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Supporting Information for

One-pot synthesis of 2-chloro-2-thio/selenocyanato ketones from β-keto acids

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1. General Information

All reactions were carried out under argon atmosphere, unless otherwise stated. All chemicals were purchased from commercial companies. All the HPLC columns were purchased from Daicel Chemical Industries. Solvents of petroleum ether (PE) and ethyl acetate (EA) were used directly in column chromatography. Toluene, THF were dried over sodium (diphenyl ketone) and distilled; CH_2Cl_2 and MeCN were distilled over CaH_2 before use. ^1H NMR spectra were recorded on a Brucker Avance400 (400 MHz) spectrometer, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm as the standard. $^{13}C\{^1H\}$ NMR spectra were recorded on a Brucker Avance400 (100 MHz) spectrometer, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm as the standard. The data is reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration, assignment). Other analyses were carried out on the following instruments. Infrared spectrometer: Bruker ALPHA FT-IR-Spektrometer. High resolution mass spectrum: AGILENT 7890A/5975C. Rotation polarity: Krüss P8000. High performance liquid chromatography: Shimadzu LC-20A. Melting point detector： Binocular microscope XT4A melting point apparatus (without correct).

2. General procedure

2.1 general procedure for the synthesis of **2a-2j**

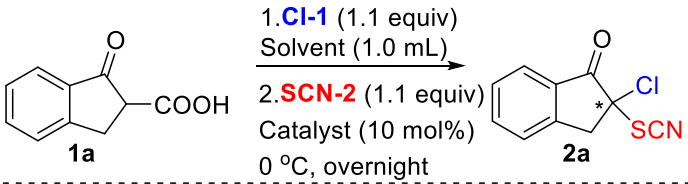
1 (0.10 mmol, 1.0 equiv), **Cl-1** (0.11 mmol, 1.1 equiv) and THF (1.0 mL) was added to a glass tube under argon atmosphere, and it was stirred 2 h at 0 ^oC. Then, **SCN-2** (0.11 mmol, 1.1 equiv) and quinine (0.01 mmol, 10 mol %) were added to the system, and the reaction system was continually stirred overnight at 0 ^oC. The reaction mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1, v/v) to afford the pure desired product.

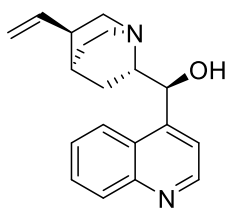
2.2 general procedure for the synthesis of **4a-4m**

3 (0.10 mmol, 1.0 equiv), **Cl-1** (0.11 mmol, 1.1 equiv) and THF (1.0 mL) was added to a glass tube under argon atmosphere, and it was stirred 2 h at 0 ^oC. Then, **SeCN-1** (0.11 mmol, 1.1 equiv) and quinine (0.01 mmol, 10 mol %) were added to the system, and the reaction system was continually stirred overnight at 0 ^oC. The reaction mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1, v/v) to afford the pure desired product.

3. Optimization of the asymmetric reaction conditions.

Table S1 Optimization of the asymmetric reaction conditions

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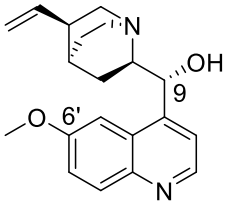
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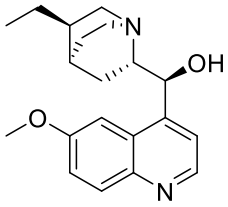
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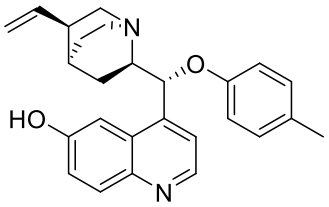
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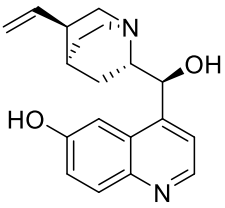
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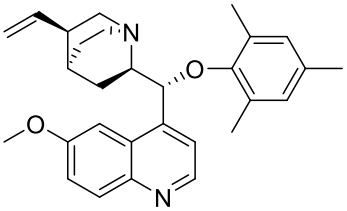
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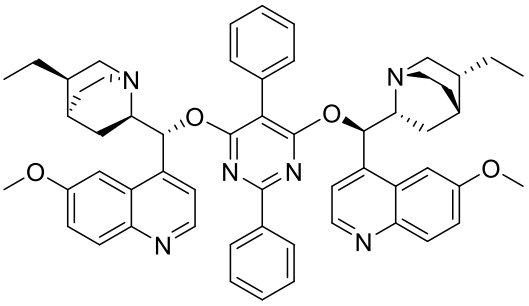
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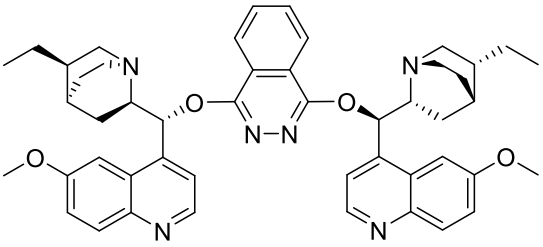
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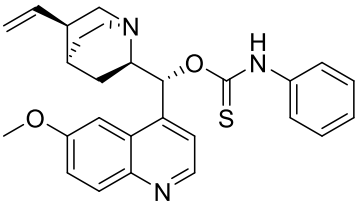
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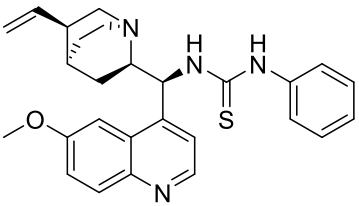
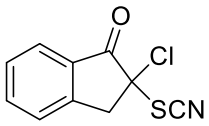

C10

entry	catalyst	solvent	Yield (%)	ee (%)
1	**C1**	THF	75	17
2	**C2**	THF	90	-30
3	**C3**	THF	74	21
4	**C4**	THF	52	7
5	**C5**	THF	37	3
6	**C6**	THF	22	0
7	**C7**	THF	76	-55
8	**C8**	THF	80	-35
9	**C9**	THF	80	40
10	**C10**	THF	50	-19
11	**C7**	Toluene	73	-53
12	**C7**	MTBE	67	-33
13	**C7**	Et_2O	89	-15
14	**C7**	CH_3CN	60	-41
15	**C7**	CH_2Cl_2	68	-41
16[c]	**C7**	THF	17	-59
17[d]	**C7**	THF	trance	-50
18[e]	**C7**	THF	57	-45

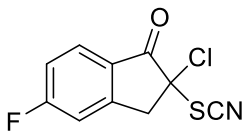
[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), Catalyst (0.01 mmol, 10 mol %), **Cl-1** (0.11 mmol, 1.1 equiv), **SCN-2** (0.11 mmol, 1.1 equiv), solvent (1.0 mL), T, overnight. [b] ee value was determined by chiral HPLC analysis on AD-H column (*n*-hexane/*iso*-propanol 90:10, v/v, 1.0 mL cm^{-1}, 254 nm). [c] **Cl-2** (0.11 mmol, 1.1 equiv) was used [d] **Cl-3** (0.11 mmol, 1.1 equiv) was used. [e] **Cl-4** (0.11 mmol, 1.1 equiv) was used.

4. Spectral data of the products



2a

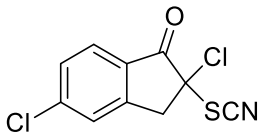
2-chloro-2-thiocyanato-2,3-dihydro-1H-inden-1-one (2a): colorless oil (20 mg, 90% yield). $[\alpha]_D^{25}$ = –17.5 (*c* 1.05, CH_2Cl_2). HPLC: on AD-H column (*n*-hexane/*iso*-propanol 90:10, v/v, 1.0 mL min^{-1}, 254 nm), t_{minor} = 9.42 min, t_{major} = 10.04 min. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 7.6 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 3.99 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 191.6, 147.2, 137.5, 130.5, 129.5, 126.7, 126.3, 107.9, 73.3, 46.6. IR (KBr): 2962, 2927, 2852, 2160, 1737, 1602, 1589, 1475, 1427, 1267 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_7ClNOS$ for $[M + H]^+$: 223.9931, found: 223.9921.



2b

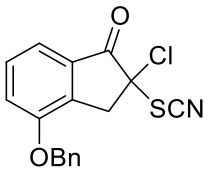
2-chloro-5-fluoro-2-thiocyanato-2,3-dihydro-1H-inden-1-one (2b): White solid (23 mg, 95% yield), mp: 113 – 115 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.96 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.23 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H),

3.99 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 189.9, 168.6 (d, *J* = 260.4 Hz), 150.3 (d, *J* = 10.7 Hz), 129.3 (d, *J* = 10.8 Hz), 126.9 (d, *J* = 1.9 Hz), 118.1 (d, *J* = 23.8 Hz), 113.3 (d, *J* = 23.3 Hz), 107.7, 73.2, 46.5. IR (KBr): 2964, 2920, 2848, 2162, 1730, 1614, 1593, 1255 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_6ClFNOS$ for $[M + H]^+$: 241.9837, found: 241.9836.



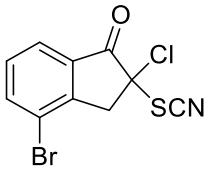
2c

2,5-dichloro-2-thiocyanato-2,3-dihydro-1H-inden-1-one (2c): White solid (24 mg, 89% yield), mp: 96 – 98 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 3.96 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 190.3, 148.6, 144.4, 130.4, 129.0, 127.7, 126.5, 107.6, 73.0, 46.2. IR (KBr): 1960, 2926, 2852, 2162, 1747, 1732, 1598, 1575, 1423, 1317, 1261 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_6Cl_2NOS$ for $[M + H]^+$: 257.9542, found: 257.9543.



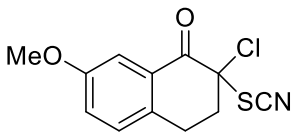
2d

4-(benzyloxy)-2-chloro-2-thiocyanato-2,3-dihydro-1H-inden-1-one (2d): White solid (31 mg, 94% yield), mp: 107 – 109 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36 – 7.19 (m, 7H), 7.10 – 7.08 (m, 1H), 5.01 (s, 2H), 3.75 (d, *J* = 4.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 191.8, 155.4, 136.4, 135.6, 131.9, 131.0, 128.8, 128.5, 127.4, 118.9, 119.1, 107.8, 73.1, 70.6, 43.6. IR (KBr): 2920, 2875, 2162, 1730, 1597, 1487, 1456, 1284, 1263 cm^{-1}. HRMS (ESI) m/z calcd $C_{17}H_{13}ClNO_2S$ for $[M + H]^+$: 330.0350, found: 330.0348.



2e

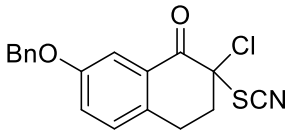
4-bromo-2-chloro-2-thiocyanato-2,3-dihydro-1H-inden-1-one (2e): Yellow solid (21 mg, 66% yield), mp: 106 – 108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 3.90 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 191.0, 147.1, 140.1, 132.6, 131.1, 125.4, 121.4, 107.4, 72.5, 47.3. IR (KBr): 2958, 2924, 2158, 1747, 1728, 1595, 1456, 1259 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_9BrClN_2OS$ for $[M + NH_4]^+$: 318.9302, found: 318.9303.



2f

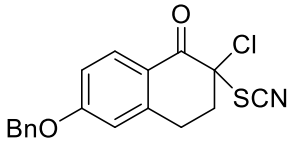
2-chloro-7-methoxy-2-thiocyanato-3,4-dihydronaphthalen-1(2H)-one (2f): Colorless oil (23 mg, 86% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 2.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 3.85 (s, 3H), 3.40 – 3.31 (m, 1H), 3.21 – 3.16

(m, 1H), 3.05 – 2.99 (m, 1H), 2.88 – 2.80 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.1, 159.1, 135.4, 130.2, 128.4, 124.3, 110.9, 109.5, 80.7, 56.7, 40.4, 26.2. IR (KBr): 3007, 2941, 2839, 2160, 1683, 1610, 1498, 1463, 1423, 1342, 1288, 1255 cm^{-1}. HRMS (ESI) m/z calcd $C_{12}H_{11}ClNO_2S$ for $[M + H]^+$: 268.0194, found: 268.0198.



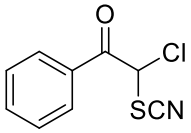
2g

7-(benzyloxy)-2-chloro-2-thiocyanato-3,4-dihydronaphthalen-1(2H)-one (2g): White solid (29 mg, 85% yield), mp: 206 – 108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 2.4 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.28 – 7.21 (m, 2H), 5.10 (s, 2H), 3.40 – 3.32 (m, 1H), 3.21 – 3.16 (m, 1H), 3.05 – 2.99 (m, 1H), 2.88 – 2.80 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 186.0, 158.2, 136.1, 135.6, 130.3, 128.7, 128.4, 128.3, 127.6, 124.8, 112.2, 109.4, 80.6, 70.4, 40.3, 28.2. IR (KBr): 2920, 2850, 2158, 1683, 1496 cm^{-1}. HRMS (ESI) m/z calcd $C_{18}H_{14}ClNNaO_2S$ for $[M + Na]^+$: 366.0326, found: 366.0334.



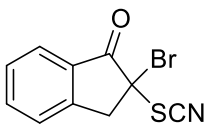
2h

6-(benzyloxy)-2-chloro-2-thiocyanato-3,4-dihydronaphthalen-1(2H)-one (2h): White solid (28 mg, 82% yield), mp: 124 – 126 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.8 Hz, 1H), 7.40 – 7.34 (m, 5H), 6.97 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.80 (s, 1H), 5.13 (s, 2H), 3.41 – 3.33 (m, 1H), 3.17 – 3.11 (m, 1H), 3.02 – 2.95(m, 1H), 2.85 – 2.77 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 184.7, 164.4, 145.5, 135.5, 132.2, 128.8, 128.5, 127.4, 120.9, 115.4, 113.6, 109.8, 80.9, 70.4, 40.2, 27.2. IR (KBr): 3089, 3064, 3034, 2926, 2868, 2158, 1674, 1597, 1454, 1352, 1273, 1224 cm^{-1}. HRMS (ESI) m/z calcd $C_{18}H_{15}ClNO_2S$ for $[M + H]^+$: 344.0507, found: 344.0498.



2i

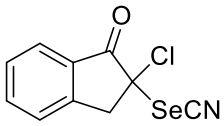
2-chloro-1-phenyl-2-thiocyanatoethan-1-one (2i): Yellow oil (16 mg, 76% yield)**.** ^1H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 7.2 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 2H), 6.76 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 189.7, 135.6, 130.6, 130.0, 129.3, 101.2, 61.4. IR (KBr): 2958, 2926, 2164, 1732, 1681, 1456, 1274 cm^{-1}. HRMS (ESI) m/z calcd C_9H_7ClNOS for $[M + H]^+$: 211.9931, found: 211.9934.



2j

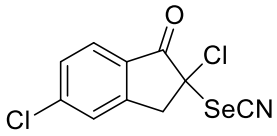
2-bromo-2-thiocyanato-2,3-dihydro-1H-inden-1-one (2j): Colorless oil (25 mg, 92% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.0 Hz, 1H), 7.77 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 4.18 – 4.06 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 192.3, 147.3, 137.4, 130.2, 129.4, 126.6, 126.2, 108.7, 61.5, 48.0. IR (KBr): 2962, 2924, 2854, 2160, 1732, 1604, 1263 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_7BrNOS$ for $[M + H]^+$: 267.9426, found:

267.9427.



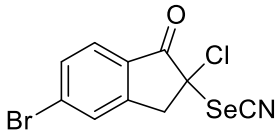
4a

2-chloro-2-selenocyanato-2,3-dihydro-1H-inden-1-one (4a): Colorless oil (22 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 4 19 – 4.01 (m, 2H). 193.2, 147.6, 137.5, 130.4, 129.4, 126.5, 126.2, 99.7, 69.4, 47.5. IR (KBr): 2962, 2926, 2852, 2156, 1737, 1716, 1602, 1261 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_7ClNOSe$ for $[M + H]^+$: 271.9376, found: 271.9378.



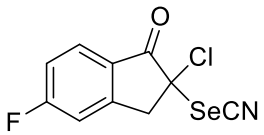
4b

2,5-dichloro-2-selenocyanato-2,3-dihydro-1H-inden-1-one (4b): White solid (21 mg, 70% yield), mp: 87 – 89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 8.4 Hz, 1H), 7.51 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.48 (s, 1H), 4.17 – 3.99 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 191.9, 148.9, 144.4, 130.3, 128.8, 127.5, 126.4, 99.5, 68.8, 47.1. IR (KBr): 2958, 2926, 2852, 2156, 1737, 1716, 1597, 1575, 1319, 1261, 1207 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_6Cl_2NOSe$ for $[M + H]^+$: 305.8986, found: 305.8985.



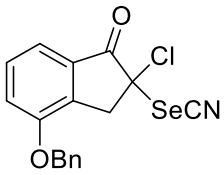
4c

5-bromo-2-chloro-2-selenocyanato-2,3-dihydro-1H-inden-1-one (4c): Yellow solid (27 mg, 77% yield), mp: 111 – 113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 14.8 Hz, 1H), 7.69 – 7.66 (m, 2H), 4.17 – 3.99 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 192.2, 148.9, 133.3, 133.2, 129.5, 129.2, 127.5, 99.4, 68.7, 47.0. IR (KBr): 2924, 2850, 2156, 1716, 1591, 1417 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_5BrClNNaOSe$ for $[M + Na]^+$: 371.8300, found: 371.8301.



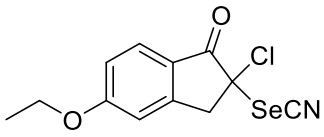
4d

2-chloro-5-fluoro-2-selenocyanato-2,3-dihydro-1H-inden-1-one (4d): Yellow solid (22 mg, 76% yield), mp: 113 – 115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 4.20 – 4.01 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 191.5, 168.7 (d, *J* = 260.3 Hz), 150.7 (d, *J* = 10.7 Hz), 129.2 (d, *J* = 10.8 Hz), 126.8 (d, *J* = 1.9 Hz), 118.0 (d, *J* = 23.8 Hz), 113.2 (d, *J* = 23.2 Hz), 99.5, 69.8, 47.4. IR (KBr): 2960, 2926, 2852, 2156, 1732, 1716, 1614, 1593, 1259 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_6ClFNOSe$ for $[M + H]^+$: 289.9282, found: 289.9278.



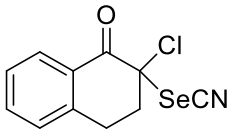
4e

4-(benzyloxy)-2-chloro-2-selenocyanato-2,3-dihydro-1H-inden-1-one (4e): White solid (35 mg, 93% yield), mp: 153 – 155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 – 7.37 (m, 7H), 7.25 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.12 – 3.93 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 193.4, 155.4, 136.7, 135.7, 131.7, 130.9, 128.8, 128.5, 127.4, 118.9, 118.0, 99.6, 70.6, 69.3, 44.3. IR (KBr): 2954, 2920, 2850, 2156, 1732, 1716, 1267 cm^{-1}. HRMS (ESI) m/z calcd $C_{17}H_{13}ClNO_2Se$ for $[M + H]^+$: 377.9795, found: 377.9794.



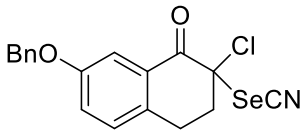
4f

5-(allyloxy)-2-chloro-2-selenocyanato-2,3-dihydro-1H-inden-1-one (4f): White solid (19 mg, 60% yield), mp: 87 – 89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.8 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.87 (s, 1H), 6.08 – 6.01 (m, 1H), 5.47 – 5.35 (m, 2H), 4.66 (d, *J* = 5.2 Hz, 2H), 4.18 – 3.97 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 191.4, 166.5, 150.8, 131.7, 128.4, 123.1, 118.8, 118.0, 110.1, 100.0, 70.2, 69.5, 47.8. IR (KBr): 2962, 2926, 2156, 1716, 1597, 1489, 1261 cm^{-1}. HRMS (ESI) m/z calcd $C_{13}H_{11}ClNO_2Se$ for $[M + H]^+$: 327.9638, found: 327.9633.



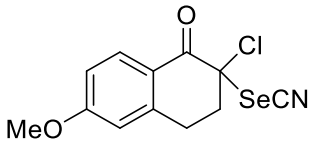
4g

2-chloro-2-selenocyanato-3,4-dihydronaphthalen-1(2H)-one (4g): Colorless oil (28 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 3.51 – 3.43 (m, 1H), 3.30 – 3.24 (m, 1H), 3.09 – 2.98 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 188.5, 143.2, 135.6, 129.4, 129.0, 127.7, 127.4, 101.7, 78.4, 41.5, 27.4. IR (KBr): 2956, 2924, 2852, 2156, 1734, 1676, 1456, 1274 cm^{-1}. HRMS (ESI) m/z calcd $C_{11}H_9ClNOSe$ for $[M + H]^+$: 285.9532, found: 285.9530.



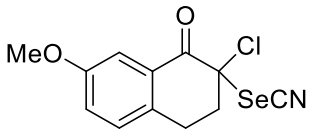
4h

7-(benzyloxy)-2-chloro-2-selenocyanato-3,4-dihydronaphthalen-1(2H)-one (4h): White solid (37 mg, 93% yield), mp: 90 – 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 2.4 Hz, 1H), 7.37 – 7.25 (m, 5H), 7.20 – 7.10 (m, 2H), 5.02 (s, 2H), 3.34 – 3.26 (m, 1H), 3.20 – 3.14 (m, 1H), 2.97 – 2.82 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 188.4, 158.1, 136.1, 136.0, 130.3, 128.7, 128.3, 128.1, 127.5, 124.8, 112.1, 101.7, 78.4, 70.4, 41.8, 26.8. IR (KBr): 2920, 2850, 2156 1732, 1716, 1267 cm^{-1}. HRMS (ESI) m/z calcd $C_{18}H_{15}ClNO_2Se$ for $[M + H]^+$: 391.9951, found: 391.9947.



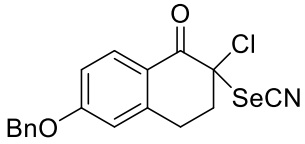
4i

2-chloro-6-methoxy-2-selenocyanato-3,4-dihydronaphthalen-1(2H)-one (4i): White solid (30 mg, 97% yield), mp: 117 – 119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.8 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 3.09 (s, 3H), 3.48 – 3.40 (m, 1H), 3.26 – 3.21 (m, 1H), 3.06 – 2.92 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 187.2, 165.5, 146.1, 132.1, 120.4, 114.8, 112.7, 102.1, 78.8, 55.7, 41.7, 27.9. IR (KBr): 2960, 2924, 2843, 2158, 1732, 1687, 1456, 1274 cm^{-1}. HRMS (ESI) m/z calcd $C_{12}H_{11}ClNO_2Se$ for $[M + H]^+$: 315.9638, found: 315.9642.



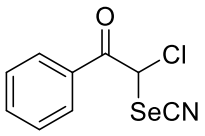
4j

2-chloro-7-methoxy-2-selenocyanato-3,4-dihydronaphthalen-1(2H)-one (4j): Colorless oil (31 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 2.4 Hz, 1H), 7.24 – 7.18 (m, 2H), 3.85 (s, 3H), 3.42 – 3.34 (m, 1H), 3.27 – 3.22 (m, 1H), 3.06 – 2.91 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 188.5, 159.0, 135.9, 130.2, 128.1, 124.3, 110.8, 101.7, 78.4, 55.6, 41.8, 26.7. IR (KBr): 2931, 2837, 2156, 1678, 1610, 1496, 1432, 1340, 1288 cm^{-1}. HRMS (ESI) m/z calcd $C_{12}H_{11}ClNO_2Se$ for $[M + H]^+$: 315.9638, found: 315.9641.



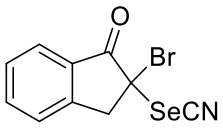
4k

6-(benzyloxy)-2-chloro-2-selenocyanato-3,4-dihydronaphthalen-1(2H)-one (4k): Pink solid (39 mg, 99% yield), mp: 141 – 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.36 (m, 5H), 7.99 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 5.16 (s, 2H), 3.47 – 3.39 (m, 1H), 3.25 – 3.20 (m, 1H), 3.05 – 2.90 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 187.1, 164.5, 146.0, 135.5, 132.1, 128.8, 128.4, 127.4, 120.6, 115.4, 113.7, 102.1, 78.8, 70.4, 41.6, 27.8. IR (KBr): 2926, 2870, 2154, 1668, 1595, 1350, 1267, 1222 cm^{-1}. HRMS (ESI) m/z calcd $C_{18}H_{15}ClNO_2Se$ for $[M + H]^+$: 391.9951, found: 391.9946.



4l

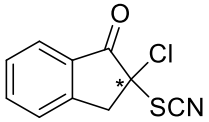
2-chloro-1-phenyl-2-selenocyanatoethan-1-one (4l): White solid (26 mg, 99% yield), mp: 76 – 78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.01 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 187.3, 135.5, 130.9, 129.7, 129.3, 109.5, 65.6. IR (KBr): 3064, 2972, 2158, 1674, 1595, 1448, 1282 cm^{-1}. HRMS (ESI) m/z calcd $C_9H_7ClNOSe$ for $[M + H]^+$: 259.9376, found: 259.9374.



4m

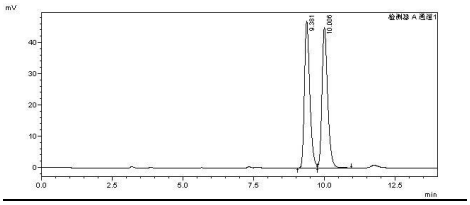
2-bromo-2-selenocyanato-2,3-dihydro-1H-inden-1-one (4m): White solid (17 mg, 55% yield), mp: 77 – 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 4.24 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 194.0, 147.9, 137.4, 129.9, 129.3, 126.5, 126.2, 100.7, 55.9, 48.8. IR (KBr): 2922, 2850, 2154, 1716, 1602, 1263 cm^{-1}. HRMS (ESI) m/z calcd $C_{10}H_6BrNNaOSe$ for $[M + Na]^+$: 337.8690, found: 337.8695.

5. Copies of HPLC chromatograms



2a

2-chloro-2-thiocyanato-2,3-dihydro-1H-inden-1-one (2a)



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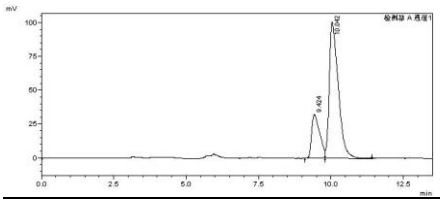
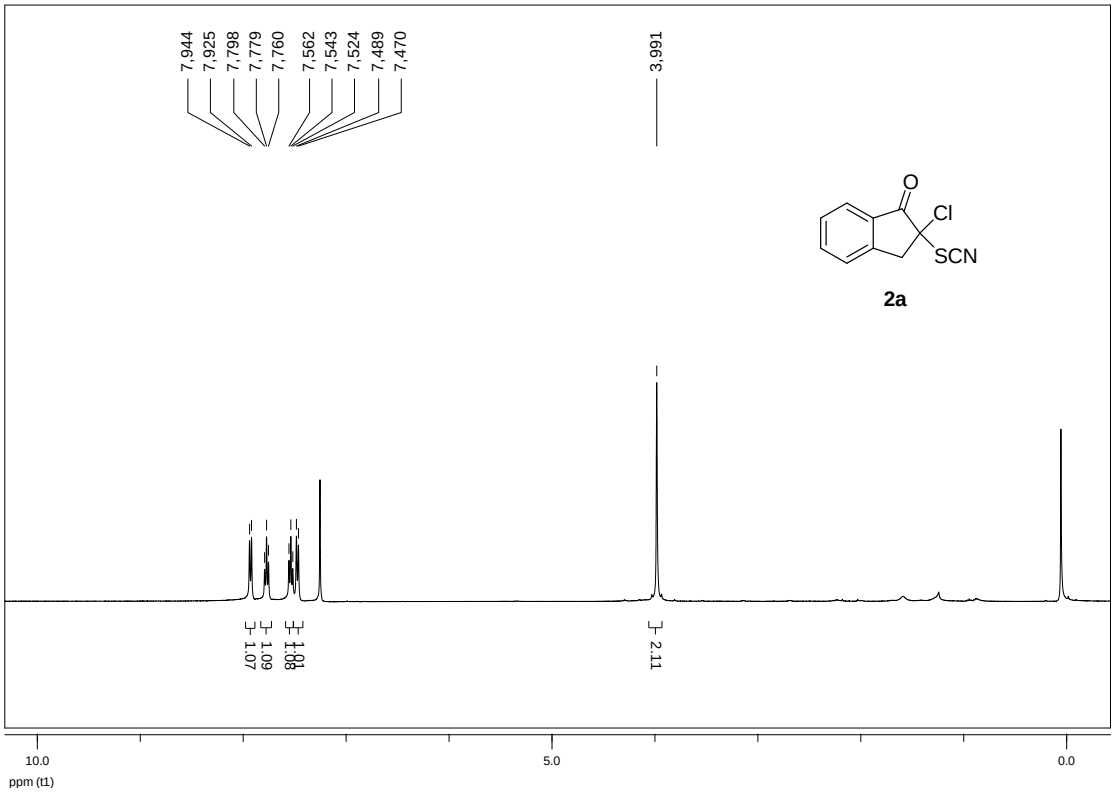
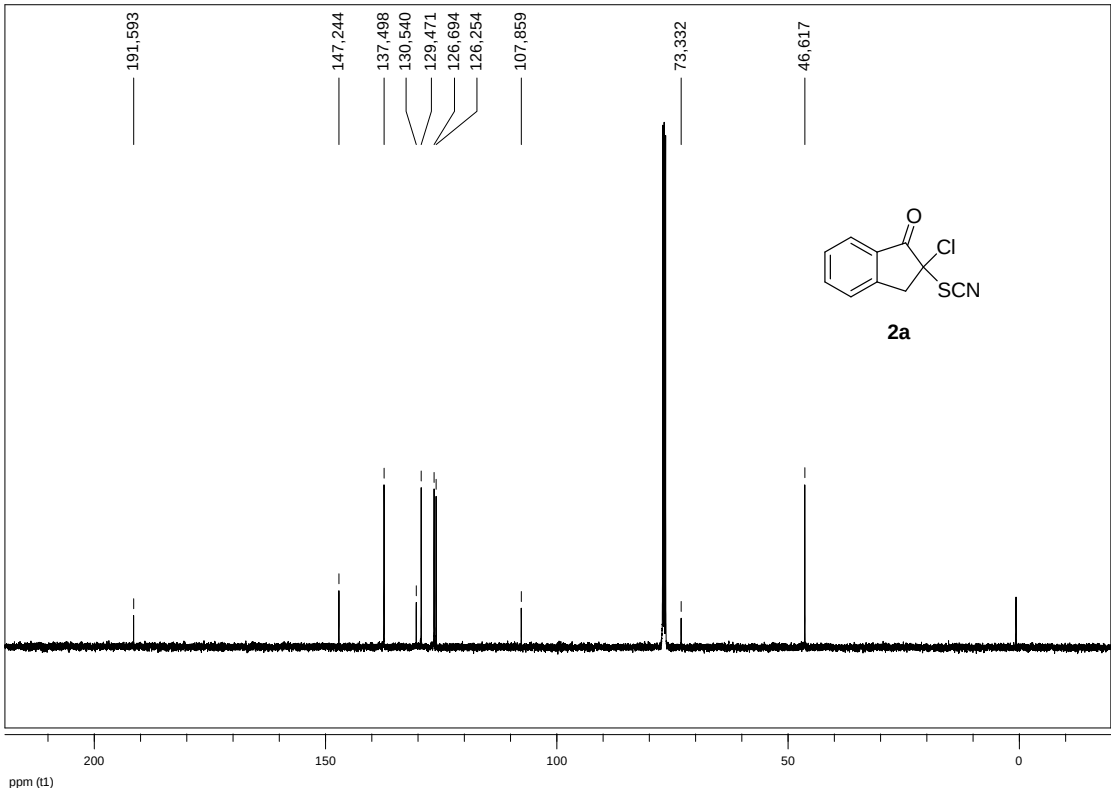
2	10.006	625673	50.286
total		1244223	100.000

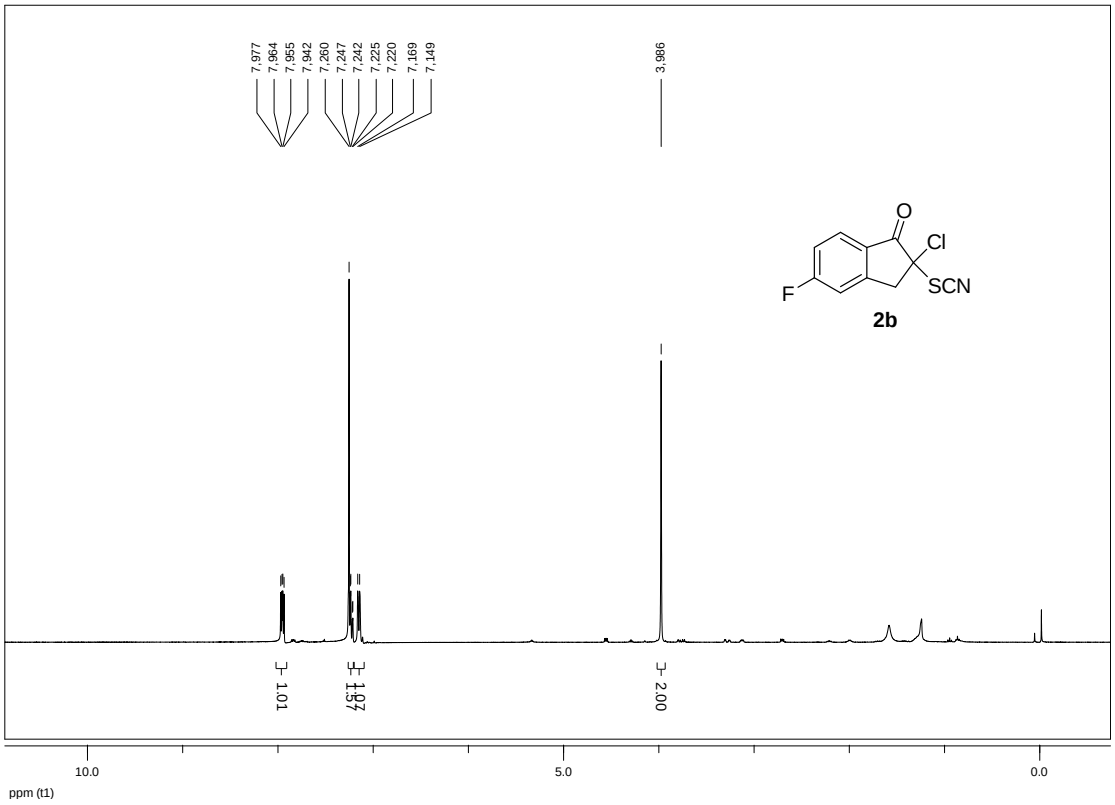


Peak	Time	Area	Area/%
1	9.424	630949	22.453
2	10.042	2179138	77.547
total		2810087	100.000

6. Copies of ^{1}H and $^{13}C\{H\}$ NMR spectra.



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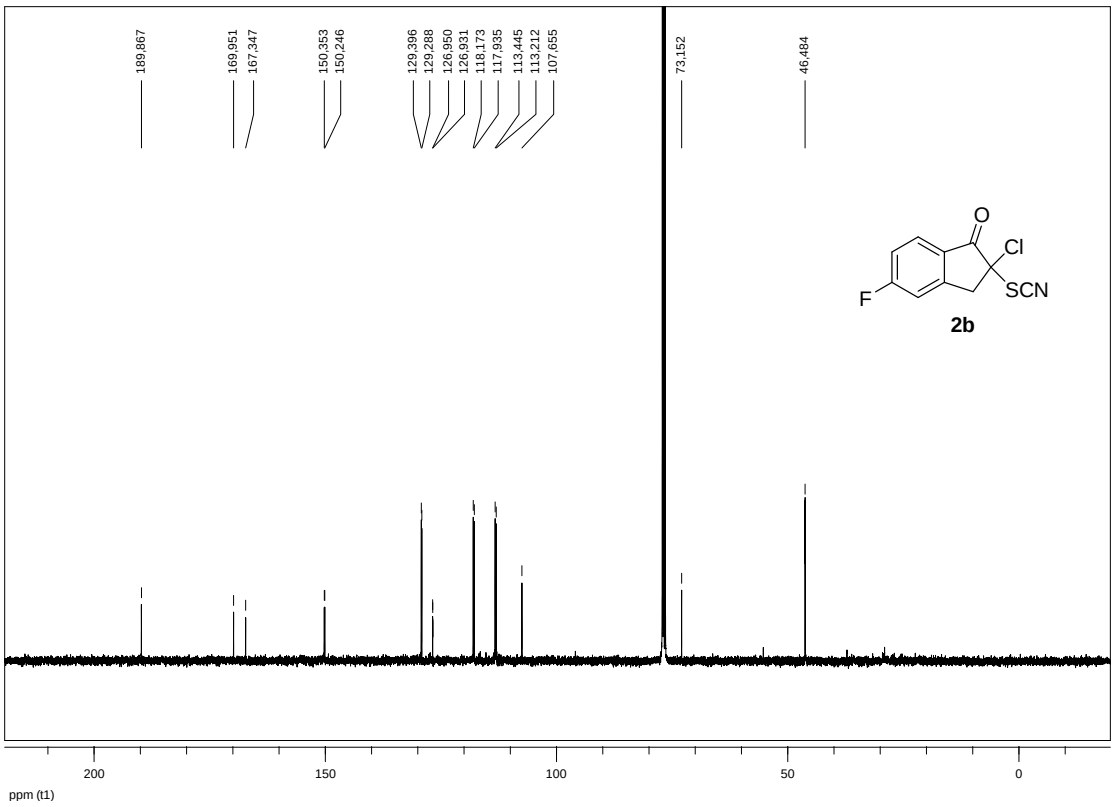
ppm (t1)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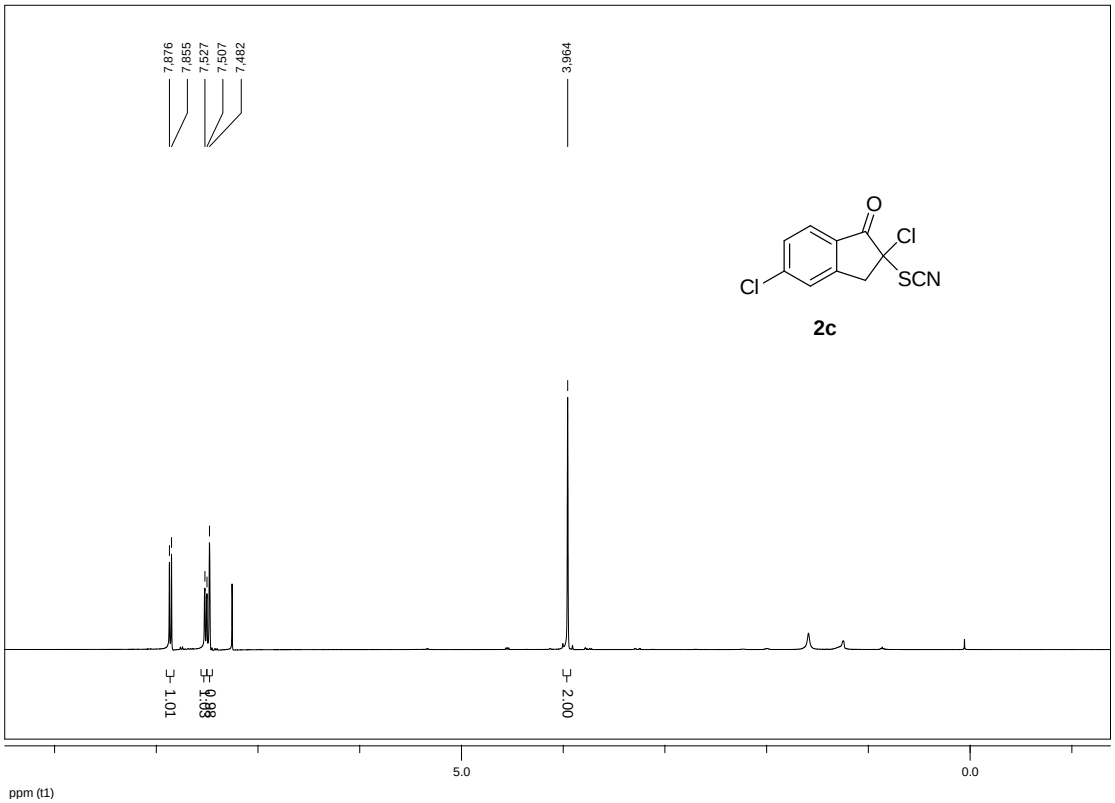
ppm (t1)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Cl
SCN
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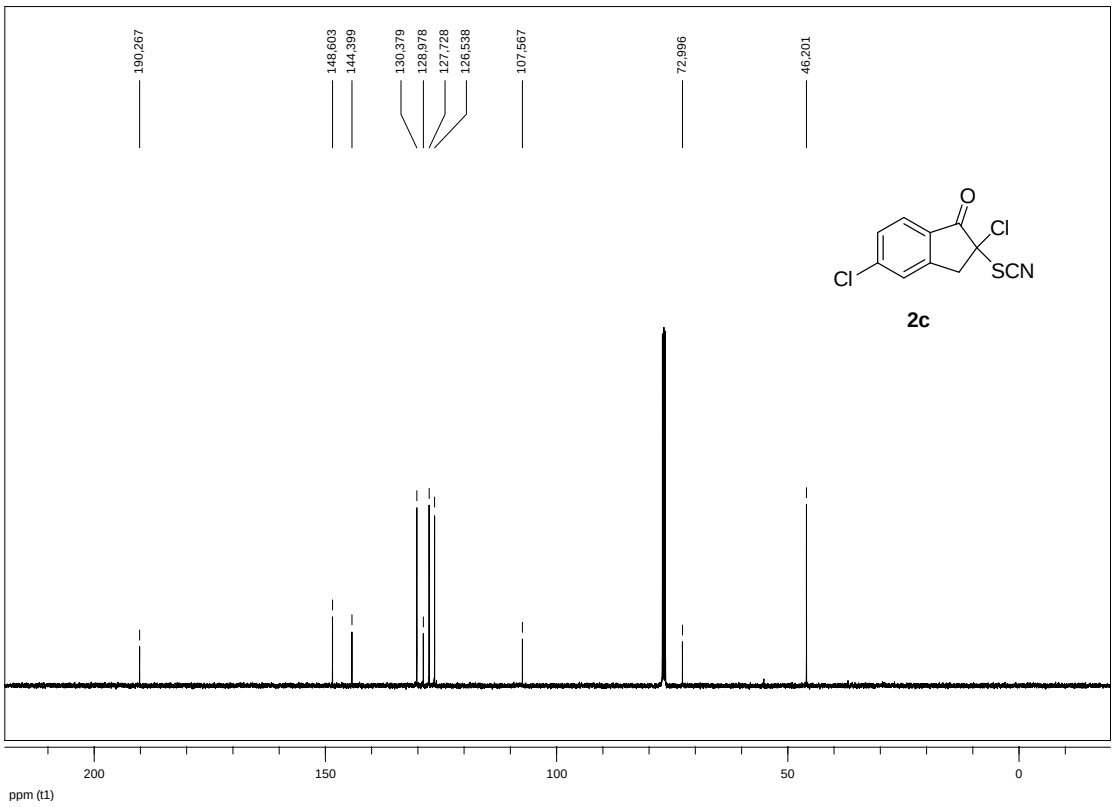
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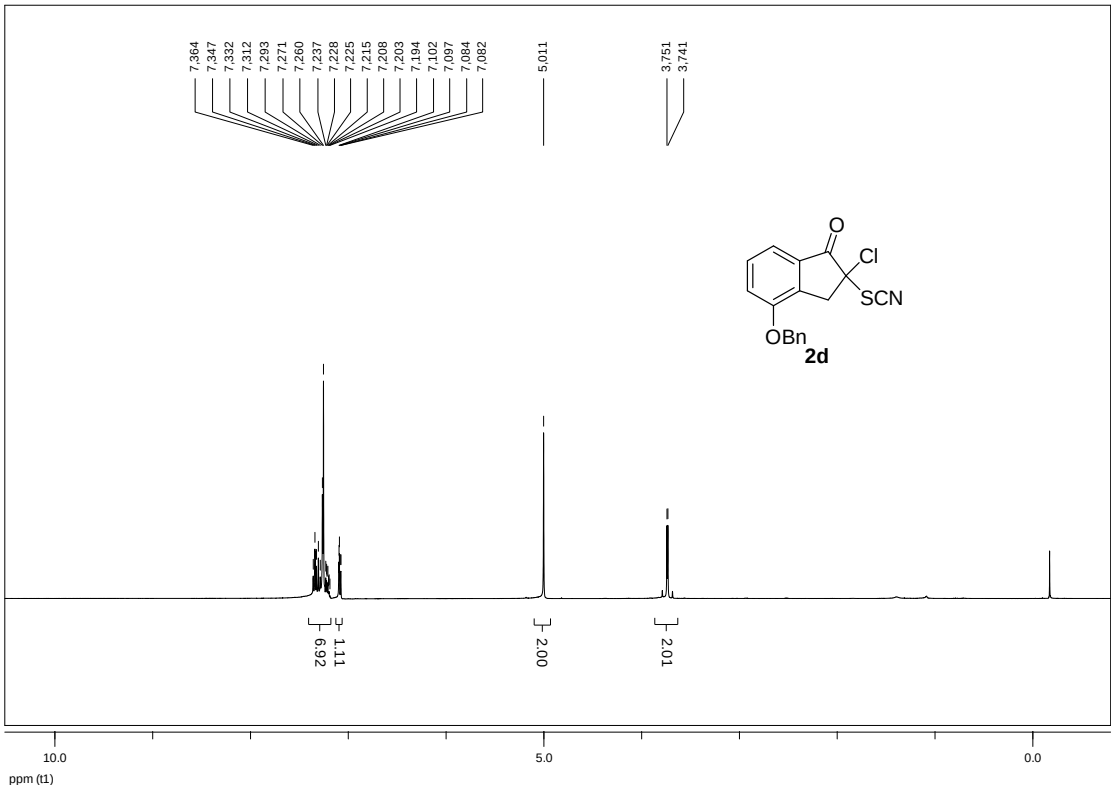
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3.741
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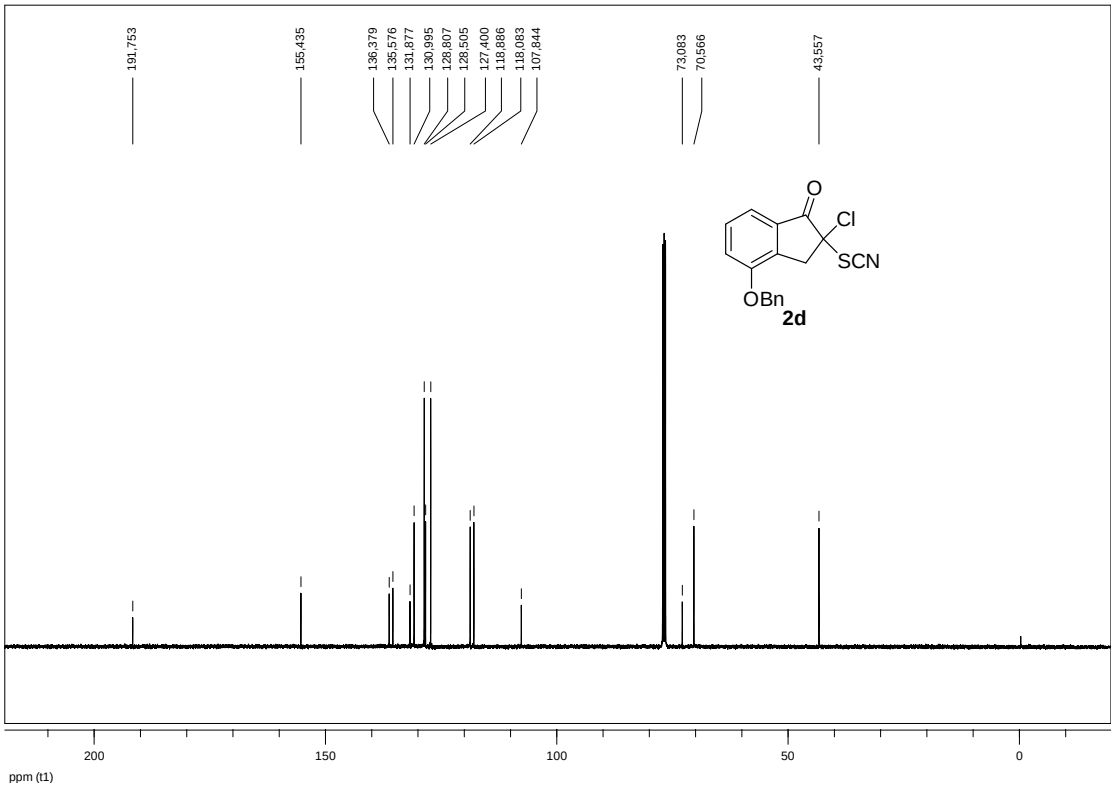
ppm (t1)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Cl
SCN
OBn
2d
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50
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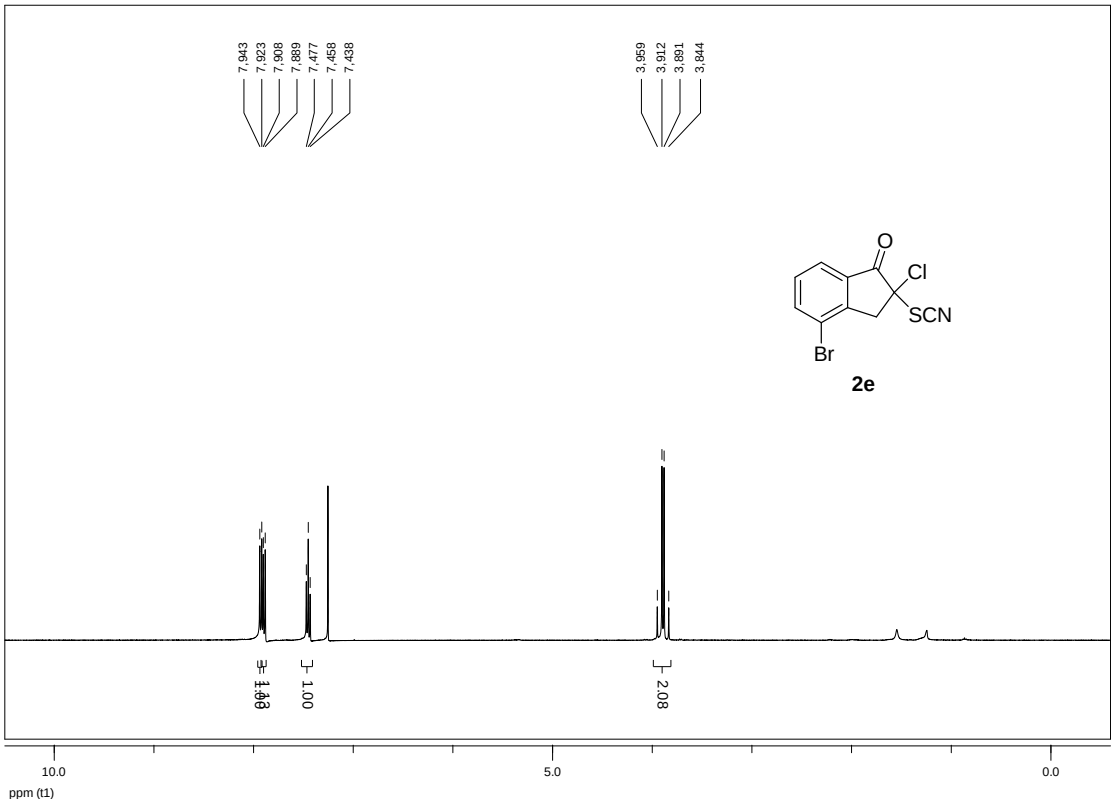
ppm (t1)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SCN
Br
2e
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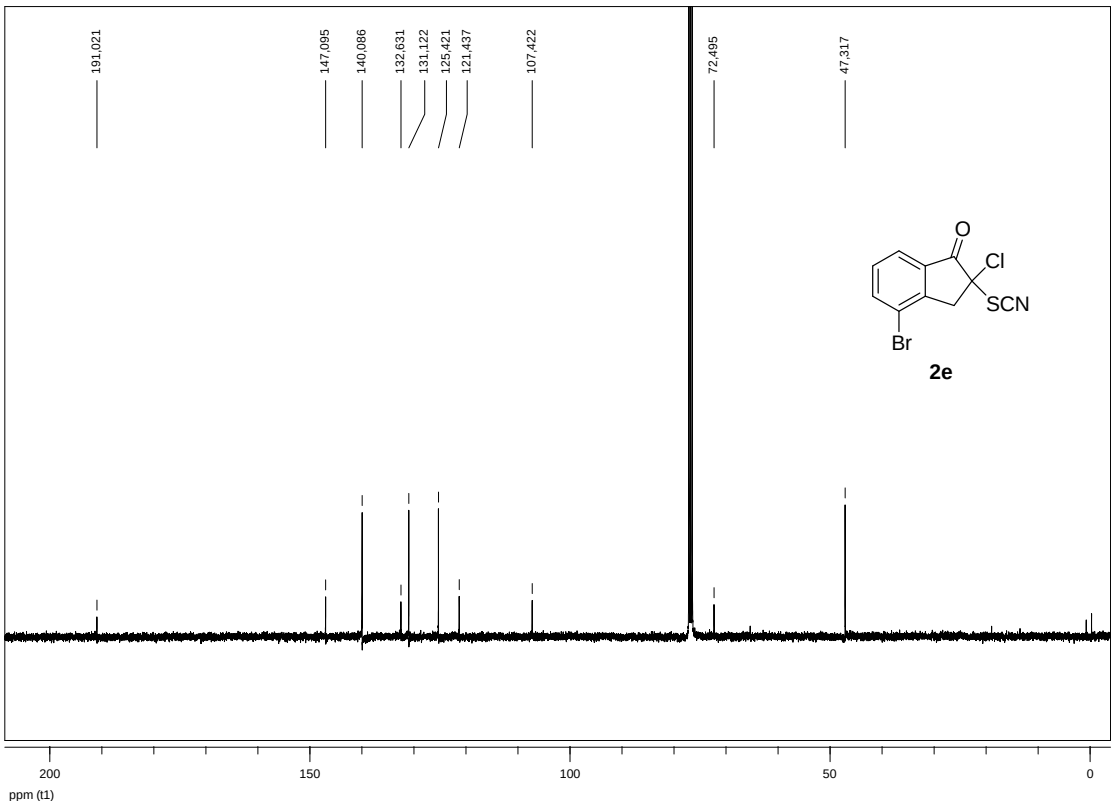
ppm (t1)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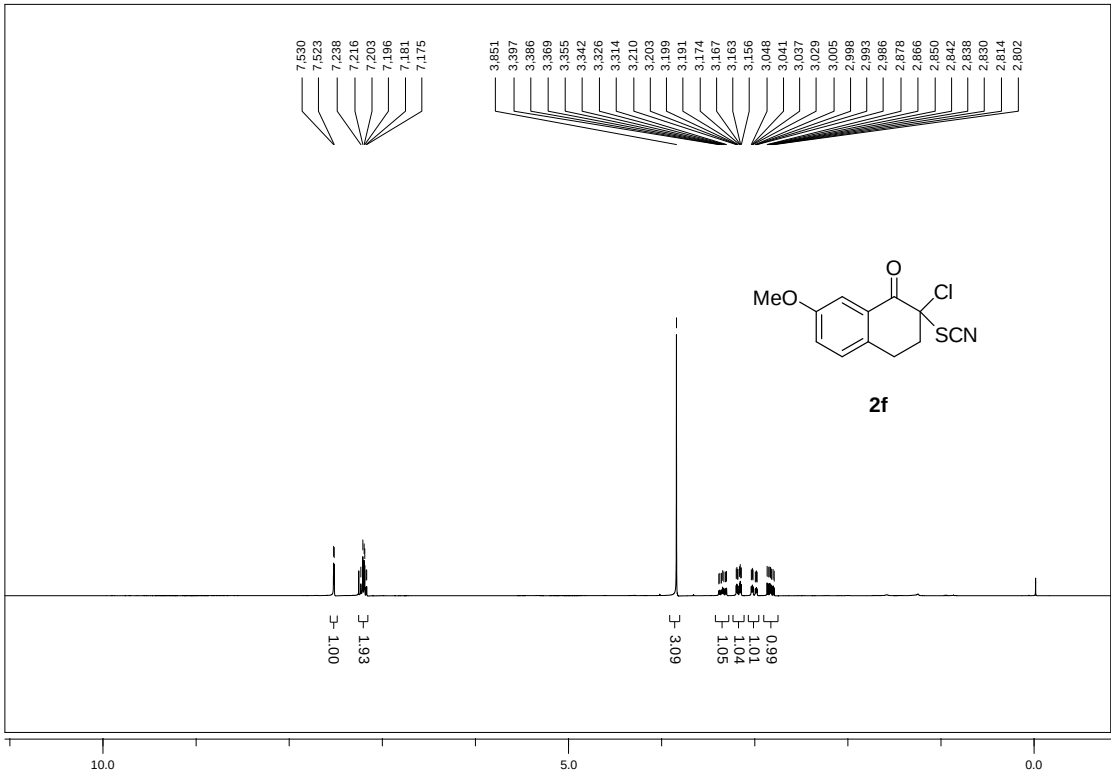
ppm (t1)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O
Cl
SCN
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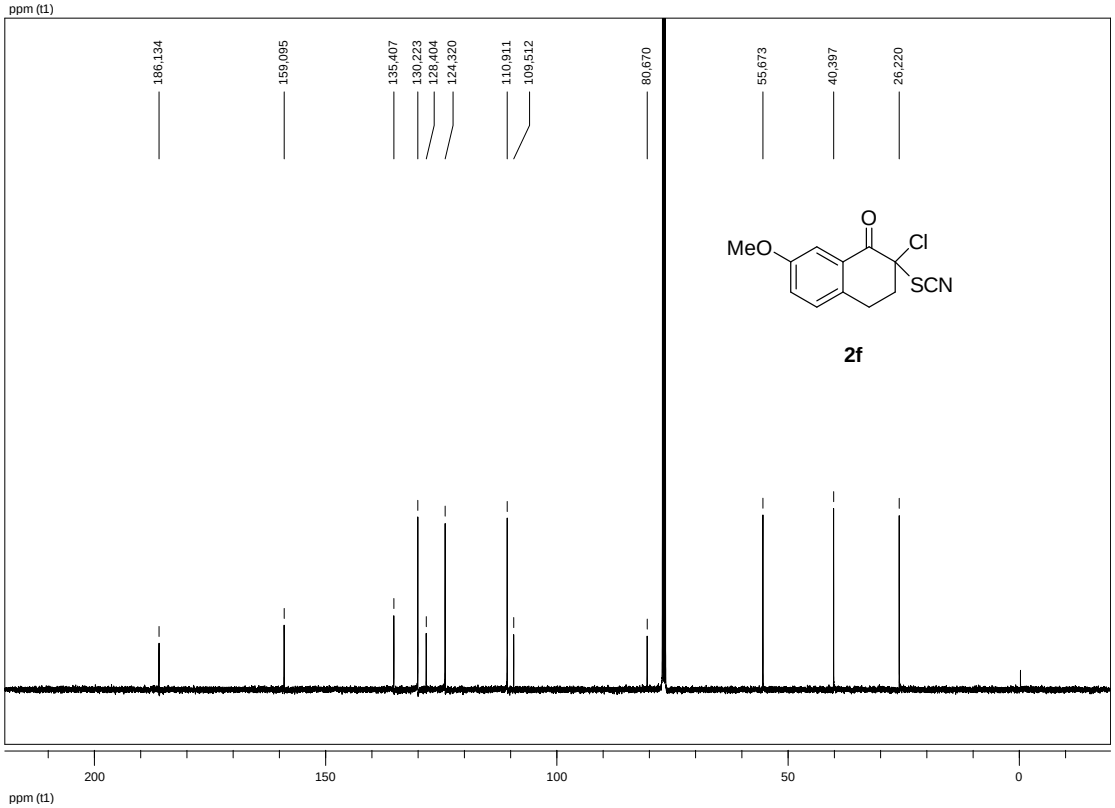
ppm (t1)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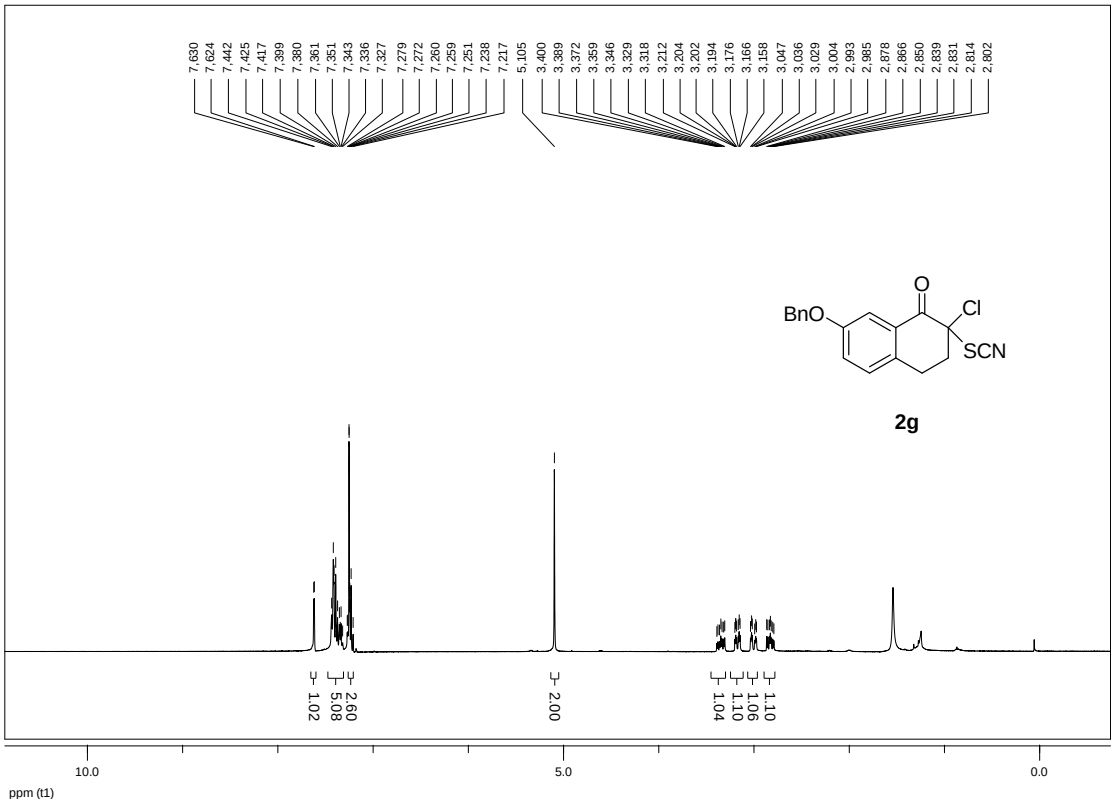
26.220
MeO
O
Cl
SCN
2f
200
150
100
50
0
ppm (t1)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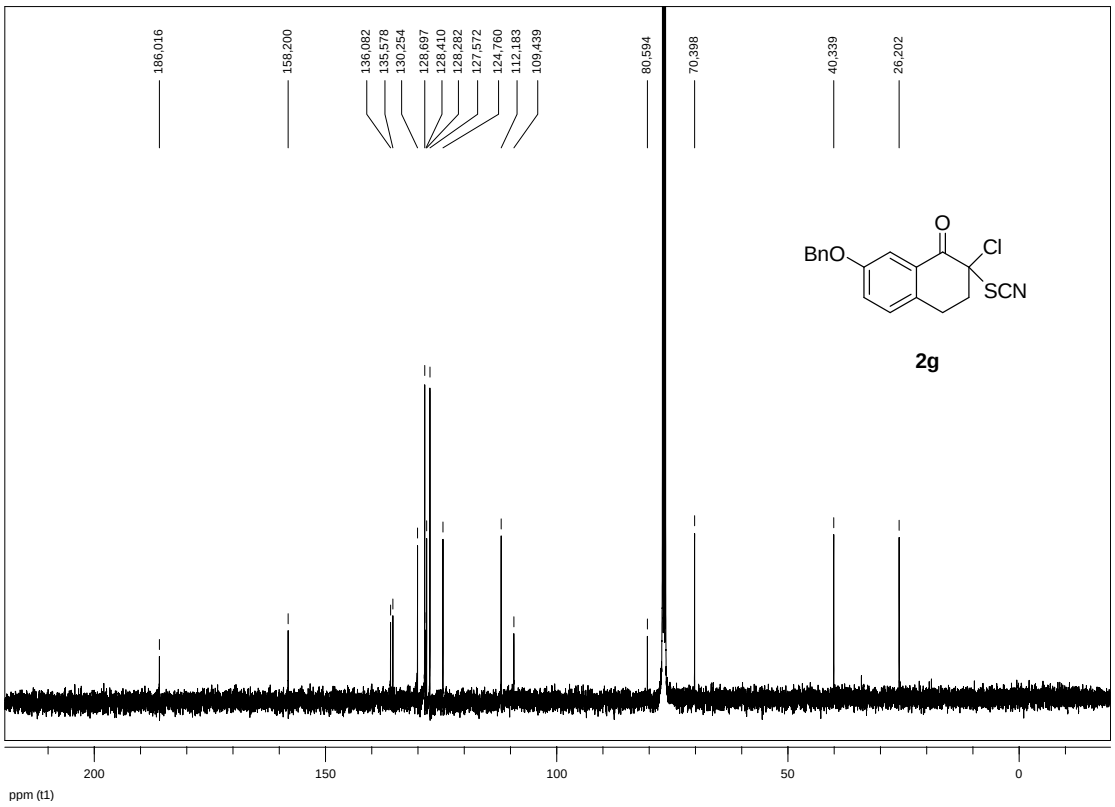
7.380
7.361
7.351
7.343
7.336
7.327
7.279
7.272
7.260
7.259
7.251
7.238
7.217
5.105
3.400
3.389
3.372
3.359
3.346
3.329
3.318
3.212
3.204
3.202
3.194
3.176
3.166
3.158
3.047
3.036
3.029
3.004
2.993
2.985
2.878
2.866
2.850
2.839
2.831
2.814
2.802
O
BnO
Cl
SCN
2g
1.02
5.08
2.60
2.00
1.04
1.10
1.06
1.10
10.0
5.0
0.0
ppm (t1)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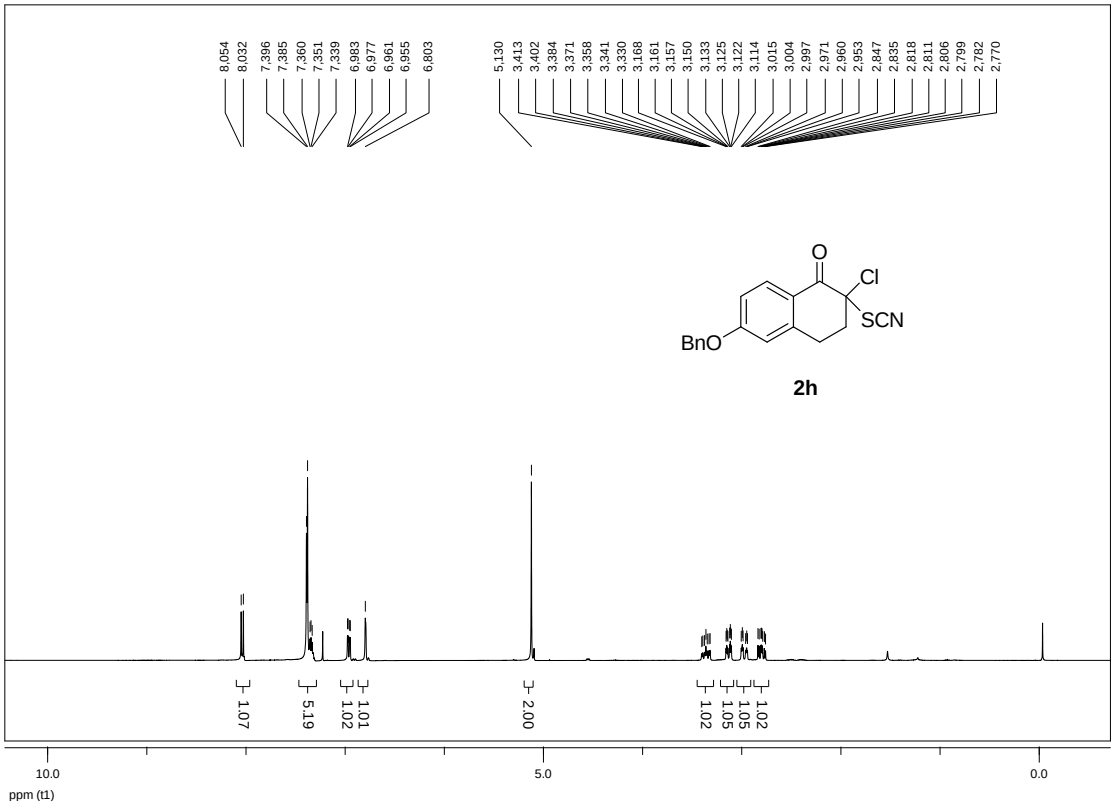
158.200
136.082
135.578
130.254
128.697
128.410
128.282
127.572
124.760
112.183
109.439
80.594
70.398
40.339
26.202
O
BnO
Cl
SCN
2g
200
150
100
50
0
ppm (t1)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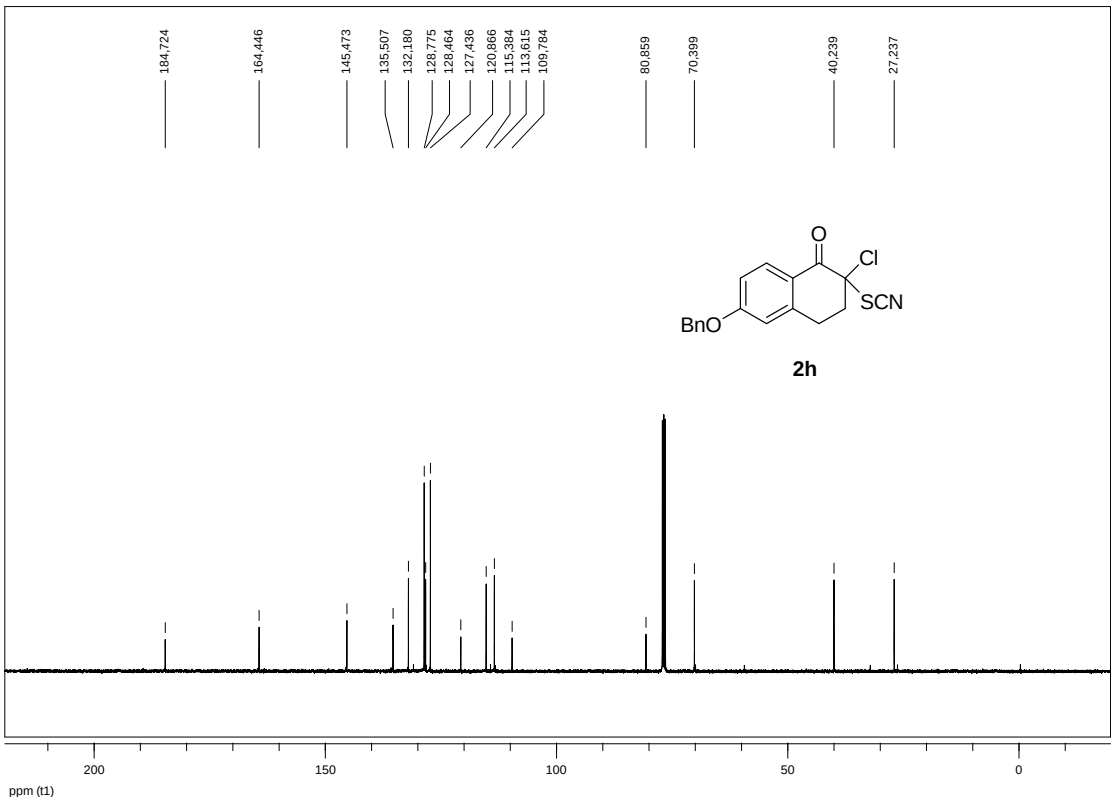
8.032
7.396
7.385
7.360
7.351
7.339
6.983
6.977
6.961
6.955
6.803
5.130
3.413
3.402
3.384
3.371
3.358
3.341
3.330
3.168
3.161
3.157
3.150
3.133
3.125
3.122
3.114
3.015
3.004
2.997
2.971
2.960
2.953
2.847
2.835
2.818
2.811
2.806
2.799
2.782
2.770
O
Cl
SCN
BnO
1.07
5.19
1.02
1.01
2.00
1.02
1.05
1.05
1.02
10.0
5.0
0.0
ppm (t1)

2h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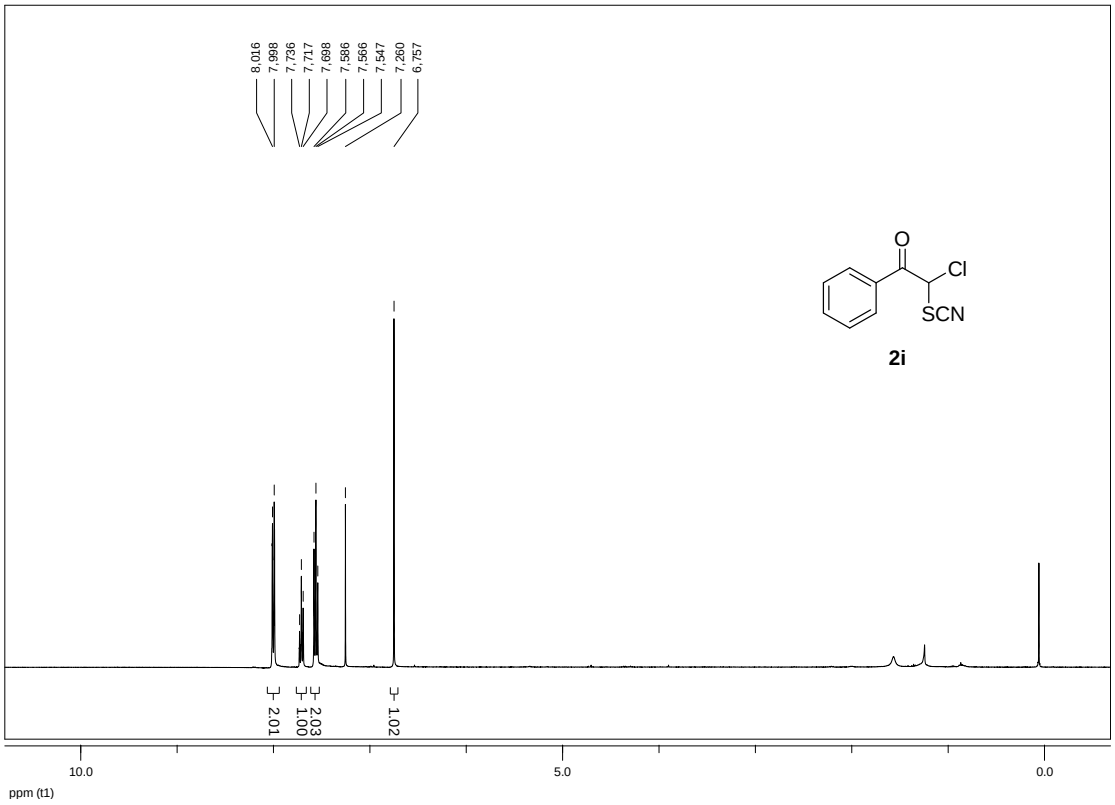
164.446
145.473
135.507
132.180
128.775
128.464
127.436
120.866
115.384
113.615
109.784
80.859
70.399
40.239
27.237
O
Cl
SCN
BnO
200
150
100
50
0
ppm (t1)

2h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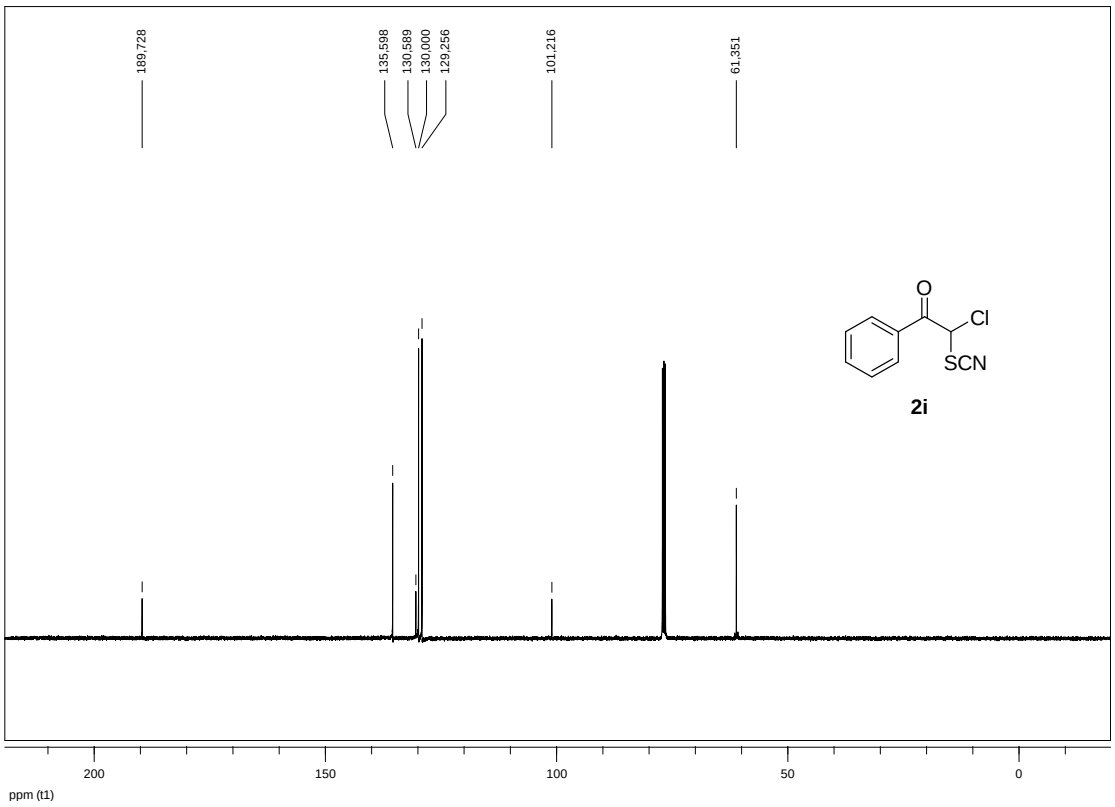
7,736
7,717
7,698
7,586
7,566
7,547
7,260
6,757
O
Cl
SCN
2i
2.01
1.00
2.03
1.02
10.0
5.0
0.0
ppm (t1)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130,589
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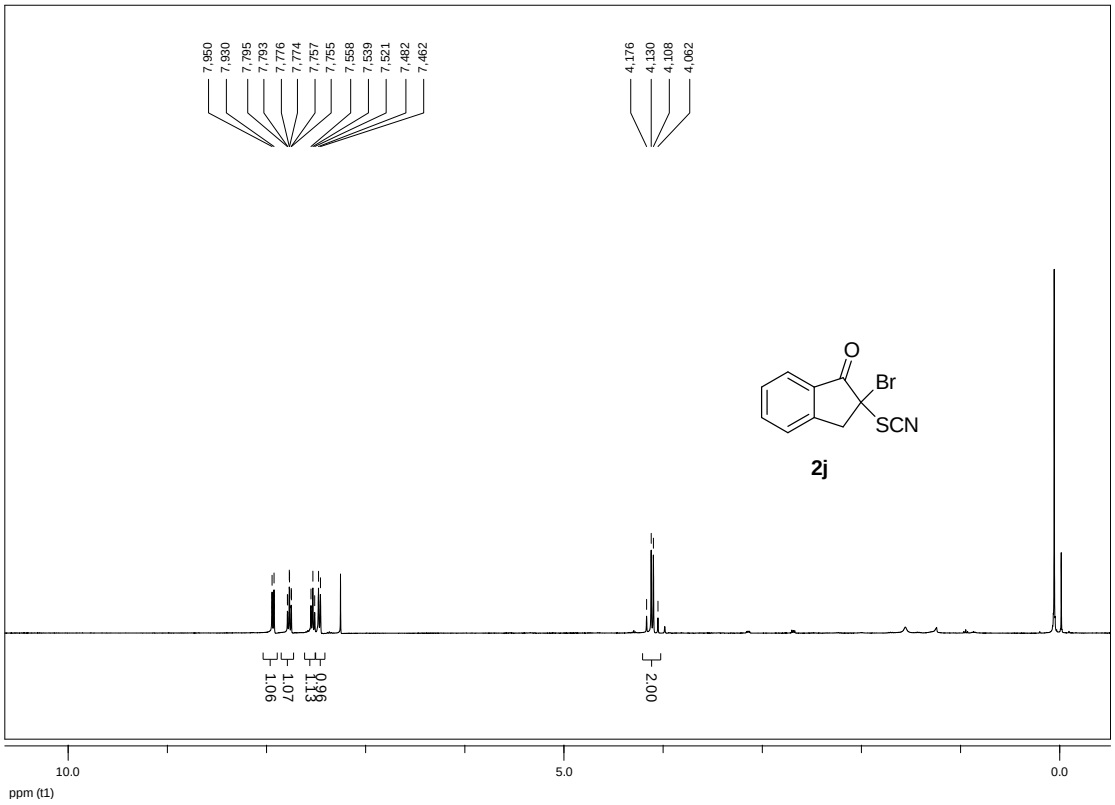
129,256
101,216
61,351
O
Cl
SCN
2i
200
150
100
50
0
ppm (t1)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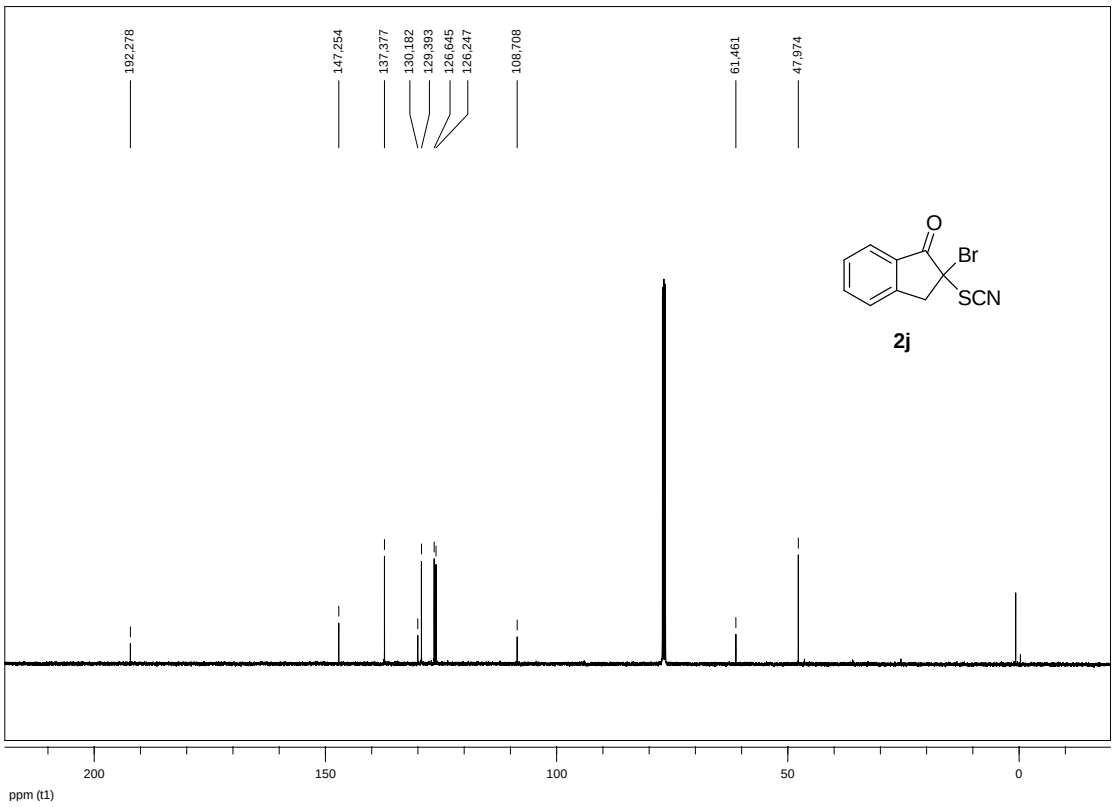
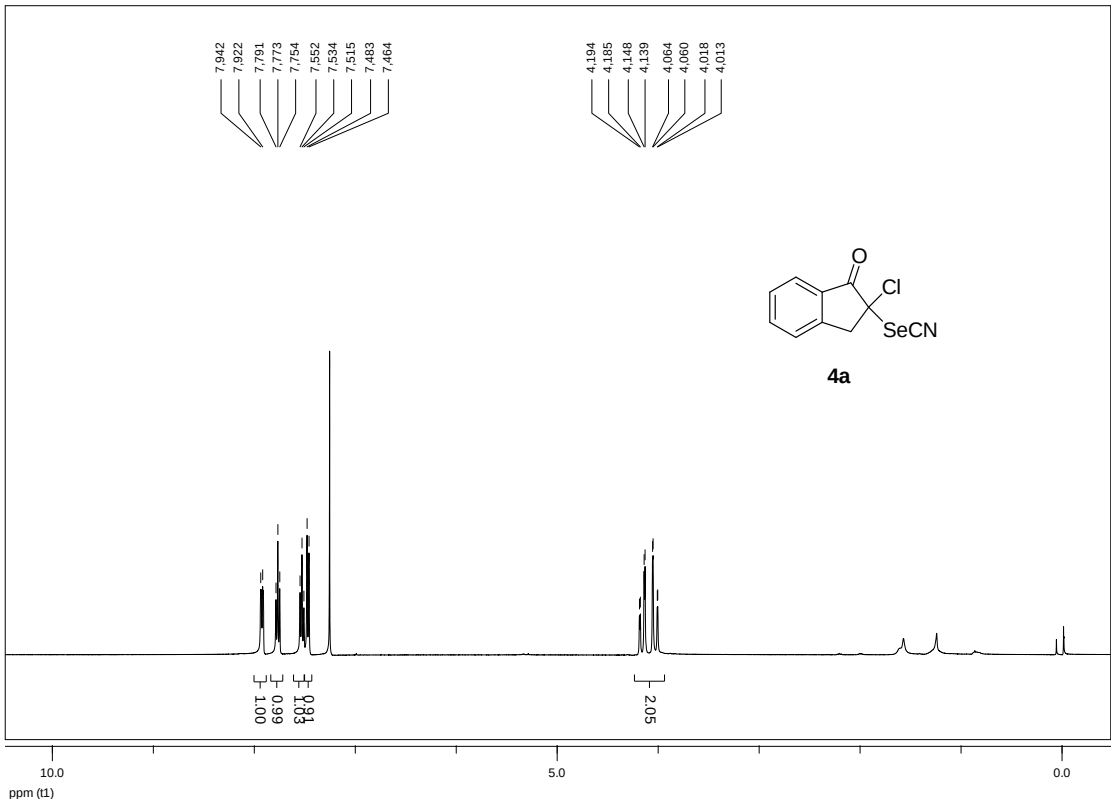
7,930
7,795
7,793
7,776
7,774
7,757
7,755
7,558
7,539
7,521
7,482
7,462
4,176
4,130
4,108
4,062
O
Br
SCN
2j
1,06
1,07
3,38
0,98
2,00
10.0
5.0
0.0
ppm (t1)


192,278
147,254
137,377
130,182
129,393
126,645
126,247
108,708
61,461
47,974
O
Br
SCN
2j
200
150
100
50
0
ppm (t1)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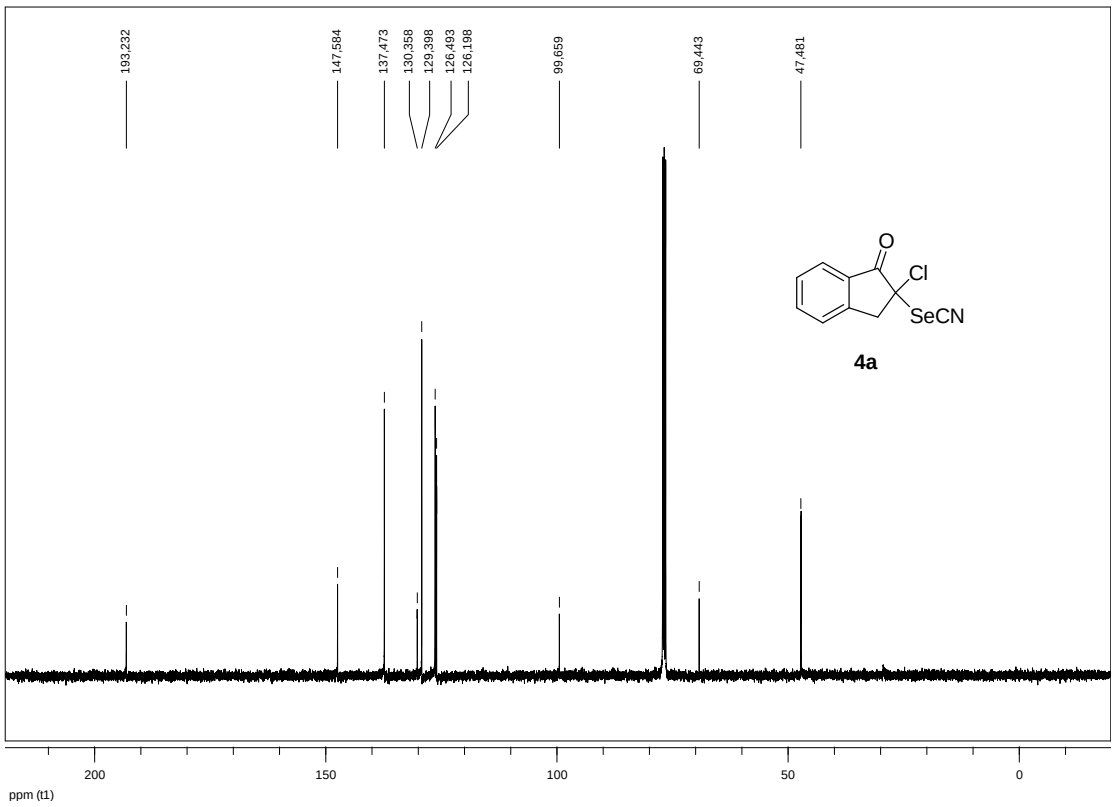
7,922
7,791
7,773
7,754
7,552
7,534
7,515
7,483
7,464
4,194
4,185
4,148
4,139
4,064
4,060
4,018
4,013
O
Cl
SeCN
4a
1,00
0,99
1,03
0,81
2,05
10.0
5.0
0.0
ppm (t1)


193,232
147,584
137,473
130,358
129,398
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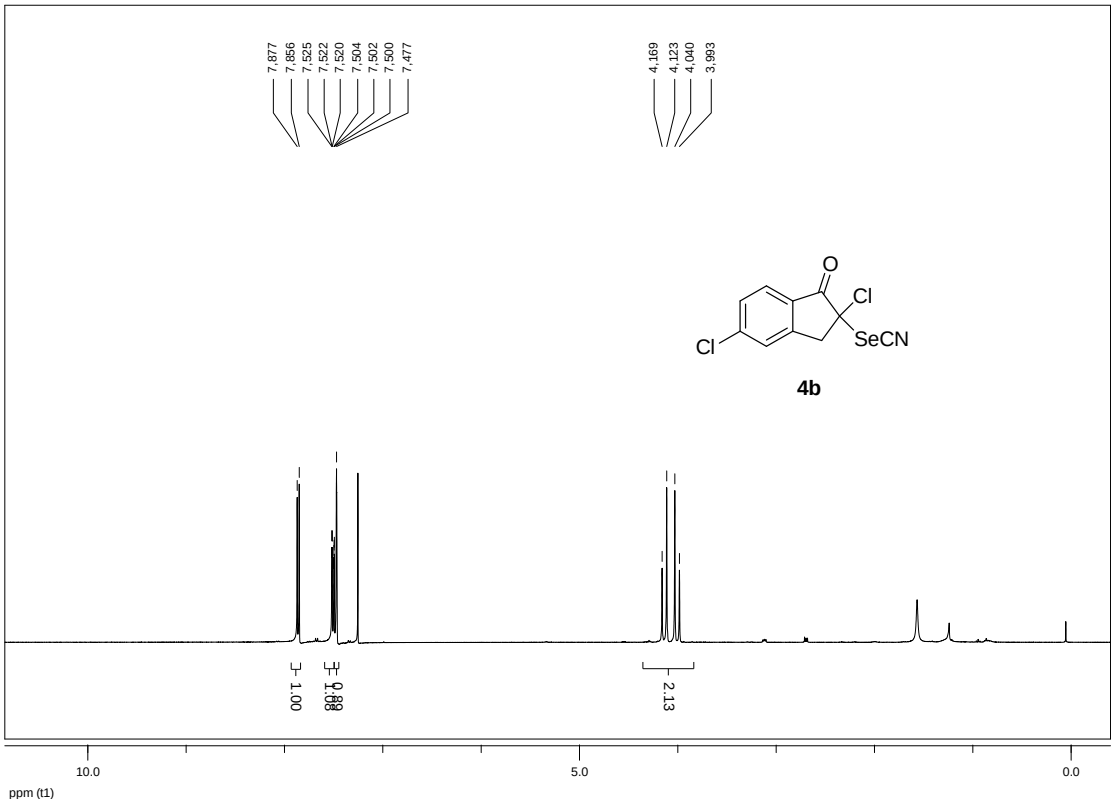
126,198
99,659
69,443
47,481
O
Cl
SeCN
4a
200
150
100
50
0
ppm (t1)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7,856
7,525
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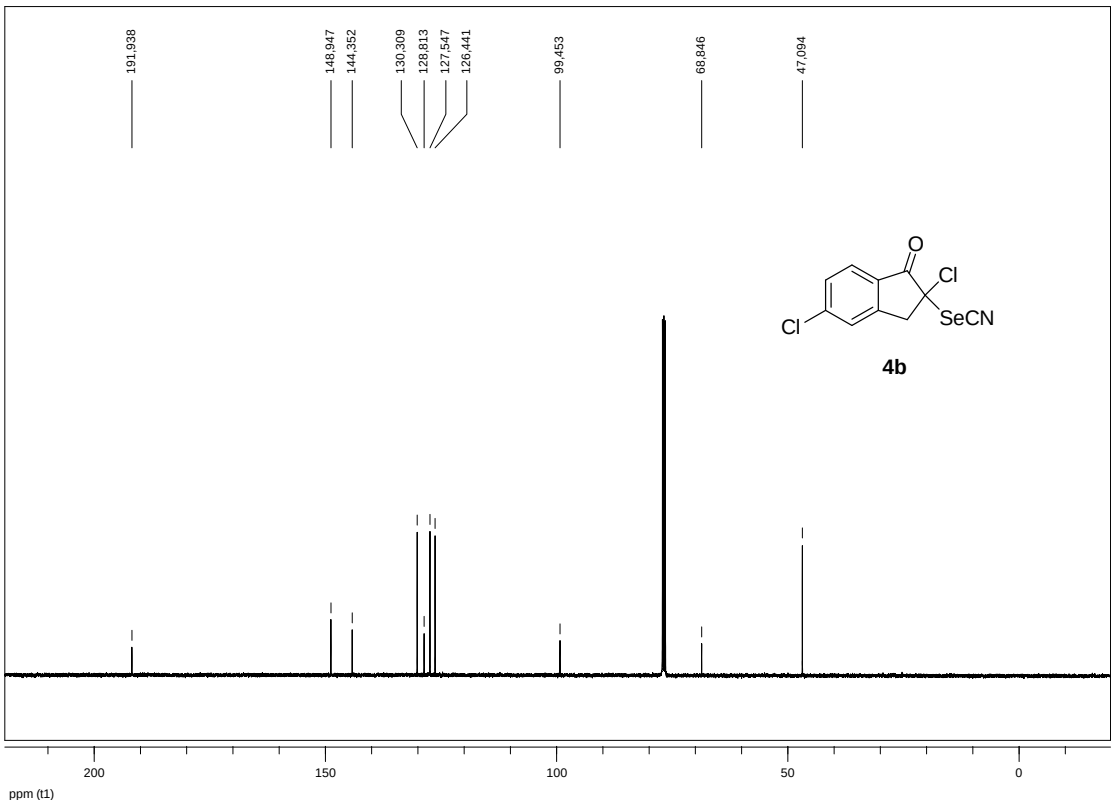
7,520
7,504
7,502
7,500
7,477
4,169
4,123
4,040
3,993
O
Cl
Cl
SeCN
4b
1.00
1.08
2.13
10.0
5.0
0.0
ppm (t1)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148,947
144,352
130,309
128,813
127,547
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47,094
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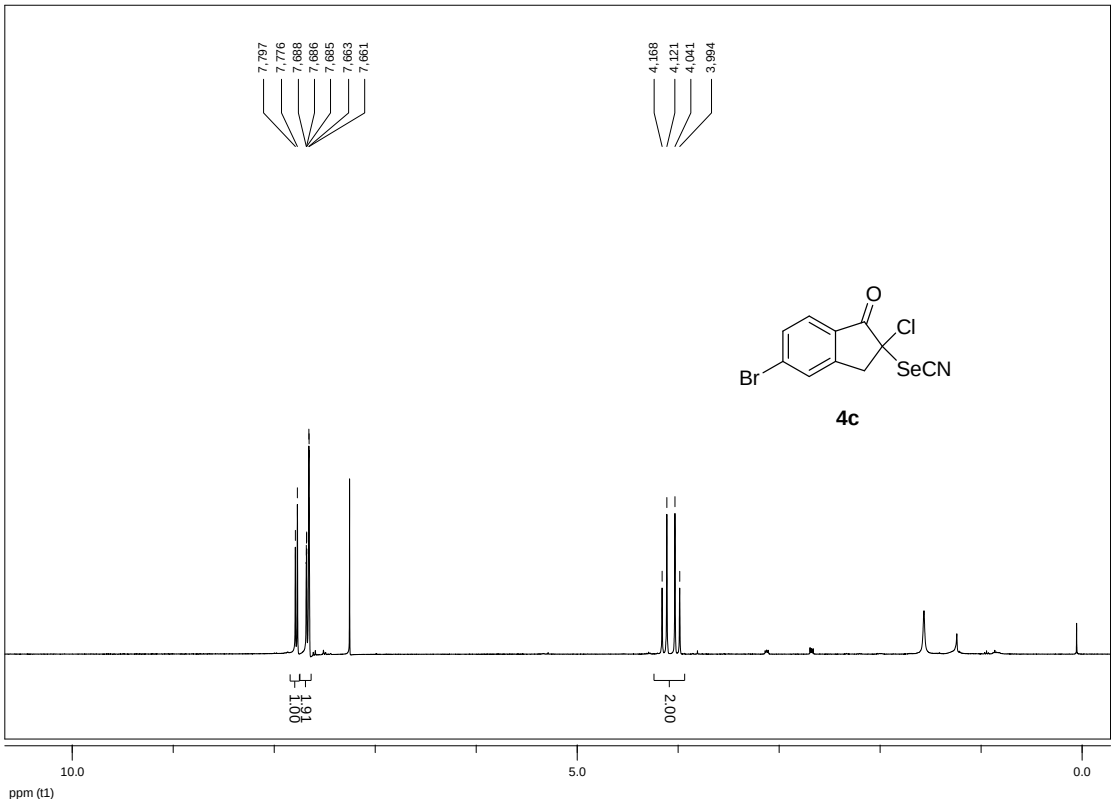
Cl
Cl
SeCN
4b
200
150
100
50
0
ppm (t1)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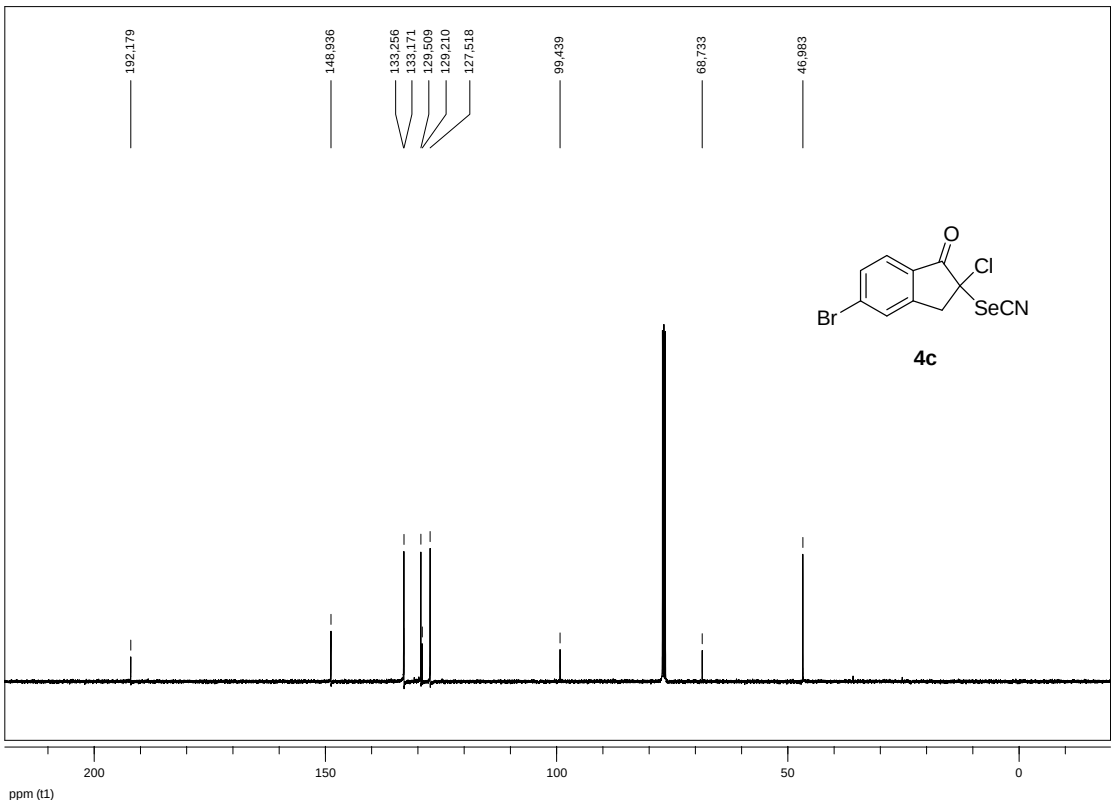
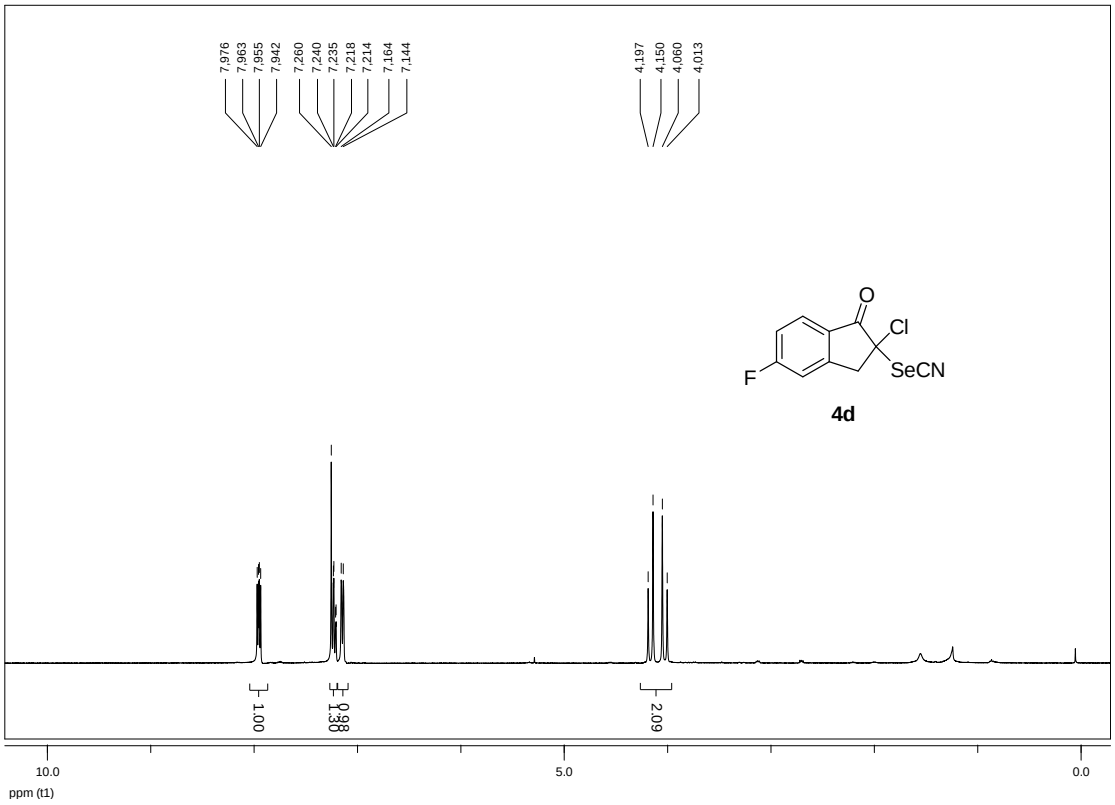
7,776
7,688
7,686
7,685
7,663
7,661
4,168
4,121
4,041
3,994
O
Cl
Br
SeCN
4c
1,91
1,00
2,00
10.0
5.0
0.0
ppm (t1)


192,179
148,936
133,256
133,171
129,509
129,210
127,518
99,439
68,733
46,983
O
Cl
Br
SeCN
4c
200
150
100
50
0
ppm (t1)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7,955
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7,260
7,240
7,235
7,218
7,214
7,164
7,144
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4,150
4,060
4,013
O
Cl
F
SeCN
4d
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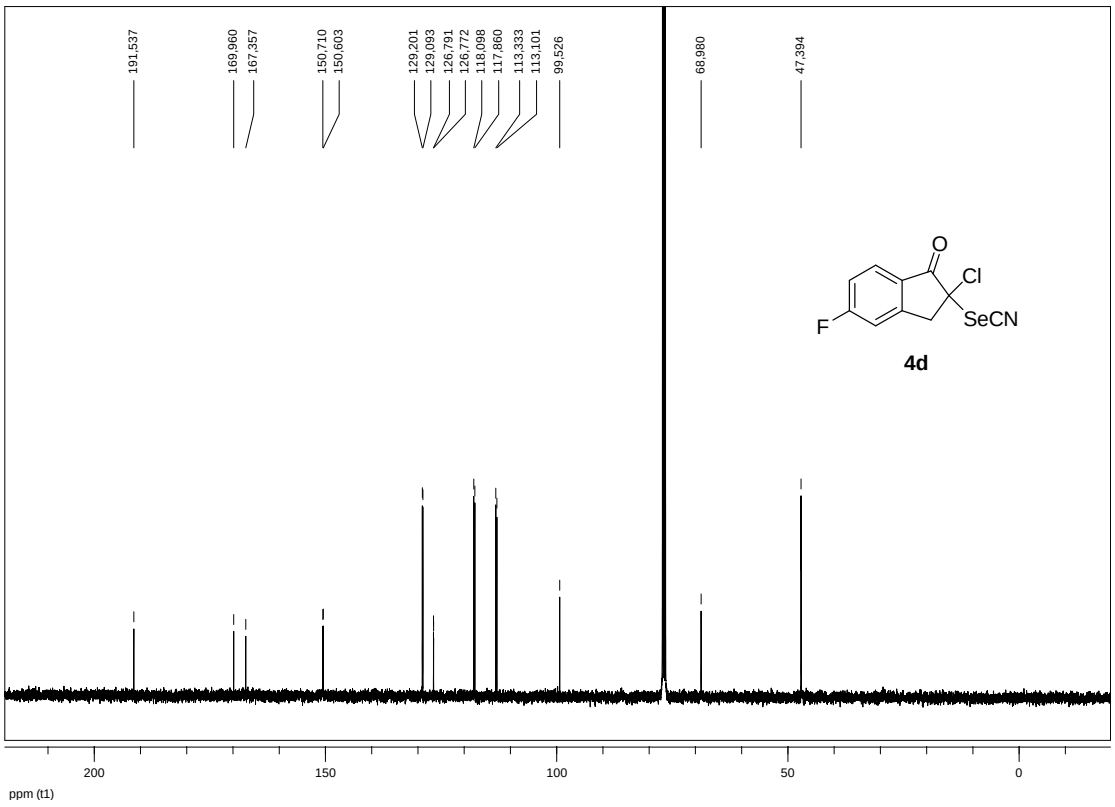
0.98
1.30
2.09
10.0
5.0
0.0
ppm (t1)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169,960
167,357
150,710
150,603
129,201
129,093
126,791
126,772
118,098
117,860
113,333
113,101
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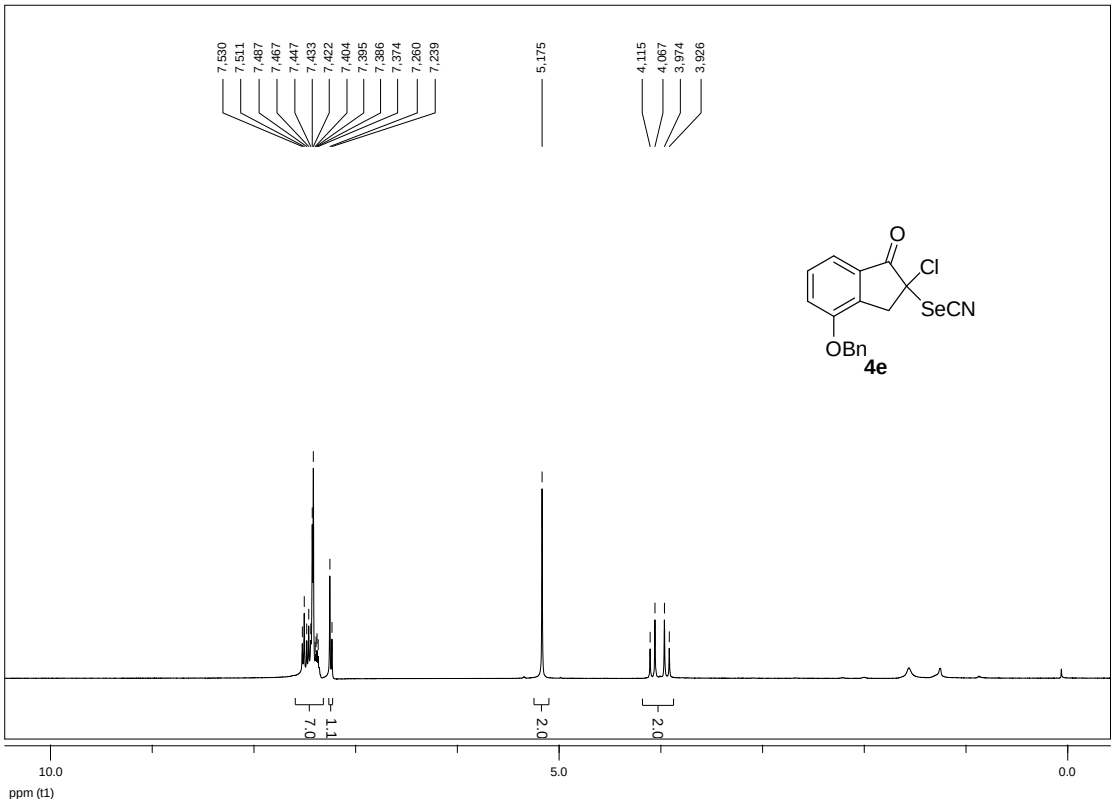
68,980
47,394
O
Cl
F
SeCN
4d
200
150
100
50
0
ppm (t1)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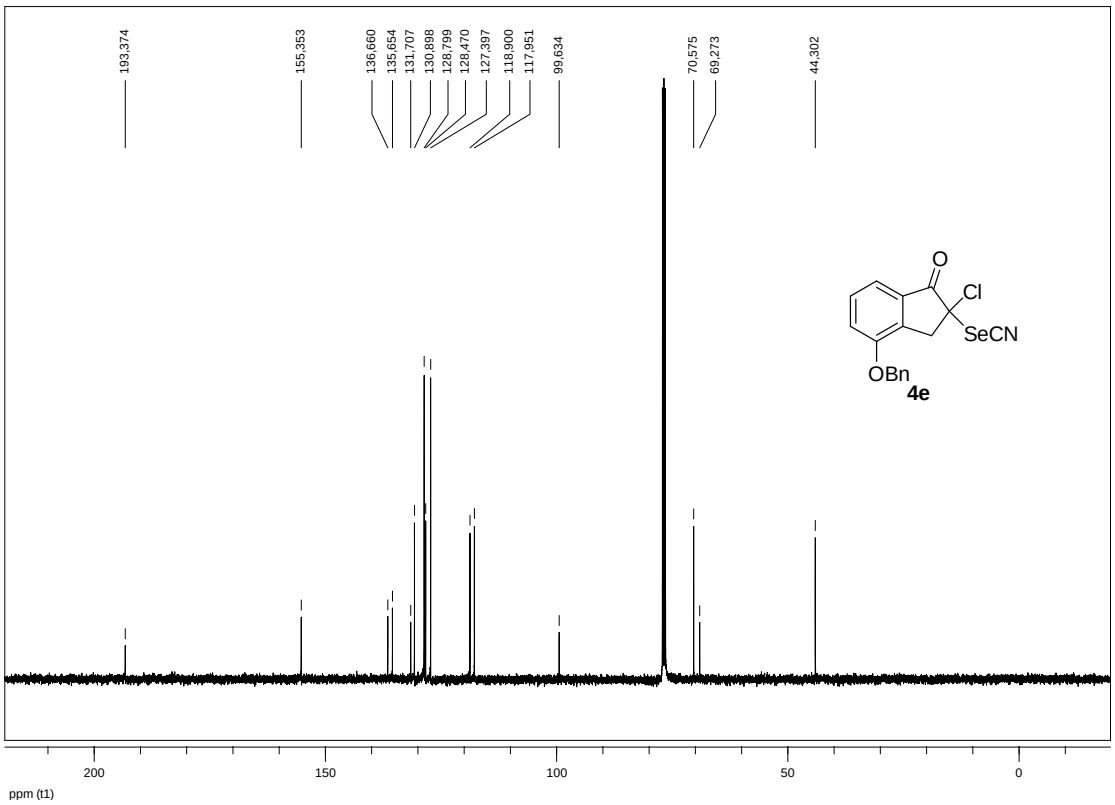
7,467
7,447
7,433
7,422
7,404
7,395
7,386
7,374
7,260
7,239
5,175
4,115
4,067
3,974
3,926
O
Cl
SeCN
OBn
4e
7,0
1,1
2,0
2,0
10.0
5.0
0.0
ppm (t1)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135,654
131,707
130,898
128,799
128,470
127,397
118,900
117,951
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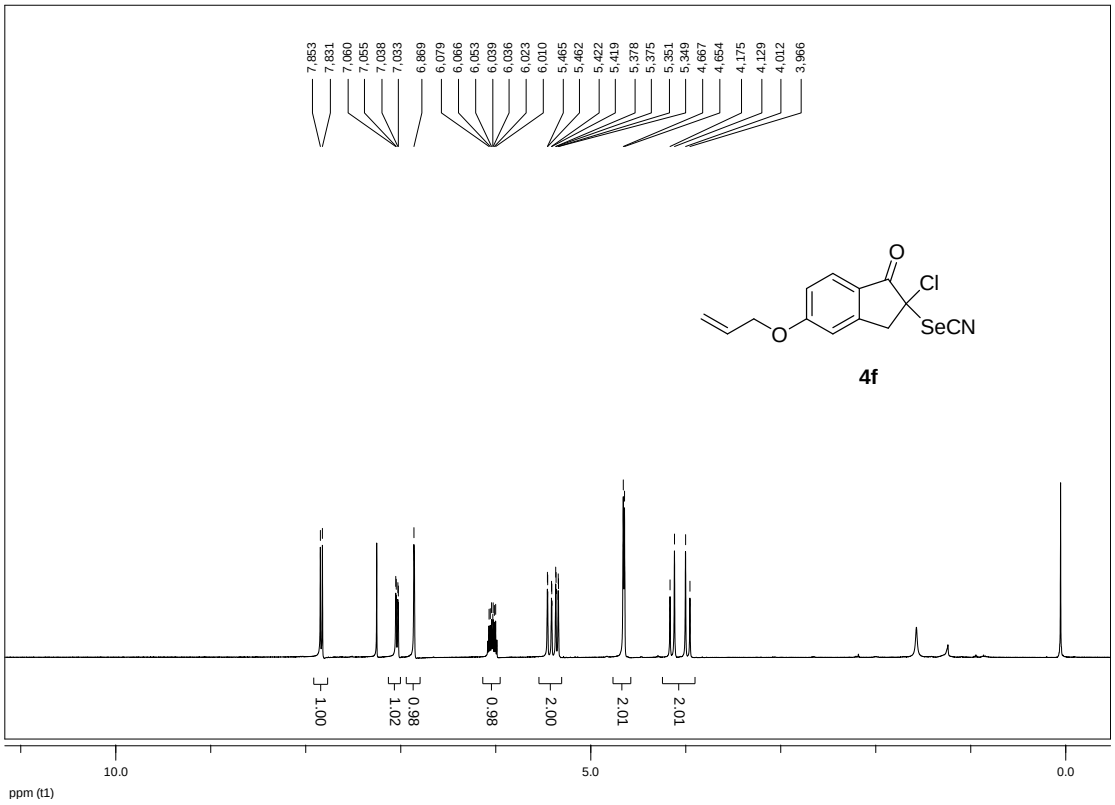
70,575
69,273
44,302
O
Cl
SeCN
OBn
4e
200
150
100
50
0
ppm (t1)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7,033
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6,079
6,066
6,053
6,039
6,036
6,023
6,010
5,465
5,462
5,422
5,419
5,378
5,375
5,351
5,349
4,667
4,654
4,175
4,129
4,012
3,966
O
Cl
SeCN
O
4f
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0.98
0.98
2.00
2.01
2.01
10.0
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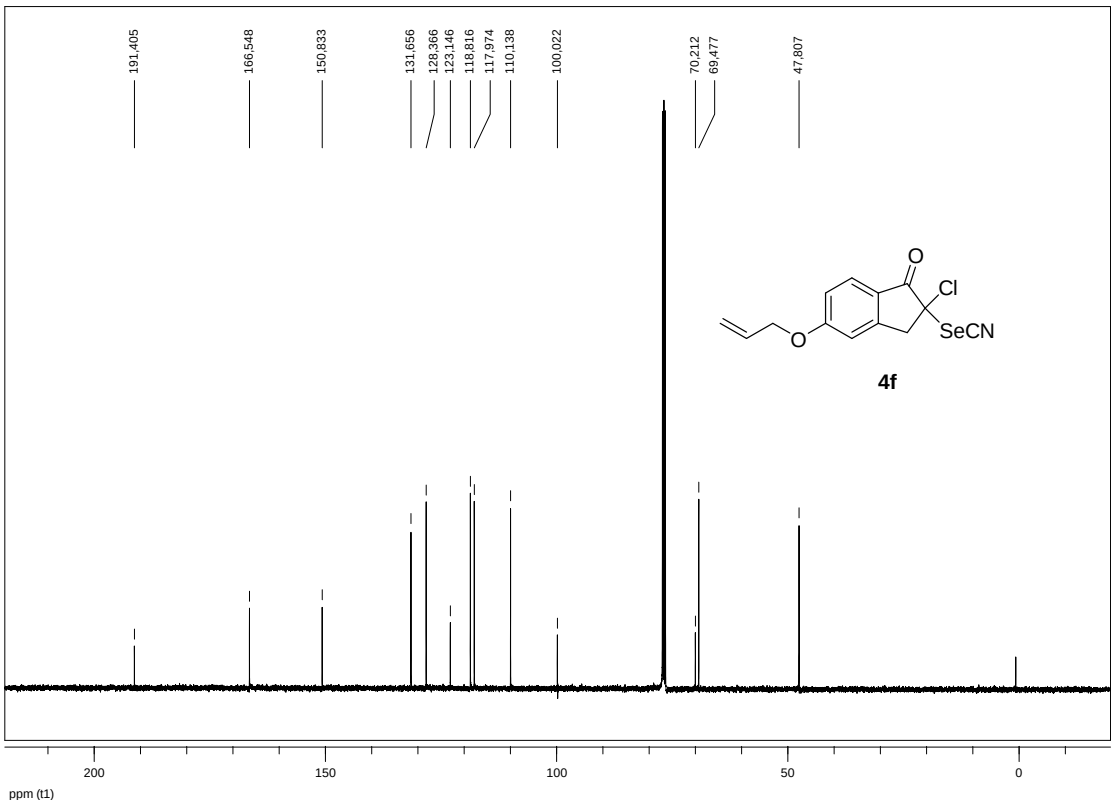
0.0
ppm (t1)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150,833
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128,366
123,146
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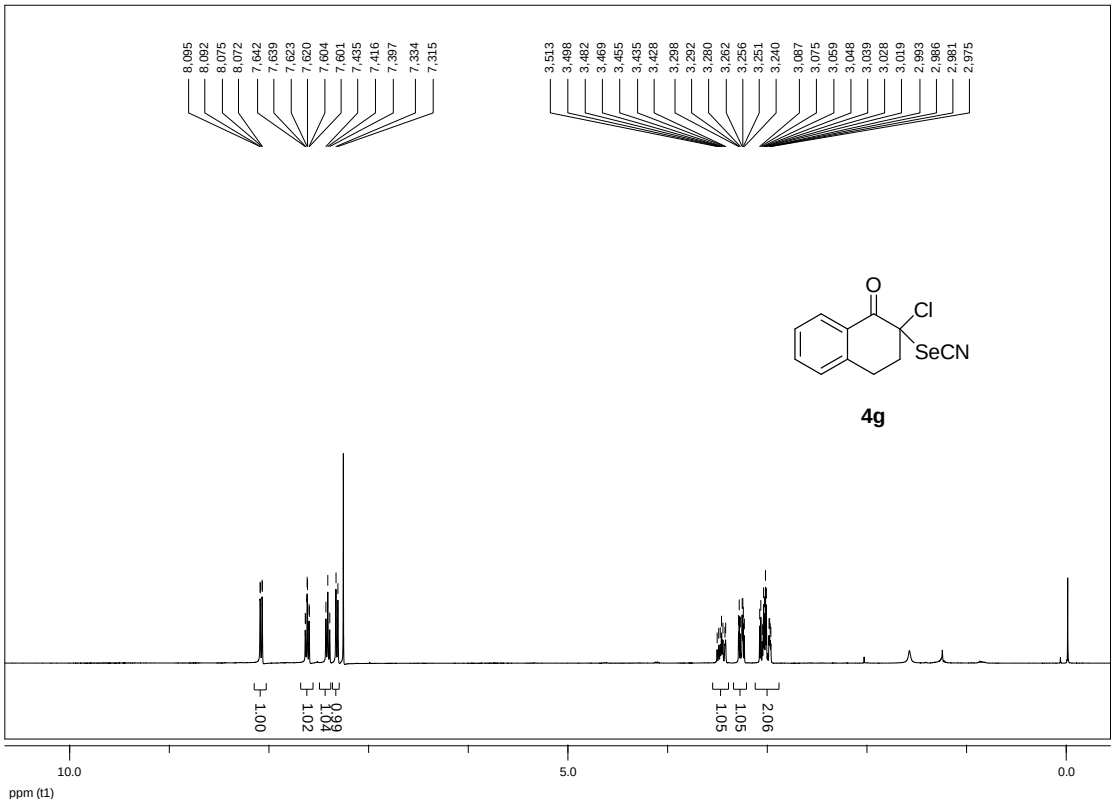
117,974
110,138
100,022
70,212
69,477
47,807
O
Cl
SeCN
O
4f
200
150
100
50
0
ppm (t1)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7,620
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7,601
7,435
7,416
7,397
7,334
7,315
3.513
3.498
3.482
3.469
3.455
3.435
3.428
3.298
3.292
3.280
3.262
3.256
3.251
3.240
3.087
3.075
3.059
3.048
3.039
3.028
3.019
2.993
2.986
2.981
2.975
O
Cl
SeCN
4g
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0.88
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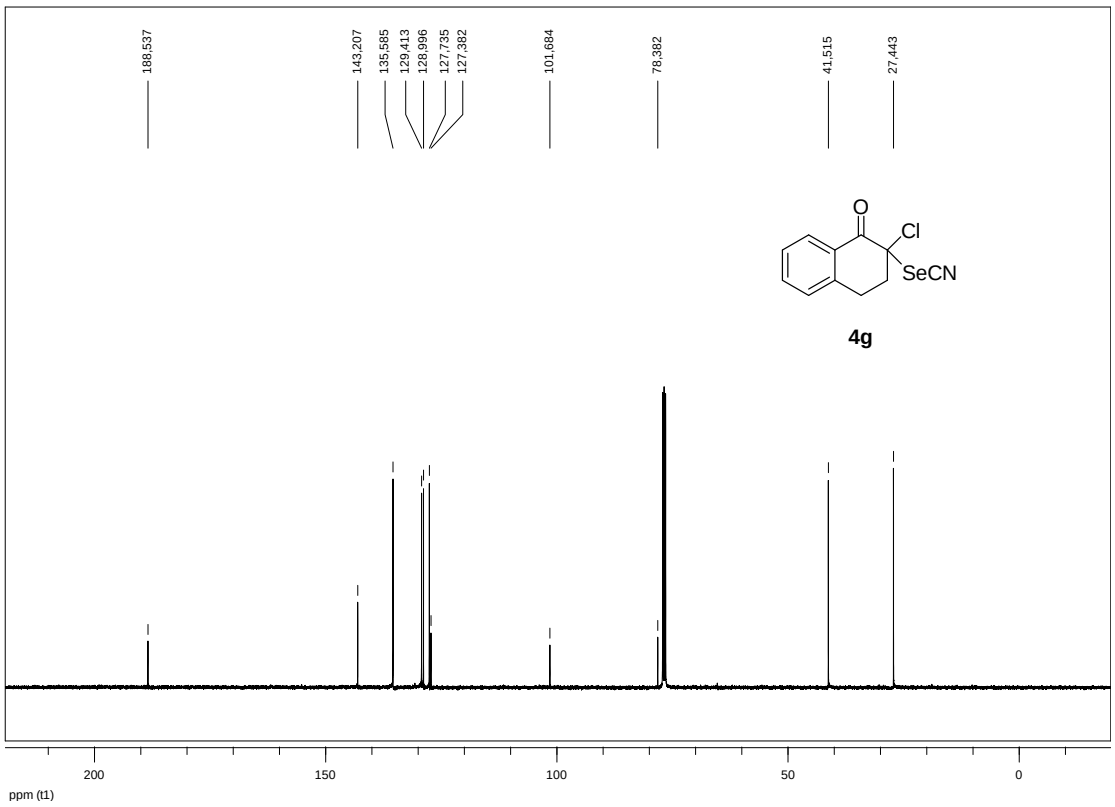
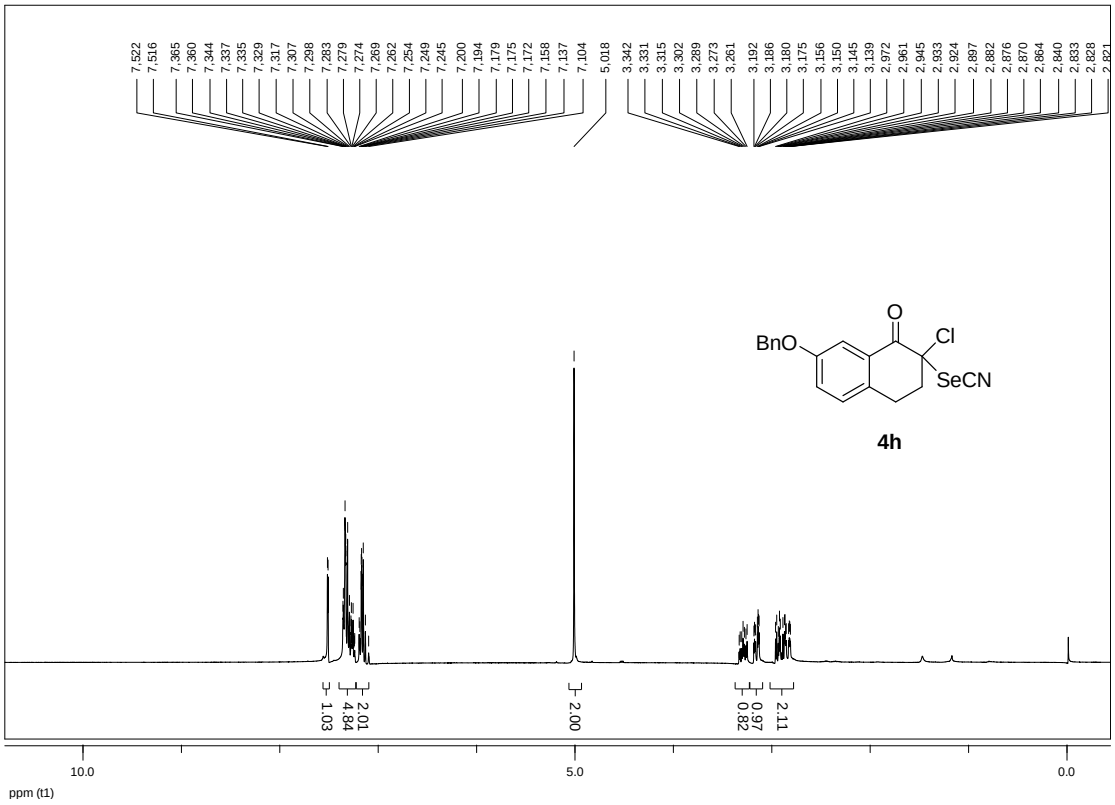
1.01
2.06
10.0
5.0
0.0
ppm (t1)


188,537
143,207
135,585
129,413
128,996
127,735
127,382
101,684
78,382
41,515
27,443
O
Cl
SeCN
4g
200
150
100
50
0
ppm (t1)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7.360
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7.335
7.329
7.317
7.307
7.298
7.283
7.279
7.274
7.269
7.262
7.254
7.249
7.245
7.200
7.194
7.179
7.175
7.172
7.158
7.137
7.104
5.018
3.342
3.331
3.315
3.302
3.289
3.273
3.261
3.192
3.186
3.180
3.175
3.156
3.150
3.145
3.139
2.972
2.961
2.945
2.933
2.924
2.897
2.882
2.876
2.870
2.864
2.840
2.833
2.828
2.821
O
BnO
Cl
SeCN
4h
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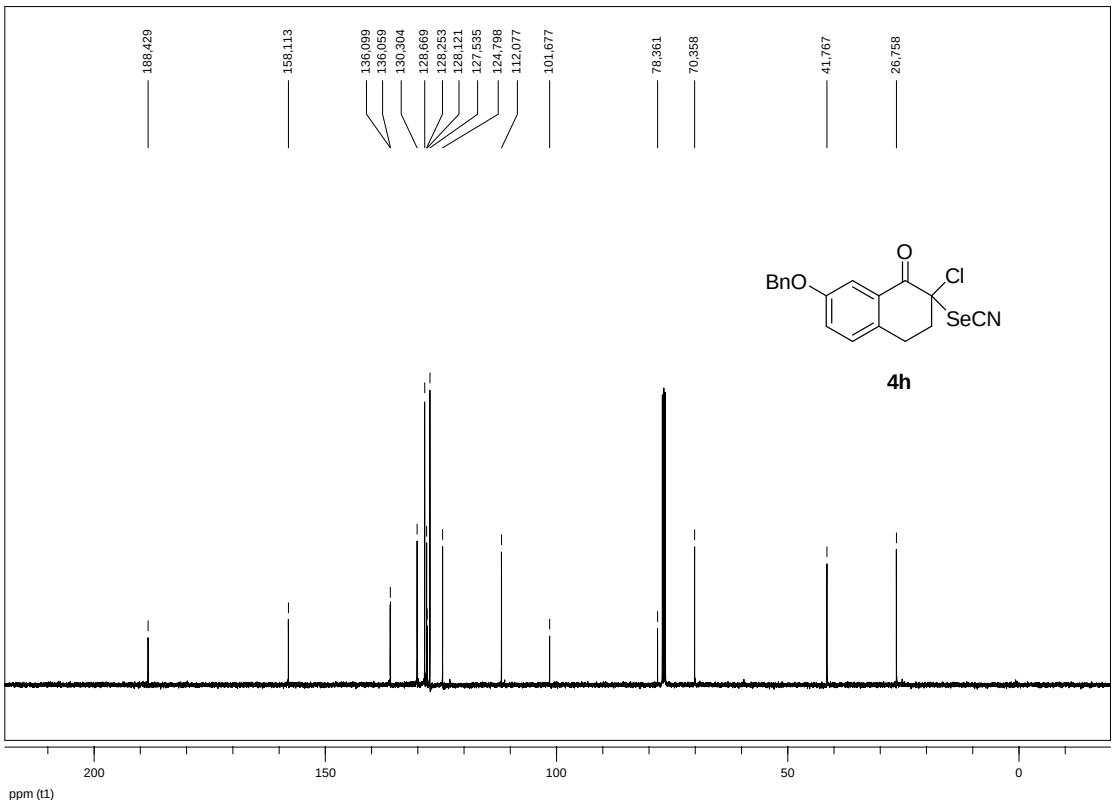
2.01
2.00
0.82
0.97
2.11
10.0
5.0
0.0
ppm (t1)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128.121
127.535
124.798
112.077
101.677
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70.358
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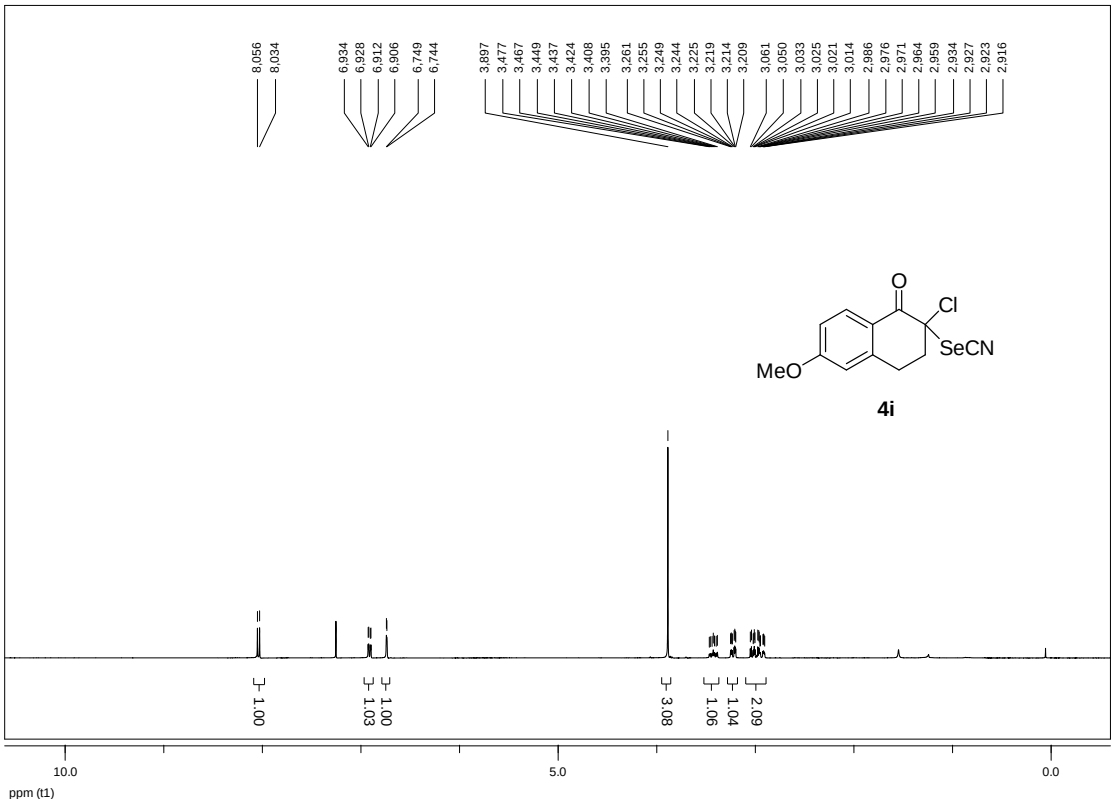
26.758
O
BnO
Cl
SeCN
4h
200
150
100
50
0
ppm (t1)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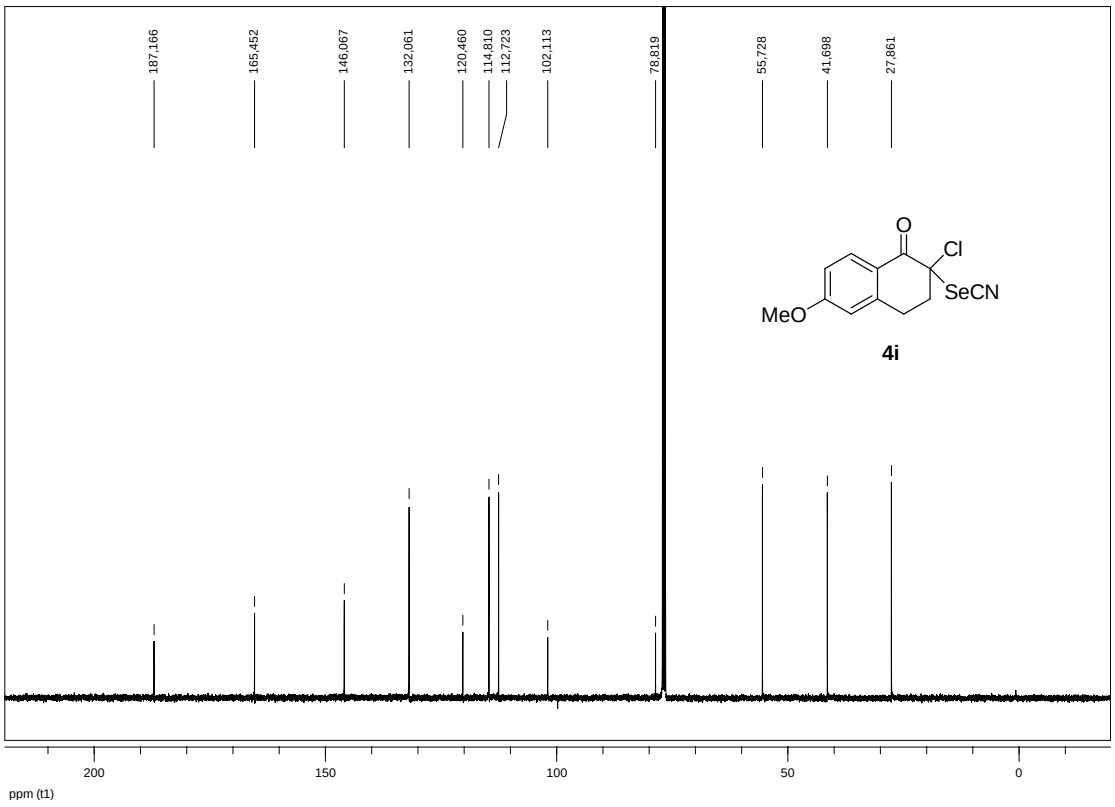
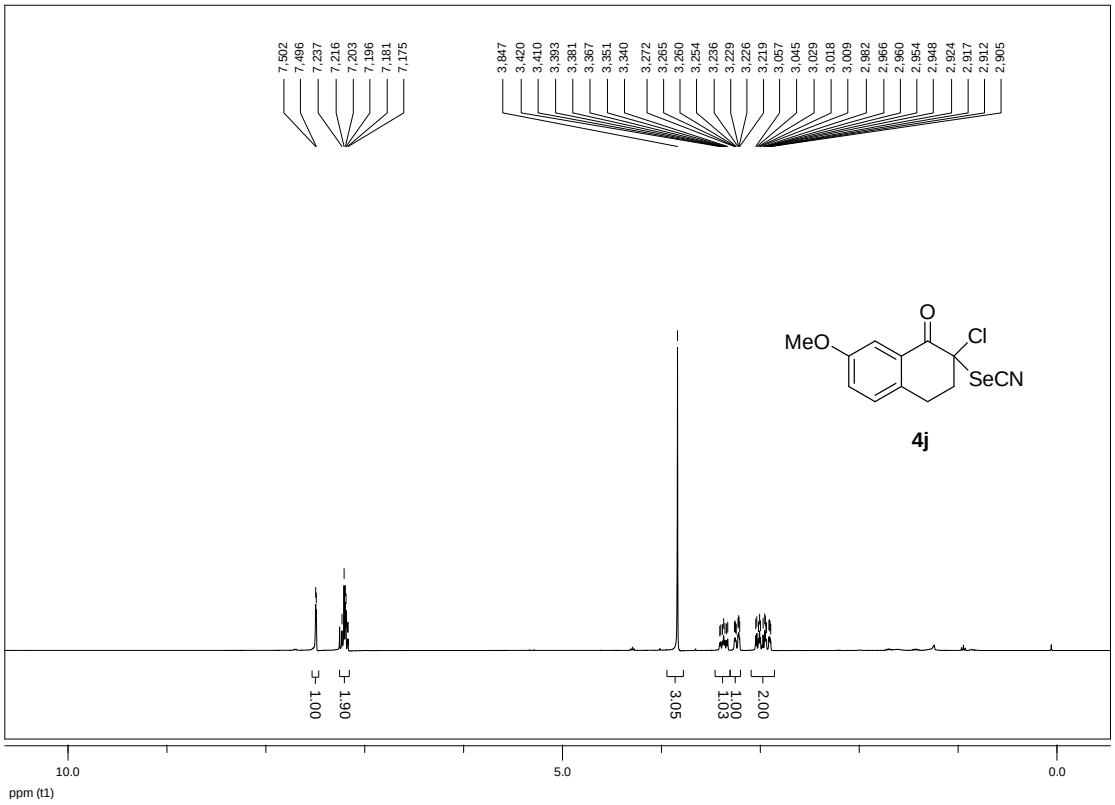
3,437
3,424
3,408
3,395
3,261
3,255
3,249
3,244
3,225
3,219
3,214
3,209
3,061
3,050
3,033
3,025
3,021
3,014
2,986
2,976
2,971
2,964
2,959
2,934
2,927
2,923
2,916
O
Cl
SeCN
MeO
4i
1,00
1,03
1,00
3,08
1,06
1,04
2,09
10.0
5.0
0.0
ppm (t1)


187,166
165,452
146,067
132,061
120,460
114,810
112,723
102,113
78,819
55,728
41,698
27,861
O
Cl
SeCN
MeO
4i
200
150
100
50
0
ppm (t1)


7.502
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7.216
7.203
7.196
7.181
7.175
3.847
3.420
3.410
3.393
3.381
3.367
3.351
3.340
3.272
3.265
3.260
3.254
3.236
3.229
3.226
3.219
3.057
3.045
3.029
3.018
3.009
2.982
2.966
2.960
2.954
2.948
2.924
2.917
2.912
2.905
O
MeO
Cl
SeCN
4j
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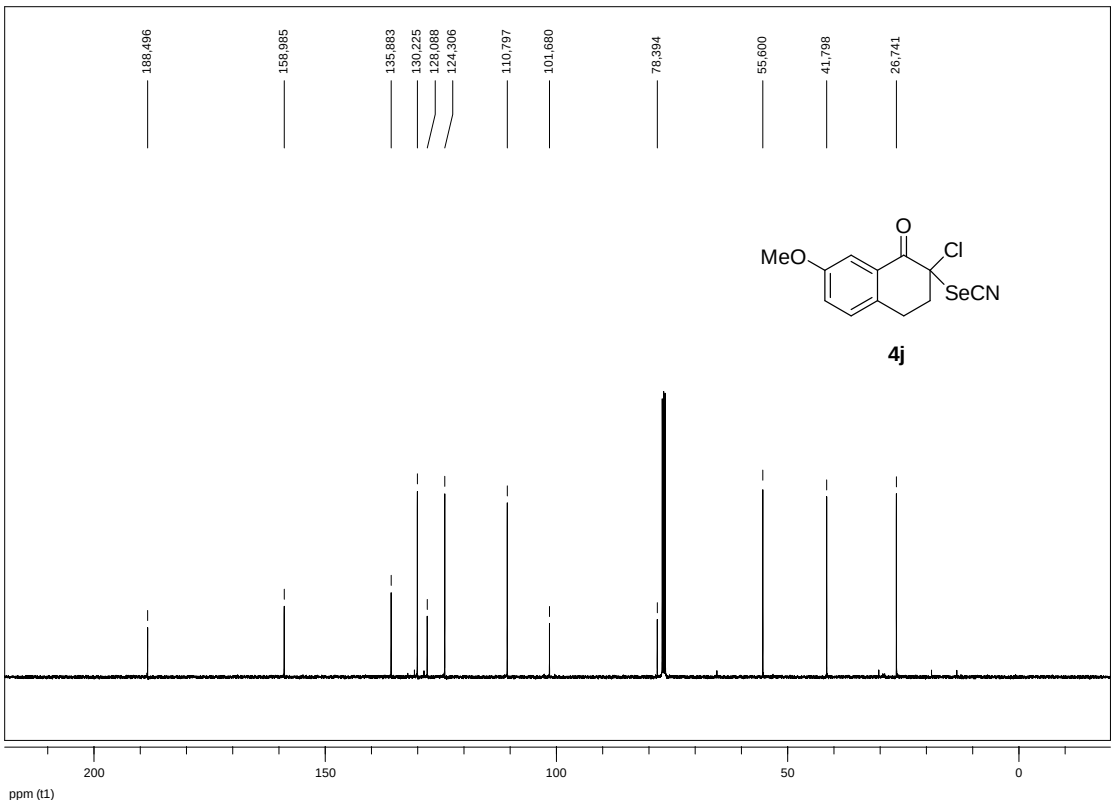
1.96
3.05
1.03
1.00
2.00
10.0
5.0
0.0
ppm (t1)


188.496
158.985
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130.225
128.088
124.306
110.797
101.680
78.394
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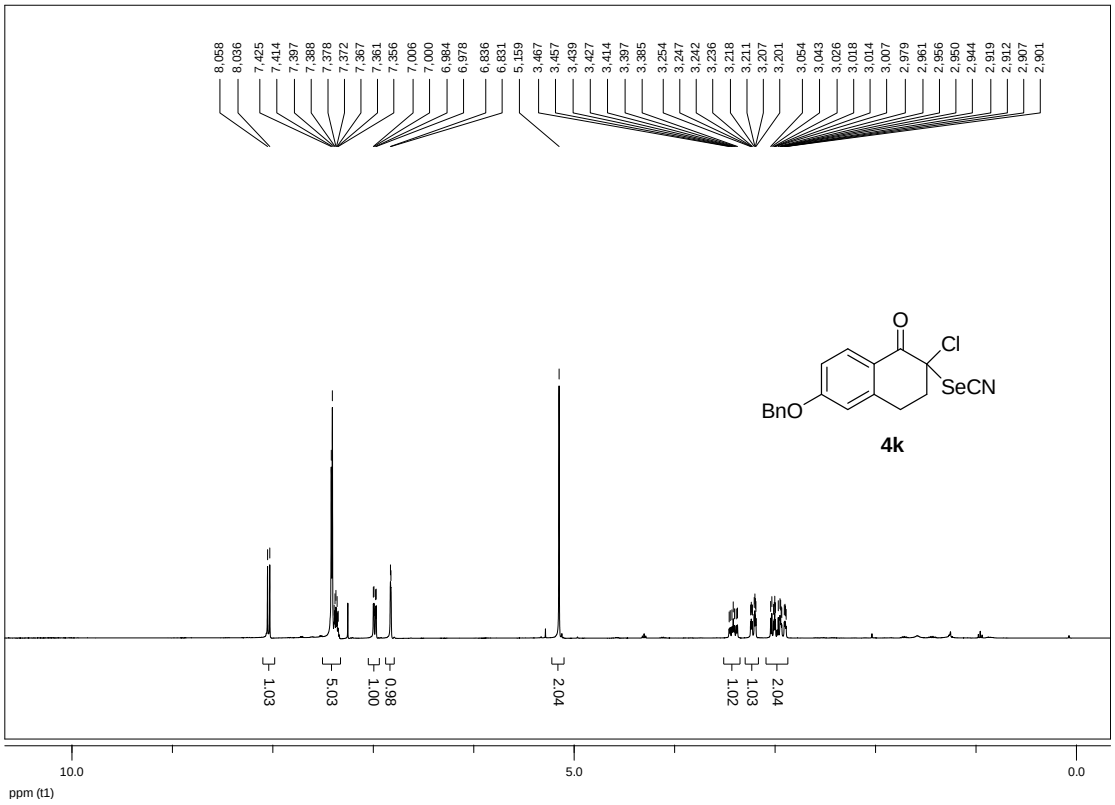
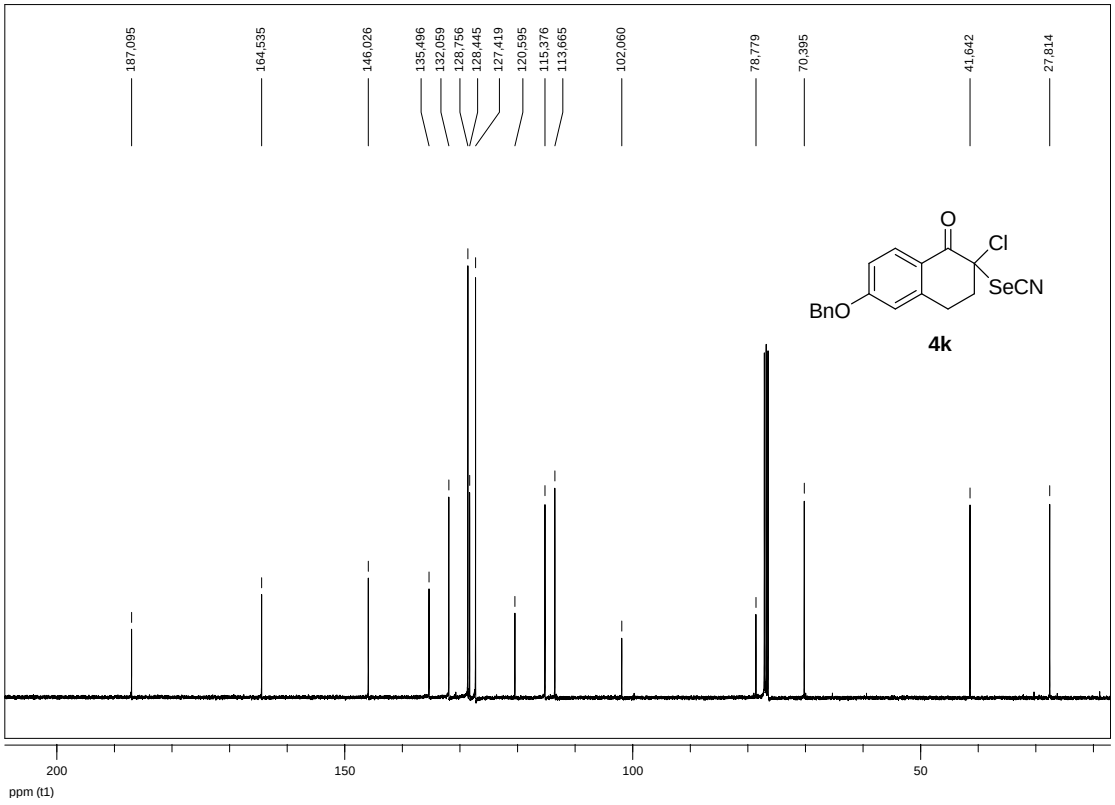
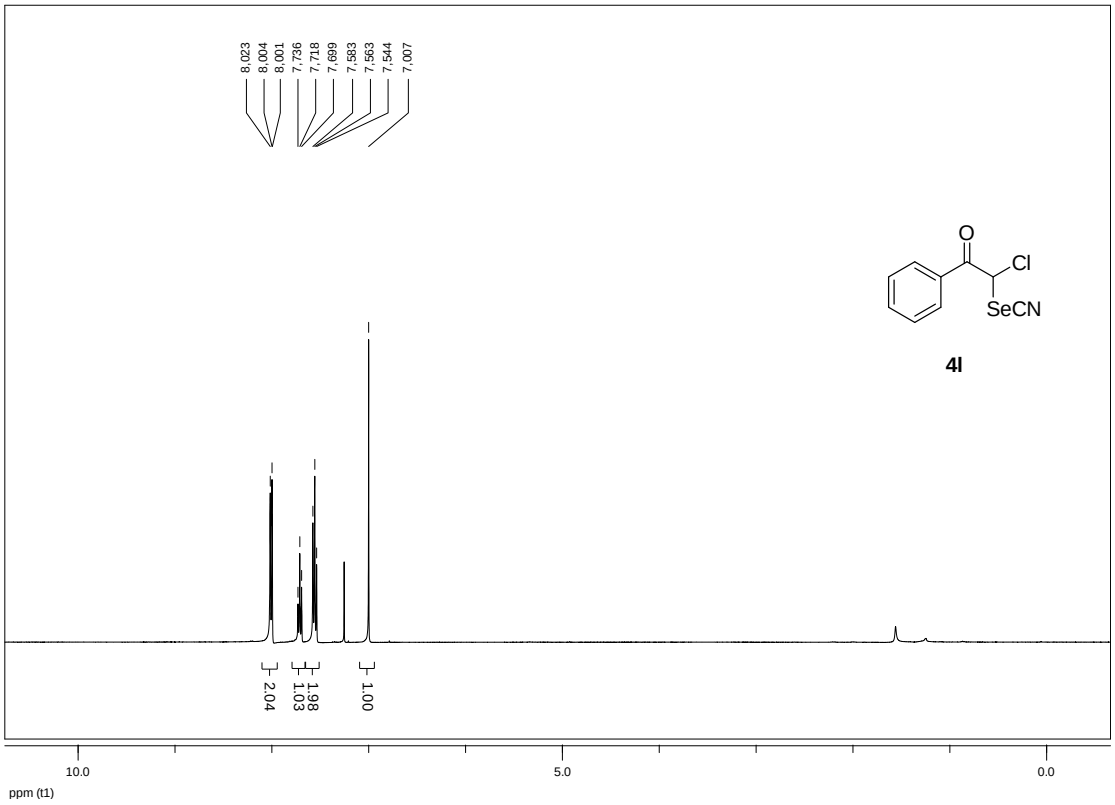
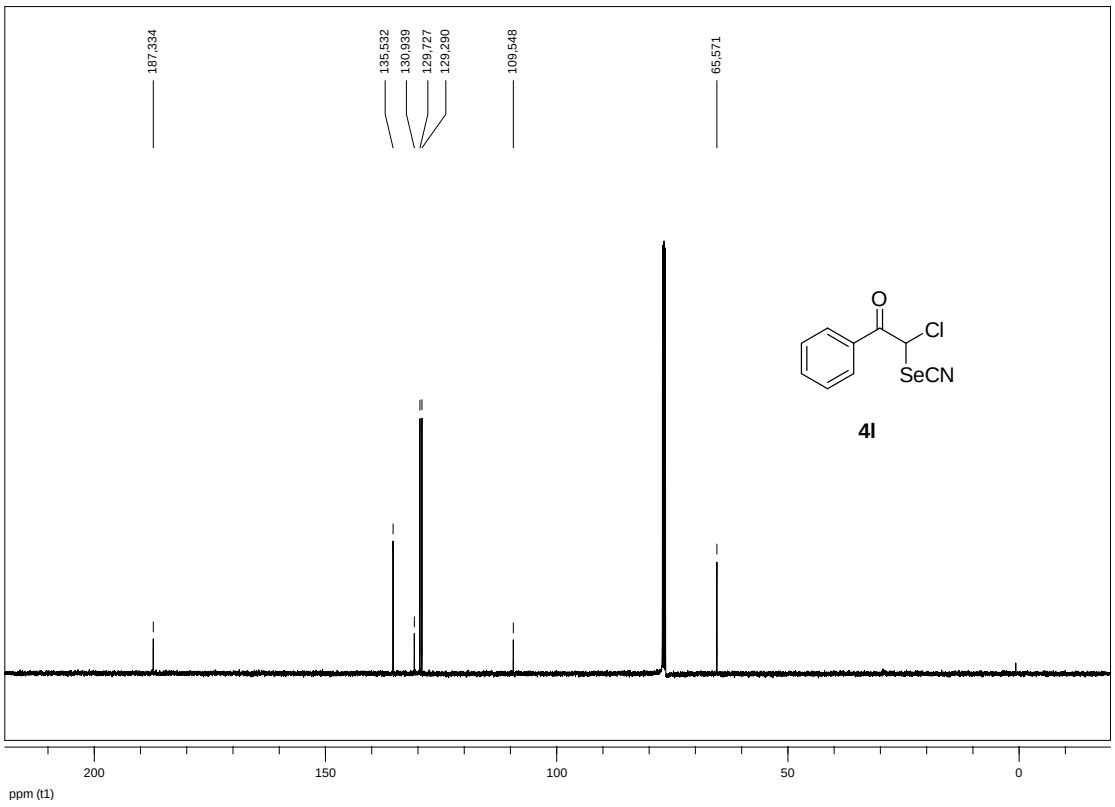
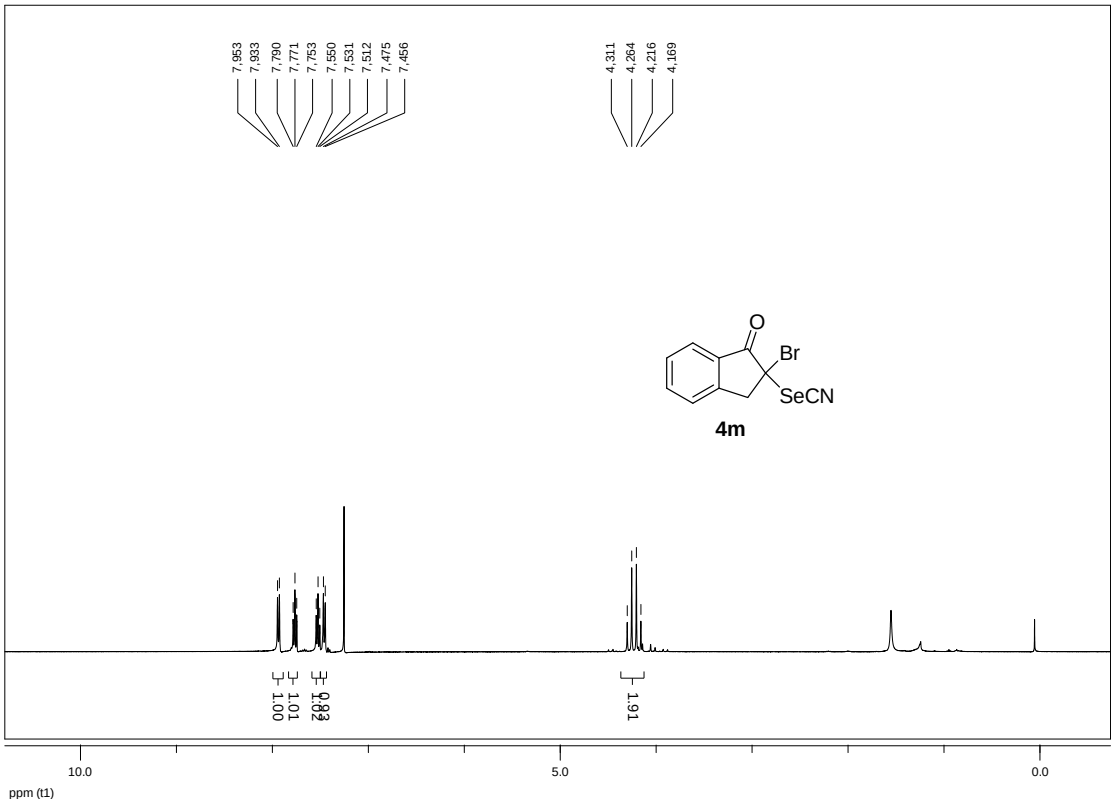
41.798
26.741
O
MeO
Cl
SeCN
4j
200
150
100
50
0
ppm (t1)

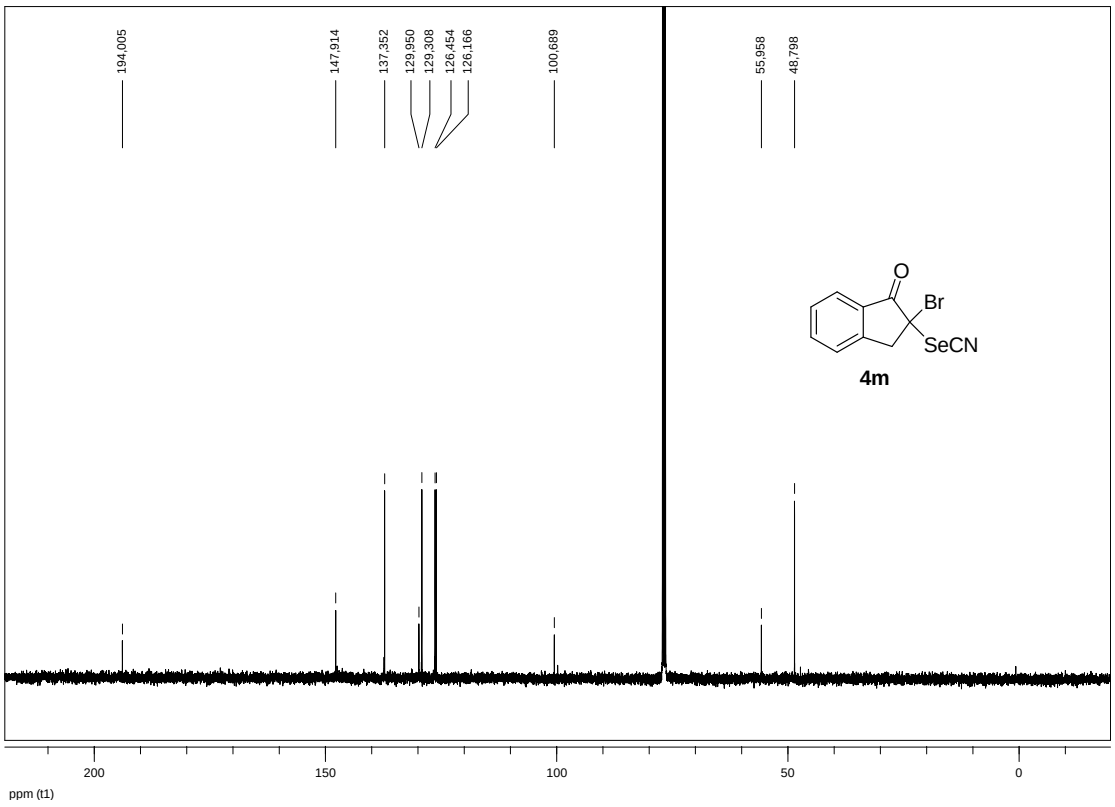

8.058
8.036
7.425
7.414
7.397
7.388
7.378
7.372
7.367
7.361
7.356
7.006
7.000
6.984
6.978
6.836
6.831
5.159
3.467
3.457
3.439
3.427
3.414
3.397
3.385
3.254
3.247
3.242
3.236
3.218
3.211
3.207
3.201
3.054
3.043
3.026
3.018
3.014
3.007
2.979
2.961
2.956
2.950
2.944
2.919
2.912
2.907
2.901
O
Cl
SeCN
BnO
4k
1.03
5.03
1.00
0.98
2.04
1.02
1.03
2.04
10.0
5.0
0.0
ppm (t1)


187.095
164.535
146.026
135.496
132.059
128.756
128.445
127.419
120.595
115.376
113.665
102.060
78.779
70.395
41.642
27.814
O
Cl
SeCN
BnO
4k
200
150
100
50
ppm (t1)


8.023
8.004
8.001
7.736
7.718
7.699
7.583
7.563
7.544
7.007
O
Cl
SeCN
4l
2.04
1.03
1.98
1.00
10.0
5.0
0.0
ppm (t1)


187.334
135.532
130.939
129.727
129.290
109.548
65.571
O
Cl
SeCN
4l
200
150
100
50
0
ppm (t1)


7,953
7,933
7,790
7,771
7,753
7,550
7,531
7,512
7,475
7,456
4,311
4,264
4,216
4,169
O
Br
SeCN
4m
1.00
1.01
0.93
0.83
1.91
10.0
5.0
0.0
ppm (t1)


194,005
147,914
137,352
129,950
129,308
126,454
126,166
100,689
55,958
48,798
O
Br
SeCN
4m
200
150
100
50
0
ppm (t1)