Electronic Supplementary Information

The CF_3-DAST-induced deacylative trifluoromethylthiolation of cyclic 1,3-diketones/lactams/lactones and its extension to deacylative pentafluorophenylthiolations

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1. Experimental Section

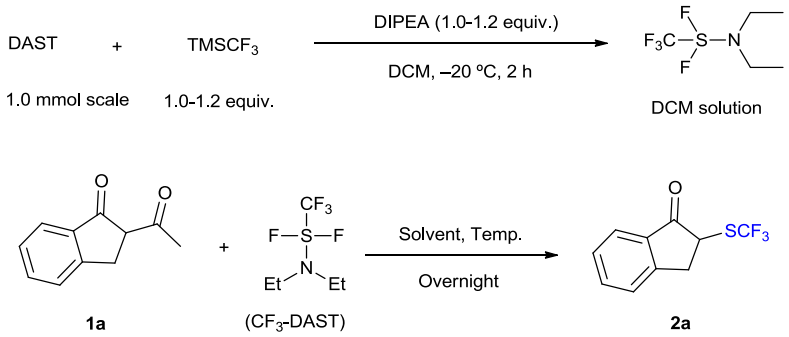
1.1 General Methods

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels though a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 μm. The ^{1}H-NMR (300 MHz), ^{19}F-NMR (282 MHz), ^{13}C-NMR (125.7 MHz) spectra for solution in $CDCl_3$ were recorded on a Buruker Avance 500, Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS (δ = 0.00). The C_6F_6 [δ = −162.2 ($CDCl_3$)] was used as internal standard for ^{19}F NMR. High resolution mass spectrometry was recorded on a Waters Synapt G2 HDMS (ESI-MS, EI-MS). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Melting point were recorded on a BUCHI M-565. All solvents were dried and distilled before use.

DAST [(Diethylamino)sulfur Trifluoride] (Purity: >90.0%) was purchased from Tokyo Chemical Industry Co., Ltd., Japan.

2. Optimization of trifluoromethylthiolation reaction condition;

2.1 Table S1. Optimization of reaction condition. [a]

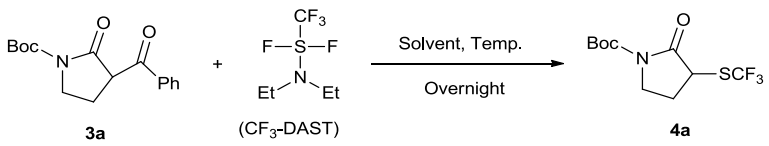


Entry	Solvent	Temp. (°C)	CF_3-DAST (equiv.)	CF_3-DAST (M)	Yield (%)[b]
1	DCM	rt	2.0	0.5	19
2	THF	rt	2.0	0.5	23
3	MeCN	rt	2.0	0.5	14
4	Toluene	rt	2.0	0.5	trace
5	DCM	reflux	2.0	0.5	trace
6	THF	reflux	2.0	0.5	trace
7	DCM	–40	2.0	0.5	64
8	Et_2O	–40	2.0	0.5	41
9	MeCN	–40	2.0	0.5	37
10	DCM	–40	2.0	1.0	59
11	DCM	–40	2.0	0.25	82
12[c]	DCM	–40	1.2	0.5	69
13[c]	DCM	–40	1.5	0.5	71

14[c]	DCM	–40	2.0	0.5	72
15[c]	DCM	–40	2.5	0.5	64
16[d]	DCM	–40	2.0	0.5	83
17[d]	DCM	–40	2.0	0.25	78

[a] The reaction of **1a** with CF_3-DAST was carried out in different solvents at different temperatures. [b] The yield was determined by ^{19}F NMR spectroscopy with an internal standard, $C_6H_5CF_3$. [c] 1.2 equivalent of base was used for preparation of reagent. [d] 1.2 equivalent of $TMSCF_3$ was used for preparation of reagent.

2.2 Table S2. Optimization of reaction condition.[a]



Entry	Solvent	Temp. (℃)	CF_3-DAST (equiv.)	Yield (%)[b]
1	DCM	rt	2.0	82
2	DCM	–40	2.0	61
3	DCM	40	2.0	78
4	DCE	rt	2.0	47
5	THF	rt	2.0	21
6	Et_2O	rt	2.0	23
7	CH_3CN	rt	2.0	88
8	DMF	rt	2.0	72
9	toluene	rt	2.0	7
10	dioxane	rt	2.0	trace
11	CH_3CN	–20	2.0	71

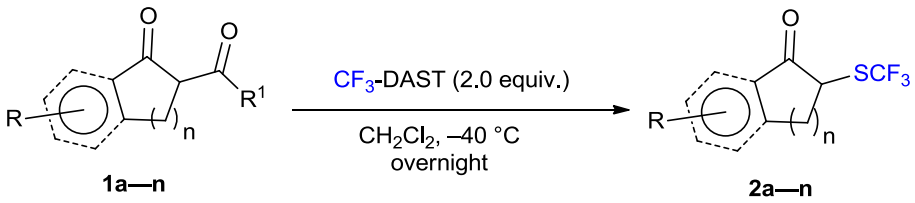
12	CH_3CN	40	2.0	66
13	CH_3CN	rt	1.2	71
14	CH_3CN	rt	1.5	78
15[c]	CH_3CN	rt	2.0	82
16[d]	CH_3CN	rt	2.0	40

[a] The reaction of **3a** with CF_3-DAST was carried out in different solvents at different temperatures. [b] The yield was determined by ^{19}F NMR spectroscopy with an internal standard, $C_6H_5CF_3$. [c] MS 4Å was added to the reaction system. [d] $MgSO_4$ was added to the reaction system.

3. Typical procedure preparation of R_f-DAST reagents

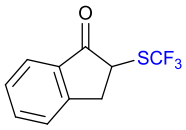
A flame-dried vessel was charged with diisopropylethylamine (1.2 equivalent) and anhydrous dichloromethane (2 mL, 0.5 M), cooled to –20 °C under the nitrogen atmosphere. The diethylamino sulfur trifluoride (DAST) (1.0 mmol, 1.0 equivalent) was added and stirred for 15 min at the same temperature, then the trimethylsilyl trifluoromethane ($TMSCF_3$) or trimethyl(perfluorophenyl)silane ($TMSC_6F_5$) (1.2 mmol, 1.2 equivalent) was added slowly by syringe. The mixture was stirred for two hours under the same reaction temperature. After two hours, the solution was directly used for next step without purification.

4. General procedure and product characterization data for Scheme 2.



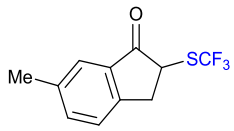
A flame-dried vessel was charged with 1,3-diketones **1a—1n** (1.0 equivalent) and anhydrous CH_2Cl_2 (0.1 M) under nitrogen gas atmosphere. The solution was cooled to –40 °C and the 0.5 M solution of CF_3-DAST in CH_2Cl_2 (2.0 equivalents taken from the solution above mentioned) was added slowly by syringe. Then the reaction mixture was stirred at –40 °C for overnight, quenched by addition of water, extracted with ethyl acetate, dried over with Na_2SO_4 and then concentrated. The crude product was purified by flash column chromatography to provide the title compound **2a—2n.**

4.1 2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (2a);



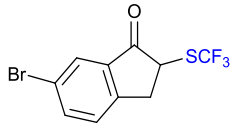
Following the general procedure, using substrate **1a—1d** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (1.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **2a** as a yellow oil in 44%—72% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.82 (d, 1H, *J* = 7.5 Hz), 7.68 (t, 1H, *J* = 7.0 Hz), 7.41—7.49 (m, 2H), 4.24 (dd, 1H, *J* = 8.1 Hz, *J* = 4.5 Hz), 3.79 (dd, 1H, *J* = 17.7 Hz, *J* = 8.1 Hz), 3.37 (dd, 1H, *J* = 17.7 Hz, *J* = 4.5 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -39.99 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 199.36, 151.96, 136.19, 134.71, 130.76 (q, *J* = 307.5 Hz), 128.44, 126.54, 124.93, 47.59, 36.49 ppm. IR (neat): 3079, 2927, 1725, 1606, 1465, 1276, 1112, 748 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_7F_3NaOS$ $[M+Na]^+$: 255.0067. Found: 255.0062. Spectroscopic data were in agreement with the literature.[1]

4.2 6-methyl-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (2e);



Following the general procedure, using 2-acetyl-6-methyl-2,3-dihydro-1H-inden-1-one **1e** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (1.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **2e** as a white solid in 73% yield. Mp: 51.7—52.9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.62 (s, 1H), 7.50 (d, 1H, *J* = 7.8 Hz), 7.37 (d, 1H, *J* = 7.8 Hz), 4.23 (dd, 1H, *J* = 8.1 Hz, *J* = 4.5 Hz) 3.74 (dd, 1H, *J* = 17.4 Hz, *J* = 8.1 Hz), 3.32 (dd, 1H, *J* = 17.4 Hz, *J* = 4.2 Hz), 2.42 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -40.00 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 199.42, 149.25, 138.55, 137.46, 134.81, 130.78 (q, *J* = 306.7 Hz), 126.18, 124.75, 47.90, 36.16, 21.24 ppm. IR (KBr): 3419, 2925, 1722, 1614, 1488, 1282, 1116, 755 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_9F_3NaOS$ $[M+Na]^+$: 269.0224. Found: 269.0224.

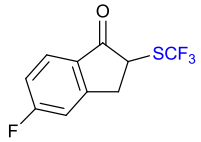
4.3 6-bromo-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (2f);



Following the general procedure, using 2-acetyl-6-bromo-2,3-dihydro-1H-inden-1-one **1f** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (1.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 25:1) to provide the title compound **2f** as a yellow oil in 41% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.94 (d, 1H, *J* = 1.0 Hz), 7.77 (dd, 1H, *J* = 8.1 Hz, *J* = 1.8 Hz), 7.37 (d, 1H, *J* = 8.1 Hz), 4.25

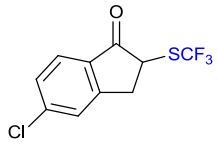
(dd, 1H, *J* = 8.1 Hz, *J* = 4.5 Hz), 3.74 (dd, 1H, *J* = 17.7 Hz, *J* = 8.1 Hz), 3.30 (dd, 1H, *J* = 17.7 Hz, *J* = 4.5 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -39.91 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 197.98, 150.28, 138.94, 136.43, 130.58 (q, *J* = 306.7 Hz), 128.06, 127.80, 122.67, 47.65, 36.05 ppm. IR (neat): 3405, 3068, 2927, 1708, 1592, 1430, 1255, 1112, 707 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_6BrF_3NaOS$ $[M+Na]^+$: 332.9173. Found: 332.9178.

4.4 5-fluoro-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (2g);



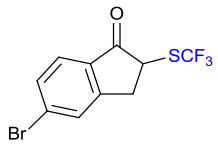
Following the general procedure, using 2-acetyl-5-fluoro-2,3-dihydro-1H-inden-1-one **1g** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (1.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **2g** as a yellow oil in 82% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.85—7.81 (m, 1H), 7.17—7.11 (m, 2H), 4.25 (dd, 1H, *J* = 8.1 Hz, *J* = 4.5 Hz), 3.78 (dd, 1H, *J* = 18.0 Hz, *J* = 8.1 Hz), 3.36 (dd, 1H, *J* = 18.0 Hz, *J* = 3.9 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -39.96 (s, 3F), -100.33 (s, 1F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 197.40, 168.04 (d, *J* = 258.9 Hz), 154.76 (d, *J* = 10.1 Hz), 131.12, 130.65 (q, *J* = 306.7 Hz) 127.40 (d, *J* = 11.3 Hz), 116.92 (d, *J* = 23.9 Hz), 113.32 (d, *J* = 22.6 Hz), 47.61, 36.35 ppm. IR (neat): 3062, 2929, 1724, 1616, 1592, 1257, 1112, 836 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_6F_4NaOS$ $[M+Na]^+$: 272.9973. Found: 272.9980.

4.5 5-chloro-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (2h);



Following the general procedure, using 2-acetyl-5-chloro-2,3-dihydro-1H-inden-1-one **1h** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (1.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **2h** as a white solid in 51% yield. Mp: 69.7—70.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.75 (d, 1H, *J* = 8.1 Hz), 7.48 (s, 1H), 7.42 (d, 1H, *J* = 8.7 Hz), 4.24 (dd, 1H, *J* = 8.1 Hz, *J* = 4.8 Hz), 3.77 (dd, 1H, *J* = 17.7 Hz, *J* = 8.1 Hz), 3.35 (dd, 1H, *J* = 18.0 Hz, *J* = 4.5 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -39.92 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 197.88, 153.19, 142.93, 133.13, 130.61 (q, *J* = 307.9 Hz), 129.33, 126.75, 126.02, 47.50, 36.12 ppm. IR (KBr): 3413, 2925, 1714, 1600, 1428, 1319, 1118, 781 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_6ClF_3NaOS$ $[M+Na]^+$: 288.9678. Found: 288.9676.

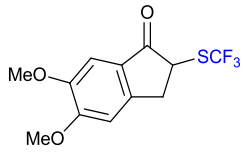
4.6 5-bromo-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (2i);



Following the general procedure, using 2-acetyl-5-bromo-2,3-dihydro-1H-inden-1-one **1i** (0.1mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (1.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide

the title compound **2i** as a yellow solid in 52% yield. Mp: 81.6—83.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.94 (s, 1H), 7.76 (d, 1H, *J* = 8.1 Hz), 7.37 (d, 1H, *J* = 8.1 Hz), 4.24 (dd, 1H, *J* = 8.1 Hz, *J* = 4.5 Hz), 3.74 (dd, 1H, *J* = 17.7 Hz, *J* = 8.1 Hz), 3.30 (dd, 1H, *J* = 17.7 Hz, *J* = 4.5 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -39.91 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 197.85, 150.15, 138.82, 136.31, 130.45 (q, *J* = 307.9 Hz), 127.93, 127.67, 122.54, 47.52, 35.92 ppm. IR (KBr): 3401, 3068, 2923, 1708, 1592, 1432, 1255, 1112, 707 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_6BrF_3NaOS$ $[M+Na]^+$: 332.9173. Found: 332.9176.

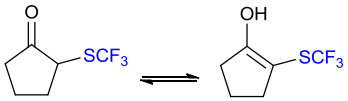
4.7 5,6-dimethoxy-2-((trifluoromethyl)thio)-2,3-dihydro-1H-inden-1-one (2j);



Following the general procedure, using 2-acetyl-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one **1j** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (1.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 10:1) to provide the title compound **2j** as a white solid in 71% yield. Mp: 106.2—107.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.20 (s, 1H), 6.87 (s, 1H), 4.22 (dd, 1H, *J* = 7.5 Hz, *J* = 3.9 Hz), 3.98 (s, 3H), 3.91 (s, 3H), 3.69 (dd, 1H, *J* = 17.4 Hz, *J* = 7.5 Hz), 3.28 (dd, 1H, *J* = 17.4 Hz, *J* = 3.6 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -40.04 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 197.68, 156.78, 150.18, 147.55, 130.84 (q, *J* = 307.9 Hz), 127.50, 107.19, 104.98, 56.54, 56.32, 47.78, 36.38 ppm. IR (KBr): 3409, 3075, 2942, 2910, 1714, 1596, 1467, 1251, 1120, 750 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{11}F_3NaO_3S$ $[M+Na]^+$:

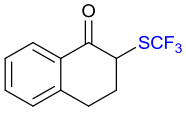
315.0279. Found: 315.0282.

4.8 2-((trifluoromethyl)thio)cyclopentanone (2k);



Following the general procedure, using 2-acetylcyclopentanone **1k** (0.5 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (5.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 50:1) to provide the title compound **2k** as a colorless oil in 21% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.14—3.07 (m, 1H), 2.54 (s, 3H), 2.44—2.40 (m, 1H), 2.18—2.09 (m, 1H), 2.04—1.91 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -37.76 (s, 3F), -42.63 (trace) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 208.36, 198.65, 129.77 (q, J = 307.9 Hz), 70.89, 37.07, 34.25, 25.71, 20.26 ppm. IR (neat): 2958, 2931, 1747, 1718, 1263, 1114, 736 cm^{-1}. HRMS (EI): Calcd. for $C_6H_7F_3OS$ $[M]^+$: 184.0170. Found: 184.0170.

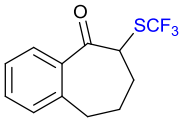
4.9 2-((trifluoromethyl)thio)-3,4-dihydronaphthalen-1(2H)-one (2l);



Following the general procedure, using 2-acetyl-3,4-dihydronaphthalen-1(2H)-one **1l** (0.2 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (2.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 30:1) to provide the title compound **2l** as a yellow oil in 15% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.04

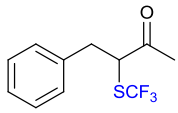
(d, 1H, *J* = 7.8 Hz), 7.52 (t, 1H, *J* = 7.5 Hz), 7.37—7.27 (m, 2H), 4.36 (dd, 1H, *J* = 10.8 Hz, *J* = 4.2 Hz), 3.15—3.11 (m, 2H), 2.74—2.65 (m, 1H), 2.46—2.33 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -39.21 (s, 3F), -41.98 (trace) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 192.25, 142.98, 134.34, 131.10, 130.76 (q, *J* = 306.7 Hz), 128.78, 128.21, 127.22, 51.77, 31.24, 28.21 ppm. IR (neat): 3062, 2931, 2850, 1687, 1600, 1455, 1288, 1114, 746 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_9F_3NaOS$ $[M+Na]^+$: 269.0224. Found: 269.0219. Spectroscopic data were in agreement with the literature.[2]

4.10 6-((trifluoromethyl)thio)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (2m);



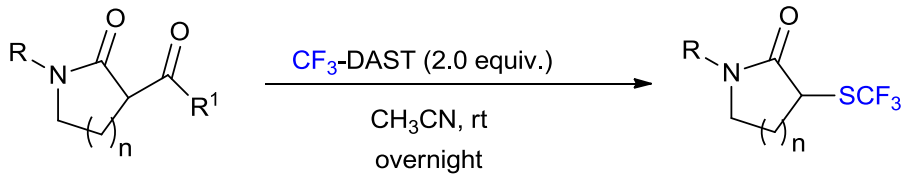
Following the general procedure, using 6-acetyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one **1m** (0.2 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (2.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 30:1) to provide the title compound **2m** as a yellow oil in 13% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.71 (d, 1H, *J* = 7.8 Hz), 7.45 (t, 1H, *J* = 7.5 Hz), 7.35—7.24 (m, 2H), 4.50 (dd, 1H, *J* = 10.2 Hz, *J* = 6.0 Hz), 3.06—3.02 (m, 2H), 2.49—2.39 (m, 1H), 2.24—2.04 (m, 2H), 1.83—1.77 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -40.33 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 199.86, 141.91, 137.46, 132.51, 130.81 (q, *J* = 306.7 Hz), 130.36, 129.49, 126.98, 53.68, 33.82, 32.25, 25.31 ppm. IR (neat): 2931, 2861, 1735, 1681, 1455, 1263, 1116, 736 cm^{-1}. HRMS (EI): Calcd. for $C_{12}H_{11}F_3OS$ $[M]^+$: 260.0483. Found: 260.0486.

4.11 4-phenyl-3-((trifluoromethyl)thio)butan-2-one (2n);



Following the general procedure, using 3-benzylpentane-2,4-dione **1n** (0.2mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (2.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 50:1) to provide the title compound **2n** as a yellow oil in 12% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.34—7.28 (m, 2H), 7.23—7.13 (m, 3H), 4.02 (dd, 1H, *J* = 8.4 Hz, *J* = 6.6 Hz), 3.25 (dd, 1H, *J* = 14.1 Hz, *J* = 9.0 Hz), 3.07 (dd, 1H, *J* = 14.1 Hz, *J* = 6.6 Hz), 2.18 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -40.39 (s, 3F) ppm. MS (ESI): Calcd. for $C_{11}H_{11}F_3OS$ $[M-H]^-$: 247. Found: 247. Spectroscopic data were in agreement with the literature.[3]

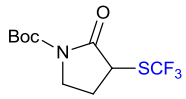
5. General procedure and product characterization data for Scheme 3.



3a—i **4a—i**

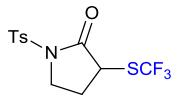
A flame-dried vessel was charged with *β*-keto esters **3a—3i** (1.0 equivalent) and anhydrous CH_3CN (0.1 M) under nitrogen gas atmosphere. The 0.5 M solution of CF_3-DAST in CH_2Cl_2 (2.0 equivalents taken from the solution above mentioned) was added slowly by syringe. Then the reaction mixture was stirred at room temperature for overnight, quenched by addition of water, extracted with ethyl acetate, dried over with Na_2SO_4 and then concentrated. The crude product was purified by flash column chromatography to provide the title compound **4a—4i.**

5.1 tert-butyl 2-oxo-3-((trifluoromethyl)thio)pyrrolidine-1-carboxylate (4a);



Following the general procedure, using substrate **3a—3c** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_3CN (1.0 mL, 0.1 M), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **4a** as a white solid in 80—84% yield. Mp: 68.5—69.3 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.17 (dd, 1H, *J* = 10.0 Hz, *J* = 8.4 Hz), 3.93—3.85 (m, 1H), 3.73—3.64 (m, 1H), 2.67—2.57 (m, 1H), 2.28—2.14 (m, 1H), 1.53 (s, 9H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -40.18 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.60, 149.79, 130.35 (q, *J* = 306.7 Hz), 84.16, 46.21, 44.41, 28.07, 27.67 ppm. IR (KBr): 2989, 2938, 1774, 1378, 1319, 1120, 846, 779 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{14}F_3NNaO_3S$ $[M+Na]^+$: 308.0544. Found: 308.0550.

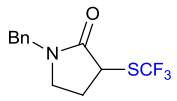
5.2 1-tosyl-3-((trifluoromethyl)thio)pyrrolidin-2-one (4d);



Following the general procedure, using 3-benzoyl-1-tosylpyrrolidin-2-one **3d** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_3CN (1.0 mL, 0.1 M), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 10:1) to provide the title compound **4d** as a white solid in 61% yield. Mp: 101.6—102.7 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.92 (d, 1H, *J* = 8.1 Hz), 7.35 (d, 1H, *J* = 8.4 Hz), 4.07—3.99 (m, 2H), 3.87—3.79 (m, 1H), 2.73—2.62 (m, 1H), 2.45 (s, 3H), 2.31—2.18 (m, 1H) ppm. ^{19}F

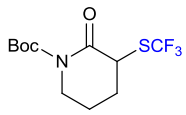
NMR (282 MHz, $CDCl_3$) δ: -40.05 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 168.18, 146.05, 134.34, 130.00 (q, *J* = 307.9 Hz), 130.02, 128.41, 45.17, 28.09, 21.90 ppm. IR (KBr): 2983, 2927, 1743, 1363, 1232, 1122, 811, 661 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{12}F_3NNaO_3S_2$ $[M+Na]^+$: 362.0108. Found: 362.0105.

5.3 1-benzyl-3-((trifluoromethyl)thio)pyrrolidin-2-one (4e);



Following the general procedure, using 3-benzoyl-1-benzylpyrrolidin-2-one **3e** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_3CN (1.0 mL, 0.1 M), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **4e** as a yellow oil in 26% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.38—7.28 (m, 3H), 7.27—7.22 (m, 2H), 4.54—4.44 (m, 2H), 4.15 (t, 1H, *J* = 8.4 Hz), 3.36—3.22 (m, 2H), 2.67—2.56 (m, 1H), 2.30—2.17 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -40.22 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 169.38, 135.60, 130.64 (q, *J* = 306.7 Hz), 129.01, 128.36, 128.12, 47.55, 44.94, 44.65, 28.49 ppm. IR (neat): 3058, 2929, 1695, 1486, 1434, 1282, 1116, 700 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{12}F_3NNaOS$ $[M+Na]^+$: 298.0489. Found: 298.0488.

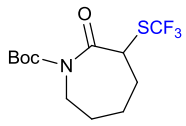
5.4 tert-butyl 2-oxo-3-((trifluoromethyl)thio)piperidine-1-carboxylate (4f);



Following the general procedure, using tert-butyl 3-benzoyl-2-oxopiperidine-1-

carboxylate **3f** (0.2 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_3CN (2.0 mL, 0.1 M), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **4f** as a yellow oil in 38% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.16 (dd, 1H, *J* = 9.3 Hz, *J* = 6.6 Hz), 3.89—3.81 (m, 1H), 3.65—3.56 (m, 1H), 2.49—2.41 (m, 1H), 2.10—1.90 (m, 3H), 1.51 (s, 9H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -39.93 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 167.69, 152.41, 130.58 (q, *J* = 307.9 Hz), 84.03, 48.25, 45.21, 29.08, 28.04, 21.41 ppm. IR (neat): 2981, 2935, 1770, 1725, 1461, 1297, 1116, 734 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{16}F_3NNaO_3S$ $[M+Na]^+$: 322.0701. Found: 322.0703.

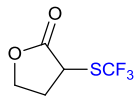
5.5 tert-butyl 2-oxo-3-((trifluoromethyl)thio)azepane-1-carboxylate (4g);



Following the general procedure, using tert-butyl 3-benzoyl-2-oxoazepane-1-carboxylate **3g** (0.2 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_3CN (2.0 mL, 0.1 M), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **4g** as a yellow oil in 15% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.43 (dd, 1H, *J* = 10.8 Hz, *J* = 2.4 Hz), 4.27—4.21 (m, 1H), 3.36—3.29 (m, 1H), 2.37—2.31 (m, 1H), 2.10—1.87 (m, 4H), 1.79—1.66 (m, 1H), 1.52 (s, 9H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -40.33 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 171.23, 152.65, 130.93 (q, *J* = 306.7 Hz), 84.19, 52.62, 45.95, 33.48, 28.06, 27.94, 27.86 ppm. IR (neat): 2977, 2935, 1768, 1725, 1459, 1257, 1116, 734 cm^{-1}. HRMS (ESI): Calcd. for

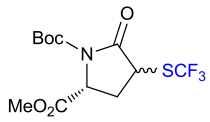
$C_{12}H_{18}F_3NNaO_3S$ [M+Na]$^+$: 336.0857. Found: 336.0860.

5.6 3-((trifluoromethyl)thio)dihydrofuran-2(3H)-one (4h);



Following the general procedure, using 3-acetyldihydrofuran-2(3H)-one **3h** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_3CN (1.0 mL, 0.1 M), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 40:1) to provide the title compound **4h** as a yellow oil in 80% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.54—4.47 (m, 1H), 4.39—4.31 (m, 1H), 4.21—4.15 (m, 1H), 2.91—2.80 (m, 1H), 2.57—2.44 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -40.16 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 172.30, 130.03 (q, J = 307.9 Hz), 66.90, 41.31, 32.03 ppm. IR (neat): 2925, 2856, 1781, 1257, 1112, 734 cm^{-1}. HRMS (EI): Calcd. for $C_5H_5F_3O_2S$ [M]$^+$: 185.9962. Found: 185.9972.

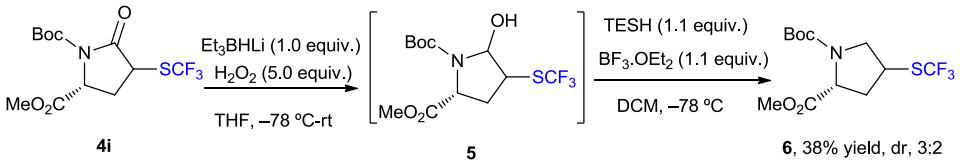
5.7 1-tert-butyl 2-methyl 5-oxo-4-((trifluoromethyl)thio)pyrrolidine-1,2-dicarboxylate (4i);



Following the general procedure, using (2R)-1-tert-butyl 2-methyl 4-acetyl-5-oxopyrrolidine-1,2-dicarboxylate **3i** (0.1 mmol, 1.0 equivalent) and CF_3-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_3CN (1.0 mL, 0.1 M), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash

column chromatography (Hex: AcOEt = 20:1) to provide the title compound **4i** as a yellow oil in 77% yield (dr; 3:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: (major) 4.67 (d, 1H, *J* = 9.3 Hz), 4.29 (dd, 1H, *J* = 11.4 Hz, *J* = 8.7 Hz), 3.82 (s, 3H), 2.70—2.62 (m, 1H), 2.54—2.47 (m, 1H), 1.51 (s, 9H). (minor) 4.62—4.58 (m, 1H), 4.16—4.10 (m, 1H), 3.80 (s, 3H), 3.07—2.84 (m, 1H), 2.30—2.23 (m, 1H), 1.48 (s, 9H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: (major) -40.00 (s, 3F), (minor) -40.76 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: (major) 170.97, 167.90, 148.95, 130.19 (q, *J* = 307.9 Hz), 84.98, 56.97, 53.17, 44.38, 31.52, 27.94, 27.91. (minor) 170.73, 167.83, 148.85, 85.01, 57.27, 53.03, 44.37, 30.98, 27.84, 27.80 ppm. IR (neat): 2981, 2938, 1795, 1752, 1311, 1255, 1116, 912, 734 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{16}F_3NNaO_5S$ $[M+Na]^+$: 366.0599. Found: 366.0602.

6. General procedure and product characterization data for Scheme 4.



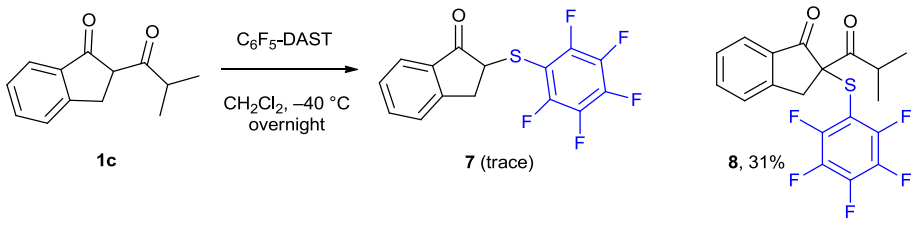
To a solution of **4i** (0.27g, 0.8 mmol) in THF (2 mL) at –78 °C was added dropwise a solution of lithium triethylhydroborate (1M in THF, 0.8 mL, 1.0 equivalent). The reaction mixture was stirred at –78 °C for 2 h and it was quenched with aq. $NaHCO_3$ (1 mL). The resulting mixture was then allowed to warm to 0 °C. A solution of hydrogen peroxide (50% in H_2O) (0.3 mL, 3.8 mmol) was added dropwise. The mixture was stirred at room temperature for 30 min and concentrated *in vacuo* to remove THF. The residue was extracted with EtOAc, and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified using flash column chromatography to provide the intermediate **5**.

To a cooled solution of the intermediate in DCM (3 mL) at –78 °C was added triethylsilane (0.15 mL, 0.88 mmol) followed by $BF_3 \cdot OEt_2$ (0.1 mL, 0.88 mmol). The reaction mixture was stirred at –78 °C for additional 2 h before it was quenched with aq. $NaHCO_3$ (2.0 mL). The resulting mixture was allowed to warm to room temperature and extracted with DCM. The combined organic layers were dried over $MgSO_4$, concentrated *in vacuo*, and purified using flash column chromatography to provide compound **6** in 38% yield (dr, 3:2).

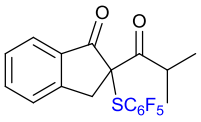
^{1}H NMR ($CDCl_3$, 300 MHz) δ: (major and minor) 4.46—4.27 (m, 1.6H), 4.12—3.82 (m, 2.7H), 3.75—3.65 (m, 6.6H), 3.46—3.36 (m, 1.8H), 2.80—2.71 (m, 1H), 2.43—2.26 (m, 1.4H), 2.09—1.99 (m, 1H), 1.45 (s, 7.8H), 1.45 (s, 9H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: (minor) -40.68 (s, 3F), (major) -40.98 (s, 3F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: (major and minor) 172.65 (d, *J* = 36.4 Hz), 172.47 (d, *J* = 38.9 Hz), 153.7 (d, *J* = 21.3 Hz), 153.1 (d, *J* = 15.0 Hz), 130.34 (q, *J* = 306.7 Hz), 130.39 (q, *J* = 306.7 Hz), 81.00, 80.95, 58.46, 58.29, 58.07, 58.01, 52.61, 52.43, 52.32, 52.25, 39.57 (d, *J* = 11.3 Hz), 39.02 (d, *J* = 20.1 Hz), 37.46, 37.38, 36.63, 36.40, 28.44, 28.31 ppm. IR (neat): 2979, 2877, 1751, 1706, 1398, 1257, 1118, 898, 763 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{18}F_3NNaO_4S$ $[M+Na]^+$: 352.0806. Found: 352.0802.

7. General procedure and product characterization data for Scheme 5.

7.1 Reaction procedure and product characterization data for 7 and 8;



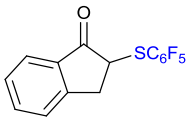
7.1.1 2-isobutyryl-2-((perfluorophenyl)thio)-2,3-dihydro-1H-inden-1-one (8);



Following the general procedure, using substrate **1c** (0.2 mmol, 1.0 equivalent) and C_6F_5-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_2Cl_2 (2.0 mL), the reaction mixture was stirred at –40 °C for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 50:1) to provide the title compound **7** (trace) and **8** (31% yield) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.77 (d, 1H, *J* = 7.8 Hz), 7.64 (t, 1H, *J* = 7.3 Hz), 7.45—7.41 (m, 2H), 3.93 (d, 1H, *J* = 17.7 Hz), 3.54—3.45 (m, 1H), 3.26 (d, 1H, *J* = 17.7 Hz), 1.21 (d, 3H, *J* = 6.6 Hz), 0.91 (d, 3H, *J* = 6.6 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -127.41—-127.53 (m, 2F), -147.80—-147.98 (m, 1F), -159.85—-160.07 (m, 2F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 205.02, 197.29, 150.93, 149.87—149.70 (m), 147.89—147.72 (m), 144.25—144.03 (m), 142.19—141.93 (m), 138.89—138.59 (m), 136.86—136.51 (m), 138.29, 134.41, 128.58, 126.38, 125.14, 105.09—104.72 (m), 69.26, 37.35, 36.55, 20.45, 19.47 ppm. IR (neat): 3585, 2977, 1712, 1513, 1484, 1265, 977, 738, 2927 cm^{-1}. MS (ESI): Calcd. for $C_{19}H_{13}F_5NaO_2S$ $[M+Na]^+$:

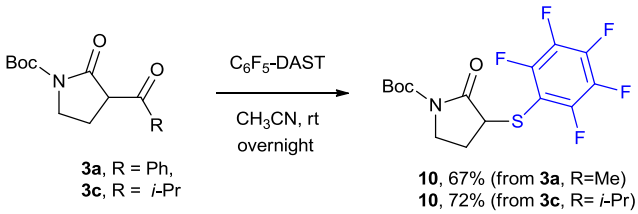
423. Found: 423.

7.1.2 2-((perfluorophenyl)thio)-2,3-dihydro-1H-inden-1-one (7);

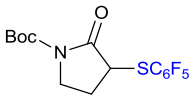


(Including addition product) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.76 (d, 1H, *J* = 7.8 Hz), 7.67—7.62 (m, 1H), 7.46-7.40 (m, 2H), 4.09—4.07 (m, 1H), 3.62 (dd, 1H, *J* = 18.6 Hz, *J* = 6.0 Hz), 3.04 (d, 1H, *J* = 17.7 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -131.63—-131.71 (m, 2F), -151.39—-151.54 (m, 1F), -161.24—-161.38 (m, 2F) ppm. MS (ESI): Calcd. for $C_{15}H_7F_5NaOS$ $[M+Na]^+$: 353. Found: 353.

7.2 Reaction procedure and product characterization data for 10;



7.2.1 tert-butyl 2-oxo-3-((perfluorophenyl)thio)pyrrolidine-1-carboxylate (10);



Following the general procedure, using tert-butyl 3-benzoyl-2-oxopyrrolidine-1-carboxylate **3a** or **3c** (0.1mmol, 1.0 equivalent) and C_6F_5-DAST (2.0 equivalent, 0.5 M solution in CH_2Cl_2) in CH_3CN (1.0 mL, 0.1 M), the reaction mixture was stirred at room temperature for overnight. The crude product was purified by flash column chromatography (Hex: AcOEt = 20:1) to provide the title compound **10** as a yellow oil in

67% —72% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.96—3.86 (m, 2H), 3.79—3.71 (m, 1H), 2.49—2.37 (m, 1H), 2.03—1.93 (m, 1H), 1.51 (s, 9H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -131.83—-131.94 (m, 2F), -150.96—-151.11 (m, 1F), -161.02—-161.19 (m, 2F) ppm. ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ: 169.85, 150.01, 149.19—149.07 (m), 147.22—147.11 (m), 143.58—143.34 (m), 141.55—141.25 (m), 138.93—138.65 (m), 136.91—136.64 (m), 106.35—105.98 (m), 83.72, 46.75, 44.29, 28.07, 24.64 ppm. IR (neat): 2981, 2931, 1781, 1724, 1513, 1305, 1153, 981, 734 cm^{-1}. HRMS (ESI): Calcd. for $C_{15}H_{14}F_5NNaO_3S$ $[M+Na]^+$: 406.0512. Found: 406.0508.

8. References;

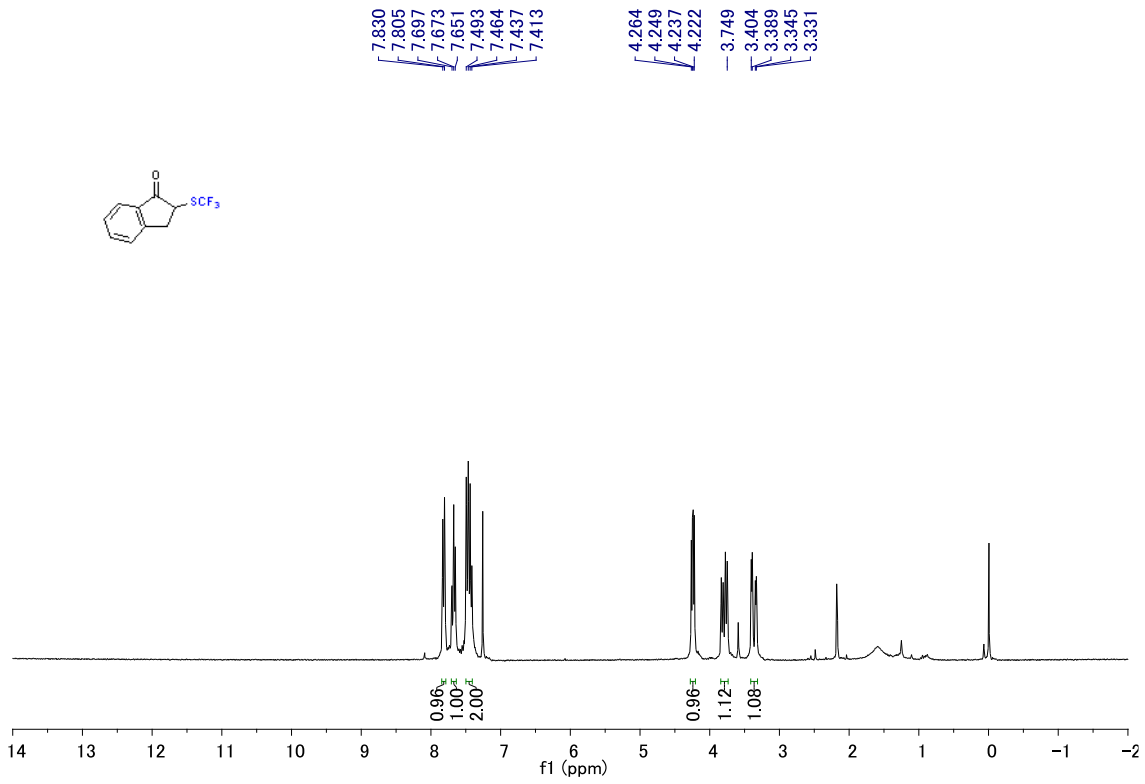
[1]. (*a*) S. Arimori, M. Takada and N. Shibata, *Org. Lett.*, 2015, **17**, 1063; (*b*) S. Alazet, L. Zimmer and T. Billard, *Chem. Eur. J*., 2014, **20**, 8589; (*c*) S. Alazet, E. Ismalaj, Q. Glenadel, D. Le Bars and T. Billard, *Eur. J. Org. Chem.*, 2015, 4607.

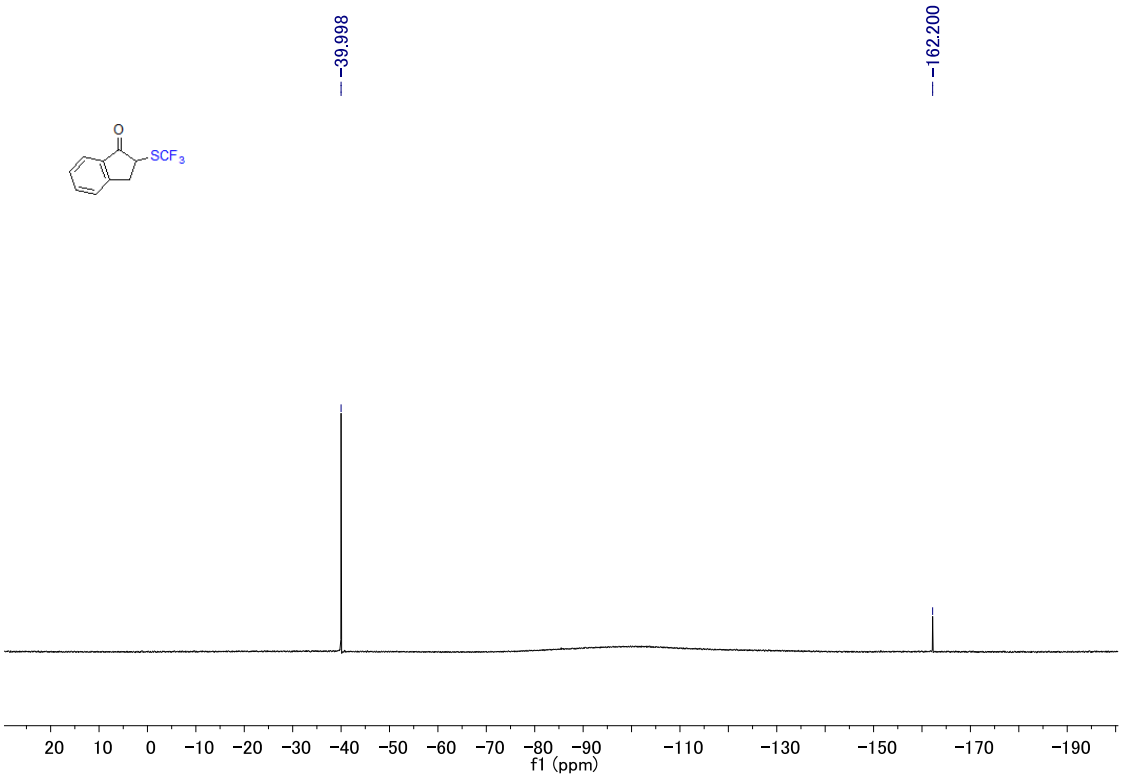
[2]. (*a*) C. Xu, B. Ma and Q. Shen, *Angew. Chem. Int. Ed.*, 2014, **53**, 9316; (*b*) A. K. Yadav and K. N. Singh, *Chem. Commun.*, 2018, **54**, 1976.

[3]. W. Wu, X. Zhang, F. Liang and S. Cao, *Org. Biomol. Chem.*, 2015, **13**, 6992.

9. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for desired compounds;

9.1 spectra for scheme 2;

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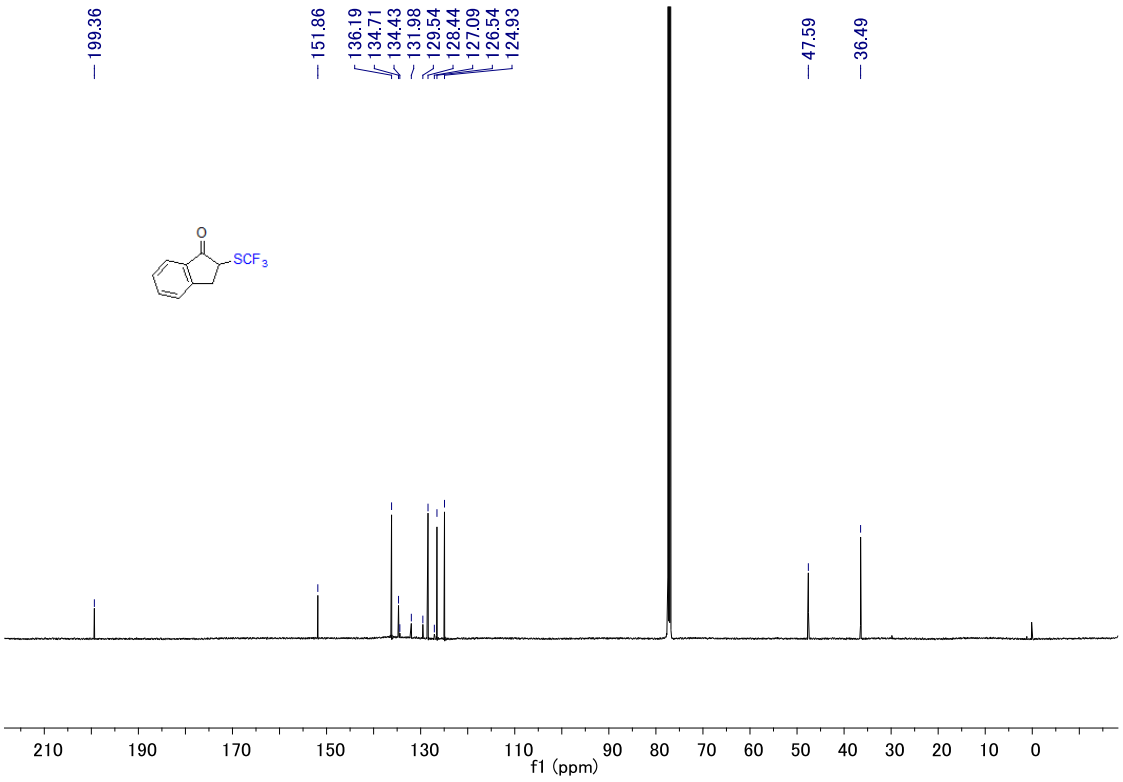
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129.54
128.44
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124.93
47.59
36.49
O
SCF3
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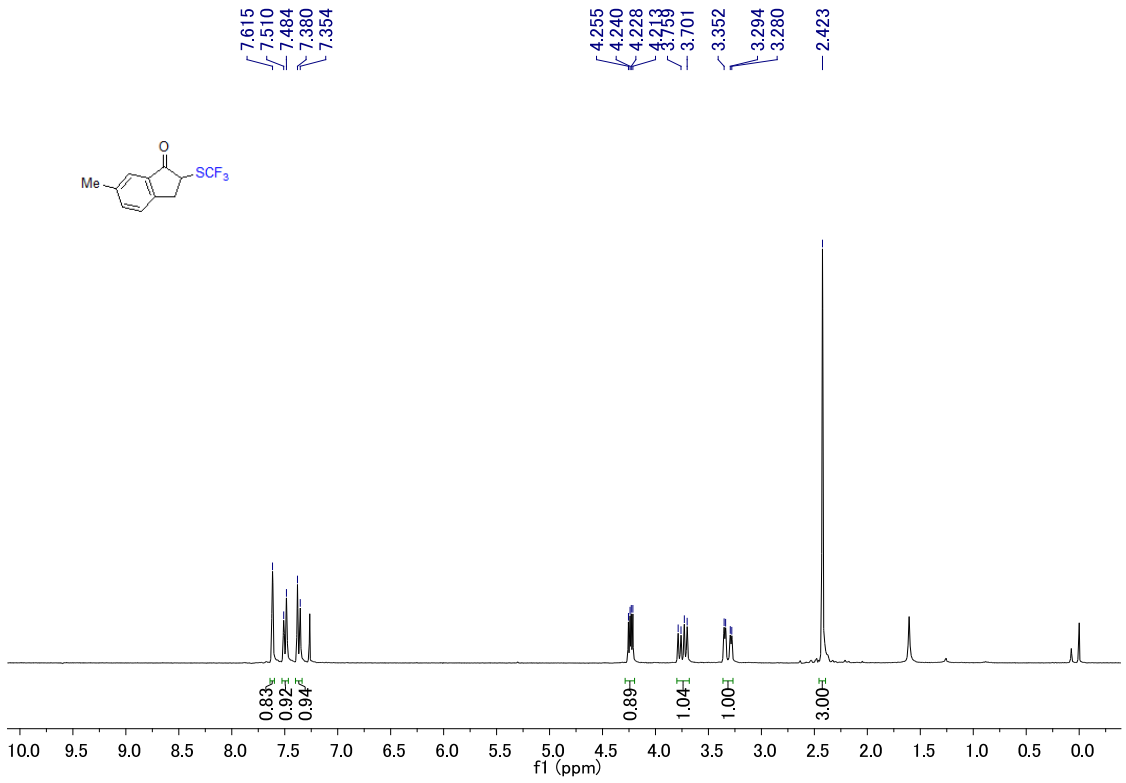
f1 (ppm)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3.294
3.280
2.423
O
Me
SCF3
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0.89
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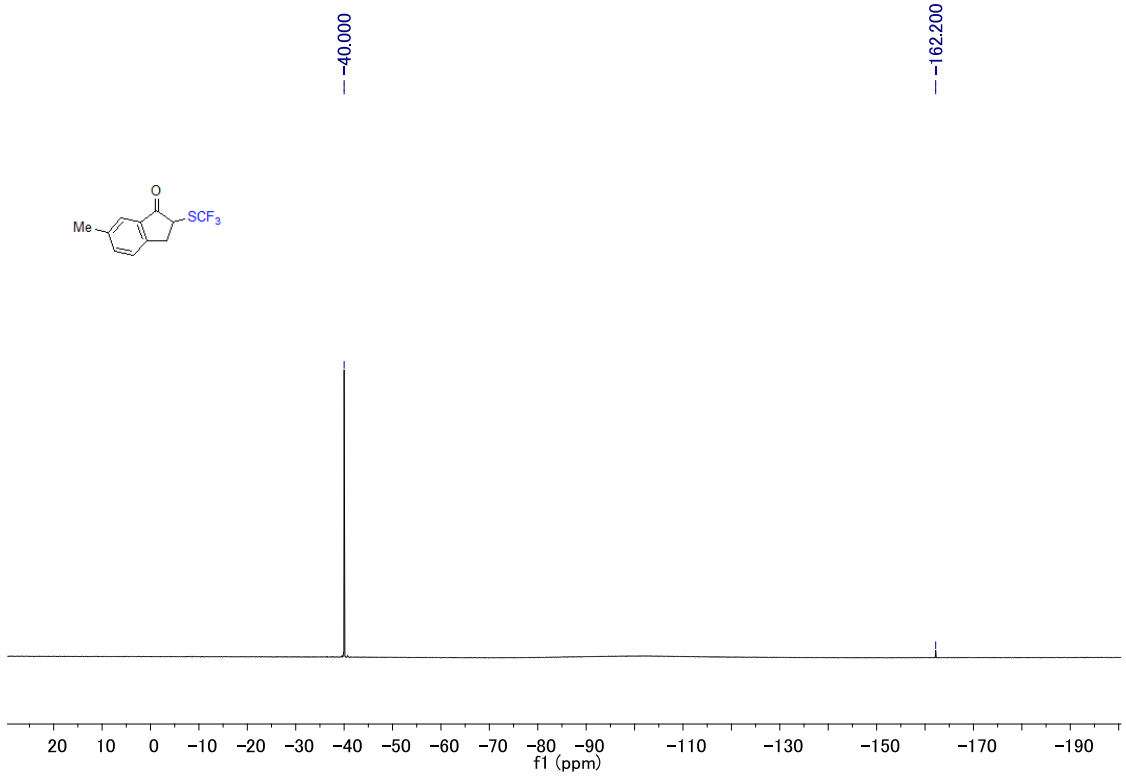
3.00
f1 (ppm)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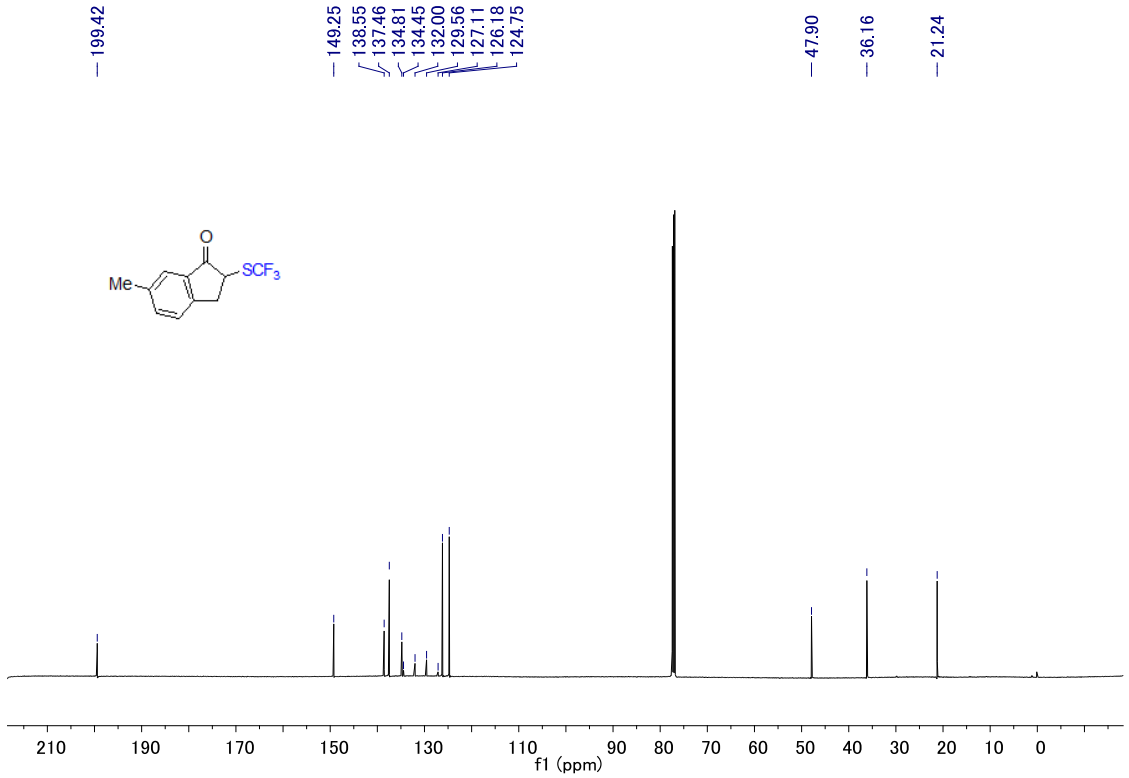
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36.16
21.24
O
Me
SCF3
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90
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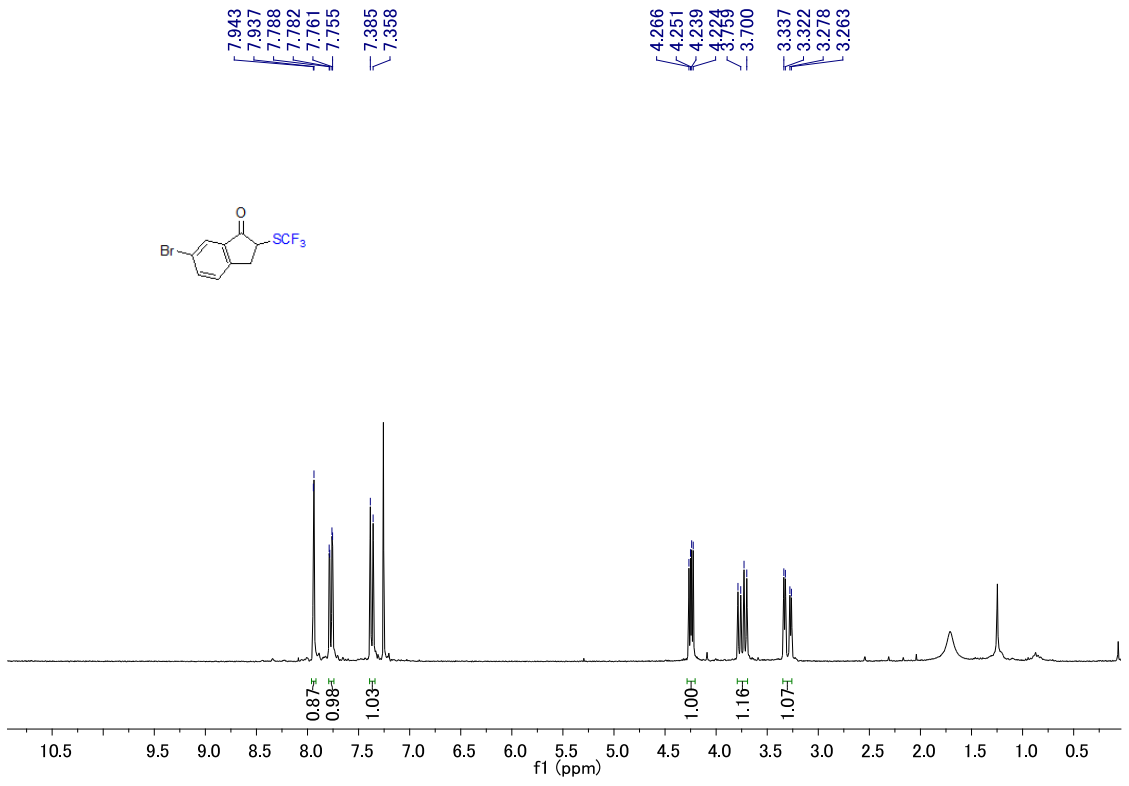
50
40
30
20
10
0
f1 (ppm)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3.759
3.700
3.337
3.322
3.278
3.263
O
Br
SCF3
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0.98
1.03
1.00
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1.07
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9.5
9.0
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8.0
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7.0
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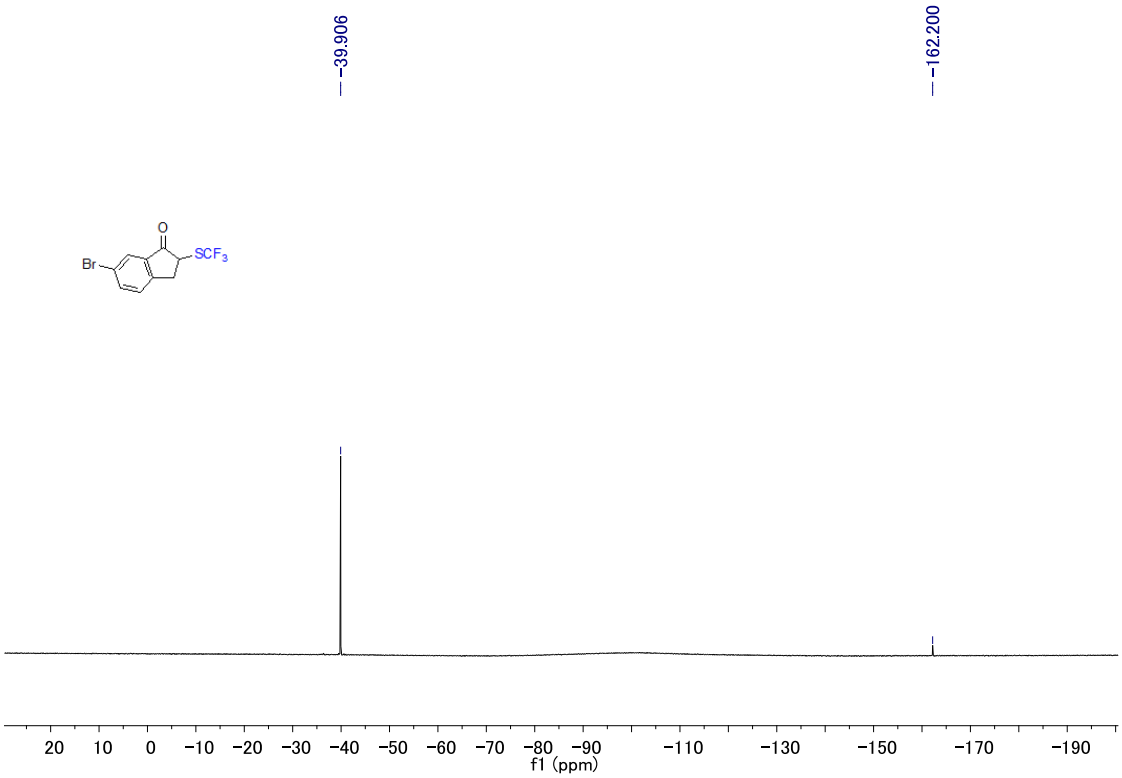
f1 (ppm)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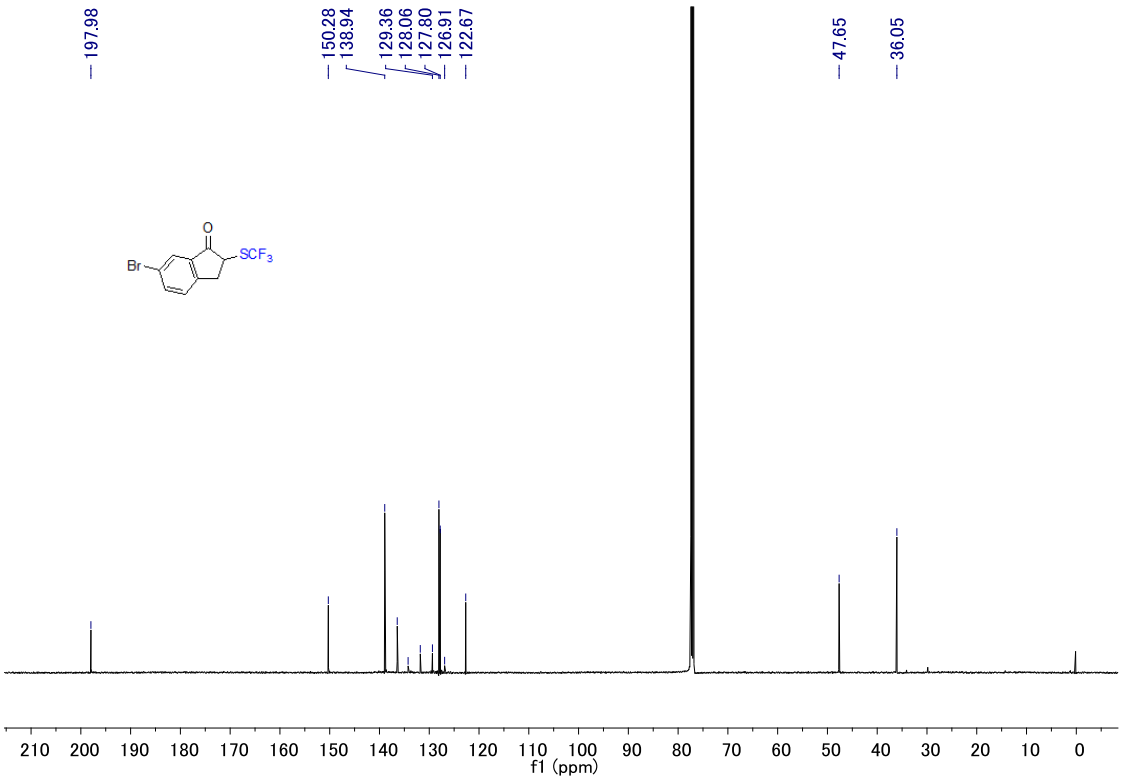
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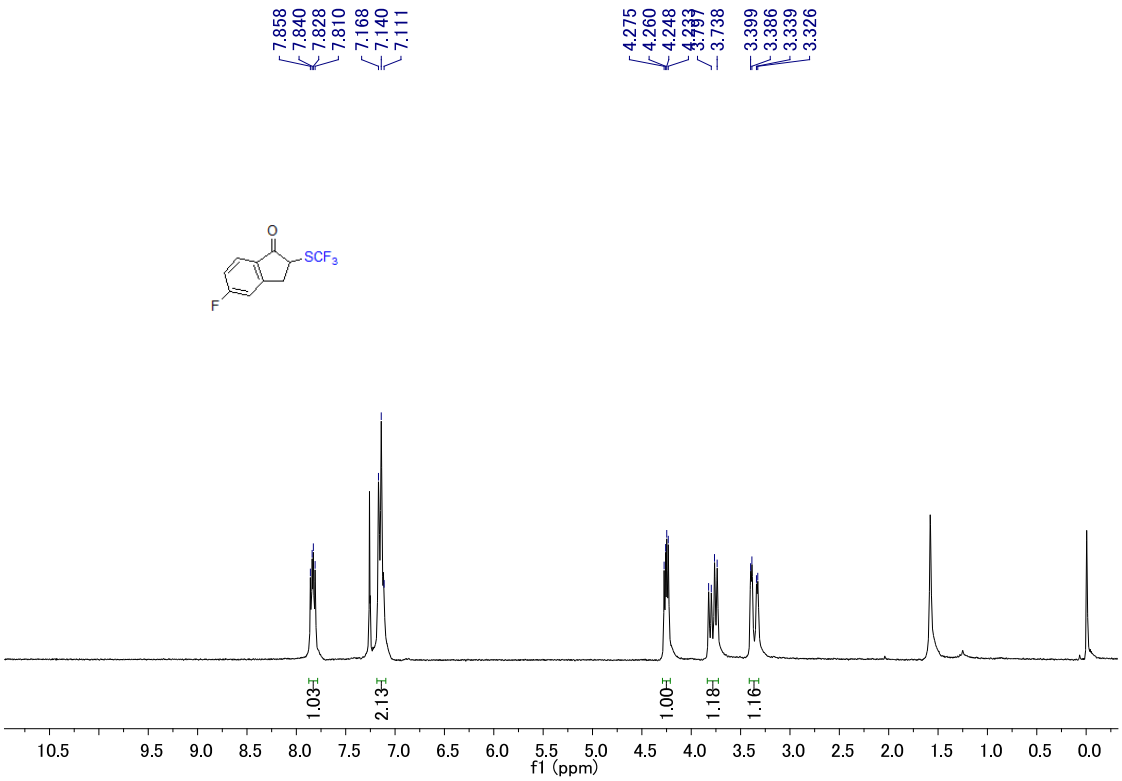
f1 (ppm)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3.386
3.339
3.326
O
SCF3
F
1.03
2.13
1.00
1.18
1.16
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
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2.0
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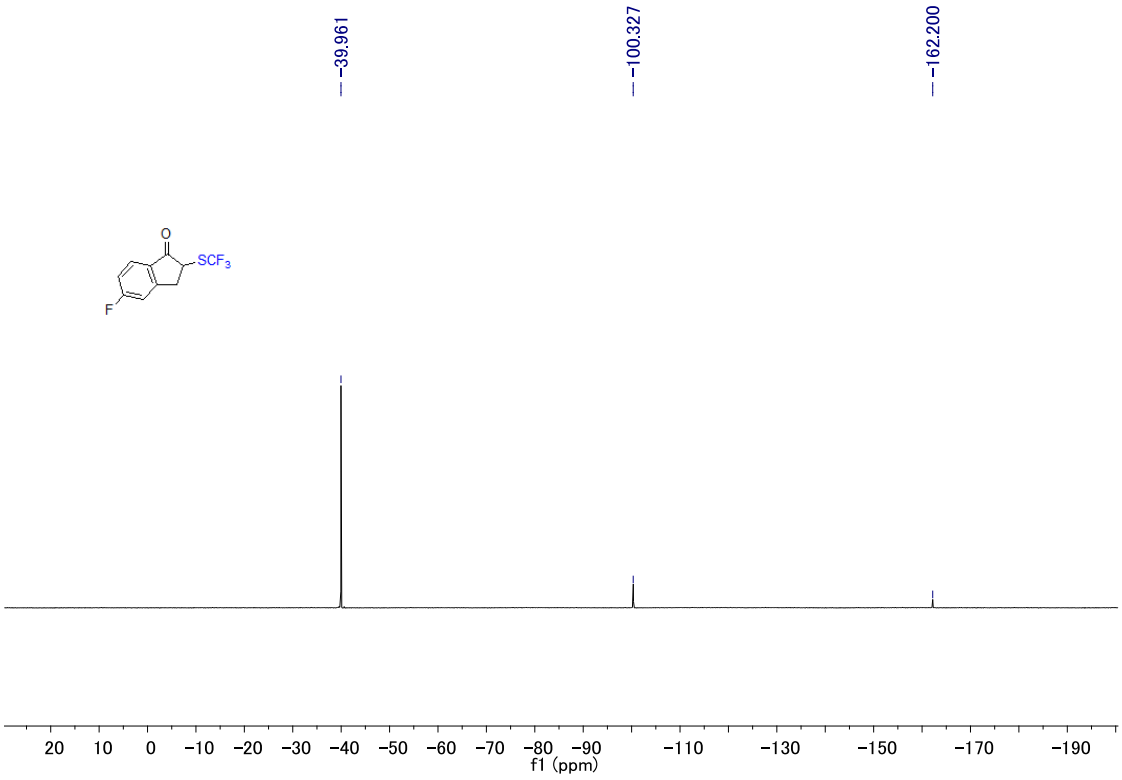
0.0
f1 (ppm)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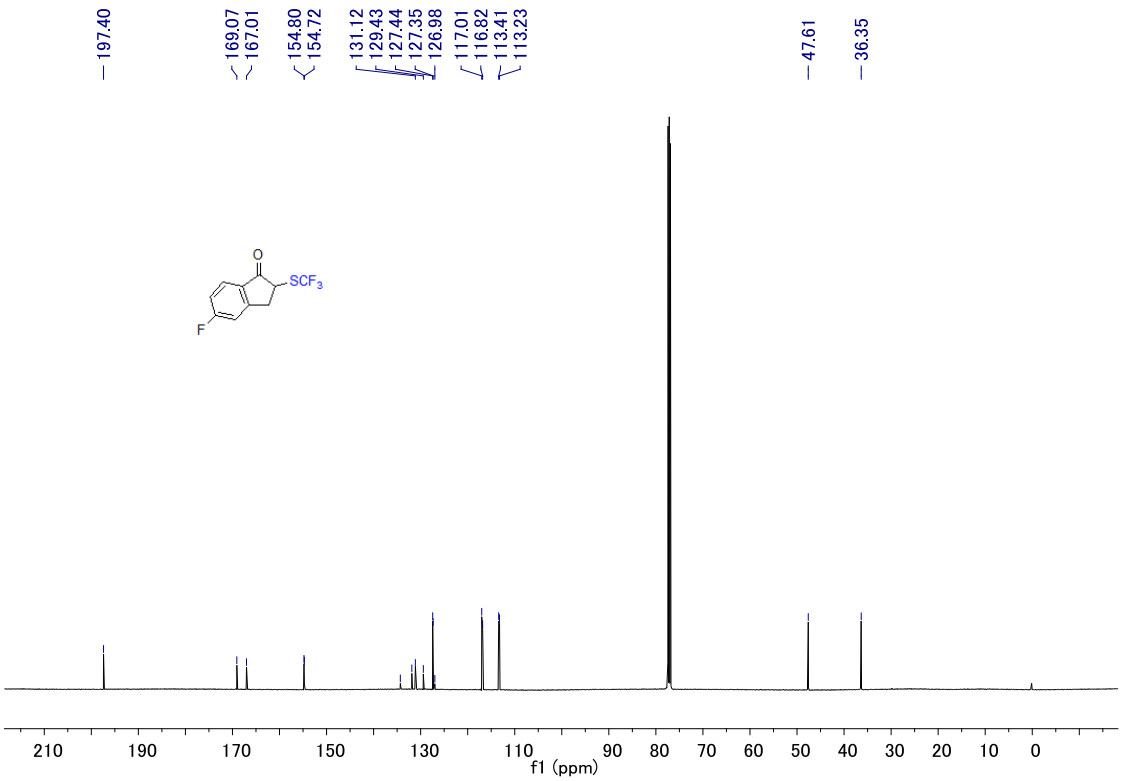
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113.41
113.23
47.61
36.35
O
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130
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90
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50
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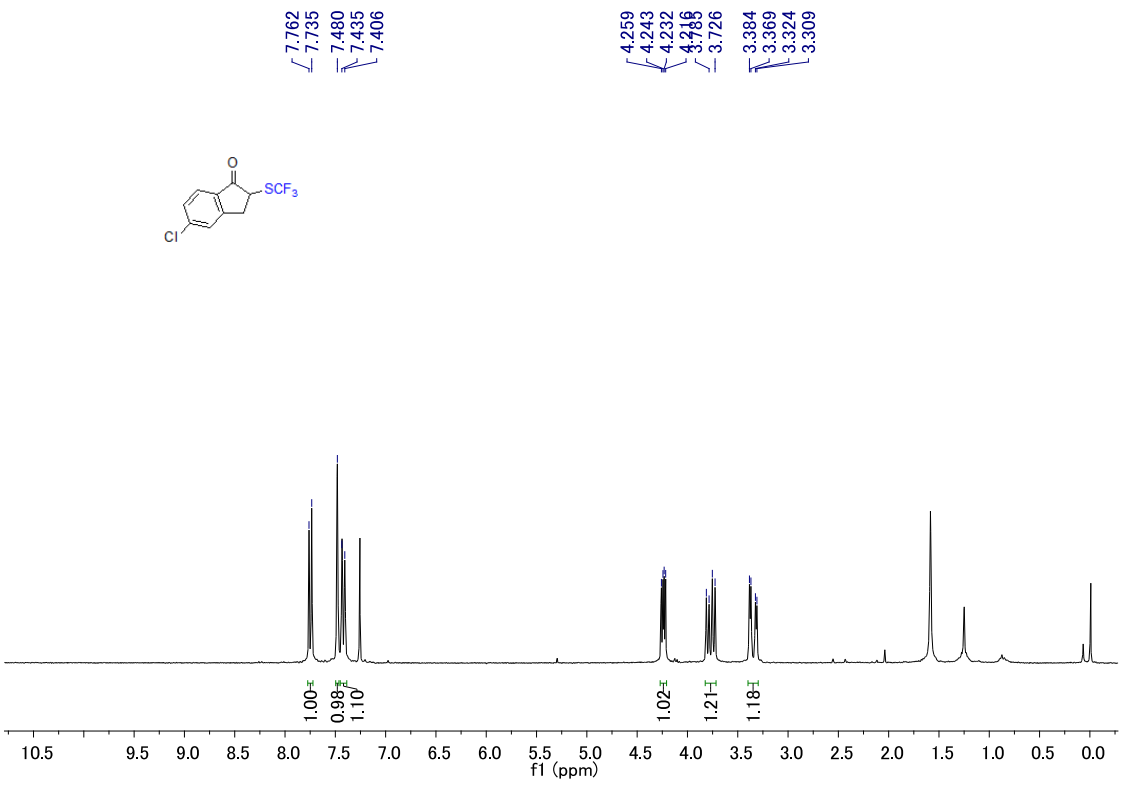
f1 (ppm)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9.5
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7.0
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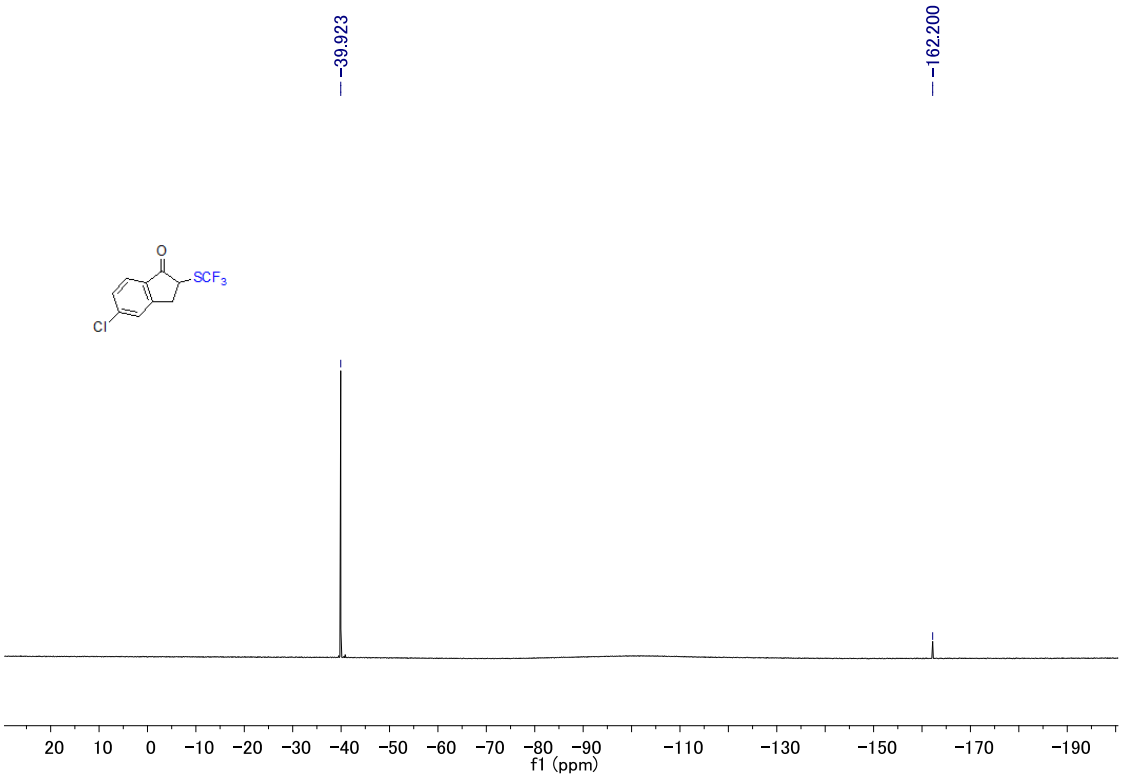
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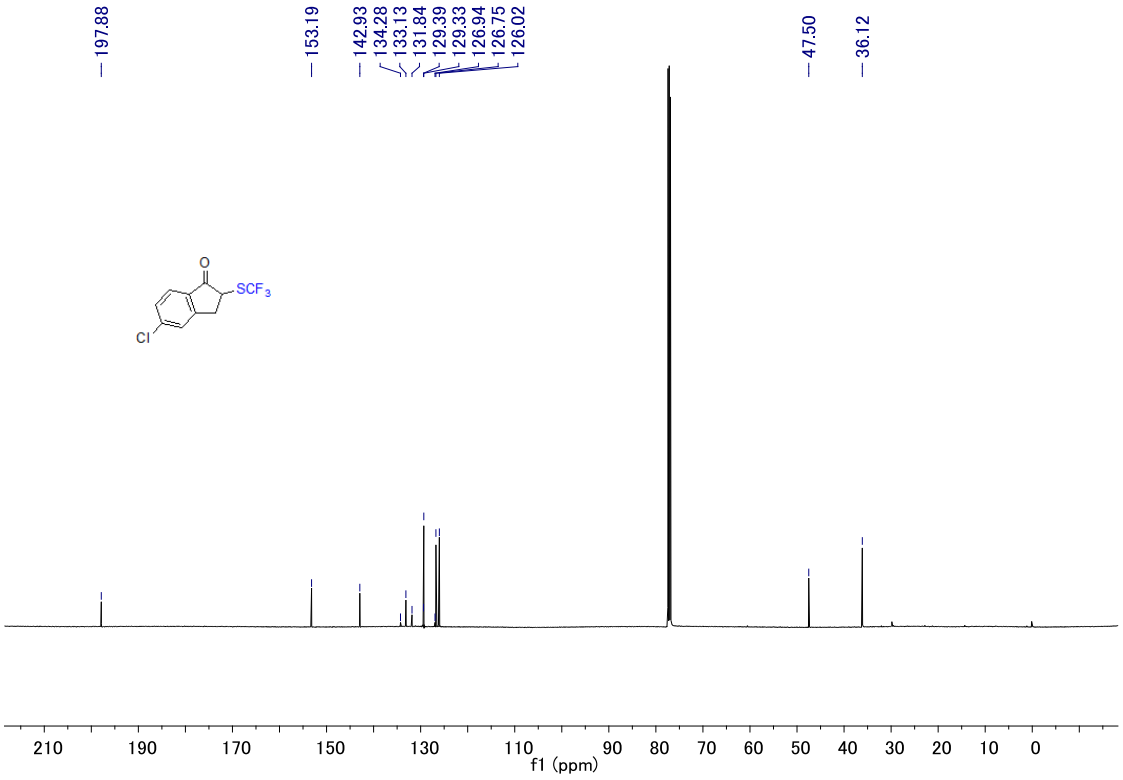
f1 (ppm)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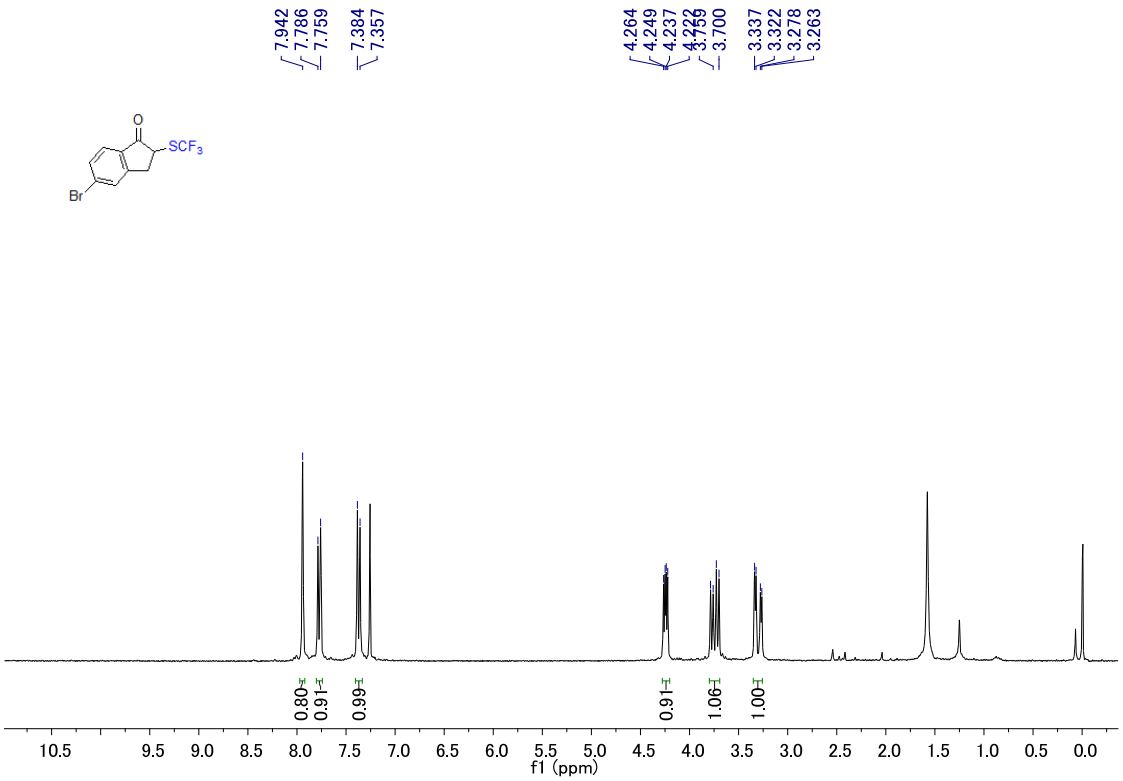
f1 (ppm)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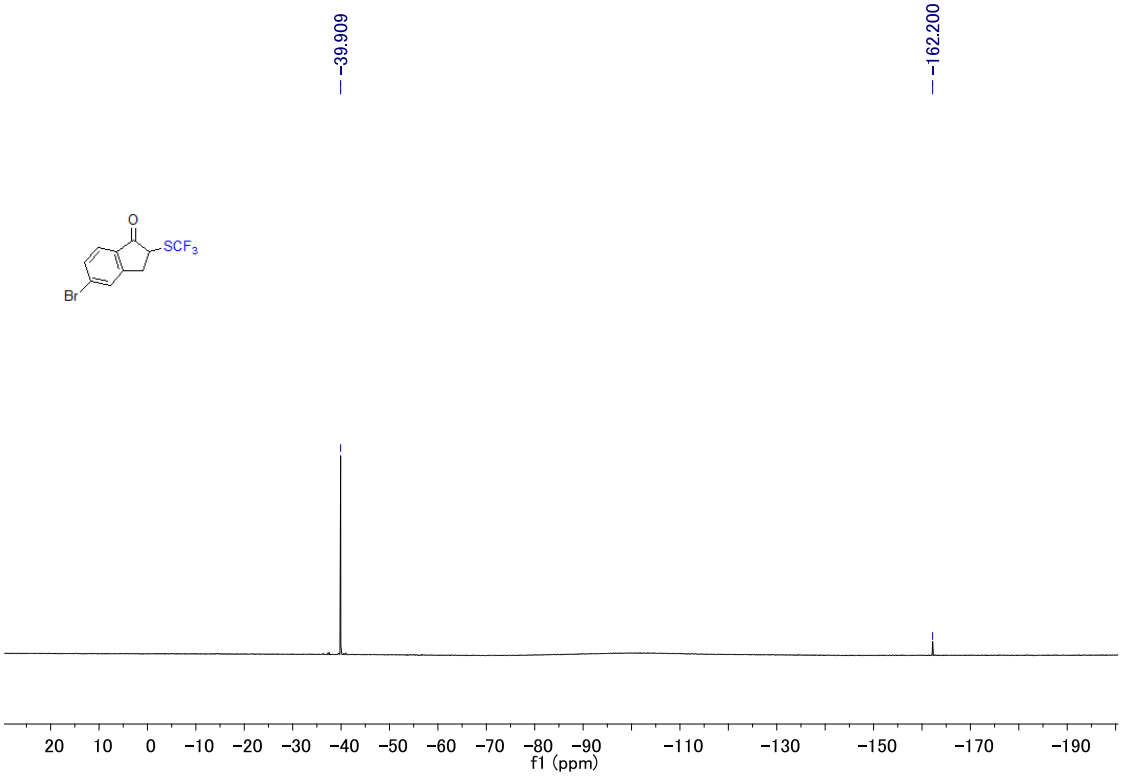
f1 (ppm)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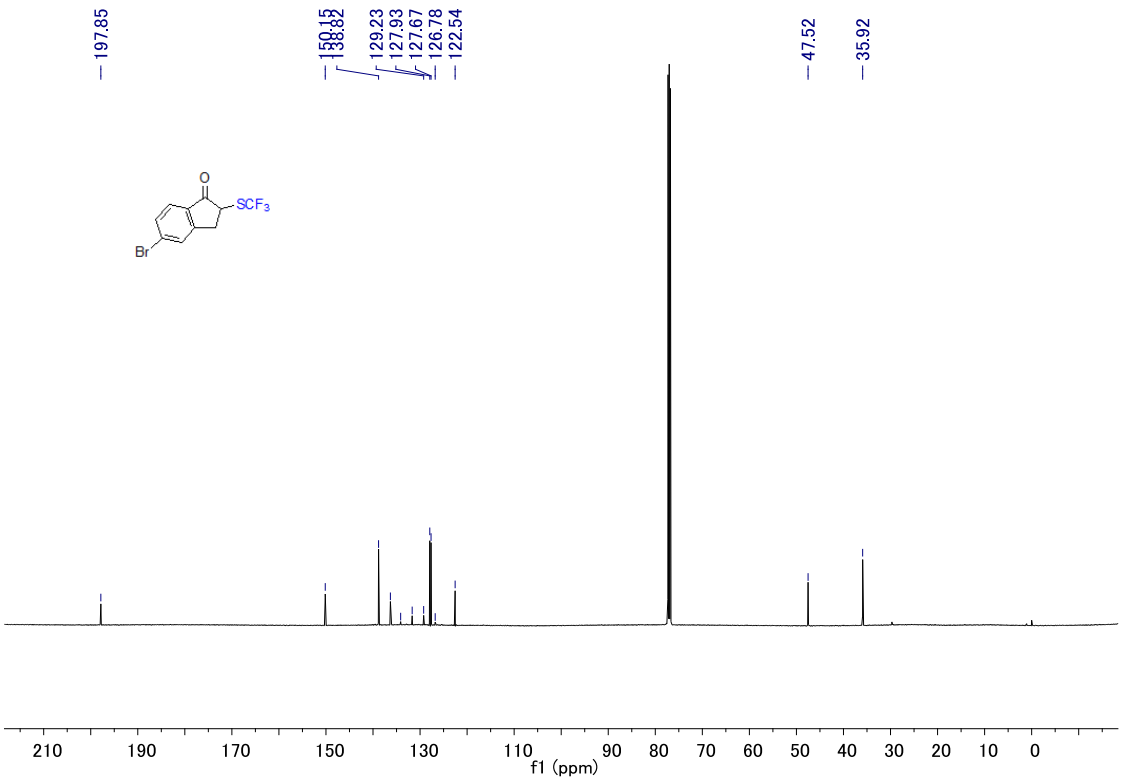
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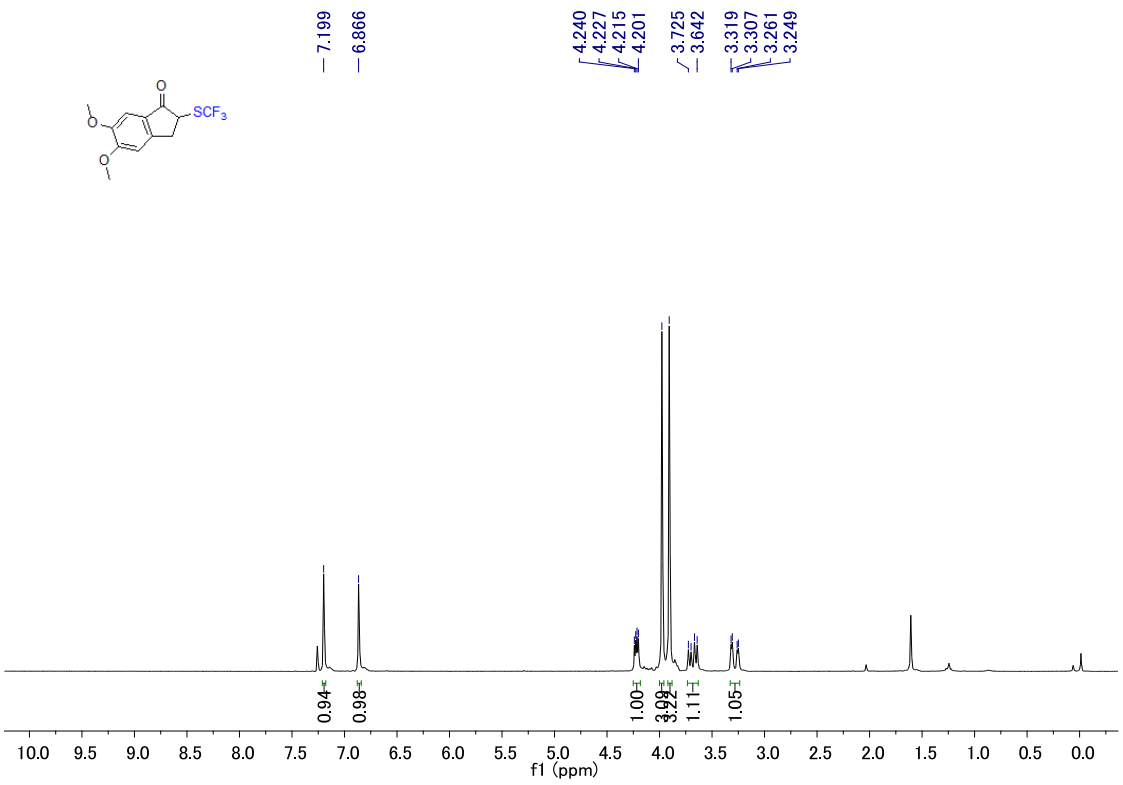
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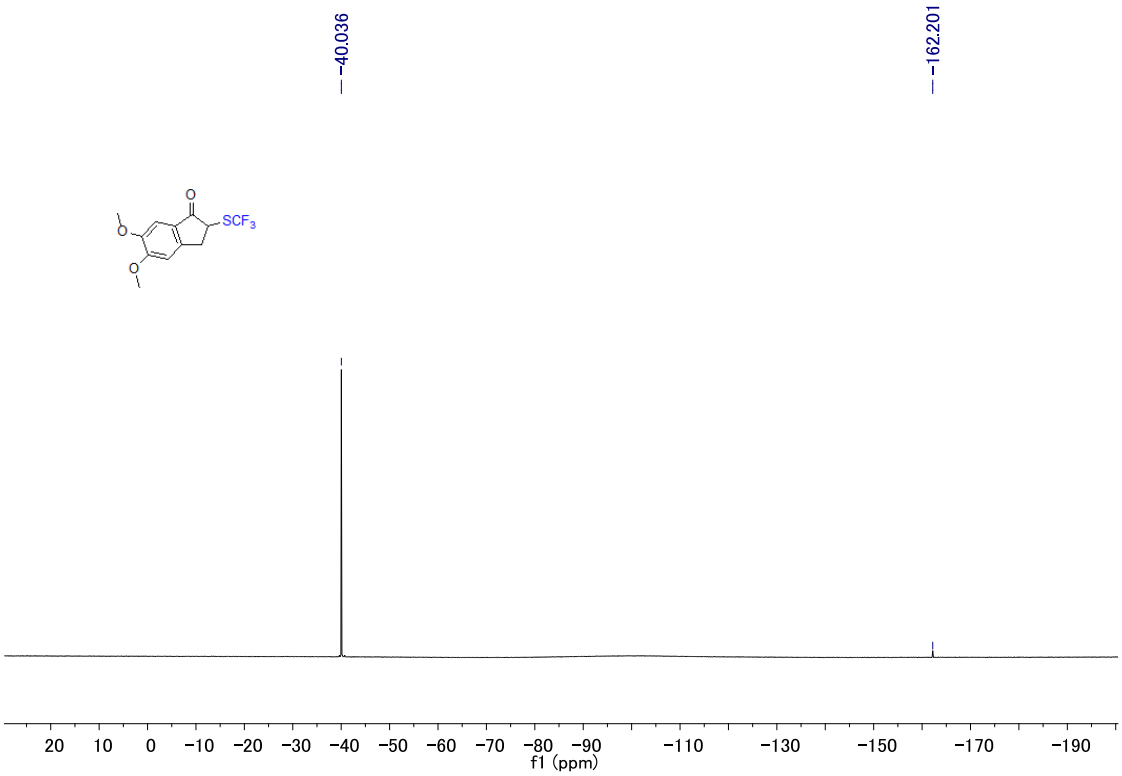
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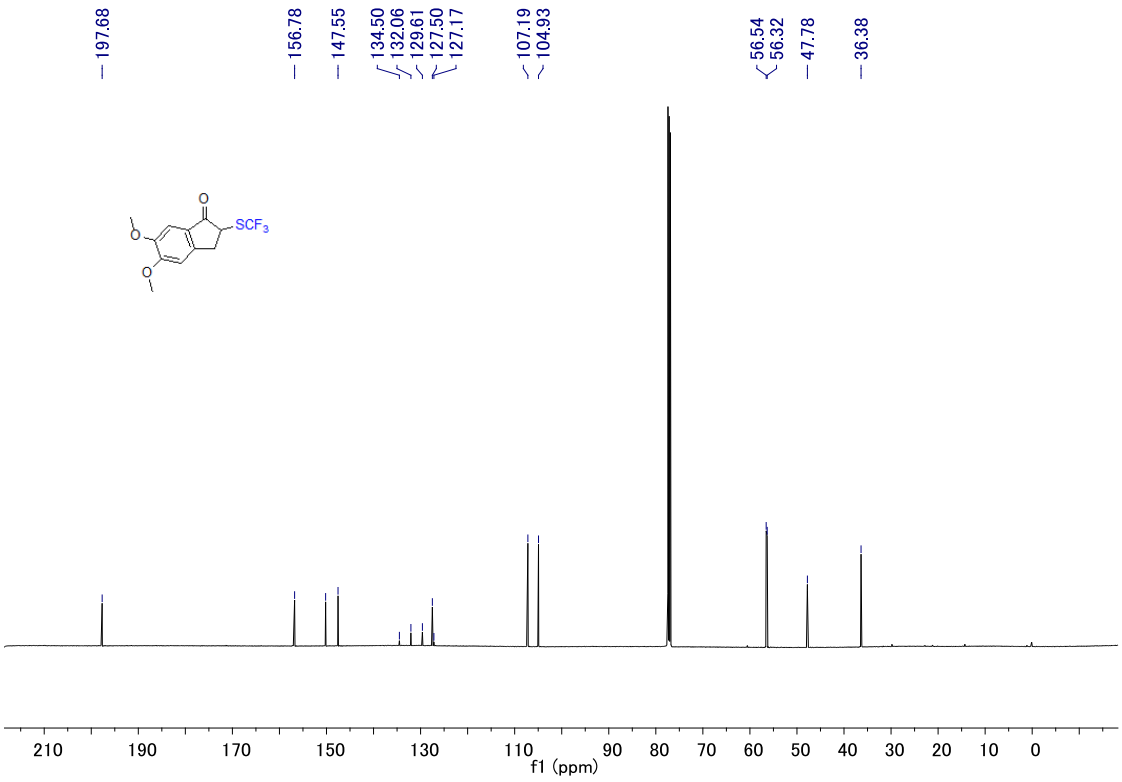
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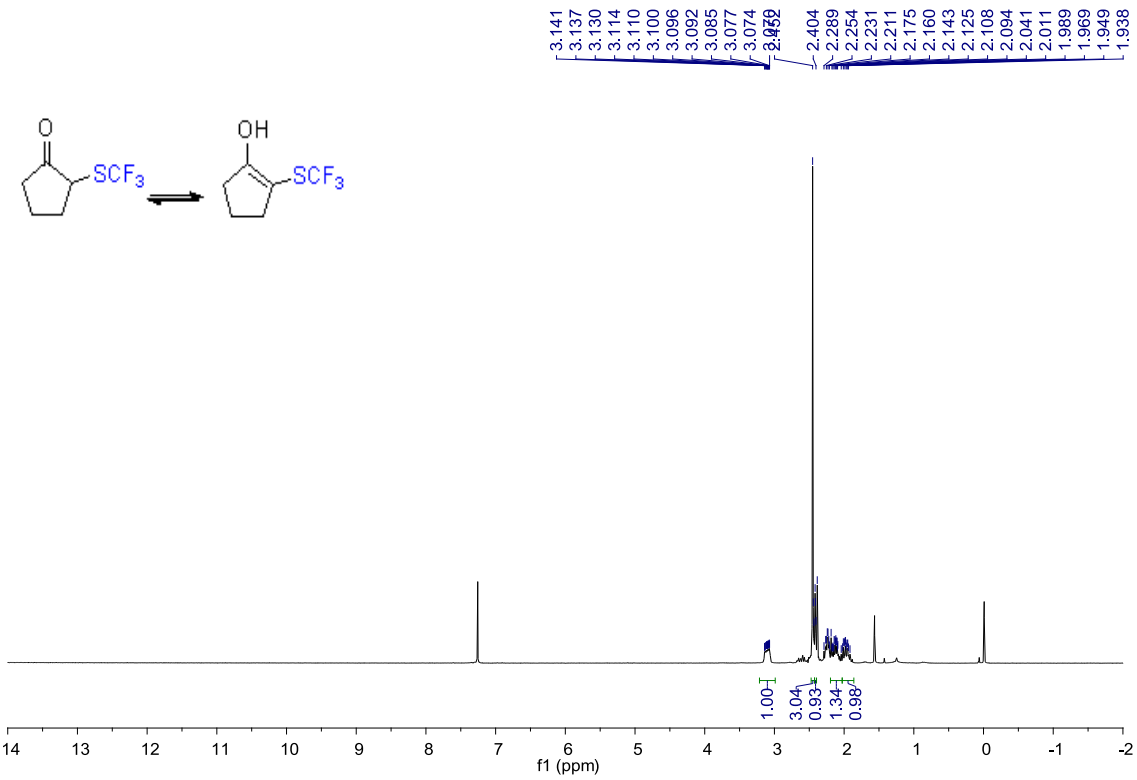
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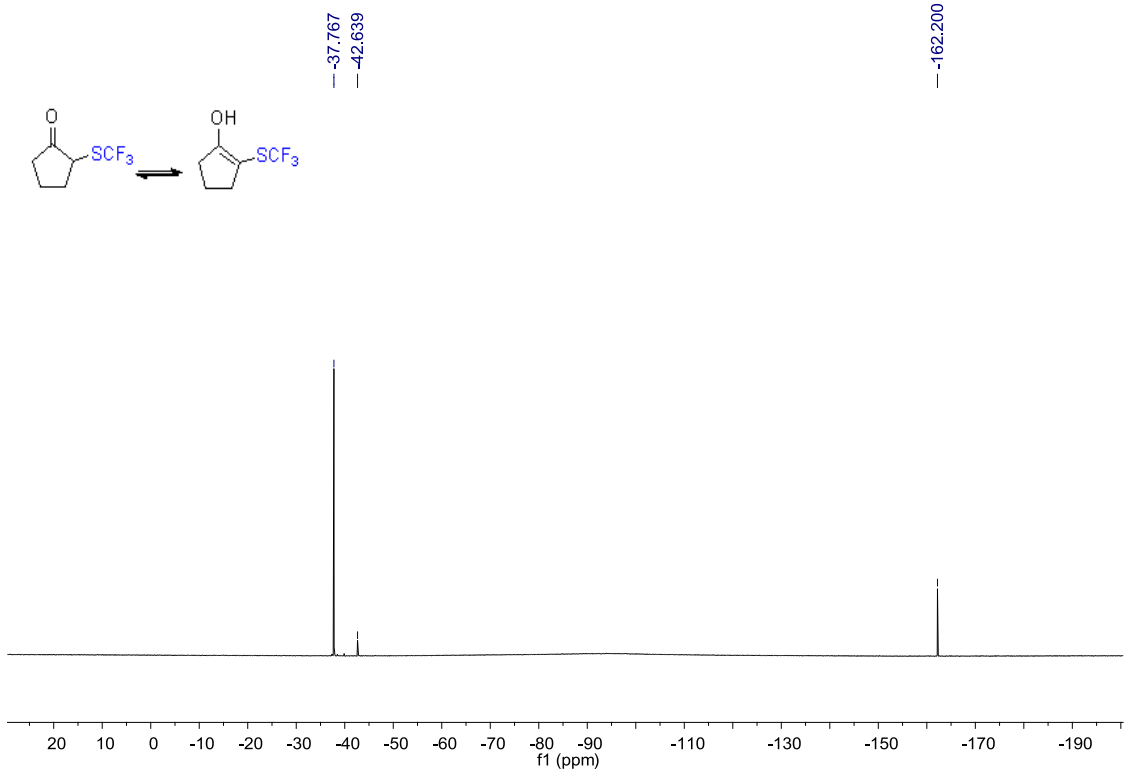
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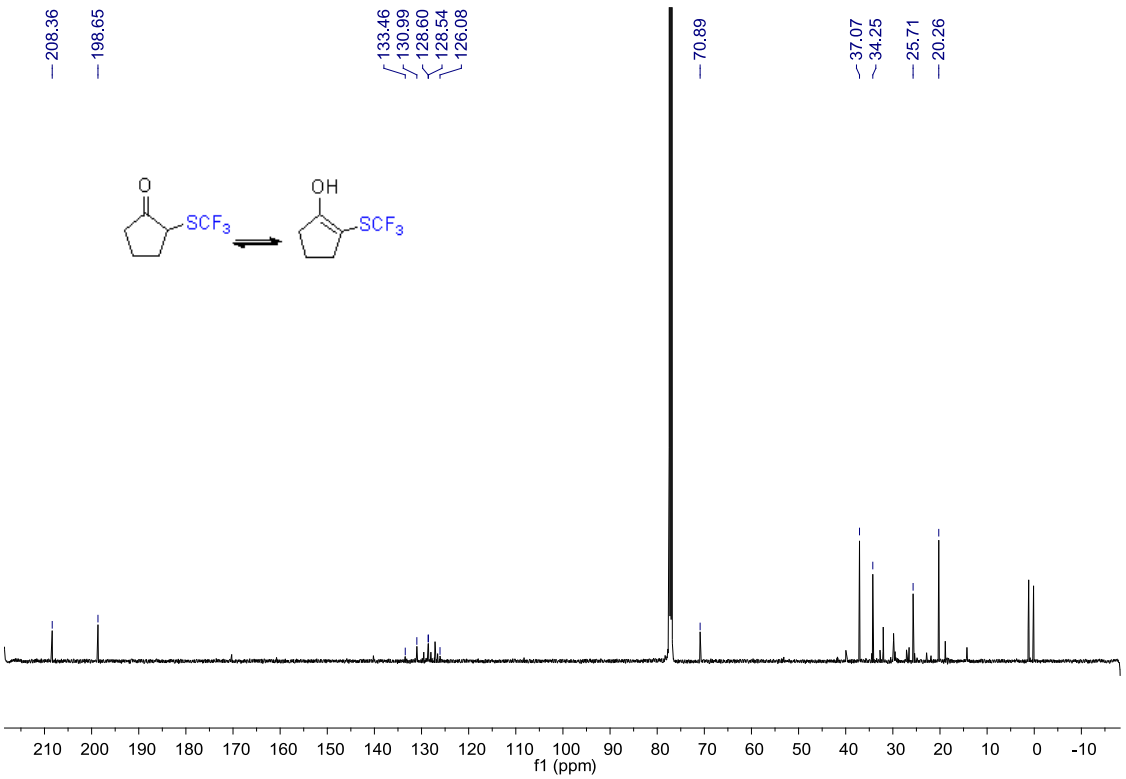
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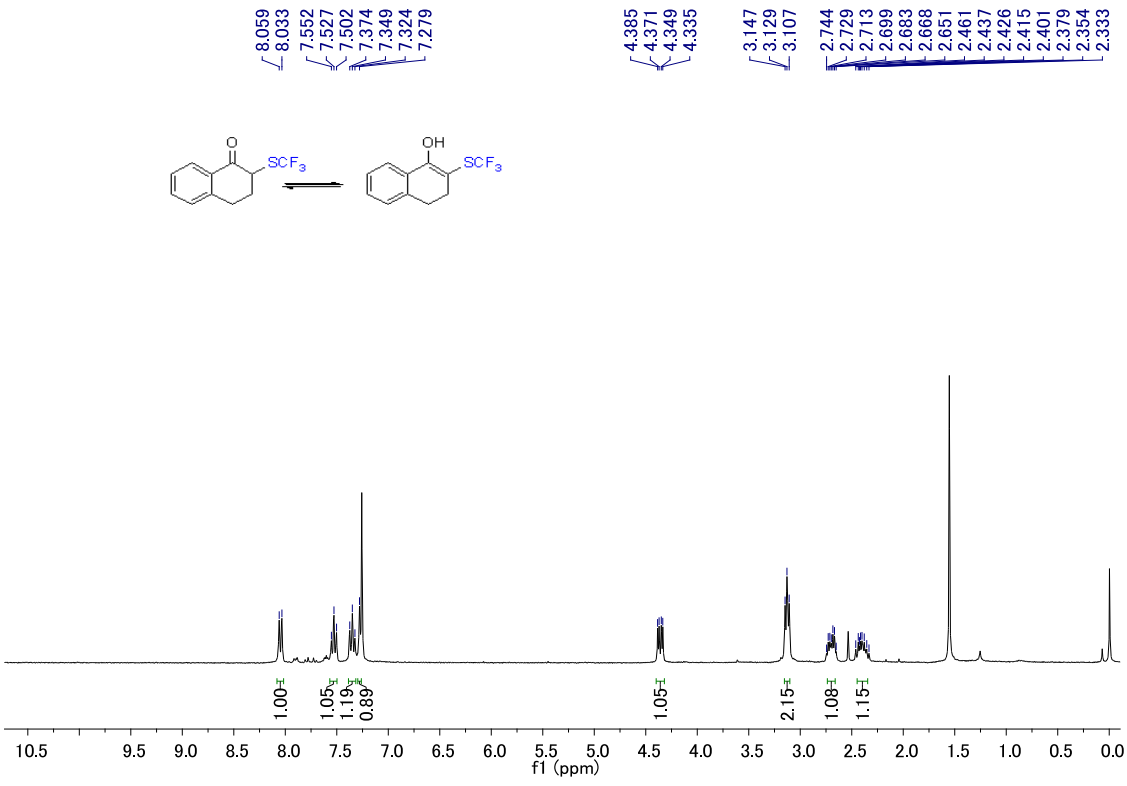
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1.15
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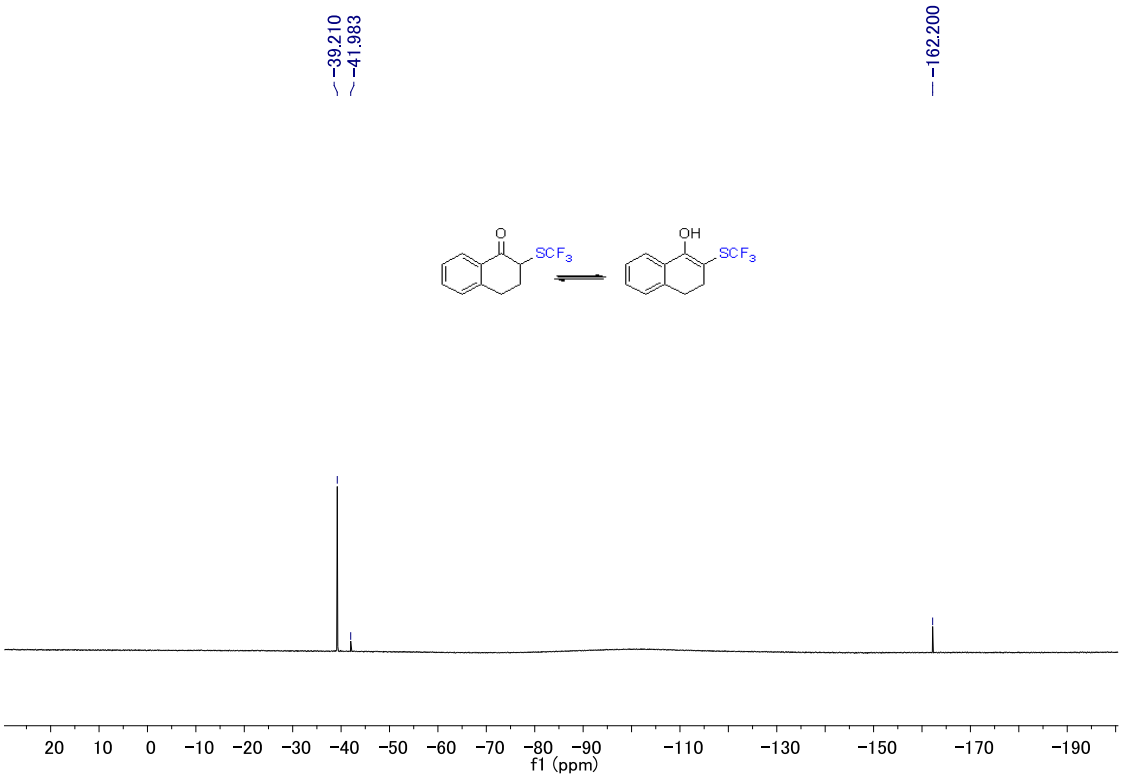
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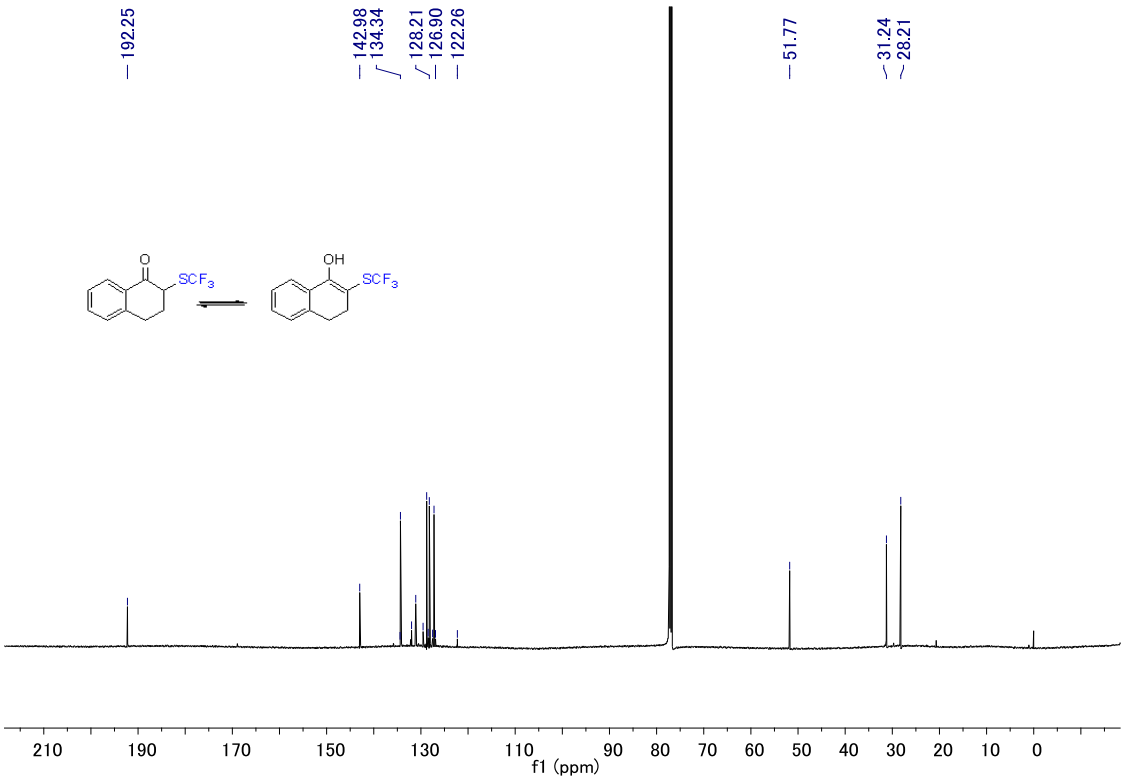
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SCF3
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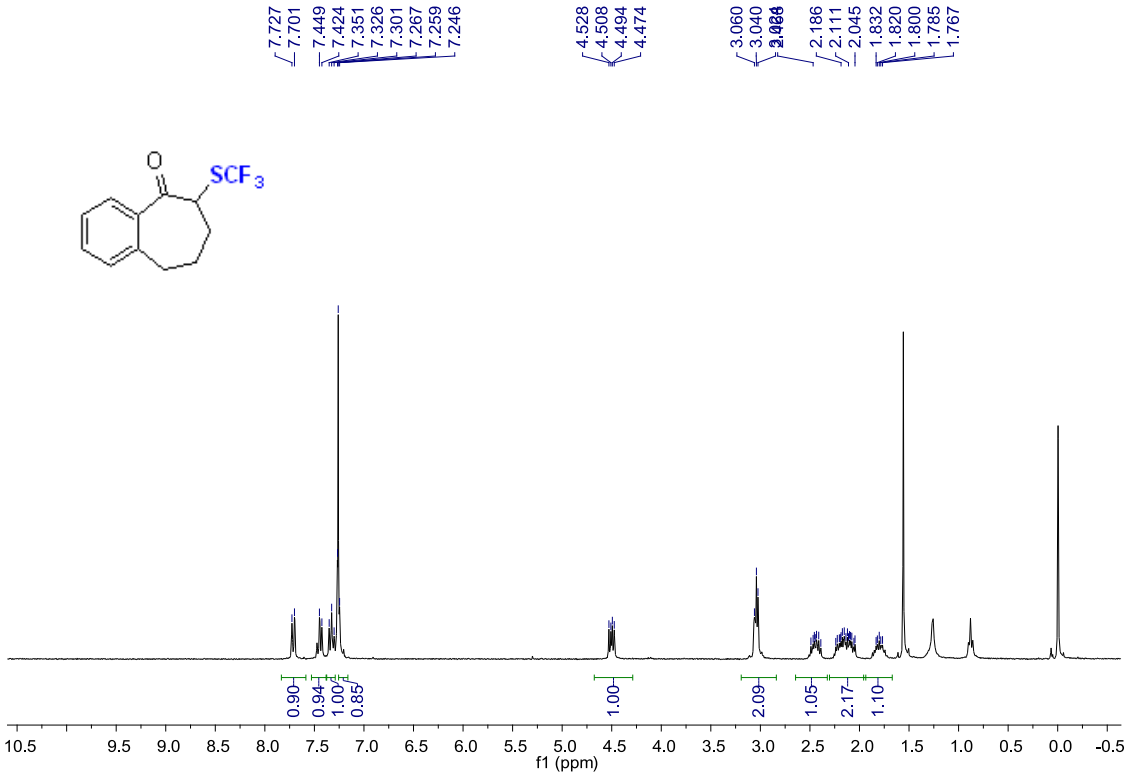
f1 (ppm)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SCF3
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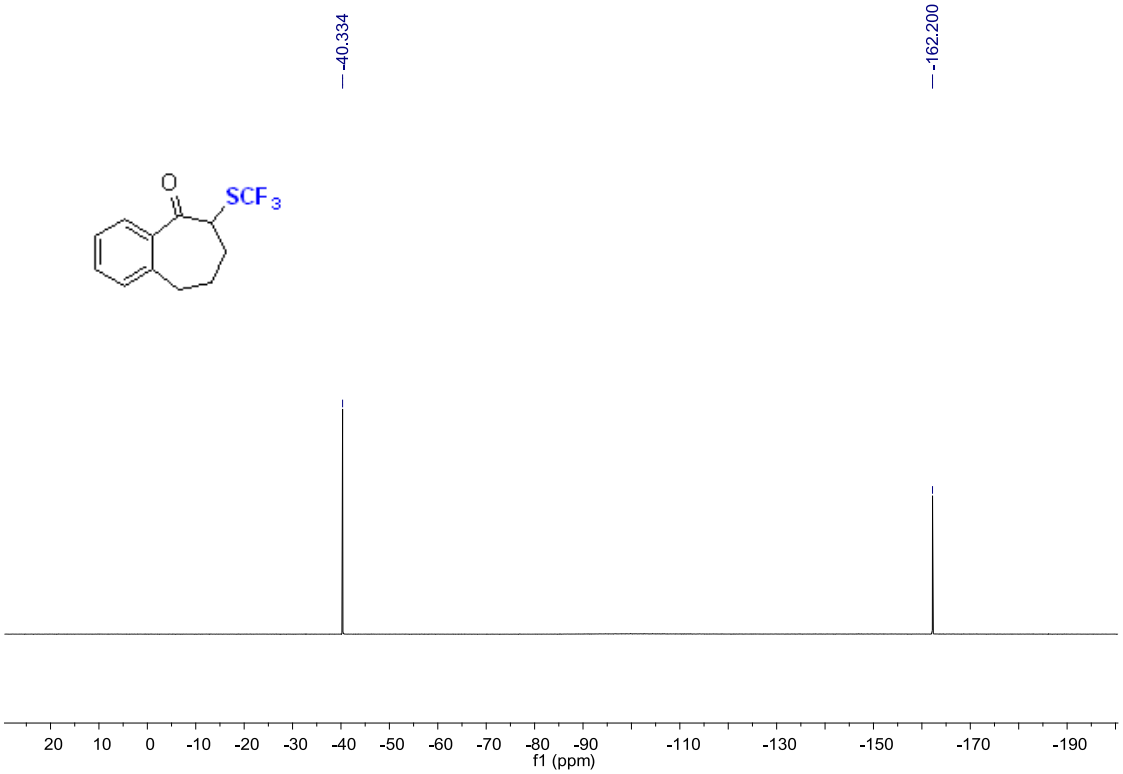
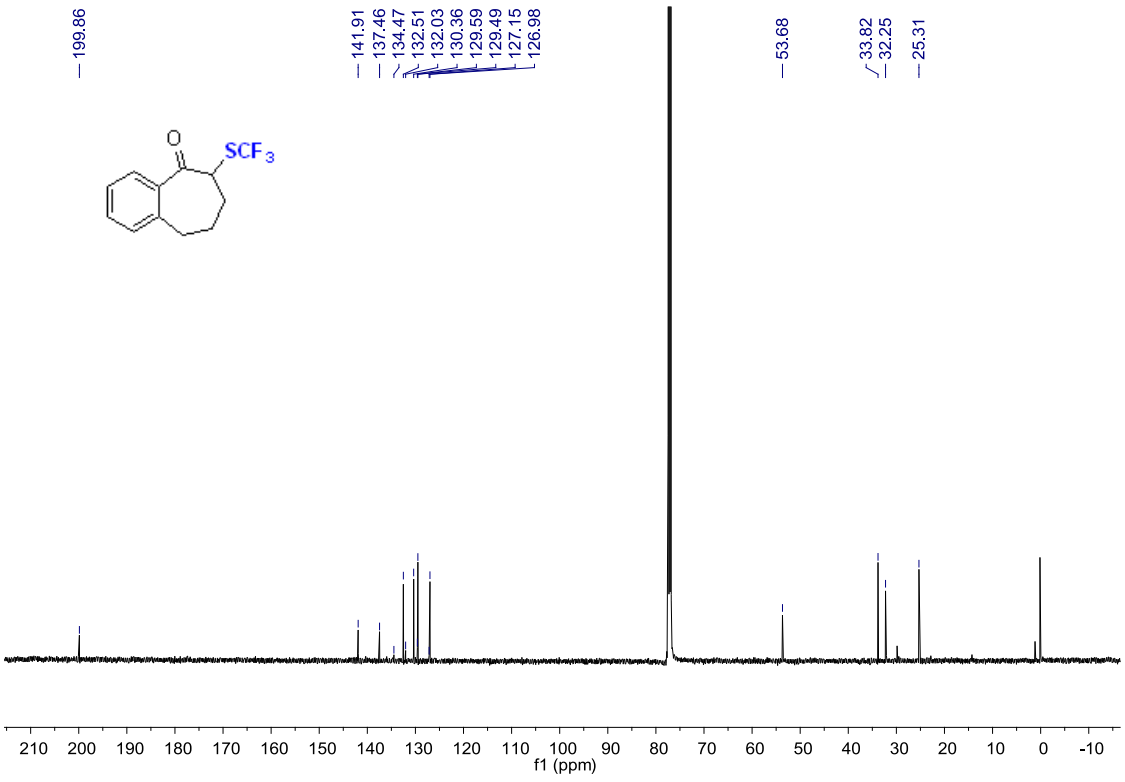
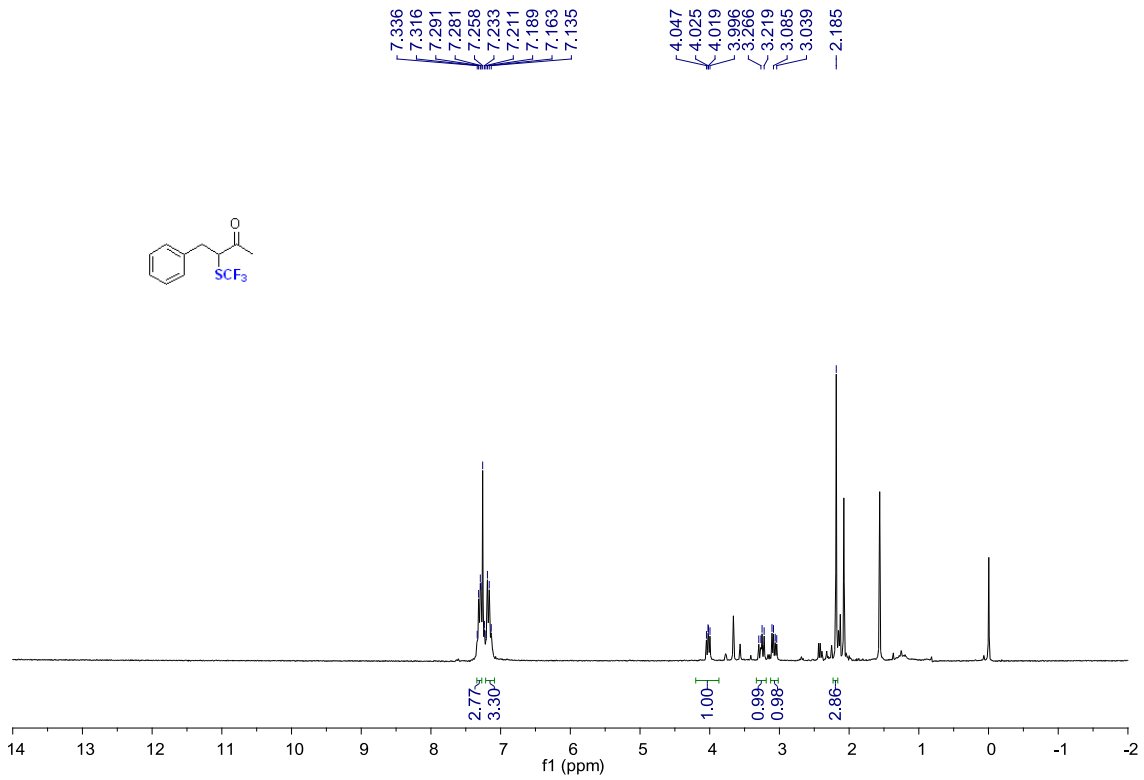
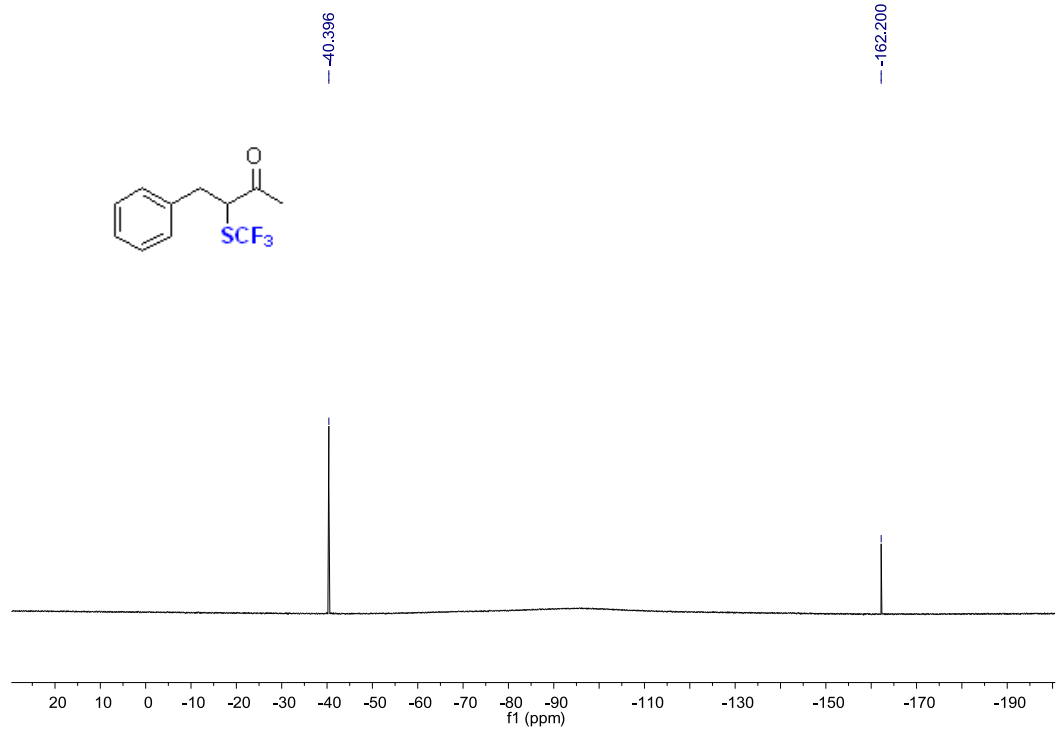
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

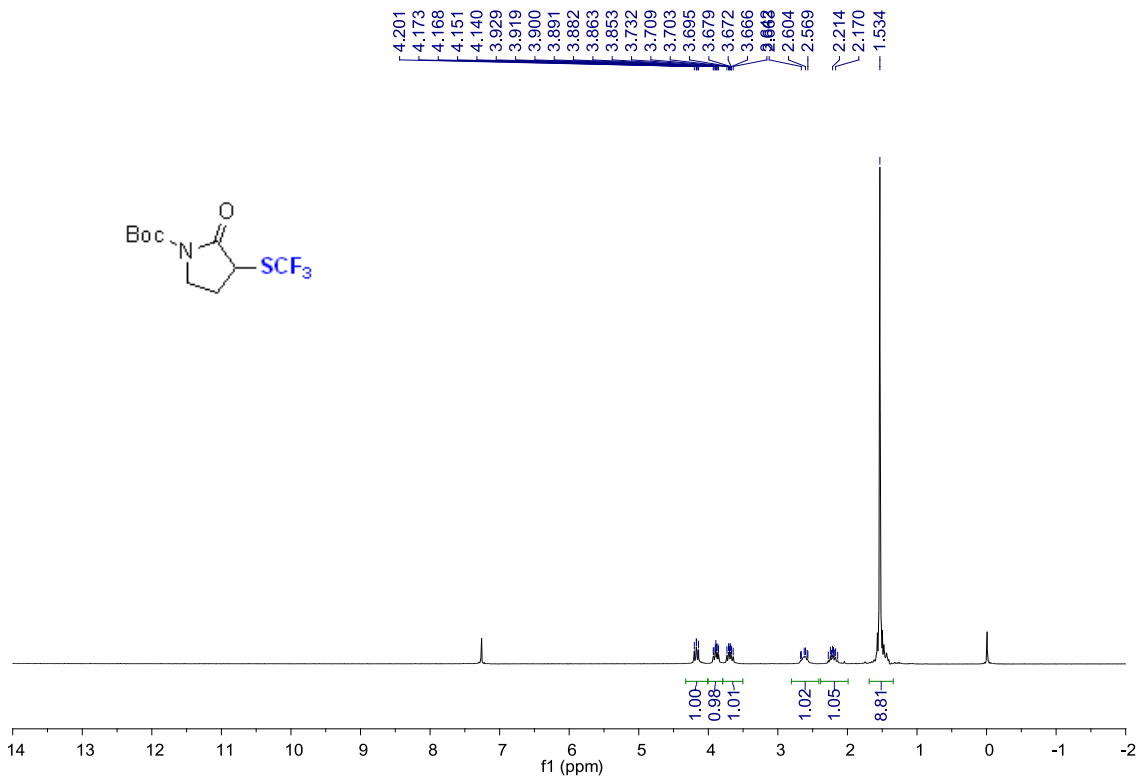

-40.334
-162.200
O
SCF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

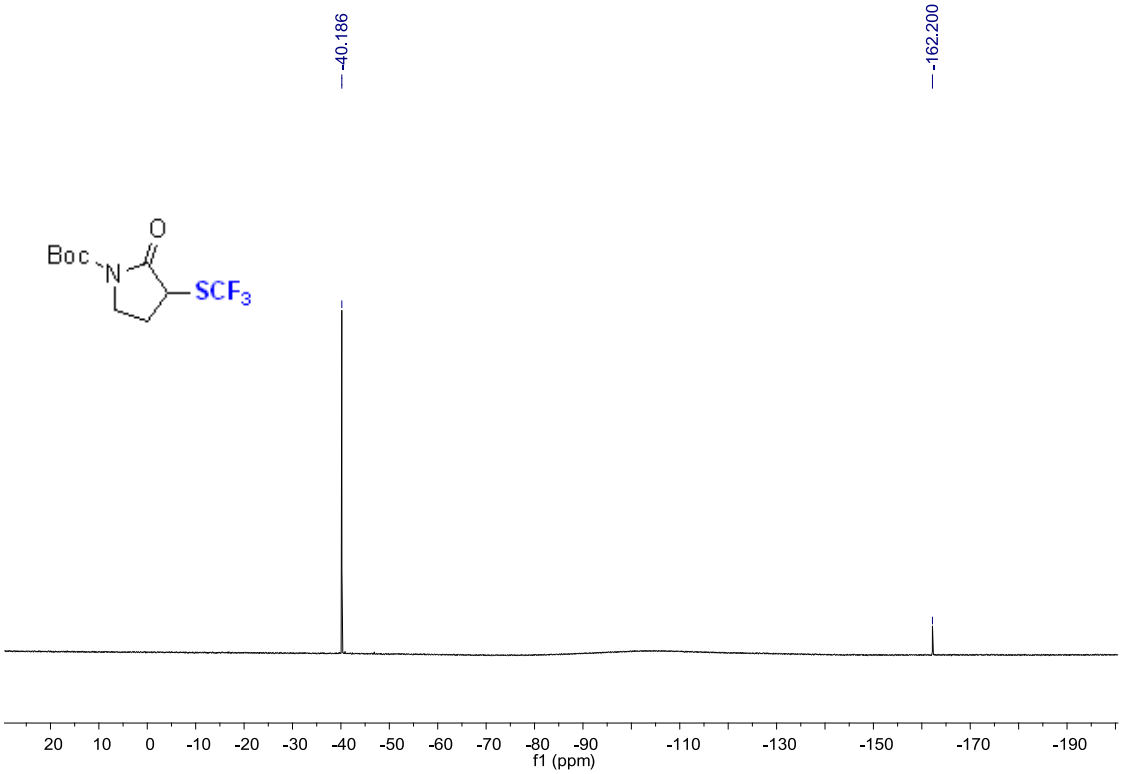

199.86
141.91
137.46
134.47
132.51
132.03
130.36
129.59
129.49
127.15
126.98
53.68
33.82
32.25
25.31
O
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

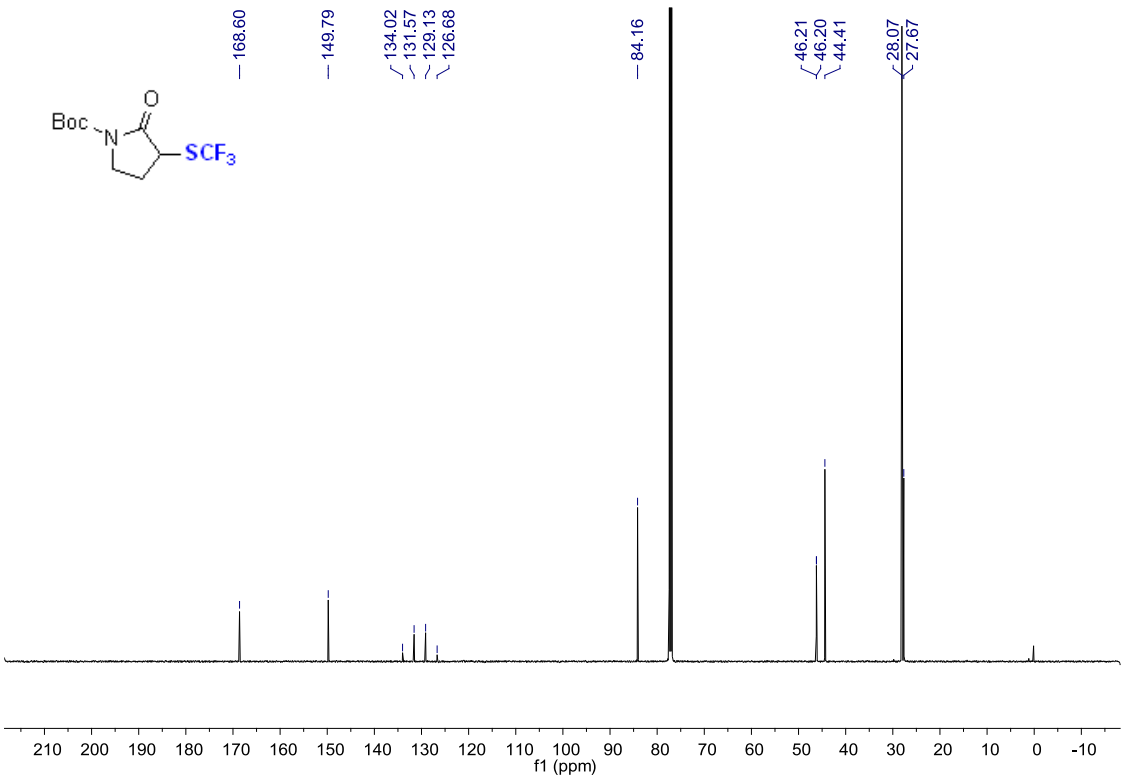

7.336
7.316
7.291
7.281
7.258
7.233
7.211
7.189
7.163
7.135
4.047
4.025
4.019
3.996
3.266
3.219
3.085
3.039
2.185
O
SCF3
2.77
3.30
1.00
0.99
0.98
2.86
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

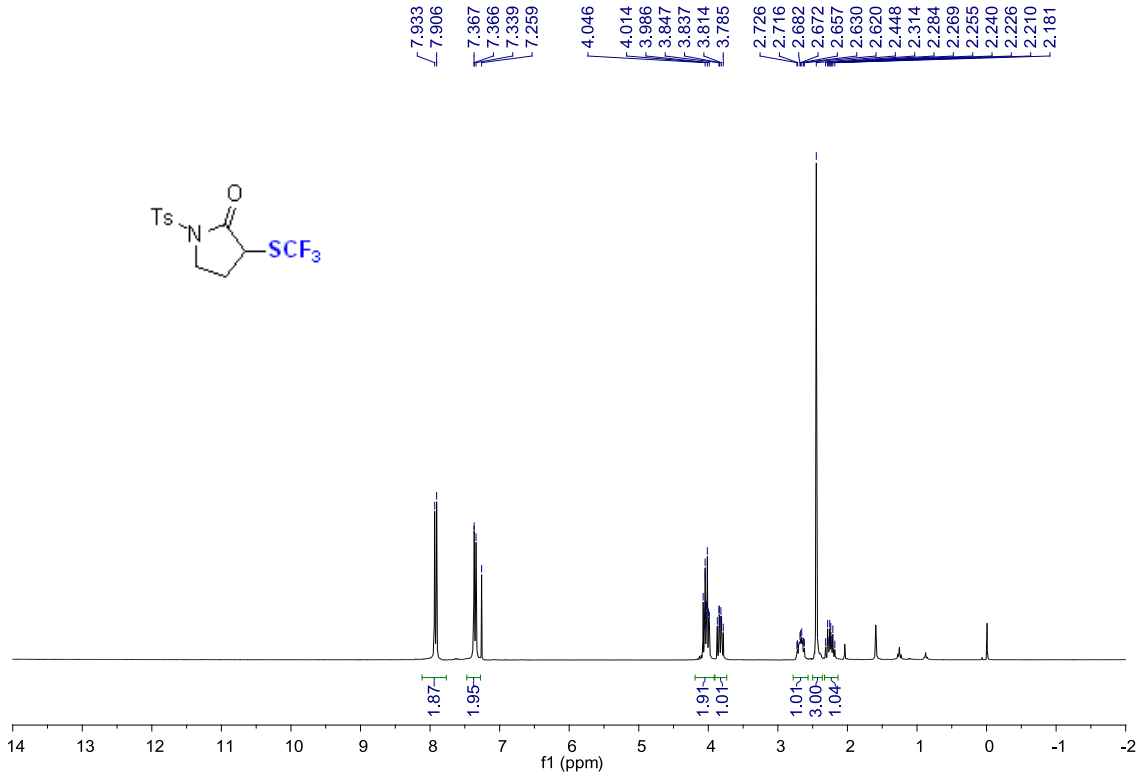

-40.396
-162.200
O
SCF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

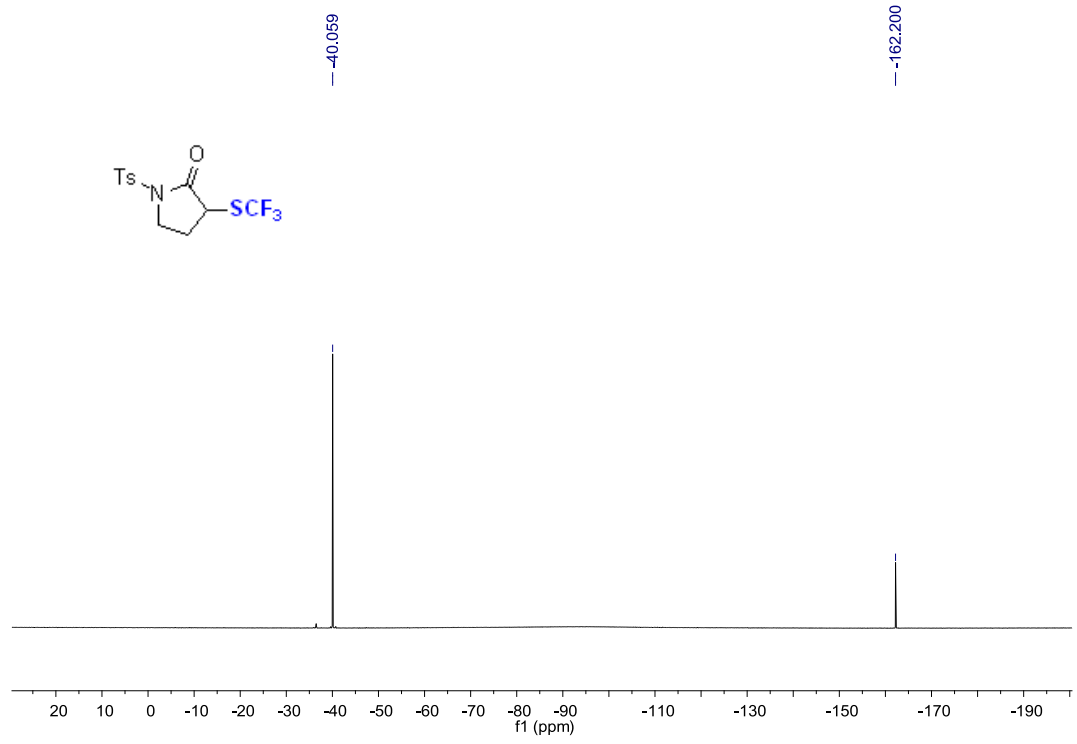
9.2 spectra for scheme 3;

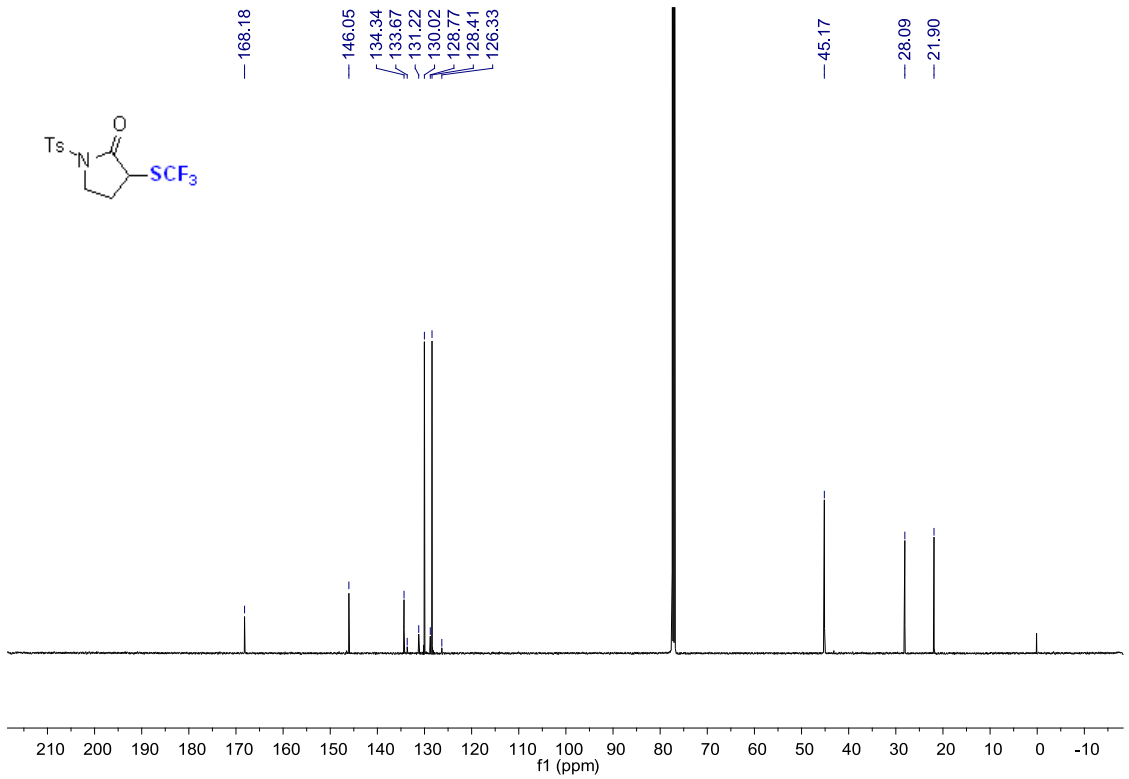


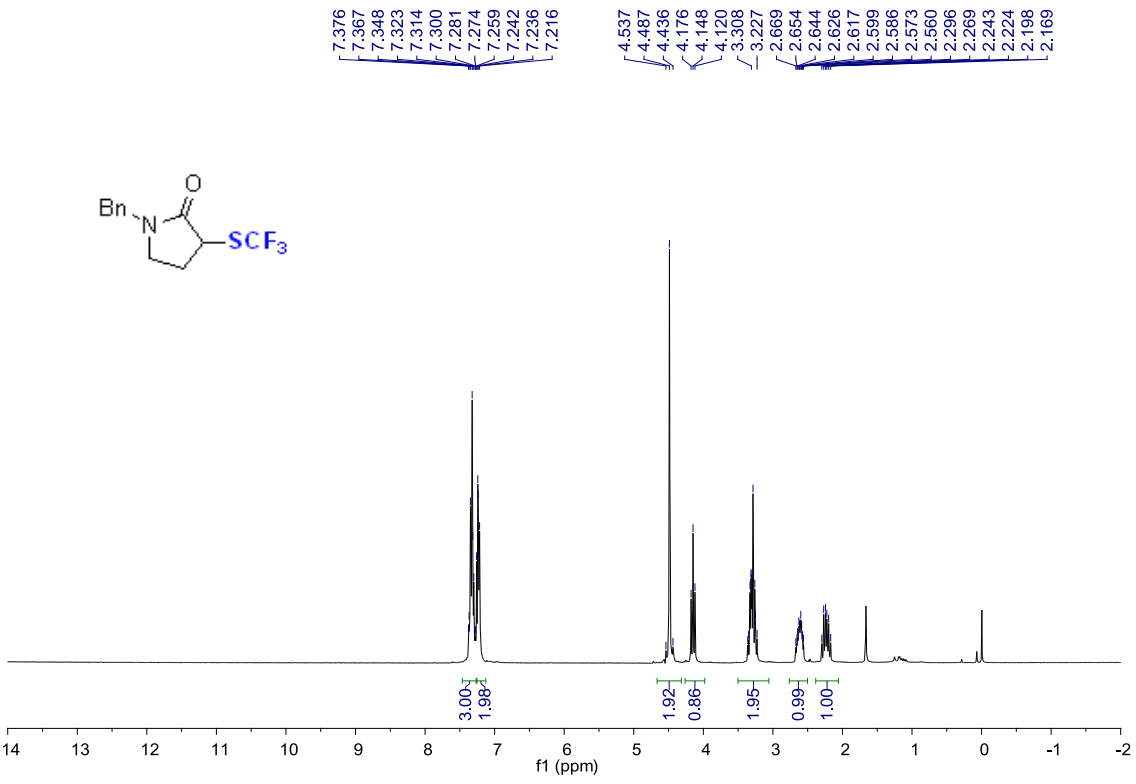

-40.186
-162.200
Boc
N
O
SCF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

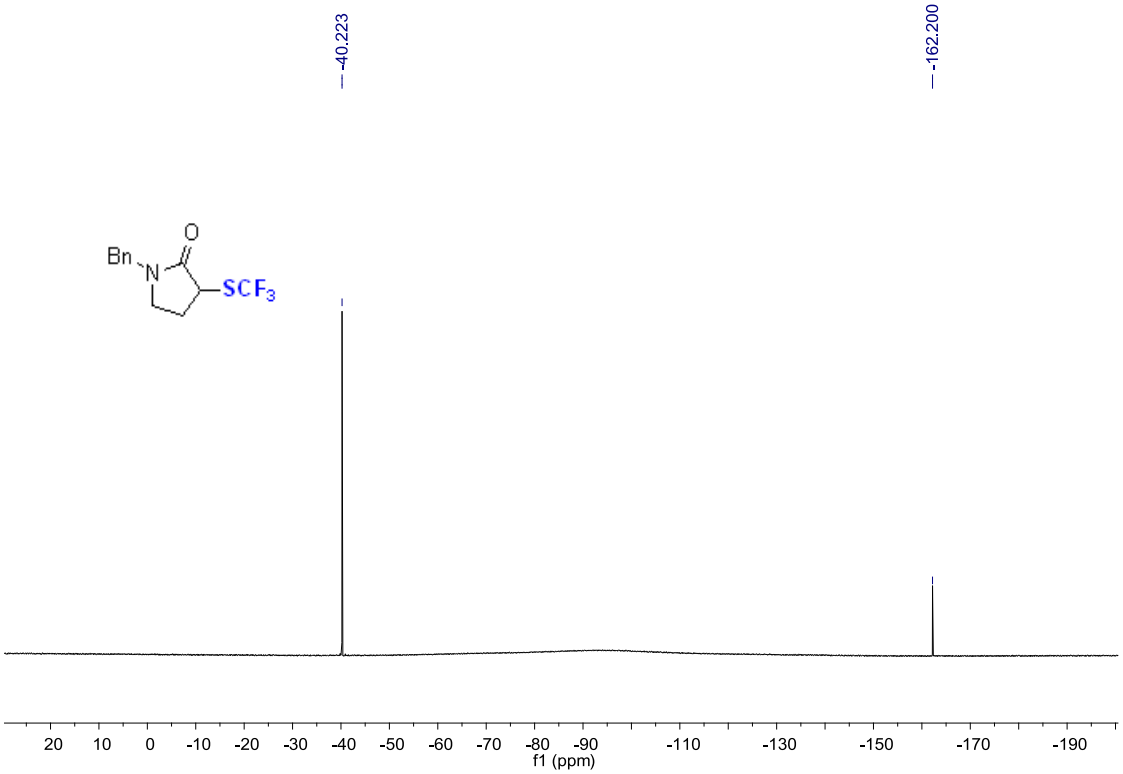

168.60
149.79
134.02
131.57
129.13
126.68
84.16
46.21
46.20
44.41
28.07
27.67
Boc
N
O
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

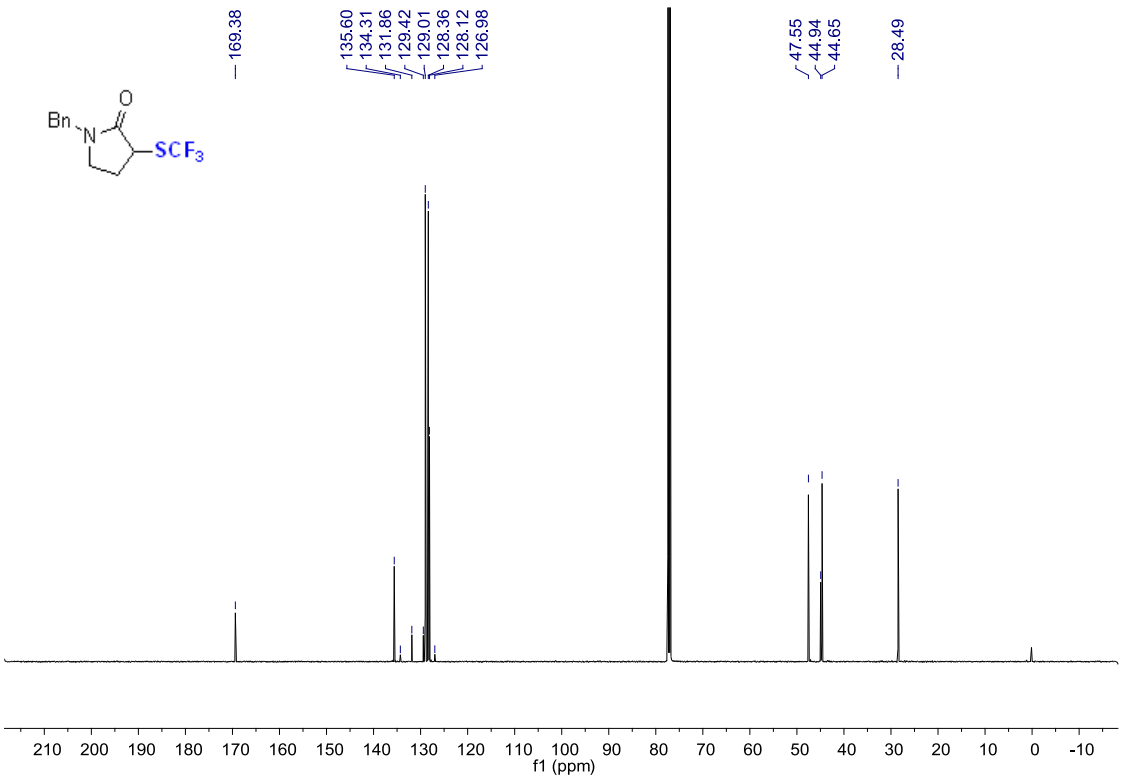

7.933
7.906
7.367
7.366
7.339
7.259
4.046
4.014
3.986
3.847
3.837
3.814
3.785
2.726
2.716
2.682
2.672
2.657
2.630
2.620
2.448
2.314
2.284
2.269
2.255
2.240
2.226
2.210
2.181
Ts
N
O
SCF3
1.87
1.95
1.91
1.01
1.01
3.00
1.04
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

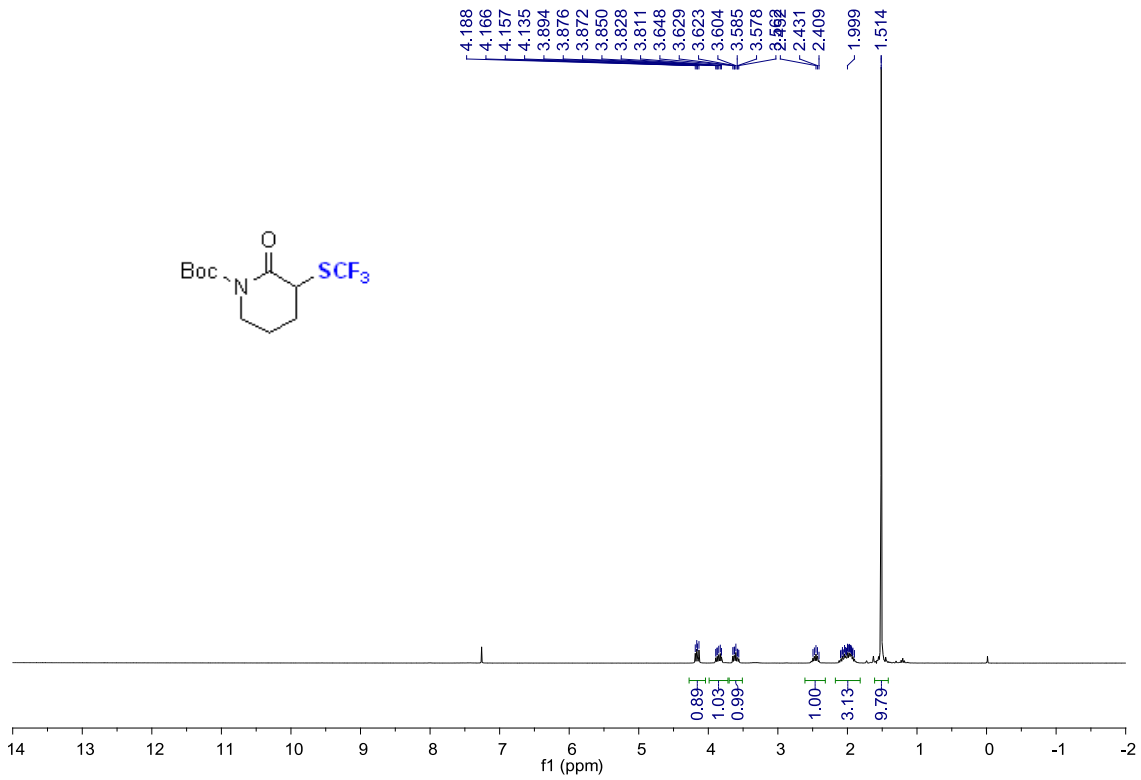

-40.059
-162.200
Ts
N
O
SCF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

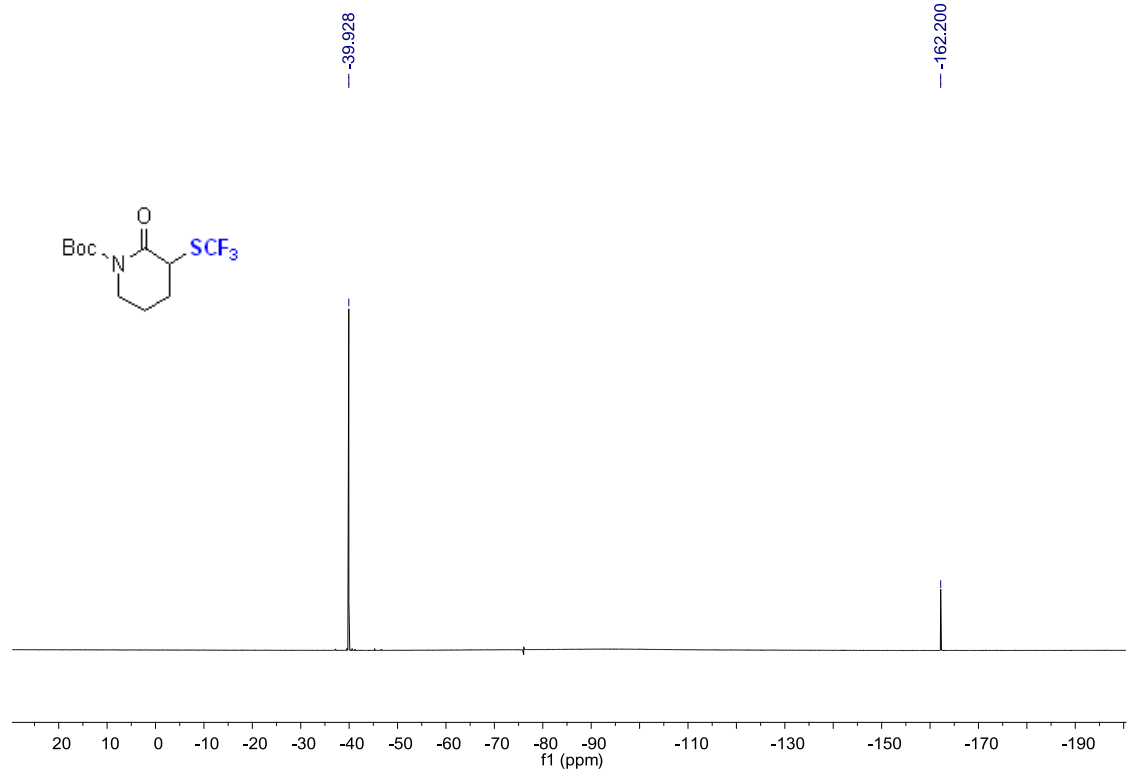

168.18
146.05
134.34
133.67
131.22
130.02
128.77
128.41
126.33
45.17
28.09
21.90
Ts
N
O
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

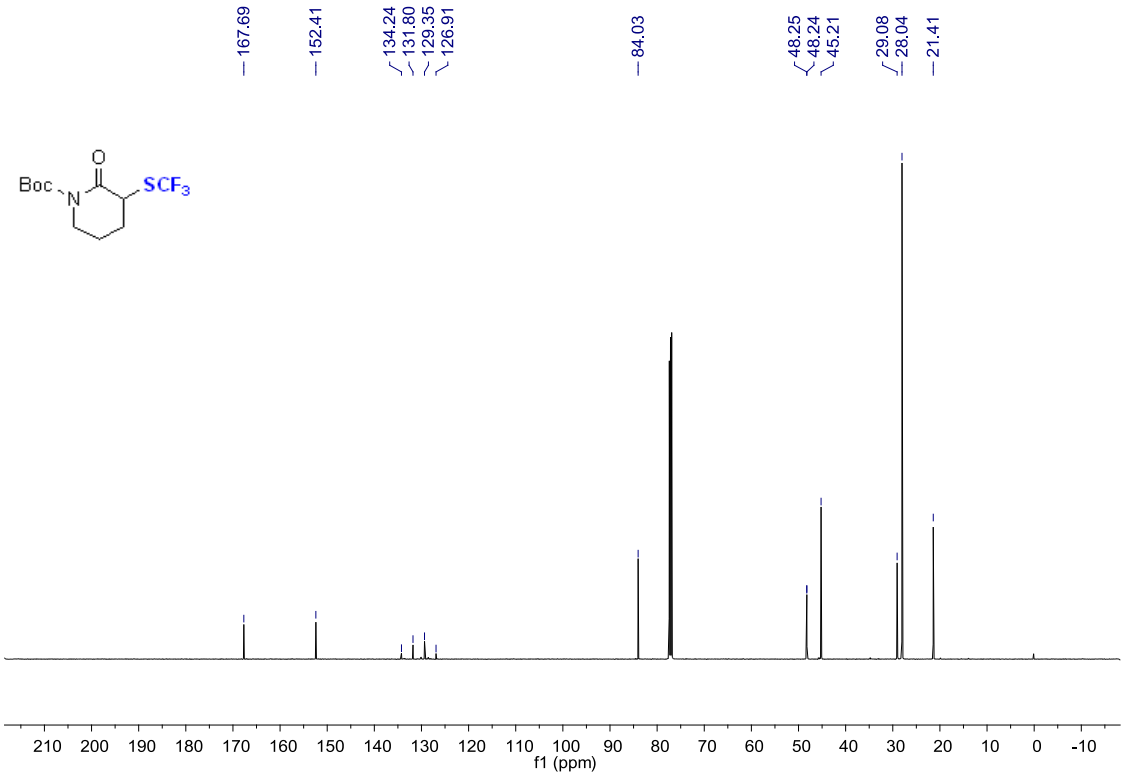

7.376
7.367
7.348
7.323
7.314
7.300
7.281
7.274
7.259
7.242
7.236
7.216
4.537
4.487
4.436
4.176
4.148
4.120
3.308
3.227
2.669
2.654
2.644
2.626
2.617
2.599
2.586
2.573
2.560
2.296
2.269
2.243
2.224
2.198
2.169
Bn
N
O
SCF3
3.00
1.98
1.92
0.86
1.95
0.99
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

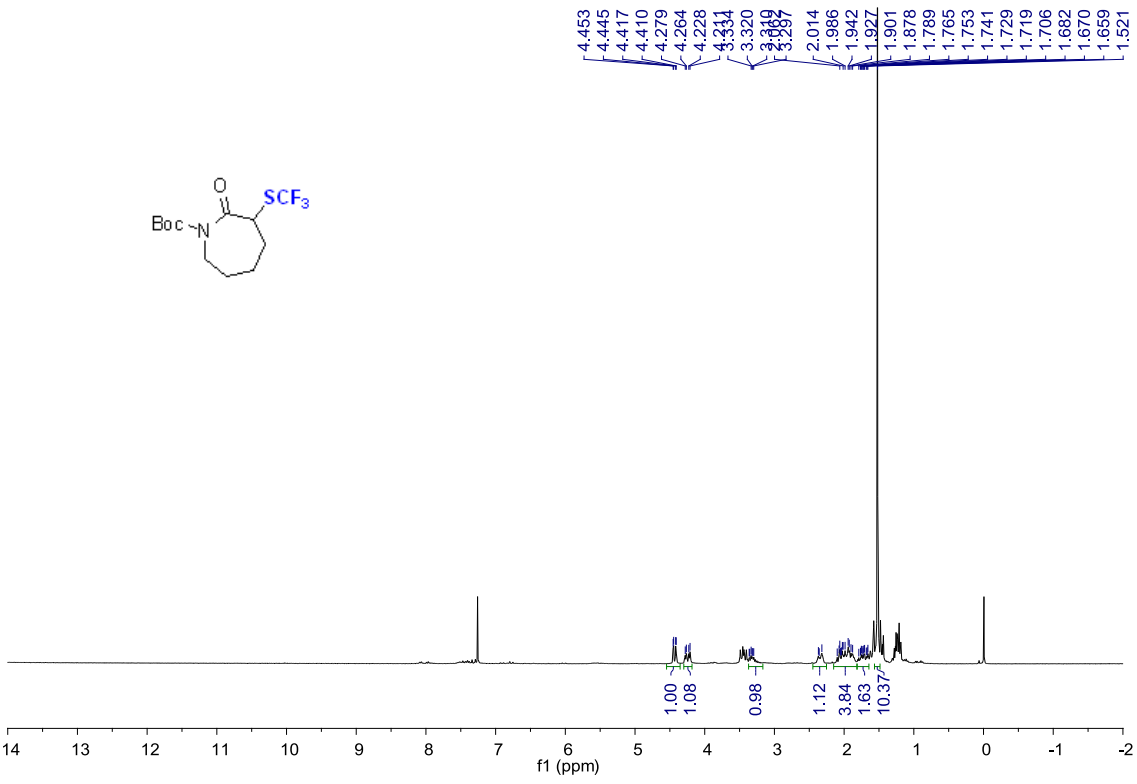

-40.223
-162.200
Bn
N
O
SCF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

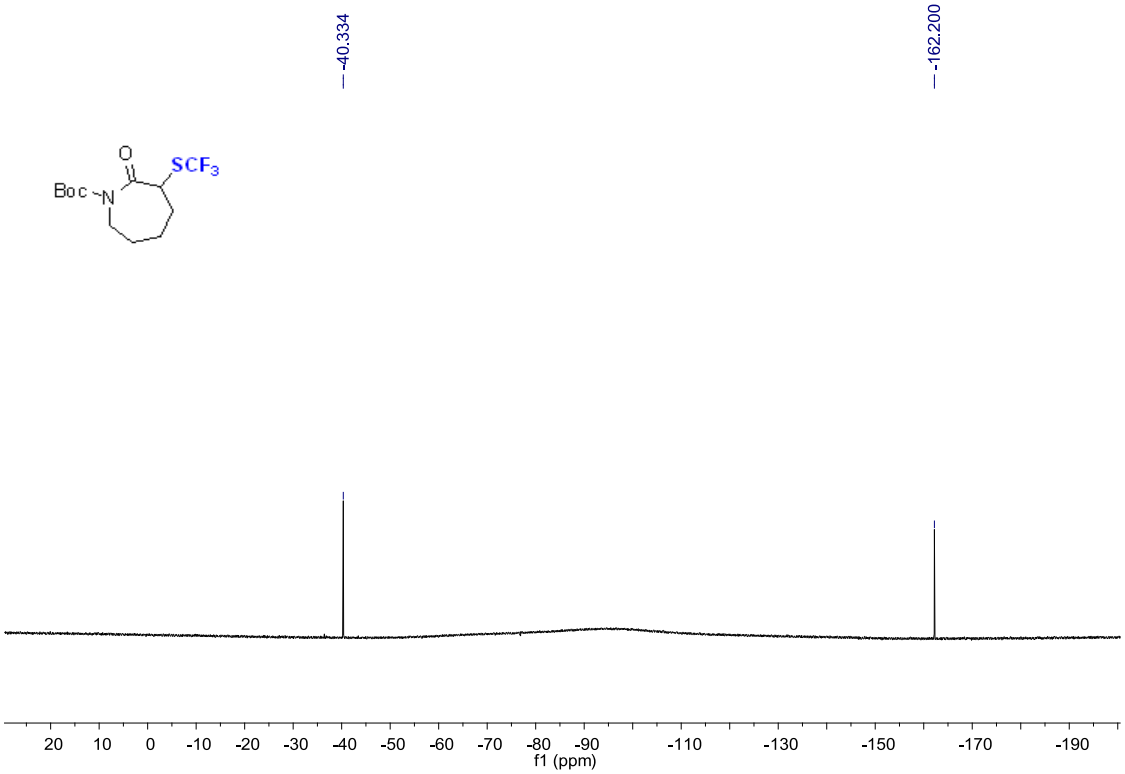

169.38
135.60
134.31
131.86
129.42
129.01
128.36
128.12
126.98
47.55
44.94
44.65
28.49
Bn
N
O
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

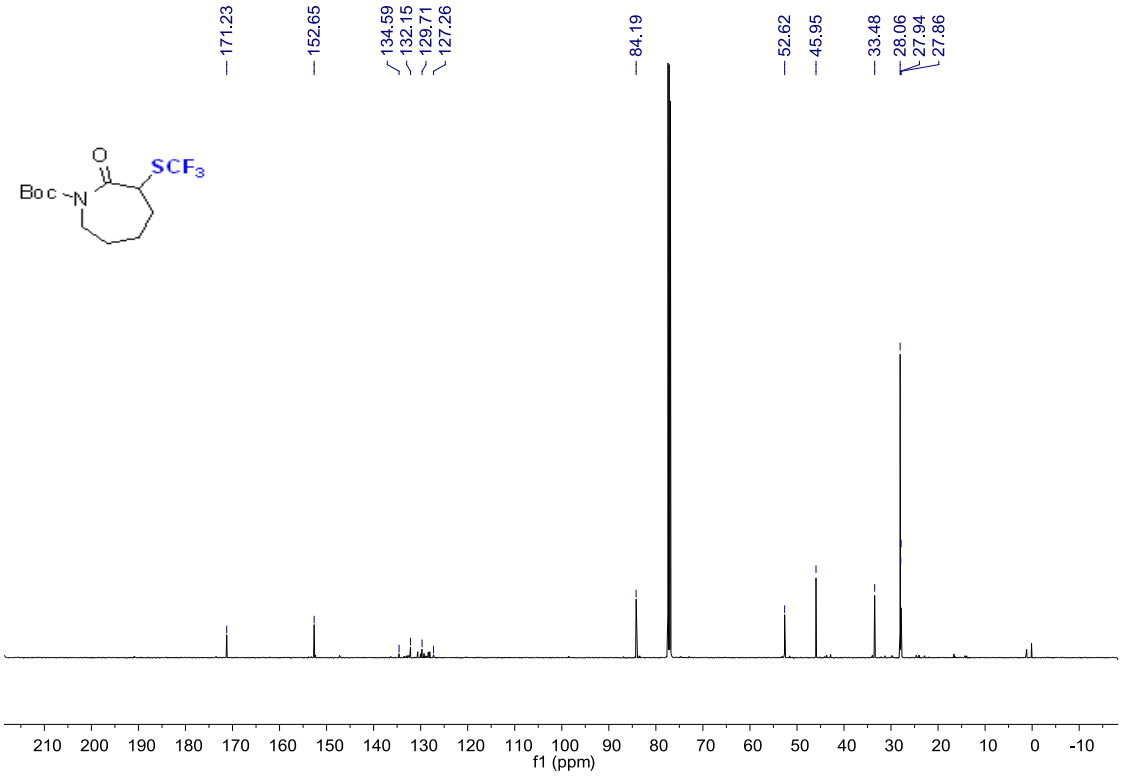

4.188
4.166
4.157
4.135
3.894
3.876
3.872
3.850
3.828
3.811
3.648
3.629
3.623
3.604
3.585
3.578
2.431
2.409
1.999
1.514
Boc
N
O
SCF3
0.89
1.03
0.99
1.00
3.13
9.79
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


-39.928
-162.200
Boc
N
O
SCF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

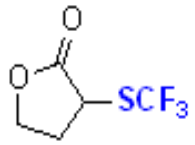

167.69
152.41
134.24
131.80
129.35
126.91
84.03
48.25
48.24
45.21
29.08
28.04
21.41
Boc
N
O
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

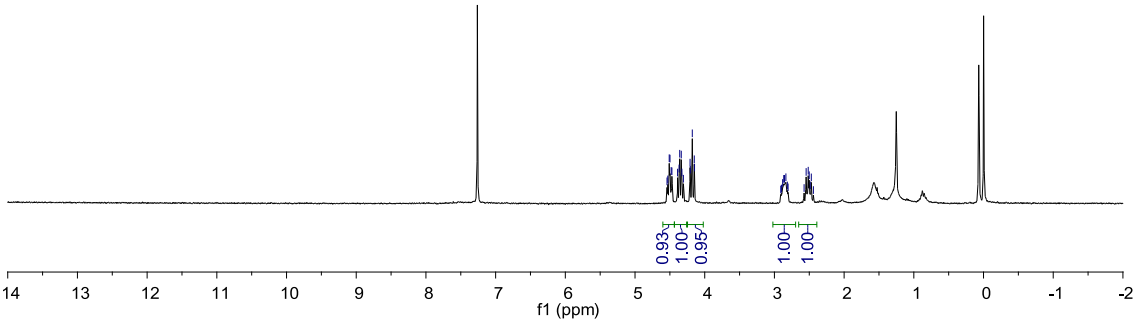

4.453
4.445
4.417
4.410
4.279
4.264
4.228
4.211
3.334
3.320
2.014
1.986
1.942
1.927
1.901
1.878
1.789
1.765
1.753
1.741
1.729
1.719
1.706
1.682
1.670
1.659
1.521
Boc
N
O
SCF3
1.00
1.08
0.98
1.12
3.84
1.63
10.37
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


-40.334
-162.200
O
SCF3
Boc
N
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

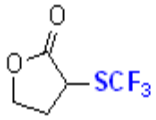

171.23
152.65
134.59
132.15
129.71
127.26
84.19
52.62
45.95
33.48
28.06
27.94
27.86
O
SCF3
Boc
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

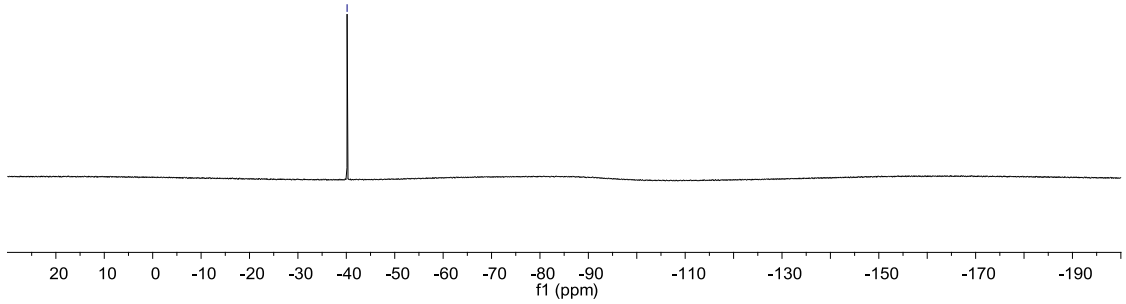

4.541
4.529
4.510
4.498
4.482
4.471
4.389
4.367
4.359
4.337
4.328
4.306
4.210
4.207
4.178
4.150
4.146
2.909
2.899
2.882
2.866
2.855
2.835
2.815
2.804
2.574
2.545
2.515
2.501
2.486
2.471
2.441

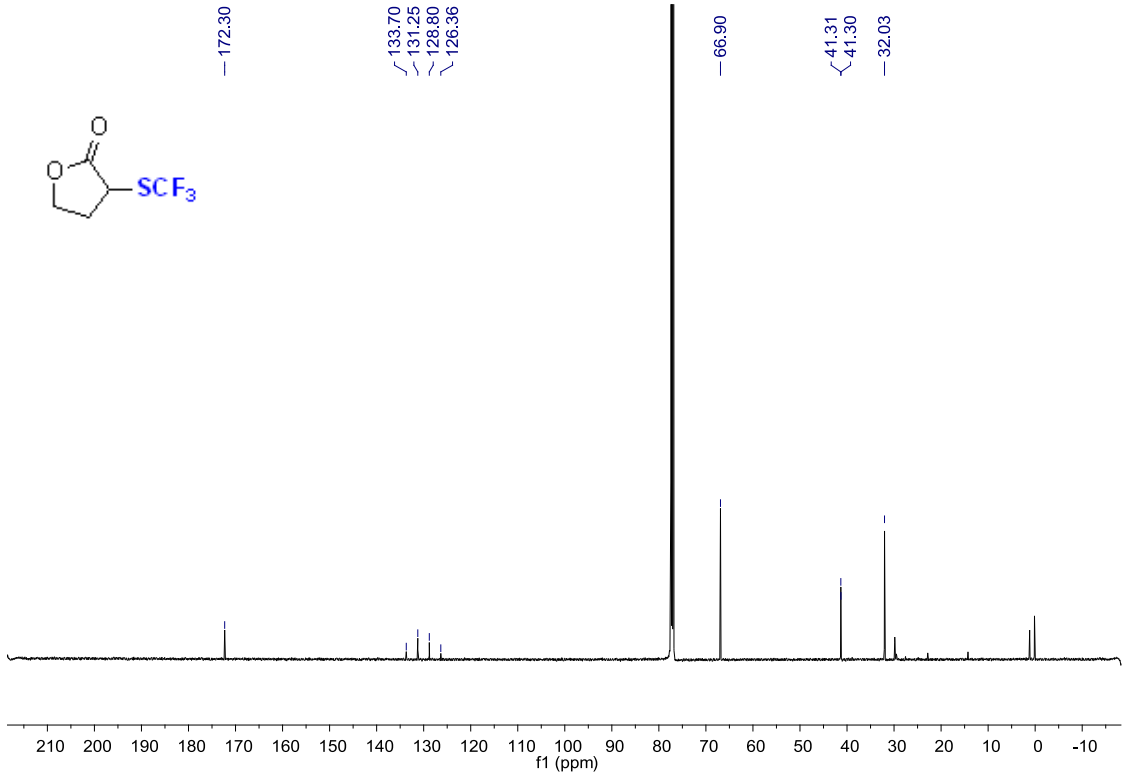

O
O
SCF3

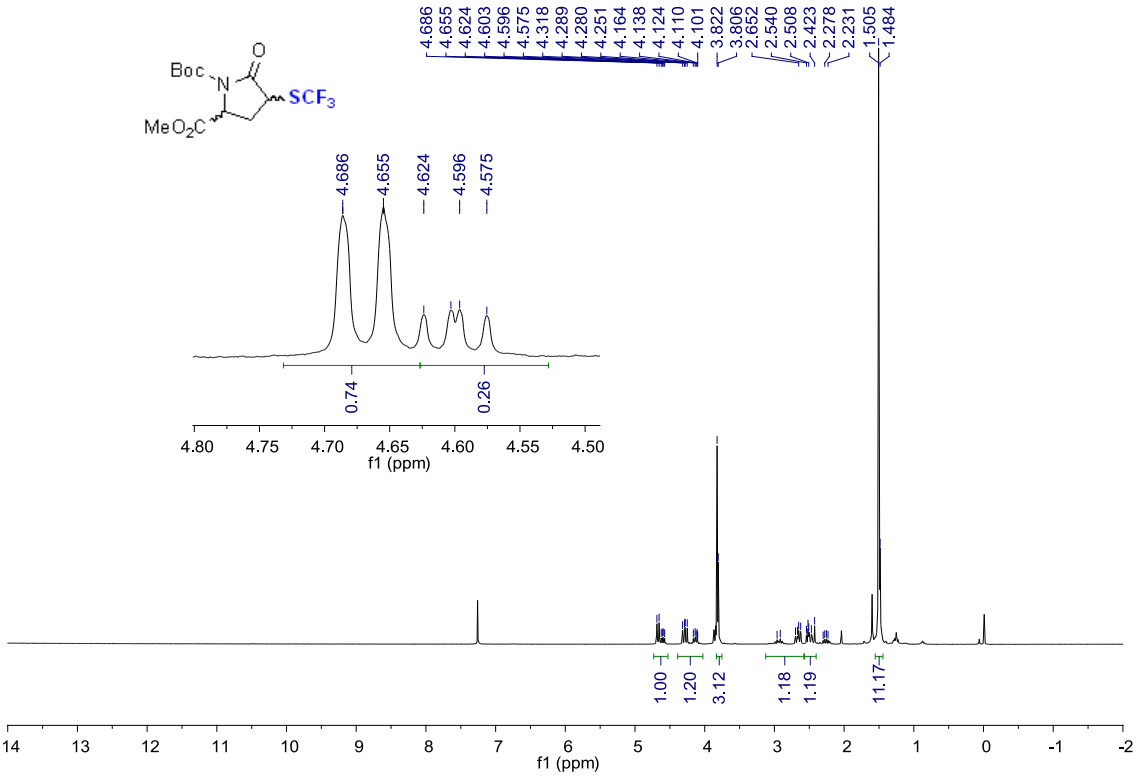

0.93
1.00
0.95
1.00
1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

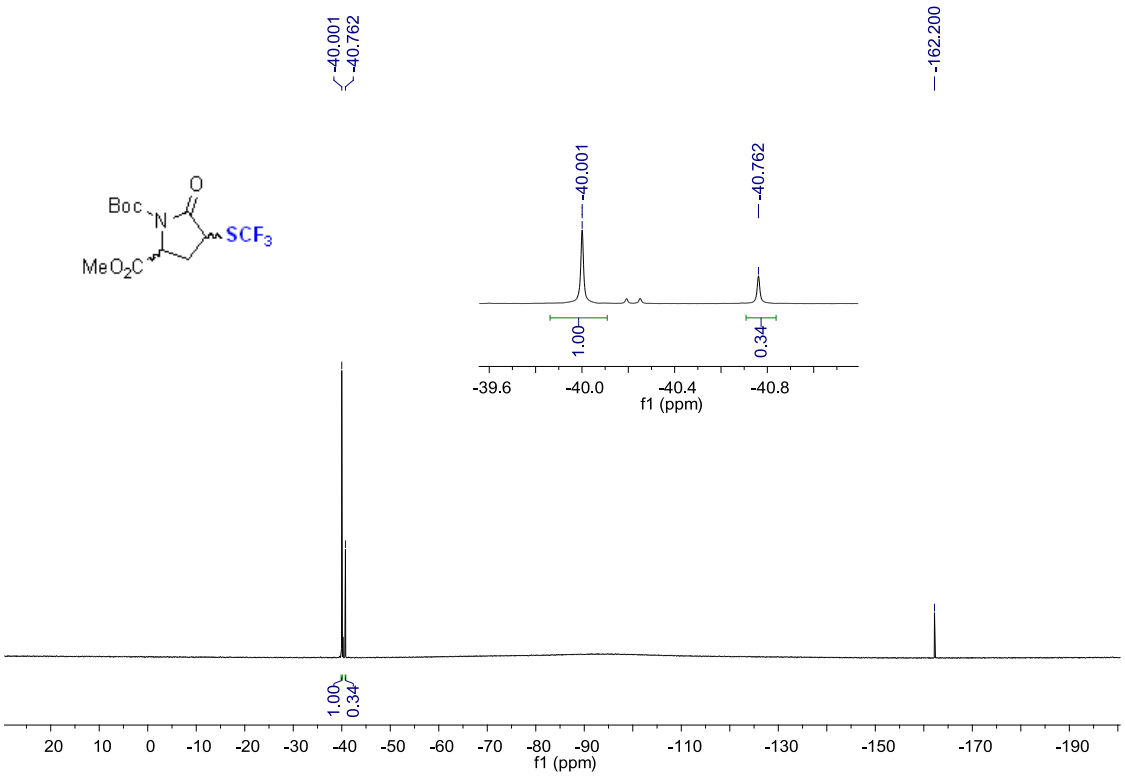

-40.160

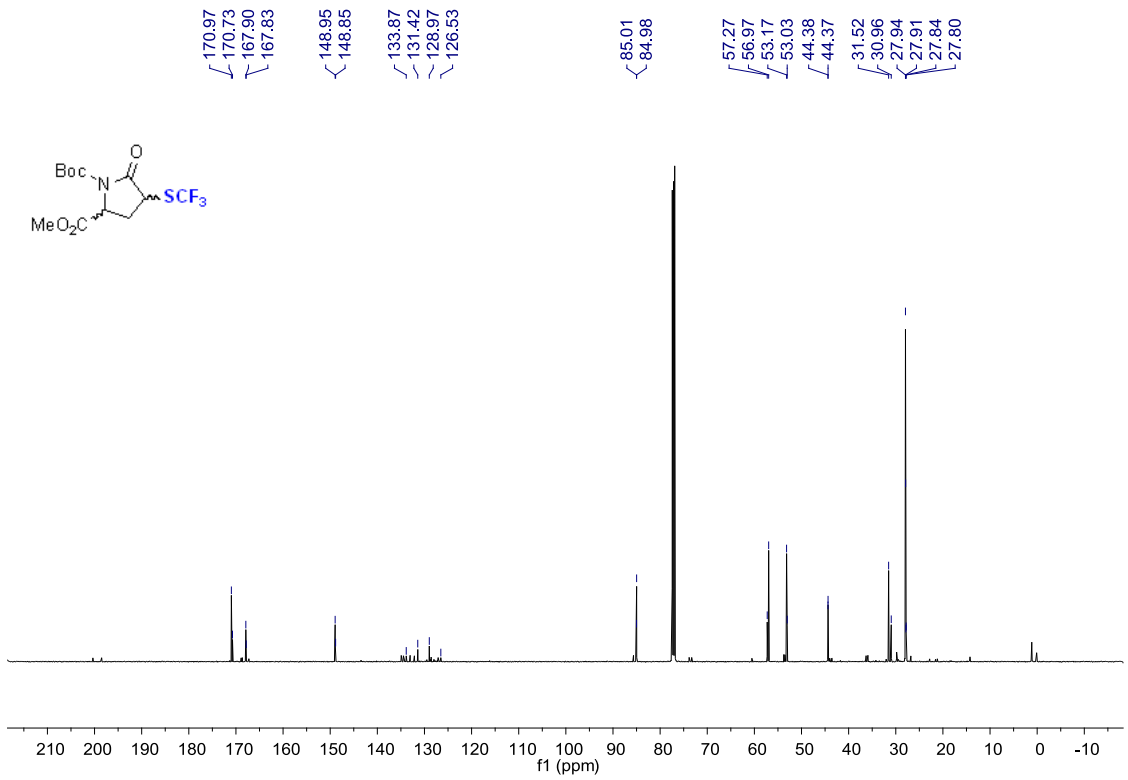

O
O
SCF3


20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
f1 (ppm)

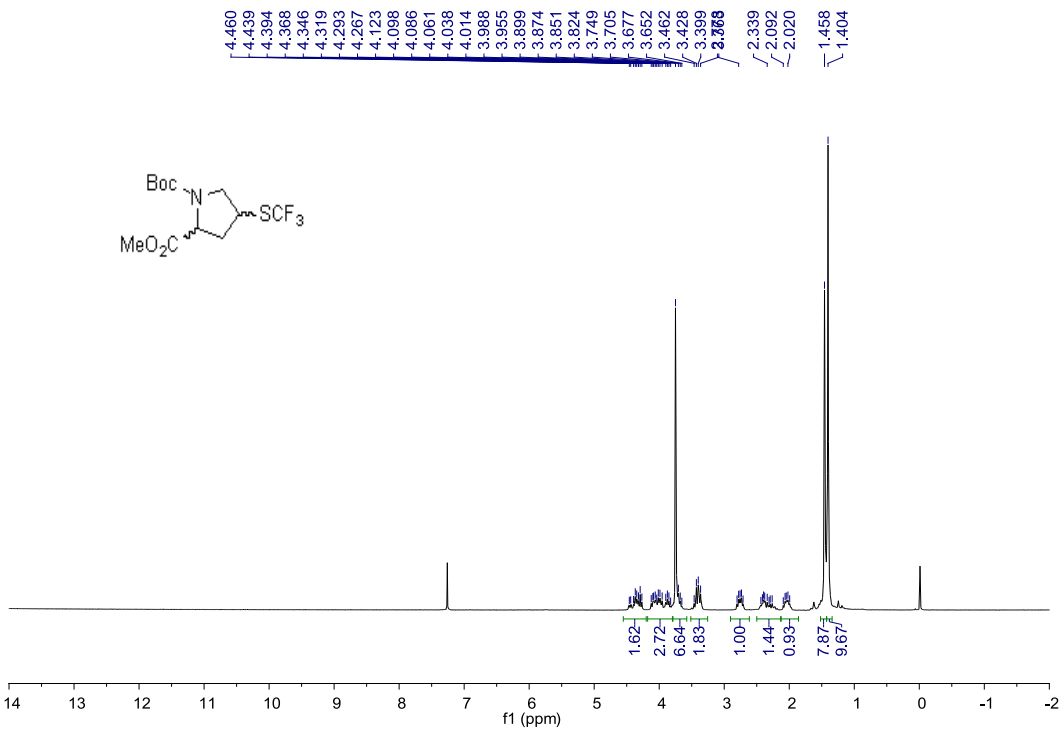

172.30
133.70
131.25
128.80
126.36
66.90
41.31
41.30
32.03
O
O
SCF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

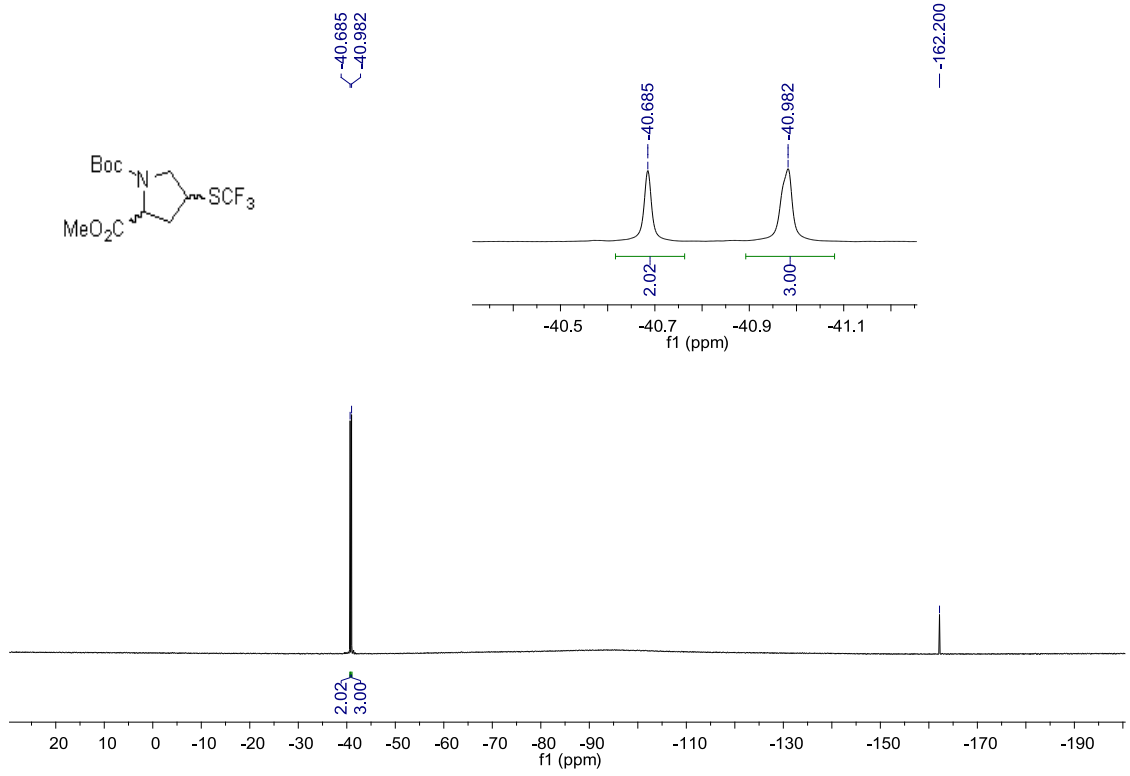

4.686
4.655
4.624
4.603
4.596
4.575
4.318
4.289
4.280
4.251
4.164
4.138
4.124
4.110
4.101
3.822
3.806
2.652
2.540
2.508
2.423
2.278
2.231
1.505
1.484
Boc
N
O
SCF3
MeO2C
4.686
4.655
4.624
4.596
4.575
0.74
0.26
4.80 4.75 4.70 4.65 4.60 4.55 4.50
f1 (ppm)
1.00
1.20
3.12
1.18
1.19
11.17
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

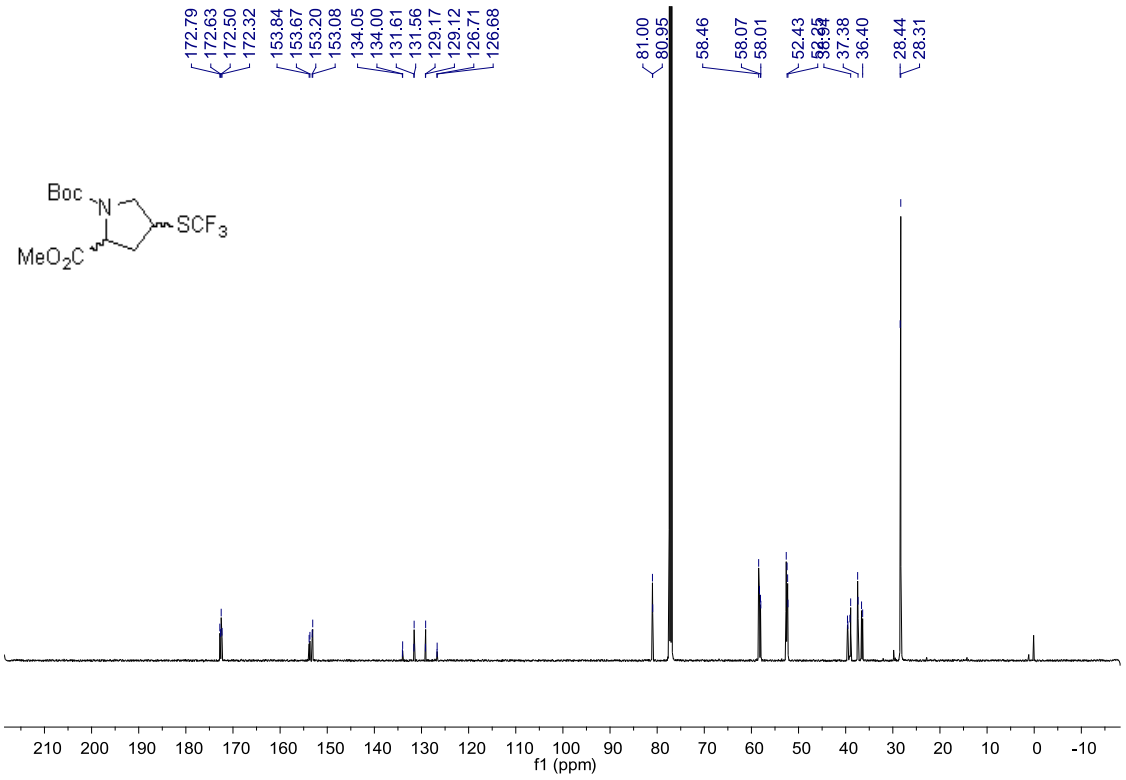

-40.001
-40.762
-162.200
Boc
N
O
SCF3
MeO2C
-40.001
-40.762
1.00
0.34
-39.6
-40.0
-40.4
-40.8
f1 (ppm)
1.00
0.34
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
f1 (ppm)


170.97
170.73
167.90
167.83
148.95
148.85
133.87
131.42
128.97
126.53
85.01
84.98
57.27
56.97
53.17
53.03
44.38
44.37
31.52
30.96
27.94
27.91
27.84
27.80
Boc
N
O
SCF3
MeO2C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

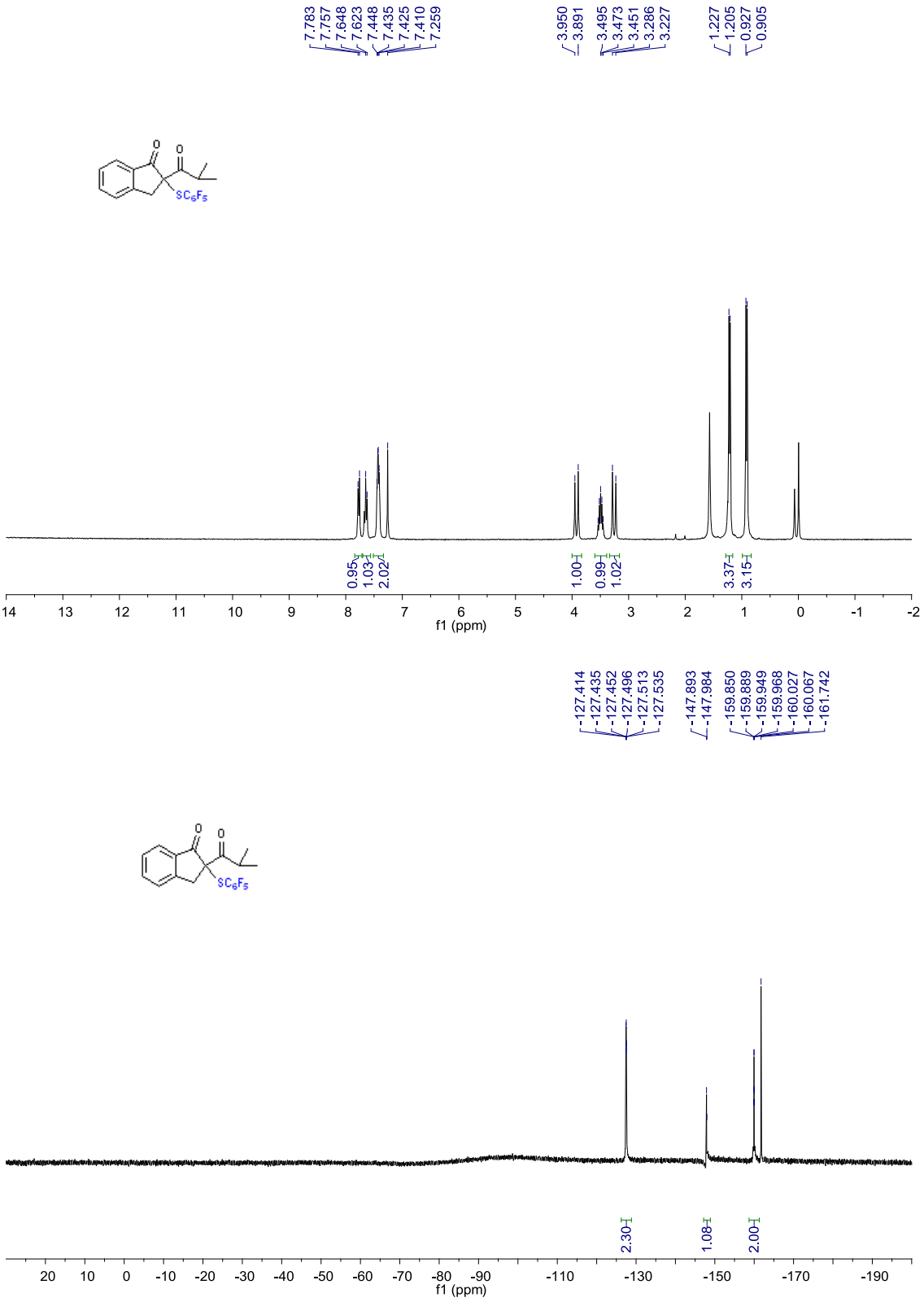
9.3 spectra for scheme 4;

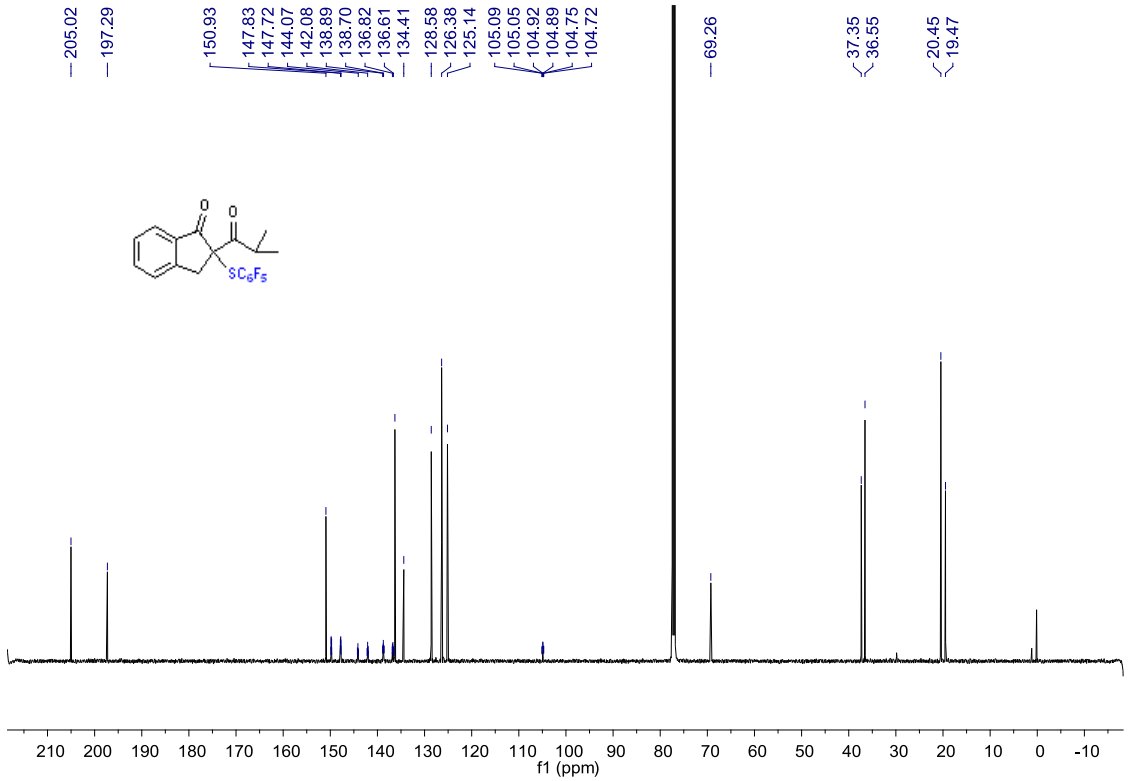


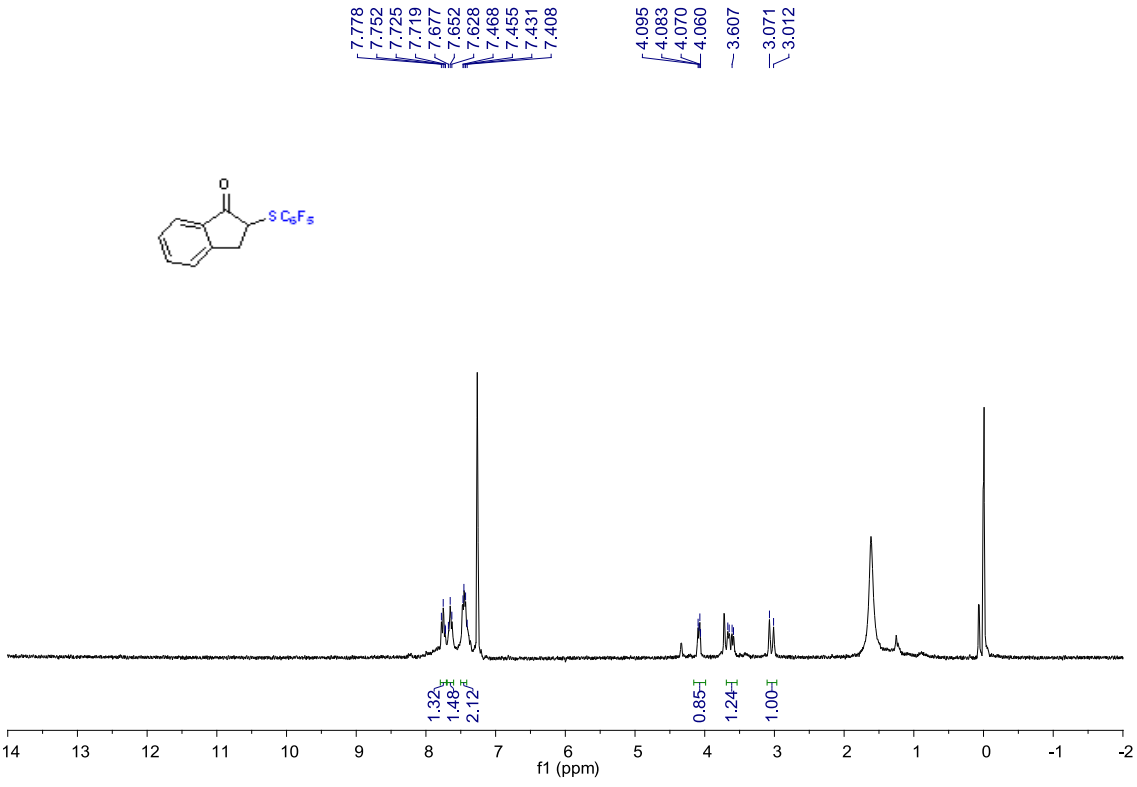


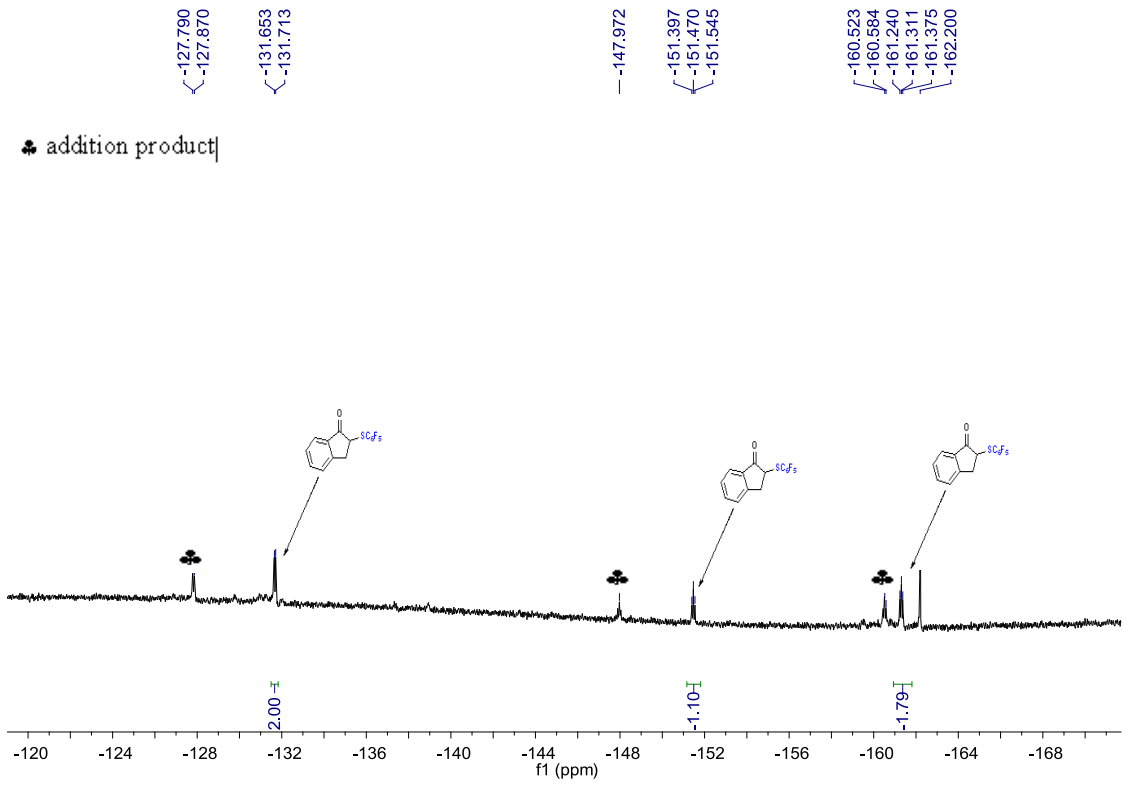

172.79
172.63
172.50
172.32
153.84
153.67
153.20
153.08
134.05
134.00
131.61
131.56
129.17
129.12
126.71
126.68
81.00
80.95
58.46
58.07
58.01
52.43
37.38
36.40
28.44
28.31
Boc
N
SCF3
MeO2C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

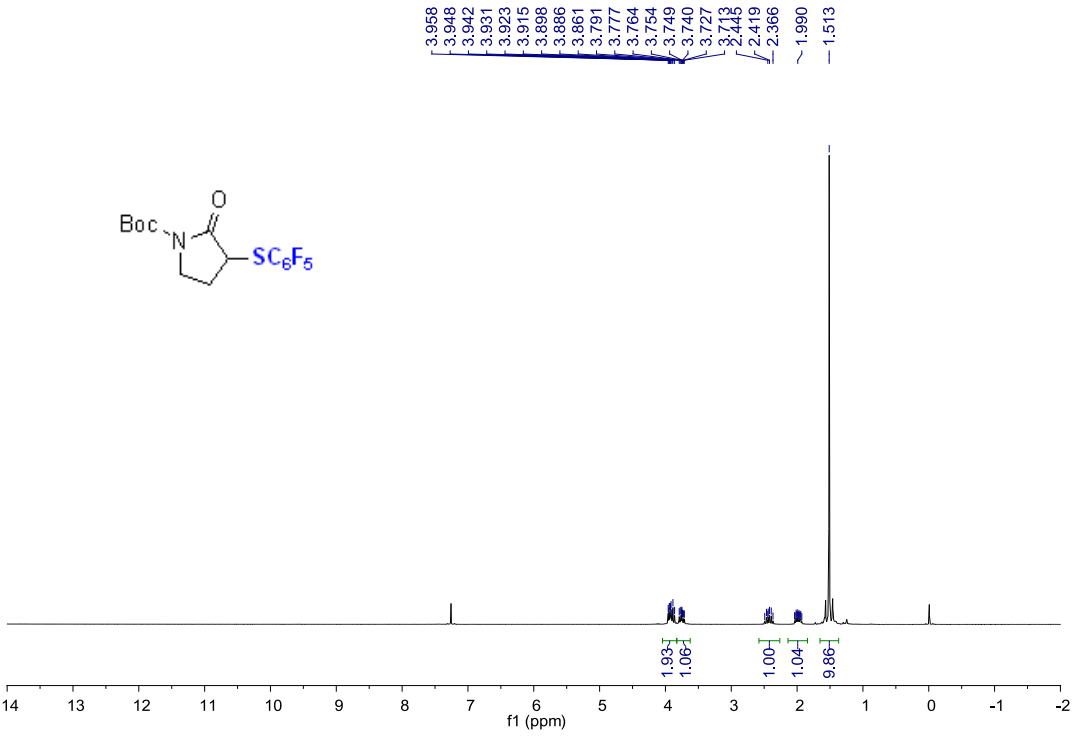
9.4 spectra for scheme 5;

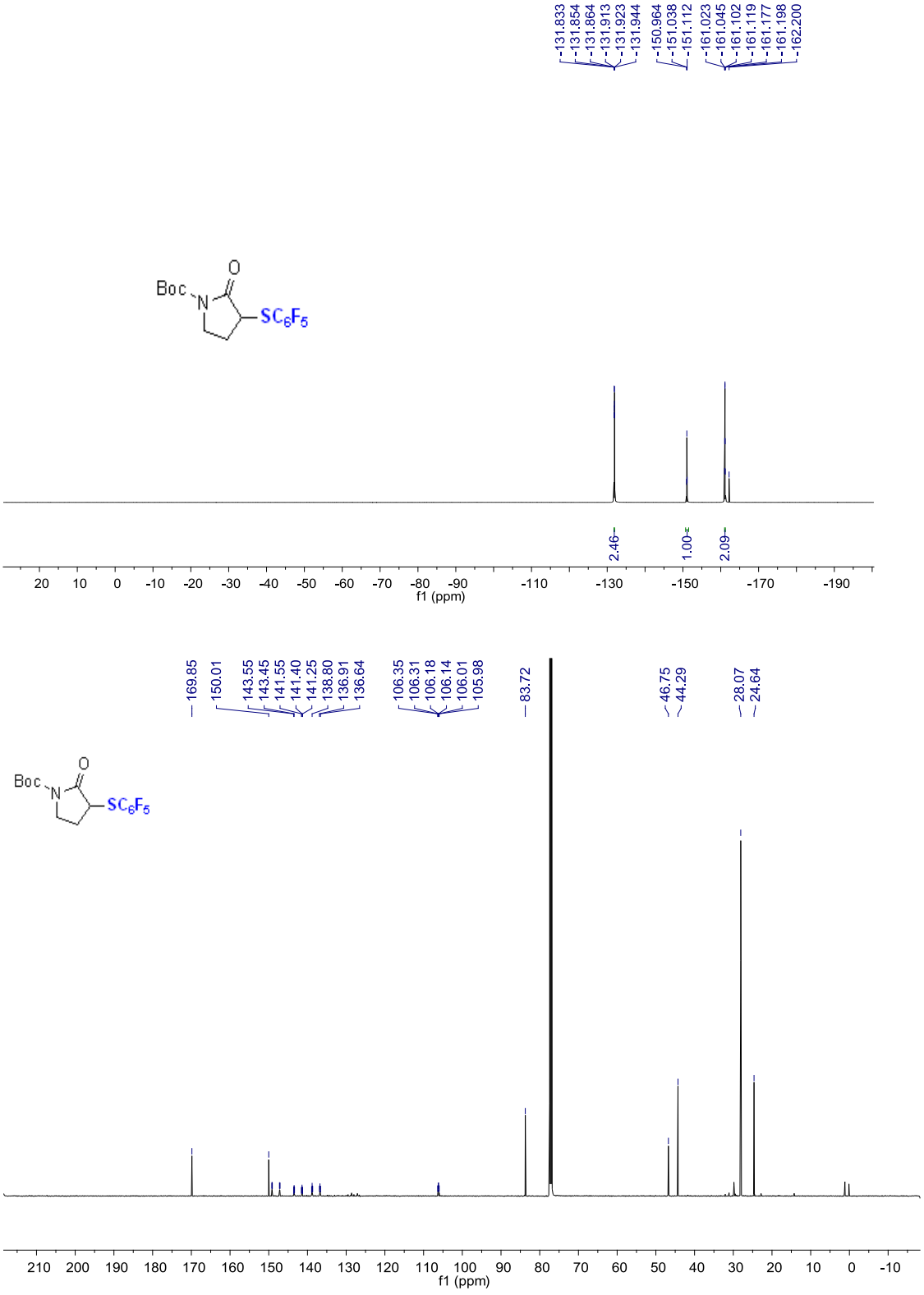



205.02
197.29
150.93
147.83
147.72
144.07
142.08
138.89
138.70
136.82
136.61
134.41
128.58
126.38
125.14
105.09
105.05
104.92
104.89
104.75
104.72
69.26
37.35
36.55
20.45
19.47
O
O
SC6F5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.778
7.752
7.725
7.719
7.677
7.652
7.628
7.468
7.455
7.431
7.408
4.095
4.083
4.070
4.060
3.607
3.071
3.012
O
S C6F5
1.32
1.48
2.12
0.85
1.24
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


-127.790
-127.870
-131.653
-131.713
-147.972
-151.397
-151.470
-151.545
-160.523
-160.584
-161.240
-161.311
-161.375
-162.200
♣ addition product
2.00
1.10
1.79
-120
-124
-128
-132
-136
-140
-144
-148
-152
-156
-160
-164
-168
f1 (ppm)


3.958
3.948
3.942
3.931
3.923
3.915
3.898
3.886
3.861
3.791
3.777
3.764
3.754
3.749
3.740
3.727
3.713
2.445
2.419
2.366
1.990
1.513
Boc
N
O
SC6F5
1.93
1.06
1.00
1.04
9.86
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


-131.833
-131.854
-131.864
-131.913
-131.923
-131.944
-150.964
-151.038
-151.112
-161.023
-161.045
-161.102
-161.119
-161.177
-161.198
-162.200
Boc
N
O
SC6F5
2.46
1.00
2.09
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)
169.85
150.01
143.55
143.45
141.55
141.40
141.25
138.80
136.91
136.64
106.35
106.31
106.18
106.14
106.01
105.98
83.72
46.75
44.29
28.07
24.64
Boc
N
O
SC6F5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)