1690, 1458, 1098, 736  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 – 7.68 (m, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.41 (m, 3H), 7.32 (dd,  $J$  = 8.0, 7.2 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.10 (d,  $J$  = 8.1 Hz, 2H), 7.04 (d,  $J$  = 8.3 Hz, 2H), 6.69 (s, 1H), 3.73 (s, 3H), 2.33 (s, 3H) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 138.4, 137.8, 135.1, 132.1 (2C), 131.3, 131.0, 129.0 (2C), 128.1, 127.9, 127.9, 124.2, 121.5, 120.6, 119.8, 119.6, 109.4, 102.5, 93.0, 87.9, 31.1, 21.4 ppm.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{24}\text{H}_{20}\text{N}]^+$  322.1590; found 322.1587.



### 2-(2-((4-Butylphenyl)ethynyl)phenyl)-1-methyl-1H-indole (**1c**):

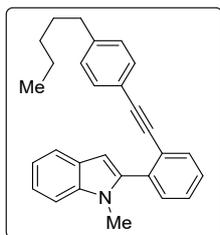
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 1-butyl-4-ethynylbenzene **8c** (95 mg, 0.6 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (14 mg, 0.02 mmol),  $\text{CuI}$  (19 mg, 0.1 mmol),  $\text{Et}_3\text{N}$  (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1c** (129.40 mg, 89%) as brown solid; mp = 68–70 °C. [TLC control (petroleum ether/ethyl acetate 98:2),  $R_f(\mathbf{7a})$  = 0.6,  $R_f(\mathbf{8c})$  = 0.7,  $R_f(\mathbf{1c})$  = 0.5 UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3054, 2926, 2248, 1915, 1509, 1460, 1009, 729  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.64 (m, 2H), 7.52 – 7.46 (m, 1H), 7.46 – 7.39 (m, 3H), 7.35 – 7.27 (m, 1H), 7.22 – 7.16 (m, 1H), 7.11 (dd,  $J$  = 8.1, 1.8 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.67 (d,  $J$  = 1.4 Hz, 1H), 3.73 (s, 3H), 2.57 (t,  $J$  = 7.4 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.37 – 1.30 (m, 2H), 0.93 (t,  $J$  = 7.3 Hz, 3H) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 140.0, 137.8, 135.1, 132.1, 131.3 (2C), 131.0, 129.3, 128.4 (2C), 128.1, 127.9, 124.2, 121.5, 120.6, 120.0, 119.6, 109.4, 102.5, 93.1, 87.8, 35.5, 33.3, 31.1, 22.2, 13.9 ppm.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{NH}_4]^+$  calcd for  $[\text{C}_{27}\text{H}_{29}\text{N}_2]^+$  381.2325; found 381.2336.



### 1-Methyl-2-(2-((4-pentylphenyl)ethynyl)phenyl)-1H-indole (**1d**):

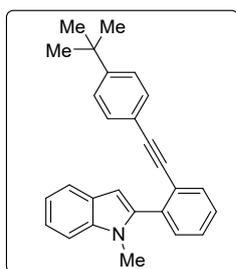
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 1-ethynyl-4-pentylbenzene **8d** (103.36 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1d** (139 mg, 92%) as yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8d**) = 0.7, *R<sub>f</sub>*(**1d**) = 0.5 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3052, 2923, 2215, 1912, 1509, 1375, 1102, 750 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 – 7.67 (m, 2H), 7.52 – 7.47 (m, 1H), 7.46 – 7.41 (m, 3H), 7.34 – 7.29 (m, 1H), 7.20 (ddd, *J* = 7.1, 2.0, 0.9 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.08 – 7.00 (m, 2H), 6.68 (d, *J* = 1.4 Hz, 1H), 3.73 (s, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.65 – 1.53 (m, 2H), 1.32 (dtd, *J* = 15.2, 8.2, 1.7 Hz, 4H), 0.91 (t, *J* = 7.1 Hz, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  143.5, 140.0, 137.8, 135.2, 132.1, 131.3 (2C), 131.0, 128.4 (2C), 128.1, 127.9, 127.9, 124.2, 121.5, 120.6, 120.0, 119.6, 109.4, 102.5, 93.1, 87.9, 35.8, 31.4, 31.0, 30.8, 22.5, 13.9 ppm.

**HRMS** (ESI) *m/z*: [M+NH<sub>4</sub>]<sup>+</sup> calcd for [C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>]<sup>+</sup> 395.2482; found 395.2498.



### 2-(2-((4-(*Tert*-butyl)phenyl)ethynyl)phenyl)-1-methyl-1H-indole (**1e**):

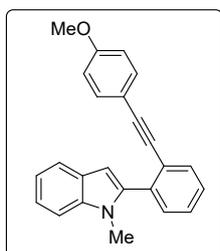
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 1-(*tert*-butyl)-4-ethynylbenzene **8e** (95 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1e** (131 mg, 90%) as yellow solid; mp = 126–128 °C. [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8e**) = 0.7, *R<sub>f</sub>*(**1e**) = 0.5 UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3051, 2955, 2215, 1919, 1510, 1350, 1014, 744  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.57 (m, 2H), 7.39 (dd,  $J$  = 7.8, 2.4 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.23 – 7.18 (m, 1H), 7.16 – 7.14 (m, 2H), 7.12 – 7.08 (m, 1H), 7.04 (d,  $J$  = 8.5 Hz, 2H), 6.58 (s, 1H), 3.62 (s, 3H), 1.19 (s, 9H) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.5, 140.0, 137.8, 135.2, 132.2, 131.2 (2C), 131.0, 128.1, 127.9, 127.9, 125.2 (2C), 124.2, 121.5, 120.6, 119.9, 119.6, 109.4, 102.5, 92.9, 87.8, 34.7, 31.1 (3C), 31.0 ppm.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{NH}_4]^+$  calcd for  $[\text{C}_{27}\text{H}_{29}\text{N}_2]^+$  381.2325; found 381.2331.



### **2-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1-methyl-1H-indole (1f):**

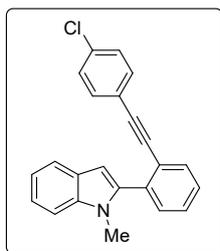
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 1-ethynyl-4-methoxybenzene **8f** (79.2 mg, 0.6 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (14 mg, 0.02 mmol),  $\text{CuI}$  (19 mg, 0.1 mmol),  $\text{Et}_3\text{N}$  (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the product **1f** (121.37 mg, 90%) as dark brown viscous oil; [TLC control (petroleum ether/ethyl acetate 96:4),  $R_f(\mathbf{7a})$  = 0.6,  $R_f(\mathbf{8f})$  = 0.7,  $R_f(\mathbf{1f})$  = 0.4 UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3053, 2926, 2214, 1699, 1459, 1249, 1100, 734  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J$  = 7.9 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.50 – 7.46 (m, 1H), 7.42 (ddd,  $J$  = 8.4, 6.4, 2.6 Hz, 3H), 7.29 (dd,  $J$  = 7.3, 3.9 Hz, 1H), 7.20 (dd,  $J$  = 7.2, 7.6 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.78 – 6.72 (m, 2H), 6.67 (s, 1H), 3.77 (s, 3H), 3.72 (s, 3H) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 140.1, 137.8, 134.9, 132.9 (2C), 131.9, 131.0, 128.1, 127.9, 127.7, 124.3, 121.5, 120.6, 119.6, 115.0, 113.9 (2C), 109.4, 102.5, 92.9, 87.3, 55.2, 31.0 ppm.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{24}\text{H}_{20}\text{NO}]^+$  338.1539; found 338.1545.



#### 2-(2-((4-Chlorophenyl)ethynyl)phenyl)-1-methyl-1H-indole (**1g**):

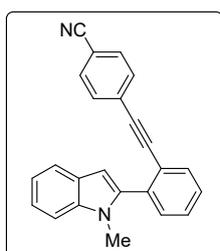
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 1-chloro-4-ethynylbenzene **8g** (82 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1g** (127 mg, 93%) as brown crystalline solid; mp = 98–100 °C. [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8g**) = 0.7, *R<sub>f</sub>*(**1g**) = 0.5 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3053, 2939, 1906, 1596, 1478, 1265, 1092, 735 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 – 7.69 (m, 2H), 7.54 – 7.42 (m, 4H), 7.36 – 7.31 (m, 1H), 7.25 – 7.18 (m, 3H), 7.14 – 7.09 (m, 2H), 6.70 (s, 1H), 3.72 (s, *J* = 0.9 Hz, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  139.4, 137.8, 135.7, 132.4, 131.9 (2C), 131.8 (2C), 131.1, 129.1, 128.3, 127.8, 122.9, 121.8, 120.7, 119.8, 118.4, 111.4, 109.4, 102.9, 92.8, 90.9, 31.0 ppm.

**HRMS** (ESI) *m/z*: [M+H<sub>2</sub>O]<sup>+</sup> calcd for [C<sub>23</sub>H<sub>18</sub>ClNO]<sup>+</sup> 359.1077; found 359.1084.



#### 4-((2-(1-Methyl-1H-indol-2-yl)phenyl)ethynyl)benzotrile (**1h**):

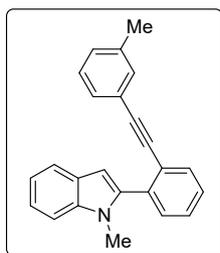
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 4-ethynylbenzotrile **8h** (76 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the product **1a** (106.28 mg, 80%) as brown viscous oil; [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8h**) = 0.7, *R<sub>f</sub>*(**1h**) = 0.4 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3055, 2923, 2222, 1924, 1601, 1461, 1159, 751 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.74 – 7.67 (m, 2H), 7.51 – 7.43 (m, 5H), 7.39 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.24 – 7.15 (m, 3H), 6.66 (s, 1H), 3.68 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CDCl<sub>3</sub>) δ 139.4, 137.8, 135.7, 132.4, 131.9 (2C), 131.8 (2C), 131.1, 129.1, 128.3, 127.8, 127.8, 122.9, 121.8, 120.7, 119.8, 118.4, 111.4, 109.4, 102.9, 92.8, 90.9, 31.0 ppm.

**HRMS** (ESI) *m/z*: [M+2(H<sub>2</sub>O)]<sup>+2</sup> calcd for [C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>]<sup>+2</sup> 184.0757; found 184.0751.



### 1-Methyl-2-(2-(*m*-tolylethynyl)phenyl)-1*H*-indole (**1i**):

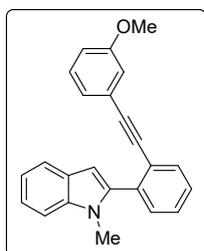
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1*H*-indole **7a** (135 mg, 0.4 mmol), 1-ethynyl-3-methylbenzene **8i** (69 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1i** (118.18 mg, 92%) as brown solid; mp = 78–80 °C. [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8i**) = 0.7, *R<sub>f</sub>*(**1i**) = 0.5 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>): *ν*<sub>max</sub> = 3048, 2924, 2207, 1926, 1699, 1457, 1159, 745 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.65 (m, 2H), 7.53 – 7.48 (m, 1H), 7.44 (ddd, *J* = 7.6, 7.8, 6.6 Hz, 3H), 7.31 (dd, *J* = 7.5, 7.6 Hz, 1H), 7.20 (dd, *J* = 7.8, 7.1 Hz, 1H), 7.15 – 6.99 (m, 3H), 6.91 (d, *J* = 0.6 Hz, 1H), 6.68 (s, 1H), 3.72 (s, 3H), 2.21 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.9, 137.9, 137.8, 135.4, 132.2, 132.0, 130.9, 129.2, 128.3, 128.2, 128.1, 128.1, 127.9, 124.1, 122.7, 121.5, 120.6, 119.6, 109.4, 102.5, 93.1, 88.2, 31.0, 21.1 ppm.

**HRMS** (ESI) *m/z*: [M+NH<sub>4</sub>]<sup>+</sup> calcd for [C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>]<sup>+</sup> 339.1856; found 339.1854.



### 2-(2-((3-Methoxyphenyl)ethynyl)phenyl)-1-methyl-1H-indole (1j):

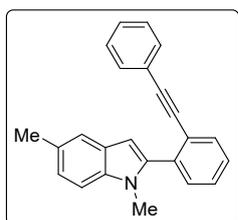
GP-2 was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 1-ethynyl-3-methoxybenzene **8j** (79 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:04) furnished the product **1a** (114.62 mg, 85%) as orange solid; mp = 68–70 °C. [TLC control (petroleum ether/ethyl acetate 96:04), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8j**) = 0.7, *R<sub>f</sub>*(**1j**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3055, 2945, 2208, 1927, 1585, 1429, 1228, 752 cm<sup>-1</sup>.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 – 7.68 (m, 2H), 7.55 – 7.49 (m, 1H), 7.48 – 7.44 (m, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.22 – 7.16 (m, 1H), 7.14 (dd, *J* = 7.9, 7.6 Hz, 1H), 6.88 – 6.80 (m, 2H), 6.70 (s, 1H), 6.57 (s, 1H), 3.73 (s, 3H), 3.57 (s, 3H) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 139.9, 137.7, 135.5, 131.9, 130.9, 129.5, 129.3, 128.2, 127.9, 125.0, 124.0, 123.8, 123.7, 121.6, 120.6, 119.6, 115.6, 109.4, 102.5, 92.9, 88.3, 55.0, 30.9 ppm.

HRMS (ESI) *m/z*: [M+K]<sup>+</sup> calcd for [C<sub>24</sub>H<sub>19</sub>KNO]<sup>+</sup> 376.1098; found 376.1118.



### 1,5-Dimethyl-2-(2-(phenylethynyl)phenyl)-1H-indole (1k):

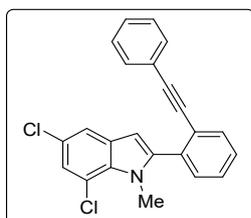
GP-2 was carried out with 2-(2-iodophenyl)-1,5-dimethyl-1H-indole **7b** (138.8 mg, 0.4 mmol), phenylacetylene **8a** (61 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1a** (113.12 mg, 92%) as brown viscous oil; [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7b**) = 0.6, *R<sub>f</sub>*(**8a**) = 0.7, *R<sub>f</sub>*(**1k**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3023, 2919, 2216, 1956, 1455, 1330, 1098, 751 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (dd, *J* = 7.8, 3.2 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.40 – 7.36 (m, 2H), 7.23 (d, *J* = 3.7 Hz, 1H), 7.22 – 7.15 (m, 5H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.54 (s, 1H), 3.65 (s, 3H), 2.47 (s, 3H) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.0, 136.4, 135.4, 132.3, 131.4 (2C), 131.1, 128.7, 128.2 (3C), 128.1 (2C), 128.0, 123.9, 123.2, 122.9, 120.2, 109.1, 102.1, 92.7, 88.5, 31.1, 21.5 ppm.

**HRMS (ESI)  $m/z$ :**  $[M+H]^+$  calcd for  $[C_{24}H_{20}N]^+$  322.1590; found 322.1587.



**5,7-Dichloro-1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole (11):**

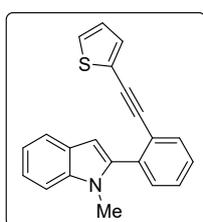
**GP-2** was carried out with 5,7-dichloro-2-(2-iodophenyl)-1-methyl-1H-indole **7c** (161 mg, 0.4 mmol), phenylacetylene **8a** (62 mg, 0.6 mmol),  $PdCl_2(PPh_3)_2$  (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol),  $Et_3N$  (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1a** (113.12 mg, 92%) as yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 98:2),  $R_f(7c) = 0.6$ ,  $R_f(8a) = 0.7$ ,  $R_f(11) = 0.5$  UV detection].

**IR (MIR-ATR, 4000–600  $cm^{-1}$ ):**  $\nu_{max} = 3064, 2950, 2216, 1957, 1457, 1269, 1034, 751 cm^{-1}$ .

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  7.64 – 7.59 (m, 1H), 7.44 (d,  $J = 1.9$  Hz, 1H), 7.40 – 7.37 (m, 3H), 7.23 – 7.16 (m, 5H), 7.14 (d,  $J = 1.9$  Hz, 1H), 6.49 (s, 1H), 3.91 (s, 3H) ppm.

**$^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  143.4, 134.2, 132.2, 131.9, 131.4 (2C), 131.2, 130.9, 128.7, 128.5, 128.4 (2C), 128.3, 124.9, 124.2, 123.1, 122.7, 118.8, 117.3, 102.9, 93.1, 87.9, 34.3 ppm.

**HRMS (ESI)  $m/z$ :**  $[M+NH_4]^+$  calcd for  $[C_{23}H_{19}Cl_2N_2]^+$  393.0920; found 393.0906.



**1-Methyl-2-(2-(thiophen-2-ylethynyl)phenyl)-1H-indole (1m):**

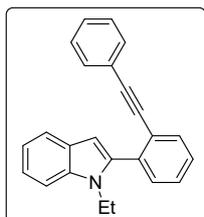
**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1H-indole **7a** (135 mg, 0.4 mmol), 2-ethynylthiophene **8k** (65 mg, 0.6 mmol),  $PdCl_2(PPh_3)_2$  (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol),  $Et_3N$  (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1a** (100.18 mg, 80%) as brown viscous oil; [TLC control (petroleum ether/ethyl acetate 98:2),  $R_f(7a) = 0.6$ ,  $R_f(8k) = 0.7$ ,  $R_f(1m) = 0.5$  UV detection].

**IR (MIR-ATR, 4000–600  $cm^{-1}$ ):**  $\nu_{max} = 3054, 2930, 1998, 1799, 1424, 1283, 1127, 750 cm^{-1}$ .

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.73 – 7.64 (m, 2H), 7.52 – 7.39 (m, 4H), 7.34 – 7.28 (m, 1H), 7.23 – 7.16 (m, 2H), 7.03 – 6.97 (m, 1H), 6.95 – 6.85 (m, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 3.73 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>) δ 139.7, 137.9, 134.9, 131.9, 131.8, 131.0, 128.2, 128.1, 127.9, 127.5, 127.0, 123.6, 122.9, 121.6, 120.6, 119.6, 109.5, 102.7, 92.3, 86.0, 31.1 ppm.

**HRMS** (ESI) *m/z*: [M+H<sub>2</sub>O]<sup>+</sup> calcd for [C<sub>21</sub>H<sub>17</sub>NOS]<sup>+</sup> 331.1025; found 331.1023.



**1-Ethyl-2-(2-(phenylethynyl)phenyl)-1H-indole (1n):**

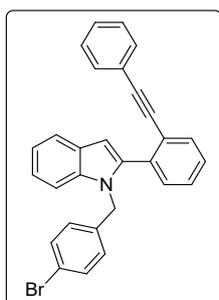
**GP-2** was carried out with 1-ethyl-2-(2-iodophenyl)-1H-indole **7d** (139 mg, 0.4 mmol), phenylacetylene **8a** (62 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1n** (90 mg, 70%) as brown viscous oil; [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7d**) = 0.6, *R<sub>f</sub>*(**8a**) = 0.7, *R<sub>f</sub>*(**1n**) = 0.5 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>): *v*<sub>max</sub> = 3054, 2931, 2245, 1953, 1676, 1371, 1138, 752 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 7.72 – 7.63 (m, 1H), 7.48 – 7.42 (m, 1H), 7.43 – 7.36 (m, 3H), 7.31 (dd, *J* = 10.6, 6.6 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.15 (m, 5H), 6.62 (d, *J* = 0.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>) δ 139.0, 136.5, 135.6, 132.1, 131.4 (2C), 130.9, 128.2 (4C), 128.1, 126.5, 124.0, 122.9, 121.4, 120.7, 119.4, 109.7, 103.1, 92.9, 88.3, 38.8, 15.1 ppm.

**HRMS** (ESI) *m/z*: [M]<sup>+</sup> calcd for [C<sub>24</sub>H<sub>19</sub>N]<sup>+</sup> 321.1512; found 321.1518.



**1-(4-Bromobenzyl)-2-(2-(phenylethynyl)phenyl)-1H-indole (1o):**

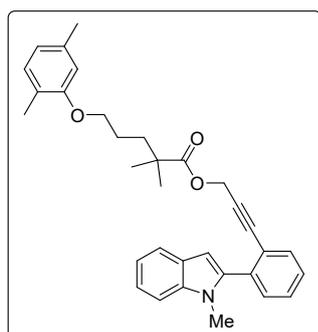
**GP-2** was carried out with 1-(4-bromobenzyl)-2-(2-iodophenyl)-1*H*-indole **7e** (195 mg, 0.4 mmol), phenylacetylene **8a** (62 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **1o** (166 mg, 90%) as brown solid; mp = 108–110 °C. [TLC control (petroleum ether/ethyl acetate 98:2), *R<sub>f</sub>*(**7e**) = 0.6, *R<sub>f</sub>*(**8a**) = 0.7, *R<sub>f</sub>*(**1o**) = 0.4 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3051, 2922, 2319, 1596, 1397, 1261, 1069, 745 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 – 7.70 (m, 1H), 7.69 – 7.63 (m, 1H), 7.44 – 7.38 (m, 2H), 7.36 (dd, *J* = 7.3, 7.8 Hz, 2H), 7.26 – 7.17 (m, 9H), 6.80 – 6.71 (m, 3H), 5.30 (s, 2H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  139.5, 137.1 (2C), 134.9, 132.3, 131.5 (2C), 131.4 (2C), 130.9, 128.3 (2C), 128.9 (2C), 128.2, 127.9 (3C), 124.0, 122.9, 121.9, 120.8, 120.8, 120.0, 110.2, 103.9, 93.1, 88.3, 47.1 ppm.

**HRMS** (ESI) *m/z*: [M+H<sub>2</sub>O]<sup>+</sup> calcd for [C<sub>29</sub>H<sub>22</sub>BrNO]<sup>+</sup> 479.0879; found 481.0859.



### **3-(2-(1-Methyl-1*H*-indol-2-yl)phenyl)prop-2-yn-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**1p**):**

**GP-2** was carried out with 2-(2-iodophenyl)-1-methyl-1*H*-indole **7a** (135 mg, 0.4 mmol), prop-2-yn-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **8m** (296 mg, 0.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5) furnished the product **1q** (176 mg, 68%) as yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 95:5), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8m**) = 0.6, *R<sub>f</sub>*(**1q**) = 0.3 UV detection].

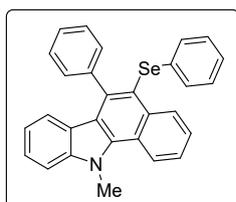
**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3050, 2928, 2204, 1731, 1508, 1260, 1128, 749 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 4.0 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.31 – 7.27 (m, 1H), 7.17 (dd, *J* = 7.8, 7.1 Hz, 1H), 7.03 (d,

$J = 7.4$  Hz, 1H), 6.69 (d,  $J = 7.4$  Hz, 1H), 6.66 – 6.54 (m, 2H), 4.75 (s, 2H), 3.86 (t,  $J = 4.6$  Hz, 2H), 3.69 (s, 3H), 2.34 (s, 3H), 2.19 (s, 3H), 1.73 – 1.54 (m, 4H), 1.15 (s, 6H) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.8, 156.9, 139.5, 137.8, 136.4, 135.2, 132.8, 131.2, 130.2, 128.5, 128.0, 127.8, 123.5, 122.8, 121.6, 120.6, 120.5, 119.6, 111.9, 109.6, 102.4, 86.4, 84.9, 67.8, 52.6, 41.9, 36.8, 30.9, 24.9, 24.9 (2C), 21.4, 15.7 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}]^+$  calcd for  $[\text{C}_{33}\text{H}_{35}\text{NO}_3]^+$  493.2611; found 493.2603.



### 11-Methyl-6-phenyl-5-(phenylselanyl)-11H-benzo[a]carbazole (3aa):

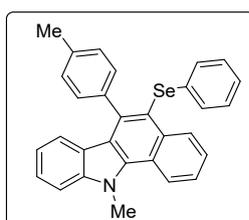
GP-2 was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (77 mg, 0.25 mmol), 1,2-diphenyldisilane **2a** (39 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 98:02) furnished the product **3aa** (106 mg, 92%) as a yellow solid, mp = 184–186 °C. [TLC control (petroleum ether/ethyl acetate 98:02),  $R_f$ (**1a**) = 0.5,  $R_f$ (**2a**) = 0.9,  $R_f$ (**3aa**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3055, 2922, 1944, 1728, 1569, 1433, 1257, 731  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (dd,  $J = 8.5, 0.9$  Hz, 1H), 8.83 (d,  $J = 8.4$  Hz, 1H), 7.65 (ddd,  $J = 8.4, 6.9, 1.4$  Hz, 1H), 7.61 – 7.46 (m, 5H), 7.42 (ddd,  $J = 8.3, 7.1, 1.1$  Hz, 1H), 7.33 – 7.29 (m, 2H), 7.09 – 6.91 (m, 6H), 6.49 (dd,  $J = 8.0, 0.7$  Hz, 1H), 4.49 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.2, 142.5, 141.0, 136.7, 135.2, 134.3, 130.9, 128.8 (2C), 128.8 (3C), 128.5 (2C), 128.3 (2C), 127.5, 126.2, 125.4, 125.1, 124.8, 122.9, 122.8, 122.5, 121.9, 119.9, 118.5, 108.9, 34.4 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $[\text{C}_{29}\text{H}_{21}\text{NNaSe}]^+$  486.0731; found 486.0739.



### 11-Methyl-5-(phenylselanyl)-6-(p-tolyl)-11H-benzo[a]carbazole (3ba):

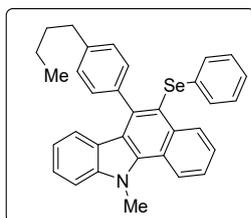
**GP-2** was carried out with 1-methyl-2-(2-(*p*-tolylethynyl)phenyl)-1*H*-indole **1b** (80.35 mg, 0.25 mmol), 1,2-diphenyldiselane **2a** (39 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3ba** (102 mg, 86%) as a orange solid, mp = 188–190 °C. [TLC control (petroleum ether/ethyl acetate 97:03), *R<sub>f</sub>*(**1b**) = 0.5, *R<sub>f</sub>*(**2a**) = 0.9, *R<sub>f</sub>*(**3ba**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3053, 2923, 1788, 1570, 1433, 1223, 1068, 737 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.87 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 7.64 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.42 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.06 – 7.01 (m, 5H), 7.00 – 6.96 (m, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.49 (s, 3H), 2.51 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.3, 141.0, 139.5, 137.1, 136.7, 135.3, 134.3, 131.0, 129.1 (2C), 128.8 (2C), 128.6 (2C), 128.4 (2C), 126.2, 125.3, 125.0, 124.7, 123.1, 122.8, 122.5, 122.33, 122.1, 119.8, 118.7, 108.8, 34.5, 21.6 ppm.

**HRMS** (ESI) *m/z*: [M+2(H<sub>2</sub>O)]<sup>+2</sup> calcd for [C<sub>30</sub>H<sub>27</sub>NO<sub>2</sub>Se]<sup>+2</sup> 256.5598; found 256.5589.



#### **6-(4-Butylphenyl)-11-methyl-5-(phenylselanyl)-11*H*-benzo[*a*]carbazole (**3ca**):**

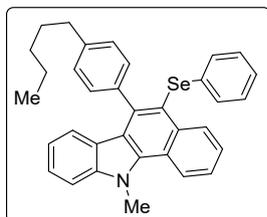
**GP-2** was carried out with 2-(2-((4-butylphenyl)ethynyl)phenyl)-1-methyl-1*H*-indole **1c** (91 mg, 0.25 mmol), 1,2-diphenyldiselane **2a** (39 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 98:02) furnished the product **3ca** (98 mg, 77%) as a yellow solid, mp = 160–162 °C. [TLC control (petroleum ether/ethyl acetate 98:02), *R<sub>f</sub>*(**1c**) = 0.5, *R<sub>f</sub>*(**2a**) = 0.9, *R<sub>f</sub>*(**3ca**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3054, 2859, 2211, 1914, 1679, 1447, 1266, 751 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.88 (dd, *J* = 8.5, 0.9 Hz, 1H), 8.82 (d, *J* = 8.3 Hz, 1H), 7.64 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.05 – 6.99 (m, 5H), 6.98 – 6.91 (m, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 4.49 (s, 3H), 2.81 – 2.63 (m, 2H), 1.78 – 1.70 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 142.1, 141.0, 139.7, 136.7, 135.3, 134.3, 131.3, 131.0, 128.8 (2C), 128.6 (4C), 128.4 (2C), 126.1, 125.3, 125.0, 124.7, 123.1, 122.8, 122.5, 122.1, 119.8, 118.8, 108.8, 35.5, 34.4, 33.5, 22.3, 14.1 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}_2\text{O}]^+$  calcd for  $[\text{C}_{33}\text{H}_{31}\text{NOSe}]^+$  537.1565; found 537.1582.



**11-Methyl-6-(4-pentylphenyl)-5-(phenylselanyl)-11H-benzo[a]carbazole (3da):**

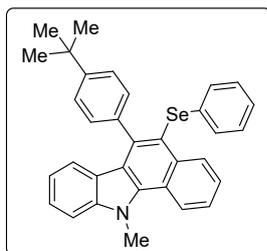
GP-2 was carried out with 1-methyl-2-(2-((4-pentylphenyl)ethynyl)phenyl)-1H-indole **1d** (94.3 mg, 0.25 mmol), 1,2-diphenyldiselenane **2a** (39 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 98:02) furnished the product **3da** (100 mg, 75%) as a yellow solid, mp = 156–158 °C. [TLC control (petroleum ether/ethyl acetate 98:02),  $R_f$ (**1d**) = 0.5,  $R_f$ (**2a**) = 0.9,  $R_f$ (**3da**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3056, 2922, 2246, 1794, 1569, 1466, 1070, 726  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (d,  $J$  = 8.5 Hz, 1H), 8.81 (d,  $J$  = 8.4 Hz, 1H), 7.64 (dd,  $J$  = 7.5, 7.8 Hz, 1H), 7.58 (dd,  $J$  = 7.6, 7.8 Hz, 1H), 7.54 (d,  $J$  = 8.3 Hz, 1H), 7.42 (t,  $J$  = 7.7 Hz, 1H), 7.30 (d,  $J$  = 7.8 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.05 (s, 5H), 6.97 (dd,  $J$  = 7.5, 7.6 Hz, 1H), 6.51 (d,  $J$  = 8.0 Hz, 1H), 4.47 (s, 3H), 2.78 (t,  $J$  = 7.6 Hz, 2H), 1.92 – 1.59 (m, 2H), 1.48 – 1.31 (m, 4H), 0.99 (t,  $J$  = 6.8 Hz, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4, 141.1, 140.0, 138.7, 135.7, 134.3, 133.3, 130.0, 127.8 (2C), 127.6 (4C), 127.4 (2C), 125.1, 124.3, 124.0, 123.7, 122.1, 121.8, 121.5, 121.1, 118.7, 117.8, 117.7, 107.8, 34.8, 33.4, 30.5, 30.0, 21.6, 13.2 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calcd for  $[\text{C}_{34}\text{H}_{31}\text{NNaSe}]^+$  556.1514; found 556.1502.



**6-(4-(tert-butyl)phenyl)-11-methyl-5-(phenylselanyl)-11H-benzo[a]carbazole (3ea):**

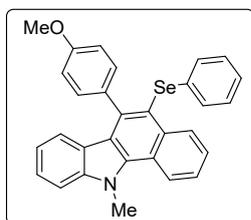
**GP-2** was carried out with 2-(2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)-1-methyl-1*H*-indole **1e** (91 mg, 0.25 mmol), 1,2-diphenyldiselenane **2a** (39 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 98:02) furnished the product **3ea** (116 mg, 90%) as a red solid, mp = 218–220 °C. [TLC control (petroleum ether/ethyl acetate 98:02), *R<sub>f</sub>* (**1e**) = 0.5, *R<sub>f</sub>* (**2a**) = 0.9, *R<sub>f</sub>* (**3ea**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 2958, 2215, 1930, 1575, 1463, 1331, 1021, 735 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.89 (d, *J* = 8.5 Hz, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.59 – 7.52 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.41 (dd, *J* = 7.6, 7.8 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.04 (s, 5H), 6.95 (dd, *J* = 7.5, 7.6 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 4.48 (s, 3H), 1.45 (s, 9H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 144.4, 141.0, 139.4, 136.7, 135.4, 134.3, 131.1, 128.8 (2C), 128.7 (2C), 128.4 (2C), 126.1, 125.3, 125.2, 125.1 (2C), 124.7, 123.1, 122.8, 122.5, 122.1, 119.8, 118.9, 118.8, 108.8, 34.7, 34.5, 31.5 (3C) ppm.

**HRMS** (ESI) *m/z*: [M+NH<sub>4</sub>]<sup>+</sup> calcd for [C<sub>33</sub>H<sub>33</sub>N<sub>2</sub>Se]<sup>+</sup> 537.1803; found 537.1807.



#### **6-(4-Methoxyphenyl)-11-methyl-5-(phenylselenanyl)-11*H*-benzo[*a*]carbazole (**3fa**):**

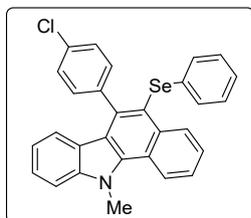
**GP-2** was carried out with 2-(2-((4-methoxyphenyl)ethynyl)phenyl)-1-methyl-1*H*-indole **1f** (84 mg, 0.25 mmol), 1,2-diphenyldiselenane **2a** (39 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 96:04) furnished the product **3fa** (105 mg, 86%) as a orange solid, mp = 180–182 °C. [TLC control (petroleum ether/ethyl acetate 96:04), *R<sub>f</sub>* (**1f**) = 0.5, *R<sub>f</sub>* (**2a**) = 0.9, *R<sub>f</sub>* (**3fa**) = 0.2, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3057, 2941, 2247, 1885, 1606, 1242, 1027, 729 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.88 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.59 – 7.53 (m, 2H), 7.45 – 7.40 (m, 1H), 7.24 – 7.19 (m, 2H), 7.08 – 6.97 (m, 8H), 6.62 (d, *J* = 8.0 Hz, 1H), 4.48 (s, 3H), 3.93 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.9, 143.9, 140.9, 136.7, 135.3, 134.9, 134.3, 134.0, 131.0, 129.9, 128.8 (2C), 128.4, 126.2, 125.3, 125.0, 124.8, 123.1, 122.8, 122.5, 122.1, 119.9, 114.1, 113.6 (2C), 108.8, 55.2, 34.4 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+2\text{H}]^{+2}$  calcd for  $[\text{C}_{30}\text{H}_{25}\text{NOSe}]^{+2}$  247.5545; found 247.5530.



#### 6-(4-Chlorophenyl)-11-methyl-5-(phenylselanyl)-11H-benzo[a]carbazole (**3ga**):

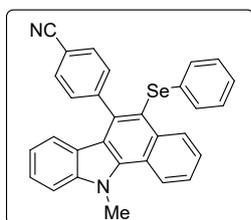
GP-2 was carried out with 2-(2-((4-chlorophenyl)ethynyl)phenyl)-1-methyl-1H-indole **1g** (85 mg, 0.25 mmol), 1,2-diphenyldiselane **2a** (39 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 98:02) furnished the product **3ga** (98 mg, 79%) as a yellow solid, mp = 178–180 °C. [TLC control (petroleum ether/ethyl acetate 98:02),  $R_f$  (**1g**) = 0.5,  $R_f$  (**2a**) = 0.9,  $R_f$  (**3ga**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3058, 2926, 2246, 1725, 1570, 1379, 1018, 731  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 (d,  $J$  = 8.5 Hz, 1H), 8.82 (d,  $J$  = 8.4 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.63 – 7.54 (m, 2H), 7.46 (d,  $J$  = 8.1 Hz, 3H), 7.23 (d,  $J$  = 8.3 Hz, 2H), 7.08 – 6.96 (m, 6H), 6.61 (d,  $J$  = 8.1 Hz, 1H), 4.47 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 141.0, 140.8, 136.8, 135.0, 134.3, 133.4, 130.9, 130.3 (2C), 128.9 (2C), 128.6 (2C), 128.4 (2C), 126.3, 125.6, 125.2, 124.9, 122.8, 122.7, 122.5, 121.8, 120.0, 118.7, 118.2, 108.9, 34.5 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}_2\text{O}]^+$  calcd for  $[\text{C}_{29}\text{H}_{22}\text{ClNOSe}]^+$  515.0550; found 515.0550.



#### 4-(11-Methyl-5-(phenylselanyl)-11H-benzo[a]carbazol-6-yl)benzonitrile (**3ha**):

GP-2 was carried out with 4-((2-(1-methyl-1H-indol-2-yl)phenyl)ethynyl)benzonitrile **1h** (83 mg, 0.25 mmol), 1,2-diphenyldiselane **2a** (39 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column

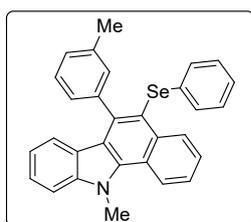
chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ha** (73 mg, 60%) as a yellow solid, mp = 198–200 °C. [TLC control (petroleum ether/ethyl acetate 95:05),  $R_f$  (**1h**) = 0.5,  $R_f$  (**2a**) = 0.9,  $R_f$  (**3ha**) = 0.2, UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3056, 2924, 2224, 1732, 1464, 1330, 1264, 735  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 (d,  $J$  = 8.5 Hz, 1H), 8.84 (d,  $J$  = 8.4 Hz, 1H), 7.74 (d,  $J$  = 8.3 Hz, 2H), 7.70 (ddd,  $J$  = 8.3, 6.9, 1.2 Hz, 1H), 7.63 (ddd,  $J$  = 8.1, 6.9, 1.1 Hz, 1H), 7.58 (d,  $J$  = 8.3 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.37 (d,  $J$  = 8.3 Hz, 2H), 7.08 – 7.03 (m, 3H), 7.00 (dd,  $J$  = 11.2, 3.9 Hz, 1H), 6.95 (dd,  $J$  = 6.7, 3.0 Hz, 2H), 6.43 (d,  $J$  = 8.0 Hz, 1H), 4.49 (s, 3H) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1, 142.0, 141.1, 136.9, 134.7, 134.3, 132.1 (2C), 130.9, 129.9 (2C), 128.9 (2C), 128.5 (2C), 126.6, 125.9, 125.5, 125.1, 122.9, 122.6, 122.3, 121.3, 120.2, 119.1, 118.2, 117.6, 111.4, 109.2, 34.5 ppm.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{K}]^+$  calcd for  $[\text{C}_{30}\text{H}_{20}\text{KN}_2\text{Se}]^+$  527.0423; found 527.0441.



### 11-Methyl-5-(phenylselanyl)-6-(*m*-tolyl)-11*H*-benzo[*a*]carbazole (**3ia**):

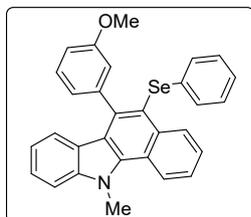
**GP-2** was carried out with 1-methyl-2-(2-(*m*-tolylethynyl)phenyl)-1*H*-indole **1i** (80 mg, 0.25 mmol), 1,2-diphenyldisilane **2a** (39 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3ia** (86 mg, 72%) as an orange solid, mp = 158–160 °C. [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$  (**1i**) = 0.5,  $R_f$  (**2a**) = 0.9,  $R_f$  (**3ia**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3058, 2924, 2247, 1573, 1379, 1251, 1026, 725  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (dd,  $J$  = 8.5, 0.9 Hz, 1H), 8.74 (d,  $J$  = 8.1 Hz, 1H), 7.56 (ddd,  $J$  = 8.4, 6.8, 1.3 Hz, 1H), 7.49 (ddd,  $J$  = 8.2, 6.8, 1.2 Hz, 1H), 7.47 (d,  $J$  = 8.3 Hz, 1H), 7.34 (ddd,  $J$  = 8.3, 7.1, 1.1 Hz, 1H), 7.29 (dd,  $J$  = 7.5, 7.8 Hz, 1H), 7.24 (d,  $J$  = 7.7 Hz, 1H), 7.03 (d,  $J$  = 7.4 Hz, 1H), 6.99 (s, 1H), 6.97 – 6.92 (m, 5H), 6.89 (ddd,  $J$  = 8.0, 7.1, 0.9 Hz, 1H), 6.44 (d,  $J$  = 8.0 Hz, 1H), 4.40 (s, 3H), 2.27 (s, 3H) ppm.

$^{13}\text{C}\{\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 142.3, 141.0, 137.8, 136.7, 135.4, 134.4, 131.0, 129.6, 128.7 (2C), 128.7 (2C), 128.2, 128.2, 126.2, 125.8, 125.3, 125.1, 124.7, 123.0, 122.8, 122.5, 122.1, 119.9, 118.7, 118.6, 108.8, 34.5, 21.6 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+2(\text{H}_2\text{O})]^{+2}$  calcd for  $[\text{C}_{30}\text{H}_{27}\text{NO}_2\text{Se}]^{+2}$  256.5598; found 256.5589.



**6-(3-Methoxyphenyl)-11-methyl-5-(phenylselanyl)-11H-benzo[a]carbazole (3ja):**

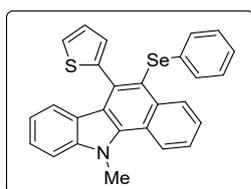
GP-2 was carried out with 2-(2-((4-butylphenyl)ethynyl)phenyl)-1-methyl-1H-indole **1j** (84 mg, 0.25 mmol), 1,2-diphenyldisilane **2a** (39 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 96:04) furnished the product **3ja** (98 mg, 80%) as a brown solid, mp = 166–168 °C. [TLC control (petroleum ether/ethyl acetate 96:04),  $R_f$  (**1j**) = 0.5,  $R_f$  (**2a**) = 0.9,  $R_f$  (**3ja**) = 0.2, UV detection].

IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3058, 2937, 2221, 1935, 1731, 1473, 1252, 742  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 (dd,  $J$  = 8.5, 1.0 Hz, 1H), 8.83 (d,  $J$  = 8.3 Hz, 1H), 7.66 (ddd,  $J$  = 8.4, 6.9, 1.3 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.46 – 7.37 (m, 2H), 7.09 – 6.97 (m, 7H), 6.95 – 6.90 (m, 1H), 6.79 (dd,  $J$  = 2.5, 1.5 Hz, 1H), 6.61 (d,  $J$  = 8.0 Hz, 1H), 4.49 (s, 3H), 3.61 (s, 3H) ppm.

$^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 143.9, 143.7, 141.0, 136.7, 135.6, 134.4, 130.9, 129.38, 128.8 (3C), 128.4 (2C), 126.3, 125.4, 125.0, 124.8, 122.9, 122.8, 122.5, 122.1, 121.2, 119.9, 118.4, 114.0, 113.5, 108.9, 55.0, 34.5 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}_2\text{O}]^+$  calcd for  $[\text{C}_{30}\text{H}_{25}\text{NO}_2\text{Se}]^+$  511.1045; found 511.1032.



**11-Methyl-5-(phenylselanyl)-6-(thiophen-2-yl)-11H-benzo[a]carbazole (3ka):**

GP-2 was carried out with 1-methyl-2-(2-(thiophen-2-ylethynyl)phenyl)-1H-indole **1k** (78 mg, 0.25 mmol), 1,2-diphenyldisilane **2a** (39 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in

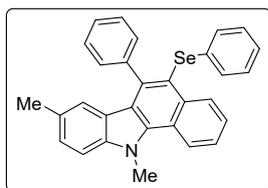
CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3ka** (76 mg, 65%) as a brown solid, mp = 200–202 °C. [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$ (**1k**) = 0.5,  $R_f$ (**2a**) = 0.9,  $R_f$ (**3ka**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3050, 2923, 1720, 1503, 1370, 1162, 1060, 733 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.89 (dd,  $J$  = 8.5, 0.7 Hz, 1H), 8.80 (d,  $J$  = 8.4 Hz, 1H), 7.65 (ddd,  $J$  = 8.3, 6.8, 1.3 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.52 (dd,  $J$  = 5.2, 1.1 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.21 (dd,  $J$  = 5.2, 3.4 Hz, 1H), 7.12 – 7.02 (m, 6H), 7.00 (dd,  $J$  = 3.4, 1.1 Hz, 1H), 6.70 (d,  $J$  = 8.0 Hz, 1H), 4.46 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  143.1, 141.0, 136.6, 136.3, 135.3, 134.1, 131.3, 128.9 (3C), 128.6 (2C), 127.0, 126.9, 126.3, 125.9, 125.6, 125.2, 125.1, 123.3, 122.7, 122.5, 121.9, 120.2, 119.5, 108.9, 34.5 ppm.

**HRMS** (ESI)  $m/z$ : [M+Na]<sup>+</sup> calcd for [C<sub>27</sub>H<sub>19</sub>NNaSSe]<sup>+</sup> 492.0296; found 492.0260.



### **8,11-Dimethyl-6-phenyl-5-(phenylselanyl)-11H-benzo[a]carbazole (**3la**):**

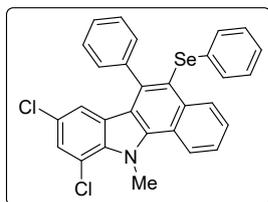
**GP-2** was carried out with 1,5-dimethyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1l** (80 mg, 0.25 mmol), 1,2-diphenyldisilane **2a** (39 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3la** (103 mg, 87%) as a brown solid, mp = 190–192 °C. [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$ (**1m**) = 0.5,  $R_f$ (**2a**) = 0.9,  $R_f$ (**3la**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3058, 2922, 2178, 1871, 1571, 1434, 1262, 746 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.89 (dd,  $J$  = 8.5, 0.8 Hz, 1H), 8.83 – 8.78 (m, 1H), 7.64 (ddd,  $J$  = 8.4, 7.9, 1.4 Hz, 1H), 7.59 – 7.46 (m, 4H), 7.43 (d,  $J$  = 8.4 Hz, 1H), 7.31 (d,  $J$  = 6.7 Hz, 2H), 7.24 (dd,  $J$  = 8.4, 1.4 Hz, 1H), 7.06 – 7.00 (m, 5H), 6.21 (s, 1H), 4.45 (s, 3H), 2.24 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.3, 142.6, 139.4, 136.8, 135.3, 134.2, 130.9, 129.0, 128.8 (2C), 128.8 (2C), 128.5 (2C), 128.3 (2C), 127.4, 126.2, 126.1, 125., 125.04, 123.0, 122.9, 122.5, 121.9, 118.3, 118.0, 108.5, 34.5, 21.5 ppm.

**HRMS (ESI)  $m/z$ :**  $[M+H]^+$  calcd for  $[C_{30}H_{24}NSe]^+$  478.1068; found 478.1096.



**8,10-Dichloro-11-methyl-6-phenyl-5-(phenylselanyl)-11H-benzo[a]carbazole (3ma):**

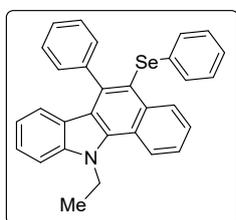
**GP-2** was carried out with 5,7-dichloro-1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1m** (94 mg, 0.25 mmol), 1,2-diphenyldiselane **2a** (39 mg, 0.125 mmol), and  $LiClO_4$  (64 mg, 0.1 M) in  $CH_3CN$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 98:02) furnished the product **3ma** (106 mg, 80%) as a orange solid, mp = 200–202 °C. [TLC control (petroleum ether/ethyl acetate 98:02),  $R_f$ (**1m**) = 0.5,  $R_f$ (**2a**) = 0.9,  $R_f$ (**3ma**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600  $cm^{-1}$ ):  $\nu_{max}$  = 3060, 2924, 2275, 1724, 1460, 1275, 1069, 747  $cm^{-1}$ .

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.88 (dd,  $J$  = 8.4, 1.0 Hz, 1H), 8.63 – 8.59 (m, 1H), 7.67 (ddd,  $J$  = 8.4, 6.9, 1.4 Hz, 1H), 7.61 (ddd,  $J$  = 8.2, 6.9, 1.3 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.51 – 7.46 (m, 2H), 7.33 (d,  $J$  = 2.0 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.07 – 7.03 (m, 3H), 7.03 – 6.99 (m, 2H), 6.22 (d,  $J$  = 1.9 Hz, 1H), 4.63 (s, 3H) ppm.

**$^{13}C\{^1H\}$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  143.4, 141.5, 140.3, 136.9, 134.9, 134.8, 131.1, 128.9 (2C), 128.7 (2C), 128.6 (2C), 128.6 (2C), 127.9, 127.3, 127.0, 126.3, 125.7, 125.5, 125.3, 123.3, 122.3, 120.6, 120.4, 118.2, 117.3, 38.5 ppm.

**HRMS (ESI)  $m/z$ :**  $[M+NH_4]^+$  calcd for  $[C_{29}H_{23}Cl_2N_2Se]^+$  549.0398; found 549.0391.



**11-Ethyl-6-phenyl-5-(phenylselanyl)-11H-benzo[a]carbazole (3na):**

**GP-2** was carried out with 1-ethyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1na** (80 mg, 0.25 mmol), 1,2-diphenyldiselane **2a** (39 mg, 0.125 mmol), and  $LiClO_4$  (64 mg, 0.1 M) in  $CH_3CN$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3na** (99 mg, 83%) as a brown

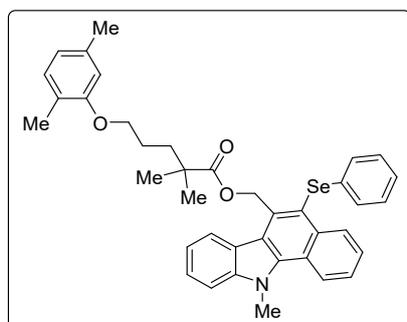
viscous oil; [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$ (**1n**) = 0.5,  $R_f$ (**2a**) = 0.7,  $R_f$ (**3na**) = 0.2, UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3056, 2926, 2248, 1951, 1512, 1470, 1025, 802  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (d,  $J$  = 8.5 Hz, 1H), 8.64 (d,  $J$  = 8.5 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.62 – 7.55 (m, 2H), 7.52 (d,  $J$  = 7.2 Hz, 1H), 7.48 (dd,  $J$  = 11.2, 4.1 Hz, 2H), 7.42 (dd,  $J$  = 7.7, 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.09 – 7.00 (m, 5H), 6.97 (dd,  $J$  = 7.6, 7.8 Hz, 1H), 6.47 (d,  $J$  = 8.1 Hz, 1H), 4.95 (q,  $J$  = 7.2 Hz, 2H), 1.79 (t,  $J$  = 7.2 Hz, 3H) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 142.5, 140.3, 135.6, 135.3, 134.3, 131.2, 128.8 (4C), 128.5 (2C), 128.3 (2C), 127.5, 126.2, 125.7, 125.1, 124.8, 123.1, 122.4, 122.2, 122.1, 119.9, 118.7, 118.6, 108.7, 40.9, 15.0 ppm.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}_2\text{O}]^+$  calcd for  $[\text{C}_{30}\text{H}_{24}\text{NSe}]^+$  478.1068; found 478.1104.



**(11-Methyl-5-(phenylselanyl)-11H-benzo[a]carbazol-6-yl)methyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3pa):**

**5-(2,5-**

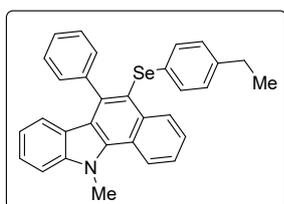
**GP-2** was carried out with 3-(2-(1-methyl-1H-indol-2-yl)phenyl)prop-2-yn-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **1p** (123 mg, 0.25 mmol), 1,2-diphenyldisilane **2a** (39 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3pa** (113 mg, 70%) as a yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$ (**1p**) = 0.5,  $R_f$ (**2a**) = 0.7,  $R_f$ (**3pa**) = 0.2, UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 2924, 2242, 1731, 1577, 1263, 1080, 747  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J$  = 7.9 Hz, 1H), 7.56 (dd,  $J$  = 7.9, 3.2 Hz, 1H), 7.42 (d,  $J$  = 8.1 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.20 – 7.12 (m, 3H), 7.10 – 7.01 (m, 3H), 7.00 (d,  $J$  = 7.5 Hz, 1H), 6.66 (d,  $J$  = 7.5 Hz, 1H), 6.57 (s, 1H), 4.65 (q,  $J$  = 15.8 Hz, 2H), 3.80 (d,  $J$  = 6.2 Hz, 2H), 3.69 (s, 3H), 2.31 (s, 3H), 2.15 (s, 3H), 1.69 – 1.54 (m, 4H), 1.05 (s, 3H), 1.03 (s, 3H) ppm.

$^{13}\text{C}\{\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9, 156.9, 144.4, 137.6, 136.4, 134.3, 133.9, 132.4, 132.0, 130.3, 130.2 (2C), 128.8, 128.7 (2C), 128.5 (2C), 128.3, 125.2, 123.7, 123.5, 122.6, 120.7, 120.6 (2C), 111.9, 109.8, 86.7, 84.6, 67.8, 52.5, 41.9, 36.8, 31.5, 24.9, 24.8, 24.8, 21.4, 15.7 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+2(\text{NH}_4)]^{+2}$  calcd for  $[\text{C}_{39}\text{H}_{47}\text{N}_3\text{O}_3\text{Se}]^{+2}$  342.6386; found 342.6402.



### 5-((4-Ethylphenyl)selanyl)-11-methyl-6-phenyl-11H-benzo[a]carbazole (**3ab**):

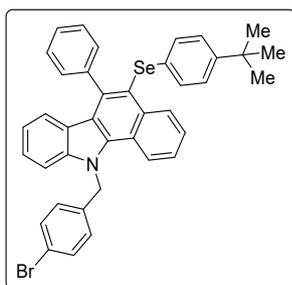
GP-2 was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (77 mg, 0.25 mmol), 1,2-bis(4-ethylphenyl)diselane **2b** (46 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3ab** (102 mg, 83%) as a brown crystalline, mp = 176–178 °C. [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$ (**1a**) = 0.5,  $R_f$ (**2b**) = 0.9,  $R_f$ (**3ab**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3053, 2959, 2340, 1943, 1723, 1478, 1120, 733  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 (dd,  $J$  = 8.4, 1.0 Hz, 1H), 8.81 (d,  $J$  = 8.3 Hz, 1H), 7.65 (ddd,  $J$  = 8.4, 6.9, 1.4 Hz, 1H), 7.61 – 7.46 (m, 5H), 7.42 (ddd,  $J$  = 8.2, 7.1, 1.1 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.01 – 6.93 (m, 3H), 6.89 (d,  $J$  = 8.4 Hz, 2H), 6.49 (d,  $J$  = 8.0 Hz, 1H), 4.48 (s, 3H), 2.51 (q,  $J$  = 7.6 Hz, 2H), 1.14 (t,  $J$  = 7.6 Hz, 3H) ppm.

$^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 142.5, 141.2, 140.9, 136.6, 134.3, 131.5, 131.1, 128.9 (2C), 128.7 (2C), 128.4 (2C), 128.3 (2C), 127.5, 126.2, 125.3, 124.7, 122.9, 122.8, 122.4, 121.9, 119.8, 118.9, 118.5, 108.8, 34.4, 28.2, 15.4 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{NH}_4]^+$  calcd for  $[\text{C}_{31}\text{H}_{29}\text{N}_2\text{Se}]^+$  509.1490; found 509.1514.



**11-(4-Bromobenzyl)-5-((4-(*tert*-butyl)phenyl)selanyl)-6-phenyl-11*H*-benzo[*a*]carbazole (3oc):**

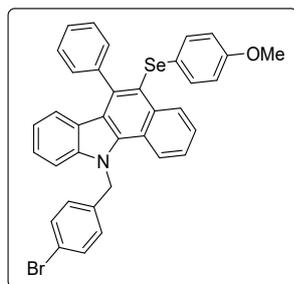
**GP-2** was carried out with 1-(4-bromobenzyl)-2-(2-((3-methoxyphenyl)ethynyl)phenyl)-1*H*-indole **1o** (115 mg, 0.25 mmol), 1,2-bis(4-(*tert*-butyl)phenyl)diselane **2c** (53 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 96:04) furnished the product **3oc** (118 mg, 70%) as a yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 97:03), *R<sub>f</sub>*(**1o**) = 0.5, *R<sub>f</sub>*(**2c**) = 0.9, *R<sub>f</sub>*(**3oc**) = 0.2, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 2960, 2245, 1706, 1588, 1390, 1243, 1072, 728 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.95 (d, *J* = 7.9 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.51 (m, 6H), 7.47 (dd, *J* = 7.6, 7.8 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.10 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.06 – 6.97 (m, 3H), 6.60 – 6.46 (m, 1H), 5.97 (s, 2H), 1.24 (s, 9H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  148.3, 143.9, 142.3, 141.3, 136.4, 136.2, 135.4, 134.5, 132.3 (2C), 131.3, 131.2, 128.9 (2C), 128.6 (2C), 128.3 (2C), 127.8 (2C), 127.6 (2C), 126.3, 125.9 (2C), 125.7, 125.2, 123.4, 122.1, 122.1, 121.6, 120.5, 119.1, 116.4, 109.0, 49.8, 34.3, 31.2 (3C) ppm.

**HRMS** (ESI) *m/z*: [M+H<sub>2</sub>O]<sup>+</sup> calcd for [C<sub>39</sub>H<sub>34</sub>BrNOSe]<sup>+</sup> 691.0984; found 691.1000.



**11-(4-Bromobenzyl)-5-((4-methoxyphenyl)selanyl)-6-phenyl-11*H*-benzo[*a*]carbazole (3od):**

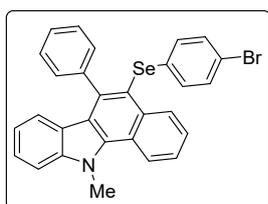
**GP-2** was carried out with 1-(4-bromobenzyl)-2-(2-((3-methoxyphenyl)ethynyl)phenyl)-1*H*-indole **1o** (115 mg, 0.25 mmol), 1,2-bis(4-methoxyphenyl)diselane **2d** (46.5 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 96:04) furnished the product **3od** (124 mg, 77%) as a yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 97:03), *R<sub>f</sub>*(**1o**) = 0.5, *R<sub>f</sub>*(**2d**) = 0.9, *R<sub>f</sub>*(**3od**) = 0.2, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3054, 2929, 2328, 1732, 1487, 1241, 1072, 738 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.97 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.64 – 7.47 (m, 6H), 7.37 – 7.35 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 3H), 7.03 (d, *J* = 8.9 Hz, 3H), 6.69 – 6.61 (m, 2H), 6.55 (d, *J* = 8.1 Hz, 1H), 5.96 (s, 2H), 3.70 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>) δ 157.9, 143.8, 142.4, 141.3, 136.3, 136.2, 134.4, 132.3 (2C), 131.2, 130.8 (2C), 129.0 (2C), 128.7 (2C), 127.8 (2C), 127.6, 126.2, 125.7, 125.2, 124.9, 123.4, 122.1, 122.1, 122.0, 121.6, 120.5, 120.5, 119.0, 114.6 (2C), 109.0, 55.1, 49.7 ppm.

**HRMS** (ESI) *m/z*: [M]<sup>+</sup> calcd for [C<sub>36</sub>H<sub>26</sub>BrNOSe]<sup>+</sup> 647.0358; found 647.0332.



**5-((4-Bromophenyl)selanyl)-11-methyl-6-phenyl-11H-benzo[a]carbazole (3ae):**

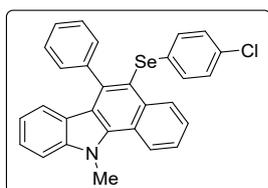
**GP-2** was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (77 mg, 0.25 mmol), 1,2-bis(4-bromophenyl)diselane **2e** (59 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3ae** (118 mg, 87%) as a brown viscous oil; [TLC control (petroleum ether/ethyl acetate 97:03), *R<sub>f</sub>*(**1a**) = 0.5, *R<sub>f</sub>*(**2e**) = 0.9, *R<sub>f</sub>*(**3ae**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>): *ν*<sub>max</sub> = 3059, 2932, 2247, 1679, 1474, 1223, 1012, 730 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.83 (dd, *J* = 8.5, 3.3 Hz, 2H), 7.70 – 7.64 (m, 1H), 7.62 – 7.57 (m, 1H), 7.54 (dd, *J* = 8.4, 7.8 Hz, 2H), 7.50 (dd, *J* = 7.3, 7.8 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.31 – 7.27 (m, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.98 (dd, *J* = 11.1, 3.9 Hz, 1H), 6.90 – 6.82 (m, 2H), 6.50 (d, *J* = 8.0 Hz, 1H), 4.48 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>) δ 144.3, 142.3, 141.0, 136.8, 134.3, 134.1, 131.8 (2C), 130.7, 130.0 (2C), 128.7 (2C), 128.4 (2C), 127.7, 126.4, 125.5, 124.9, 122.9, 122.9, 122.6, 121.9, 119.9, 118.9, 118.5, 118.0, 108.9, 34.5 ppm.

**HRMS** (ESI) *m/z*: [M]<sup>+</sup> calcd for [C<sub>29</sub>H<sub>20</sub>BrNSe]<sup>+</sup> 540.9939; found 540.9954.



**5-((4-Chlorophenyl)selanyl)-11-methyl-6-phenyl-11H-benzo[a]carbazole (3af):**

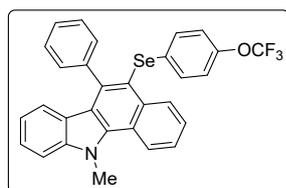
**GP-2** was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **1a** (77 mg, 0.25 mmol), 1,2-bis(4-chlorophenyl)diselane **2f** (48 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3af** (107 mg, 86%) as a brown solid, mp = 158–160 °C. [TLC control (petroleum ether/ethyl acetate 97:03), *R<sub>f</sub>*(**1a**) = 0.5, *R<sub>f</sub>*(**2f**) = 0.9, *R<sub>f</sub>*(**3af**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3057, 2926, 2034, 1728, 1503, 1224, 1086, 745 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.87 – 8.80 (m, 2H), 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.57 – 7.46 (m, 4H), 7.42 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.03 – 6.95 (m, 3H), 6.94 – 6.87 (m, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.49 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.3, 142.3, 141.0, 136.8, 134.1, 133.5, 131.0, 130.7, 129.7 (2C), 128.9 (2C), 128.7 (2C), 128.4 (2C), 127.7, 126.4, 125.5, 124.9, 122.9, 122.9, 122.6, 121.9, 119.9, 118.5, 118.2, 108.9, 34.5 ppm.

**HRMS** (ESI) *m/z*: [M+H<sub>2</sub>O]<sup>+</sup> calcd for [C<sub>29</sub>H<sub>22</sub>ClNOSe]<sup>+</sup> 515.0550; found 515.0549.



### 11-Methyl-6-phenyl-5-((4-(trifluoromethoxy)phenyl)selanyl)-11*H*-benzo[*a*]carbazole

#### (**3ag**):

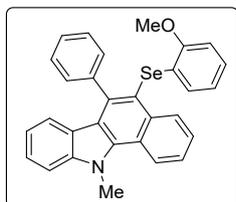
**GP-2** was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1*H*-indole **1a** (77 mg, 0.25 mmol), 1,2-bis(4-(trifluoromethoxy)phenyl)diselane **2g** (60 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 96:04) furnished the product **3ag** (100 mg, 73%) as a brown crystalline, mp = 160–162 °C. [TLC control (petroleum ether/ethyl acetate 96:04), *R<sub>f</sub>*(**1a**) = 0.5, *R<sub>f</sub>*(**2g**) = 0.9, *R<sub>f</sub>*(**3ag**) = 0.2, UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3056, 2926, 2107, 1728, 1480, 1254, 1164, 742 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.85 (dd, *J* = 8.5, 8.4 Hz, 2H), 7.67 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.61 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.57 – 7.41 (m, 5H), 7.29 – 7.26 (m, 2H), 7.02 – 6.94 (m, 3H), 6.89 (dd, *J* = 8.8, 0.8 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.49 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.0 (q,  $J = 1.8$  Hz), 144.3, 142.2, 141.0, 139.9 (q,  $J = 249.5$  Hz), 136.8, 134.1, 133.6, 130.7, 129.7 (2C), 128.8 (2C), 128.4 (2C), 127.7 (2C), 126.4, 125.5, 124.9, 122.9, 122.9, 122.6, 121.9, 121.5, 119.9, 118.6, 118.3, 108.9, 34.5 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}]^+$  calcd for  $[\text{C}_{30}\text{H}_{20}\text{F}_3\text{NOSe}]^+$  547.0657; found 547.0680.



### 5-((2-Methoxyphenyl)selanyl)-11-methyl-6-phenyl-11H-benzo[a]carbazole (**3ah**):

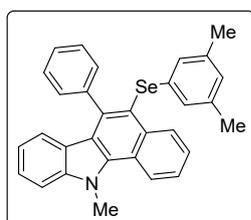
GP-2 was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (77 mg, 0.25 mmol), 1,2-bis(2-methoxyphenyl)diselane **2h** (46 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 96:04) furnished the product **3ah** (98 mg, 80%) as a brown solid, mp = 180–182 °C. [TLC control (petroleum ether/ethyl acetate 96:04),  $R_f$  (**1a**) = 0.5,  $R_f$  (**2h**) = 0.9,  $R_f$  (**3ah**) = 0.2, UV detection].

IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3057, 2840, 2052, 1672, 1504, 1237, 1061, 744  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 8.9$  Hz, 2H), 7.64 (ddd,  $J = 8.4, 7.9, 1.3$  Hz, 1H), 7.57 – 7.53 (m, 2H), 7.50 – 7.39 (m, 4H), 7.35 – 7.30 (m, 2H), 7.05 – 6.95 (m, 2H), 6.77 (dd,  $J = 8.1, 1.0$  Hz, 1H), 6.54 (ddd,  $J = 7.6, 7.9, 1.1$  Hz, 1H), 6.47 (d,  $J = 8.0$  Hz, 1H), 6.42 (dd,  $J = 7.7, 1.5$  Hz, 1H), 4.49 (s, 3H), 3.86 (s, 3H) ppm.

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 144.8, 142.4, 140.9, 136.8, 134.5, 131.1, 128.6 (2C), 128.3 (2C), 128.3, 127.5, 126.2, 125.7, 125.4, 124.7, 124.4, 122.9, 122.9, 122.5, 121.9, 121.40, 119.8, 118.7, 116.8, 109.8, 108.8, 55.7, 34.5 ppm.

HRMS (ESI)  $m/z$ :  $[\text{M}+\text{NH}_4]^+$  calcd for  $[\text{C}_{30}\text{H}_{27}\text{N}_2\text{OSe}]^+$  511.1283; found 511.1246.



### 5-((3,5-Dimethylphenyl)selanyl)-11-methyl-6-phenyl-11H-benzo[a]carbazole (**3ai**):

GP-2 was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (77 mg, 0.25 mmol), 1,2-bis(3,5-dimethylphenyl)diselane **2i** (46 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1

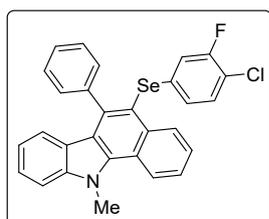
M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3ai** (104 mg, 85%) as a yellow solid, mp = 200–202 °C. [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f(\mathbf{1a}) = 0.5$ ,  $R_f(\mathbf{2i}) = 0.9$ ,  $R_f(\mathbf{3ai}) = 0.3$ , UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max} = 3052, 1727, 1564, 1433, 1330, 1164, 1026, 731$  cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 (dd,  $J = 8.5, 1.0$  Hz, 1H), 8.82 (d,  $J = 8.3$  Hz, 1H), 7.65 (ddd,  $J = 8.4, 6.9, 1.5$  Hz, 1H), 7.61 – 7.57 (m, 1H), 7.55 (d,  $J = 8.6$  Hz, 1H), 7.52 – 7.47 (m, 3H), 7.44 – 7.40 (m, 1H), 7.33 – 7.29 (m, 2H), 7.02 – 6.92 (m, 1H), 6.68 – 6.64 (m, 3H), 6.50 (d,  $J = 8.0$  Hz, 1H), 4.49 (s, 3H), 2.10 (s, 6H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.0, 142.5, 140.9, 138.2 (2C), 136.6, 134.7, 134.4, 131.1, 128.9 (2C), 128.3 (2C), 127.5, 127.2, 126.2 (2C), 126.1, 125.2, 124.7, 122.9, 122.8, 122.4, 121.9, 119.8, 118.6, 118.5, 108.8, 34.4, 21.1 (2C) ppm.

**HRMS** (ESI)  $m/z$ : [M+NH<sub>4</sub>]<sup>+</sup> calcd for [C<sub>31</sub>H<sub>29</sub>N<sub>2</sub>Se]<sup>+</sup> 509.1490; found 509.1472.



**5-((4-Chloro-3-fluorophenyl)selanyl)-11-methyl-6-phenyl-11H-benzo[a]carbazole (**3aj**):**

**GP-2** was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (77 mg, 0.25 mmol), 1,2-bis(4-chloro-3-fluorophenyl)diselane **2j** (52 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3aj** (96 mg, 75%) as a yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f(\mathbf{1a}) = 0.5$ ,  $R_f(\mathbf{2j}) = 0.9$ ,  $R_f(\mathbf{3aj}) = 0.3$ , UV detection].

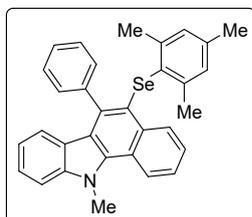
**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max} = 3057, 2927, 2346, 1726, 1504, 1394, 1030, 745$  cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.84 (d,  $J = 8.3$  Hz, 1H), 8.80 (dd,  $J = 8.5, 0.8$  Hz, 1H), 7.68 (ddd,  $J = 8.3, 6.8, 1.3$  Hz, 1H), 7.61 (ddd,  $J = 8.1, 6.8, 1.1$  Hz, 1H), 7.54 (ddd,  $J = 7.2, 6.5, 4.8$  Hz, 2H), 7.51 – 7.47 (m, 2H), 7.43 (ddd,  $J = 7.1, 7.8, 3.6$  Hz, 1H), 7.29 (d,  $J = 6.9$  Hz, 2H), 7.05 (dd,  $J = 8.5, 7.5$  Hz, 1H), 7.00 – 6.95 (m, 1H), 6.73 (ddd,  $J = 9.4, 5.1, 2.0$  Hz, 2H), 6.49 (d,  $J = 8.0$  Hz, 1H), 4.49 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  158.1 (d,  $J = 251.6$  Hz), 144.5, 142.2, 141.8, 136.9, 135.7 (d,  $J = 5.8$  Hz), 133.9, 131.3, 130.5, 130.4, 128.6, 128.4, 128.3, 127.8, 126.7, 125.6, 124.9,

124.7 (d,  $J = 3.5$  Hz), 122.9 (d,  $J = 9.9$  Hz), 122.7, 122.1, 120.0, 118.5, 117.6, 116.4 (d,  $J = 23.0$  Hz), 110.2, 34.5 ppm.

**HRMS** (ESI)  $m/z$ :  $[M+H_2O]^+$  calcd for  $[C_{29}H_{21}ClFNOSe]^+$  533.0455; found 533.0427.



### 5-(Mesitylselanyl)-11-methyl-6-phenyl-11H-benzo[a]carbazole (**3ak**):

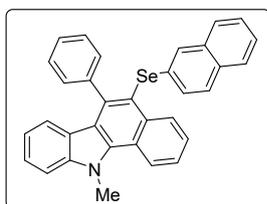
**GP-2** was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (77 mg, 0.25 mmol), 1,2-dimesityldiselane **2k** (49 mg, 0.125 mmol), and  $LiClO_4$  (64 mg, 0.1 M) in  $CH_3CN$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3ak** (108 mg, 86%) as a orange solid, mp = 236–238 °C. [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$  (**1a**) = 0.5,  $R_f$  (**2k**) = 0.9,  $R_f$  (**3ak**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600  $cm^{-1}$ ):  $\nu_{max}$  = 3056, 2925, 1892, 1728, 1463, 1250, 1081, 742  $cm^{-1}$ .

**$^1H$  NMR** (600 MHz,  $CDCl_3$ )  $\delta$  8.80 (d,  $J = 8.5$  Hz, 1H), 8.77 (d,  $J = 8.4$  Hz, 1H), 7.65 – 7.58 (m, 1H), 7.57 – 7.51 (m, 1H), 7.50 (d,  $J = 8.2$  Hz, 1H), 7.47 (dd,  $J = 7.5, 7.7$  Hz, 1H), 7.41 – 7.35 (m, 3H), 7.16 – 7.09 (m, 2H), 6.89 (dd,  $J = 7.5, 7.8$  Hz, 1H), 6.66 (s, 2H), 6.35 (d,  $J = 8.0$  Hz, 1H), 4.44 (s, 3H), 2.19 (s, 3H), 1.99 (s, 6H).

**$^{13}C\{^1H\}$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.6, 141.3, 141.1 (2C), 140.9, 136.5, 135.9, 133.9, 131.7, 129.8, 129.2 (2C), 128.6 (2C), 128.2 (2C), 127.3, 125.4, 125.0, 124.6, 122.8, 122.5, 122.4, 121.9, 121.1, 119.6, 118.8, 108.7, 34.4, 23.8 (2C), 20.8 ppm.

**HRMS** (ESI)  $m/z$ :  $[M]^+$  calcd for  $[C_{32}H_{27}NSe]^+$  505.1303; found 505.1329.



### 11-Methyl-5-(naphthalen-2-ylselanyl)-6-phenyl-11H-benzo[a]carbazole (**3al**):

**GP-2** was carried out with 1-methyl-2-(2-(phenylethynyl)phenyl)-1H-indole **1a** (77 mg, 0.25 mmol), 1,2-di(naphthalen-2-yl)diselane **2l** (51 mg, 0.125 mmol), and  $LiClO_4$  (64 mg, 0.1 M) in  $CH_3CN$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column

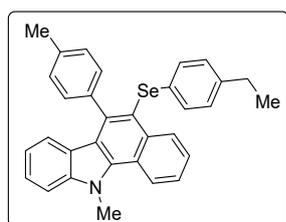
chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3al** (102 mg, 80%) as a orange viscous oil; [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$ (**1a**) = 0.5,  $R_f$ (**2l**) = 0.9,  $R_f$ (**3al**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3051, 2925, 2302, 1896, 1554, 1300, 1127, 739  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.93 (d,  $J$  = 8.5 Hz, 1H), 8.84 (d,  $J$  = 8.5 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.65 (dd,  $J$  = 7.6, 7.8 Hz, 1H), 7.58 – 7.51 (m, 4H), 7.49 – 7.40 (m, 5H), 7.34 (dd,  $J$  = 7.5, 5.4 Hz, 4H), 7.17 (dd,  $J$  = 8.6, 1.3 Hz, 1H), 6.99 (dd,  $J$  = 10.4, 4.6 Hz, 1H), 6.53 (dd,  $J$  = 7.9, 2.9 Hz, 1H), 4.50 (s, 3H) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 142.4, 141.1, 136.8, 134.4, 134.0, 132.9, 131.4, 130.9, 128.8 (2C), 128.4 (2C), 128.0, 127.6, 127.6, 126.8 (2C), 126.4, 126.3, 126.1, 125.4, 125.0, 124.8, 123.0, 122.9, 122.5, 122.0, 119.9, 118.6, 118.3, 108.9, 34.5 ppm.

**HRMS** (ESI)  $m/z$ :  $[\text{M}]^+$  calcd for  $[\text{C}_{33}\text{H}_{23}\text{NSe}]^+$  513.0990; found 513.0985.



### 5-((4-Ethylphenyl)selanyl)-11-methyl-6-(*p*-tolyl)-11*H*-benzo[*a*]carbazole (**3bb**):

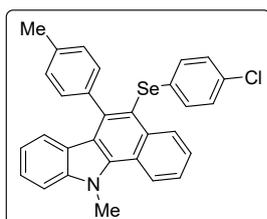
**GP-2** was carried out with 1-methyl-2-(2-(*p*-tolylethynyl)phenyl)-1*H*-indole **1b** (80 mg, 0.25 mmol), 1,2-bis(4-ethylphenyl)diselane **2b** (46 mg, 0.125 mmol), and  $\text{LiClO}_4$  (64 mg, 0.1 M) in  $\text{CH}_3\text{CN}$  (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3bb** (107 mg, 85%) as a brown solid, mp = 130–132 °C. [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$ (**1b**) = 0.5,  $R_f$ (**2b**) = 0.9,  $R_f$ (**3bb**) = 0.3, UV detection].

**IR** (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  = 3052, 2924, 2308, 1724, 1600, 1477, 1020, 739  $\text{cm}^{-1}$ .

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (d,  $J$  = 7.9 Hz, 1H), 8.81 (d,  $J$  = 8.2 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.59 – 7.51 (m, 2H), 7.42 (ddd,  $J$  = 8.3, 7.1, 1.1 Hz, 1H), 7.29 (d,  $J$  = 7.9 Hz, 2H), 7.20 (d,  $J$  = 7.9 Hz, 2H), 7.01 – 6.85 (m, 5H), 6.56 (d,  $J$  = 8.0 Hz, 1H), 4.48 (s, 3H), 2.51 (s, 3H), 2.52 – 2.44 (q,  $J$  = 7.6 Hz, 2H), 1.13 (t,  $J$  = 7.6 Hz, 3H) ppm.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 141.2, 141.0, 139.6, 137.0, 136.6, 134.3, 131.6, 131.1, 129.1 (2C), 128.7 (2C), 128.6 (2C), 128.4 (2C), 126.1, 125.2, 124.7, 123.1, 122.8, 122.4, 122.1, 119.8, 119.1, 118.7, 108.8, 34.5, 28.2, 21.6, 15.4 ppm.

**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{K}]^+$  calcd for  $[\text{C}_{32}\text{H}_{27}\text{KNSe}]^+$  544.0940; found 544.0983.



### 5-((4-Chlorophenyl)selanyl)-11-methyl-6-(*p*-tolyl)-11*H*-benzo[*a*]carbazole (**3bf**):

**GP-2** was carried out with 1-methyl-2-(2-(*p*-tolylethynyl)phenyl)-1*H*-indole **1b** (80 mg, 0.25 mmol), 1,2-bis(4-chlorophenyl)diselane **2f** (48 mg, 0.125 mmol), and LiClO<sub>4</sub> (64 mg, 0.1 M) in CH<sub>3</sub>CN (6 mL) at 7 mA for 1 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03) furnished the product **3bf** (111 mg, 87%) as a orange viscous oil; [TLC control (petroleum ether/ethyl acetate 97:03),  $R_f$ (**1b**) = 0.5,  $R_f$ (**2f**) = 0.9,  $R_f$ (**3bf**) = 0.3, UV detection].

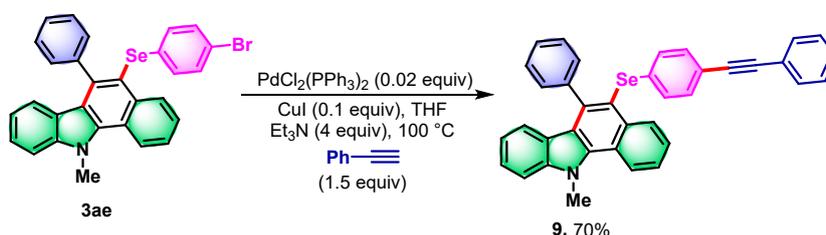
**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3053, 2924, 2110, 1700, 1504, 1378, 1088, 740 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.87 – 8.78 (m, 2H), 7.69 – 7.62 (m, 1H), 7.60 – 7.53 (m, 2H), 7.43 (ddd,  $J$  = 8.3, 7.1, 1.1 Hz, 1H), 7.30 (d,  $J$  = 7.7 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.04 – 6.97 (m, 3H), 6.95 – 6.89 (m, 2H), 6.56 (d,  $J$  = 8.0 Hz, 1H), 4.48 (s, 3H), 2.52 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  144.4, 141.0, 139.4, 137.2, 136.8, 134.1, 133.6, 130.9, 130.7, 129.7 (2C), 129.1 (2C), 128.9 (2C), 128.5 (2C), 126.3, 125.4, 124.8, 123.0, 122.9, 122.6, 122.0, 119.9, 118.7, 118.3, 108.9, 34.4, 21.5 ppm.

**HRMS** (ESI)  $m/z$ : [M]<sup>+</sup> calcd for [C<sub>30</sub>H<sub>22</sub>ClNSe]<sup>+</sup> 511.0601; found 511.0586.

**Scheme S3:** Synthetic applications through coupling reactions of **3ae**.

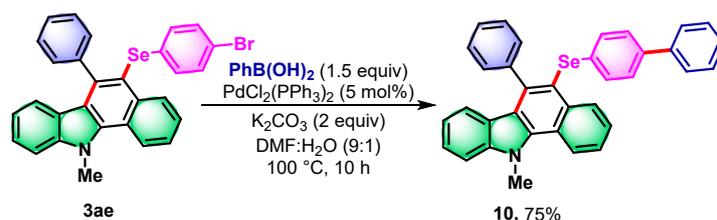


### 11-Methyl-6-phenyl-5-((4-(phenylethynyl)phenyl)selanyl)-11*H*-benzo[*a*]carbazole (**9**):

In an oven-dried Schlenk tube equipped with a magnetic stir bar, were added 5-((4-bromophenyl)selanyl)-11-methyl-6-phenyl-11*H*-benzo[*a*]carbazole **3ae** (108 mg, 0.2 mmol, 1 equiv), phenylacetylene **8a** (31 mg, 0.3 mmol, 1.5 equiv), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (14 mg, 0.02 mmol), CuI (19 mg, 0.1 mmol), Et<sub>3</sub>N (404 mg, 4 mmol), and toluene (0.5 mL), allowed the reaction mixture to stir at 100 °C for 2 h in an oil bath. The resulting mixture was then poured into a

saturated aqueous solution of NH<sub>4</sub>Cl (15 mL), extracted with ethyl acetate (2 × 15 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3) furnished the product **9** (79 mg, 70%) as yellow viscous oil; [TLC control (petroleum ether/ethyl acetate 97:3), *R<sub>f</sub>*(**3ae**) = 0.6, *R<sub>f</sub>*(**8a**) = 0.7, *R<sub>f</sub>*(**9**) = 0.4 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 2953, 2865, 2276, 2150, 1460, 1378, 1069, 754 cm<sup>-1</sup>.  
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 – 8.79 (m, 2H), 7.68 (dd, *J* = 7.6, 8.1 Hz, 1H), 7.60 (dd, *J* = 7.7, 7.9 Hz, 1H), 7.58 – 7.47 (m, 6H), 7.44 (dd, *J* = 7.6, 8.1 Hz, 1H), 7.32 (d, *J* = 6.2 Hz, 5H), 7.24 – 7.18 (m, 2H), 7.05 – 6.91 (m, 3H), 6.53 (dd, *J* = 9.7, 5.3 Hz, 1H), 4.49 (s, 3H).  
**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  144.4, 142.3, 141.0, 136.8, 136.5, 134.2, 131.8 (2C), 131.4 (2C), 130.8, 128.7 (2C), 128.4 (2C), 128.3 (2C), 128.2 (2C), 128.1, 127.7, 126.4, 125.5, 124.9, 123.3, 122.9, 122.9, 122.6, 121.9, 119.9, 119.7, 118.6, 117.9, 108.9, 89.3, 89.3, 34.5 ppm.  
**HRMS** (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for [C<sub>37</sub>H<sub>25</sub>NNaSe]<sup>+</sup> 586.1044; found 586.1086.



### 5-((1,1'-Biphenyl)-4-ylselanyl)-11-methyl-6-phenyl-11*H*-benzo[*a*]carbazole (**10**):

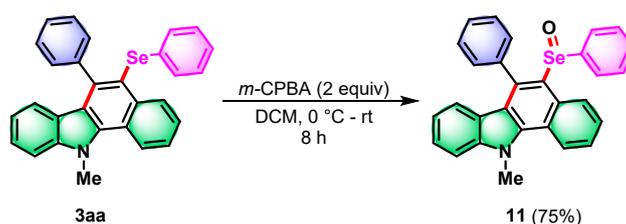
In an oven-dried Schlenk tube equipped with a magnetic stir bar, were added 5-((4-bromophenyl)selanyl)-11-methyl-6-phenyl-11*H*-benzo[*a*]carbazole **3ae** (108 mg, 0.2 mmol, 1 equiv), phenylboronic acid (36.6 mg, 0.3 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (35 mg, 0.02 mmol), K<sub>2</sub>CO<sub>3</sub> (130 mg, 0.4 mmol), followed by DMF:H<sub>2</sub>O (9:1) under nitrogen atmosphere and allowed the reaction mixture to stir at 100 °C for 10 h in an oil bath. The resulting mixture was then poured into a saturated aqueous solution of NH<sub>4</sub>Cl (15 mL), extracted with ethyl acetate (2 × 15 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the product **10** (81 mg, 75%) as yellow viscous oil, [TLC control (petroleum ether/ethyl acetate 94:6), *R<sub>f</sub>*(**7a**) = 0.6, *R<sub>f</sub>*(**8a**) = 0.7, *R<sub>f</sub>*(**10**) = 0.3 UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3057, 2957, 2246, 1804, 1553, 1378, 1016, 723 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.92 (dd, *J* = 8.5, 0.8 Hz, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.64 – 7.58 (m, 1H), 7.58 – 7.46 (m, 6H), 7.45 – 7.40 (m, 1H), 7.38 – 7.31 (m, 4H), 7.30 – 7.27 (m, 3H), 7.10 – 7.05 (m, 2H), 6.98 (dd, *J* = 7.4, 7.3 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 4.50 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>) δ 144.3, 142.4, 141.1, 140.6, 137.9, 136.8, 134.5, 134.3, 131.0, 128.8 (2C), 128.8 (2C), 128.7 (2C), 128.4 (2C), 127.6, 127.4 (2C), 127.0, 126.7 (2C), 126.3, 125.4, 124.8, 122.9, 122.8, 122.5, 122.0, 119.9, 118.6, 118.4, 108.9, 34.5 ppm.

**HRMS** (ESI) *m/z*: [M+H<sub>2</sub>O]<sup>+</sup> calcd for [C<sub>35</sub>H<sub>27</sub>NOSe]<sup>+</sup> 557.1252; found 557.1301.



### Synthesis of 11-methyl-6-phenyl-5-(phenylselenonyl)-11H-benzo[a]carbazole (11):

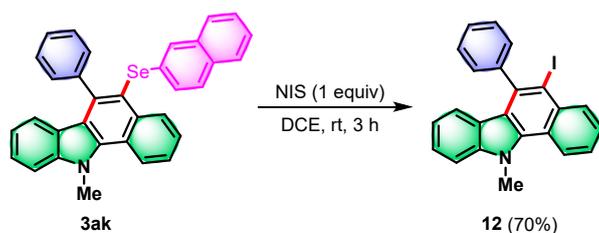
In an oven-dried Schlenk tube equipped with a magnetic stir bar, 3-Chloroperoxybenzoic acid, *m*-CPBA (52 mg, 0.3 mmol) was added to a solution of 11-methyl-6-phenyl-5-(phenylselenanyl)-11H-benzo[a]carbazole **3aa** (70 mg, 0.15 mmol) dissolved in dichloromethane (3 mL) at 0 °C. The reaction mixture was cooled at 0 °C. Then, the reaction mixture was stirred vigorously for 8 h. The resulting mixture was then poured into a saturated aqueous solution of NH<sub>4</sub>Cl (15 mL), extracted with ethyl acetate (2 × 15 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Purification of the crude mixture by silica gel column chromatography (DCM/MeOH 100:0 to 94:6) furnished the product **11** (54 mg, 75%) as brown viscous oil.

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max}$  = 3054, 2924, 2254, 1553, 1379, 1263, 1068, 728 cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.01 (dd, *J* = 8.5, 0.6 Hz, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 7.69 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.67 – 7.60 (m, 4H), 7.59 – 7.54 (m, 3H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.40 – 7.31 (m, 3H), 7.02 (ddd, *J* = 8.0, 7.2, 0.9 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.44 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>) δ 142.6, 141.3, 141.2, 137.9, 137.7, 130.9, 130.1, 130.0, 129.7, 129.5, 129.2 (2C), 128.9, 128.8, 127.1, 126.9 (2C), 126.8, 126.3, 125.8, 125.2, 123.4, 122.8, 122.7, 121.6, 120.4, 116.8, 109.2, 34.5 ppm.

**HRMS** (ESI) *m/z*: [M+NH<sub>4</sub>]<sup>+</sup> calcd for [C<sub>29</sub>H<sub>25</sub>N<sub>2</sub>OSe]<sup>+</sup> 497.1127; found 497.1129.



### Synthesis of 5-iodo-11-methyl-6-phenyl-11H-benzo[*a*]carbazole (**12**):

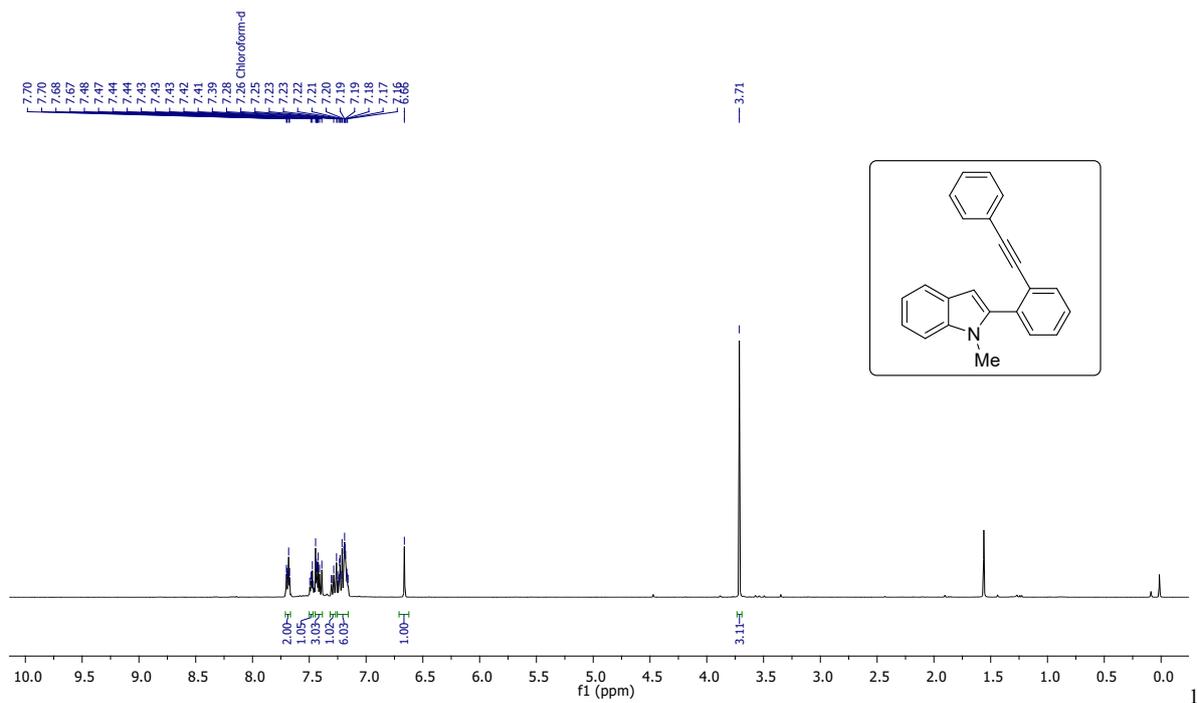
In an oven-dried Schlenk tube equipped with a magnetic stir bar, were added 11-methyl-5-(naphthalen-2-ylselanyl)-6-phenyl-11H-benzo[*a*]carbazole **3ak** (76 mg, 0.15 mmol, 1 equiv), NIS (33 mg, 0.15 mmol), and DCE (2 mL), allowed the reaction mixture to stir at room temperature for 3 h. The resulting mixture was then poured into a saturated aqueous solution of NH<sub>4</sub>Cl (15 mL), extracted with ethyl acetate (2 × 15 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3) furnished the product **12** (45 mg, 70%) as yellow viscous oil. [TLC control (petroleum ether/ethyl acetate 97:3),  $R_f(\mathbf{3ak}) = 0.5$ ,  $R_f(\mathbf{12}) = 0.4$  UV detection].

**IR** (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{max} = 3055, 2926, 2291, 2027, 1718, 1429, 1160, 905$  cm<sup>-1</sup>.

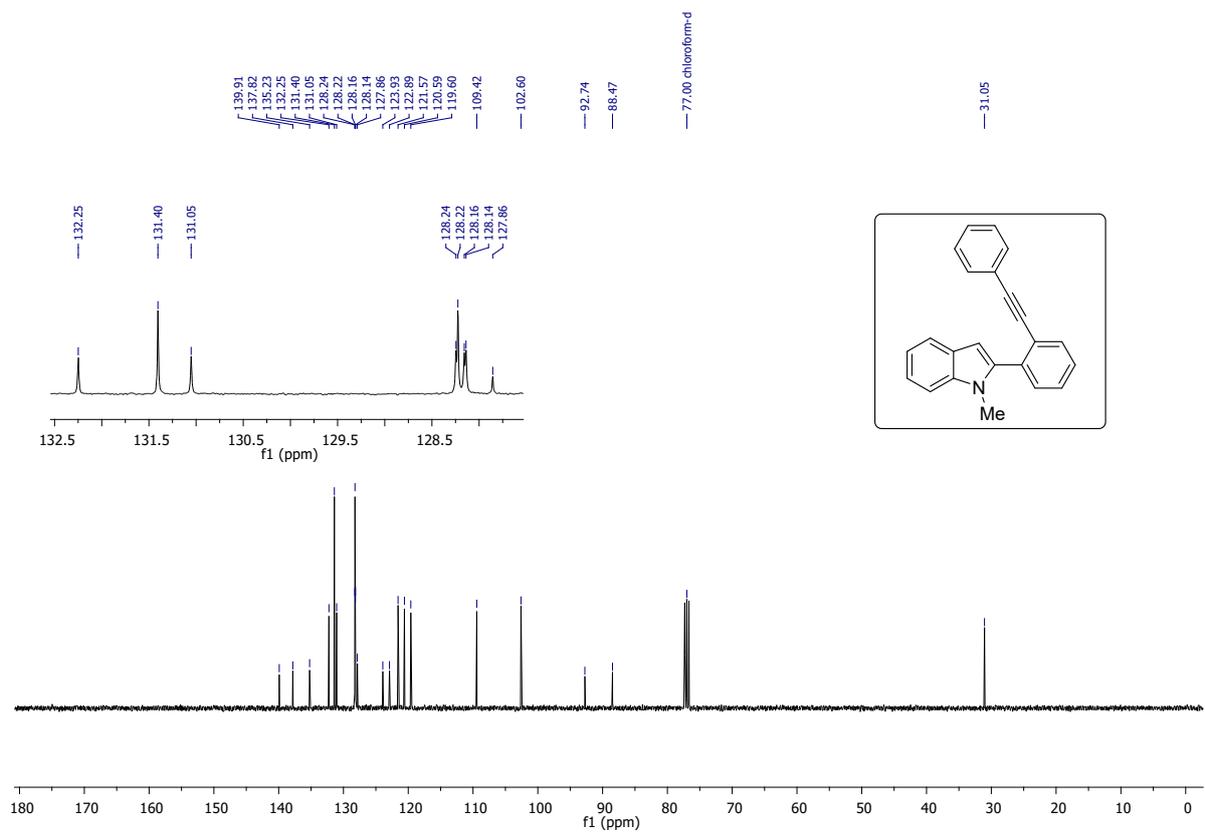
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.80 – 8.71 (m, 1H), 8.68 – 8.51 (m, 1H), 7.69 – 7.65 (m, 2H), 7.65 – 7.59 (m, 3H), 7.52 (d,  $J = 8.3$  Hz, 1H), 7.44 – 7.36 (m, 3H), 6.95 (ddd,  $J = 8.0, 7.1, 0.9$  Hz, 1H), 6.44 (d,  $J = 8.0$  Hz, 1H), 4.44 (s, 3H) ppm.

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  145.5, 142.1, 140.9, 134.8, 133.1, 129.4 (2C), 129.1, 128.8 (2C), 128.0, 126.6, 125.7, 124.9, 122.6, 122.5, 122.4, 121.9, 119.7, 118.9, 108.8, 96.0, 34.5 ppm.

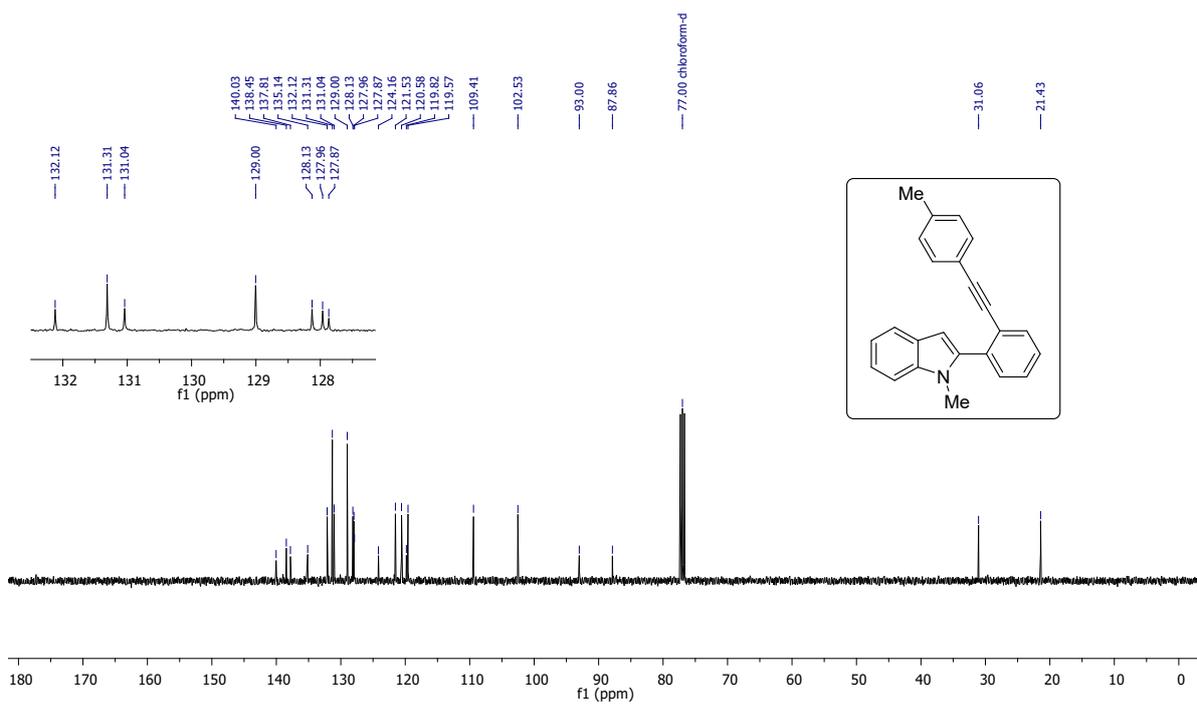
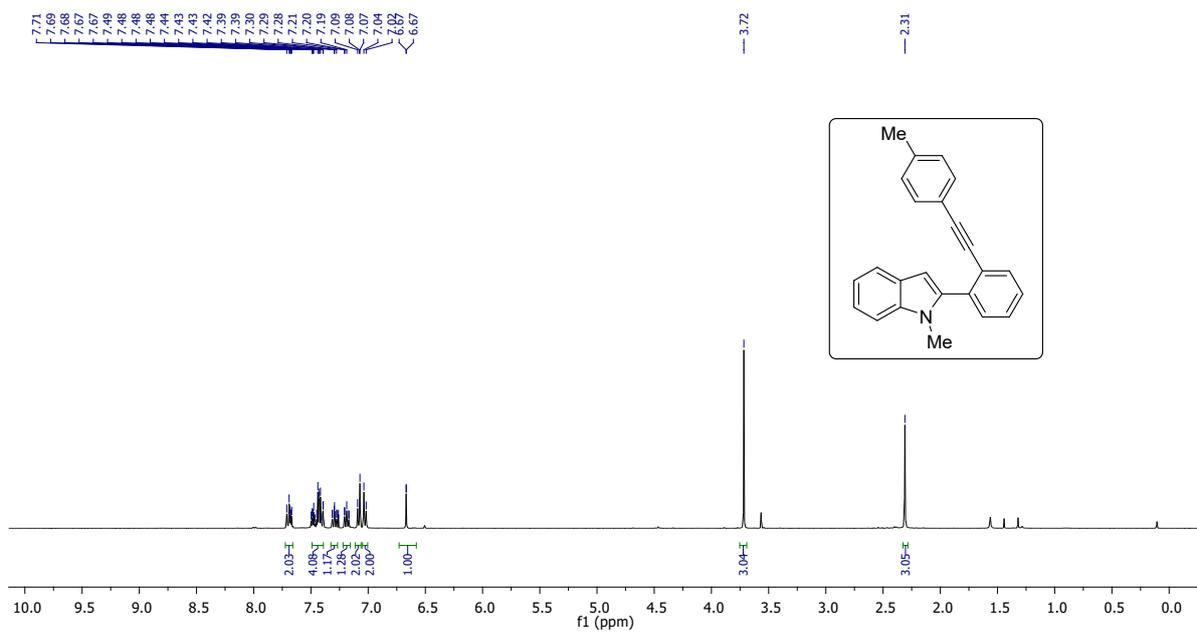
**HRMS** (ESI)  $m/z$ : [M+ NH<sub>4</sub>]<sup>+</sup> calcd for [C<sub>23</sub>H<sub>20</sub>IN<sub>2</sub>]<sup>+</sup> 451.0666; found 451.0684.

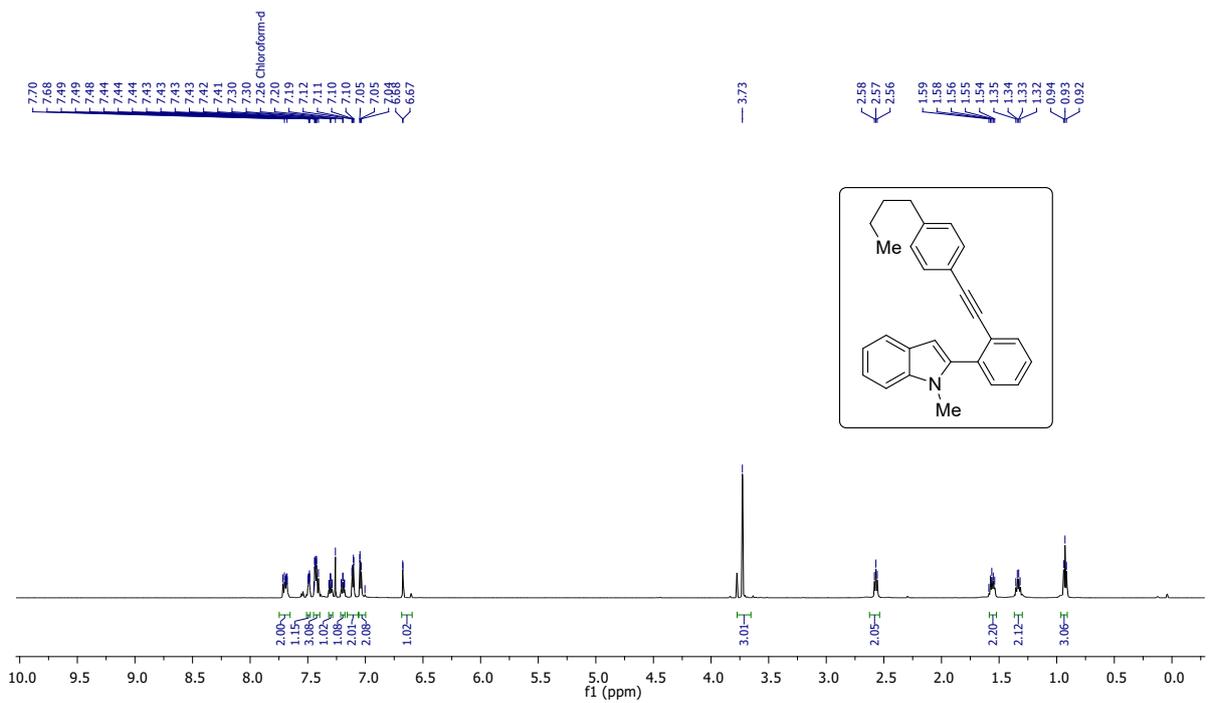


<sup>1</sup>H NMR (400 MHz) spectrum of **1a** in CDCl<sub>3</sub>

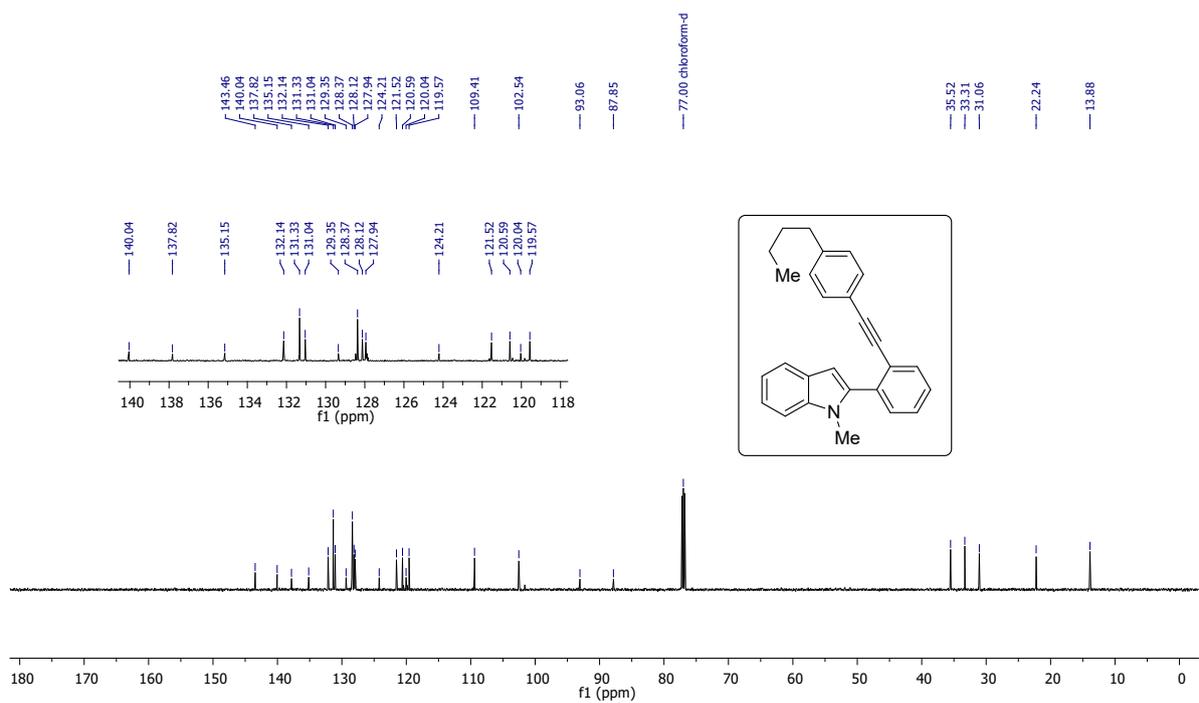


<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz) spectrum of **1a** in CDCl<sub>3</sub>

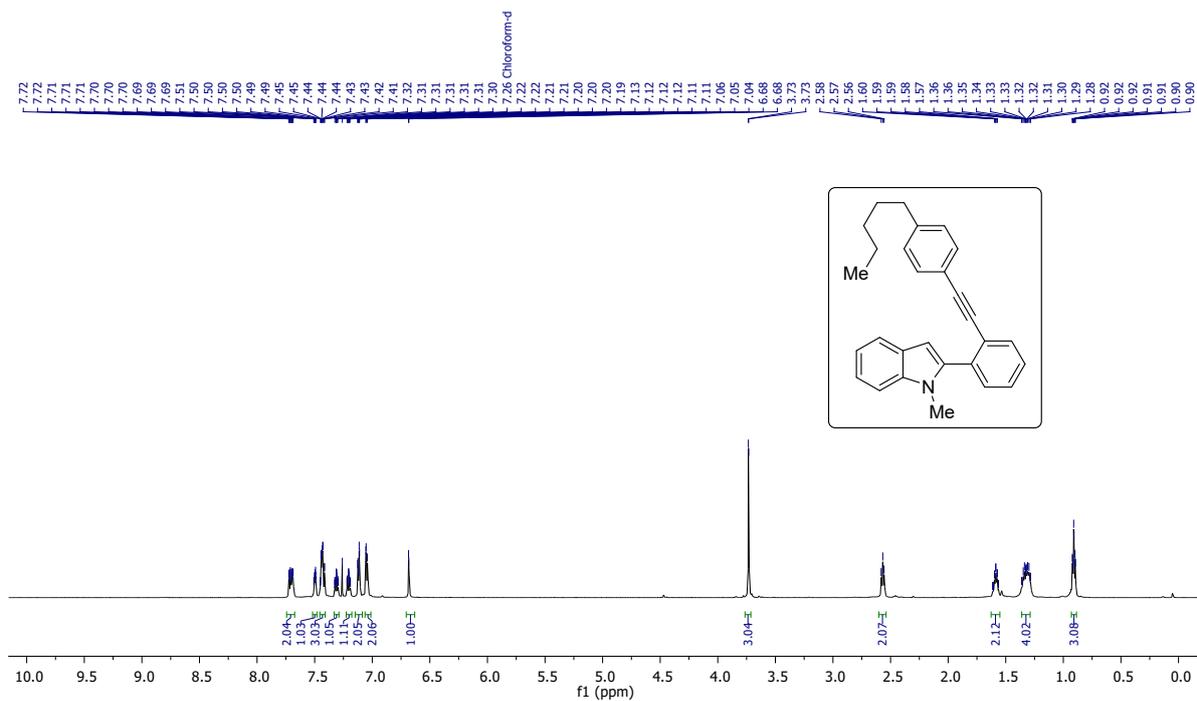




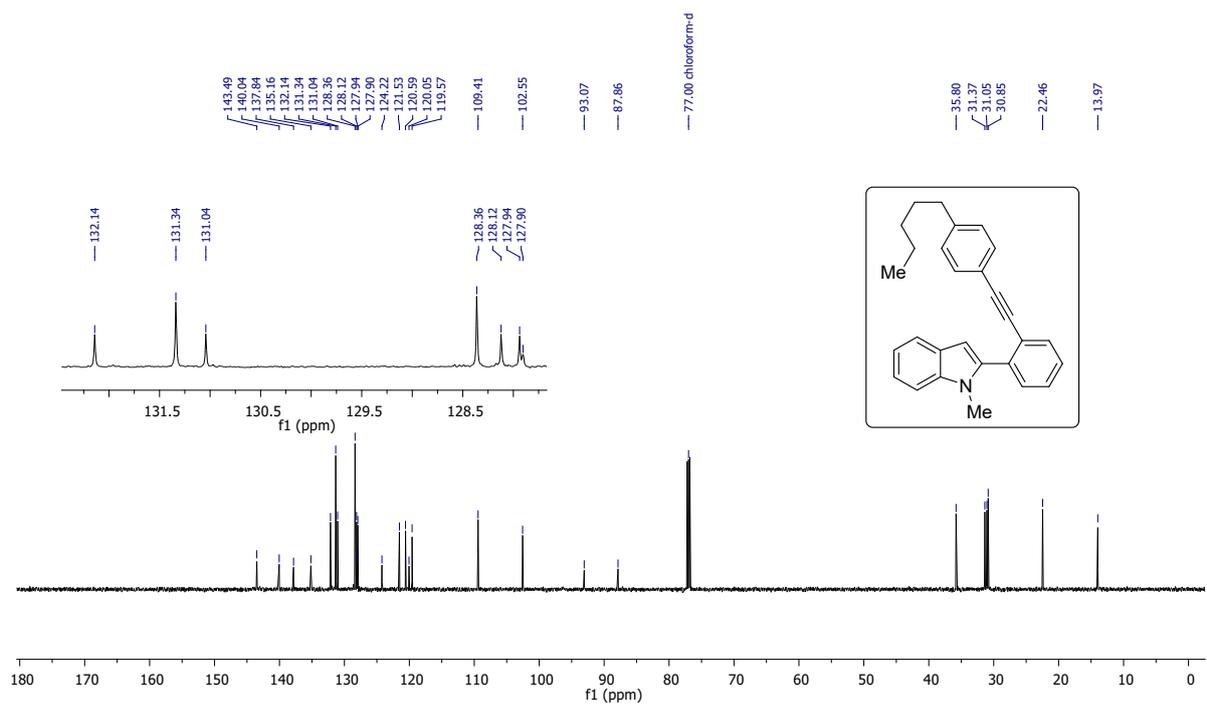
$^1\text{H}$  NMR (600 MHz) spectrum of **1c** in  $\text{CDCl}_3$



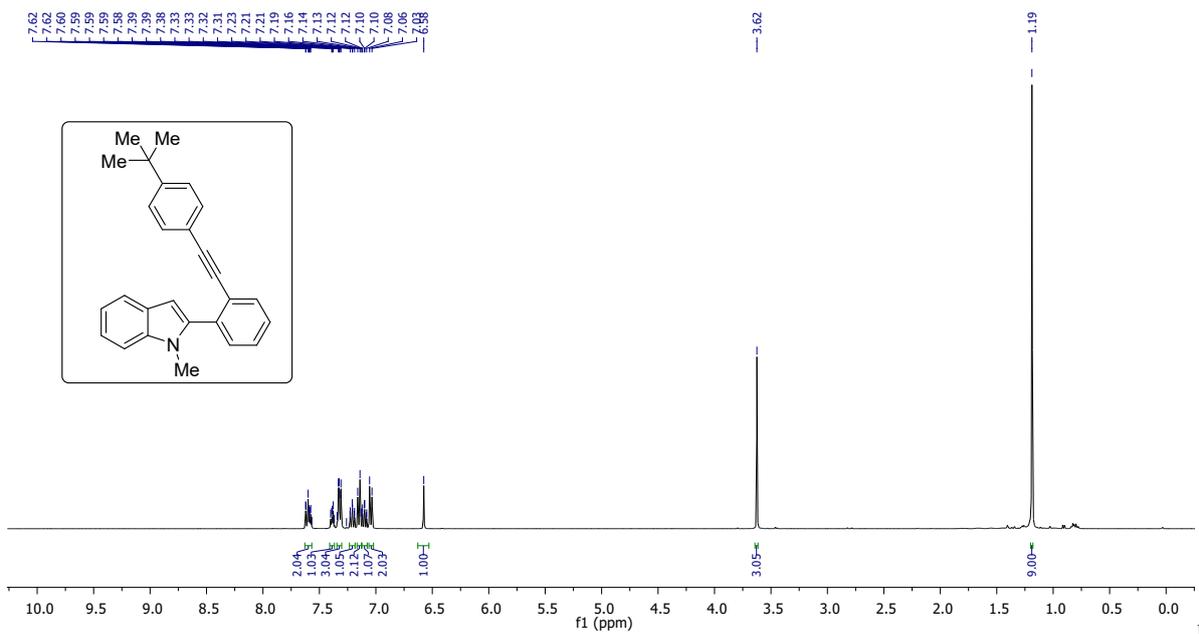
$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of **1c** in  $\text{CDCl}_3$



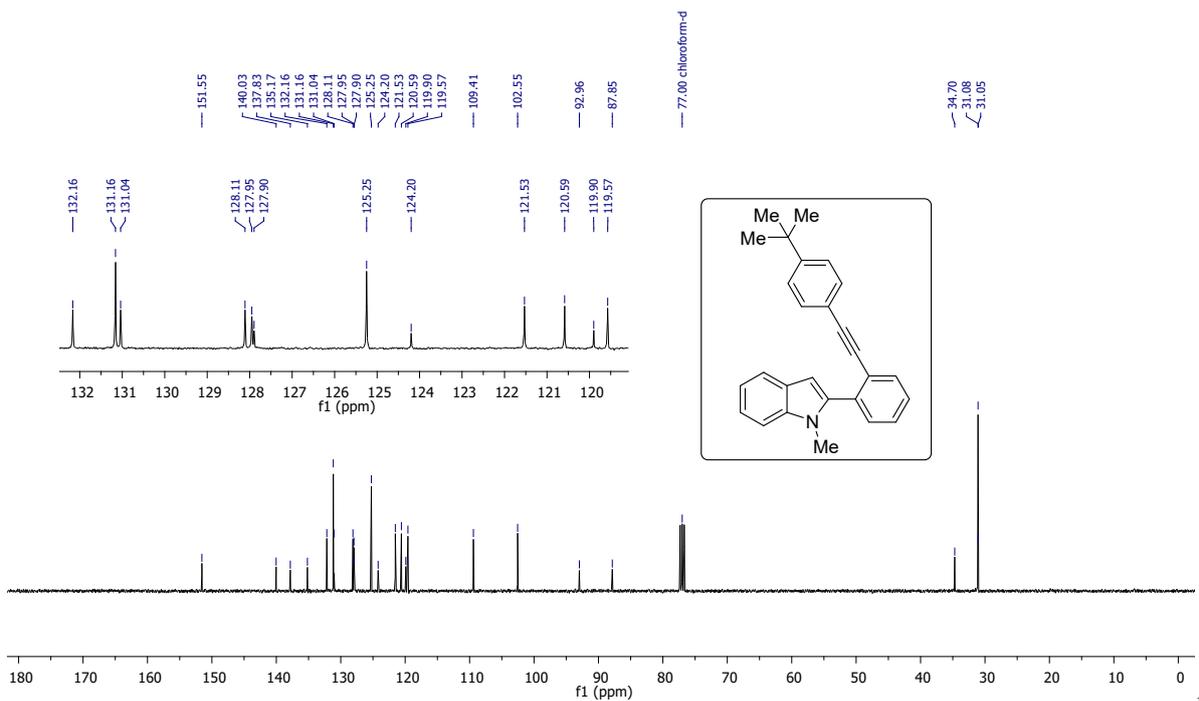
$^1\text{H}$  NMR (600 MHz) spectrum of **1d** in  $\text{CDCl}_3$



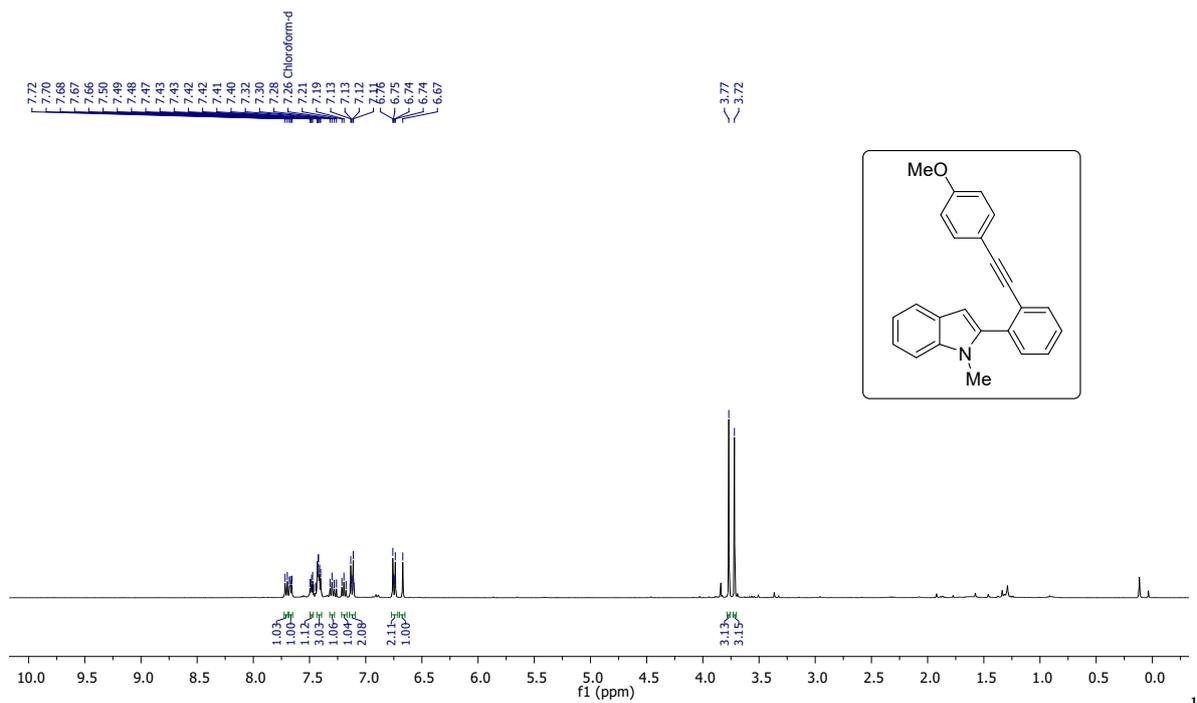
$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of **1d** in  $\text{CDCl}_3$



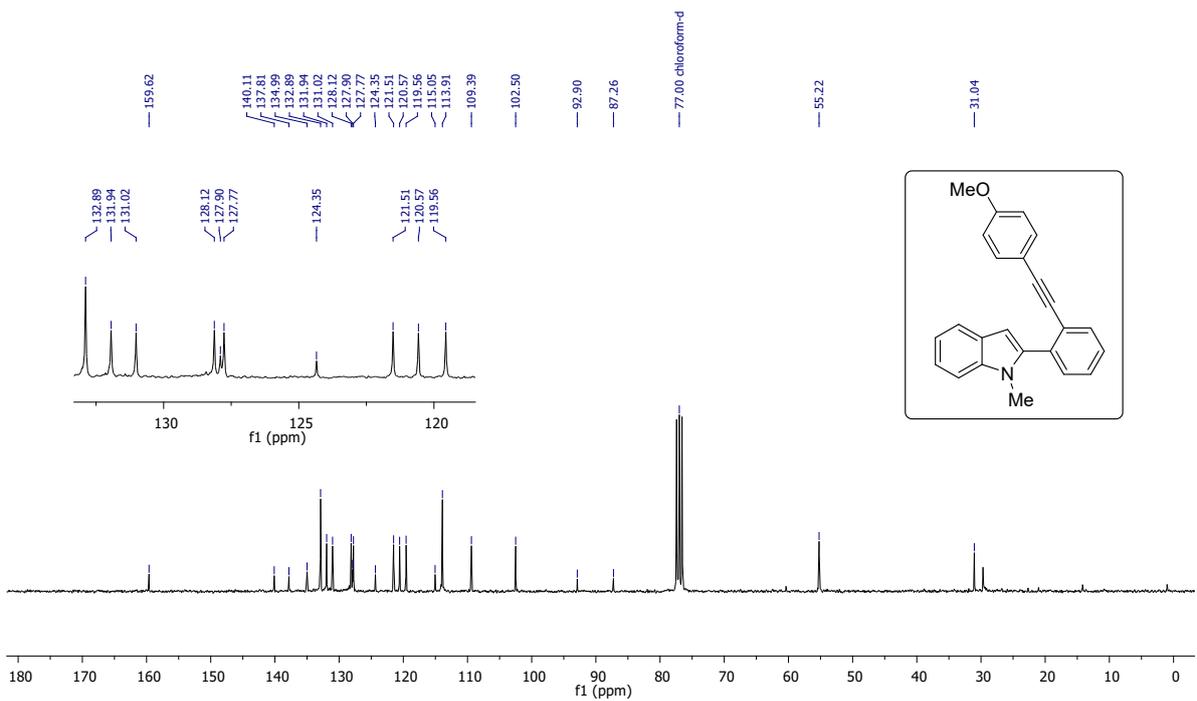
<sup>1</sup>H NMR (400 MHz) spectrum of **1e** in CDCl<sub>3</sub>



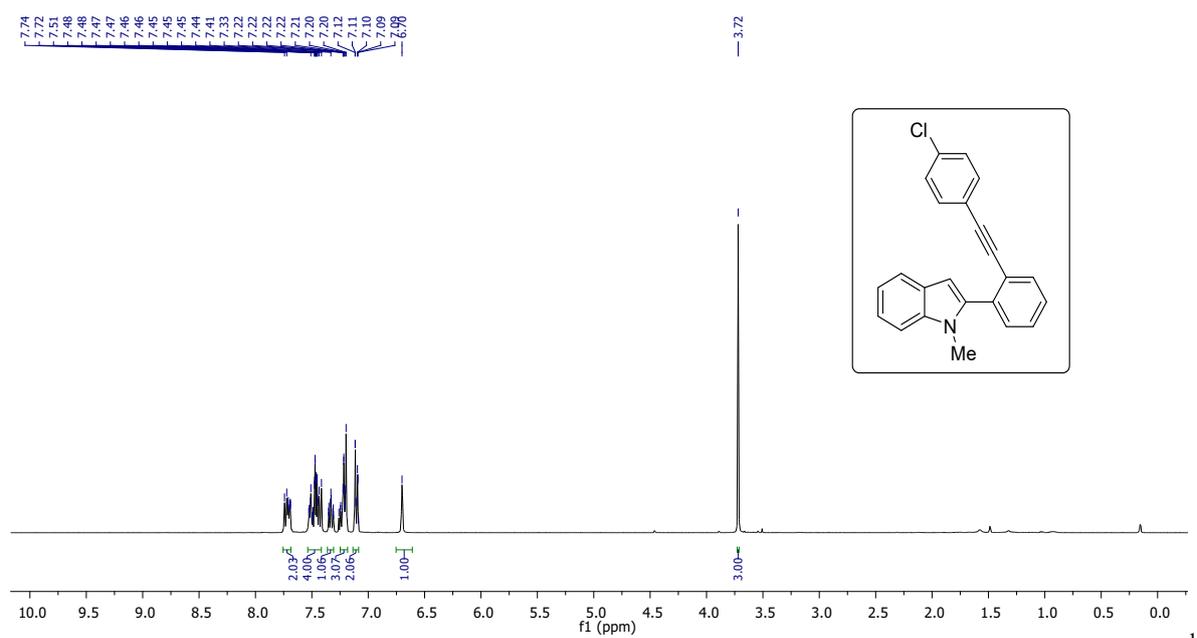
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz) spectrum of **1e** in CDCl<sub>3</sub>



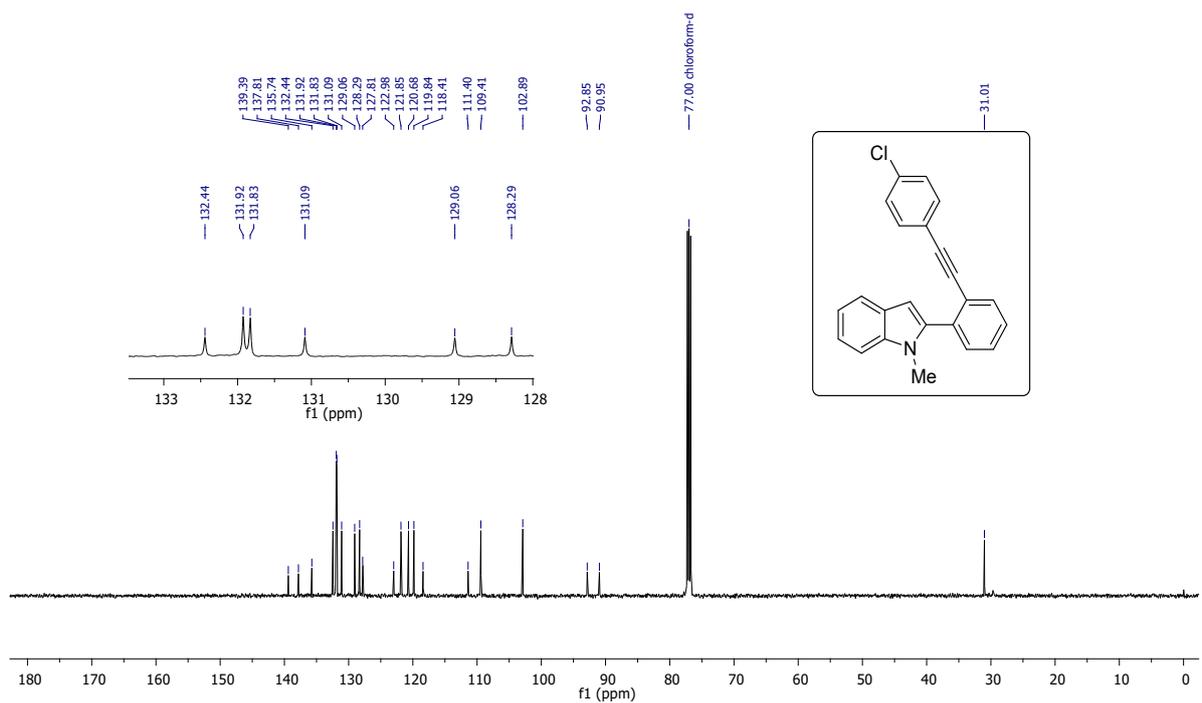
H NMR (400 MHz) spectrum of **1f** in CDCl<sub>3</sub>



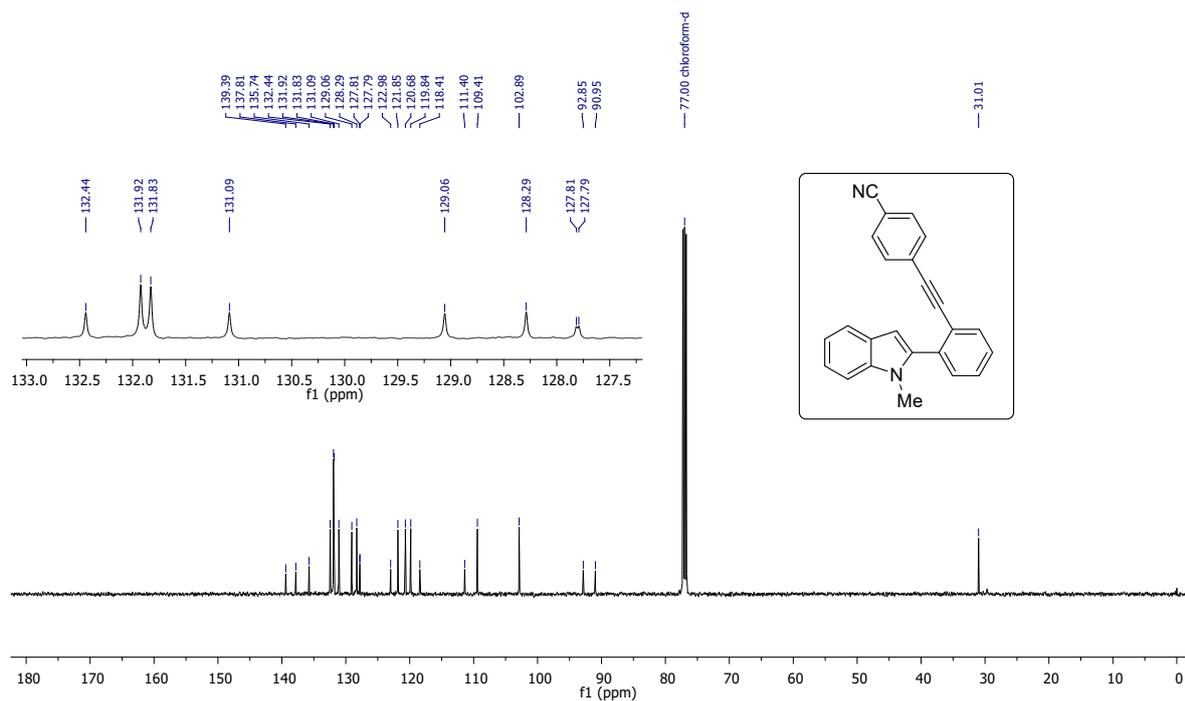
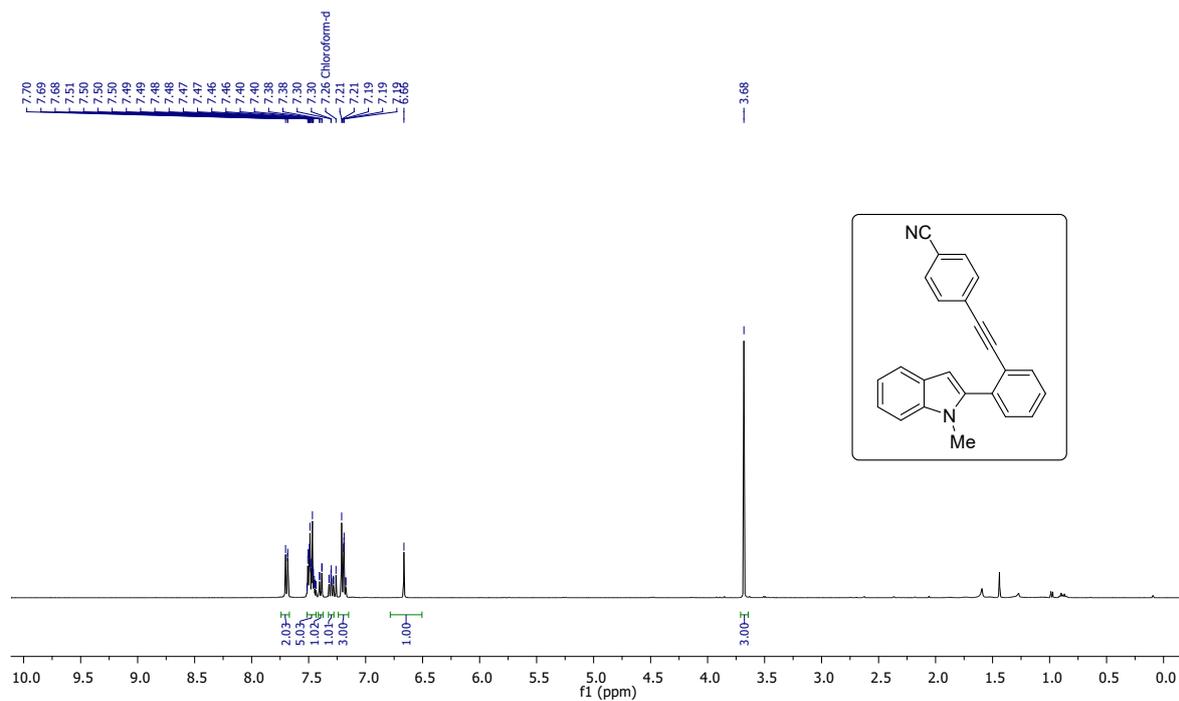
<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz) spectrum of **1f** in CDCl<sub>3</sub>



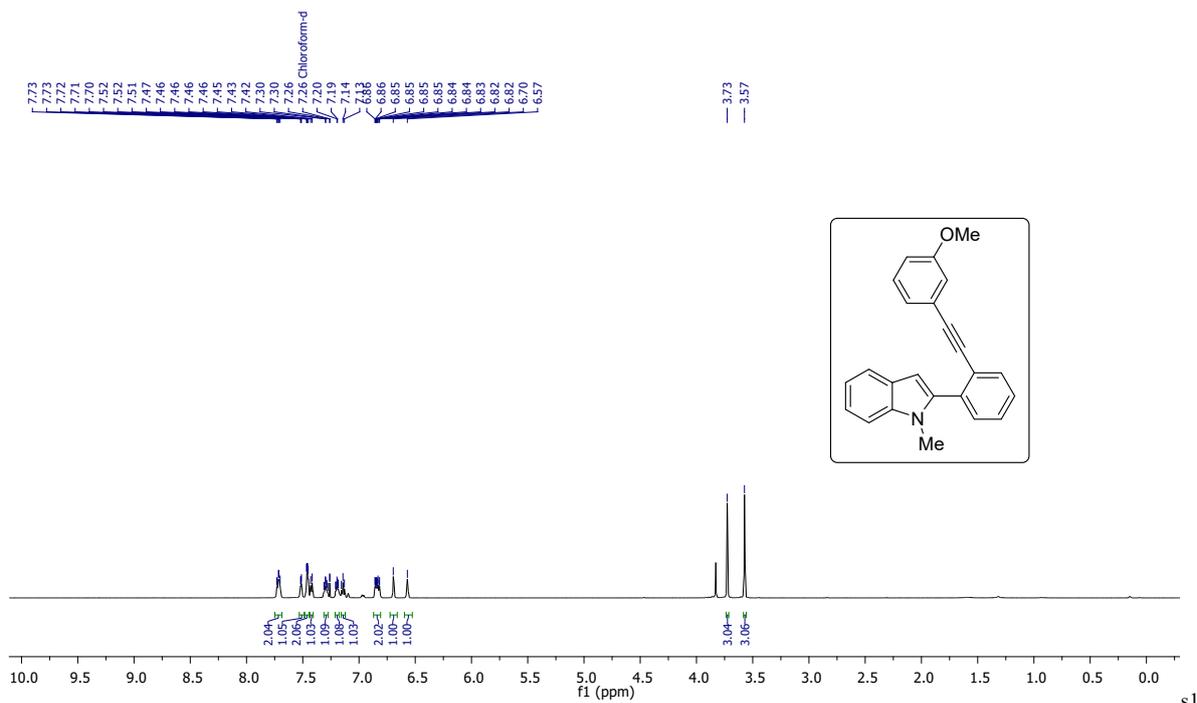
H NMR (400 MHz) spectrum of **1g** in CDCl<sub>3</sub>



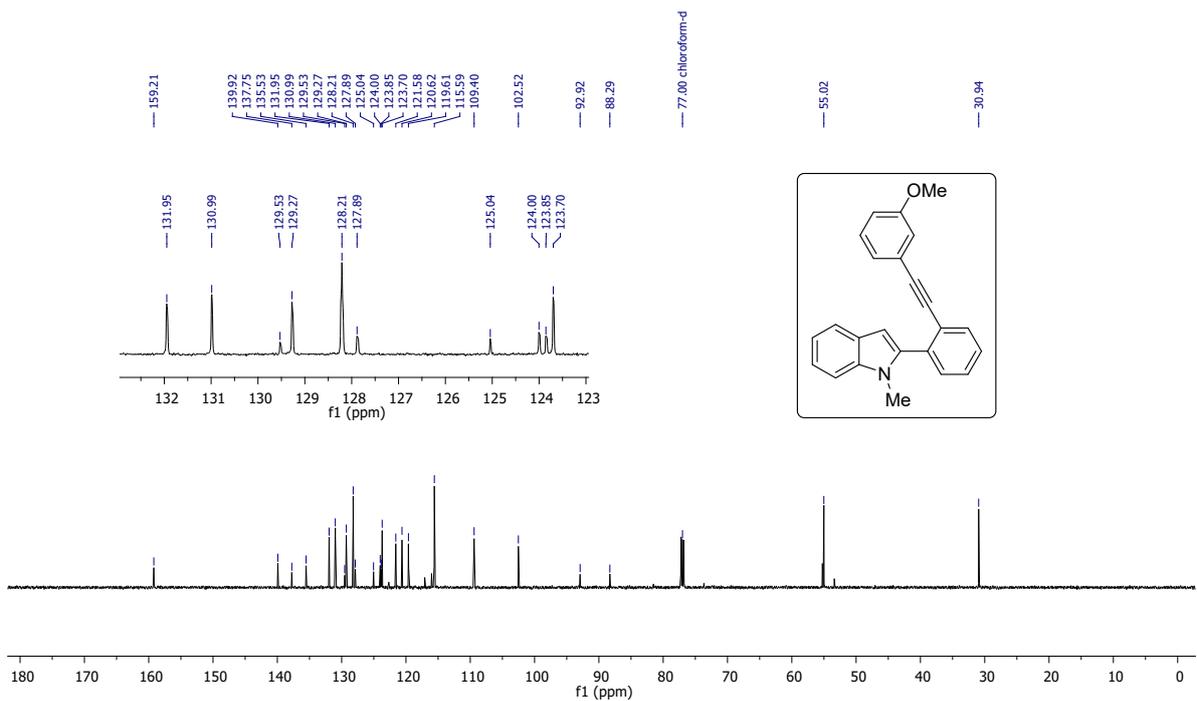
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz) spectrum of **1g** in CDCl<sub>3</sub>



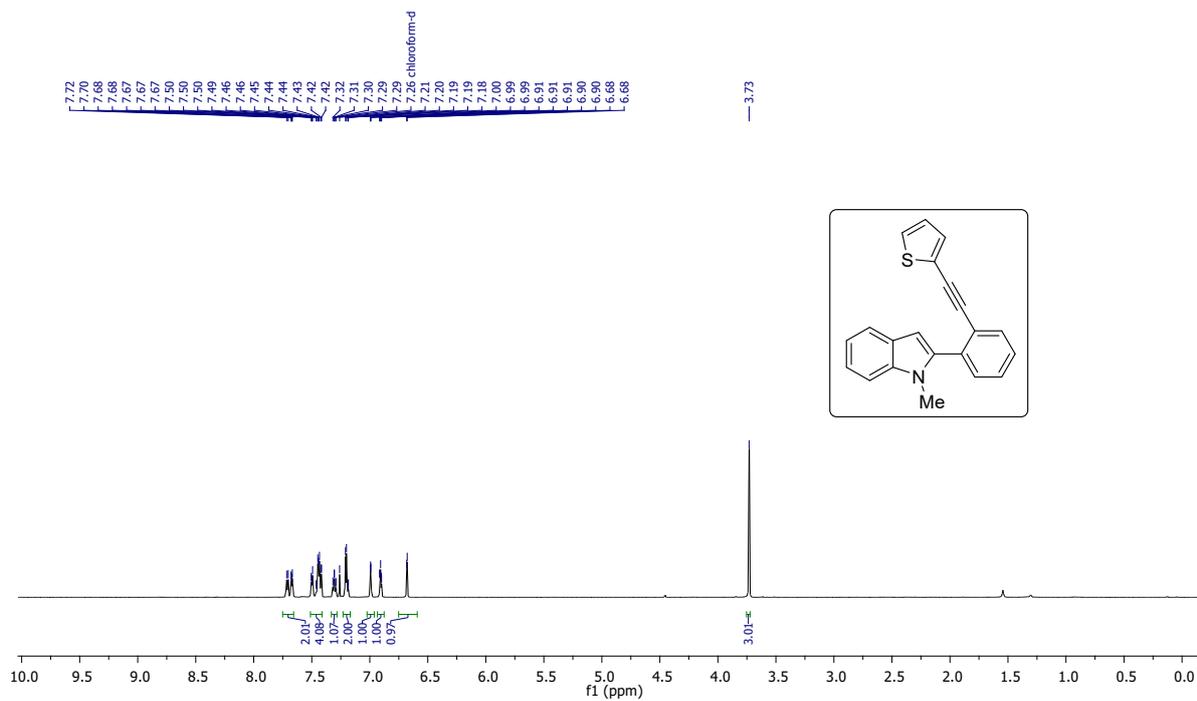




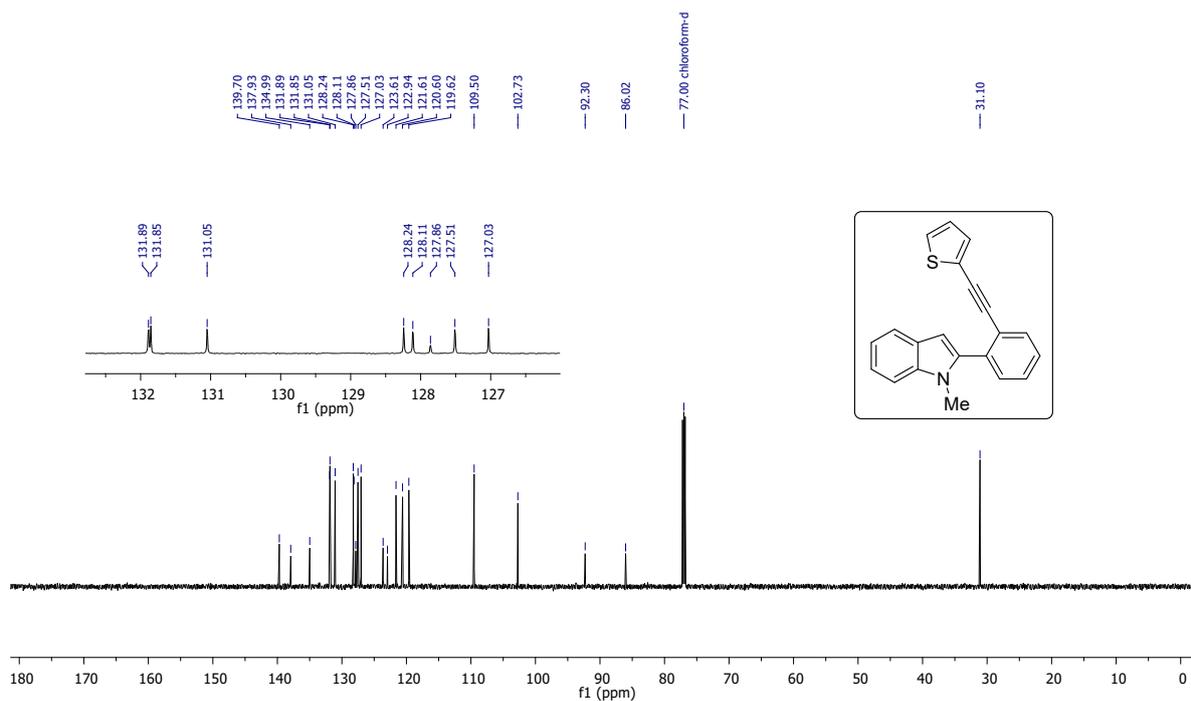
H NMR (600 MHz) spectrum of **1j** in CDCl<sub>3</sub>



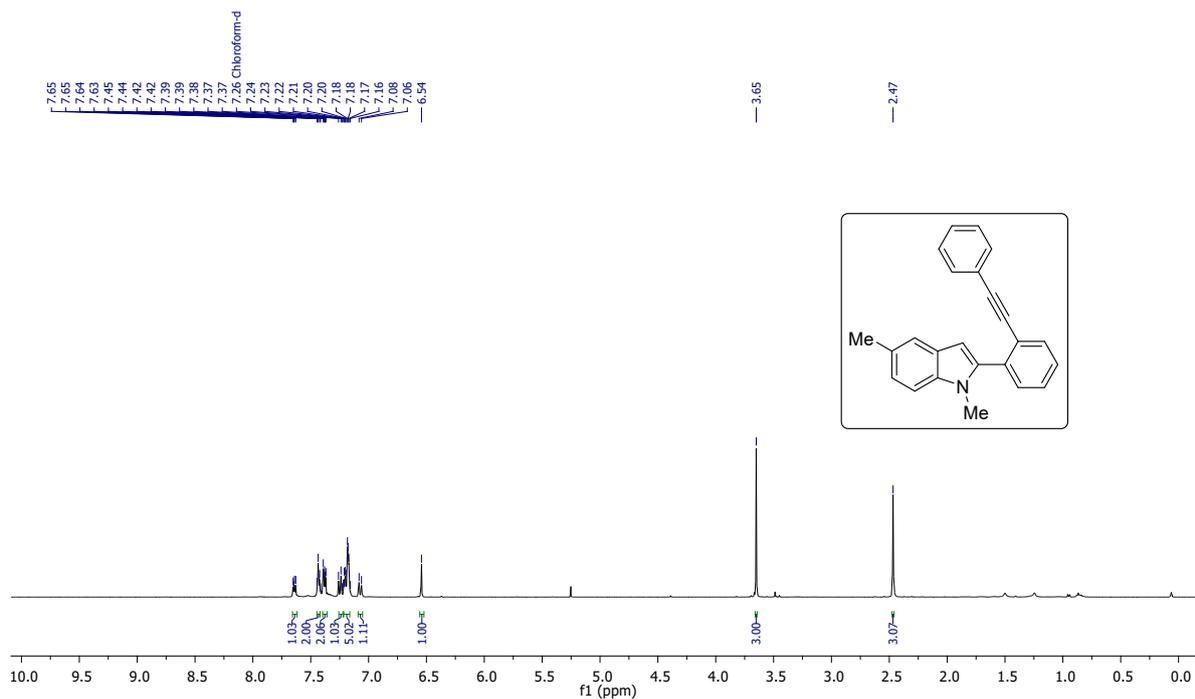
<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz) spectrum of **1j** in CDCl<sub>3</sub>



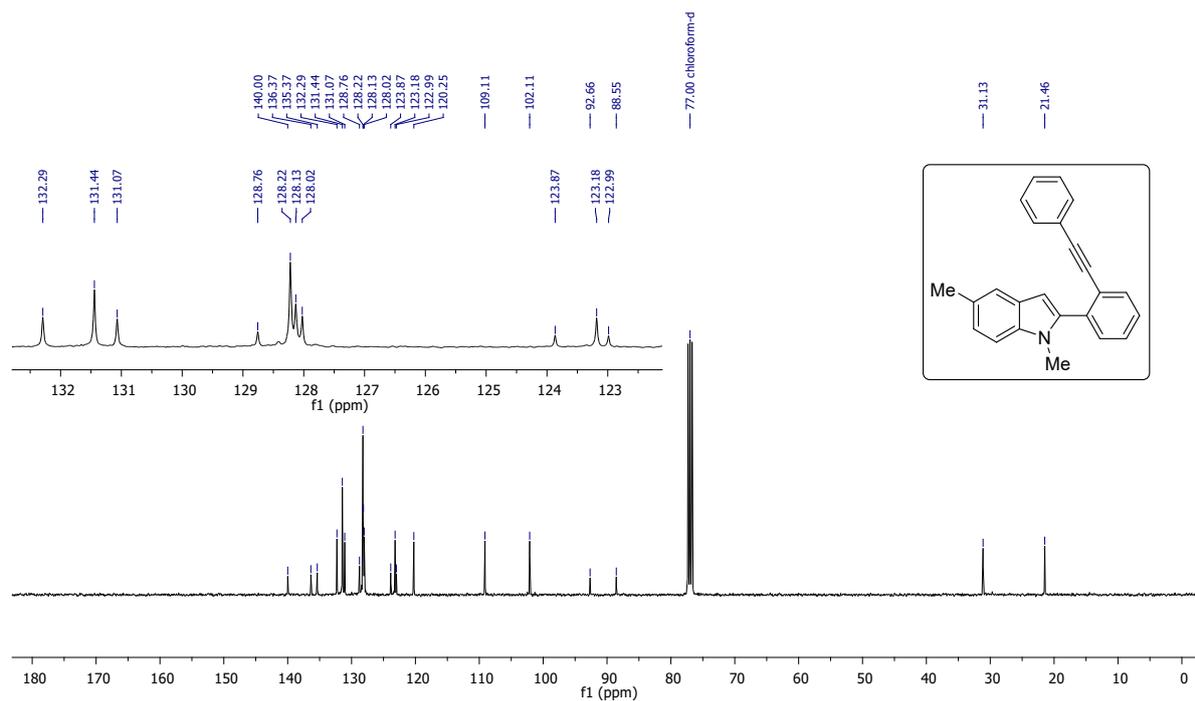
$^1\text{H}$  NMR (600 MHz) spectrum of **1k** in  $\text{CDCl}_3$



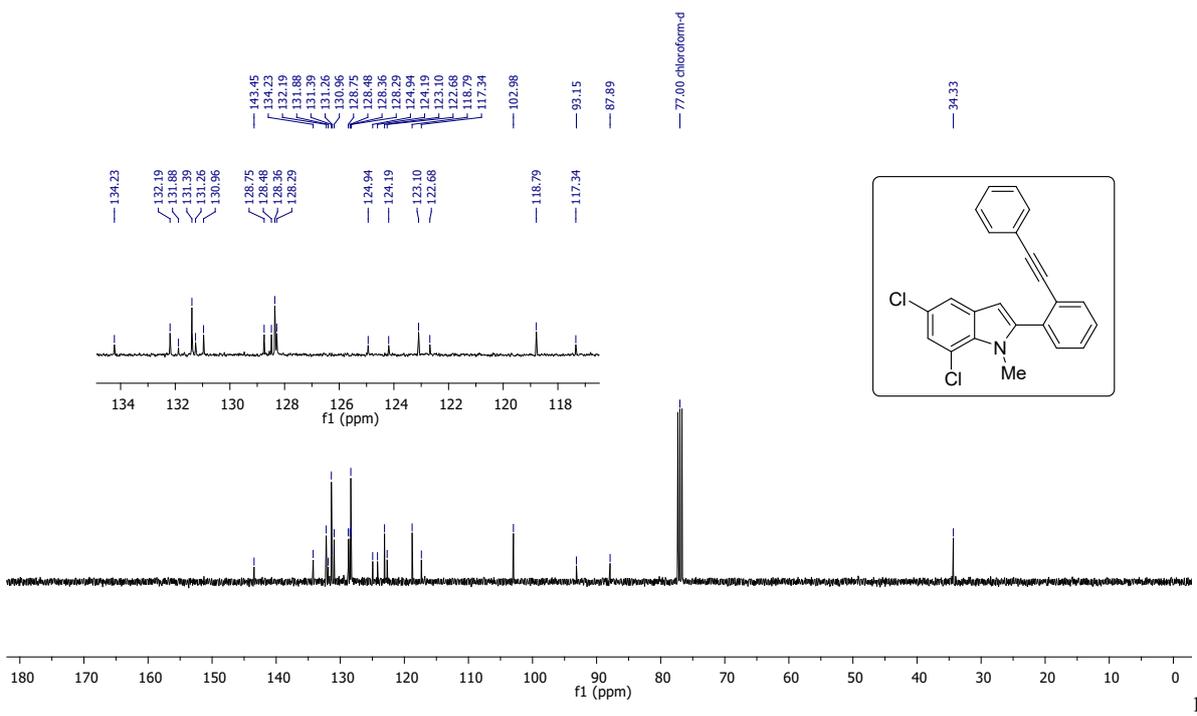
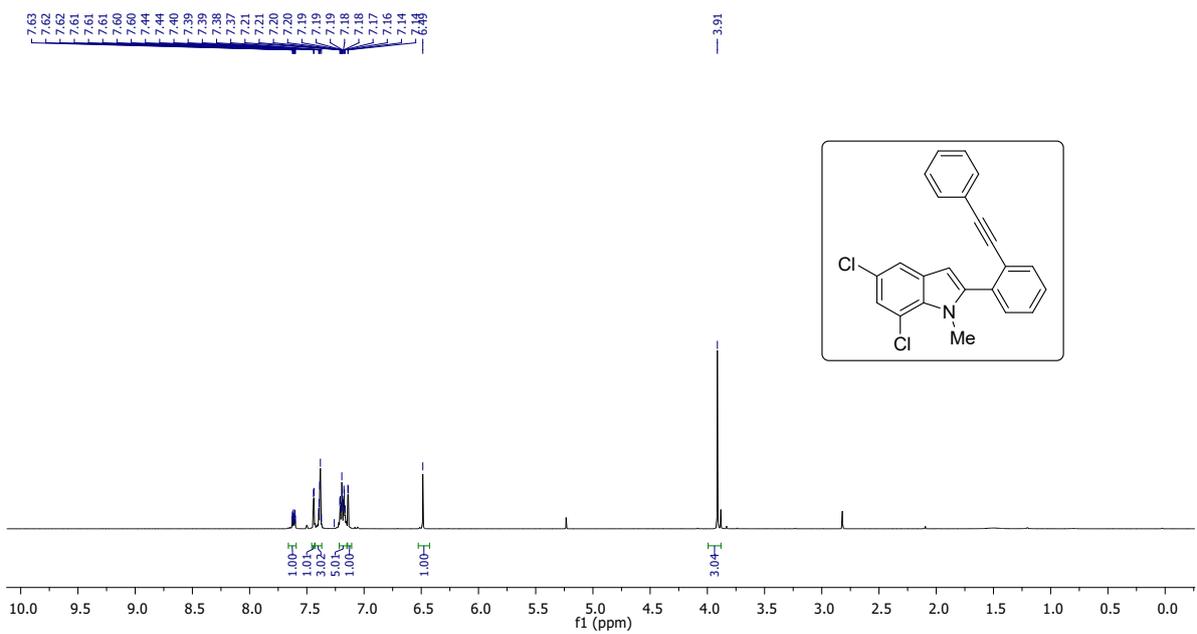
$^{13}\text{C}$  NMR (151 MHz) spectrum of **1k** in  $\text{CDCl}_3$



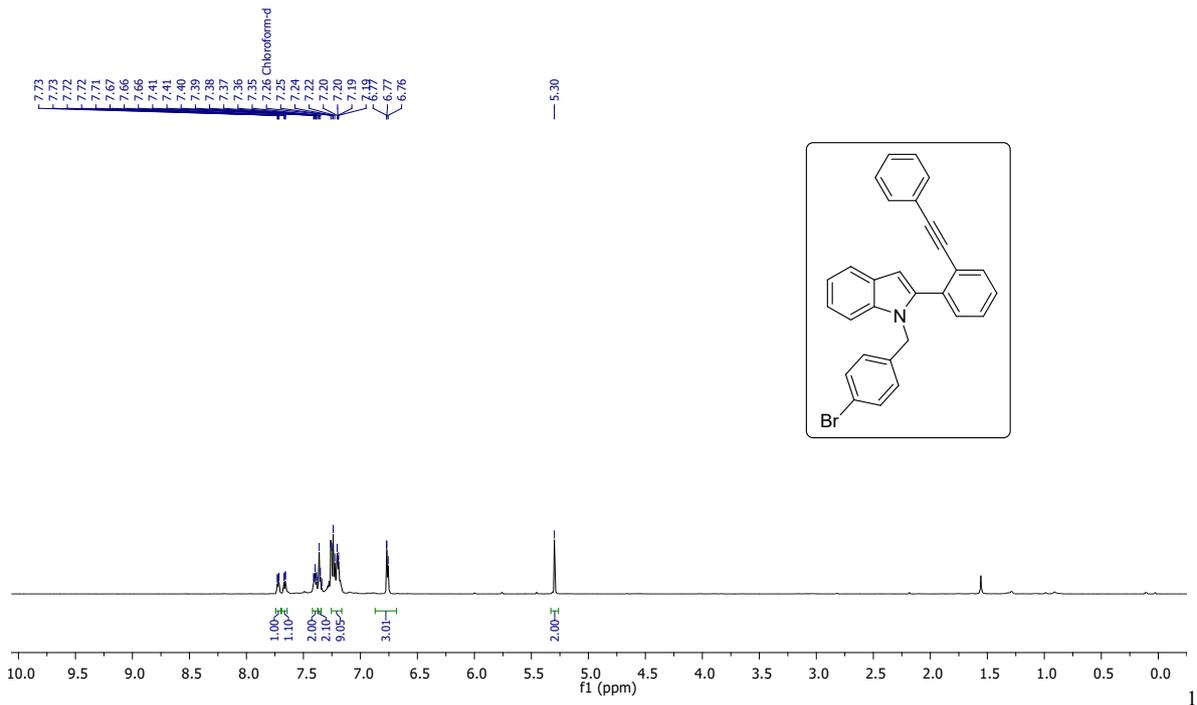
$^1\text{H}$  NMR (400 MHz) spectrum of **11** in  $\text{CDCl}_3$



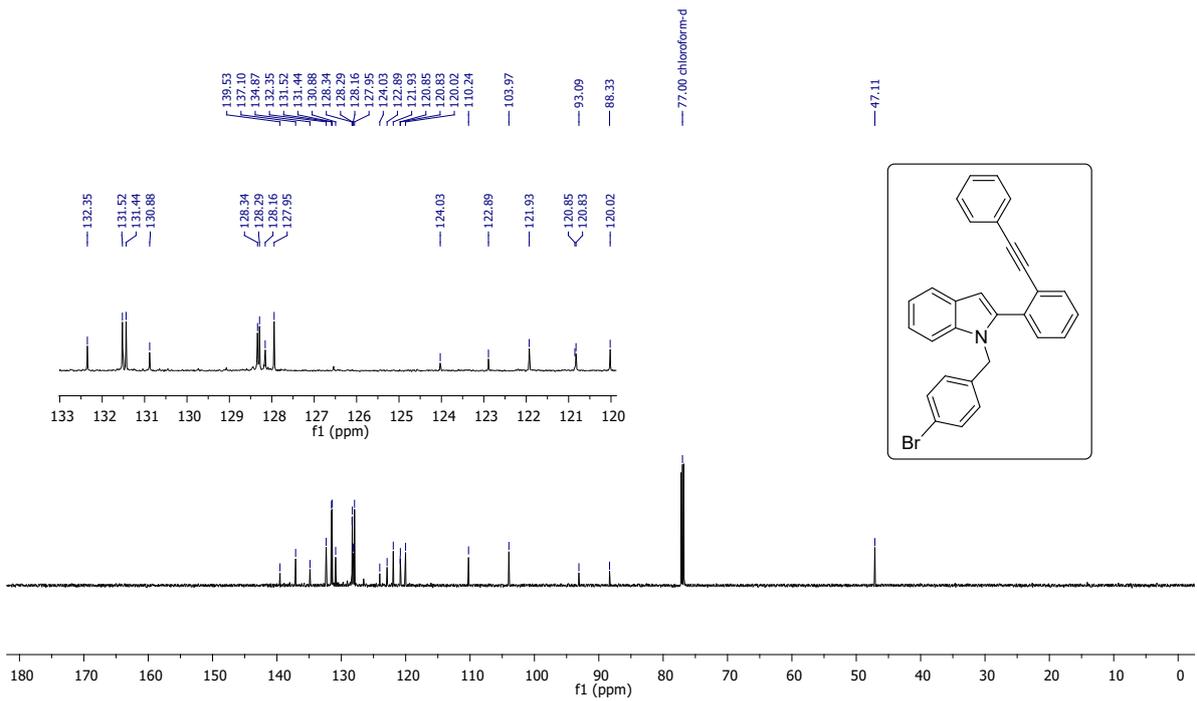
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz) spectrum of **11** in  $\text{CDCl}_3$



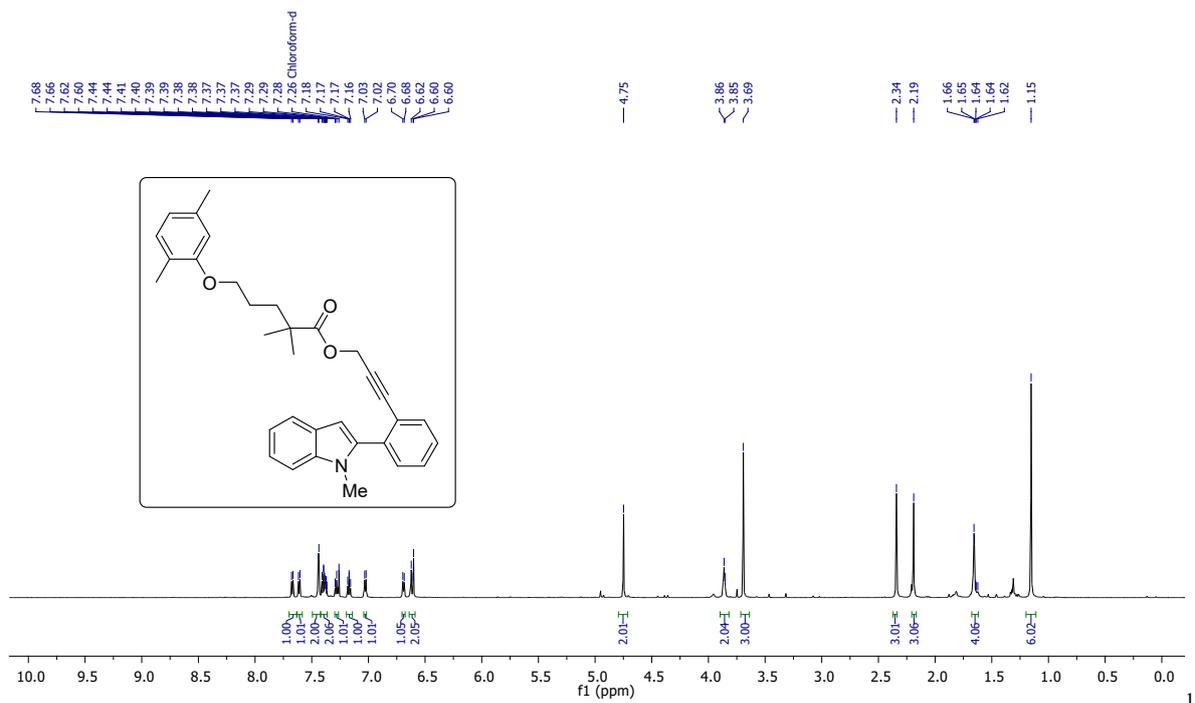




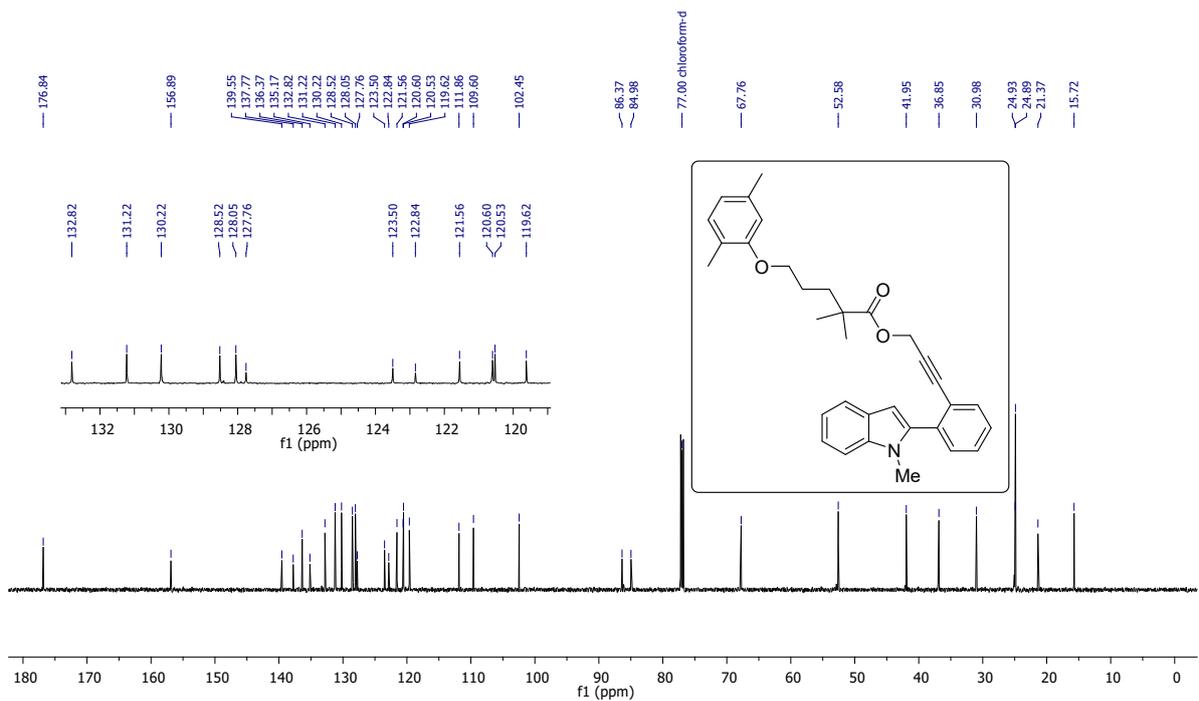
H NMR (600 MHz) spectrum of **10** in CDCl<sub>3</sub>



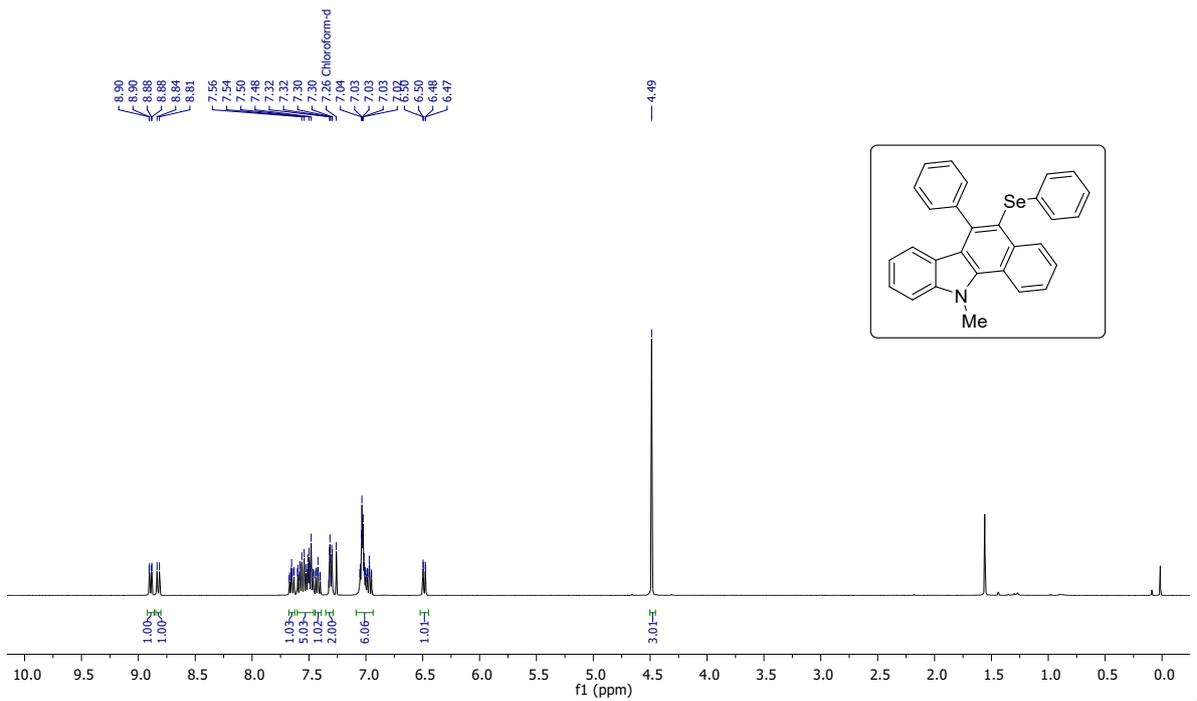
<sup>13</sup>C {<sup>1</sup>H} NMR (151 MHz) spectrum of **10** in CDCl<sub>3</sub>



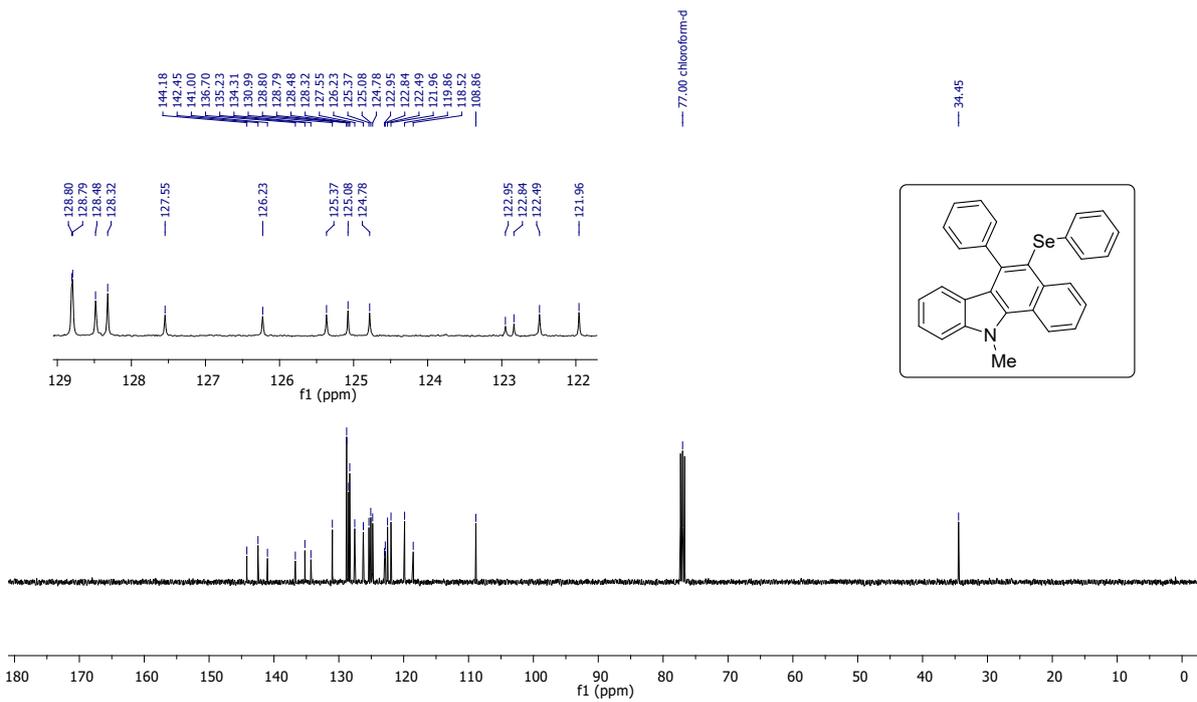
**<sup>1</sup>H NMR (600 MHz) spectrum of **1p** in CDCl<sub>3</sub>**



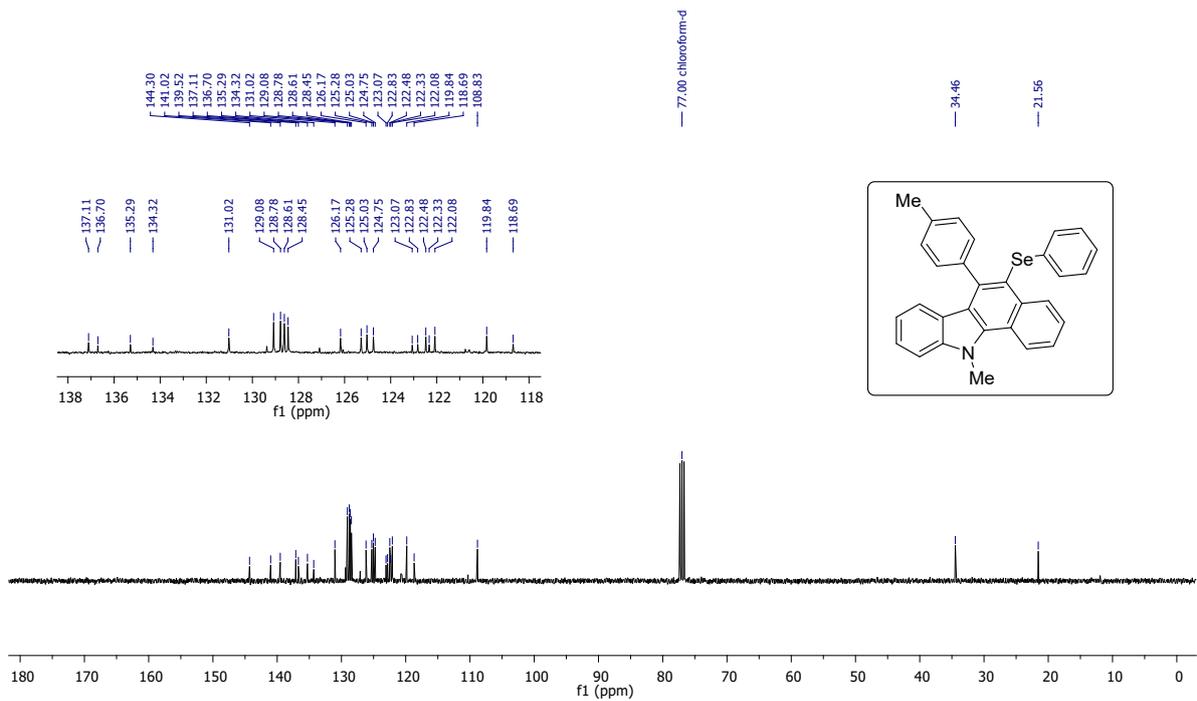
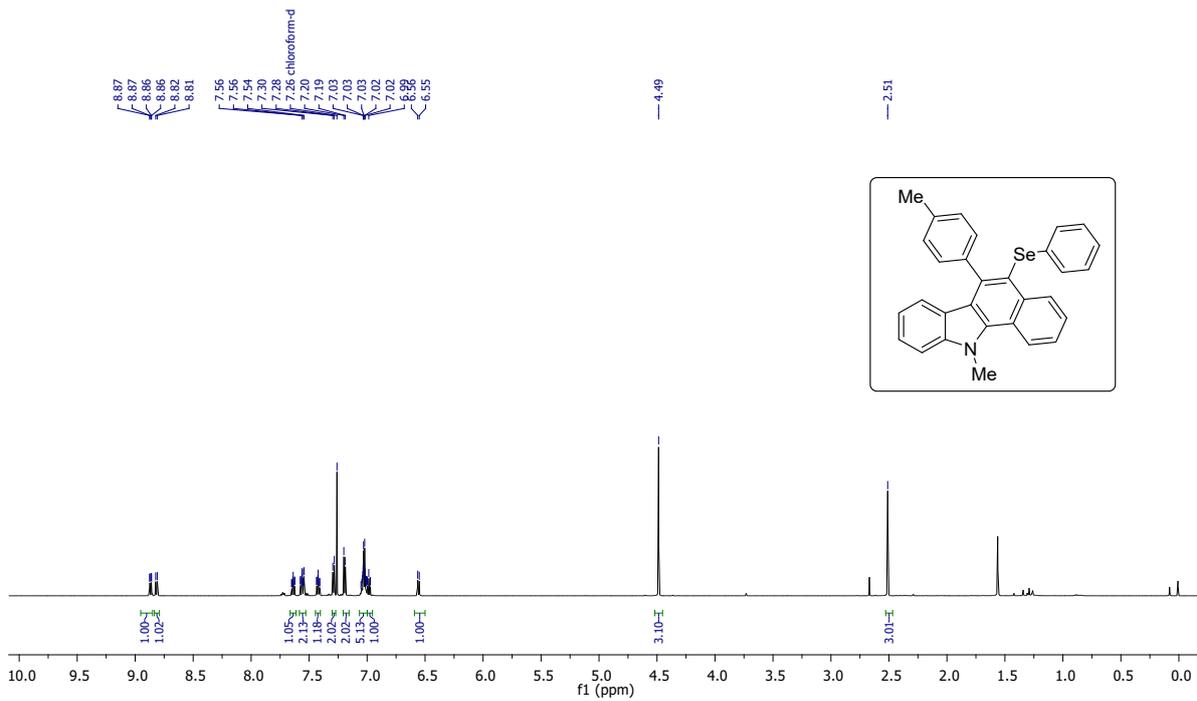
**<sup>13</sup>C {<sup>1</sup>H} NMR (151 MHz) spectrum of **1p** in CDCl<sub>3</sub>**

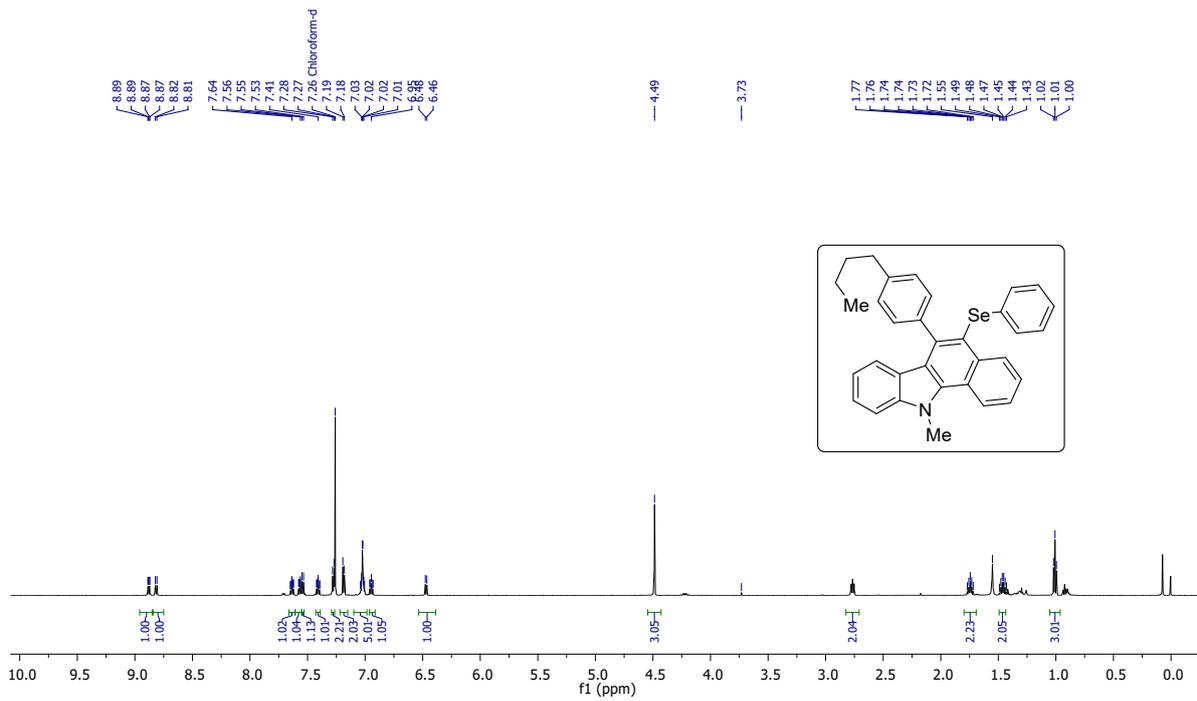


<sup>1</sup>H NMR (400 MHz) spectrum of **3aa** in CDCl<sub>3</sub>

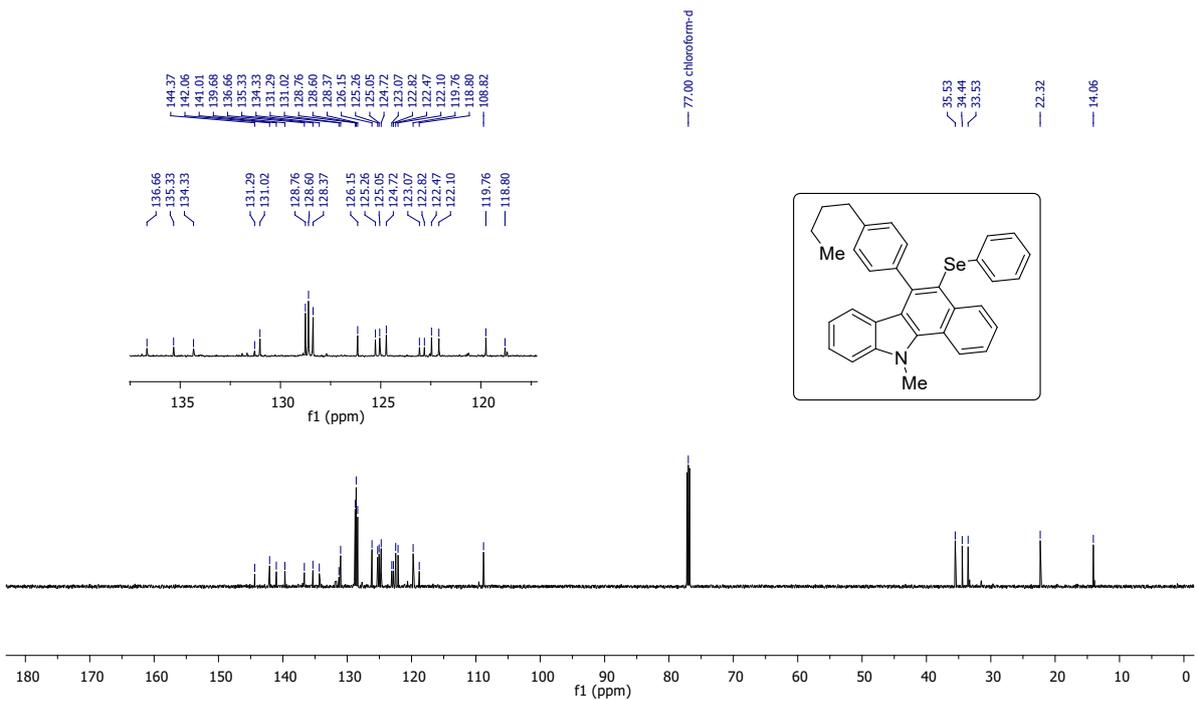


<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz) spectrum of **3aa** in CDCl<sub>3</sub>

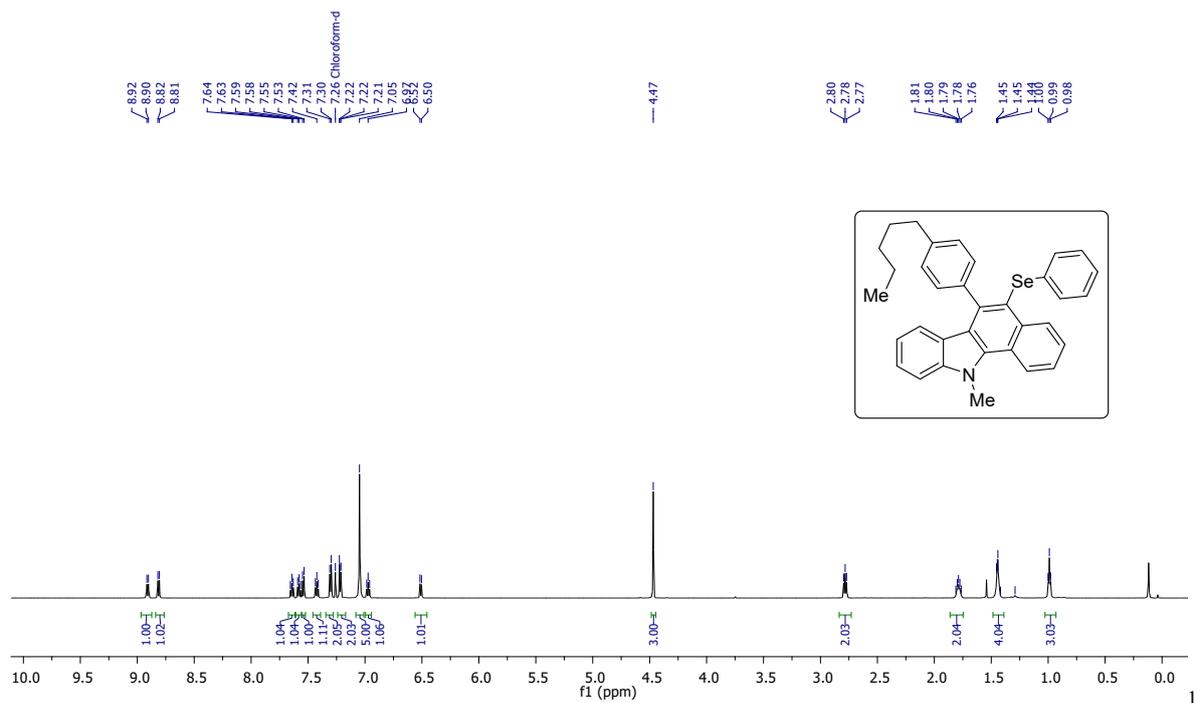




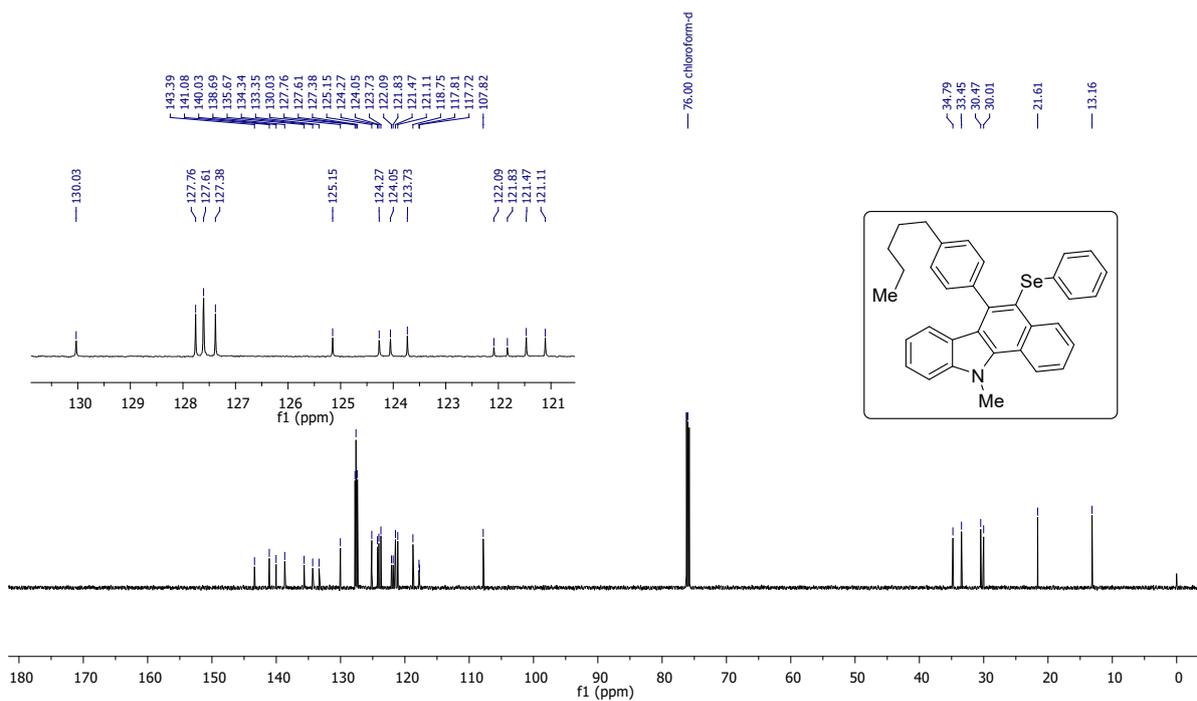
<sup>1</sup>H NMR (600 MHz) spectrum of **3ca** in CDCl<sub>3</sub>



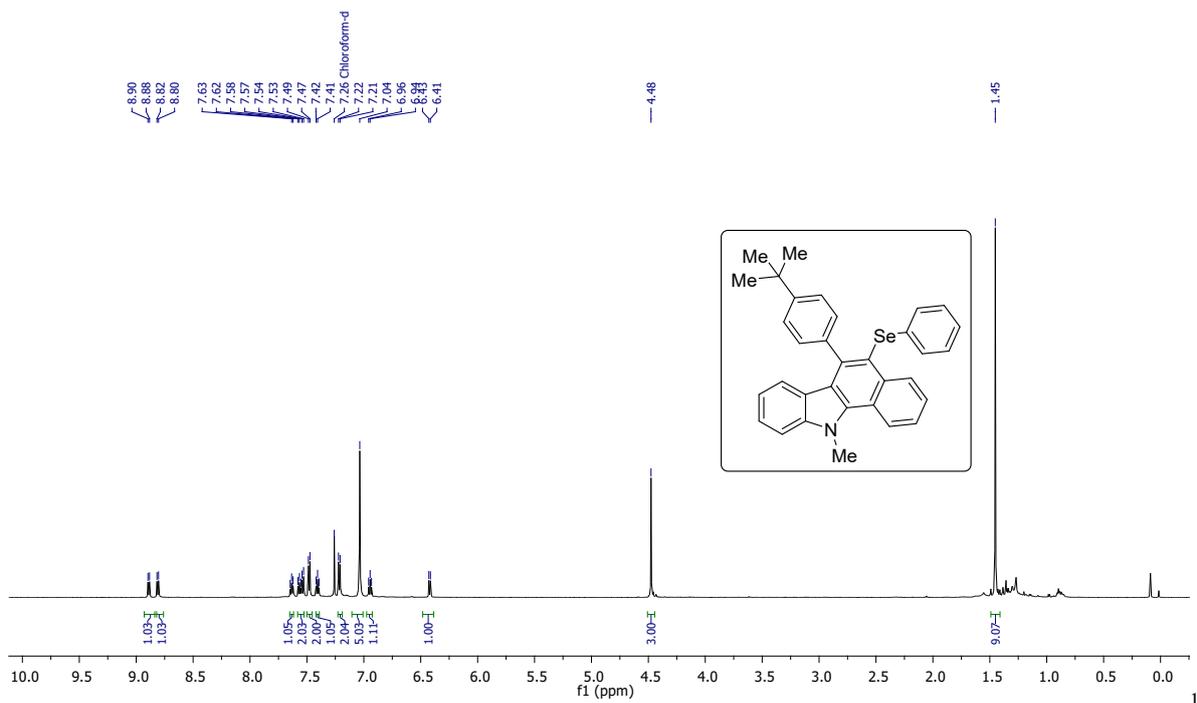
<sup>13</sup>C {<sup>1</sup>H} NMR (151 MHz) spectrum of **3ca** in CDCl<sub>3</sub>



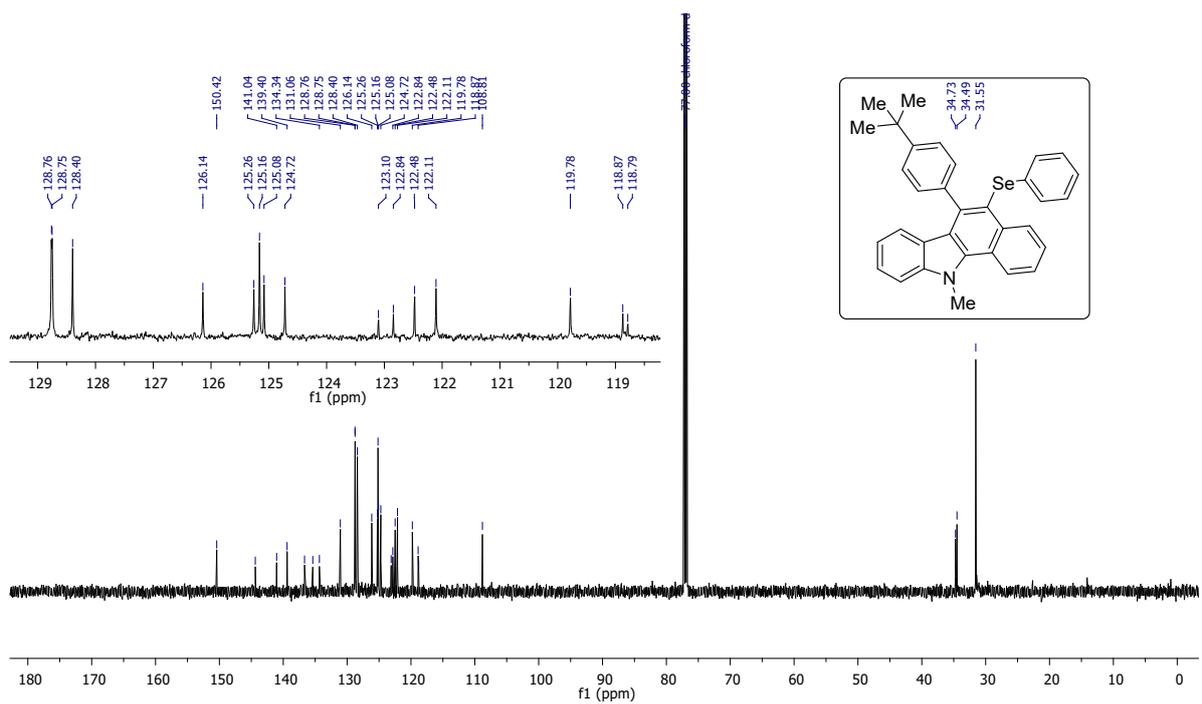
<sup>1</sup>H NMR (600 MHz) spectrum of **3da** in CDCl<sub>3</sub>



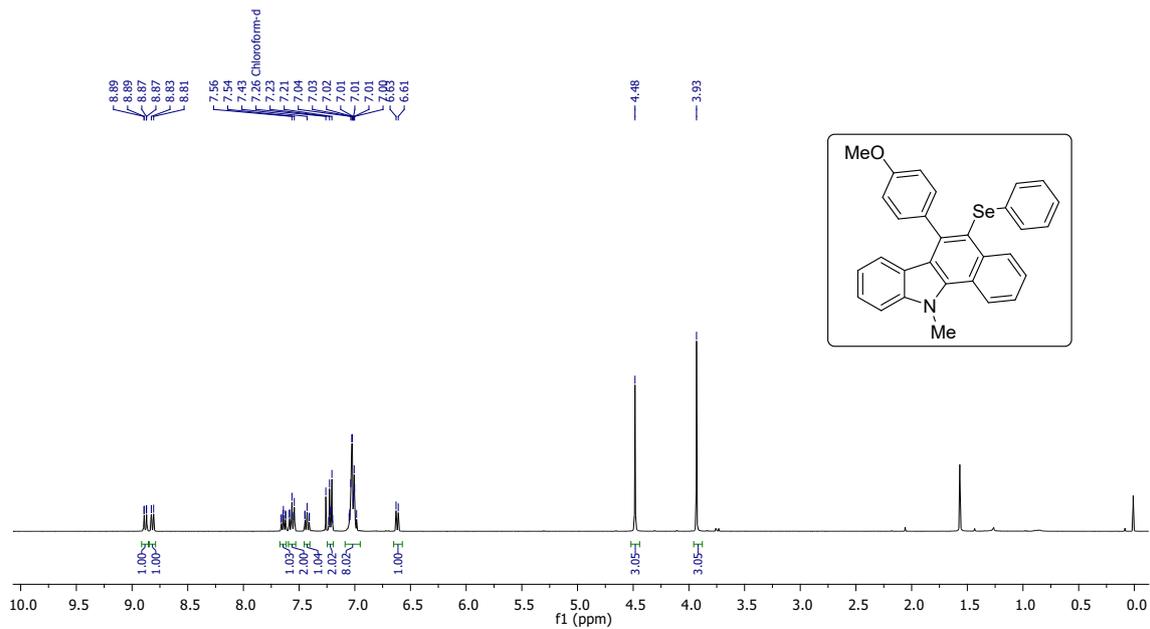
<sup>13</sup>C {<sup>1</sup>H} NMR (151 MHz) spectrum of **3da** in CDCl<sub>3</sub>



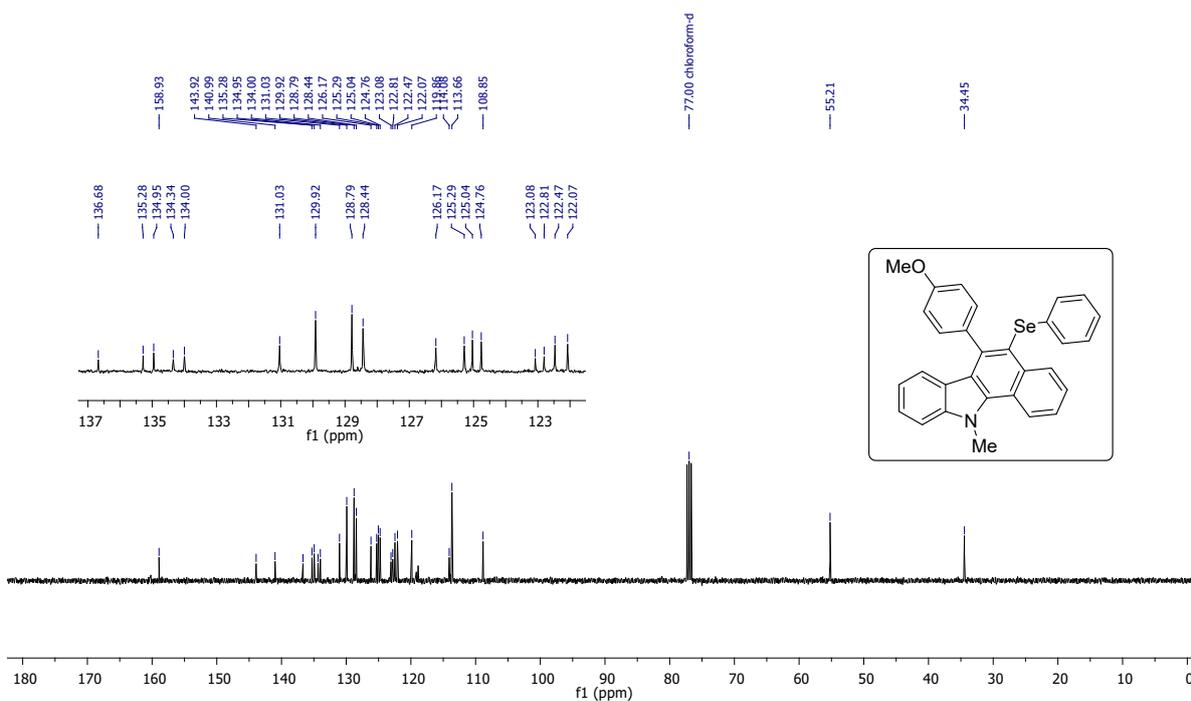
<sup>1</sup>H NMR (600 MHz) spectrum of **3ea** in CDCl<sub>3</sub>



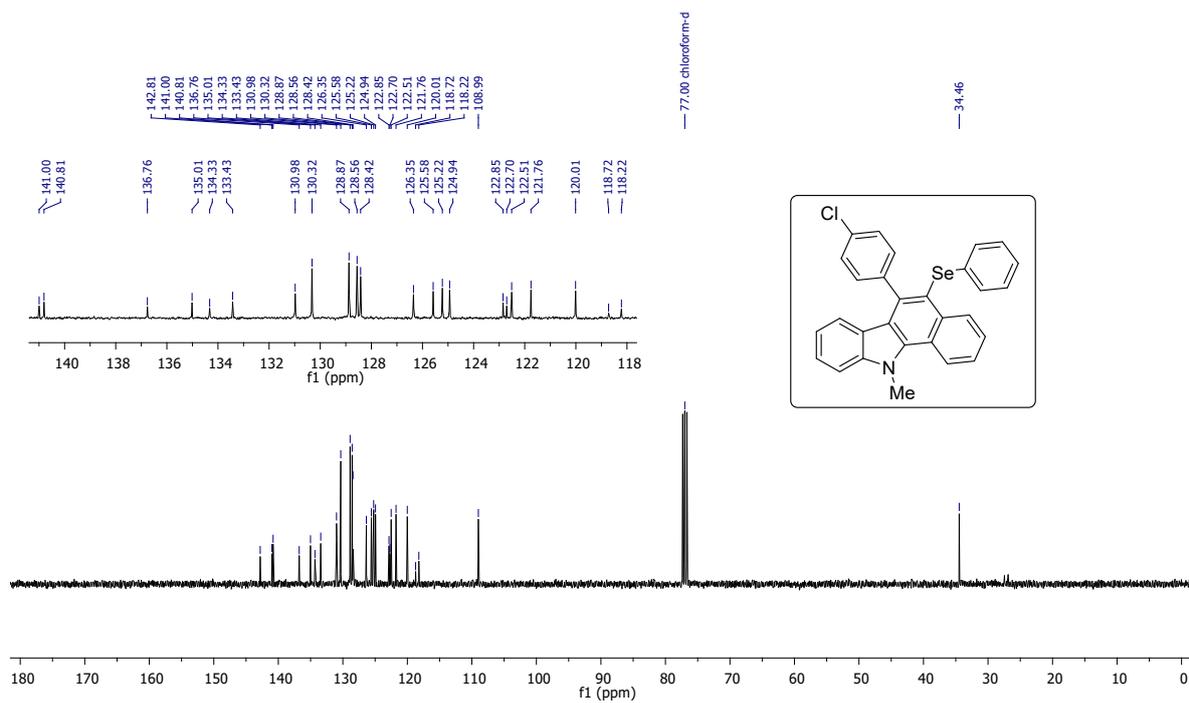
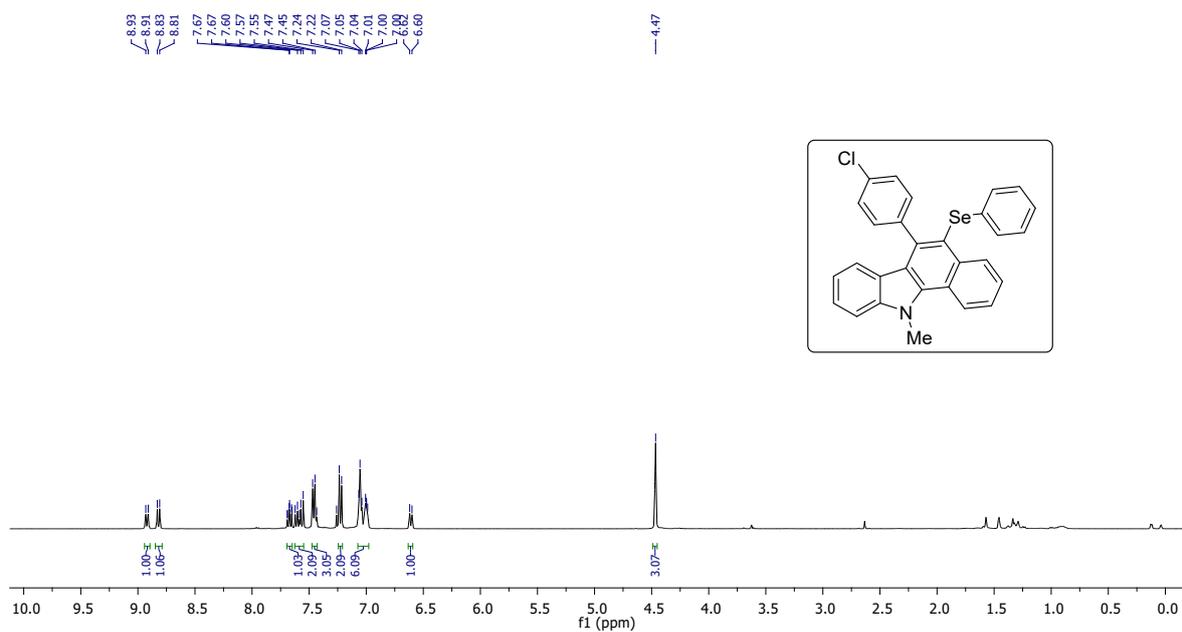
<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz) spectrum of **3ea** in CDCl<sub>3</sub>

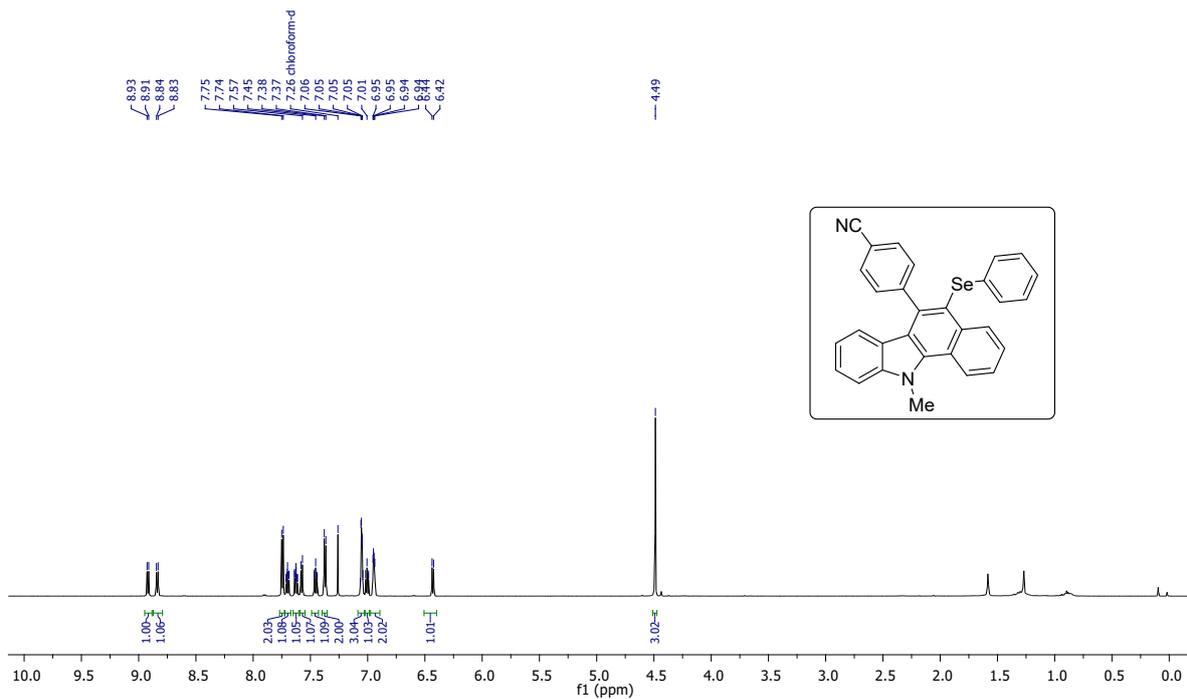


$^1\text{H}$  NMR (400 MHz) spectrum of **3fa** in  $\text{CDCl}_3$

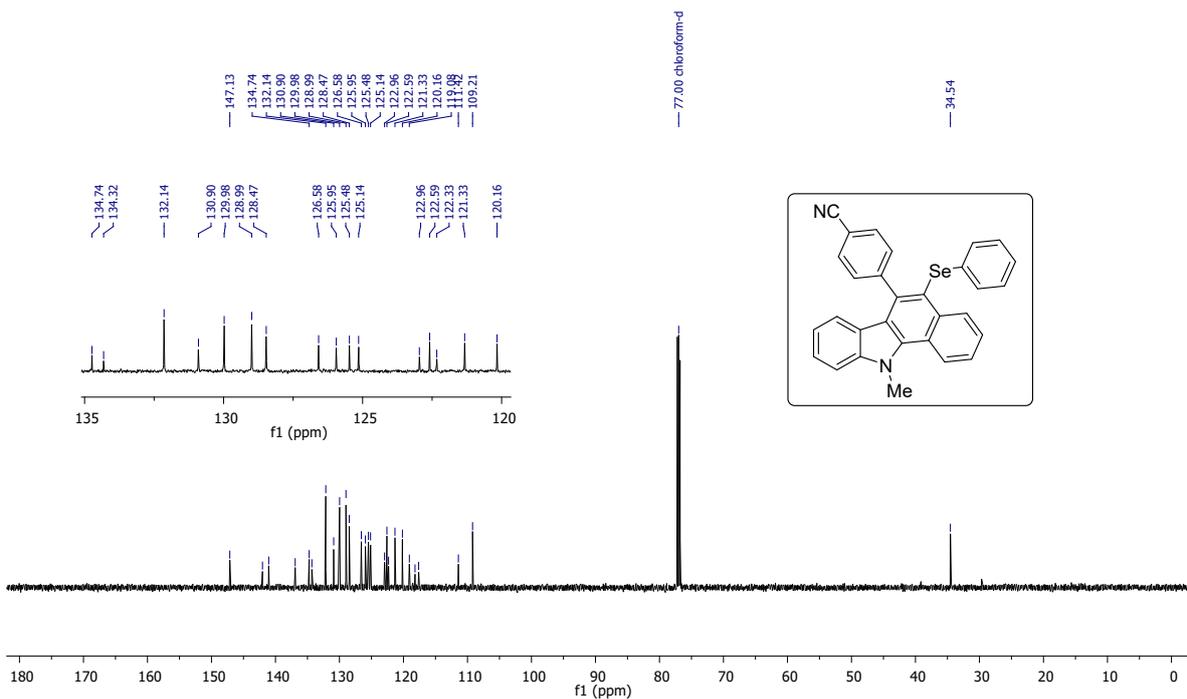


$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz) spectrum of **3fa** in  $\text{CDCl}_3$

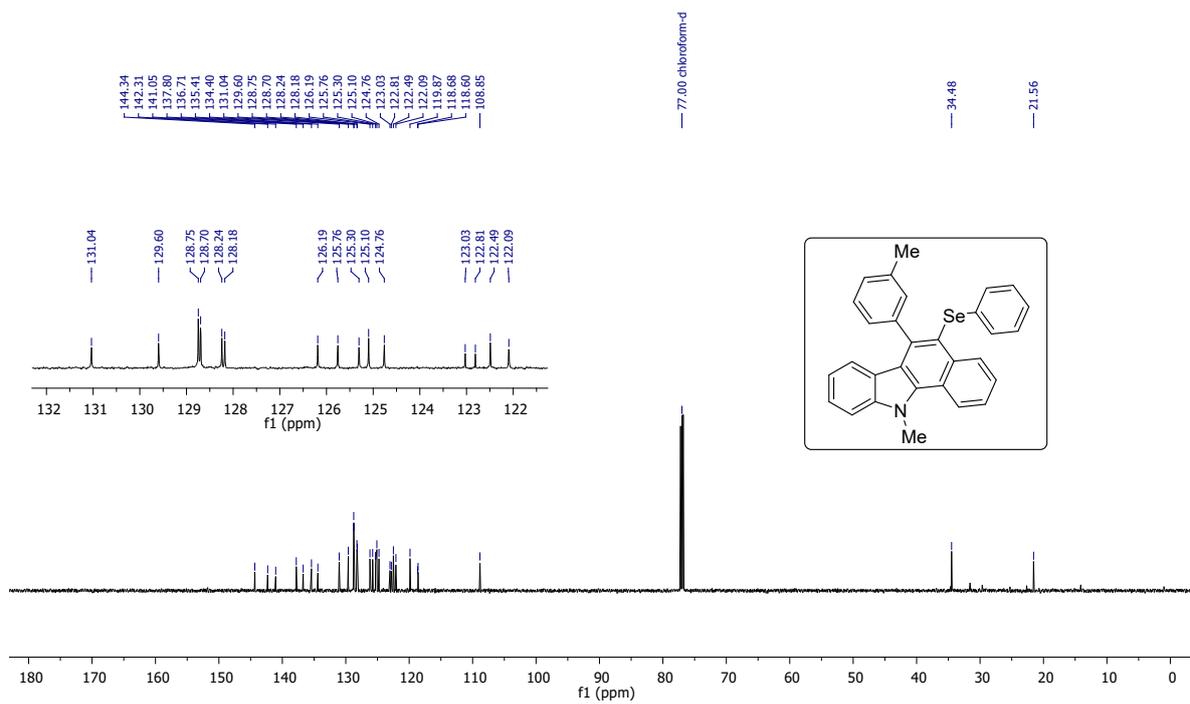
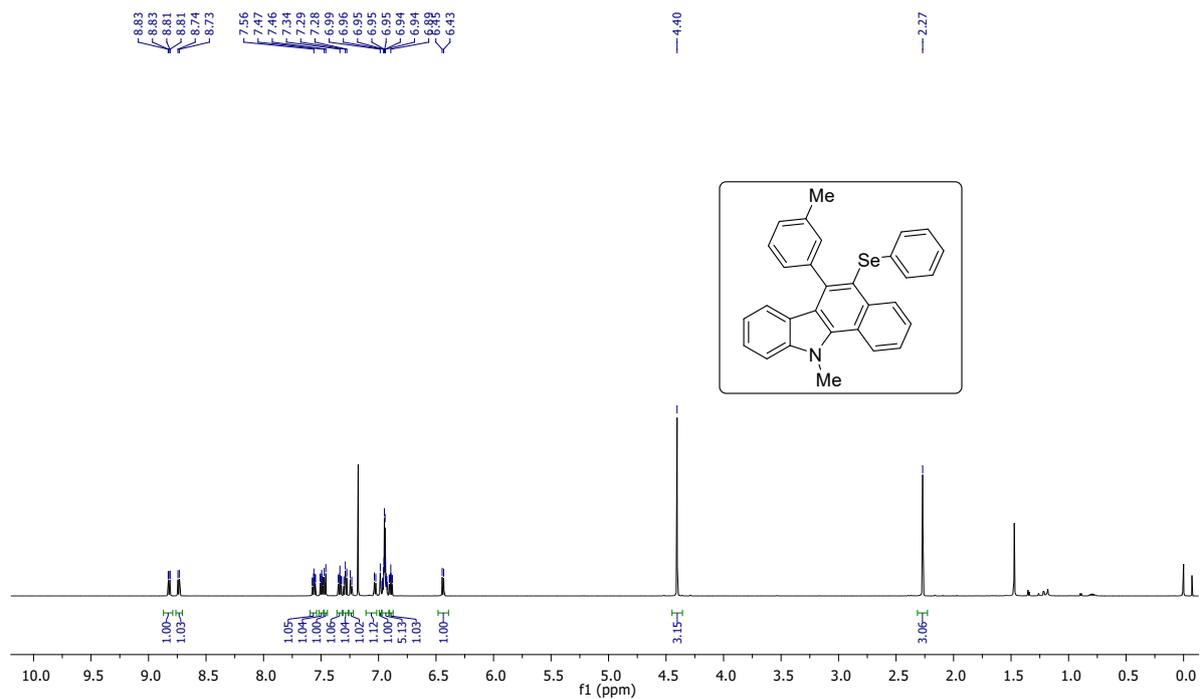


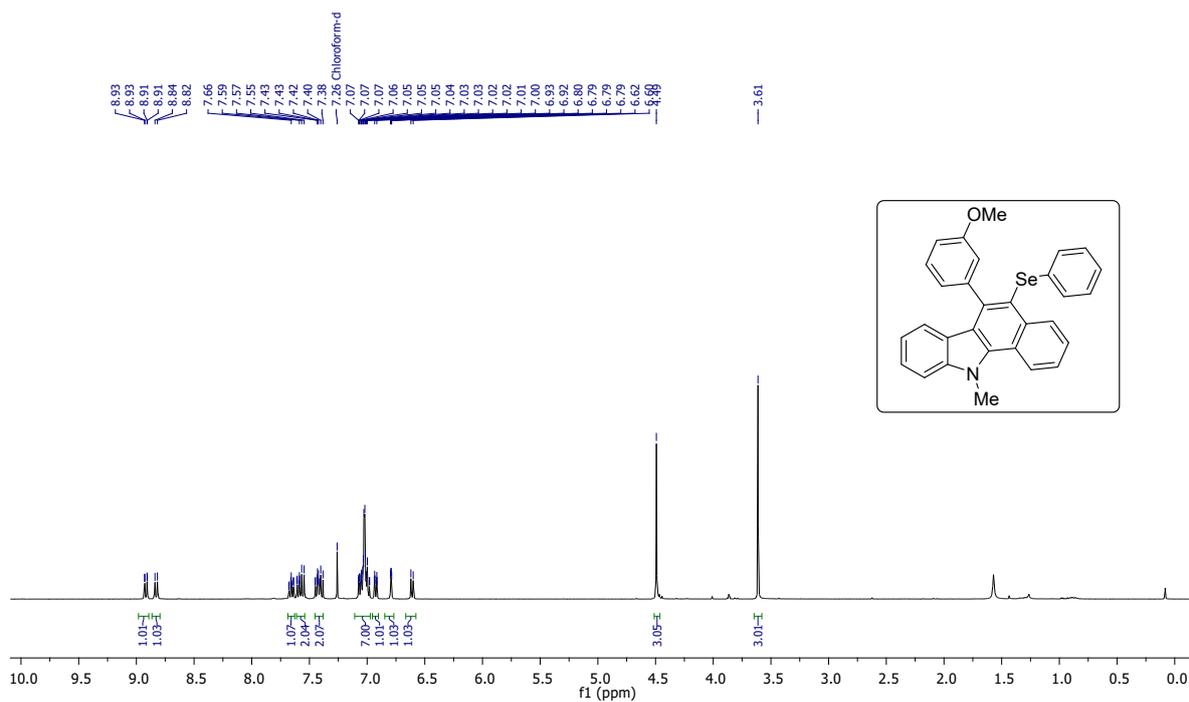


$^1\text{H NMR}$  (600 MHz) spectrum of **3ha** in  $\text{CDCl}_3$

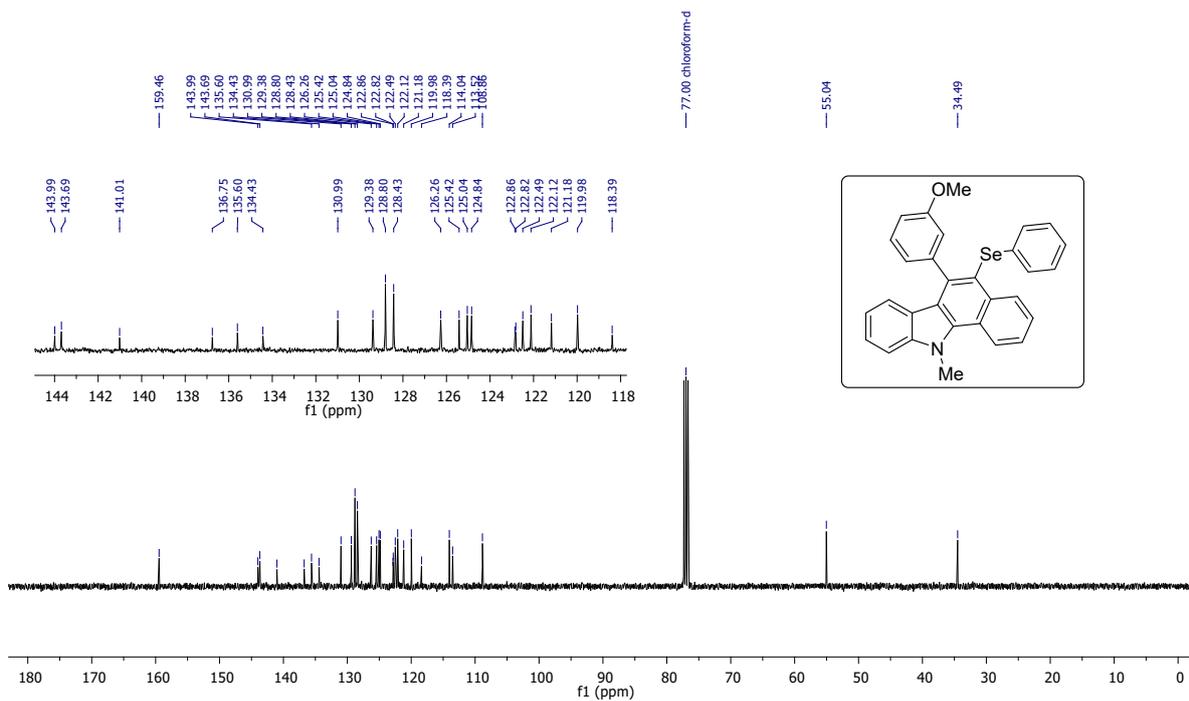


$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of **3ha** in  $\text{CDCl}_3$

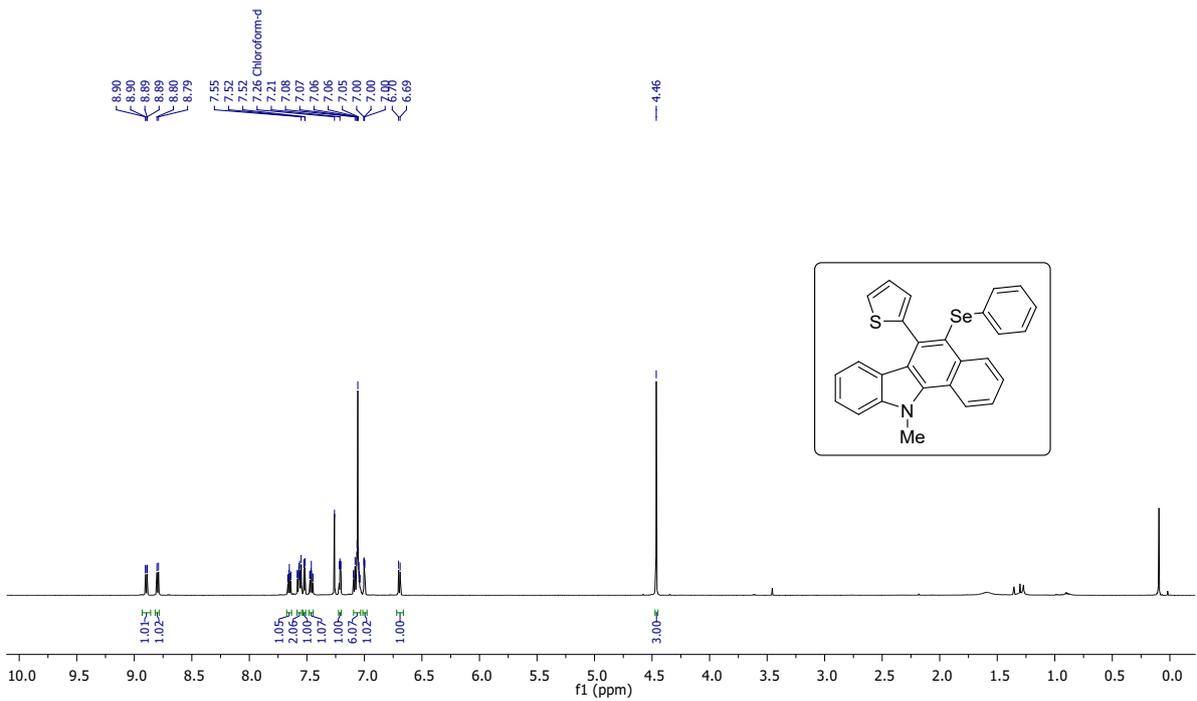




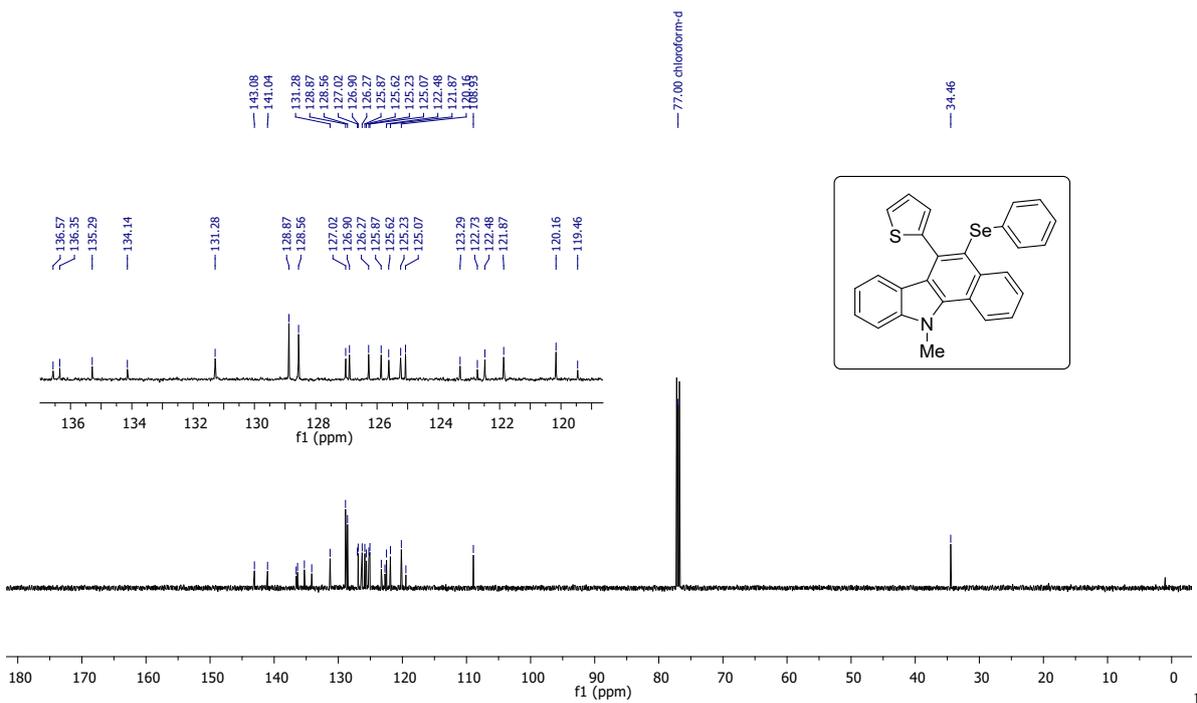
**<sup>1</sup>H NMR (400 MHz) spectrum of 3ja in CDCl<sub>3</sub>**



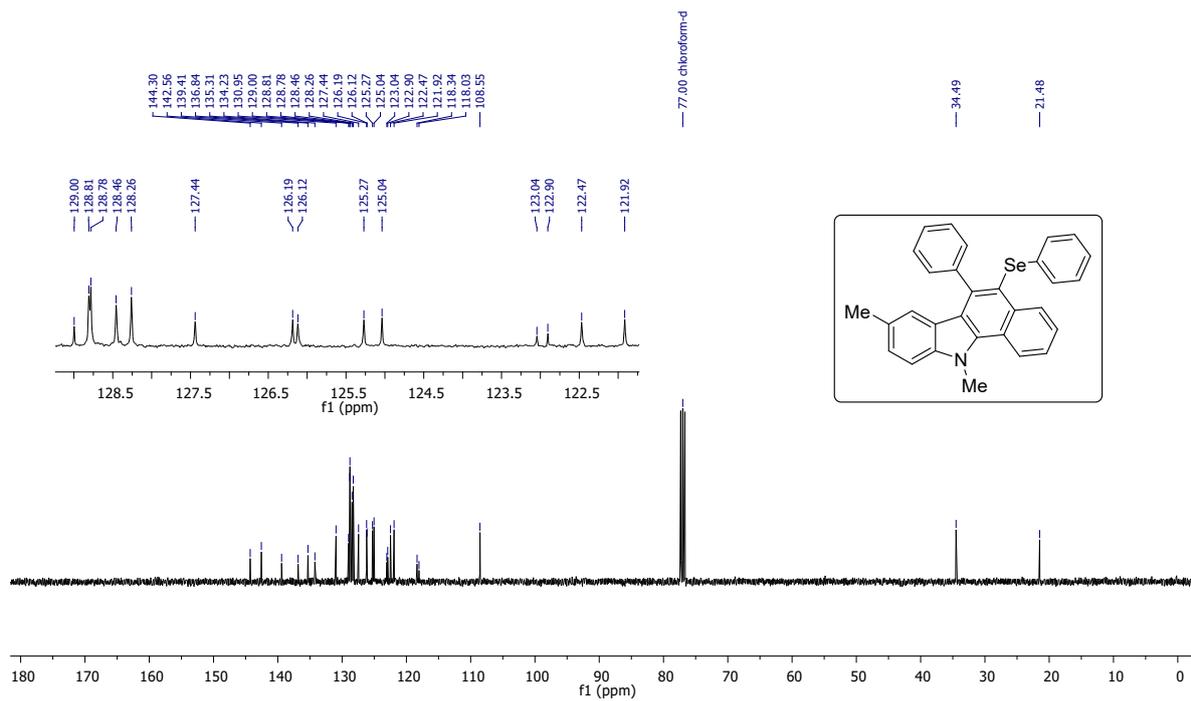
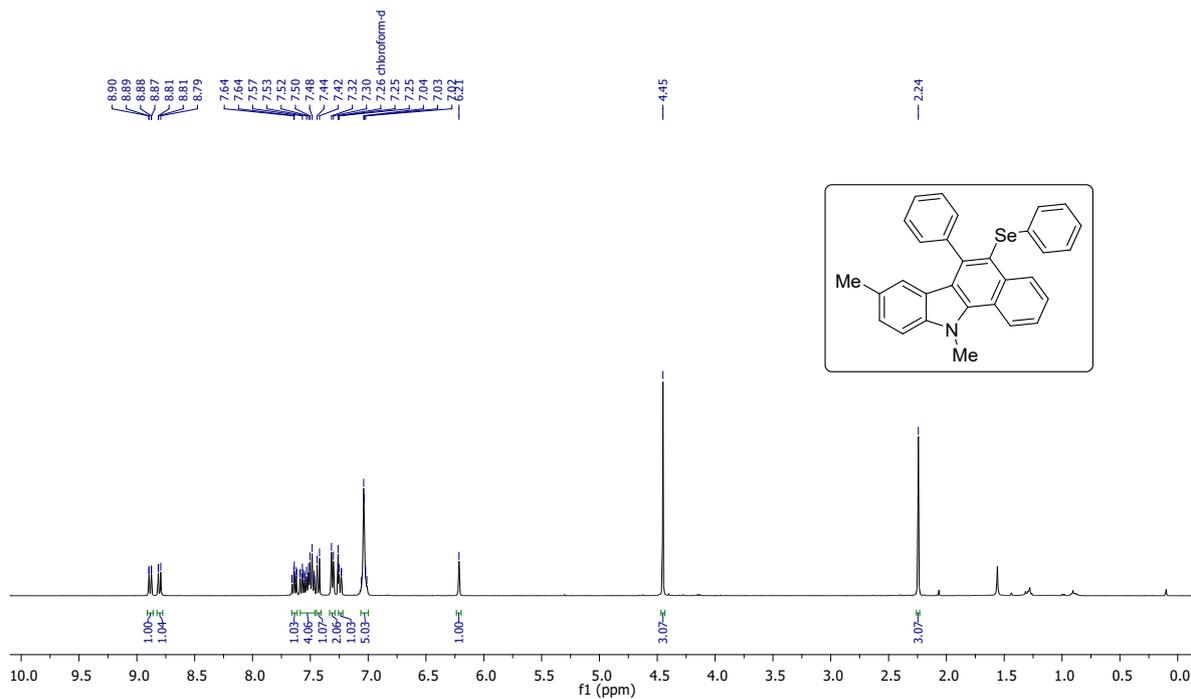
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz) spectrum of 3ja in CDCl<sub>3</sub>**

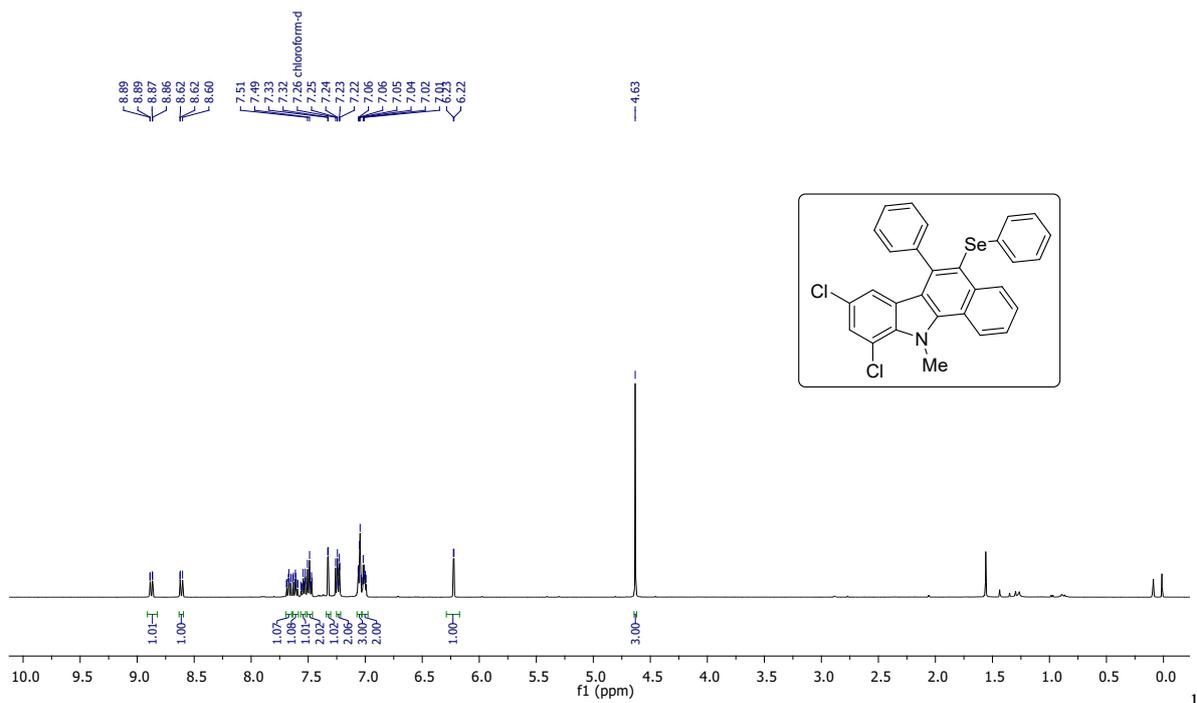


<sup>1</sup>H NMR (600 MHz) spectrum of **3ka** in CDCl<sub>3</sub>

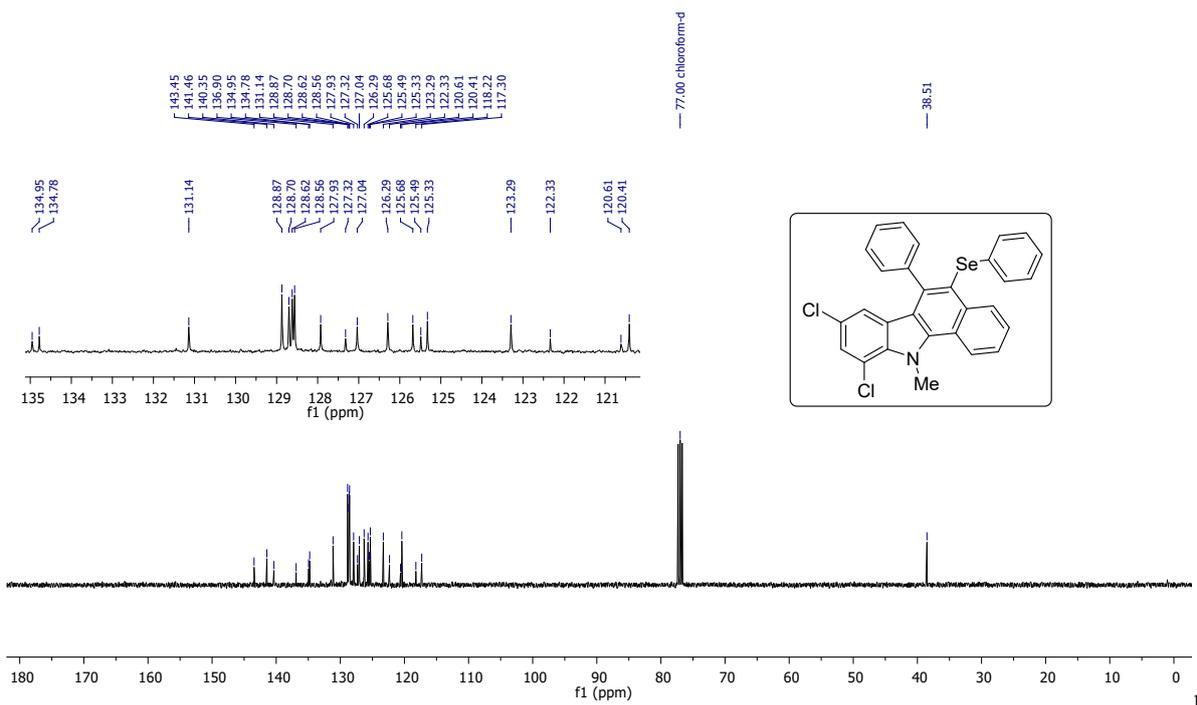


<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz) spectrum of **3ka** in CDCl<sub>3</sub>

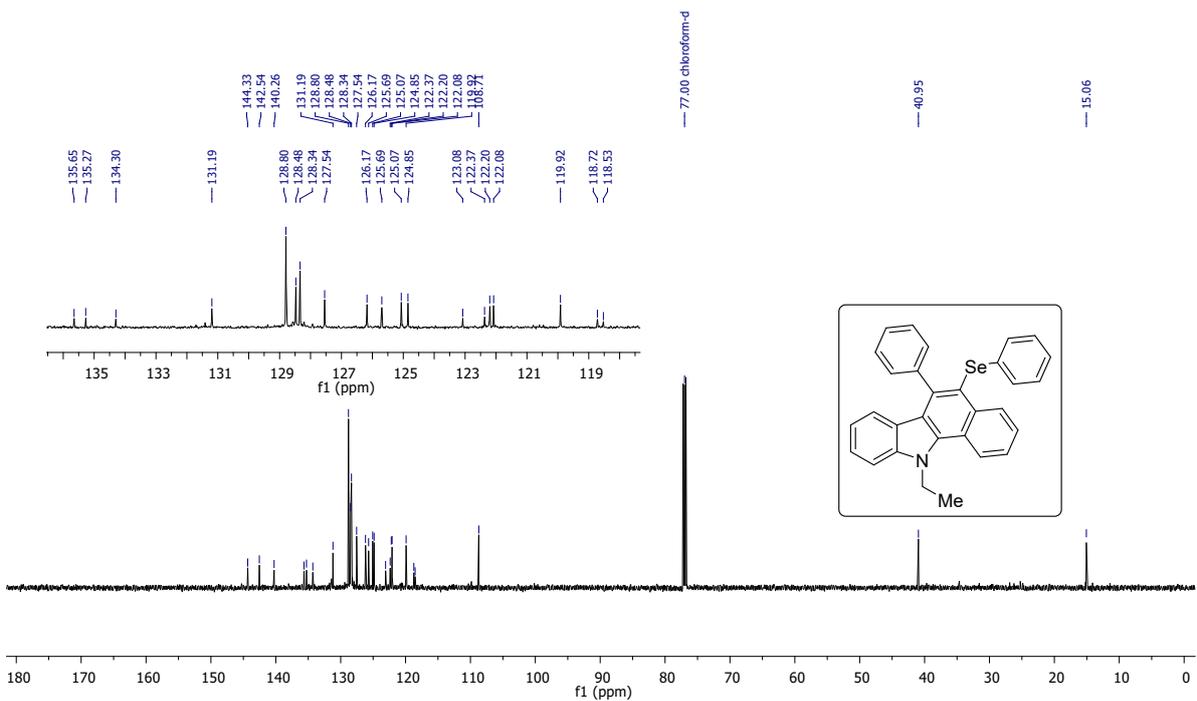
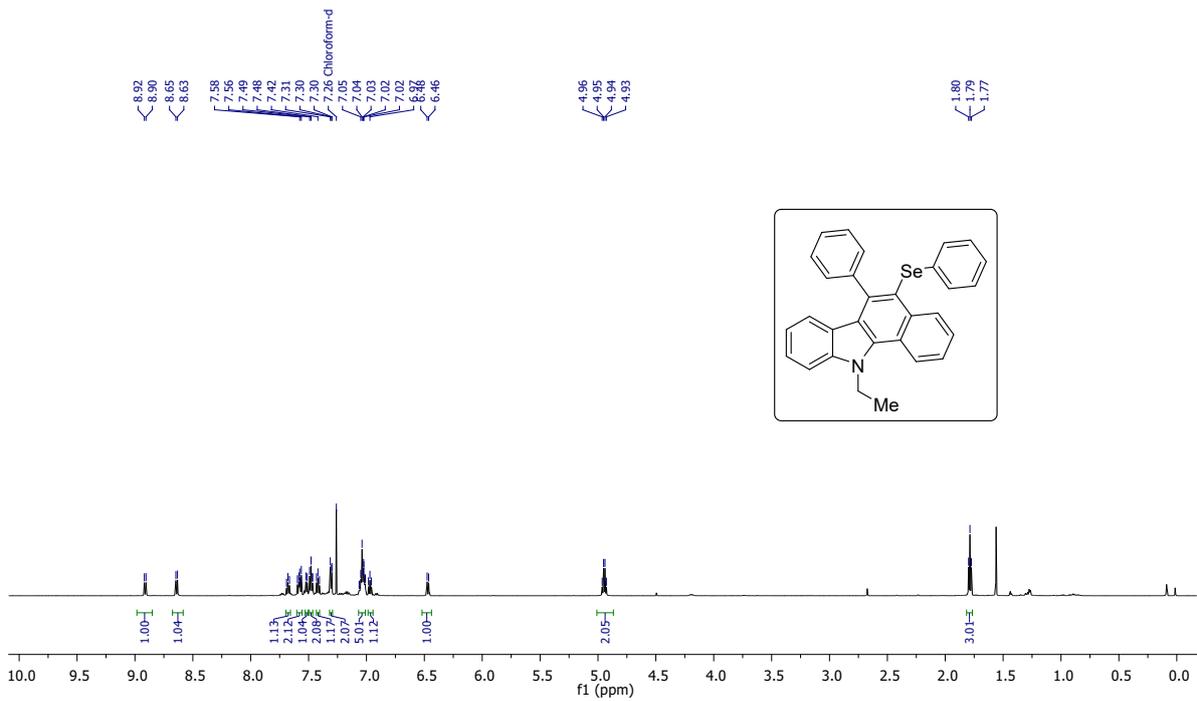


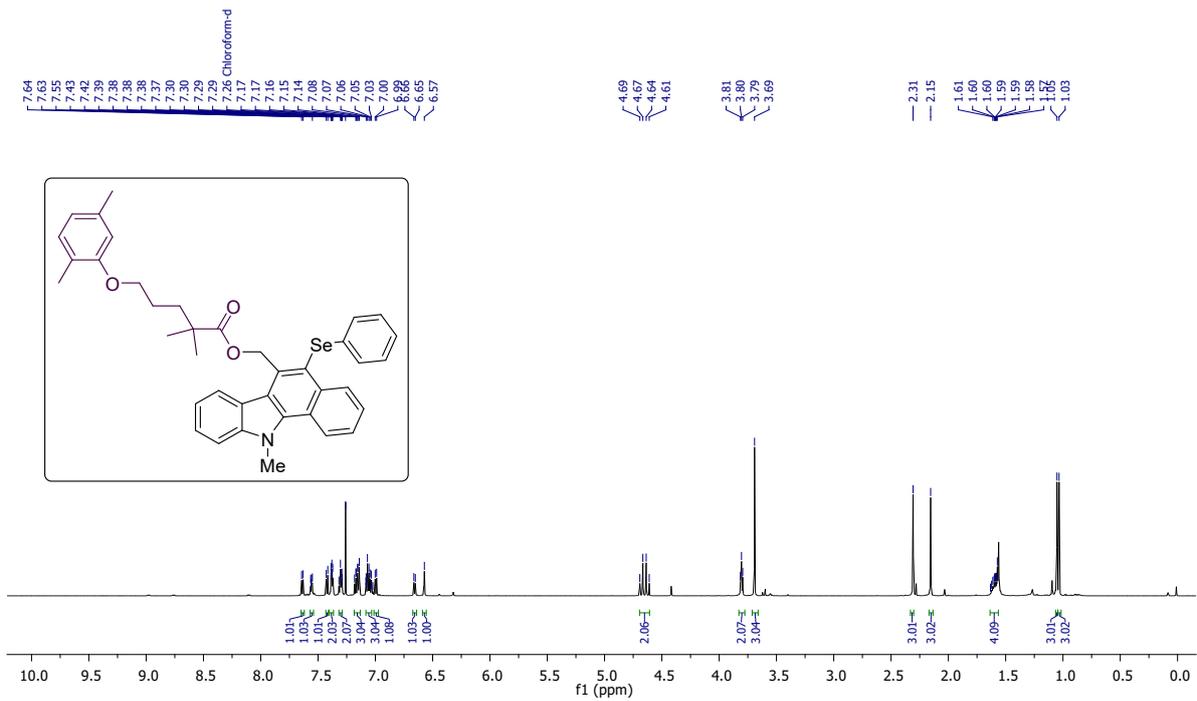


<sup>1</sup>H NMR (400 MHz) spectrum of **3ma** in CDCl<sub>3</sub>

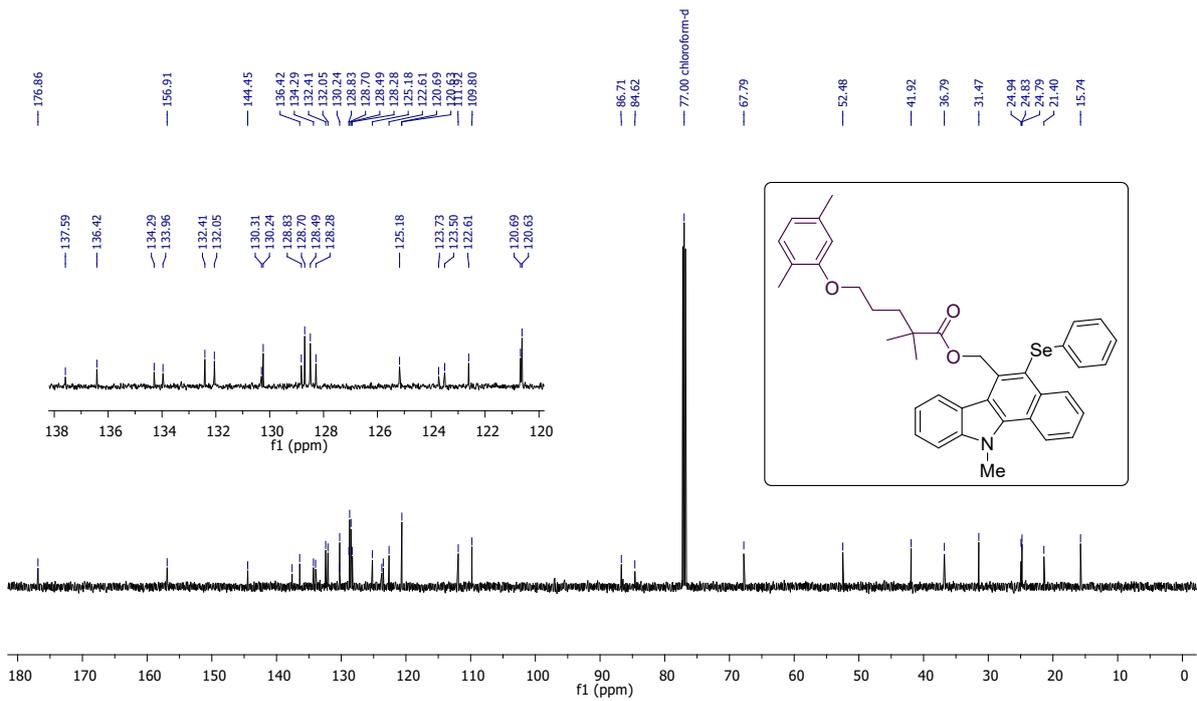


<sup>13</sup>C NMR (101 MHz) spectrum of **3ma** in CDCl<sub>3</sub>

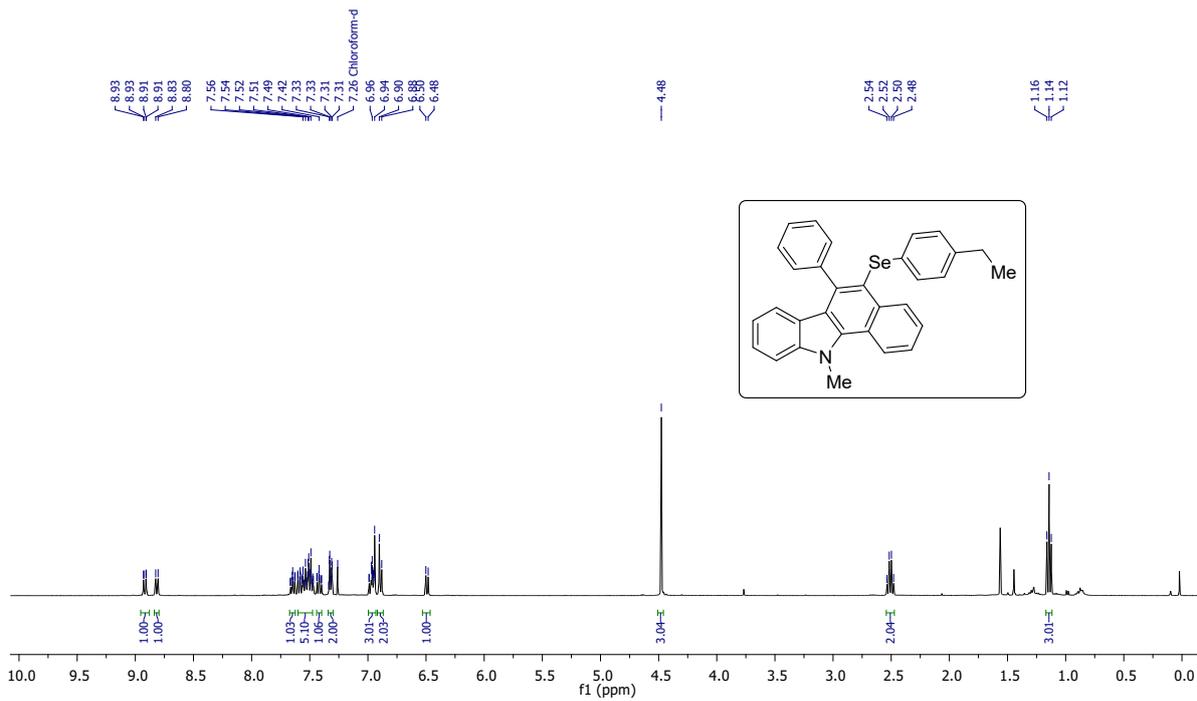




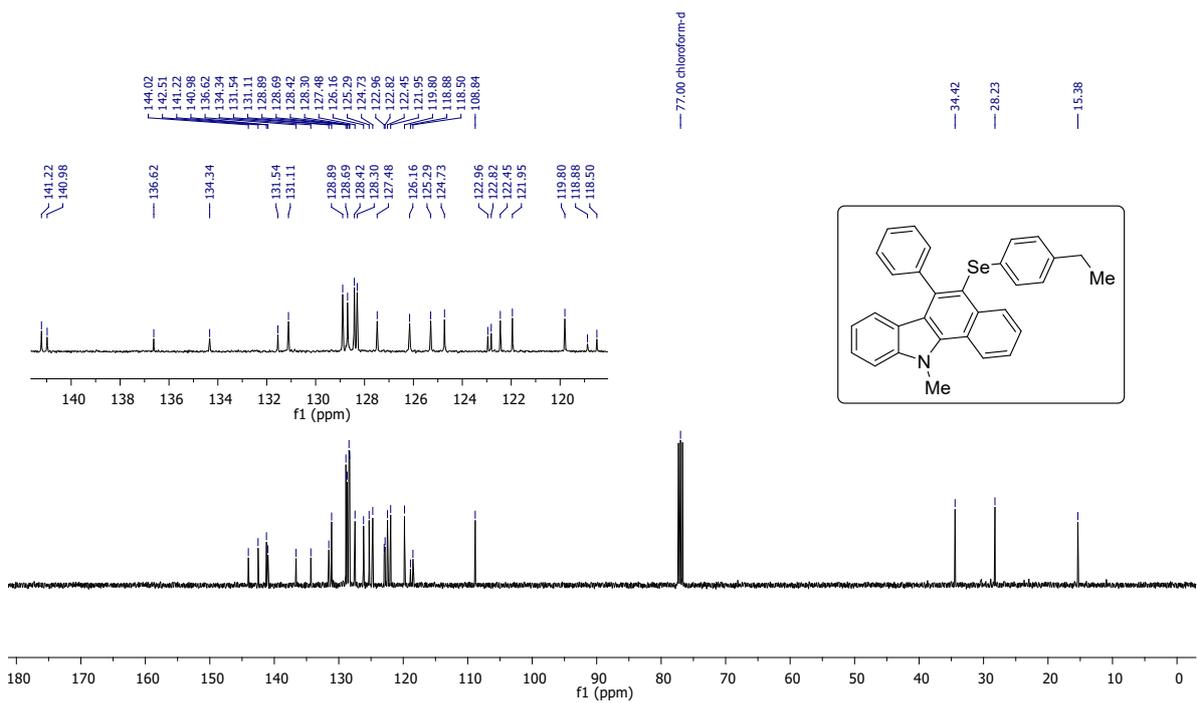
<sup>1</sup>H NMR (600 MHz) spectrum of **30a** in CDCl<sub>3</sub>



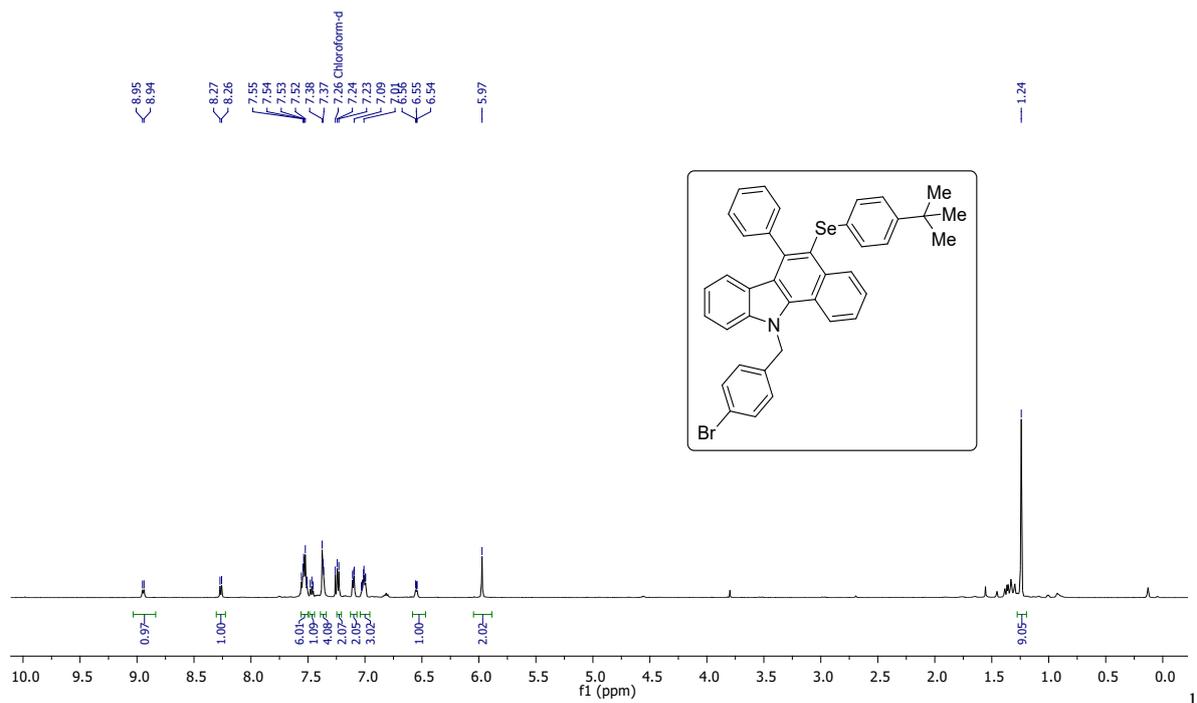
<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz) spectrum of **30a** in CDCl<sub>3</sub>



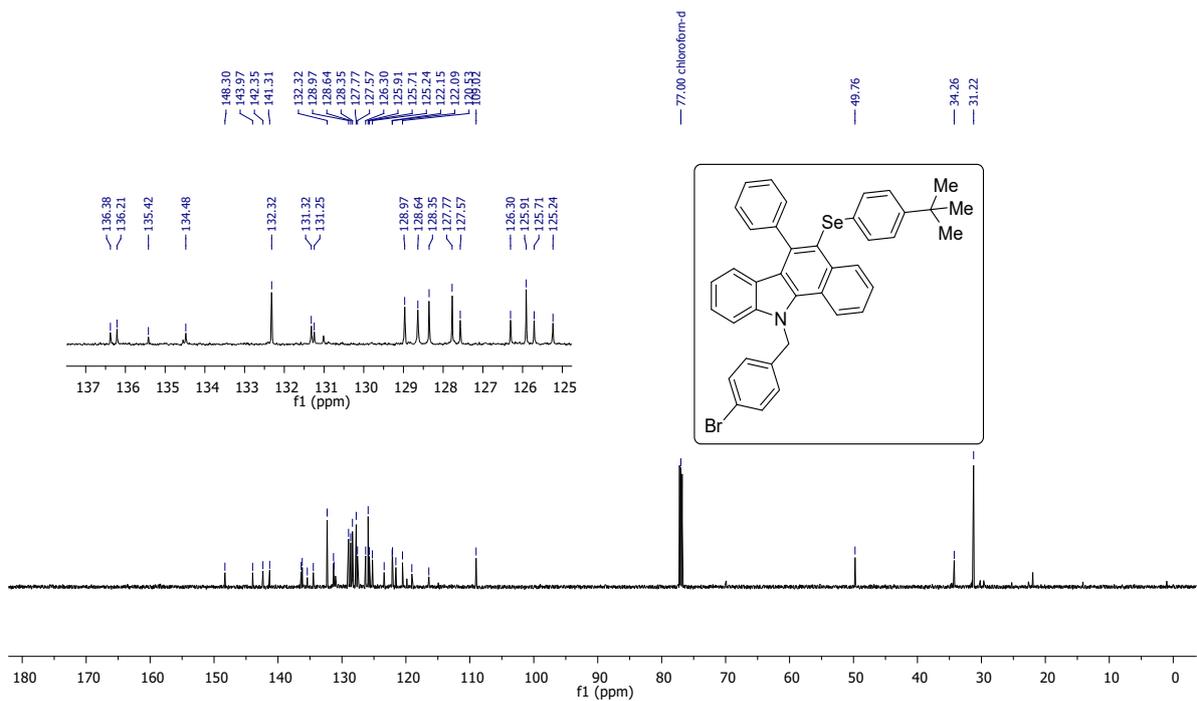
<sup>1</sup>H NMR (400 MHz) spectrum of **3ab** in CDCl<sub>3</sub>



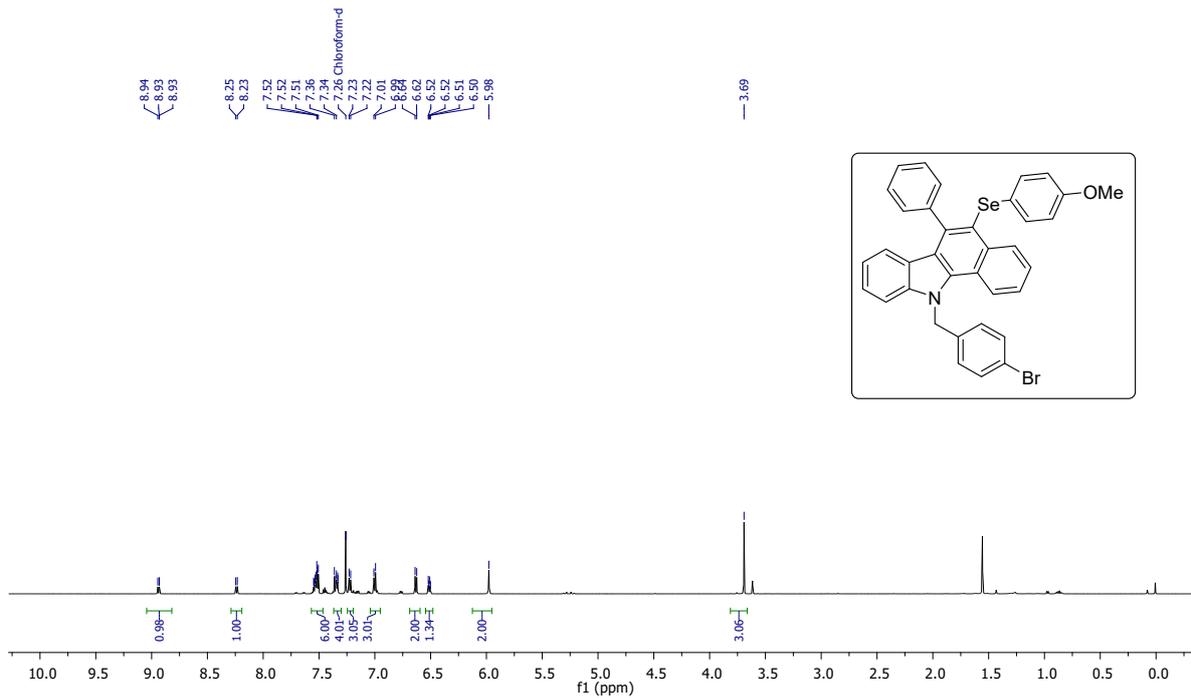
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz) spectrum of **3ab** in CDCl<sub>3</sub>



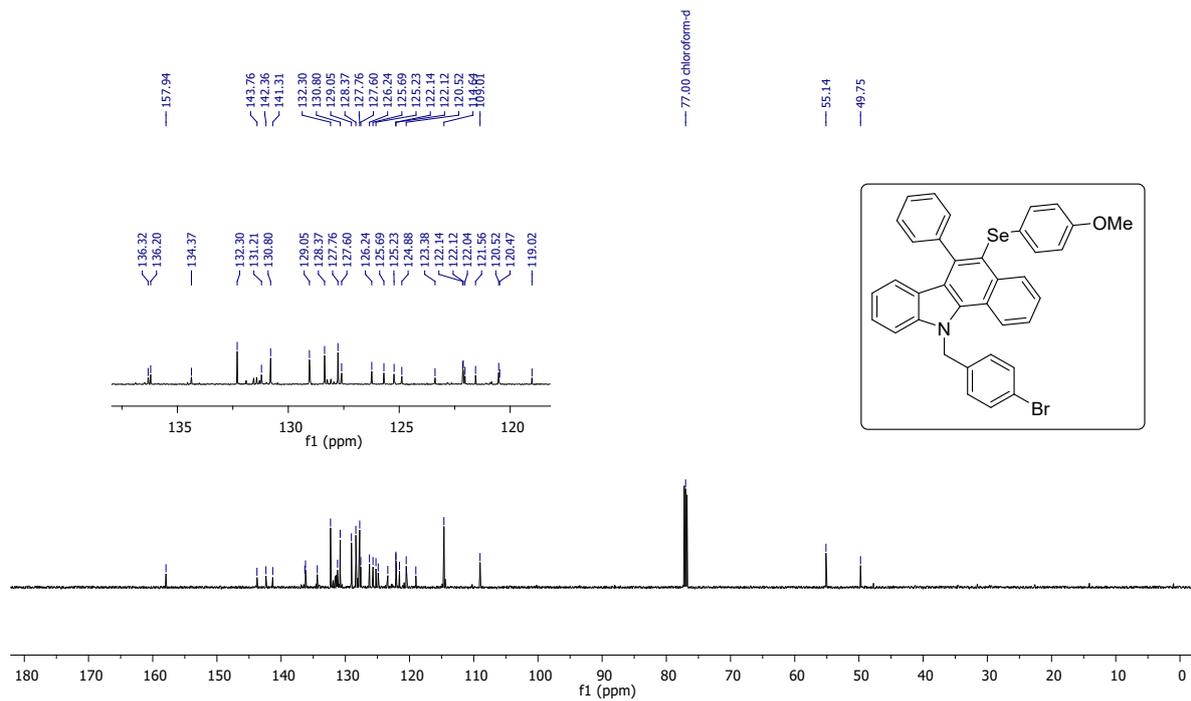
<sup>1</sup>H NMR (600 MHz) spectrum of **3ac** in CDCl<sub>3</sub>



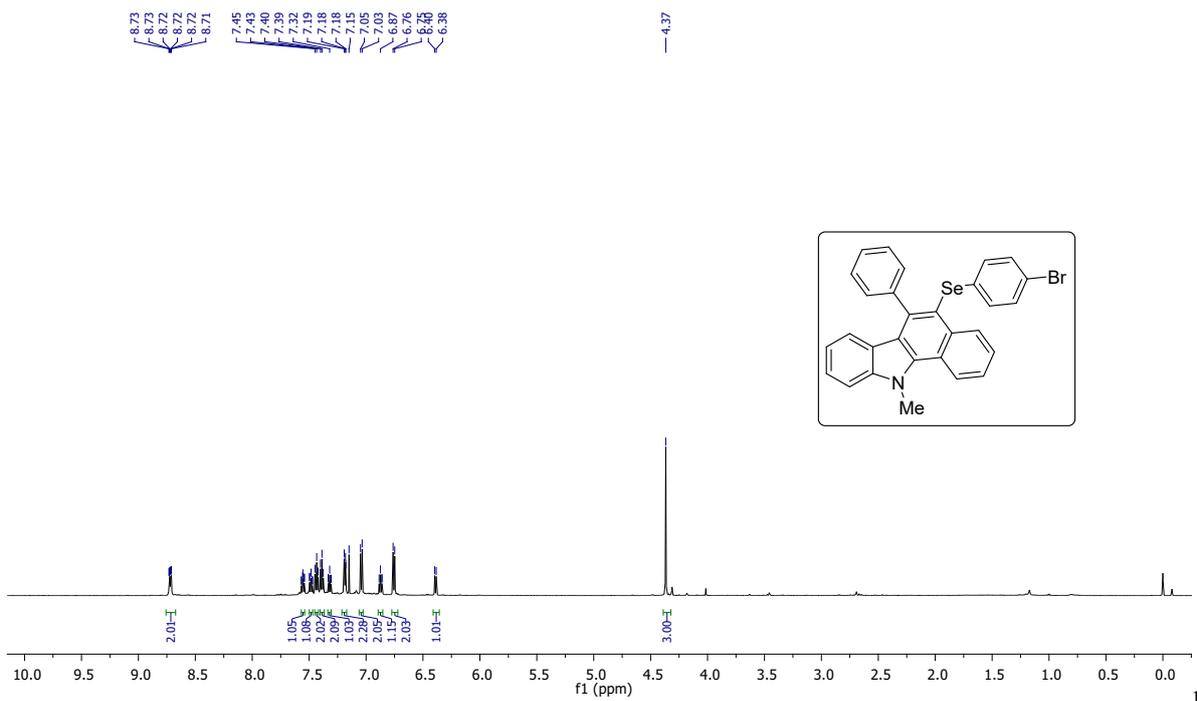
<sup>13</sup>C {<sup>1</sup>H} NMR (151 MHz) spectrum of **3ac** in CDCl<sub>3</sub>



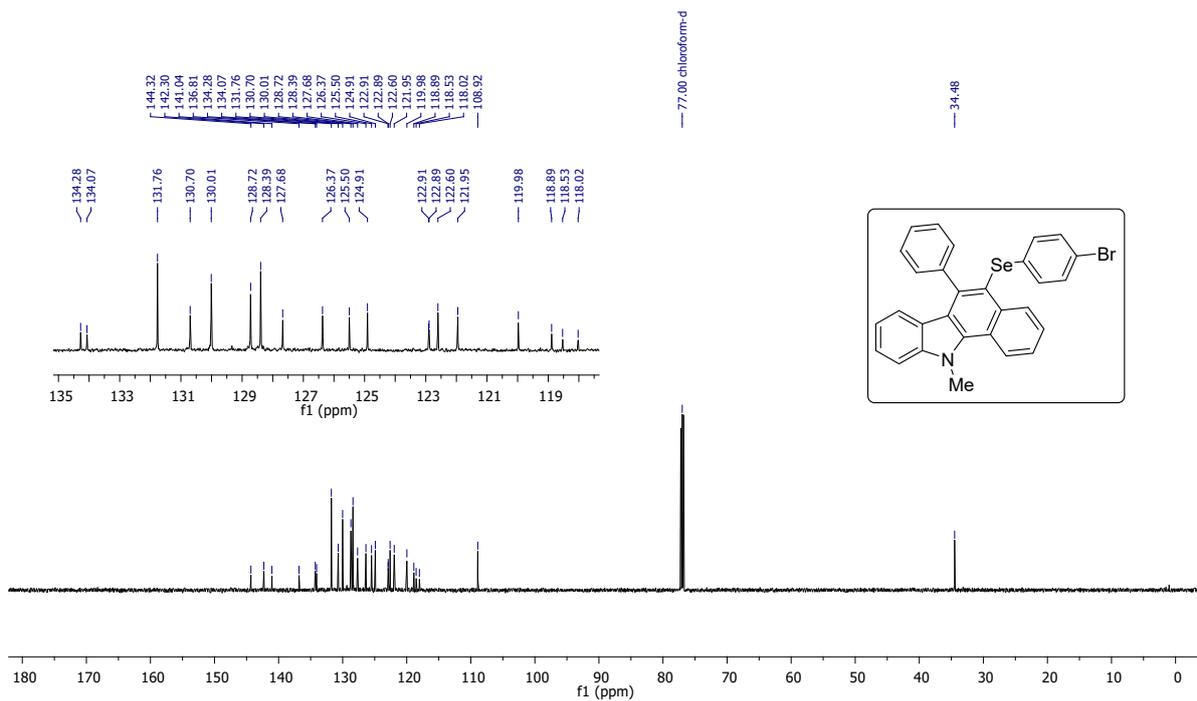
<sup>1</sup>H NMR (600 MHz) spectrum of **3od** in CDCl<sub>3</sub>



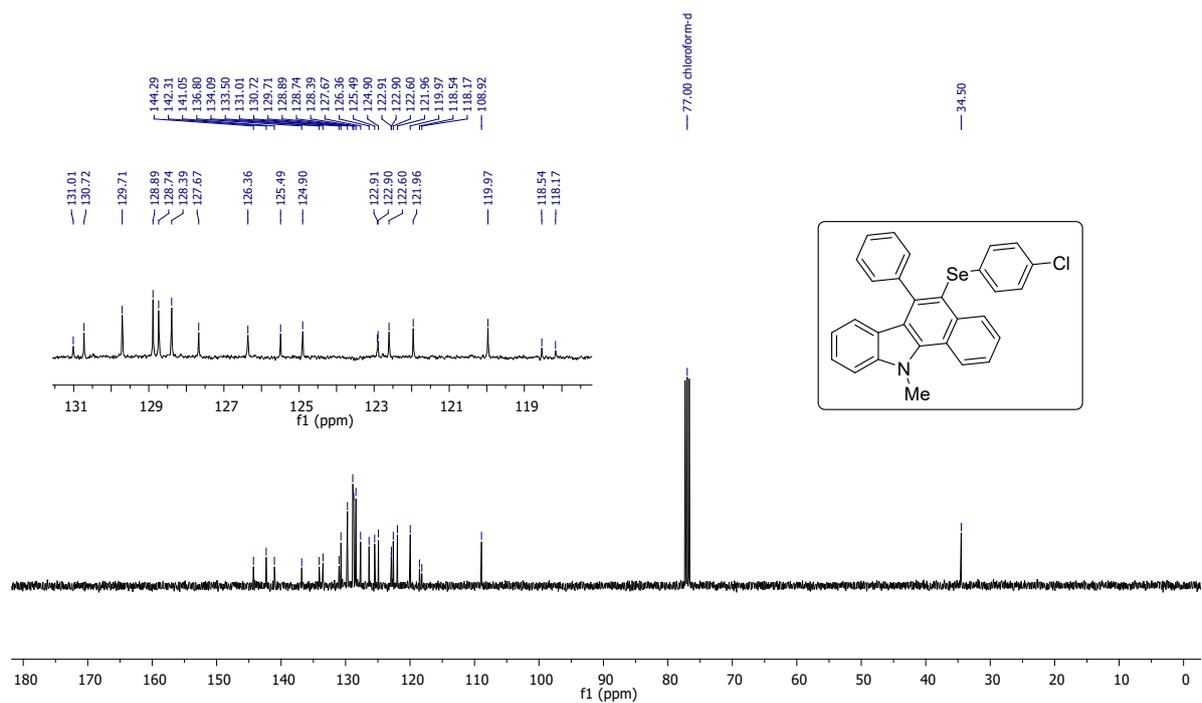
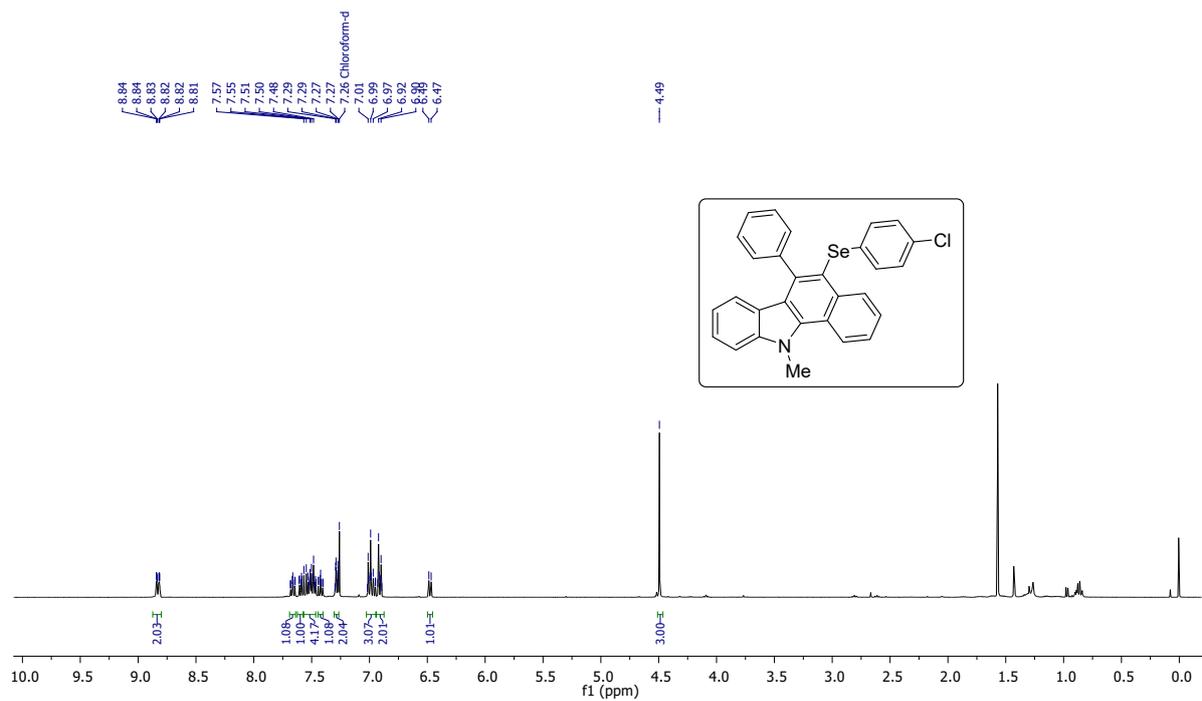
<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz) spectrum of **3od** in CDCl<sub>3</sub>

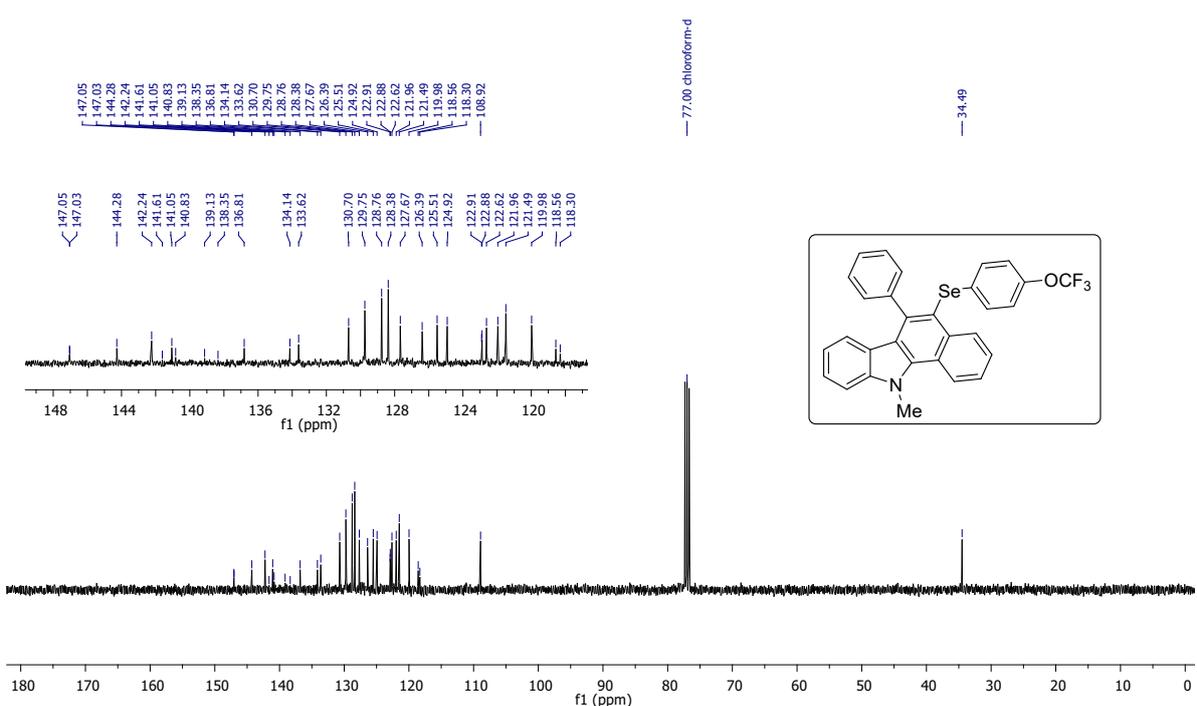
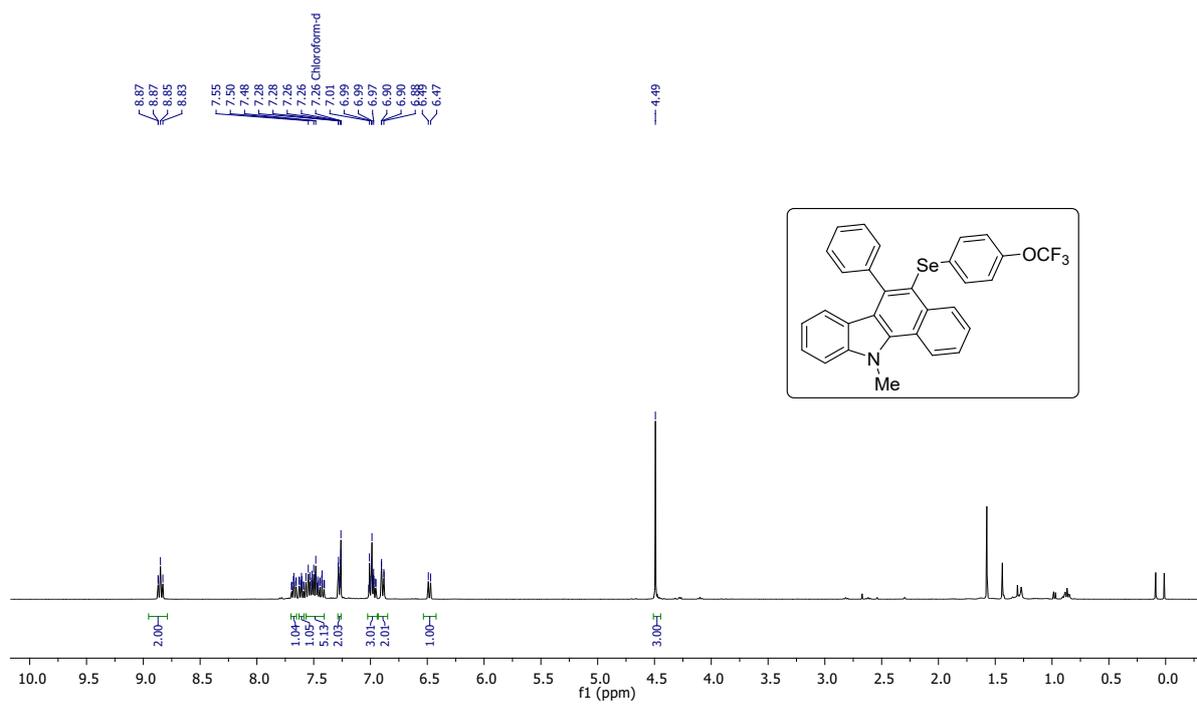


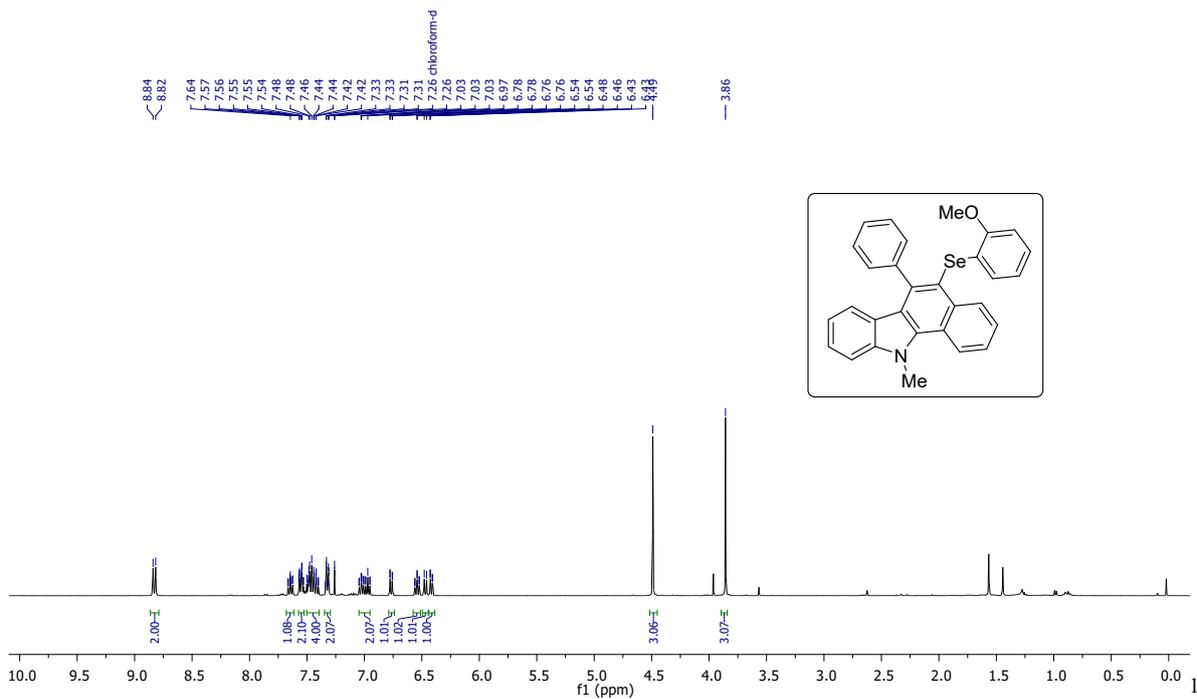
$^1\text{H}$  NMR (600 MHz) spectrum of **3ae** in  $\text{CDCl}_3$



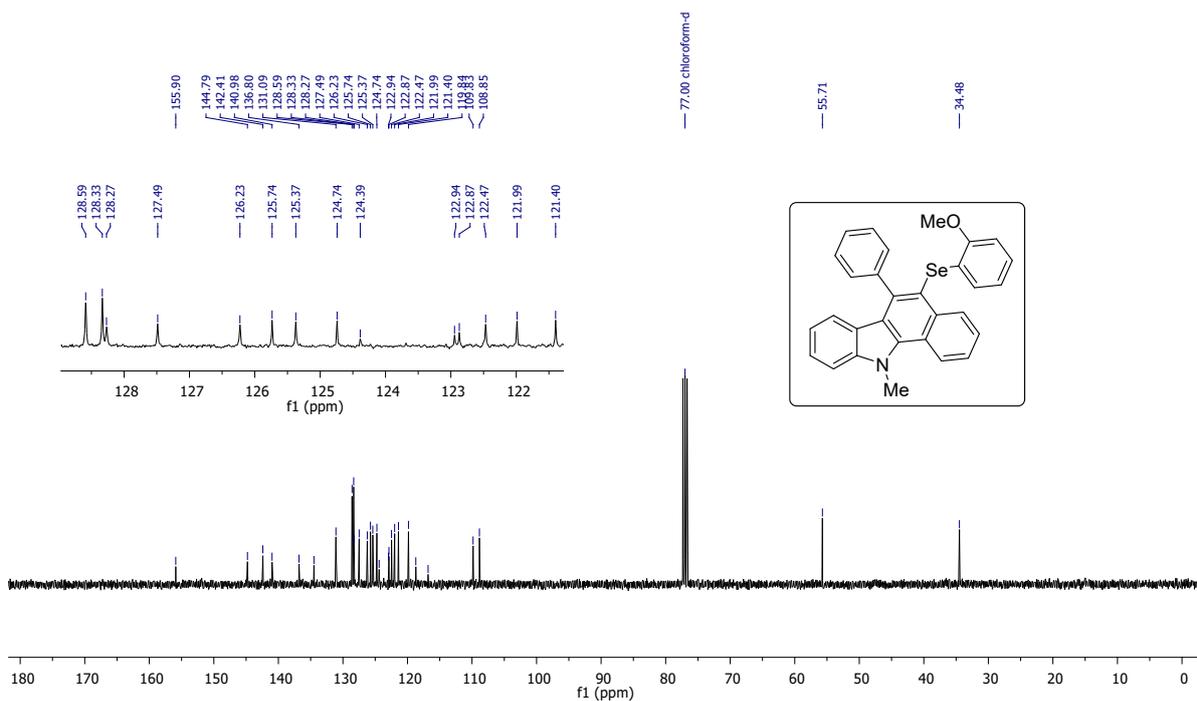
$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of **3ae** in  $\text{CDCl}_3$



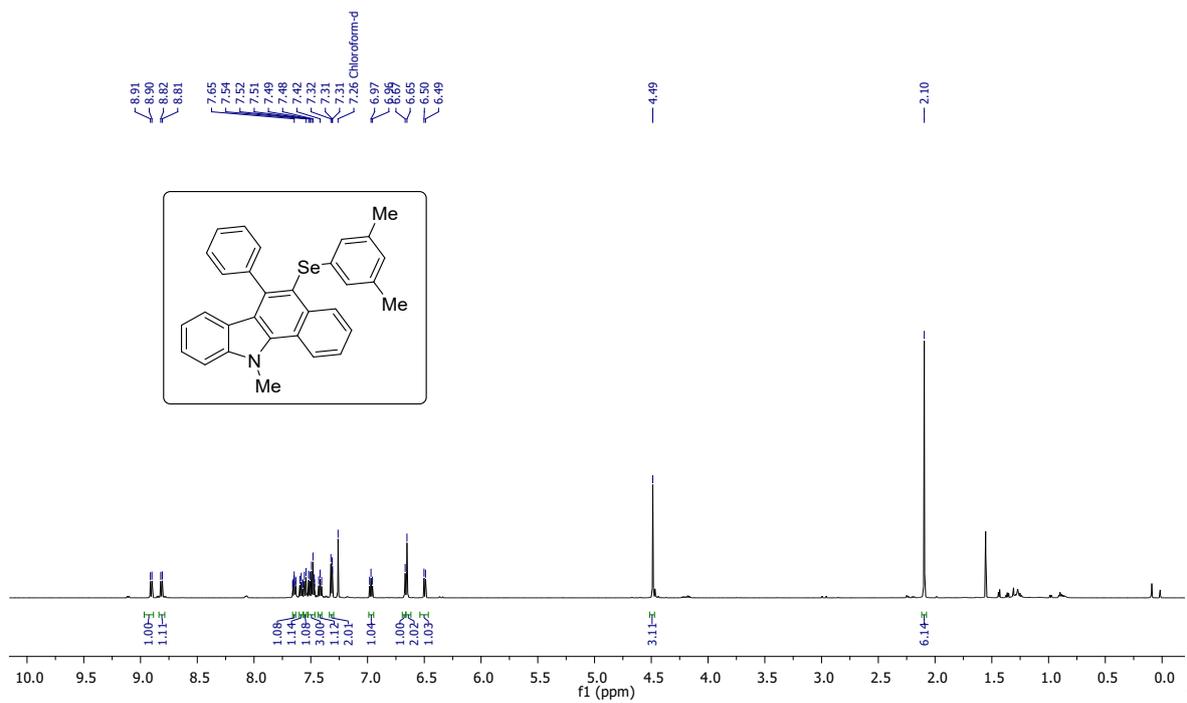




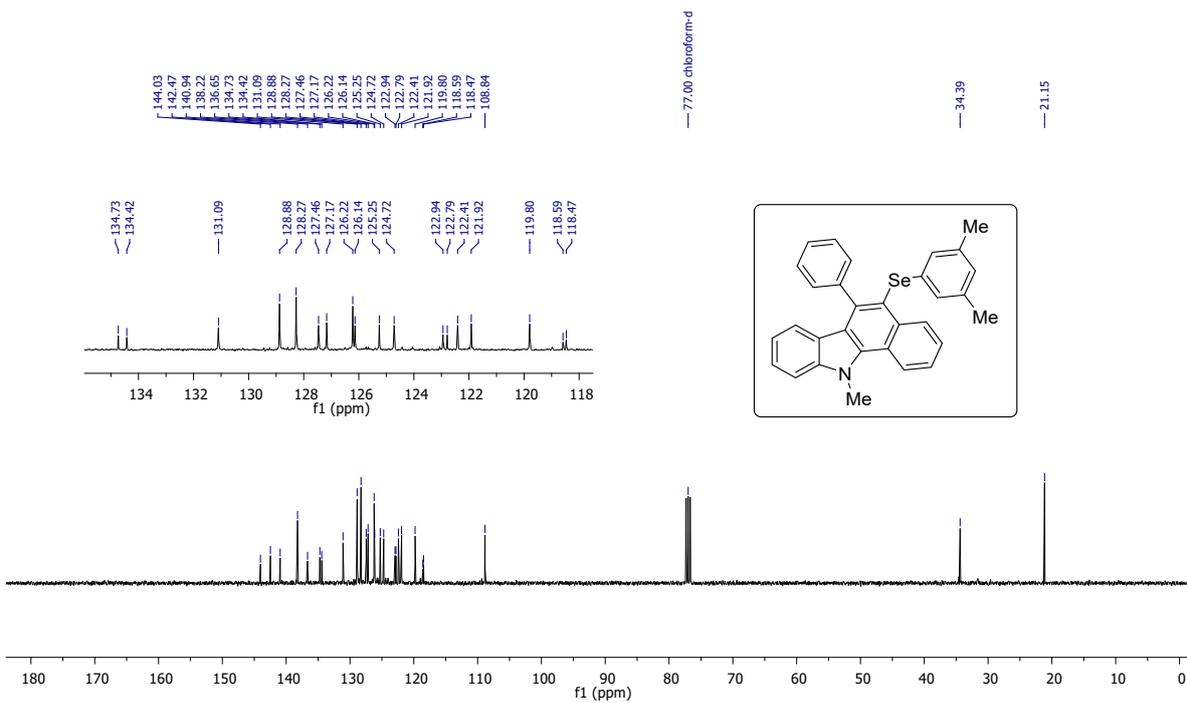
<sup>1</sup>H NMR (400 MHz) spectrum of **3ah** in CDCl<sub>3</sub>



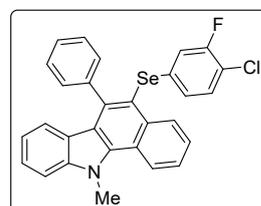
<sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz) spectrum of **3ah** in CDCl<sub>3</sub>

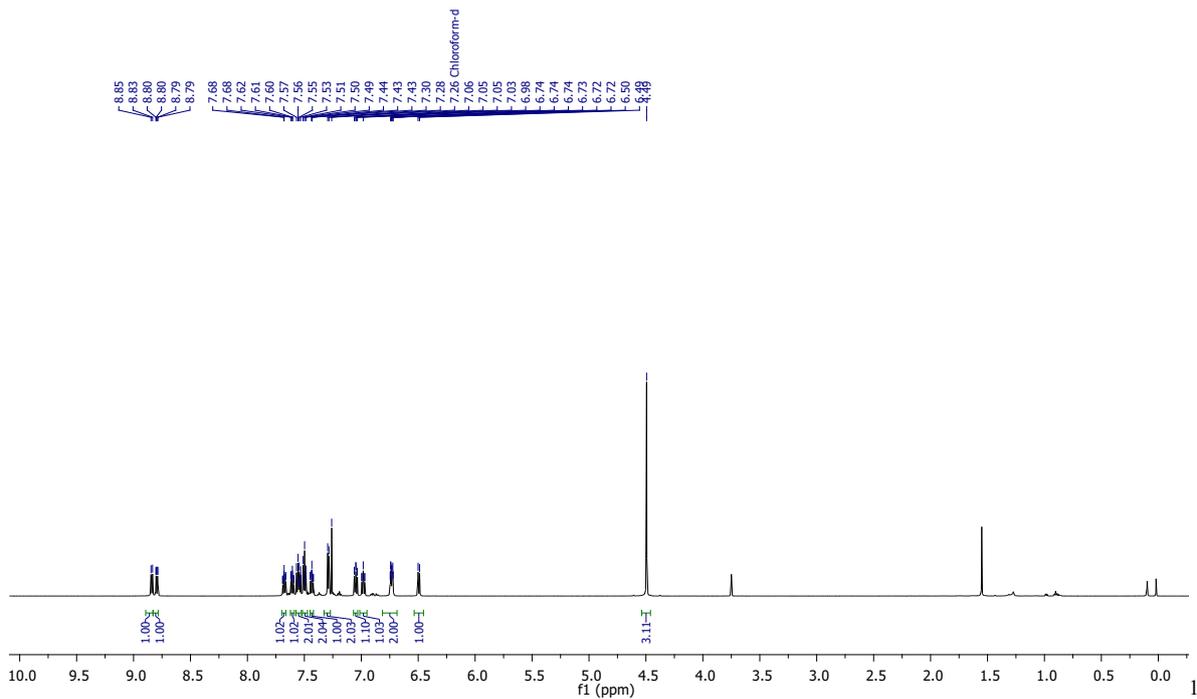


<sup>1</sup>H NMR (600 MHz) spectrum of **3ai** in CDCl<sub>3</sub>

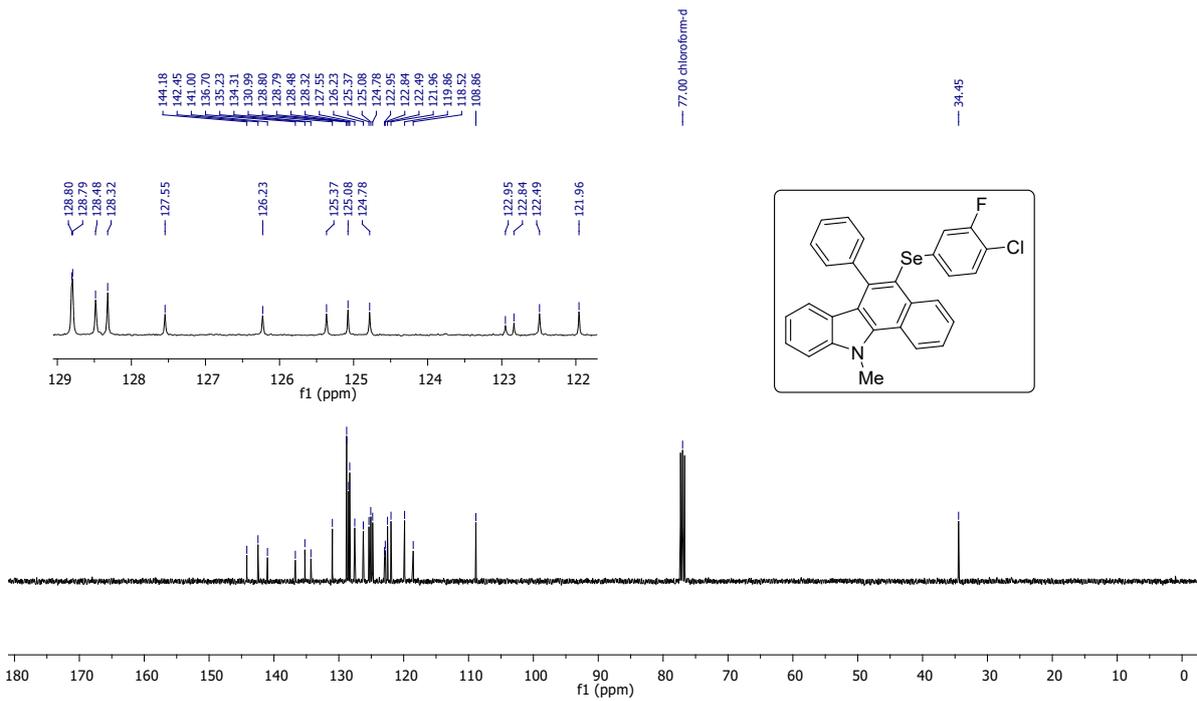


<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz) spectrum of **3ai** in CDCl<sub>3</sub>

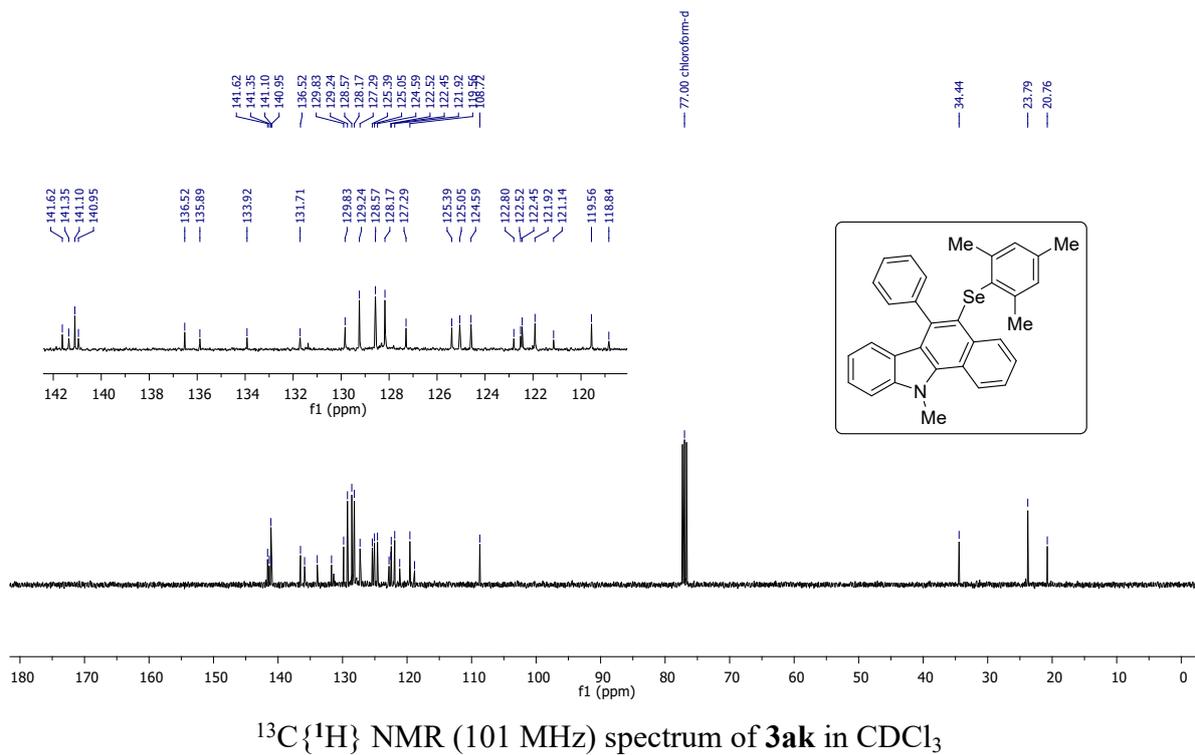
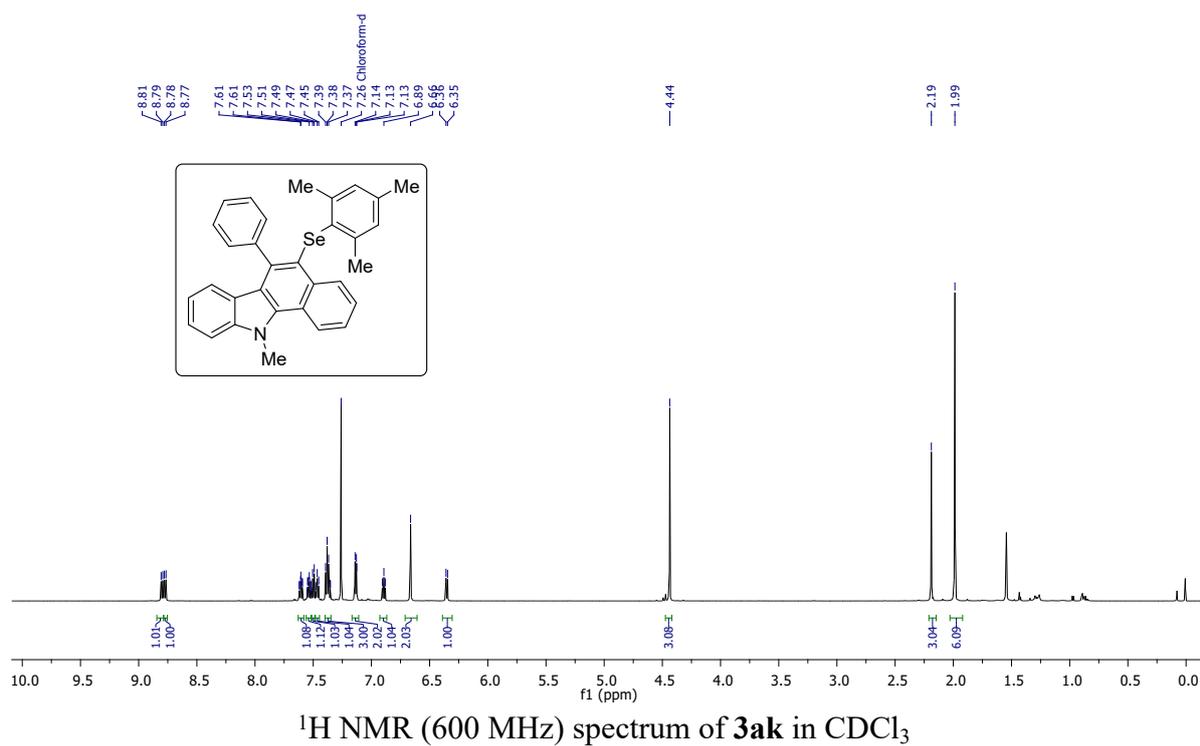


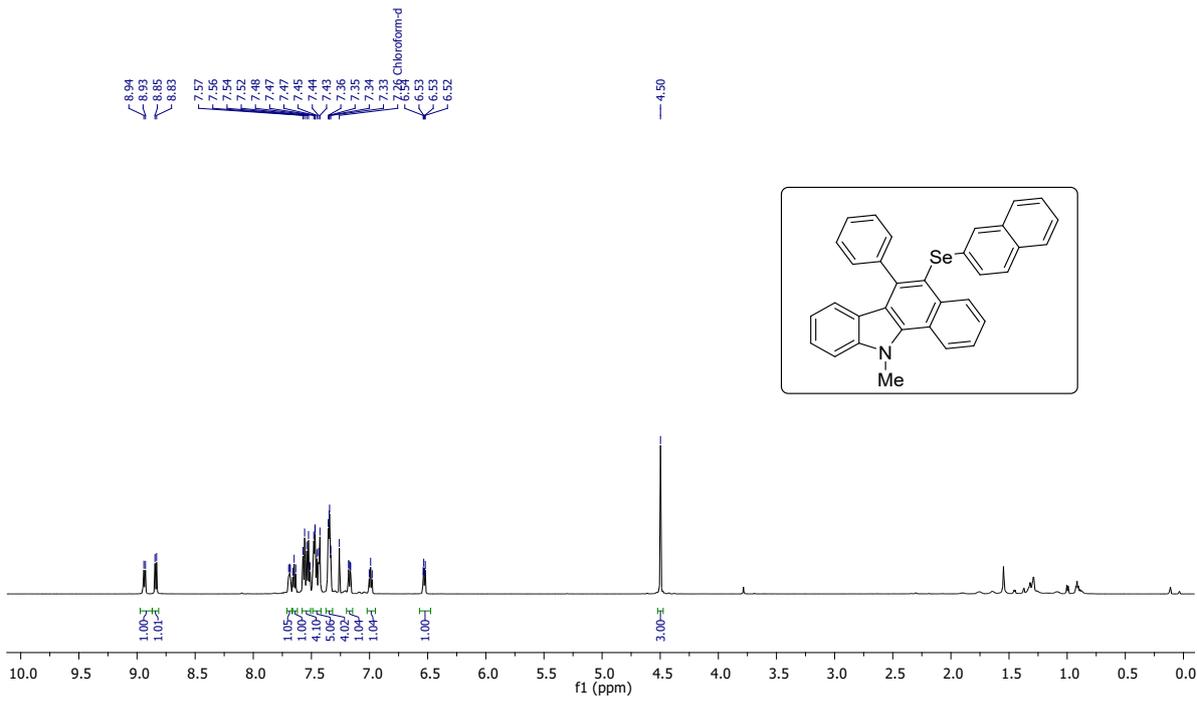


$^1\text{H}$  NMR (400 MHz) spectrum of **3aj** in  $\text{CDCl}_3$

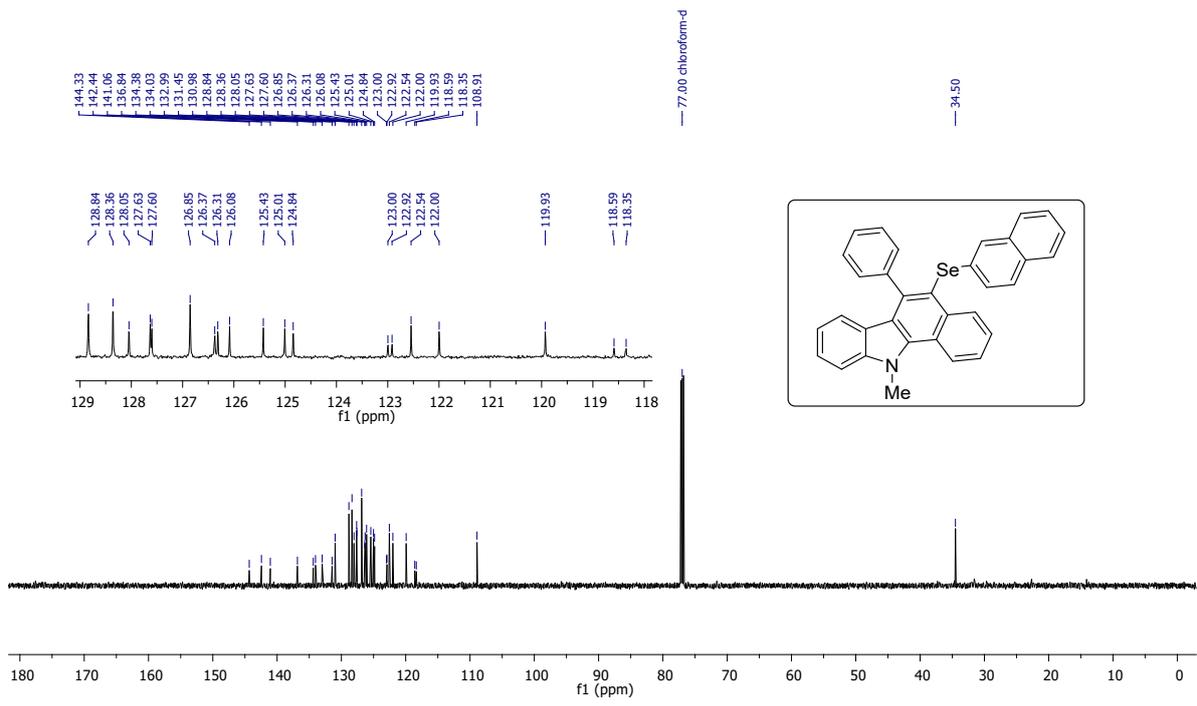


$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz) spectrum of **3aj** in  $\text{CDCl}_3$

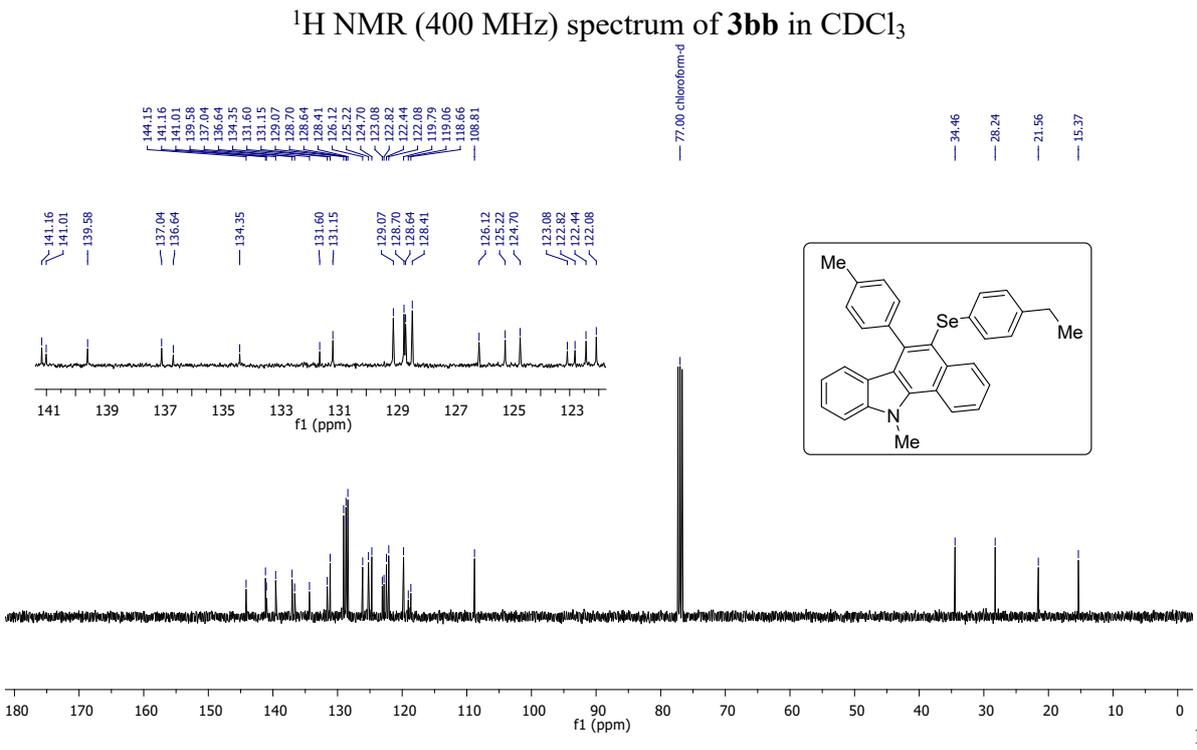
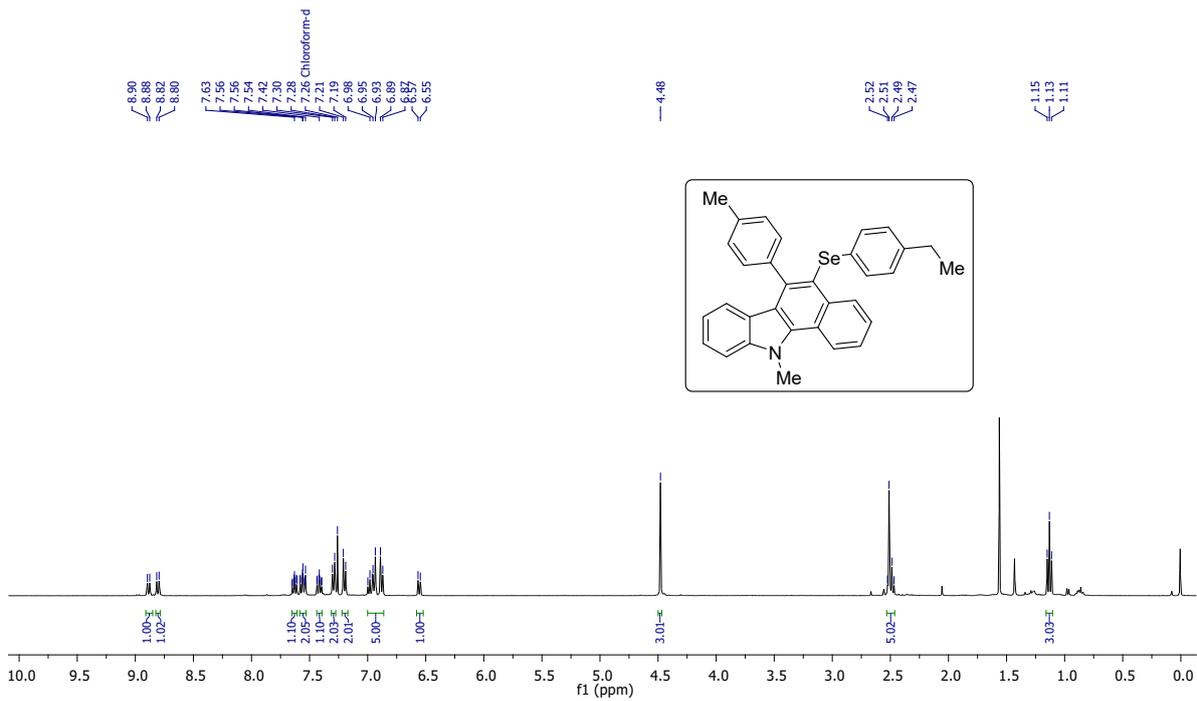


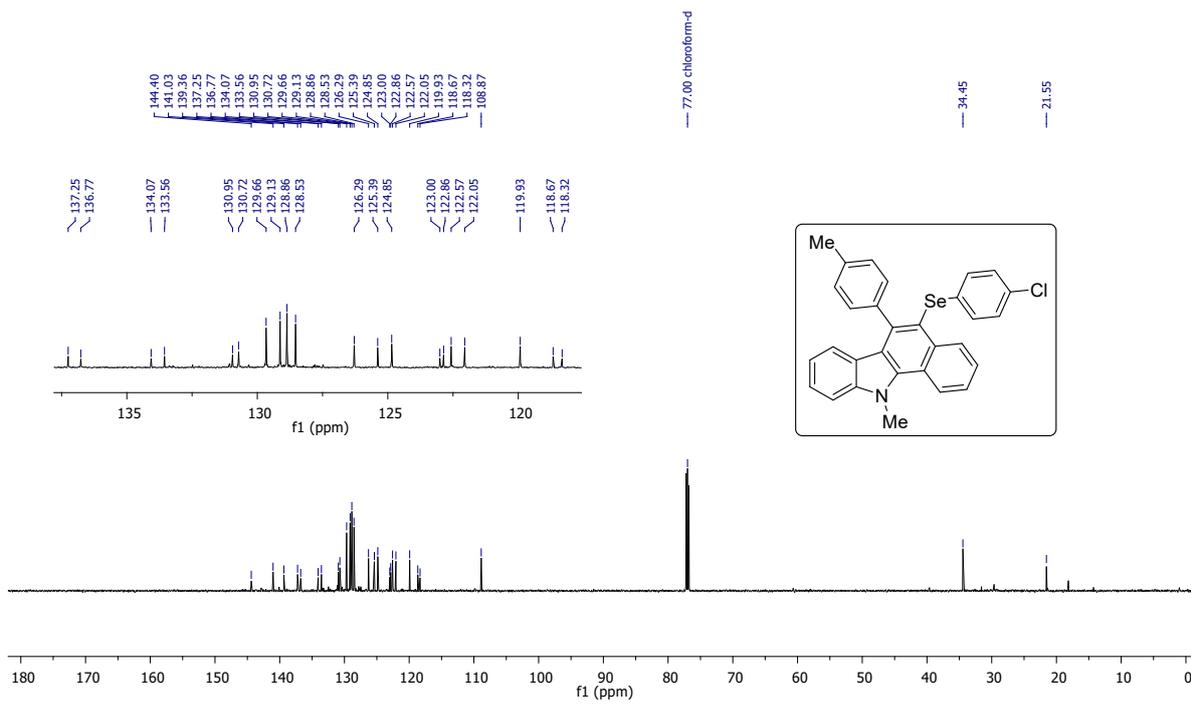
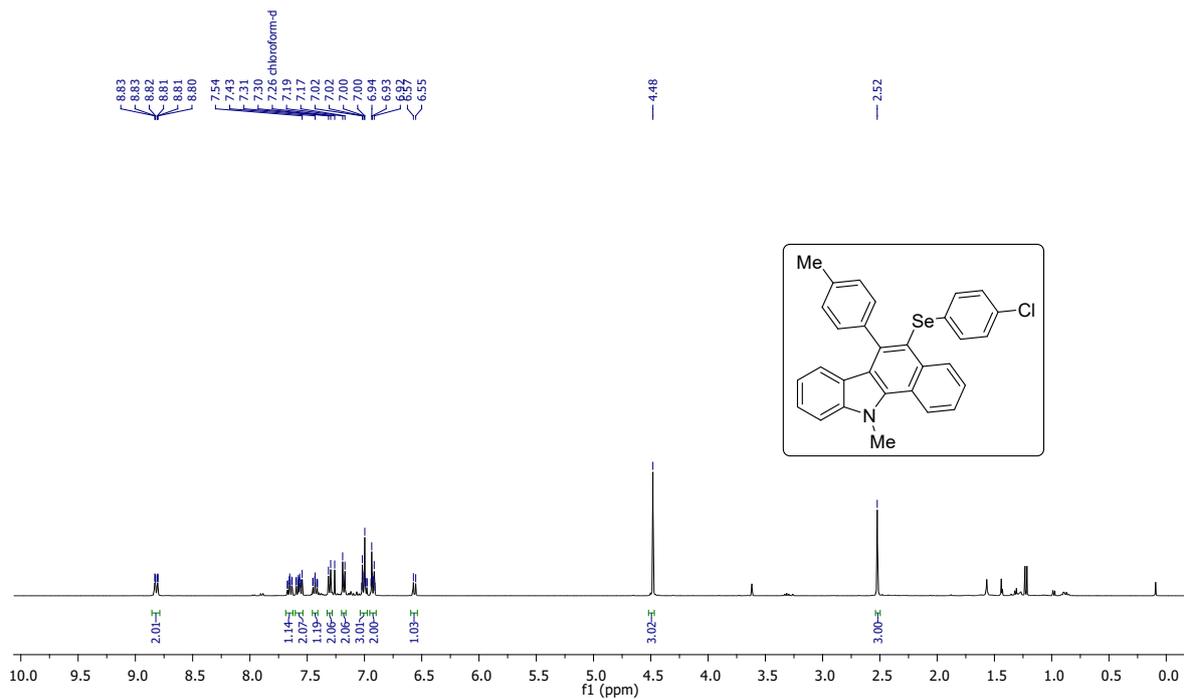


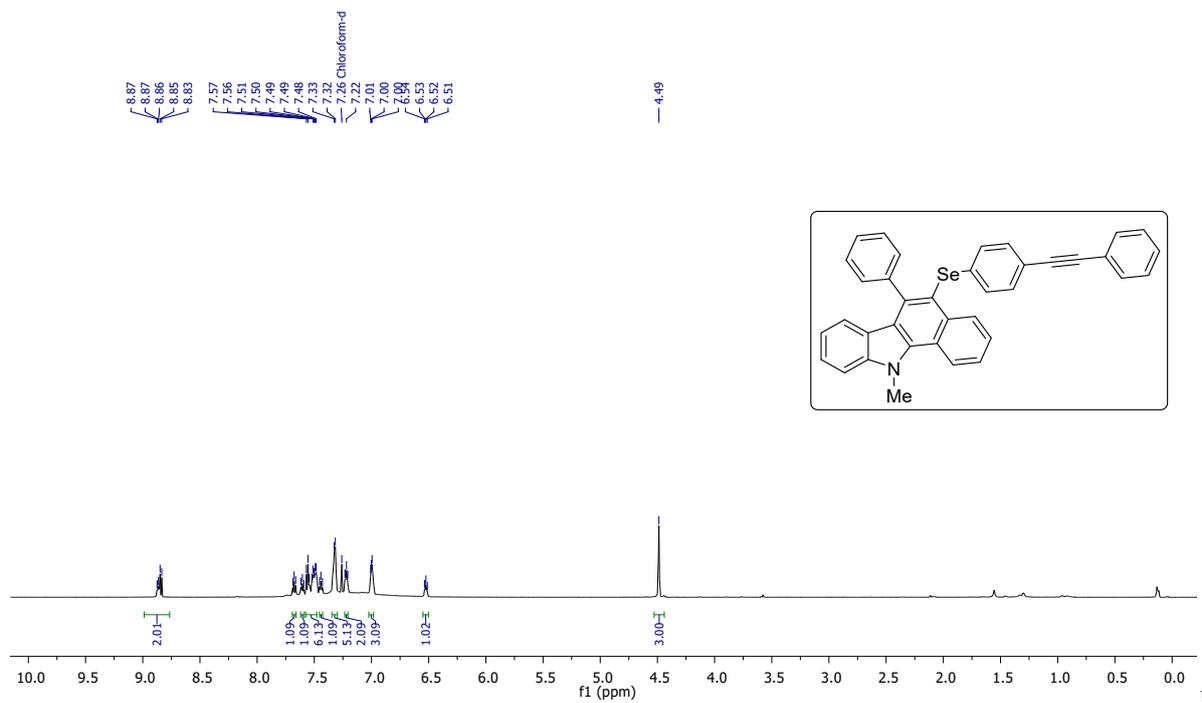
$^1\text{H}$  NMR (600 MHz) spectrum of **3al** in  $\text{CDCl}_3$



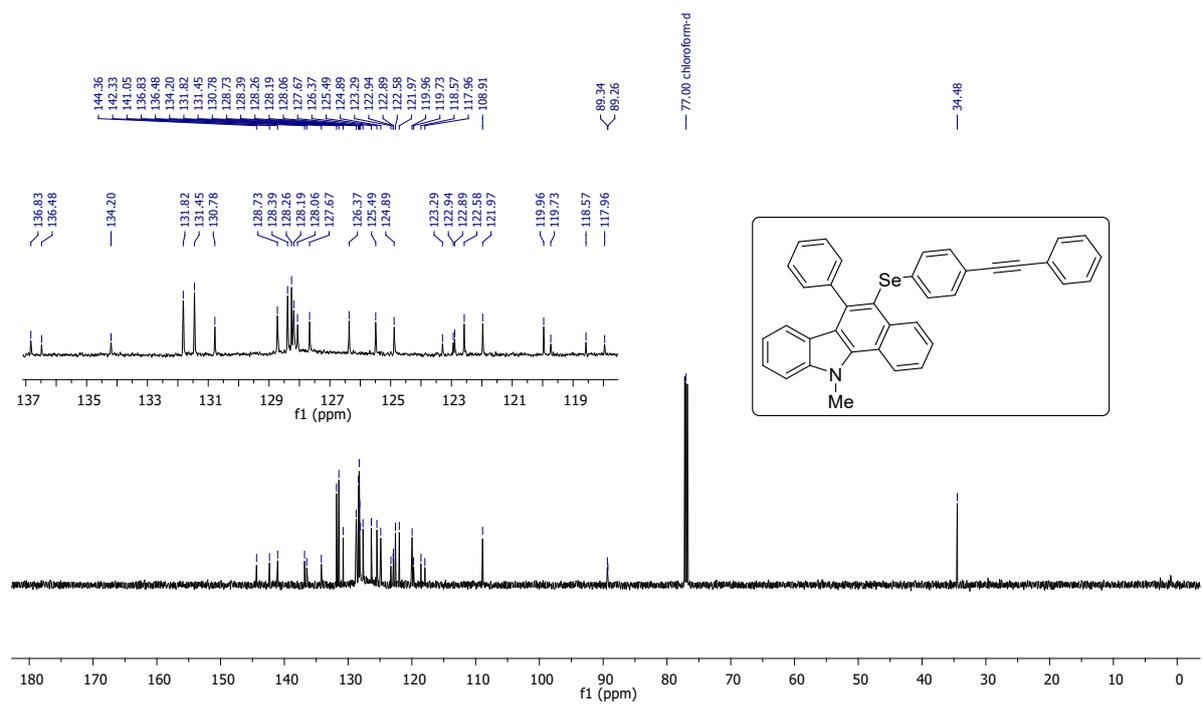
$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of **3al** in  $\text{CDCl}_3$



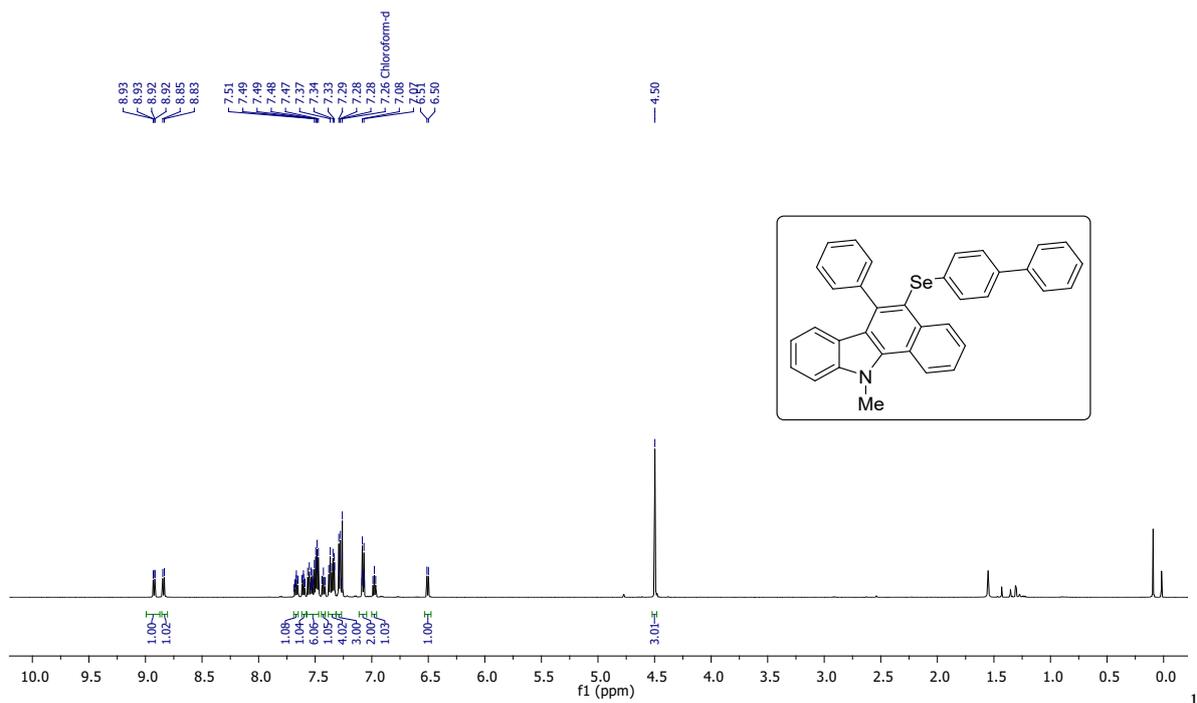




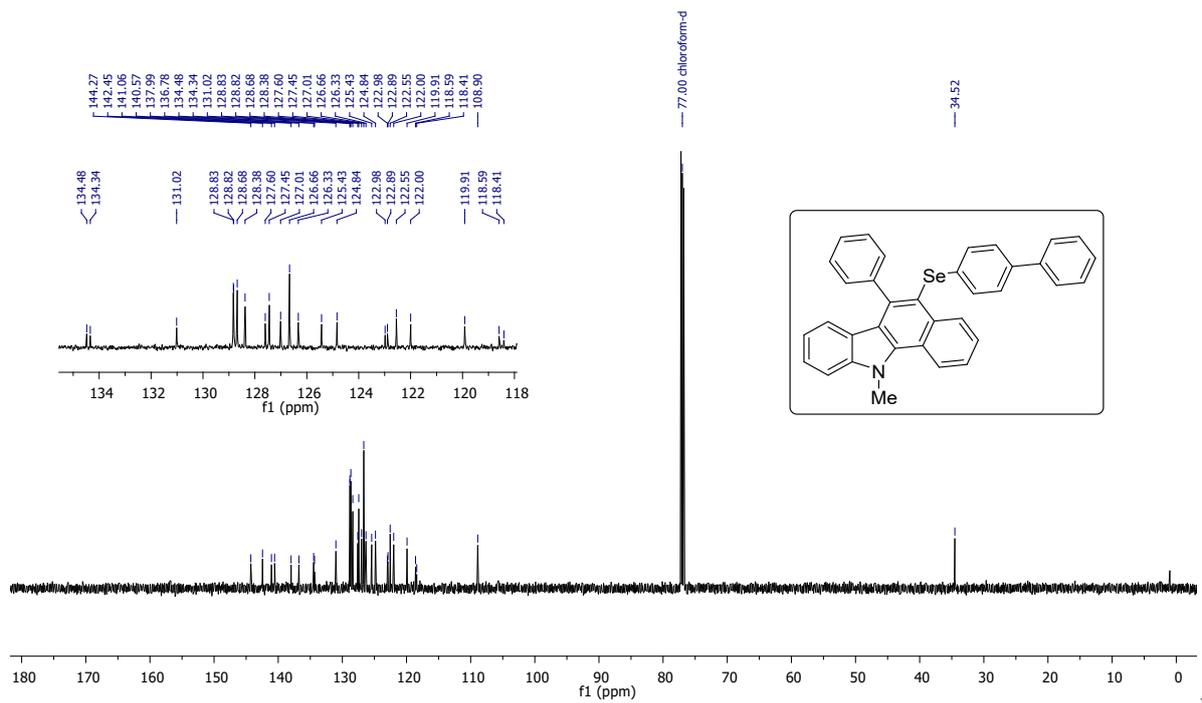
$^1\text{H}$  NMR (600 MHz) spectrum of **9** in  $\text{CDCl}_3$



$^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of **9** in  $\text{CDCl}_3$

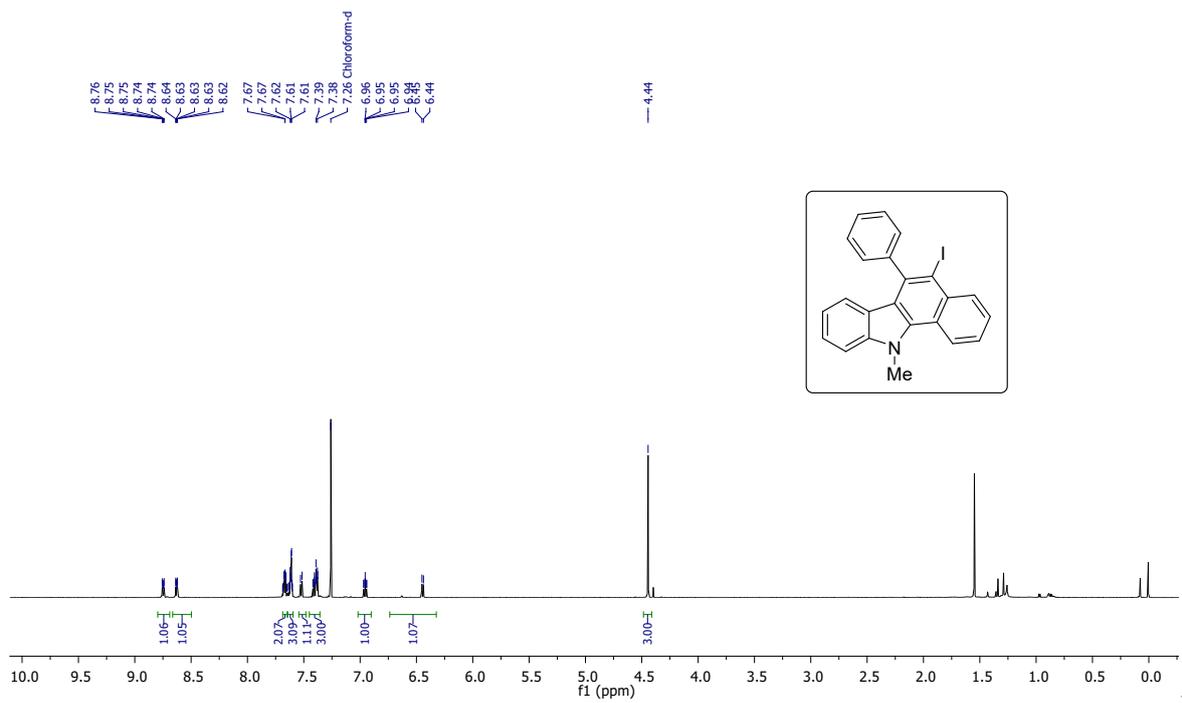


<sup>1</sup>H NMR (600 MHz) spectrum of **10** in CDCl<sub>3</sub>

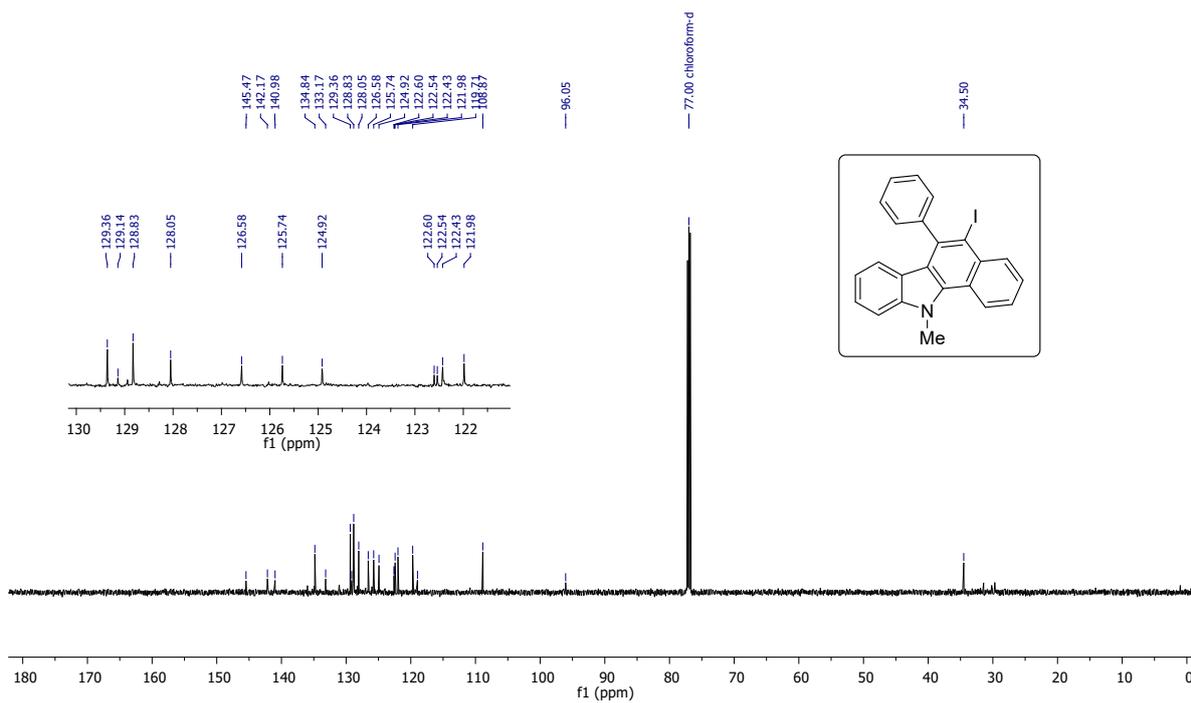


<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz) spectrum of **10** in CDCl<sub>3</sub>





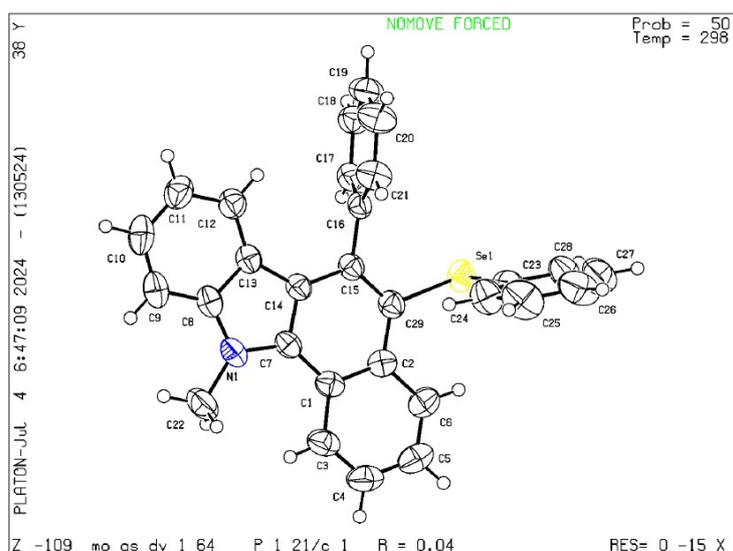
H NMR (600 MHz) spectrum of **12** in CDCl<sub>3</sub>



<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz) spectrum of **12** in CDCl<sub>3</sub>

## 2. X-Ray crystal structure of compound 3aa:

Crystal of compounds **3aa** were obtained by dissolving the product in Hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture and allowing the solvent to slowly evaporate at room temperature. A suitable crystal was selected and mounted onto the cryoloop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,8 the structure was solved with the SHELXT9 structure solution program using Intrinsic Phasing and refined with the SHELXL10 refinement package using Least Squares minimization.



**Figure S2:** X-ray diagram of compound **3aa** with ellipsoid shown at the 50% contour percent probability level (CCDC: 2526228).

**Table S5:** Crystal data and structure refinement for **3aa** (CCDC: 2526228).

<b>Table S5 Crystal data and structure refinement for 3aa.</b>	
Identification code	<b>3aa</b>
Empirical formula	C <sub>29</sub> H <sub>21</sub> NSe
Formula weight	462.43
Temperature/K	298
Crystal system	monoclinic
Space group	P21/c
a/Å	13.2855(10)
b/Å	16.1469(10)
c/Å	10.9297(9)
α/°	90
β/°	112.099(2)
γ/°	90

Volume/Å <sup>3</sup>	2172.4(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.414
$\mu/\text{mm}^{-1}$	1.745
F(000)	944.0
Crystal size/mm <sup>3</sup>	0.36 × 0.21 × 0.19
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/°	4.16 to 54.312
Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 19, -14 ≤ l ≤ 14
Reflections collected	34592
Independent reflections	4794 [R <sub>int</sub> = 0.0639, R <sub>sigma</sub> = 0.0377]
Data/restraints/parameters	4794/0/281
Goodness-of-fit on F <sup>2</sup>	1.031
Final R indexes [ $I \geq 2\sigma(I)$ ]	R1 = 0.0365, wR2 = 0.0926
Final R indexes [all data]	R1 = 0.0483, wR2 = 0.0998
Largest diff. peak/hole / e Å <sup>-3</sup>	0.61/-0.67

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