Supporting Information

Synthesis of 1,4-Benzodioxepines via Electrochemical Oxyselenenylation of 2-*O*-tethered Alkenyl Phenylmethanol and Diselenides

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Contents:

1. General Information.

All reactions were carried out under N_2 conditions unless otherwise stated. Reagents were purchased commercially and used directly without further purification unless otherwise stated. The solvents were distilled from the appropriate drying reagents. Column chromatography was performed using silica gel (200-300 mesh). ^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were obtained on Bruker AV-600 instrument in $CDCl_3$ with TMS as internal standard. Multiplicities were reported by use of the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS (ESI) spectra were recorded on a 1200-6520 Q-TOF/Agilent mass spectrometer using electrospray ionization.

2. General Procedures for the Preparation of substrates.

General Information General Procedure for Preparation of Substrates **1**[1] :
A solution of 2-(hydroxymethyl)phenol (2.0 mmol) (ArOH) in DMF (5.0 mL) was treated with K_2CO_3 (5.0 mmol) and allyl bromide or 3-bromo-2-methylprop-1-ene (2.5 mmol). The mixture was stirred 4 hours at 80 °C. Then it was cooled to room temperature and poured into saturated aqueous NH_4Cl and extracted 4 times with EtOAc. The organic phases were evaporated and then subjected to column chromatography to afford the starting materials **1**.
General Procedure for the Preparation of Substrates **2**[2]:
To a stirred solution of Se metal powder (2.0 mmol) and halides (1.0 mmol) in dry DMSO (2.0 mL) was added CuO powder (10.0 mol%) followed by KOH (2.0 equiv) under nitrogen atmosphere at 90 ℃ in an oil bath. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was allowed to cool, which was subjected to column chromatographic separation to give pure diselenides.

[1] (a) P. V. Navaratne, A. J. Grenning, *Org. Biomol. Chem*. 2017, **15**, 69. (b) K. Hirano, A. T. Biju, I. Piel and F. Glorius, *J. Am. Chem. Soc.* 2009, **131**, 14190.
[2] D. Singh, A. M. Deobald, L. R. S. Camargo, G. Tabarelli, O. E. D. Rodrigues and A. L. Braga, *Org. Lett.*, 2010, **12**, 3288.

3. General Procedures for the Preparation of Products.

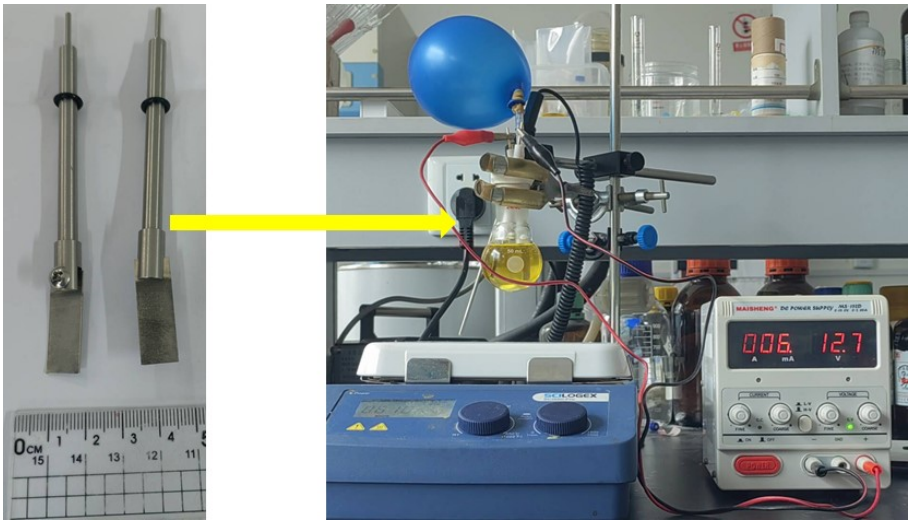
Procedure for the Synthesis of 3

Under N_2 atmosphere, a 10-mL electrolytic bath was charged with **1** (0.2 mmol), RSeSeR **2** (0.13 mmol), $LiBF_4$ (0.3 mmol, 28.2 mg). The flask was equipped with two platinum plates (1 cm x 1 cm) as anode and cathode respectively, then dry CH_3CN (3 mL) were added. The mixture was stirred at room temperature and electrolyzed at a constant current of 6 mA for 2 - 4 h. After the substrate was consumed (monitored by TLC), the reaction mixture was concentrated under reduced pressure, and the residue was purified through silica gel chromatography with petroleum ether/ ethyl acetate as eluent (eluent, petroleum ether/ethyl acetate = 25:1 to 10:1) to obtain the desired product **3**.

Gram-scale reaction:

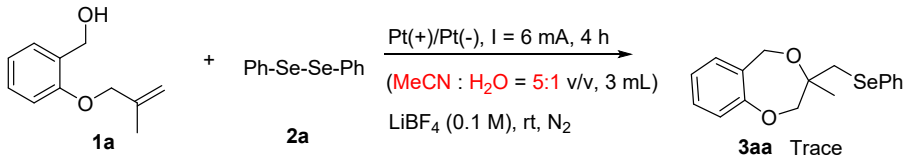
Under N_2 a 100-mL electrolytic bath was charged with **1a** (5.6 mmol, 1.0 g), PhSeSePh **2a** (3.64 mmol, 1.2 g), $LiBF_4$ (6 mmol, 564 mg). The flask was equipped with two platinum plates (2 cm x 1 cm) as anode and cathode respectively, then dry CH_3CN (60 mL) were added. The mixture was stirred at room temperature and electrolyzed at a constant current of 6 mA for 12 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified through silica gel chromatography with petroleum ether/ethyl acetate as eluent (eluent, petroleum ether/ethyl acetate = 25:1 to 10:1) to obtain the desired product **3aa** (1.16 g).

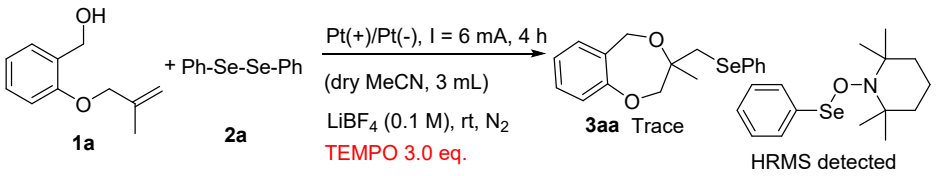
Under N_2 a 100-mL three-necked round-bottomed flask was charged with **1g** (4.0 mmol, 1.0 g), PhSeSePh **2a** (2.63 mmol, 0.8 g), $LiBF_4$ (6 mmol, 564 mg). The flask was equipped with two platinum plates (2 cm x 1 cm) as anode and cathode respectively, then dry CH_3CN (60 mL) were added. The mixture was stirred at room temperature and electrolyzed at a constant current of 6 mA for 12 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified through silica gel chromatography with petroleum ether/ ethyl acetate as eluent (eluent, petroleum ether/ethyl acetate = 25:1 to 10:1) to obtain the desired product **3ga** (1.20 g).

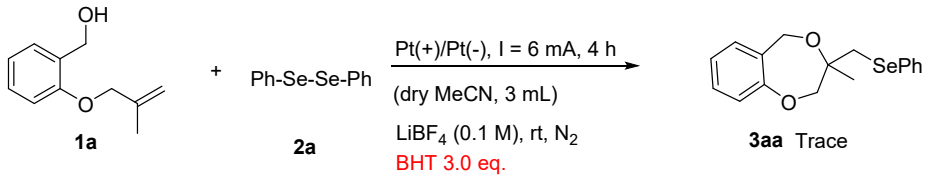


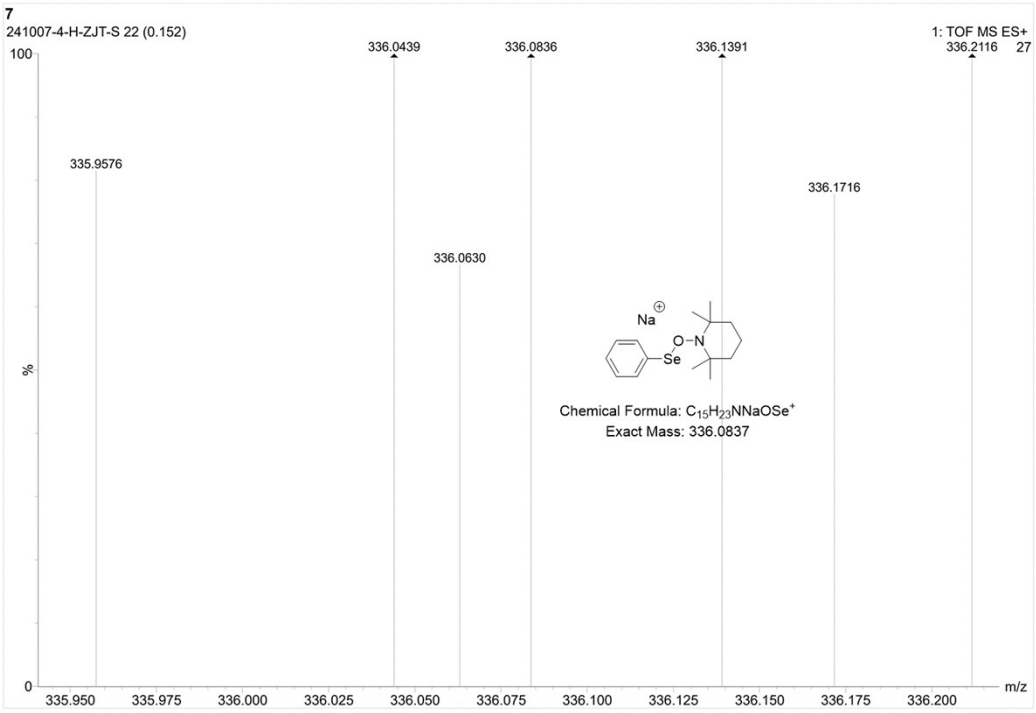
4. Mechanism study

Control experiments:









This reaction did not work when the solvent is MeCN:H_2O (5:1 v/v), which means that the reaction is water sensitive. To probe the possible reaction mechanism, the 2,2,6,6-tetramethylpiperidine N-oxide (TEMPO) and 2,6-di-tert-butyl-4-methylphenol (BHT), which are radical scavengers, was added to the reaction system respectively, the formation of the desired product **3aa** was prohibited, indicating that a free radical was involved in the reaction.

Cyclic voltammetry (CV) experiments

We probed the mechanism by means of a series of cyclic voltammetric (CV) analyses. As depicted in Fig. S1, the oxidative peak of **1a** was observed at 1.5 V *vs*. Ag/AgCl (curve b) in dry MeCN and the oxidative peak of **2a** at 1.0 V vs. Ag/AgCl (curve c). The compound **2a** was found to be oxidized at 1.0 V *vs*. Ag/AgCl (curve c, d). It could be concluded that the diphenyl diselenide **2a** was oxidized preferentially at a low potential which was lower than the oxidation potential of **1a**.

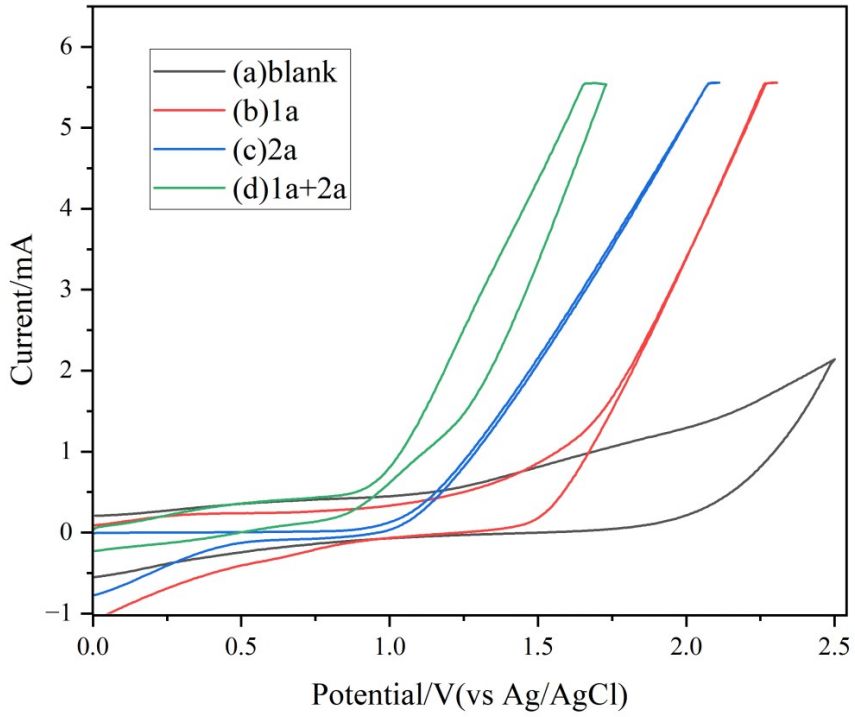
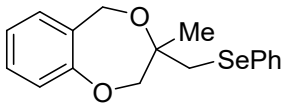


Figure S1. CVs (0.1 V/s) in dry MeCN and $LiBF_4$ (0.1 M) of: background (a); **1a** (0.2 mmol, b); **2a** (0.13 mmol, c); **1a** (0.2 mmol) + **2a** (0.13 mmol) (d). The voltammogram was obtained with Pt plates (1 cm × 1 cm) as the working and counter electrode and Ag/AgCl electrode as the reference electrode at room temperature.

5. Characterization of data for the electrolysis products.



3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

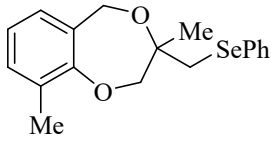
Compound 3aa.

Yield = 65%; 44 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 5.8 Hz, 2H), 7.28 (q, *J* = 7.5 Hz, 3H), 7.22 (t, *J* = 6.8 Hz, 1H), 7.09 (d, *J* = 6.1 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 2H), 4.76 (q, *J* = 14.7 Hz, 2H), 4.17 (d, *J* = 13.0 Hz, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 3.53 (d, *J* = 12.2 Hz, 1H), 3.20 (d, *J* = 12.1 Hz, 1H), 1.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.9, 132.7, 130.8, 130.1, 129.1, 128.85, 128.83, 126.9, 122.7, 119.8, 78.3, 77.0, 65.3, 34.9, 21.5.

HRMS (ESI) calculated for $C_{17}H_{18}NaO_2Se$ [M+Na]+: 357.0364; found: 357.0369.



3,9-dimethyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

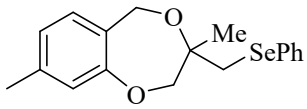
Compound 3ba.

Yield = 68%; 47 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.32 – 7.24 (m, 3H), 7.10 (d, *J* = 6.6 Hz, 1H), 6.95 (d, *J* = 5.6 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 4.78 – 4.68 (m, 2H), 4.17 (d, *J* = 12.8 Hz, 1H), 4.02 (d, *J* = 12.9 Hz, 1H), 3.56 (d, *J* = 11.8 Hz, 1H), 3.22 (d, *J* = 13.2 Hz, 1H), 2.25 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4, 132.7, 130.8, 130.4, 130.3, 129.1, 128.9, 126.9, 126.5, 122.5, 78.1, 76.8, 65.4, 34.9, 21.5, 16.0.

HRMS (ESI) calculated for $C_{18}H_{21}O_2Se$ [M+H]+: 349.0701; found: 349.0710.



3,7-dimethyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

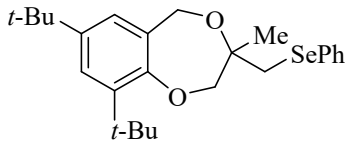
Compound 3ca.

Yield = 66%; 46 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 3H), 7.00 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.92 – 6.86 (m, 2H), 4.74 (d, *J* = 14.7 Hz, 1H), 4.67 (d, *J* = 14.6 Hz, 1H), 4.12 (d, *J* = 13.0 Hz, 1H), 4.01 (d, *J* = 12.9 Hz, 1H), 3.53 (d, *J* = 12.1 Hz, 1H), 3.18 (d, *J* = 12.6 Hz, 1H), 2.29 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9, 132.7, 132.3, 130.8, 130.1, 129.30, 129.27, 129.1, 126.9, 119.5, 78.2, 77.3, 65.3, 34.9, 21.5, 20.5.

HRMS (ESI) calculated for $C_{18}H_{21}O_2Se$ [M+H]+: 349.0701; found: 349.0718



7,9-di-*tert*-butyl-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

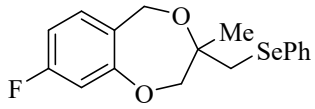
Compound 3da.

Yield = 72%; 64 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.03 (d, *J* = 2.5 Hz, 1H), 4.80 (d, *J* = 14.1 Hz, 1H), 4.62 (d, *J* = 14.1 Hz, 1H), 4.12 (d, *J* = 12.6 Hz, 1H), 3.87 (d, *J* = 12.6 Hz, 1H), 3.59 (d, *J* = 12.2 Hz, 1H), 3.28 (d, *J* = 12.2 Hz, 1H), 1.40 (s, 3H), 1.39 (s, 9H), 1.32 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 145.2, 140.0, 132.8, 131.7, 130.9, 129.1, 126.9, 124.23, 123.4, 77.8, 77.4, 66.2, 35.1, 34.7, 34.4, 31.5, 30.3, 21.9.

HRMS (ESI) calculated for $C_{25}H_{35}O_2Se$ [M+H]+: 447.1797; found: 447.1808.



8-fluoro-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

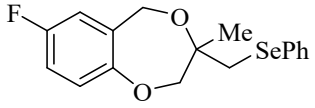
Compound 3ea.

Yield = 70%; 49 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.05 – 6.99 (m, 1H), 6.72 – 6.66 (m, 2H), 4.76 – 4.67 (m, 2H), 4.18 (d, *J* = 13.1 Hz, 1H), 4.08 (d, *J* = 13.1 Hz, 1H), 3.48 (d, *J* = 12.2 Hz, 1H), 3.18 (d, *J* = 12.2 Hz, 1H), 1.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.55 (d, *J* = 246.5 Hz), 159.92 (d, *J* = 11.6 Hz), 132.7, 130.7, 129.62 (d, *J* = 9.9 Hz), 129.1, 127.0, 125.81 (d, *J* = 3.3 Hz), 109.46 (d, *J* = 20.9 Hz), 107.33 (d, *J* = 23.1 Hz), 78.5, 76.8, 64.7, 34.9, 21.4.

HRMS (ESI) calculated for $C_{17}H_{18}FO_2Se$ [M+H]+: 353.0451; found: 353.0456.



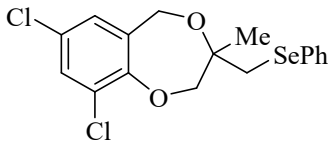
7-fluoro-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

Compound 3fa.

Yield = 65%; 45 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.28 (d, *J* = 6.4 Hz, 3H), 6.94 (dd, *J* = 8.8, 4.8 Hz, 1H), 6.88 (td, *J* = 8.3, 3.1 Hz, 1H), 6.80 (dd, *J* = 8.5, 3.1 Hz, 1H), 4.71 (d, *J* = 14.8 Hz, 1H), 4.65 (d, *J* = 14.8 Hz, 1H), 4.12 (d, *J* = 13.0 Hz, 1H), 4.00 (d, *J* = 13.0 Hz, 1H), 3.50 (d, *J* = 12.2 Hz, 1H), 3.17 (d, *J* = 12.2 Hz, 1H), 1.40 (s, 3H).

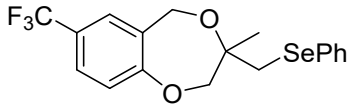
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.07 (d, *J* = 241.6 Hz), 155.16 (d, *J* = 2.6 Hz), 132.7, 132.02 (d, *J* = 6.6 Hz), 130.7, 129.1, 127.0, 121.05 (d, *J* = 8.3 Hz), 115.13 (d, *J* = 10.1 Hz), 114.98 (d, *J* = 11.7 Hz), 78.4, 77.4, 64.8, 34.8, 21.4.
^{19}F NMR (565 MHz, CDCl3) δ -120.9.
HRMS (ESI) calculated for $C_{17}H_{18}FO_2Se$ [M+H]+: 353.0451; found: 353.0456.



7,9-dichloro-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

Compound 3ga.

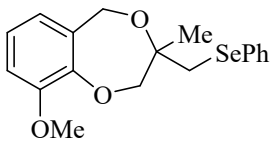
Yield = 87%; 70 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.33 – 7.24 (m, 4H), 6.99 (d, *J* = 2.6 Hz, 1H), 4.73 – 4.63 (m, 2H), 4.21 (d, *J* = 13.0 Hz, 1H), 4.09 (d, *J* = 13.0 Hz, 1H), 3.50 (d, *J* = 12.3 Hz, 1H), 3.17 (d, *J* = 12.3 Hz, 1H), 1.42 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5, 133.4, 132.8, 130.5, 129.2, 129.0, 127.6, 127.13, 127.11, 126.0, 78.4, 77.6, 64.6, 34.7, 21.3.
HRMS (ESI) calculated for $C_{17}H_{17}Cl_2O_2Se$ [M+H]+: 402.9765; found: 402.9782.



3-methyl-3-((phenylselanyl)methyl)-7-(trifluoromethyl)-2,3-dihydro-5*H*-benzo[e][1,4]dioxepine.

Compound 3ha.

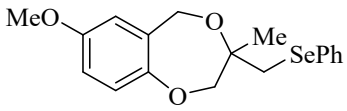
Yield = 72%; 58 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 2H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.25 – 7.08 (m, 4H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.68 (s, 2H), 4.14 (d, *J* = 13.2 Hz, 1H), 4.05 (d, *J* = 13.2 Hz, 1H), 3.34 (d, *J* = 12.3 Hz, 1H), 3.10 (d, *J* = 12.3 Hz, 1H), 1.32 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 132.8, 130.6, 129.6, 129.1, 127.1, 126.0 (q, *J* = 3.3 Hz), 125.9 (q, *J* = 3.4 Hz), 124.6 (q, *J* = 32.6 Hz), 124.0 (q, *J* = 271.4 Hz), 120.1, 78.7, 76.2, 64.8, 34.9, 21.2.
^{19}F NMR (565 MHz, $CDCl_3$) δ -61.8.
HRMS (ESI) calculated for $C_{18}H_{18}F_3O_2Se$ [M+H]+: 403.0419; found: 403.0439.



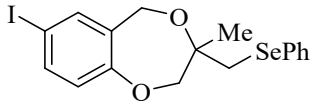
9-methoxy-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

Compound 3ia.

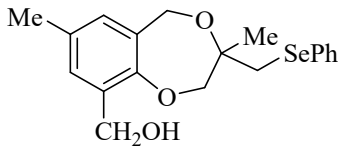
Yield = 60%; 44 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.30 – 7.24 (m, 3H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 9.7 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 4.80 – 4.68 (m, 2H), 4.25 – 4.08 (m, 2H), 3.88 (s, 3H), 3.58 (d, *J* = 12.2 Hz, 1H), 3.14 (d, *J* = 12.2 Hz, 1H), 1.42 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 150.5, 148.2, 132.7, 131.7, 130.8, 129.1, 126.9, 122.9, 120.5, 111.5, 78.2, 77.9, 65.2, 56.1, 34.9, 21.5.
HRMS (ESI) calculated for $C_{18}H_{21}O_3Se$ [M+H]+: 365.0650; found: 365.0666.



7-methoxy-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.
Compound 3ja.
Yield = 57%; 41 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.31 – 7.23 (m, 3H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.74 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.65 (d, *J* = 3.0 Hz, 1H), 4.73 (d, *J* = 14.5 Hz, 1H), 4.65 (d, *J* = 14.6 Hz, 1H), 4.08 (d, *J* = 12.8 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 3.78 (s, 3H), 3.54 (d, *J* = 12.1 Hz, 1H), 3.17 (d, *J* = 12.2 Hz, 1H), 1.40 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 155.1, 153.1, 132.7, 131.8, 130.8, 129.1, 126.9, 120.6, 113.9, 113.6, 78.2, 77.8, 65.4, 55.7, 34.8, 21.5.
HRMS (ESI) calculated for $C_{18}H_{21}O_3Se$ [M+H]+: 365.0650; found: 365.0666.



7-iodo-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.
Compound 3ka.
Yield = 71%; 65 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.47 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.38 (d, *J* = 2.2 Hz, 1H), 7.28 (s, 3H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.67 (d, *J* = 6.0 Hz, 2H), 4.15 (d, *J* = 13.1 Hz, 1H), 4.05 (d, *J* = 13.1 Hz, 1H), 3.45 (d, *J* = 12.3 Hz, 1H), 3.17 (d, *J* = 12.2 Hz, 1H), 1.39 (d, *J* = 5.7 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.8, 137.5, 137.3, 132.8, 132.4, 130.6, 129.2, 129.1, 127.0, 122.0, 85.2, 78.5, 64.4, 34.8, 21.3.
HRMS (ESI) calculated for $C_{17}H_{18}IO_2Se$ [M+H]+: 460.9511; found: 460.9516.



(3,7-dimethyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepin-9-

yl)methanol.

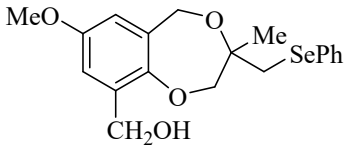
Compound 3la.

Yield = 45%; 34 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 4.75 – 4.59 (m, 4H), 4.17 (d, *J* = 12.8 Hz, 1H), 4.02 (d, *J* = 12.8 Hz, 1H), 3.48 (d, *J* = 12.3 Hz, 1H), 3.22 (d, *J* = 12.3 Hz, 1H), 2.28 (s, 3H), 2.11 (s, 1H), 1.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 132.8, 132.3, 131.1, 130.7, 130.3, 129.1, 128.9, 128.7, 127.0, 78.2, 77.1, 65.2, 61.7, 34.8, 21.5, 20.5.

HRMS (ESI) calculated for $C_{19}H_{22}NaO_3Se$ [M+Na]+: 401.0626; found: 401.0638.



(7-methoxy-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepin-9-yl)methanol.

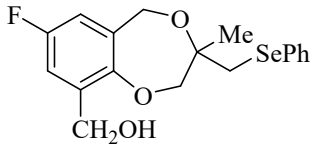
Compound 3ma.

Yield = 46%; 36 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 3H), 6.80 (d, *J* = 3.1 Hz, 1H), 6.60 (d, *J* = 3.1 Hz, 1H), 4.73 (d, *J* = 14.5 Hz, 1H), 4.70 – 4.61 (m, 3H), 4.14 (d, *J* = 12.7 Hz, 1H), 3.97 (d, *J* = 12.7 Hz, 1H), 3.78 (s, 3H), 3.49 (d, *J* = 12.3 Hz, 1H), 3.22 (d, *J* = 12.3 Hz, 1H), 1.61 (s, 1H), 1.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 150.9, 132.8, 132.5, 132.0, 130.7, 129.1, 127.0, 113.4, 112.9, 78.2, 77.6, 65.2, 61.7, 55.7, 34.7, 21.5.

HRMS (ESI) calculated for $C_{19}H_{22}NaO_4Se$ [M+Na]+: 417.0576; found: 417.0582.



(7-fluoro-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepin-9-yl)methanol.

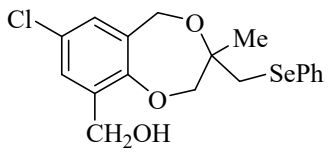
Compound 3na.

Yield = 64%; 49 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.1, 2.2 Hz, 2H), 7.29 (d, *J* = 6.7 Hz, 3H), 6.98 (dd, *J* = 8.5, 3.2 Hz, 1H), 6.74 (dd, *J* = 8.3, 3.2 Hz, 1H), 4.73 – 4.59 (m, 4H), 4.16 (d, *J* = 12.7 Hz, 1H), 4.01 (d, *J* = 12.8 Hz, 1H), 3.45 (d, *J* = 12.3 Hz, 1H), 3.21 (d, *J* = 12.3 Hz, 1H), 2.07 (s, 1H), 1.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.82 (d, *J* = 242.7 Hz), 152.72 (d, *J* = 2.2 Hz), 133.41 (d, *J* = 7.2 Hz), 132.8, 132.08 (d, *J* = 6.6 Hz), 130.6, 129.1, 127.1, 114.30 (d, *J* = 23.1 Hz), 114.08 (d, *J* = 23.1 Hz), 78.4, 77.2, 64.7, 60.9, 34.7, 21.3.

HRMS (ESI) calculated for $C_{18}H_{20}FO_3Se$ [M+H]+: 383.0556; found: 383.0561.



(7-chloro-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepin-9-yl)methanol

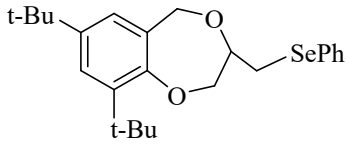
Compound 3oa.

Yield = 50%; 39 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.28 (s, 3H), 7.24 (d, *J* = 2.7 Hz, 1H), 7.01 (d, *J* = 2.7 Hz, 1H), 4.69 (s, 2H), 4.62 (d, *J* = 6.1 Hz, 2H), 4.20 (d, *J* = 12.9 Hz, 1H), 4.06 (d, *J* = 13.0 Hz, 1H), 3.42 (d, *J* = 12.4 Hz, 1H), 3.22 (d, *J* = 12.4 Hz, 1H), 1.73 (s, 1H), 1.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 133.1, 132.9, 131.6, 130.5, 129.1, 127.8, 127.5, 127.2, 78.5, 77.2, 64.6, 61.0, 34.8, 21.3.

HRMS (ESI) calculated for $C_{18}H_{19}ClNaO_3Se$ [M+Na]+: 421.0080; found: 421.0089.



7,9-di-*tert*-butyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

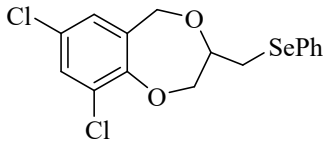
Compound 3pa.

Yield = 55%; 48 mg; colorless oil.

^{1}H NMR (600 MHz, CDCl3) δ 7.61 – 7.55 (m, 2H), 7.34 – 7.26 (m, 4H), 7.09 (d, *J* = 2.5 Hz, 1H), 4.77 (d, *J* = 13.1 Hz, 1H), 4.68 (d, J = 13.2 Hz, 1H), 4.46 (dd, J = 12.4, 1.8 Hz, 1H), 4.16 – 4.08 (m, 1H), 3.55 (dd, J = 12.4, 9.1 Hz, 1H), 3.08 (dd, J = 12.6, 6.9 Hz, 1H), 2.91 (dd, J = 12.6, 6.3 Hz, 1H), 1.40 (s, 9H), 1.32 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 145.5, 140.5, 132.8, 132.7, 129.2, 127.1, 124.5, 123.7, 80.8, 76.5, 72.5, 35.1, 34.4, 31.5, 30.3, 28.4.

HRMS (ESI) calculated for $C_{24}H_{33}O_2Se$ [M+H]+: 433.1640; found: 433.1648



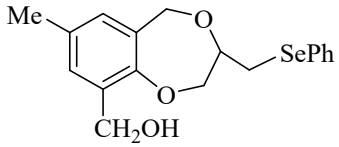
7,9-dichloro-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

Compound 3qa.

Yield = 85%; 66 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 2H), 7.35 (dd, *J* = 2.5, 0.5 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.08 (d, *J* = 2.5 Hz, 1H), 4.68 (q, *J* = 13.7 Hz, 2H), 4.57 (dd, *J* = 12.6, 1.9 Hz, 1H), 4.11 – 4.07 (m, 1H), 3.70 (dd, *J* = 12.7, 8.7 Hz, 1H), 3.08 (dd, *J* = 12.7, 6.8 Hz, 1H), 2.91 (dd, *J* = 12.7, 6.3 Hz, 1H).

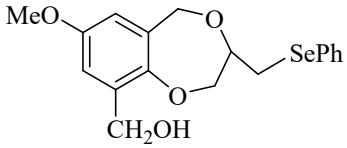
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.9, 135.2, 132.9, 129.6, 129.34, 129.30, 128.4, 127.51, 127.43, 127.0, 81.4, 76.6, 71.1, 28.0.
HRMS (ESI) calculated for $C_{16}H_{15}Cl_2O_2Se$ [M+H]+: 388.9609; found: 88.9612.



(7-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepin-9-yl)methanol.

Compound 3ra.

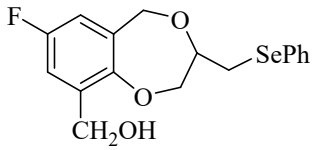
Yield = 48%; 35 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.31 – 7.28 (m, 3H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 2.5 Hz, 1H), 4.77 – 4.66 (m, 3H), 4.60 (d, *J* = 12.6 Hz, 1H), 4.50 (dd, *J* = 12.5, 1.8 Hz, 1H), 4.10 – 4.03 (m, 1H), 3.67 (dd, *J* = 12.5, 8.6 Hz, 1H), 3.09 (dd, *J* = 12.6, 6.8 Hz, 1H), 2.92 (dd, *J* = 12.6, 6.4 Hz, 1H), 2.31 (s, 3H), 1.89 (s, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 155.3, 133.0, 132.9, 132.2, 131.9, 129.8, 129.3, 129.2, 129.1, 127.2, 81.3, 76.3, 71.7, 61.6, 28.3, 20.6.
HRMS (ESI) calculated for $C_{18}H_{20}NaO_3Se$ [M+Na]+: 387.0470; found: 387.0476.



(7-methoxy-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepin-9-yl)methanol.

Compound 3sa.

Yield = 41%; 31 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.34 – 7.26 (m, 3H), 6.83 (d, *J* = 3.1 Hz, 1H), 6.68 (d, *J* = 3.1 Hz, 1H), 4.74 (dd, *J* = 25.0, 13.2 Hz, 2H), 4.63 (dd, *J* = 26.9, 13.3 Hz, 2H), 4.47 (dd, *J* = 12.5, 1.8 Hz, 1H), 4.07 (q, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.63 (dd, *J* = 12.5, 8.8 Hz, 1H), 3.08 (dd, *J* = 12.7, 6.9 Hz, 1H), 2.91 (dd, *J* = 12.6, 6.3 Hz, 1H), 1.99 (s, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 155.2, 151.1, 133.5, 133.2, 132.9, 129.8, 129.2, 127.3, 113.9, 113.0, 81.5, 76.4, 71.7, 61.5, 55.7, 28.2.
HRMS (ESI) calculated for $C_{18}H_{20}NaO_4Se$ [M+Na]+: 403.0419; found: 403.0427.



(7-fluoro-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepin-9-yl)methanol.

Compound 3ta.

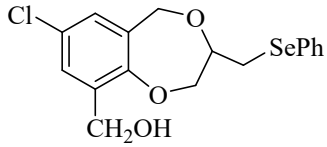
Yield = 53%; 39 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.35 – 7.26 (m, 3H), 7.03 (dd, *J* = 8.5, 3.2 Hz, 1H), 6.83 (dd, *J* = 8.2, 3.2 Hz, 1H), 4.74 (d, *J* = 13.4 Hz, 1H), 4.70 (d, *J* = 13.7 Hz, 1H), 4.63 (dd, *J* = 17.1, 13.4 Hz, 2H), 4.48 (d, *J* = 12.5 Hz, 1H), 4.09 – 4.04 (m, 1H), 3.65 (dd, *J* = 12.6, 8.7 Hz, 1H), 3.08 (dd, *J* = 12.7, 6.9 Hz, 1H), 2.91 (dd, *J* = 12.7, 6.3 Hz, 1H), 2.20 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.16 (d, *J* = 243.2 Hz), 153.1, 134.27 (d, *J* = 7.2 Hz), 133.99 (d, *J* = 7.2 Hz), 132.9, 129.7, 129.2, 127.3, 114.81 (d, *J* = 23.1 Hz), 114.38 (d, *J* = 23.7 Hz), 81.5, 76.2, 71.2, 60.8, 28.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -119.1.

HRMS (ESI) calculated for $C_{17}H_{17}FNaO_3Se$ [M+Na]+: 391.0219; found: 391.0230.



(7-chloro-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepin-9-yl)methanol.

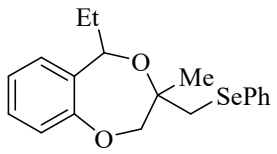
Compound 3ua.

Yield = 54%; 41 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.32 – 7.28 (m, 4H), 7.11 (d, *J* = 2.7 Hz, 1H), 4.76 – 4.61 (m, 4H), 4.52 (dd, *J* = 12.6, 1.8 Hz, 1H), 4.10 – 4.03 (m, 1H), 3.72 – 3.66 (m, 1H), 3.09 (dd, *J* = 12.7, 6.7 Hz, 1H), 2.92 (dd, *J* = 12.7, 6.5 Hz, 1H), 1.83 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 134.0, 133.8, 132.9, 129.6, 129.2, 128.3, 128.0, 127.4, 81.3, 76.2, 71.0, 60.9, 28.1.

HRMS (ESI) calculated for $C_{17}H_{17}ClNaO_3Se$ [M+Na]+: 406.9924; found:406.9932.



5-ethyl-3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

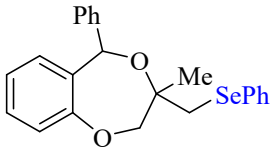
Compound 3va.

Yield = 38%; 27 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.48 (m, 2H), 7.40 – 7.16 (m, 5H), 7.15 – 6.77 (m, 2H), 4.88 (m , 1H), 4.28 (d, *J* =12.6 Hz, 1H), 3.78 (d, *J* = 12.6 Hz, 1H), 3.33 (d, *J* =12.0 Hz, 2H), 2.25 – 2.00 (m, 1H), 2.00 – 1.72 (m, 1H), 1.42 (m, 3H), 1.12 (dt, *J* = 9.7, 7.3 Hz, 3H). dr. = 1.5:1.

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 134.2, 132.5, 131.2, 129.0, 128.5, 126.8, 126.2, 123.1, 120.4, 77.5, 71.1, 33.5, 26.0, 24.0, 19.5, 10.9.

HRMS (ESI) calculated for $C_{19}H_{22}NaO_2Se$ [M+Na]+: 385.0677; found: 385.0686.



3-methyl-5-phenyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

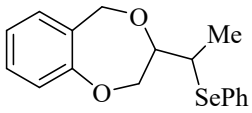
Compound 3wa.

Yield = 32%; 26 mg; colorless oil. d.r. = 1.6:1

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.23 (m, 10H), 7.22 – 7.13 (m, 1H), 7.06 (dd, *J* = 18.4, 7.9 Hz, 1H), 6.93 – 6.73 (m, 1H), 6.42 (dd, *J* = 18.3, 7.7 Hz, 1H), 6.10 (d, *J* = 9.4 Hz, 1H), 4.41 (d, *J* = 12.8 Hz, 1H), 3.91 (d, *J* = 12.8 Hz, 1H), 3.86 – 3.25 (m, 2H), 1.49 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 140.4, 135.2, 132.6, 130.9, 129.2, 129.1, 128.7, 128.2, 127.9, 127.6, 126.8, 123.0, 120.2, 77.9, 77.4, 73.9, 33.6, 24.0.

HRMS (ESI) calculated for $C_{23}H_{23}O_2Se$ [M+H]+: 411.0858; found: 411.0862.



3-(1-(phenylselanyl)ethyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

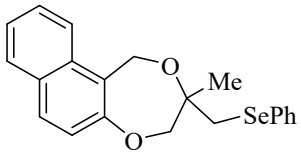
Compound 3xa.

Yield = 62 %; 41 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.26 (m, *J* = 7.8, 1.6 Hz, 1H), 7.22 – 7.12 (m, 4H), 7.07 (dd, *J* = 14.2, 7.6 Hz, 2H), 4.79 (d, *J* = 12.8 Hz, 1H), 4.50 (d, *J* = 12.8 Hz, 1H), 4.43 – 4.24 (m, 2H), 4.13 (q, *J* = 6.4 Hz, 1H), 3.28 (t, *J* = 4.8 Hz, 1H), 1.40 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 134.3, 132.8, 130.7, 130.1, 129.9, 129.1, 127.5, 124.7, 121.9, 76.6, 76.4, 68.0, 52.5, 20.0.

HRMS (ESI) calculated for $C_{17}H_{19}O_2Se$ [M+H]+:335.0545; found: 355.0550.



3-methyl-3-((phenylselanyl)methyl)-3,4-dihydro-1*H*-naphtho[2,1-*e*][1,4]dioxepine.

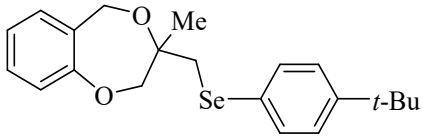
Compound 3ya.

Yield = 45%; 34 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.54 – 7.46 (m, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.34 – 7.23 (m, 4H), 7.16 (d, *J* = 8.8 Hz, 1H), 5.41 – 5.11 (m, 2H), 4.30 (d, *J* = 13.0 Hz, 1H), 4.23 (d, *J* = 13.1 Hz, 1H), 3.56 (d, *J* = 12.2 Hz, 1H), 3.26 (d, *J* = 12.2 Hz, 1H), 1.47 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.1, 132.7, 131.8, 130.8, 129.9, 129.1, 128.8, 128.5, 127.0, 126.6, 123.9, 121.7, 120.75, 120.3, 78.5, 76.6, 60.4, 35.3, 21.4.

HRMS (ESI) calculated for $C_{21}H_{20}NaO_2Se$ [M+Na]+: 407.0521; found: 407.0529.



3-(((4-(*tert*-butyl)phenyl)selanyl)methyl)-3-methyl-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

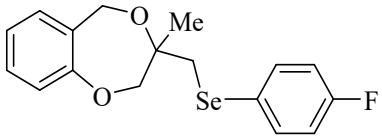
Compound 3ab.

Yield = 62%; 48 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.30 (m, 2H), 7.27 – 7.15 (m, 2H), 7.10 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.98 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.89 (dd, *J* = 10.5, 4.4 Hz, 2H), 4.68 (d, *J* = 14.7 Hz, 1H), 4.61 (d, *J* = 14.7 Hz, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 3.95 (d, *J* = 13.0 Hz, 1H), 3.39 (d, *J* = 12.1 Hz, 1H), 3.06 (d, *J* = 12.1 Hz, 1H), 1.31 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 150.3, 132.8, 132.8, 130.1, 128.8, 127.1, 126.2, 122.7, 119.8, 78.3, 77.1, 65.3, 35.1, 34.5, 31.2, 21.5.

HRMS (ESI) calculated for $C_{21}H_{27}O_2Se$ [M+H]+: 391.1171; found: 391.1176.



3-(((4-fluorophenyl)selanyl)methyl)-3-methyl-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

Compound 3ac.

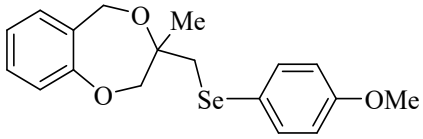
Yield = 58%; 40 mg; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.89 (dd, *J* = 12.3, 5.8 Hz, 4H), 4.83 – 4.51 (m, 2H), 4.05 (d, *J* = 13.0 Hz, 1H), 3.96 (d, *J* = 13.0 Hz, 1H), 3.38 (d, *J* = 12.2 Hz, 1H), 3.04 (d, *J* = 12.2 Hz, 1H), 1.30 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.36 (d, *J* = 247.1 Hz), 158.9, 135.37 (d, *J* = 7.7 Hz), 130.0, 128.83 (d, *J* = 8.6 Hz), 125.16 (d, *J* = 3.3 Hz), 122.8, 119.7, 116.3, 116.2, 78.2, 76.9, 65.3, 35.9, 21.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -114.7.

HRMS (ESI) calculated for $C_{17}H_{18}FO_2Se$ [M+H]+: 353.0451; found: 353.0459

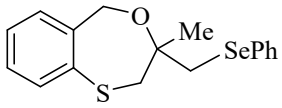


3-(((4-methoxyphenyl)selanyl)methyl)-3-methyl-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.

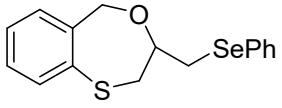
Compound 3ad.

Yield = 51%; 37 mg; colorless oil.

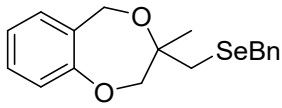
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.32 (m, 2H), 7.10 (td, *J* = 7.7, 1.6 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 2H), 6.81 – 6.47 (m, 2H), 4.63 (dd, *J* = 37.0, 14.7 Hz, 2H), 4.05 (d, *J* = 13.0 Hz, 1H), 3.94 (d, *J* = 13.0 Hz, 1H), 3.72 (s, 3H), 3.33 (d, *J* = 12.3 Hz, 1H), 3.00 (d, *J* = 12.3 Hz, 1H), 1.30 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 159.0, 135.5, 130.1, 128.7, 122.7, 120.6, 119.7, 114.8, 78.3, 65.2, 55.3, 36.1, 21.4.
HRMS (ESI) calculated for $C_{18}H_{21}O_3Se$ [M+H]+: 365.0650; found: 365.066.



3-methyl-3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]oxathiepine. Compound 3za.
Yield = 78%; 54 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.45 – 7.32 (m, 1H), 7.29 – 6.82 (m, 6H), 4.67 (m, 2H), 3.48 (s, 1H), 3.16 (d, *J* = 12.0 Hz, 1H), 2.91 (d, *J* = 14.7 Hz, 1H), 2.84 (d, *J* = 14.7 Hz, 1H), 1.42 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 141.2, 135.8, 131.9, 130.2, 129.7, 128.5, 128.0, 126.8, 126.4, 125.9, 75.9, 65.7, 42.1, 36.5, 23.5.
HRMS (ESI) calculated for $C_{17}H_{18}NaOSSe$ [M+Na]+ : 373.0136; found: 373.0144.

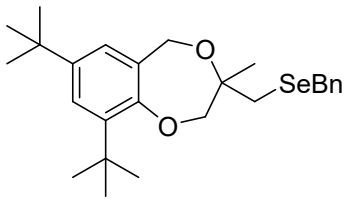


3-((phenylselanyl)methyl)-2,3-dihydro-5*H*-benzo[*e*][1,4]oxathiepine. Compound 3aaa.
Yield = 76%; 51 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (ddd, *J* = 9.3, 7.3, 1.3 Hz, 3H), 7.34 – 6.90 (m, 6H), 5.03 – 4.37 (m, 2H), 4.10 – 3.69 (m, 1H), 3.07 (dd, *J* = 12.5, 6.9 Hz, 1H), 2.91 (dd, *J* = 14.4, 1.3 Hz, 1H), 2.84 (dd, *J* = 12.5, 6.2 Hz, 1H), 2.62 (dd, *J* = 14.4, 9.6 Hz, 1H).
^{13}C NMR (150 MHz, CDCl3) δ 143.2, 136.8, 132.9, 132.8, 132.2, 130.0, 129.7, 129.2, 128.1, 127.8, 127.1, 83.4, 74.5, 38.8, 32.9.
HRMS (ESI) calculated for $C_{16}H_{16}NaOSSe$ [M+Na]+: 358.9979; found: 358.9986.



3-((benzylselanyl)methyl)-3-methyl-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine. Compound 3ae.
Yield = 78%; 54 mg; colorless oil.
1H NMR (600 MHz, CDCl3) δ 7.25 – 7.17 (m, 4H), 7.15 – 7.08 (m, 2H), 6.98 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.91 – 6.86 (m, 2H), 4.68 (d, *J* = 14.7 Hz, 1H), 4.61 (d, *J* = 14.7 Hz, 1H), 4.03 (d, *J* = 12.9 Hz, 1H), 3.94 (d, *J* = 13.1 Hz, 1H), 3.78 (s, 2H), 2.89 (d, *J* = 12.4 Hz, 1H), 2.66 (d, *J* = 12.5 Hz, 1H), 1.49 (s, 1H), 1.23 (s, 3H).

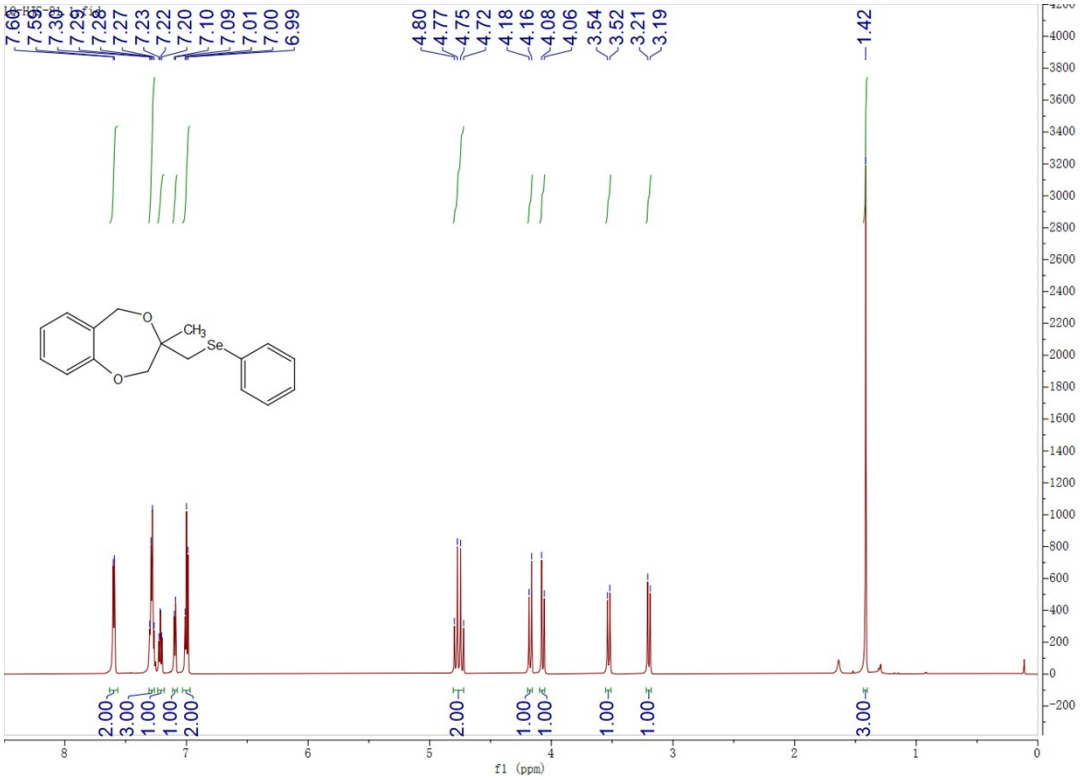
13C NMR (150 MHz, CDCl3) δ 158.9, 139.2, 129.9, 129.0, 128.7, 128.5, 126.7, 122.6, 119.7, 78.6, 65.1, 30.5, 28.5, 21.1.
HRMS (ESI) calculated for $C_{18}H_{20}NaO_2Se$ [M+Na]+: 371.0521; found: 371.0528.

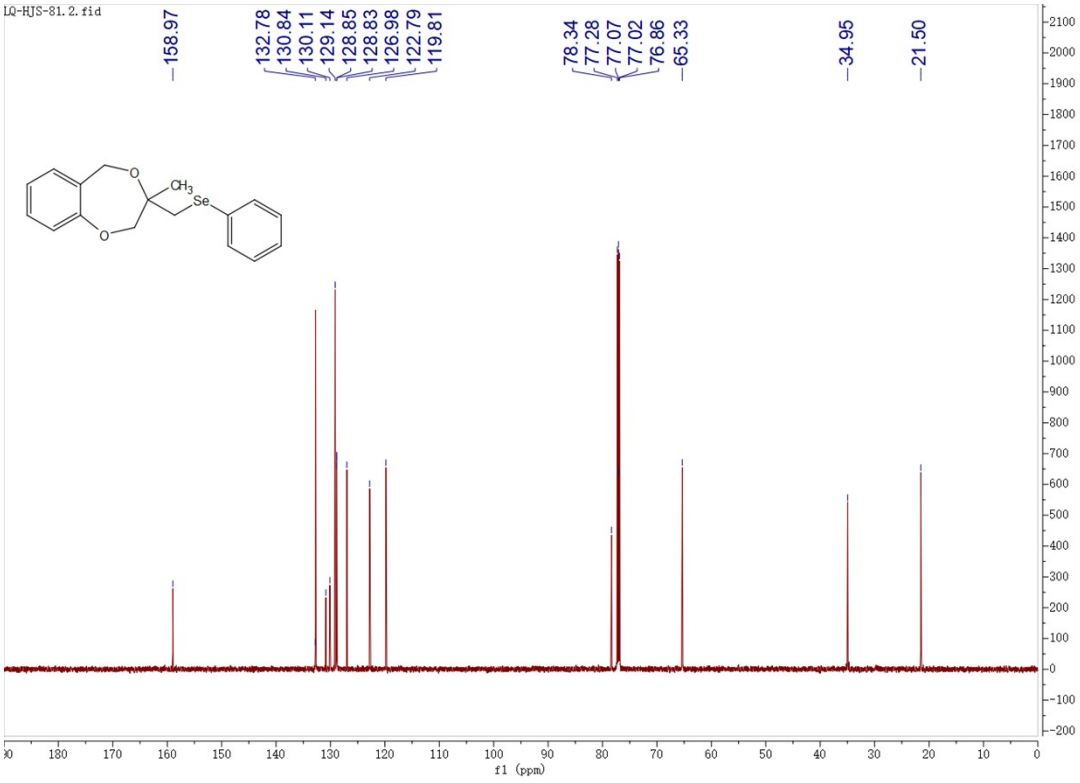


3-((benzylselanyl)methyl)-7,9-di-*tert*-butyl-3-methyl-2,3-dihydro-5*H*-benzo[*e*][1,4]dioxepine.
Compound 3de.
Yield = 74%; 68 mg; colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 5H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 4.64 (d, *J* = 14.0 Hz, 1H), 4.55 (d, *J* = 14.0 Hz, 1H), 3.96 (d, *J* = 12.5 Hz, 1H), 3.83 – 3.76 (m, 2H), 3.73 (d, *J* = 12.5 Hz, 1H), 2.93 (d, *J* = 12.4 Hz, 1H), 2.72 (d, *J* = 12.5 Hz, 1H), 1.30 (s, 9H), 1.22 (s, 3H), 1.21 (s, 9H).
^{13}C NMR (150 MHz, CDCl3) δ 156.7, 145.1, 139.9, 139.4, 131.7, 128.9, 128.5, 126.7, 124.1, 123.4, 77.9, 77.6, 66.0, 35.1, 34.4, 31.5, 30.3, 28.4, 21.5.
HRMS (ESI) calculated for $C_{26}H_{36}NaO_2Se$ [M+Na]+: 483.1773; found: 483.1779.

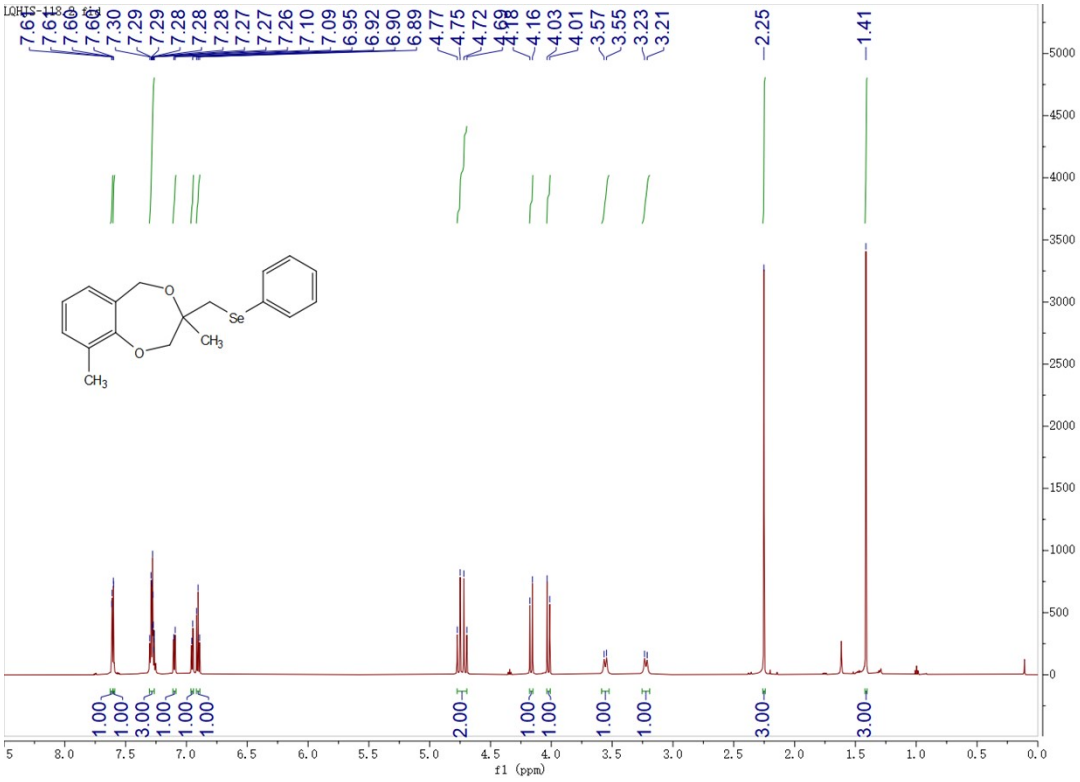
6. ^{1}H NMR and ^{13}C NMR Spectra for Products.

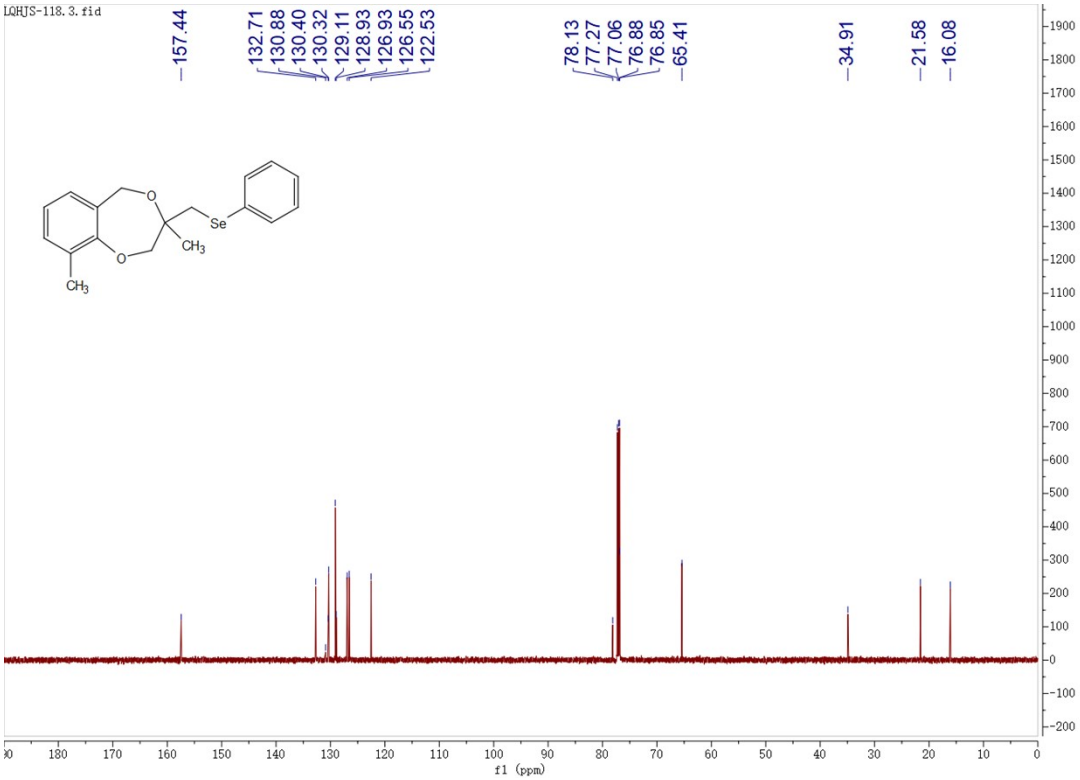
Compound 3aa ^{1}H NMR and ^{13}C NMR



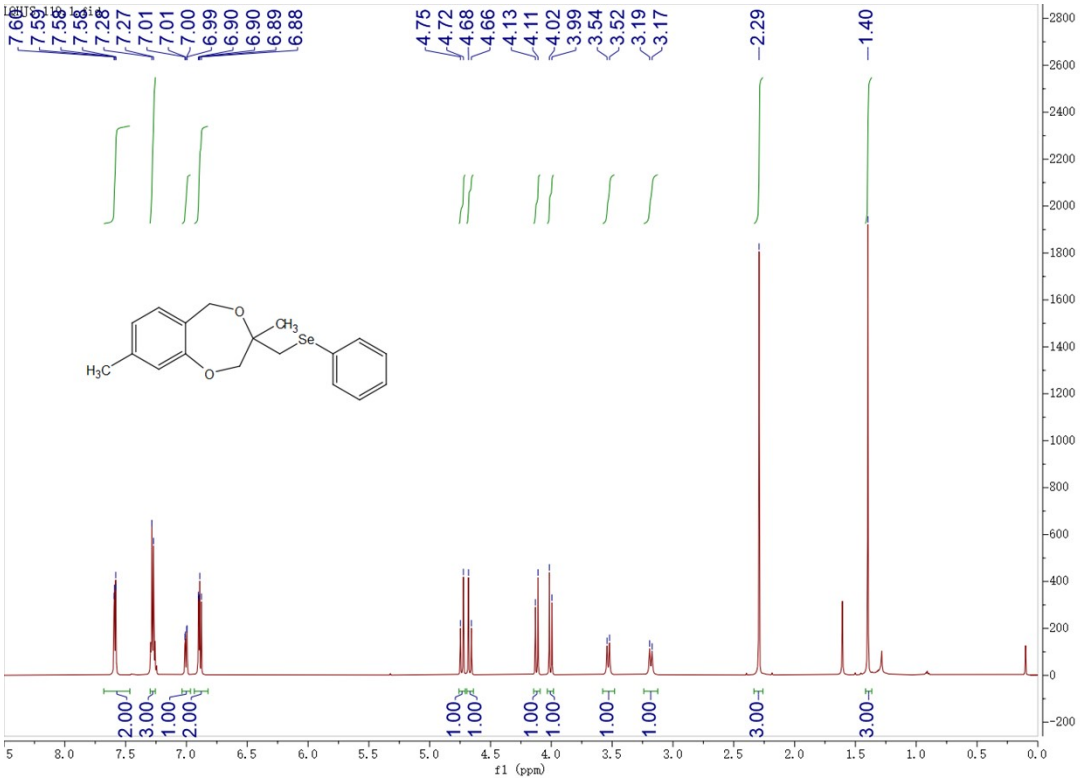


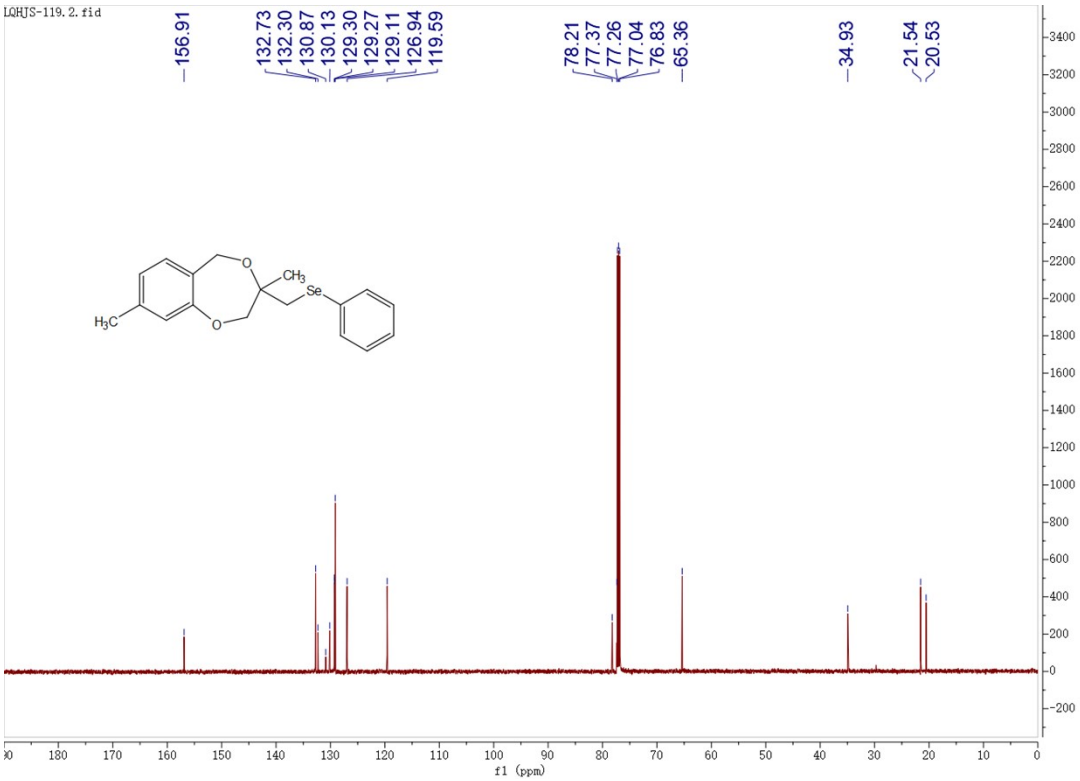
Compound 3ba ^{1}H NMR and ^{13}C NMR



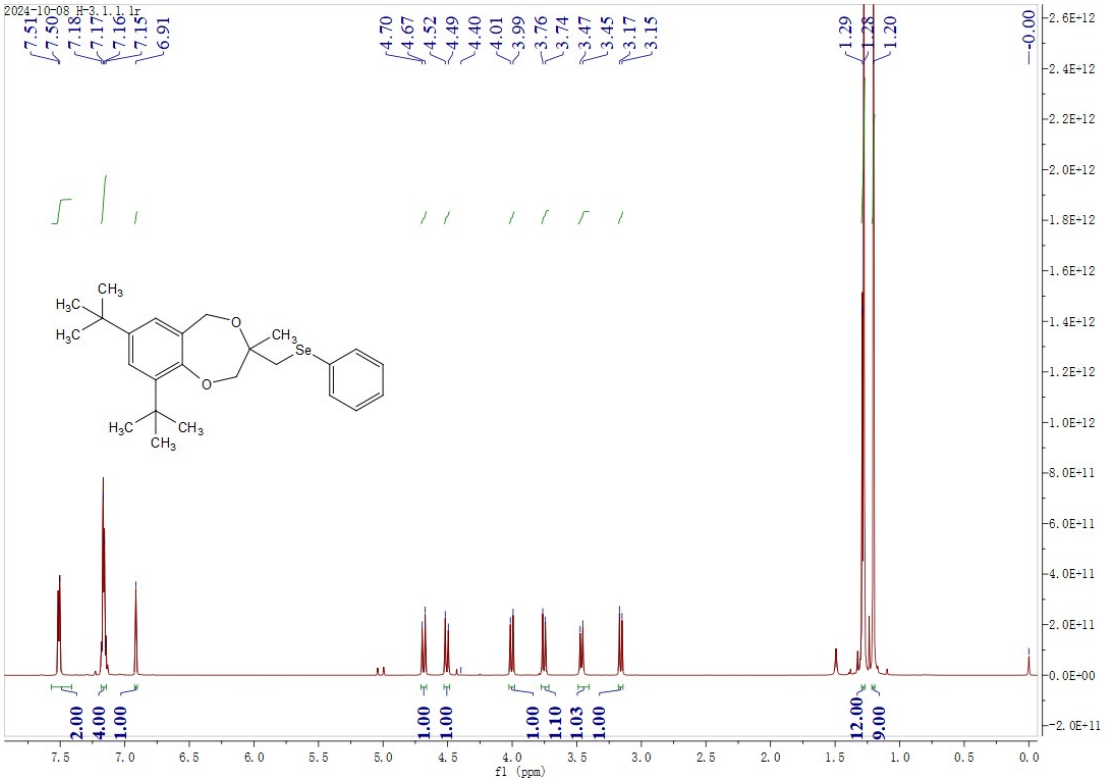


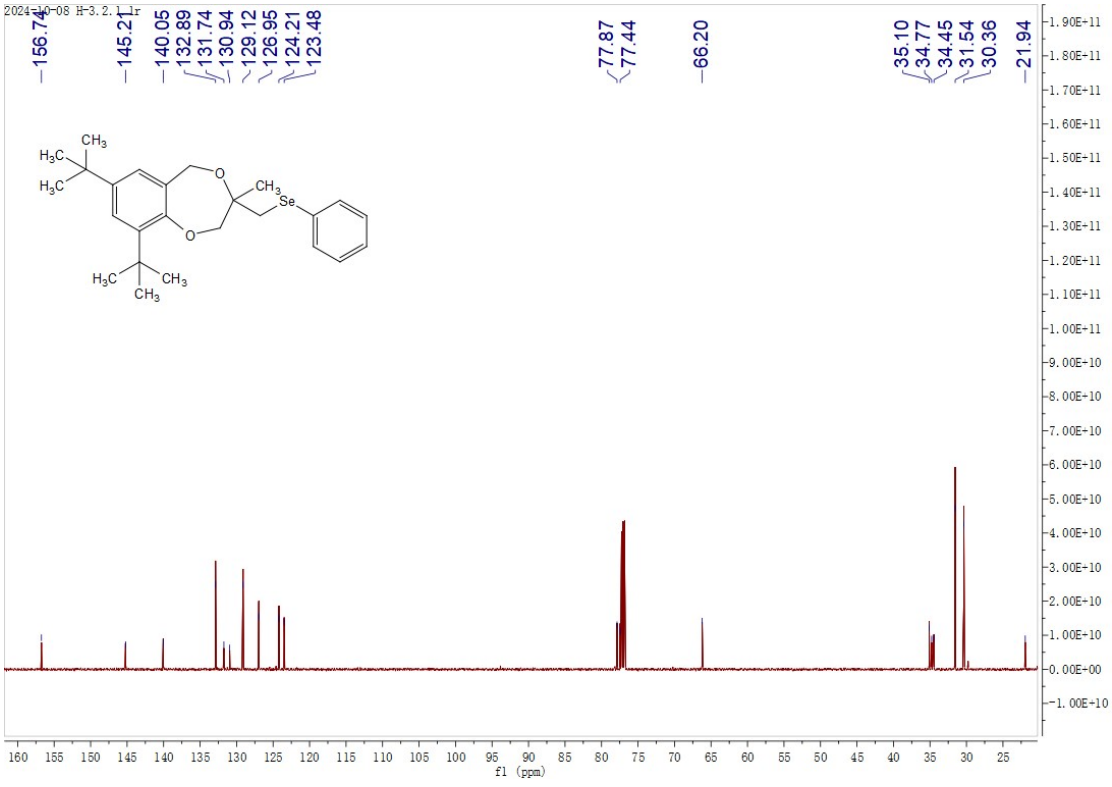
Compound 3ca ^{1}H NMR and ^{13}C NMR



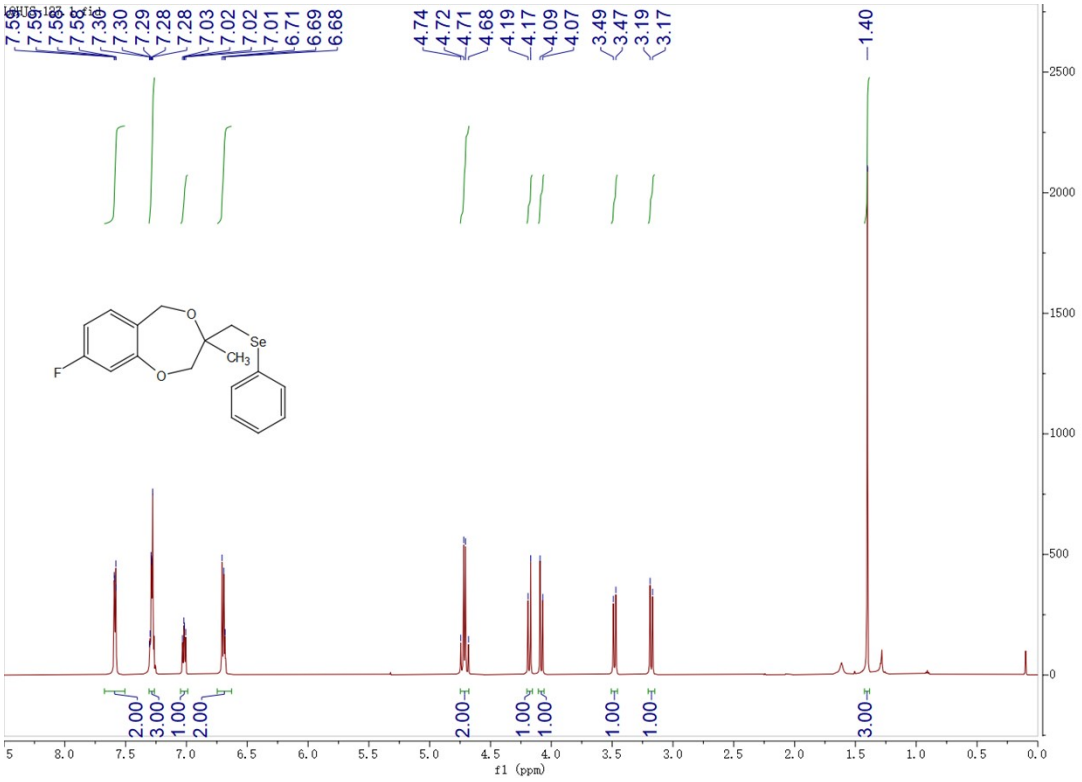


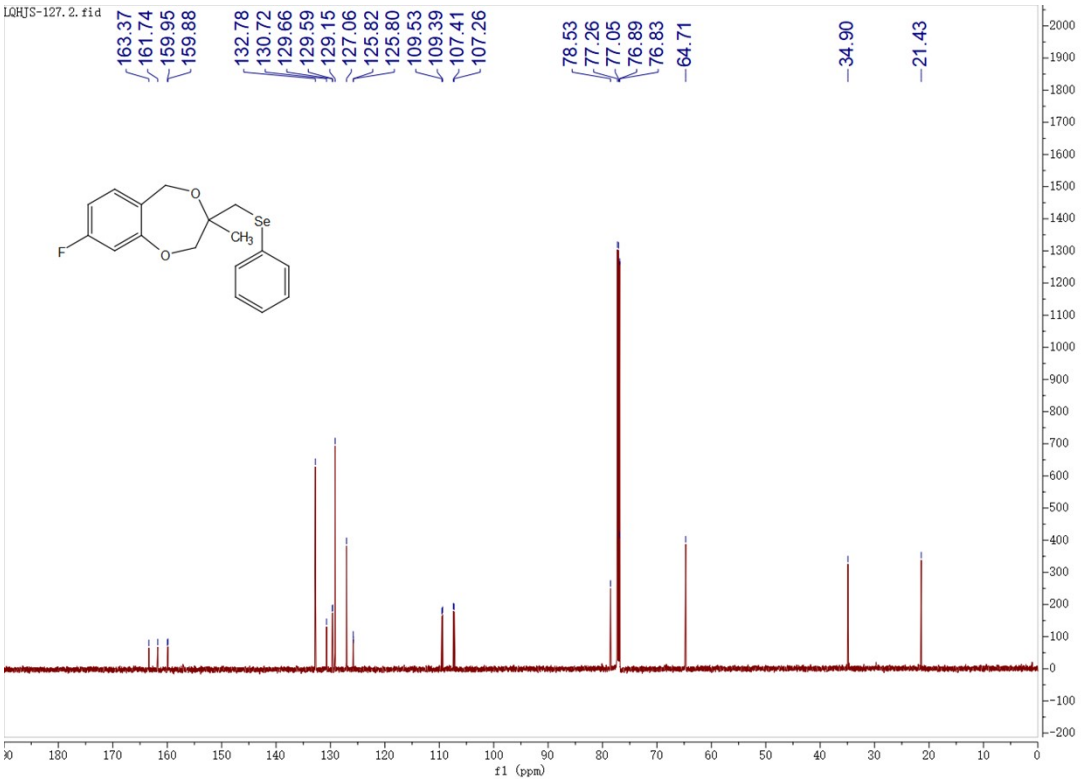
Compound 3da ^{1}H NMR and ^{13}C NMR



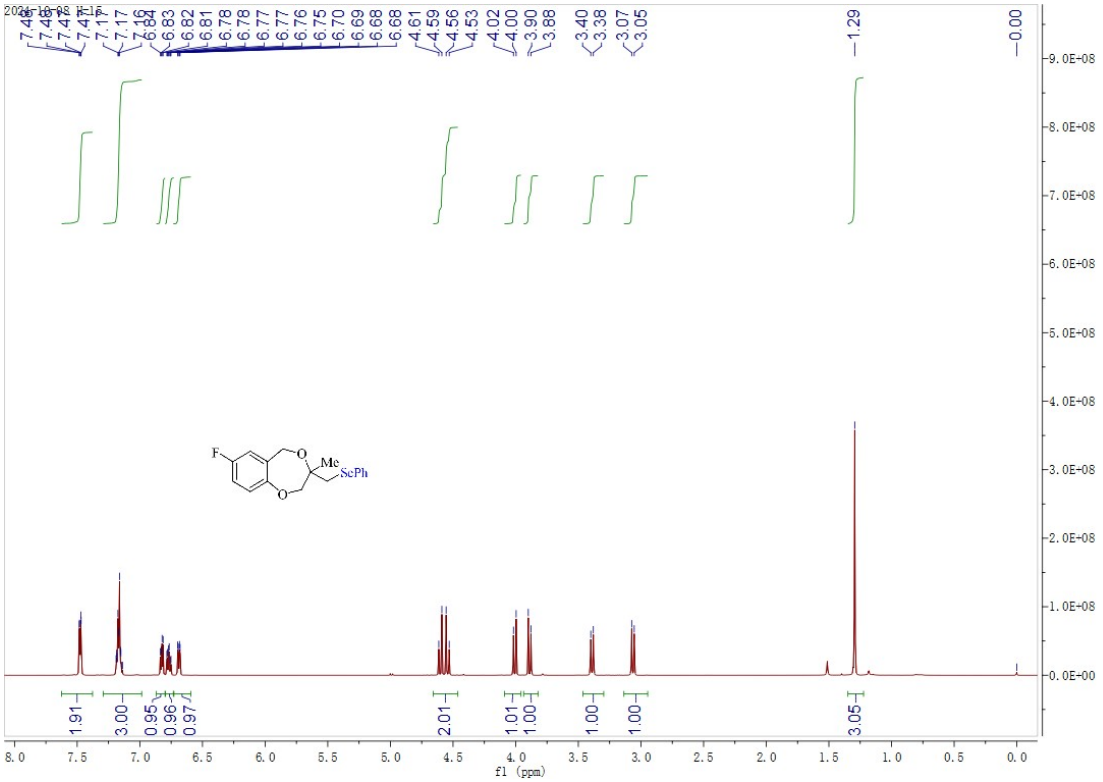


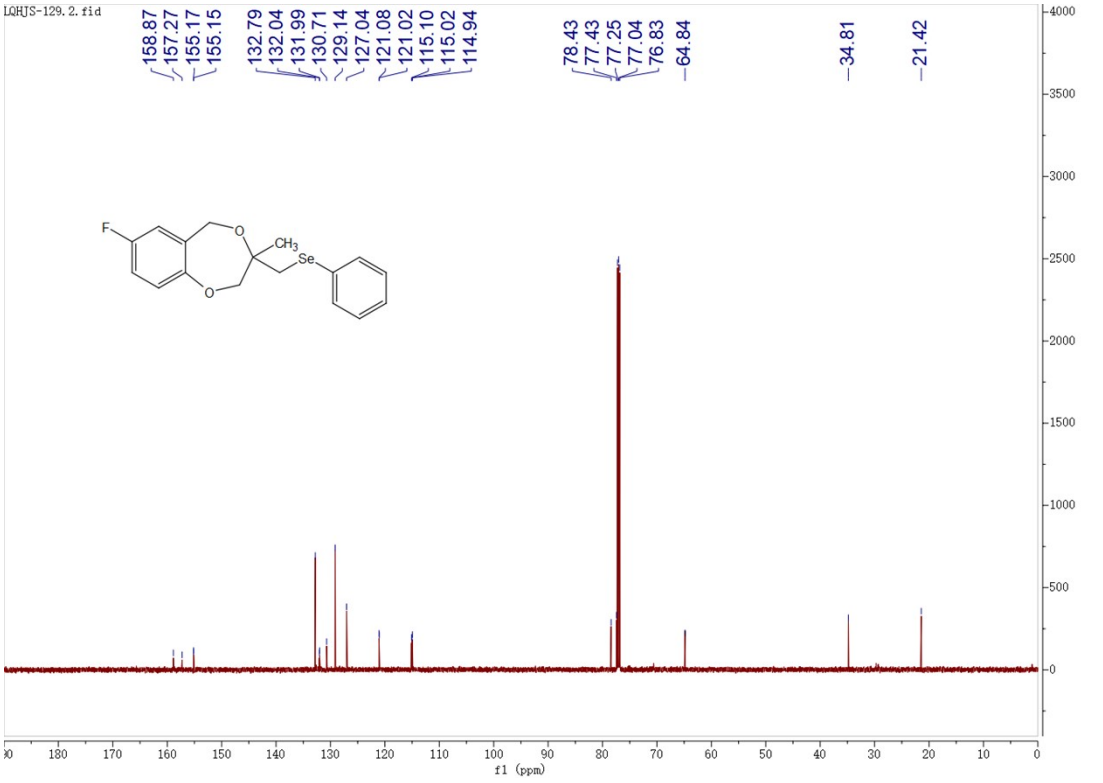
Compound 3ea ^{1}H NMR and ^{13}C NMR

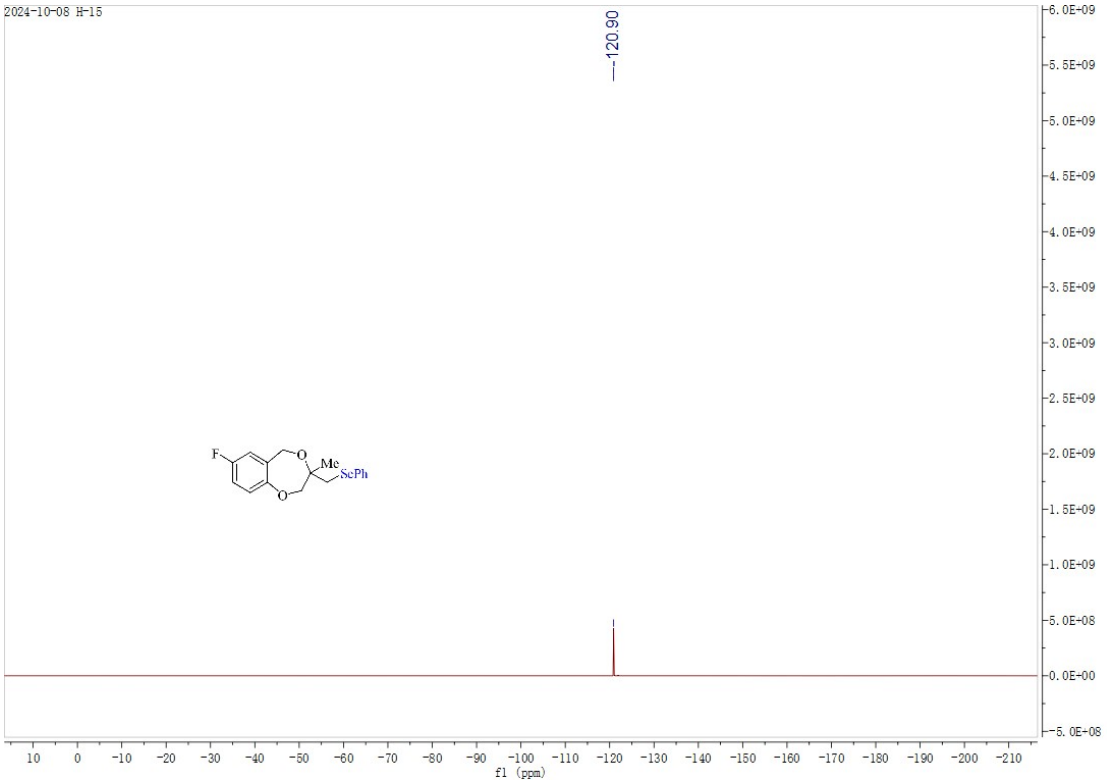




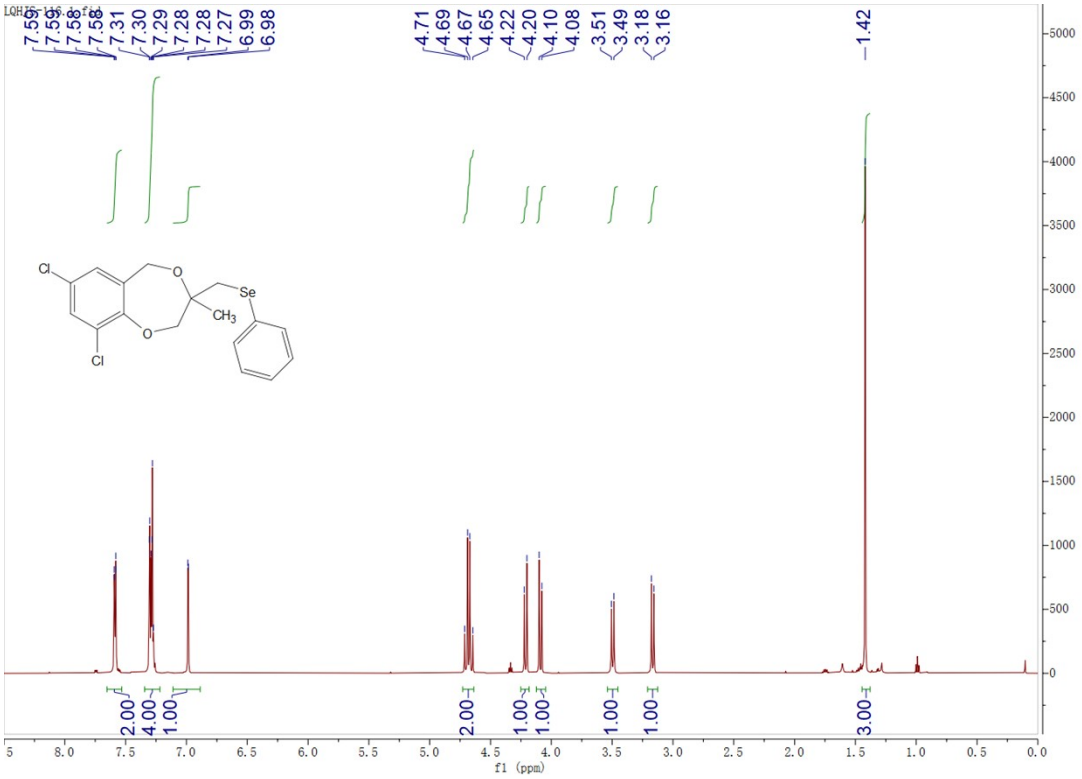
Compound 3fa ^{1}H NMR, ^{13}C NMR and ^{19}F NMR

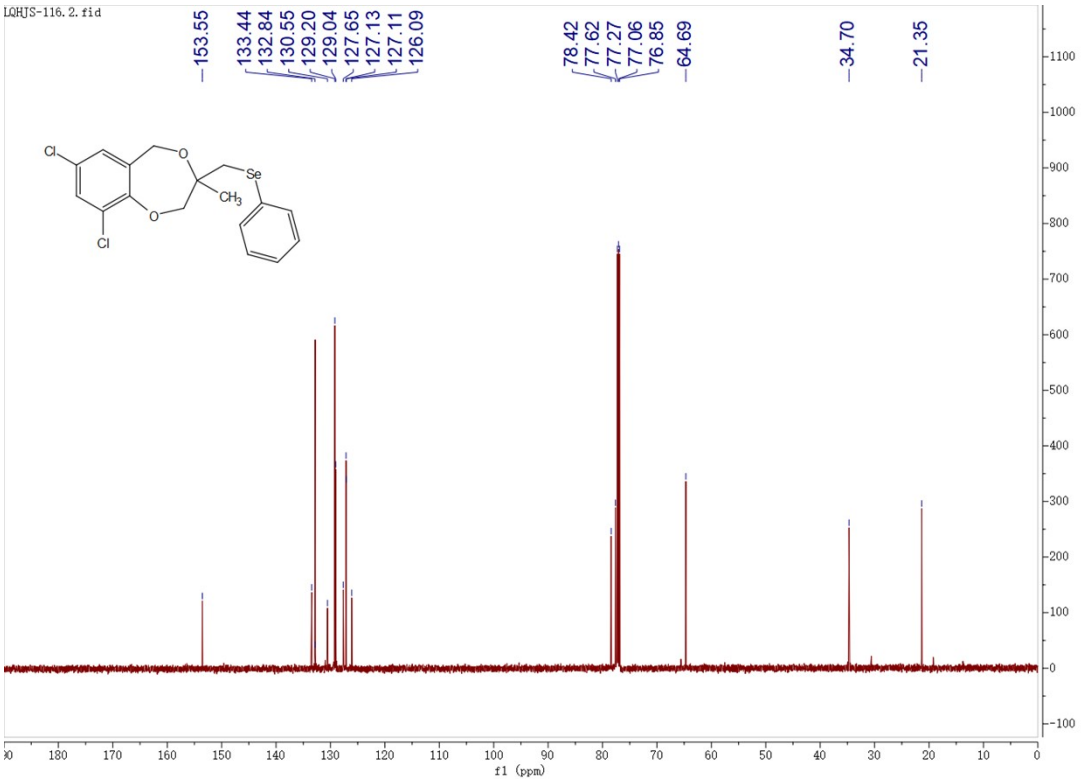




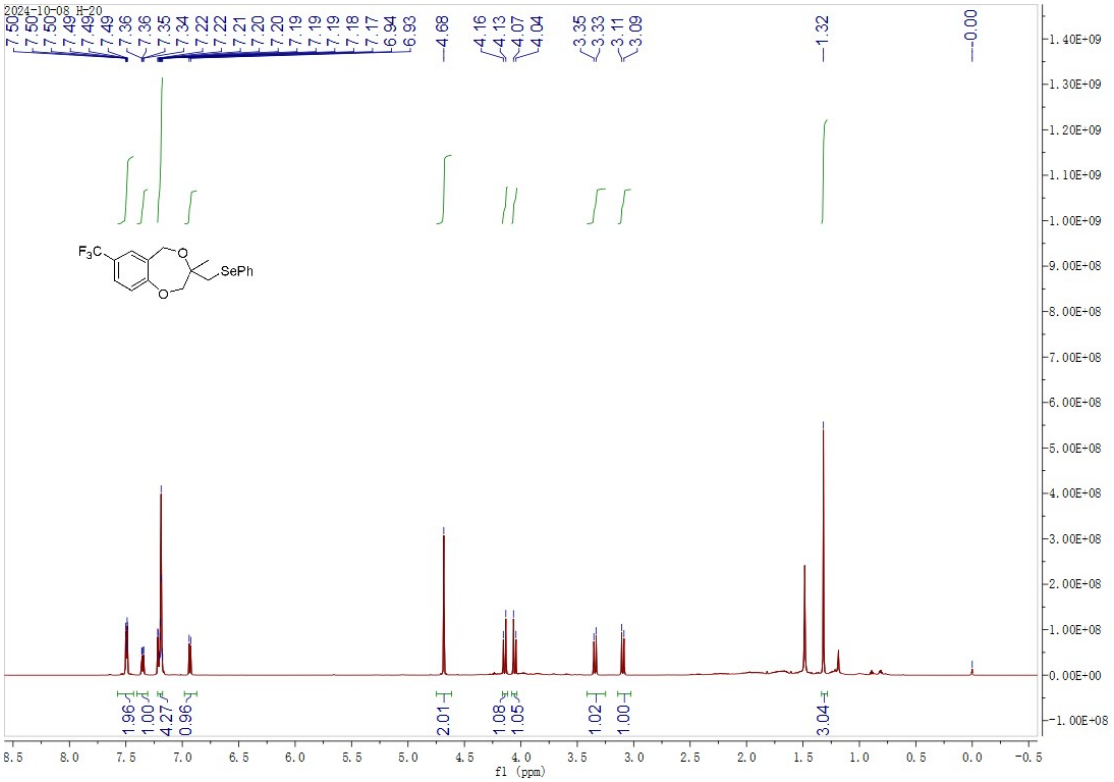

2024-10-08 H-15
-120.90
F
O
Me
SePh
O
6.0E-09
5.5E-09
5.0E-09
4.5E-09
4.0E-09
3.5E-09
3.0E-09
2.5E-09
2.0E-09
1.5E-09
1.0E-09
5.0E-08
0.0E-00
-5.0E-08
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

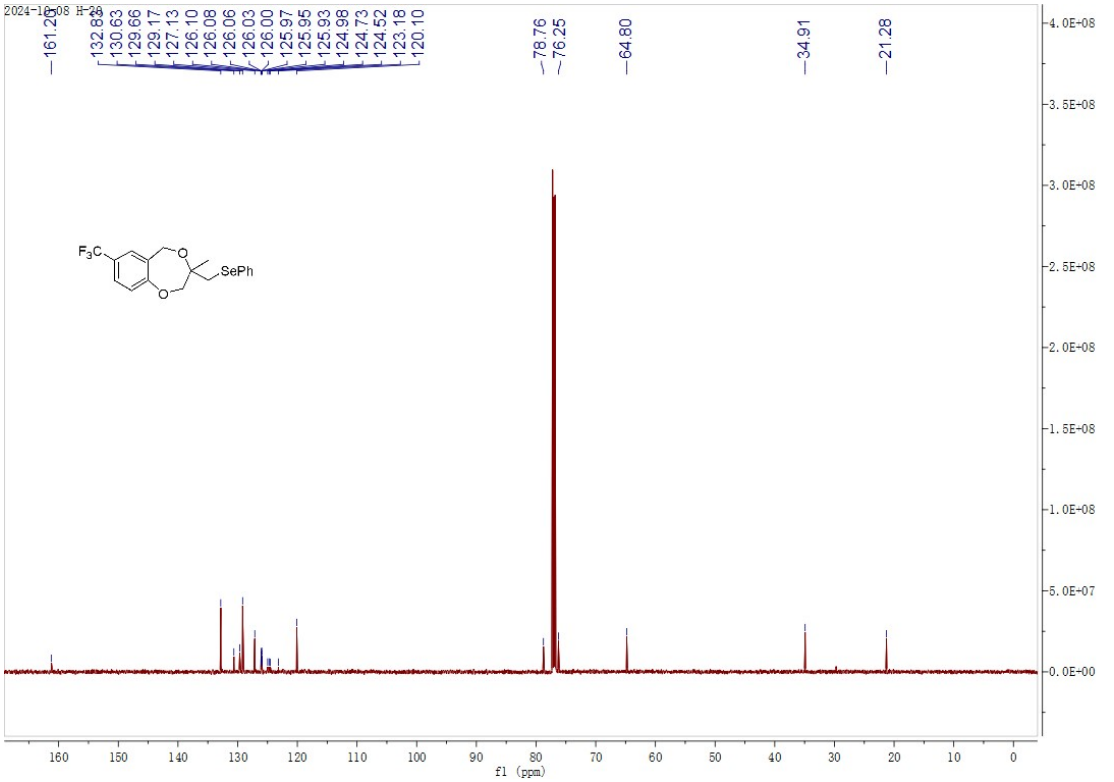
Compound 3ga ^{1}H NMR and ^{13}C NMR

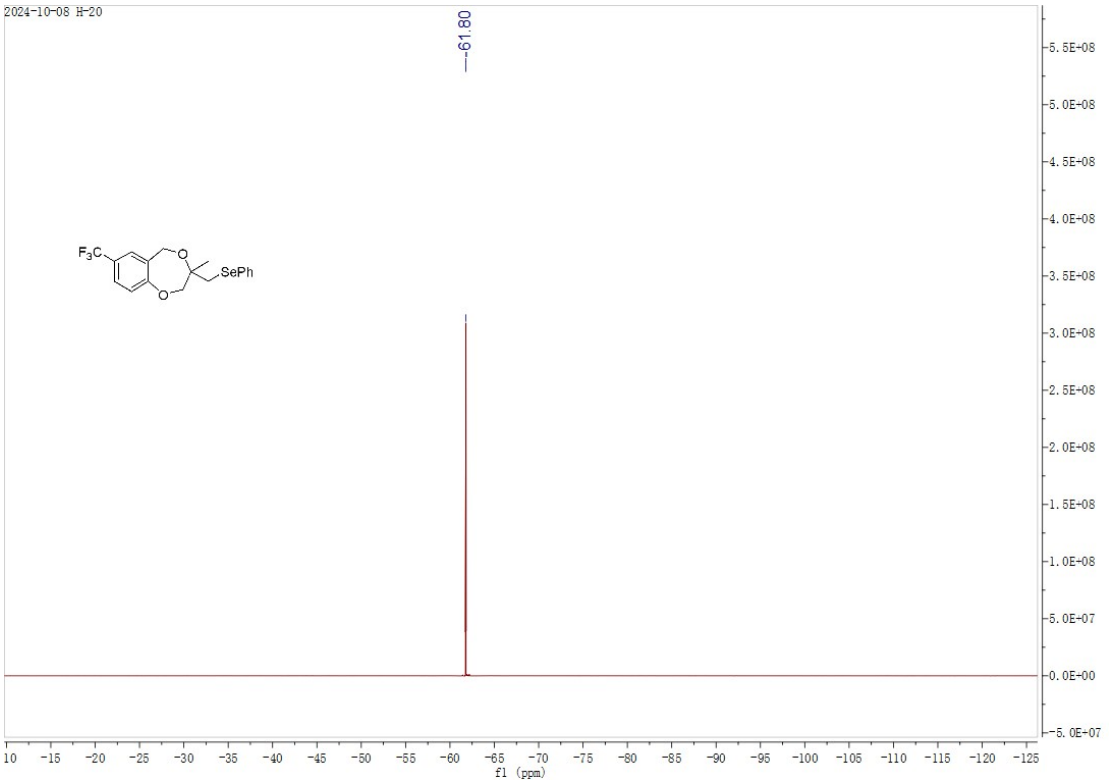




Compound 3ha ^{1}H NMR, ^{13}C NMR and ^{19}F NMR






2024-10-08 H-20
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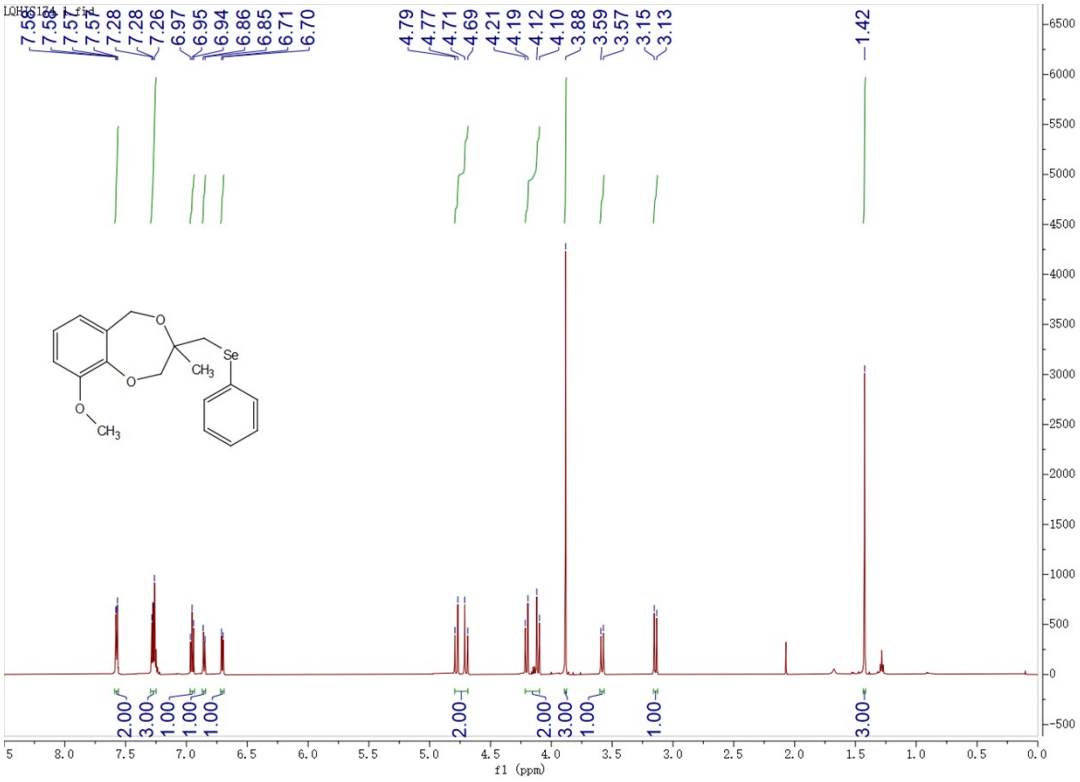
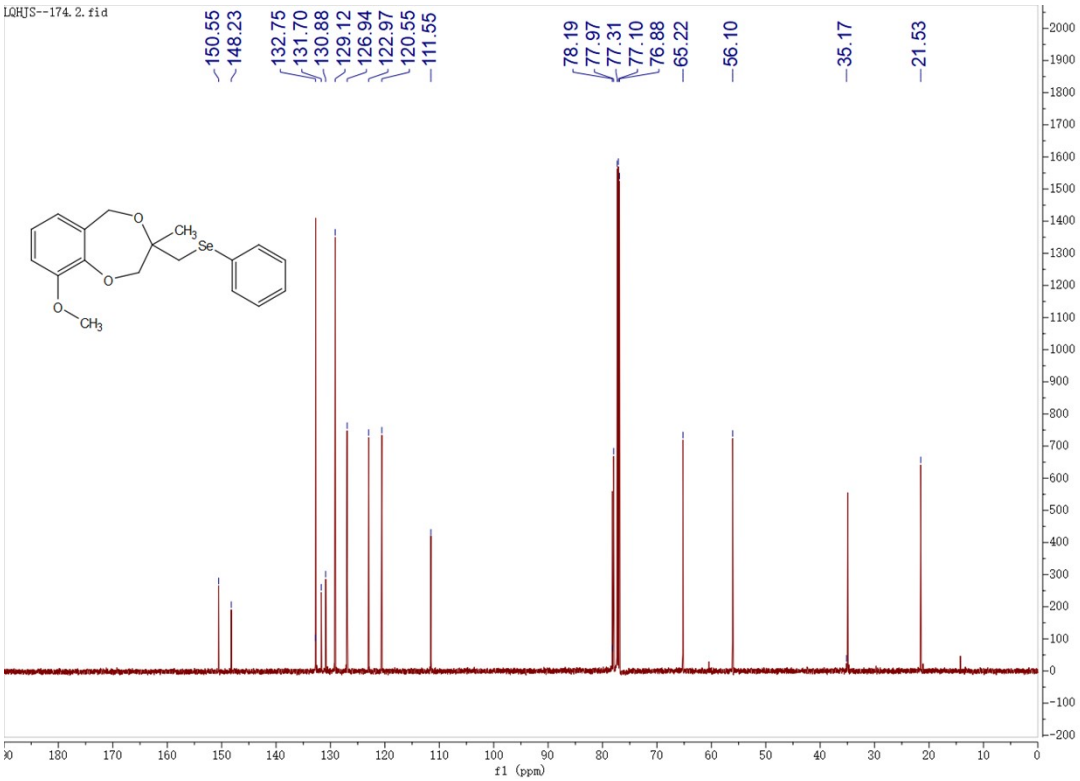
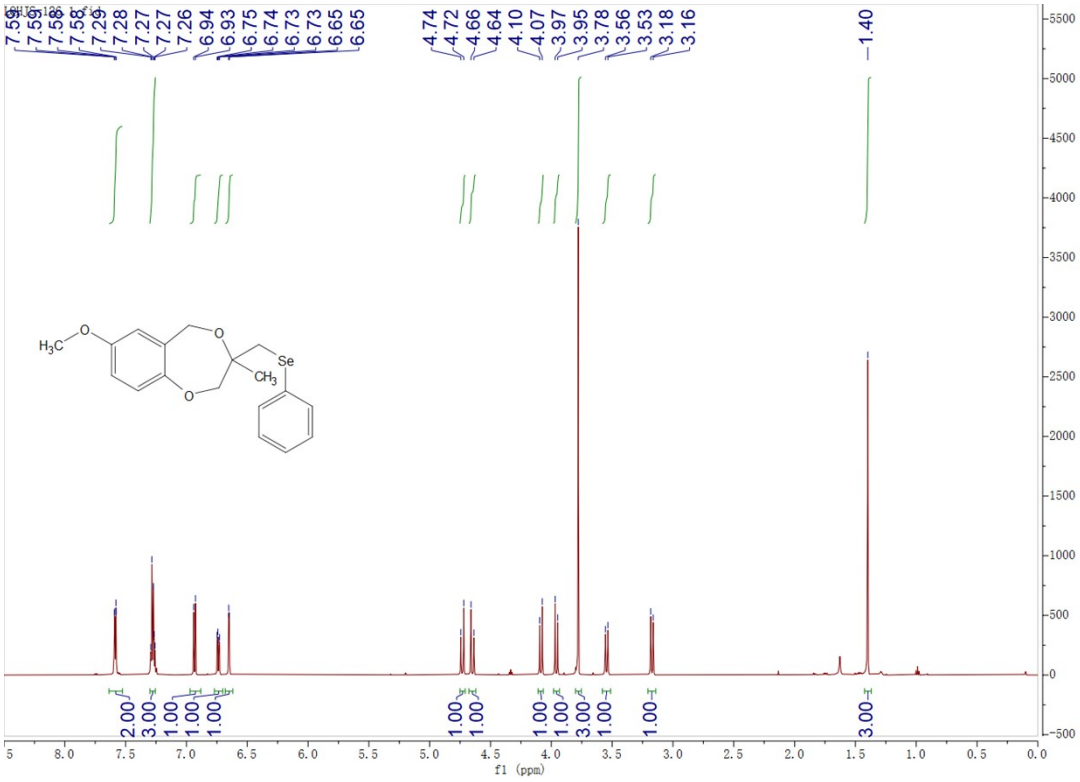
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
f1 (ppm)

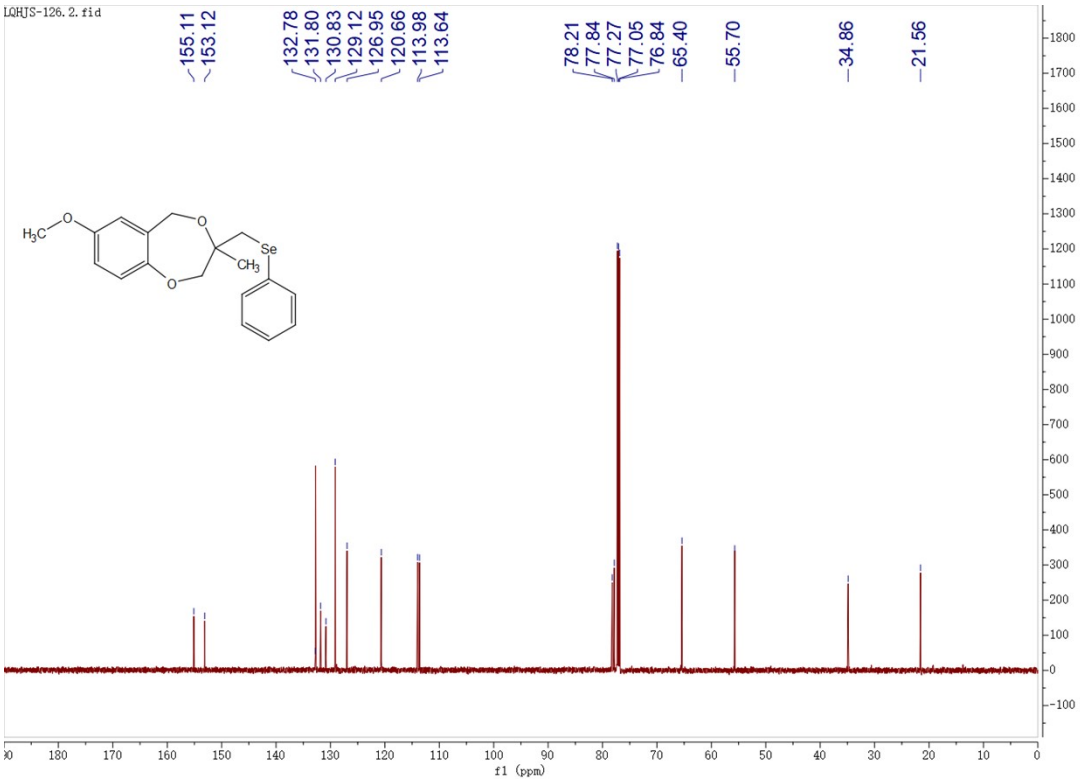
Compound 3ia ^{1}H NMR and ^{13}C NMR



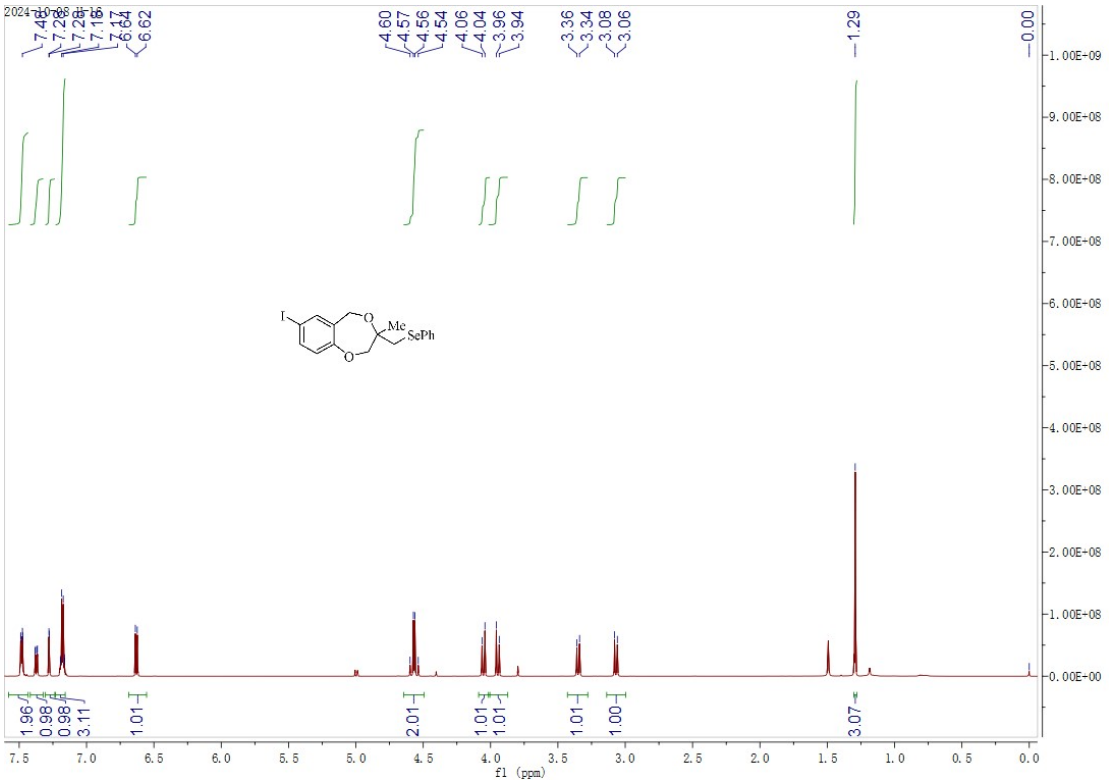


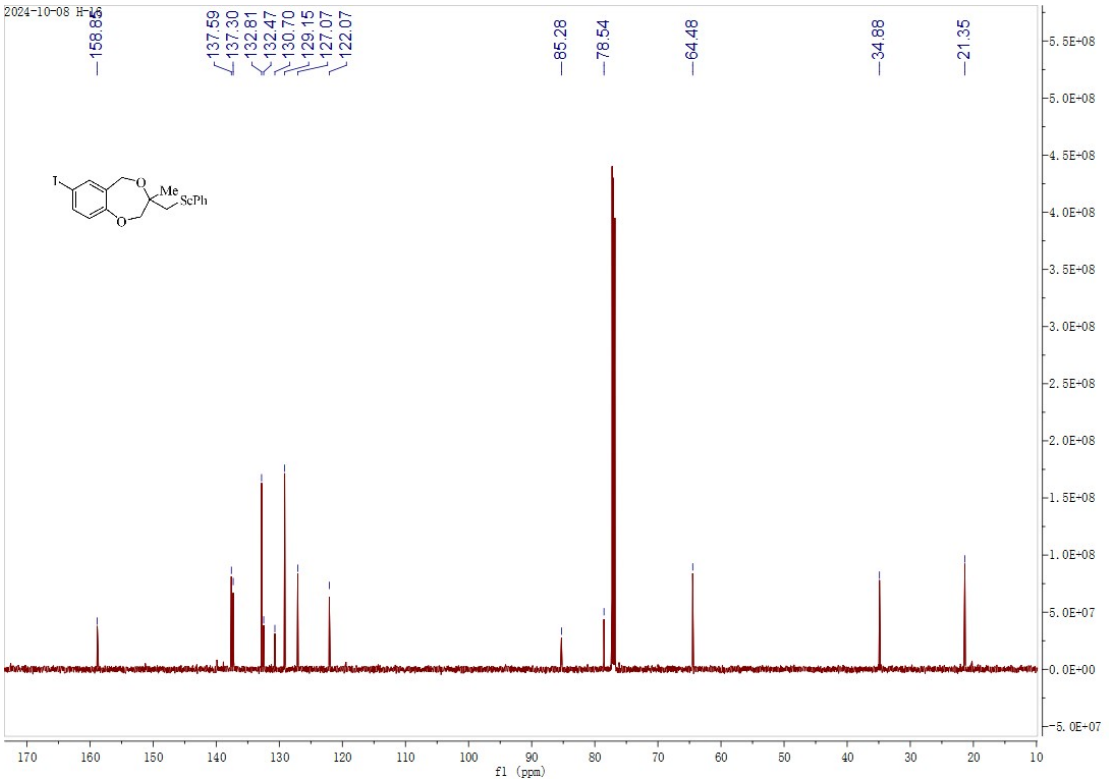
Compound 3ja ^{1}H NMR and ^{13}C NMR



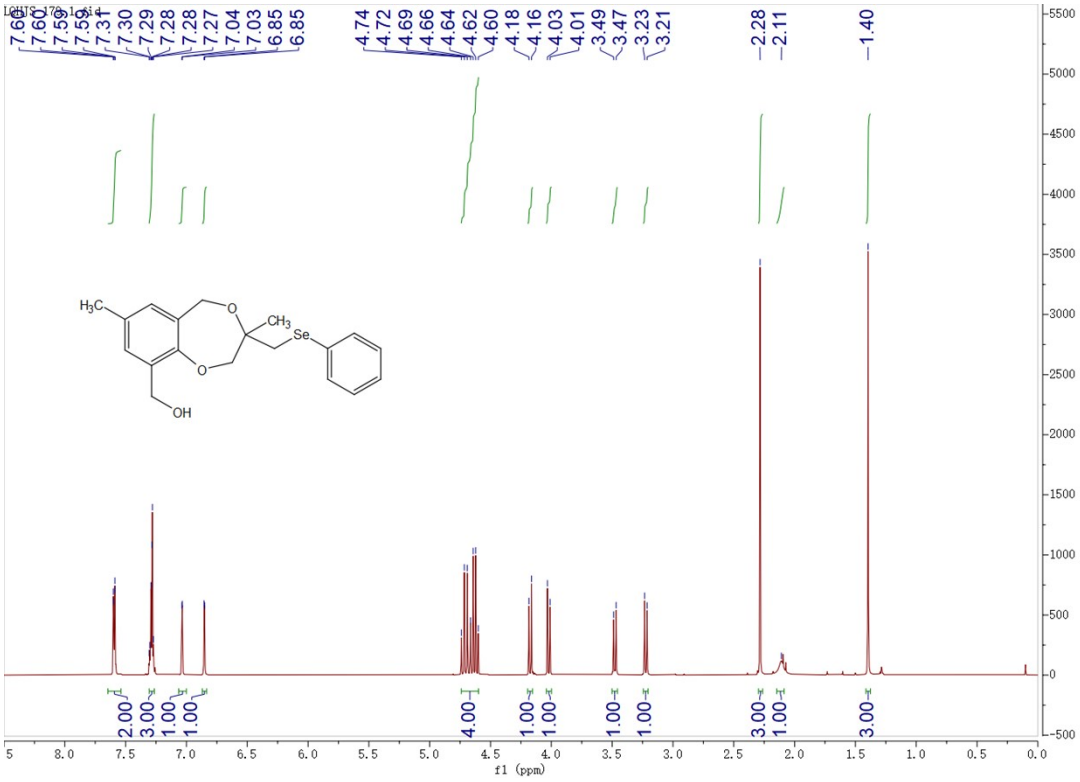


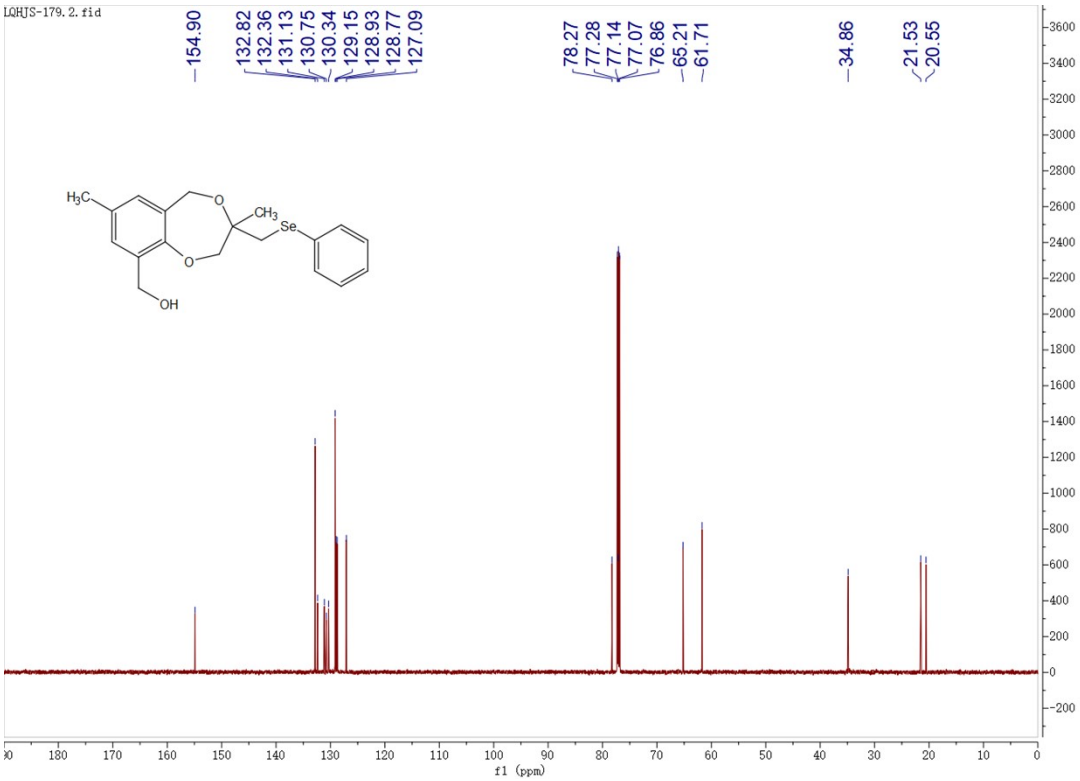
Compound 3ka ^{1}H NMR and ^{13}C NMR



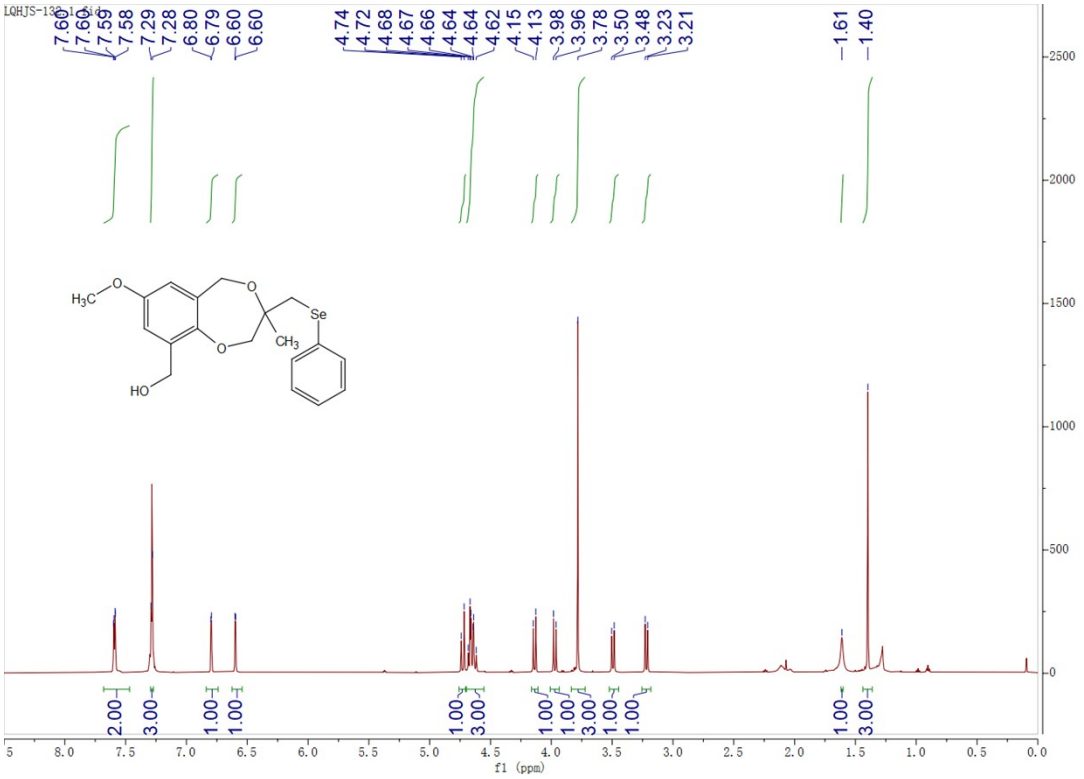


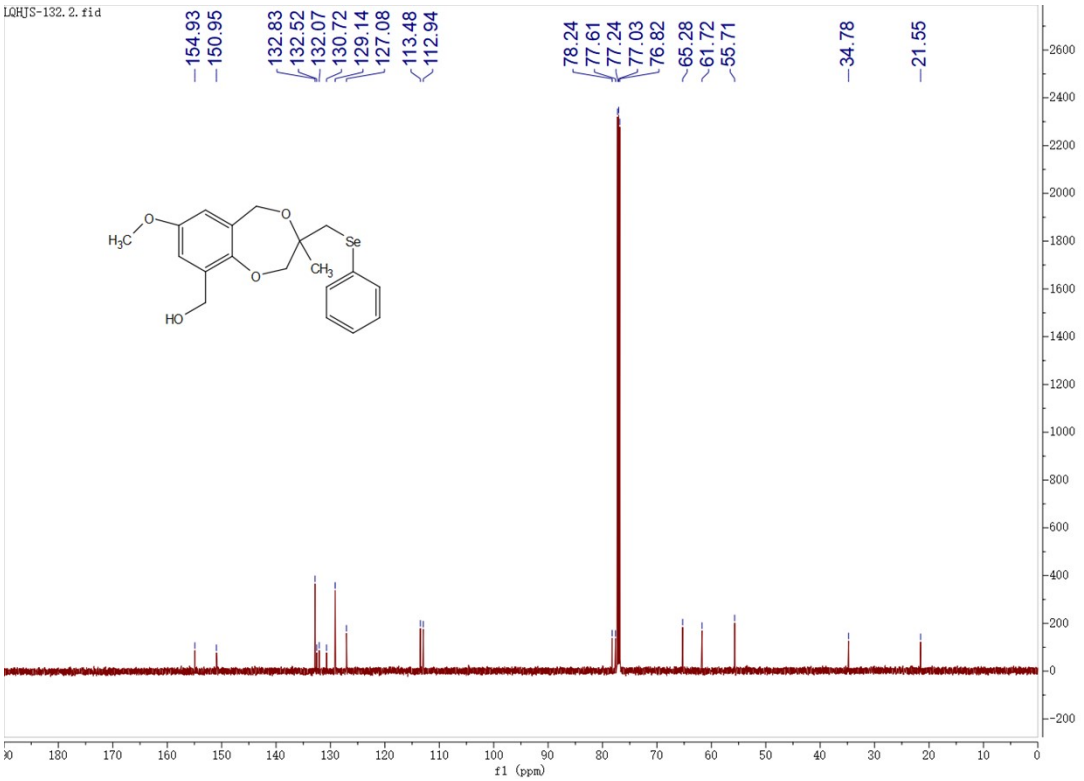
Compound 3la ^{1}H NMR and ^{13}C NMR



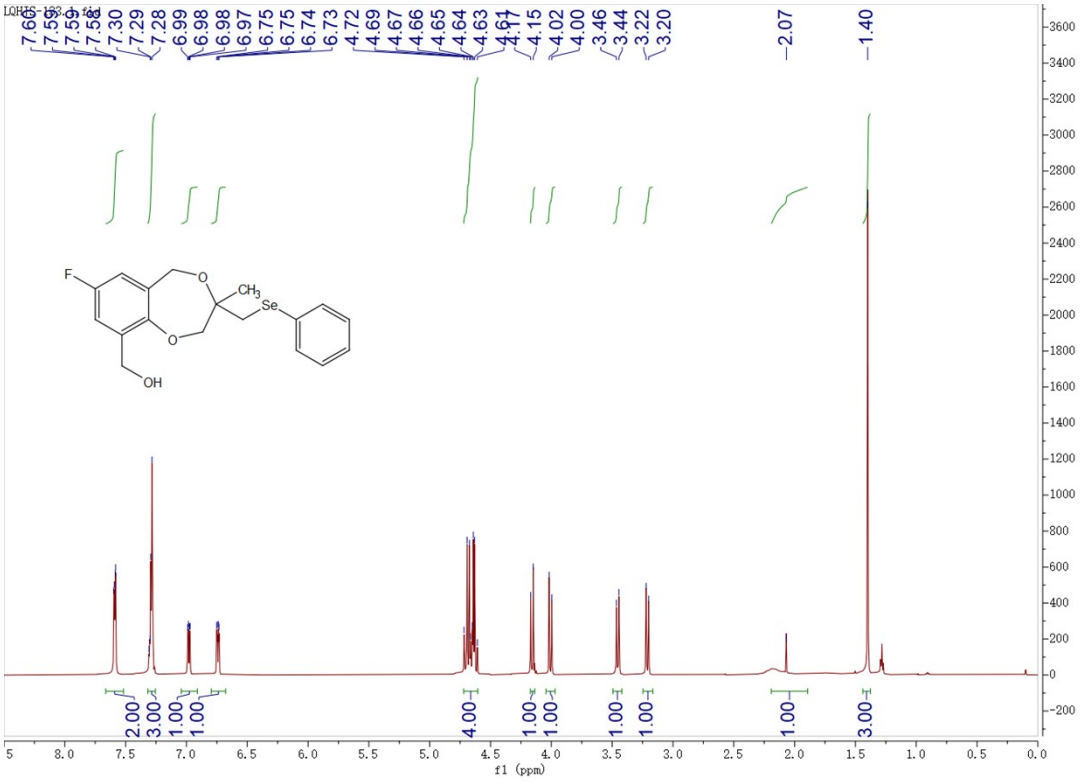


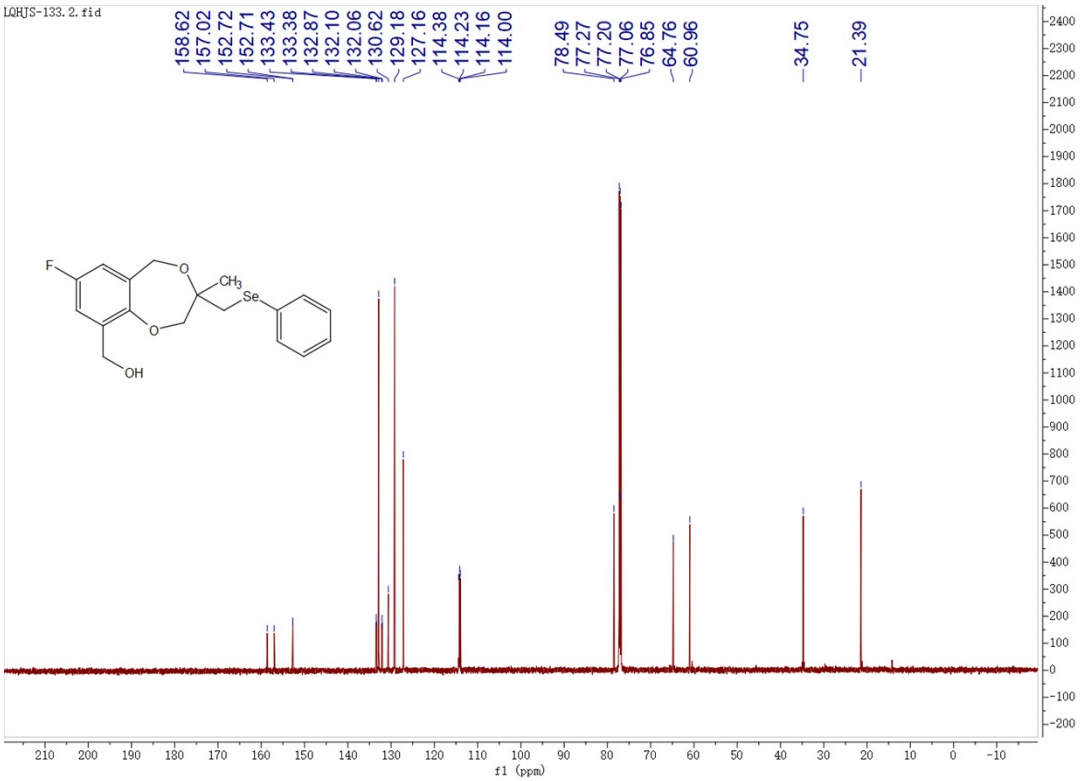
Compound 3ma ^{1}H NMR and ^{13}C NMR



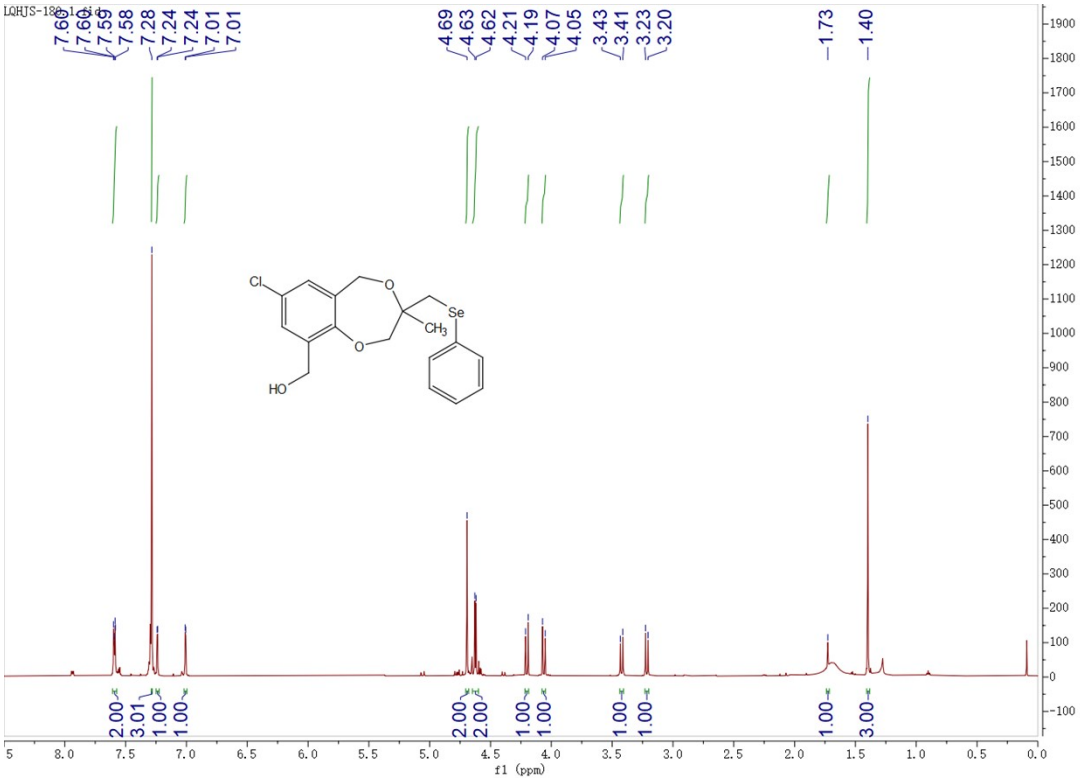


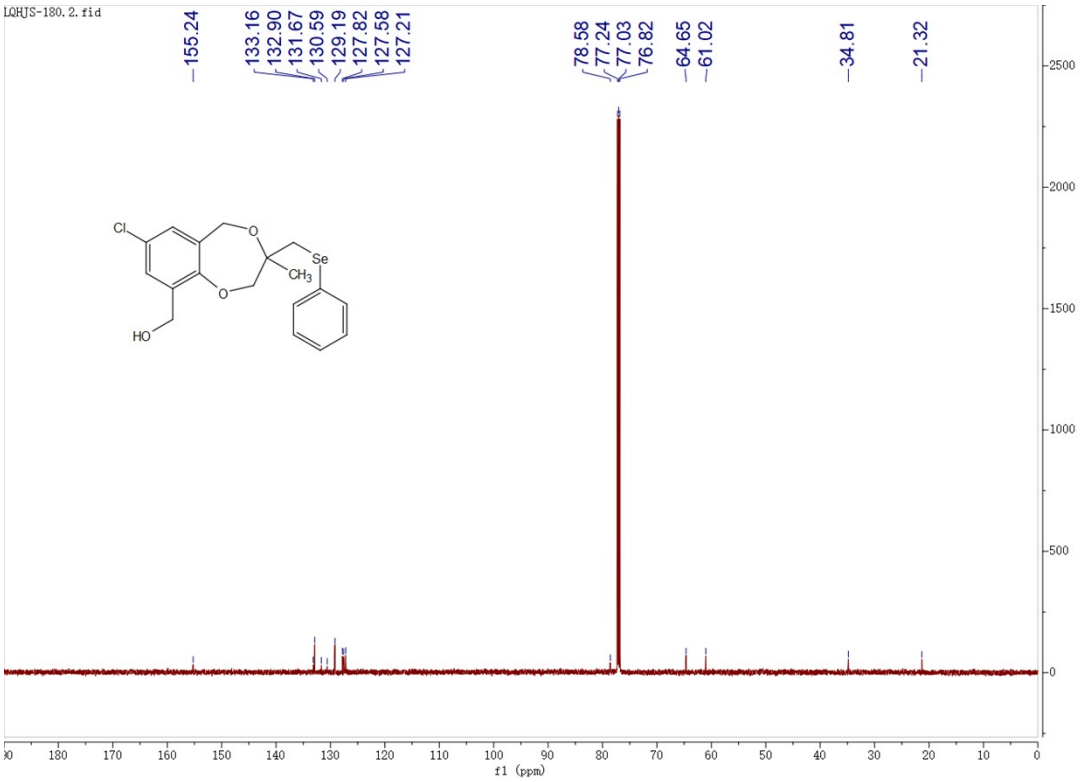
Compound 3na ^{1}H NMR and ^{13}C NMR



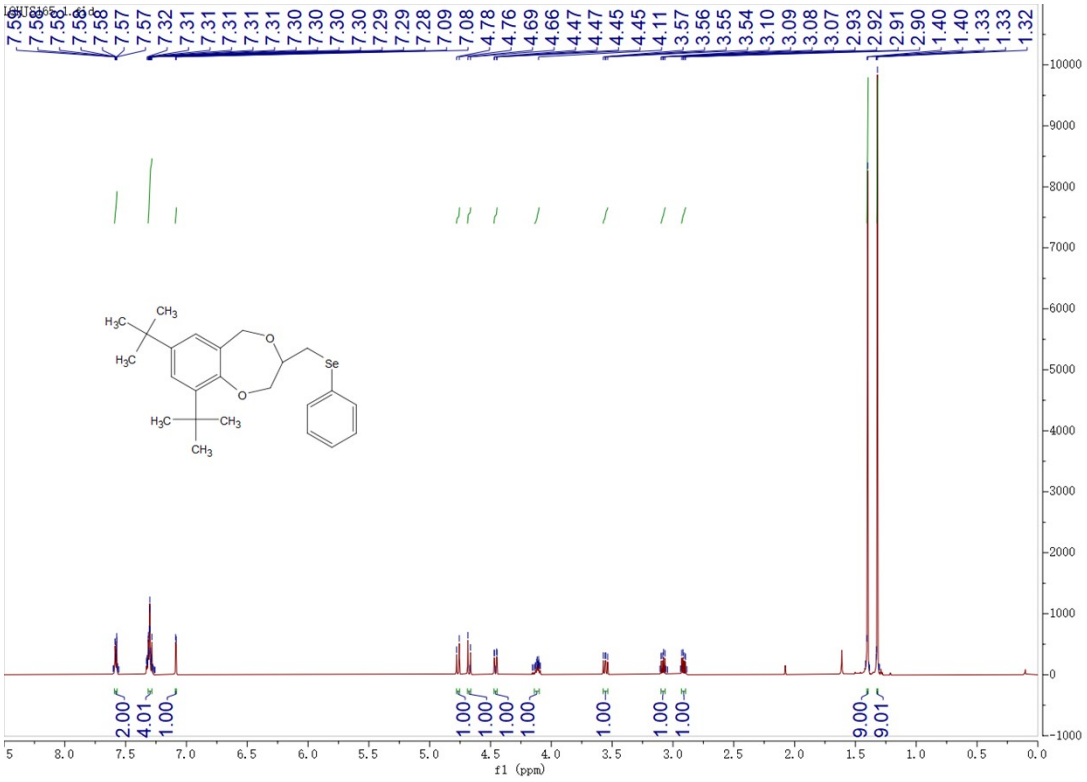


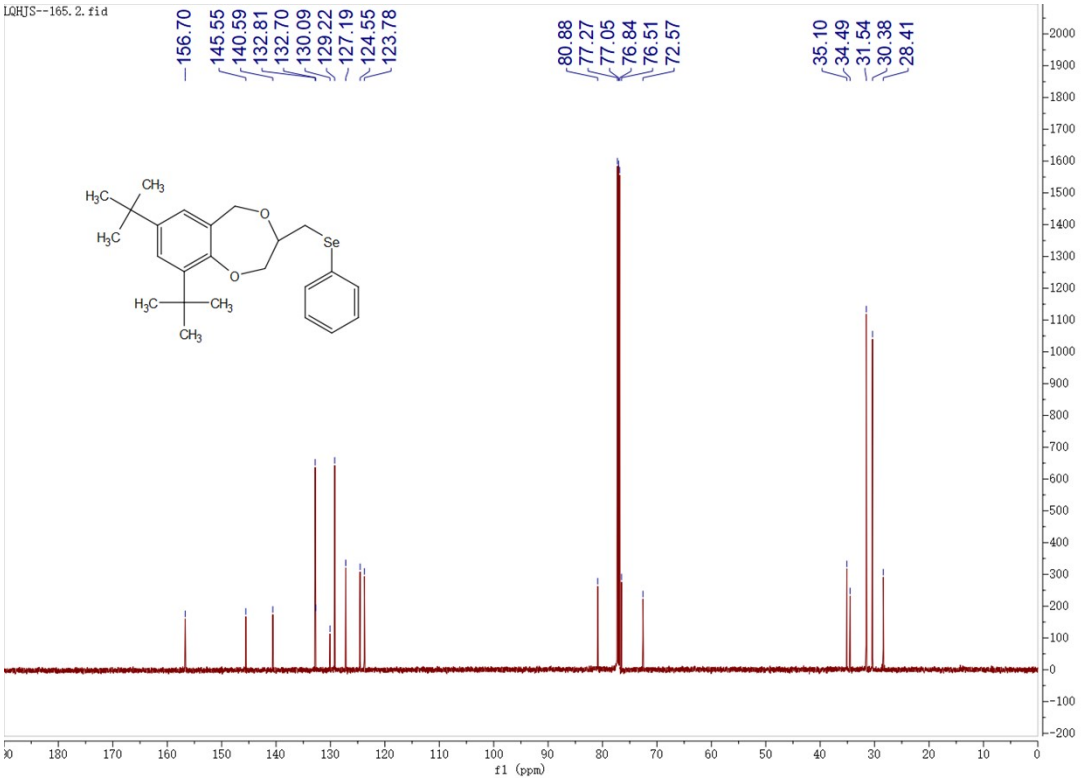
Compound 3oa ^{1}H NMR and ^{13}C NMR



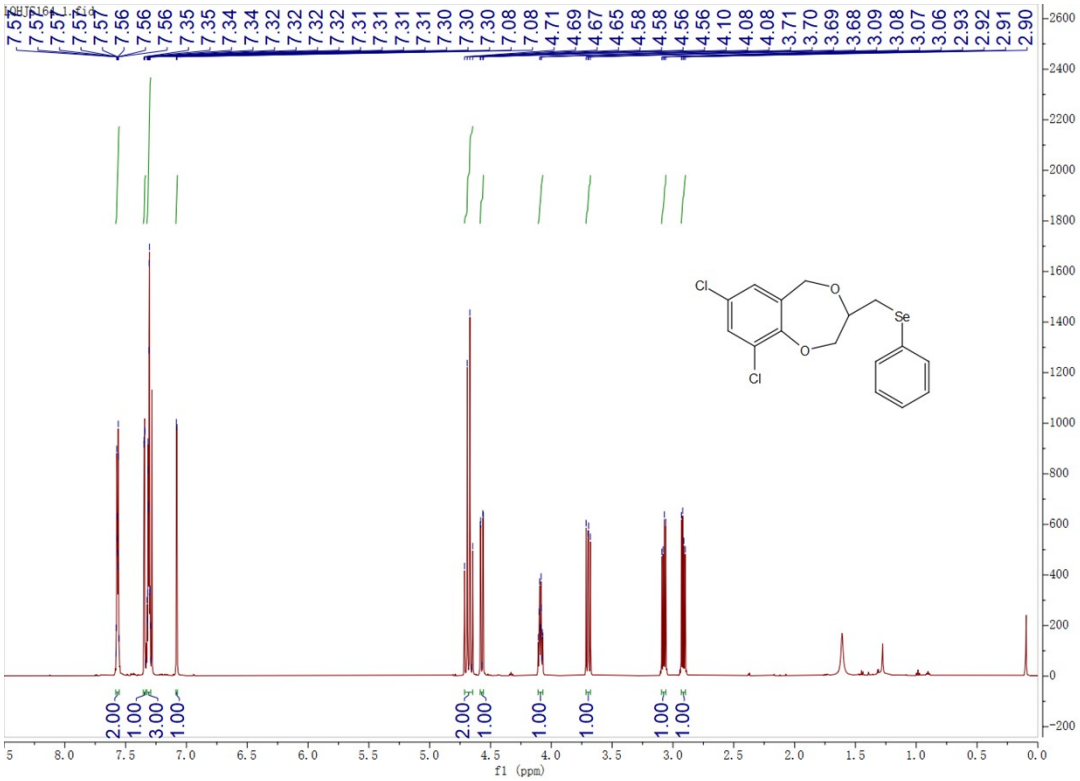


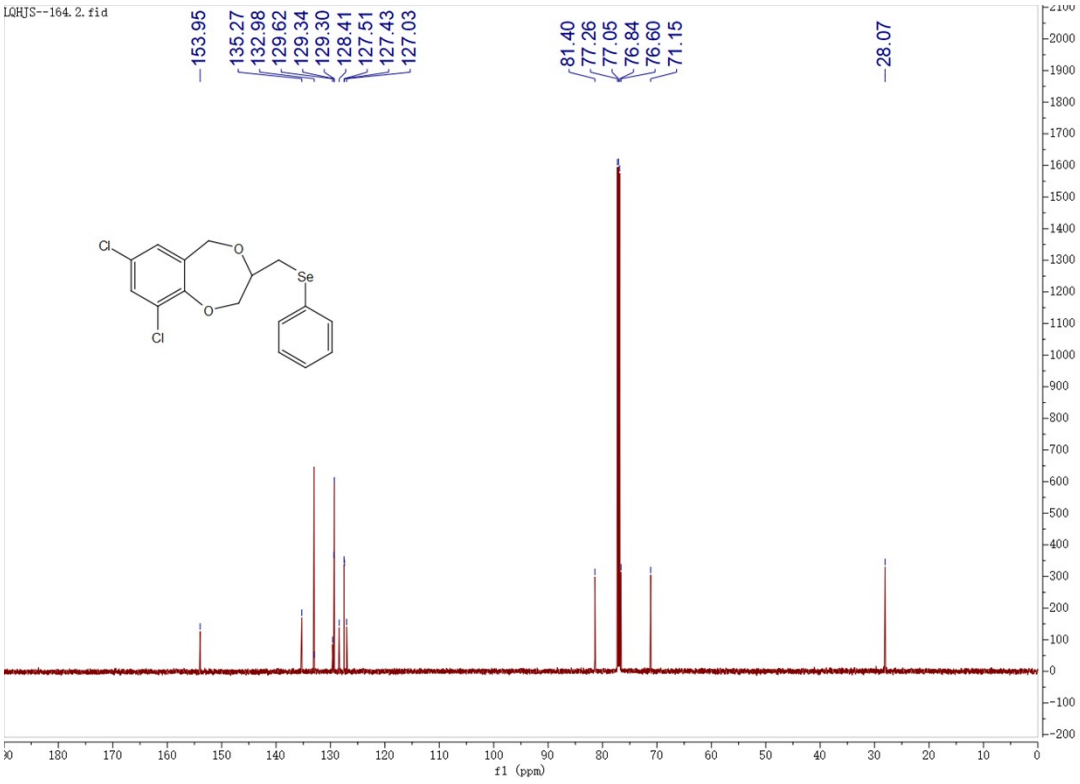
Compound 3pa ^{1}H NMR and ^{13}C NMR



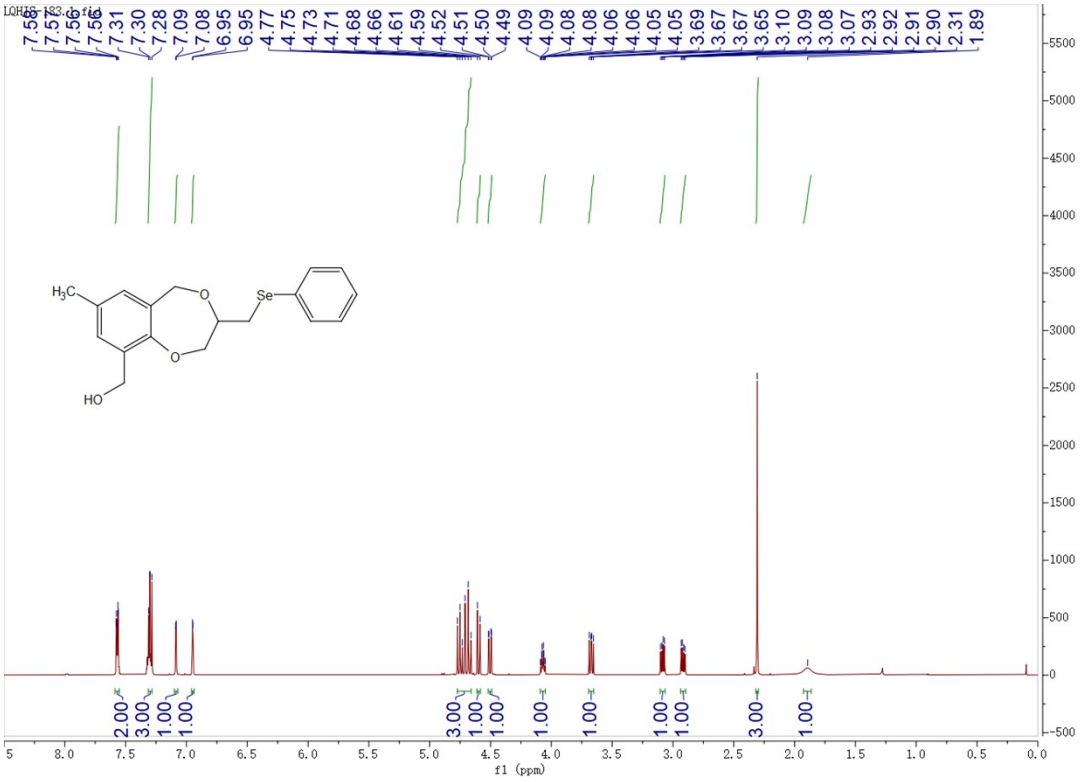


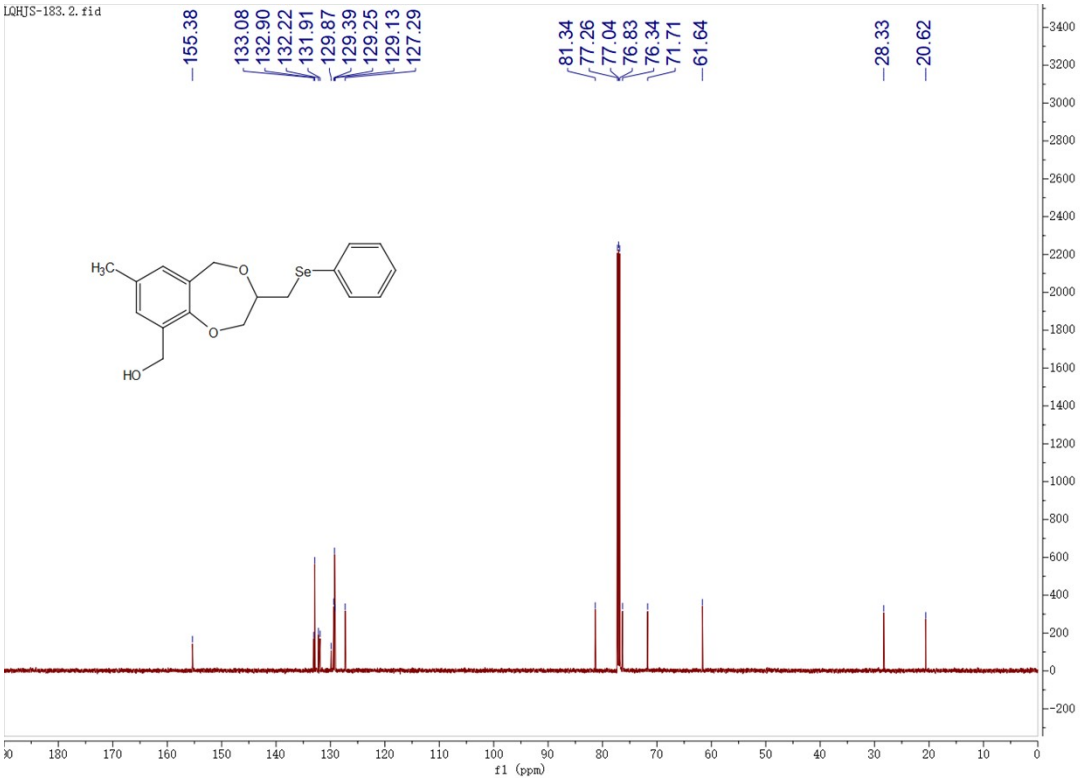
Compound 3qa ^{1}H NMR and ^{13}C NMR



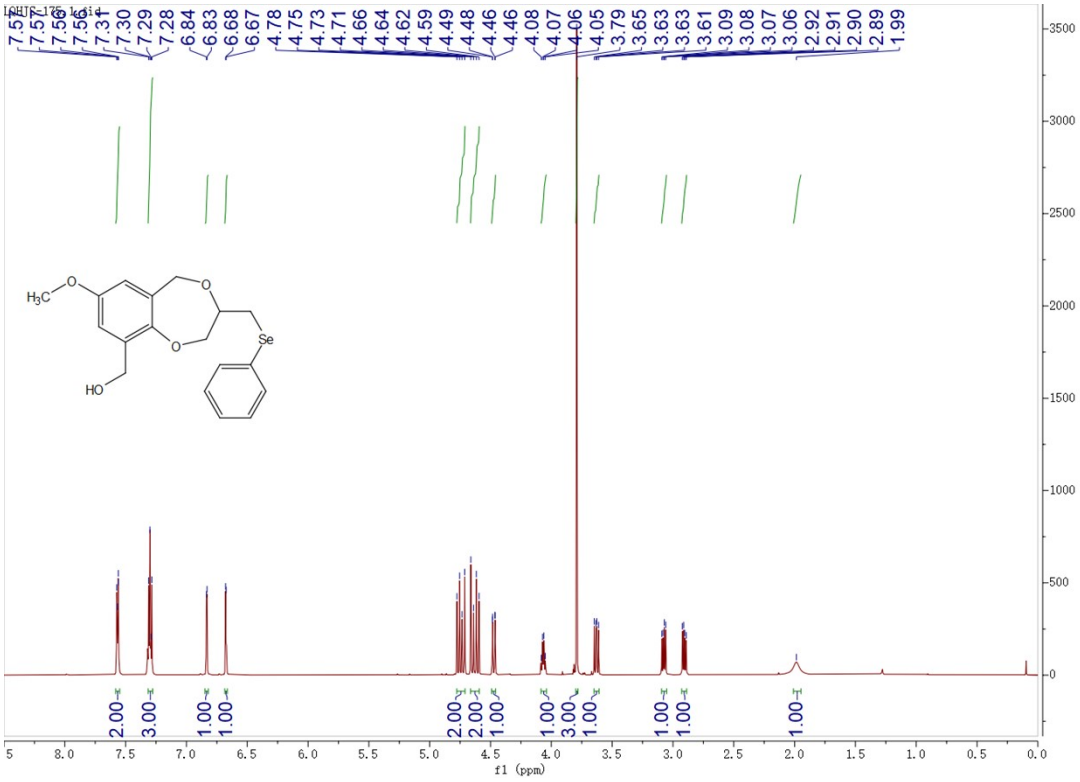


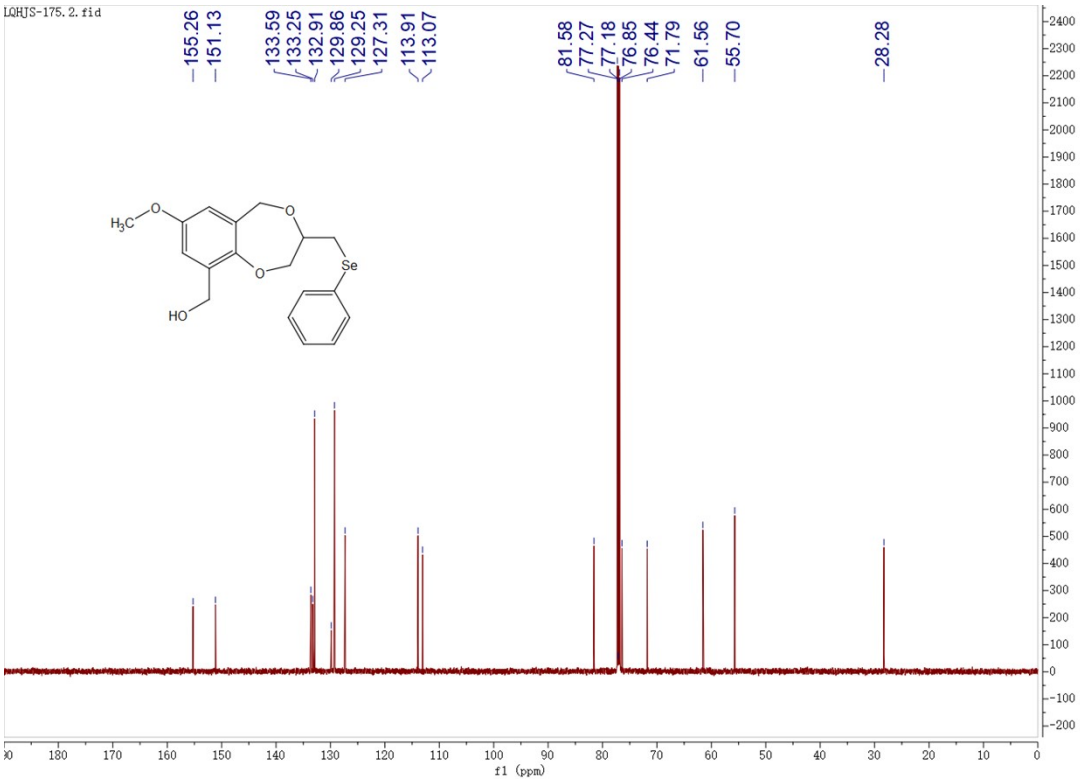
Compound 3ra ^{1}H NMR and ^{13}C NMR



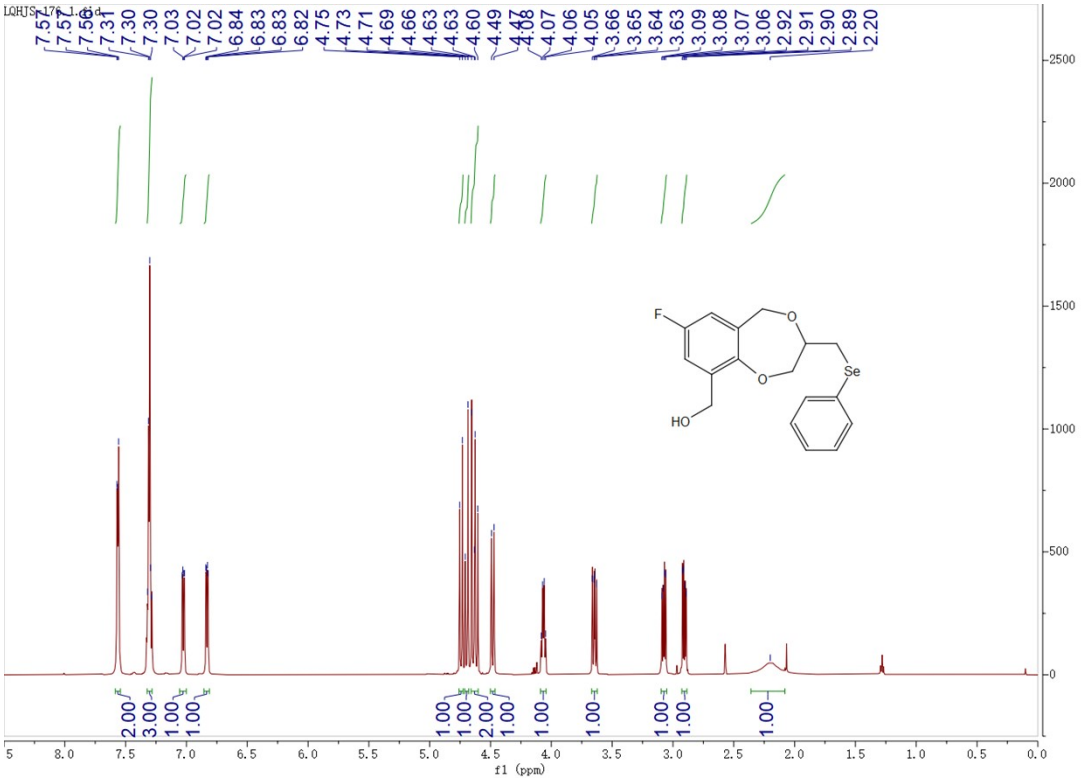


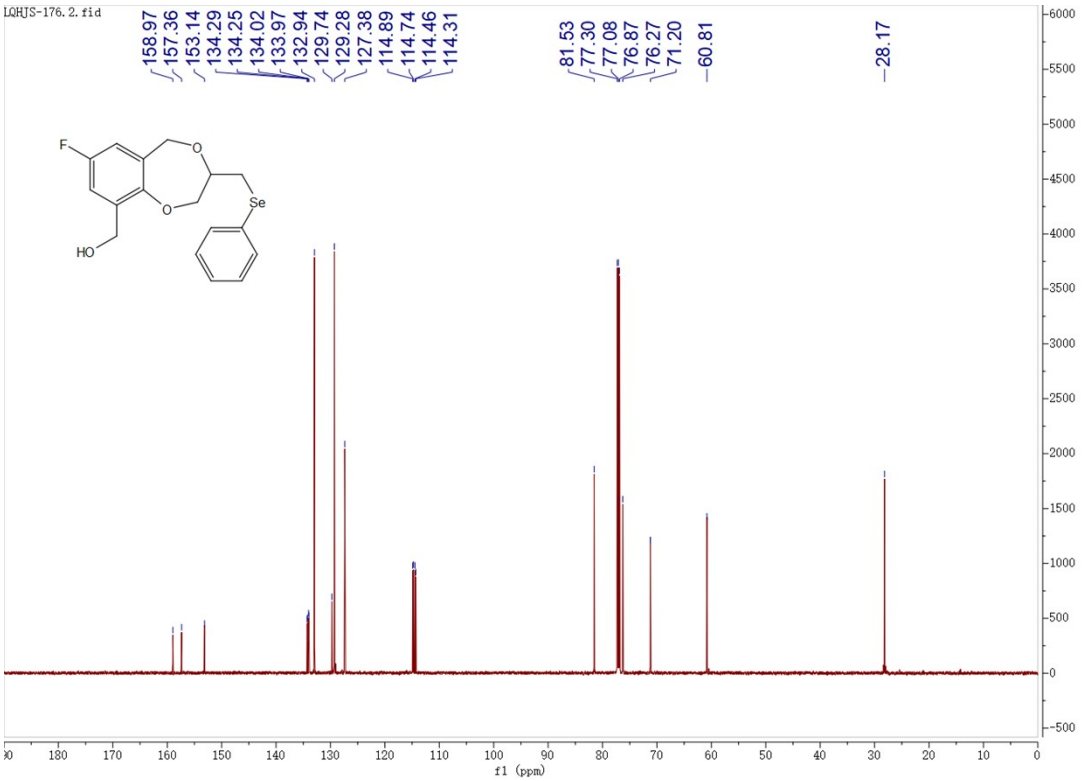
Compound 3sa ^{1}H NMR and ^{13}C NMR

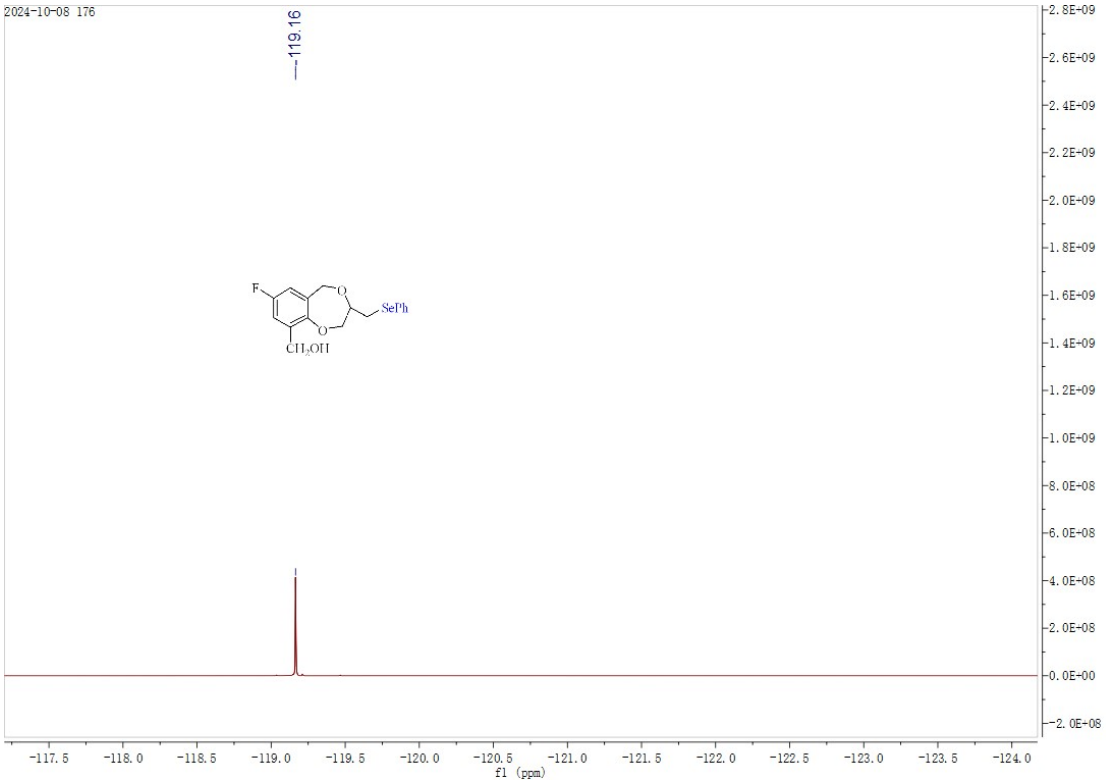




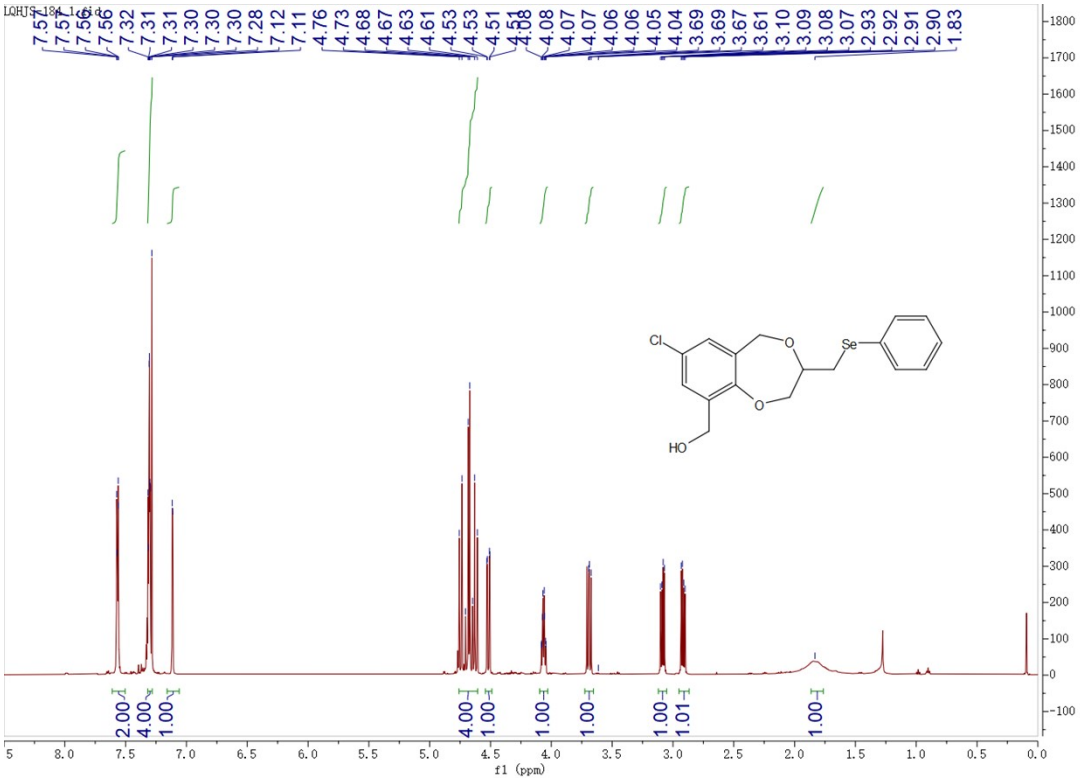
Compound 3ta ^{1}H NMR, ^{13}C NMR and ^{19}F NMR

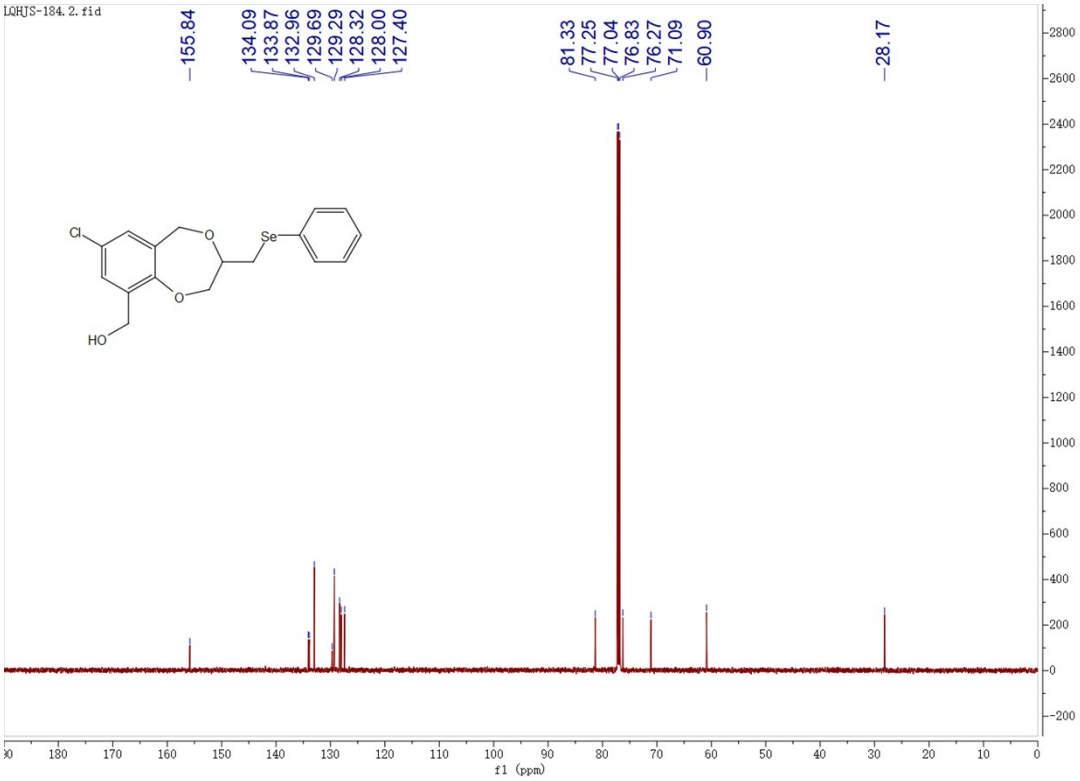




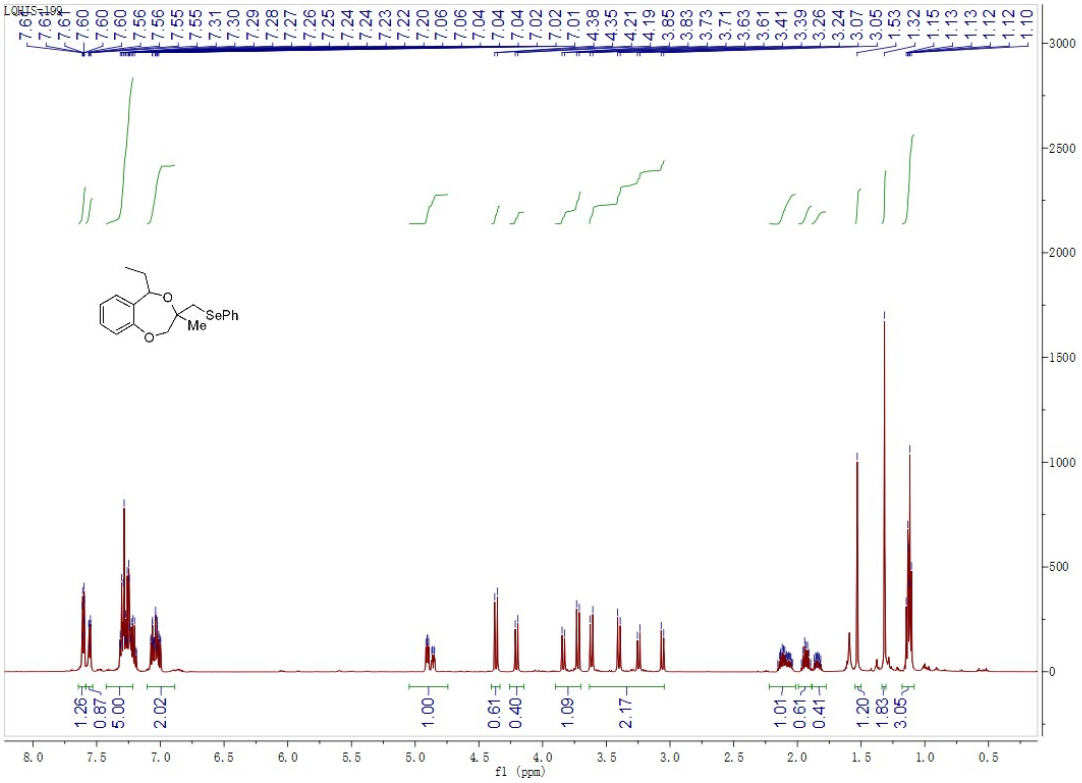

2024-10-08 176
-119.16
F
SePh
CH2OH
2.8E-09
2.6E-09
2.4E-09
2.2E-09
2.0E-09
1.8E-09
1.6E-09
1.4E-09
1.2E-09
1.0E-09
8.0E-08
6.0E-08
4.0E-08
2.0E-08
0.0E-00
-2.0E-08
-117.5
-118.0
-118.5
-119.0
-119.5
-120.0
-120.5
-121.0
-121.5
-122.0
-122.5
-123.0
-123.5
-124.0
f1 (ppm)

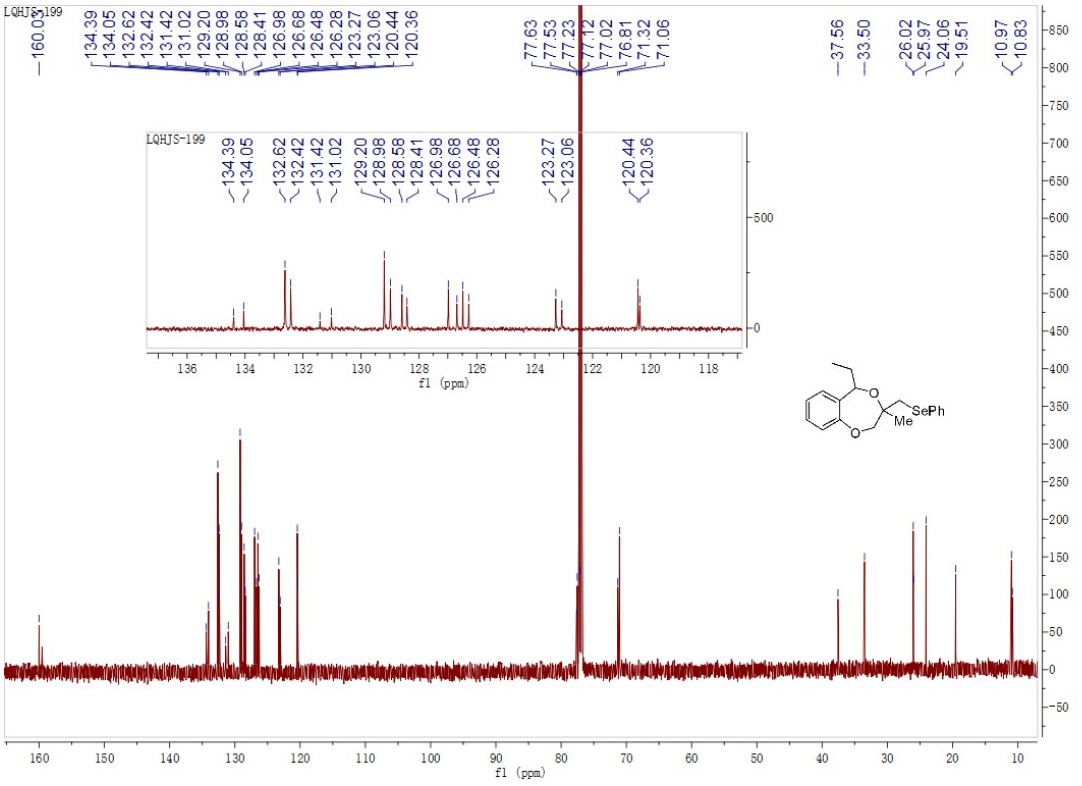
Compound 3ua ^{1}H NMR and ^{13}C NMR



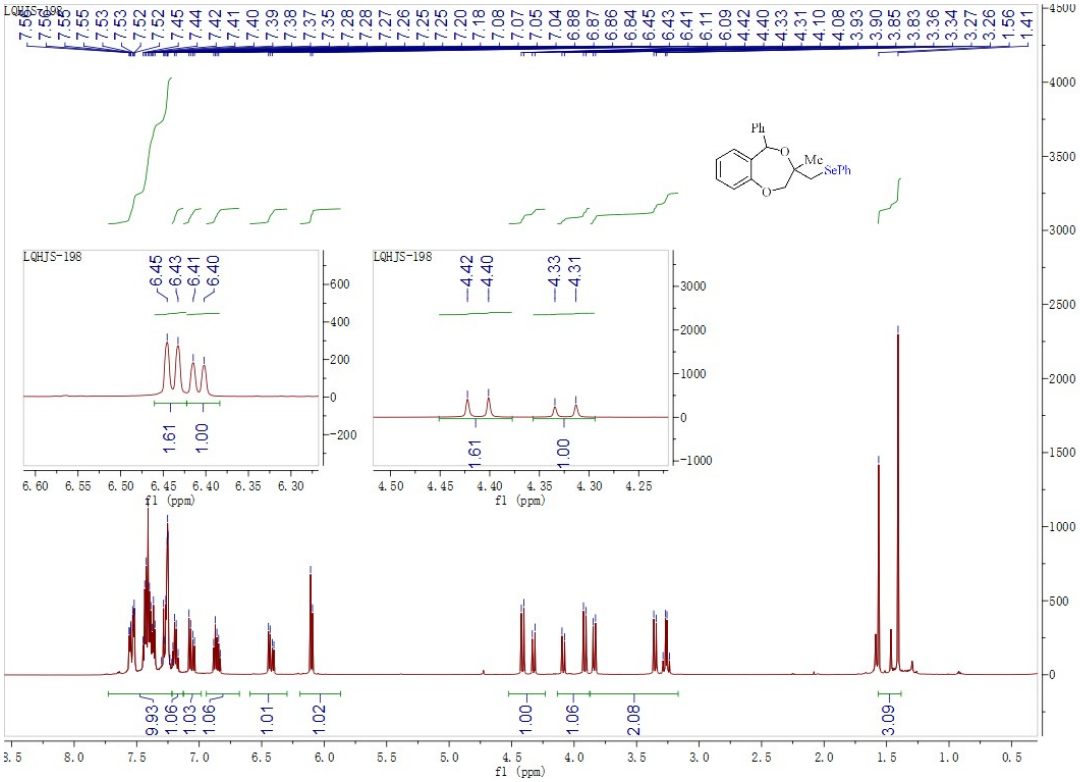


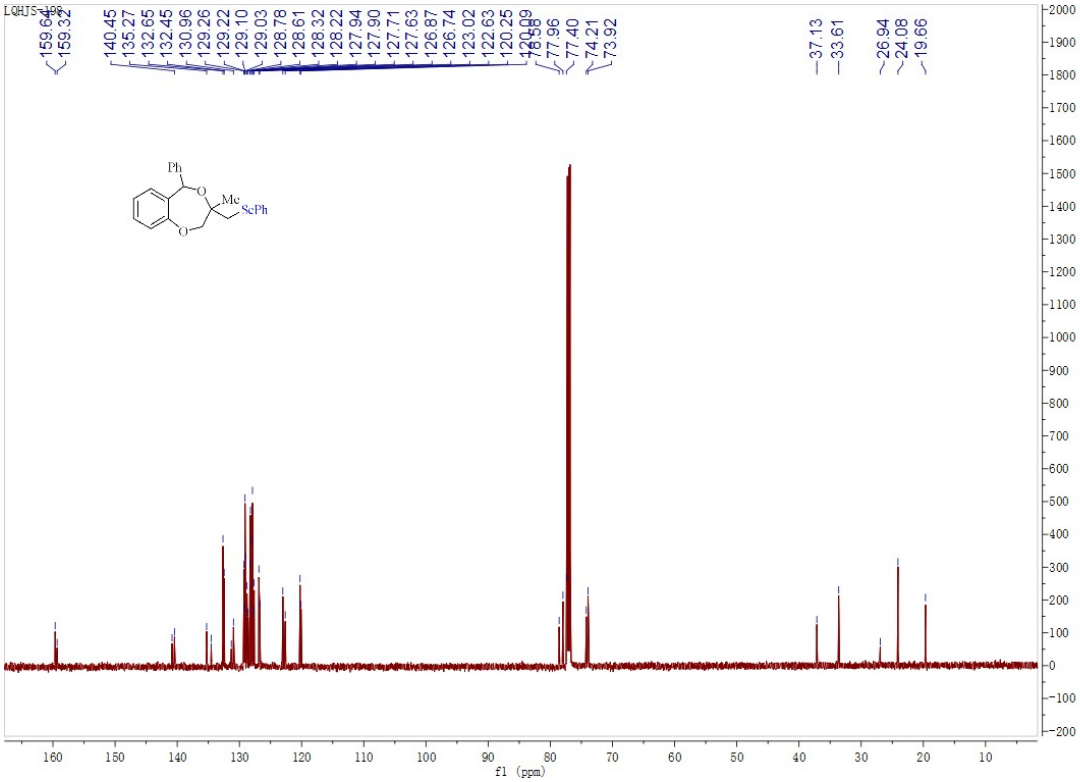
Compound 3va ^{1}H NMR and ^{13}C NMR



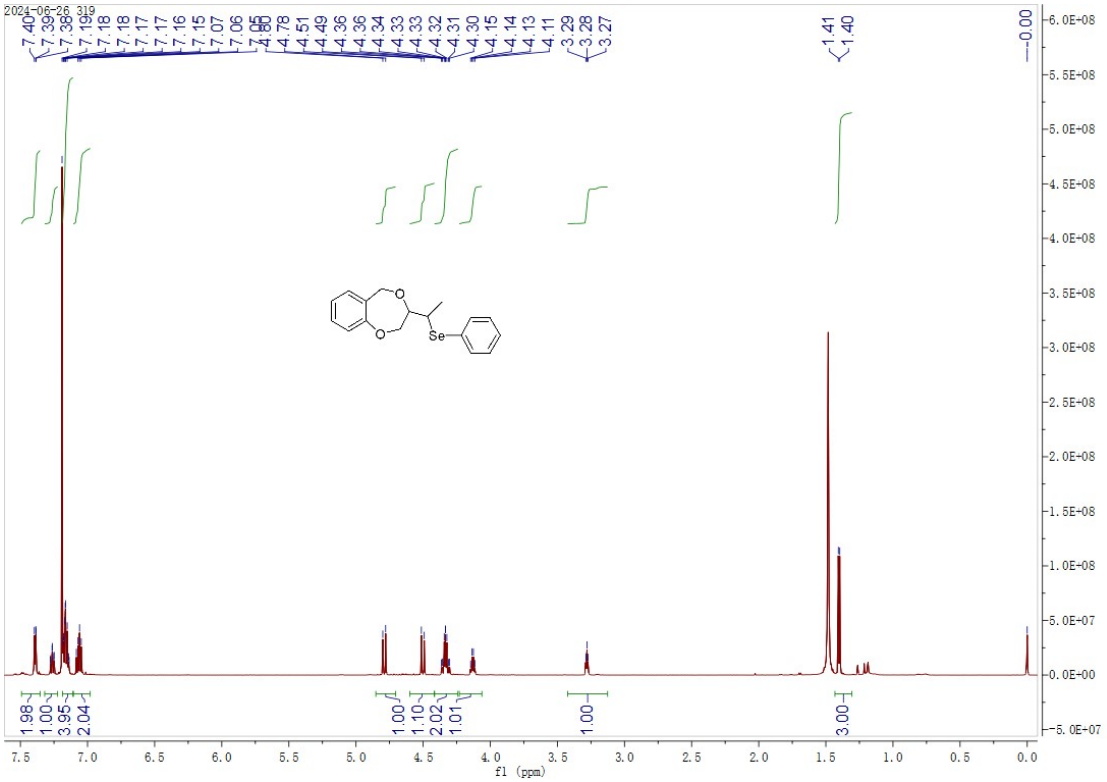


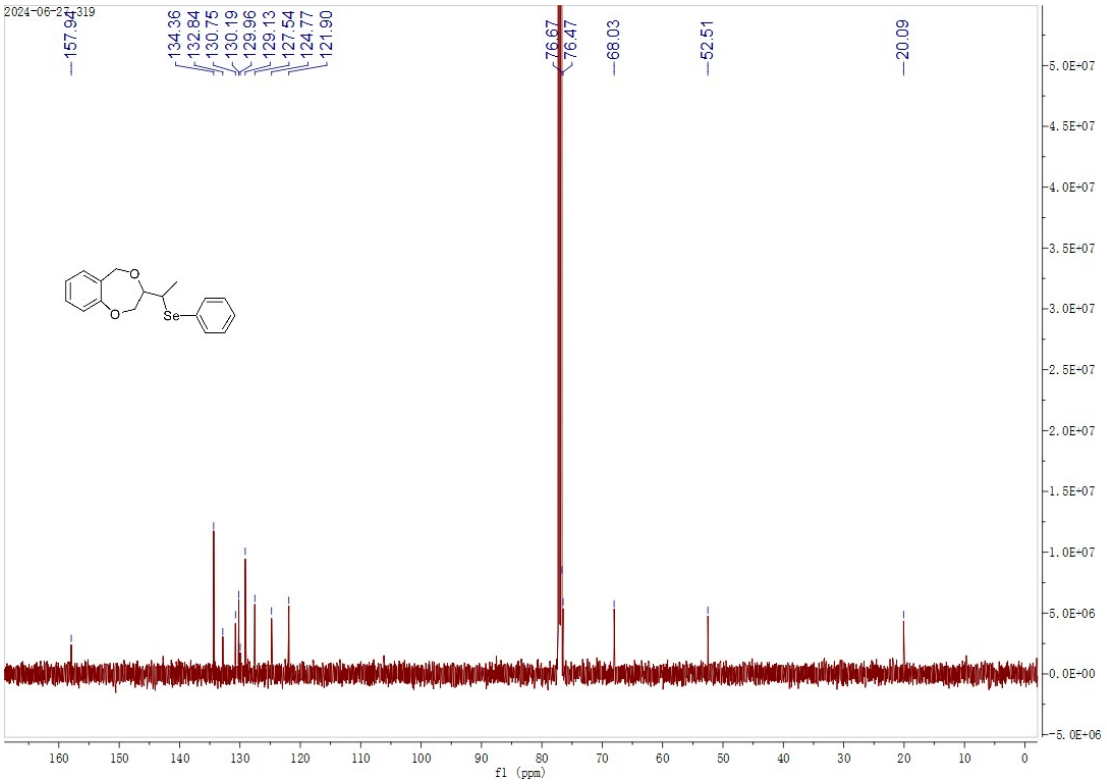
Compound 3wa ^{1}H NMR and ^{13}C NMR



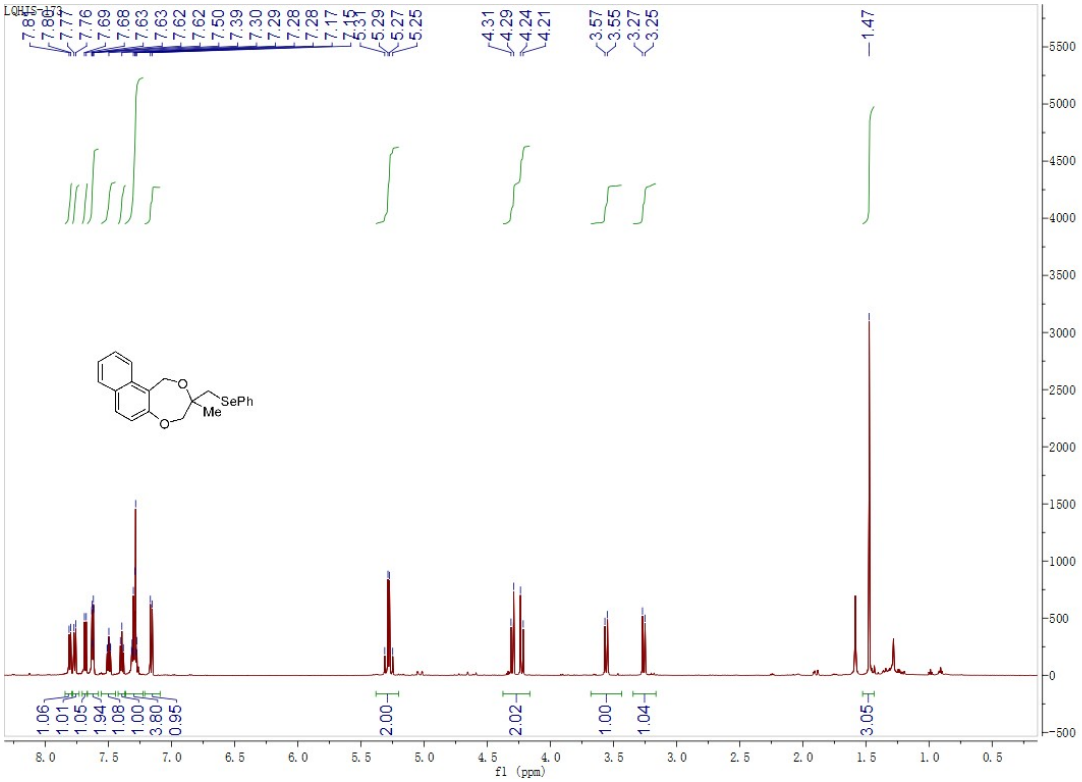


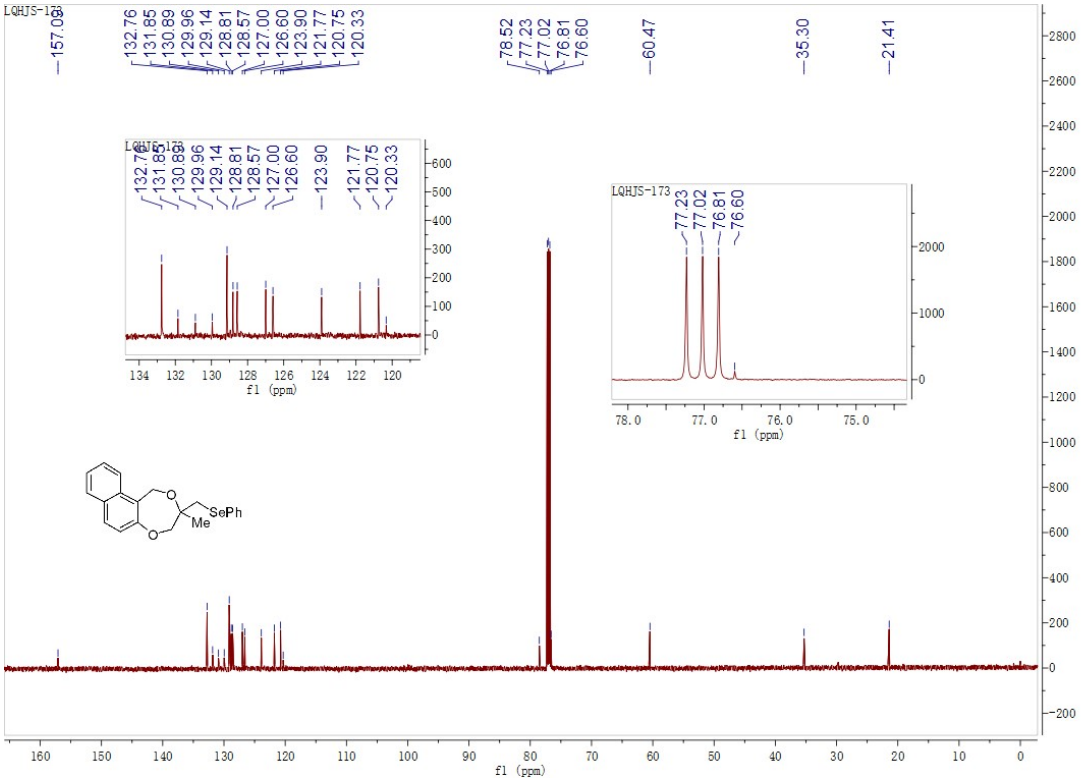
Compound 3xa ^{1}H NMR and ^{13}C NMR



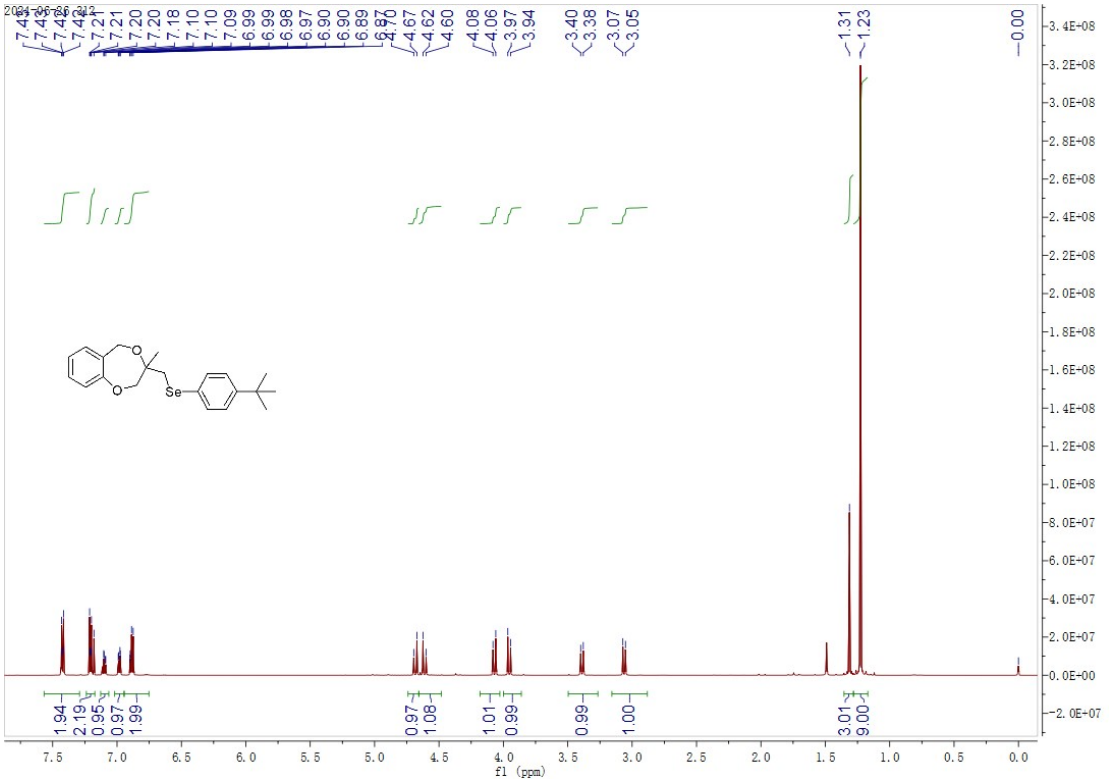


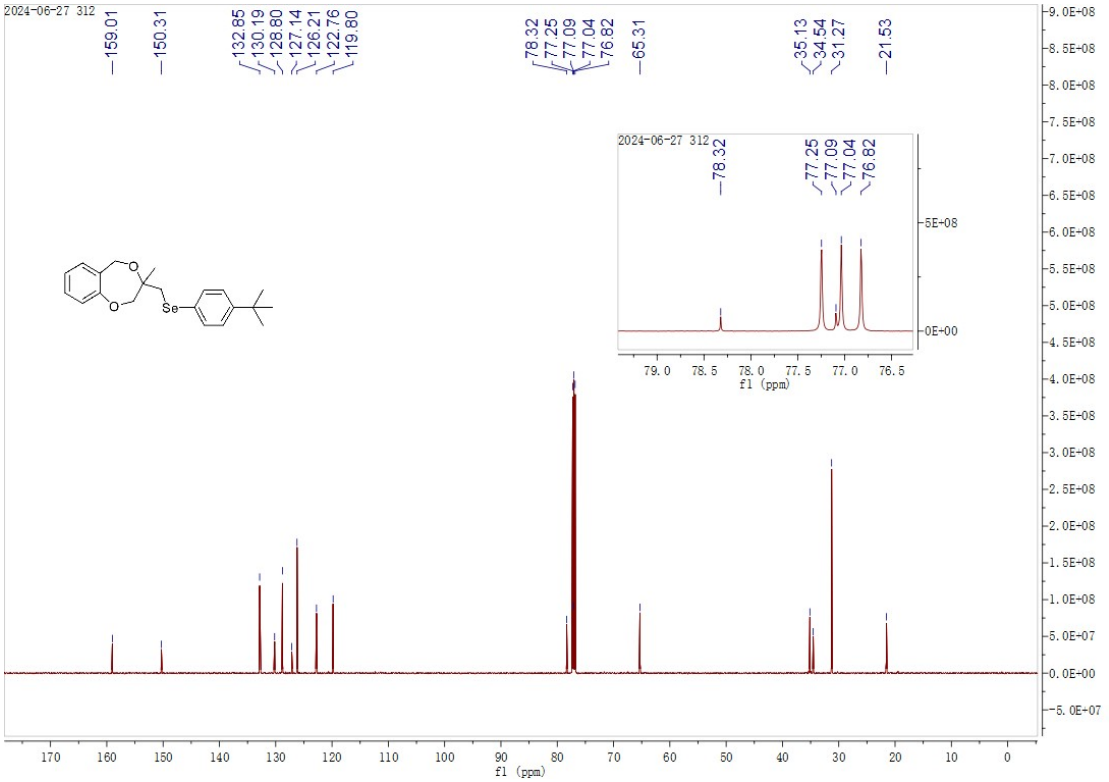
Compound 3ya ^{1}H NMR and ^{13}C NMR



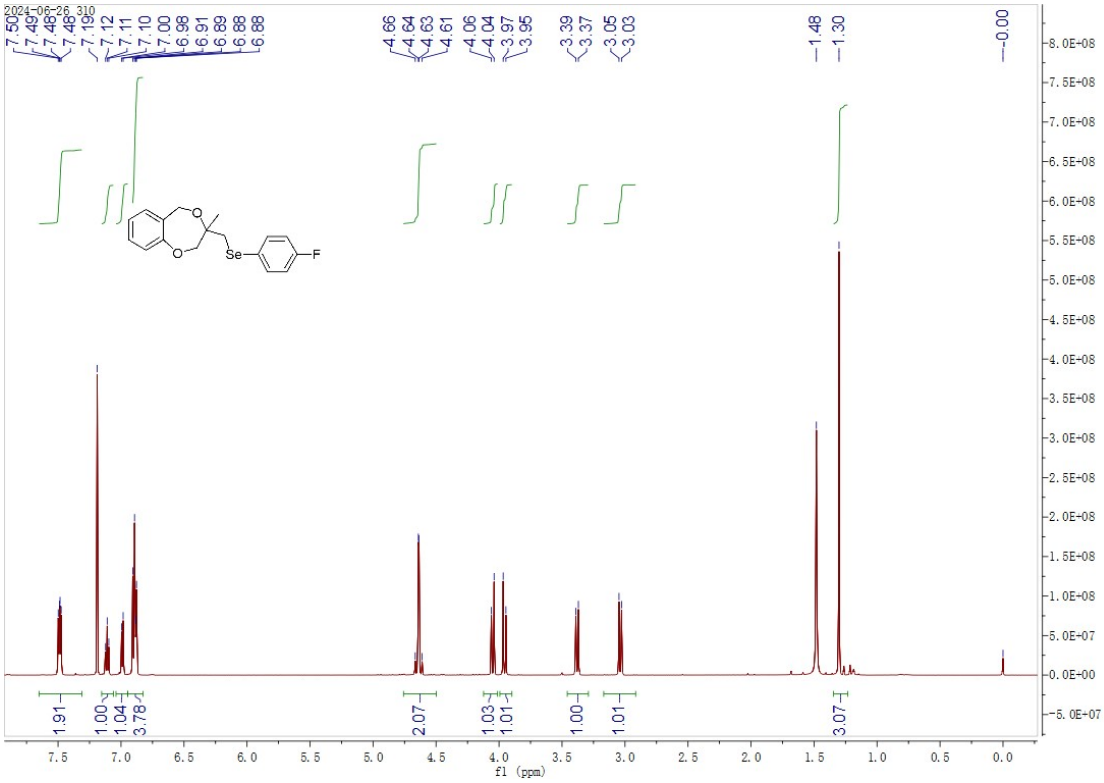


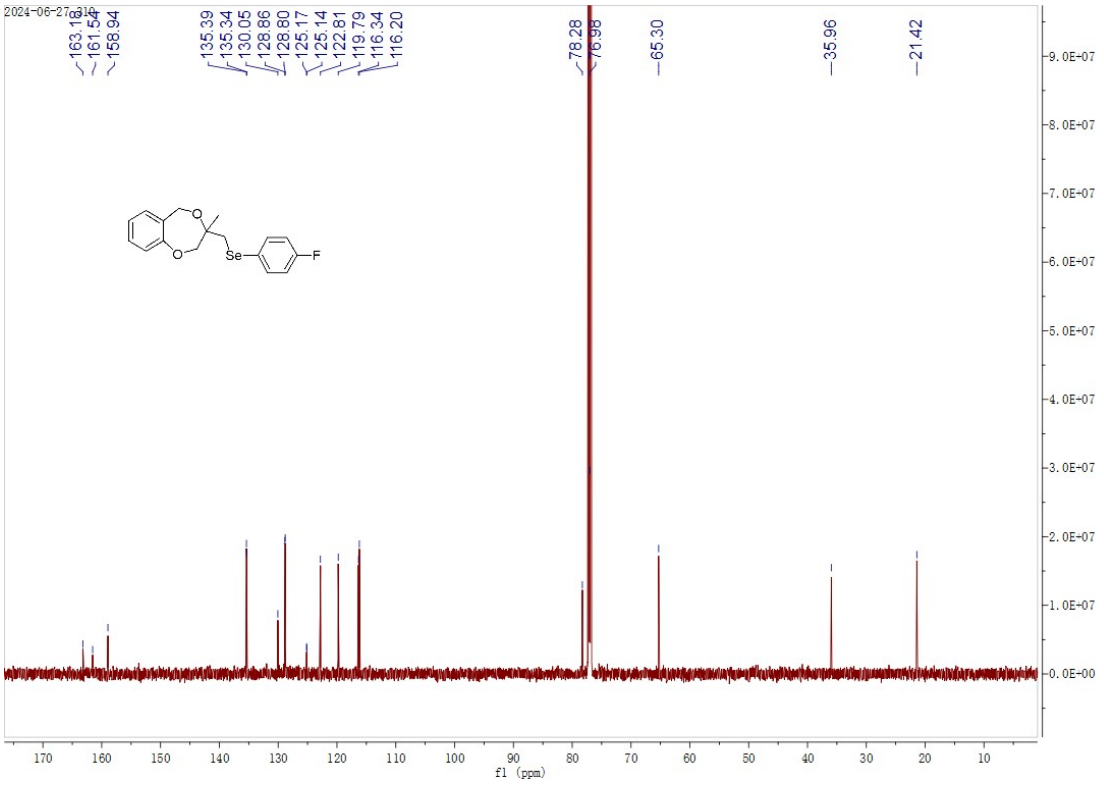
Compound 3ab ^{1}H NMR and ^{13}C NMR

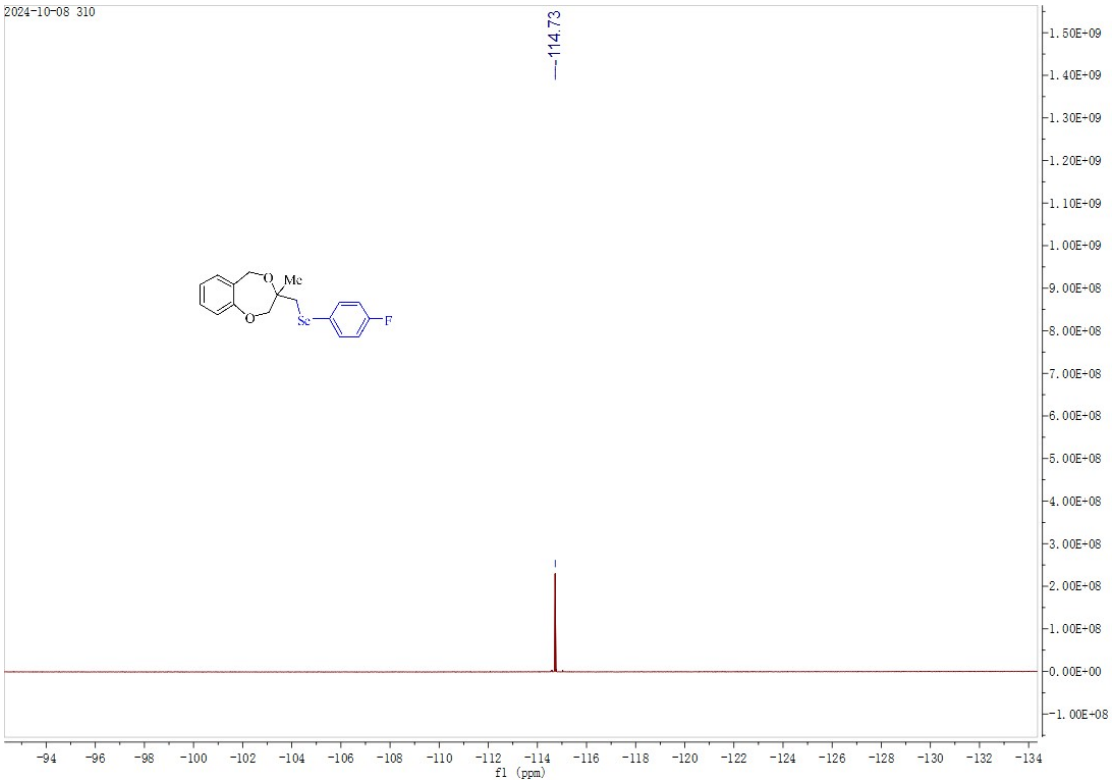




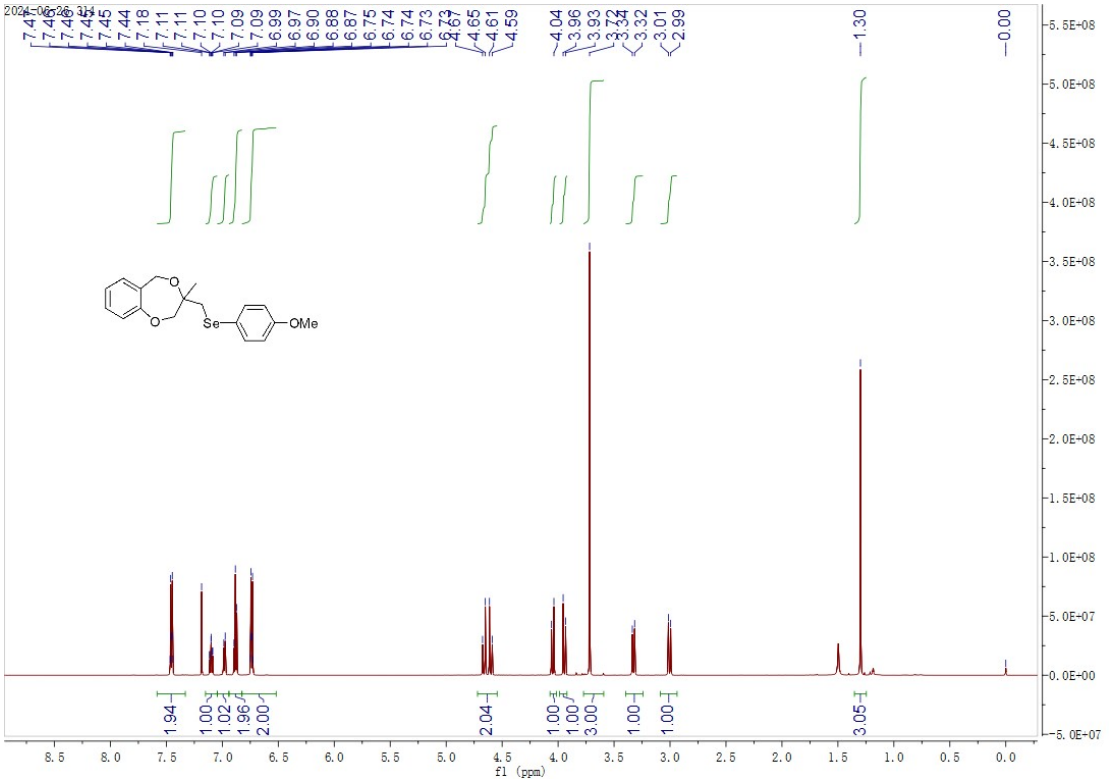
Compound 3ac ^{1}H NMR, ^{13}C NMR and ^{19}F NMR

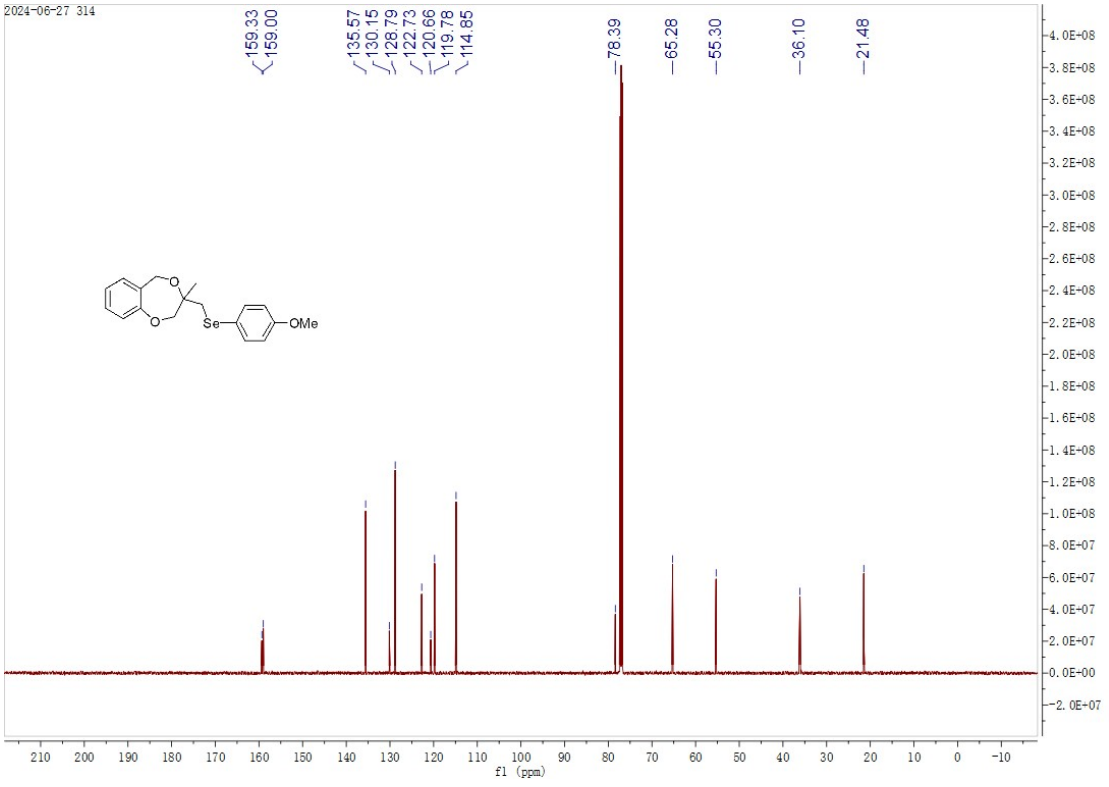




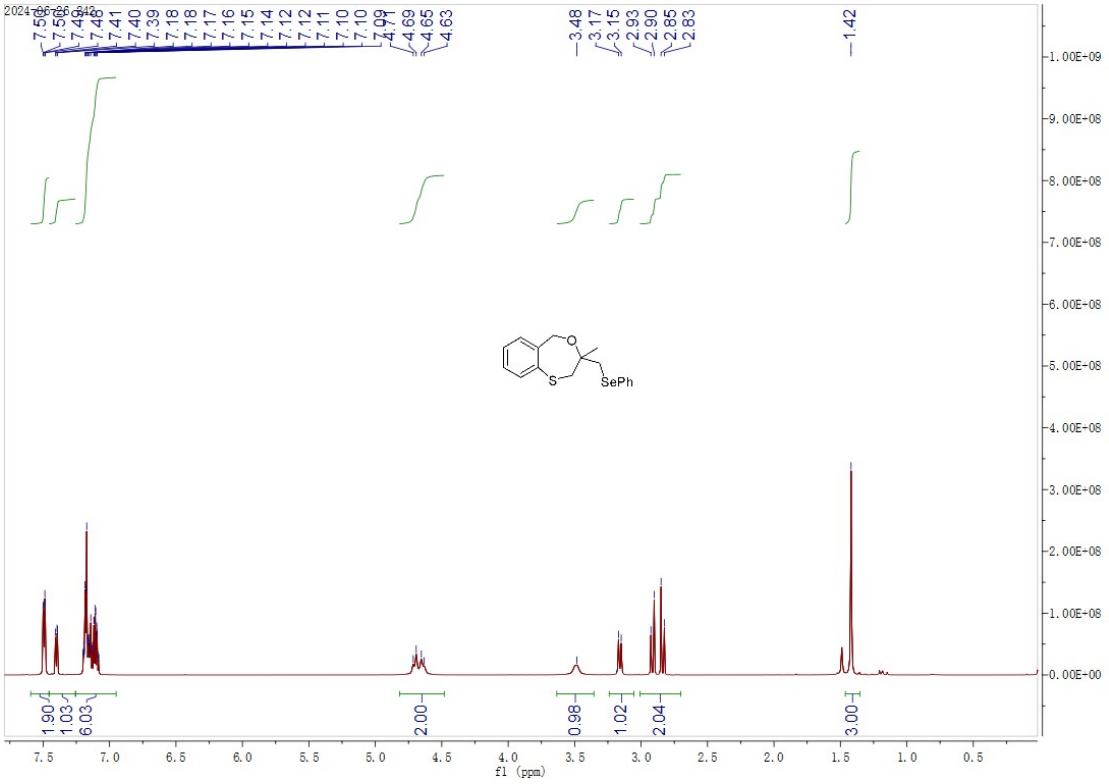

2024-10-08 310
-114.73
Me
O
O
Se
F
1.50E-09
1.40E-09
1.30E-09
1.20E-09
1.10E-09
1.00E-09
9.00E-08
8.00E-08
7.00E-08
6.00E-08
5.00E-08
4.00E-08
3.00E-08
2.00E-08
1.00E-08
0.00E+00
-1.00E-08
-94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134
f1 (ppm)

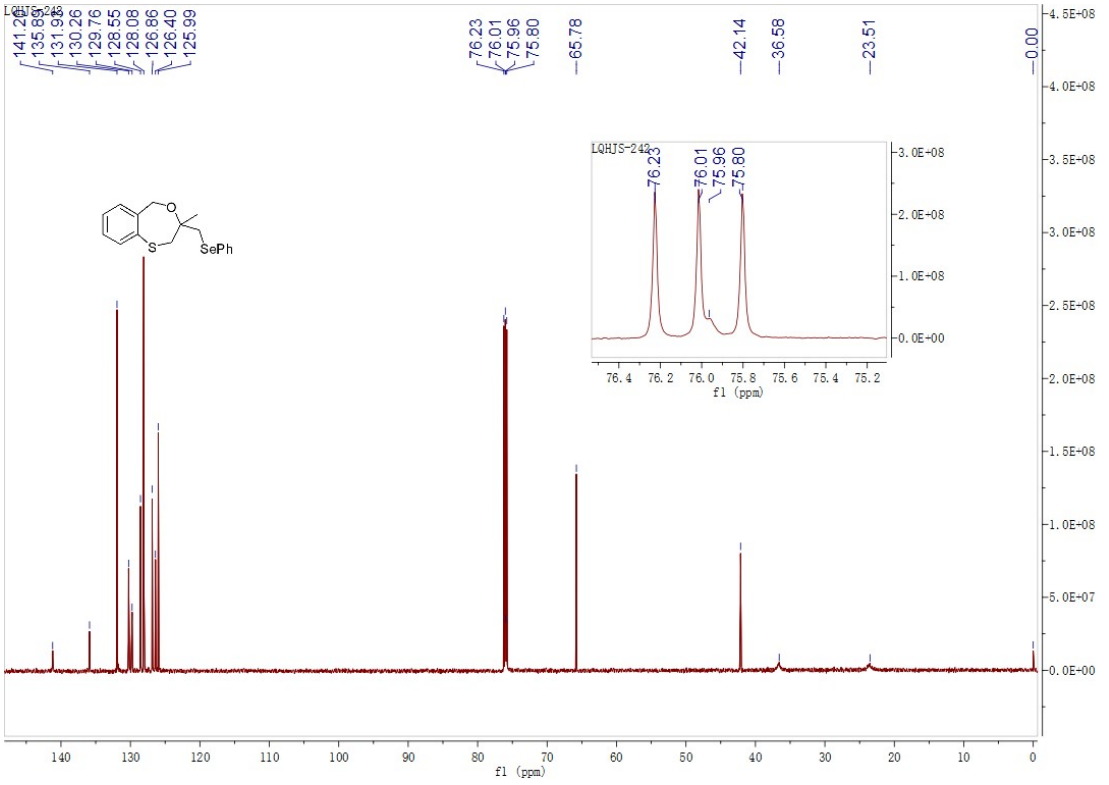
Compound 3ad ^{1}H NMR and ^{13}C NMR



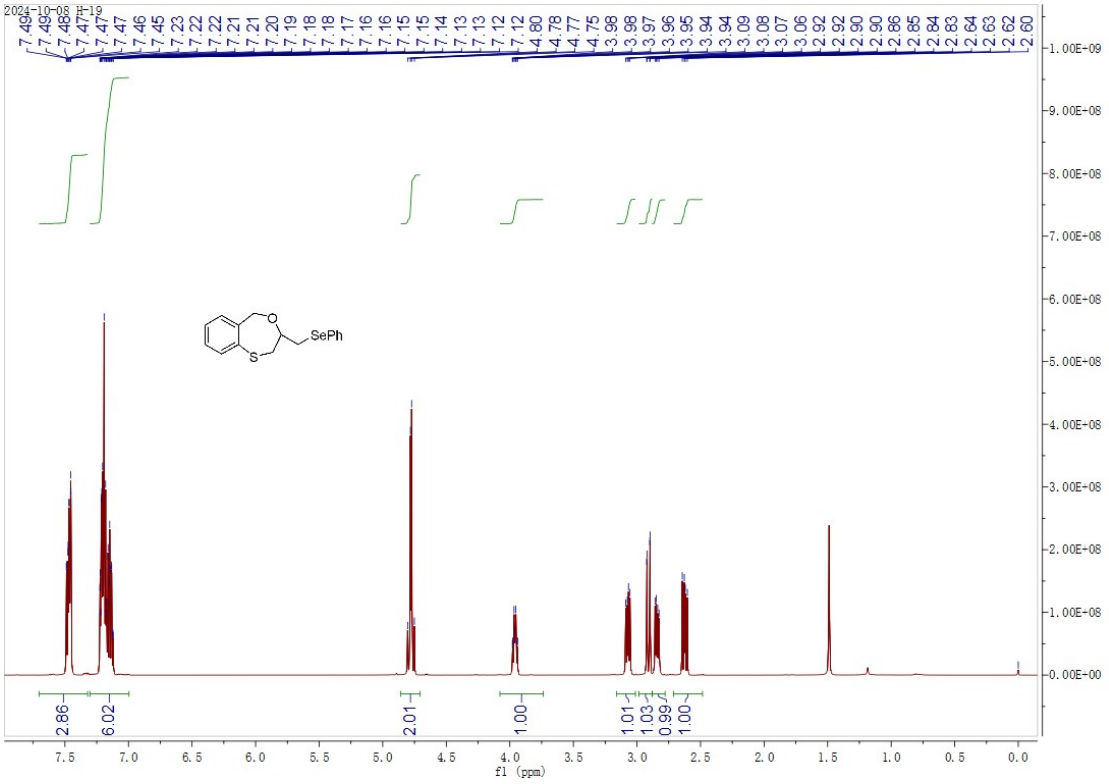


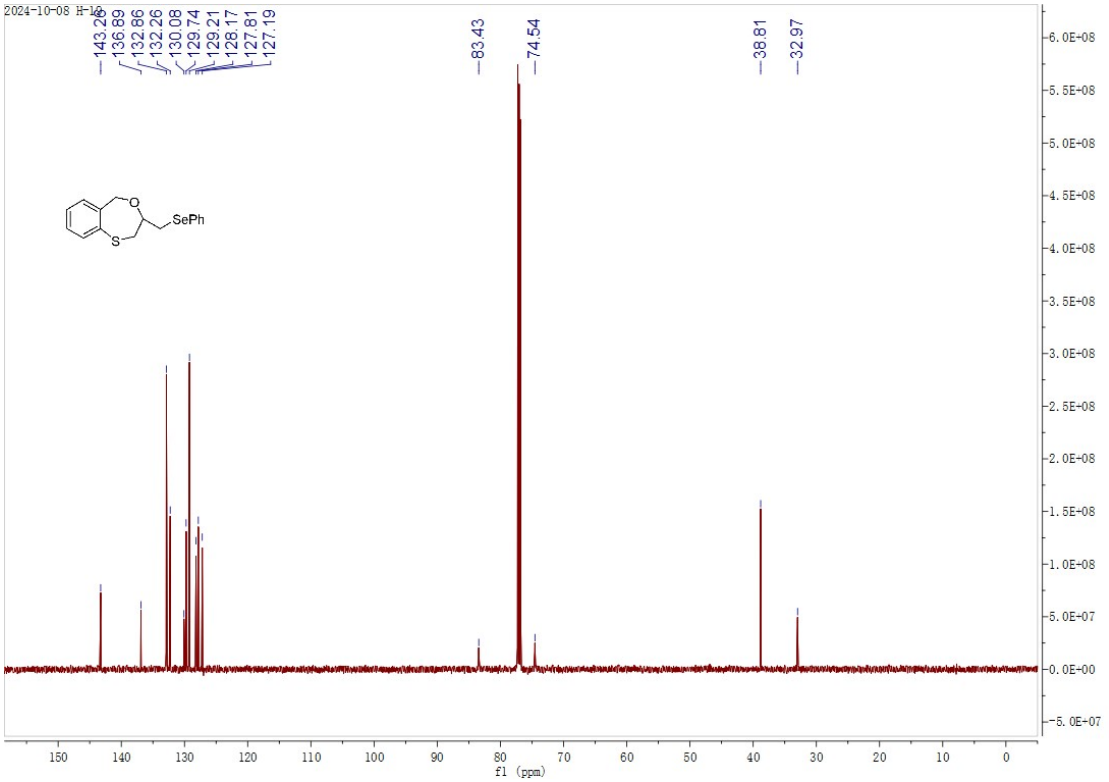
Compound 3za ^{1}H NMR and ^{13}C NMR



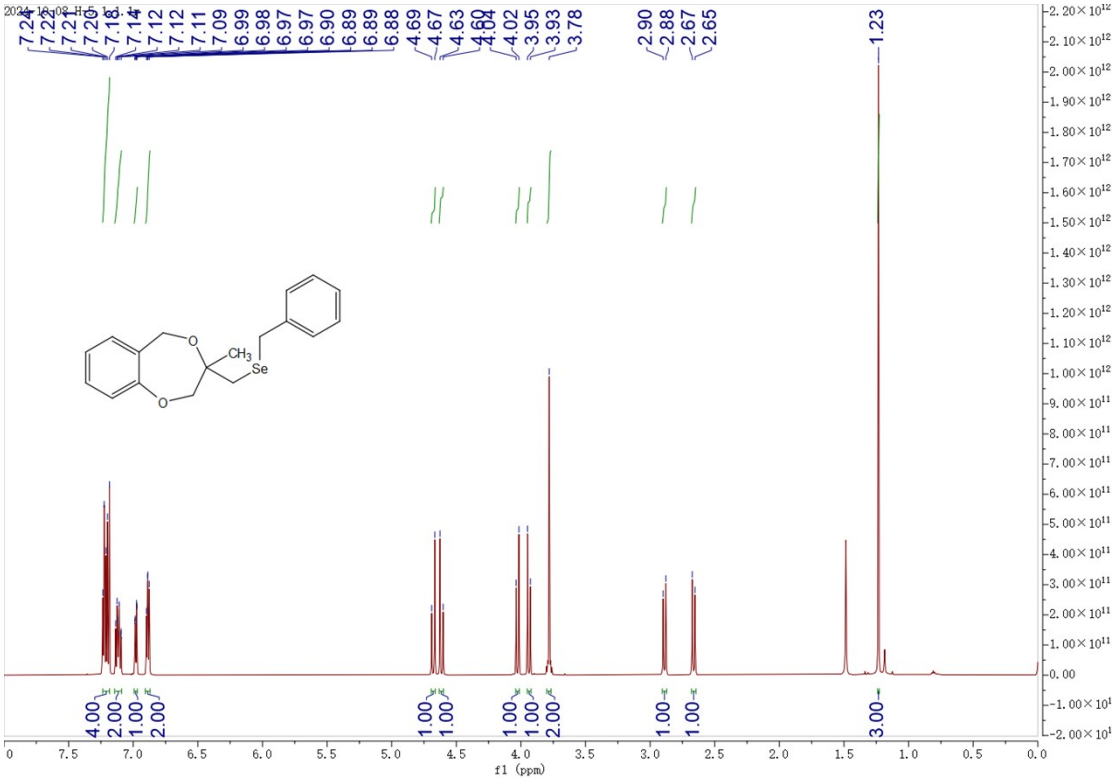


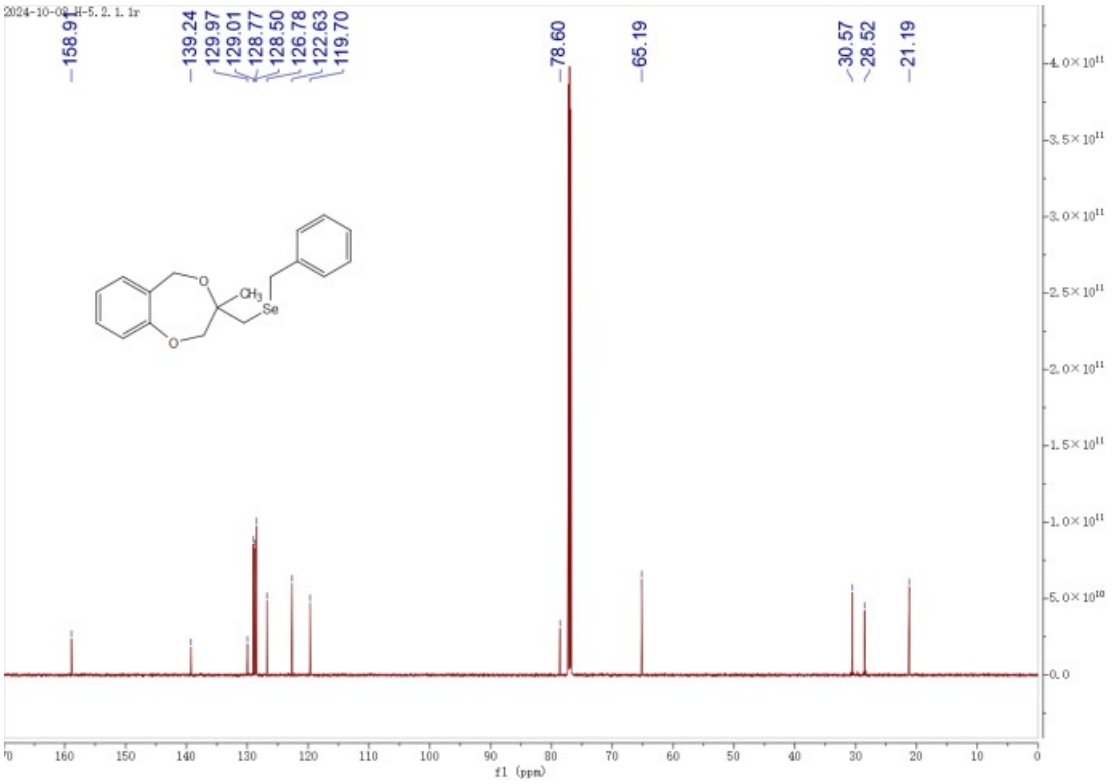
Compound 3aaa ^{1}H NMR and ^{13}C NMR





Compound 3ae ^{1}H NMR and ^{13}C NMR





Compound 3de ^{1}H NMR and ^{13}C NMR