Supporting Information for

Synthesis of Selenated Isochromenones by $AgNO_3$-Catalyzed Radical Cyclization of Alkynylaryl Esters, Selenium Powder and $ArB(OH)_2$

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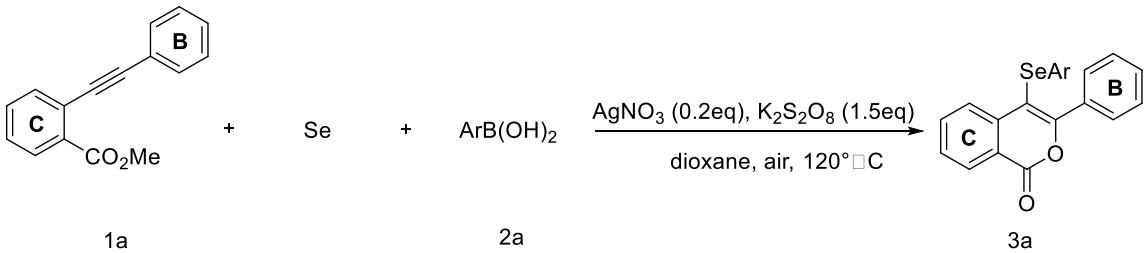
1. General Information

All reagents and solvents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros and Meryer. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300−400 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on a 500 MHz Bruker AVANCE spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C and 470 MHz for ^{19}F), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. Analysis of crude reaction mixture was done on the Varian 4000 GC/MS and Agilent 7890A/5975C. High-resolution mass spectra were recorded on a micrOTOF-Q II 10410 mass spectrometer.

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. The methyl 2-(arylethynylene)benzoate[1] and ethyl 2-(phenylethynyl)benzoate[2], isopropyl 2-(phenylethynyl)benzoate[2], phenyl 2-(phenylethynyl)benzoate[3], [1,1'-biphenyl]-4-yl 2-(phenylethynyl)benzoate[3] were prepared according to corresponding literature procedures.

2. General experimental proceduce

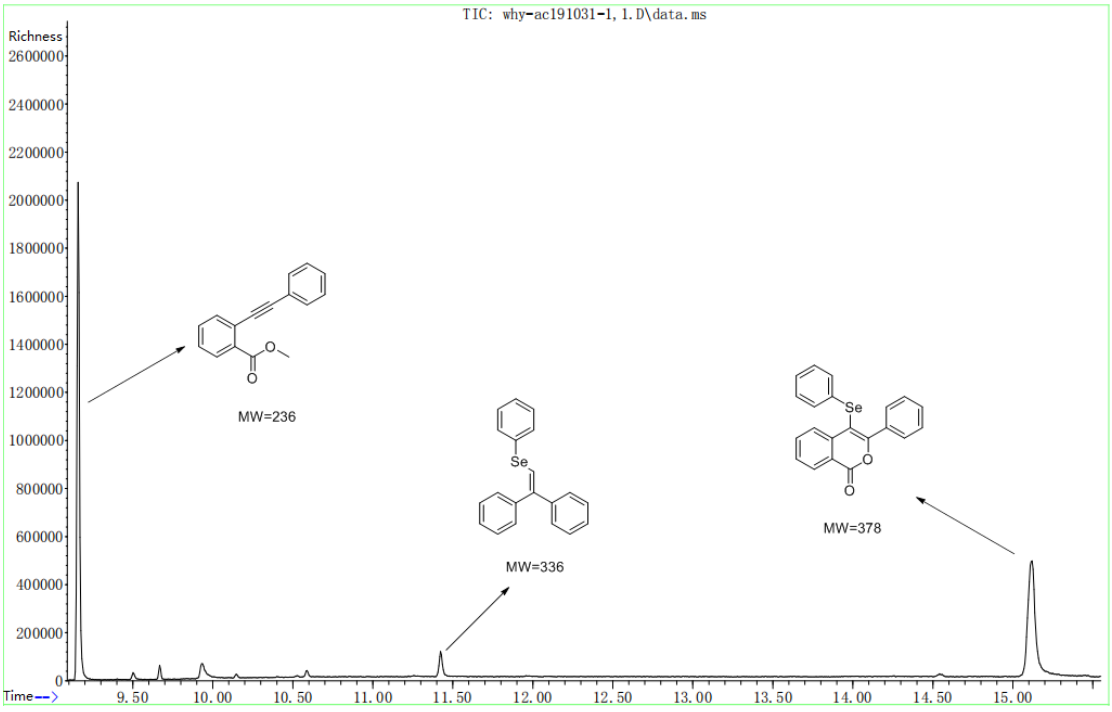


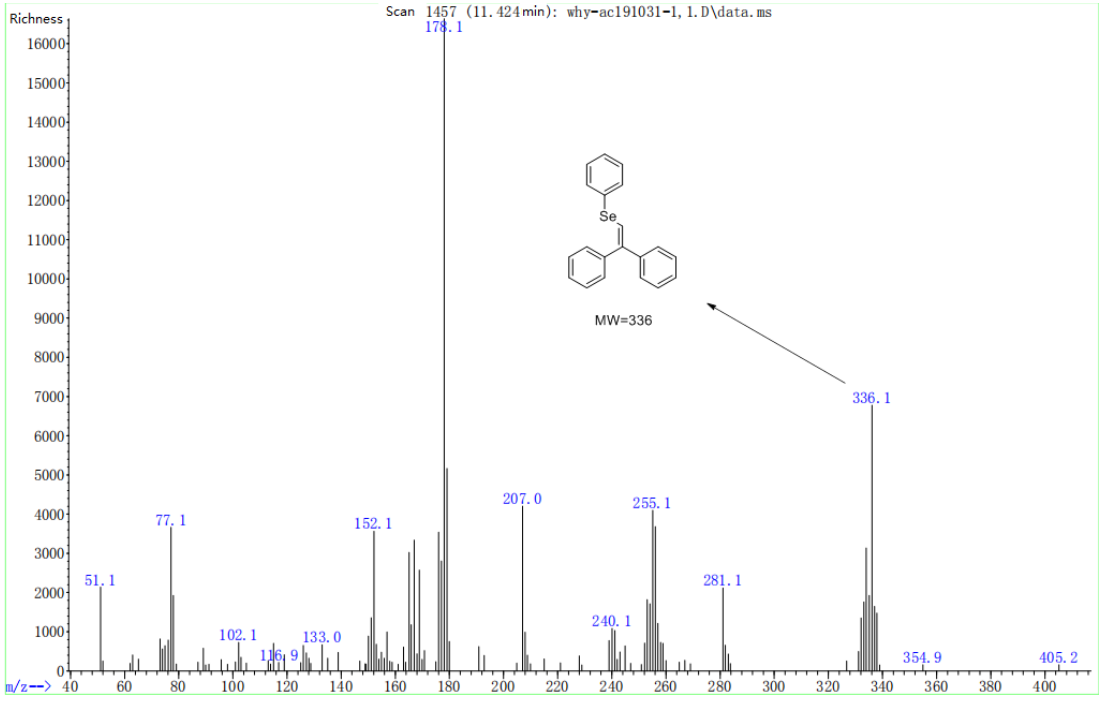
1a 2a 3a

A 25 mL Schlenk tube equipped with a stir bar was charged with $AgNO_3$ (0.06 mmol), 2a (0.6 mmol), Se (0.6 mmol), 1a (0.3 mmol) and dioxane (2 mL) was added in turn to the Schlenk tube , The reaction mixture was stirred at 120 °C for 20 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether, filtered

through a pad of silica gel and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

3. GC-MS data

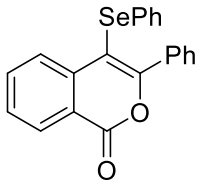




The GC-MS shows an m/z peak of 336, which is in good agreement with that of a selenium radical intermediate.

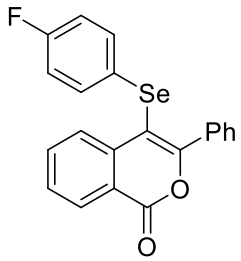
4. Characterization of products in details

3-phenyl-4-(phenylselanyl)-1H-isochromen-1-one (3a) [4]



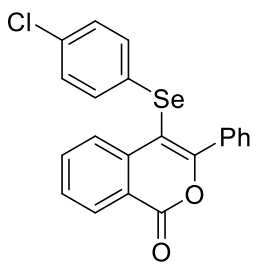
White solid (104 mg, 92% yield); EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.36 (m, 1H), 8.06-8.05 (m, 1H), 7.73-7.70 (m, 1H), 7.67-7.65 (m, 2H), 7.55-7.52 (m, 1H), 7.46-7.40 (m, 3H), 7.21-7.15 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.6, 138.5, 135.3, 134.1, 131.8, 130.1, 129.7, 129.6, 129.5, 128.9, 128.7, 128.3, 127.8, 126.5, 120.9, 104.8.

4-((4-fluorophenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3ba) [4]



White solid (60.6 mg, 51% yield); EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.35 (m, 1H), 8.07-8.05 (m, 1H), 7.75-7.72 (m, 1H), 7.65-7.63 (m, 2H), 7.56-7.53 (m, 1H), 7.47-7.40 (m, 3H), 7.17-7.14 (m, 2H), 6.90-6.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.0 Hz), 161.6, 159.5, 138.3, 135.4, 134.0, 131.3 (d, *J* = 8.8 Hz), 130.2, 129.8, 129.7, 128.8, 128.1, 127.9, 126.0 (d, *J* = 3.8 Hz), 120.9, 116.7 (d, *J* = 21.3 Hz), 105.4. ^{19}F NMR (470 MHz, CDCl3) δ -115.2 (s, 1F).

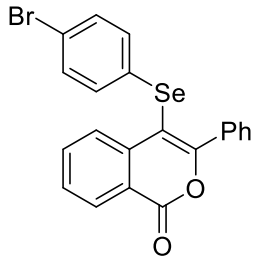
4-((4-chlorophenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3ca) [4]



White solid (102.6 mg, 83% yield); EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38-8.36 (m, 1H), 8.01-8.00 (m, 1H), 7.74-7.71 (m, 1H), 7.64-7.62 (m, 2H),

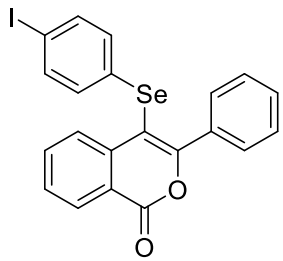
7.57-7.54 (m, 1H), 7.47-7.40 (m, 3H), 7.16-7.14 (m, 2H), 7.12-7.10 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 159.8, 138.2, 135.4, 133.9, 132.7, 130.3, 130.2, 130.0, 129.9, 129.6, 129.5, 128.8, 128.0, 127.9, 120.9, 104.7.

4-((4-bromophenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3da)



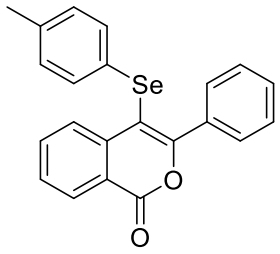
White solid (101.2 mg, 74% yield); mp 105.0-106.4 ºC; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38-8.36 (m, 1H), 8.00-7.99 (m, 1H), 7.74-7.71 (m, 1H), 7.64-7.62 (m, 2H), 7.57-7.54 (m, 1H), 7.46-7.41 (m, 3H), 7.31-7.29 (m, 2H), 7.06-7.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 159.9, 138.1, 135.5, 133.9, 132.5, 130.7, 130.5, 130.3, 129.9, 129.6, 128.9, 128.0, 127.9, 120.9, 120.6, 104.5. HRMS (ESI): calculated for $C_{21}H_{14}BrO_2Se$ $[M+H]^+$ 456.9337, found 456.9320.

4-((4-iodophenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3ea)



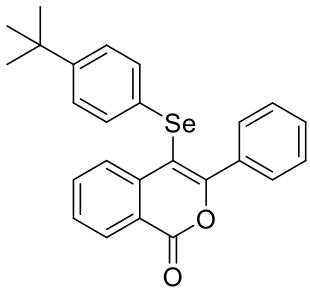
White solid (54.4 mg, 36% yield); mp 106.8-107.4 ºC; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.36 (m, 1H), 7.99-7.98 (m, 1H), 7.73-7.70 (m, 1H), 7.64-7.62 (m, 2H), 7.56-7.53 (m, 1H), 7.49-7.39 (m, 5H), 6.93-6.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 159.9, 138.4, 138.1, 135.5, 133.9, 131.8, 130.6, 130.3, 129.9, 129.6, 128.9, 128.0, 127.9, 120.9, 104.3, 91.5. HRMS (ESI): calculated for $C_{21}H_{14}IO_2Se$ $[M+H]^+$ 504.9198, found 504.9193.

3-phenyl-4-(p-tolylselanyl)-1H-isochromen-1-one (3fa) [4]



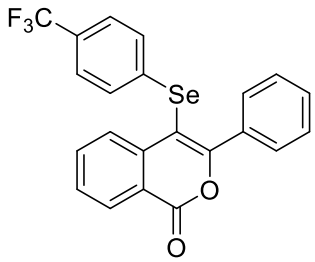
White solid (108 mg, 92% yield); EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.36 (m, 1H), 8.09-8.08 (m, 1H), 7.71-7.69 (m, 3H), 7.54-7.51 (m, 1H), 7.45-7.40 (m, 3H), 7.12-7.11 (m, 2H), 7.02-7.00 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.4, 138.6, 136.5, 135.3, 134.2, 130.3, 130.1, 129.8, 129.7, 129.2, 128.6, 128.4, 128.0, 127.8, 120.9, 105.2, 21.0.

4-((4-(tert-butyl)phenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3ga)



White solid (86 mg, 66% yield); mp 102.0-102.4 °C; EtOAc/PE = 1/40.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.36 (m, 1H), 8.11-8.10 (m, 1H), 7.73-7.68 (m, 3H), 7.55-7.52 (m, 1H), 7.44-7.40 (m, 3H), 7.22-7.21 (m, 2H), 7.14-7.13 (m, 2H), 1.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.4, 149.8, 138.7, 135.3, 134.2, 130.0, 129.8, 129.7, 128.9, 128.6, 128.4, 128.1, 127.8, 126.6, 120.9, 105.1, 34.5, 31.2. HRMS (ESI): calculated for $C_{25}H_{23}O_2Se$ $[M+H]^+$ 435.0858, found 435.0858.

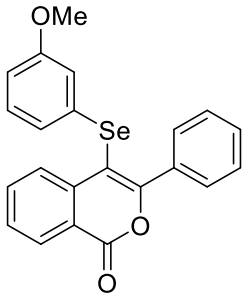
3-phenyl-4-((4-(trifluoromethyl)phenyl)selanyl)-1H-isochromen-1-one (3ha)



White solid (92 mg, 69% yield); mp 91.9-92.0 °C; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39-8.38 (m, 1H), 7.97-7.95 (m, 1H), 7.74-7.71 (m, 1H), 7.64-7.62 (m, 2H), 7.58-7.55 (m, 1H), 7.45-7.39 (m, 5H), 7.30-7.29 (m, 2H); ^{13}C NMR (125

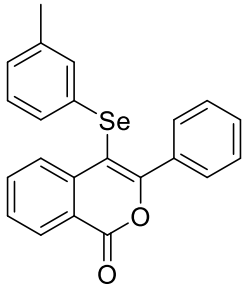
MHz, $CDCl_3$) δ 161.4, 160.3, 138.0, 137.2, 135.6, 133.8, 130.4, 130.0, 129.5, 129.0, 128.7 (q, *J* = 32.5 Hz), 128.5, 127.9, 127.8, 126.2 (q, *J* = 3.8 Hz), 124.0(q, *J* =270.0 Hz), 120.9, 103.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.6 (s, 1F). HRMS (ESI): calculated for $C_{22}H_{14}O_2Se$ $[M+H]^+$ 447.0106, found 447.0106.

4-((3-methoxyphenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3ia)



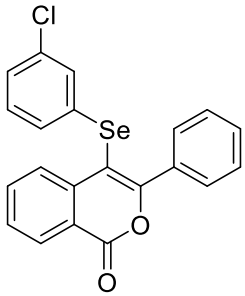
White solid (50 mg, 41% yield); mp 96.2-96.4 °C; EtOAc/PE = 1/40. ^1H NMR (500 MHz, $CDCl_3$) δ 8.37-8.35 (m, 1H), 8.06-8.05 (m, 1H), 7.73-7.67 (m, 3H), 7.55-7.52 (m, 1H), 7.44-7.39 (m, 3H), 7.12-7.09 (m, 1H), 6.80-6.78 (m, 1H), 6.76 (s, 1H), 6.71-6.69 (m, 1H), 3.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 160.2, 159.7, 138.5, 135.4, 134.1, 133.0, 130.3, 130.1, 129.7, 128.7, 128.3, 127.8, 121.1, 120.8, 114.7, 112.0, 104.7, 55.2. HRMS (ESI): calculated for $C_{22}H_{17}O_3Se$ $[M+H]^+$ 409.0338, found 409.0330.

3-phenyl-4-(m-tolylselanyl)-1H-isochromen-1-one (3ja)



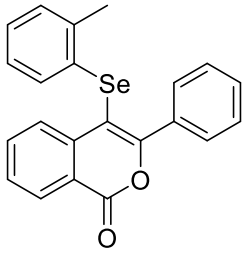
White solid (92 mg, 78% yield); mp 86.4-86.8 °C; EtOAc/PE = 1/40. ^1H NMR (500 MHz, $CDCl_3$) δ 8.37-8.36 (m, 1H), 8.07-8.06 (m, 1H), 7.73-7.67 (m, 3H), 7.55-7.52 (m, 1H), 7.44-7.39 (m, 3H), 7.08-7.03 (m, 2H), 6.99-6.96 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.5, 139.3, 138.6, 135.3, 134.1, 131.6, 130.1, 129.7, 129.6, 129.5, 129.3, 128.7, 128.3, 127.8, 127.4, 126.0, 120.9, 104.9, 21.3. HRMS (ESI): calculated for $C_{22}H_{17}O_2Se$ $[M+H]^+$ 393.0389, found 393.0392.

4-((3-chlorophenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3ka)



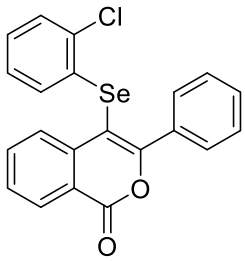
White solid (105 mg, 85% yield); mp 92.0-93.3 ºC; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38-8.37 (m, 1H), 8.01-8.00 (m, 1H), 7.75-7.72 (m, 1H), 7.65-7.63 (m, 2H), 7.57-7.54 (m, 1H), 7.47-7.40 (m, 3H),7.18 (s, 1H), 7.14-7.04 (m, 3H), ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 160.0, 138.1, 135.5, 135.3, 133.9, 133.5, 130.4, 129.9, 129.6, 128.9, 128.6, 128.0, 127.9, 126.9, 126.8, 120.9, 104.4. HRMS (ESI): calculated for $C_{21}H_{13}ClO_2Se$ $[M+H]^+$ 412.9842, found 412.9848.

3-phenyl-4-(o-tolylselanyl)-1H-isochromen-1-one (3la)



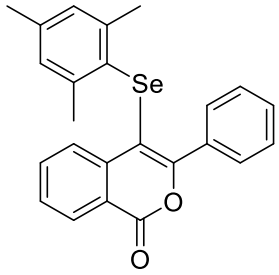
White solid (93 mg, 79% yield); mp 114.8-115.4 ºC; EtOAc/ PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39-8.38 (m, 1H), 7.96-7.95 (m, 1H), 7.71-7.66 (m, 3H), 7.56-7.53 (m, 1H), 7.45-7.37 (m, 3H), 7.17-7.15 (m, 1H),7.11-7.08 (m, 1H), 6.97-6.96 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.7, 138.5, 136.5, 135.4, 134.1, 132.7, 130.4, 130.1, 129.7, 129.6, 128.7, 128.3, 127.9, 127.8, 127.1, 126.2, 120.9, 104.1, 21.3. HRMS (ESI): calculated for $C_{22}H_{17}O_2Se$ $[M+H]^+$ 393.0389, found 393.0382.

4-((2-chlorophenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3ma)



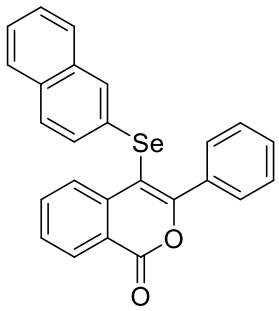
White solid (86 mg, 70% yield); EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39-8.38 (m, 1H), 7.94-7.92 (m, 1H), 7.72-7.69 (m, 1H), 7.65-7.64 (m, 2H), 7.57-7.54 (m, 1H), 7.45-7.37 (m, 3H), 7.35-7.33 (m, 1H), 7.13-7.10 (m, 1H), 7.04-7.01(m 1H), 6.92-6.90 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 160.4, 138.1, 135.6, 133.8, 132.7, 132.5, 130.3, 129.8, 129.7, 129.5, 128.9, 128.7, 128.0, 127.9, 127.7, 127.2, 120.9, 103.7.

4-(mesitylselanyl)-3-phenyl-1H-isochromen-1-one (3na)



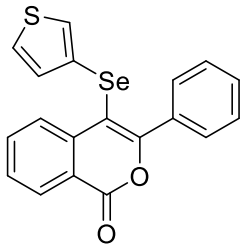
White solid (89 mg, 71% yield); mp 101.6-102.1 ºC; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33-8.31 (m, 1H), 7.84-7.83 (m, 1H), 7.65-7.62 (m, 1H), 7.51-7.46 (m, 3H), 7.45-7.37 (m, 3H), 6.71 (s, 2H), 2.18 (s, 6H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 156.1, 141.1, 138.6, 137.7, 134.8, 134.2, 129.8, 129.7, 129.6, 129.1, 128.4, 128.1, 127.7, 127.3, 120.7, 107.3, 23.7, 20.7. HRMS (ESI): calculated for $C_{24}H_{21}O_2Se$ $[M+H]^+$ 421.0702, found 421.0707.

4-(naphthalen-2-ylselanyl)-3-phenyl-1H-isochromen-1-one (3oa)



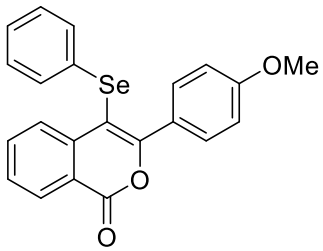
White solid (59 mg, 46% yield); mp 103.5-104.1 ºC; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40-8.39 (m, 1H), 8.10-8.09 (m, 1H), 7.77-7.76 (m, 1H), 7.73-7.72 (m, 2H), 7.69-7.63 (m, 4H), 7.54-7.51 (m, 1H), 7.46-7.39 (m, 5H), 7.33-7.30 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.8, 138.5, 135.4, 134.1, 134.0, 132.0, 130.2, 129.8, 129.7, 129.4, 129.0, 128.8, 128.3, 127.9, 127.8, 127.3, 127.1, 126.7, 126.6, 125.9, 120.9, 104.7. HRMS (ESI): calculated for $C_{25}H_{17}O_2Se$ $[M+H]^+$ 429.0389, found 429.0396.

3-phenyl-4-(thiophen-3-ylselanyl)-1H-isochromen-1-one (3pa)



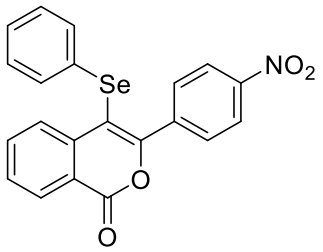
White solid (61mg, 53% yield); mp 95.5-97.2 ºC; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35-8.33 (m, 1H), 8.17-8.16 (m, 1H), 7.76-7.73 (m, 1H), 7.66-7.65 (m, 2H), 7.55-7.52 (m, 1H), 7.45-7.41 (m, 3H), 7.25-7.22 (m, 1H), 6.96 (s, 1H), 6.83-6.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 158.9, 138.5, 135.2, 134.1, 130.1, 129.9, 129.7, 129.5, 128.7, 128.2, 127.8, 126.7, 124.1, 123.8, 120.9, 105.8. HRMS (ESI): calculated for $C_{19}H_{13}SO_2Se$ $[M+H]^+$ 384.9796, found 384.9796.

3-(4-methoxyphenyl)-4-(phenylselanyl)-1H-isochromen-1-one (3ab) [4]



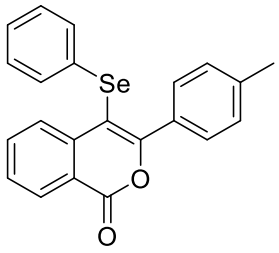
White solid (95 mg, 78% yield); EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35-8.34 (m, 1H), 8.04-8.02 (m, 1H), 7.70-7.65 (m, 3H), 7.52-7.49 (m, 1H), 7.20-7.15 (m, 5H), 6.92-6.90 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 161.1, 159.5, 138.8, 135.3, 132.0, 131.4, 129.6, 129.5, 128.7, 128.4, 128.2, 126.4, 126.3, 120.7, 113.2, 103.8, 55.3.

3-(4-nitrophenyl)-4-(phenylselanyl)-1H-isochromen-1-one (3ac)



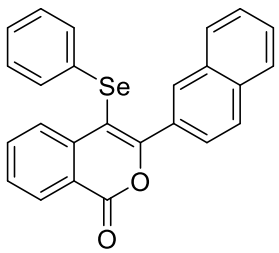
Yellow solid (82 mg, 65% yield); mp 106.7-107.4 °C; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.36 (m, 1H), 8.23-8.21 (m, 2H), 8.10-8.09 (m, 1H), 7.84-7.83 (m, 2H), 7.77-7.74 (m, 1H), 7.61-7.58 (m, 1H), 7.19-7.18 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 156.8, 148.4, 139.9, 137.9, 135.7, 131.2, 130.8, 129.9, 129.8, 129.5, 129.0, 128.5, 127.0, 123.0, 121.0, 106.8. HRMS (ESI): calculated for $C_{21}H_{14}NO_4Se$ $[M+H]^+$ 424.0083, found 424.0076.

4-(phenylselanyl)-3-(p-tolyl)-1H-isochromen-1-one (3ad) [4]



White solid (82 mg, 70% yield); EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.35 (m, 1H), 8.05-8.03 (m, 1H), 7.71-7.68 (m, 1H), 7.59-7.57 (m, 2H), 7.54-7.51 (m, 1H), 7.22-7.15 (m, 7H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 159.8, 140.4, 138.6, 135.3, 132.0, 131.2, 129.7, 129.6, 129.5, 128.8, 128.5, 128.4, 128.2, 126.4, 120.8, 104.3, 21.5.

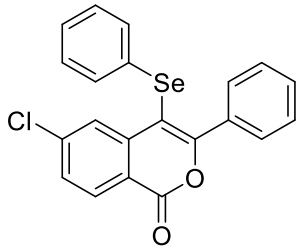
3-(naphthalen-2-yl)-4-(phenylselanyl)-1H-isochromen-1-one (3ae)



White solid (114 mg, 89% yield); mp 94.9-96.3 °C; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40-8.39 (m, 1H), 8.17 (s, 1H), 8.12-8.10 (m, 1H), 7.87-7.82 (m, 3H),

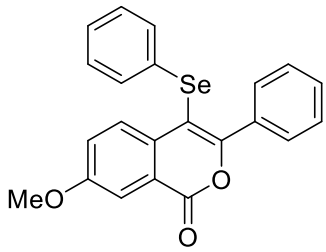
7.78-7.72 (m, 2H), 7.57-7.51 (m, 3H), 7.24-7.18 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.6, 138.6, 135.4, 133.9, 132.3, 132.0, 131.4, 130.1, 129.8, 129.5, 129.0, 128.8, 128.7, 128.3, 127.7, 127.4, 127.3, 126.6, 126.5, 126.4, 120.9, 105.2. HRMS (ESI): calculated for $C_{25}H_{17}O_2Se$ $[M+H]^+$ 429.0389, found 429.0386.

6-chloro-3-phenyl-4-(phenylselanyl)-1H-isochromen-1-one (3af) [4]



White solid (108 mg, 87% yield); EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29-8.28 (m, 1H), 8.08 (s, 1H), 7.66-7.64 (m, 2H), 7.49-7.39 (m, 4H), 7.21-7.18 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 160.8, 142.4, 140.3, 133.8, 131.4, 131.3, 130.4, 129.7, 129.6, 129.3, 129.2, 128.0, 127.9, 126.9, 119.2, 104.1.

7-methoxy-3-phenyl-4-(phenylselanyl)-1H-isochromen-1-one (3ag)



White solid (99 mg, 81% yield); mp 109.8-110.7 ºC; EtOAc/PE = 1/40. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.96 (m, 1H), 7.78-7.77 (m, 1H), 7.66-7.65 (m, 2H), 7.43-7.38 (m, 3H), 7.28-7.27 (m, 1H), 7.19-7.15 (m, 5H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 159.9, 157.5, 134.0, 132.1, 131.9, 130.0, 129.9, 129.7, 129.5, 128.9, 127.8, 126.4, 124.6, 122.0, 110.3, 104.5, 55.8. HRMS (ESI): calculated for $C_{22}H_{17}O_3Se$ $[M+H]^+$ 409.0338, found 409.033.

Reference:

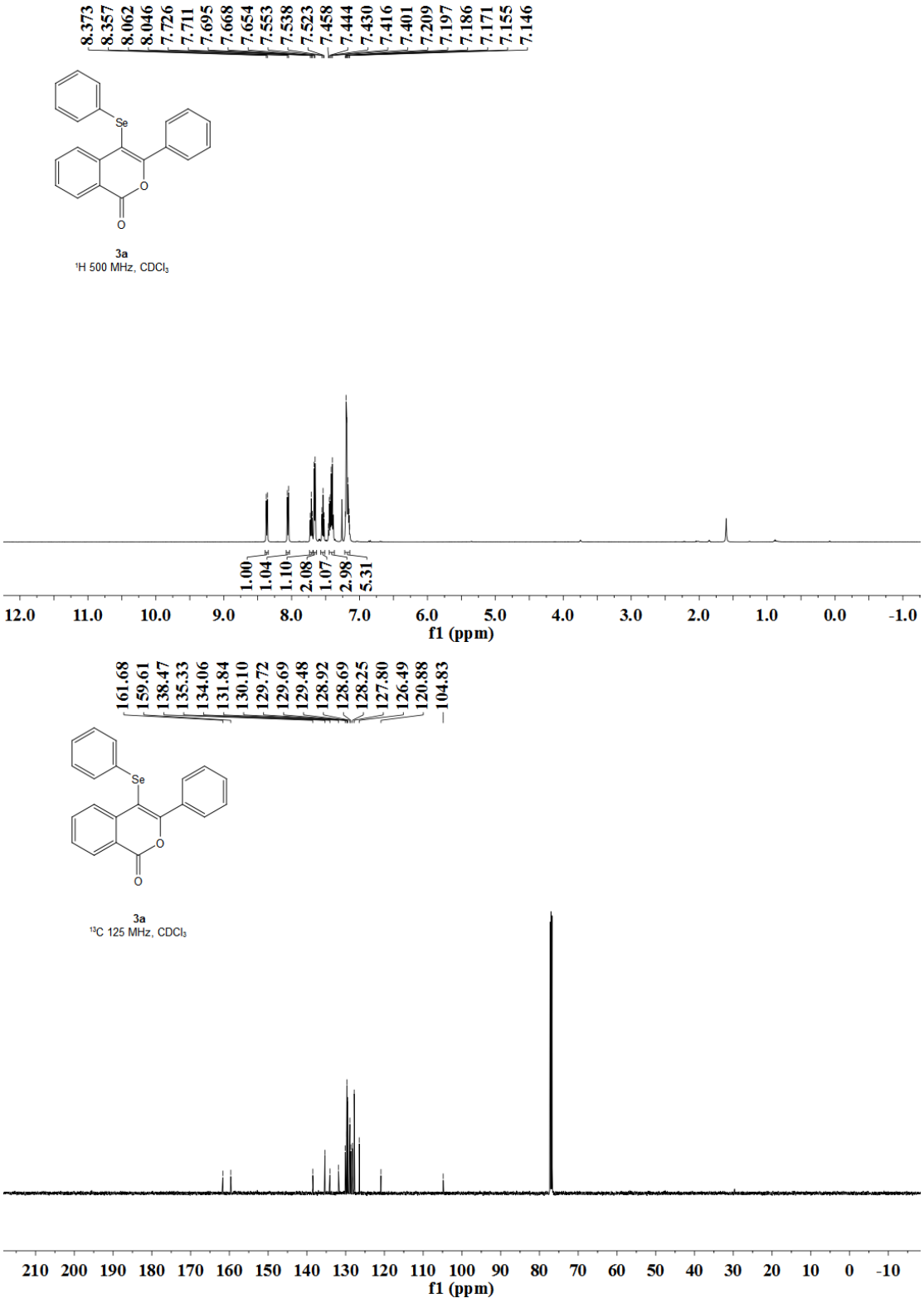
[1] Lv, J. H.; Zhao, B.L.; Liu, L.; Han, Y.; Yuan, Y.; Shi, Z. Z. Boron Trichloride-Mediated Synthesis of Indoles via the Aminoboration of Alkynes.. Adv. Synth. Catal., **2018**, 360, (21), 4054-4059.

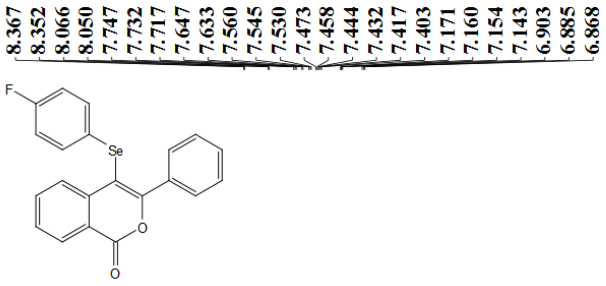
[2] Norseeda, K.; Chaisan, N.; Thongsornkleeb, C.; Tummatorn, J.; Ruchirawat. S. Metal-Free Synthesis of 4-Chloroisocoumarins by TMSCl-Catalyzed NCS-Induced Chlorinative Annulation of 2-Alkynylaryloate Esters. *J. Org. Chem*. 2019, 84, 16222-16236.

[3] Dohi, T.; Koseki, D.; Sumida, K.; Okada, K.; Mizuno, S.; Kato, A.; Morimoto, K.; Kita. Y. Metal-Free O-Arylation of Carboxylic Acid by ActiveDiaryliodonium(III) Intermediates Generated in situ from Iodosoarenes. *Adv. Synth. Catal.* **2017**, 359, 3503-3508.

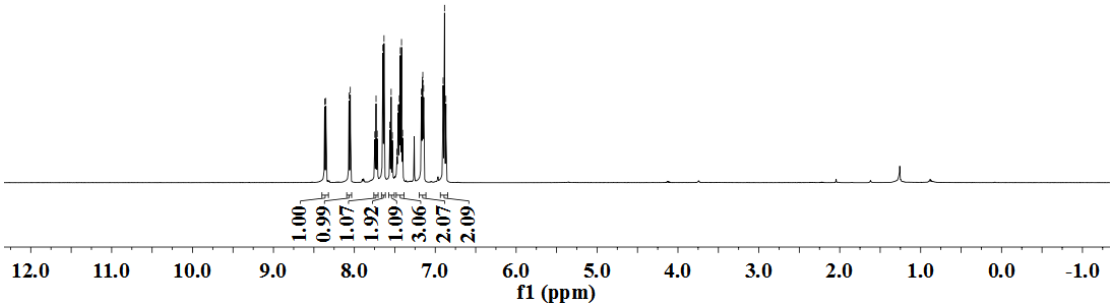
[4] Speranca, A.; Godoi, B.; Pinton, S.; Back, D. F.; Menezes, P. H.; Zeni, G. Regioselective Synthesis of Isochromenones by Iron(III)/PhSeSePh Mediated Cyclization of 2-Alkynylaryl Esters. *J. Org. Chem*. 2011, 76, 6789-6797.

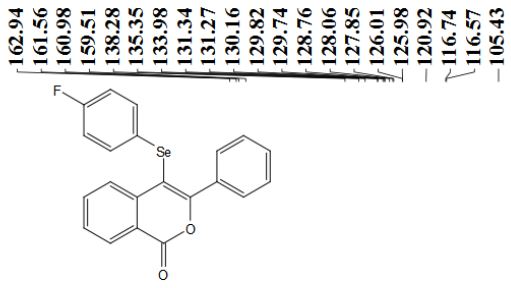
5. ^{1}H, ^{13}C and ^{19}F NMR spectra of products



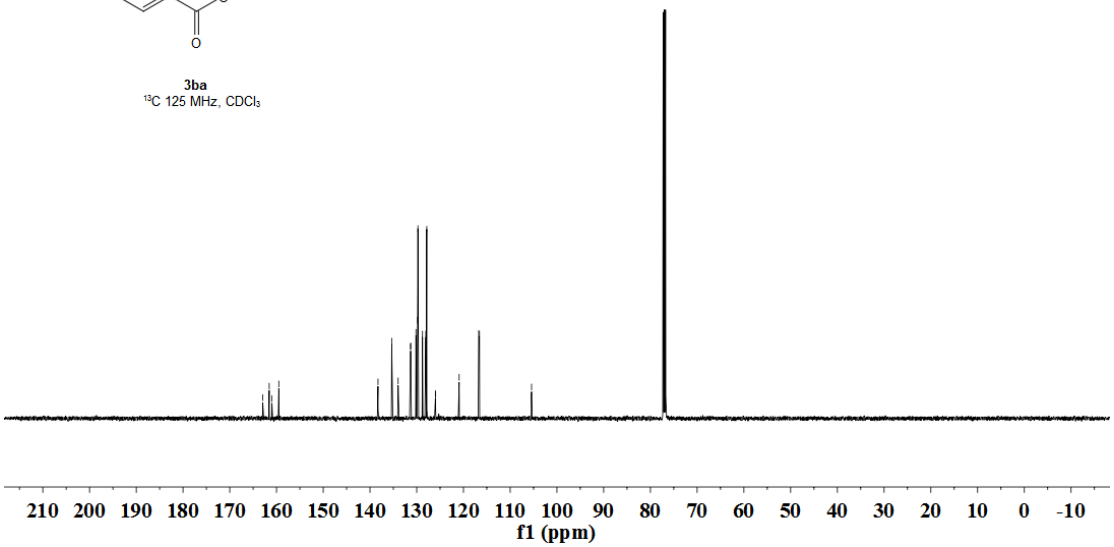


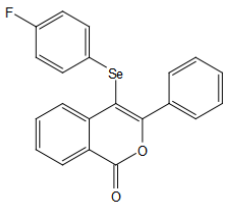
3ba
^{1}H 500 MHz, $CDCl_3$



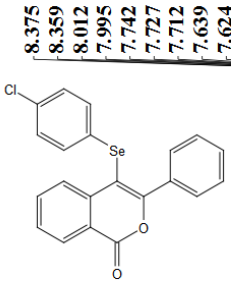


3ba
^{13}C 125 MHz, $CDCl_3$

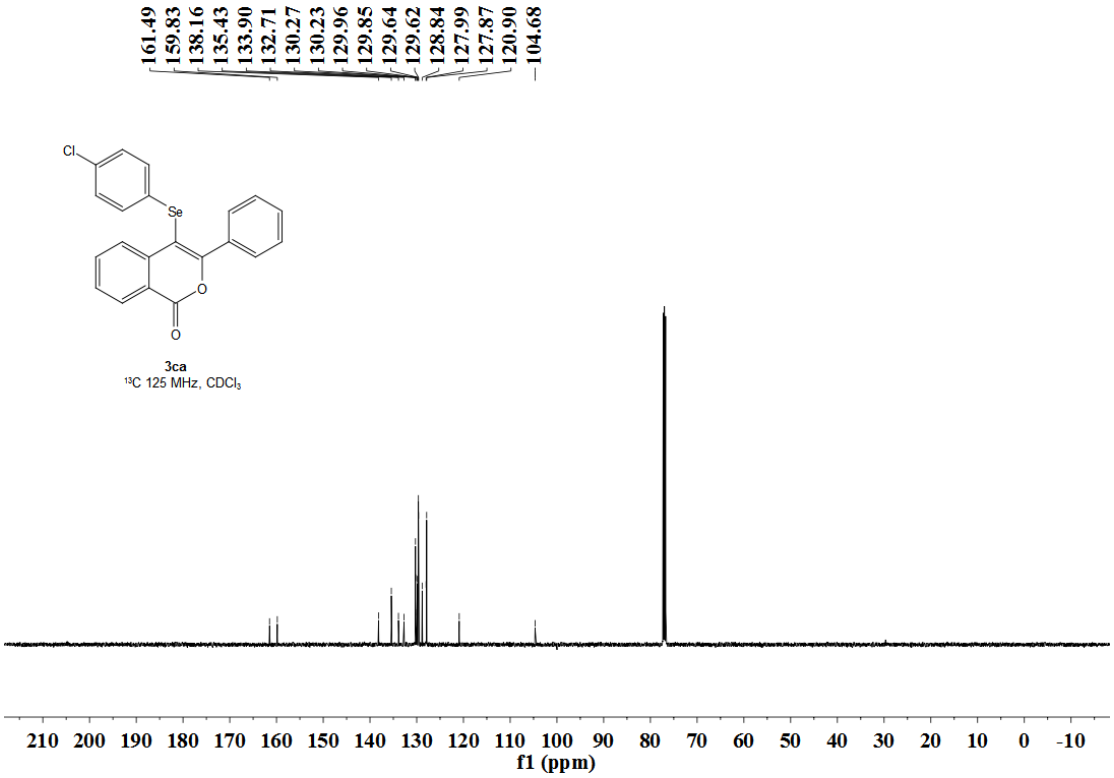


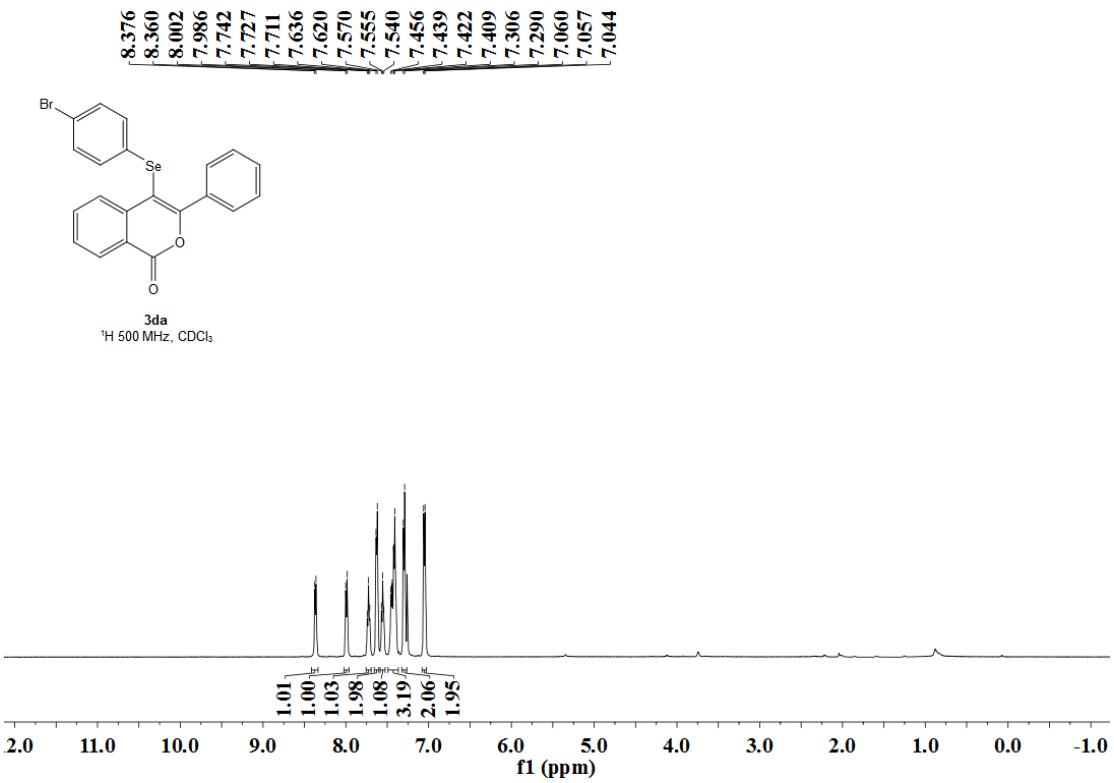


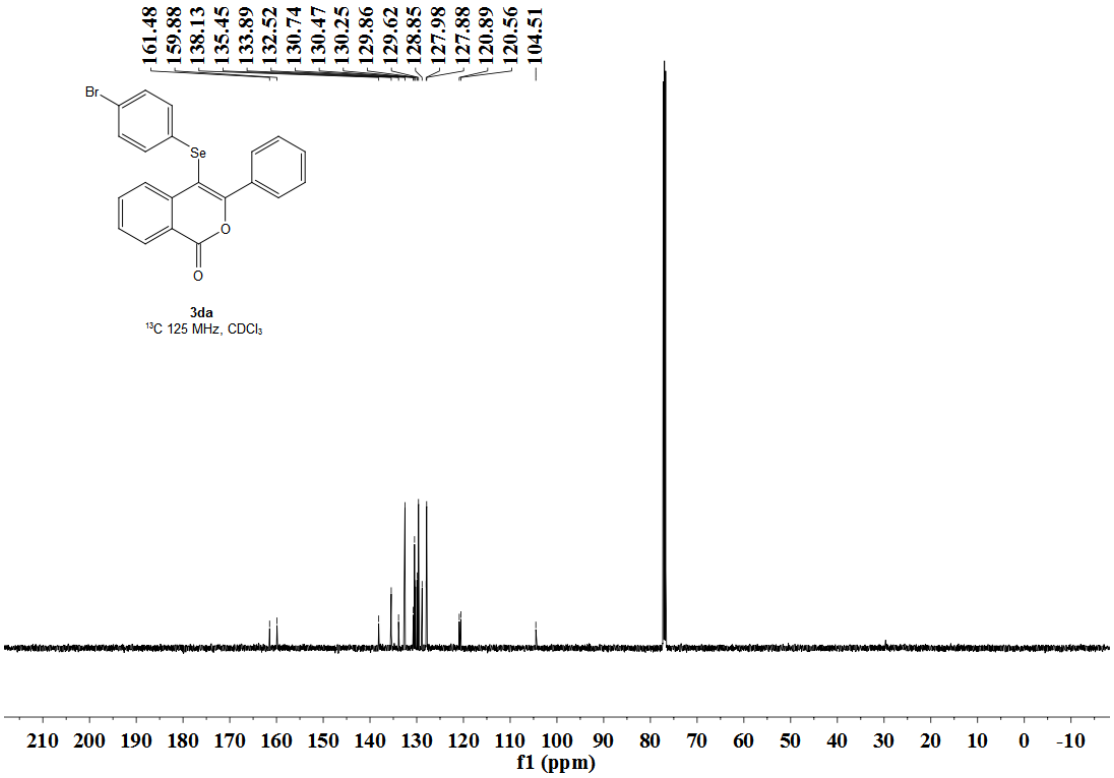
3ba
^{19}F 470 MHz, $CDCl_3$



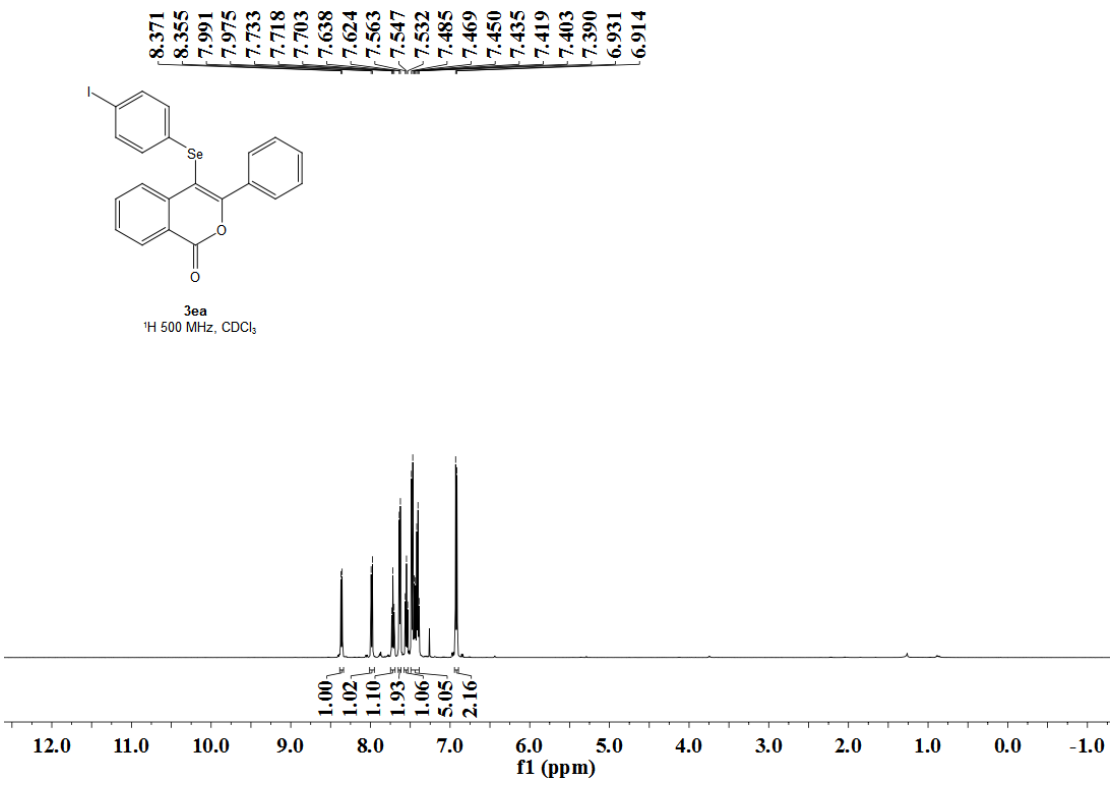
3ca
^{1}H 500 MHz, $CDCl_3$


161.49
159.83
138.16
135.43
133.90
132.71
130.27
130.23
129.96
129.85
129.64
129.62
128.84
127.99
127.87
120.90
104.68
Cl
Se
O
O
3ca
13C 125 MHz, CDCl3
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)

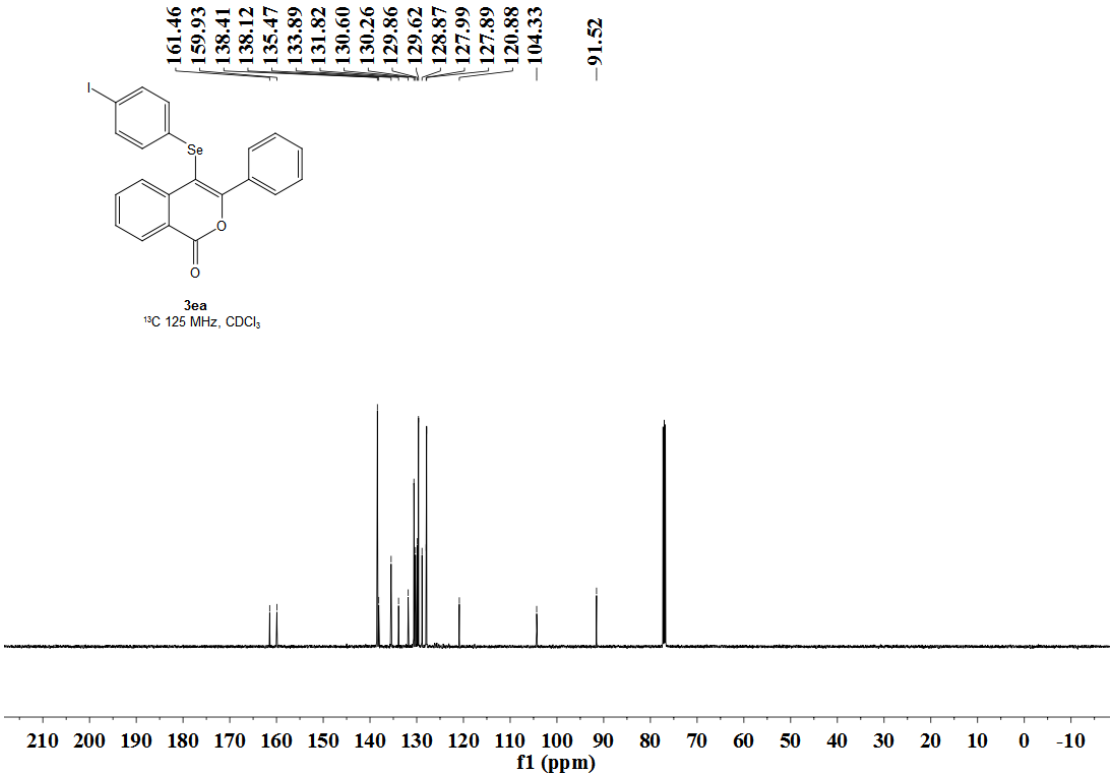

8.376
8.360
8.002
7.986
7.742
7.727
7.711
7.636
7.620
7.570
7.555
7.540
7.456
7.439
7.422
7.409
7.306
7.290
7.060
7.057
7.044
Br
Se
O
O
3da
1H 500 MHz, CDCl3
1.01
1.00
1.03
1.98
1.08
3.19
2.06
1.95
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)



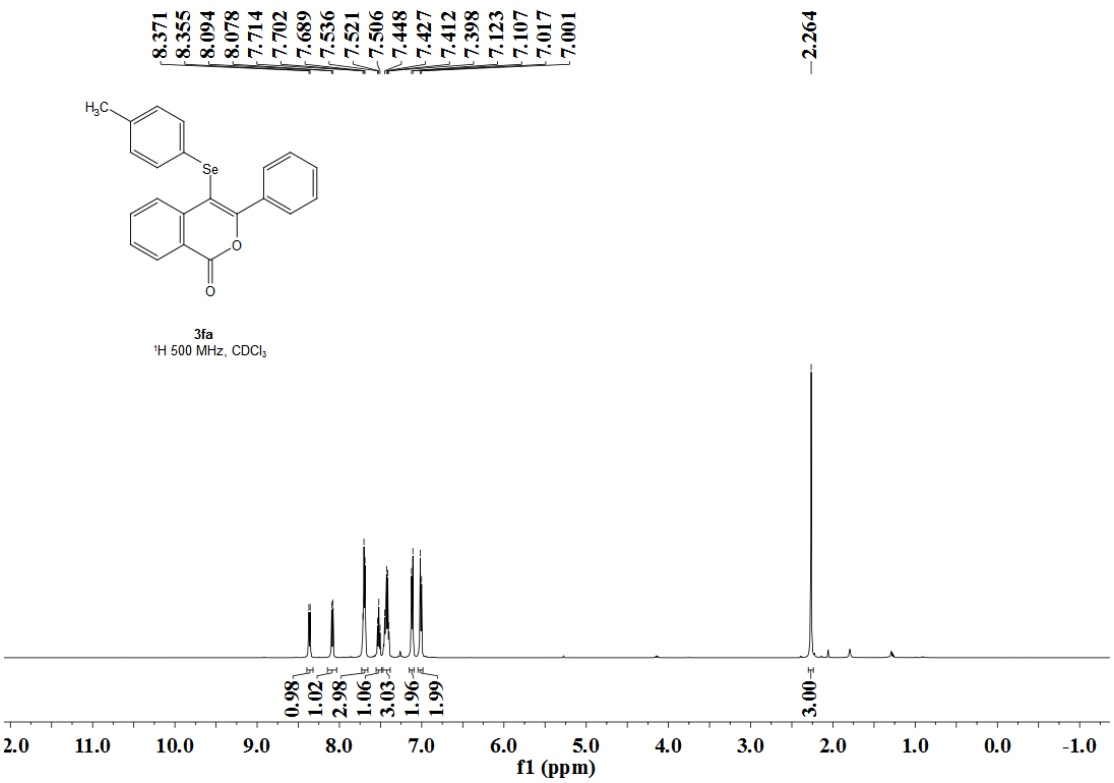
3da
^{13}C 125 MHz, $CDCl_3$



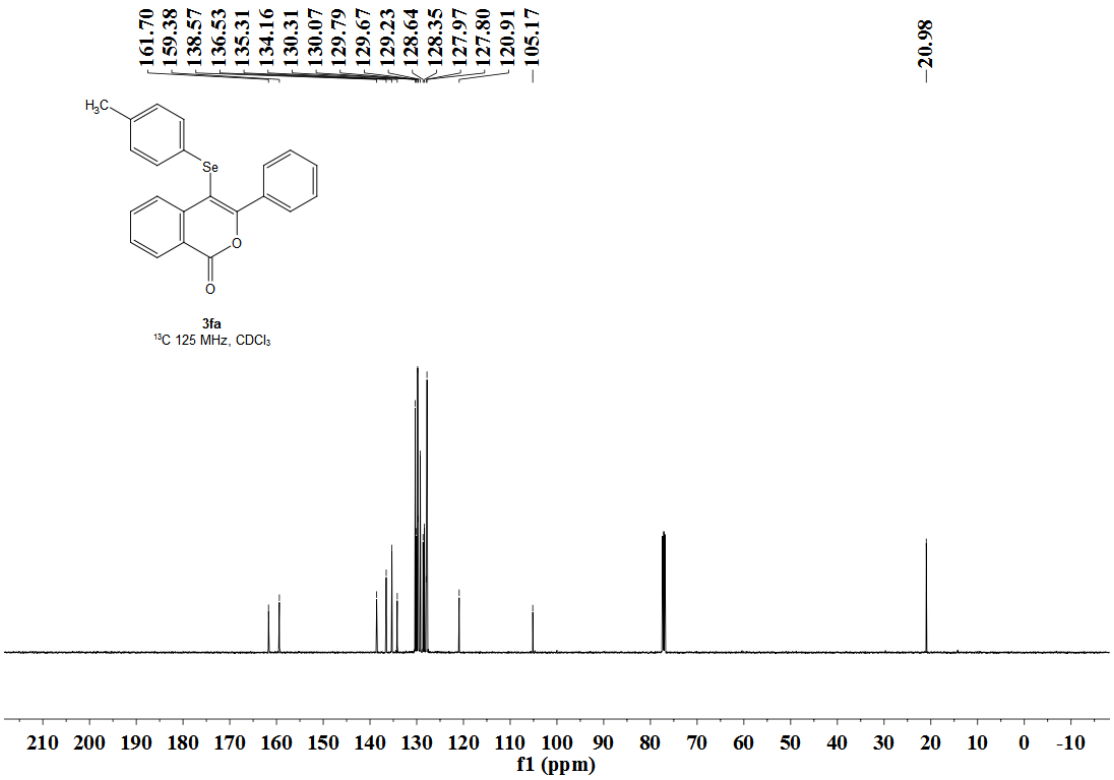
3ea
^{1}H 500 MHz, $CDCl_3$



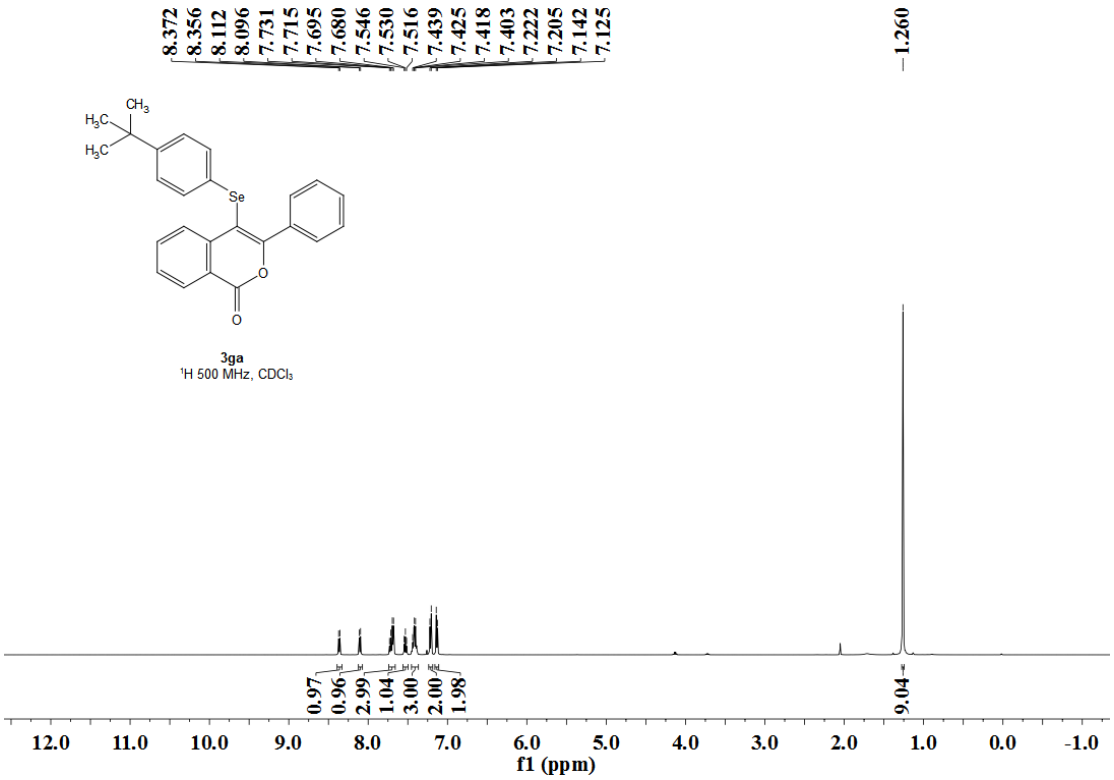
3ea
^{13}C 125 MHz, $CDCl_3$



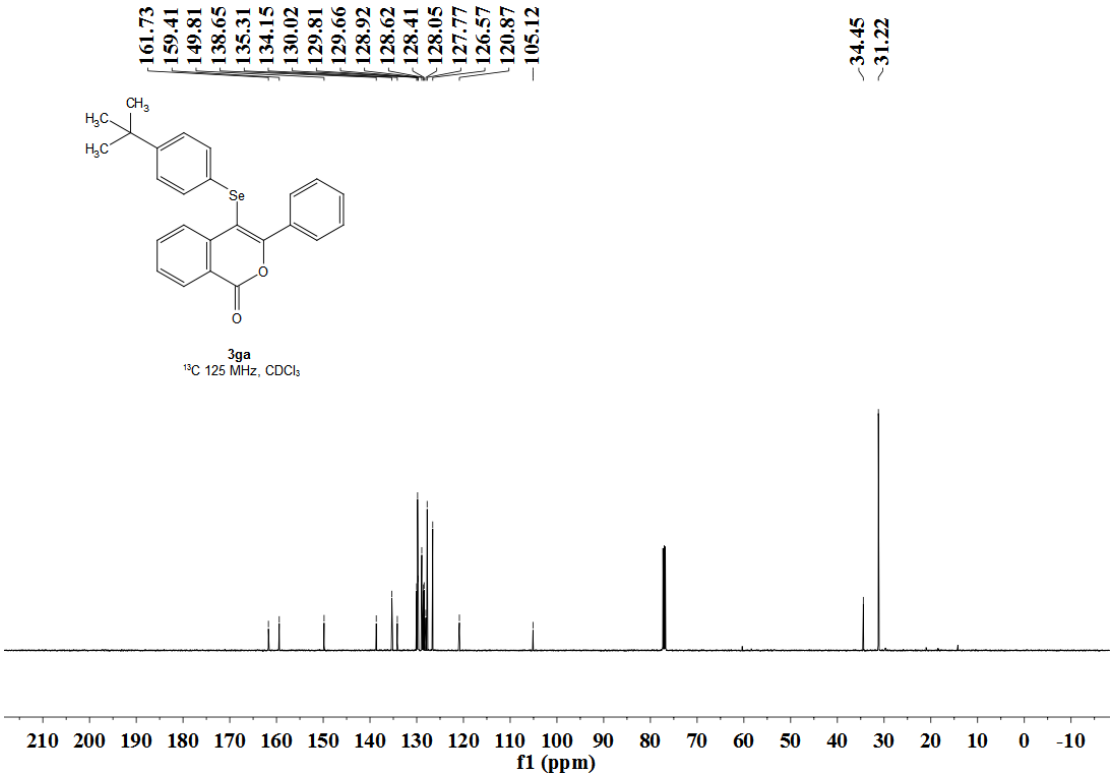
3fa
^{1}H 500 MHz, $CDCl_3$



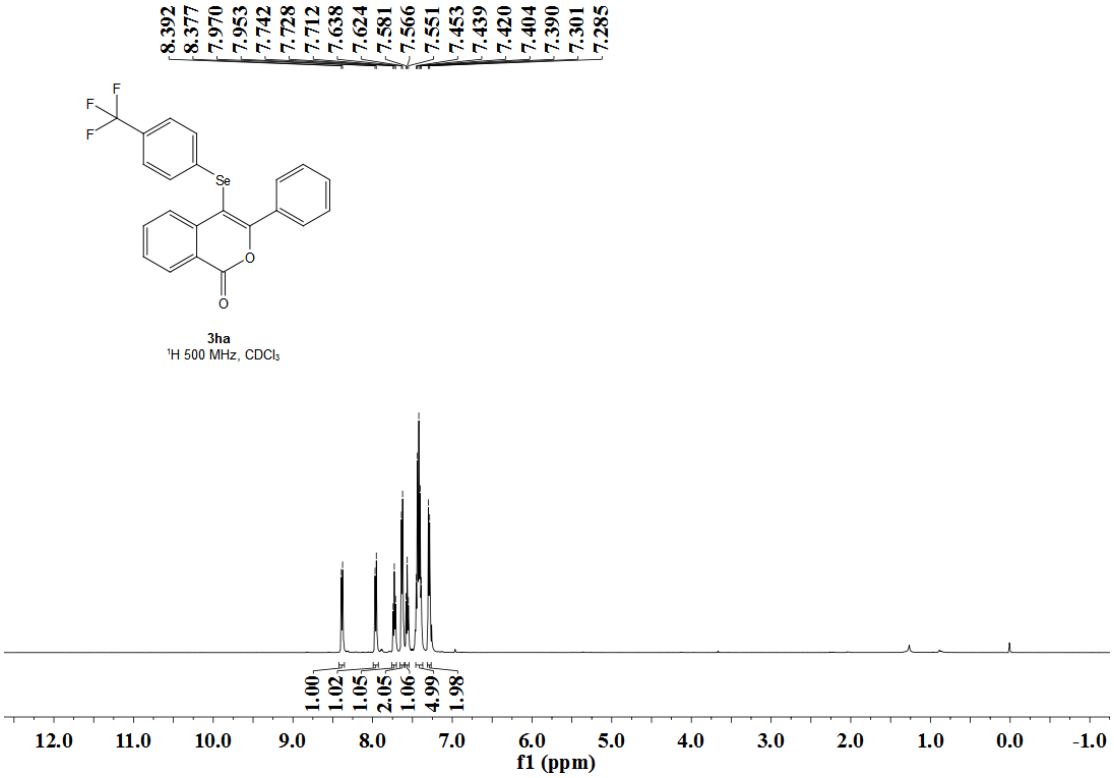
3fa
^{13}C 125 MHz, $CDCl_3$



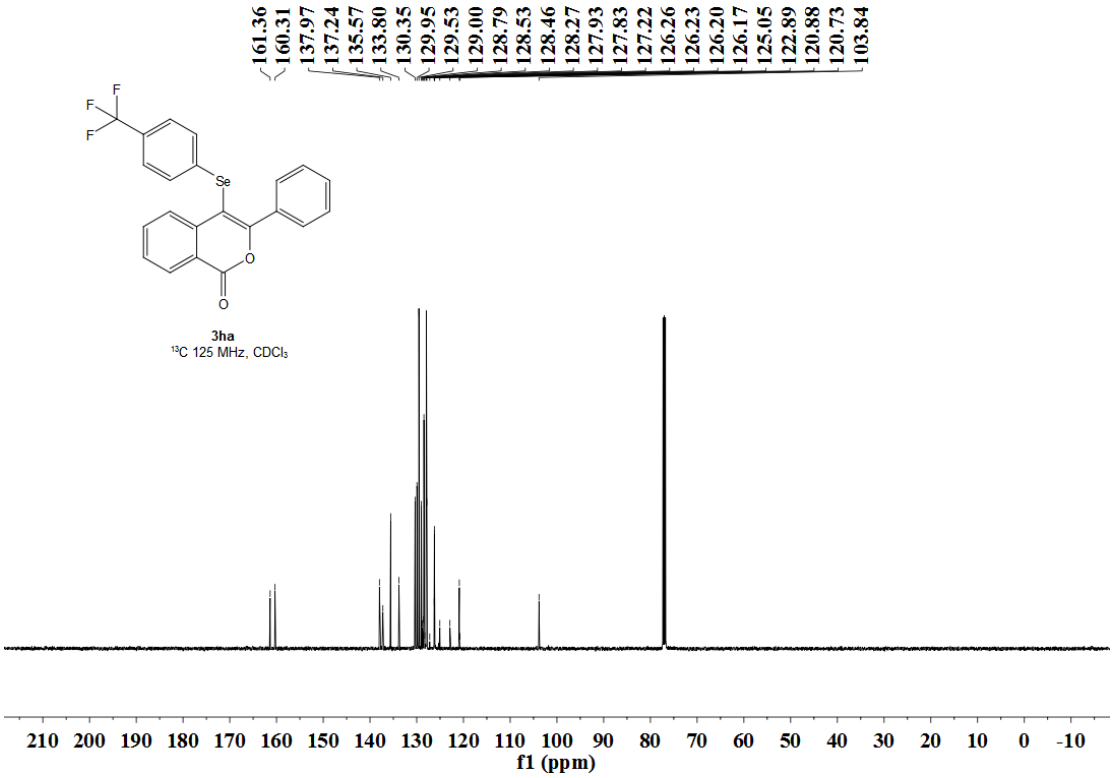
3ga
^{1}H 500 MHz, $CDCl_3$

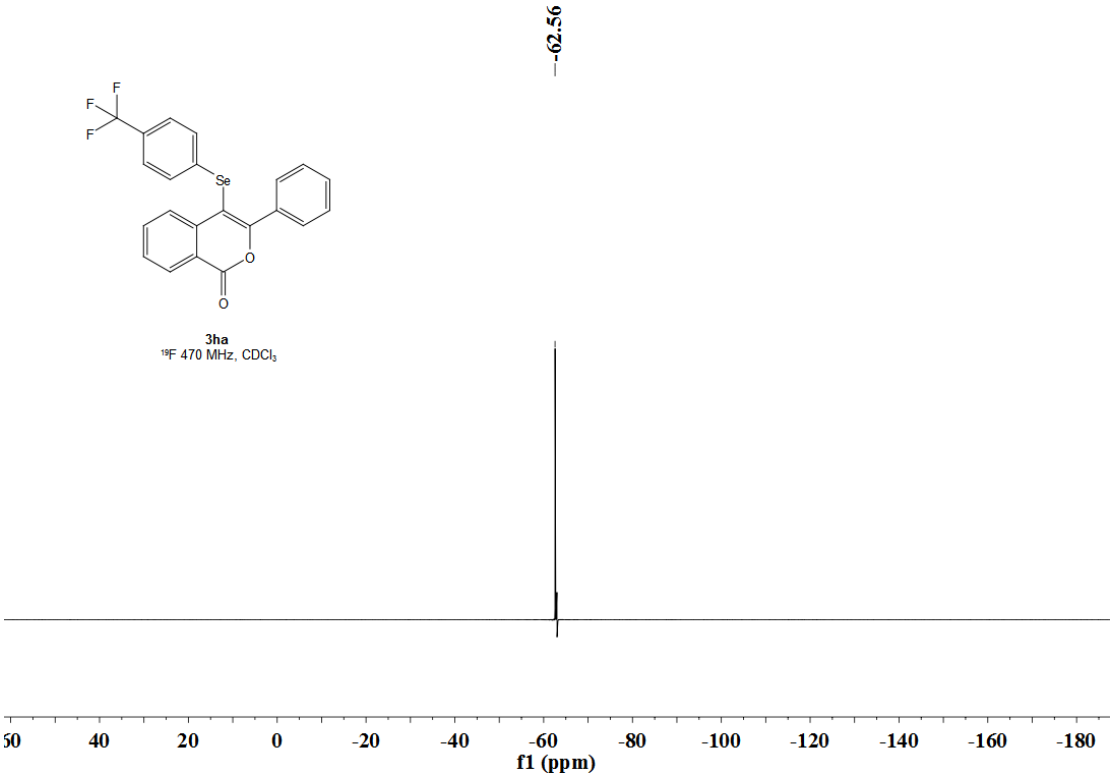


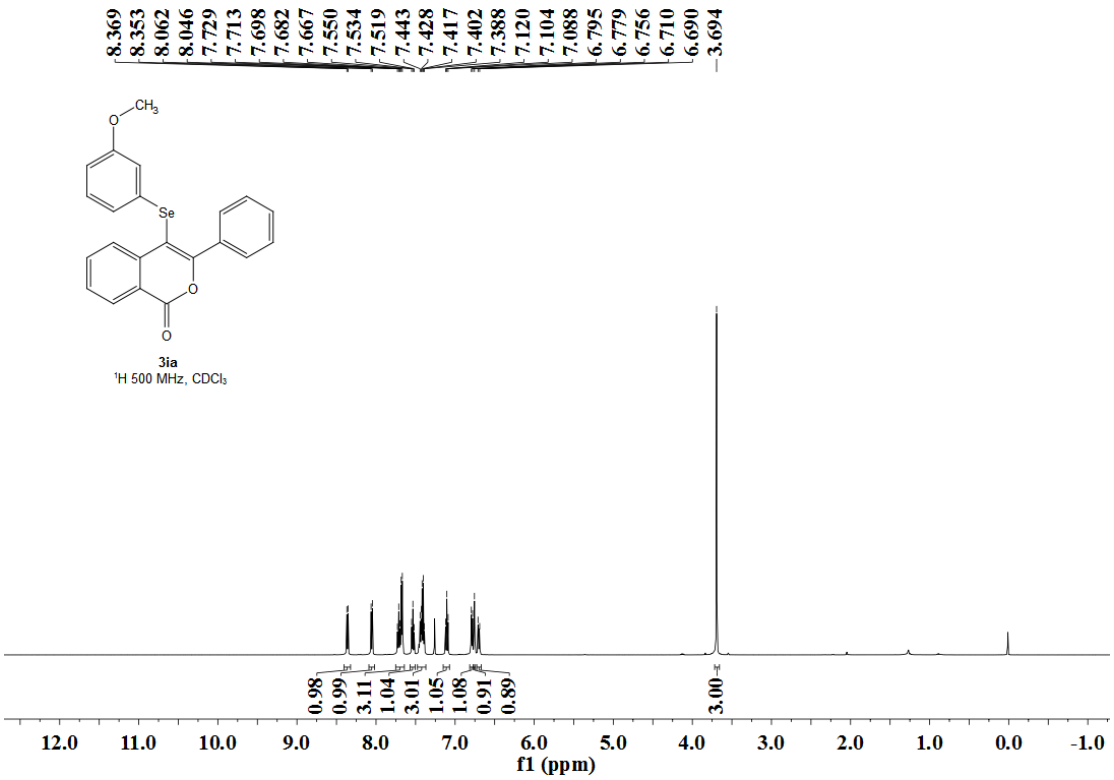
3ga
^{13}C 125 MHz, $CDCl_3$

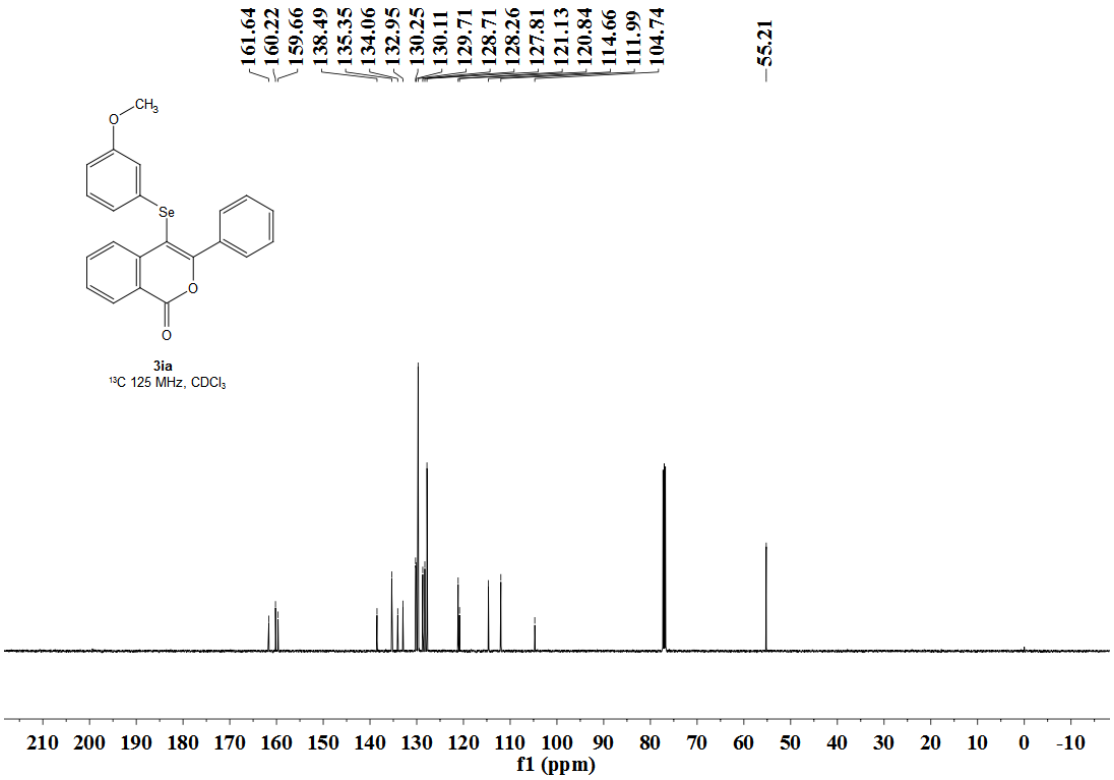


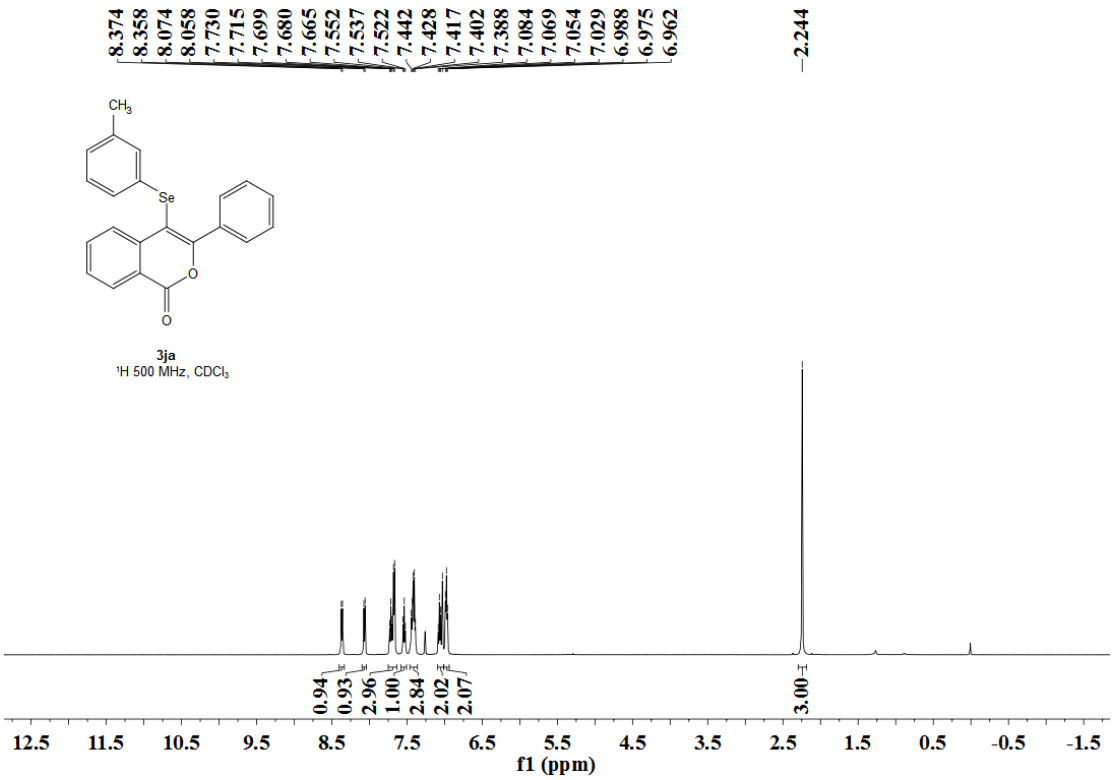
3ha
^{1}H 500 MHz, $CDCl_3$

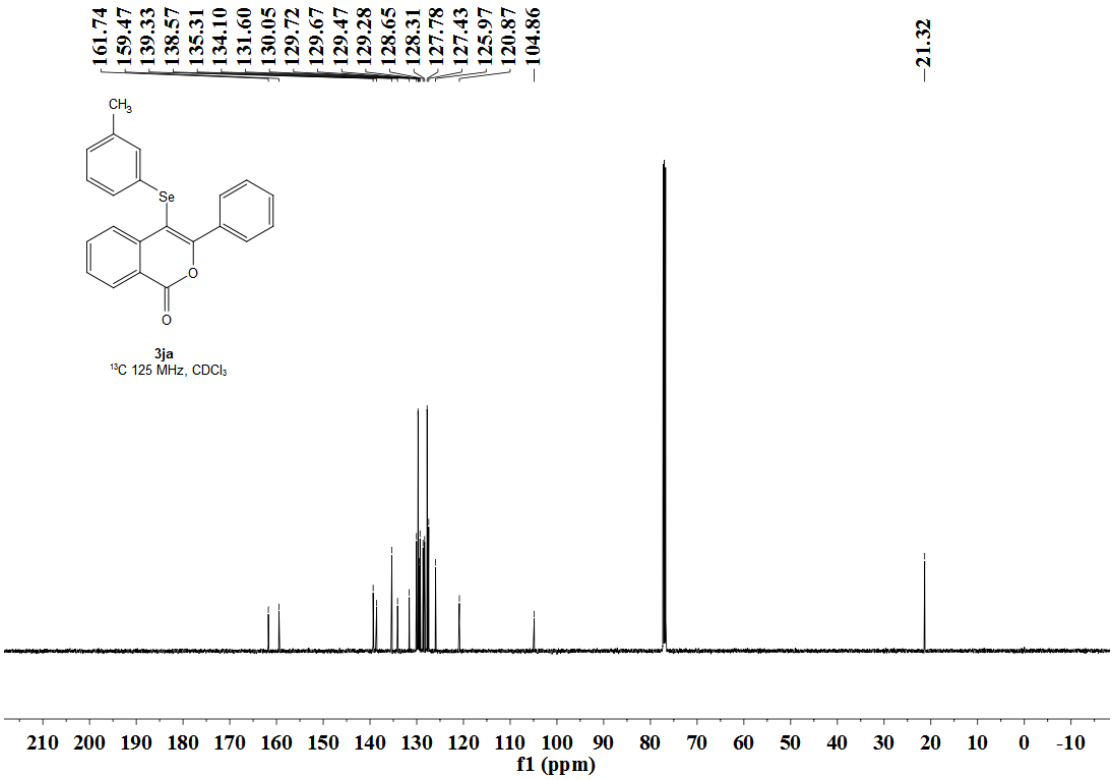

161.36
160.31
137.97
137.24
135.57
133.80
130.35
129.95
129.53
129.00
128.79
128.53
128.46
128.27
127.93
127.83
127.22
126.26
126.23
126.20
126.17
125.05
122.89
120.88
120.73
103.84
F
F
F
Se
O
O
3ha
13C 125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

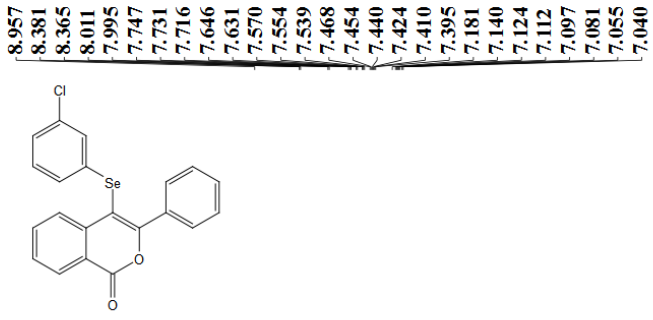

-62.56
F
F
F
Se
O
O
3ha
19F 470 MHz, CDCl3
50 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)


8.369
8.353
8.062
8.046
7.729
7.713
7.698
7.682
7.667
7.550
7.534
7.519
7.443
7.428
7.417
7.402
7.388
7.120
7.104
7.088
6.795
6.779
6.756
6.710
6.690
3.694
O
CH3
Se
O
O
3ia
1H 500 MHz, CDCl3
0.98
0.99
3.11
1.04
3.01
1.05
1.08
0.91
0.89
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

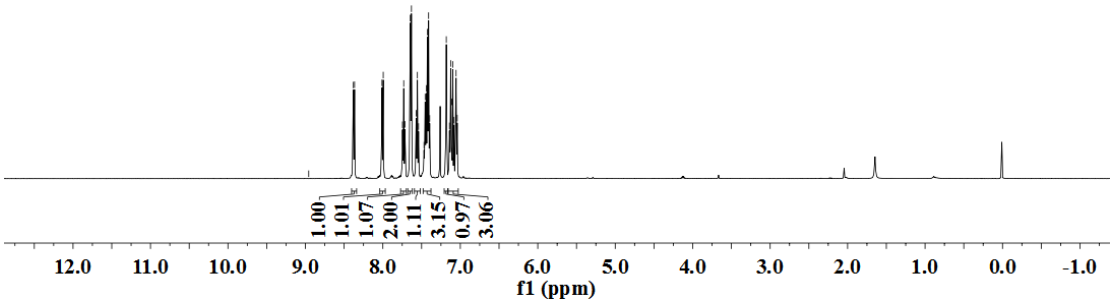

161.64
160.22
159.66
138.49
135.35
134.06
132.95
130.25
130.11
129.71
128.71
128.26
127.81
121.13
120.84
114.66
111.99
104.74
55.21
O
CH3
Se
O
O
3ia
13C 125 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

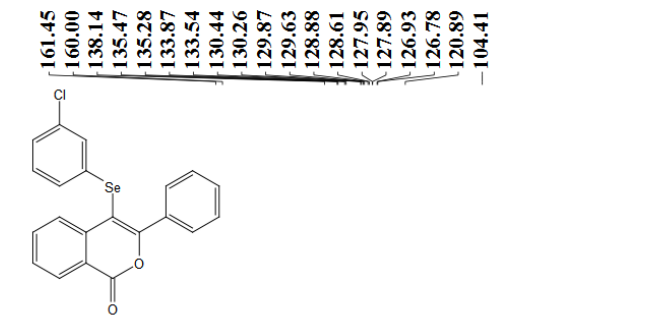

8.374
8.358
8.074
8.058
7.730
7.715
7.699
7.680
7.665
7.552
7.537
7.522
7.442
7.428
7.417
7.402
7.388
7.084
7.069
7.054
7.029
6.988
6.975
6.962
2.244
CH3
Se
O
O
3ja
1H 500 MHz, CDCl3
0.94
0.93
2.96
1.00
2.84
2.02
2.07
3.00
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
f1 (ppm)


161.74
159.47
139.33
138.57
135.31
134.10
131.60
130.05
129.72
129.67
129.47
129.28
128.65
128.31
127.78
127.43
125.97
120.87
104.86
21.32
CH3
Se
O
O
3ja
13C 125 MHz, CDCl3
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)

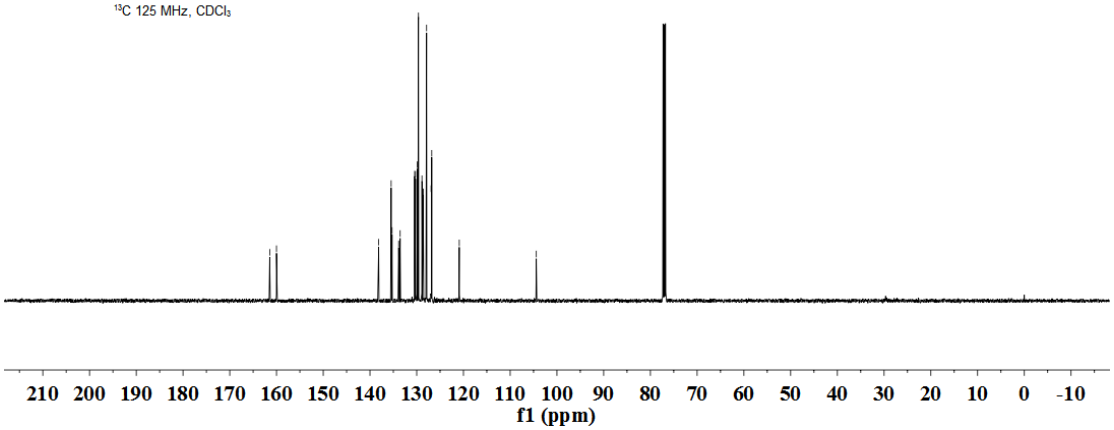


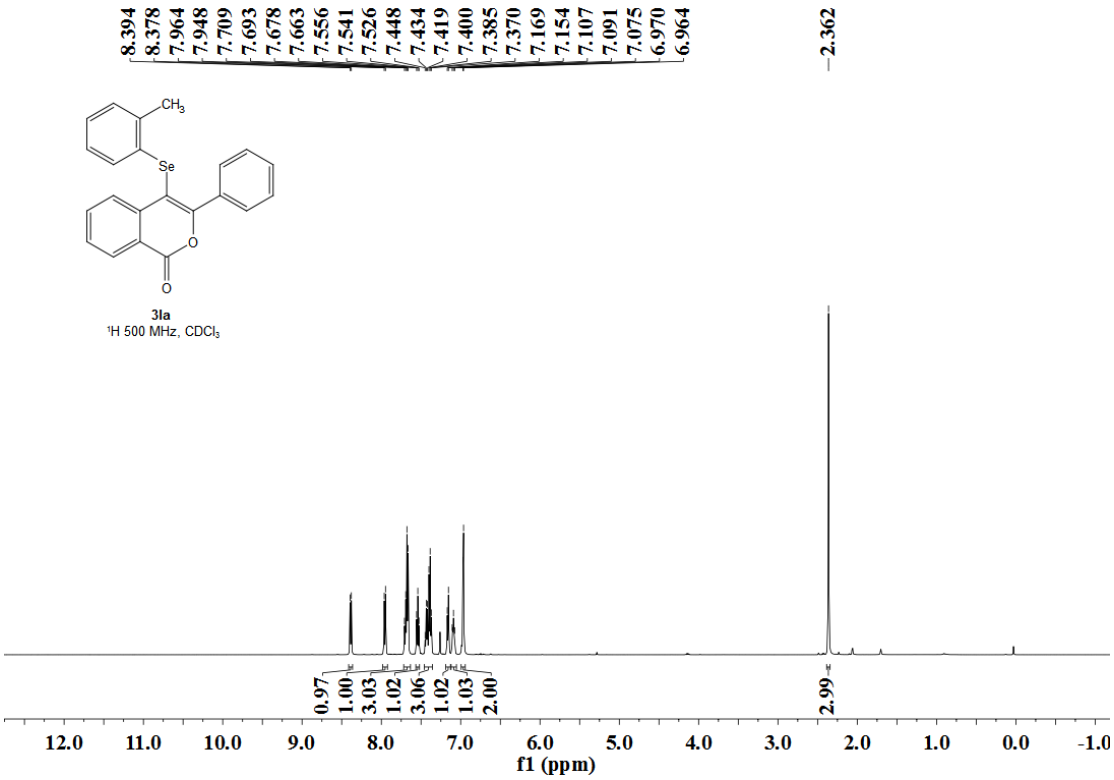
3ka
^{1}H 500 MHz, $CDCl_3$



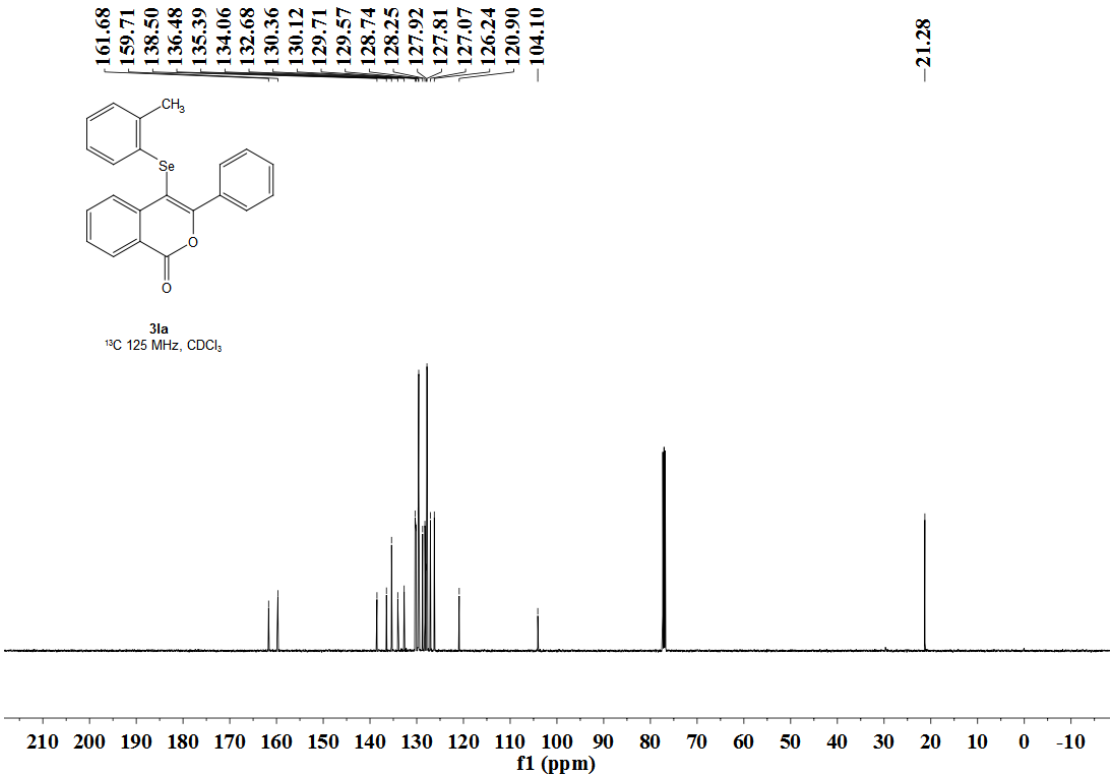


3ka
^{13}C 125 MHz, $CDCl_3$

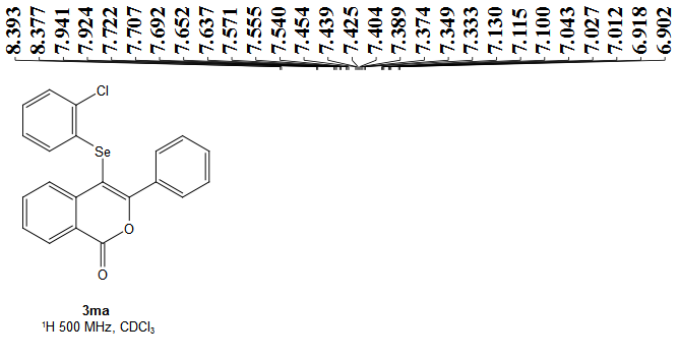




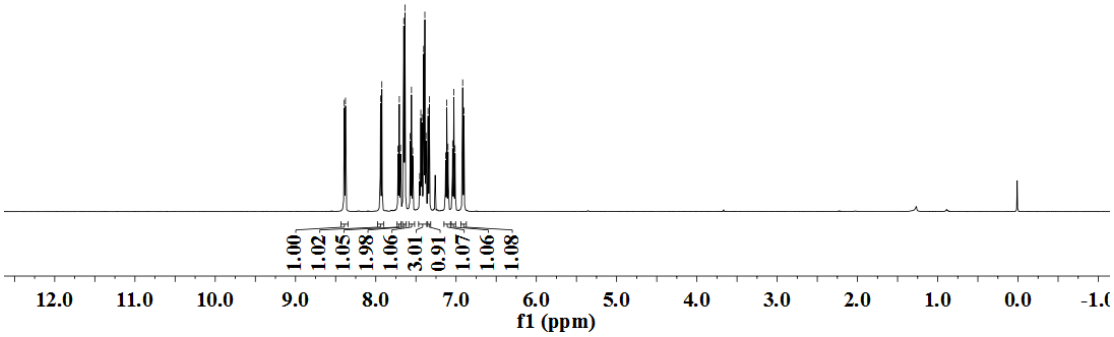
3la
^{1}H 500 MHz, $CDCl_3$

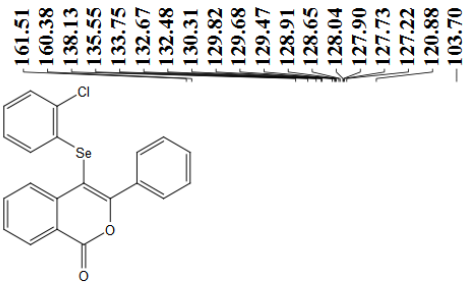


3la
^{13}C 125 MHz, $CDCl_3$

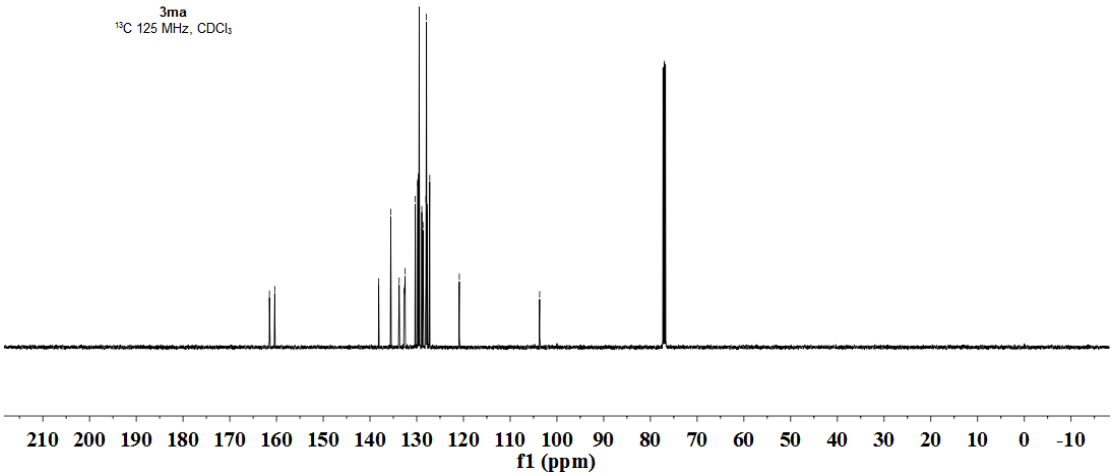


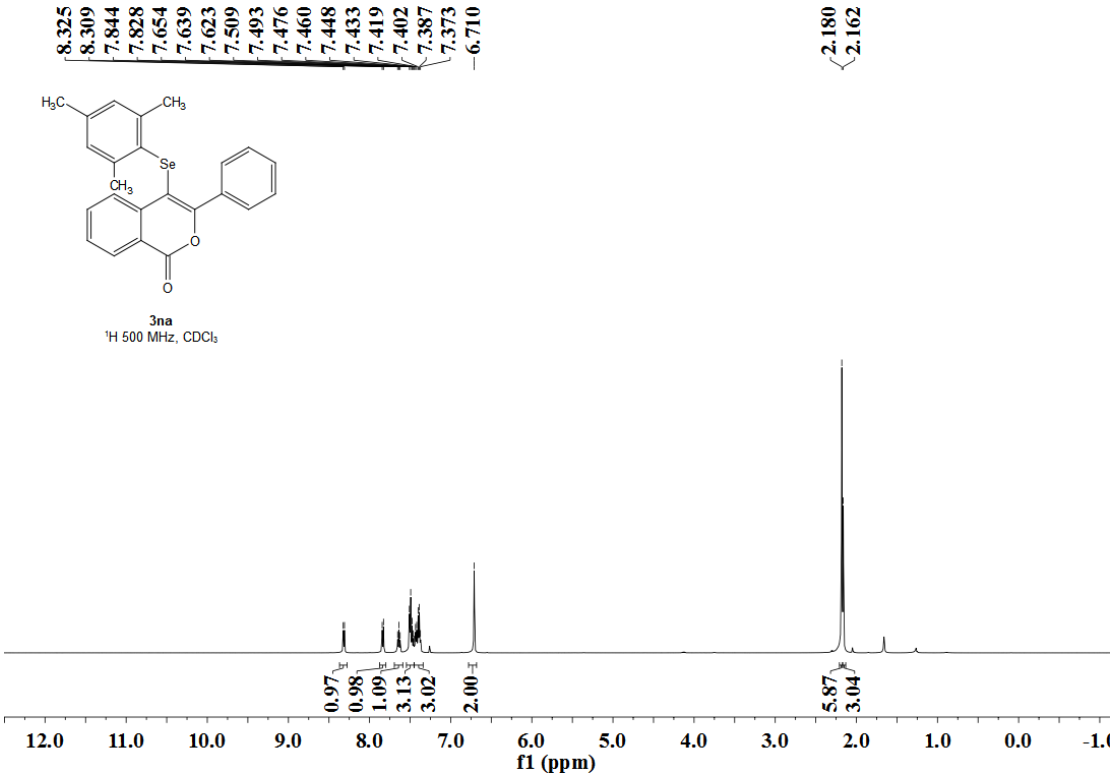
3ma
^{1}H 500 MHz, $CDCl_3$



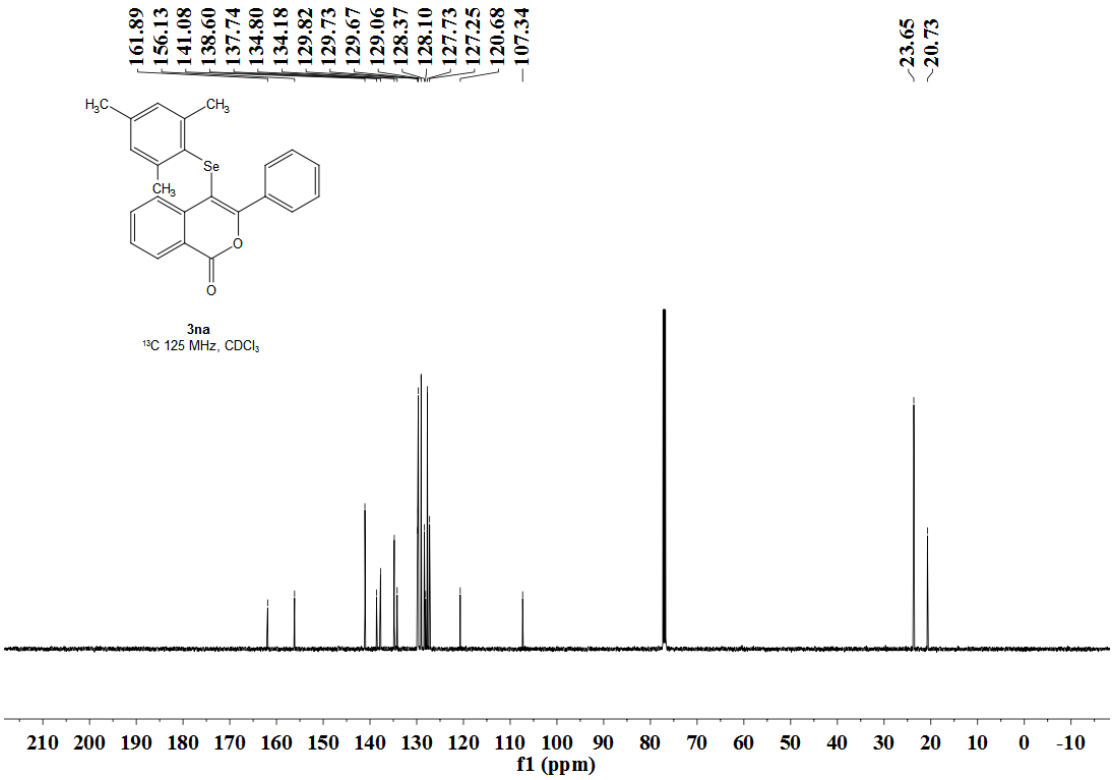


3ma
^{13}C 125 MHz, $CDCl_3$

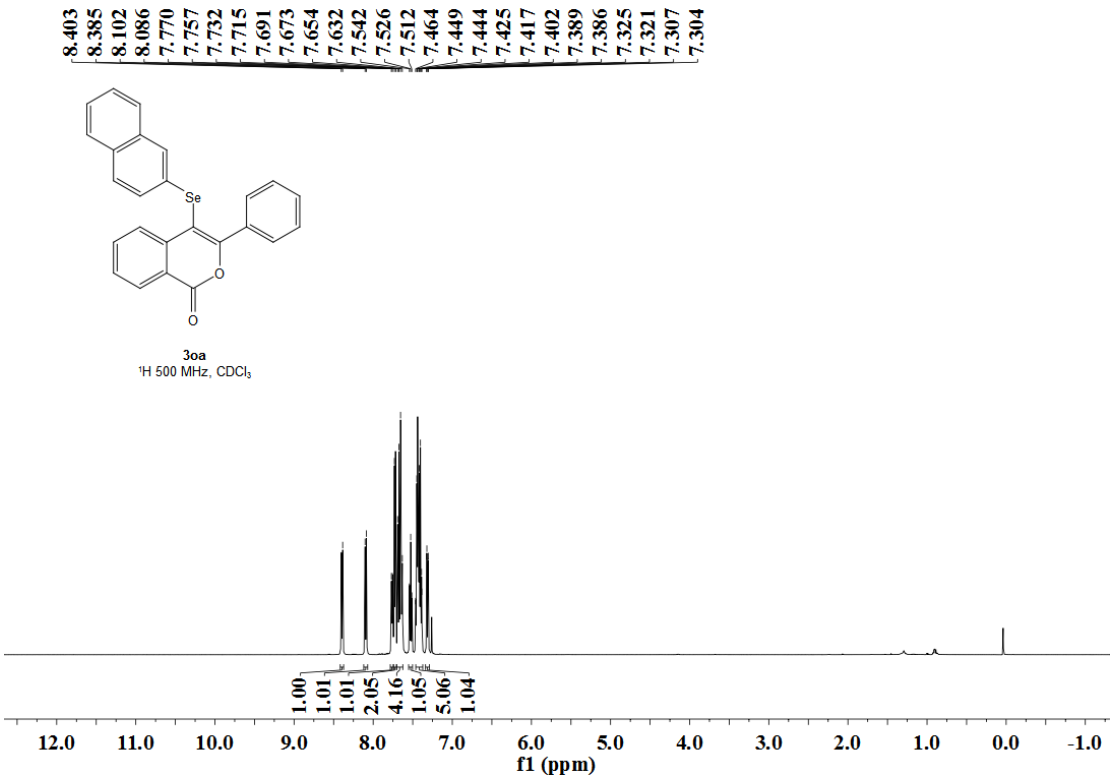


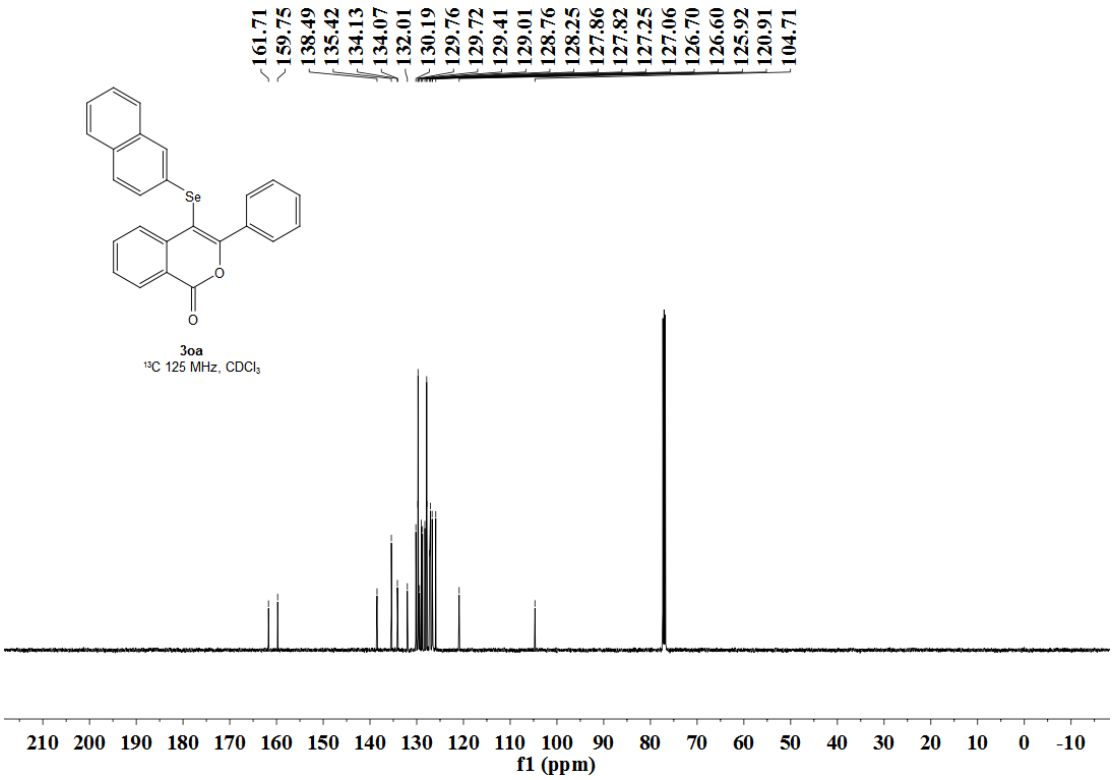


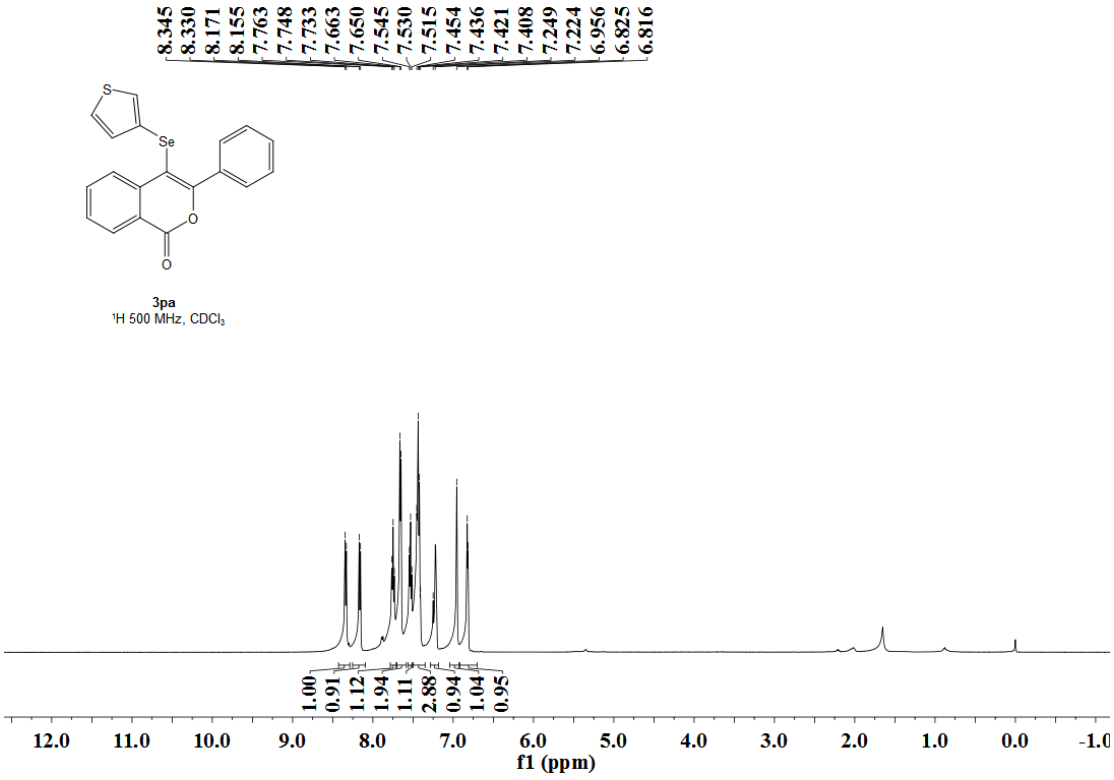
3na
^{1}H 500 MHz, $CDCl_3$



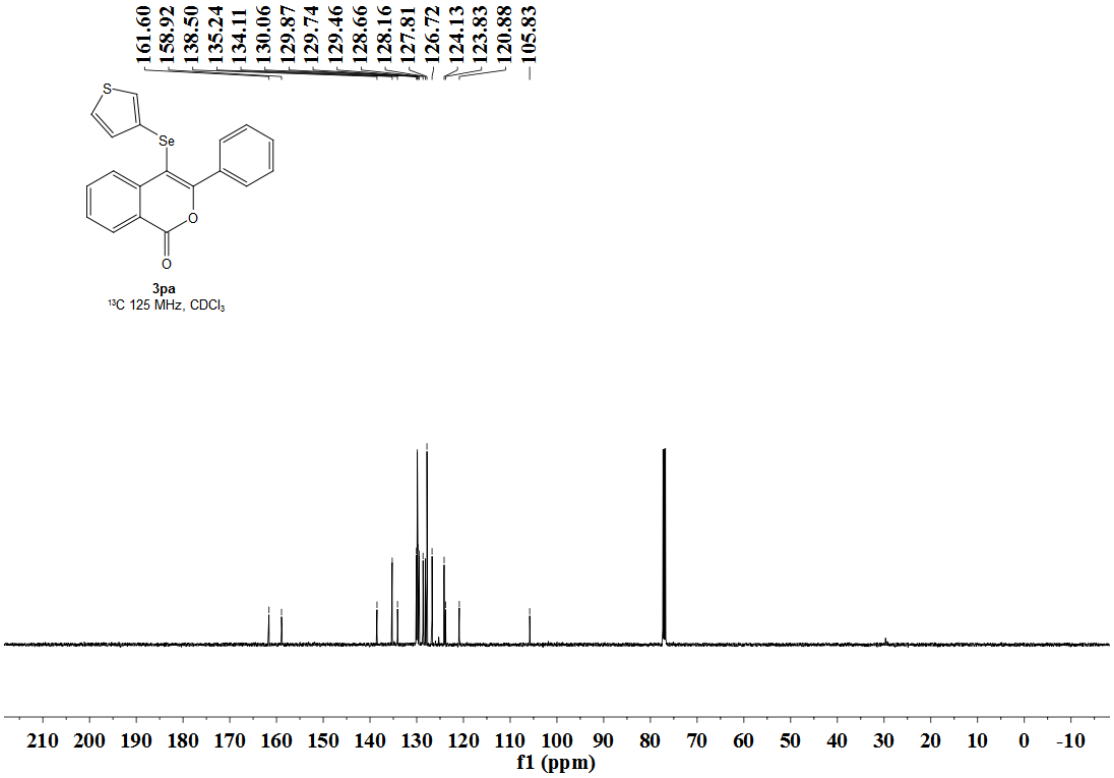
3na
^{13}C 125 MHz, $CDCl_3$


8.403
8.385
8.102
8.086
7.770
7.757
7.732
7.715
7.691
7.673
7.654
7.632
7.542
7.526
7.512
7.464
7.449
7.444
7.425
7.417
7.402
7.389
7.386
7.325
7.321
7.307
7.304
Se
O
O
3oa
1H 500 MHz, CDCl3
1.00
1.01
1.01
2.05
4.16
1.05
5.06
1.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

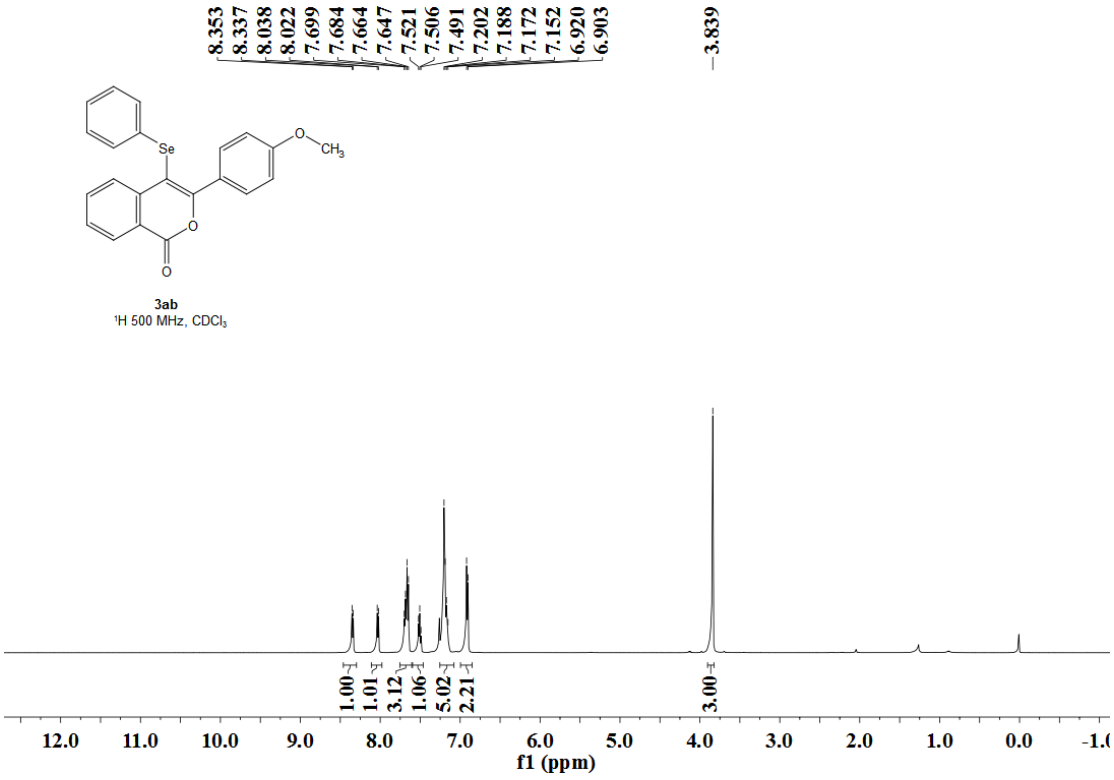

161.71
159.75
138.49
135.42
134.13
134.07
132.01
130.19
129.76
129.72
129.41
129.01
128.76
128.25
127.86
127.82
127.25
127.06
126.70
126.60
125.92
120.91
104.71
Se
O
O
3oa
13C 125 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

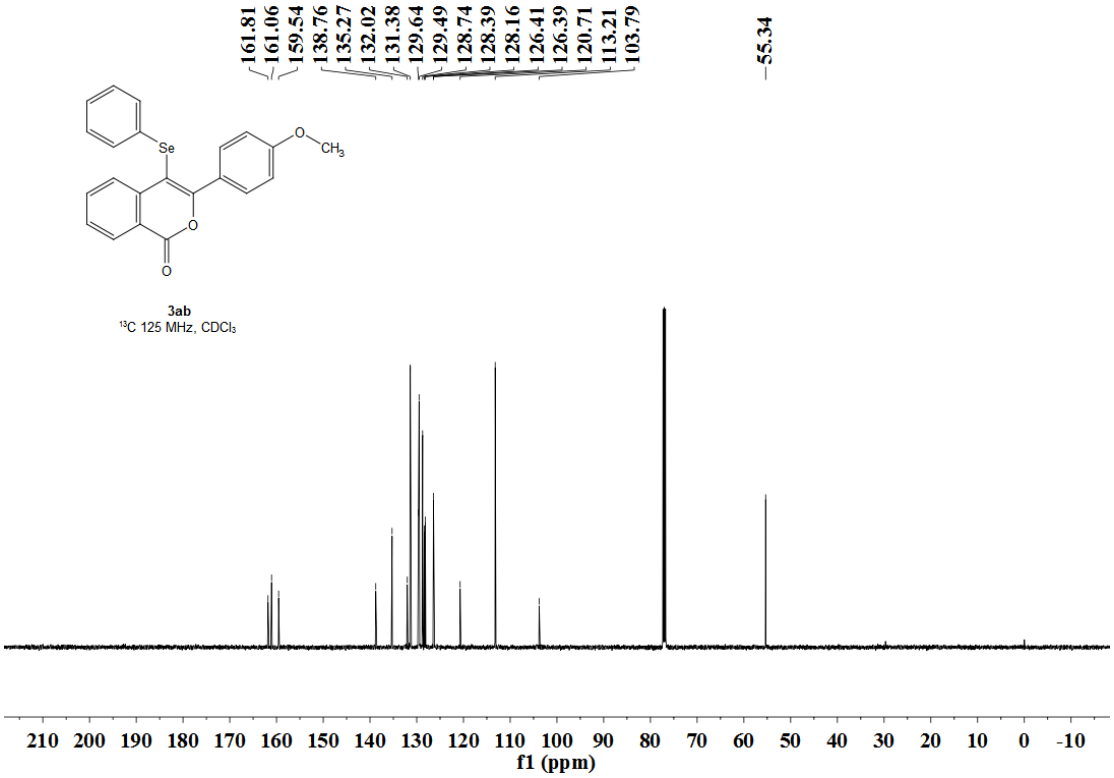


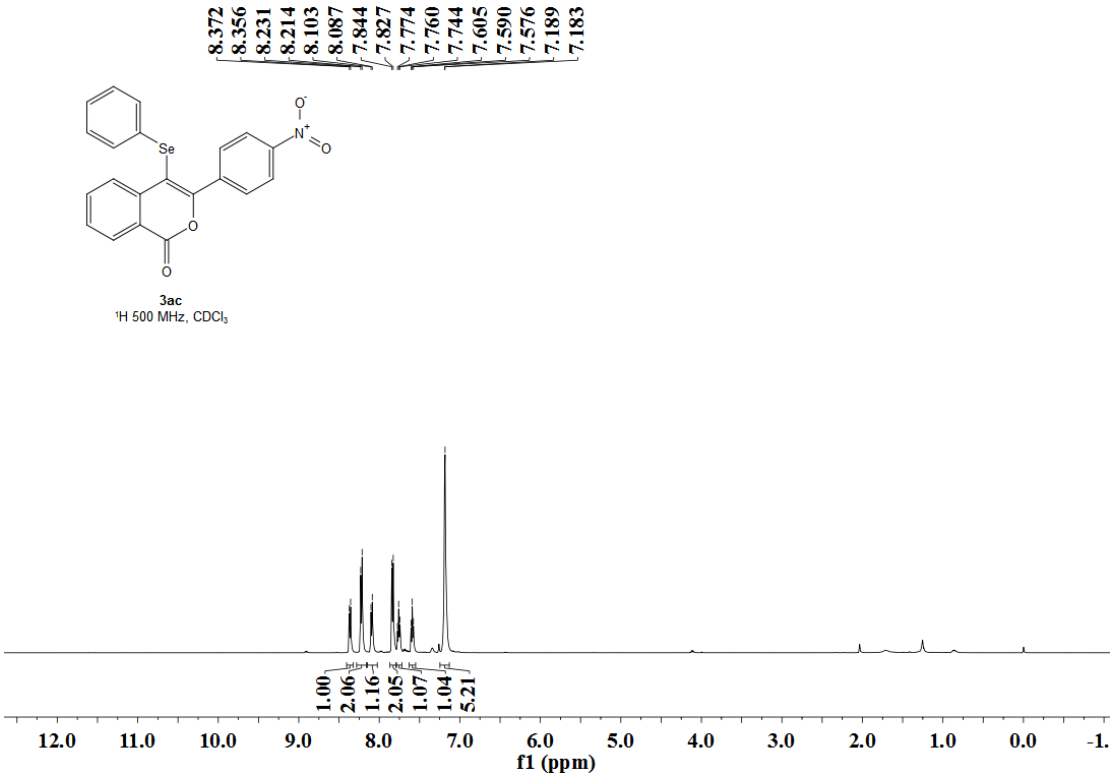
3pa
^{1}H 500 MHz, $CDCl_3$

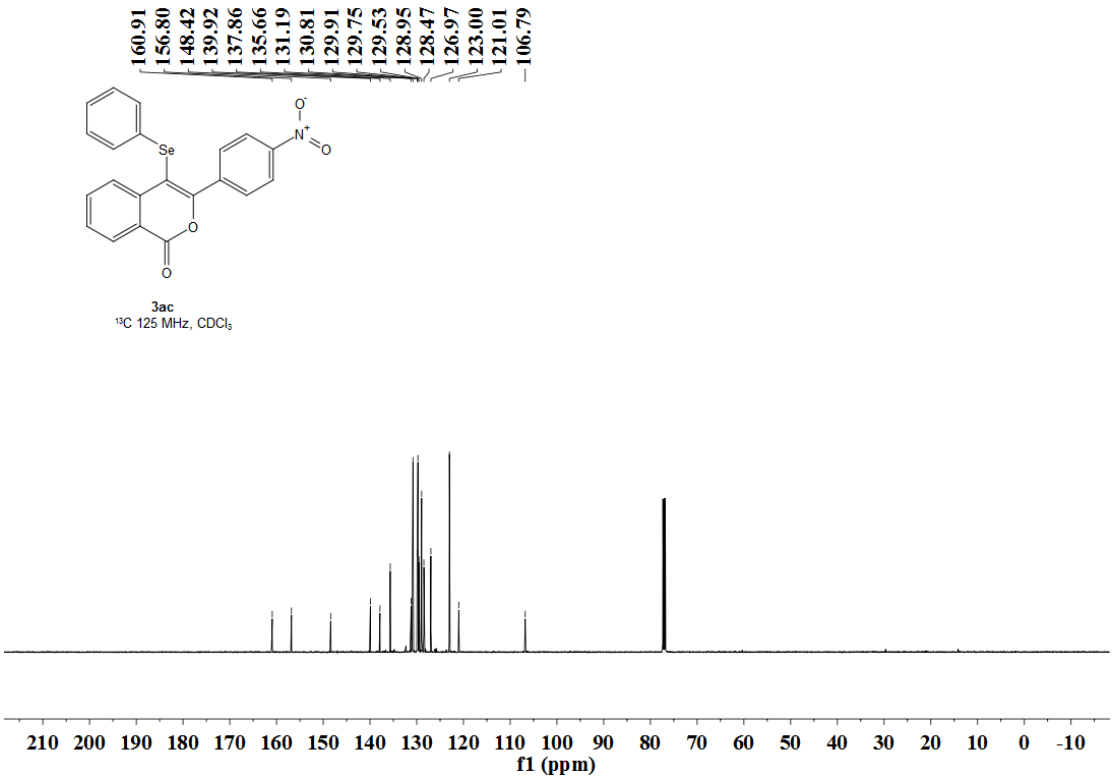


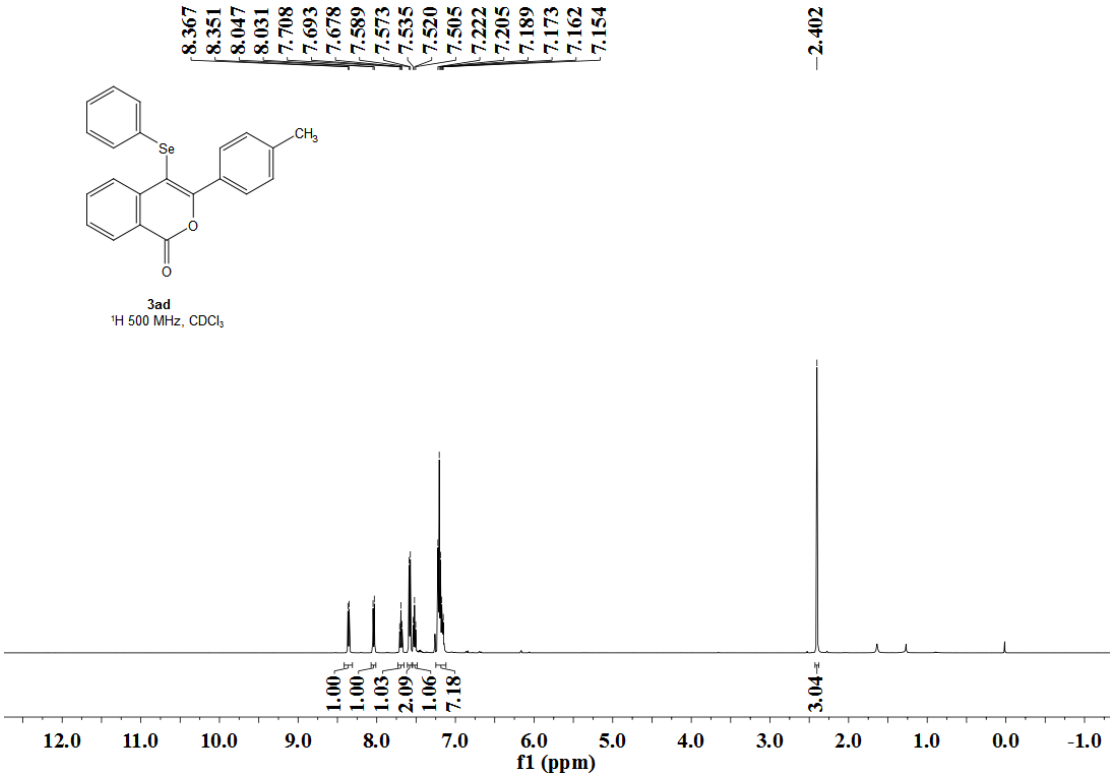
3pa
^{13}C 125 MHz, $CDCl_3$

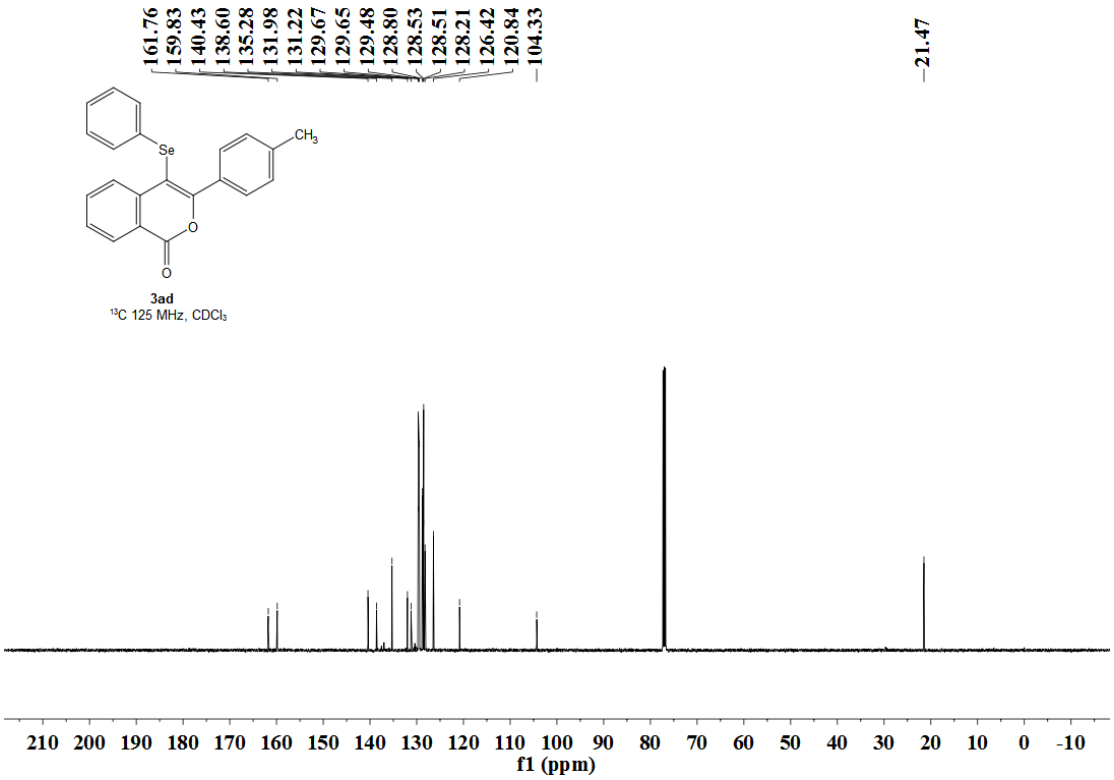

8.353
8.337
8.038
8.022
7.699
7.684
7.664
7.647
7.521
7.506
7.491
7.202
7.188
7.172
7.152
6.920
6.903
3.839
Se
O
CH3
O
O
3ab
1H 500 MHz, CDCl3
1.00
1.01
3.12
1.06
5.02
2.21
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

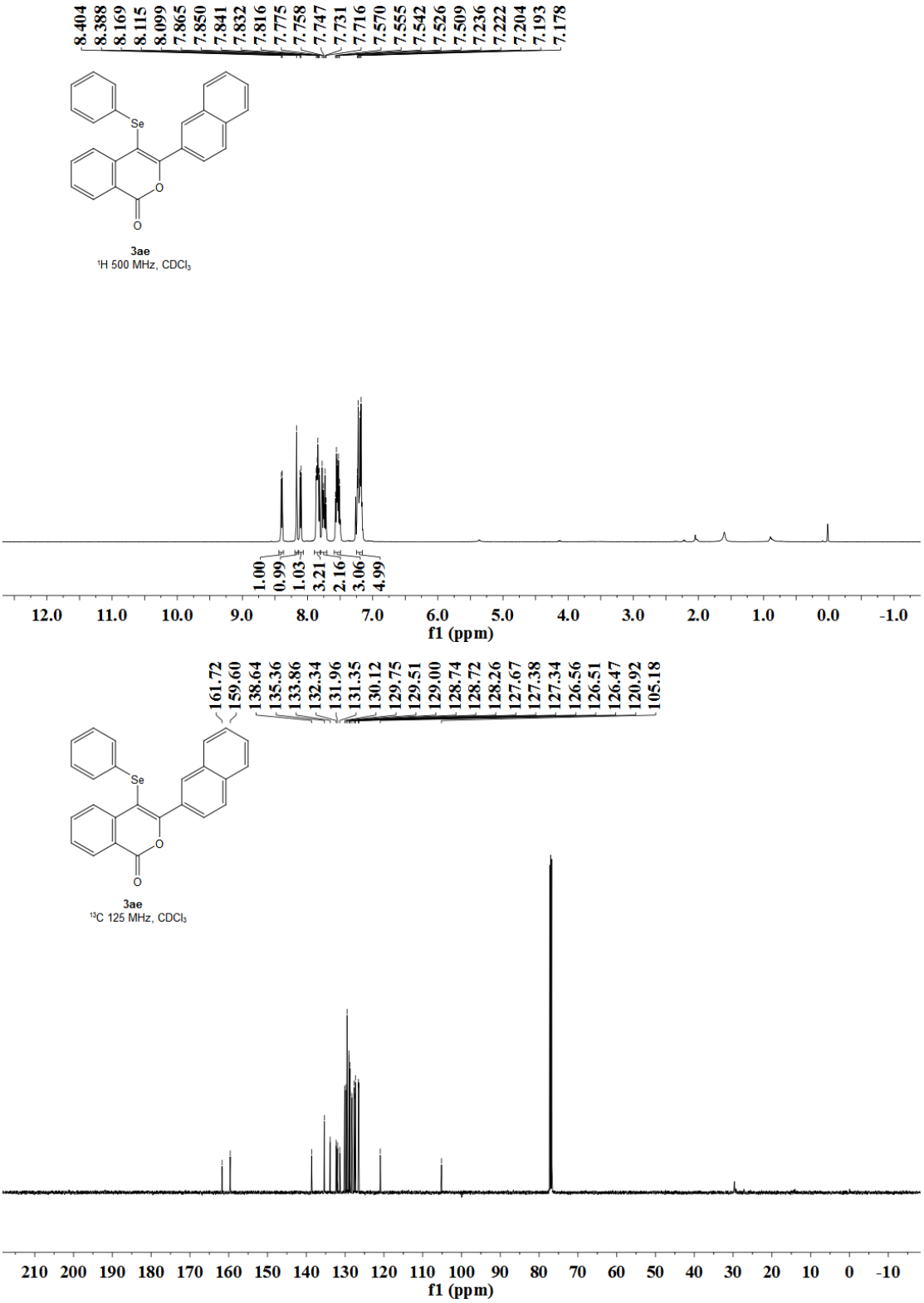

161.81
161.06
159.54
138.76
135.27
132.02
131.38
129.64
129.49
128.74
128.39
128.16
126.41
126.39
120.71
113.21
103.79
55.34
Se
O
CH3
O
O
3ab
13C 125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

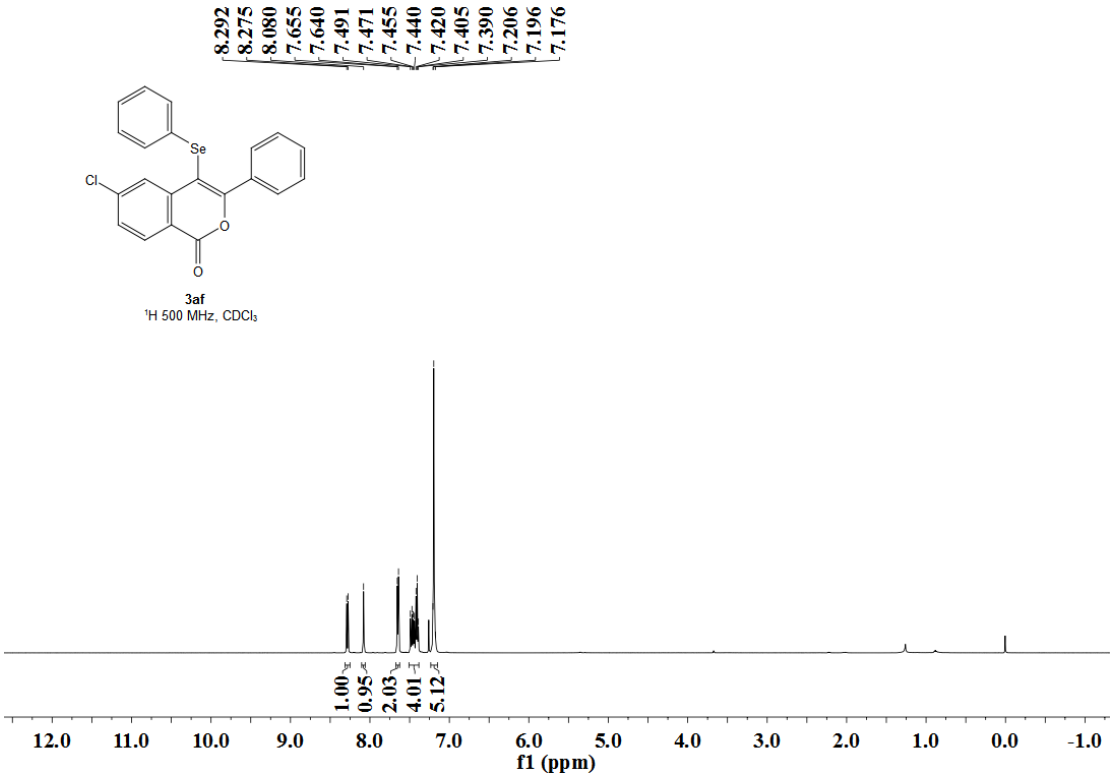

8.372
8.356
8.231
8.214
8.103
8.087
7.844
7.827
7.774
7.760
7.744
7.605
7.590
7.576
7.189
7.183
Se
O
O
O
N
O
3ac
1H 500 MHz, CDCl3
1.00
2.06
1.16
2.05
1.07
1.04
5.21
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

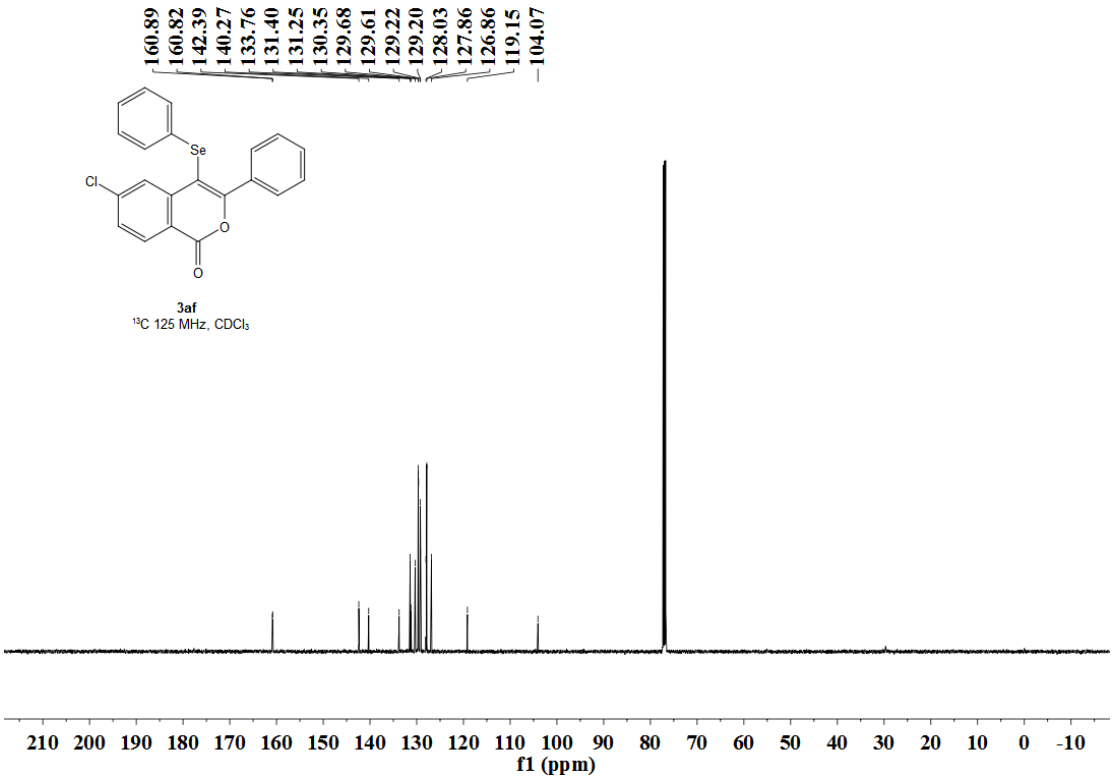

160.91
156.80
148.42
139.92
137.86
135.66
131.19
130.81
129.91
129.75
129.53
128.95
128.47
126.97
123.00
121.01
106.79
Se
O
O
O
N
O
3ac
13C 125 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

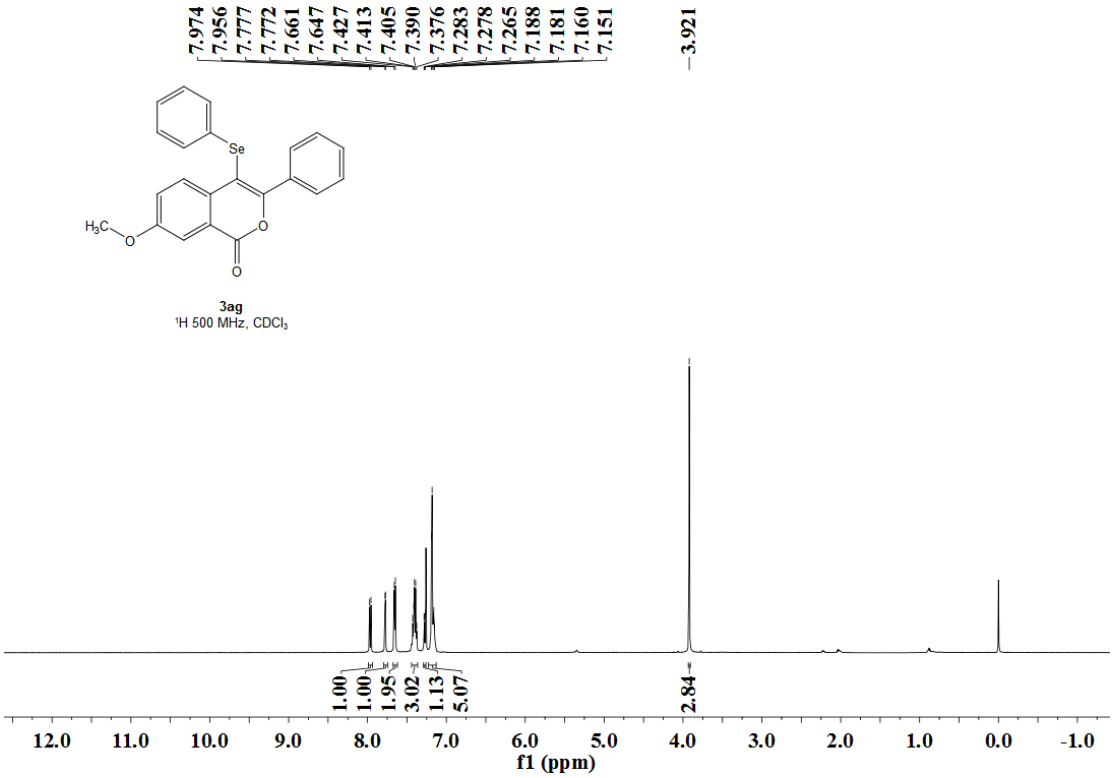

8.367
8.351
8.047
8.031
7.708
7.693
7.678
7.589
7.573
7.535
7.520
7.505
7.222
7.205
7.189
7.173
7.162
7.154
2.402
Se
CH3
O
O
3ad
1H 500 MHz, CDCl3
1.00
1.00
1.03
2.09
1.06
7.18
3.04
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

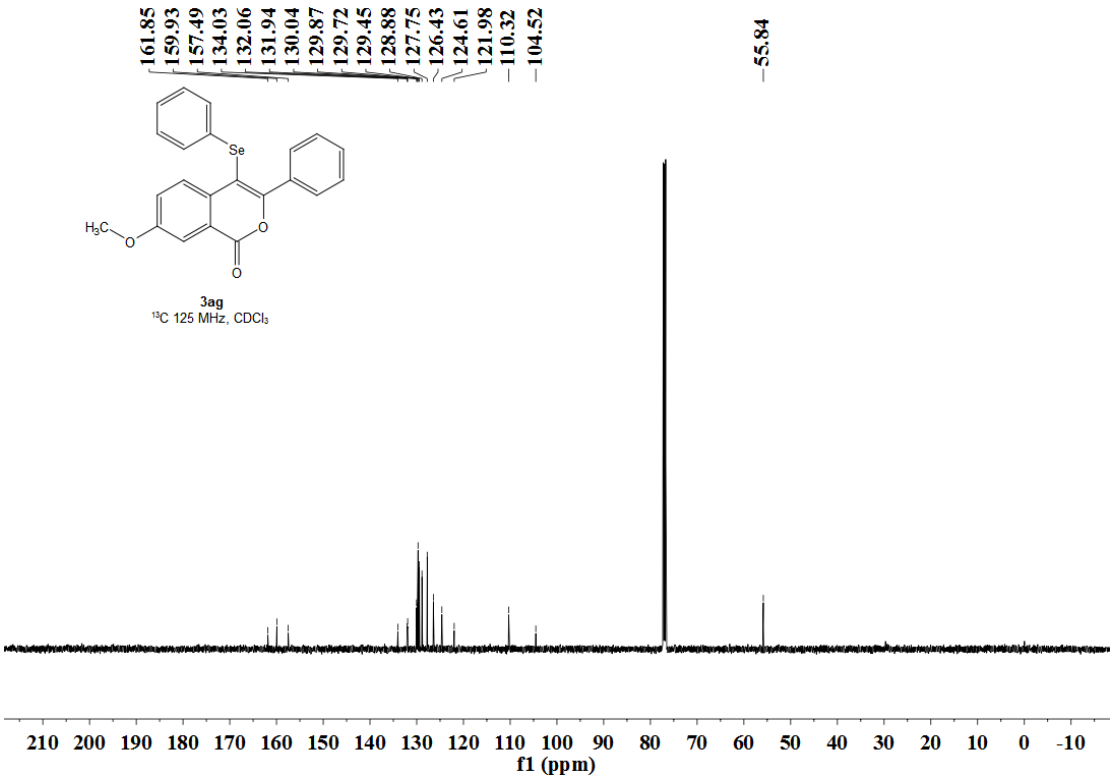

161.76
159.83
140.43
138.60
135.28
131.98
131.22
129.67
129.65
129.48
128.80
128.53
128.51
128.21
126.42
120.84
104.33
21.47
Se
CH3
O
O
3ad
13C 125 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.404
8.388
8.169
8.115
8.099
7.865
7.850
7.841
7.832
7.816
7.775
7.758
7.747
7.731
7.716
7.570
7.555
7.542
7.526
7.509
7.236
7.222
7.204
7.193
7.178
Se
O
O
3ae
1H 500 MHz, CDCl3
1.00
0.99
1.03
3.21
2.16
3.06
4.99
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
161.72
159.60
138.64
135.36
133.86
132.34
131.96
131.35
130.12
129.75
129.51
129.00
128.74
128.72
128.26
127.67
127.38
127.34
126.56
126.51
126.47
120.92
105.18
Se
O
O
3ae
13C 125 MHz, CDCl3
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)


8.292
8.275
8.080
7.655
7.640
7.491
7.471
7.455
7.440
7.420
7.405
7.390
7.206
7.196
7.176
Se
Cl
O
O
3af
¹H 500 MHz, CDCl₃
1.00
0.95
2.03
4.01
5.12
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


160.89
160.82
142.39
140.27
133.76
131.40
131.25
130.35
129.68
129.61
129.22
129.20
128.03
127.86
126.86
119.15
104.07
Se
Cl
O
O
3af
¹³C 125 MHz, CDCl₃
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)


7.974
7.956
7.777
7.772
7.661
7.647
7.427
7.413
7.405
7.390
7.376
7.283
7.278
7.265
7.188
7.181
7.160
7.151
3.921
Se
H3C
O
O
O
3ag
1H 500 MHz, CDCl3
1.00
1.00
1.95
3.02
1.13
5.07
2.84
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


161.85
159.93
157.49
134.03
132.06
131.94
130.04
129.87
129.72
129.45
128.88
127.75
126.43
124.61
121.98
110.32
104.52
55.84
Se
H3C
O
O
O
3ag
13C 125 MHz, CDCl3
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)