Electronic Supplementary Material (ESI) for RSC Advances.

PIFA-Mediated Selenylative Spirocyclization of Indolyl Ynones: Facile Access to Selenated Spiro[cyclopentenone-1,3'-indoles]

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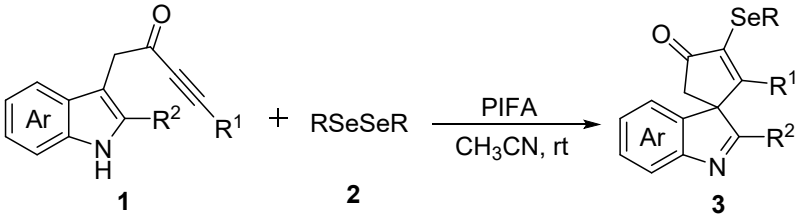
1. General information

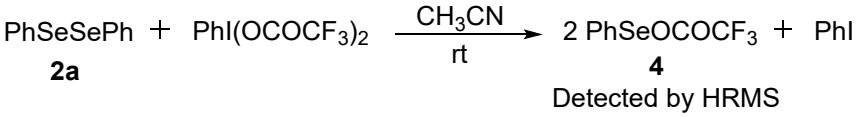
Unless otherwise stated, all commercial materials and solvents were used directly without further purification. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400MHz, ^{13}C 100MHz, ^{19}F NMR 376 MHz), using $CDCl_3$ (spectra were referenced to the solvent peaks ^{1}H: residual $CDCl_3$ = 7.26 ppm, ^{13}C: $CDCl_3$ = 77.0 ppm)) as the solvent. High-resolution mass spectra (HRMS) were measured on ESI-TOF. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluent. Thin-layer chromatography (TLC) was carried out on 4×5 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). Starting materials diselenides **2** [S1] and indol-ynones **1** [S2] were prepared according to the literatures.

2. General procedure for the synthesis of 3



To a solution of RSeSeR (0.1 mmol) in MeCN (2 mL) was added PIFA (0.12 mmol) at rt. The mixture was stirred for 2 min. Then substrate **1** (0.2 mmol) was added to this solution in one portion and the reaction mixture was stirred for another 3 min until the completion of the starting material (monitored by TLC). The resulting mixture was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 20:1 to 4:1) as eluent to afford the corresponding compounds **3**.

3. Mechanism Exploration



To a solution of PhSeSePh (0.1 mmol) in DCE (2 mL) was added PIFA (0.1 mmol) at rt. The reaction mixture was stirred for 2 min, and compound **4** was detected by HRMS (Figure S1). HRMS (ESI) m/z calcd for $C_8H_5F_3NaO_2Se$ $[M+Na]^+$ 292.9299, found 292.9298.

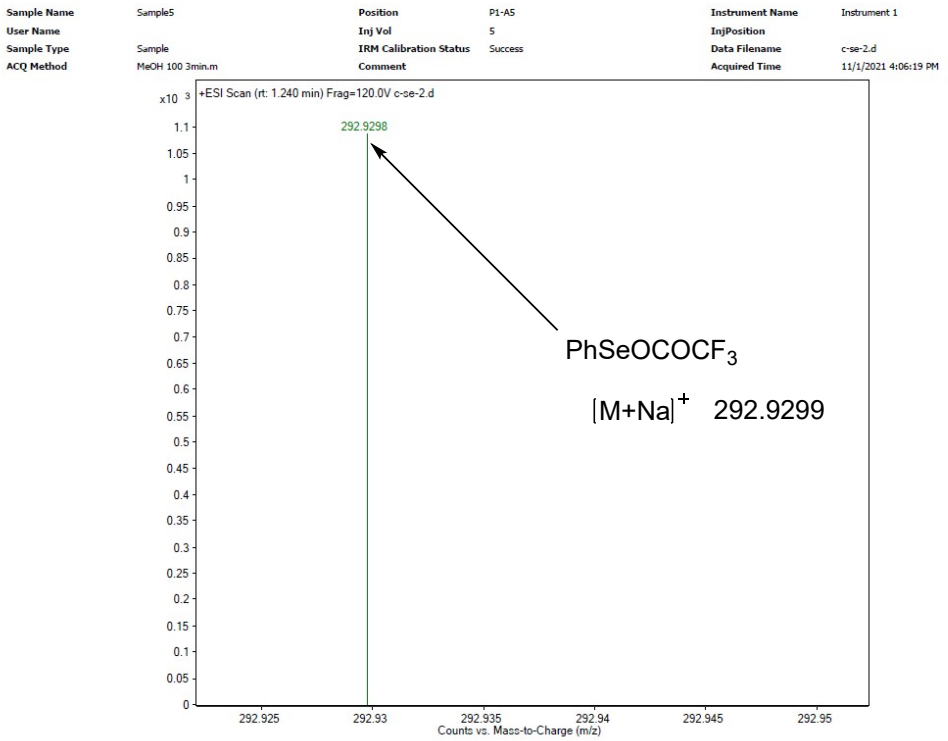
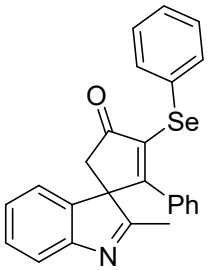


Figure. S1

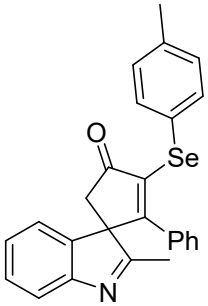
Characterization of compounds 3

2'-Methyl-2-phenyl-3-(phenylselanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3aa)[S3]



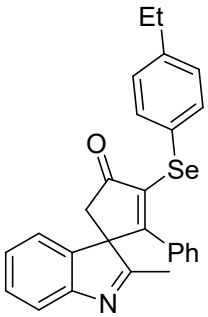
Brown solid. 76.4 mg, Yield: 89%, mp 153-155 °C. column chromatography eluent, EtOAc/PE = 1:15 → 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.24 – 7.21 (m, 2H), 7.19 – 7.12 (m, 4H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.72 (dd, *J* = 8.2, 1.0 Hz, 2H), 2.94 (d, *J* = 18.7 Hz, 1H), 2.86 (d, *J* = 18.7 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 181.3, 173.0, 155.1, 140.5, 135.6, 133.2, 133.1, 130.0, 129.1, 129.1, 128.2, 128.1, 127.7, 126.8, 126.5, 121.8, 120.6, 68.3, 43.1, 15.9. HRMS (ESI): Calcd for $C_{25}H_{20}NOSe$ $[M+H]^+$: 430.0705; found: 430.0704.

2'-Methyl-2-phenyl-3-(p-tolylselanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3ab)



Brown solid. 77.1 mg, Yield: 87%, mp 165-166 °C. column chromatography eluent, EtOAc/PE = 1:15 → 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.16 (m, 3H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 2.94 (d, *J* = 18.7 Hz, 1H), 2.86 (d, *J* = 18.7 Hz, 1H), 2.28 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 181.3, 172.5, 155.2, 140.6, 137.8, 135.9, 133.7, 133.2, 129.9, 129.9, 129.1, 128.2, 126.9, 126.4, 124.2, 121.8, 120.6, 68.3, 43.1, 21.1, 15.9. HRMS (ESI): Calcd for $C_{26}H_{22}NOSe$ $[M+H]^+$: 444.0861; found: 444.0865.

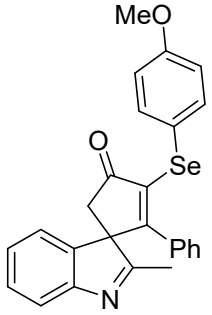
3-((4-Ethylphenyl)selanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3ac)



Brown solid. 78.6 mg, Yield: 86%, mp 172-173 °C. column chromatography eluent, EtOAc/PE = 1:15 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H),

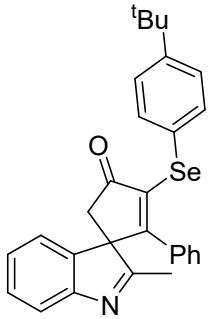
6.73 (d, *J* = 7.6 Hz, 2H), 2.95 (d, *J* = 18.7 Hz, 1H), 2.87 (d, *J* = 18.7 Hz, 1H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.21 (s, 3H), 1.18 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 181.3, 172.3, 155.1, 144.1, 140.6, 135.9, 133.7, 133.1, 129.9, 129.1, 128.6, 128.1, 126.8, 126.4, 124.3, 121.8, 120.6, 68.3, 43.1, 28.5, 15.9, 15.4. HRMS (ESI): Calcd for $C_{27}H_{24}NOSe$ $[M+H]^+$: 458.1018; found: 458.1015.

3-((4-Methoxyphenyl)selanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3ad)



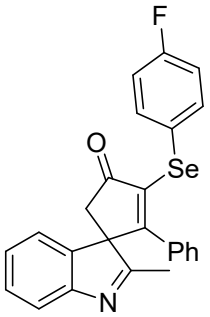
Brown solid. 74.4 mg, Yield: 81%, mp 138-140 ℃. column chromatography eluent, EtOAc/PE = 1:15 → 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.23 – 7.13 (m, 3H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.70 – 6.64 (m, 4H), 3.72 (s, 3H), 2.90 (d, *J* = 18.7 Hz, 1H), 2.82 (d, *J* = 18.7 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 181.6, 171.7, 159.7, 154.8, 140.4, 136.4, 136.0, 133.1, 129.9, 129.1, 128.2, 126.8, 126.5, 121.8, 120.5, 117.6, 114.7, 68.2, 55.3, 43.1, 15.8. HRMS (ESI): Calcd for $C_{26}H_{22}NO_2Se$ $[M+H]^+$: 460.0810; found: 460.0812.

3-((4-(Tert-butyl)phenyl)selanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3ae)



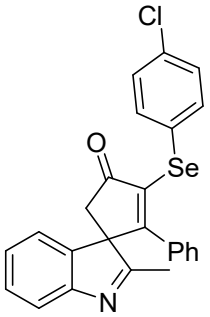
Brown solid. 80.5 mg, Yield: 83%, mp 175-177 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.30 – 7.22 (m, 4H), 7.17 – 7.11 (m, 3H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.73 – 6.67 (m, 2H), 2.97 (d, *J* = 18.7 Hz, 1H), 2.88 (d, *J* = 18.7 Hz, 1H), 2.22 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 181.6, 171.9, 154.9, 150.9, 140.5, 136.0, 133.3, 133.0, 129.8, 129.1, 128.1, 126.8, 126.5, 126.1, 124.0, 121.8, 120.6, 68.4, 43.0, 34.5, 31.2, 15.9. HRMS (ESI): Calcd for $C_{29}H_{28}NOSe$ $[M+H]^+$: 486.1331; found: 486.1331.

3-((4-Fluorophenyl)selanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3af)



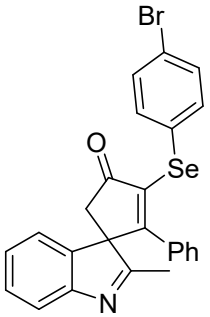
Brown solid. 81.4 mg, Yield: 91%, mp 115-116 ℃. column chromatography eluent, EtOAc/PE = 1:15 → 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.26 – 7.15 (m, 3H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.85 – 6.78 (m, 2H), 6.70 – 6.63 (m, 2H), 2.93 (d, *J* = 18.7 Hz, 1H), 2.85 (d, *J* = 18.7 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 181.4, 172.3, 162.7 (d, *J* = 248.5 Hz), 154.8, 140.3, 136.1 (d, *J* = 8.1 Hz), 135.9, 133.0, 130.1, 129.2, 128.3, 126.7, 126.6, 122.1 (d, *J* = 3.6 Hz), 121.7, 120.6, 116.2 (d, *J* = 21.8 Hz), 68.3, 43.0, 15.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.12. HRMS (ESI): Calcd for $C_{25}H_{18}FNOSe$ $[M+H]^+$: 448.0610; found: 448.0610.

3-((4-Chlorophenyl)selanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3ag)



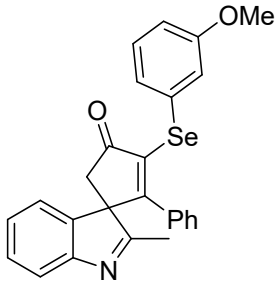
Brown solid. 81.5 mg, Yield: 88%, mp 159-161 ℃. column chromatography eluent, EtOAc/PE = 1:10 → 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 7.13 – 7.04 (m, 4H), 6.71 – 6.65 (m, 2H), 2.95 (d, *J* = 18.8 Hz, 1H), 2.86 (d, *J* = 18.8 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 181.2, 172.9, 154.9, 140.3, 135.4, 134.9, 134.2, 132.9, 130.2, 129.3, 129.2, 128.3, 126.7, 126.6, 125.9, 121.7, 120.7, 68.3, 43.0, 15.9. HRMS (ESI): Calcd for $C_{25}H_{19}Cl^{37}NOSe$ $[M+H]^+$: 464.0315; found: 464.0314, $C_{25}H_{19}Cl^{35}NOSe$ $[M+H]^+$: 462.0323; found: 462.0325.

3-((4-Bromophenyl)selanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3ah)



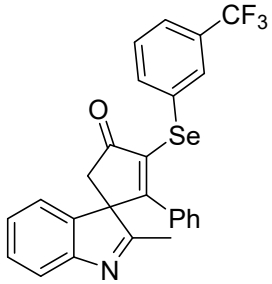
Brown solid. 85.2 mg, Yield: 84%, mp 153-154 ℃. column chromatography eluent, EtOAc/PE = 1:10 → 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.19 (m, 7H), 7.10 (t, *J* = 7.7 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 2.98 (d, *J* = 18.8 Hz, 1H), 2.89 (d, *J* = 18.7 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 181.5, 172.7, 154.4, 140.2, 135.4, 135.1, 132.9, 132.1, 130.2, 129.3, 128.3, 126.7, 126.7, 126.6, 122.3, 121.8, 120.6, 68.3, 43.0, 15.8. HRMS (ESI): Calcd for $C_{25}H_{19}Br^{79}NOSe$ $[M+H]^+$: 507.9810; found: 507.9808, $C_{25}H_{19}Br^{81}NOSe$ $[M+H]^+$: 509.9789; found: 509.9790.

3-((3-Methoxyphenyl)selanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3ai)



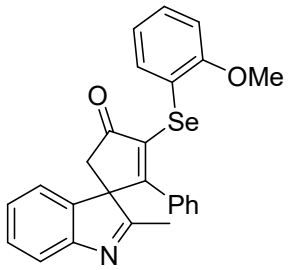
Brown solid. 73.5 mg, Yield: 80%, mp 129-130 ℃. column chromatography eluent, EtOAc/PE = 1:15 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.24 – 7.21 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 3H), 6.96 – 6.91 (m, 1H), 6.90 – 6.86 (m, 1H), 6.75 – 6.67 (m, 3H), 3.70 (s, 3H), 2.96 (d, *J* = 18.7 Hz, 1H), 2.87 (d, *J* = 18.7 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 181.3, 173.1, 159.6, 155.0, 140.5, 135.5, 133.1, 130.0, 129.8, 129.2, 128.9, 128.2, 126.8, 126.5, 125.2, 121.8, 120.6, 118.5, 68.4, 55.2, 43.1, 15.9. HRMS (ESI): Calcd for $C_{26}H_{22}NO_2Se$ $[M+H]^+$: 460.0810; found: 460.0813.

2'-Methyl-2-phenyl-3-((3-(trifluoromethyl)phenyl)selanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3aj)



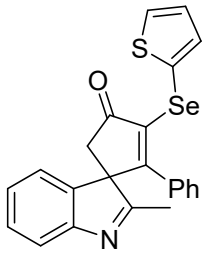
Brown solid. 84.5 mg, Yield: 85%, mp 145-146 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 9.7 Hz, 3H), 7.40 – 7.37 (m, 2H), 7.25 – 7.20 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.69 – 6.64 (m, 2H), 2.98 (d, *J* = 18.8 Hz, 1H), 2.89 (d, *J* = 18.8 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 180.8, 173.6, 155.2, 140.2, 136.4, 135.1, 132.8, 130.2, 129.7 (q, *J* = 3.9 Hz), 129.3, 129.0, 128.3, 126.6, 126.6, 124.4 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.1 Hz),121.7, 120.7, 68.4, 43.0, 15.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.84. HRMS (ESI): Calcd for $C_{26}H_{19}F_3NOSe$ $[M+H]^+$: 498.0578; found: 498.0578.

3-((2-Methoxyphenyl)selanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3ak)



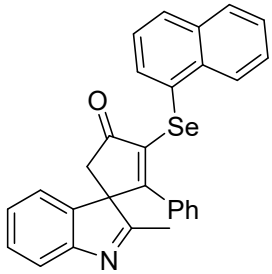
Brown solid. 67.9 mg, Yield: 74%, mp 157-159 °C. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.39 (td, *J* = 7.4, 1.6 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.19 – 7.10 (m, 2H), 7.02 (dd, *J* = 10.6, 4.8 Hz, 2H), 6.80 (td, *J* = 7.5, 1.1 Hz, 1H), 6.74 (dd, *J* = 5.2, 3.4 Hz, 2H), 6.70 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.78 (s, 3H), 2.99 (d, *J* = 18.7 Hz, 1H), 2.89 (d, *J* = 18.7 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 181.6, 172.3, 157.7, 155.0, 140.7, 134.3, 132.9, 132.8, 129.9, 129.1, 129.0, 128.0, 126.6, 126.4, 121.8, 121.3, 120.6, 116.8, 110.6, 68.5, 55.7, 43.1, 15.9. HRMS (ESI): Calcd for $C_{26}H_{22}NO_2Se$ $[M+H]^+$: 460.0810; found: 460.0811.

2'-Methyl-2-phenyl-3-(thiophen-2-ylselanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3al)



Brown solid. 67.0 mg, Yield: 77%, mp 145-146 °C. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.29 (dd, *J* = 5.3, 1.1 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.11 (t, *J* = 7.7 Hz, 2H), 7.05 (dd, *J* = 3.5, 1.1 Hz, 1H), 6.81 (dd, *J* = 5.3, 3.6 Hz, 1H), 6.76 – 6.71 (m, 2H), 2.91 (d, *J* = 18.7 Hz, 1H), 2.83 (d, *J* = 18.7 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 181.1, 172.9, 155.1, 140.3, 136.6, 135.9, 132.9, 131.2, 130.1, 129.1, 128.3, 127.7, 126.8, 126.4, 121.9, 120.8, 120.6, 68.2, 43.0, 15.9. HRMS (ESI): Calcd for $C_{23}H_{18}NOSSe$ $[M+H]^+$: 436.0269; found: 436.0265.

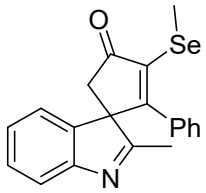
2'-Methyl-3-(naphthalen-1-ylselanyl)-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3am)



Brown solid. 69.9 mg, Yield: 73%, mp 176-178 °C. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 1H), 7.71 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.63 (dd, *J* = 12.4, 5.1 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.06 –

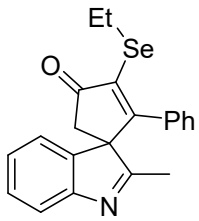
6.98 (m, 2H), 6.85 (dd, *J* = 10.8, 4.9 Hz, 2H), 6.48 – 6.43 (m, 2H), 2.91 (d, *J* = 18.8 Hz, 1H), 2.81 (d, *J* = 18.8 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 181.3, 172.0, 154.8, 140.3, 135.9, 134.6, 134.0, 133.8, 132.6, 129.5, 129.4, 129.0, 128.7, 127.8, 127.7, 126.8, 126.3, 126.3, 126.2, 126.1, 125.4, 121.9, 120.4, 68.5, 42.7, 15.8. HRMS (ESI): Calcd for $C_{29}H_{22}NOSe$ $[M+H]^+$: 480.0861; found: 480.0863.

2'-Methyl-3-(methylselanyl)-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3an)



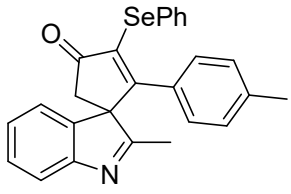
Brown solid. 67.5 mg, Yield: 92%, mp 86-88 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.37 (td, *J* = 7.7, 1.9 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 2H), 6.84 (d, *J* = 7.3 Hz, 2H), 2.94 (d, *J* = 18.7 Hz, 1H), 2.88 (d, *J* = 18.7 Hz, 1H), 2.23 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 181.6, 169.4, 155.0, 140.5, 134.6, 133.5, 130.1, 129.1, 128.4, 126.8, 126.4, 121.8, 120.6, 68.0, 43.4, 15.8, 5.9. HRMS (ESI): Calcd for $C_{20}H_{18}NOSe$ $[M+H]^+$: 368.0548; found: 368.0546.

3-(Ethylselanyl)-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3ao)



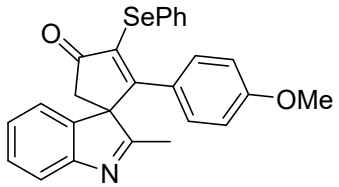
Brown solid. 68.6 mg, Yield: 90%, mp 101-103 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.26 – 7.20 (m, 3H), 7.19 – 7.12 (m, 2H), 6.85 – 6.77 (m, 2H), 2.97 – 2.83 (m, 4H), 2.19 (s, 3H), 1.32 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 181.5, 170.6, 155.1, 140.7, 133.8, 133.6, 130.1, 129.1, 128.4, 126.8, 126.4, 121.8, 120.6, 68.2, 43.4, 19.2, 15.9, 15.8. HRMS (ESI): Calcd for $C_{21}H_{20}NOSe$ $[M+H]^+$: 382.0705; found: 382.0705.

2'-Methyl-3-(phenylselanyl)-2-(p-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3ba)



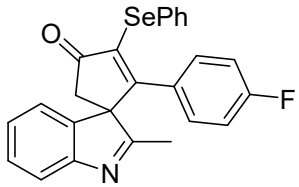
Brown solid. 79.8 mg, Yield: 90%, mp 113-114 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.25 – 7.14 (m, 5H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.65 (d, *J* = 7.9 Hz, 2H), 2.92 (d, *J* = 18.7 Hz, 1H), 2.84 (d, *J* = 18.7 Hz, 1H), 2.20 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 181.6, 173.4, 155.2, 140.8, 140.6, 134.7, 133.0, 130.3, 129.1, 129.1, 129.0, 128.4, 127.6, 126.9, 126.5, 121.8, 120.6, 68.2, 43.2, 21.4, 16.0. HRMS (ESI): Calcd for $C_{26}H_{22}NOSe$ $[M+H]^+$: 444.0861; found: 444.0862.

2-(4-Methoxyphenyl)-2'-methyl-3-(phenylselanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3ca)



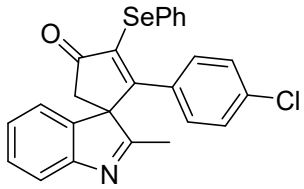
Brown solid. 79.0 mg, Yield: 86%, mp 134-136 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 3H), 7.25 – 7.13 (m, 5H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 8.7 Hz, 2H), 3.68 (s, 3H), 2.91 (d, *J* = 18.6 Hz, 1H), 2.82 (d, *J* = 18.6 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 182.0, 172.6, 161.2, 155.0, 141.2, 133.6, 132.8, 129.1, 129.0, 128.6, 127.6, 126.5, 125.5, 121.7, 120.7, 113.7, 68.2, 55.2, 43.4, 15.9. HRMS (ESI): Calcd for $C_{26}H_{22}NOSe$ $[M+H]^+$: 460.0810; found: 460.0811.

2-(4-Fluorophenyl)-2'-methyl-3-(phenylselanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3da)



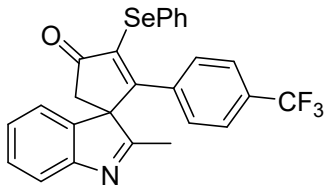
Brown solid. 77.8 mg, Yield: 87%, mp 142-143 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.38 (dd, *J* = 19.2, 7.3 Hz, 3H), 7.30 – 7.11 (m, 5H), 6.80 – 6.68 (m, 4H), 2.97 (d, *J* = 18.8 Hz, 1H), 2.89 (d, *J* = 18.7 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 181.2, 171.3, 163.4 (d, *J* = 251.7 Hz), 155.1, 140.3, 135.9, 133.3, 129.3, 129.1, 129.0 (d, *J* = 8.6 Hz), 127.8, 127.8, 126.6, 121.7, 120.8, 115.4 (d, *J* = 21.8 Hz), 68.3, 43.0, 15.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.43. HRMS (ESI): Calcd for $C_{25}H_{18}FNOSe$ $[M+H]^+$: 448.0610; found: 448.0613.

2-(4-Chlorophenyl)-2'-methyl-3-(phenylselanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3ea)



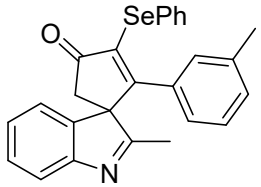
Brown solid. 77.8 mg, Yield: 84%, mp 174-175 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.26 – 7.10 (m, 5H), 7.02 – 6.97 (m, 2H), 6.65 – 6.59 (m, 2H), 2.94 (d, *J* = 18.8 Hz, 1H), 2.87 (d, *J* = 18.8 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 181.0, 171.0, 155.1, 140.2, 136.4, 136.0, 133.5, 131.4, 129.3, 129.1, 128.5, 128.1, 127.9, 127.6, 126.6, 121.8, 120.8, 68.3, 42.9, 15.9. HRMS (ESI): Calcd for $C_{25}H_{19}Cl^{37}NOSe$ $[M+H]^+$: 464.0315; found: 464.0317, $C_{25}H_{19}Cl^{35}NOSe$ $[M+H]^+$: 462.0323; found: 462.0326.

2'-Methyl-3-(phenylselanyl)-2-(4-(trifluoromethyl)phenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3fa)



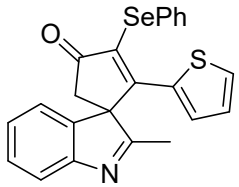
Brown solid. 79.5 mg, Yield: 80%, mp 152-153 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.32 – 7.21 (m, 6H), 7.15 (t, *J* = 7.0 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 3.01 (d, *J* = 19.0 Hz, 1H), 2.93 (d, *J* = 18.7 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 180.6, 169.8, 155.1, 139.8, 137.7, 136.4, 133.9, 131.27 (q, *J* = 32.7 Hz), 129.4, 129.1, 128.1, 127.0, 127.0, 126.6, 125.06 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.4 Hz), 121.8, 120.8, 68.4, 42.6, 15.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.12. HRMS (ESI): Calcd for $C_{26}H_{19}F_3NOSe$ $[M+H]^+$: 498.0578; found: 498.0581.

2'-Methyl-3-(phenylselanyl)-2-(m-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3ga)



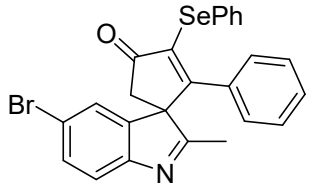
Brown solid. 75.3 mg, Yield: 85%, mp 108-109 ℃. column chromatography eluent, EtOAc/PE = 1:15 → 1:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 6.4 Hz, 3H), 7.28 – 7.16 (m, 5H), 7.03 – 6.89 (m, 2H), 6.50 (d, *J* = 8.6 Hz, 2H), 2.96 (d, *J* = 18.7 Hz, 1H), 2.88 (d, *J* = 18.7 Hz, 1H), 2.21 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 181.3, 173.1, 155.2, 140.6, 137.7, 135.3, 133.2, 133.0, 130.8, 129.1, 129.0, 128.1, 127.6, 127.5, 126.4, 123.8, 121.8, 120.6, 68.3, 43.0, 21.3, 16.0. HRMS (ESI): Calcd for $C_{26}H_{22}NOSe$ $[M+H]^+$: 444.0861; found: 444.0864.

2'-Methyl-3-(phenylselanyl)-2-(thiophen-2-yl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3ha)



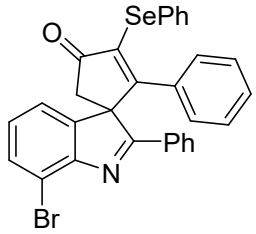
Brown solid. 63.5 mg, Yield: 73%, mp 110-112 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 6.4 Hz, 3H), 7.28 – 7.16 (m, 5H), 7.03 – 6.89 (m, 2H), 6.50 (d, *J* = 8.6 Hz, 2H), 2.96 (d, *J* = 18.7 Hz, 1H), 2.88 (d, *J* = 18.7 Hz, 1H), 2.21 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 181.3, 173.1, 155.2, 140.6, 137.7, 135.3, 133.2, 133.0, 130.8, 129.1, 129.0, 128.1, 127.6, 127.5, 126.4, 123.8, 121.8, 120.6, 68.3, 43.0, 21.3, 16.0. HRMS (ESI): Calcd for $C_{23}H_{18}NOSe$ $[M+H]^+$: 436.0269; found: 436.0271.

5'-Bromo-2'-methyl-2-phenyl-3-(phenylselanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3ja)



Brown solid. 93.3 mg, Yield: 92%, mp 173-174 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.32 (m, 4H), 7.17 – 7.09 (m, 6H), 6.74 (d, *J* = 6.3 Hz, 2H), 2.92 (d, *J* = 18.6 Hz, 1H), 2.83 (d, *J* = 18.3 Hz, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 181.9, 171.6, 154.1, 142.7, 136.2, 133.5, 132.8, 132.2, 130.2, 129.1, 128.4, 127.9, 127.8, 126.8, 125.1, 122.0, 120.0, 68.5, 43.0, 16.0. HRMS (ESI): Calcd for $C_{25}H_{19}Br^{79}NOSe$ $[M+H]^+$: 507.9810; found: 507.9812, $C_{25}H_{19}Br^{81}NOSe$ $[M+H]^+$: 509.9789; found: 509.9791.

7'-Bromo-2,2'-diphenyl-3-(phenylselanyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3ka)



Brown solid. 85.2 mg, Yield: 84%, mp 151-153 ℃. column chromatography eluent, EtOAc/PE = 1:20 → 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.21 – 7.06 (m, 8H), 6.74 (dd, *J* = 5.2, 3.4 Hz, 2H), 2.93 (d, *J* = 18.7 Hz, 1H), 2.84 (d, *J* = 18.7 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 183.0, 171.6, 153.4, 142.3, 136.2, 133.4, 132.9, 132.5, 130.2, 129.1, 128.4, 127.8, 127.8, 126.7, 120.78, 114.4, 69.8, 43.2, 16.2. HRMS (ESI): Calcd for $C_{25}H_{19}Br^{79}NOSe$ $[M+H]^+$: 507.9810; found: 507.9809, $C_{25}H_{19}Br^{81}NOSe$ $[M+H]^+$: 509.9789; found: 509.9787.

References

[S1] (a) X. Ma, Q. Wang, X. Feng, Z. Mo, Y. Pan, Y. Chen, M. Xin and Y. Xu, *Green Chem.,* 2019, **21**, 3547; (b) A.-D. Sonawane, R.-A. Sonawane, M. Ninomiya and M. Koketsu, *Adv. Synth. Catal.,* 2020, **362**, 3485.

[S2] (a) M.-J. James, J.-D. Cuthbertson, P. O'Brien, R.-J.-K. Taylor and W.-P. Unsworth, *Angew. Chem., Int. Ed.,* 2015, **54**, 7640; (b) A.-K. Clarke, M.-J. James, P. O'Brien, R.-J.-K. Taylor and W.-P. Unsworth, *Angew. Chem., Int. Ed.,* 2016, **55**, 13798; (c) S.-J. Chambers, G. Coulthard, W.-P. Unsworth, P. O'Brien and R.-J.-K. Taylor, *Chem. Eur. J.* 2016, **22**, 1.

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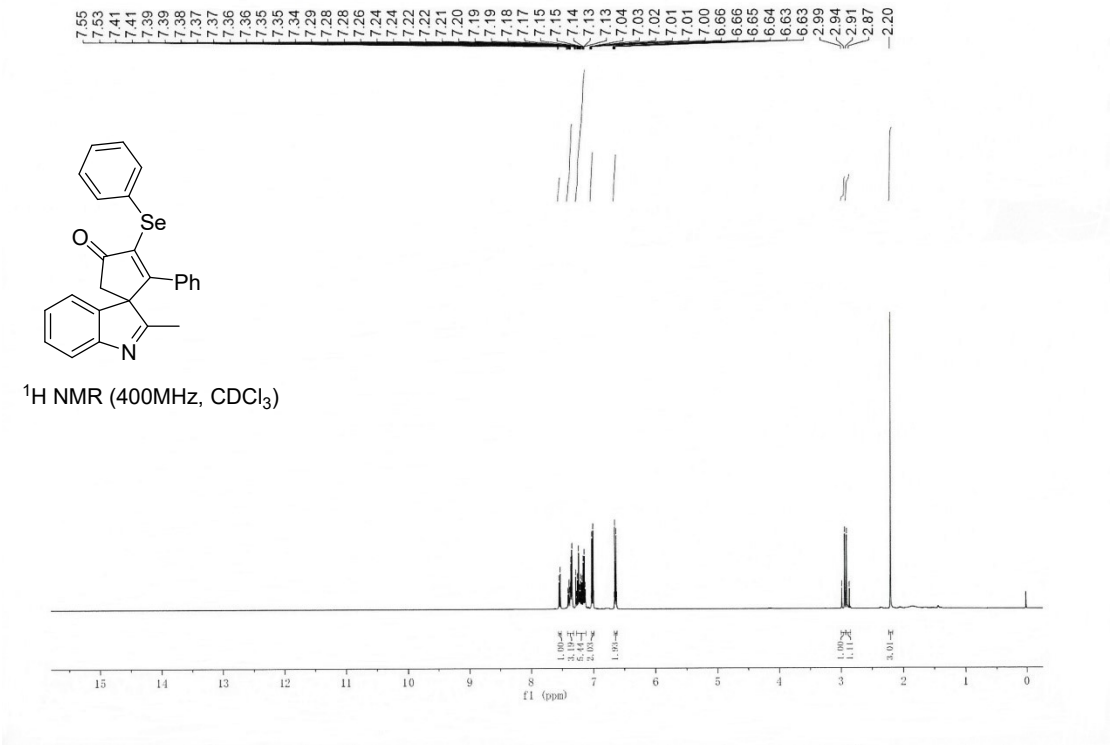
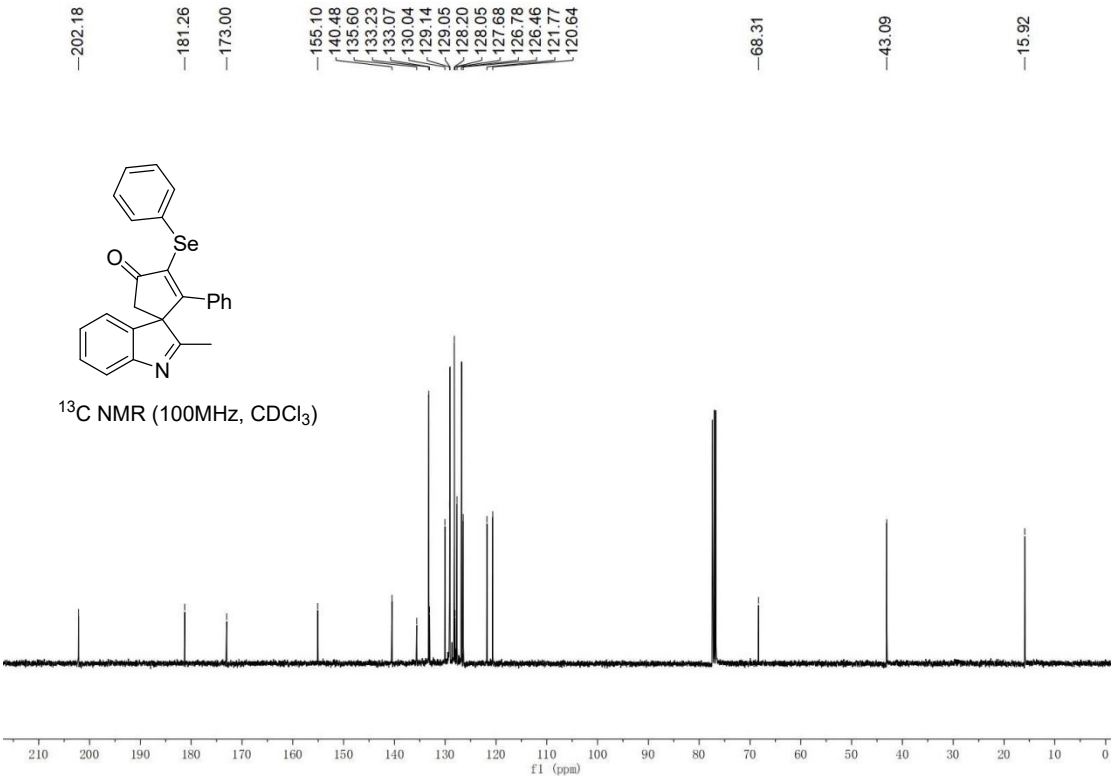
Copies of the ^{1}H, ^{13}C and ^{19}F NMR Spectra

^{1}H NMR spectrum of **3aa**



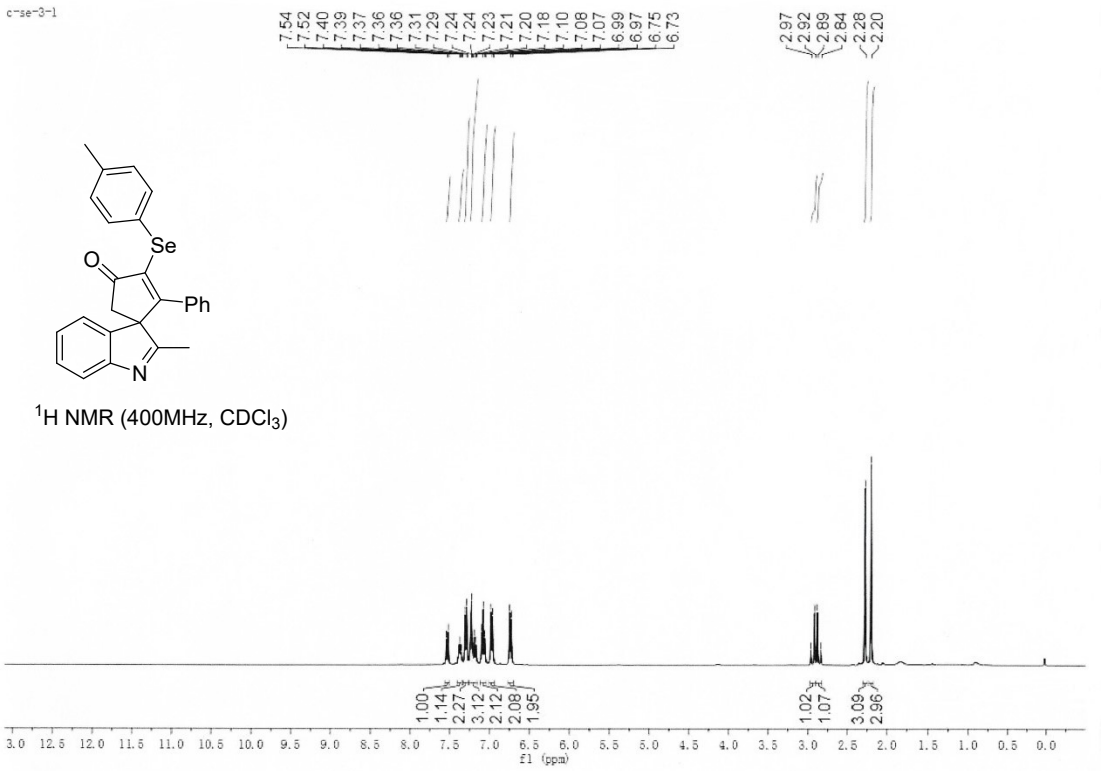
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3aa**



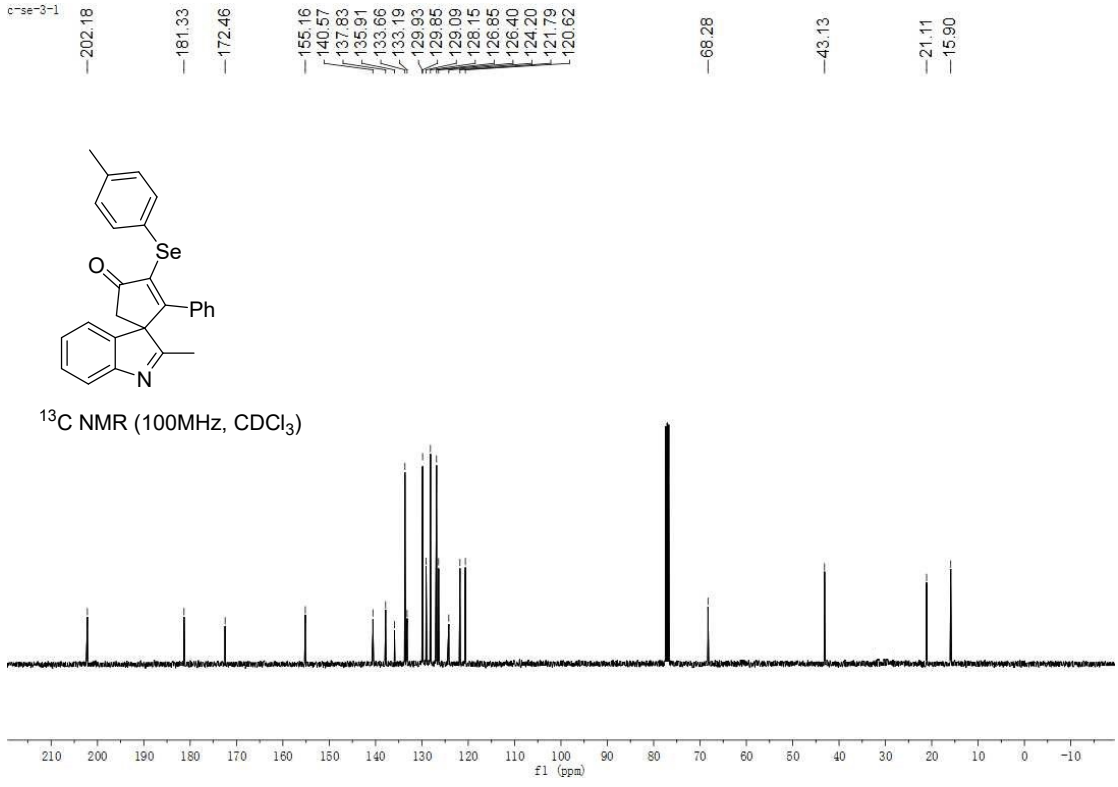
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ab**



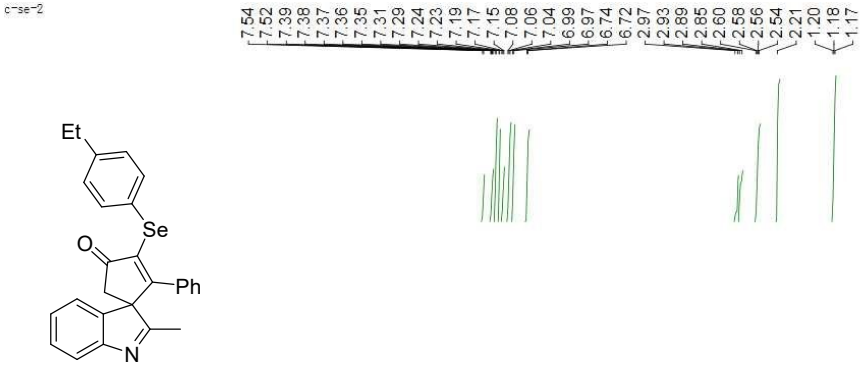
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ab**

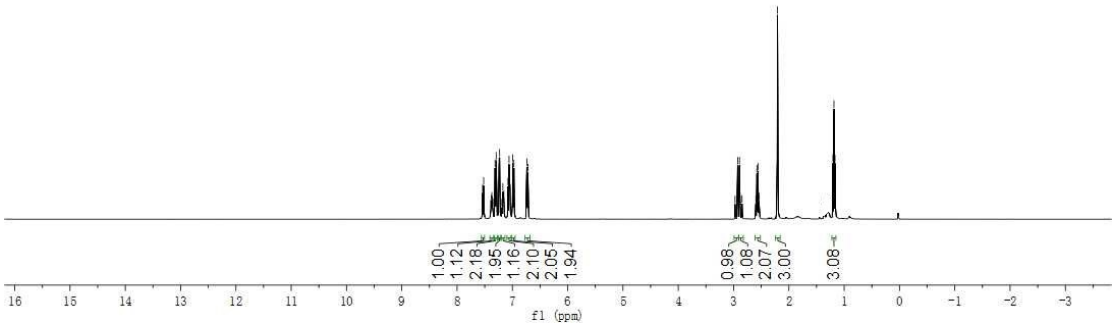


^{13}C NMR (100MHz, $CDCl_3$)

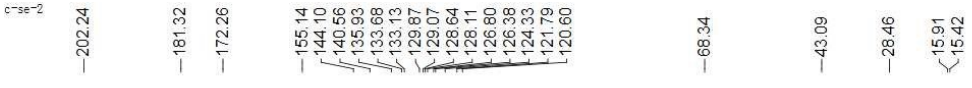
^{1}H NMR spectrum of **3ac**

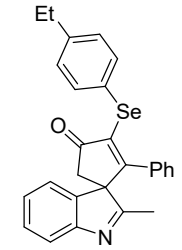


^{1}H NMR (400MHz, $CDCl_3$)

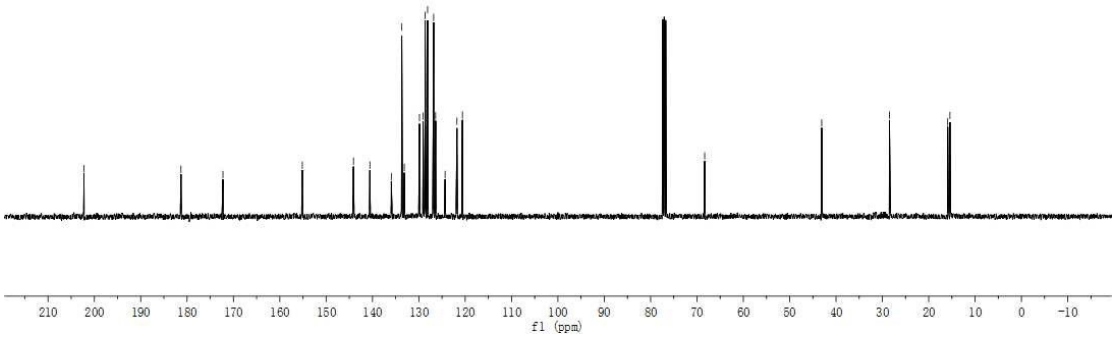


^{13}C NMR spectrum of **3ac**

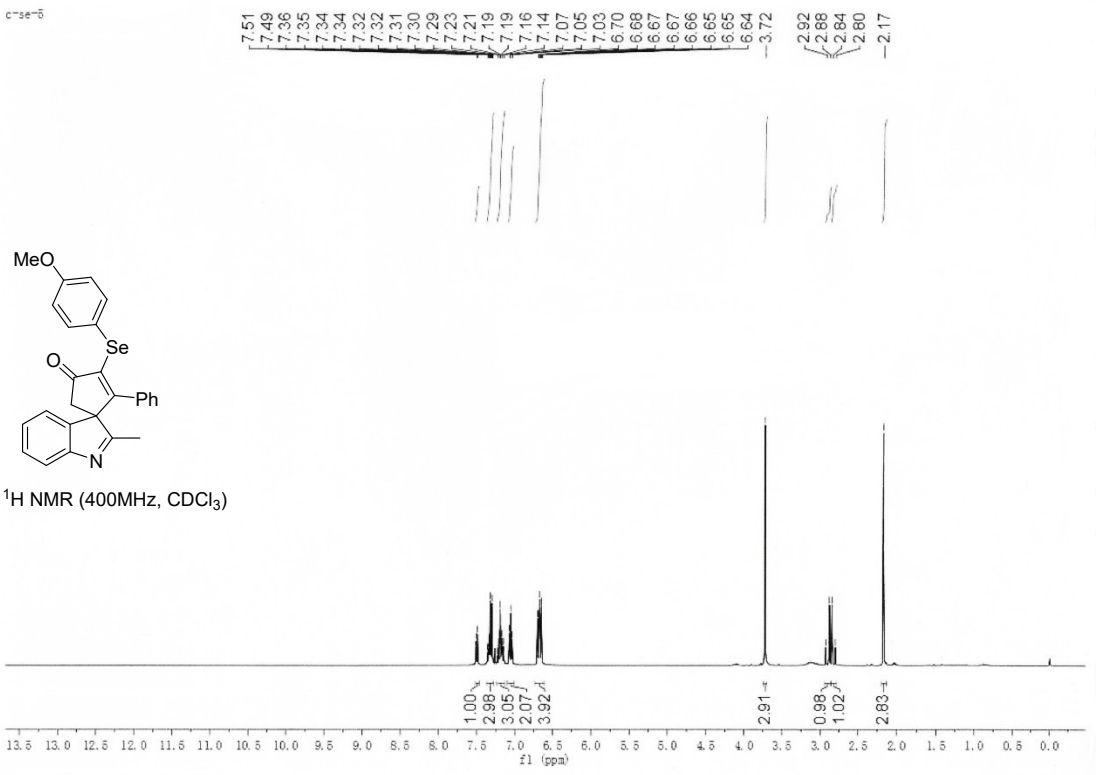




^{13}C NMR (100MHz, $CDCl_3$)

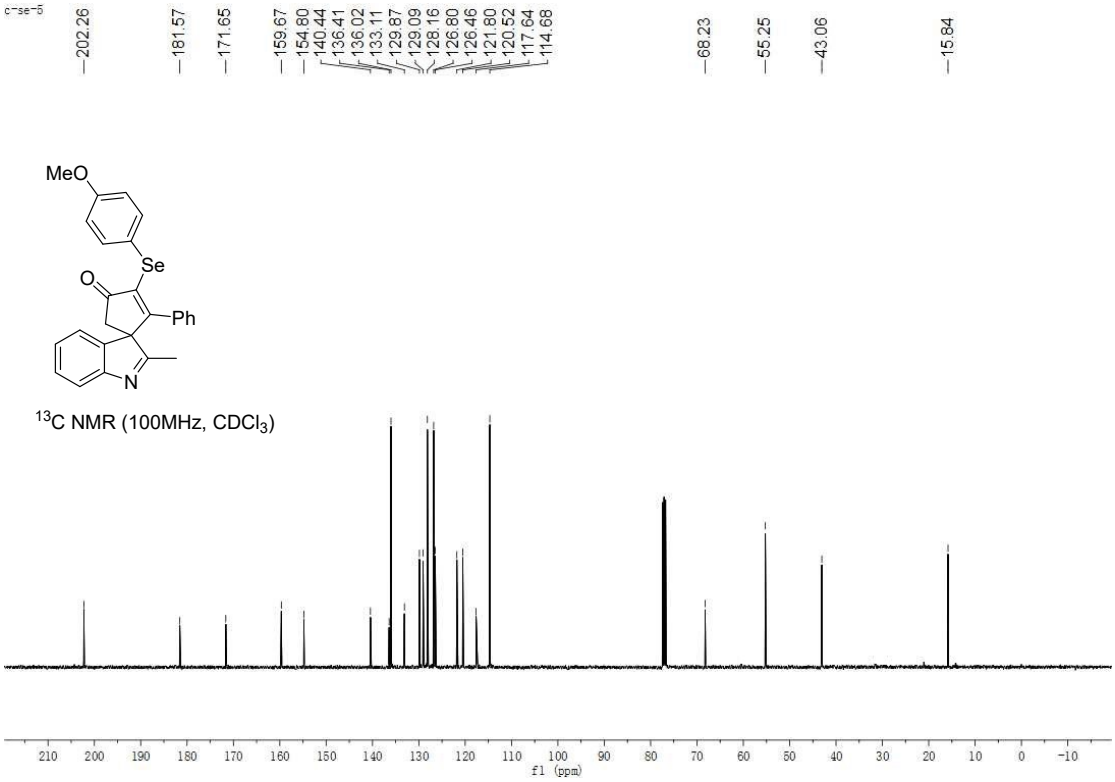


^{1}H NMR spectrum of **3ad**



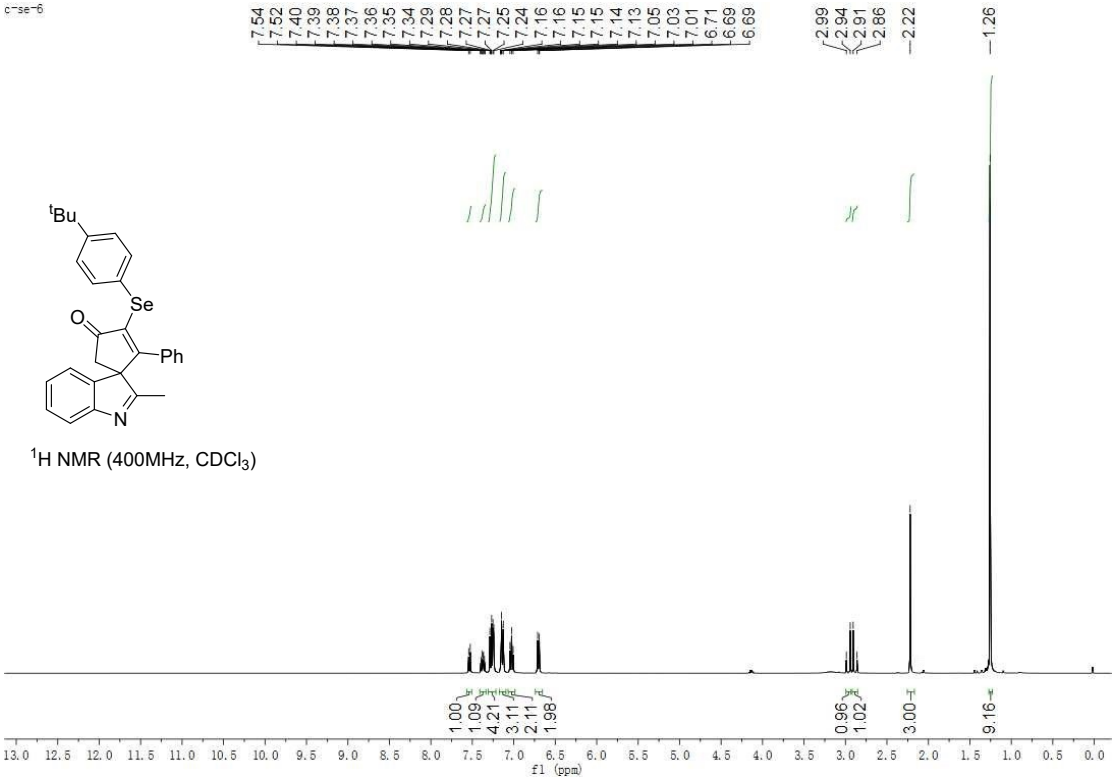
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ad**



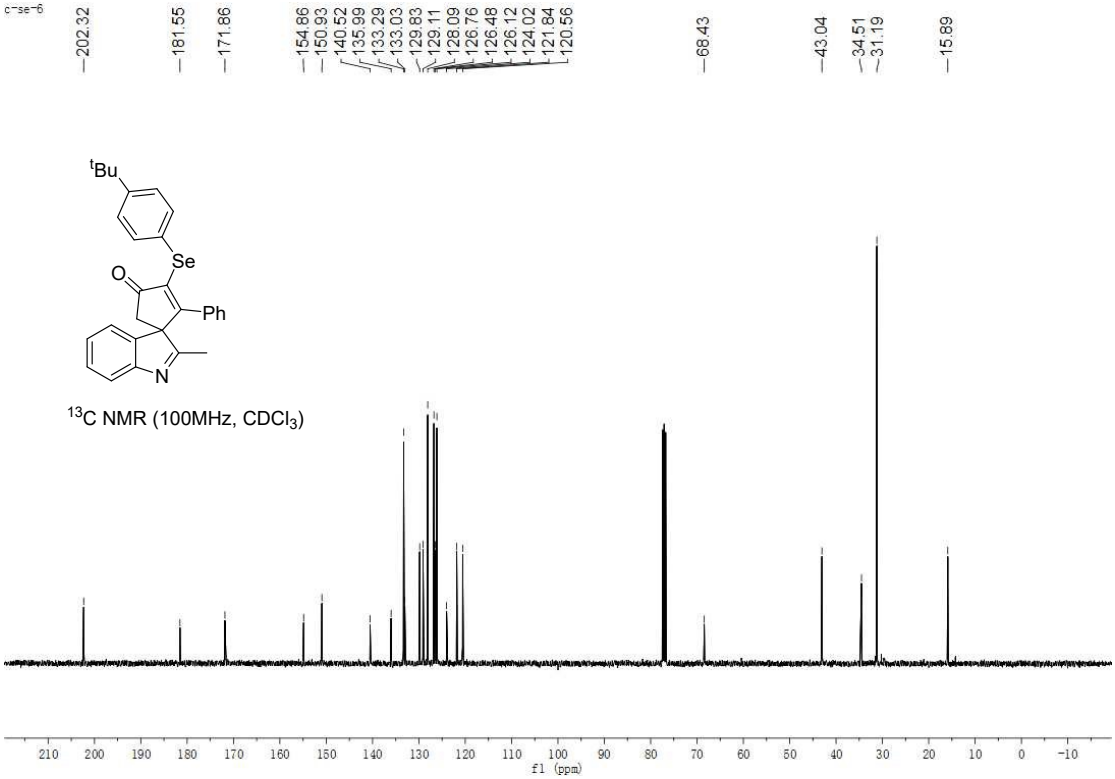
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ae**



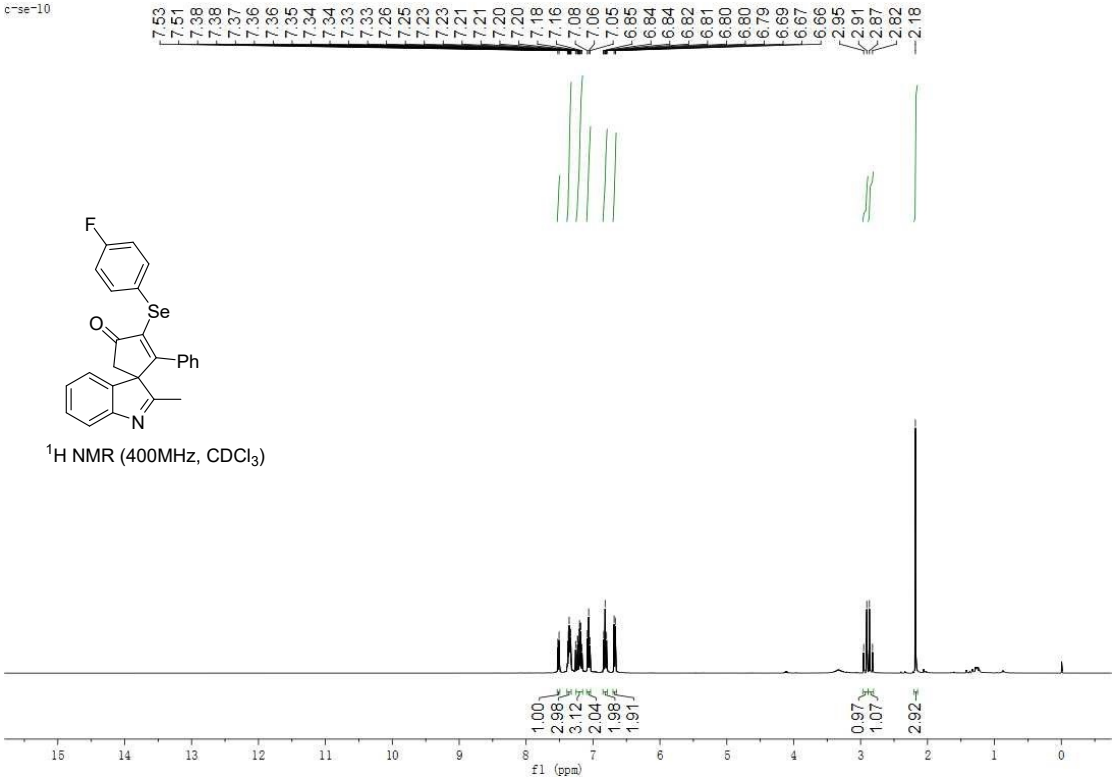
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ae**



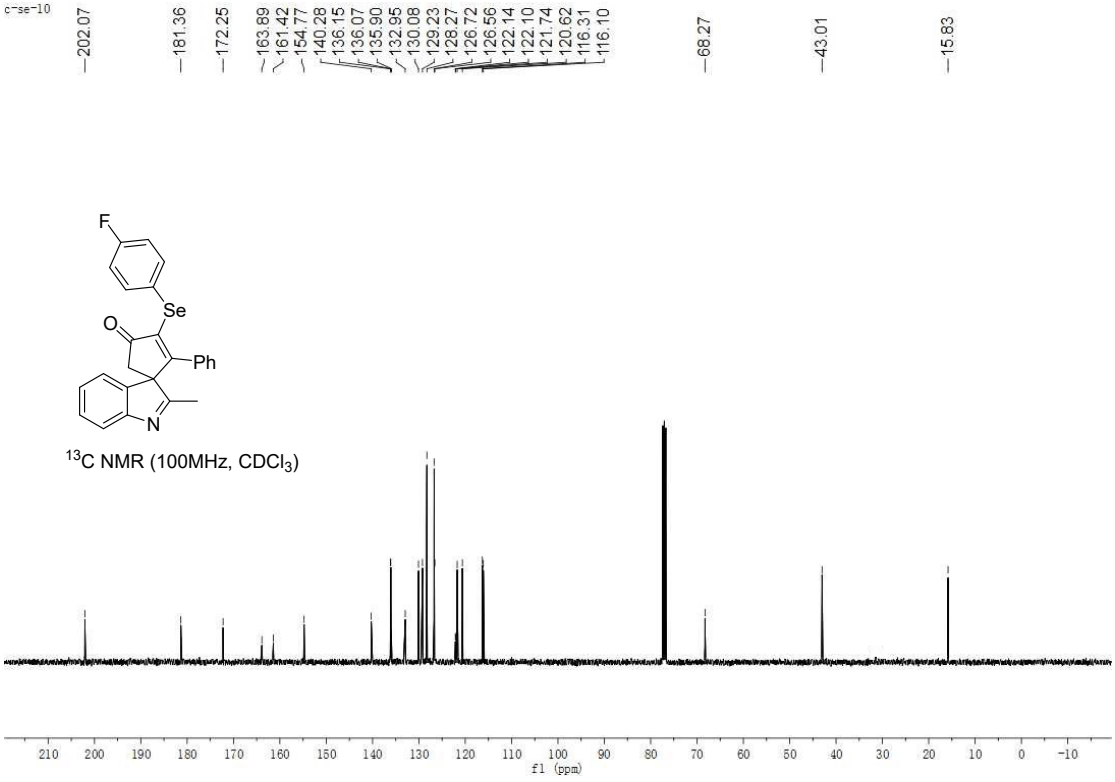
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3af**



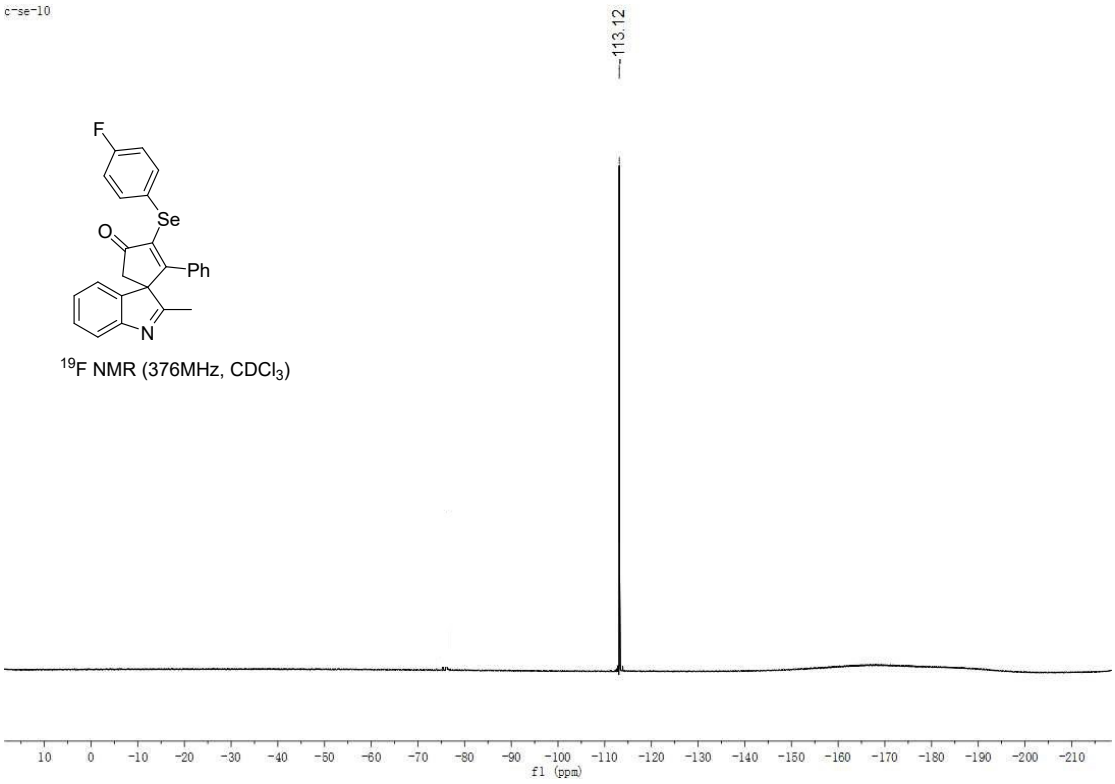
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3af**



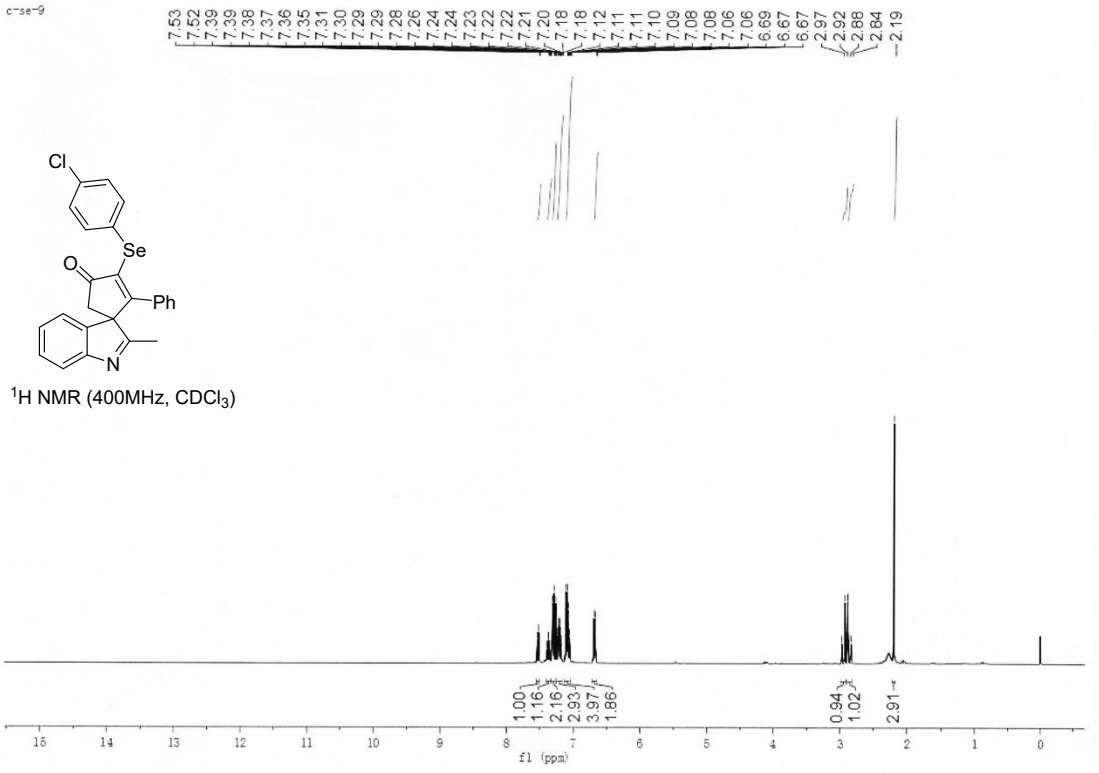
^{13}C NMR (100MHz, $CDCl_3$)

^{19}F NMR spectrum of **3af**



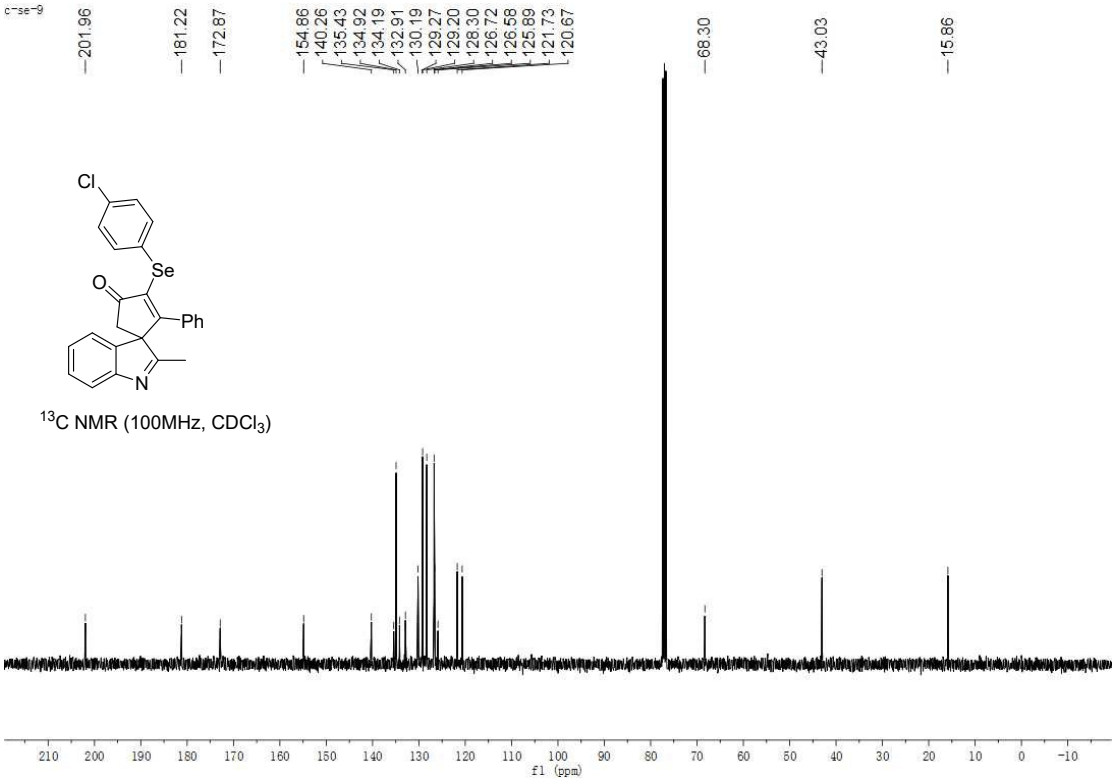
^{19}F NMR (376MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ag**

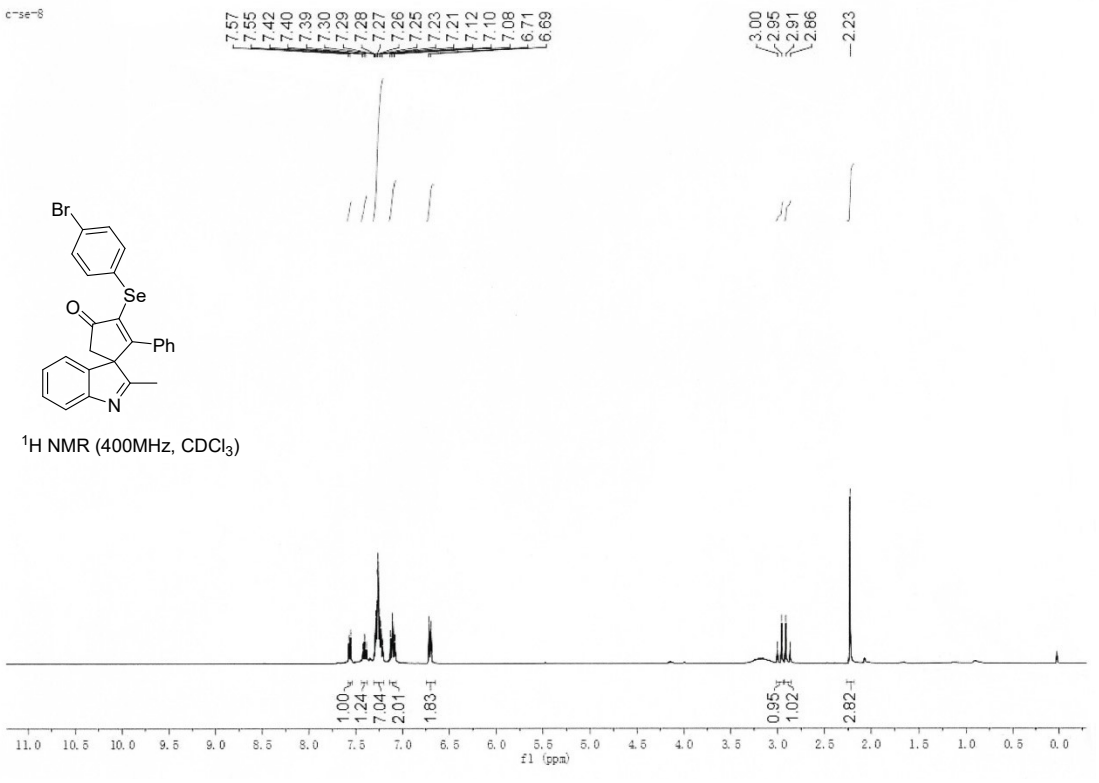


^{1}H NMR (400MHz, $CDCl_3$)

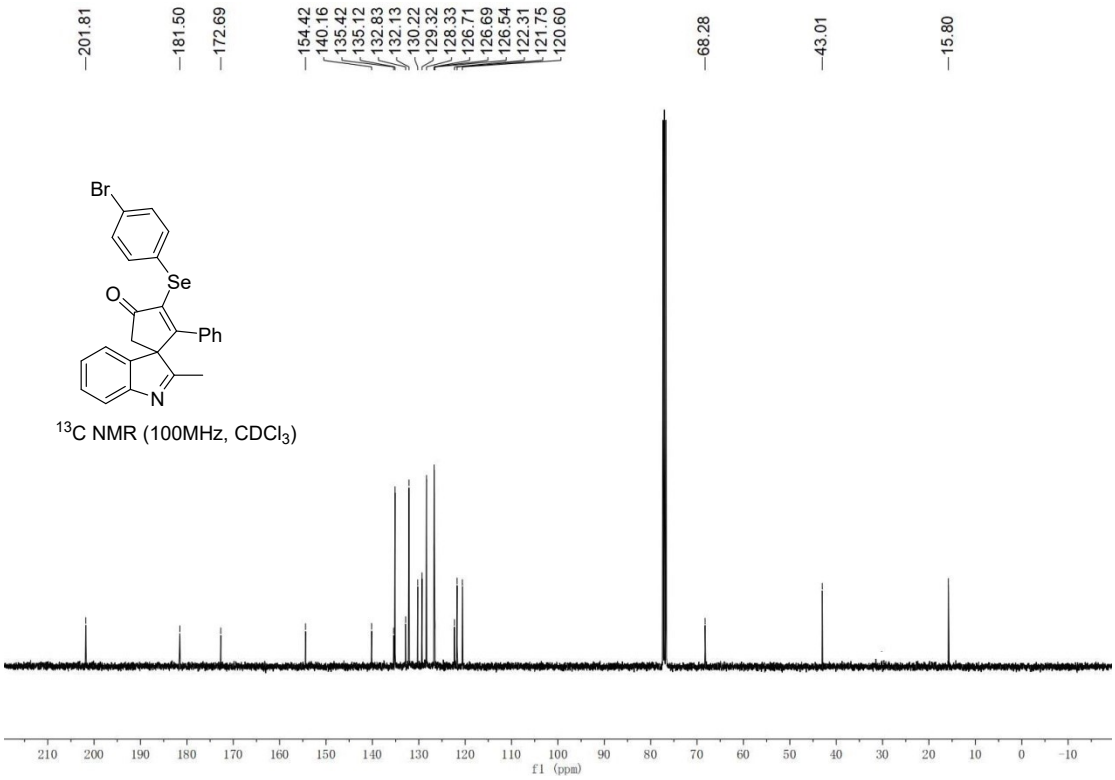
^{13}C NMR spectrum of **3ag**



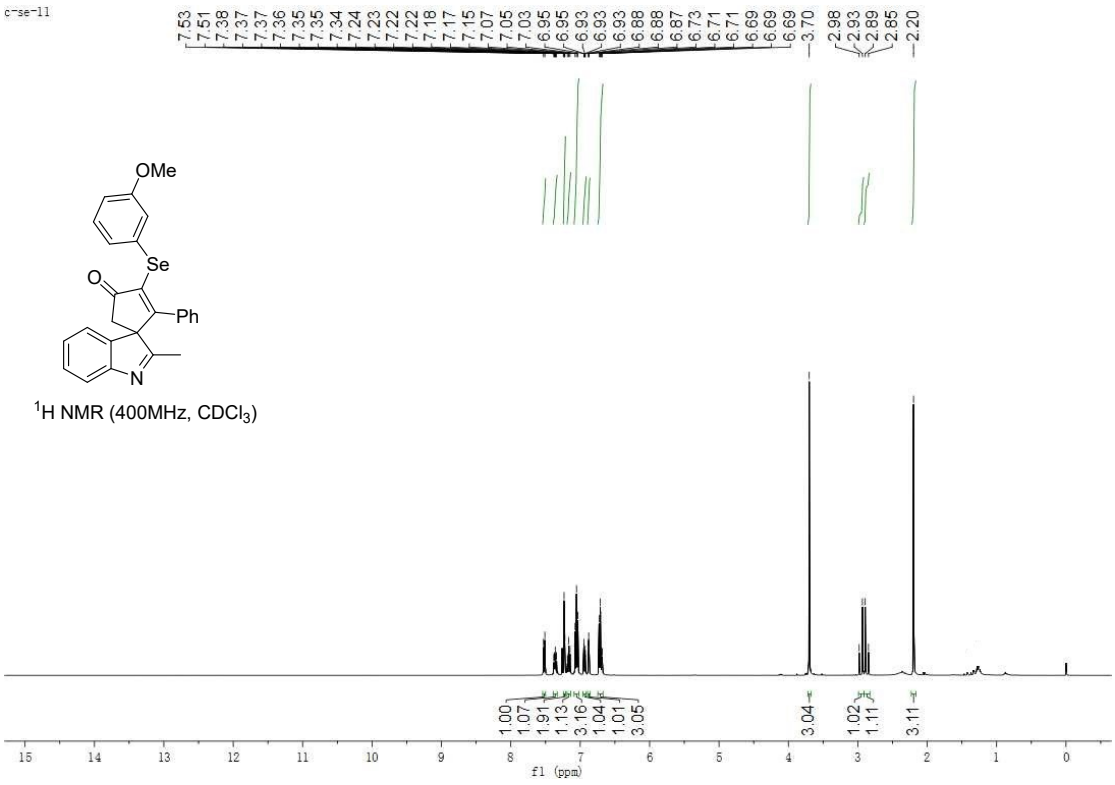
^{1}H NMR spectrum of **3ah**



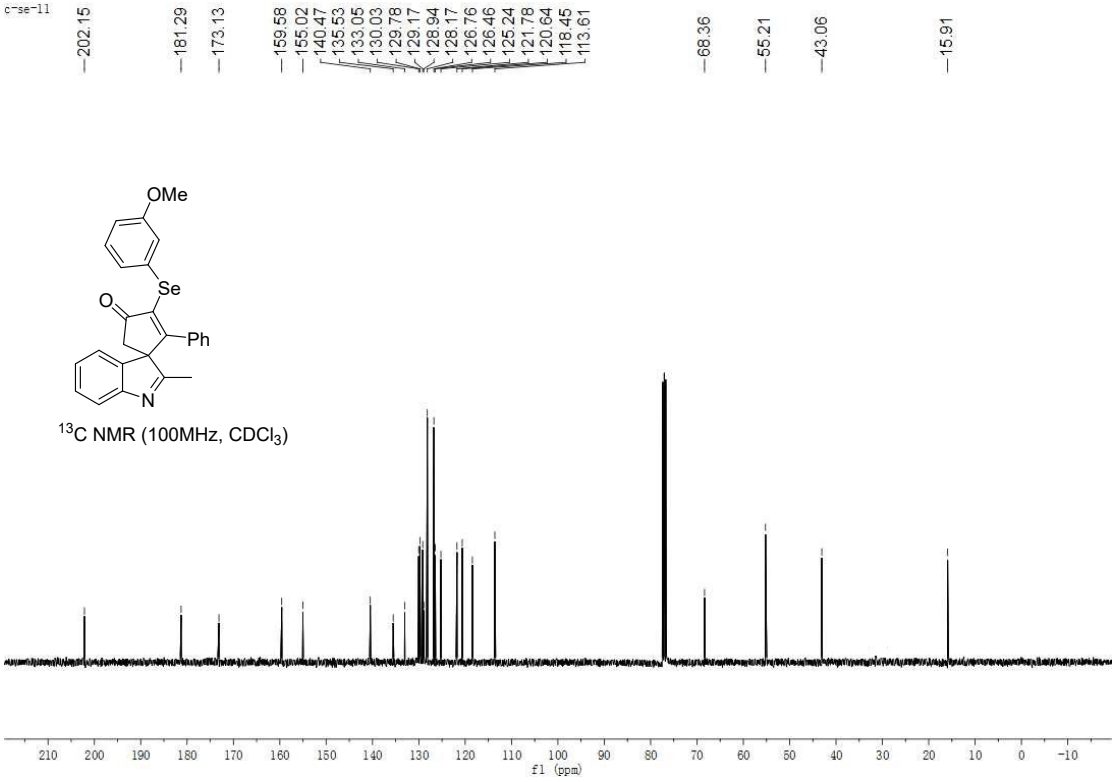
^{13}C NMR spectrum of **3ah**



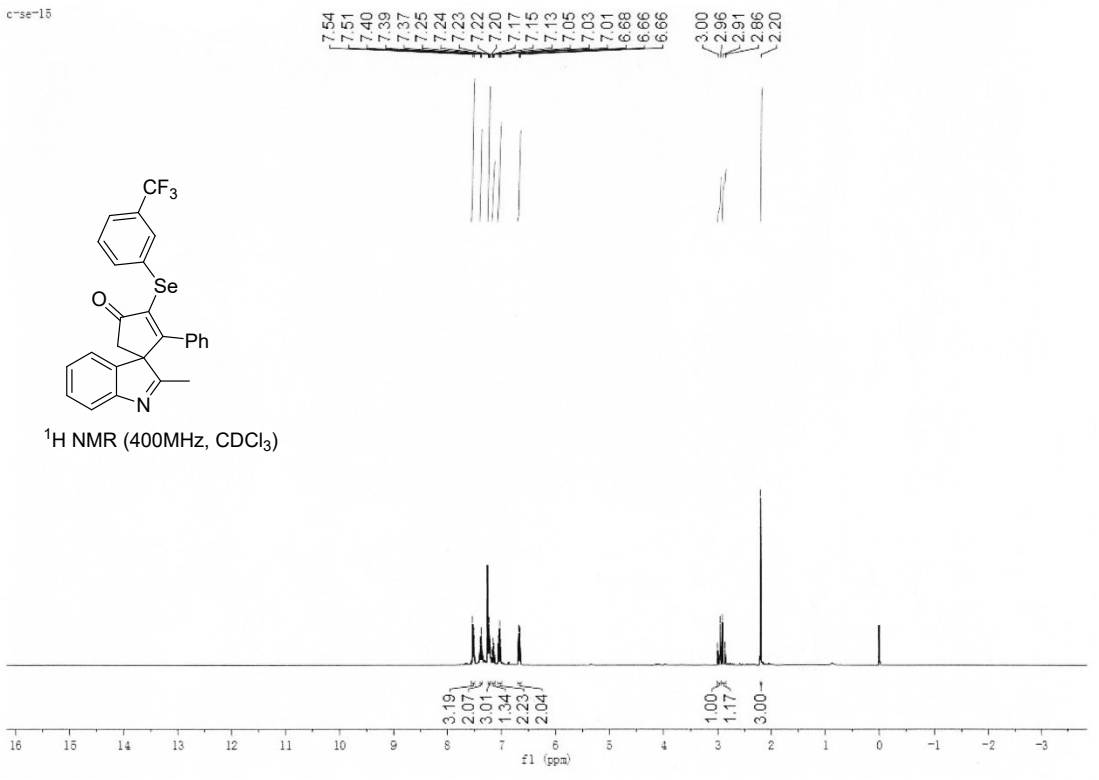
^{1}H NMR spectrum of **3ai**



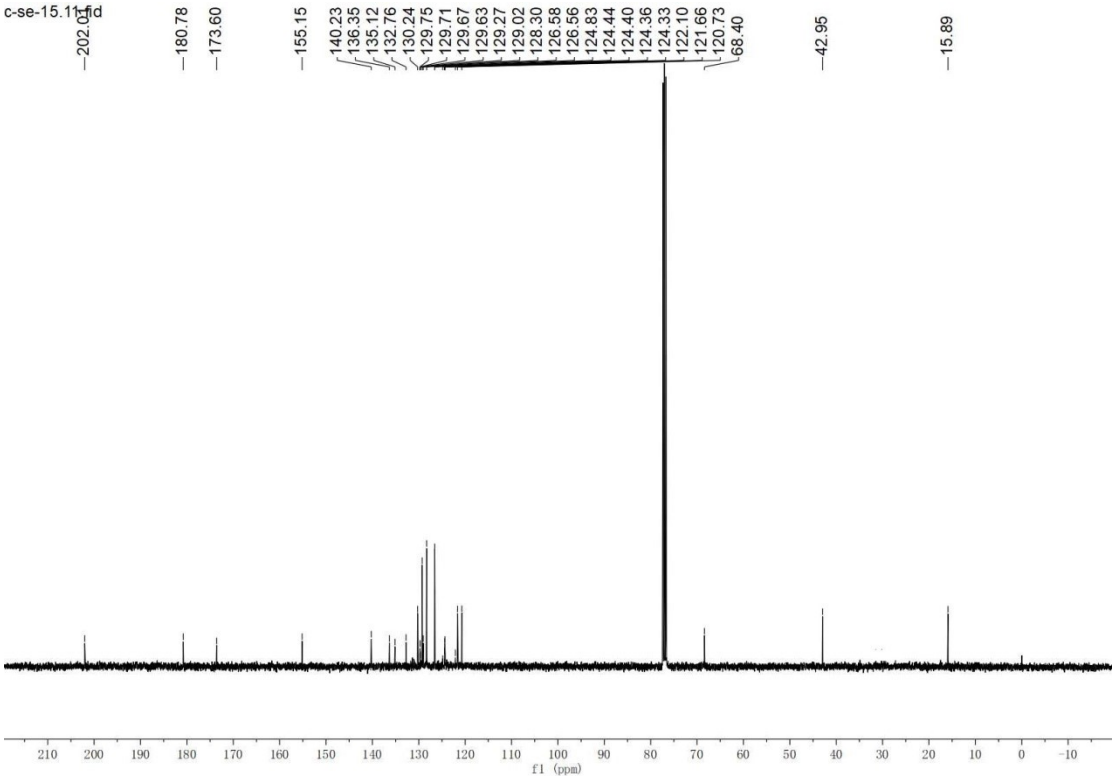
^{13}C NMR spectrum of **3ai**



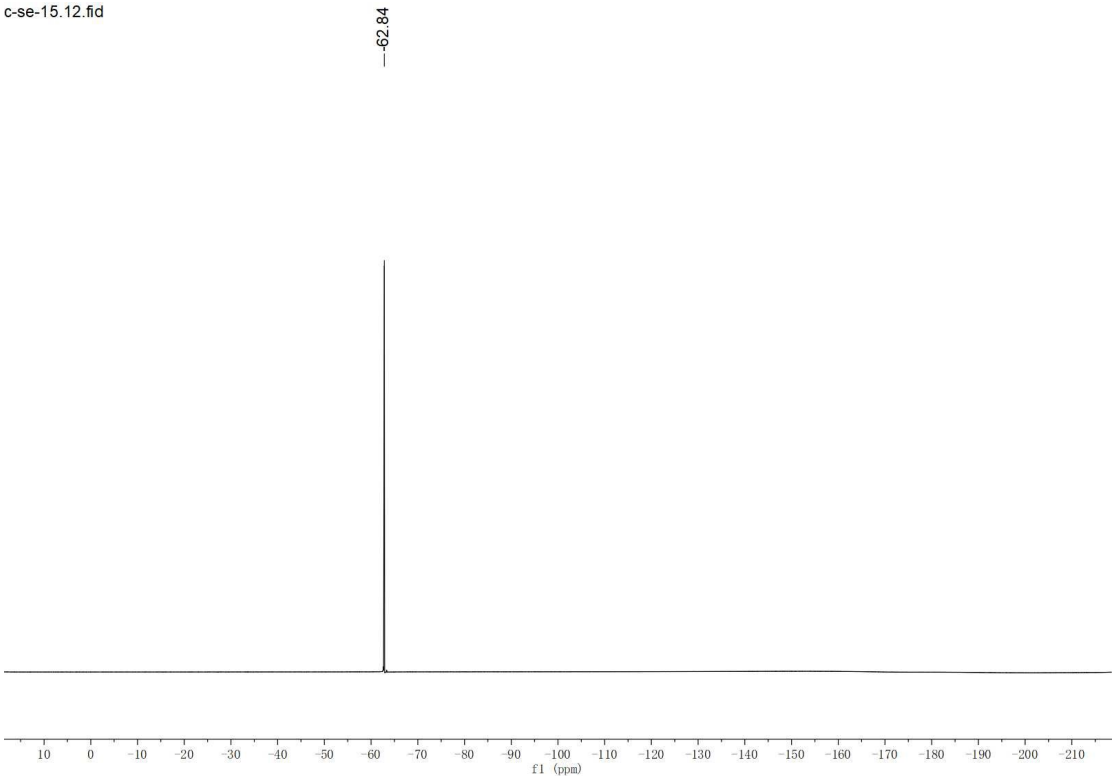
^{1}H NMR spectrum of **3aj**



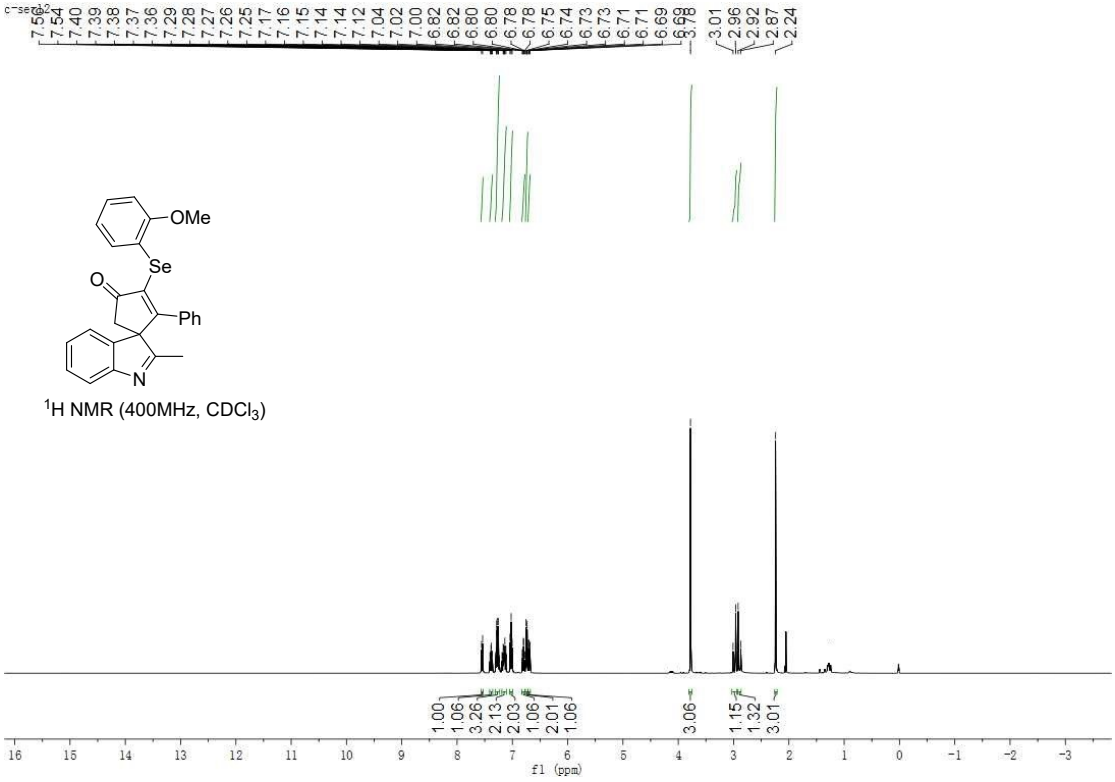
^{13}C NMR spectrum of **3aj**



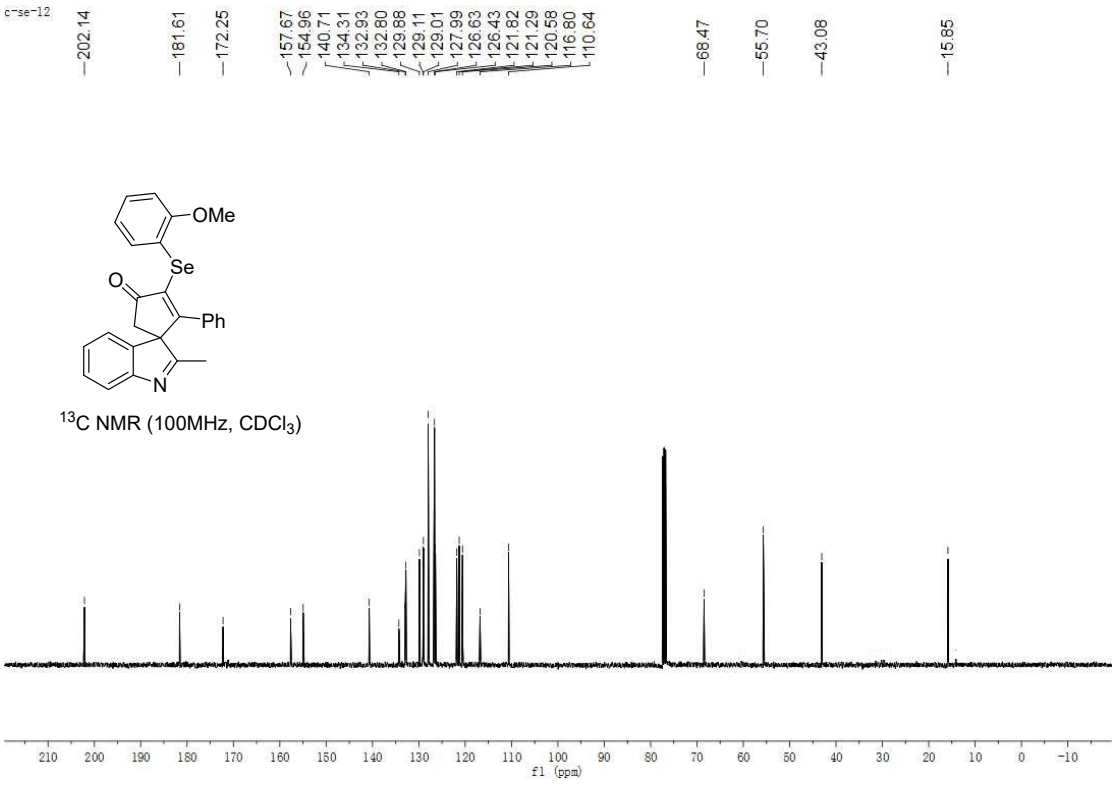
^{19}F NMR spectrum of **3aj**



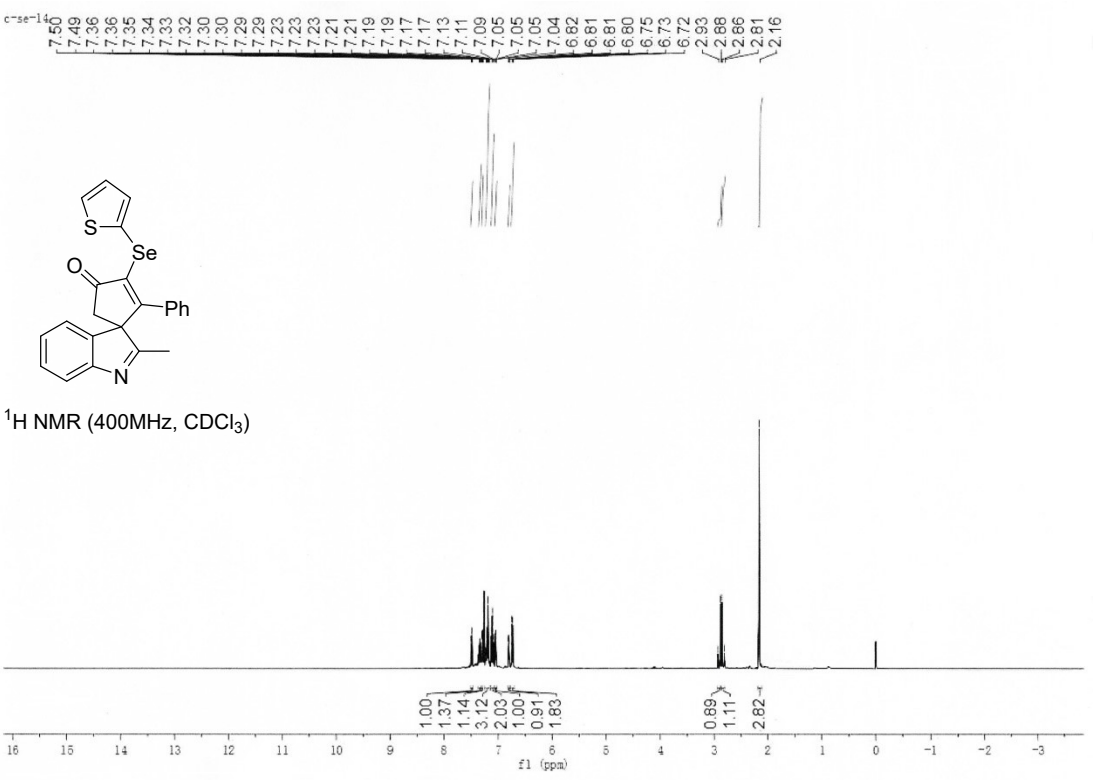
^{1}H NMR spectrum of **3ak**



^{13}C NMR spectrum of **3ak**

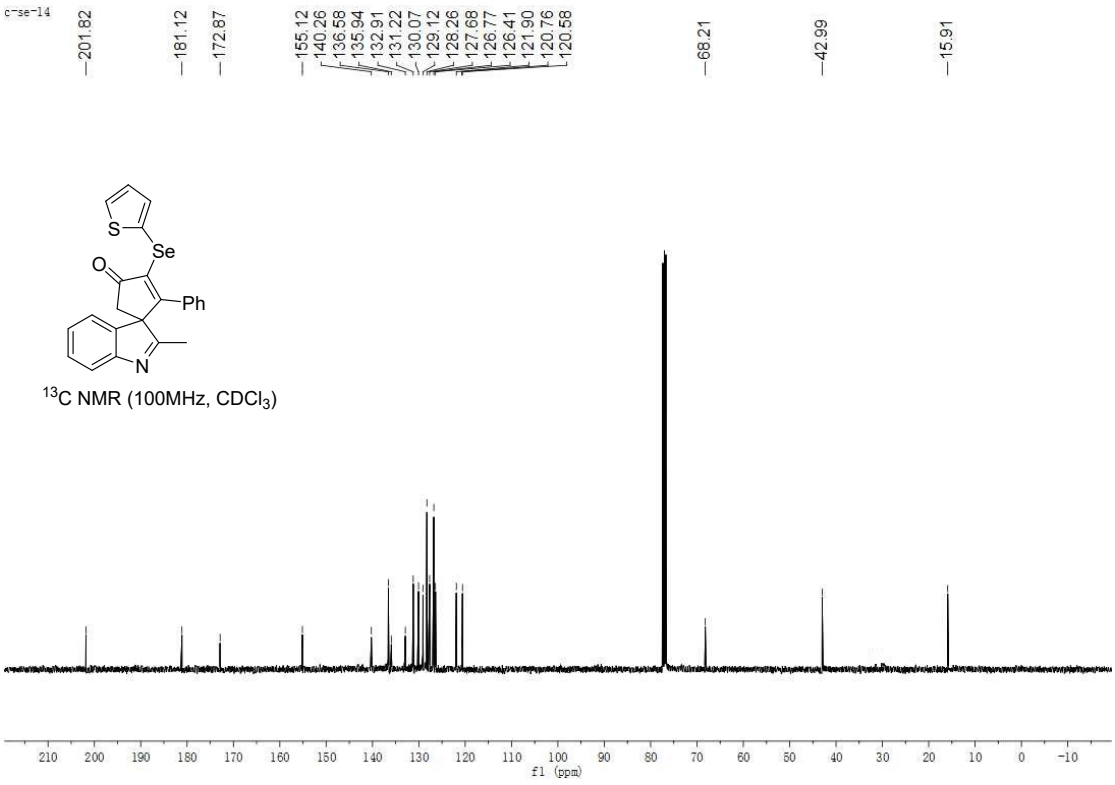


^{1}H NMR spectrum of **3al**



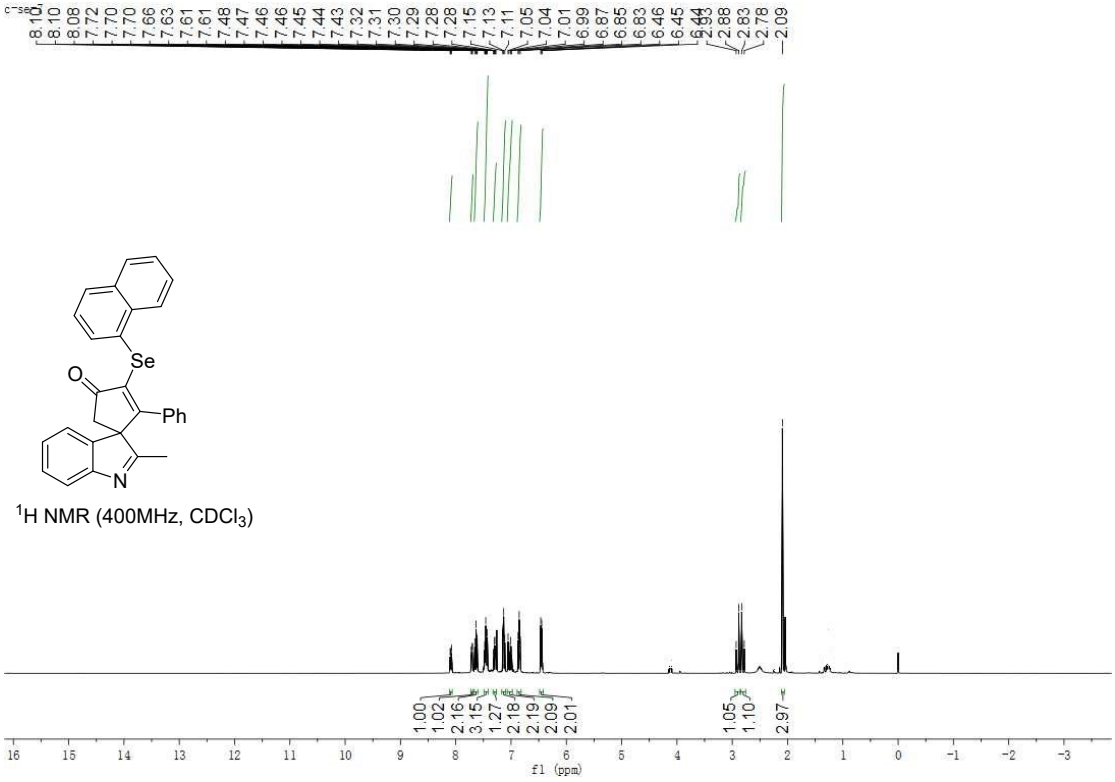
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3al**



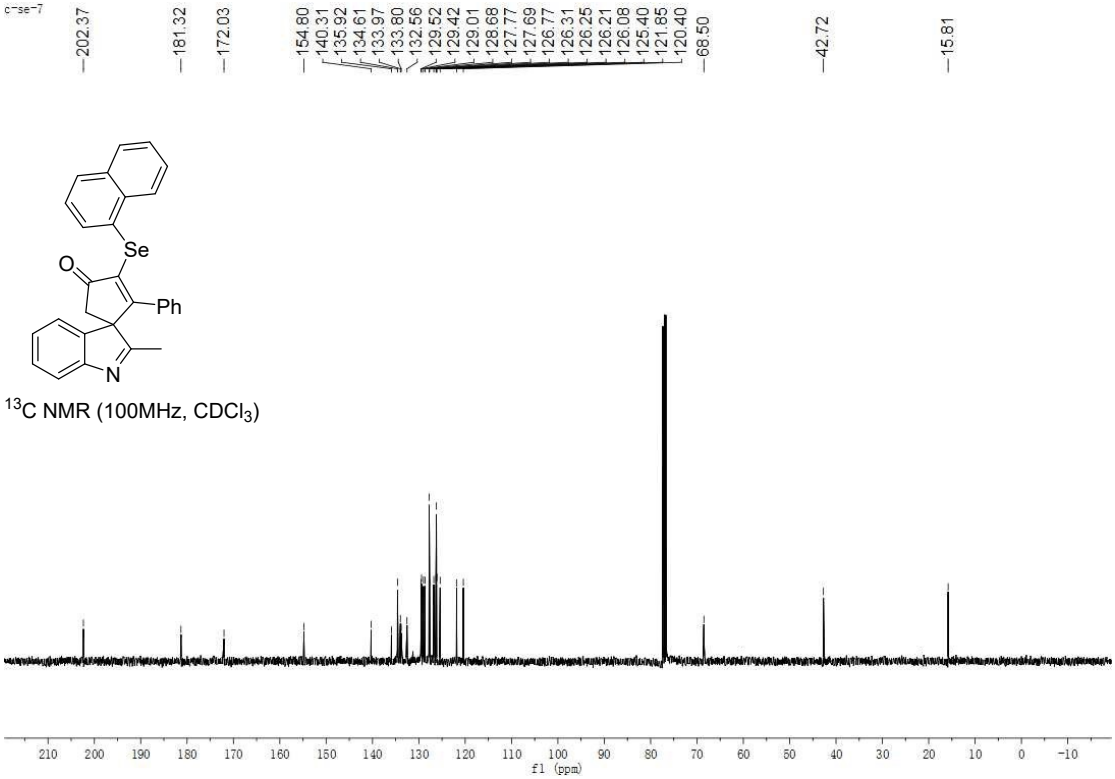
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3am**



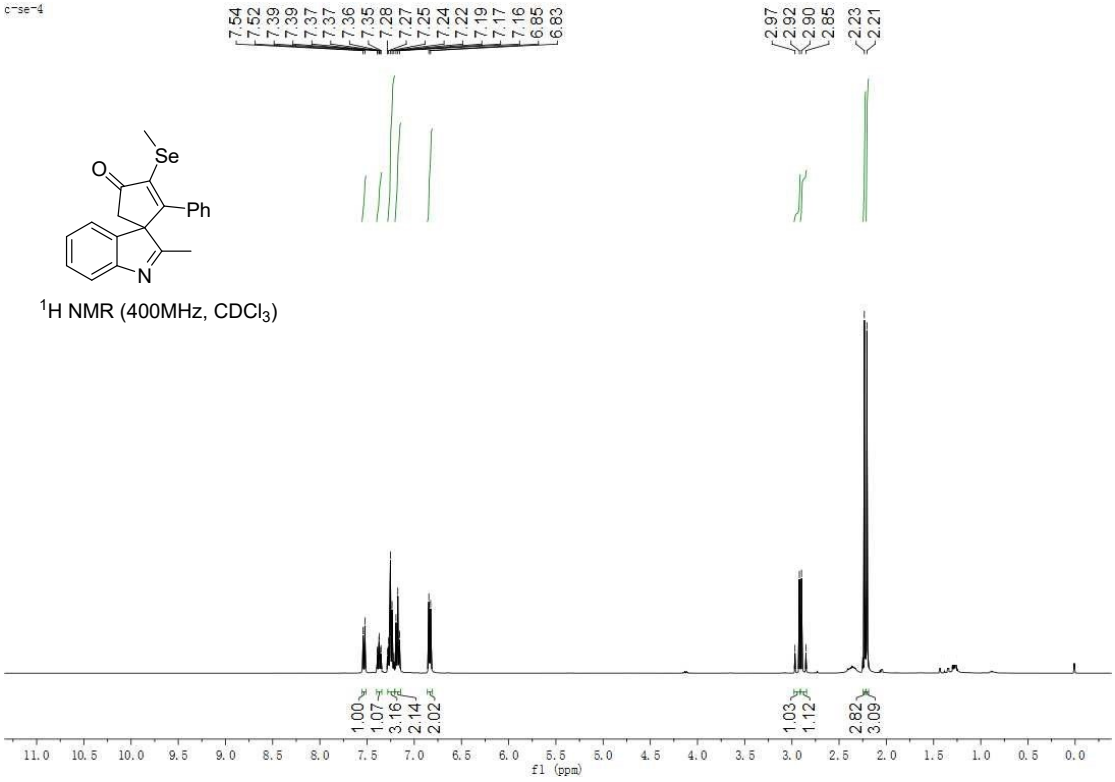
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3am**



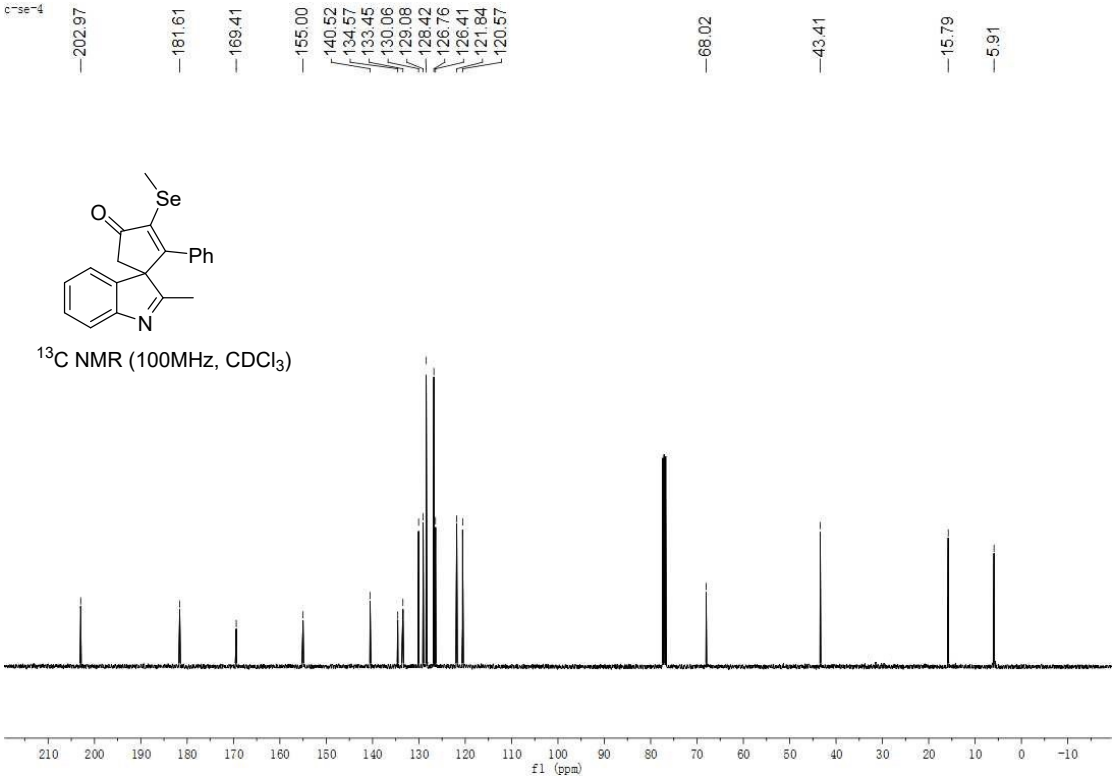
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3an**



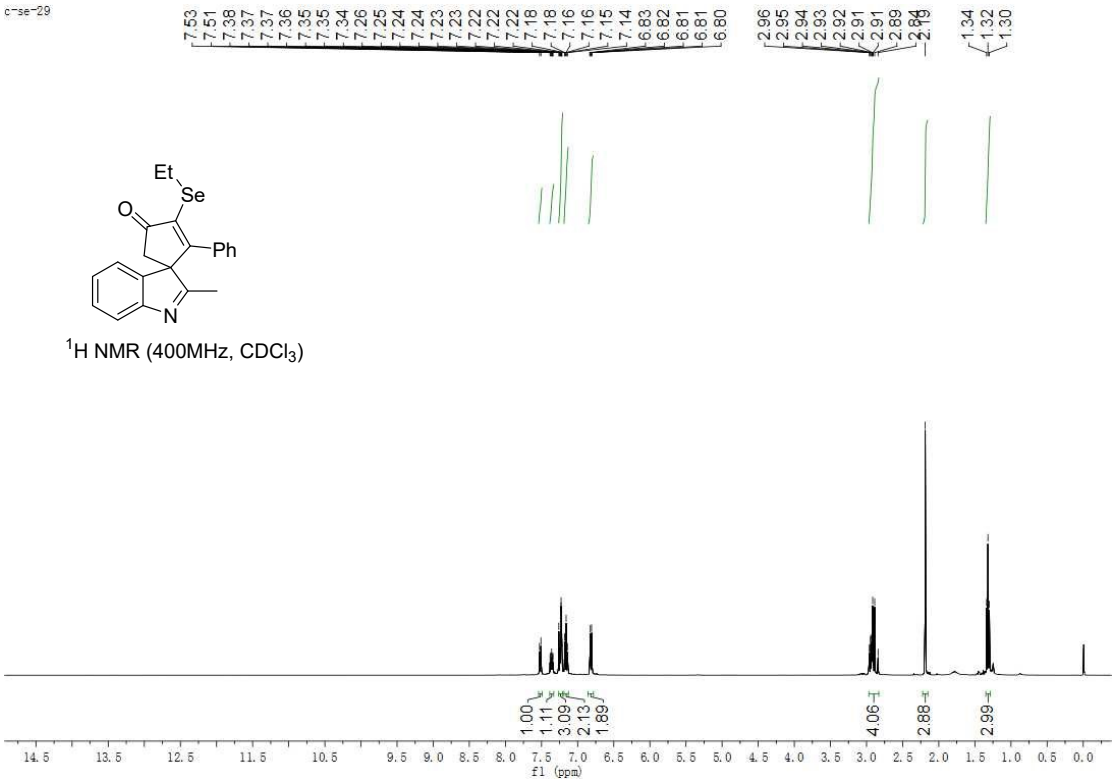
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3an**



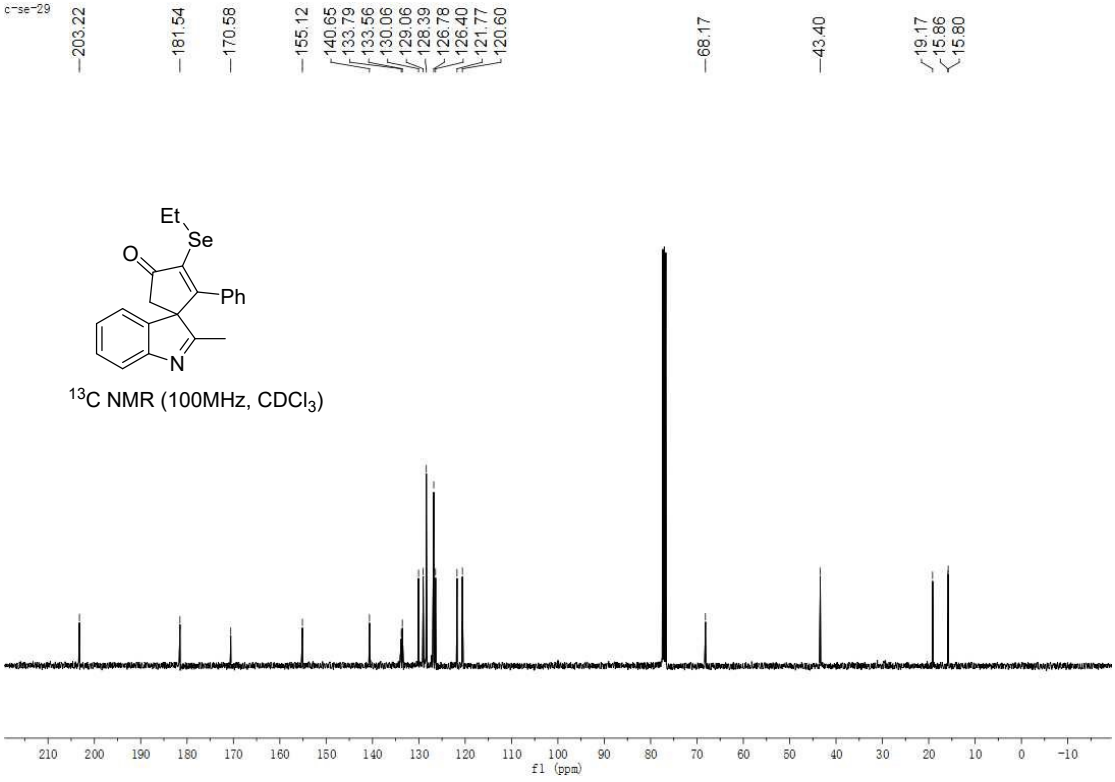
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ao**



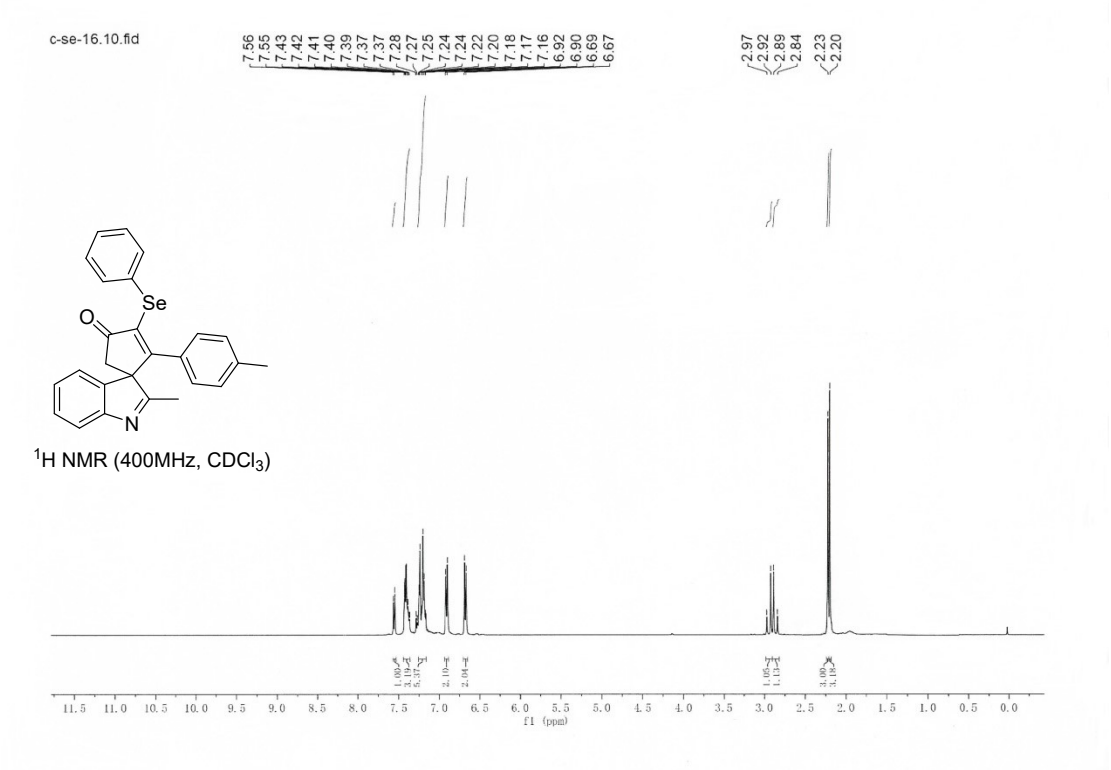
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ao**

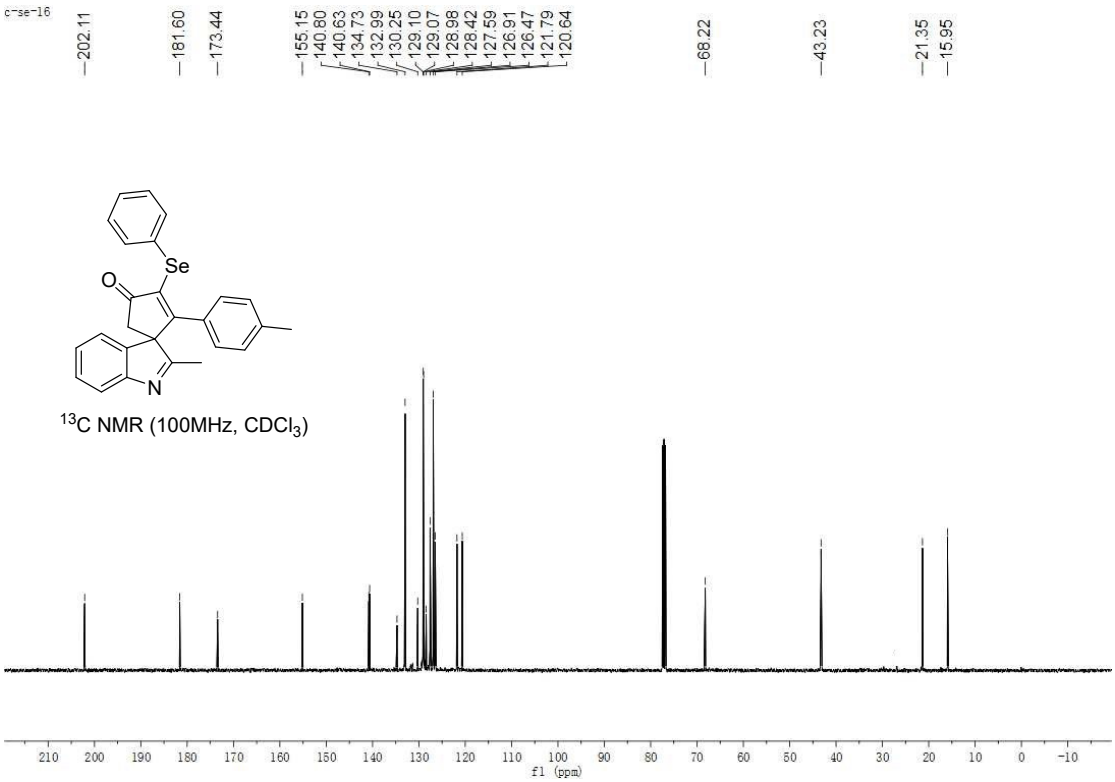


^{13}C NMR (100MHz, $CDCl_3$)

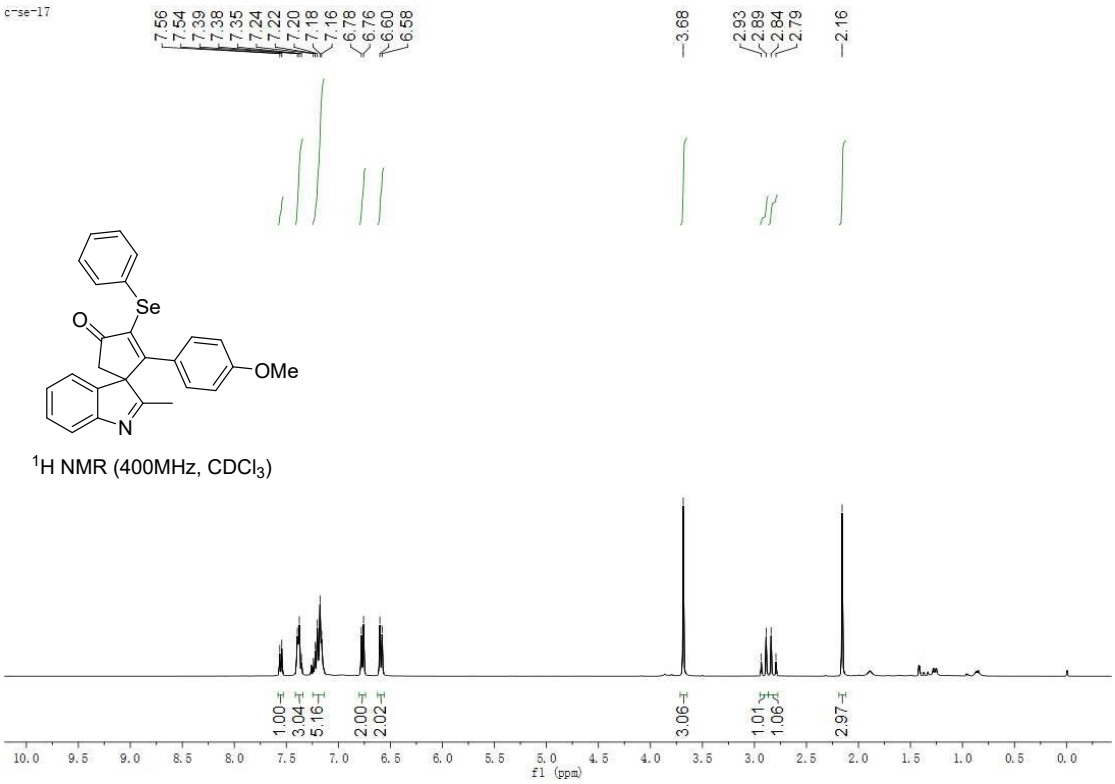
^{1}H NMR spectrum of **3ba**



^{13}C NMR spectrum of **3ba**

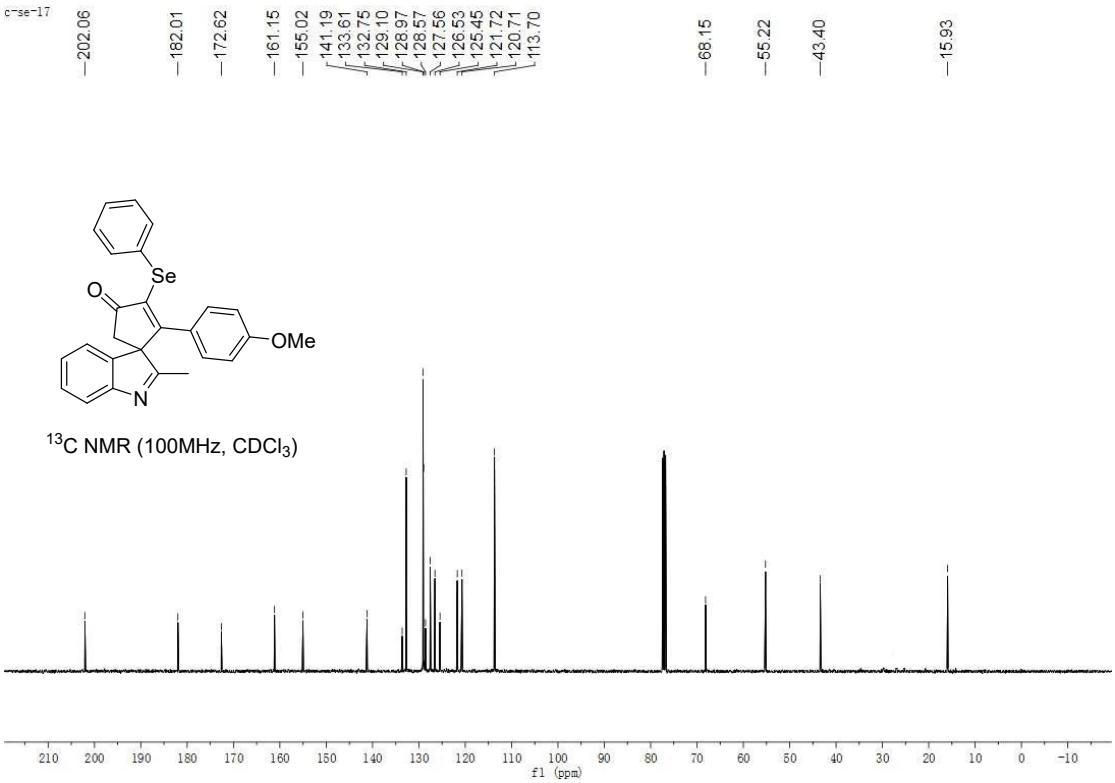


^{1}H NMR spectrum of **3ca**



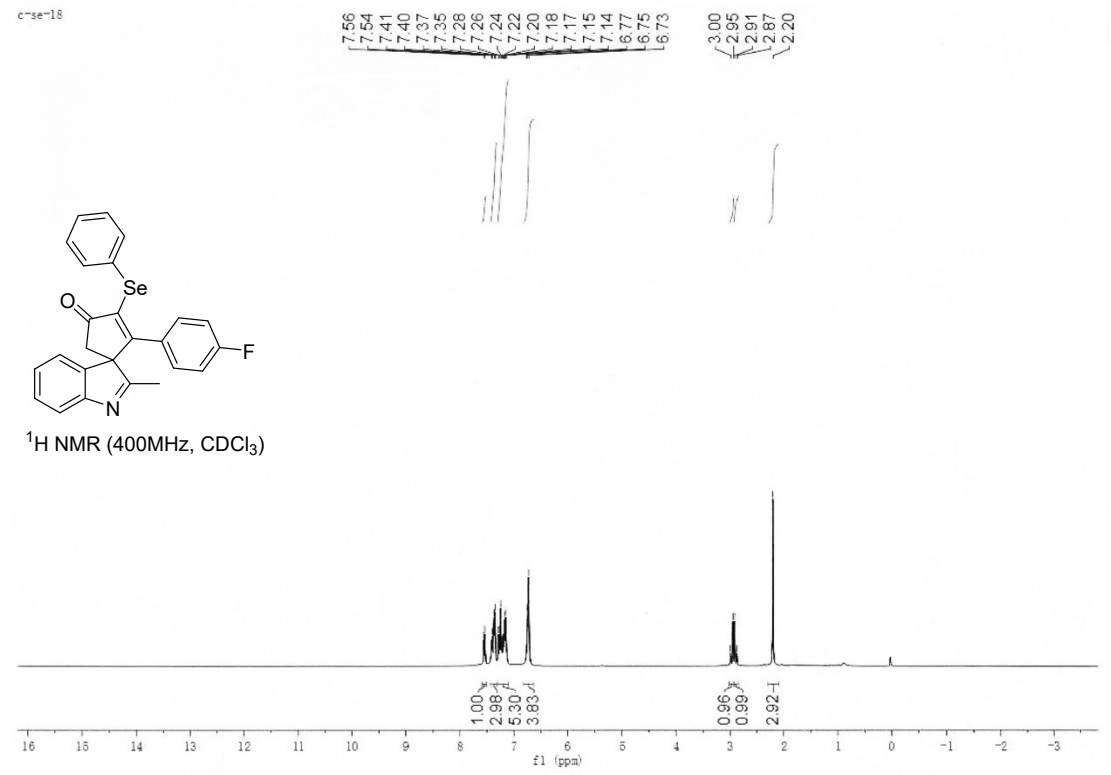
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ca**



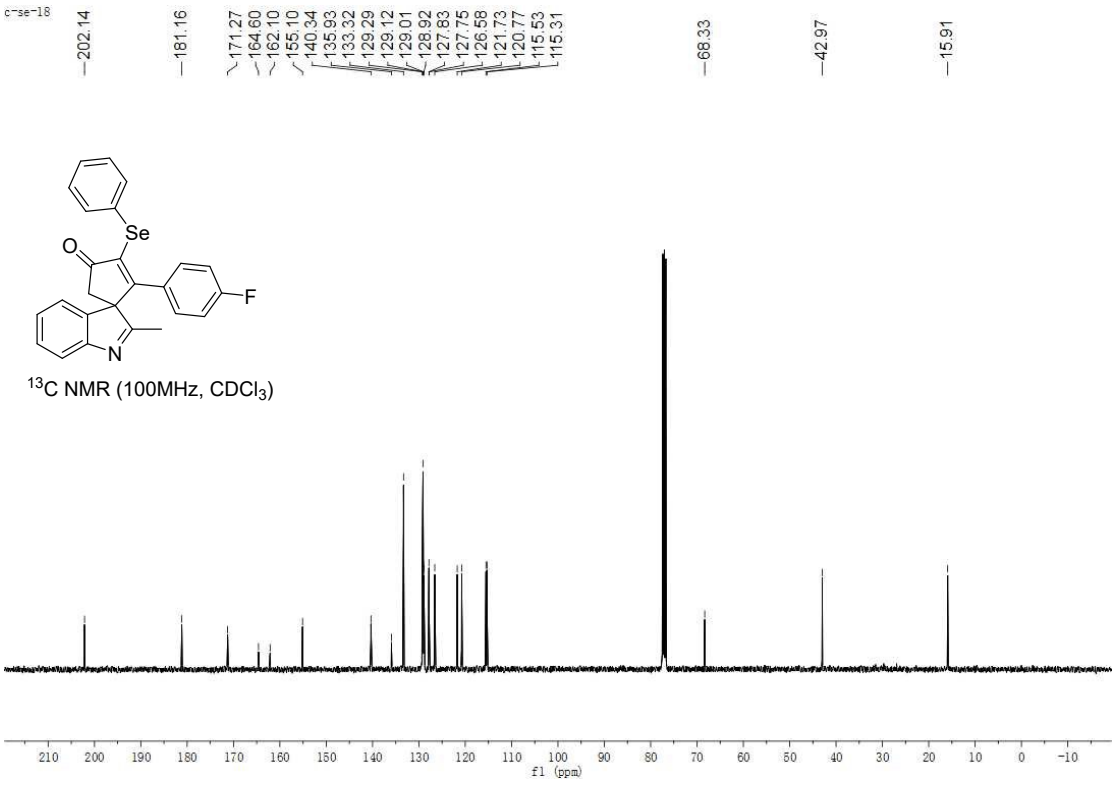
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3da**



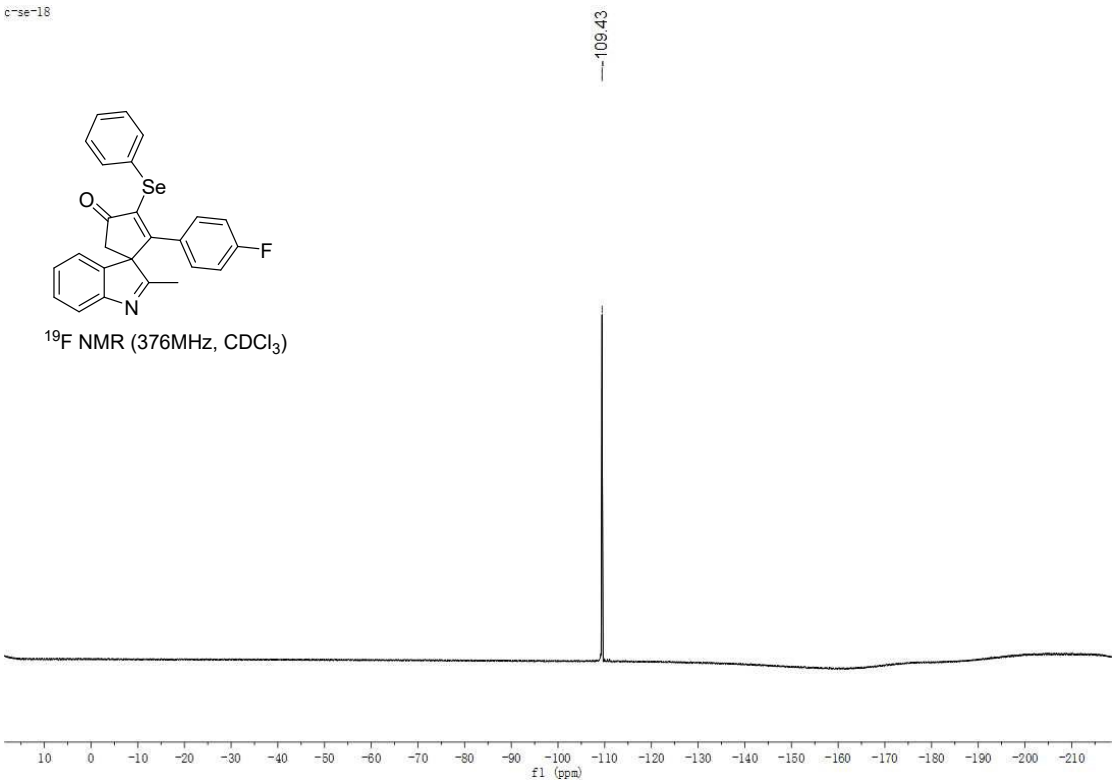
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3da**



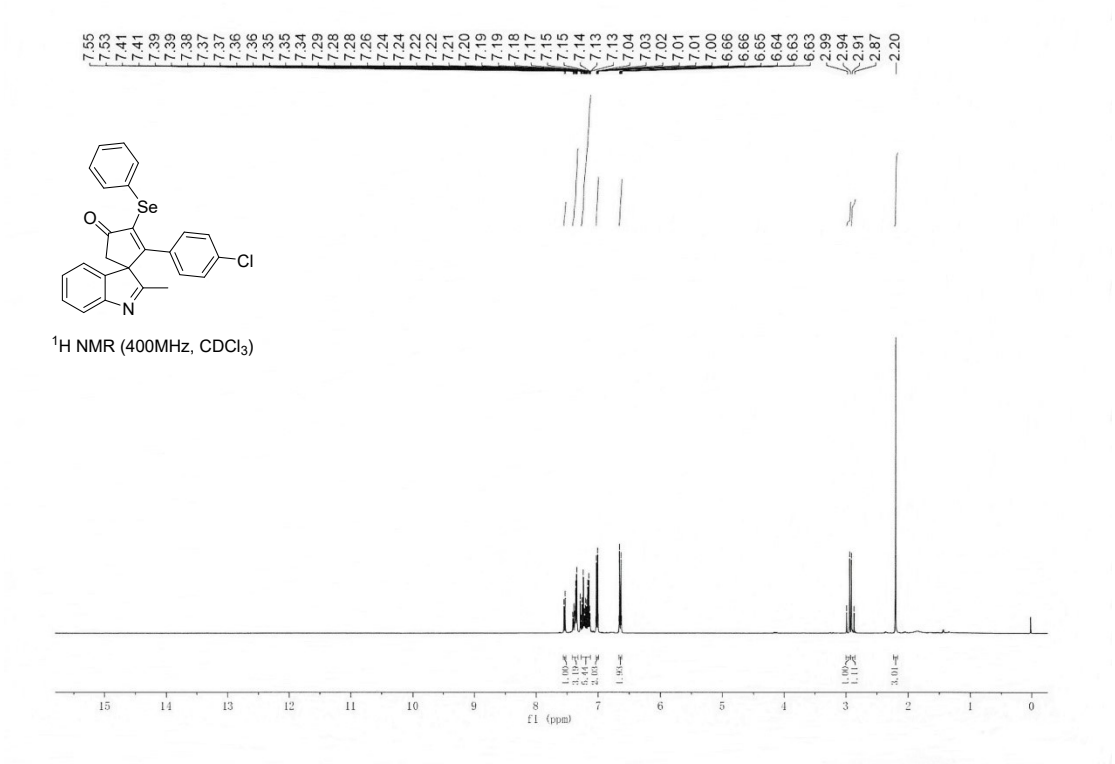
^{13}C NMR (100MHz, $CDCl_3$)

^{19}F NMR spectrum of **3da**



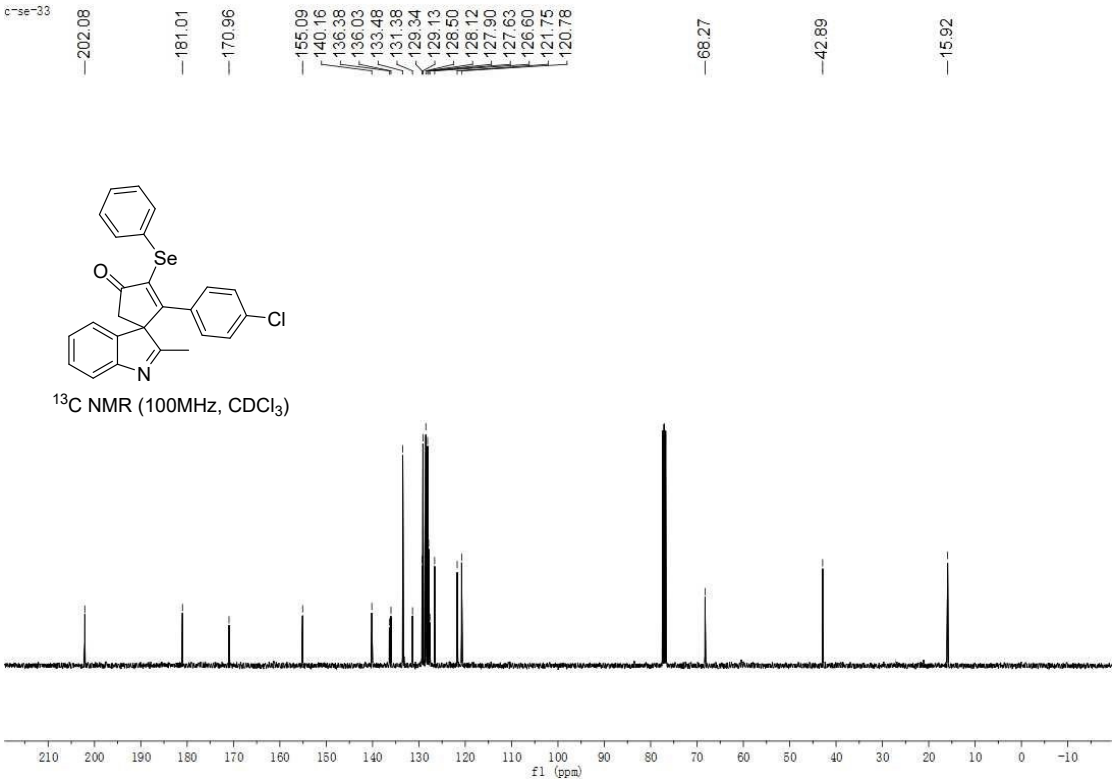
^{19}F NMR (376MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ea**

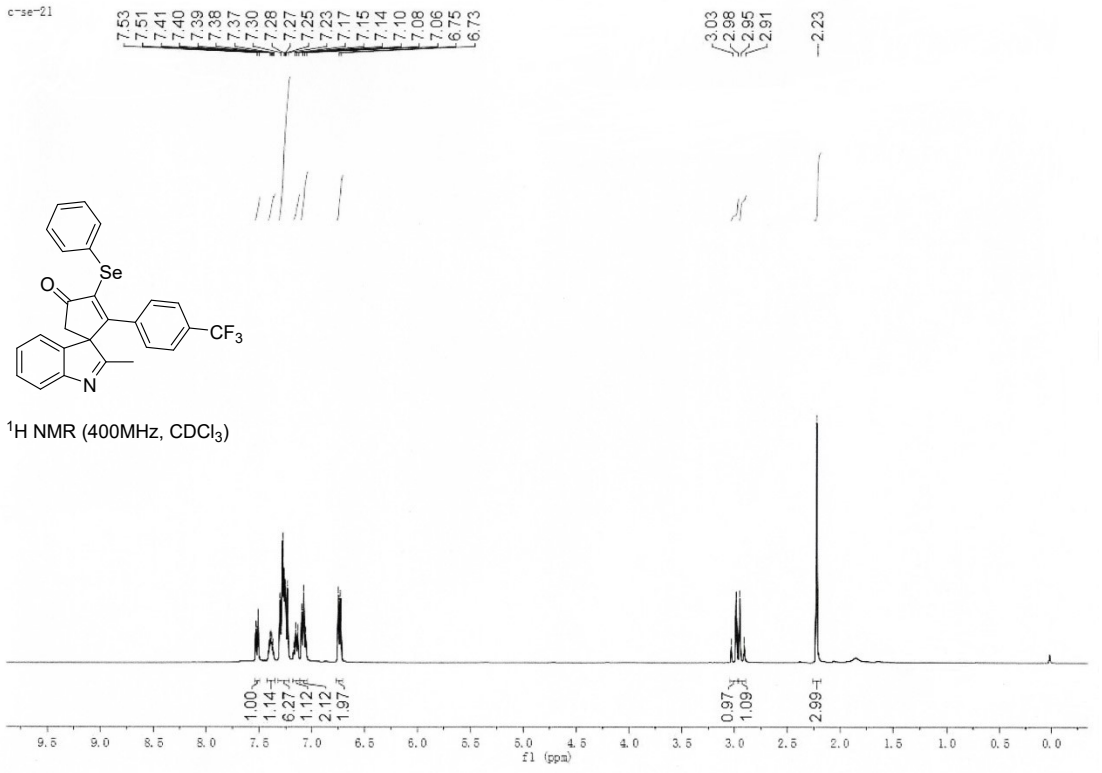


^{1}H NMR (400MHz, $CDCl_3$)

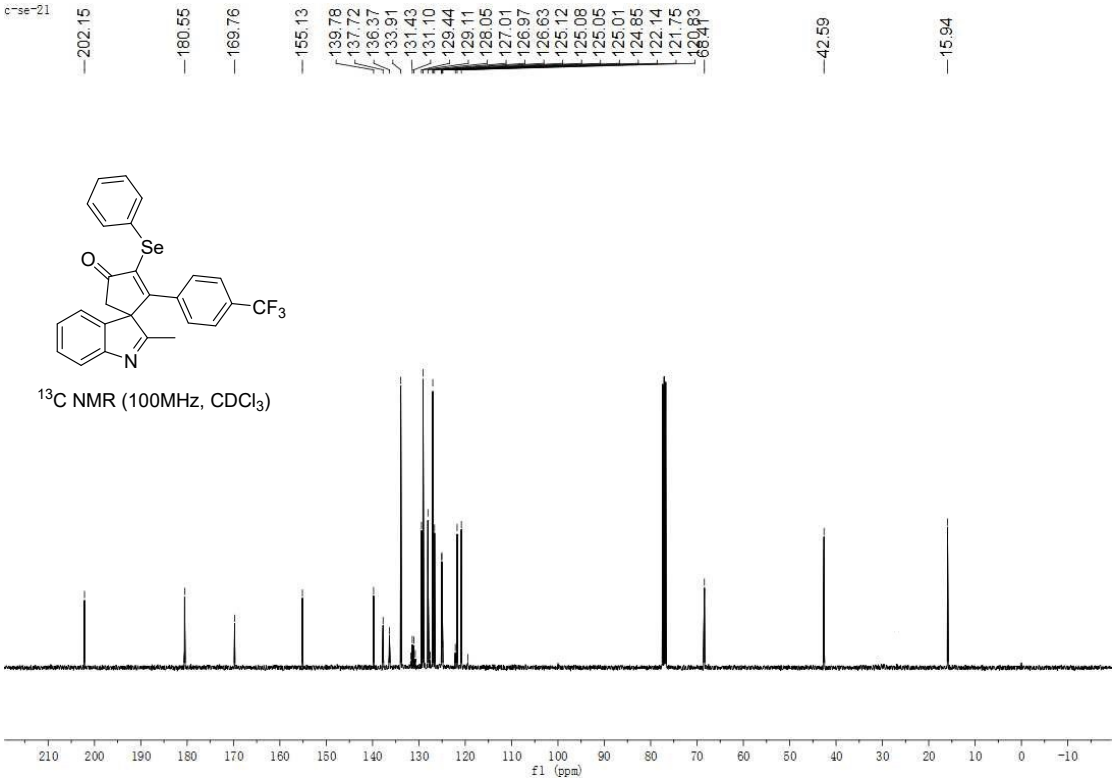
^{13}C NMR spectrum of **3ea**



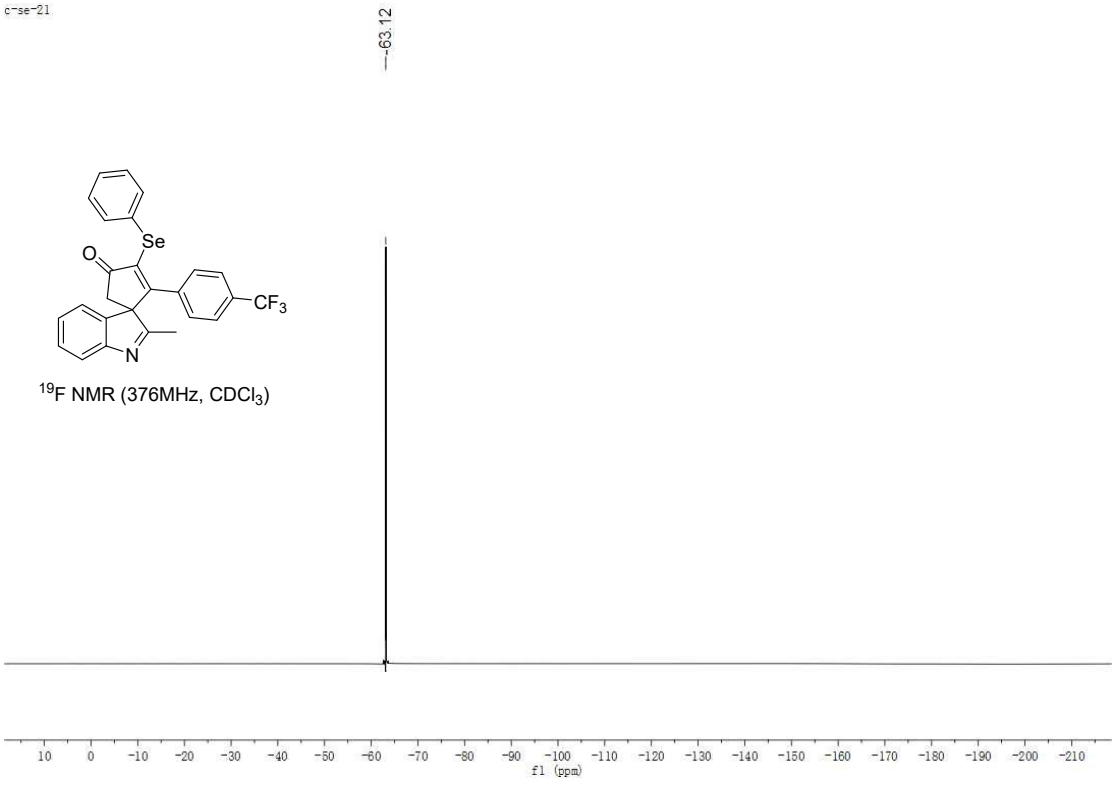
^{1}H NMR spectrum of **3fa**



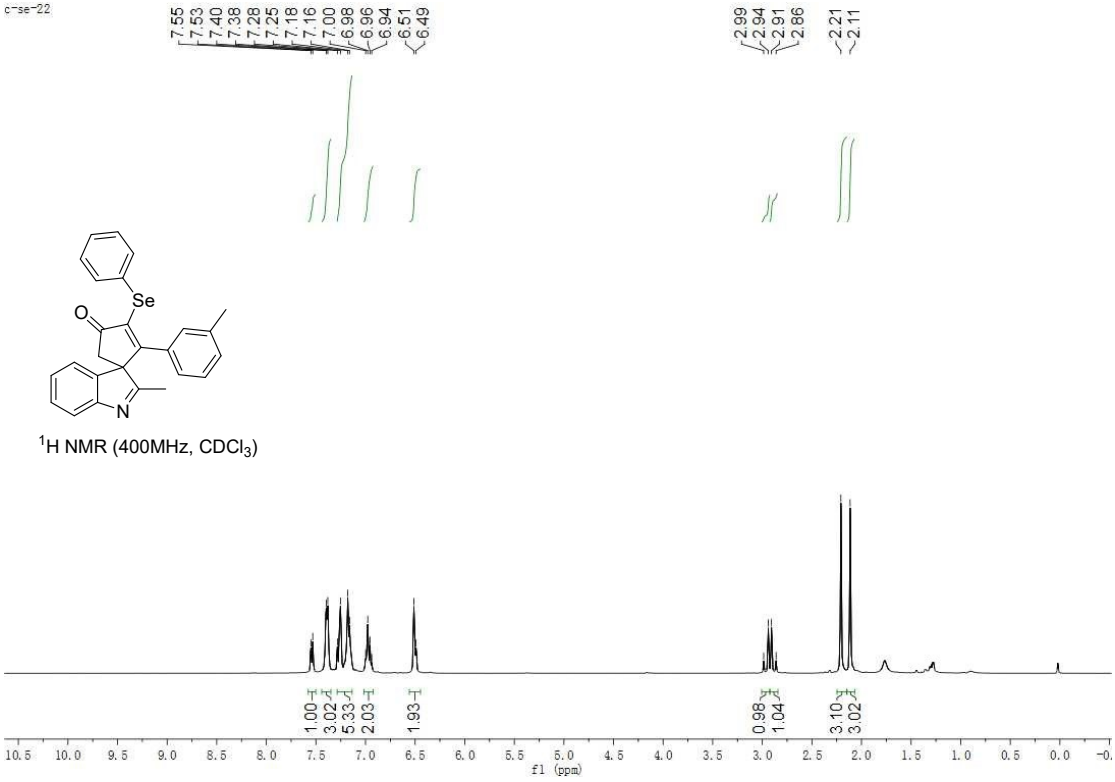
^{13}C NMR spectrum of **3fa**



^{19}F NMR spectrum of **3fa**

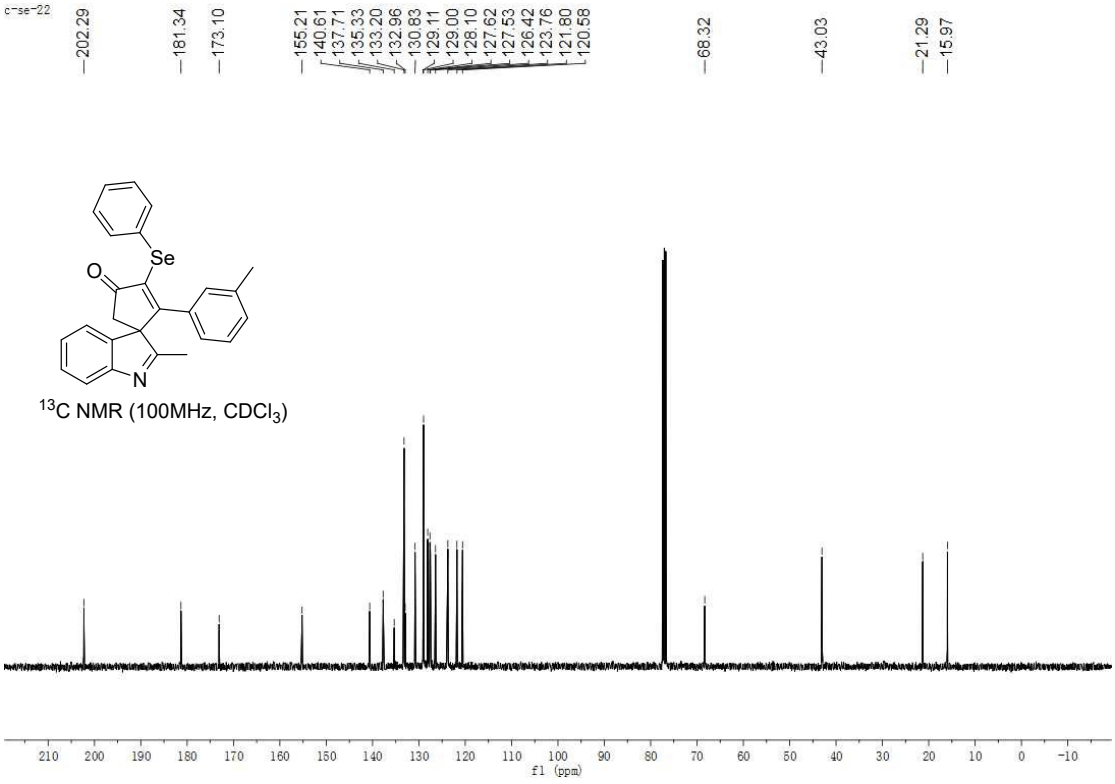


^{1}H NMR spectrum of **3ga**



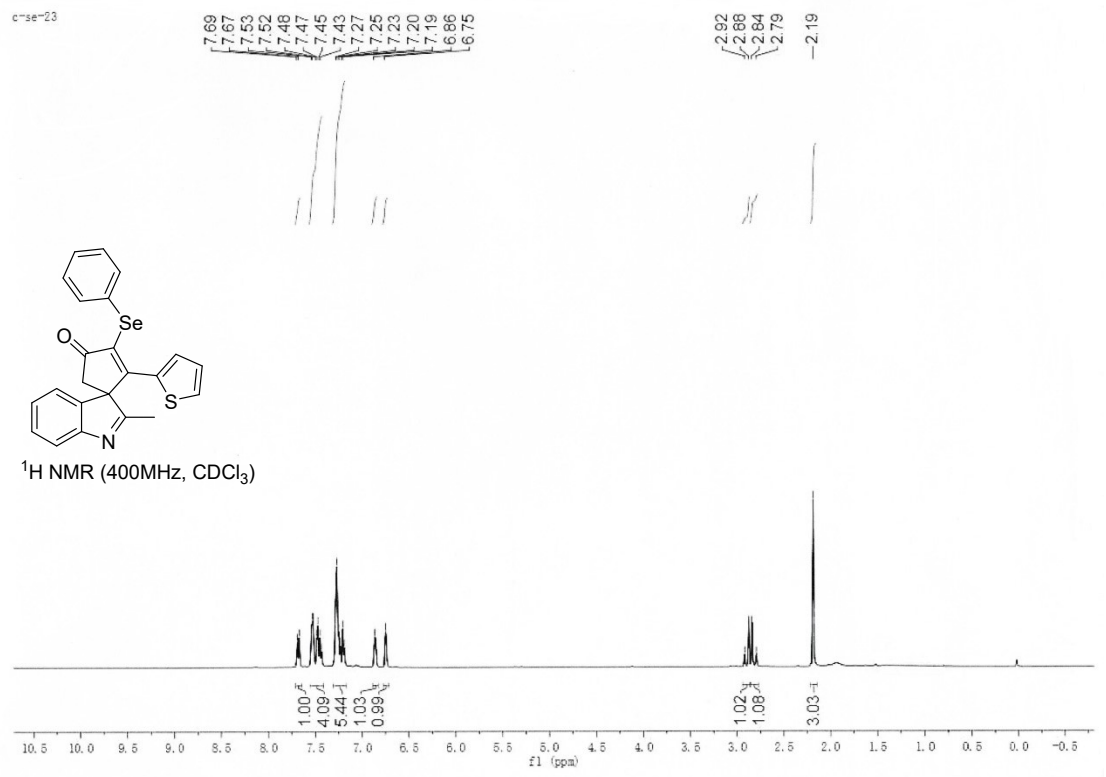
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ga**



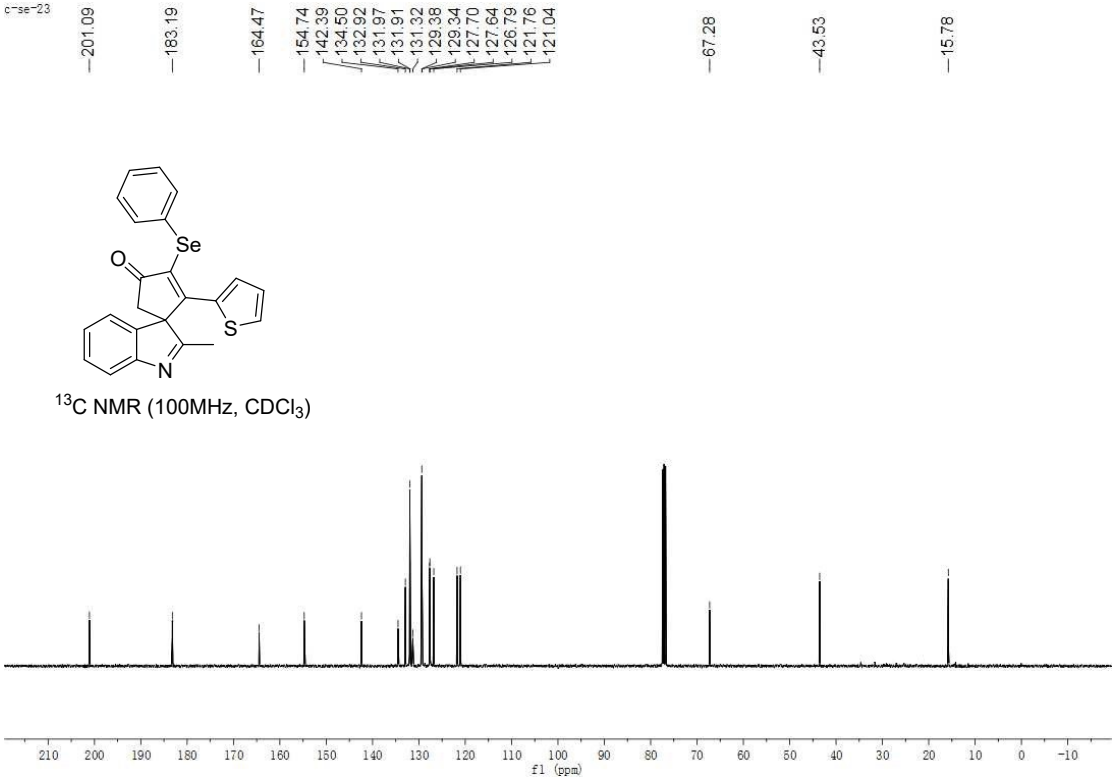
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ha**



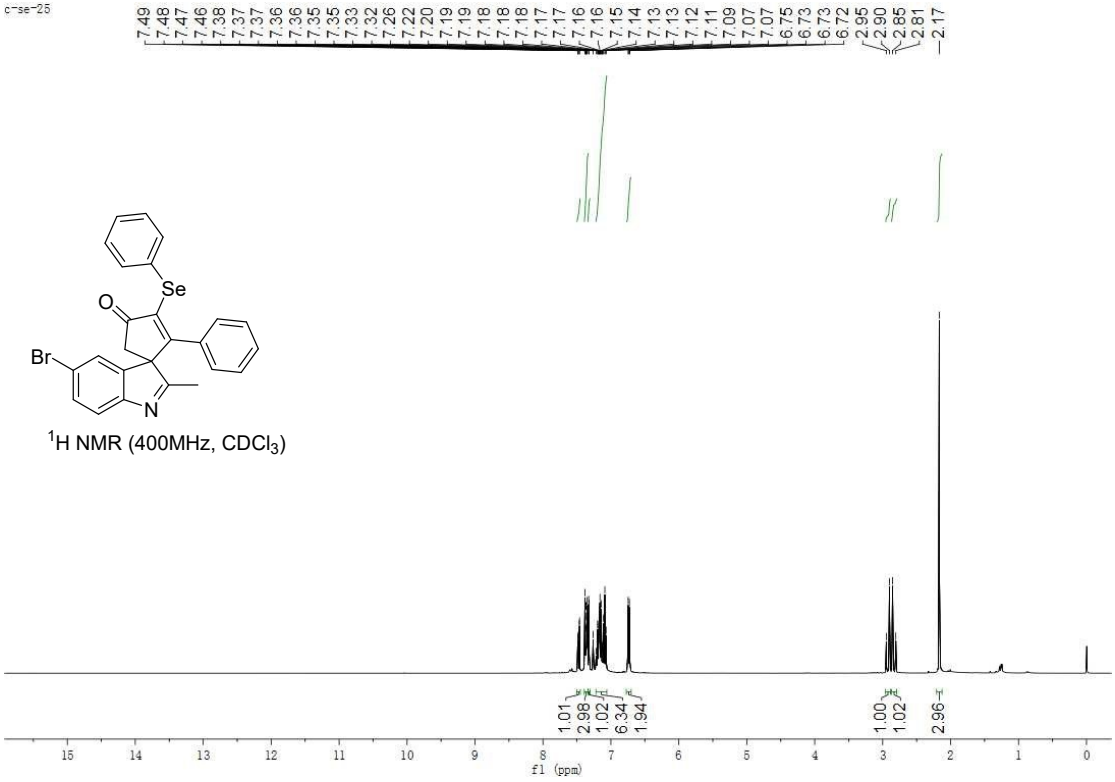
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ha**



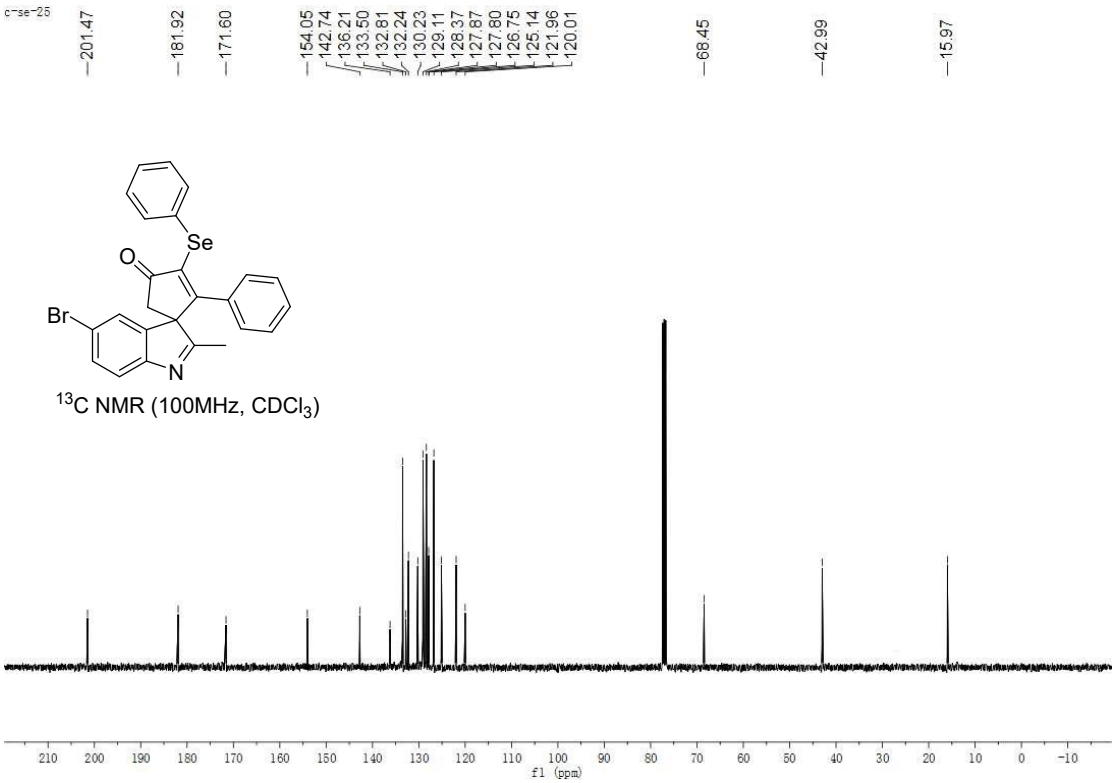
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ja**



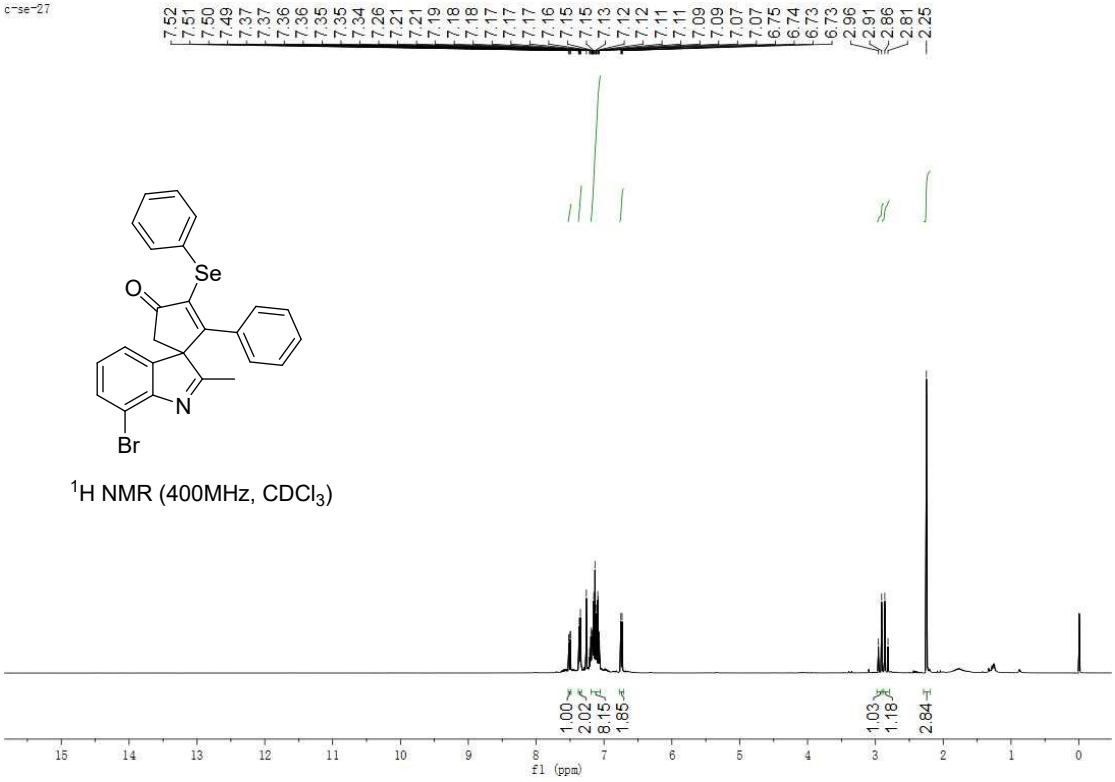
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ja**



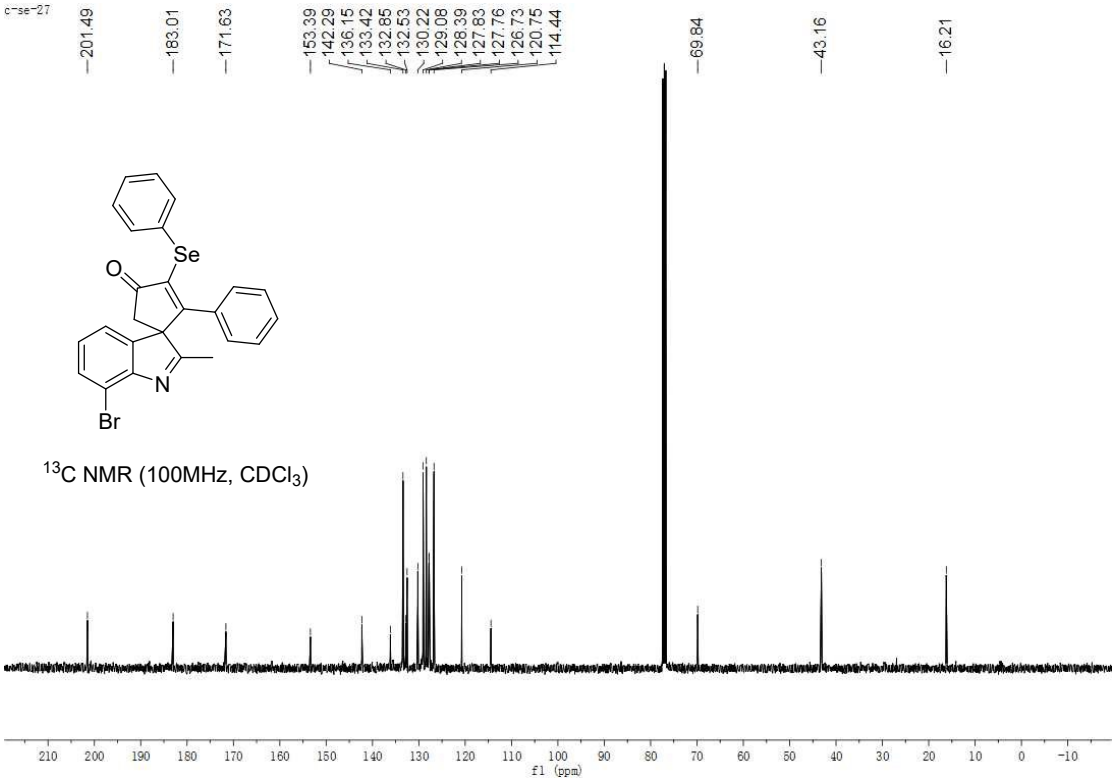
^{13}C NMR (100MHz, $CDCl_3$)

^{1}H NMR spectrum of **3ka**



^{1}H NMR (400MHz, $CDCl_3$)

^{13}C NMR spectrum of **3ka**



^{13}C NMR (100MHz, $CDCl_3$)