Palladium/Norbornene-Catalyzed *Ortho*-Acylation and *Ipso*-Selenation via C(O)-Se Bond Cleavage: Synthesis of α-Carbonyl Selane

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General Information

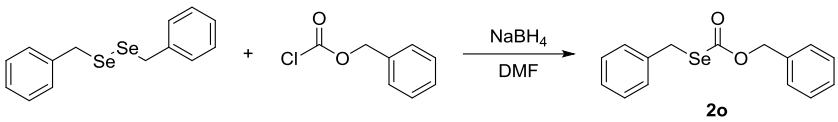
Nuclear magnetic resonan ce spectroscopies were recorded on Bruker-400 MHz instruments. ^{1}H NMR was internally referenced to tetramethylsilane (0.0 ppm) or residue of $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm) signal; ^{13}C NMR was referenced to the residue of $CDCl_3$ (77.00 ppm) or DMSO-d_6 (39.50 ppm). High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF (Waters Corporation). All reactions were performed under an inert atmosphere of nitrogen in sealed tube, unless otherwise stated. 1,3-Dichloropropane (DCP) and 1,3-dimethyl-2-imidazolidinone (DMI) were distilled over calcium hydride under an atmosphere of nitrogen.

All the selenoates except **2o** and **2p** are known compounds, which were prepared according to the literatures.[1-3]

General Procedure for Palladium/NBE-Catalyzed α-Acyl Selenides Synthesis

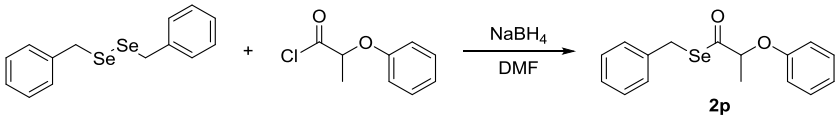
A flame-dried sealed tube was charged with aryl iodide **1** (0.20 mmol, 1.0 equiv), selenate **2** (0.30 mmol, 1.5 equiv), $PdCl_2$ (3.5 mg, 0.02 mmol, 10 mol %), TFP (11.6 mg, 0.05 mmol, 25 mol %), norbornene (56.5 mg, 0.60 mmol, 3.0 equiv), K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv) and 1,3-dichloropropane (4.0 ml, 0.050 mol/L). After the reaction being heated in an oil bath at 100 ºC for 16 h, the reaction mixture was cooled to room temperature and filtered through a pad of celite with EtOAc as the eluent. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane) to give the corresponding selenides **3**.

O,Se-dibenzyl carbonoselenoate (2o)



To a solution of 1,2-dibenzyldiselane (0.680 g, 2.0 mmol) in DMF (20 mL) was added $NaBH_4$ (75.6 mg, 2.0 mmol, 1.0 equiv), and the solution was stirred at room temperature for 30 min. Benzyl chloroformate (0.717 g, 4.2 mmol, 2.1 equiv) was added and stirred for 3 h. The reaction was quenched by the addition of H_2O (40 mL) and extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1) to give O,Se-dibenzyl carbonoselenoate (**2o**) (0.330 g, 1.1 mmol, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, 10 H), 5.28 (s, 2 H), 4.17 (s, 2 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 138.3, 135.0, 128.9, 128.63, 128.61, 128.5, 127.2, 126.7, 69.5, 30.7; **HRMS (ESI)** calcd. for $C_{15}H_{14}O_2SeNa$ $[M+Na]^+$ 329.0057, found 329.0062.

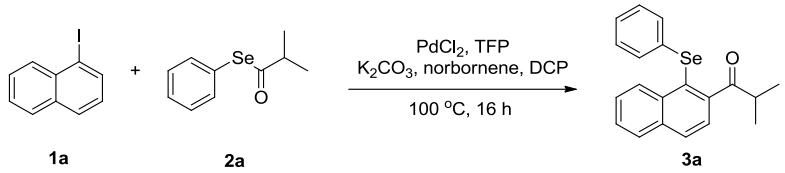
Se-benzyl 2-phenoxypropaneselenoate (2p)



To a solution of 1,2-dibenzyldiselane (0.680 g, 2.0 mmol) in DMF (20 mL) was added $NaBH_4$ (75.6 mg, 2 mmol, 1.0 equiv), and the solution was stirred at room temperature for 30 min. 2-Phenoxypropanoyl chloride (0.775 g, 4.2 mmol, 2.1 equiv)

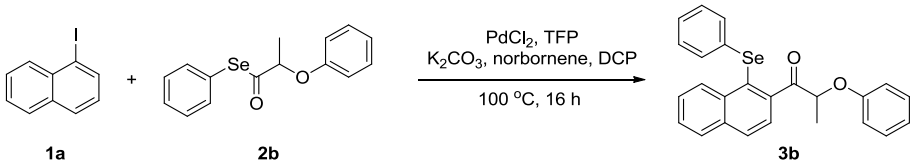
was added and stirred for 3 h. The reaction was quenched by the addition of H_2O (40 mL) and extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1) to give Se-benzyl 2-phenoxypropaneselenoate (**2p**) (0.240 g, 0.75 mmol, 38%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 - 7.27 (m, 3 H), 7.25 - 7.16 (m, 3 H), 7.22 - 7.16 (m, 1 H), 7.00 (t, *J* = 7.2 Hz, 1 H), 6.95 - 6.86 (m, 2 H), 4.73 (q, *J* = 6.4 Hz, 1 H), 4.12 (d, *J* = 12.4 Hz, 1 H), 4.08 (d, *J* = 12.4 Hz, 1 H), 1.55 (d, *J* = 6.0 Hz, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 206.9, 157.3, 138.7, 129.6, 128.9, 128.6, 126.9, 122.2, 115.6, 81.6, 27.6, 18.8; **HRMS (ESI)** calcd. for $C_{16}H_{16}O_2SeNa$ $[M+Na]^+$ 343.0213, found 343.0207.

Isopropyl 1-(phenylselanyl)-2-naphthoate (3a)



The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2a** (68.1 mg, 0.30 mmol, 1.5 equiv) afforded **3a** (58.7 mg, 83%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.4 Hz, 1 H), 7.98 (d, *J* = 8.4 Hz, 1 H), 7.88 - 7.85 (m, 1 H), 7.58 - 7.48 (m, 2 H), 7.40 (d, *J* = 8.0 Hz, 1 H), 7.21 - 7.07 (m, 5 H), 3.33 (hept, *J* = 6.8 Hz, 1 H), 1.24 (d, *J* = 6.8 Hz, 6 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.8, 146.2, 133.5, 133.0, 131.8, 129.6, 128.21, 128.17, 127.7, 127.5, 126.9, 126.1, 125.2, 122.7, 121.8, 40.3, 17.3; **HRMS (ESI)** calcd. for $C_{20}H_{19}OSe$ $[M+H]^+$ 355.0601, found 355.0600.

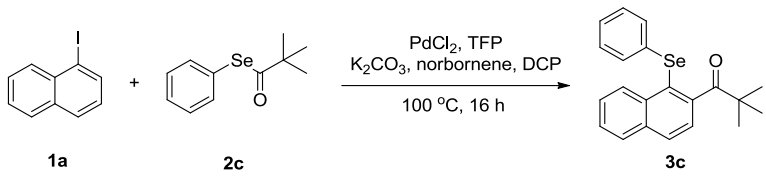
2-phenoxy-1-(1-(phenylselanyl)naphthalen-2-yl)propan-1-one (3b)



The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2b** (91.6 mg, 0.30 mmol, 1.5 equiv) afforded **3b** (63.0 mg, 73%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1 H), 7.97

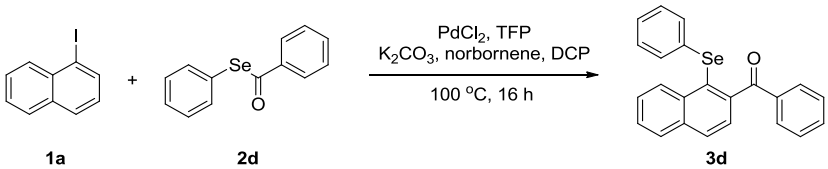
(d, J = 8.4 Hz, 1 H), 7.87 (d, J = 7.6 Hz, 1 H), 7.58 - 7.46 (m, 3 H), 7.17 (t, J = 8.0 Hz, 2 H), 7.10 - 7.05 (m, 5 H), 6.91 (t, J = 7.2 Hz, 1 H), 6.82 (d, J = 8.4 Hz, 2 H), 5.47 (q, J = 6.8 Hz, 1 H), 1.63 (d, J = 6.8 Hz, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.6, 157.4, 144.8, 134.34, 134.28, 132.7, 130.5, 129.4, 129.29, 129.28, 129.0, 128.6, 128.0, 127.4, 126.3, 124.0, 123.9, 121.5, 115.8, 78.5, 17.4; **HRMS (ESI)** calcd. for $C_{25}H_{20}O_2SeNa$ $[M+Na]^+$ 455.0526, found 455.0524.

2,2-dimethyl-1-(1-(phenylselanyl)naphthalen-2-yl)propan-1-one (3c)



The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2c** (72.4 mg, 0.30 mmol, 1.5 equiv) afforded **3c** (50.0 mg, 68%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 - 8.36 (m, 1 H), 7.96 (d, J = 8.4 Hz, 1 H), 7.90 - 7.84 (m, 1 H), 7.63 - 7.50 (m, 2 H), 7.30 (d, J = 8.4 Hz, 1 H), 7.20 - 7.15 (m, 2 H), 7.12 - 7.06 (m, 3 H), 1.31 (s, 9 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.6, 147.4, 134.5, 133.5, 132.5, 130.4, 129.6, 129.1, 128.7, 128.6, 127.9, 126.8, 126.2, 122.5, 121.9, 44.7, 27.8; **HRMS (ESI)** calcd. for $C_{21}H_{21}OSe$ $[M+H]^+$ 369.0758, found 369.0760.

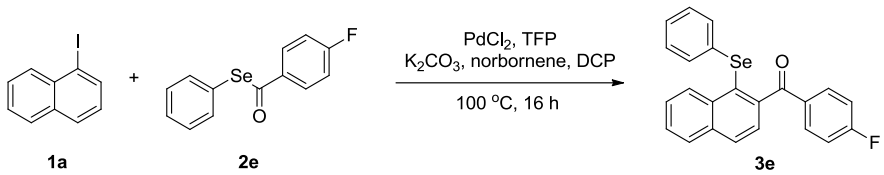
Phenyl(1-(phenylselanyl)naphthalen-2-yl)methanone (3d)



The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2d** (78.4 mg, 0.30 mmol, 1.5 equiv) afforded **3d** (43.4 mg, 56%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 - 8.48 (m, 1 H), 8.03 (d, J = 8.3 Hz, 1 H), 7.97 - 7.89 (m, 1 H), 7.76 (d, J = 7.6 Hz, 2 H), 7.62 - 7.55 (m, 2 H), 7.55 – 7.45 (m, 2 H), 7.35 (t, J = 7.6 Hz, 2 H), 7.11 - 7.07 (m, 2 H), 7.06 - 7.02 (m, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.1, 145.2, 137.2, 134.6, 134.2, 133.2, 132.7, 130.6, 129.94, 129.91, 129.0, 128.9, 128.7, 128.4, 128.1, 127.2, 126.3, 124.5, 124.2;

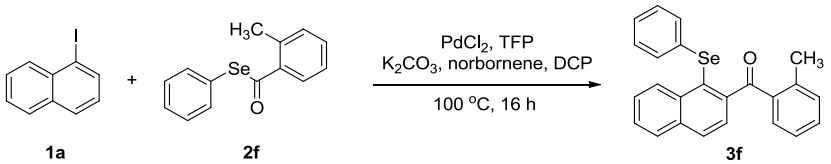
HRMS (ESI) calcd. for $C_{23}H_{16}OSeNa$ $[M+Na]^+$ 411.0264, found 411.0264.

(4-fluorophenyl)(1-(phenylselanyl)naphthalen-2-yl)methanone (3e)



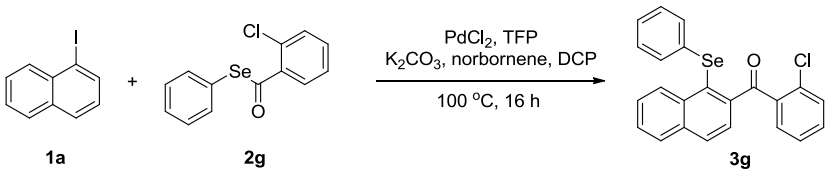
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2e** (83.8 mg, 0.30 mmol, 1.5 equiv) 16 h afforded **3e** (47.0 mg, 58%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 - 8.50 (m, 1 H), 8.04 (d, *J* = 12.4 Hz, 1 H), 7.96 - 7.89 (m, 1 H), 7.80 - 7.70 (m, 2 H), 7.65 - 7.55 (m, 2 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.14 - 7.03 (m, 5 H), 7.00 (t, *J* = 8.4 Hz, 2 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.6, 165.8 (d, *J* = 257.6 Hz), 144.8, 134.7, 134.2, 133.7 (d, *J* = 2.0 Hz), 132.7, 132.5 (d, *J* = 9.1 Hz), 130.7, 129.9, 129.0, 128.9, 128.7, 128.2, 127.3, 126.4, 124.5, 124.0, 115.5 (d, *J* = 22.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.6; **HRMS (ESI)** calcd. for $C_{23}H_{16}FOSe$ $[M+H]^+$ 407.0350, found 407.0352.

(1-(phenylselanyl)naphthalen-2-yl)(*o*-tolyl)methanone (3f)



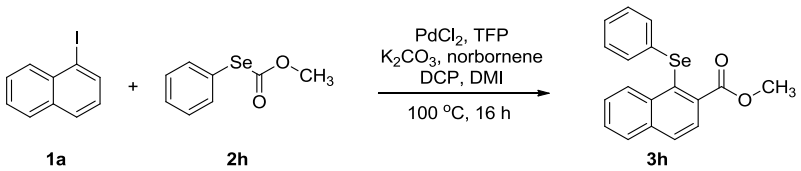
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) afforded **3f** (69.0 mg, 86%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.6 Hz, 1 H), 8.03 (d, *J* = 8.0 Hz, 1 H), 7.95 -7.85 (m, 1 H), 7.62 - 7.49 (m, 3 H), 7.34 - 7.27 (m, 2 H), 7.17 (d, *J* = 8.0 Hz, 1 H), 7.11 - 7.00 (m, 5 H), 7.00 - 6.92 (m, 1 H), 2.68 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.5, 146.4, 140.0, 137.2, 134.7, 134.3, 132.8, 131.9, 131.8, 131.7, 130.5, 129.7, 128.9, 128.6, 128.0, 127.2, 126.1, 125.1, 124.9, 124.8, 21.6; **HRMS (ESI)** calcd. for $C_{24}H_{19}OSe$ $[M+H]^+$ 403.0601, found 403.0604.

(2-chlorophenyl)(1-(phenylselanyl)naphthalen-2-yl)methanone (3g)



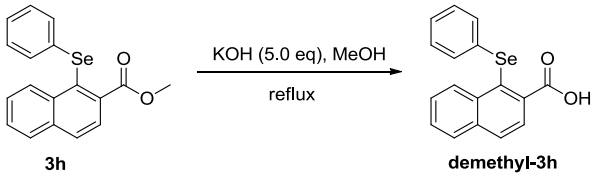
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2g** (88.7 mg, 0.30 mmol, 1.5 equiv) afforded **3g** (76.8 mg, 91%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.64 - 7.50 (m, 3 H), 7.39 (d, *J* = 7.6 Hz, 1 H), 7.38 - 7.27 (m, 2 H), 7.10 (t, *J* = 7.6 Hz, 1 H), 7.05 - 7.00 (m, 5 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 145.0, 137.7, 134.8, 134.6, 133.1, 132.9, 132.2, 131.7, 130.9, 130.5, 129.5, 129.3, 128.9, 128.6, 128.0, 127.7, 126.2, 126.1, 125.9, 125.4; **HRMS (ESI)** calcd. for $C_{23}H_{16}ClOSe$ $[M+H]^+$ 423.0055, found 423.0054.

Methyl 1-(phenylselanyl)-2-naphthoate (3h)



The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2h** (64.5 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3h** (36.9 mg, 54%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 12.8 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.65 (d, *J* = 12.4 Hz, 1 H), 7.57 - 7.45 (m, 2 H), 7.23 - 7.21 (m, 2 H), 7.15 - 7.07 (m, 3 H), 3.92 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.4, 138.3, 134.6, 134.4, 132.9, 130.3, 130.1, 129.8, 129.1, 128.5, 127.8, 127.4, 126.3, 124.4, 52.5; **HRMS (ESI)** calcd. for $C_{18}H_{14}O_2SeNa$ $[M+Na]^+$ 365.0057, found 365.0054.

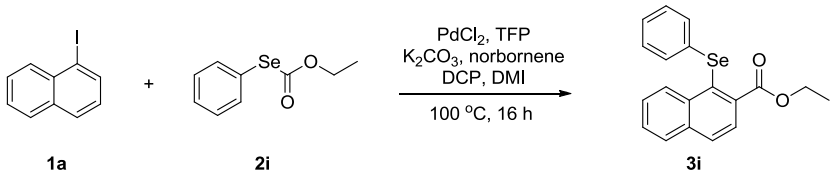
1-(phenylselanyl)-2-naphthoic acid (demethyl-3h)



Potassium hydroxide (0.137 g, 2.45 mmol) was added to the solution of **3h** (0.155 g,

0.45 mmol) in methanol (5 ml), and refluxed at 85 °C overnight. After being cooled to room temperature, the reaction was quenched with HCl (1 M) to pH ~ 1-2, then extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solid was filtered off and the solution was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford **demethyl-3h** (0.143 g, 93%). M.p. 191.7-192.8 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.29 (d, *J* = 7.6 Hz, 1 H), 8.00 (d, *J* = 8.4 Hz, 1 H), 7.96 - 7.90 (m, 1 H), 7.64 (d, *J* = 8.4 Hz, 1 H), 7.54 - 7.45 (m, 2 H), 7.27 - 7.20 (m, 2 H), 7.19 - 7.10 (m, 3 H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 172.6, 145.9, 133.54, 133.52, 133.3, 129.9, 129.6, 129.1, 128.7, 128.6, 127.2, 126.1, 125.9, 125.0, 122.8. **HRMS (ESI)** calcd. for $C_{17}H_{12}O_2SeNa$ $[M+Na]^+$ 350.9900, found 350.9903.

Ethyl 1-(phenylselanyl)-2-naphthoate (3i)



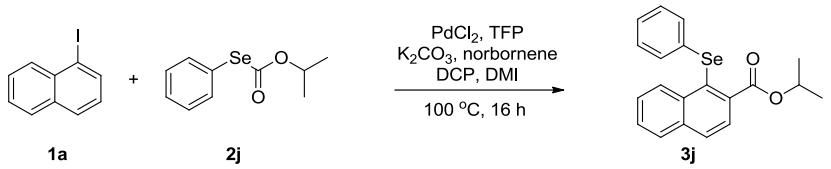
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2i** (68.7 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3i** (49.0 mg, 69%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 12.4 Hz, 1 H), 7.85 (d, *J* = 8.4 Hz, 1 H), 7.65 (d, *J* = 12.8 Hz, 1 H), 7.57 - 7.46 (m, 2 H), 7.24 - 7.19 (m, 2 H), 7.15 - 7.08 (m, 3 H), 4.39 (q, *J* = 7.2 Hz, 2 H), 1.32 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1, 138.8, 134.54, 134.47, 133.1, 130.2, 130.1, 129.7, 129.1, 128.5, 127.7, 127.4, 126.9, 126.2, 124.3, 61.8, 14.1; **HRMS (ESI)** calcd. for $C_{19}H_{16}O_2SeNa$ $[M+Na]^+$ 379.0213, found 379.0216.

Procedure for 2.70 mmol Scale Synthesis of 3i

A flame-dried sealed tube was charged with 1-iodonaphthalene **1a** (0.686 g, 2.70 mmol, 1.0 equiv), selenate **2i** (0.916 g, 4.00 mmol, 1.5 equiv), $PdCl_2$ (48 mg, 0.27 mmol, 10 mol %), TFP (0.128 g, 0.55 mmol, 22 mol %), norbornene (0.283 g, 8.10 mmol, 3.0 equiv), K_2CO_3 (1.10 g, 8.10 mmol, 3.0 equiv), 1,3-dichloropropane (50 ml) and DMI (2.5 ml). After stirring at 100 °C for 16 h, the reaction mixture was cooled to room

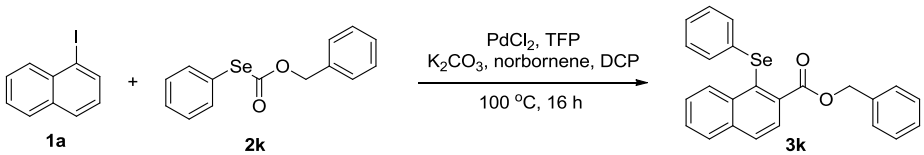
temperature and filtered through a pad of celite with EtOAc as the eluent to get rid of the solid. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 4:1) to give **3l** (0.672 g, 70%). The analytic data were identical with the compound obtained at 0.20 mmol scale reaction.

Isopropyl 1-(phenylselanyl)-2-naphthoate (3j)



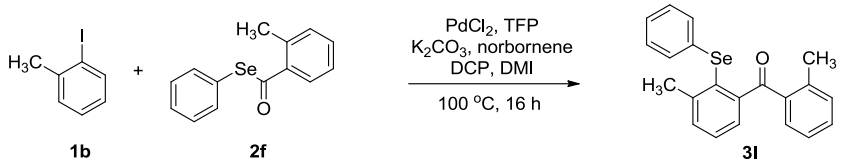
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2j** (72.9 mg, 0.30 mmol, 1.5 equiv) afforded **3j** (45.8 mg, 62%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 12.4 Hz, 1 H), 7.85 (d, *J* = 8.4 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.56 - 7.41 (m, 2 H), 7.23 - 7.20 (m, 2 H), 7.16 - 7.03 (m, 3 H), 5.29 (hept, *J* = 6.0 Hz, 1 H), 1.33 (d, *J* = 6.0 Hz, 6 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 139.3, 134.51, 134.45, 133.1, 130.2, 130.0, 129.6, 129.0, 128.5, 127.7, 127.3, 126.3, 126.1, 124.2, 69.7, 21.7; **HRMS (ESI)** calcd. for $C_{20}H_{19}O_2Se$ $[M+H]^+$ 371.0550, found 371.0545.

Benzyl 1-(phenylselanyl)-2-naphthoate (3k)



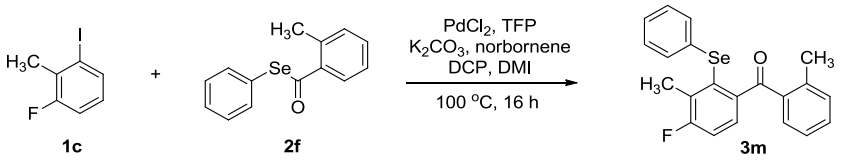
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2k** (87.4 mg, 0.30 mmol, 1.5 equiv) afforded **3k** (52.6 mg, 63%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.4 Hz, 1 H), 7.94 (d, *J* = 8.4 Hz, 1 H), 7.85 (d, *J* = 7.2 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.56 - 7.46 (m, 2 H), 7.37 - 7.35 (m, 2 H), 7.34 - 7.30 (m, 3 H), 7.19 - 7.18 (m, 2 H), 7.14 - 7.04 (m, 3 H), 5.36 (s, 2 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 138.4, 135.3, 134.6, 134.5, 133.0, 130.2, 130.1, 129.7, 129.1, 128.5, 128.3, 127.8, 127.5, 127.1, 126.2, 124.4, 67.6; **HRMS (ESI)** calcd. for $C_{24}H_{18}O_2SeNa$ $[M+Na]^+$ 441.0370, found 441.0374.

(3-methyl-2-(phenylselanyl)phenyl)(o-tolyl)methanone (3l)



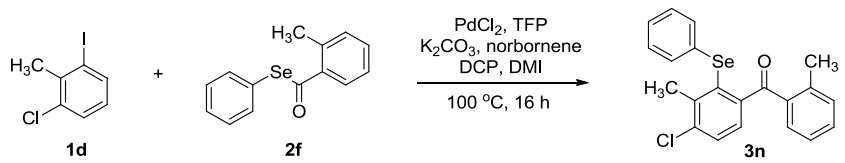
The reaction of 1-iodo-2-methylbenzene **1b** (43.6 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3l** (56.3 mg, 77%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.39 (m, 1 H) , 7.39 - 7.37 (m, 1 H), 7.33 - 7.27 (m, 2 H), 7.25 - 7.19 (m, 2 H), 7.13 - 7.00 (m, 6 H), 2.61 (s, 3 H), 2.36 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.6, 147.9, 144.0, 139.9, 137.3, 132.4, 131.81, 131.76, 131.63, 131.59, 129.8, 129.04, 128.97, 126.8, 126.2, 125.9, 125.1, 23.0, 21.5; **HRMS (ESI)** calcd. for $C_{21}H_{18}OSeNa$ $[M+Na]^+$ 389.0421, found 389.0422.

(4-fluoro-3-methyl-2-(phenylselanyl)phenyl)(o-tolyl)methanone (3m)



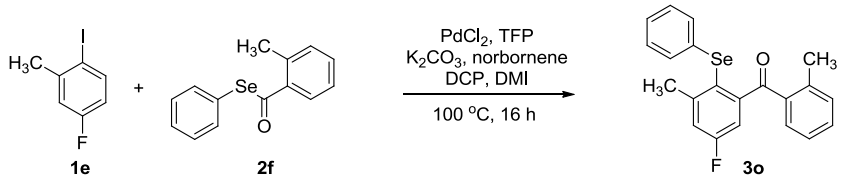
The reaction of 1-fluoro-3-iodo-2-methylbenzene **1c** (47.2 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3m** (66.7 mg, 87%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 - 7.28 (m, 2 H), 7.25 - 7.23 (m, 1 H), 7.22 - 7.14 (m, 2 H), 7.14 - 7.03 (m, 6 H), 2.59 (s, 3 H), 2.26 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.6, 161.8 (d, J = 252.5 Hz), 143.4 (d, J = 4.0 Hz), 139.7, 137.5, 132.1, 131.7 (d, J = 13.1 Hz), 131.4, 131.1, 130.9, 130.6 (d, J = 2.0 Hz), 130.3, 129.1, 127.38 (d, J = 9.1 Hz), 126.6, 125.2, 115.65 (d, J = 23.2 Hz), 21.34, 14.94 (d, J = 4.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.3; **HRMS (ESI)** calcd. for $C_{21}H_{17}FOSeNa$ $[M+Na]^+$ 407.0326, found 407.0323.

(4-chloro-3-methyl-2-(phenylselanyl)phenyl)(o-tolyl)methanone (3n)



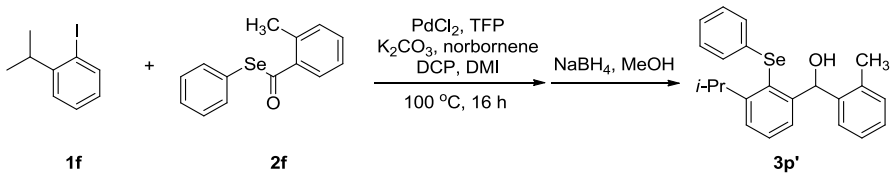
The reaction of 1-chloro-3-iodo-2-methylbenzene **1d** (50.5 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3n** (70.4 mg, 88%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1 H), 7.35 - 7.29 (m, 1 H), 7.26 - 7.21 (m, 2 H), 7.18 (d, *J* = 6.8 Hz, 1 H), 7.15 - 7.09 (m, 3 H), 7.09 - 6.98 (m, 3 H), 2.61 (s, 3 H), 2.47 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.5, 146.4, 141.6, 140.0, 137.0, 136.5, 132.1, 131.9, 131.8, 131.6, 130.1, 130.0, 129.2, 129.1, 126.6, 126.5, 125.2, 21.5, 20.8; **HRMS (ESI)** calcd. for $C_{21}H_{17}ClOSeNa$ $[M+Na]^+$ 423.0031, found 423.0028.

(5-fluoro-3-methyl-2-(phenylselanyl)phenyl)(o-tolyl)methanone (3o)



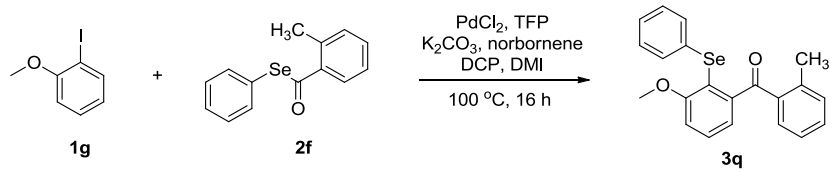
The reaction of 4-fluoro-1-iodo-2-methylbenzene **1e** (47.2 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3o** (46.0 mg, 60%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.2 Hz, 1 H), 7.26-7.24 (m, 1 H), 7.20 (d, *J* = 8.0 Hz, 1 H), 7.15 - 7.07 (m, 4 H), 7.07 - 6.99 (m, 4 H), 2.63 (s, 3 H), 2.38 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.0, 162.8 (d, *J* = 22.5 Hz), 149.9 (d, *J* = 7.1 Hz), 147.1 (d, *J* = 8.1 Hz), 140.2, 136.5, 132.1, 132.0 (d, *J* = 2.0 Hz), 131.8, 129.6, 129.0, 126.3, 125.2, 121.5, 121.4, 118.5 (d, *J* = 21.2 Hz), 112.9 (d, *J* = 23.2 Hz), 23.2, 21.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.6; **HRMS (ESI)** calcd. for $C_{21}H_{17}FOSeNa$ $[M+Na]^+$ 407.0326, found 407.0326.

(3-isopropyl-2-(phenylselanyl)phenyl)(*o*-tolyl)methanol (3p)



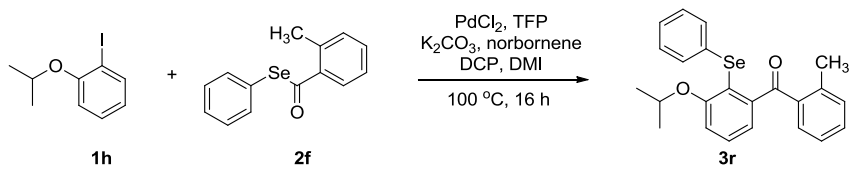
The reaction of 1-iodo-2-isopropylbenzene **1f** (49.2 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **the corresponding ketone** (petroleum ether : dichloromethane = 3 : 1), which was purified after the reduction with $NaBH_4$ (15.1 mg, 0.4 mmol) in MeOH (4.0 mL) as alcohol **3p'** (47.4 mg, 60% yield for two steps) (petroleum ether:ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.30 (m, 3 H), 7.21 - 7.03 (m, 9 H), 6.52 (d, *J* = 4.0 Hz, 1 H), 3.74 (hept, *J* = 6.8 Hz, 1 H), 2.43 (d, *J* = 4.4 Hz, 1 H), 2.07 (s, 3 H), 1.17 (d, *J* = 7.2 Hz, 3 H), 1.14 (d, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.1, 147.5, 141.2, 141.0, 135.7, 133.6, 130.21, 130.16, 129.2, 128.9, 127.3, 126.5, 126.0, 125.94, 125.92, 73.4, 33.8, 24.21, 24.17, 19.3; **HRMS (ESI)** calcd. for $C_{23}H_{24}OSeNa$ $[M+Na]^+$ 419.0890, found 419.0893.

(3-methoxy-2-(phenylselanyl)phenyl)(o-tolyl)methanone (3q)



The reaction of 1-iodo-2-methoxybenzene **1g** (46.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3q** (24.4 mg, 32%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 - 7.36 (m, 2 H), 7.34 - 7.28 (m, 2 H), 7.25 - 7.18 (m, 2 H), 7.14 - 7.00 (m, 6 H), 2.61 (s, 3 H), 2.36 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.6, 147.9, 144.0, 139.9, 137.3, 132.5, 131.82, 132.77, 131.64, 131.60, 129.8, 129.1, 129.0, 126.8, 126.2, 125.9, 125.1, 23.0, 21.5; **HRMS (ESI)** calcd. for $C_{21}H_{19}O_2Se$ $[M+H]^+$ 383.0550, found 383.0542.

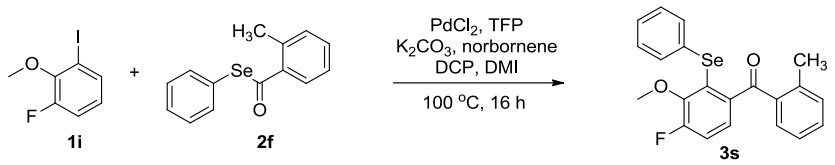
(3-isopropoxy-2-(phenylselanyl)phenyl)(o-tolyl)methanone (3r)



The reaction of 1-iodo-2-isopropoxybenzene **1h** (52.2 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL)

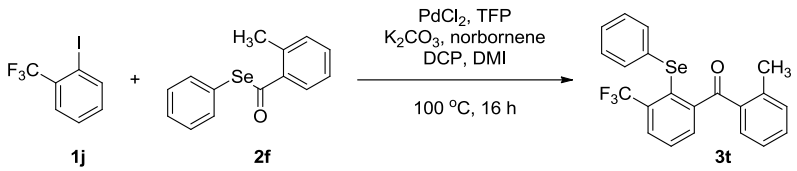
afforded **3r** (46.7 mg, 57%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 - 7.31 (m, 2 H), 7.30 - 7.25 (m, 2 H), 7.24 - 7.24 (m, 2 H), 7.14 - 7.05 (m, 4 H), 7.00 (d, *J* = 7.2 Hz, 1 H), 6.95 (d, *J* = 12.4 Hz, 1 H), 4.49 (hept, *J* = 6.0 Hz, 1 H), 2.62 (s, 3 H), 1.06 (d, *J* = 6.0 Hz, 6 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.0, 157.8, 147.7, 139.7, 137.4, 133.0, 131.7, 131.64, 131.61, 131.5, 129.6, 128.5, 126.3, 125.2, 120.2, 117.8, 114.4, 70.5, 21.4, 21.3; **HRMS (ESI)** calcd. for $C_{23}H_{22}O_2SeNa$ $[M+Na]^+$ 433.0683, found 433.0680.

(4-fluoro-3-methoxy-2-(phenylselanyl)phenyl)(*o*-tolyl)methanone (3s)



The reaction of 1-fluoro-3-iodo-2-methoxybenzene **1i** (50.4 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3s** (52.7 mg, 66%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 - 7.32 (m, 1 H), 7.33 - 7.26 (m, 3 H), 7.22 (d, *J* = 7.6, Hz, 1 H), 7.20 - 7.07 (m, 6 H), 3.63 (d, *J* = 2.0 Hz, 3 H), 2.55 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.8, 156.7 (d, *J* = 256.5 Hz), 148.7 (d, *J* = 11.1 Hz), 141.9 (d, *J* = 4.0 Hz), 139.6, 137.2, 132.10, 132.06, 131.7 (d, *J* = 3.0 Hz), 131.2, 128.9, 127.1, 125.7 (d, *J* = 1.0 Hz), 125.3, 124.6 (d, *J* = 8.1 Hz), 117.1, 116.9, 60.8 (d, *J* = 6.1 Hz), 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.9; **HRMS (ESI)** calcd. for $C_{21}H_{18}FO_2Se$ $[M+H]^+$ 401.0455, found 401.0455.

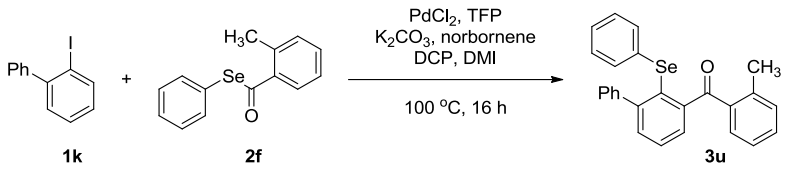
(2-(phenylselanyl)-3-(trifluoromethyl)phenyl)(o-tolyl)methanone (3t)



The reaction of 1-iodo-2-(trifluoromethyl)benzene **1j** (54.4 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.8 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3t** (30.0 mg, 36%) (petroleum ether : dichloromethane = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.63 (t, *J* = 7.6 Hz, 1 H), 7.57 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.35 - 7.28 (m, 1 H), 7.23 (d, *J* = 7.2 Hz, 1 H), 7.12 – 7.02 (m, 5

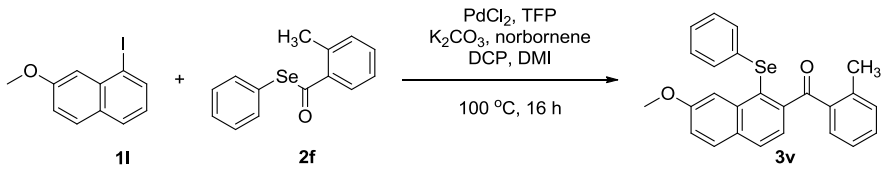
H), 6.99 (d, J = 4.0 Hz, 2 H), 2.55 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 150.2, 140.5, 135.8, 135.5, 135.2, 132.04 (q, J = 30 Hz), 132.02, 130.6, 129.5, 128.9, 127.9 (q, J = 6.1 Hz), 126.7, 125.2, 124.7, 123.74, 123.73, 122.0, 21.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.0. **HRMS (ESI)** calcd. for $C_{21}H_{16}F_3OSe$ $[M+H]^+$ 421.0318, found 421.0323.

(2-(phenylselanyl)-[1,1'-biphenyl]-3-yl)(*o*-tolyl)methanone (3u)



The reaction of 2-iodo-1,1'-biphenyl **1k** (56.0 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.8 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3u** (36.0 mg, 42%) (petroleum ether : dichloromethane = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 - 7.44 (m, 1 H), 7.43 - 7.35 (m, 3 H), 7.33 (d, J = 8.0 Hz, 1 H), 7.28 (d, J = 7.2 Hz, 1 H), 7.22 - 7.17 (m, 3 H), 7.16 - 7.12 (m, 3 H), 7.02 - 6.97 (m, 1 H), 6.90 (t, J = 8.0 Hz, 2 H), 6.80 - 6.70 (m, 2 H), 2.60 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 147.8, 147.1, 141.6, 139.9, 137.3, 132.7, 132.5, 131.9, 131.8, 131.7, 131.6, 129.3, 128.41, 128.38, 128.2, 127.7, 127.5, 127.0, 126.3, 125.2, 21.4. **HRMS (ESI)** calcd. for $C_{26}H_{21}OSe$ $[M+H]^+$ 429.0758, found 429.0760.

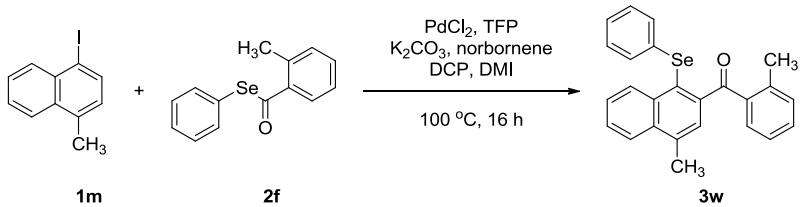
(7-methoxy-1-(phenylselanyl)naphthalen-2-yl)(o-tolyl)methanone (3v)



The reaction of 1-iodo-7-methoxynaphthalene **1l** (56.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.8 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3v** (71.0 mg, 82%) (petroleum ether : dichloromethane = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1 H), 7.79 (d, J = 7.2 Hz, 1 H), 7.70 (d, J = 2.4 Hz, 1 H), 7.41 (d, J = 8.0 Hz, 1 H), 7.34 - 7.27 (m, 2 H), 7.22 (d, J = 7.6 Hz, 1 H), 7.18 (dd, J = 8.8, 2.4 Hz, 1 H), 7.13 - 7.08 (m, 2 H), 7.06 - 7.02 (m, 3 H), 7.00 (t, J = 7.6 Hz, 1 H), 3.70 (s, 3 H), 2.69 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.7, 159.1, 146.5,

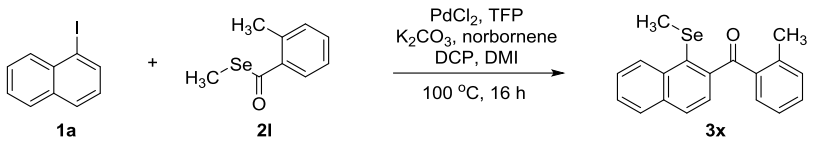
140.0, 137.3, 136.0, 132.6, 131.9, 131.8, 131.7, 130.14, 130.10, 129.9, 129.7, 128.9, 126.3, 125.1, 123.8, 122.5, 120.2, 107.1, 55.2, 21.6. **HRMS (ESI)** calcd. for $C_{25}H_{21}O_2Se$ $[M+H]^+$ 433.0707, found 433.0708.

(4-methyl-1-(phenylselanyl)naphthalen-2-yl)(o-tolyl)methanone (3w)



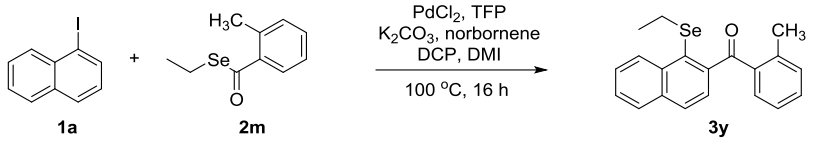
The reaction of 1-iodo-4-methylnaphthalene **1m** (53.6 mg, 0.20 mmol, 1.0 equiv), selenoester **2f** (82.8 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3w** (60.0 mg, 72%) (petroleum ether : dichloromethane = 3 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.4 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.63 - 7.57 (m, 1 H), 7.57 - 7.50 (m, 1 H), 7.41 (s, 1 H), 7.29 - 7.24 (m, 2 H), 7.18 (d, J = 8.0 Hz, 1 H), 7.04 - 6.98 (m, 5 H), 6.94 (t, *J* = 8.4 Hz,1 H), 2.78 (s, 3 H), 2.68 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.7, 146.3, 134.0, 137.5, 137.2, 134.6, 133.6, 133.0, 131.9, 131.8, 131.7, 129.5, 128.8, 127.6, 127.1, 126.0, 125.4, 125.1, 124.7, 122.4, 21.6, 19.7. **HRMS (ESI)** calcd. for $C_{25}H_{21}OSe$ $[M+H]^+$ 417.0758, found 417.0757.

(1-(methylselanyl)naphthalen-2-yl)(*o*-tolyl)methanone (3x)



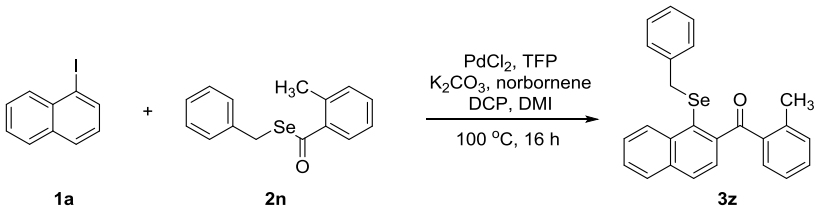
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2l** (63.9 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3x** (31.9 mg, 47%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.70 - 7.62 (m, 1 H), 7.63 - 7.55 (m, 1 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 7.40 - 7.30 (m, 2 H), 7.19 (d, *J* = 7.2 Hz, 1 H), 7.09 (t, *J* = 7.6 Hz, 1 H), 2.75 (s, 3 H), 1.97 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.7, 145.9, 140.2, 137.6, 134.4, 134.1, 131.9, 131.8, 131.7, 129.7, 128.8, 128.5, 127.8, 127.1, 126.2, 125.1, 124.4, 21.7, 10.0; **HRMS (ESI)** calcd. for $C_{19}H_{16}OSeNa$ $[M+Na]^+$ 363.0264, found 363.0267.

(1-(ethylselanyl)naphthalen-2-yl)(*o*-tolyl)methanone (3y)



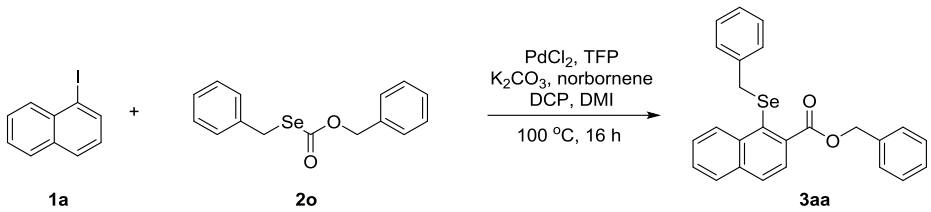
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2m** (68.1 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3y** (41.7 mg, 59%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.8 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.69 - 7.55 (m, 2 H), 7.49 (d, *J* = 8.4 Hz, 1 H), 7.41 - 7.30 (m, 2 H), 7.20 (d, *J* = 7.2 Hz, 1 H), 7.08 (t, *J* = 8.0 Hz, 1 H), 2.75 (s, 3 H), 2.64 (q, *J* = 8.0 Hz, 2 H), 1.12 (t, *J* = 7.6 Hz, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.8, 146.4, 140.1, 137.8, 135.0, 134.0, 131.9, 131.74, 131.67, 129.6, 128.70, 128.68, 127.6, 127.0, 125.4, 125.1, 124.4, 24.1, 21.7, 15.4; **HRMS (ESI)** calcd. for $C_{20}H_{18}OSeNa$ $[M+Na]^+$ 377.0421, found 377.0418.

(1-(benzylselanyl)naphthalen-2-yl)(*o*-tolyl)methanone (3z)



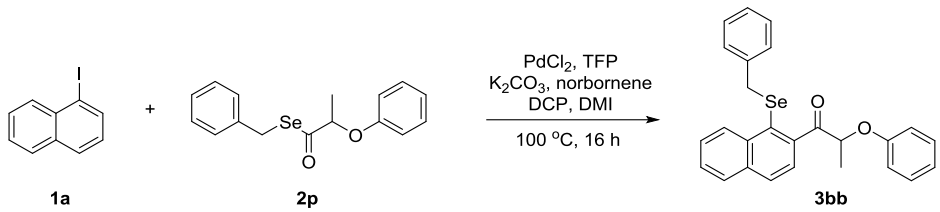
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2n** (86.8 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3z** (49.0 mg, 59%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 - 8.43 (m, 1 H), 7.96 (d, *J* = 8.4 Hz, 1 H), 7.93 - 7.85 (m, 1 H), 7.64 - 7.54 (m, 2 H), 7.48 (d, *J* = 8.4 Hz, 1 H), 7.43 - 7.32 (m, 2 H), 7.17 - 7.00 (m, 5 H), 6.94 - 6.79 (m, 2 H), 3.76 (s, 2 H), 2.73 (s, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.6, 146.4, 140.2, 137.9, 137.8, 135.0, 134.0, 131.9, 131.67, 131.66, 129.9, 128.7, 128.6, 128.3, 127.7, 127.0, 126.8, 125.8, 125.2, 124.5, 33.8, 21.6; **HRMS (ESI)** calcd. for $C_{25}H_{20}OSeNa$ $[M+Na]^+$ 439.0577, found 439.0580.

Benzyl 1-(benzylselanyl)-2-naphthoate (3aa)



The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2o** (91.6 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3aa** (36.2 mg, 42%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 - 8.52 (m, 1 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.85 - 7.80 (m, 1 H), 7.59 - 7.52 (m, 3 H), 7.49 (d, *J* = 7.2 Hz, 2 H), 7.44 - 7.33 (m, 3 H), 7.15 - 7.02 (m, 3 H), 7.02 - 6.80 (m, 2 H), 5.41 (s, 2 H), 4.00 (s, 2 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 138.6, 138.4, 135.6, 135.0, 134.2, 129.7, 129.6, 128.7, 128.6, 128.4, 128.3, 128.2, 127.9, 127.5, 127.2, 126.7, 124.2, 67.4, 34.0; **HRMS (ESI)** calcd. for $C_{25}H_{20}O_2SeNa$ $[M+Na]^+$ 455.0526, found 455.0525.

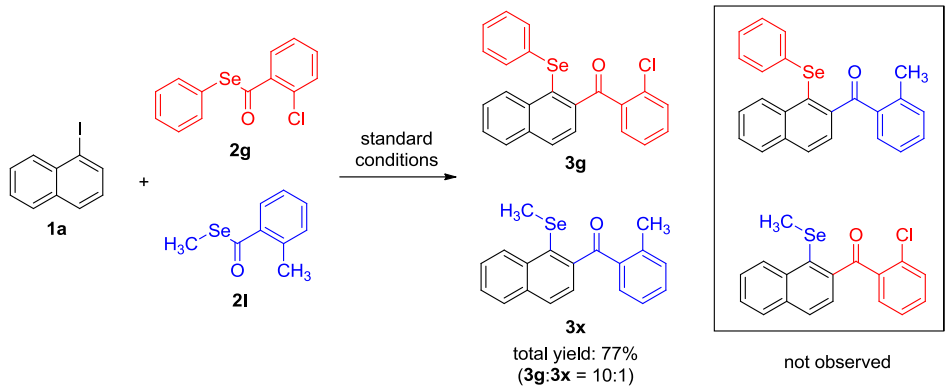
1-(1-(benzylselanyl)naphthalen-2-yl)-2-phenoxypropan-1-one (3bb)



The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoester **2p** (95.8 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded **3bb** (53.5 mg, 60%) (petroleum ether : dichloromethane = 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 - 8.49 (m, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.87 - 7.80 (m, 1 H), 7.60 - 7.52 (m, 2 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 7.30 - 7.18 (m, 2 H), 7.14 - 7.06 (m, 3 H), 7.00 - 6.97 (m, 2 H), 6.96 - 6.91 (m, 3 H), 5.45 (q, *J* = 6.8 Hz, 1 H), 4.01 (d, *J* = 10.8 Hz, 1 H), 3.96 (d, *J* = 10.8 Hz, 1 H), 1.57 (d, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.8, 157.6, 144.8, 138.0, 134.7, 133.9, 129.9, 129.4, 128.8, 128.7, 128.5, 128.4, 127.6, 127.2, 126.9, 125.0, 123.6, 121.5, 116.0, 78.9, 34.5, 17.6; **HRMS (ESI)** calcd. for $C_{26}H_{22}O_2SeNa$ $[M+Na]^+$ 469.0683, found 469.0684.

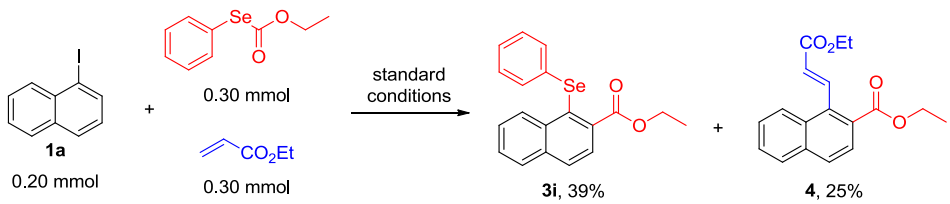
Control experiments

a) The Crossover Reaction



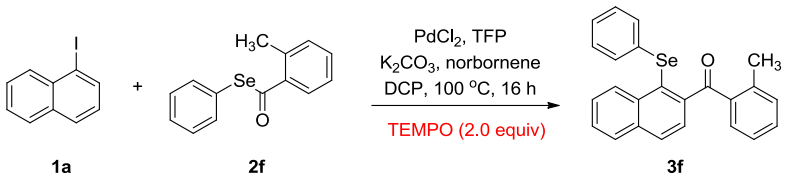
The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), selenoesters **2g** (88.7 mg, 0.30 mmol, 1.5 equiv) and **2l** (63.9 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) and DMI (0.20 mL) afforded a mixture of **3g** and **3x** (62.0 mg) (petroleum ether : dichloromethane = 4 : 1). The analysis of the ^{1}H NMR of the mixture indicated the ratio of **3g** : **3x** was 10 : 1, thus the calculated total yield was 77%.

b) The Trapping Reaction



The reaction of 1-iodonaphthalene **1a** (50.8 mg, 0.20 mmol, 1.0 equiv), *O*-ethyl *Se*-phenyl carbonoselenoate (68.7 mg, 0.30 mmol, 1.5 equiv) and ethyl acrylate (30.0 mg, 0.30 mmol, 1.5 equiv) in DCP (4.0 mL) afforded a mixture of **3i** (27.7 mg, 39%) and **4** (14.9 mg, 25%) (petroleum ether : dichloromethane = 3 : 1). The spectrum data of (*E*)-ethyl 1-(3-ethoxy-3-oxoprop-1-en-1-yl)-2-naphthoate **4** is : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 16.4 Hz, 1 H), 8.18 (d, *J* = 8.0 Hz, 1 H), 7.96 (d, *J* = 8.4 Hz, 1 H), 7.90 - 7.80 (m, 2 H), 7.64 - 7.51 (m, 2 H), 6.09 (d, *J* = 16.4 Hz, 1 H), 4.39 (q, *J* = 7.2 Hz, 2 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 1.42 - 1.38 (m, 3 H), 1.38 - 1.34 (m, 3 H). **^{13}C NMR** (101 MHz, CDCl3) δ 167.5, 166.2, 143.4, 136.0, 135.0, 130.9, 128.5, 128.2, 127.9, 127.1, 127.0, 126.7, 125.6, 125.0, 61.4, 60.7, 14.3, 14.2. **HRMS (ESI)** calcd. for $C_{18}H_{18}O_4Na$ $[M+Na]^+$ 321.1103, found 321.1105.

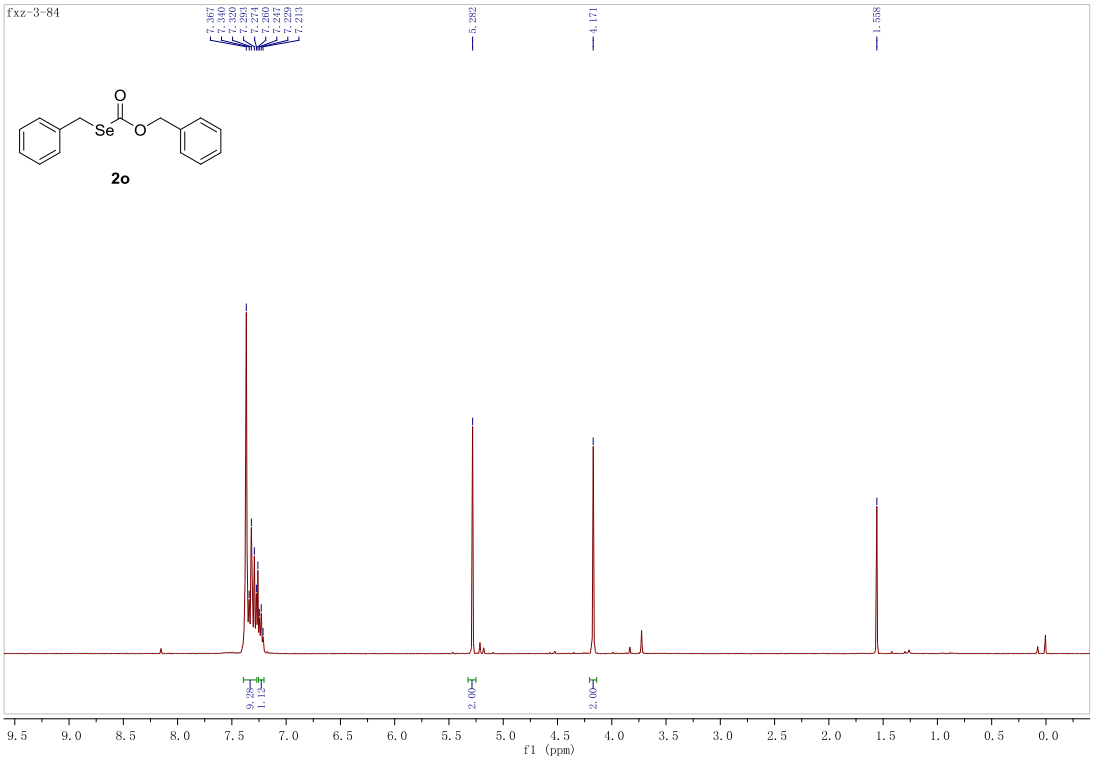
c) The Reaction in the Presence of TEMPO



A flame-dried sealed tube was charged with 1-iodonaphthalene **1a** (50.8 mg, 0.2 mmol, 1.0 equiv), selenate **2f** (82.6 mg, 0.30 mmol, 1.5 equiv), TEMPO (62.5 mg, 0.4 mmol, 2.0 euiv), $PdCl_2$ (3.5 mg, 0.02 mmol, 10 mol %), TFP (11.6 mg, 0.05 mmol, 25 mol %), norbornene (56.5 mg, 0.60 mmol, 3.0 equiv), K_2CO_3 (82.9 mg, 0.60 mmol, 3.0 equiv) and 1,3-dichloropropane (4.0 ml). The reaction was stirred at 100 ^oC in an oil bath for 16 h. After being cooled to room temperature, the mixture was filtered through a pad of celite with EtOAc as the eluent. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 4:1) to give **3f** (63.4 mg, 79%).

References:

1. P. G. Gassman, A. Miura, T. Miura. *J. Org. Chem.* **1982**, *47*, 951.
2. W. Munbunjong, E. H. Lee, P. Ngernmaneerat, S. J. Kim, G. Singh, W. Chavasiri, D. O. Jang, *Tetrahedron* **2009**, *65*, 2467.
3. B. Movassagh, A. Tatar, *Org. Prep. Proc. Int.* **2008**, *40*, 477.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7.320
7.293
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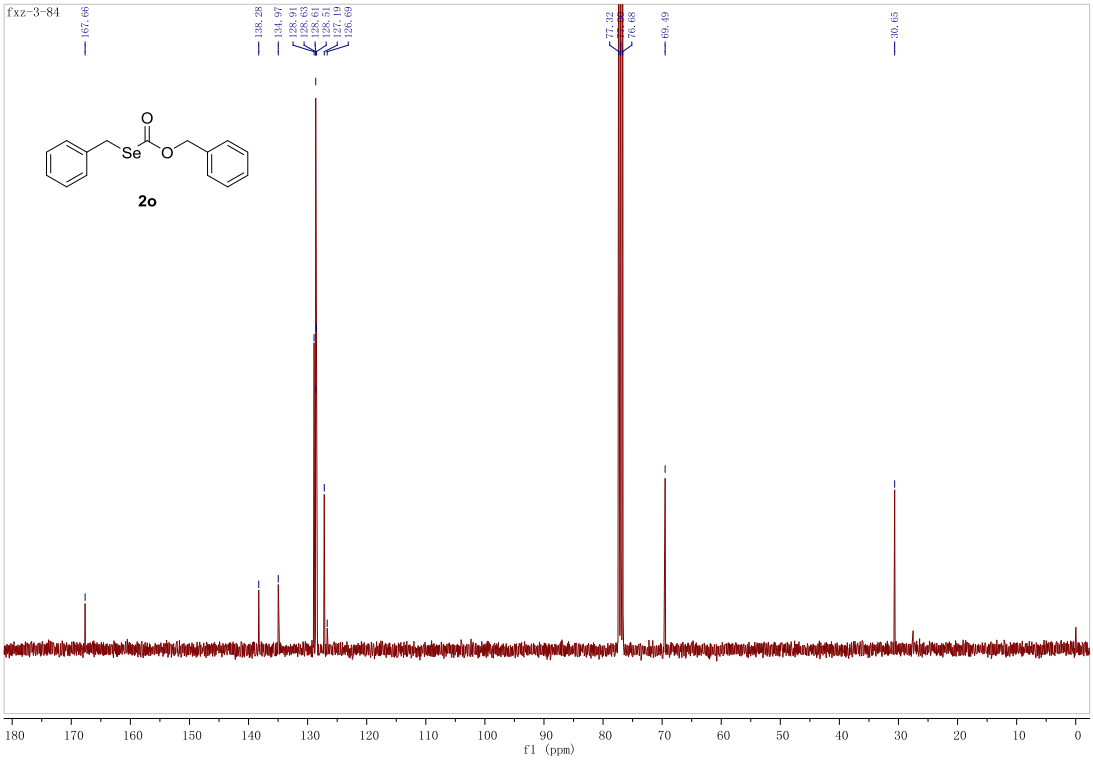
7.247
7.229
7.209
7.210
5.282
4.171
1.558
Se
O
O
2o
9.28
1.12
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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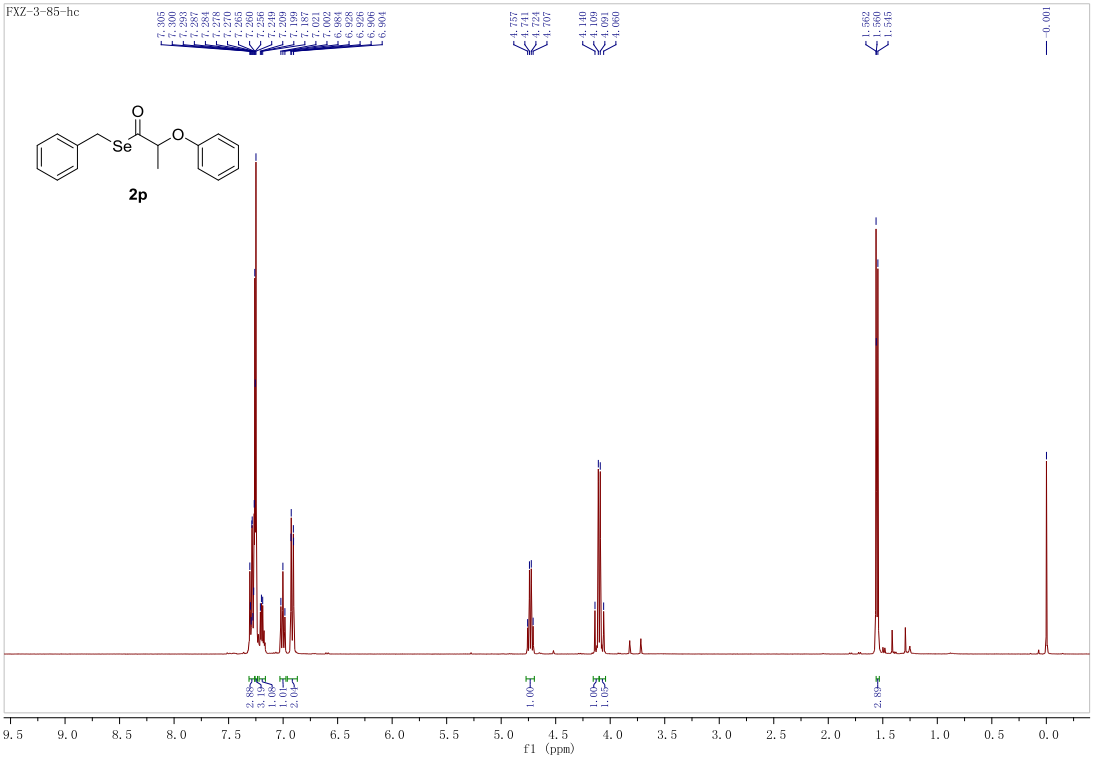
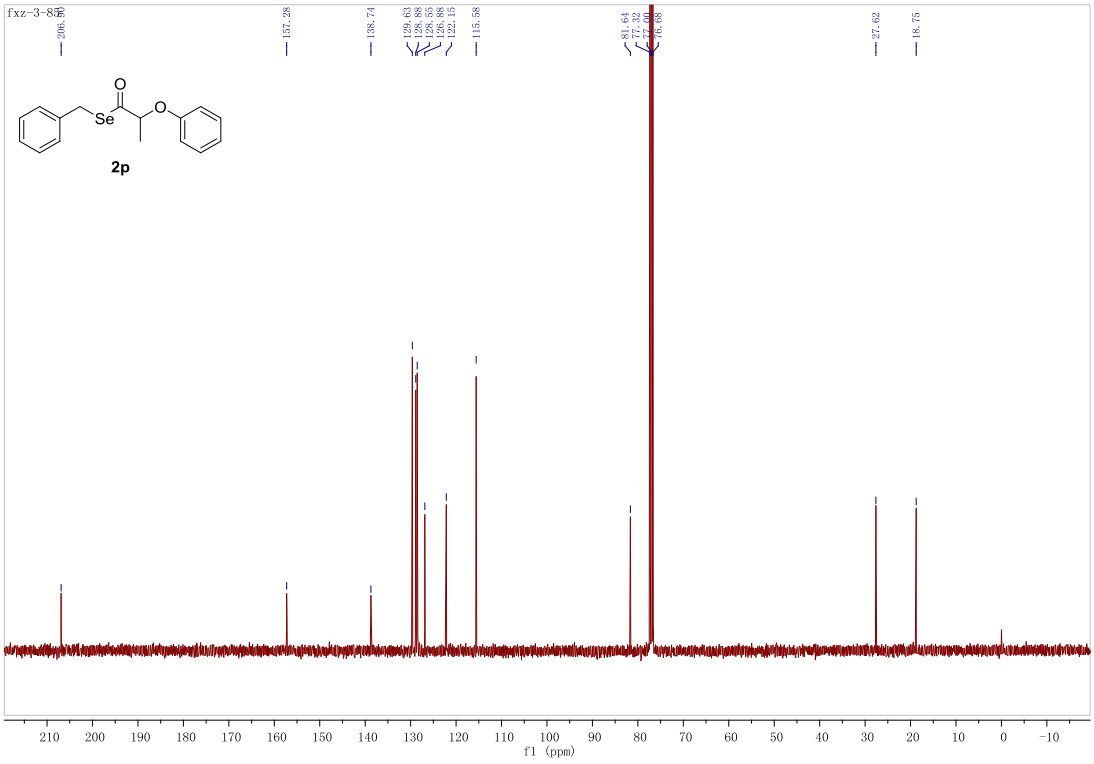
138.28
134.97
128.91
128.63
128.51
128.37
127.19
126.69
77.32
76.68
69.49
30.65
Se
O
O
2o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


FXZ-3-85-hc
2p
f1 (ppm)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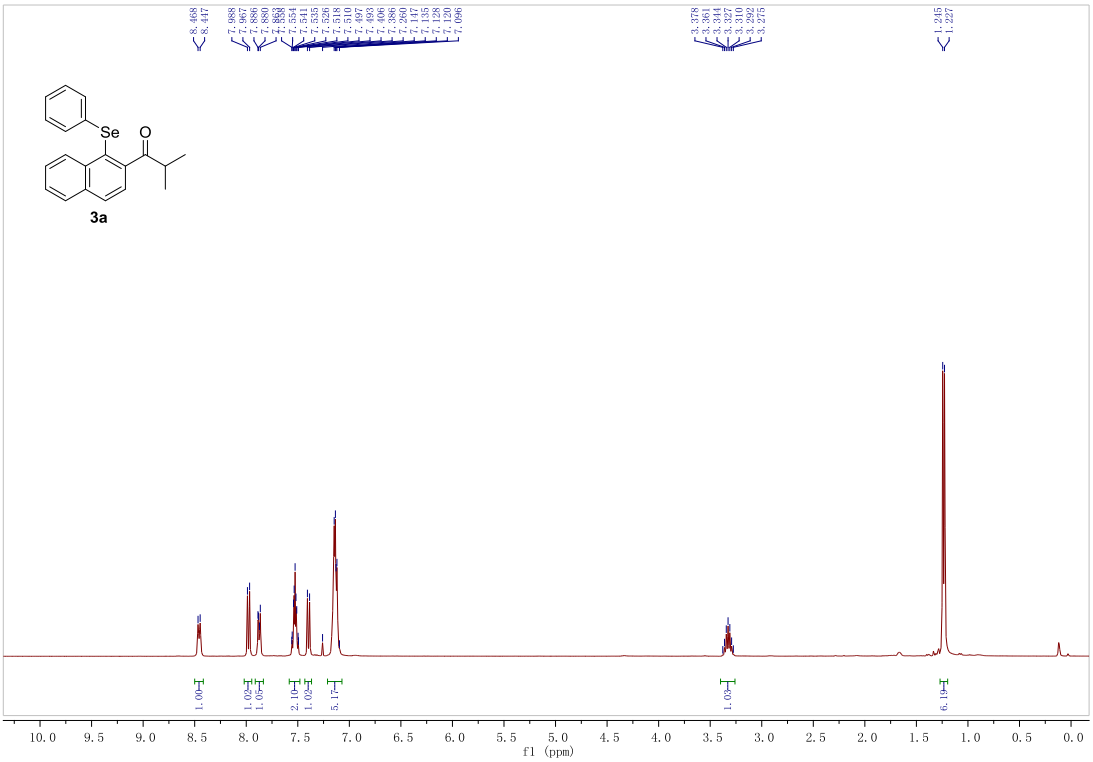
f1 (ppm)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7.880
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7.541
7.535
7.526
7.518
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7.469
7.406
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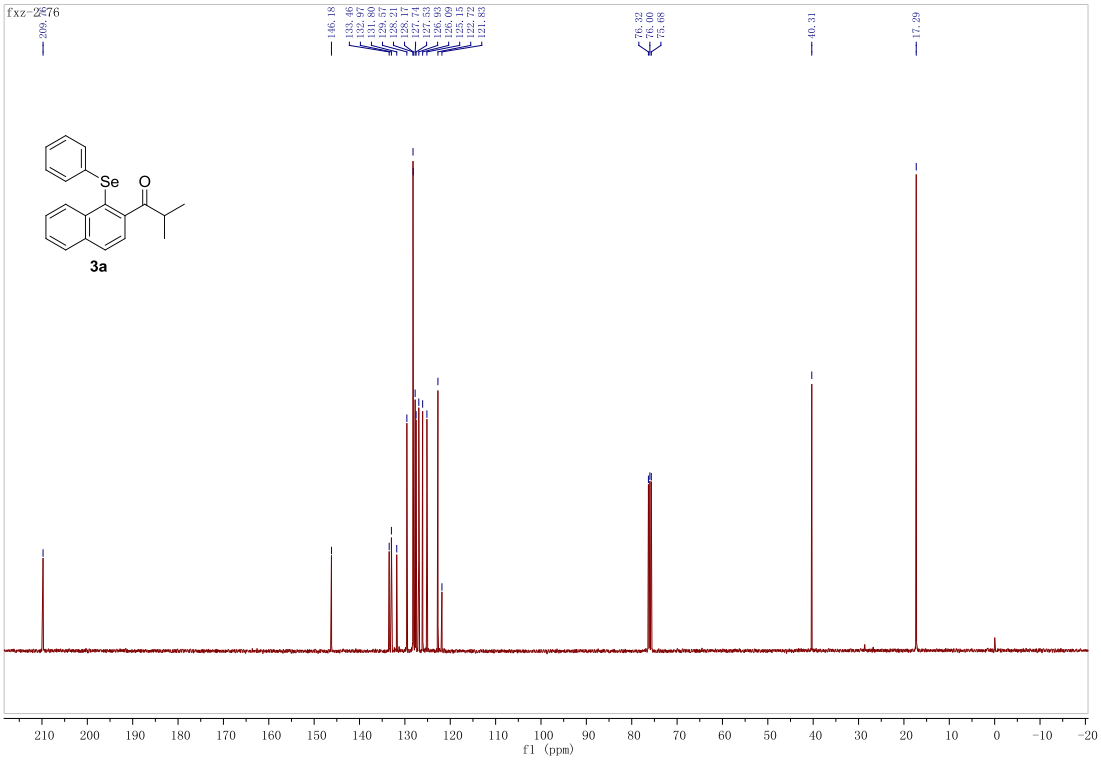
7.147
7.135
7.128
7.120
7.096
3.378
3.361
3.344
3.327
3.310
3.292
3.275
1.245
1.227
Se
O
3a
1.00
1.02
1.05
2.10
1.02
5.17
1.03
6.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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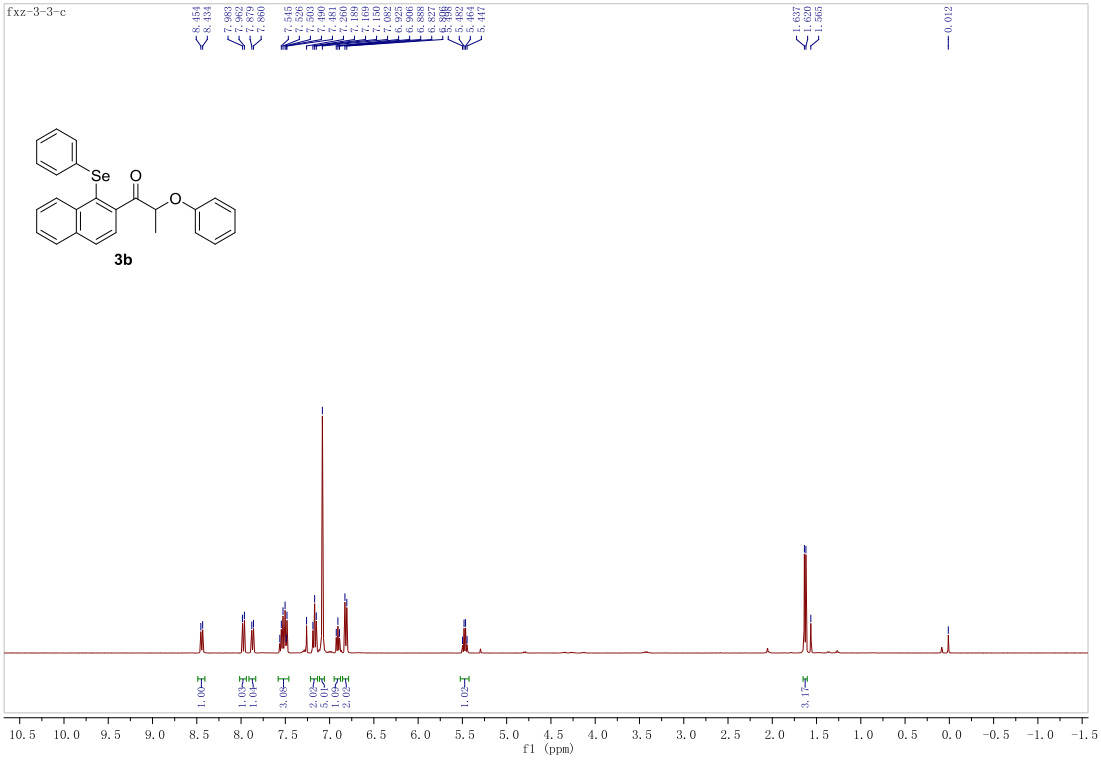
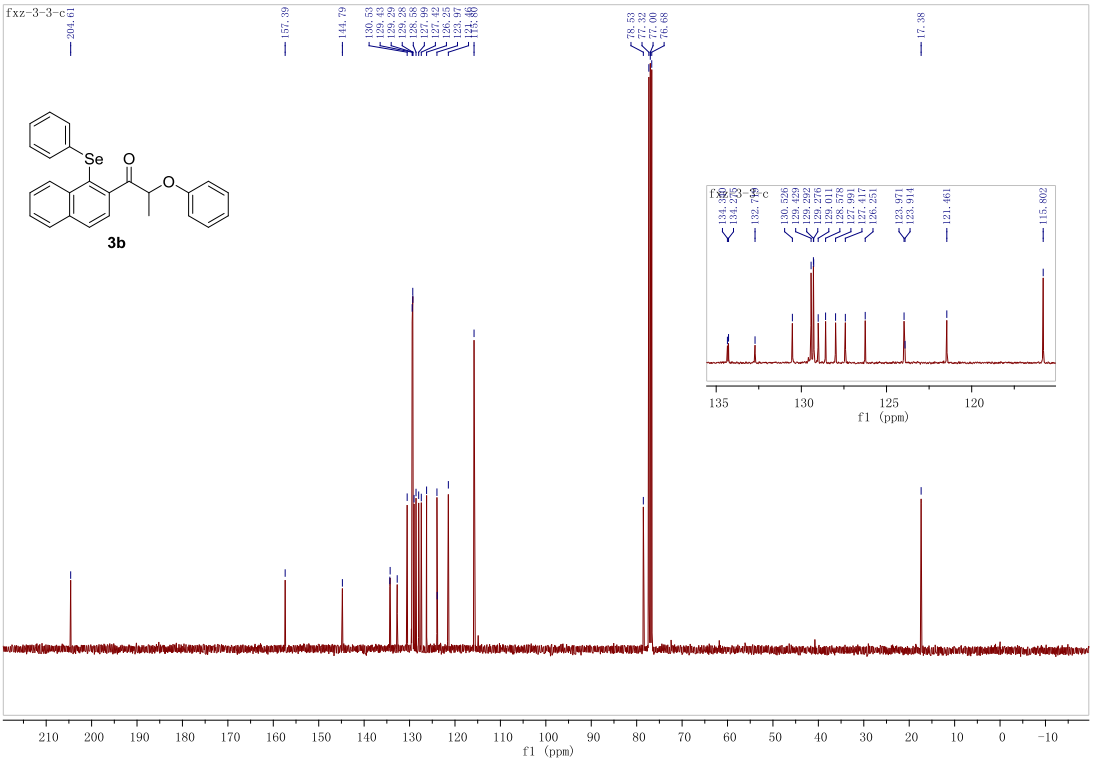
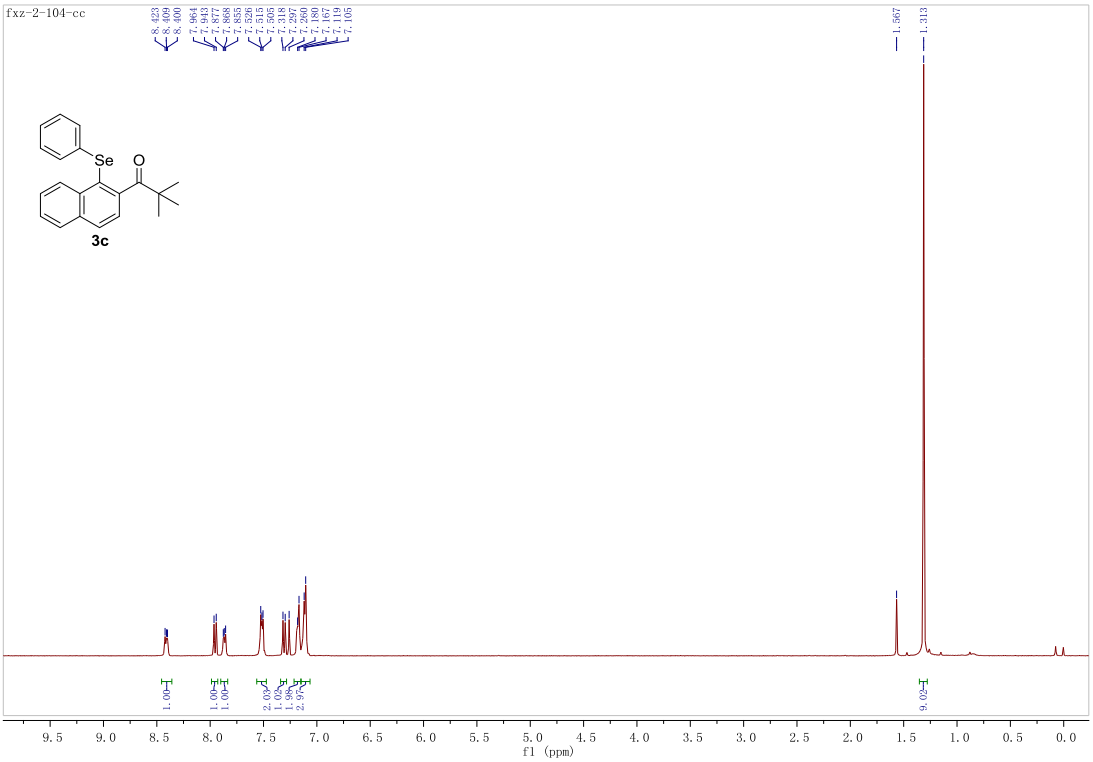
128.21
128.17
127.74
127.53
126.53
126.09
125.15
122.72
121.83
76.32
76.00
75.68
40.31
17.29
Se
O
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)


fxz-3-3-c
Se
O
O
3b
f1 (ppm)


fxz-3-3-c
Se
O
O
3b
f1 (ppm)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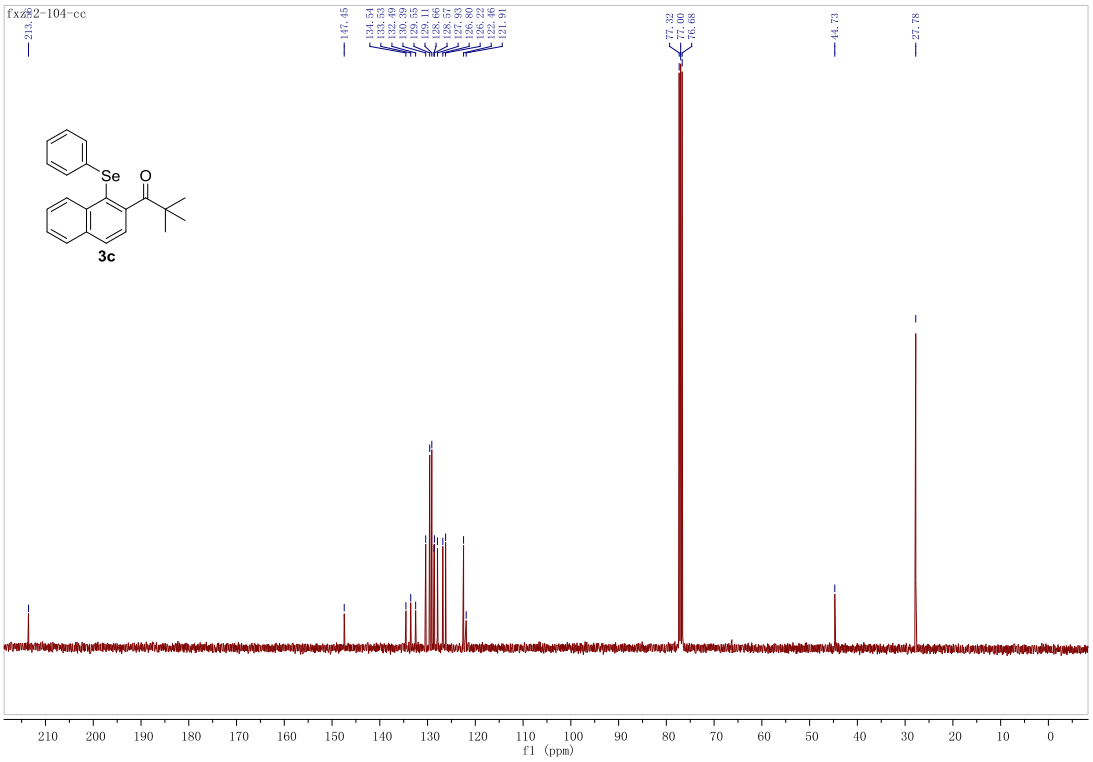
7.515
7.505
7.318
7.297
7.260
7.189
7.180
7.167
7.119
7.105
1.567
1.313
Se
O
3c
1.00
1.00
1.06
2.03
1.02
1.98
2.97
9.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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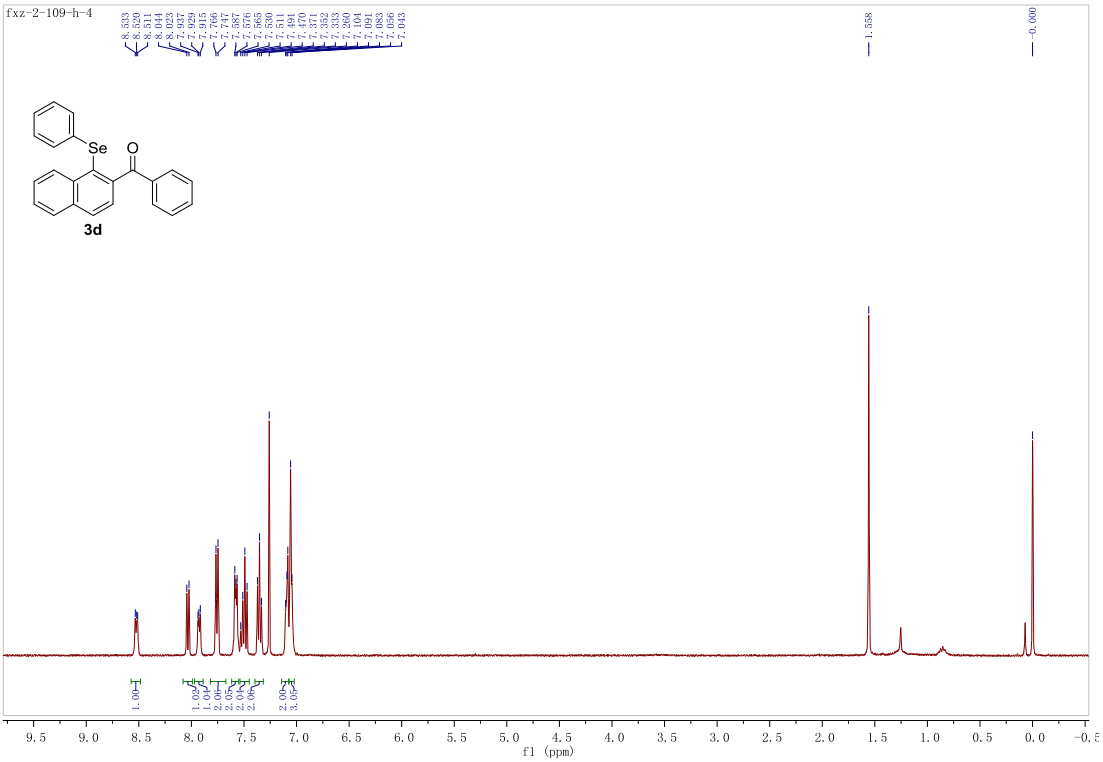
134.54
133.53
132.49
130.39
129.55
129.11
128.66
128.57
127.93
126.80
126.22
122.46
121.91
77.32
77.09
76.68
44.73
27.78
Se
O
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.511
8.044
8.023
7.937
7.929
7.915
7.906
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7.587
7.576
7.565
7.530
7.511
7.491
7.470
7.357
7.352
7.333
7.260
7.104
7.094
7.083
7.056
7.043
1.558
-0.000
Se
O
3d
1.00
1.02
1.04
2.06
2.05
2.04
2.06
2.06
3.05
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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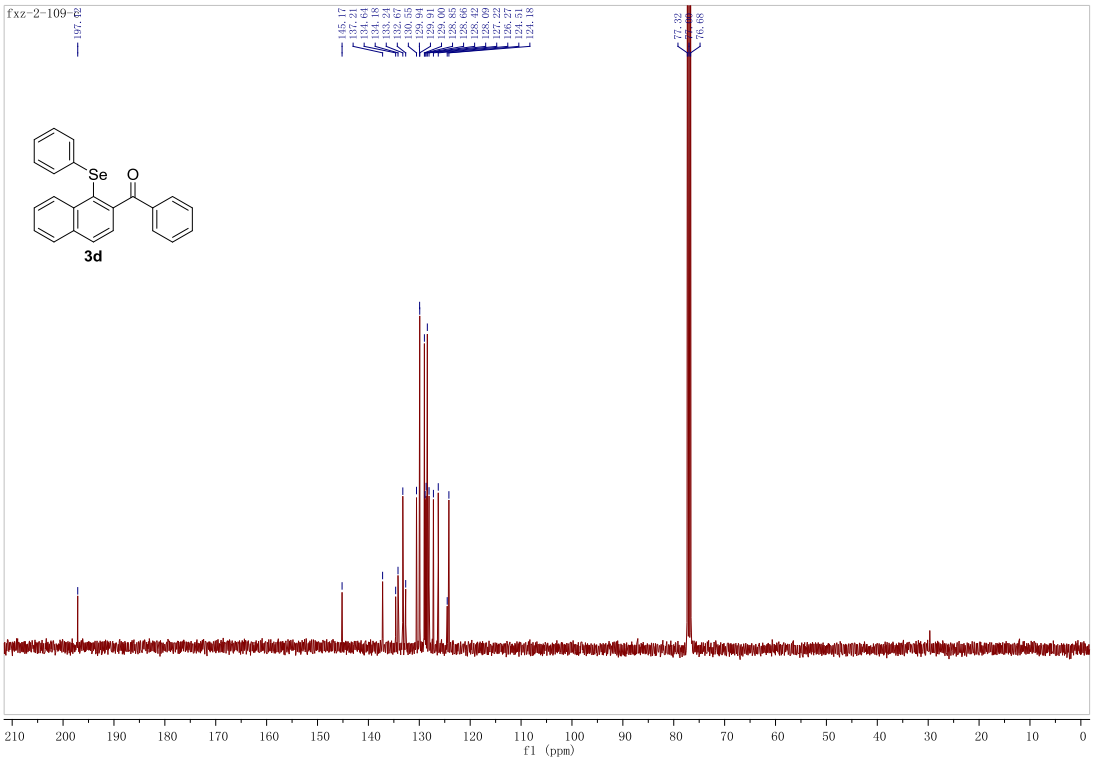
f1 (ppm)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129.00
128.85
128.66
128.42
128.09
127.22
126.27
124.51
124.18
77.32
76.68
Se
O
3d
210
200
190
180
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50
40
30
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10
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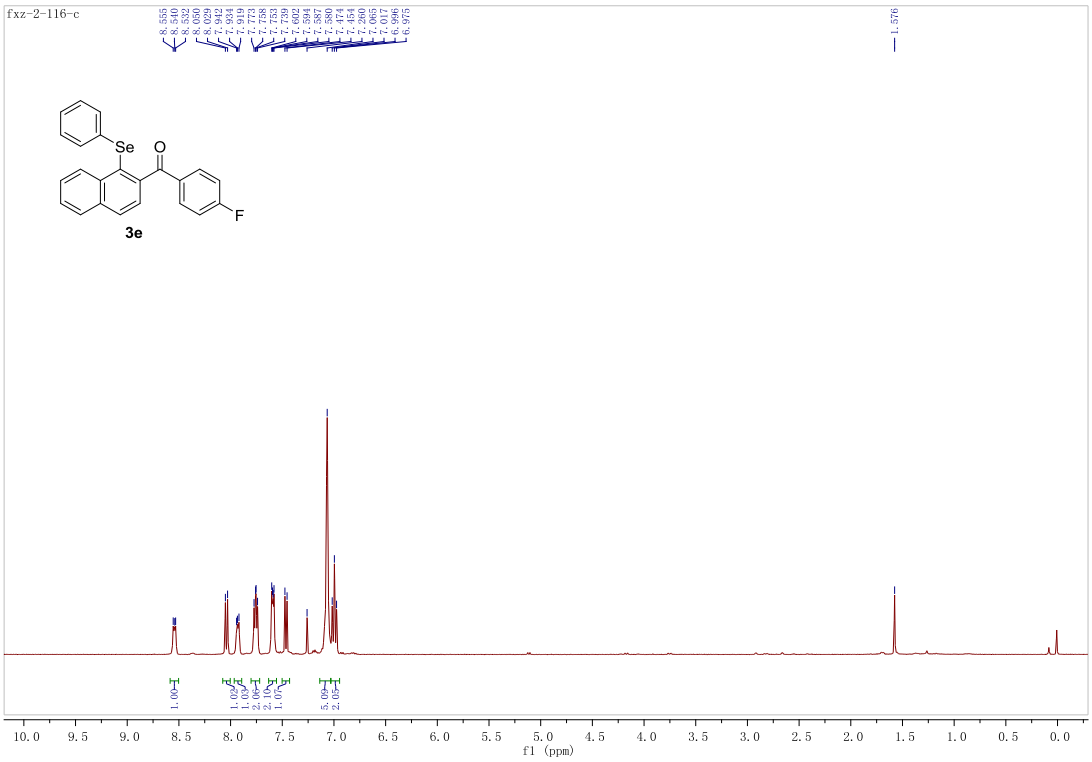
f1 (ppm)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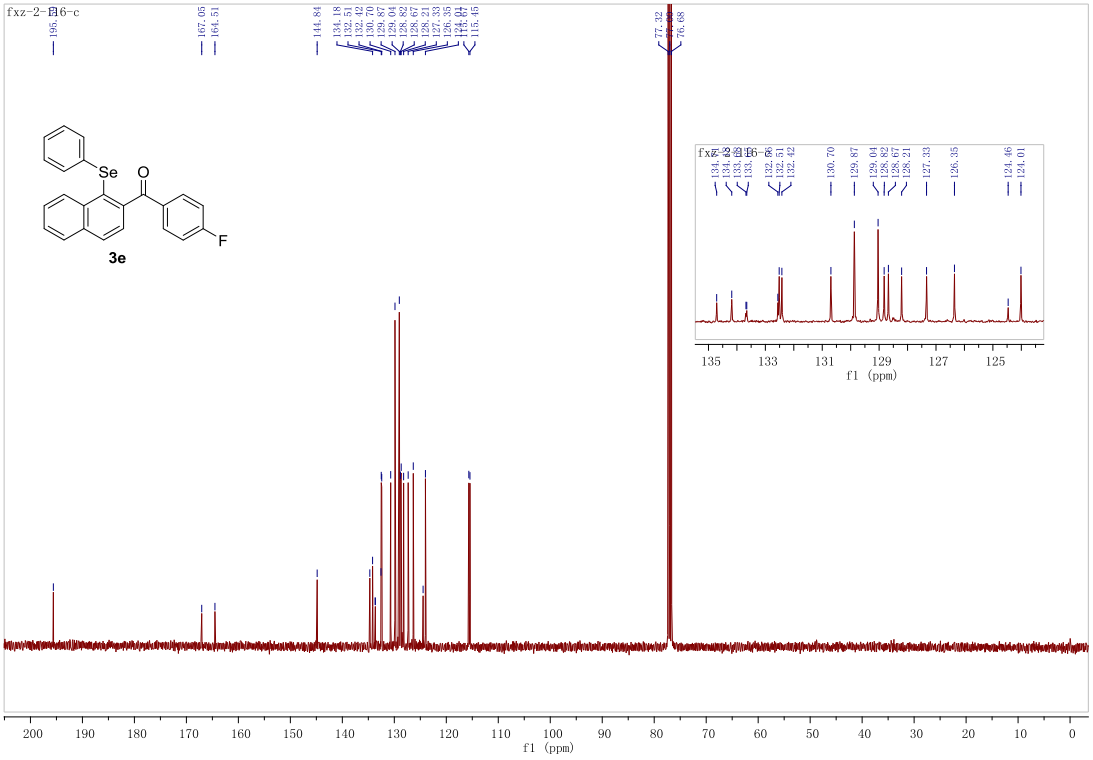
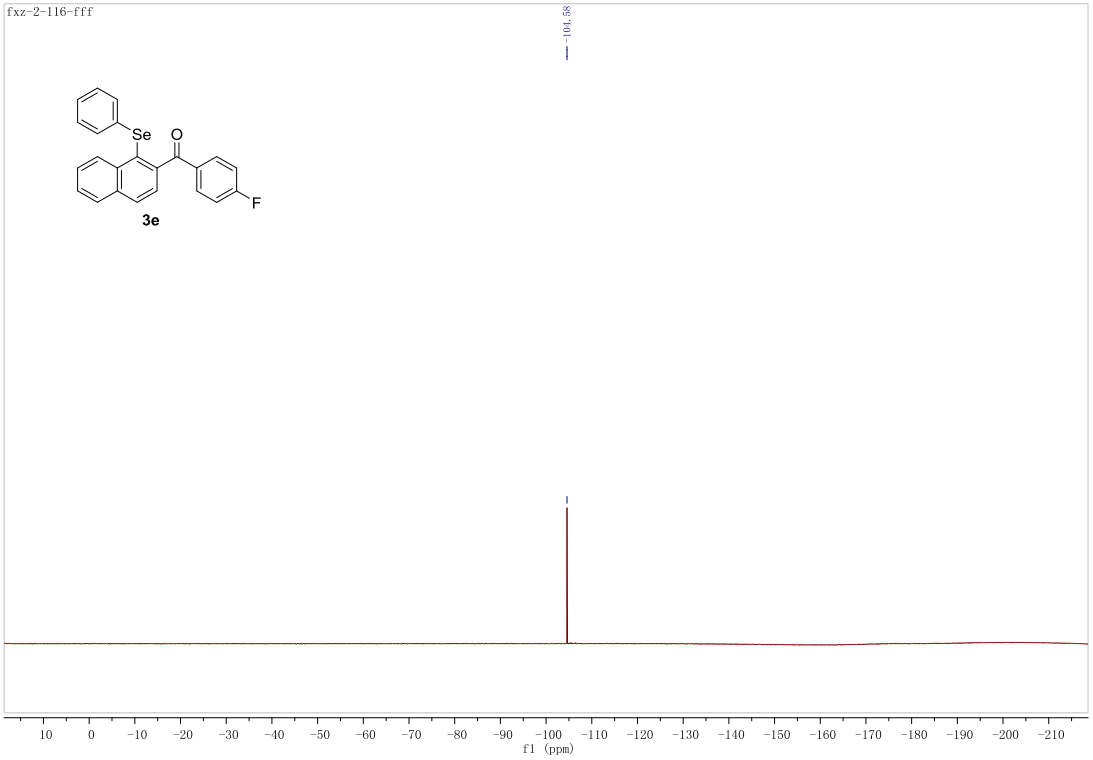
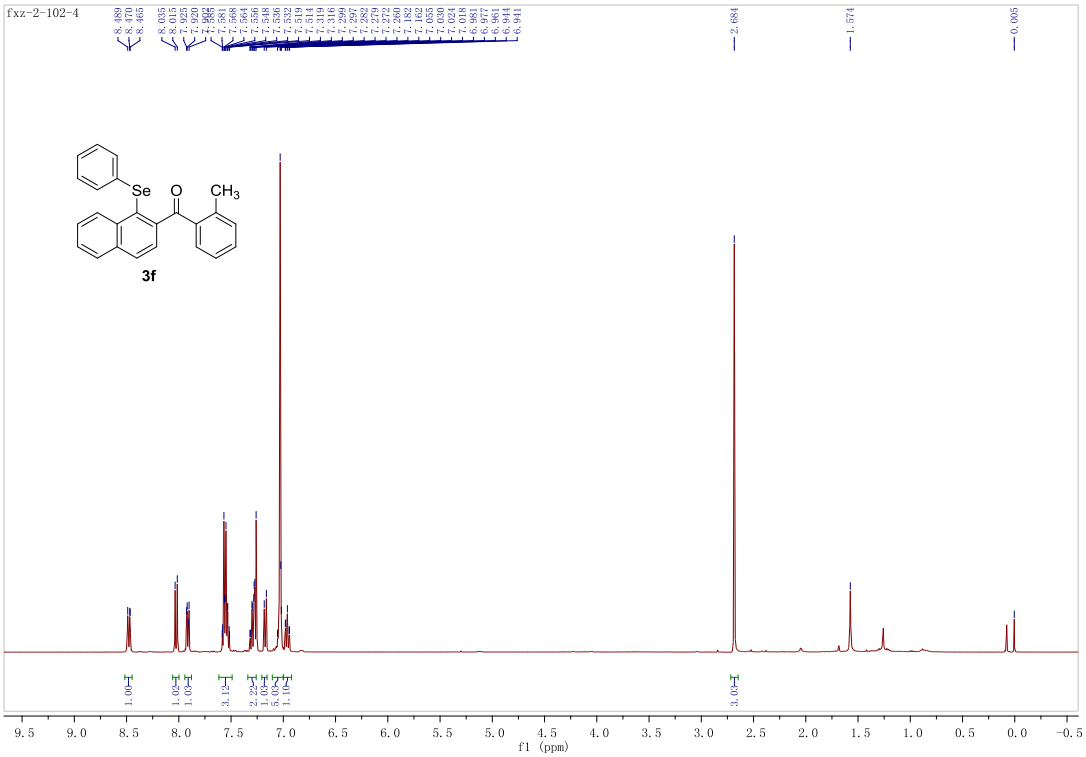
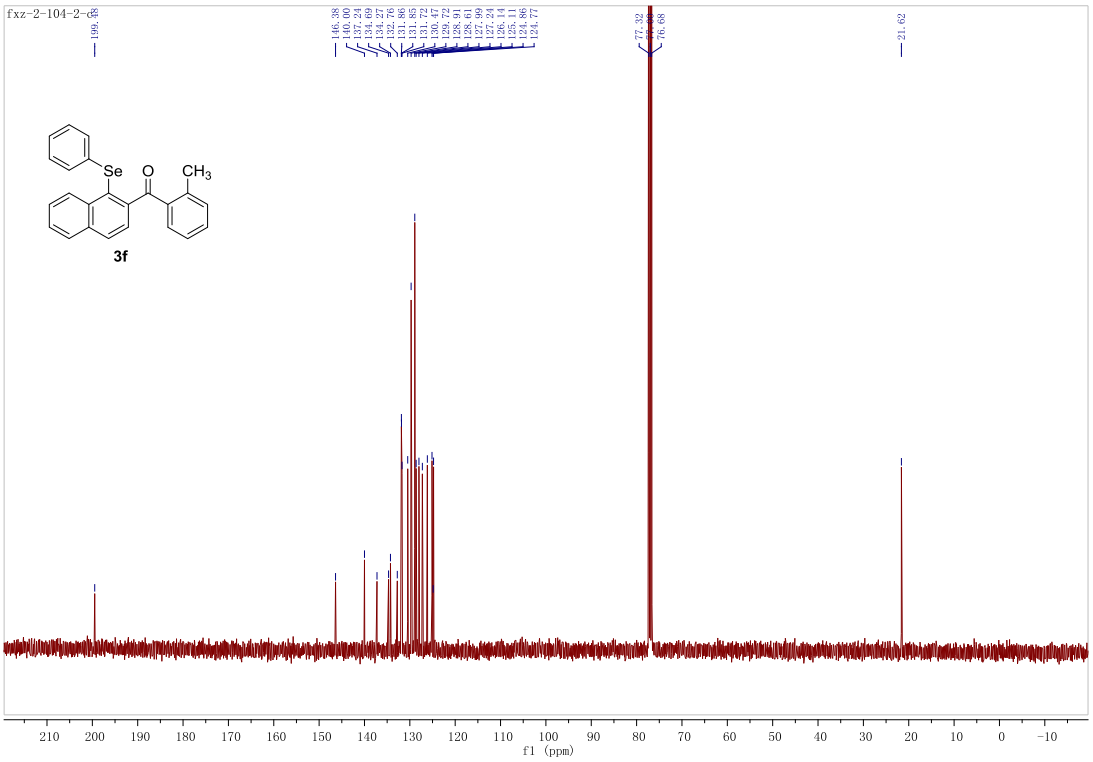
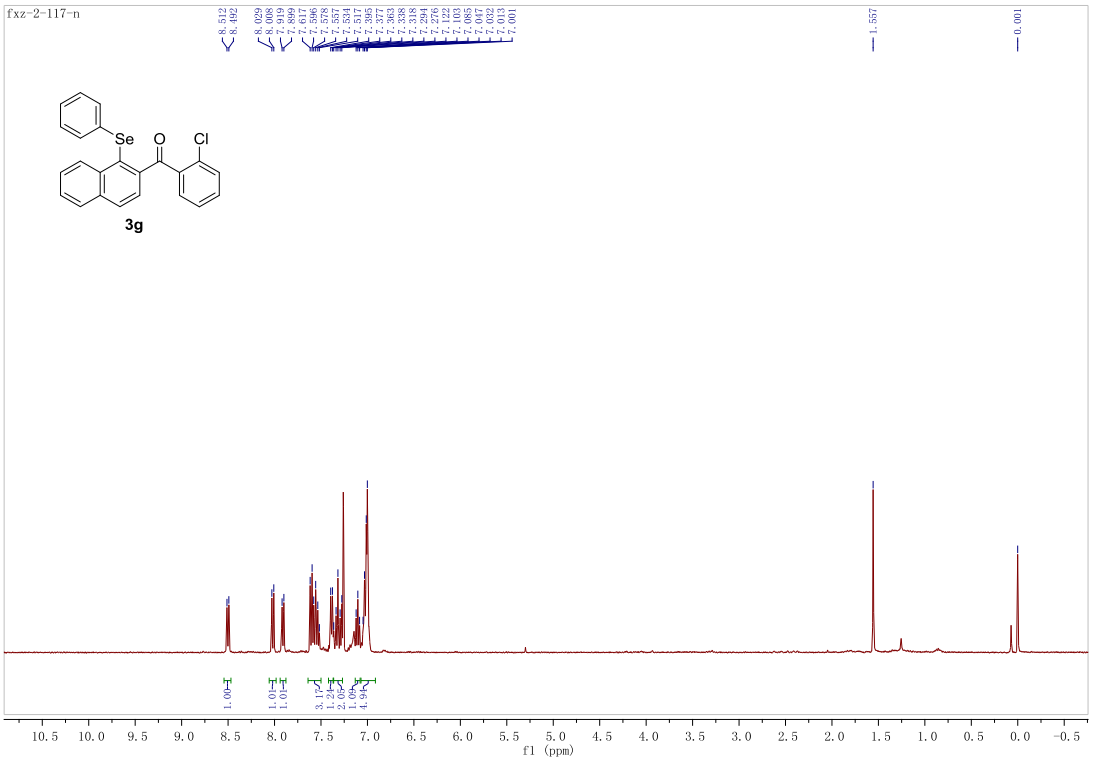
O
F
3e
f1 (ppm)

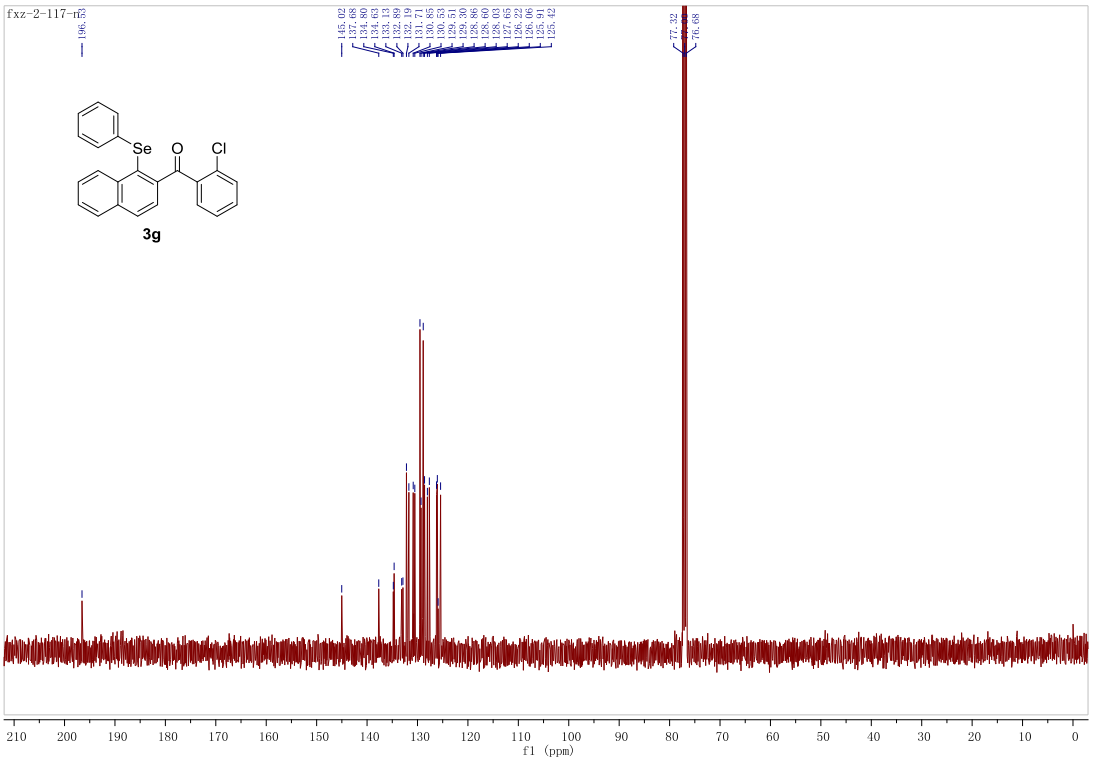

fxz-2-116-c
Se
O
F
3e
f1 (ppm)

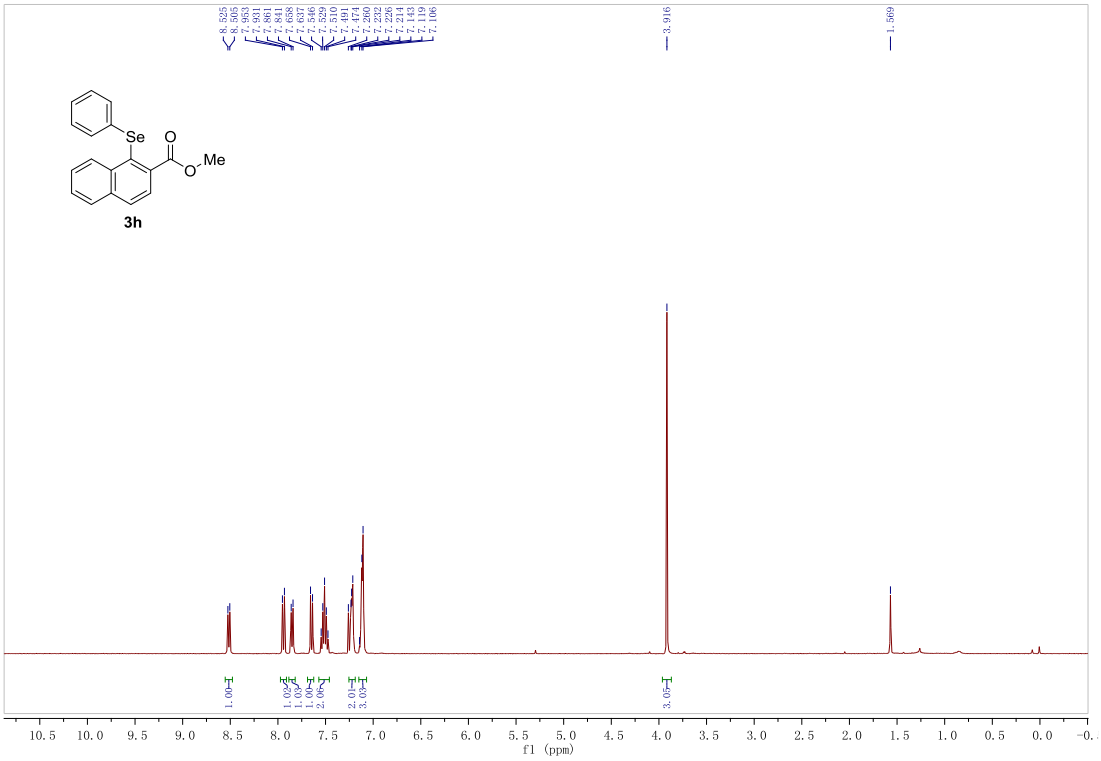

fxz-2-116-fff
-104.58
Se
O
F
3e
f1 (ppm)

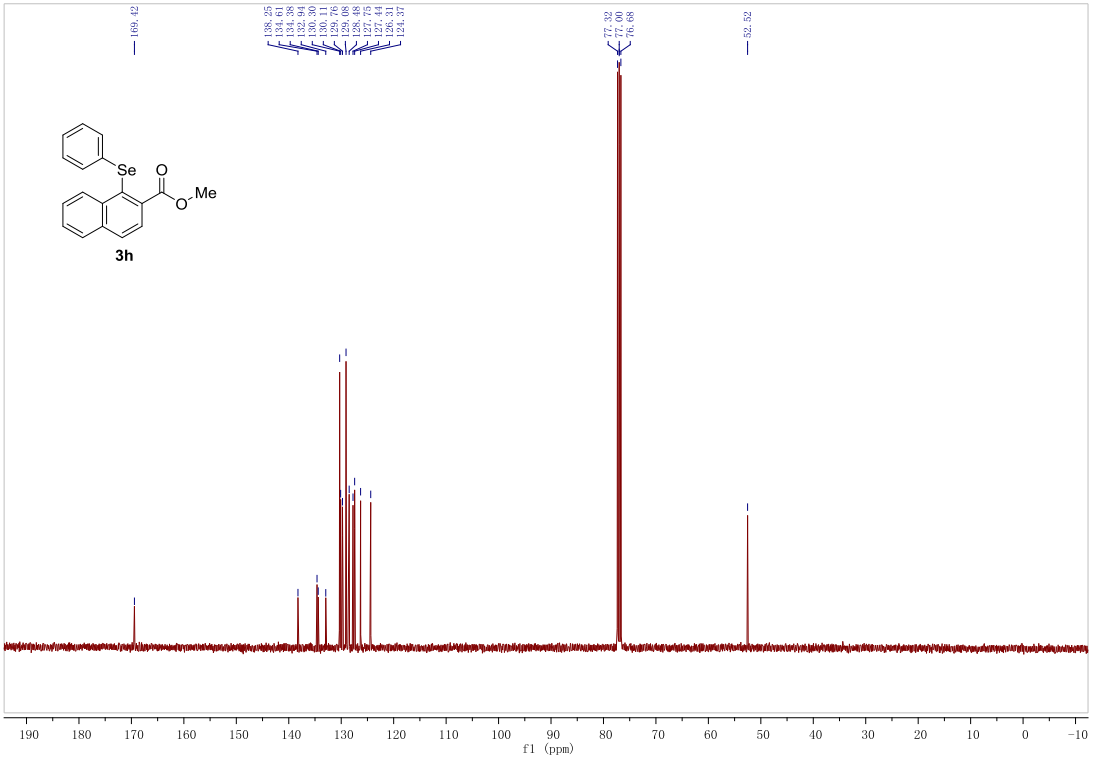

fxz-2-102-4
8.480
8.470
8.465
8.035
8.015
7.925
7.920
7.581
7.568
7.564
7.556
7.548
7.536
7.532
7.514
7.511
7.319
7.316
7.309
7.299
7.297
7.282
7.279
7.272
7.269
7.182
7.162
7.055
7.030
7.024
7.018
6.981
6.977
6.964
6.944
6.941
2.684
1.574
0.005
Se
O
CH3
3f
1.00
1.02
1.03
3.12
2.22
1.03
5.03
1.10
3.03
f1 (ppm)

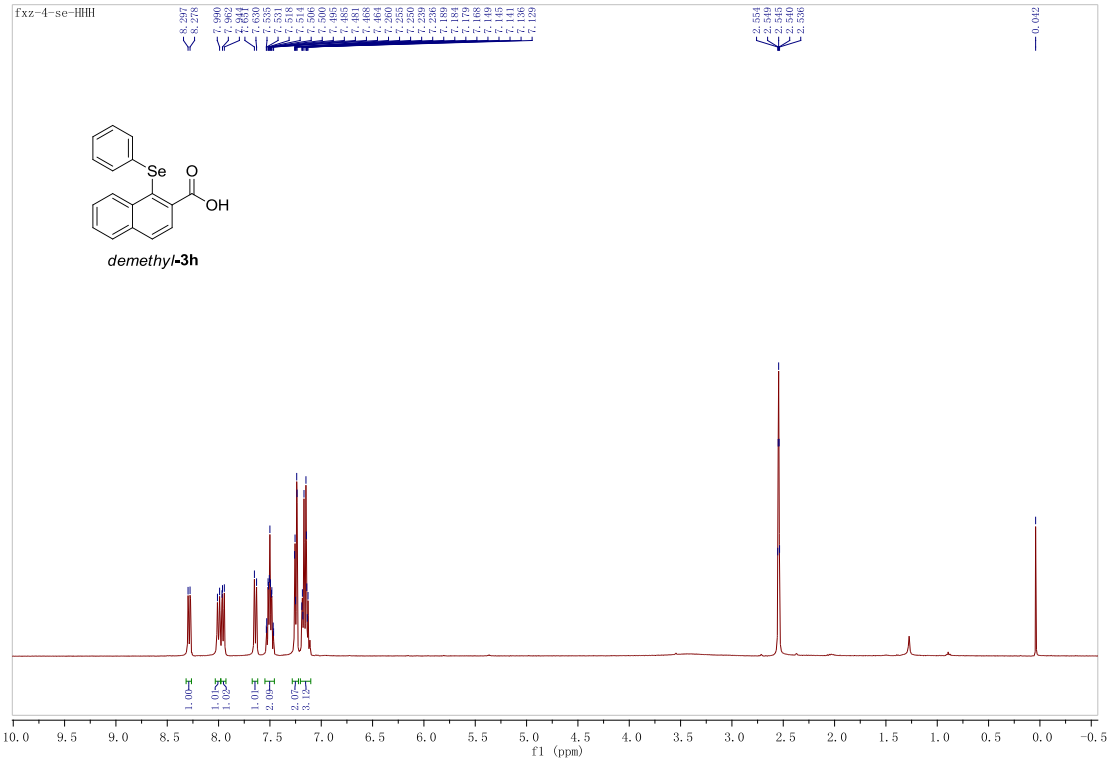

fxz-2-104-2-c
199.35
146.38
140.00
137.24
134.69
134.27
132.76
131.86
131.85
131.72
130.47
129.72
128.91
128.41
127.99
127.24
126.14
125.11
124.86
124.77
77.32
77.00
76.68
21.62
Se
O
CH3
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


fxz-2-117-n
8.512
8.492
8.029
8.008
7.919
7.899
7.617
7.596
7.578
7.557
7.534
7.517
7.396
7.377
7.363
7.338
7.318
7.294
7.276
7.122
7.103
7.085
7.047
7.032
7.013
7.001
1.557
0.001
1.00
1.01
1.01
3.17
2.24
2.22
1.09
4.94
Se
O
Cl
3g
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

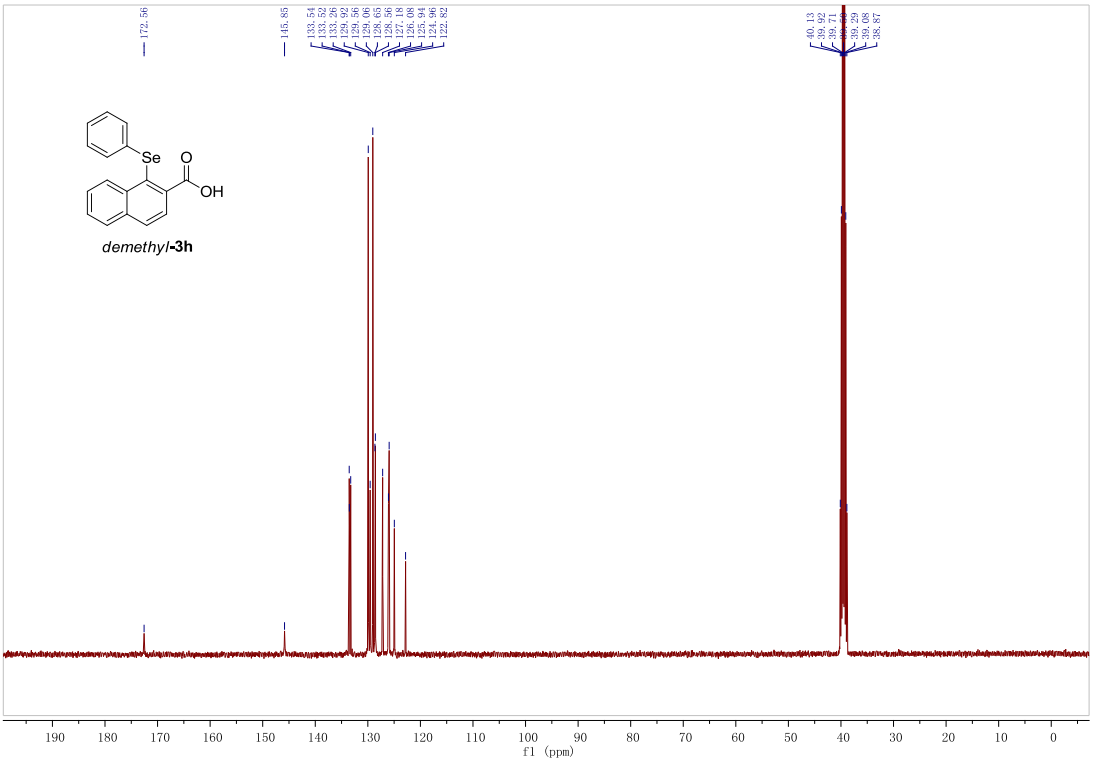

fxz-2-117-13
196.53
145.02
137.68
134.80
134.63
133.13
132.89
132.19
131.71
130.85
130.53
129.71
129.30
128.86
128.69
128.03
127.65
126.22
126.06
125.91
125.42
77.32
76.68
Se
O
Cl
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

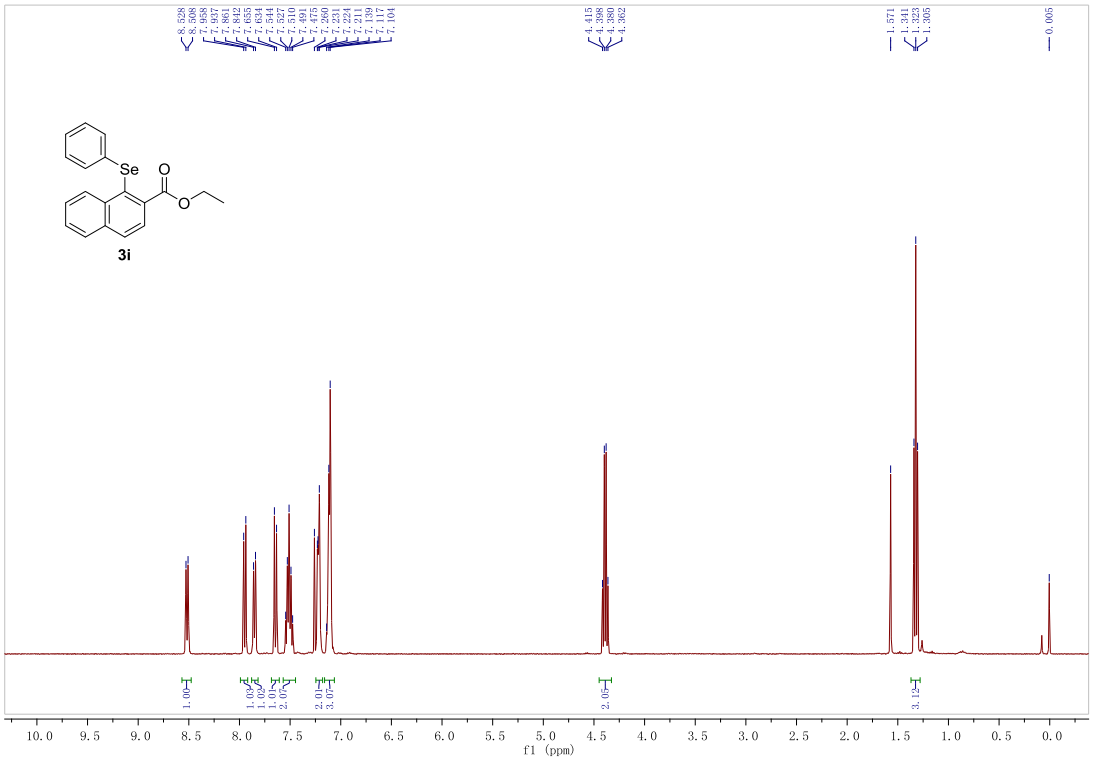

8.525
8.505
7.953
7.941
7.861
7.841
7.638
7.627
7.549
7.529
7.510
7.491
7.474
7.260
7.232
7.226
7.214
7.143
7.119
7.106
3.916
1.569
Se
O
O
Me
3h
1.00
1.02
1.00
2.00
2.01
3.03
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

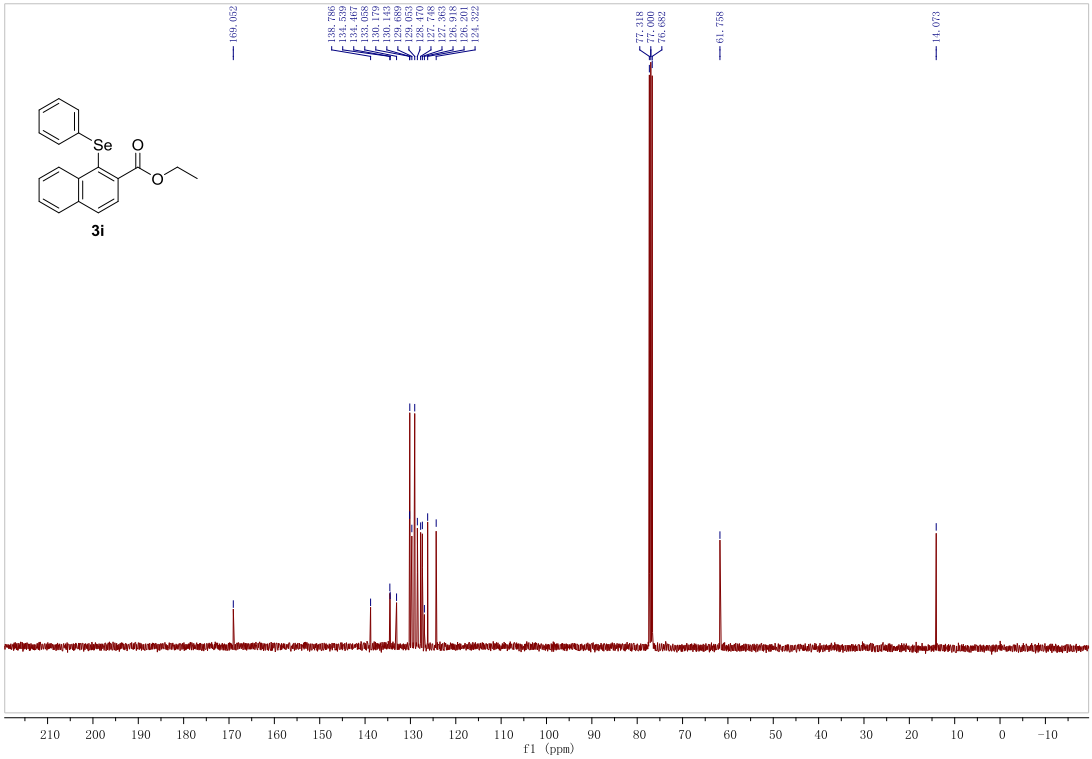

169.42
138.25
134.61
134.38
132.94
131.90
130.11
129.76
129.08
128.48
127.75
127.44
126.31
124.37
77.32
77.00
76.68
52.52
Se
O
O
Me
3h
f1 (ppm)

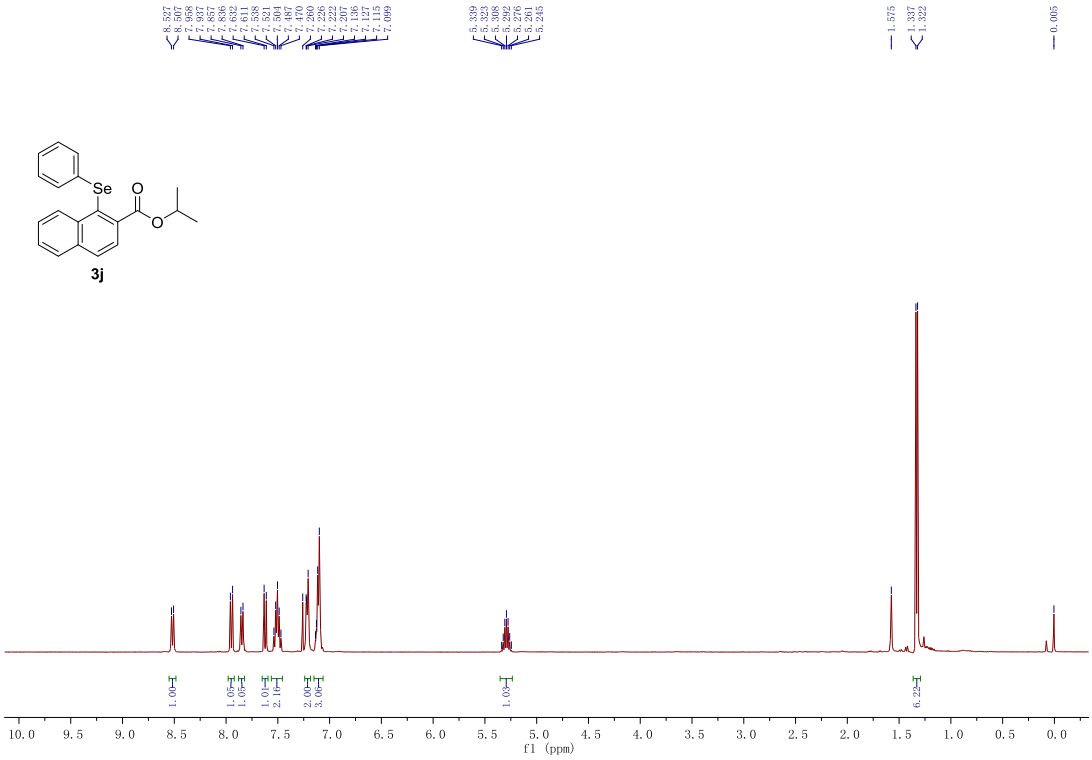

fxz-4-se-HHH
8.297
8.278
7.990
7.962
7.630
7.535
7.531
7.518
7.514
7.506
7.496
7.485
7.481
7.468
7.464
7.260
7.255
7.250
7.239
7.226
7.189
7.184
7.179
7.165
7.149
7.145
7.141
7.136
7.129
2.554
2.549
2.545
2.540
2.536
0.042
Se
O
OH
demethyl-3h
1.00
1.01
1.02
1.01
2.00
2.07
3.19
f1 (ppm)

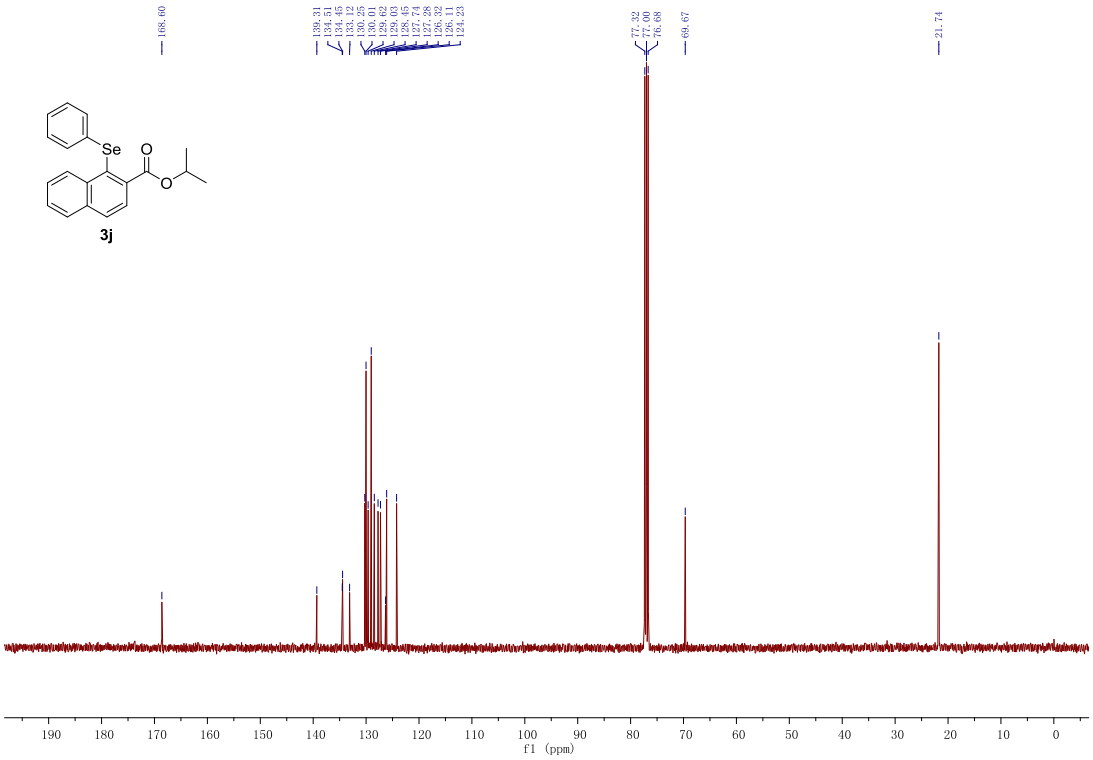
.

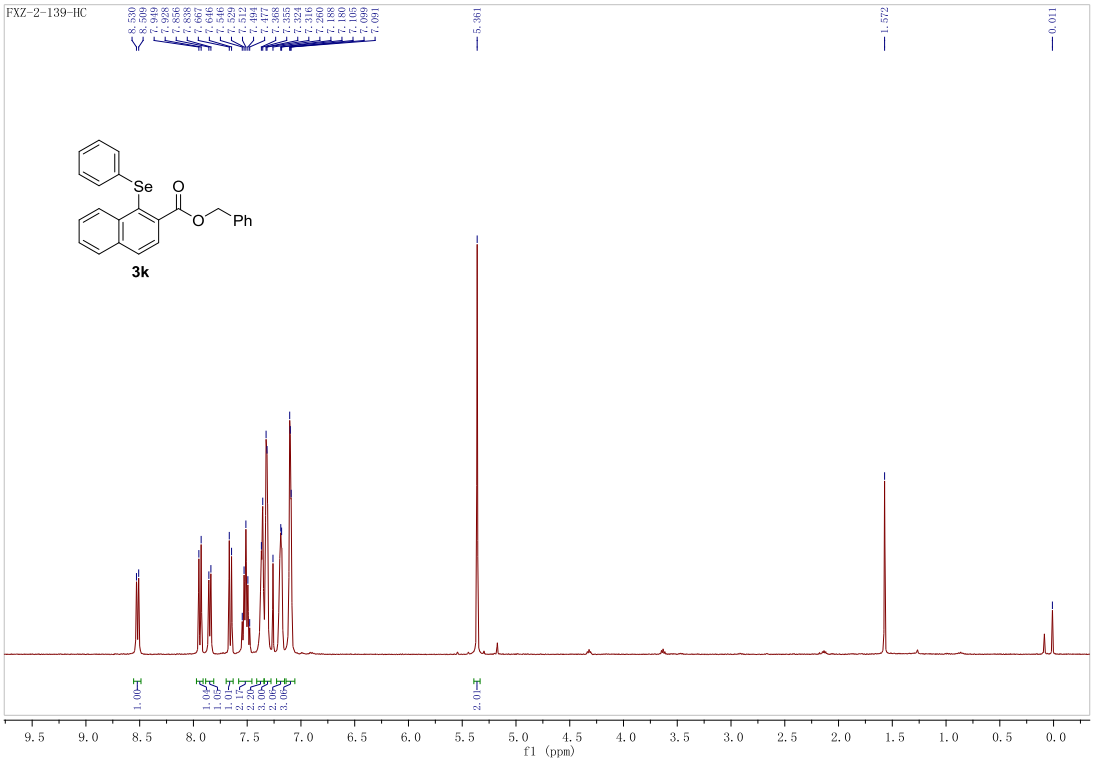

172.56
145.85
133.54
133.52
133.26
129.92
129.56
129.46
128.65
128.56
127.18
126.06
125.94
124.96
122.82
40.13
39.92
39.71
39.50
39.29
39.08
38.87
Se
O
OH
demethyl-3h
f1 (ppm)

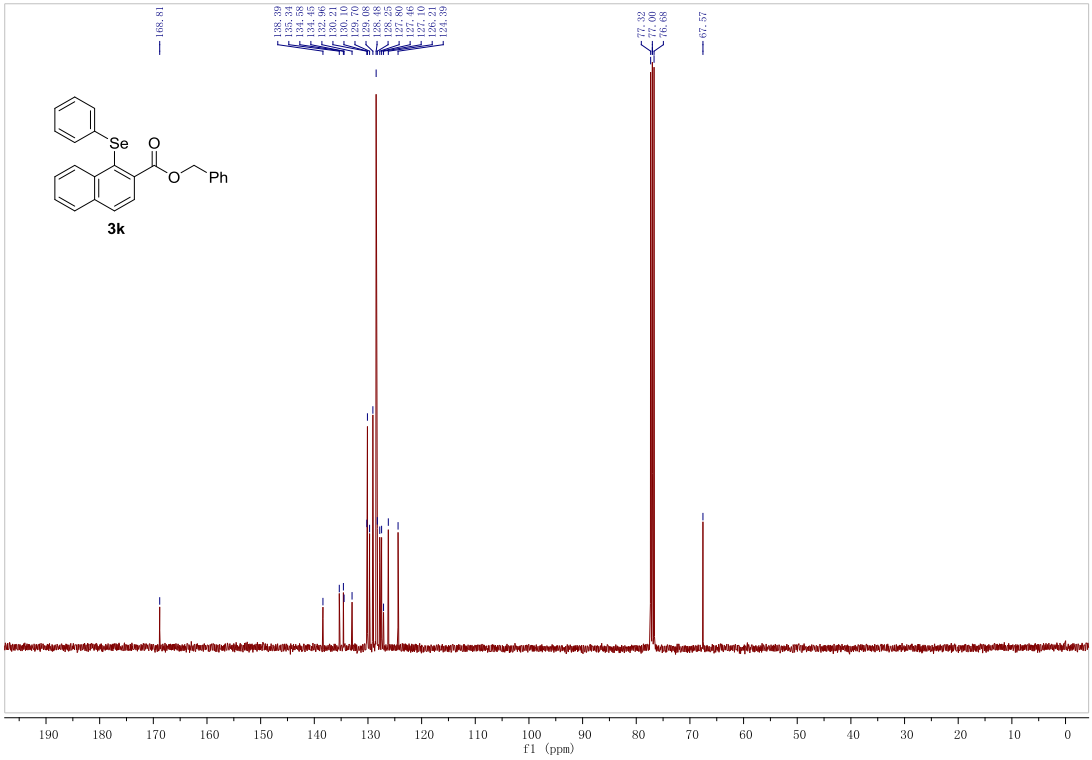

8.528
8.508
7.958
7.937
7.861
7.842
7.655
7.634
7.544
7.527
7.510
7.491
7.475
7.390
7.231
7.224
7.211
7.199
7.117
7.104
4.415
4.398
4.380
4.362
1.571
1.341
1.323
1.305
0.005
Se
O
O
3i
1.00
1.02
1.01
2.07
2.01
3.07
2.05
3.12
f1 (ppm)

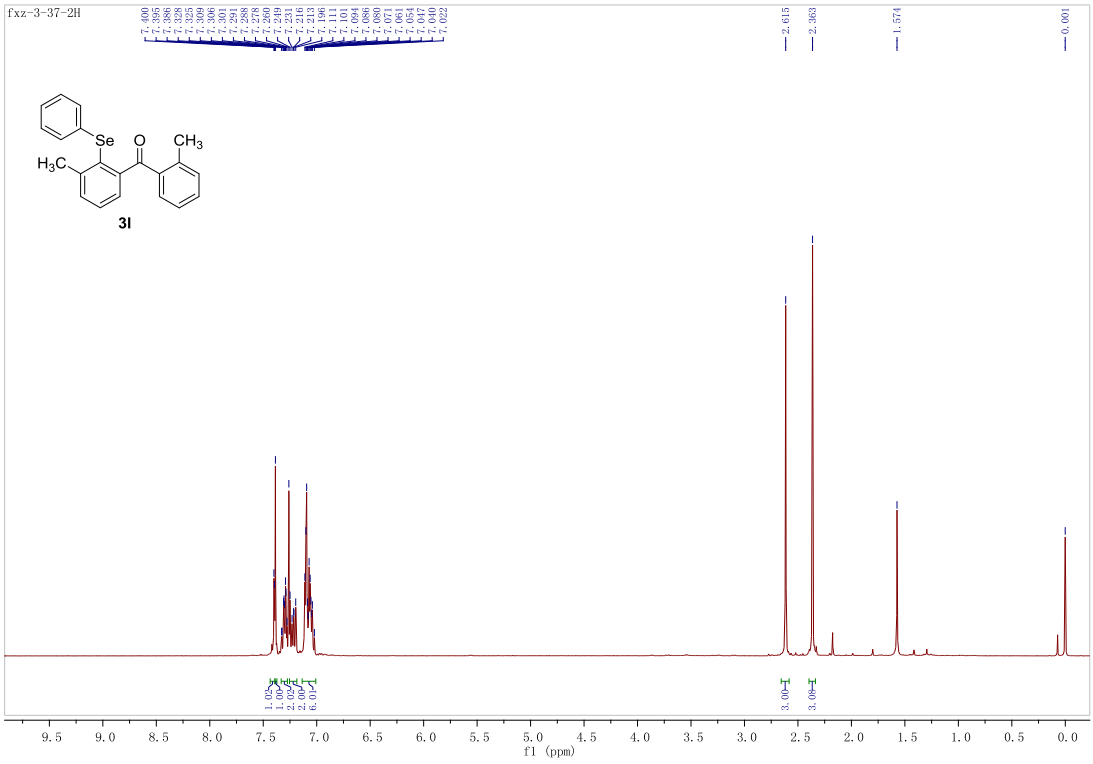

169.052
138.786
134.539
134.407
133.058
130.179
130.143
129.689
129.055
128.470
127.748
127.363
126.948
126.201
124.322
77.318
77.000
76.682
61.758
14.073
Se
O
O
3i
f1 (ppm)


8.527
8.507
7.958
7.957
7.857
7.836
7.632
7.611
7.598
7.521
7.504
7.487
7.470
7.249
7.226
7.222
7.207
7.196
7.127
7.115
7.099
5.339
5.323
5.308
5.292
5.276
5.261
5.245
1.575
1.337
1.322
0.005
Se
O
O
3j
1.00
1.05
1.05
1.01
2.16
2.00
3.00
1.03
6.22
f1 (ppm)


168.60
139.31
134.51
134.45
133.12
130.25
130.01
129.82
129.03
128.45
127.74
127.28
125.32
126.11
124.23
77.32
77.00
76.68
69.67
21.74
Se
O
O
3j
f1 (ppm)


FXZ-2-139-HC
8.530
8.509
7.949
7.928
7.856
7.835
7.697
7.646
7.546
7.529
7.512
7.494
7.477
7.368
7.355
7.324
7.316
7.260
7.188
7.180
7.105
7.099
7.091
5.361
1.572
0.011
Se
O
O
Ph
3k
1.00
1.00
1.01
1.07
2.17
2.25
3.00
2.06
2.06
2.00
2.00
2.00
f1 (ppm)


168.81
138.39
135.34
134.58
134.45
132.96
130.21
130.10
129.70
129.08
128.48
128.25
127.80
127.66
127.46
127.10
126.21
124.39
77.32
77.00
76.68
67.57
Se
O
O
Ph
3k
f1 (ppm)


fxz-3-37-2H
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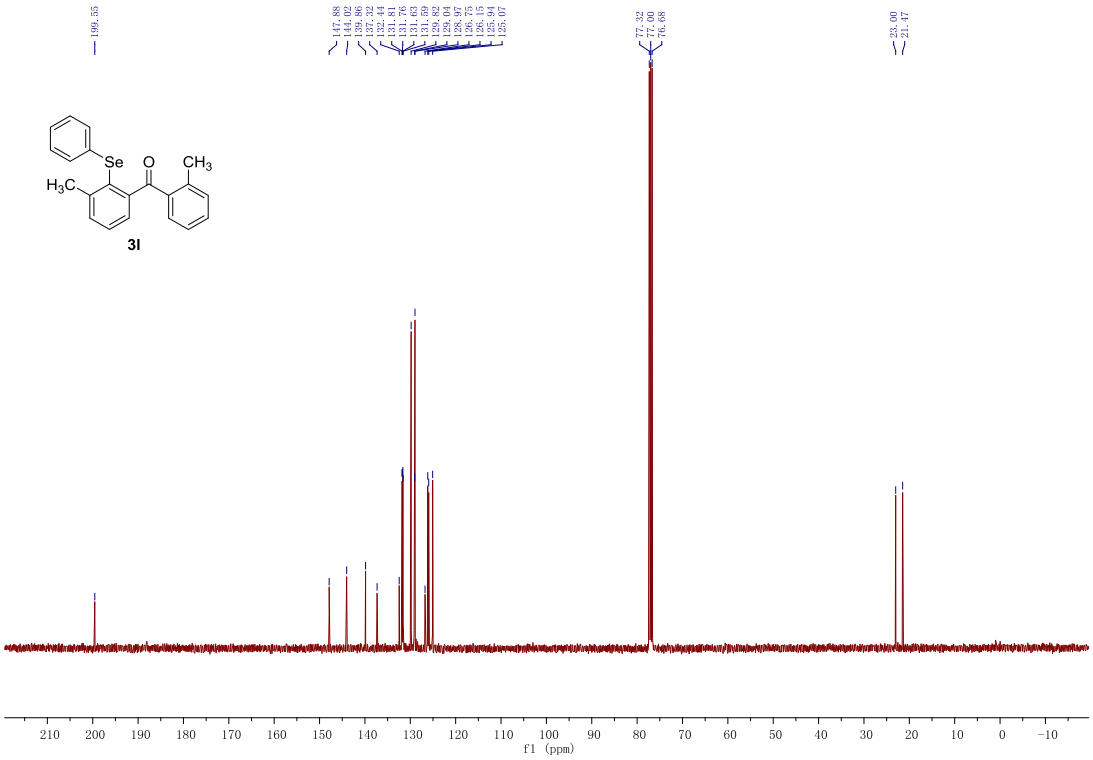
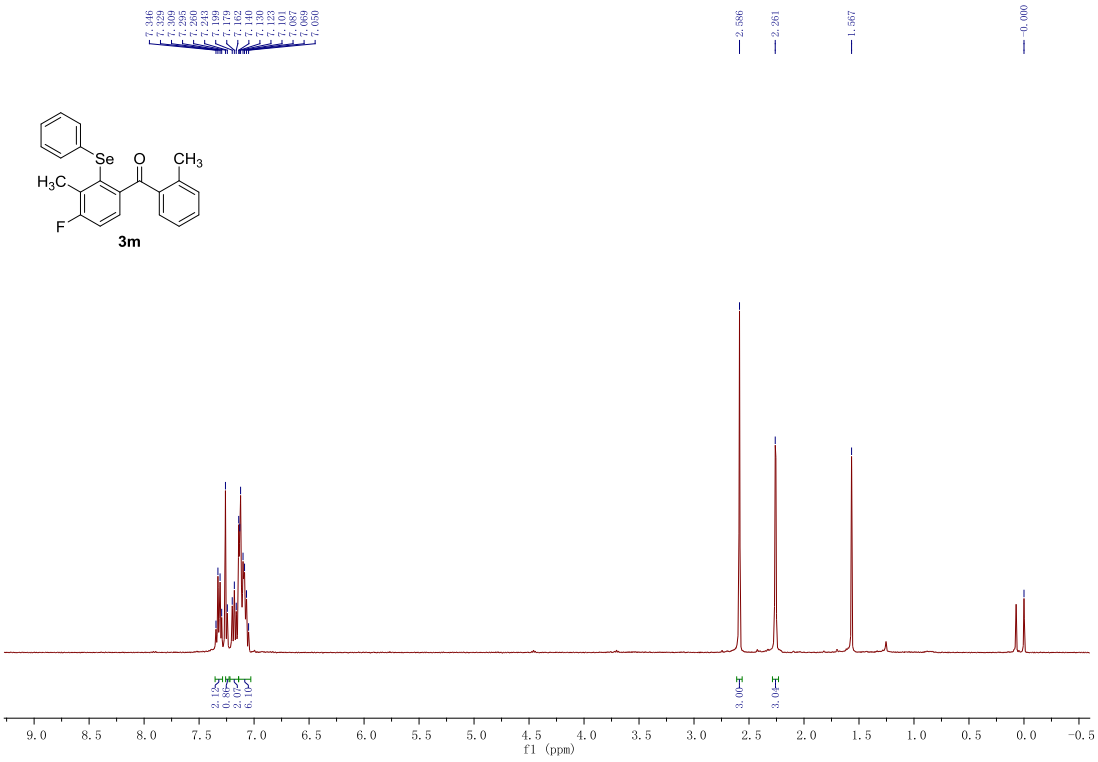
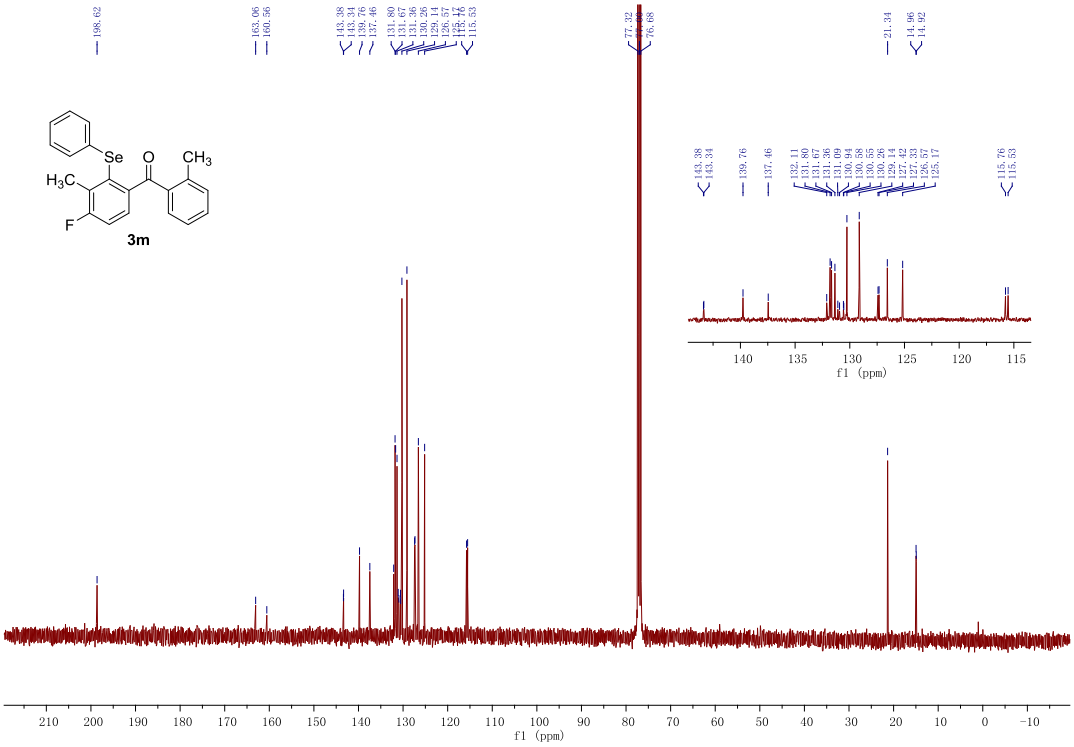
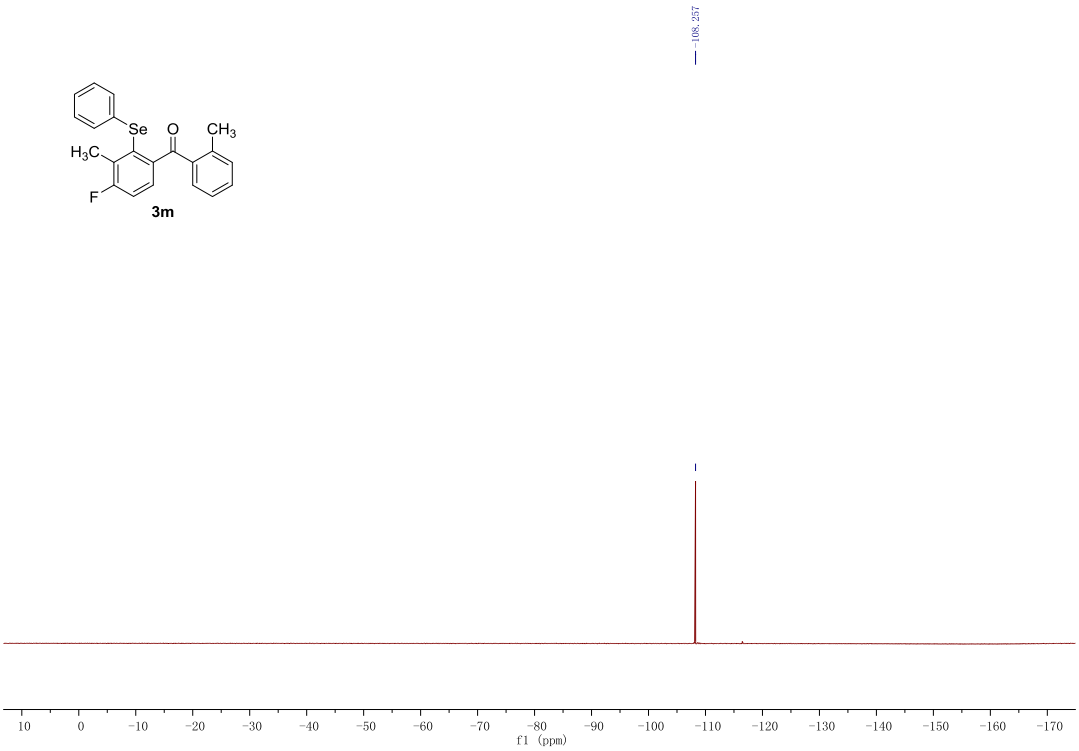
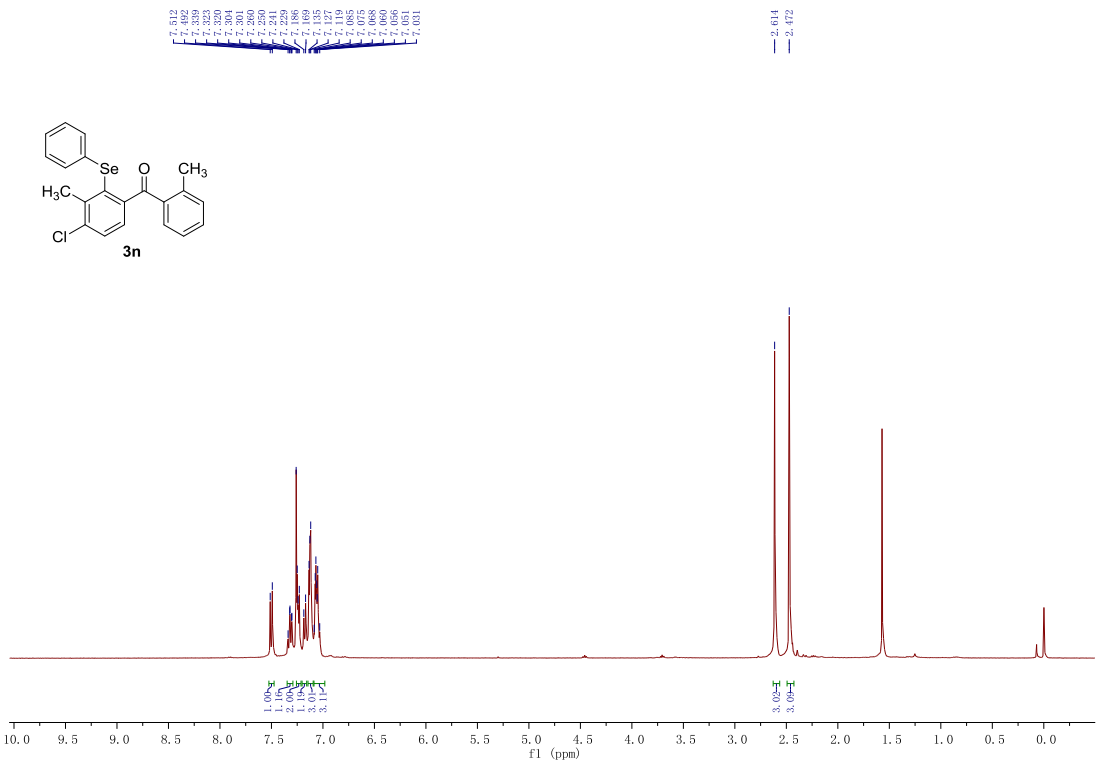
7.395
7.386
7.328
7.325
7.309
7.306
7.301
7.291
7.288
7.278
7.260
7.249
7.231
7.216
7.213
7.196
7.111
7.101
7.094
7.086
7.080
7.071
7.061
7.054
7.047
7.040
7.022
2.615
2.363
1.574
0.001
Se
O
CH3
H3C
3l
1.02
1.00
2.02
2.00
6.07
3.00
3.08
f1 (ppm)

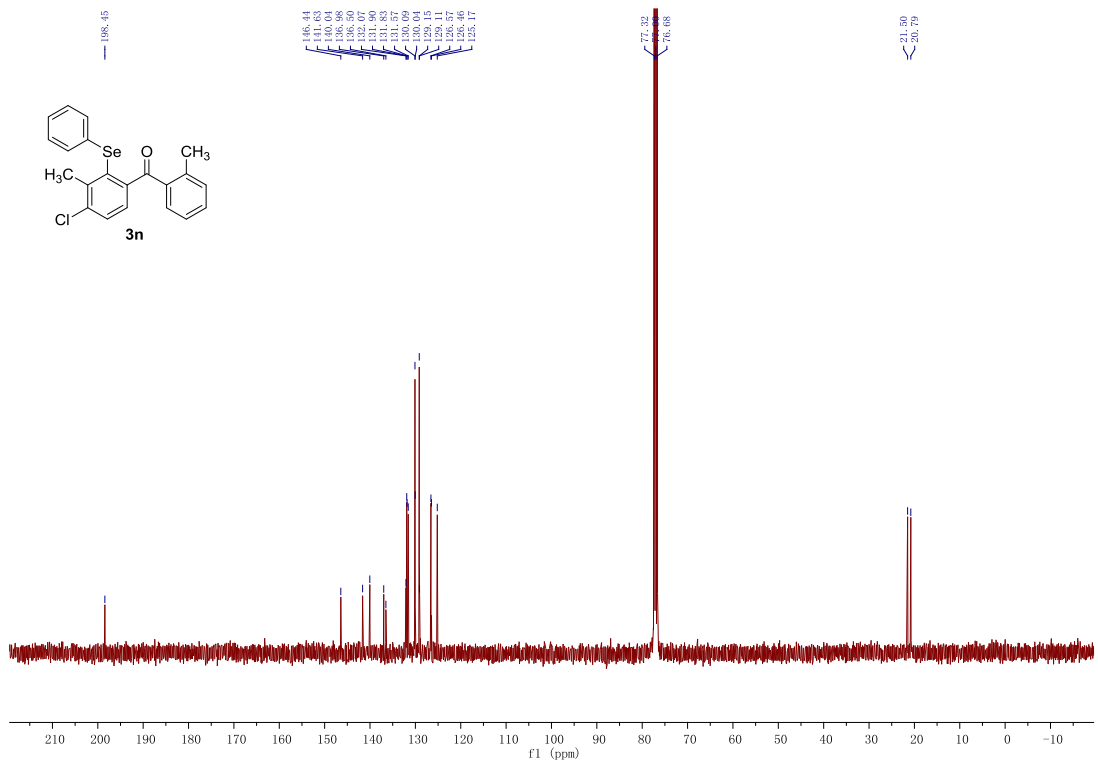

199.55
147.88
144.02
139.86
137.32
132.44
131.81
131.76
131.63
131.09
129.82
129.04
128.97
128.75
126.15
125.94
125.07
77.32
77.00
76.68
23.00
21.47
Se
O
CH3
H3C
3l
f1 (ppm)

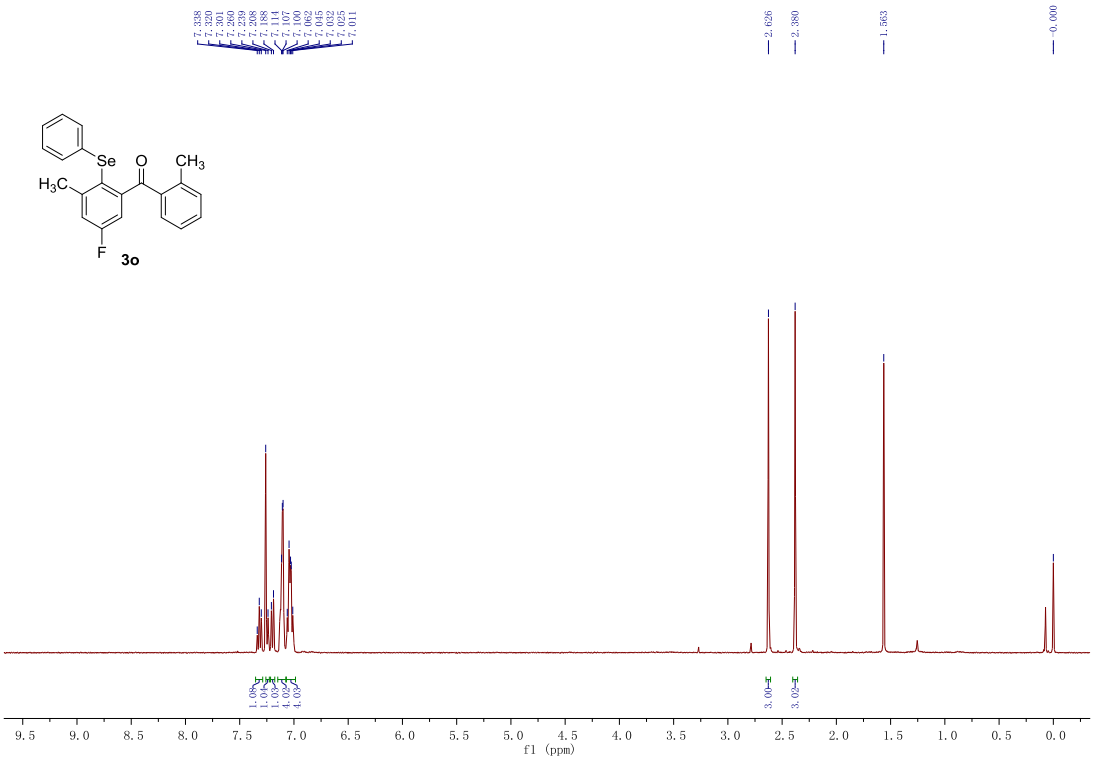

7.346
7.329
7.309
7.295
7.260
7.243
7.199
7.179
7.162
7.140
7.130
7.123
7.101
7.087
7.069
7.050
2.586
2.261
1.567
-0.000
Se
O
CH3
H3C
F
3m
2.13
0.86
2.05
6.10
3.00
3.04
f1 (ppm)

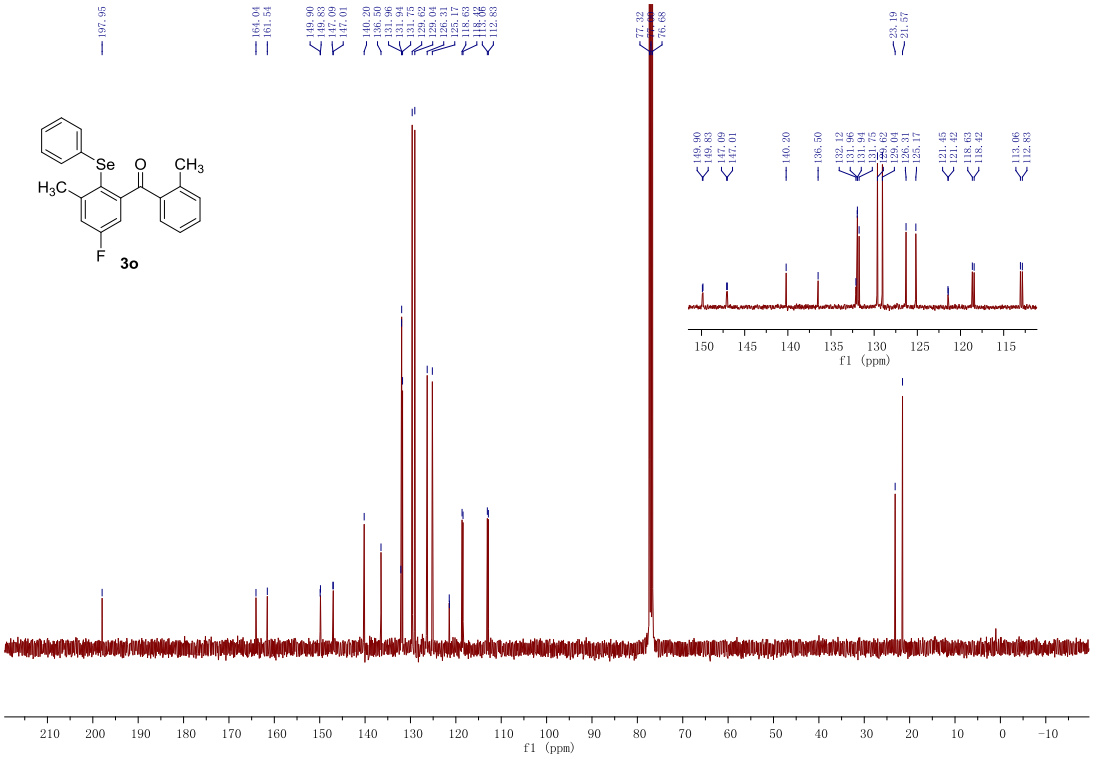

198.62
163.06
160.56
143.38
143.34
139.76
137.46
131.80
131.67
131.36
130.26
129.14
126.57
125.17
115.53
77.32
76.68
21.34
14.96
14.92
Se
O
CH3
H3C
F
3m
f1 (ppm)


-108.257
Se
O
CH3
H3C
F
3m
f1 (ppm)


7.512
7.492
7.339
7.323
7.320
7.304
7.301
7.260
7.259
7.241
7.229
7.188
7.169
7.155
7.127
7.119
7.085
7.075
7.068
7.060
7.056
7.051
7.031
2.614
2.472
Se
O
CH3
H3C
Cl
3n
1.00
1.16
2.06
2.19
3.01
3.11
3.02
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

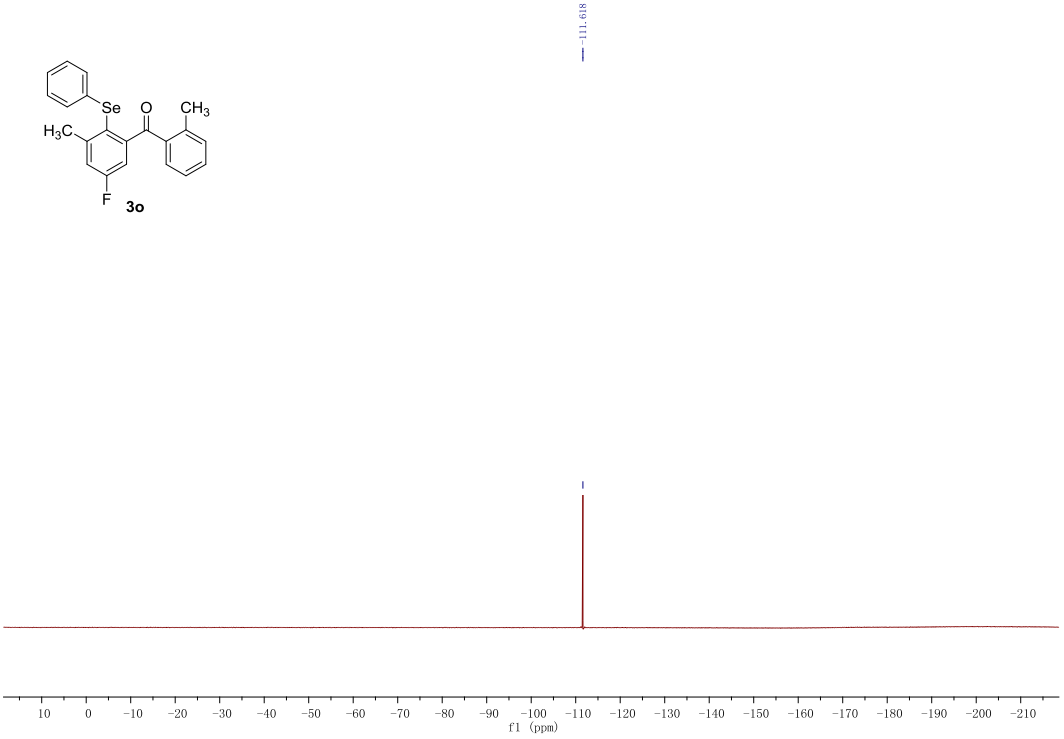

198.45
146.44
141.63
140.04
136.98
135.50
132.07
131.90
131.83
131.57
130.09
130.04
129.15
129.11
126.57
126.46
125.17
77.32
76.68
21.50
20.79
Se
O
CH3
H3C
Cl
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

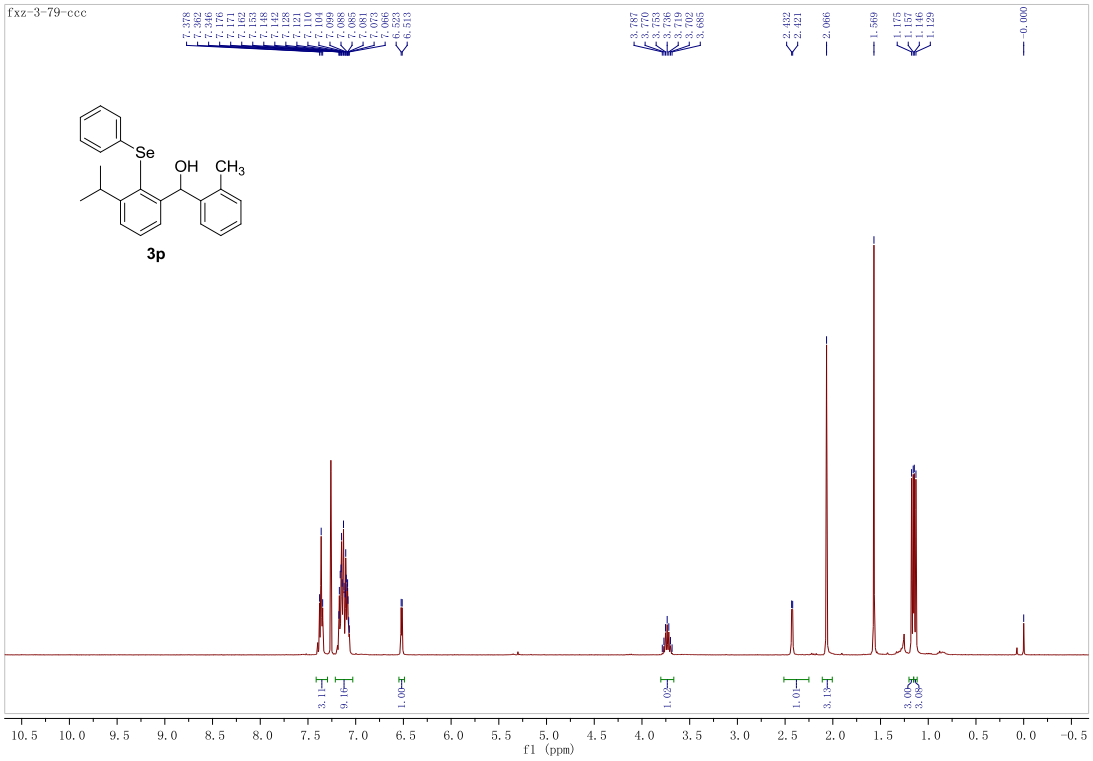

7.338
7.320
7.301
7.290
7.209
7.208
7.188
7.114
7.107
7.104
7.062
7.045
7.032
7.015
7.011
2.626
2.380
1.563
0.000
Se
O
CH3
H3C
F
3o
1.08
1.04
1.03
4.02
4.00
3.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

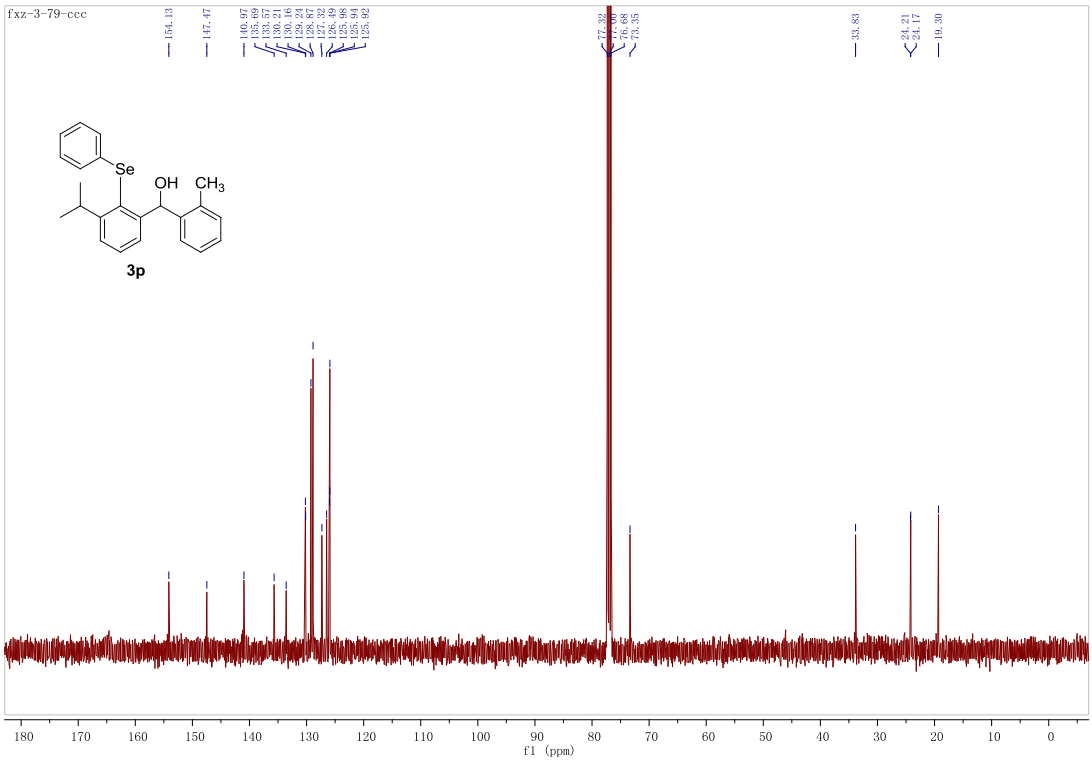

197.95
164.04
161.54
149.90
149.83
147.09
147.01
140.20
136.50
131.96
131.94
131.75
129.62
129.04
126.31
125.17
121.45
121.42
118.63
118.42
113.06
112.83
77.32
76.68
23.19
21.57
Se
O
CH3
H3C
F
3o
150 145 140 135 130 125 120 115
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

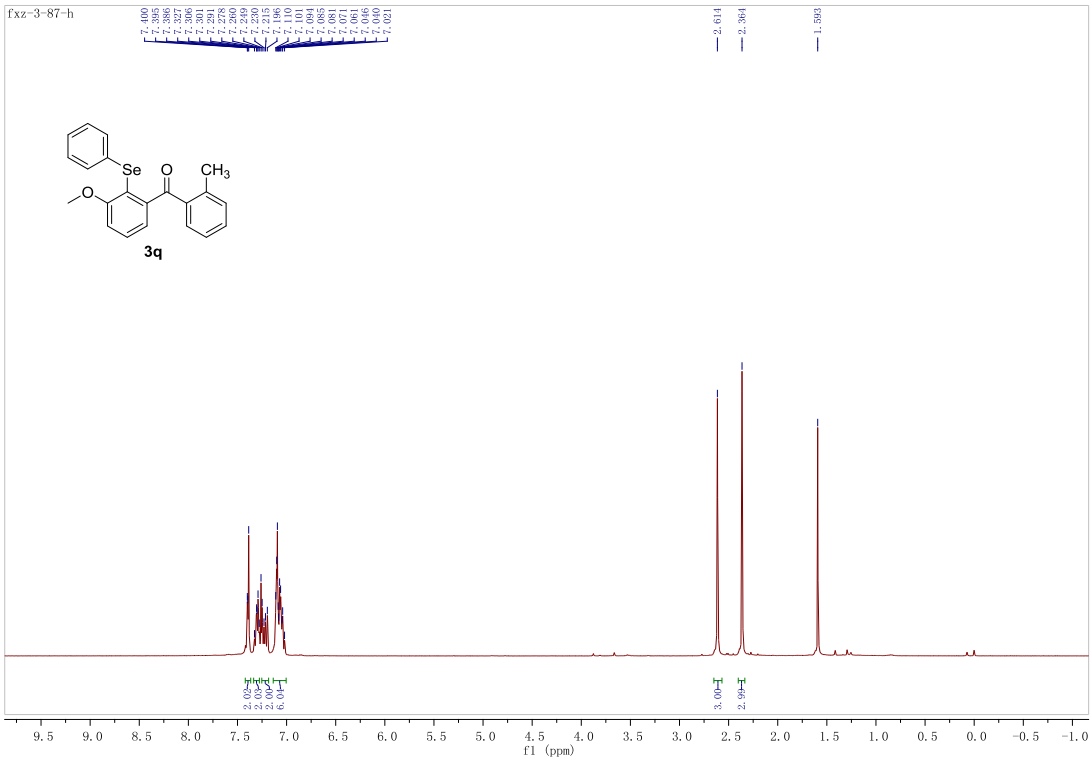
Se
O
CH3
H3C
F

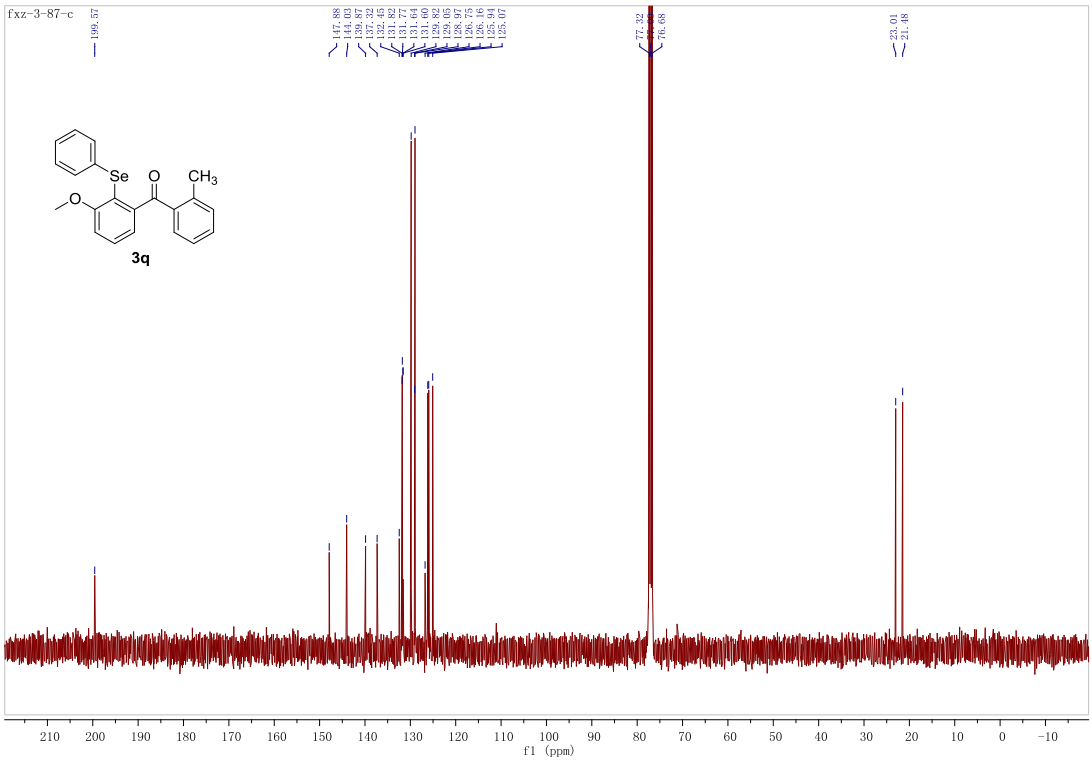
3o

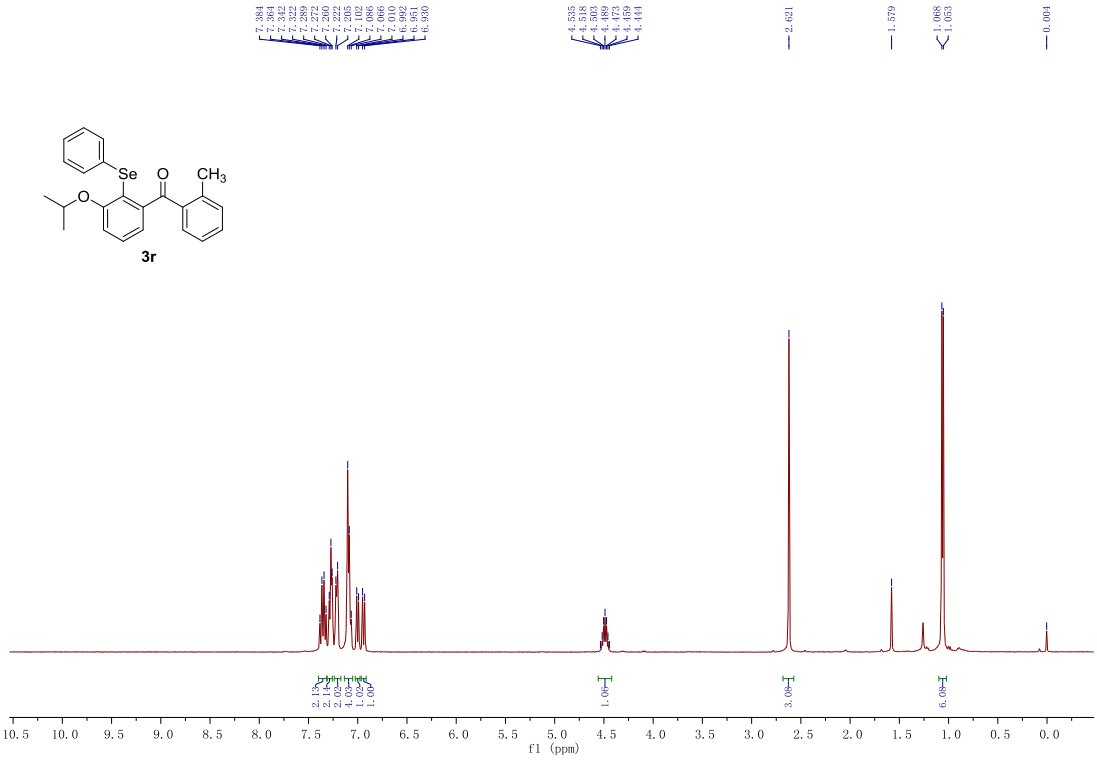

-111.618
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

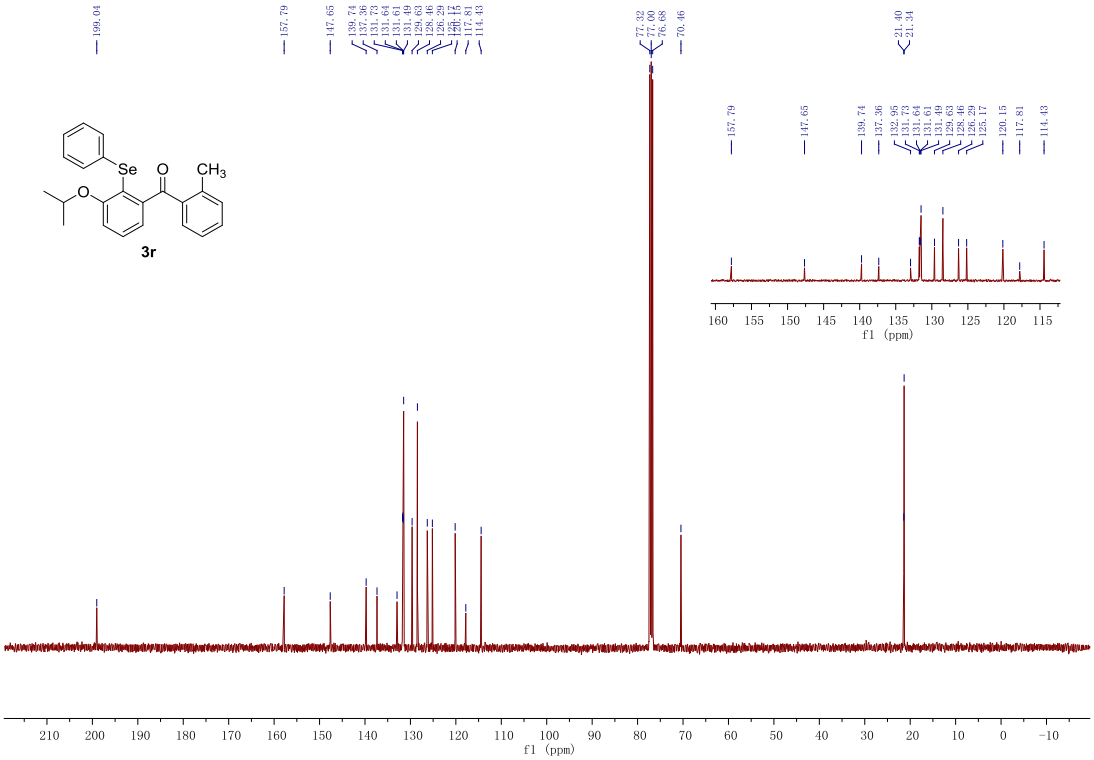

fxz-3-79-ccc
7.378 7.362 7.346 7.176 7.171 7.167 7.162 7.153 7.148 7.142 7.128 7.121 7.110 7.104 7.099 7.088 7.085 7.081 7.073 7.066 7.057 6.513
3.787 3.770 3.753 3.736 3.719 3.702 3.685
2.432 2.421
2.066
1.569
1.175 1.157 1.146 1.129
-0.000
Se
OH
CH3
3p
3.11 9.10 1.00 1.02 1.01 3.13 3.00 3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

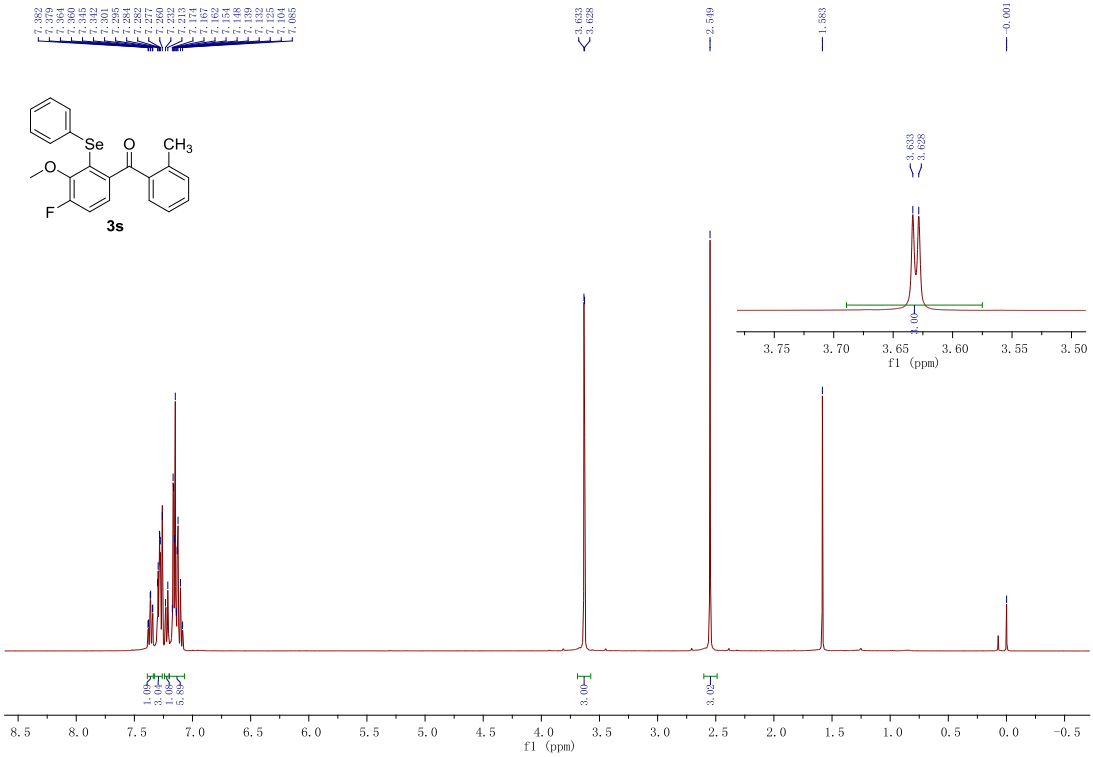

fxz-3-79-ccc
154.13
147.47
140.97
135.69
133.57
130.21
130.16
129.34
128.87
127.32
126.49
125.98
125.44
125.92
77.32
77.00
76.68
73.35
33.83
24.21
24.17
19.30
Se
OH
CH3
3p
f1 (ppm)

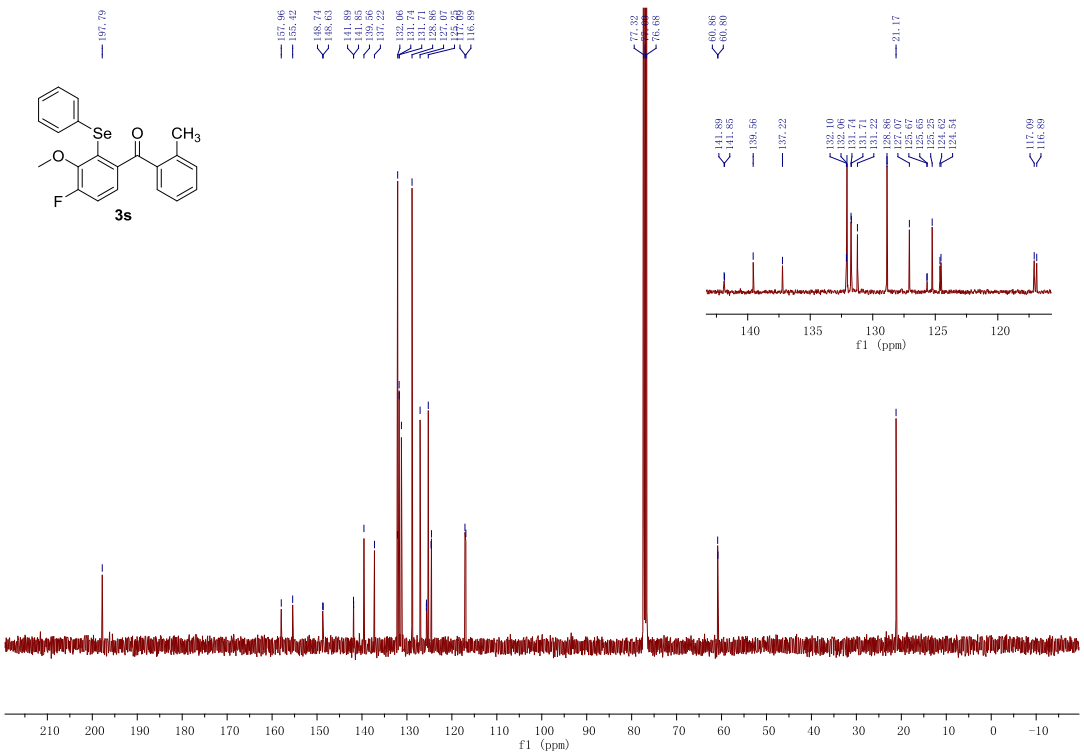

fxz-3-87-h
7.400
7.395
7.386
7.327
7.306
7.301
7.291
7.278
7.260
7.249
7.239
7.229
7.215
7.196
7.110
7.101
7.094
7.085
7.081
7.071
7.061
7.046
7.040
7.021
2.614
2.364
1.593
Se
O
CH3
O
3q
2.02
2.02
2.02
6.01
3.00
2.99
f1 (ppm)

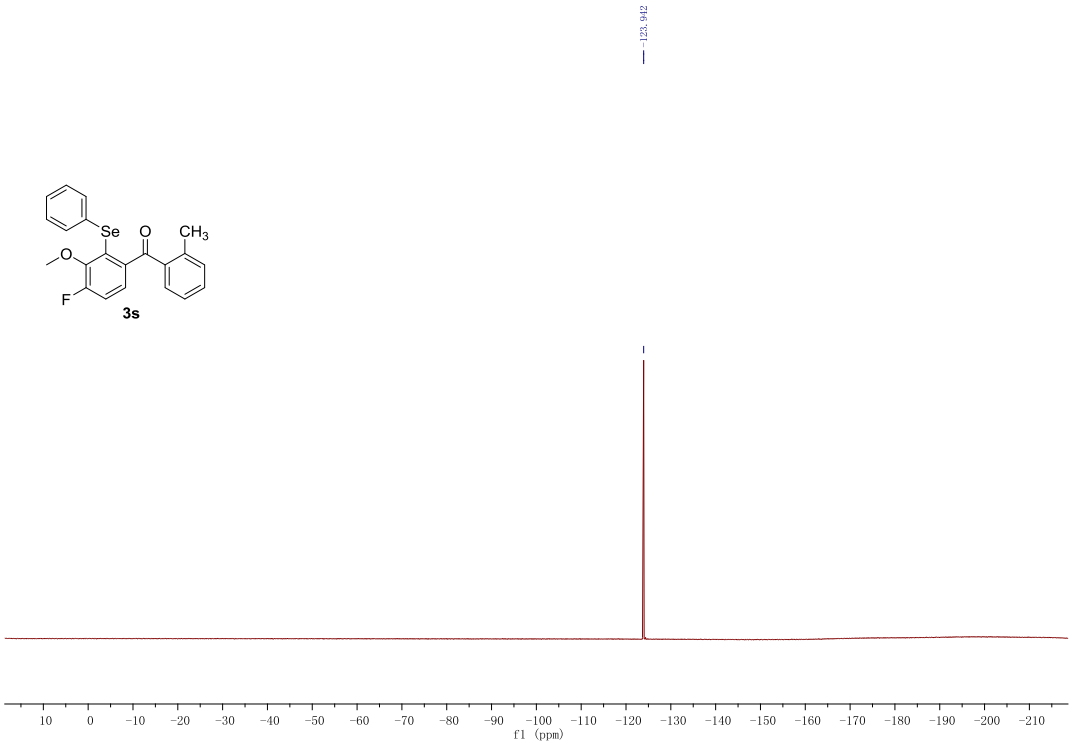

fxz-3-87-c
199.57
147.88
144.03
139.87
137.32
132.45
131.82
131.77
131.64
131.60
129.82
129.05
128.97
128.75
126.45
125.94
125.07
77.32
76.68
23.01
21.48
Se
O
CH3
O
3q
f1 (ppm)

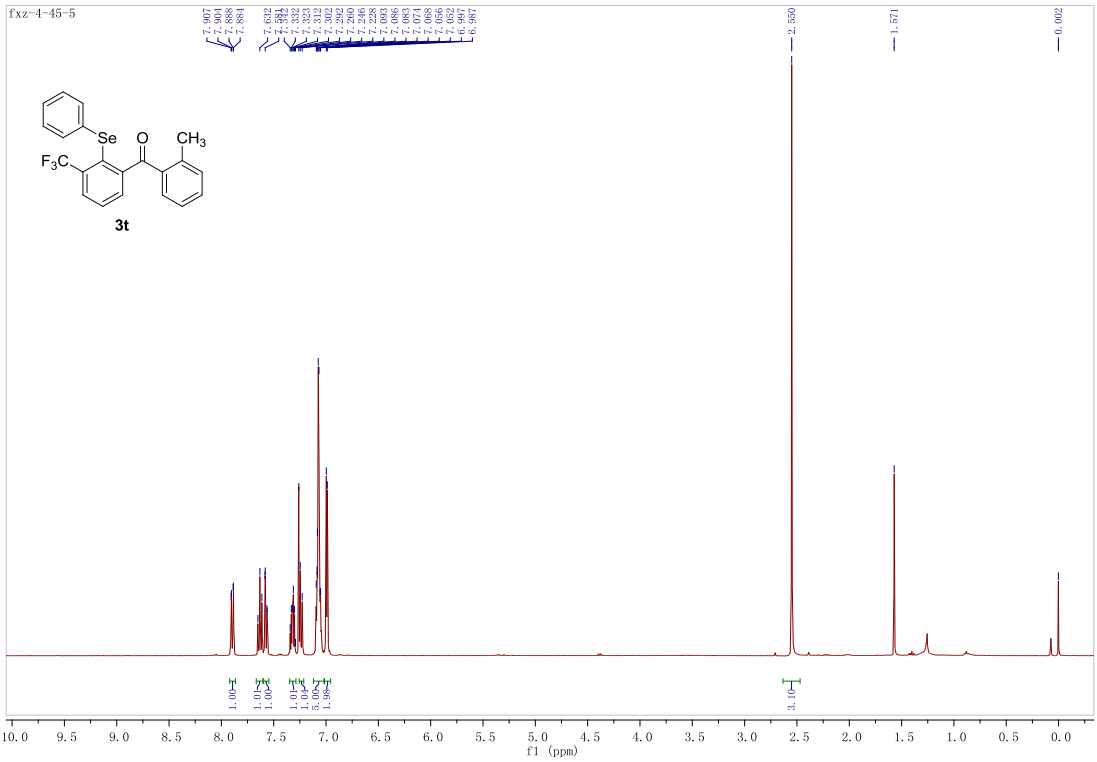

7.384
7.364
7.342
7.322
7.299
7.272
7.260
7.222
7.205
7.102
7.086
7.010
6.992
6.951
6.930
4.535
4.518
4.503
4.489
4.473
4.459
4.444
2.621
1.579
1.068
1.053
0.004
Se
O
CH3
O
3r
2.15
2.14
2.02
4.03
1.02
1.00
1.00
3.09
6.09
f1 (ppm)

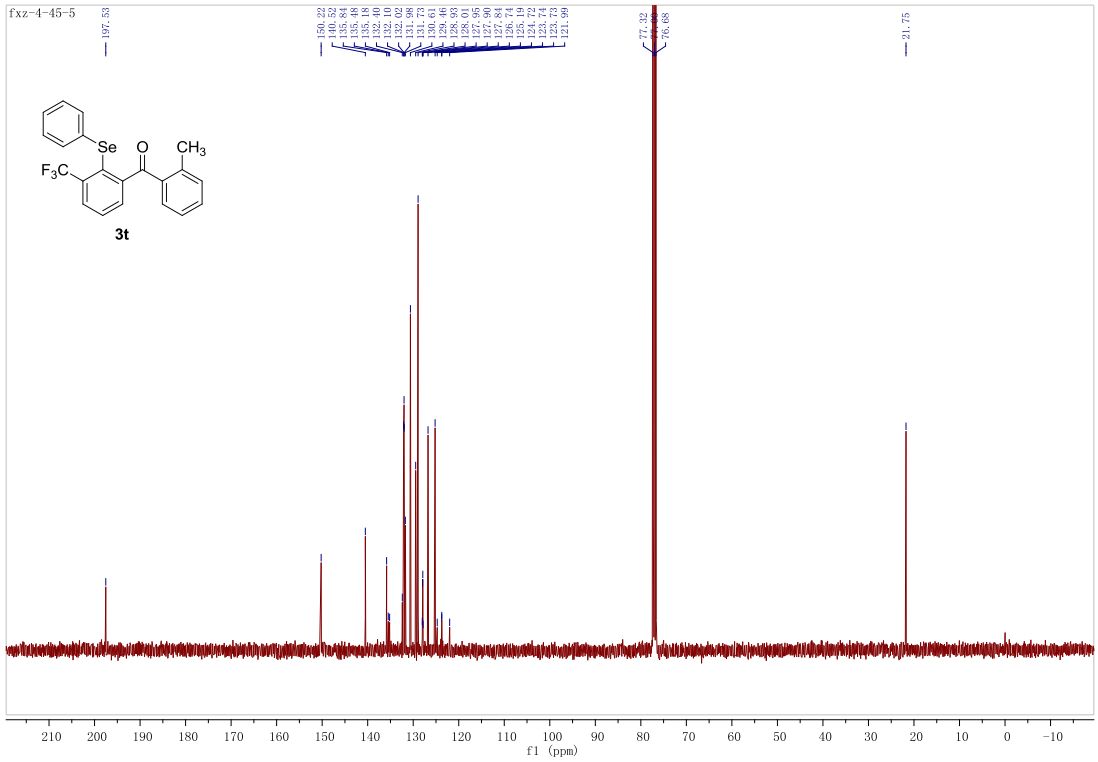

3r
f1 (ppm)

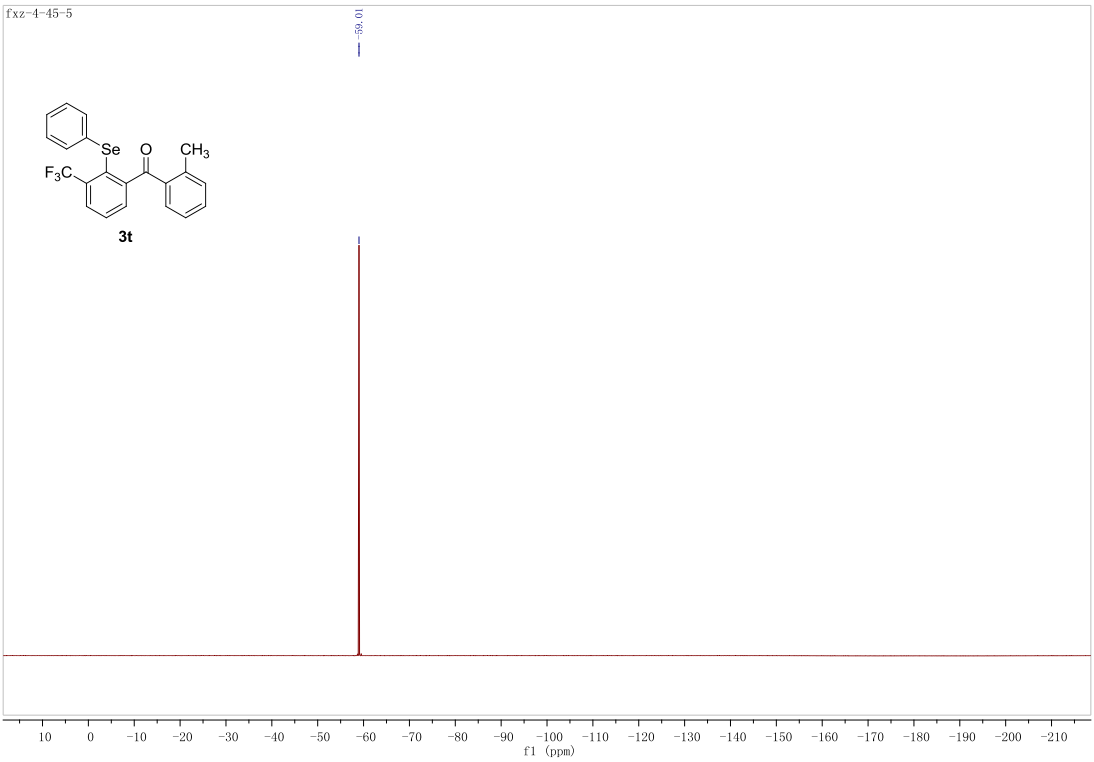

3s
f1 (ppm)

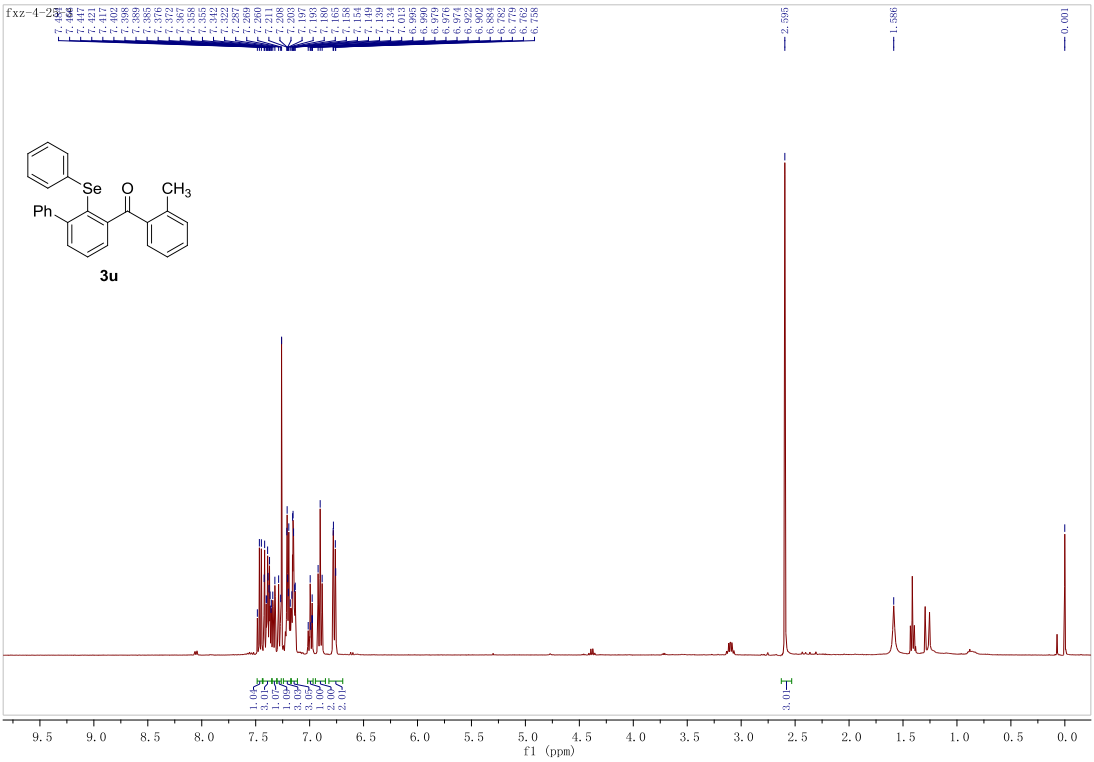

197.79
157.96
155.42
148.74
146.63
141.89
141.85
139.56
137.22
132.06
131.74
131.71
131.71
129.86
127.07
125.25
124.62
116.89
77.32
76.68
60.86
60.80
21.17
141.89
141.85
139.56
137.22
132.10
132.06
131.74
131.71
131.22
128.86
127.07
125.67
125.65
125.25
124.62
124.54
117.09
116.89
Se
O
CH3
O
F
3s
f1 (ppm)

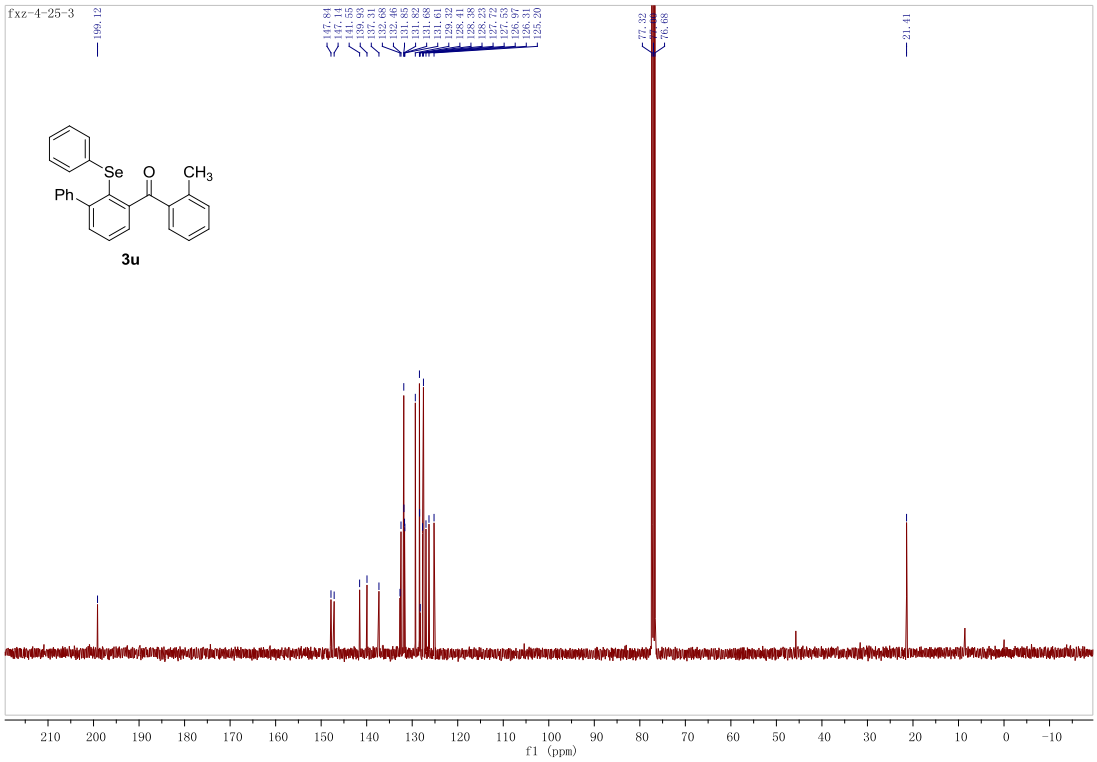

-123.942
Se
O
CH3
O
F
3s
f1 (ppm)

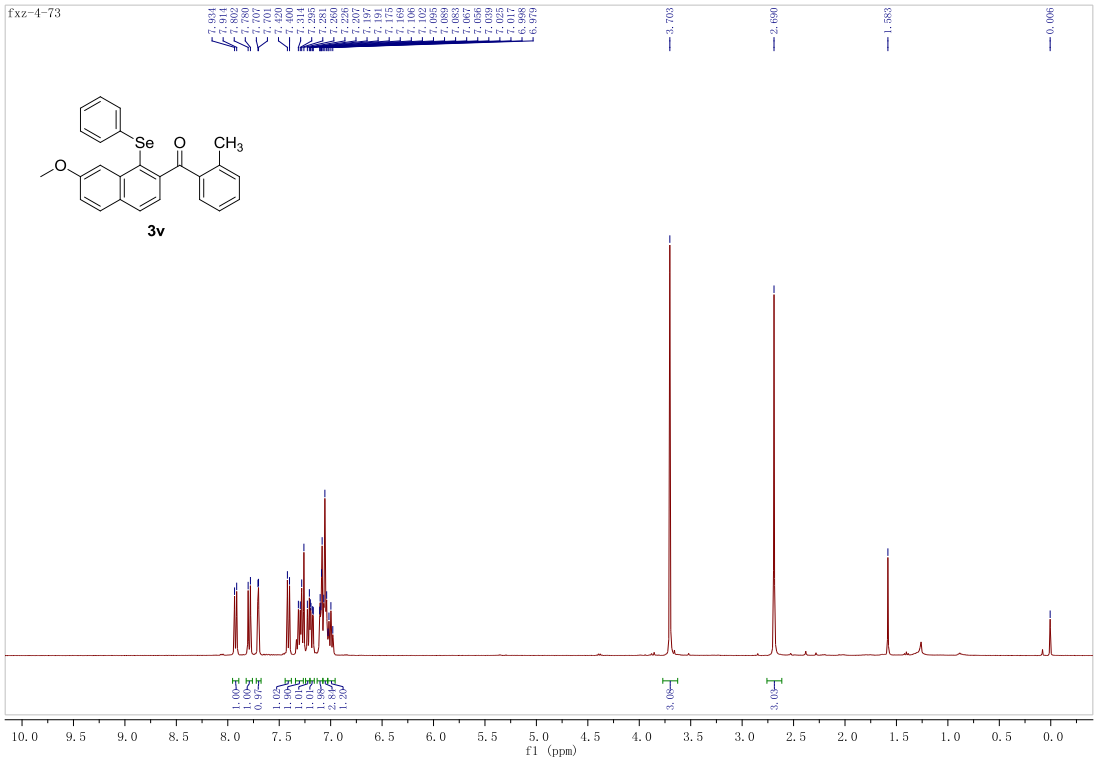

fxz-4-45-5
Se
O
CH3
F3C
3t
f1 (ppm)

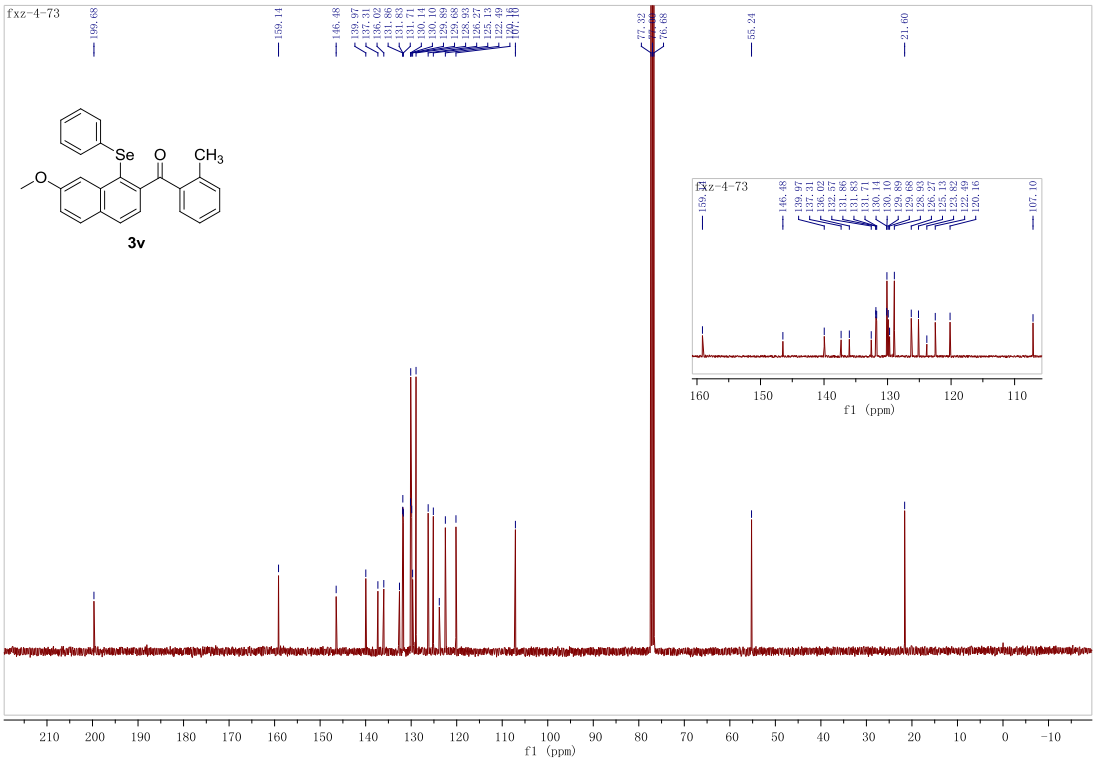

fxz-4-45-5
Se
O
CH3
F3C
3t
f1 (ppm)

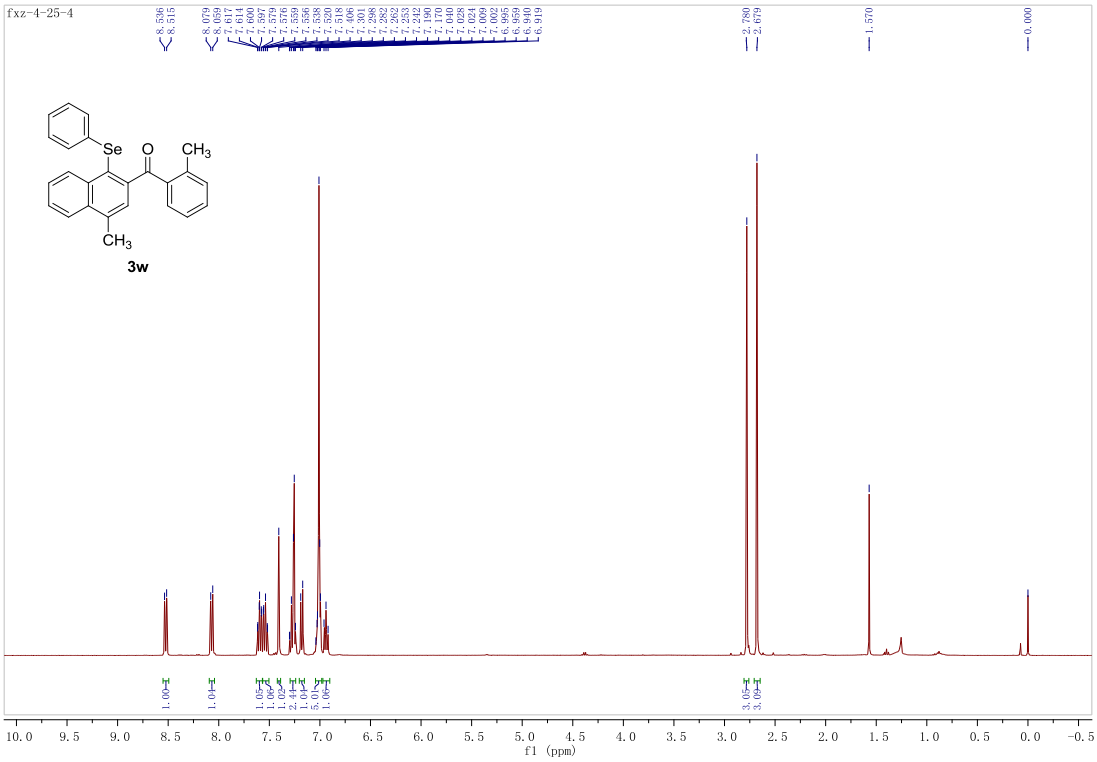

fxz-4-45-5
-59.01
Se
O
CH3
F3C
3t
f1 (ppm)

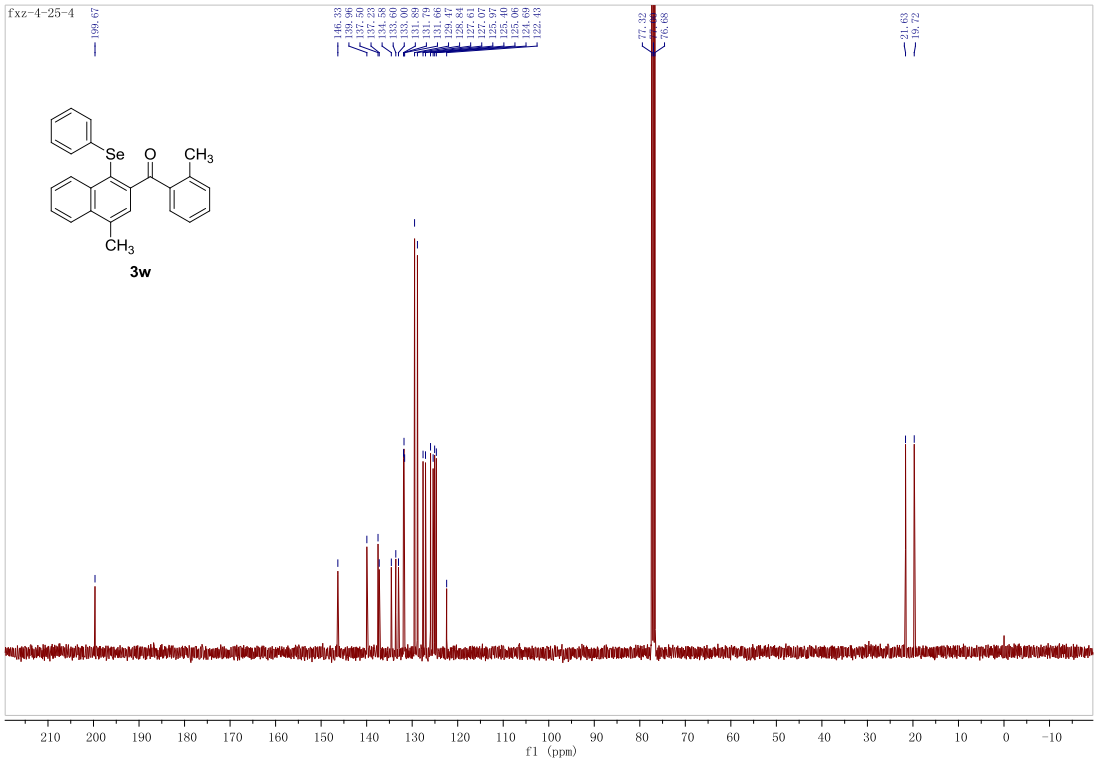

2.595
1.586
0.001
Se
O
CH3
Ph
3u
f1 (ppm)

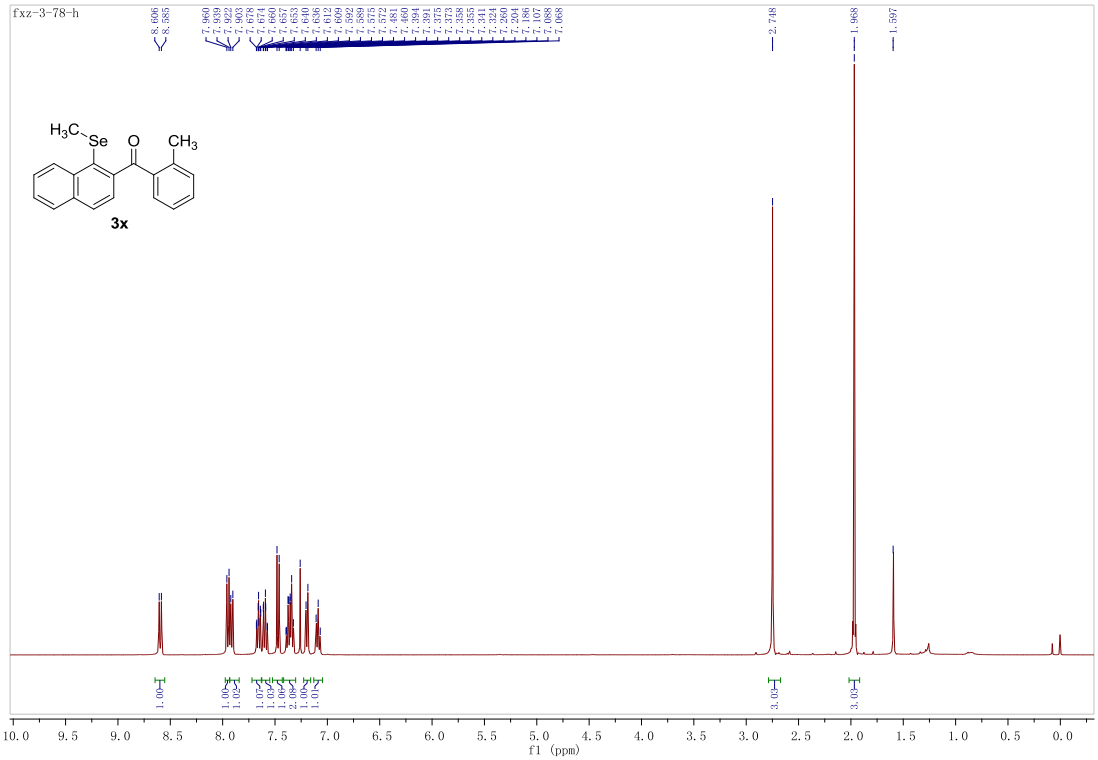

fxz-4-25-3
199.12
147.84
147.14
141.55
139.93
137.31
132.58
132.46
131.85
131.82
131.68
131.61
129.32
128.41
128.38
128.25
127.72
127.53
126.97
126.31
125.20
77.32
76.68
21.41
Se
O
CH3
Ph
3u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


fxz-4-73
7.934
7.914
7.802
7.789
7.707
7.701
7.420
7.400
7.314
7.295
7.281
7.260
7.226
7.207
7.197
7.191
7.175
7.169
7.149
7.102
7.095
7.089
7.083
7.067
7.056
7.039
7.025
7.017
6.998
6.979
3.703
2.690
1.583
0.006
Se
O
CH3
O
3v
1.00
1.00
0.97
1.02
1.05
1.04
1.01
1.00
2.94
1.20
3.08
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


fxz-4-73
199.68
159.14
146.48
139.97
137.31
136.02
131.86
131.83
131.71
130.14
130.10
129.89
129.68
128.93
126.27
125.13
122.49
120.16
77.32
76.68
55.24
21.60
Se
O
CH3
O
3v
107.10
f1 (ppm)


fxz-4-25-4
8.536
8.515
8.079
8.059
7.617
7.614
7.600
7.597
7.579
7.559
7.556
7.538
7.520
7.518
7.406
7.301
7.298
7.282
7.262
7.253
7.242
7.190
7.170
7.040
7.028
7.024
7.009
7.002
6.995
6.959
6.940
6.919
2.780
2.679
1.570
0.000
Se
O
CH3
CH3
3w
1.00
1.04
1.05
1.02
1.02
2.44
1.04
5.01
1.00
3.05
3.09
f1 (ppm)


fxz-4-25-4
199.67
146.33
139.96
137.50
137.23
134.58
133.60
133.00
131.89
131.79
131.66
129.47
128.84
127.61
127.07
125.97
125.40
125.06
124.69
122.43
77.32
76.68
21.63
19.72
Se
O
CH3
CH3
3w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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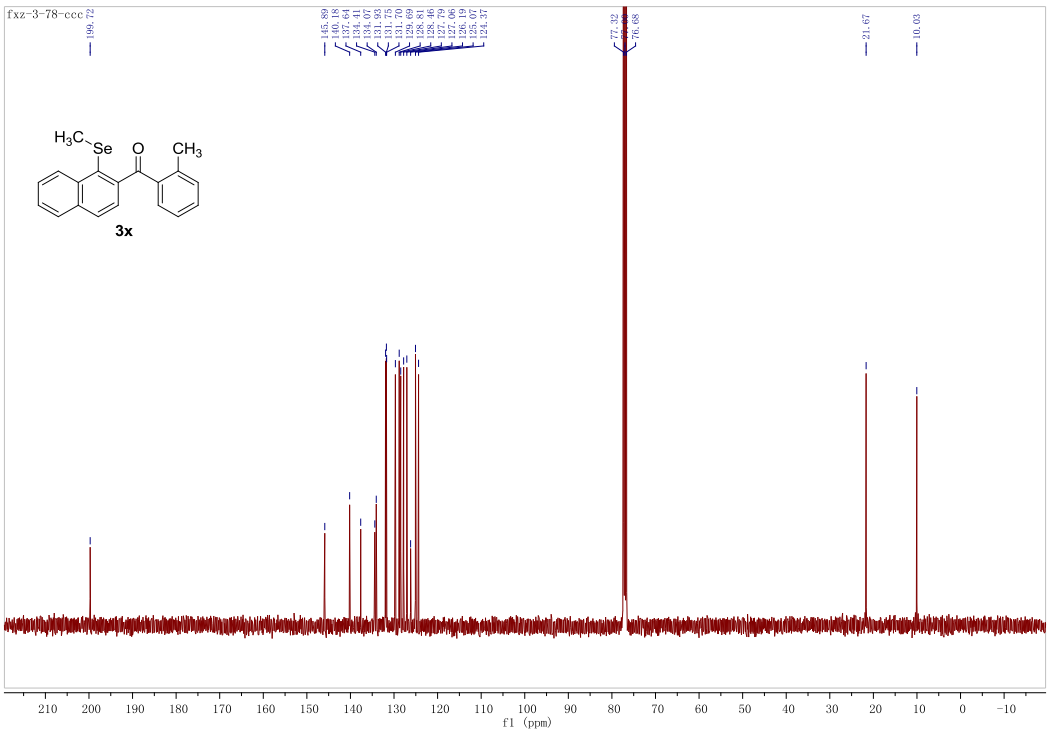
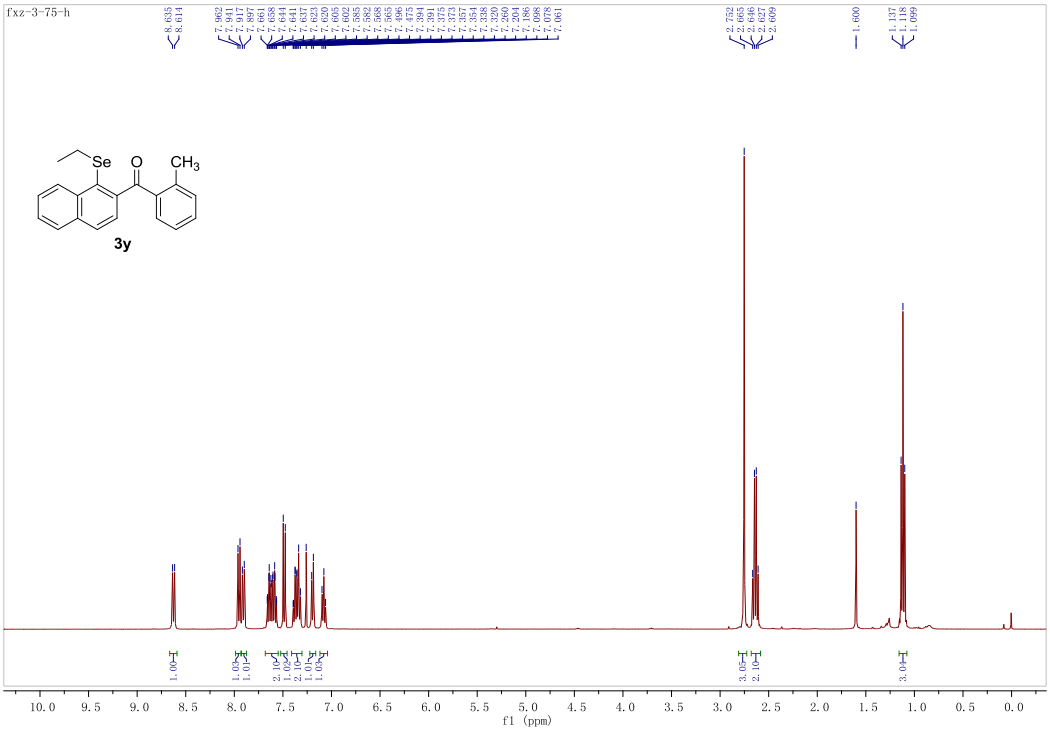
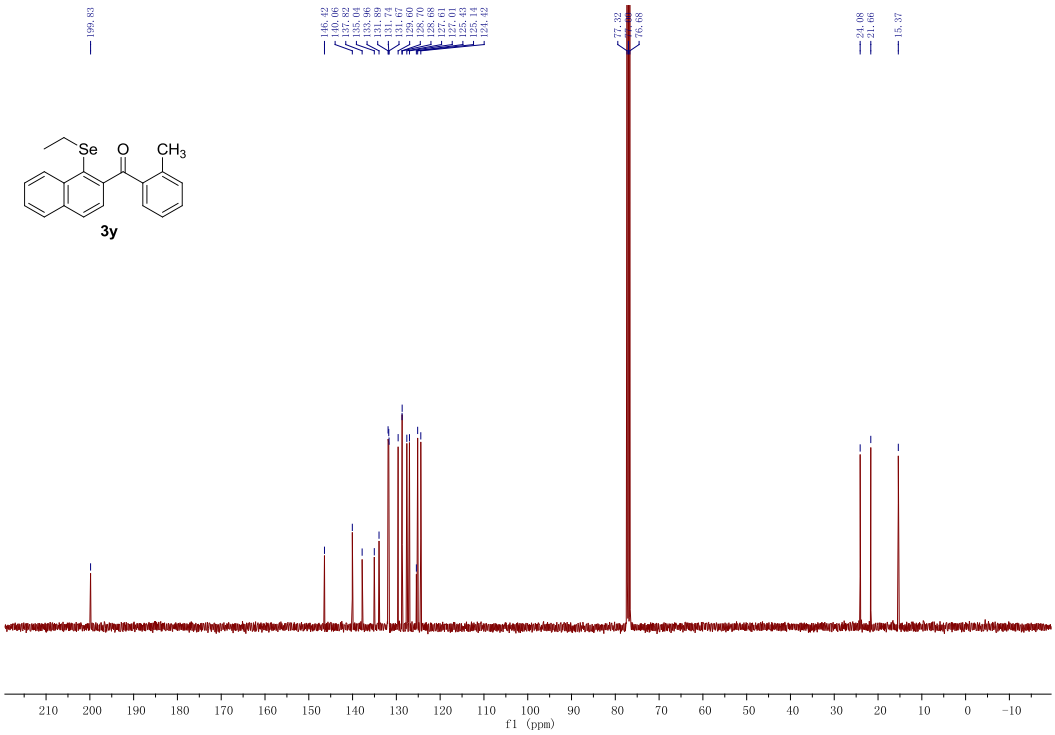
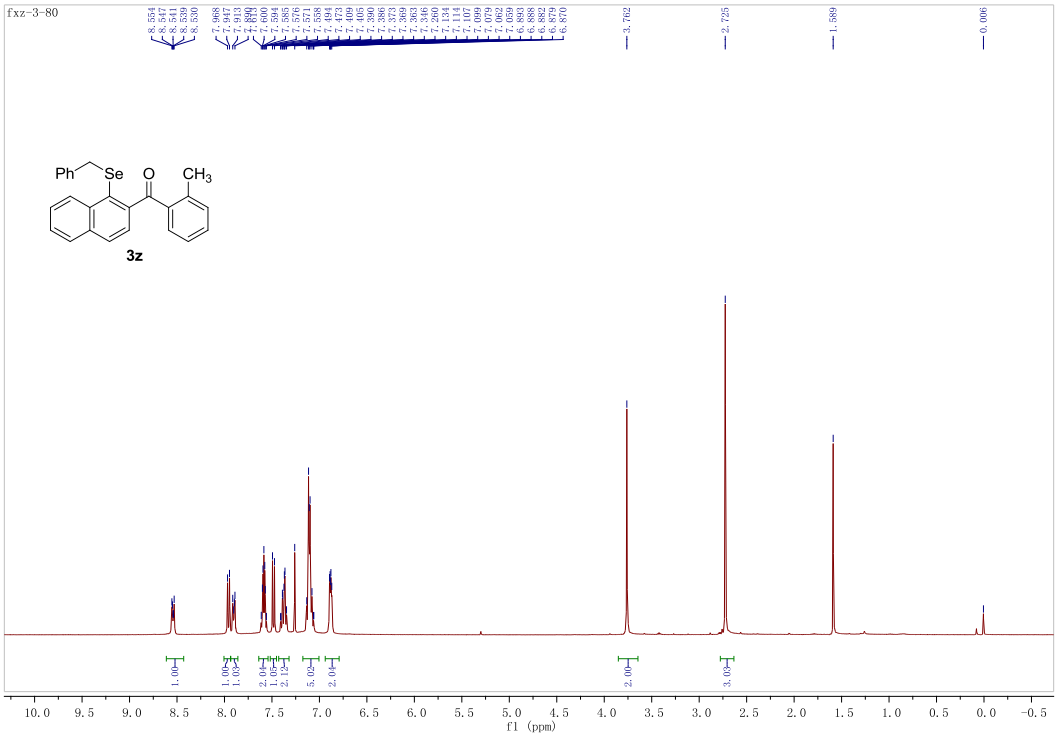
8.585
7.960
7.939
7.922
7.903
7.753
7.674
7.660
7.657
7.653
7.649
7.636
7.612
7.609
7.592
7.589
7.575
7.572
7.481
7.460
7.394
7.391
7.375
7.373
7.358
7.355
7.341
7.324
7.290
7.204
7.186
7.107
7.088
7.068
2.748
1.968
1.597
H3C
Se
O
CH3
3x
1.00
1.00
1.02
1.05
1.03
1.09
2.06
1.04
1.01
3.03
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


fxz-3-78-ccc
3x
f1 (ppm)


fxz-3-75-h
3y
f1 (ppm)


199.83
146.42
140.06
137.82
135.04
133.96
131.94
131.74
131.67
129.60
129.70
128.68
127.61
127.01
125.43
125.14
124.42
77.32
76.68
24.08
21.66
15.37
Se
O
CH3
3y
f1 (ppm)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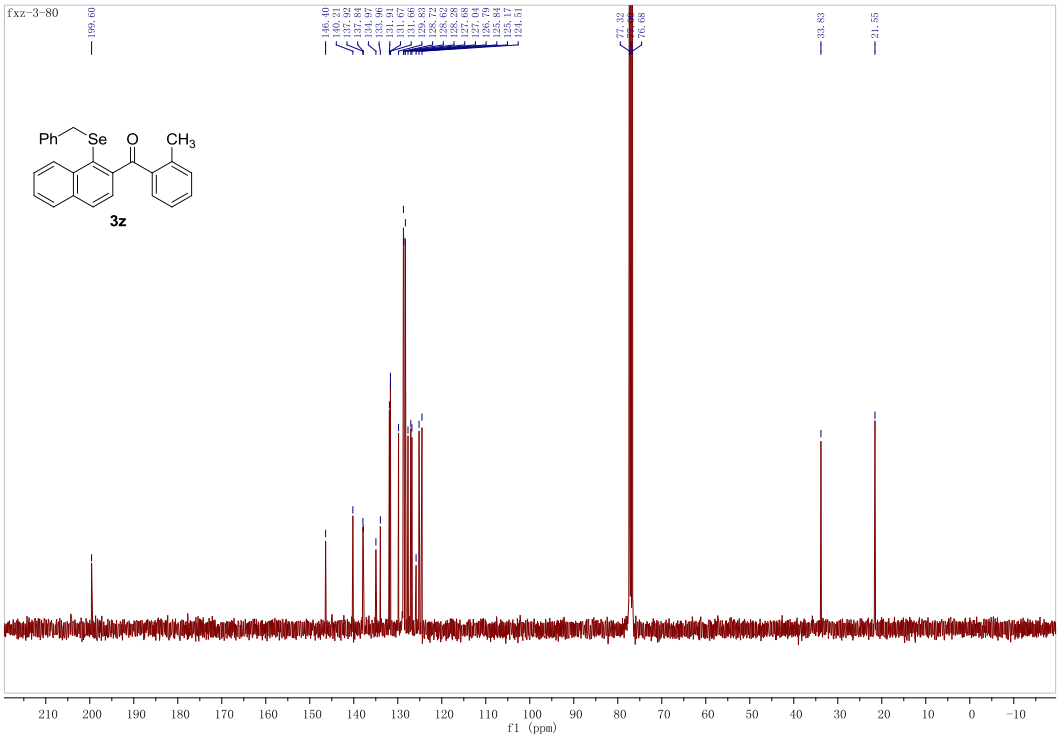
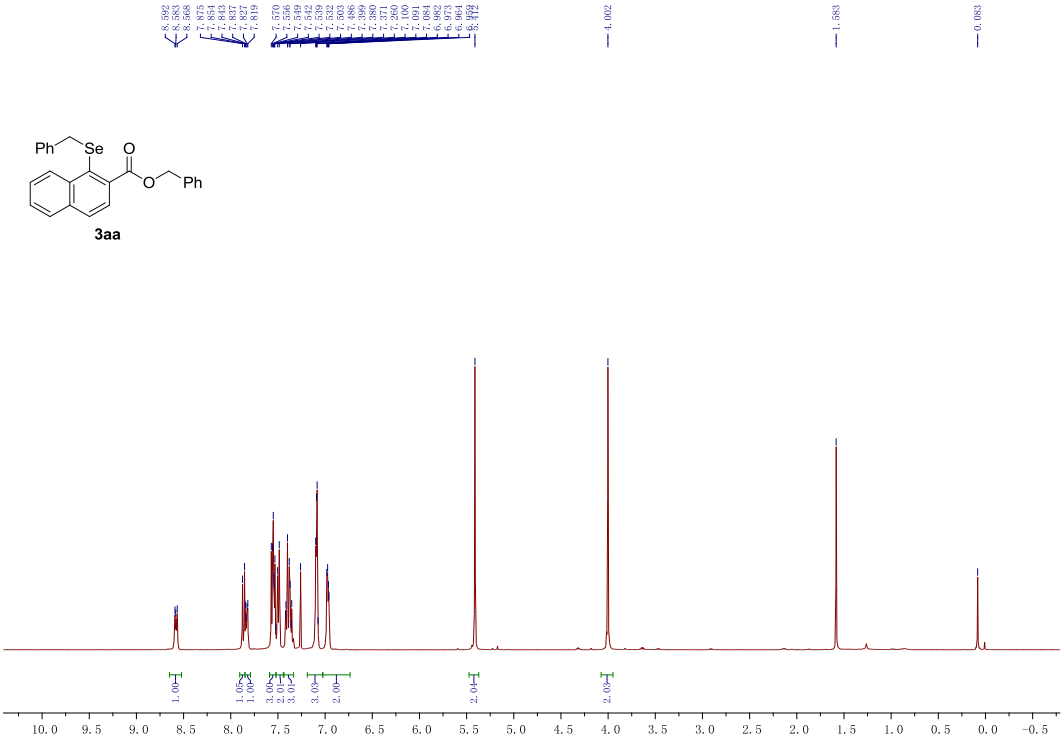
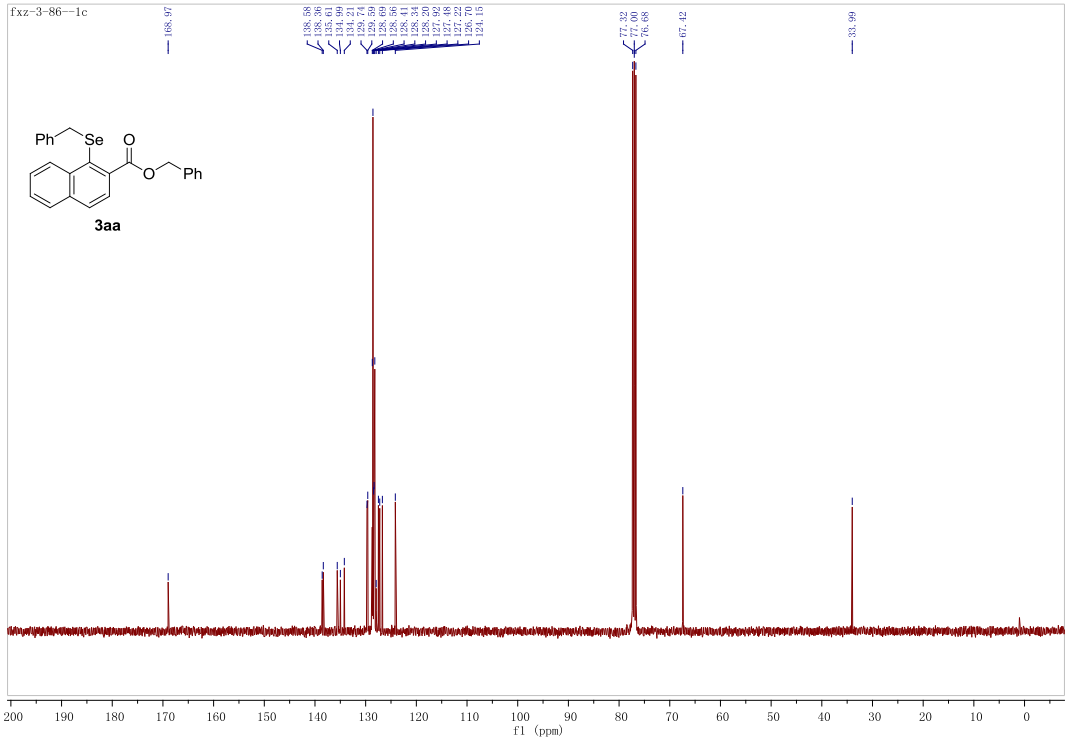
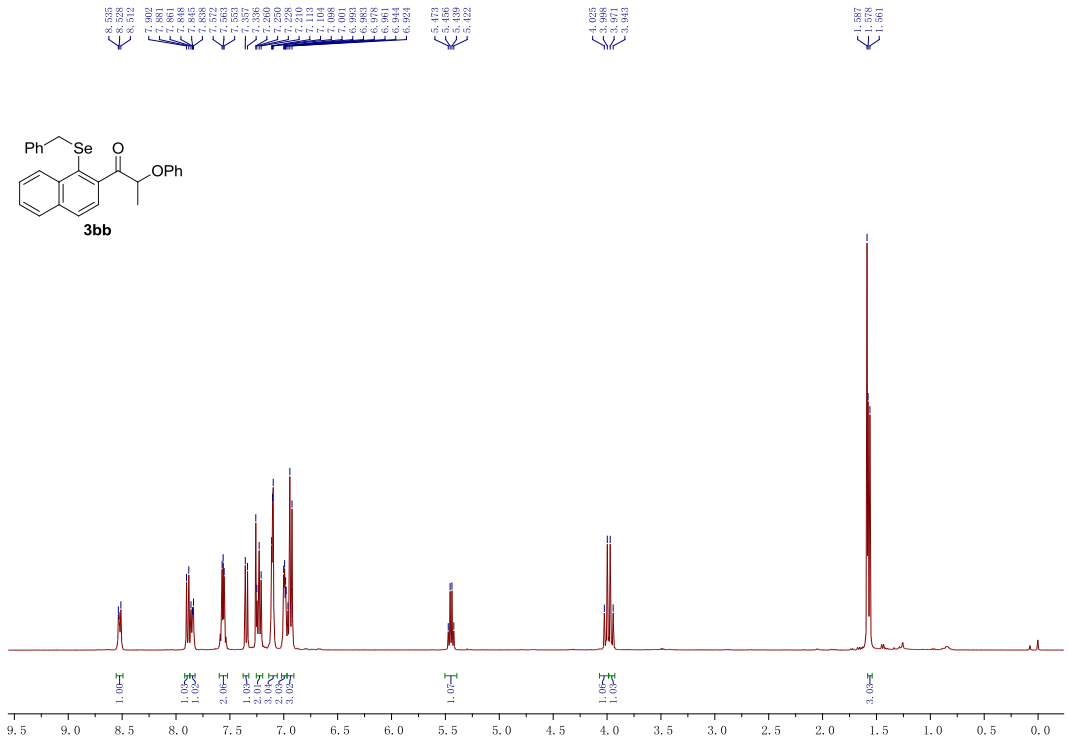
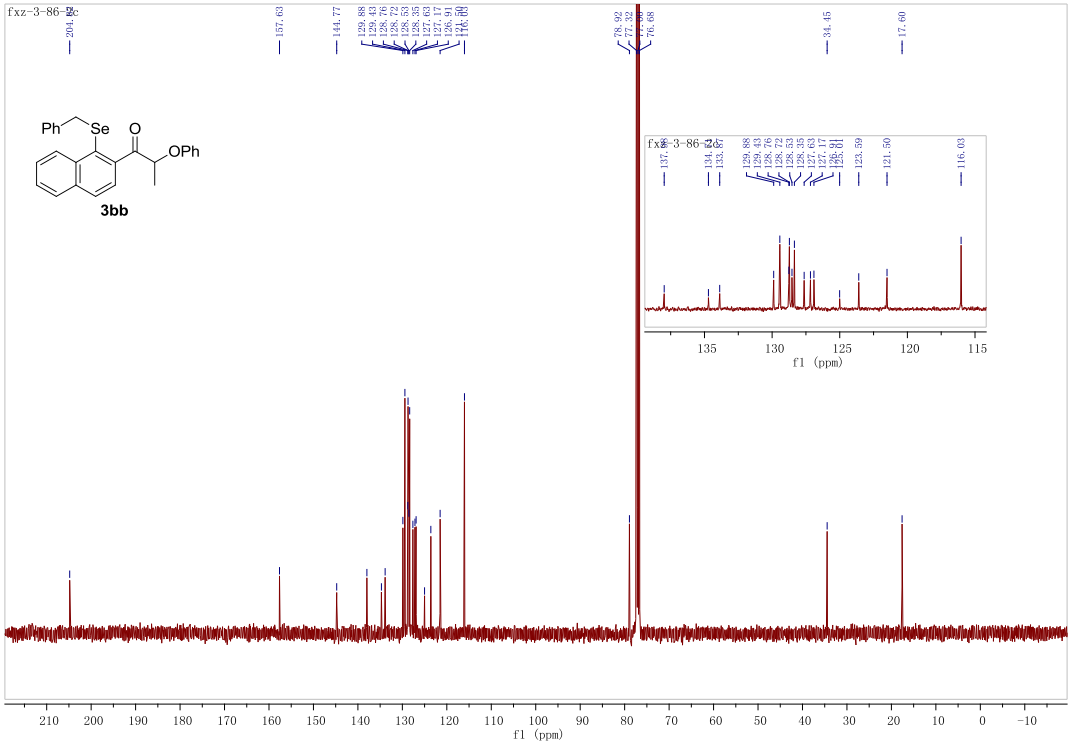
8.547
8.541
8.539
8.530
7.968
7.947
7.913
7.900
7.600
7.594
7.585
7.576
7.571
7.558
7.494
7.473
7.449
7.405
7.390
7.388
7.373
7.369
7.363
7.346
7.299
7.134
7.114
7.107
7.079
7.069
7.062
7.059
6.893
6.886
6.882
6.879
6.870
3.762
2.725
1.589
0.006
Ph
Se
O
CH3
3z
1.00
1.00
1.00
2.04
1.05
2.12
5.02
2.00
2.00
3.03
f1 (ppm)

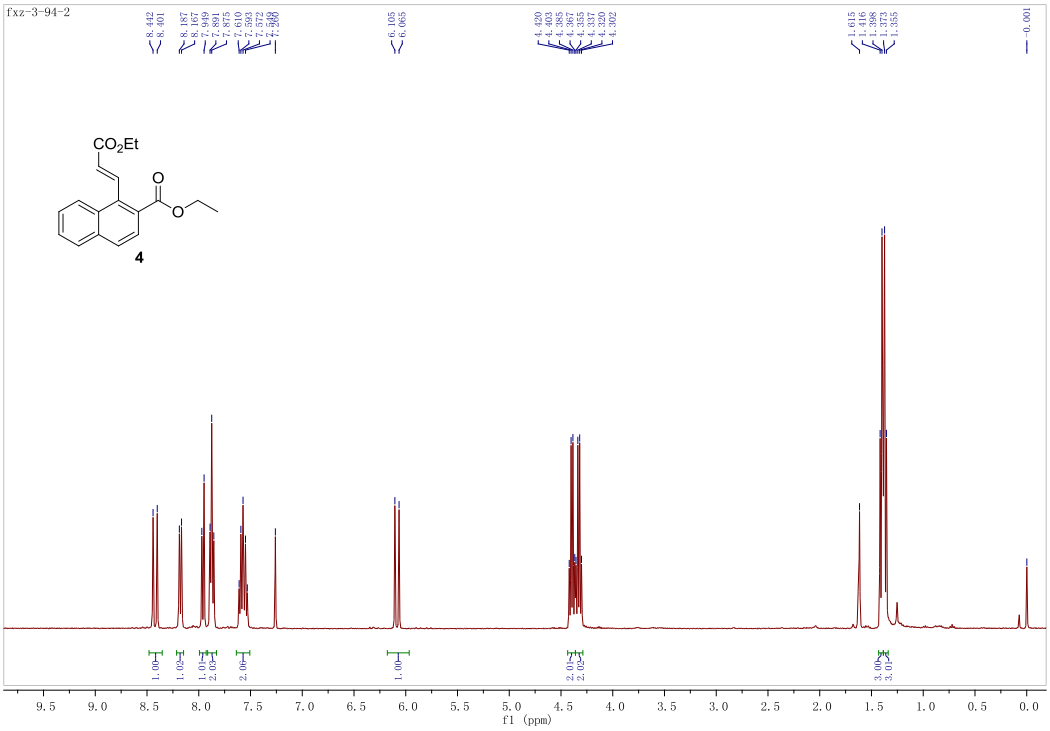

fxz-3-80
199.60
146.40
140.21
137.92
137.84
134.97
134.46
131.91
131.67
131.66
129.85
128.72
128.62
125.28
127.68
127.04
126.79
125.84
125.57
124.51
77.32
77.00
76.68
33.83
21.55
Ph
Se
O
CH3
3z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

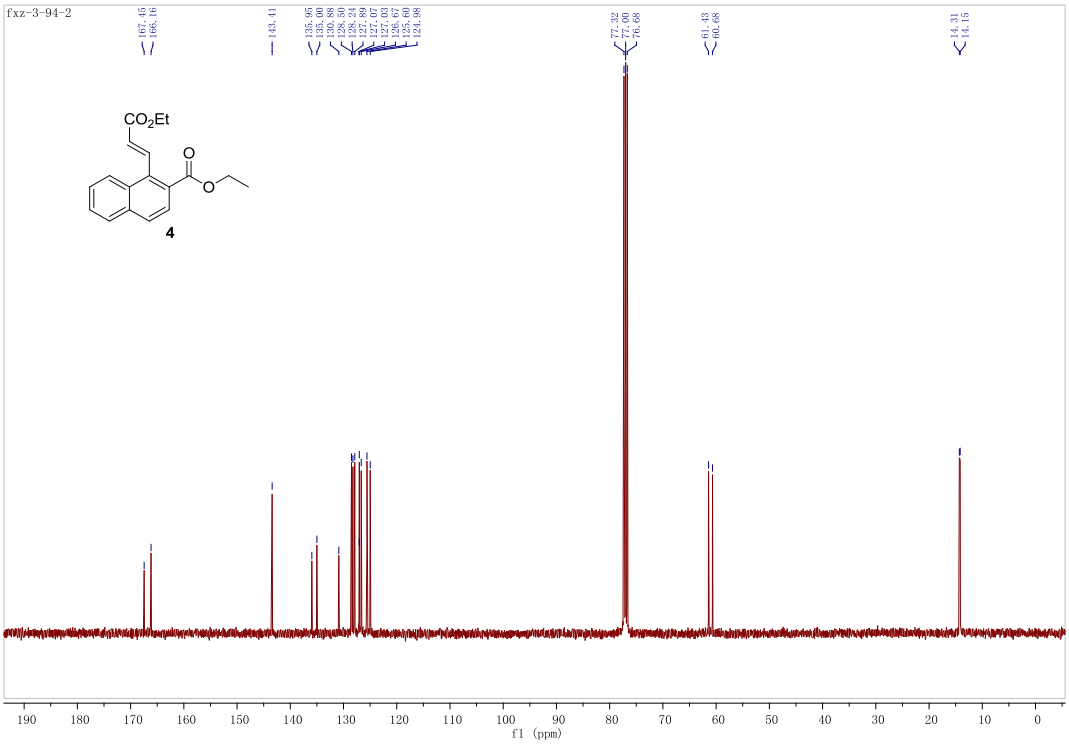

8.592
8.583
8.568
7.875
7.854
7.843
7.837
7.827
7.819
7.570
7.536
7.549
7.542
7.539
7.532
7.503
7.496
7.399
7.380
7.371
7.260
7.100
7.091
7.084
6.992
6.973
6.964
5.472
5.442
4.002
1.583
0.083
Ph
Se
O
O
Ph
3aa
1.00
1.05
1.00
3.00
2.01
3.01
3.03
2.00
2.04
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


fxz-3-86--1c
168.97
138.58
136.36
135.41
134.99
134.21
129.74
129.69
128.69
128.56
128.41
128.34
128.30
127.92
127.48
127.22
126.70
124.15
77.32
77.00
76.68
67.42
33.99
Ph
Se
O
O
Ph
3aa
f1 (ppm)


8.535
8.529
8.512
7.902
7.881
7.861
7.848
7.845
7.838
7.572
7.563
7.553
7.537
7.336
7.260
7.250
7.228
7.210
7.113
7.104
7.098
7.091
6.993
6.983
6.978
6.961
6.944
6.924
5.473
5.456
5.439
5.422
4.025
3.998
3.971
3.943
1.587
1.578
1.561
Ph
Se
O
OPh
3bb


fxz-3-86-13c
Ph
Se
O
OPh
3bb
f1 (ppm)


fxz-3-94-2
CO2Et
O
O
4
f1 (ppm)


fxz-3-94-2
167.45
166.16
143.41
135.95
135.00
130.88
129.30
128.24
127.89
127.07
127.03
125.67
125.60
124.98
77.32
77.00
76.68
61.43
60.68
14.31
14.15
CO2Et
O
O
4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)