

# Electronic Supplementary Information

*for*

## Visible-light induced selenocyclization of 2-ethynylanilines under ambient conditions: simple FeBr<sub>3</sub> as a dual-functional catalyst

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# 1. General and experimental details

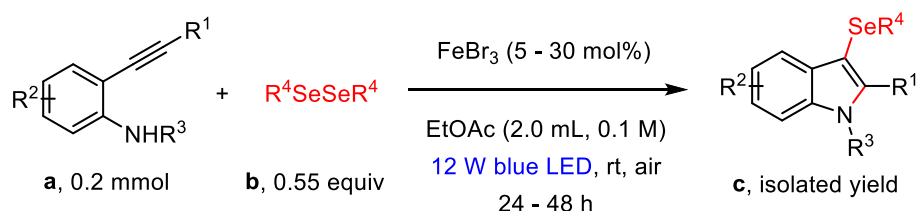
## 1.1 General information

All commercially available reagents (AR grade) were directly used as received without further purification. All yields of products refer to the isolated yields after chromatography that performed on 200 ~ 300 mesh silica gel with PE (petroleum ether) / EtOAc or PE / DCM (dichloromethane) as eluents. The household blue or white LED lamps used in the visible-light induced reactions (12 W and 3 W) were purchased from AoweiGuang Co, Ltd., China.

$^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (101 MHz) and  $^{19}\text{F}$  NMR (376 MHz) spectra were recorded on a Bruker AV-400 spectrometer with  $\text{CDCl}_3$  as the solvent. For  $^1\text{H}$  NMR, the signal of additional tetramethylsilane (TMS,  $\delta = 0.00$  ppm) serves as the internal standard; for proton decoupled  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR, the signal of  $\text{CDCl}_3$  ( $\delta = 77.16$  ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, hept = heptet, m = multiplet, br = broad), coupling constant  $J$  (in Hz), and integration. For certain -NHAr substrates with minor inseparable indoles, only the data of the major compounds are reported.

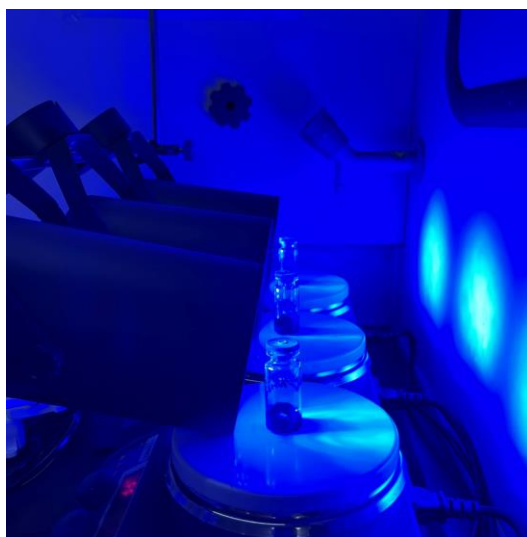
The UV-vis absorption spectra were collected using a UV-2600 UV-VIS spectrophotometer (Shimadzu Instrument Co., Ltd.), within a wavelength range of 350 - 600 nm. HR-MS spectra were recorded on an Agilent 6546 LC/Q-TOF Agilent. Melting points of solid compounds were recorded on a microscopic melting point apparatus (WRX-4, Shanghai Yice Instruments) without correction.

## 1.2 General procedure for the visible-light induced, Fe-catalyzed selenocyclization



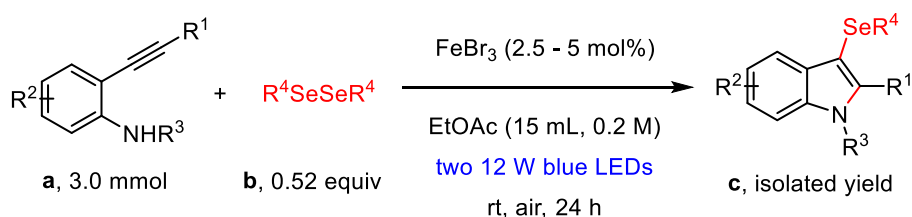
To a 10 mL glass vial with a magnetic stir bar was added substrates **a** (0.2 mmol, 1.0 equiv) and **b** (0.11 mmol, 0.55 equiv), followed by catalyst  $\text{FeBr}_3$  (0.01 – 0.06 mmol, 0.05 – 0.30 equiv) and

solvent EtOAc (2.0 mL, 0.1 M). In case of poor solubility, additional DCM (2.0 mL) was added as co-solvent. The vial was closed with a rubber septum and then placed under the irradiation of a 12 W blue LED lamp (the distance to the vial was approx. 1.5 cm) with 500 rpm magnetic stirring. After the indicated time as determined by TLC analysis (24 – 48 h), the reaction mixture was transferred to a flask to have the solvent removed under reduced pressure. Further purification by column chromatography on silica gel (eluted with EtOAc/PE or DCM/PE) afforded the desired product **c**.



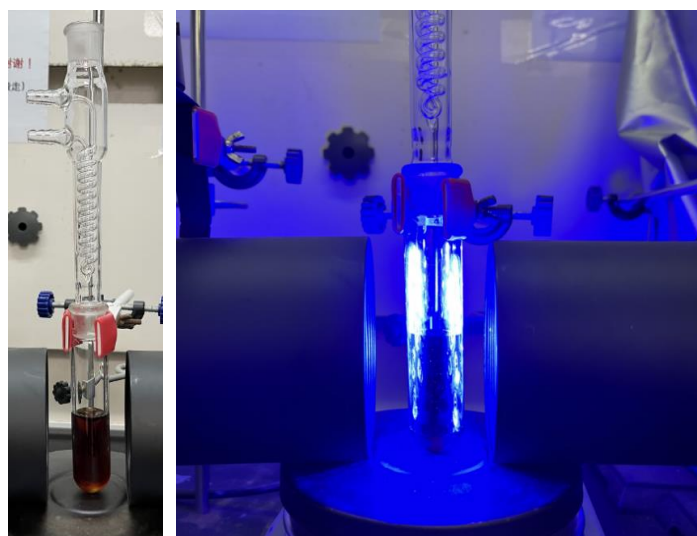
**Fig. S1** Setup for the visible-light induced, Fe-catalyzed selenocyclization.

### 1.3 Procedure for the visible-light induced selenocyclization in gram-scale



Substrates **a** (3.0 mmol, 1.0 equiv), **b** (1.56 mmol, 0.52 equiv), catalyst  $\text{FeBr}_3$  (0.075 – 0.15 mmol, 0.025 – 0.05 equiv) and solvent EtOAc (15 mL, 0.2 M) were added to a 25 mL reaction tube with a magnetic stir bar. The reaction tube was then equipped with a reflux condenser and subjected to irradiation by two 12 W blue LED lamps (approx. 1 cm) with 500 rpm magnetic stirring. Upon completion as revealed by TLC analysis (24 h), the resulting mixture was transferred to a flask to

have the solvent removed under reduced pressure. Further purification by column chromatography on silica gel afforded the desired product **c**.



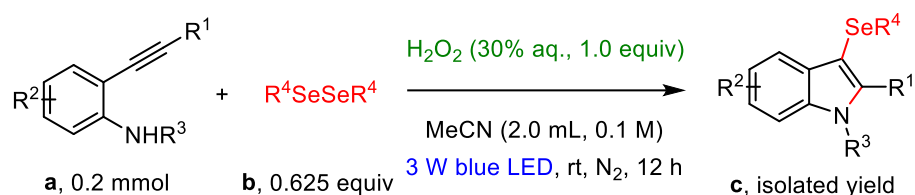
**Fig. S2** Setup for the visible-light induced selenocyclization in gram-scale.

• This procedure has been applied to the following reactions:

**1c**: 1.480 g, 2.945 mmol, **98% yield**.

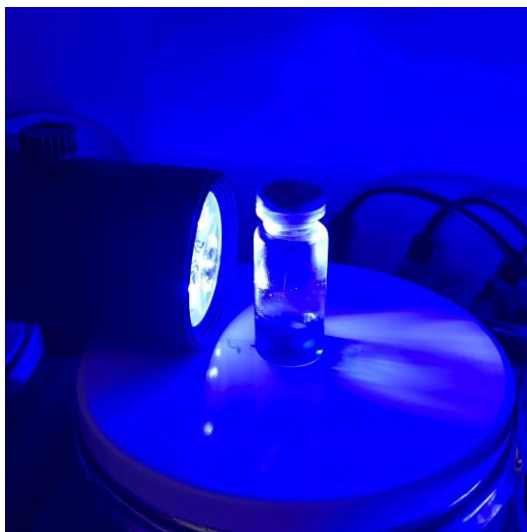
**13c**: 1.151 g, 2.712 mmol, **90% yield**.

#### 1.4 General procedure for the visible-light induced selenocyclization with H<sub>2</sub>O<sub>2</sub> <sup>[1]</sup>



To a 10 mL glass vial with a magnetic stir bar was added substrates **a** (0.2 mmol, 1.0 equiv) and **b** (0.125 mmol, 0.625 equiv), followed by solvent MeCN (2.0 mL, 0.1 M) and 30% H<sub>2</sub>O<sub>2</sub> aqueous solution (22.7 mg, 0.2 mmol, 1.0 equiv). The vial was closed with a rubber septum, degassed using freeze-pump-thaw technique and refilled with nitrogen atmosphere. The vial was then tightly sealed and placed under the irradiation of a 3 W blue LED lamp (the distance to the vial was approx. 1 cm) with 500 rpm magnetic stirring. After 12 h, the septum was removed, and the reaction mixture was transferred to a flask to have the solvent removed under reduced pressure. Further purification by

column chromatography on silica gel (eluted with EtOAc/PE or DCM/PE) afforded the desired product **c**.



**Fig. S3** Setup for the visible-light induced selenocyclization with H<sub>2</sub>O<sub>2</sub>

• This method has been applied to the following reactions:

**1c**: 95.6 mg, 0.190 mmol, **95% yield**.

**4c**: **trace** (negligible conversion of **4a**).

**6c**: 5.9 mg, 0.010 mmol, **5% yield** (low conversion of **6a**).

**7c**: 43.9 mg, 0.087 mmol, **43% yield** (incomplete conversion of **7a**; and side-products with large R<sub>f</sub> values were observed by TLC analysis).

**11c**: 65.6 mg, 0.117 mmol, **59% yield** (incomplete conversion of **11a**).

**13c**: 27.2 mg, 0.064 mmol, **32% yield** (incomplete conversion of **13a**; and side-products with large R<sub>f</sub> values were observed by TLC analysis).

## 1.5 Procedures for substrate synthesis

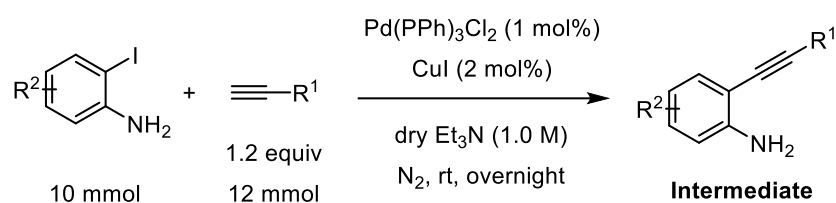
2-Ethynylanilines **1a** – **12a**, **30a** – **31a**, **39a** were prepared according to the methods described in our previous work,<sup>[2]</sup> and the characterization data were in good agreement with those reported therein. 2-Ethynylanilines **13a** – **24a** were prepared by the following protocol (see section S1.5.1), among which only **13a**<sup>[3]</sup> and **15a**<sup>[4]</sup> were known compounds.

Diselenides **2b** – **4b** were synthesized by a reported method,<sup>[5]</sup> and the characterization data were in good agreement with those reported therein; while diselenides **5b** and **6b** were purchased from commercial sources.

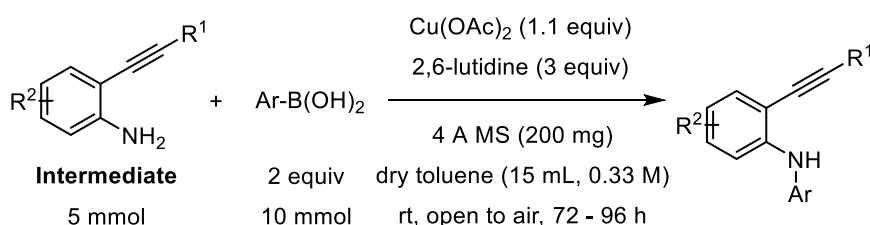
Indoles **1a'**,<sup>[2]</sup> **13a'**<sup>[3]</sup> and **39a'** as substrates for comparison were prepared using literature methods or purchased from commercial sources.

Finally, the synthesis of **32a** – **34a**, **37a** are described in the following sections (S1.5.2 – 1.5.4)

### 1.5.1 General produce for Sonogashira and Chan-Lam cross-coupling



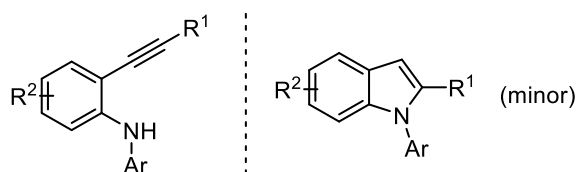
To an oven-dried 50 mL flask with a magnetic stir bar was added 2-iodoaniline derivative (10 mmol, 1 equiv), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (70.2 mg, 0.1 mmol, 1 mol%) and CuI (38.0 mg, 0.2 mmol, 2 mol%). Then the flask was closed with a septum, and the atmosphere inside was replaced with N<sub>2</sub>. Dry Et<sub>3</sub>N (10 mL, 1.0 M) and specific terminal alkyne (12 mmol, 1.2 equiv) were successively added via syringe (solid alkynes were added after dissolution in minimized amount of dry THF or DMF). The mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was filtered through a short pad of silica gel, concentrated under reduced pressure, and subjected to column chromatography (eluted with EtOAc/PE) to yield the 2-ethynylaniline **intermediate** (yields were generally ≥ 90% for this step).



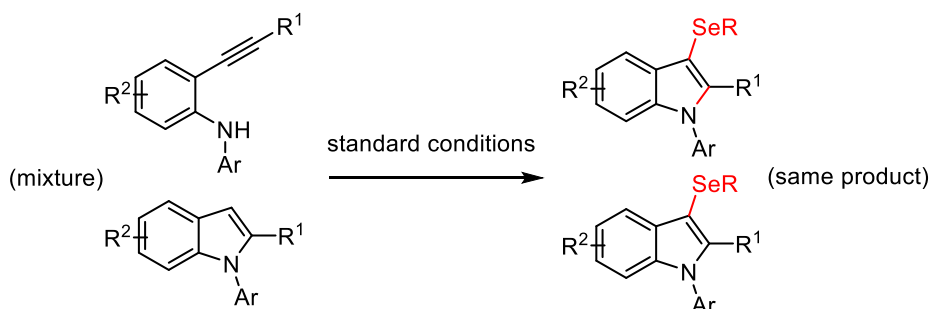
To an oven-dried 50 mL round-bottom flask was added the specific unprotected 2-ethynylaniline **intermediate** (5 mmol, 1 equiv) and aryl boronic acid (10 mmol, 2 equiv), followed by Cu(OAc)<sub>2</sub> (1.0 g, 5.5 mmol, 1.1 equiv) and pre-activated, powdered 4Å molecular

sieve (200 mg). After addition of dry toluene (15 mL, 0.33 M) and 2,6-lutidine (1.75 mL, 15 mmol, 3 equiv), the flask was equipped with a drying tube containing granular anhydrous CaCl<sub>2</sub>. The system was then stirred under ambient conditions for 72 - 96 h. Upon completion, the insoluble matters were removed by filtration through a short silica gel pad, and the filtrate was then concentrated under reduced pressure. Further purification of the resulting mixture by column chromatography on silica gel (eluted with EtOAc/PE) afforded the desired *N*-arylated 2-ethynylaniline (yields ranged from 40% to 90%).

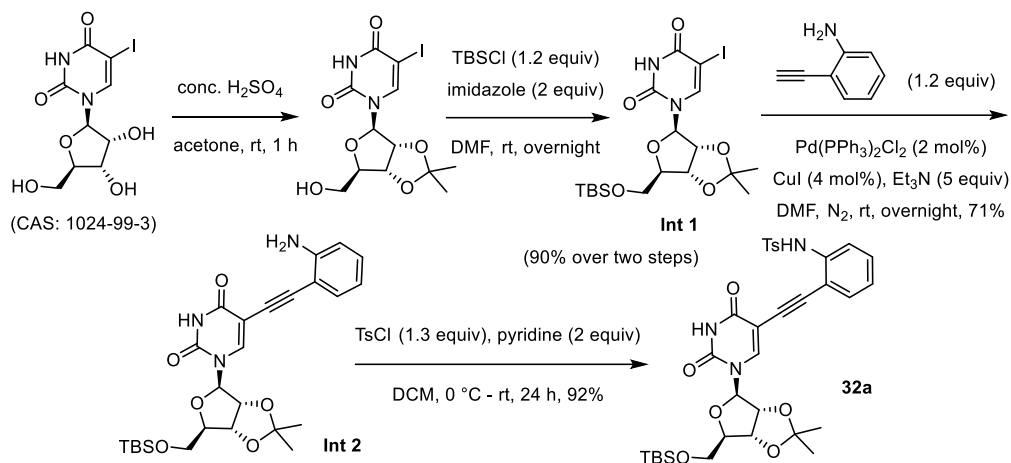
- It should be noted that in certain cases, the title -NHAr products **a** were isolated with minor *N*-aryl indoles **a'** (ratios of **a** : **a'** ranged from 1:0 to 1:0.16 by <sup>1</sup>H NMR) as Cu-catalyzed cyclization side products (**a** and **a'** were almost inseparable chromatographically):



However, the comparison experiment with indole **13a'** as the substrate instead of **13a** (see Figure 1c, reaction 2 in the main text) had proven that electron-rich indoles **a'** are also competent substrates to undergo direct C3 selenylation under our established standard conditions to access the same products **c**. **Therefore, minor indole impurities with identical molecular weights would not affect the real yields of the *N*-aryl-3-selenylindoles:**



### 1.5.2 Synthesis of 32a



To a suspension of 5-iodouridine (3.70 g, 10 mmol, 1 equiv) in acetone (120 mL) was added concentrated  $\text{H}_2\text{SO}_4$  (1.0 mL), the reaction mixture was stirred for 1 h at room temperature, during which the solid was gradually dissolved. TLC analysis indicated the complete conversion, the mixture was then extracted with EtOAc/water, washed with saturated  $\text{NaHCO}_3$  aq., dried over anhydrous  $\text{Na}_2\text{SO}_4$  and had the solvent removed under reduced pressure. The crude product was dissolved in 50 mL dry DMF, and imidazole (1.36 g, 20 mmol, 2 equiv) was then added. Under magnetic stirring, TBSCl (2.1 mL, 12 mmol, 1.2 equiv) was added dropwise to the solution, and the system was stirred overnight at ambient temperature. The mixture was extracted with EtOAc/water, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then had the solvent removed under reduced pressure. Further column chromatography afforded **Int 1** as a light yellow solid (4.72 g, 90%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.17 (s, 1H), 7.93 (s, 1H), 5.86 (d,  $J = 2.9$  Hz, 1H), 4.71 (qd,  $J = 6.1, 2.4$  Hz, 2H), 4.37 (q,  $J = 2.5$  Hz, 1H), 3.91 (dd,  $J = 11.7, 2.3$  Hz, 1H), 3.79 (dd,  $J = 11.6, 3.1$  Hz, 1H), 1.58 (s, 3H), 1.35 (s, 3H), 0.90 (s, 9H), 0.12 (s, 6H).

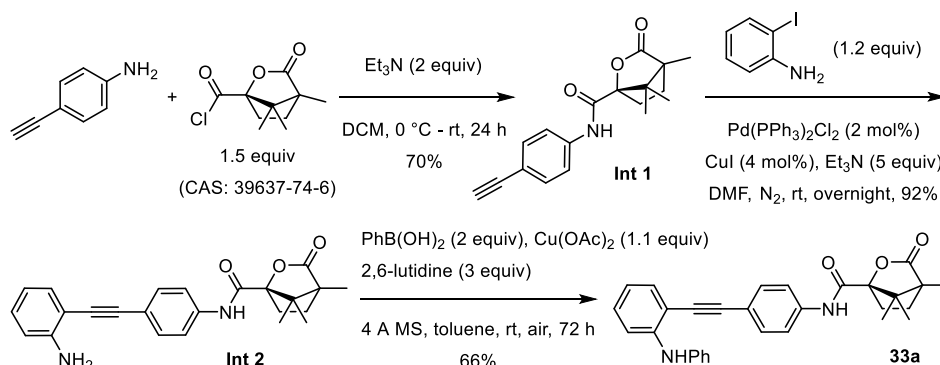
To an oven-dried 50 mL flask with a magnetic stir bar was added **Int 1** (2.62 g, 5 mmol, 1 equiv),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (71 mg, 0.1 mmol, 2 mol%) and  $\text{CuI}$  (38 mg, 0.2 mmol, 4 mol%). Then the flask was closed with a septum, and the atmosphere inside was replaced with  $\text{N}_2$ . Dry DMF (10 mL),  $\text{Et}_3\text{N}$  (3.5 mL, 25 mmol, 5 equiv) and 2-ethynylaniline (0.7 mL, 6 mmol, 1.2 equiv) were successively added via syringe. The mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was filtered through a short pad of silica gel, concentrated under reduced pressure, and subjected to column chromatography to yield **Int 2** as a brown solid (1.82 g, 71%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.20 (br, 1H), 7.91 (d,  $J = 1.4$  Hz, 1H), 7.19 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.12 (ddt,  $J = 8.7, 7.5, 2.3$  Hz, 1H), 6.71 (t,  $J = 7.5$  Hz, 1H),



6.63 (tt,  $J = 7.5, 1.4$  Hz, 1H), 5.99 (s, 1H), 4.77 (dd,  $J = 6.1, 2.4$  Hz, 1H), 4.71 (dd,  $J = 6.1, 3.1$  Hz, 1H), 4.40 (s, 1H), 3.97 (dd,  $J = 11.6, 2.2$  Hz, 1H), 3.82 (dd,  $J = 11.6, 2.7$  Hz, 1H), 1.61 (s, 3H), 1.37 (s, 3H), 0.93 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H).

To an oven-dried 100 mL flask with a magnetic stir bar was added **Int 2** (1.54 g, 3 mmol, 1 equiv), pyridine (0.5 mL, 6 mmol, 2 equiv) and dry DCM (20 mL), after which the system was cooled to 0 °C with ice-water bath. Subsequently, *p*-toluenesulfonyl chloride (0.74 g, 3.9 mmol, 1.3 equiv) was slowly added to the solution with vigorous stirring. Then the reaction mixture was allowed to room temperature and stirred for 24 h. Aqueous HCl solution (1 M) was added to quench the remaining pyridine and the mixture was then extracted with water/DCM. The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Further purification by column chromatography afforded **32a** as a white solid (1.84 g, 92%). See section S2.1 for the characterization data.

### 1.5.3 Synthesis of 33a



To an oven-dried 100 mL flask with a magnetic stir bar was added 4-ethynylaniline (1.17 g, 10 mmol, 1 equiv), Et<sub>3</sub>N (3.0 mL, 20 mmol, 2 equiv) and dry DCM (25 mL), after which the system was cooled to 0 °C with ice-water bath. Subsequently, (-)-Camphanoyl chloride (3.25 g, 15 mmol, 1.5 equiv) was slowly added to the solution with vigorous stirring. Then the reaction mixture was allowed to room temperature and stirred for 24 h. Water was added to the mixture and the aqueous phase was extracted with DCM for three times. The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Further purification by column chromatography afforded **Int 1** as a light yellow solid (2.08 g, 70%).

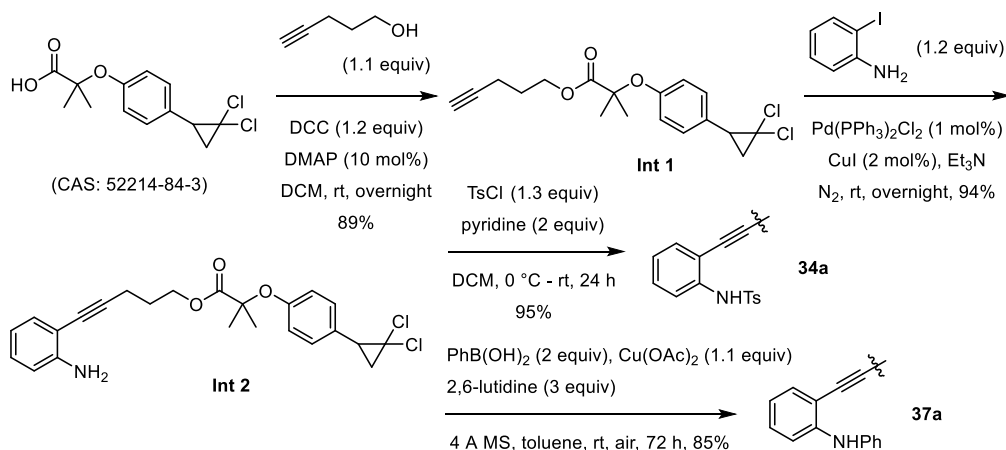
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (s, 1H), 7.61 – 7.54 (m, 2H), 7.52 – 7.43 (m, 2H), 3.07 (s, 1H),

2.68 – 2.53 (m, 1H), 2.08 – 1.93 (m, 2H), 1.81 – 1.70 (m, 1H), 1.17 (s, 3H), 1.15 (s, 3H), 0.98 (s, 3H).

To an oven-dried 50 mL flask with a magnetic stir bar was added 2-iodoaniline (1.58 g, 7.2 mmol, 1.2 equiv), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (85 mg, 0.12 mmol, 2 mol%) and CuI (46 mg, 0.24 mmol, 4 mol%). Then the flask was closed with a septum, and the atmosphere inside was replaced with N<sub>2</sub>. Dry DMF (5 mL), Et<sub>3</sub>N (4.2 mL, 30 mmol, 5 equiv) and **Int 1** (1.78 g, 6 mmol, 1 equiv, dissolved in 5 mL dry DMF) were successively added via syringe. The mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was filtered through a short pad of silica gel, concentrated under reduced pressure, and subjected to column chromatography to yield **Int 2** as a light yellow solid (2.14 g, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.36 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.19 – 7.06 (m, 1H), 6.74 (dt, *J* = 11.3, 5.7 Hz, 2H), 2.61 (ddt, *J* = 15.3, 8.2, 4.2 Hz, 1H), 2.01 (td, *J* = 13.0, 4.7 Hz, 2H), 1.75 (ddt, *J* = 12.2, 8.0, 4.8 Hz, 1H), 1.18 (s, 3H), 1.15 (s, 3H), 0.99 (s, 3H).

To an oven-dried 50 mL round-bottom flask was added **Int 2** (1.94 g, 5 mmol, 1 equiv) and phenyl boronic acid (1.22 g, 10 mmol, 2 equiv), followed by Cu(OAc)<sub>2</sub> (1.0 g, 5.5 mmol, 1.1 equiv) and pre-activated, powdered 4Å molecular sieve (200 mg). After addition of dry toluene (15 mL) and 2,6-lutidine (1.75 mL, 15 mmol, 3 equiv), the flask was equipped with a drying tube containing granular anhydrous CaCl<sub>2</sub>. The system was then stirred under ambient conditions for 72 h. Upon completion, the insoluble matters were removed by filtration through a short silica gel pad, and the filtrate was then concentrated under reduced pressure. Further purification of the resulting mixture by column chromatography on silica gel afforded **33a** as a white solid (1.53 g, 66%). See section S2.1 for the characterization data.

#### 1.5.4 Synthesis of 34a/37a



To an oven-dried 100 mL flask with a magnetic stir bar was added Ciprofibrate (2.89 g, 10 mmol, 1 equiv), pent-4-yn-1-ol (0.92 g, 11 mmol, 1.1 equiv) and dry DCM (30 mL). Subsequently, dicyclohexylcarbodiimide (DCC, 2.48 g, 12 mmol, 1.2 equiv) and then 4-dimethylaminopyridine (DMAP, 122 mg, 1 mmol, 10 mol%) were slowly added to the solution with vigorous stirring. The reaction mixture was stirred overnight. The reaction solvent was evaporated under reduced pressure and the residue was filtered through a short pad of silica gel (rinsed with cold EtOAc). The filtrate was then concentrated under reduced pressure, and further purification by column chromatography afforded **Int 1** as a colorless oil (3.16 g, 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 – 7.06 (m, 2H), 6.85 – 6.74 (m, 2H), 4.25 (t, *J* = 6.2 Hz, 2H), 2.83 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.09 (td, *J* = 7.1, 2.6 Hz, 2H), 1.98 – 1.90 (m, 2H), 1.84 – 1.74 (m, 3H), 1.61 (s, 6H).

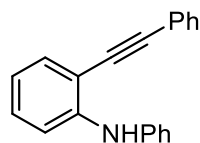
To an oven-dried 50 mL flask with a magnetic stir bar was added 2-iodoaniline (2.11 g, 9.6 mmol, 1.2 equiv), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (113 mg, 0.16 mmol, 2 mol%) and CuI (61 mg, 0.32 mmol, 4 mol%). Then the flask was closed with a septum, and the atmosphere inside was replaced with N<sub>2</sub>. Dry Et<sub>3</sub>N (10 mL) and **Int 1** (2.84 g, 8 mmol, 1 equiv, dissolved in 2 mL dry THF) were successively added via syringe. The mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was filtered through a short pad of silica gel, concentrated under reduced pressure, and subjected to column chromatography to yield **Int 2** as a light brown oil (3.36 g, 94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.09 (dd, *J* = 8.4, 6.6 Hz, 3H), 6.85 – 6.76 (m, 2H), 6.74 – 6.61 (m, 2H), 4.33 (t, *J* = 6.2 Hz, 2H), 2.80 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.38 (t, *J* = 6.9 Hz, 2H), 1.97 – 1.83 (m, 3H), 1.74 (t, *J* = 7.9 Hz, 1H), 1.62 (s, 6H).

To an oven-dried 100 mL flask with a magnetic stir bar was added **Int 2** (1.34 g, 3 mmol, 1 equiv), pyridine (0.5 mL, 6 mmol, 2 equiv) and dry DCM (20 mL), after which the system was cooled to 0 °C with ice-water bath. Subsequently, *p*-toluenesulfonyl chloride (0.74 g, 3.9 mmol, 1.3 equiv) was slowly added to the solution with vigorous stirring. Then the reaction mixture was allowed to room temperature and stirred for 24 h. Aqueous HCl solution (1 M) was added to quench the remaining pyridine and the mixture was then extracted with water/DCM. The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Further purification by column chromatography afforded **34a** as a light brown oil (1.71 g, 95%). See section S2.1 for the characterization data.

To an oven-dried 50 mL round-bottom flask was added **Int 2** (1.34 g, 3 mmol, 1 equiv) and phenyl boronic acid (0.73 g, 10 mmol, 2 equiv), followed by Cu(OAc)<sub>2</sub> (0.6 g, 3.3 mmol, 1.1 equiv) and pre-activated, powdered 4Å molecular sieve (120 mg). After addition of dry toluene (9 mL) and 2,6-lutidine (1.05 mL, 9 mmol, 3 equiv), the flask was equipped with a drying tube containing granular anhydrous CaCl<sub>2</sub>. The system was then stirred under ambient conditions for 72 h. Upon completion, the insoluble matters were removed by filtration through a short silica gel pad, and the filtrate was then concentrated under reduced pressure. Further purification of the resulting mixture by column chromatography on silica gel afforded **37a** as a light yellow oil (1.33 g, 85%). See section S2.1 for the characterization data.

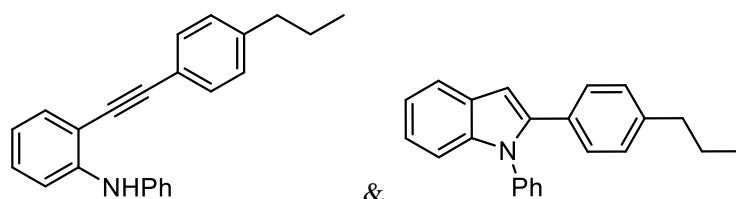
## 2. Characterization data

### 2.1 Characterization data for substrates



**13a:** *N*-phenyl-2-(phenylethynyl)aniline <sup>[3]</sup>

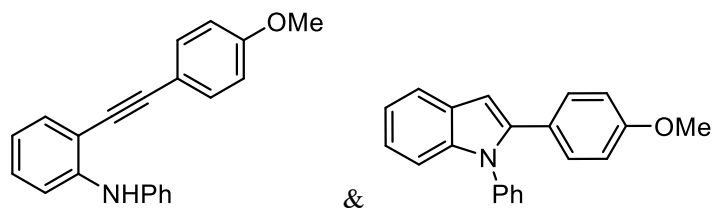
- With negligible corresponding indole **13a'**.
- Light yellow oil.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 – 7.49 (m, 2H), 7.47 (dd,  $J$  = 7.7, 1.6 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.26 – 7.16 (m, 4H), 7.03 (t,  $J$  = 7.3 Hz, 1H), 6.87 – 6.77 (m, 1H), 6.51 (s, 1H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.98, 141.78, 132.76, 131.66, 129.64, 129.55, 128.58, 123.16, 122.70, 120.43, 119.35, 113.56, 110.28, 95.74, 85.79.



**14a:** *N*-phenyl-2-((4-propylphenyl)ethynyl)aniline

**14a':** 1-phenyl-2-(4-propylphenyl)-1*H*-indole

- **14a** : **14a'** = 1 : 0.13 (by <sup>1</sup>H-NMR)
- Light yellow oil.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 – 7.41 (m, 3H), 7.32 (t,  $J$  = 7.9 Hz, 2H), 7.28 – 7.12 (m, 6H), 7.03 (t,  $J$  = 7.4 Hz, 1H), 6.81 (t,  $J$  = 7.4 Hz, 1H), 6.52 (s, 1H), 2.60 (t,  $J$  = 7.6 Hz, 2H), 1.64 (q,  $J$  = 7.4 Hz, 2H), 0.94 (t,  $J$  = 7.4 Hz, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.88, 143.56, 141.83, 132.68, 131.57, 129.54, 129.44, 128.76, 122.62, 120.38, 120.30, 119.32, 113.48, 110.51, 95.97, 85.08, 38.10, 24.50, 13.89.
- **HRMS** (ESI) calculated for C<sub>23</sub>H<sub>22</sub>N<sup>+</sup>  $m/z$  [M+H]<sup>+</sup>: 312.1747, found: 312.1753.



**15a**: 2-((4-methoxyphenyl)ethynyl)-*N*-phenylaniline [4]

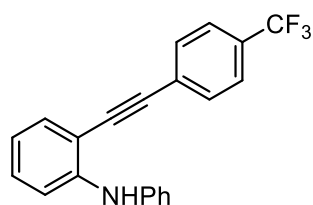
**15a'**: 2-(4-methoxyphenyl)-1-phenyl-1*H*-indole [6]

• **15a** : **15a'** = 1 : 0.08 (by <sup>1</sup>H-NMR)

• Light yellow oil.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.42 (m, 3H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.14 (m, 4H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.84 – 6.78 (m, 1H), 6.51 (s, 1H), 3.82 (s, 3H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 159.88, 144.76, 141.86, 133.13, 132.60, 129.53, 129.29, 122.57, 120.32, 119.34, 115.22, 114.21, 113.51, 110.67, 95.72, 84.38, 55.46.



**16a**: *N*-phenyl-2-((4-(trifluoromethyl)phenyl)ethynyl)aniline

• With negligible corresponding indole **16a'**.

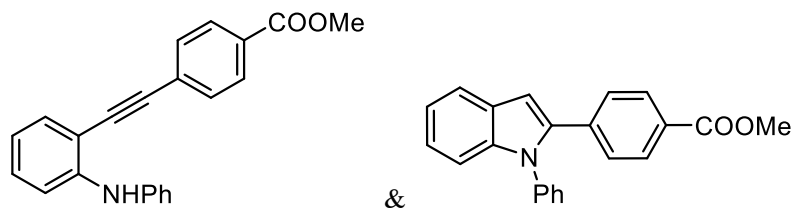
• Light brown oil.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 (s, 4H), 7.50 – 7.45 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.18 (m, 4H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.87 – 6.80 (m, 1H), 6.43 (s, 1H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.29, 141.60, 133.00, 131.83, 130.26, 130.17 (q, *J* = 32.9 Hz), 129.62, 127.01, 125.51 (q, *J* = 3.7 Hz), 124.05 (d, *J* = 272.3 Hz), 122.97, 121.71, 120.62, 119.50, 113.85, 109.57, 94.29, 88.39.

• **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.74.

• **HRMS** (ESI) calculated for C<sub>21</sub>H<sub>15</sub>F<sub>3</sub>N<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 338.1151, found: 338.1155.



**17a:** methyl 4-((2-(phenylamino)phenyl)ethynyl)benzoate

**17a':** methyl 4-(1-phenyl-1*H*-indol-2-yl)benzoate [7]

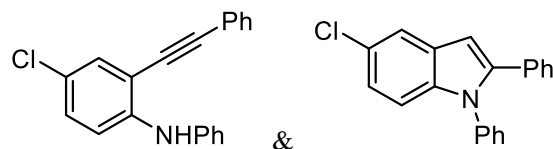
• **17a : 17a'** = 1 : 0.16 (by <sup>1</sup>H-NMR)

• Yellow solid, m. p.: N/A (mixture).

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.03 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.58 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.48 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.28 – 7.16 (m, 5H), 7.12 – 7.00 (m, 1H), 6.84 (ddd, *J* = 8.1, 6.8, 1.8 Hz, 1H), 3.93 (s, 3H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.65, 145.26, 141.60, 132.97, 131.50, 130.20, 129.74, 129.70, 129.61, 127.87, 122.95, 120.63, 119.45, 113.75, 109.67, 94.98, 88.94, 52.41.

• **HRMS** (ESI) calculated for C<sub>22</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> *m/z* [M+H]<sup>+</sup>: 328.1332, found: 328.1338.



**18a:** 4-chloro-*N*-phenyl-2-(phenylethynyl)aniline

**18a':** 5-chloro-1,2-diphenyl-1*H*-indole [6]

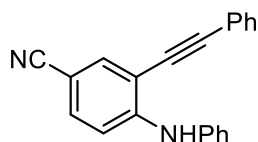
• **18a : 18a'** = 1 : 0.13 (by <sup>1</sup>H-NMR)

• Light yellow oil.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.43 (d, *J* = 2.3 Hz, 1H), 7.38 – 7.29 (m, 5H), 7.21 – 7.10 (m, 4H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.43 (s, 1H).

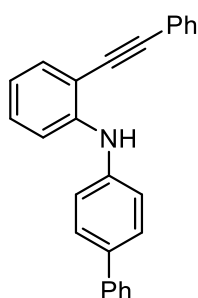
• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.70, 141.32, 131.97, 131.71, 129.65, 129.58, 128.90, 128.63, 123.54, 123.15, 122.63, 120.66, 114.55, 111.58, 96.62, 84.51.

• **HRMS** (ESI) calculated for C<sub>20</sub>H<sub>15</sub>ClN<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 304.0888, found: 304.0895.



**19a:** 4-(phenylamino)-3-(phenylethynyl)benzonitrile

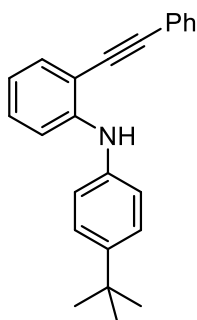
- With negligible corresponding indole **19a'**.
- Light yellow solid, **m. p.:** 99 – 101 °C.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 2.0 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.46 – 7.34 (m, 6H), 7.29 – 7.23 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 6.88 (s, 1H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 148.88, 139.30, 136.57, 133.41, 131.81, 129.91, 129.27, 128.74, 125.28, 123.12, 122.19, 119.39, 111.94, 109.81, 100.98, 97.30, 83.31.
- **HRMS** (ESI) calculated for C<sub>21</sub>H<sub>15</sub>N<sub>2</sub><sup>+</sup> *m/z* [M+H]<sup>+</sup>: 295.1230, found: 295.1239.



**20a:** *N*-(2-(phenylethynyl)phenyl)-[1,1'-biphenyl]-4-amine

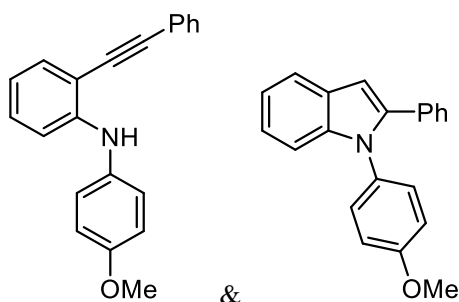
- With negligible corresponding indole **20a'**.
- White solid, **m. p.:** 88 – 91 °C.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.52 (m, 6H), 7.49 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.43 (td, *J* = 7.7, 1.6 Hz, 2H), 7.38 – 7.19 (m, 8H), 6.85 (td, *J* = 7.5, 1.3 Hz, 1H), 6.58 (s, 1H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 144.68, 141.18, 140.86, 135.42, 132.82, 131.68, 129.68, 128.92, 128.61, 128.19, 126.98, 126.82, 123.13, 120.32, 119.60, 113.93, 110.56, 95.85, 85.74.
- **HRMS** (ESI) calculated for C<sub>26</sub>H<sub>20</sub>N<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 346.1590, found: 346.1599.





**21a:** *N*-(4-(*tert*-butyl)phenyl)-2-(phenylethynyl)aniline

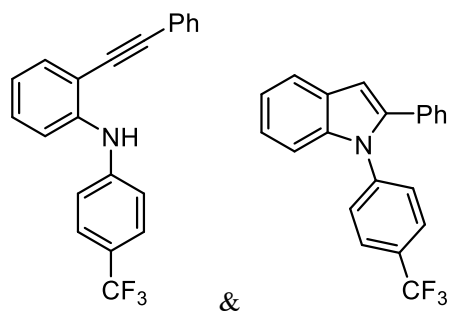
- With negligible corresponding indole **21a'**.
- Light yellow oil.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 – 7.48 (m, 2H), 7.46 (d,  $J$  = 7.9 Hz, 1H), 7.39 – 7.30 (m, 5H), 7.24 – 7.13 (m, 4H), 6.79 (td,  $J$  = 7.6, 7.0, 1.7 Hz, 1H), 6.47 (s, 1H), 1.33 (s, 9H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.94, 145.51, 139.05, 132.66, 131.64, 129.65, 128.57, 128.51, 126.37, 123.22, 120.67, 118.88, 113.22, 109.76, 95.63, 85.89, 34.45, 31.59.
- **HRMS** (ESI) calculated for C<sub>24</sub>H<sub>24</sub>N<sup>+</sup>  $m/z$  [M+H]<sup>+</sup>: 326.1903, found: 326.1905.



**22a:** *N*-(4-methoxyphenyl)-2-(phenylethynyl)aniline

**22a':** 1-(4-methoxyphenyl)-2-phenyl-1*H*-indole <sup>[8]</sup>

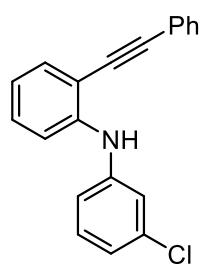
- **22a** : **22a'** = 1 : 0.08 (by <sup>1</sup>H-NMR)
- Light yellow oil.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.49 (m, 2H), 7.48 – 7.41 (m, 1H), 7.40 – 7.29 (m, 3H), 7.21 – 7.11 (m, 3H), 6.99 – 6.87 (m, 3H), 6.80 – 6.70 (m, 1H), 6.34 (s, 1H), 3.81 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.43, 146.92, 134.40, 132.61, 131.67, 129.77, 128.57, 128.49, 124.73, 123.27, 118.21, 114.84, 112.05, 108.73, 95.47, 85.94, 55.70.
- **HRMS** (ESI) calculated for C<sub>21</sub>H<sub>18</sub>NO<sup>+</sup>  $m/z$  [M+H]<sup>+</sup>: 300.1383, found: 300.1388.



**23a**: 2-(phenylethynyl)-*N*-(4-(trifluoromethyl)phenyl)aniline

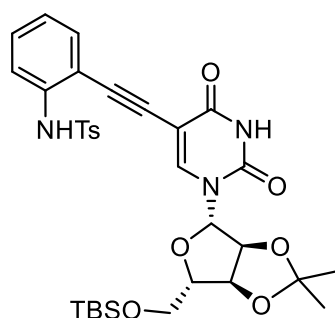
**23a'**: 2-phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-indole <sup>[8]</sup>

- **23a** : **23a'** = 1 : 0.04 (by <sup>1</sup>H-NMR)
- Light yellow solid, m. p.: N/A (mixture).
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.46 (m, 5H), 7.40 – 7.32 (m, 4H), 7.31 – 7.17 (m, 3H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.61 (s, 1H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.43, 142.87, 133.03, 131.67, 129.61, 128.81, 128.64, 126.86 (q, *J* = 3.9 Hz), 124.60 (q, *J* = 271.1 Hz), 123.18 (q, *J* = 32.7 Hz), 122.85, 121.29, 117.59, 115.84, 112.46, 96.19, 85.35.
- **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -61.59.
- **HRMS** (ESI) calculated for C<sub>21</sub>H<sub>15</sub>F<sub>3</sub>N<sup>+</sup> m/z [M+H]<sup>+</sup>: 338.1151, found: 338.1151.



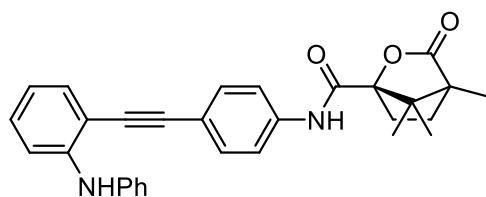
**24a**: *N*-(3-chlorophenyl)-2-(phenylethynyl)aniline

- With negligible corresponding indole **24a'**.
- Light yellow oil.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.45 (m, 3H), 7.40 – 7.32 (m, 3H), 7.31 – 7.17 (m, 4H), 7.06 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.97 (dd, *J* = 7.9, 2.1 Hz, 1H), 6.89 (td, *J* = 7.4, 1.5 Hz, 1H), 6.48 (s, 1H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.81, 143.40, 135.18, 132.91, 131.69, 130.53, 129.67, 128.72, 128.62, 122.97, 122.20, 120.39, 119.30, 117.60, 114.62, 111.33, 95.98, 85.46.
- **HRMS** (ESI) calculated for C<sub>20</sub>H<sub>15</sub>ClN<sup>+</sup> m/z [M+H]<sup>+</sup>: 304.0888, found: 304.0894.



**32a:** *N*-(2-((1-((3*aS*,4*S*,6*S*,6*aS*)-6-(((*tert*-butyldimethylsilyl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)phenyl)-4-methylbenzenesulfonamide

- White solid, **m. p.:** 182 – 185 °C.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.46 (br, 1H), 8.26 (s, 1H), 7.96 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.19 (t, *J* = 7.2 Hz, 3H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.01 (d, *J* = 2.8 Hz, 1H), 4.77 (dd, *J* = 6.1, 2.3 Hz, 1H), 4.74 – 4.68 (m, 1H), 4.44 (q, *J* = 2.3 Hz, 1H), 3.98 (dd, *J* = 11.7, 2.1 Hz, 1H), 3.83 (dd, *J* = 11.6, 2.6 Hz, 1H), 2.33 (s, 3H), 1.62 (s, 3H), 1.38 (s, 3H), 0.91 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.56, 148.87, 143.72, 140.85, 139.15, 136.77, 130.16, 129.99, 129.61, 127.59, 124.96, 123.57, 118.83, 114.32, 112.66, 99.55, 92.96, 91.42, 87.91, 87.03, 85.87, 80.77, 63.63, 27.39, 26.13, 25.42, 21.66, 18.53, -5.13, -5.31.
- **HRMS** (ESI) calculated for C<sub>33</sub>H<sub>42</sub>N<sub>3</sub>O<sub>8</sub>SSi<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 668.2456, found: 668.2459.



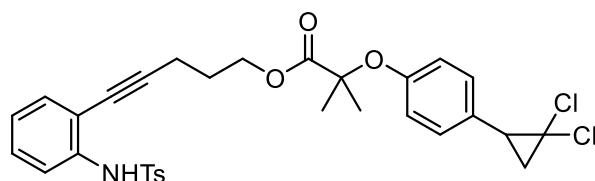
**33a:** (1*S*)-4,7,7-trimethyl-3-oxo-*N*-(4-((2-(phenylamino)phenyl)ethynyl)phenyl)-2-oxabicyclo[2.2.1]heptane-1-carboxamide

- With negligible corresponding indole **33a**<sup>?</sup>.
- White solid, **m. p.:** 184 – 186 °C.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.16 (m, 4H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.83

(t,  $J = 7.4$  Hz, 1H), 6.46 (s, 1H), 2.68 – 2.55 (m, 1H), 2.08 – 1.95 (m, 2H), 1.82 – 1.70 (m, 1H), 1.18 (s, 3H), 1.16 (s, 3H), 1.00 (s, 3H).

•  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.97, 165.46, 144.94, 141.75, 136.95, 132.75, 132.52, 129.64, 129.56, 122.72, 120.44, 119.81, 119.58, 119.39, 113.62, 110.24, 95.26, 92.49, 85.82, 55.65, 54.62, 30.68, 29.21, 16.90, 16.74, 9.87.

• **HRMS** (ESI) calculated for  $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_3^+$   $m/z$   $[\text{M}+\text{H}]^+$ : 465.2173, found: 465.2178.



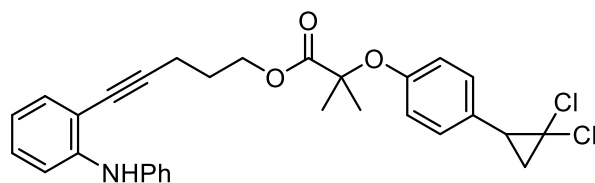
**34a:** 5-(2-((4-methylphenyl)sulfonamido)phenyl)pent-4-yn-1-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate

• Light brown oil.

•  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.62 (m, 2H), 7.59 – 7.47 (m, 1H), 7.25 – 7.17 (m, 5H), 7.10 (d,  $J = 8.7$  Hz, 2H), 6.99 (td,  $J = 7.6, 1.2$  Hz, 1H), 6.85 – 6.78 (m, 2H), 4.28 (t,  $J = 6.1$  Hz, 2H), 2.80 (dd,  $J = 10.7, 8.3$  Hz, 1H), 2.35 (s, 3H), 2.30 (t,  $J = 7.0$  Hz, 2H), 1.94 – 1.81 (m, 3H), 1.75 (t,  $J = 7.9$  Hz, 1H), 1.64 (s, 6H).

•  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.41, 155.14, 144.11, 137.82, 136.39, 132.24, 129.90, 129.74, 129.24, 128.27, 127.40, 124.31, 119.48, 118.33, 114.51, 95.87, 79.27, 76.35, 63.88, 61.03, 34.91, 27.68, 25.90, 25.62, 21.68, 16.24.

• **HRMS** (ESI) calculated for  $\text{C}_{31}\text{H}_{32}\text{Cl}_2\text{NO}_5\text{S}^+$   $m/z$   $[\text{M}+\text{H}]^+$ : 600.1373, found: 600.1379.



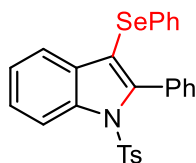
**37a:** 5-(2-(phenylamino)phenyl)pent-4-yn-1-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate

• With negligible corresponding indole **37a**?

• Light yellow oil.

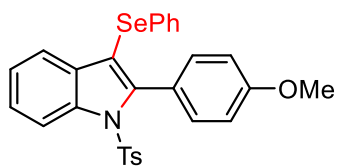
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 – 7.26 (m, 3H), 7.25 – 7.11 (m, 4H), 7.08 (d,  $J$  = 8.5 Hz, 2H), 7.01 (t,  $J$  = 7.3 Hz, 1H), 6.82 – 6.73 (m, 3H), 6.42 (s, 1H), 4.33 (t,  $J$  = 6.0 Hz, 2H), 2.78 (dd,  $J$  = 10.7, 8.3 Hz, 1H), 2.38 (t,  $J$  = 6.9 Hz, 2H), 1.94 – 1.82 (m, 3H), 1.71 (t,  $J$  = 7.9 Hz, 1H), 1.62 (s, 6H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  174.40, 155.12, 144.90, 141.95, 132.80, 129.88, 129.48, 129.00, 128.23, 122.47, 120.28, 119.29, 118.34, 113.58, 110.83, 94.73, 79.27, 78.01, 64.01, 61.01, 34.90, 27.81, 25.87, 25.66, 25.56, 16.37.
- **HRMS** (ESI) calculated for C<sub>30</sub>H<sub>30</sub>Cl<sub>2</sub>NO<sub>3</sub><sup>+</sup>  $m/z$  [M+H]<sup>+</sup>: 522.1597, found: 522.1605.

## 2.2 Characterization data for products



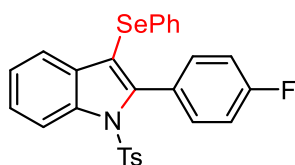
**1c**: 2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-indole <sup>[9]</sup>

- White solid, **m. p.**: 164 – 165 °C.
- Following the General Procedure: **1a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 98.6 mg, 0.196 mmol, **98% yield**.
- **[Gram-scale]** Following the General Procedure of gram-scale synthesis: **1a** (3.0 mmol) and **1b** (1.56 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> (0.15 mmol) under the irradiation of two 12 W blue LEDs for 24 h.
- 1.480 g, 2.945 mmol, **98% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d,  $J$  = 8.4 Hz, 1H), 7.48 – 7.36 (m, 5H), 7.35 – 7.23 (m, 5H), 7.12 – 7.01 (m, 5H), 6.98 – 6.90 (m, 2H), 2.34 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  145.02, 137.68, 135.15, 132.25, 131.94, 131.78, 131.05, 129.54, 129.40, 129.32, 129.14, 127.28, 127.05, 126.19, 125.84, 124.78, 121.35, 116.42, 110.67, 21.75.



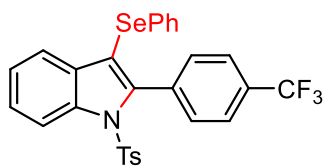
**2c:** 2-(4-methoxyphenyl)-3-(phenylselanyl)-1-tosyl-1*H*-indole <sup>[9]</sup>

- White solid, **m. p.:** 170 – 172 °C.
- Following the General Procedure: **2a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 104.0 mg, 0.195 mmol, **98% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.35 (m, 2H), 7.33 – 7.19 (m, 5H), 7.12 – 6.99 (m, 5H), 6.96 – 6.86 (m, 4H), 3.87 (s, 3H), 2.34 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 160.43, 145.14, 144.94, 137.71, 135.18, 133.16, 132.38, 132.11, 129.49, 129.23, 129.13, 127.03, 126.10, 125.68, 124.78, 123.15, 121.20, 116.54, 112.76, 110.25, 55.36, 21.74.



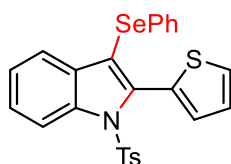
**3c:** 2-(4-fluorophenyl)-3-(phenylselanyl)-1-tosyl-1*H*-indole <sup>[9]</sup>

- White solid, **m. p.:** 142 – 143 °C.
- Following the General Procedure: **3a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 20 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 90.9 mg, 0.175 mmol, **87% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.37 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.33 – 7.23 (m, 5H), 7.05 (m, 7H), 6.95 – 6.87 (m, 2H), 2.33 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.37 (*J* = 249.3 Hz), 145.16, 143.83, 137.64, 135.11, 133.62 (*J* = 8.3 Hz), 132.16, 131.77, 129.58, 129.35, 129.19, 126.97 (*J* = 3.6 Hz), 126.91, 126.28, 125.99, 124.87, 121.35, 116.41, 114.47 (*J* = 21.8 Hz), 110.95, 21.71.



**4c:** 3-(phenylselanyl)-1-tosyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indole

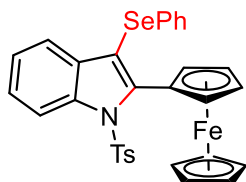
- White solid, **m. p.:** 216 – 218 °C.
- Following the General Procedure: **4a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 30 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 103.7 mg, 0.182 mmol, **91% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.40 (m, 4H), 7.35 – 7.23 (m, 3H), 7.14 – 7.07 (m, 3H), 7.07 – 7.00 (m, 2H), 6.95 – 6.87 (m, 2H), 2.34 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.35, 143.11, 137.77, 134.83, 132.24, 132.05, 131.54, 130.99 (q, *J* = 32.6 Hz), 129.67, 129.52, 129.27, 126.93, 126.47, 126.36, 125.07, 124.25 (q, *J* = 3.8 Hz), 124.20 (q, *J* = 272.5 Hz), 121.58, 116.47, 112.01, 21.75.
- **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.53.
- **HRMS** (ESI) calculated for C<sub>28</sub>H<sub>21</sub>F<sub>3</sub>NO<sub>2</sub>SSe<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 572.0405, found: 572.0408.



**5c:** 3-(phenylselanyl)-2-(thiophen-2-yl)-1-tosyl-1*H*-indole <sup>[9]</sup>

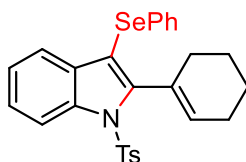
- White solid, **m. p.:** 139 – 141 °C.
- Following the General Procedure: **5a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 98.7 mg, 0.194 mmol, **97% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.36 (m, 5H), 7.29 – 7.23 (m, 1H), 7.14 – 6.99 (m, 9H), 2.35 (s, 3H).

•  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.07, 137.89, 137.36, 135.19, 132.37, 131.86, 131.74, 130.75, 129.79, 129.61, 129.18, 128.80, 127.10, 126.43, 126.38, 126.20, 124.72, 121.48, 116.32, 113.07, 21.77.



**6c:** 2-(ferrocen-1-yl)-3-(phenylselanyl)-1-tosyl-1*H*-indole <sup>[9]</sup>

- Red solid, **m. p.:** 193 – 195 °C.
- Following the General Procedure: **6a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 48 h.
- 94.7 mg, 0.155 mmol, **78% yield**.
- $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (t,  $J = 7.2$  Hz, 1H), 7.38 – 7.30 (m, 1H), 7.23 – 7.14 (m, 2H), 7.13 – 6.92 (m, 7H), 6.77 (t,  $J = 7.1$  Hz, 2H), 5.03 (s, 2H), 4.44 (s, 2H), 4.17 (s, 5H), 2.31 (s, 3H).
- $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.71, 144.47, 139.13, 134.64, 133.33, 132.25, 129.18, 129.07, 128.91, 127.36, 125.98, 125.48, 125.21, 120.58, 118.54, 111.98, 72.69, 70.46, 68.29, 21.78.

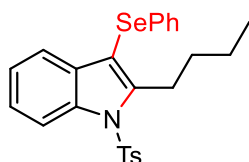


**7c:** 2-(cyclohex-1-en-1-yl)-3-(phenylselanyl)-1-tosyl-1*H*-indole <sup>[9]</sup>

- Light yellow solid, **m. p.:** 125 – 127 °C.
- Following the General Procedure: **7a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 24 h.
- 64.1 mg, 0.127 mmol, **63% yield**.
- $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (dd,  $J = 8.4, 3.9$  Hz, 1H), 7.58 (dd,  $J = 8.4, 3.1$  Hz, 2H), 7.37 – 7.29 (m, 2H), 7.21 – 7.11 (m, 3H), 7.10 – 7.01 (m, 5H), 5.43 (s, 1H), 2.85 – 2.53 (m, 1H), 2.33 (s, 3H), 2.25 – 2.13 (m, 2H), 2.11 – 1.89 (m, 1H), 1.88 – 1.57 (m, 4H).

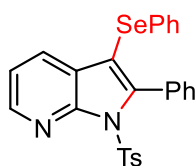


- $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.34, 144.92, 137.13, 135.64, 132.57, 132.22, 132.10, 130.91, 129.61, 129.55, 129.11, 126.99, 126.13, 125.29, 124.30, 121.27, 115.64, 108.44, 30.81, 25.70, 22.74, 21.92, 21.73.



**8c:** 2-butyl-3-(phenylselanyl)-1-tosyl-1*H*-indole <sup>[9]</sup>

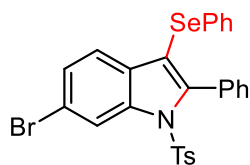
- White solid, **m. p.:** 77 – 79 °C.
- Following the General Procedure: **8a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 24 h.
- 86.2 mg, 0.179 mmol, **89% yield**.
- $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (d,  $J = 8.3$  Hz, 1H), 7.61 (d,  $J = 8.0$  Hz, 2H), 7.42 (d,  $J = 7.7$  Hz, 1H), 7.30 (t,  $J = 7.8$  Hz, 1H), 7.24 – 7.16 (m, 3H), 7.14 – 6.96 (m, 5H), 3.33 – 3.15 (m, 2H), 2.36 (s, 3H), 1.64 (p,  $J = 7.6$  Hz, 2H), 1.38 (h,  $J = 7.4$  Hz, 2H), 0.89 (t,  $J = 7.3$  Hz, 3H).
- $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.33, 145.03, 137.21, 136.02, 132.08, 132.01, 129.97, 129.19, 128.94, 126.46, 126.08, 124.99, 124.33, 120.71, 115.40, 108.11, 33.40, 28.45, 22.83, 21.73, 13.91.



**9c:** 2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-pyrrolo[2,3-*b*]pyridine <sup>[9]</sup>

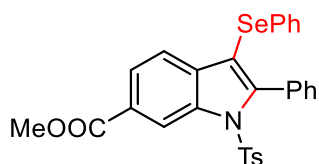
- White solid, **m. p.:** 185 – 186 °C.
- Following the General Procedure: **9a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 24 h.
- 96.2 mg, 0.191 mmol, **96% yield**.
- $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 – 8.47 (m, 1H), 7.84 (dd,  $J = 8.4, 2.3$  Hz, 2H), 7.70 (d,  $J = 7.8$  Hz, 1H), 7.53 – 7.35 (m, 5H), 7.24 – 7.16 (m, 3H), 7.15 – 7.02 (m, 5H), 2.37 (s, 3H).

- $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.44, 145.67, 145.23, 144.89, 135.91, 131.40, 131.27, 131.04, 130.07, 129.56, 129.49, 129.44, 129.28, 128.14, 127.58, 126.62, 124.42, 120.08, 106.57, 21.78.



**10c:** 6-bromo-2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-indole <sup>[9]</sup>

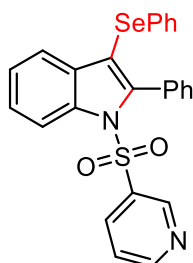
- White solid, **m. p.:** 162 – 164 °C.
- Following the General Procedure: **10a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 24 h.
- 113.5 mg, 0.195 mmol, **98% yield**.
- $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 – 8.48 (m, 1H), 7.49 – 7.42 (m, 1H), 7.41 – 7.34 (m, 3H), 7.33 – 7.24 (m, 5H), 7.16 – 7.00 (m, 5H), 6.97 – 6.88 (m, 2H), 2.36 (s, 3H).
- $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.39, 145.29, 138.22, 135.02, 131.79, 131.50, 131.04, 130.55, 129.69, 129.54, 129.23, 128.06, 127.34, 127.12, 126.42, 122.47, 119.44, 119.28, 110.24, 21.78.



**11c:** methyl 2-phenyl-3-(phenylselanyl)-1-tosyl-1*H*-indole-6-carboxylate <sup>[9]</sup>

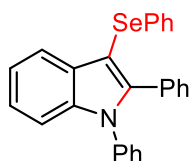
- White solid, **m. p.:** 136 – 138 °C.
- Following the General Procedure: **11a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 36 h.
- 105.5 mg, 0.188 mmol, **94% yield**.
- $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.12 – 9.01 (m, 1H), 7.96 (dd,  $J = 8.2, 1.4$  Hz, 1H), 7.52 – 7.44 (m, 2H), 7.40 (t,  $J = 7.5$  Hz, 2H), 7.35 – 7.27 (m, 4H), 7.14 – 7.00 (m, 5H), 6.94 (d,  $J = 7.4$  Hz, 2H), 3.98 (s, 3H), 2.34 (s, 3H).

- $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.37, 147.71, 145.37, 137.11, 135.86, 134.99, 131.70, 131.45, 130.55, 129.67, 129.61, 129.22, 127.59, 127.36, 127.14, 126.45, 125.87, 121.11, 118.06, 110.43, 52.45, 21.74.



**12c:** 2-phenyl-3-(phenylselanyl)-1-(pyridin-3-ylsulfonyl)-1*H*-indole <sup>[9]</sup>

- White solid, **m. p.:** 160 – 162 °C.
- Following the General Procedure: **12a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 48 h.
- 90.7 mg, 0.185 mmol, **93% yield**.
- $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (dd,  $J = 4.8, 1.6$  Hz, 1H), 8.63 (d,  $J = 2.4$  Hz, 1H), 8.36 (d,  $J = 8.4$  Hz, 1H), 7.67 (dt,  $J = 8.1, 2.0$  Hz, 1H), 7.51 – 7.38 (m, 5H), 7.36 – 7.19 (m, 4H), 7.13 – 7.02 (m, 3H), 6.96 (dd,  $J = 7.8, 1.9$  Hz, 2H).
- $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.32, 147.72, 144.35, 137.35, 134.59, 134.54, 132.35, 131.74, 131.35, 130.62, 129.75, 129.66, 129.26, 127.56, 126.49, 126.33, 125.37, 123.46, 121.72, 116.31, 112.03.



**13c:** 1,2-diphenyl-3-(phenylselanyl)-1*H*-indole

- Light yellow solid, **m. p.:** 96 – 98 °C.
- Following the General Procedure: (1) **13a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 24 h; (2) **13a'** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol%  $\text{FeBr}_3$  under the irradiation of a 12 W blue LED for 24 h.
- (1) 78.3 mg, 0.184 mmol, **92% yield**; (2) 76.2 mg, 0.180 mmol, **90% yield**.

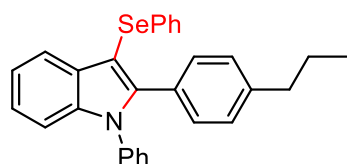
• **[Gram-scale]** Following the General Procedure of gram-scale synthesis: **13a** (3.0 mmol) and **1b** (1.56 mmol) as substrates, with 2.5 mol% FeBr<sub>3</sub> (0.075 mmol) under the irradiation of two 12 W blue LEDs for 24 h.

• 1.151 g, 2.712 mmol, **90% yield**.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.19 (m, 11H), 7.18 – 7.08 (m, 3H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.13, 138.47, 138.19, 134.28, 131.27, 131.17, 131.02, 129.35, 129.14, 128.83, 128.25, 128.16, 127.84, 127.60, 125.62, 123.43, 121.67, 121.01, 110.98, 99.03.

• **HRMS** (ESI) calculated for C<sub>26</sub>H<sub>20</sub>NSe<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 426.0755, found: 426.0747.



**14c**: 1-phenyl-3-(phenylselanyl)-2-(4-propylphenyl)-1*H*-indole

• Light yellow solid, **m. p.**: 144 – 145 °C.

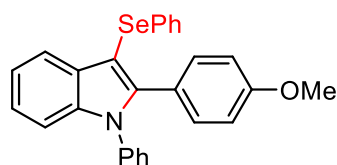
• Following the General Procedure: **14a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.

• 87.9 mg, 0.188 mmol, **94% yield**.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.29 (m, 4H), 7.28 – 7.18 (m, 6H), 7.17 – 7.07 (m, 5H), 7.02 (d, *J* = 7.7 Hz, 2H), 2.52 (t, *J* = 7.7 Hz, 2H), 1.65 – 1.54 (m, 2H), 0.89 (dt, *J* = 8.9, 4.4 Hz, 3H).

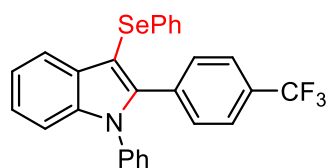
• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.32, 142.78, 138.43, 138.30, 134.40, 131.06, 130.96, 129.28, 129.11, 128.78, 128.44, 128.16, 127.94, 127.49, 125.55, 123.25, 121.58, 120.91, 110.92, 98.64, 37.90, 24.26, 13.96.

• **HRMS** (ESI) calculated for C<sub>29</sub>H<sub>26</sub>NSe<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 468.1225, found: 468.1225.



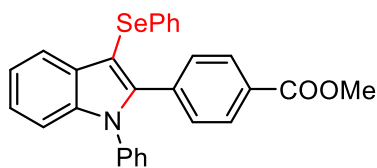
**15c:** 2-(4-methoxyphenyl)-1-phenyl-3-(phenylselanyl)-1*H*-indole

- White solid, **m. p.:** 135 – 137 °C.
- Following the General Procedure: **15a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 77.8 mg, 0.171 mmol, **86% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.64 (m, 1H), 7.41 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.19 (m, 6H), 7.17 – 7.06 (m, 5H), 6.80 – 6.69 (m, 2H), 3.75 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 159.48, 145.10, 138.37, 138.28, 134.42, 132.36, 131.07, 129.36, 129.14, 128.67, 128.18, 127.52, 125.55, 123.52, 123.20, 121.59, 120.81, 113.38, 110.89, 98.44, 55.25.
- **HRMS** (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NOSe<sup>+</sup> m/z [M+H]<sup>+</sup>: 456.0861, found: 456.0861.



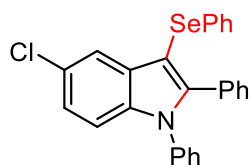
**16c:** 1-phenyl-3-(phenylselanyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-indole

- Light yellow solid, **m. p.:** 119 – 121 °C.
- Following the General Procedure: **16a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 73.9 mg, 0.150 mmol, **75% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.79 – 7.70 (m, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.31 (m, 4H), 7.30 – 7.19 (m, 6H), 7.17 – 7.09 (m, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.15, 138.64, 137.79, 134.88, 133.85, 131.39, 130.93, 129.96 (q, *J* = 32.7 Hz), 129.61, 129.28, 128.82, 128.06, 127.96, 125.88, 124.81 (q, *J* = 3.9 Hz), 124.12 (q, *J* = 272.4 Hz), 124.02, 121.98, 121.25, 111.11, 100.13.
- **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.59.
- **HRMS** (ESI) calculated for C<sub>27</sub>H<sub>19</sub>F<sub>3</sub>NSe<sup>+</sup> m/z [M+H]<sup>+</sup>: 494.0629, found: 494.0633.



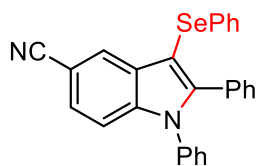
**17c:** methyl 4-(1-phenyl-3-(phenylselanyl)-1*H*-indol-2-yl)benzoate

- White solid, **m. p.:** 137 – 138 °C.
- Following the General Procedure: **17a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 91.3 mg, 0.189 mmol, **95% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (dd,  $J$  = 8.2, 1.6 Hz, 2H), 7.79 – 7.70 (m, 1H), 7.40 – 7.28 (m, 6H), 7.27 – 7.17 (m, 6H), 7.16 – 7.07 (m, 3H), 3.84 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.82, 143.62, 138.63, 137.87, 135.87, 133.90, 131.11, 131.00, 129.53, 129.50, 129.20, 129.02, 128.90, 128.01, 127.81, 125.82, 123.90, 121.89, 121.19, 111.04, 100.12, 52.22.
- **HRMS** (ESI) calculated for C<sub>28</sub>H<sub>22</sub>NO<sub>2</sub>Se<sup>+</sup>  $m/z$  [M+H]<sup>+</sup>: 484.0810, found: 484.0812.



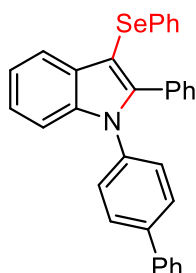
**18c:** 5-chloro-1,2-diphenyl-3-(phenylselanyl)-1*H*-indole

- Light yellow oil.
- Following the General Procedure: **18a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 85.5 mg, 0.186 mmol, **93% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (s, 1H), 7.40 – 7.31 (m, 3H), 7.26 – 7.07 (m, 14H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.37, 137.76, 136.85, 133.85, 132.28, 131.05, 130.80, 129.46, 129.24, 128.79, 128.49, 127.99, 127.91, 127.88, 127.43, 125.83, 123.73, 120.31, 112.16, 98.49.
- **HRMS** (ESI) calculated for C<sub>26</sub>H<sub>19</sub>ClNSe<sup>+</sup>  $m/z$  [M+H]<sup>+</sup>: 460.0366, found: 460.0360.



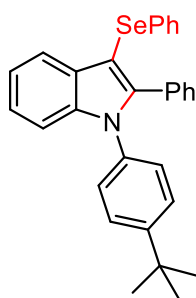
**19c:** 1,2-diphenyl-3-(phenylselanyl)-1*H*-indole-5-carbonitrile

- White solid, **m. p.:** 184 – 186 °C.
- Following the General Procedure: **19a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 86.6 mg, 0.193 mmol, **96% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.05 (s, 1H), 7.47 – 7.29 (m, 6H), 7.26 – 7.11 (m, 11H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 147.34, 140.04, 137.08, 133.01, 131.00, 130.93, 130.16, 129.62, 129.32, 129.21, 128.83, 128.39, 128.02, 127.94, 126.39, 126.27, 126.23, 120.38, 111.98, 104.72, 99.96.
- **HRMS** (ESI) calculated for C<sub>27</sub>H<sub>19</sub>N<sub>2</sub>Se<sup>+</sup> m/z [M+H]<sup>+</sup>: 451.0708, found: 451.0709.



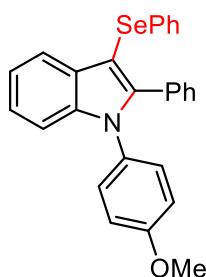
**20c:** 1-([1,1'-biphenyl]-4-yl)-2-phenyl-3-(phenylselanyl)-1*H*-indole

- White solid, **m. p.:** 189 – 191 °C.
- Following the General Procedure: **20a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 80.3 mg, 0.160 mmol, **80% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 4H), 7.51 – 7.33 (m, 5H), 7.31 – 7.21 (m, 10H), 7.19 – 7.09 (m, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 145.08, 140.27, 140.08, 138.46, 137.34, 134.26, 131.27, 131.21, 131.09, 129.16, 129.04, 128.87, 128.35, 128.31, 127.94, 127.90, 127.82, 127.19, 125.65, 123.49, 121.74, 121.06, 111.05, 99.24.
- **HRMS** (ESI) calculated for C<sub>32</sub>H<sub>24</sub>NSe<sup>+</sup> m/z [M+H]<sup>+</sup>: 502.1068, found: 502.1071.



**21c:** 1-(4-(tert-butyl)phenyl)-2-phenyl-3-(phenylselanyl)-1*H*-indole

- White solid, **m. p.:** 149 – 151 °C.
- Following the General Procedure: **21a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 80.4 mg, 0.167 mmol, **84% yield**.
- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 – 7.63 (m, 1H), 7.34 (t, *J* = 8.4 Hz, 3H), 7.27 – 7.17 (m, 9H), 7.16 – 7.05 (m, 5H), 1.31 (s, 9H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.57, 145.16, 138.56, 135.40, 134.37, 131.35, 131.17, 130.96, 129.11, 128.78, 128.14, 127.75, 127.55, 126.17, 125.56, 123.27, 121.53, 120.90, 111.15, 98.66, 34.77, 31.46.
- **HRMS** (ESI) calculated for C<sub>30</sub>H<sub>28</sub>NSe<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 482.1381, found: 482.1385.



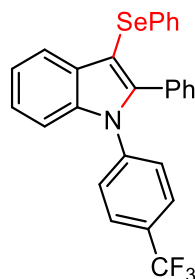
**22c:** 1-(4-methoxyphenyl)-2-phenyl-3-(phenylselanyl)-1*H*-indole

- White solid, **m. p.:** 126 – 127 °C.
- Following the General Procedure: **22a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 79.1 mg, 0.174 mmol, **87% yield**.
- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 (dd, *J* = 6.6, 2.3 Hz, 1H), 7.29 – 7.17 (m, 10H), 7.16 – 7.05 (m, 5H), 6.89 – 6.83 (m, 2H), 3.79 (s, 3H).



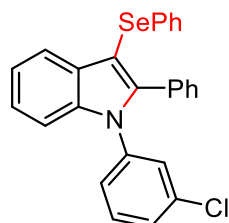
• <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.77, 145.34, 138.80, 134.36, 131.32, 131.17, 130.92, 130.86, 129.25, 129.11, 128.76, 128.17, 127.82, 125.56, 123.27, 121.51, 120.89, 114.50, 110.99, 98.41, 77.48, 77.16, 76.84, 55.54.

• HRMS (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NOSe<sup>+</sup> m/z [M+H]<sup>+</sup>: 456.0861, found: 456.0867.



**23c**: 2-phenyl-3-(phenylselanyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-indole

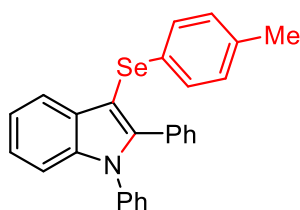
- White solid, **m. p.**: 154 – 156 °C.
- Following the General Procedure: **23a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 91.6 mg, 0.186 mmol, **93% yield**.
- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.31 – 7.18 (m, 9H), 7.18 – 7.10 (m, 3H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.69, 141.38, 138.04, 133.82, 131.20, 131.13, 130.84, 129.42 (q, *J* = 32.7 Hz), 129.20, 129.04, 128.60, 128.22, 128.14, 126.55 (q, *J* = 3.6 Hz), 125.83, 123.92 (q, *J* = 272.1 Hz), 123.91, 122.18, 121.32, 110.63, 100.58.
- <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.40.
- HRMS (ESI) calculated for C<sub>27</sub>H<sub>19</sub>F<sub>3</sub>NSe<sup>+</sup> m/z [M+H]<sup>+</sup>: 494.0629, found: 494.0623.



**24c**: 1-(3-chlorophenyl)-2-phenyl-3-(phenylselanyl)-1*H*-indole

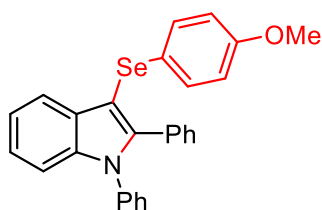
- Light yellow oil.

- Following the General Procedure: **24a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 75.2 mg, 0.164 mmol, **82% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.19 (m, 13H), 7.18 – 7.09 (m, 3H), 7.08 – 7.03 (m, 1H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 144.86, 139.38, 138.22, 134.86, 133.98, 131.12, 131.06, 130.90, 130.30, 129.17, 128.94, 128.51, 128.19, 128.04, 127.83, 126.44, 125.74, 123.74, 122.00, 121.18, 110.74, 99.91.
- **HRMS** (ESI) calculated for C<sub>26</sub>H<sub>19</sub>ClNSe<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 460.0366, found: 460.0369.



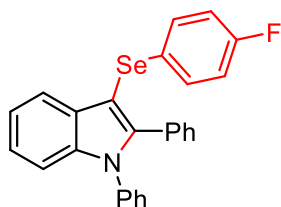
**25c**: 1,2-diphenyl-3-(p-tolylselanyl)-1*H*-indole

- Light yellow oil.
- Following the General Procedure: **13a** (0.2 mmol) and **2b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 71.5 mg, 0.157 mmol, **82% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.72 (dd, *J* = 6.4, 2.5 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.19 (d, *J* = 7.6 Hz, 9H), 7.18 – 7.14 (m, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 2.25 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 144.93, 138.42, 138.21, 135.45, 131.33, 131.20, 131.05, 130.29, 129.96, 129.33, 129.13, 128.20, 128.15, 127.82, 127.54, 123.36, 121.61, 121.03, 110.93, 99.42, 21.10.
- **HRMS** (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NSe<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 440.0912, found: 440.0913.



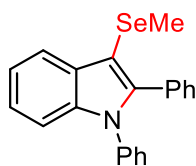
**26c:** 3-((4-methoxyphenyl)selanyl)-1,2-diphenyl-1*H*-indole

- Light yellow oil.
- Following the General Procedure: **13a** (0.2 mmol) and **3b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 81.8 mg, 0.180 mmol, **90% yield**.
- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 – 7.71 (m, 1H), 7.40 – 7.15 (m, 15H), 6.75 – 6.67 (m, 2H), 3.72 (s, 3H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.42, 144.63, 138.36, 138.21, 131.42, 131.28, 131.00, 129.31, 128.18, 128.13, 127.81, 127.51, 123.88, 123.32, 121.57, 120.97, 114.90, 110.92, 100.36, 55.37.
- HRMS (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NOSe<sup>+</sup> m/z [M+H]<sup>+</sup>: 456.0861, found: 456.0864.



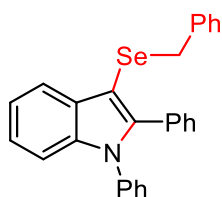
**27c:** 3-((4-fluorophenyl)selanyl)-1,2-diphenyl-1*H*-indole

- Light yellow oil.
- Following the General Procedure: **13a** (0.2 mmol) and **4b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 78.9 mg, 0.178 mmol, **89% yield**.
- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 7.1 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.28 – 7.17 (m, 11H), 6.90 – 6.80 (m, 2H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.66 (d, *J* = 244.8 Hz), 144.99, 138.41, 138.09, 131.22, 131.17, 131.00 (d, *J* = 7.7 Hz), 130.80, 129.36, 128.37, 128.32, 128.13, 127.88, 127.64, 123.48, 121.72, 120.81, 116.21 (d, *J* = 21.7 Hz), 111.05, 99.52.
- <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -117.28.
- HRMS (ESI) calculated for C<sub>26</sub>H<sub>19</sub>FNSe<sup>+</sup> m/z [M+H]<sup>+</sup>: 444.0661, found: 444.0660.



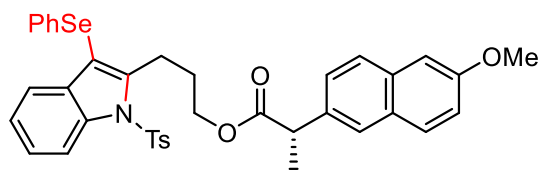
**28c:** 3-(methylselanyl)-1,2-diphenyl-1*H*-indole

- White solid, **m. p.:** 153 – 155 °C.
- Following the General Procedure: **13a** (0.2 mmol) and **5b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 61.3 mg, 0.169 mmol, **85% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.31 – 7.20 (m, 9H), 7.17 (dd, *J* = 7.2, 1.8 Hz, 2H), 2.10 (s, 3H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.41, 138.25, 138.20, 131.69, 131.26, 130.78, 129.25, 128.09, 128.04, 127.82, 127.38, 123.17, 121.25, 120.68, 110.94, 100.88, 9.01.
- **HRMS** (ESI) calculated for C<sub>21</sub>H<sub>18</sub>NSe<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 364.0599, found: 364.0599.



**29c:** 3-(benzylselanyl)-1,2-diphenyl-1*H*-indole

- Light yellow oil.
- Following the General Procedure: **13a** (0.2 mmol) and **6b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 69.6 mg, 0.159 mmol, **79% yield**.
- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.82 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.36 – 7.23 (m, 6H), 7.21 – 7.09 (m, 8H), 6.95 – 6.87 (m, 4H), 3.86 (s, 2H).
- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 144.90, 139.37, 138.22, 138.19, 131.30, 131.24, 131.10, 129.22, 128.90, 128.24, 128.09, 127.85, 127.53, 127.38, 126.57, 123.13, 121.35, 120.71, 110.91, 99.88, 31.75.
- **HRMS** (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NSe<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 440.0912, found: 440.0915.



**30c:** 3-(3-(phenylselanyl)-1-tosyl-1*H*-indol-2-yl)propyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate <sup>[9]</sup>

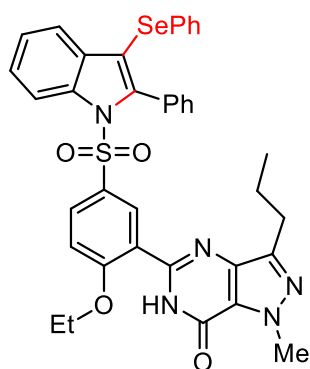
- Light yellow oil.

- Following the General Procedure: **30a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 48 h.

- 126.9 mg, 0.182 mmol, **91% yield**.

- **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.62 (m, 3H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.34 – 7.28 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.05 (m, 5H), 7.05 – 6.98 (m, 2H), 6.93 (d, *J* = 7.3 Hz, 2H), 4.16 (dt, *J* = 11.3, 6.0 Hz, 1H), 4.08 (dt, *J* = 11.3, 6.0 Hz, 1H), 3.90 (s, 3H), 3.84 (q, *J* = 7.1 Hz, 1H), 3.28 (ddd, *J* = 8.8, 6.6, 2.2 Hz, 2H), 2.32 (s, 3H), 2.00 (hept, *J* = 6.5 Hz, 2H), 1.57 (d, *J* = 7.3 Hz, 3H).

- **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  174.80, 157.69, 145.61, 145.12, 137.19, 135.95, 135.71, 133.80, 131.94, 131.71, 129.99, 129.49, 129.22, 129.08, 129.03, 127.26, 126.57, 126.41, 126.19, 126.17, 125.26, 124.43, 120.85, 118.98, 115.39, 108.96, 105.71, 64.32, 55.43, 45.66, 30.10, 25.61, 21.69, 18.68.



**31c:** 5-(2-ethoxy-5-((2-phenyl-3-(phenylselanyl)-1*H*-indol-1-yl)sulfonyl)phenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-*d*]pyrimidin-7-one <sup>[9]</sup>

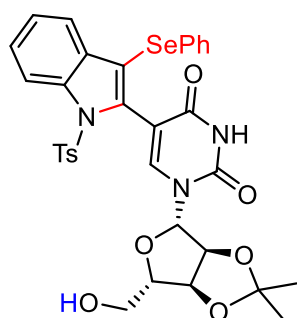
- White solid, **m. p.:** 173 – 175 °C.

• Following the General Procedure: **31a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 36 h; additional 2 mL DCM was added as co-solvent.

• 140.6 mg, 0.195 mmol, **97% yield**.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.71 (s, 1H), 8.56 (d, *J* = 2.5 Hz, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 7.54 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.48 – 7.36 (m, 7H), 7.30 – 7.22 (m, 1H), 7.06 – 6.93 (m, 5H), 6.91 (d, *J* = 8.9 Hz, 1H), 4.32 – 4.23 (m, 5H), 2.90 (t, *J* = 7.6 Hz, 2H), 1.83 (h, *J* = 7.4 Hz, 2H), 1.59 (t, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 7.3 Hz, 3H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 160.00, 153.61, 147.13, 146.02, 144.75, 138.32, 137.47, 132.23, 131.69, 131.61, 131.22, 131.12, 131.06, 130.52, 129.69, 129.34, 129.09, 127.40, 126.28, 125.93, 124.91, 124.54, 121.50, 121.03, 116.19, 112.81, 111.09, 66.33, 38.37, 27.63, 22.43, 14.59, 14.18.



**32c**: 1-((3a*S*,4*S*,6*S*,6a*S*)-6-(hydroxymethyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-5-(3-(phenylselanyl)-1-tosyl-1*H*-indol-2-yl)pyrimidine-2,4(1*H*,3*H*)-dione (**dr** = **1:1**)

• White solid, **m. p.**: 91 – 93 °C.

• Following the General Procedure: **32a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 30 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h; additional 2 mL DCM was added as co-solvent.

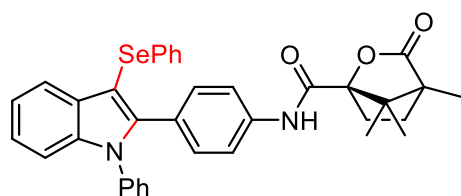
• 43.4 mg, 0.061 mmol, **31% yield**.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.32 (s, 0.5H), 9.25 (s, 0.5H), 8.08 (d, *J* = 8.4 Hz, 0.5H), 8.03 (d, *J* = 8.4 Hz, 0.5H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.29 (m, 3H), 7.29 – 7.15 (m, 4H), 7.15 – 7.07 (m, 4H), 5.74 (d, *J* = 2.9 Hz, 0.5H), 5.61 (d, *J* = 2.7 Hz, 0.5H), 5.04 (dd, *J* = 6.2, 2.8 Hz, 0.5H), 4.90 (dd, *J* = 6.3, 2.7 Hz, 0.5H), 4.71 (qd, *J* = 6.5, 2.9 Hz, 1H), 4.35 (d, *J* = 3.1 Hz, 0.5H), 4.24 (d, *J* =

3.2 Hz, 0.5H), 3.87 – 3.63 (m, 2H), 2.50 – 2.15 (m, 4H), 1.58 (s, 1.5H), 1.57 (s, 1.5H), 1.38 (s, 1.5H), 1.34 (s, 1.5H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 161.87, 161.60, 150.01, 149.97, 145.55, 143.67, 142.91, 137.08, 136.96, 135.37, 135.06, 134.89, 134.49, 131.89, 131.35, 131.30, 130.47, 129.98, 129.62, 129.53, 129.40, 127.39, 127.31, 126.79, 126.58, 126.22, 126.06, 124.42, 121.52, 115.21, 114.56, 114.15, 113.16, 112.30, 107.36, 106.85, 95.65, 93.97, 87.35, 86.61, 84.76, 84.19, 80.77, 80.39, 62.74, 62.58, 27.34, 25.42, 25.36, 21.73.

• **HRMS** (ESI) calculated for C<sub>33</sub>H<sub>32</sub>N<sub>3</sub>O<sub>8</sub>SSe<sup>+</sup> m/z [M+H]<sup>+</sup>: 710.1070, found: 710.1078.



**33c:** (1*S*)-4,7,7-trimethyl-3-oxo-*N*-(4-(1-phenyl-3-(phenylselanyl)-1*H*-indol-2-yl)phenyl)-2-oxabicyclo[2.2.1]heptane-1-carboxamide (**dr** = **2:1**)

• White solid, **m. p.:** 189 – 192 °C.

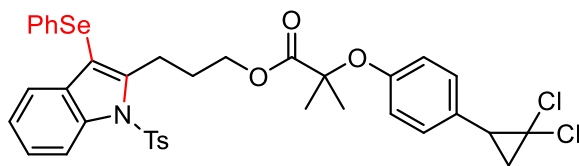
• Following the General Procedure: **33a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 30 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h; additional 2 mL DCM was added as co-solvent.

• 95.1 mg, 0.153 mmol, **77% yield**.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 1H), 7.71 (t, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 3H), 7.36 – 7.29 (m, 2H), 7.28 – 7.20 (m, 7H), 7.19 – 7.06 (m, 3H), 2.65 – 2.50 (m, 1H), 2.03 – 1.91 (m, 2H), 1.78 – 1.67 (m, 1H), 1.14 (s, 3H), 1.13 (s, 3H), 0.96 (s, 3H).

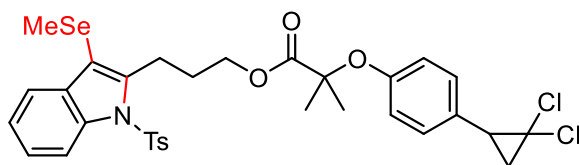
• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 177.99, 165.41, 165.37, 144.45, 144.35, 138.50, 138.10, 138.01, 136.79, 136.73, 134.23, 133.97, 133.87, 132.91, 131.94, 131.91, 131.31, 131.05, 130.85, 129.54, 129.48, 129.45, 129.19, 128.76, 128.18, 127.81, 127.74, 127.40, 125.69, 123.60, 123.51, 121.80, 121.73, 120.98, 120.85, 119.09, 119.05, 111.05, 110.97, 99.18, 98.76, 92.47, 55.63, 54.53, 30.67, 29.20, 16.88, 16.73, 9.85.

• **HRMS** (ESI) calculated for C<sub>36</sub>H<sub>33</sub>N<sub>2</sub>O<sub>3</sub>Se<sup>+</sup> m/z [M+H]<sup>+</sup>: 621.1651, found: 621.1661.



**34c:** 3-(3-(phenylselanyl)-1-tosyl-1*H*-indol-2-yl)propyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate

- Light yellow viscous oil.
- Following the General Procedure: **34a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 36 h.
- 125.3 mg, 0.166 mmol, **83% yield**.
- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.26 – 7.14 (m, 3H), 7.11 – 7.02 (m, 5H), 7.01 – 6.95 (m, 2H), 6.85 – 6.78 (m, 2H), 4.22 (t, *J* = 6.2 Hz, 2H), 3.35 – 3.22 (m, 2H), 2.78 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.34 (s, 3H), 2.02 (dq, *J* = 13.1, 6.2 Hz, 2H), 1.89 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.73 (t, *J* = 7.9 Hz, 1H), 1.59 (s, 6H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.18, 155.07, 145.37, 145.21, 137.15, 135.71, 131.89, 131.68, 130.03, 129.73, 129.27, 128.97, 128.26, 126.40, 126.24, 125.31, 124.46, 120.85, 119.13, 115.35, 108.91, 79.42, 64.94, 61.00, 34.92, 30.04, 25.90, 25.59, 25.55, 21.70.
- HRMS (ESI) calculated for C<sub>37</sub>H<sub>35</sub>Cl<sub>2</sub>NNaO<sub>5</sub>SSe<sup>+</sup> *m/z* [M+Na]<sup>+</sup>: 778.0670, found: 778.0681.



**35c:** 3-(3-(methylselanyl)-1-tosyl-1*H*-indol-2-yl)propyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate

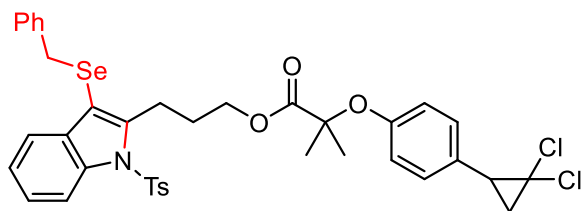
- Light yellow viscous oil.
- Following the General Procedure: **34a** (0.2 mmol) and **5b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.
- 124.2 mg, 0.179 mmol, **90% yield**.



• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.21 – 8.11 (m, 1H), 7.62 – 7.53 (m, 3H), 7.34 – 7.26 (m, 2H), 7.18 – 7.07 (m, 4H), 6.89 – 6.81 (m, 2H), 4.28 (t, *J* = 6.3 Hz, 2H), 3.36 – 3.25 (m, 2H), 2.81 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.31 (s, 3H), 2.13 – 2.02 (m, 5H), 1.91 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.76 (t, *J* = 7.9 Hz, 1H), 1.64 (s, 6H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 174.28, 155.05, 145.06, 143.47, 136.86, 135.78, 131.80, 129.99, 129.73, 128.26, 126.37, 125.01, 124.11, 120.53, 119.08, 115.22, 110.05, 79.41, 65.04, 60.99, 34.90, 30.15, 25.89, 25.59, 25.55, 25.38, 21.66, 8.51.

• **HRMS** (ESI) calculated for C<sub>32</sub>H<sub>33</sub>Cl<sub>2</sub>NNaO<sub>5</sub>SSe<sup>+</sup> *m/z* [M+Na]<sup>+</sup>: 716.0514, found: 716.0522.



**36c**: 3-(3-(benzylselanyl)-1-tosyl-1*H*-indol-2-yl)propyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate

• Light yellow viscous oil.

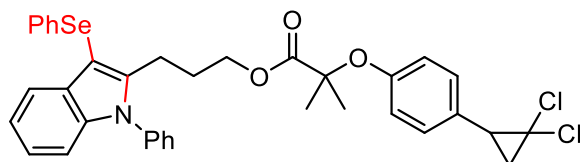
• Following the General Procedure: **34a** (0.2 mmol) and **6b** (0.11 mmol) as substrates, with 10 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.

• 141.9 mg, 0.184 mmol, **92% yield**.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.22 (m, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.01 (m, 3H), 6.97 (t, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 7.0 Hz, 2H), 4.13 (t, *J* = 6.3 Hz, 2H), 3.76 (s, 2H), 3.00 – 2.87 (m, 2H), 2.80 (dd, *J* = 10.7, 8.4 Hz, 1H), 2.33 (s, 3H), 1.90 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.80 – 1.67 (m, 3H), 1.61 (s, 6H).

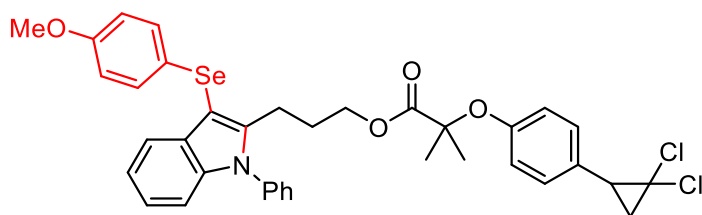
• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 174.17, 155.05, 145.09, 145.06, 139.07, 136.70, 135.92, 132.02, 129.98, 129.72, 128.57, 128.29, 128.26, 126.75, 126.45, 124.97, 124.10, 120.50, 119.13, 115.07, 108.43, 79.38, 65.07, 61.00, 34.90, 31.27, 29.85, 25.89, 25.59, 25.55, 24.95, 21.68.

• **HRMS** (ESI) calculated for C<sub>38</sub>H<sub>37</sub>Cl<sub>2</sub>NNaO<sub>5</sub>SSe<sup>+</sup> *m/z* [M+Na]<sup>+</sup>: 792.0827, found: 792.0833.



**37c:** 3-(1-phenyl-3-(phenylselanyl)-1*H*-indol-2-yl)propyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate

- Light yellow viscous oil.
- Following the General Procedure: **37a** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 48 h.
- 120.0 mg, 0.177 mmol, **89% yield**.
- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.60 (m, 1H), 7.58 – 7.46 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.27 – 7.19 (m, 2H), 7.18 – 7.08 (m, 5H), 7.07 – 7.00 (m, 3H), 6.76 – 6.66 (m, 2H), 3.96 (t, *J* = 6.2 Hz, 2H), 2.87 (dd, *J* = 9.2, 6.6 Hz, 2H), 2.78 (dd, *J* = 10.7, 8.4 Hz, 1H), 1.90 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.73 (t, *J* = 7.9 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.59 – 1.52 (m, 1H), 1.46 (s, 6H).
- <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.06, 154.99, 145.18, 138.75, 137.61, 133.98, 130.54, 129.93, 129.70, 129.16, 128.73, 128.57, 128.31, 128.21, 125.66, 122.66, 121.29, 120.04, 118.84, 110.55, 97.61, 79.22, 64.67, 60.99, 34.89, 28.79, 25.90, 25.45, 23.06.
- HRMS (ESI) calculated for C<sub>36</sub>H<sub>34</sub>Cl<sub>2</sub>NO<sub>3</sub>Se<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 678.1075, found: 678.1081.



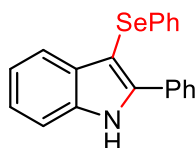
**38c:** 3-(3-((4-methoxyphenyl)selanyl)-1-phenyl-1*H*-indol-2-yl)propyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate

- Light yellow viscous oil.
- Following the General Procedure: **37a** (0.2 mmol) and **3b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 36 h.
- 96.0 mg, 0.136 mmol, **68% yield**.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 (dd, *J* = 6.7, 2.3 Hz, 1H), 7.57 – 7.46 (m, 3H), 7.36 – 7.32 (m, 2H), 7.25 – 7.21 (m, 2H), 7.18 – 7.13 (m, 2H), 7.07 – 7.01 (m, 3H), 6.73 (dd, *J* = 8.7, 3.3 Hz, 4H), 3.97 (t, *J* = 6.3 Hz, 2H), 3.73 (s, 3H), 2.96 – 2.83 (m, 2H), 2.79 (dd, *J* = 10.7, 8.4 Hz, 1H), 1.91 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.74 (t, *J* = 7.9 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.48 (s, 6H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 174.11, 158.43, 155.02, 144.70, 138.68, 137.68, 131.11, 130.56, 129.91, 129.73, 128.68, 128.34, 128.26, 123.69, 122.57, 121.20, 120.05, 118.89, 114.97, 110.51, 98.89, 79.26, 64.75, 61.00, 55.40, 34.92, 28.82, 25.92, 25.48, 23.06.

• **HRMS** (ESI) calculated for C<sub>37</sub>H<sub>36</sub>Cl<sub>2</sub>NO<sub>4</sub>Se<sup>+</sup> *m/z* [M+H]<sup>+</sup>: 708.1181, found: 708.1189.



**39c**: 2-phenyl-3-(phenylselanyl)-1*H*-indole <sup>[10]</sup>

• Light brown oil.

• Following the General Procedure: **39a'** (0.2 mmol) and **1b** (0.11 mmol) as substrates, with 5 mol% FeBr<sub>3</sub> under the irradiation of a 12 W blue LED for 24 h.

• 66.9 mg, 0.192 mmol, **96% yield**.

• **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.46 (s, 1H), 7.71 – 7.61 (m, 3H), 7.42 – 7.31 (m, 4H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.13 (m, 3H), 7.11 – 7.02 (m, 3H).

• **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 142.21, 136.24, 134.16, 132.15, 132.08, 129.17, 128.72, 128.62, 128.35, 125.54, 123.37, 121.22, 121.00, 111.15, 95.85.

### 3. Mechanistic studies

#### 3.1 Control experiments

• **Procedure for control reactions in dark:** A 10-mL glass vial with a magnetic stir bar wrapped with tin foil was quickly charged with specific reaction components and closed with a rubber septum. Another piece of tin foil was then covered to make sure the system was completely away from light. The resulting system was stirred under ambient conditions (or in 45 °C/80°C oil bath) for indicated time with 500 rpm stirring.



**Fig S4** Setup for control reactions in dark

• **Procedure for control reactions under N<sub>2</sub> atmosphere:** A 10-mL reaction tube with a magnetic stir bar was charged with specific reaction components and closed with a rubber septum. The system atmosphere was then replaced using a combination of pump and N<sub>2</sub> balloon (**Fig S5a**). After being bubbled with N<sub>2</sub> for 10 min (**Fig S5b**), 2 mL EtOAc was transferred to the reaction system via syringe. The resulting system was then sealed, equipped with a N<sub>2</sub> balloon, and subjected to irradiation with a 12 W blue LED under ambient conditions with 500 rpm stirring (**Fig S5c and S5d**).

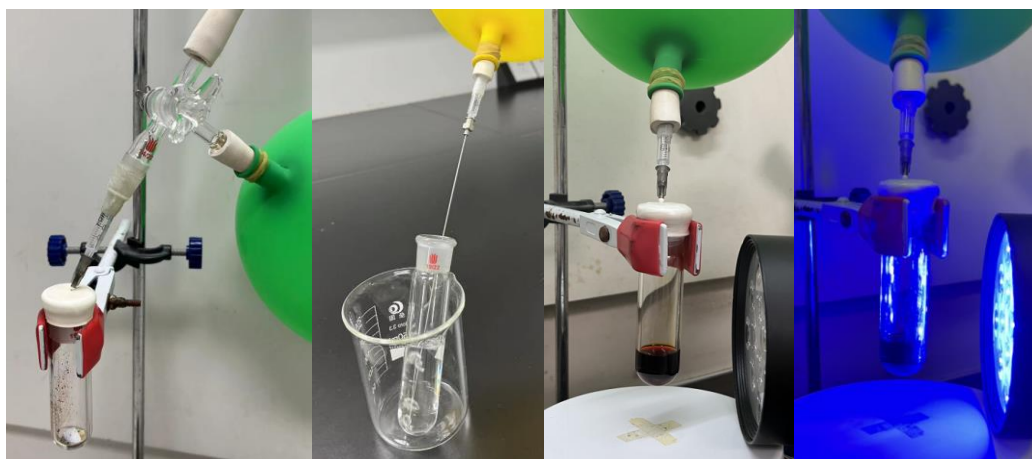
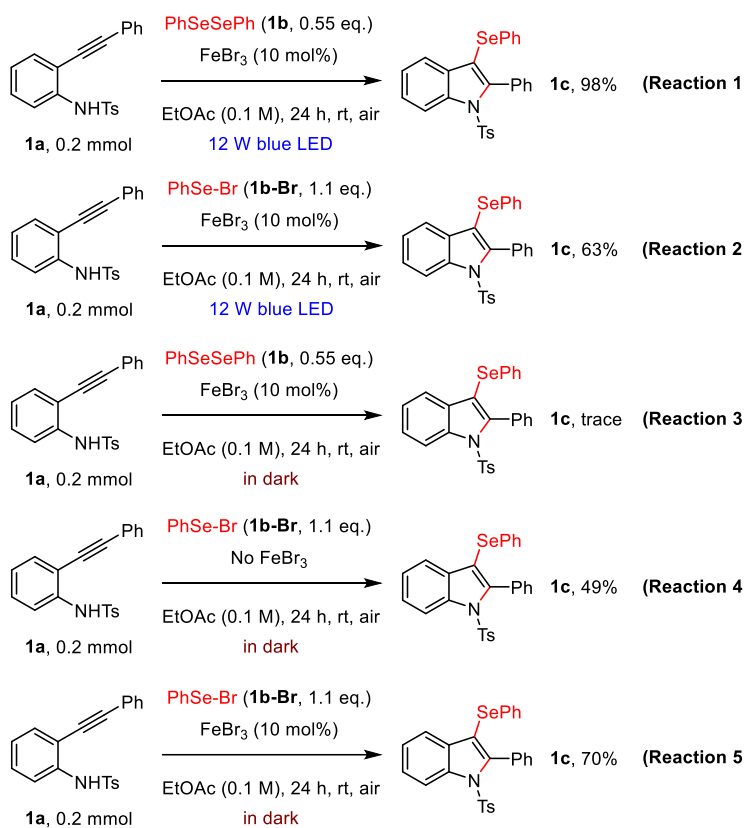


Fig S5 Setup for control reactions under N<sub>2</sub> atmosphere

### 3.1.1 Control experiments with 1a

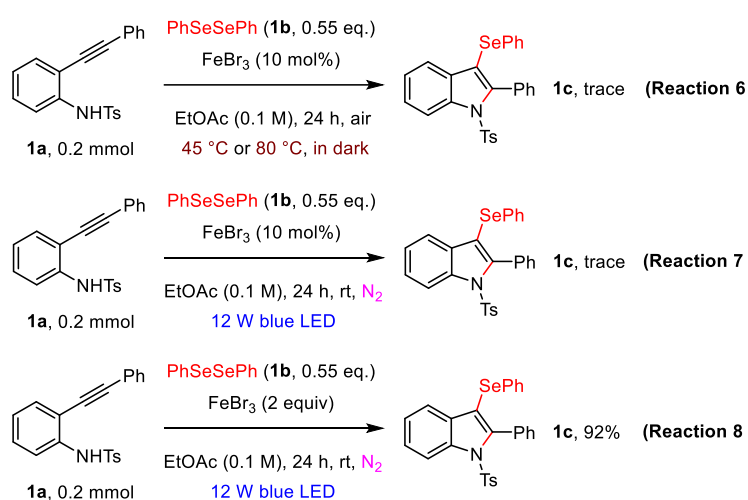


- **Reaction 1:** The result was taken from Table 1 (entry 10) in the main text.
- **Reaction 2:** Incomplete conversion of **1a** after 24 h irradiation, along with some visible side products observed upon TLC analysis. The isolated yield of **1c** was **63%**.
- **Reaction 3:** Negligible conversion of **1a** after stirring for 24 h in dark.

• **Reaction 4:** Clean but moderate conversion of **1a** after stirring for 24 h in dark. The isolated yield of **1c** was **49%**.

• **Reaction 5:** Nearly complete conversion of **1a** after stirring for 24 h in dark, along with some visible side products observed upon TLC analysis. The isolated yield of **1c** was **70%**.

These results indicate that: 1) *in-situ* generated RSe-Br may act as the key reaction intermediate in the visible-light induced, Fe-catalyzed selenocyclization; 2) FeBr<sub>3</sub> can accelerate the conversion of 2-ethynylanilines with RSe-Br in dark.



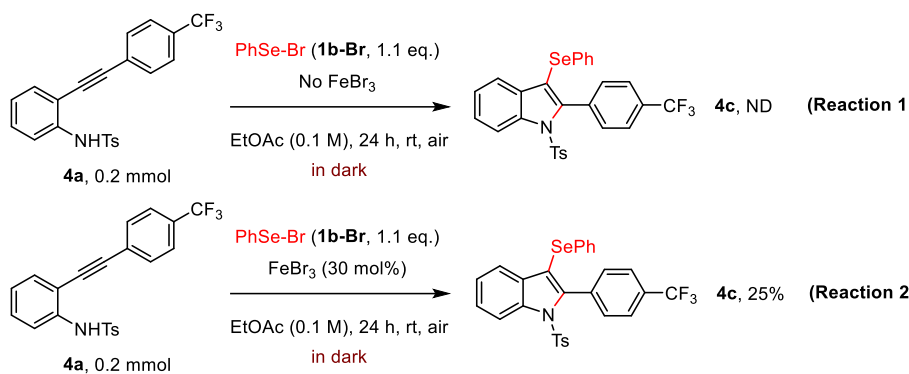
• **Reaction 6:** Negligible conversion of **1a** after stirring for 24 h in dark.

• **Reaction 7:** Negligible conversion of **1a** after stirring for 24 h under irradiation.

• **Reaction 8:** Full conversion of **1a** after stirring for 24 h under irradiation, and the isolated yield of **1c** was 92%.

These results indicate that: 1) visible-light irradiation plays an indispensable role in the successful transformation, heating alone cannot trigger such a reaction; 2) air plays a crucial role in this catalytic transformation, possibly as an oxidant; 3) Under N<sub>2</sub> atmosphere, the use of stoichiometric FeBr<sub>3</sub> also leads to clean conversion of **1a**, which is in accordance with the mechanistic proposal that FeBr<sub>3</sub> undergoes a photo-induced LMCT process to generate bromine radical (but herein it serves as a sacrificial reagent in the absence of air for its regeneration).

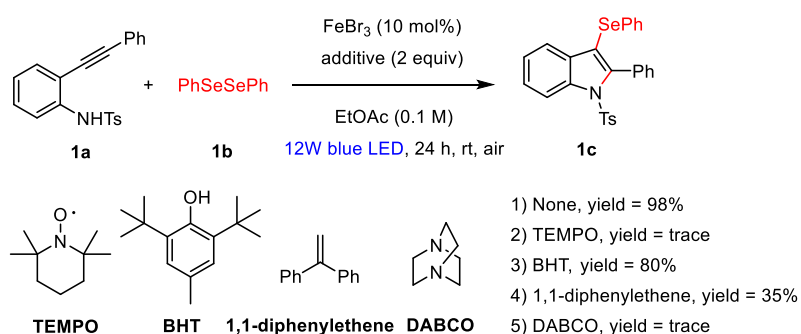
### 3.1.2 Control experiments with 4a



- **Reaction 1:** No conversion of **4a** was observed upon TLC analysis after stirring for 24 h in dark.
- **Reaction 2:** Clean but low conversion of **4a** after stirring for 24 h in dark. The isolated yield of **4c** was **25%**.

These results indicate that:  $\text{FeBr}_3$  can indeed enable the reaction of inert 2-ethynylaniline **4a** (possibly due to the deactivation effect by  $-\text{Ts}$  and  $-\text{CF}_3$  that makes the C-C triple bond less electron-rich) with **1b-Br** in dark.

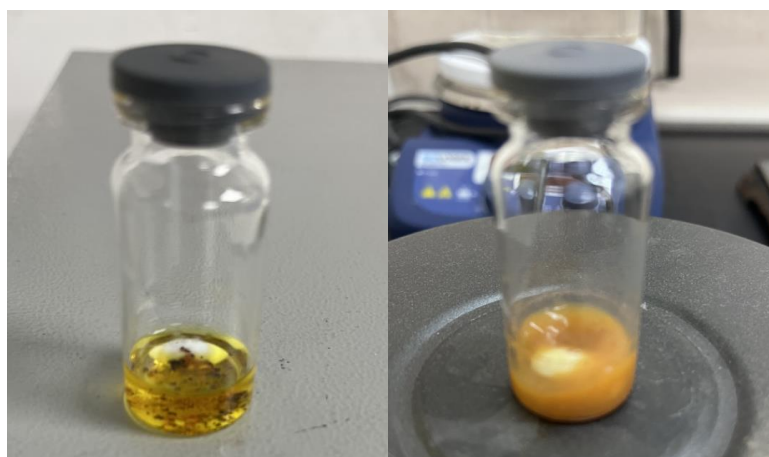
### 3.1.3 Quenching experiments



In the quenching experiments, additional scavengers were added in 2 equiv to the model reaction systems under standard conditions. All three radical scavengers (TEMPO, BHT and 1,1-diphenylethene) showed negative influence on the isolated yield of **1c**, but no corresponding adducts were detected or isolated. The reactions 2-4 were monitored by TLC (only reaction 4 showed a complex system, while the other two were clean with only spots of reaction components and product), and the resulting systems were subjected to GC-MS and HRMS analysis, but unfortunately, no sign of anticipated adducts (either Se-containing or Br-containing) was observed.

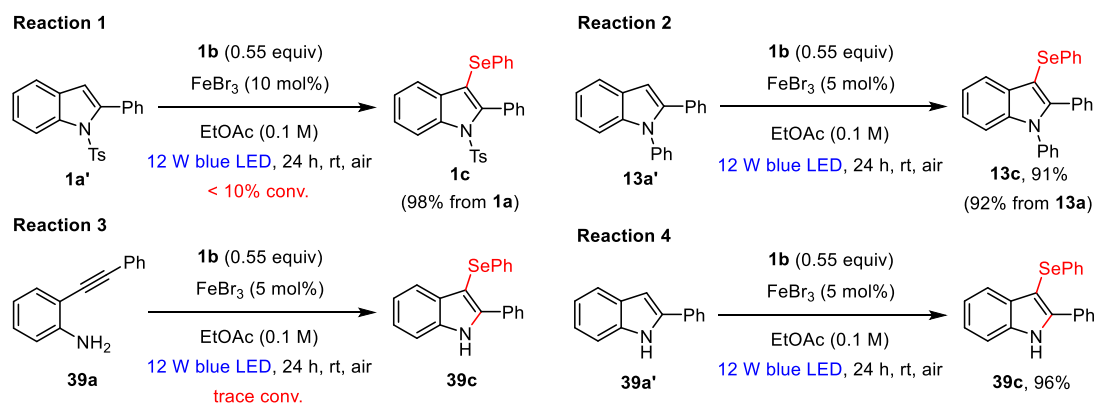
These results indicate that there might be radical intermediates involved in the visible-light induced, Fe-catalyzed selenocyclization, but the decisive evidence is still lacking.

Another experiment was conducted with DABCO as a possible singlet oxygen quencher, which also provided negligible conversion of **1a** (reaction 5). However, upon mixing DABCO with FeBr<sub>3</sub> in this system, the solid FeBr<sub>3</sub> did not dissolve, and the system appeared to be a heterogeneous one upon stirring (**the reaction systems without this additive is typically a transparent red solution**). Such a result is possibly due to the instant Lewis base-acid interaction between DABCO and FeBr<sub>3</sub> that may disable catalyst FeBr<sub>3</sub>. Nevertheless, the irradiation was still carried out and kept for 24 h, which resulted in negligible conversion of **1a**.



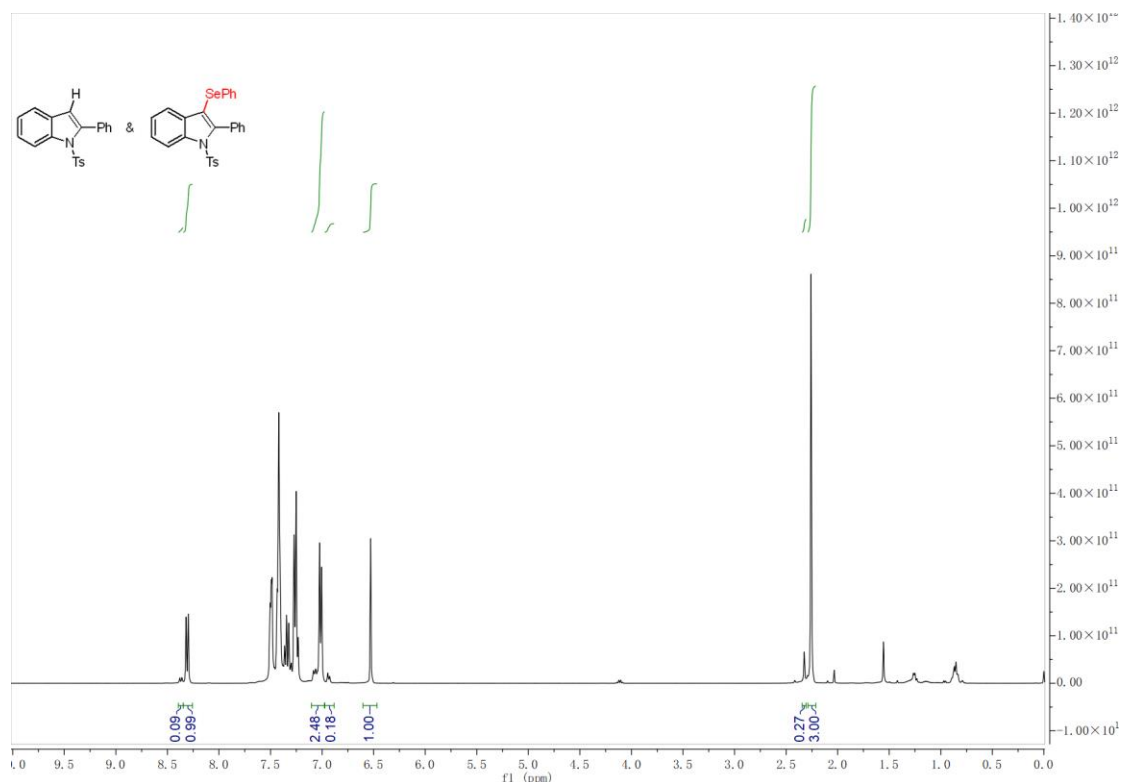
On the basis of such a result, while the quenching of singlet oxygen by DABCO is possible, the deactivation of catalyst FeBr<sub>3</sub> is more likely the reason.

### 3.1.4 Comparison experiments



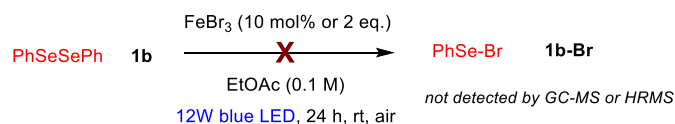
• **Reaction 1**: The reaction between indole **1a'** and **1b** ended in low conversion after irradiation for 24 h. Since **1a'** and **1c** are inseparable via column chromatography, the <sup>1</sup>H NMR of their mixture was recorded, the ratio of **1a'** and **1c** is 1:0.09 (< 10% conversion of **1a'**):





- **Reaction 2:** The reaction between indole **13a'** and **1b** proceeded smoothly under the standard conditions with 5 mol% FeBr<sub>3</sub>. The isolated yield of **13c** was **91%**.
- **Reaction 3:** The reaction between unprotected 2-ethynylaniline **39a** and **1b** only presented negligible conversion under the standard conditions with 5 mol% FeBr<sub>3</sub>.
- **Reaction 4:** The reaction between indole **39a'** and **1b** proceeded smoothly under the standard conditions with 5 mol% FeBr<sub>3</sub>. The isolated yield of **39c** was **96%**.

### 3.1.5 Attempts to detect the putative selenyl bromide formed *in situ*

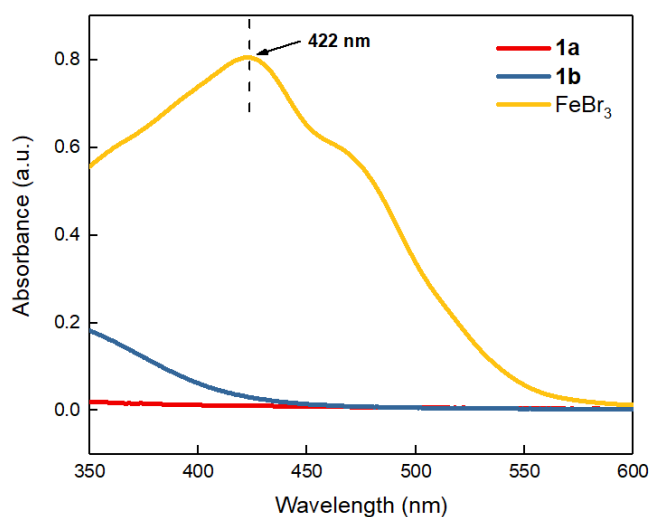


- The model reactions were conducted in the absence of substrate **1a**, with either catalytic or stoichiometric FeBr<sub>3</sub>. Unfortunately, the corresponding selenyl bromide (**1b-Br**) was not detected in both reaction systems.

## 3.2 UV-vis spectroscopic studies

• For the UV-vis absorption spectra collection, EtOAc served as the solvent and was used for blank test. The single-component samples of **1a**, **1b** and FeBr<sub>3</sub> were prepared in 1.8×10<sup>-4</sup> mol/L concentration.

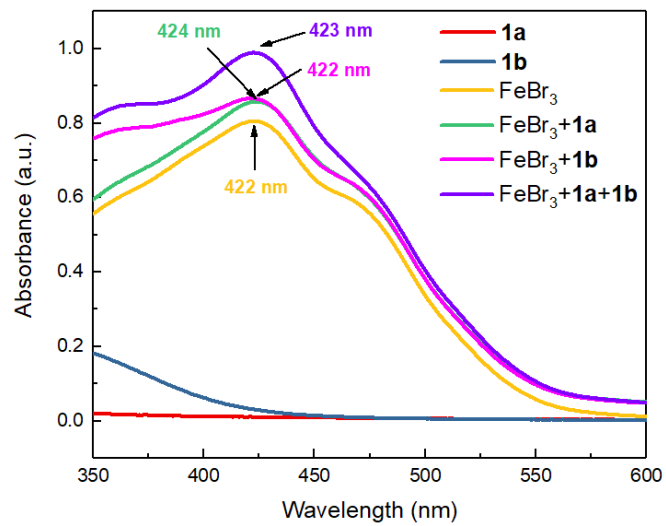
**As shown in Fig S6:** (1) **1a** has nearly no absorption within the tested region (350 – 600 nm); (2) **1b** shows absorption peak majorly in the purple light to UV light region (< 400 nm); (3) as for FeBr<sub>3</sub>, strong absorption is observed throughout the 350 – 500 nm region, and the λ<sub>max</sub> appeared at 422 nm.



**Fig S6** UV-vis spectra of three single-component samples

• The double- as well as triple-component samples were also collected. For these samples, the concentration of each component in the solution was 1.8×10<sup>-4</sup> mol/L (in 1:1 or 1:1:1 molar ratio).

**As shown in Fig S7:** (1) Compared with single FeBr<sub>3</sub>, all the double- and triple-component samples showed somewhat enhanced absorbance; (2) the λ<sub>max</sub> showed negligible shift when FeBr<sub>3</sub> was mixed with other components; (3) no new peak was observed when FeBr<sub>3</sub> was mixed with other components.



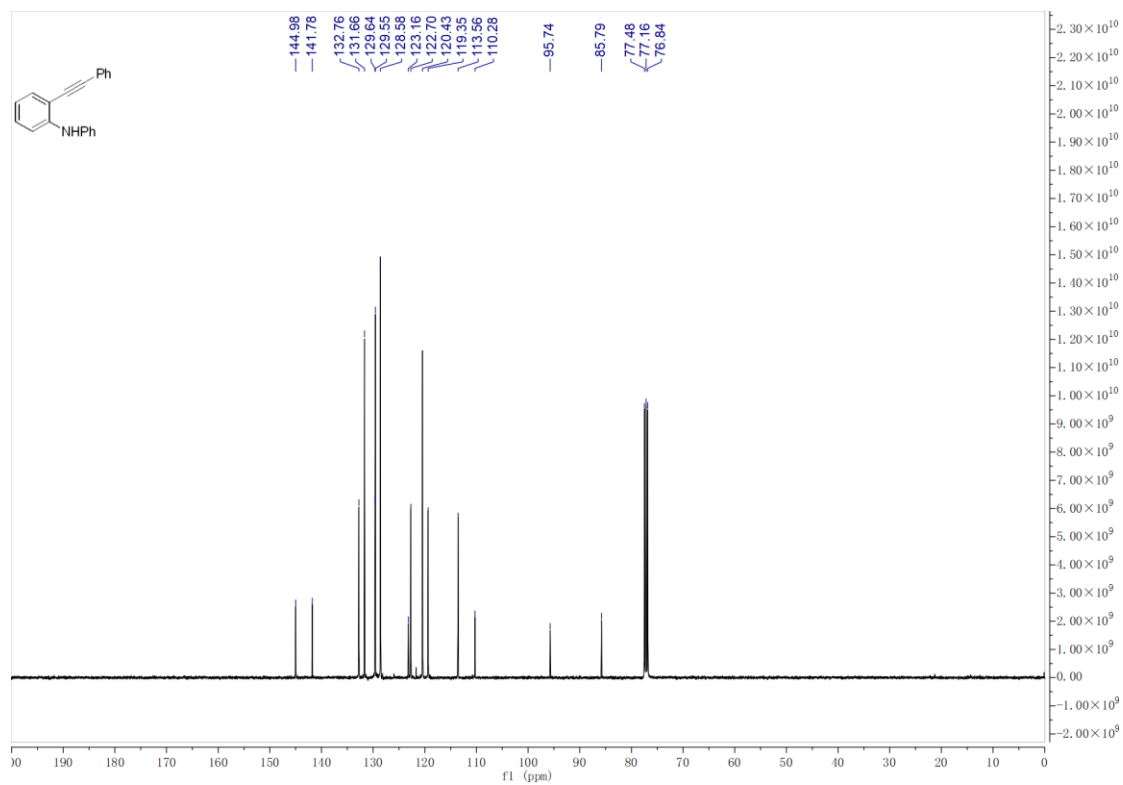
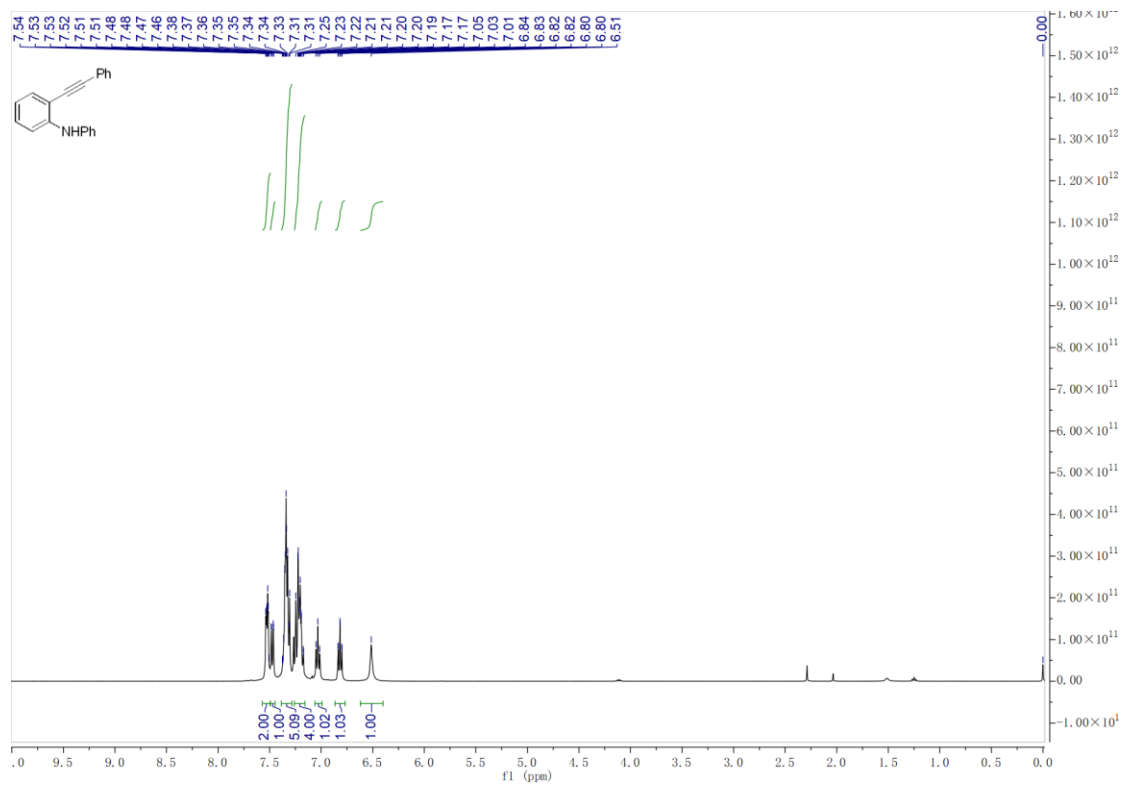
**Fig S7** UV-vis spectra of all samples

## 4. References

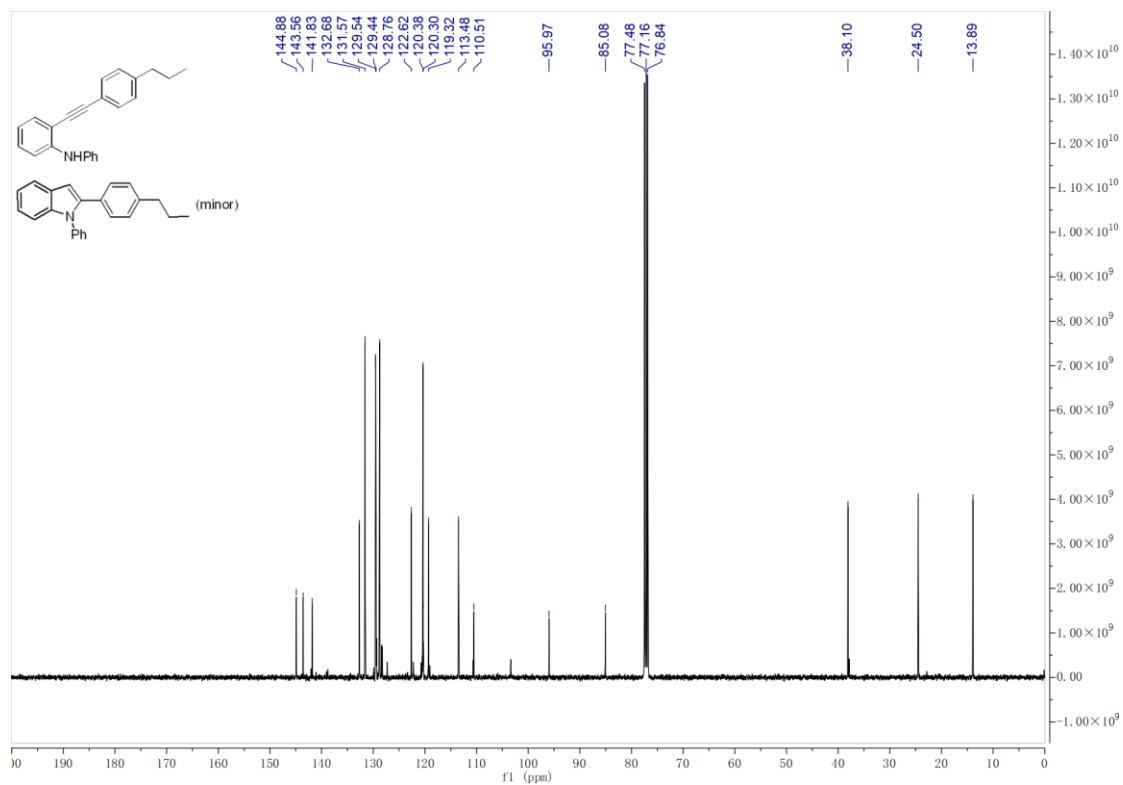
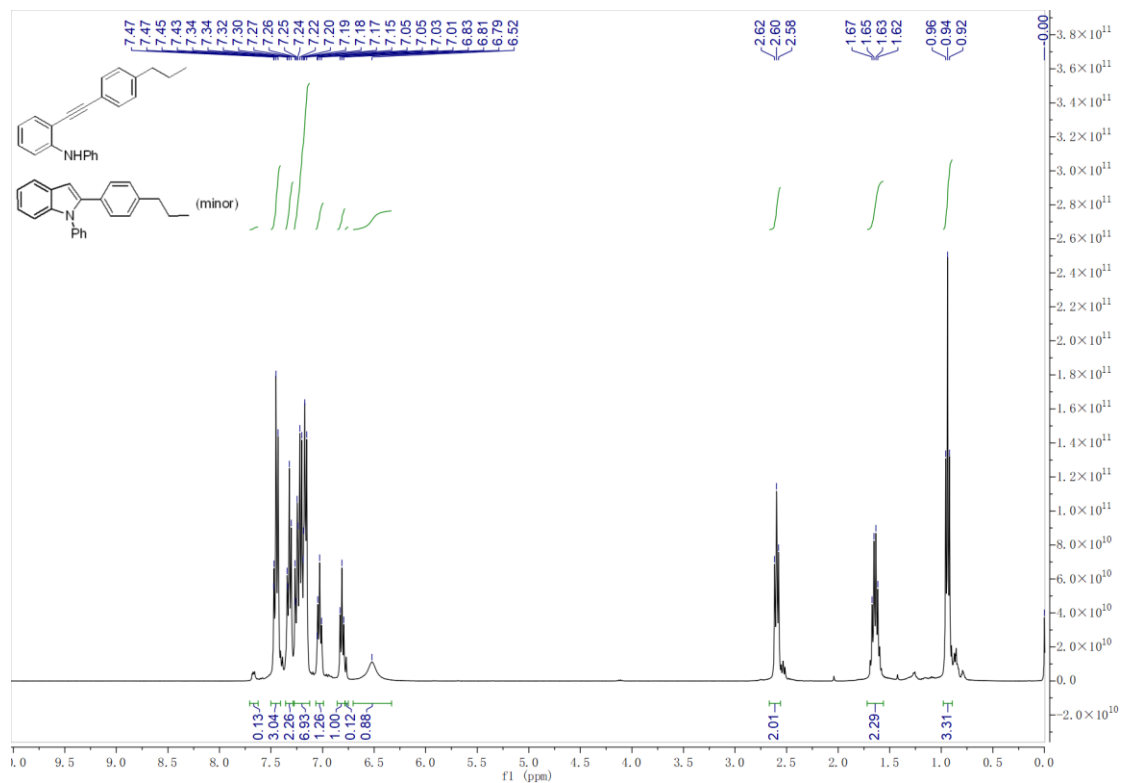
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## 5. Copies of NMR spectra

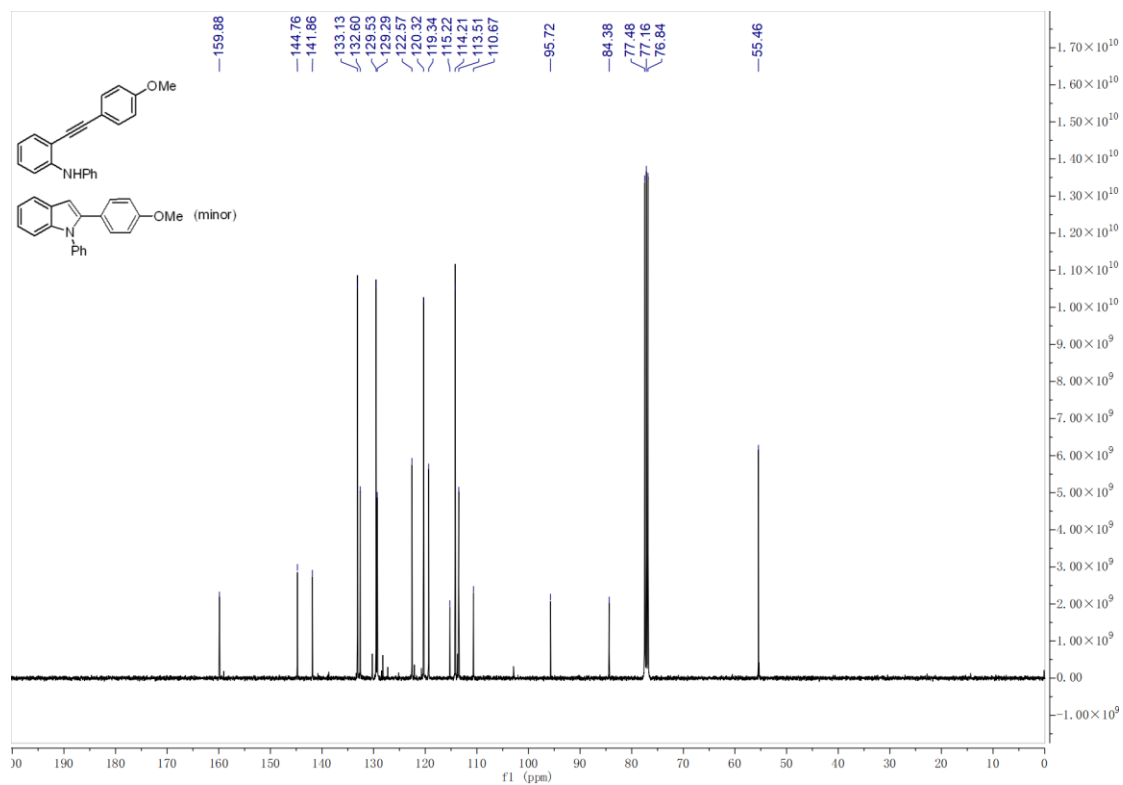
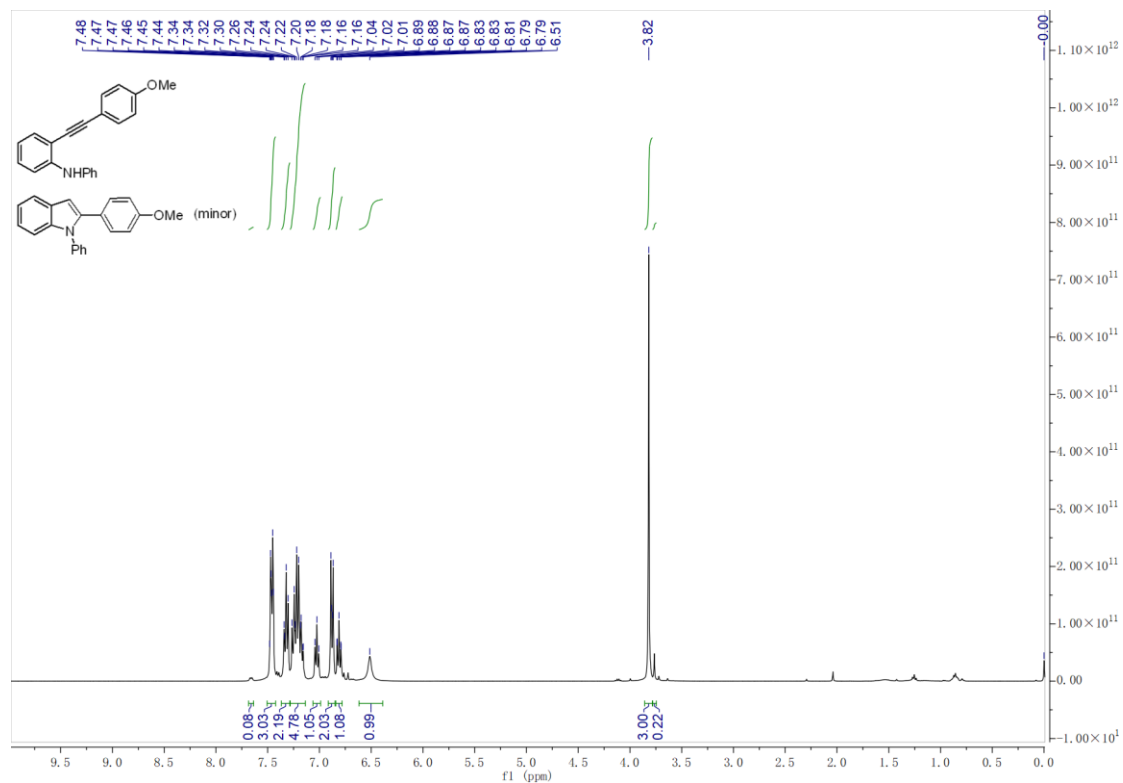
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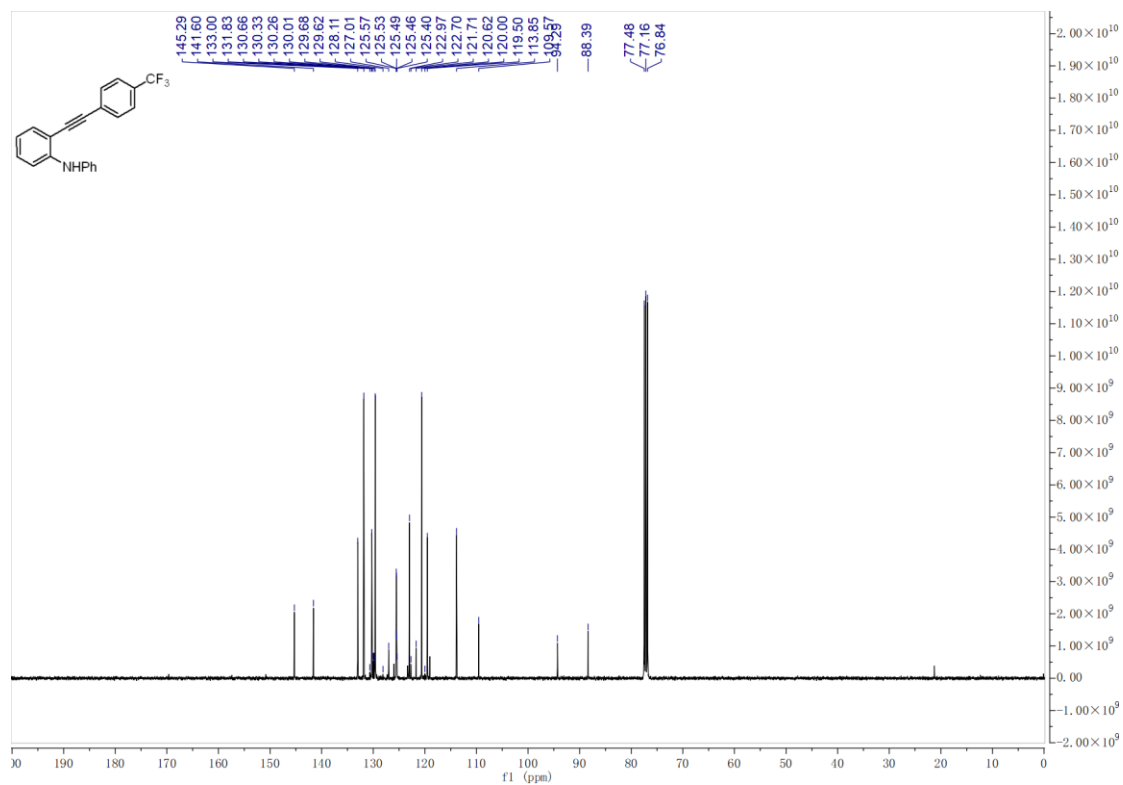
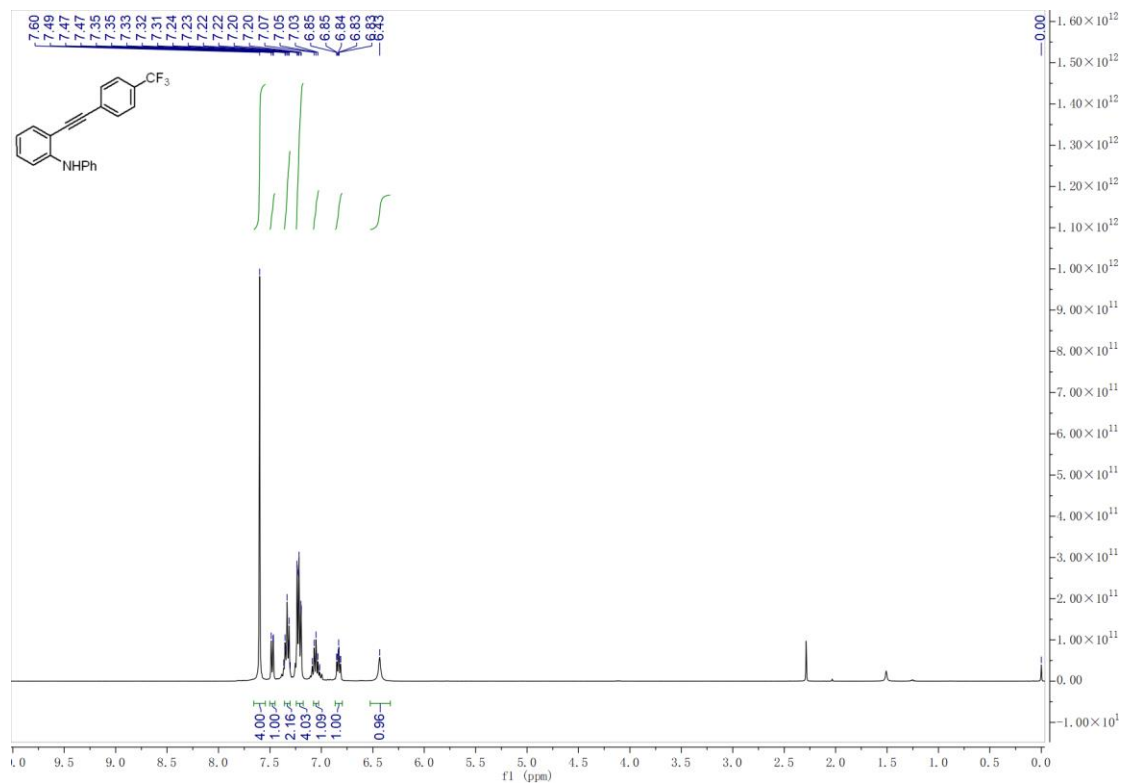
**14a : 14a'** = 1 : 0.13, <sup>1</sup>H NMR & <sup>13</sup>C NMR



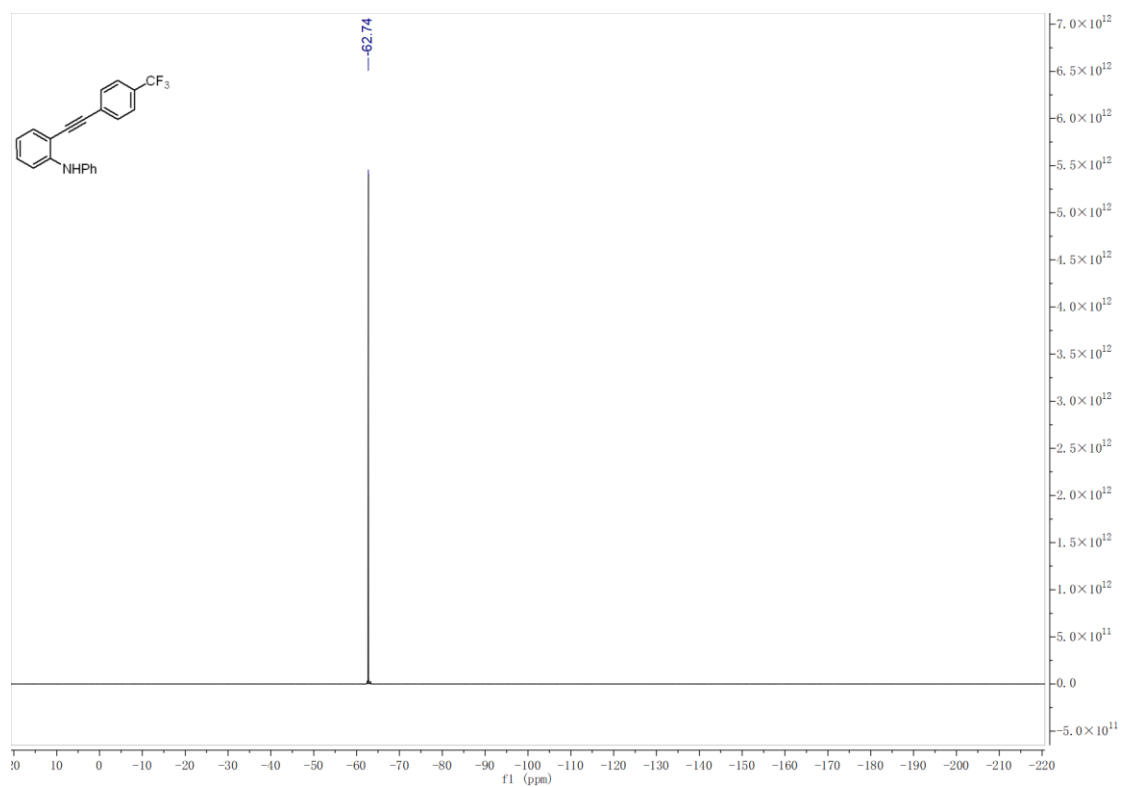
15a : 15a' = 1 : 0.08, <sup>1</sup>H NMR & <sup>13</sup>C NMR



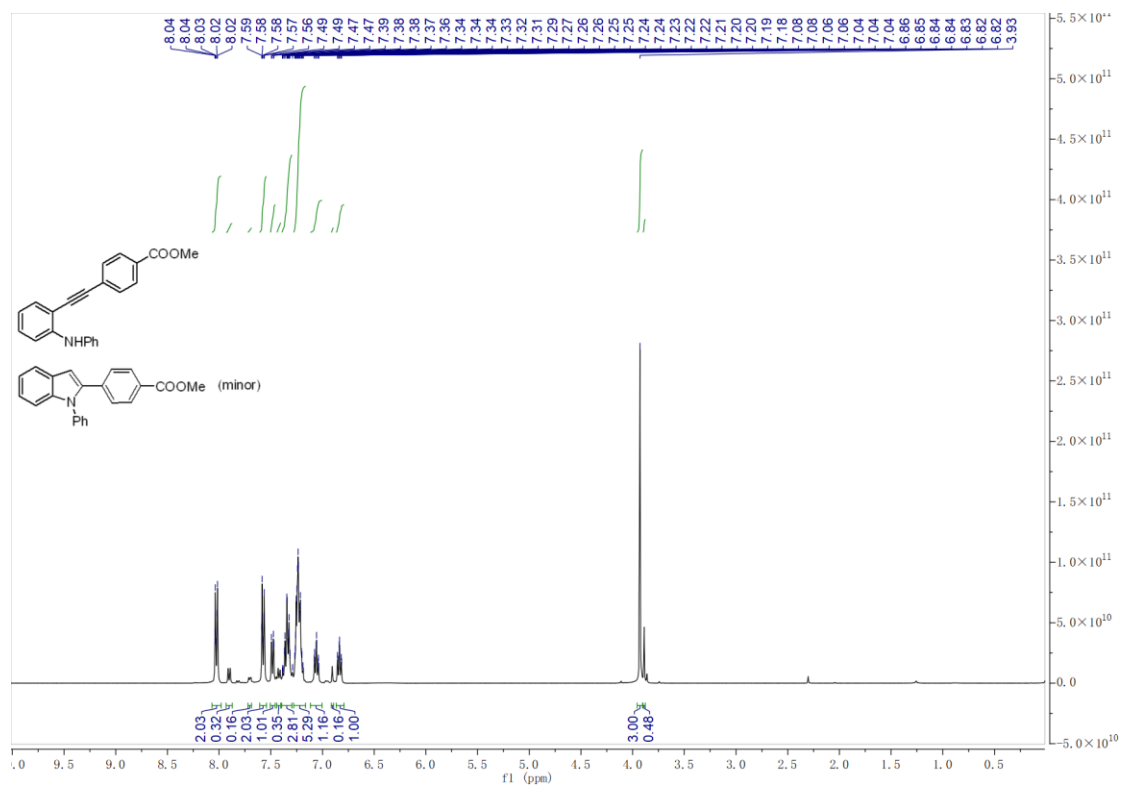
16a, <sup>1</sup>H NMR & <sup>13</sup>C NMR & <sup>19</sup>F NMR

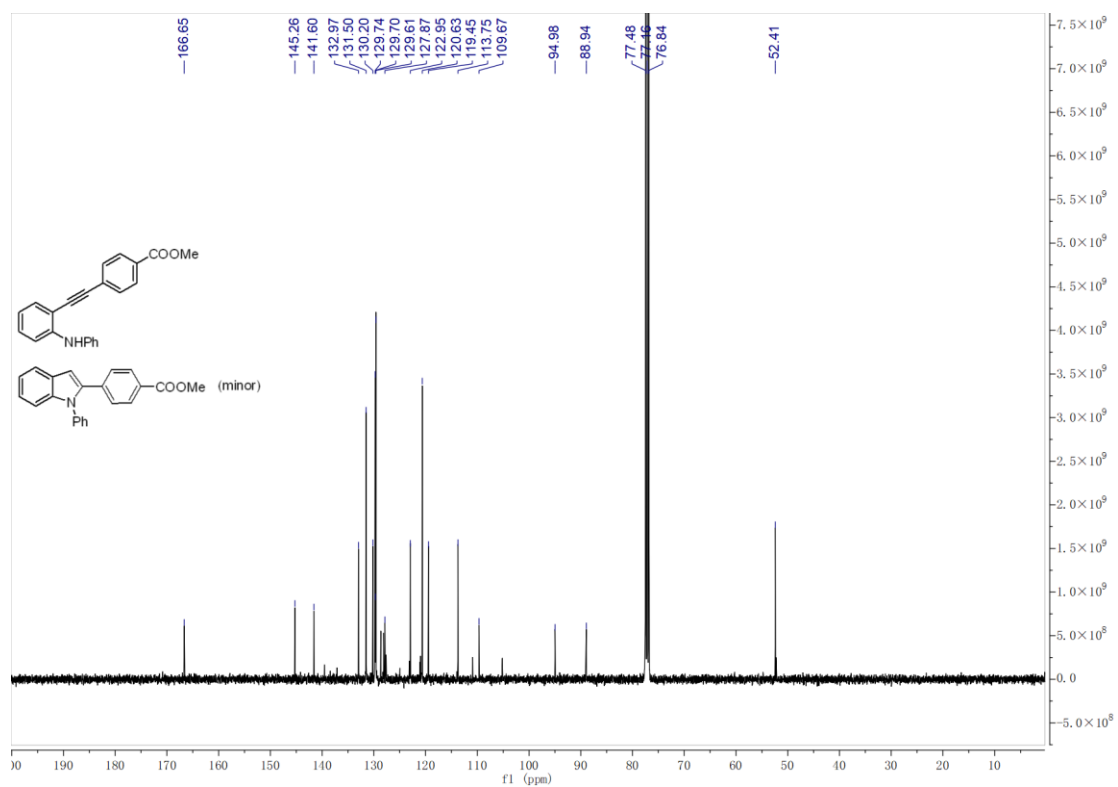




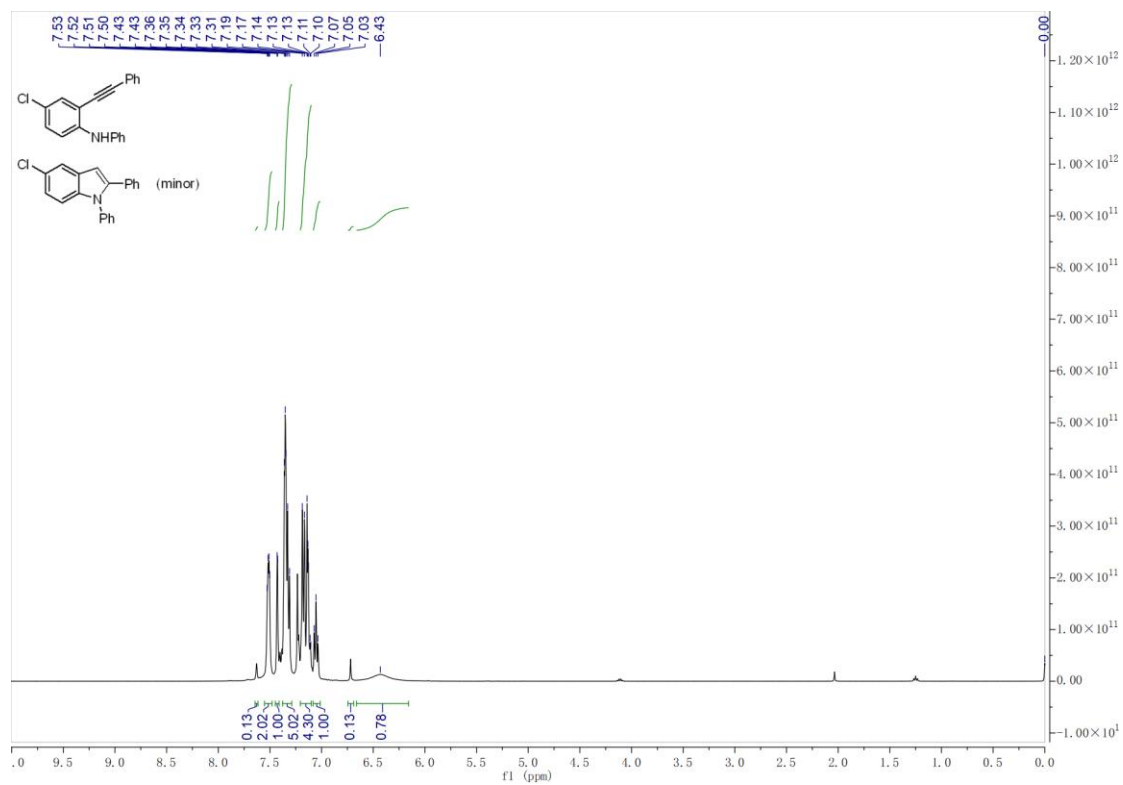


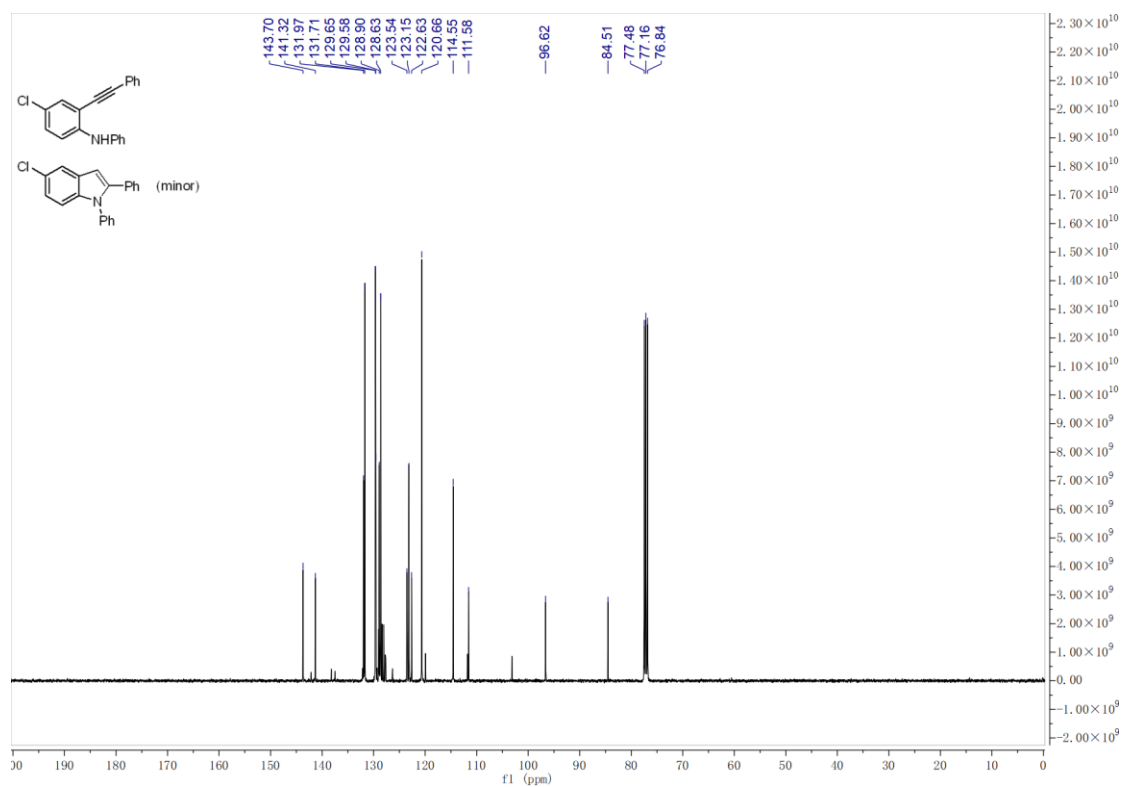
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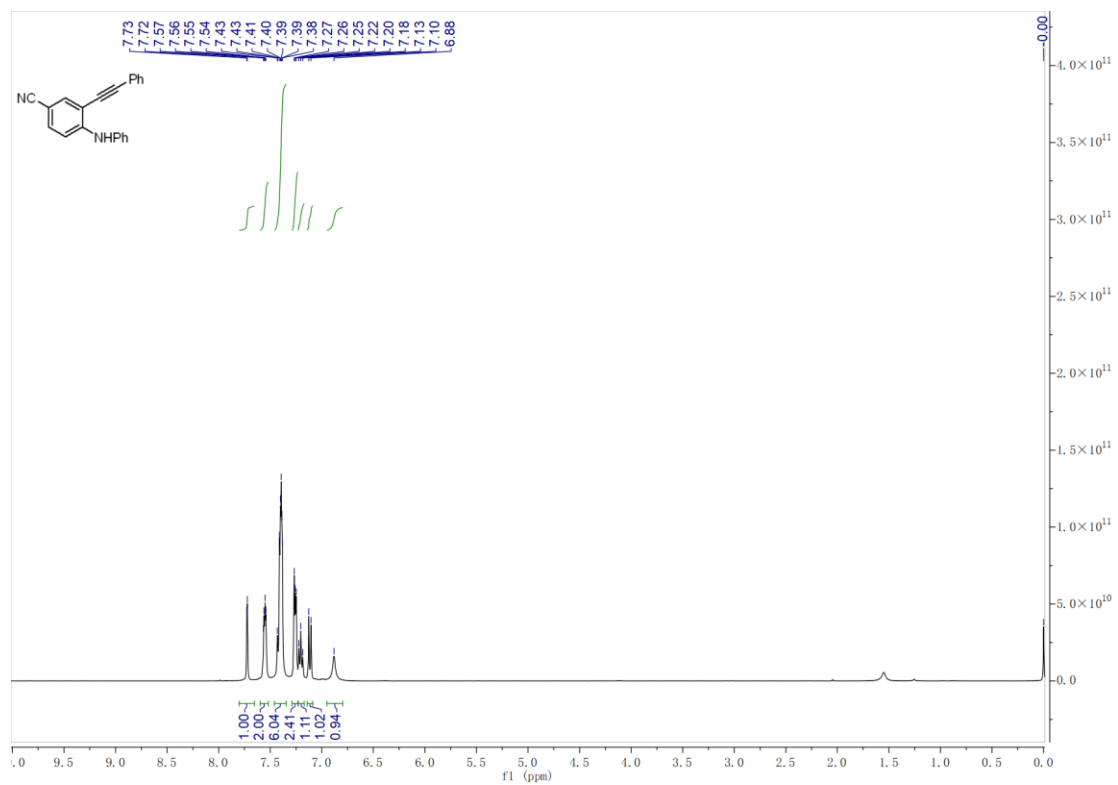


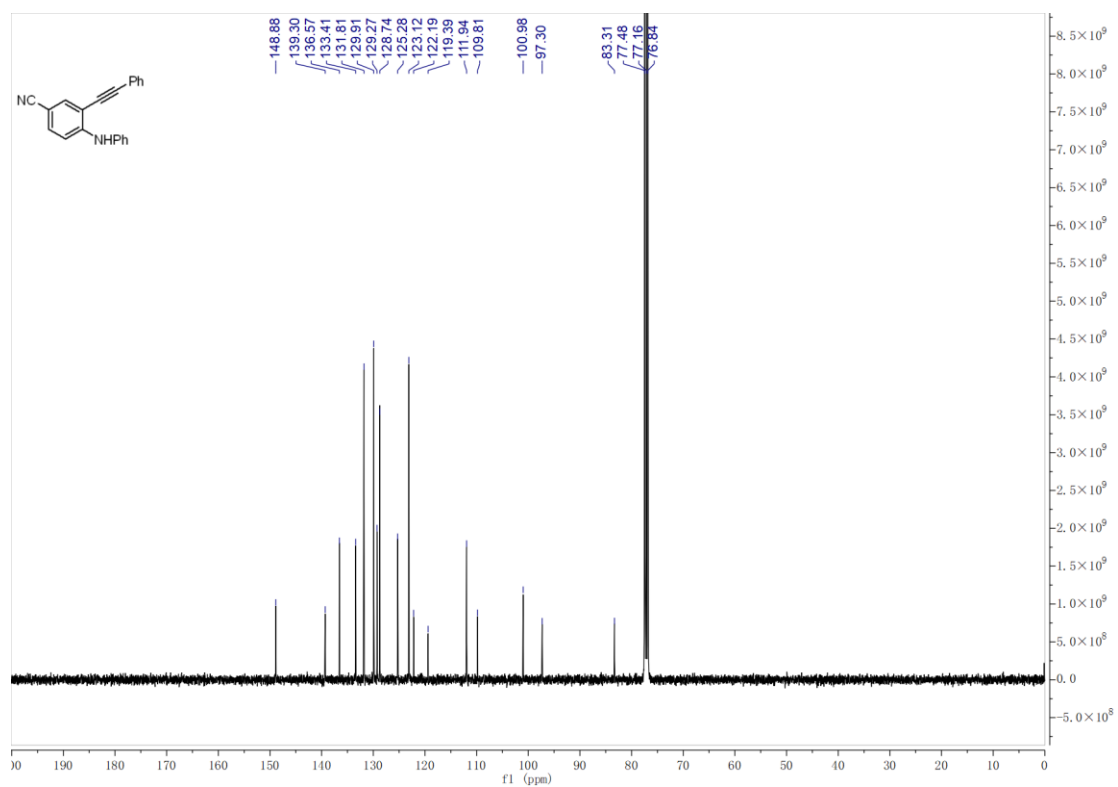
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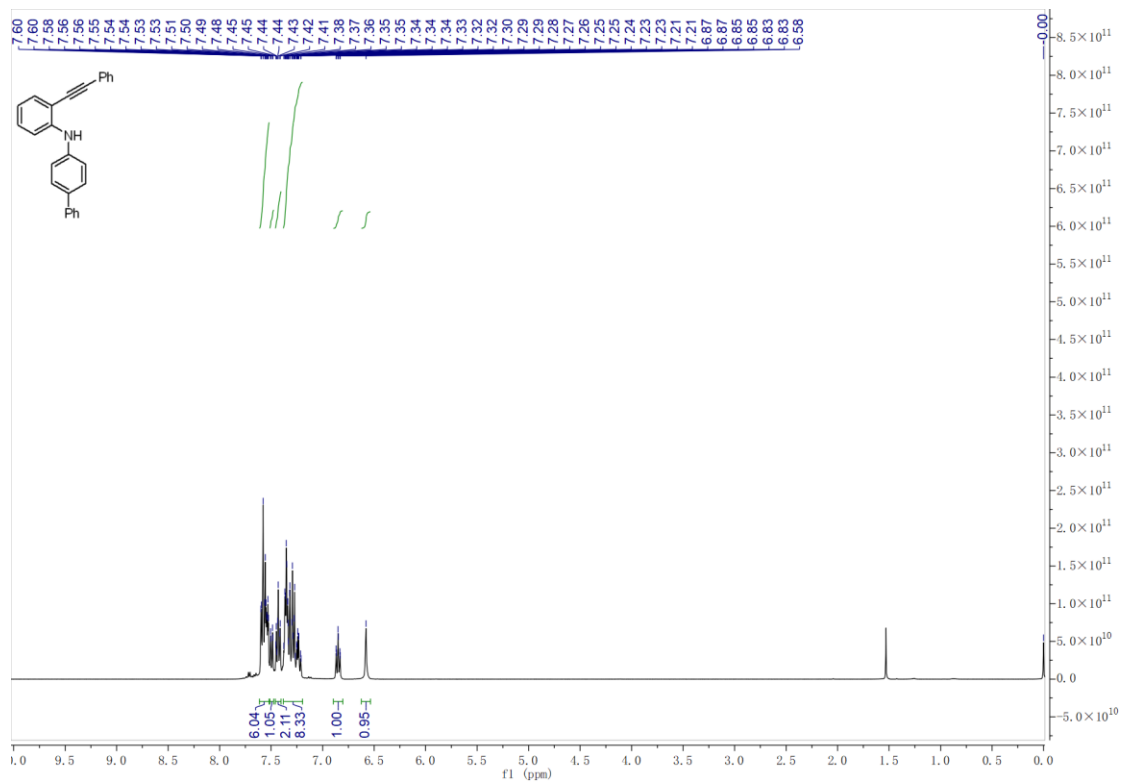


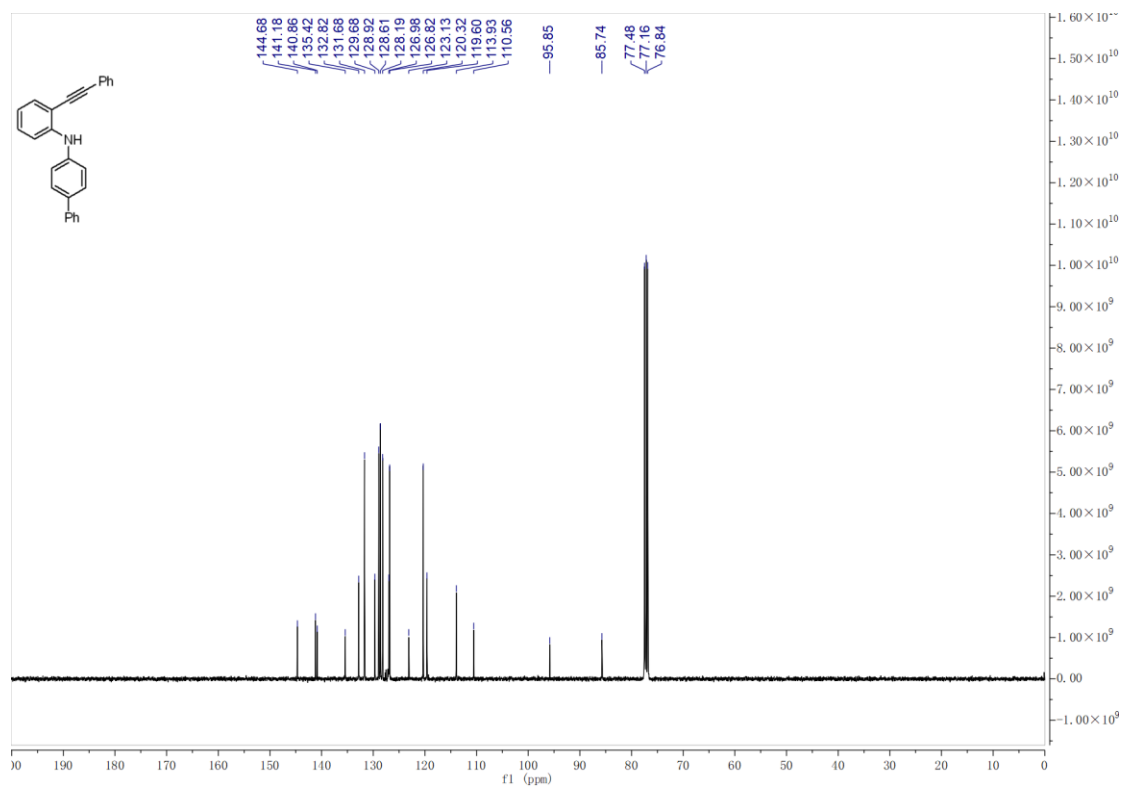
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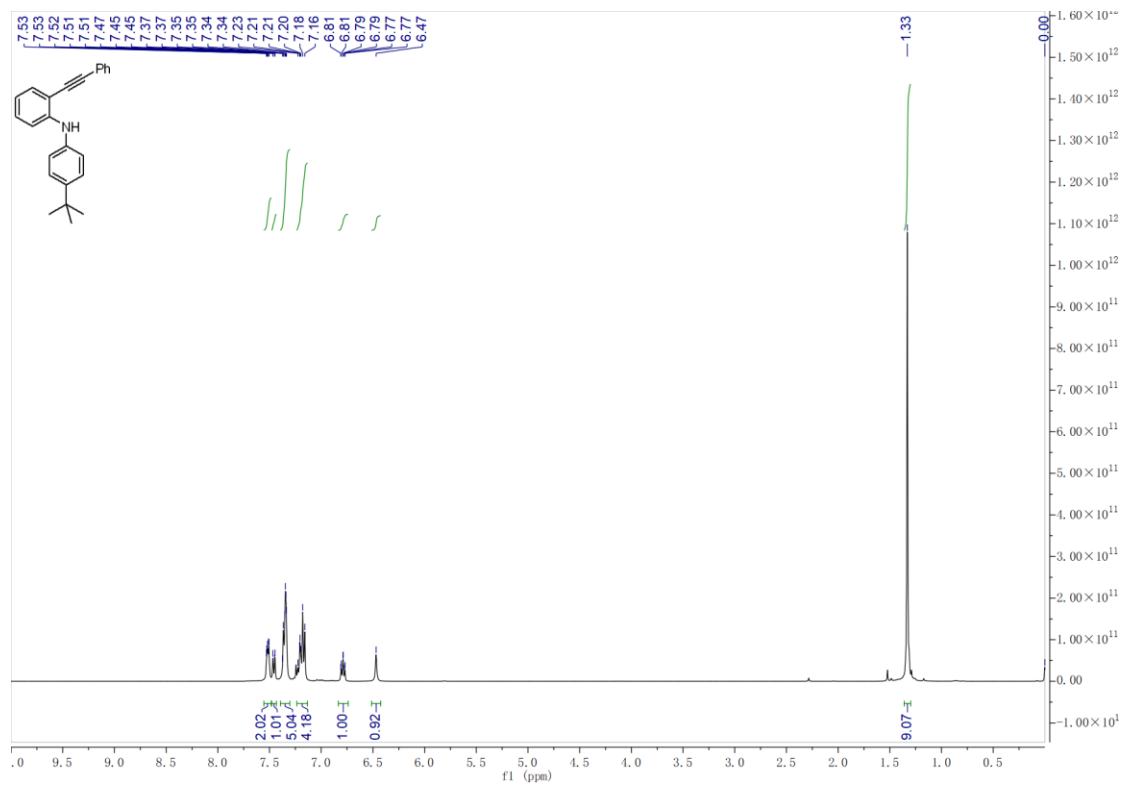


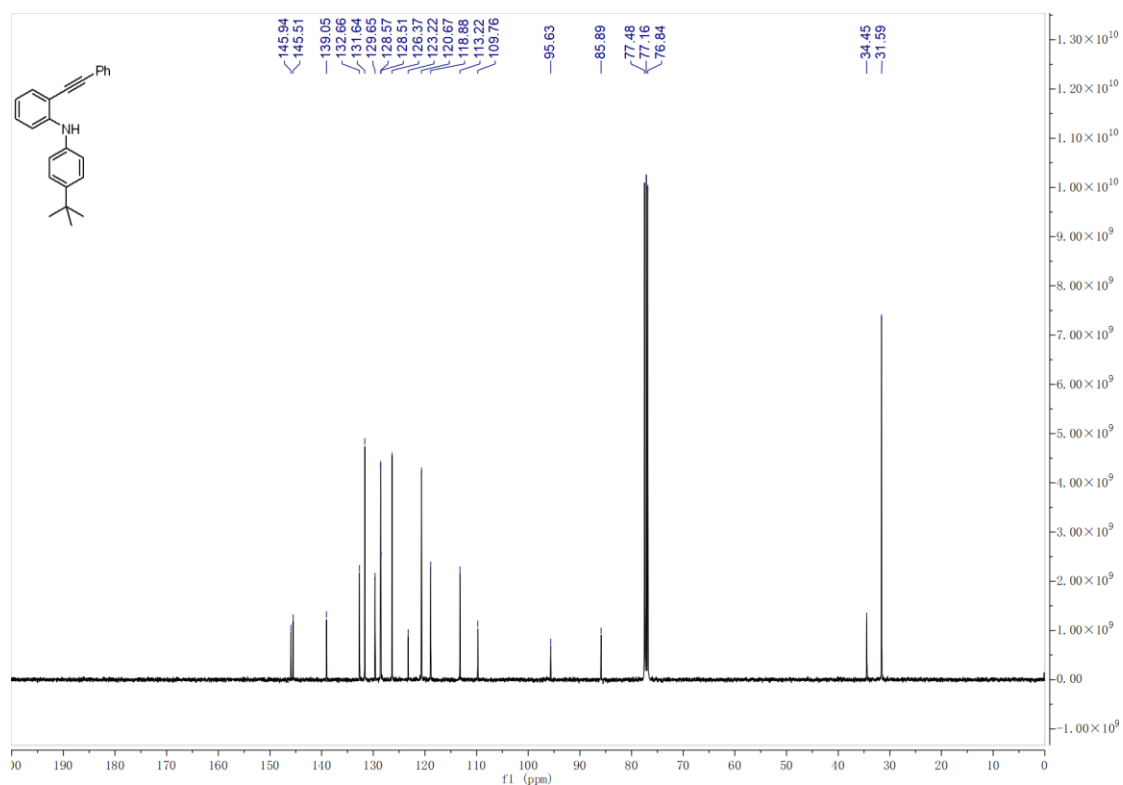
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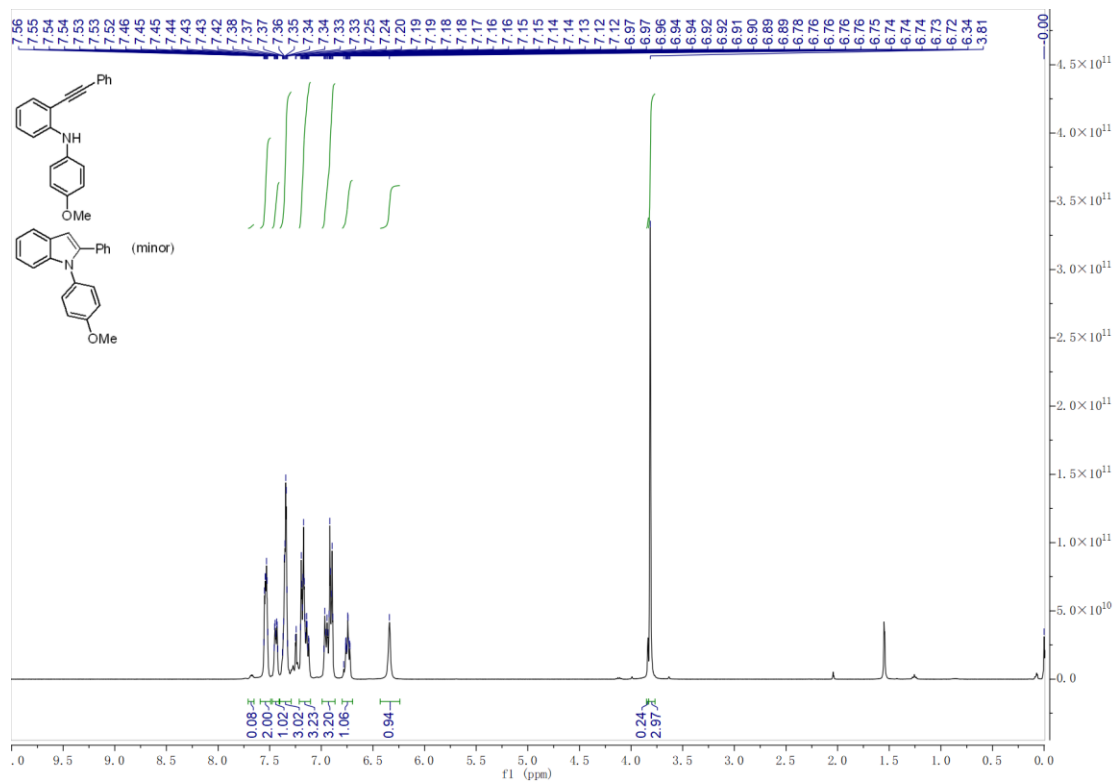


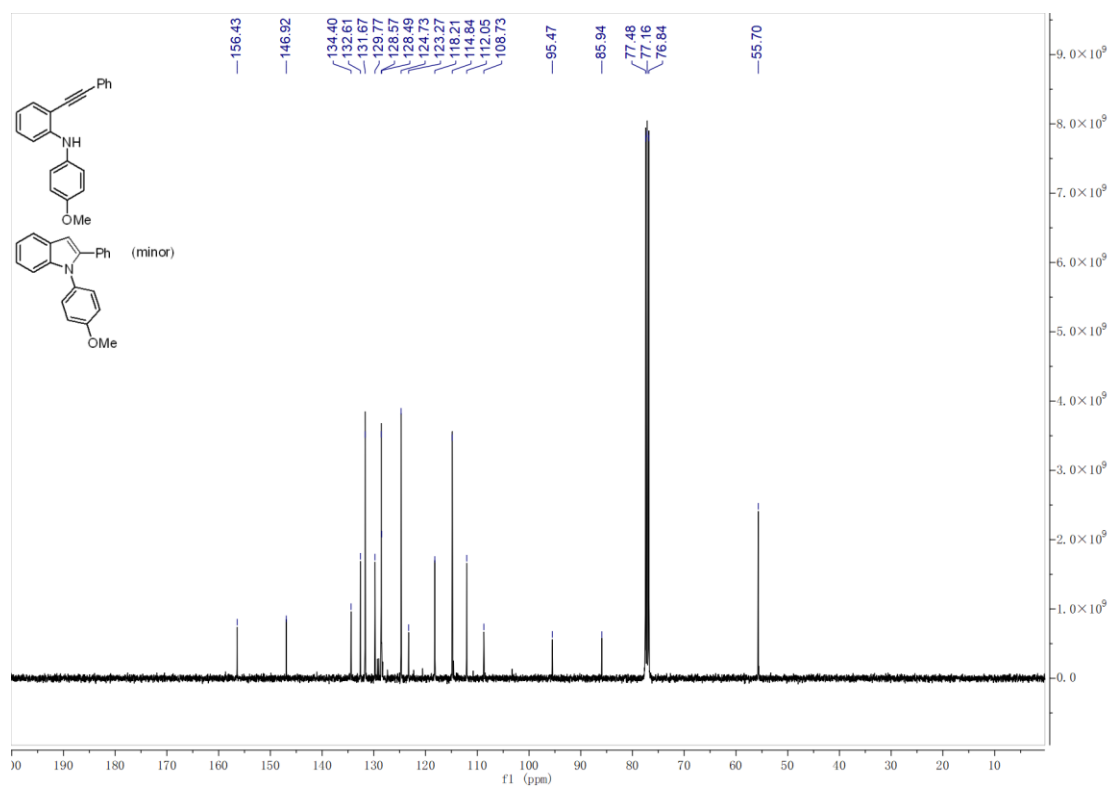
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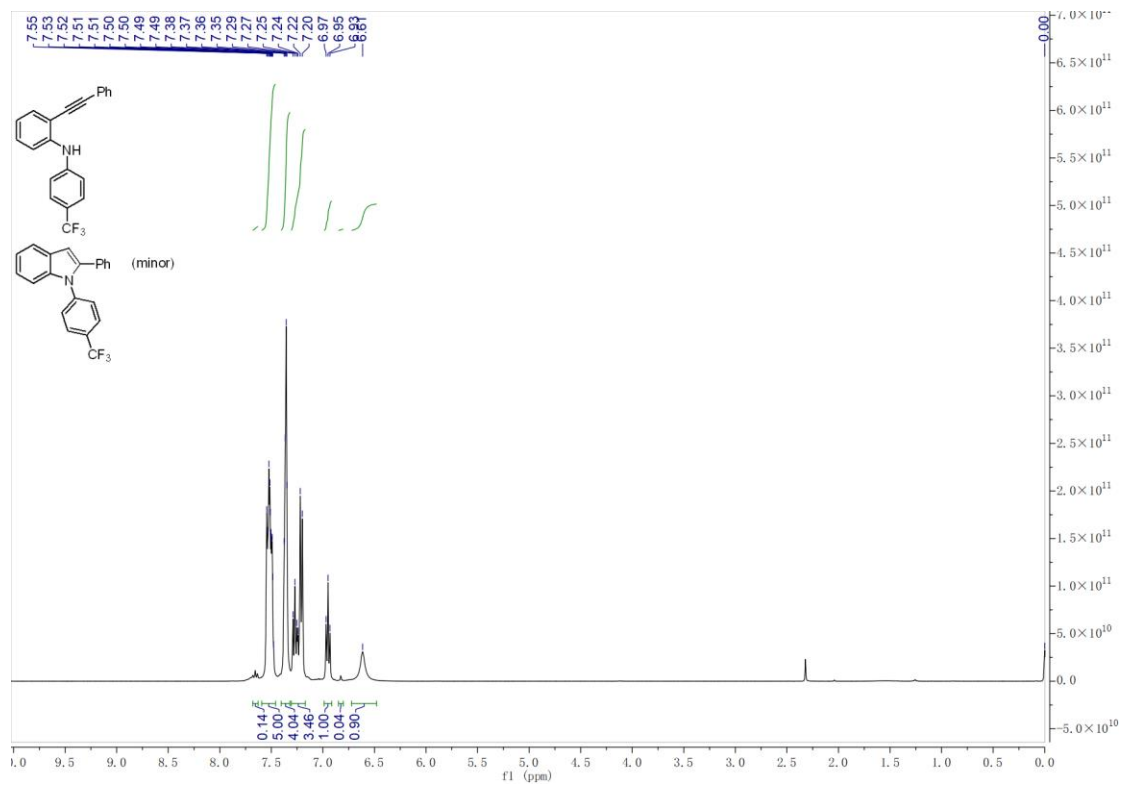


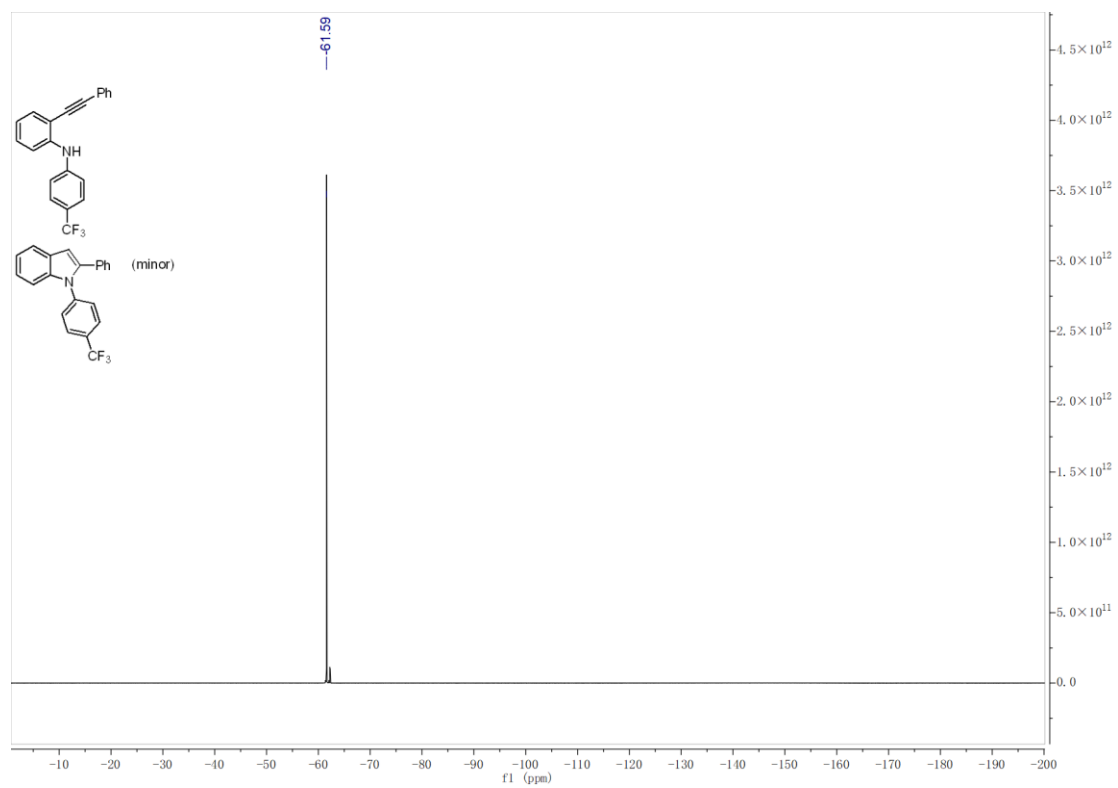
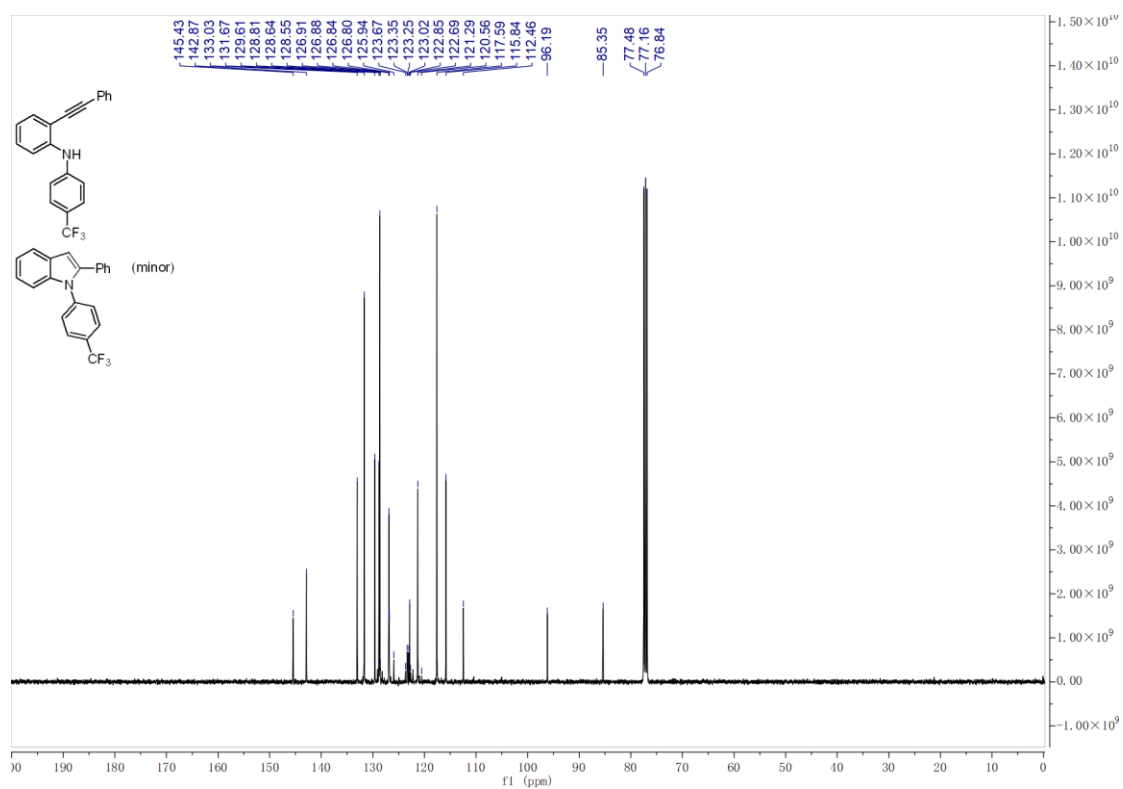
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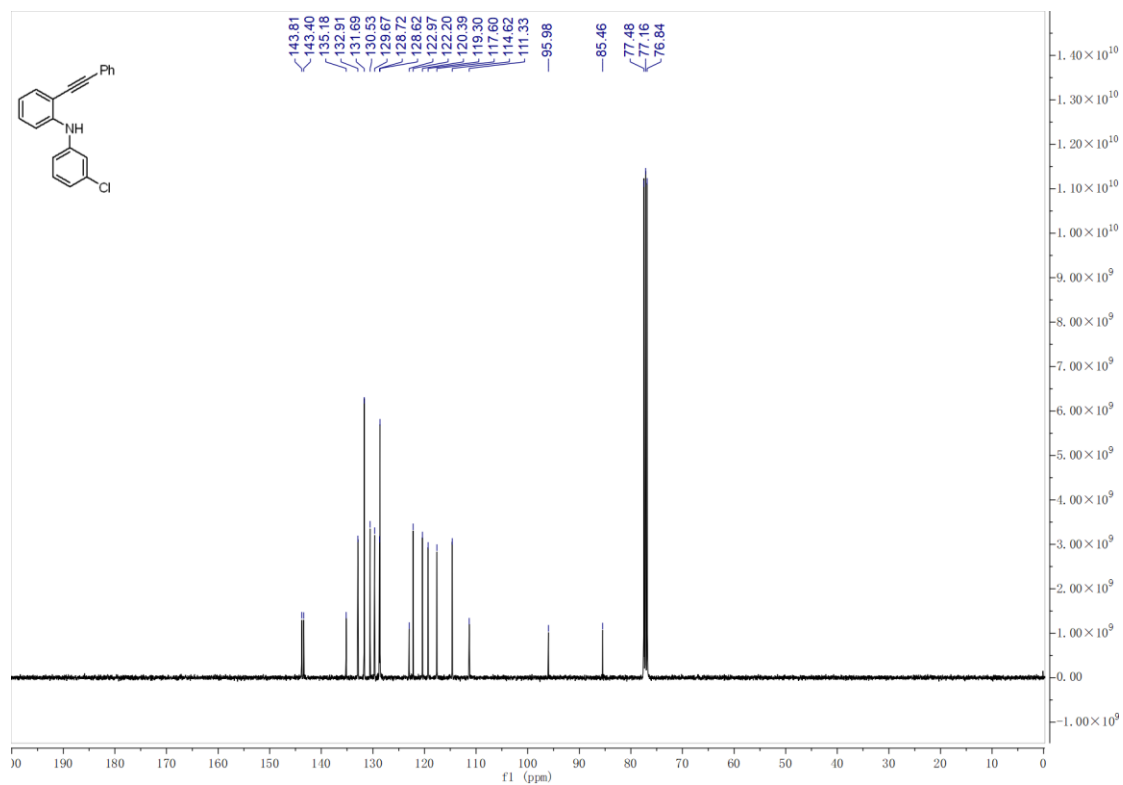
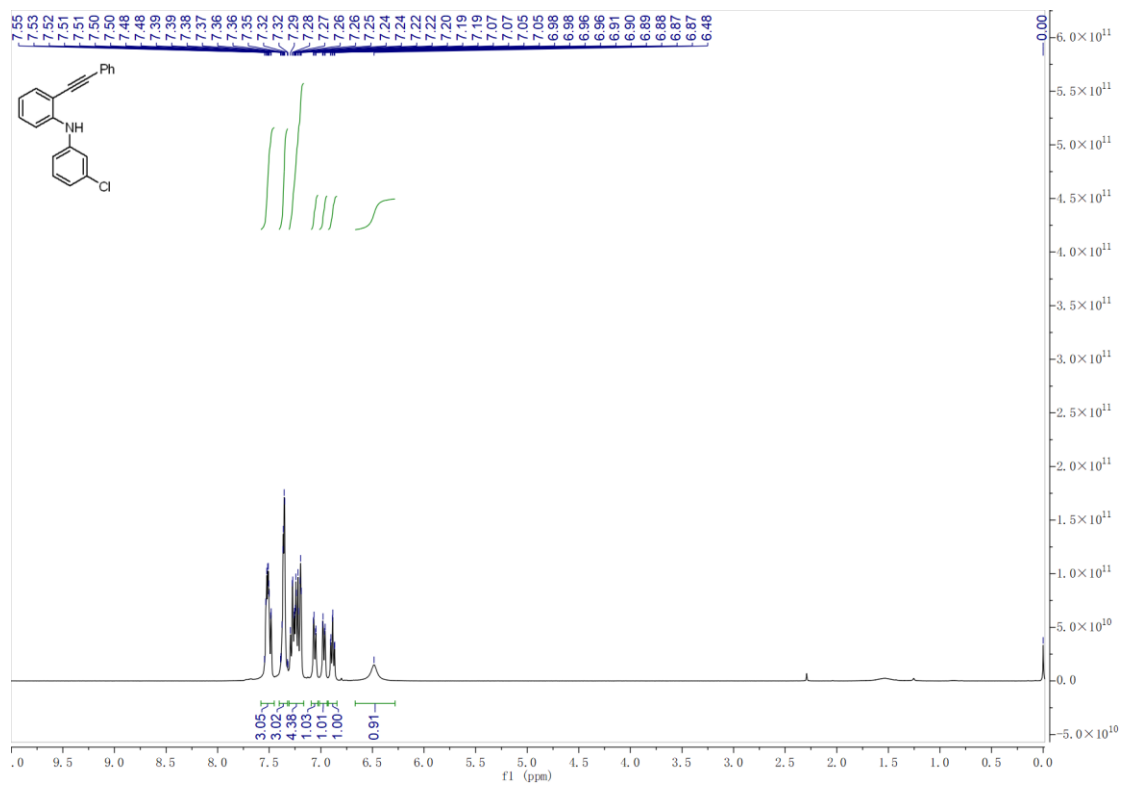
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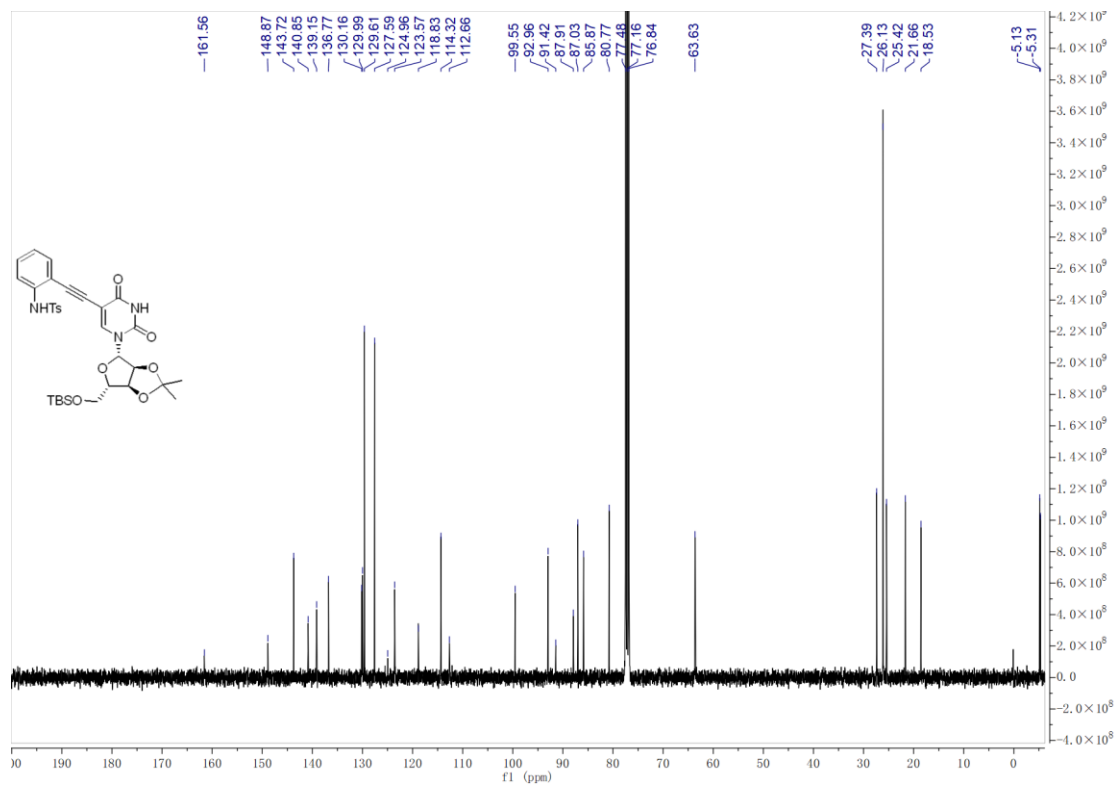
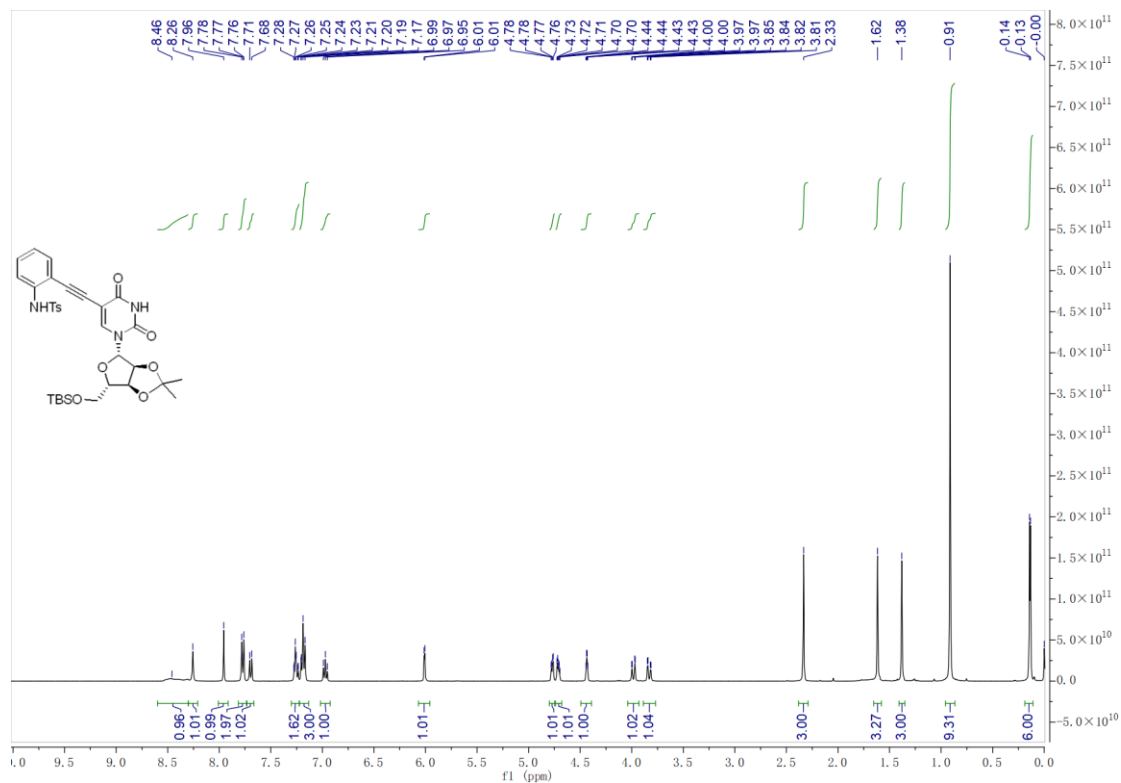




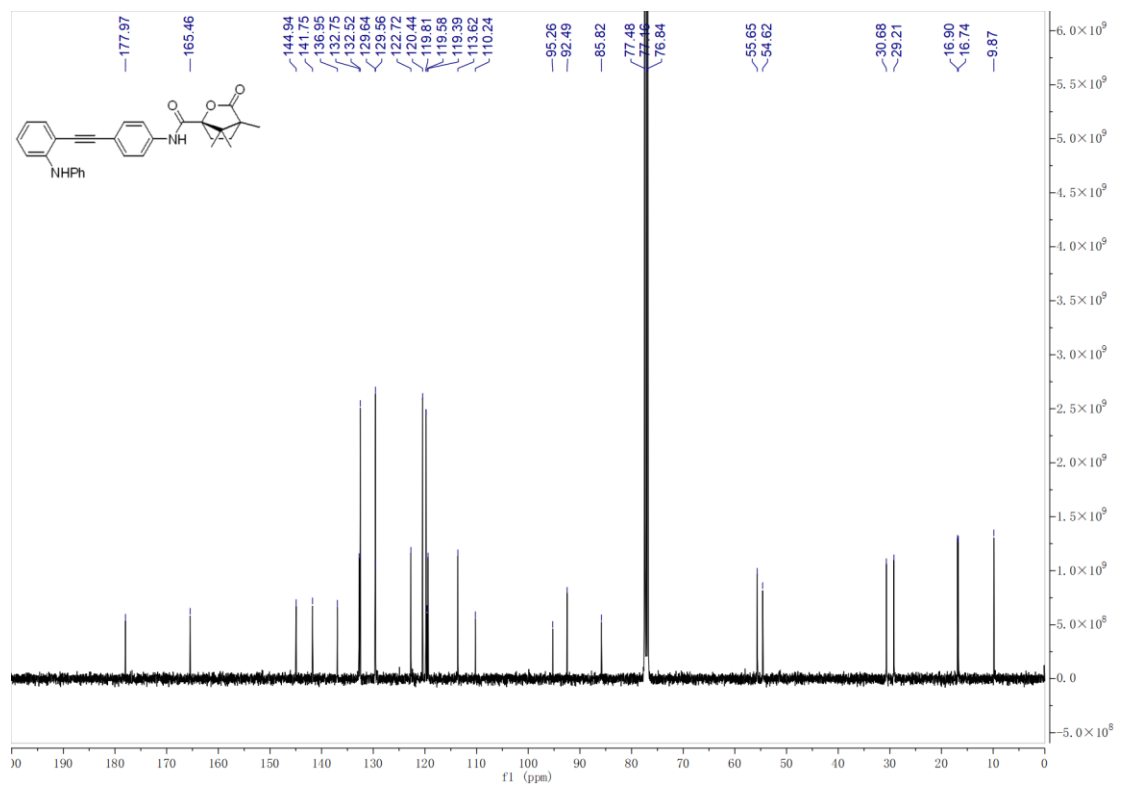
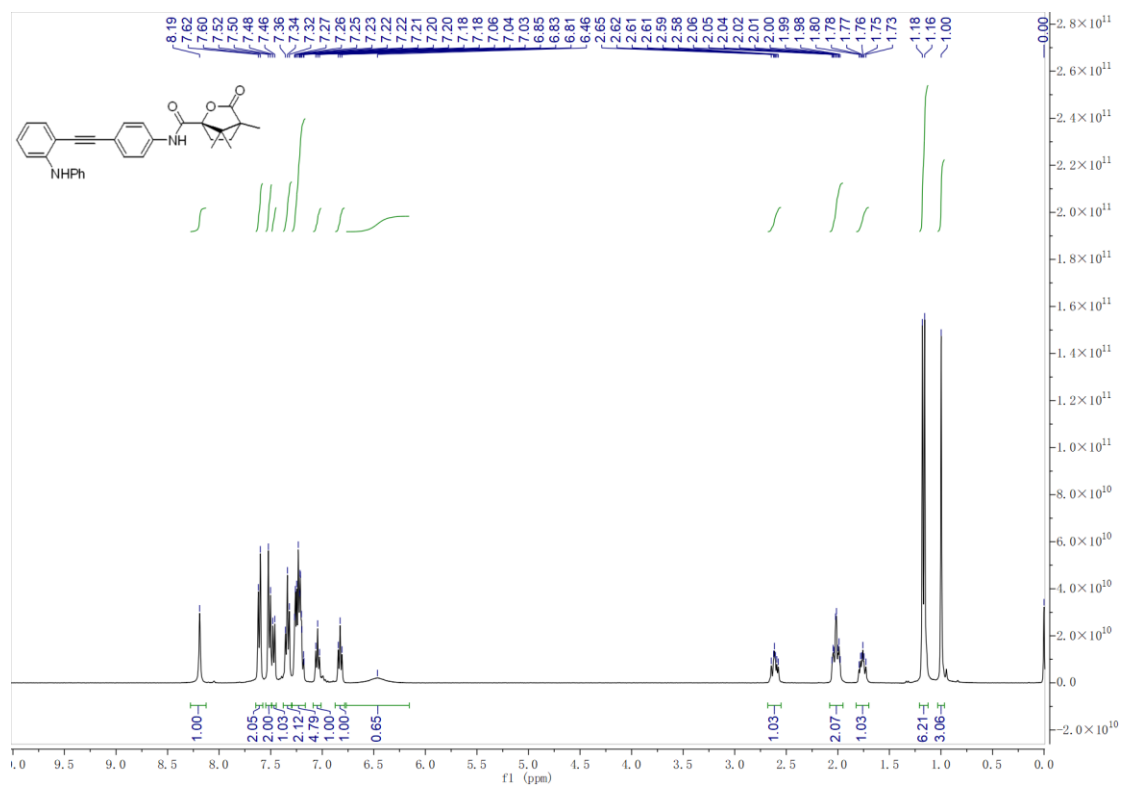
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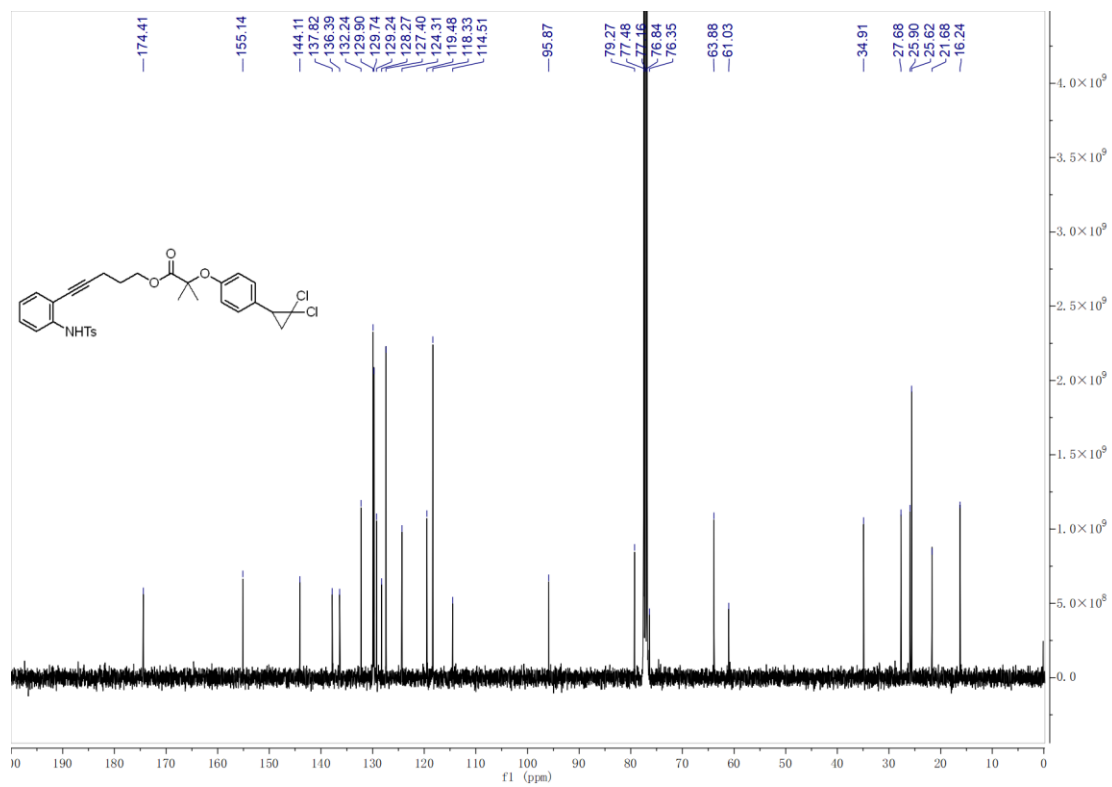
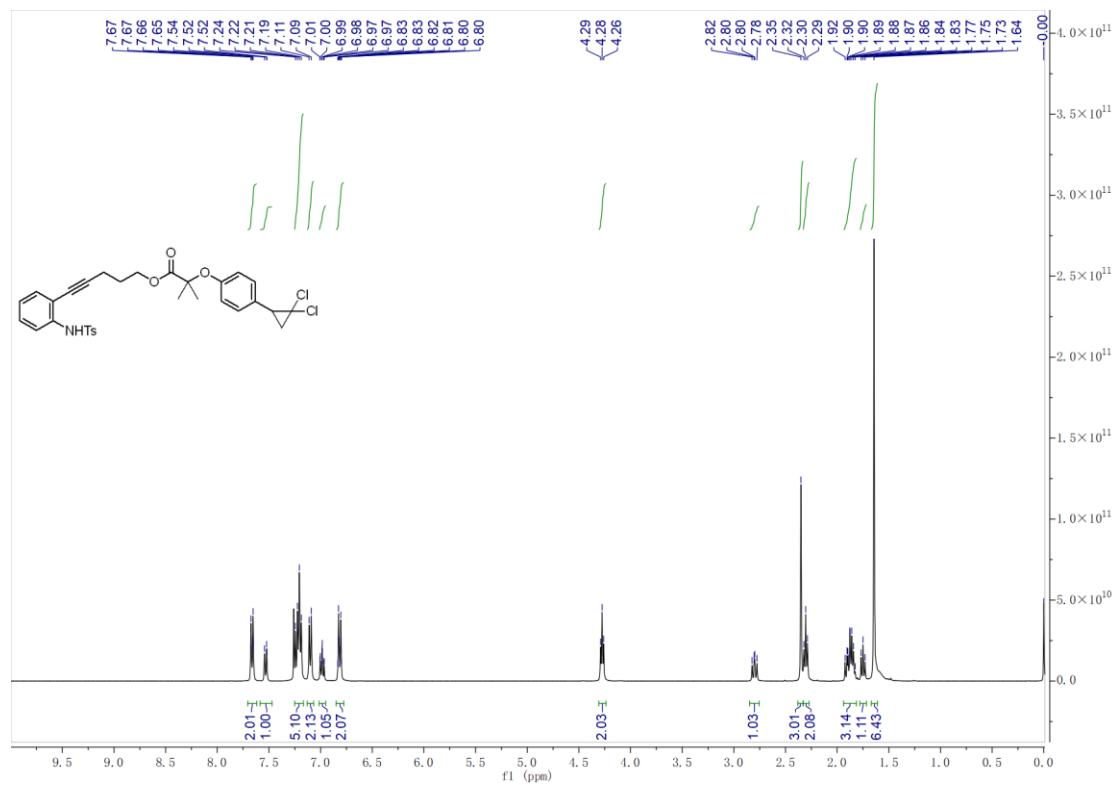
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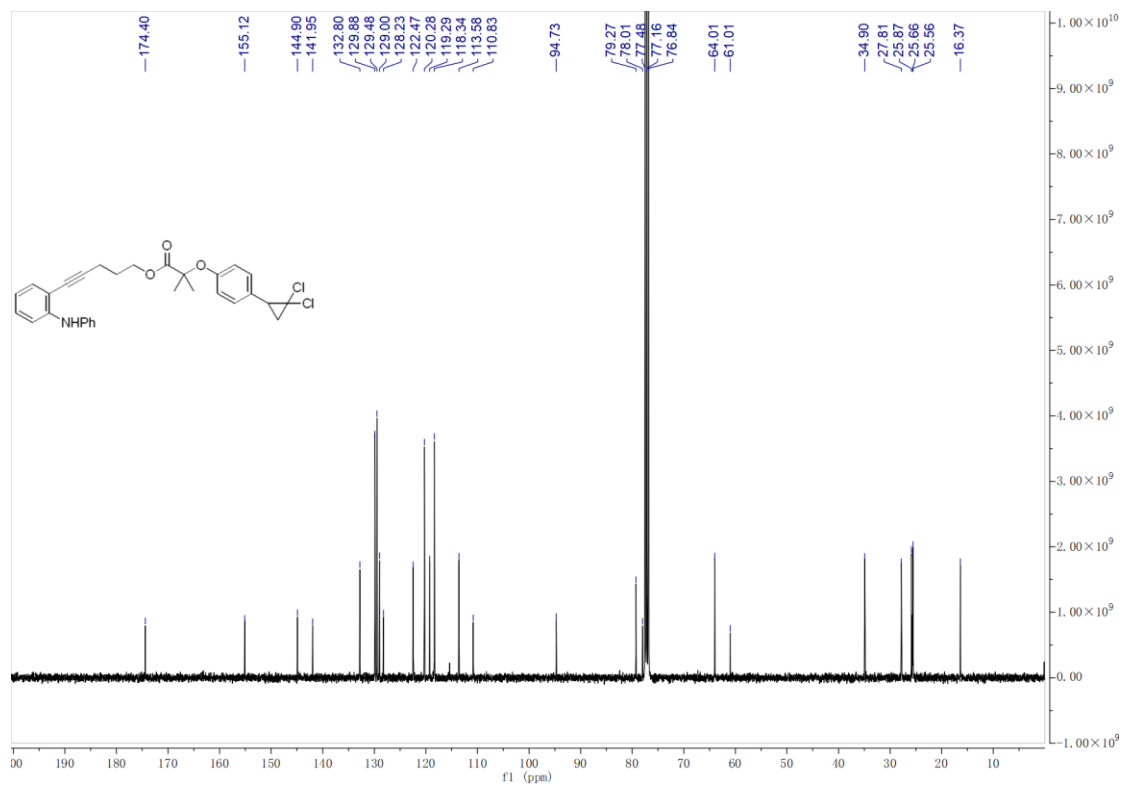
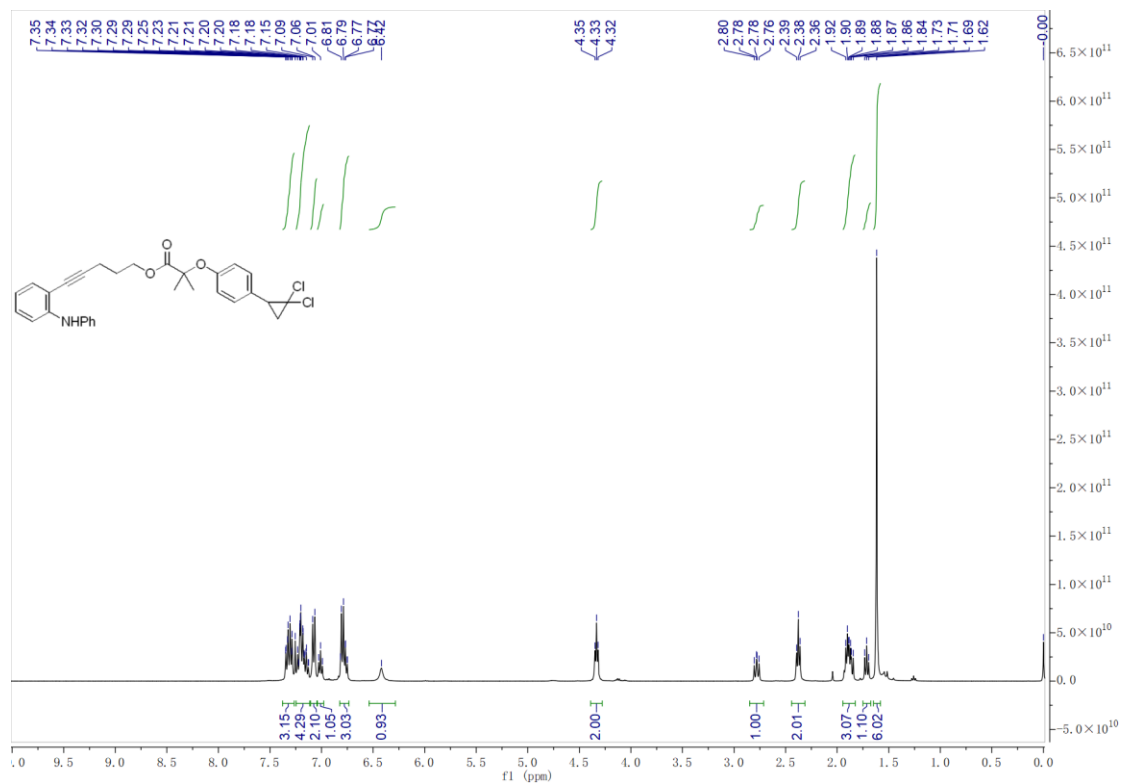
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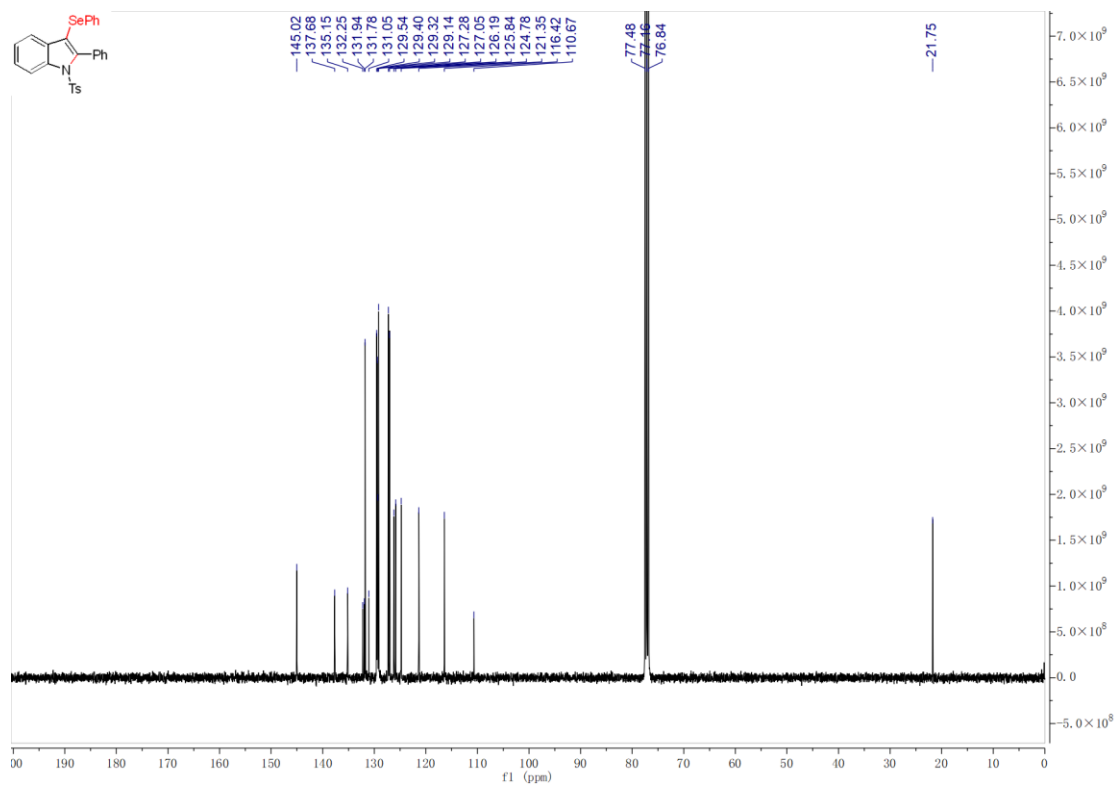
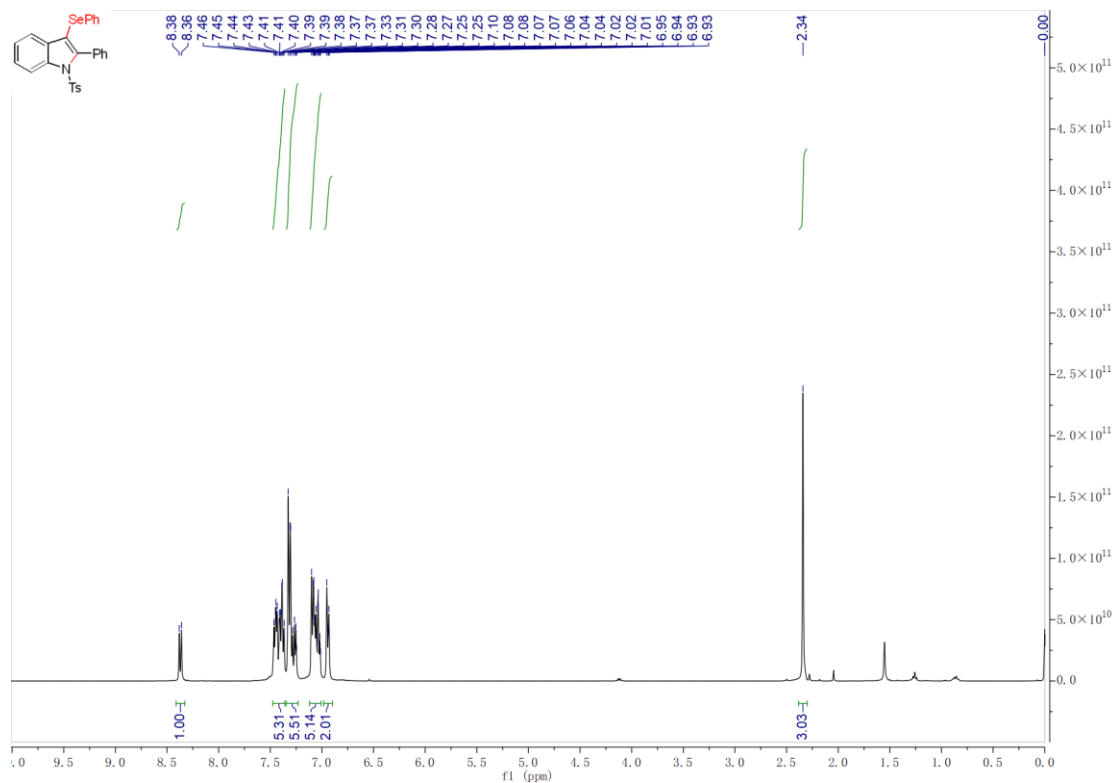
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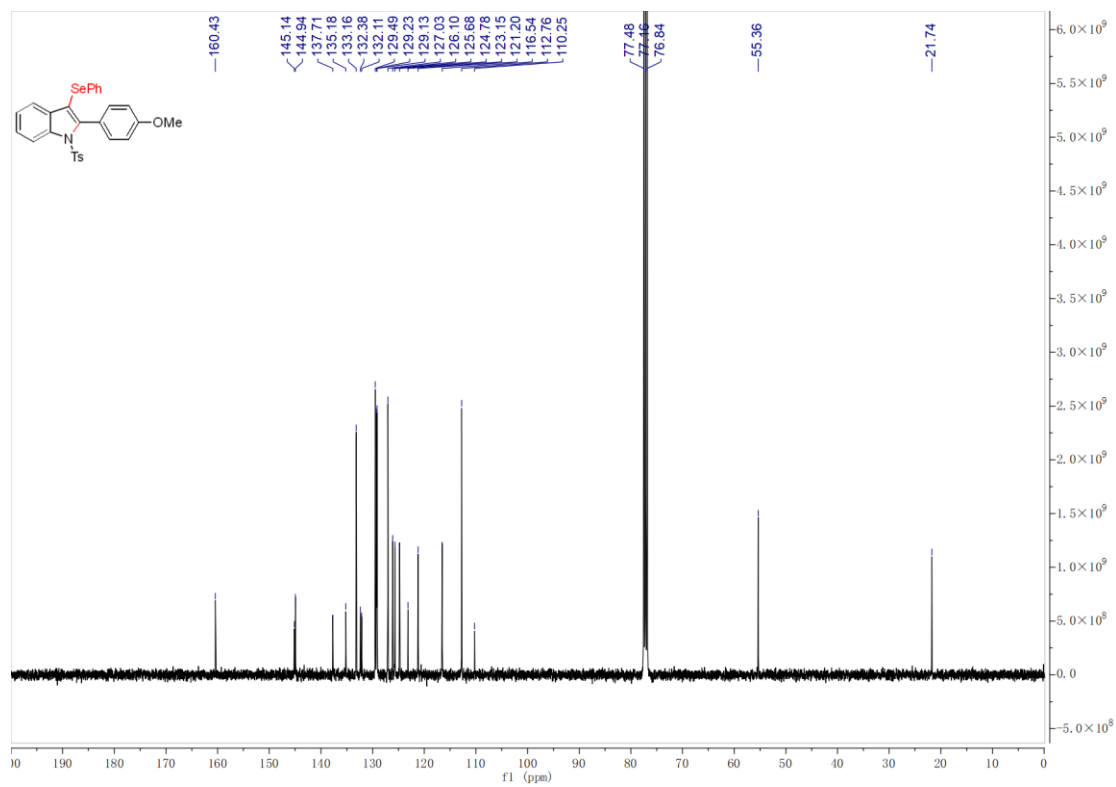
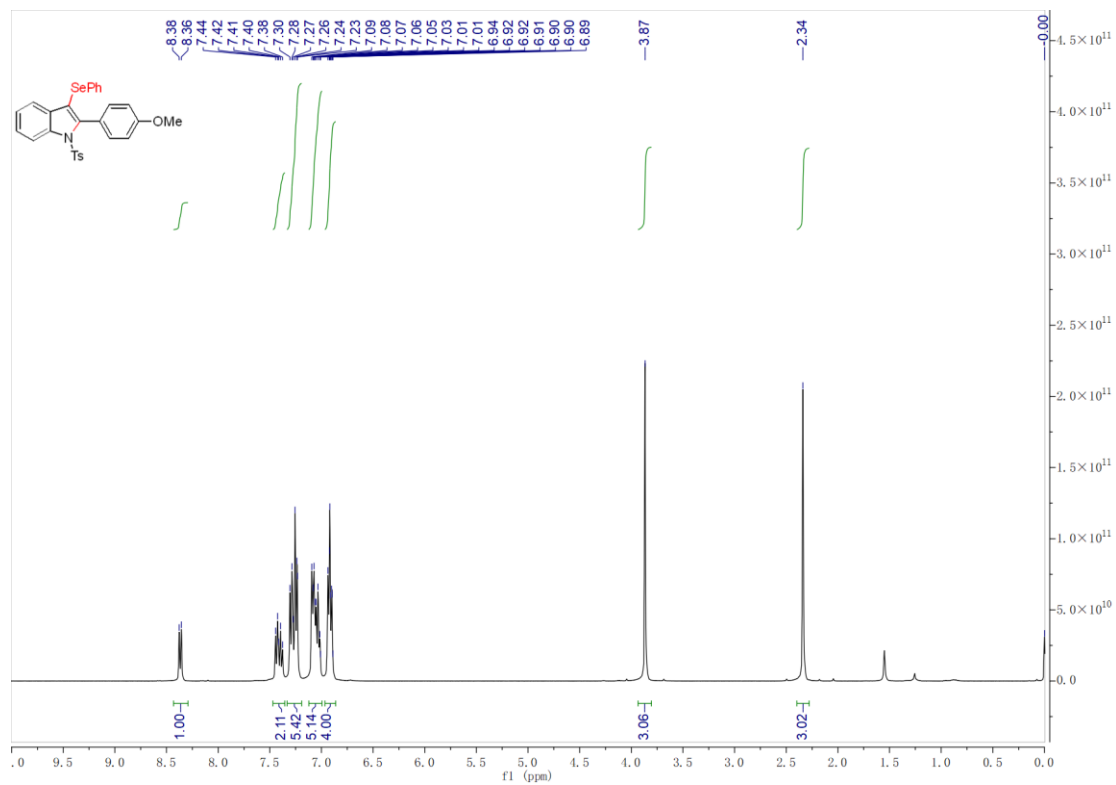
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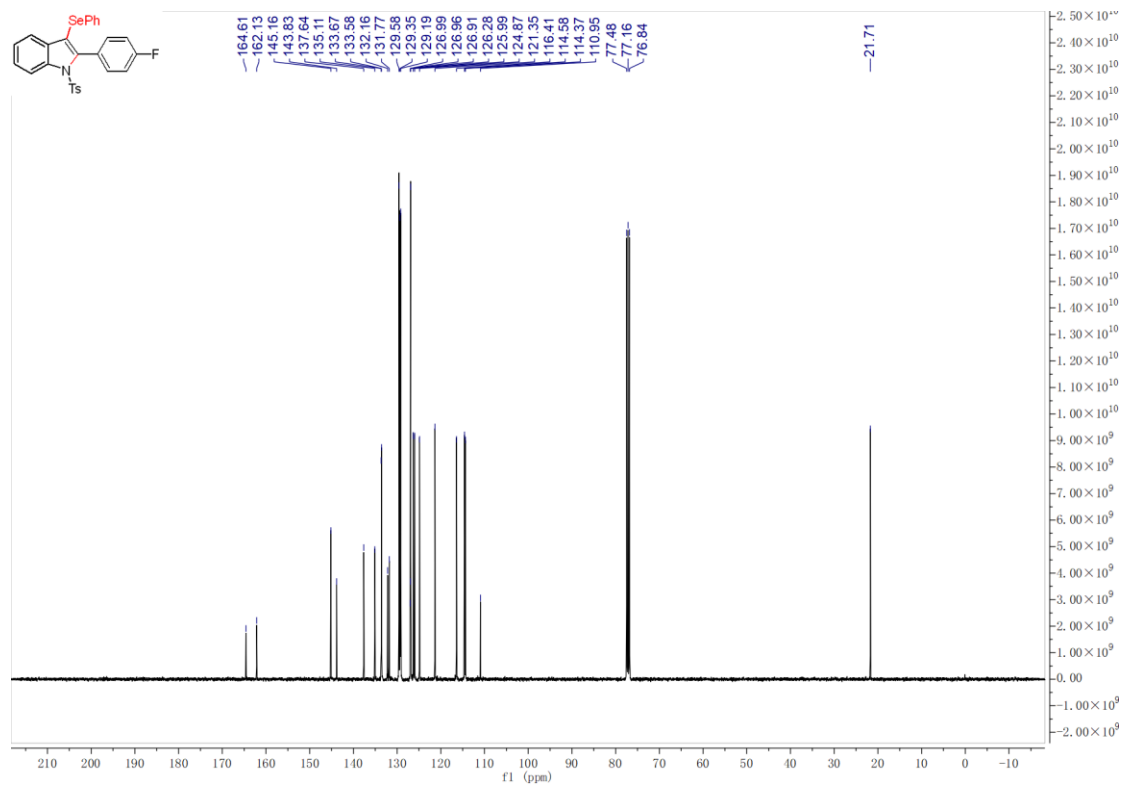
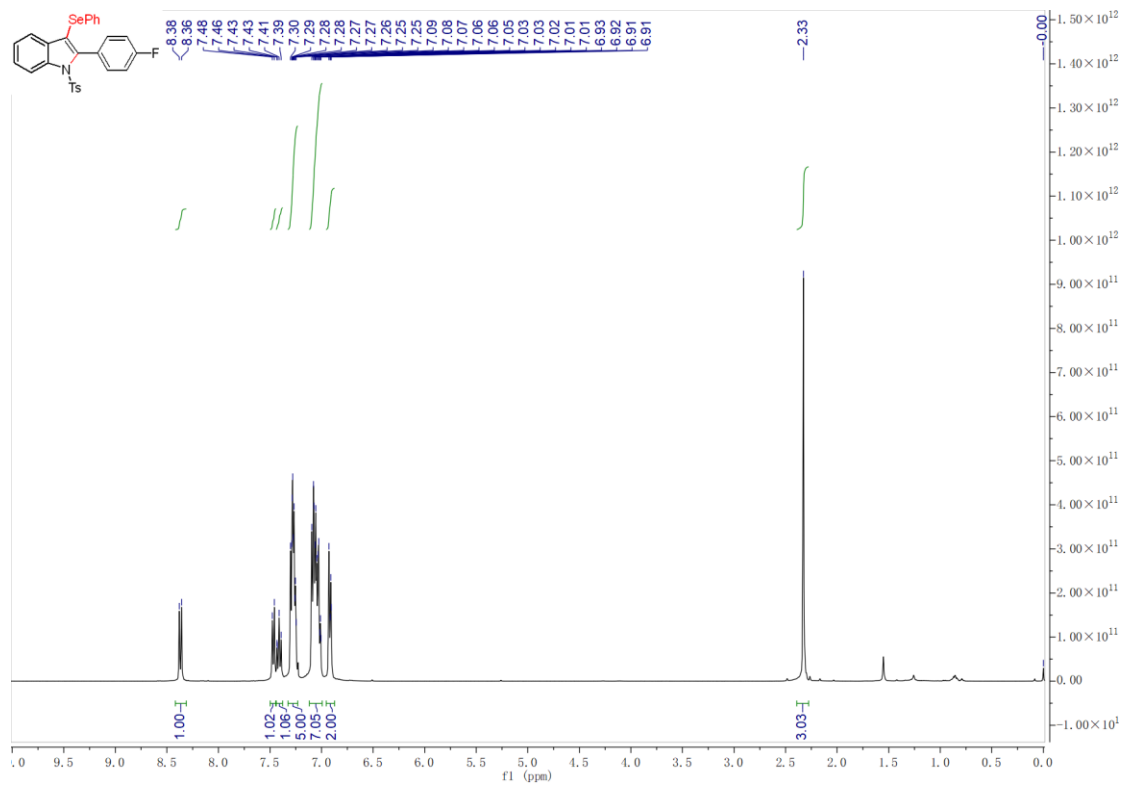
1c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



2c, <sup>1</sup>H NMR & <sup>13</sup>C NMR

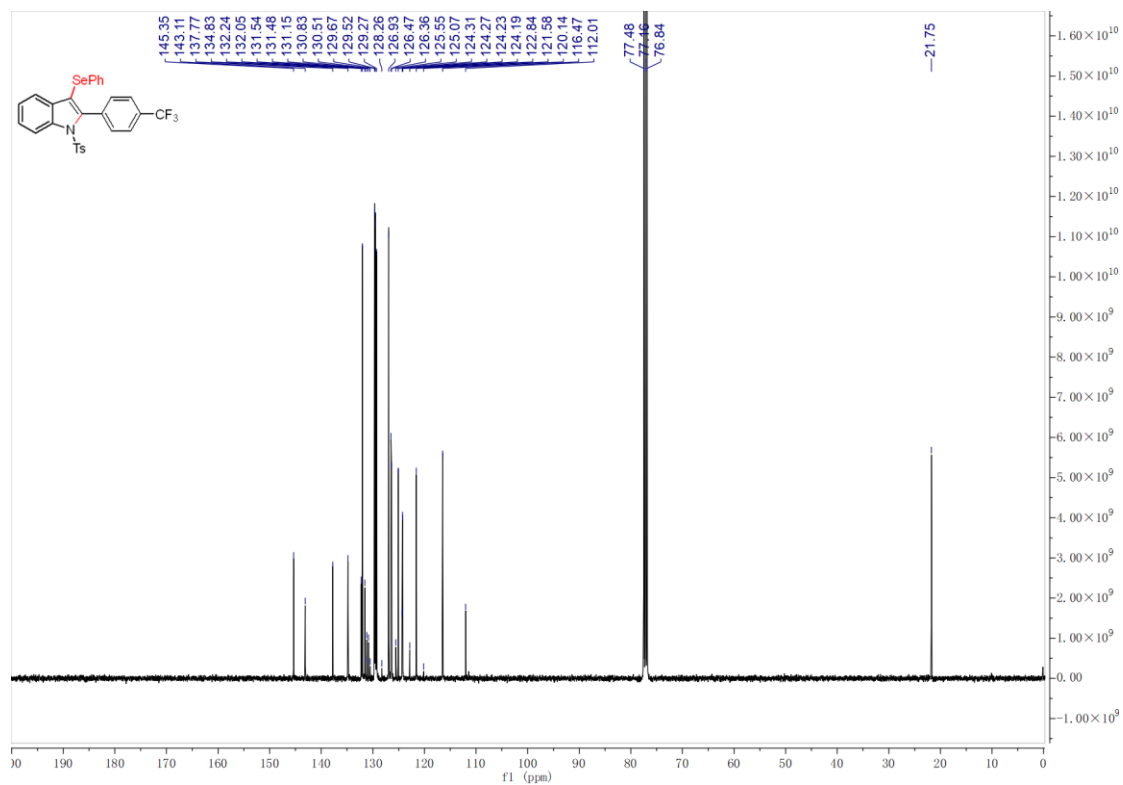
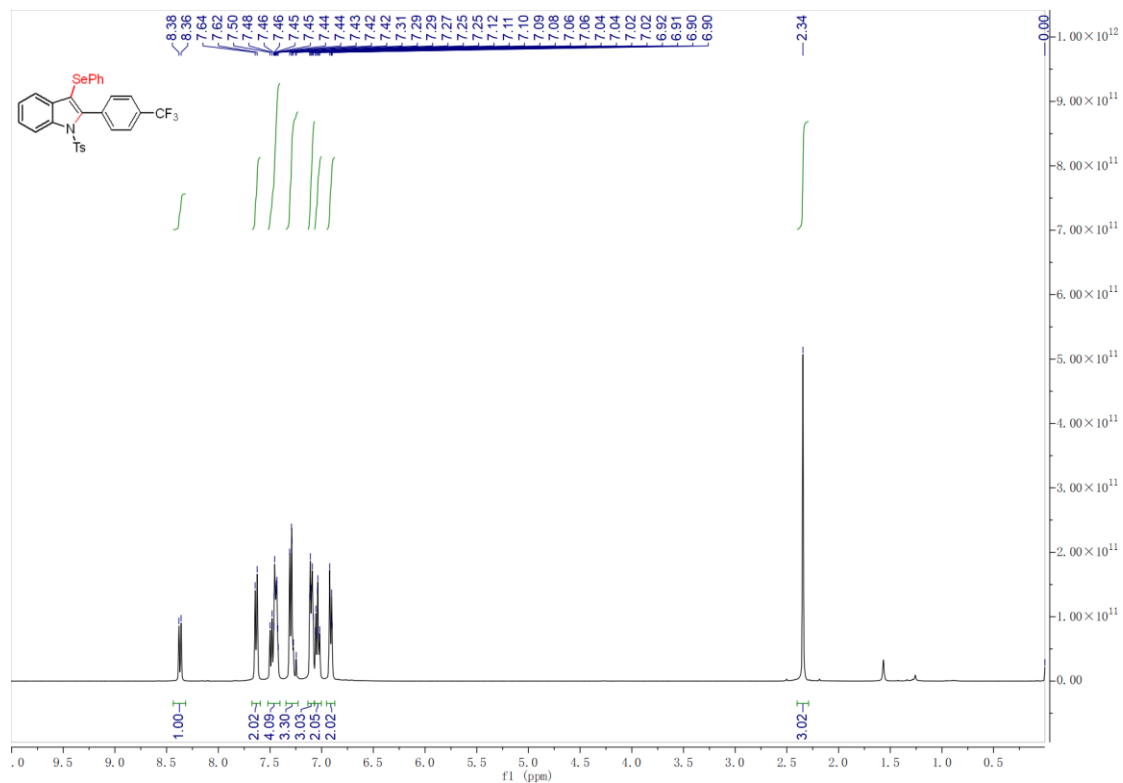


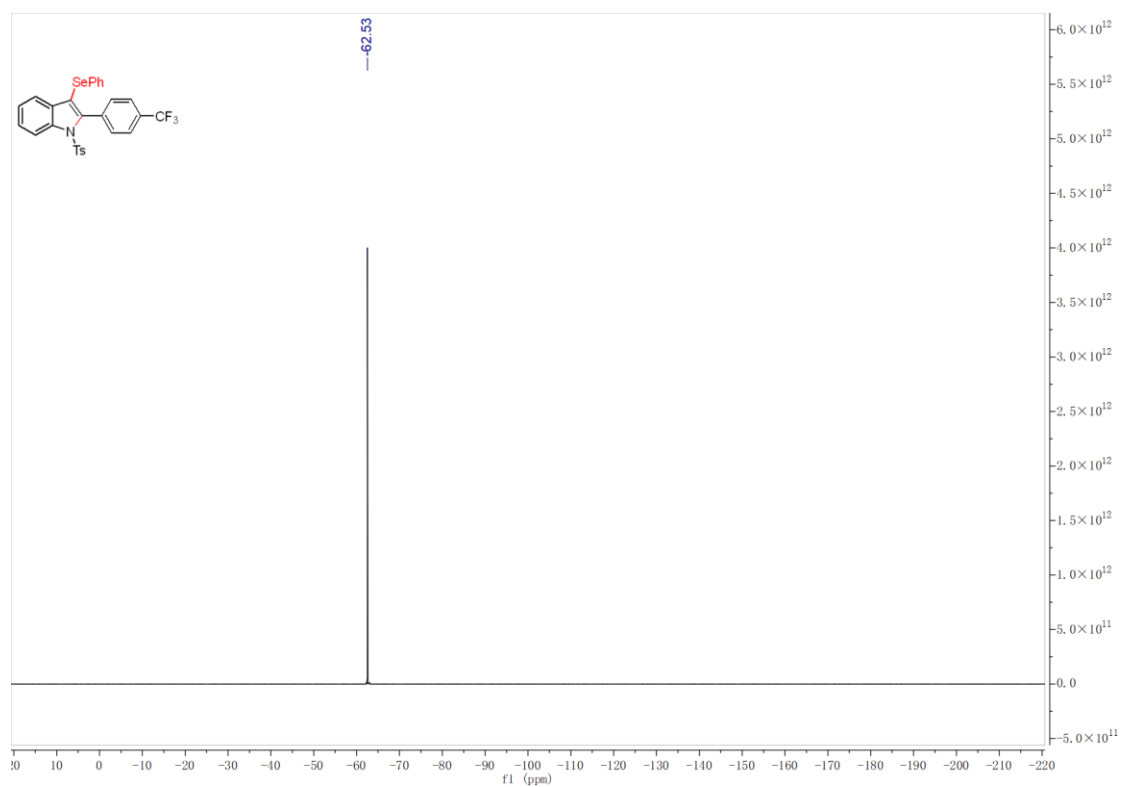
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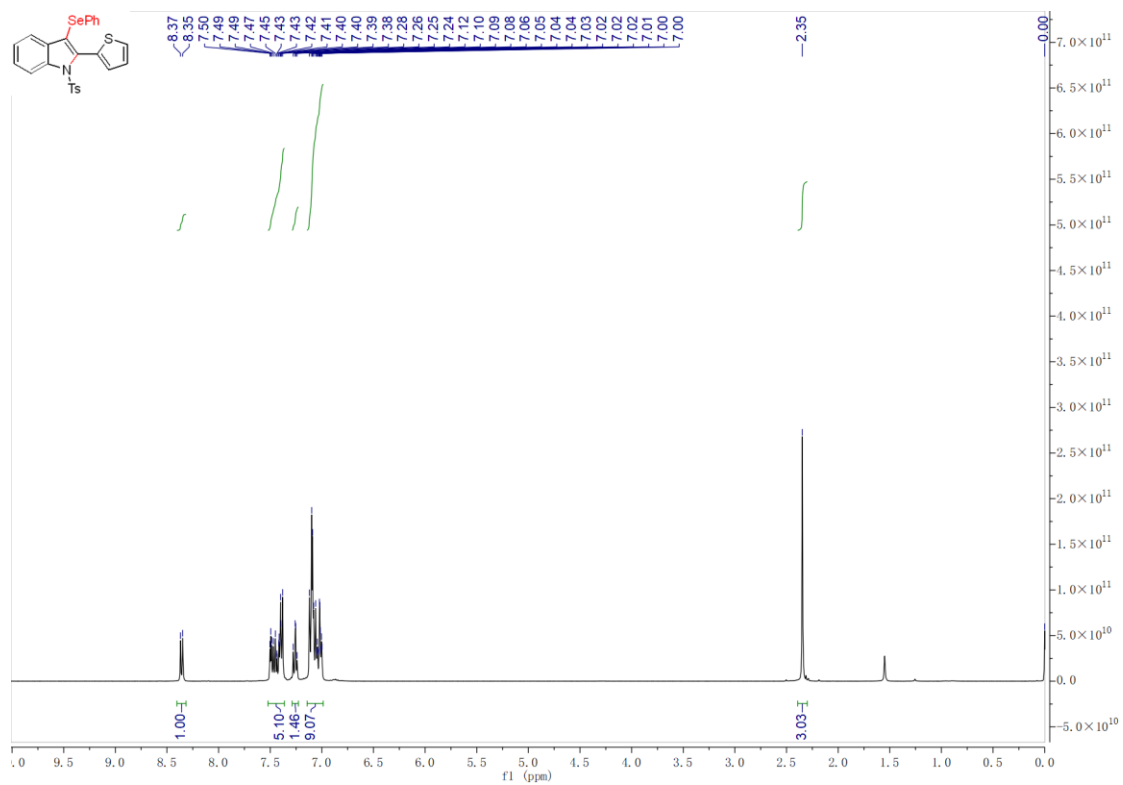


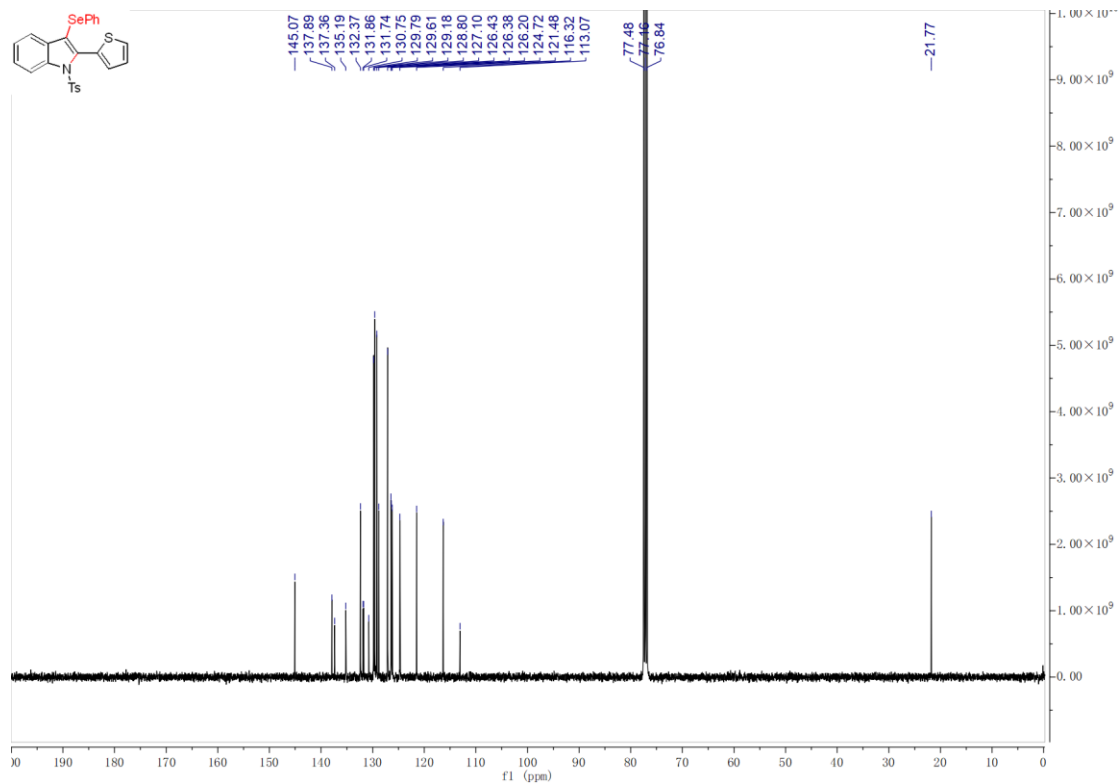
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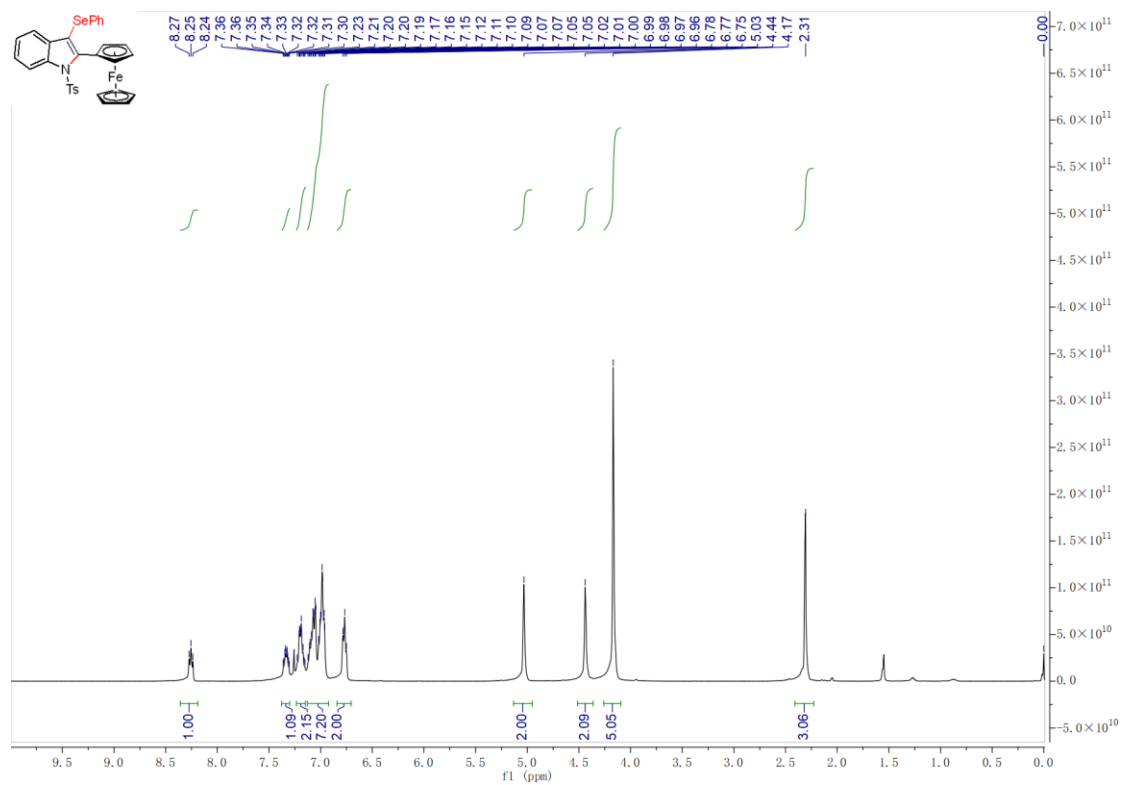


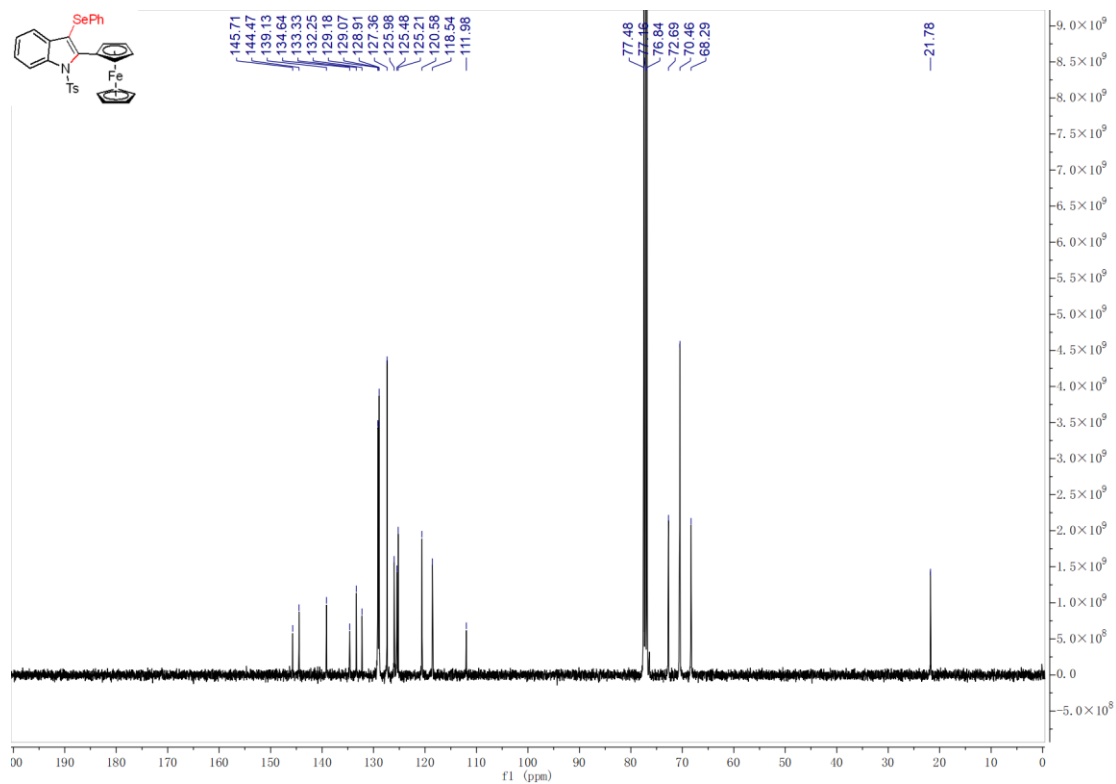
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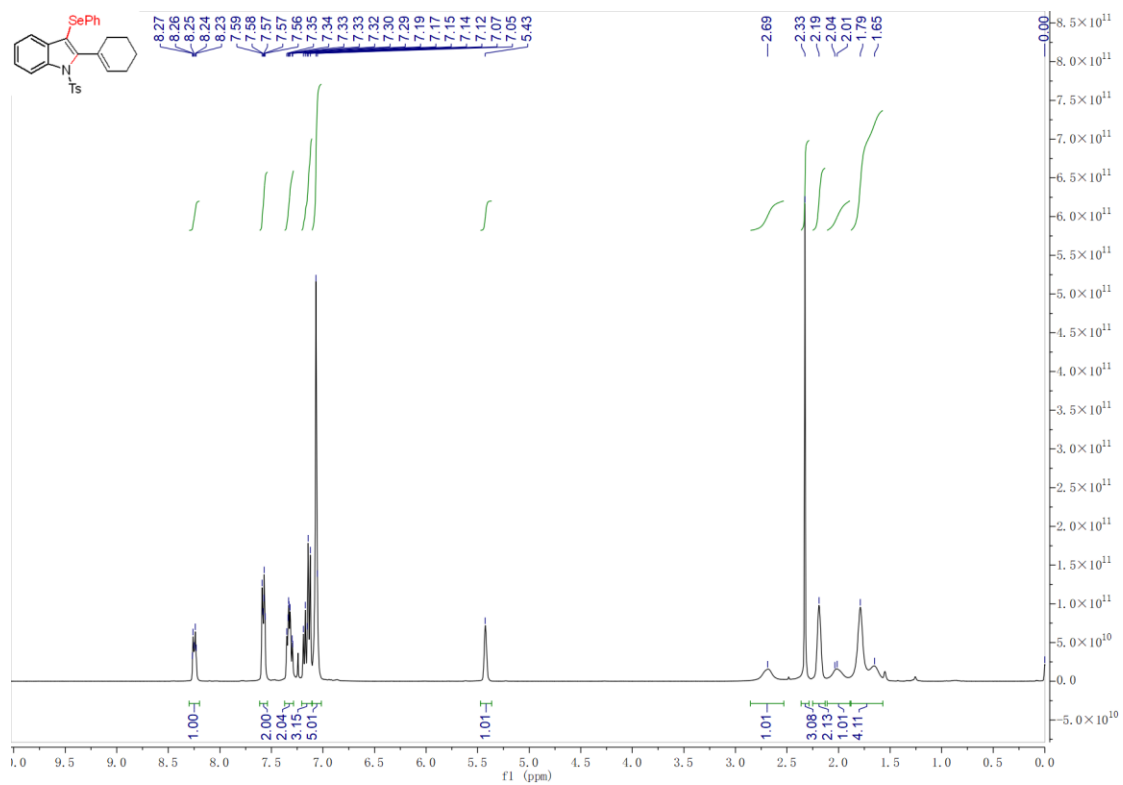


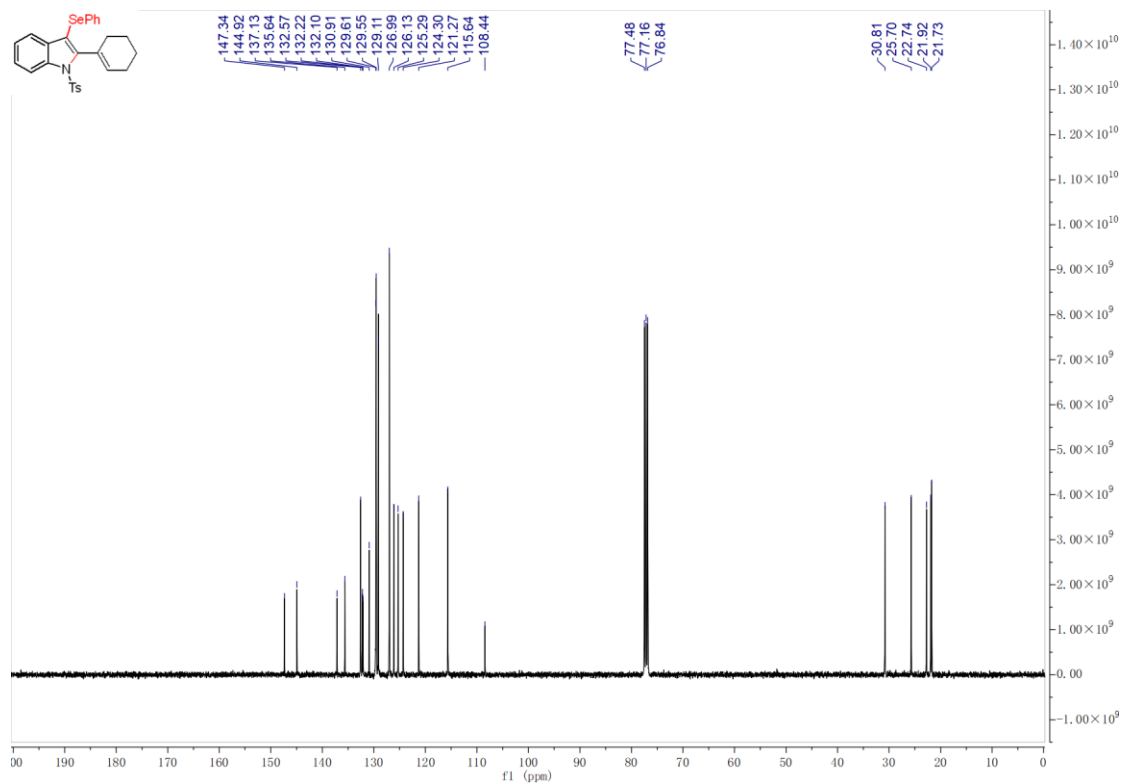
**6c, <sup>1</sup>H NMR & <sup>13</sup>C NMR**



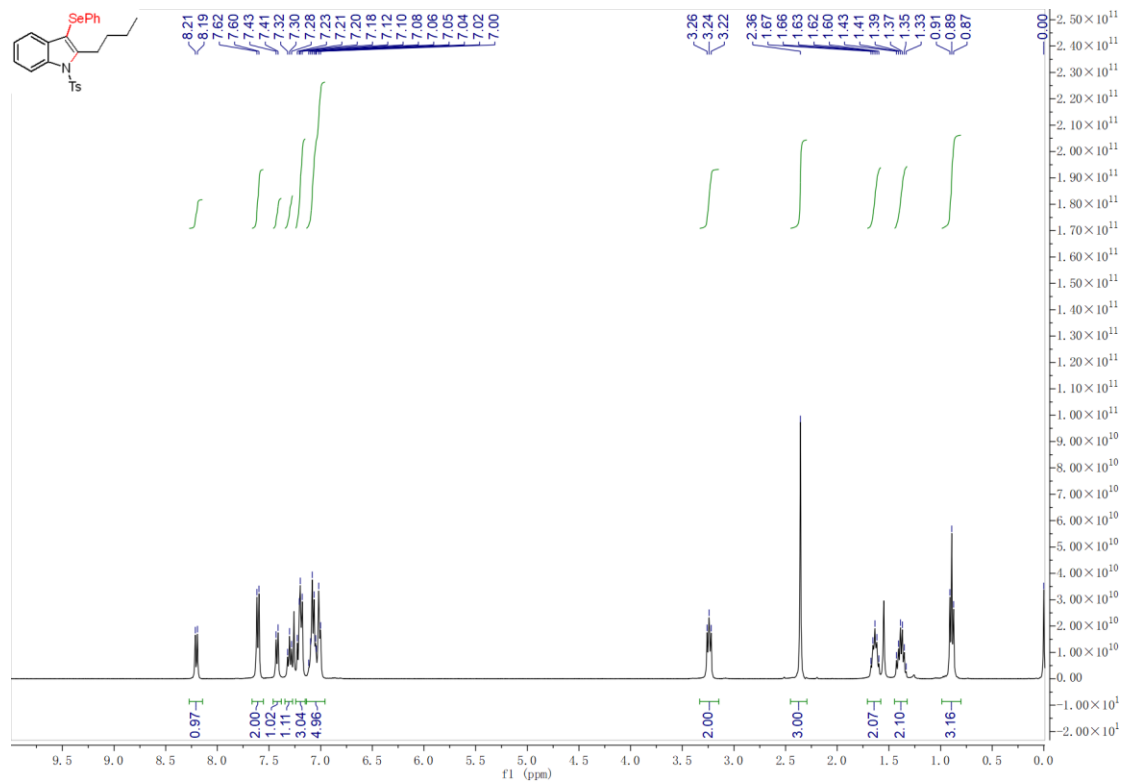


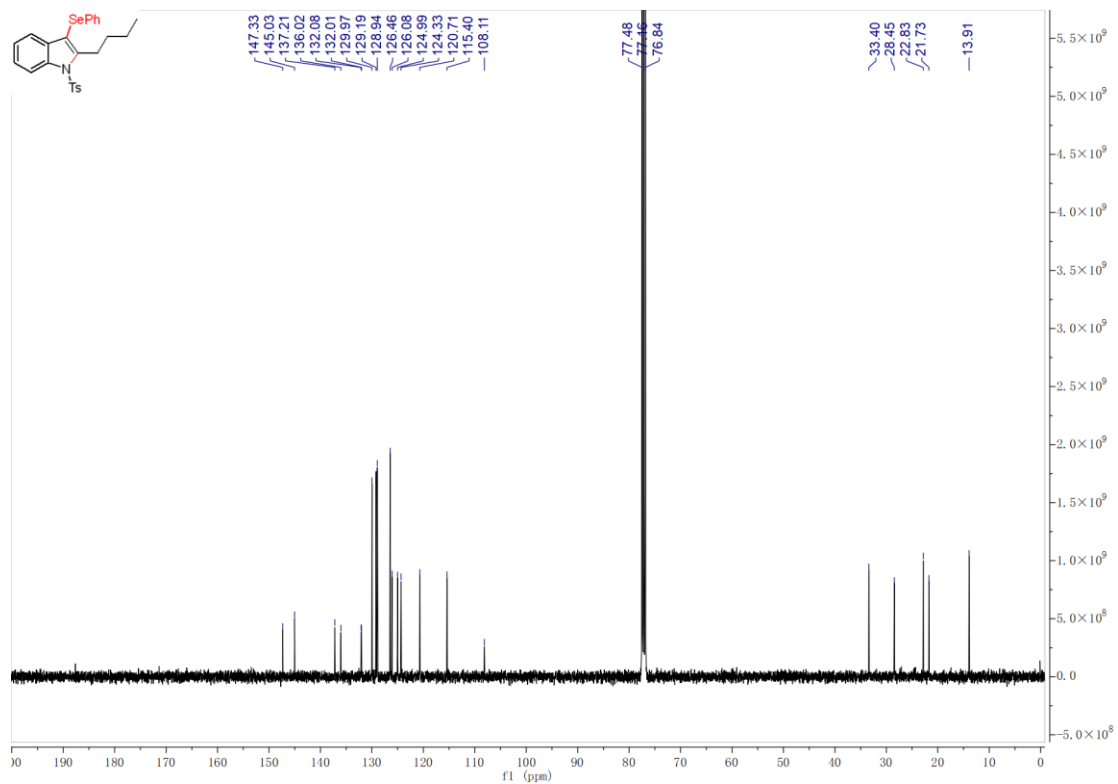
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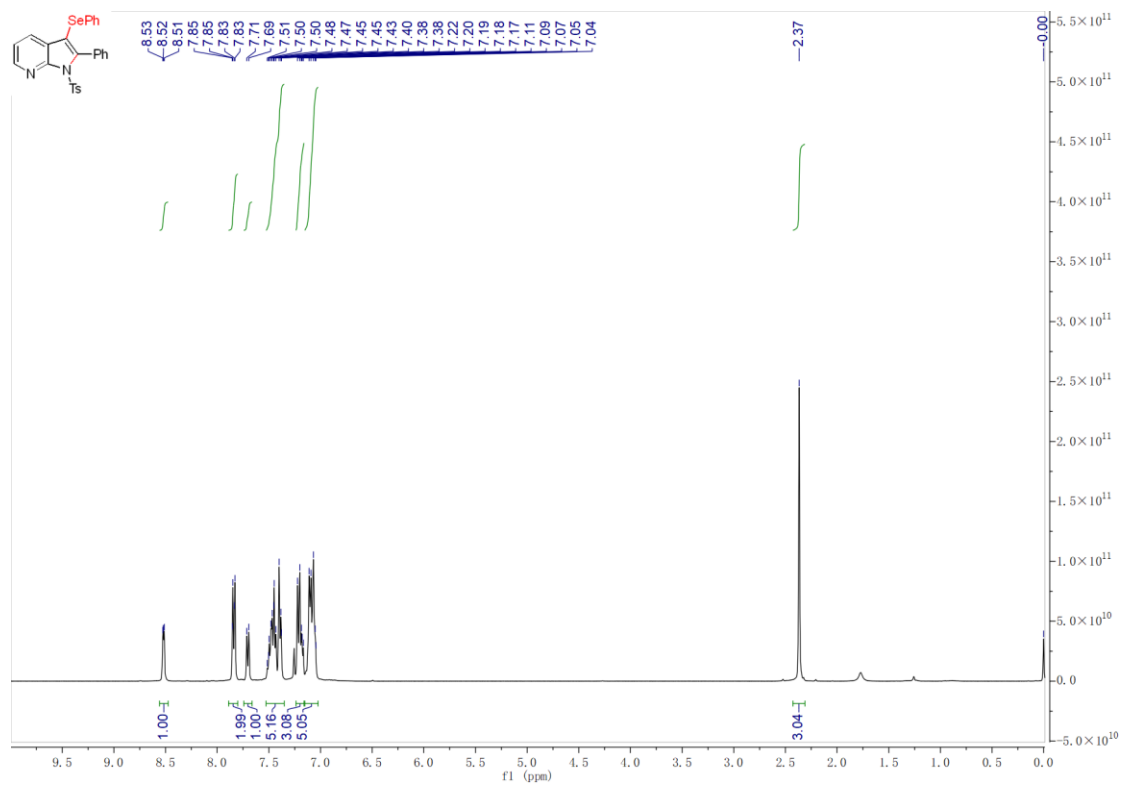


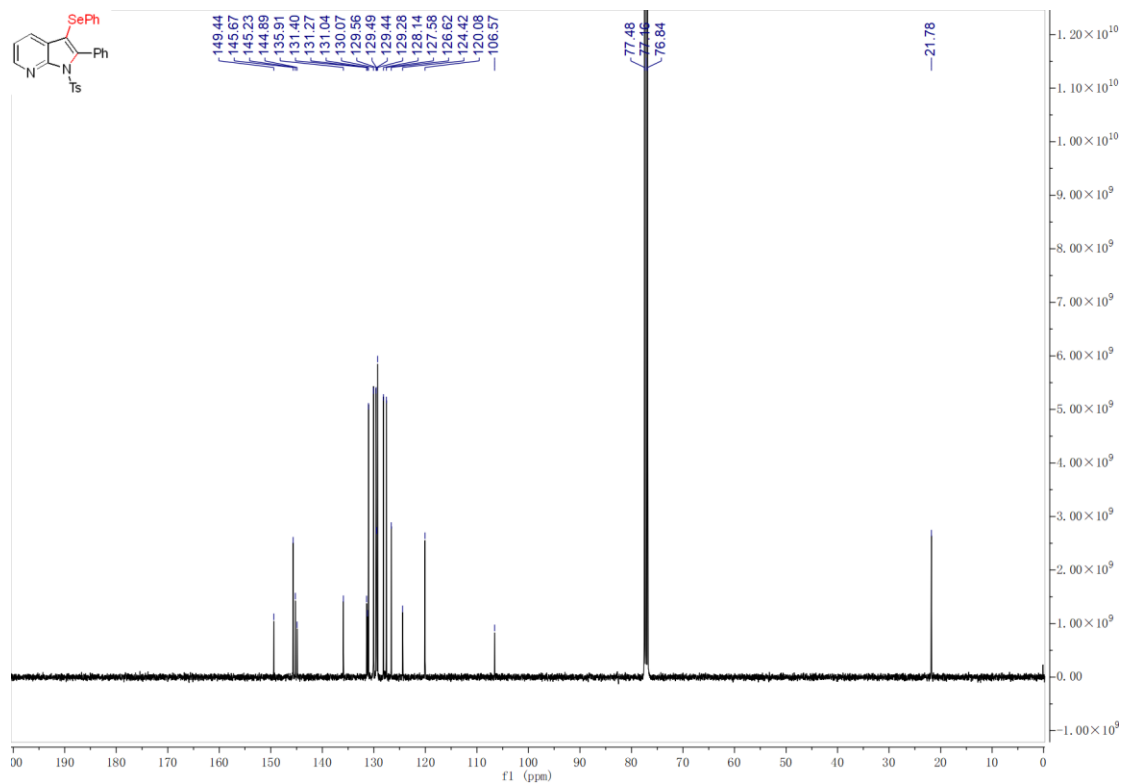
**8c, <sup>1</sup>H NMR & <sup>13</sup>C NMR**



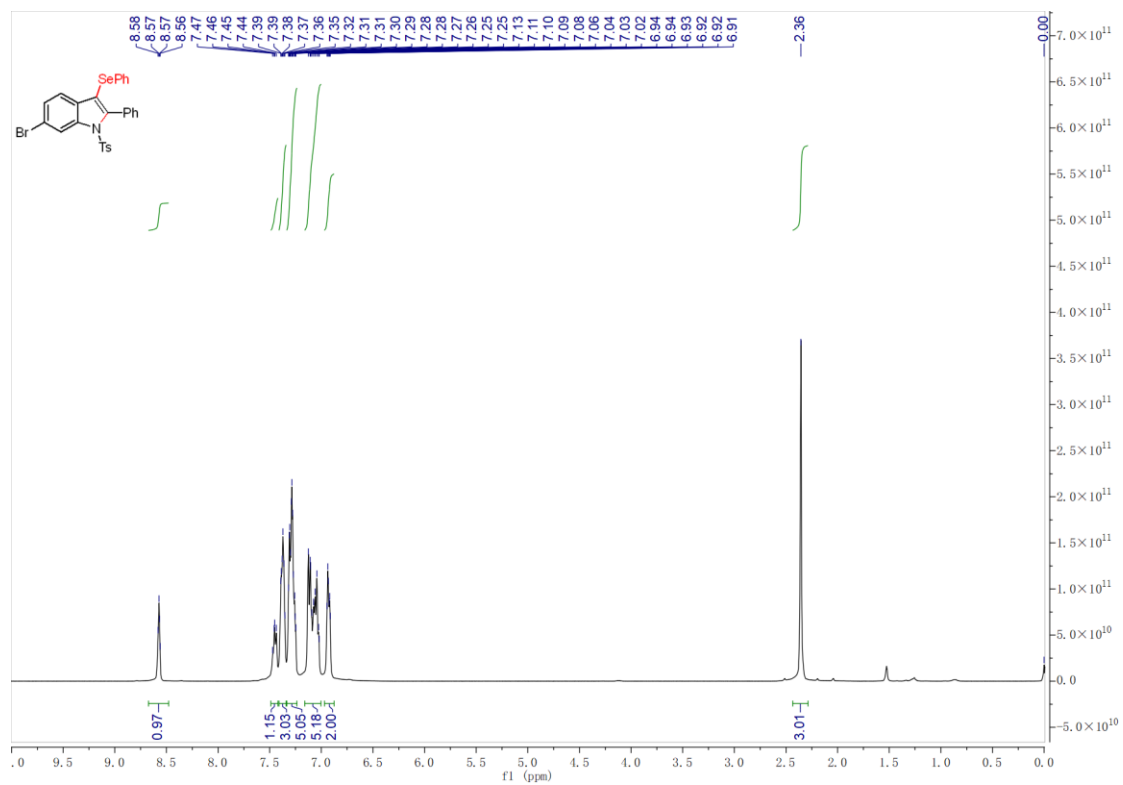


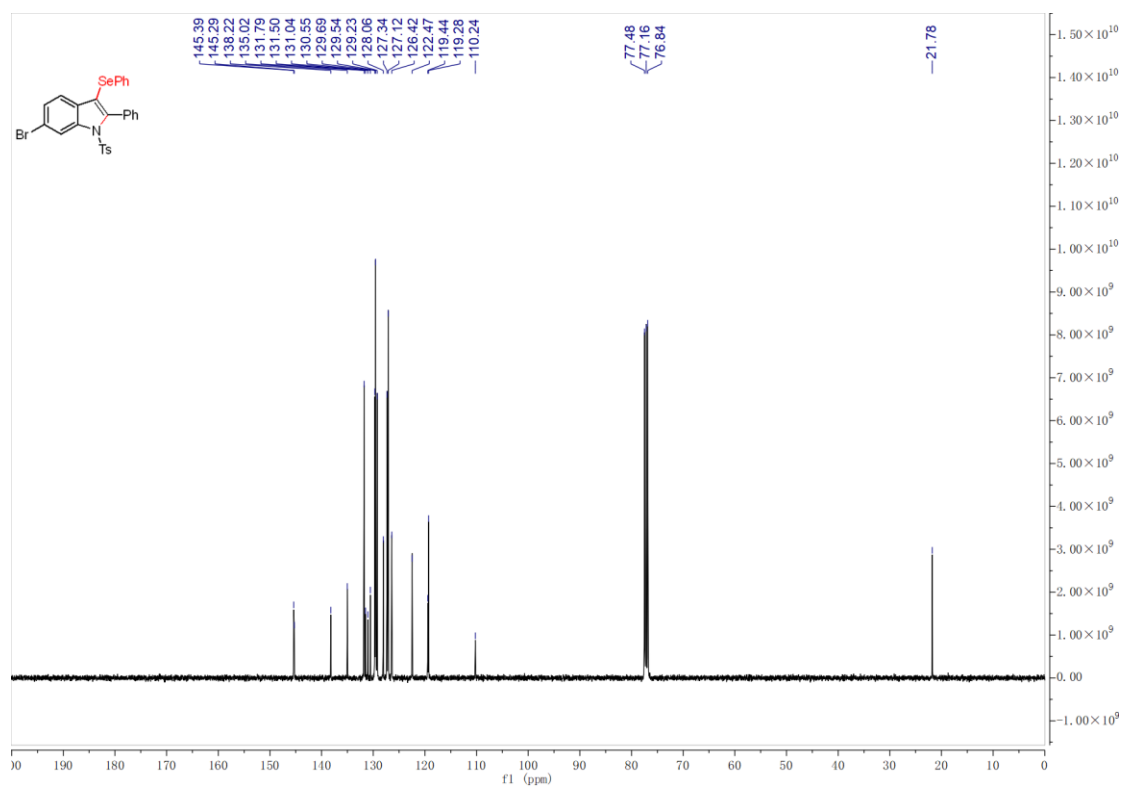
**9c, <sup>1</sup>H NMR & <sup>13</sup>C NMR**



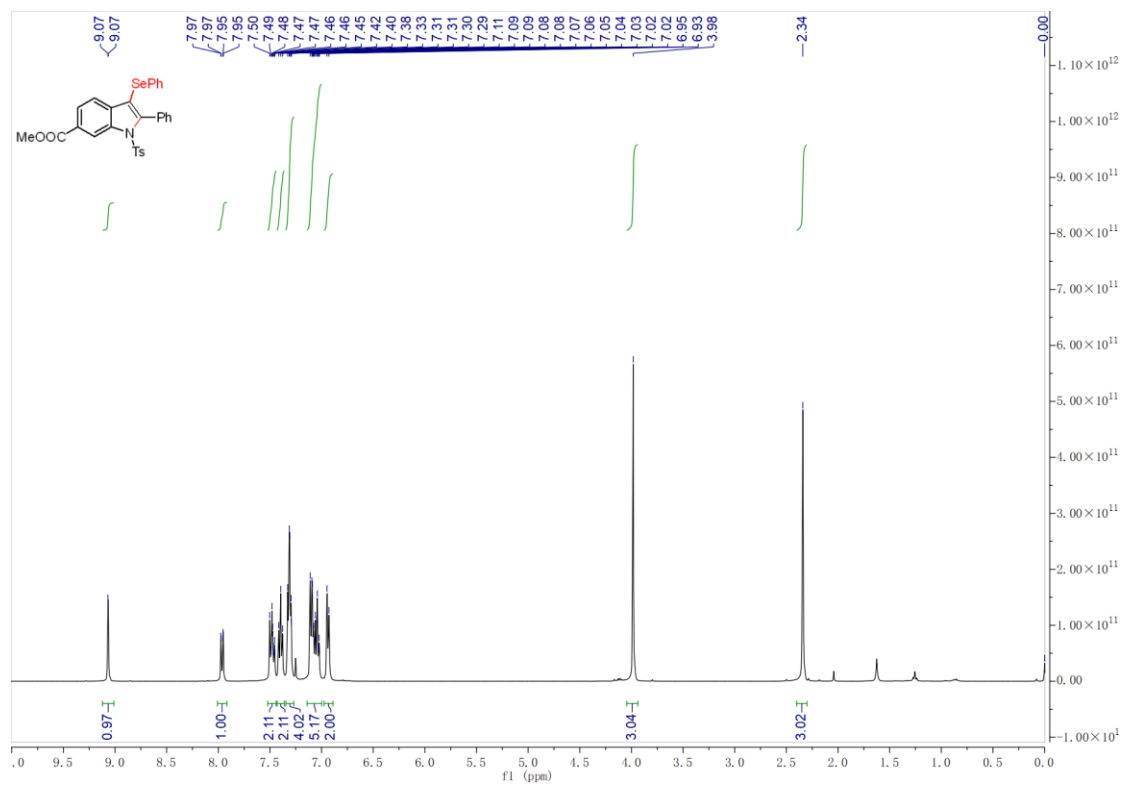


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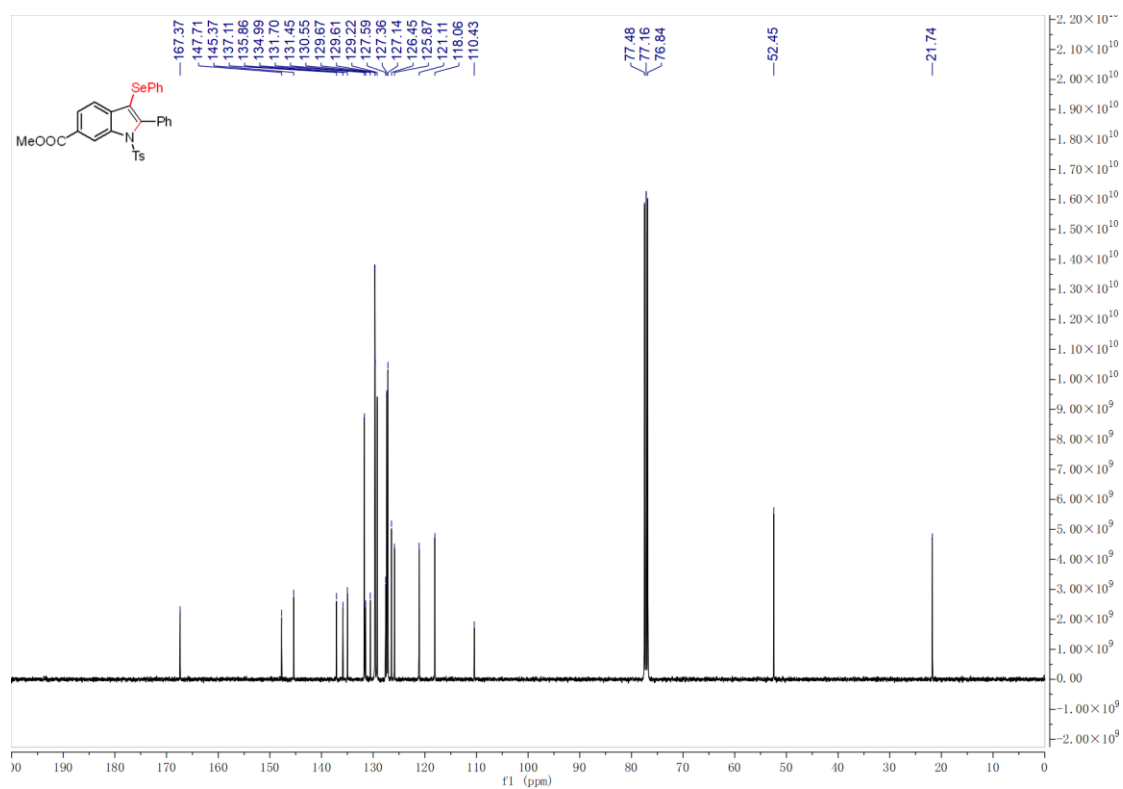




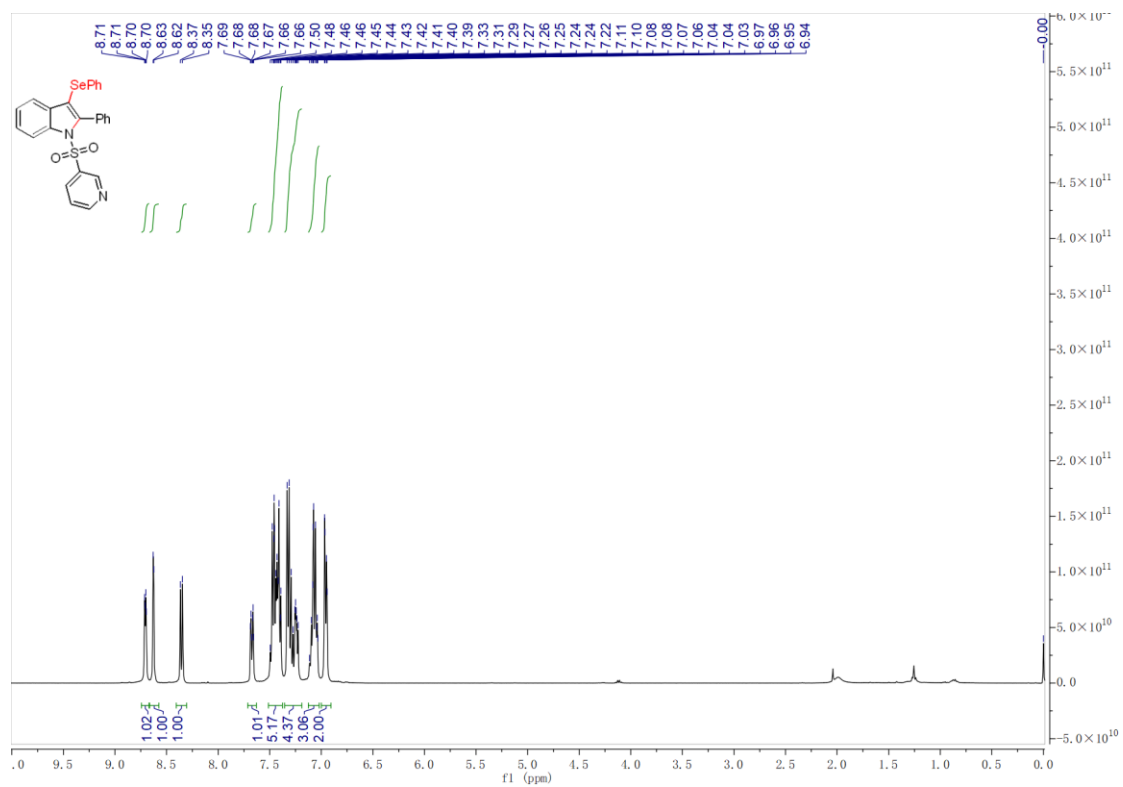
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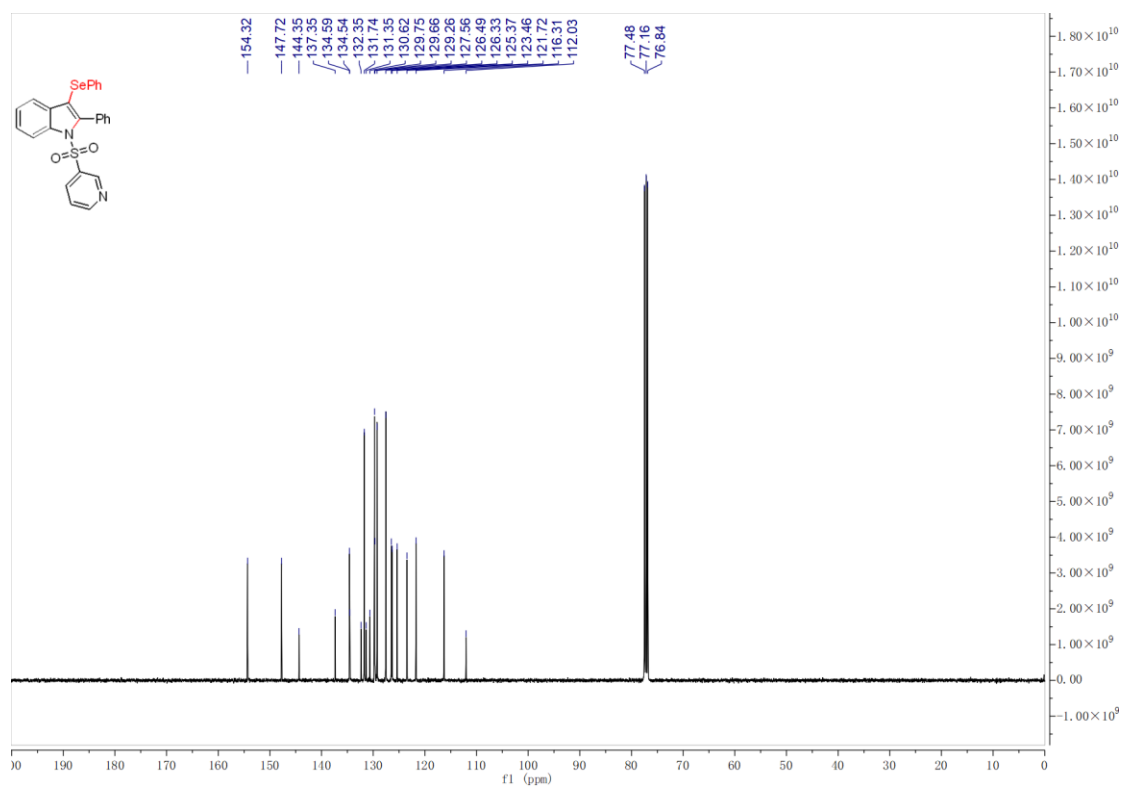




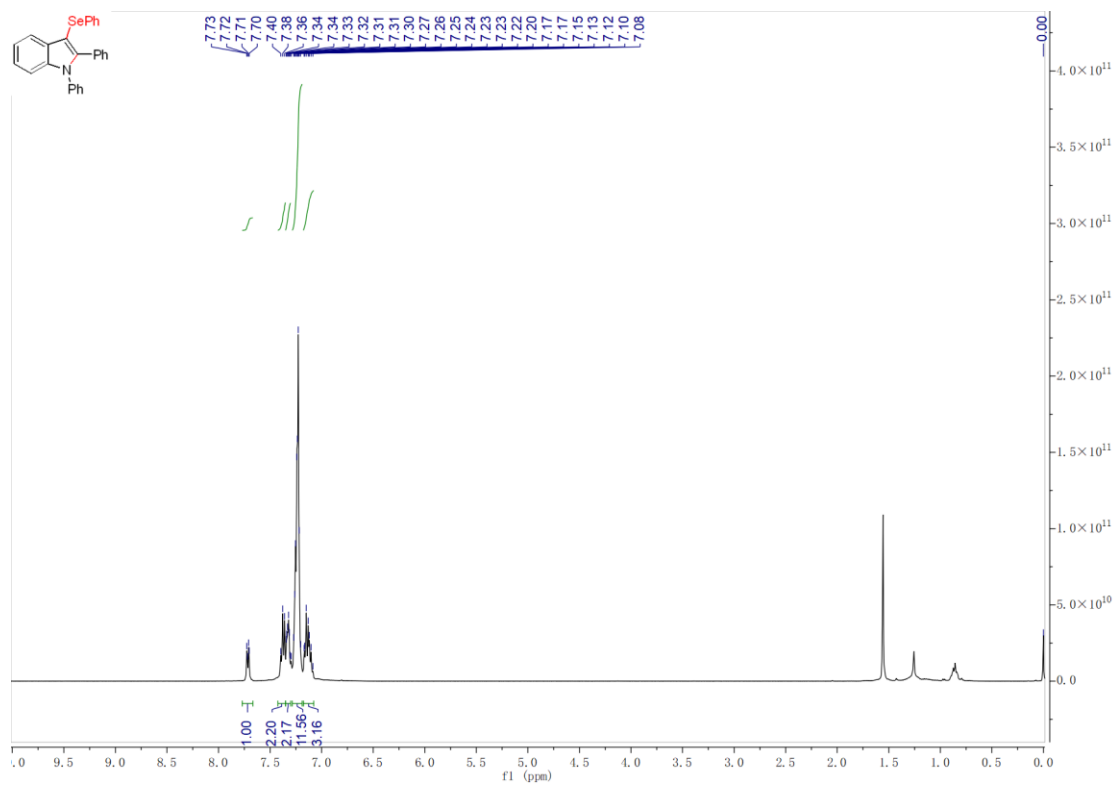


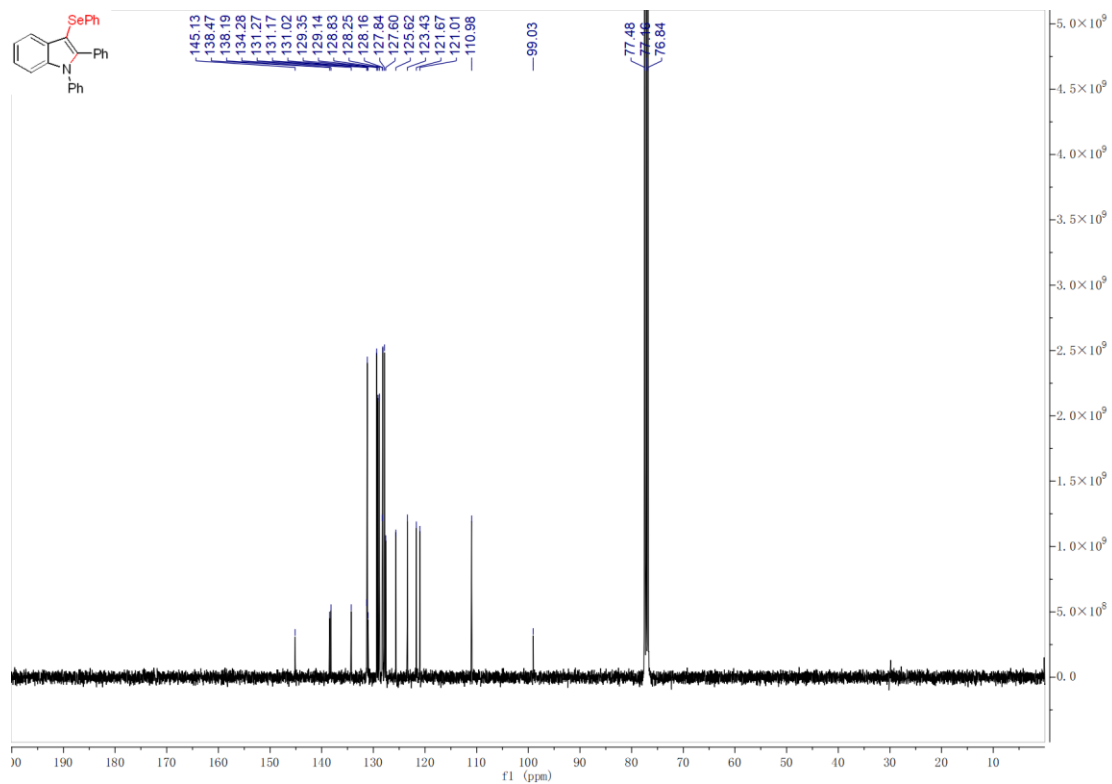
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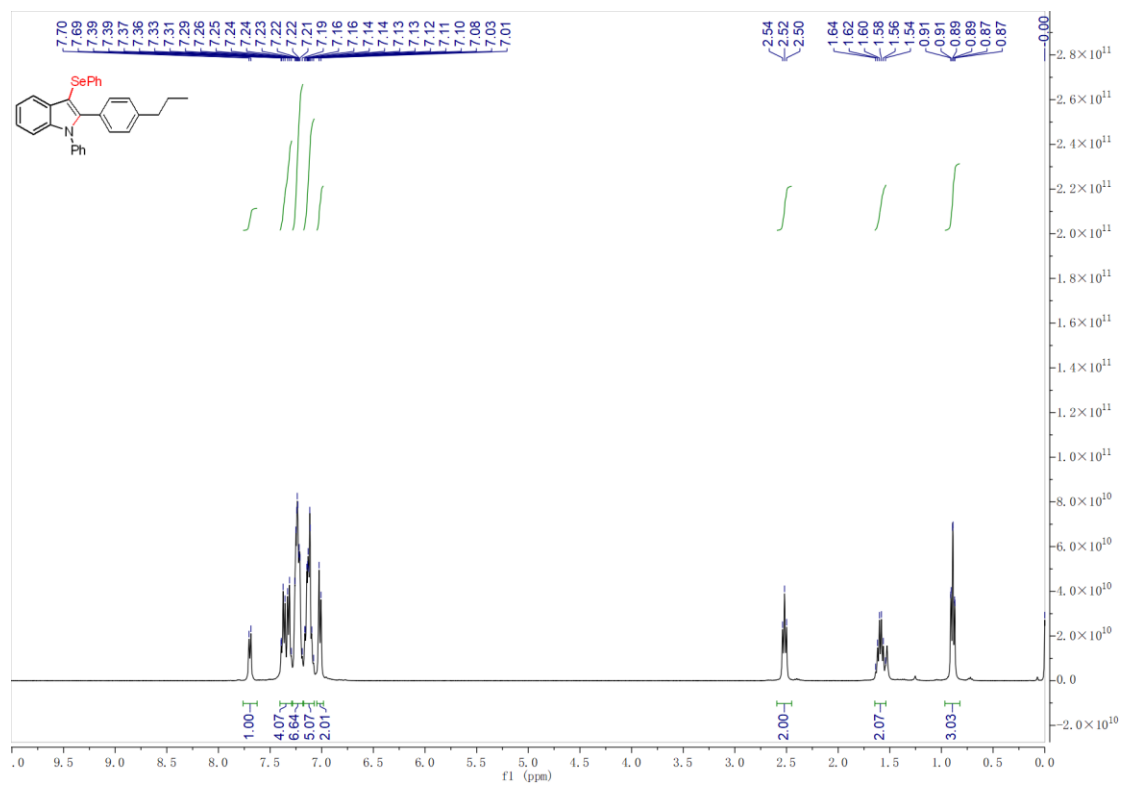


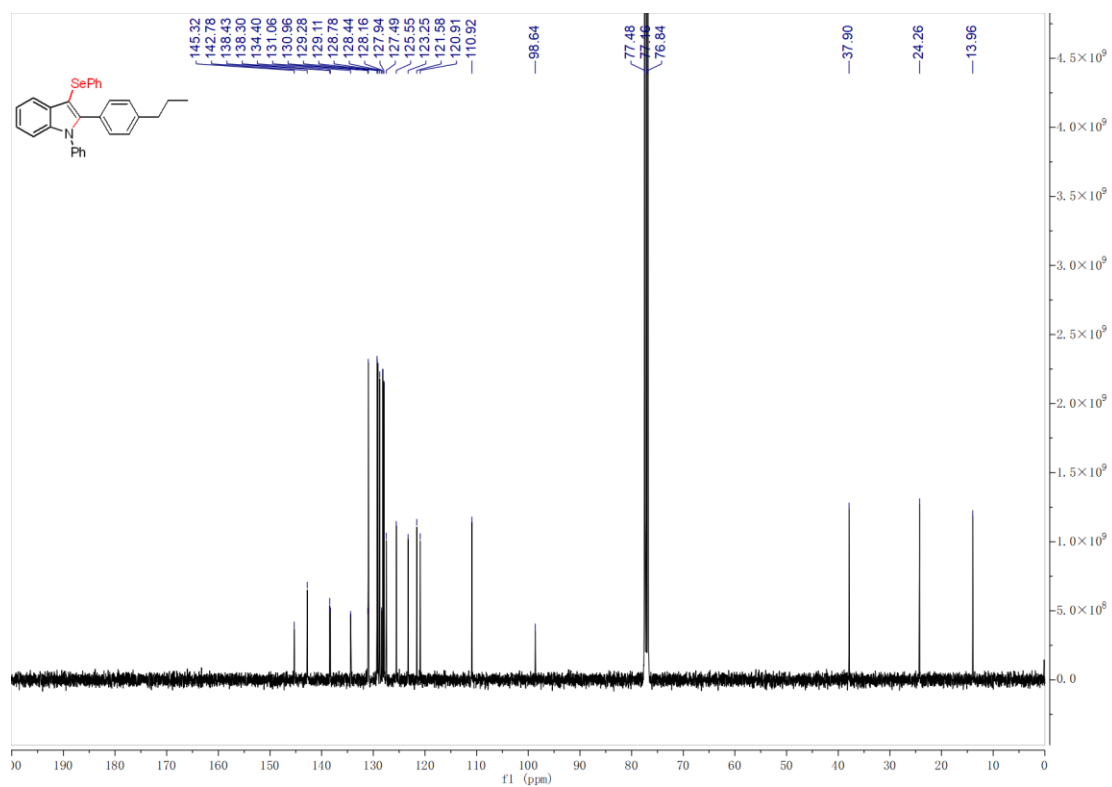
**13c**, <sup>1</sup>H NMR & <sup>13</sup>C NMR



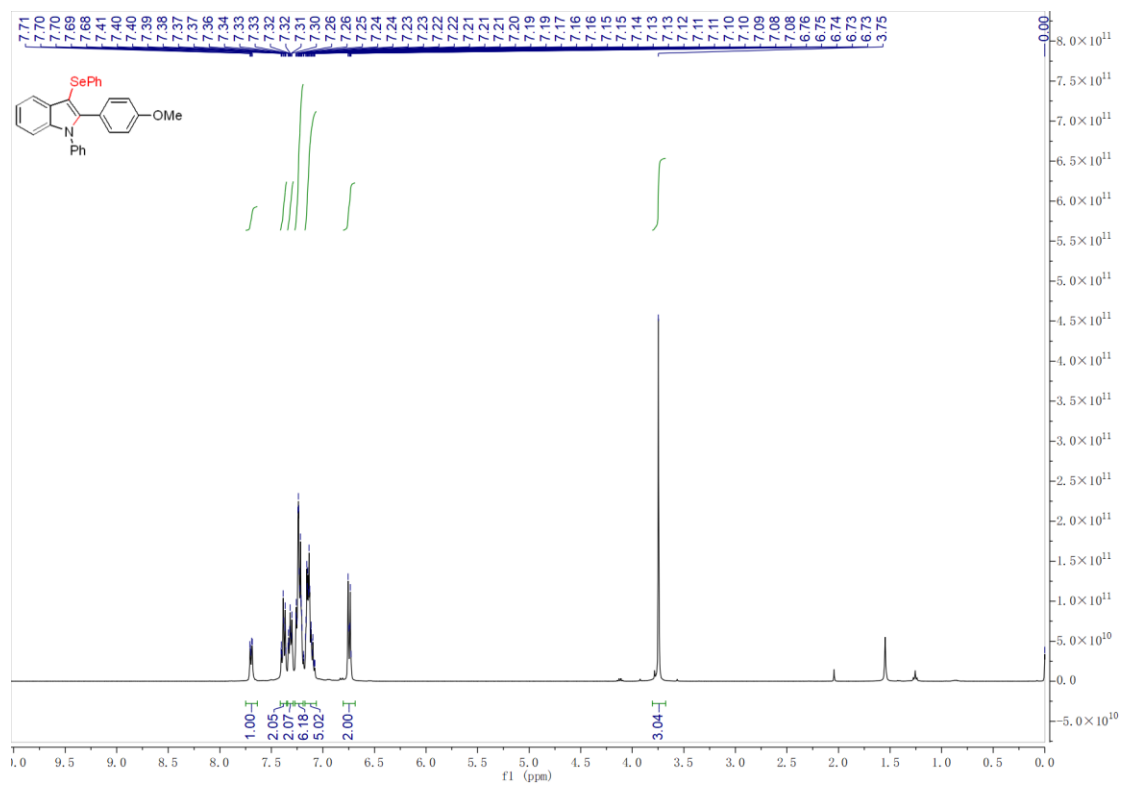


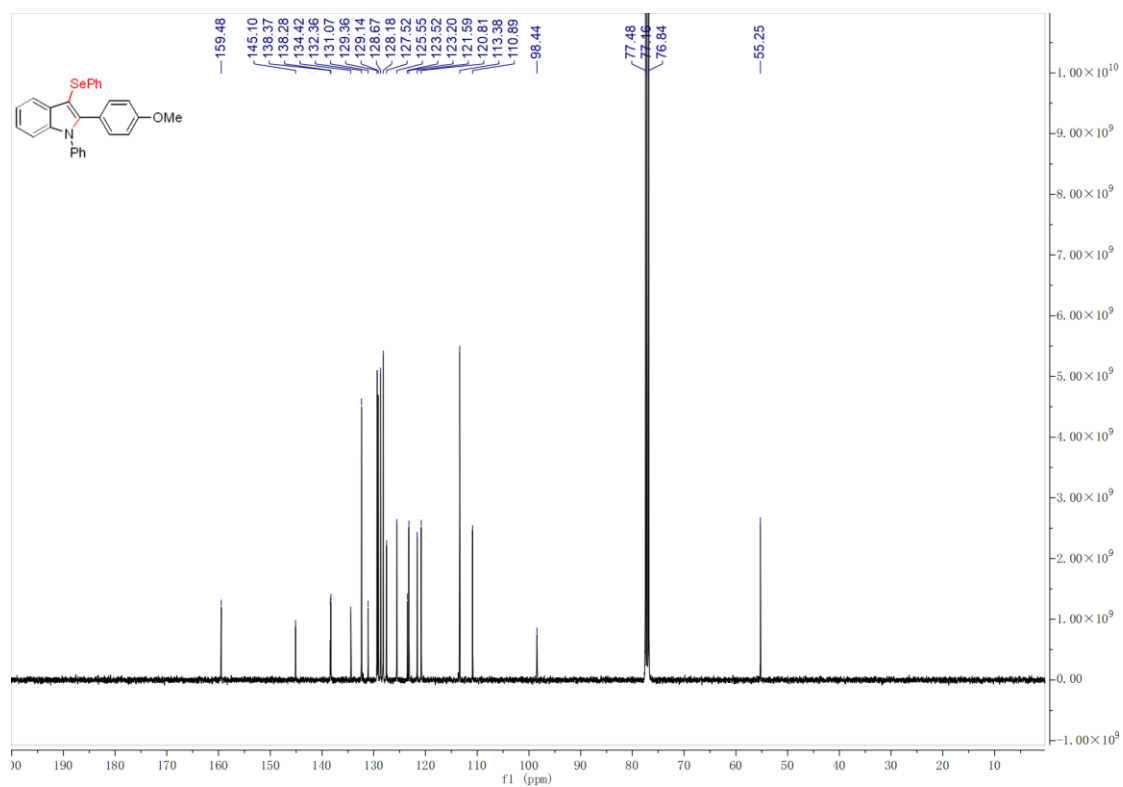
**14c, <sup>1</sup>H NMR & <sup>13</sup>C NMR**



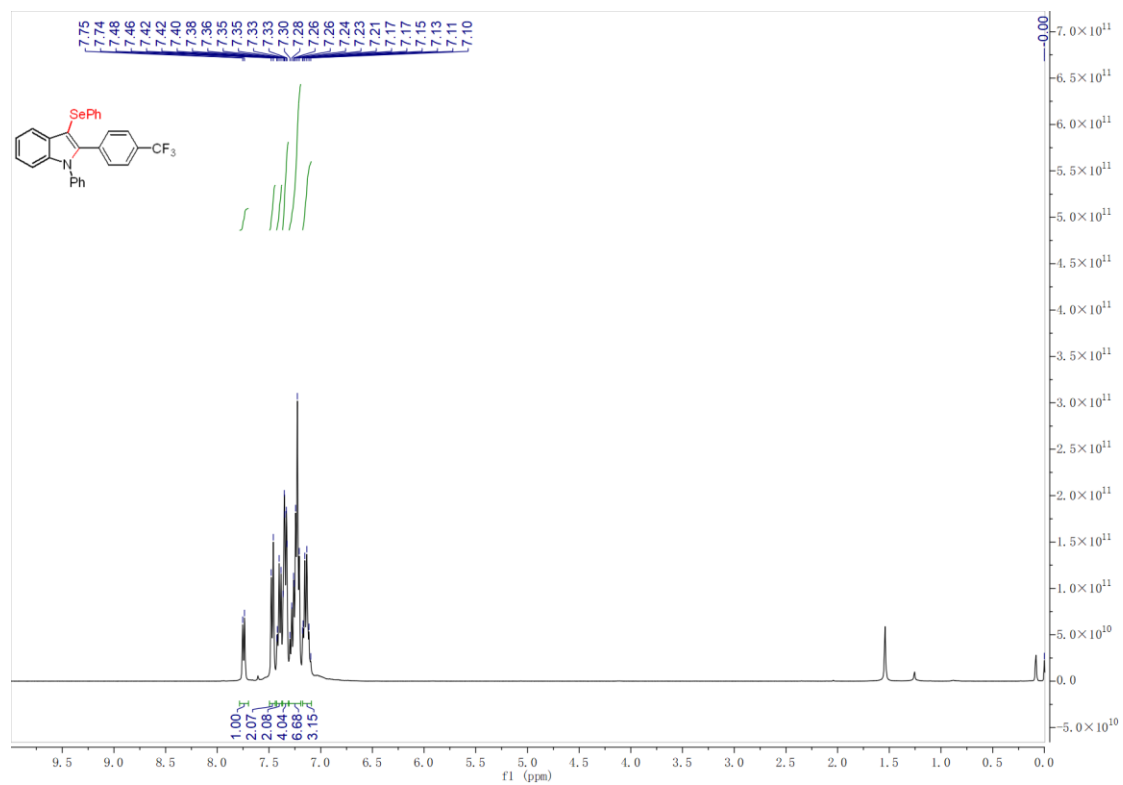


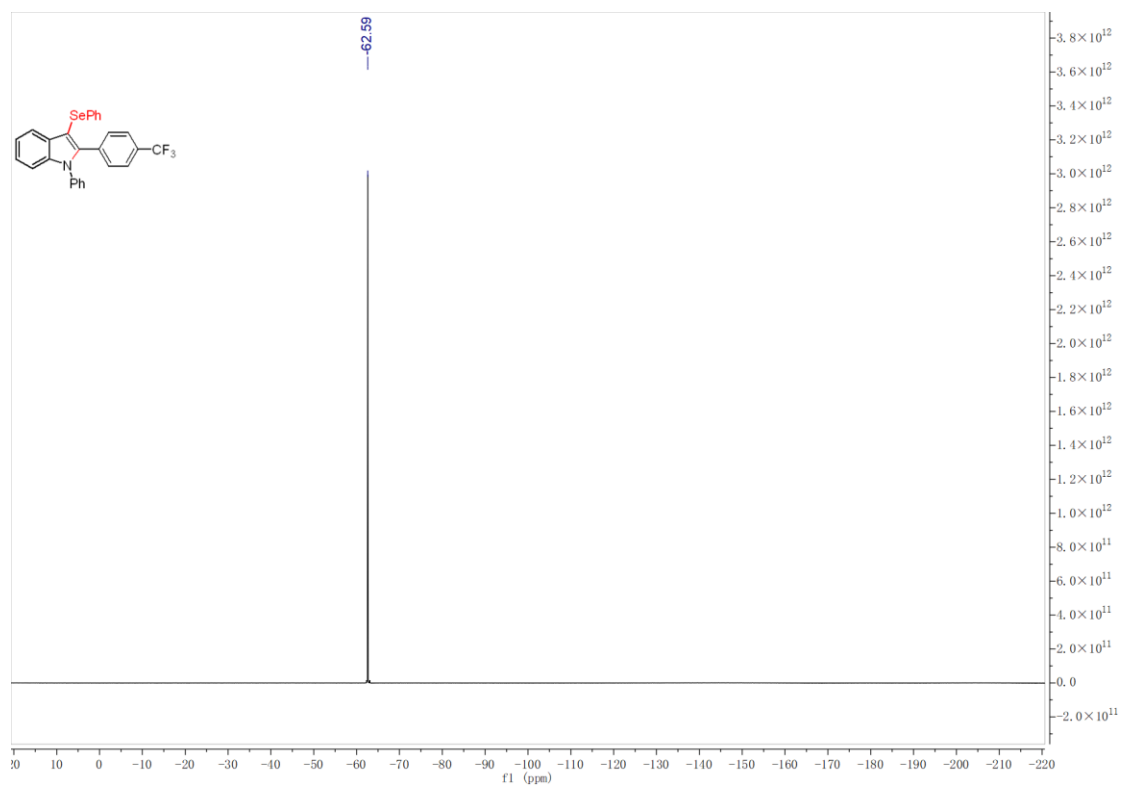
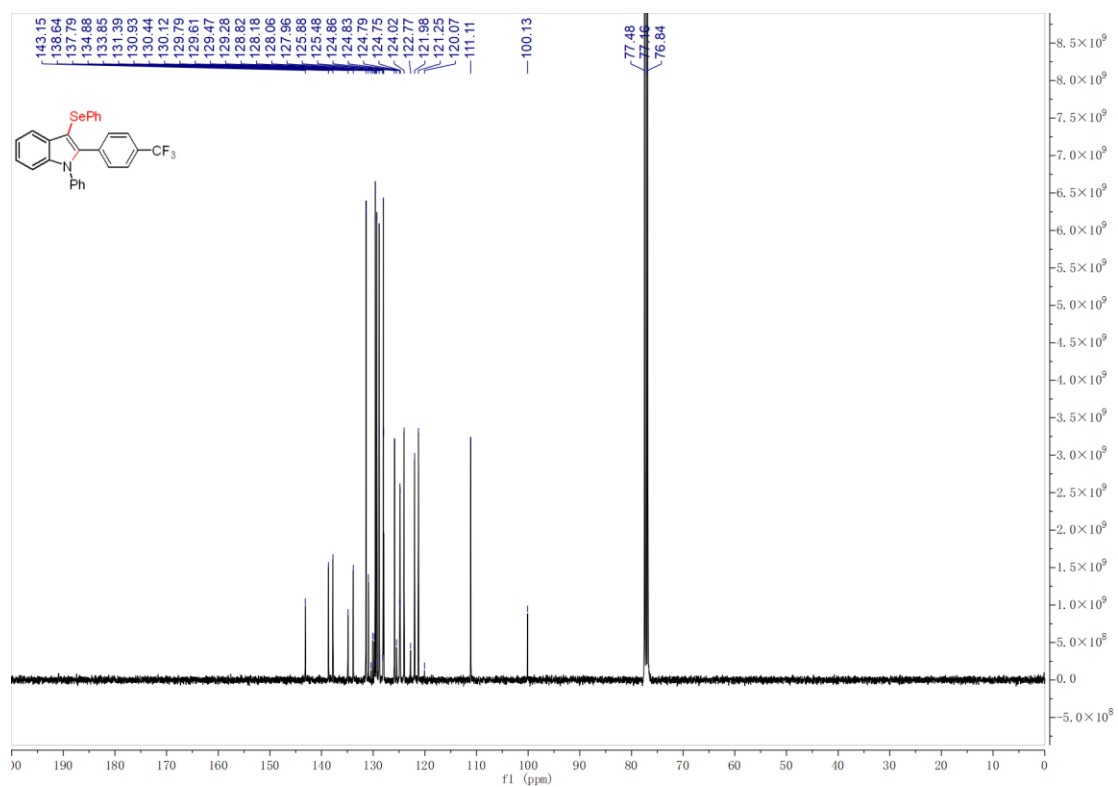
**15c, <sup>1</sup>H NMR & <sup>13</sup>C NMR**



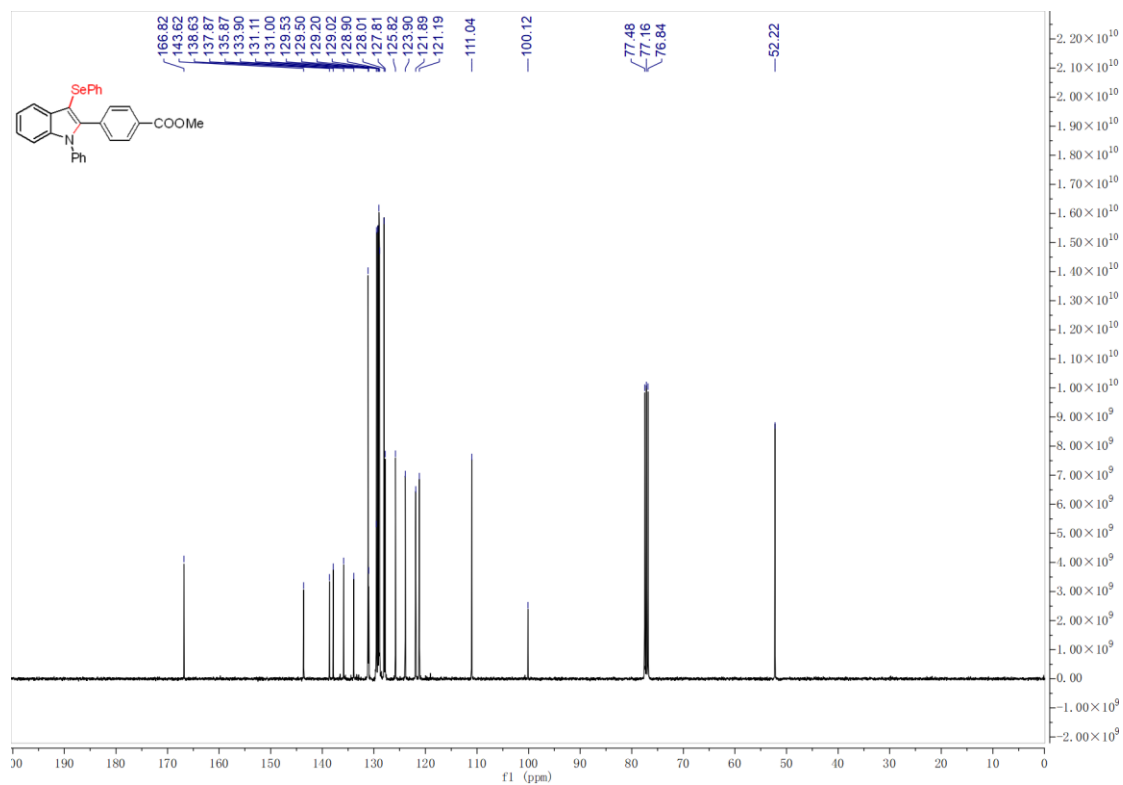
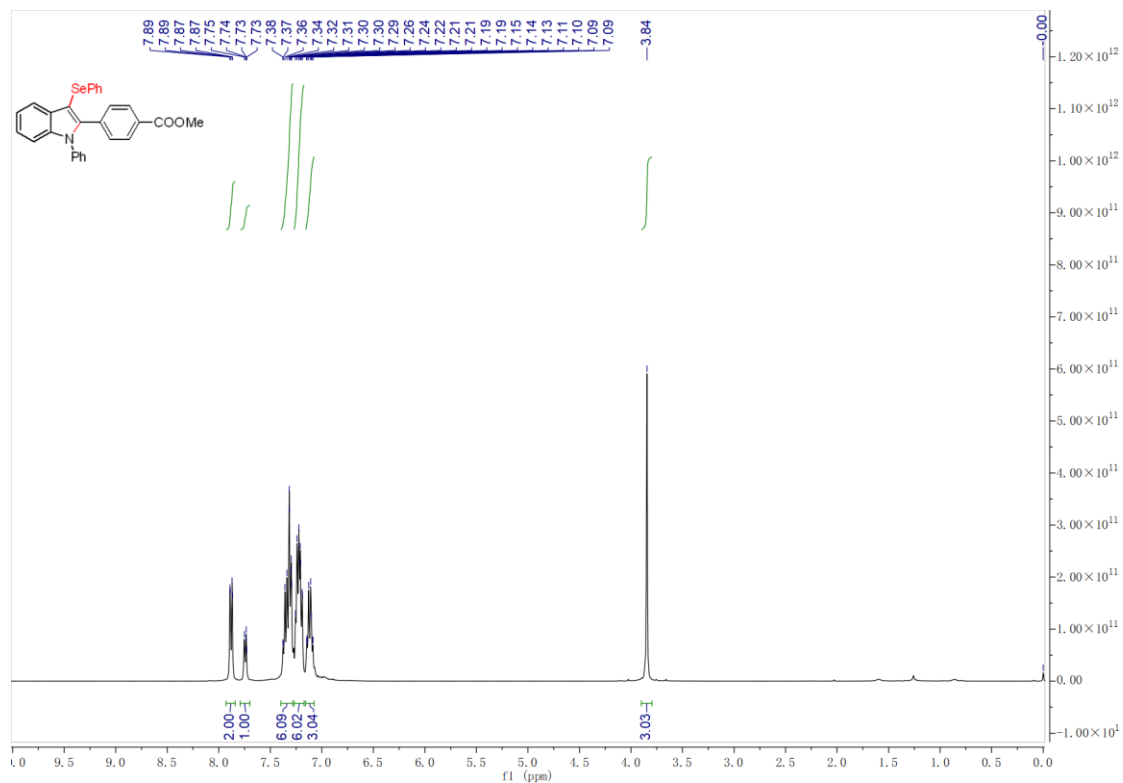


**16c**, <sup>1</sup>H NMR & <sup>13</sup>C NMR & <sup>19</sup>F NMR

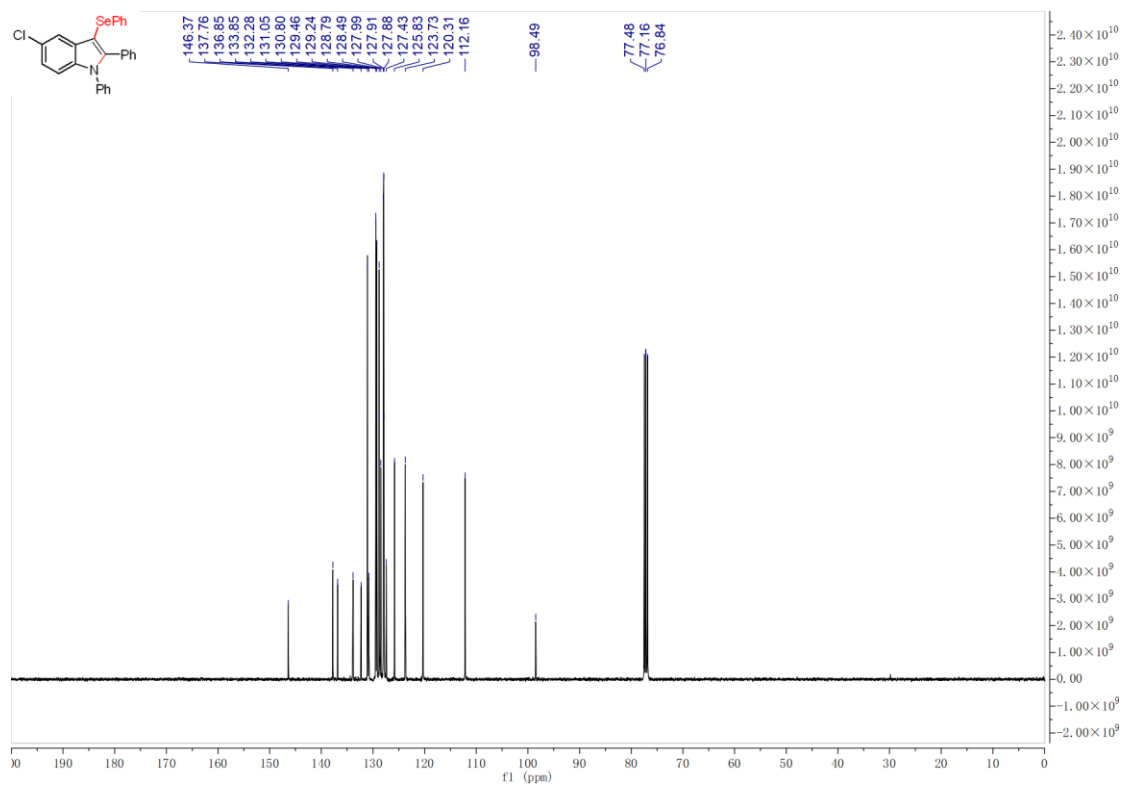
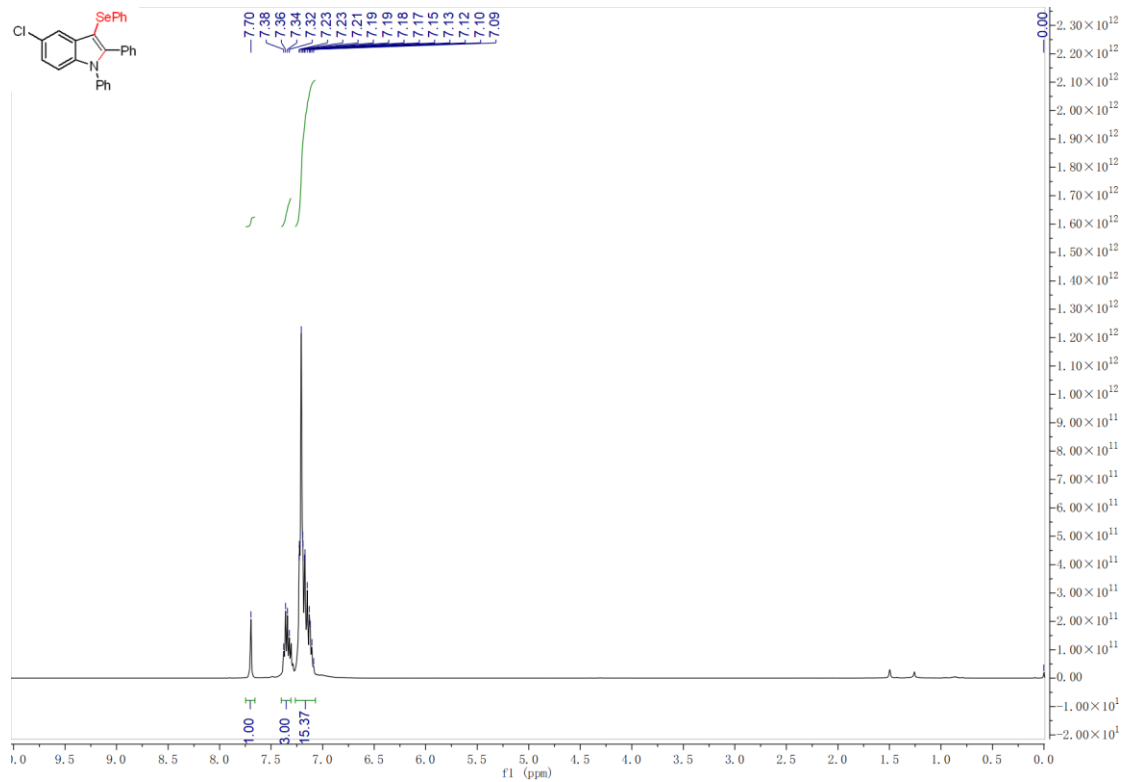




17c, <sup>1</sup>H NMR & <sup>13</sup>C NMR

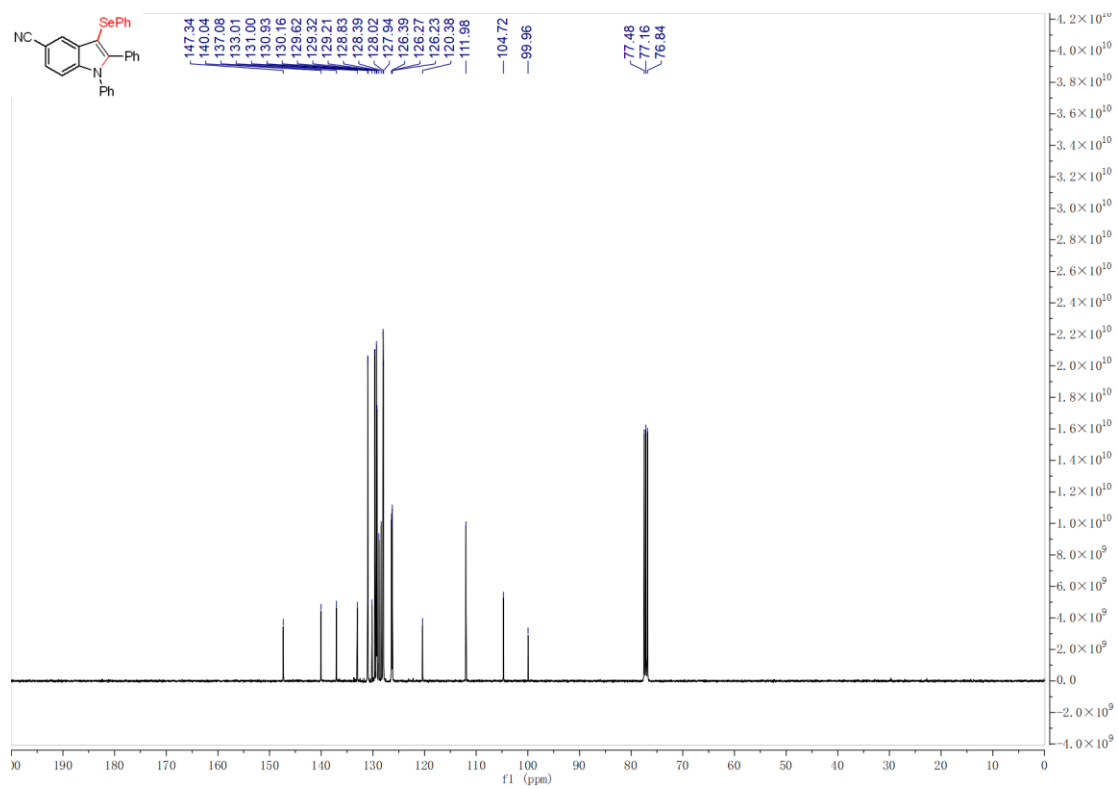
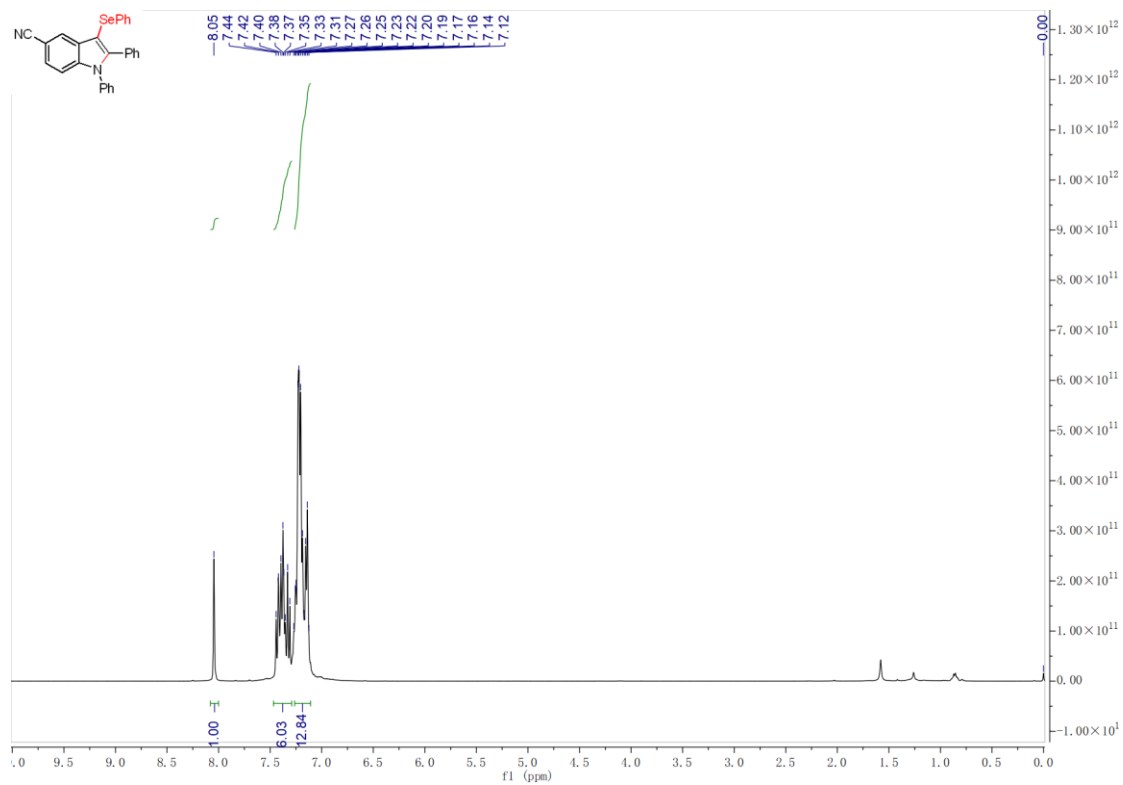


**18c**,  $^1\text{H}$  NMR &  $^{13}\text{C}$  NMR

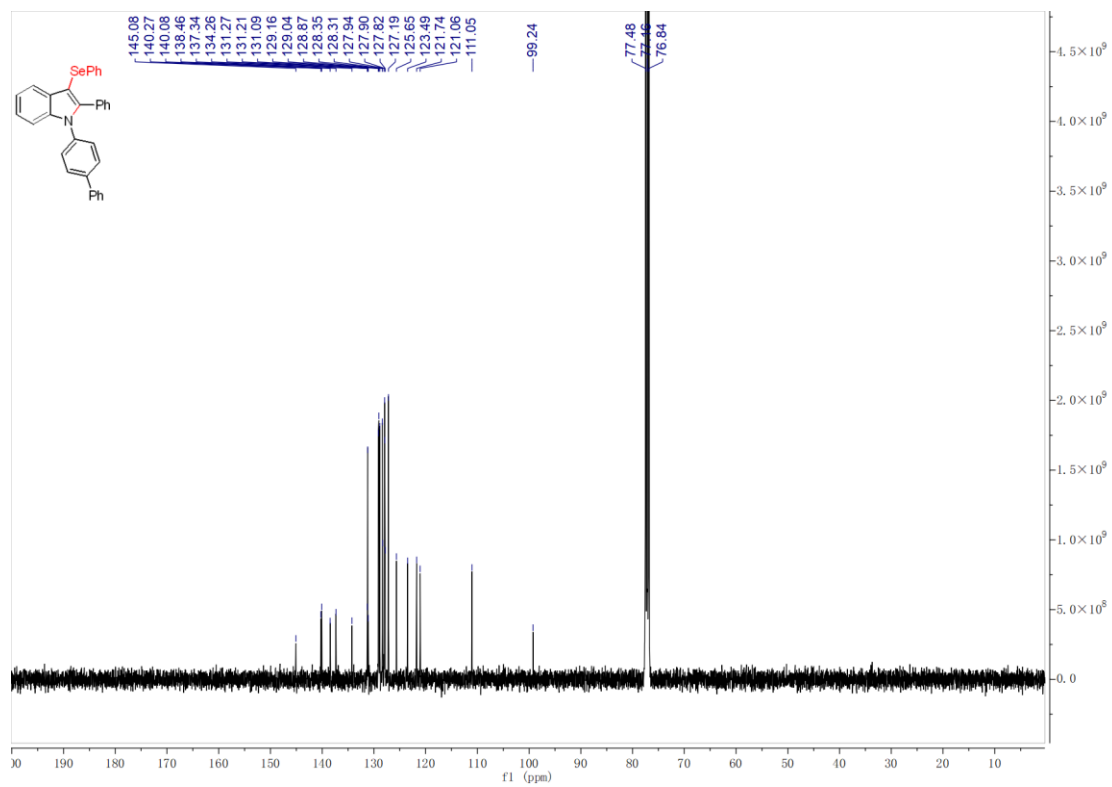
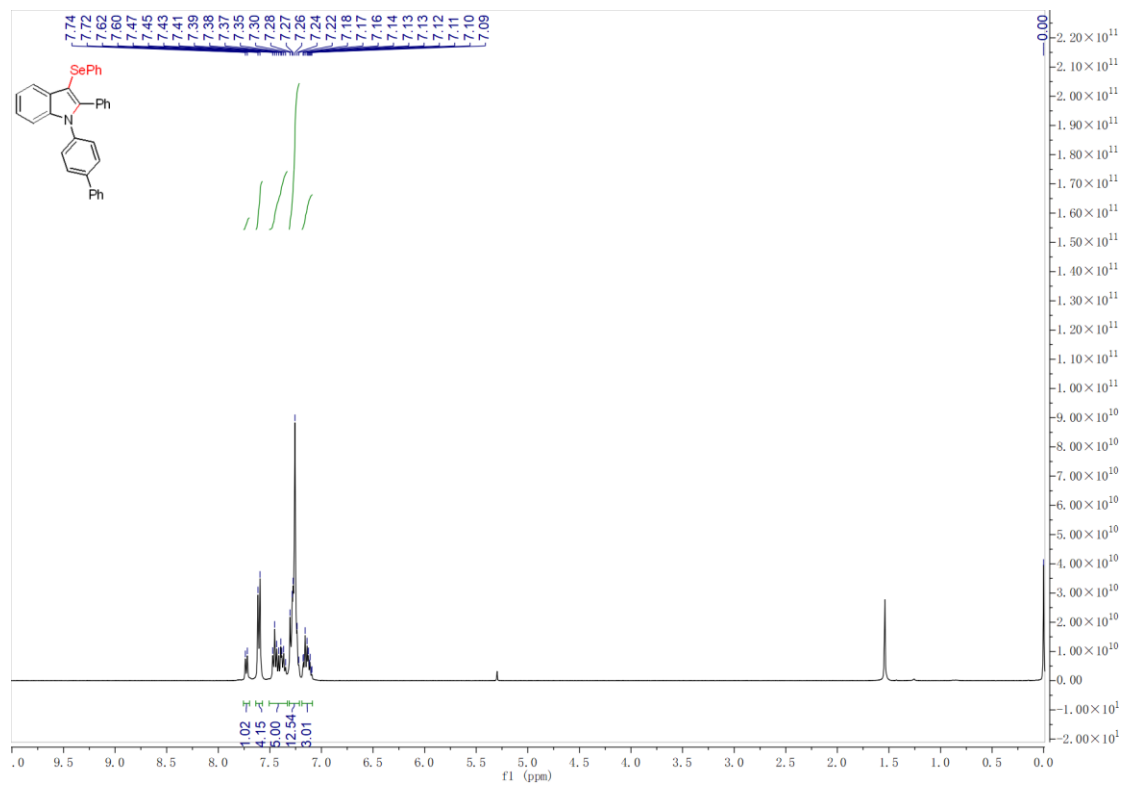




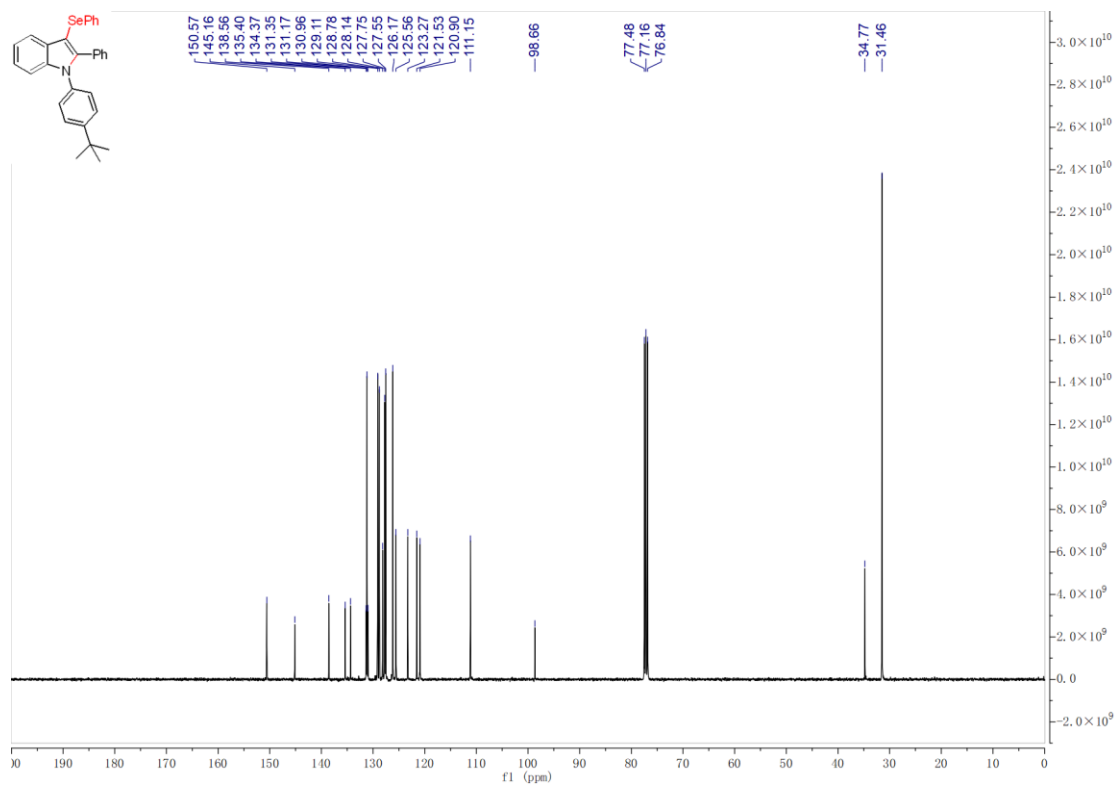
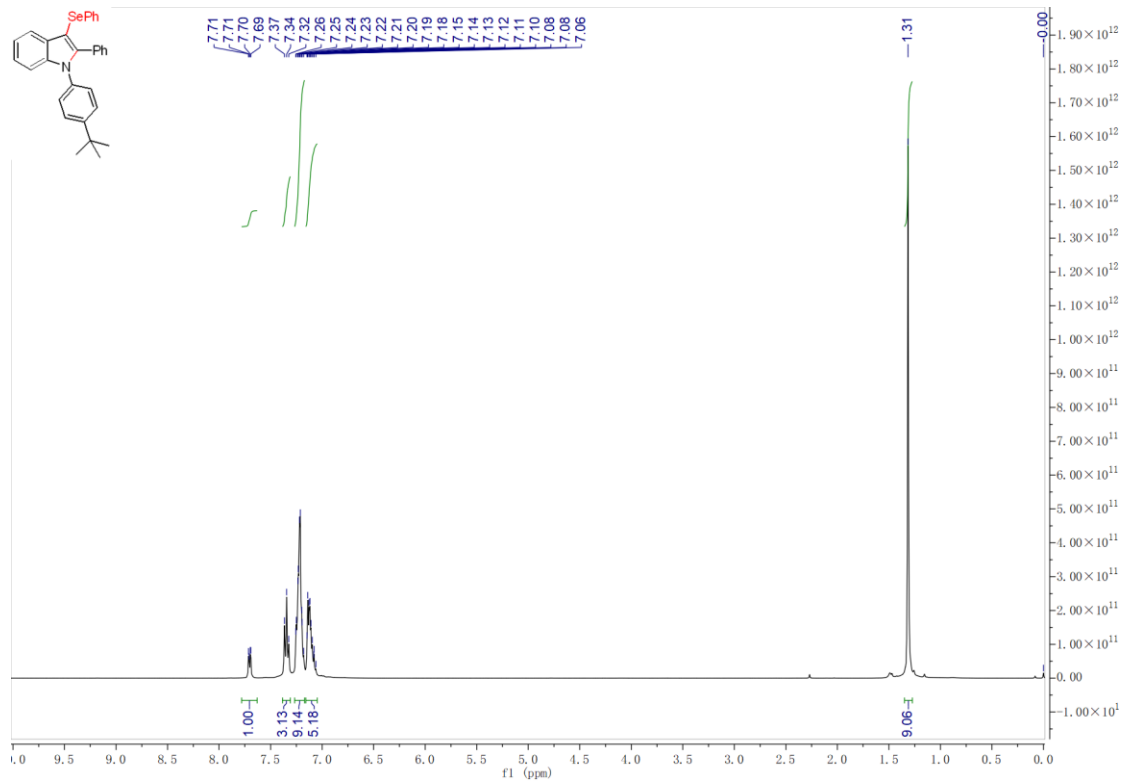
# 19c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



20c, <sup>1</sup>H NMR & <sup>13</sup>C NMR

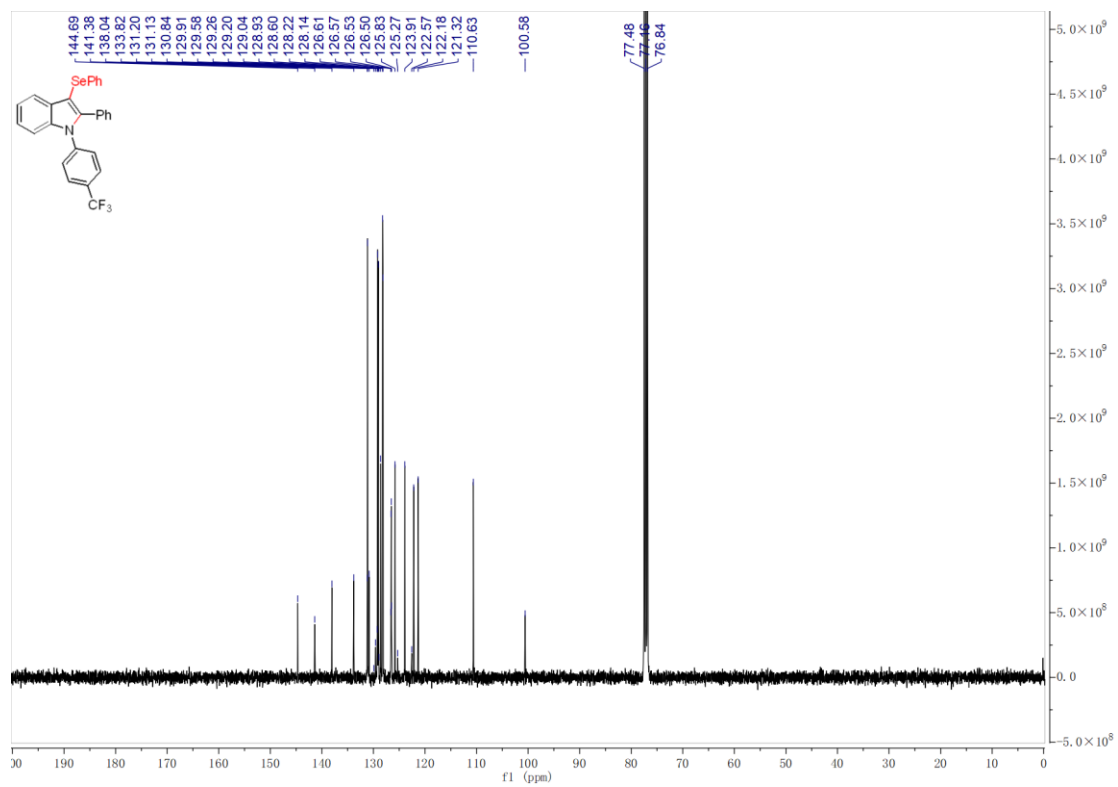
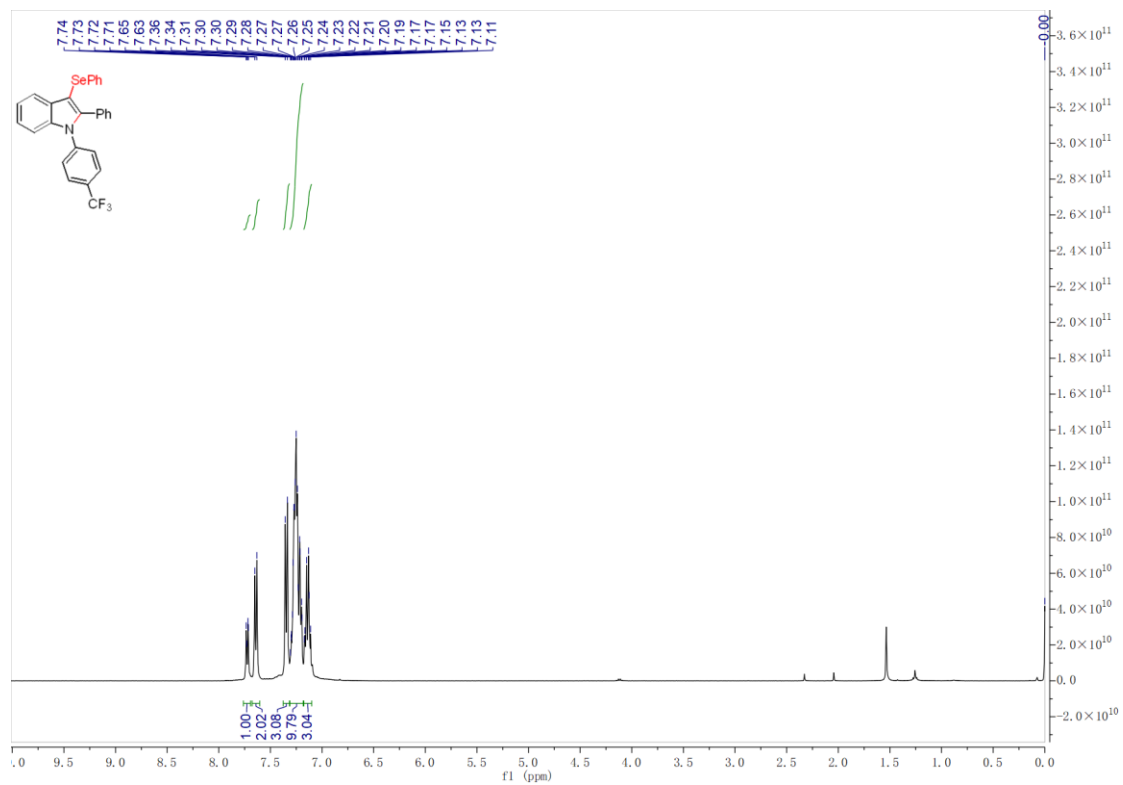


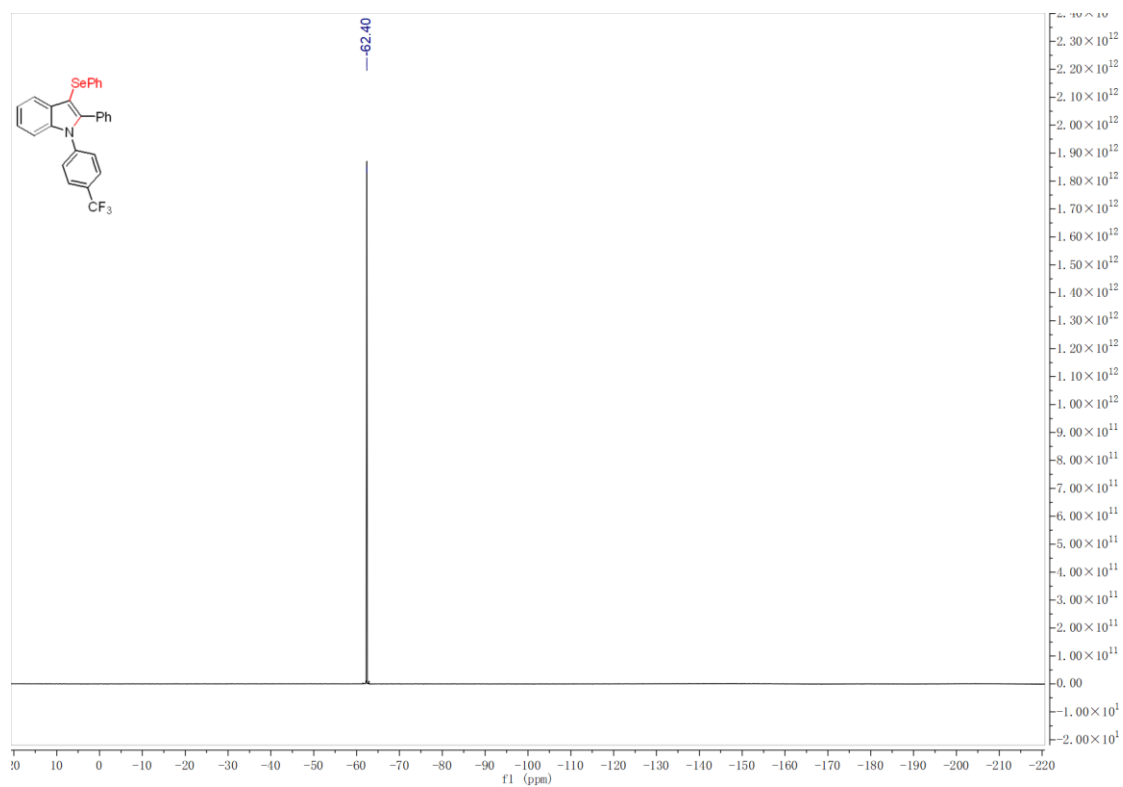
21c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



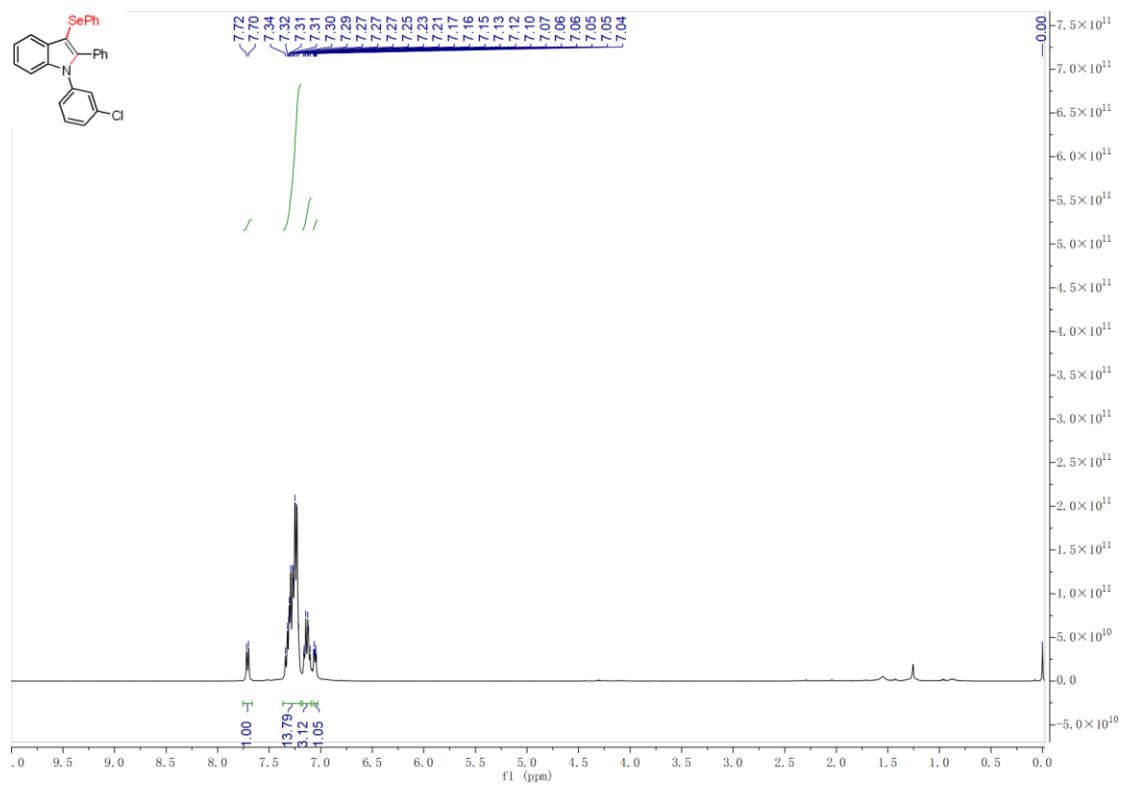


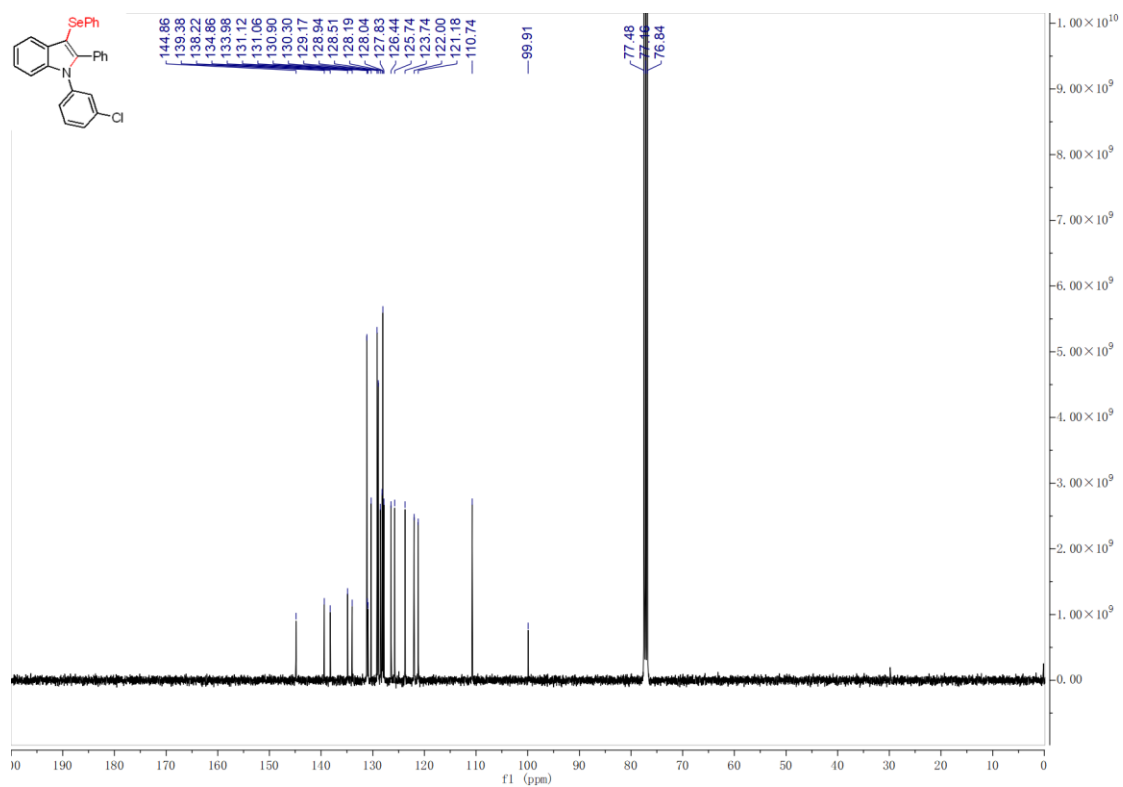
23c, <sup>1</sup>H NMR & <sup>13</sup>C NMR & <sup>19</sup>F NMR



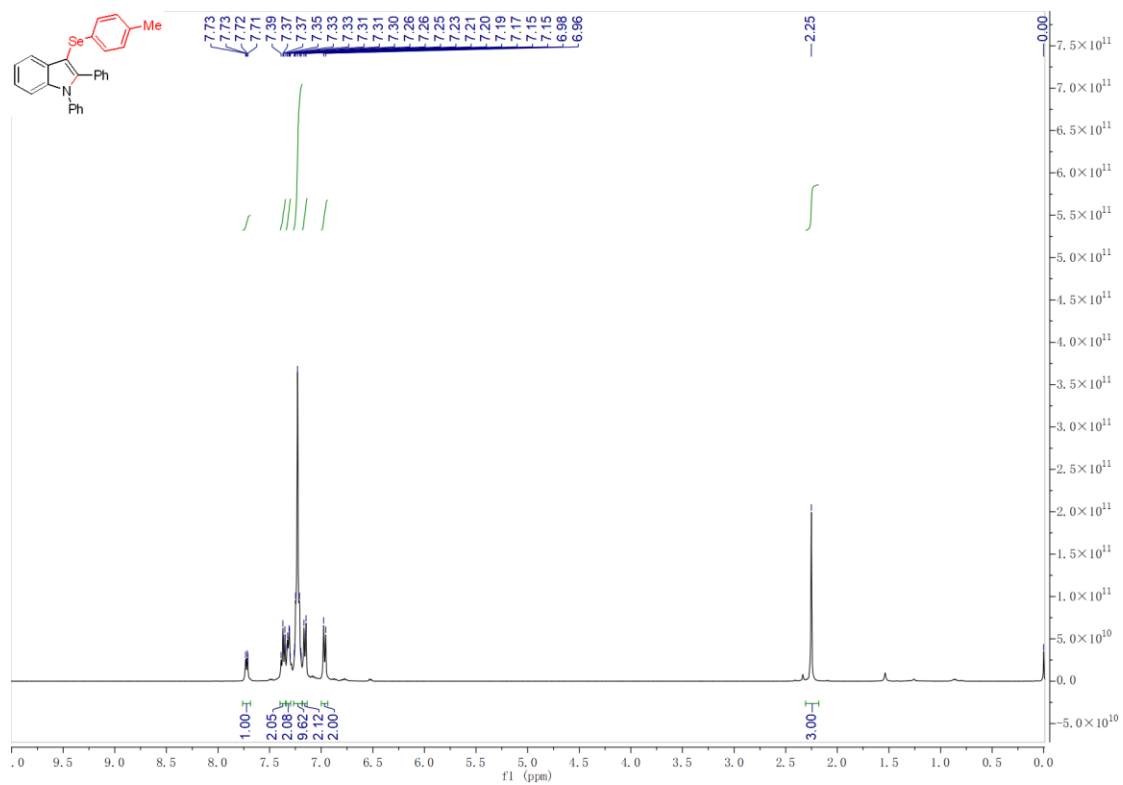


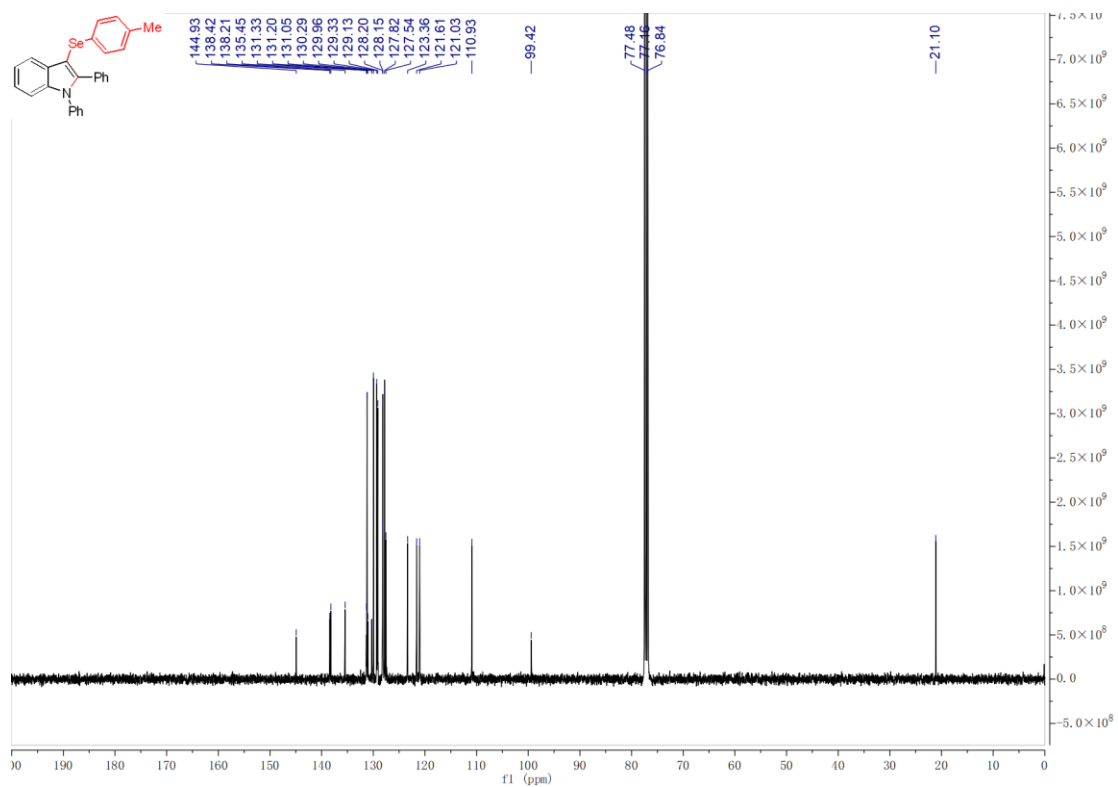
**24c,  $^1\text{H}$  NMR &  $^{13}\text{C}$  NMR**



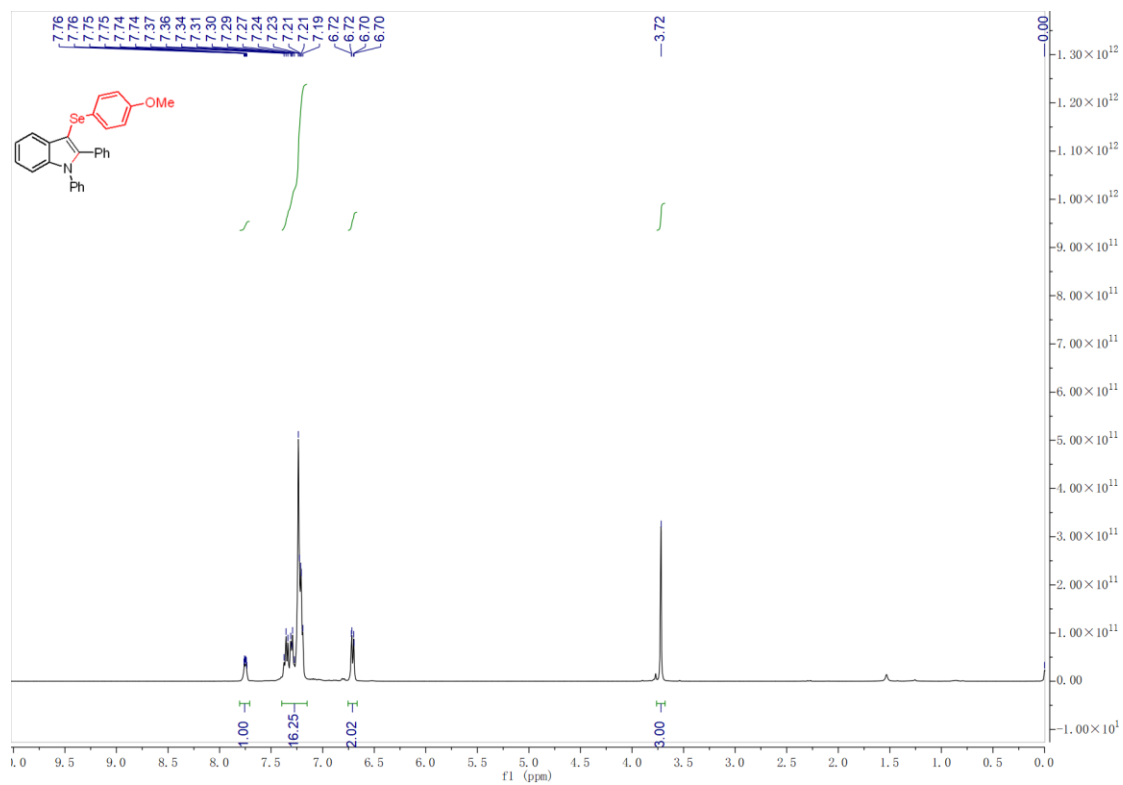


**25c, <sup>1</sup>H NMR & <sup>13</sup>C NMR**

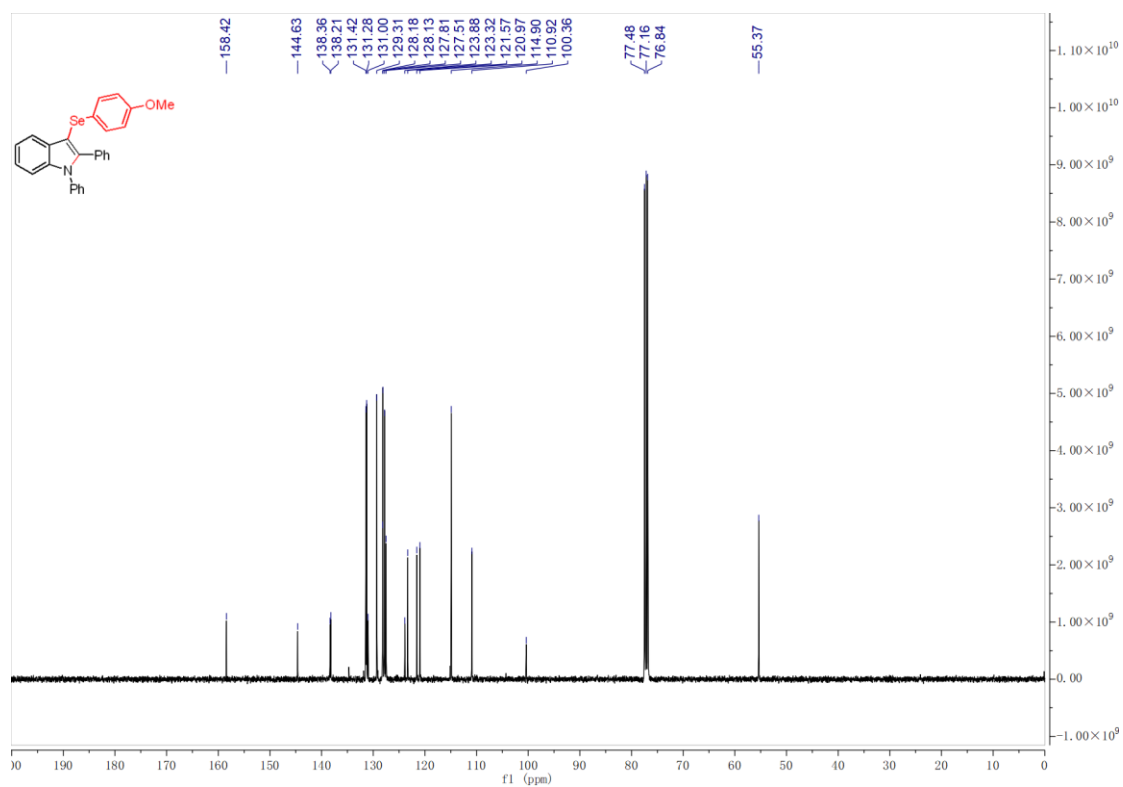




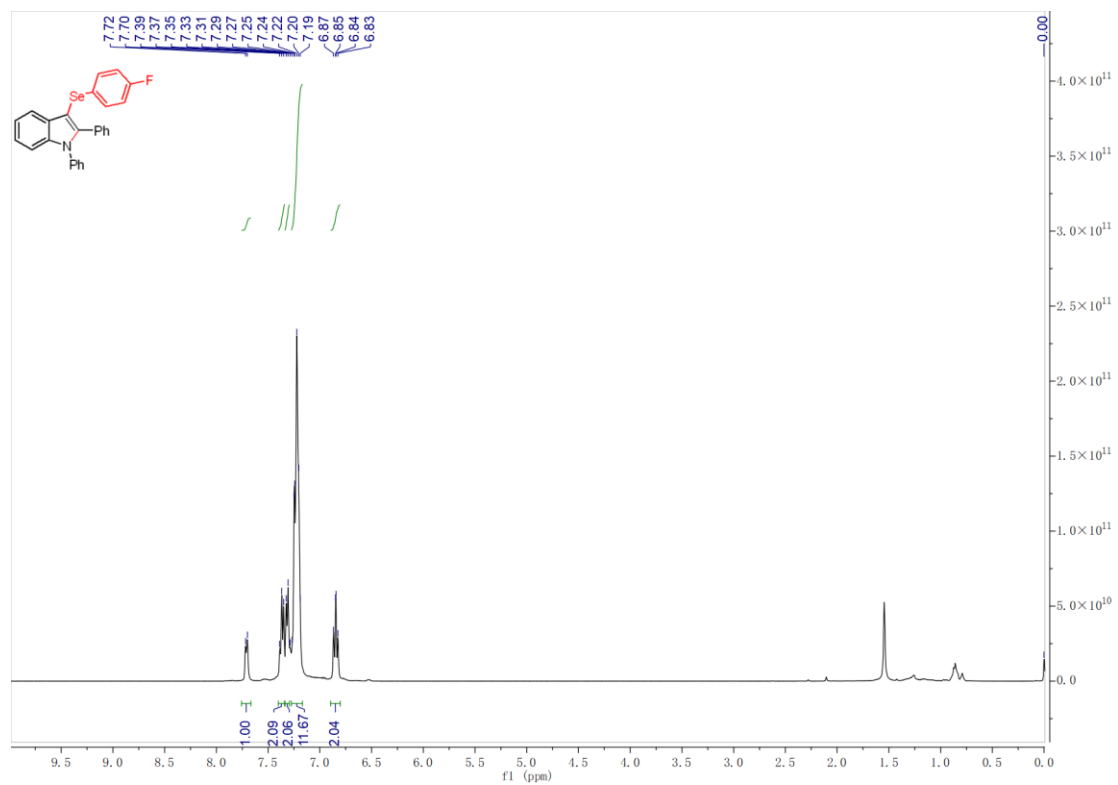
**26c, <sup>1</sup>H NMR & <sup>13</sup>C NMR**

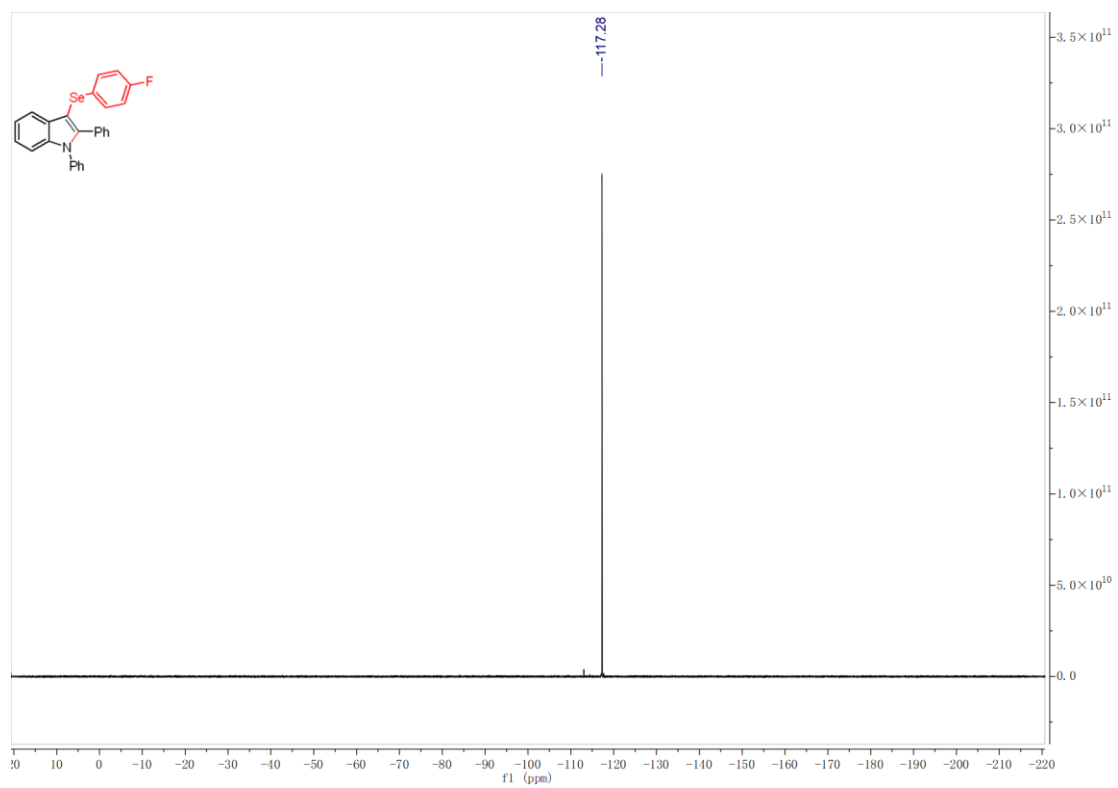
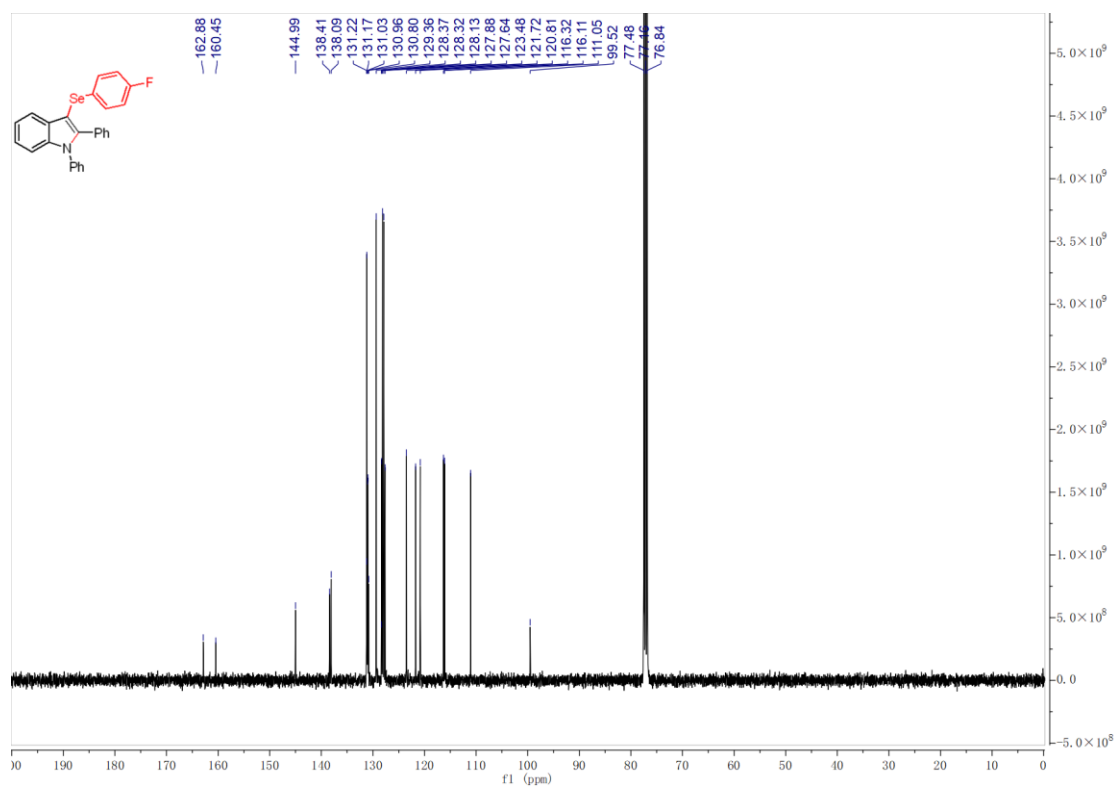




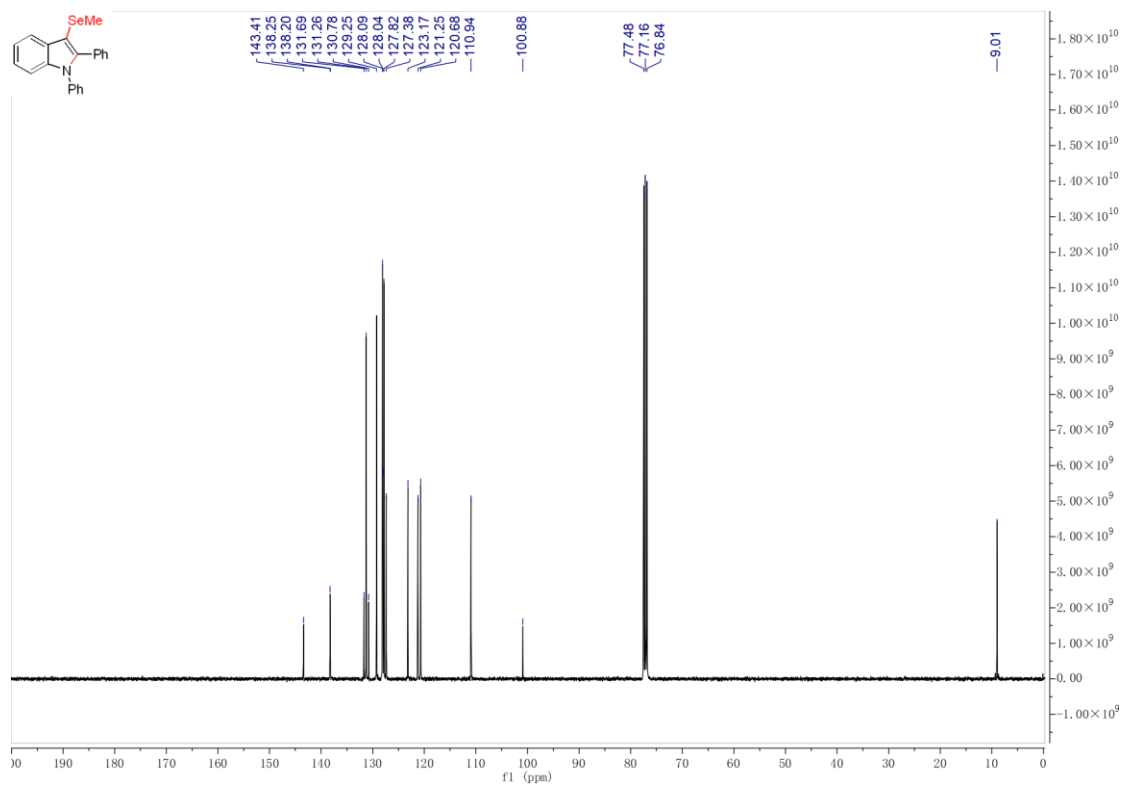
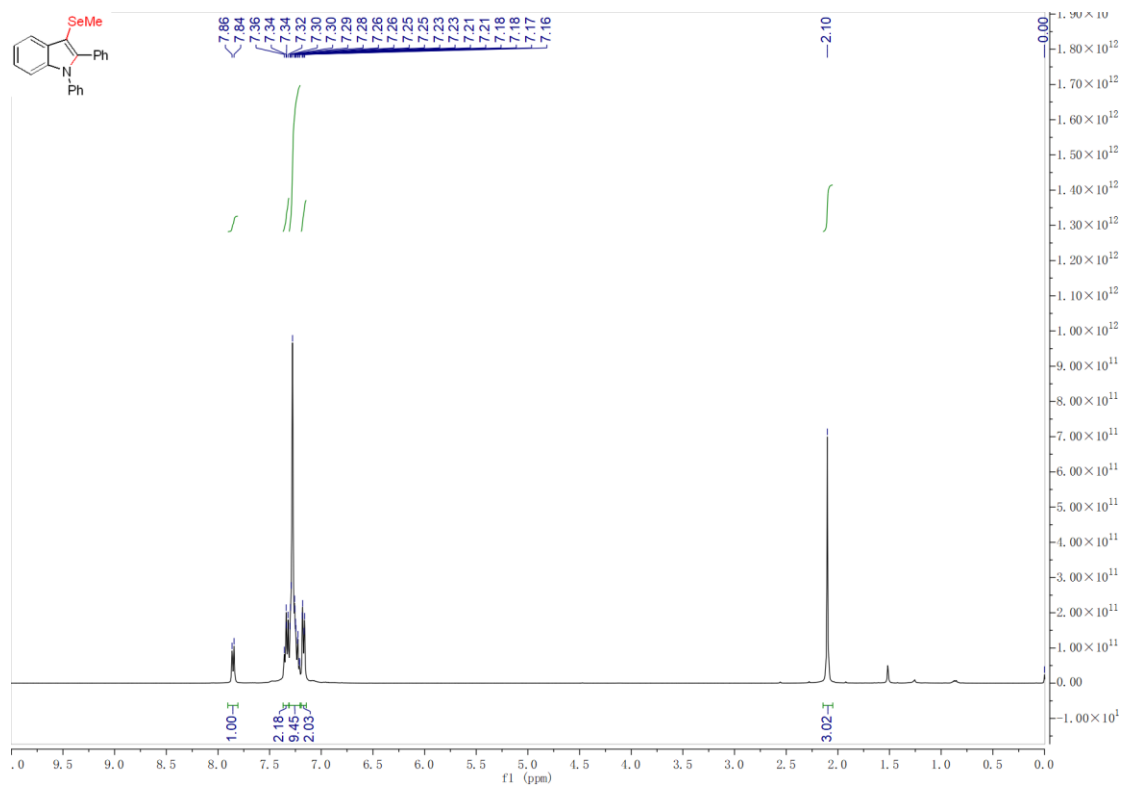


27c, <sup>1</sup>H NMR & <sup>13</sup>C NMR & <sup>19</sup>F NMR

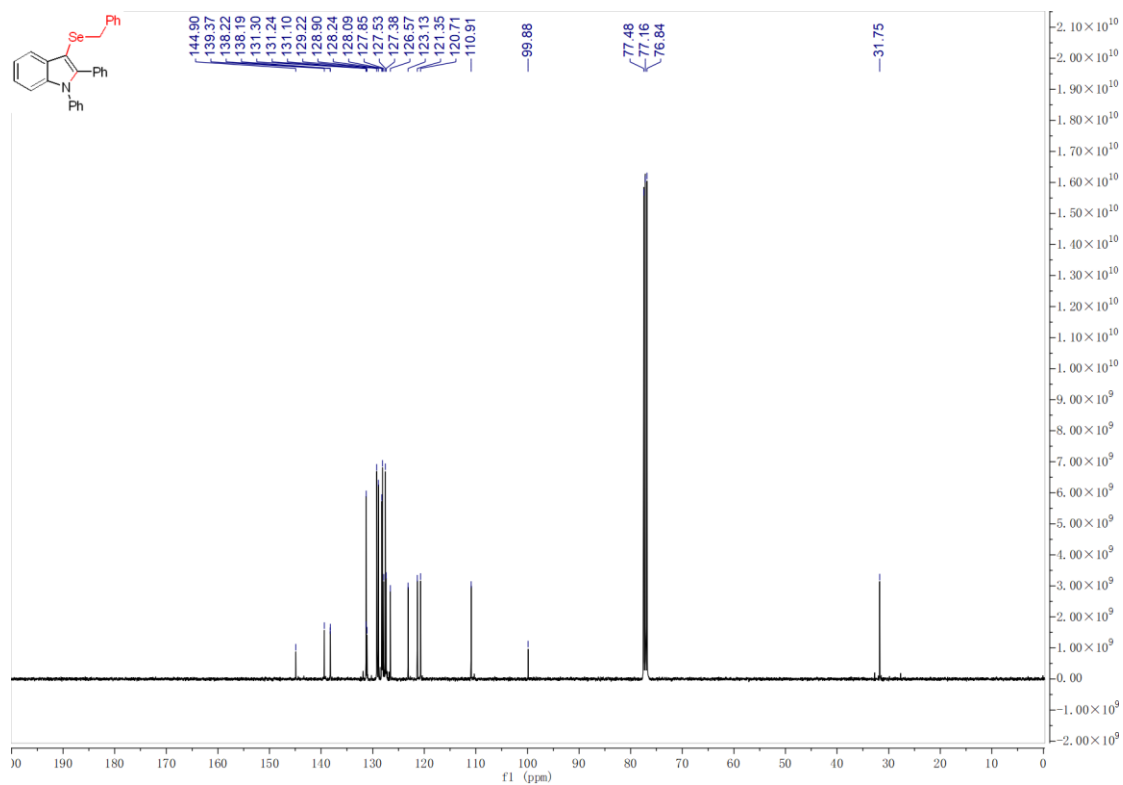
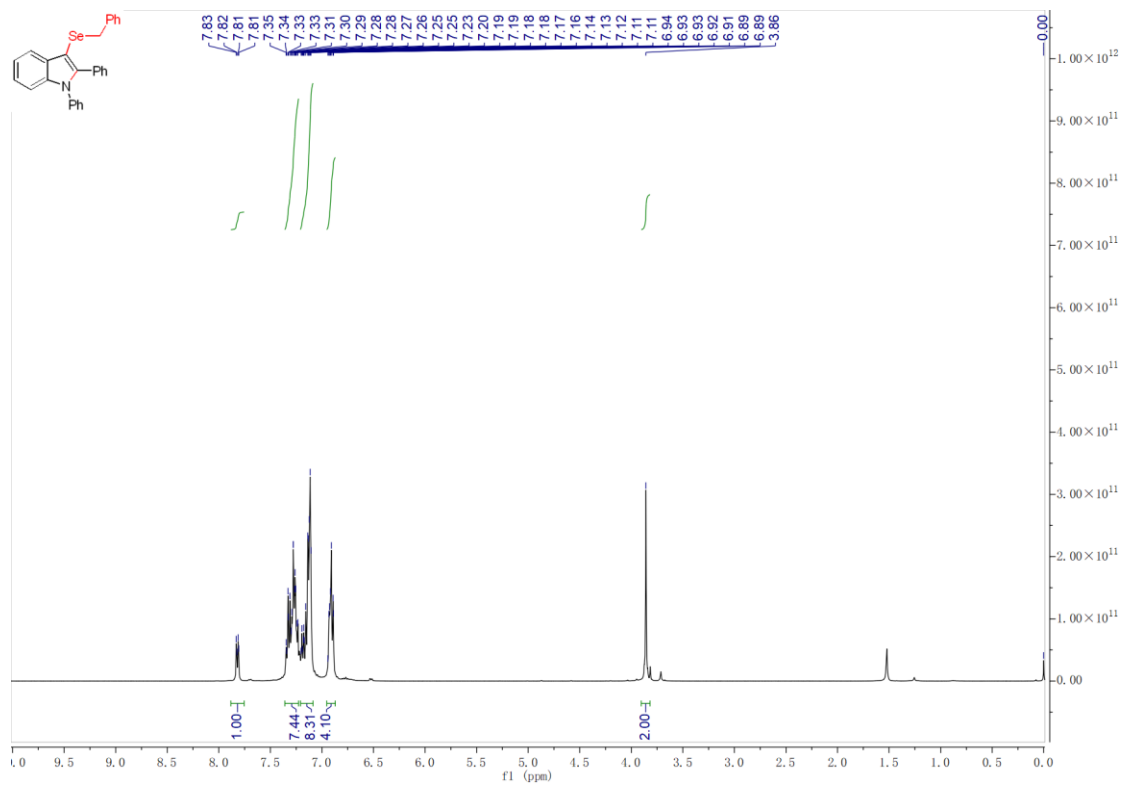




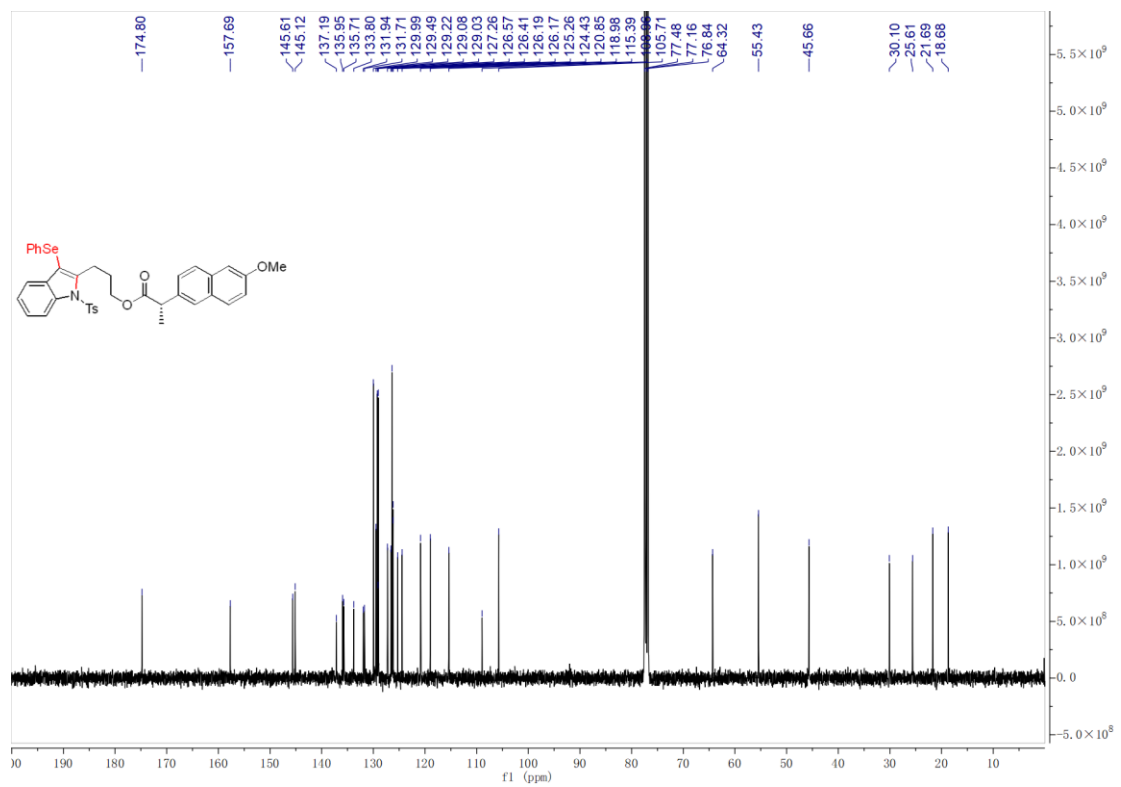
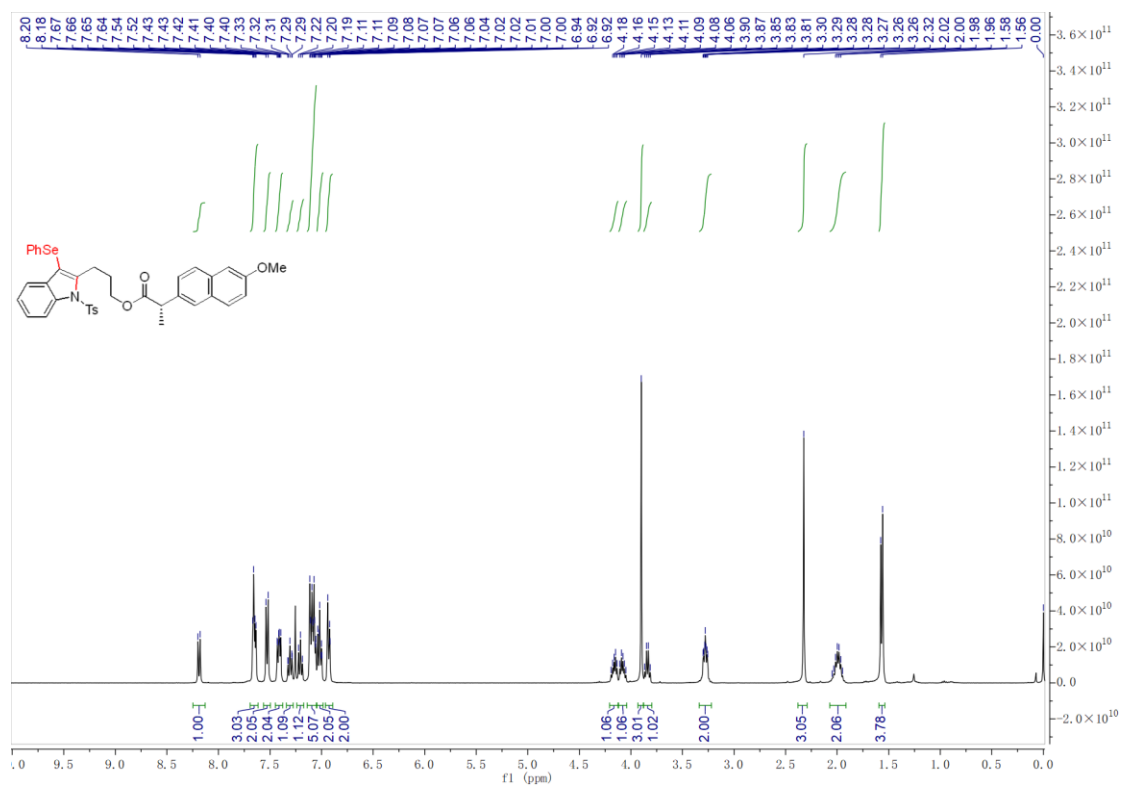
**28c**,  $^1\text{H}$  NMR &  $^{13}\text{C}$  NMR



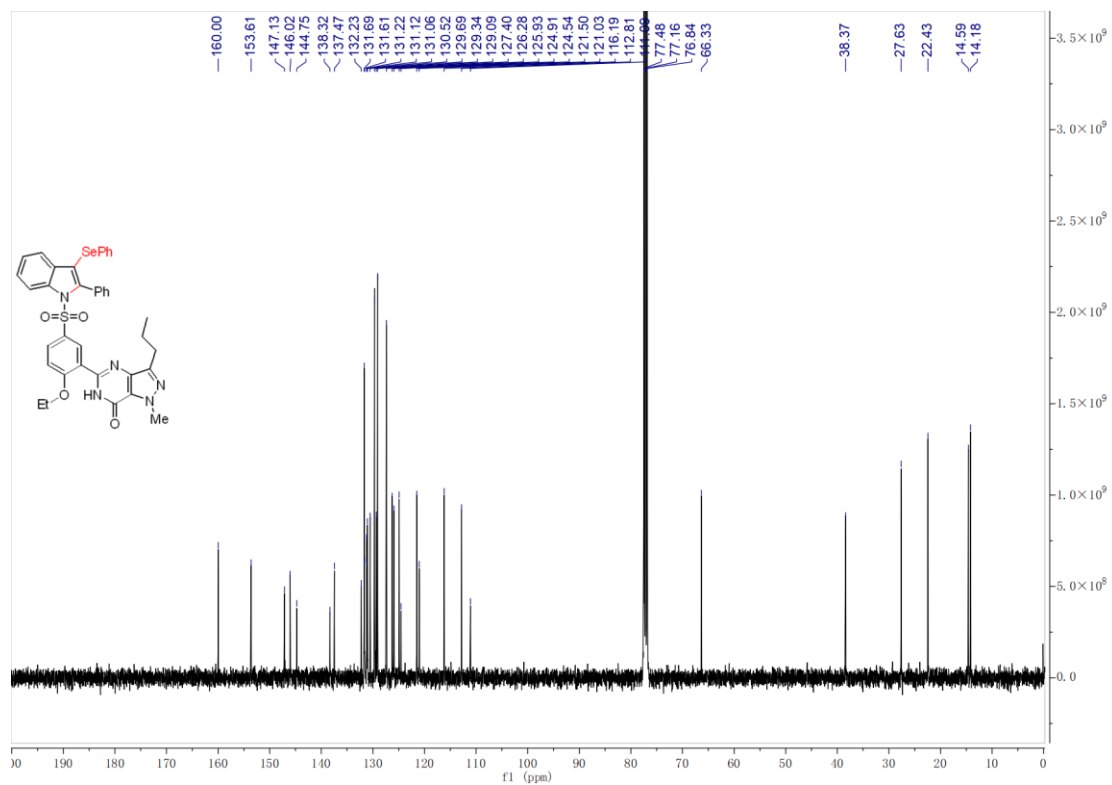
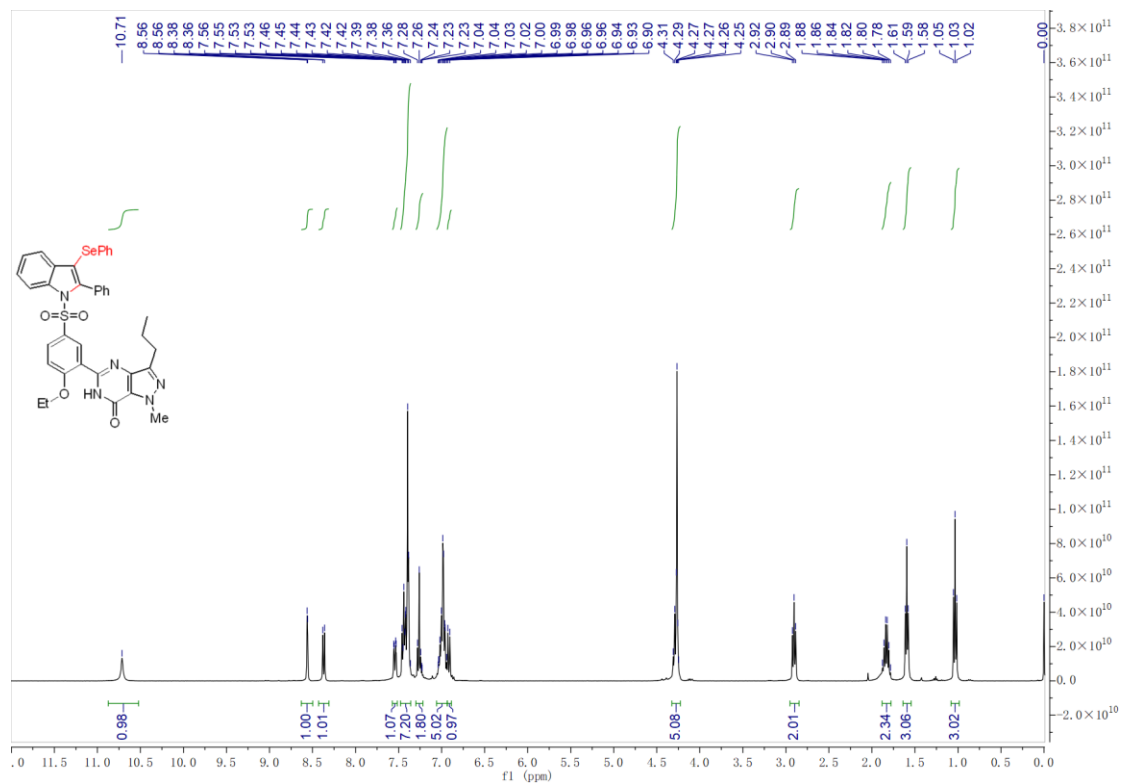
29c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



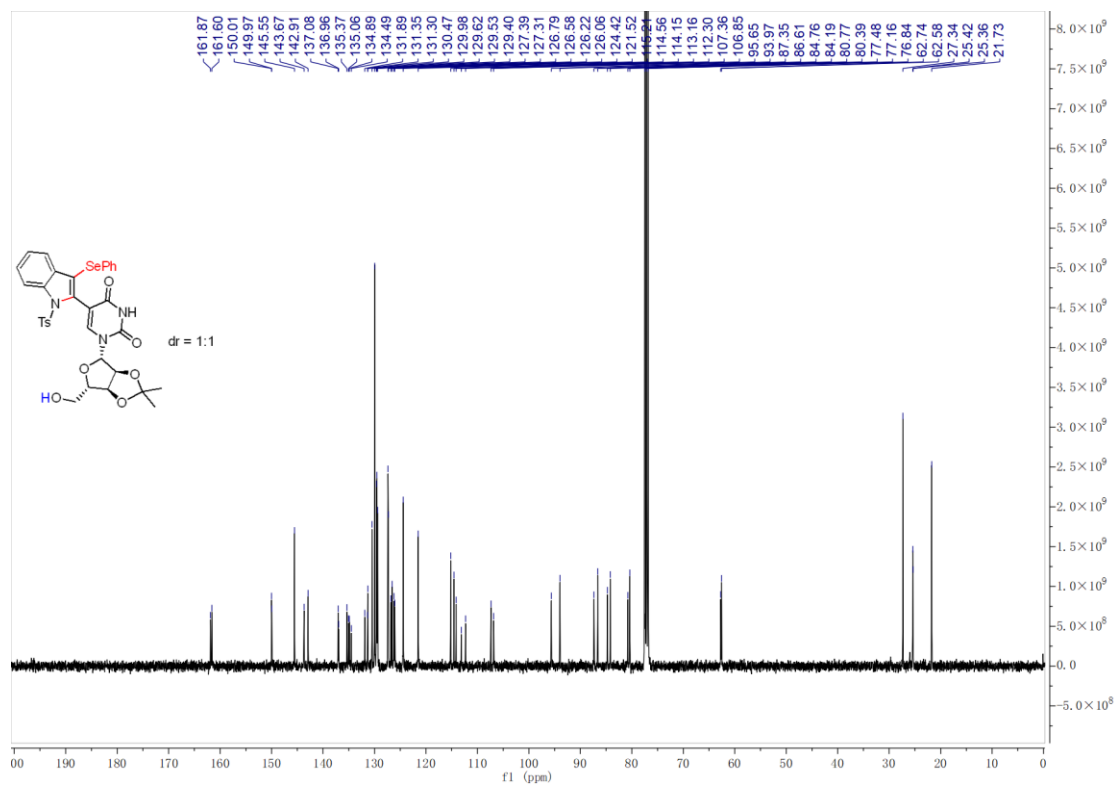
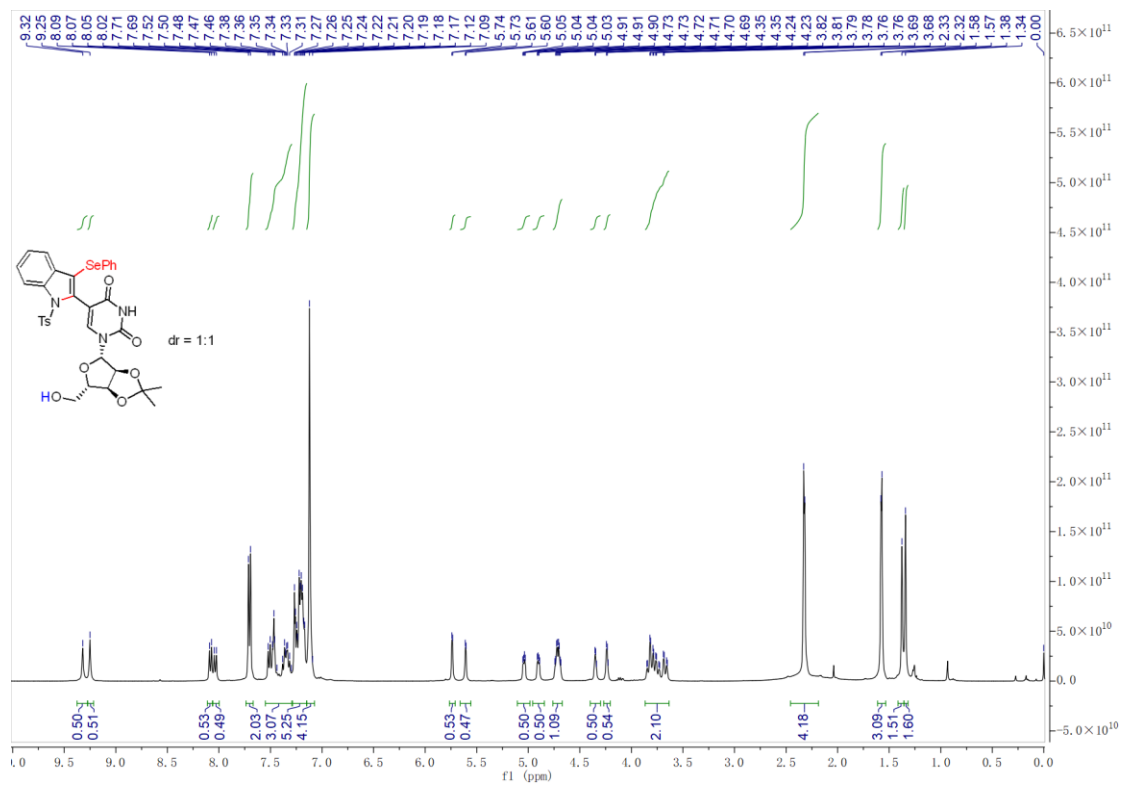
**30c**,  $^1\text{H}$  NMR &  $^{13}\text{C}$  NMR



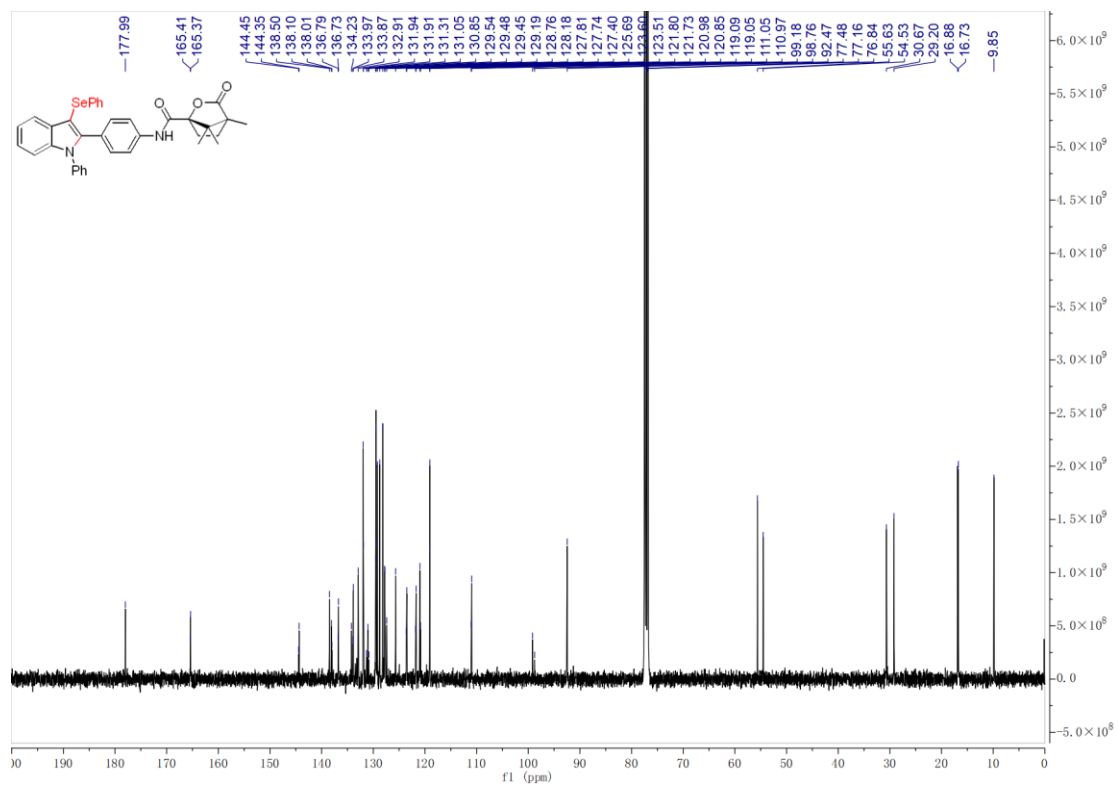
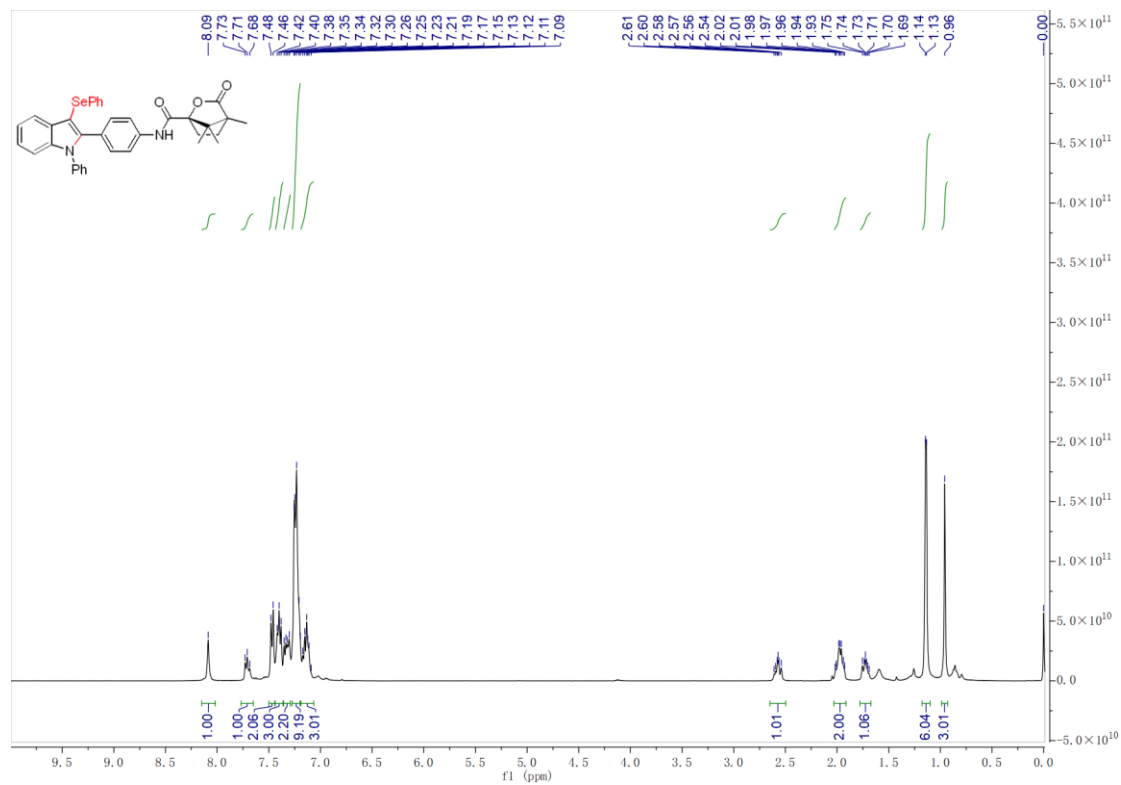
31c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



32c, <sup>1</sup>H NMR & <sup>13</sup>C NMR

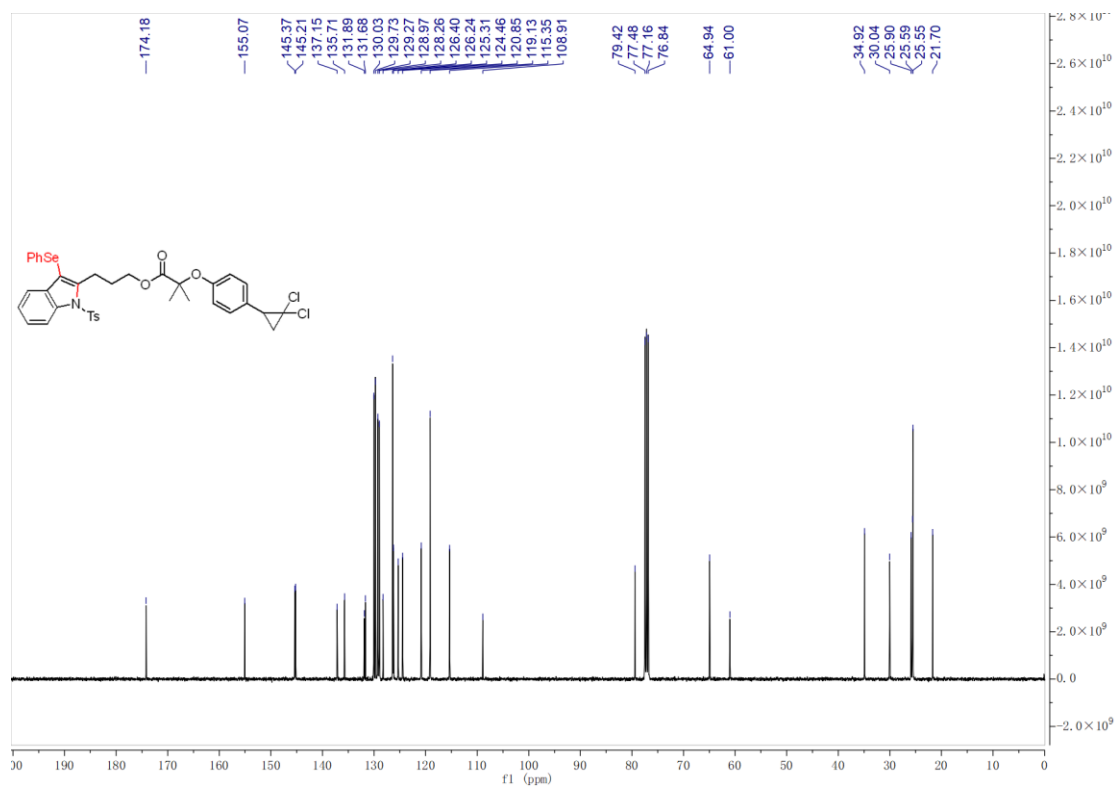
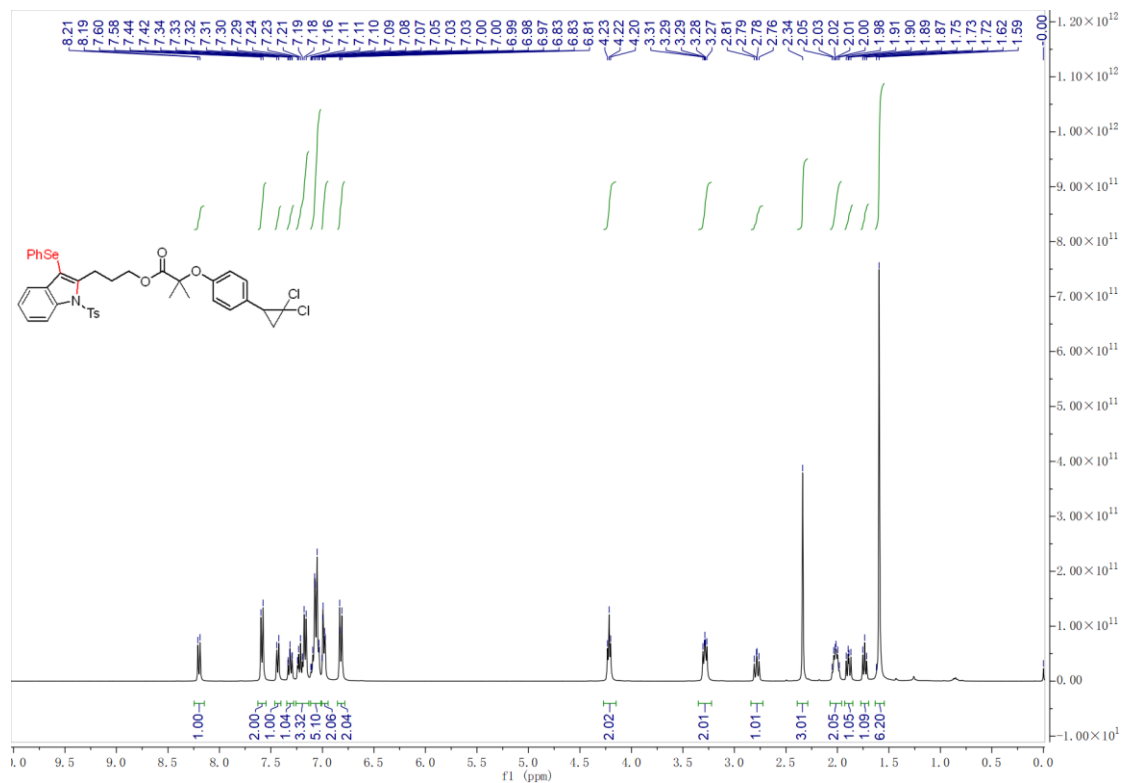


33c, <sup>1</sup>H NMR & <sup>13</sup>C NMR

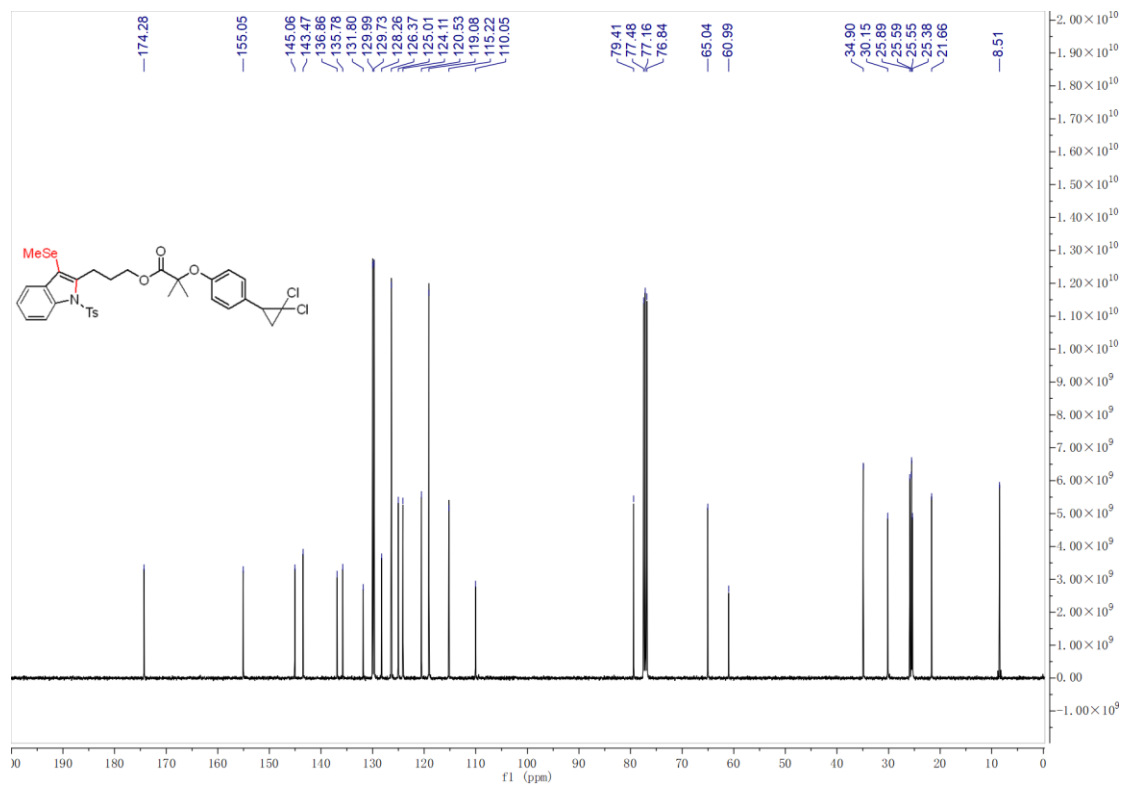
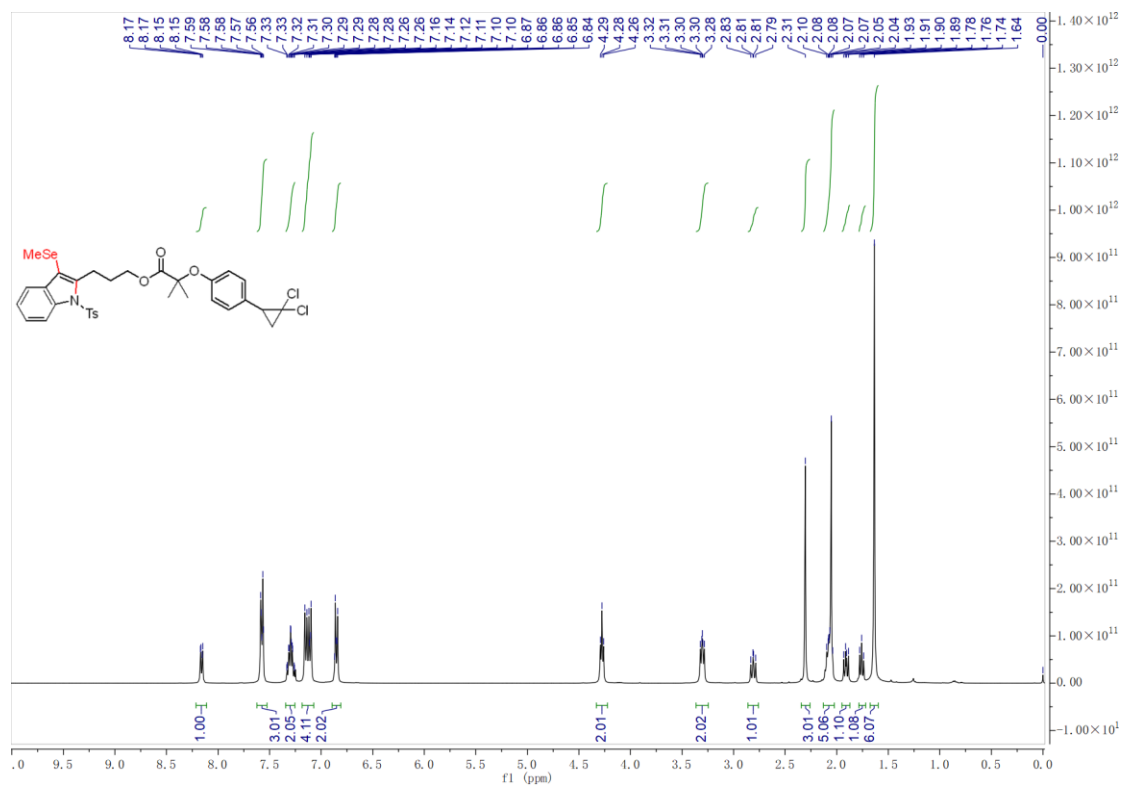




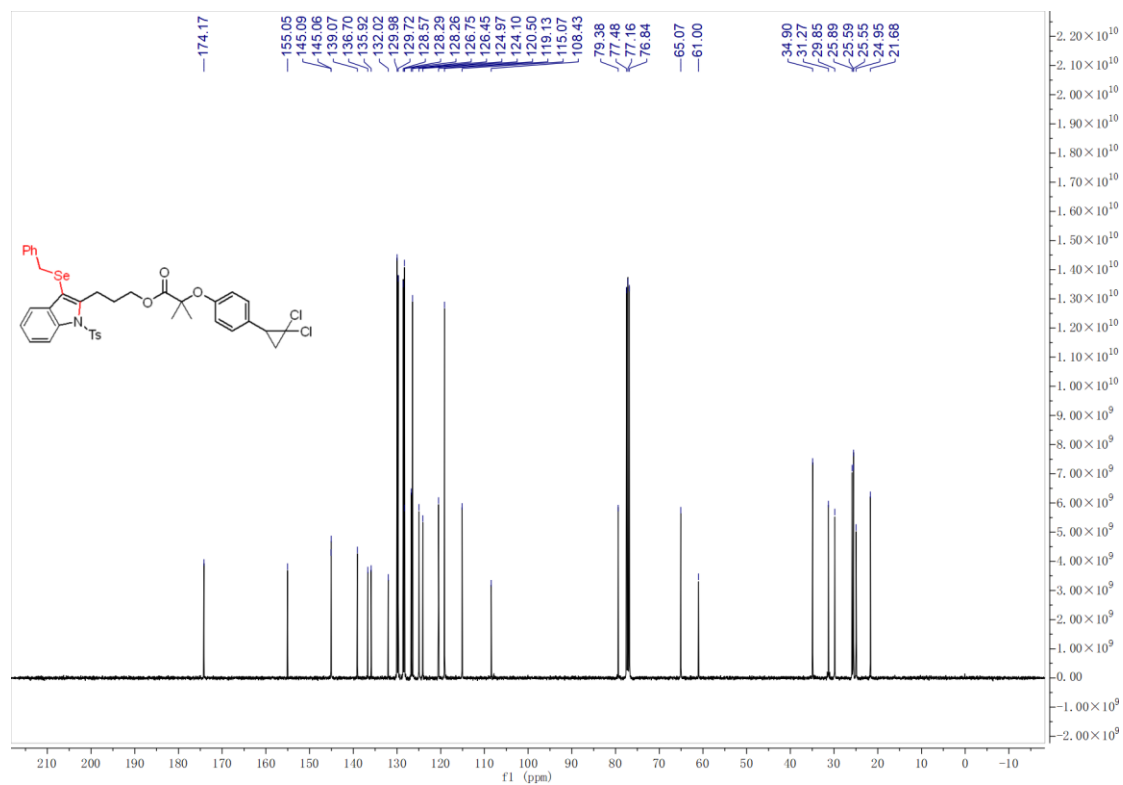
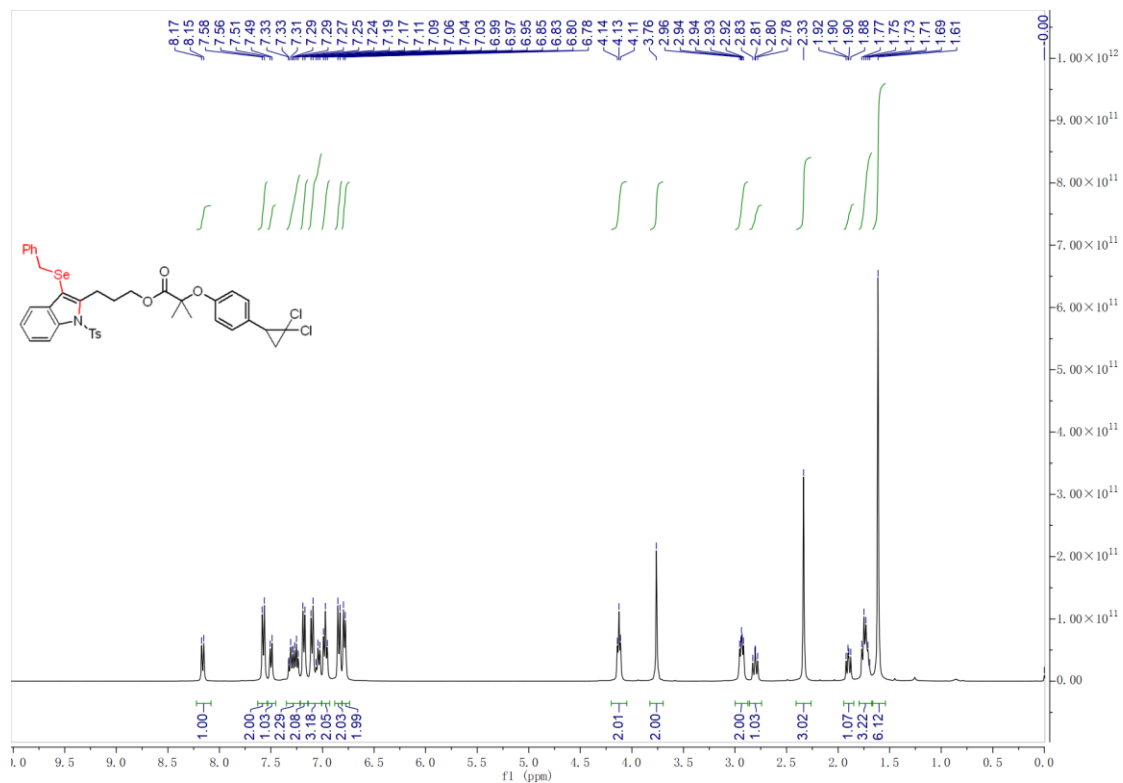
34c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



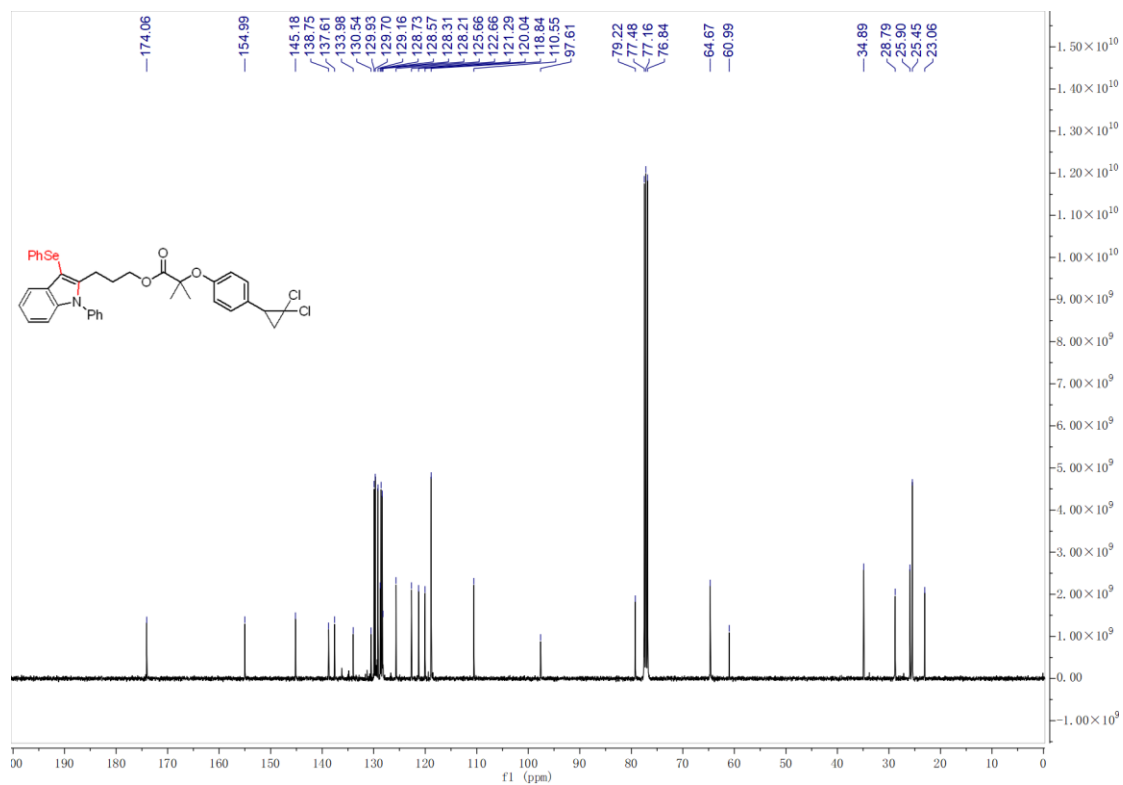
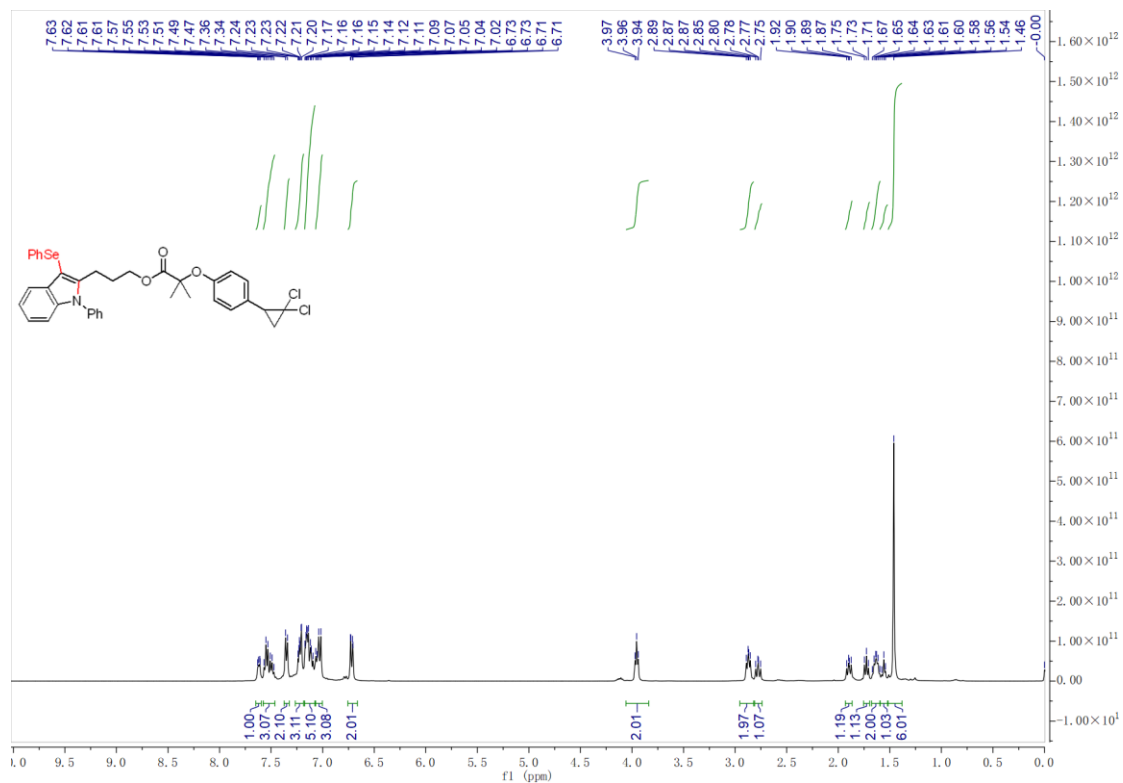
35c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



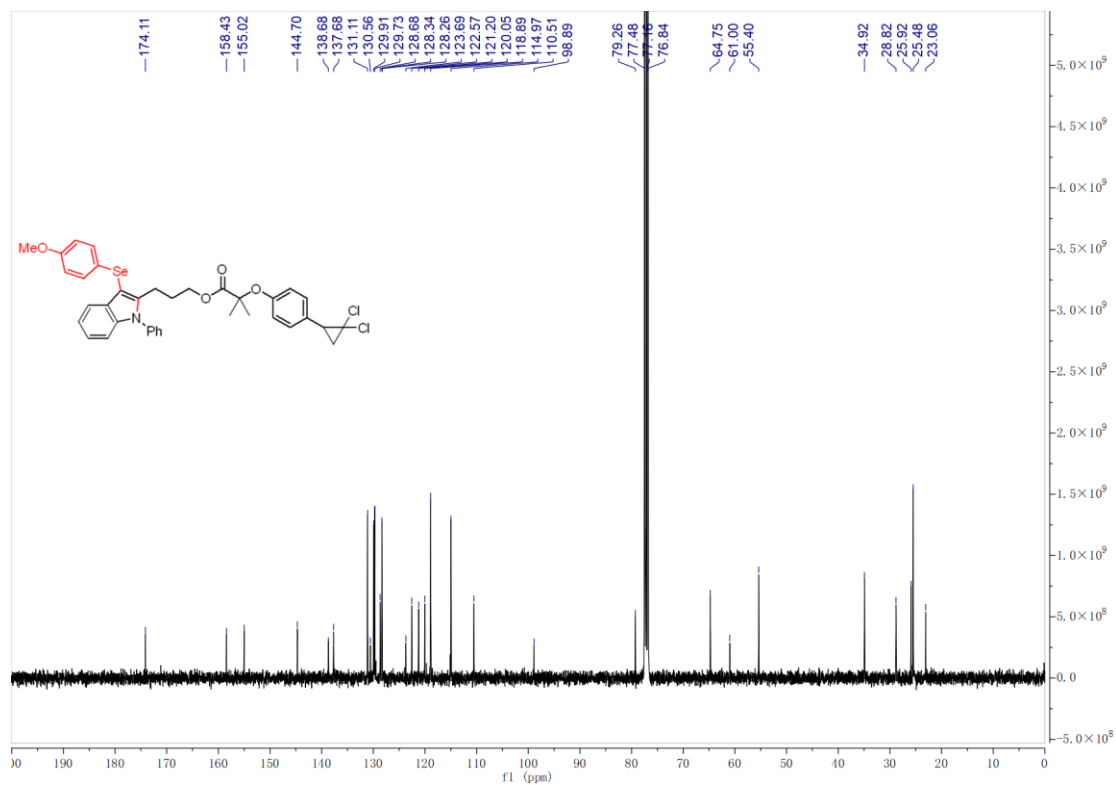
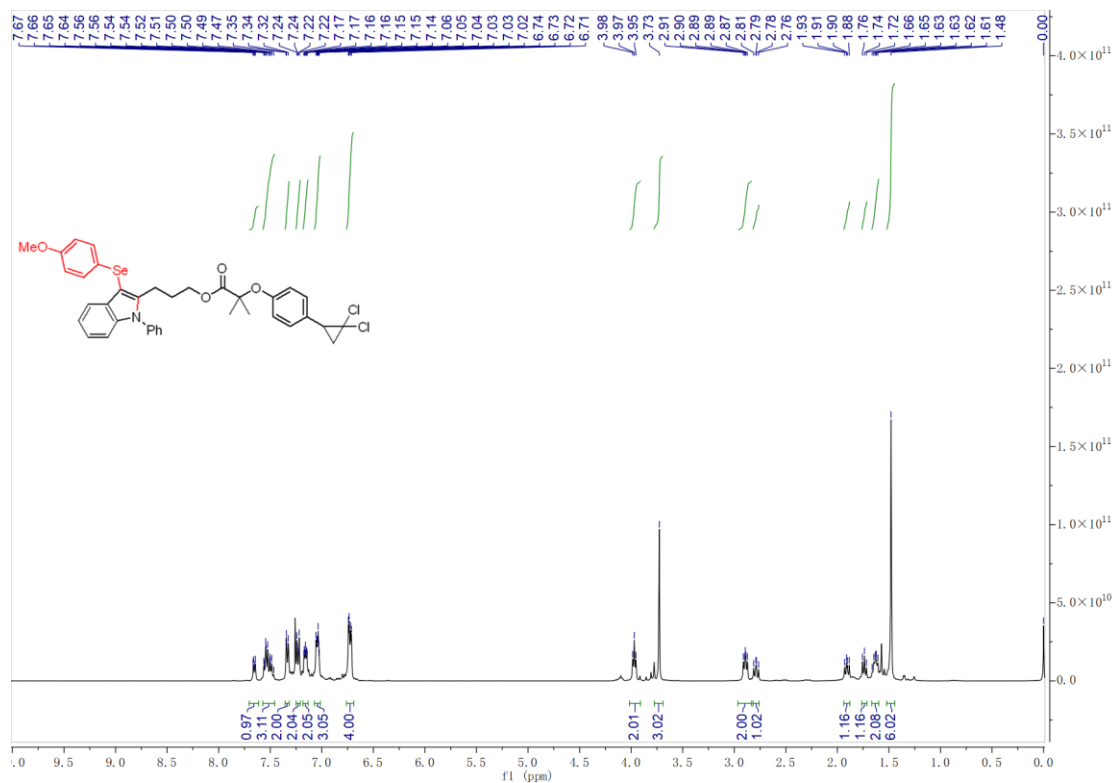
36c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



37c, <sup>1</sup>H NMR & <sup>13</sup>C NMR



**38c**,  $^1\text{H}$  NMR &  $^{13}\text{C}$  NMR



39c, <sup>1</sup>H NMR & <sup>13</sup>C NMR

