Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Selenocyanobenziodoxolone: A Practical Electrophilic Selenocyanation Reagent and Its Application for Solid-state Synthesis of α-Carbonyl Selenocyanates

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Supporting Information

Contents

1. General Information

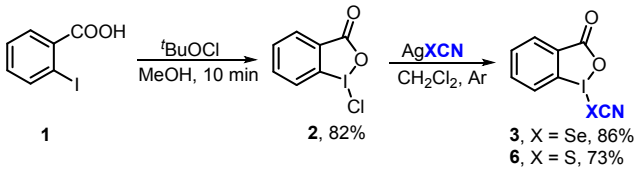
Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 300 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 75 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Infrared spectra (IR) were measured by FT-IR apparatus. ^{19}F NMR data were collected at 282 MHz with complete proton decoupling. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ESI^{+} mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh). All solvents and commercially available reagents were either purified via literature procedures or used without further purification.

The *N*-acetyl-*α*-arylenamines derivatives and silyl enol ethers derivatives were prepared according to the reported procedure. [1] , [2]

Caution: the hypervalent iodine compounds have a hazardous of explosion after grinding. Thus, a safty sheild is necessary before carrying out the reaction.

2. Experimental Procedures and Characterization Data

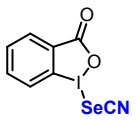
2.1 Synthetic procedure for the synthesis of selenocyanobenziodoxolone 3 (BI-SeCN) and thiocyanobenziodoxolone 6 (BI-SCN)



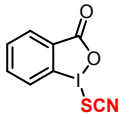
To a solution of 2-iodobenzoic acid **1** (3 g, 12.1 mmol) in anhydrous methanol (50 mL) was added *tert*-butyl hypochlorite. The mixture was stirred vigorously at room temperature for 10 min. Then, the white precipitate was filtered and dried under vacuum to yield 1-chlorobenziodoxolone **2** as white solid (2.8 g, 9.9 mmol, 82% yield).

To a stir solution of 1-chlorobenziodoxolone **2** (2 g, 7.1 mmol) in dichloromethane (35 mL), silver selenocyanate (1.8 g, 8.5 mmol, 1.2 equiv.) was added under Ar atmosphere. The flask was covered with thin-foil and stirred at room temperature for 48 h. After the completion of the reaction, the undissolved solid was filtered off and the residue was concentrated under high vacuum to give the BI-SeCN as a yellow solid (2.2 g, 6.1 mmol). Synthesized using the same

procedure with silver thiocyanate in 7.1 mmol scale to afford the BI-SCN as a white solid (1.6 g, 5.2 mmol). Those reagents were used in the next step without further purification and preserved at 0 ℃.



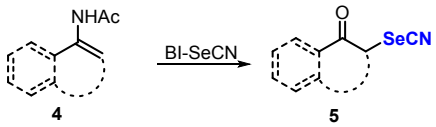
Selenocyanobenziodoxolone (**3**): yellow solid (86% yield, 2.2 g, 6.1 mmol); m.p. 97-99 °C; **IR (KBr)** ν 2517, 1799, 1654, 1467, 1270, 1018, 879, 732 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H); **^{13}C NMR (75 MHz, DMSO-d_6)** δ 168.6, 141.0, 137.4, 132.9, 130.5, 128.6, 102.4, 94.5; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_8H_4NO_2SeINa$ $[M+Na]^+$ 375.8344, found 375.8340.



Thiocyanobenziodoxolone (**6**): white solid (73% yield, 1.6 g, 5.2 mmol); m.p. 74-75 °C; **IR (KBr)** ν 2053, 1794, 1679, 1465, 1270, 1008, 894, 732 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.03-8.10 (m, 2H), 7.48 (td, *J* = 7.5, 1.2 Hz, 1H), 7.23 (td, *J* = 7.8, 1.7 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.2, 142.0, 133.6, 133.1, 132.1, 128.1, 107.0, 94.7; **HRMS (TOF- ESI$^+$) m/z**: calcd for $C_8H_4NO_2SINa$ $[M+Na]^+$ 327.8900, found 327.8907.

2.2 General procedure for the synthesis of α-carbonyl selenocyanate compounds.

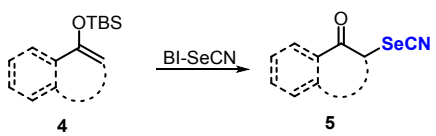
General Procedure 1



The *N*-acetyl-α-arylenamine (0.1 mmol) and BI-SeCN (52.9 mg, 0.15 mmol, 1.5 equiv.) was ground togather with agate mortar at room temperature for the given time. After the completion of the reaction, the mixture was dissolved in EtOAc (2 mL). Then the mixture was extracted with EtOAc (2×2 mL) and washed with saturated aqueous $NaHCO_3$. The combined organic phase were dried (Na_2SO_4) and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography (PE:EtOAc = 9:1-5:1) to afford the desired selenocyanate compound as a white solid.

Caution: This reaction should be carried out behind a safety shield!

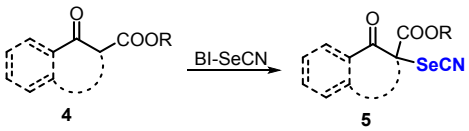
General Procedure 2



The silyl enol ether (0.1 mmol) and BI-SeCN (52.9 mg, 0.15 mmol, 1.5 equiv.) was ground togather with agate mortar at room temperature for the given time. After the completion of the reaction, the mixture was dissolved in EtOAc (2 mL). Then the mixture was extracted with EtOAc (2×2 mL) and washed with saturated aqueous $NaHCO_3$. The combined organic phase were dried (Na_2SO_4) and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography (PE:EtOAc = 9:1-5:1) to afford the desired selenocyanate compound as a white solid.

Caution: This reaction should be carried out behind a safety shield!

General Procedure 3

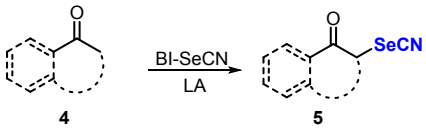


4 **5**

The *β*-keto ester (0.1 mmol) and BI-SeCN (52.9 mg, 0.15 mmol, 1.5 equiv.) was ground togather with agate mortar at room temperature for the given time. After the completion of the reaction, the mixture was dissolved in EtOAc (2 mL). Then the mixture was extracted with EtOAc (2×2 mL) and washed with saturated aqueous $NaHCO_3$. The combined organic phase were dried (Na_2SO_4) and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography with PE:EtOAc = 9:1-5:1 to afford the desired selenocyanate compound as a white solid.

Caution: This reaction should be carried out behind a safety shield!

General Procedure 4



4 **5**

The ketone (0.1 mmol), BI-SeCN (52.9 mg, 0.15 mmol, 1.5 equiv.) and Lewis acid (0.01 mmol) was ground togather with agate mortar at room temperature for the given time. After the completion of the reaction, the mixture was dissolved in EtOAc (2 mL). Then the mixture was extracted with EtOAc (2×2 mL) and washed with saturated aqueous $NaHCO_3$. The combined organic phase were dried (Na_2SO_4) and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography with (PE:EtOAc = 9:1-5:1) to afford the desired selenocyanate compound as a white solid.

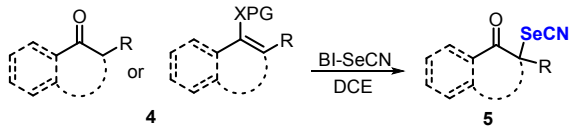
Various lewis acids were screnned under grinding conditions. Pleasingly, scandium(III) triflate performed the best and afforded the desired product **5aa** in 92% yield (Table S-1, entry 5).

Table S-1 Screening of the lewis acids

entry	LA	t (h)	Yield (%)
1	$Mg(OTf)_2$	0.5	nr
2	$Zn(OTf)_2$	0.5	64
3	$Cu(OTf)_2$	0.5	71
4	$Yb(OTf)_2$	0.5	80
5	$Sc(OTf)_2$	0.5	92

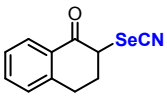
Caution: This reaction should be carried out behind a safety shield!

General Procedure 5

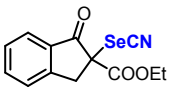


To a stir solution of *N*-acetyl-α-arylenamines/silyl enol ethers/*β*-keto esters (0.1 mmol) in DCE (1 mL), BI-SeCN (52.9 mg, 0.15 mmol, 1.5 equiv.) was added. After the completion of the reaction, the mixture was extracted with EtOAc (2×2 mL) and washed with saturated aqueous $NaHCO_3$. The combined organic phase were dried (Na_2SO_4) and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography (PE:EtOAc = 9:1-5:1) to afford the desired selenocyanate compound as a white solid.

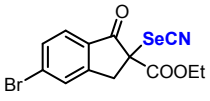
Caution: This reaction should be carried out behind a safety shield!



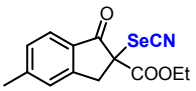
2-Selenocyanato-3,4-dihydronaphthalen-1(2*H*)-one (**5aa**): Obtained in 99% yield (24.8 mg, 0.099 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 79-80 °C (lit. 82-83 °C); **IR (KBr)** ν 2906, 2512, 2148, 1797, 1594, 1457, 896, 739 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 6.0 Hz, 2H), 5.31 (dd, *J* = 12.6, 5.1 Hz, 1H), 3.16-3.27 (m, 1H), 3.07-3.12 (m, 1H), 2.64-2.70 (m, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 194.2, 144.1, 135.0, 130.5, 129.0, 127.8, 127.4, 102.5, 53.2, 32.6, 30.3; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{11}H_9NOSeNa$ $[M+Na]^+$ 273.9742, found 273.9753.



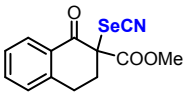
Ethyl 1-Oxo-2-selenocyanato-2,3-dihydro-1*H*-indene-2-carboxylate (**5ab**): Obtained in 83% yield (25.6 mg, 0.083 mmol) according to procedure 3 after column chromatography as a white solid by using *β*-keto ester; m.p. 114-115 °C; **IR (KBr)** ν 2938, 2509, 2148, 1791, 1599, 1472, 1180, 751, 694 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.49-7.56 (m, 2H), 4.19-4.34 (m, 3H), 3.84 (d, *J* = 18.6 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.0, 167.4, 151.1, 136.9, 132.9, 128.9, 126.2, 125.8, 100.7, 64.3, 61.6, 41.0, 13.9; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{13}H_{11}NO_3SeNa$ $[M+Na]^+$ 331.9796, found 331.9813.



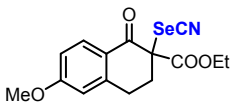
Ethyl 1-Oxo-2-selenocyanato-5-bromo-2,3-dihydro-1*H*-indene-2-carboxylate (**5ac**): Obtained in 65% yield (25.1 mg, 0.065 mmol) according to procedure 3 after column chromatography as a white solid by using *β*-keto ester; m.p. 117-118 °C; **IR (KBr)** ν 2983, 2148, 1716, 1594, 1427, 1183, 829, 575 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.02 (s, 1H), 7.84 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.15 (d, *J* = 18.6 Hz, 1H), 3.77 (d, *J* = 18.6 Hz, 1H), 1.28 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 194.8, 167.0, 149.7, 139.7, 134.7, 128.5, 127.7, 123.1, 100.6, 64.5, 61.6, 40.6, 13.9; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{13}H_{10}NO_3SeBrNa$ $[M+Na]^+$ 409.8901, found 409.8900.



Ethyl 1-Oxo-2-selenocyanato-5-methyl-2,3-dihydro-1*H*-indene-2-carboxylate (**5ad**): Obtained in 93% yield (30.0 mg, 0.093 mmol) according to procedure 3 after column chromatography as a white solid by using *β*-keto ester; m.p. 147-148 °C; **IR (KBr)** ν 2990, 2519, 1796, 1674, 1577,1465, 1013, 874, 732 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.70 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 4.29 (q, *J* = 6.9 Hz, 2H), 4.16 (d, *J* = 18.3 Hz, 1H), 3.78 (d, *J* = 18.3 Hz, 1H), 2.46 (s, 3H), 1.28 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 196.0, 167.6, 148.6, 139.1, 138.3, 133.1, 125.8, 125.6, 100.8, 64.2, 62.1, 40.7, 21.1, 13.9; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{14}H_{13}NO_3SeNa$ $[M+Na]^+$ 345.9953, found 345.9944.

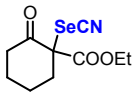


Methyl 1-Oxo-2-selenocyanato-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**5ae**): Obtained in 88% yield (28.4 mg, 0.088 mmol) according to procedure 3 after column chromatography as a white solid by using *β*-keto ester; m.p. 141-143 °C; **IR (KBr)** ν 2958, 2153, 1799, 1671, 1477, 1308, 961,879 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 3.82 (s, 3H), 3.25-3.33 (m, 1H), 3.06-3.19 (m, 2H), 2.72-2.82 (m, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.5, 167.8, 143.5, 135.3, 130.0, 129.1, 128.4, 127.5, 101.8, 64.2, 54.0, 35.0, 27.9; **HRMS (TOF-ESI$^+$) m/z**: $C_{13}H_{11}NO_3SeNa$ $[M+Na]^+$ 331.9796, found 331.9803.

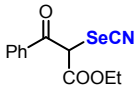


Ethyl 1-Oxo-2-selenocyanato-6-methoxyl-1,2,3,4-tetrahydronaphthalene -2-carboxylate (**5af**): Obtained in 79% yield (27.9 mg, 0.079 mmol) according to procedure 3 after column chromatography as a white solid by

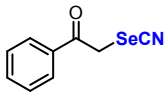
using *β*-keto ester; m.p. 132-133 °C; **IR (KBr)** ν 2947, 2516, 2153, 1657, 1342, 1067, 1013, 883 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 9.0 Hz, 1H), 6.89 (dd, *J* = 2.1, 8.7 Hz, 1H), 6.72 (s, 1H), 4.25-4.34 (m, 2H), 3.89 (s, 3H), 3.21-3.29 (m, 1H), 2.99-3.15 (m, 2H), 2.69-2.79 (m, 1H), 1.27 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 190.0, 167.6, 165.1, 146.2, 130.9, 123.5, 114.4, 112.7, 102.3, 64.5, 63.2, 55.7, 35.0, 28.4, 13.8; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{15}H_{15}NO_4SeNa$ $[M+Na]^+$ 376.0059, found 376.0039.



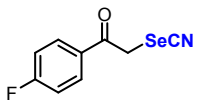
Ethyl 1-selenocyanato-2-oxo-cyclohexanecarboxylate (**5ag**): Obtained in 81% yield (22.3 mg, 0.081 mmol) according to procedure 3 after column chromatography as a colorless oil by using *β*-keto ester; **IR (KBr)** ν 2923, 2856, 2155, 1796, 1454, 1203, 869, 547 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 4.25-4.31 (m, 2H), 2.90 (dd, *J* = 12.9, 2.4 Hz, 1H), 2.50-2.69 (m, 2H), 2.25 (td, *J* = 13.2, 3.6 Hz, 1H), 2.03-2.07 (m, 1H), 1.85 (d, *J* = 13.2 Hz, 1H), 1.66-1.75 (m, 1H), 1.45-1.59 (m, 1H), 1.22 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 205.5, 167.6, 102.7, 66.8, 63.3, 38.7, 26.7, 23.9, 14.1; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{10}H_{13}NO_3SeNa$ $[M+Na]^+$ 297.9953, found 297.9953.



Ethyl 3-oxo-3-phenyl-2-selenocyanatopropanoate (**5ah**): Obtained in 84% yield (25.0 mg, 0.084 mmol) according to procedure 3 after column chromatography as a colorless oil by using *β*-keto ester; **IR (KBr)** ν 2978, 2155, 1796, 1734, 1450, 1235, 876, 684 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 6.37 (s, 1H), 4.17-4.23 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (75 MHz, DMSO-d_6)** δ 191.5, 167.2, 135.3, 133.9, 129.6, 129.4, 103.3, 63.0, 51.8, 14.2; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{12}H_{11}NO_3SeNa$ $[M+Na]^+$ 319.9796, found 319.9800.

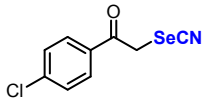


1-Phenyl-2-selenocyanatoethanone (**5ai**): Obtained in 89% yield (20.0 mg, 0.089 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 81-82 °C (lit. 48-49 °C); **IR (KBr)** ν 2955, 2514, 2155, 1796, 1462, 1268, 884, 734 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 4.96 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 193.2, 134.9, 133.8, 129.2, 128.8, 101.9, 38.5; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_9H_7NOSeNa$ $[M+Na]^+$ 247.9585, found 247.9571.

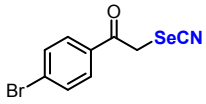


1-(4-Fluorophenyl)-2-selenocyanatoethanone (**5aj**): Obtained in 83% yield (20.2 mg, 0.083 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 118-119 °C (lit. 112-113 °C); **IR (KBr)** ν 2990, 2158, 1657, 1412, 1290, 1000, 824, 581 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.99-8.04 (m, 2H), 7.22 (t, *J* = 8.4 Hz, 2H), 4.92 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.6, 166.7 (d, $^1J_{C\text{-}F}$ = 257.3 Hz), 131.6 (d, $^2J_{C\text{-}F}$ = 9.8 Hz), 130.3 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 116.5 (d, $^2J_{C\text{-}F}$ = 22.5 Hz),

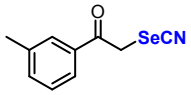
101.7, 38.1; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_9H_6NOSeFNa$ $[M+Na]^+$ 265.9491, found 265.9499.



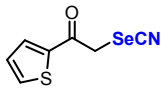
1-(4-Chlorophenyl)-2-selenocyanatoethanone (**5ak**): Obtained in 71% yield (18.4 mg, 0.071 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 162-164 °C; **IR (KBr)** ν 2985, 2155, 1796, 1657, 1399, 1178, 816, 579 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 8.04-8.15 (m, 2H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.41 (t, *J* = 8.7 Hz, 1H), 4.79 (d, *J* = 7.2 Hz, 2H); **^{13}C NMR (75 MHz, DMSO-*d*$_6$)** δ 193.4 (d, *J* = 29.3 Hz), 139.5, 133.4, 132.4 (d, *J* = 9.8 Hz), 131.2, 129.5, 116.4 (d, *J* = 21.8 Hz), 104.3, 35.6 (d, *J* = 12.0 Hz); **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_9H_6NOSeClNa$ $[M+Na]^+$ 281.9195, found 281.9204.



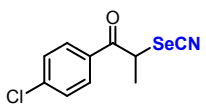
1-(4-Bromophenyl)-2-selenocyanatoethanone (**5al**): Obtained in 66% yield (20.0 mg, 0.066 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 184-186 °C (lit. 144-145 °C); **IR (KBr)** ν 2509, 1794, 1652, 1465, 1397, 1008, 871, 739 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 4.77 (s, 2H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 192.2, 132.6, 132.5, 130.5, 130.1, 101.5, 37.9; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_9H_6NOSeBrNa$ $[M+Na]^+$ 325.8690, found 325.8679.



1-(3-Methylphenyl)-2-selenocyanatoethanone (**5am**): Obtained in 84% yield (20.1 mg, 0.084 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 84-85 °C (lit. 43-44 °C); **IR (KBr)** ν 2983, 2153, 1799, 1599, 1380, 1290, 1043, 786 cm^{-1}; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.76-7.78 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 4.95 (s, 2H), 2.46 (s, 3H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 193.4, 139.2, 135.7, 133.8, 129.2, 129.0，126.0, 101.9, 38.6, 21.3; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{10}H_9NOSeNa$ $[M+Na]^+$ 261.9742, found 261.9742.

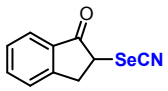


2-Selenocyanato-1-(thiophen-2-yl)ethanone (**5an**): Obtained in 99% yield (22.9 mg, 0.099 mmol) according to procedure 2 after column chromatography as a white solid by using silyl enol ethers; m.p. 101-102 °C (lit. 100-101 °C); **IR (KBr)** ν 2936, 2158, 1794, 1629, 1350, 1298, 941, 836 cm^{-1}; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.82 (d, *J* = 3.9 Hz, 2H), 7.23 (t, *J* = 3.9 Hz, 1H), 4.77 (s, 2H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 185.4, 140.2, 136.3, 134.3, 128.8, 101.4, 36.7; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_7H_5NOSSeNa$ $[M+Na]^+$ 253.9149, found 253.9143.

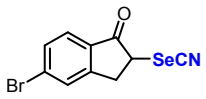


1-(4-Chlorophenyl)-2-selenocyanatopropan-1-one (**5ao**): Obtained in 95% yield (25.9 mg, 0.095 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 72-73 °C (lit. 70-71 °C); **IR (KBr)** ν 2921, 2514, 2160, 1791, 1440, 1230, 844, 752 cm^{-1}; **^{1}H NMR (300 MHz,**

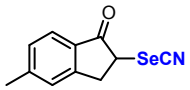
DMSO-d_6) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 5.18 (dd, *J* = 13.2, 6.6 Hz, 1H), 1.77 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 195.8, 141.4, 131.1, 130.3, 129.6, 102.3, 48.3, 21.2; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{10}H_8NOSeClNa$ $[M+Na]^+$ 295.9352, found 295.9332.



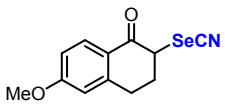
2-Selenocyanato-2,3-dihydro-1H-inden-1-one (**5ap**): Obtained in 93% yield (22.0 mg, 0.093 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 131-133 °C; **IR (KBr)** ν 2965, 2517, 2153, 1794, 1604, 1460, 1325, 754 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 4.45 (dd, *J* = 8.1, 3.6 Hz, 1H), 3.88 (dd, *J* = 18.0, 8.1 Hz, 1H), 3.29-3.30 (m, 1H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 199.8, 151.7, 136.4, 134.0, 128.6, 126.5, 125.0, 99.8, 44.2, 35.6; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{10}H_7NOSeNa$ $[M+Na]^+$ 259.9585, found 259.9578.



5-Bromo-2-selenocyanato-2,3-dihydro-1*H*-inden-1-one (**5aq**): Obtained in 86% yield (27.1 mg, 0.086 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 123-125°C; **IR (KBr)** ν 2923, 2856, 2155, 1796, 1445, 1245, 869, 547 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 7.93 (dd, *J* = 8.1, 1.5 Hz,, 1H), 7.88 (s, 1H), 7.59 (d, *J* = 8.1 Hz,1H), 4.47 (dd, *J* = 8.1, 3.6 Hz, 1H), 3.84 (dd, *J* = 18.3, 8.1 Hz, 1H), 3.25 (d, *J* = 3.0 Hz, 1H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 198.5, 150.2, 139.1, 135.8, 128.0, 127.8, 122.8, 99.5, 43.9, 35.3; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{10}H_6NOSeBrNa$ $[M+Na]^+$ 337.8690, found 337.8683.

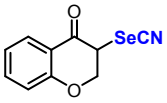


5-Methyl-2-selenocyanato-2,3-dihydro-1*H*-inden-1-one (**5ar**): Obtained in 82% yield (20.6 mg, 0.082 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 104-106 °C; **IR (KBr)** ν 2965, 2153, 1696, 1574, 1278, 1110, 826, 724 cm^{-1}; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.65 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 4.47 (dd, *J* = 7.8, 3.6 Hz, 1H), 3.84 (dd, *J* = 18.0, 7.8 Hz, 1H), 3.44-3.50 (m, 1H), 2.45 (s, 3H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 199.8, 149.1, 138.8, 137.7, 134.1, 126.2, 124.8, 99.9, 44.6, 35.3, 21.1; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{11}H_9NOSeNa$ $[M+Na]^+$ 273.9742, found 273.9748.

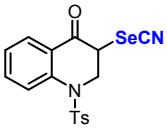


6-Methoxyl-2-selenocyanato-3,4-dihydronaphthalen-1(2*H*)-one (**5as**): Obtained in 99% yield (27.8 mg, 0.099 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 125-126 °C; **IR (KBr)** ν 2511, 2149, 1793, 1651, 1592, 1356, 1255, 1104,1021, 893 cm^{-1}; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.99 (d, *J* = 9.0 Hz, 1H), 6.89 (dd, *J* = 8.7, 1.8 Hz, 1H), 6.76 (s, 1H), 4.99 (dd, *J* = 13.5, 5.1 Hz, 1H), 3.90 (s, 3H), 3.13-3.17 (m, 2H), 2.87-2.92 (m, 1H), 2.48-2.60 (m, 1H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 192.6, 164.9, 146.8, 130.4, 124.0, 114.1, 112.8, 102.8, 55.7, 53.1,

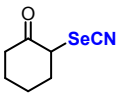
32.6, 30.7; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{12}H_{11}NO_2SeNa$ $[M+Na]^+$ 303.9847, found 303.9832.



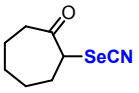
2-Selenocyanato chromanone (**5at**): Obtained in 91% yield (23.0 mg, 0.091 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 93-94 °C; **IR (KBr)** ν 2928, 2851, 2153, 1799, 1664, 1602, 1203, 1140, 998, 599 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 7.5, 15.0 Hz, 2H), 4.92 (dd, *J* = 11.7, 4.2 Hz, 1H), 4.82-4.86 (m, 1H), 4.70 (dd, *J* = 11.4, 7.2 Hz, 1H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 187.7, 161.7, 137.5, 127.6, 122.6, 119.2, 118.2, 99.6, 71.2, 47.1; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{10}H_7NO_2SeNa$ $[M+Na]^+$ 275.9534, found 275.9520.



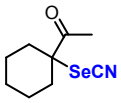
N-Tosyl-2-selenocyanato-2,3-dihydro-4(1*H*)-quinolinone (**5au**): Obtained in 47% yield (19.1 mg, 0.047 mmol) according to procedure 1 after column chromatography as a white solid by using enamine; m.p. 114-116 °C; **IR (KBr)** ν 2921, 2155, 1679, 1602, 1475, 1370, 1223, 1163, 881, 754 cm^{-1}; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.95 (t, *J* = 8.7 Hz, 2H), 7.65-7.72 (m, 3H), 7.35 (t, *J* = 7.8 Hz, 3H), 4.88 (dd, *J* = 14.1, 4.8 Hz, 1H), 4.46 (dd, *J* = 13.2, 5.1 Hz, 1H), 4.20 (t, *J* = 18.9 Hz, 1H), 2.46 (s, 3H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 189.2, 145.4, 142.6, 136.2, 130.6, 128.4, 127.0, 126.0, 124.3, 123.1, 99.7, 52.2, 47.0, 21.7; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{17}H_{14}N_2O_3SSeNa$ $[M+Na]^+$ 428.9783, found 428.9797.



2-Selenocyanato cyclohexanone (**5av**): Obtained in 86% yield (17.4 mg, 0.086 mmol) according to procedure 1 after column chromatography as a colorless oil by using enamine; **IR (KBr)** ν 2933, 2856, 2148, 1794, 1450, 1340, 1200, 1098, 939, 891 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 5.04 (dd, *J* = 12.6, 6.3 Hz, 1H), 2.54-2.59 (m, 2H), 2.40-2.45 (m, 1H), 2.00-2.08 (m, 2H), 1.87-1.91 (m, 1H), 1.62-1.77 (m, 2H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 207.8, 103.6, 55.9, 41.2, 37.0, 26.8, 25.6; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_7H_9NOSeNa$ $[M+Na]^+$ 225.9742, found 225.9741.

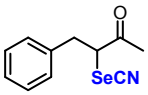


2-Selenocyanato cycloheptanone (**5aw**): Obtained in 81% yield (17.6 mg, 0.081 mmol) according to procedure 1 after column chromatography as a colorless oil by using enamine; **IR (KBr)** ν 2923, 2861, 2150, 1794, 1670, 1447, 1123, 1026, 879, 694 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-*d*$_6$)** δ 5.22 (dd, *J* = 10.5, 3.6 Hz, 1H), 2.63-2.72 (m, 1H), 2.36-2.47 (m, 2H), 2.02 (dd, *J* = 25.5, 12.0 Hz, 1H), 1.80-1.84 (m, 2H), 1.68-1.72 (m, 2H), 1.53-1.61 (m, 1H), 1.34-1.45 (m, 1H); **^{13}C NMR (75 MHz, CDCl$_3$)** δ 211.5, 104.9, 59.6, 41.5, 32.8, 29.2, 28.9, 23.9; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_8H_{11}NOSeK$ $[M+K]^+$ 255.9637, found 255.9657.

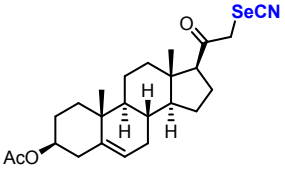


1-Cyclohexyl-1-selenocyanatoethanone (**5ax**): Obtained in 71% yield (16.4 mg, 0.071 mmol) according to procedure 1 after column chromatography as a white solid

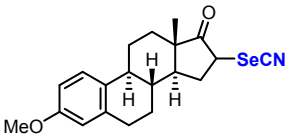
by using enamine; m.p. 43-44 °C; **IR (KBr)** ν 2930, 2856, 2145, 1699, 1455, 1360, 1183, 1123, 894, 654 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 2.35 (s, 3H), 2.01-2.08 (m, 4H), 1.55-1.66 (m, 2H), 1.35-1.46 (m, 4H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 203.1, 102.4, 64.9, 32.6, 24.8, 24.7, 23.8; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_9H_{13}NOSeNa$ $[M+Na]^+$ 254.0055, found 254.0061.



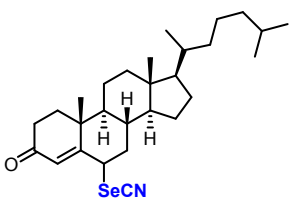
3-Selenocyanato-4-phenyl-2-butanone (**5ay**): Obtained in 83% yield (21.0 mg, 0.083 mmol) according to procedure 1 after column chromatography as a white solid, by using enamine; m.p. 57-58 °C; **IR (KBr)** ν 2921, 2846, 2517, 2155, 1799, 1647, 1465, 1270, 874,694 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 7.31-7.35 (m, 2H), 7.24-7.27 (m, 3H), 4.41 (dd, J = 9.0, 6.0 Hz, 1H), 3.38-3.43 (m, 1H), 3.01 (dd, J = 14.7, 9.3 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR (75 MHz, DMSO-d_6)** δ 202.7, 138.5, 129.5, 128.8, 127.2, 103.5, 53.6, 36.1, 28.0; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{11}H_{11}NOSeNa$ $[M+Na]^+$ 275.9898, found 275.9899.



Pregnenolone acetate selenocyanate derivative (**5az**): Obtained in 92% yield (42.6 mg, 0.092 mmol) according to procedure 2 after column chromatography as a white solid by using silyl enol ethers; m.p. 153-154 °C; **IR (KBr)** ν 2940, 2155, 1799, 1724, 1465, 1370, 1248, 1028, 874, 607 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.39 (d, J = 3.6 Hz, 1H), 4.61-4.64 (m, 1H), 4.30 (s, 2H), 2.67 (t, J = 8.1 Hz, 1H), 2.34-2.36 (m, 2H), 2.15-2.21 (m, 1H), 2.05 (s, 3H),2.00-2.04 (m, 2H), 1.88-1.91 (m, 2H), 1.77-1.79 (m, 2H), 1.62-1.65 (m, 3H), 1.53-1.56 (m, 1H), 1.47-1.50 (m, 2H), 1.18- 1.32 (m, 3H), 1.04 (s, 3H), 0.67 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.7, 170.6, 139.7, 122.1, 101.8, 73.8, 62.0, 56.7, 49.7, 45.0, 41.4, 38.7, 38.0, 37.0, 36.6, 31.8, 31.6, 27.7, 24.4, 23.4, 21.4, 21.0, 19.3, 13.5; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{24}H_{33}NO_3SeK$ $[M+K]^+$ 502.1257, found 502.1244.



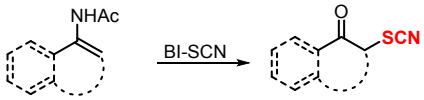
Estrone selenocyanate derivative (**5ba**): Obtained in 87% yield (33.8 mg, 0.087 mmol) according to procedure 2 after column chromatography as a white solid by using silyl enol ethers; m.p. 134-135 °C; **IR (KBr)** ν 2928, 2153, 1796, 1724, 1609, 1499, 1377, 1255, 869, 669 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.21 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 7.3 Hz, 1H), 6.68 (s, 1H), 4.65 (d, J = 6.8 Hz, 1H), 3.80 (s, 3H), 2.93-2.94 (m, 2H), 2.43-2.50 (m, 2H), 2.32-2.39 (m, 1H), 1.91-2.05 (m, 3H), 1.45-1.67 (m, 5H), 1.07 (d, J = 13.8 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 213.5, 157.8, 137.5, 131.4, 126.3, 113.9, 111.7, 101.3, 55.2, 48.4, 47.5, 45.7, 43.7, 37.9, 31.7, 31.3, 29.4, 26.3, 25.6, 14.0; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{20}H_{23}NO_2SeNa$ $[M+Na]^+$ 412.0786, found 412.0758.



Cholesterol selenocyanate derivative (**5bb**): Obtained in 73% yield (35.7 mg, 0.073 mmol) according to procedure 2 after column chromatography as a white solid by using silyl enol ethers; m.p. 100-101 °C; **IR (KBr)** ν 2938, 2148, 1799, 1649, 1562, 1467, 1228, 1013,

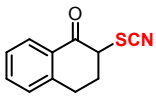
874, 667 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 5.95 (s, 1H), 4.83 (s, 1H), 2.54-2.63 (m, 2H), 2.08-2.22 (m, 3H), 1.52-1.89 (m, 8H), 1.43 (s, 3H), 1.28-1.35 (m, 6H), 1.09-1.19 (m, 6H), 1.01-1.06 (m, 2H), 0.94 (d, *J* = 6.3 Hz, 3H), 0.90 (s, 3H), 0.88 (s, 3H), 0.77 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 198.5, 163.1, 128.4, 102.0, 56.1, 55.2, 52.6, 49.8, 42.5, 39.5, 39.3, 38.2, 37.4, 37.1, 36.1, 35.7, 34.1, 31.6, 28.0, 24.1, 23.8, 22.8, 22.5, 21.2, 20.9, 18.6, 12.0; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{28}H_{43}NOSeNa$ $[M+Na]^+$ 512.2402, found 512.2417.

2.3 Synthetic procedure for the synthesis of 2-thiocyanato-3,4-dihydronaphthalen-1(2*H*)-one (7)



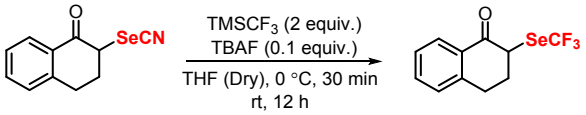
The *N*-acetyl-α-arylenamines **4a** (0.1 mmol) and BI-SCN (36.6 mg, 0.15 mmol, 1.5 equiv.) was ground togather with agate mortar at room temperature for the given time. After the completion of the reaction, the mixture was dissolved in EtOAc (2 mL). Then the mixture was extracted with EtOAc (2×2 mL) and washed with saturated aqueous $NaHCO_3$. The combined organic phase were dried (Na_2SO_4) and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography (PE:EtOAc = 9:1-5:1) to afford the desired selenocyanate compound as a white solid.

Caution: This reaction should be carried out behind a safety shield!



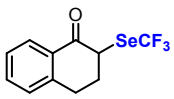
2-thiocyanato-3,4-dihydronaphthalen-1(2*H*)-one (**7**): white solid (64% yield, 13.0 mg, 0.064 mmol); m.p. 56-57 °C (lit. 56-58 °C); **IR (KBr)** ν 2923,1796, 1607, 1460, 1225, 1150, 983, 764 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.41-7.43 (m, 2H), 5.17 (dd, *J* = 13.2, 4.8 Hz, 1H), 3.22 (dd, *J* = 12.3, 4.2 Hz, 1H), 3.09-3.14 (m, 1H), 2.61-2.66 (m, 1H), 2.33 (dd, *J* = 12.3, 4.2 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 191.7, 143.5, 134.9, 130.6, 129.0, 128.0, 127.5, 111.8, 55.8, 31.5, 29.1; **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{11}H_9NOSK$ $[M+K]^+$ 242.0036, found 242.0026.

2.4 Synthetic procedure for the synthesis of 2-trifluoromethylselenocyanato-3,4-dihydronaphthalen-1(2*H*)-one (8)



To a dry two-neck flask were added α-selenocyanate tetralone (25.0 mg, 0.1 mmol) and dry THF (2 mL). The flask was evacuated and refilled with Ar three times. After the reaction was cooled to 0 °C, $TMSCF_3$ (28.4 mg, 0.2 mmol, 2.0 equiv.) and TBAF in 1 M THF (20 μL, 0.02

mmol, 0.2 equiv.) were added dropwise respectively. After 30 min at 0 °C under Ar atmosphere, the reaction was allowed to warm to 23 °C and stirred for 12 h. The reaction mixture was then extracted with EtOAc (2×2 mL) and washed with brine. The combined organic layers were dried ($MgSO_4$) and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography (PE:EtOAc = 19:1) to afford the desired product as a colorless liquid.



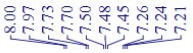
2-Trifluoromethylselenocyanato-3,4-dihydronaphthalen-1(2*H*)-one (**8**): colorless oil (83% yield, 24.4 mg, 0.083 mmol); **IR (KBr)** ν 2923, 2512, 2153, 1671, 1450, 1320, 891, 742 cm^{-1}; **^{1}H NMR (300 MHz, DMSO-d_6)** δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 5.13 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.15-3.18 (m, 1H), 3.01-3.06 (m, 1H), 2.60-2.66 (m, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ 193.6, 143.2, 134.3, 131.0, 128.8, 128.1, 127.2, 122.9 (d, $^1J_{C\text{-}F}$ = 329.2 Hz), 49.4, 31.5, 29.0; **^{19}F NMR (282 MHz, $CDCl_3$)** δ -32.2 (s); **HRMS (TOF-ESI$^+$) m/z**: calcd for $C_{11}H_9F_3OSeNa$ $[M+Na]^+$ 316.9663, found 316.9649.

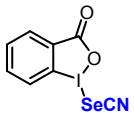
3. References

[1] Z.-H., Guan; Z.-Y., Zhang; Z.-H. , Ren; Y.-Y. , Wang; X., Zhang. *J. Org. Chem.* **2011,** 76, (1), 339-341.

[2] (a) Hata, K.; Arichi, N.; Yamaoka, Y.; Yamada, K.; Takemoto, Y.; Takasu, K. *Asian J. Org. Chem.* **2014,** 3, (6), 706-710; (b) Zhu, J.; W.-C. , Cui; Wang, S.; Z.-J. , Yao. *J. Org. Chem.* **2018,** 83 (23), pp 14600–14609.

4. Spectra





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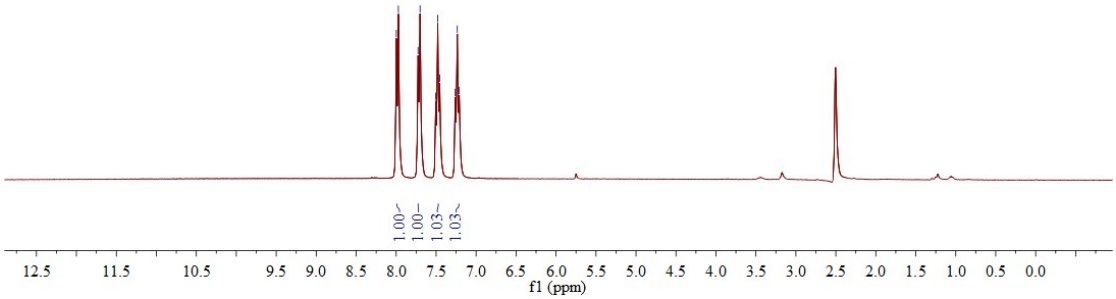

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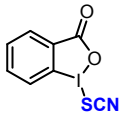

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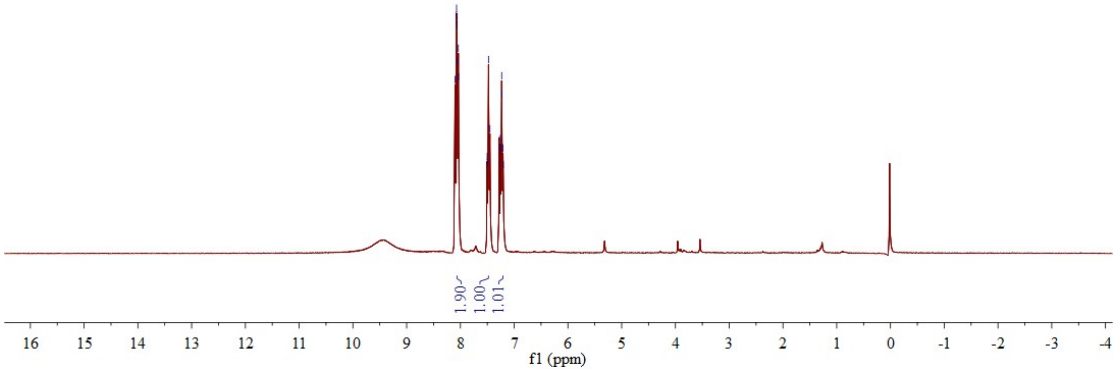

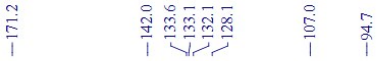

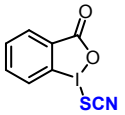

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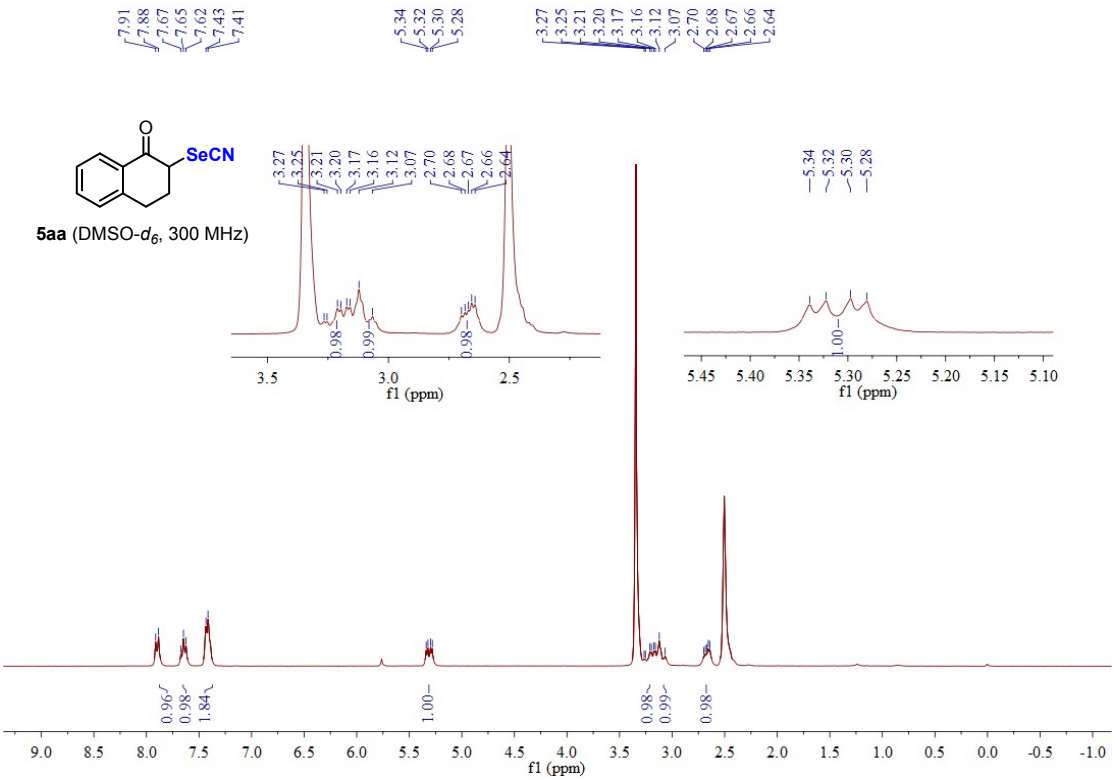
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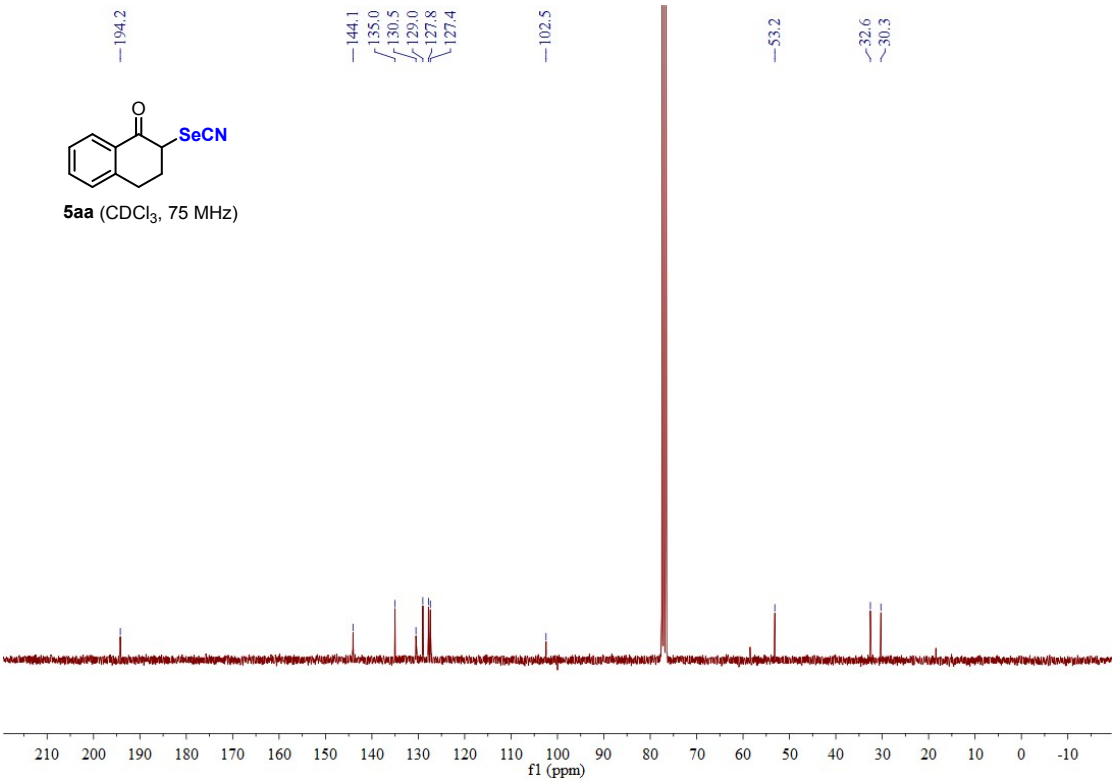
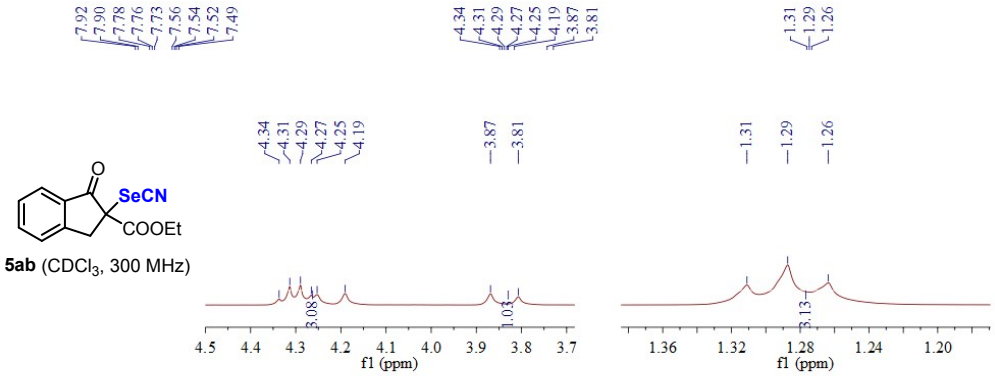
5aa (DMSO-d6, 300 MHz)
f1 (ppm)


SeCN
5aa (CDCl3, 75 MHz)
f1 (ppm)



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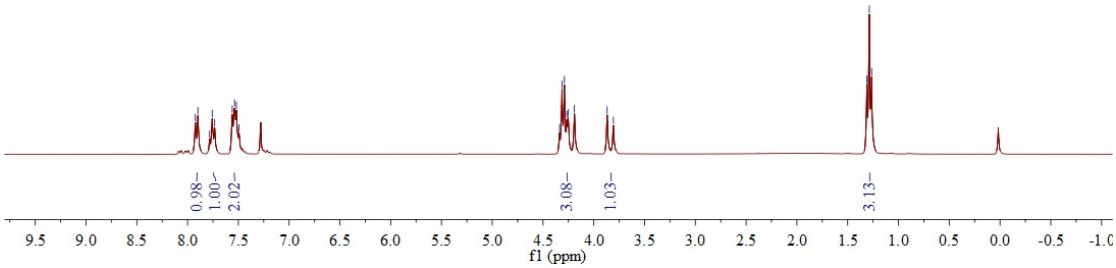

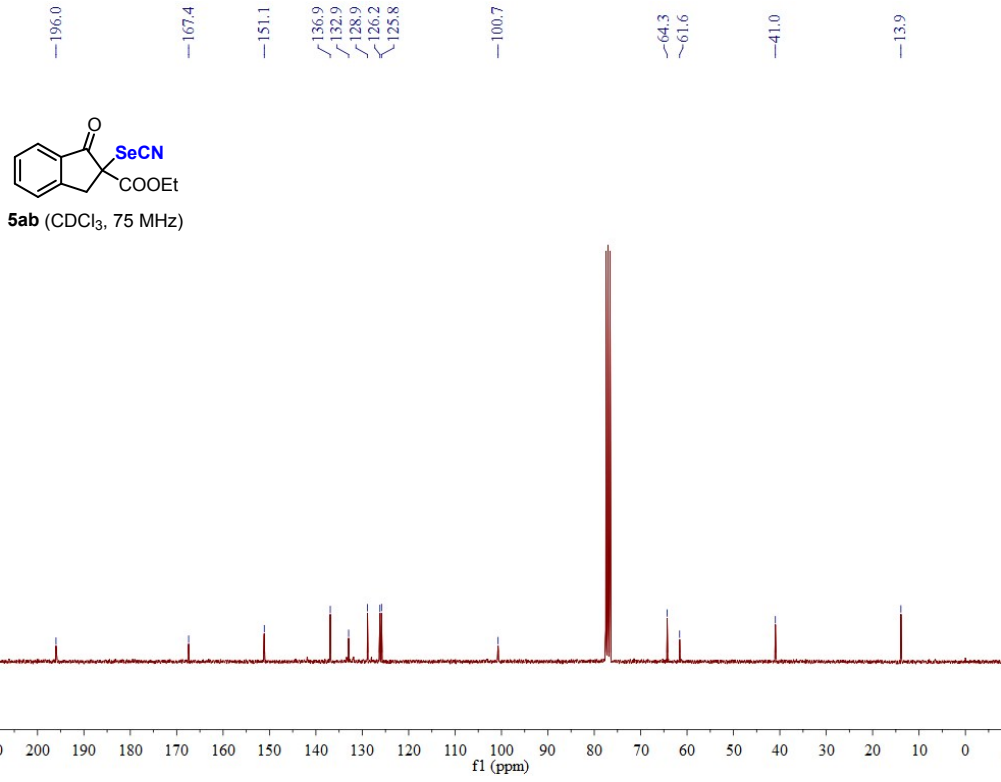

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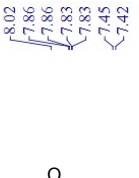

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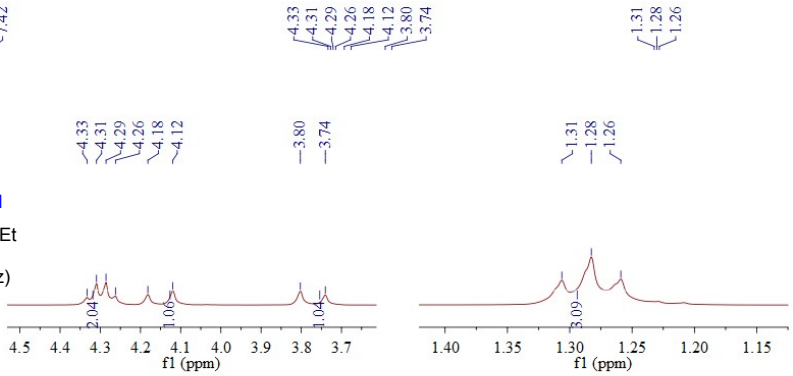

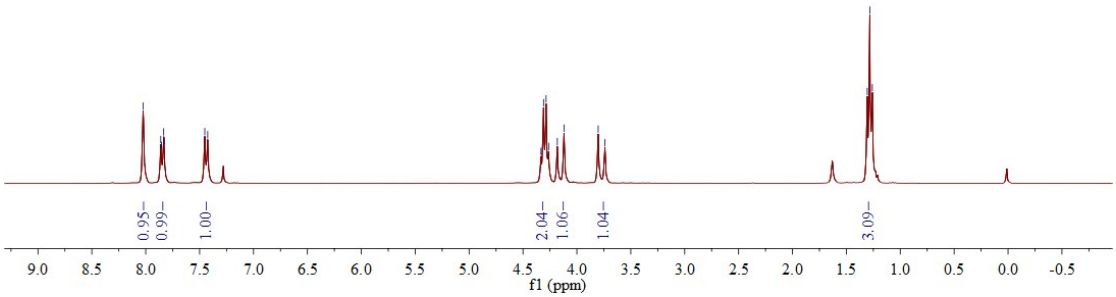

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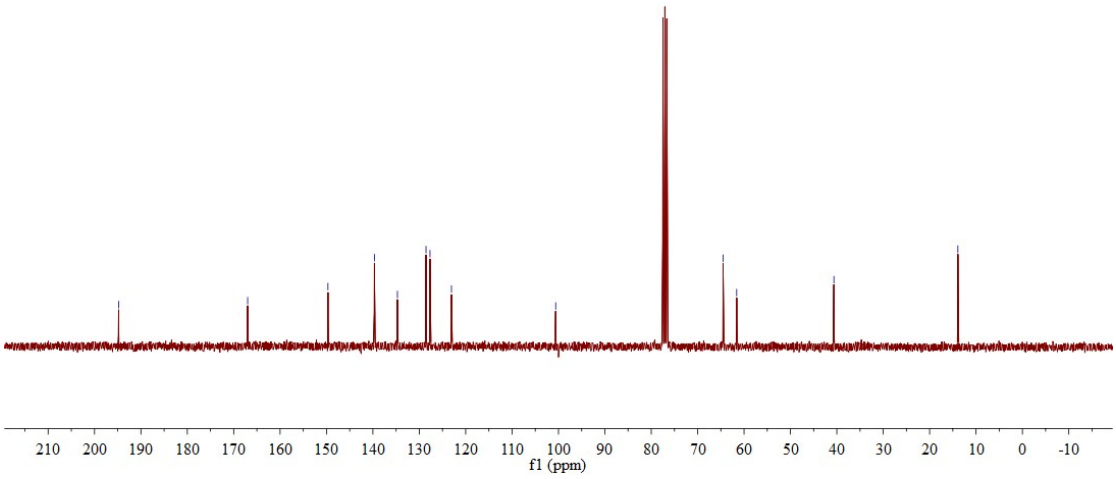

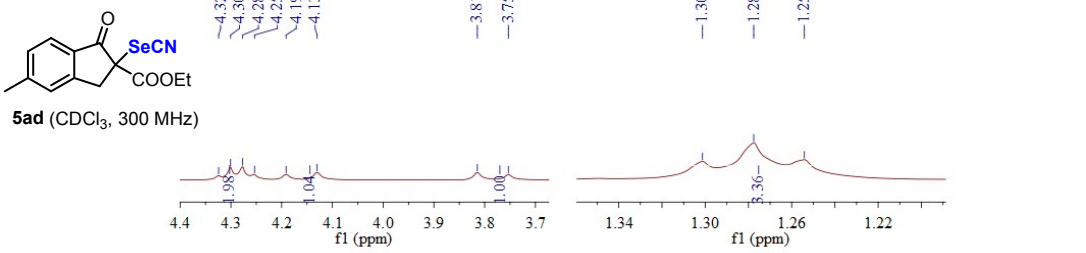

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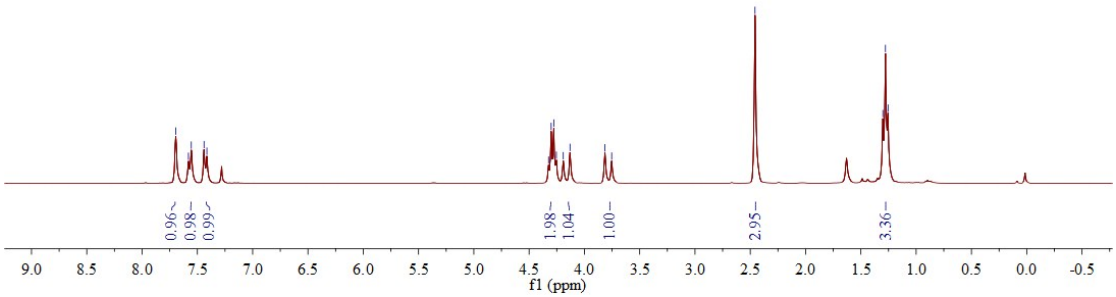

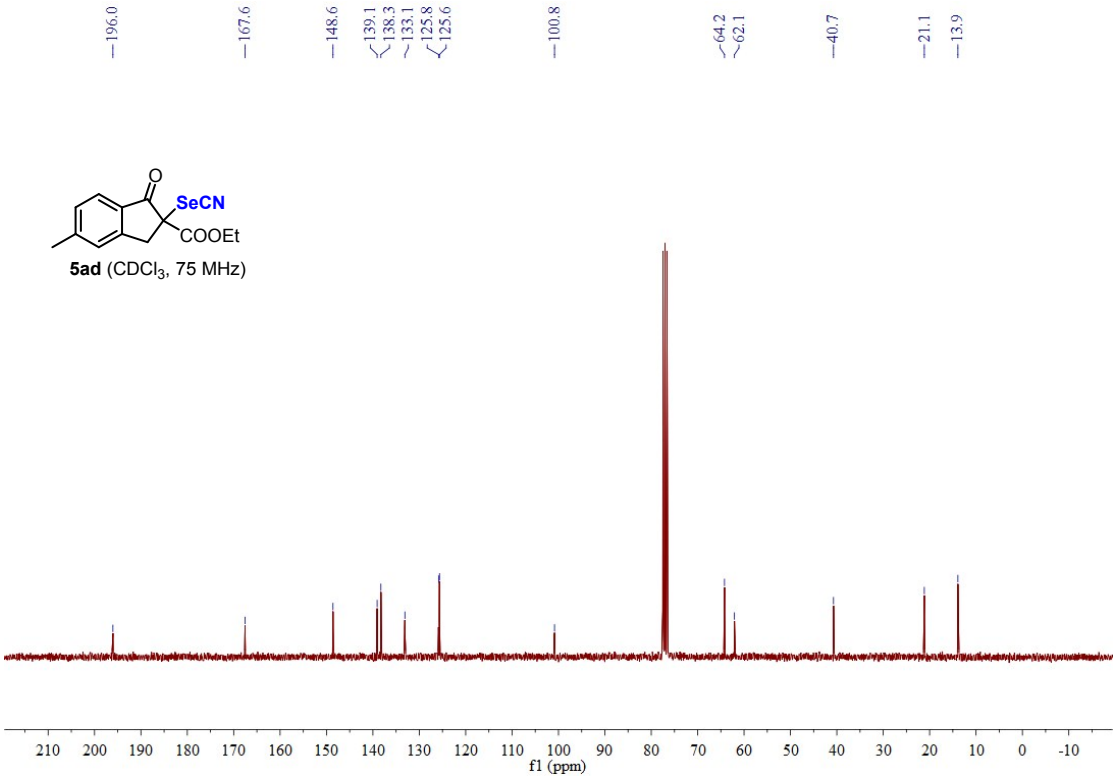

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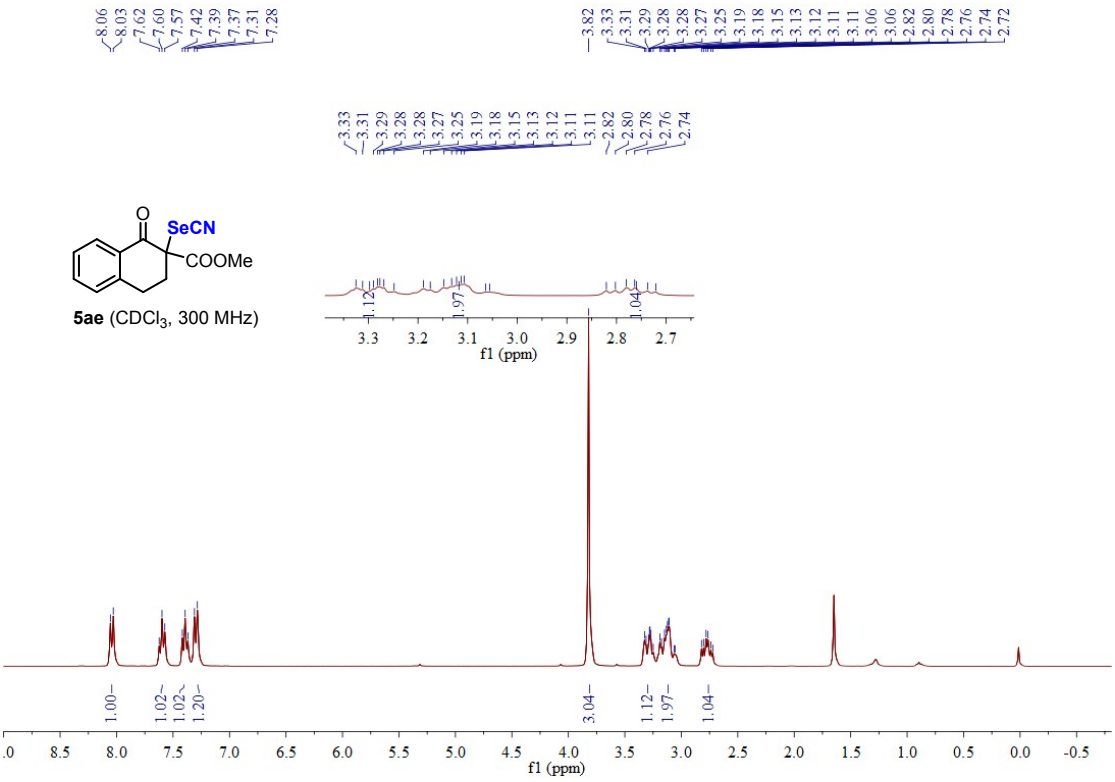

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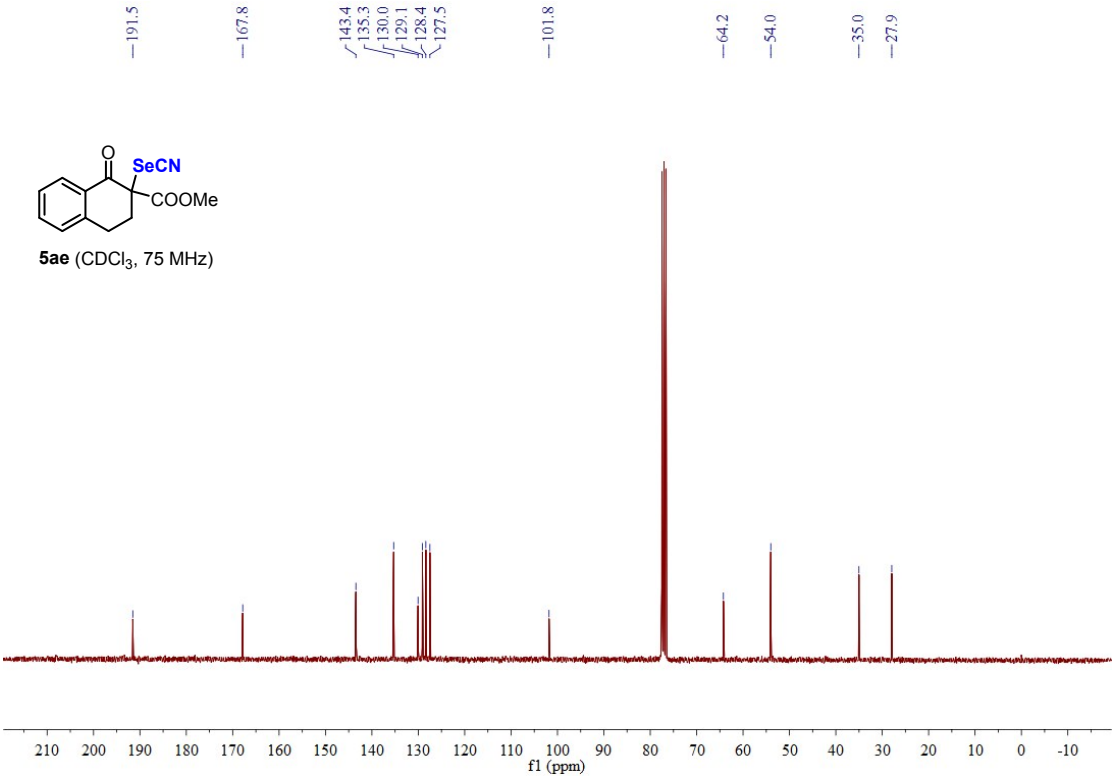

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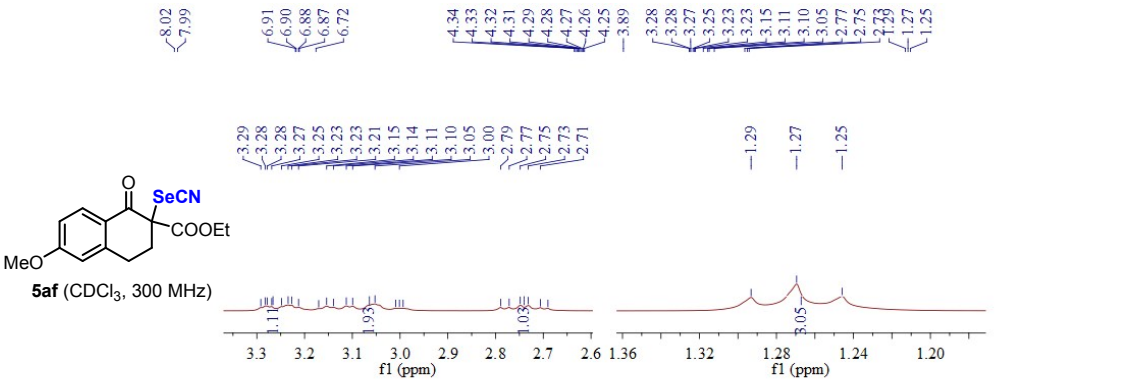

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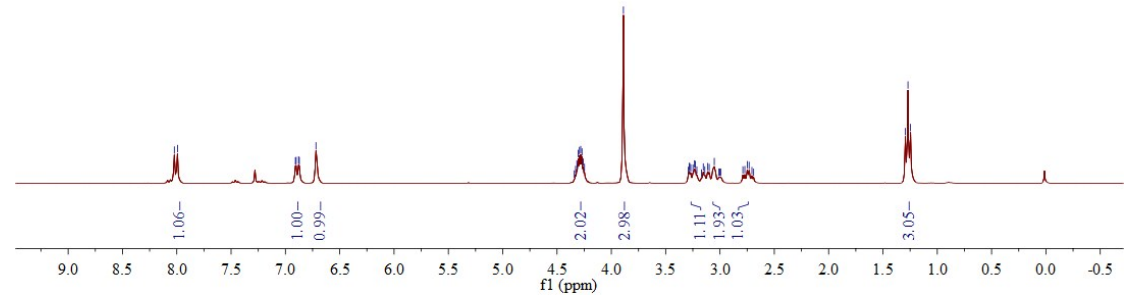

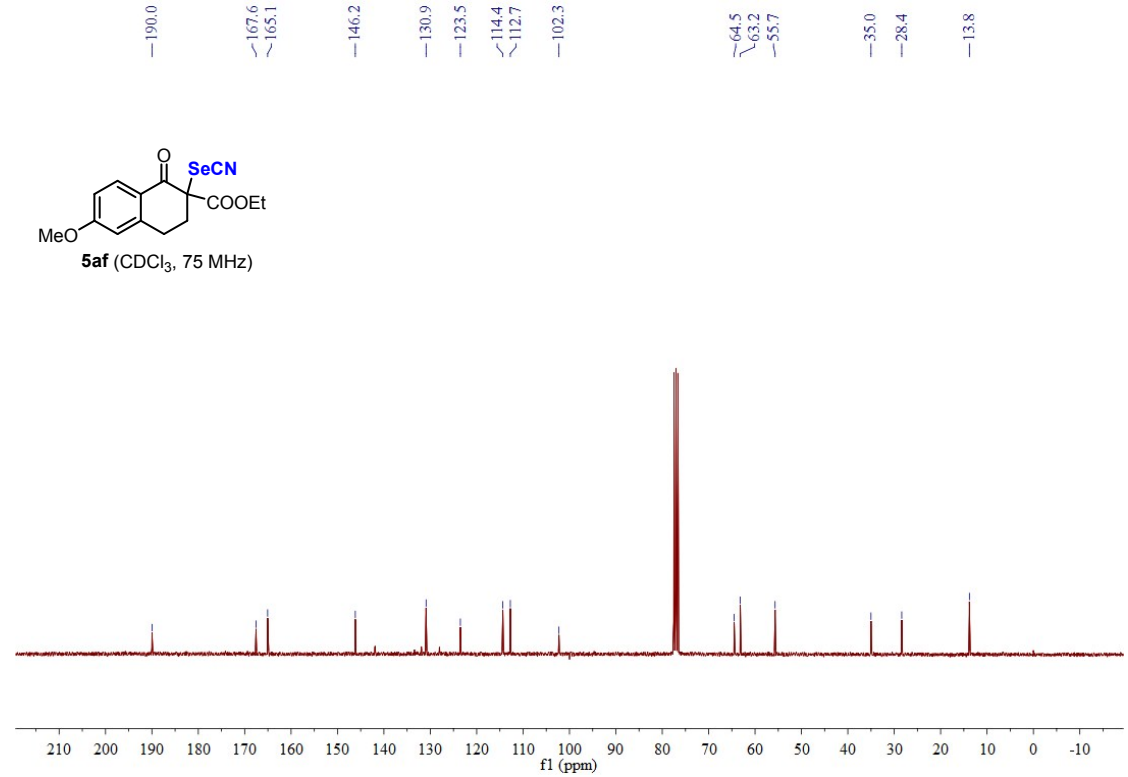

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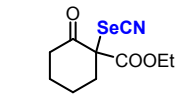

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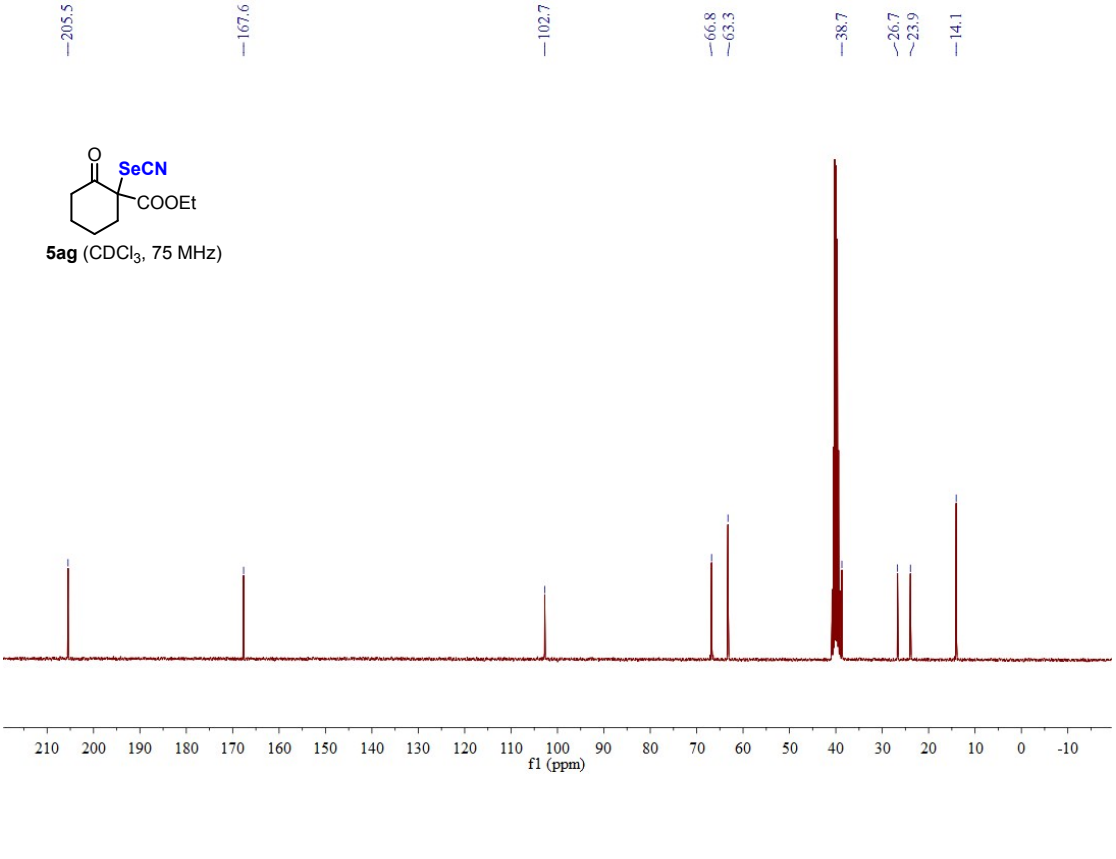

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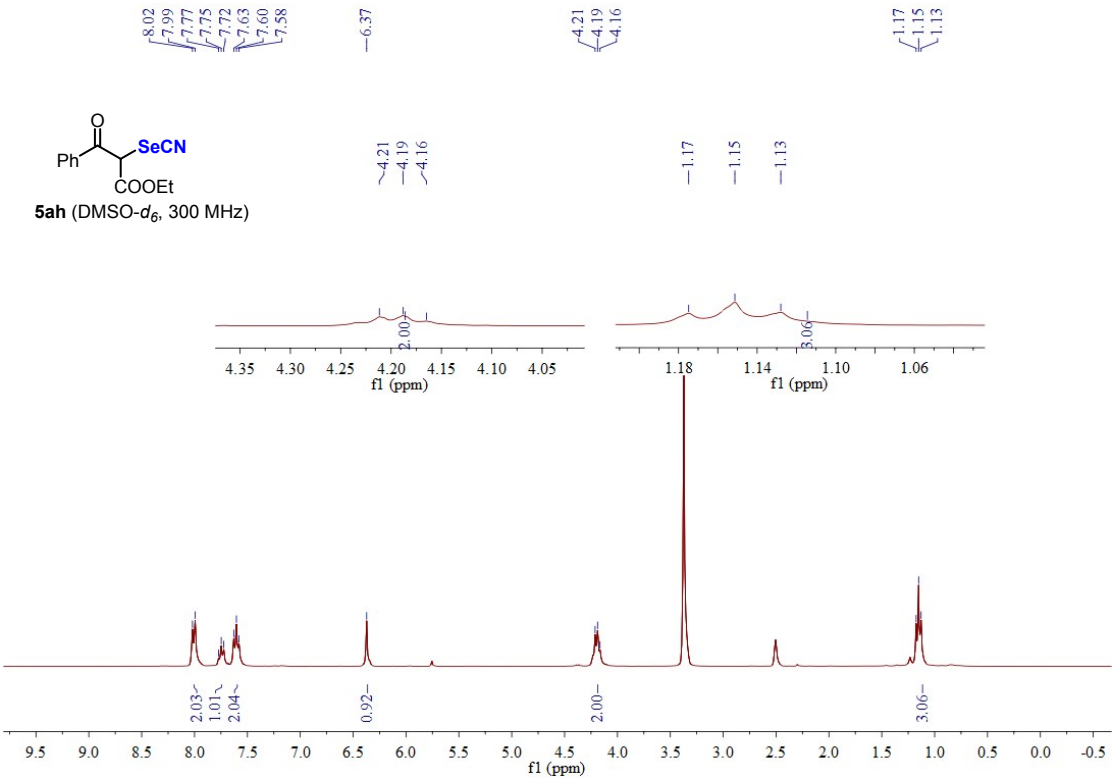

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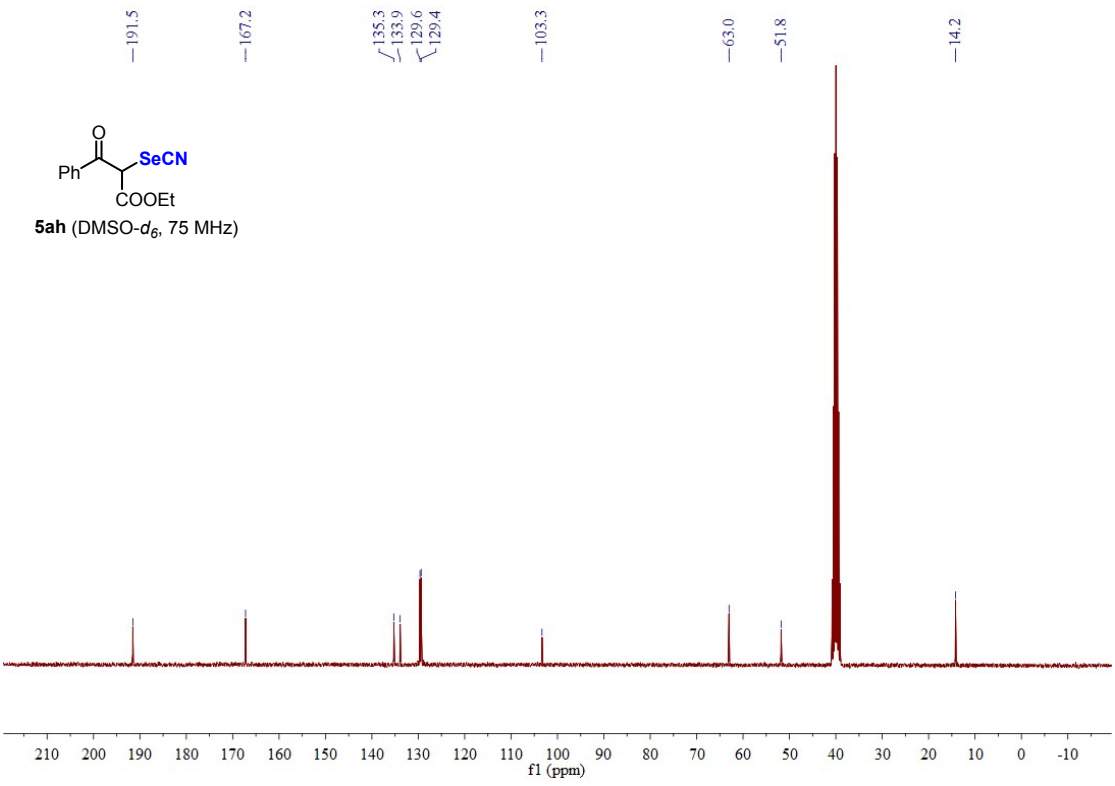

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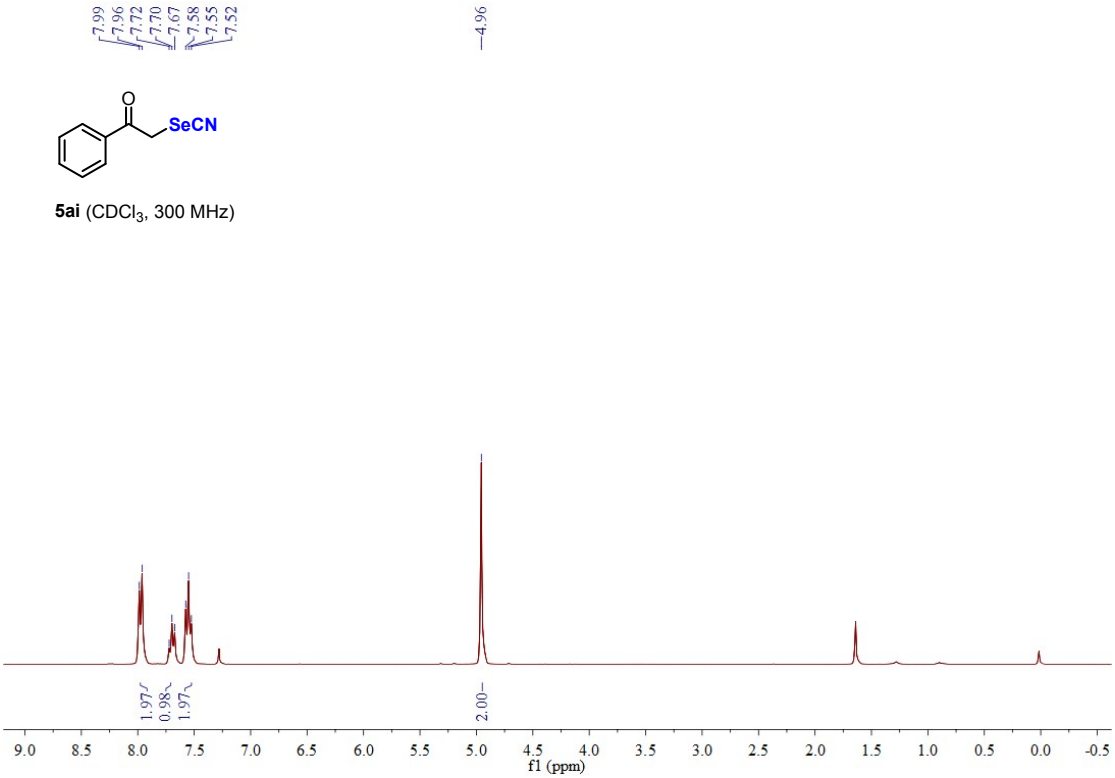

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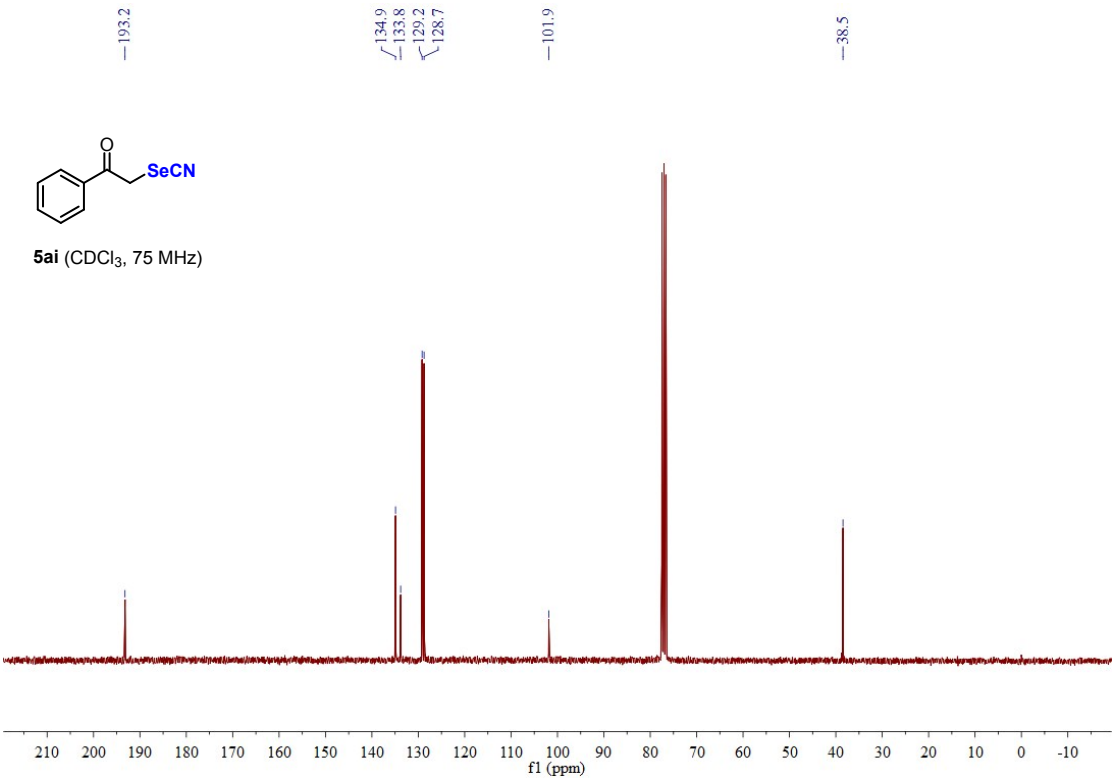

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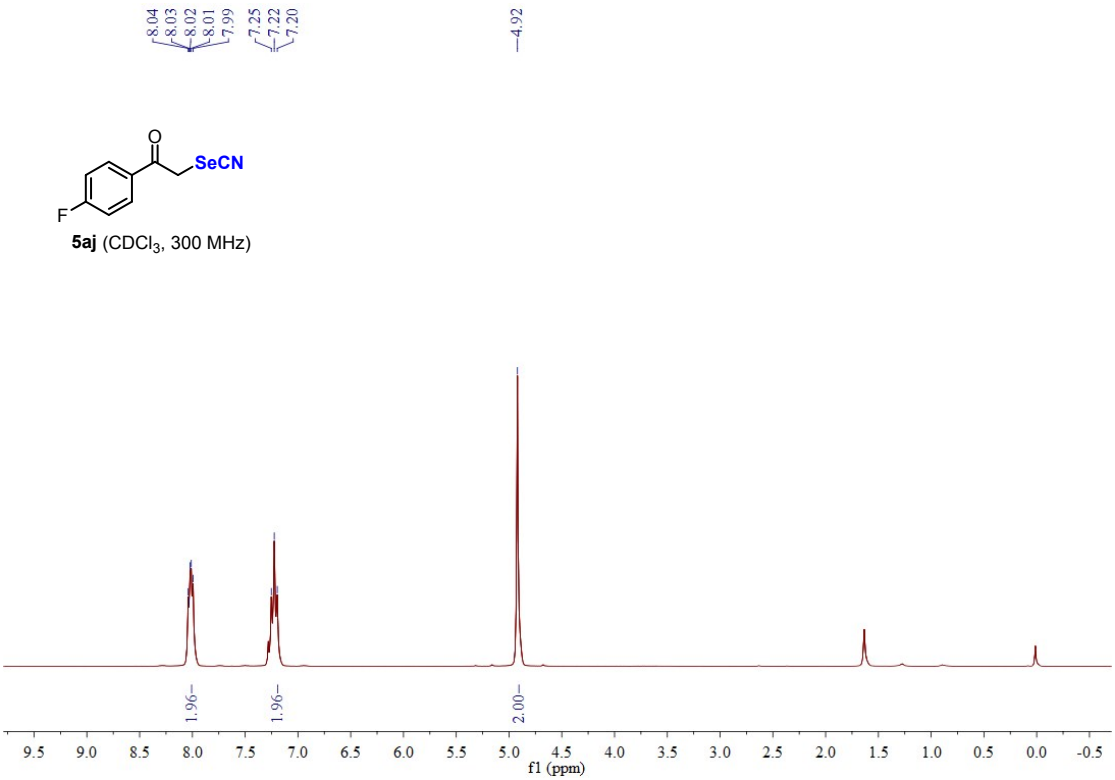
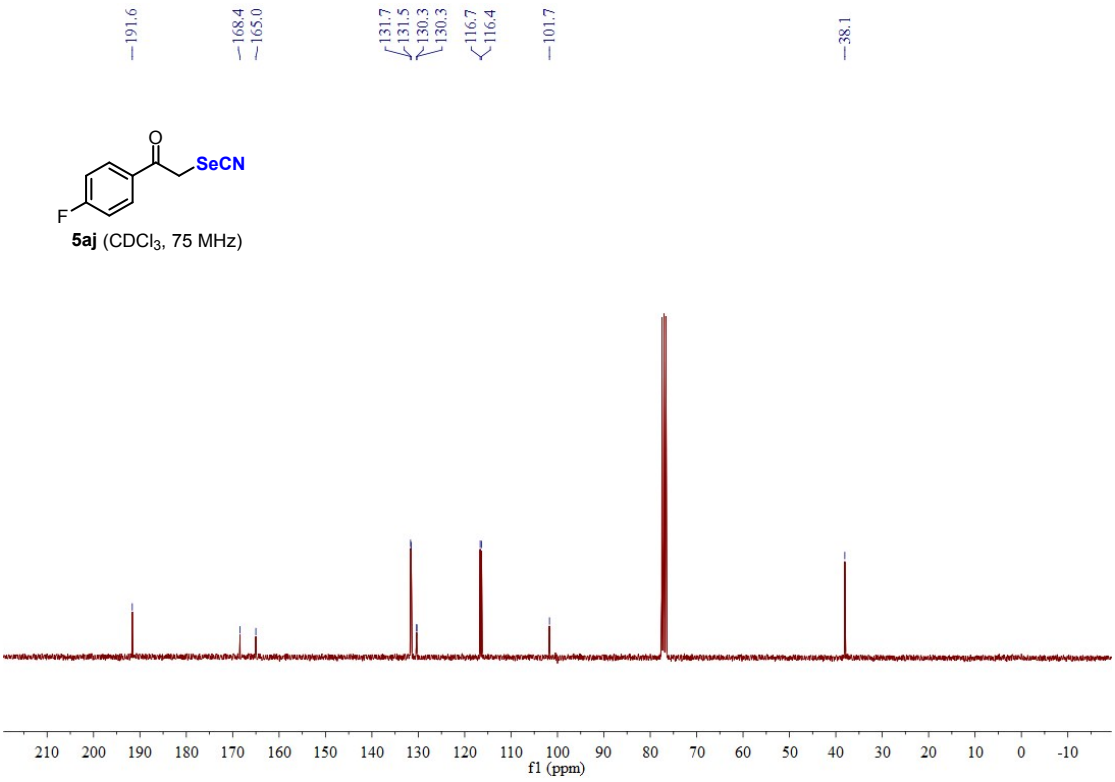
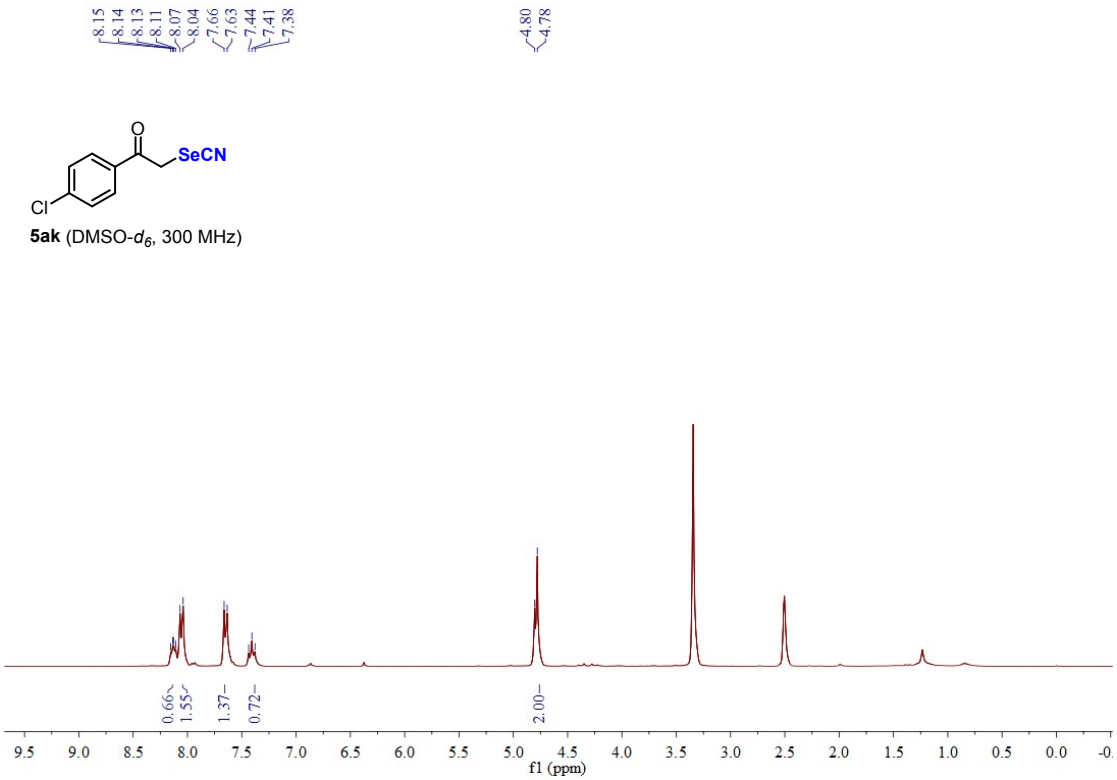


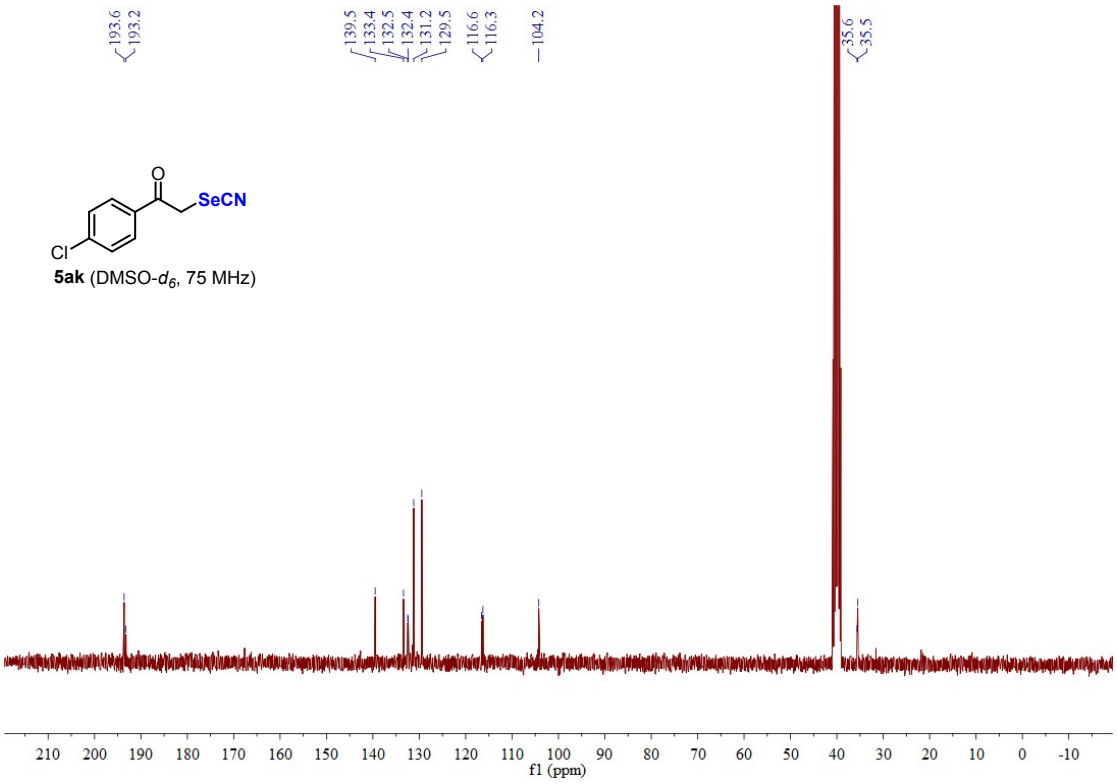
5aj ($CDCl_3$, 300 MHz)



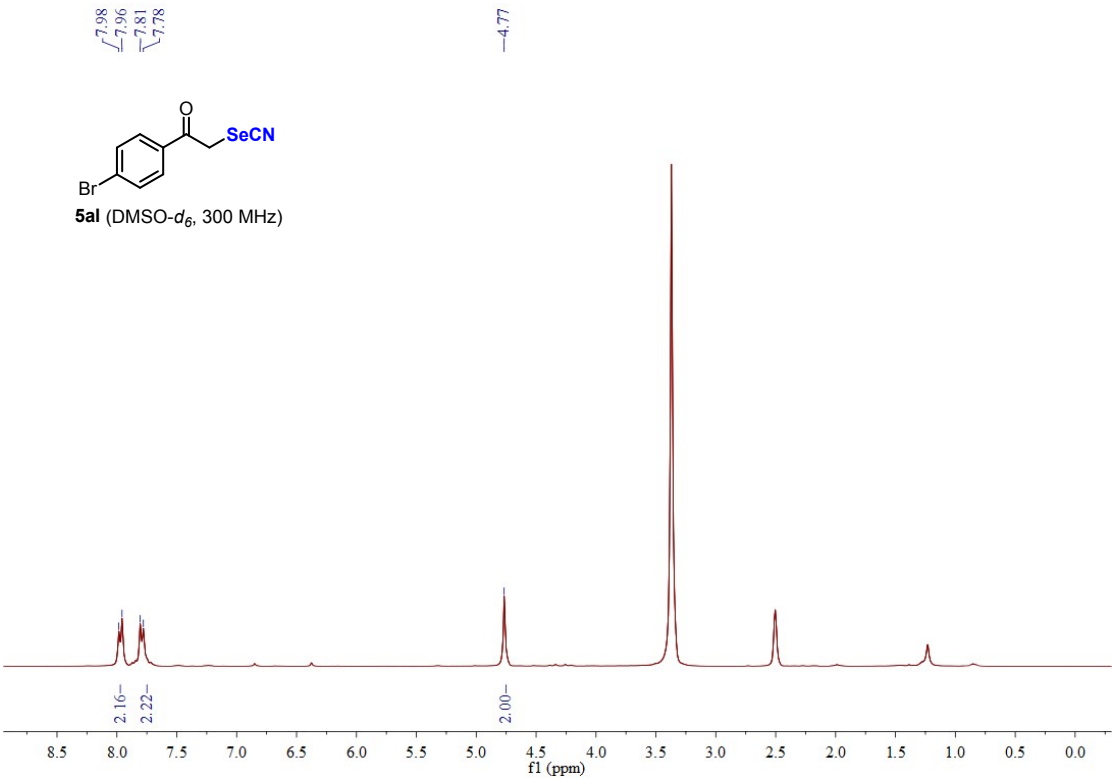
5aj ($CDCl_3$, 75 MHz)



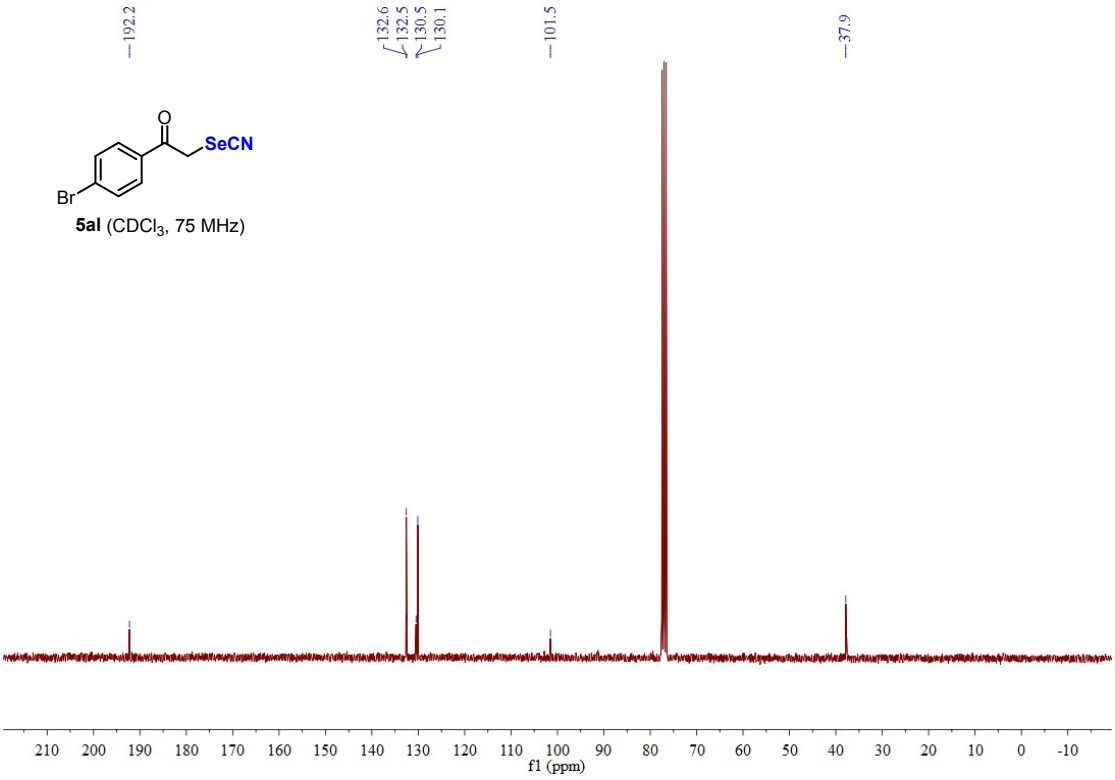
5ak (DMSO-d_6, 300 MHz)



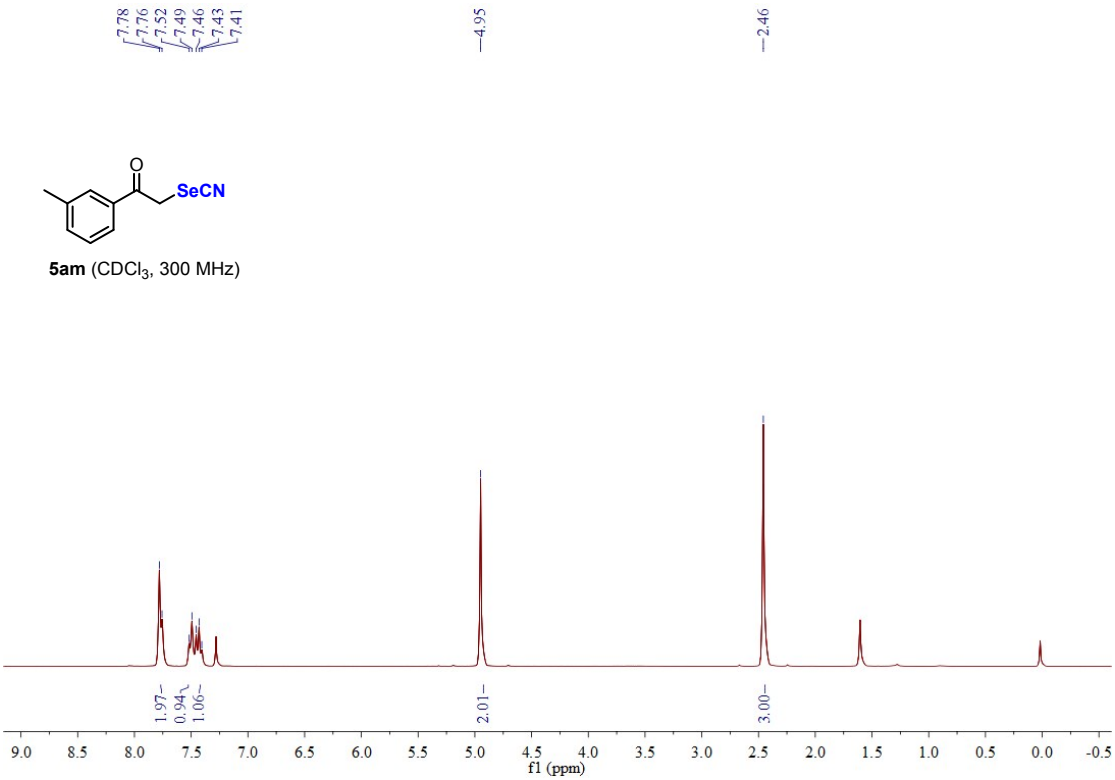
5ak (DMSO-d_6, 75 MHz)



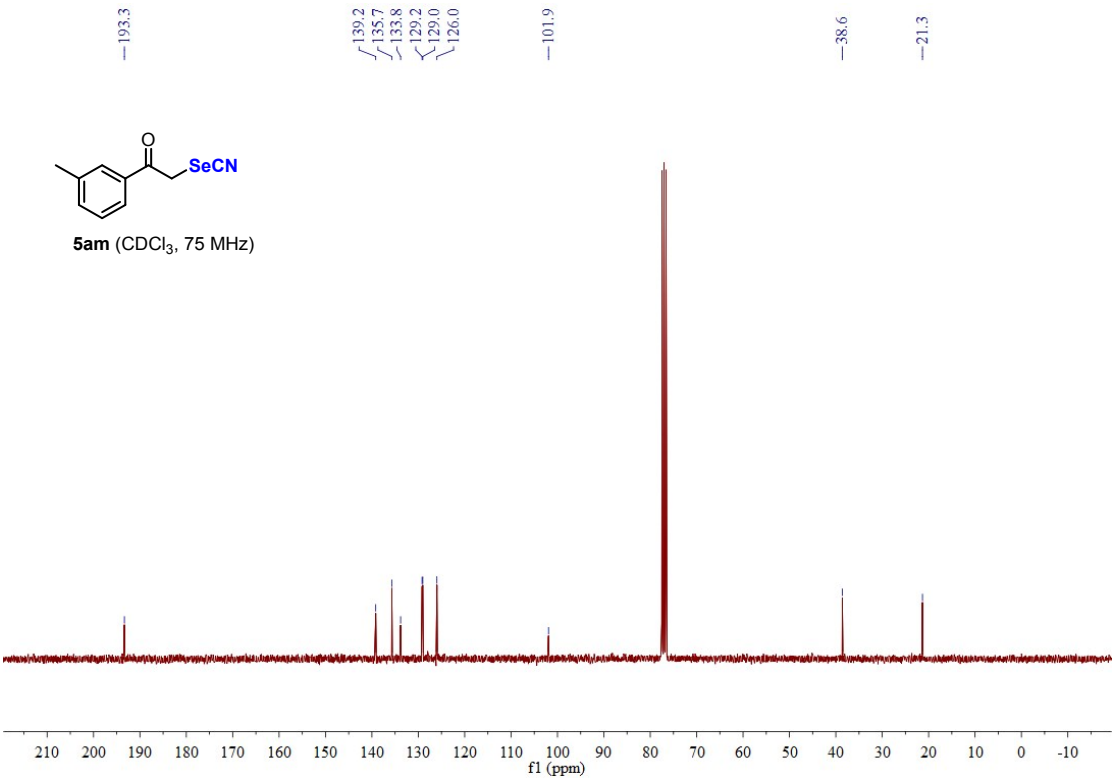
5al (DMSO-d_6, 300 MHz)



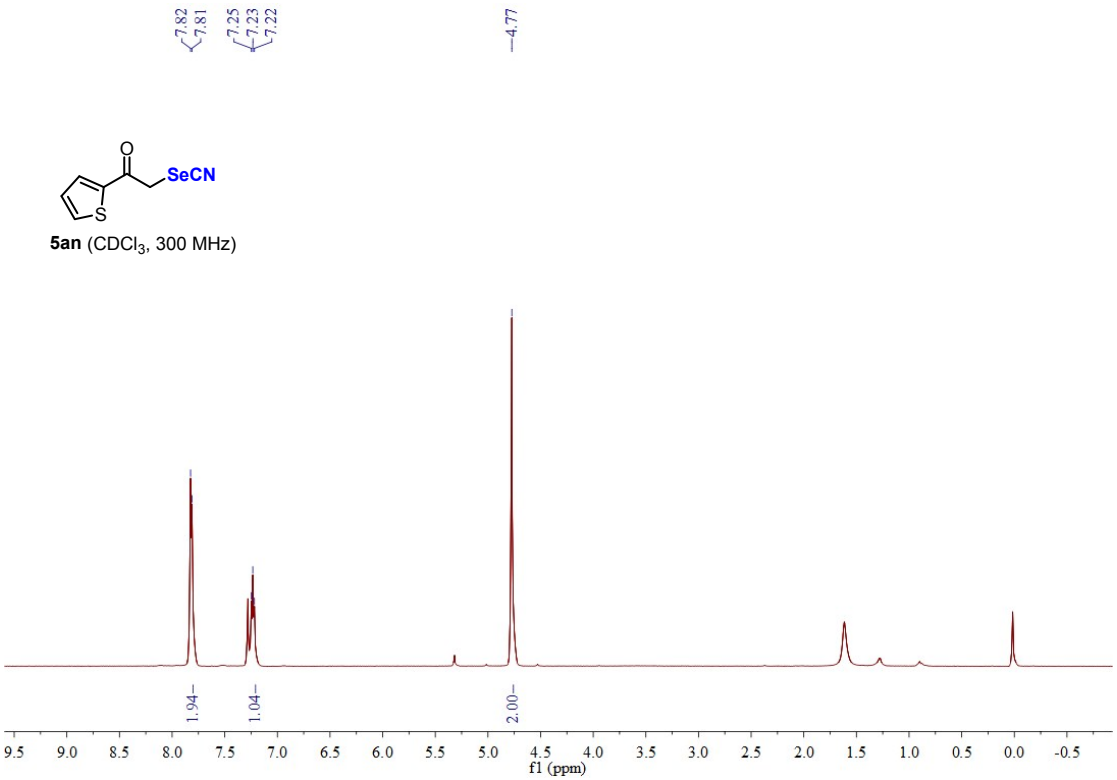
5al ($CDCl_3$, 75 MHz)



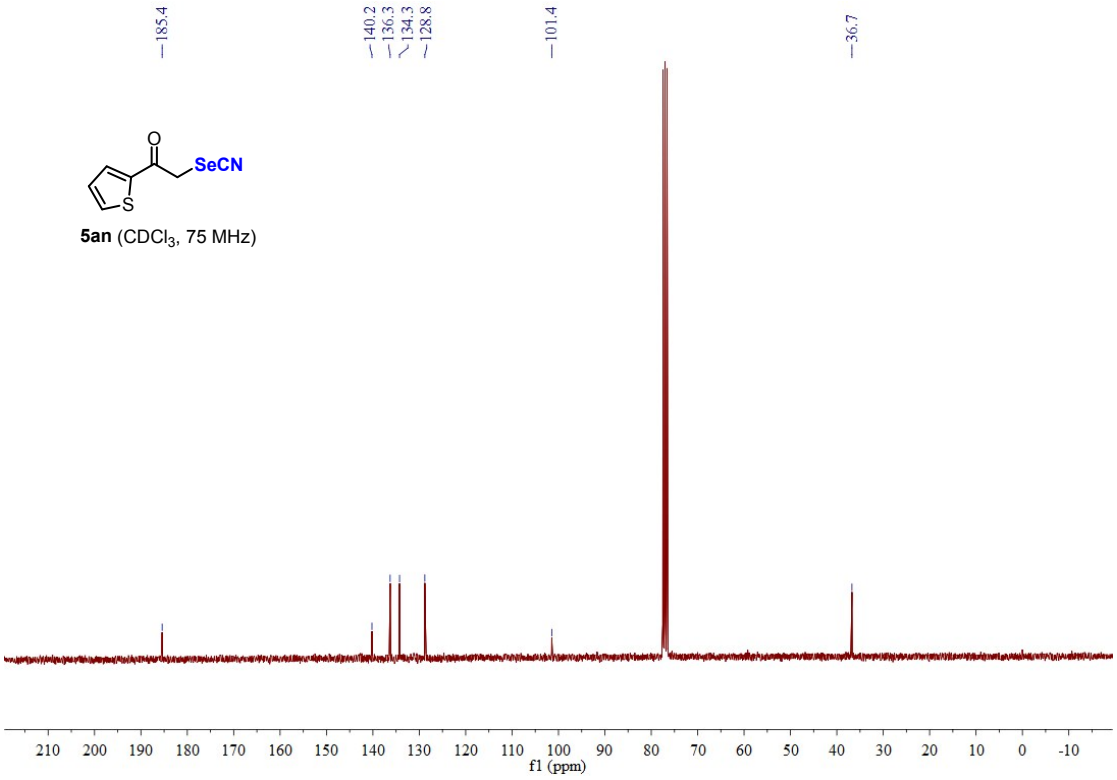
5am ($CDCl_3$, 300 MHz)



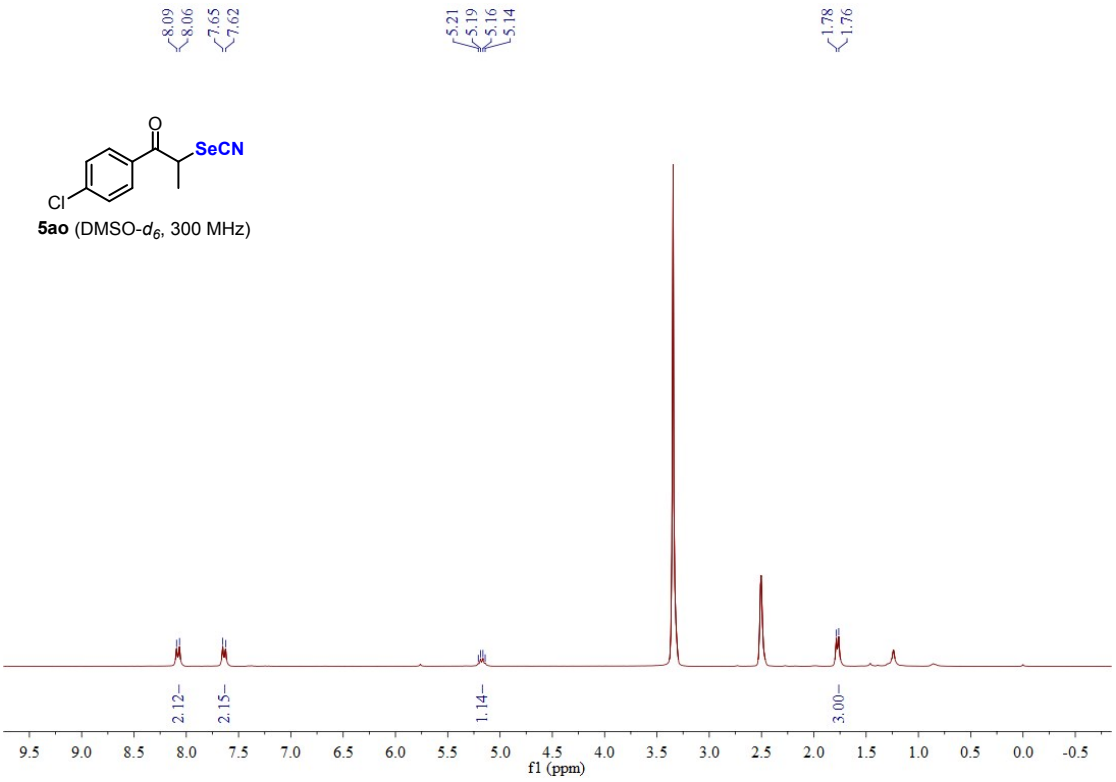
5am ($CDCl_3$, 75 MHz)



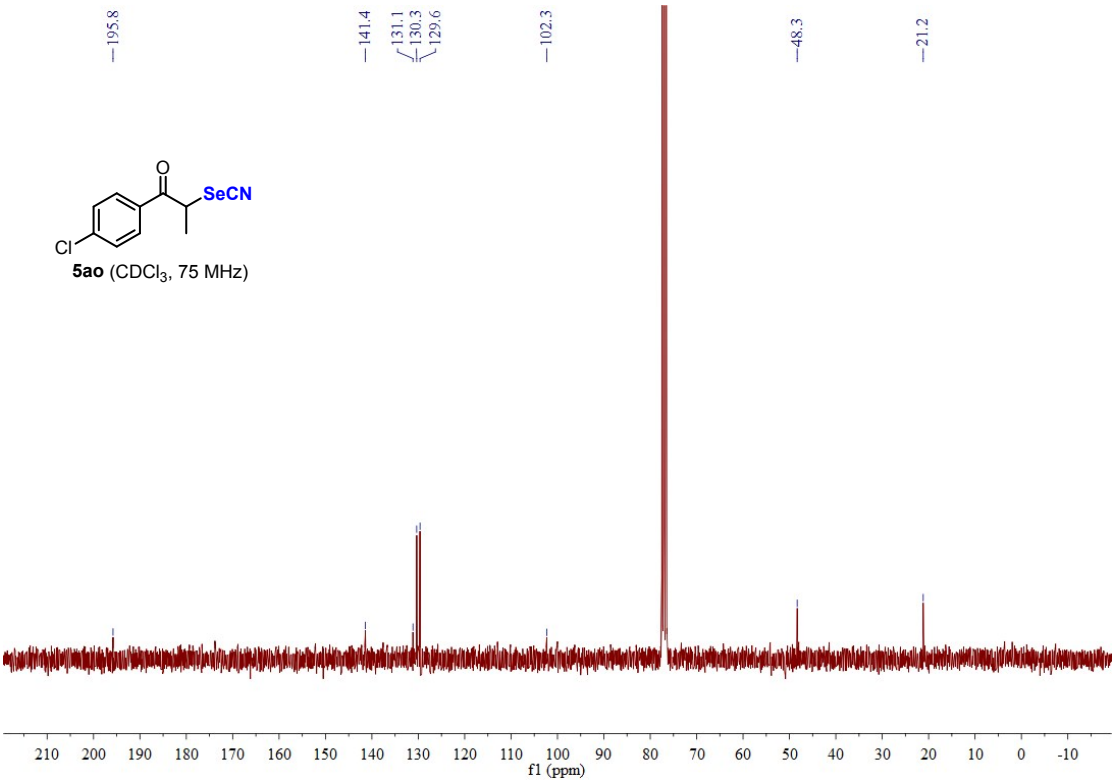
5an ($CDCl_3$, 300 MHz)



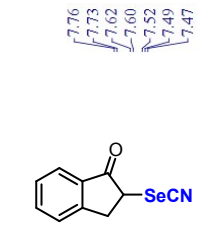
5an ($CDCl_3$, 75 MHz)



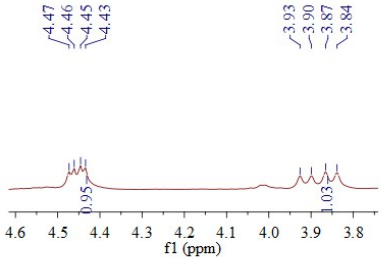
5ao (DMSO-d_6, 300 MHz)

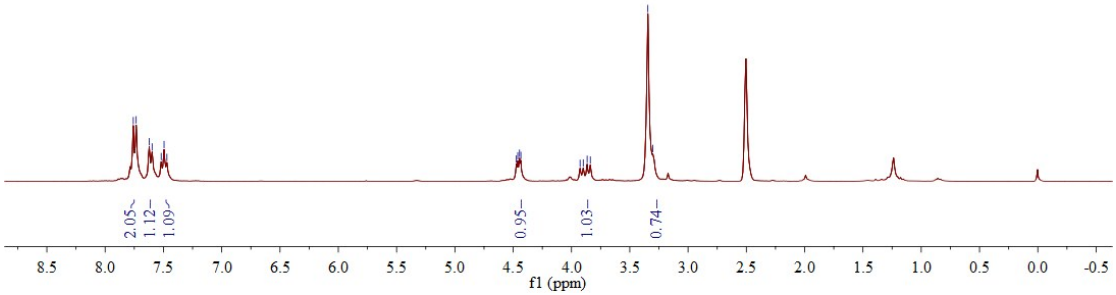


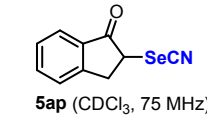
5ao ($CDCl_3$, 75 MHz)



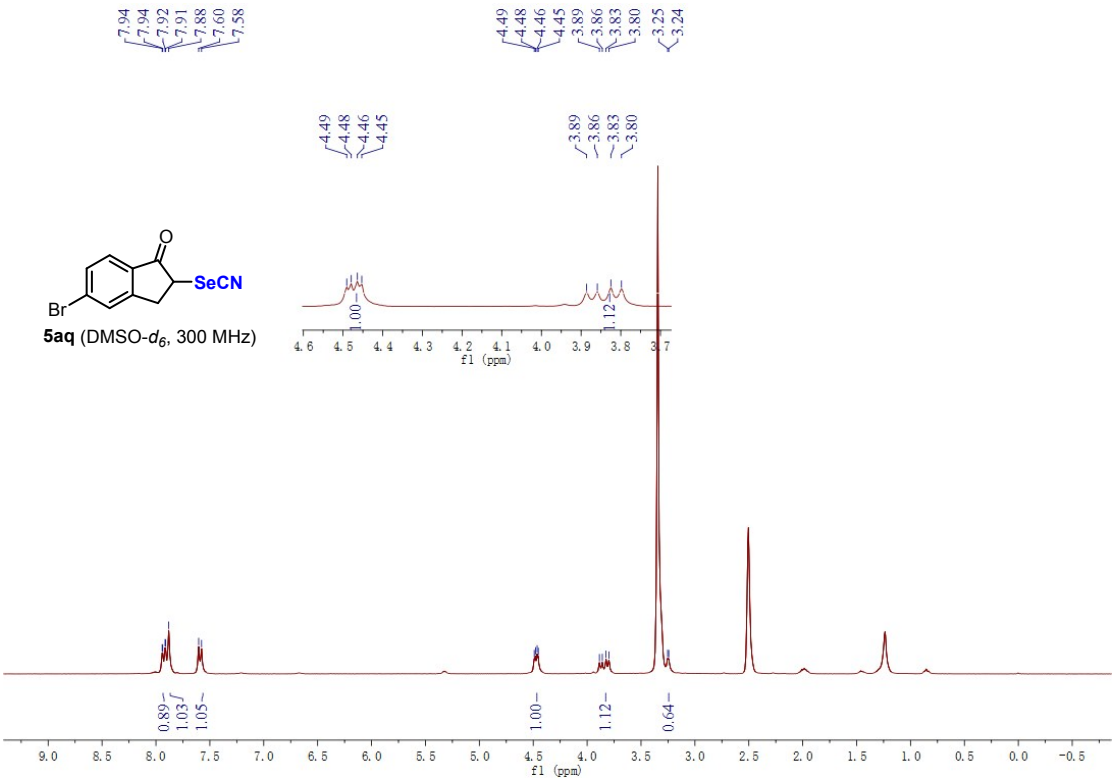
5ap (DMSO-d_6, 300 MHz)



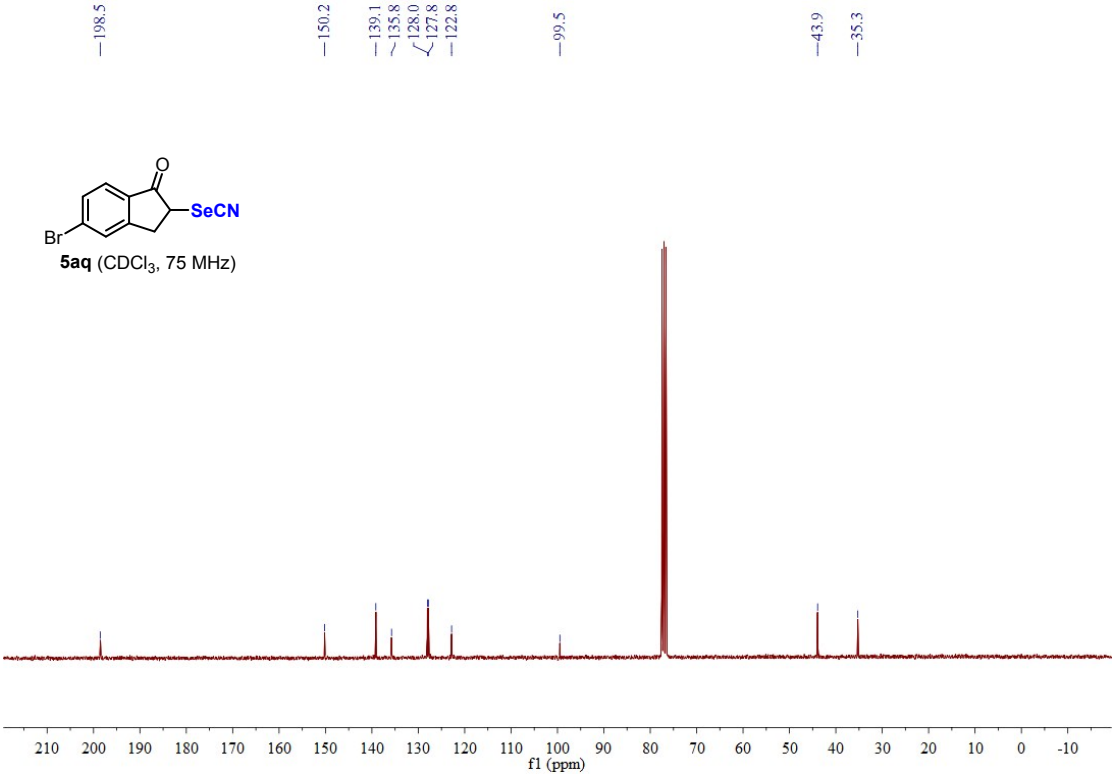




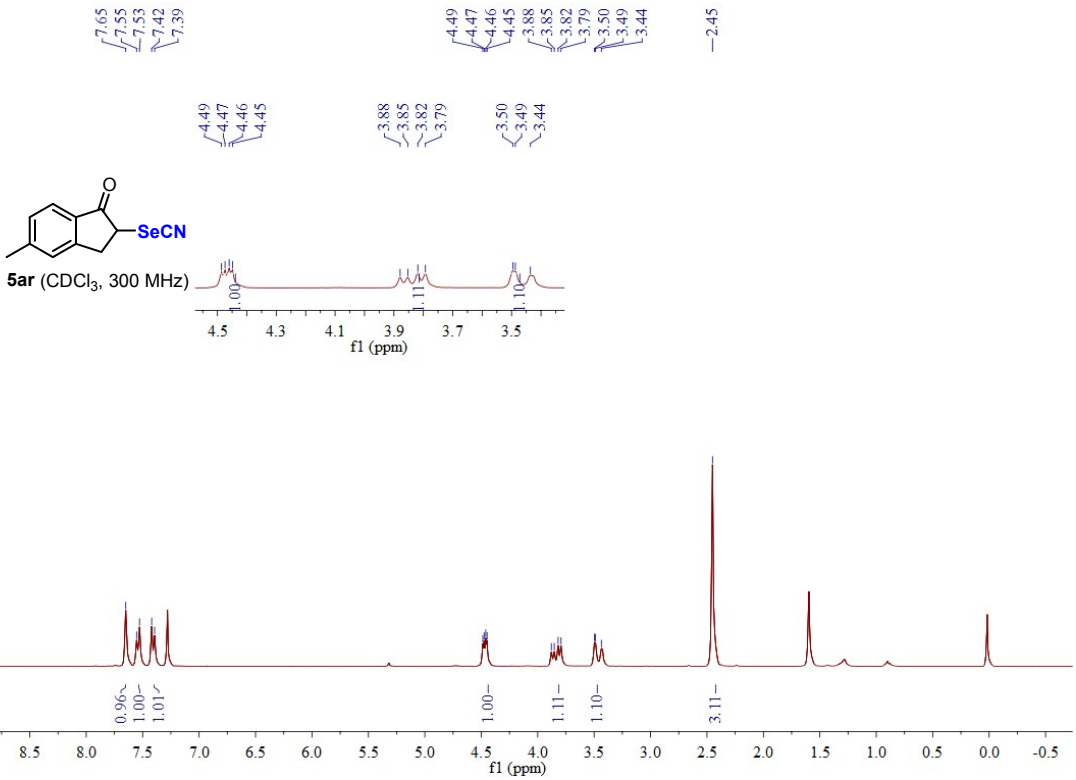
5ap ($CDCl_3$, 75 MHz)

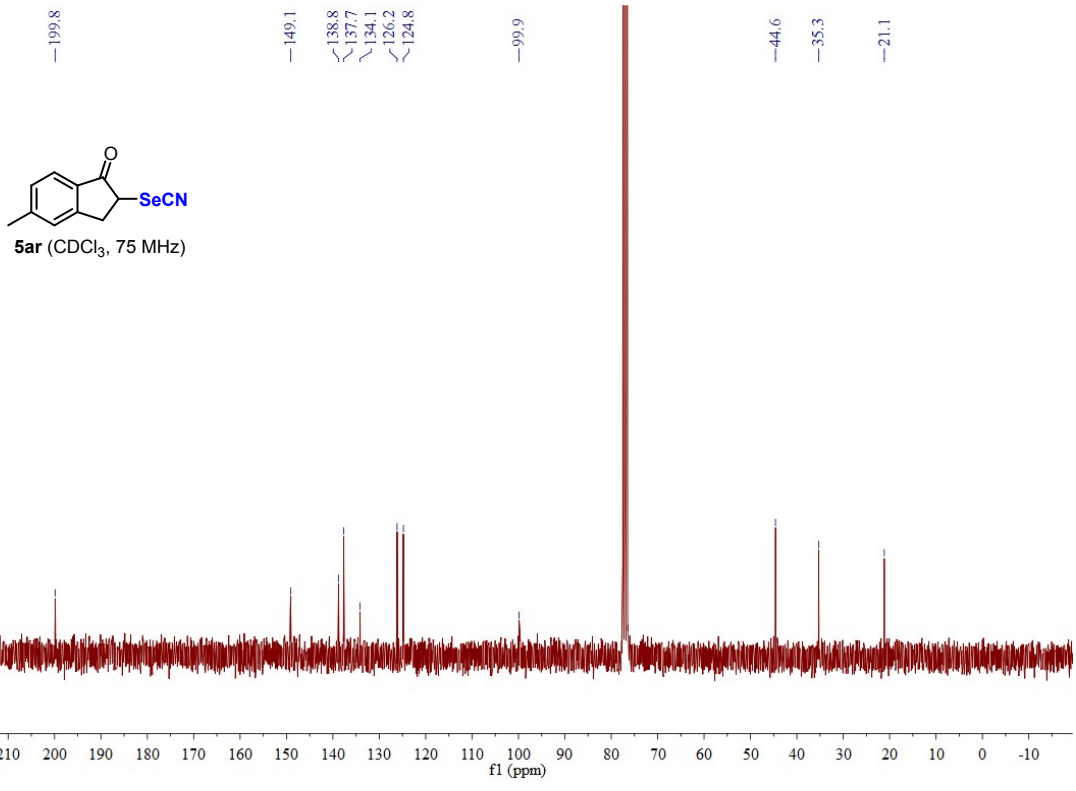


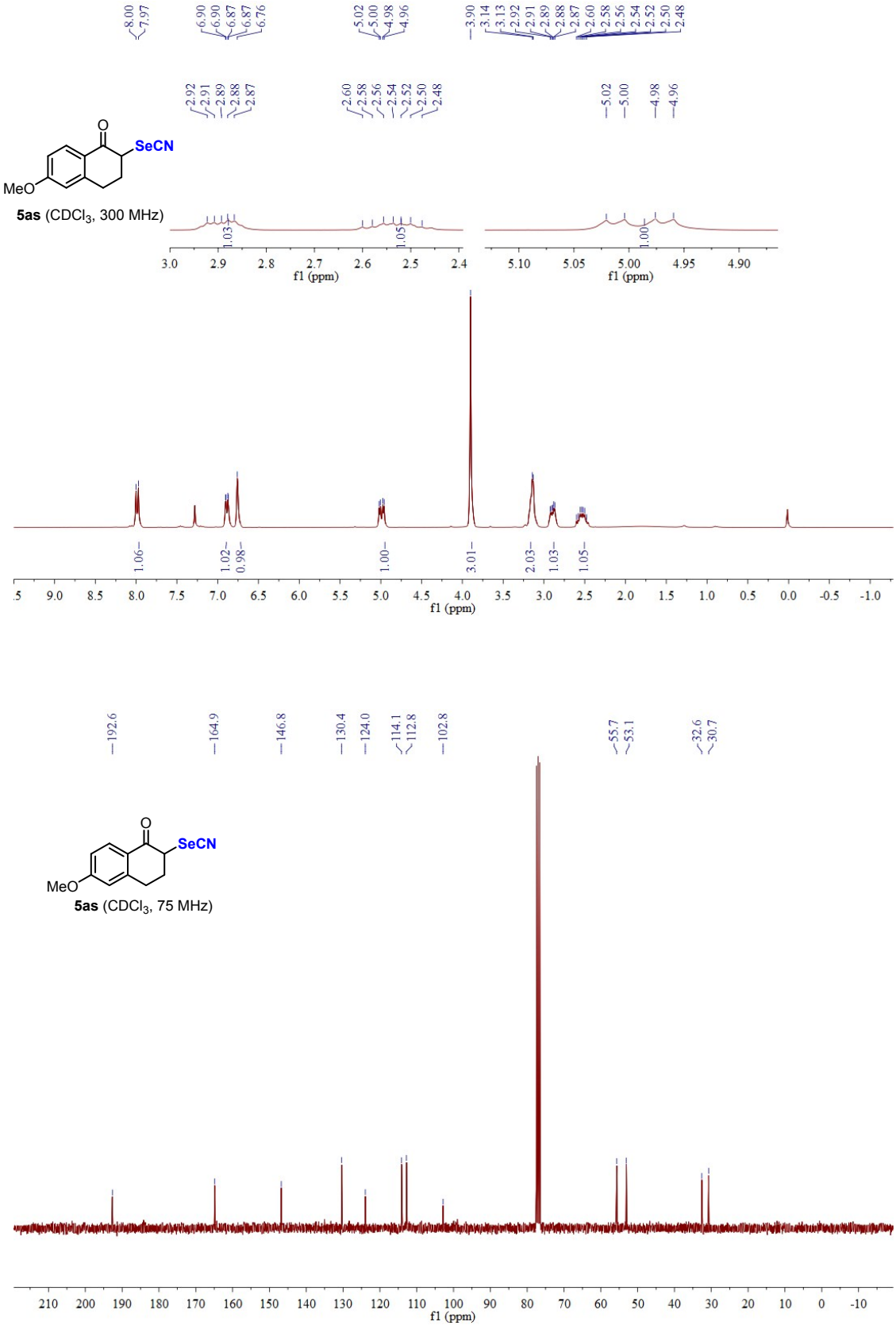
5aq (DMSO-d_6, 300 MHz)

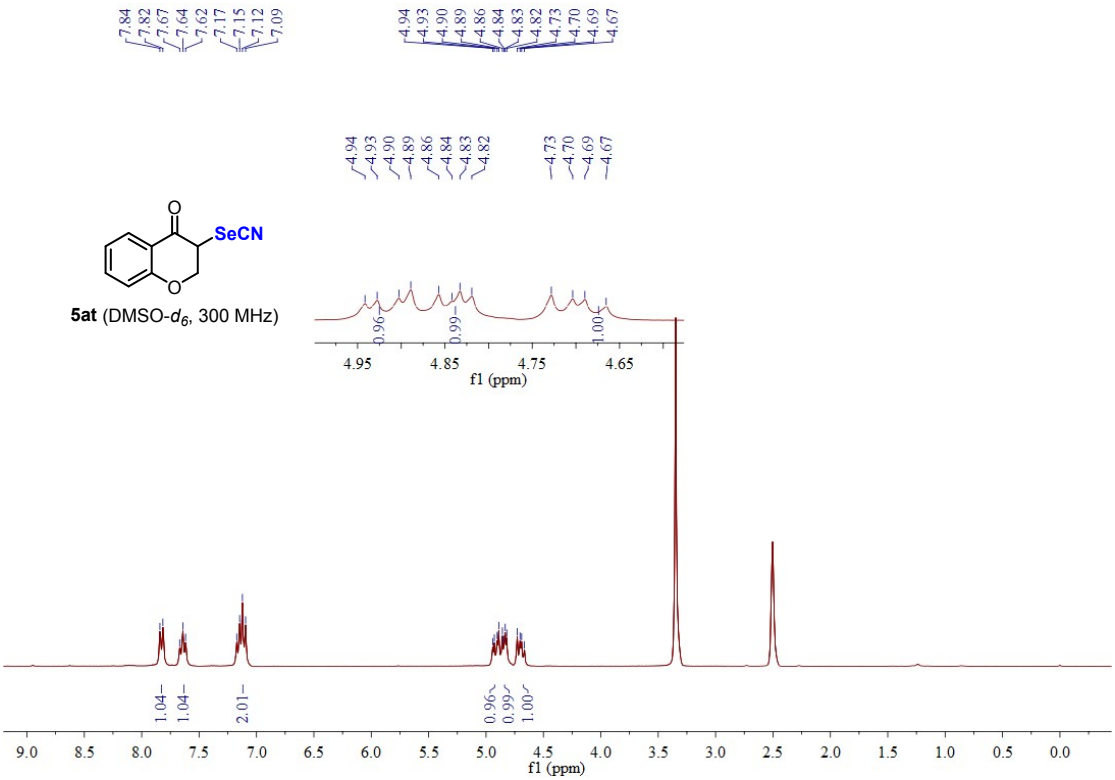


5aq ($CDCl_3$, 75 MHz)

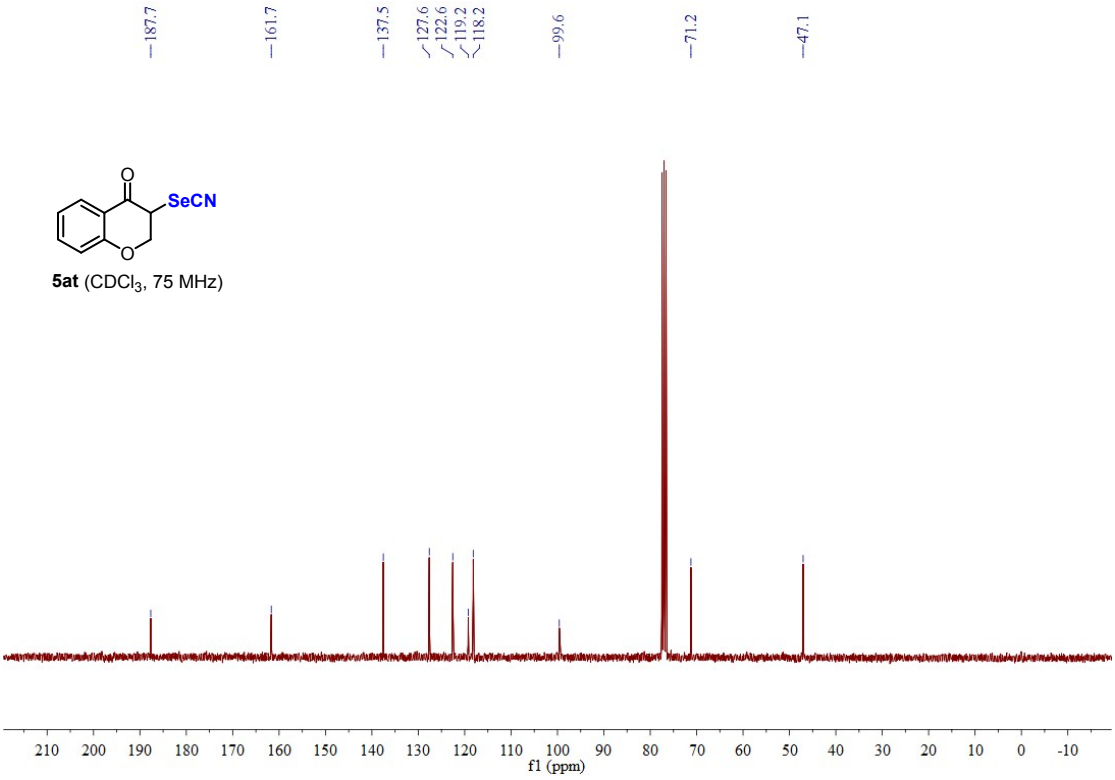

7.65
7.55
7.53
7.42
7.39
4.49
4.47
4.46
4.45
3.88
3.85
3.82
3.79
3.50
3.49
3.44
2.45
SeCN
5ar (CDCl3, 300 MHz)
1.00
1.11
1.10
f1 (ppm)
0.96
1.00
1.01
3.11


199.8
149.1
138.8
137.7
134.1
126.2
124.8
99.9
44.6
35.3
21.1
SeCN
5ar (CDCl3, 75 MHz)
f1 (ppm)

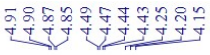

8.00
7.97
6.90
6.90
6.87
6.87
6.76
5.02
5.00
4.98
4.96
3.90
3.14
3.13
2.92
2.91
2.89
2.88
2.87
2.60
2.58
2.56
2.54
2.52
2.50
2.48
O
SeCN
MeO
5as (CDCl3, 300 MHz)
1.03
1.05
1.00
f1 (ppm)
1.06
1.02
0.98
1.00
3.01
2.03
1.03
1.05
f1 (ppm)
192.6
164.9
146.8
130.4
124.0
114.1
112.8
102.8
55.7
53.1
32.6
30.7
O
SeCN
MeO
5as (CDCl3, 75 MHz)
f1 (ppm)

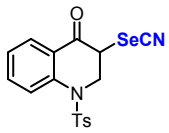


5at (DMSO-d_6, 300 MHz)

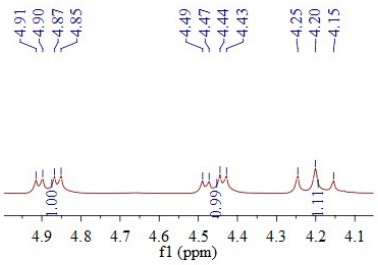


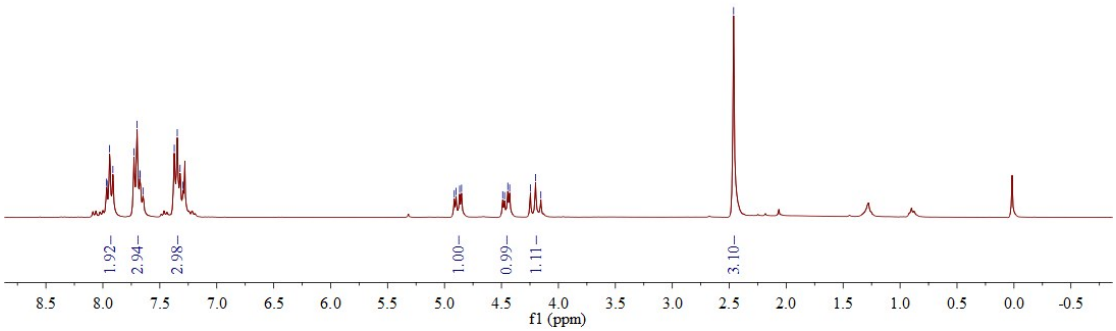
5at ($CDCl_3$, 75 MHz)

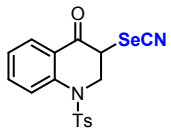




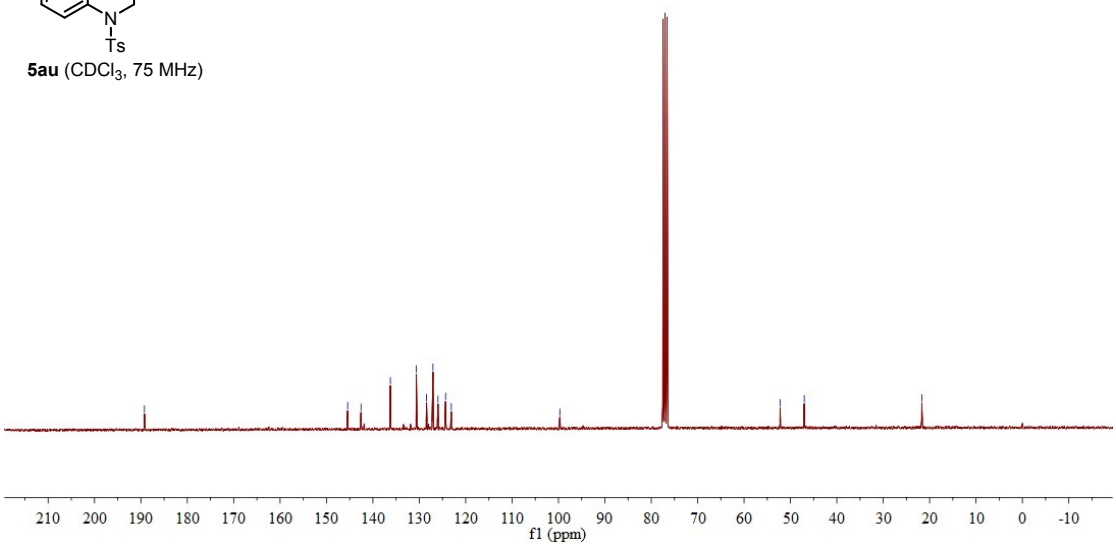
5au ($CDCl_3$, 300 MHz)

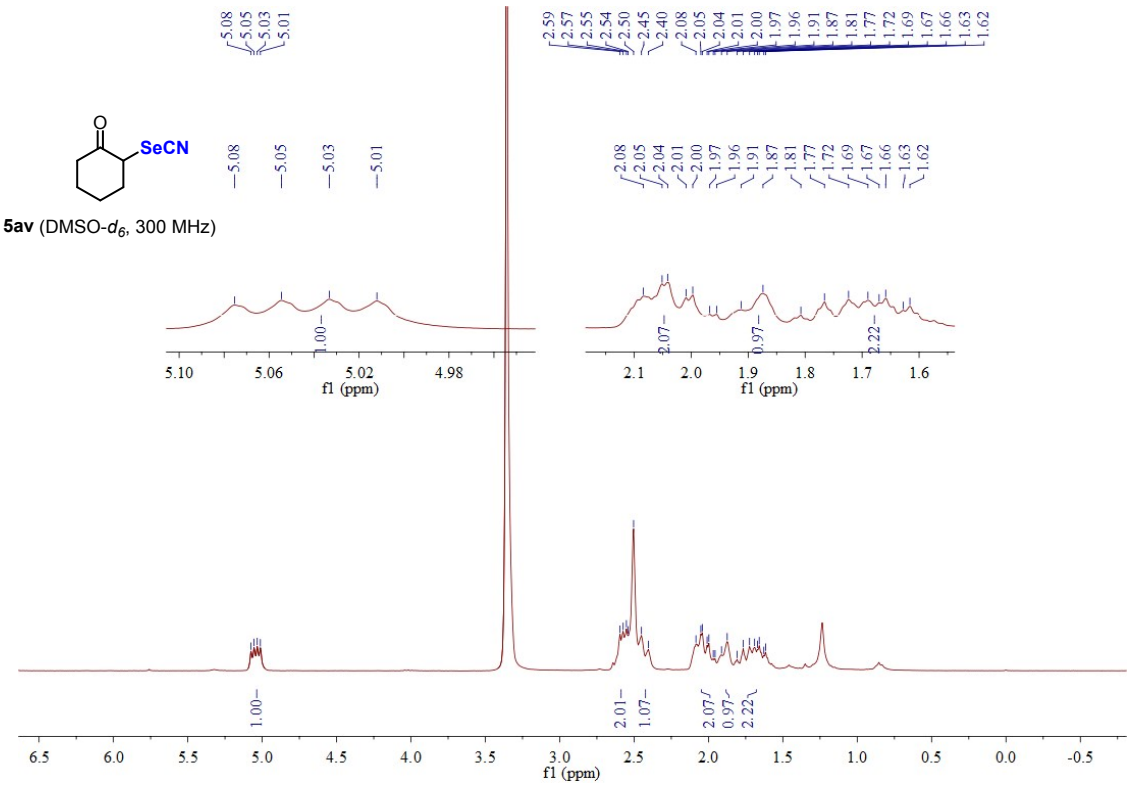




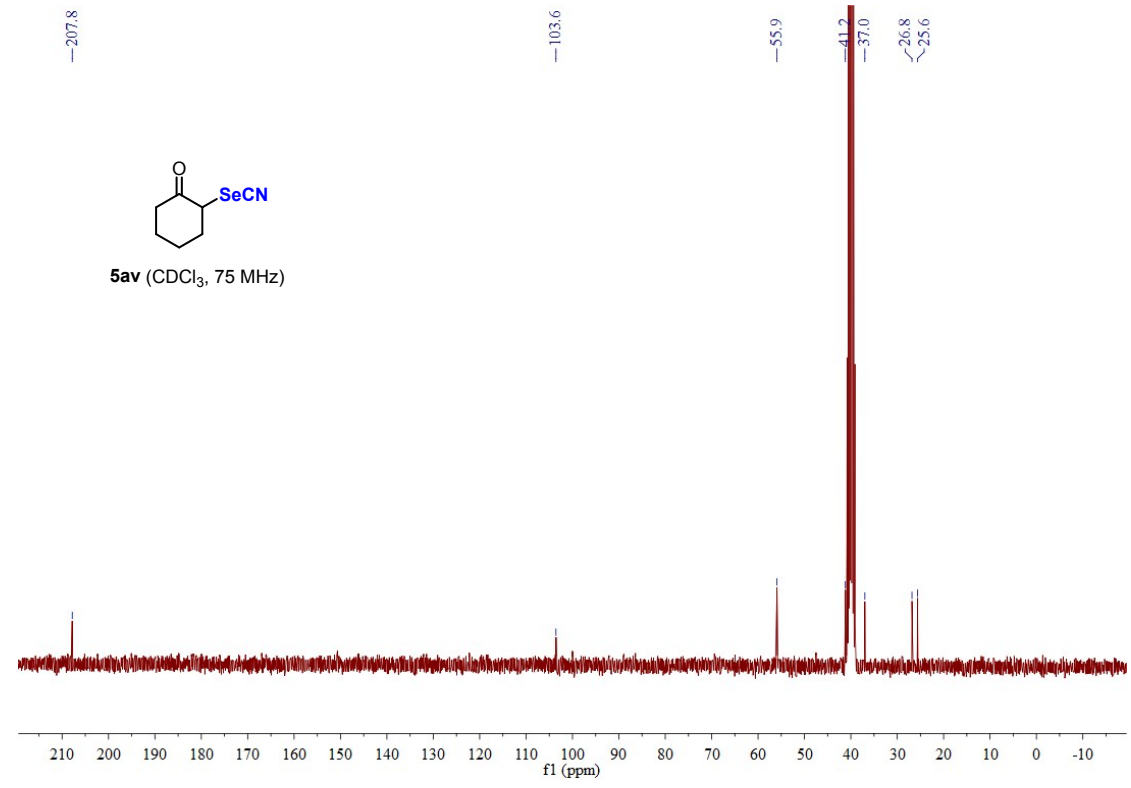


5au ($CDCl_3$, 75 MHz)

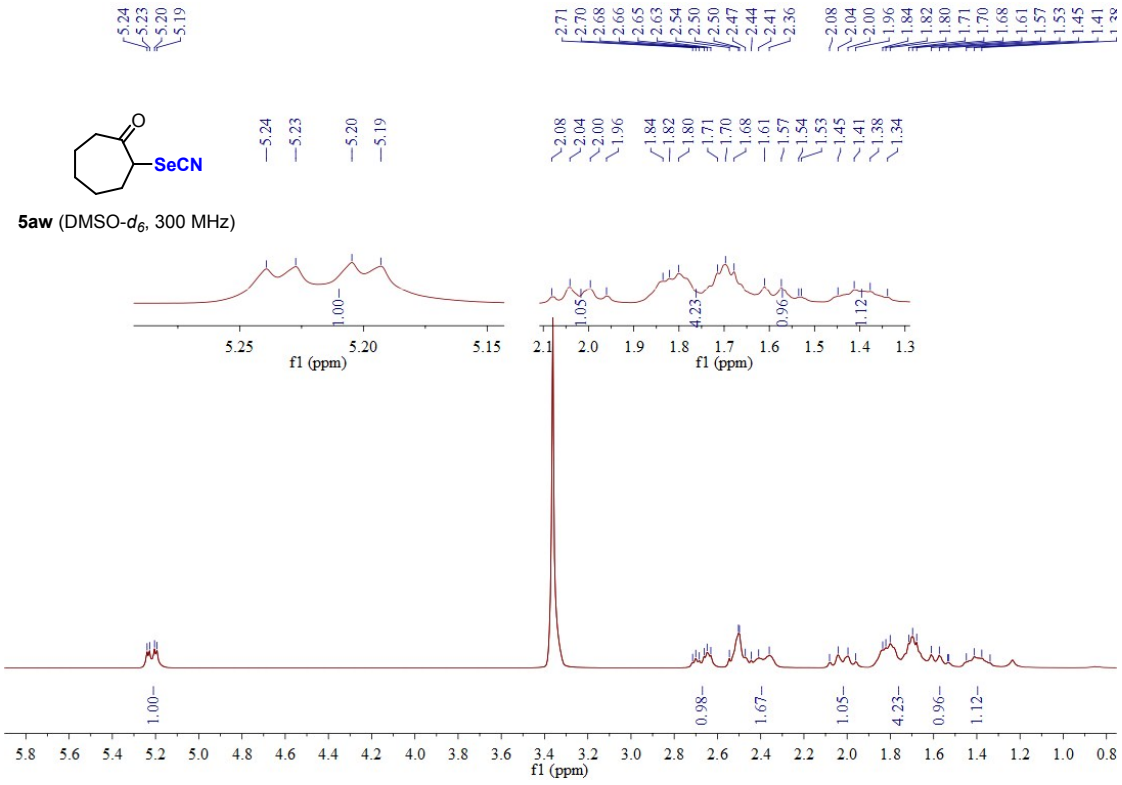




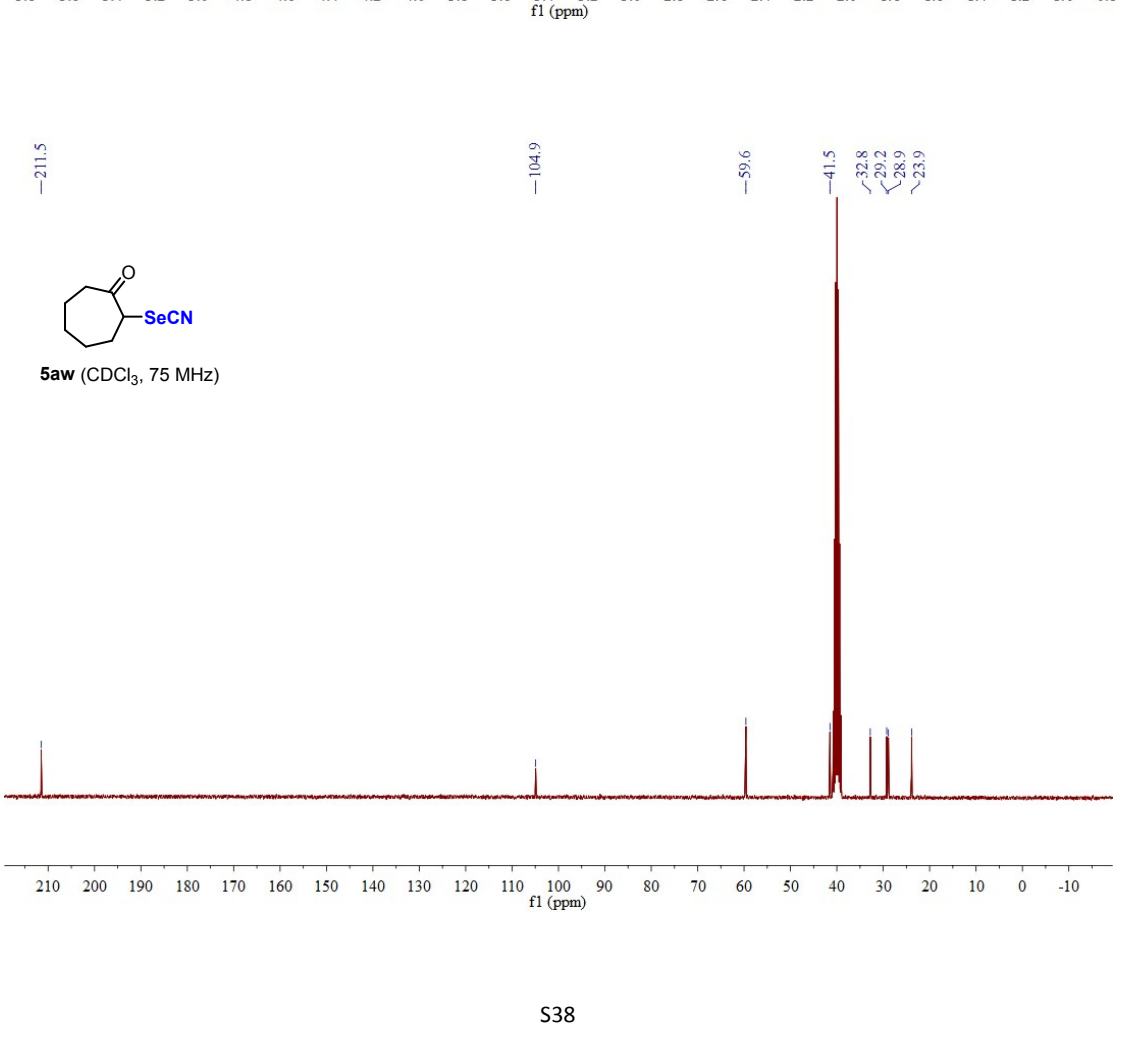
5av (DMSO-d_6, 300 MHz)



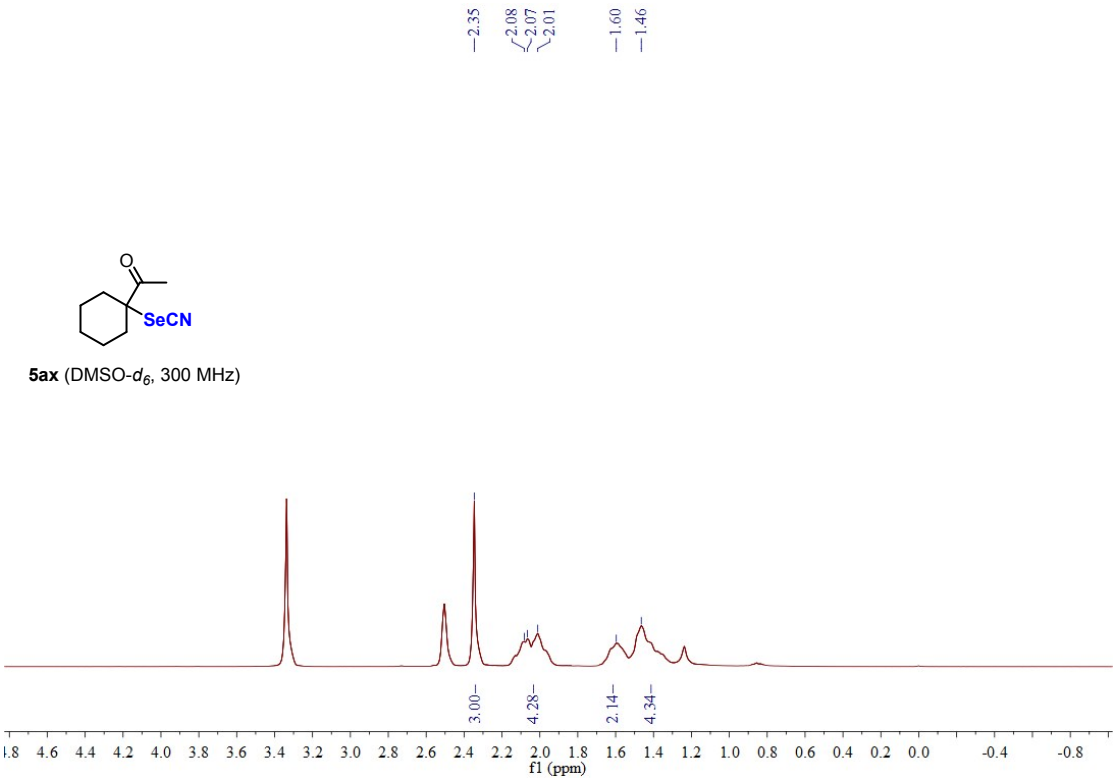
5av ($CDCl_3$, 75 MHz)



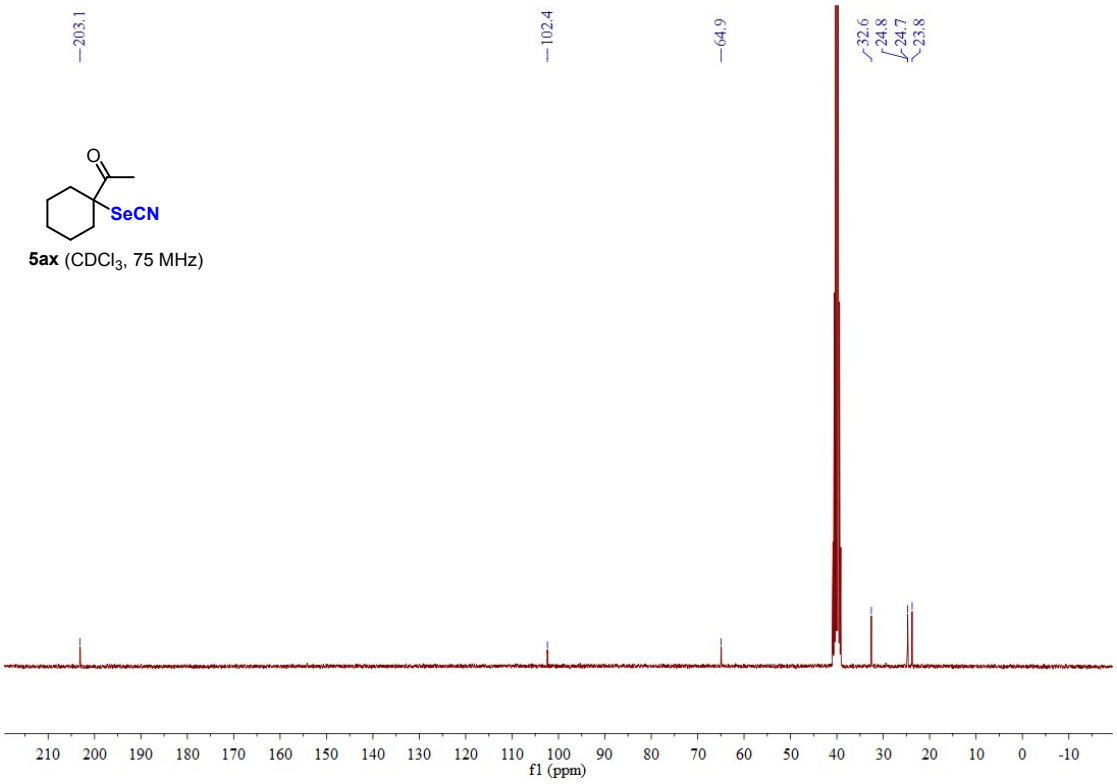
5aw (DMSO-d_6, 300 MHz)



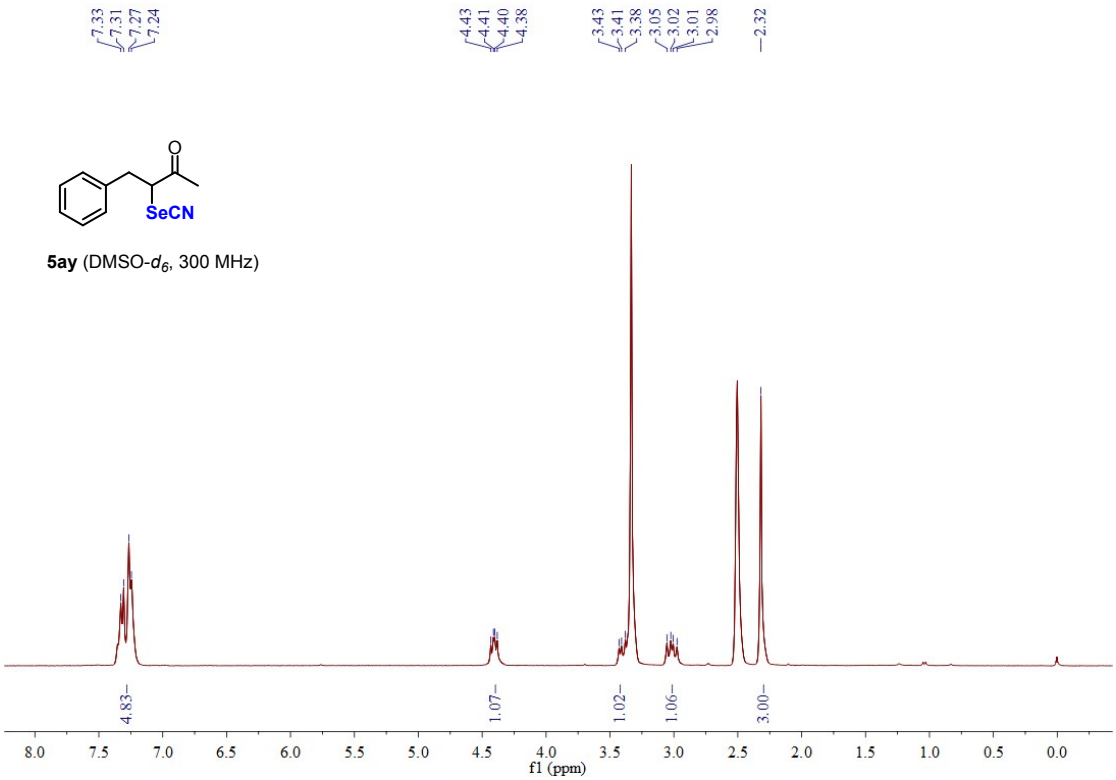
5aw ($CDCl_3$, 75 MHz)



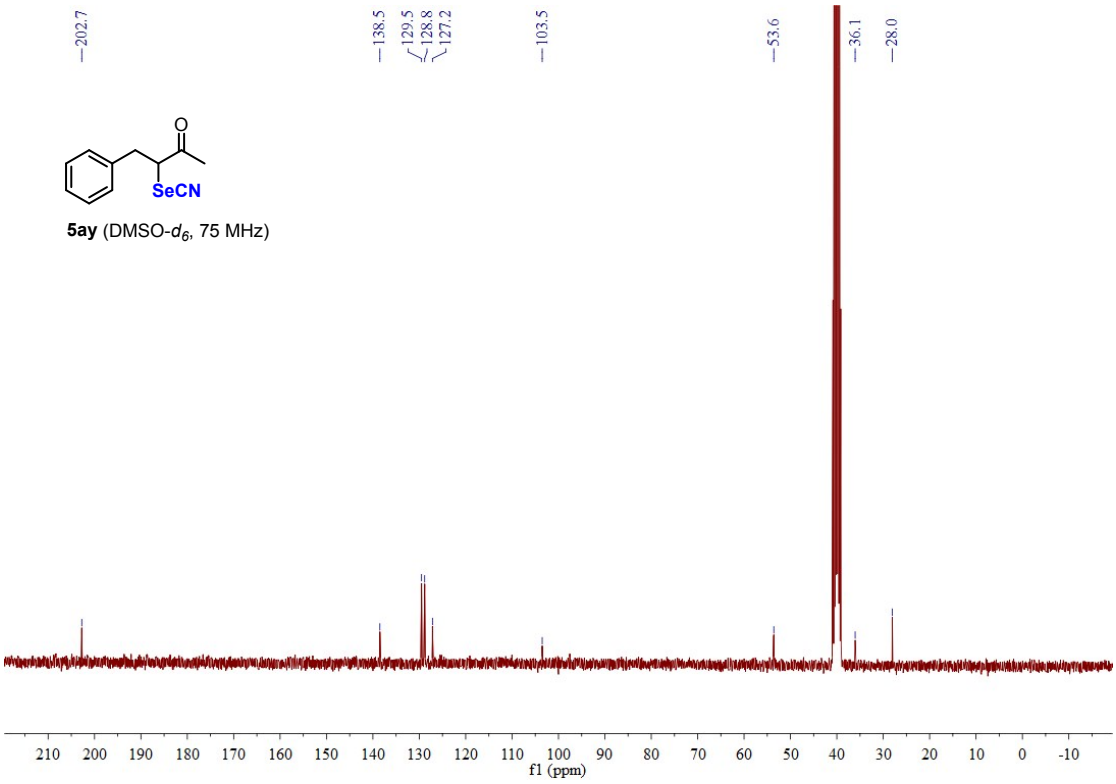
5ax (DMSO-d_6, 300 MHz)



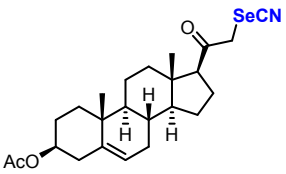
5ax ($CDCl_3$, 75 MHz)



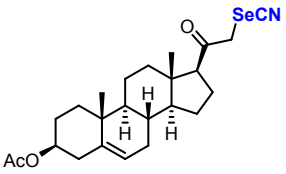
5ay (DMSO-d_6, 300 MHz)



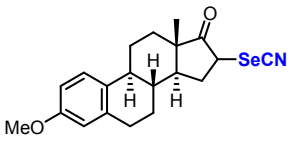
5ay (DMSO-d_6, 75 MHz)



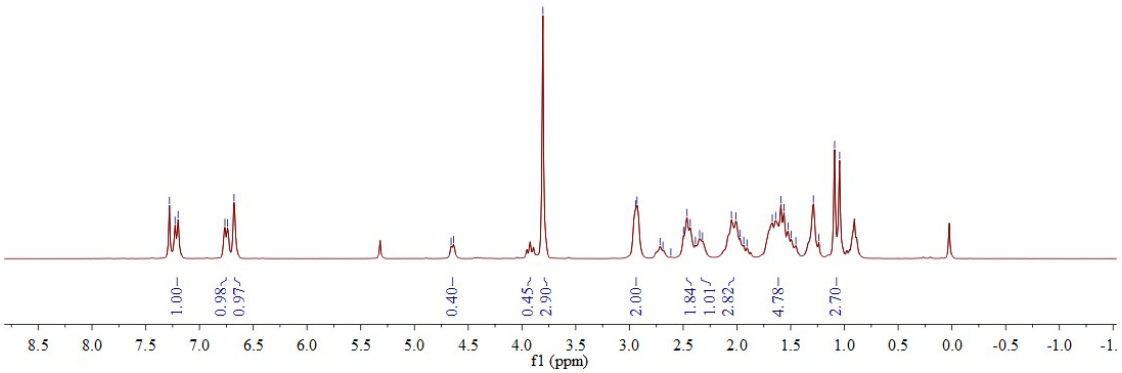
5az ($CDCl_3$, 300 MHz)

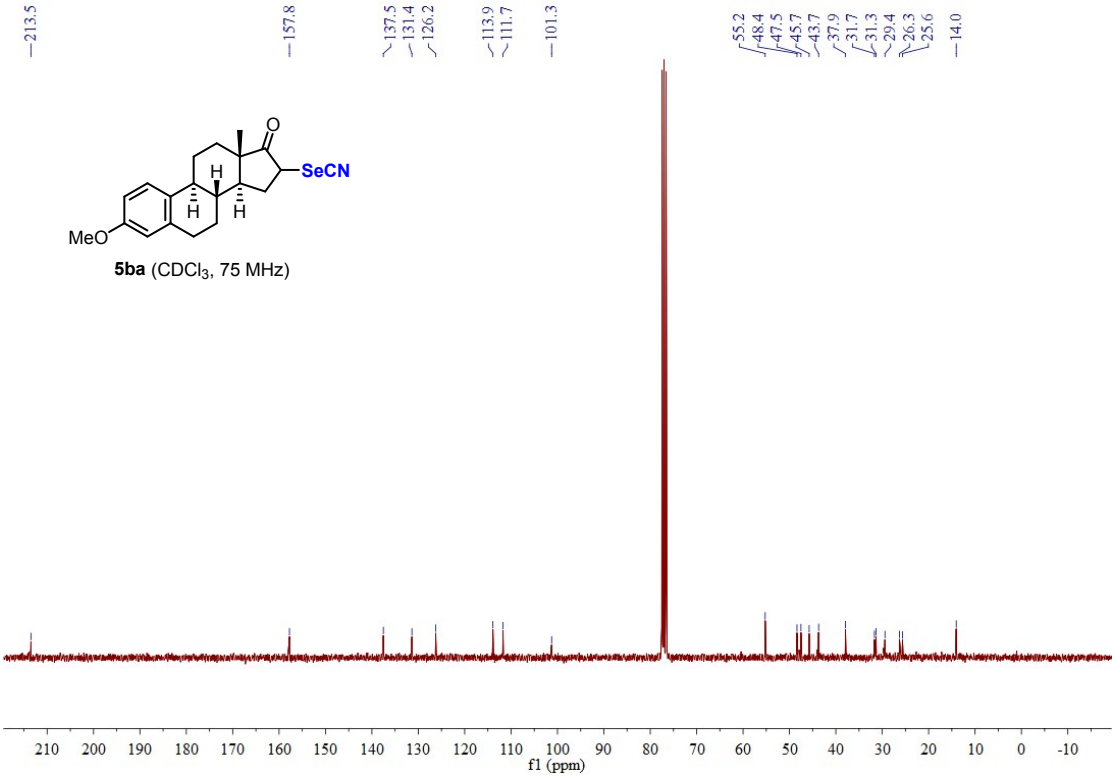


5az ($CDCl_3$, 75 MHz)

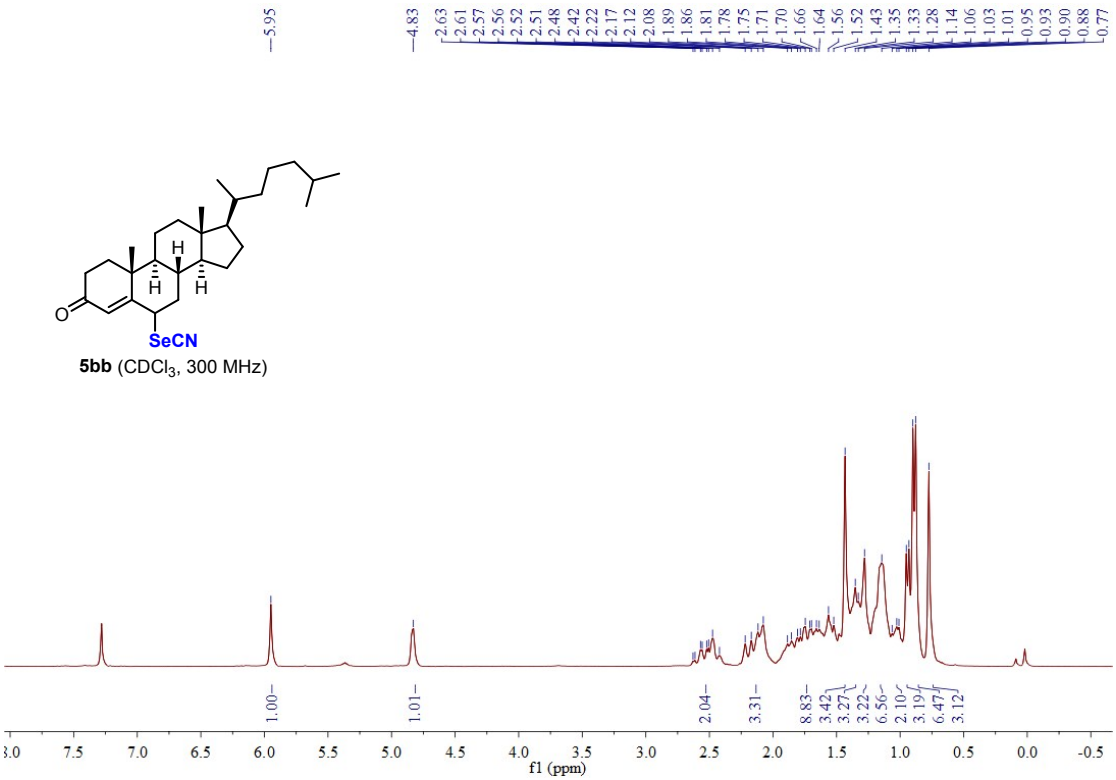


5ba ($CDCl_3$, 300 MHz)

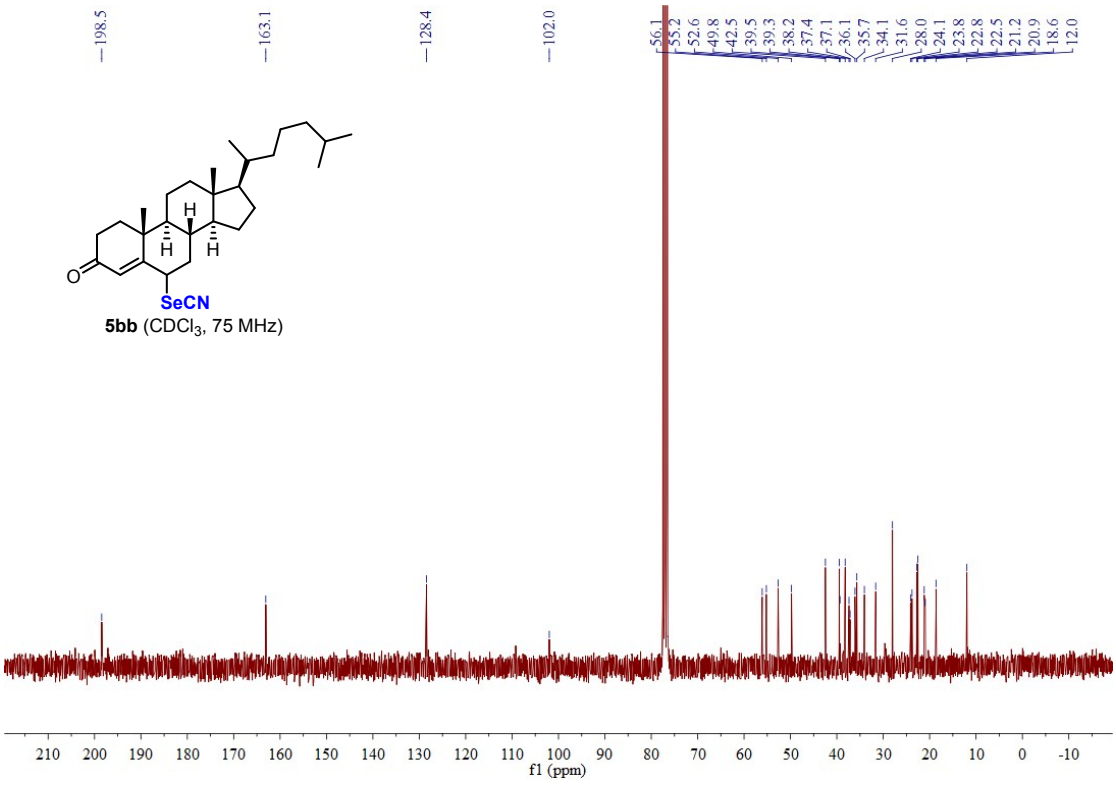




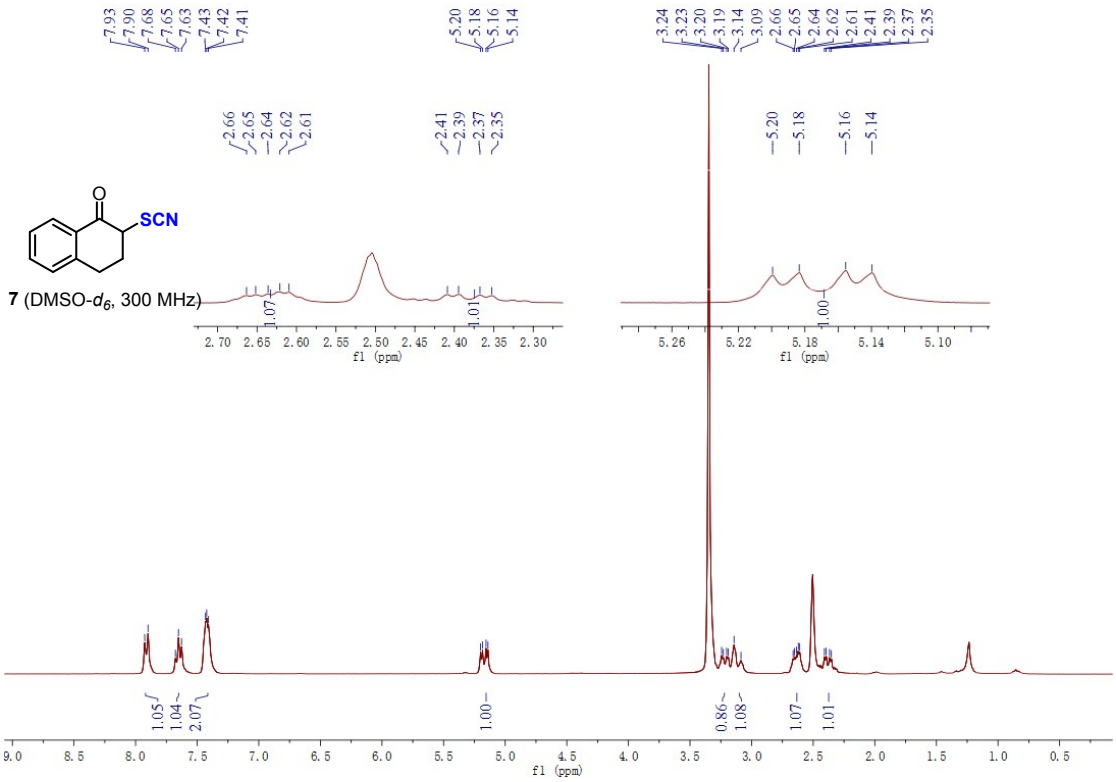
5ba ($CDCl_3$, 75 MHz)



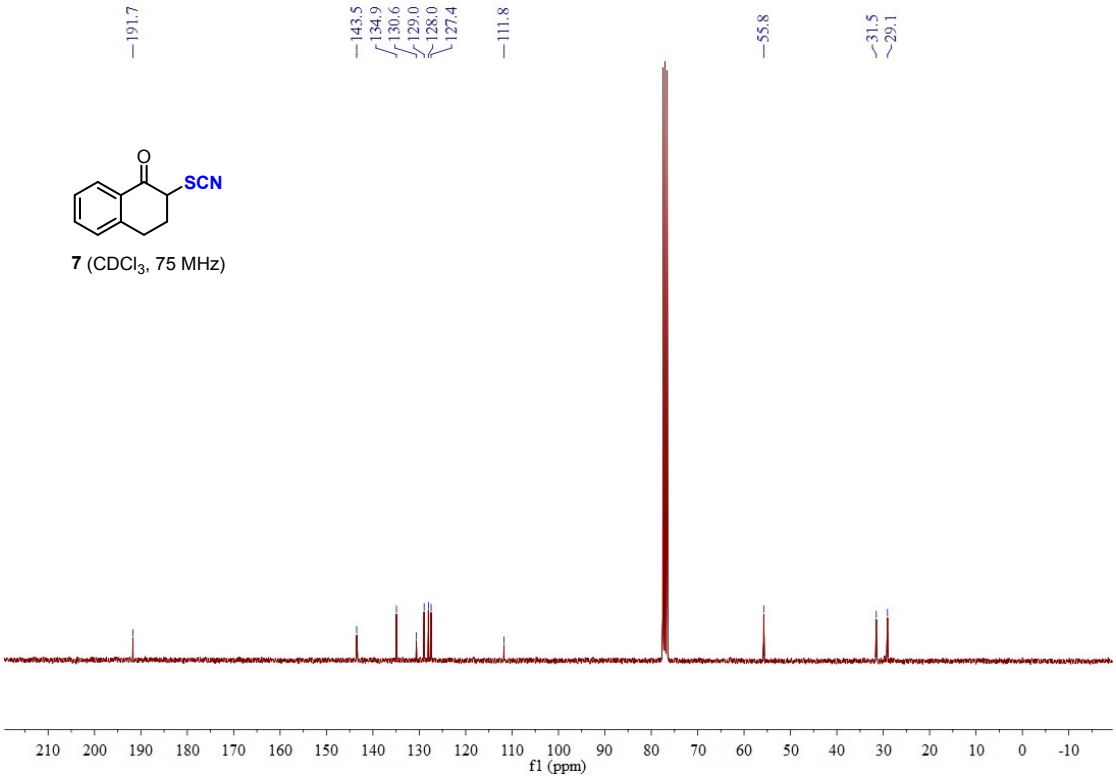
5bb ($CDCl_3$, 300 MHz)



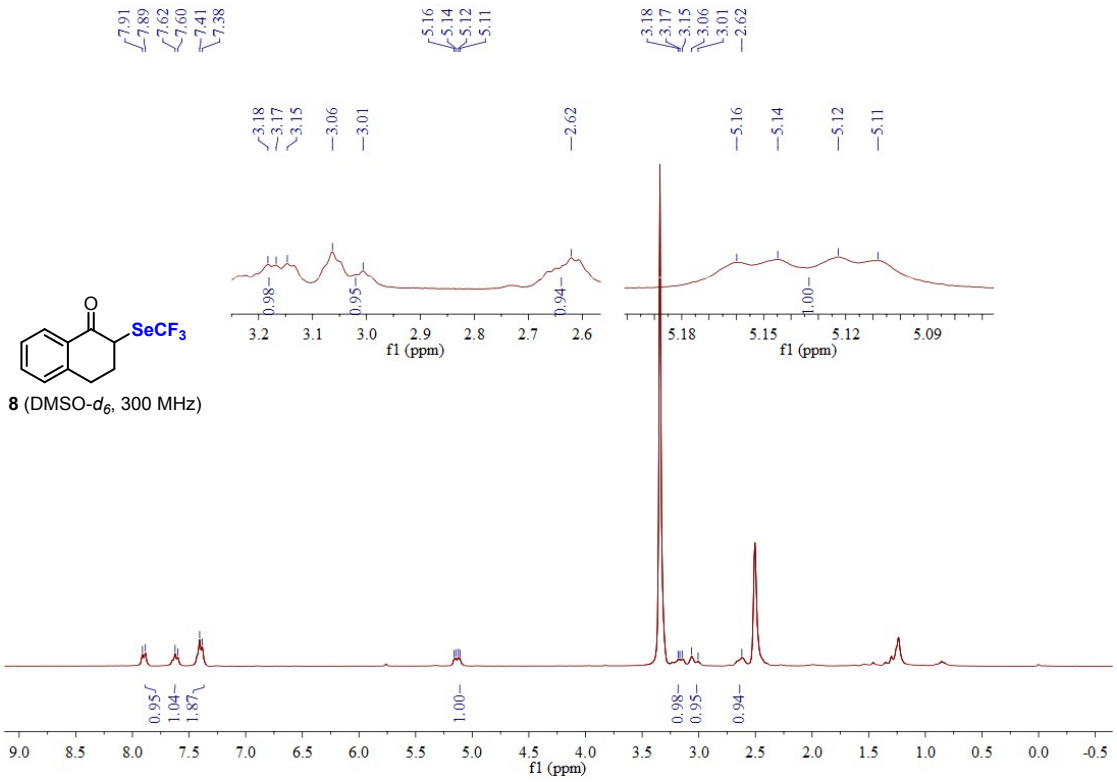
5bb ($CDCl_3$, 75 MHz)



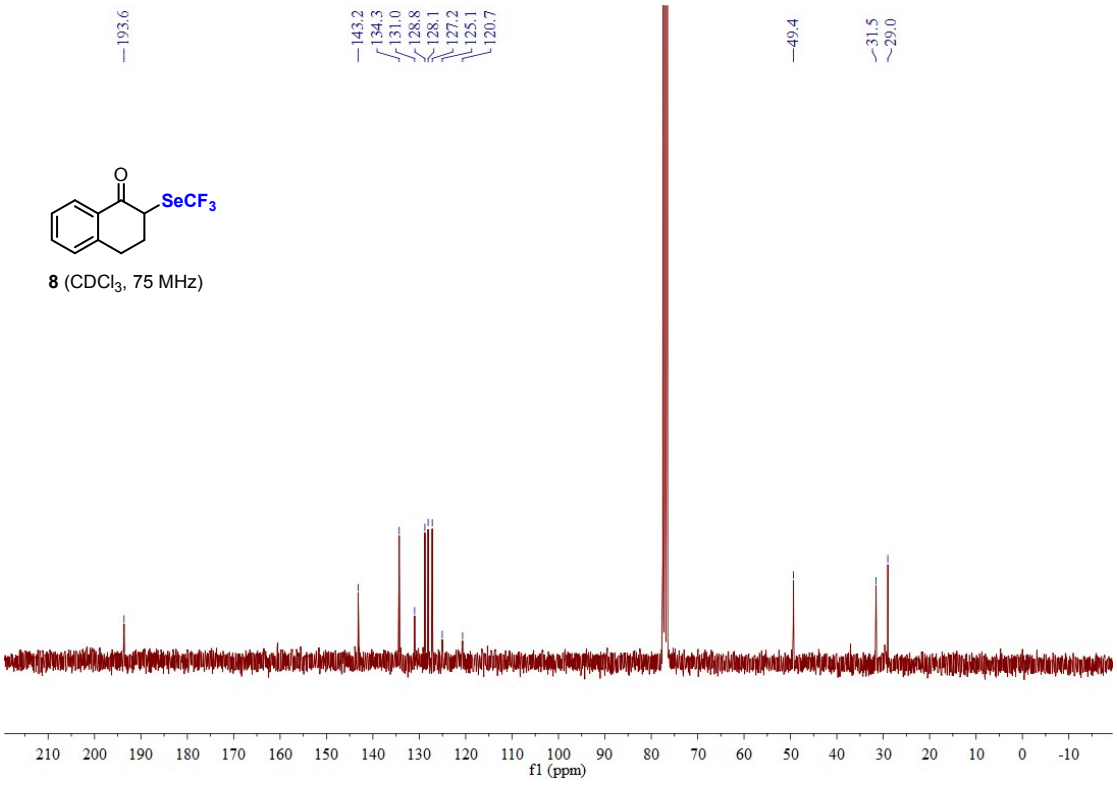
7 (DMSO-d_6, 300 MHz)



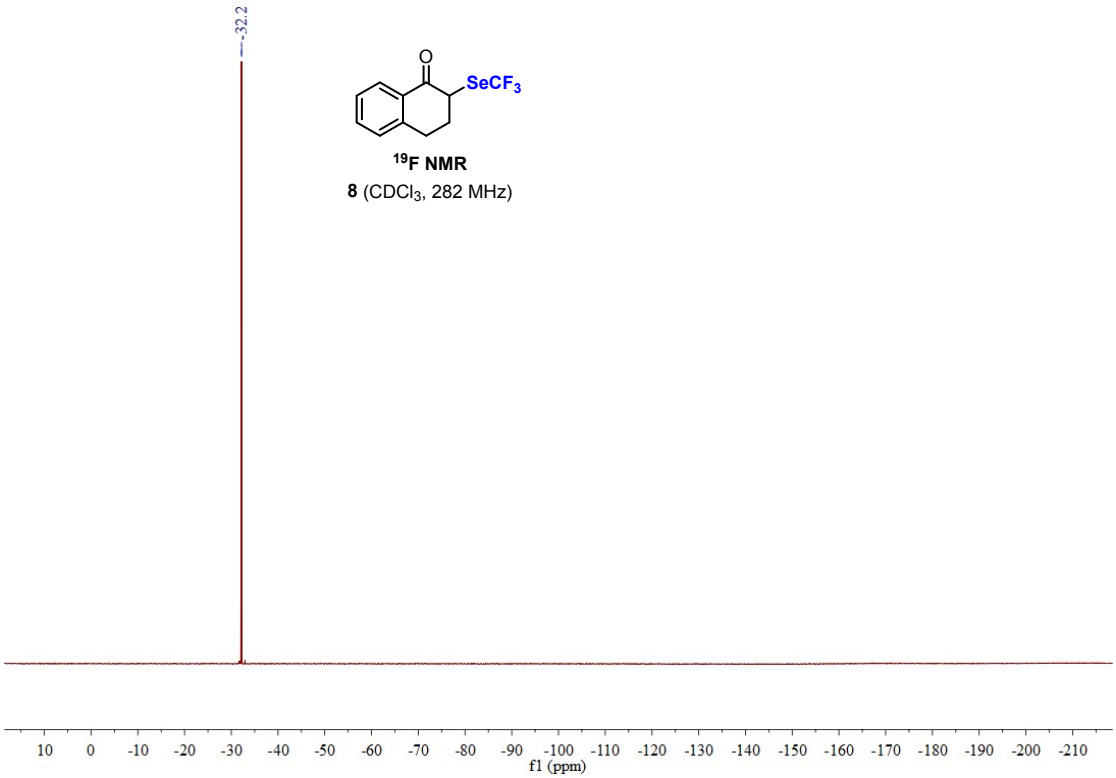
7 ($CDCl_3$, 75 MHz)



8 (DMSO-d_6, 300 MHz)



8 ($CDCl_3$, 75 MHz)



^{19}F NMR

8 ($CDCl_3$, 282 MHz)

5. X-Ray Crystal Structures

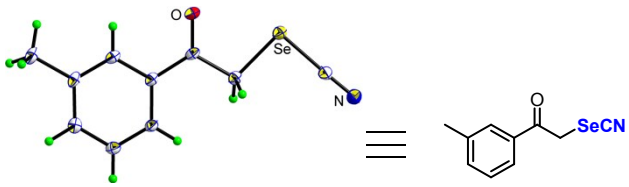


Fig. S1 X-ray structures of **5am** (with 20% probability level)

Compound 5am		**CCDC: 1899043**
Bond precision: C-C = 0.0046 Å		Wavelength = 0.71073
a = 5.4632(4)	b = 16.8139(11)	c = 10.7302(7)
alpha = 90.00	beta = 98.574(2)	gamma = 90.00
Cell setting: monoclinic		Moiety formula: $C_{10}H_9NOSe$
Cell volume = 974.64(11)		Space group: P2(1)/c
Data completeness = 1.000		Theta(max) = 27.520
R(reflections) = 0.0387(1520)		WR2(reflections) = 0.0859(2238)
S = 1.026		Radiation type: MoK\a
Measurement device type: CCD area detector		Measurement method: phi and omega scans
Structure solution: SHELXS-97		Structure refinement: SHELXL-97
Solution primary: direct		Solution secondary: difmap
Solution hydrogens: geom		Hydrogen treatment: mixed

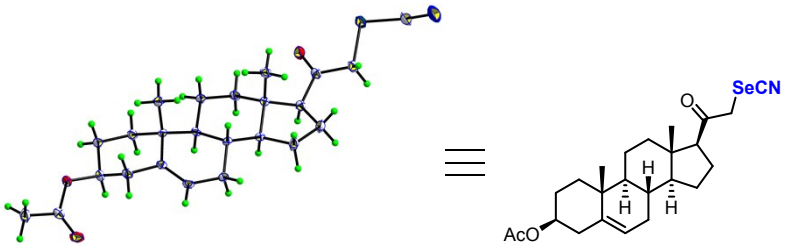


Fig. S2 X-ray structures of **5az** (with 20% probability level)

Compound 5az	**CCDC: 1899044**	**Flack parameter: 0.014(8)**
Bond precision: C-C = 0.0039 Å	Wavelength = 0.71073	
a = 10.1323(6)	b = 7.4394(5)	c = 15.4852(10)
alpha = 90.00	beta = 100.787(2)	gamma = 90.00
Cell setting: monoclinic	Moiety formula: $C_{24}H_{33}NO_3Se$	
Cell volume = 1146.62(13)	Space group: P2(1)	
Data completeness = 1.78/0.96	Theta(max) = 27.550	
R(reflections) = 0.0362(4061)	WR2(reflections) = 0.0849(5088)	
S = 1.023	Radiation type: MoK\a	
Measurement device type: CCD area detector	Measurement method: phi and omega scans	
Structure solution: SHELXS-97	Structure refinement: SHELXL-97	
Solution primary: direct	Solution secondary: difmap	
Solution hydrogens: geom	Hydrogen treatment: mixed	