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General Considerations

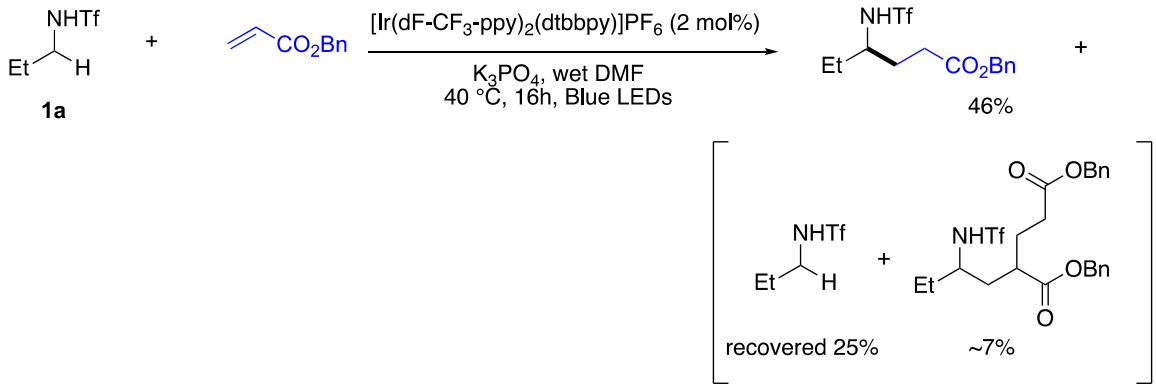
Commercial reagents and anhydrous solvents were purchased from Sigma-Aldrich, Alfa and TCI, and were used as received unless otherwise indicated. All catalytic reactions were carried out under N_2 with oven-dried vials. Thin layer chromatography was performed on SiliCycle® 250 μm, 60 Å plates. Silica gel column chromatography was performed on SiliCycle®SilicaFlash® P60, 40-63 μm, 60 Å. Visualization was accomplished with Seebach's "magic" stain.

Unless otherwise noted, ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were taken on a Bruker 400 MHz spectrometer at ambient temperature and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to chloroform at 7.26 ppm for ^{1}H and relative to $CDCl_3$ at 77.16 for ^{13}C. Data for ^{1}H, and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported as follows: chemical shift (δ ppm). Several spectra are from mixtures of rotamers and deconvolution is not possible. High resolution mass spectra (HRMS) were obtained from Columbia University Mass Spectrometry Facility on a JOEL JMSHX110HF mass spectrometer using ESI^{+}/ESI^{-} /$ASAP^{-}$ ionization model. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer. Stern-Volmer luminescence quenching experiments were conducted on a Perkin Elmer LS-55.

All alkenes were purchased from Aldrich and used as received. All trifluoromethanesulfonamide substrates were synthesized according to the general methods as shown below.

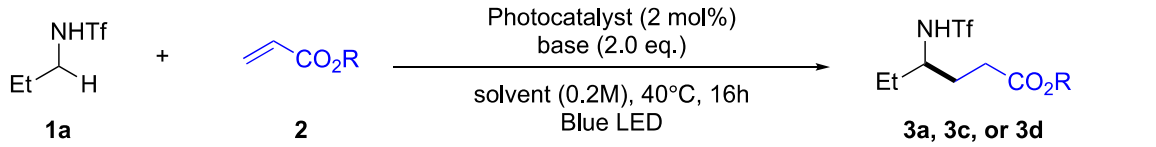
Reaction Discovery, Optimization, and Control Reactions

Initial Result:



Optimization:

Reactions were run on 0.1mmol scale (**1a**), with alkene (0.15 or 0.3 mmol), photocatalyst (2.0 mol%), base (0.2 mmol) in solvent (0.2M) at 40 °C for 16h.



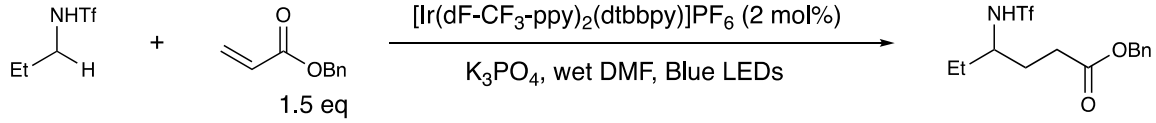
3a:R=^{t}Bu, **3c**=Et, **3d**: R=CH_2Ph

	Photocatalyst	R	solvent	base	yield
1	$[Ir\{dF\text{-}(CF_3)ppy\}_2(bpy)]PF_6$	CH_2Ph	DMF	K_3PO_4	16%
2	$[Ir\{dF\text{-}(CF_3)ppy\}_2(3,3'(CF_3)_2bpy)]PF_6$	CH_2Ph	DMF	K_3PO_4	38%
3	$[Ir\{dF\text{-}(CF_3)ppy\}_2(dtbbpy)]PF_6$	CH_2Ph	DMF	K_3PO_4	58%
4	$[Ir\{dF\text{-}(CH_3)ppy\}_2(dtbbpy)]PF_6$	CH_2Ph	DMF	K_3PO_4	65%
5	$[Ir\{dFppy\}_2(dtbbpy)]PF_6$	CH_2Ph	DMF	K_3PO_4	64%
6	$[Ir\{dF\text{-}(CH_3)ppy\}_2(dtbbpy)]PF_6$	Et	DMF	K_3PO_4	65%
7	$[Ir\{dF\text{-}(CH_3)ppy\}_2(dtbbpy)]PF_6$	*t*Bu	DMF	K_3PO_4	68%
8	$[Ir\{dF\text{-}(CH_3)ppy\}_2(dtbbpy)]PF_6$	*t*Bu	DMF	quinuclidine	77%
9	$[Ir\{dF\text{-}(CF_3)ppy\}_2(dtbbpy)]PF_6$	*t*Bu	DMF	quinuclidine	71%
10	$[Ir\{dF\text{-}(OMe)ppy\}_2(dtbbpy)]PF_6$	*t*Bu	DMF	quinuclidine	70%
11	$[Ir\{dFppy\}_2(dtbbpy)]PF_6$	*t*Bu	DMF	quinuclidine	68%

12	[Ir{dF-(CH_3)ppy}$_2$(dtbbpy)]PF_6	*t*Bu	DMF	DABCO	17%
13	[Ir{dF-(CH_3)ppy}$_2$(dtbbpy)]PF_6	*t*Bu	DMF	3-OAc-qunuclidine	50%
14	[Ir{dF-(CH_3)ppy}$_2$(dtbbpy)]PF_6	*t*Bu	DMF	3-OH-quinuclidine	trace
15	[Ir{dF-(CH_3)ppy}$_2$(dtbbpy)]PF_6	*t*Bu	DMF	Et_3N	0%
16	[Ir{dF-(CH_3)ppy}$_2$(dtbbpy)]PF_6	*t*Bu	toluene	quinuclidine	48%
17	[Ir{dF-(CH_3)ppy}$_2$(dtbbpy)]PF_6	*t*Bu	CF_3Ph	quinuclidine	32%

Table S1. Reaction Optimization

Control Reactions:



Trial	Deviation from Std Conditions	Yield Desired Pdt (%)
a	No photocatalyst	0
b	No base	0
c	No light	0

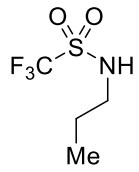
Table S2. Control Reactions

Trifluoromethanesulfonamide Synthesis and Characterization

Procedure A: To a solution of amine (1.0 equiv.) and NEt_3 (1.5 equiv.) in DCM (0.25 M) was added trifluoromathanesulfonic anhydride (1.0 equiv.) at 0 °C. The mixture was slowly warmed to ambient temperature and stirred overnight. The reaction was quenched with sat. NH_4Cl aq. Organic compounds were extracted with DCM twice. The combined organic layer was washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography using hexane/EtOAc as an eluent.

1,1,1-trifluoro-*N*-propylmethanesulfonamide (1a)

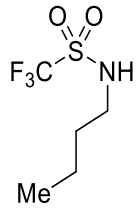
Prepared according to **Procedure A** from commercially available propylamine (1.00 g, 16.9 mmol). Colorless oil (2.28 g, 71% yield). R_f = 0.37 (9:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.20 (brs, 1H), 3.25 (t, *J* = 7.0 Hz, 2H), 1.63 (sext, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 119.7 (q, *J* = 319), 46.1, 23.4, 10.6; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.6; **IR (neat)** 3313(*s*), 2973(*m*), 2884(*m*), 1431(*s*), 1365(*s*), 1229(*s*), 1187(*s*), 1142(*s*), 1069(*s*), 1012(*s*), 609(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_4H_8F_3NO_2S$; expected $(M-H)^-$ *m*/*z* 190.0150, observed $(M-H)^-$ *m*/*z* 190.0148.

***N*-butyl-1,1,1-trifluoromethanesulfonamide (1b)**

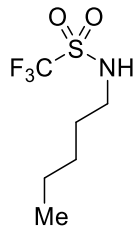
Prepared according to **Procedure A** from commercially available butylamine (731 mg, 10.0 mmol). Colorless oil (1.31 g, 64% yield). R_f = 0.38 (9:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.17 (brs, 1H), 3.28 (q, *J* = 6.6Hz, 2H), 1.58 (m, 2H), 1.38 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 119.7 (q, *J* = 319), 44.2, 32.0, 19.3, 13.3; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.5; **IR (neat)** 3312(*s*), 2964(*m*), 2878(*m*), 1430(*s*), 1367(*s*), 1228(*s*), 1187(*s*), 1144(*s*), 1073(*s*), 1035(*s*), 609(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_5H_{10}F_3NO_2S$; expected $(M-H)^-$ *m*/*z* 204.0306, observed $(M-H)^-$ *m*/*z* 204.0310.

1,1,1-trifluoro-*N*-pentylmethanesulfonamide (1c)

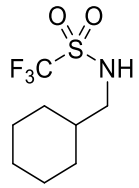
Prepared according to **Procedure A** from commercially available amylamine (871 mg, 10.0 mmol). Colorless oil (1.44 g, 66% yield). R_f = 0.37 (9:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.67 (brs, 1H), 3.30 (t, *J* = 6.9 Hz, 2H), 1.62 (tt, *J* = 7.4, 7.4 Hz, 2H), 1.38-1.32 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 119.7 (q, *J* = 319), 44.5, 29.7, 28.2, 22.0, 13.7; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.5; **IR (neat)** 3311(*s*), 2960(*m*), 2935(m), 2868(*m*), 1430(*s*), 1367(*s*), 1229(*s*), 1188(*s*), 1144(*s*), 1063(*s*), 610(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_6H_{12}F_3NO_2S$; expected $(M-H)^-$ *m*/*z* 218.0463, observed $(M-H)^-$ *m*/*z* 218.0462.

***N*-(cyclohexylmethyl)-1,1,1-trifluoromethanesulfonamide (1d)**

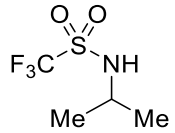
Prepared according to **Procedure A** from commercially available Cyclohexanemethylamine (226 mg, 2.00 mmol). Colorless oil (235 mg, 48% yield). R_f = 0.51 (7:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.15 (brs, 1H), 3.13 (d, *J* =6.8 Hz, 2H), 1.79-1.68 (m, 5H), 1.58-1.48 (m, 1H), 1.32-1.12 (m, 3H), 1.00-0.91 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 119.7 (q, *J* = 319), 50.4, 38.1, 30.1, 26.0, 25.5; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.3; **IR (neat)** 3311(*s*), 2928(*s*), 2855(*m*), 1433(*s*), 1368(*s*), 1229(*s*), 1187(*s*), 1142(*s*), 1061(*s*), 1049(*s*), 609(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_8H_{14}F_3NO_2S$; expected $(M-H)^+$ *m*/*z* 244.0619, observed $(M-H)^+$ *m*/*z* 244.0628;

1,1,1-trifluoro-*N*-isopropylmethanesulfonamide (1e)

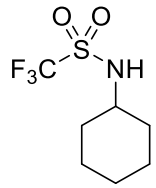
Prepared according to **Procedure A** from commercially available Isopropylamine (1.00 g, 16.9 mmol). Colorless oil (2.11 g, 65% yield). R_f = 0.42 (7:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.18 (brs, 1H), 3.84-3.76 (m, 1H), 1.27 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 119.6 (q, *J* = 319), 48.6, 23.9; **^{19}F NMR** ($CDCl_3$, 376 MHz): −78.2; **IR (neat)** 3304(*s*), 2985(*m*), 1468(*m*), 1432(*s*), 1368(*s*), 1228(*s*), 1186(*s*), 1150(*s*), 1014(*s*), 901(*s*), 615(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_4H_8F_3NO_2S$; expected $(M-H)^-$ *m*/*z* 190.0150, observed $(M-H)^-$ *m*/*z* 190.0147.

_N_-cyclohexyl-1,1,1-trifluoromethanesulfonamide (1f)

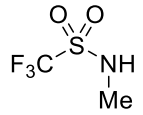
Prepared according to **Procedure A** from commercially available Cyclohexylamine (992 mg, 10.0 mmol). White solid (1.86 g, 81% yield). R_f = 0.55 (9:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.11 (brs, 1H), 3.51-3.45 (m, 1H), 2.06-2.00 (m, 2H), 1.78-1.72 (m, 2H), 1.63-1.59 (m, 1H), 1.42-1.29 (m, 4H), 1.23-1.14 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 119.6 (q, *J* = 319), 54.9, 34.3, 24.8, 24.6; **^{19}F NMR** ($CDCl_3$, 376 MHz): −78.1; **IR (neat)** 3277(*s*), 2933(*s*), 2859(*m*), 1453(*s*), 1376(*s*), 1222(*s*), 1177(*s*), 1139(*s*), 1063(*s*), 1029(*s*), 892(*s*), 610(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_7H_{12}F_3NO_2S$; expected $(M-H)^+$ *m*/*z* 230.0463, observed $(M-H)^+$ *m*/*z* 230.0467;

1,1,1-trifluoro-_N_-methylmethanesulfonamide (1g)

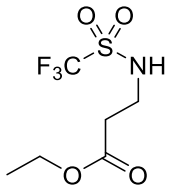
Prepared according to **Procedure A** from commercially methanamine hydrochloride (675 mg, 10 mmol). Colorless oil (183.8 mg, 11% yield). R_f = 0.65 (6:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.94 (brs, 1H), 2.98 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 119.9 (q, *J* = 321 Hz), 30.23; **^{19}F NMR** ($CDCl_3$, 376 MHz): −76.9; **IR (neat)** 3643.05 (brs), 3326.57 (brs), 1419.70 (m), 1361.55 (s), 1230.15 (s), 1186.38 (s), 1151.52 (s), 1074.90 (s), 852.52 (s), 606.70 (s), 521.87 (m), 461.18 (m) cm^{-1}; **MS (ESI, negative)**: M = $C_2H_4F_3NO_2S$; expected $(M-H)^-$ *m*/*z* 162.11, observed $(M-H)^-$ *m*/*z* 162.0.

ethyl 3-((trifluoromethyl)sulfonamido)propanoate (1h)

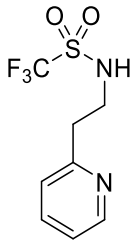
Prepared according to **Procedure A** from commercially available β-Alanine Ethyl Ester Hydrochloride (479 mg, 3.12 mmol). Colorless oil (265 mg, 34% yield). R_f = 0.50 (3:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.22 (brs, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.58-3.50 (m, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.0, 119.6 (q, *J* = 321 Hz), 61.4, 39.8, 34.6, 14.0; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.7; **IR (neat)** 3260(*s*), 2987(*s*), 1716(*s*), 1434(*s*), 1373(*s*), 1185(*s*), 1146(*s*), 1050(*m*), 950(*s*), 816(*m*), 607(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_6H_{10}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 248.0204, observed $(M-H)^-$ *m*/*z* 248.0210.

1,1,1-trifluoro-N-(2-(pyridin-2-yl)ethyl)methanesulfonamide (1i)

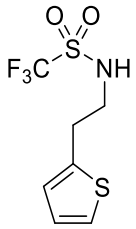
Prepared according to **Procedure A** from commercially available 2-(2-Pyridyl)ethylamine (488 mg, 4.00 mmol). White solid (568 mg, 56% yield). R_f = 0.45 (1:2 hex:EtOAc).



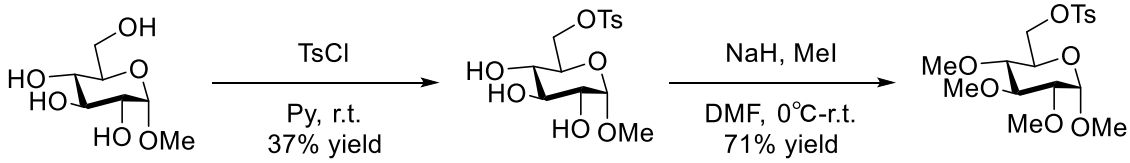
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.47 (d, *J* = 4.7 Hz, 1H), 8.30 (brs, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.24-7.20 (m, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 158.1, 148.7, 137.4, 123.8, 122.3, 119.9 (q, *J* = 320), 43.4, 36.9; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.7; **IR (neat)** 3028(*s*), 2629(*s*), 1597(*m*), 1438(*s*), 1366(*s*), 1222(*s*), 1175(*s*), 1077(*s*), 1008(*s*), 932(*s*), 767(*s*), 597(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_8H_9F_3N_2O_2S$; expected $(M-H)^-$ *m*/*z* 253.0259, observed $(M-H)^-$ *m*/*z* 253.0262.

1,1,1-trifluoro-*N*-(2-(thiophen-2-yl)ethyl)methanesulfonamide (1j)

Prepared according to **Procedure A** from commercially available 2-Thiopheneethylamine (508 mg, 4.00 mmol). Colorless oil (598 mg, 58% yield). R_f = 0.53 (6:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.01 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.92 (dd, *J* = 3.4, 0.9 Hz, 1H), 5.18 (brs, 1H), 3.59 (t, *J* = 6.5 Hz, 2H), 3.15 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 138.8, 127.4, 126.3, 124.8, 119.6 (q, *J* = 321 Hz), 45.5, 30.8; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.4; **IR (neat)** 3308(*s*), 2919(*s*), 1426(*s*), 1368(*s*), 1229(*s*), 1188(*s*), 1143(*s*), 1070(*s*), 849(*s*), 702(*s*), 609(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_7H_8F_3NO_2S_2$; expected $(M-H)^+$ *m*/*z* 257.9870, observed $(M-H)^+$ *m*/*z* 257.9873;



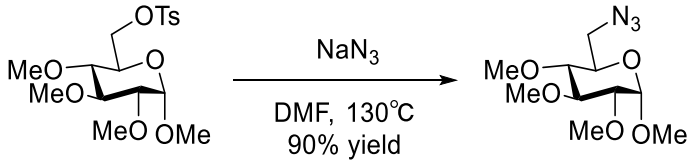
A solution of the Methyl α-D-Glucoside (2.38 g, 12.3 mmol) in dry pyridine (15.0 ml) was cooled to 0 ºC in an ice bath with stirring. A solution of p-toluenesulfonyl chloride

(2.80 g, 14.7 mmol) was added at 0 °C. The mixture was slowly allowed to warm to rt and stir overnight. The solvent was removed *in vacuo*, then the reaction was quenched with water. The aqueous layer was extracted with EtOAc (20 mL×3), and the organic layer was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give crude ((2*R*,3*S*,4*S*,5*R*,6*S*)-3,4,5-trihydroxy-6-methoxytetrahydro-2*H*-pyran-2-yl)methyl 4-methylbenzenesulfonate, which was directly used for next step without further purification.

To a solution of ((2*R*,3*S*,4*S*,5*R*,6*S*)-3,4,5-trihydroxy-6-methoxytetrahydro-2*H*-pyran-2-yl)methyl 4-methylbenzenesulfonate (1.48 g, 4.26 mmol) and MeI (2.12 g, 14.91 mmol) in anhydrous DMF (15 mL) was added NaH (60% dispersion in mineral oil, 596 mg, 14.91 mmol) at 0 °C in four portions over 1 h. The resulting mixture was allowed to warm to ambient temperature over 12 h. Excess NaH was quenched by addition of EtOAc and the solvent was removed *in vacuo*. The residue was suspended in EtOAc, washed with H_2O, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by flash column chromatography using hexane/EtOAc as the eluent to provide the desired product (1.16 g, 26%).

((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)methyl 4-methylbenzenesulfonate

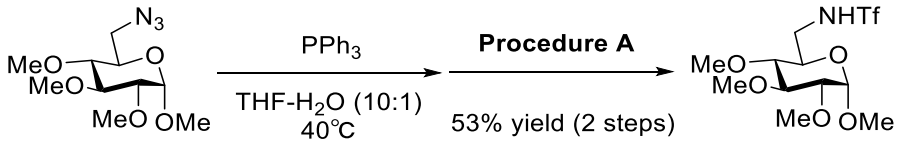
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.68 (d, *J* = 3.6 Hz, 1H), 4.23–4.15 (m, 2H), 3.61–3.56 (m, 1H), 3.55 (s, 3H), 3.43–3.36 (m, 4H), 3.42 (s, 3H), 3.30 (s, 3H), 3.08–2.99 (m, 2H), 2.41 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 114.9, 133.1, 129.8, 128.0, 97.4, 83.4, 81.6, 78.9, 68.7, 68.5, 60.8, 60.5, 59.0, 55.3, 21.7 ppm; **IR (neat)** 2913(*s*), 2834(*s*), 1597(*s*), 1446(*s*), 1360(*s*), 1175(*s*), 1041(*s*), 901(*s*), 832(*s*), 745(*s*), 615(*s*) cm^{-1}; **HRMS-ESI** (positive): M = $C_{17}H_{26}O_8S$; expected $(M+Na)^+$ *m*/*z* 413.1246, observed $(M+Na)^+$ *m*/*z* 413.1248.



To a solution of NaN_3 (344.7 mg, 5.30 mmol) in DMF (1.0 mL) was added a solution of ((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)methyl 4-methylbenzenesulfonate (1.03 g, 2.65 mmol) in dry DMF (6.0 mL). The mixture was stirred at 130 °C for 12h. After cooling down to room temperature, the reaction was quenched with water. Organic compounds were extracted with EtOAc (20 mL×3), and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by flash column chromatography using hexane/EtOAc as the eluent to provide (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(azidomethyl)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran (618 mg, 90%).

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(azidomethyl)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.79 (d, *J* = 3.5 Hz, 1H), 3.64–3.60 (m, 1H), 3.58 (s, 3H), 3.50 (s, 3H), 3.48 (s, 3H), 3.48–3.43 (m, 2H), 3.40 (s, 3H), 3.38–3.30 (m, 1H), 3.16 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.03 (t, *J* = 9.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 97.4, 83.4, 81.8, 80.3, 70.0, 60.8, 60.6, 59.0, 55.3, 51.4; **IR (neat)** 2914(*s*), 2833(*s*), 2096(*s*), 1446(*s*), 1328(*s*), 1286(*s*), 1157(*s*), 1097(*s*), 991(*s*), 841(*m*), 554(*s*) cm^{-1}; **HRMS-ESI** (positive): M = $C_{10}H_{19}N_3O_5$; expected $(M+Na)^+$ *m*/*z* 284.1223, observed $(M+Na)^+$ *m*/*z* 284.1224.

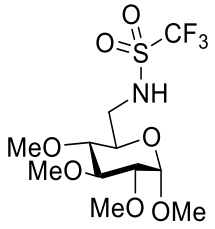


1,1,1-trifluoro-*N*-(((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)methyl)methanesulfonamide (1k)

To a solution of PPh_3 (828.0 mg, 5.16 mmol) in THF/H_2O (10/1) (22.0 mL) was added (2*R*,3*R*,4*S*,5*R*,6*S*)-2-(azidomethyl)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran (410.4 mg, 1.58 mmol). The mixture was stirred at 40 °C for 12 h. After cooled to room temperature, the solvent was removed *in vacuo*. Hexene (30 mL) was added and the mixture was sonicated until a slurry is formed. The slurry was filtered and the filtrate was concentrated *in vacuo* to give crude ((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-

2*H*-pyran-2-yl)methanamine, which was directly used for next step without further purification.

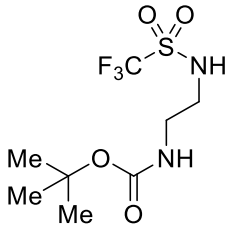
Prepared according to **Procedure A** from crude ((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)methanamine (387 mg, 1.58 mmol). White solid (305 mg, 53% yield). R_f = 0.44 (1:1 hex:EtOAc)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.49 (brs, 1H), 4.78 (d, *J* = 3.5 Hz, 1H), 3.64-3.54 (m, 2H), 3.61 (s, 3H), 3.57 (s, 3H), 3.51-3.39 (m, 2H), 3.51 (s, 3H), 3.40 (s, 3H), 3.15 (dd, *J* = 9.6, 3.6 Hz, 1H), 2.99 (t, *J* = 9.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 119.6 (q, *J* = 321 Hz), 97.6, 83.1, 81.7, 80.2, 68.8, 60.7, 60.5, 59.1, 55.4, 44.9; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.3; **IR (neat)** 3161(*s*), 2925(*s*), 2838(*m*), 1446(*s*), 1374(*s*), 1230(*s*), 1185(*s*), 1149(*s*), 1094(*s*), 987(*s*), 881(*m*), 601(*s*) cm^{-1}**; HRMS-ASAP** (negative): M = $C_{11}H_{20}F_3NO_7S$; expected $(M-H)^-$ *m*/*z* 366.0834, observed $(M-H)^-$ *m*/*z* 366.0833;

***tert*-butyl (2-((trifluoromethyl)sulfonamido)ethyl)carbamate (1l)**

Prepared according to **Procedure A** from commercially available *N*-Boc-ethylenediamine (500 mg, 3.12 mmol). White solid (~ 1:3 mixture of rotamers, 360 mg, 40% yield). R_f = 0.39 (3:1 hex:EtOAc).

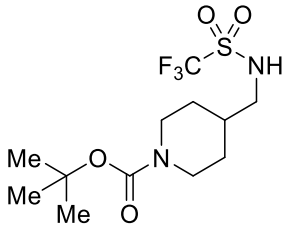


^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.98 (brs, 1H), 5.56 (brs, 0.25H), 5.10 (brs, 0.75H), 3.39-3.30 (m, 4H), 1.45 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 157.3, 119.8 (q, *J* = 321 Hz), 80.68, 45.1, 40.4, 28.2; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.5; **IR (neat)** 3418(*s*)**,** 3118(*s*),

2990(*s*), 2934(*m*), 1687(*s*), 1531(*s*), 1278(*s*), 1256(*s*), 1177(*s*), 1087(*s*), 1063(*s*), 990(*s*), 823(*s*), 583(*s*) cm^{-1}**; HRMS-ASAP** (negative): M = $C_8H_{15}F_3N_2O_4S$; expected $(M-H)^-$ *m*/*z* 291.0626, observed $(M-H)^-$ *m*/*z* 291.0630.

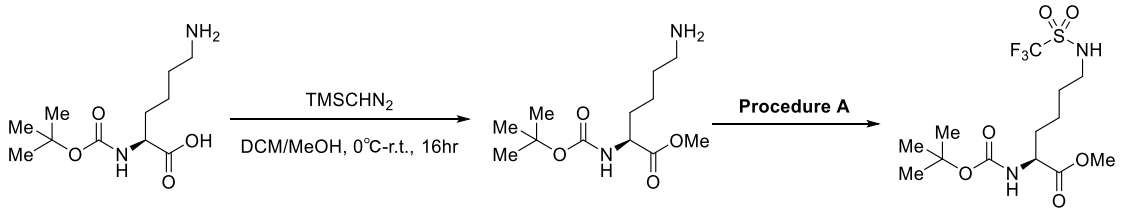
***tert*-butyl 4-(((trifluoromethyl)sulfonamido)methyl)piperidine-1-carboxylate (1m)**

Prepared according to **Procedure A** from commercially available 1-Boc-4-(aminomethyl)piperidine (857 mg, 4.0 mmol). White solid (702 mg, 51% yield). R_f = 0.47 (3:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.50 (brs, 1H), 4.09(d, *J* = 12.0 Hz, 2H), 3.14 (t, *J* = 5.9 Hz, 2H), 2.67 (t, *J* = 11.2 Hz, 2H), 1.73-1.64 (m, 3H), 1.42 (s, 9H), 1.17-1.06 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 154.9, 119.8 (q, *J* = 321.4 Hz), 78.0, 49.4, 43.4 (brs), 36.7, 29.2, 28.4; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ −77.3; **IR (neat)** 3130(*s*), 2977(*m*), 2931(*m*), 1658(*s*), 1431(*s*), 1367(*s*), 1226(*s*), 1178(*s*), 1057(*s*), 859(*s*), 602(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{12}H_{21}F_3N_2O_4S$; expected $(M-H)^-$ *m*/*z* 345.1096, observed $(M-H)^-$ *m*/*z* 345.1099.

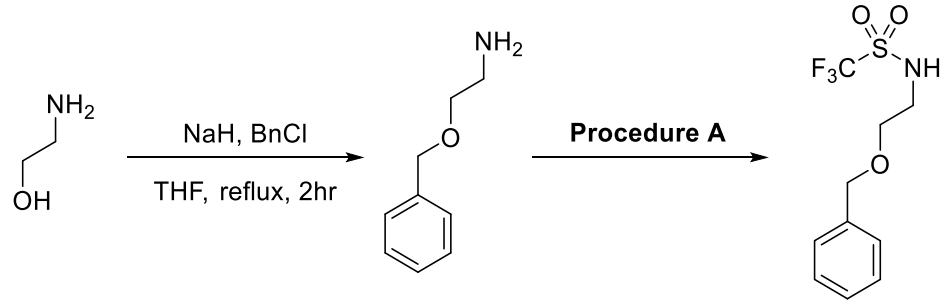
methyl N^2-(tert-butoxycarbonyl)-N^6-((trifluoromethyl)sulfonyl)-L-lysinate (1n)



A solution of Boc-Lys-OH (246 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) and MeOH (1.3 mL) was charged with $(CH_3)_3SiCHN_2$ (2.0 M solution in hexane, 1.0 mL, 2.00 mmol) at 0 °C and the resulting mixture was stirred at the same temperature for 1 h and at room

temperature for another 1 h. The solvent was removed under reduced pressure to afford crude product as a yellow oil, which was directly used for the next step without further purification. **methyl *N*^{2}-(tert-butoxycarbonyl)-*N*^{6}-((trifluoromethyl)sulfonyl)-L-lysinate** was then synthesized according to **Procedure A**. White solid (227 mg, 59% yield for 2 steps). R_f = 0.38 (4:1 hex:EtOAc). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.53 (brs, 1H), 5.18 (d, 1H), 4.31 (brs, 1H), 3.76 (s, 3H), 3.40-4.24 (m, 2H), 1.86-1.61 (m, 4H), 1.53-1.44 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.14, 156.09, 119.8 (q, *J* = 321 Hz), 80.70, 52.71, 52.65, 44.13, 32.92, 28.79, 28.45, 21.92; **^{19}F NMR** ($CDCl_3$, 376 MHz): −76.37; **IR (neat)** 3191(*s*), 2947(*s*), 1687(*s*), 1511(*s*), 1440(*s*), 1367(*s*), 1227(*s*), 1179(*s*), 1077(*s*), 858(*m*), 605(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{13}H_{23}F_3N_2O_6S$; expected $(M-H)^-$ *m*/*z* 391.1151, observed $(M-H)^-$ *m*/*z* 391.1151.

***N*-(2-(benzyloxy)ethyl)-1,1,1-trifluoromethanesulfonamide (1o)**

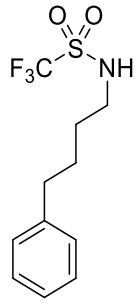


To a solution of Ethanolamine (1.00 g, 16.4 mmol) in THF (20 mL) was added NaH (60% dispersion in mineral oil, 654 mg, 16.4 mmol) at 0 °C. The temperature was then raised to reflux and the solution aged for 30 min, at which point, benzyl chloride (1.86 g, 14.7 mmol) was added dropwise. The solution was aged at reflux for 2 h, then cooled to 20 °C and quenched with water (10 mL). The mixture was extracted with EtOAc (10 mL×3), and the organic layer was combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give crude *O*-Benzylethanolamine, which was directly used for the next step without further purification. ***N*-(2-(benzyloxy)ethyl)-1,1,1-trifluoromethanesulfonamide** was then synthesized according to **Procedure A**. Colorless oil (705 mg, 15% yield for 2 steps). R_f = 0.48 (6:1 hex:EtOAc).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43-7.33 (m, 5H), 5.29 (brs, 1H), 4.57 (s, 2H), 3.63 (t, *J* = 4.6 Hz, 2H), 3.50 (q, *J* = 5.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 137.1, 128.6, 128.2, 128.0, 119.7 (q, *J* = 321 Hz), 73.4, 68.5, 44.0; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.5; **IR (neat)** 3312(*s*), 2872(*s*), 1496(*s*), 1371(*s*), 1229(*s*), 1188(*s*), 1147(*s*), 1080(*s*), 1024(*s*), 804(*s*), 607(*s*) cm^{-1}**; HRMS-ASAP** (negative): M = $C_{10}H_{12}F_3NO_3S$; expected $(M-H)^-$ *m*/*z* 282.0412, observed $(M-H)^-$ *m*/*z* 282.0413.

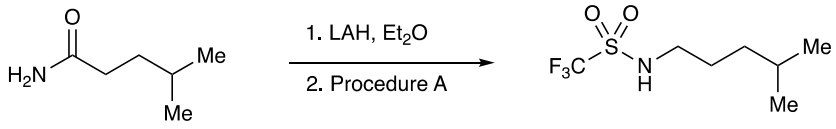
1,1,1-trifluoro-*N*-(4-phenylbutyl)methanesulfonamide (1p)

Prepared according to **Procedure A** from commercially available 4-Phenylbutylamine (893 mg, 5.99 mmol). Colorless oil (768 mg, 46% yield). R_f = 0.57 (7:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.33 (m, 2H), 7.27-7.21 (m, 3H), 5.06 (brs, 1H), 3.33 (q, *J* = 6.6 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 1.77-1.61 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 141.5, 128.5, 128.4, 126.1, 119.7 (q, *J* = 319), 44.3, 35.1, 29.6, 27.9; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.3; **IR (neat)** 3313(*s*), 3027(*m*), 2938(*m*), 2862(*s*), 1603(*m*), 1495(*s*), 1427(*s*), 1368(*s*), 1229(*s*), 1188(*s*), 1144(*s*), 1070(*s*), 747(*s*), 700(*s*), 610(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{11}H_{14}F_3NO_2S$; expected $(M-H)^-$ *m*/*z* 280.0619, observed $(M-H)^-$ *m*/*z* 280.0623.

1,1,1-trifluoro-*N*-(4-methylpentyl)methanesulfonamide (1q)

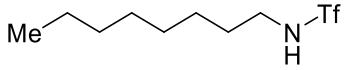


4-methylpentanamide was prepared according to literature procedure.[1] To a solution of amide (3.12g, 27.08 mmol) in Et_2O at 0 °C was added LAH (3.5g, 94.78 mmol) in portions. The mixture was warmed to rt and stirred overnight. The reaction was cooled back down to 0 °C and water was added slowly (1mL per 1g LAH), followed by 15% NaOH (1 mL per 1g LAH), and then again water (3 mL per 1g LAH). The mixture was brought back up to rt, stirred for ~20 min, and then filtered. The solvent in the filtrate was then removed under reduced pressure to afford the crude product. This crude amine was carried forward without further purification and 1,1,1-trifluoro-*N*-(4-methylpentyl)methanesulfonamide was prepared according to **Procedure A**. Colorless oil (2.213 g, 35% yield). R_f = 0.30 (9:1 hex:EtOAc).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.97 (brs, 1H), 3.28 (t, *J* = 7.2 Hz, 2H), 1.64-1.52 (m, 3H), 1.25-1.19 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 119.83 (q, *J* = 319.0 Hz), 44.94, 35.42, 28.20, 27.71, 22.49; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -77.41;

1,1,1-trifluoro-*N*-octylmethanesulfonamide (1r)

Prepared according to **Procedure A** from commercially available octylamine (2g, 15.48mmol). Light yellow oil (2.10 g, 52% yield). Rf = 0.85 (4:1 hex:EtOAc).

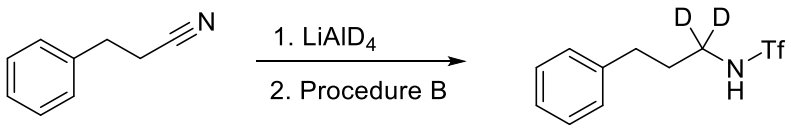


^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.17 (brs, 1H), 3.27 (t, *J* = 7.21 Hz, 2H), 1.59 (p, *J* = 7.2 Hz, 2H), 1.39-1.16 (m, 10H), 0.87 (t, *J* = 6.51 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 119.85 (q, *J* = 321.1 Hz), 44.64, 31.82, 30.20, 29.17, 29.06, 26.30, 22.70, 14.08; **^{19}F NMR** ($CDCl_3$, 376 MHz δ -77.6. IR ($CDCl_3$) cm^{-1}; **IR ($CDCl_3$)** 3313.56 (brs), 2928.18 (m), 2857.71 (m), 1428.01 (m), 1369.64 (s), 1265.46 (m), 1230.16 (s), 1191.88 (s), 1145.76 (s), 1068.87 (m), 895.10 (m), 739.75 (s) cm^{-1}; **HRMS-ASAP** (negative); M = $C_9H_{18}F_3NO_2S$; expected $(M-H)^-$ *m/z* 260.0932, observed $(M-H)^-$ *m/z* 260.0935.

[1] Chu, J. C. K.; Rovis, T. *Nature* **2016**, *539*, 272-275.

1,1,1-trifluoro-*N*-(3-phenylpropyl-1,1-d_2-)methanesulfonamide (1s-D_2)

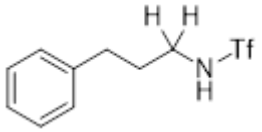
3-phenylpropan-1,1-d_2-1-amine was prepared according to a previously reported literature procedure.[2] **1s-D_2** was prepared according to **Procedure A** (1.096g 3-phenylpropan-1,1-d_2-1-amine, 7.99 mmol). Clear oil (835.5mg, 40%). Rf = 0.70 (4:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.29 (m, 2H), 7.26-7.17 (m, 3H), 4.82 (brs, 1H), 2.72-2.68 (m, 2H), 1.96-1.92 (m, 2H); **^{2}H NMR** ($CHCl_3$, 400 MHz) δ 3.30 (s, 2H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 140.33, 128.85, 128.44, 126.59, 119.79 (q, *J* = 322.2 Hz), 43.58 (pent, *J* = 21.2 Hz), 32.62, 31.64; **^{19}F NMR** ($CDCl_3$, 376 MHz δ -77.3. **IR ($CDCl_3$)** 3314.43 (brs), 2938.11 (brs), 1495.87 (m), 1416.24 (s), 1358.29 (s), 1231.76 (s), 1190.10 (s), 1148.79 (s), 1030.21 (s), 834.29 (m), 740.40 (s), 700.68 (s), 606.16 (s), 513.89 (m), 477.47 (m) cm^{-1}; **HRMS-ASAP** (negative); M = $C_{10}H_{10}D_2F_3NO_2S$ expected $(M-H)^-$ *m/z* 268.0588, observed $(M-H)^-$ *m/z* 268.0584.

1,1,1-trifluoro-*N*-(3-phenylpropyl)methanesulfonamide (3s-H_2)

Prepared according to **Procedure A** from commercially available 3-phenyl propylamine (1.0g, 7.4 mmol). Light yellow oil (777.7 mg, 39% yield). Rf = 0.70 (4:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.30 (m, 2H), 7.25-7.17 (m, 3H), 4.73 (brs, 1H), 3.33 (q, *J* = 6.7 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.96 (t, *J* =7.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 140.29, 128.87, 128.44, 128.43, 126.62, 119.79 (q, *J* = 322.2 Hz), 44.17, 32.71, 31.89; **^{19}F NMR** ($CDCl_3$, 376 MHz δ -77.27. **IR ($CDCl_3$)** 3313.66 (brs), 2945.32 (brs), 1437.77 (m), 1368.27 (s), 1229.42 (s), 1189.35 (s), 1144.50 (s), 1070.92 (m),

[2] Chia, P.-Y.; Huang, S.-L.; Liu, Y.-H.; Lin, Y.-C.; *Chem. Asian. J.* **2016**, 11, 1098.

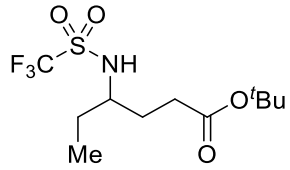
970.06 (m), 896.34 (m), 837.95 (m), 742.36 (s), 700.39 (s), 609.51 (s), 478.23 (m) cm^{-1}; **HRMS-ASAP** (negative); M = $C_{10}H_{12}F_3NO_2S$ expected $(M-H)^-$ *m/z* 266.0463, observed $(M-H)^-$ *m*/*z* 266.0460.

Photoredox-Catalyzed α-C(*sp*^{3})-H Alkylation (Alkene and Trifluoromethanesulfonmide Scope)

Procedure B: Trifluoromethanesulfonamide (0.10 mmol, 1.0 equiv.), alkene (1.2–5.0 equiv.), quinuclidine (2.0 equiv.), and $[Ir\{dF\text{-}(CH_3)ppy\}_2(dtbbpy)]PF_6$ (2.0 mol %) were placed into an oven-dried vial (4 mL). After an addition of DMF (0.50 mL), the resulting mixture was illuminated with a blue LED (Kessil, 34W) for 16 h (the distance between the vial and the LED was about 2 cm and the temperature was ~40 °C). After careful acidification with aq. HCl (0.5 M), organics were extracted with EtOAc (2 mL × 3) and concentrated *in vacuo*. The residue was directly subjected to flash silica gel column chromatography.

tert-butyl 4-((trifluoromethyl)sulfonamido)hexanoate (3aa)

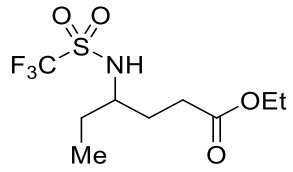
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (24.5 mg, 77% yield). R_f = 0.50 (4:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.60 (brs, 1H), 3.54-3.48 (m, 1H), 2.45-2.31 (m, 2H), 1.93-1.84 (m, 1H), 1.81-1.72 (m, 1H), 1.69-1.58 (m, 2H), 1.45 (s, 9H), 0.70 (t, *J* = 7.4, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 173.2, 119.7 (q, *J* = 319), 57.4, 31.4, 29.0, 28.6, 28.0, 9.5; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.5; **IR (neat)** 3208(*s*), 2976(*m*), 1699(*s*), 1456(*s*), 1369(*s*), 1227(*s*), 1185(*s*), 1150(*s*), 1013(*s*), 907(*m*), 775(*m*), 614(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{11}H_{20}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 318.0987, observed $(M-H)^-$ *m*/*z* 318.0981.

ethyl 4-((trifluoromethyl)sulfonamido)hexanoate (3ab)

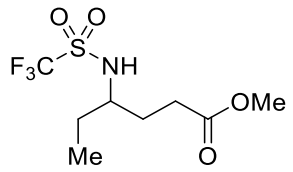
Prepared according to **Procedure B** (with 3.0 equiv. of ethyl acrylate). Colorless oil (18.4 mg, 63% yield). R_f = 0.34 (4:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.19 (d, *J* = 8.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.58-3.49 (m, 1H), 2.52-2.40 (m, 2H), 1.99-1.91 (m, 1H), 1.86-1.77 (m, 1H), 1.71-1.59 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.7, 119.6 (q, *J* = 321 Hz), 61.1, 57.4, 30.3, 29.1, 28.7, 14.1, 9.6; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.5; **IR (neat)** 3221(*s*), 2973(*m*), 2922(*s*), 1710(*s*), 1437(*s*), 1373(*s*), 1184(*s*), 1018(*s*), 906(*m*), 775(*m*), 615(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_9H_{16}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 290.0674, observed $(M-H)^-$ *m*/*z* 290.0678.

methyl 4-((trifluoromethyl)sulfonamido)hexanoate (3ac)

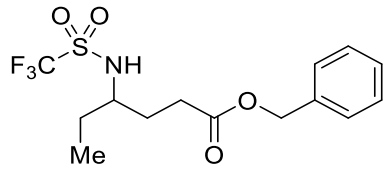
Prepared according to **Procedure B** (with 3.0 equiv. of methyl acrylate). Colorless oil (14.2 mg, 51% yield). R_f = 0.26 (5:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.17 (d, *J* = 8.1 Hz, 1H), 3.71 (s, 3H), 3.57-3.48 (m, 1H), 2.55-2.41 (m, 2H), 1.99-1.91 (m, 1H), 1.86-1.77 (m, 1H), 1.69-1.60 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 174.1, 119.6 (q, *J* = 321 Hz), 57.4, 52.0, 30.0, 29.1, 28.7, 9.6; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.5; **IR (neat)** 3227(*s*), 2923(*m*), 2852(*m*), 1716(*s*), 1438(*s*), 1372(*s*), 1184(*s*), 1013(*s*), 896(*m*), 775(*m*), 616(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_8H_{14}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 276.0517, observed $(M-H)^-$ *m*/*z* 276.0522.

benzyl 4-((trifluoromethyl)sulfonamido)hexanoate (3ad)

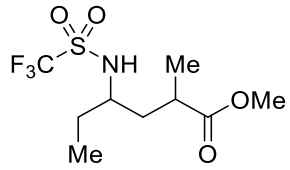
Prepared according to **Procedure B** (with 3.0 equiv. of Benzyl acrylate). Colorless oil (21.0 mg, 59% yield). R_f = 0.31 (9:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42-7.34 (m, 5H), 5.32 (brs, 1H), 5.17 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 3.55 (brs, 1H), 2.60-2.48 (m, 2H), 2.03-1.95 (m, 1H), 1.89-1.80 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.4, 135.5, 128.6, 128.4, 128.4, 119.6 (q, *J* = 321 Hz), 66.9, 57.4, 30.3, 29.2, 28.7, 9.6; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.5; **IR (neat)** 3234(*s*), 2938(*m*), 1712(*s*), 1455(*s*), 1372(*s*), 1227(*s*), 1184(*s*), 1011(*s*), 908(*m*), 750(*s*), 615(*s*) cm^{-1}**; HRMS-ASAP** (negative): M = $C_{14}H_{18}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 352.0830, observed $(M-H)^-$ *m*/*z* 352.0833.

methyl 2-methyl-4-((trifluoromethyl)sulfonamido)hexanoate (3ae)

Prepared according to **Procedure B** (with 3.0 equiv. of methyl methacrylate). Colorless oil (~1.7:1 mixed diastereomers, 19.9 mg, 68% yield). R_f = 0.42 (7:1 hex:EtOAc).

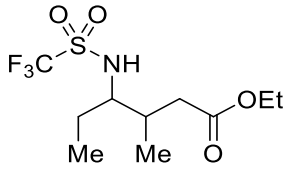


^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.17 (brs, 1H), 3.70 (s, 3H), 3.54 (brs, 1H), 2.70-2.54 (m, 1H), 2.06-1.94 (m, 1H), 1.73-1.51 (m, 3H), 1.22 (d, *J* = 7.1 Hz, 3H), 0.98-0.94 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 177.3, 176.7, 119.6 (q, *J* = 321 Hz), 119.6 (q, *J* = 321 Hz), 56.5, 56.1, 52.1, 52.0, 38.5, 37.9, 36.6, 35.6, 29.1, 28.4, 18.0, 17.8, 9.6, 9.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.61, -77.64; **IR (neat)** 3225(*s*), 2974(*m*), 1712(*s*), 1455(*s*), 1372(*s*), 1227(*s*), 1185(*s*), 1148(*s*), 1019(*s*), 901(*m*), 774(*m*), 615(*s*) cm^{-1}; **HRMS-ASAP**

(negative): M = $C_9H_{16}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 290.0674, observed $(M-H)^-$ *m*/*z* 290.0680.

ethyl 3-methyl-4-((trifluoromethyl)sulfonamido)hexanoate (3af)

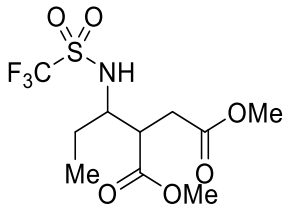
Prepared according to **Procedure B** (with 5.0 equiv. of ethyl crotonate). Colorless oil (~2.3:1 mixed diastereomers, 9.7 mg, 32% yield). R_f = 0.42 (4:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.23 (d, *J* = 8.9 Hz, 0.64H), 5.43 (d, *J* = 9.6 Hz, 0.25H), 4.19-4.12 (m, 2H), 3.49-3.36 (m, 1H), 2.45 (dd, *J* = 15.9, 6.5 Hz, 2H), 2.36-2.31 (m, 2H), 1.72-1.49 (m, 2H), 1.27 (td, *J* = 7.21, 2.2 Hz, 3H), 1.05-0.96 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.7, 173.1, 119.7 (q, *J* = 319 Hz), 119.6 (q, *J* = 319 Hz), 61.6, 61.4, 61.2, 60.9, 37.8, 37.3, 33.4, 32.7, 25.8, 25.1, 16.8, 15.7, 14.1, 14.1, 10.6, 9.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ –77.3, –77.4; **IR (neat)** 3227(*s*), 2974(*m*), 1708(*s*), 1455(*s*), 1373(*s*), 1227(*s*), 1184(*s*), 1148(*s*), 1014(*s*), 918(*m*), 774(*m*), 617(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{10}H_{18}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 304.0830, observed $(M-H)^-$ *m*/*z* 304.0836.

methyl 3-(2-methoxyacetyl)-4-((trifluoromethyl)sulfonamido)hexanoate (3ag)

Prepared according to **Procedure B** (with 3.0 equiv. of dimethyl maleate). Colorless oil (~2.4:1 mixed diastereomers, 17.6 mg, 53% yield). R_f = 0.26 (3:1 hex:EtOAc).

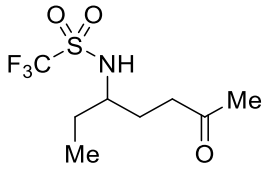


^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.76 (brs, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 3.71-3.62 (m, 1H), 2.85-2.65 (m, 1H), 2.49 (dd, *J* = 16.9, 5.8 Hz, 1H), 1.69-1.58 (m, 1H), 1.55-1.43 (m, 1H), 1.01 (td, *J* = 7.4, 4.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.6, 172.1, 171.8,

171.4, 119.5 (q, *J* = 320 Hz), 119.5 (q, *J* = 319 Hz), 58.0, 57.9, 52.6, 52.5, 52.3, 52.2, 45.4, 42.9, 33.7, 32.6, 27.9, 25.3, 10.5, 10.2; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.4, -77.6; **IR (neat)** 3234(*s*), 2957(*m*), 1718(*s*), 1438(*s*), 1375(*s*), 1227(*s*), 1186(*s*), 1148(*s*), 1013(*s*), 920(*m*), 779(*m*), 614(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{10}H_{16}F_3NO_6S$; expected $(M-H)^-$ *m*/*z* 334.0572, observed $(M-H)^-$ *m*/*z* 334.0578.

1,1,1-trifluoro-*N*-(6-oxoheptan-3-yl)methanesulfonamide (3ah)

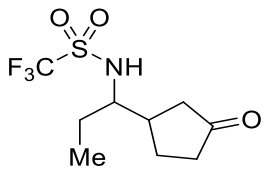
Prepared according to **Procedure B** (with 1.2 equiv. of 3-Buten-2-one). Colorless oil (17.9 mg, 69% yield). R_f = 0.18 (5:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.21 (brs, 1H), 3.51-3.44 (m, 1H), 2.75-2.57 (m, 2H), 2.21 (s, 3H), 1.95-1.87 (m, 1H), 1.80-1.71 (m, 1H), 1.69-1.61 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 208.8, 119.6 (q, *J* = 321 Hz), 57.6, 39.5, 30.0, 29.1, 27.7, 9.6; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.4; **IR (neat)** 3196(*s*), 2972(*m*), 1705(*s*), 1456(*s*), 1369(*s*), 1227(*s*), 1185(*s*), 1149(*s*), 1015(*s*), 942(*m*), 774(*m*), 614(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_8H_{14}F_3NO_3S$; expected $(M-H)^-$ *m*/*z* 260.0568, observed $(M-H)^-$ *m*/*z* 250.0570.

1,1,1-trifluoro-*N*-(1-(3-oxocyclopentyl)propyl)methanesulfonamide (3ai)

Prepared according to **Procedure B** (with 3.0 equiv. of 2-cyclopenten-1-one). Colorless oil (~1:1 mixed diastereomers, 15.7 mg, 58% yield). R_f = 0.18 (4:1 hex:EtOAc).

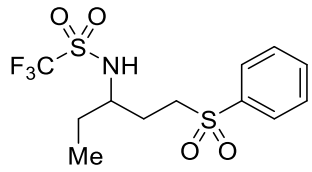


^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.24 (brs, 1H), 3.55-3.48 (m, 1H), 2.44-2.32 (m, 3H), 2.28-1.94 (m, 3H), 1.94-1.52 (m, 3H), 1.02 (td, *J* = 7.5, 2.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$,

100 MHz) δ 217.3, 217.2, 119.5 (q, *J* = 321 Hz), 119.5 (q, *J* = 321 Hz), 61.2, 61.0, 42.1, 41.6, 41.2, 41.1, 38.63, 38.4, 26.9, 26.4, 26.4, 26.0, 9.3, 9.2; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.17, -77.21; **IR (neat)** 3139(*s*), 2972(*m*), 1732(*s*), 1456(*s*), 1368(*s*), 1227(*s*), 1185(*s*), 1148(*s*), 1009(*s*), 906(*m*), 776(*m*), 602(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_9H_{14}F_3NO_3S$; expected $(M-H)^-$ *m*/*z* 272.0568, observed $(M-H)^-$ *m*/*z* 272.0569.

1,1,1-trifluoro-*N*-(1-(phenylsulfonyl)pentan-3-yl)methanesulfonamide (3aj)

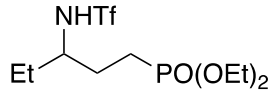
Prepared according to **Procedure B** (with 3.0 equiv. of phenyl vinyl sulfone). White solid (26.3 mg, 73% yield). R_f = 0.26 (2:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95-7.93 (m, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 2H), 5.47 (s, 1H), 3.57-3.51 (m, 1H), 3.31-3.17 (m, 2H), 2.16-2.06 (m, 1H), 2.03-1.93 (m, 1H), 1.72-1.61 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 138.6, 134.1, 129.5, 128.0, 119.5 (q, *J* = 321 Hz), 56.4, 52.7, 28.5, 27.7, 9.7; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.4; **IR (neat)** 3212(*s*), 2973(*m*), 1447(*s*), 1372(*s*), 1304(*s*), 1187(*s*), 1143(*s*), 1085(*s*), 1013(*m*), 740(*s*), 615(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{12}H_{16}F_3NO_4S_2$; expected $(M-H)^+$ *m*/*z* 358.0395, observed $(M-H)^+$ *m*/*z* 358.0402;

diethyl (3-((trifluoromethyl)sulfonamido)pentyl)phosphonate (3ak)

Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (11.4 mg, 32%). R_f = 0.25 (1:1 hex:EtOAc).

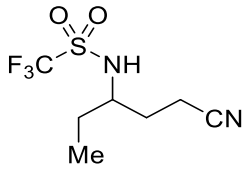


^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32 (d, *J* = 8.9 Hz, 1H), 4.17-4.05 (m, 4H), 3.53-3.45 (m, 1H), 2.01-1.76 (m, 4H), 1.71-1.59 (m, 2H), 1.33 (td, *J* = 7.1, 2.3 Hz, 6H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 119.92 (q, *J* = 320.0 Hz), 62.32 (d, *J* = 6.7 Hz), 57.34 (d, *J* = 13.4 Hz), 27.97, 27.43 (d, *J* = 4.2 Hz), 21.41 (d, *J* = 142.9 Hz), 16.32 (d, *J* =

5.9 Hz), 16.47 (d, *J* = 6.1 Hz), 10.16; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ 77.72; **IR (CDCl$_3$ solution)** 3045 (*m*), 2980 (*m*), 2885 (*m*), 1723 (*w*), 1478 (*m*), 1370 (*s*), 1186 (*s*), 1027 (*s*), 969 (*s*), 789 (*m*), 613 (*s*), 511 (*m*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{10}H_{21}F_3NO_5PS$; expected $(M-H)^-$ *m*/*z* 354.0752, observed $(M-H)^-$ *m*/*z* 354.0753.

***N*-(1-cyanopentan-3-yl)-1,1,1-trifluoromethanesulfonamide (3al)**

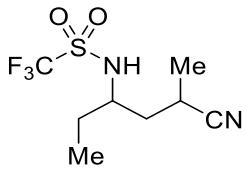
Prepared according to **Procedure B** (with 3.0 equiv. of acrylonitrile). Colorless oil (12.9 mg, 53% yield). R_f = 0.38 (2:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.14 (brs, 1H), 3.58-3.51 (m, 1H), 2.58-2.43 (m, 2H), 2.06-1.98 (m, 1H), 1.90-1.81 (m, 1H), 1.76-1.59 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 119.5 (q, *J* = 321 Hz), 119.0, 56.9, 30.8, 28.1, 13.9, 9.7; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.4; **IR (neat)** 3189(*s*), 2975(*m*), 2942(*s*), 2253(*s*), 1437(*s*), 1370(*s*), 1227(*s*), 1186(*s*), 1147(*s*), 1013(*s*), 896(*s*), 774(*m*), 615(*s*), 576(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_7H_{11}F_3N_2O_2S$; expected $(M-H)^-$ *m*/*z* 243.0415, observed $(M-H)^-$ *m*/*z* 243.0419.

***N*-(5-cyanohexan-3-yl)-1,1,1-trifluoromethanesulfonamide (3am)**

Prepared according to **Procedure B** (with 3.0 equiv. of methacrylonitrile) in 0.3 mmol scale.



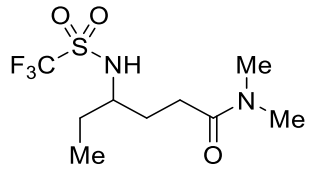
Major isomer: Colorless oil (34.9 mg, 45% yield). R_f = 0.32 (4:1 hex:EtOAc).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.66-3.59 (m, 1H), 2.01-1.94 (m, 1H), 1.83-1.71 (m, 2H), 1.69-1.58 (m, 1H), 1.41 (d, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$,

100 MHz) δ 122.4, 119.5 (q, *J* = 321 Hz), 55.5, 39.3, 28.2, 21.9, 17.8, 9.6; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.4; **IR (neat)** 3195(*s*), 2978(*m*), 2885(*m*), 2245(*s*), 1457(*s*), 1372(*s*), 1227(*s*), 1187(*s*), 1148(*s*), 1019(*s*), 844(*s*), 774(*m*), 615(*s*), 576(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_8H_{13}F_3N_2O_2S$; expected $(M-H)^-$ *m*/*z* 257.0572, observed $(M-H)^-$ *m*/*z* 257.0574.

Minor isomer: Colorless oil (13.2 mg, 17% yield). R_f = 0.27 (4:1 hex:EtOAc). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.12 (d, *J* = 8.4 Hz, 1H), 3.63-3.54 (m, 1H), 2.80-2.71 (m, 1H), 1.86 (ddd, *J* = 14.6, 10.9, 3.8 Hz, 1H), 1.70-1.53 (m, 3H), 1.31 (d, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 122.1, 119.5 (q, *J* = 321 Hz), 56.1, 40.1, 28.5, 22.5, 18.3, 9.6; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.3; **IR (neat)** 3165(*s*), 2984(*m*), 2888(*m*), 2250(*s*), 1459(*s*), 1370(*s*), 1229(*s*), 1186(*s*), 1152(*s*), 1027(*s*), 855 (*s*), 771(*m*), 609(*s*), 575(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_8H_{13}F_3N_2O_2S$; expected $(M-H)^-$ *m*/*z* 257.0572, observed $(M-H)^-$ *m*/*z* 257.0572.

_N_,_N_-dimethyl-4-((trifluoromethyl)sulfonamido)hexanamide (3an)

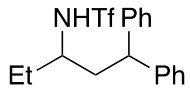
Prepared according to **Procedure B** (with 3.0 equiv. of *N*,*N*-Dimethylacrylamide). Colorless oil (10.9 mg, 38% yield). R_f = 0.34 (EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (d, *J* = 6.8 Hz, 1H), 3.51-3.43 (m, 1H), 3.03 (s, 3H), 2.97 (s, 3H), 2.60-2.52 (m, 1H), 2.46-2.39 (m, 1H), 2.02-1.85 (m, 2H), 1.73-1.61 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.11, 119.85 (q, *J* = 321.5 Hz), 57.61, 37.27, 35.83, 29.54, 29.08, 27.94, 9.55; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.6; **IR (neat)** 3071(*s*), 2970(*m*), 2938(*m*), 1619(*s*), 1461(*s*), 1367(*s*), 1225(*s*), 1180(*s*), 1151(*s*), 1014(*s*), 910(*m*), 777(*m*), 610(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_9H_{17}F_3N_2O_3S$; expected $(M-H)^-$ *m*/*z* 289.0834, observed $(M-H)^-$ *m*/*z* 289.0833.

***N*-(1,1-diphenylpentan-3-yl)-1,1,1-trifluoromethanesulfonamide (3ao)**

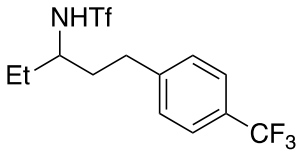
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). The reactions were conducted in triplicate (3 x 0.1mmol reaction vials), combined, and isolated via a Teledyne ISCO CombiFlash® Rf+ LumenTM instrument using RediSep® Rf high performance silica. The yields are reported on a 0.1 mmol scale (average of 3 runs). White solid (13.6 mg, 37% yield). R_f = 0.45 (9:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32-7.29 (m, 4H), 7.27-7.24 (m, 2H), 7.21 (tq, *J* = 6.6, 1.5 Hz, 4H), 4.48 (d, *J* = 9.4 Hz, 1H), 4.07 (t, *J* = 7.9 Hz, 1H), 3.50-3.43 (m, 1H), 2.38-2.27 (m, 2H), 1.78-1.69 (m, 1H), 1.61-1.52 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 143.51, 128.97, 128.95, 127.89, 127.70, 126.94, 126.87, 119.63 (q, *J* = 320.9 Hz), 56.39, 47.59, 41.23, 28.00, 9.41; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ 76.59; **IR ($CDCl_3$ solution)** 3302.69 (*br*), 3027.84 (*w*), 2928.41 (*m*), 1708.81 (*m*), 1599.03 (*m*), 1493.66 (*m*), 1427.79 (*m*), 1371.14 (*s*), 1226.75 (*s*), 1190.03 (*s*), 1145.94 (*s*), 1023.28 (*m*), 750.84 (*m*), 700.44 (*s*), 616.01 (*s*,) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{18}H_{20}F_3NO_2S$; expected $(M-H)^-$ *m*/*z* 370.1089, observed $(M-H)^-$ *m*/*z* 370.1093.

1,1,1-trifluoro-N-(1-(4-(trifluoromethyl)phenyl)pentan-3-yl)methanesulfonamide (3ap)

Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). The reactions were conducted in triplicate (3 x 0.1mmol reaction vials), combined, and isolated via a Teledyne ISCO CombiFlash® Rf+ LumenTM instrument using RediSep® Rf high performance silica. The yields are reported on a 0.1 mmol scale (average of 3 runs). White solid (11.9 mg, 33% yield). R_f = 0.4 (9:1 hex:EtOAc).

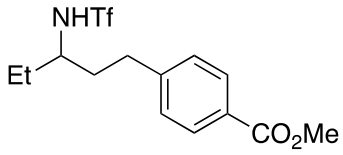


^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 3.61-3.52 (m, 1H), 2.84-2.69 (m, 2H), 1.98-1.88 (m, 1H), 1.88-1.80 (m, 1H), 1.79-1.68 (m, 1H), 1.66-1.57 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$,

126 MHz) δ 144.93, 128.75, 128.76 (q, *J* = 34.0 Hz), 125.71 (q, *J* = 3.7 Hz), 124.36 (q, *J* = 271.9 Hz), 119.70 (q, *J* = 320.7 Hz), 57.80, 36.90, 31.82, 28.48, 9.76; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -62.44, -77.42; **IR ($CDCl_3$ solution)** 3288 (*br*), 2950 (*m*), 1616 (*m*), 1424 (*s*), 1374 (*s*), 1326 (*s*), 1226 (*s*), 1194 (*s*), 1126 (*s*), 1066 (*s*), 1018 (*s*), 840 (*m*), 820 (*m*), 618 (*s*), 516 (*m*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{13}H_{15}F_6NO_2S$; expected $(M-H)^-$ *m*/*z* 362.0649, observed $(M-H)^-$ *m*/*z* 362.0646.

Methyl 4-(3-((trifluoromethyl)sulfonamide)pentyl)benzoate (3aq)

Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). The reactions were conducted in triplicate (3 x 0.1mmol reaction vials), combined, and isolated via a Teledyne ISCO CombiFlash® Rf+ LumenTM instrument using RediSep® Rf high performance silica. The yields are reported on a 0.1 mmol scale (average of 3 runs). White solid (11.2 mg, 33% yield). R_f = 0.2 (9:1hex:EtOAc).

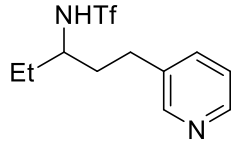


^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, *J* =8.4 Hz, 2H), 7.25 (d, 2H), 4.70 (d, *J* =9.4 Hz, 1H), 3.91 (s, 3H), 3.60-3.52 (m, 1H), 2.84-2.68 (m, 2H), 1.99-1.90 (m, 1H), 1.89-1.79 (m, 1H), 1.76-1.67 (m, 1H), 1.66-1.56 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.04, 146.21, 129.95, 128.30, 128.28, 119.58 (q, *J* = 320.8 Hz), 57.66, 52.07, 36.56, 31.86, 28.29, 9.59; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -77.46; **IR ($CDCl_3$ solution)** 3208 (*br*), 2954 (*m*), 1700 (*s*), 1612 (*s*), 1434 (*s*), 1374 (*s*), 1284 (*s*), 1228 (*s*), 1186 (*s*), 1148 (*s*), 1116 (*s*) 1016 (*s*), 768 (*s*), 708 (*s*), 616 (*s*), 574(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{14}H_{18}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 352.0830, observed $(M-H)^-$ *m*/*z* 352.0829.

1,1,1-trifluoro-*N*-(1-(pyridine-3-yl)pentan-3-yl)methanesulfonamide (3ar)

Prepared according to **Procedure B** (with 3.0 equiv of 3-vinylpyridine). After acidifying with 0.5M HCl and extraction by EtOAc, the aqueous layer was basified to a pH>7 with sat. $NaHCO_3$ and extracted by EtOAc. The combined organic layers were then washed

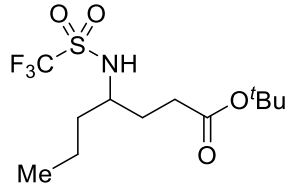
with brine. The reactions were conducted in triplicate (3 x 0.1mmol reaction vials), combined, and isolated via a Teledyne ISCO CombiFlash® Rf+ LumenTM instrument using RediSep® Rf high performance silica. The yields are reported on a 0.1 mmol scale (average of 3 runs). Colorless oil (9.7 mg, 33% yield). R_f = 0.3 (7:3 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.53 (brs, 1H), 8.49 (d, *J* = 5.0 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.26-7.17 (m, 2H), 3.60 (quint, 1H), 3.11-3.04 (m, 1H), 2.99-2.92 (m, 1H), 2.12-1.98 (m, 2H), 1.82-1.62 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 160.50, 148.24, 137.64, 123.82, 121.87, 120.16 (q, *J* = 322.0 Hz,), 57.17, 32.87, 31.58, 28.75, 9.96; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.5**. IR** ($CDCl_3$) 2936.12 (brs), 2636.72 (brs), 1598.28 (m), 1482.14 (m), 1440.91 (m), 1365.93 (s), 1223.12 (s), 1180.60 (s), 1151.19 (s), 1120.09 (s), 1052.80 (s), 1024.38 (s), 768.96 (m), 605.13 (s), 404.06 (m) cm^{-1}; **HRMS-ASAP** (negative); M = $C_{11}H_{15}F_3N_2O_2S$; expected $(M-H)^-$ *m/z* 295.0728, observed $(M-H)^-$ *m/z* 295.0731.

***tert*-butyl 4-((trifluoromethyl)sulfonamido)heptanoate (3ba)**

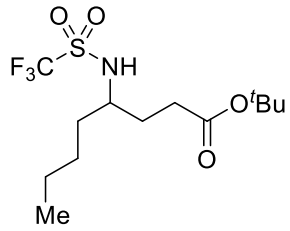
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (25.1 mg, 75% yield). R_f = 0.39 (6:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.52 (brs, 1H), 3.59 (brs, 1H), 2.48-2.33 (m, 2H), 1.97-1.88 (m, 1H), 1.82-1.73 (m, 1H), 1.63-1.56 (m, 2H), 1.47 (s, 9H), 1.46-1.38 (m, 2H), 0.97 (t, *J* = 7.3, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 173.1, 119.6 (q, *J* = 319), 81.4, 56.0, 38.0, 31.4, 29.4, 28.0, 18.5, 13.6; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.4; **IR (neat)** 3205(*s*), 2967(*m*), 1700(*s*), 1448(*s*), 1369(*s*), 1227(*s*), 1185(*s*), 1150(*s*), 1034(*m*), 994(*m*), 754(*m*), 614(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{12}H_{22}F_3NO_4S$; expected $(M-H)^-$ *m/z* 332.1143, observed $(M-H)^-$ *m/z* 332.1143.

***tert*-butyl 4-((trifluoromethyl)sulfonamido)octanoate (3ca)**

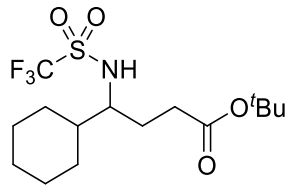
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (24.4 mg, 70% yield). R_f = 0.45 (8:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.52 (brs, 1H), 3.56 (brs, 1H), 2.45-2.31 (m, 2H), 1.94-1.86 (m, 1H), 1.80-1.71 (m, 1H), 1.61-1.56 (m, 2H), 1.45 (s, 9H), 1.38-1.29 (m, 4H), 0.91 (t, *J* = 6.9, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 173.2, 119.6 (q, *J* = 319), 81.4, 56.1, 35.5, 31.4, 29.4, 28.0, 27.3, 22.4, 13.8; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.5; **IR (neat)** 3194(*s*), 2934(*m*), 2869(*m*), 1729(*s*), 1701(*s*), 1457(*s*), 1370(*s*), 1227(*s*), 1150(*s*), 1055(*m*), 994(*m*), 843(*m*), 615(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{13}H_{24}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 346.1300, observed $(M-H)^-$ *m*/*z* 346.1302;

***tert*-butyl 4-cyclohexyl-4-((trifluoromethyl)sulfonamido)butanoate (3da)**

Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). White solid (24.0 mg, 64% yield). R_f = 0.53 (7:1 hex:EtOAc).

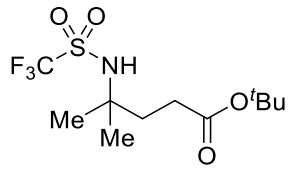


^{1}H NMR ($CDCl_3$, 400 MHz) δ5.41 (brs, 1H), 3.42 (brs, 1H), 2.46-2.32 (m, 2H), 1.94-1.70 (m, 7H), 1.70-1.60 (m, 1H), 1.47 (s, 9H), 1.32-0.99 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.1, 119.6 (q, *J* = 321 Hz), 81.4, 60.8, 42.3, 31.5, 28.7, 28.2, 28.0, 26.2, 26.2, 26.2, 26.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.2; **IR (neat)** 3216(*s*), 2929(*s*), 2855(*m*), 1728(*s*), 1700(*s*), 1448(*s*), 1368(*s*), 1227(*s*), 1185(*s*), 1148(*s*), 1049(*m*), 988(*m*), 843(*m*),

604(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{15}H_{26}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 372.1456, observed $(M-H)^-$ *m*/*z* 372.1456;

***tert*-butyl 4-methyl-4-((trifluoromethyl)sulfonamido)pentanoate (3ea)**

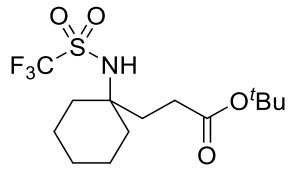
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). White solid (14.0 mg, 44% yield). R_f = 0.44 (7:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.10 (brs, 1H), 2.45 (t, *J* = 6.9 Hz, 2H), 1.90 (t, *J* = 6.8 Hz, 2H), 1.48 (s, 9H), 1.45 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 173.9, 119.3 (q, *J* = 321 Hz), 81.9, 59.4, 37.8, 30.1, 28.0, 27.7; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.8; **IR (neat)** 3210(*s*), 2980(*m*), 2925(*m*), 1700(*s*), 1440(*s*), 1367(*s*), 1227(*s*), 1187(*s*), 1146(*s*), 1003(*s*), 843(*m*), 625(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{11}H_{20}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 318.0987, observed $(M-H)^-$ *m*/*z* 318.0993;

***tert*-butyl 3-(1-((trifluoromethyl)sulfonamido)cyclohexyl)propanoate (3fa)**

Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-Butyl acrylate). White solid (15.7 mg, 44% yield). R_f = 0.42 (7:1 hex:EtOAc).

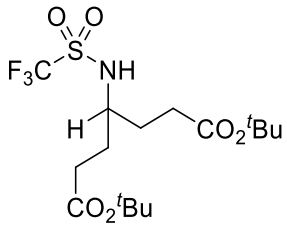


^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.34 (brs, 1H), 2.37 (t, *J* = 7.3 Hz, 2H), 2.06 (t, *J* = 7.3 Hz, 2H), 1.99-1.93 (m, 2H), 1.71-1.59 (m, 4H), 1.54-1.42 (m, 4H), 1.48 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 173.2, 119.2 (q, *J* = 319 Hz), 81.3, 62.9, 35.6, 32.0, 29.4, 28.0, 24.9, 22.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.8; **IR (neat)** 3243(*s*), 2935(*m*), 2867(*m*), 1701(*s*), 1453(*s*), 1368(*s*), 1223(*s*), 1187(s), 1144(*s*), 993(*s*), 844(*m*), 626(*s*) cm^{-1};

HRMS-ASAP (negative): M = $C_{14}H_{24}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 358.1300, observed $(M-H)^-$ *m*/*z* 358.1300;

di-*tert*-butyl 4-((Trifluoromethyl)sulfonamide)heptanedioate (3ga)

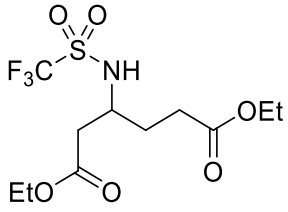
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Clear oil (14.3 mg, 34% yield). Rf = 0.50 (4:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.15 (brs, 1H), 3.63 (brs, 1H), 2.45-2.33 (m, 4H), 1.89-1.82 (m, 4H), 1.45 (s, 18H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.06, 119.87 (q, *J* = 321.4 Hz), 81.55, 55.41, 31.36, 30.00, 28.16; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ 77.25; **IR ($CDCl_3$)** 3208.66 (brs), 2919.32 (m), 2850.26 (m), 1722.07 (m), 1458.12 (m), 1369.93 (s), 1229.05 (s), 1149.75 (s), 1081.43 (m) 908.68 (s), 844.08 (m), 733.95 (s), 648.83 (m), 615.65 (m) cm^{-1}; **MS (ESI, negative)**: M = $C_{16}H_{28}F_3NO_6S$; expected $(M-H)^-$ *m*/*z* 418.16, observed $(M-H)^-$ *m*/*z* 418.2.

diethyl 3-((trifluoromethyl)sulfonamido)hexanedioate (3hb)

Prepared according to **Procedure B** (with 1.5 equiv. of ethyl acrylate). Colorless oil (12.4 mg, 36% yield). R_f = 0.36 (3:1 hex:EtOAc).

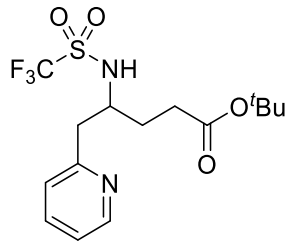


^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.32 (d, *J* = 9.3 Hz, 1H), 4.17 (dq, *J* = 14.5, 7.1 Hz, 4H), 3.85 (tq, *J* = 9.4, 4.6 Hz, 1H), 2.77-2.59 (m, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 2.06-1.88 (m, 2H), 1.30-1.25 (m, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.9, 171.2, 119.6 (q, *J* = 321 Hz), 61.4, 61.0, 52.1, 38.8, 30.5, 29.7, 29.2, 14.1, 14.0; **^{19}F NMR** ($CDCl_3$, 376 MHz):

−77.8; **IR (neat)** 3219(*s*), 2920(*m*), 2850(*m*), 1732(*s*), 1711(*s*), 1438(*s*), 1376(*s*), 1228(*s*), 1147(*s*), 1022(*m*), 857(*m*), 614(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{11}H_{18}F_3NO_6S$; expected $(M-H)^-$ *m*/*z* 348.0729, observed $(M-H)^-$ *m*/*z* 348.0734.

***tert*-butyl 5-(pyridin-2-yl)-4-((trifluoromethyl)sulfonamido)pentanoate (3ia)**

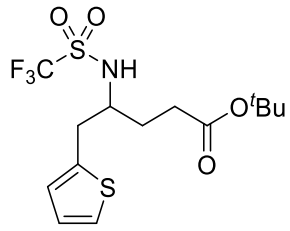
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). White solid (21.0 mg, 55% yield). R_f = 0.63 (1:2 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (d, *J* = 4.2 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.21 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 4.00-3.95 (m, 1H), 3.27 (dd, *J* = 15.4, 4.4 Hz, 1H), 2.94 (dd, *J* = 15.4, 4.2 Hz, 1H), 2.43-2.30 (m, 2H), 1.77-1.71 (m, 2H), 1.43 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.3, 157.8, 148.8, 137.3, 124.6, 122.2, 119.9 (q, *J* = 320 Hz),80.8, 54.8, 40.0, 31.7, 29.8, 28.0; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.7; **IR (neat)** 3348(*s*), 1719(*s*), 1364(*s*), 1370(*s*), 1223(*s*), 1188(*s*), 1150(*s*), 996(*s*), 769(*m*), 603(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{15}H_{21}F_3N_2O_4S$; expected $(M-H)^-$ *m*/*z* 381.1096, observed $(M-H)^-$ *m*/*z* 381.1103.

***tert*-butyl 5-(thiophen-2-yl)-4-((trifluoromethyl)sulfonamido)pentanoate (3ja)**

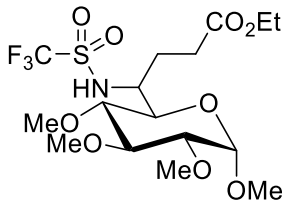
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). White solid (22.7 mg, 59% yield). R_f = 0.44 (6:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.99 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.89 – 6.87 (m, 1H), 5.57 (d, *J* = 6.8 Hz, 1H), 3.86-3.78 (m, 1H), 3.22-3.13 (m, 2H), 2.49-2.30 (m, 2H), 1.92-1.72 (m, 2H), 1.45 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.0, 136.9, 127.3, 125.0, 119.6 (q, *J* = 321 Hz), 81.6, 56.3, 36.2, 31.5, 28.4, 28.0; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.4; **IR (neat)** 3194(*s*), 2979(*m*), 2929(*m*), 1698(*s*), 1434(*s*), 1370(*s*), 1227(*s*), 1187(*s*), 1148(*s*), 1073(*m*), 994(*m*), 844(*m*), 700(*s*), 614(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{14}H_{20}F_3NO_4S_2$; expected $(M-H)^-$ *m/z* 386.0708, observed $(M-H)^-$ *m/z* 386.0710.

ethyl-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)-4-((trifluoromethyl)sulfonamido)butanoate (3kb)

Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). White solid (~1:1 mixed diastereomers, 31.7 mg, 68% yield). R_f = 0.45 (1:1 hex:EtOAc)

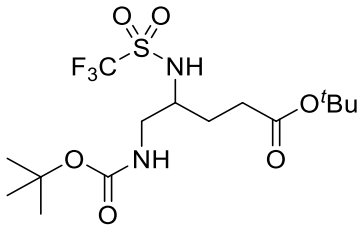


major isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.38 (d, *J* = 9.6 Hz, 1H), 4.82 (d, *J* = 3.6 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.94 (q, *J* = 7.5 Hz, 1H), 3.64 (s, 3H), 3.63 (s, 3H), 3.61-3.53 (m, 2H), 3.54 (s, 3H), 3.43 (s, 3H), 3.21-3.16 (m, 2H), 2.54-2.40 (m, 2H), 2.10-1.94 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.42, 119.48 (q, *J* = 320.5), 97.76, 83.77, 81.67, 78.64, 70.24, 60.76, 60.67, 60.25, 59.19, 55.19, 55.67, 54.63, 30.55, 28.13, 14.13; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.30; **IR ($CDCl_3$ solution)** 3320 (*br*), 2940 (*m*), 1734 (*s*), 1448 (*s*), 1374 (*s*), 1230 (*s*), 1190 (*s*), 1152 (*s*), 1096 (*s*), 1052 (*s*), 1030 (*s*), 620 (*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{16}H_{28}F_3NO_9S$; expected $(M-H)^-$ *m/z* 466.1359, observed $(M-H)^-$ *m/z* 466.1350.

***tert*-butyl 5-((*tert*-butoxycarbonyl)amino)-4-((trifluoromethyl)sulfonamido)pentanoate (3la)**

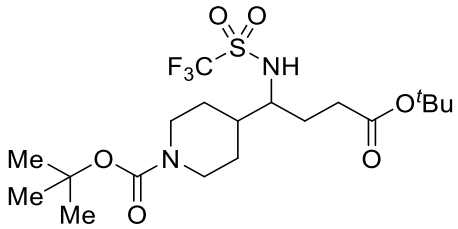
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (22.1 mg, 53% yield). R_f = 0.40 (3:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.86 (brs, 1H), 4.98 (brs, 1H), 3.65-3.59 (m, 1H), 3.35-3.23 (m, 2H), 2.46-2.32 (m, 2H), 1.92-1.76 (m, 2H), 1.44 (s, 18H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 172.7, 157.5, 119.7 (q, *J* = 321 Hz), 81.3, 80.7, 56.6, 44.5, 31.2, 28.2, 28.0, 27.8; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.1; **IR (neat)** 3155(*s*), 2978(*m*), 2933(*m*), 1692(*s*), 1520(*s*), 1454(*s*), 1368(*s*), 1228(*s*), 1184(*s*), 1149(*s*), 998(*m*), 845(*m*), 613(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{15}H_{27}F_3N_2O_6S$; expected $(M-H)^-$ *m*/*z* 419.1464, observed $(M-H)^-$ *m*/*z* 419.1461;

***tert*-butyl 4-(4-(tert-butoxy)-4-oxo-1-((trifluoromethyl)sulfonamido)butyl)piperidine-1-carboxylate (3ma)**

Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-Butyl acrylate). Colorless oil (33.2 mg, 70% yield). R_f = 0.46 (3:1 hex:EtOAc).

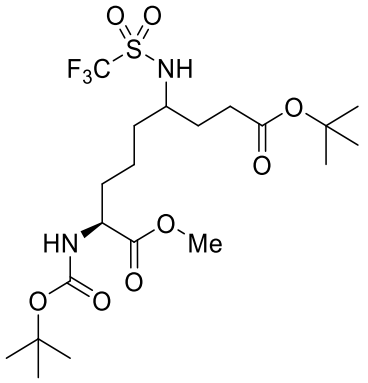


^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.14 (brs, 1H), 4.11 (brs, 2H), 3.38 (dt, *J* = 9.2, 4.8 Hz, 2H), 2.58 (t, *J* = 9.2 Hz, 2H), 2.38-2.24 (m, 2H), 1.86-1.78 (m, 1H), 1.73-1.58 (m, 4H), 1.38 (s, 9H), 1.37 (s, 9H), 1.26-1.12 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 173.0, 154.7, 119.6 (q, *J* = 319 Hz), 81.6, 79.4, 59.9, 43.8 (brs), 41.0, 31.4, 28.4, 28.0, 27.6

(brs), 26.0; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.1; **IR (neat)** 3132(*s*), 2976(*m*), 2864(*m*), 1728(*s*), 1694(*s*), 1660(*s*), 1428(*s*), 1367(*s*), 1184(*s*), 1063(*s*), 857(*m*) $cm^{-1;}$ **HRMS-ASAP** (negative): M = $C_{19}H_{33}F_3N_2O_6S$; expected $(M-H)^-$ *m*/*z* 473.1933, observed $(M-H)^-$ *m*/*z* 473.1932;

9-(*tert*-butyl) 1-methyl (2*S*)-2-((*tert*-butoxycarbonyl)amino)-6-((trifluoromethyl)sulfonamido)nonanedioate (3na)

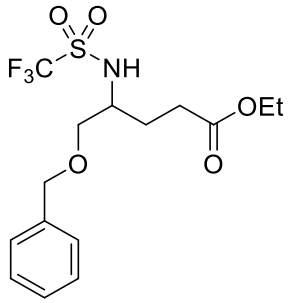
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (~1:1 mixed diastereomers, 30.2 mg, 58% yield). R_f = 0.46 (2:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.01 (dd, *J* = 20.0, 7.9 Hz, 1H), 5.14 (dd, *J* = 25.1, 8.3 Hz, 1H), 4.29 (brs, 1H), 3.74 (s, 3H), 3.63-3.42 (m, 1H), 2.47-2.26 (m, 2H), 2.44-2.29 (m, 8H), 1.44-1.43 (m, 18H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 173.27, 173.19, 173.03, 156.14, 155.71, 119.7 (q, *J* = 321.2 Hz), 81.56, 81.40, 80.57, 80.35, 55.87, 55.80, 53.05, 52.60, 52.54, 35.00, 34.08, 33.06, 32.89, 31.47, 31.43, 30.62, 29.50, 28.43, 28.16, 21.12, 21.01; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.16, –77.35; **IR (neat)** 3186(*s*), 2977(*s*), 1704(*s*), 1511(*s*), 1445(*s*), 1367(*s*), 1227(*s*), 1152(*s*), 1053(*m*), 998(*m*), 846(*m*), 613(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{20}H_{35}F_3N_2O_8S$; expected $(M-H)^-$ *m/z* 519.1988, observed $(M-H)^-$ *m/z* 519.1984.

ethyl 5-(benzyloxy)-4-((trifluoromethyl)sulfonamido)pentanoate (3oa)

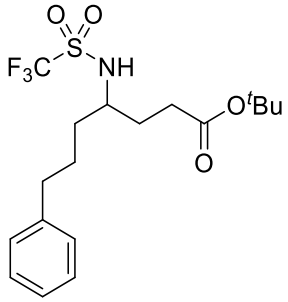
Prepared according to **Procedure B** (with 1.5 equiv. of Ethyl acrylate). Colorless oil (22.2 mg, 58% yield). R_f = 0.29 (6:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.32 (m, 5H), 5.55 (d, *J* = 9.0 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.80-3.72 (m, 1H), 3.62-3.55 (m, 2H), 2.53-2.40 (m, 2H), 2.10-1.94 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 173.2, 137.2, 128.6, 128.1, 127.8, 119.6 (q, *J* = 321 Hz), 73.6, 71.4, 60.9, 55.1, 30.3, 27.5, 14.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.6; **IR (neat)** 3214(*s*), 2876(*m*), 1712(*s*), 1442(*s*), 1227(*s*), 1184(*s*), 1147(*s*), 1015(*s*), 1055(*s*), 910(*m*), 741(*s*), 698(*s*), 609(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{15}H_{20}F_3NO_5S$; expected $(M-H)^-$ *m*/*z* 382.0936, observed $(M-H)^-$ *m*/*z* 382.0939;

***tert*-butyl 7-phenyl-4-((trifluoromethyl)sulfonamido)heptanoate (3pa)**

Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Colorless oil (30.4 mg, 74% yield). R_f = 0.38 (7:1 hex:EtOAc).

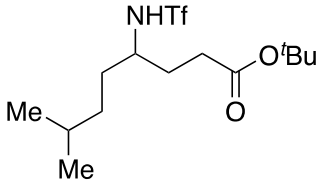


^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31-7.26 (m, 2H), 7.22-7.15 (m, 3H), 5.60 (brs, 1H), 3.58 (brs, 1H), 2.56 (t, *J* = 7.5, 2H), 2.42-2.26 (m, 2H), 1.95-1.83 (m, 1H), 1.79-1.66 (m, 3H), 1.65-1.58 (m, 2H), 1.44 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 173.1, 141.5, 128.4, 128.3, 126.0, 119.6 (q, *J* = 319), 81.5, 56.0, 35.4, 35.3, 31.3, 29.4, 28.0, 26.9; **^{19}F NMR** ($CDCl_3$, 376 MHz): −77.4; **IR (neat)** 3219(*s*), 2978(*m*), 2933(*m*), 1727(*s*), 1699(*s*), 1453(*s*), 1369(*s*), 1227(*s*), 1186(*s*), 1147(*s*), 1005(*m*), 843(*m*), 749(*s*), 615(*s*) cm^{-1};

HRMS-ASAP (negative): M = $C_{18}H_{26}F_3NO_4S$; expected $(M-H)^-$ *m*/*z* 408.1456, observed $(M-H)^-$ *m*/*z* 408.1457;

***tert*-butyl 7-methyl-4-((trifluoromethyl)sulfonamido)octanoate (3qa)**

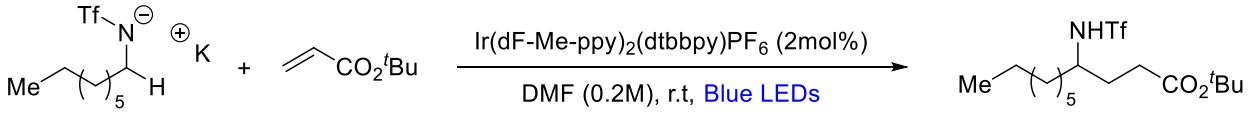
Prepared according to **Procedure B** (with 3.0 equiv. of *tert*-butyl acrylate). Light yellow oil (23.9 mg, 65% yield). R_f = 0.4 (9:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.74 (d, *J* = 8.8 Hz, 1H), 3.57-3.48 (m, 1H), 2.41-2.32 (m, 2H), 1.93-1.85 (m,1H), 1.80-1.70 (m,1H), 1.61-1.48 (m, 3H), 1.44 (s, 9H), 1.29-1.17 (m, 2H), 0.88 (dd, *J* = 6.6, 1.3 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.32, 119.80 (q, *J* = 321.1 Hz), 81.55, 56.54, 34.32, 33.75, 31.63, 29.74, 28.13, 22.59, 22.4; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ 77.50; **IR ($CDCl_3$ solution)** 3213(*w*, *br*), 2949(*w*), 1699(*s*), 1455(*s*), 1369(*s*), 1227(*s*), 1186(*s*), 1150(*s*), 1063(*m*), 995(*m*), 844(*m*), 756(*m*), 616(*s*) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{14}H_{26}F_3NO_4S$: expected $(M-H)^-$ *m*/*z* 360.1456, observed $(M-H)^-$ *m*/*z* 360.1455.

***tert*-butyl 4-((trifluoromethyl)sulfonamide)undecanoate (3ra)**

Prepared according to **Procedure B** (1,1,1-trifluoro-*N*-octylmethanesulfonamide and KH were pre-stirred for 1.5h) with 3.0 equiv of *tert*-butyl acrylate. Colorless oil (22.4 mg, 58% yield). R_f = 0.4 (7:3 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.77 (d, 1H), 3.54 (brs, 1H), 2.43-2.30 (m, 2H), 1.93-1.85 (m, 1H), 1.79-1.70 (m, 1H), 1.57 (q, *J* =7.5Hz, 2H), 1.44 (s, 9H), 1.37-1.26 (m, 10H), 0.87 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 1001 MHz) δ 173.33, 119.80 (q, *J* = 321.1 Hz), 81.53, 56.32, 35.92, 31.84, 31.64, 29.84, 29.40, 29.19, 28.12, 25.37, 22.72, 14.15.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -77.5. **MS (ESI, negative):** M = $C_{16}H_{30}F_3NO_4S$: expected $(M-H)^-$ *m/z* 388.18, observed $(M-H)^-$ *m/z* 388.2.

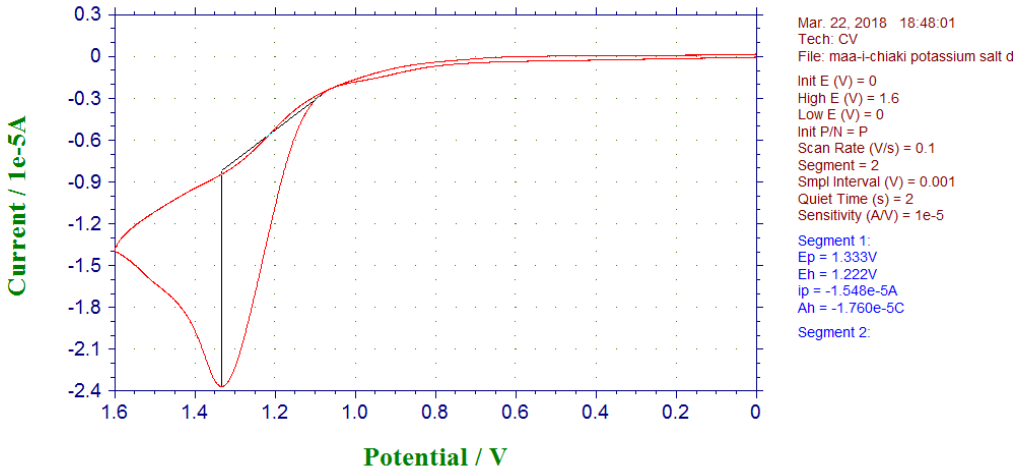
Mechanistic Investigations

1. Cyclic Voltammetry (CV) Study: a glassy electrode, a Pt mesh counter electrode and an Ag/AgCl reference electrode were used and measurement was taken in a 10 mM solution of a specific compound in DMF containing 0.1 M NBu_4PF_6.

a. CV study of amide **1a**: no oxidation was observed even at voltage >2V vs Ag/AgCl.

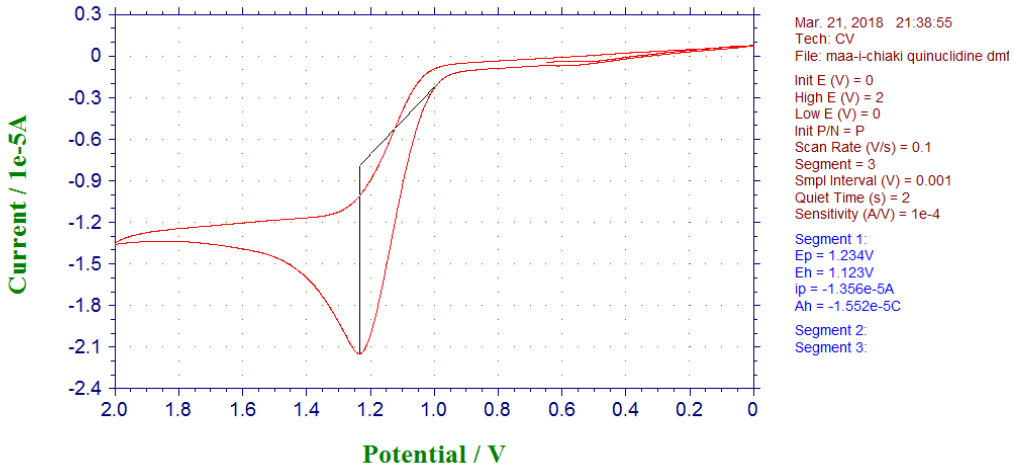
b. CV study of **1a** potassium salt: **1a** potassium salt was prepared by treatment of **1a** with 1.0 equiv of KH in DMF (0.1 M). As shown below, E_p and $E_{1/2}$ of **1a** potassium salt were determined to be 1.33 V and 1.22 V vs Ag/AgCl (i.e. 1.28 V and 1.17 V vs SCE in DMF).

Figure S1. CV Potassium Salt of Triflamide 1a



c. CV study of quinuclidine: As shown below E_p and $E_{1/2}$ were determined to be 1.23 V and 1.12 V vs Ag/AgCl (i.e. 1.18 V and 1.07 V vs SCE in DMF).

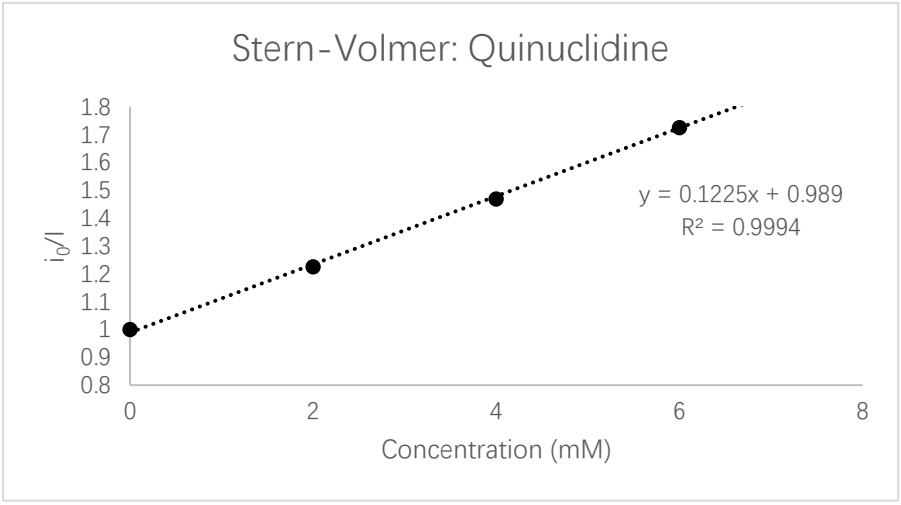
Figure S2. CV of Quinuclidine



2. Stern-Volmer

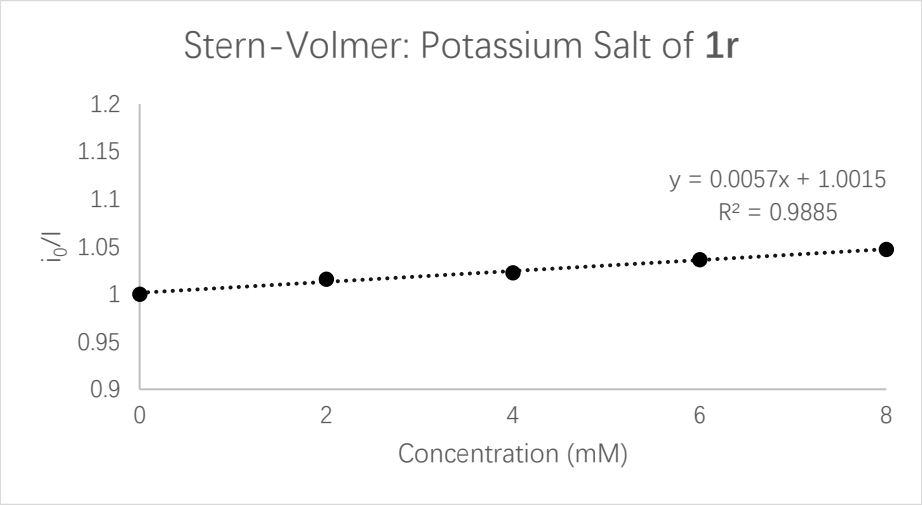
Stern-Volmer experiments were conducted with 0.01 mM Ir[(dF-Me-ppy)$_2$(dtbbpy)]PF$_6$ and varying amounts of quinuclidine, **1a**, or potassium salt of **1r**. The solutions were irradiated at 380 nm and emission was measured at 520 nm.

		Quinuclidine Concentration				
Run		0.0 mM	2.0 mM	4.0 mM	6.0 mM	8.0 mM
1	I_0/I	1	1.276872	1.541653	1.826741	2.083945
2	I_0/I	1	1.203439	1.450313	1.692283	1.942088
3	I_0/I	1	1.196164	1.413874	1.658337	1.897209
	I_0/I_{avg}	1	1.225492	1.468614	1.725787	1.974414



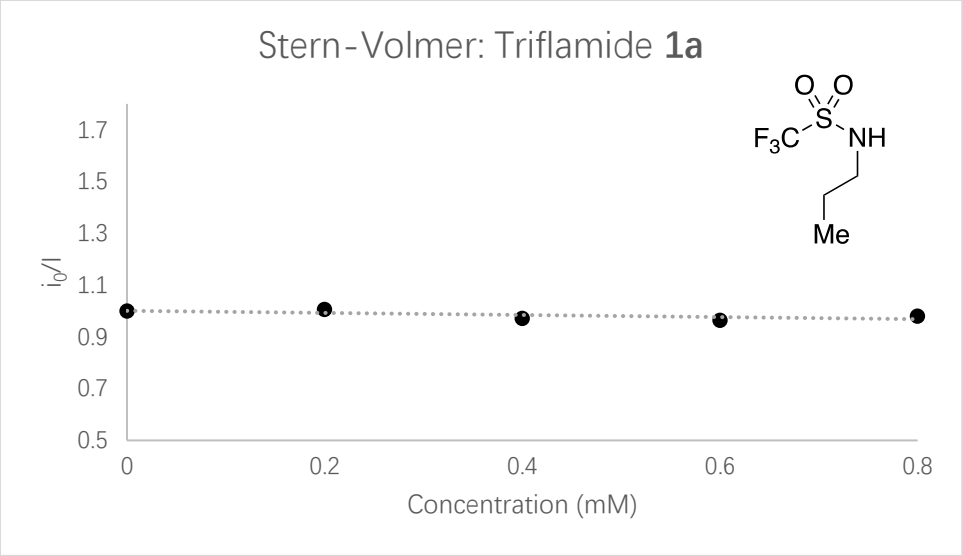
Potassium Salt of **1r** Concentration

Run		0.0 mM	2.0 mM	4.0 mM	6.0 mM	8.0 mM
1	I_0/I	1	1.011224	1.02079	1.039604	1.057669
2	I_0/I	1	1.02097	1.024548	1.033015	1.036779
	I_0/I_{avg}	1	1.016097	1.022669	1.03631	1.047224

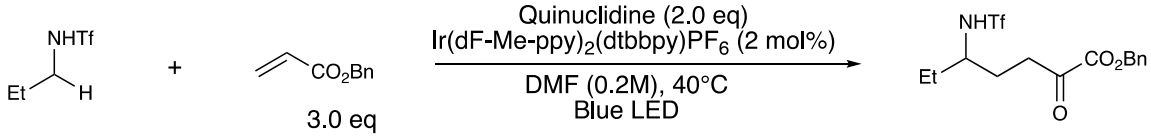


Triflamide **1a** Concentration

	0.0 mM	0.2 mM	0.4 mM	0.6 mM	0.8 mM
I_0/I	1	1.010333	0.969121	0.963478	0.97934
I_0/I	1	1.001819	0.974922	0.965405	0.981578
I_0/I_{avg}	1	1.006076	0.972021	0.964441	0.980459

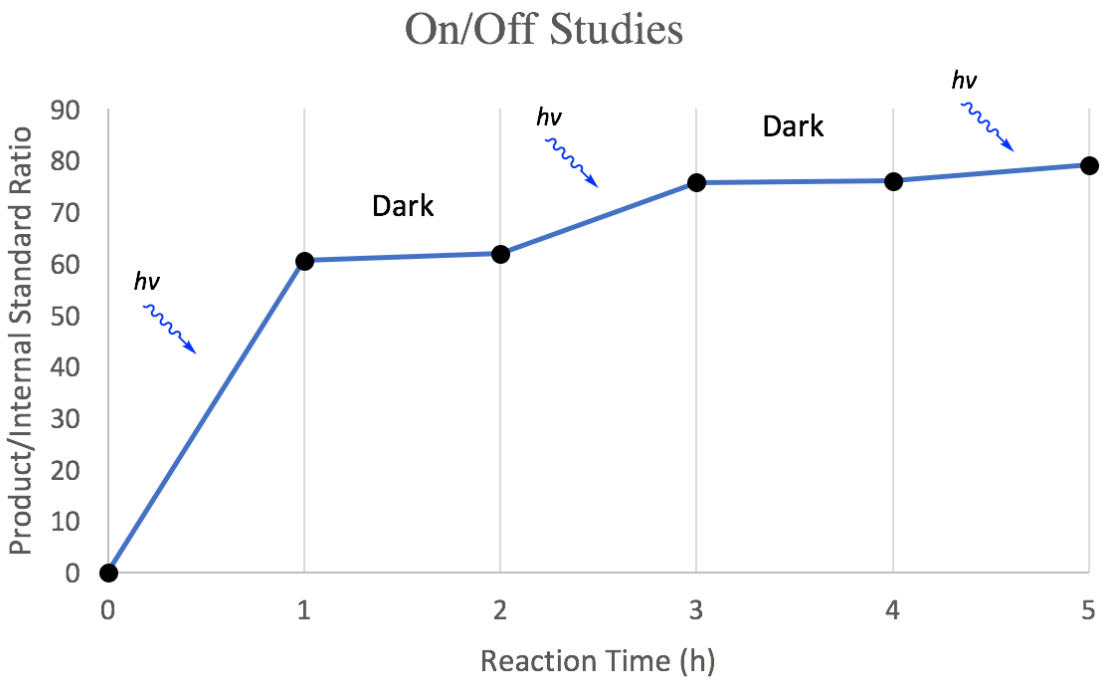


3. On/Off Studies



The above reaction was set up according to Procedure B (19.1 mg of starting material, 2 mol% [Ir] photocatalyst, 3.0 equiv. of alkene, 2 equiv. quinuclidine, 0.5 mL DMF; run under an atmosphere of argon). The reaction was irradiated with Blue LED for one hour. An aliquot (20 μL) was taken and added to a vial containing internal standard Mesitylene. The yield was determined by UPLC-MS diode-array. The reaction was then covered by aluminum foil and stirred for an hour. Yield was determined in the same way. The reaction was monitored for 5 hours.

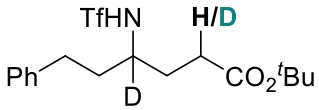
Figure S3. On/Off Study



4.0 Deuterium Incorporation

***tert*-butyl 6-phenyl-4-((trifluoromethyl)sulfonamide)hexanoate-4-d** with incorporated ***tert*-butyl 6-phenyl-4-((trifluoromethyl)sulfonamide)hexanoate-2,4-d_2 (3sa)**

Quinuclidine Conditions: Prepared according to **Procedure B** (with 3.0 equiv *tert*-butyl acrylate). Colorless oil (26.85mg, 68% yield)



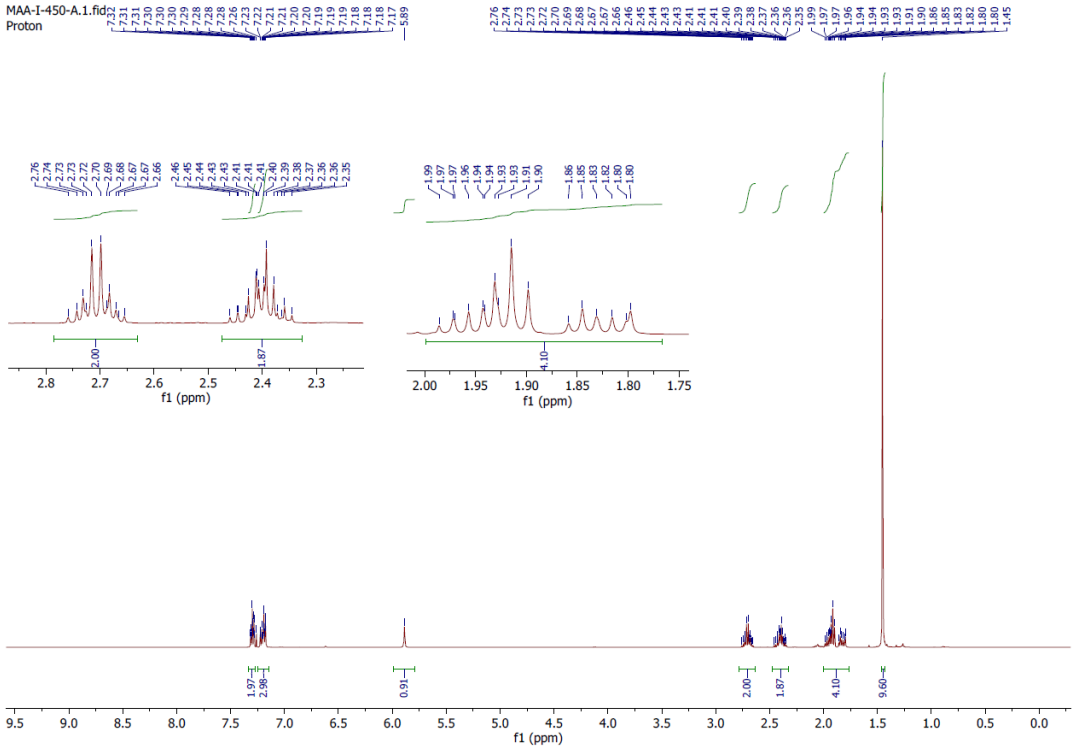
Quinuclidine: 6% D (68% yield)

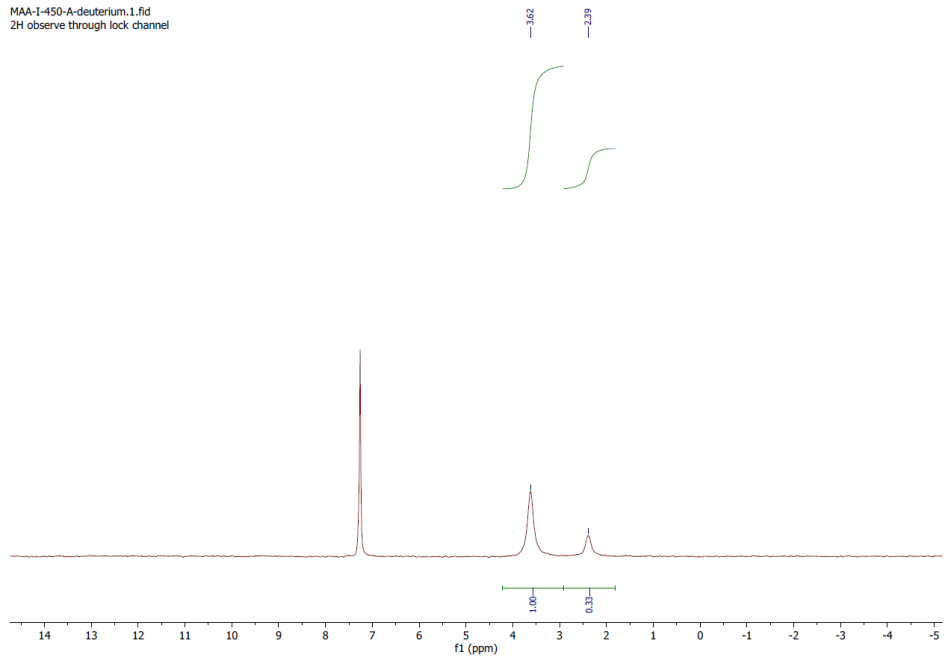
K_3PO_4 Conditions: Prepared according to an adjusted **Procedure B** (2.0 equiv. of K_3PO_4 instead of quinuclidine; 3.0 equiv. *tert*-butyl acrylate). Colorless oil (23.6mg, 60% yield)

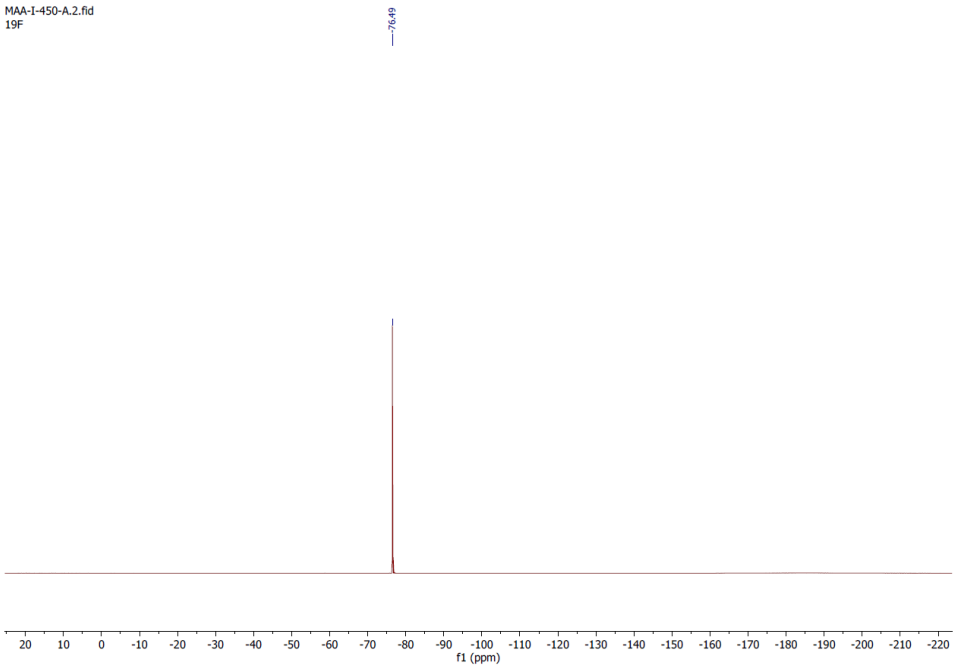
Quinuclidine Conditions - NMRs

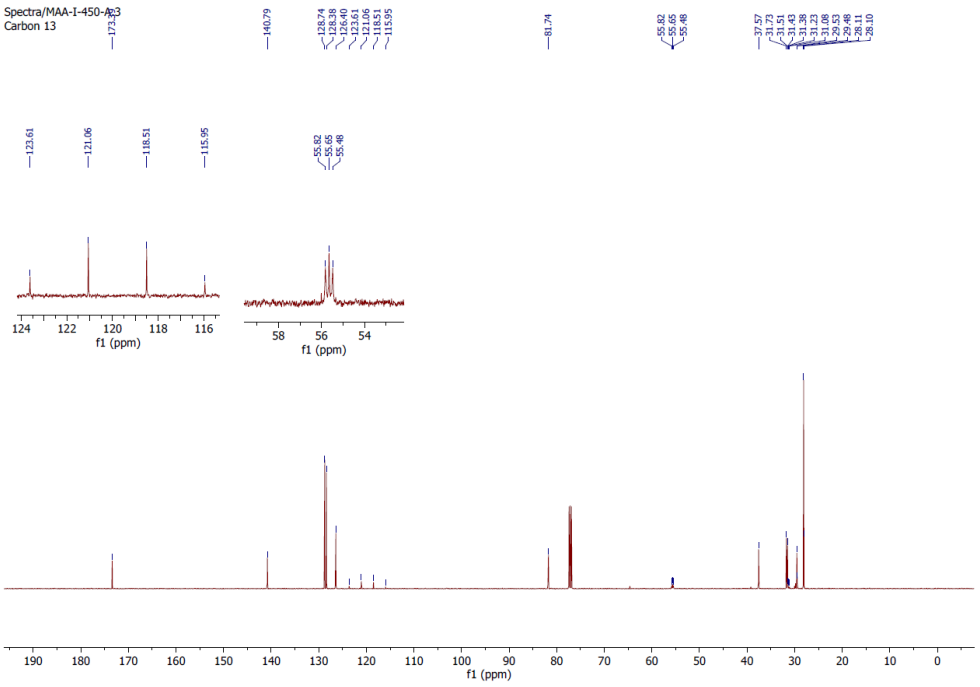
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.28 (m, 2H), 7.23-7.17 (m, 3H), 5.89 (s, 1H), 2.76-2.66 (m, 2H), 2.46-2.35 (m, 1.87), 1.99-1.80 (m, 4H), 1.45 (s, 9H); **^{2}H NMR** ($CDCl_3$, 400

MHz) δ 3.62 (1H), 2.39 (0.33H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.39, 140.79, 128.74, 128.38, 126.40, 119.17 (q, *J* = 321.0 Hz), 81.74, 55.65 (t, *J* = 20.8), 37.57, 31.73, 31.51, 31.43, 31.38, 31.23, 31.08, 29.53, 29.48, 28.11, 28.10; (13C-2H coupling) **^{19}F NMR** ($CDCl_3$, 376 MHz) 76.49; **IR (neat)** 3208.93 (brs), 2979.14 (m), 1698.46 (s), 1423.23 (m), 1367.78 (s), 1228.71 (s), 1188.32 (s), 1148.61 (s), 1000.44 (m), 843.25 (m), 744.89 (m), 699.78 (m), 614.12 (s), 514.14 (m) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{17}H_{23}DF_3NO_4S$ (major) $C_{17}H_{22}D_2F_3NO_4S$ (minor); expected $(M-H)^-$ *m/z* 395.1363 (major) 396.1425 (minor), observed $(M-H)^-$ *m/z* 395.1357 (major) 396.1405 (minor).

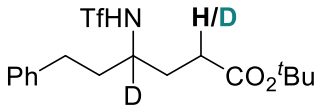



MAA-I-450-A-deuterium.1.fid
2H observe through lock channel
3.62
2.39
1.00
0.33
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)


MAA-I-450-A.2.fid
19F
-76.49
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

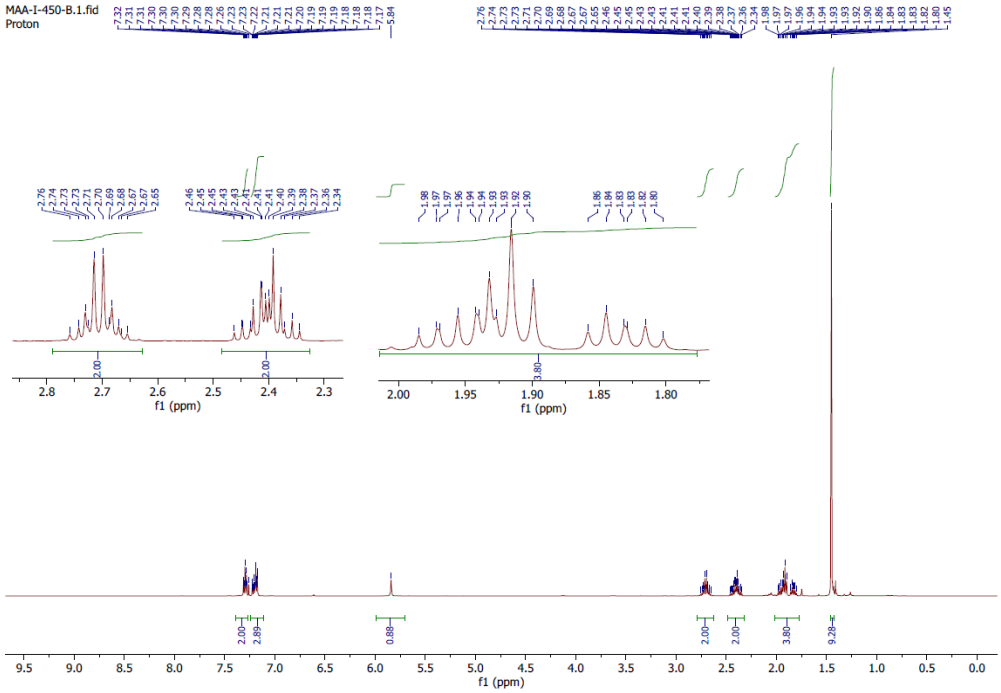


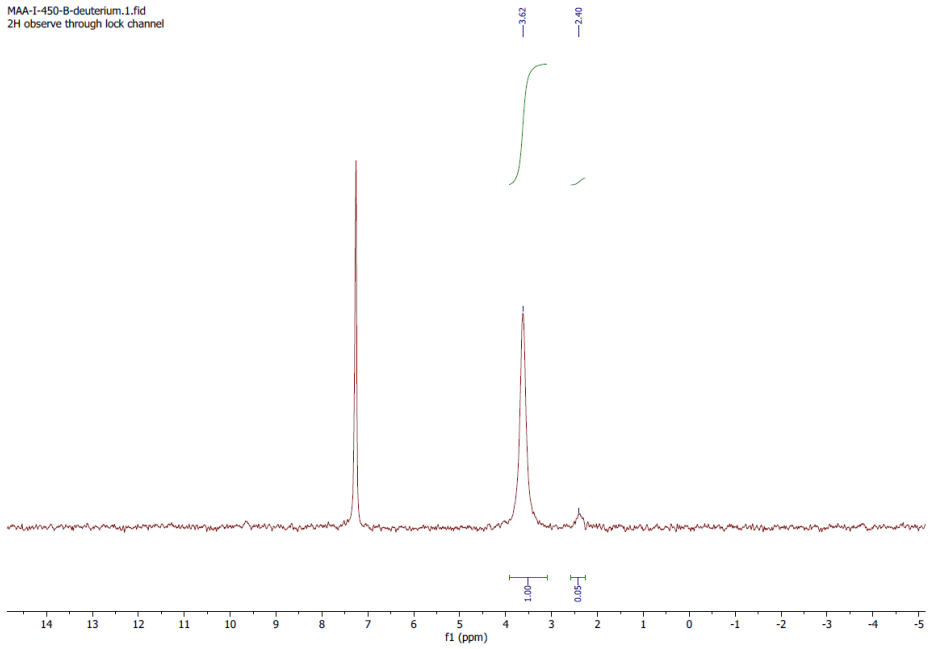
K_3PO_4 Conditions

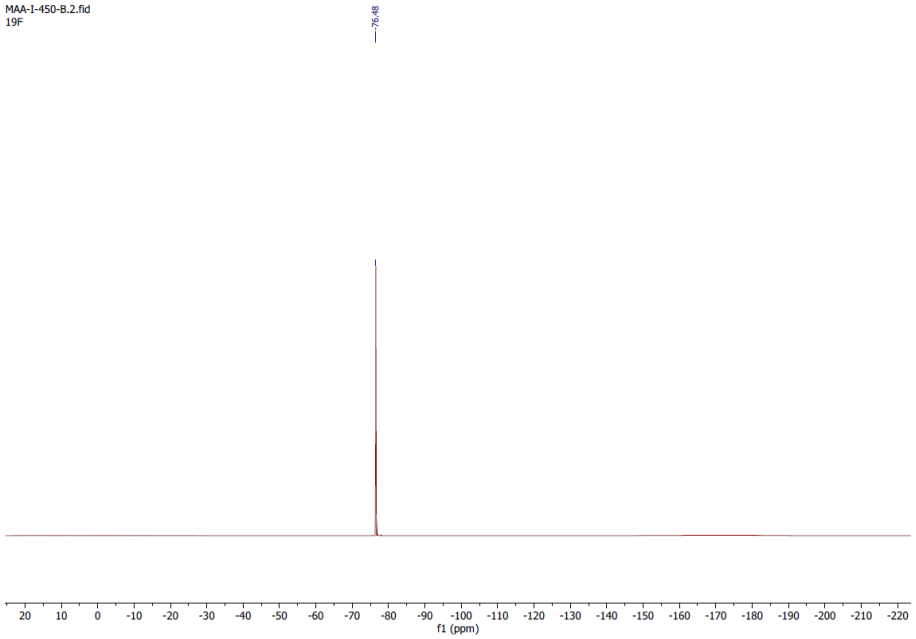


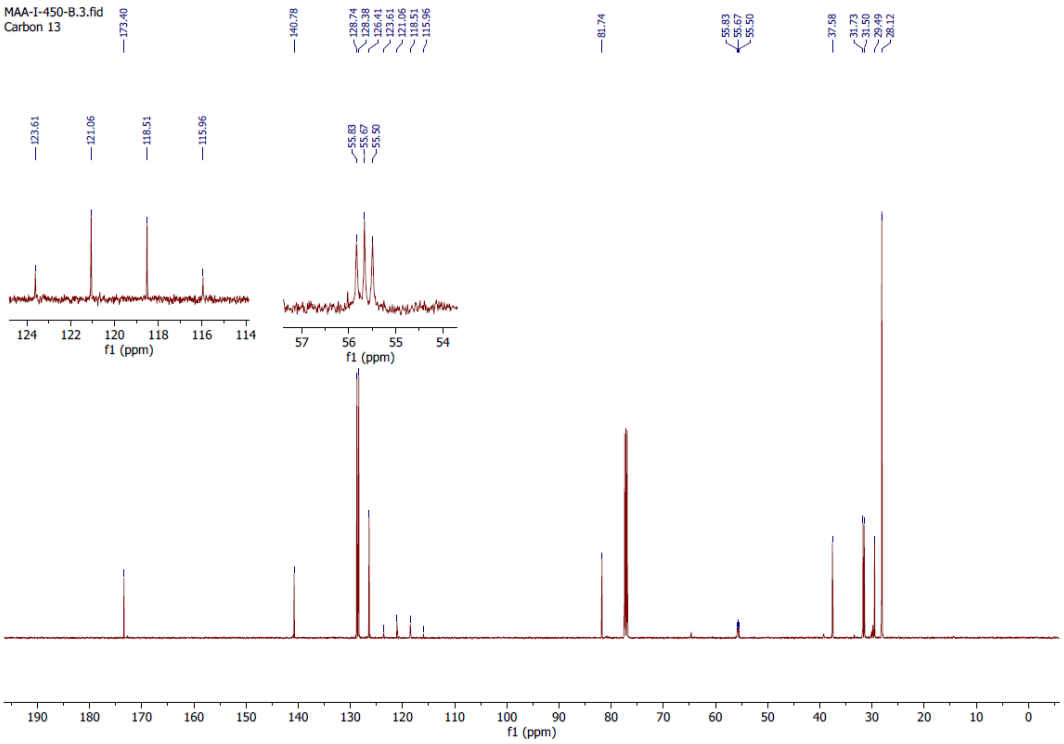
K_3PO_4: <1% **D** (60% yield)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.28 (m, 2H), 7.23-7.17 (m, 3H), 5.84 (s, 1H), 2.76-2.65 (m, 2H), 2.46-2.34 (m, 2H), 1.98-1.80 (m, 4H), 1.45 (s, 9H); **^{2}H NMR** ($CDCl_3$, 400 MHz) δ 3.62 (1H), 2.40 (0.05H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 173.40, 140.78, 128.74, 128.38, 126.41, 119.17 (q, *J* = 321.0 Hz), 81.74, 55.67 (t, *J* = 20.8), 37.57, 31.73, 31.50, 29.49, 28.12; (13C-2H coupling) **^{19}F NMR** ($CDCl_3$, 376 MHz) 76.48; **IR ($CDCl_3$)** 3209.93 (brs), 2979.25 (brs), 1698.83 (s), 1433.92 (m), 1367.82 (s), 1229.03 (m), 1189.13 (s), 1148.96 (s), 1001.02 (m), 844.02 (m), 740.21 (m), 700.22 (m), 614.33 (s) cm^{-1}; **HRMS-ASAP** (negative): M = $C_{17}H_{23}DF_3NO_4S$ (major) $C_{17}H_{22}D_2F_3NO_4S$ (minor); expected $(M-H)^-$ *m/z* 395.1363 (major) 396.1425 (minor), observed $(M-H)^-$ *m/z* 395.1365 (major) 396.1401 (minor).

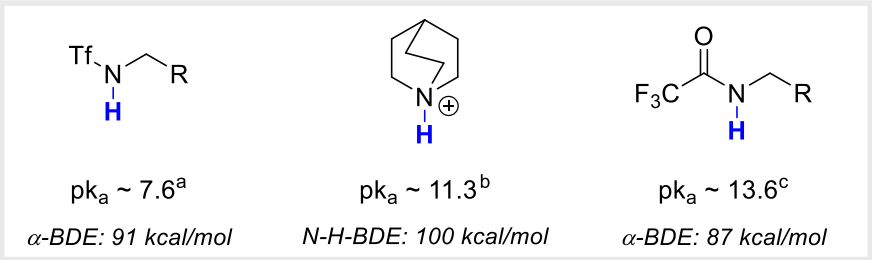

MAA-I-450-B.1.fid
Proton
f1 (ppm)


MAA-I-450-B-deuterium.1.fid
2H observe through lock channel
f1 (ppm)

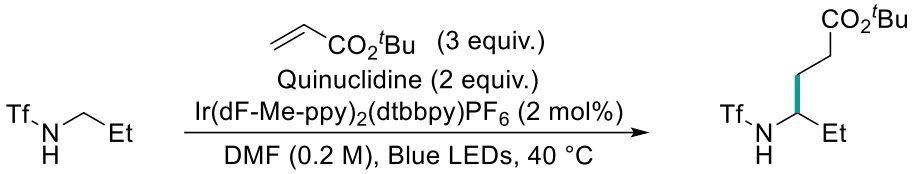

MAA-I-450-B.2.fid
19F
-76.48
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


MAA-I-450-B.3.fid
Carbon 13
173.40
140.78
128.74
128.38
126.41
123.61
121.06
118.51
115.96
81.74
55.83
55.67
55.50
37.58
31.73
31.50
29.49
28.12
123.61
121.06
118.51
115.96
55.83
55.67
55.50
124 122 120 118 116 114
f1 (ppm)
57 56 55 54
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5.0 Hydridic α-hydrogens

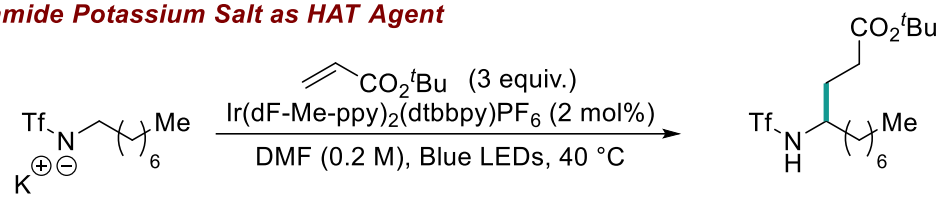


Triflamide - Quinuclidine Conditions



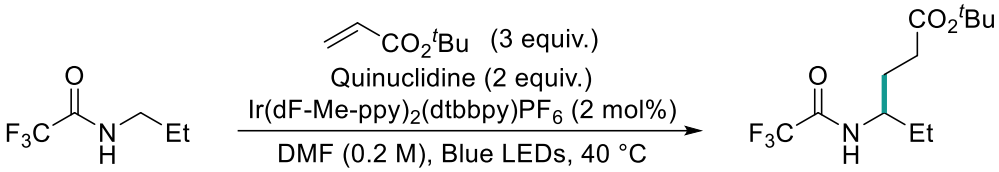
3a **3aa *(77%)***

Triflamide Potassium Salt as HAT Agent



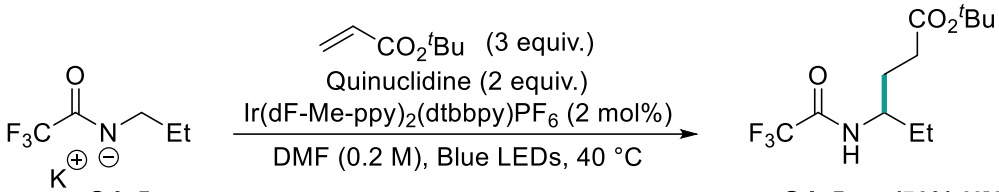
3r **3ra *(57%)***

Trifluoroacetamide - Quinuclidine Conditions



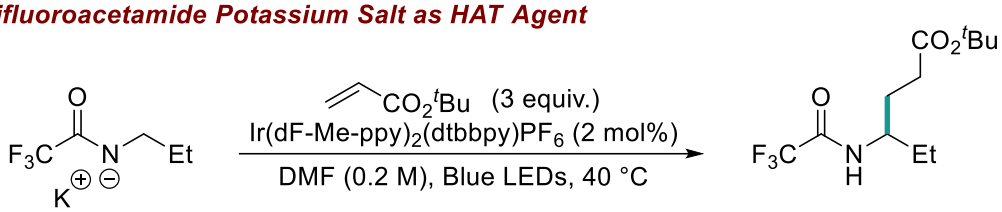
S.I. 5a **S.I. 5aa *(0%)***

Trifluoroacetamide Potassium Salt - Quinuclidine Conditions



S.I. 5a **S.I. 5aa *(53% NMR)***

Trifluoroacetamide Potassium Salt as HAT Agent



S.I. 5a **S.I. 5aa *(51% NMR)***

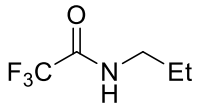
a) Trepka, R.D; Harrington, J.K; Belisle, J.W; *J. Org. Chem.* **1974**, *39*, 8, 1094.

b) Aggarwal, V.K; Emmel, I.; Fulford, S.Y.; *J. Org. Chem.* **2003**, *68*, 692.

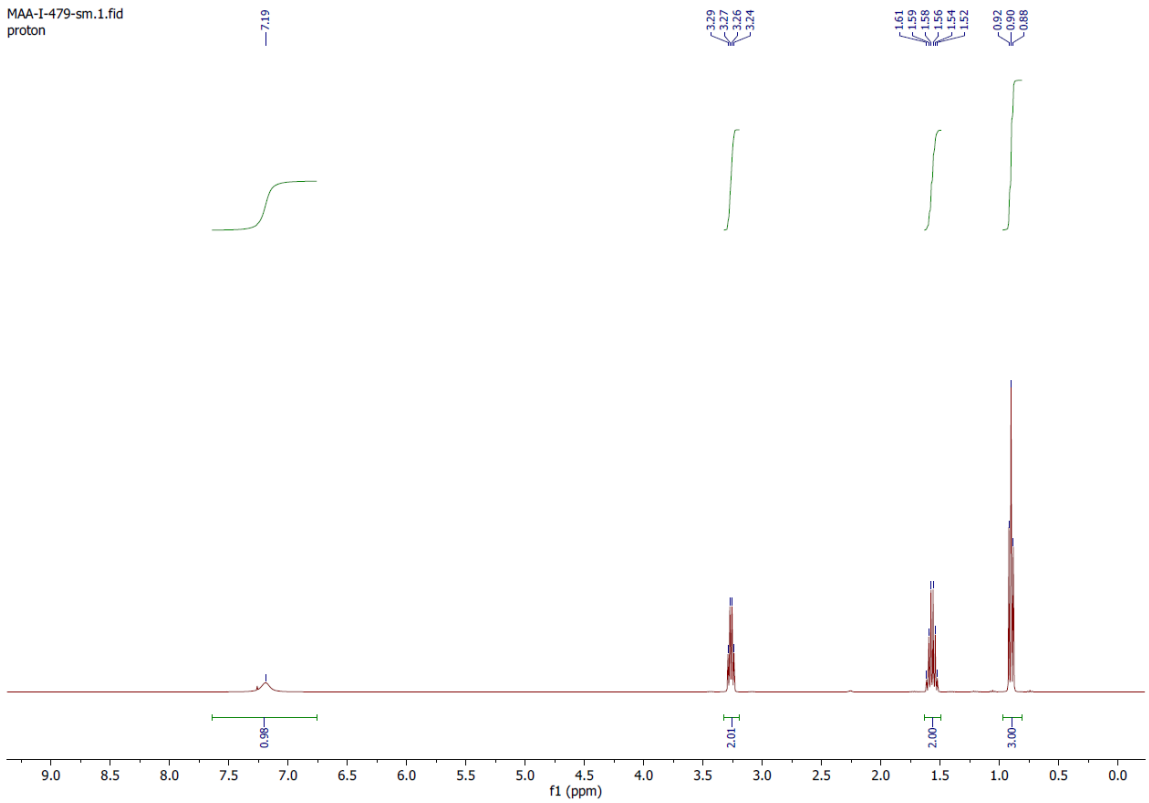
c) Li, J. J. Named Reactions for Functional Group Transformation 423–437 (Wiley, 2007).

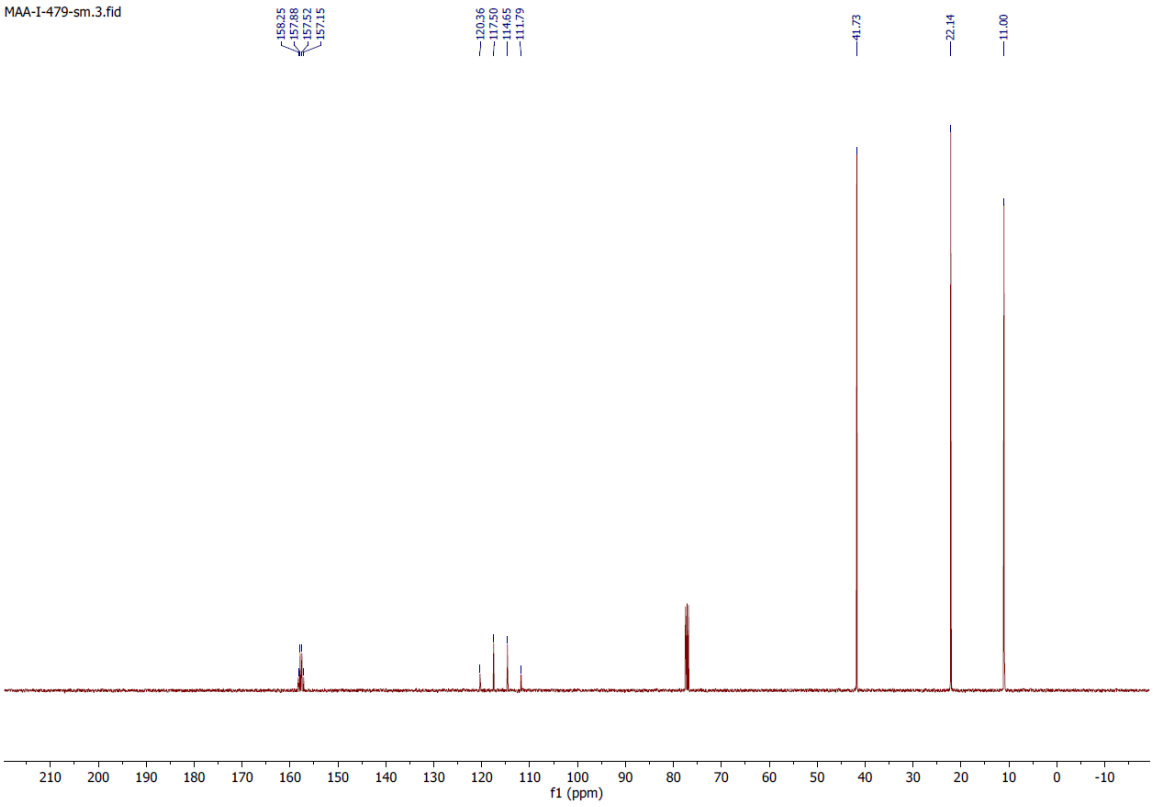
2,2,2-trifluoro-*N*-propylacetamide (S.I. 5a)

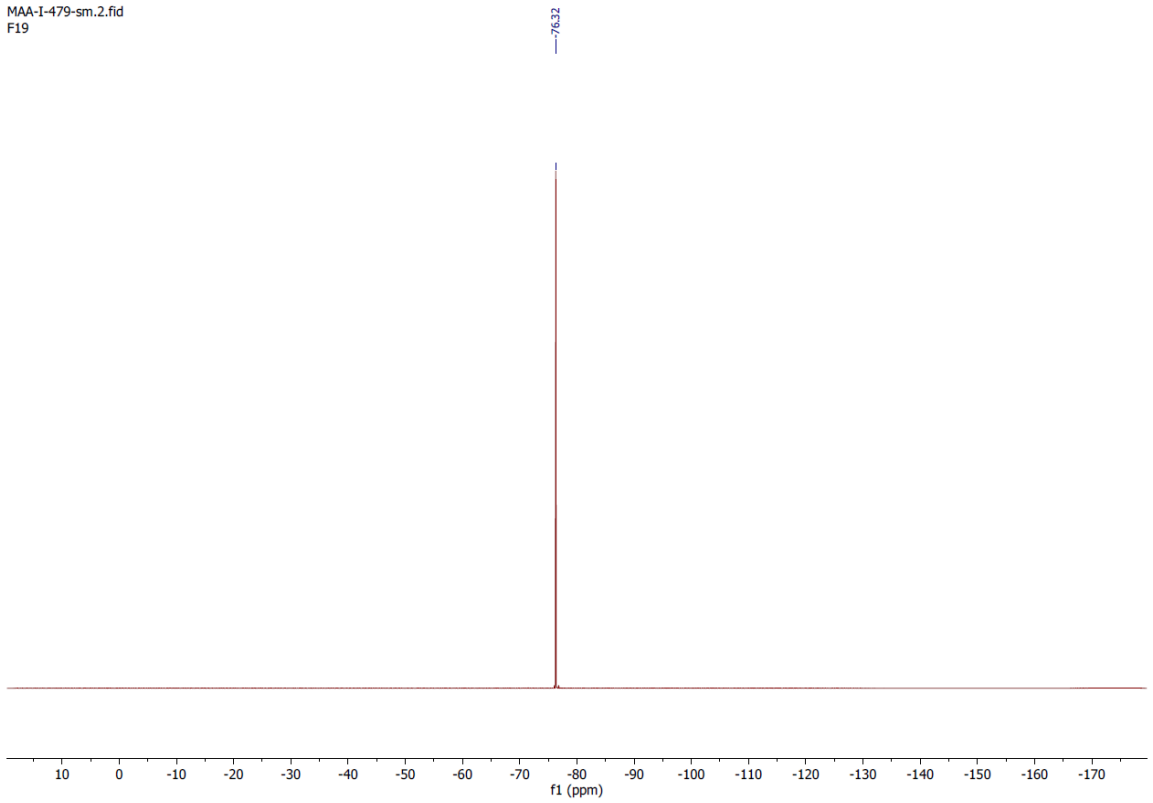
Prepared according to **Procedure A** from commercially available propylamine (591 mg, 10 mmol). Colorless oil (826.0 m g, 53% yield). R_f = 0.75 (6:1 hex:EtOAc).



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (brs,1H), 3.26 (q, *J* = 6.8 Hz, 2H), 1.57 (h, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.70 (q, *J* = 36.7 Hz), 116.08 (q, *J* = 287.3 Hz), 41.73, 22.14, 11.00; **^{19}F NMR** ($CDCl_3$, 376 MHz): −76.32; **IR (neat)** 3304.22 (brs), 3106.04 (brs), 2971.16 (brs), 1702.07 (s), 1560.97 (m), 1462.27 (m), 1371.40 (m), 1347.95 (m), 1252.39 (m), 1156.49 (s), 920.60 (m), 721.91 (s), (525.08 (m) cm^{-1}; **MS (ESI, positive)**: M = $C_5H_8F_3NO$; expected $(M+H)^+$ 156.0 *m/z*, observed $(M+H)^+$ *m/z* 156.0.

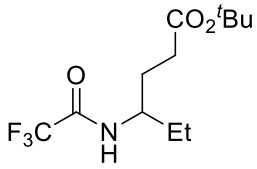



MAA-I-479-sm.3.fid
158.25
157.88
157.52
157.15
120.36
117.50
114.65
111.79
41.73
22.14
11.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

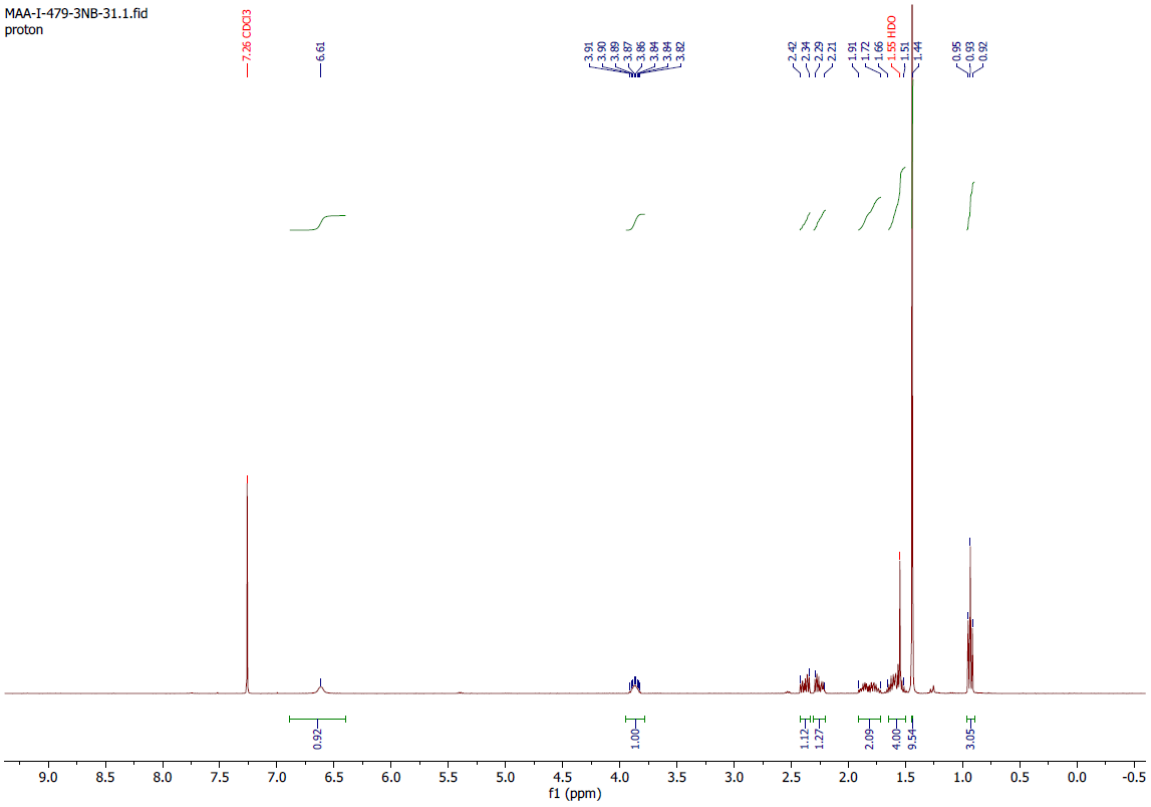

MAA-I-479-sm.2.fid
F19
-76.32
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

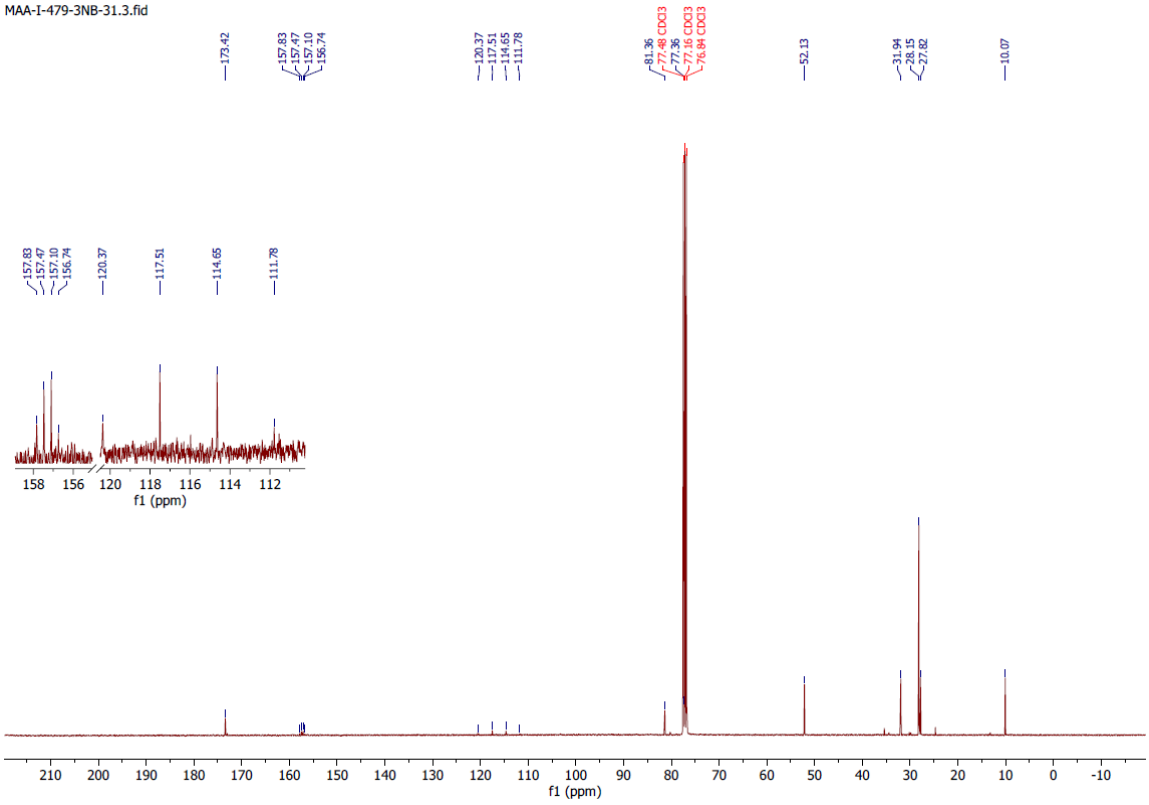
***tert*-butyl 4-(2,2,2,-trifluoroacetamido)hexanoate (S.I. 5aa)**

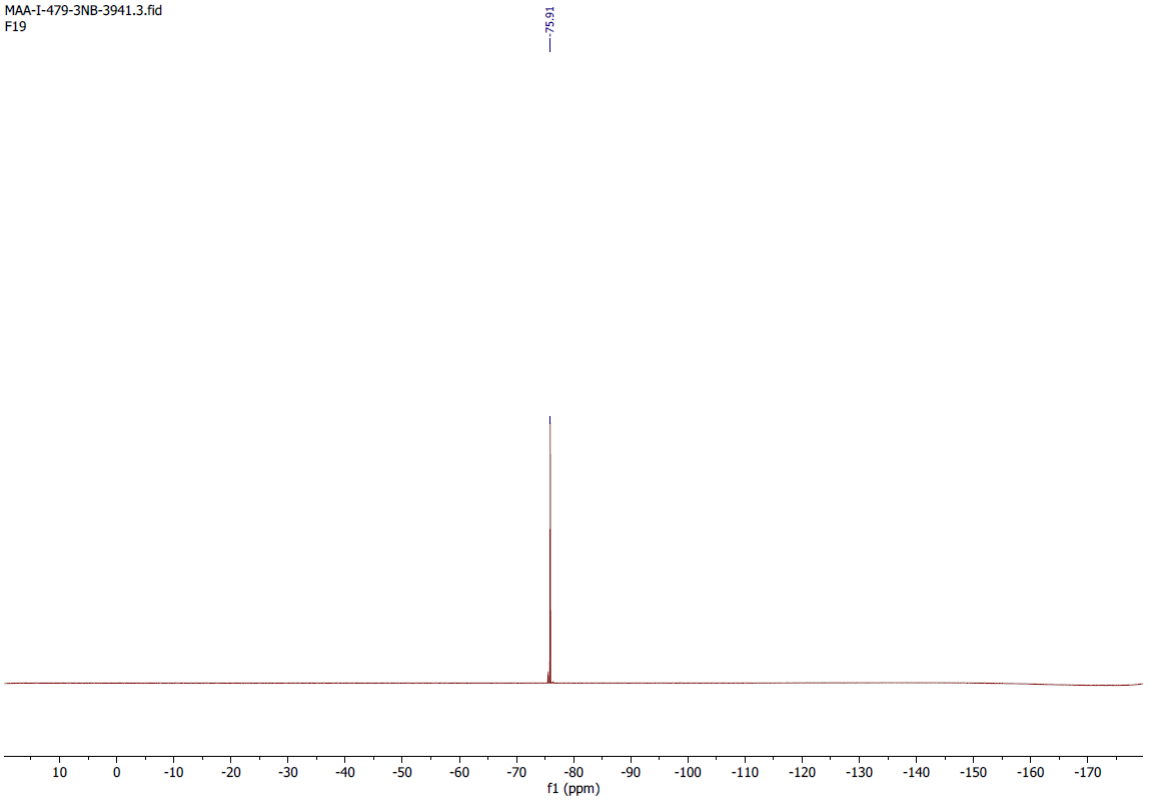
Prepared according to **Procedure B** (with 3.0 equiv of *tert*-butyl acrylate). Colorless oil R_f = 0.65 (100% CH_2Cl_2). Purified via column chromatography (7:3 hex:CH_2Cl_2 to 2:8 hex:CH_2Cl_2).



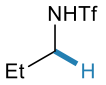
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.61 (brs, 1H), 3.86 (ddd, *J* = 14.7, 8.5, 4.7 Hz, 1H), 1.42-2.34 (m, 1H), 2.29-2.21 (m, 1H), 1.91-1.72 (m, 2H), 1.66-1.51 (m, 2H), 1.44 (s, 9H), 0.93 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 173.42, 157.29 (q, *J* = 36.5 Hz), 116.08 (q, *J* = 288.0 Hz), 81.36, 77.36, 52.13, 31.94, 28.15, 27.82, 10.07; **^{19}F NMR** ($CDCl_3$, 376 MHz): −75.91; **IR (neat)** 3307.24 (brs), 2972.29 (m), 2927.40 (m), 1704.08 (s), 1551.45 (m), 1457.54 (m), 1368.34 (m), 1255.73 (m), 1209.03 (s), 1156.05 (s), 908.79 (s), 845.05 (m), 732.80 (s), 648.87 (m) cm^{-1};



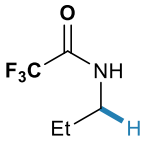

MAA-I-479-3NB-31.3.fid
173.42
157.83
157.47
157.10
156.74
120.37
117.51
114.65
111.78
81.36
77.48 CDCl3
77.36
77.16 CDCl3
76.84 CDCl3
52.13
31.94
28.15
27.82
10.07
158 156 120 118 116 114 112
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MAA-I-479-3NB-3941.3.fid
F19
-75.91
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

6.0 Computational Details



1,1,1-trifluoro-*N*-propylmethanesulfonamide



2,2,2-trifluoro-*N*-propylacetamide

DFT calculations[3] were performed using Jaguar, version 9.4[4], program and the results were produced with Maestro[5]. 1,1,1-trifluoro-*N*-propylmethanesulfonamide and 2,2,2-trifluoro-*N*-propylacetamide (and their corresponding α-radical species) were optimized using B3LYP/6-311+G**[6,7] Frequency calculations at the same level of theory were performed. Single point energies were determined using B3LYP/aug-ccPVTZ(-f). Bond dissociation energies for the α-C-H bond were determined by calculating the difference in energies between the optimized starting substrates and their radical energies plus hydrogen atom energies. All computations were completed in the gas phase.

$$BDE = [E(radical) + E(H)] - E(molecule)$$

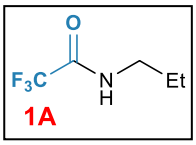
[3] Kohn, W.; Sham, L. J. Phys. Rev. A 1965, 140, A1133-S1138.

[4] (a) Jaguar, version 9.4, Schrodinger, Inc., New York, NY, 2016. (b) Bochevarov, A.D.; Harder, E.; Hughes, T.F.; Greenwood, J.R.; Braden, D.A.; Philipp, D.M.; Rinaldo, D.; Halls, M.D.; Zhang, J.; Friesner, R.A., "Jaguar: A high-performance quantum chemistry software program with strengths in life and materials sciences," Int. J. Quantum Chem., 2013, 113(18), 2110-2142.

[5] Schrodinger Release 2016-4: Maestro, Schrodinger, LLC, New York, NY, 2017.

[6] (a) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. J. Phys. Chem. 1994, 98, 11623- 11267. (b) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652. (c) Becke, A. D. J. Chem. Phys. 1993, 98, 1372-1377. (d) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785-791.

[7] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. J. Chem. Phys. 1980, 72, 650-654.



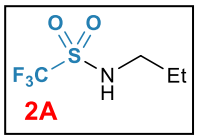
$E_{tot\_ZPE\_corrected}$

1A = -392176.5 kcal/mol

$1A_{\alpha\text{-rad}}$ = -391774.2 kcal/mol

H_{atom} = -315.108 kca/mol

α-C-H BDE: 87 kcal/mol



$E_{tot\_ZPE\_corrected}$

2A = -665317.8 kcal/mol

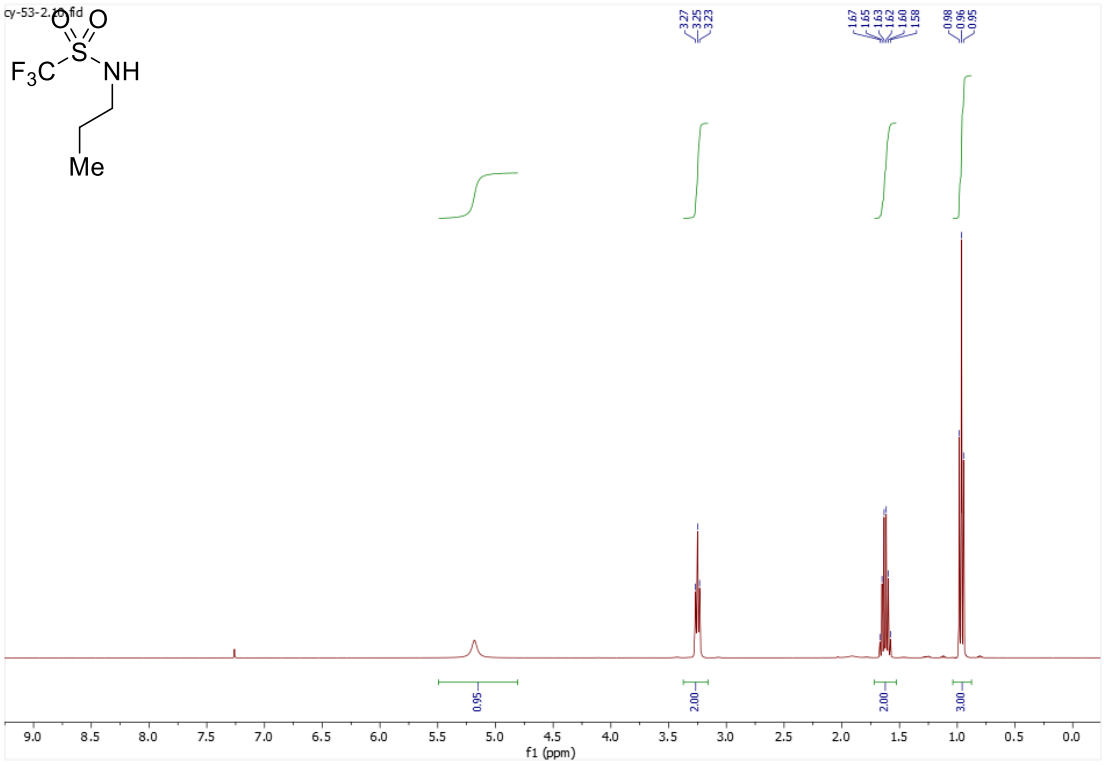
$2A_{\alpha\text{-rad}}$ = -664912.2 kcal/mol

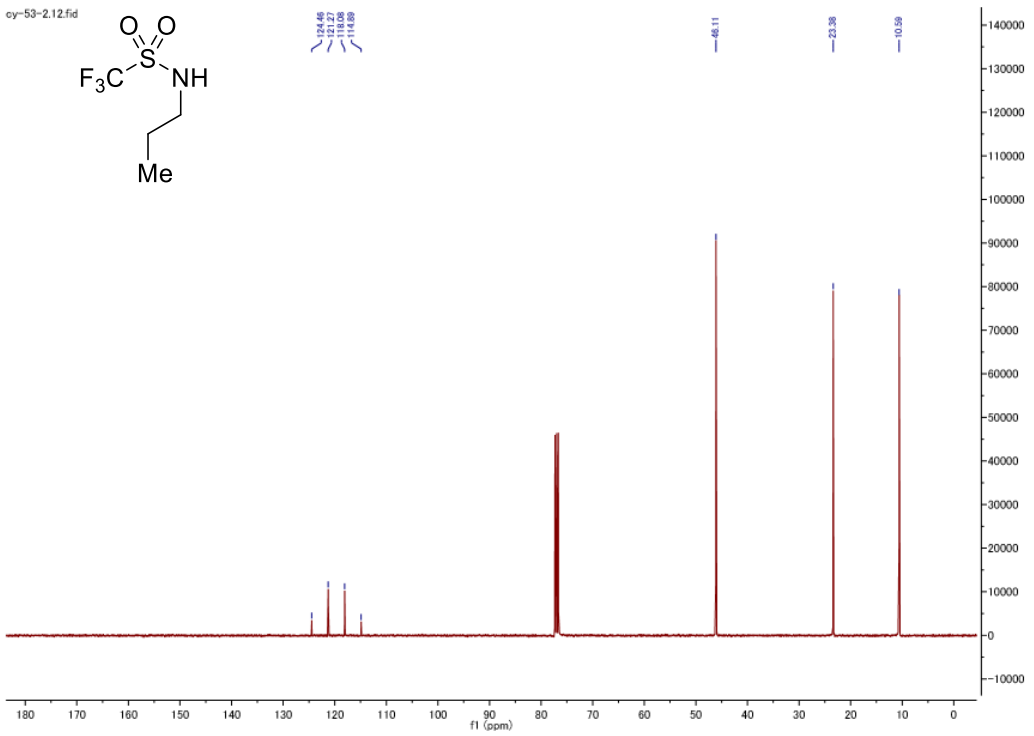
H_{atom} = -315.108 kca/mol

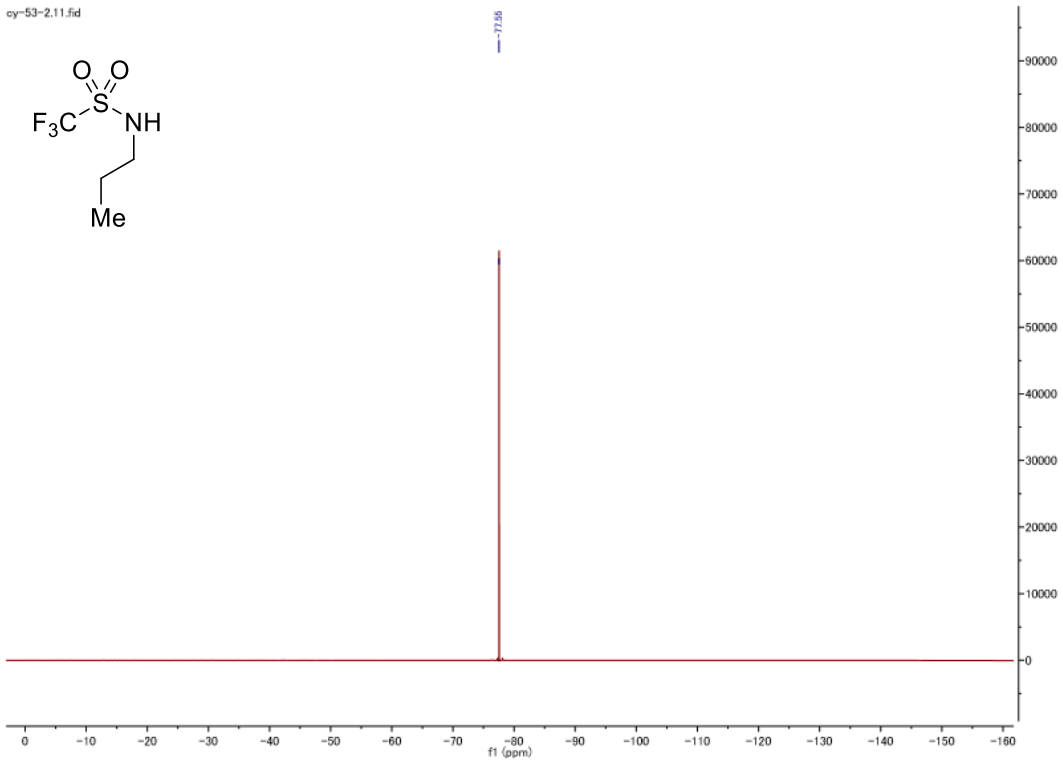
α-C-H BDE: 91 kcal/mol

NMR spectra

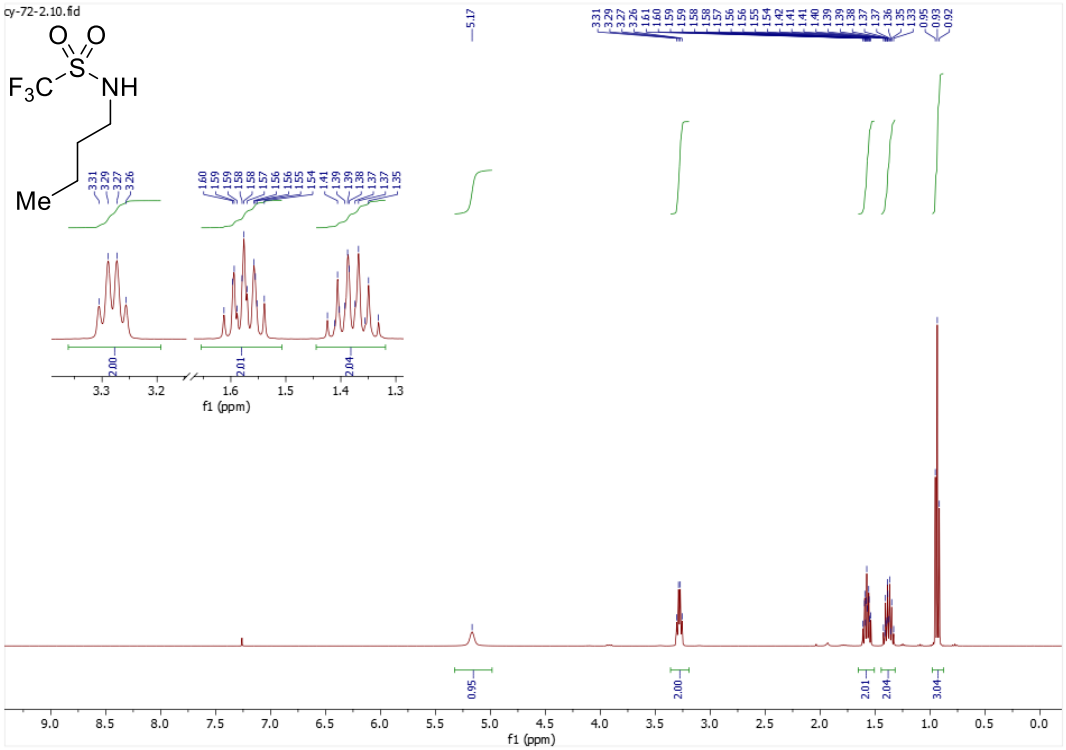
1,1,1-trifluoro-*N*-propylmethanesulfonamide (1a)

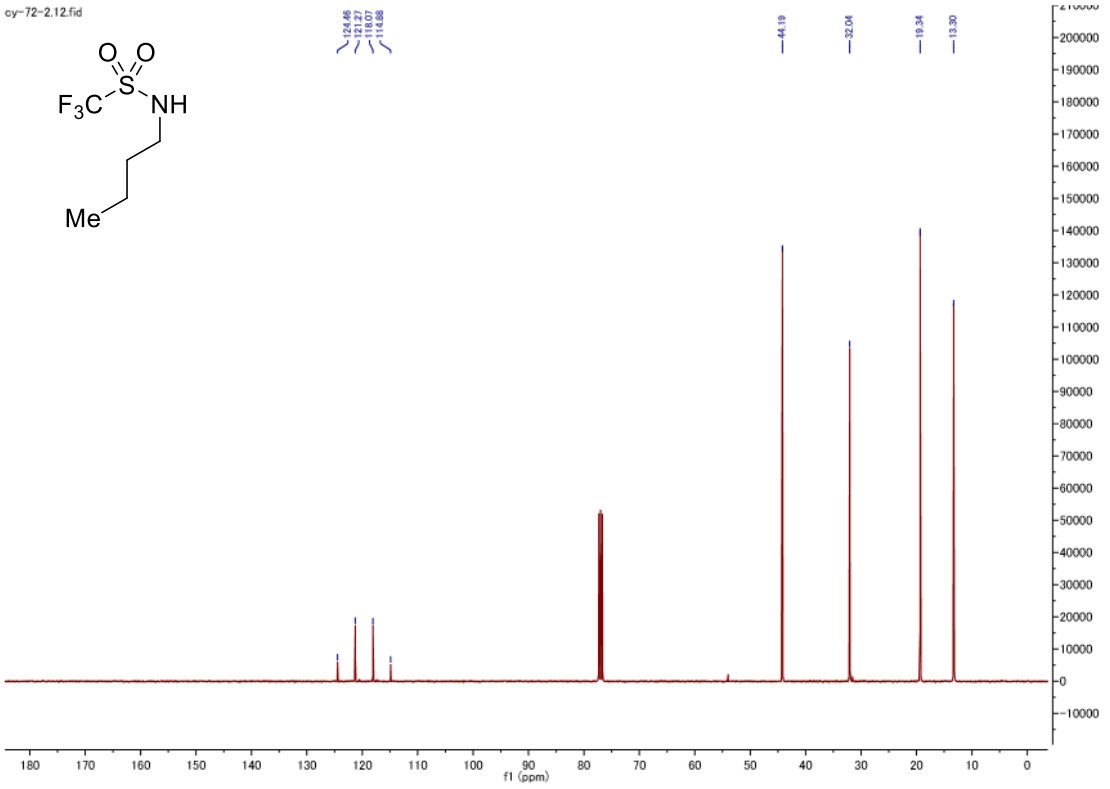


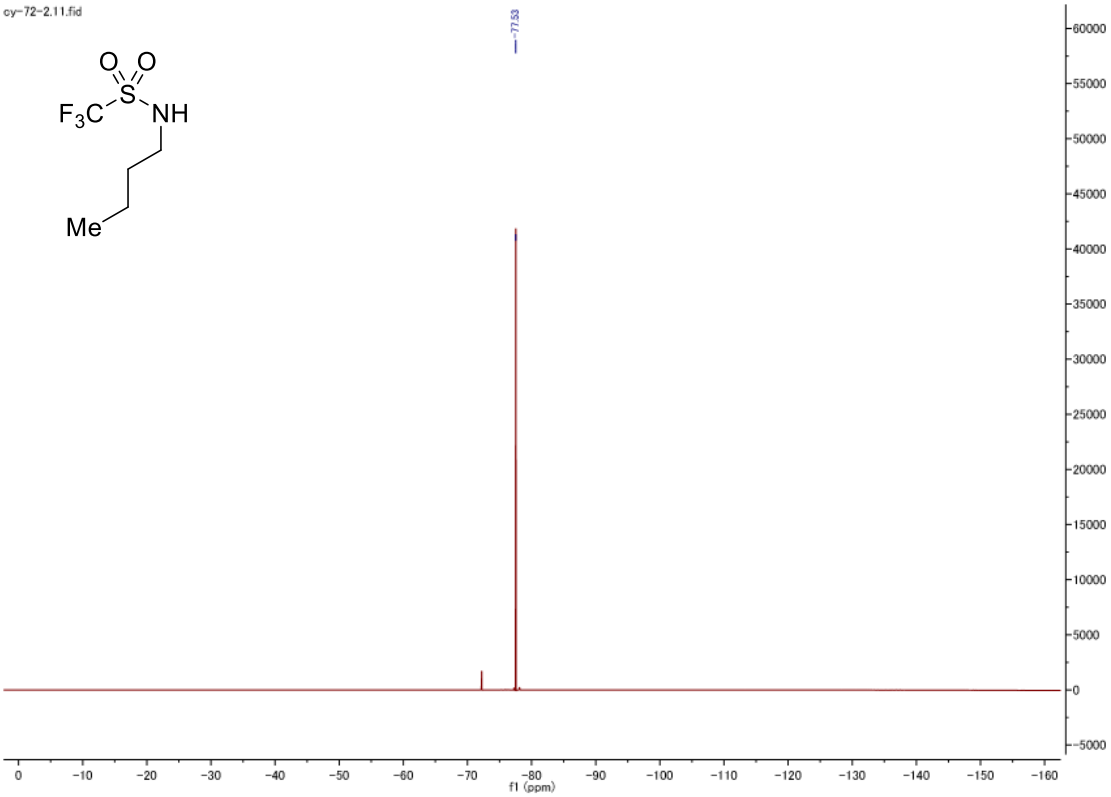




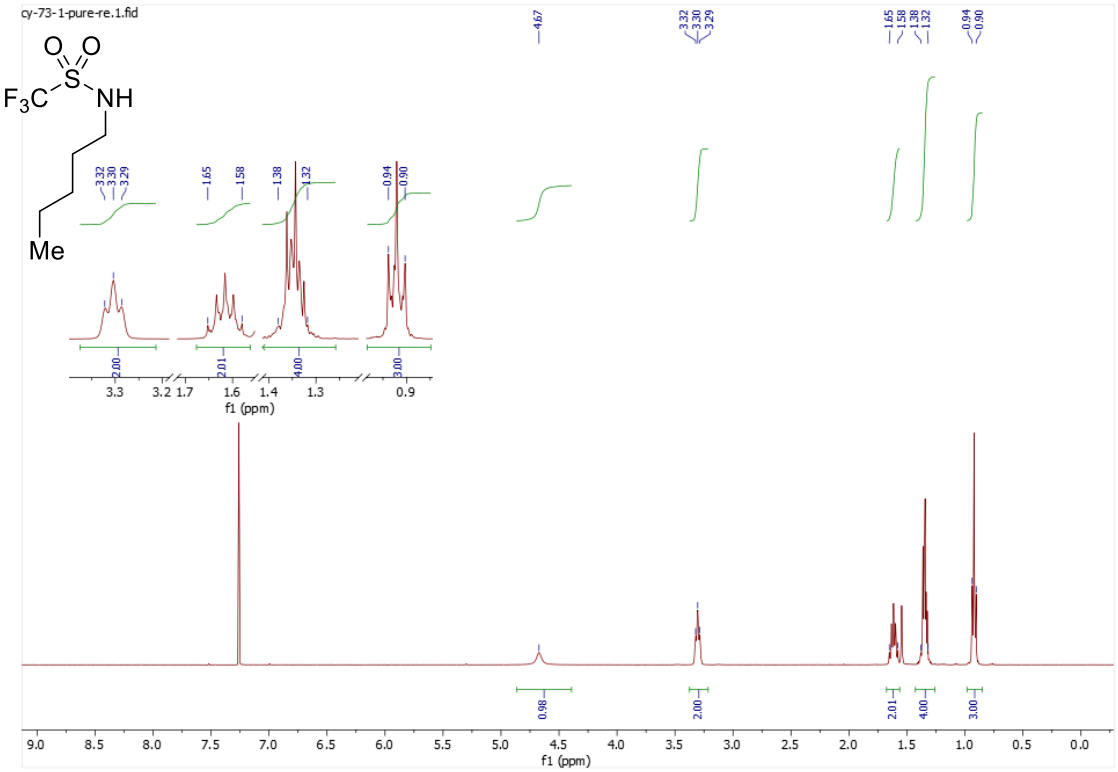
***N*-butyl-1,1,1-trifluoromethanesulfonamide (1b)**

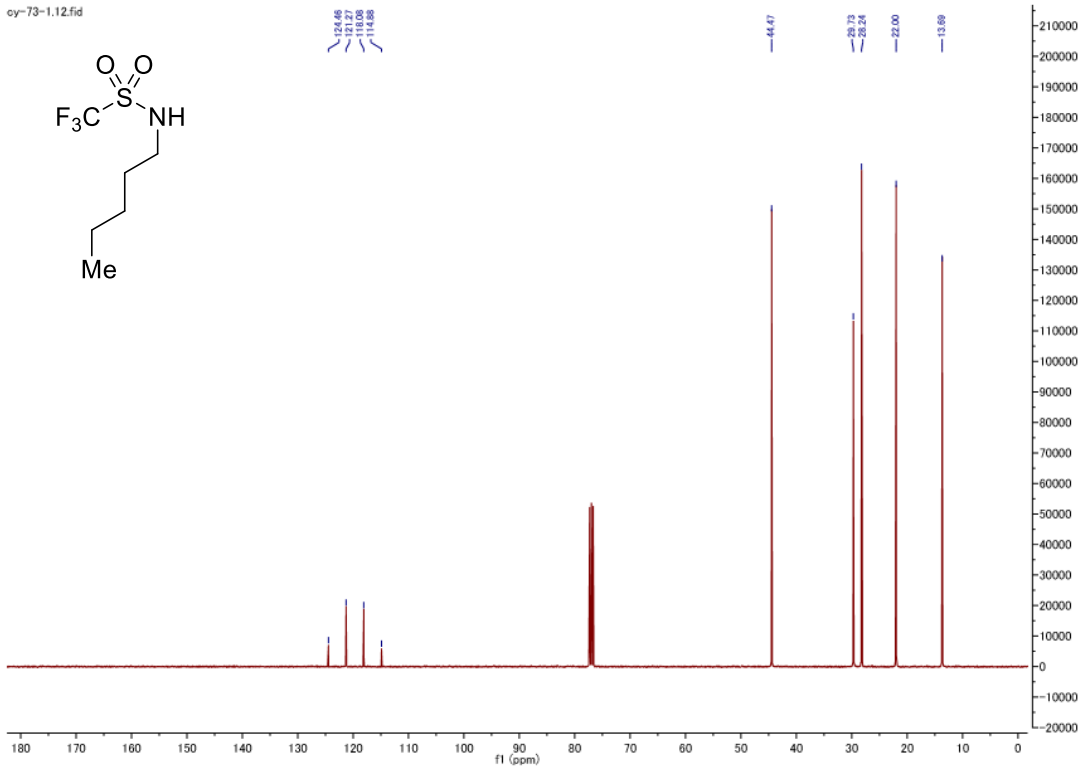


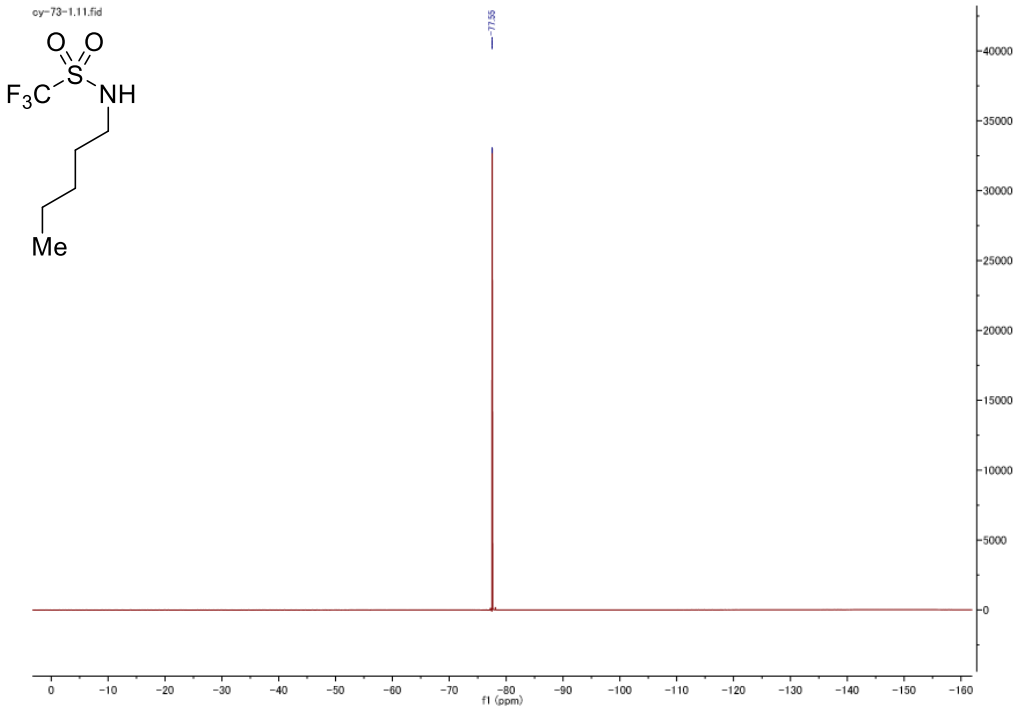

cy-72-2.12.fid
124.46
121.27
118.07
114.88
44.19
32.04
19.34
13.30
O
O
S
F3C
NH
Me
f1 (ppm)


cy-72-2.11.fid
77.53
O
O
S
F3C
NH
Me
f1 (ppm)

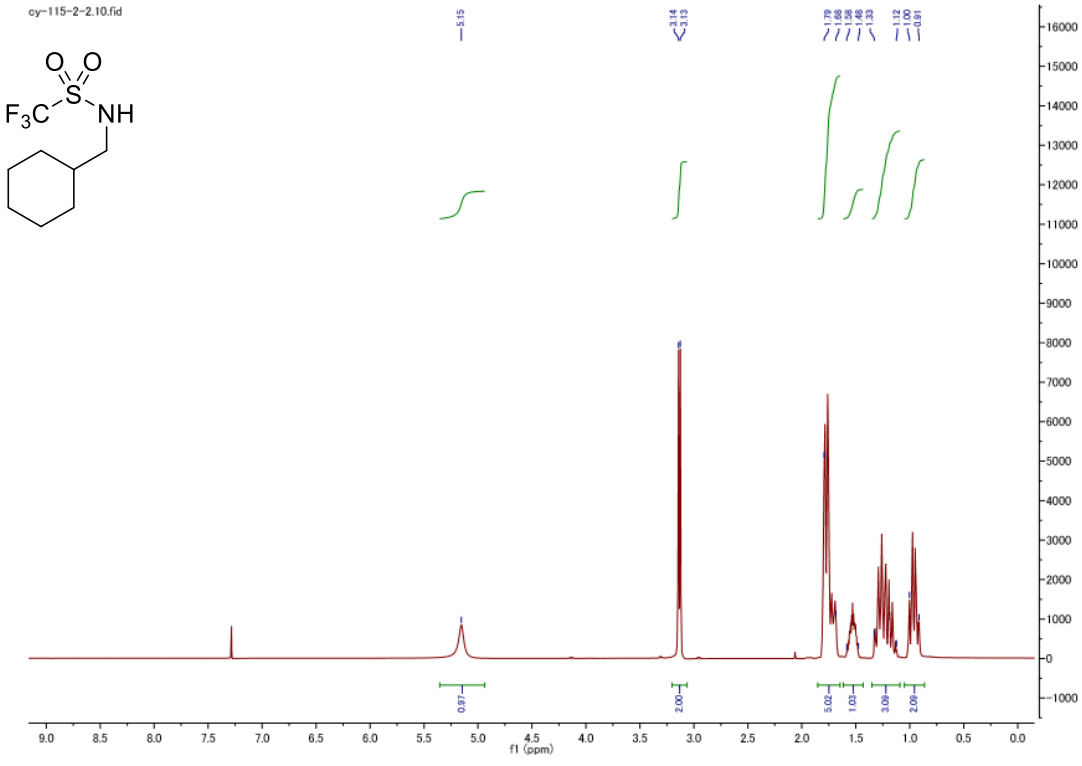
1,1,1-trifluoro-*N*-pentylmethanesulfonamide (1c)

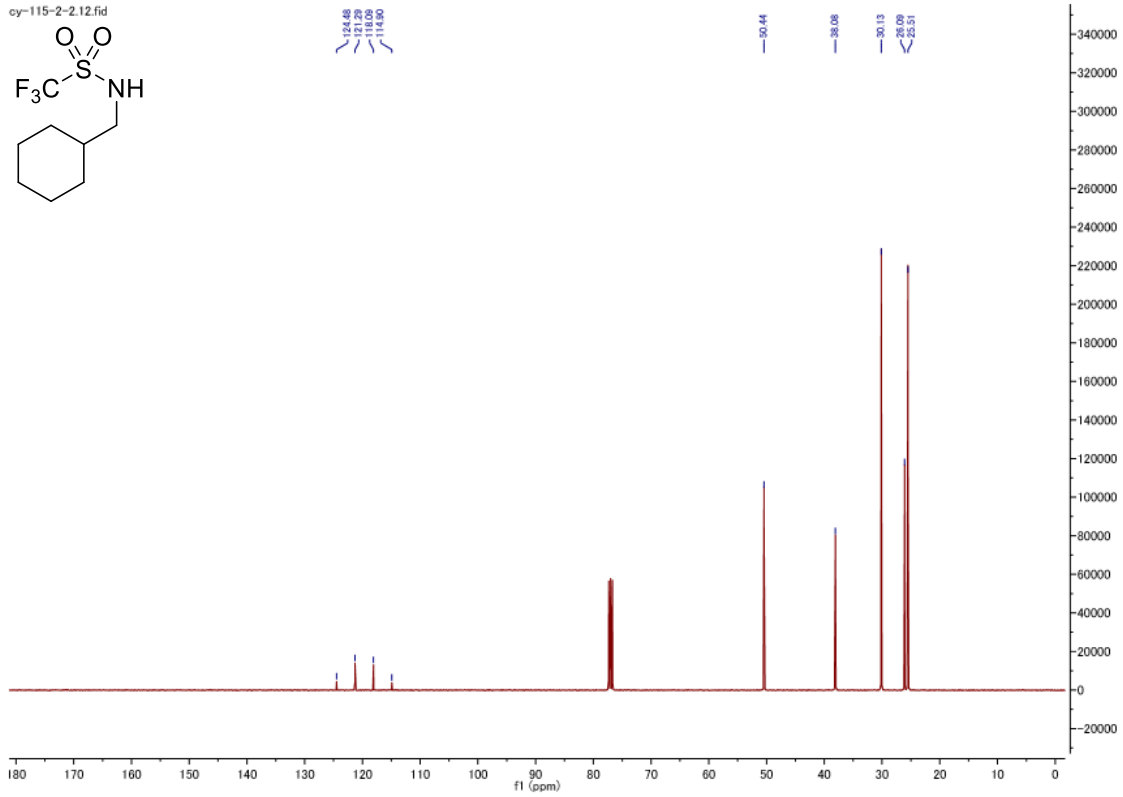


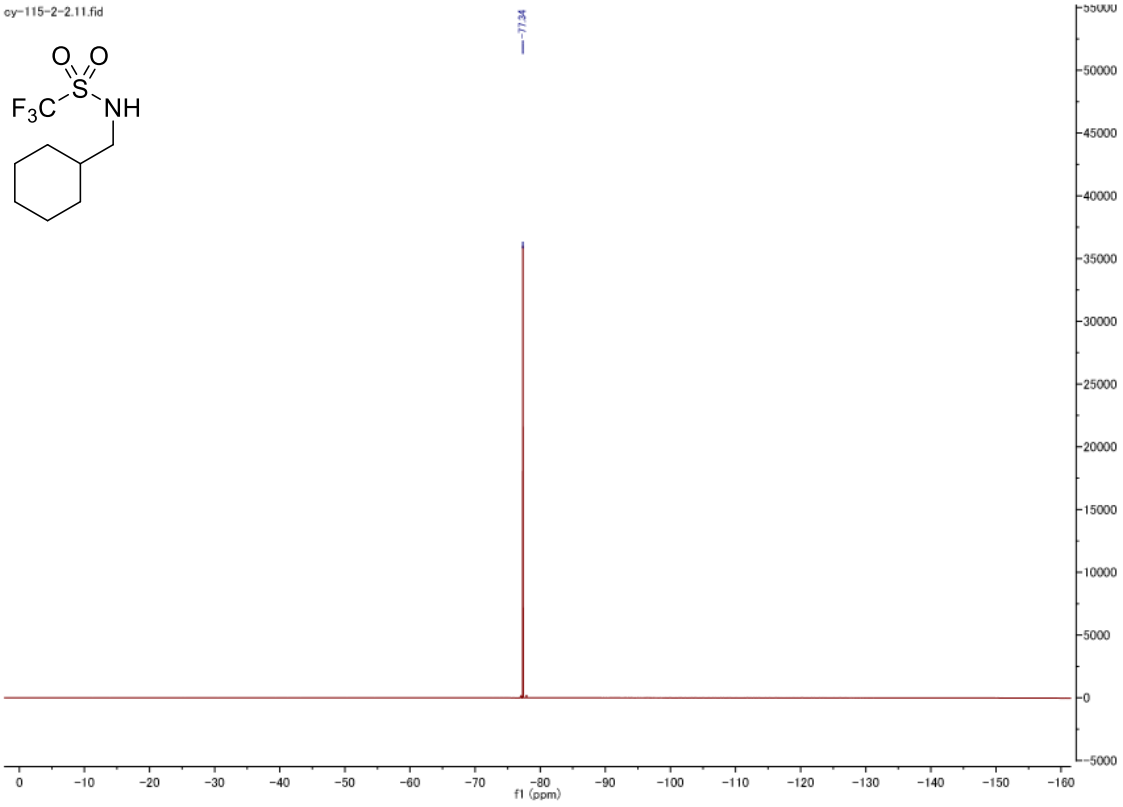




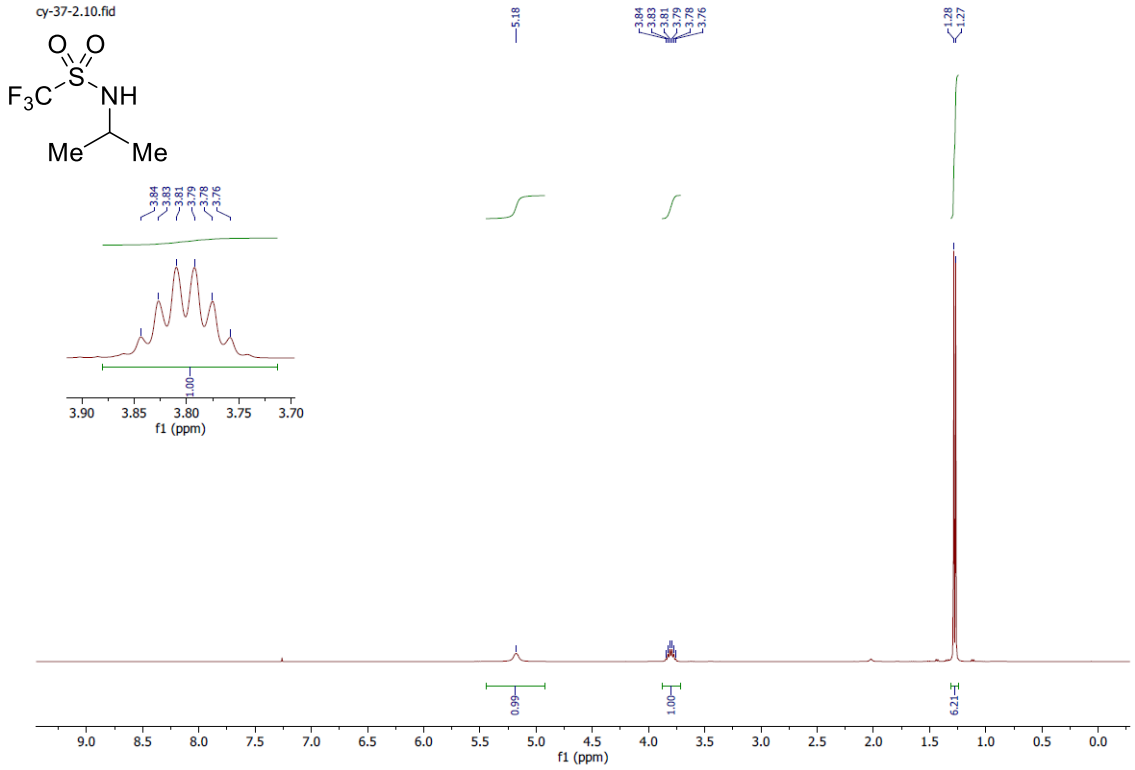
***N*-(cyclohexylmethyl)-1,1,1-trifluoromethanesulfonamide (1d)**

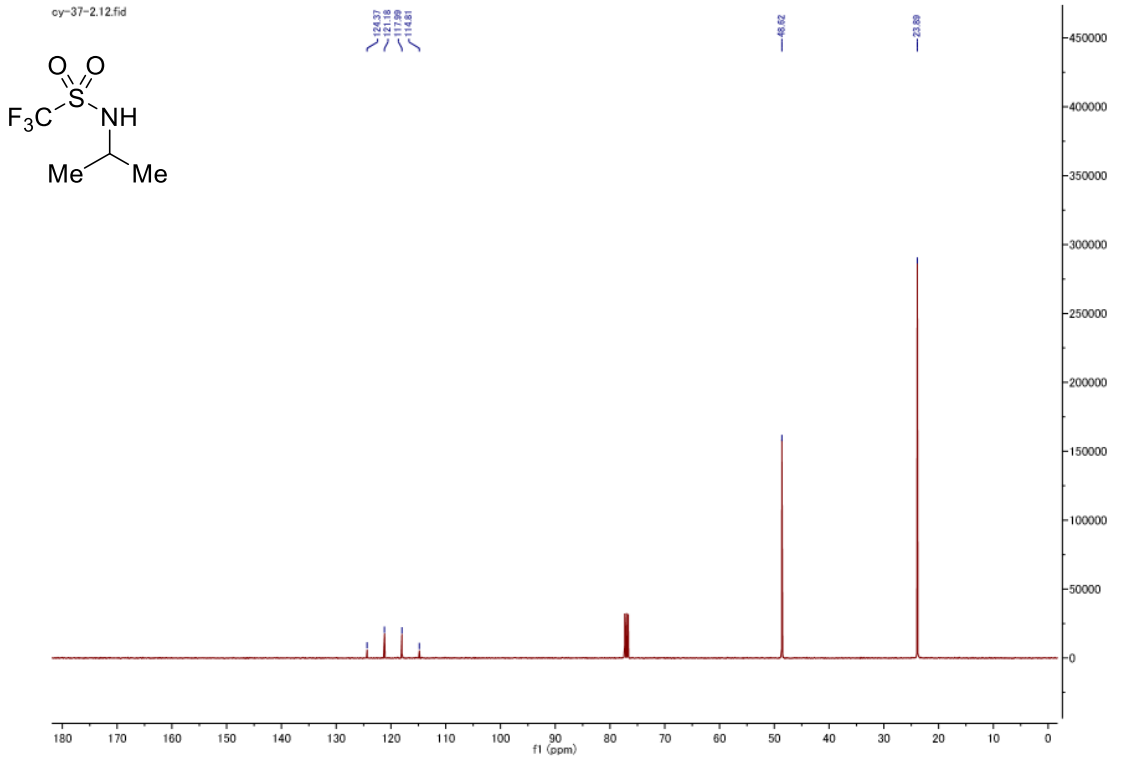


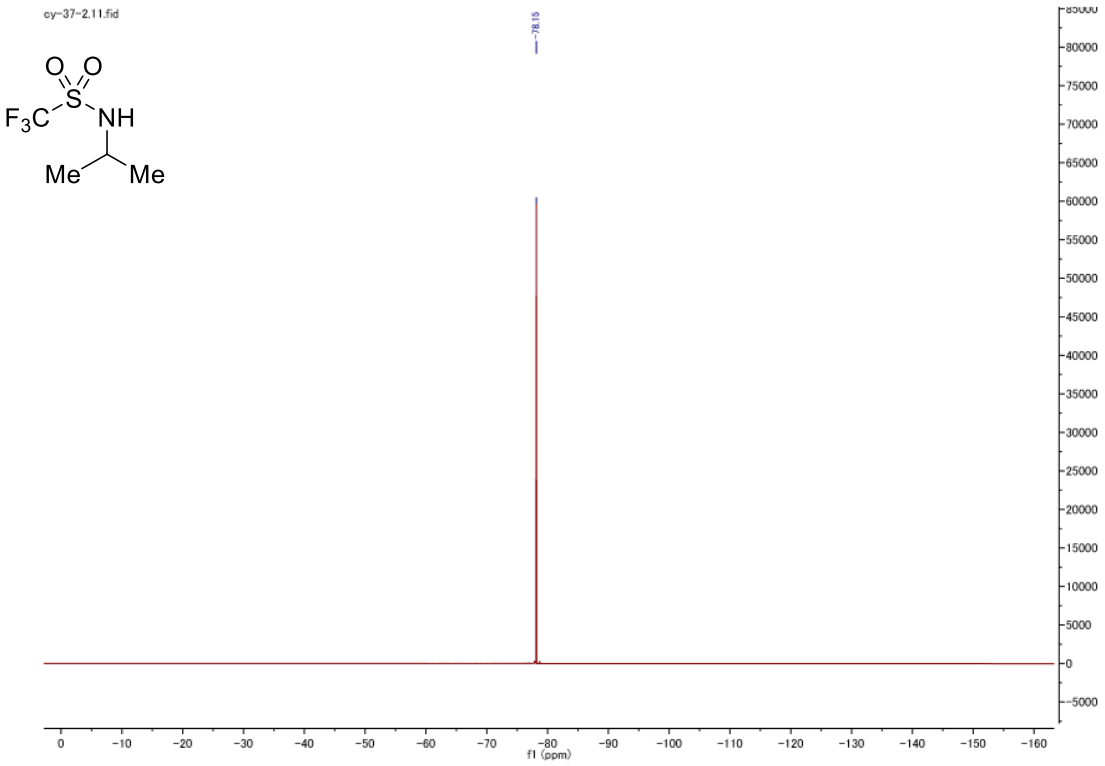

cy-115-2-2.12.fid
124.48
121.39
118.09
114.90
50.44
38.08
30.13
25.09
25.51
f1 (ppm)


cy-115-2-2.11.fid
-77.34
f1 (ppm)

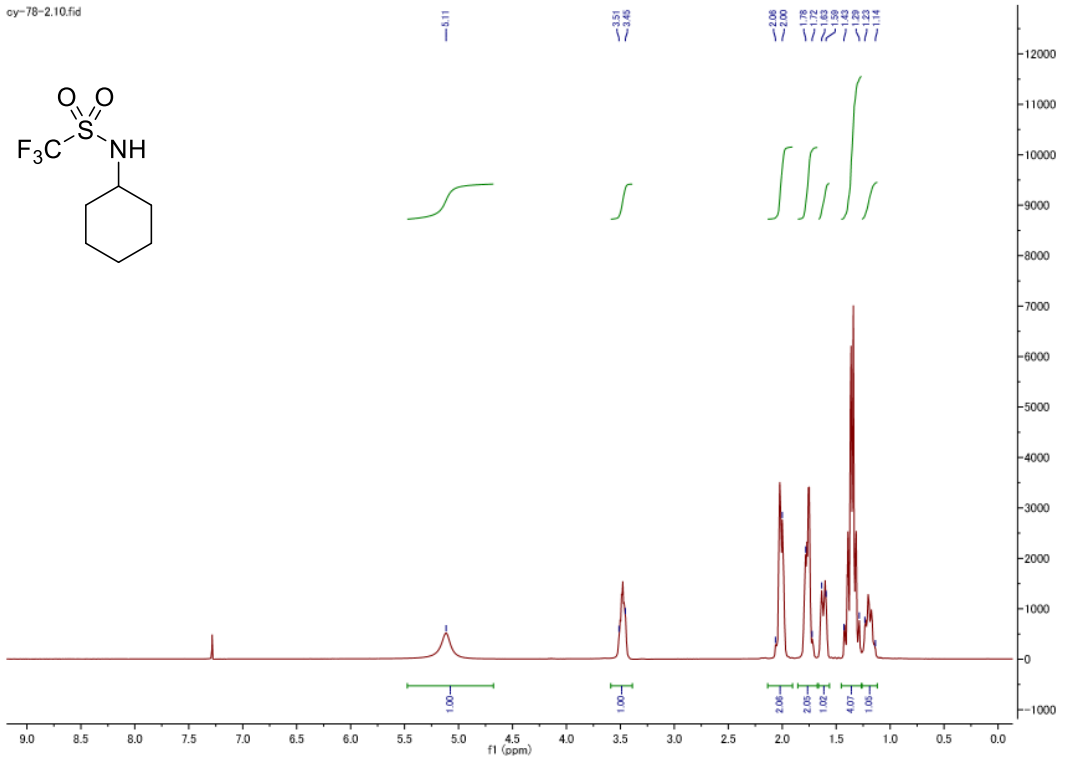
1,1,1-trifluoro-*N*-isopropylmethanesulfonamide (1e)

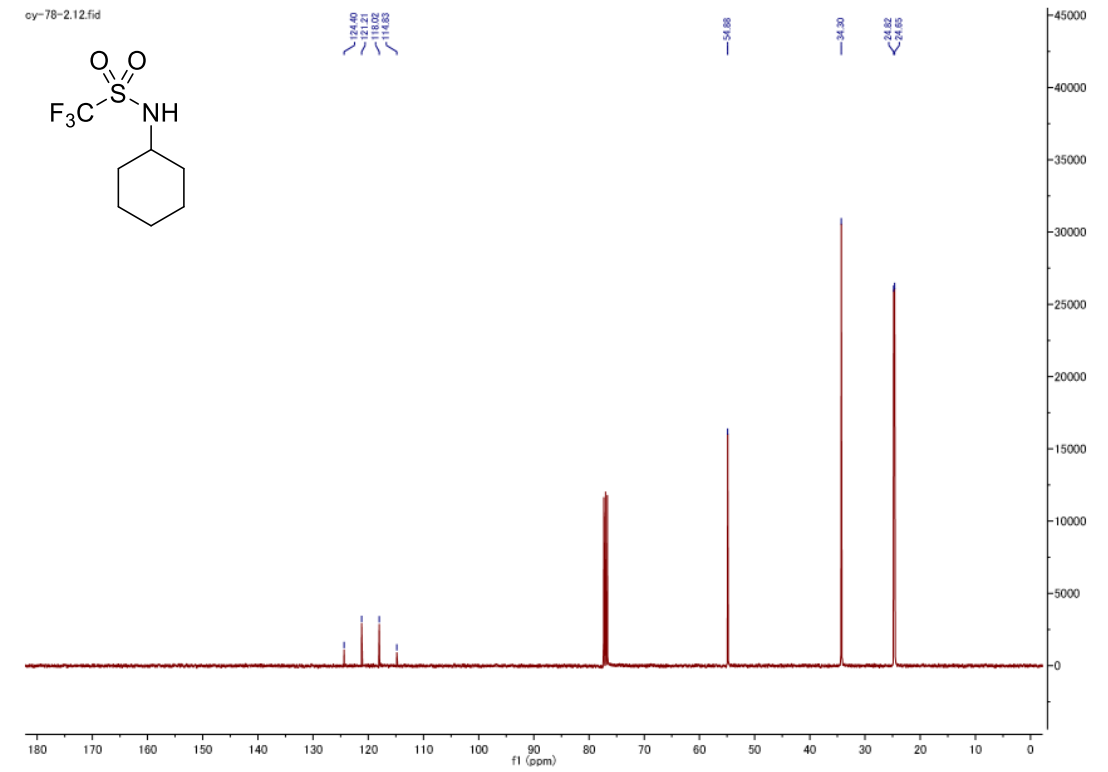


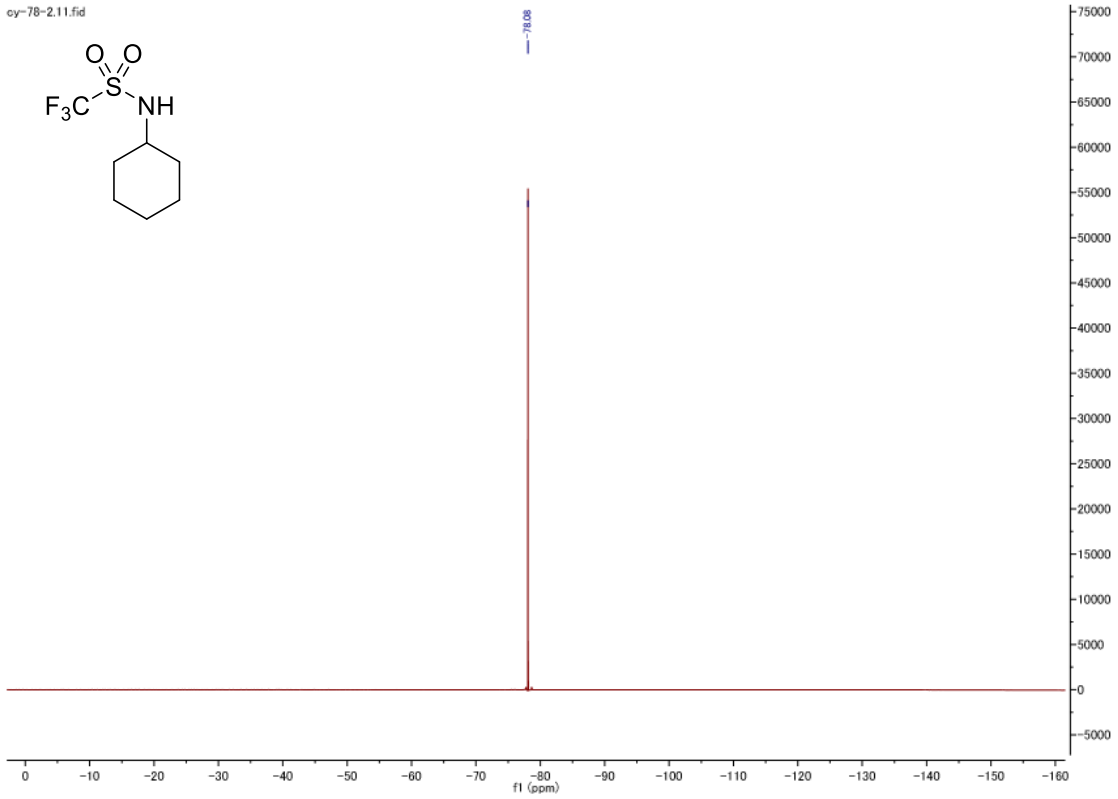




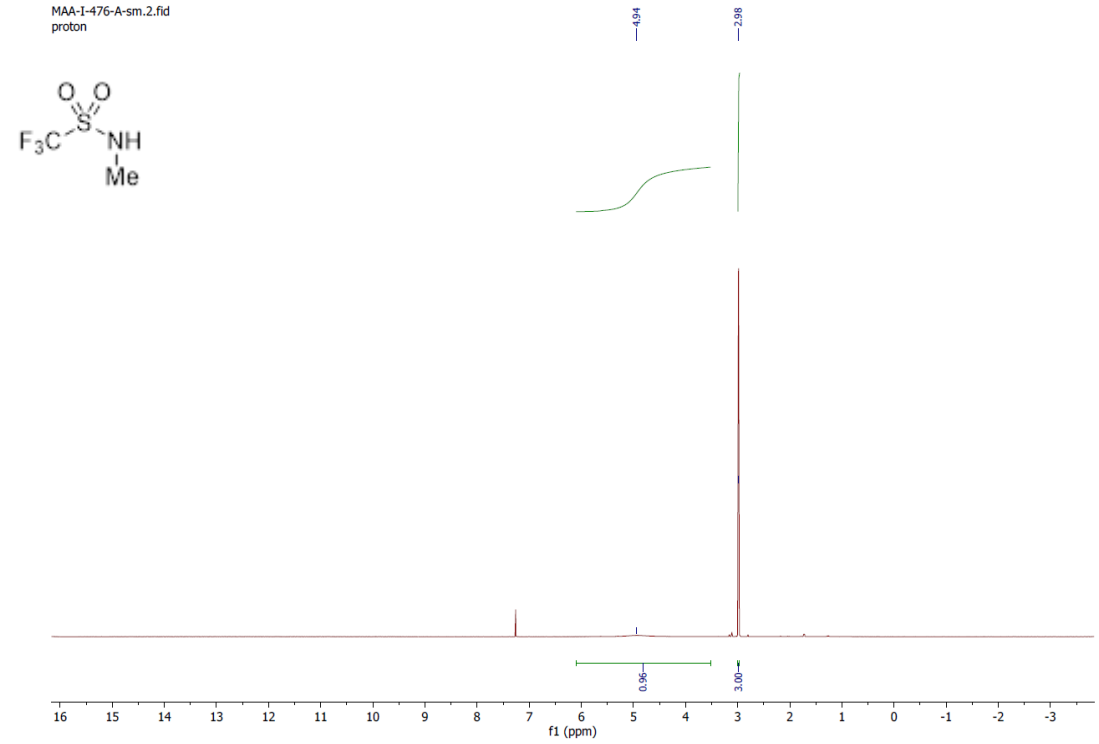
***N*-cyclohexyl-1,1,1-trifluoromethanesulfonamide (1f)**

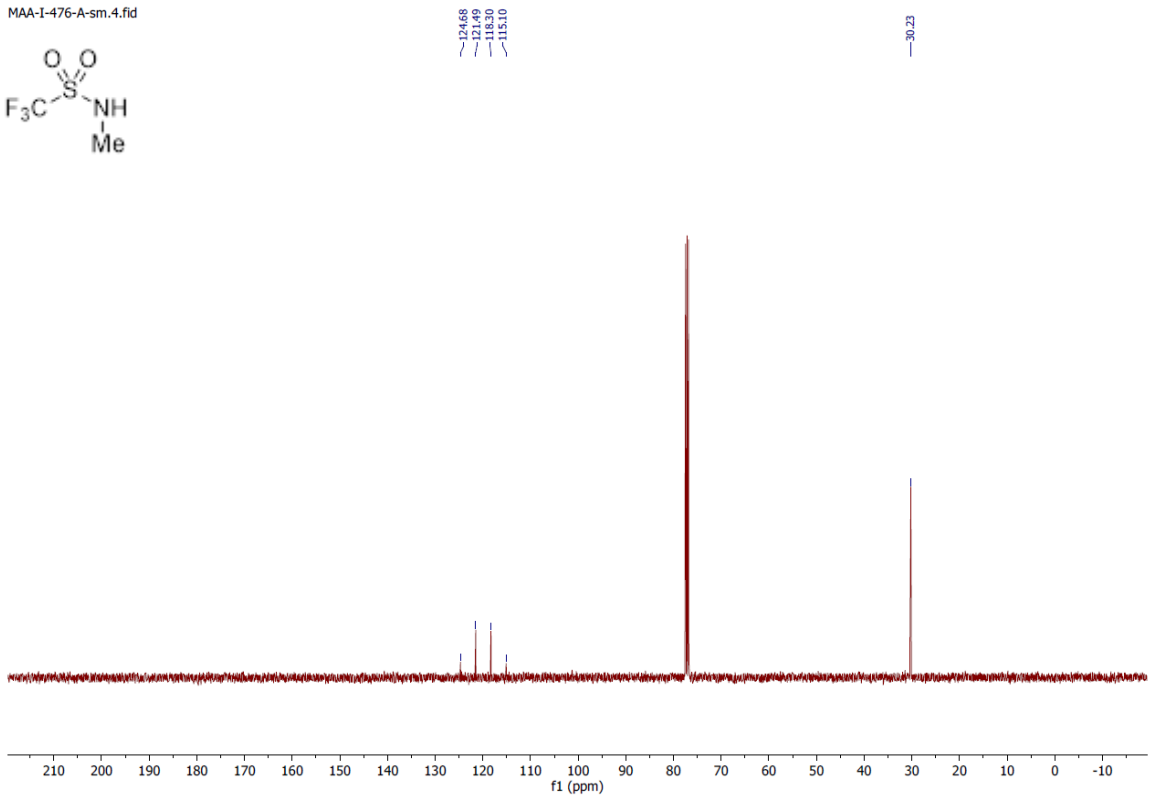


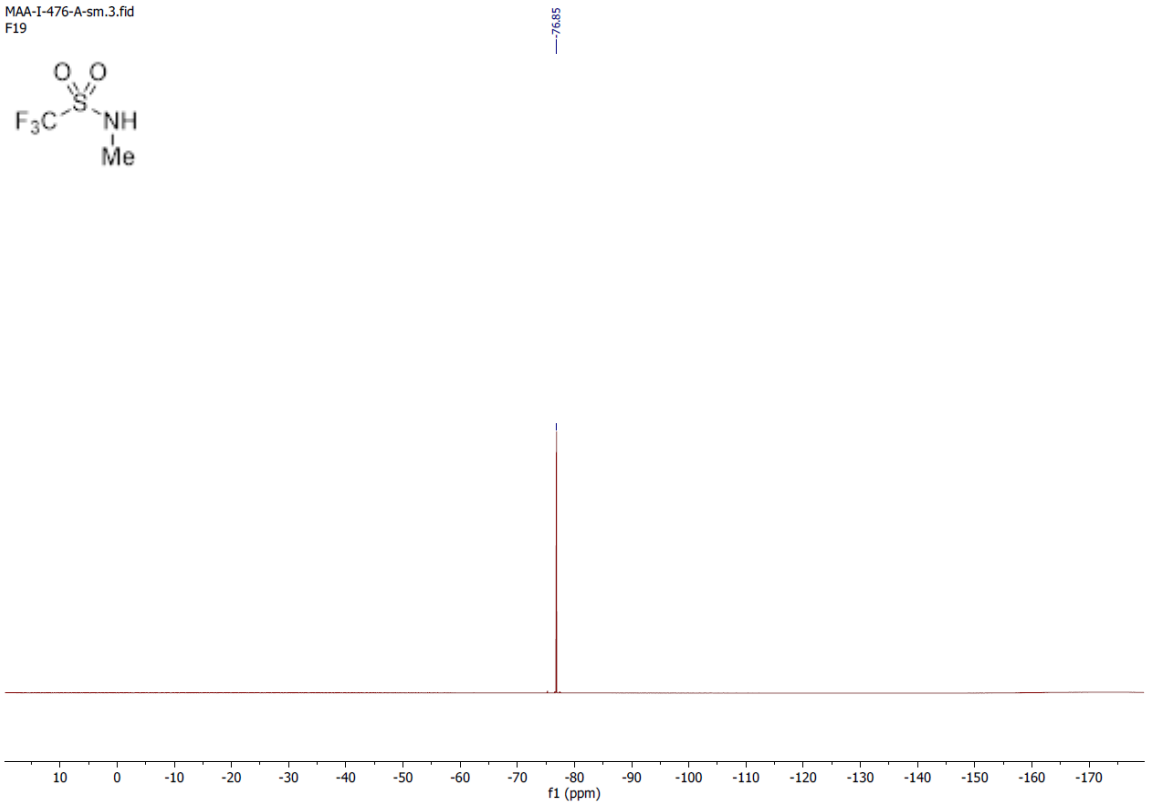

cy-78-2.12.fid
124.40
121.21
118.02
114.83
54.88
34.30
24.82
24.65
f1 (ppm)


cy-78-2.11.fid
-78.08
f1 (ppm)

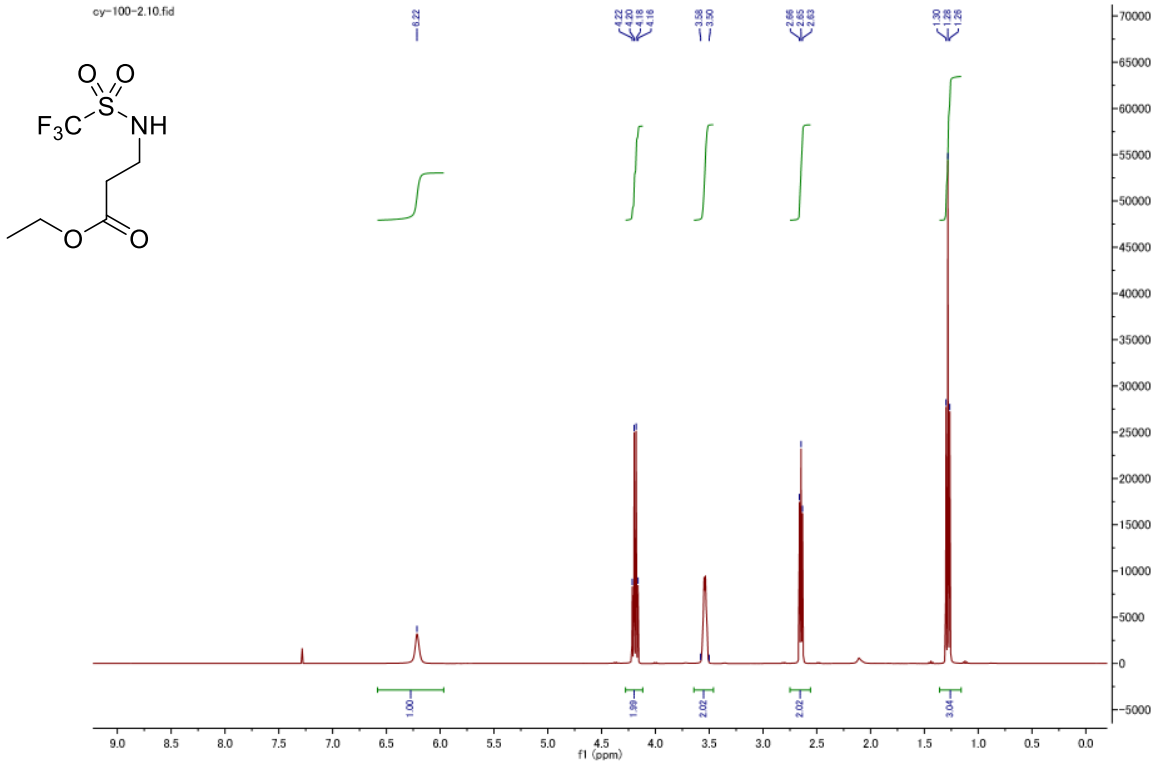
1,1,1-trifluoro-*N*-methylmethanesulfonamide (1g)

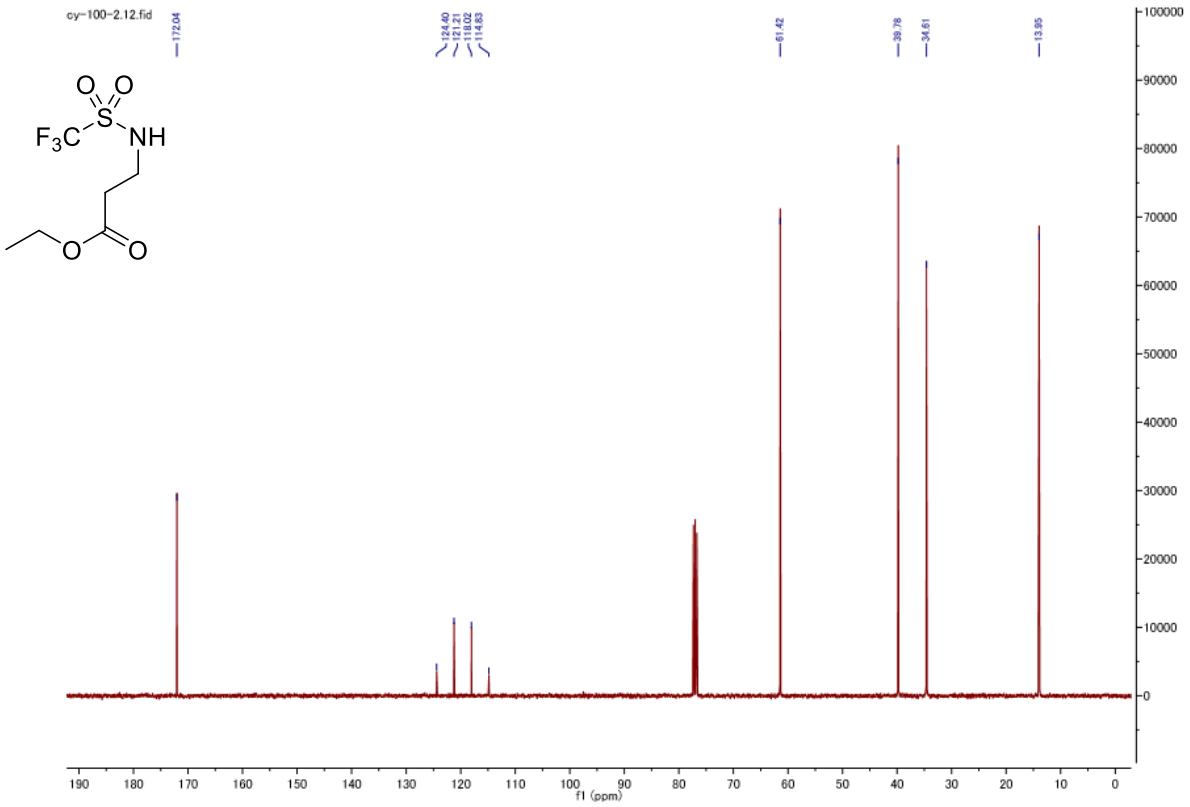


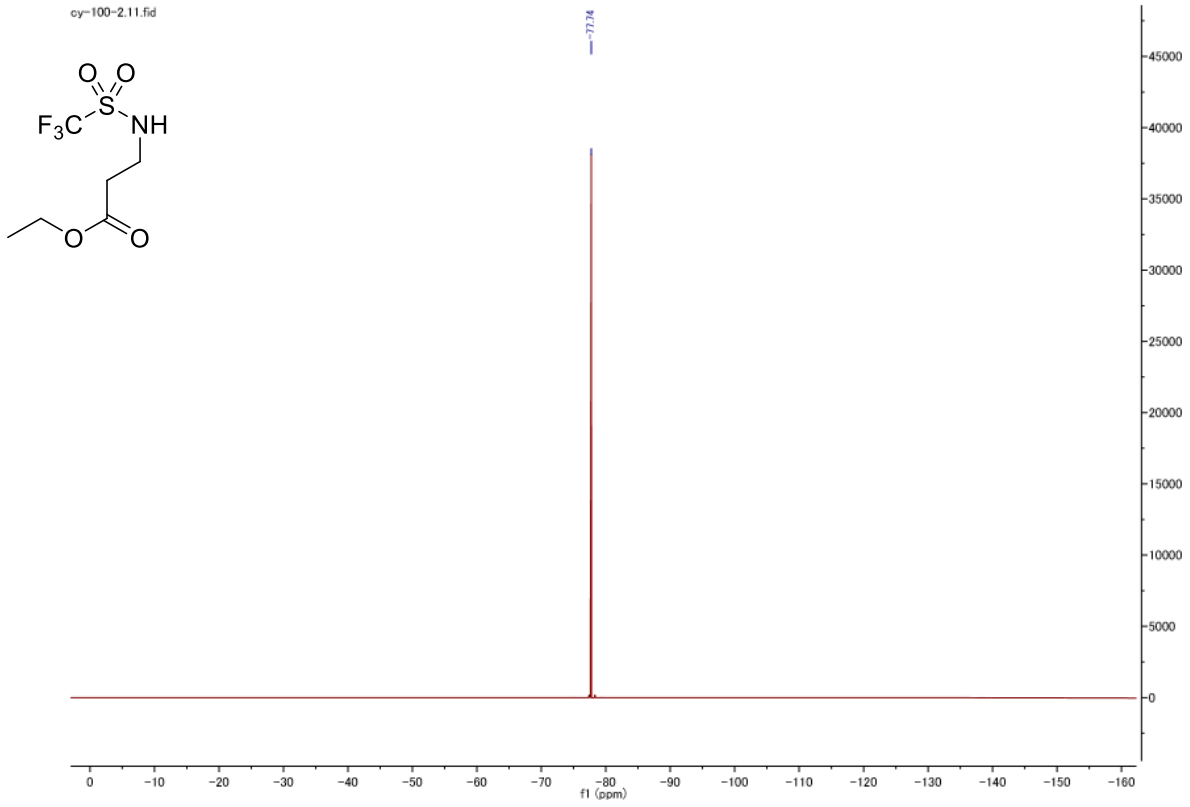




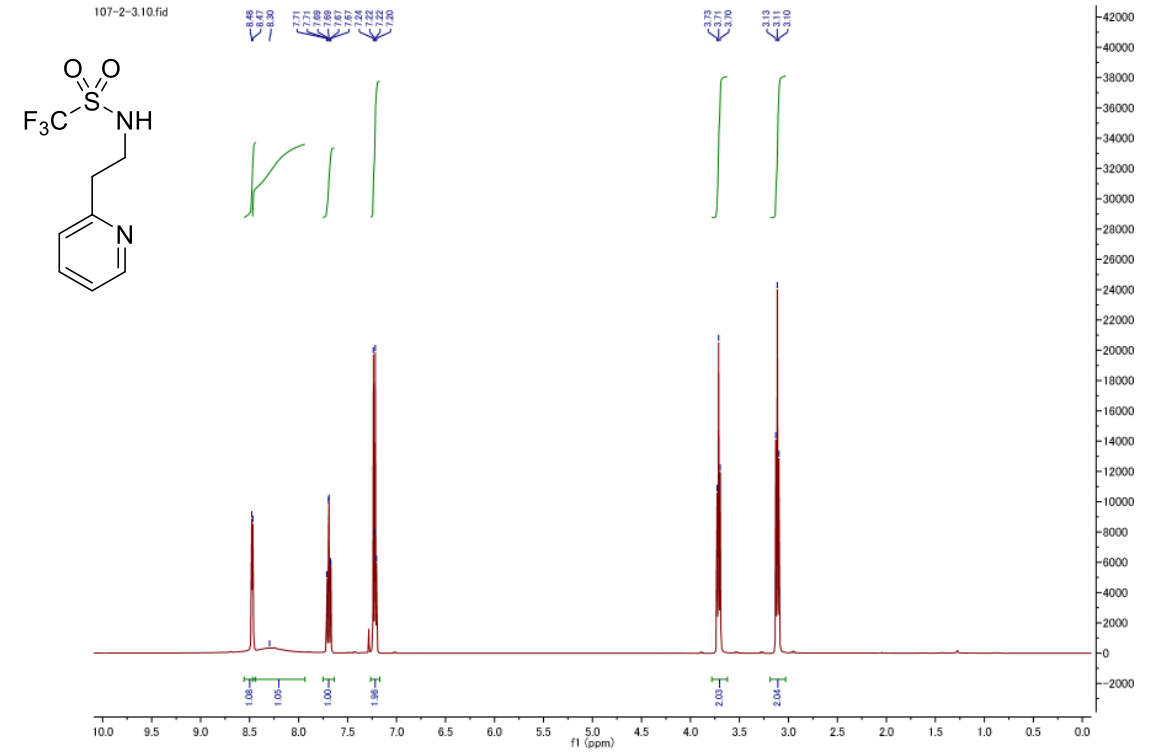
ethyl 3-((trifluoromethyl)sulfonamido)propanoate (1h)

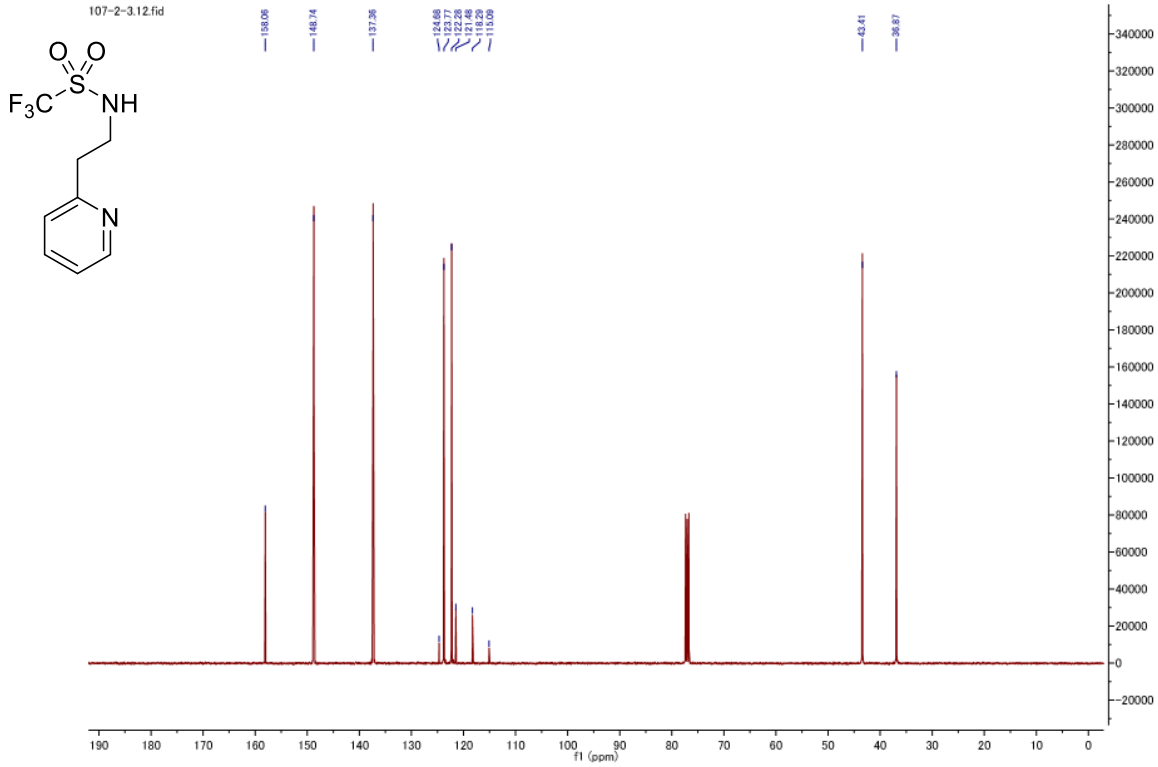


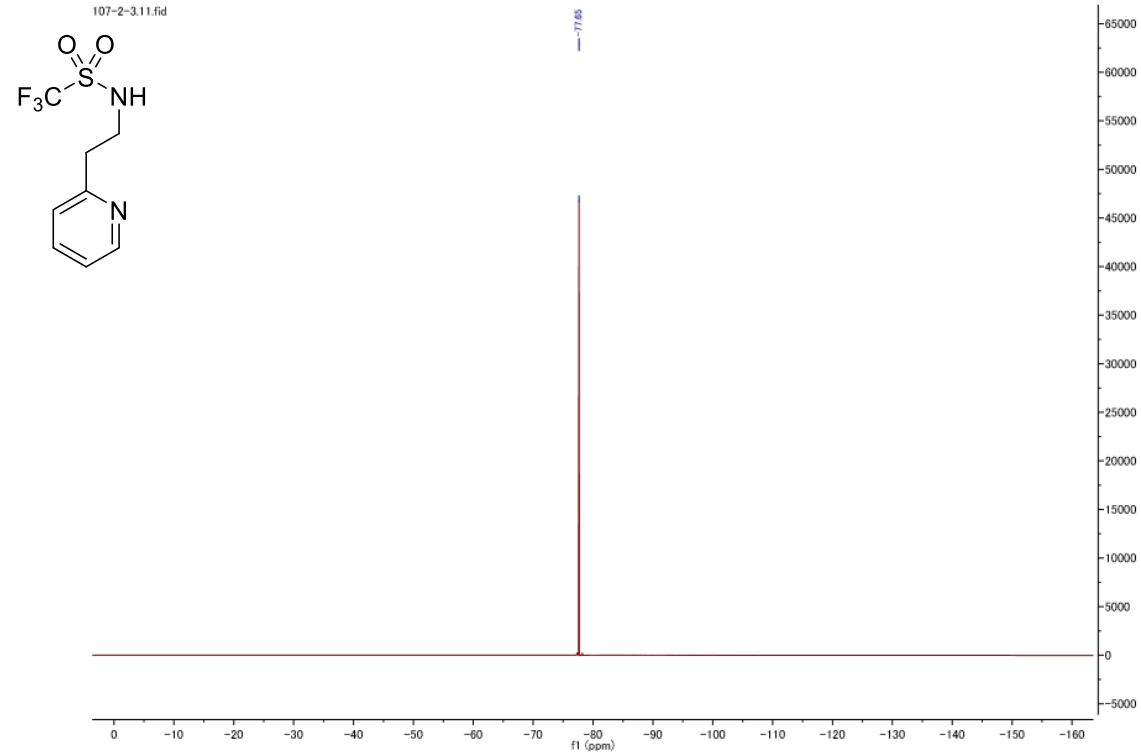

cy-100-2.12.fid
172.04
124.40
121.21
118.02
114.83
61.42
39.78
34.61
13.95
f1 (ppm)


cy-100-2.11.fid
77.74
f1 (ppm)

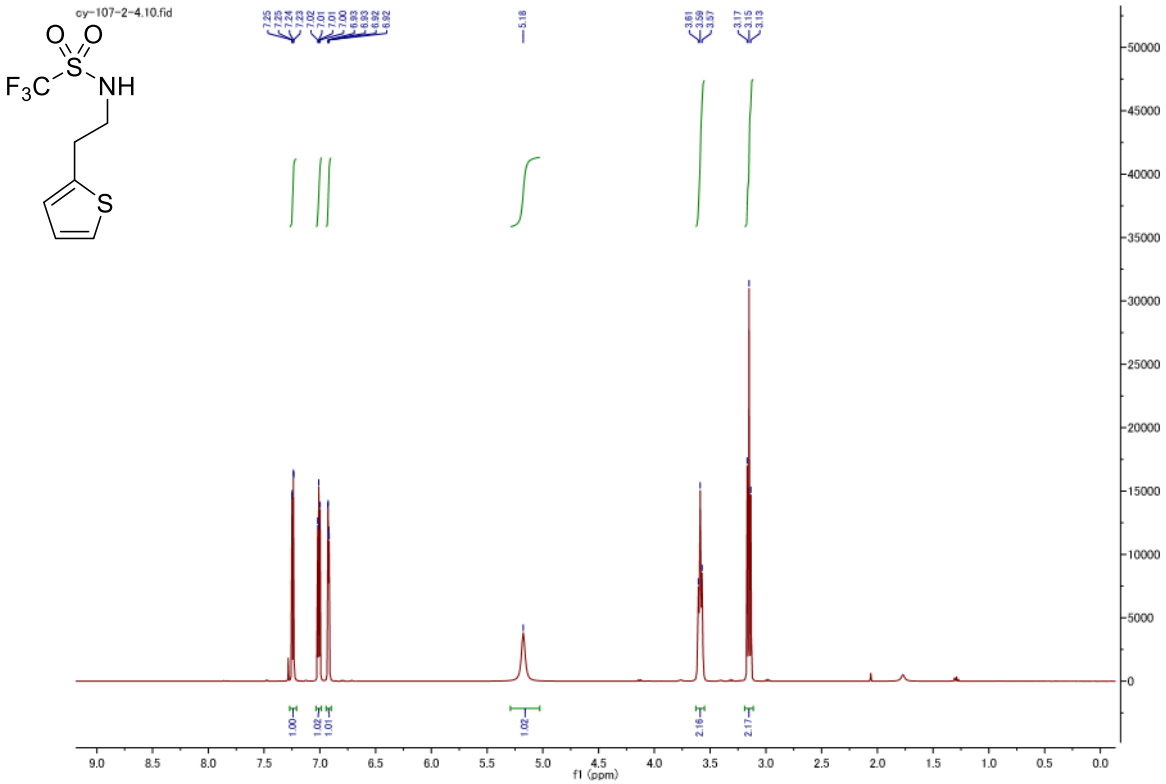
1,1,1-trifluoro-N-(2-(pyridin-2-yl)ethyl)methanesulfonamide (1i)

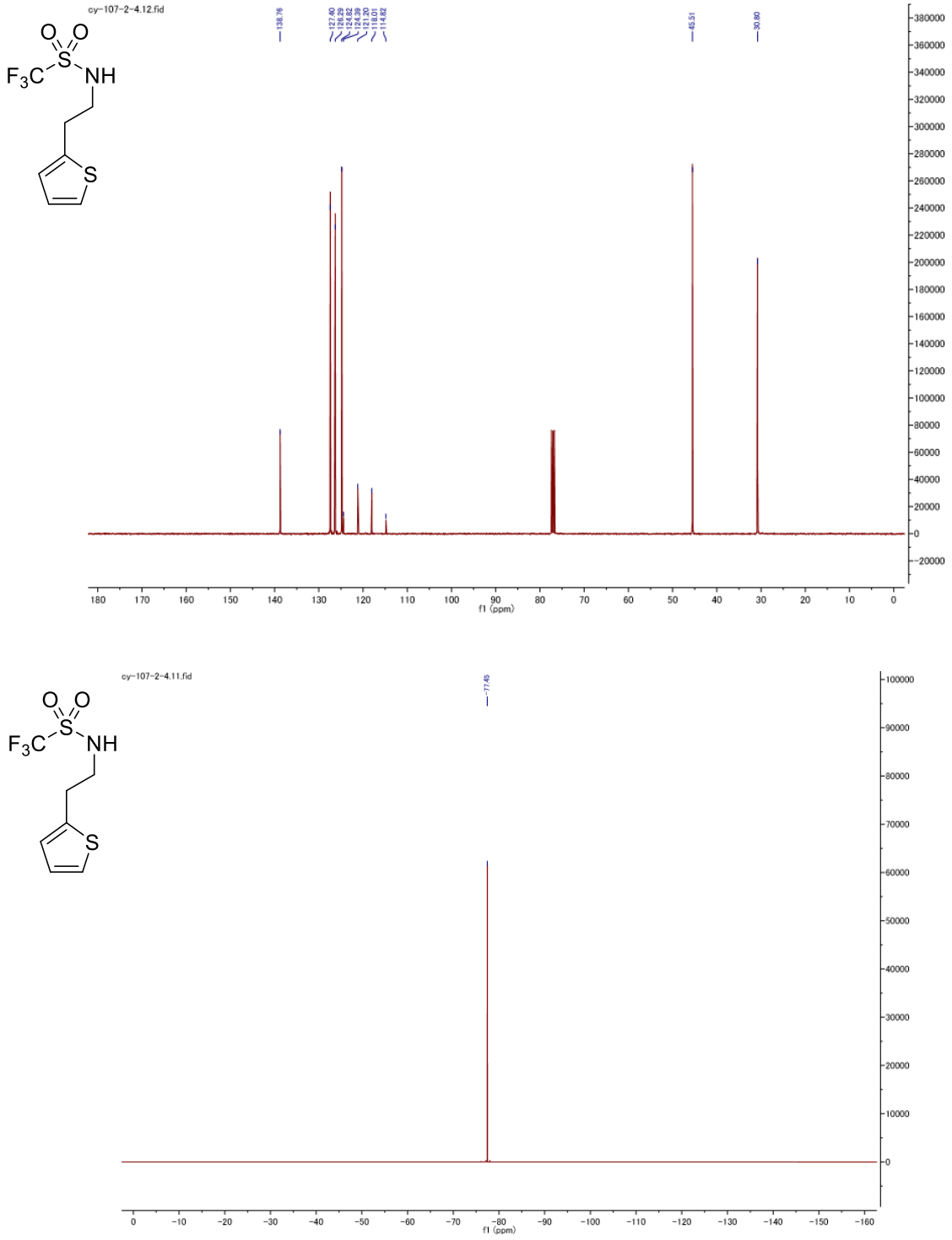




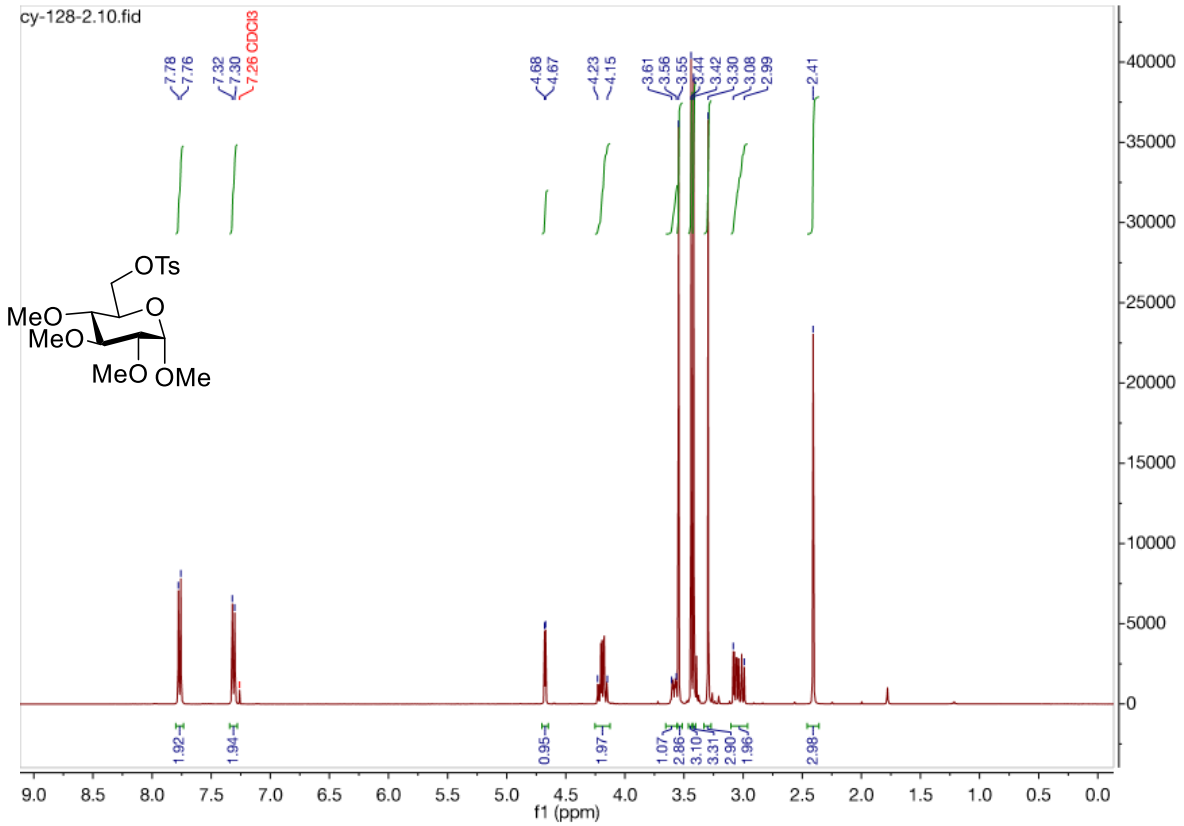


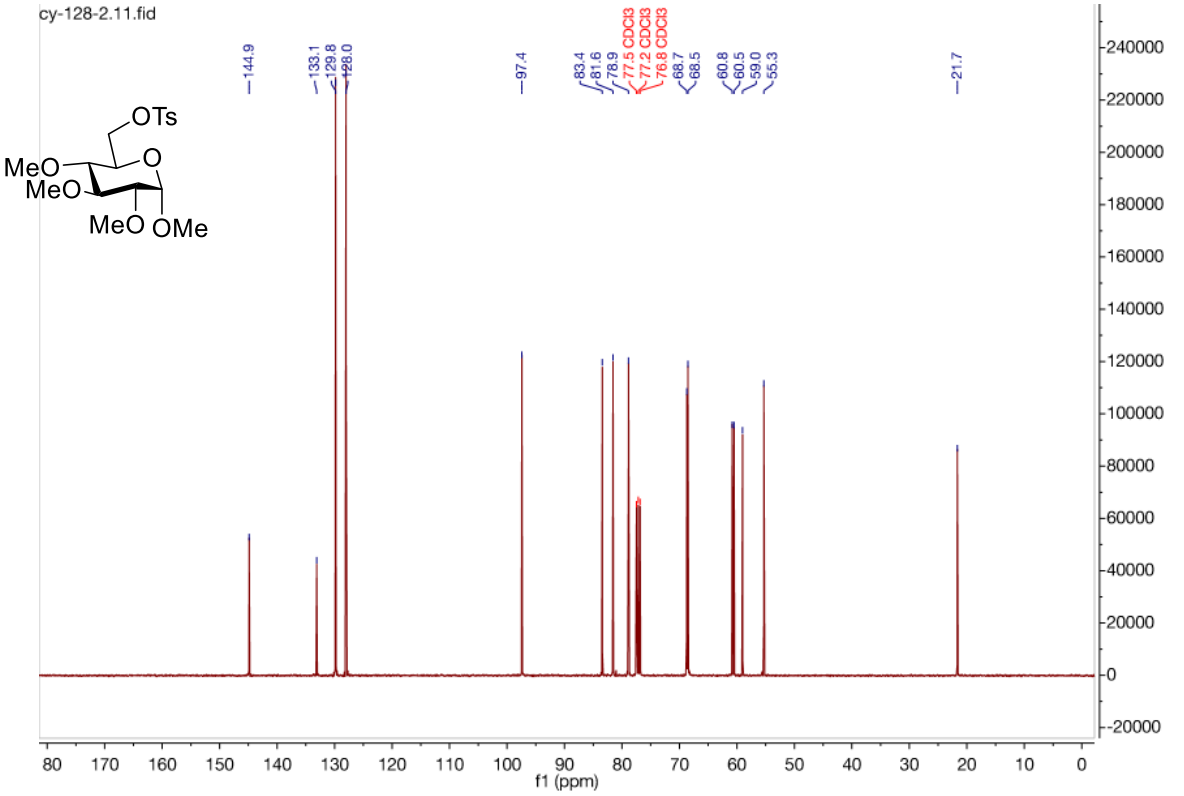
1,1,1-trifluoro-*N*-(2-(thiophen-2-yl)ethyl)methanesulfonamide (1j)

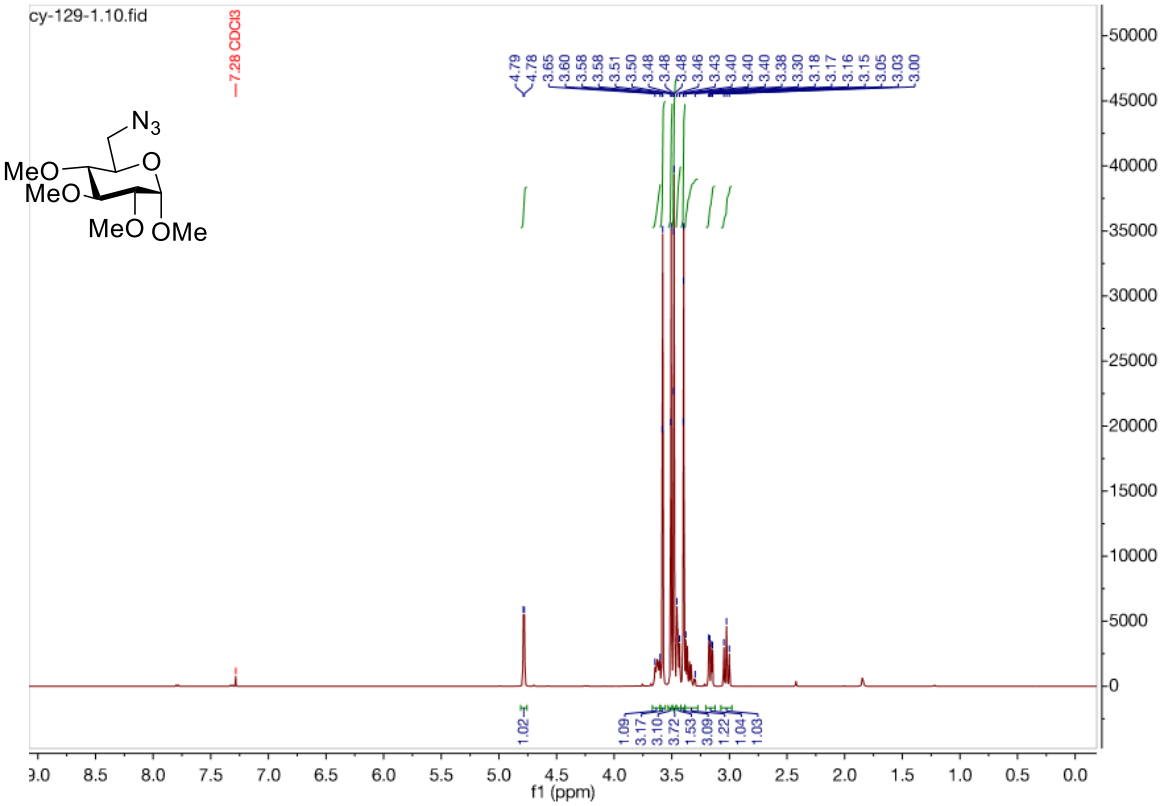


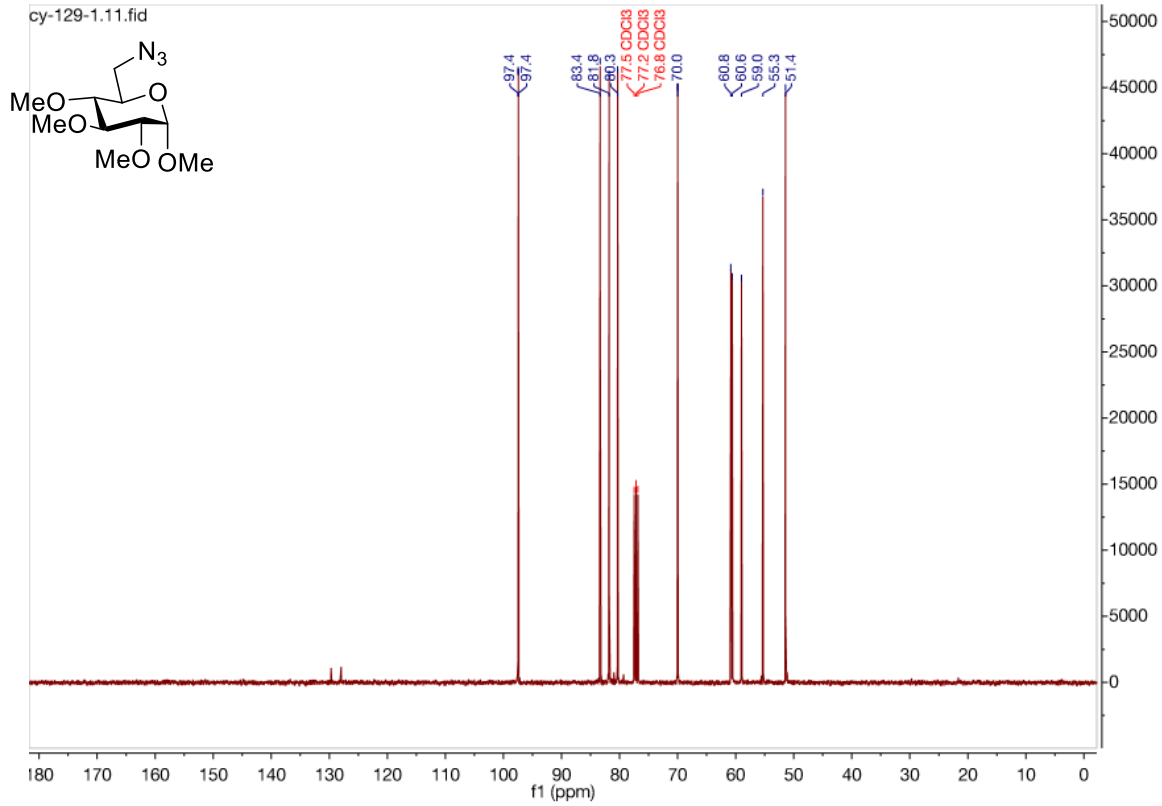


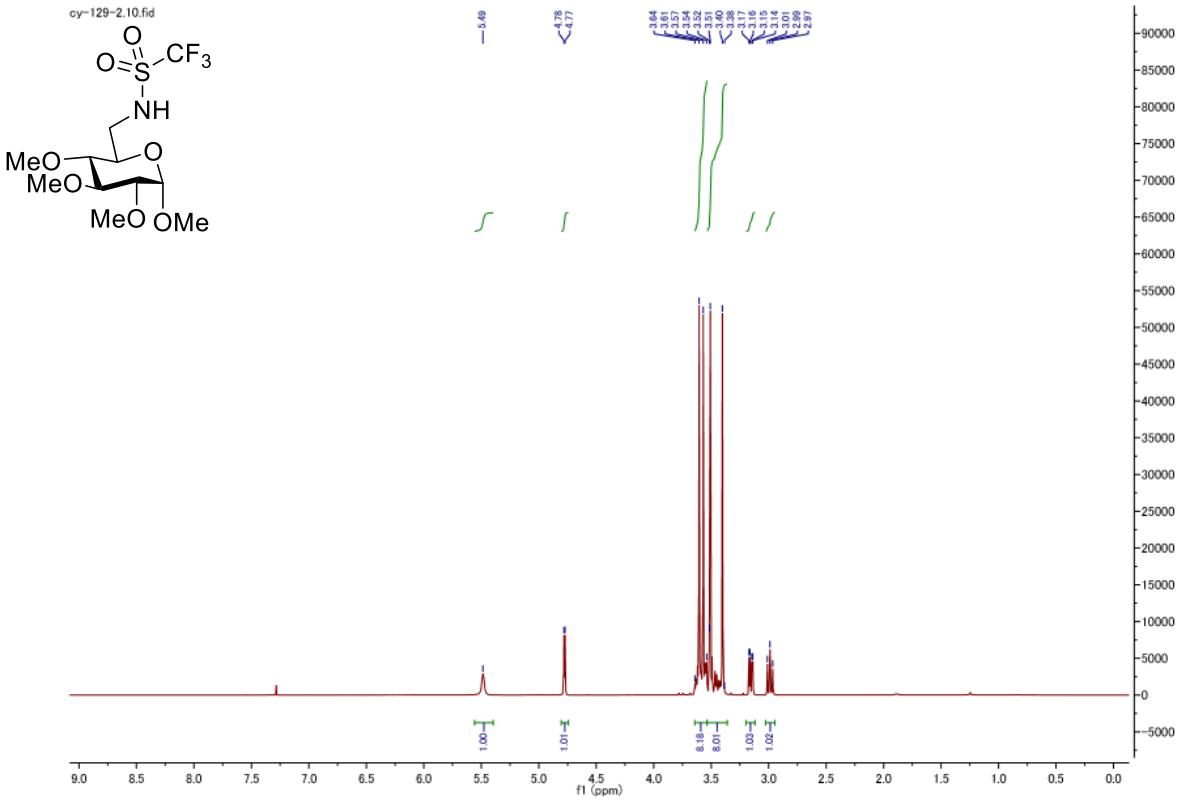
1,1,1-trifluoro-*N*-(((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)methyl)methanesulfonamide (1k)

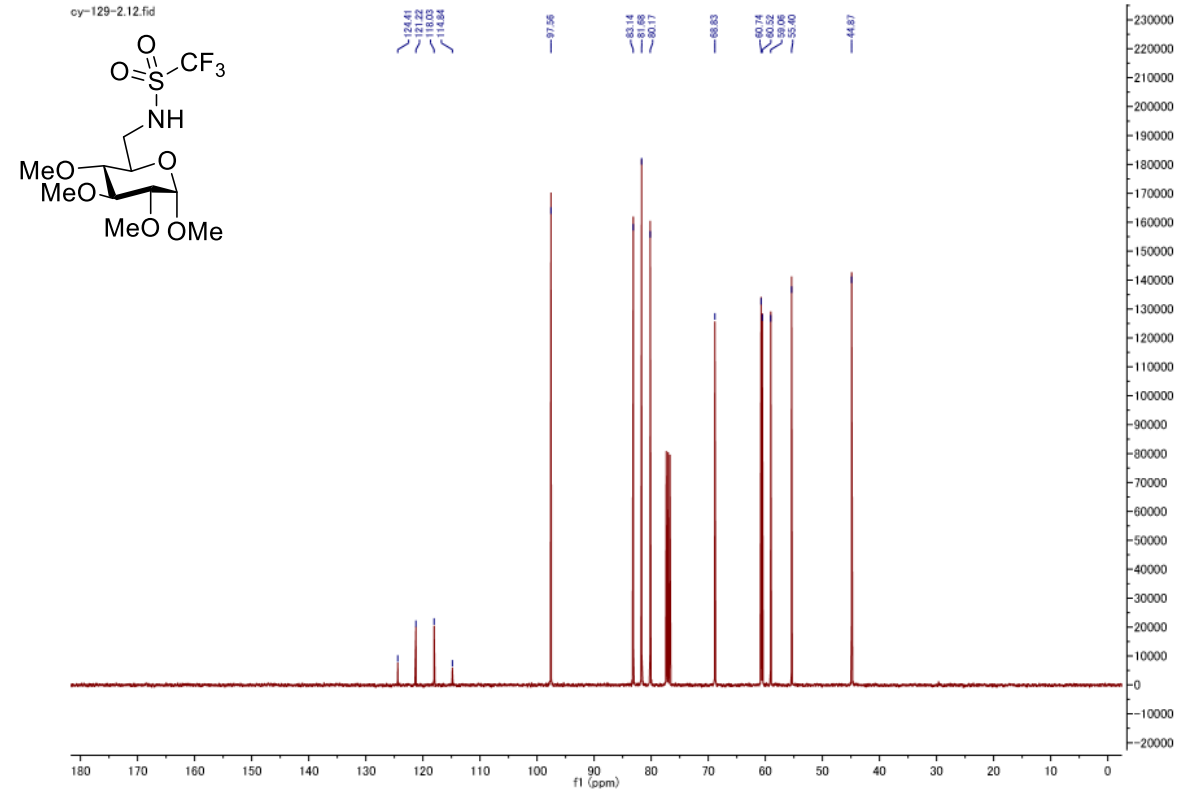

cy-128-2.10.fid
7.78
7.76
7.32
7.30
7.26 CDCl3
4.68
4.67
4.23
4.15
3.61
3.56
3.55
3.44
3.42
3.30
3.08
2.99
2.41
OTs
O
MeO
MeO
MeO
OMe
1.92
1.94
0.95
1.97
1.07
2.86
3.10
3.31
2.90
1.96
2.98
f1 (ppm)

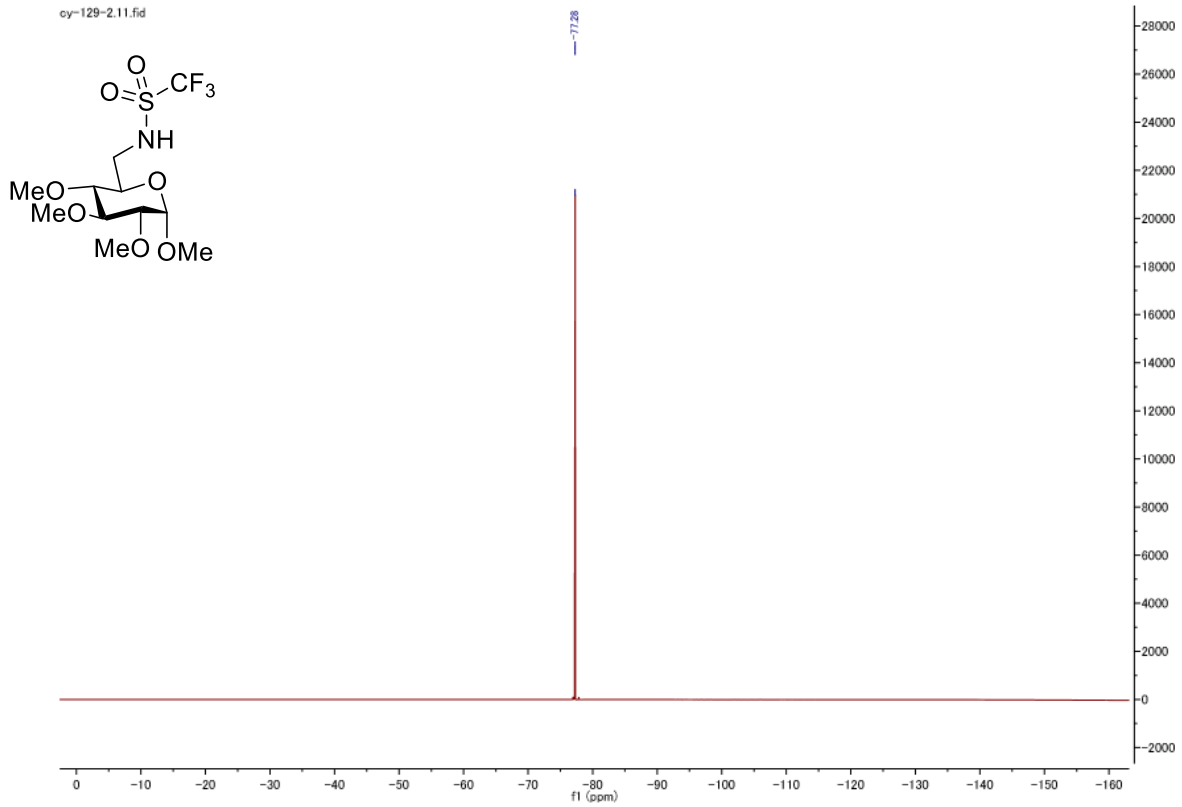

cy-128-2.11.fid
144.9
133.1
129.8
128.0
97.4
83.4
81.6
78.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
68.7
68.5
60.8
60.5
59.0
55.3
21.7
OTs
O
MeO
MeO
MeO
OMe
f1 (ppm)


cy-129-1.10.fid
7.28 CDCl3
N3
MeO
MeO
O
MeO OMe
4.79
4.78
3.65
3.60
3.58
3.58
3.51
3.50
3.48
3.48
3.48
3.46
3.43
3.40
3.40
3.40
3.38
3.30
3.18
3.17
3.16
3.15
3.05
3.03
3.00
1.02
1.09
3.17
3.10
3.72
1.53
3.09
1.22
1.04
1.03
f1 (ppm)

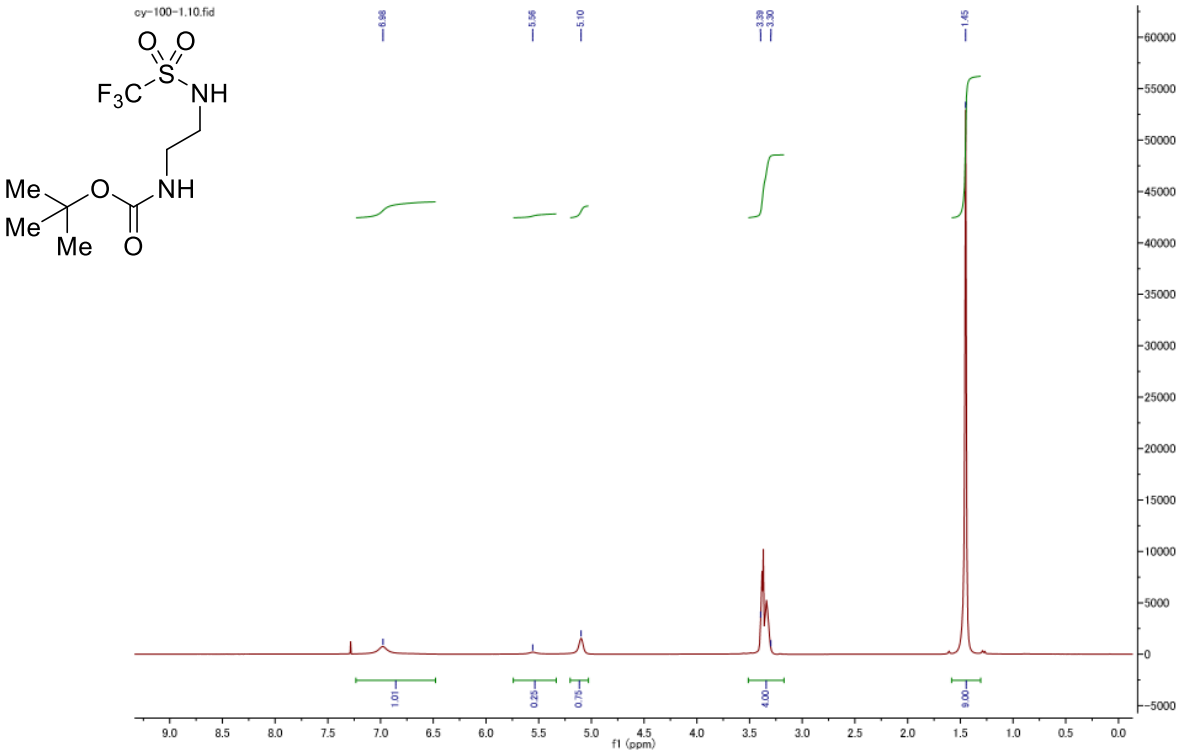

cy-129-1.11.fid
N3
MeO
MeO
O
MeO OMe
97.4
97.4
83.4
81.8
80.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
70.0
60.8
60.6
59.0
55.3
51.4
f1 (ppm)

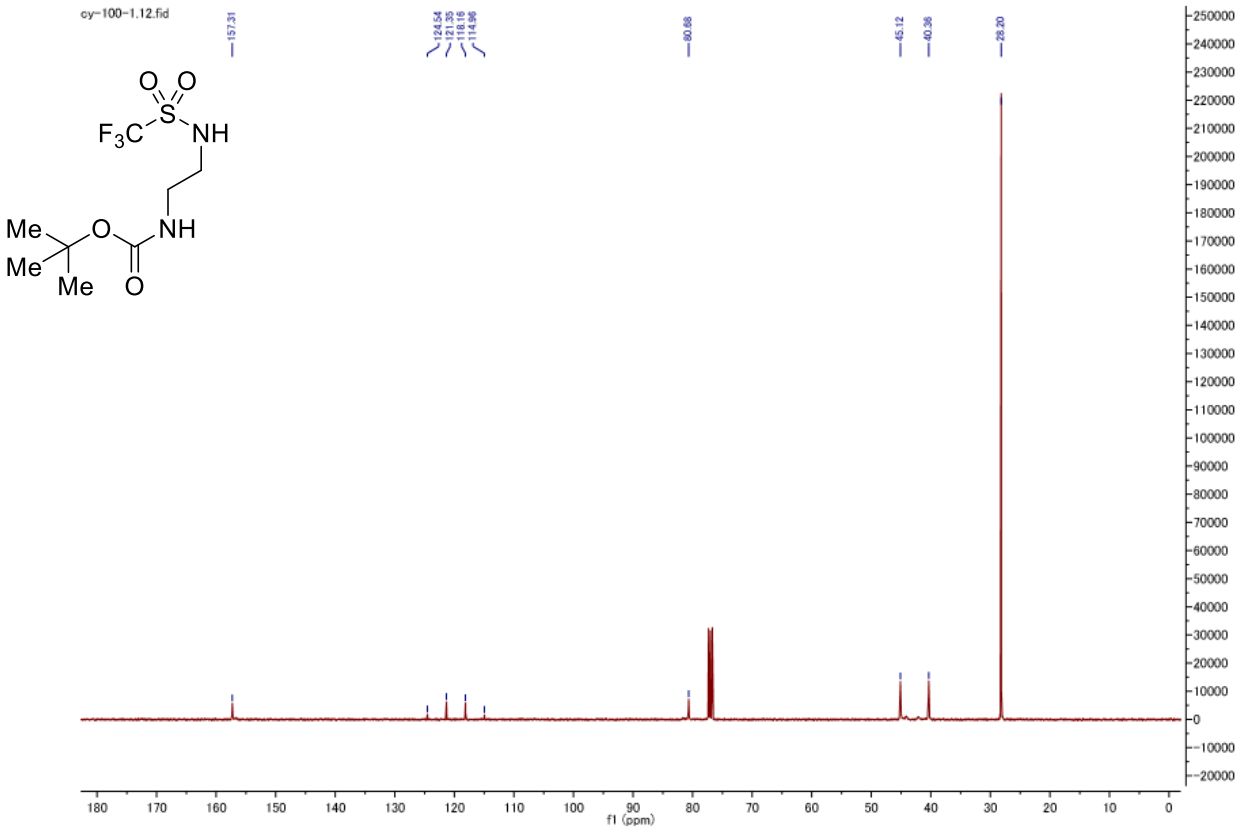

cy-129-2.10.fid
MeO
MeO
MeO
OMe
NH
CF3
f1 (ppm)

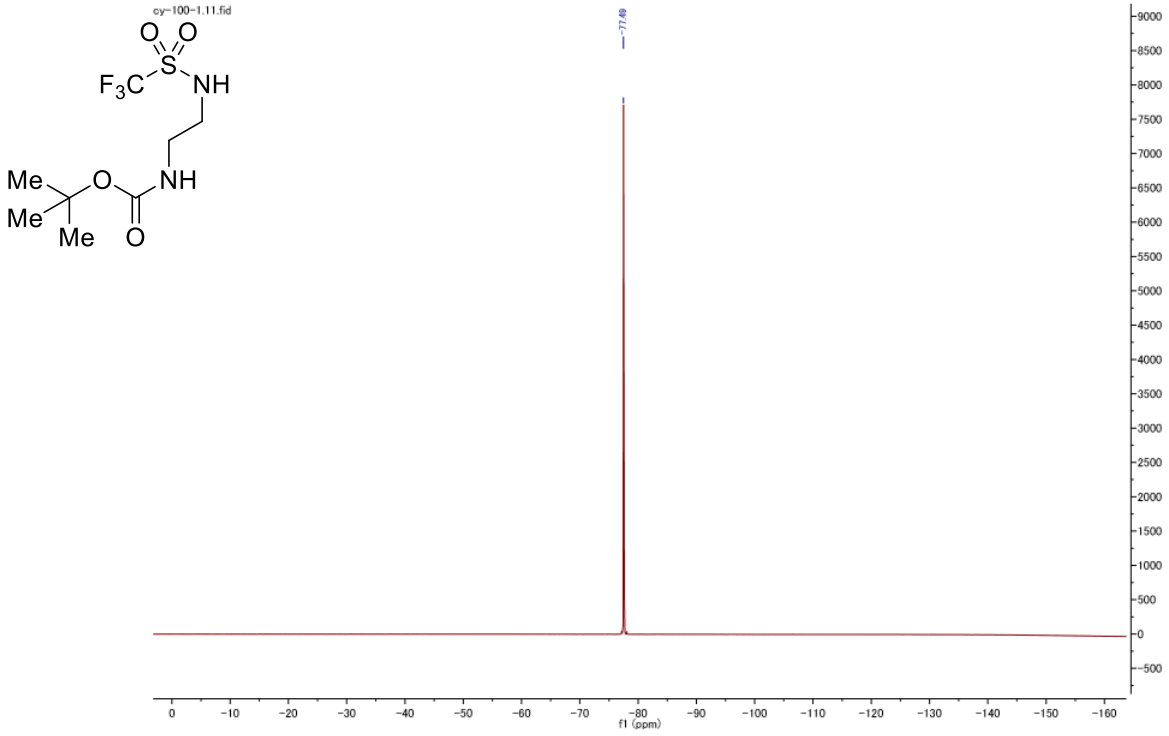

cy-129-2.12.fid
MeO
MeO
MeO
OMe
NH
CF3
f1 (ppm)



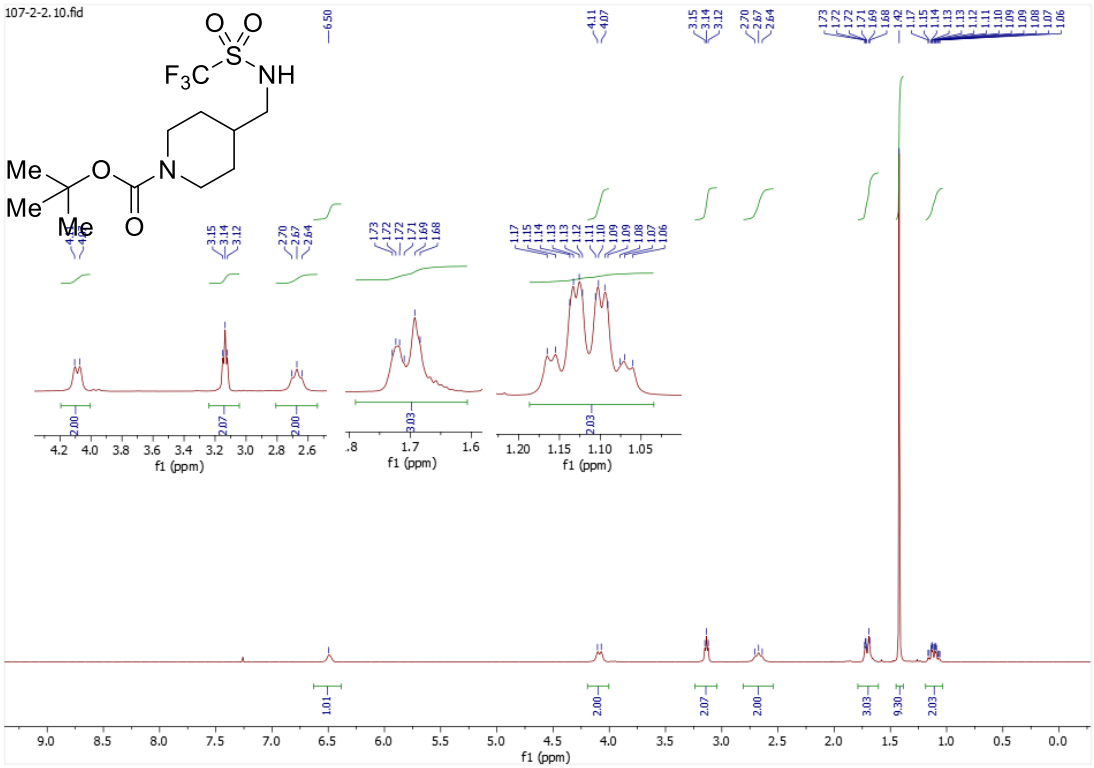
***tert*-butyl (2-((trifluoromethyl)sulfonamido)ethyl)carbamate (1l)**

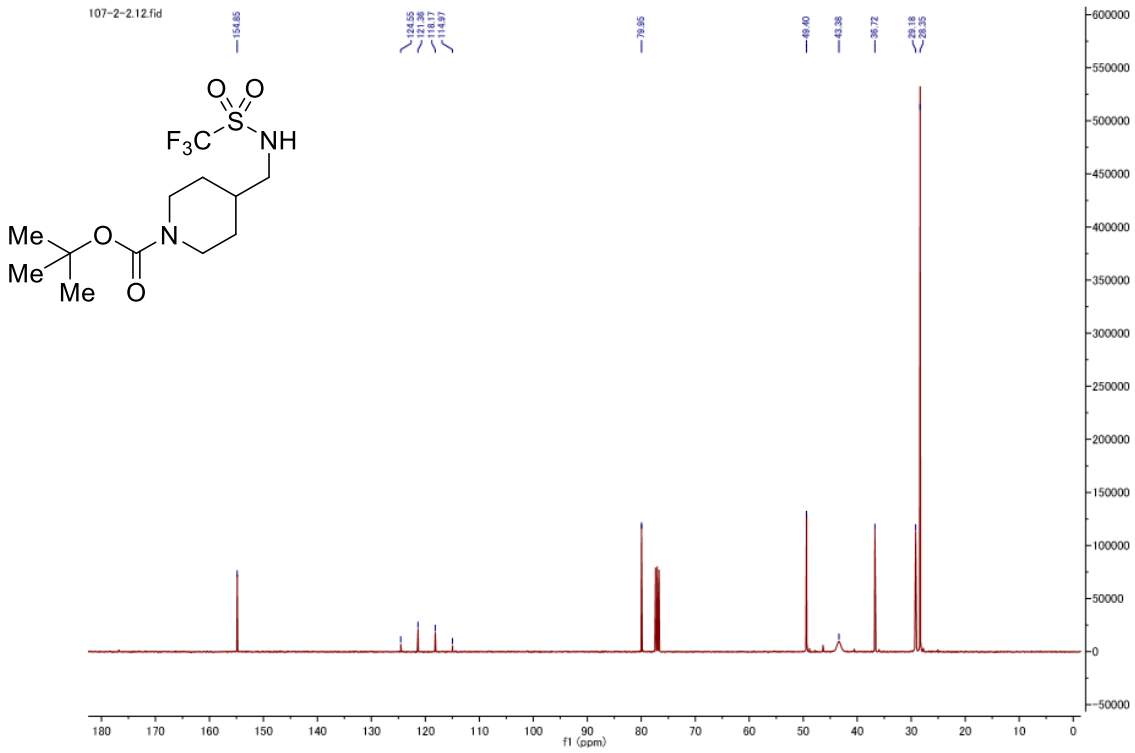


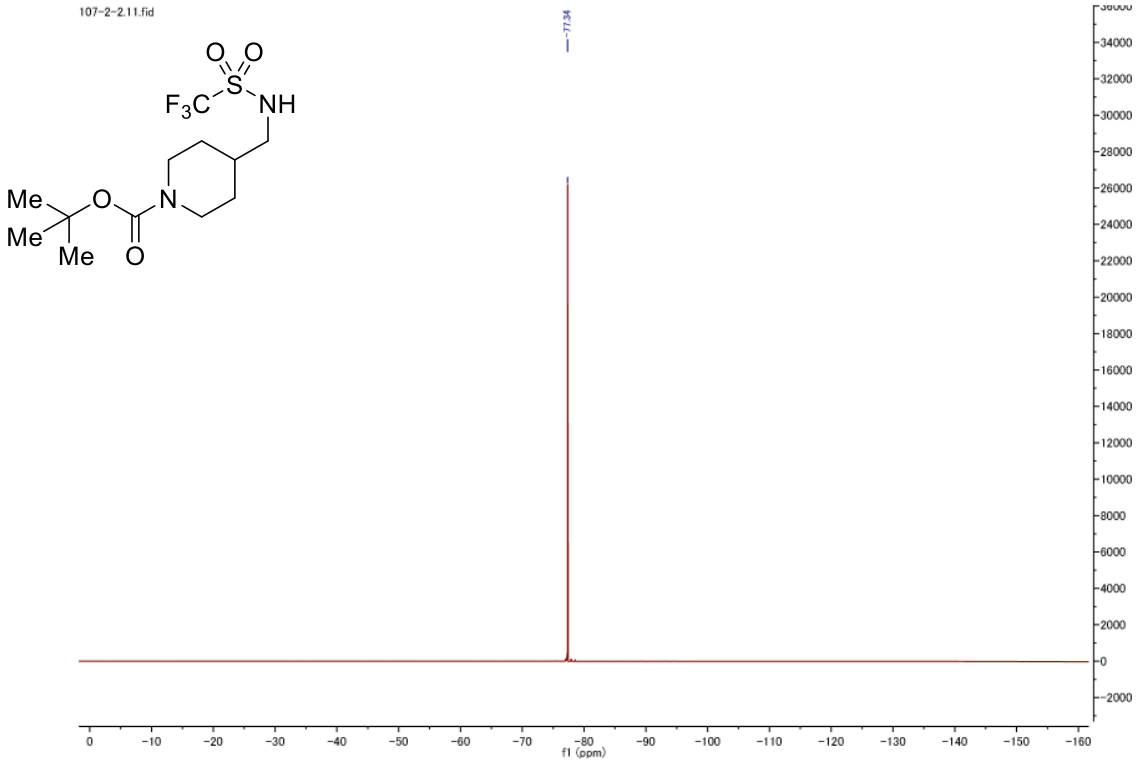

cy-100-1.12.fid
157.31
124.54
121.35
118.16
114.96
80.68
45.12
40.36
28.20
O
O
S
F3C
NH
Me
Me
Me
O
NH
O
f1 (ppm)


cy-100-1.11.fid
77.49
O
O
S
F3C
NH
Me
Me
Me
O
NH
O
f1 (ppm)

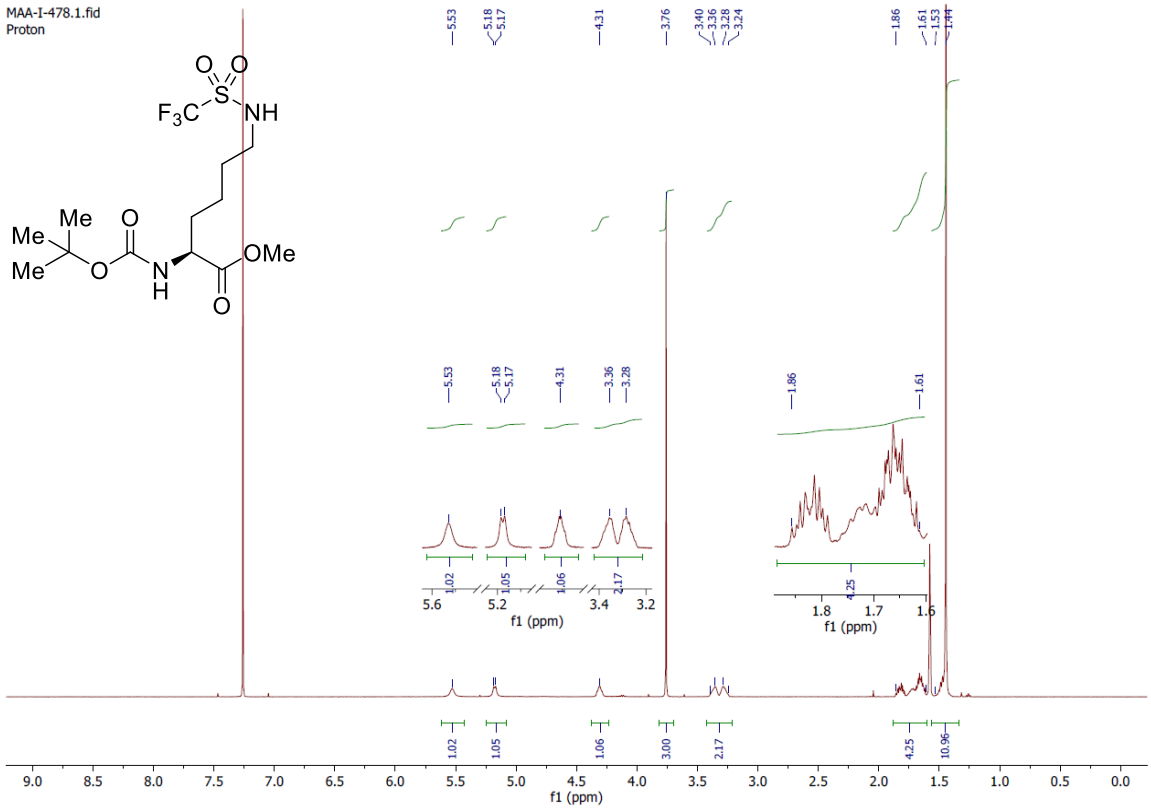
***tert*-butyl 4-(((trifluoromethyl)sulfonamido)methyl)piperidine-1-carboxylate (1m)**

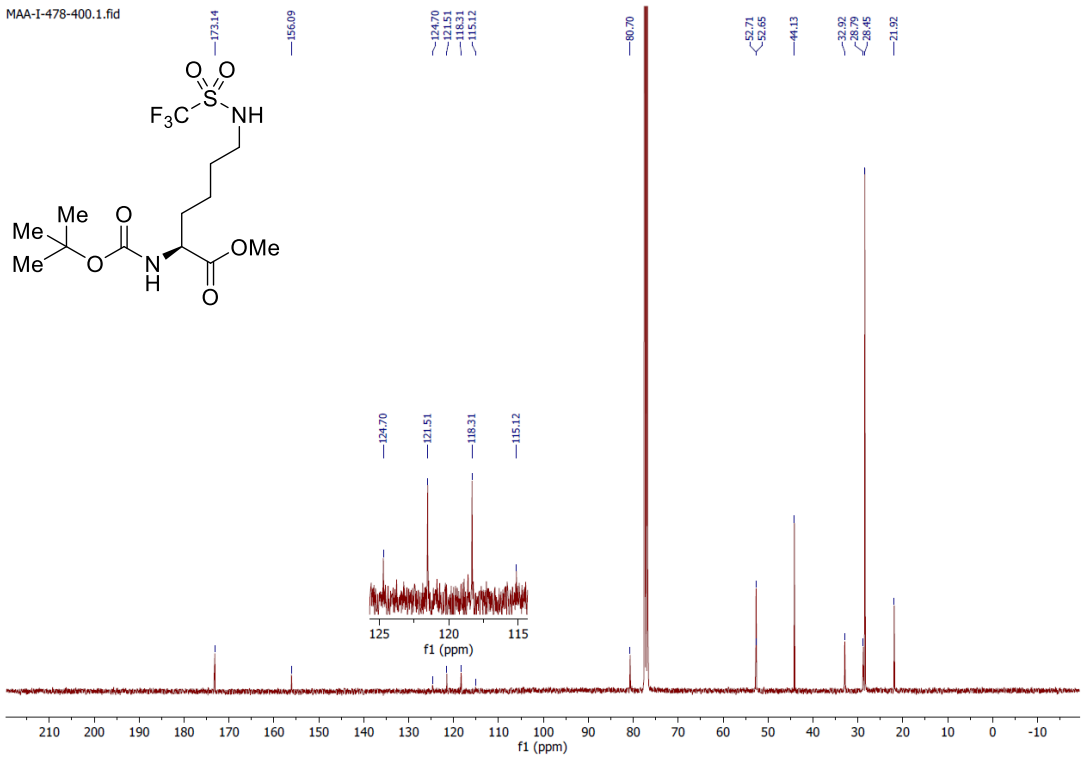


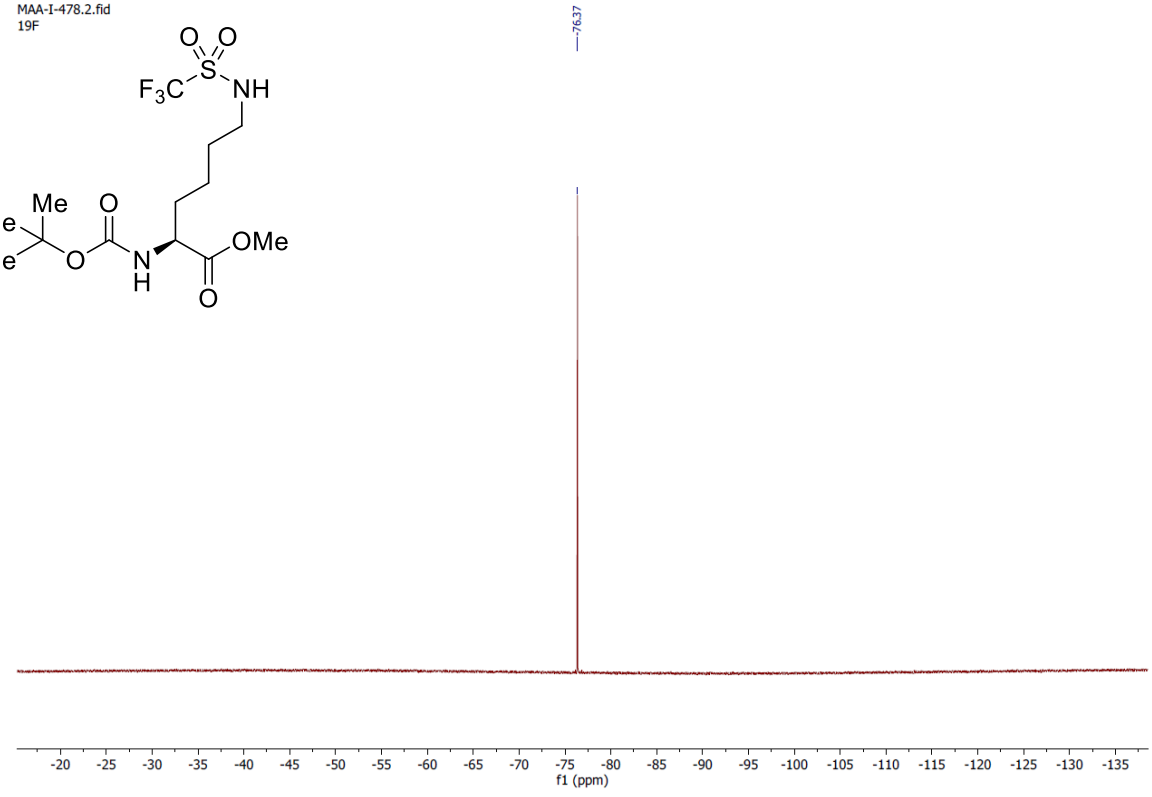




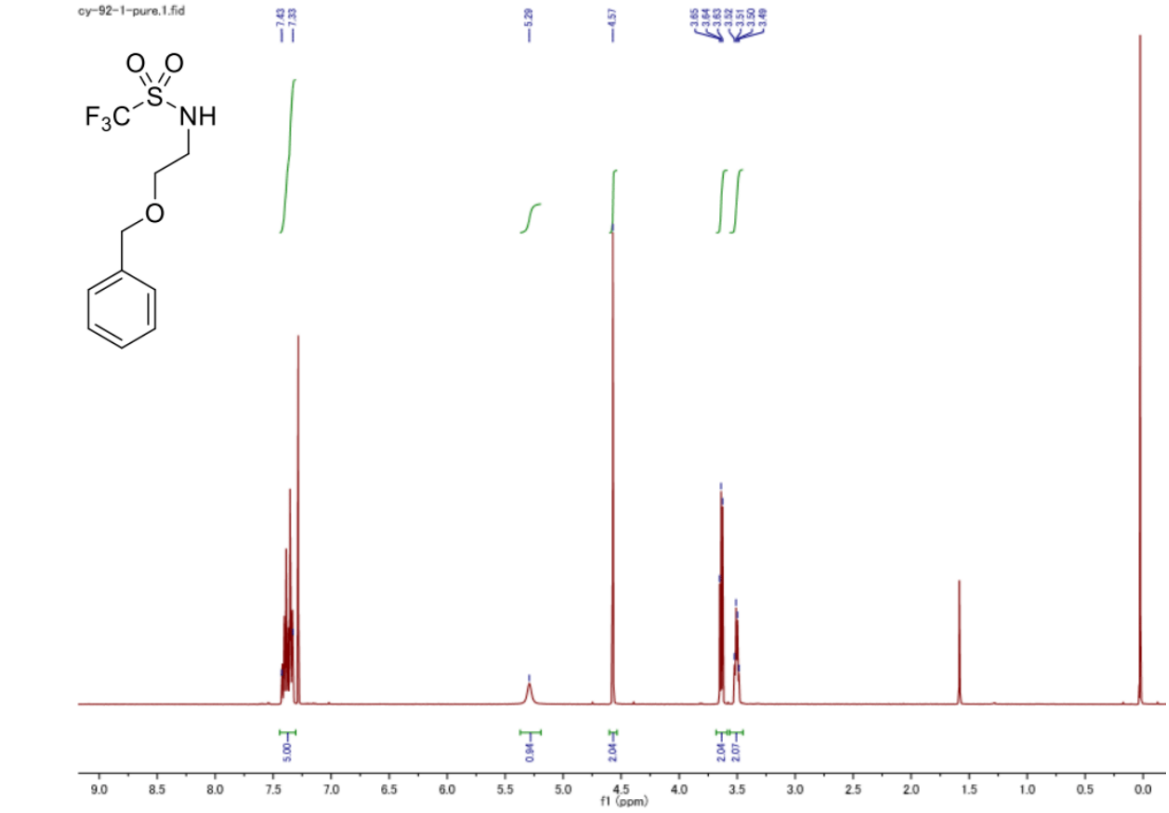
methyl N^2-(tert-butoxycarbonyl)-N^6-((trifluoromethyl)sulfonyl)-L-lysinate (1n)

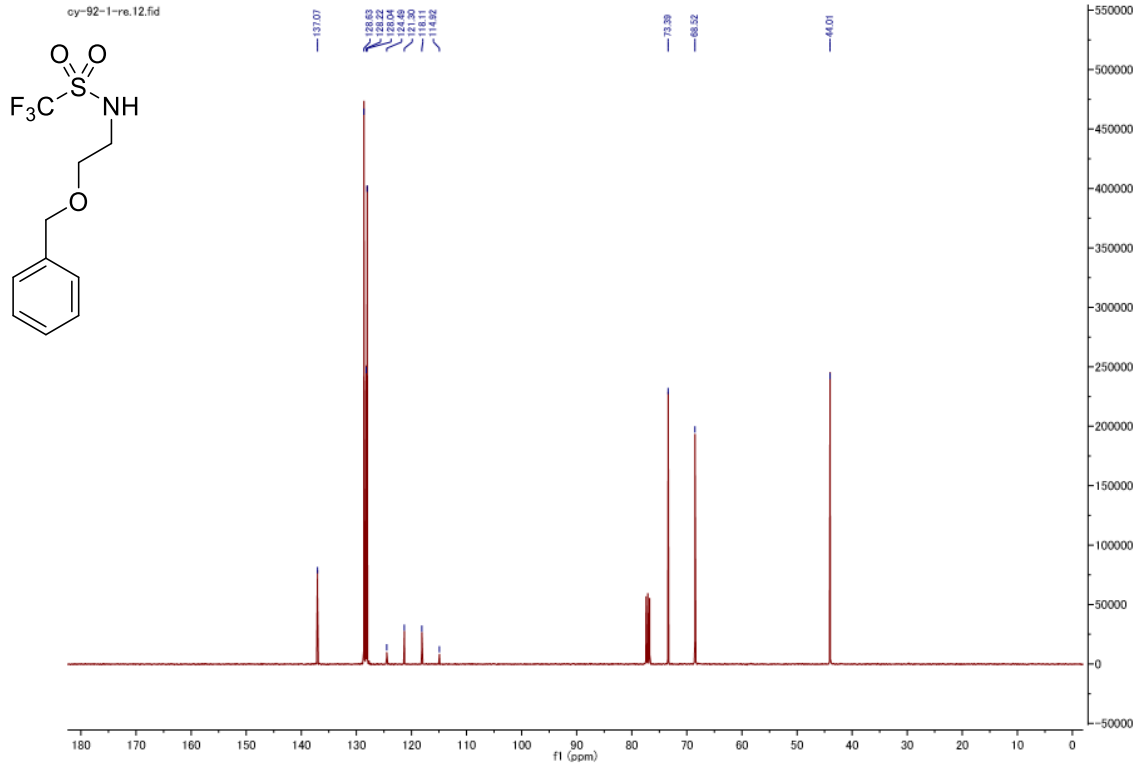


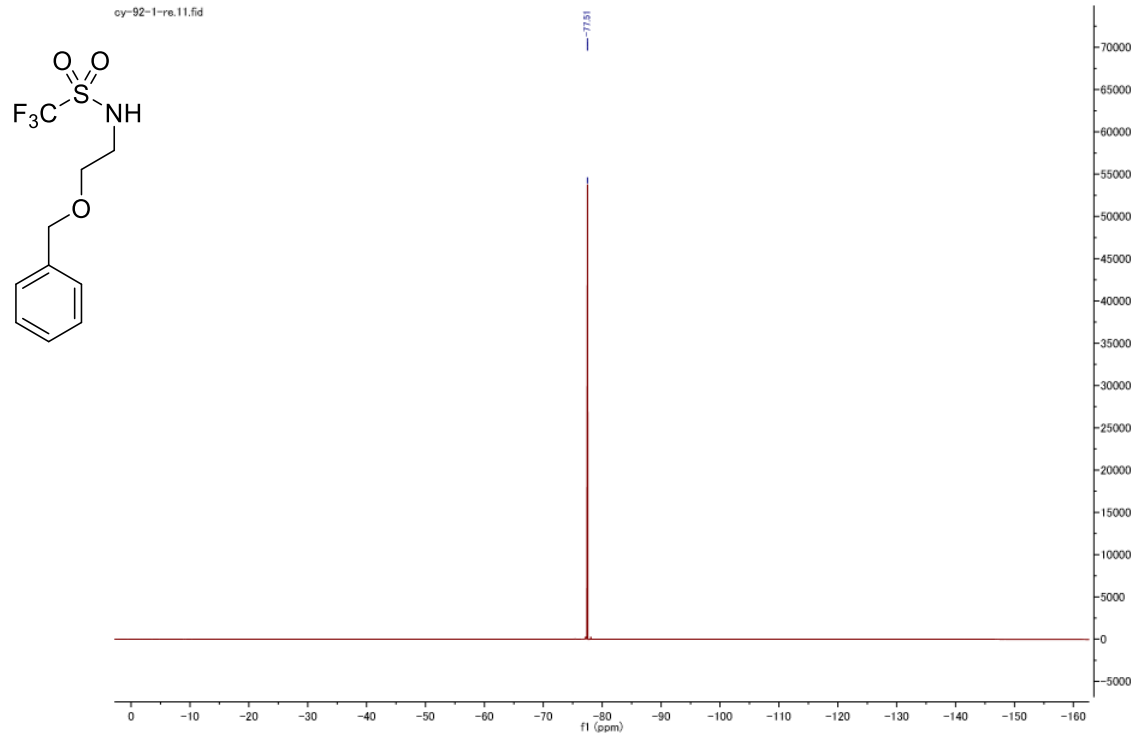

MAA-I-478-400.1.fid
173.14
156.09
124.70
121.51
118.31
115.12
80.70
52.71
52.65
44.13
32.92
28.79
28.45
21.92
f1 (ppm)


MAA-I-478.2.fid
19F
-76.37
f1 (ppm)

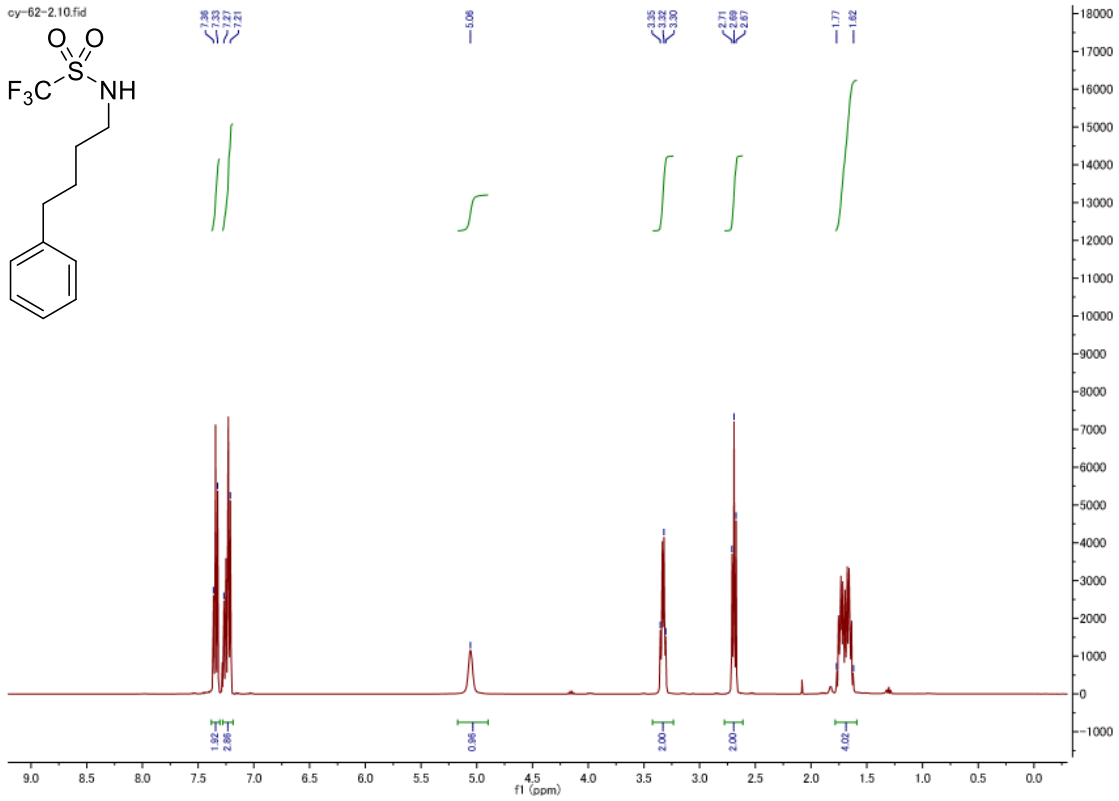
***N*-(2-(benzyloxy)ethyl)-1,1,1-trifluoromethanesulfonamide (1o)**

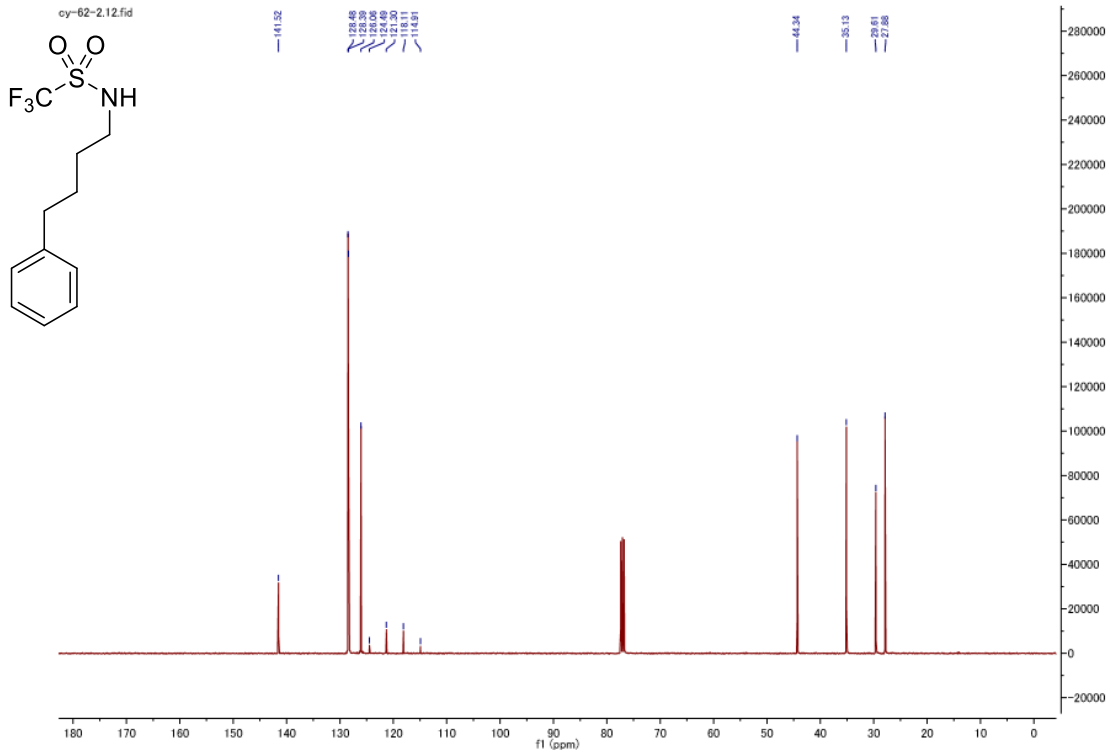


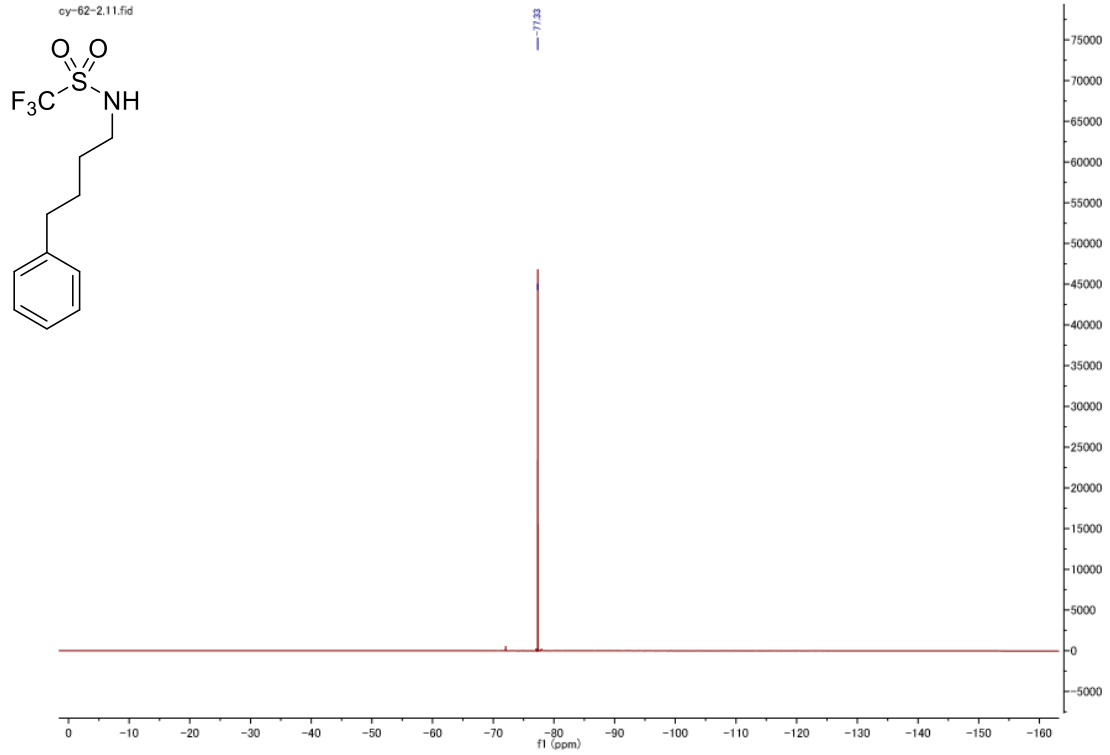




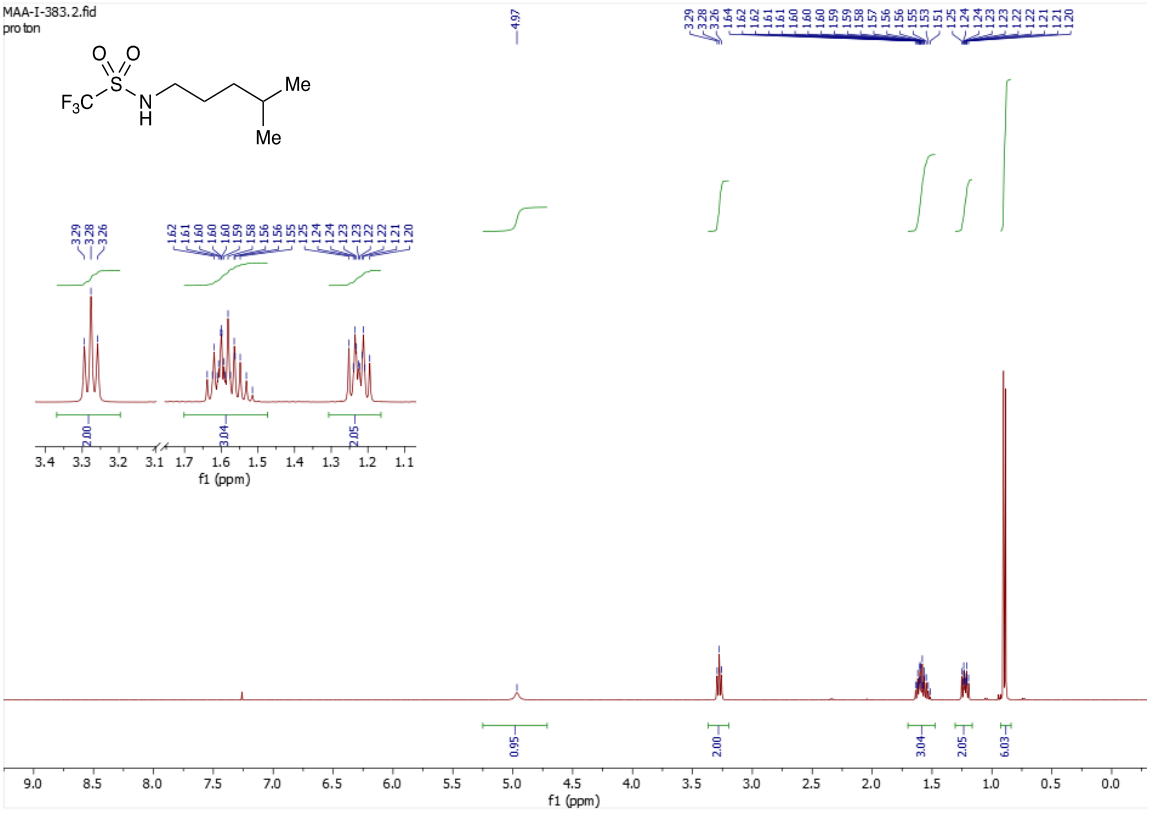
1,1,1-trifluoro-*N*-(4-phenylbutyl)methanesulfonamide (1p)

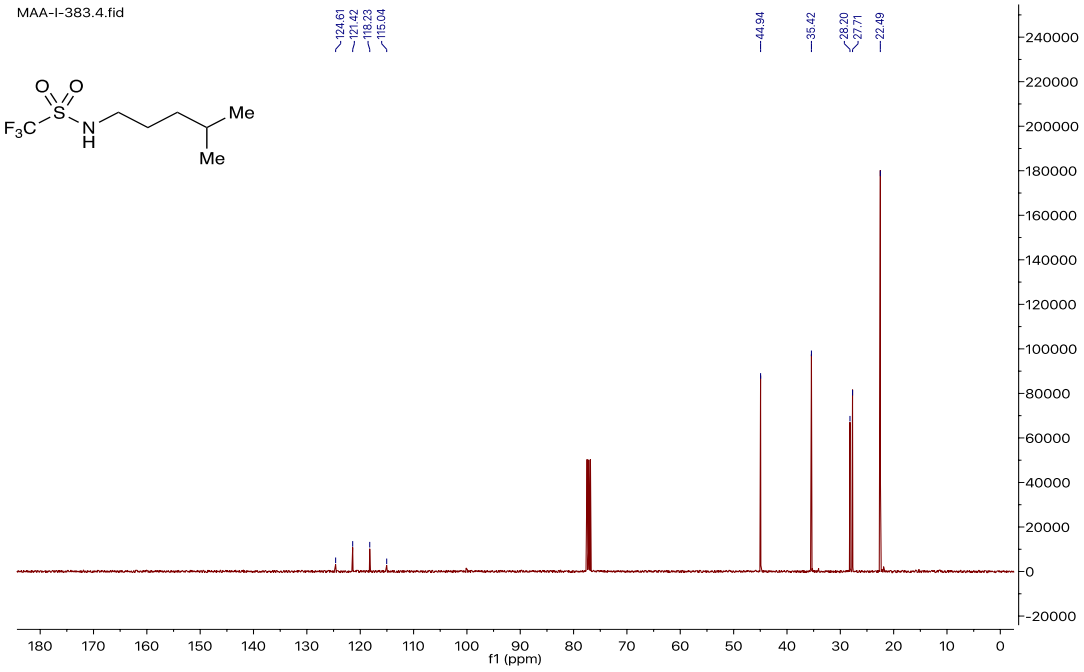


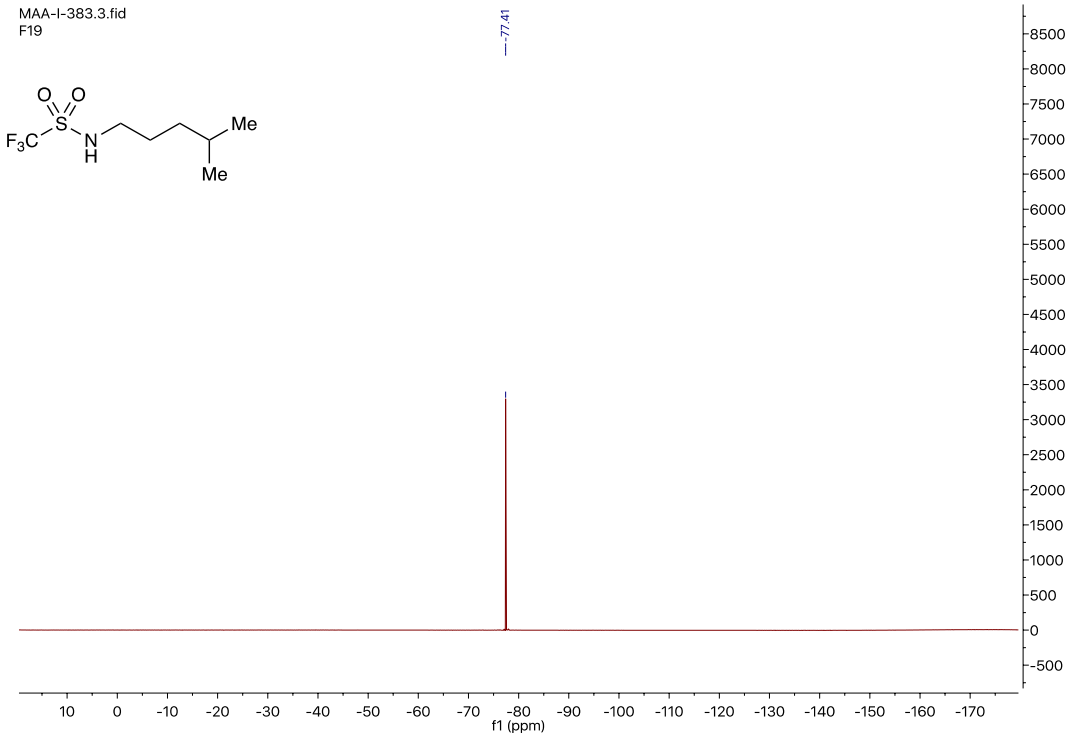

cy-62-2.12.fid
141.52
128.48
128.39
126.08
125.66
121.30
118.11
114.61
44.34
35.13
29.61
27.88
f1 (ppm)


cy-62-2.11.fid
77.33
f1 (ppm)

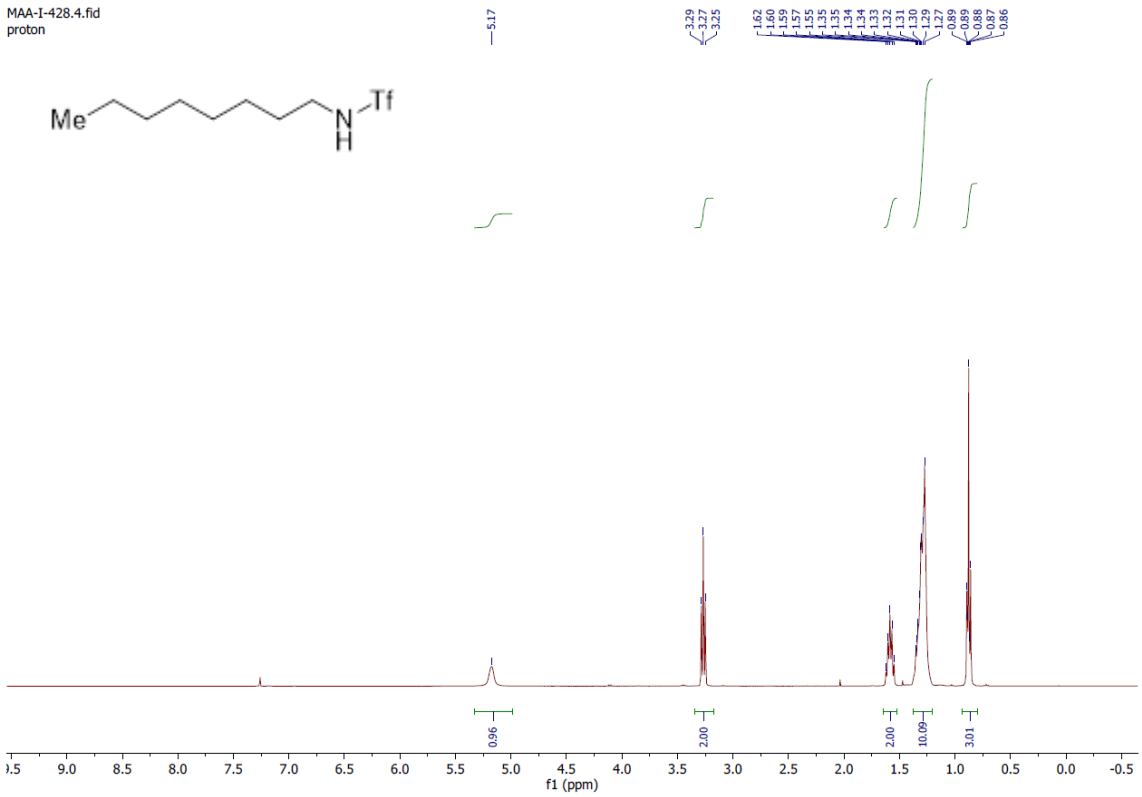
1,1,1-trifluoro-*N*-(4-methylpentyl)methanesulfonamide (1q)



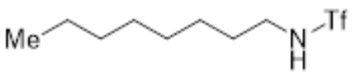




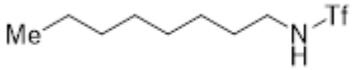
1,1,1-trifluoro-*N*-octylmethanesulfonamide (1r)



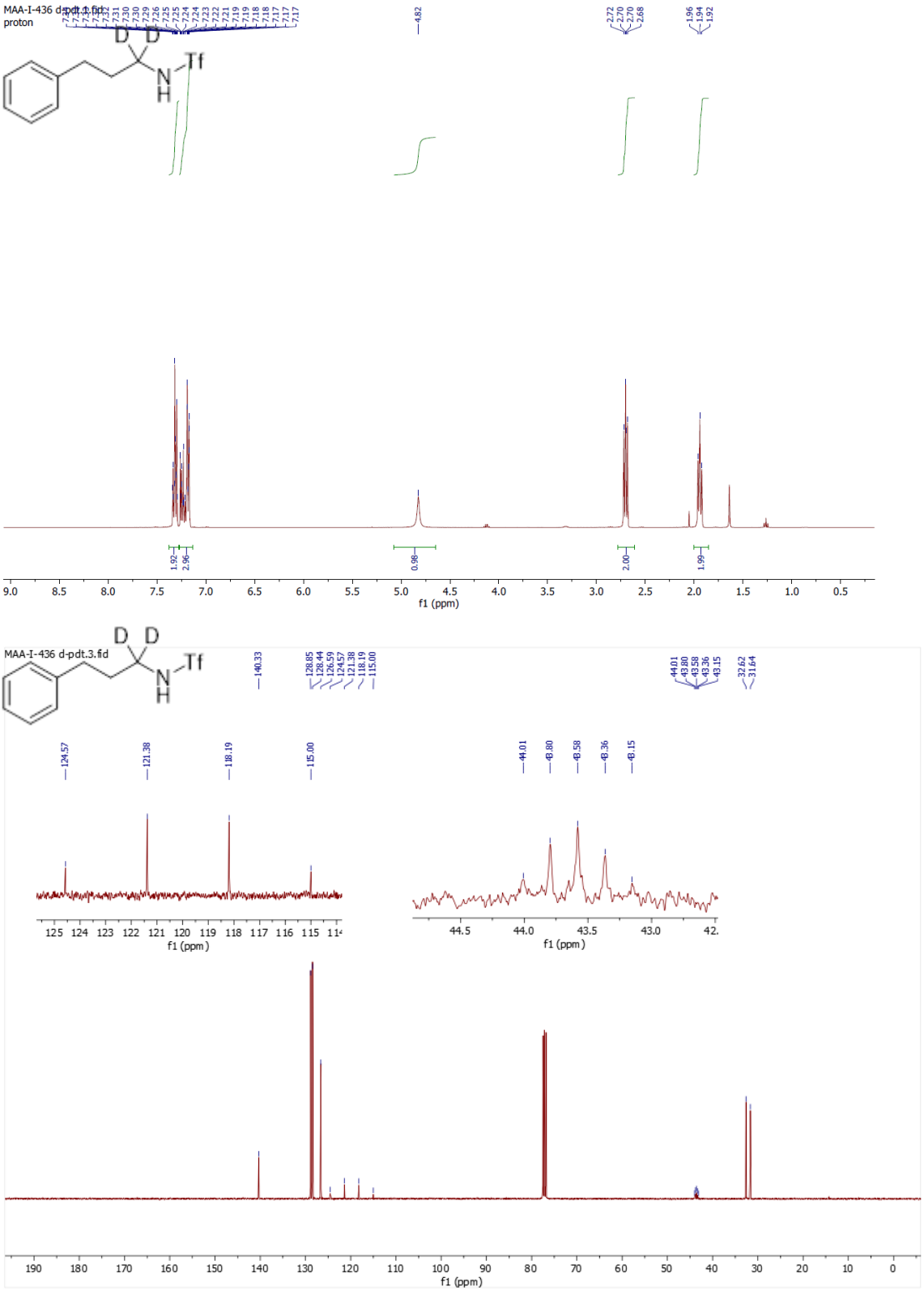
MAA-I-428.6.fid

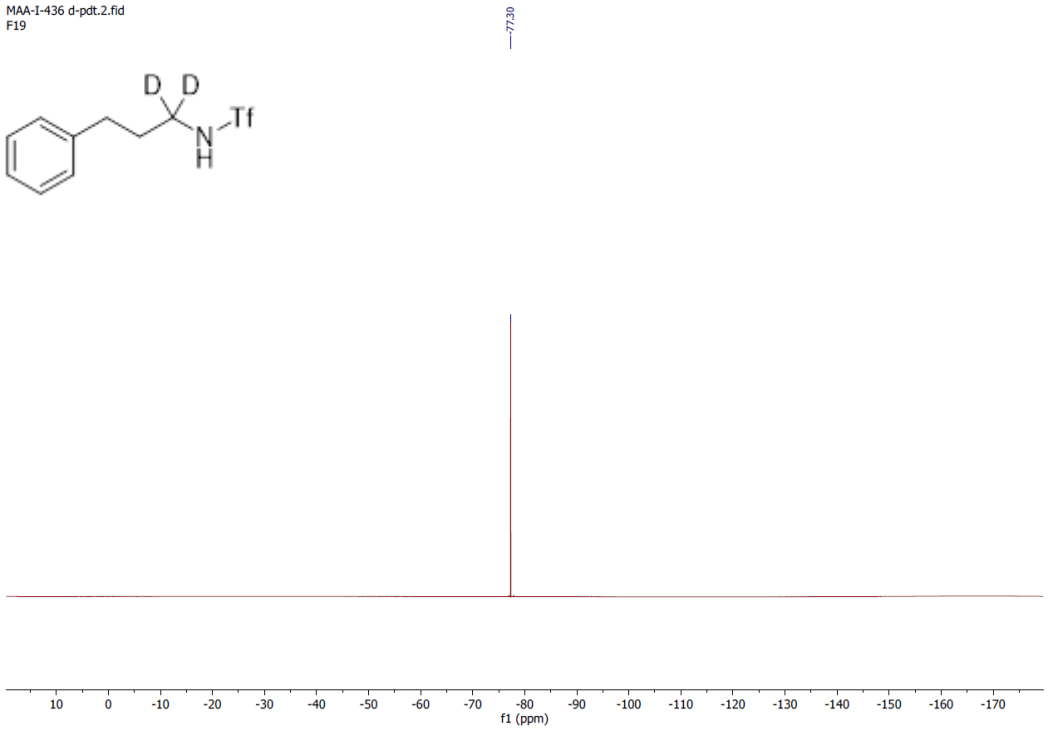


MAA-I-428.5.fid
F19

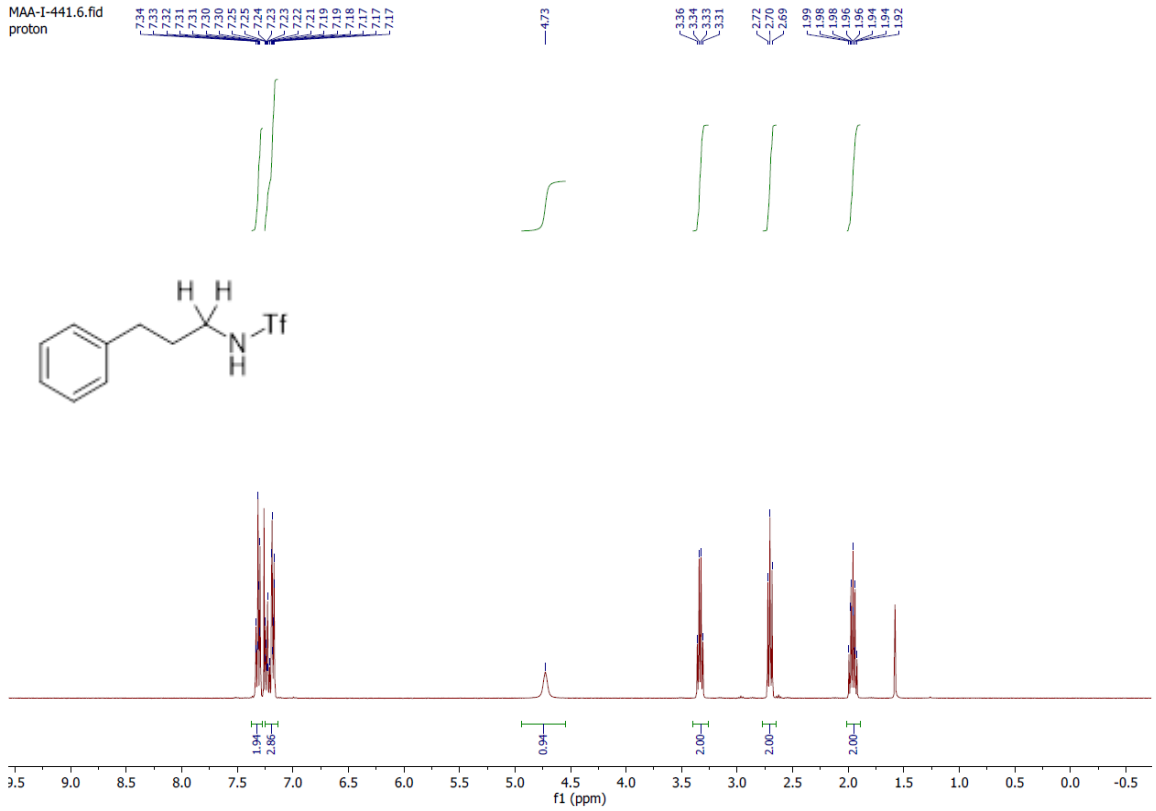


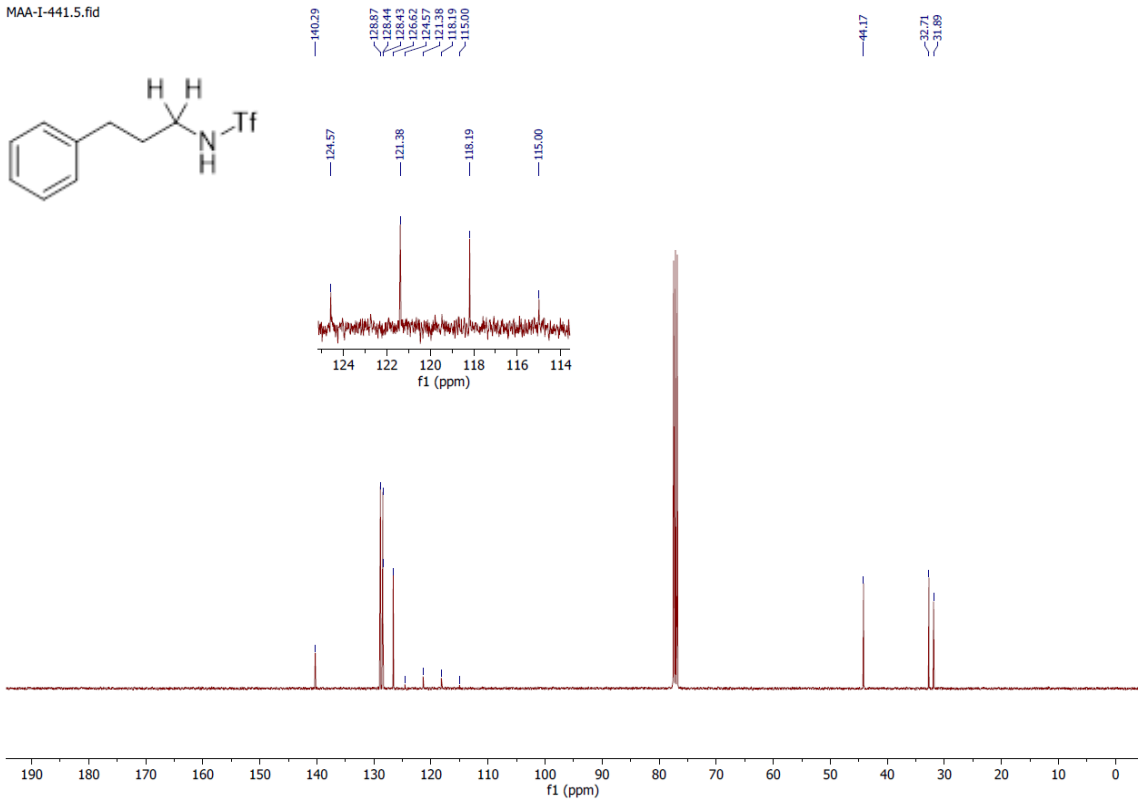
1,1,1-trifluoro-*N*-(3-phenylpropyl-1,1-d_2-)methanesulfonamide (1s-D_2)

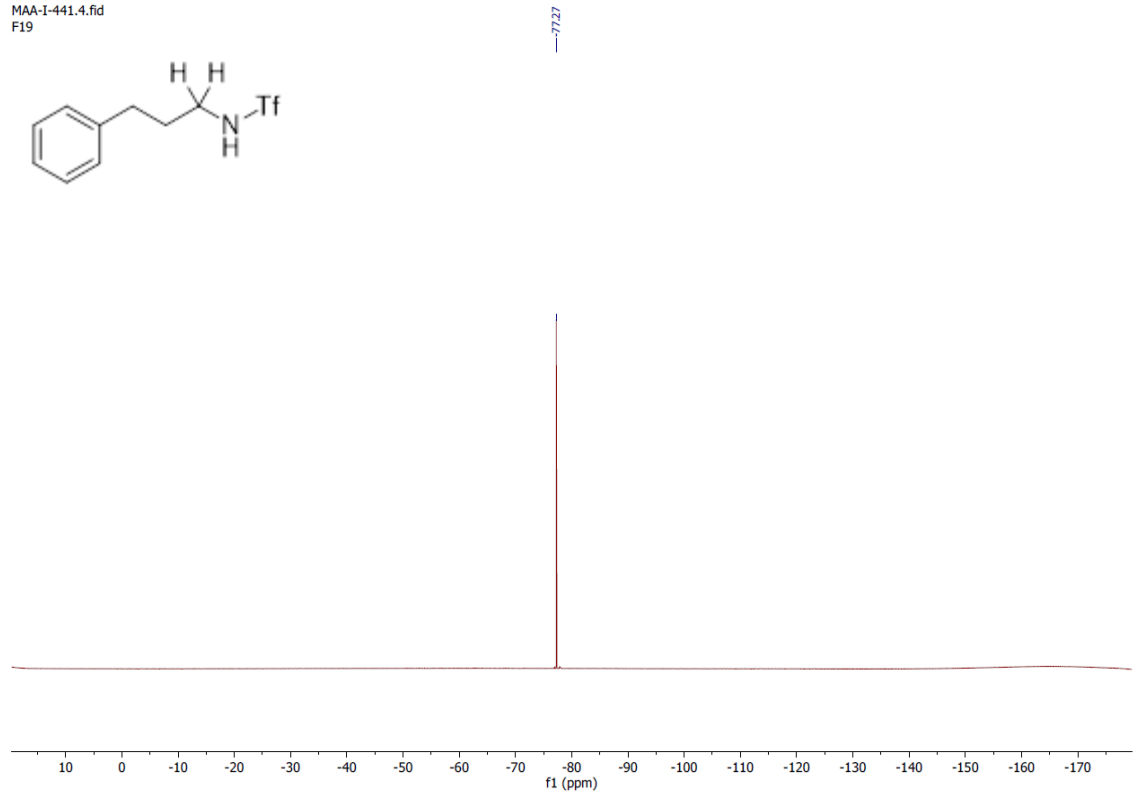




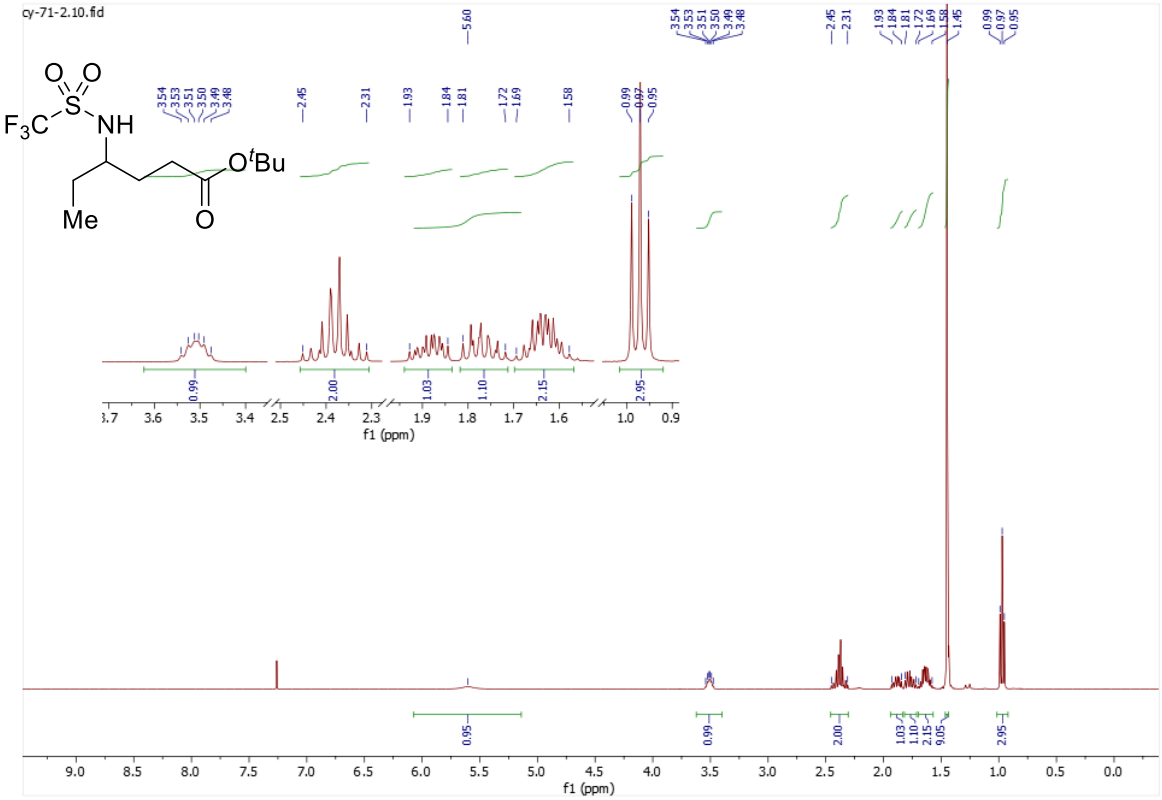
1,1,1-trifluoro-*N*-(3-phenylpropyl)methanesulfonamide (3s-H_2)

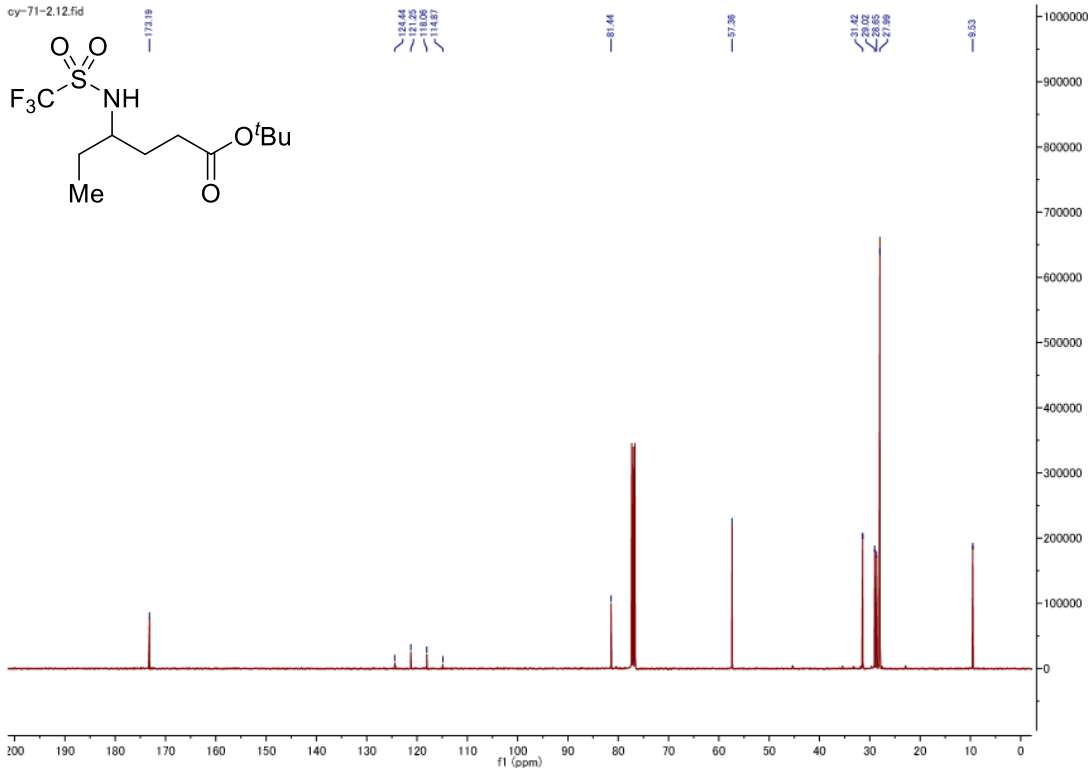


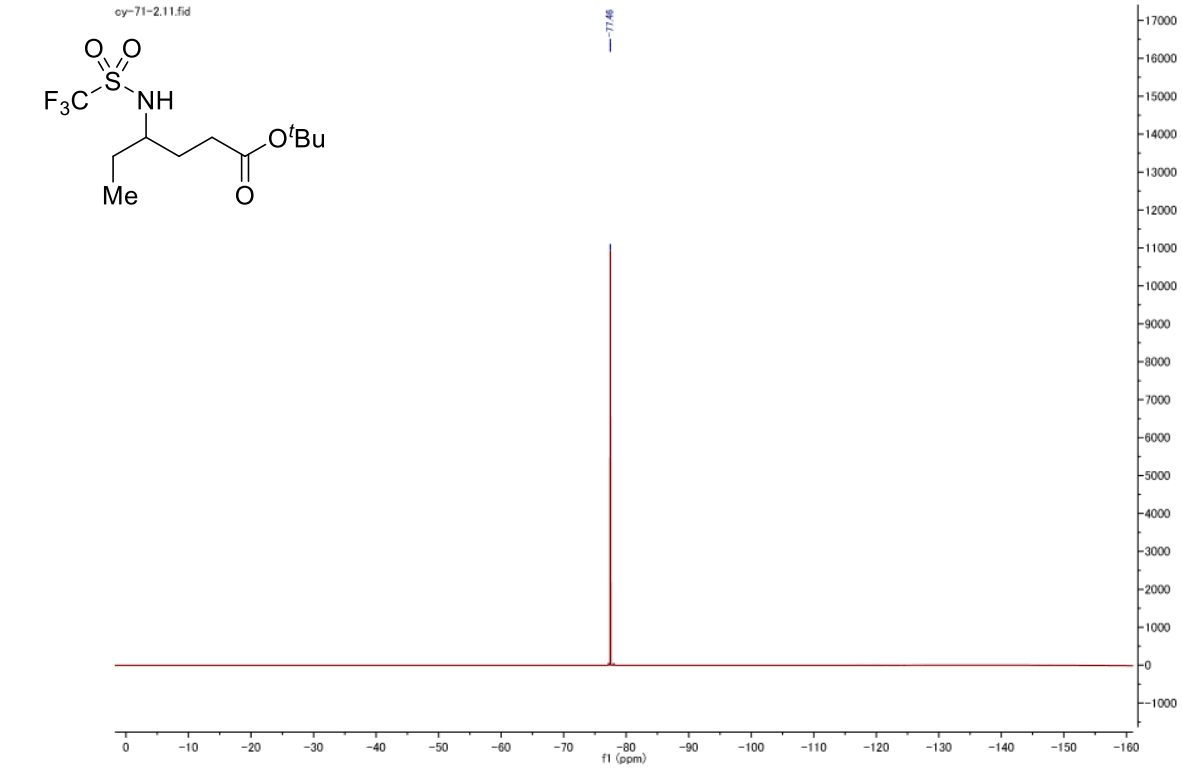

MAA-I-441.5.fid
140.29
128.87
128.44
128.43
126.62
124.57
121.38
118.19
115.00
44.17
32.71
31.89
H H
N
H
Tf
124.57
121.38
118.19
115.00
124 122 120 118 116 114
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MAA-I-441.4.fid
F19
-77.27
H H
N
H
Tf
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

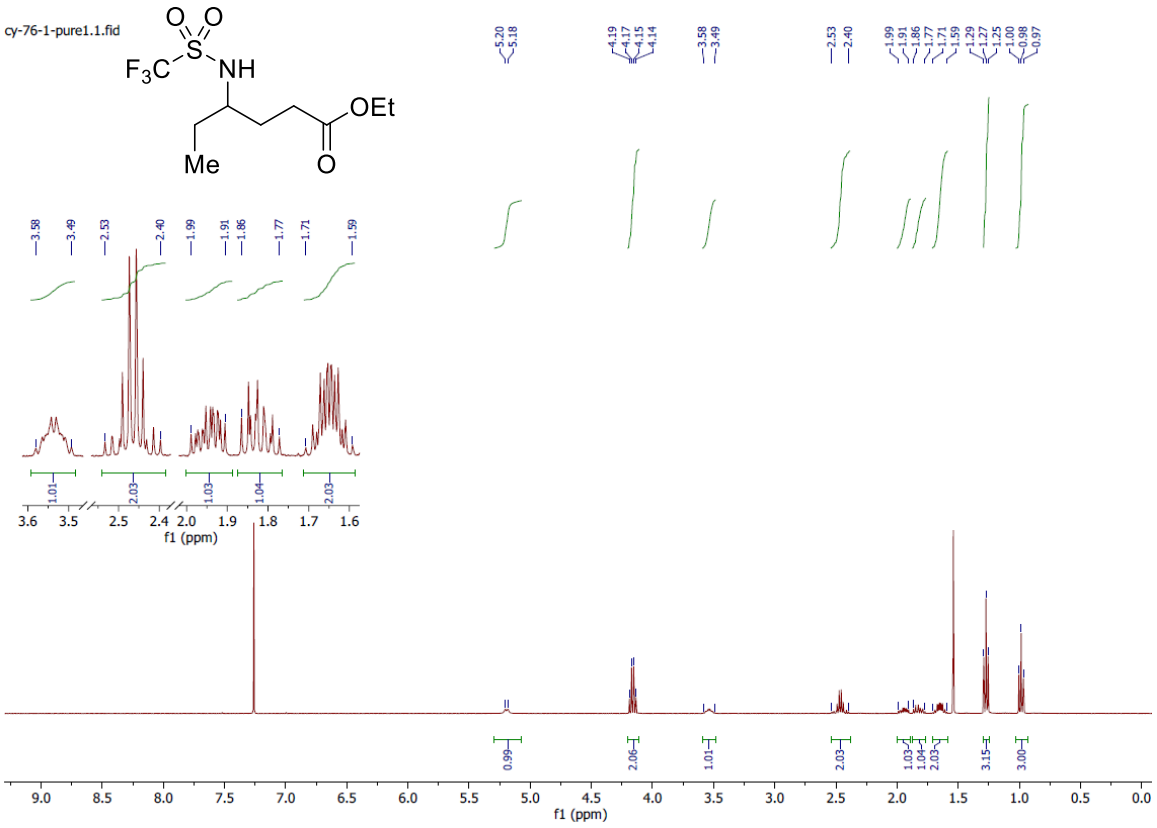
***tert*-butyl 4-((trifluoromethyl)sulfonamido)hexanoate (3aa)**

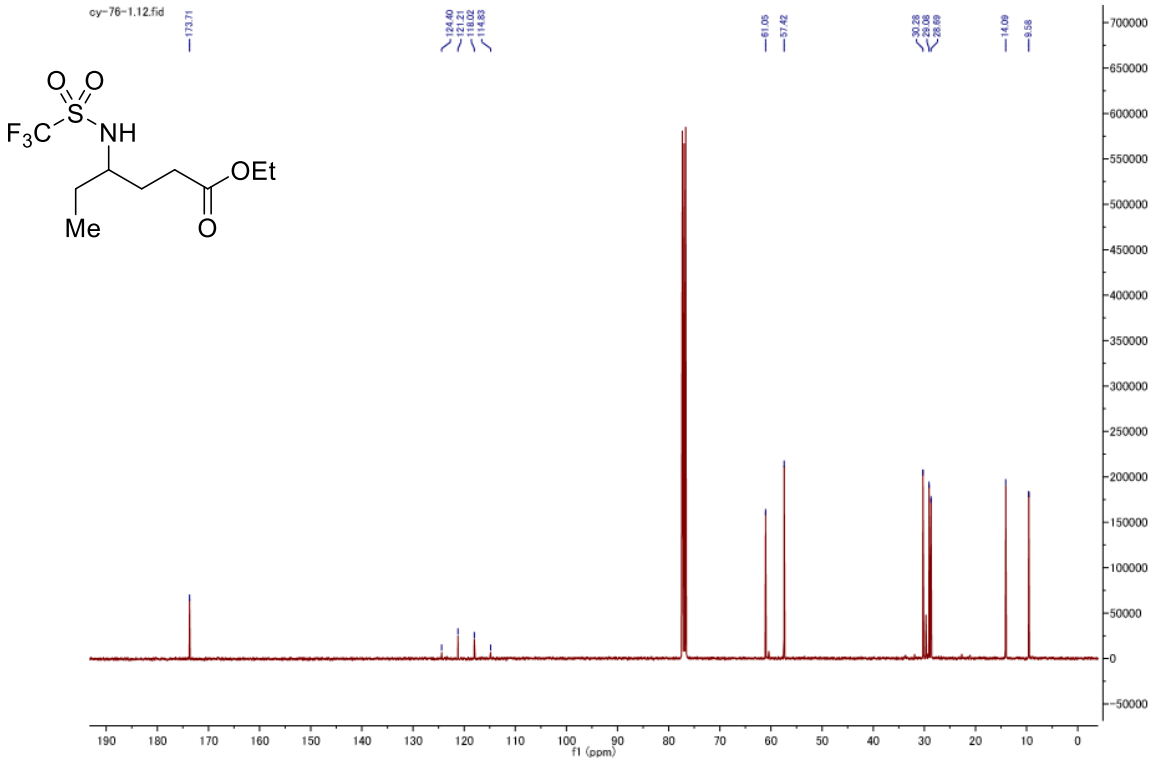


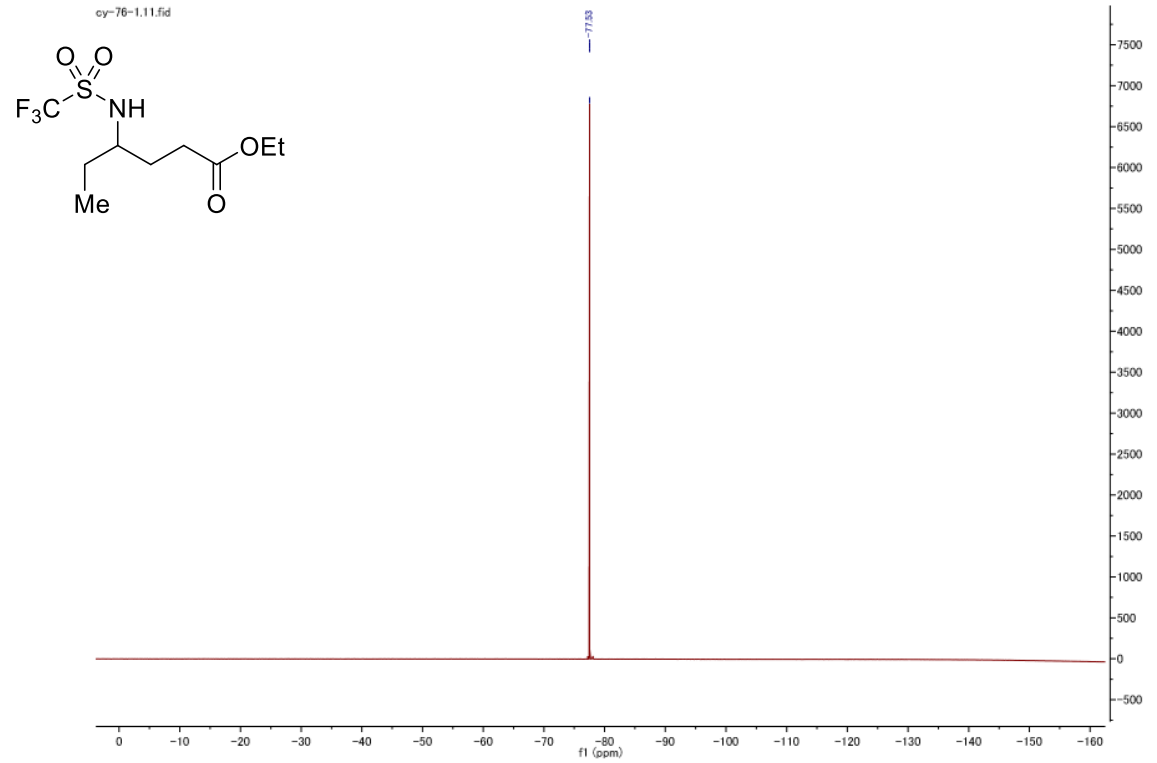




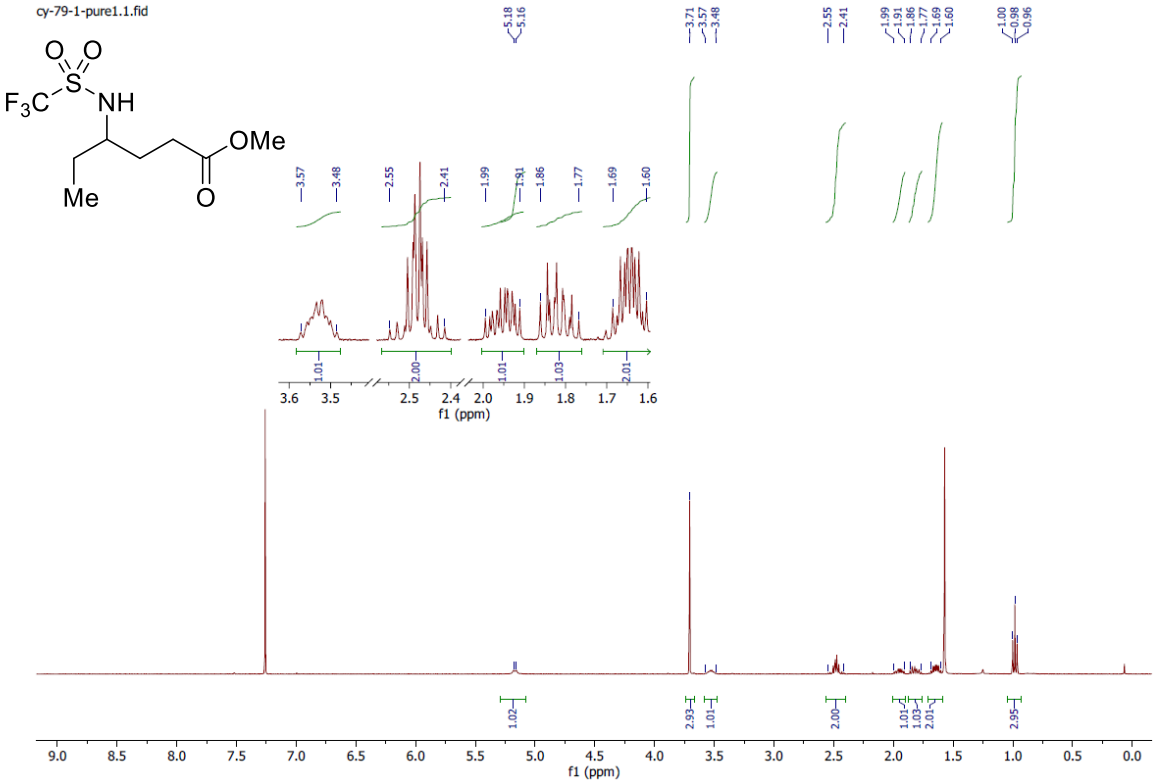
ethyl 4-((trifluoromethyl)sulfonamido)hexanoate (3ab)

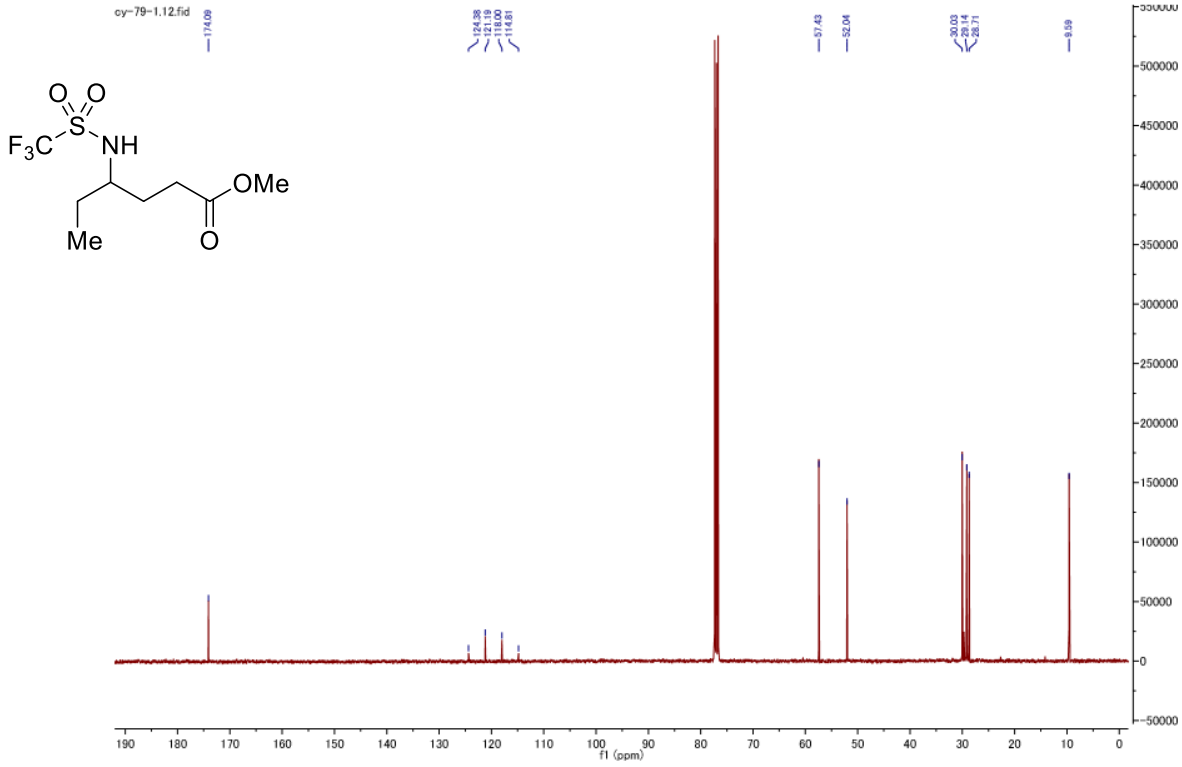


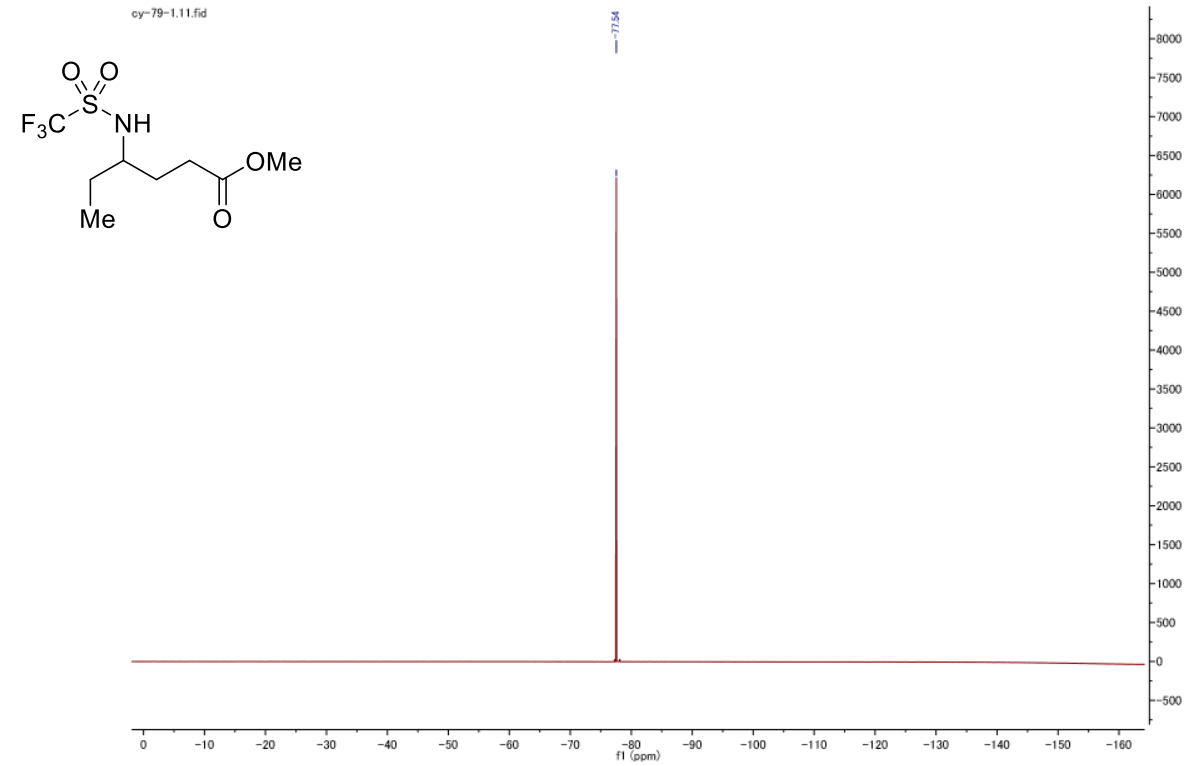

cy-76-1.12.fid
173.71
124.40
121.21
118.02
114.83
61.05
57.42
30.28
29.06
28.69
14.09
8.58
O
O
S
F3C
NH
OEt
Me
O
f1 (ppm)


cy-76-1.11.fid
-77.53
O
O
S
F3C
NH
OEt
Me
O
f1 (ppm)

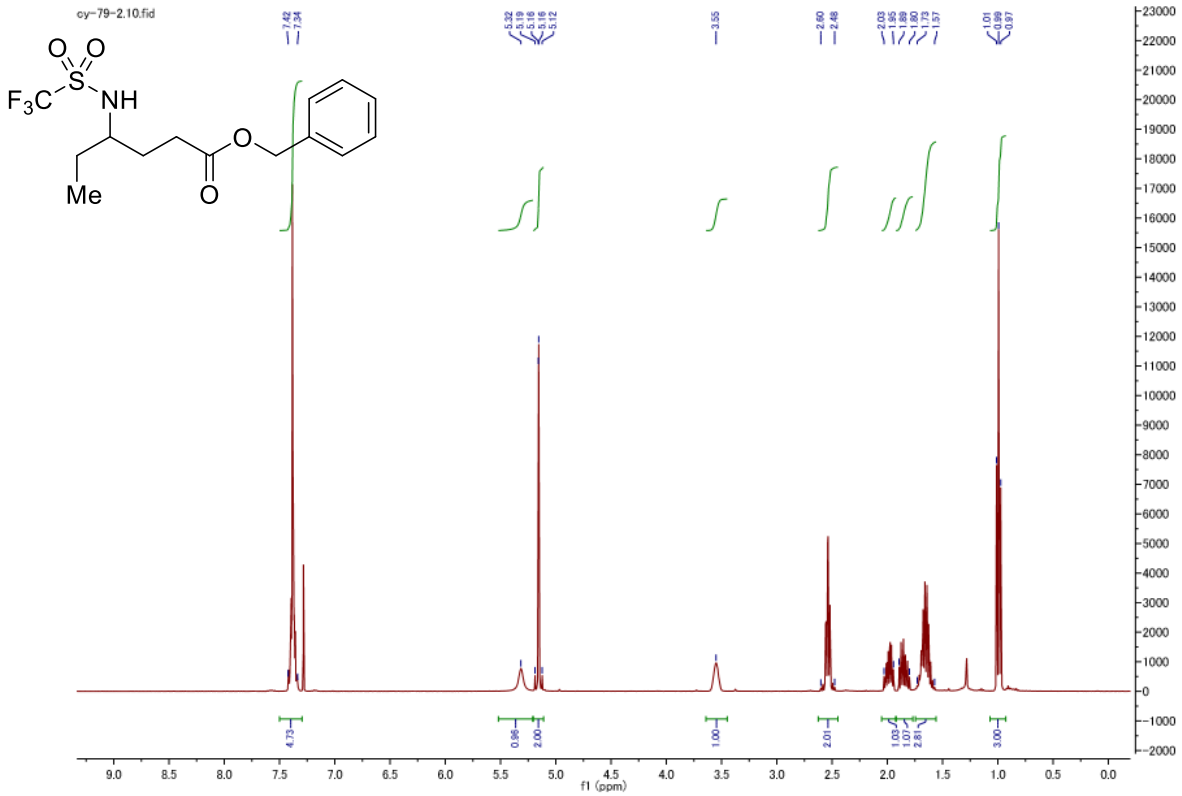
methyl 4-((trifluoromethyl)sulfonamido)hexanoate (3ac)

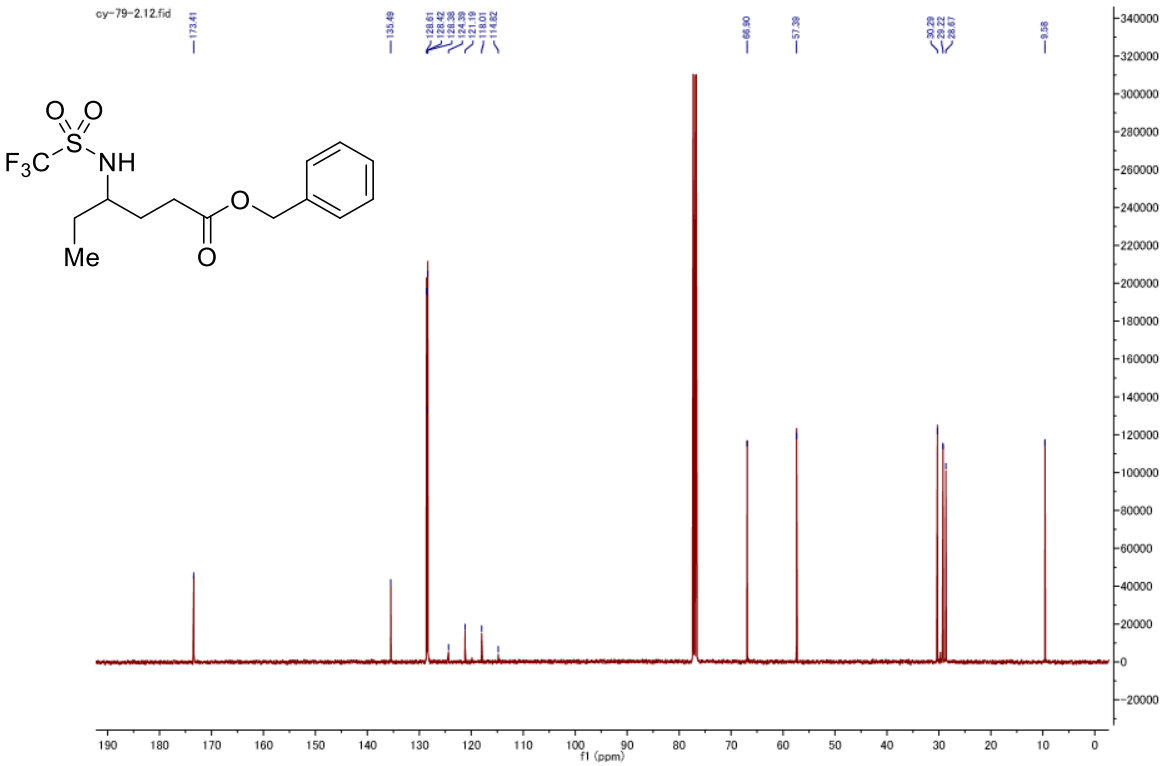


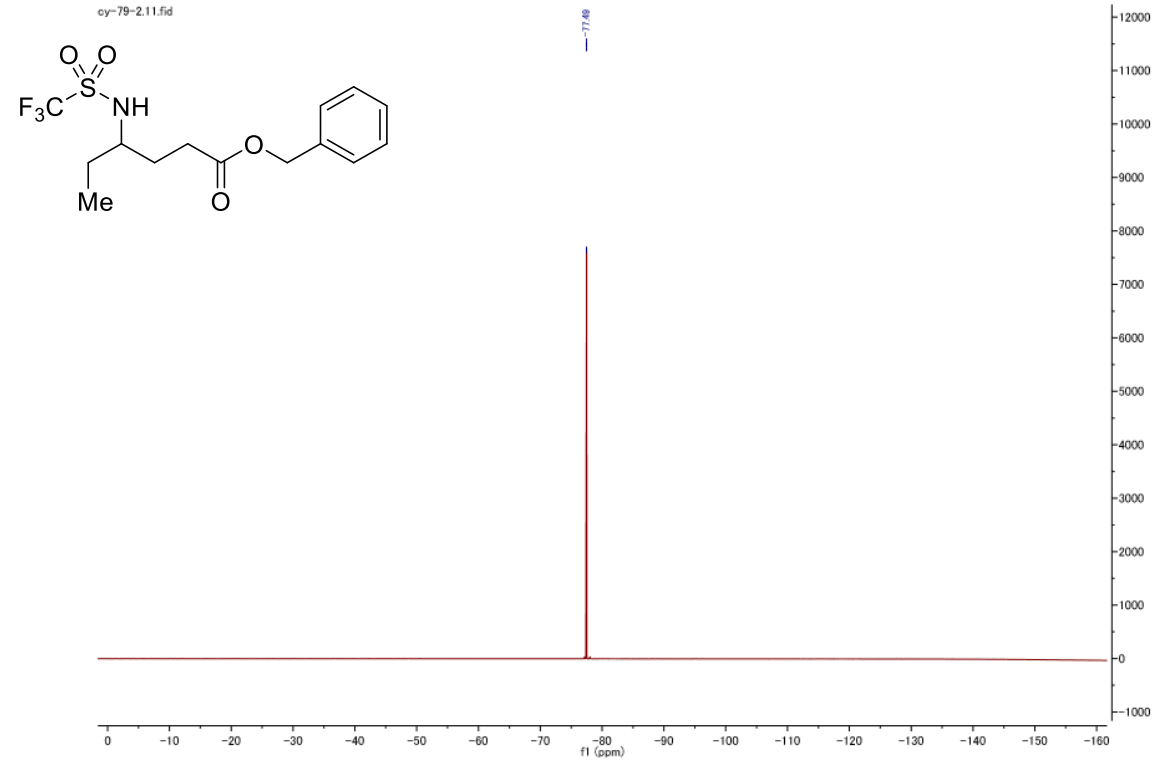




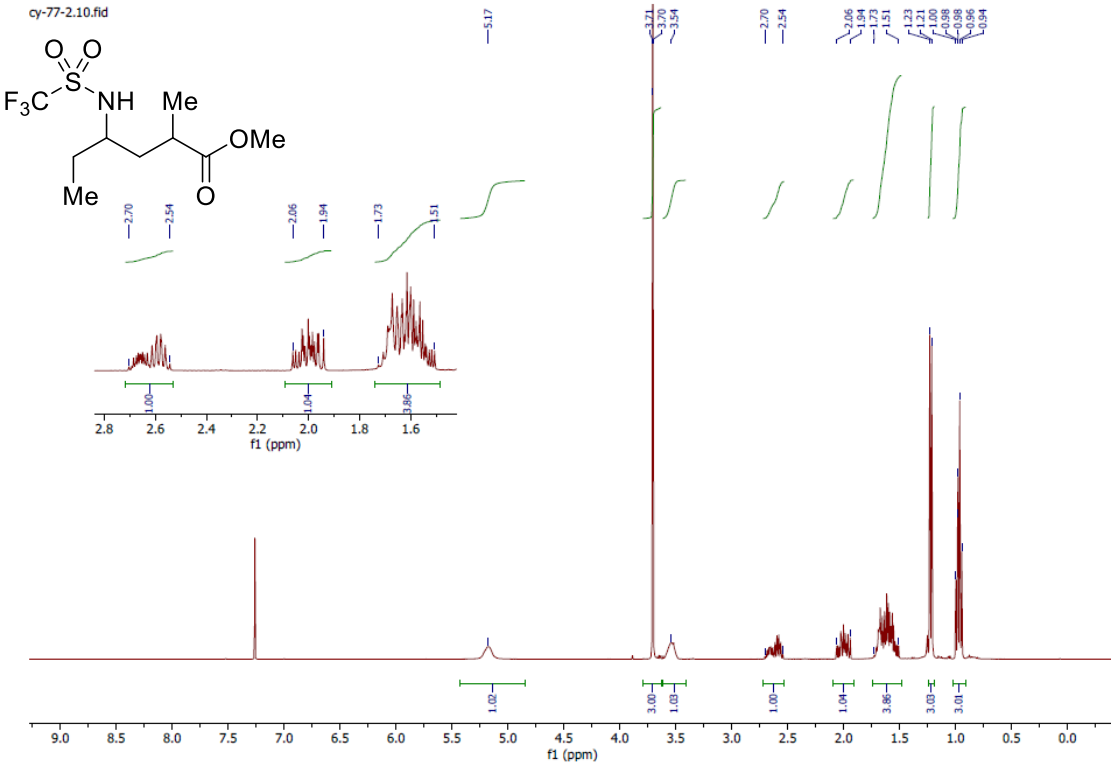
benzyl 4-((trifluoromethyl)sulfonamido)hexanoate (3ad)

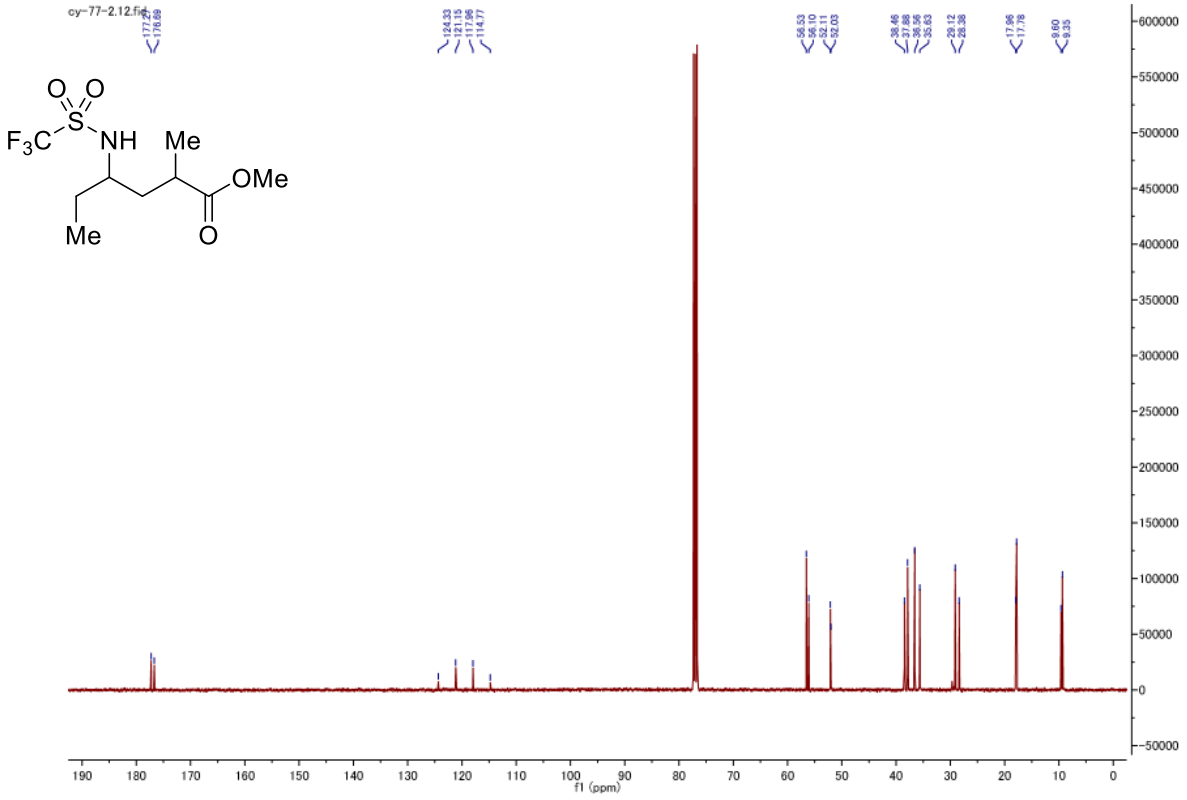


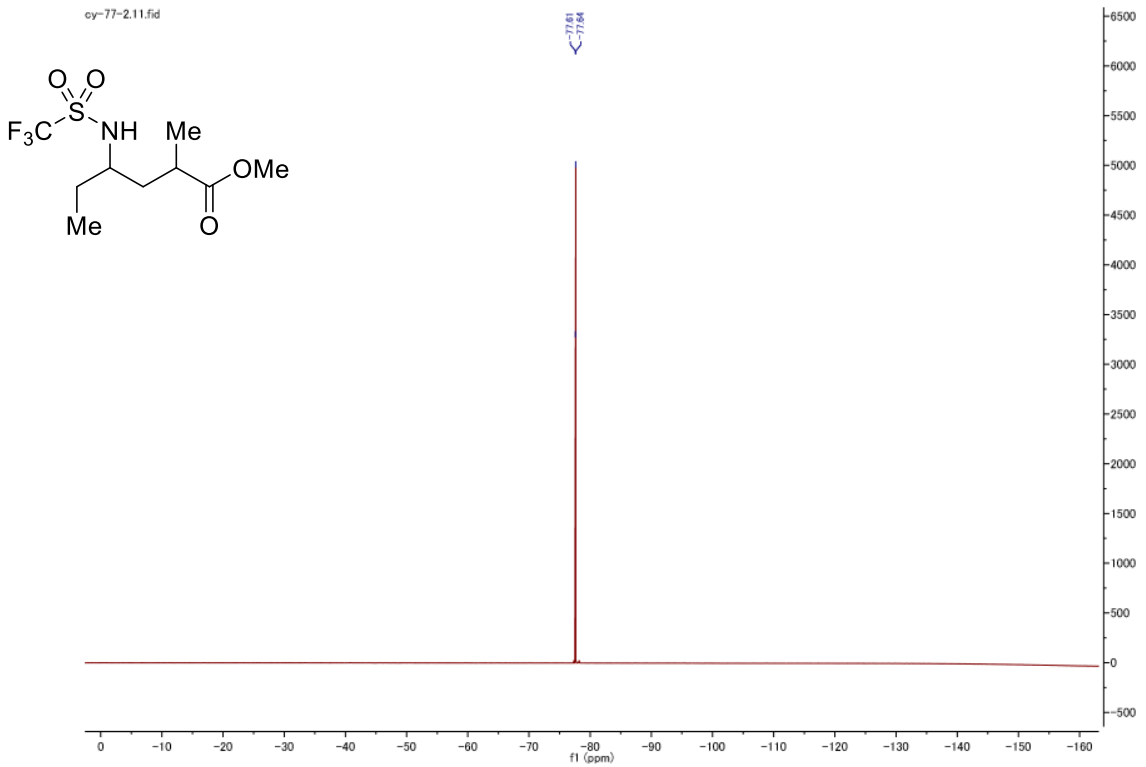

cy-79-2.12.fid
O
O
S
F3C
NH
O
Me
O
f1 (ppm)


cy-79-2.11.fid
O
O
S
F3C
NH
O
Me
O
f1 (ppm)

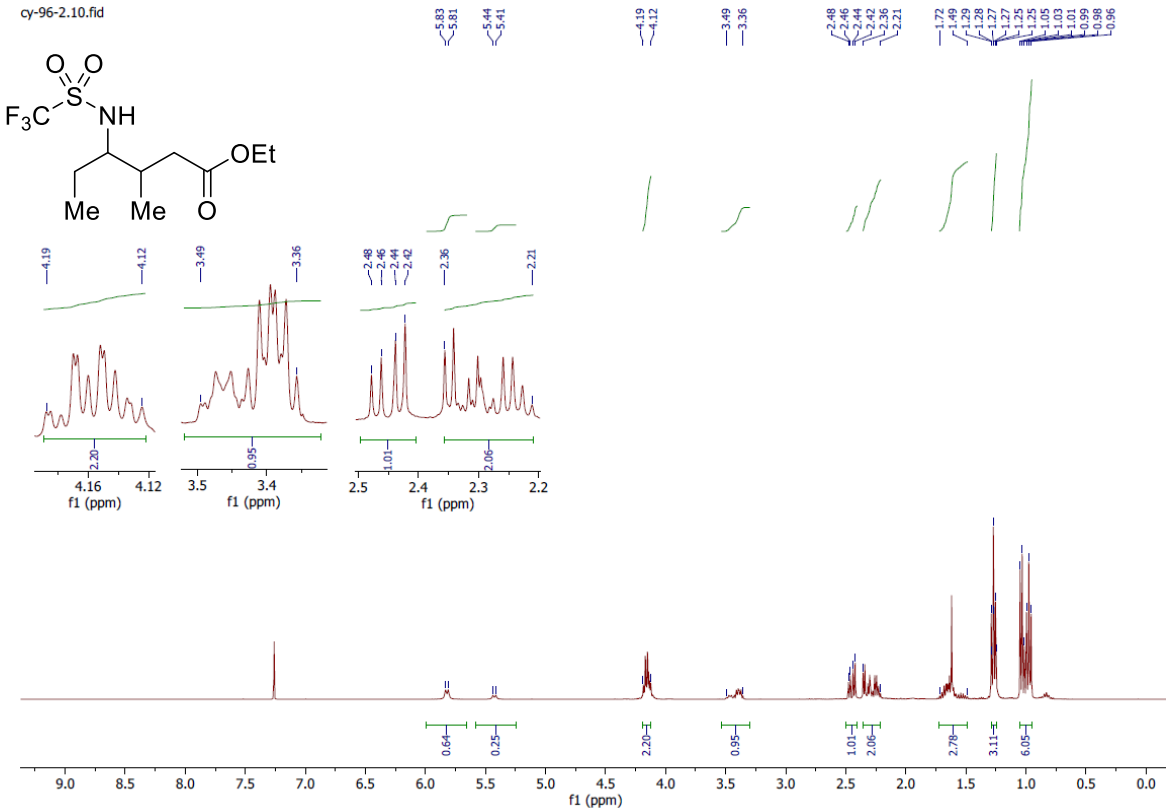
methyl 2-methyl-4-((trifluoromethyl)sulfonamido)hexanoate (3ae)

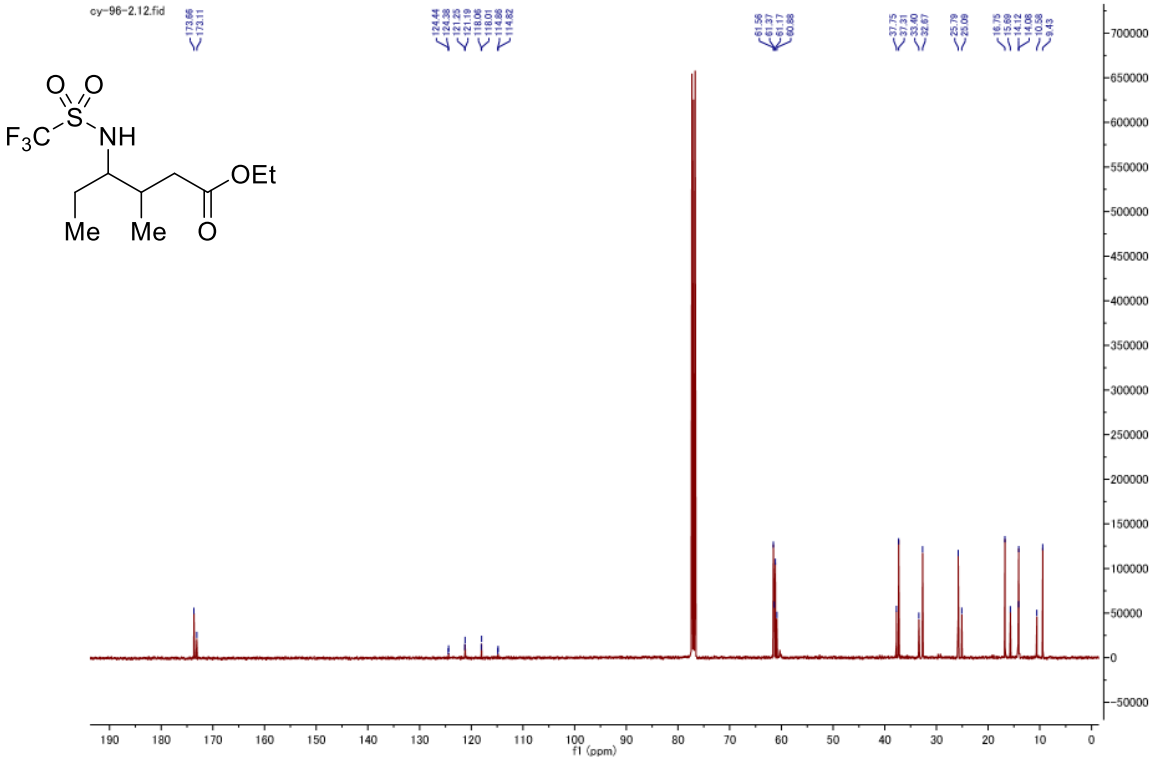


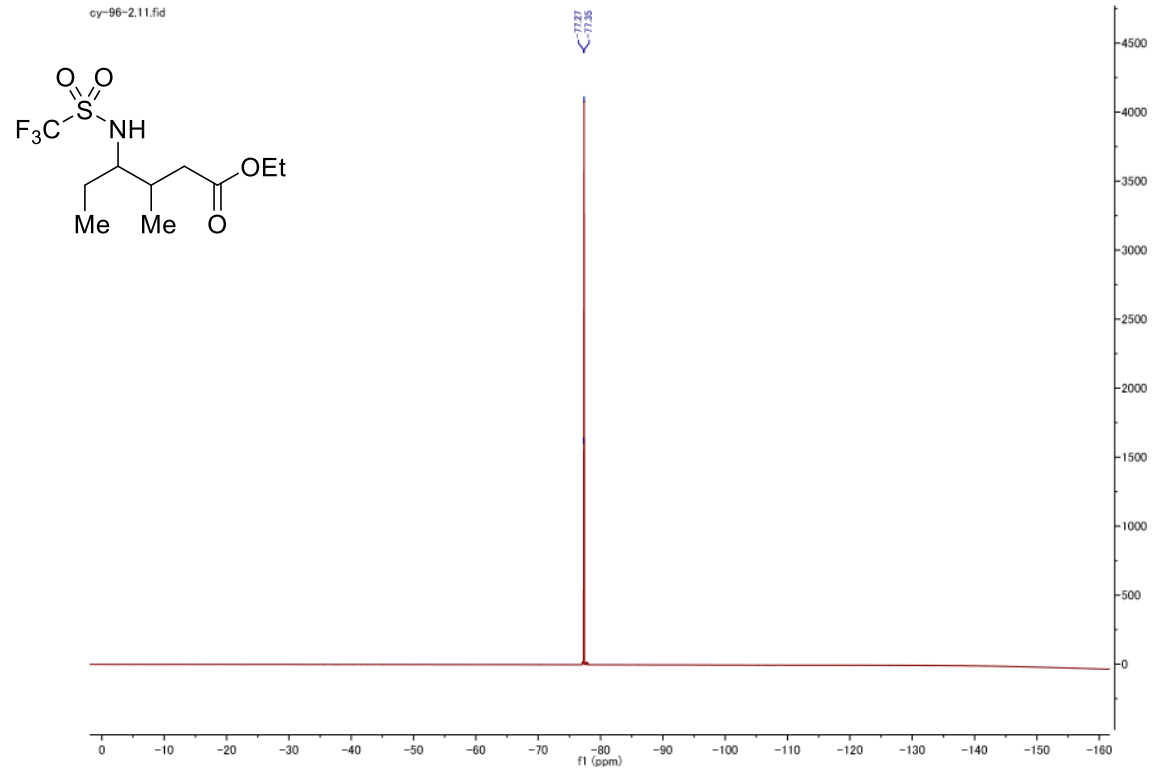




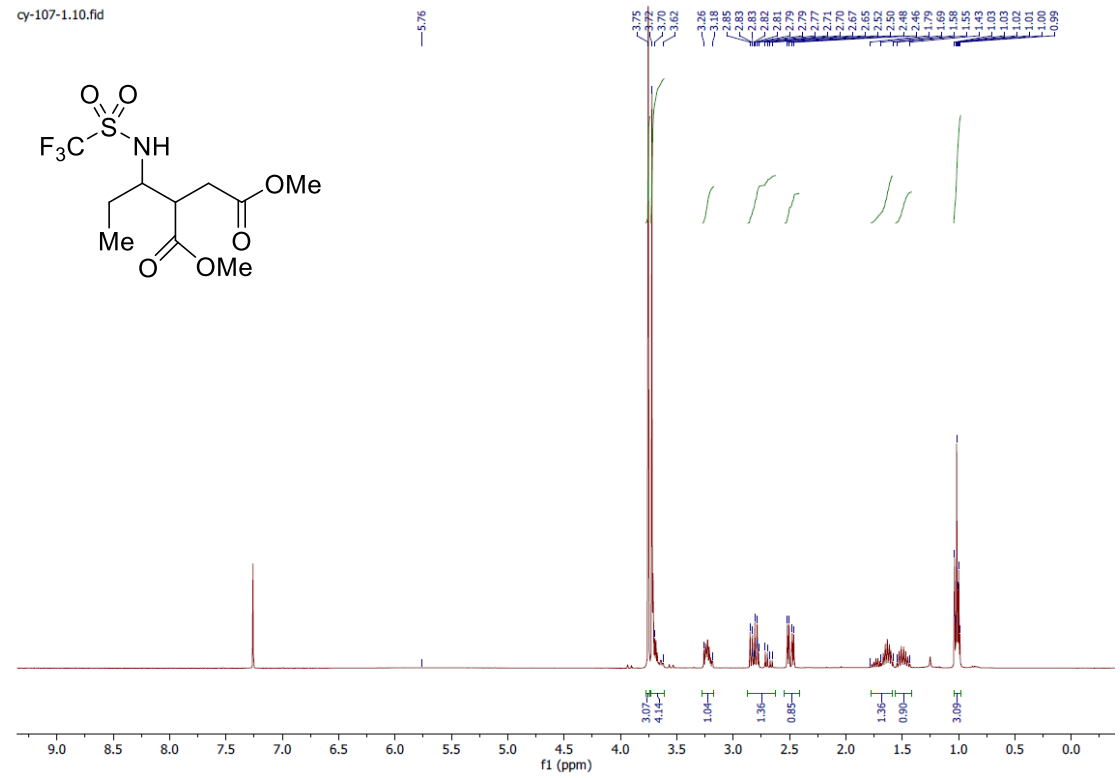
ethyl 3-methyl-4-((trifluoromethyl)sulfonamido)hexanoate (3af)

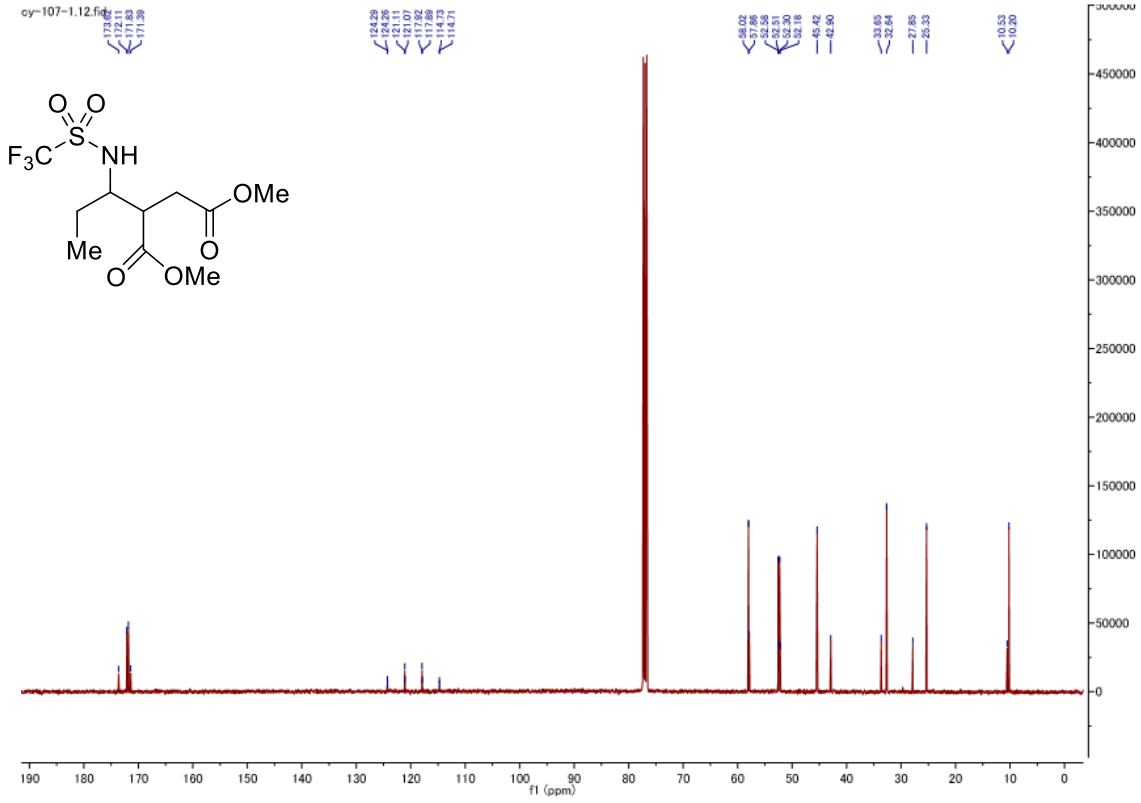


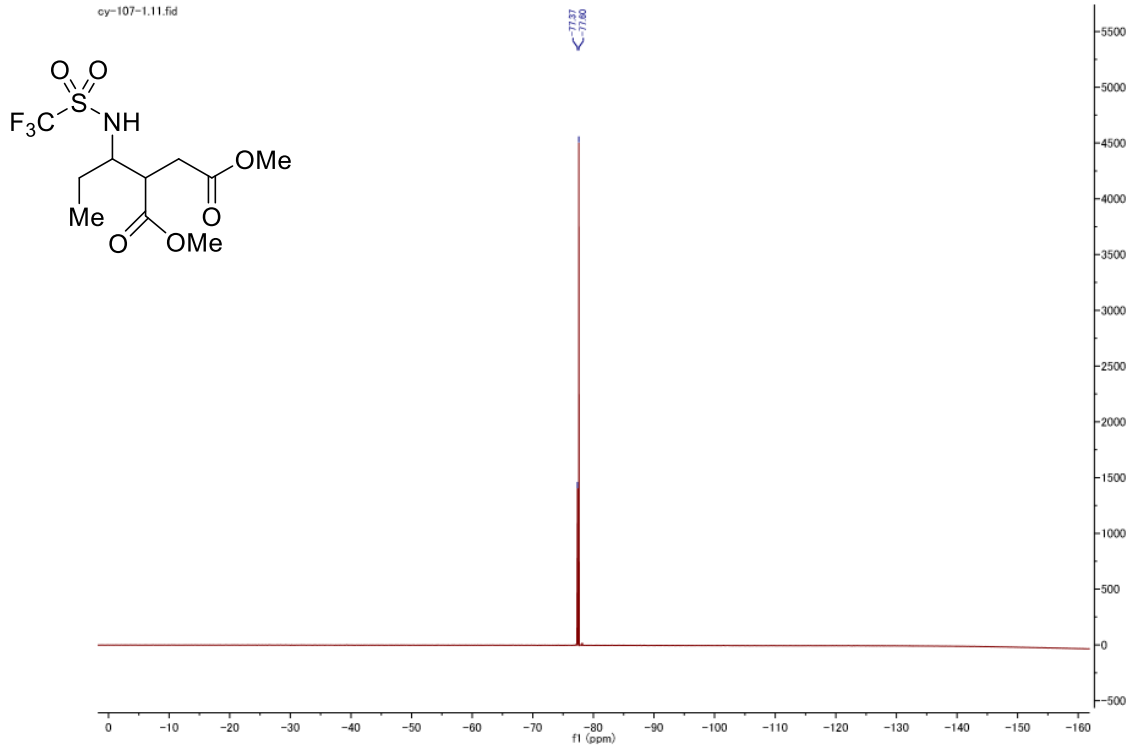

cy-96-2.12.fid
O
O
S
F3C
NH
OEt
Me
Me
O
f1 (ppm)


cy-96-2.11.fid
O
O
S
F3C
NH
OEt
Me
Me
O
f1 (ppm)

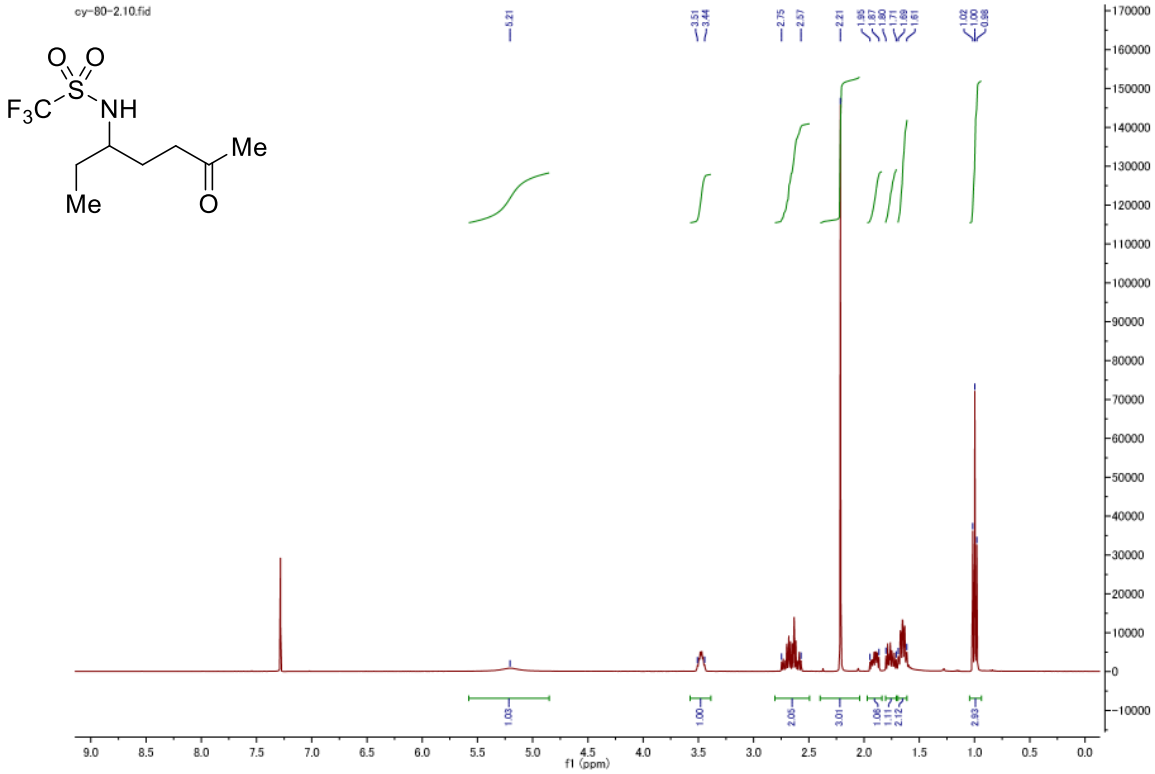
methyl 3-(2-methoxyacetyl)-4-((trifluoromethyl)sulfonamido)hexanoate (3ag)

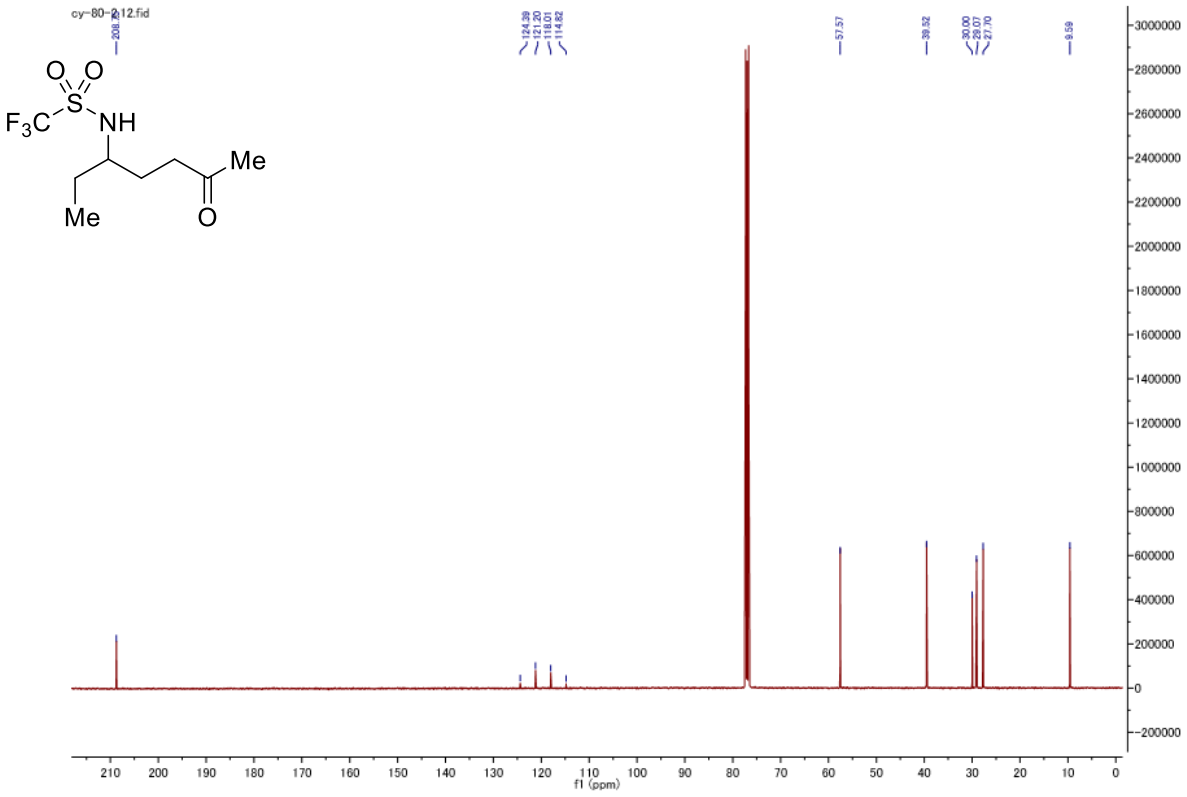


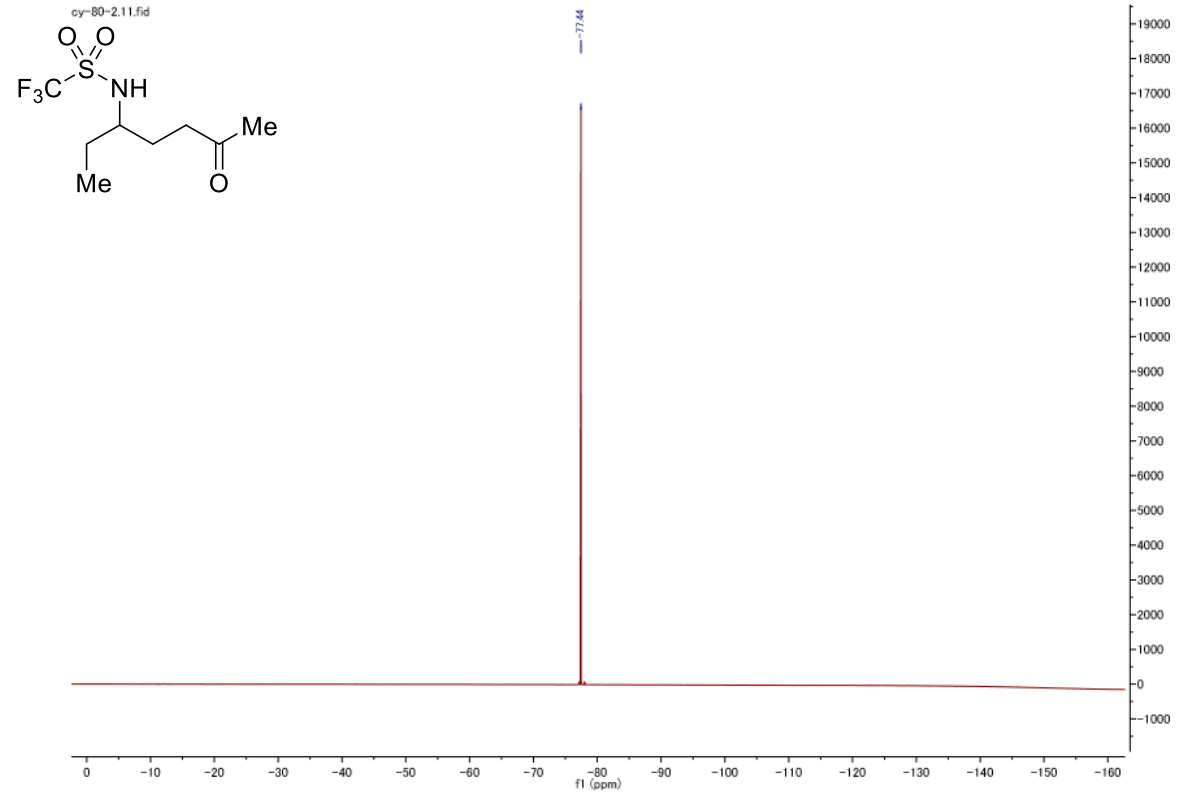




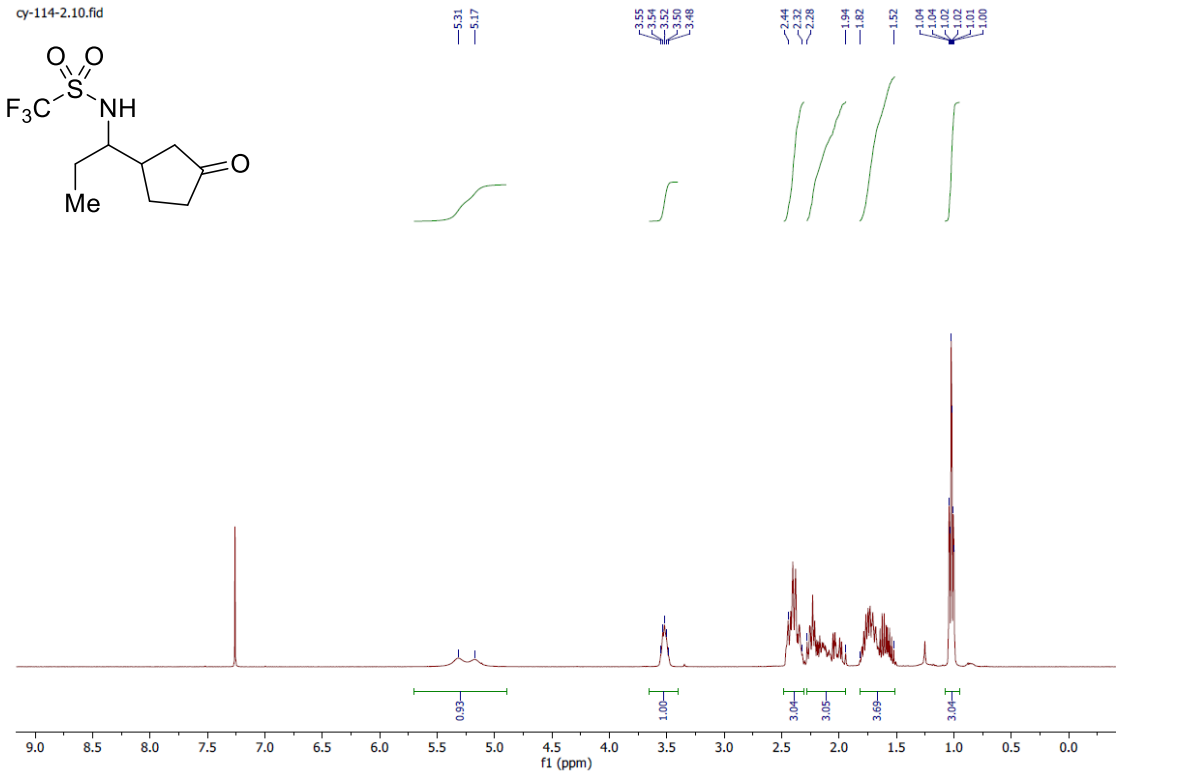
1,1,1-trifluoro-*N*-(6-oxoheptan-3-yl)methanesulfonamide (3ah)

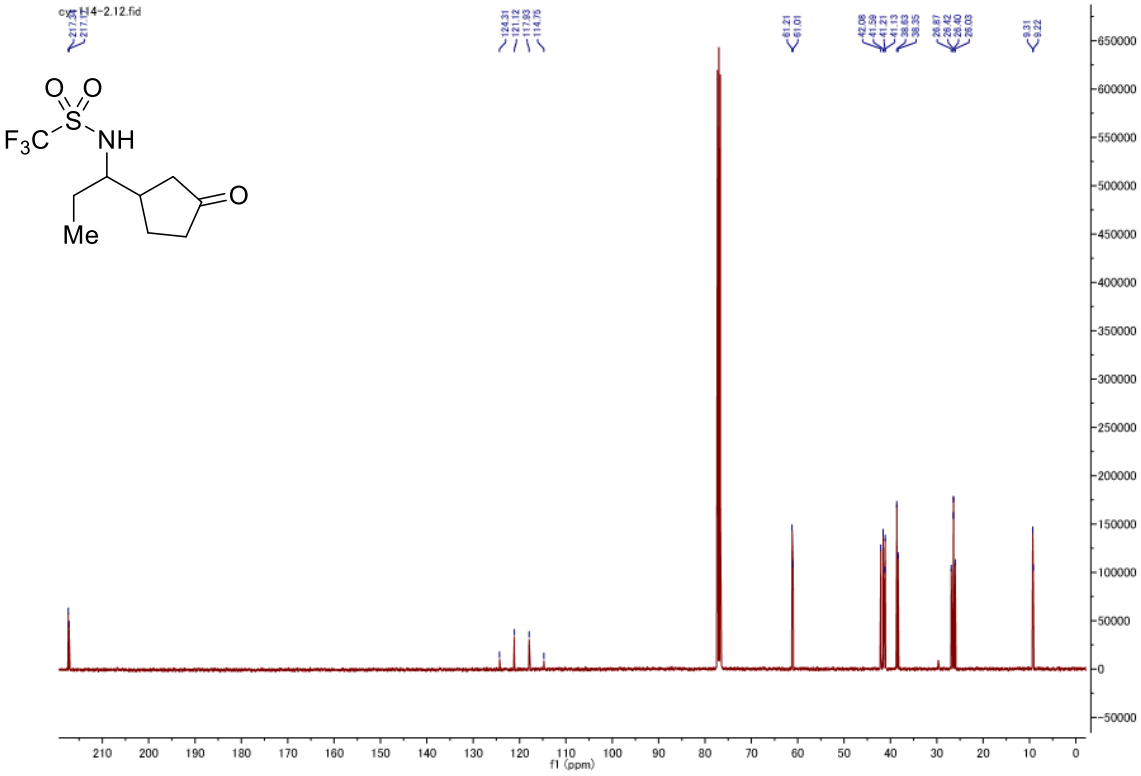


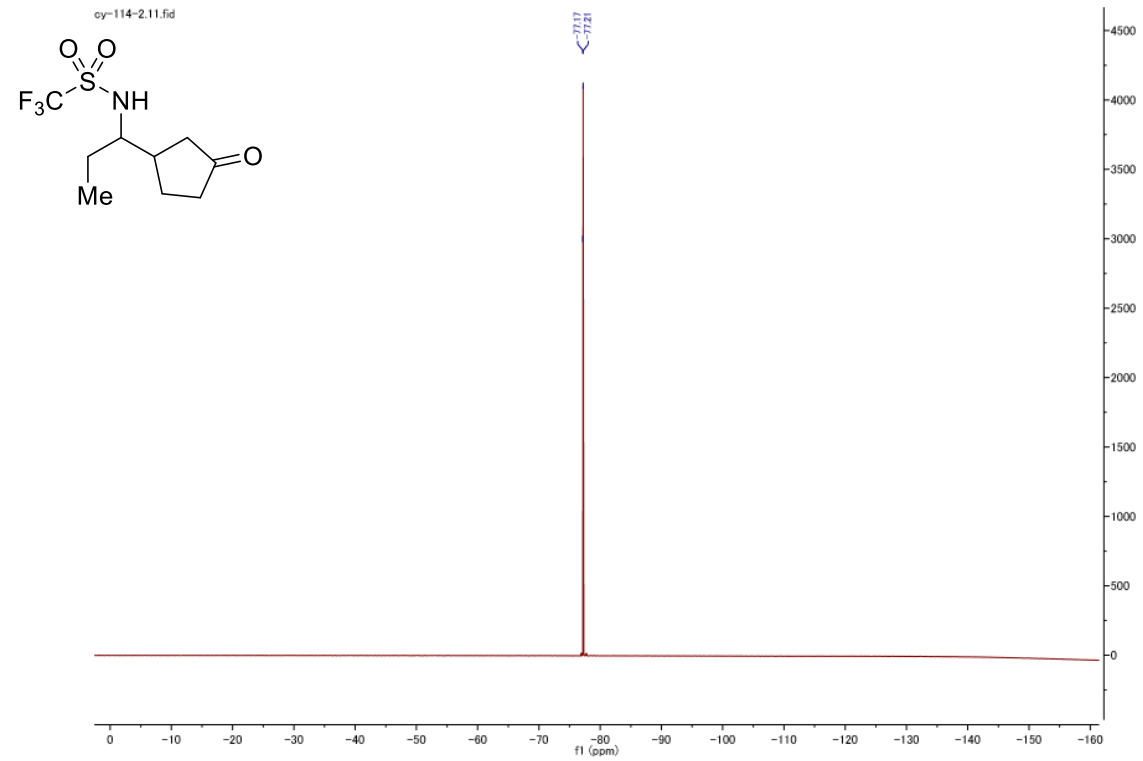

cy-80-2.12.fid
208.82
124.39
121.20
118.01
114.82
57.57
39.52
30.00
29.07
27.70
9.59
O
O
S
F3C
NH
Me
Me
O
f1 (ppm)


cy-80-2.11.fid
77.44
O
O
S
F3C
NH
Me
Me
O
f1 (ppm)

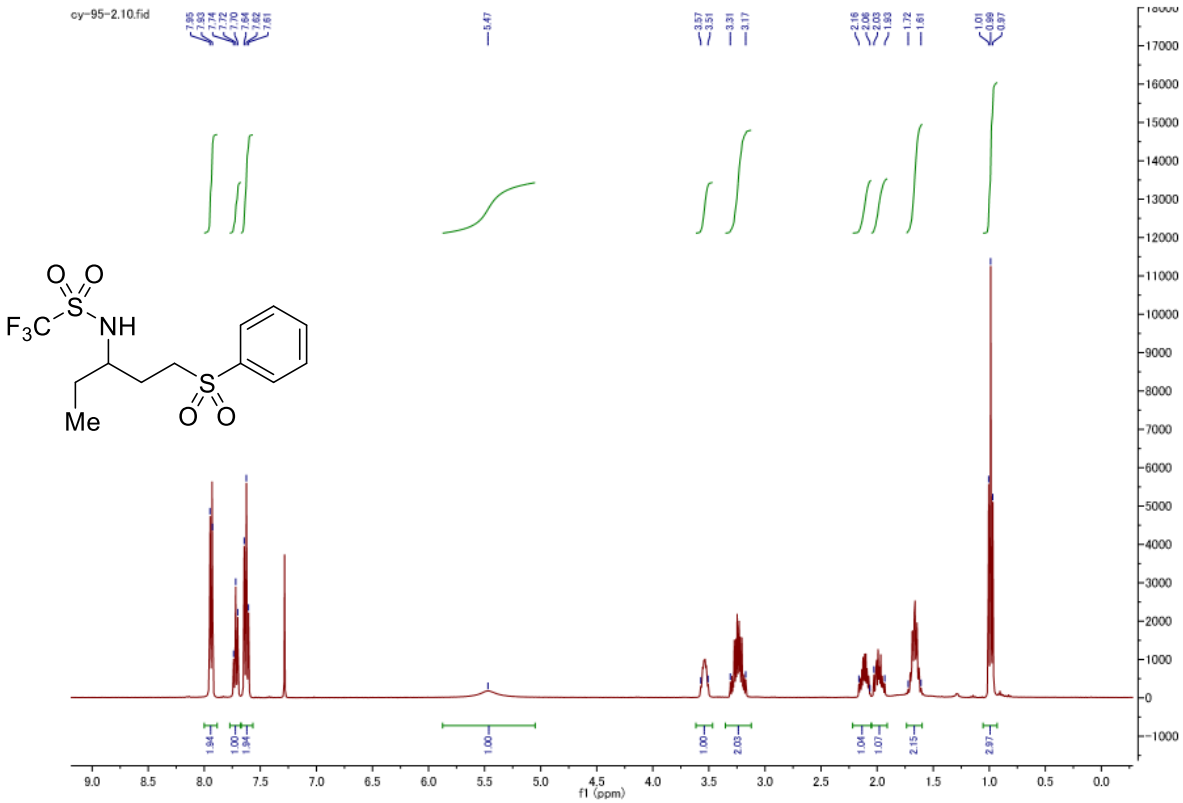
1,1,1-trifluoro-*N*-(1-(3-oxocyclopentyl)propyl)methanesulfonamide (3ai)

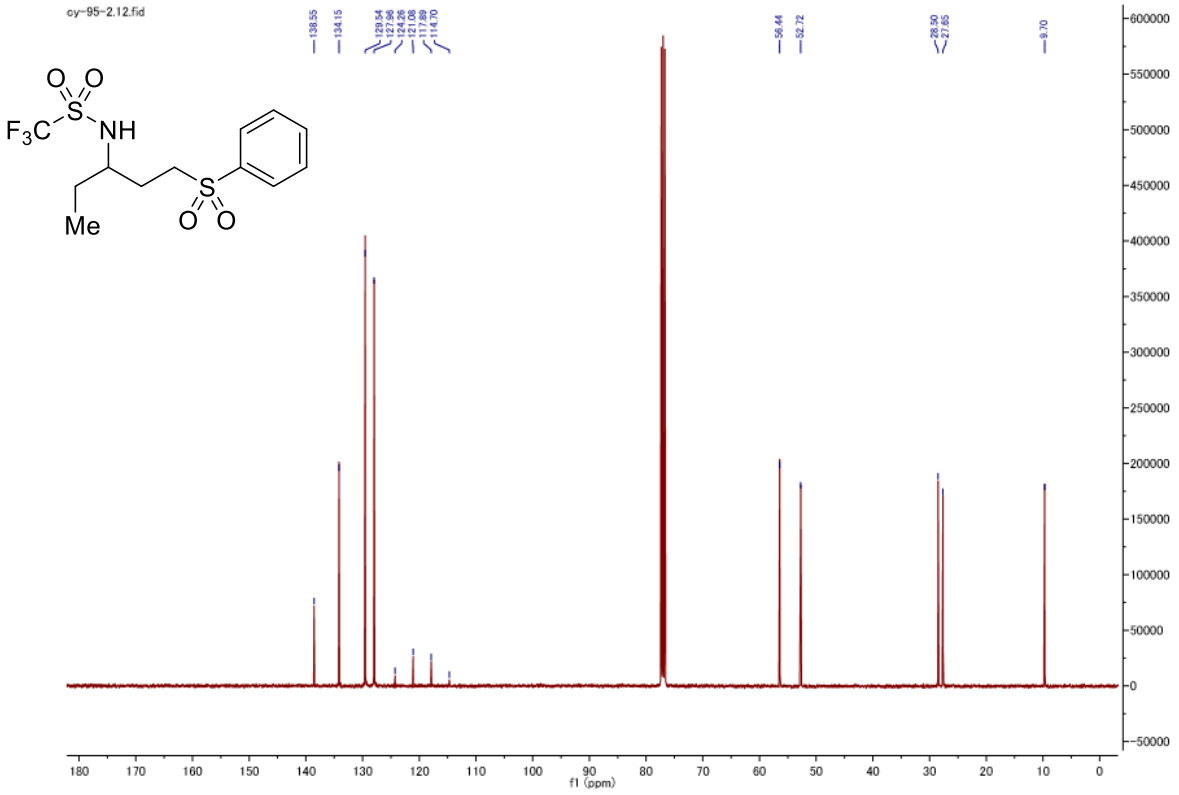


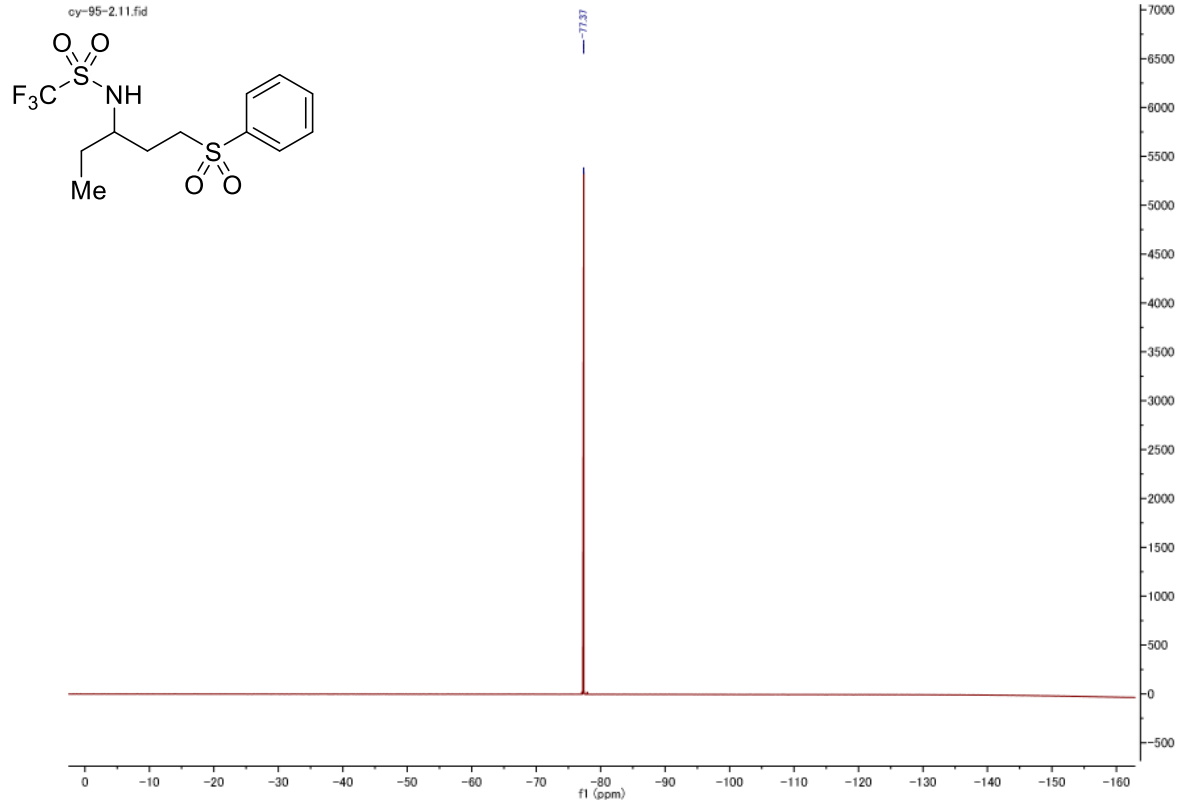




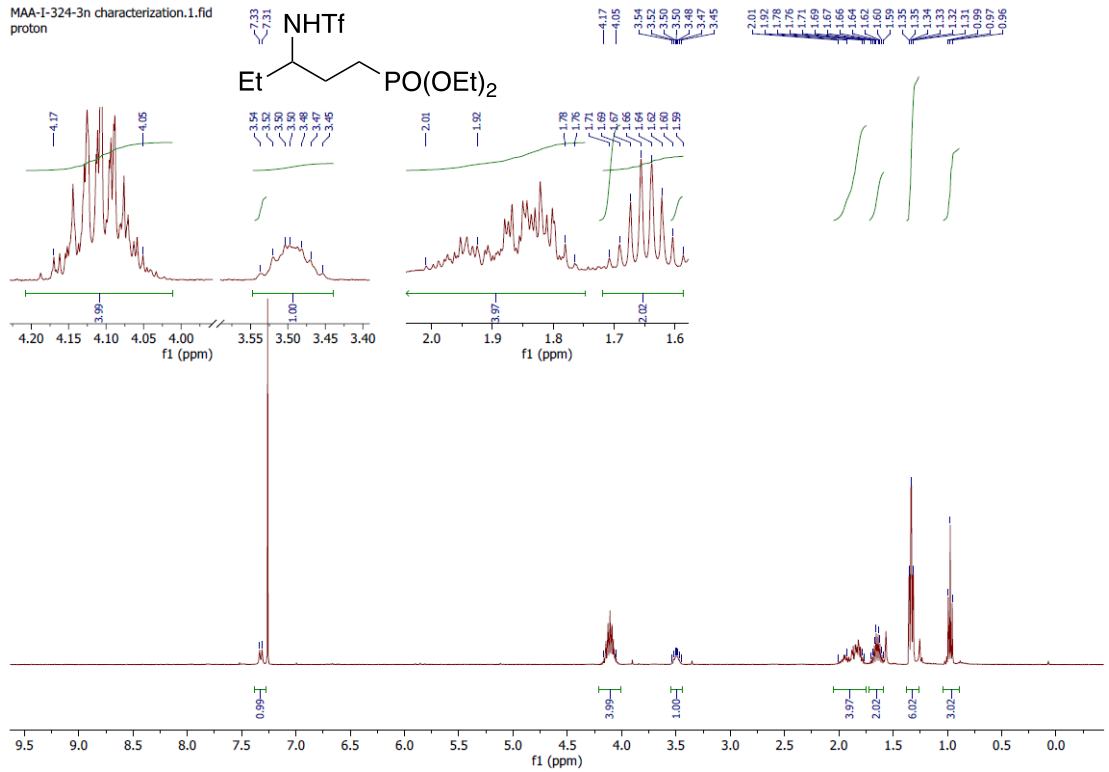
1,1,1-trifluoro-*N*-(1-(phenylsulfonyl)pentan-3-yl)methanesulfonamide (3aj)

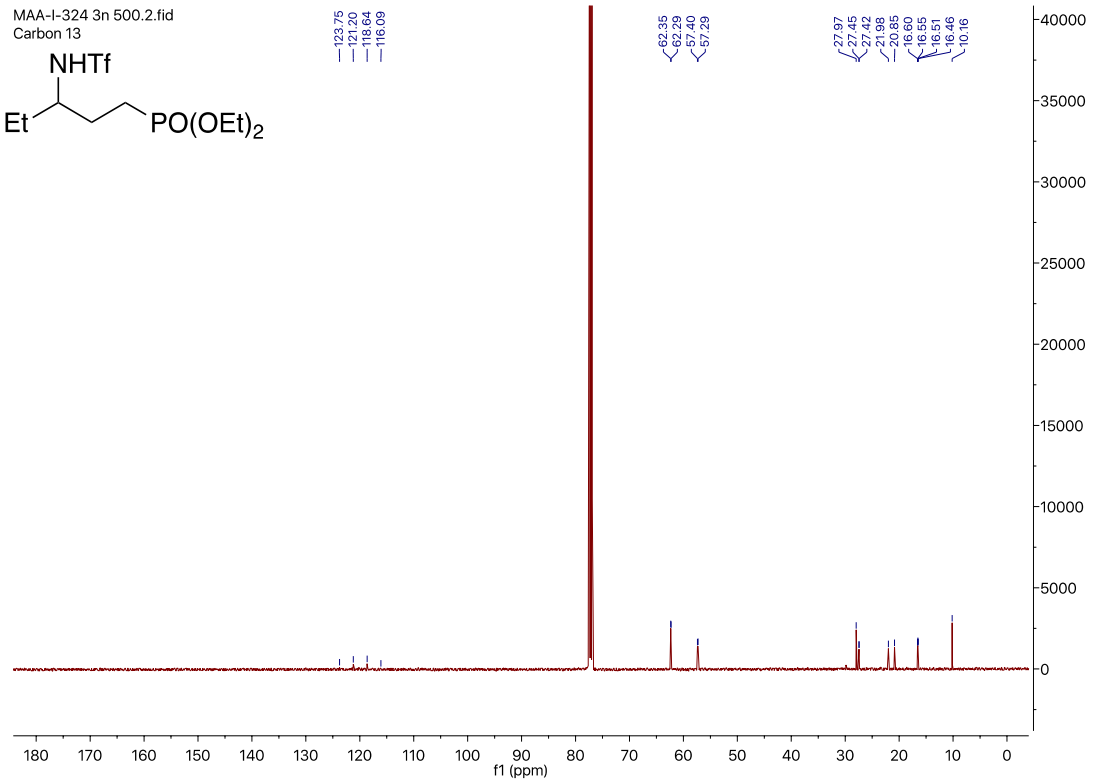


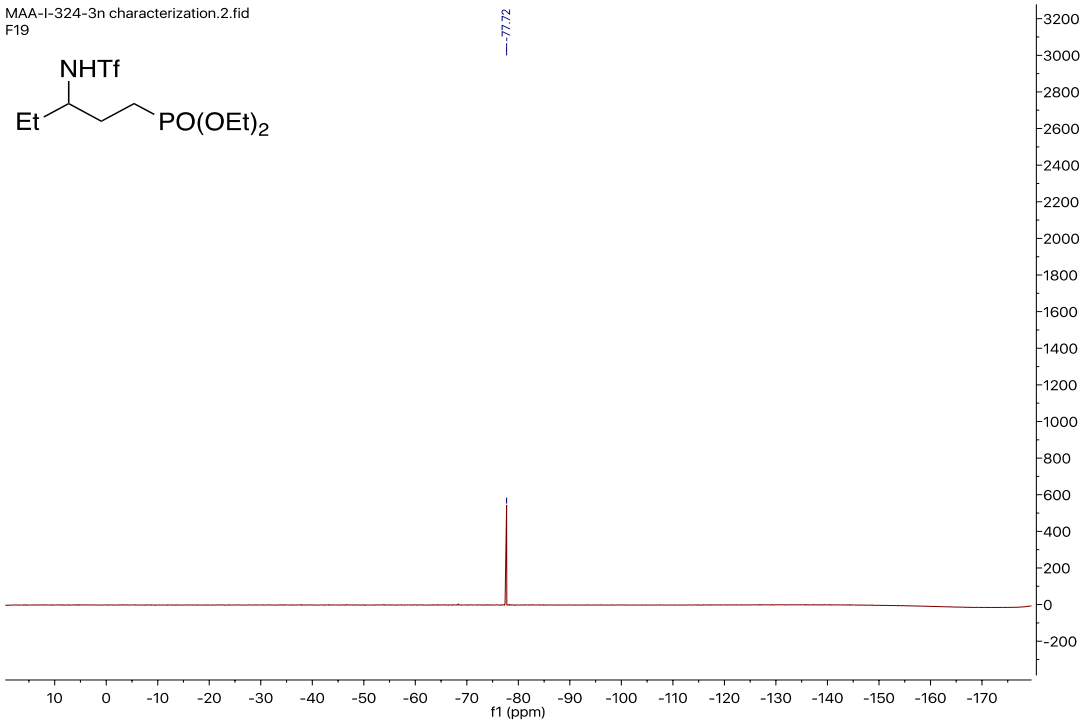

cy-95-2.12.fid
138.55
134.15
129.54
127.96
124.35
121.08
117.89
114.70
56.44
52.72
28.50
27.65
9.70
f1 (ppm)


cy-95-2.11.fid
77.37
f1 (ppm)

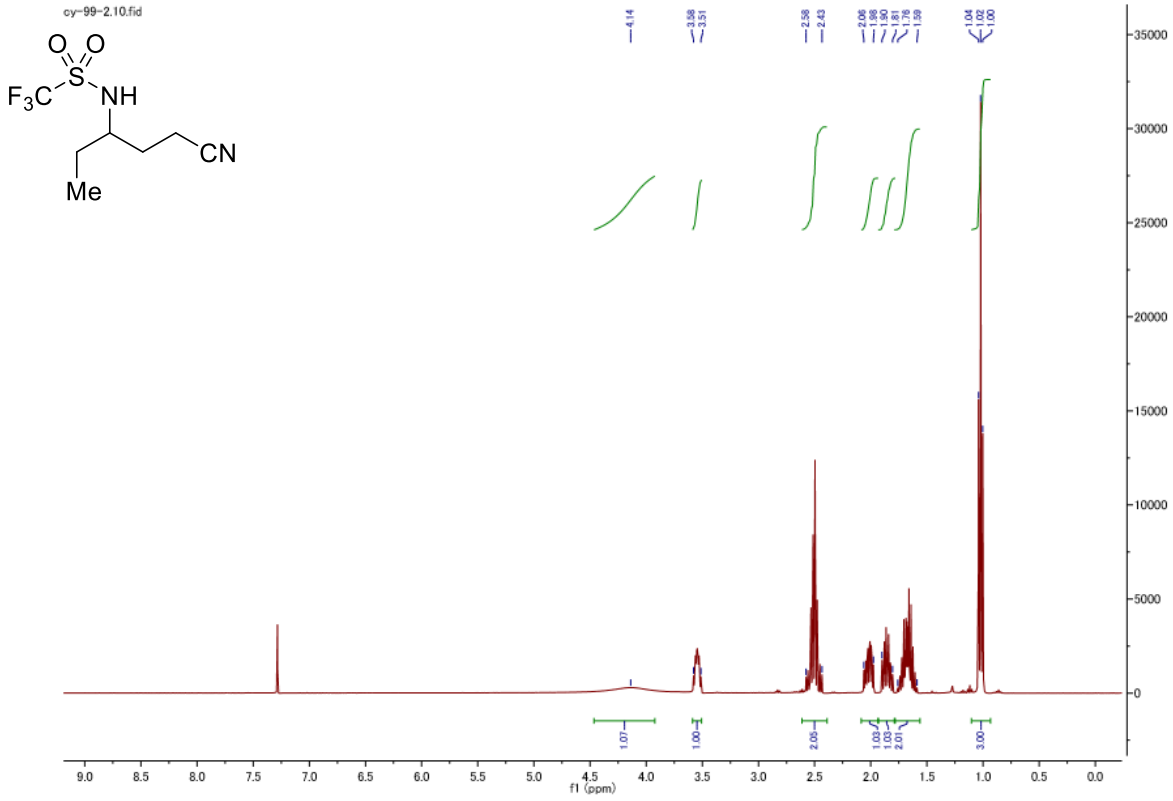
diethyl (3-((trifluoromethyl)sulfonamido)pentyl)phosphonate (3ak)

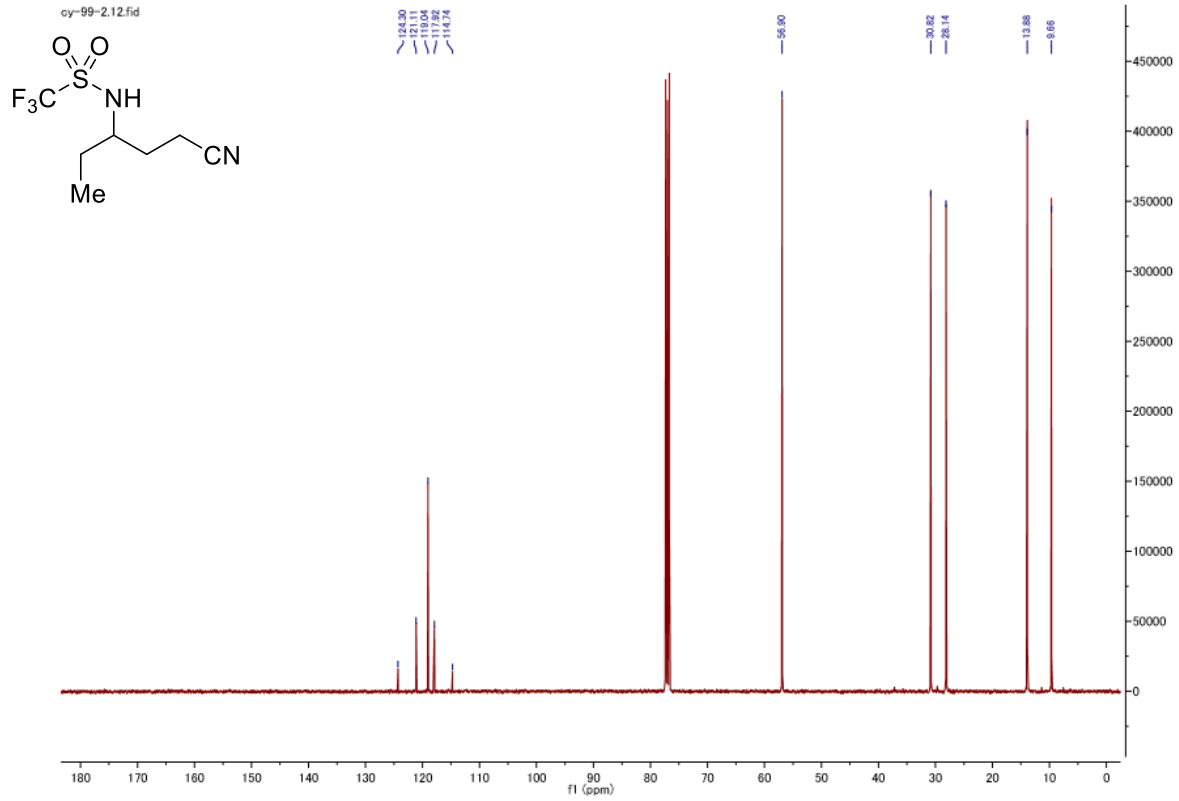


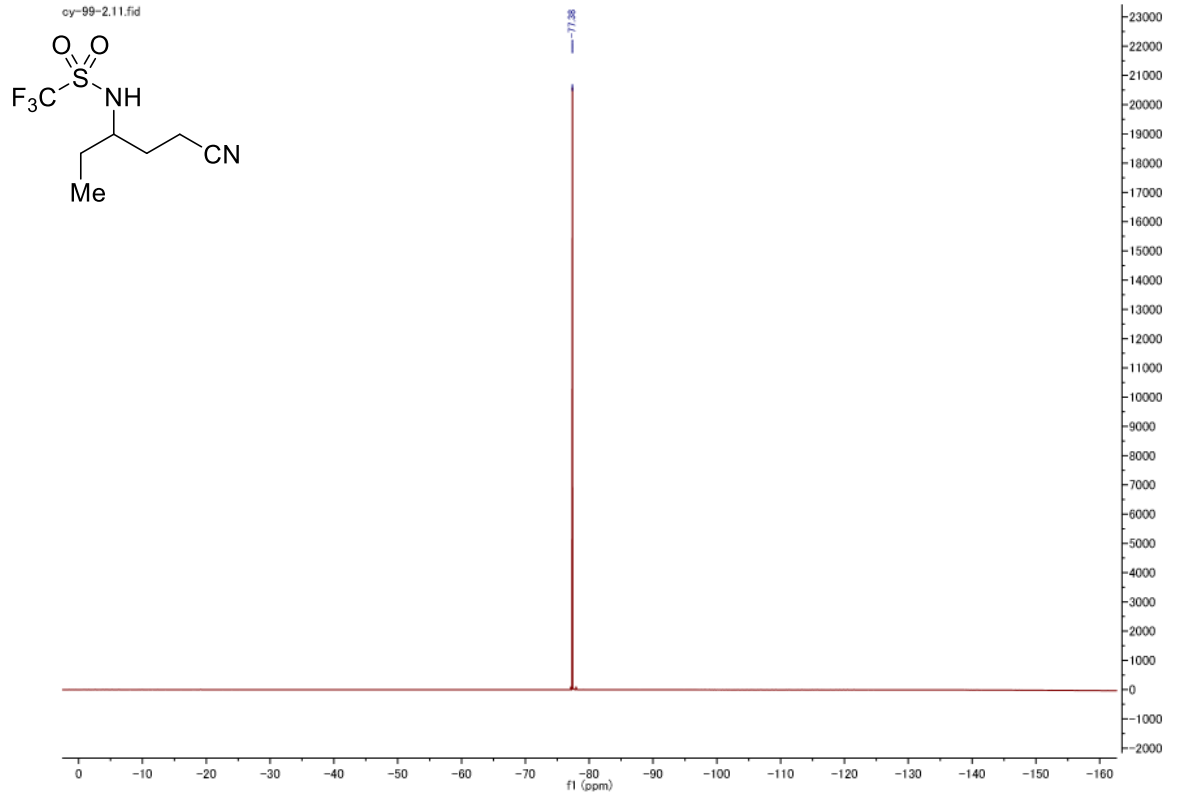




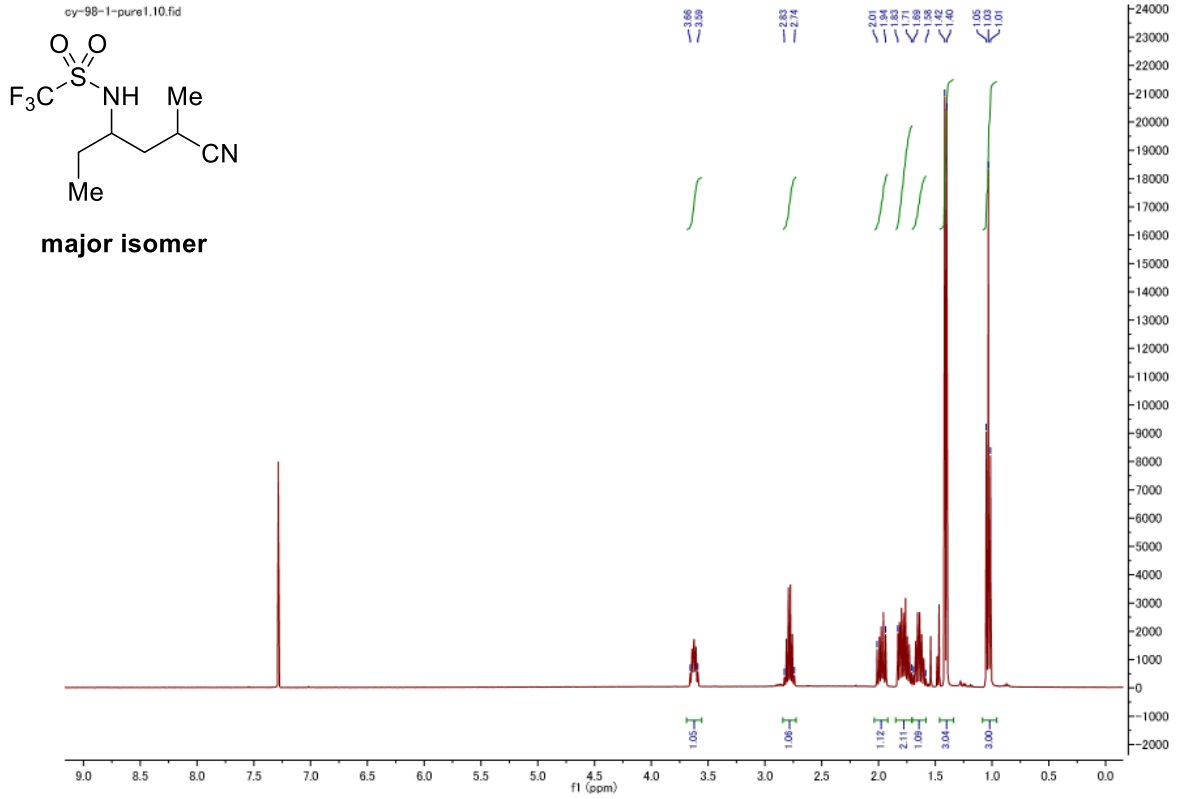
***N*-(1-cyanopentan-3-yl)-1,1,1-trifluoromethanesulfonamide (3al)**

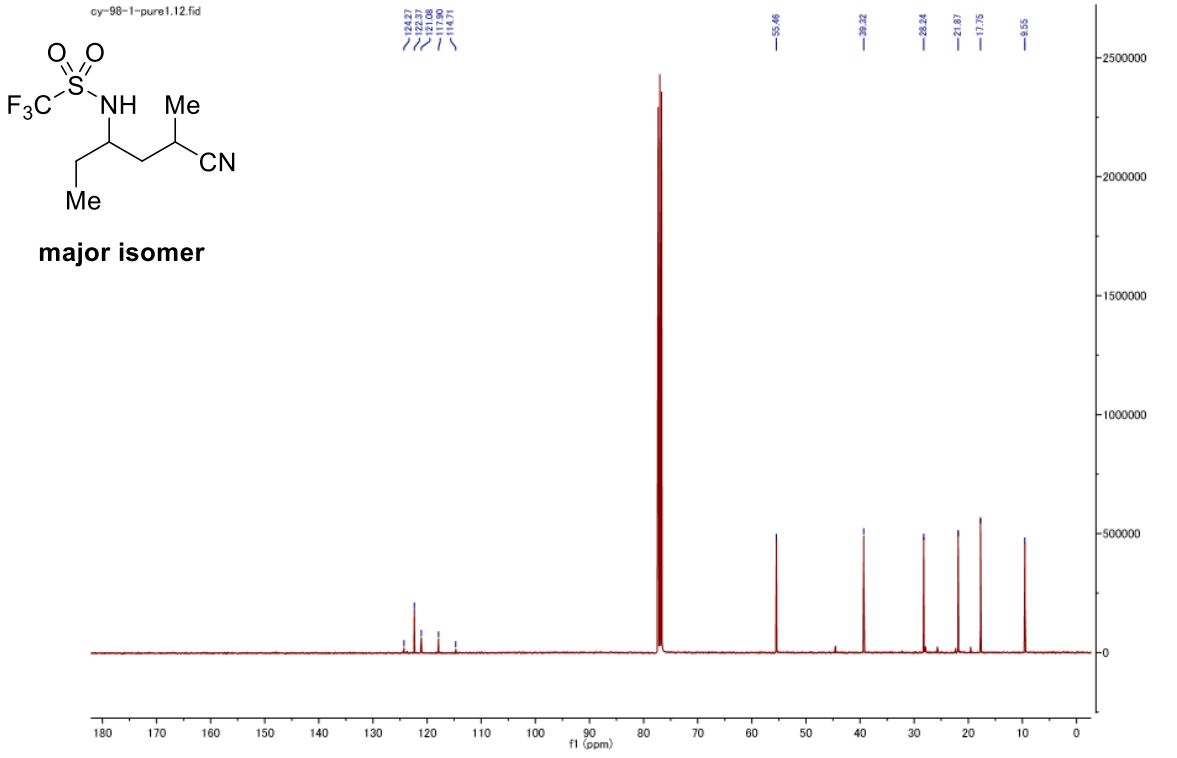


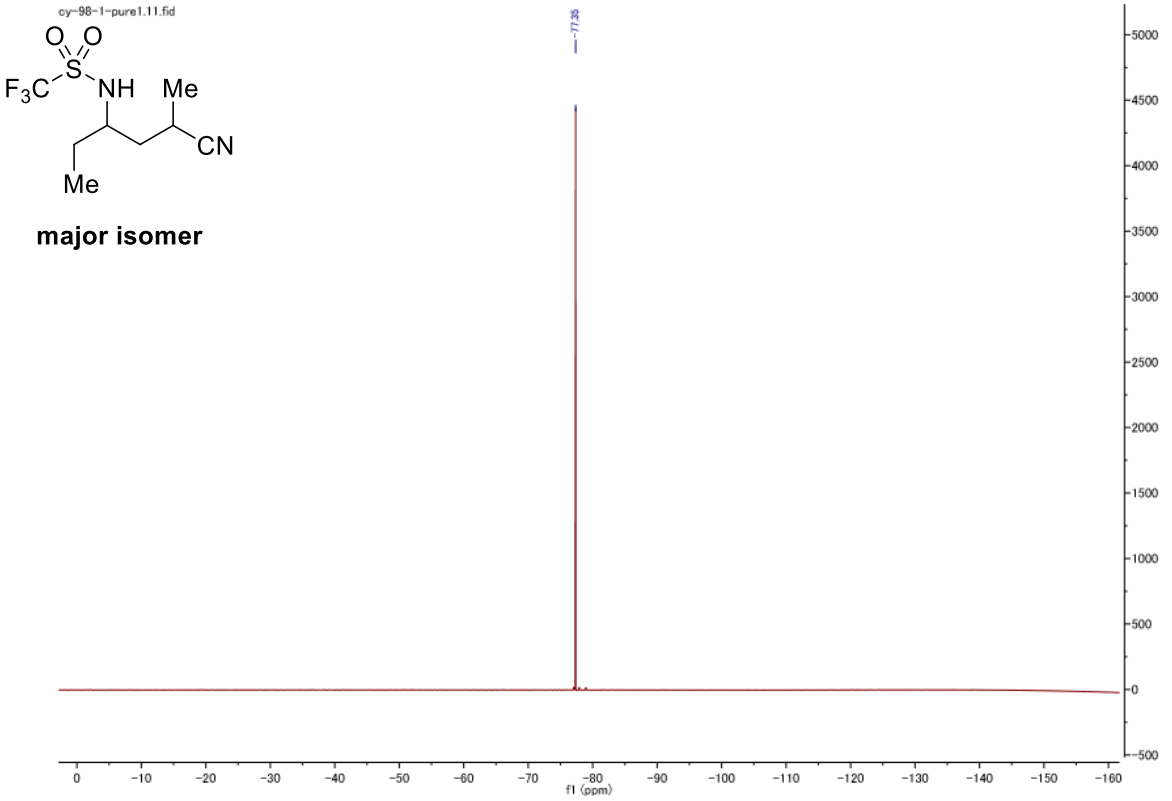

cy-99-2.12.fid
O
O
S
F3C
NH
CN
Me
124.30
121.11
119.64
117.82
114.74
56.90
30.82
28.14
13.88
9.66
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

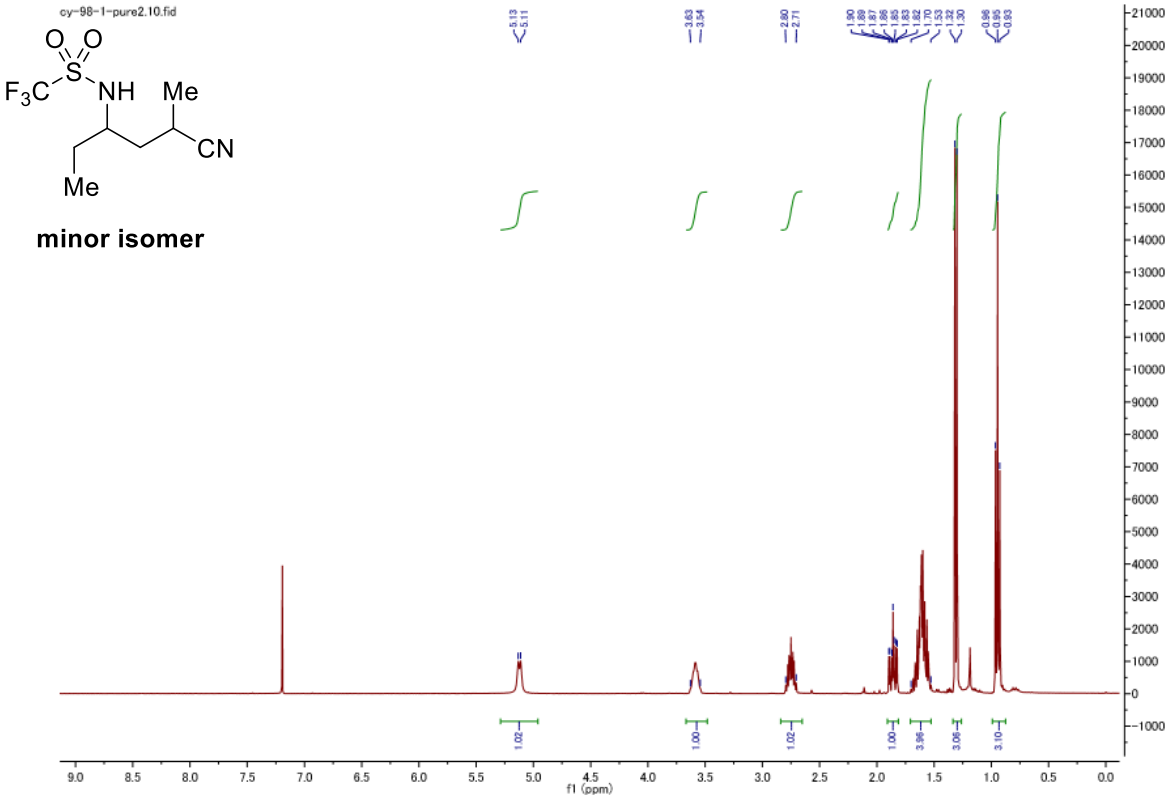

cy-99-2.11.fid
O
O
S
F3C
NH
CN
Me
77.38
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

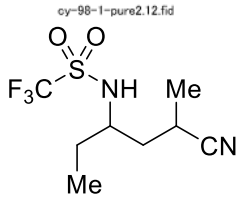
***N*-(5-cyanohexan-3-yl)-1,1,1-trifluoromethanesulfonamide (3am)**



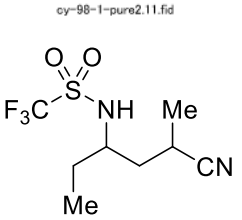



cy-98-1-pure1.11.fid
major isomer
f1 (ppm)


cy-98-1-pure2.10.fid
minor isomer
f1 (ppm)

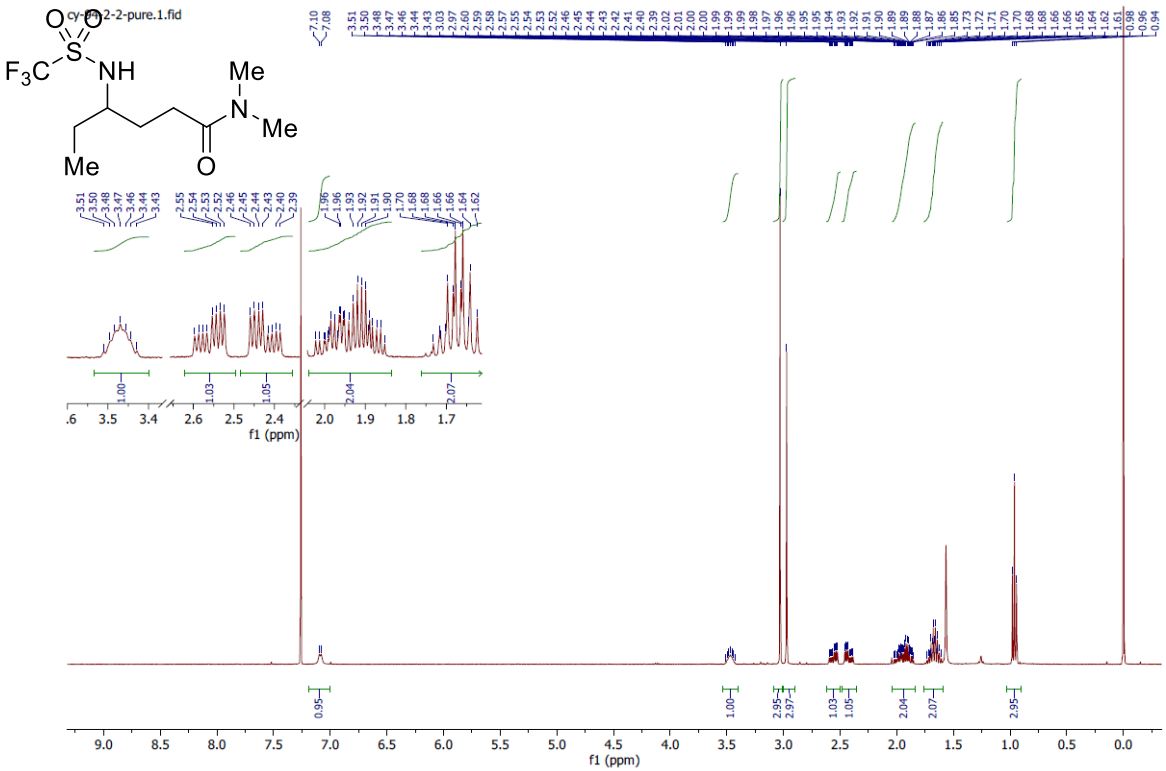


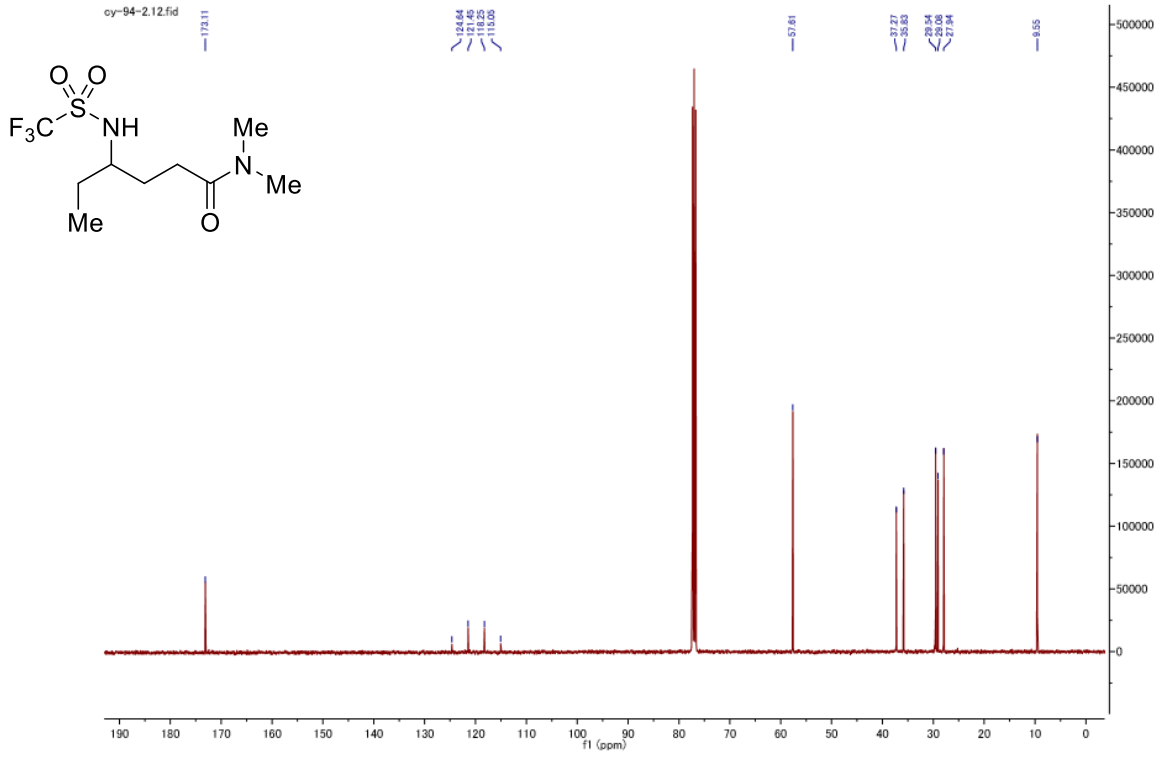
minor isomer

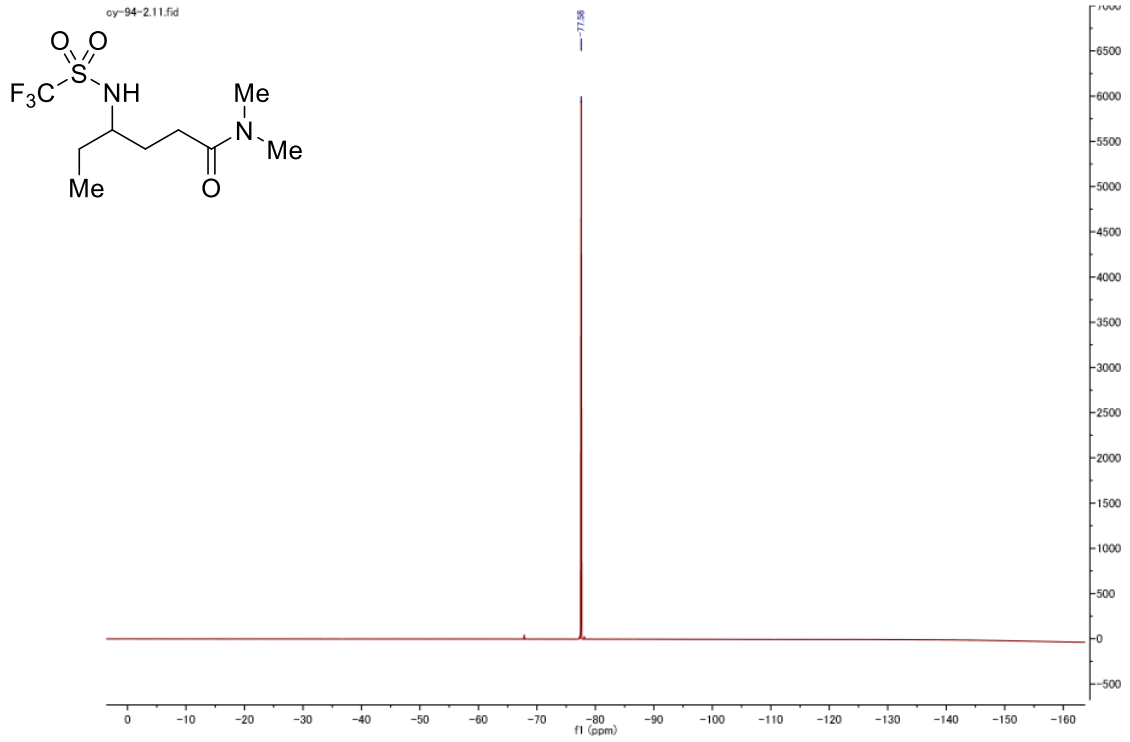


minor isomer

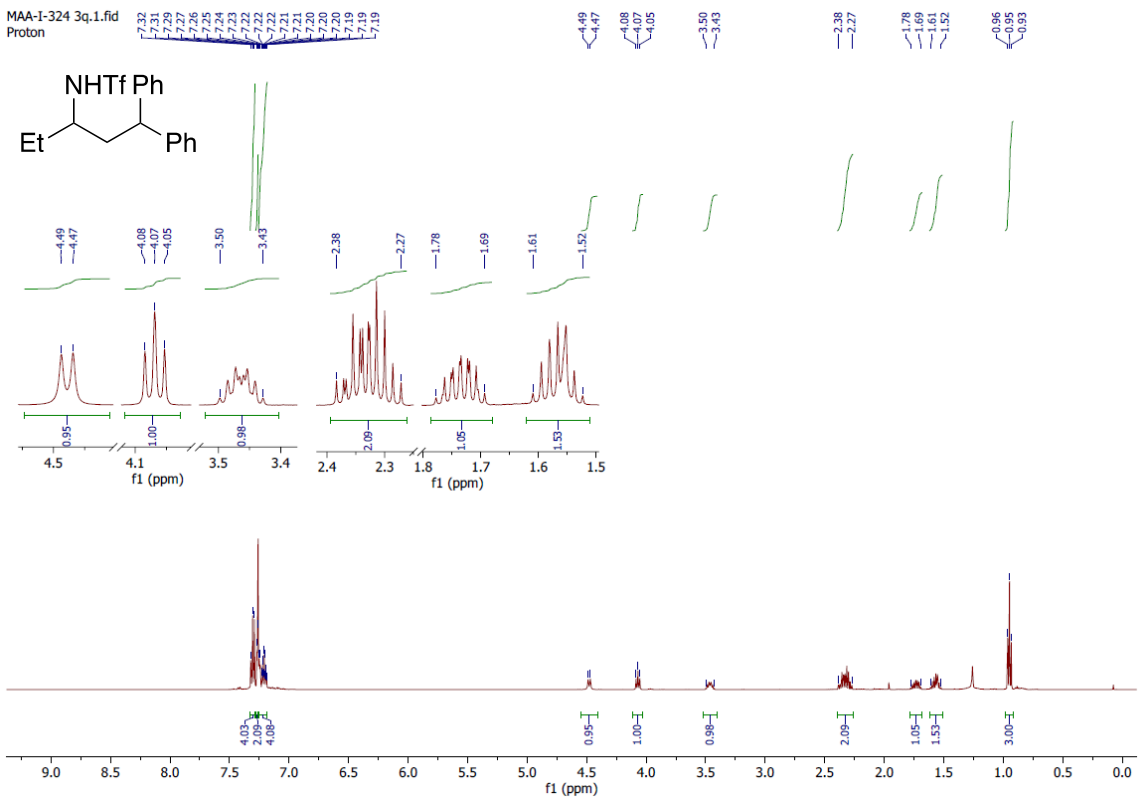
***N,N*-dimethyl-4-((trifluoromethyl)sulfonamido)hexanamide (3an)**

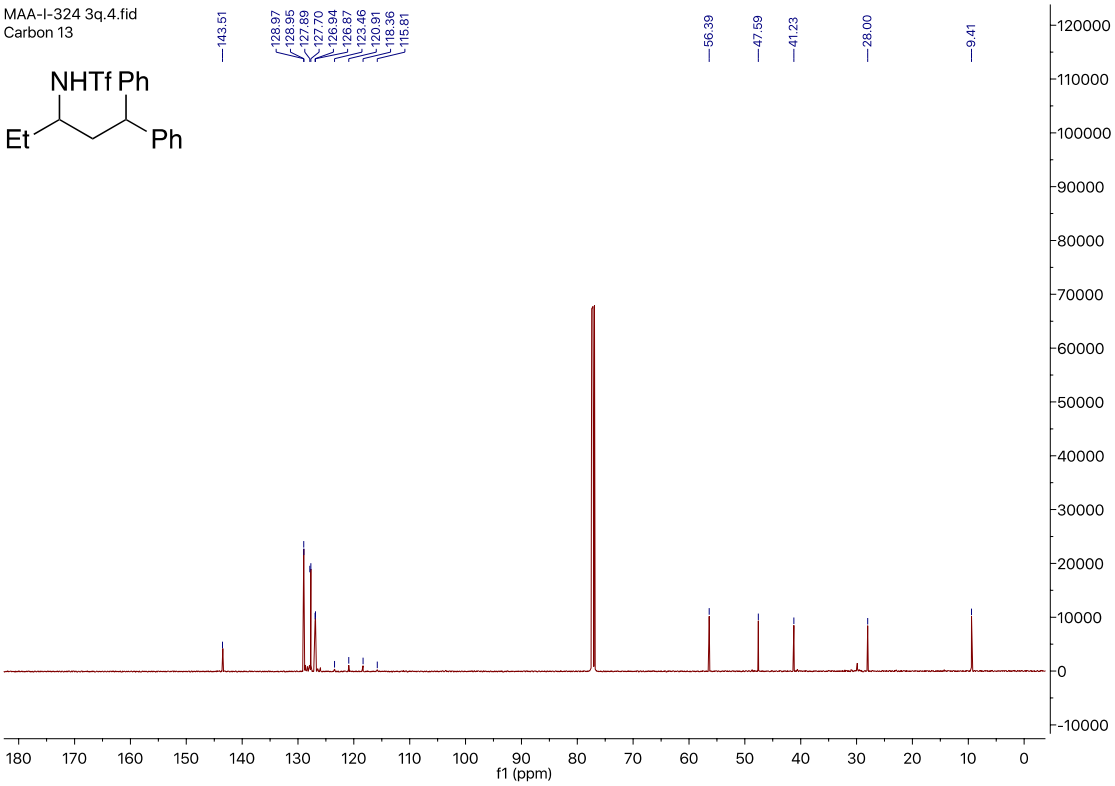


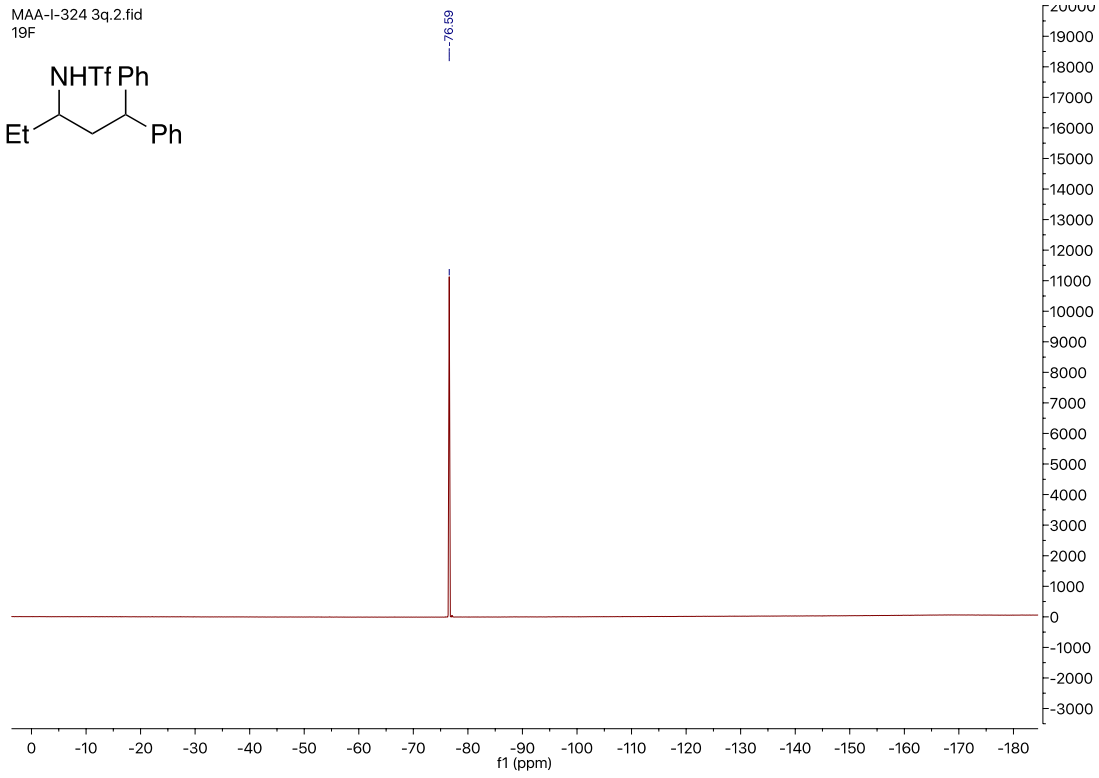




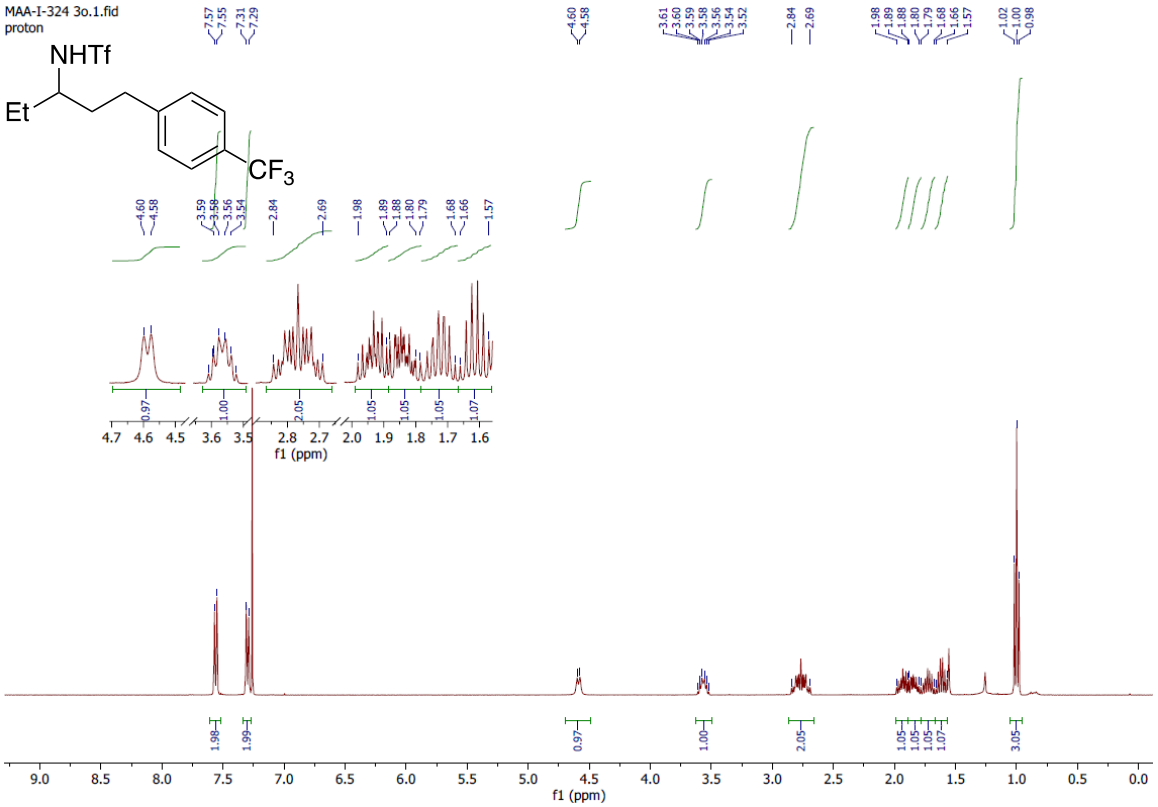
***N*-(1,1-diphenylpentan-3-yl)-1,1,1-trifluoromethanesulfonamide (3ao)**

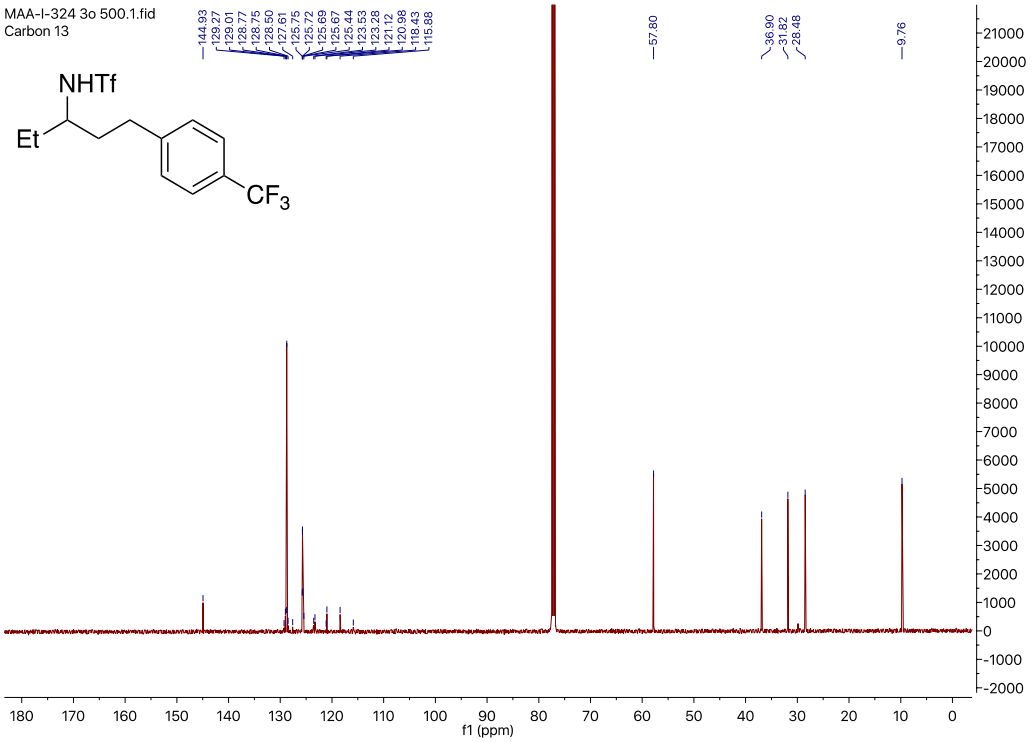


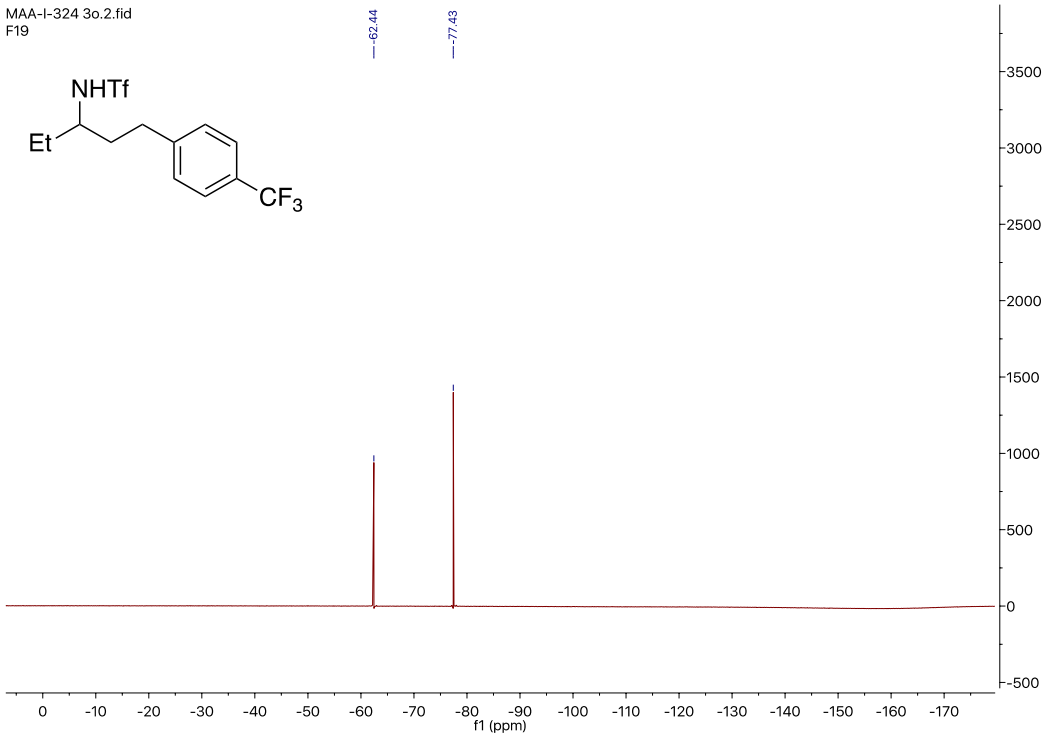

MAA-I-324 3q.4.fid
Carbon 13
NHTf Ph
Et
Ph
143.51
128.97
128.95
127.89
127.70
126.94
126.87
123.46
120.91
118.36
115.81
56.39
47.59
41.23
28.00
9.41
f1 (ppm)


MAA-I-324 3q.2.fid
19F
NHTf Ph
Et
Ph
-76.59
f1 (ppm)

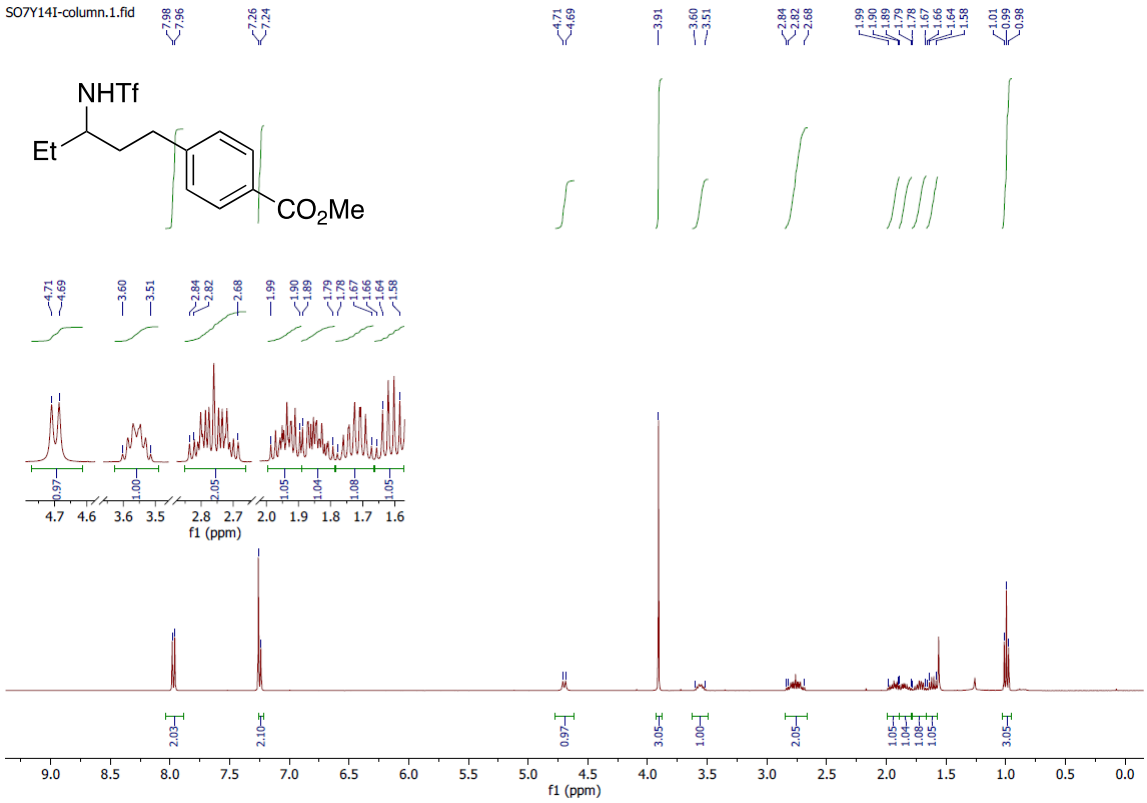
1,1,1-trifluoro-N-(1-(4-(trifluoromethyl)phenyl)pentan-3-yl)methanesulfonamide (3ap)

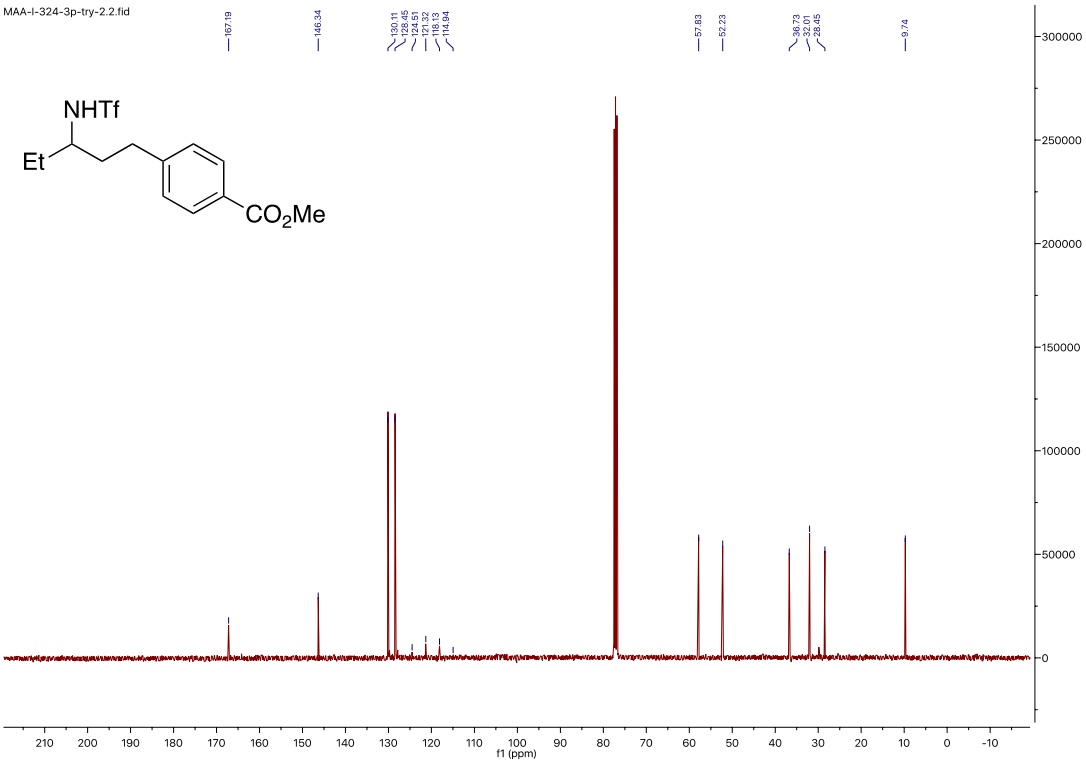


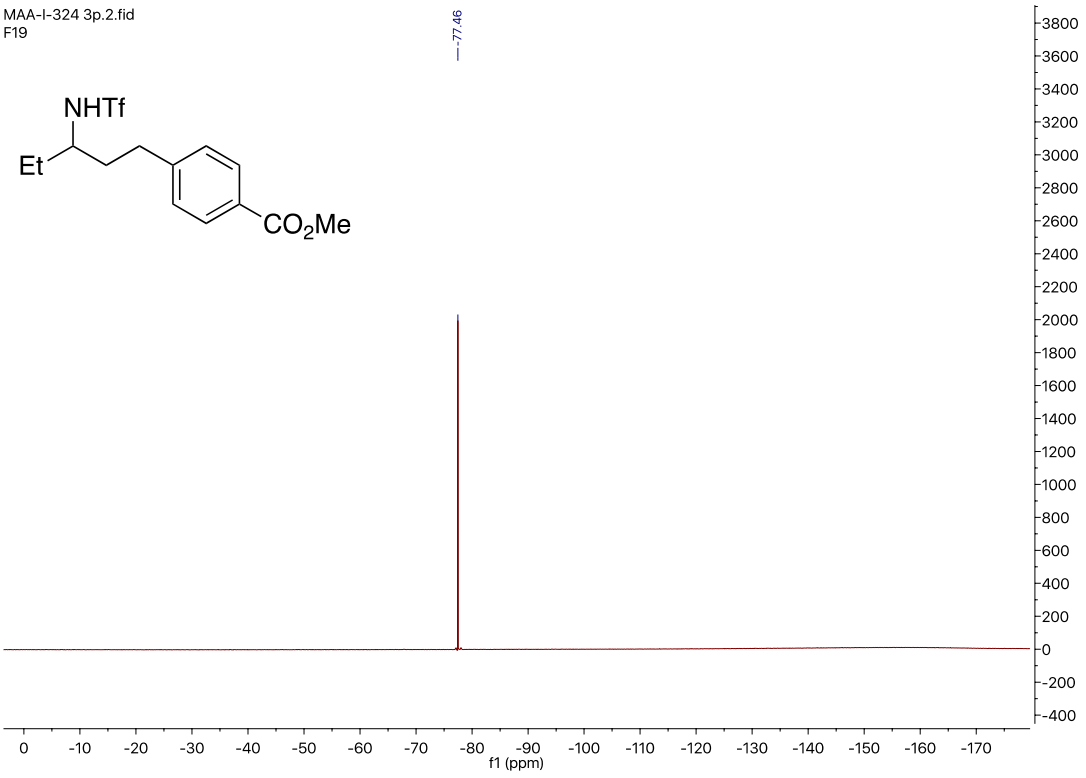




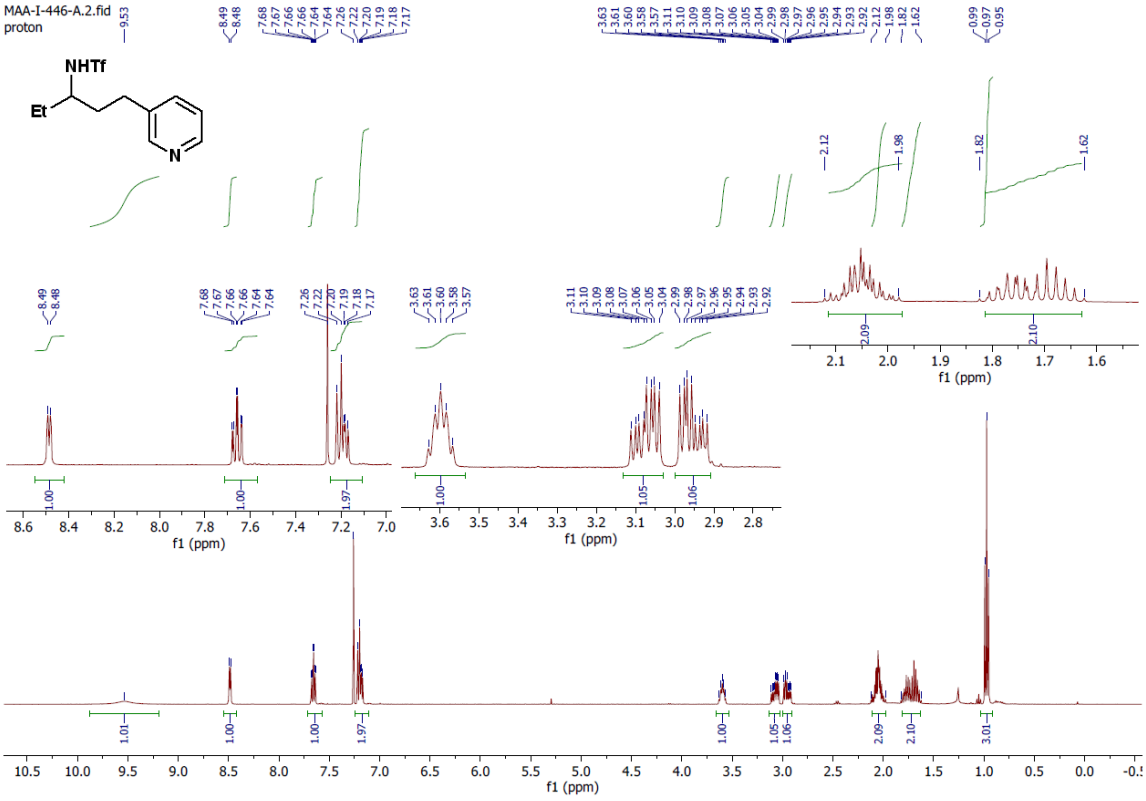
Methyl 4-(3-((trifluoromethyl)sulfonamide)pentyl)benzoate (3aq)

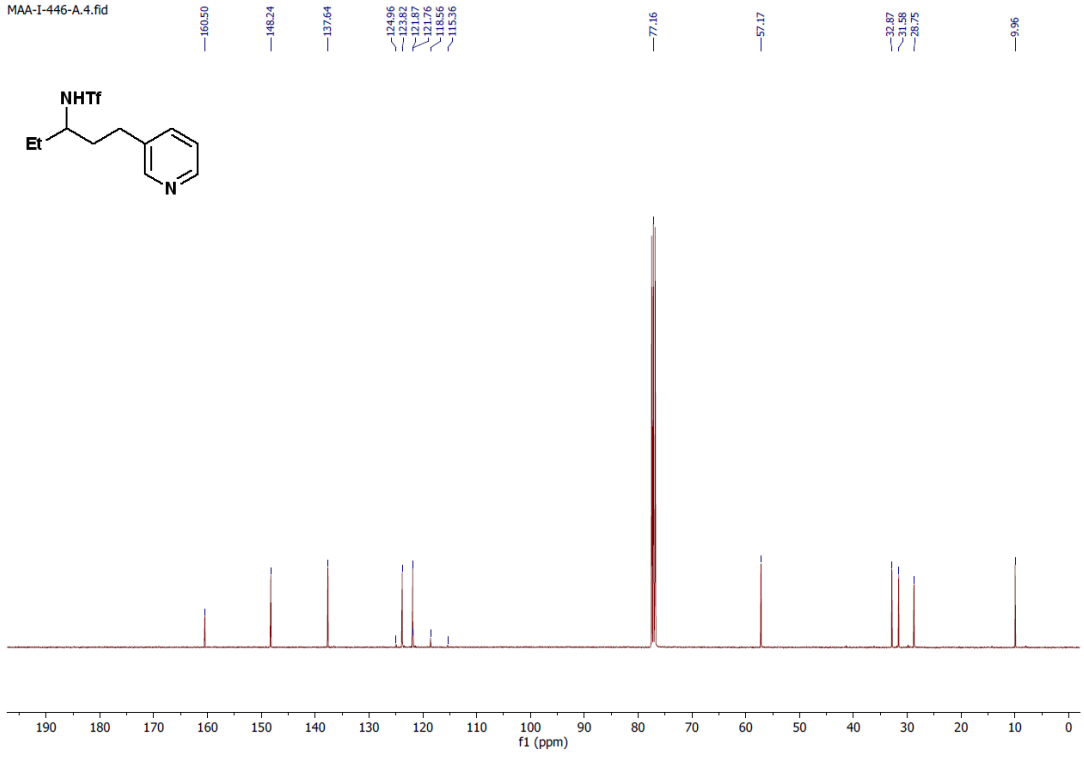


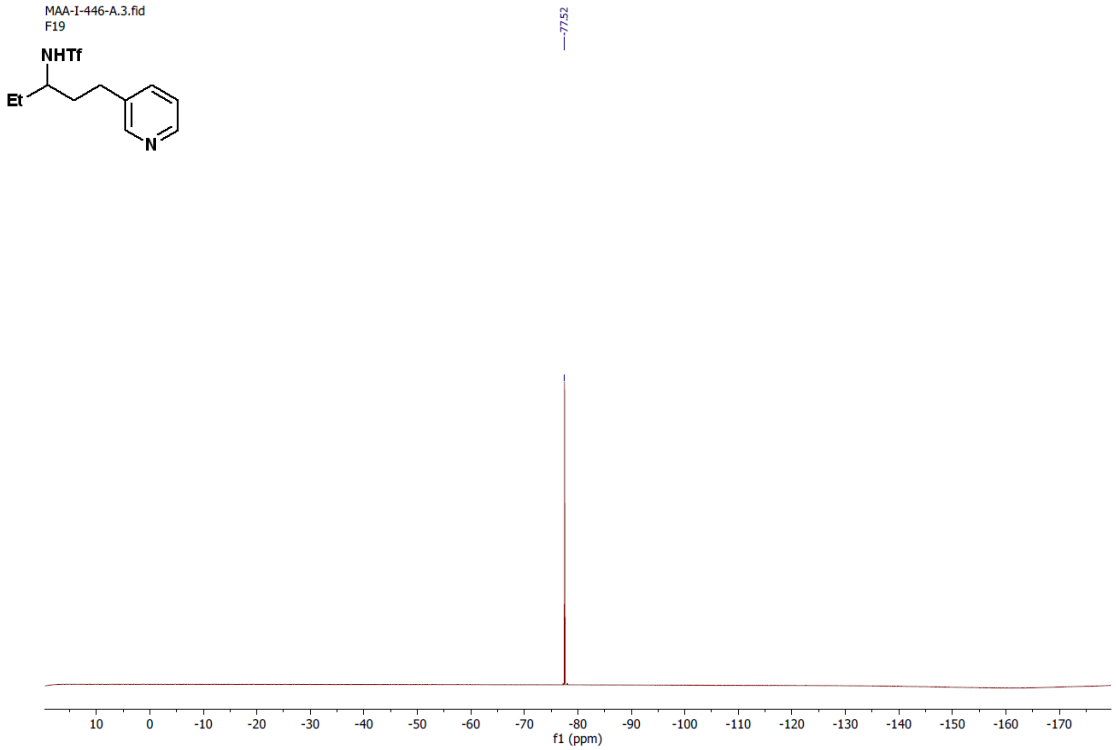

MAA-I-324-3p-try-2.2.fid
167.19
146.34
130.11
128.45
124.51
121.32
118.53
114.94
57.83
52.23
36.73
32.01
28.45
9.74
NHTf
Et
CO2Me
f1 (ppm)


MAA-I-324 3p.2.fid
F19
-77.46
NHTf
Et
CO2Me
f1 (ppm)

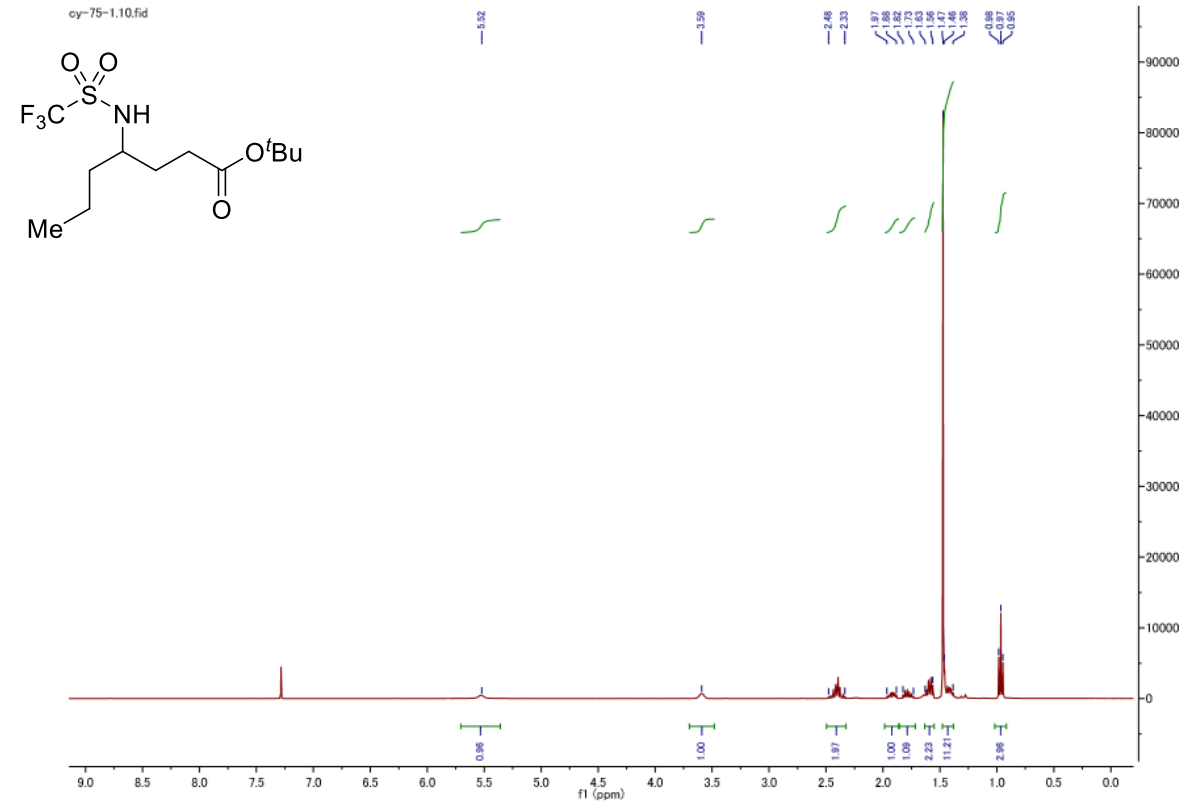
1,1,1-trifluoro-*N*-(1-(pyridine-3-yl)pentan-3-yl)methanesulfonamide (3ar)

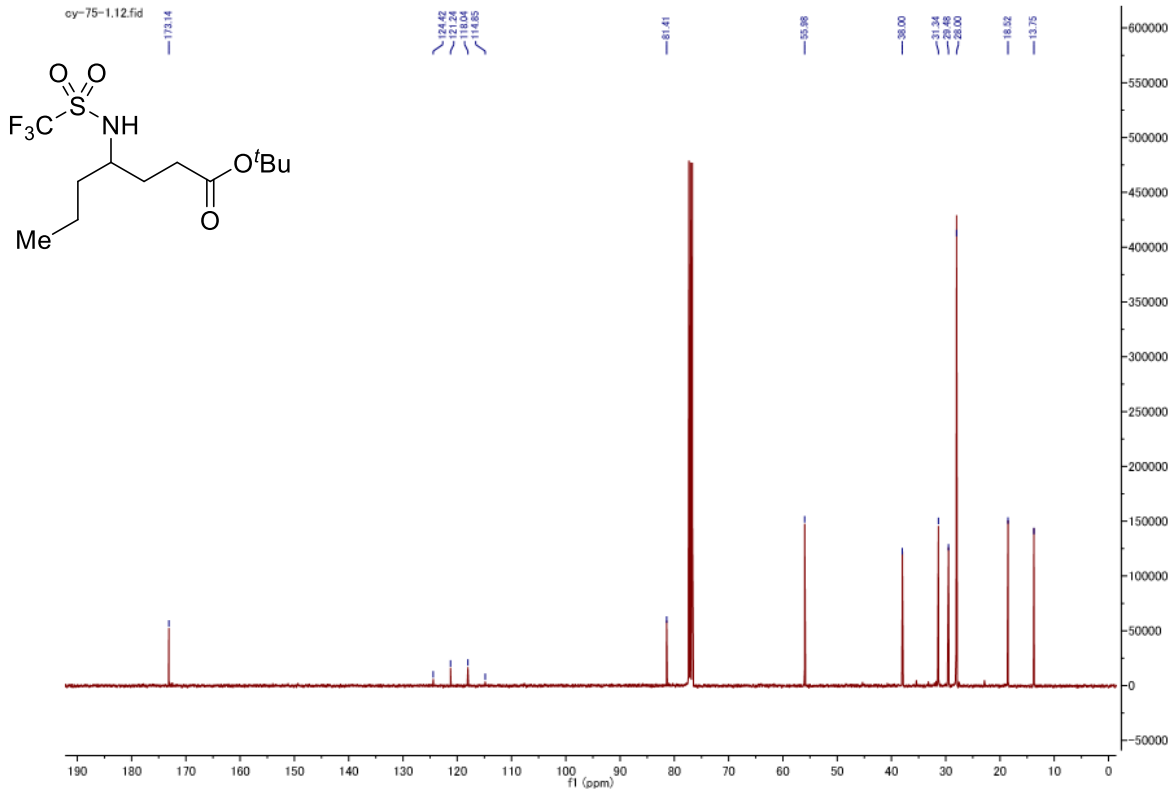


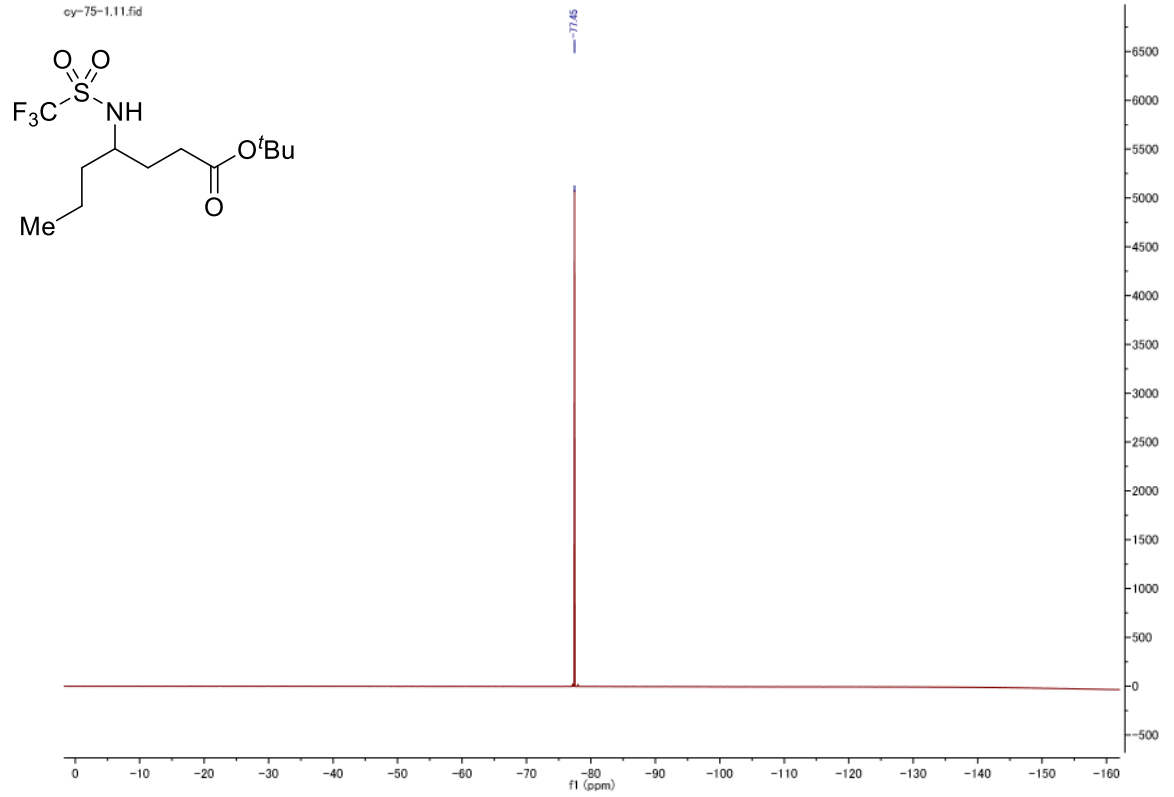




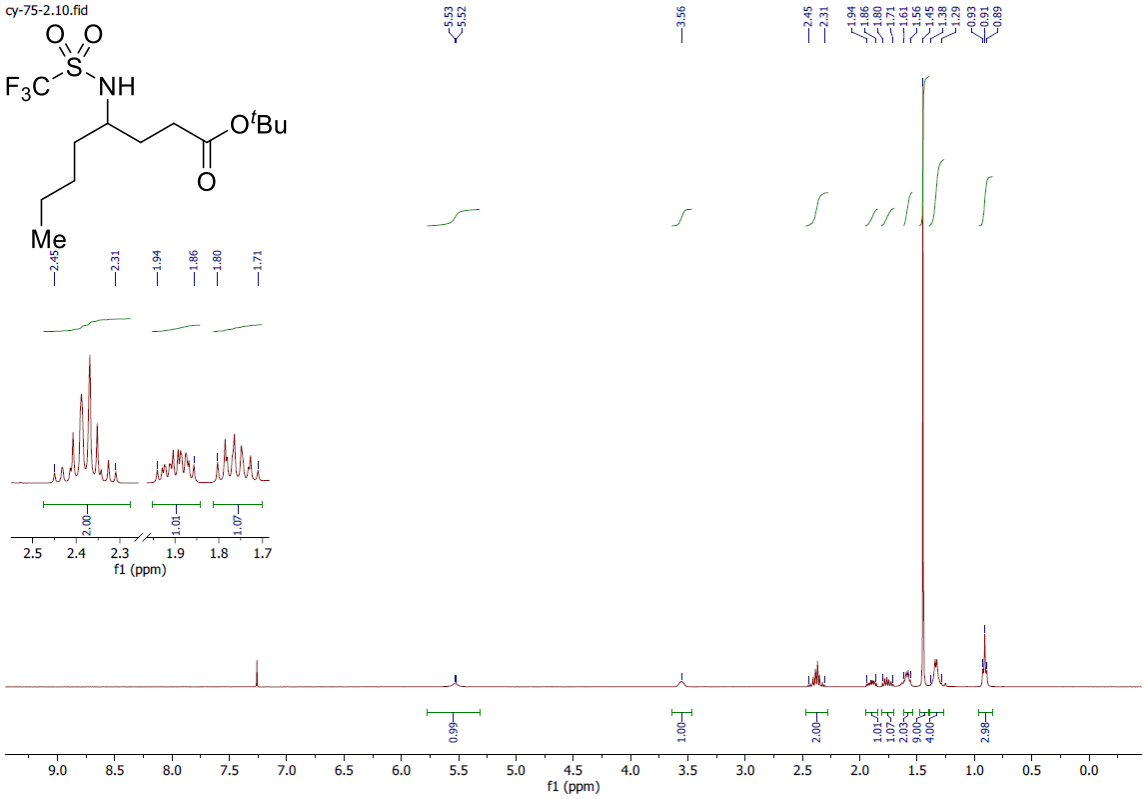
tert-butyl 4-((trifluoromethyl)sulfonamido)heptanoate (3ba)

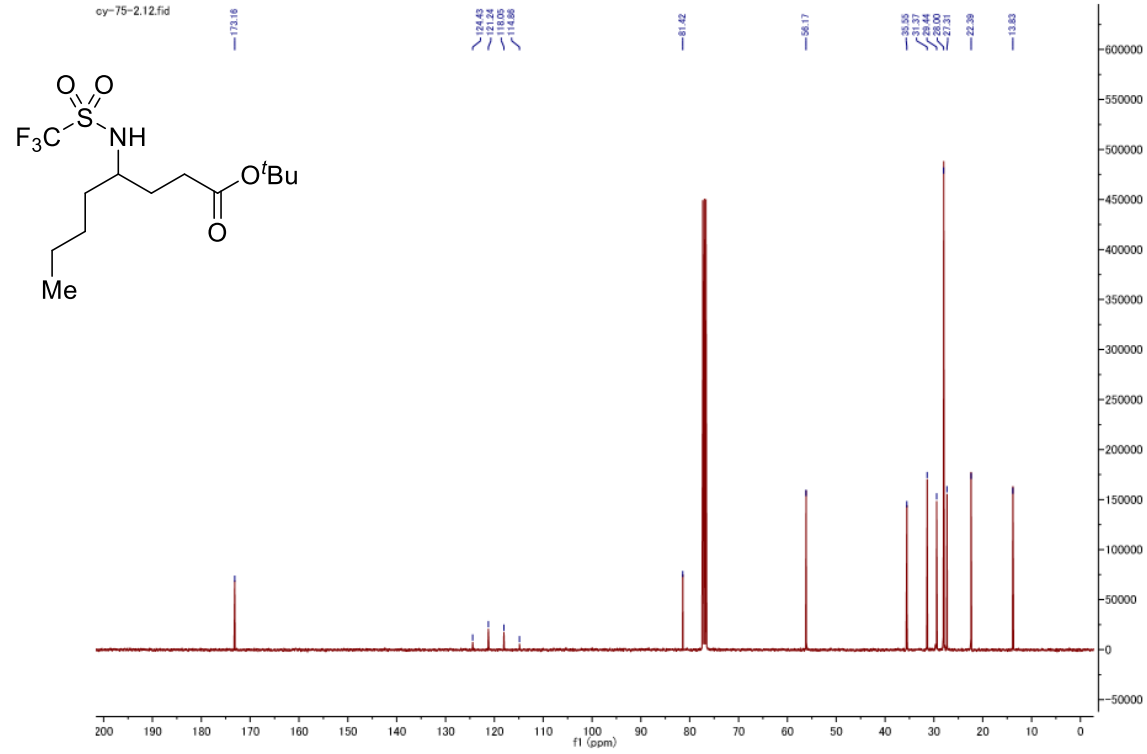


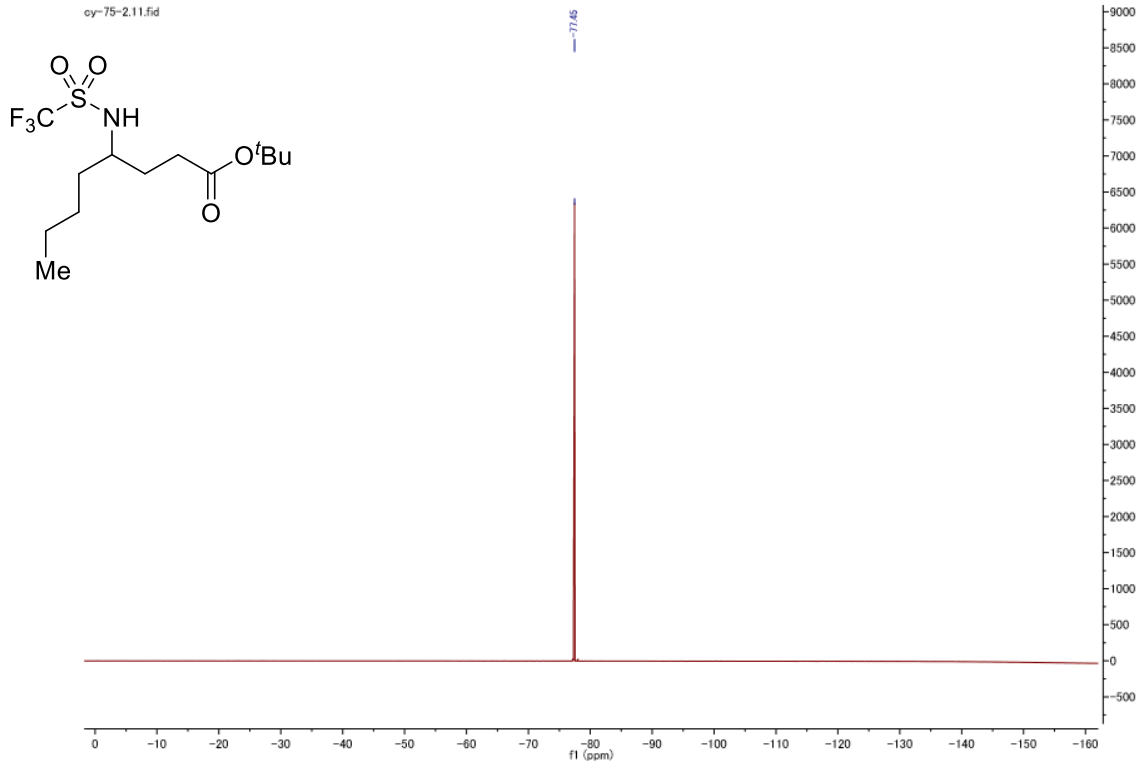

cy-75-1.12.fid
O
O
S
F3C
NH
OtBu
O
Me
173.14
134.42
121.24
119.04
114.85
81.41
55.98
38.00
31.34
29.48
28.00
18.52
13.75
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


cy-75-1.11.fid
O
O
S
F3C
NH
OtBu
O
Me
77.45
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

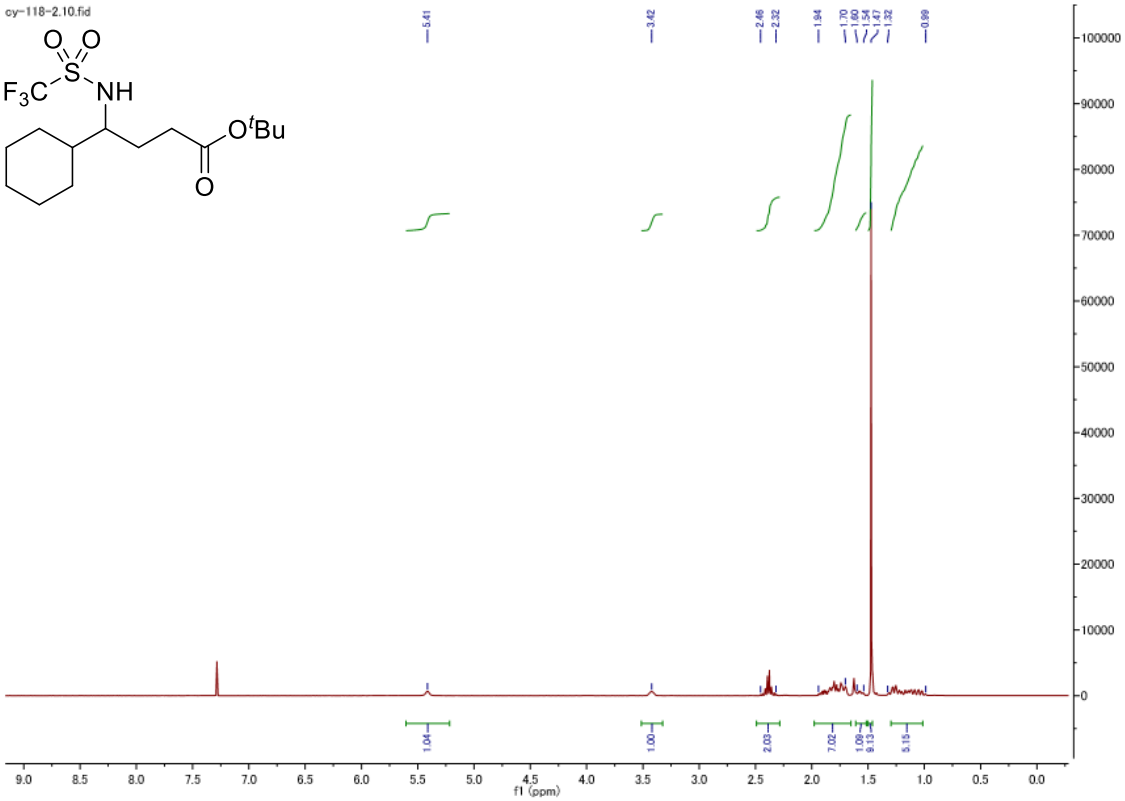
tert-butyl 4-((trifluoromethyl)sulfonamido)octanoate (3ca)

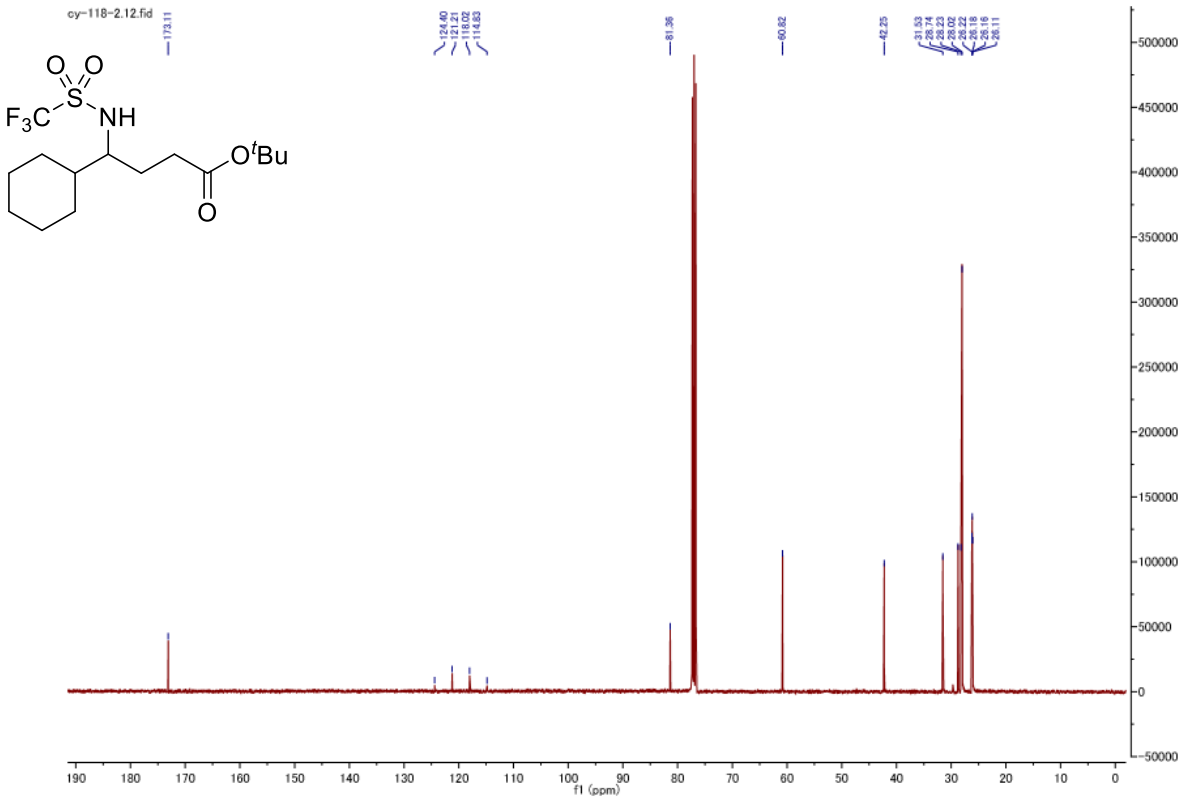


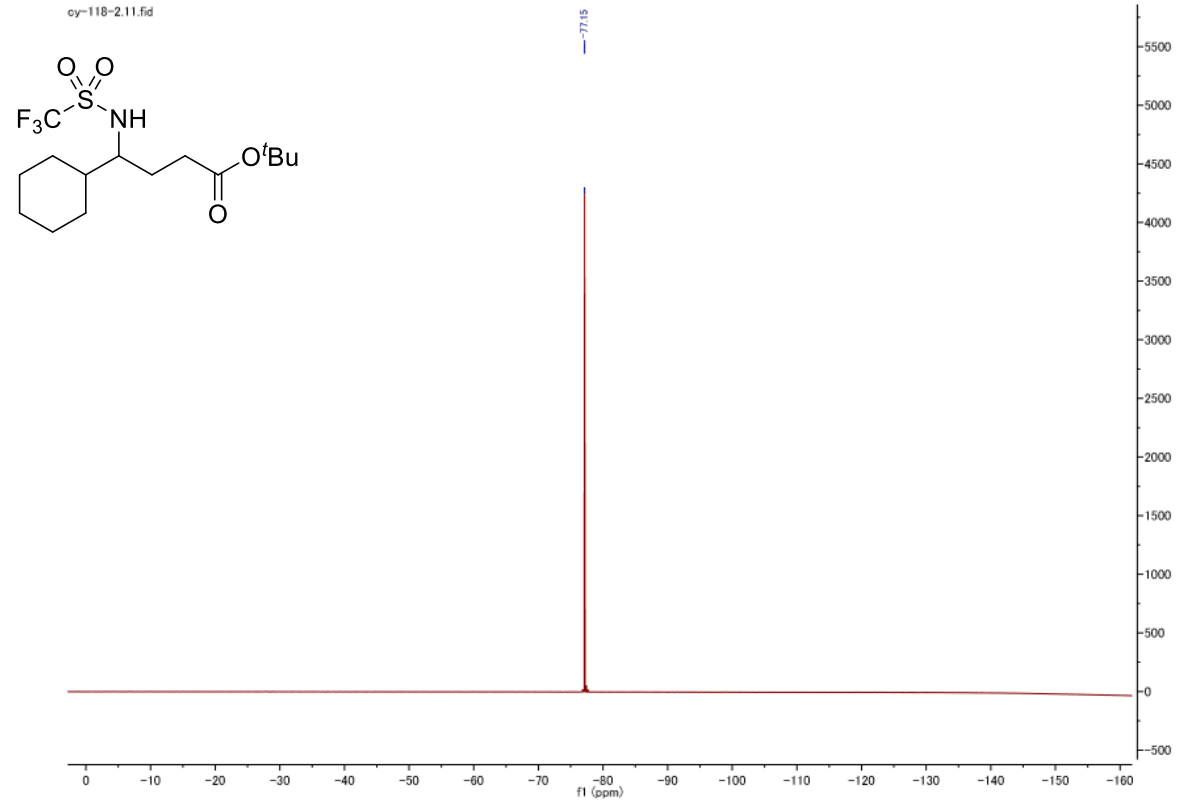




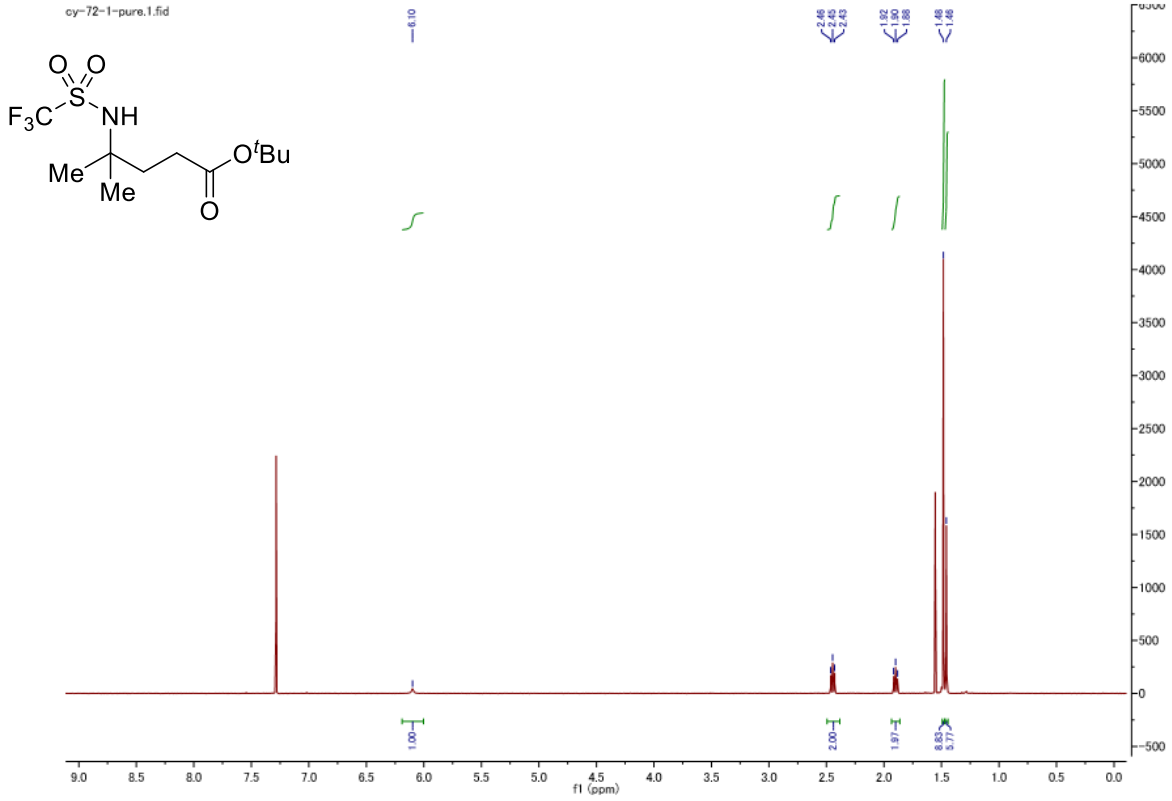
***tert*-butyl 4-cyclohexyl-4-((trifluoromethyl)sulfonamido)butanoate (3da)**

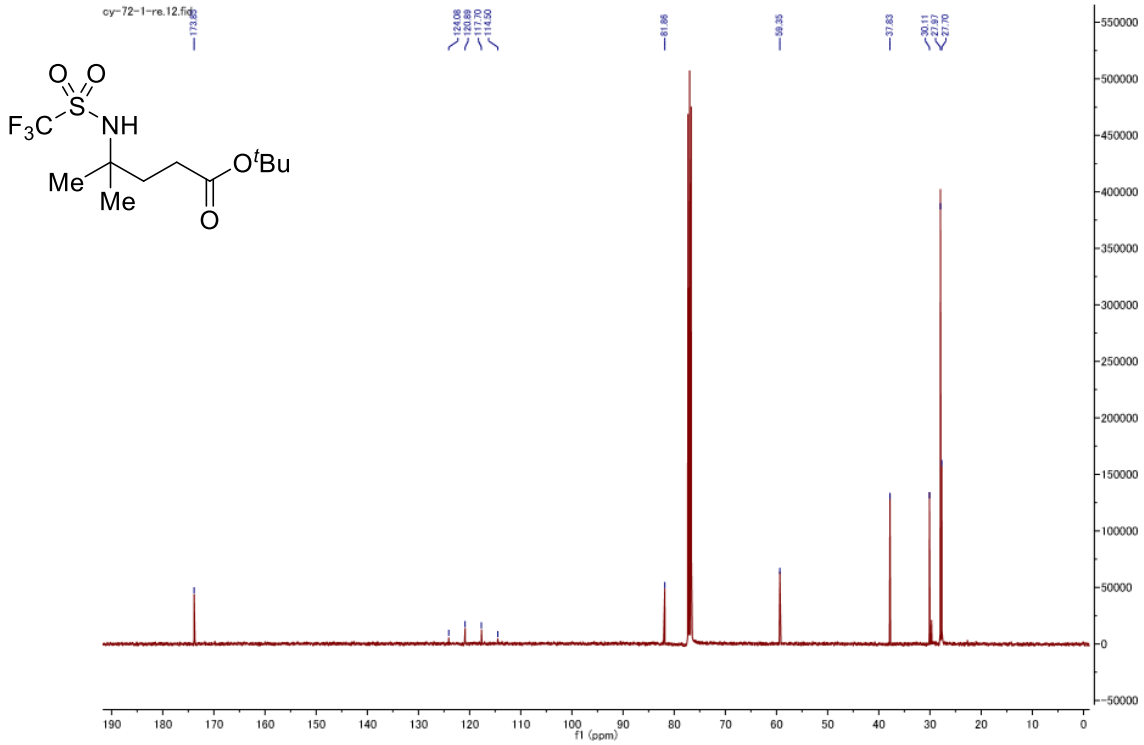


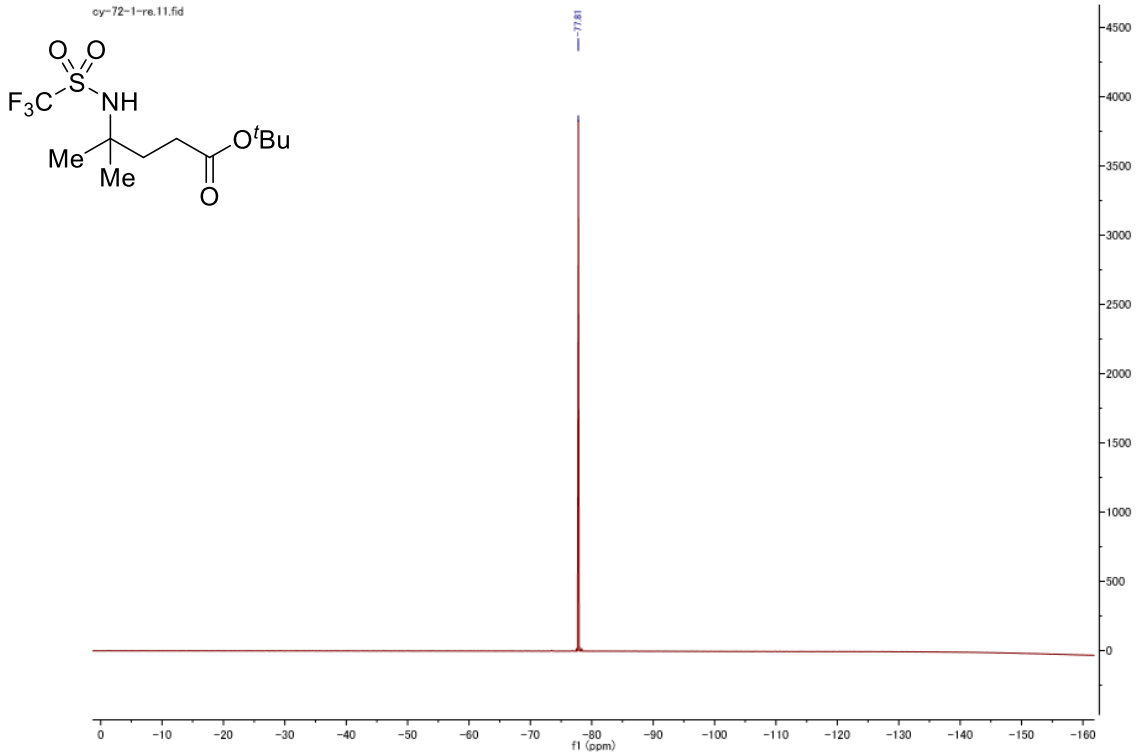

cy-118-2.12.fid
O
O
S
F3C
NH
OtBu
O
173.11
124.40
121.21
118.02
114.83
81.36
60.62
42.25
31.53
28.74
28.23
28.02
26.22
26.18
26.16
26.11
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


cy-118-2.11.fid
O
O
S
F3C
NH
OtBu
O
-77.15
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

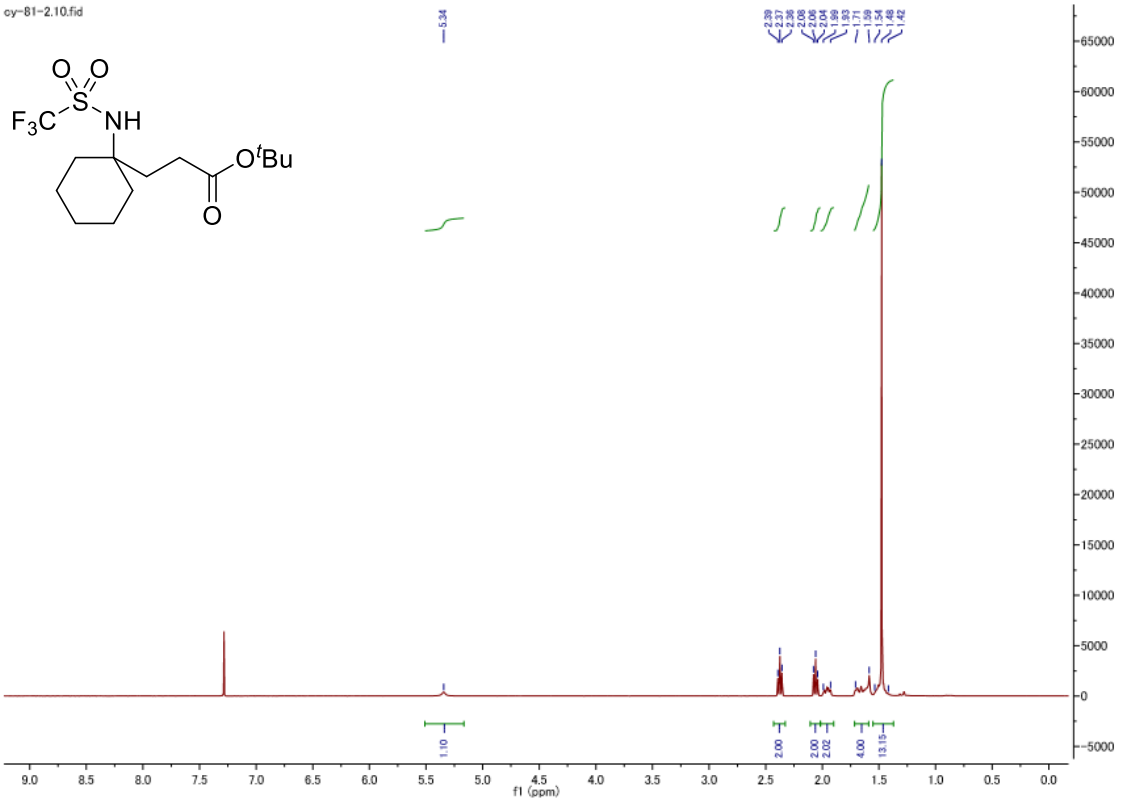
***tert*-butyl 4-methyl-4-((trifluoromethyl)sulfonamido)pentanoate (3ea)**

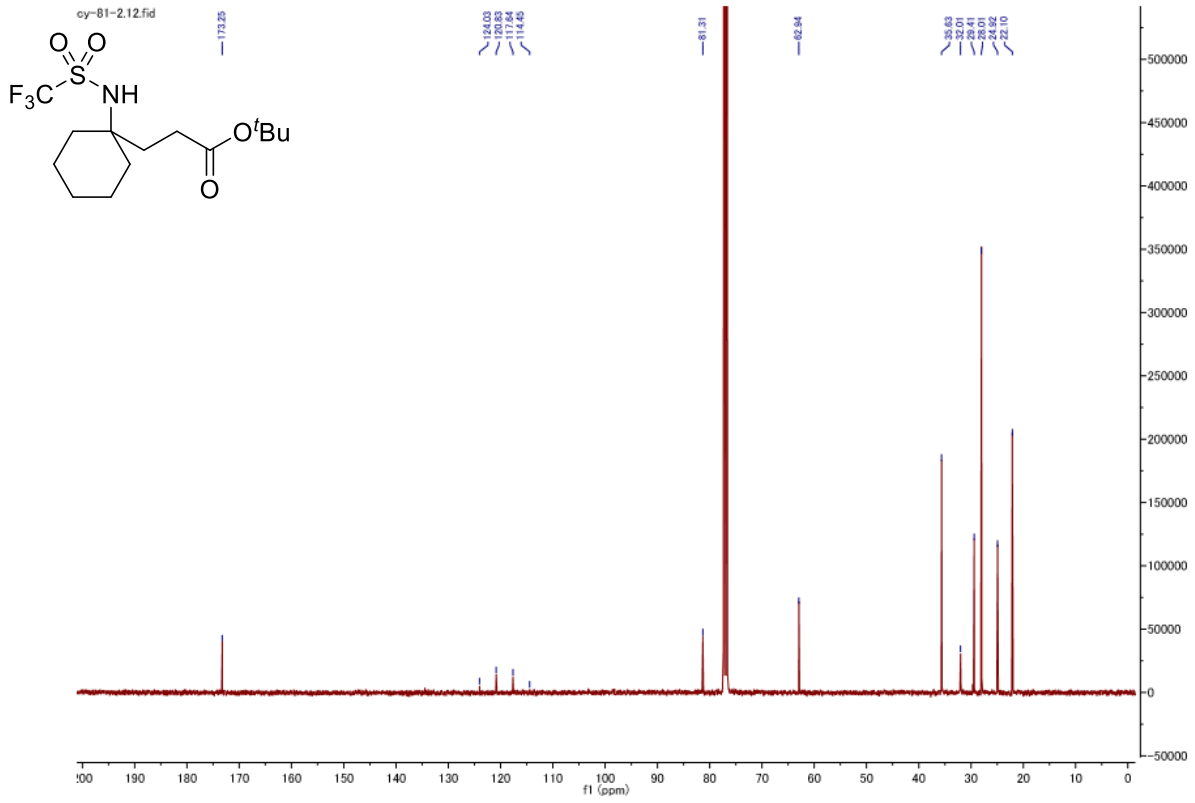


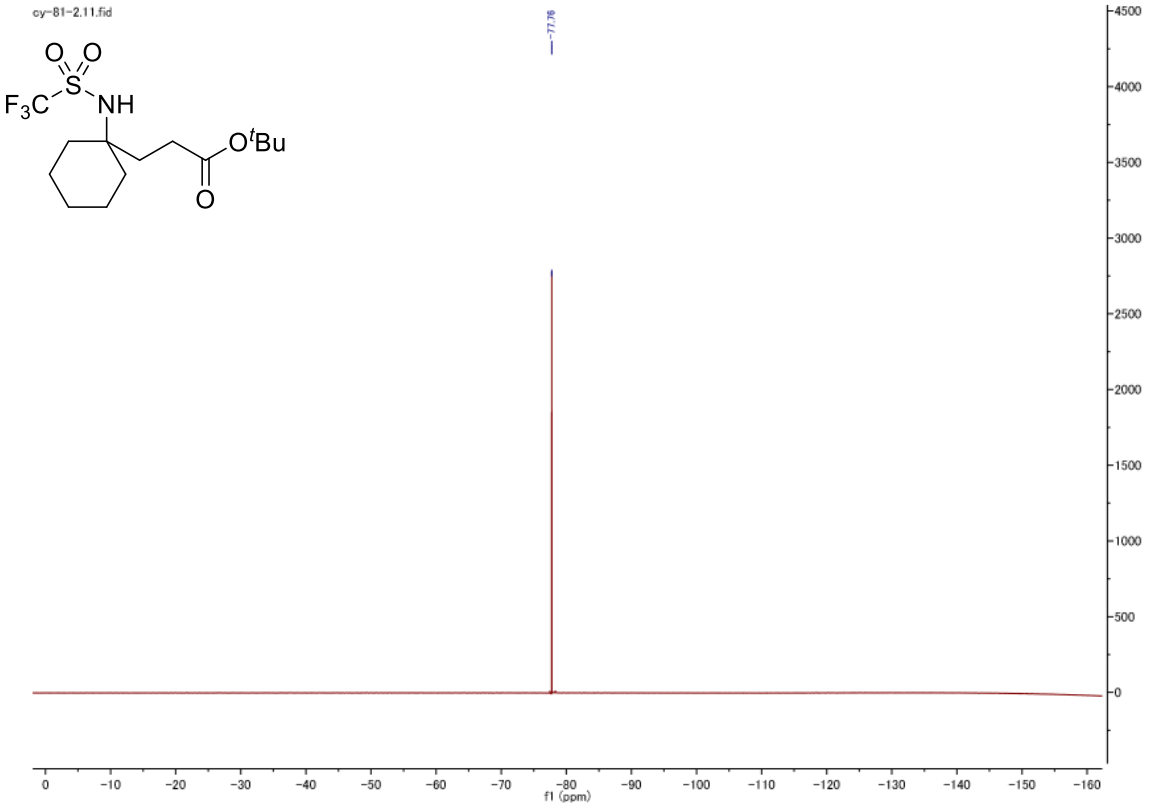




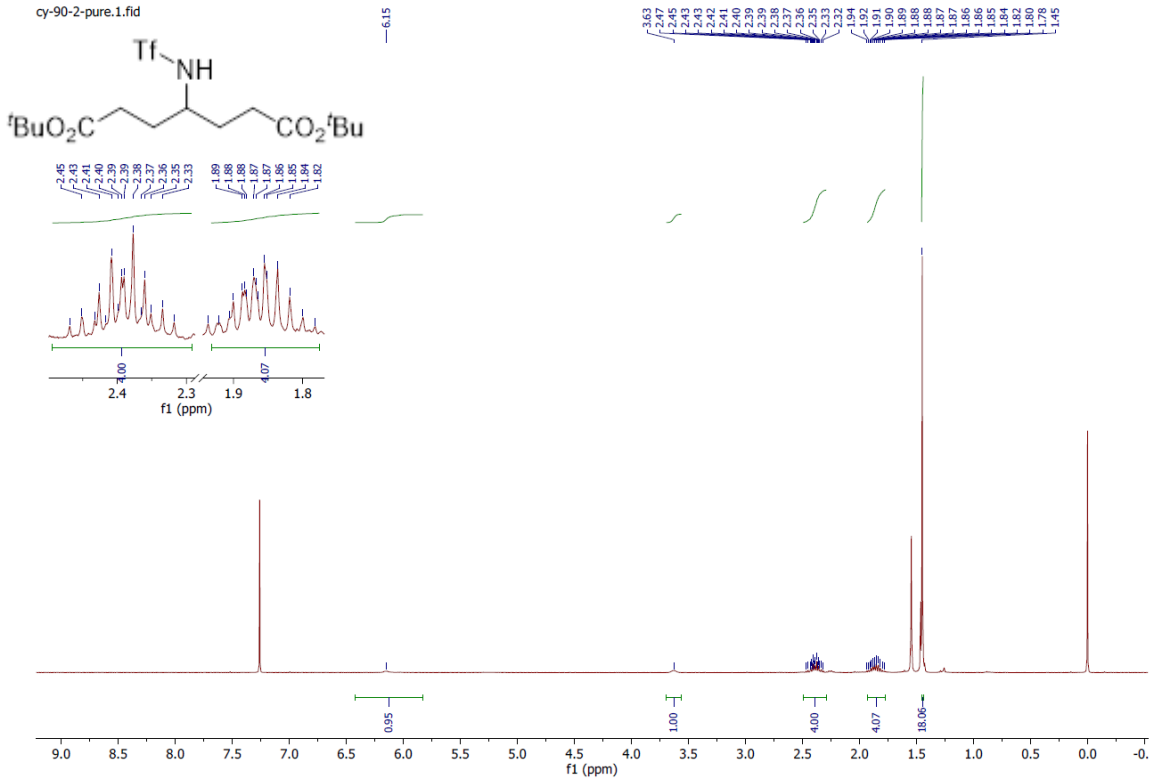
***tert*-butyl 3-(1-((trifluoromethyl)sulfonamido)cyclohexyl)propanoate (3fa)**

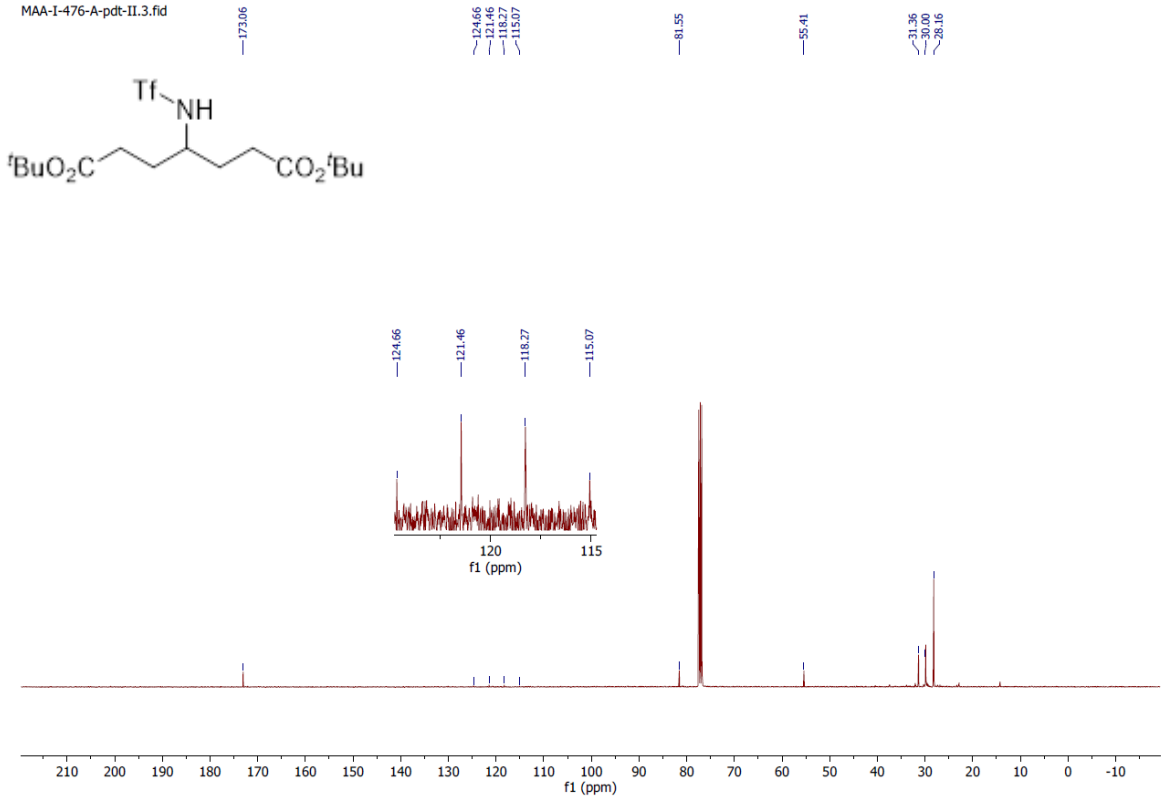


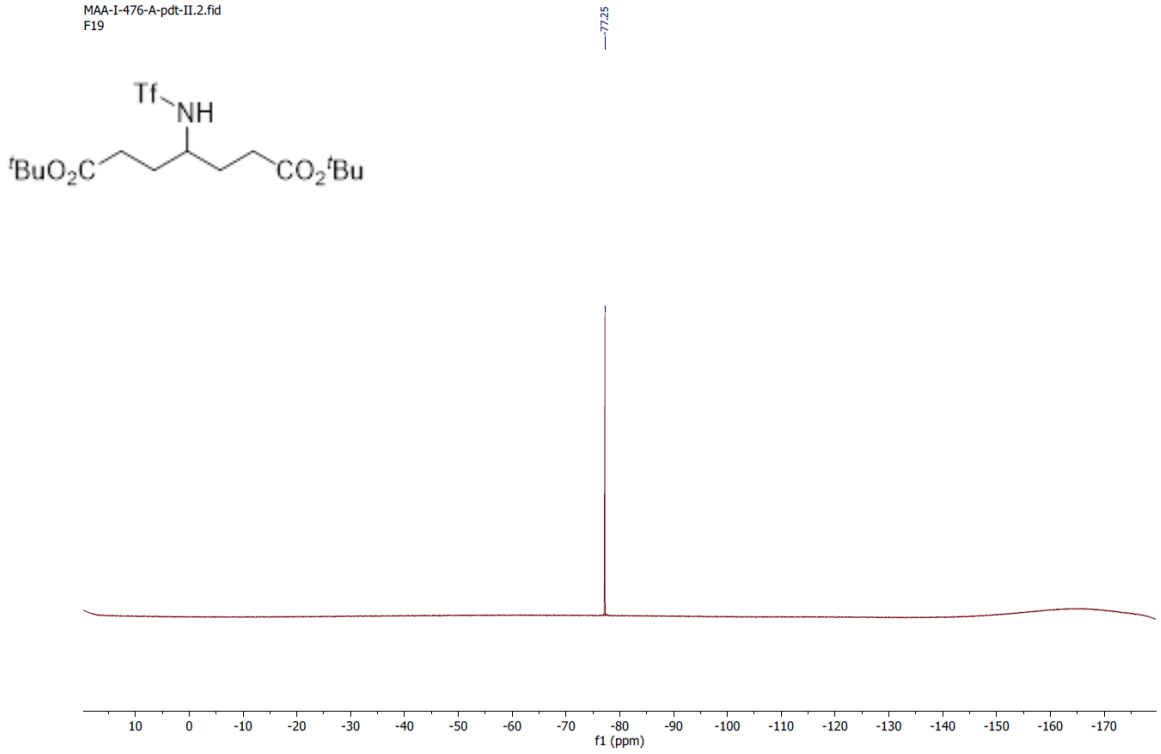

cy-81-2.12.fid
O
O
S
F3C
NH
OtBu
O
173.25
124.03
120.83
117.64
114.45
81.31
62.84
35.63
32.01
29.41
28.01
24.92
22.10
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


cy-81-2.11.fid
O
O
S
F3C
NH
OtBu
O
77.76
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

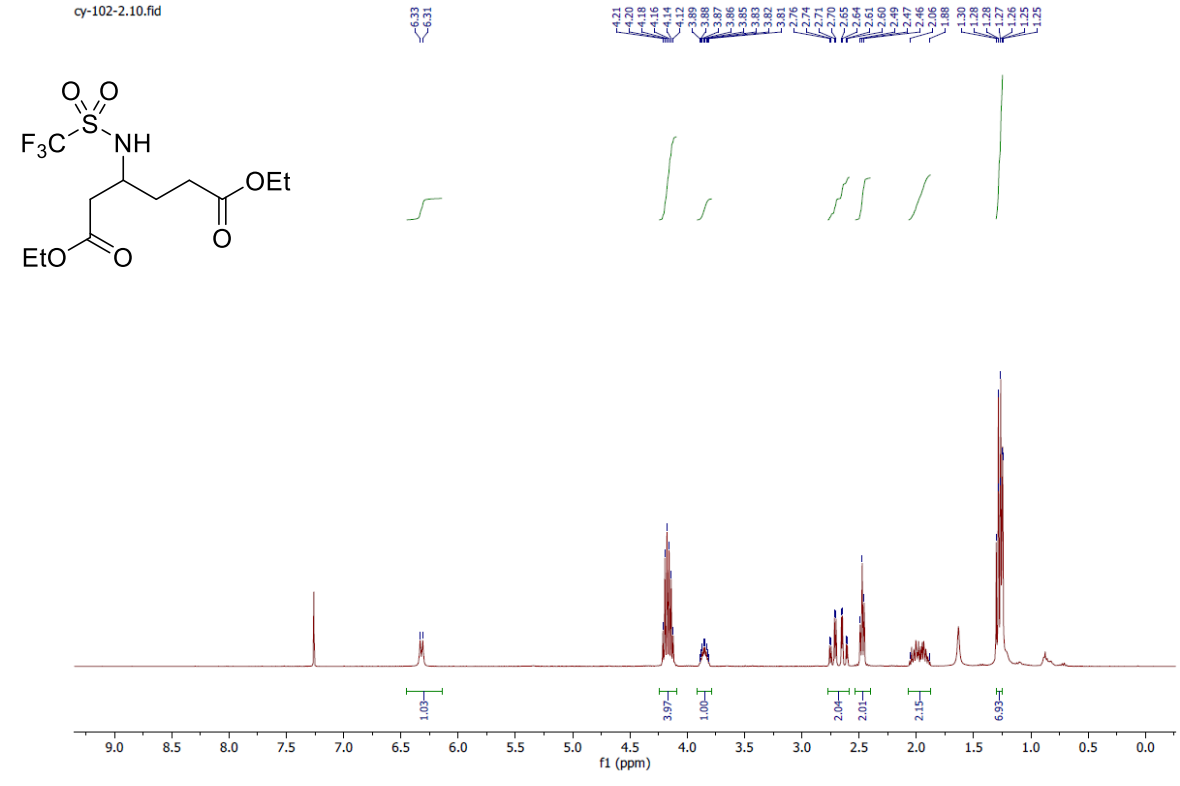
di-*tert*-butyl 4-((Trifluoromethyl)sulfonamide)heptanedioate (3ga)

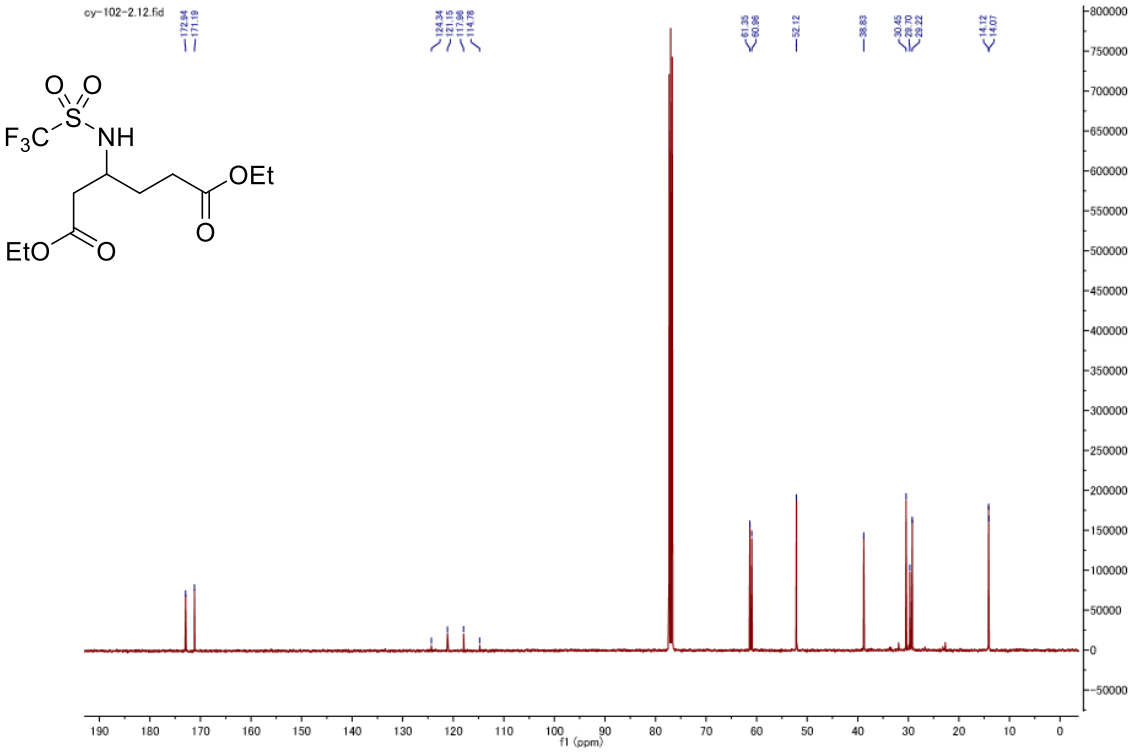


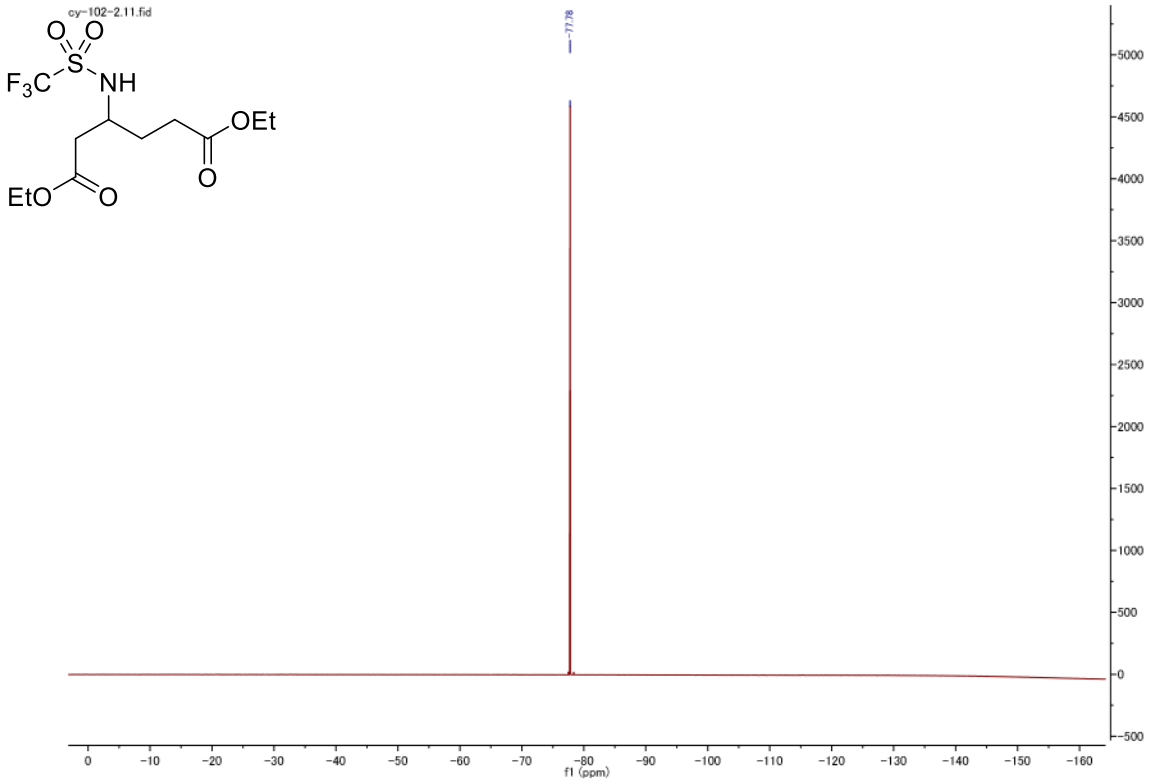




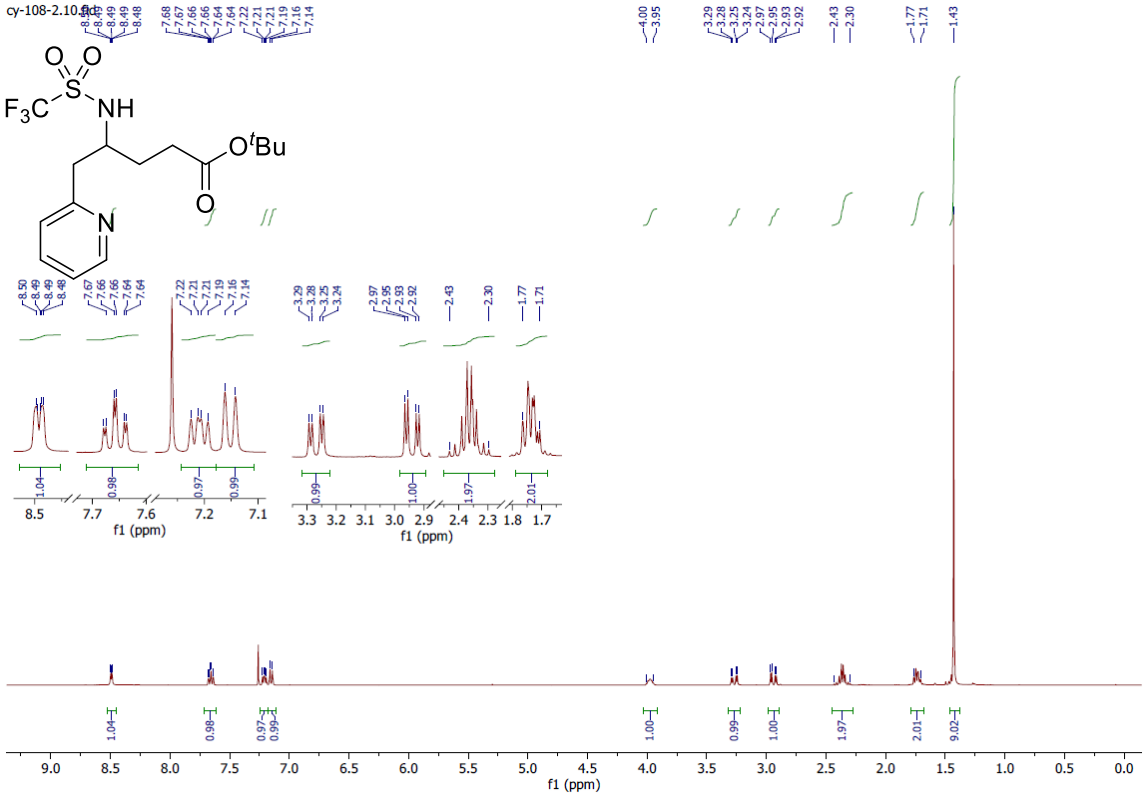
diethyl 3-((trifluoromethyl)sulfonamido)hexanedioate (3hb)

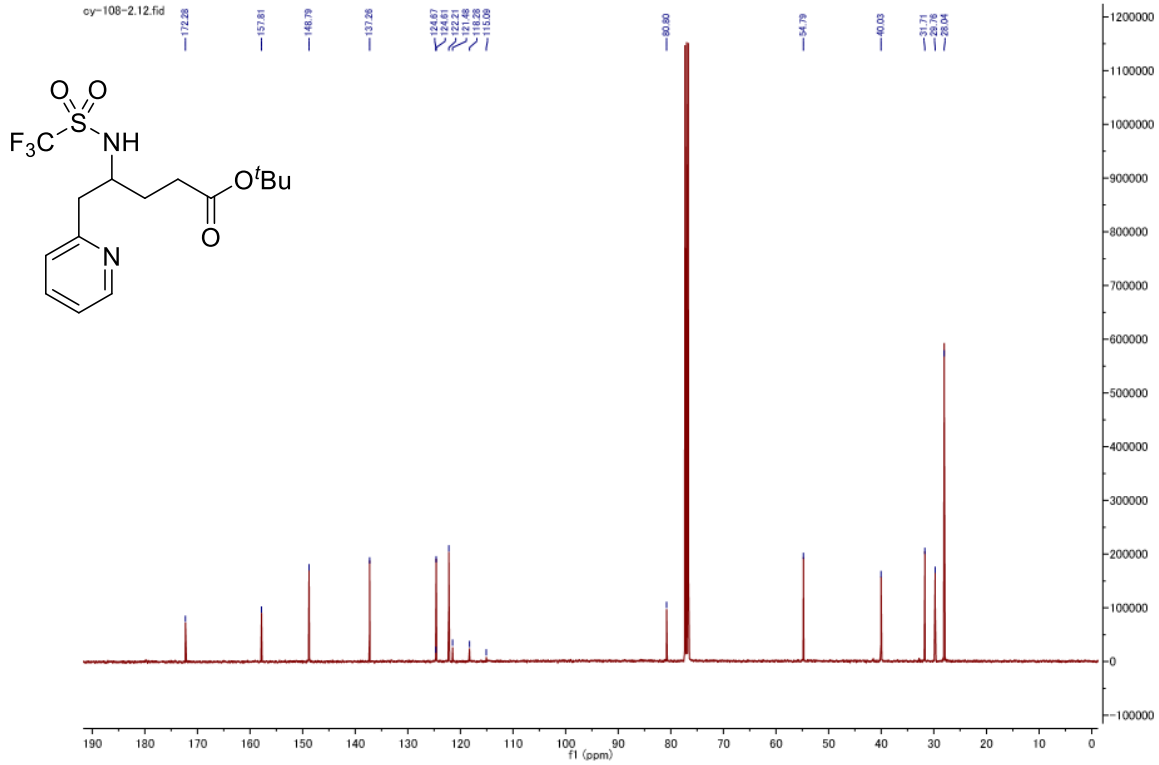


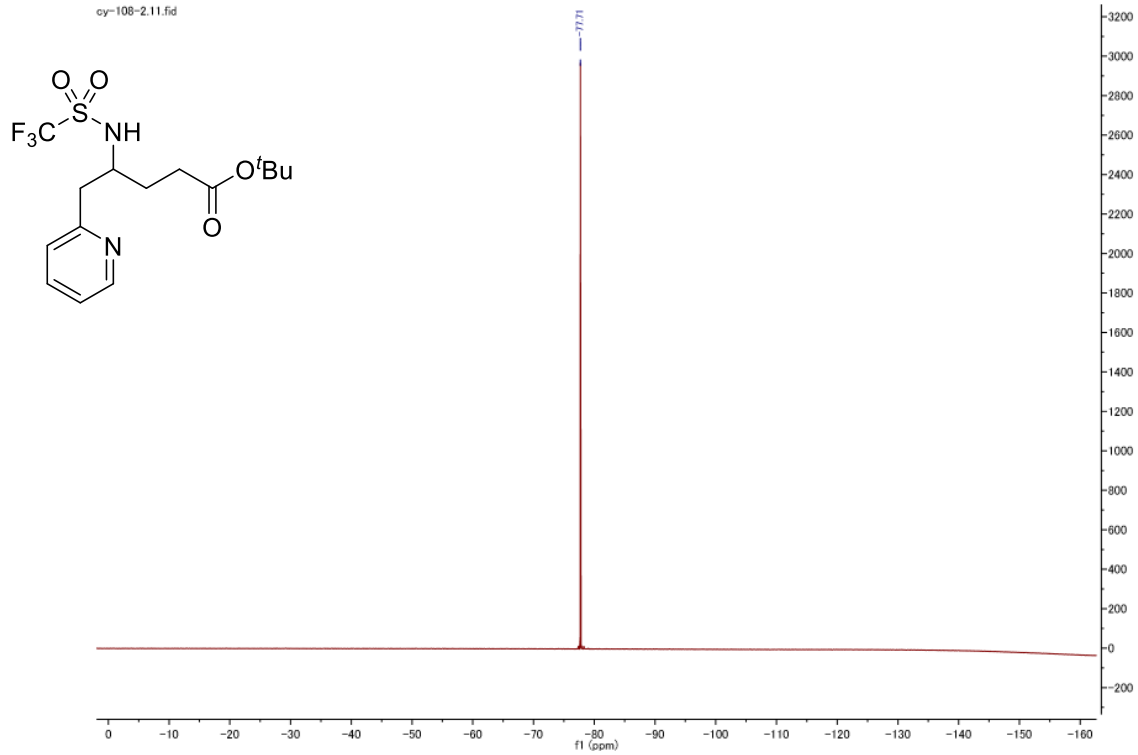

cy-102-2.12.fid
O
O
S
F3C
NH
OEt
O
EtO
O
f1 (ppm)


cy-102-2.11.fid
O
O
S
F3C
NH
OEt
O
EtO
O
f1 (ppm)

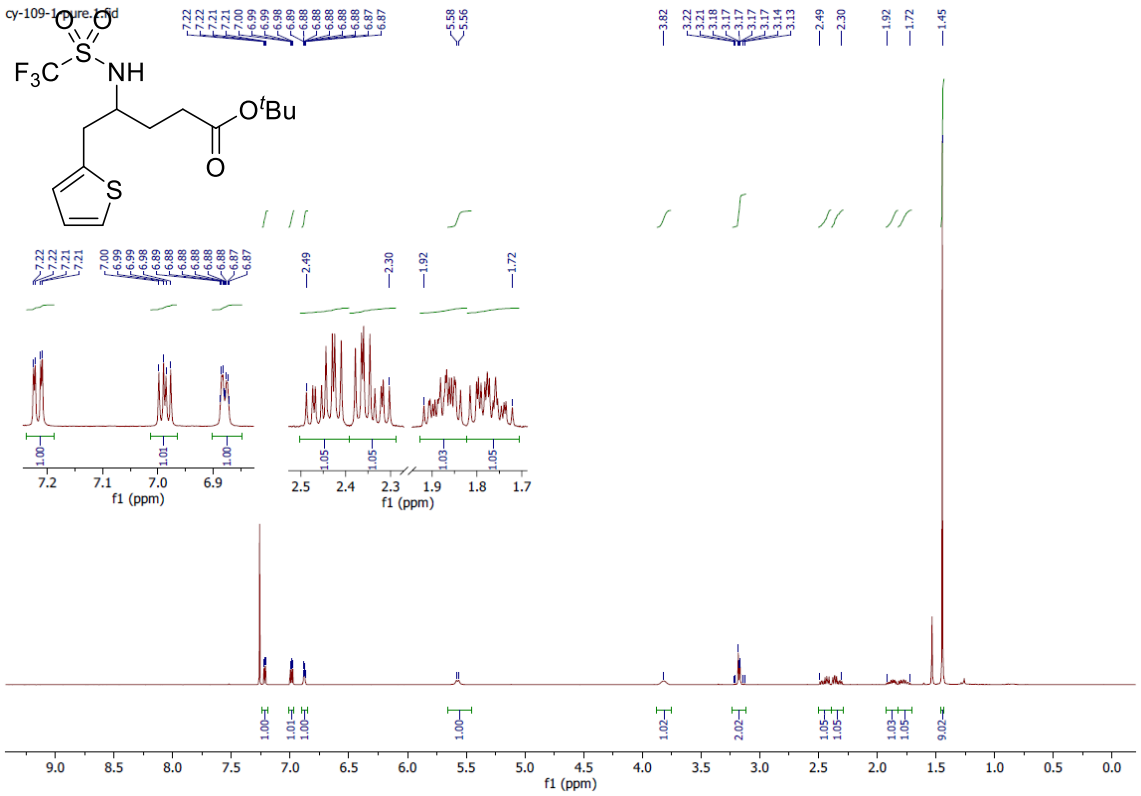
***tert*-butyl 5-(pyridin-2-yl)-4-((trifluoromethyl)sulfonamido)pentanoate (3ia)**

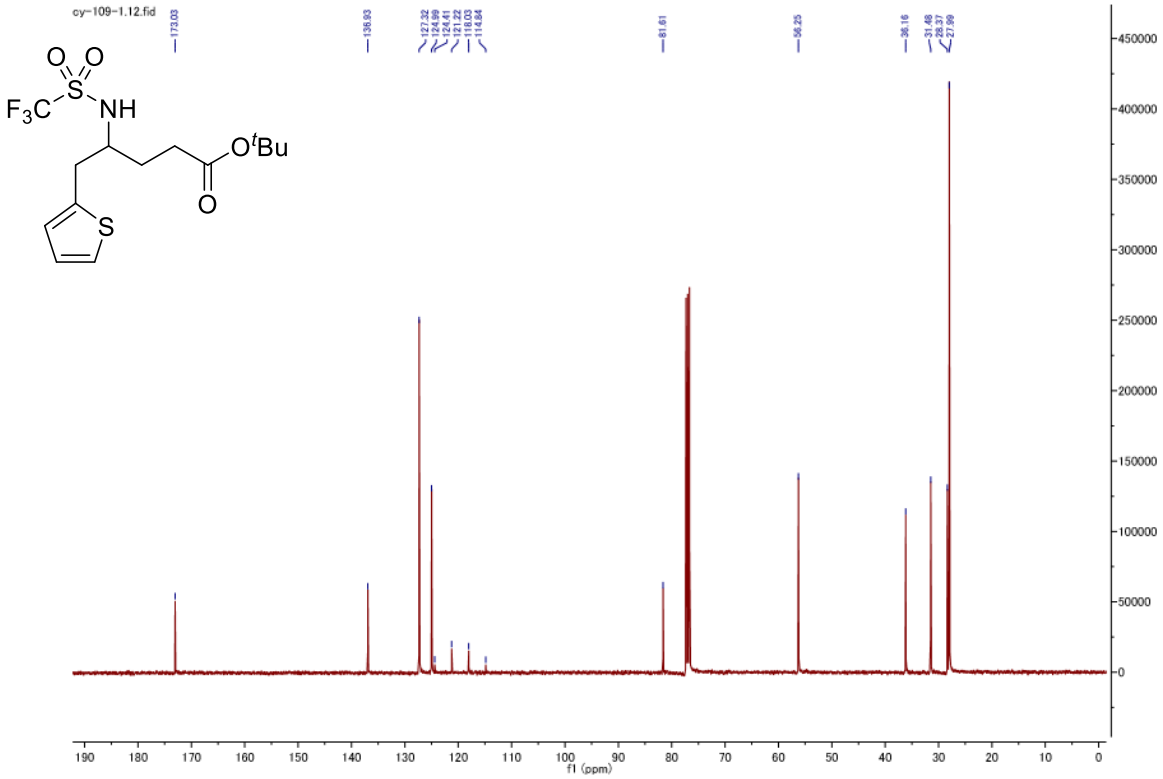


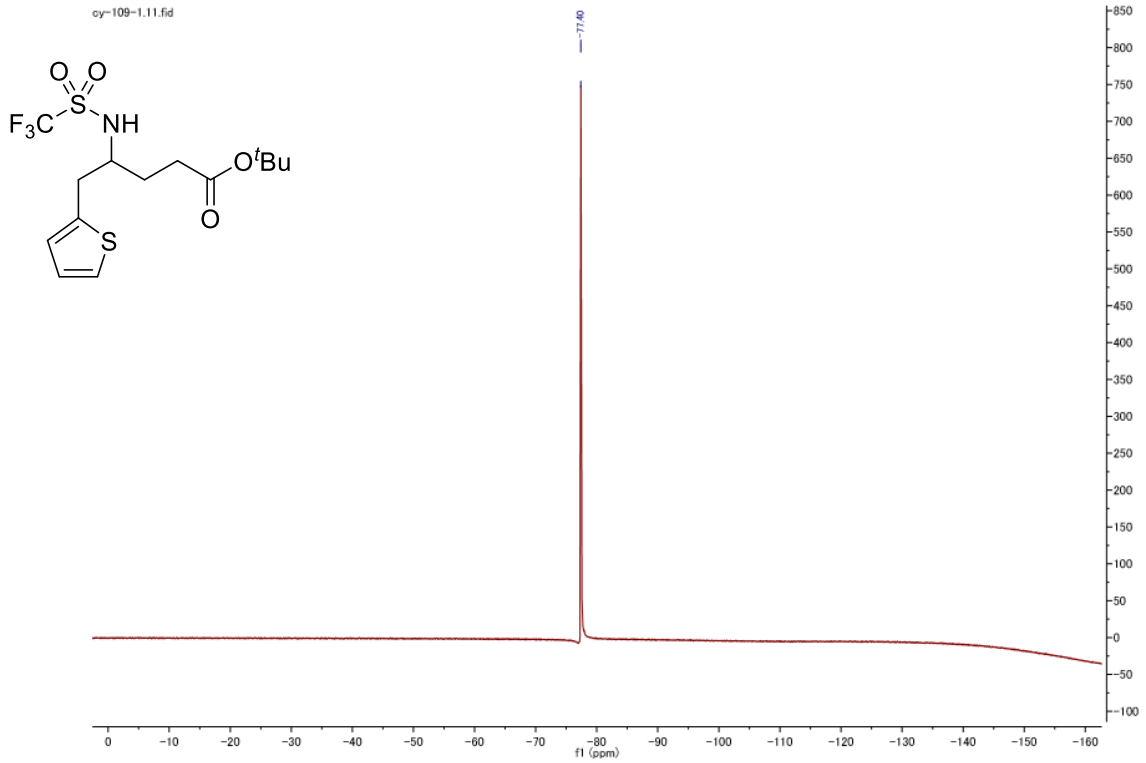




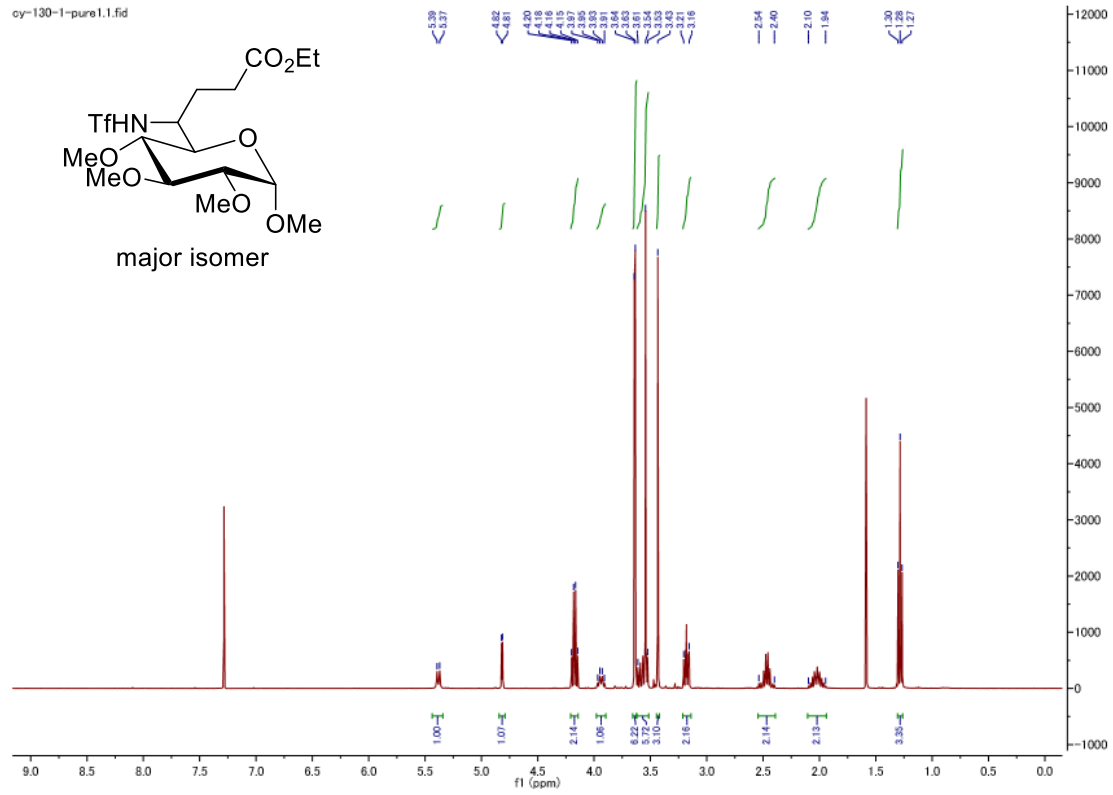
tert-butyl 5-(thiophen-2-yl)-4-((trifluoromethyl)sulfonamido)pentanoate (3ja)

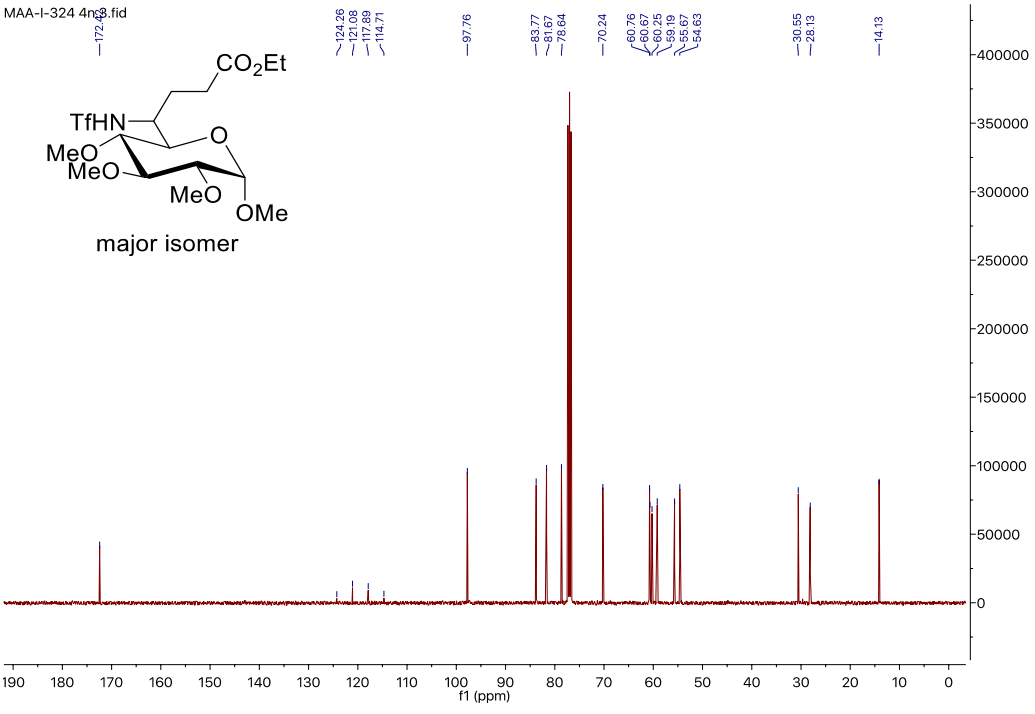


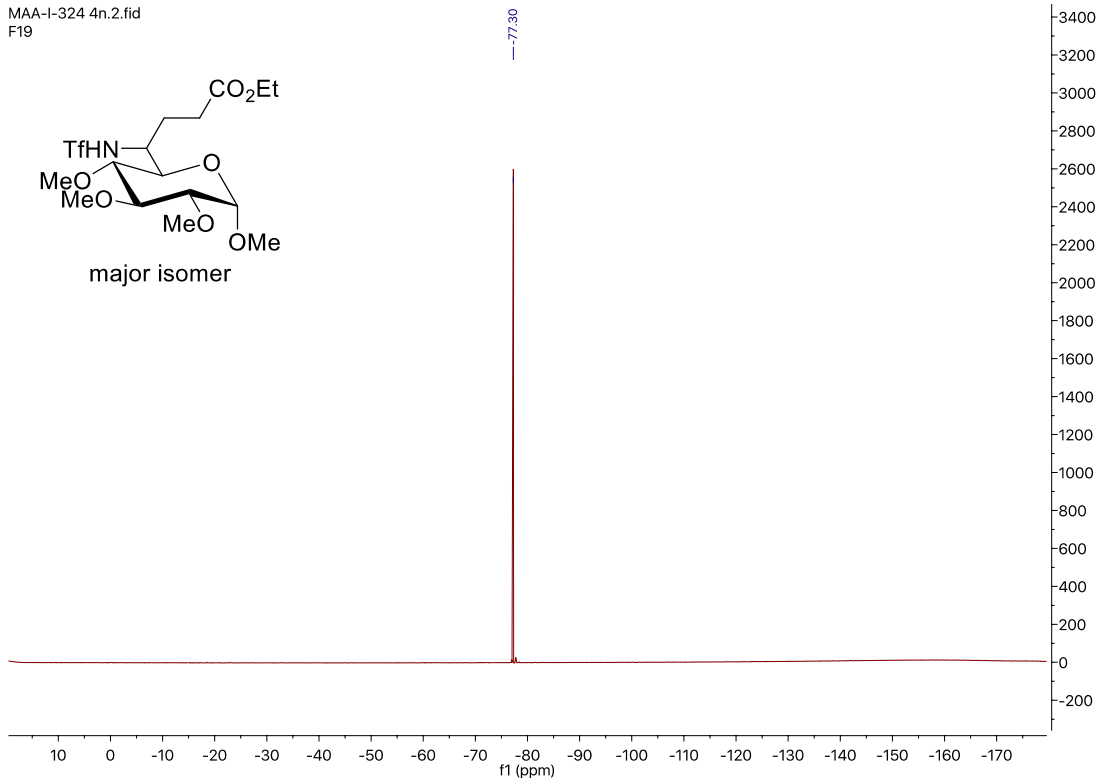

cy-109-1.12.fid
O
O
F3C
S
NH
O
tBu
O
S
173.03
136.93
127.32
124.99
124.41
121.22
116.03
114.64
81.61
56.25
36.16
31.48
28.37
27.99
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


cy-109-1.11.fid
O
O
F3C
S
NH
O
tBu
O
S
77.40
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

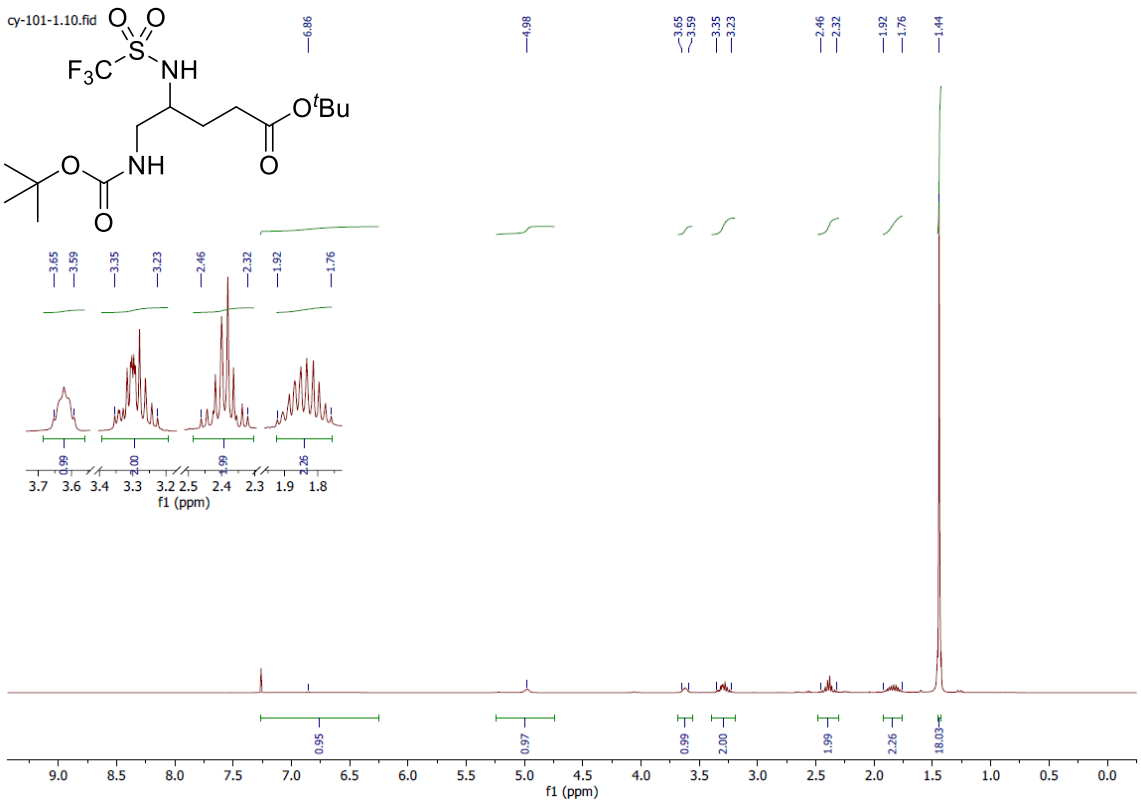
ethyl-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2*H*-pyran-2-yl)-4-((trifluoromethyl)sulfonamido)butanoate (3kb)

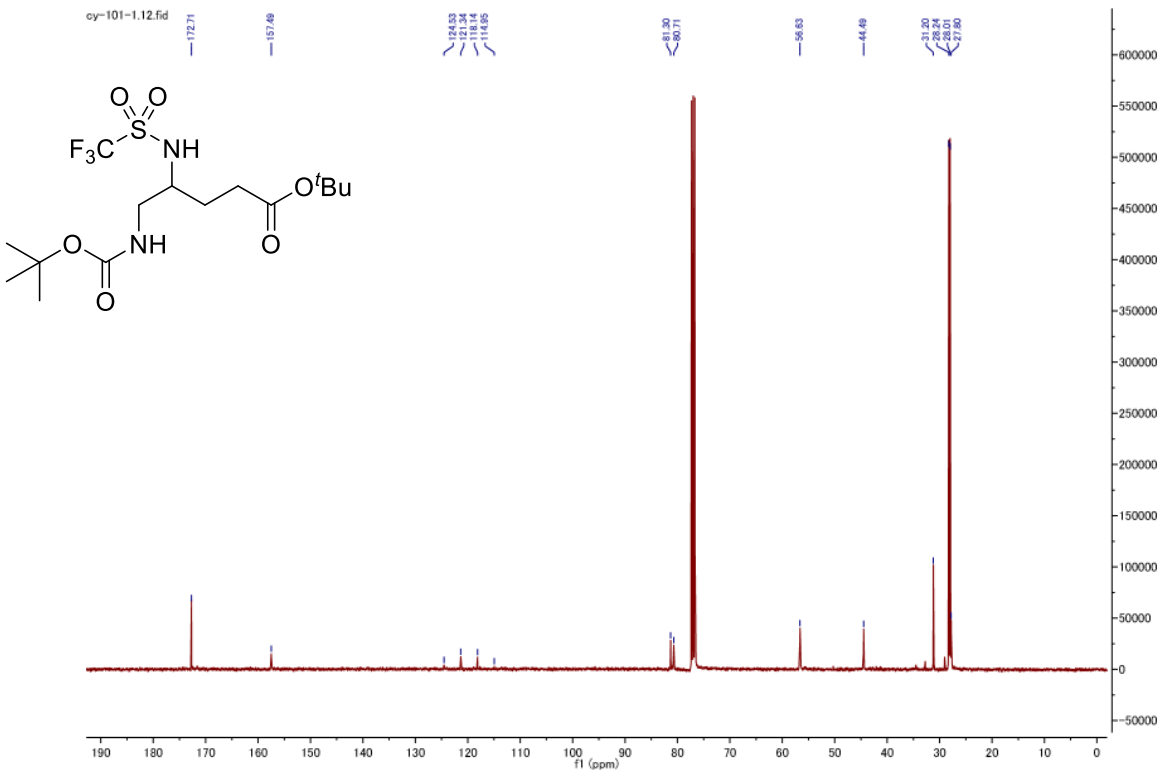


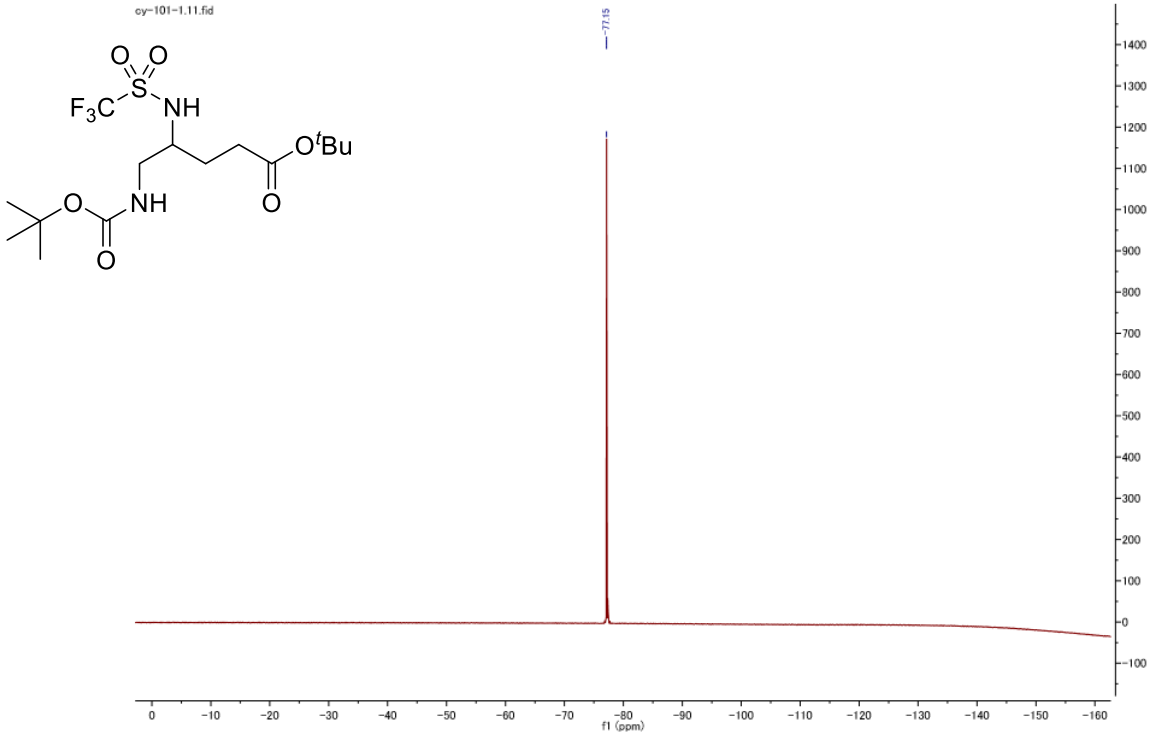




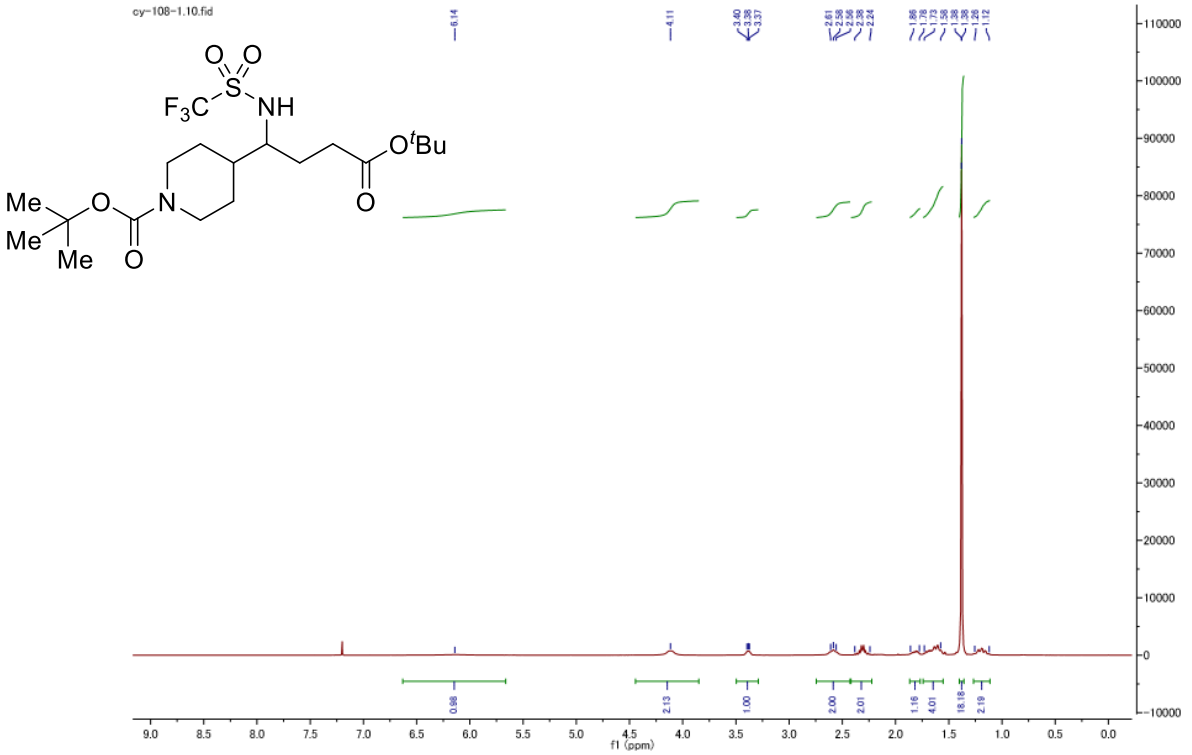
***tert*-butyl 5-((*tert*-butoxycarbonyl)amino)-4-((trifluoromethyl)sulfonamido)pentanoate (3la)**

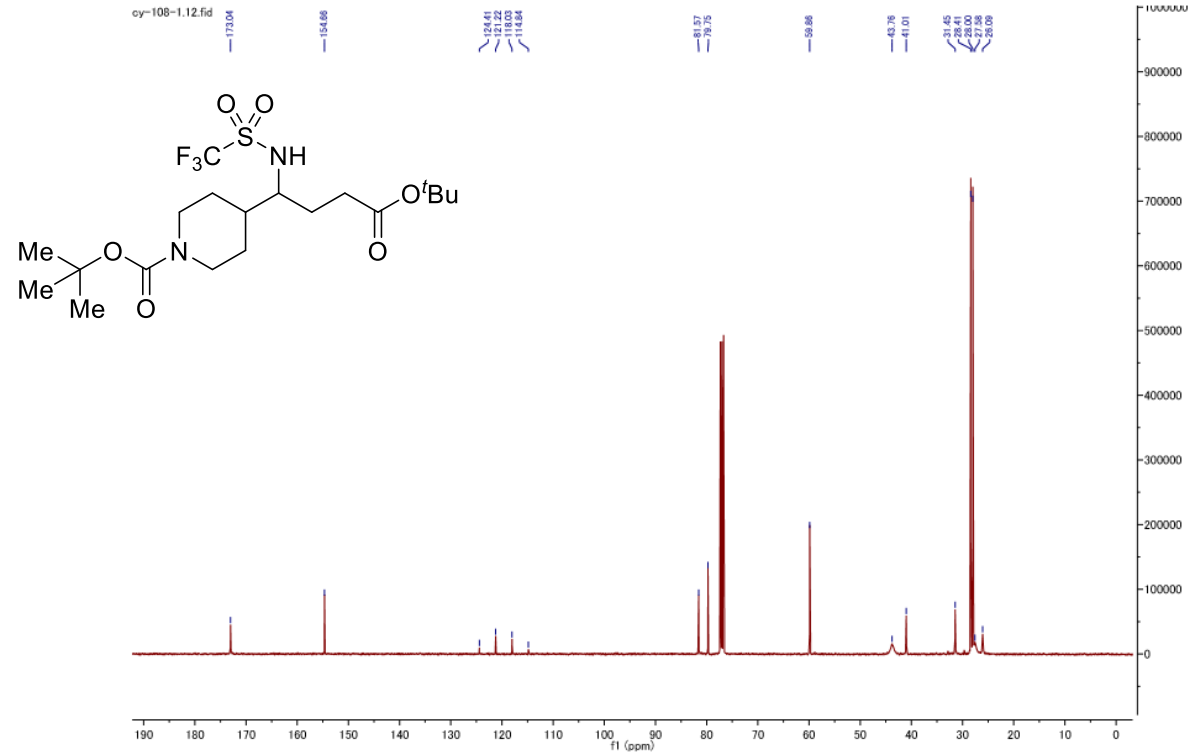


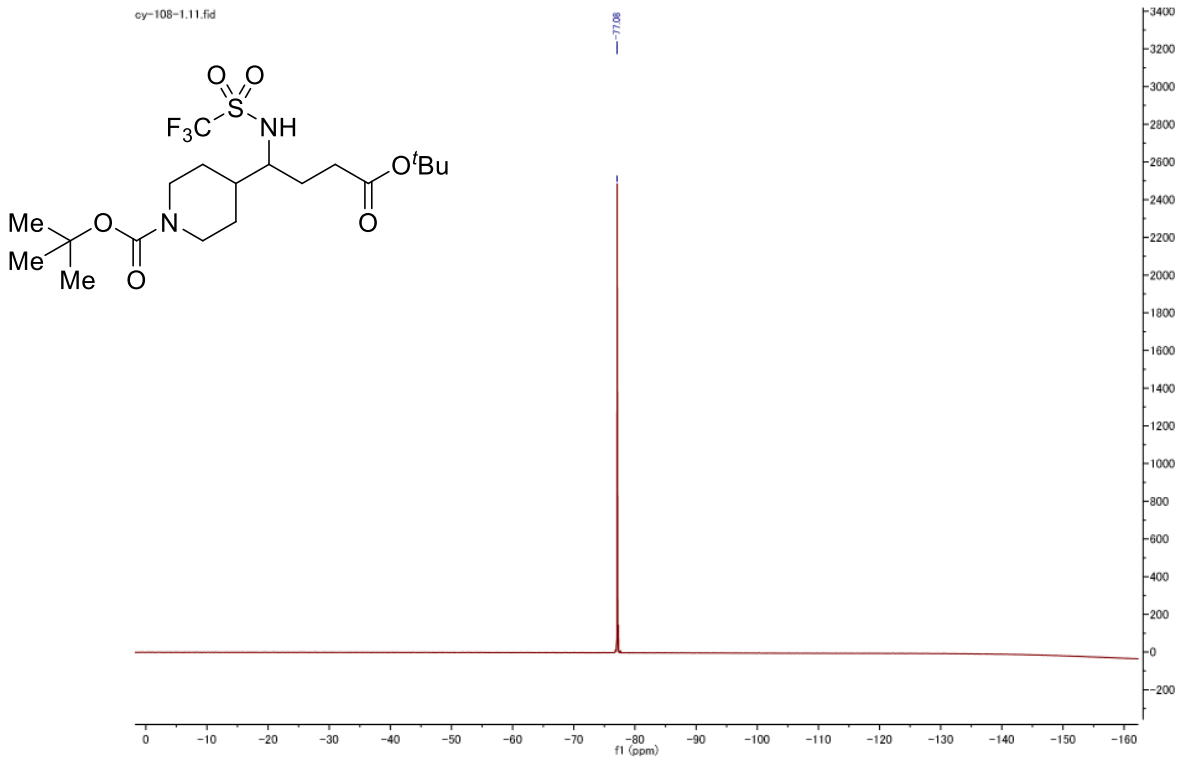

cy-101-1.12.fid
172.71
157.49
124.53
121.34
118.14
114.95
81.30
80.71
56.63
44.49
31.20
28.24
28.01
27.80
O
O
S
F3C
NH
OtBu
O
NH
O
O
f1 (ppm)


cy-101-1.11.fid
77.15
O
O
S
F3C
NH
OtBu
O
NH
O
O
f1 (ppm)

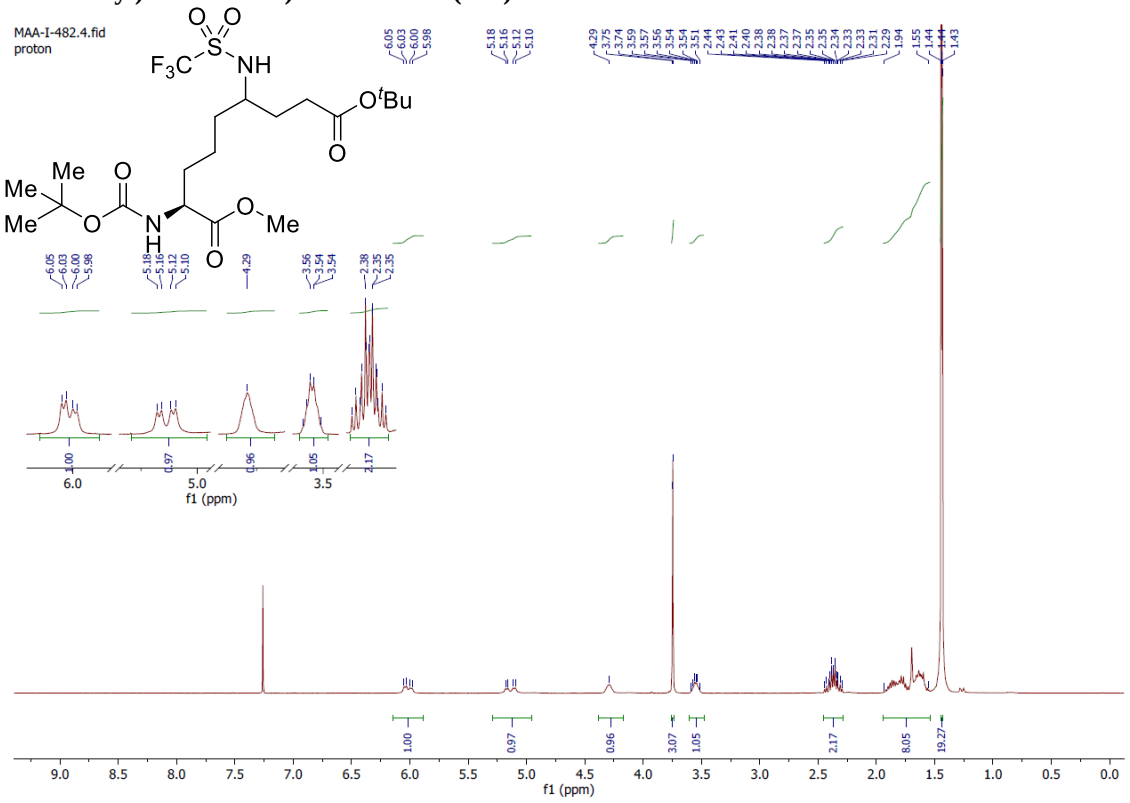
***tert*-butyl 4-(4-(tert-butoxy)-4-oxo-1-((trifluoromethyl)sulfonamido)butyl)piperidine-1-carboxylate (3ma)**

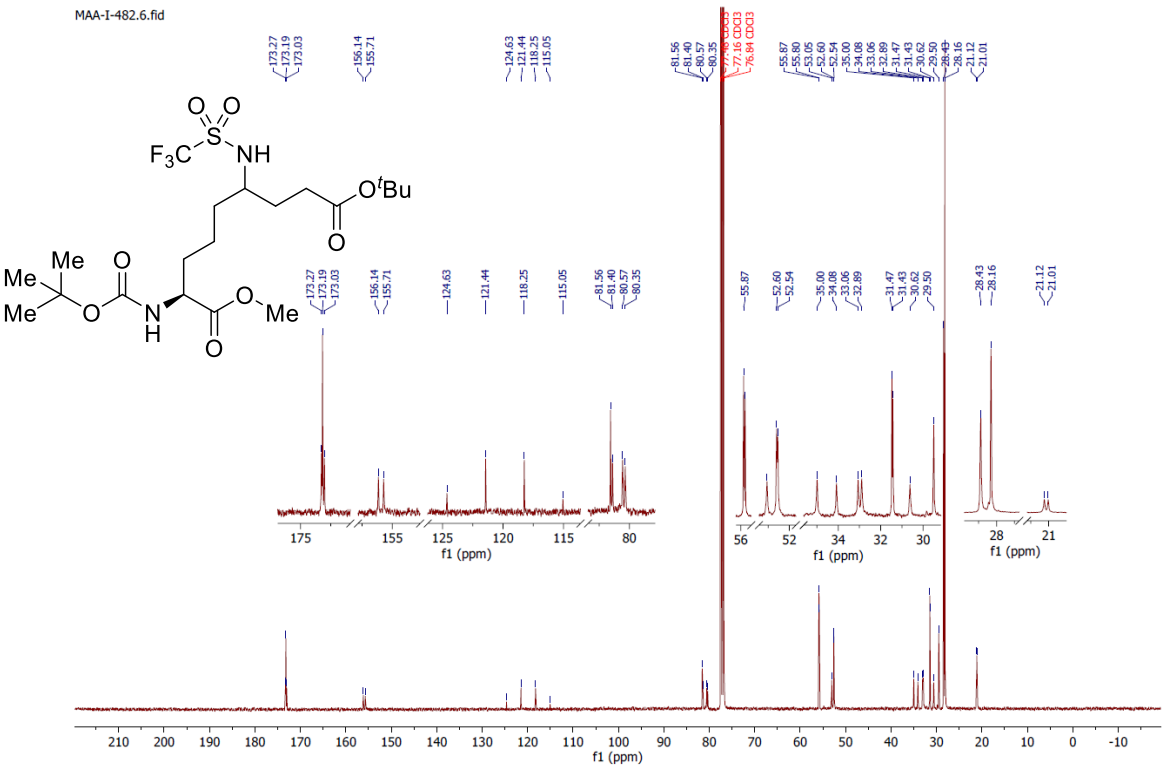


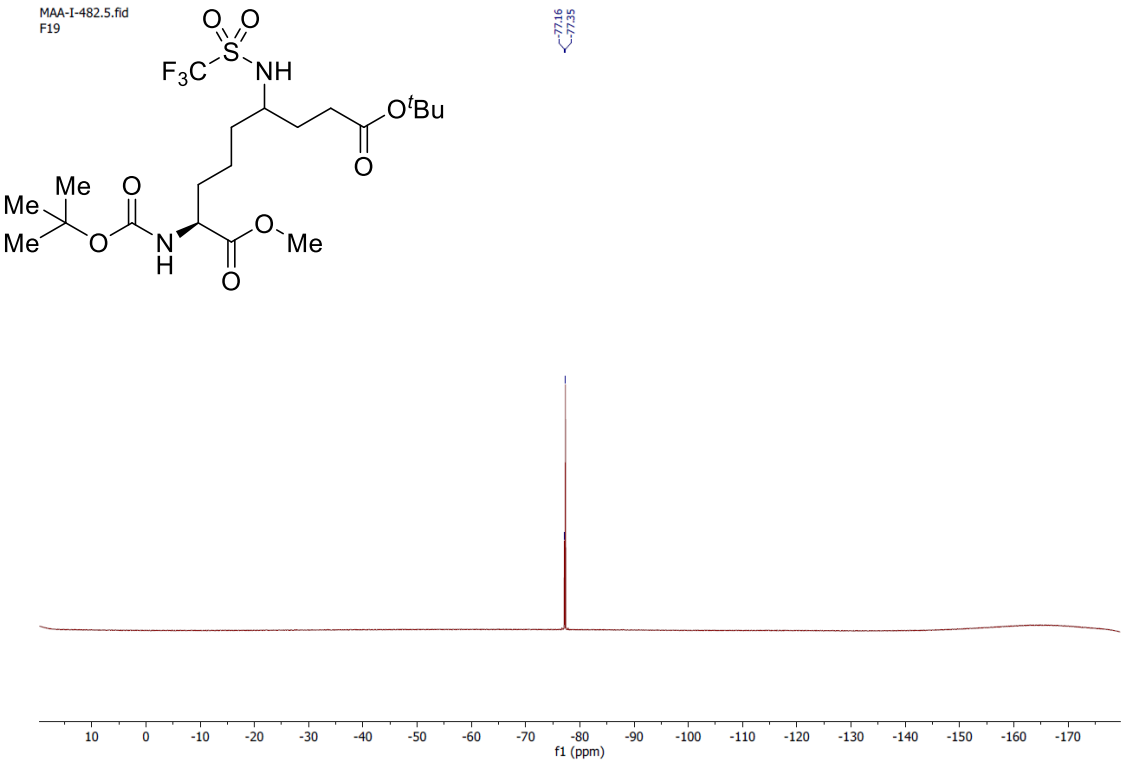




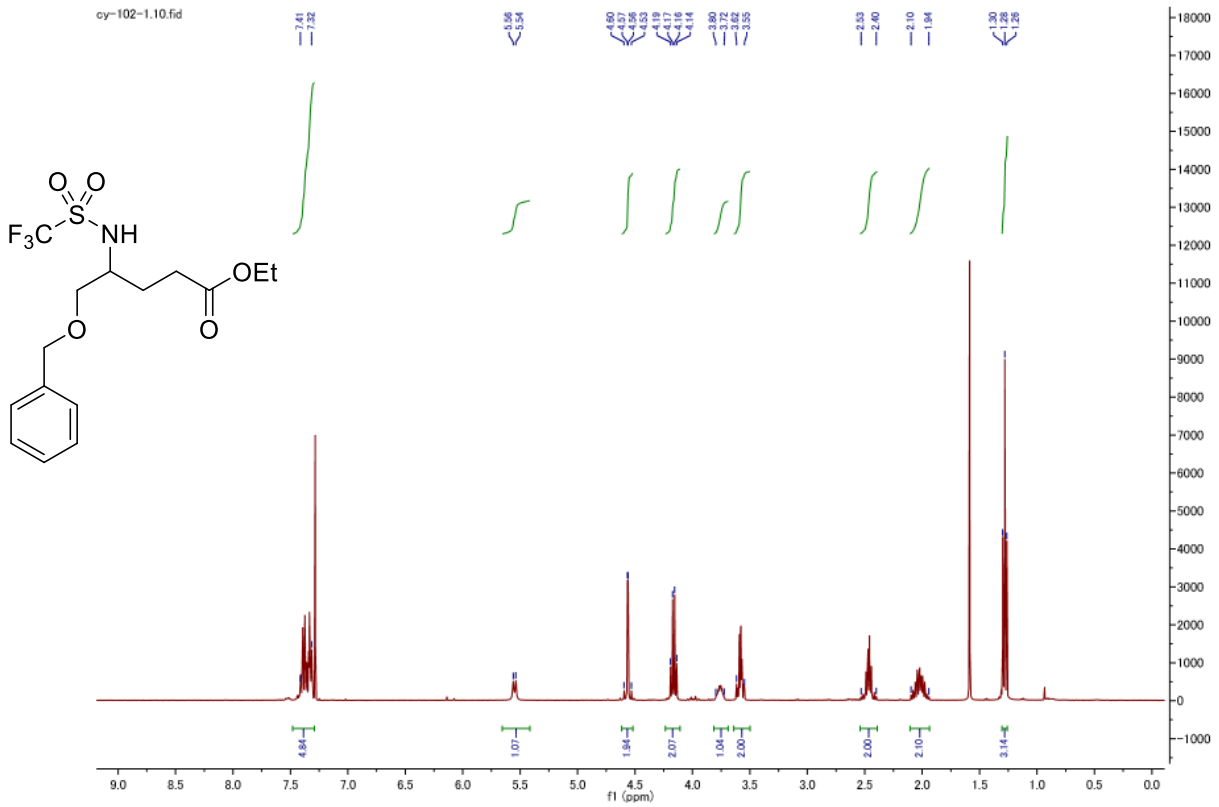
9-(*tert*-butyl) 1-methyl (2*S*)-2-((*tert*-butoxycarbonyl)amino)-6-((trifluoromethyl)sulfonamido)nonanedioate (3na)

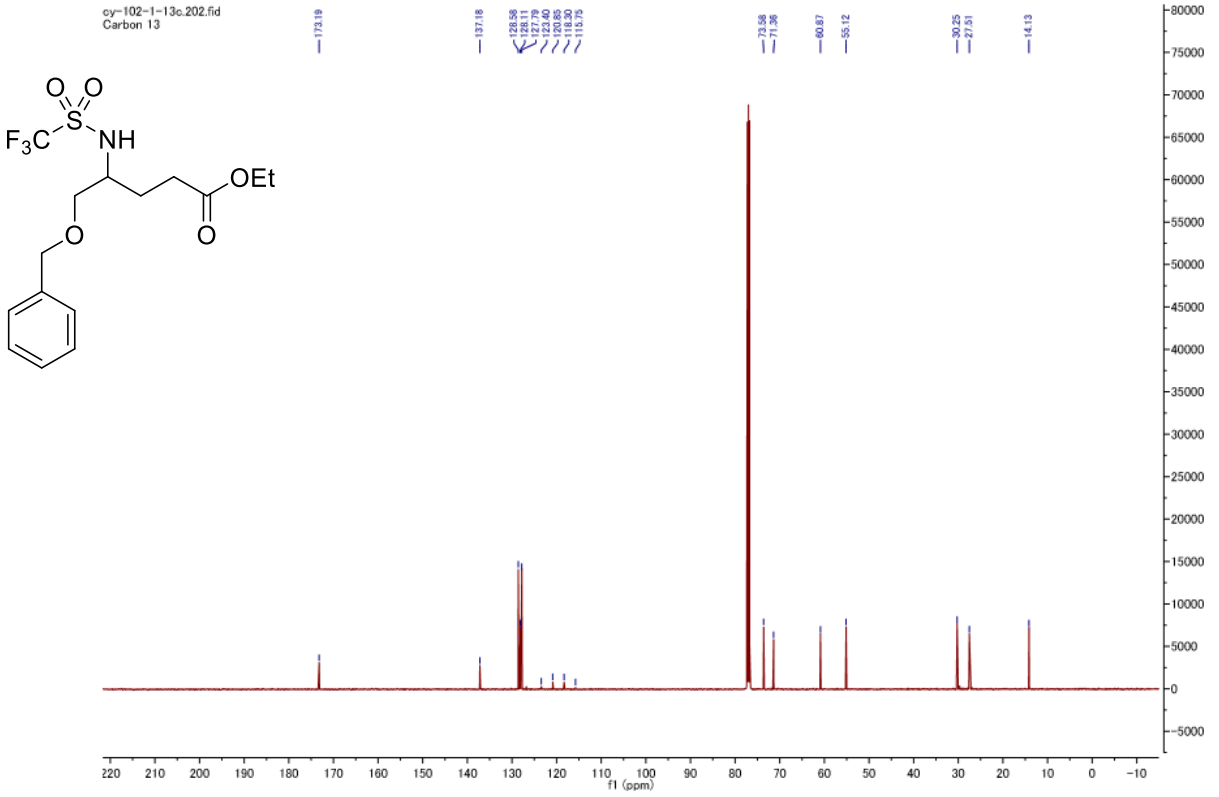


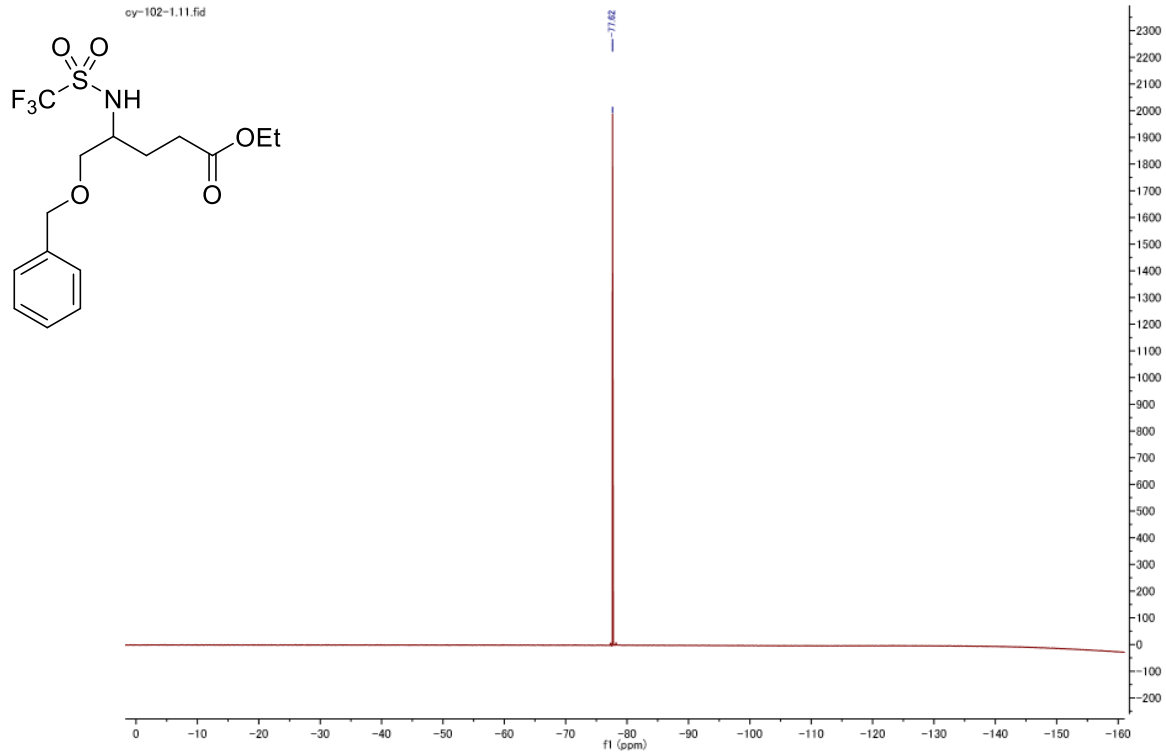




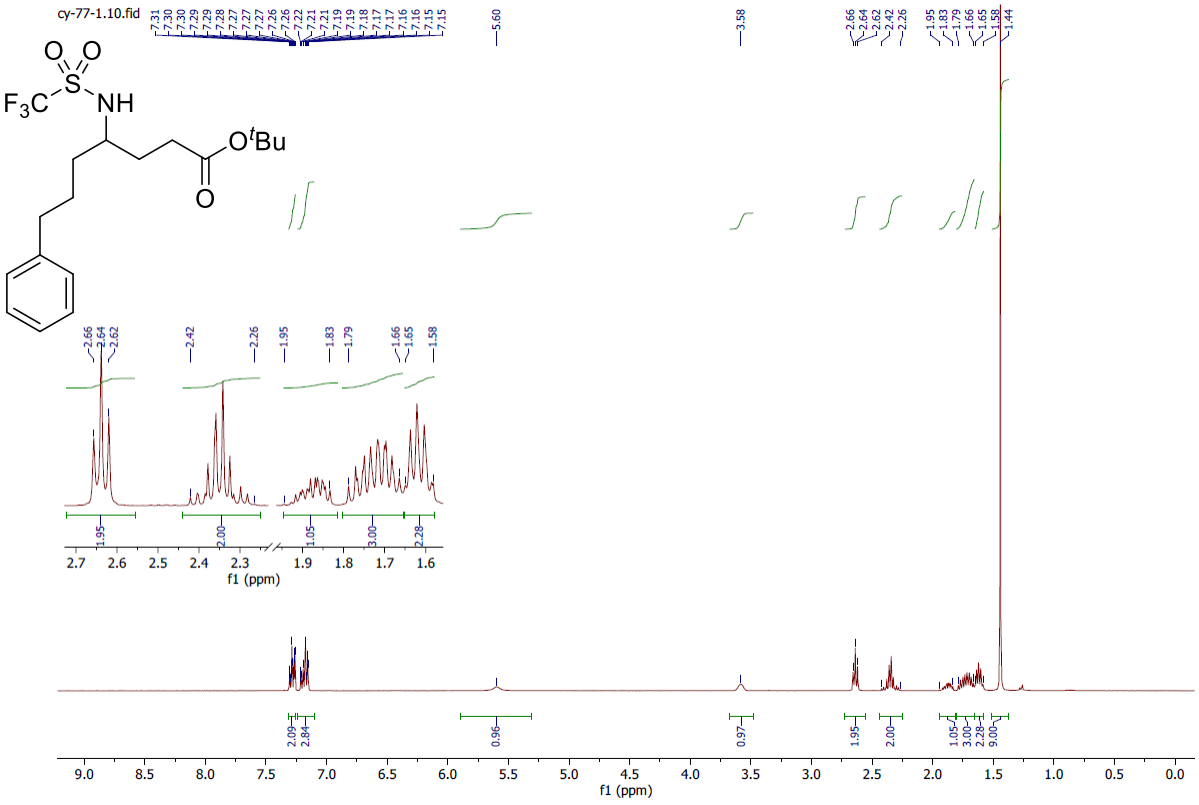
ethyl 5-(benzyloxy)-4-((trifluoromethyl)sulfonamido)pentanoate (3oa)

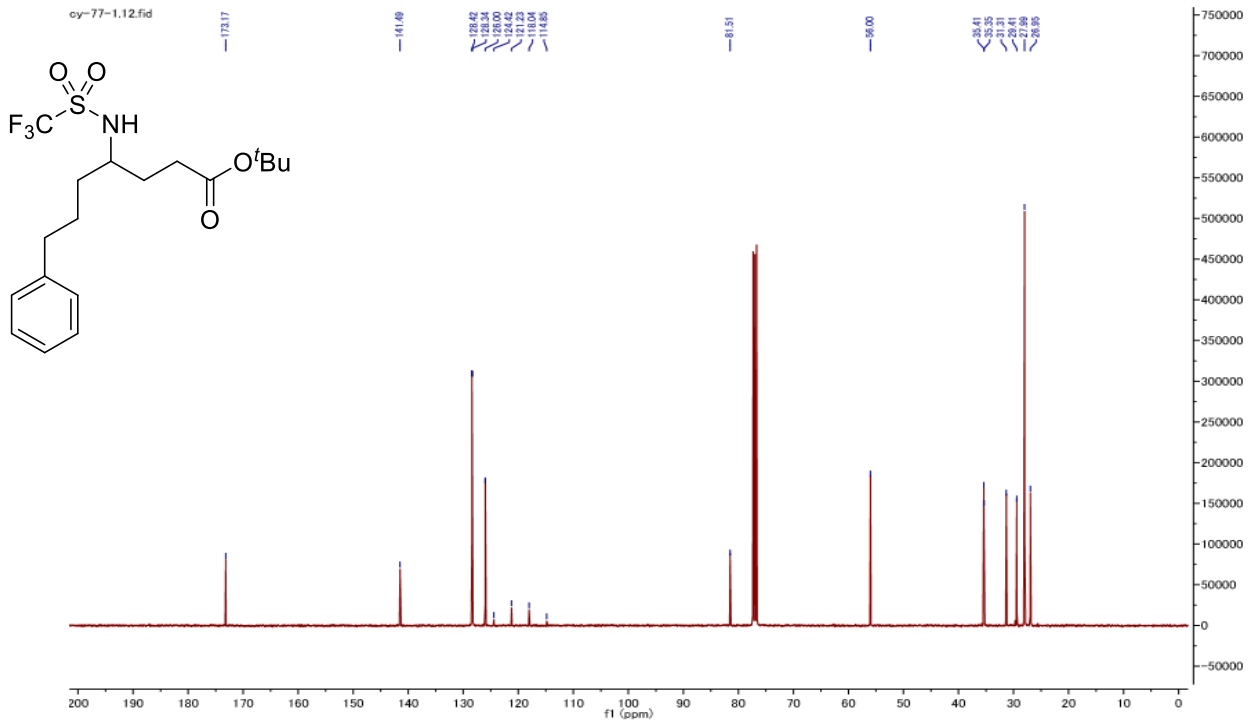

cy-102-1.10.fid
F3C
S
NH
OEt
O
f1 (ppm)

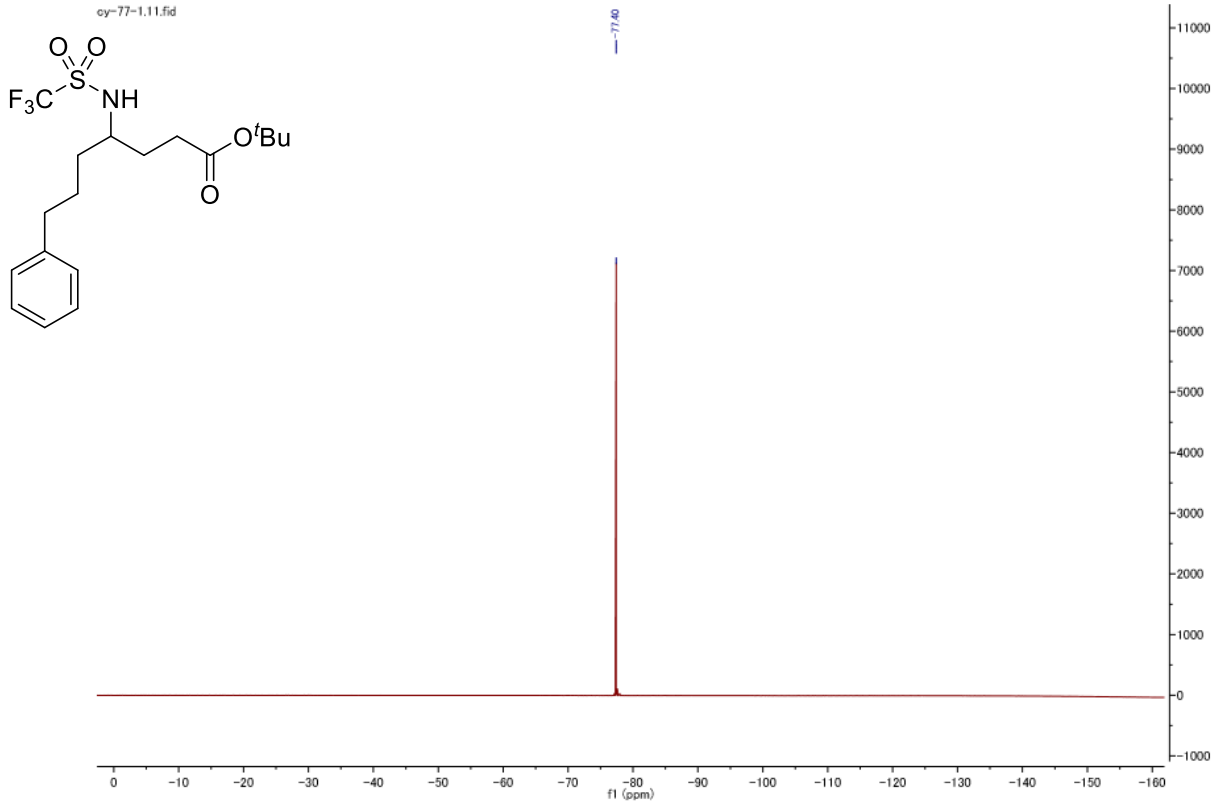

cy-102-1-13c.202.fid
Carbon 13
F3C
S
NH
OEt
O
f1 (ppm)



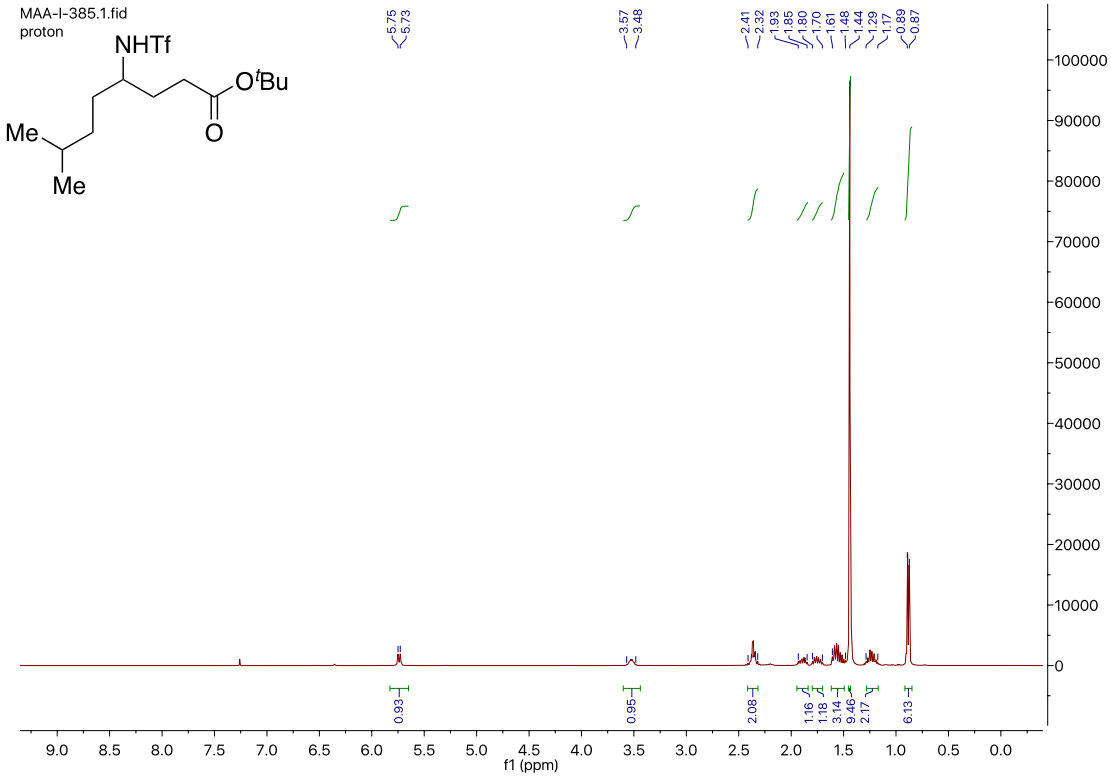
***tert*-butyl 7-phenyl-4-((trifluoromethyl)sulfonamido)heptanoate (3pa)**

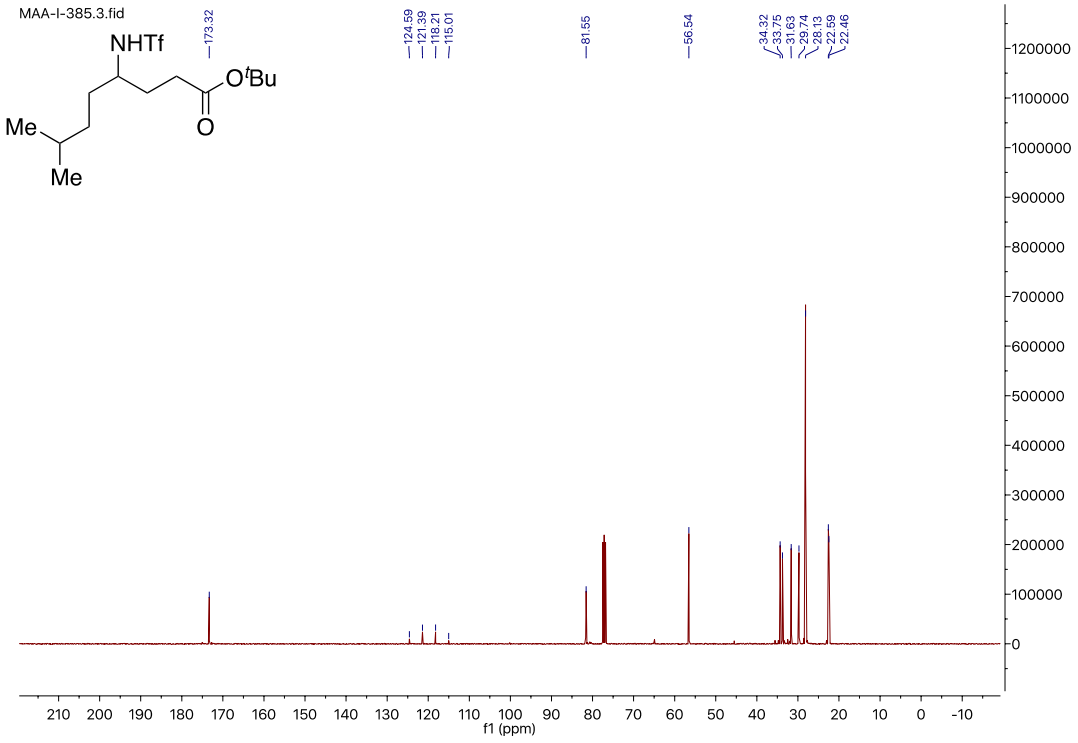


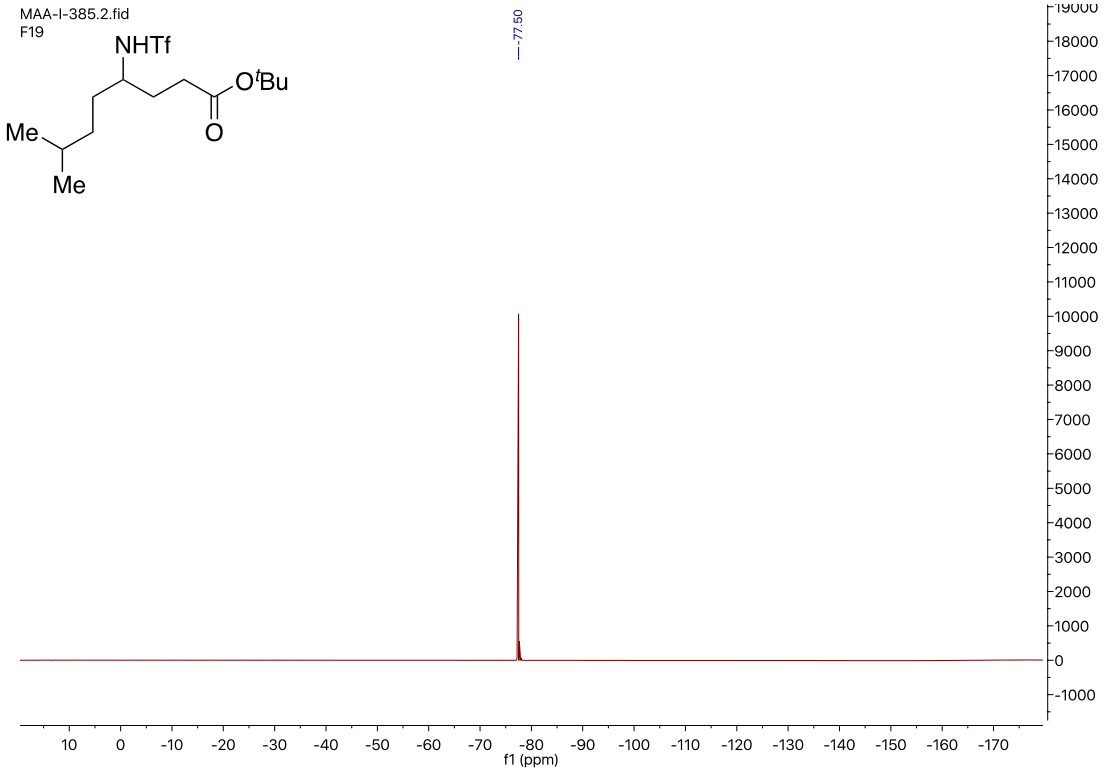

cy-77-1.12.fid
O
O
S
F3C
NH
OtBu
O
173.17
141.48
128.42
128.34
128.00
126.42
121.23
118.04
114.85
81.51
56.00
35.41
35.35
31.31
29.41
27.99
26.95
f1 (ppm)


cy-77-1.11.fid
O
O
S
F3C
NH
OtBu
O
77.40
f1 (ppm)

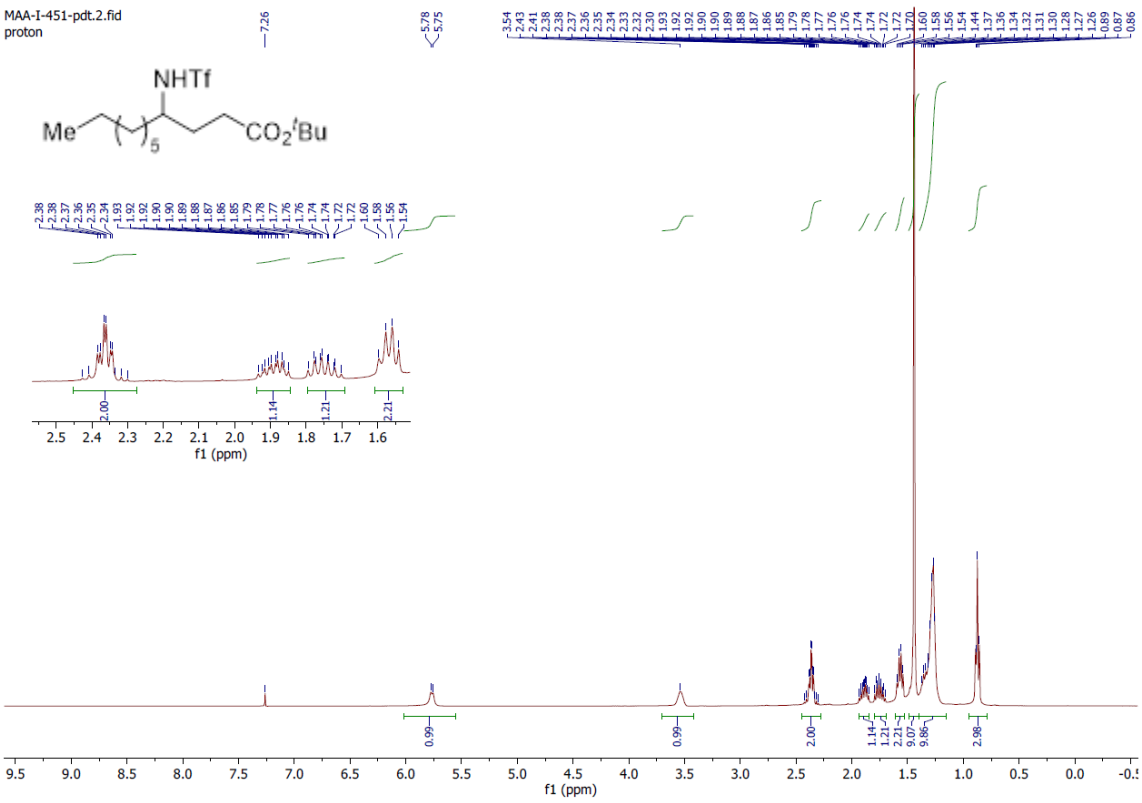
tert-butyl 7-methyl-4-((trifluoromethyl)sulfonamido)octanoate (3qa)

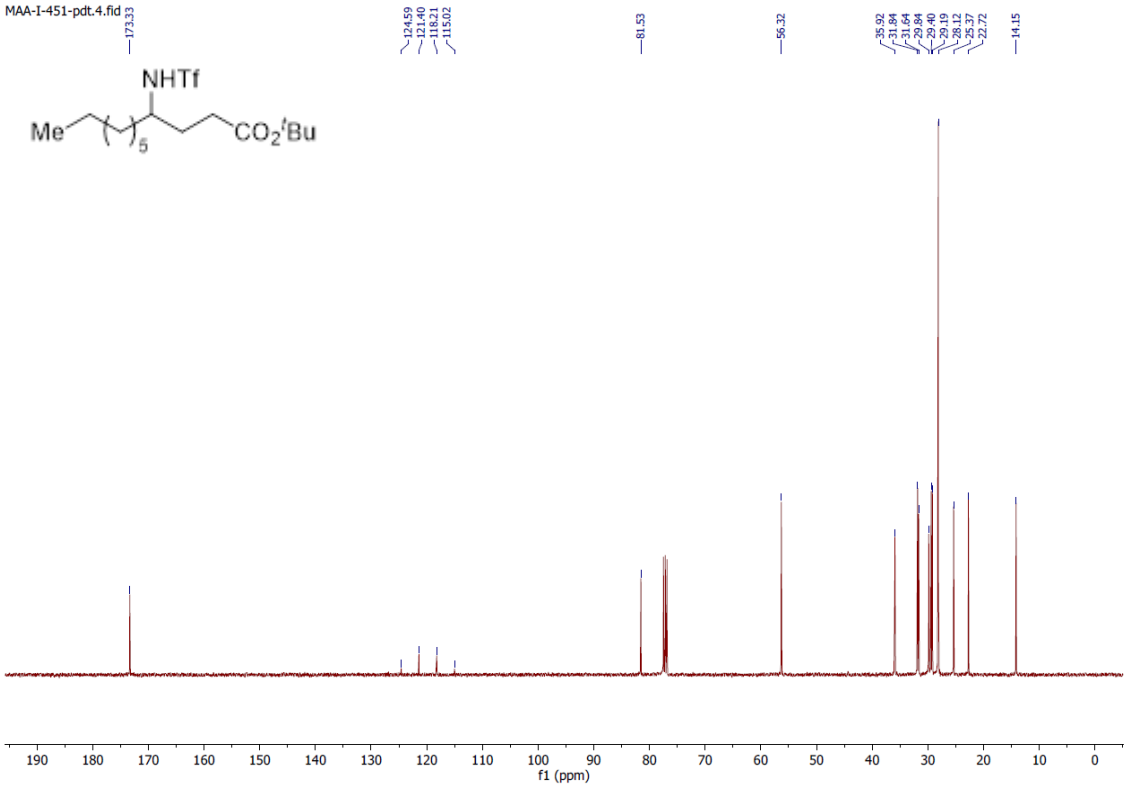


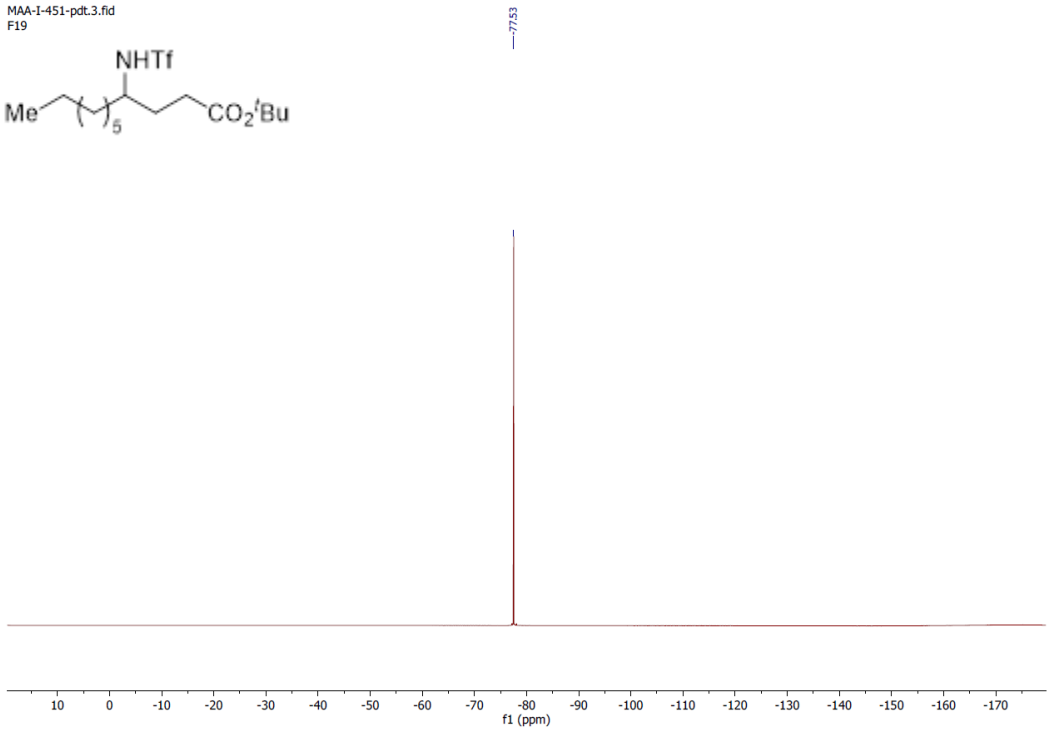




***tert*-butyl 4-((trifluoromethyl)sulfonamide)undecanoate (3ra)**




MAA-I-451-pdt.4.fid
173.33
124.59
121.40
118.21
115.02
81.53
56.32
35.92
31.84
31.64
29.84
29.40
29.19
28.12
25.37
22.72
14.15
NHTf
Me
5
CO2tBu
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MAA-I-451-pdt.3.fid
F19
77.53
NHTf
Me
5
CO2tBu
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)