Supporting Information

Regioselective Alkylative Cross-Coupling of Remote Unactivated C(sp3)-H Bonds

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Materials and Methods:

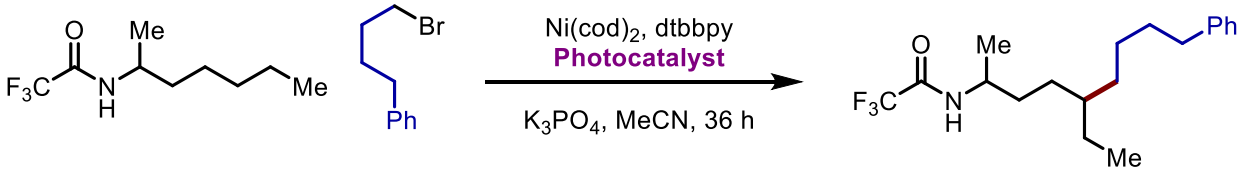
Unless otherwise noted, all reactions were performed in oven-dried glassware and carried out under an atmosphere of argon or nitrogen with magnetic stirring. All photochemical reactions were run in 1.0 dram vials fitted with Teflon caps under irradiation from a Blue H150 Kessil 35W LED lamp with Teflon stir-bars under vigorous magnetic stirring. All photochemical reactions were set-up in a nitrogen glovebox, though can also be performed with suitable All column chromatography was performed using a Teledyne Isco Combiflash using CombiFlash gold pre-packed columns outfitted with an ELSD detector. As most of the compounds listed do not exhibit an UV trace, ELSD was integral to the separation of product while thin layer chromatography was performed on SiliCycle® 250 µm 60 Å plates. Visualization was accomplished with 254 nm UV light, Seebach's stain, or I_2.

^{1}H NMR spectra were recorded on Bruker 400 or 500 MHz spectrometers at ambient temperature. Chemical shift is reported in parts per million (ppm) from $CDCl_3$ (7.26 ppm) with multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constants (Hz). ^{13}C NMR was recorded on Bruker 500 MHz spectrometers (125 MHz) at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ (77.2 ppm). Mass spectra were recorded on an Agilent 7890B GC System 5977B MSD GCMS with an EI ionization method. Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR Spectrometer.

Unless otherwise mentioned, all starting materials were obtained from commercial sources including Sigma-Aldrich, TCI, Matrix, Alfa-Aesar, and Oakwood Scientific. Anhydrous Ni(glyme)Cl_2, 4,4'-di-methyl-2,2'-dipyridyl, anhydrous acetonitrile, and anhydrous K_3PO_4 were obtained from Millipore-Sigma. $Ni(COD)_2$ was obtained through Strem. Photocatalysts used in this studied were either synthesized through known methods or bought from commercial sources. $[Ir(dF\text{-}CF_3ppy)_2(dtbbpy)]PF_6$, in particular, was synthesized according to a reported literature procedure[i] or purchased from Aspira Scientific.

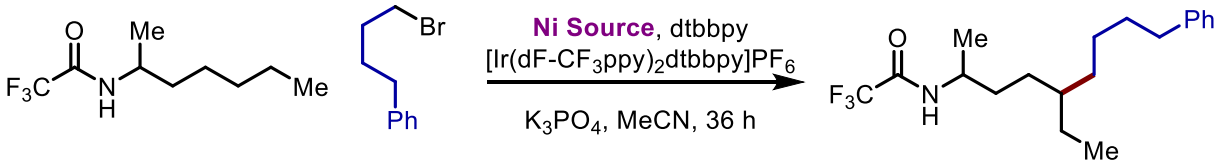
Extended Optimization Studies:

Table S1: Photocatalyst optimization



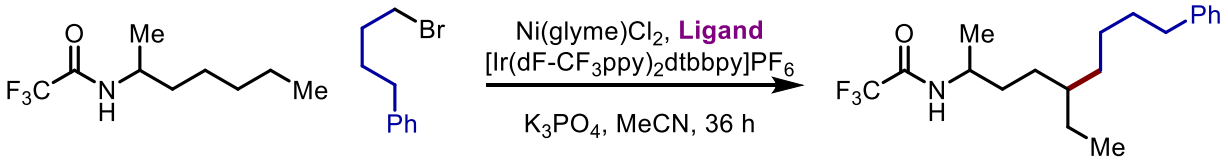
Entry	Photocatalyst (1 mol%)	Yield
1	$[Ir(dF\text{-}CF_3ppy)_2dtbbpy]PF_6$:	74%
2	4Cz-IPN (5 mol%):	73%
3	4Cz-TPN (5 mol%):	52%
4	$[Ir(ppy)_2dtbbpy]PF_6$:	15%
5	$[Ir((dF\text{-}Me)ppy)_2dtbbpy]PF_6$:	54%
6	$[Ir((dF\text{-}CF_3)ppy)_2(5,5'\text{-}dCF_3)bpy]PF_6$:	61%
7	$Ru(bpy_3)Cl_2$:	0%
8	$Ir(ppy)_3$:	0%

Table S2: Nickel Precatalyst Optimization



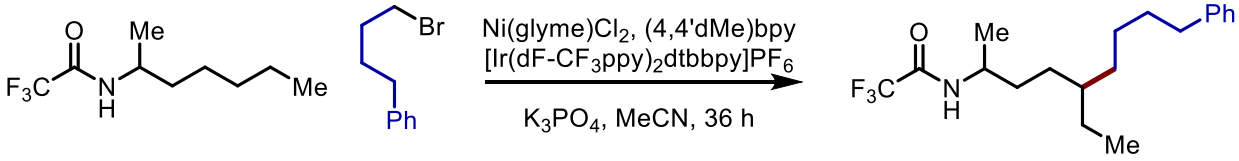
Entry	Nickel Source (10 mol%)	Yield
1	$Ni(cod)_2$	63%
2	$Ni(glyme)Cl_2$	78%
3	$Ni(acac)_2$	trace
4	$NiBr_2$	trace
5	$Ni(OAc)_{2\text{-}4}H_2O$	43%
6	$Ni(PPh_3)_2Cl_2$	20%

Table S3: Ligand Optimization



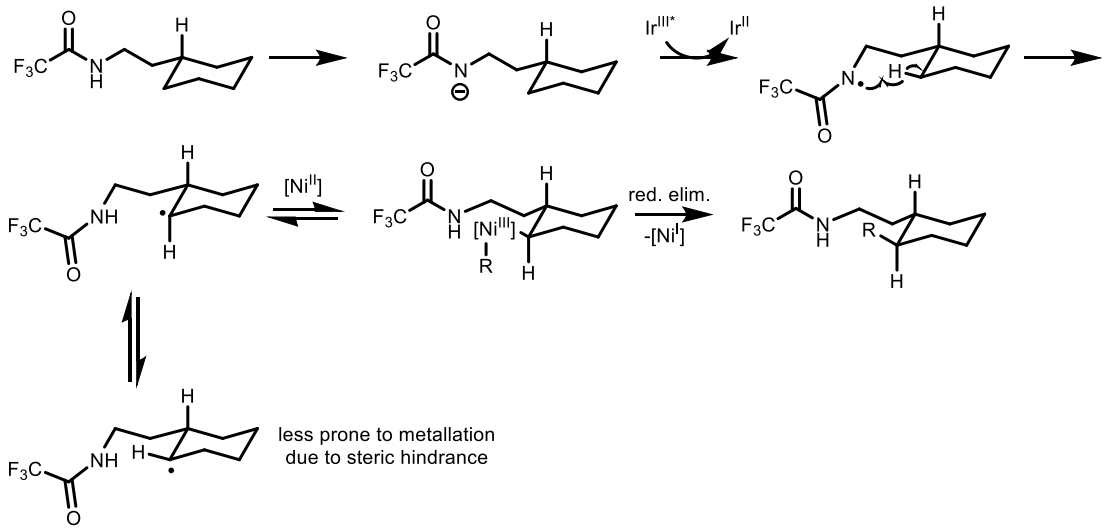
Entry	Ligand	Yield
1	bpy	62%
2	dtbbpy	70%
3	(4,4'-dMe)bpy	76%
4	(6, 6'-dMe)bpy	0%
5	acridine	12%
6	2, 9-neocuproin	0%
7	Bathocuproin	0%
8	(diBn-BOX)	0%

Table S4: Relative Equivalents



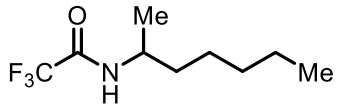
Entry	Equivilents of alkyl bromide	Yield
1	4	30%
2	2	70%
3	1	55%
4	0.5	15%
5	0.25	12%
6	2 (2 aliquots, start, 18 h)	36%
7	2 (4 aliquots, start, 6 h, 12 h, 18 h, 24 h)	32%

Scheme S5: Model for origin of stereoselectivity from cyclic systems.

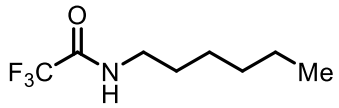


Starting Material Synthesis and characterization Data:

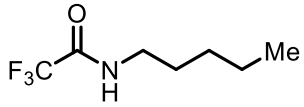
Procedure A: To a stirring solution of amine (5 mmol) in dichloromethane (50 mL, 0.1 M), triethylamine (10 mmol, 2.0 equiv) was added under N_2. The resulting solution was cooled with an ice bath and trifluoroacetic anhydride (5.5 mmol, 1.1 equiv) was added dropwise. After complete addition, the reaction was warmed to room temperature and the solution was allowed to stir for 12 hours. The reaction was quenched with slow addition of 1 M HCl and extracted with dichloromethane (3 x 10 mL). The organic layer was then washed with concentrated $NaHCO_3$ (50 mL) before being passed through a short silica plug and concentrated to afford the intended trifluoroacetamide without need for further chromatography.



1a - 2,2,2-trifluoro-N-(heptan-2-yl)acetamide
Prepared using procedure A from commercially available heptan-2-amine.
Yield 82%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.01 (s, 1H), 4.02 (dq, *J* = 8.5, 6.6 Hz, 1H), 1.63 – 1.43 (m, 2H), 1.37 – 1.25 (m, 6H), 1.21 (d, *J* = 6.6 Hz, 3H), 0.96 – 0.82 (m, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.65 (q, *J* = 36.7 Hz), 116.08 (q, *J* = 288.2 Hz), 46.71, 36.51, 31.64, 25.65, 22.66, 20.57, 14.13.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.12.
IR (film) ν_{max} 3293, 3099, 2960, 2932, 2862, 1696, 1556, 1156, 1182, 724
LRMS (EI) m/z calculated 211.12, found 211.2

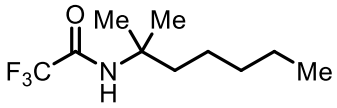


1b - 2,2,2-trifluoro-N-hexylacetamide
Prepared using procedure A from commercially available hexylamine. Structure previously reported by Xu *et al.*[2]
Yield 90%

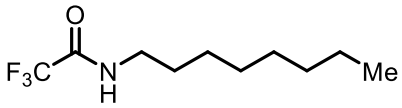


1c - 2,2,2-trifluoro-N-pentylacetamide

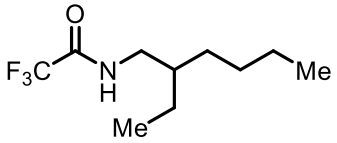
Prepared using procedure A from commercially available pentylamine. Structure previously reported by Milan *et al.*[1]
Yield 92%



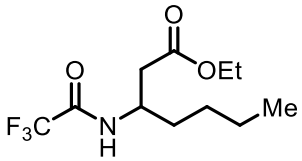
1d - 2,2,2-trifluoro-N-(2-methylheptan-2-yl)acetamide
Prepared according to previously published procedure from Chu *et al*.[3]
Yield 17% (3 steps)



1e - 2,2,2-trifluoro-N-octylacetamide
Prepared using procedure A from commercially available octylamine. Structure previously reported by Xu *et al.*[2]
Yield 88%

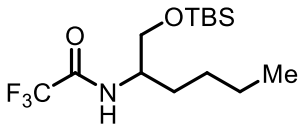


1f - N-(2-ethylhexyl)-2,2,2-trifluoroacetamide
Prepared using procedure A from commercially available 2-ethylhexan-1-amine.
Yield 83%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.24 (s, 1H), 3.31 (td, *J* = 6.2, 2.1 Hz, 2H), 1.53 (p, *J* = 6.2 Hz, 1H), 1.40 – 1.22 (m, 8H), 0.95 – 0.87 (m, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.49 (d, *J* = 36.1 Hz), 116.11 (q, *J* = 288.1 Hz), 43.00, 39.22, 30.96, 28.90, 24.25, 23.07, 14.15, 10.92.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.00.
IR (film) ν_{max} 3303, 3108, 2962, 2931, 2863, 1700, 1558, 1157, 1180, 722
LRMS (EI) [$C_{10}H_{18}F_3NO$] m/z calculated 225.13, found 225.2

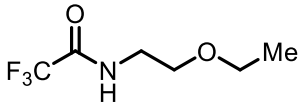


1g - ethyl 3-(2,2,2-trifluoroacetamido)heptanoate
Prepared using procedure A from commercially available ethyl 3-aminoheptanoate.
Yield 72%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (s, 1H), 4.30 – 4.22 (m, 1H), 4.19 (qd, *J* = 7.1, 0.8 Hz, 2H), 2.81 – 2.44 (m, 2H), 1.70 – 1.52 (m, 2H), 1.34 (ddt, *J* = 7.8, 6.0, 4.3 Hz, 4H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.57, 156.63 (q, *J* = 36.9 Hz), 115.88 (q, *J* = 288.0 Hz), 61.07, 46.83, 37.49, 33.33, 28.15, 22.27, 13.97 (d, *J* = 30.4 Hz).
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.21.
IR (film) ν_{max} 3295, 3103, 2959, 2931, 2863, 1730, 1701, 1556, 1174, 725, 700

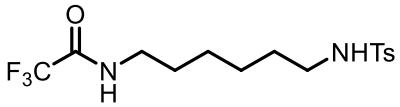
LRMS (EI) [$C_{11}H_{18}F_3NO_3$] m/z calculated 269.12, found 269.1



1h - N-(1-((tert-butyldimethylsilyl)oxy)hexan-2-yl)-2,2,2-trifluoroacetamide
From commercially available 2-aminohexan-1-ol (1.00 g, 8.53 mmol) 1-((tert-butyldimethylsilyl)oxy)hexan-2-amine was prepared by the portionwise addition of 1.5 equivalents (1.93 g) tert-Butyldimethylsilyl Chloride to a stirring solution of amino alcohol in dichloromethane (.1 M) at room temperature. After stirring for two hours, the reaction mixture was quenched with H_2O and extracted three times dichloromethane. The organic layers were combined and washed with H_2O and brine and dried over Na_2SO_4. The solution was concentrated *en vacuo* to give 1-((tert-butyldimethylsilyl)oxy)hexan-2-amine which was carried through without further purification. **2h** was prepared using procedure A from 1-((tert-butyldimethylsilyl)oxy)hexan-2-amine.
Yield 63%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.52 (d, *J* = 9.1 Hz, 1H), 3.98 (dtd, *J* = 10.5, 6.9, 3.2 Hz, 1H), 3.78 – 3.57 (m, 2H), 1.65 – 1.53 (m, 2H), 1.34 (dddd, *J* = 17.2, 13.9, 6.9, 5.0 Hz, 4H), 0.91 (s, 7H), 0.08 (d, *J* = 2.5 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.63 (q, *J* = 36.5 Hz), 115.97 (q, *J* = 288.1 Hz), 63.48, 51.28, 30.75, 27.95, 25.73, 22.46, 18.18, 13.89, -5.62 (d, *J* = 7.2 Hz).
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.21.
IR (film) ν_{max} 3305, 3104, 2932, 2859, 1702, 1557, 1161, 833, 774
LRMS (EI) [$C_{14}H_{28}F_3NO_2Si$] m/z calculated 327.18 found 327.0

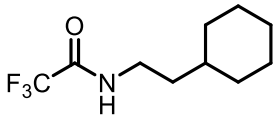


1i - N-(2-ethoxyethyl)-2,2,2-trifluoroacetamide
Prepared using procedure A from commercially available 2-ethoxyethan-1-amine.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.75 (s, 1H), 3.83 – 3.30 (m, 7H), 1.24 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.21 (q, *J* = 37.0 Hz), 115.84 (q, *J* = 287.6 Hz), 67.80, 66.69, 39.75, 14.99.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.09.
IR (film) ν_{max} 3308, 3100, 2980, 2939, 2875, 1706, 1556, 1153, 1117, 723
LRMS (EI) [$C_6H_{10}F_3NO_2$] m/z calculated 185.15 found 185.9

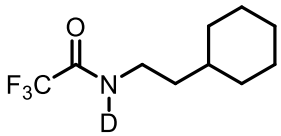


1j - 2,2,2-trifluoro-N-(6-((4-methylphenyl)sulfonamido)hexyl)acetamide
To a vigorously stirred solution of 20.0 g (172 mmol) hexane-1,6-diamine was added dropwise 1 equivalent (1.22 g, 8.6 mmol) of ethyl 2,2,2-trifluoroacetate at 0 ºC overnight. The resulting solution was washed with a 1:1 mixture of brine and water until diamine was absent by TLC. The solution was then dried over Na_2SO_4 and concentrated to a white paste. This paste was then dissolved in dichloromethane (0.1 M) at 0 ºC. 2 equivalents (1.36 g, 17.2 mmol) of pyridine was added along with 1.5 equivalents (2.46 g, 12.9 mmol) of 4-Toluenesulfonyl chloride. The solution was permitted to warm to room temperature overnight. The product was purified by silica gel chromatography 20-40% EtOAc:Hexane.
Yield 38%
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H), 4.87 (t, *J* = 6.2 Hz, 1H), 3.34 (q, *J* = 6.8 Hz, 2H), 2.93 (q, *J* = 6.7 Hz, 2H), 2.44 (s, 3H), 1.61 – 1.43 (m, 4H), 1.39-1.25 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.33 (q, *J* = 36.7 Hz), 143.51, 136.80, 129.76, 127.03, 115.90 (q, *J* = 287.8 Hz), 42.81, 39.59, 29.26, 28.61, 25.78, 25.67, 21.51.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.88.
IR (film) ν_{max} 3295, 3095, 2927, 2849, 1707, 1560, 1150, 1183, 1091, 722

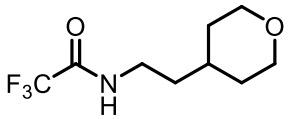
LRMS (ESI+APCI) [$C_{15}H_{21}F_3N_2O_3S$] m/z ([M+H]$^+$) calculated 367.12 found 367.1



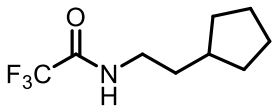
1k - N-(2-cyclohexylethyl)-2,2,2-trifluoroacetamide
Prepared using procedure A from commercially available 2-cyclohexylethan-1-amine.
Yield 92%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.21 (s, 1H), 3.43 – 3.33 (m, 2H), 1.75 – 1.63 (m, 3H), 1.52 – 1.43 (m, 2H), 1.35 – 1.10 (m, 3H), 1.00 – 0.87 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.27 (q, *J* = 38.6, 37.6 Hz), 116.05 (q, *J* = 287.8 Hz), 38.07, 36.57, 35.42, 33.20, 26.55, 26.27.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.08.
IR (film) ν_{max} 3303, 3106, 2924, 2853, 1700, 1560, 1449, 1157, 723
LRMS (EI) [$C_{10}H_{16}F_3NO$] m/z calculated 223.12 found 223.1



1k-N(d) - N-(2-cyclohexylethyl)-2,2,2-trifluoroacetamide-d
Prepared through portion wise addition of KH (40.1 mg, 1.0 equiv.) to 10 mL THF solution of 223 mg (1mmol) **1k.** The solution was allowed to stir for 6 hours under nitrogen atmosphere. The reaction was quenched via dropwise addition of DCl (1.0 M, Et_2O). The solvent was removed under reduced pressure to afford the N-deuterated product product which was verified by the absence of the N-H signal in the ^{1}H NMR spectrum.
Yield 96%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.43 – 3.33 (m, 2H), 1.75 – 1.63 (m, 3H), 1.52 – 1.43 (m, 2H), 1.35 – 1.10 (m, 3H), 1.00 – 0.87 (m, 2H).

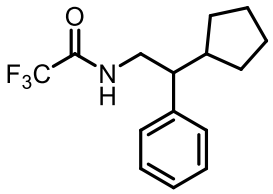


1l - 2,2,2-trifluoro-N-(2-(tetrahydro-2H-pyran-4-yl)ethyl)acetamide
Prepared using procedure A from commercially available 2-(tetrahydro-2H-pyran-4-yl)ethan-1-amine.
Yield 88%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.73 (s, 1H), 3.96 – 3.90 (m, 2H), 3.42 – 3.31 (m, 4H), 1.67 – 1.48 (m, 5H), 1.29 (ddt, *J* = 16.8, 10.7, 4.6 Hz, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.47 (q, *J* = 36.8 Hz), 116.01 (q, *J* = 287.8 Hz), 67.91, 37.44, 36.06, 32.84, 32.66.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.05.
IR (film) ν_{max} 3295, 3095, 2924, 2849, 1706, 1560, 1181, 1149, 1091, 722
LRMS (EI) [$C_9H_{14}F_3NO_2$] m/z calculated 223.12 found 223.1

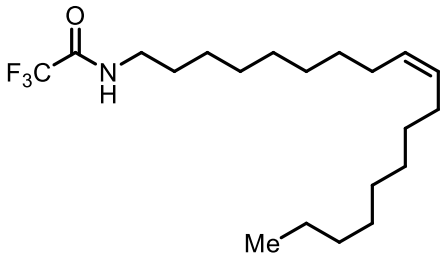


1m - N-(2-cyclopentylethyl)-2,2,2-trifluoroacetamide
Prepared using procedure A from commercially available 2-cyclopentylethan-1-amine.
Yield 87%

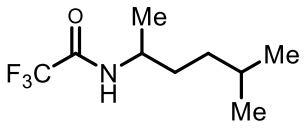
^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.38 (dt, *J* = 7.8, 6.0 Hz, 2H), 1.85 – 1.75 (m, 3H), 1.67 – 1.49 (m, 6H), 1.18 – 1.04 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.28 (q, *J* = 36.6 Hz), 116.06 (q, *J* = 287.8 Hz), 39.66, 37.73, 35.36, 32.71, 25.23.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.09.
IR (film) ν_{max} 3304, 3102, 2950, 2868, 1700, 1559, 1181, 1152, 720, 691
LRMS (EI) [$C_9H_{14}F_3NO$] m/z calculated 209.10 found 209.2



1n - N-(2-cyclopentyl-2-phenylethyl)-2,2,2-trifluoroacetamide
Prepared using procedure A from commercially available 2-cyclopentyl-2-phenylethan-1-amine.
Yield 78%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.21 – 7.09 (m, 2H), 6.01 (s, 1H), 3.93 (ddd, *J* = 13.5, 7.2, 4.4 Hz, 1H), 3.31 (ddd, *J* = 13.5, 10.5, 4.6 Hz, 1H), 2.57 (td, *J* = 10.4, 4.5 Hz, 1H), 2.15 – 1.92 (m, 2H), 1.75 – 1.65 (m, 1H), 1.65 – 1.28 (m, 3H), 1.09 – 0.94 (m, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.10 (q, *J* = 36.7 Hz), 141.71, 129.08, 128.04, 127.37, 115.89 (q, *J* = 288.0 Hz), 51.56, 44.57, 43.90, 31.80, 31.47, 25.53, 24.82.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.28.
IR (film) ν_{max} 3310, 3105, 3030, 2952, 2869, 1703, 1556, 1452, 1160, 724, 700
LRMS (EI) [$C_{15}H_{18}F_3NO$] m/z calculated 285.13 found 285.1



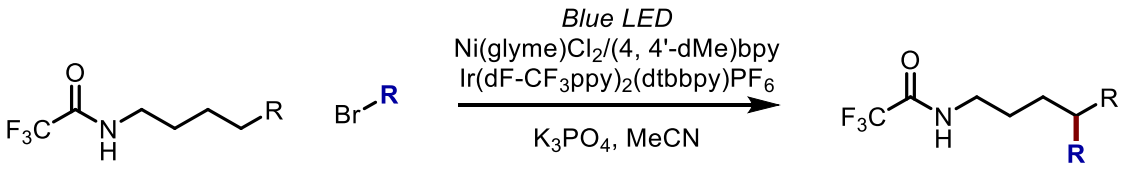
1o - (Z)-2,2,2-trifluoro-N-(octadec-9-en-1-yl)acetamide
Prepared using procedure A from commercially available (Z)-octadec-9-en-1-amine.
Yield 66%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.30 (s, 1H), 5.39 – 5.30 (m, 2H), 3.35 (q, *J* = 6.8 Hz, 2H), 2.06 – 1.92 (m, 3H), 1.58 (p, *J* = 7.2 Hz, 2H), 1.41 – 1.18 (m, 23H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.33 (q, *J* = 36.6 Hz), 130.22, 129.90, 116.07 (q, *J* = 287.8 Hz), 40.18, 32.09, 29.95, 29.88, 29.84, 29.71, 29.51, 29.50, 29.34, 29.29, 29.14, 27.40, 27.34, 26.84, 22.86, 14.28.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.07.
IR (film) ν_{max} 3305, 3107, 2924, 2855, 1703, 1557, 1464, 1182, 1163, 722
LRMS (EI) [$C_{20}H_{36}F_3NO$] m/z calculated 363.27, found 363.3



1p - 2,2,2-trifluoro-N-(5-methylhexan-2-yl)acetamide

Prepared using procedure A from commercially available 5-methylhexan-2-amine. Prepared according to previously published procedure from Chu *et al*.[3]
Yield 75%

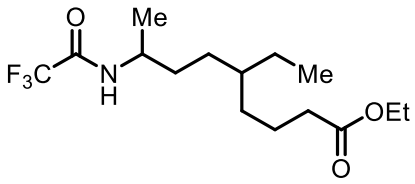
Standard Reaction Conditions:



To an oven-dried vial, $[Ir(dF\text{-}CF_3ppy)_2dtbbpy]PF_6$ (0.001 mmol, 0.01 equiv.), 4, 4'-dimethyl-2, 2'-bipyridine (0.012 mmol, 0.12 equiv.), trifluoroacetamide (0.1 mmol, 1 equiv.), and K_3PO_4 (0.4 mmol, 4 equiv) were added sequentially. The vial was charged with a stir bar and transferred to a glovebox, where the solids were backfilled with an inert atmosphere. In the glovebox, $Ni(glyme)Cl_2$ (0.01 mmol, 0.1 equiv) was added followed by anhydrous acetonitrile (0.75 mL, 0.13 M) and the reaction was stirred for roughly 5 minutes to insure complexation between nickel and the ligand. Subsequently add alkyl bromide (0.11 mmol, 1.1 equiv.) and seal tightly. Place ~2-6 inches from a blue Kessil lamp and irradiate and stir for 36 hours at room temperature. Upon completion, reactions were run through a short silica plug and concentrated *in vacuo*. Products were purified using flash column chromatography using EtOAc:Hexanes as an eluent.

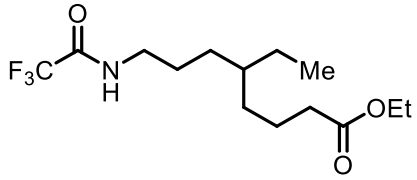
Characterization Data of Products:

Note: The following compound characterization is listed with isolated yield defined as a ratio of diastereomers where relevant. Listing of ^1H and ^{13}C follows with a comment on whether they are resolved or not. Some reactions lead to trace amounts of alkene impurities, whose composition is further denoted. Efforts to further purify these products met with failure, not surprising given that these largely non-polar, modestly functionalized alkanes often without a UV reporter group.

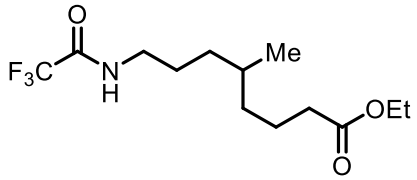


3aa - ethyl 5-ethyl-8-(2,2,2-trifluoroacetamido)nonanoate
Prepared using procedure B from compound **2c.**
Yield 73% 1:1 dr

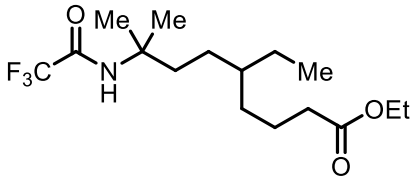
Mix of diastereomers ~3:1 Maj:Min, ^{1}H peaks unresolved, ^{13}C Major diastereomer selected, contains 6% impurity of unsaturated product
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.33 – 5.84 (m, 1H), 4.31 – 3.85 (m, 3H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.44 (m, 4H), 1.42 – 1.15 (m, 10H), 0.86 (dt, *J* = 20.2, 6.9 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.83, 156.63 (q, *J* = 36.4 Hz), 116.11 (q, *J* = 287.6 Hz), 60.45, 44.83, 41.17, 35.80, 34.65, 34.28, 33.06, 21.90, 21.04, 19.67, 14.42, 11.00.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.13.
IR (film) ν_{max} 3309, 3096, 2960, 2932, 2873, 1700, 1553, 1155, 724
LRMS (EI) [$C_{15}H_{26}F_3NO_3$] m/z calculated 325.19, found 325.2



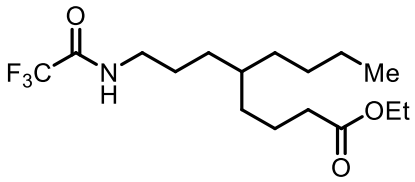
3ba - ethyl 5-ethyl-8-(2,2,2-trifluoroacetamido)octanoate
Prepared using procedure B from compound **2b.**
Yield 46%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.46 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.34 (q, *J* = 6.8 Hz, 2H), 2.28 (t, *J* = 7.3 Hz, 2H), 1.57 (ddt, *J* = 14.5, 11.9, 7.3 Hz, 3H), 1.31 – 1.22 (m, 92H), 0.86 – 0.81 (m, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.01, 157.38 (q, *J* = 36.9 Hz), 116.07 (q, *J* = 287.9 Hz), 60.46, 40.48, 38.41, 34.68, 32.45, 29.95, 26.18, 22.04, 14.41, 10.92.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.05.
IR (film) ν_{max} 3322, 3102, 2919, 2854, 1705, 1554, 1155, 1035, 722
LRMS (EI) [$C_{14}H_{24}F_3NO_3$] m/z calculated 311.17, found 311.1



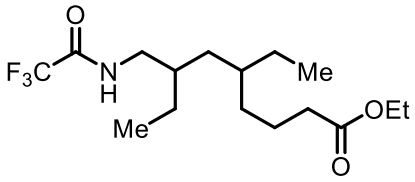
3ca - ethyl 5-methyl-8-(2,2,2-trifluoroacetamido)octanoate
Prepared using procedure B from compound **2a.**
Yield 55%, contains 6% impurity of unsaturated product
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.51 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.38 – 3.28 (m, 2H), 2.27 (ddd, *J* = 7.8, 7.1, 2.3 Hz, 2H), 1.66 – 1.51 (m, 4H), 1.48 – 1.40 (m, 1H), 1.39 – 1.21 (m, 6H), 1.21 – 1.08 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.00, 157.38 (q, *J* = 36.8 Hz), 116.06 (q, *J* = 287.8 Hz), 60.43, 40.39, 36.27, 34.63, 33.72, 32.34, 26.55, 22.45, 19.52, 14.40.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.05.
IR (film) ν_{max} 3324, 3102, 2935, 2873, 1706, 1554, 1156, 1034, 722
LRMS (EI) [$C_{13}H_{22}F_3NO_3$] m/z calculated 297.16, found 297.1



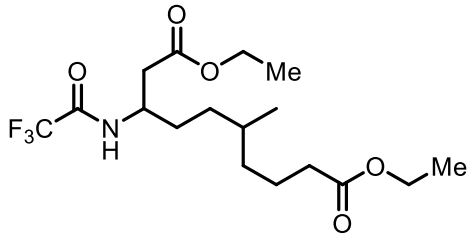
3da - ethyl 5-ethyl-8-methyl-8-(2,2,2-trifluoroacetamido)nonanoate
Prepared using procedure B from compound **2d.**
Yield 82%, contains 7% impurity of unsaturated product
^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.99 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.57 (m, 5H), 1.40 (dz, 6H), 1.35 – 1.21 (m, 9H), 0.85 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.77, 156.17 (q, *J* = 35.7 Hz), 115.79 (q, *J* = 289.7 Hz), 60.45, 56.04, 43.60, 35.15, 34.64, 34.42, 27.46, 27.07, 26.94, 22.18, 14.42, 10.77.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.35.
IR (film) ν_{max} 3330, 3086, 2966, 2936, 2876, 1711, 1551, 1179, 1152, 723
LRMS (EI) [$C_{15}H_{26}F_3NO_3$] m/z calculated 325.19, found 325.3



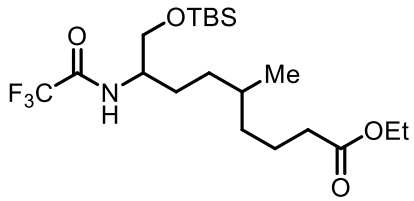
3ea - ethyl 5-(3-(2,2,2-trifluoroacetamido)propyl)nonanoate
Prepared using procedure B from compound **2e.**
Yield 55%, contains 4% impurity of unsaturated product
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.46 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.37 (q, *J* = 6.8 Hz, 2H), 2.30 (t, *J* = 7.3 Hz, 2H), 2.25 – 1.90 (m, 1H), 1.64 – 1.51 (m, 3H), 1.44 – 1.16 (m, 14H), 0.91 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.03, 157.38 (q, *J* = 36.5 Hz), 116.08 (q, *J* = 288.1 Hz), 60.47, 40.50, 36.98, 34.69, 33.20, 32.93, 30.40, 29.01, 26.15, 23.20, 22.02, 14.42, 14.27.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.04.
IR (film) ν_{max} 3321, 3102, 2929, 2861, 1705, 1554, 1156, 722
LRMS (EI) [$C_{16}H_{28}F_3NO_3$] m/z calculated 339.20, found 339.2



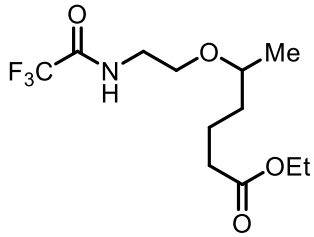
3fa - ethyl 5-ethyl-7-((2,2,2-trifluoroacetamido)methyl)nonanoate
Prepared using procedure B from compound **2f.**
Yield 63% 1:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.42 (s, 1H), 4.12 (qd, *J* = 7.2, 1.4 Hz, 2H), 3.41 – 3.12 (m, 2H), 2.36 – 2.21 (m, 2H), 1.68 – 1.47 (m, 3H), 1.40 – 1.08 (m, 12H), 0.99 – 0.78 (m, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.90, 157.69 (q, *J* = 18.6 Hz), 116.13 (q, *J* = 287.9 Hz), 60.51, 43.26, 41.79, 38.09, 35.88, 34.56, 32.90, 26.00, 24.72, 21.68, 20.98, 14.38, 10.77.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -74.92, -75.01.
IR (film) ν_{max} 3321, 3104, 2961, 2932, 2875, 1705, 1554, 1156, 1032, 723
LRMS (EI) [$C_{16}H_{28}F_3NO_3$] m/z calculated 339.20, found 339.2



3ga - diethyl 6-methyl-3-(2,2,2-trifluoroacetamido)decanedioate
Prepared using procedure B from compound **2g.**
Yield 70% 1:1 dr
Mix of diastereomers ~2:1 Maj:Min, ^{1}H peaks unresolved, ^{13}C Major diastereomer selected, contains 6% impurity of unsaturated product
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 (s, 1H), 4.32 (dh, *J* = 9.6, 5.0 Hz, 1H), 4.15 (dq, *J* = 26.6, 7.1 Hz, 4H), 2.67 – 2.50 (m, 2H), 2.31 – 2.23 (m, 2H), 1.73 – 1.63 (m, 1H), 1.60 – 1.49 (m, 2H), 1.48 – 1.38 (m, 1H), 1.39 – 1.22 (m, 11H), 0.89 – 0.80 (m, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.83, 171.75, 156.74 (q, *J* = 36.8 Hz), 116.03 (q, *J* = 288.1 Hz), 61.29, 60.46, 45.02, 37.91, 37.48, 35.71, 34.58, 32.15, 25.72, 21.79, 14.42, 14.29, 10.58.^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.17, -75.22.
IR (film) ν_{max} 3321, 3096, 2964, 2937, 2876, 1710, 1553, 1158, 911, 729, 648
LRMS (EI) [$C_{17}H_{28}F_3NO_5$] m/z calculated 383.19, found 383.2

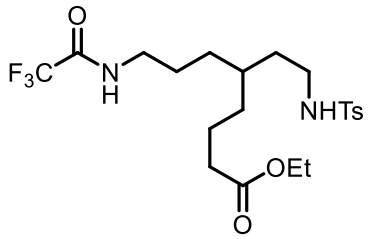


3ha - ethyl 9-((tert-butyldimethylsilyl)oxy)-5-methyl-8-(2,2,2-trifluoroacetamido)nonanoate
Prepared using procedure B from compound **2h.**
Yield 49% 1:1 dr
3:1 mix of diastereomers isolated, ^{1}H peaks unresolved, ^{13}C Major diastereomer selected
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.46 (d, *J* = 8.8 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.08 (td, *J* = 7.4, 6.5, 3.5 Hz, 1H), 3.74 – 3.58 (m, 2H), 2.33 – 2.26 (m, 2H), 1.68 – 1.49 (m, 4H), 1.45 – 1.31 (m, 5H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.96 – 0.82 (m, 12H), 0.08 (d, *J* = 1.7 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.65, 156.55 (q, *J* = 36.7 Hz), 115.94 (q, *J* = 288.2 Hz), 63.74, 60.24, 49.29, 35.29, 34.72, 34.50, 32.56, 32.28, 25.74, 21.73, 18.18, 14.25, 10.43, -5.59 (d, *J* = 12.2 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.09, -76.12.
IR (film) ν_{max} 3317, 2932, 2860, 1708, 1553, 1162, 838, 778, 726
LRMS (EI) [$C_{20}H_{38}F_3NO_4Si$] m/z calculated 441.61, found 442.3

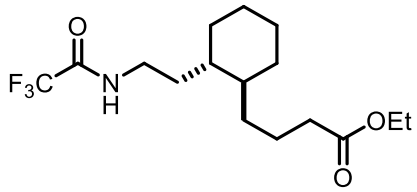


3ia - ethyl 5-(2-(2,2,2-trifluoroacetamido)ethoxy)hexanoate
Prepared using procedure B from compound **2i.**

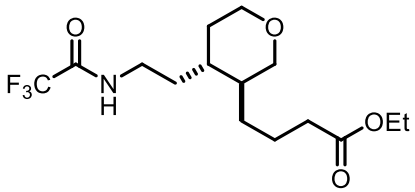
Yield 62%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.93 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.66 (ddd, *J* = 9.3, 5.9, 3.4 Hz, 1H), 3.57 (m, 2H), 3.52 – 3.43 (m, 2H), 2.34 (td, *J* = 7.3, 3.0 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.60 – 1.45 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 6.1 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.64, 157.21 (q, *J* = 37.0 Hz), 115.89 (q, *J* = 288.1, 287.6 Hz), 75.63, 65.71, 60.38, 40.07, 35.68, 34.07, 20.82, 19.41, 14.22.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.09.
IR (film) ν_{max} 3327, 3099, 2930, 2861, 1709, 1555, 1178, 1151, 722, 654, 549
LRMS (EI) [$C_{13}H_{22}F_3NO_4$] m/z calculated 299.13, found 299.1



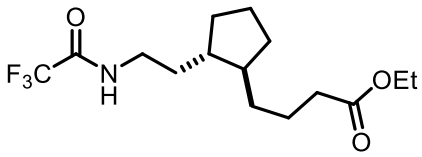
3ja - ethyl 5-(2-((4-methylphenyl)sulfonamido)ethyl)-8-(2,2,2-trifluoroacetamido)octanoate
Prepared using procedure B from compound **2j.**
Yield 49%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.64 (m, 2H), 7.32 – 7.28 (m, 2H), 6.61 (s, 1H), 6.42 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.37 (p, *J* = 6.5 Hz, 2H), 3.11 (p, 2H), 2.42 (s, 3H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.89 – 1.76 (m, 2H), 1.63 – 1.53 (m, 4H), 1.36 (m, 5H), 1.25 (t, *J* = 7.2 Hz, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.09, 157.26 (q, *J* = 36.8 Hz), 143.25, 136.56, 129.70, 127.09, 115.91 (q, *J* = 287.9 Hz), 60.54, 48.38, 47.85, 39.54, 31.10, 28.58, 28.25, 25.67, 25.57, 24.15, 21.48, 14.19.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -74.99.
IR (film) ν_{max} 3320, 3101, 2924, 2856, 1706, 1554, 1159, 863, 722
LRMS (ESI+APCI) [$C_{21}H_{31}F_3N_2O_5S$] m/z ([M+H]$^+$) calculated 481.19 found 481.1



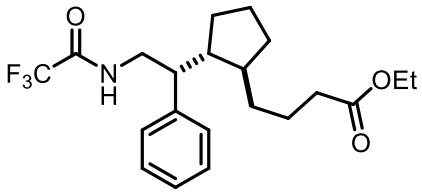
3ka - ethyl 4-((1S,2S)-2-(2-(2,2,2-trifluoroacetamido)ethyl)cyclohexyl)butanoate
Prepared using procedure B from compound **1k.**
Yield 68% >20:1 dr
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.67 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.46 – 3.21 (m, 2H), 2.41 – 2.09 (m, 2H), 1.88 – 1.61 (m, 6H), 1.59 – 1.28 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.22 – 1.15 (m, 2H), 1.14 – 0.91 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.15, 157.38 (q, *J* = 36.5 Hz), 116.09 (q, *J* = 287.9 Hz), 60.47, 41.06, 38.89, 37.96, 34.54, 32.66, 32.44, 31.85, 31.56, 26.16, 26.12, 21.30, 14.37.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.95.
IR (film) ν_{max} 3320, 3101, 2924, 2856, 1706, 1554, 1159, 722
LRMS (EI) [$C_{16}H_{26}F_3NO_3$] m/z calculated 337.19, found 337.2



3la - ethyl 4-((3S,4R)-4-(2-(2,2,2-trifluoroacetamido)ethyl)tetrahydro-2H-pyran-3-yl)butanoate
Prepared using procedure B from compound **2l.**
Yield 52% >20:1 dr, contains 15% impurity of unsaturated product
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.56 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.94 (qd, *J* = 11.7, 4.1 Hz, 2H), 3.43 – 3.31 (m, 3H), 3.12 – 3.03 (m, 1H), 2.37 – 2.21 (m, 2H), 2.02 – 1.88 (m, 1H), 1.75 – 1.65 (m, 2H), 1.58 – 1.42 (m, 3H), 1.41 – 1.31 (m, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.21 – 1.10 (m, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.81, 157.49 (q, *J* = 36.8 Hz), 116.06 (q, *J* = 288.3, 287.0 Hz), 71.91, 68.00, 60.64, 40.37, 37.53, 36.82, 34.35, 32.13, 31.45, 28.84, 21.68, 14.40.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -74.99.
IR (film) ν_{max} 3307, 3092, 2928, 2854, 1709, 1555, 1153, 1096, 723
LRMS (EI) [$C_{15}H_{24}F_3NO_4$] m/z calculated 480.19, found 481.1

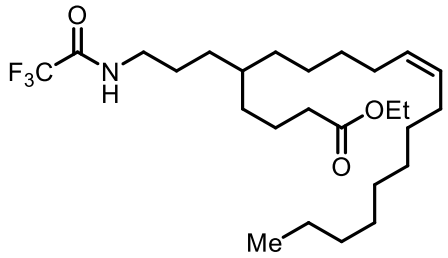


3ma - ethyl 4-(2-(2-(2,2,2-trifluoroacetamido)ethyl)cyclopentyl)butanoate
Prepared using procedure B from compound **2m.**
Yield 58% 16:1 dr, 9:1 mix of diastereomers isolated, ^{1}H peaks unresolved, ^{13}C Major diastereomer selected
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.35 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.27 (m, 2H), 2.39 – 2.20 (m, 2H), 1.89 – 1.79 (m, 2H), 1.78 – 1.62 (m, 2H), 1.61 – 1.45 (m, 5H), 1.43 – 1.29 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3jH), 1.22 – 1.11 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.98, 157.28 (q, *J* = 36.4 Hz), 116.05 (q, *J* = 287.9 Hz), 60.45, 45.84, 43.46, 39.51, 34.64, 34.45, 34.42, 23.93, 23.83, 14.43.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.06.
IR (film) ν_{max} 3322, 3102, 2943, 2868, 1708, 1556, 1180, 1161, 723
LRMS (EI) [$C_{15}H_{24}F_3NO_3$] m/z calculated 337.19, found 337.2

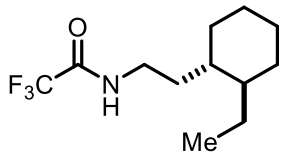


3na - ethyl 4-(2-(1-phenyl-2-(2,2,2-trifluoroacetamido)ethyl)cyclopentyl)butanoate
Prepared using procedure B from compound **2n.**
Yield 37% >20:1:1:1 dr
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.32 – 7.25 (m, 1H), 7.18 – 7.12 (m, 2H), 6.07 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.96 (ddd, *J* = 12.8, 7.3, 4.8 Hz, 1H), 3.39 (ddd, *J* = 13.4, 10.7, 4.5 Hz, 1H), 2.79 (ddd, *J* = 10.6, 8.2, 4.8 Hz, 1H), 2.35 (td, *J* = 7.3, 5.3 Hz, 2H), 1.84 – 1.37 (m, 10H), 1.31 – 1.27 (m, 5H), 1.19 – 1.11 (m, 1H), 0.95 – 0.79 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.73, 156.97 (q, *J* = 36.3, 35.8 Hz), 140.18, 128.79, 128.44, 127.24, 120.28 – 111.15 (q, *J* = 287.7 Hz), 60.30, 49.14, 48.56, 43.91, 42.48, 35.67, 34.41, 31.81, 29.93, 24.06, 23.64, 14.26.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.13.

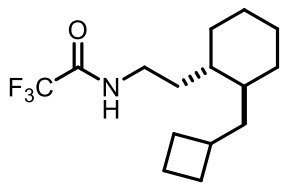
IR (film) ν_{max} 3324, 3088, 3029, 2938, 2868, 1711, 1554, 1177, 1160, 703
LRMS (EI) [$C_{21}H_{28}F_3NO_3$] m/z calculated 339.17, found 339.2



3oa - ethyl (Z)-5-(3-(2,2,2-trifluoroacetamido)propyl)nonadec-10-enoate
Prepared using procedure B from compound **2o.**
Yield 35%
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.39 (s, 1H), 5.43 – 5.25 (m, 1H), 4.13 (qd, *J* = 7.1, 1.7 Hz, 2H), 3.36 (dq, *J* = 13.5, 6.8 Hz, 2H), 2.35 – 2.19 (m, 2H), 2.07 – 1.90 (m, 4H), 1.65 – 1.46 (m, 7H), 1.33 – 1.19 (m, 38H), 0.88 (t, *J* = 6.8 Hz, 5H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.94, 130.75, 130.29, 60.54, 38.10, 37.00, 35.15, 34.52, 33.45, 33.42, 32.84, 32.80, 32.76, 32.74, 32.09, 29.84, 29.68, 29.51, 29.38, 22.87, 21.93, 21.92, 14.43, 14.30.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.04.
IR (film) ν_{max} 3320, 3100, 2924, 2854, 1707, 1553, 1161, 722
LRMS (ESI+APCI) [$C_{26}H_{46}F_3NO_3$] m/z ([M+H]$^+$) calculated 478.34 found 478.3

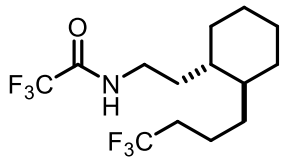


3kb - N-(2-(2-ethylcyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available bromoethane.
Yield 65% 14:1 trans:cis dr
Mix of diastereomers (1.6:1 isolated)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.30 (s, 1H), 3.52 – 3.26 (m, 2H), 1.89 – 1.68 (m, 5H), 1.63 – 1.46 (m, 2H), 1.46 – 1.36 (m, 1H), 1.30 – 1.13 (m, 4H), 1.08 – 0.93 (m, 3H), 0.86 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.08 (q, *J* = 36.4 Hz), 115.87 (q, *J* = 287.9 Hz), 42.48, 38.79, 37.89, 33.02, 32.55, 31.68, 30.84, 26.07, 26.02, 25.58, 10.44.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.99, -76.01.
IR (film) ν_{max} 3302, 3106, 2923, 2855, 1700, 1557, 1179, 1157, 722
LRMS (EI) [$C_{12}H_{20}F_3NO$] m/z calculated 225.13, found 225.2

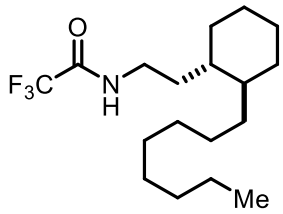


3kc - N-(2-(2-(cyclobutylmethyl)cyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available (Bromomethyl)cyclobutane.
Yield 42% >20:1 dr

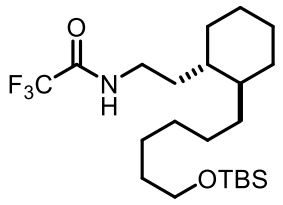
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.24 (s, 1H), 3.43 (ddt, *J* = 15.2, 10.6, 5.2 Hz, 1H), 3.30 (ddt, *J* = 13.0, 9.6, 6.3 Hz, 1H), 2.34 (qd, *J* = 8.3, 6.2 Hz, 1H), 2.01 (ddq, *J* = 22.6, 11.3, 3.9 Hz, 2H), 1.87 – 1.71 (m, 5H), 1.70 – 1.49 (m, 5H), 1.36 (dtt, *J* = 16.9, 8.3, 4.2 Hz, 1H), 1.17 (m, 3H), 1.01 (m, 3H), 0.89 (qd, *J* = 11.4, 10.8, 5.3 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.06 (q, *J* = 36.7 Hz), 115.88 (q, *J* = 287.9 Hz), 40.92, 39.97, 39.58, 37.95, 33.91, 32.75, 31.65, 29.71, 28.71, 25.92, 25.89, 18.64.z
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.05.
IR (film) ν_{max} 3300, 3106, 2924, 2854, 1700, 1557, 1157, 1178, 722
LRMS (EI) [$C_{15}H_{24}F_3NO$] m/z calculated 291.18, found 291.1



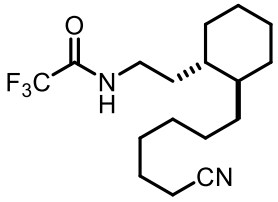
3kd - 2,2,2-trifluoro-N-(2-(2-(4,4,4-trifluorobutyl)cyclohexyl)ethyl)acetamide
Prepared using procedure B from compound **1k** and commercially available 4-bromo-1,1,1-trifluorobutane.
Yield 57% >20:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.24 (s, 1H), 3.44 (ddt, *J* = 13.6, 9.8, 5.5 Hz, 1H), 3.30 (ddt, *J* = 13.3, 9.2, 6.2 Hz, 1H), 2.15 – 1.94 (m, 2H), 1.87 – 1.74 (m, 3H), 1.74 – 1.67 (m, 2H), 1.67 – 1.51 (m, 3H), 1.51 – 1.31 (m, 2H), 1.26 – 1.14 (m, 3H), 1.12 – 0.92 (m, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.31 (q, *J* = 36.9 Hz), 127.35 (d, *J* = 276.5 Hz), 116.02 (q, *J* = 287.9 Hz), 41.11, 39.37, 38.00, 34.24 (q, *J* = 28.3 Hz), 32.78, 32.46, 31.71, 31.36, 26.00 (d, *J* = 3.2 Hz), 19.00 (q, *J* = 3.0 Hz).
^{19}F NMR (471 MHz, Chloroform-*d*) δ -65.43 (t, *J* = 10.9 Hz), -75.08.
IR (film) ν_{max} 3450, 3305, 3106, 2926, 2858, 1701, 1557, 1253, 1180, 1151, 722, 658
LRMS (EI) [$C_{14}H_{21}F_6NO$] m/z calculated 333.15, found 333.2



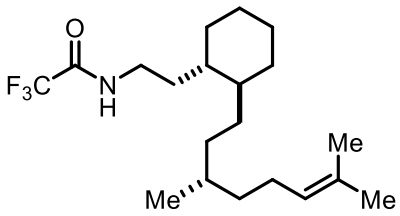
3ke - 2,2,2-trifluoro-N-(2-((2-octylcyclohexyl)ethyl)acetamide
Prepared using procedure B from compound **1k** and commercially available 1-bromooctane.
Yield 62% >20:1 dr
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.19 (s, 1H), 3.51 – 3.21 (m, 2H), 1.88 – 1.62 (m, 5H), 1.53 – 0.94 (m, 24H), 0.8f8 (t, *J* = 5.9 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.23 (q, *J* = 36.9 Hz), 116.06 (q, *J* = 288.1 Hz), 41.44, 39.53, 38.12, 33.51, 32.84, 32.10, 31.88, 31.69, 30.33, 29.87, 29.53, 26.50, 26.19, 22.87, 14.29.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.07.
IR (film) ν_{max} 3300, 3106, 2922, 2854, 1700, 1558, 1161, 1180, 722
LRMS (EI) [$C_{18}H_{32}F_3NO$] m/z calculated 335.24, found 335.3



3kf - N-(2-(2-(6-((tert-butyldimethylsilyl)oxy)hexyl)cyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available ((6-bromohexyl)oxy)(tert-butyl)dimethylsilane.
Yield 48% >20:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.24 (s, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 3.47 – 3.38 (m, 1H), 3.30 (ddt, *J* = 13.0, 9.5, 6.3 Hz, 1H), 1.79 (ddt, *J* = 23.3, 13.4, 2.9 Hz, 3H), 1.72 – 1.64 (m, 2H), 1.54 – 1.42 (m, 3H), 1.41 – 1.15 (m, 9H), 1.15 – 0.91 (m, 5H), 0.89 (s, 9H), 0.04 (s, 5H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.24 (q, *J* = 36.6 Hz), 116.05 (q, *J* = 288.0 Hz), 63.50, 41.41, 39.50, 38.10, 33.40, 33.04, 32.80, 31.84, 31.66, 30.07, 26.44, 26.18, 26.17, 26.03, 18.57, -5.08.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.05.
IR (film) ν_{max} 3307, 3105, 2928, 2856, 1703, 1207, 1164, 908, 834, 776, 731
LRMS (ESI+APCI) [$C_{22}H_{42}F_3NO_2Si$] m/z ([M+H]$^+$) calculated 438.29 found 438.3

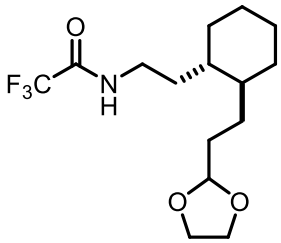


3kg - N-(2-(2-(6-cyanohexyl)cyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available 7-bromoheptanenitrile.
Yield 48% >20:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.48 (s, 1H), 3.41 (ddt, *J* = 13.5, 10.4, 5.5 Hz, 1H), 3.28 (ddt, *J* = 13.0, 9.7, 6.2 Hz, 1H), 2.34 (t, *J* = 7.0 Hz, 2H), 1.85 – 1.61 (m, 7H), 1.51 – 1.27 (m, 4H), 1.19 (dddd, *J* = 10.4, 8.5, 4.6, 2.3 Hz, 2H), 1.11 – 0.91 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.05 (q, *J* = 36.7 Hz), 119.96, 115.94 (q, *J* = 287.9 Hz), 41.37, 39.56, 38.14, 33.19, 32.89, 31.98, 31.81, 29.23, 28.73, 26.31, 26.02, 26.03, 25.49, 17.46.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.05.
IR (film) ν_{max} 3318, 3104, 2923, 2854, 2252, 1707, 1556, 1179, 1159, 909, 729, 648
LRMS (EI) [$C_{17}H_{27}F_3N_2O$] m/z calculated 332.21, found 332.2

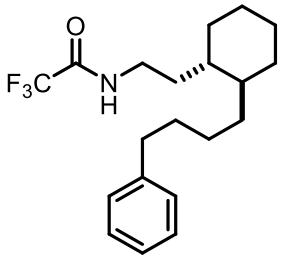


3kh - N-(2-(2-(3,7-dimethyloct-6-en-1-yl)cyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available (S)-8-bromo-2,6-dimethyloct-2-ene.
Yield 34% 20:1 trans:cis, 1:1 dr, contains 2% impurity of unsaturated product
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.19 (s, 1H), 5.10 (t, *J* = 6.8 Hz, 1H), 3.37 (ddt, *J* = 47.3, 13.7, 8.2 Hz, 2H), 1.96 (s, 2H), 1.84 – 1.66 (m, 7H), 1.56 (s, 3H), 1.30 (dd, *J* = 25.8, 8.8 Hz, 5H), 1.22 – 1.08 (m, 5H), 1.05 – 0.96 (m, 3H), 0.91 – 0.80 (m, 5H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.23 (q, *J* = 36.9 Hz), 131.92, 124.20, 116.06 (q, *J* = 288.1 Hz), 41.44, 39.53, 38.12, 33.51, 32.84, 32.10, 31.88, 31.69, 30.33, 29.87, 29.53, 26.50, 26.19, 26.19, 22.87, 14.29.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.04.

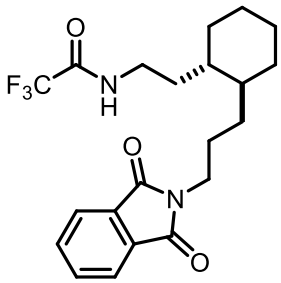
IR (film) ν_{max} 3302, 3105, 2921, 2854, 1702, 1562, 1161, 1180, 723
LRMS (EI) [$C_{20}H_{34}F_3NO$] m/z calculated 361.26, found 361.3



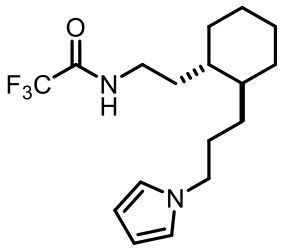
3ki - N-(2-(2-(2-(1,3-dioxolan-2-yl)ethyl)cyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available 2-(2-bromoethyl)-1,3-dioxolane. Due to coelution with homocoupled bromide product with desired product, the integrations for some ^{1}H NMR peaks have inflated integrations. The yield was adjusted according to normalized integrations.
Yield 61% >20:1 dr
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.37 (s, 1H), 5.10 – 4.69 (m, 2H), 4.00 – 3.90 (m, 4H), 3.90 – 3.78 (m, 4H), 3.48 – 3.23 (m, 2H), 1.89 – 1.75 (m, 2H), 1.68 (dddd, *J* = 12.1, 8.8, 5.2, 3.1 Hz, 6H), 1.46 (ddd, *J* = 7.6, 4.7, 3.4 Hz, 3H), 1.40 – 1.31 (m, 1H), 1.25 – 1.15 (m, 2H), 1.11 (ddd, *J* = 8.8, 6.1, 3.1 Hz, 1H), 0.98 (t, *J* = 11.0 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.26 (d, *J* = 36.7 Hz), 116.06 (d, *J* = 287.6 Hz), 104.68, 65.00, 40.99, 39.19, 38.01, 33.99, 32.62, 31.72, 31.45, 30.51, 26.07, 26.04, 24.17.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.94.
IR (film) ν_{max} 3312, 3097, 2920, 2853, 1708, 1559, 1153, 1178, 1035, 721
LRMS (EI) [$C_{15}H_{24}F_3NO_3$] m/z calculated 323.17, found 323.1



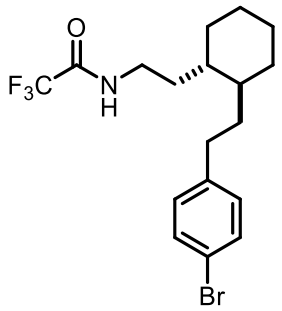
3kj -2,2,2-trifluoro-N-(2-(2-(4-phenylbutyl)cyclohexyl)ethyl)acetamide
Prepared using procedure B from compound **1k** and commercially available (4-bromobutyl)benzene.
Yield 54% >20:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 6.27 (s, 1H), 3.40 (ddt, *J* = 14.9, 9.9, 5.0 Hz, 1H), 3.28 (ddt, *J* = 13.1, 9.5, 6.3 Hz, 1H), 2.62 (ddd, *J* = 8.6, 6.7, 4.7 Hz, 2H), 1.72-1.83 (m, 3H), 1.72 – 1.45
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.24 (q, *J* = 36.6 Hz), 142.89, 128.58, 128.41, 125.77, 116.04 (q, *J* = 287.9 Hz), 41.35, 39.45, 38.07, 36.07, 33.27, 32.75, 31.95, 31.81, 31.67, 26.15, 26.14, 26.02.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.02.
IR (film) ν_{max} 3304, 3087, 3063, 3027, 2923, 2854, 1701, 1559, 1159, 739, 724, 698
LRMS (EI) [$C_{20}H_{28}F_3NO$] m/z calculated 355.21, found 355.2



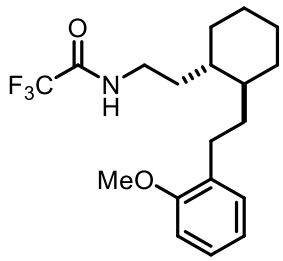
3kk - N-(2-((1S,2S)-2-(3-(1,3-dioxoisoindolin-2-yl)propyl)cyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available 2-(3-bromopropyl)isoindoline-1,3-dione.
Yield 69% >20:1 dr
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.54 (s, 1H), 3.65 (t, *J* = 6.7 Hz, 2H), 3.36 (dh, *J* = 13.6, 7.5, 7.1 Hz, 2H), 1.81 – 1.49 (m, 8H), 1.37 (dq, *J* = 13.7, 8.0 Hz, 1H), 1.25 – 1.06 (m, 5H), 0.98 (p, *J* = 10.0 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.74, 157.29 (q, *J* = 36.7 Hz), 134.14, 132.26, 123.36, 116.09 (q, *J* = 288.0 Hz), 40.57, 39.11, 38.44, 37.94, 32.58, 31.54, 31.37, 30.28, 25.94, 25.92, 25.25.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.87.
IR (film) ν_{max} 3339, 3091, 2922, 2852, 2256, 1772, 1704, 1552, 1397, 1156, 909, 718, 529
LRMS (ESI+APCI) [$C_{21}H_{25}F_3N_2O_3$] m/z ([M+H]$^+$) calculated 411.18 found 411.2



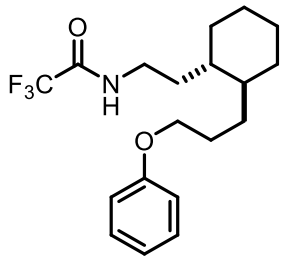
3kl - N-(2-((2-(3-(1H-pyrrol-1-yl)propyl)cyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available 1-(3-bromopropyl)-1H-pyrrole.
Yield 56% >20:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.66 (t, *J* = 2.1 Hz, 2H), 6.20 (s, 1H), 6.13 (t, *J* = 2.1 Hz, 2H), 3.90 (ddd, *J* = 13.4, 7.0, 6.2 Hz, 1H), 3.81 (dt, *J* = 13.8, 7.1 Hz, 1H), 3.32 (ddt, *J* = 13.3, 10.5, 5.4 Hz, 1H), 3.21 (ddt, *J* = 13.0, 9.7, 6.3 Hz, 1H), 1.80 – 1.62 (m, 7H), 1.56 (dtt, *J* = 13.0, 6.6, 2.8 Hz, 1H), 1.43 (dddd, *J* = 13.5, 11.1, 5.5, 2.5 Hz, 1H), 1.31 – 0.93 (m, 9H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.20 (q, *J* = 36.6 Hz), 120.83, 116.05 (q, *J* = 287.9 Hz), 107.97, 49.99, 41.05, 39.13, 37.85, 32.55, 31.80, 31.69, 29.98, 28.19, 26.16, 26.16.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -74.99.
IR (film) ν_{max} 3315, 3102, 2922, 2855, 1702, 1551, 1158, 1088, 721, 518
LRMS (EI) [$C_{17}H_{25}F_3N_2O$] m/z calculated 330.19, found 330.2



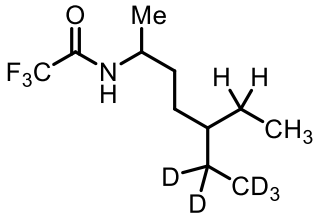
3km - N-(2-((1S,2S)-2-(4-bromophenethyl)cyclohexyl)ethyl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1k** and commercially available 1-bromo-4-(2-bromoethyl)benzene.
Yield 43% >20:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.39 (m, 2H), 7.11 – 7.02 (m, 2H), 6.21 (s, 1H), 3.43 (ddt, *J* = 15.3, 10.5, 5.3 Hz, 1H), 3.30 (ddt, *J* = 13.1, 9.6, 6.3 Hz, 1H), 2.66 (ddd, *J* = 13.8, 10.7, 5.2 Hz, 1H), 2.46 (ddd, *J* = 13.8, 10.6, 6.2 Hz, 1H), 1.94 – 1.66 (m, 5H), 1.47 – 1.34 (m, 2H), 1.30 – 1.20 (m, 2H), 1.19 – 1.00 (m, 4fH), 0.90 (h, *J* = 6.9, 5.4 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.08 (q, *J* = 36.5 Hz), 141.75, 131.40, 130.09, 119.40, 115.84 (q, J = 288.0 Hz), 40.77, 39.26, 37.84, 35.13, 32.58, 32.15, 31.49, 31.30, 25.85, 25.82.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.95.
IR (film) ν_{max} 3303, 3104, 2923, 2855, 1701, 1553, 1487, 1160, 1180, 1072, 1011, 802, 722
LRMS (EI) [$C_{18}H_{23}BrF_3NO$] m/z calculated 405.09/407.09, found 405.1/407.1



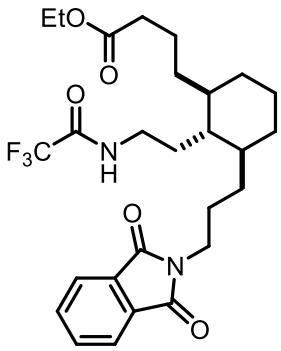
3kn - 2,2,2-trifluoro-N-(2-((2-(2-methoxyphenethyl)cyclohexyl)ethyl)acetamide
Prepared using procedure B from compound **1k** and commercially available 1-(2-bromoethyl)-2-methoxybenzene.
Yield 58% >20:1 dr
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.05 (m, 2H), 6.93 – 6.82 (m, 2H), 6.19 (s, 1H), 3.81 (s, 3H), 3.43 – 3.25 (m, 2H), 2.67 (td, *J* = 12.2, 11.1, 5.1 Hz, 1H), 2.52 – 2.42 (m, 1H), 1.93 – 1.64 (m, 5H), 1.50 – 1.33 (m, 2H), 1.27 – 0.88 (m, 7H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.55, 131.49, 129.85, 127.12, 120.64, 116.06 (q, *J* = 287.9 Hz), 110.47, 55.41, 41.39, 39.17, 38.00, 33.73, 32.61, 31.83, 31.70, 27.10, 26.20, 26.19.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.06.
IR (film) ν_{max} 3307, 3104, 2922, 2854, 1702, 1553, 1493, 1461, 1205, 1158, 1031, 750, 724
LRMS (EI) [$C_{19}H_{26}F_3NO_2$] m/z calculated 357.19, found 357.2



3ko - 2,2,2-trifluoro-N-(2-(2-(3-phenoxypropyl)cyclohexyl)ethyl)acetamide
Prepared using procedure B from compound **1k** and commercially available (3-bromopropoxy)benzene.
Yield 54% >20:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (dd, *J* = 8.7, 7.4 Hz, 2H), 6.95 – 6.91 (m, 1H), 6.89 (dd, *J* = 8.8, 1.1 Hz, 2H), 6.21 (s, 1H), 4.02 – 3.88 (m, 2H), 3.42 (ddt, *J* = 13.4, 10.2, 5.4 Hz, 1H), 3.30 (ddt, *J* = 13.1, 9.6, 6.4 Hz, 1H), 1.75-1.91 (m, 4H), 1.62-1.74 (m, 4H), 1.46 – 1.18 (m, 4H), 1.18 – 0.91 (m, 4H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.14, 157.25 (q, *J* = 36.8 Hz), 129.62, 120.75, 117.18 (q, *J* = 287.9 Hz), 114.67, 68.19, 41.12, 39.42, 38.05, 32.71, 31.79, 31.64, 29.60, 26.14, 26.13, 26.08.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.02.
IR (film) ν_{max} 3306, 3100, 3040, 2920, 2853, 1701, 1600, 1552, 1496, 1205, 1158, 1035, 753, 691, 512
LRMS (EI) [$C_{19}H_{26}F_3NO_2$] m/z calculated 357.19, found 357.2

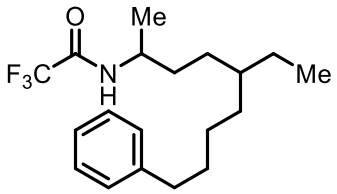


3ap - N-(5-ethylheptan-2-yl-6,6,7,7,7-d5)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **2c** and commercially available bromoethane-d_5.
Yield 42% 1:1 dr
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.01 (s, 1H), 4.10 (hept, *J* = 6.6 Hz, 1H), 1.51 – 1.16 (m, 11H), 0.89 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.62 (q, *J* = 36.7 Hz), 116.09 (q, *J* = 288.1 Hz), 44.87, 40.85, 35.44, 29.89, 21.11, 20.54, 19.74, 14.53, 11.23 – 10.87 (m).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.08.
^{2}H NMR (61 MHz, Chloroform-*d*) δ 1.29 (s, 2H), 0.80 (s, 3H).
IR (film) ν_{max} 3295, 3100, 2959, 2921, 2852, 2220, 2097, 2073, 1698, 1556, 1185, 1162, 725
LRMS (EI) [$C_{11}H_{15}D_5F_3NO$] m/z calculated 244.18, found 244.3

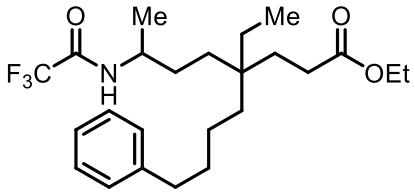


4a - ethyl 4-(3-(3-(1,3-dioxoisoindolin-2-yl)propyl)-2-(2-(2,2,2-trifluoroacetamido)ethyl)cyclohexyl)butanoate
Prepared using procedure B from compound **3kk** and commercially available ethyl 4-bromobutanoate.
Yield 45% >20:1:1:1 dr

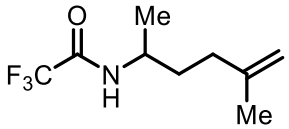
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.80 – 7.68 (m, 2H), 6.73 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.79 – 3.64 (m, 2H), 3.31 (dtd, *J* = 23.6, 13.0, 6.4 Hz, 1H), 2.41 – 2.23 (m, 2H), 1.89 – 1.46 (m, 12H), 1.27 (t, *J* = 7.1 Hz, 4H), 1.24 – 1.11 (m, 3H), 1.02 – 0.83 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.85, 168.66, 157.07 (q, *J* = 36.8 Hz), 133.97, 132.09, 123.19, 115.93 (q, *J* = 288.0 Hz), 60.27, 43.74, 39.88, 39.67, 38.18, 37.18, 34.43, 32.85, 31.90, 31.81, 30.69, 28.29, 25.69, 25.38, 21.57, 14.23.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.90.
IR (film) ν_{max} 3339, 3090, 2927, 2858, 1771, 1705, 1553, 1397, 1370, 1177, 1155, 720
LRMS (ESI+APCI) [$C_{27}H_{35}F_3N_2O_5$] m/z ([M+H]$^+$) calculated 525.25, found 525.2



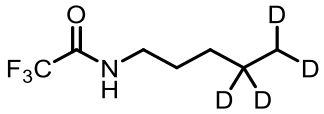
3aj - N-(5-ethyl-9-phenylnonan-2-yl)-2,2,2-trifluoroacetamide
Prepared using procedure B from compound **1c** and commercially available (4-bromobutyl)benzene.
Yield 68% 1:1 dr, contains 5% impurity unsaturated product
10:1 mixture of diastereomers isolated
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 4H), 5.96 (s, 1H), 4.10 (p, *J* = 7.0 Hz, 1H), 2.74 – 2.52 (m, 2H), 1.69 – 1.53 (m, 2H), 1.52 – 1.10 (m, 14H), 0.96 – 0.80 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.40 (q, *J* = 36.5 Hz), 142.67, 128.39, 128.25, 125.62, 115.90 (q, *J* = 288.1 Hz), 44.69, 41.14, 35.86, 35.73, 34.17, 33.30, 31.68, 25.93, 20.86, 19.49, 14.35.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.04.
IR (film) ν_{max} 3294, 3088, 3027, 2929, 2858, 1696, 1556, 1455, 1158, 1182, 744, 725, 697
LRMS (EI) [$C_{19}H_{28}F_3NO$] m/z calculated 343.21, found 434.2



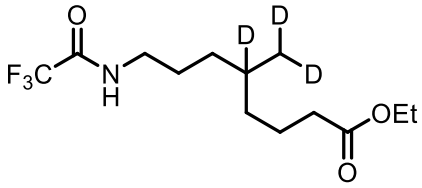
4b - ethyl 4-ethyl-8-phenyl-4-(3-(2,2,2-trifluoroacetamido)butyl)octanoate
Synthesized according to conditions reported by Chu *et al*,[3] compound **3cj** was reacted with commercially available ethyl acrylate.
Yield 61% 1:1 dr
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (s, 1H), 4.33 (m, 1H), 4.26 – 3.97 (m, 4H), 2.67 – 2.52 (m, 2H), 2.28 (tt, *J* = 7.4, 2.3 Hz, 4H), 1.68 – 1.50 (m, 4H), 1.48 – 1.39 (m, 1H), 1.39 – 1.30 (m, 2H), 1.30 – 1.21 (m, 8H), 0.88 – 0.77 (m, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.81, 171.72, 156.74 (q, *J* = 36.8 Hz), 116.03 (q, *J* = 288.0 Hz), 61.27, 60.44, 45.02, 37.93, 37.48, 35.69, 34.57, 32.59, 32.14, 25.71, 21.78, 14.27, 10.57.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -75.17, -75.22.
IR (film) ν_{max} 3311, 3089, 2930, 2862, 1701, 1552, 1155, 1177, 724, 699
LRMS (EI) [$C_{24}H_{36}F_3NO_3$] m/z calculated 443.26, found 443.3



5a - 2,2,2-trifluoro-N-(5-methylhex-5-en-2-yl)acetamide
Prepared using procedure B from compound **1p** utilizing ethyl 4-bromobutanoate as an oxidant.
Yield 40%
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.05 (s, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 4.11 – 3.98 (m, 1H), 2.15 – 2.00 (m, *J* = 7.6 Hz, 2H), 1.80 – 1.60 (m, 5H), 1.25 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.66 (q, *J* = 37.0 Hz), 144.66, 116.06 (q, *J* = 288.1 Hz), 111.04, 46.53, 34.18, 34.05, 22.51, 20.45.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.05.
LRMS (EI) [$C_9H_{14}F_3NO$] m/z calculated 209.10, found 209.1



1c-d$_4$ - 2,2,2-trifluoro-N-(pentyl-4,4,5,5-d$_4$)acetamide
Prepared from the commercially available 2-(pent-4-yn-1-yl)isoindoline-1,3-dione, (5.00 g, 23.4 mmol) which was subjected to ten percent Pd/C (2.5 grams, 2.34 mmol) in MeOH (0.05M) under an atmosphere of D_2 overnight at room temperature to form the corresponding alkane. The product was dried under vacuum and used for the subsequent step without further purification. The phthalimide alkane was then subjected to 3.5 equivalents (1.18 g, 23.4 mmol) hydrazine monohydrate in 150 mL EtOH at room temperature. The mixture was then refluxed overnight. Three equivalents (8.00 g, 70.2 mmol) of trifluoroacetic acid was then added. EtOH was then removed *en vacuo* and to the resulting white solid was added 50 mL 1 M NaOH in H_2O slowly. The mixture was then extracted with DCM three times, washed with brine and dried over Na_2SO_4. The solvent was removed by careful evaporation and the product was subjected to procedure A without further purification to form **1q**.
Yield 15% (3 steps)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.20 (s, 1H), 3.36 (q, *J* = 6.8 Hz, 2H), 1.59 (tt, *J* = 8.4, 6.6 Hz, 2H), 1.32 (q, *J* = 9.4, 8.0 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 1H).
^{2}H NMR (61 MHz, Chloroform-*d*) δ 1.30 (s, 2H), 0.88 (s, 2H).



3ca-d$_3$ - ethyl 5-(methyl-d)-8-(2,2,2-trifluoroacetamido)octanoate-4,5,6,7-d4
Prepared using procedure B from compound **1q**.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.39 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.37 (td, *J* = 8.2, 2.8 Hz, 2H), 2.29 (t, *J* = 7.3 Hz, 2H), 1.68 – 1.48 (m, 6H), 1.37 – 1.18 (m, 7H), 0.93 – 0.75 (m, 1H).
^{2}H NMR (61 MHz, Chloroform-d) δ 1.33 (s, 1H), 0.84 (s, 2H).

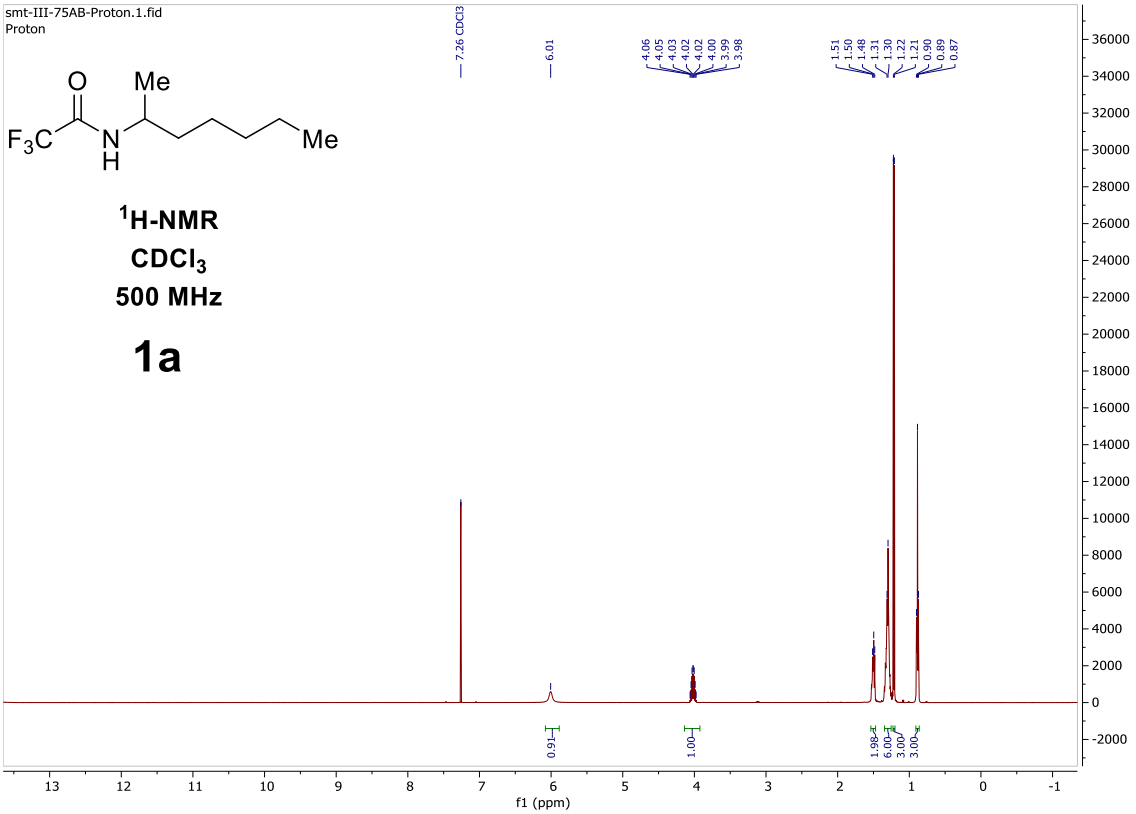
References:

(1) Milan, M.; Carboni, G.; Salamone, M.; Costas, M.; Bietti, M. Tuning Selectivity in Aliphatic C–H Bond Oxidation of N-Alkylamides and Phthalimides Catalyzed by Manganese Complexes. *ACS Catal.* **2017**, *7*, 5903–5911.

(2) Xu, B.; Tambar, U. K. Remote Allylation of Unactivated C(Sp3)–H Bonds Triggered by Photogenerated Amidyl Radicals. *ACS Catal.* **2019**, *9*, 4627–4631.

(3) Chu, J. C. K.; Rovis, T. Amide-Directed Photoredox-Catalysed C–C Bond Formation at Unactivated Sp^3 C–H Bonds. *Nature* **2016**, *539*, 272–275.

NMR Spectra: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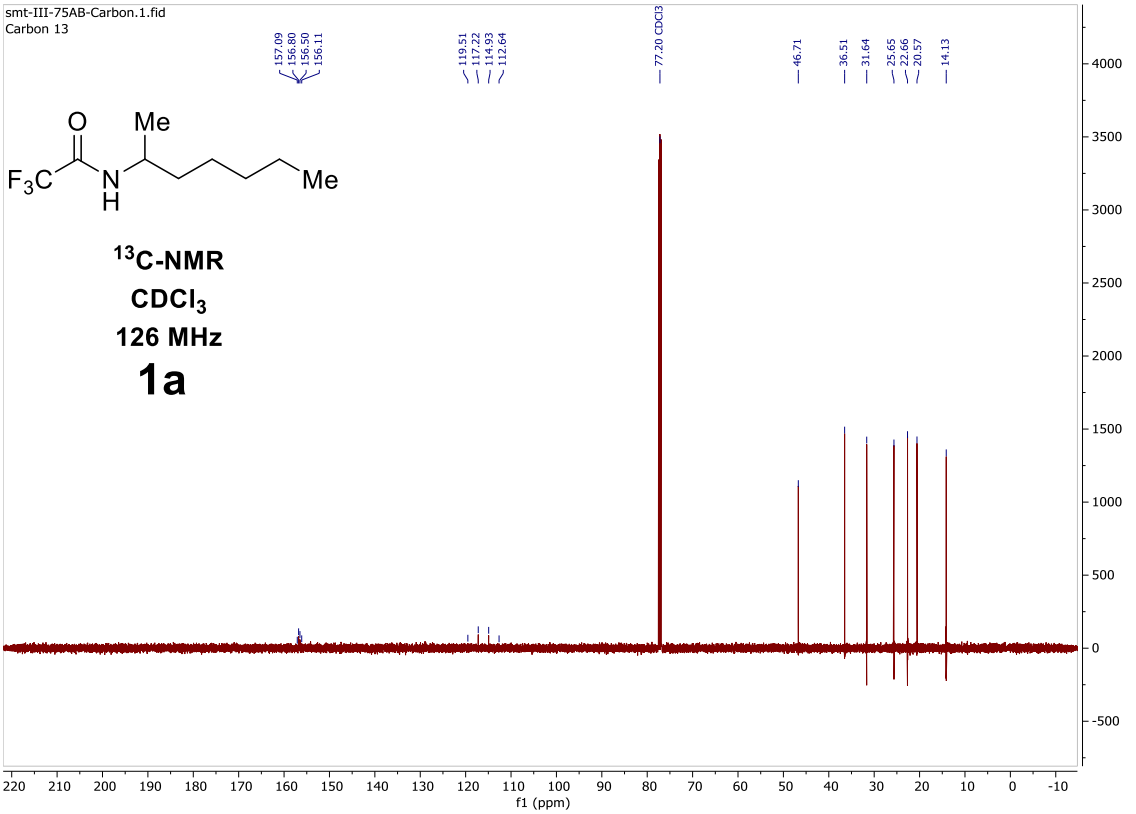
6.01
4.06
4.05
4.03
4.02
4.02
4.00
3.99
3.98
1.51
1.50
1.48
1.31
1.30
1.22
1.21
0.90
0.89
0.87
O
Me
F3C
N
H
Me
1H-NMR
CDCl3
500 MHz
1a
0.91
1.00
1.98
6.00
3.00
3.00
f1 (ppm)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31.64
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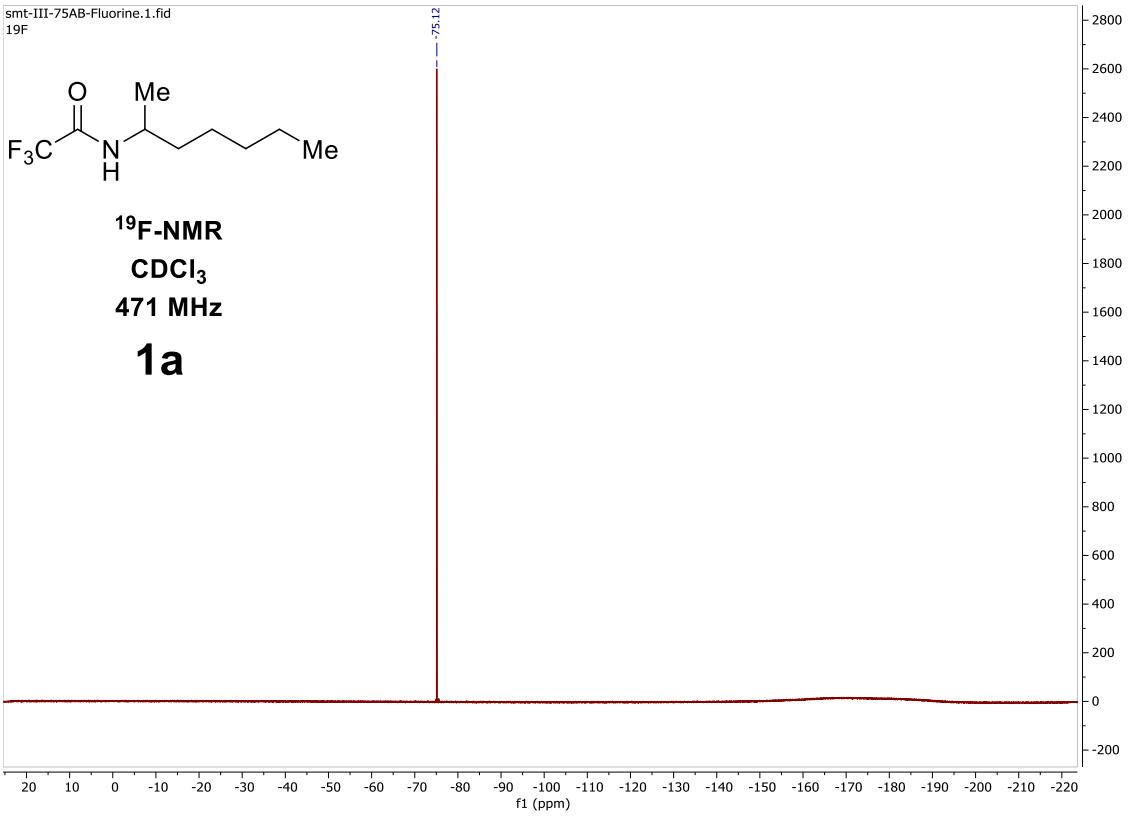
13C-NMR
CDCl3
126 MHz
1a
f1 (ppm)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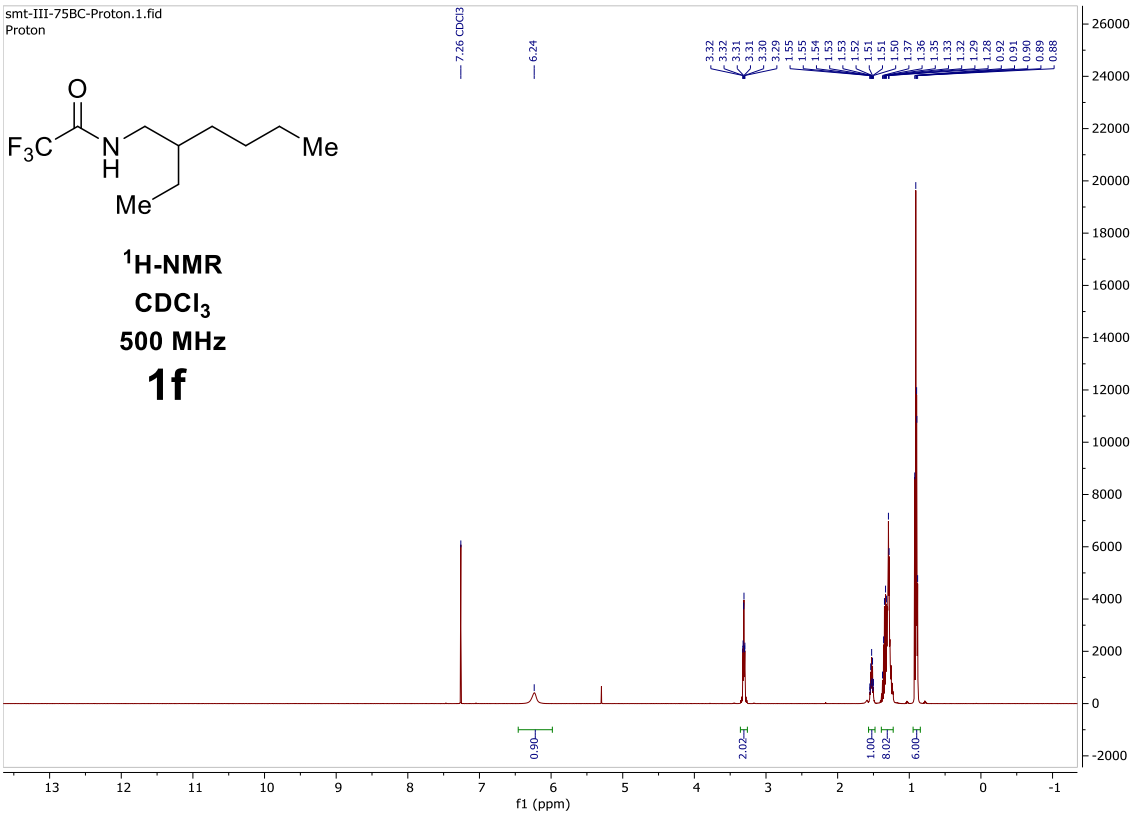
1a
f1 (ppm)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Proton
7.26 CDCl3
6.24
O
F3C
N
H
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Me
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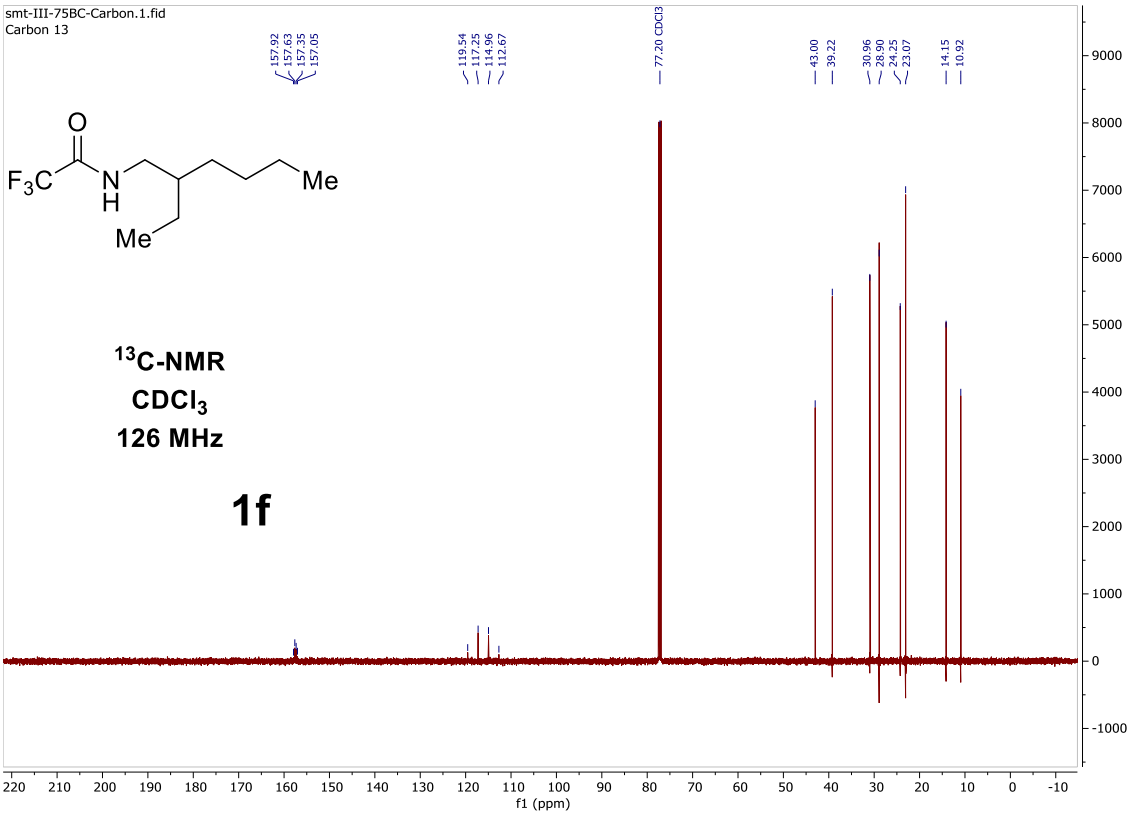
500 MHz
1f
0.90
2.02
1.00
8.02
6.00
f1 (ppm)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39.22
30.96
28.90
24.25
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F3C
N
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Me
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13C-NMR
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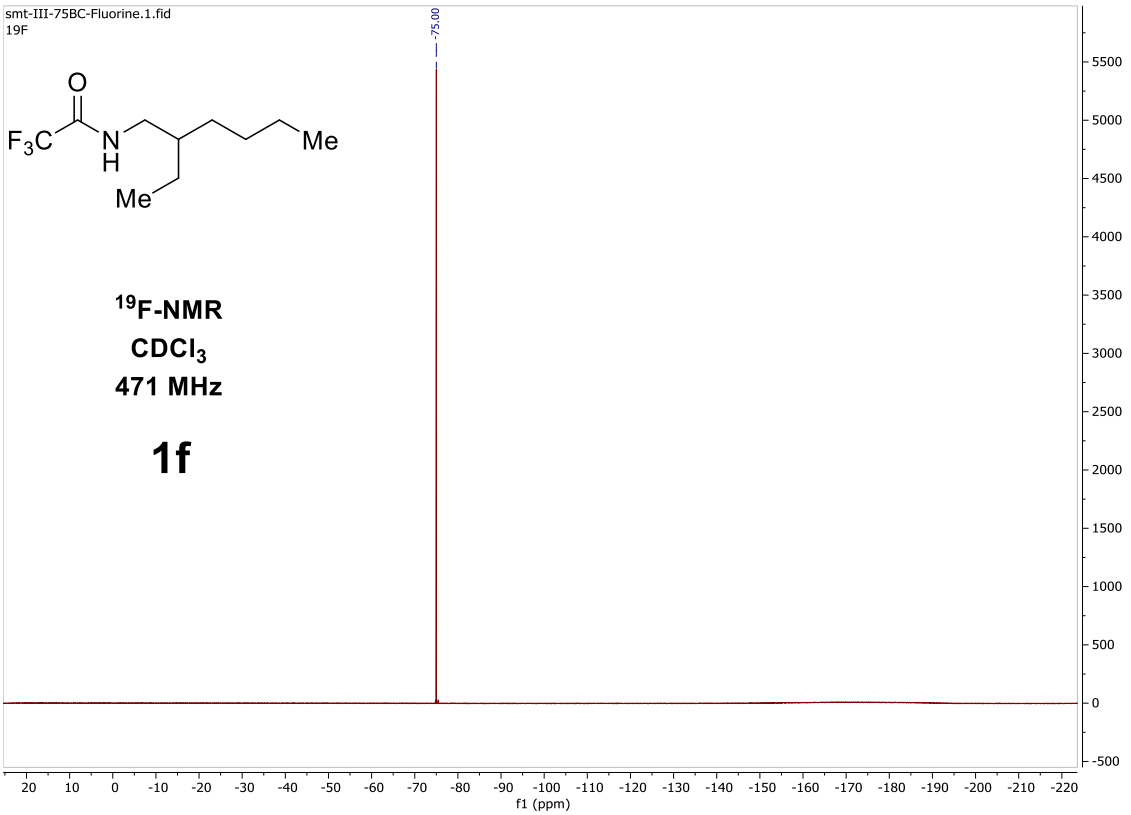
126 MHz
1f
f1 (ppm)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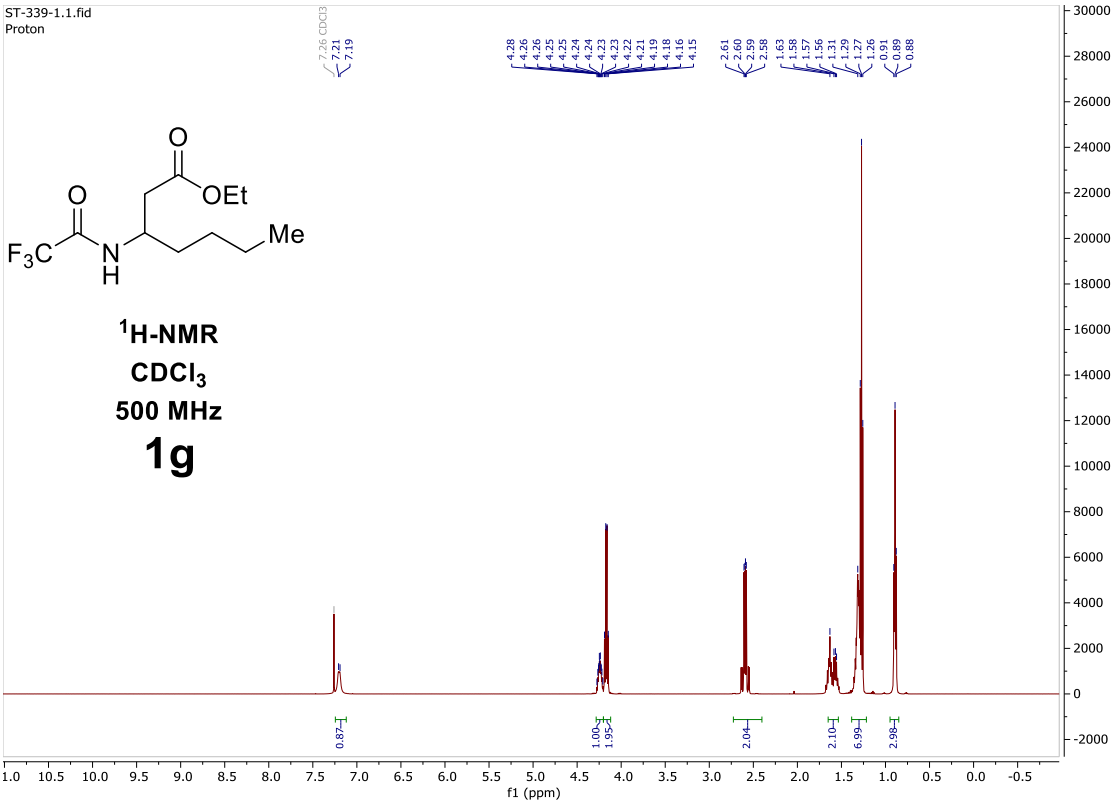
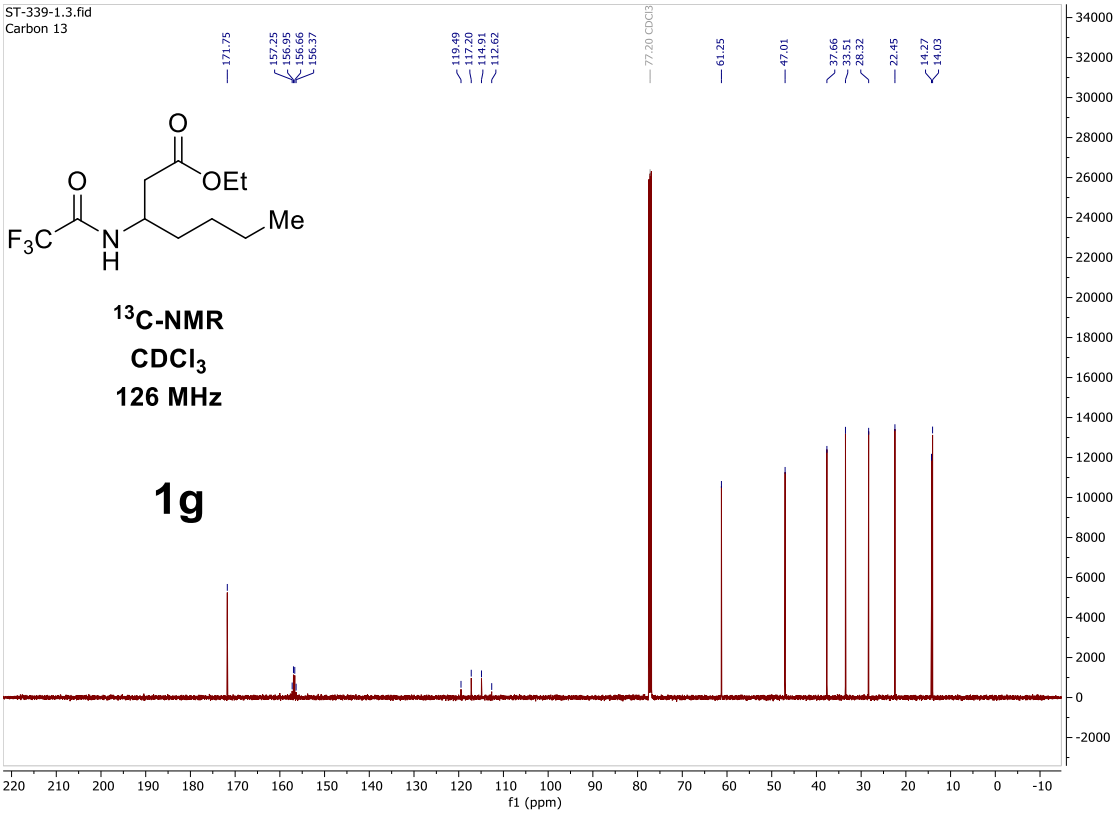
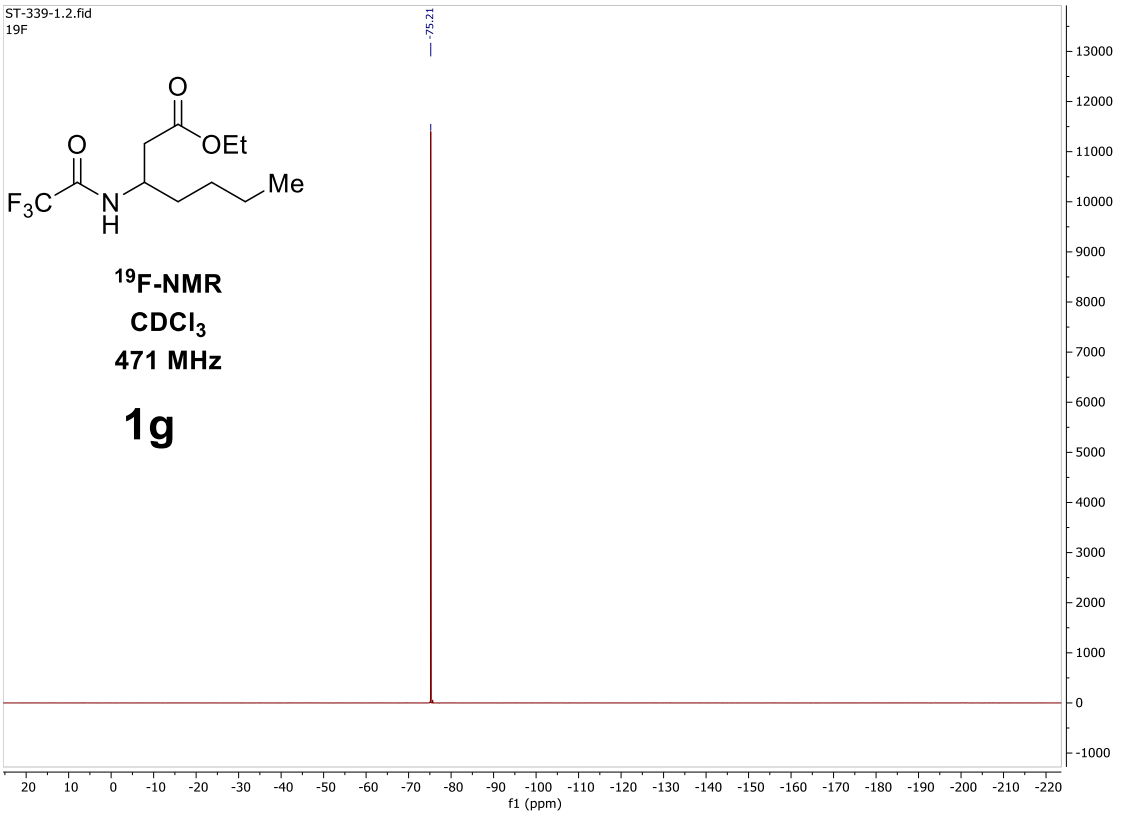
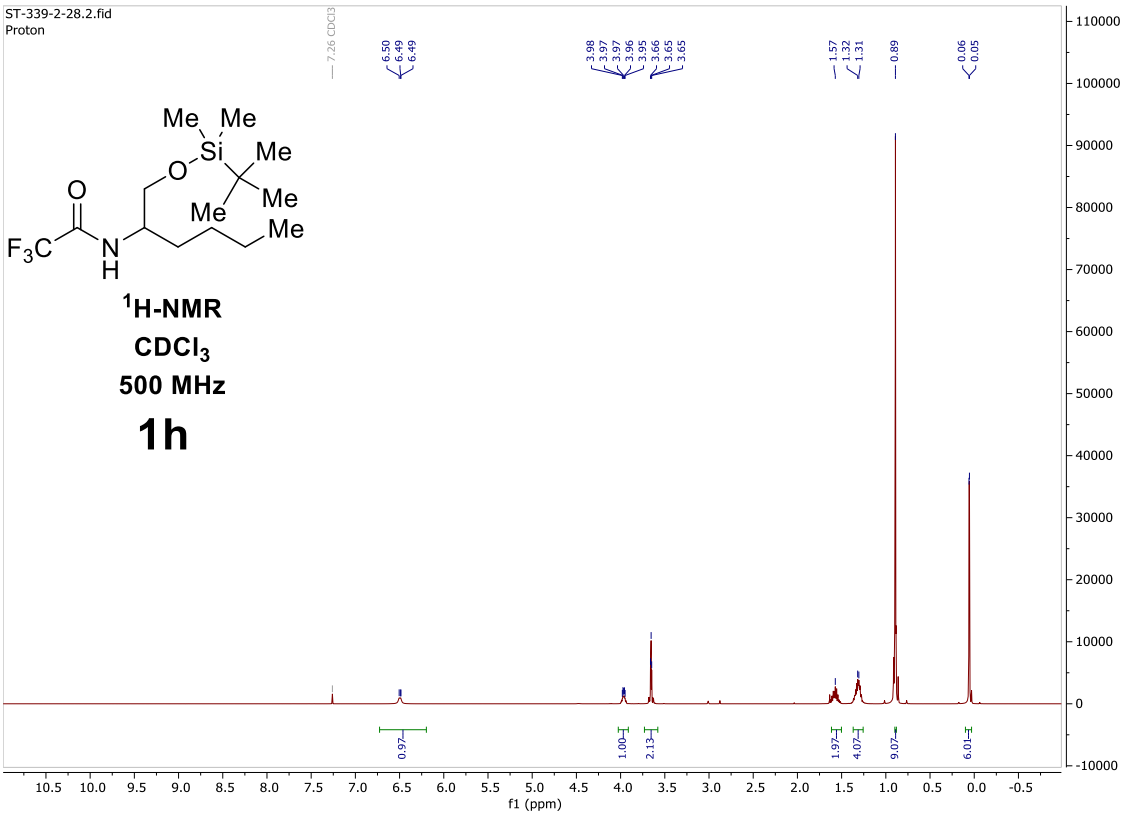
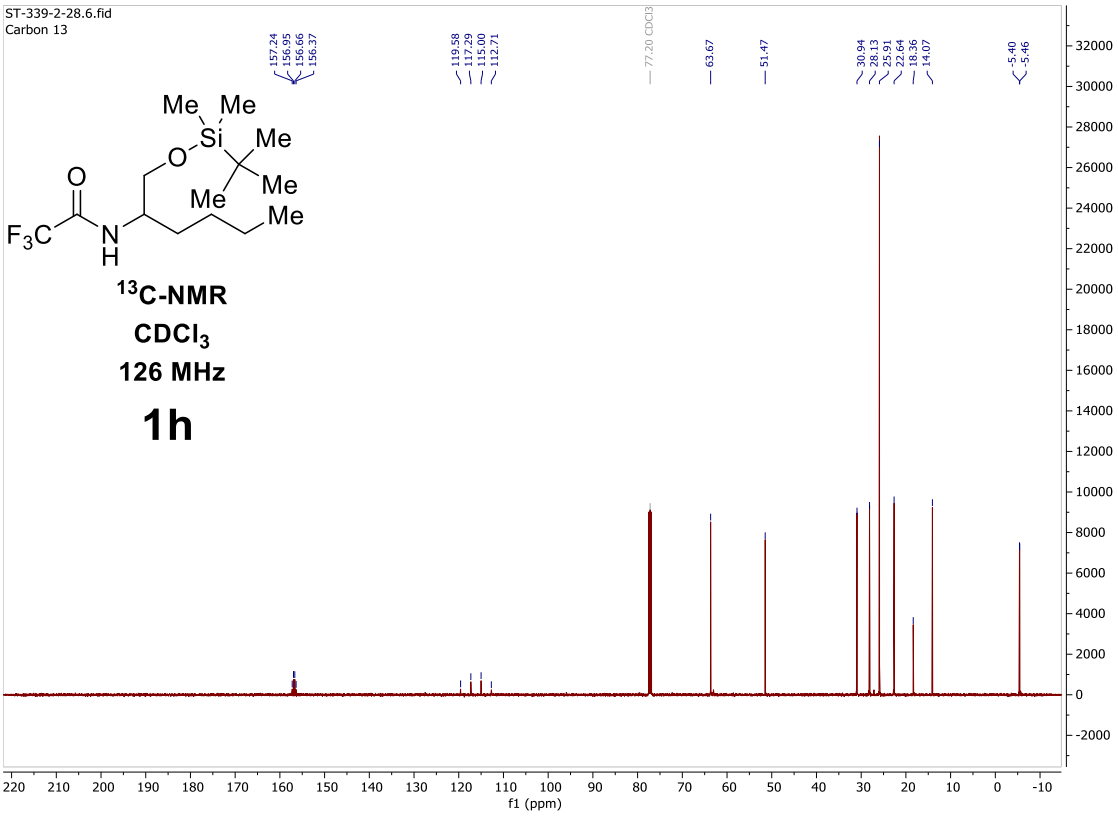
1f
f1 (ppm)

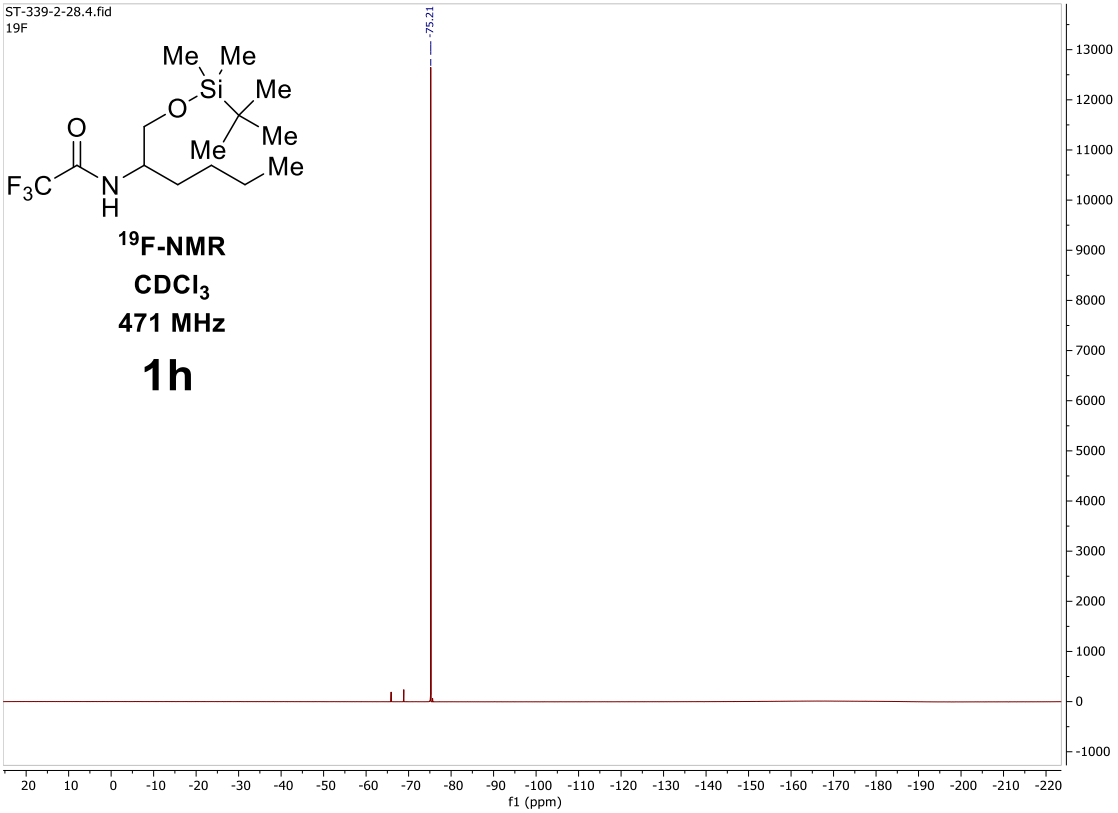

ST-339-1.1.fid
Proton
7.26 CDCl3
7.21
7.19
4.28
4.26
4.26
4.26
4.25
4.25
4.24
4.24
4.23
4.23
4.22
4.21
4.19
4.18
4.16
4.15
2.61
2.60
2.59
2.58
1.63
1.58
1.57
1.55
1.31
1.29
1.27
1.26
0.91
0.89
0.88
O
O
OEt
F3C
N
H
Me
1H-NMR
CDCl3
500 MHz
1g
0.87
1.00
1.95
2.04
2.10
6.99
2.98
f1 (ppm)

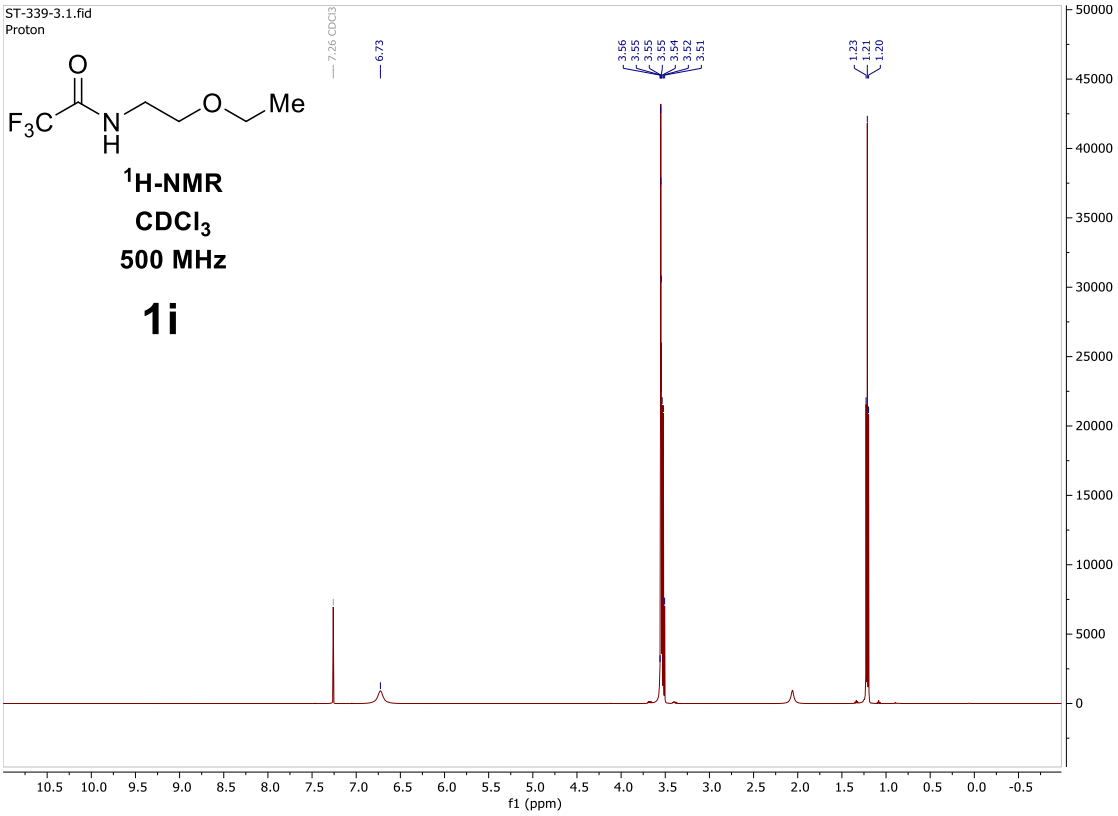

ST-339-1.3.fid
Carbon 13
171.75
157.25
156.95
156.66
156.37
119.49
117.20
114.91
112.62
77.20 CDCl3
61.25
47.01
37.66
33.51
28.32
22.45
14.27
14.03
O
O
OEt
F3C
N
H
Me
13C-NMR
CDCl3
126 MHz
1g
f1 (ppm)

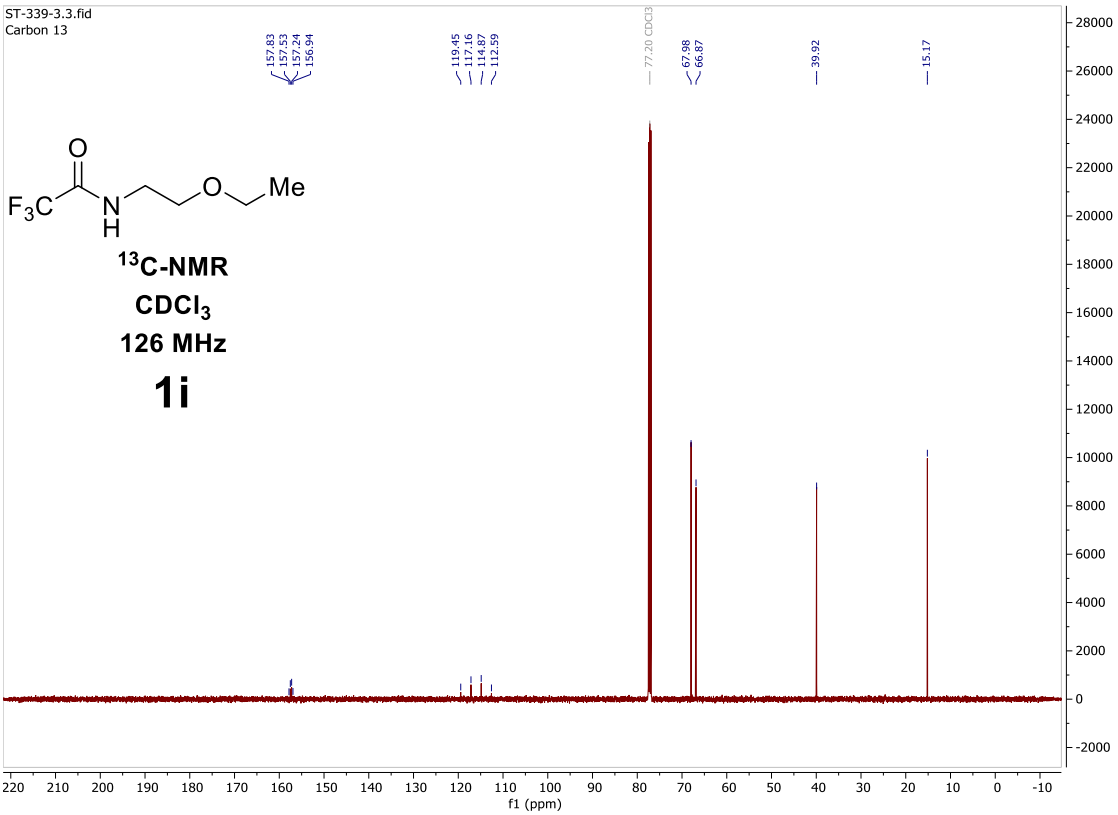

ST-339-1.2.fid
19F
-75.21
O
OEt
O
F3C
N
H
Me
19F-NMR
CDCl3
471 MHz
1g
f1 (ppm)

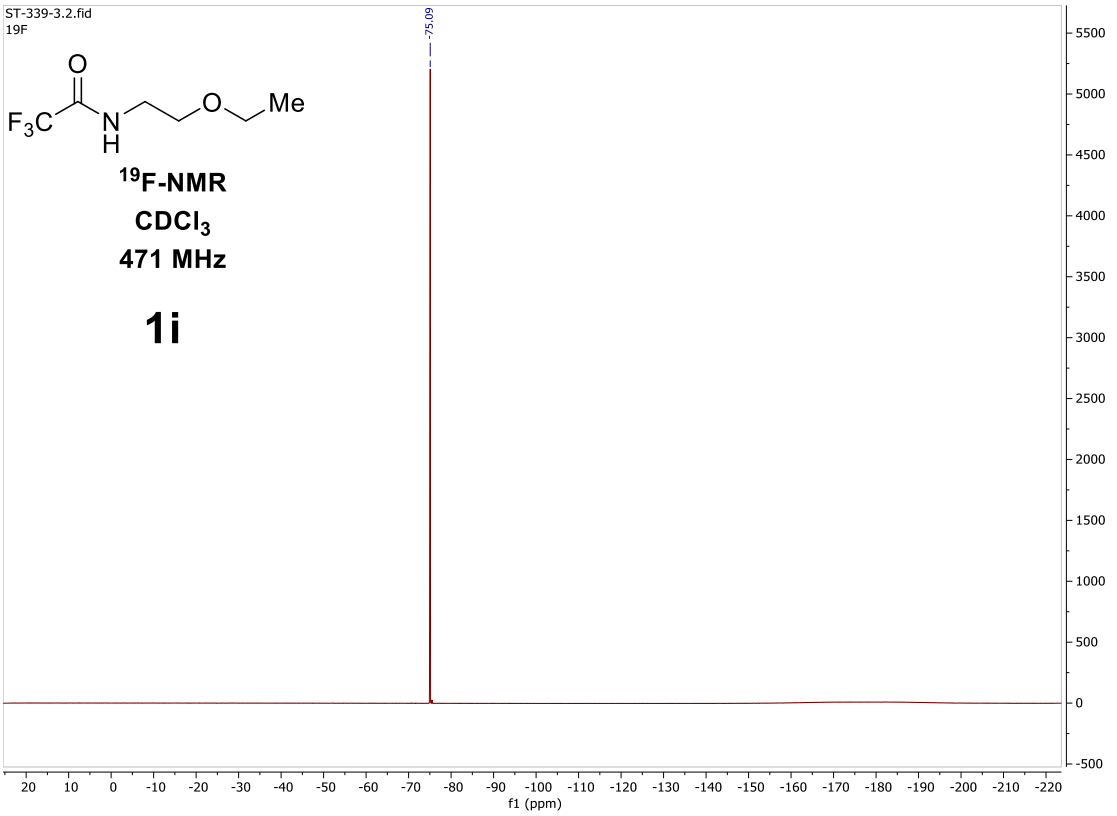

ST-339-2-28.2.fid
Proton
7.26 CDCl3
6.50
6.49
6.49
3.98
3.97
3.97
3.96
3.95
3.66
3.65
3.65
1.57
1.32
1.31
0.89
0.06
0.05
Me
Me
Si
Me
O
Me
Me
Me
O
F3C
N
H
0.97
1.00
2.13
1.97
4.07
9.07
6.01
1H-NMR
CDCl3
500 MHz
1h
f1 (ppm)

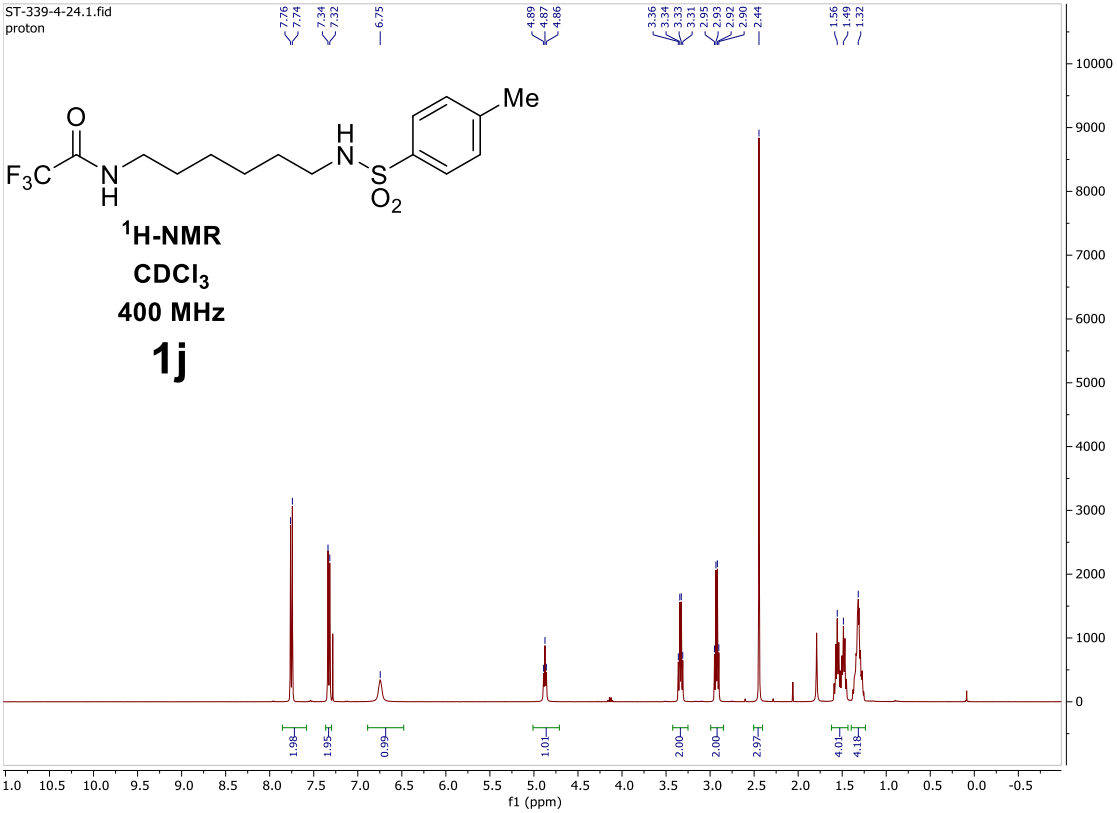

ST-339-2-28.6.fid
Carbon 13
157.24
156.95
156.66
156.37
119.58
117.29
115.00
112.71
77.20 CDCl3
63.67
51.47
30.94
28.13
25.91
22.64
18.36
14.07
-5.40
-5.46
Me Me
Si
Me
O
Me
Me
Me
O
F3C
N
H
13C-NMR
CDCl3
126 MHz
1h
f1 (ppm)

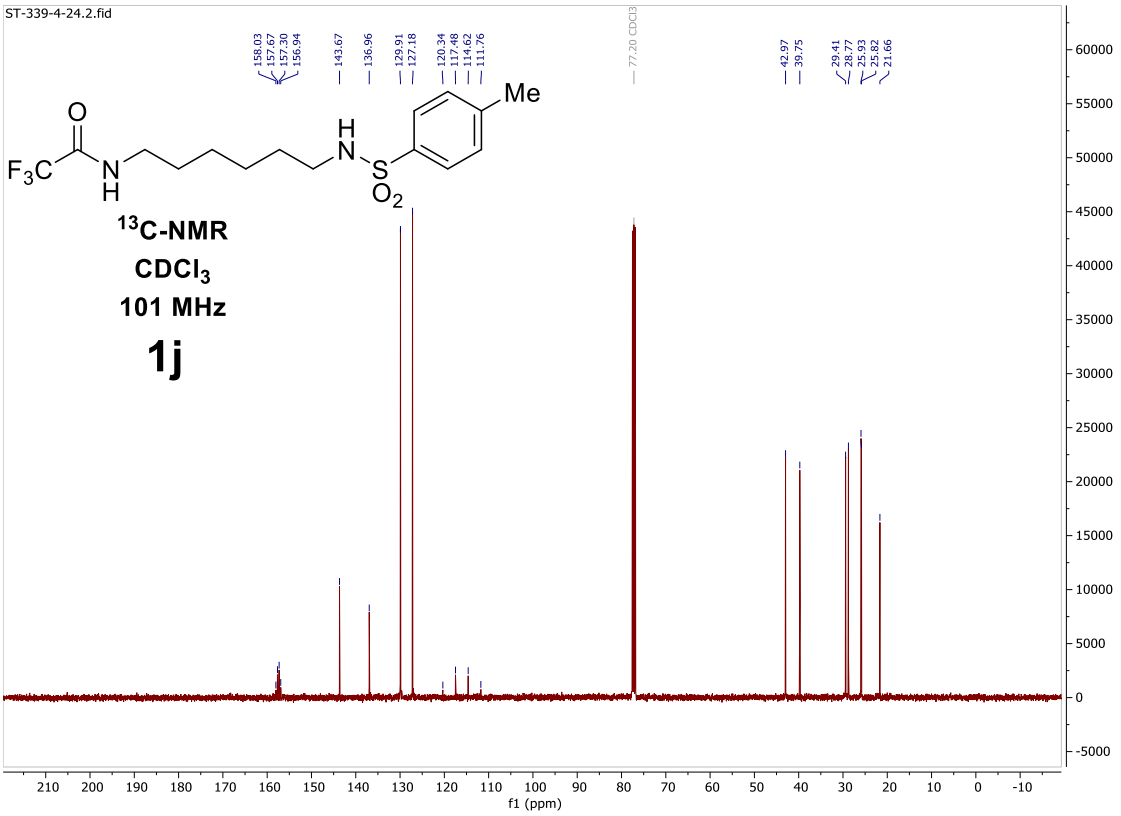

ST-339-2-28.4.fid
19F
-75.21
Me Me
Si
Me
O
Me
Me
Me
O
F3C
N
H
19F-NMR
CDCl3
471 MHz
1h
f1 (ppm)

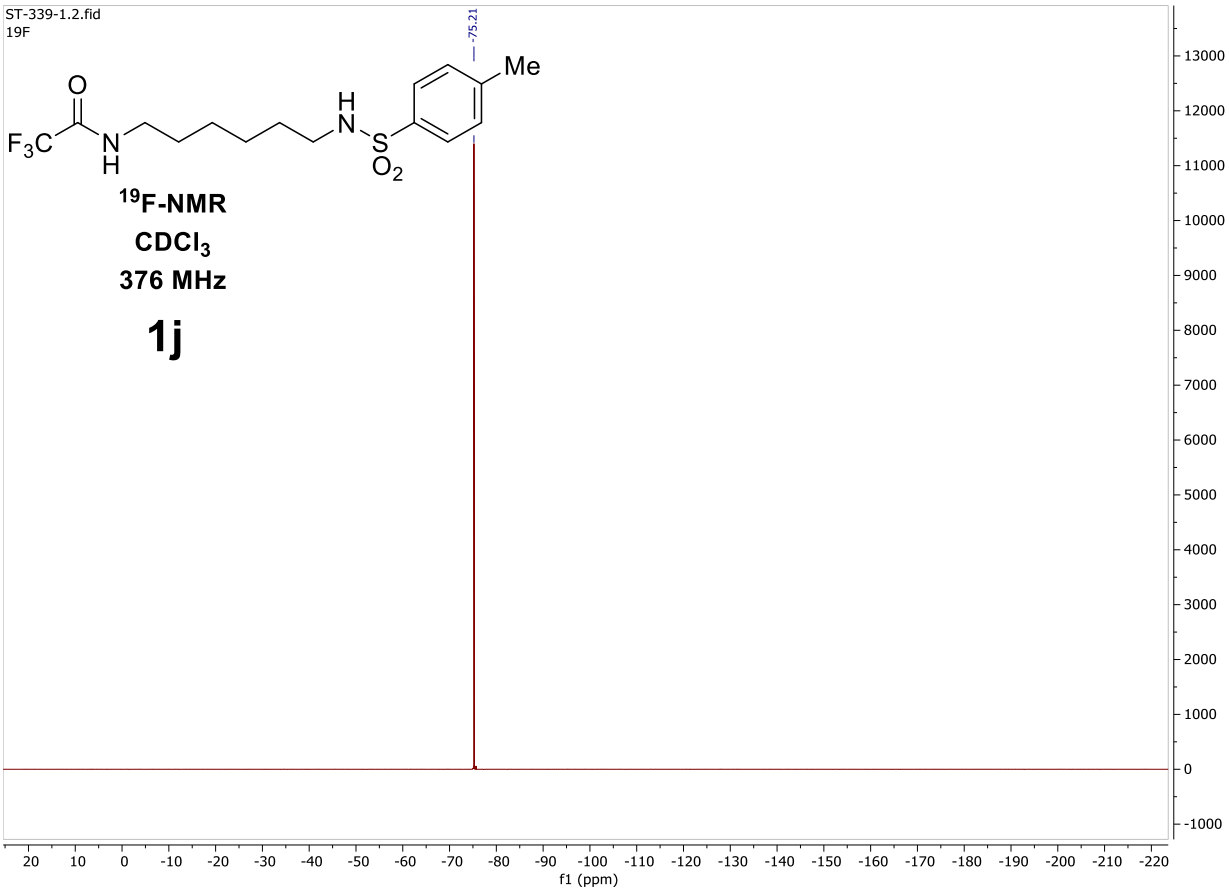

ST-339-3.1.fid
Proton
7.26 CDCl3
6.73
3.56
3.55
3.55
3.55
3.55
3.54
3.52
3.51
1.23
1.21
1.20
F3C
O
N
H
O
Me
1H-NMR
CDCl3
500 MHz
1i
f1 (ppm)

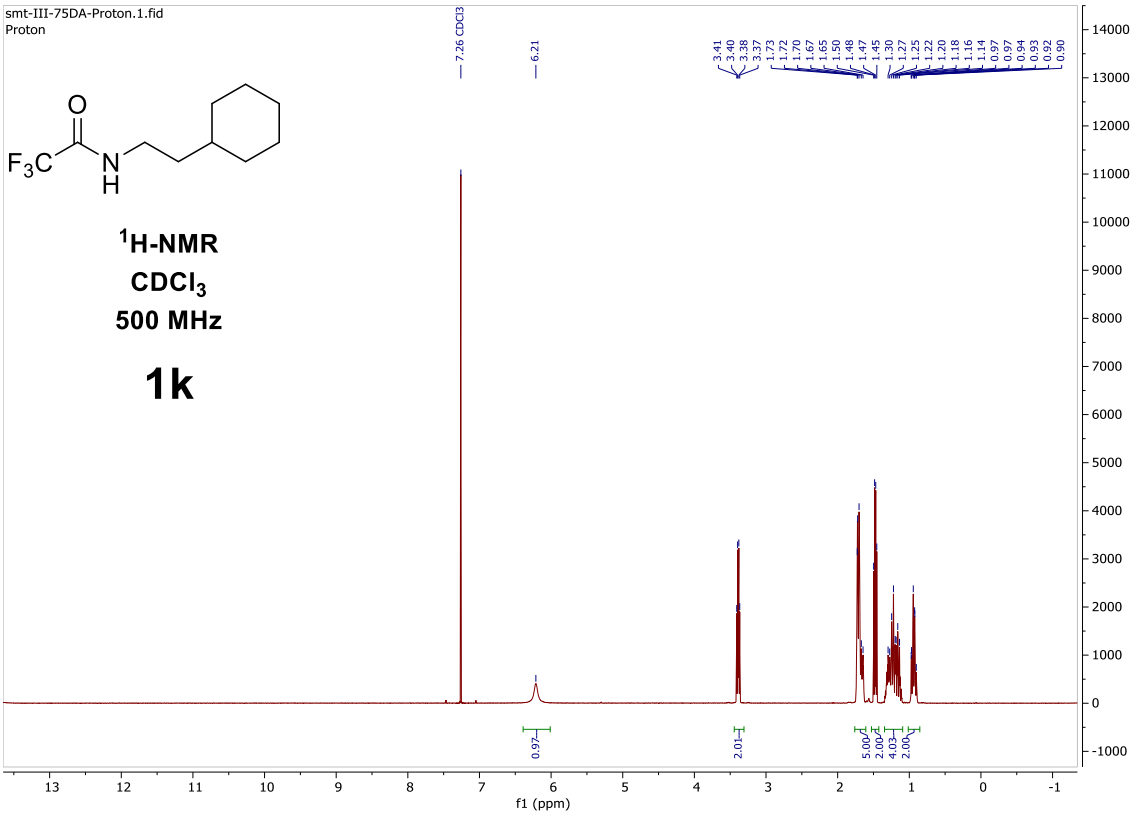

ST-339-3.3.fid
Carbon 13
157.83
157.53
157.24
156.94
119.45
117.16
114.87
112.59
77.20 CDCl3
67.98
66.87
39.92
15.17
F3C
O
N
H
O
Me
13C-NMR
CDCl3
126 MHz
1i
f1 (ppm)

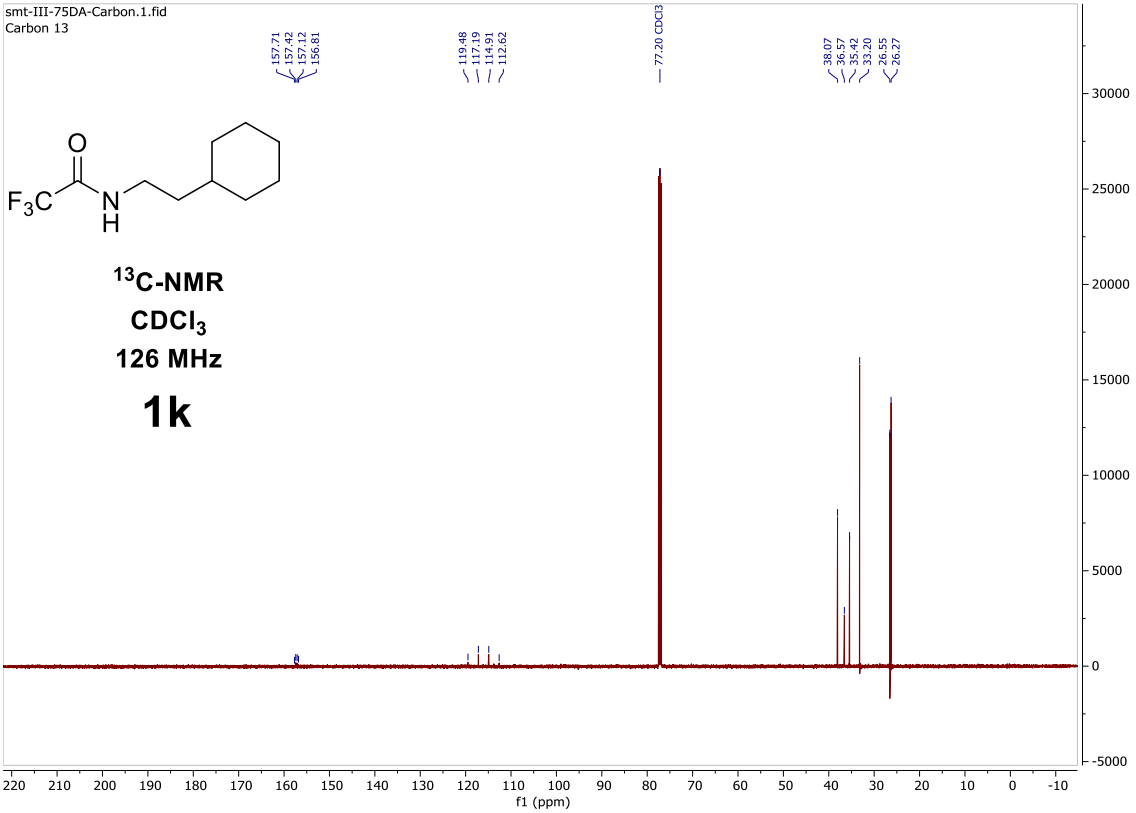

ST-339-3.2.fid
19F
-75.09
^{19}F-NMR
$CDCl_3$
471 MHz
1i
f1 (ppm)

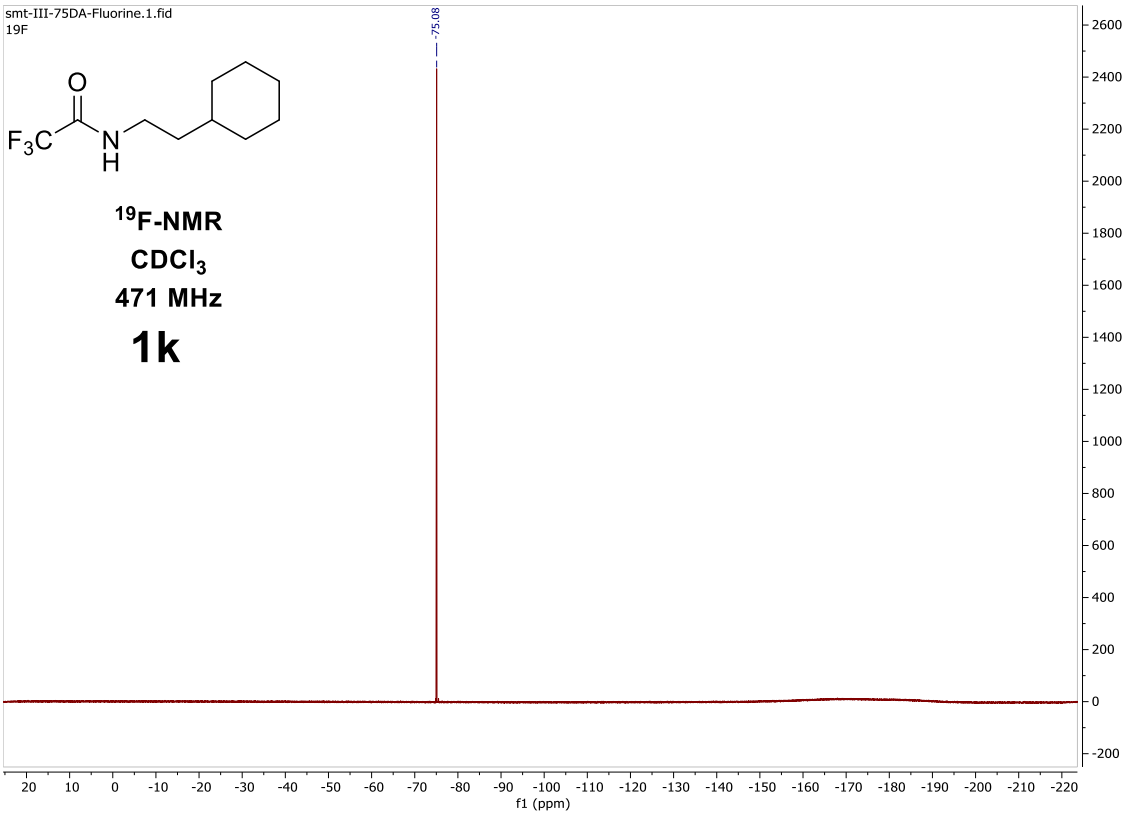

ST-339-4-24.1.fid
proton
^{1}H-NMR
$CDCl_3$
400 MHz
1j
f1 (ppm)

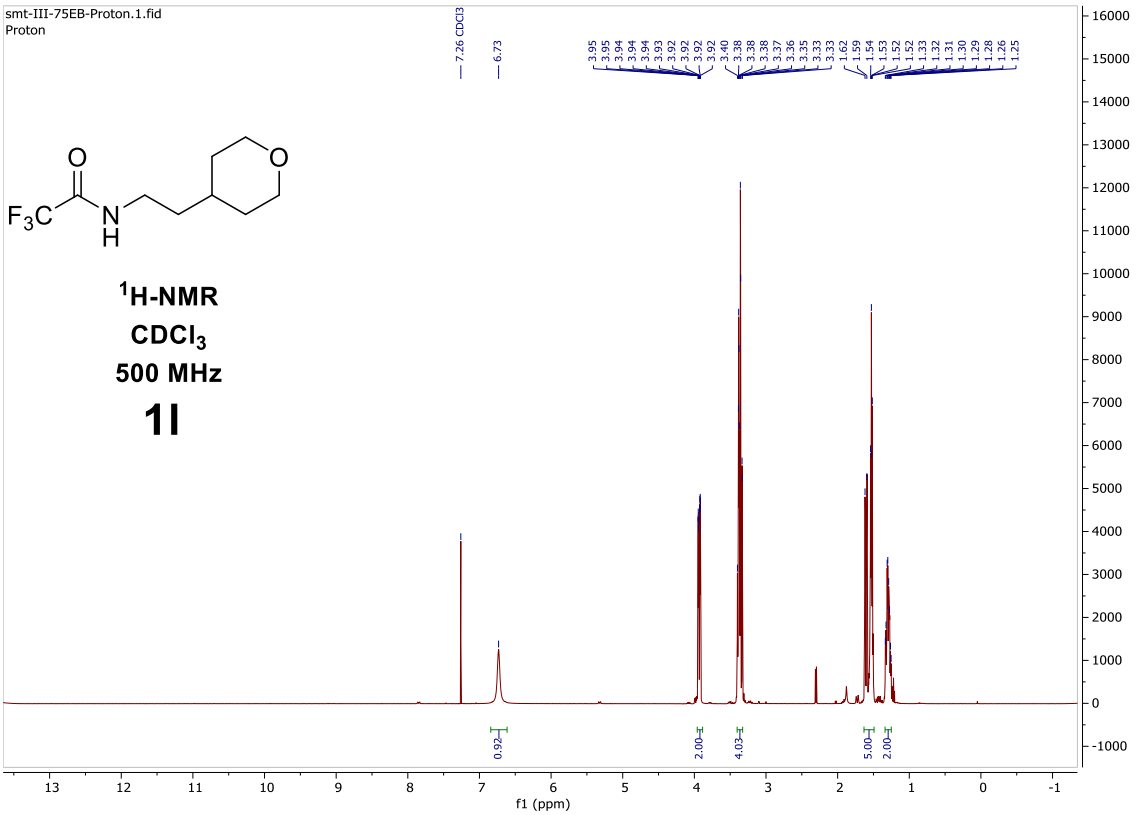

ST-339-4-24.2.fid
158.03
157.67
157.30
156.94
143.67
136.96
129.91
127.18
120.34
117.48
114.62
111.76
77.20 CDCl3
42.97
39.75
29.41
28.77
25.93
25.32
21.66
Me
^{13}C-NMR
CDCl$_3$
101 MHz
1j
f1 (ppm)

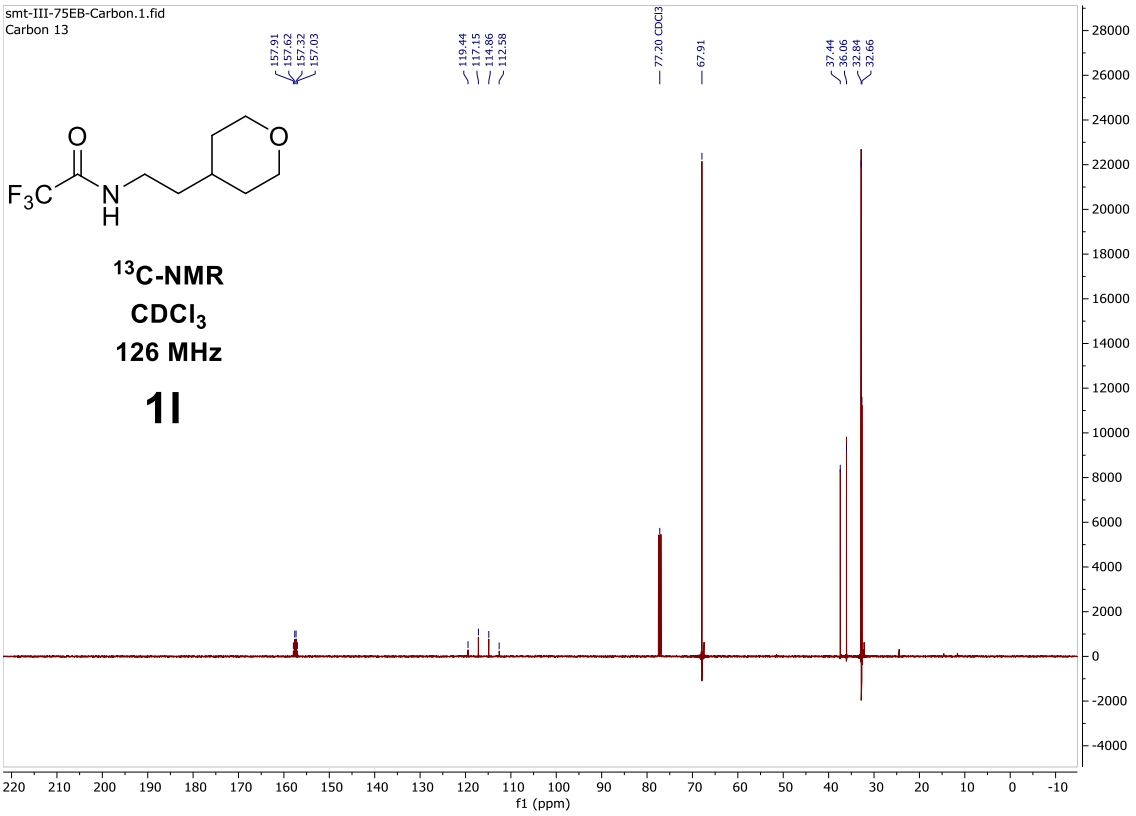

ST-339-1.2.fid
19F
-75.21
Me
^{19}F-NMR
CDCl$_3$
376 MHz
1j
f1 (ppm)

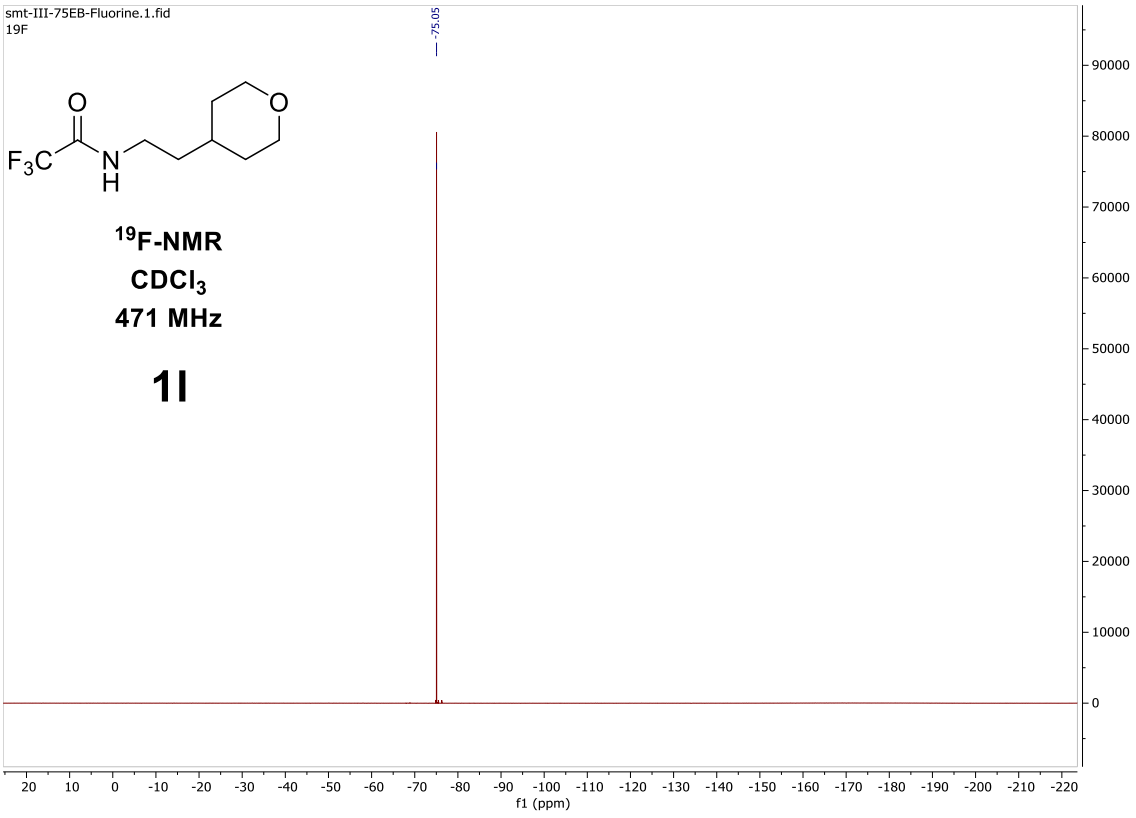

smt-III-75DA-Proton.1.fid
Proton
7.26 CDCl3
6.21
3.41
3.40
3.38
3.37
1.73
1.72
1.70
1.67
1.65
1.50
1.48
1.47
1.45
1.30
1.27
1.25
1.22
1.20
1.18
1.16
1.14
0.97
0.97
0.94
0.93
0.92
0.90
O
F3C
N
H
1H-NMR
CDCl3
500 MHz
1k
0.97
2.01
5.00
2.00
4.03
2.00
f1 (ppm)

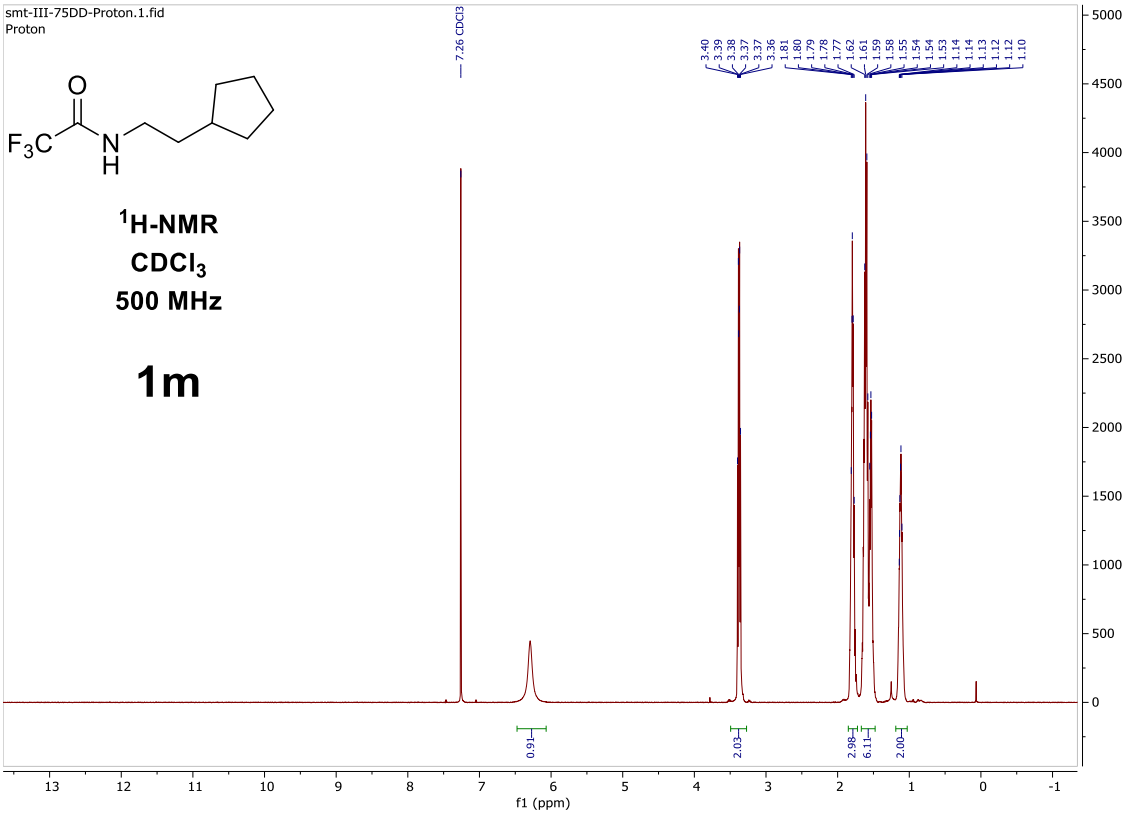

smt-III-75DA-Carbon.1.fid
Carbon 13
157.71
157.42
157.12
156.81
119.48
117.19
114.91
112.62
77.20 CDCl3
38.07
36.57
35.42
33.20
26.55
26.27
O
F3C
N
H
13C-NMR
CDCl3
126 MHz
1k
f1 (ppm)

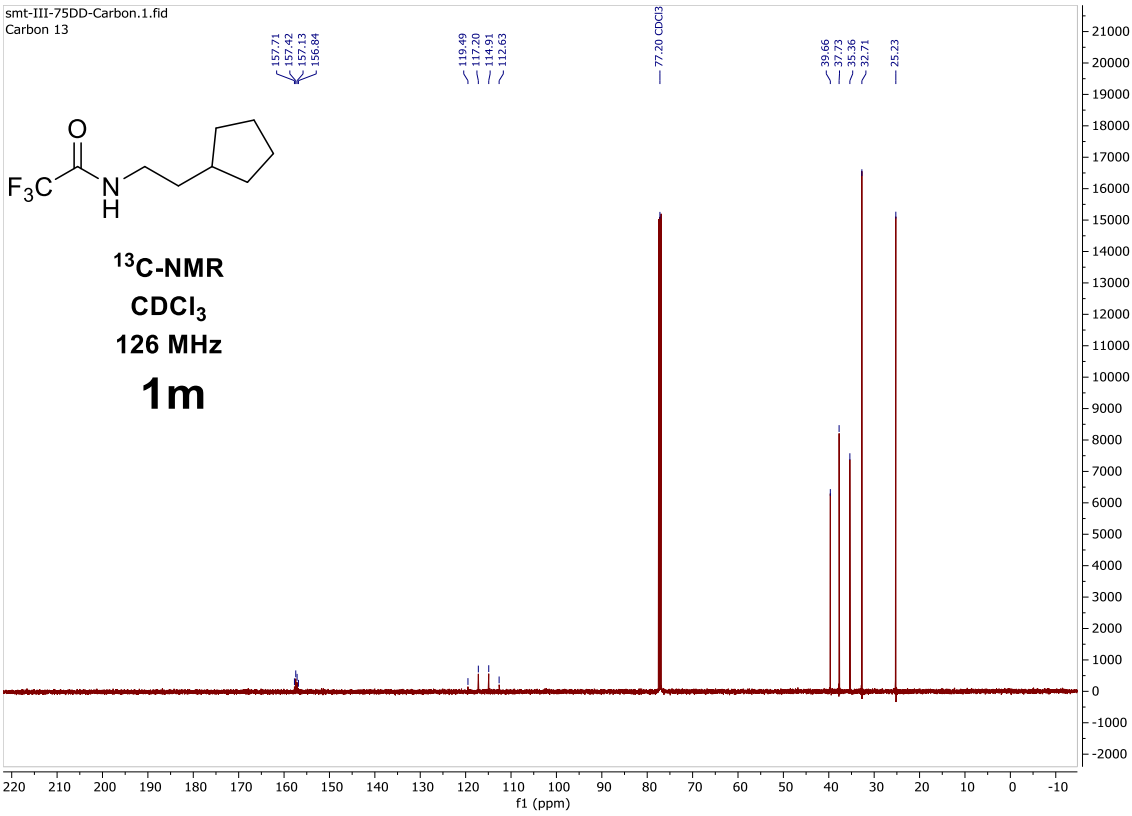

smt-III-75DA-Fluorine.1.fid
19F
-75.08
F3C
O
N
H
19F-NMR
CDCl3
471 MHz
1k
f1 (ppm)

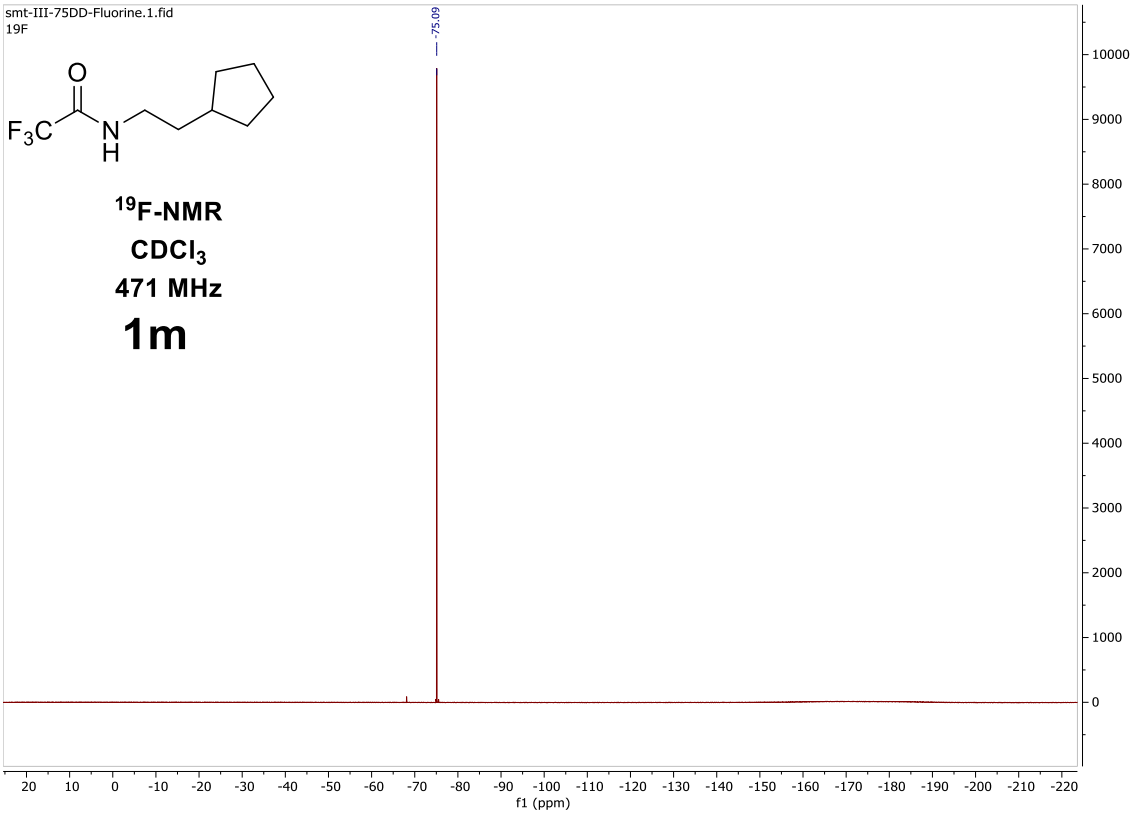

smt-III-75EB-Proton.1.fid
Proton
7.26 CDCl3
6.73
0.92
2.00
4.03
5.00
2.00
F3C
O
N
H
O
1H-NMR
CDCl3
500 MHz
1l
f1 (ppm)

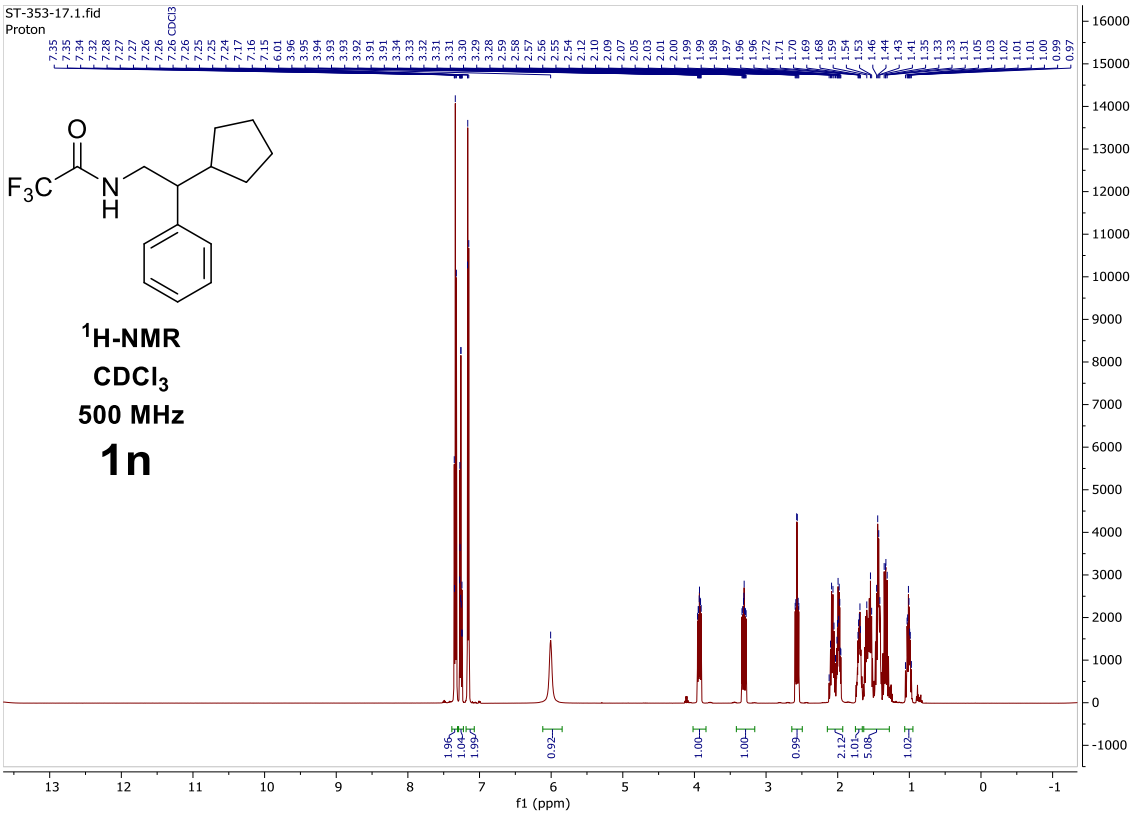

smt-III-75EB-Carbon.1.fid
Carbon 13
157.91
157.62
157.32
157.03
119.44
117.15
114.86
112.58
77.20 CDCl3
67.91
37.44
36.06
32.84
32.66
O
O
F3C
N
H
13C-NMR
CDCl3
126 MHz
1l
f1 (ppm)

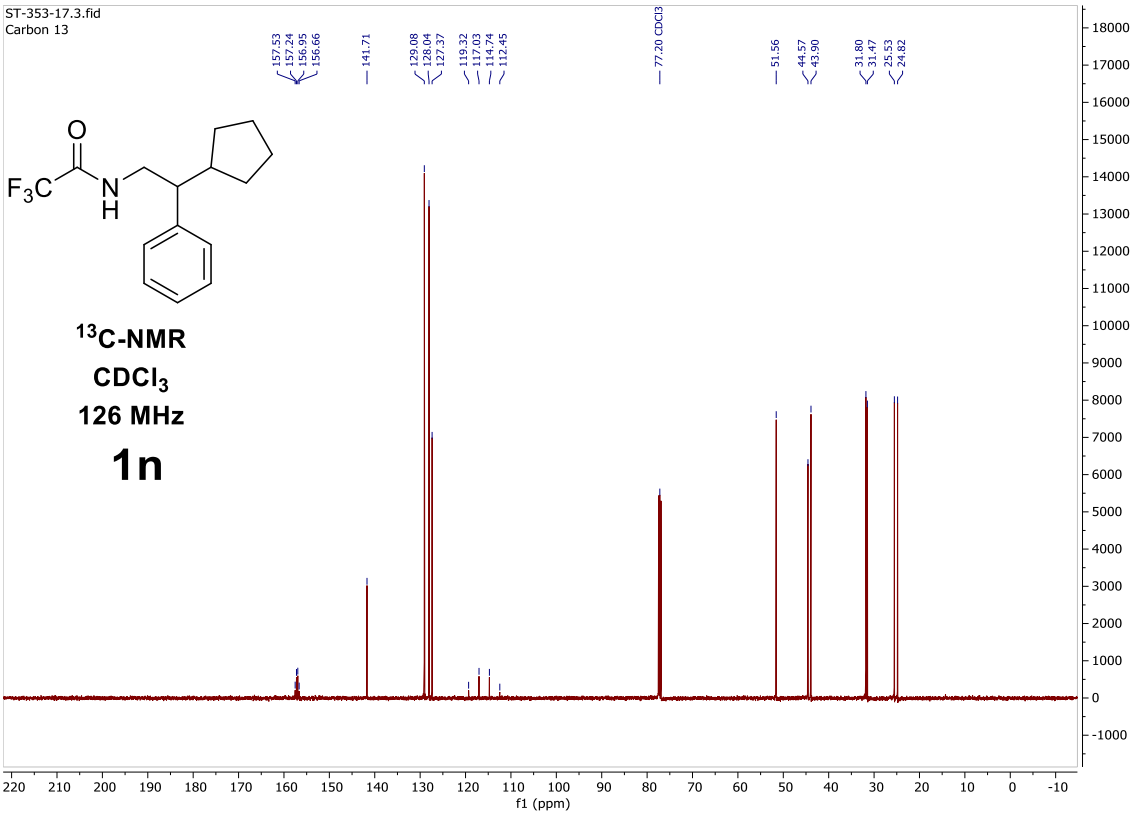

smt-III-75EB-Fluorine.1.fid
19F
-75.05
O
O
F3C
N
H
19F-NMR
CDCl3
471 MHz
1l
f1 (ppm)

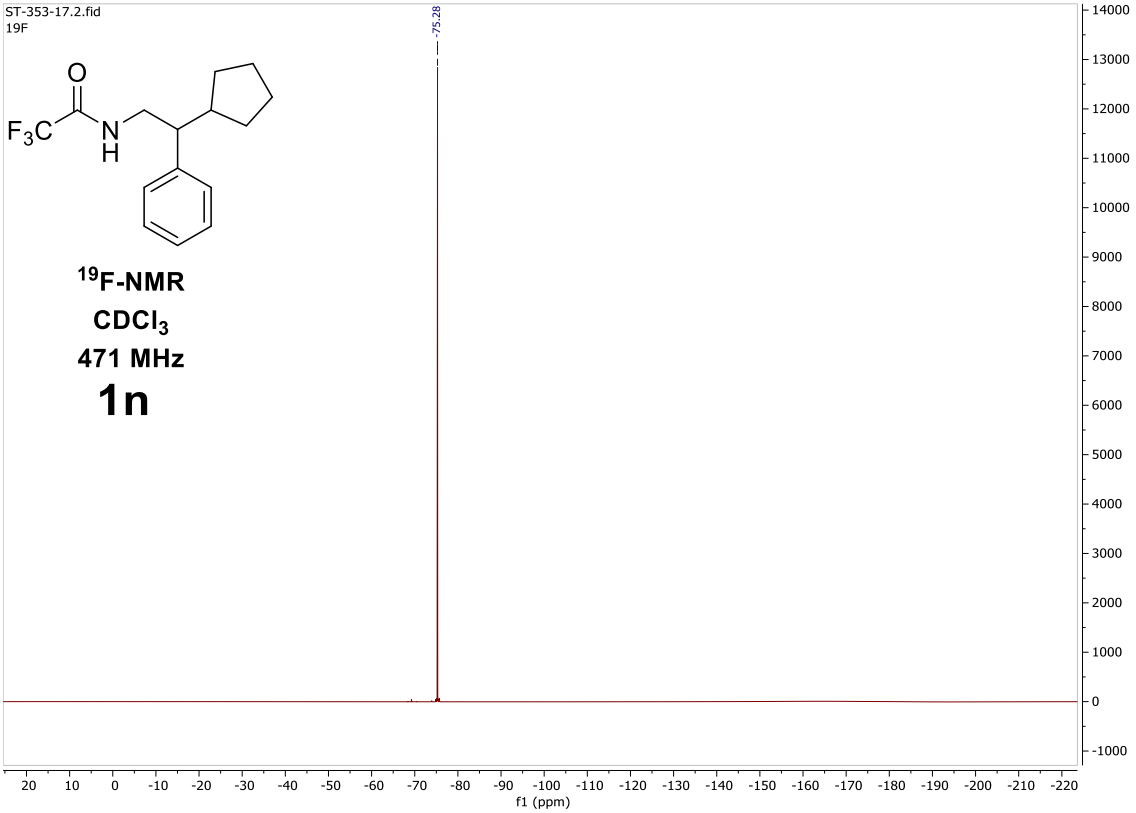

smt-III-75DD-Proton.1.fid
Proton
7.26 CDCl3
3.40
3.39
3.38
3.37
3.37
3.36
1.81
1.80
1.79
1.78
1.77
1.62
1.61
1.59
1.58
1.55
1.54
1.54
1.53
1.14
1.14
1.13
1.12
1.12
1.10
0.91
2.03
2.98
6.11
2.00
f1 (ppm)
1H-NMR
CDCl3
500 MHz
1m

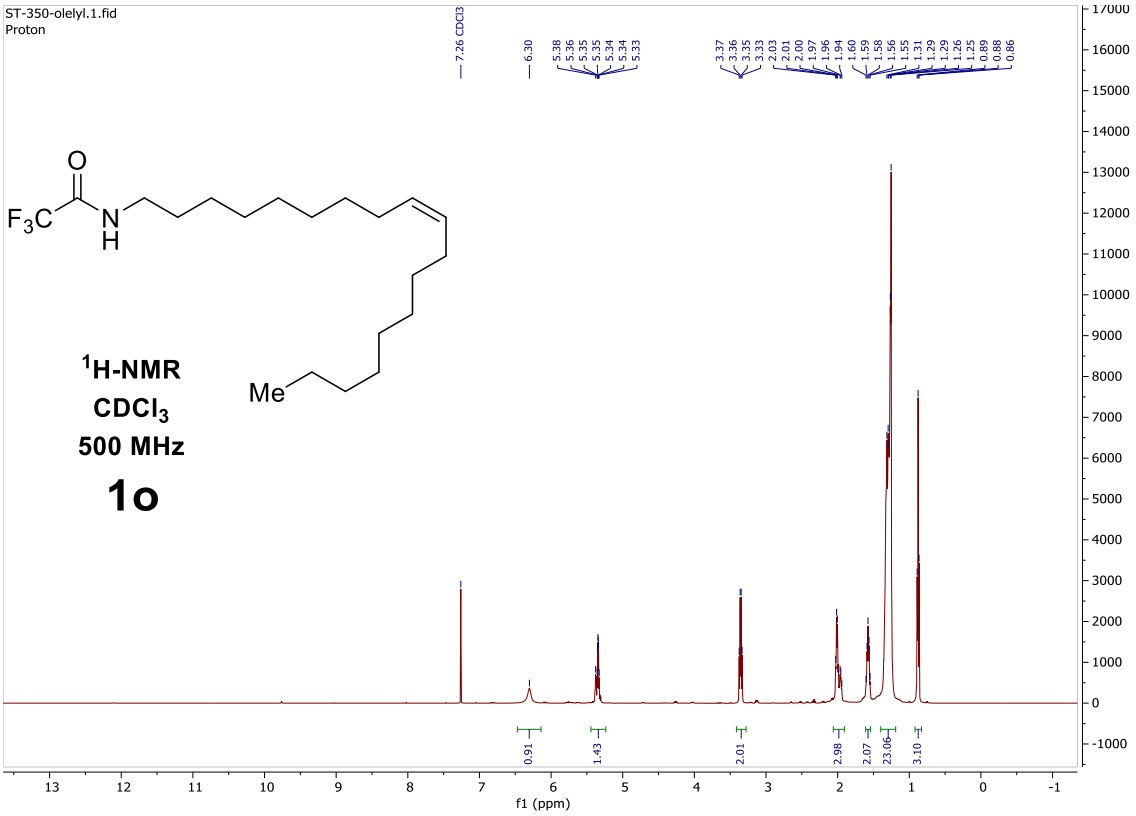

smt-III-75DD-Carbon.1.fid
Carbon 13
157.71
157.42
157.13
156.84
119.49
117.20
114.91
112.63
77.20 CDCl3
39.66
37.73
35.36
32.71
25.23
f1 (ppm)
13C-NMR
CDCl3
126 MHz
1m

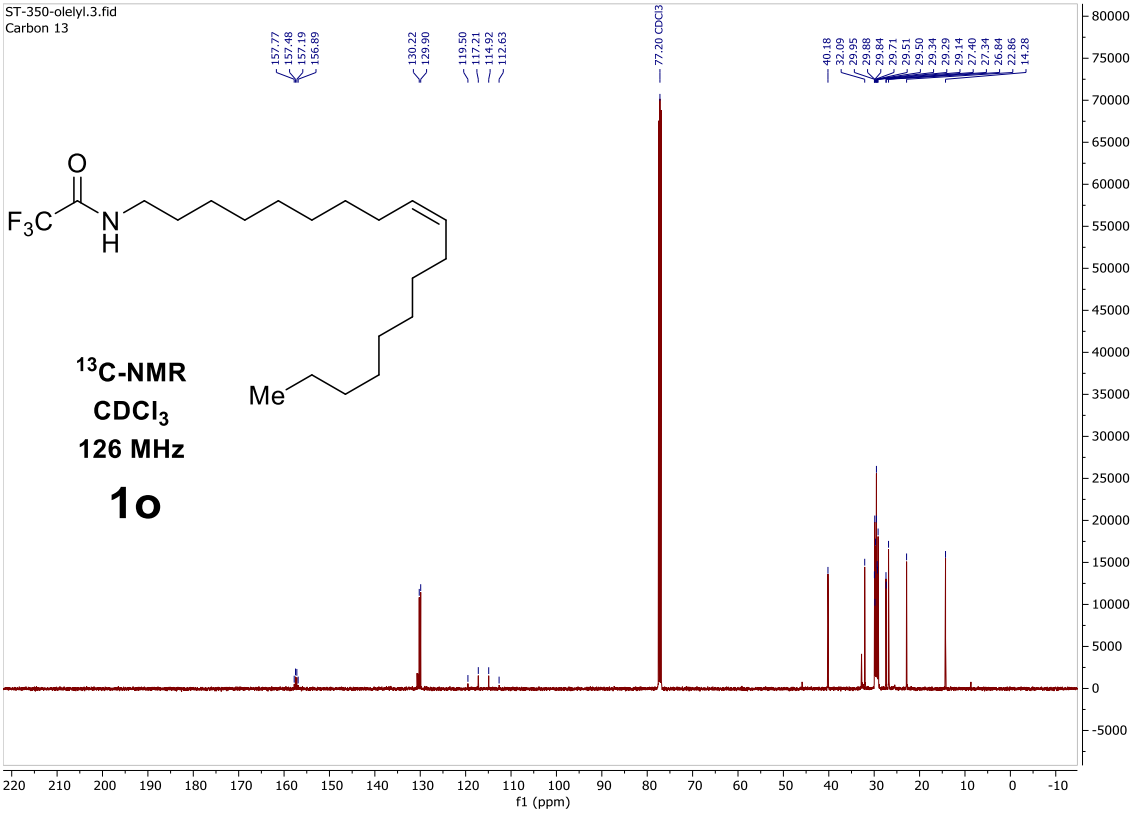

smt-III-75DD-Fluorine.1.fid
19F
-75.09
O
F3C
N
H
19F-NMR
CDCl3
471 MHz
1m
f1 (ppm)

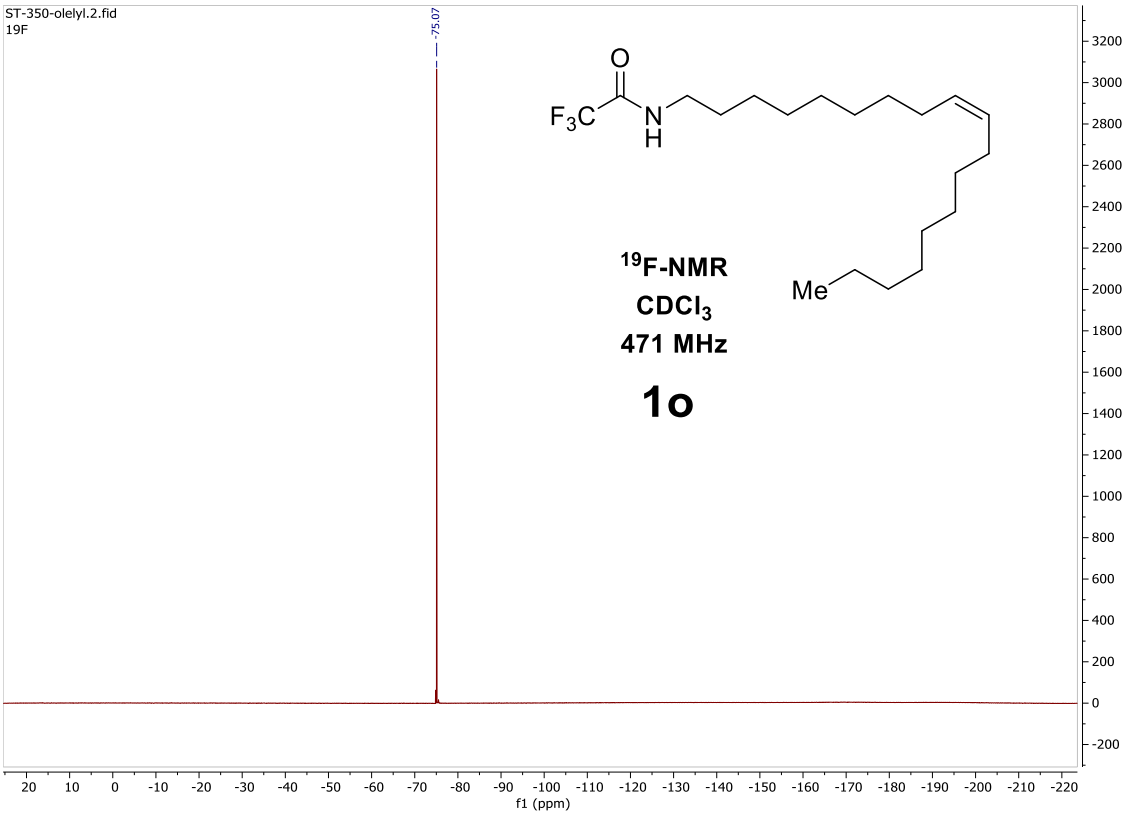

ST-353-17.1.fid
Proton
CDCl3
O
F3C
N
H
1H-NMR
CDCl3
500 MHz
1n
1.96
1.04
1.99
0.92
1.00
1.00
0.99
2.12
1.01
5.08
1.02
f1 (ppm)

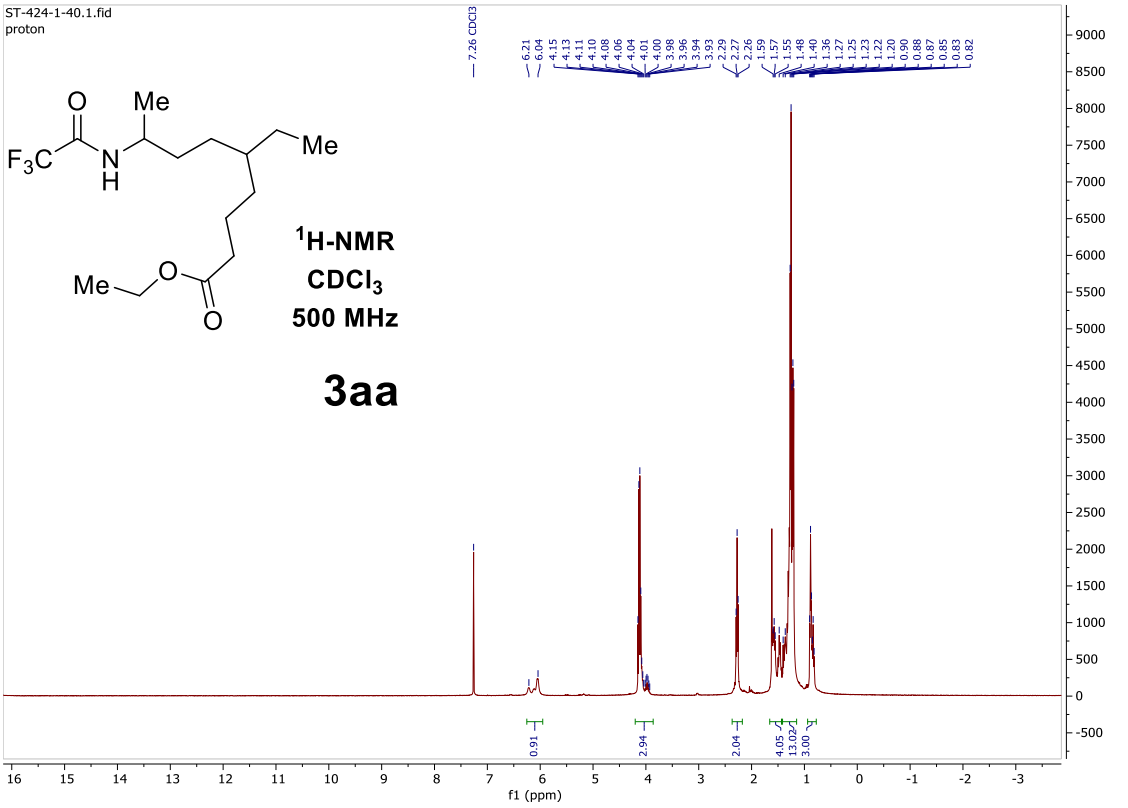

ST-353-17.3.fid
Carbon 13
157.53
157.24
156.95
156.66
141.71
129.08
128.84
127.37
119.32
117.03
114.74
112.45
77.20 CDCl3
51.56
44.57
43.90
31.80
31.47
25.53
24.82
O
F3C
N
H
13C-NMR
CDCl3
126 MHz
1n
f1 (ppm)

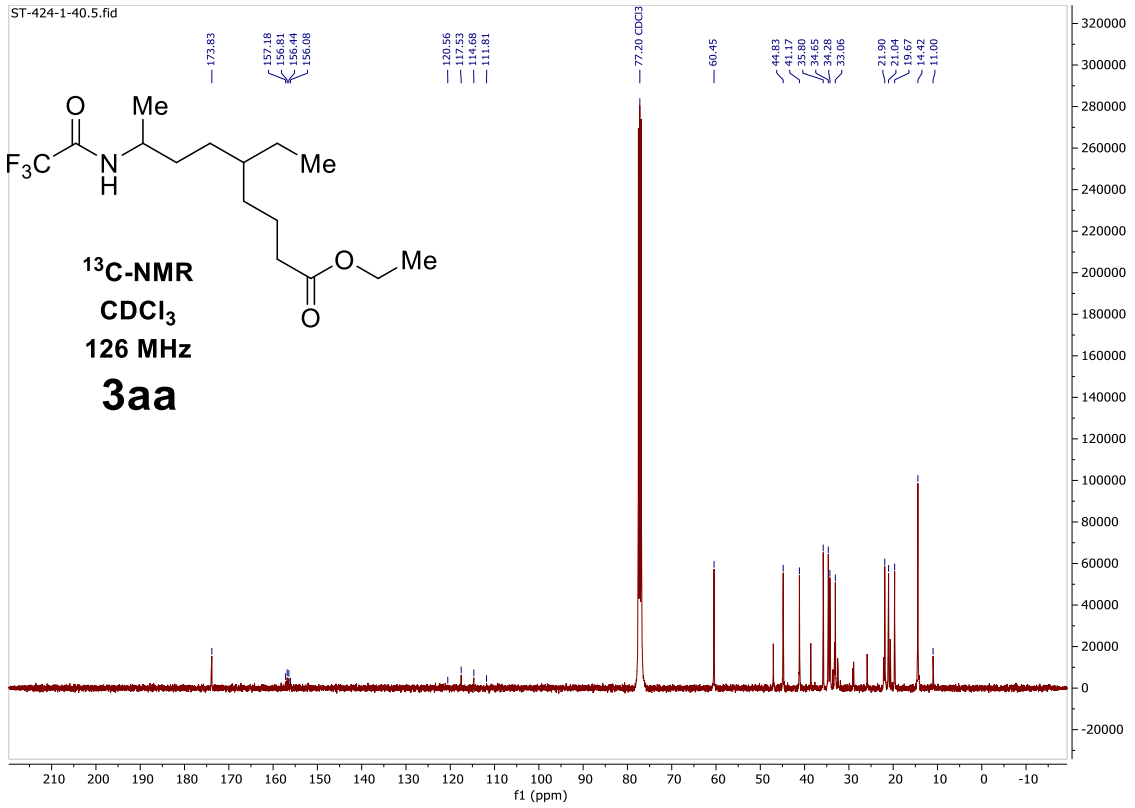

ST-353-17.2.fid
19F
-75.28
O
F3C
N
H
19F-NMR
CDCl3
471 MHz
1n
f1 (ppm)

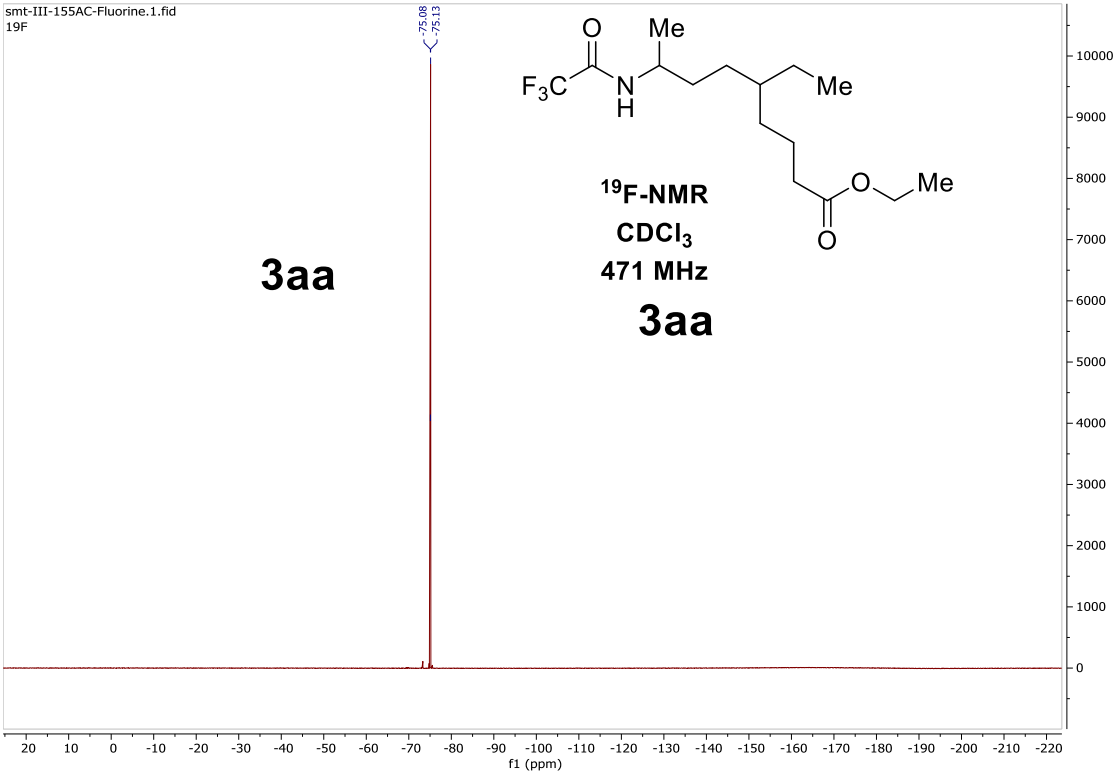

ST-350-olelyl.1.fid
Proton
7.26 CDCl3
6.30
5.38
5.36
5.35
5.35
5.34
5.34
5.33
3.37
3.36
3.35
3.33
2.03
2.01
2.00
1.97
1.96
1.94
1.60
1.59
1.58
1.56
1.55
1.31
1.29
1.29
1.26
1.25
0.89
0.88
0.86
O
F3C
N
H
Me
1H-NMR
CDCl3
500 MHz
1o
0.91
1.43
2.01
2.98
2.07
23.06
3.10
f1 (ppm)

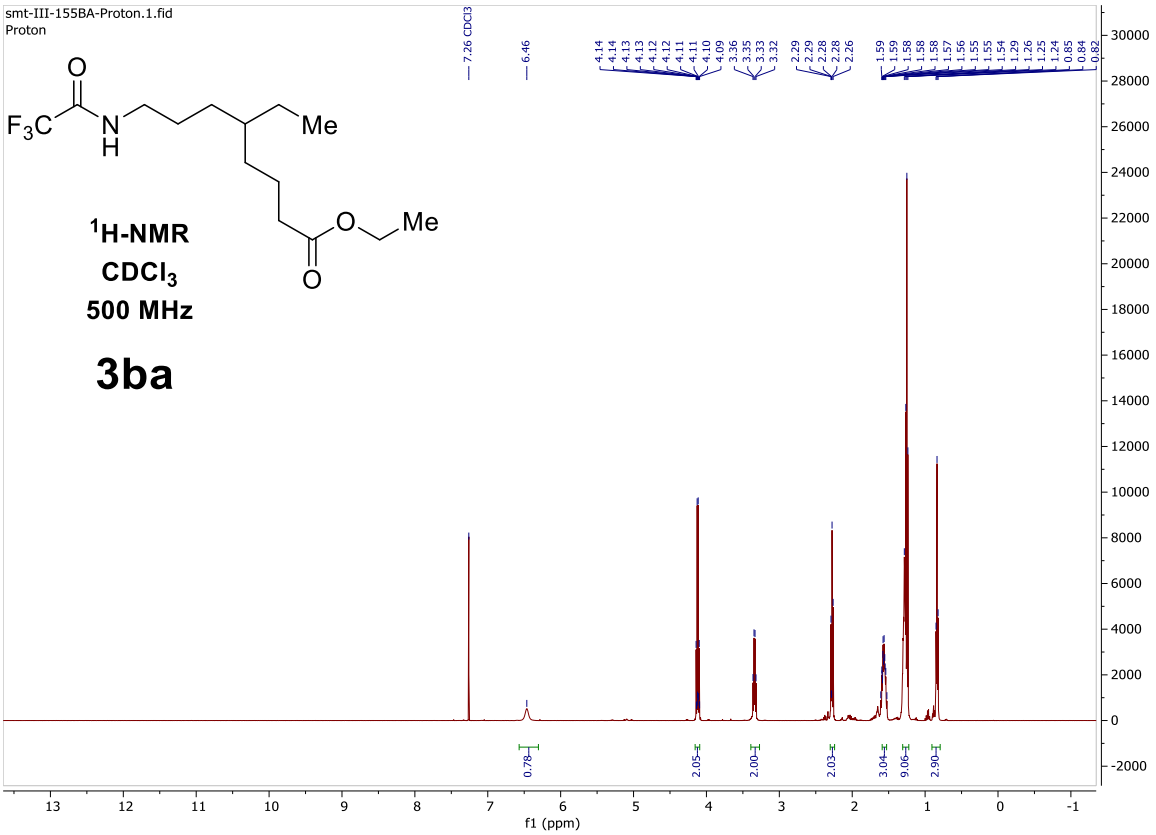

ST-350-olelyl.3.fid
Carbon 13
157.77
157.48
157.19
156.89
130.22
129.90
119.50
117.21
114.92
112.63
77.20 CDCl3
40.18
32.09
29.95
29.88
29.84
29.71
29.51
29.50
29.34
29.29
29.14
27.40
27.34
26.84
22.86
14.28
O
F3C
N
H
Me
13C-NMR
CDCl3
126 MHz
1o
f1 (ppm)

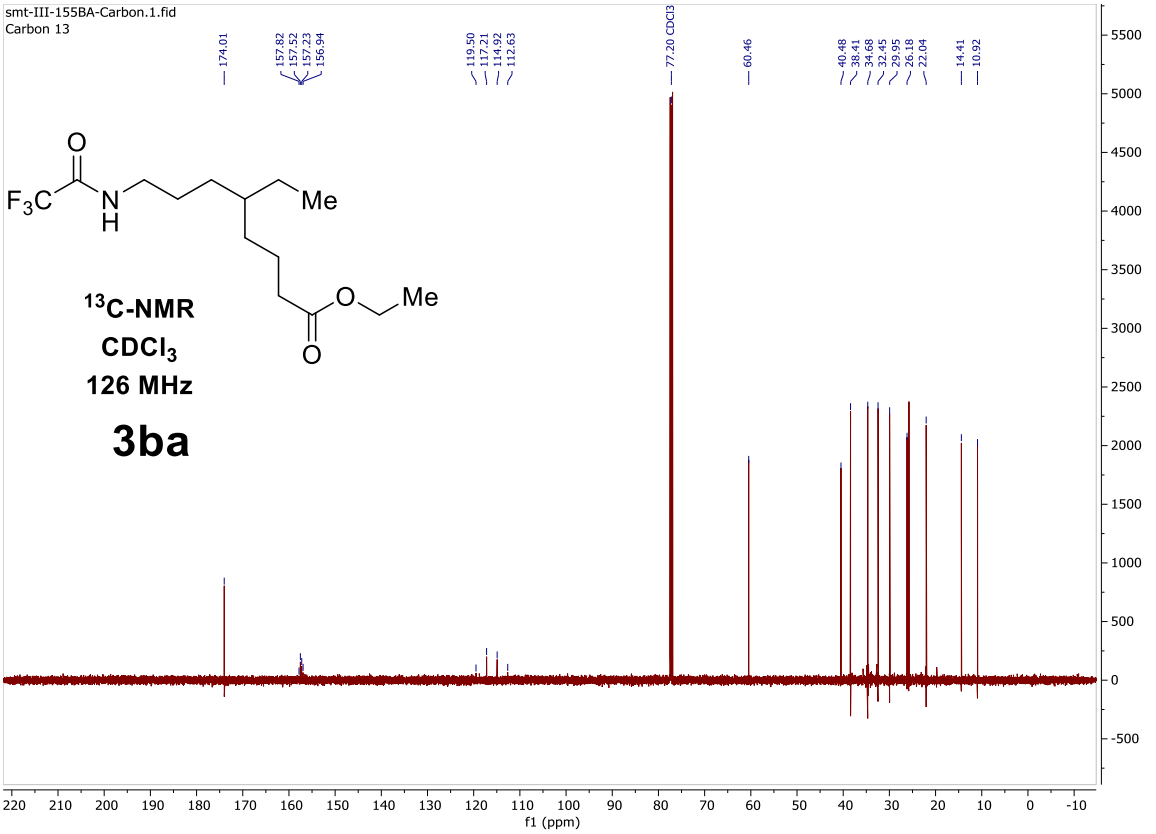

ST-350-olelyl.2.fid
19F
-75.07
O
F3C
N
H
Me
19F-NMR
CDCl3
471 MHz
1o
f1 (ppm)

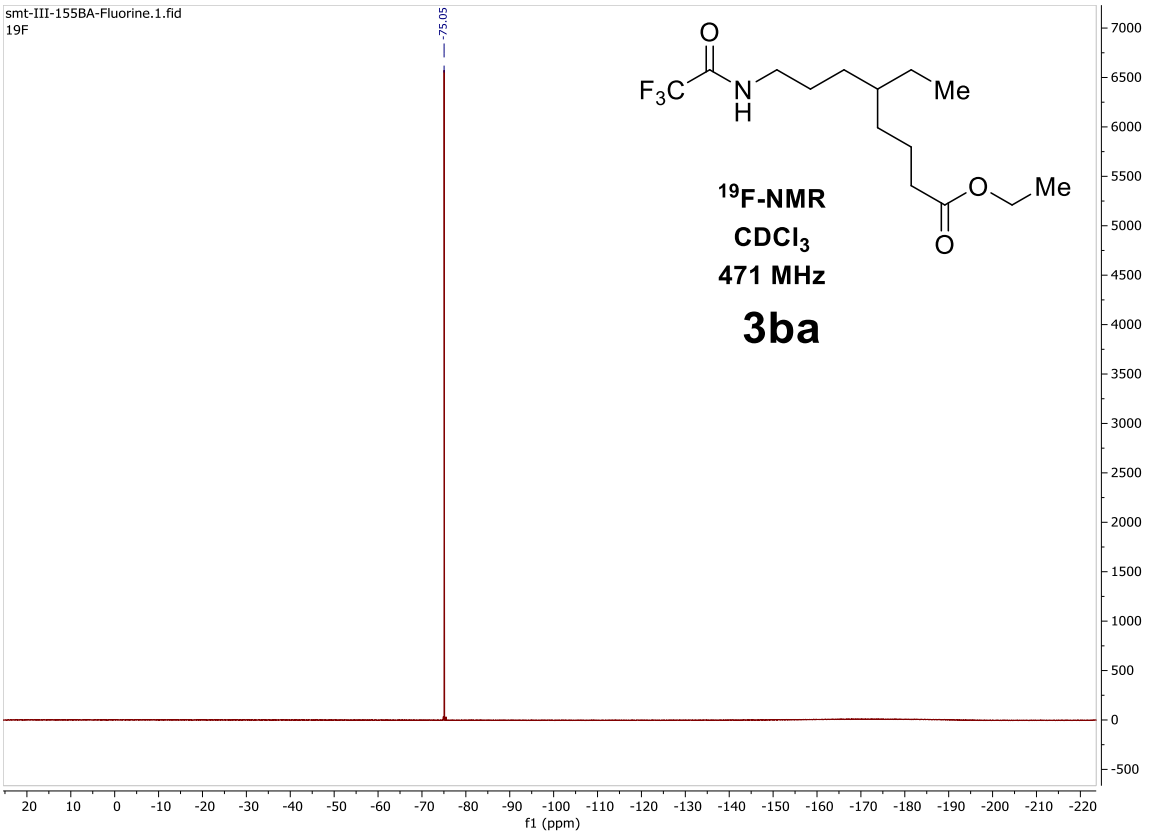

ST-424-1-40.1.fid
proton
7.26 CDCl3
O
Me
F3C
N
H
Me
Me
O
O
1H-NMR
CDCl3
500 MHz
3aa
0.91
2.94
2.04
4.05
13.02
3.00
f1 (ppm)

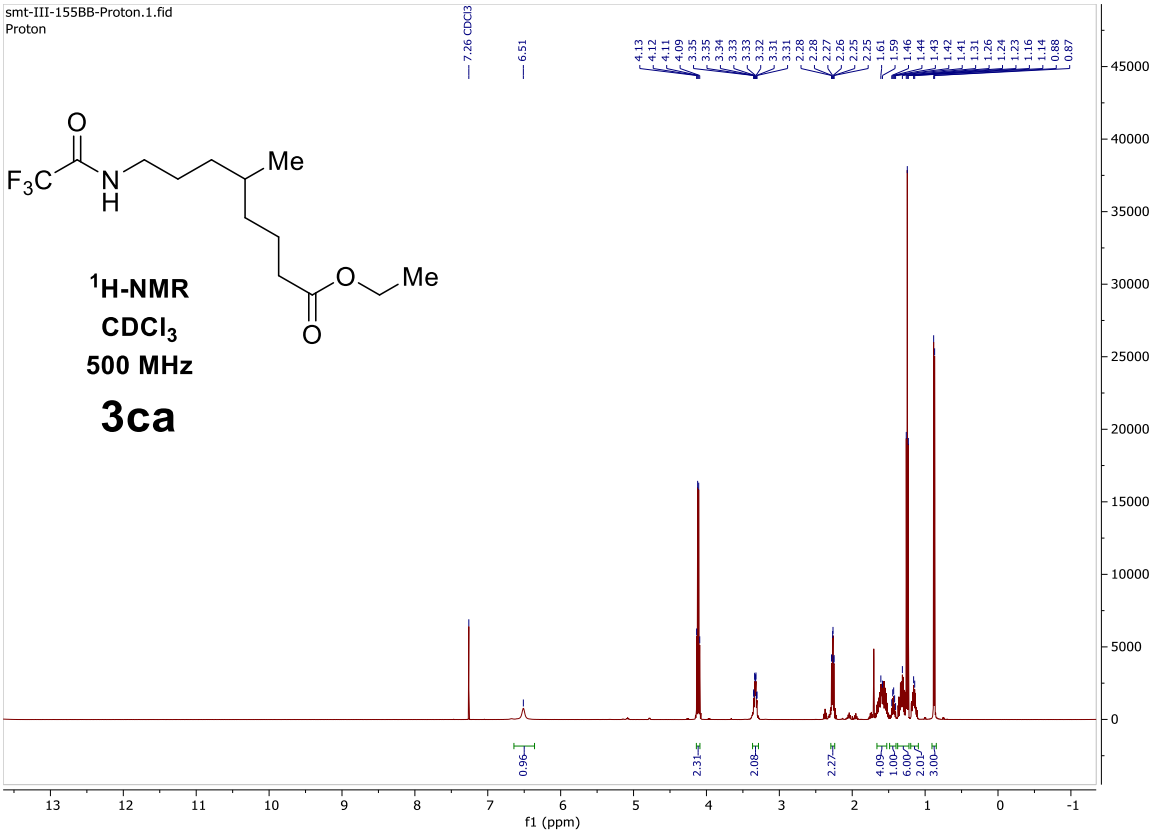

ST-424-1-40.5.fid
173.83
157.18
156.81
156.44
156.08
120.56
117.53
114.68
111.81
77.20 CDCl3
60.45
44.83
41.17
35.80
34.65
34.28
33.06
21.90
21.04
19.67
14.42
11.00
F3C
O
N
H
Me
Me
O
Me
O
13C-NMR
CDCl3
126 MHz
3aa
f1 (ppm)

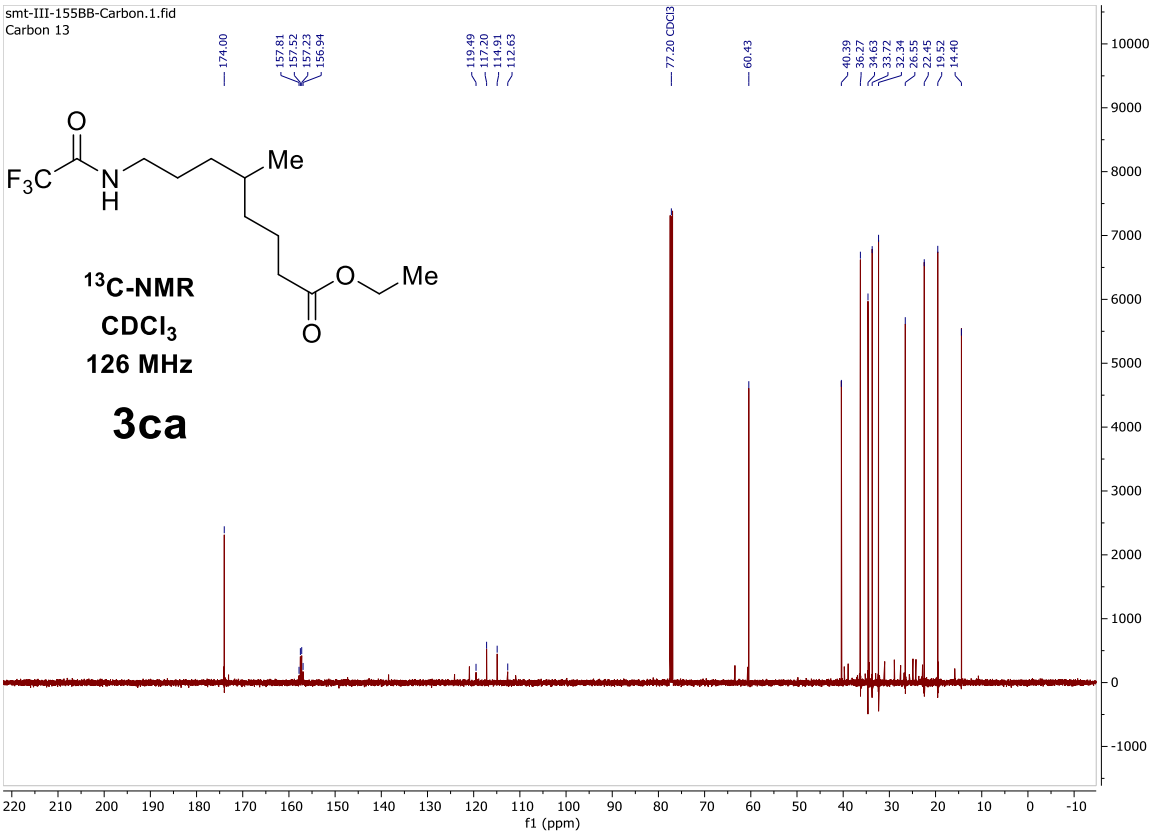

smt-III-155AC-Fluorine.1.fid
19F
-75.08
-75.13
F3C
O
N
H
Me
Me
O
Me
O
19F-NMR
CDCl3
471 MHz
3aa
3aa
f1 (ppm)

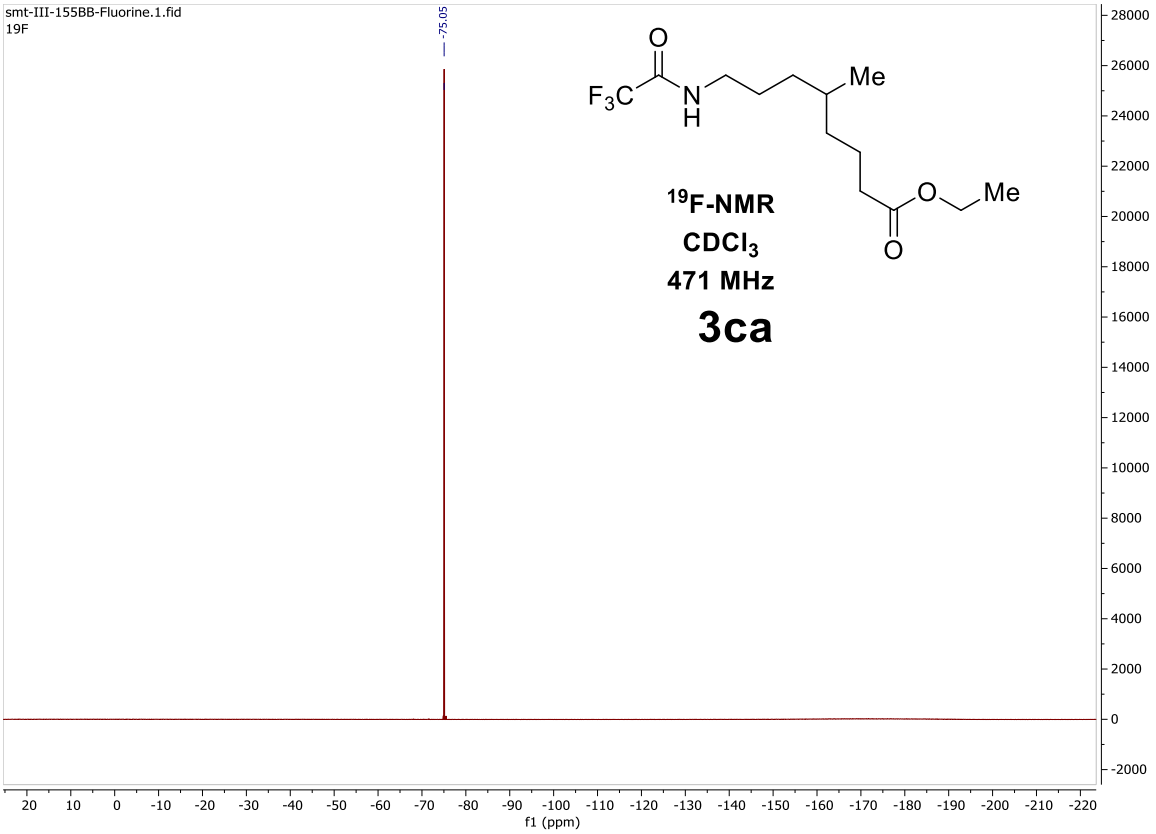

smt-III-155BA-Proton.1.fid
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3ba
f1 (ppm)

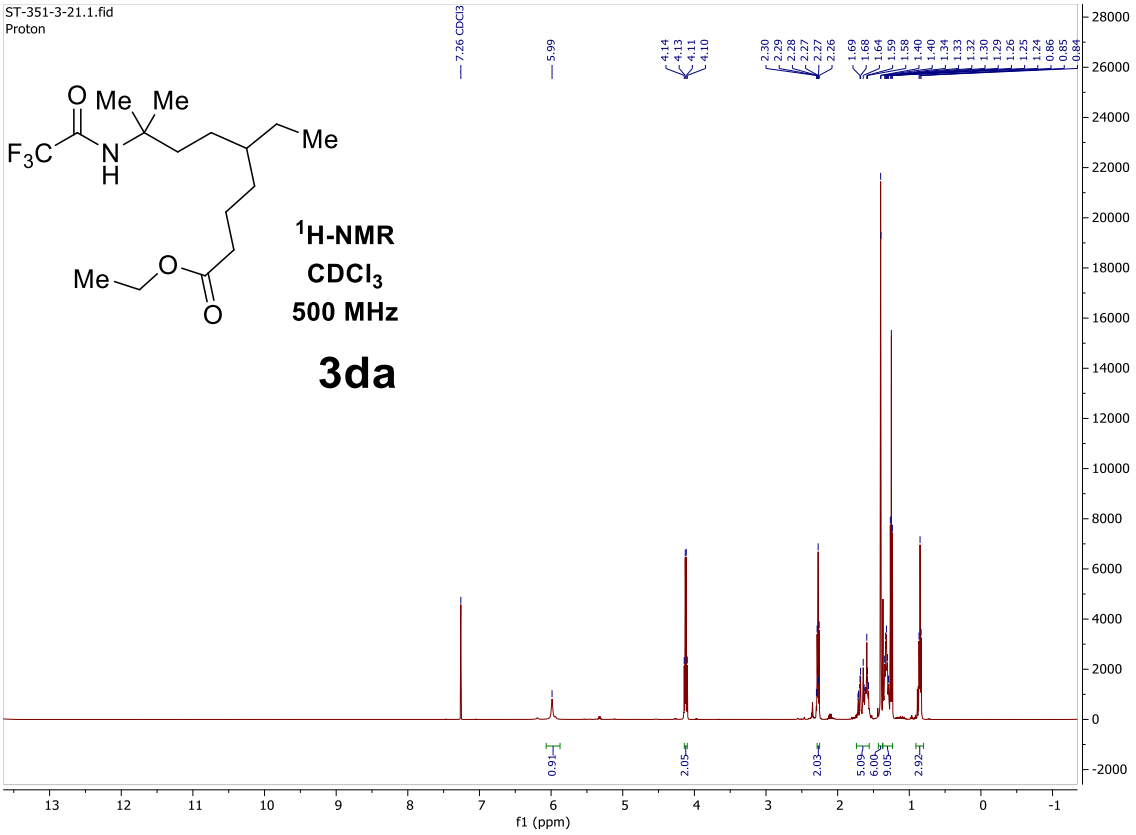

smt-III-155BA-Carbon.1.fid
Carbon 13
^{13}C-NMR
$CDCl_3$
126 MHz
3ba
f1 (ppm)

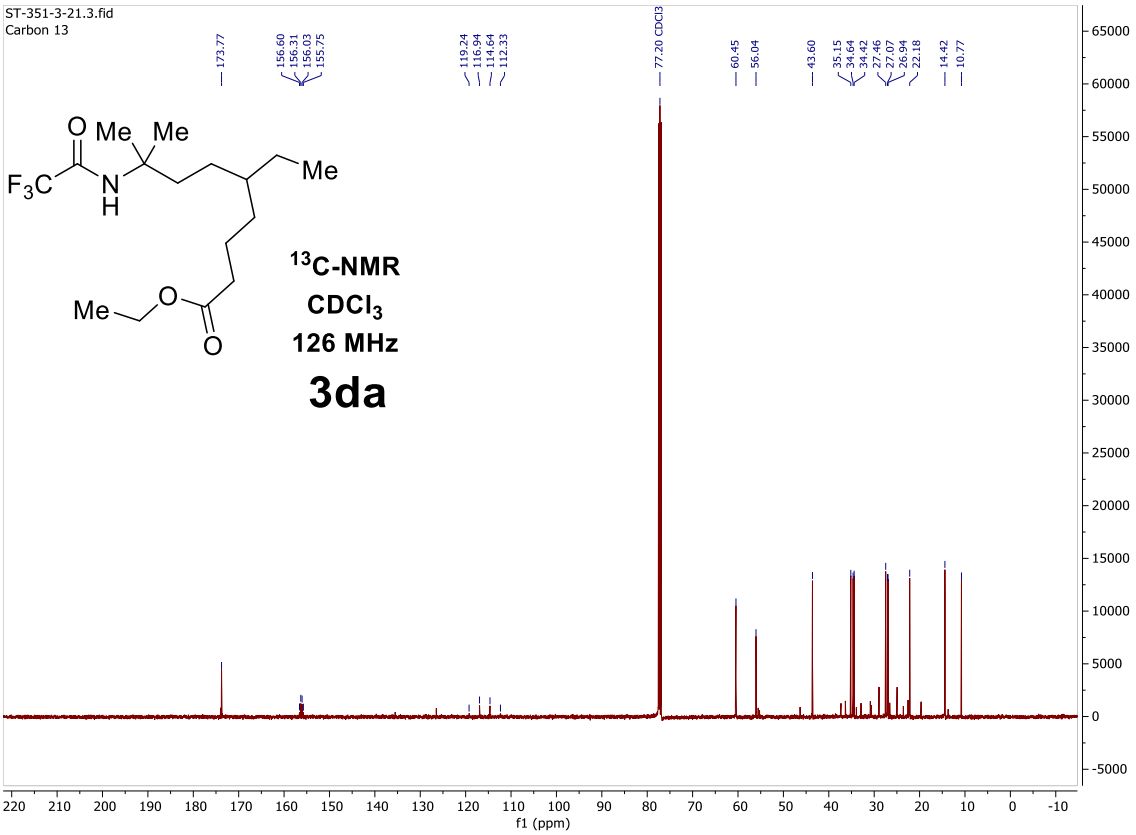

smt-III-155BA-Fluorine.1.fid
19F
-75.05
F3C
N
H
O
Me
O
Me
O
19F-NMR
CDCl3
471 MHz
3ba
f1 (ppm)

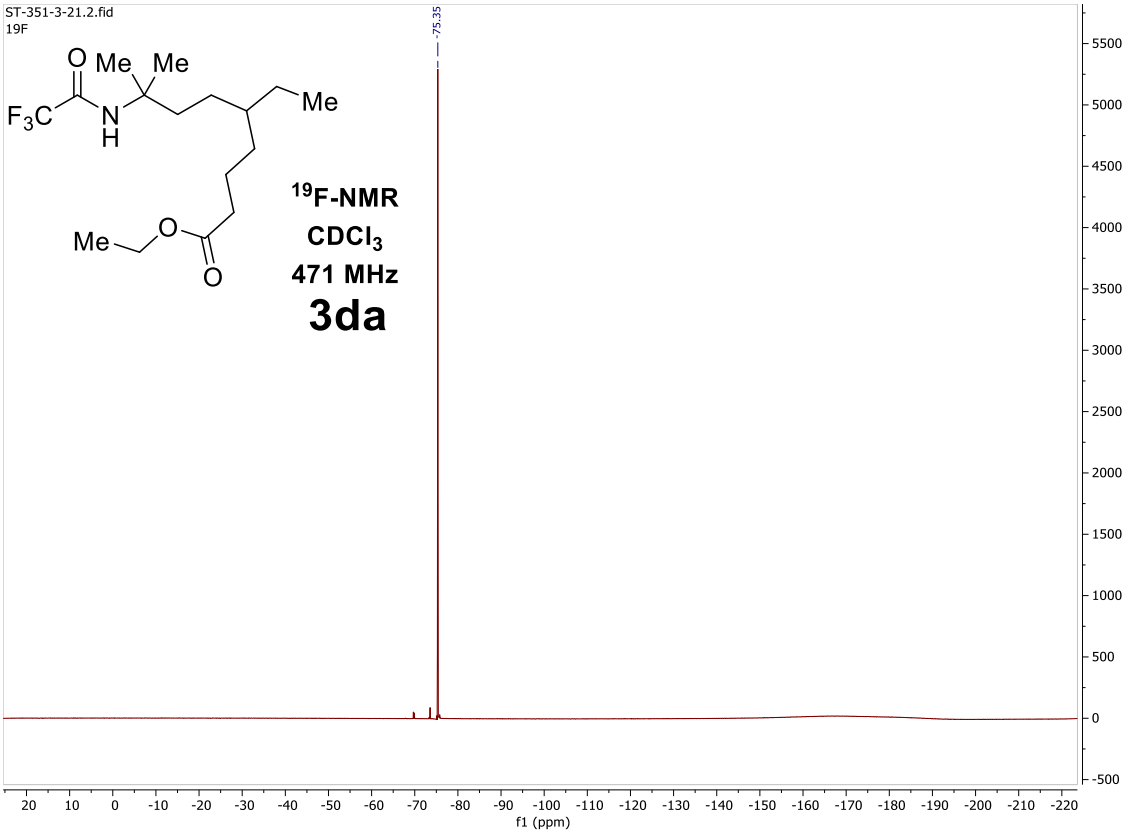

smt-III-155BB-Proton.1.fid
Proton
7.26 CDCl3
6.51
F3C
N
H
O
Me
O
Me
O
1H-NMR
CDCl3
500 MHz
3ca
0.96
2.31
2.08
2.27
4.09
1.00
6.00
2.01
3.00
f1 (ppm)

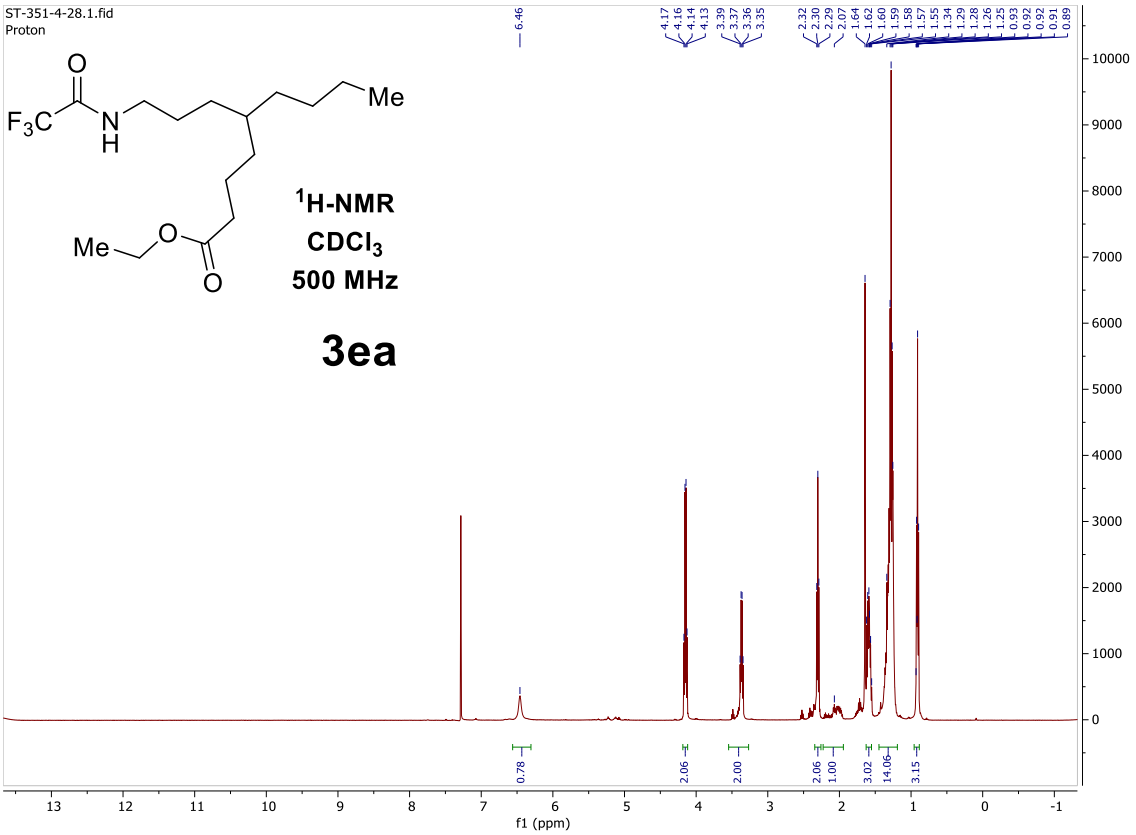

smt-III-155BB-Carbon.1.fid
Carbon 13
174.00
157.81
157.52
157.23
156.94
119.49
117.20
114.91
112.63
77.20 CDCl3
60.43
40.39
36.27
34.63
33.72
32.34
26.55
22.45
19.52
14.40
F3C
N
H
Me
O
Me
13C-NMR
CDCl3
126 MHz
3ca
f1 (ppm)

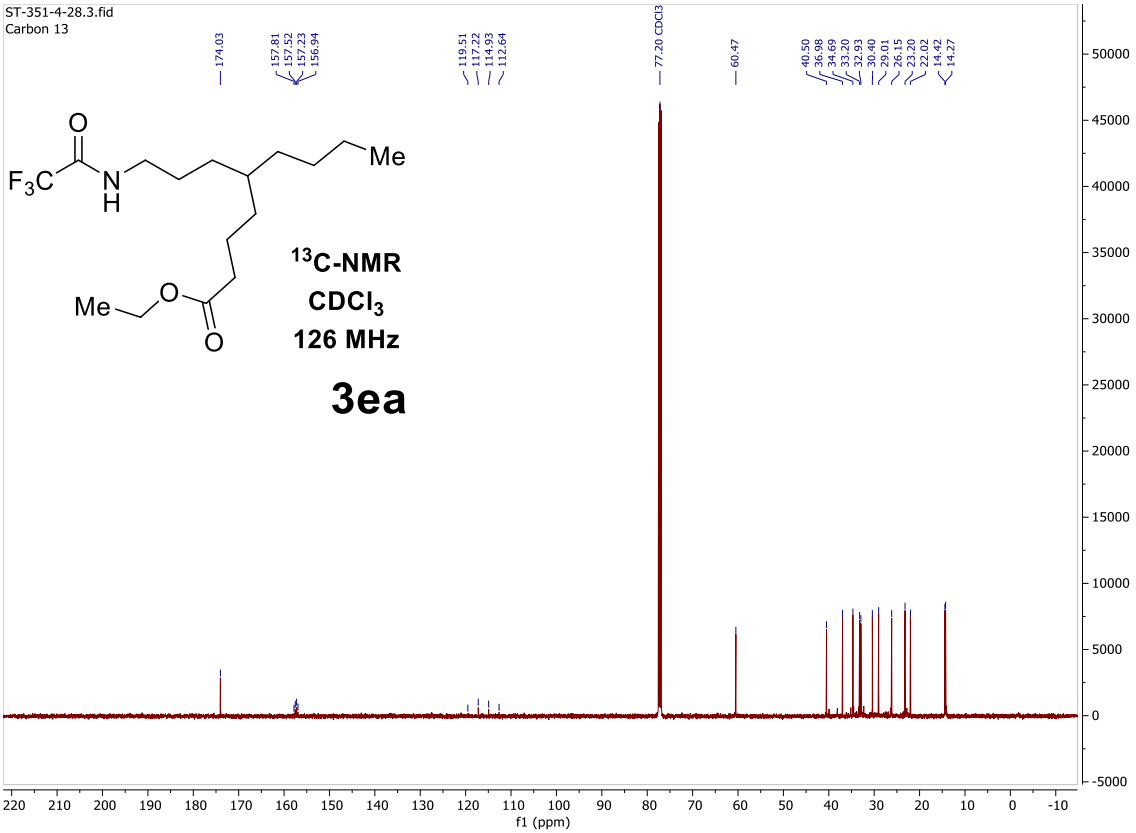

smt-III-155BB-Fluorine.1.fid
19F
-75.05
F3C
N
H
Me
O
Me
19F-NMR
CDCl3
471 MHz
3ca
f1 (ppm)

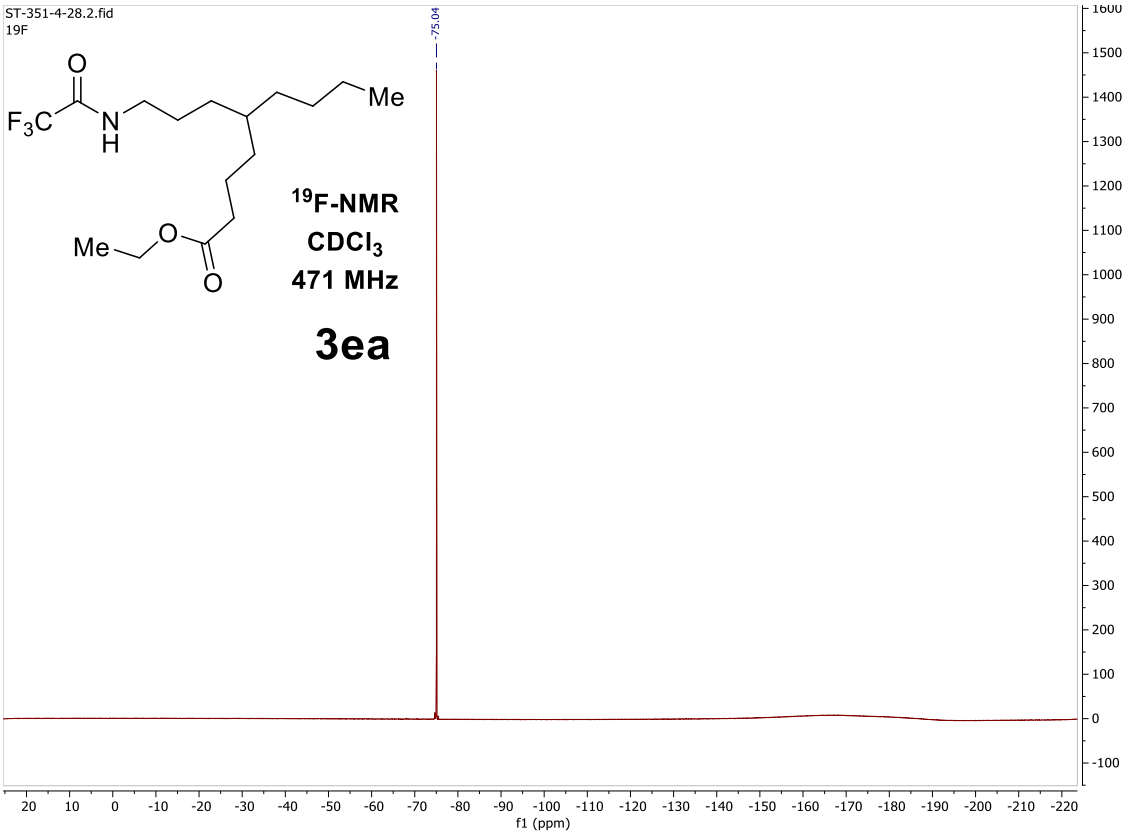

ST-351-3-21.1.fid
Proton
7.26 CDCl3
5.99
4.14
4.13
4.11
4.10
2.30
2.29
2.28
2.27
2.27
2.26
1.69
1.68
1.64
1.59
1.58
1.40
1.40
1.34
1.33
1.32
1.30
1.29
1.26
1.25
1.24
0.86
0.85
0.84
O
Me
Me
F3C
N
H
Me
Me
O
O
O
1H-NMR
CDCl3
500 MHz
3da
0.91
2.05
2.03
5.09
6.00
9.05
2.92
f1 (ppm)

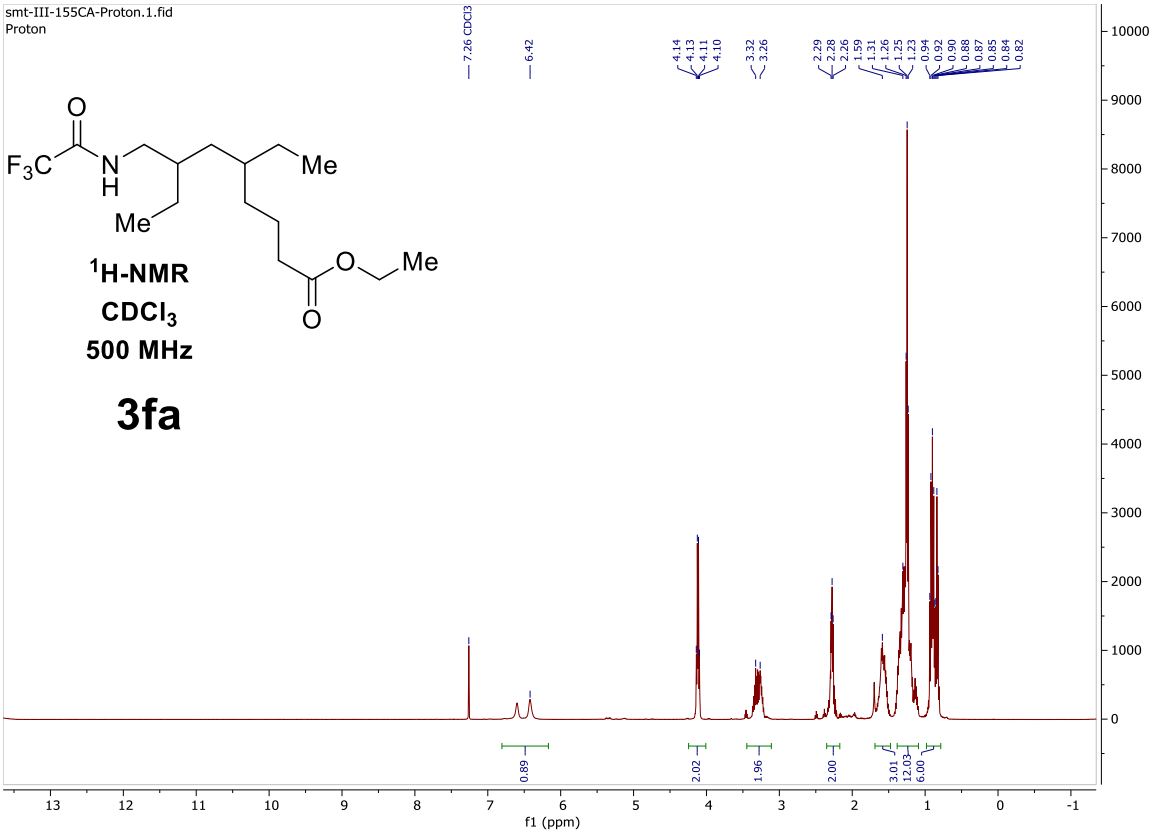

ST-351-3-21.3.fid
Carbon 13
173.77
156.60
156.31
156.03
155.75
119.24
116.94
114.64
112.33
77.20 CDCl3
60.45
56.04
43.60
35.15
34.64
34.42
27.46
27.07
26.94
22.18
14.42
10.77
13C-NMR
CDCl3
126 MHz
3da
f1 (ppm)

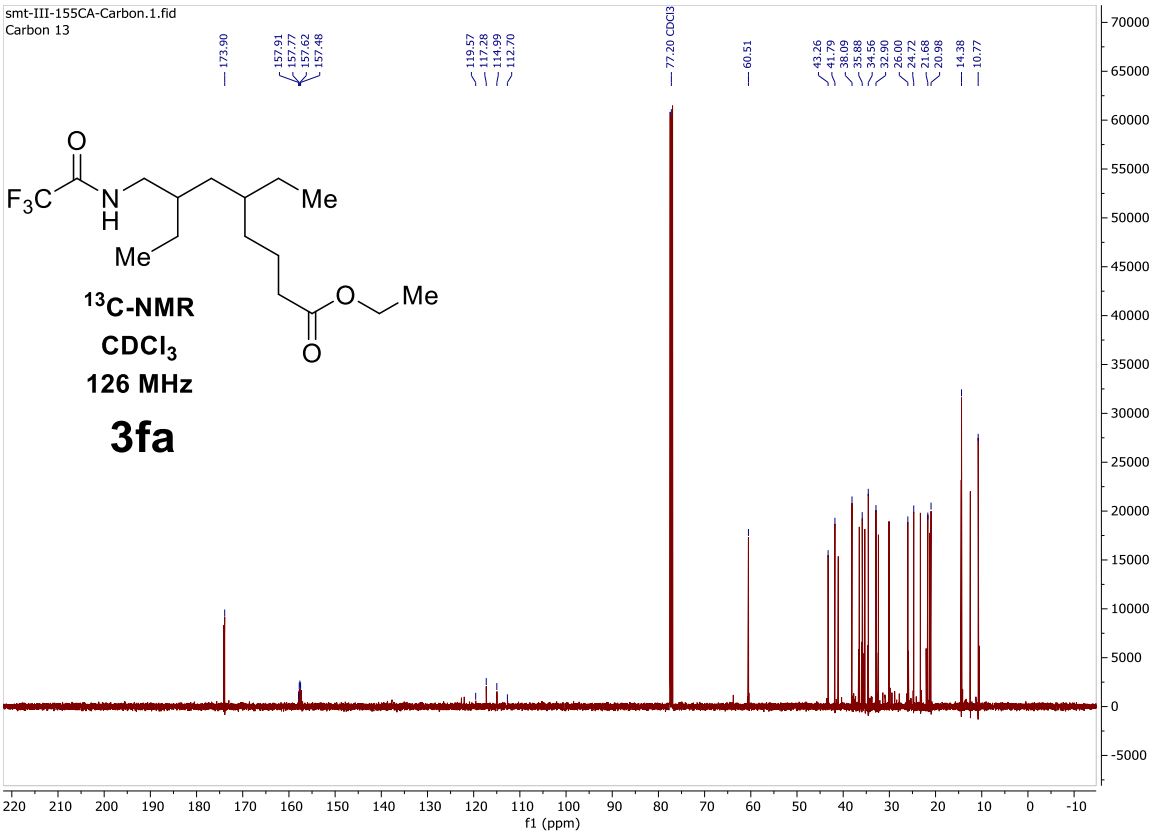

ST-351-3-21.2.fid
19F
-75.35
19F-NMR
CDCl3
471 MHz
3da
f1 (ppm)

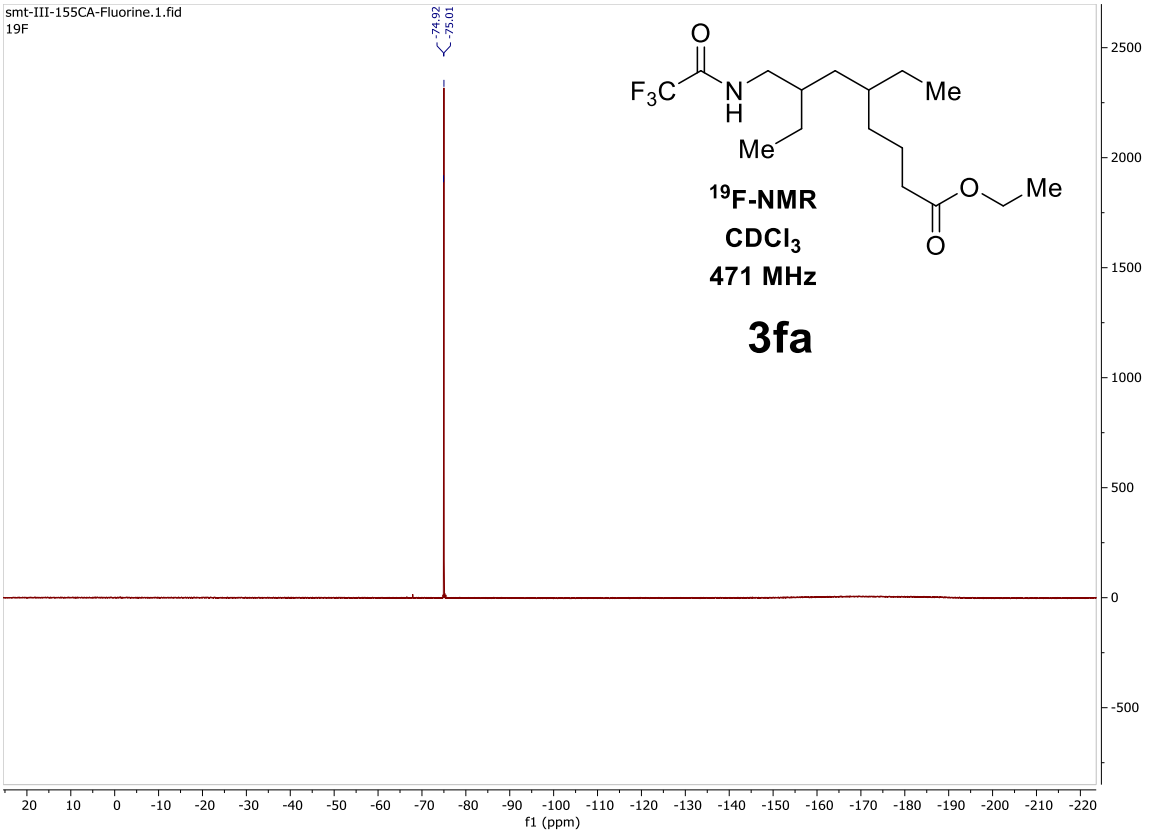

ST-351-4-28.1.fid
Proton
^{1}H-NMR
CDCl$_3$
500 MHz
3ea
f1 (ppm)

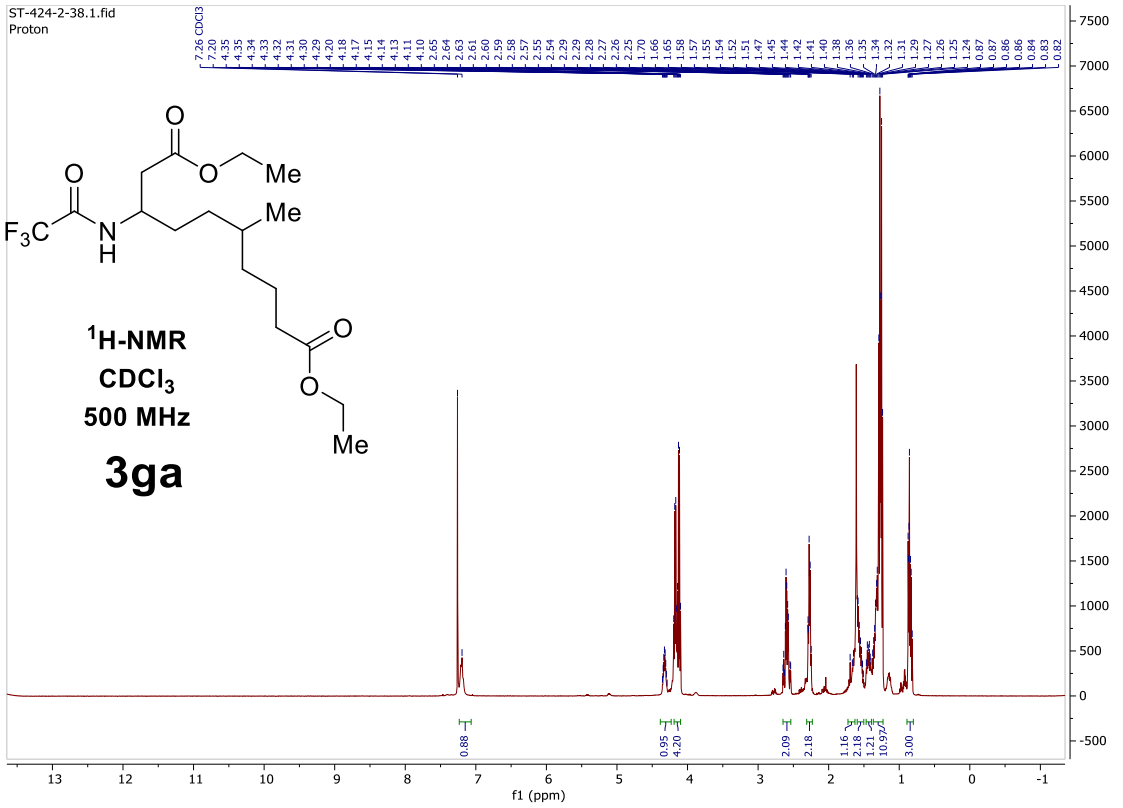

ST-351-4-28.3.fid
Carbon 13
^{13}C-NMR
CDCl$_3$
126 MHz
3ea
f1 (ppm)

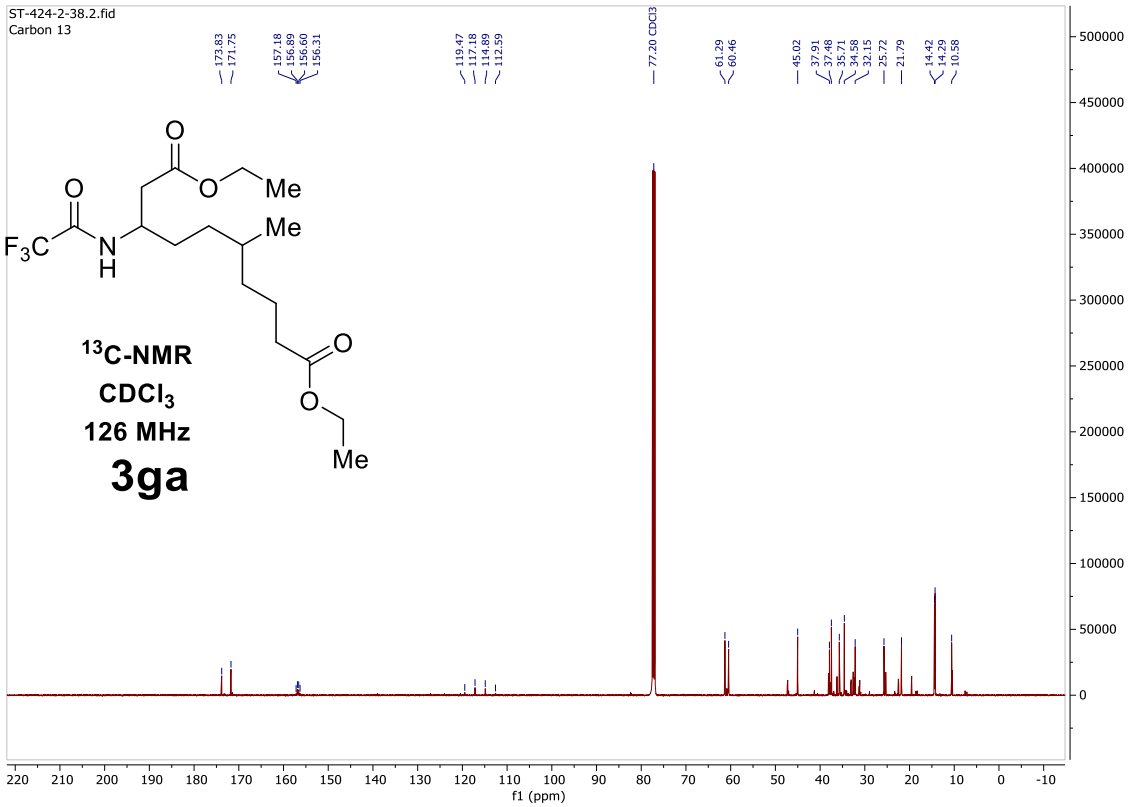

ST-351-4-28.2.fid
19F
-75.04
^{19}F-NMR
$CDCl_3$
471 MHz
3ea
f1 (ppm)

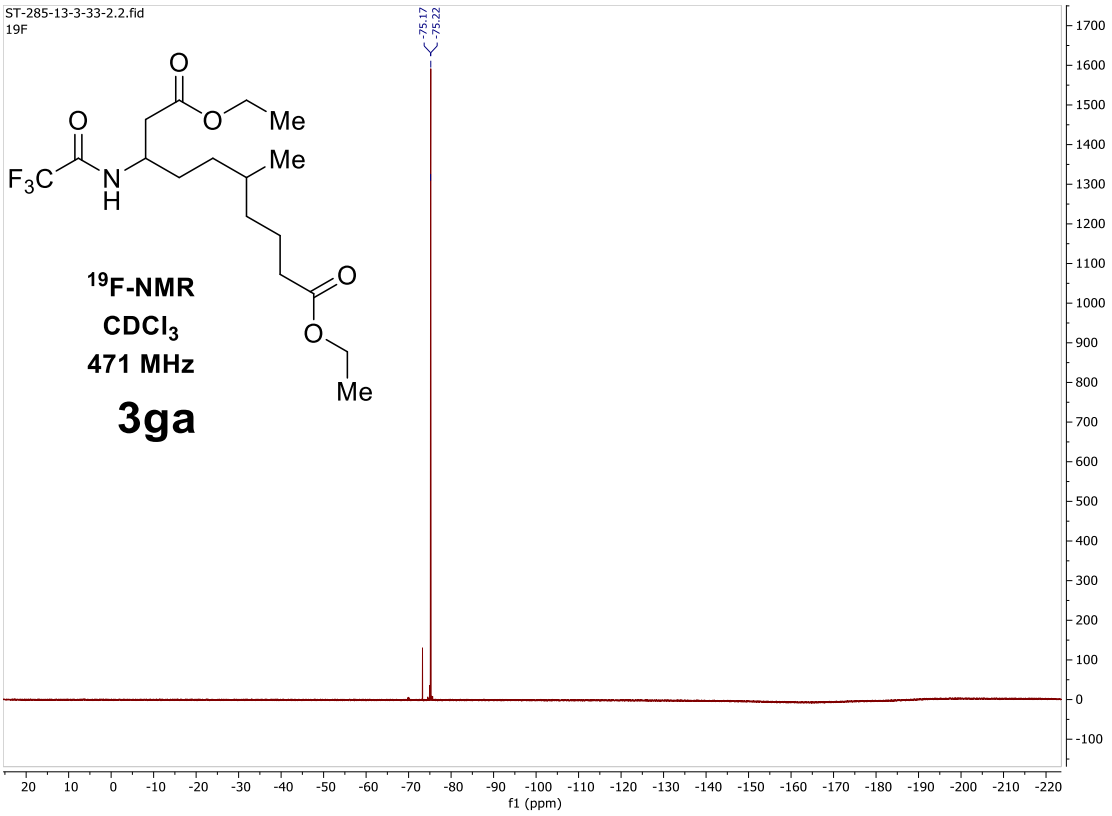

smt-III-155CA-Proton.1.fid
Proton
7.26 CDCl3
6.42
^{1}H-NMR
$CDCl_3$
500 MHz
3fa
0.89
2.02
1.96
2.00
3.01
12.03
6.00
f1 (ppm)

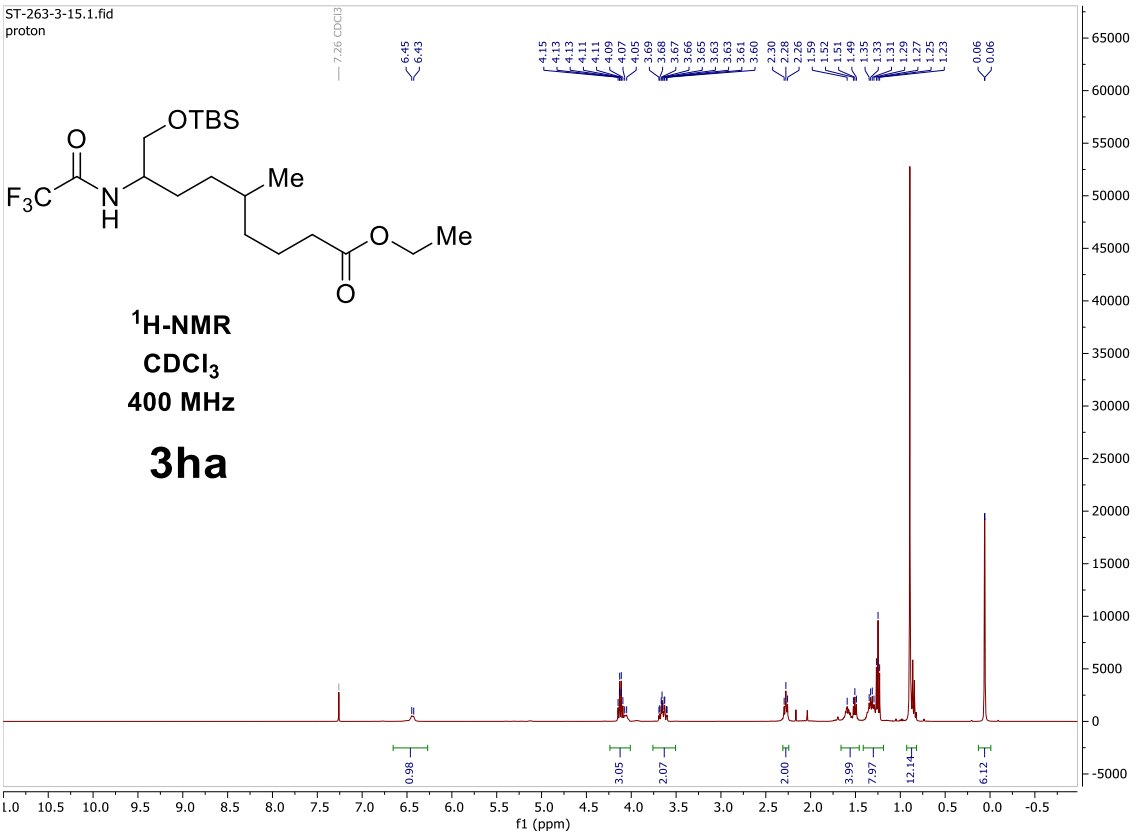

smt-III-155CA-Carbon.1.fid
Carbon 13
173.90
157.91
157.77
157.62
157.48
119.57
117.28
114.99
112.70
77.20 CDCl3
60.51
43.26
41.79
38.09
35.88
34.56
32.90
26.00
24.72
21.68
20.98
14.38
10.77
F3C
N
H
O
Me
Me
O
Me
O
13C-NMR
CDCl3
126 MHz
3fa
f1 (ppm)

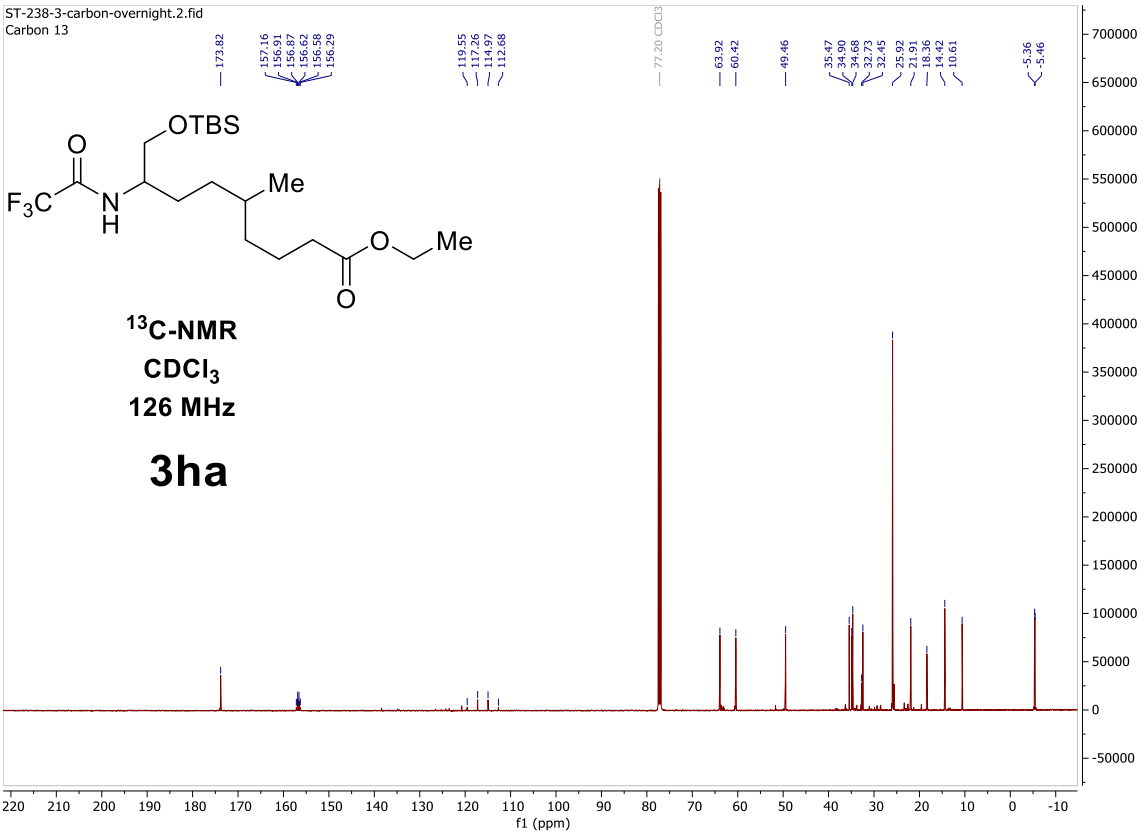

smt-III-155CA-Fluorine.1.fid
19F
-74.92
-75.01
F3C
N
H
O
Me
Me
O
Me
O
19F-NMR
CDCl3
471 MHz
3fa
f1 (ppm)

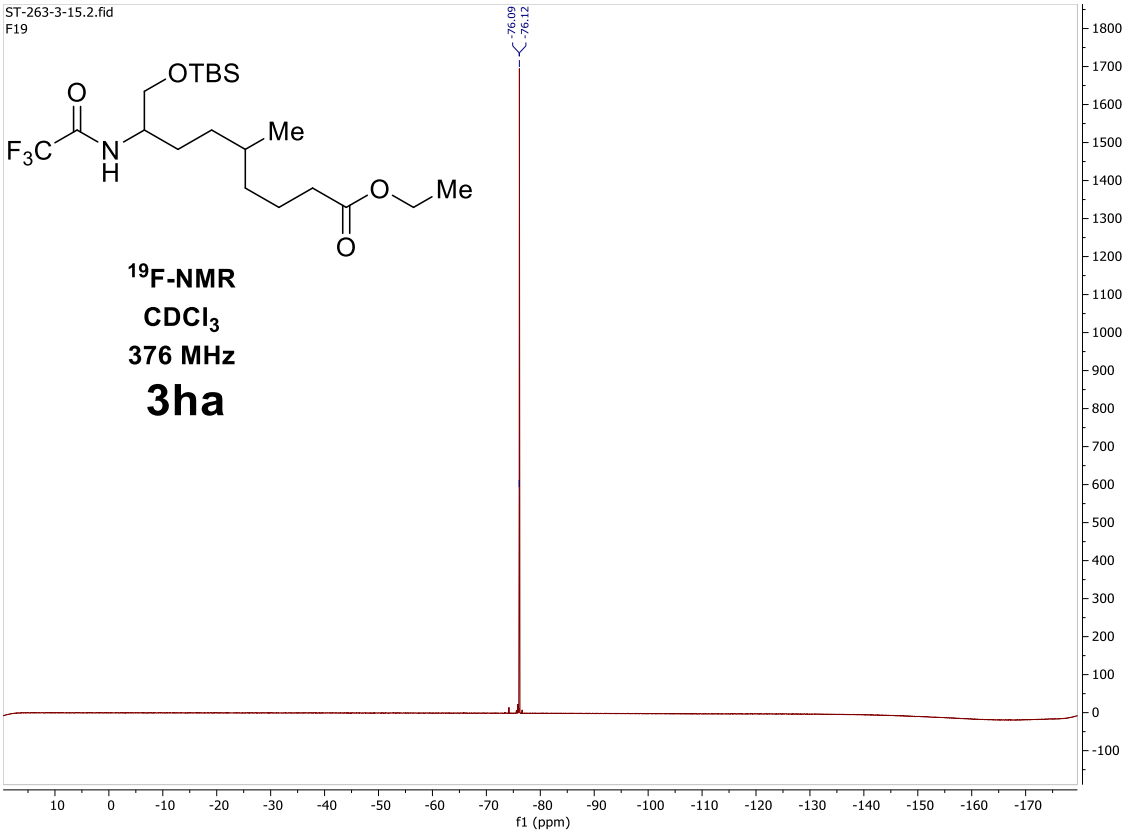

ST-424-2-38.1.fid
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3ga
f1 (ppm)

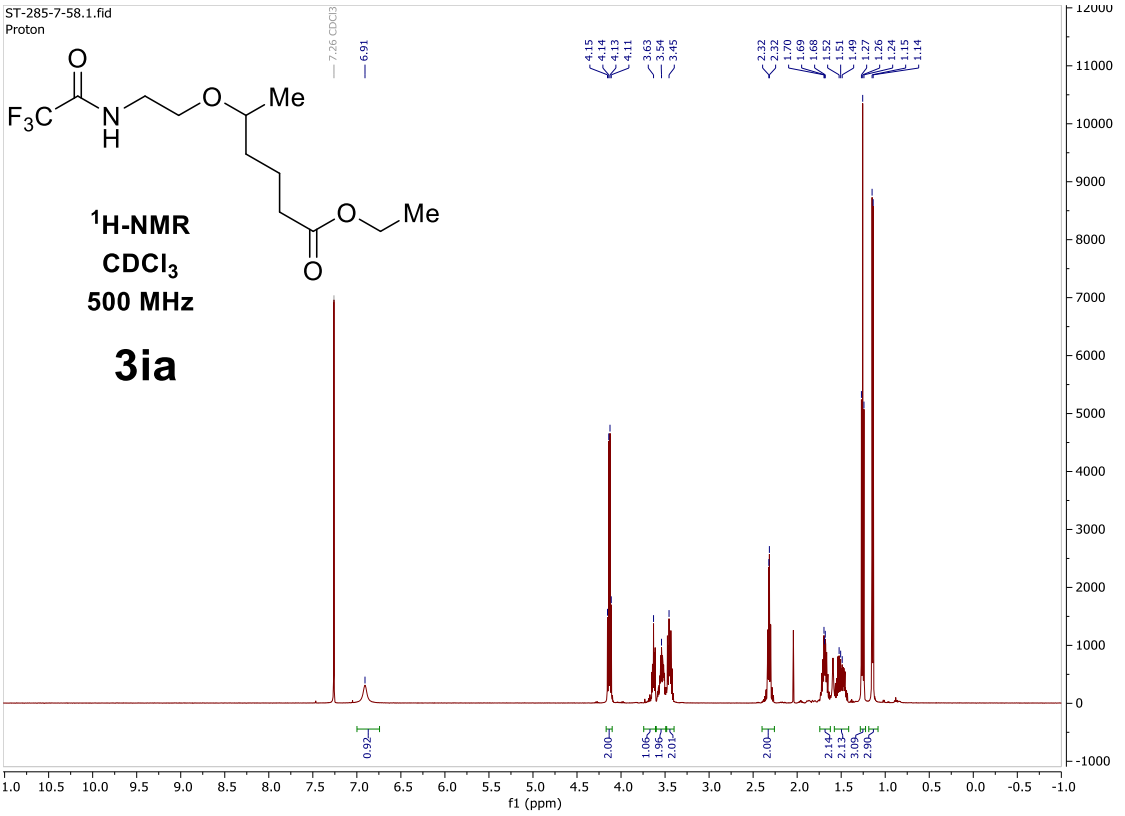

ST-424-2-38.2.fid
Carbon 13
^{13}C-NMR
$CDCl_3$
126 MHz
3ga
f1 (ppm)

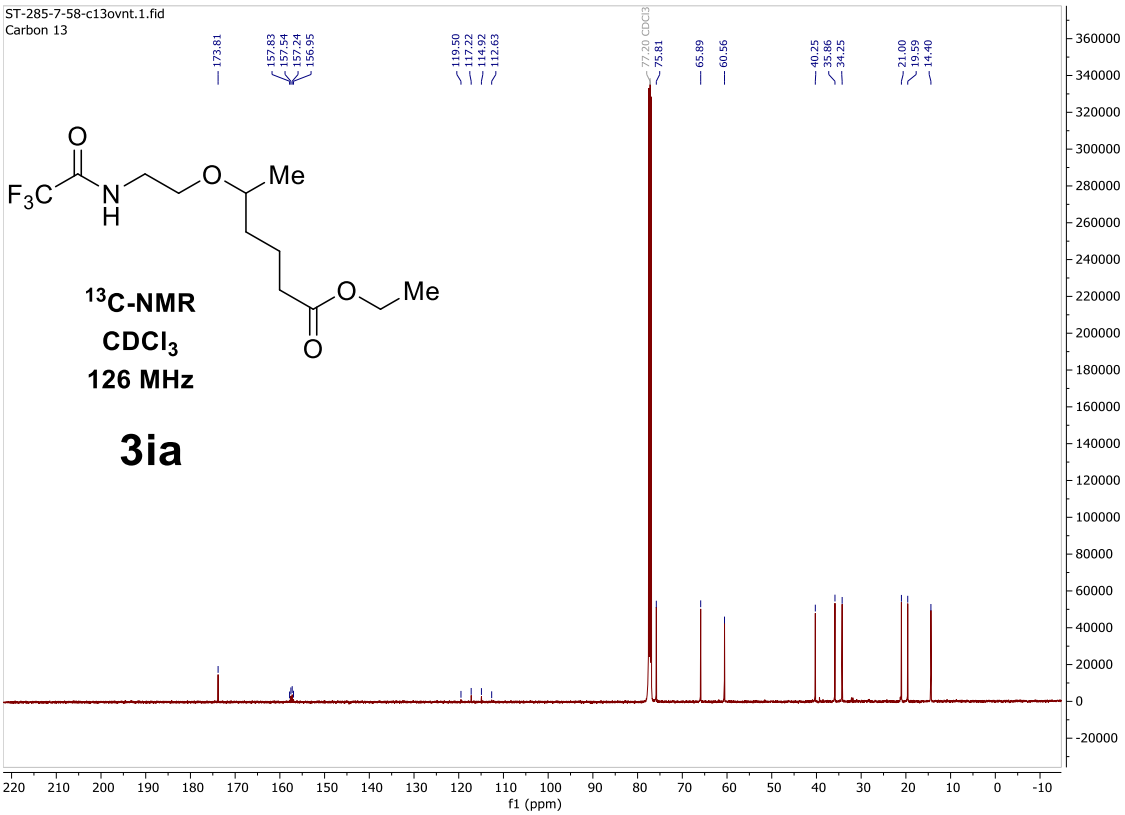

ST-285-13-3-33-2.2.fid
19F
-75.17
-75.22
^{19}F-NMR
$CDCl_3$
471 MHz
3ga
f1 (ppm)

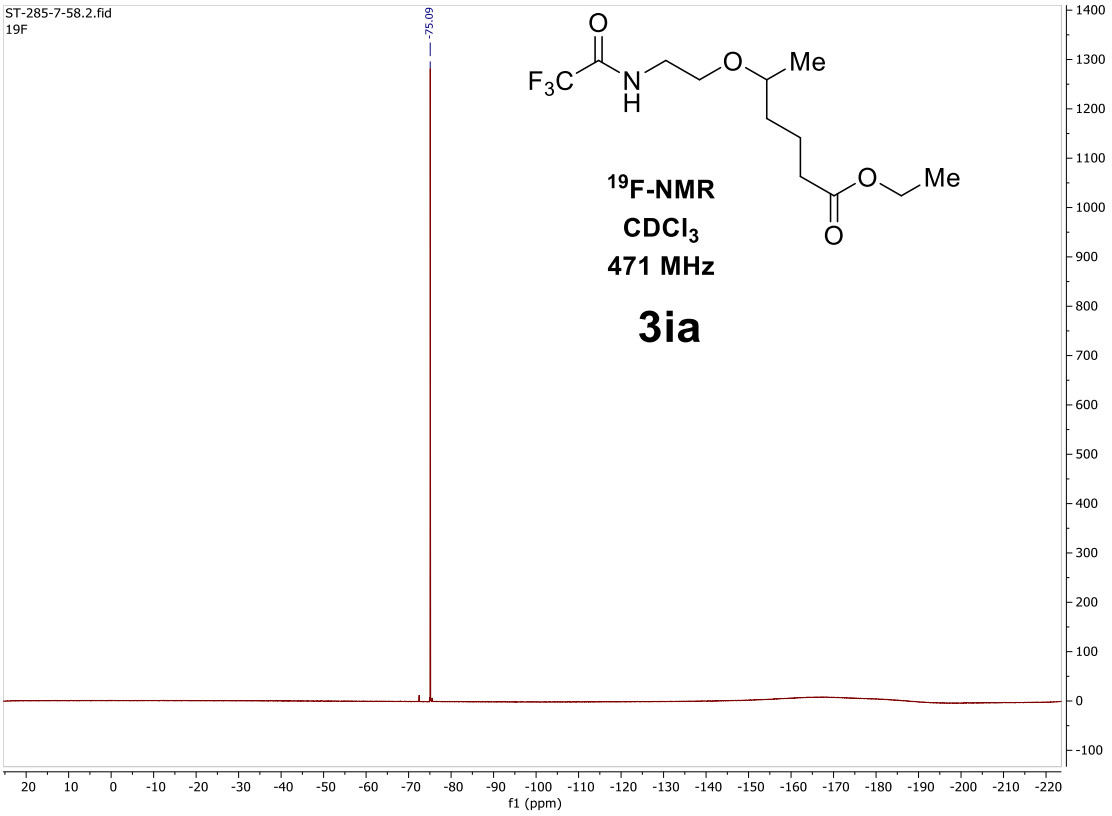

ST-263-3-15.1.fid
proton
7.26 CDCl3
^{1}H-NMR
$CDCl_3$
400 MHz
3ha
0.98
3.05
2.07
2.00
3.99
7.97
12.14
6.12
f1 (ppm)

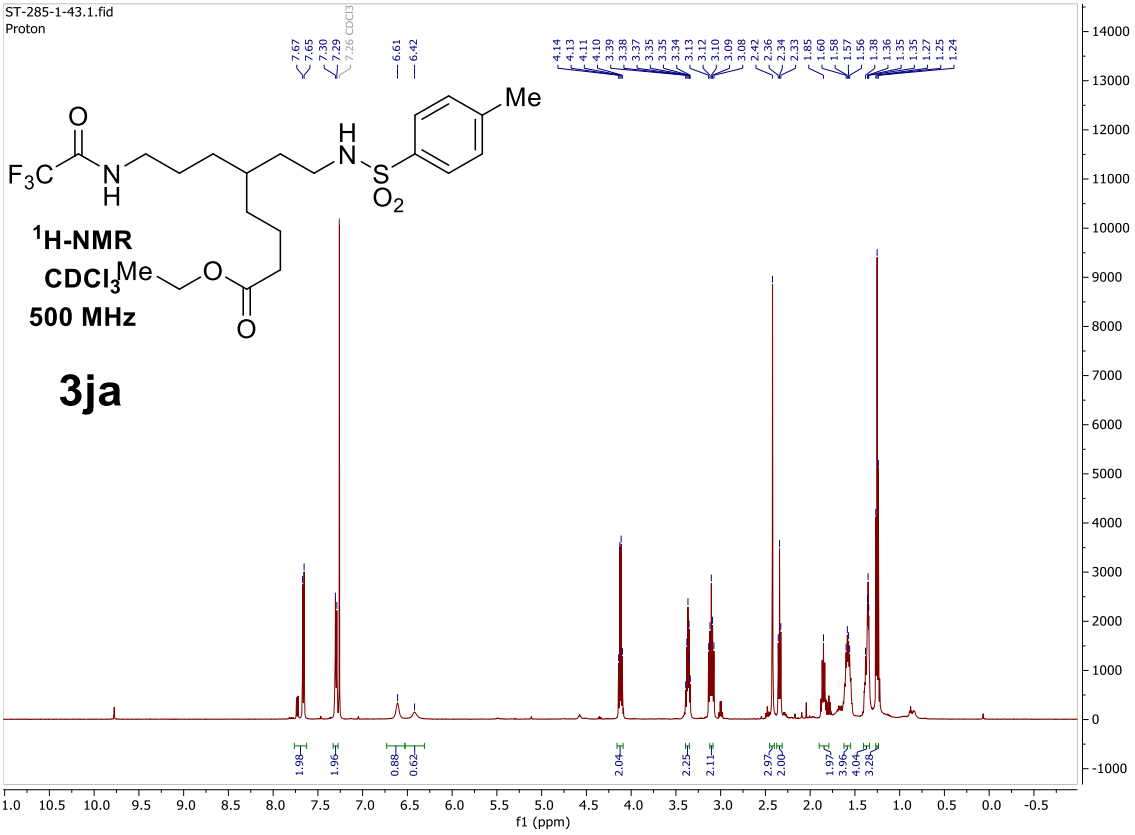

ST-238-3-carbon-overnight.2.fid
Carbon 13
173.82
157.16
156.91
156.87
156.62
156.58
156.29
119.55
117.26
114.97
112.68
77.20 CDCl3
63.92
60.42
49.46
35.47
34.90
34.68
32.73
32.45
25.92
21.91
18.36
14.42
10.61
-5.36
-5.46
OTBS
O
F3C
N
H
Me
O
Me
O
13C-NMR
CDCl3
126 MHz
3ha
f1 (ppm)

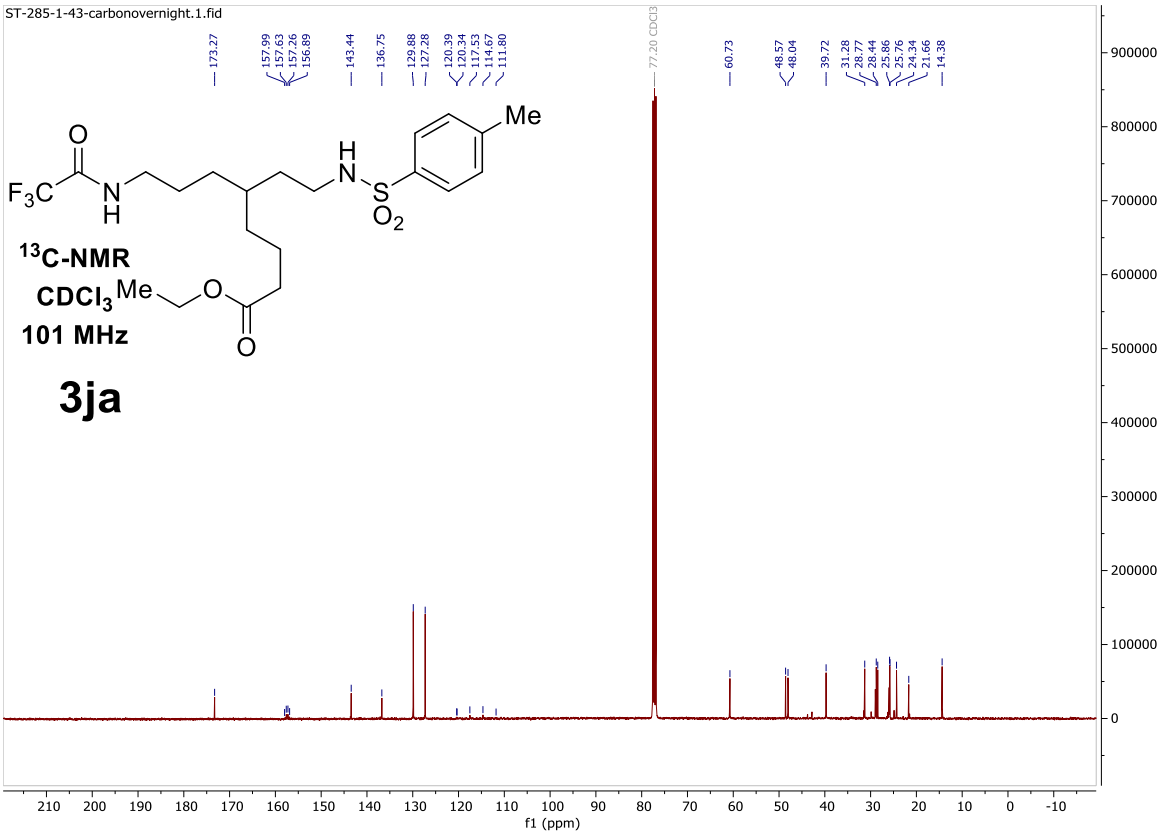

ST-263-3-15.2.fid
F19
-76.09
-76.12
OTBS
O
F3C
N
H
Me
O
Me
O
19F-NMR
CDCl3
376 MHz
3ha
f1 (ppm)

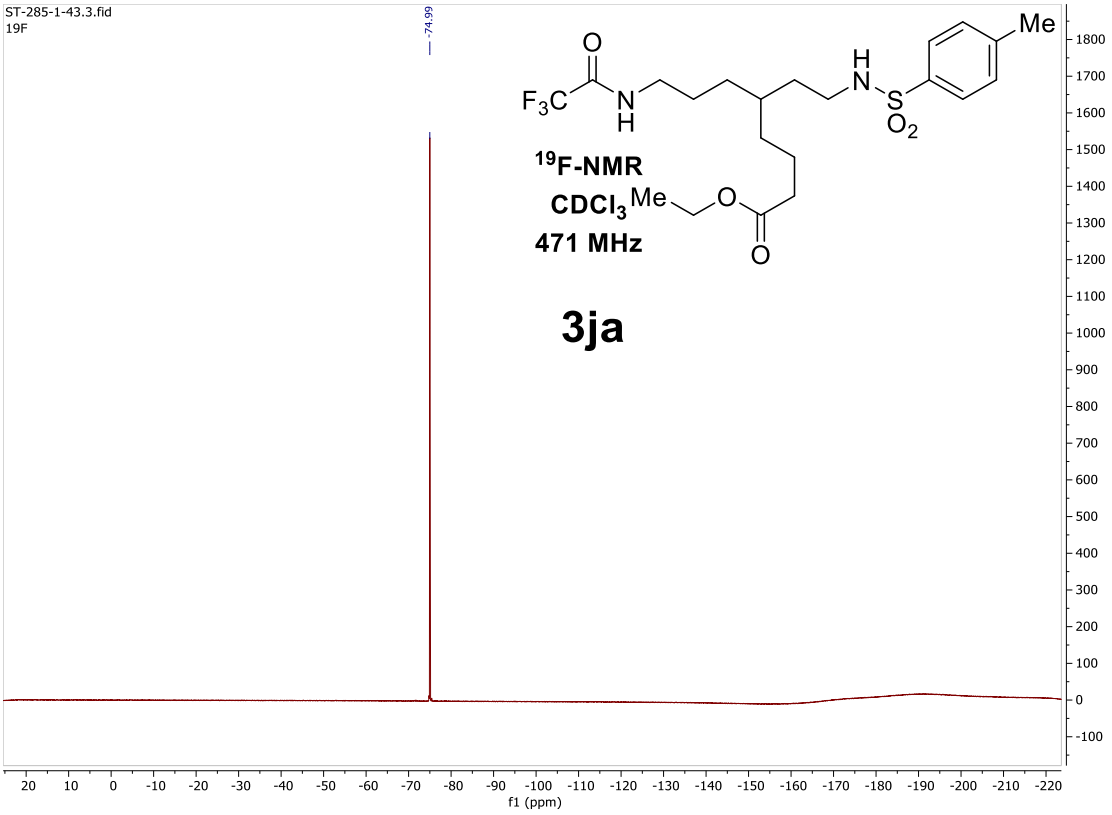

ST-285-7-58.1.fid
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3ia
f1 (ppm)

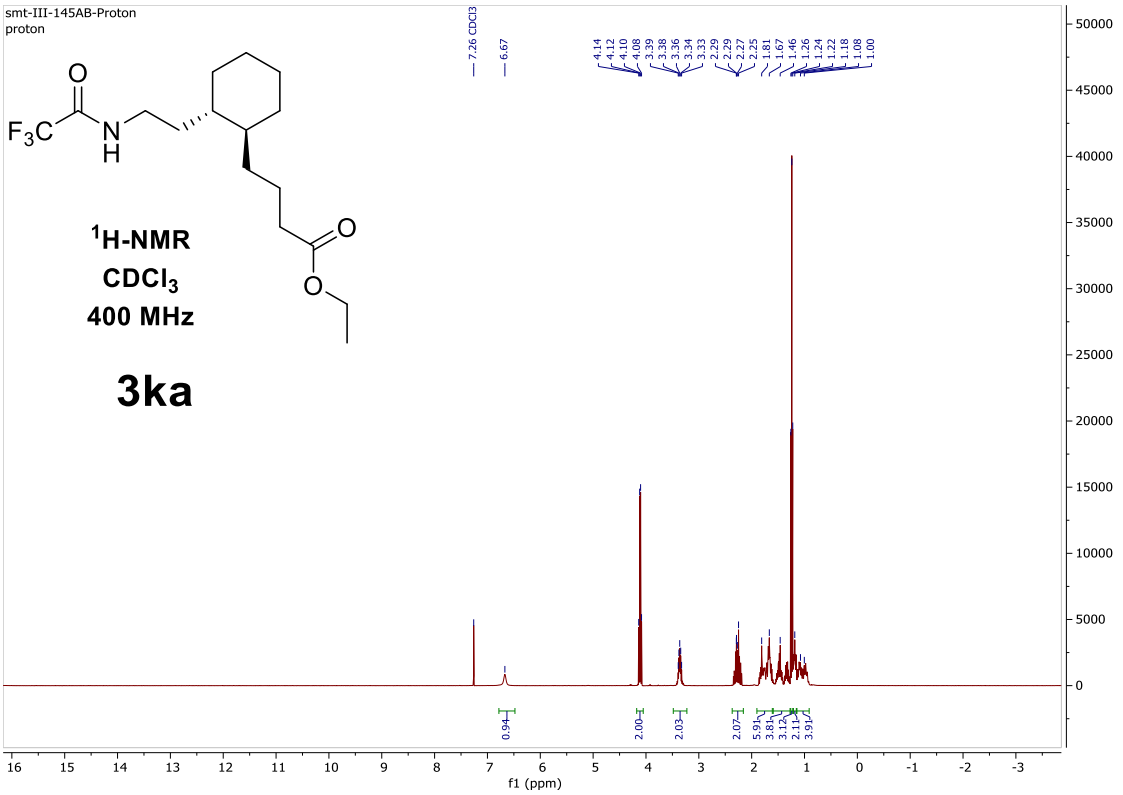

ST-285-7-58-c13ovnt.1.fid
Carbon 13
^{13}C-NMR
$CDCl_3$
126 MHz
3ia
f1 (ppm)

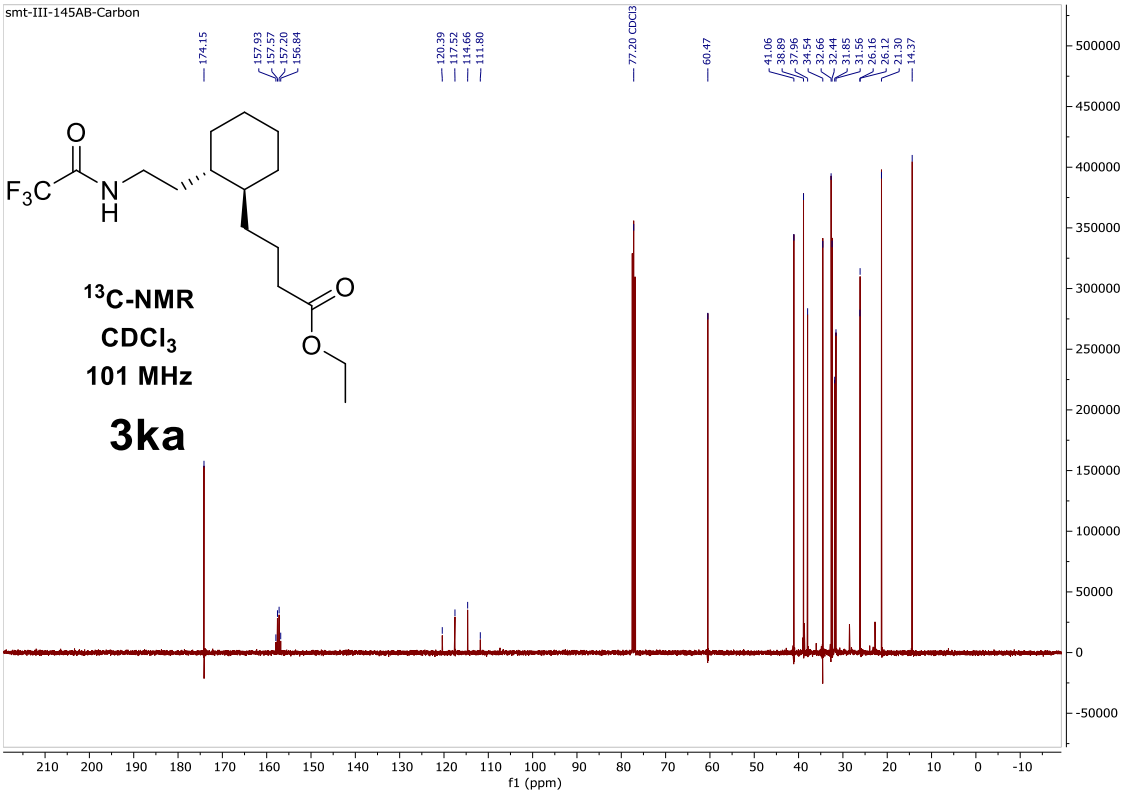

ST-285-7-58.2.fid
19F
-75.09
^{19}F-NMR
$CDCl_3$
471 MHz
3ia
f1 (ppm)

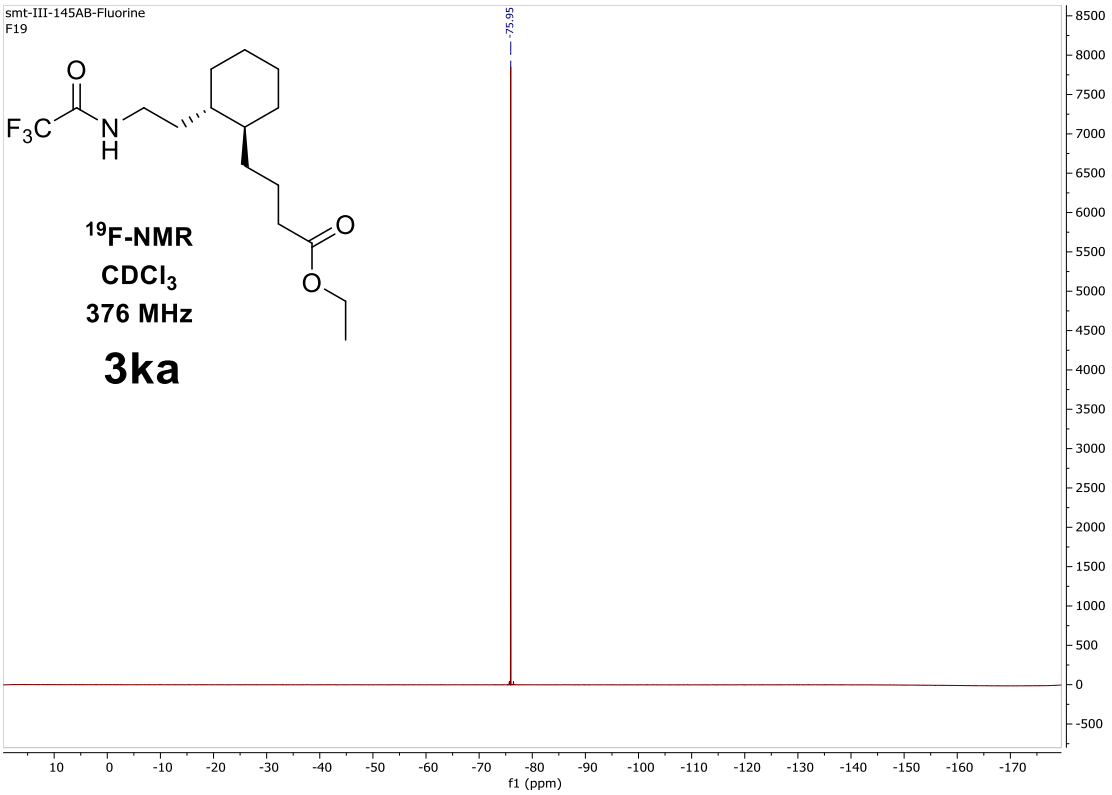

ST-285-1-43.1.fid
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3ja
f1 (ppm)

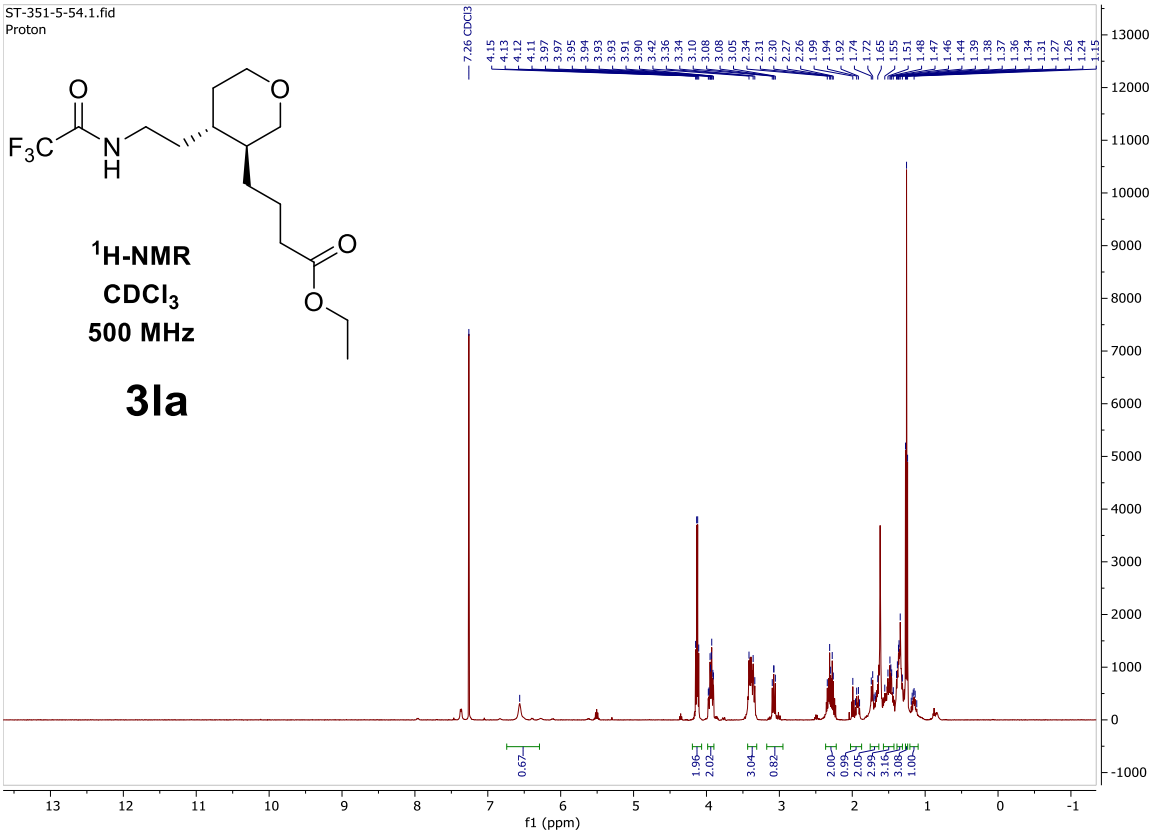

ST-285-1-43-carbonovernight.1.fid
173.27
157.99
157.63
157.26
156.89
143.44
136.75
129.88
127.28
120.39
120.34
117.53
114.67
111.80
77.20 CDCl3
60.73
48.57
48.04
39.72
31.28
28.77
28.44
25.86
25.76
24.34
21.66
14.38
Me
O
F3C
N
H
H
N
S
O2
13C-NMR
CDCl3
Me
O
O
101 MHz
3ja
f1 (ppm)

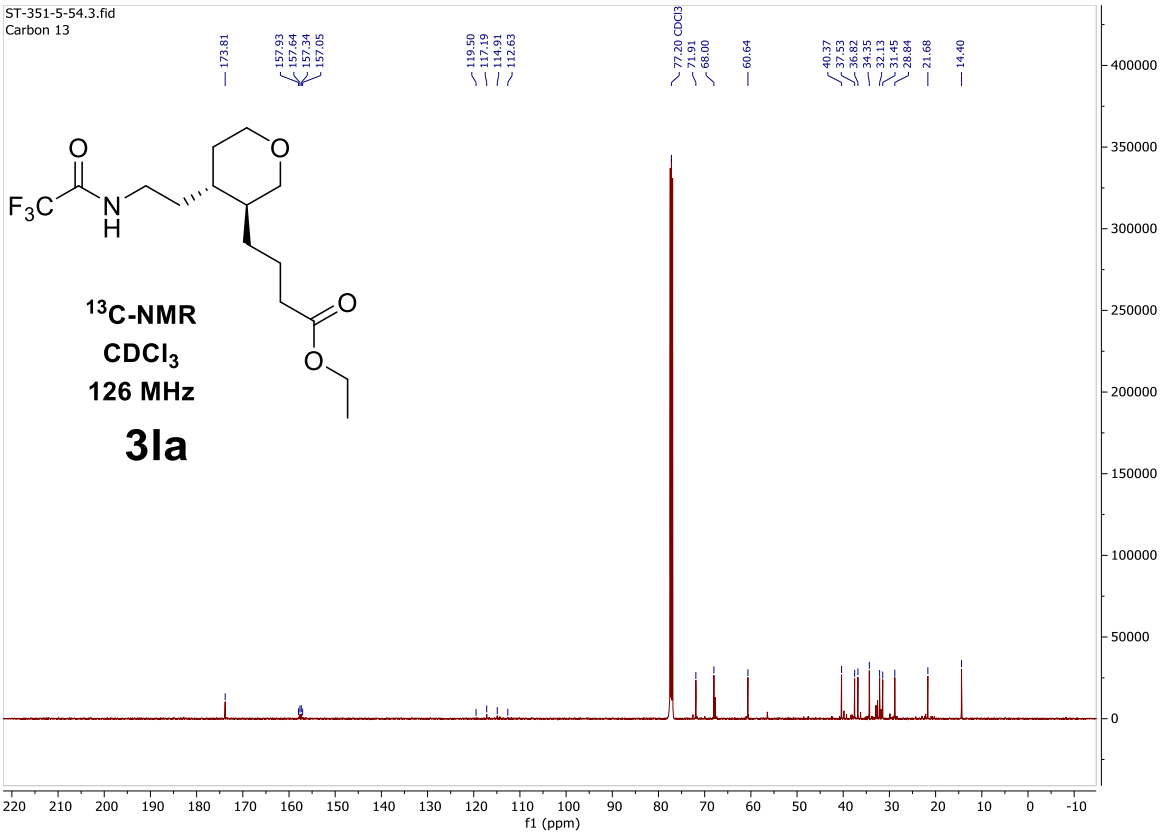

ST-285-1-43.3.fid
19F
-74.99
Me
O
F3C
N
H
H
N
S
O2
19F-NMR
CDCl3
Me
O
O
471 MHz
3ja
f1 (ppm)

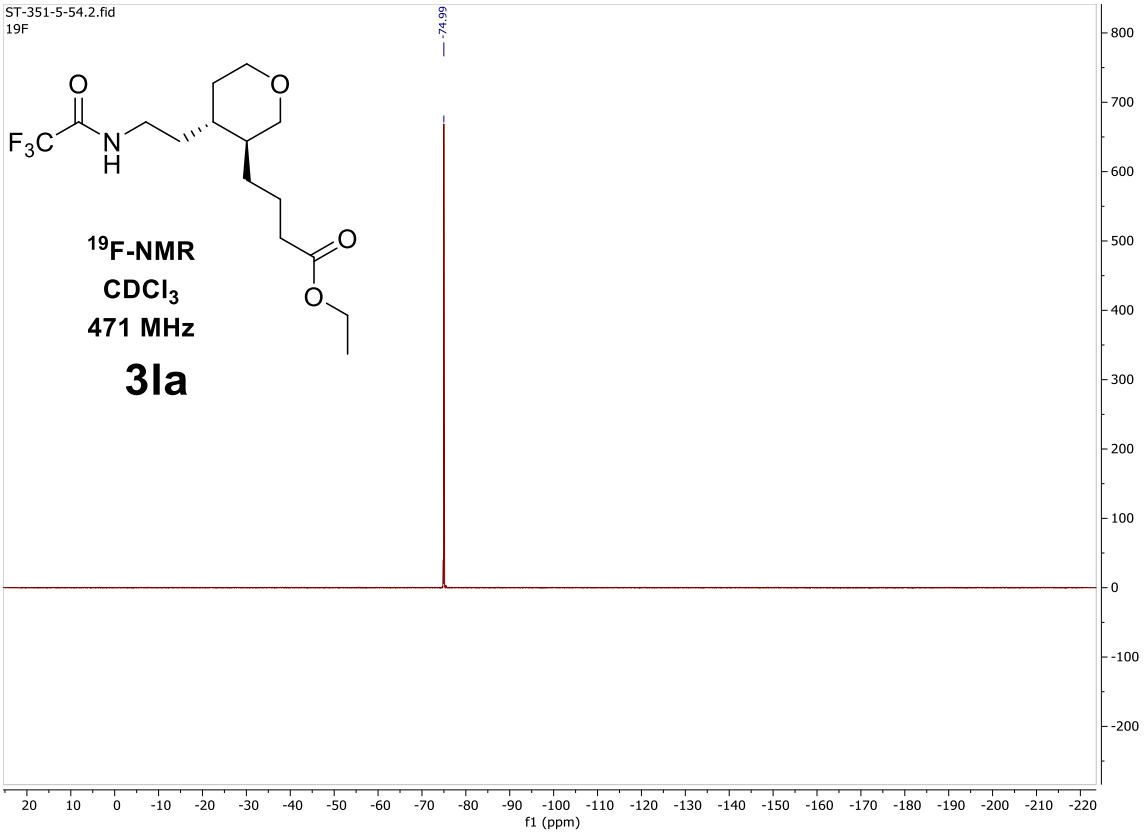

smt-III-145AB-Proton
proton
^{1}H-NMR
$CDCl_3$
400 MHz
3ka
f1 (ppm)

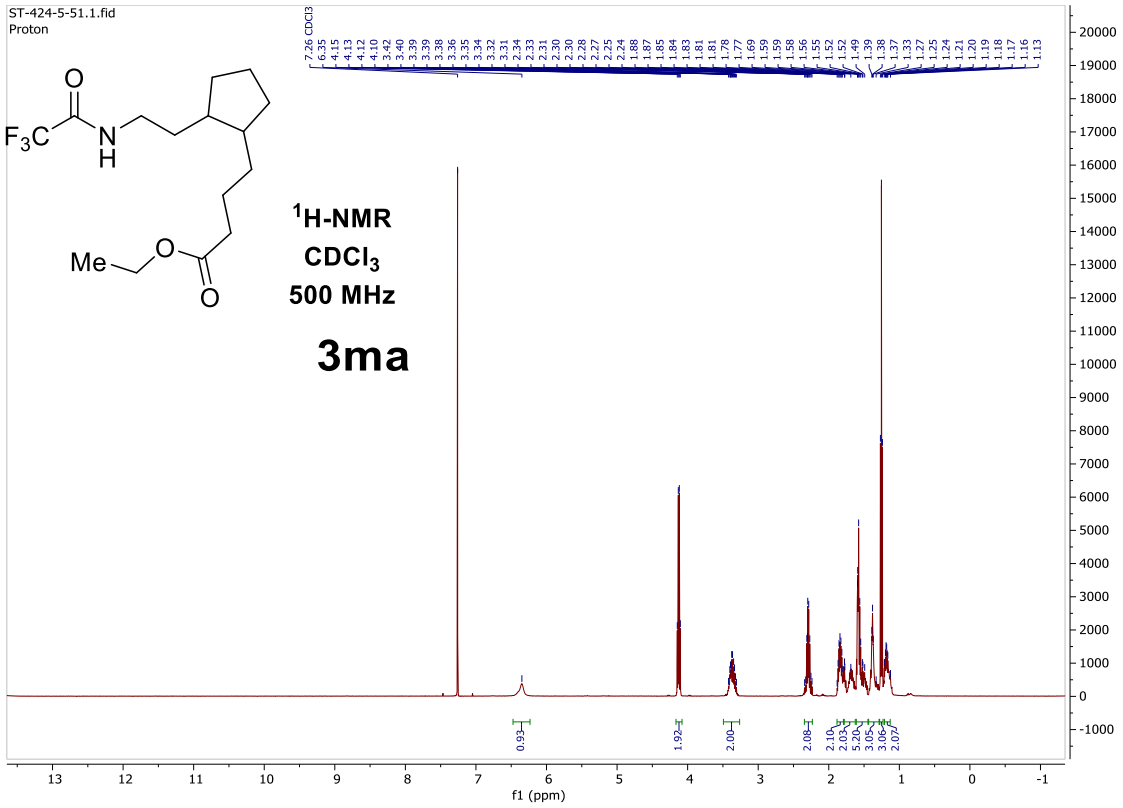

smt-III-145AB-Carbon
^{13}C-NMR
$CDCl_3$
101 MHz
3ka
f1 (ppm)

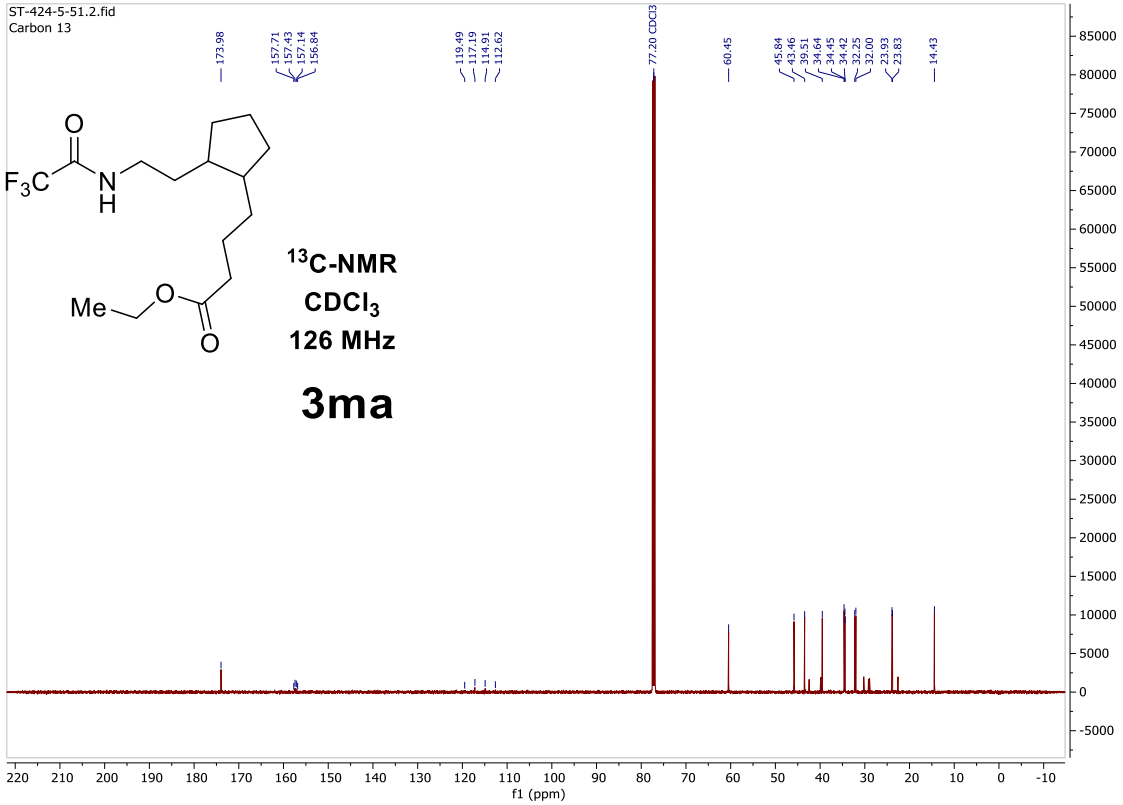

smt-III-145AB-Fluorine
F19
-75.95
^{19}F-NMR
$CDCl_3$
376 MHz
3ka
f1 (ppm)

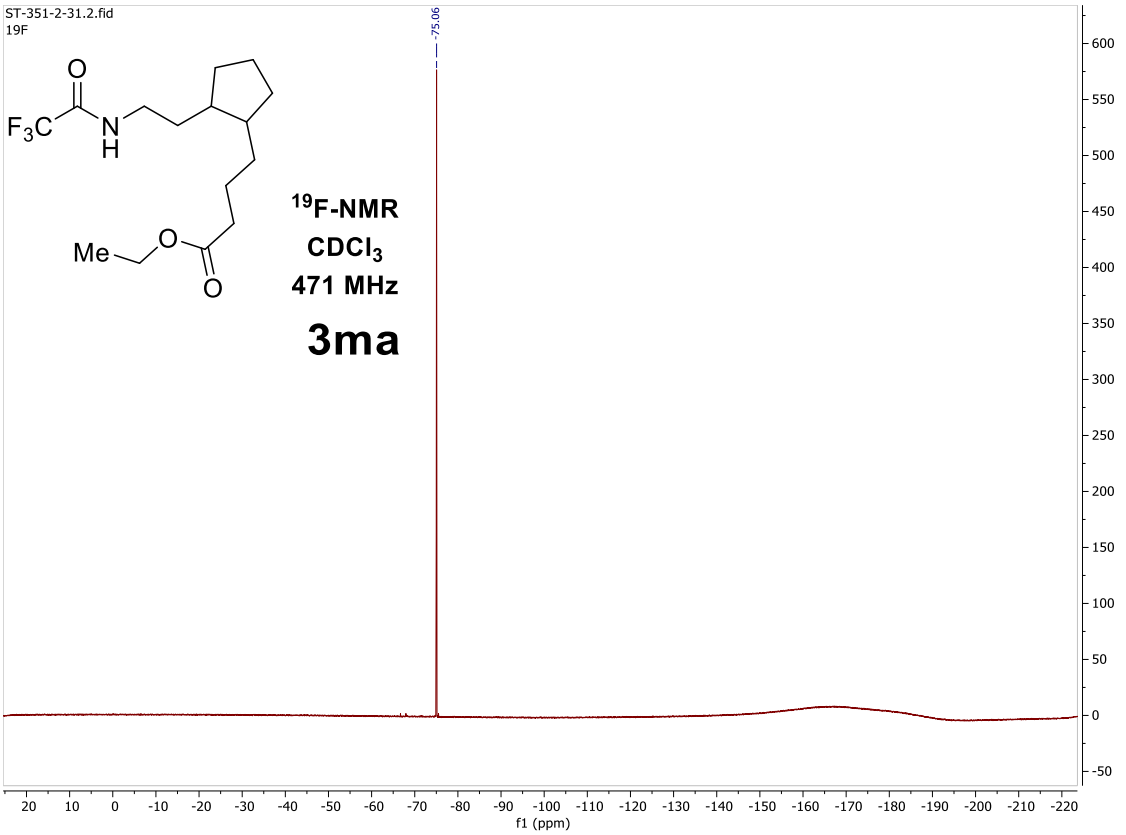

ST-351-5-54.1.fid
Proton
7.26 CDCl3
^{1}H-NMR
$CDCl_3$
500 MHz
3la
f1 (ppm)

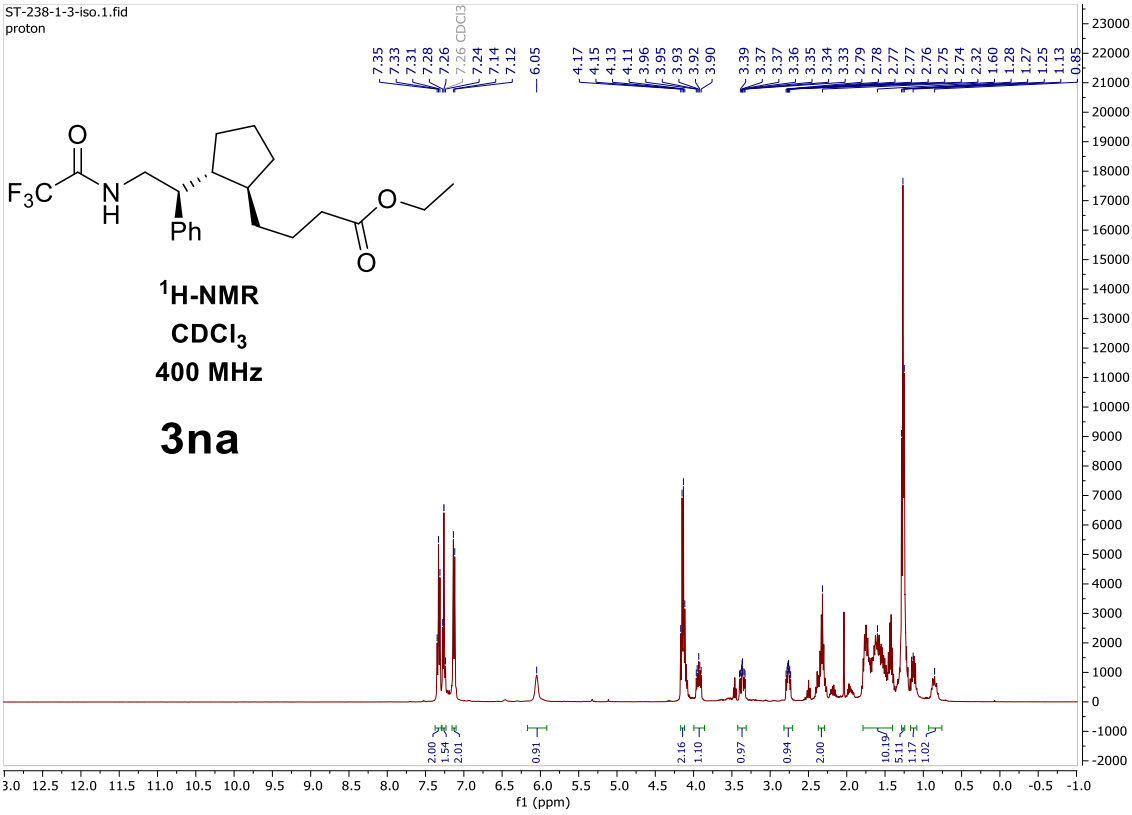

ST-351-5-54.3.fid
Carbon 13
173.81
157.93
157.64
157.34
157.05
119.50
117.19
114.91
112.63
77.20 CDCl3
71.91
68.00
60.64
40.37
37.53
36.82
34.35
32.13
31.45
28.84
21.68
14.40
13C-NMR
CDCl3
126 MHz
3la
f1 (ppm)

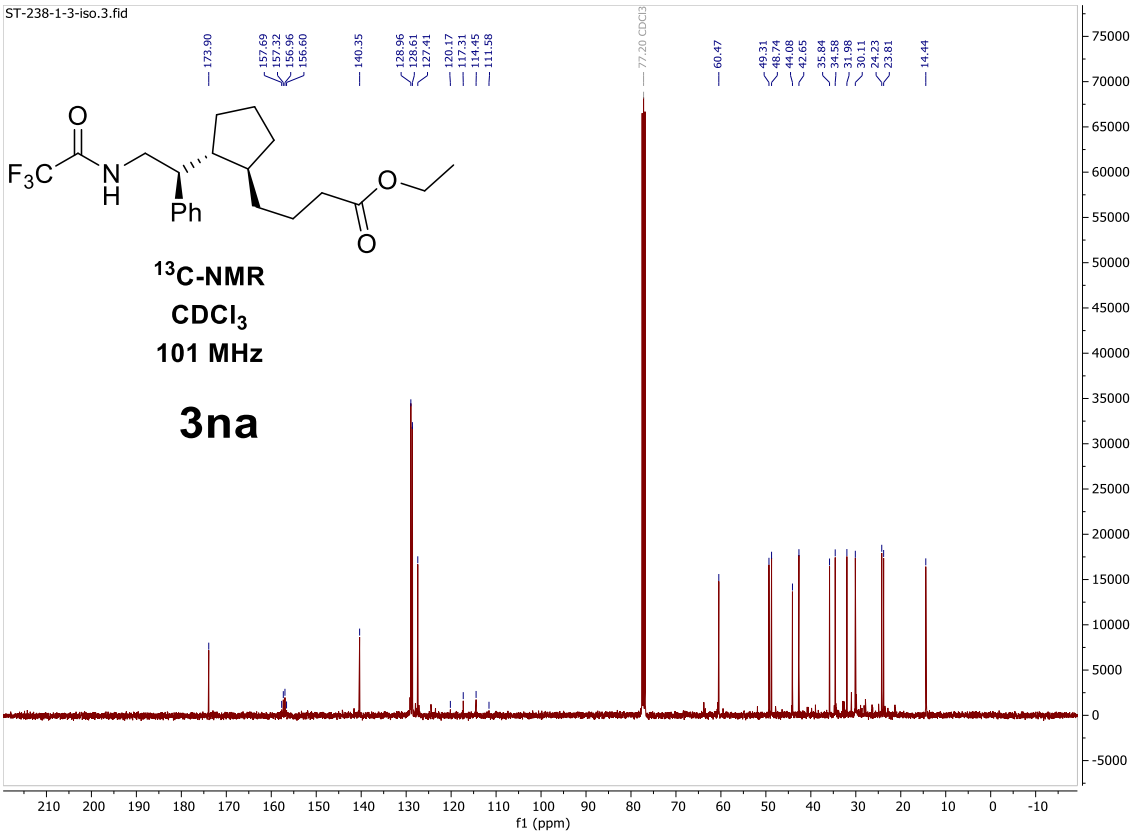

ST-351-5-54.2.fid
19F
-74.99
19F-NMR
CDCl3
471 MHz
3la
f1 (ppm)

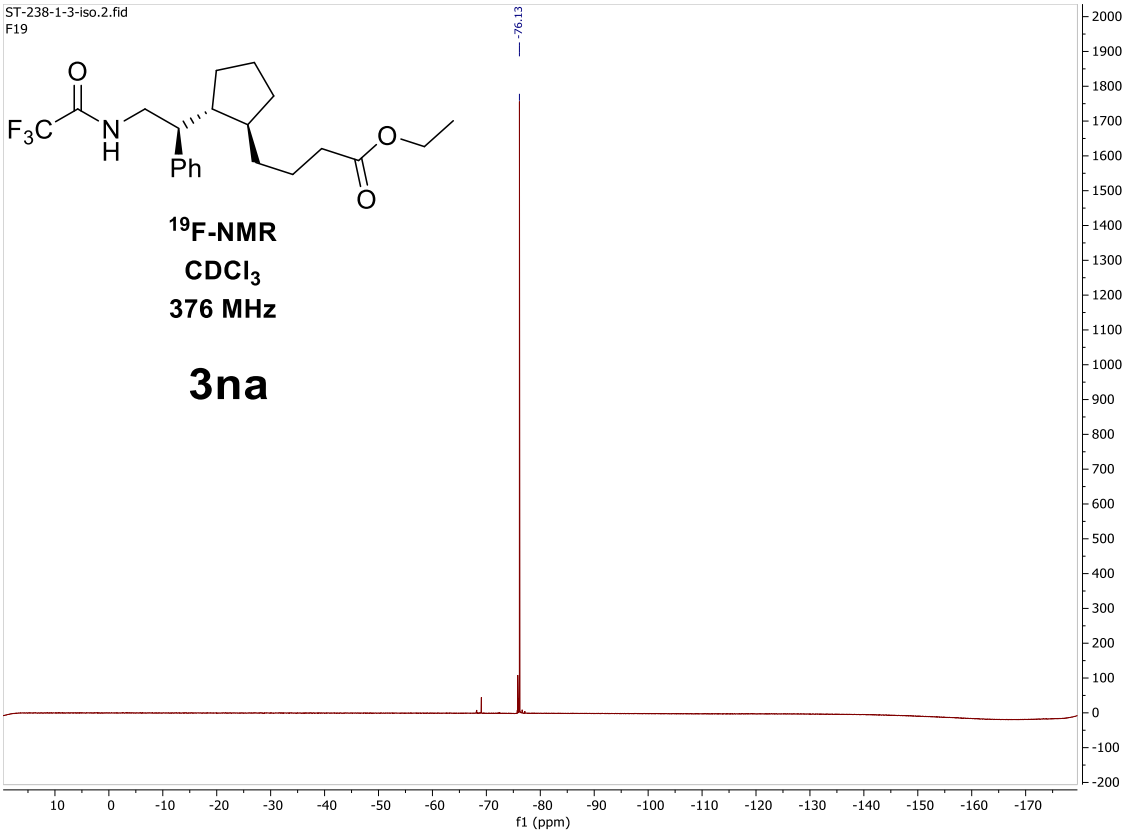

ST-424-5-51.1.fid
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3ma
f1 (ppm)

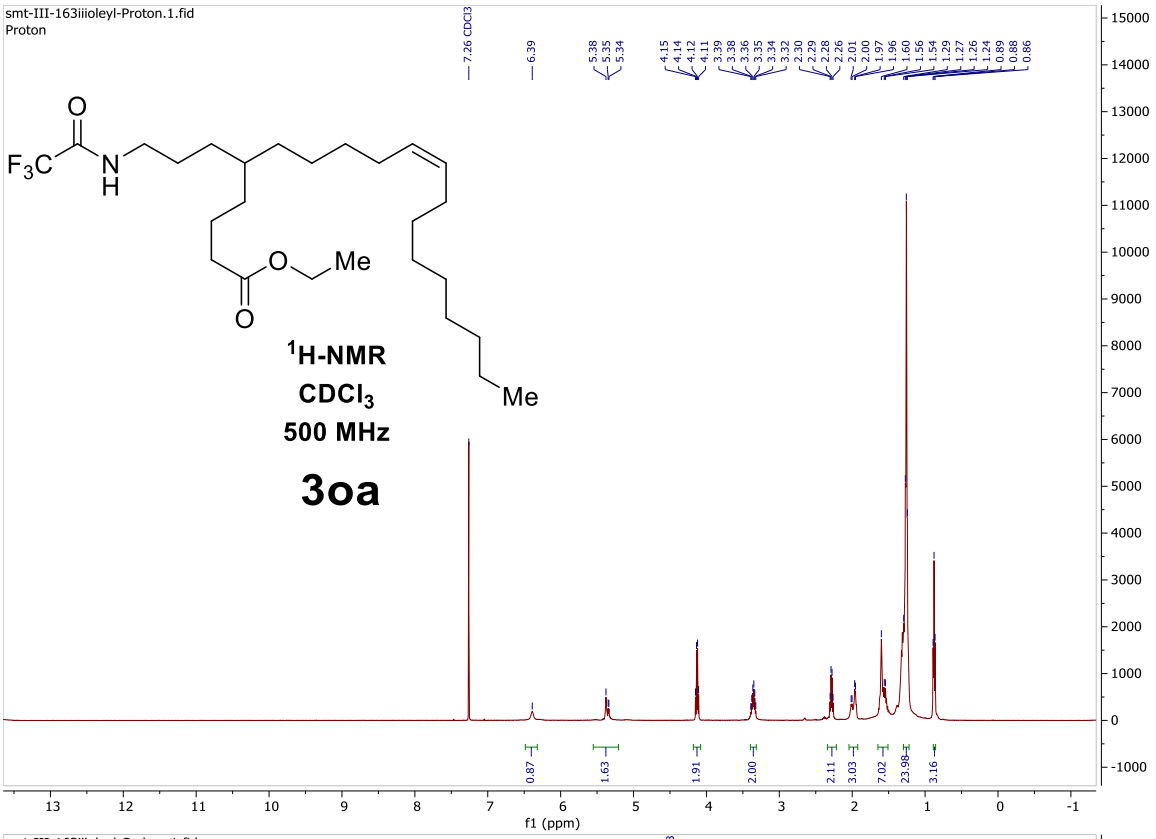

ST-424-5-51.2.fid
Carbon 13
^{13}C-NMR
$CDCl_3$
126 MHz
3ma
f1 (ppm)

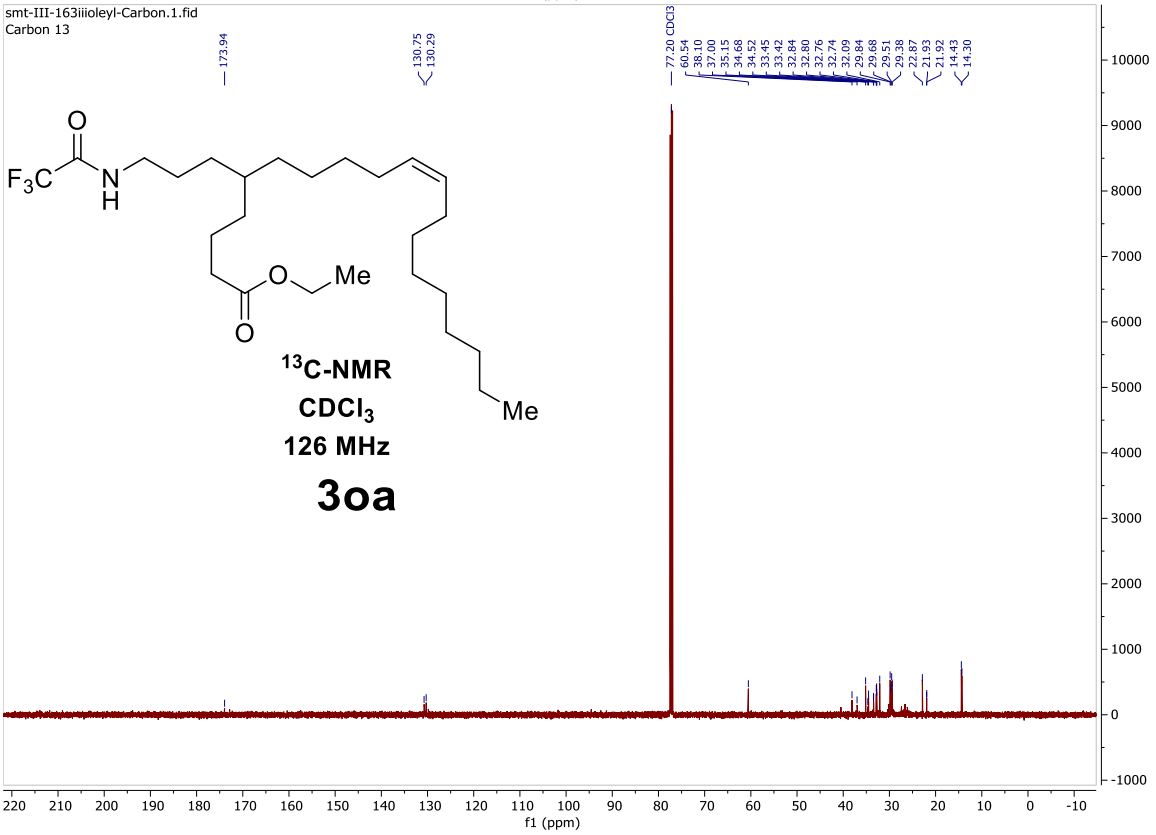

ST-351-2-31.2.fid
19F
75.06
^{19}F-NMR
$CDCl_3$
471 MHz
3ma
f1 (ppm)

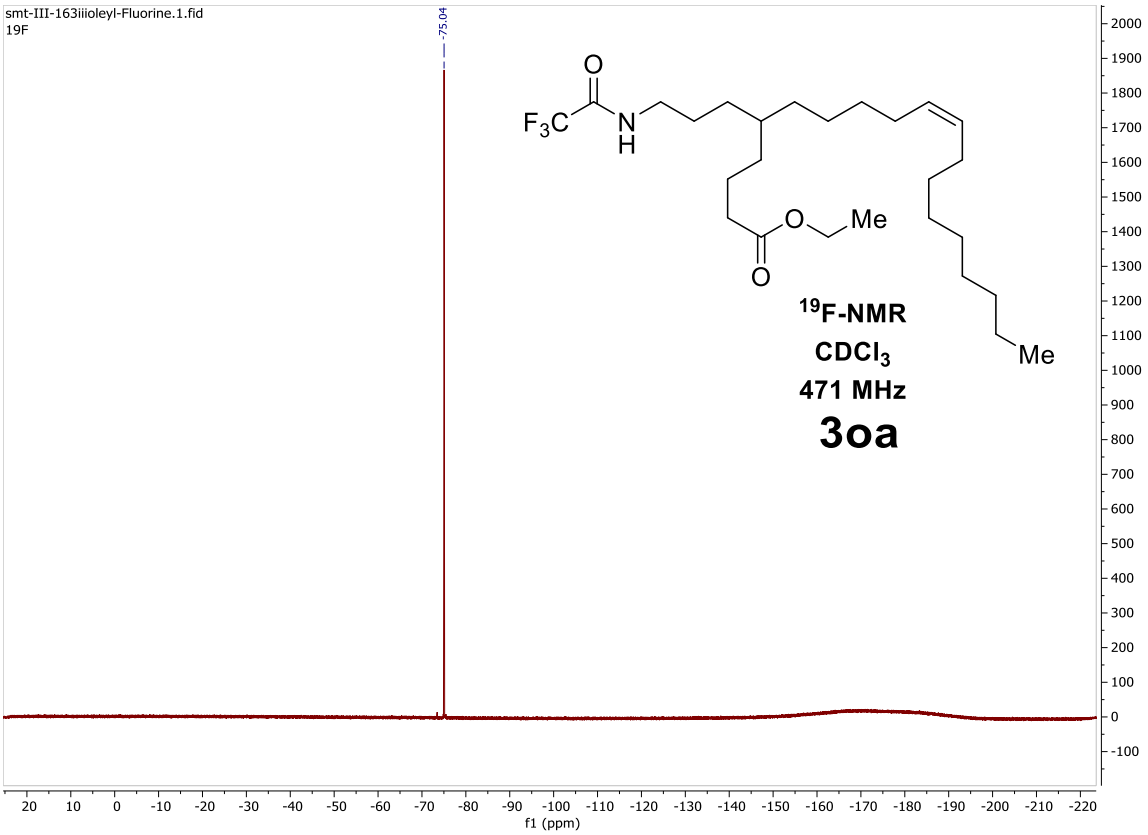

ST-238-1-3-iso.1.fid
proton
7.26 CDCl3
^{1}H-NMR
$CDCl_3$
400 MHz
3na
f1 (ppm)

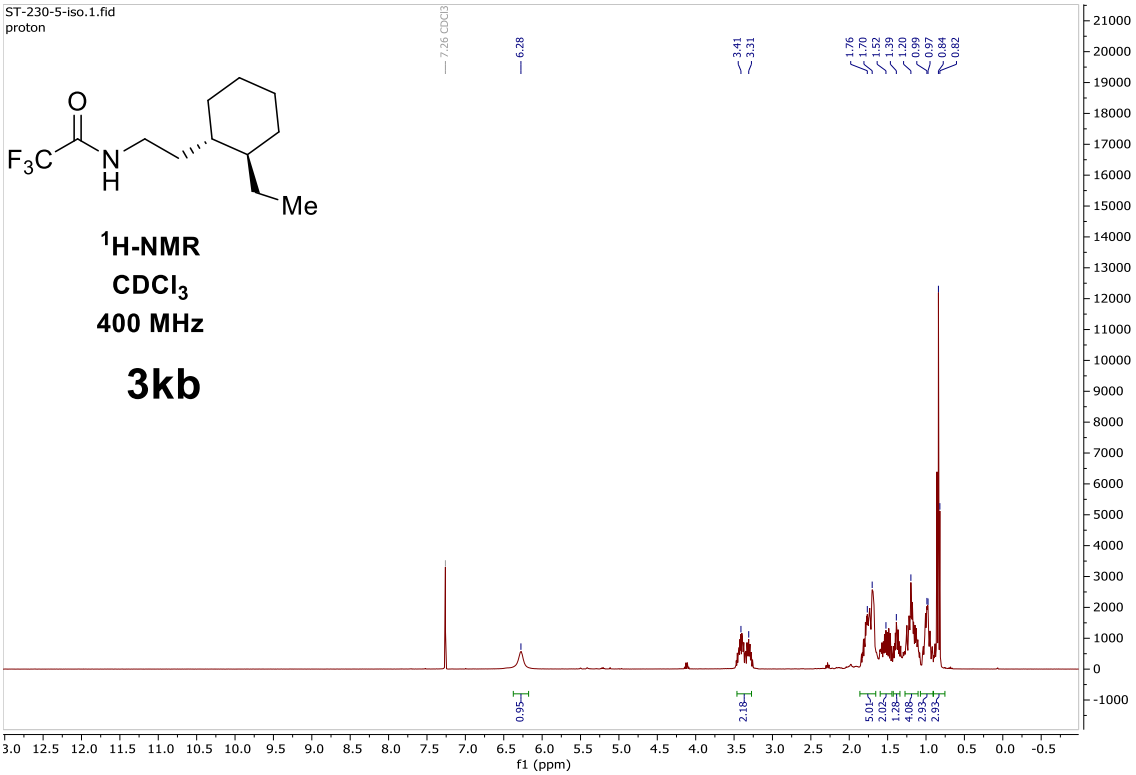

ST-238-1-3-iso.3.fid
173.90
157.69
157.32
156.96
156.60
140.35
128.96
128.61
127.41
120.17
117.31
114.45
111.58
77.20 CDCl3
60.47
49.31
48.74
44.08
42.65
35.84
34.58
31.96
30.11
24.33
23.81
14.44
F3C
O
N
H
Ph
O
O
13C-NMR
CDCl3
101 MHz
3na
f1 (ppm)

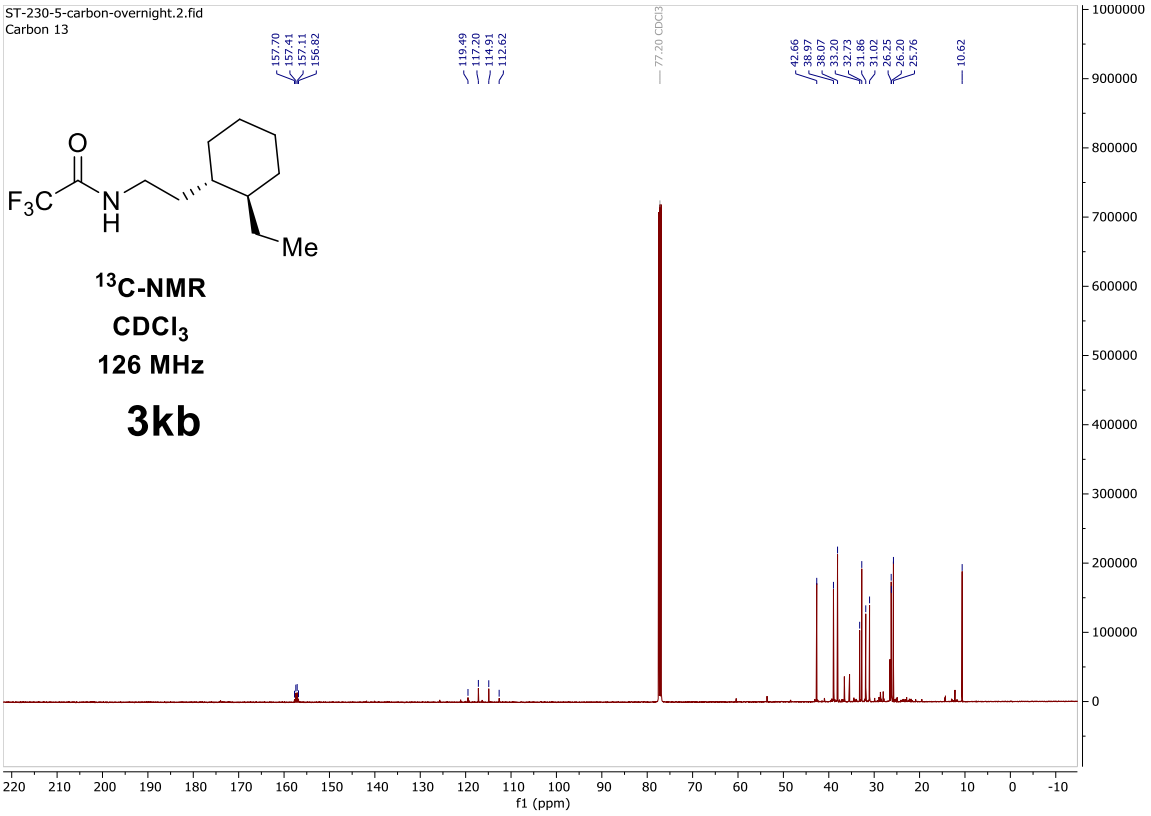

ST-238-1-3-iso.2.fid
F19
-76.13
F3C
O
N
H
Ph
O
O
19F-NMR
CDCl3
376 MHz
3na
f1 (ppm)

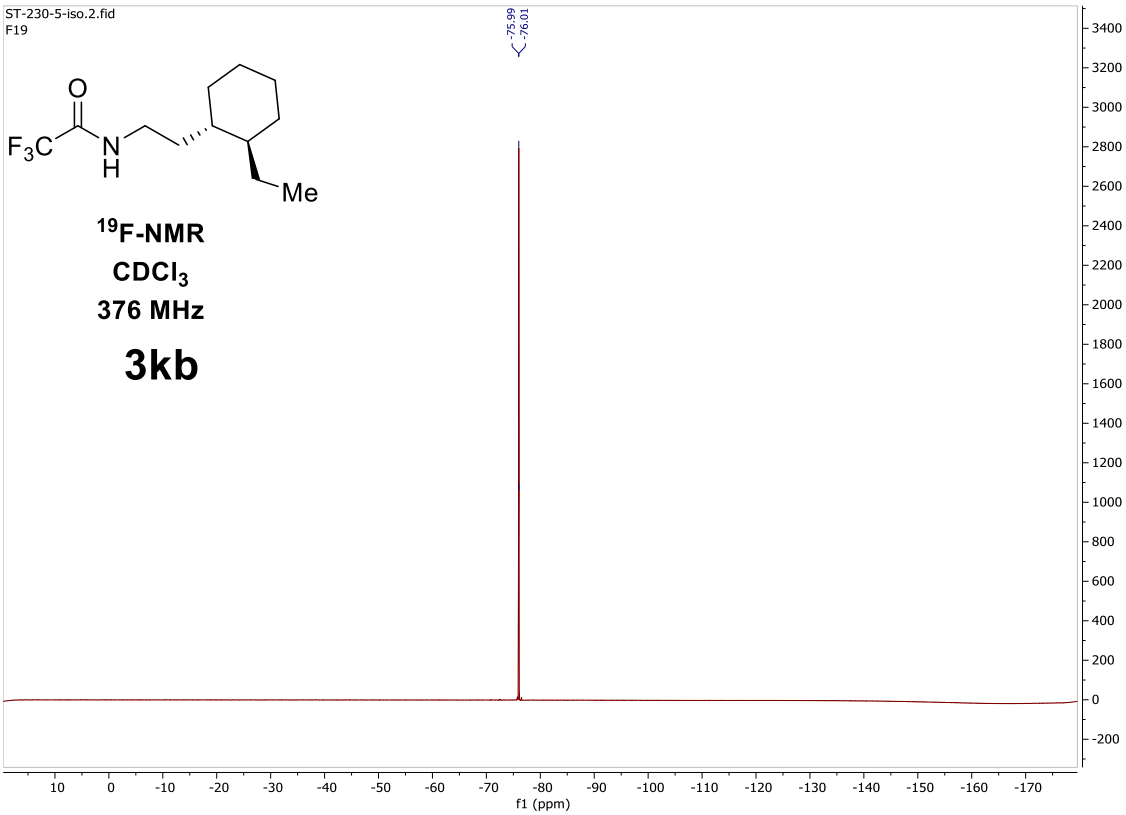

smt-III-163iiioleyl-Proton.1.fid
Proton
7.26 CDCl3
6.39
5.38
5.35
5.34
4.15
4.14
4.12
4.11
3.39
3.38
3.36
3.35
3.34
3.32
2.30
2.29
2.28
2.26
2.01
2.00
1.97
1.96
1.60
1.56
1.54
1.29
1.27
1.26
1.24
0.89
0.88
0.86
F3C
N
H
O
O
O
Me
Me
1H-NMR
CDCl3
500 MHz
3oa
0.87
1.63
1.91
2.00
2.11
3.03
7.02
23.98
3.16
f1 (ppm)

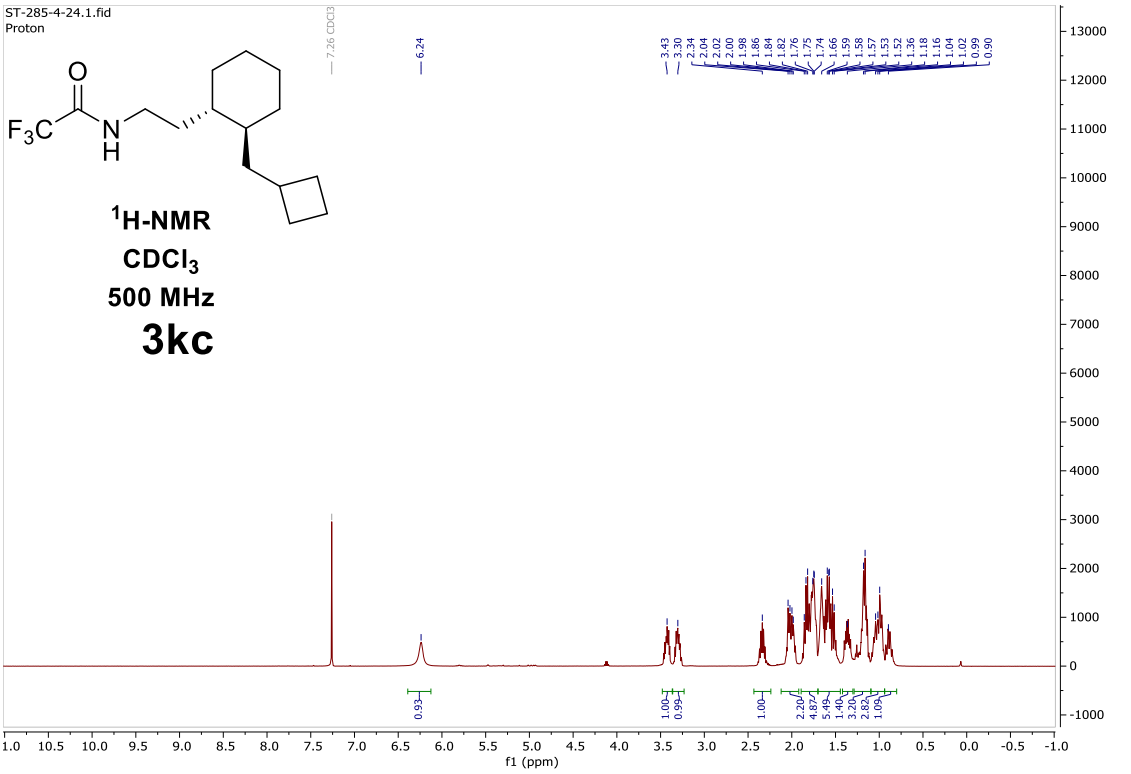

smt-III-163iiioleyl-Carbon.1.fid
Carbon 13
173.94
130.75
130.29
77.20 CDCl3
60.54
38.10
37.00
35.15
34.68
34.52
33.45
33.42
32.84
32.80
32.76
32.74
32.09
29.84
29.68
29.51
29.38
22.87
21.93
21.92
14.43
14.30
F3C
N
H
O
O
O
Me
Me
13C-NMR
CDCl3
126 MHz
3oa
f1 (ppm)

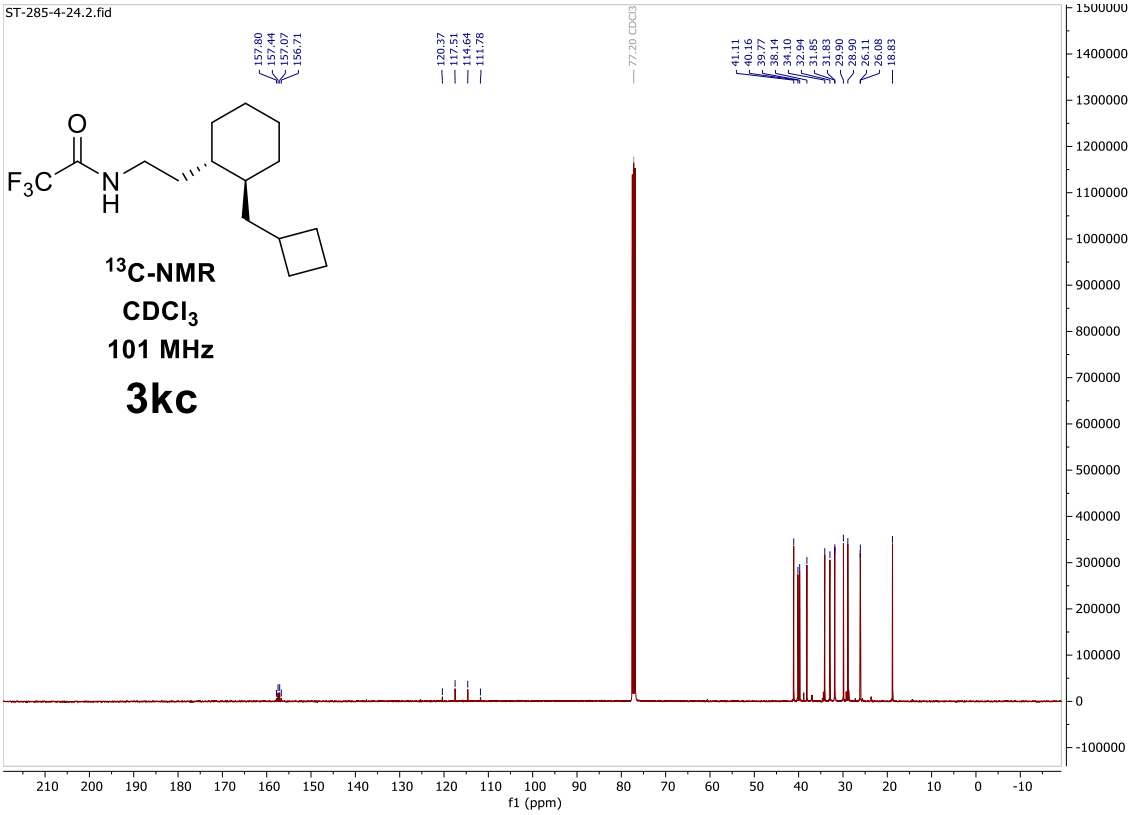

smt-III-163iiioleyl-Fluorine.1.fid
19F
-75.04
^{19}F-NMR
$CDCl_3$
471 MHz
3oa
f1 (ppm)

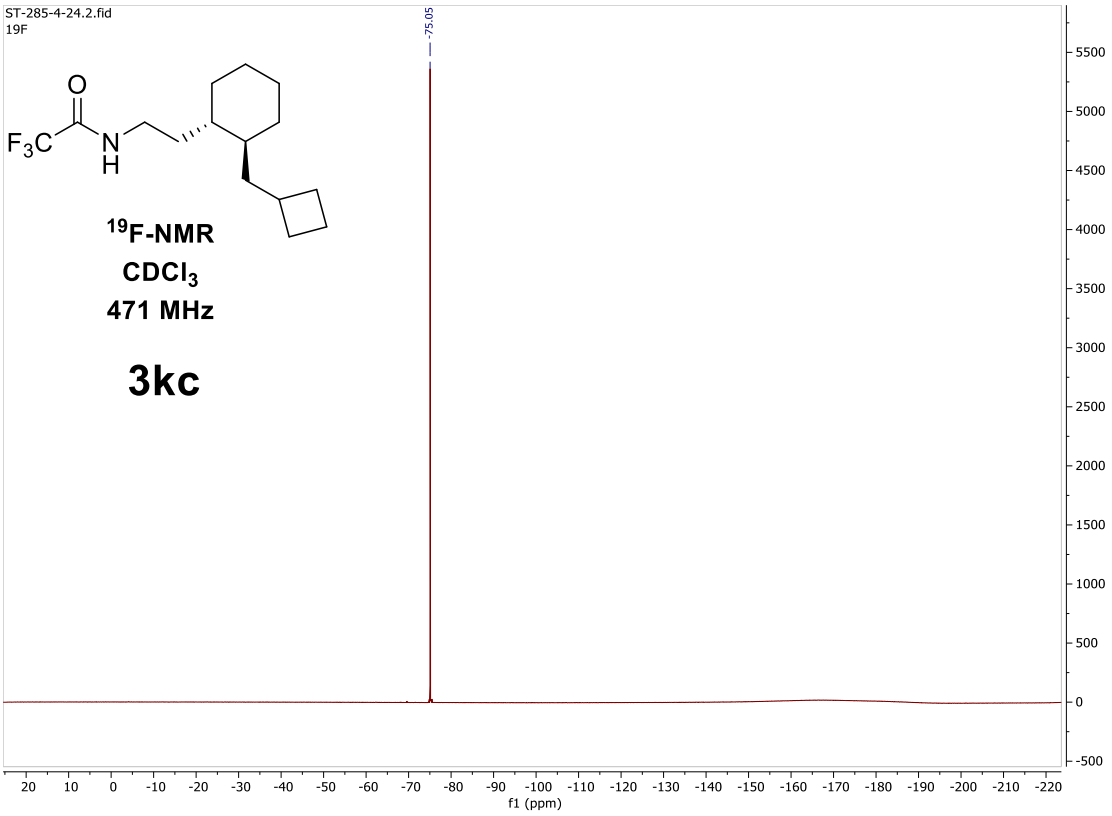

ST-230-5-iso.1.fid
proton
7.26 CDCl3
6.28
3.41
3.31
1.76
1.70
1.52
1.39
1.30
0.99
0.97
0.84
0.82
^{1}H-NMR
$CDCl_3$
400 MHz
3kb
0.95
2.18
5.01
2.02
1.28
4.08
2.93
2.93
f1 (ppm)

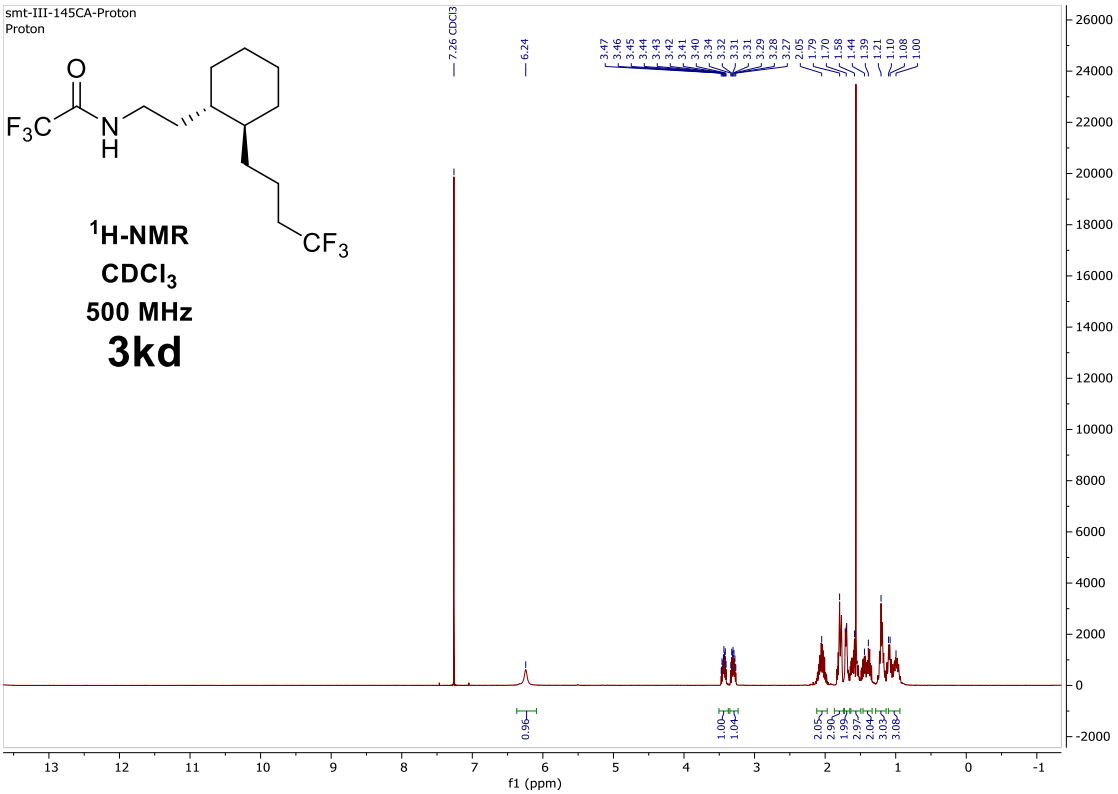

ST-230-5-carbon-overnight.2.fid
Carbon 13
157.70
157.41
157.11
156.82
119.49
117.20
114.91
112.62
77.20 CDCl3
42.66
38.97
38.07
33.20
32.23
31.86
31.02
26.25
26.20
25.76
10.62
Me
13C-NMR
CDCl3
126 MHz
3kb
f1 (ppm)

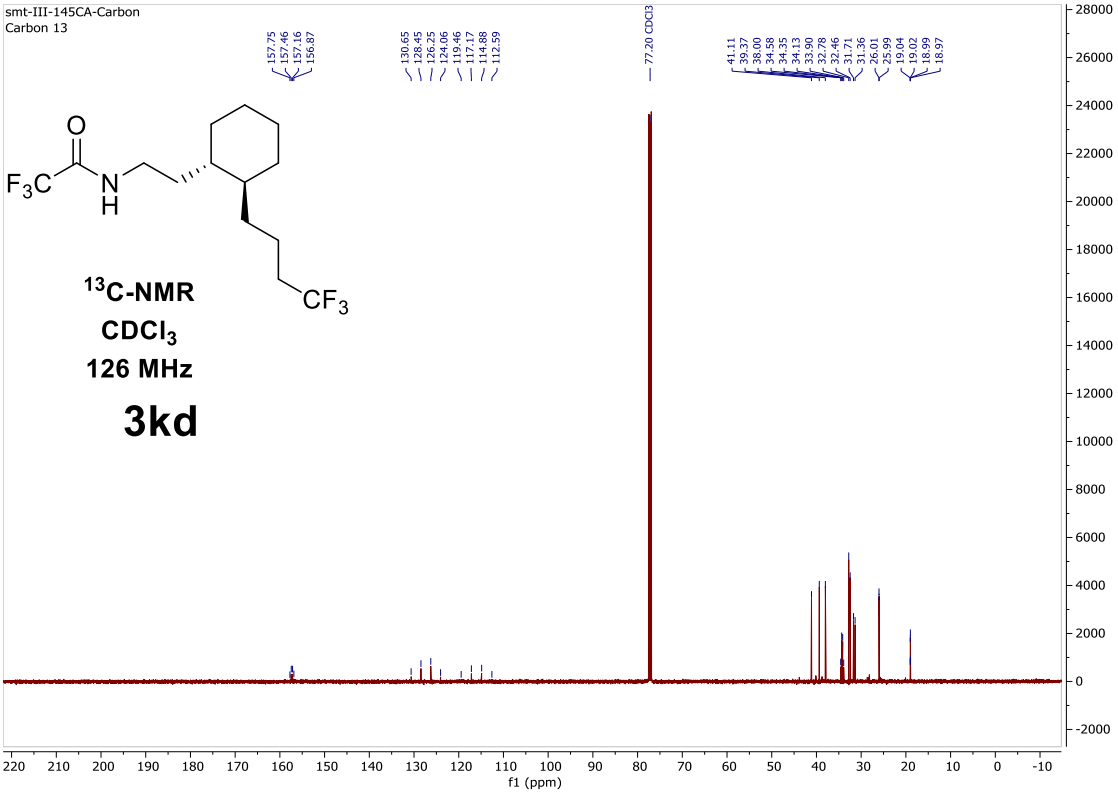

ST-230-5-iso.2.fid
F19
-75.99
-76.01
Me
19F-NMR
CDCl3
376 MHz
3kb
f1 (ppm)

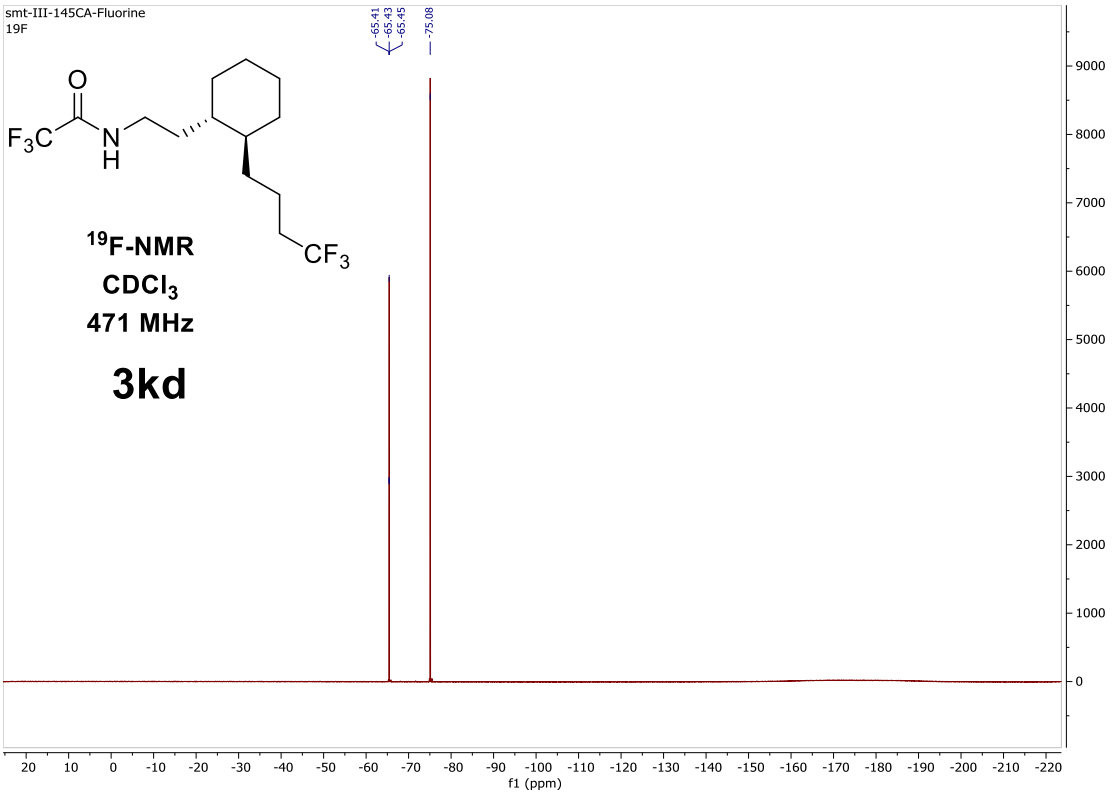

ST-285-4-24.1.fid
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3kc
f1 (ppm)

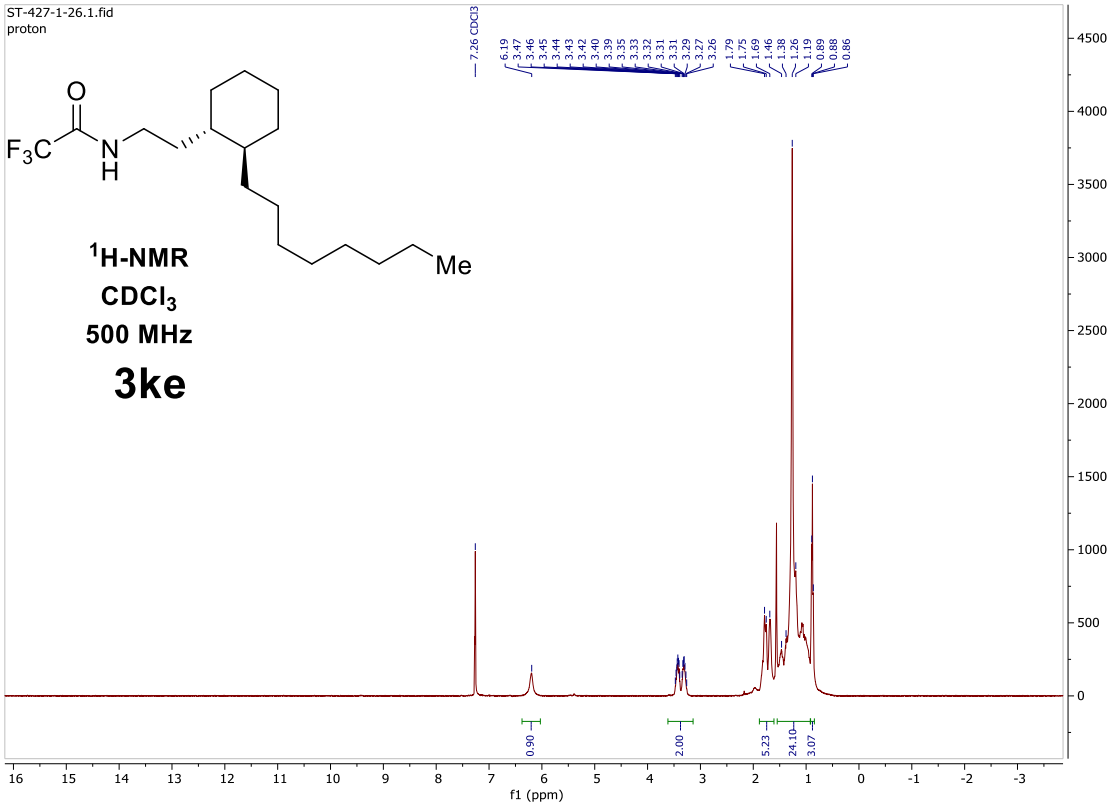

ST-285-4-24.2.fid
^{13}C-NMR
$CDCl_3$
101 MHz
3kc
f1 (ppm)

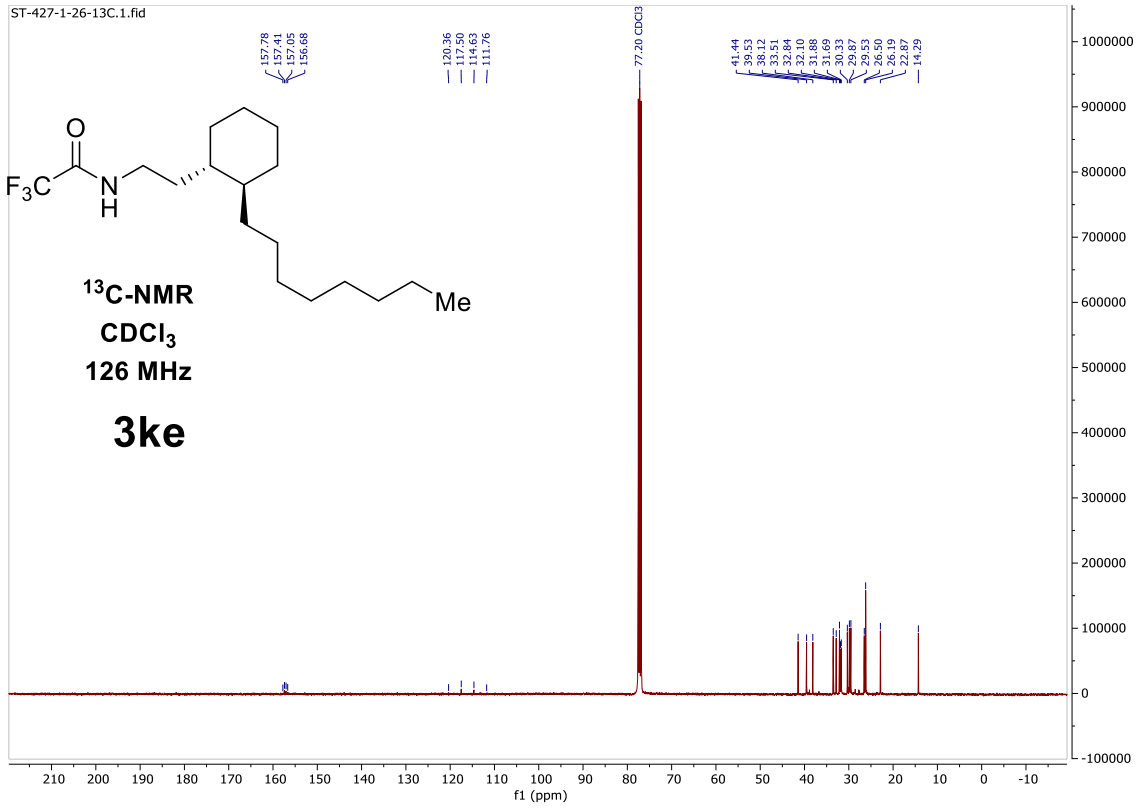

ST-285-4-24.2.fid
19F
-75.05
O
F3C
N
H
19F-NMR
CDCl3
471 MHz
3kc
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

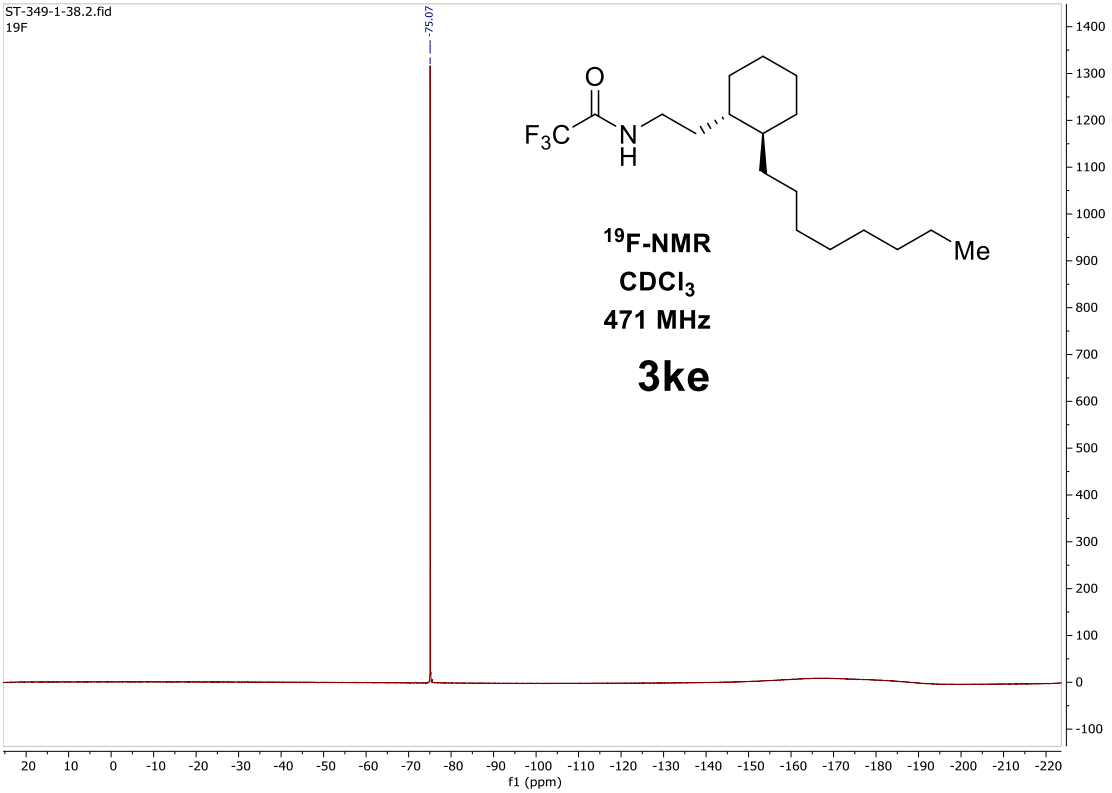

smt-III-145CA-Proton
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3kd
f1 (ppm)

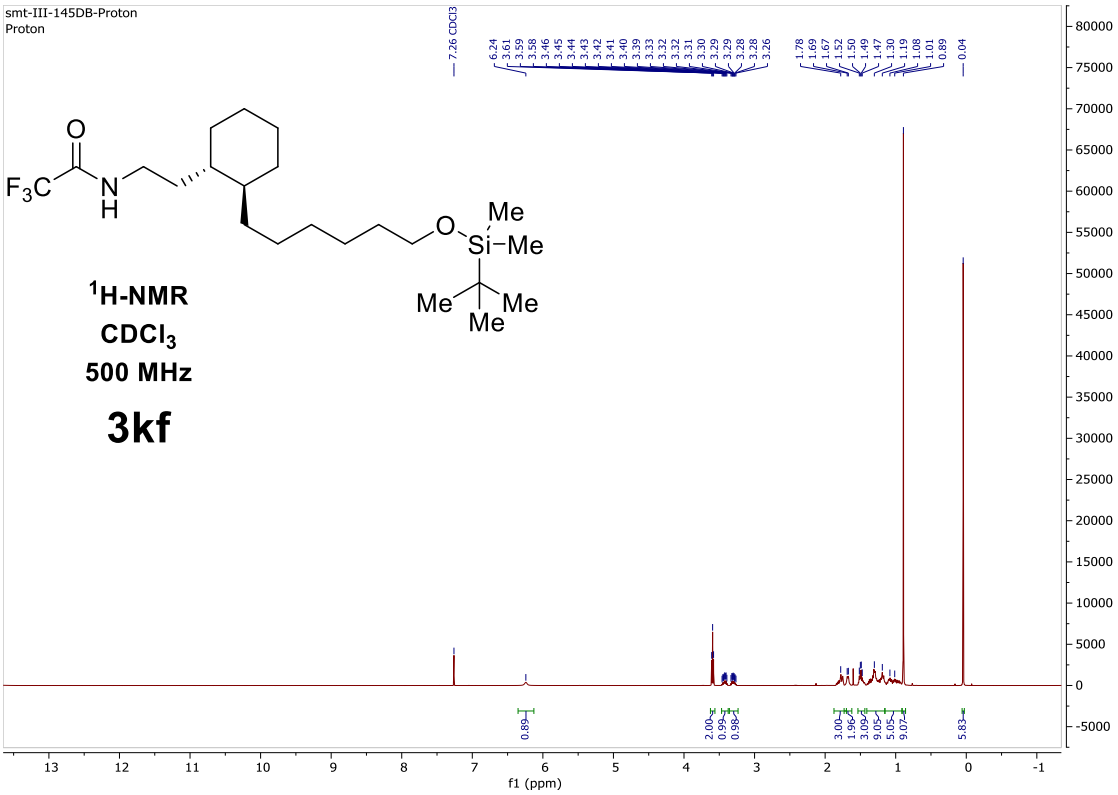

smt-III-145CA-Carbon
Carbon 13
^{13}C-NMR
$CDCl_3$
126 MHz
3kd
f1 (ppm)

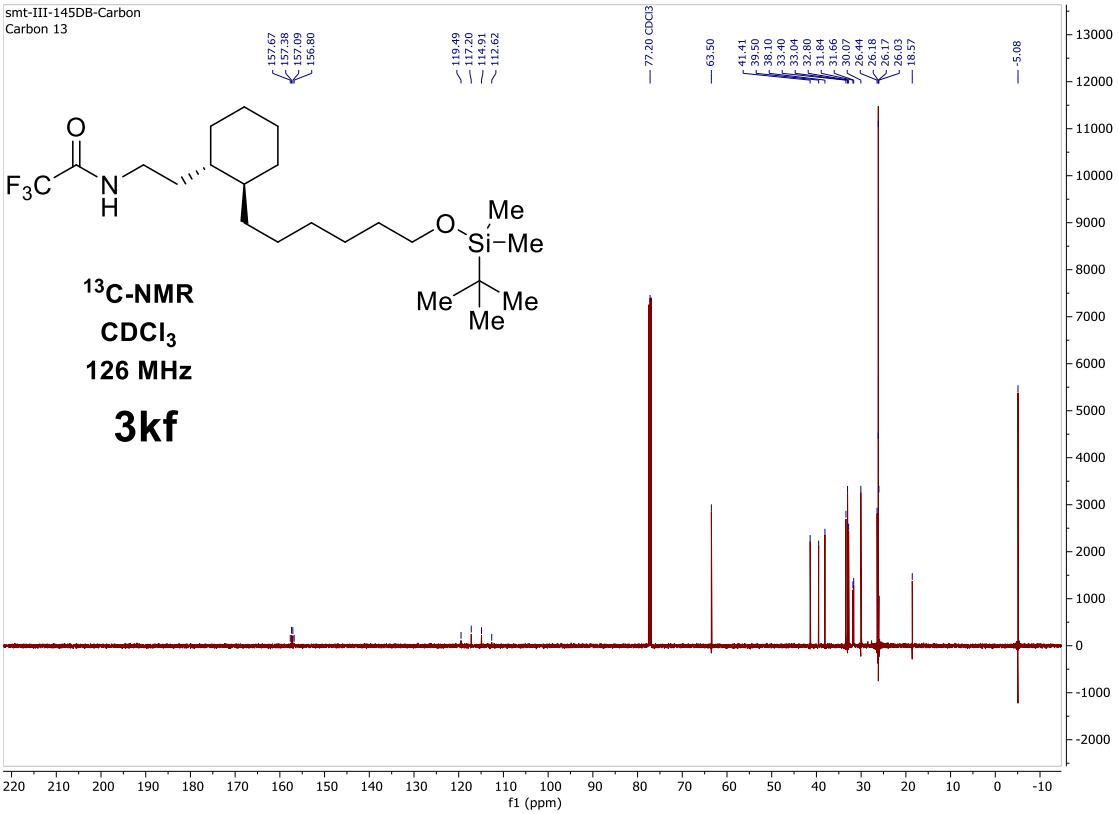

smt-III-145CA-Fluorine
19F
-65.41
-65.43
-65.45
-75.08
F3C
O
N
H
CF3
19F-NMR
CDCl3
471 MHz
3kd
f1 (ppm)

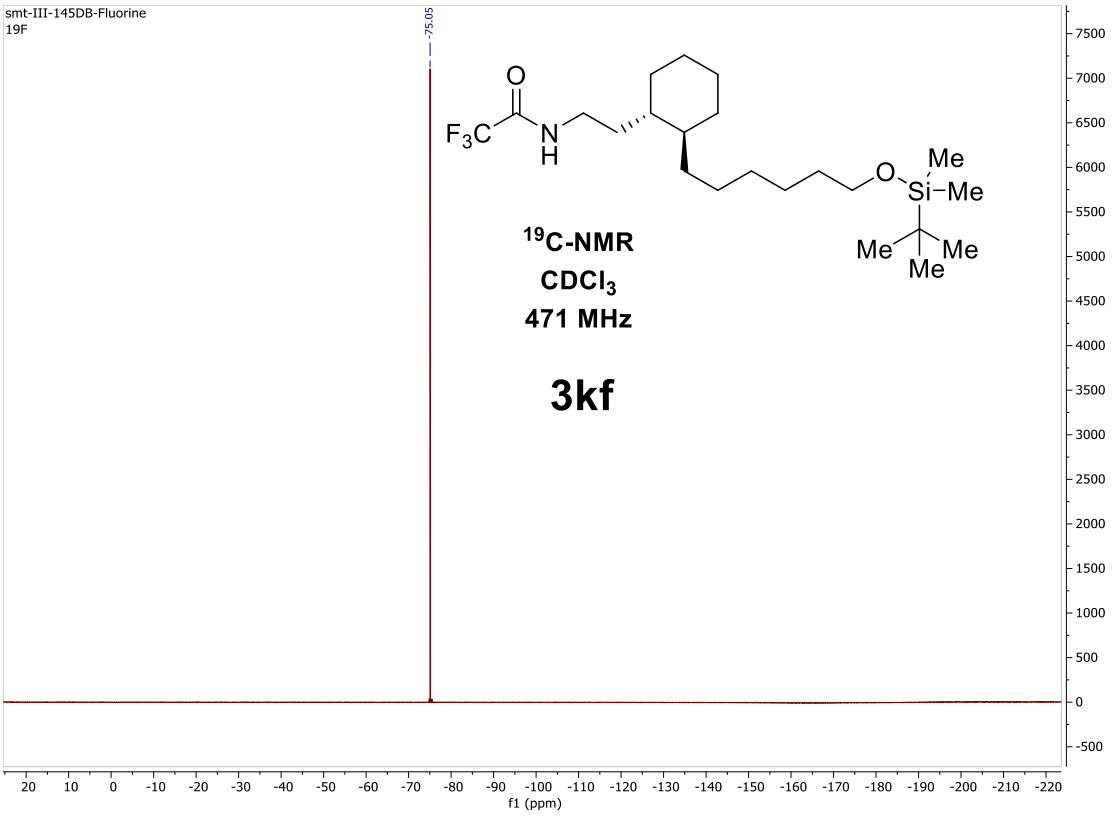

ST-427-1-26.1.fid
proton
7.26 CDCl3
6.19
3.47
3.46
3.45
3.44
3.43
3.42
3.40
3.39
3.35
3.33
3.32
3.31
3.31
3.29
3.27
3.26
1.79
1.75
1.69
1.46
1.38
1.26
1.19
0.89
0.88
0.86
F3C
O
N
H
Me
1H-NMR
CDCl3
500 MHz
3ke
0.90
2.00
5.23
24.10
3.07
f1 (ppm)

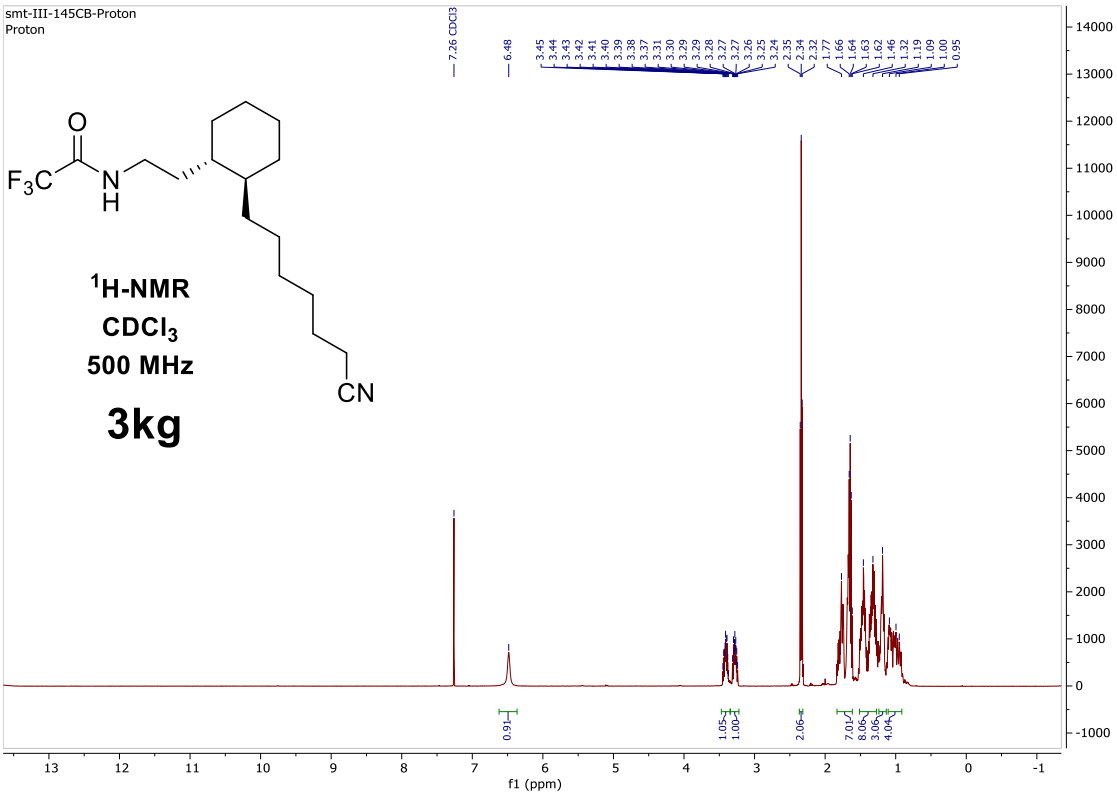

ST-427-1-26-13C.1.fid
157.78
157.41
157.05
156.68
120.36
117.50
114.63
111.76
77.20 CDCl3
41.44
39.53
39.12
33.51
32.84
32.10
31.88
31.69
30.33
29.87
29.53
26.50
26.19
22.87
14.29
Me
13C-NMR
CDCl3
126 MHz
3ke
f1 (ppm)

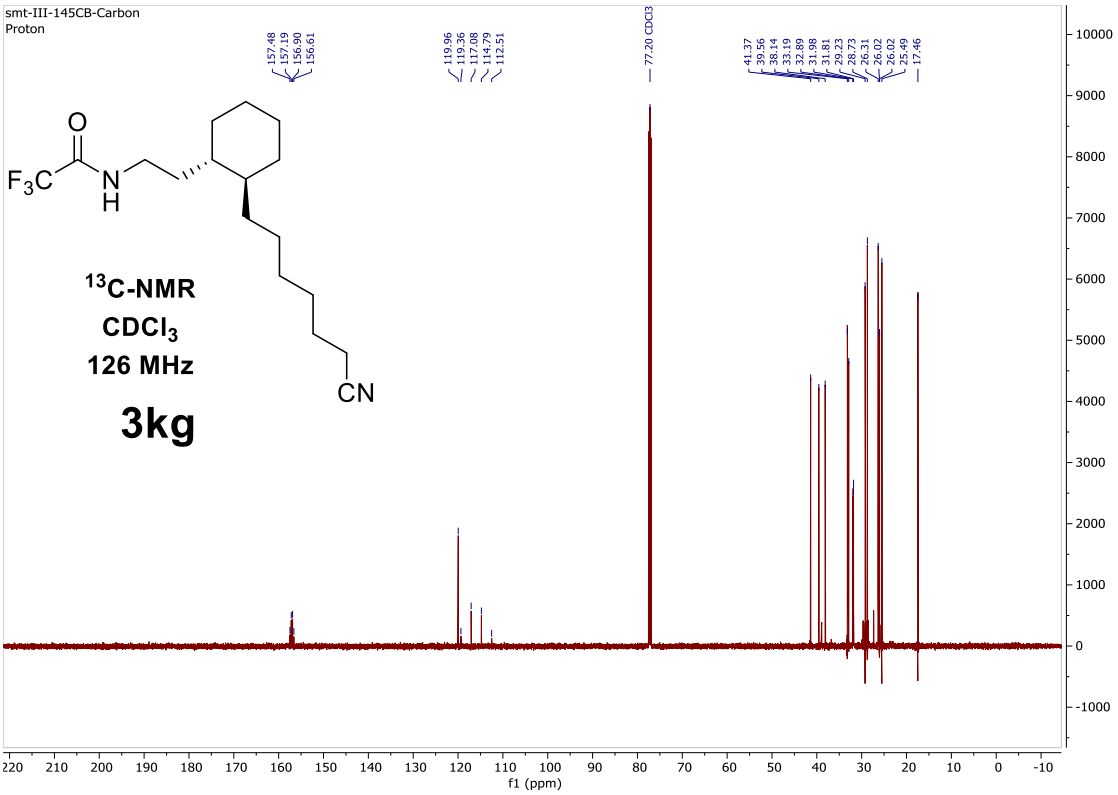

ST-349-1-38.2.fid
19F
-75.07
Me
19F-NMR
CDCl3
471 MHz
3ke
f1 (ppm)

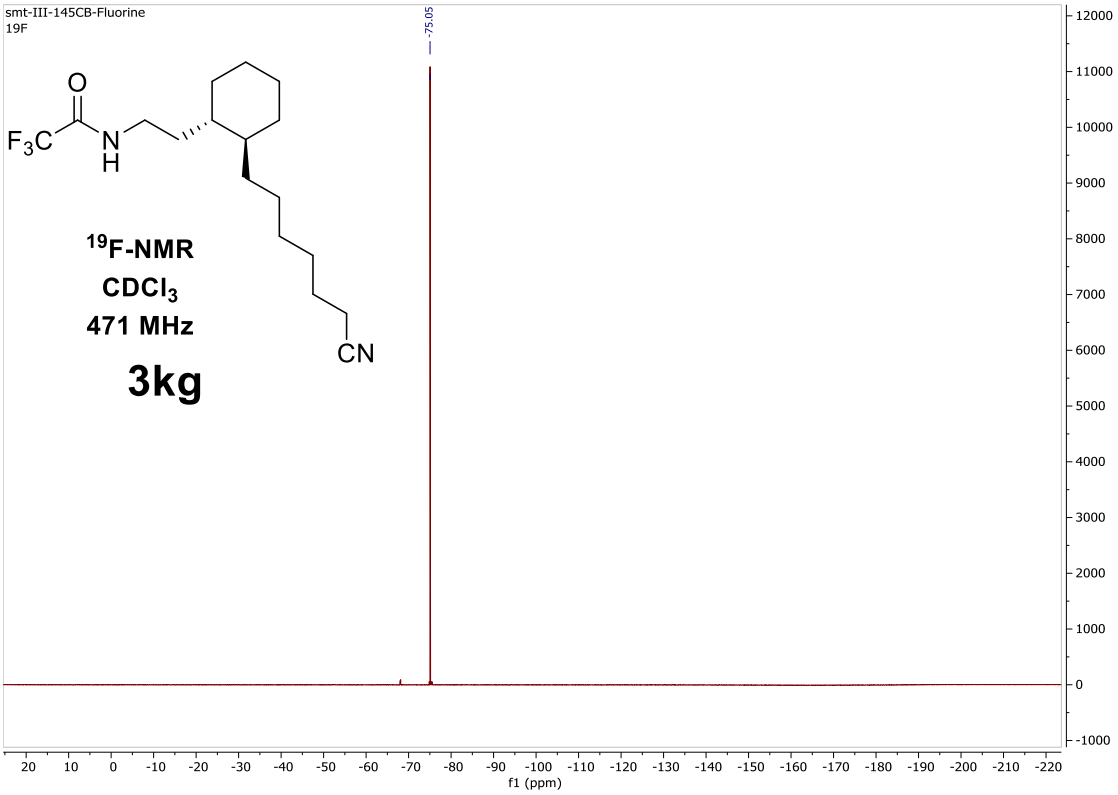

smt-III-145DB-Proton
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3kf
f1 (ppm)

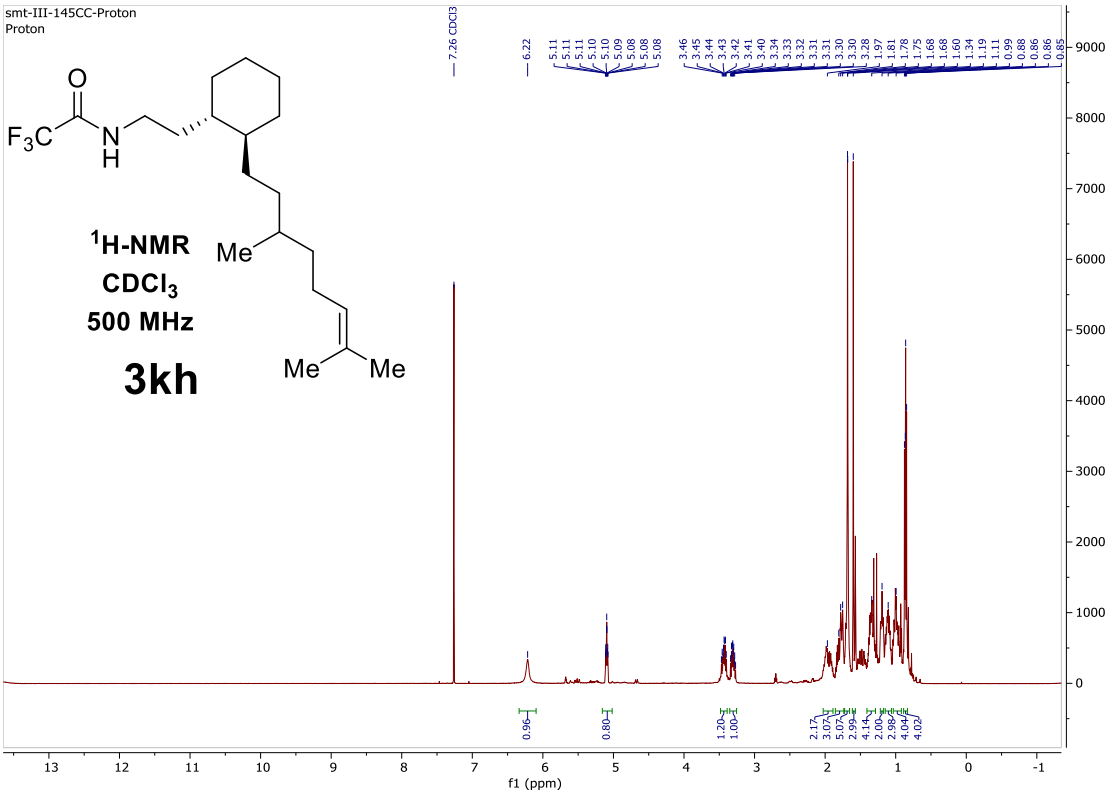

smt-III-145DB-Carbon
Carbon 13
^{13}C-NMR
$CDCl_3$
126 MHz
3kf
f1 (ppm)

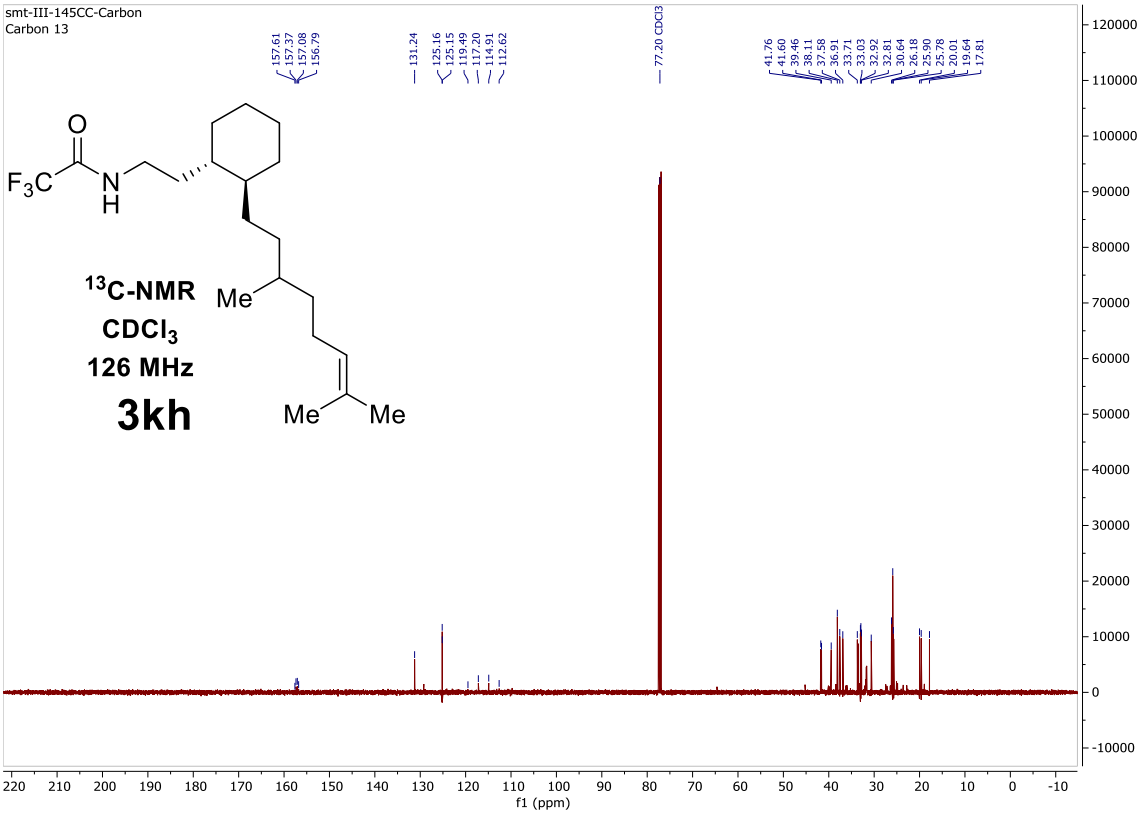

smt-III-145DB-Fluorine
19F
-75.05
^{19}C-NMR
$CDCl_3$
471 MHz
3kf
f1 (ppm)

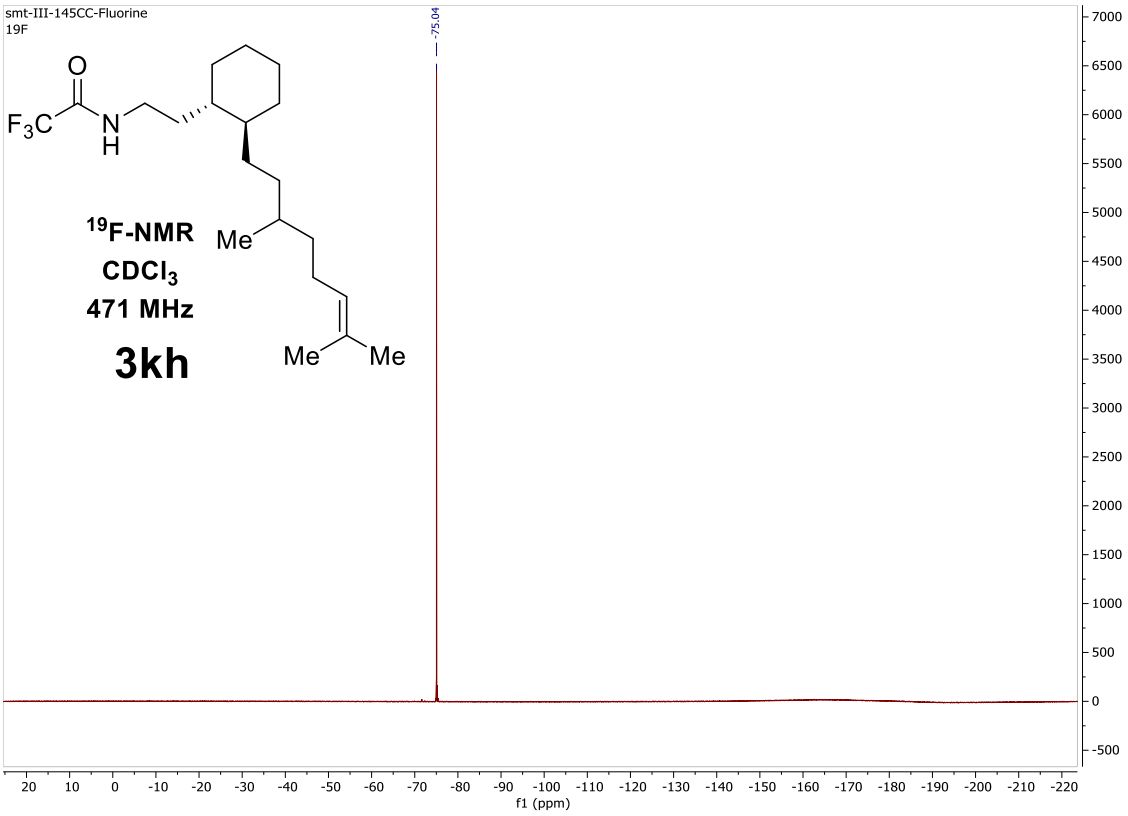

smt-III-145CB-Proton
Proton
7.26 CDCl3
6.48
^{1}H-NMR
$CDCl_3$
500 MHz
3kg
CN
f1 (ppm)

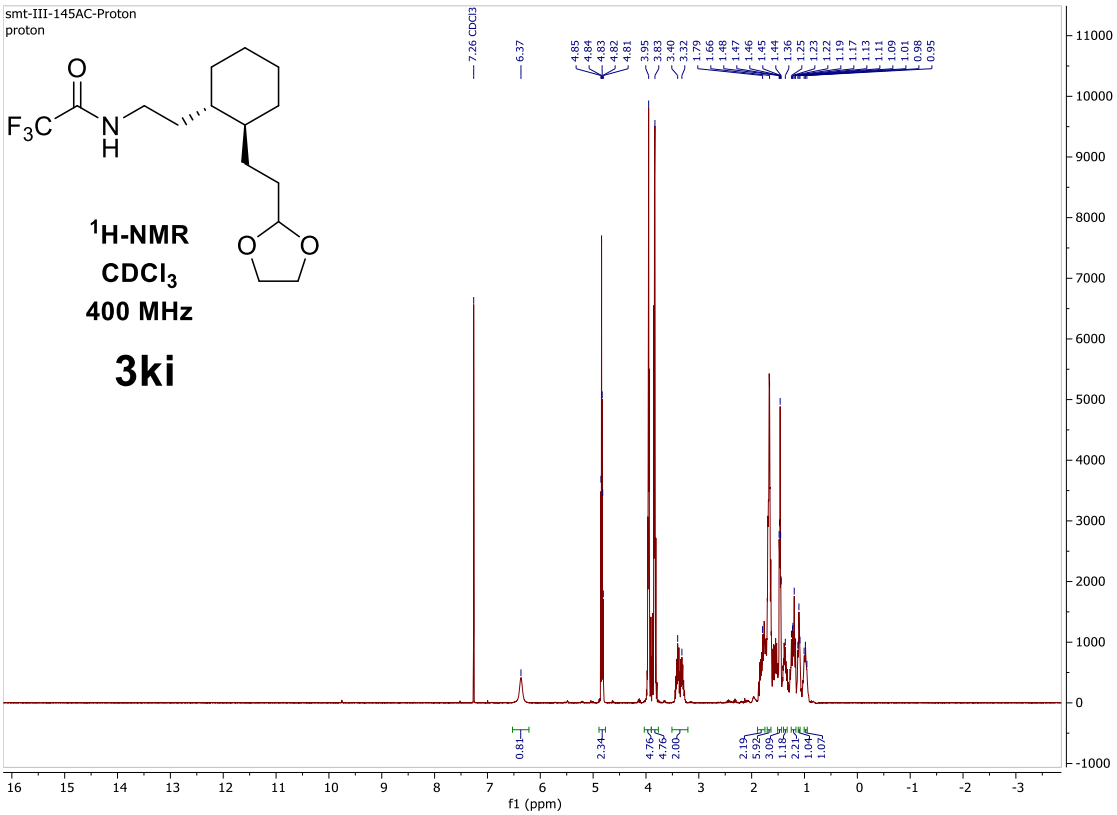

smt-III-145CB-Carbon
Proton
157.48
157.19
156.90
156.61
119.96
119.36
117.08
114.79
112.51
77.20 CDCl3
41.37
39.56
38.14
33.19
32.89
31.98
31.81
29.23
28.73
26.31
26.02
26.02
25.49
17.46
O
F3C
N
H
CN
13C-NMR
CDCl3
126 MHz
3kg
f1 (ppm)

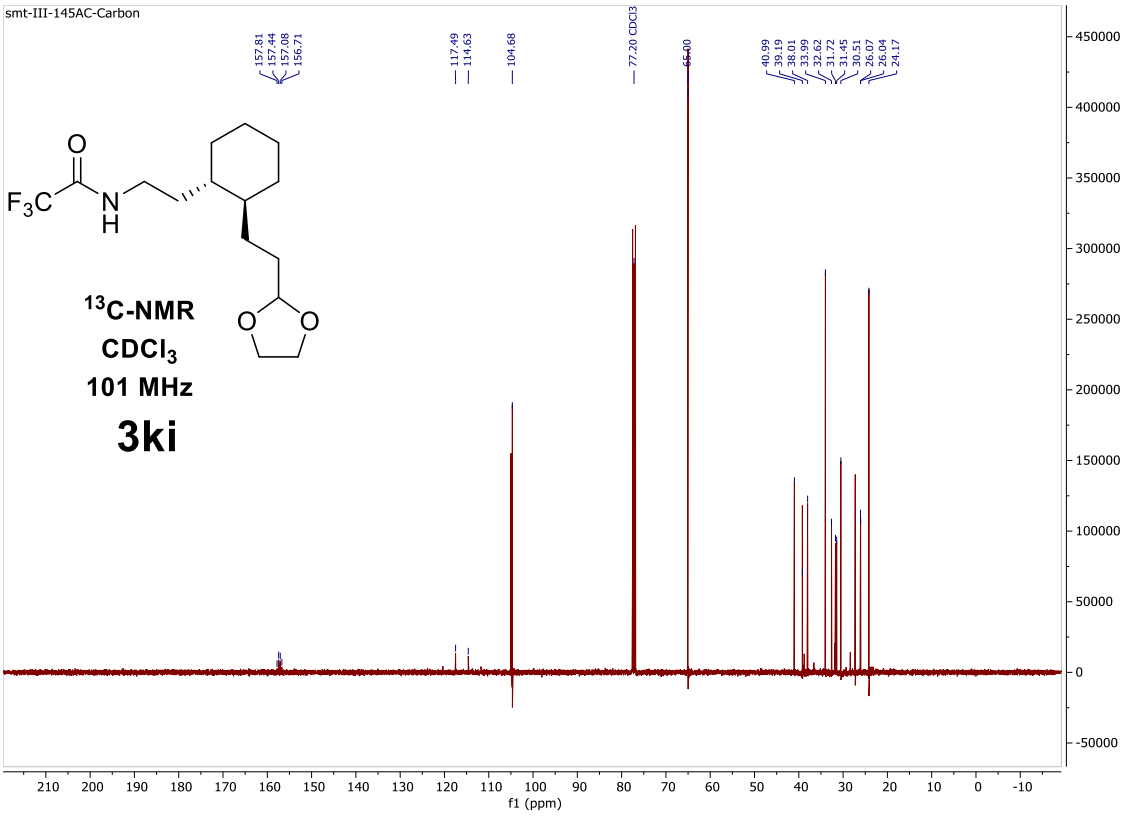

smt-III-145CB-Fluorine
19F
-75.05
O
F3C
N
H
CN
19F-NMR
CDCl3
471 MHz
3kg
f1 (ppm)

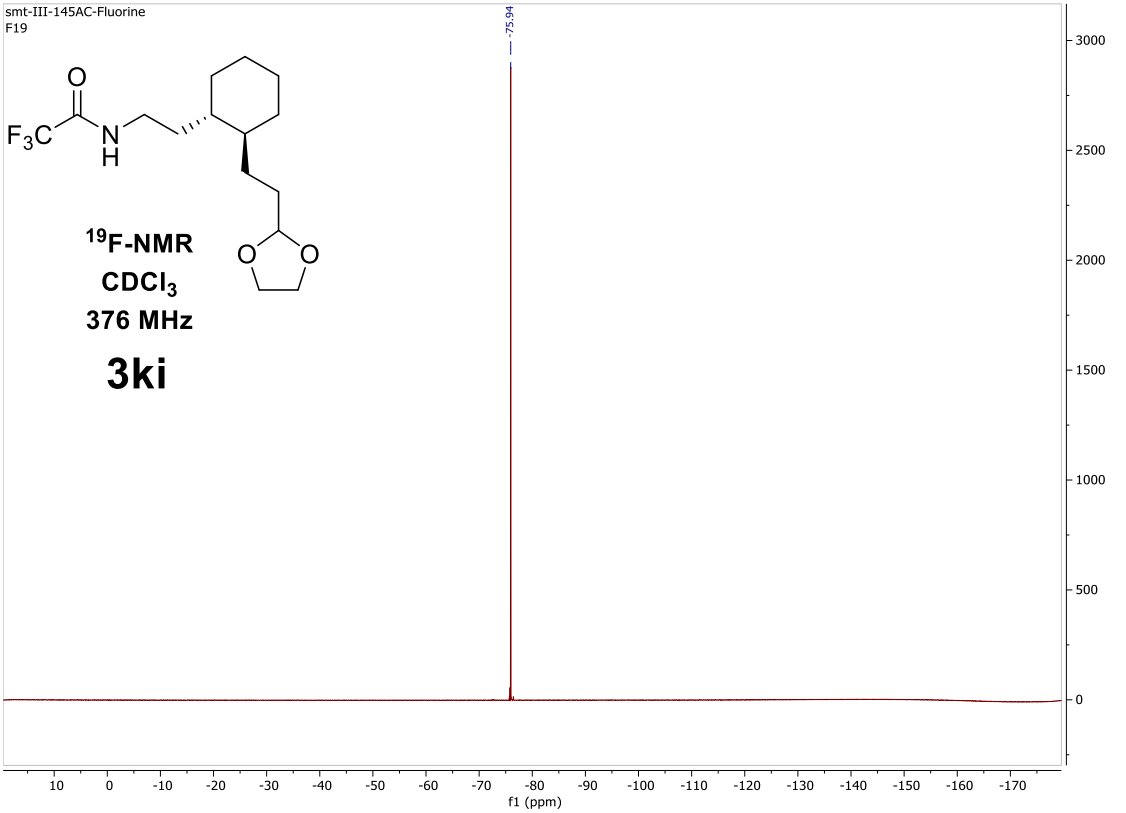

smt-III-145CC-Proton
Proton
7.26 CDCl3
6.22
f1 (ppm)
1H-NMR
CDCl3
500 MHz
3kh

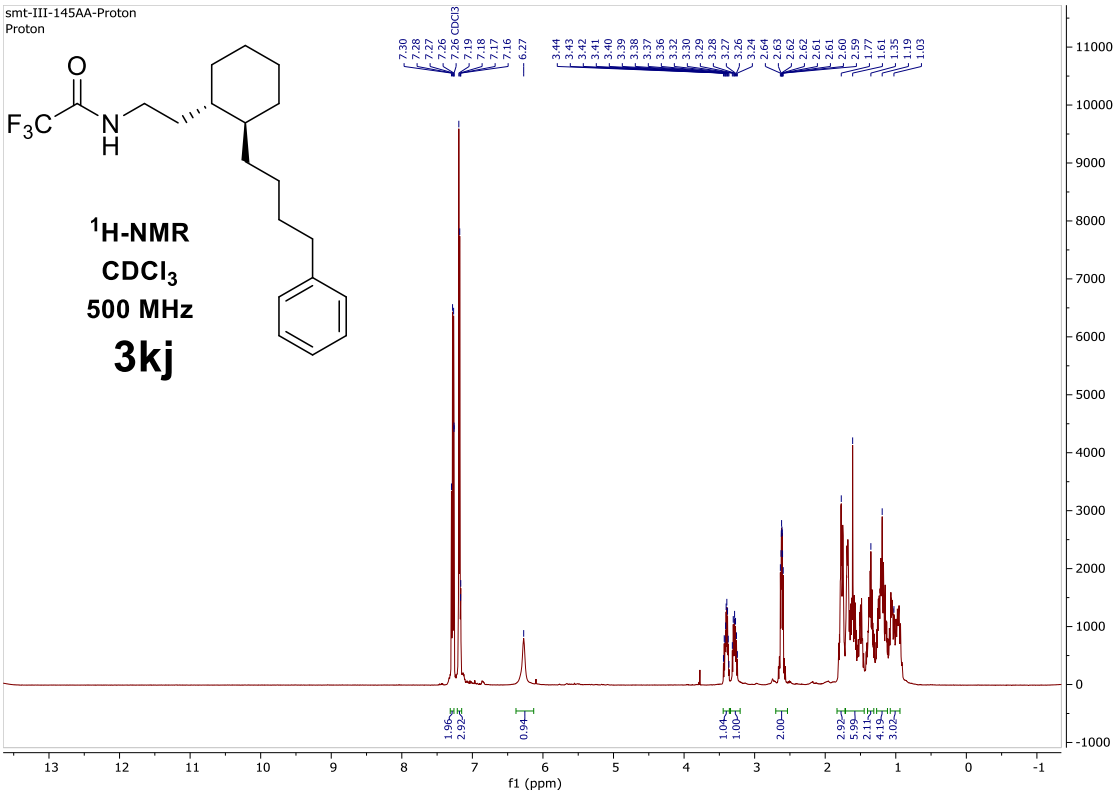

smt-III-145CC-Carbon
Carbon 13
157.61
157.37
157.08
156.79
131.24
125.16
125.15
119.49
117.20
114.91
112.62
77.20 CDCl3
41.76
41.60
39.46
38.11
37.58
36.91
33.71
33.23
32.92
32.81
30.64
26.18
25.90
25.78
20.01
19.64
17.81
f1 (ppm)
13C-NMR
CDCl3
126 MHz
3kh

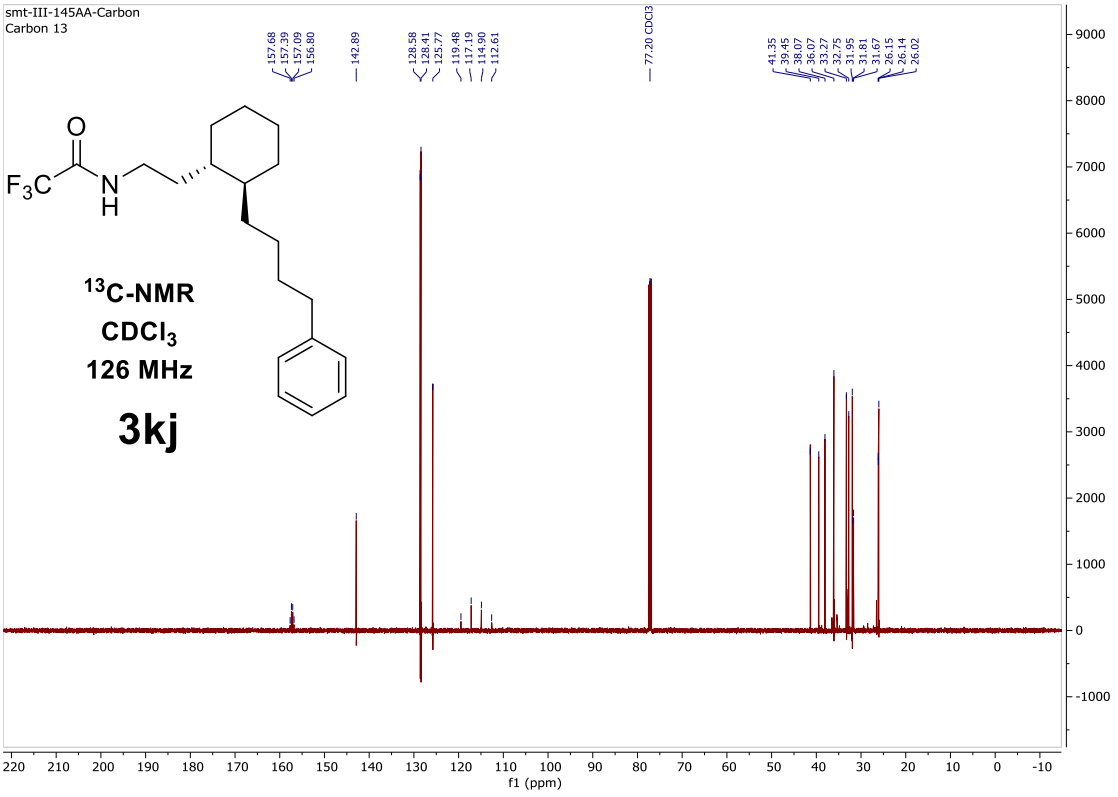

smt-III-145CC-Fluorine
19F
-75.04
^{19}F-NMR
$CDCl_3$
471 MHz
3kh
f1 (ppm)

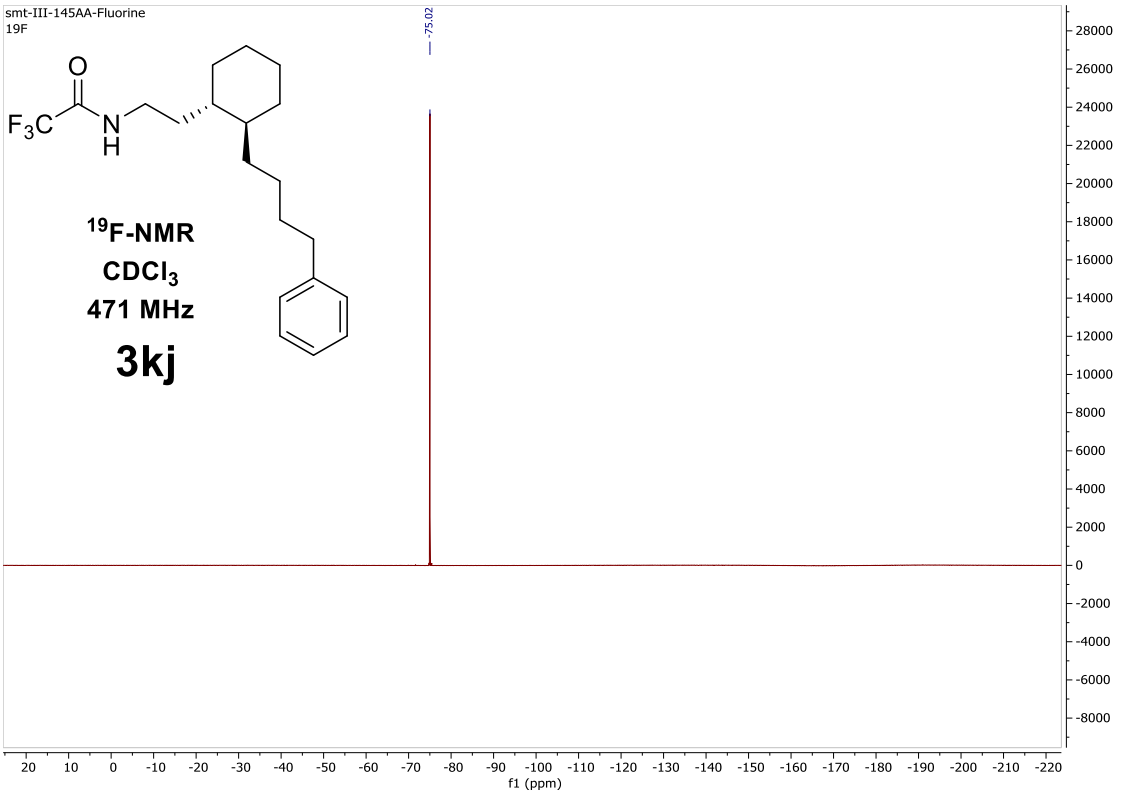

smt-III-145AC-Proton
proton
7.26 CDCl3
6.37
^{1}H-NMR
$CDCl_3$
400 MHz
3ki
f1 (ppm)

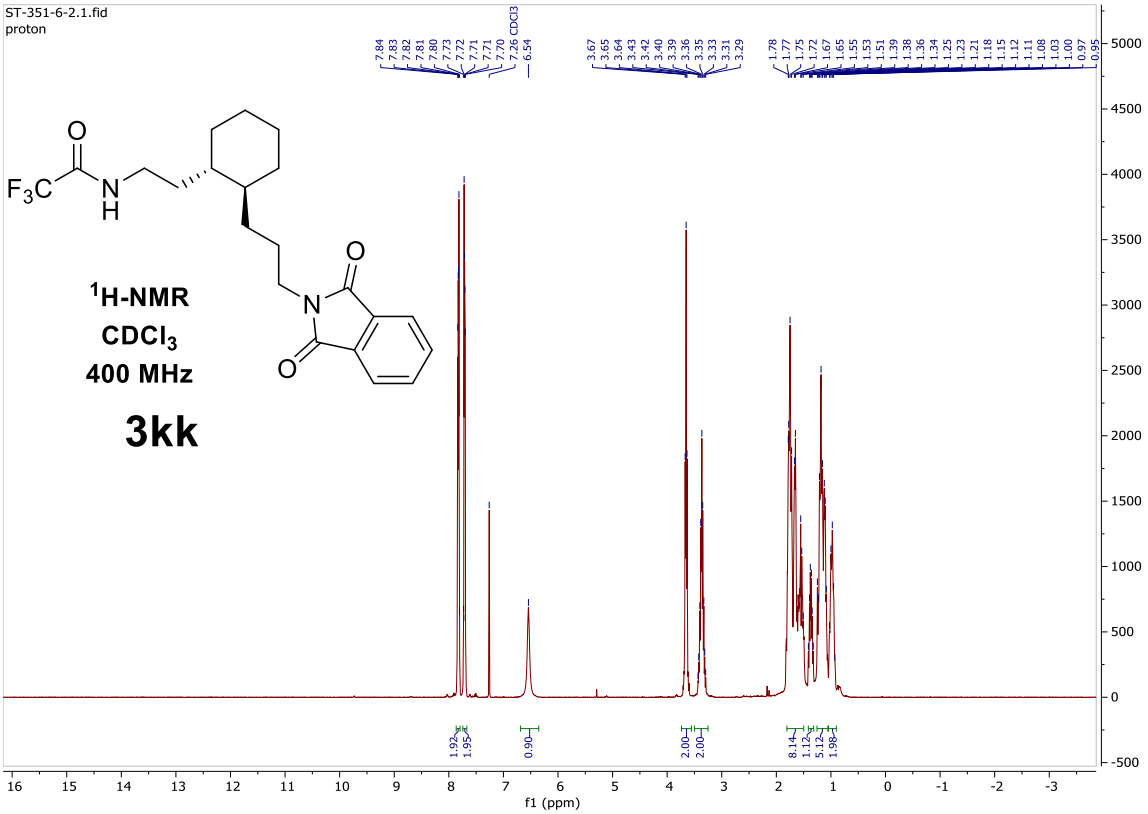

smt-III-145AC-Carbon
157.81
157.44
157.08
156.71
117.49
114.63
104.68
77.20 CDCl3
65.00
40.99
39.19
38.01
33.99
32.62
31.72
31.45
30.51
26.07
26.04
24.17
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O
F3C
N
H
O
O
13C-NMR
CDCl3
101 MHz
3ki

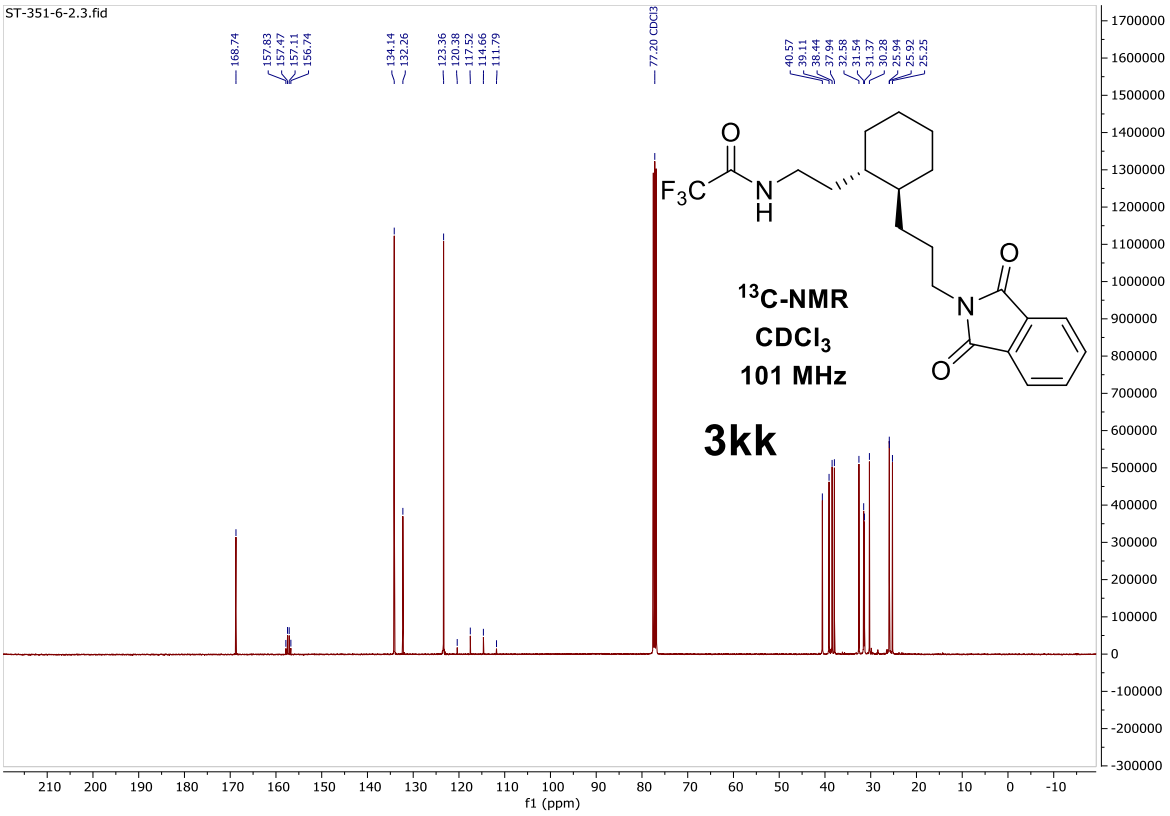

smt-III-145AC-Fluorine
F19
-75.94
3000
2500
2000
1500
1000
500
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)
O
F3C
N
H
O
O
19F-NMR
CDCl3
376 MHz
3ki

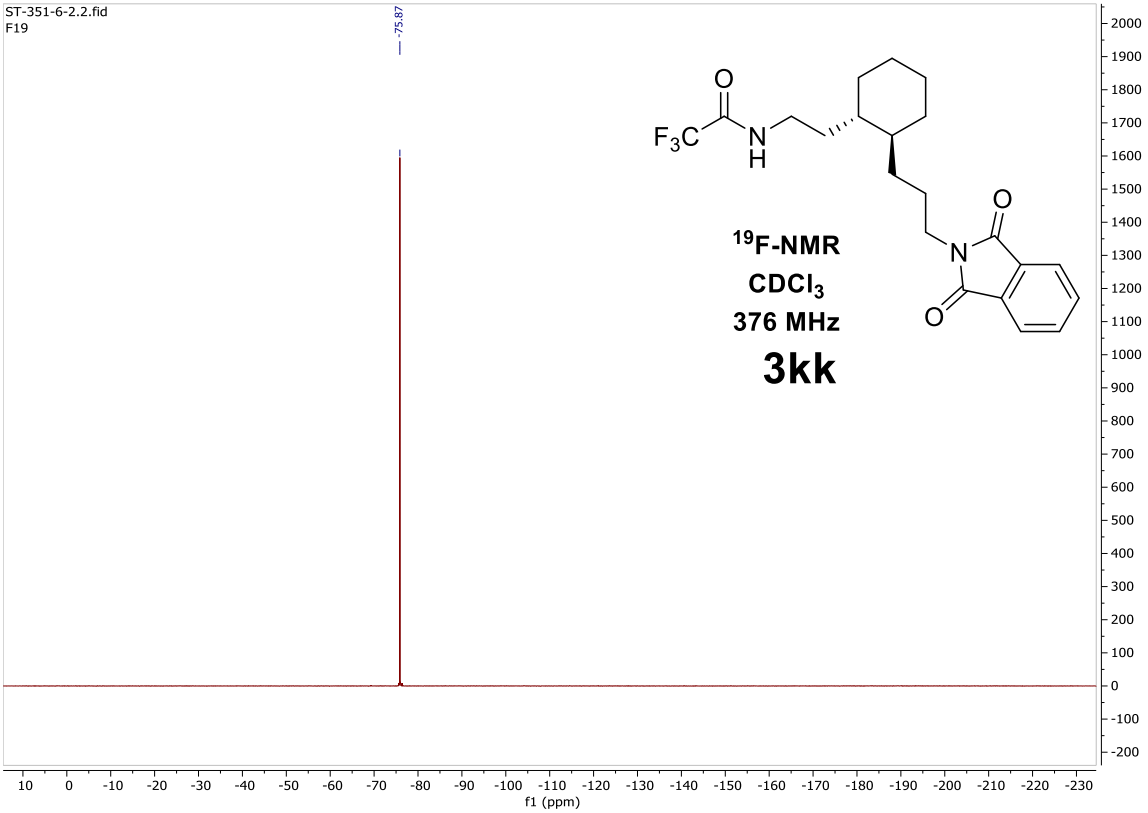

smt-III-145AA-Proton
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3kj
f1 (ppm)

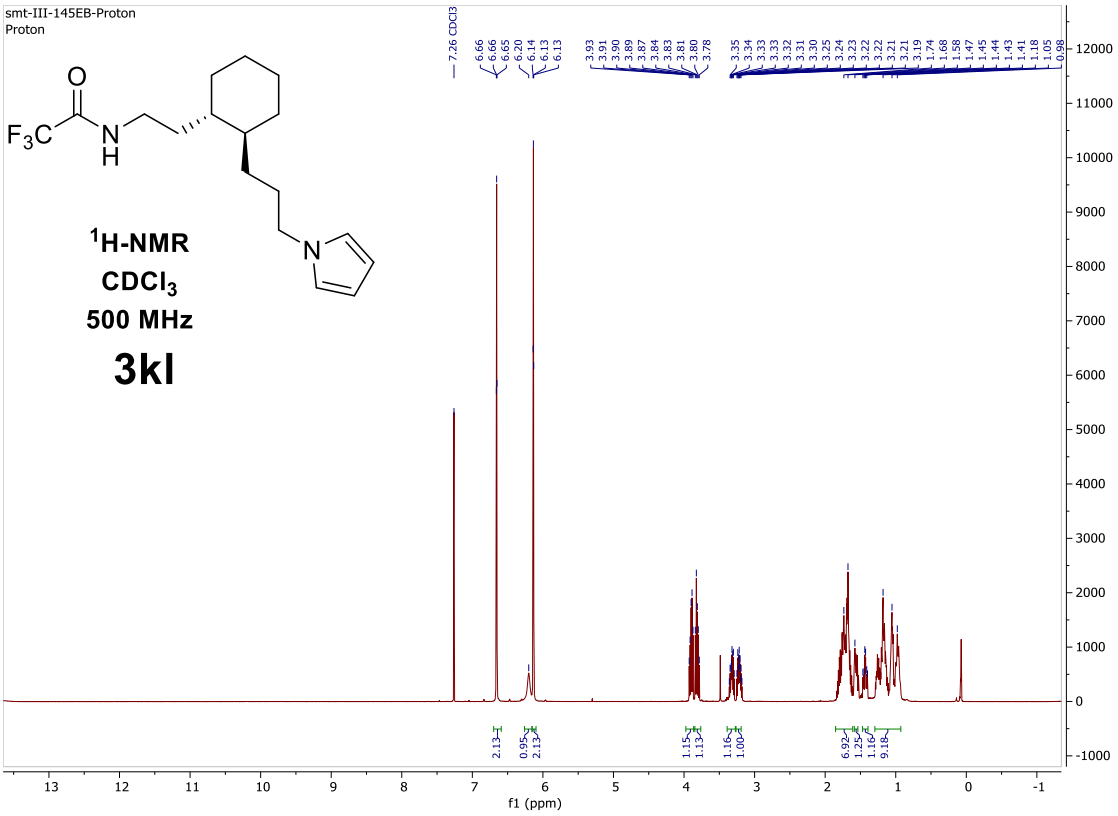

smt-III-145AA-Carbon
Carbon 13
^{13}C-NMR
$CDCl_3$
126 MHz
3kj
f1 (ppm)

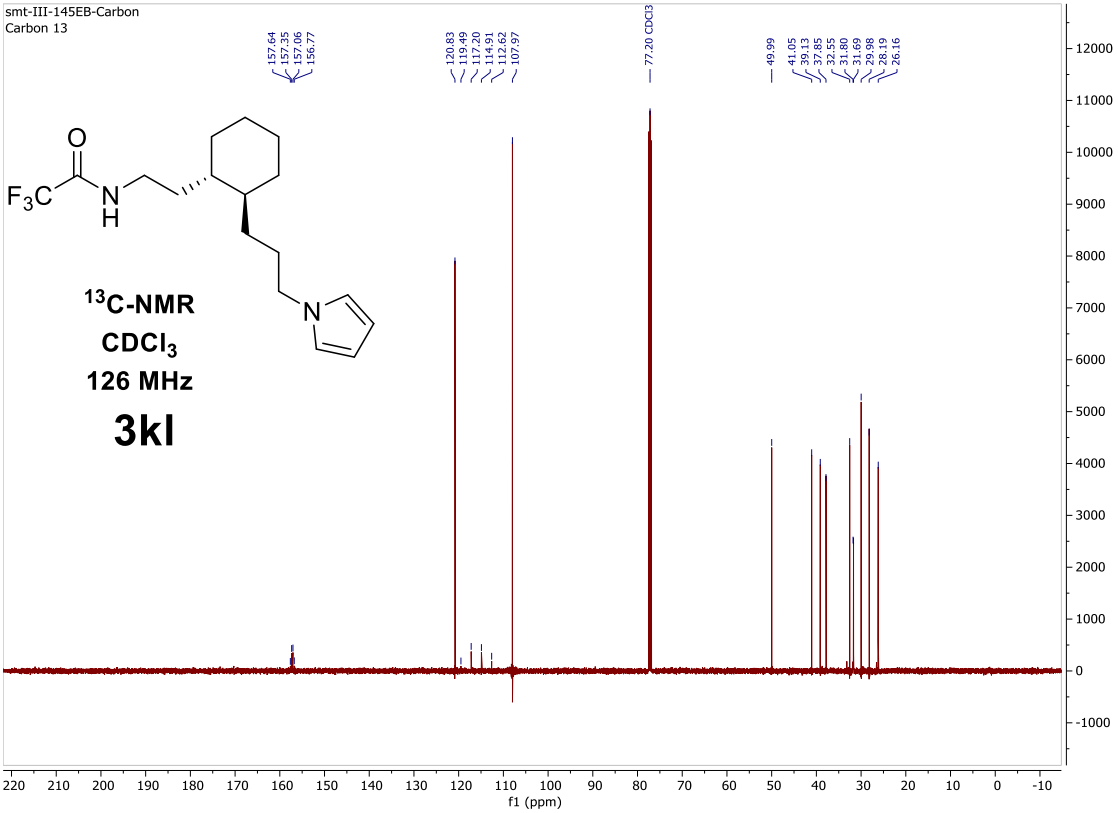

smt-III-145AA-Fluorine
19F
-75.02
^{19}F-NMR
$CDCl_3$
471 MHz
3kj
f1 (ppm)

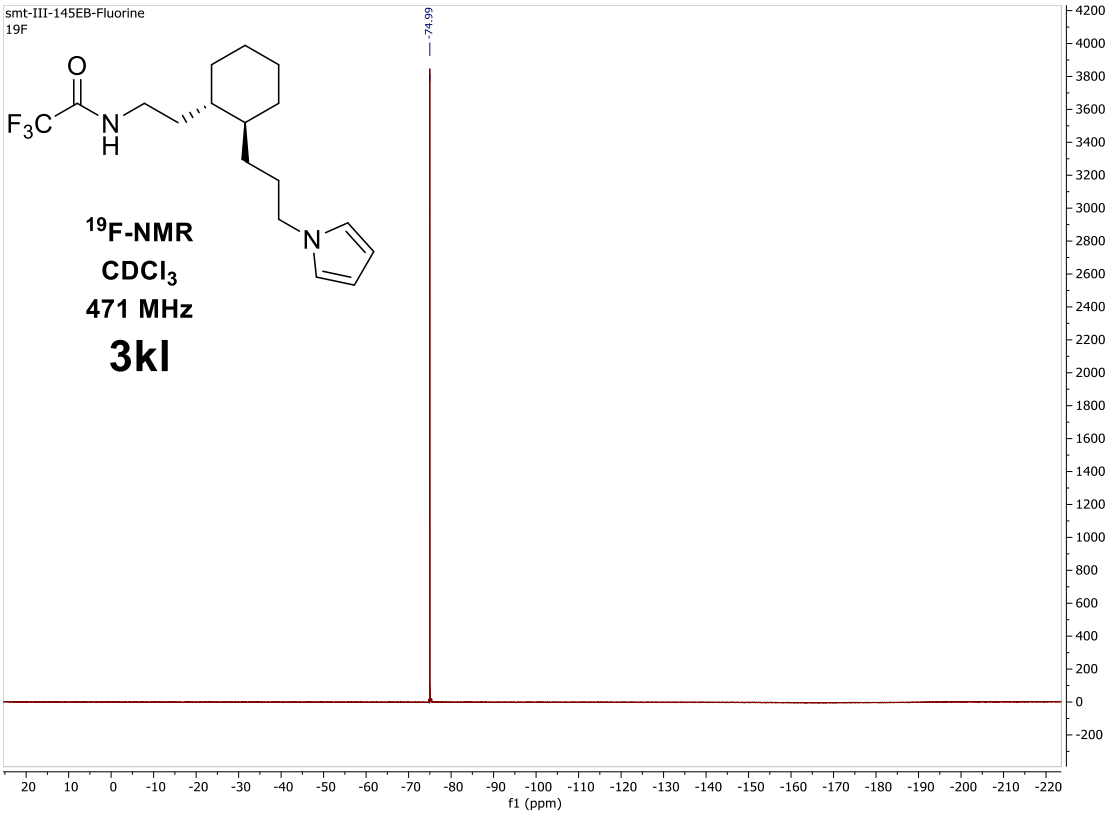

ST-351-6-2.1.fid
proton
^{1}H-NMR
$CDCl_3$
400 MHz
3kk
f1 (ppm)

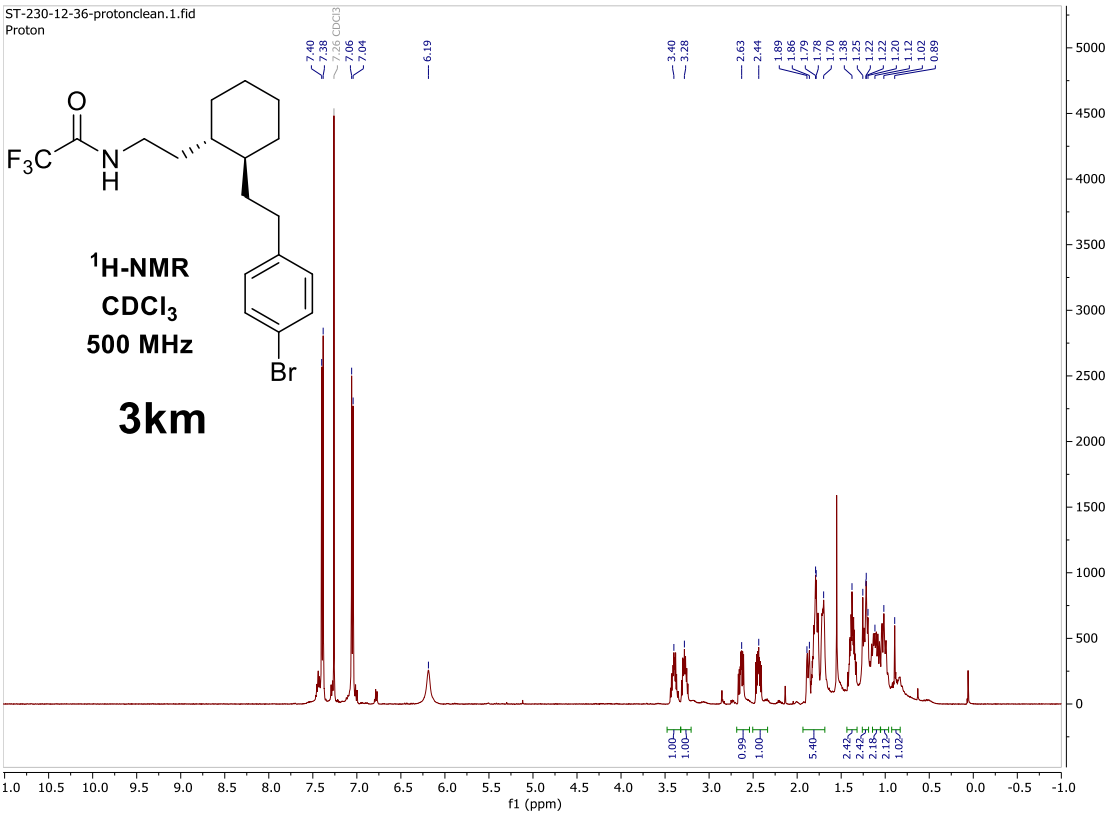

ST-351-6-2.3.fid
168.74
157.83
157.47
157.11
156.74
134.14
132.26
123.36
120.38
117.52
114.66
111.79
77.20 CDCl3
40.57
39.11
38.44
37.94
32.58
31.54
31.37
30.28
25.94
25.92
25.25
F3C
N
H
O
O
N
O
13C-NMR
CDCl3
101 MHz
3kk
f1 (ppm)

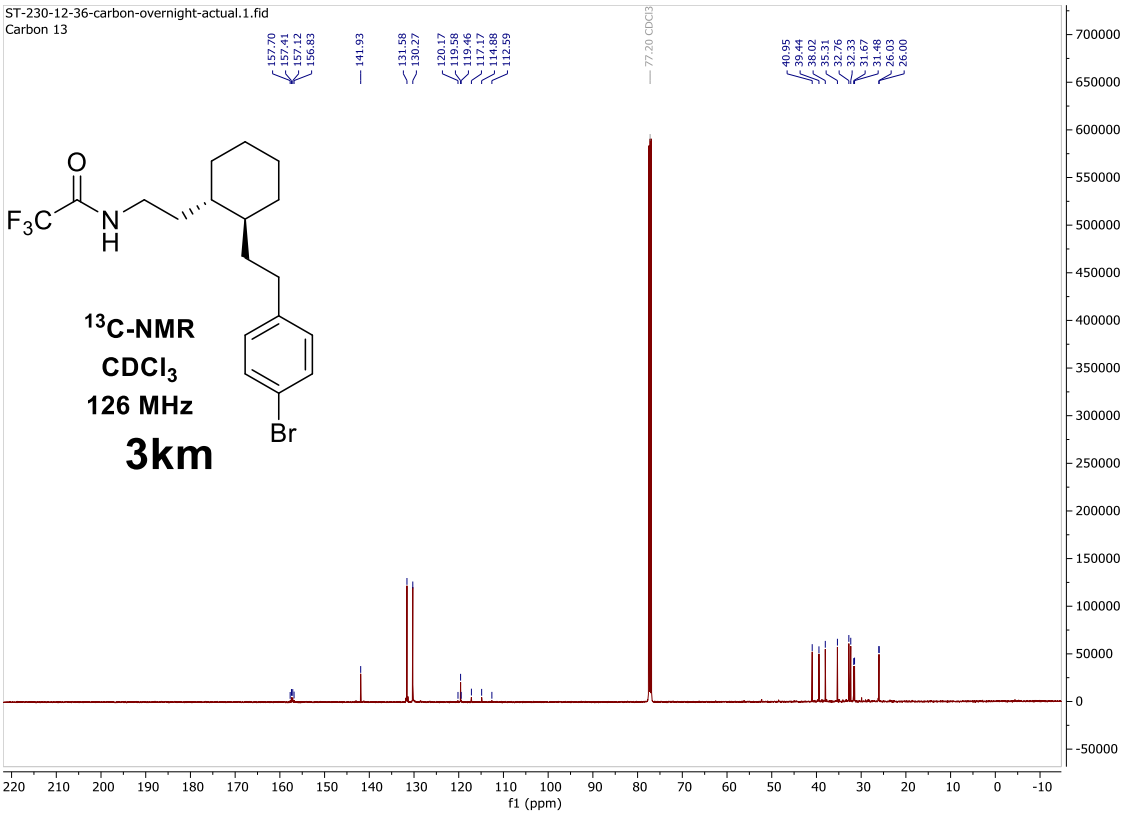

ST-351-6-2.2.fid
F19
-75.87
F3C
N
H
O
O
N
O
19F-NMR
CDCl3
376 MHz
3kk
f1 (ppm)

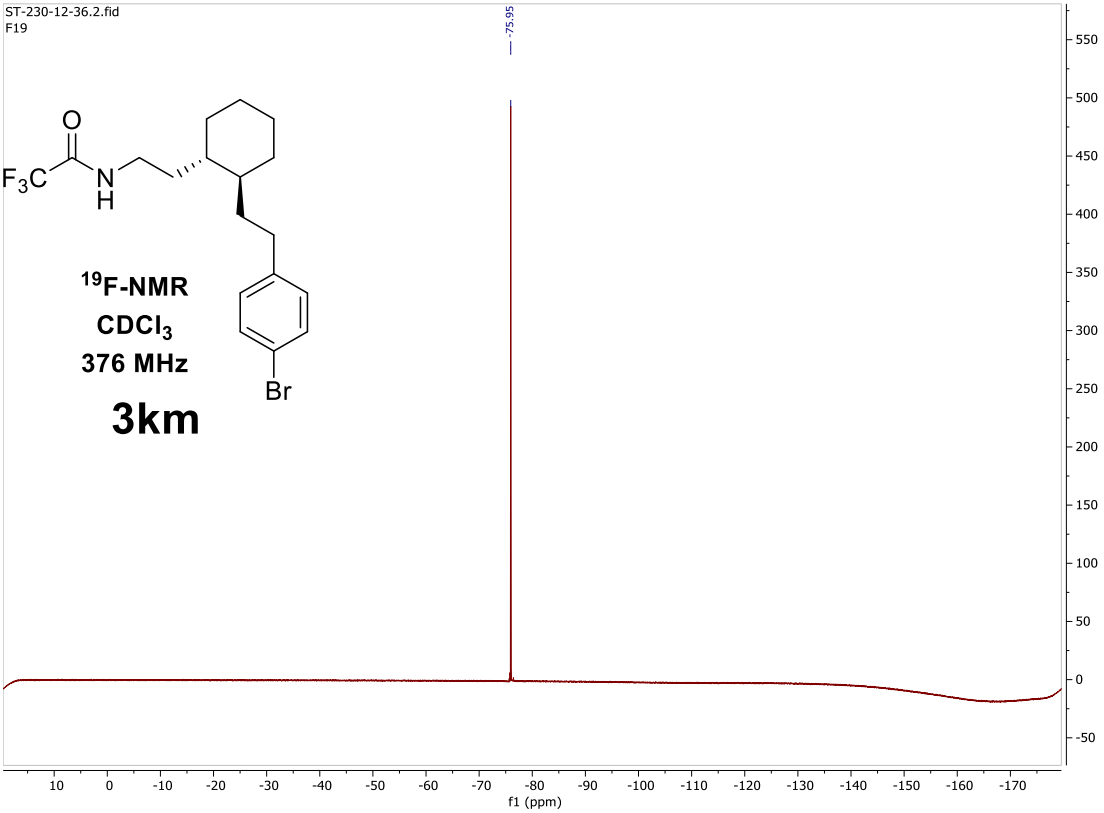

smt-III-145EB-Proton
Proton
^{1}H-NMR
$CDCl_3$
500 MHz
3kl
f1 (ppm)

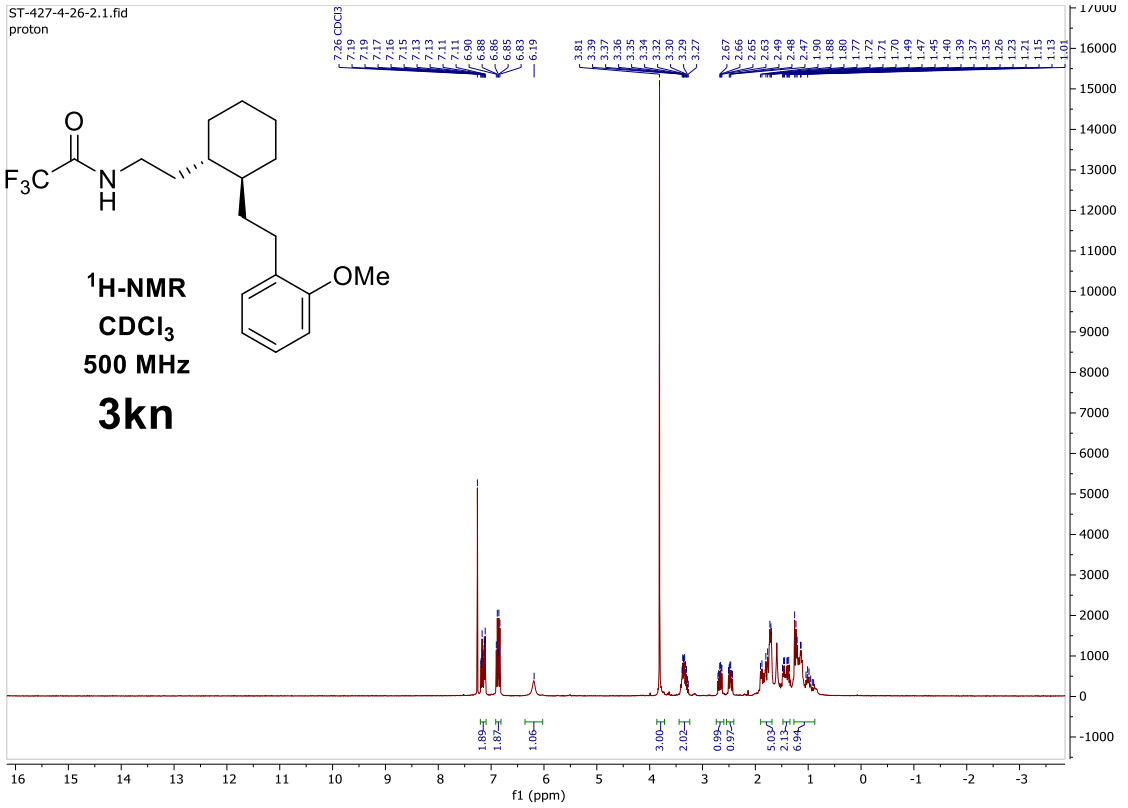

smt-III-145EB-Carbon
Carbon 13
^{13}C-NMR
$CDCl_3$
126 MHz
3kl
f1 (ppm)

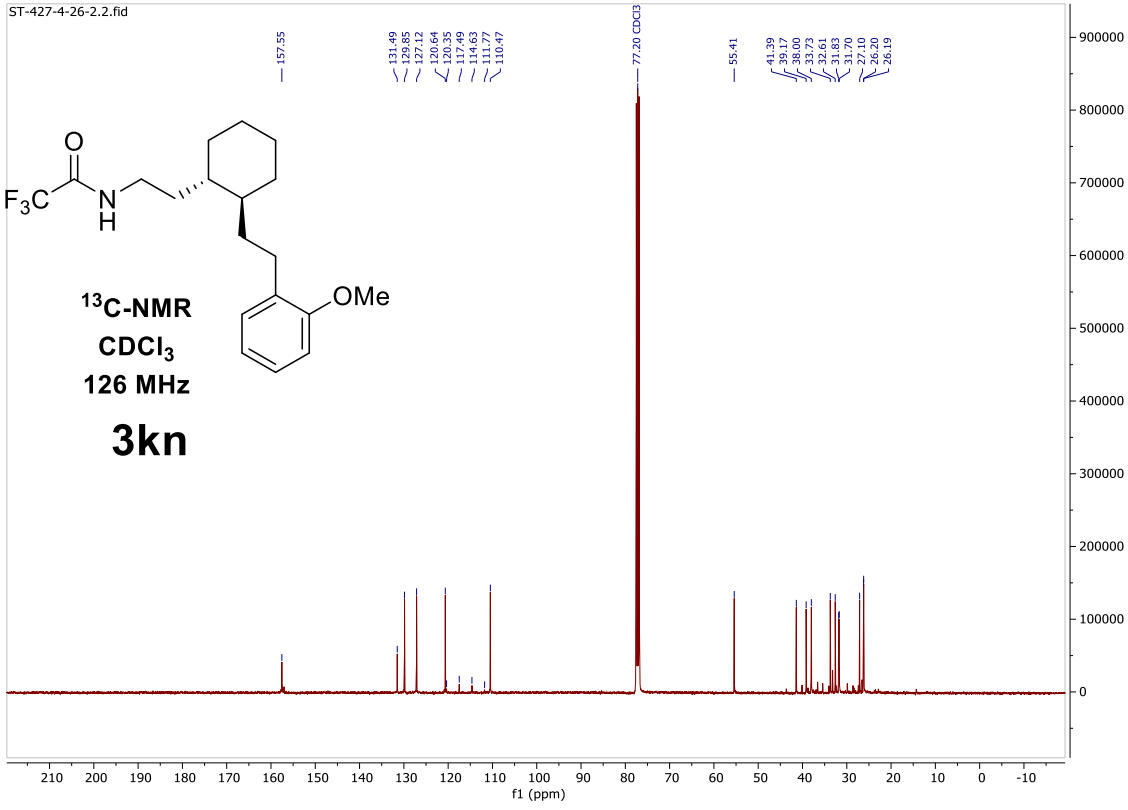

smt-III-145EB-Fluorine
19F
-74.99
^{19}F-NMR
$CDCl_3$
471 MHz
3kl
f1 (ppm)

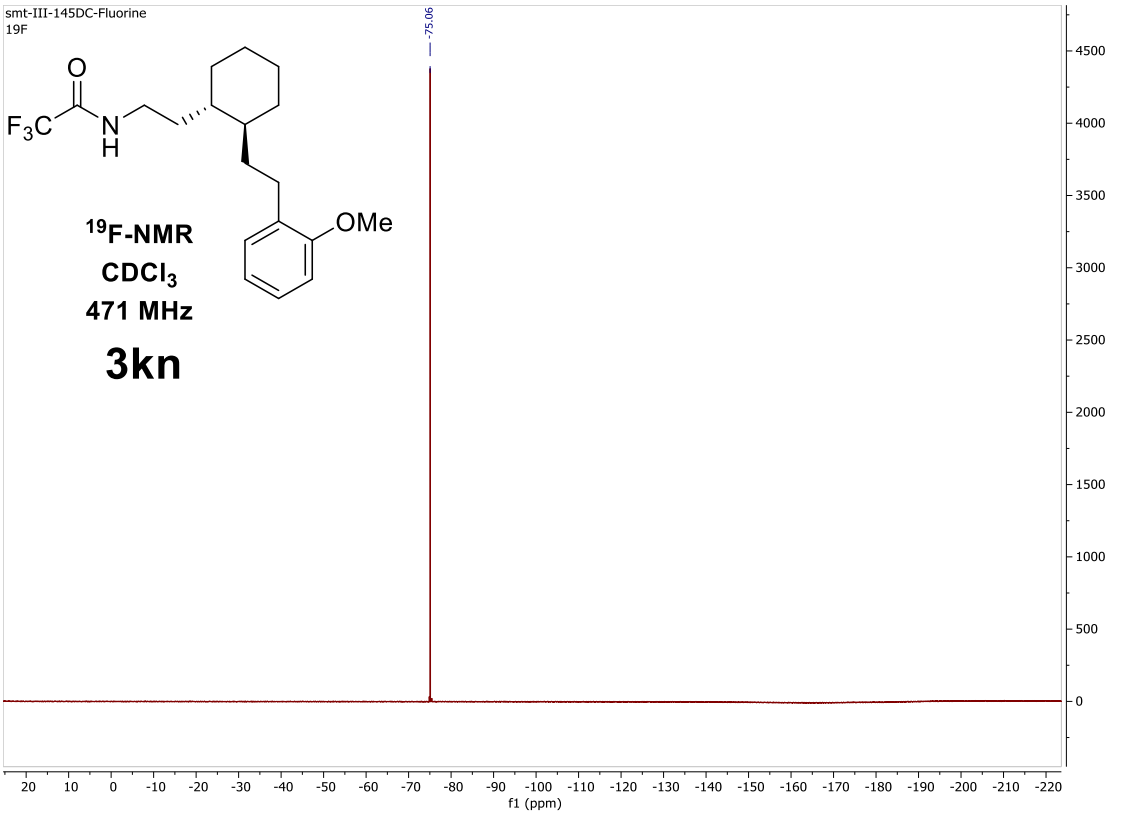

ST-230-12-36-protonclean.1.fid
Proton
7.40
7.38
7.26 CDCl3
7.06
7.04
6.19
3.40
3.28
2.63
2.44
1.89
1.86
1.79
1.78
1.70
1.38
1.25
1.22
1.22
1.20
1.12
1.02
0.89
^{1}H-NMR
$CDCl_3$
500 MHz
3km
1.00
1.00
0.99
1.00
5.40
2.43
2.43
2.18
2.12
1.02
f1 (ppm)

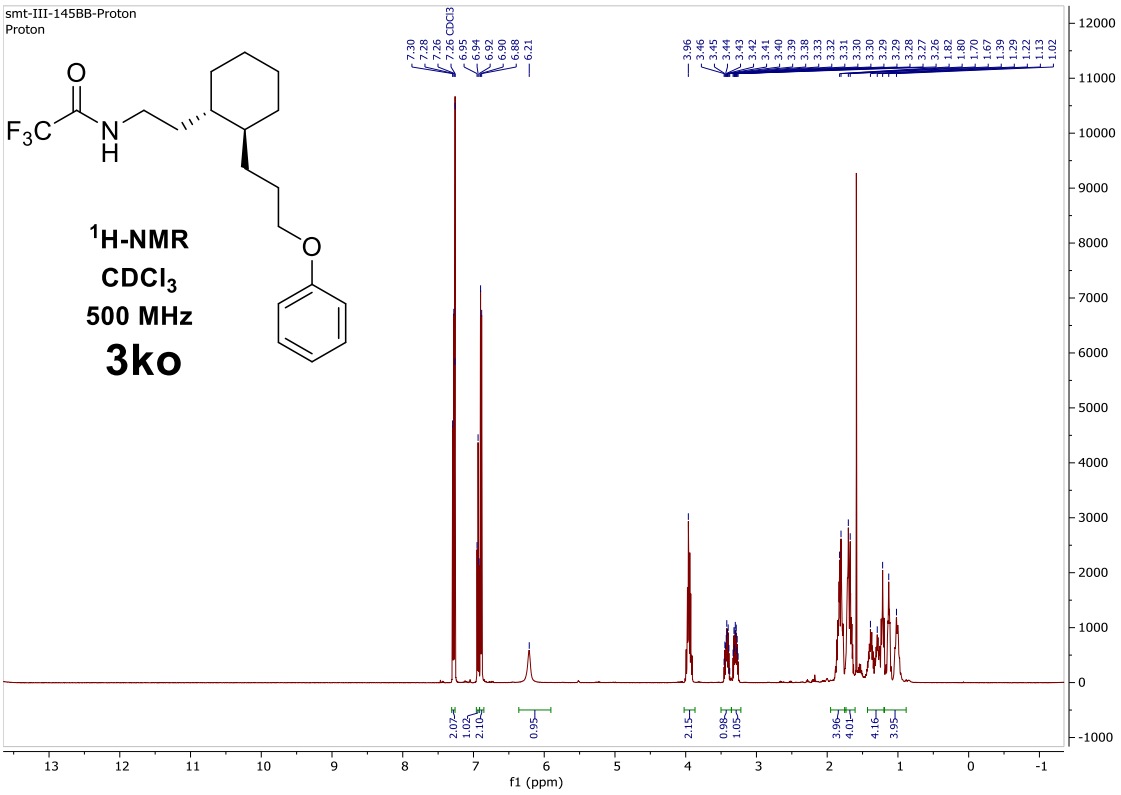

ST-230-12-36-carbon-overnight-actual.1.fid
Carbon 13
157.70
157.41
157.12
156.83
141.93
131.58
130.27
120.17
119.58
119.46
117.17
114.88
112.59
77.20 CDCl3
40.95
39.44
38.02
35.31
32.76
32.33
31.67
31.48
26.03
26.00
O
F3C
N
H
Br
13C-NMR
CDCl3
126 MHz
3km
f1 (ppm)

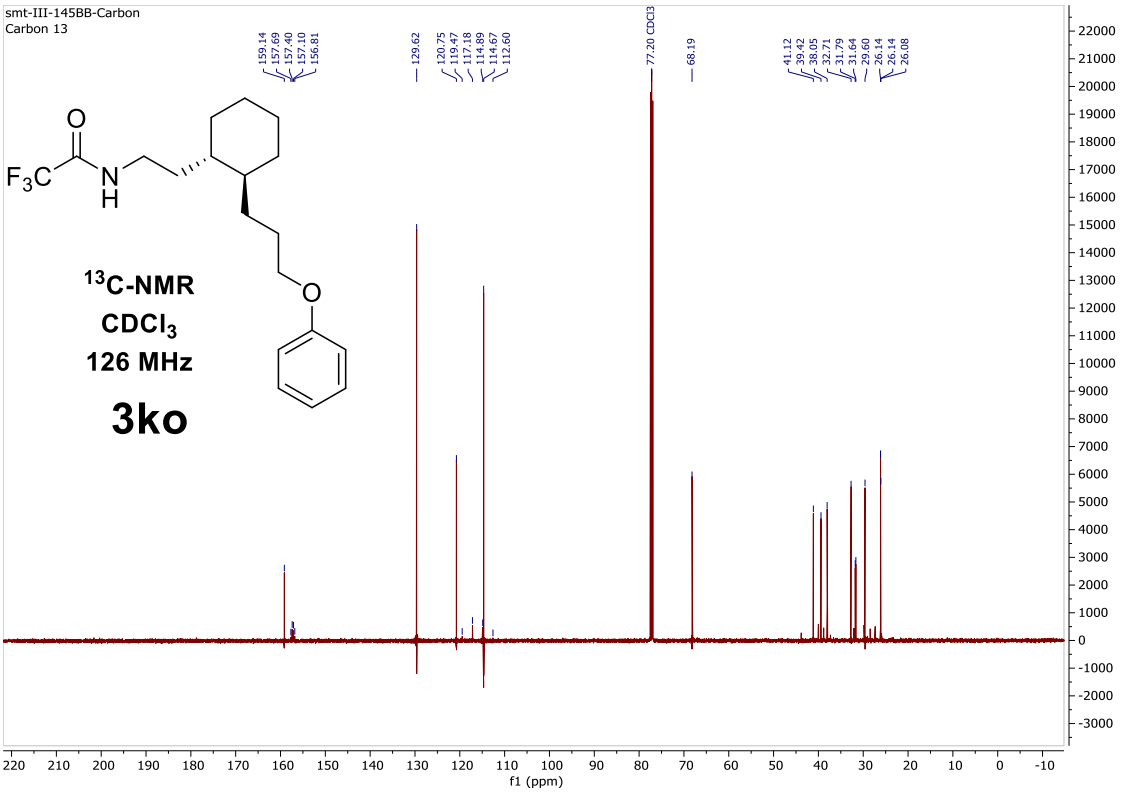

ST-230-12-36.2.fid
F19
-75.95
O
F3C
N
H
Br
19F-NMR
CDCl3
376 MHz
3km
f1 (ppm)

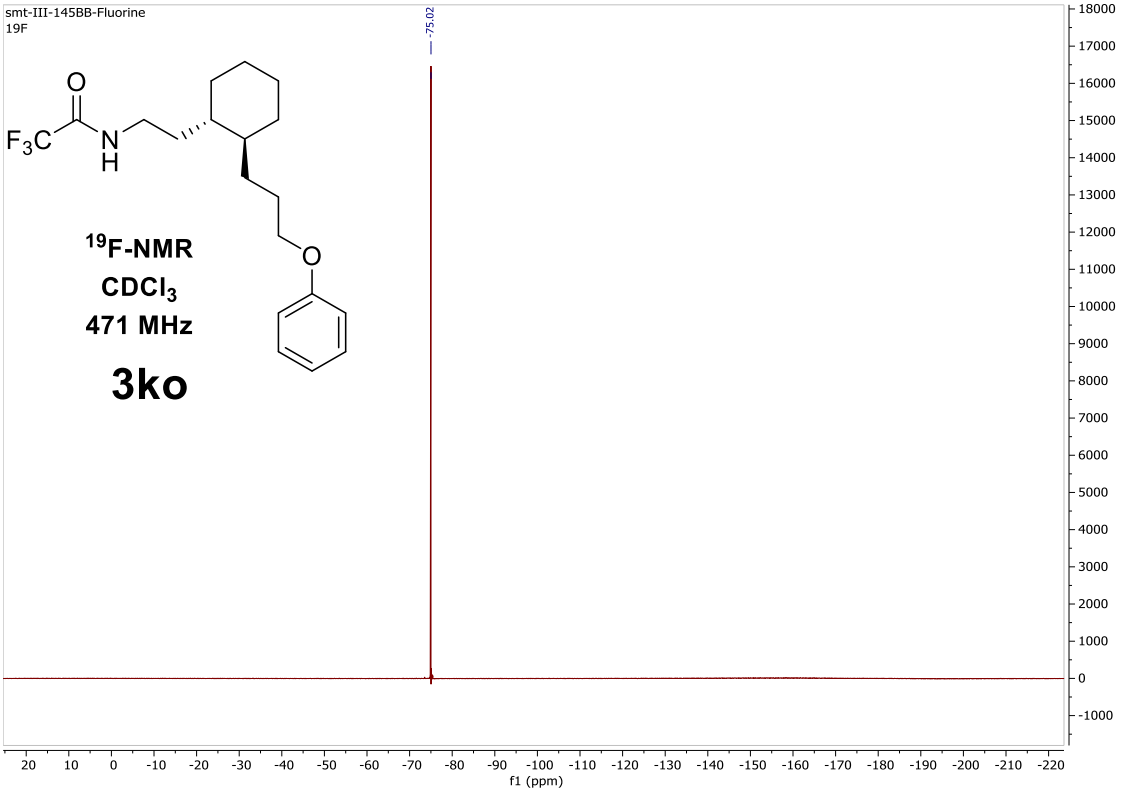

ST-427-4-26-2.1.fid
proton
^{1}H-NMR
$CDCl_3$
500 MHz
3kn
f1 (ppm)

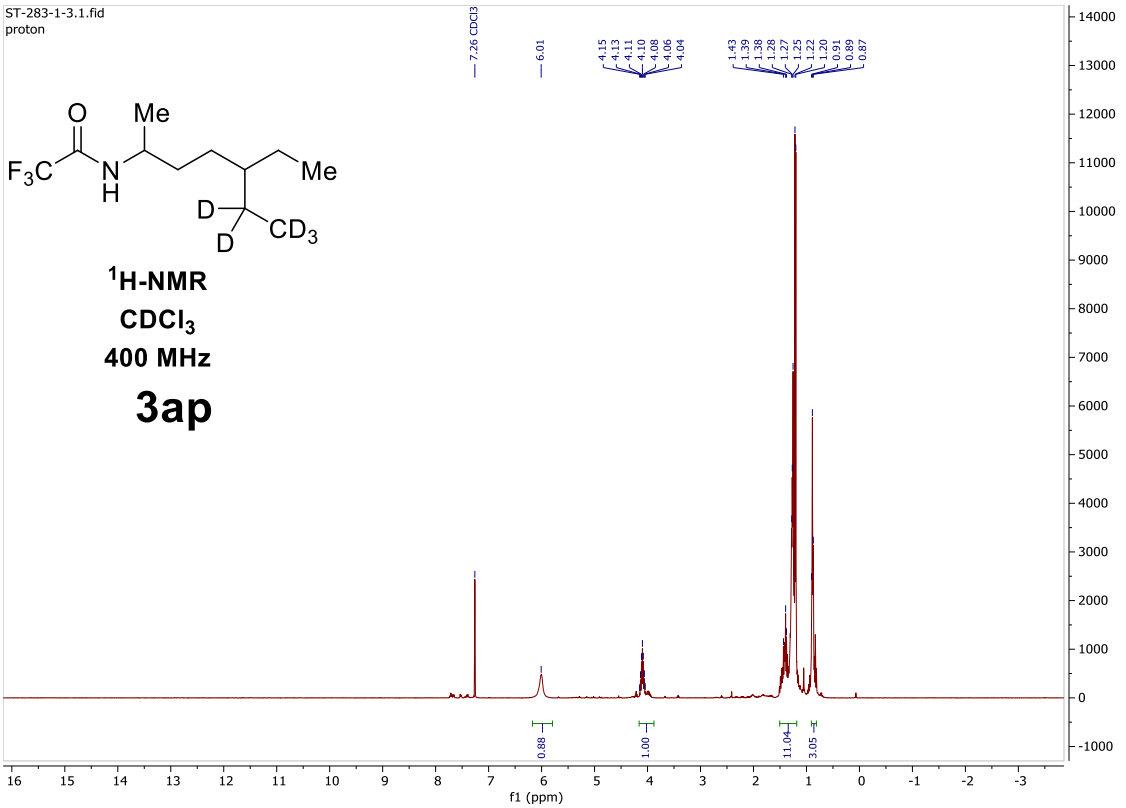

ST-427-4-26-2.2.fid
^{13}C-NMR
$CDCl_3$
126 MHz
3kn
f1 (ppm)

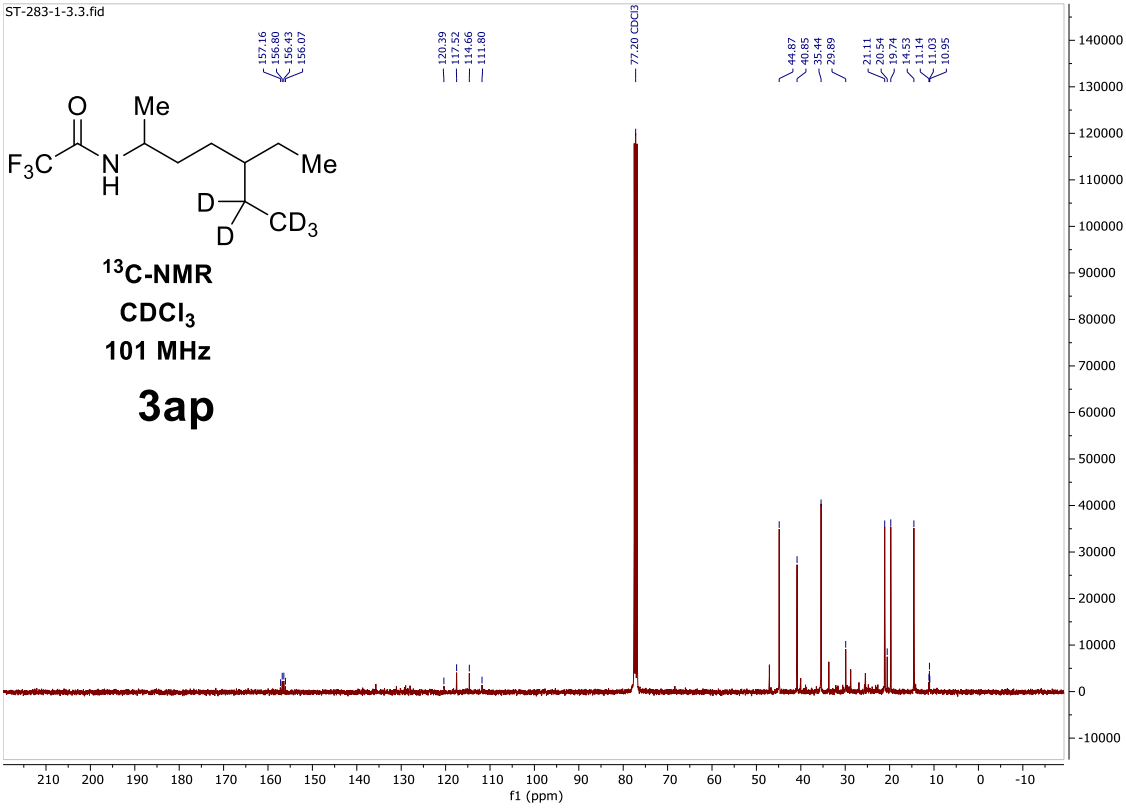

smt-III-145DC-Fluorine
19F
-75.06
O
F3C
N
H
OMe
19F-NMR
CDCl3
471 MHz
3kn
f1 (ppm)

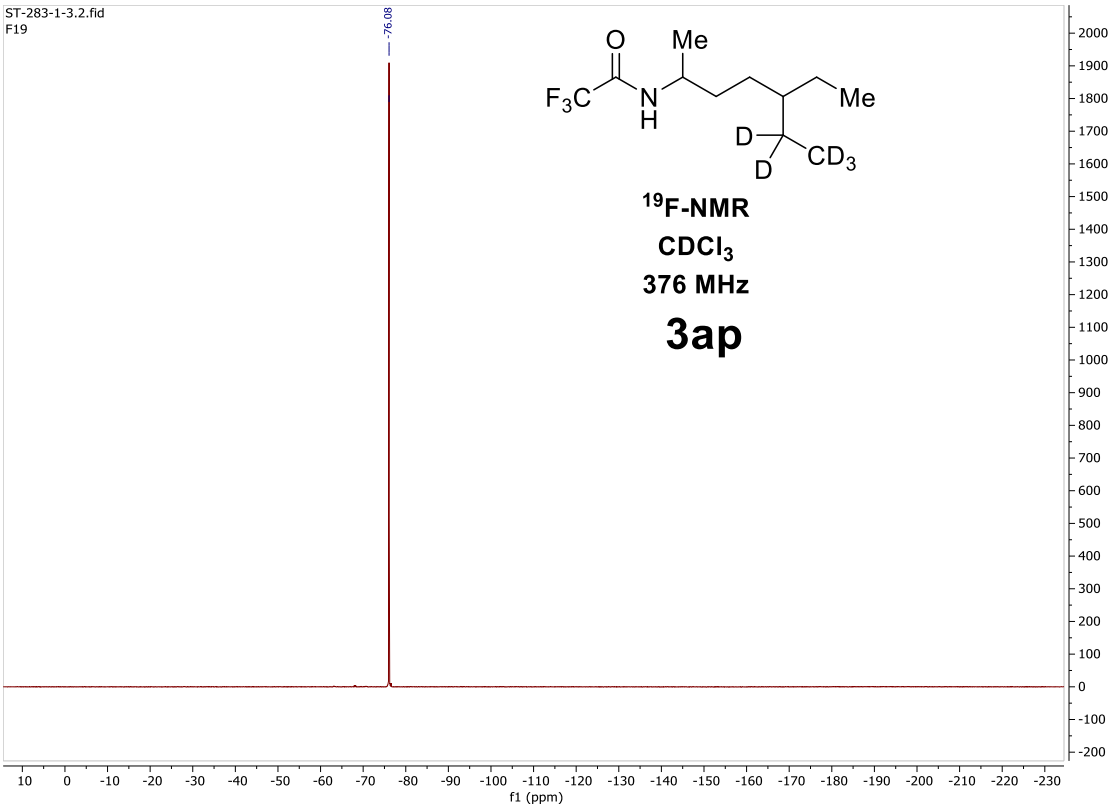

smt-III-145BB-Proton
Proton
7.30
7.28
7.26
7.26 CDCl3
6.95
6.94
6.92
6.90
6.88
6.21
3.96
3.46
3.45
3.44
3.43
3.42
3.41
3.40
3.39
3.38
3.33
3.32
3.31
3.30
3.30
3.29
3.29
3.29
3.28
3.27
3.26
1.82
1.80
1.70
1.67
1.38
1.29
1.22
1.13
1.02
O
F3C
N
H
O
1H-NMR
CDCl3
500 MHz
3ko
2.07
1.02
2.10
0.95
2.15
0.98
1.05
3.96
4.01
4.16
3.95
f1 (ppm)

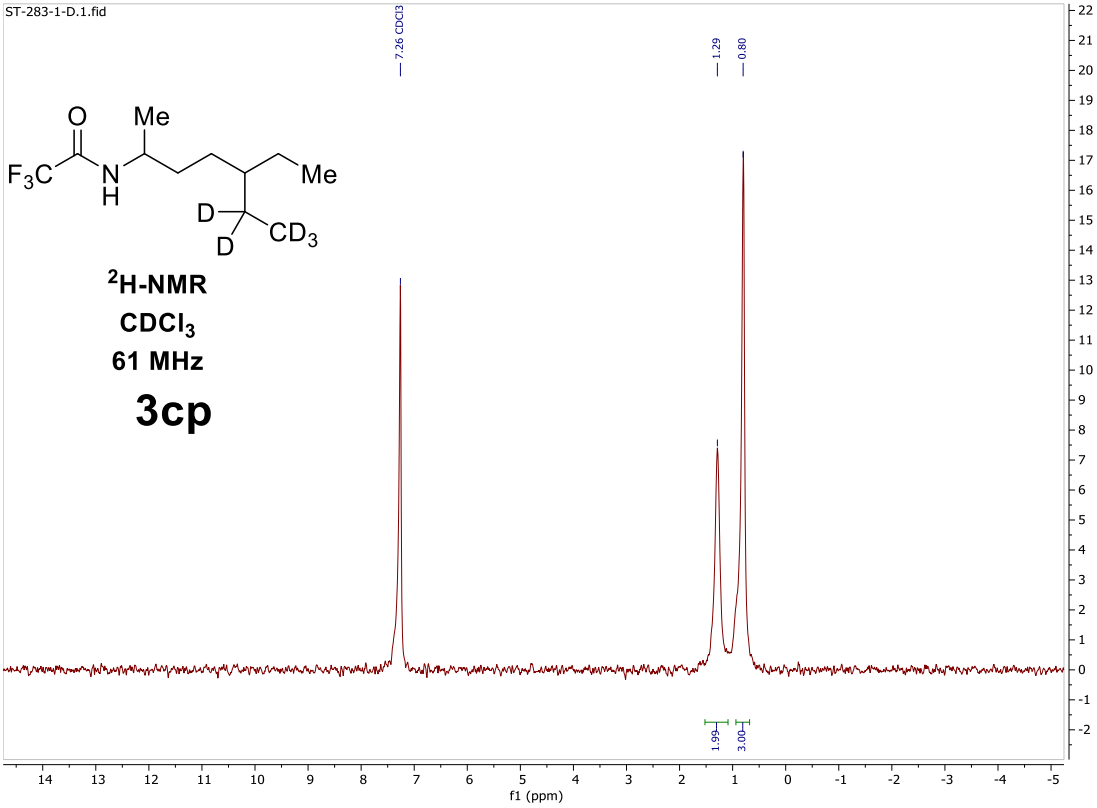

smt-III-145BB-Carbon
Carbon 13
159.14
157.69
157.40
157.10
156.81
129.62
120.75
119.47
117.18
114.89
114.67
112.60
77.20 CDCl3
68.19
41.12
39.42
38.05
32.71
31.79
31.64
29.60
26.14
26.14
26.08
13C-NMR
CDCl3
126 MHz
3ko
f1 (ppm)

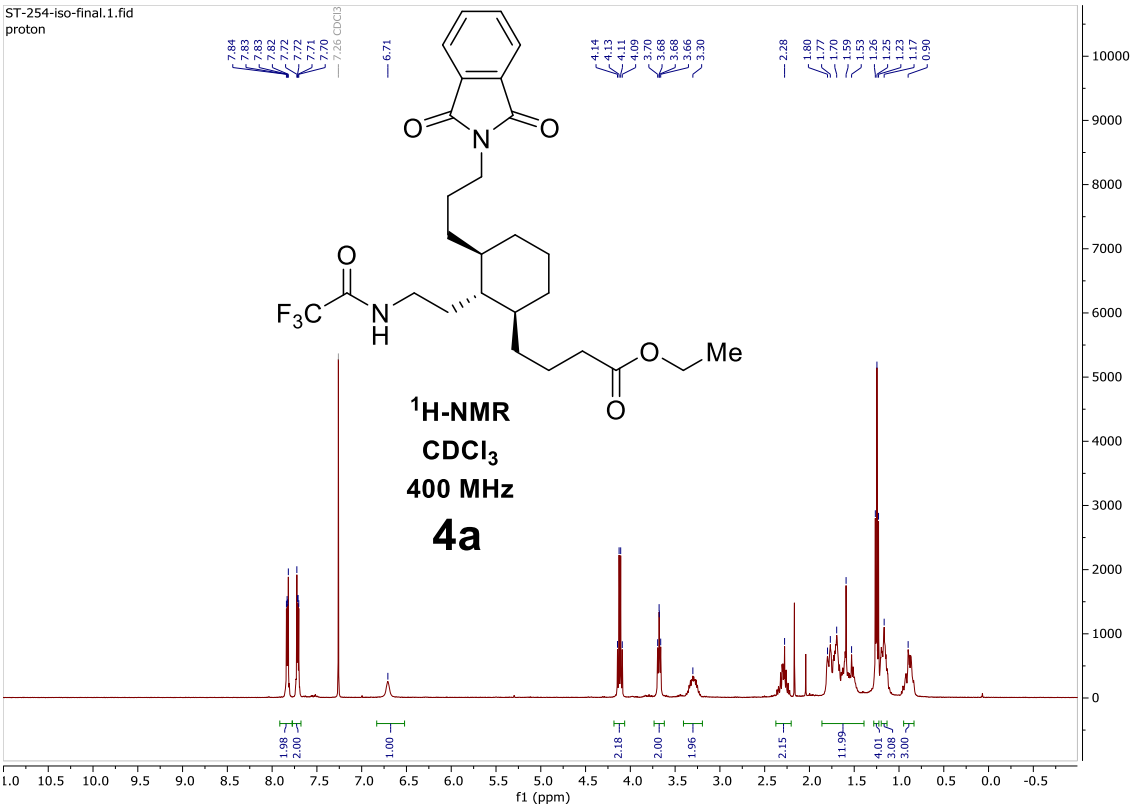

smt-III-145BB-Fluorine
19F
-75.02
19F-NMR
CDCl3
471 MHz
3ko
f1 (ppm)

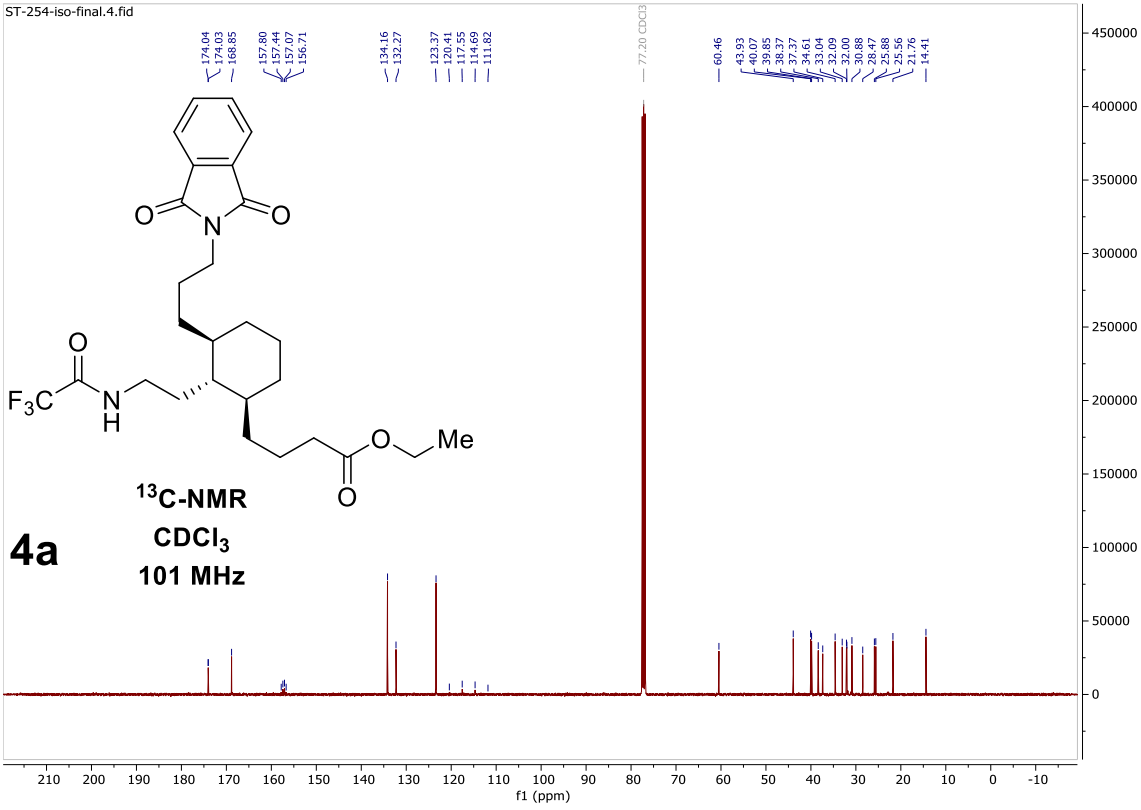

ST-283-1-3.1.fid
proton
7.26 CDCl3
6.01
4.15
4.13
4.11
4.10
4.08
4.06
4.04
1.43
1.39
1.38
1.28
1.27
1.25
1.22
1.20
0.91
0.89
0.87
0.88
1.00
11.04
3.05
f1 (ppm)
1H-NMR
CDCl3
400 MHz
3ap

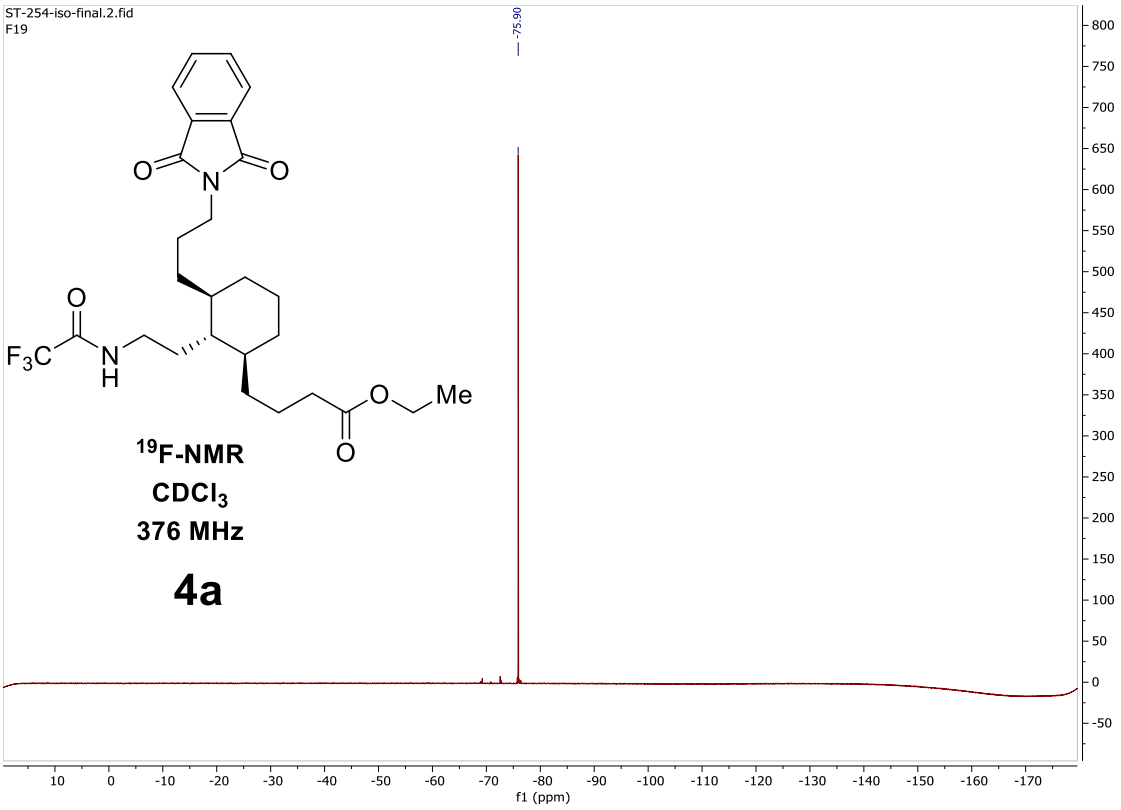

ST-283-1-3.3.fid
157.16
156.80
156.43
156.07
120.39
117.52
114.66
111.80
77.20 CDCl3
44.87
40.55
35.44
29.89
21.11
20.54
19.74
14.53
11.14
11.03
10.95
f1 (ppm)
13C-NMR
CDCl3
101 MHz
3ap

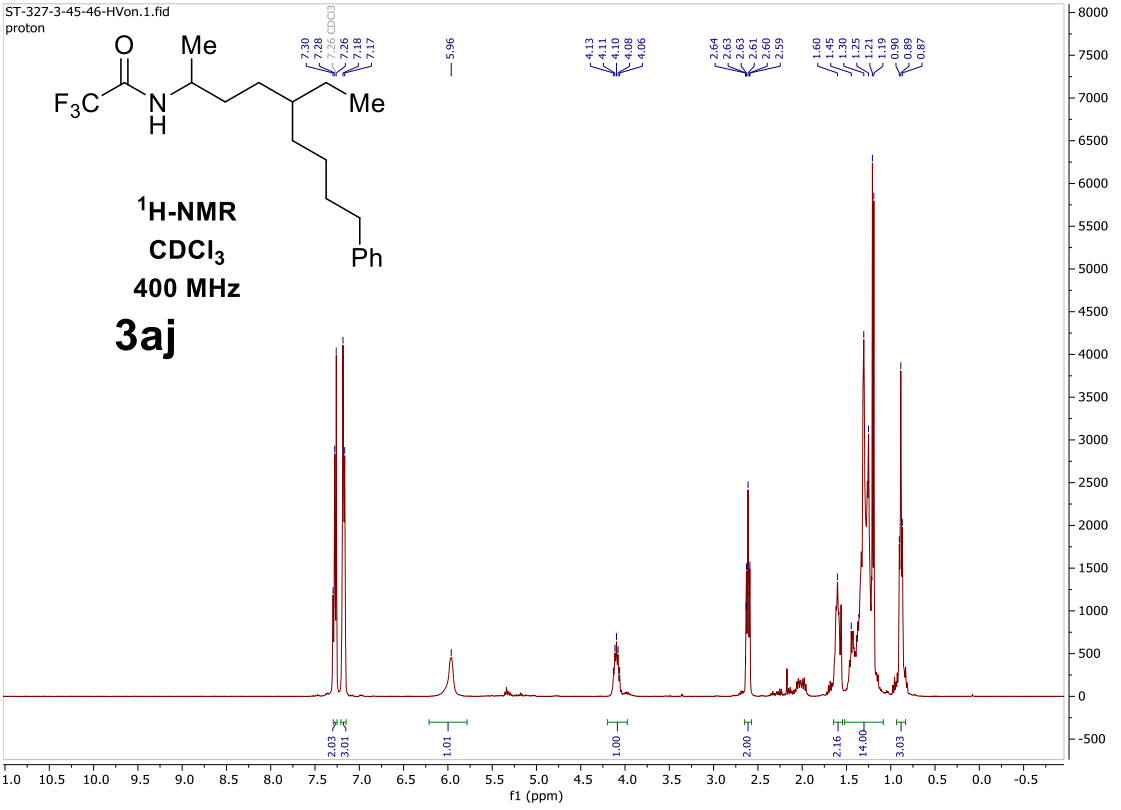

ST-283-1-3.2.fid
F19
-76.08
O
Me
F3C
N
H
Me
D
D
CD3
19F-NMR
CDCl3
376 MHz
3ap
f1 (ppm)

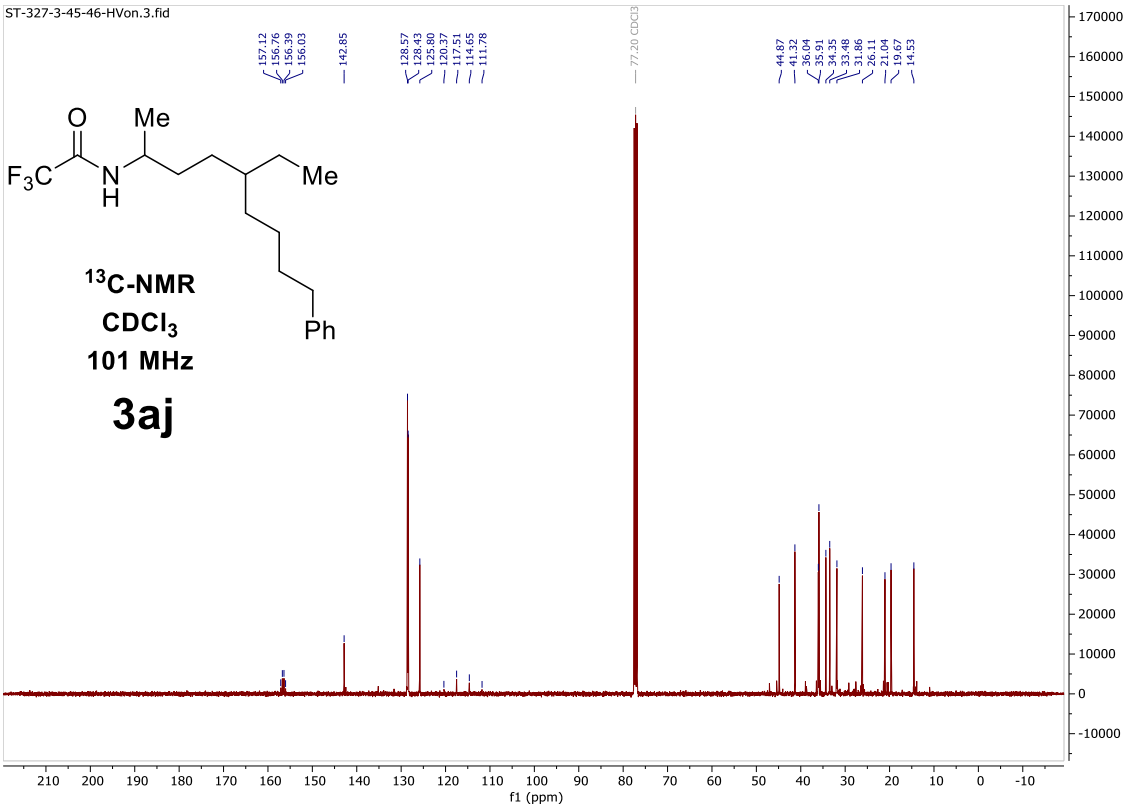

ST-283-1-D.1.fid
7.26 CDCl3
1.29
0.80
O
Me
F3C
N
H
Me
D
D
CD3
2H-NMR
CDCl3
61 MHz
3cp
1.99
3.00
f1 (ppm)

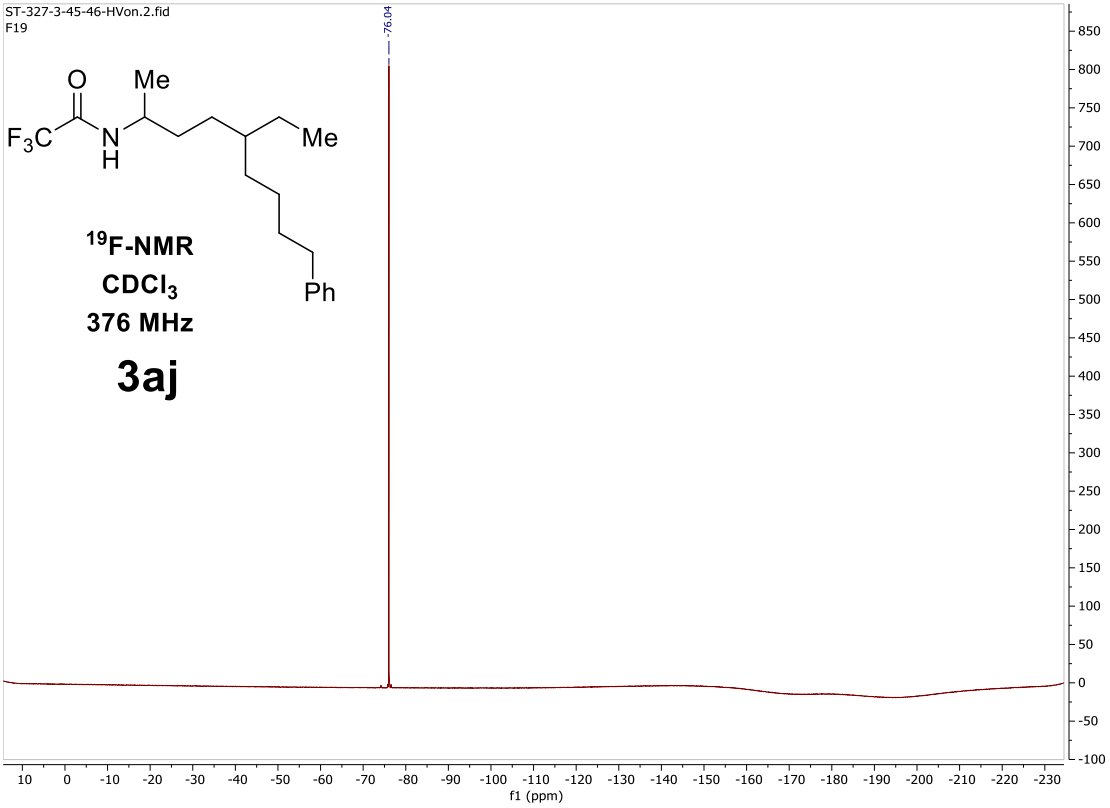

ST-254-iso-final.1.fid
proton
^{1}H-NMR
CDCl$_3$
400 MHz
4a
f1 (ppm)

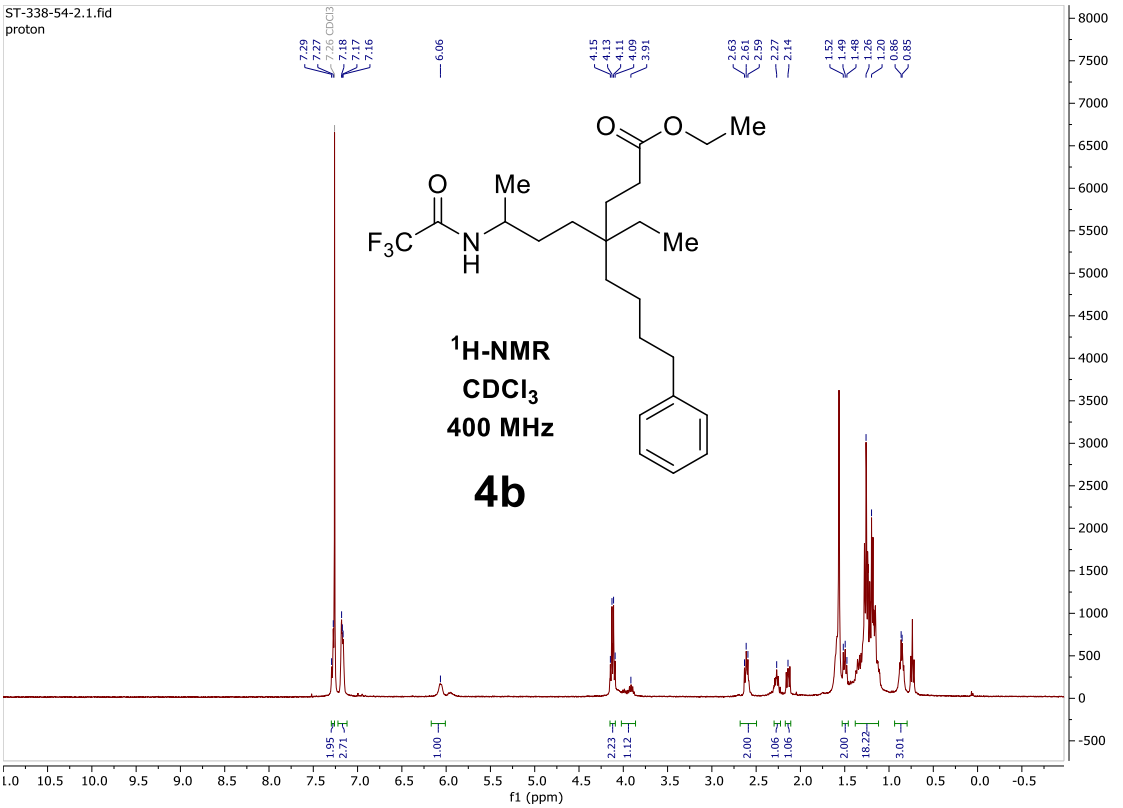

ST-254-iso-final.4.fid
^{13}C-NMR
CDCl$_3$
101 MHz
4a
f1 (ppm)

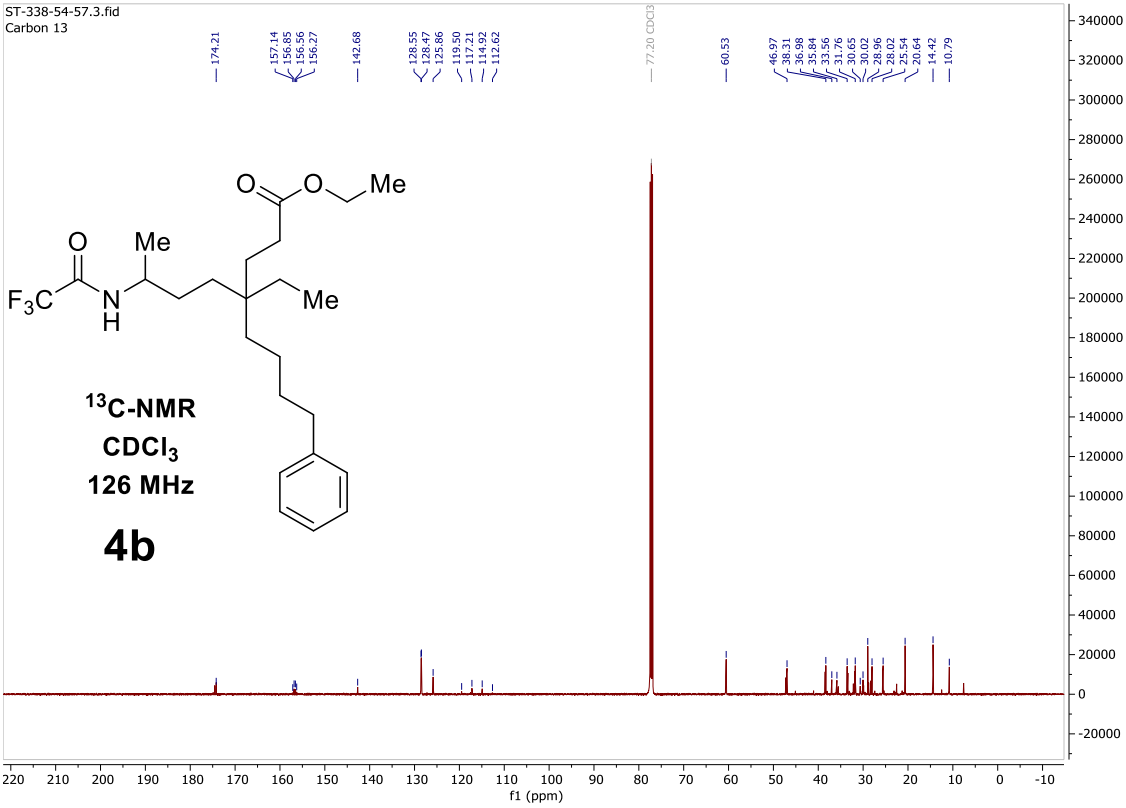

ST-254-iso-final.2.fid
F19
-75.90
^{19}F-NMR
$CDCl_3$
376 MHz
4a
f1 (ppm)

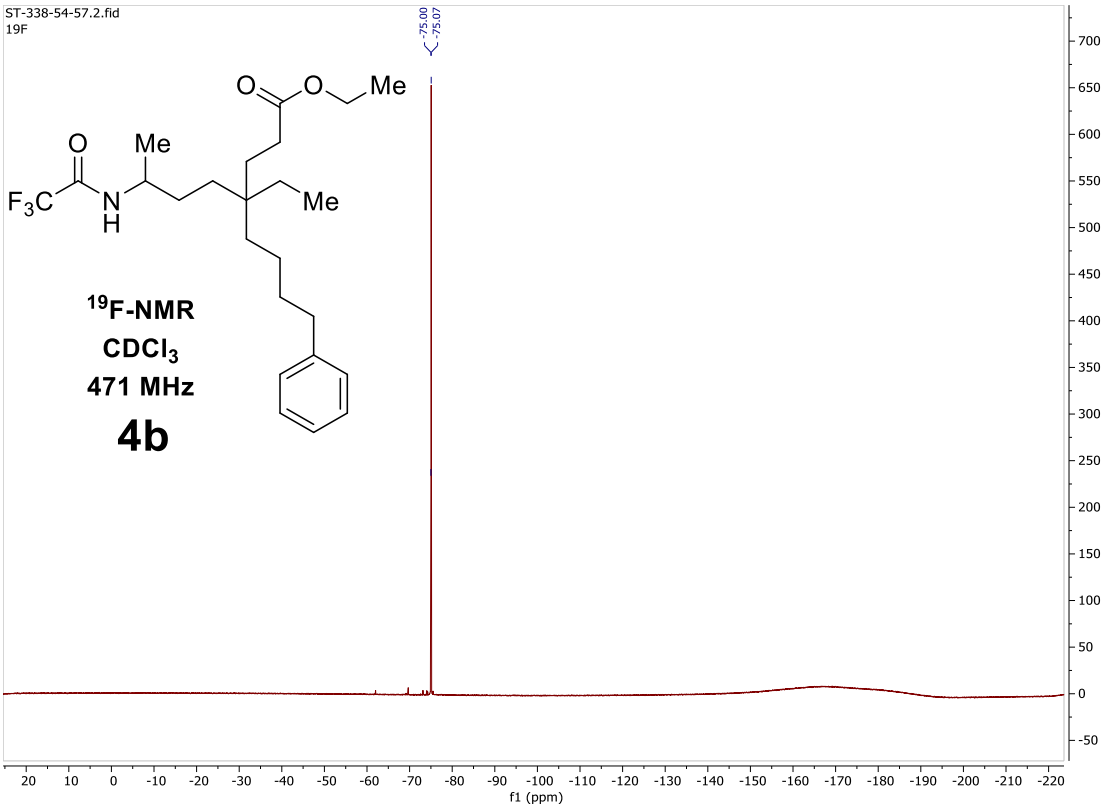

ST-327-3-45-46-HVon.1.fid
proton
^{1}H-NMR
$CDCl_3$
400 MHz
3aj
f1 (ppm)

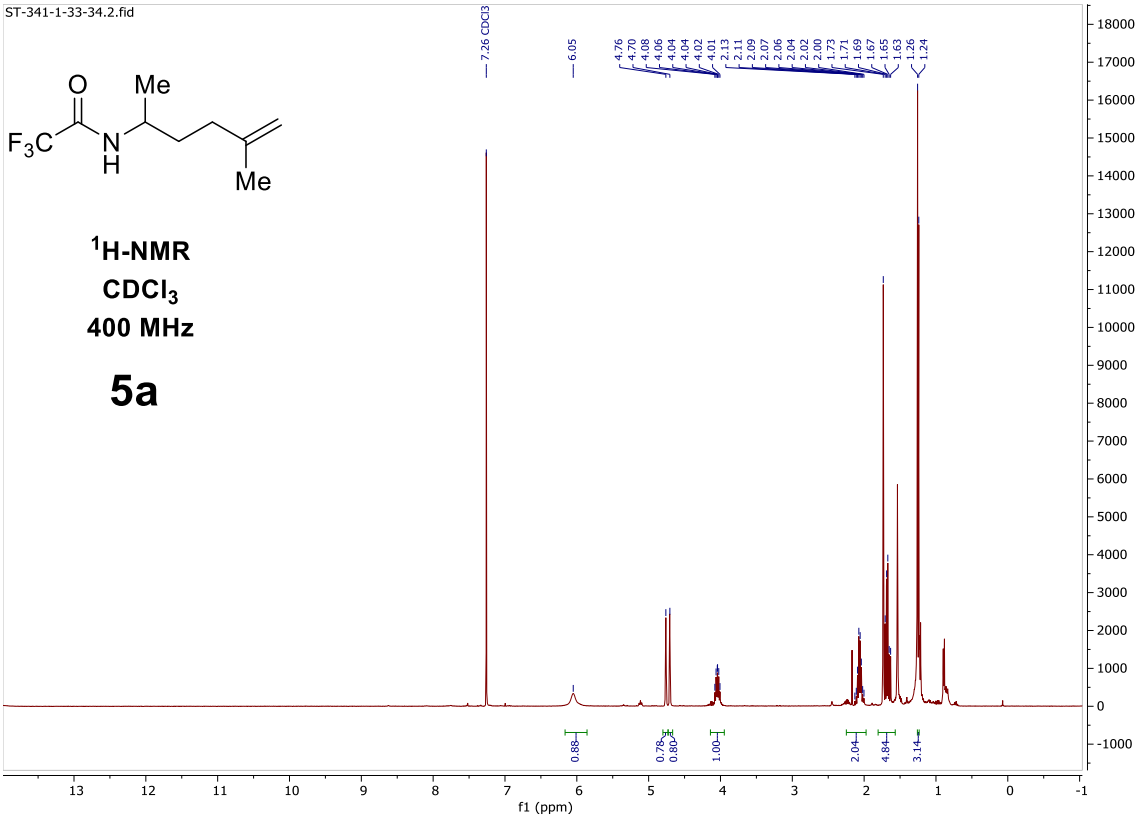

ST-327-3-45-46-HVon.3.fid
157.12
156.76
156.39
156.03
142.85
128.57
128.43
125.80
120.37
117.51
114.65
111.78
77.20 CDCl3
44.87
41.32
36.04
35.91
34.35
33.48
31.86
26.11
21.04
19.67
14.53
O
Me
F3C
N
H
Me
Ph
13C-NMR
CDCl3
101 MHz
3aj
f1 (ppm)

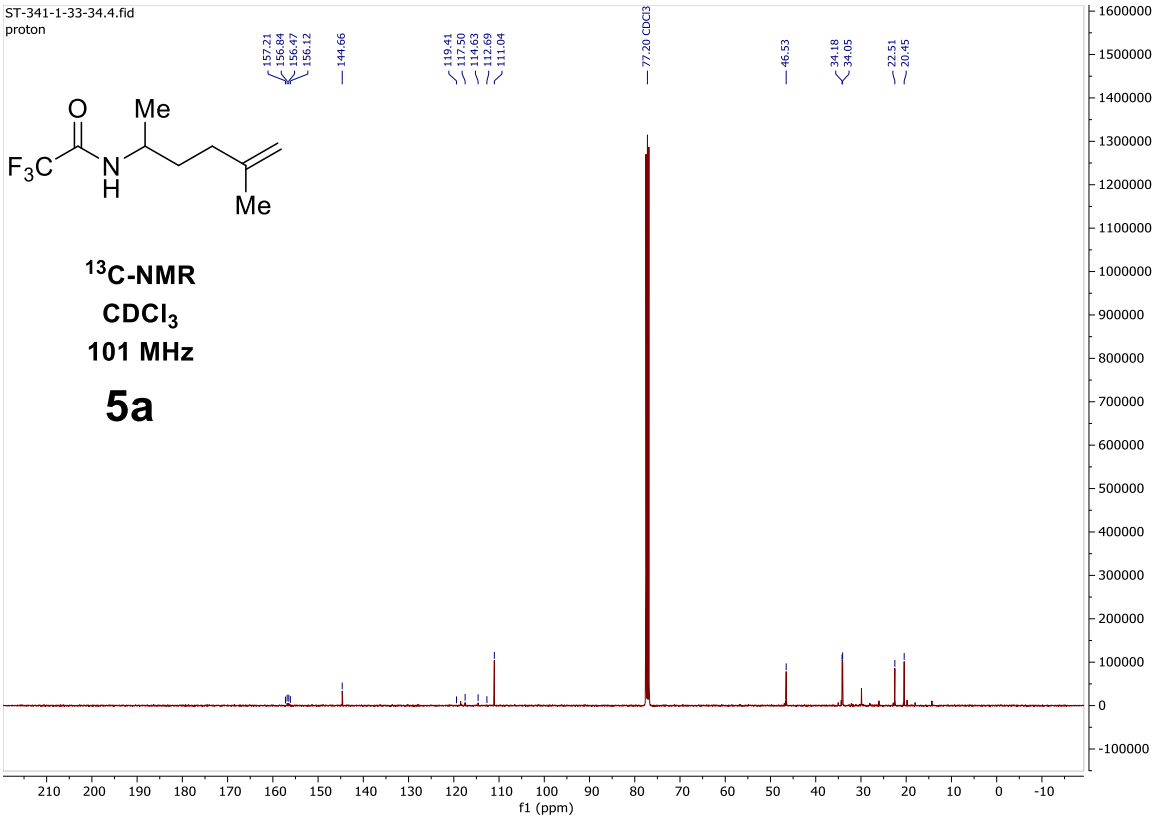

ST-327-3-45-46-HVon.2.fid
F19
76.04
O
Me
F3C
N
H
Me
Ph
19F-NMR
CDCl3
376 MHz
3aj
f1 (ppm)

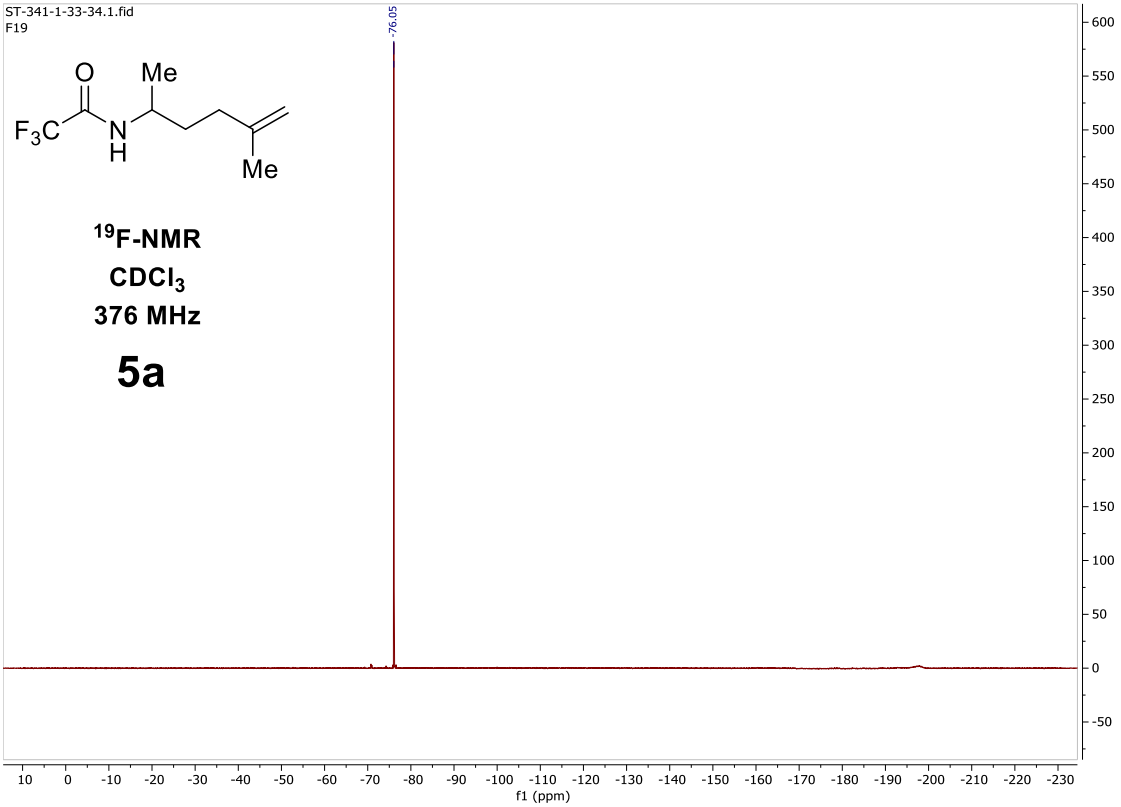

ST-338-54-2.1.fid
proton
^{1}H-NMR
CDCl$_3$
400 MHz
4b

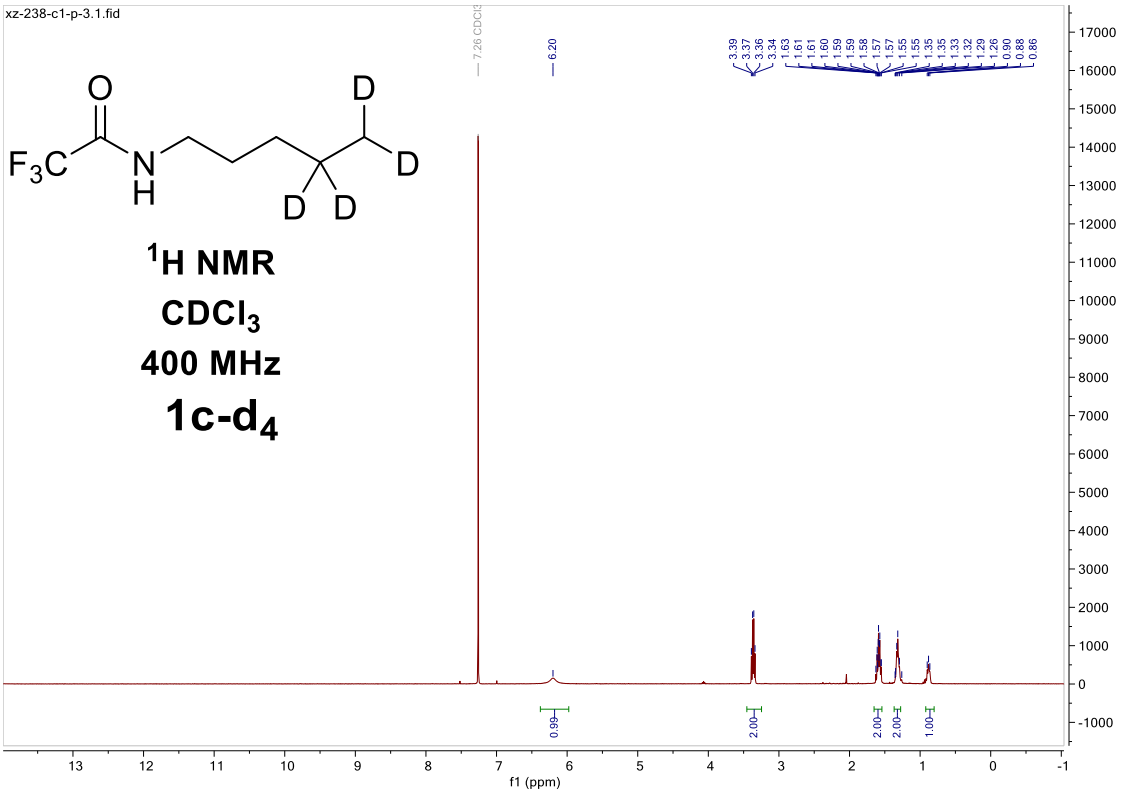

ST-338-54-57.3.fid
Carbon 13
^{13}C-NMR
CDCl$_3$
126 MHz
4b

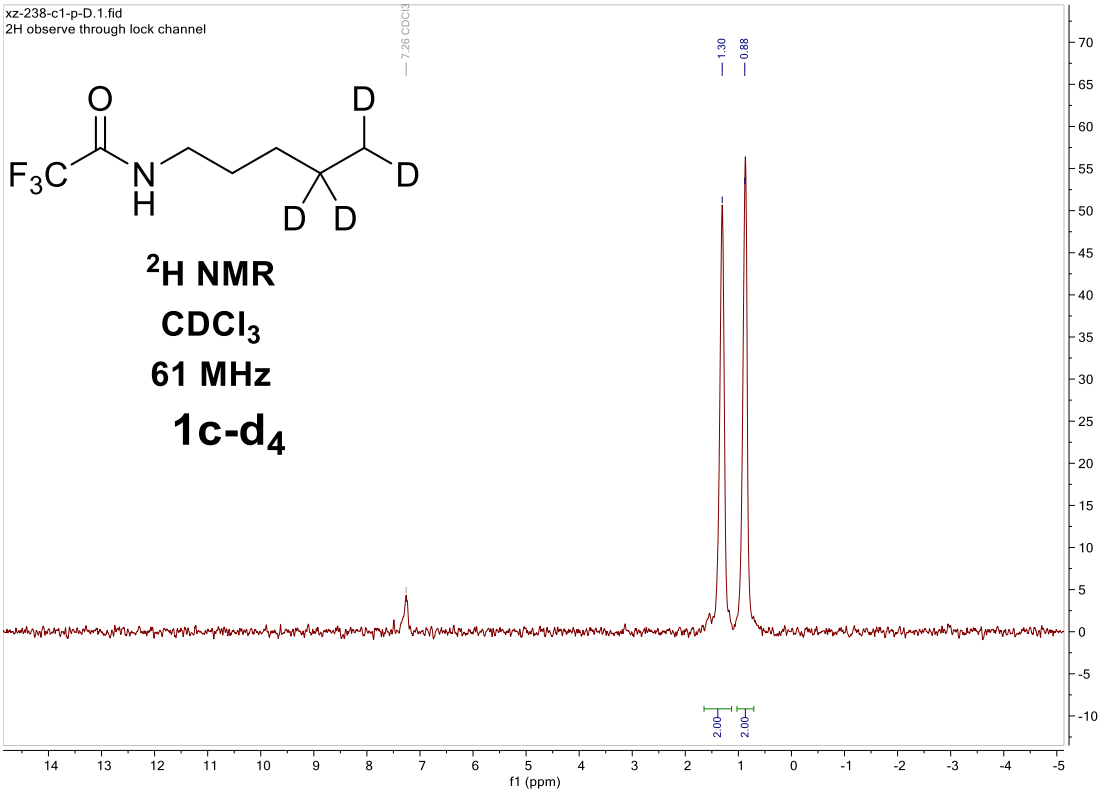

ST-338-54-57.2.fid
19F
-75.00
-75.07
O
O
Me
O
Me
F3C
N
H
Me
19F-NMR
CDCl3
471 MHz
4b
f1 (ppm)

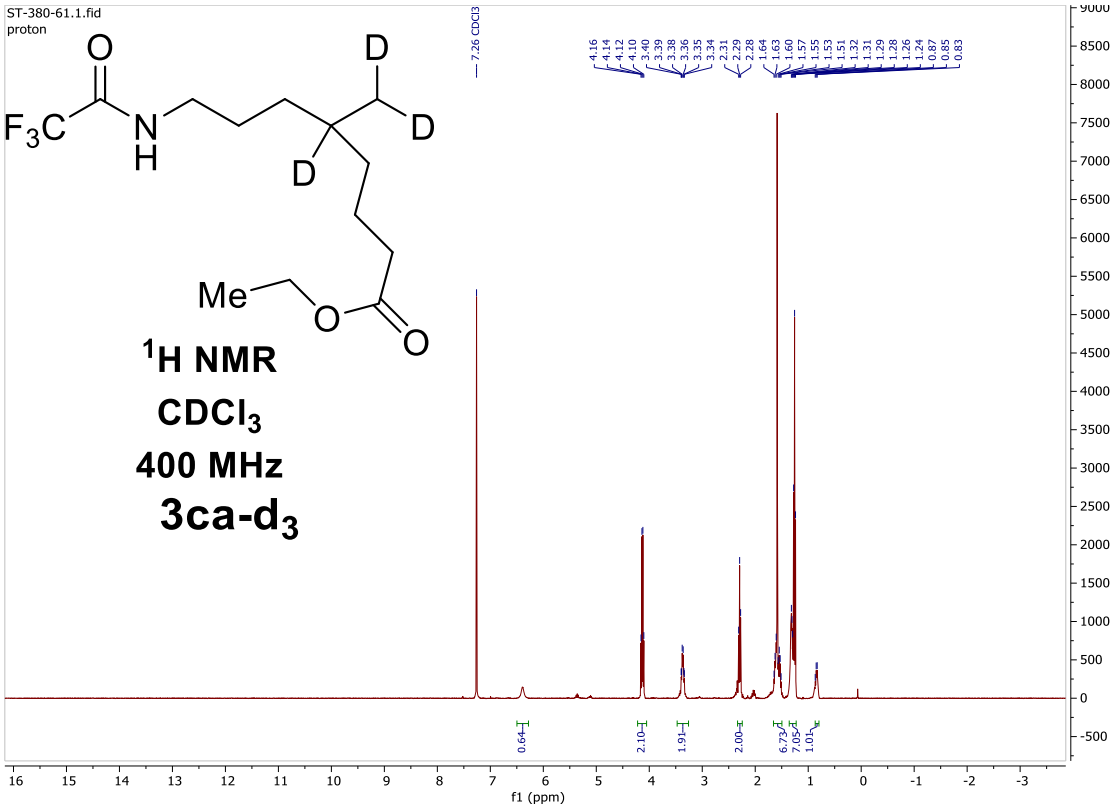

ST-341-1-33-34.2.fid
7.26 CDCl3
6.05
4.76
4.70
4.08
4.06
4.04
4.04
4.02
4.01
2.13
2.11
2.09
2.07
2.06
2.04
2.02
2.00
1.73
1.71
1.69
1.67
1.65
1.63
1.26
1.24
O
Me
F3C
N
H
Me
1H-NMR
CDCl3
400 MHz
5a
0.88
0.78
0.80
1.00
2.04
4.84
3.14
f1 (ppm)

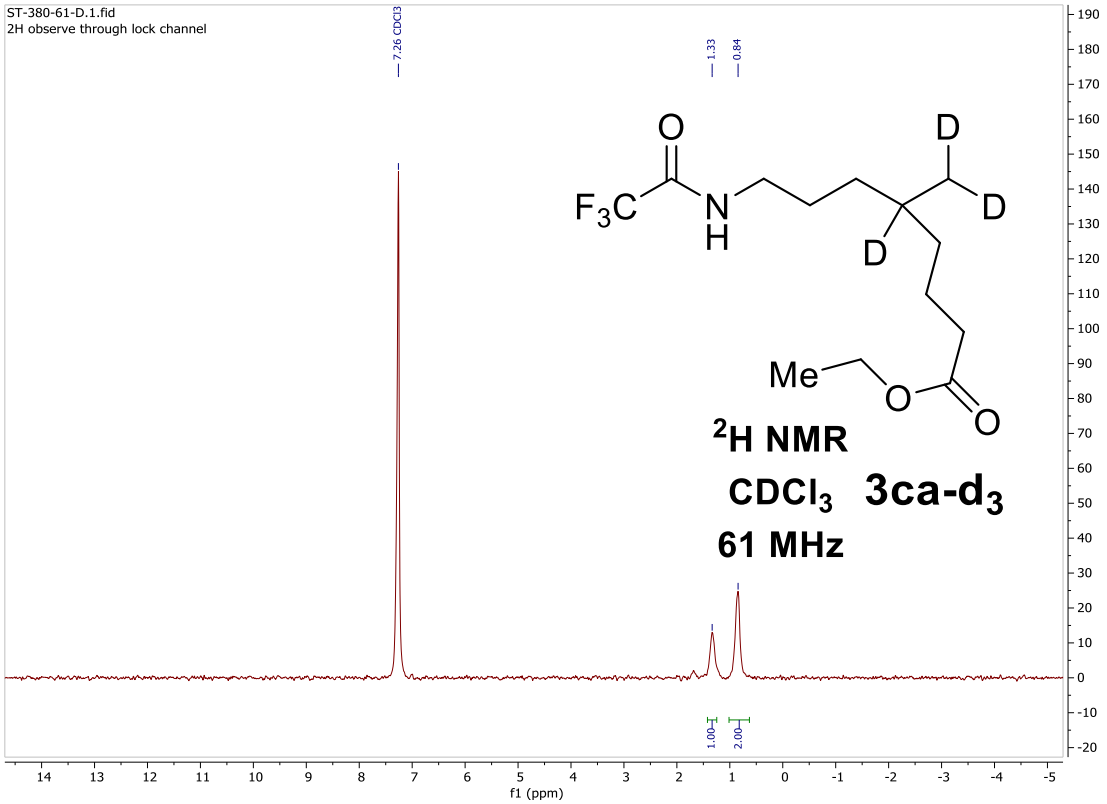

ST-341-1-33-34.4.fid
proton
157.21
156.84
156.47
156.12
144.66
119.41
117.50
114.63
112.69
111.04
77.20 CDCl3
46.53
34.18
34.05
22.51
20.45
O
Me
F3C
N
H
Me
13C-NMR
CDCl3
101 MHz
5a
f1 (ppm)


ST-341-1-33-34.1.fid
F19
-76.05
O
Me
F3C
N
H
Me
19F-NMR
CDCl3
376 MHz
5a
f1 (ppm)


xz-238-c1-p-3.1.fid
7.26 CDCl3
6.20
3.39
3.37
3.36
3.34
1.63
1.61
1.61
1.60
1.59
1.59
1.58
1.57
1.57
1.55
1.55
1.35
1.35
1.33
1.32
1.29
1.26
0.90
0.88
0.86
O
F3C
N
H
D
D
D
D
1H NMR
CDCl3
400 MHz
1c-d4
0.99
2.00
2.00
2.00
1.00
f1 (ppm)


xz-238-c1-p-D.1.fid
2H observe through lock channel
7.26 CDCl3
1.30
0.88
O
F3C
N
H
D
D
D
D
2H NMR
CDCl3
61 MHz
1c-d4
2.00
2.00
f1 (ppm)


ST-380-61.1.fid
proton
7.26 CDCl3
4.16
4.14
4.12
4.10
3.40
3.39
3.38
3.36
3.35
3.34
2.31
2.29
2.28
1.64
1.63
1.60
1.57
1.55
1.53
1.51
1.32
1.31
1.29
1.28
1.26
1.24
0.87
0.85
0.83
O
D
F3C
N
H
D
D
Me
O
O
1H NMR
CDCl3
400 MHz
3ca-d3
0.64
2.10
1.91
2.00
6.73
7.05
1.01
f1 (ppm)


ST-380-61-D.1.fid
2H observe through lock channel
7.26 CDCl3
1.33
0.84
O
D
F3C
N
H
D
D
Me
O
O
2H NMR
CDCl3 3ca-d3
61 MHz
1.00
2.00
f1 (ppm)