Supporting Information

Site-Selective Defluorinative sp^3 C–H Alkylation of Secondary Amides

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General Considerations

Analytical methods. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 MHz, Bruker 400 MHz and Bruker 500 MHz at 20 °C. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were calibrated using the residual solvent peak of $CHCl_3$ (7.26 ppm), unless otherwise indicated. All ^{13}C NMR spectra are reported in ppm relative to TMS, were calibrated using the signal of residual $CHCl_3$ (77.16 ppm), ^{19}F NMR was obtained with ^{1}H decoupling unless otherwise indicated. Coupling constants, *J* are reported in Hertz. Melting points were measured using open glass capillaries in a Büchi B540 apparatus. Infrared spectra (FT-IR) measurements were carried out on a Bruker Optics FT-IR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm^{-1} resolution using a one bounce ATR accessory with diamond windows. Mass spectra were recorded on a Waters LCT Premier spectrometer or in a MicroTOF Focus, Bruker Daltonics spectrometer. UV/Vis absorption spectra were recorded using a Agilent Technologies Cary 300 UV/Vis spectrophotometer and UV-1800PC spectrophotometer in quartz cuvettes with a path length of 1.0 cm. Bulk electrolysis was conducted on a PARSTAT 2273 potentiometer using a 3-electrode cell configuration at room temperature, The same electrodes were used as for CV experiments, namely a glassy carbon working electrode, platinum flag counter electrode and Ag/AgCl (KCl sat.) reference electrode. Flash chromatography was performed with EM Science silica gel 60 (230-400 mesh). Thin layer chromatography was used to monitor reaction progress and analysed fractions from column chromatography. To this purpose TLC Silica gel 60 F_{254} aluminium sheets from Merck were used and visualization was achieved using UV irradiation and/or staining with Potassium Permanganate or Cerium Molybdate solution. The yields reported refer to isolated yields and represent an average of at least two independent runs. The procedures described in this section are representative. Thus, the yields may differ slightly from those given in the tables of the manuscript.

Reagents. Commercially available materials were used as received without further purification. $NiBr_2$·diglyme (97% purity) were purchased from Aldrich. 5,5'-Di-Me-2,2'-bipyridine (97% purity) was purchased from Aldrich. Anhydrous K_3PO_4 was purchased from Aldrich (99% purity). Anhydrous 1,4-dioxane (99.5% purity) and toluene (99.5% purity) was purchased from Across.

The defluorinative α sp^3 C-H alkylation of amides was performed with 451 nm LEDs (OSRAM Oslon® SSL 80 royal- blue LEDs), which were installed at the bottom of a custom-made 8 flat-bottom Schlenk tubes holder, equipped with a cooling system (the temperature was set at 15 °C) and a magnetic stirrer (~ 900 rpm).

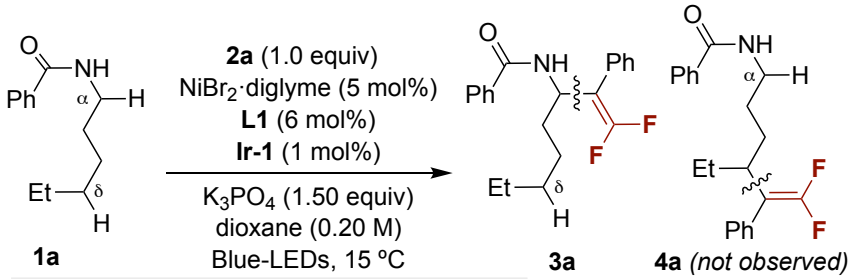
The defluorinative δ sp^3 C-H alkylation of amides was performed with 451 nm Kessil light (DiCon Fiberoptics, Inc., 40 W), equipped with a fan cooling system (the thermostat was set at 35-40 °C) and a magnetic stirrer (~ 900 rpm).

Optimization of the Reaction Conditions

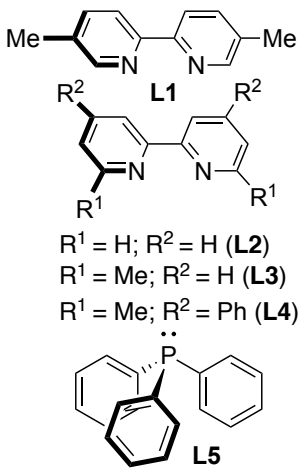
Optimization of the reaction conditions for the α sp^3 C-H defluorinative alkylation of secondary amides

General procedure for the reaction of 1a with 2a: An oven-dried 8 mL Schlenk tube containing a stirring bar was charged with **1a** (41.0 mg, 0.20 mmol, 2 equiv), Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (**Ir**-1; 1.1 mg, 0.01 equiv), **L** (0.06 equiv) and the base (0.150 mmol, 1.5 equiv). The tube was then introduced in the nitrogen-filled glovebox where the nickel catalyst (0.05 equiv) was added followed by 0.5 mL of the solvent. Then, the tube was brought outside the glovebox, and **2a** (17.2 mg, 0.10 mmol, 1 equiv) was added to the reaction mixture under N_2 atmosphere. Then, the tube was stirred at 15 °C under blue LED irradiation with a cooling system for 36 hours. At that time, the reaction was quenched by the addition of EtOAc (5 mL). The mixture was filtered through a silica plug, and the solvent was removed under vacuum. Then, nitromethane (5.4 μL, 0.10 mmol) was added as internal standard, and the mixture was analyzed by ^{1}H NMR.

Table S1. Optimization of α sp^3 C–H defluorinative alkylation of secondary amides.[a]

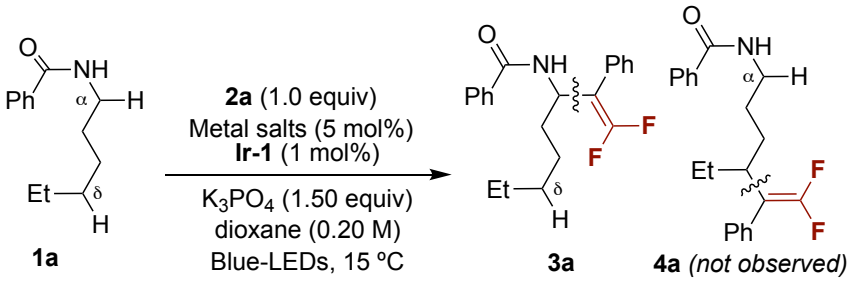


entry	deviation standard conditions	**3a** (%)[b]
1	none	90 (87)[c]
2	**L2** instead of **L1**	88
3	**L3** instead of **L1**	12
4	**L4** instead of **L1**	0
5	**L5** instead of **L1**	0
6	using Ni(cod)$_2$	11
7	using *fac*-Ir(ppy)$_3$PF$_6$ (4-CzIPN)	0
8	PhMe as solvent	0
9	Cs_2CO_3 instead of K_3PO_4	50
10	no NiBr$_2$·diglyme, **Ir-1** or light	0
11	no **L1**	43
12	no K_3PO_4	67



[a] **1a** (0.20 mmol), **2a** (0.10 mmol), NiBr$_2$·diglyme (5 mol%), **Ir-1** (1 mol%), **L1** (6 mol%), K_3PO_4 (0.15 mmol), dioxane (0.20 M) at 15 °C for 36 h. [b] ^{1}H NMR yields using $MeNO_2$ as internal standard. [c] Isolated yield

Table S2. Screening the metal source for α *sp*^{3} C–H defluorinative alkylation [a]



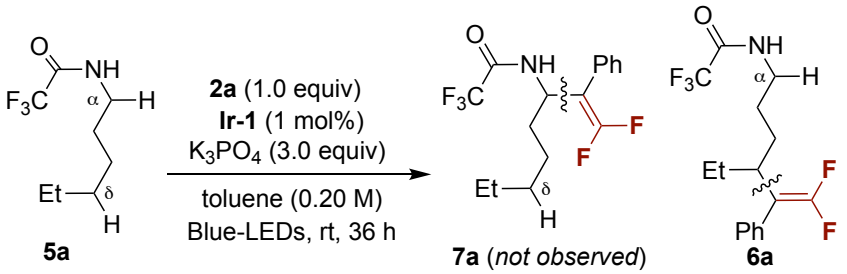
entry	metal salts	**3a** (%)[b]
1	$FeCl_2$	0
2	CuCl	0
3	$Cu(OAc)_2$	0
4	$CeCl_3$	0
5	$CoCl_2$	0
6	$ZnCl_2$	0
7	$CrCl_3$	0
8	$AlCl_3$	0
9	AgF	0
10	$MnBr_2$	7

[a] **1a** (0.20 mmol), **2a** (0.10 mmol), metal salts (5 mol%), **Ir-1** (1 mol%), K_3PO_4 (0.15 mmol), dioxane (0.20 M) at 15 ºC for 36 h. [b] ^{1}H NMR yields using $MeNO_2$ as internal standard.

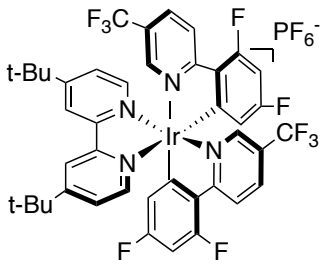
Optimization of the reaction conditions for the δ sp^3 C-H defluorinative alkylation of secondary amides

General procedure for the reaction of 5a with 2a: To an 8 mL vial equipped with a stirring bar was added **5a** (38.5 mg, 0.20 mmol, 2 equiv) and **Ir-1** (1.1 mg, 0.01 equiv). The vial was then introduced in the nitrogen-filled glovebox where the base (0.30 mmol, 3.0 equiv) was added followed by 0.5 mL of the solvent. Then the tube was brought outside the glovebox, and **2a** (0.10 mmol, 1 equiv) was added to the reaction mixture under N_2 atmosphere. The reaction was stirred and irradiated using 451 nm Kessil light (40 W) equipped with a fan cooling system for 36 h. The reaction was quenched by the addition of EtOAc (5 mL). The mixture was filtered through a silica plug and the solvent was removed under vacuum. Then, nitromethane (5.4 μL, 0.10 mmol) was added as internal standard and the reaction mixture was analyzed by ^{1}H NMR.

Table S3. Optimization of δ sp^3 C–H defluorinative alkylation of secondary amides.[a]



entry	deviation standard conditions	**6a** (%)[b]
1	none	84 (78)[c]
2	using *fac*-Ir(ppy)$_3$PF$_6$	0
3	using Ir(dFppy)$_2$(bpy)PF$_6$	80
4	using Ir(Fppy)$_2$(bpy)PF$_6$	56
5	K_2HPO_4 instead of K_3PO_4	0
6	Cs_2CO_3 instead of K_3PO_4	84
7	1,4-dioxane as solvent	71
8	MeCN as solvent	60
9	K_3PO_4 (1.50 equiv)	72
10	no K_3PO_4	0
11	no **Ir-1** or light	0

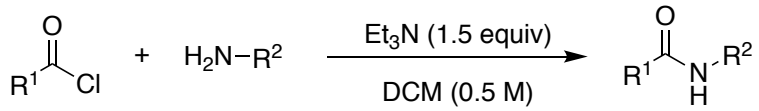


Ir-1

[a] **5a** (0.20 mmol), **2a** (0.10 mmol), **Ir-1** (1 mol%), K_3PO_4 (0.30 mmol), toluene (0.2 M) at rt for 36 h. [b] ^{1}H NMR yields using nitromethane as internal standard. [c] Isolated yield.

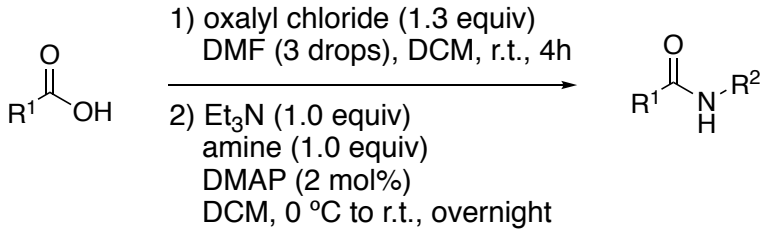
Synthesis of Starting Materials

General procedure A for the synthesis of secondary amides



Amine (1.0 equiv) and Et_3N (1.5 equiv) were added to a round-bottomed flask containing a stirring bar and dichloromethane (0.5 M). The mixture was then stirred and cooled down using an ice bath. Subsequently, the corresponding acyl chloride (1.0 equiv) was added dropwise by syringe. After the addition, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The reaction was then washed with saturated NaCl solution, 1 M HCl solution and water, and the resulting organic phases were dried over $MgSO_4$. The mixture was then purified by flash column chromatography, eluting with hexane/EtOAc.[1]

General procedure B for the synthesis of secondary amides

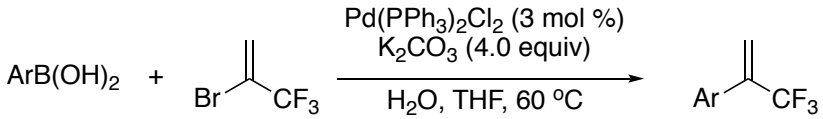


To a 100 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added benzoic acid (5.0 mmol, 1.0 equiv). The flask was backfilled with N_2 three times before adding DCM (25 mL, 0.2 M). The mixture was then cooled down to 0 ºC using an ice bath prior to addition of oxalyl chloride (0.55 mL, 6.5 mmol, 1.3 equiv) and DMF (3-5 drops). The reaction was then allowed to warm to room temperature and stirred for 4 hours. The crude was concentrated under reduced pressure, and the residue was then taken up in fresh DCM (25 mL, 0.2 M) and cooled to 0 ºC. Et_3N (0.70 mL, 5.0 mmol, 1.0 equiv) was added dropwise followed by addition of the amine (5.0 mmol, 1.0 equiv) and DMAP (12 mg, 0.1 mmol, 0.02 equiv). The reaction was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with 10 mL H_2O and 25 mL DCM. The organic phases were washed with 1M HCl (25 mL × 2), 1M NaOH (25 mL × 2), dried with 25 mL brine, and then over Na_2SO_4. The solvent was removed under vacuum and the crude was purified by silica gel chromatography.[1]

General procedure for synthesis of trifluoromethyl amides

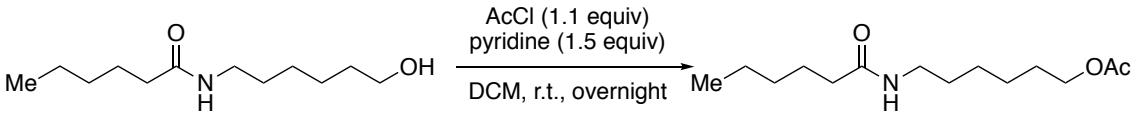
To a stirring solution of amine (3 mmol) in dichloromethane (30 mL, 0.1 M), triethylamine (6 mmol, 2.0 equiv) was added dropwise under N_2. The resulting solution was cooled with an ice bath and trifluoroacetic anhydride (3.3 mmol, 1.1 equiv) was added dropwise. Then, the reaction was warmed to room temperature and 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 $NaHCO_3$ (30 mL) before being passed through a short silica plug and concentrated to afford the corresponding trifluoroacetamide without the need for further purification. [2]

General procedure for synthesis of trifluoromethylated alkenes



To a Schlenk tube equipped a magnetic stir bar, boronic acid (5 mmol, 1.0 equiv), and $Pd(PPh_3)_2Cl_2$ (63.2 mg, 3 mol%) were added sequentially. The vessel was evacuated and filled with argon (three times), and then THF (15 mL, degased) and aqueous K_2CO_3 (2.0 M, 10 mL, degased) were added. After the addition of 2-bromo-3,3,3-trifluoropropene (1.04 mL, 10 mmol, 2.0 equiv), the reaction mixture was stirred at 60 °C overnight under argon atmospheres. The resulting mixture was cooled to room temperature, quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3×15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired trifluoromethylated alkene.[3]

Synthesis of 6-hexanamidohexyl acetate (1r)



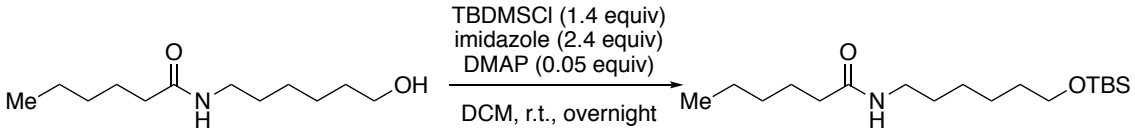
Int 1 **1r**

To a 25 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added **Int 1** (646 mg, 3.0 mmol, 1.0 equiv). The flask was backfilled with N_2 three times before adding DCM (15 mL, 0.2 M) and cooling to 0 ºC in an ice bath. Acetyl chloride (0.23 mL, 3.3 mmol, 1.1 equiv) was then added followed by pyridine (0.36 mL, 4.5 mmol, 1.5 equiv). The reaction was then allowed to warm to room temperature and

stirred overnight. The reaction was quenched with water and extracted with DCM (20 mL × 3), washed with 80 mL brine. Then, the organics were dried over Na_2SO_4. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography hexane/EtOAc 1/1 to 100% EtOAc to give the title compound as a pale yellow oil (625 mg, 2.43 mmol, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (s, 1H), 3.96 (t, *J* = 6.7 Hz, 2H), 3.46 – 2.82 (m, 2H), 2.10 – 2.05 (m, 2H), 1.95 (s, 3H), 1.59 – 1.49 (m, 4H), 1.45 – 1.39 (m, 2H), 1.33 – 1.12 (m, 8H), 0.80 (t, J = 6.8 Hz, 3H) ppm.**^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.3, 171.2, 64.3, 39.3, 36.7, 31.4, 29.5, 28.5, 26.5, 25.6, 25.5, 22.4, 20.9, 13.9 ppm. **HRMS** calcd. for ($C_{14}H_{28}NO_3$) $[M+H]^+$: 258.2064, found 258.2056. **IR (neat):** 3294, 2931, 2860, 1739, 1642, 1234, 1037, 731.

Synthesis of N-(6-((tert-butyldimethylsilyl)oxy)hexyl)hexanamide (1s)

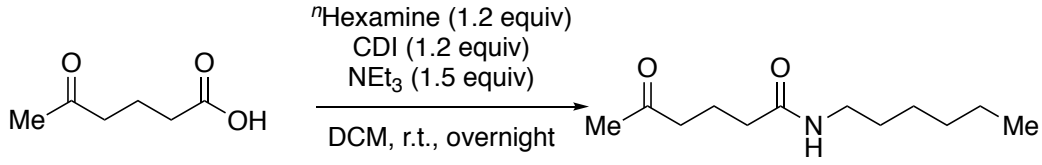


Int 1 **1s**

To a 25 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added **Int 1** (320 mg, 1.5 mmol, 1.0 equiv). The flask was backfilled with N_2 three times before adding DCM (7.5 mL, 0.2 M). TBDMSCl (320 mg, 2.1 mmol, 1.4 equiv) was then added followed by imidazole (240 mg, 3.6 mmol, 2.4 equiv) and DMAP (9 mg, 0.075 mmol, 0.05 equiv). The reaction was stirred overnight at room temperature. Then the reaction was quenched with water and extracted with Et_2O (20 mL × 3), washed with 20mL water and 40 mL brine. Then, the organics were dried over Na_2SO_4. The solvent was removed under vacuum and the crude reaction mixture was purified by silica gel chromatography hexane/EtOAc 2/1 to give the title compound as a colorless oil (461 mg, 1.4 mmol, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (s, 1H), 3.59 (t, *J* = 6.5 Hz, 2H), 3.35 – 3.14 (m, 2H), 2.20 – 2.09 (m, 2H), 1.70 – 1.57 (m, 2H), 1.56 – 1.43 (m, 4H), 1.41 – 1.21 (m, 8H), 0.95 – 0.83 (m, 12H), 0.04 (s, 6H) ppm.**^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.3, 63.2, 39.5, 36.8, 32.8, 31.6, 29.8, 26.8, 26.0, 25.8, 25.6, 22.5, 18.4, 14.0, -5.2 ppm. **HRMS** calcd. for ($C_{18}H_{40}NO_2Si$) $[M+H]^+$: 330.2823, found 330.2816. **IR (neat):** 3290, 2929, 2857, 1643, 1551, 1253, 1096, 834.

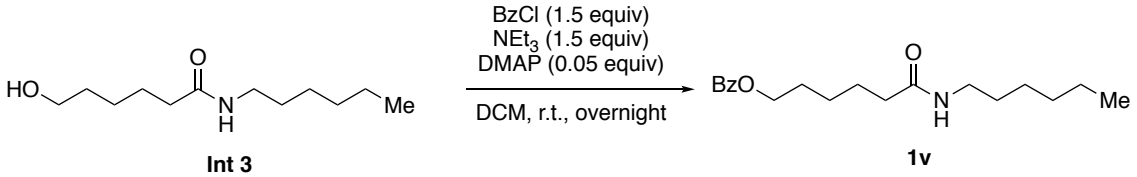
Synthesis of *N*-hexyl-5-oxohexanamide (1z)



1z

To a 50 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added 5-oxohexanoic acid (1.30 g, 10.0 mmol, 1.0 equiv). The flask was backfilled with N_2 three times before adding DCM (20 mL, 0.5 M) and CDI (1.95 g, 12.0 mmol, 1.2 equiv). The mixture was stirred at room temperature for 1 h. ^{n}Hexamine (1.55 mL, 12.0 mmol, 1.2 equiv) was then added followed by NEt_3 (2.10 mL, 15.0 mmol, 1.5 equiv). The reaction was then stirred overnight. The reaction was quenched with aqueous 2 M HCl and stirred for another 15 minutes. Then the mixture was extracted with DCM (20 mL × 3), washed with 30 mL aqueous 2 M HCl, 30mL water, 40 mL saturated aqueous $NaHCO_3$, and 30 mL brine sequentially. Then, the organics were dried over Na_2SO_4. The solvent was removed under vacuum and give the title compound as a pale yellow solid (1.40 g, 6.56 mmol, 66% yield), which can be used directly without further purification. M.P.: 63-64 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.58 (s, 1H), 3.22 (td, J = 7.2, 5.7 Hz, 2H), 2.51 (t, J = 7.0 Hz, 2H), 2.18 (t, J = 7.3 Hz, 2H), 2.13 (s, 3H), 1.95 – 1.81 (m, 2H), 1.52 – 1.40 (m, 2H), 1.35 – 1.21 (m, 6H), 0.91 – 0.83 (m, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.7, 172.4, 42.5, 39.5, 35.4, 31.5, 29.9, 29.6, 26.6, 22.6, 19.8, 14.0 ppm. **HRMS** calcd. for ($C_{12}H_{24}NO_2$) $[M+H]^+$: 214.1802, found 214.1795. **IR (neat):** 3284, 2922, 2853, 1703, 1638, 1370, 1157, 713.

Synthesis of 6-(hexylamino)-6-oxohexyl benzoate (1v)



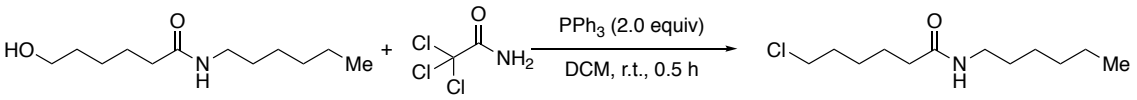
Int 3 **1v**

To a 25 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added **Int 3** (650 mg, 3.0 mmol, 1.0 equiv). The flask was backfilled with N_2 three times before adding DCM (15 mL, 0.2 M) and cooling to 0 °C in an ice bath. Benzoyl chloride (630 mg, 4.5 mmol, 1.5 equiv) was then added followed by NEt_3 (460 mg, 4.5 mmol, 1.5 equiv) and DMAP (18 mg, 0.15 mmol, 0.05 equiv). The reaction was then allowed to warm to room temperature and stirred for 1 hour. The reaction was

quenched with water and extracted with DCM (20 mL × 3), washed with 80 mL brine. Then the organics were dried over Na_2SO_4. The solvent was removed under vacuum and the crude reaction mixture was purified by silica gel chromatography hexane/EtOAc 1/1 to give the title compound as a colorless oil (741 mg, 2.31 mmol, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.54 – 7.47 (m, 1H), 7.43 – 7.34 (m, 2H), 5.92 (t, *J* = 5.8 Hz, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.18 (td, *J* = 7.2, 5.6 Hz, 2H), 2.16 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.58 (m, 4H), 1.50 – 1.34 (m, 4H), 1.32 – 1.11 (m, 6H), 0.86 – 0.77 (m, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.8, 166.6, 132.9, 130.3, 129.5, 128.3, 64.8, 39.5, 36.5, 31.5, 29.6, 28.5, 26.6, 25.8, 25.5, 22.5, 14.0 ppm. **HRMS** calcd. for ($C_{19}H_{30}NO_3$) $[M+H]^+$: 320.2220, found 320.2219. **IR (neat):** 3301, 2929, 2859, 1718, 1641, 1271, 1115, 709.

Synthesis of 6-chloro-*N*-hexylhexanamide (1w)

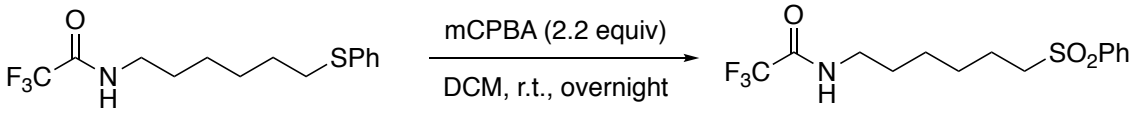


Int 3 **1w**

To a stirred solution of **Int 3** (650 mg, 3.0 mmol, 1.0 equiv) and PPh_3 (1.57 g, 6.0 mmol, 2.0 equiv) in dry DCM(10 mL, 0.3 M) was added 2,2,2-trichloroacetamide (970 mg, 6.0 mmol, 2.0 equiv) under Ar. The reaction mixture was stirring at rt for 30 min, then quenched with cold water. The aqueous phase was extracted with DCM (3 x 10 mL), the combined organic phases were dried over $MgSO_4$, then concentrated. The residue was purified by flash column chromatography (Hexane/EtOAc = 1:1) to provide **1w** (400 mg, 1.73 mmol, 57%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (s, 1H), 3.53 (t, *J* = 6.6 Hz, 2H), 3.31 – 3.17 (m, 2H), 2.17 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.71 (m, 2H), 1.72 – 1.63 (m, 2H), 1.55 – 1.41 (m, 4H), 1.37 – 1.22 (m, 6H), 0.92 – 0.83 (m, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.8, 77.7, 44.9, 39.6, 36.6, 32.3, 31.5, 29.6, 26.7, 26.6, 25.1, 22.6, 14.1 ppm. **HRMS** calcd. for ($C_{12}H_{25}ClNO$) $[M+H]^+$: 234.1619, found 234.1615. **IR (neat):** 3293, 2929, 2859, 1640, 1549, 1459, 730.

Synthesis of 2,2,2-trifluoro-*N*-(6-(phenylsulfonyl)hexyl)acetamide (5d)

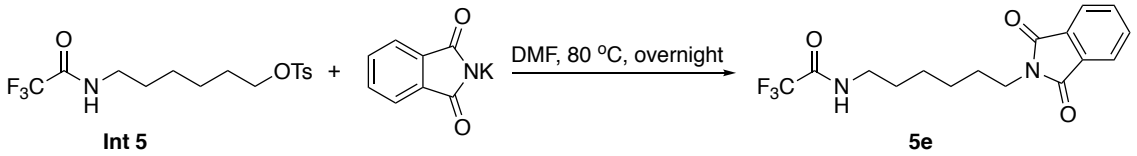


Int 4 **5d**

To a 25 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added **Int 4** (1.37 g, 4.5 mmol, 1.0 equiv) and DCM (45 mL, 0.1 M) and cooling to 0 ºC in an ice bath. *m*CPBA (1.71 g 75%, 9.9 mmol, 2.2 equiv) was then added. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with water and extracted with DCM (20 mL × 3), washed with 80 mL saturated aqueous $NaHCO_3$ and 50 mL brine sequentially. Then, the organics were dried over Na_2SO_4. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography hexane/EtOAc 3/1 to give the title compound as a colorless oil (1.08 g, 3.20 mmol, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.68 – 7.60 (m, 1H), 7.59 – 7.49 (m, 2H), 6.98 (s, 1H), 3.27 (q, *J* = 6.8 Hz, 2H), 3.09 – 3.00 (m, 2H), 1.74 – 1.60 (m, 2H), 1.56 – 1.45 (m, 2H), 1.41 – 1.31 (m, 2H), 1.31 – 1.21 (m, 2H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.98 ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.4 (q, *J* = 36.7 Hz), 139.0, 133.9, 129.4, 128.0, 116.0 (q, *J* = 287.7 Hz), 56.0, 39.6, 28.5, 27.7, 26.0, 22.5 ppm. **HRMS** calcd. for ($C_{14}H_{18}F_3NNaO_3S$) $[M+Na]^+$: 360.0852, found 360.0855. **IR (neat):** 3326, 2941, 2864, 1708, 1556, 1140, 1085, 721.

Synthesis of *N*-(6-(1,3-dioxoisoindolin-2-yl)hexyl)-2,2,2-trifluoroacetamide (5e)

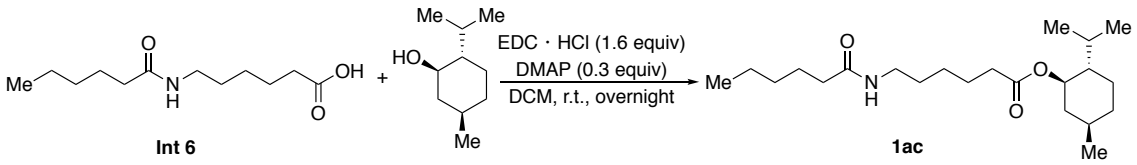


Int 5 **5e**

To a 25 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added **Int 5** (735 mg, 2.0 mmol, 1.0 equiv). The flask was backfilled with N_2 three times before adding DMF (5 mL, 0.4 M). Potassium phthalimide (437 mg, 2.4 mmol, 1.2 equiv) was then added. The reaction was then heated to 80 ºC and stirred at this temperature overnight. The reaction was quenched with brine and extracted with $CHCl_3$ (20 mL × 3). The combined organic phase was washed with 80 mL water and 80 mL brine. Then, the organics were dried over Na_2SO_4. The solvent was removed under vacuum and the crude reaction mixture was purified by silica gel chromatography

hexane/EtOAc 3/1 to give the title compound as a white solid (560 mg, 1.64 mmol, 82% yield). M.P.: 117-118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.73 – 7.65 (m, 2H), 6.88 (s, 1H), 3.65 (t, *J* = 7.1 Hz, 2H), 3.32 (q, *J* = 6.7 Hz, 2H), 1.72 – 1.60 (m, 2H), 1.61 – 1.51 (m, 2H), 1.44 – 1.28 (m, 4H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.02 ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 157.4 (q, *J* = 36.8 Hz), 134.1, 132.1, 123.3, 116.0 (d, *J* = 287.8 Hz), 39.7, 37.6, 28.7, 28.4, 26.1, 25.9 ppm. **HRMS** calcd. for ($C_{16}H_{17}F_3N_2NaO_3$) $[M+Na]^+$: 365.1083, found 365.1085. **IR (neat):** 3304, 2930, 2862, 1692, 1560, 1401, 1162, 720.

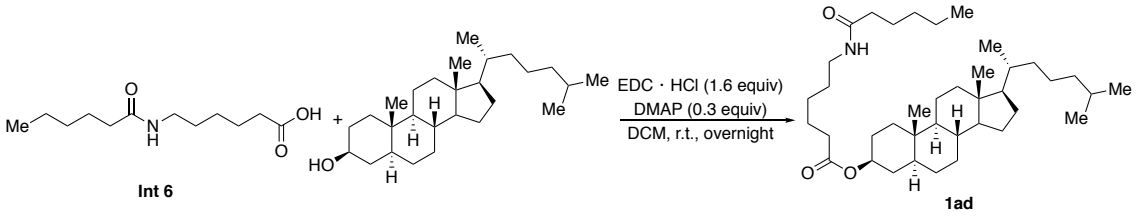
Synthesis of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 6-hexanamidohexanoate (1ac)



To a 50 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added **Int 6** (690 mg, 3.0 mmol, 1.0 equiv), (*L*)-menthol (750 mg, 4.8 mmol, 1.6 equiv), EDC•HCl (920 mg, 4.8 mmol, 1.6 equiv), and DMAP (110 mg, 0.90 mmol, 0.3 equiv) sequentially. The flask was backfilled with N_2 three times before adding DCM (15 mL, 0.2 M). The reaction was stirred overnight. Then the reaction was quenched with water and extracted with DCM (20 mL × 3), washed with 80 mL brine. Then, the organics were dried over Na_2SO_4. The solvent was removed under vacuum and the crude reaction mixture was purified by silica gel chromatography hexane/EtOAc 1/1 to give the title compound as a colorless oil (400 mg, 1.09 mmol, 36% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (s, 1H), 4.63 (td, *J* = 10.9, 4.4 Hz, 1H), 3.20 (q, *J* = 6.5 Hz, 2H), 2.24 (t, *J* = 7.4 Hz, 2H), 2.11 (t, *J* = 7.6 Hz, 2H), 1.97 – 1.87 (m, 1H), 1.85 – 1.72 (m, 1H), 1.69 – 1.52 (m, 6H), 1.52 – 1.39 (m, 3H), 1.37 – 1.17 (m, 7H), 1.06 – 0.88 (m, 2H), 0.89 – 0.77 (m, 10H), 0.71 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.3, 173.2, 74.1, 47.1, 41.0, 39.2, 36.8, 34.5, 34.3, 31.5, 31.4, 29.3, 26.4, 26.3, 25.6, 24.7, 23.5, 22.5, 22.1, 20.8, 16.4, 14.0 ppm. **HRMS** calcd. for ($C_{22}H_{42}NO_3$) $[M+H]^+$: 368.3159, found 368.3158. **IR (neat):** 3294, 2928, 2868, 1730, 1644, 1547, 1456, 1169.

Synthesis of (3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 6-hexanamidohexanoate (1ad)

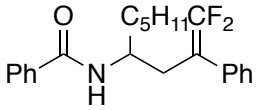


To a 50 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added **Int 6** (690 mg, 3.0 mmol, 1.0 equiv), 5α-Cholestan-3β-ol (1.87 g, 4.8 mmol, 1.6 equiv), EDC•HCl (920 mg, 4.8 mmol, 1.6 equiv), and DMAP (110 mg, 0.90 mmol, 0.3 equiv) sequentially. The flask was backfilled with N_2 three times before adding DCM (15 mL, 0.2 M) and the reaction was stirred overnight. Then, the reaction was quenched with water and extracted with DCM (20 mL × 3), washed with 80 mL brine. Then, the organics were dried over Na_2SO_4. The solvent was removed under vacuum and the crude reaction mixture was purified by silica gel chromatography hexane/EtOAc 1/1 to give the title compound as a white solid (1.28 g, 2.13 mmol, 71% yield). M.P.: 104-105 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.50 (s, 1H), 4.68 (tt, *J* = 11.4, 4.9 Hz, 1H), 3.24 (td, *J* = 7.1, 5.7 Hz, 2H), 2.26 (t, *J* = 7.4 Hz, 2H), 2.19 – 2.11 (m, 2H), 1.96 (dt, *J* = 12.5, 3.4 Hz, 1H), 1.85 – 1.72 (m, 3H), 1.70 (t, *J* = 3.6 Hz, 1H), 1.68 – 1.59 (m, 5H), 1.58 – 1.43 (m, 7H), 1.39 – 1.20 (m, 16H), 1.18 – 1.04 (m, 7H), 1.02 – 0.94 (m, 3H), 0.91 – 0.88 (m, 6H), 0.87 – 0.86 (m, 3H), 0.85 (d, *J* = 1.8 Hz, 3H), 0.81 (s, 3H), 0.64 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.4, 173.3, 73.7, 56.5, 56.4, 54.3, 44.8, 42.7, 40.1, 39.6, 39.3, 36.9, 36.8, 36.3, 35.9, 35.6, 34.5, 34.2, 32.1, 31.6, 29.3, 28.7, 28.3, 28.1, 27.6, 26.4, 25.60, 24.7, 24.3, 23.9, 22.9, 22.7, 22.5, 21.3, 18.8, 14.0, 12.3, 12.2 ppm. **HRMS** calcd. for ($C_{39}H_{70}NO_3$) $[M+H]^+$: 600.5350, found 600.5334. **IR (neat):** 3328, 2934, 2867, 1738, 1644, 1554, 1231, 1183.

Defluorinative α/δ sp^3 C-H alkylation of secondary amides

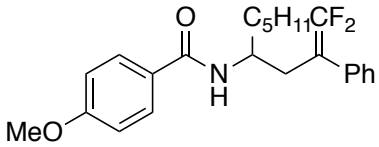
General procedure A: An oven-dried 8 mL Schlenk tube containing a stirring bar was charged with **1** (0.40 mmol, 2 equiv), **Ir-1** (2.2 mg, 0.01 equiv), **L1** (2.2 mg, 0.06 equiv), and $NiBr_2$·diglyme (3.6 mg, 0.05 equiv). The tube was then introduced in the nitrogen-filled glovebox where K_3PO_4 (64 mg, 0.30 mmol, 1.5 equiv) was added followed by 1.0 mL 1,4-dioxane. Then the tube was brought outside the glovebox, and **2** (0.20 mmol, 1 equiv) was added to the reaction mixture under N_2 atmosphere. Then the tube was stirred at 15 °C under irradiation of blue LEDs with a cooling system for 36 hours. The reaction was quenched by the addition of EtOAc (5 mL), and the reaction mixture was concentrated under vacuum prior to purification by flash chromatography column on silica gel.

General procedure B: To an 8 mL vial equipped with a stirring bar was added **5** (0.40 mmol, 2.0 equiv), **Ir-1** (2.2 mg, 0.01 equiv). The vial was then introduced in the nitrogen-filled glovebox where K_3PO_4 (128 mg, 0.60 mmol, 3.0 equiv) was added followed by 1.0 mL toluene. Then the tube was brought outside the glovebox, and **2** (0.20 mmol, 1 equiv) was added to the reaction mixture under N_2 atmosphere. The reaction was stirred and irradiated using 451 nm Kessil light (40 W), equipped with a fan cooling system for 72 hours. The reaction was quenched by addition of EtOAc (5 mL), and the mixture was concentrated under vacuum prior to purification by flash chromatography on silica gel.

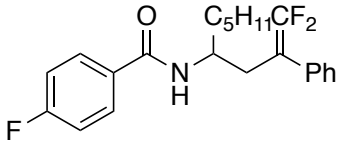


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)benzamide (**3a**) Following General Procedure A, *N*-hexylbenzamide (1a) (82.1 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (2a) (34.4 mg, 0.20 mmol) were used, affording the title compound as a white solid (63.0 mg, 87% yield) by using Hexane/EtOAc (8:1) as eluent. M.P.: 102-103 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 3H), 7.39 – 7.30 (m, 6H), 7.29 – 7.21 (m, 1H), 5.77 (d, *J* = 8.9 Hz, 1H), 4.37 – 3.89 (m, 1H), 2.77 – 2.62 (m, 2H), 1.67 – 1.53 (m, 1H), 1.54 – 1.42 (m, 1H), 1.41 – 1.11 (m, 6H), 0.90 – 0.80 (m, 3H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.49 (d, *J* = 41.4 Hz), δ -90.62 (d, *J* = 41.4 Hz) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 154.5 (dd, *J* = 290.2, 288.0 Hz), 134.7, 133.7 (d, *J* = 2.5 Hz), 131.3, 128.8, 128.5, 128.4, 127.6, 126.8, 90.0 (dd, *J* = 19.7, 16.3 Hz), 49.1 (t, *J* = 2.8 Hz), 34.5, 33.3, 31.7, 25.7, 22.6, 14.1 ppm. **HRMS** calcd. for ($C_{22}H_{26}F_2NO$) $[M+H]^+$:

358.1977, found 358.1984. **IR (neat):** 3238, 3065, 2932, 2856, 1704, 1628, 1542, 1225, 692.

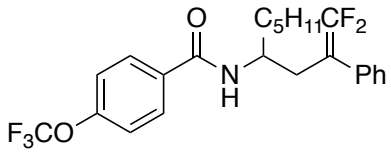


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-4-methoxybenzamide (**3b**) Following General Procedure A, N-hexyl-4-methoxybenzamide (**1b**) (94.1 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a white solid (75.0 mg, 96% yield) by using Hexane/EtOAc (6:1) as eluent. M.P.: 82-83 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.38 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 6.85 – 6.76 (m, 2H), 5.70 (d, *J* = 8.9 Hz, 1H), 4.25 – 4.10 (m, 1H), 3.81 (s, 3H), 2.80 – 2.54 (m, 2H), 1.65 – 1.51 (m, 1H), 1.53 – 1.40 (m, 1H), 1.37 – 1.17 (m, 6H), 0.89 – 0.80 (m, 3H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.66 (d, *J* = 41.4 Hz), δ -90.68 (d, *J* = 41.4 Hz) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.5, 162.1, 154.5 (dd, *J* = 290.3, 288.0 Hz), 133.8 (d, *J* = 2.2 Hz), 128.8, 128.6, 128.5 (t, *J* = 3.0 Hz), 127.6, 127.0, 113.7, 90.0 (dd, *J* = 19.4, 16.5 Hz), 55.4, 49.0 (t, *J* = 2.7 Hz), 34.5, 33.2, 31.7, 25.7, 22.6, 14.1 ppm.**HRMS** calcd. for ($C_{23}H_{28}F_2NO_2$) $[M+H]^+$: 388.2083, found 388.2067. **IR (neat):** 3234, 2932, 2857, 1738, 1605, 1506, 1026, 692.

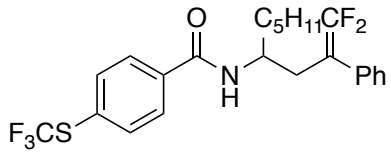


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-4-fluorobenzamide (**3c**) Following General Procedure A, 4-fluoro-N-hexylbenzamide (**1c**) (89.3 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.43 mg, 0.20 mmol) were used, affording the title compound as a white solid (50.0 mg, 67% yield) by using Hexane/EtOAc (8:1) as eluent. M.P.: 83-84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 3H), 7.35 – 7.31 (m, 3H), 7.28 – 7.20 (m, 1H), 7.00 (t, *J* = 8.6 Hz, 2H), 5.59 (d, *J* = 8.9 Hz, 1H), 4.26 – 4.10 (m, 1H), 2.76 – 2.62 (m, 2H), 1.65 – 1.54 (m, 1H), 1.52 – 1.43 (m, 1H), 1.34 – 1.22 (m, 6H), 0.88 – 0.82 (m, 3H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.05, -90.07, -108.30 ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.0, 163.5, 154.5 (dd, *J* = 290.0, 288.2 Hz), 133.8 (d, *J* = 1.5 Hz), 130.7 (d, *J* = 3.1 Hz), 129.1 (d, *J* = 8.9 Hz), 128.9, 128.5 (t, *J* = 3.0 Hz), 127.7, 115.5 (d, *J* = 21.9 Hz), 89.9 (dd, *J* = 19.7, 16.3 Hz), 49.3 (t, *J* = 2.8 Hz), 34.6, 33.2,

31.75, 25.7, 22.6, 14.1. **HRMS** calcd. for ($C_{22}H_{25}F_3NO$) $[M+H]^+$: 376.1883, found 376.1887. **IR (neat):** 3242, 2955, 2929, 2857, 1713, 1631, 1504, 1228, 853, 692.

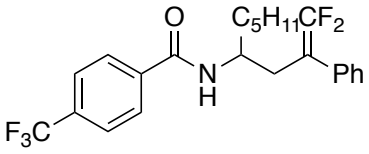


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-4-(trifluoromethoxy)benzamide (**3d**) Following General Procedure A, N-hexyl-4-(trifluoromethoxy)benzamide (**1d**) (115.7 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as white solid (70.0 mg, 79% yield) by using Hexane/EtOAc (8:1) as eluent. M.P.:70-71 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.36 – 7.28 (m, 4H), 7.28 – 7.20 (m, 1H), 7.18 – 7.06 (m, 2H), 5.93 (d, *J* = 8.8 Hz, 1H), 4.36 – 4.08 (m, 1H), 2.73 – 2.66 (m, 2H), 1.64 – 1.50 (m, 1H), 1.53 – 1.41 (m, 1H), 1.35 – 1.19 (m, 6H), 0.87 – 0.82 (m, 3H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.55, -90.09 ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.8, 154.5 (t, *J* = 289.2 Hz), 151.4 (q, *J* = 1.8 Hz), 133.8, 133.2, 128.9, 128.7, 128.4 (t, *J* = 3.0 Hz), 127.6, 120.5, 120.4 (q, *J* = 258.2 Hz), 89.9 (t, *J* = 18.1 Hz), 49.4 (t, *J* = 2.7 Hz), 34.5, 33.2, 31.7, 25.7, 22.6, 14.0 ppm. **HRMS** calcd. for ($C_{23}H_{25}F_5NO_2$) $[M+H]^+$: 442.1800, found 442.1807. **IR (neat):** 3265, 2933, 2860, 1735, 1637, 1548, 1240, 695.

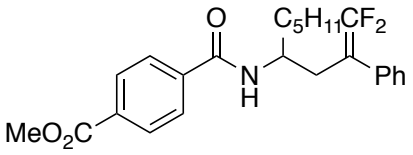


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-4-((trifluoromethyl)thio)benzamide (**3e**) Following General Procedure A, N-hexyl-4-((trifluoromethyl)thio)benzamide (1e) (122.1 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (2a) (34.4 mg, 0.20 mmol) were used, affording the title compound as an oil (86.3 mg, 94% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.36 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 5.61 (d, *J* = 8.9 Hz, 1H), 4.28 – 4.12 (m, 1H), 2.78 – 2.64 (m, 2H), 1.66 – 1.55 (m, 1H), 1.54 – 1.42 (m, 1H), 1.37 – 1.22 (m, 6H), 0.90 – 0.82 (m, 3H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.89, -89.95 ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 154.5 (t, *J* = 289.3 Hz), 136.9, 136.0, 133.8, 128.9, 128.8 (q, *J* = 156.4 Hz), 128.4 (t, *J* = 3.0 Hz), 127.8, 127.7, 125.1, 89.9 (t, *J* = 18.0 Hz), 49.5, 34.5, 33.1, 31.7, 25.7, 22.6, 14.1. **HRMS** calcd. for ($C_{23}H_{25}F_5NOS$) $[M+H]^+$:

458.1572, found 458.1567. **IR (neat):** 2930, 2860, 1727, 1637, 1231, 1111, 1015, 761, 692.

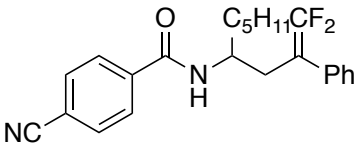


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-4-(trifluoromethyl)benzamide (**3f**) Following General Procedure A, N-hexyl-4-(trifluoromethyl)benzamide (**1f**) (109.3 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a white solid (66.0 mg, 77% yield) by using Hexane/EtOAc (10:1) as eluent. M.P.: 88-89 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.29 – 7.22 (m, 1H), 5.79 (d, *J* = 8.9 Hz, 1H), 4.30 – 4.14 (m, 1H), 2.76 – 2.58 (m, 2H), 1.65 – 1.55 (m, 1H), 1.55 – 1.43 (m, 1H), 1.35 – 1.23 (m, 6H), 0.87 – 0.83 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.08, -90.34. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.80, 154.53 (t, *J* = 289.4 Hz), 137.97, 133.83, 133.13 (q, *J* = 32.8 Hz), 128.96, 128.44 (q, *J* = 4.3, 3.6 Hz), 127.72, 127.27, 125.53 (q, *J* = 3.7 Hz), 123.79 (q, *J* = 272.5 Hz), 89.85 (t, *J* = 18.1 Hz), 49.54 (t, *J* = 2.8 Hz), 34.51, 33.14, 31.71, 25.73, 22.60, 14.07.**HRMS** calcd. for ($C_{23}H_{25}F_5NO$) $[M+H]^+$: 426.1851, found 426.1844. **IR (neat):** 3285, 2929, 2855, 1736, 1644, 1546, 1123, 694.

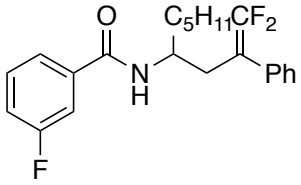


methyl 4-((1,1-difluoro-2-phenylnon-1-en-4-yl)carbamoyl)benzoate (**3g**) Following General Procedure A, methyl 4-(hexylcarbamoyl)benzoate (**1g**) (105.3 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (72.2 mg, 87% yield) by using Hexane/EtOAc (8:1) as eluent. M.P.: 79-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.47 – 7.41 (m, 2H), 7.35 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 5.89 (d, *J* = 9.0 Hz, 1H), 4.27 – 4.12 (m, 1H), 3.91 (s, 3H), 2.78 – 2.53 (m, 2H), 1.64 – 1.53 (m, 1H), 1.52 – 1.44 (m, 1H), 1.34 – 1.20 (m, 6H), 0.86 – 0.81 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.95 (d, *J* = 41.4 Hz), δ -90.07 (d, *J* = 41.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.40, 166.20, 154.46 (dd, *J* = 290.4, 288.4 Hz), 138.59, 133.76 (d, *J* = 2.4 Hz), 132.53, 129.69, 128.88, 128.41 (t, *J* = 3.8 Hz), 127.68, 126.83, 89.87 (dd, *J* = 19.6, 16.5 Hz), 52.42, 49.43 (t, *J* = 2.8 Hz), 34.42, 33.09, 31.68, 25.69, 22.56, 14.05. **HRMS** calcd. for

($C_{24}H_{28}F_2NO_3$) $[M+H]^+$: 416.2032, found 416.2034. **IR (neat):** 2930, 2859, 1723, 1638, 1541, 1275, 1105, 696.

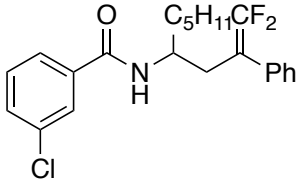


4-cyano-N-(1,1-difluoro-2-phenylnon-1-en-4-yl)benzamide (**3h**) Following General Procedure A, 4-cyano-N-hexylbenzamide (**1h**) (92.1 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (62.1 mg, 81% yield) by using Hexane/EtOAc (6:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.27 – 7.22 (m, 1H), 5.67 (d, *J* = 8.9 Hz, 1H), 4.22 (d, *J* = 6.5 Hz, 1H), 2.79 – 2.62 (m, 2H), 1.66 – 1.56 (m, 1H), 1.56 – 1.43 (m, 1H), 1.34 – 1.21 (m, 6H), 0.87 – 0.83 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.78. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.15, 154.51 (dd, *J* = 289.6, 288.5 Hz), 138.57, 133.86 (d, *J* = 1.6 Hz), 132.37, 128.98, 128.43 (t, *J* = 2.9 Hz), 127.74, 127.48, 118.13, 114.96, 89.65 (dd, *J* = 19.6, 16.4 Hz), 49.70 (t, *J* = 2.7 Hz), 34.49, 33.05, 31.68, 25.71, 22.59, 14.08. **HRMS** calcd. for ($C_{23}H_{24}F_2N_2NaO$) $[M+Na]^+$: 405.1749, found 405.1753. **IR (neat):** 3237, 2930, 2858, 2230, 1729, 1633, 1548, 1232, 695.

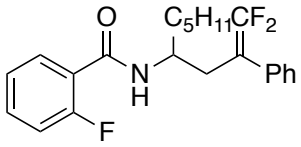


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-3-fluorobenzamide (**3i**) Following General Procedure A, 3-fluoro-N-hexylbenzamide (**1i**) (89.3 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (62.5 mg, 83% yield) by using Hexane/EtOAc (10:1) as eluent. M.P.: 82-83 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 4H), 7.30 – 7.21 (m, 2H), 7.20 – 7.10 (m, 3H), 5.73 (d, *J* = 8.9 Hz, 1H), 4.30 – 3.77 (m, 1H), 2.86 – 2.49 (m, 2H), 1.65 – 1.54 (m, 1H), 1.53 – 1.43 (m, 1H), 1.35 – 1.21 (m, 6H), 0.87 – 0.83 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.06, -111.81. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.73 (d, *J* = 2.5 Hz), 162.69 (d, *J* = 247.5 Hz), 154.45 (t, *J* = 289.3 Hz), 136.97 (d, *J* = 6.7 Hz), 133.73, 130.07 (d, *J* = 7.9 Hz), 128.86, 128.41 (t, *J* = 3.0 Hz), 127.70, 122.25 (d, *J* = 3.0 Hz), 118.27 (d, *J* = 21.3 Hz), 114.14 (d, *J* = 22.8 Hz), 89.90 (t,

J = 18.1 Hz), 49.33 (t, J = 2.8 Hz), 34.43, 33.11, 31.69, 25.68, 22.56, 14.04. **HRMS** calcd. for ($C_{22}H_{25}F_3NO$) $[M+H]^+$: 376.1883, found 376.1879. **IR (neat):** 3238, 3071, 2933, 2857, 1706, 1631, 1548, 1227, 691.

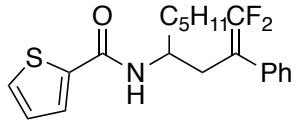


3-chloro-N-(1,1-difluoro-2-phenylnon-1-en-4-yl)benzamide (**3j**) Following General Procedure A, 3-chloro-N-hexylbenzamide (**1j**) (95.9 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (52.0 mg, 59% yield) by using Hexane/EtOAc (8:1) as eluent. M.P.: 85-86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 1H), 7.31 – 7.25 (m, 6H), 7.24 – 7.19 (m, 2H), 5.67 (d, J = 8.9 Hz, 1H), 4.22 – 4.11 (m, 1H), 2.71 – 2.61 (m, 2H), 1.60 – 1.51 (m, 1H), 1.50 – 1.40 (m, 1H), 1.30 – 1.17 (m, 6H), 0.84 – 0.79 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.36 (d, J = 33.8 Hz), δ -90.45 (d, J = 33.8 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.69, 154.48 (dd, J = 290.2, 288.0 Hz), 136.45, 134.64, 133.79 (d, J = 2.0 Hz), 131.40, 129.80, 128.93, 128.42 (t, J = 3.0 Hz), 127.82, 127.00, 124.95, 89.87 (dd, J = 19.2, 16.9 Hz), 49.46 (t, J = 2.8 Hz), 34.47, 33.08, 31.72, 25.70, 22.59, 14.08. **HRMS** calcd. for ($C_{22}H_{24}ClF_2NNaO$) $[M+Na]^+$: 414.1407, found 414.1400. **IR (neat):** 3065, 2929, 2858, 1723, 1636, 1541, 1236, 696.

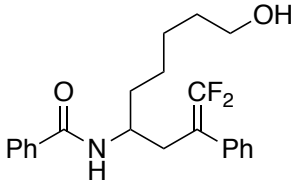


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-2-fluorobenzamide (**3k**) Following General Procedure A, 2-fluoro-N-hexylbenzamide (**1k**) (89.3 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (52.0 mg, 70% yield) by using Hexane/EtOAc (10:1) as eluent. M.P.: 79-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (td, J = 7.8, 1.8 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.36 – 7.27 (m, 4H), 7.25 – 7.17 (m, 2H), 7.06 (dd, J = 12.2, 8.2 Hz, 1H), 6.34 (d, J = 8.7 Hz, 1H), 4.25 – 4.07 (m, 1H), 2.76 – 2.63 (m, 2H), 1.66 – 1.53 (m, 1H), 1.54 – 1.40 (m, 1H), 1.39 – 1.18 (m, 6H), 0.87 – 0.82 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.52 (d, J = 41.1 Hz), -90.81 (dd, J = 41.3, 3.4 Hz), -114.08 (d, J = 3.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) 162.91 (d, J = 3.2 Hz), 160.69 (d, J = 246.8 Hz),

154.54 (dd, J = 290.0, 289.0 Hz), 133.38, 133.19 (d, J = 9.2 Hz), 132.15 (d, J = 2.2 Hz), 128.67, 128.43 (t, J = 3.1 Hz), 127.56, 124.84 (d, J = 3.3 Hz), 121.25 (d, J = 11.6 Hz), 116.03 (d, J = 25.0 Hz), 90.02 (dd, J = 21.1, 14.9 Hz), 48.94 (t, J = 2.9 Hz), 34.32, 33.11, 31.71, 25.50, 22.58, 14.08. **HRMS** calcd. for ($C_{22}H_{24}F_3NNaO$) $[M+Na]^+$: 397.1702, found 397.1688. **IR (neat):** 3259, 3065, 2952, 2856, 1703, 1630, 1540, 1224, 757.

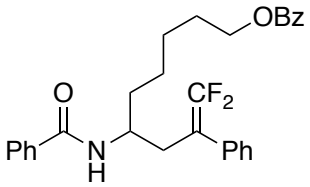


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)thiophene-2-carboxamide (**3l**) Following General Procedure A, N-hexylthiophene-2-carboxamide (**1l**) (84.5 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (50.4 mg, 69% yield) by using Hexane/EtOAc (10:1) as eluent. M.P.: 123-124 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 5.0, 1.1 Hz, 1H), 7.37 – 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 7.13 (dd, J = 3.7, 1.1 Hz, 1H), 6.99 (dd, J = 5.0, 3.7 Hz, 1H), 5.53 (d, J = 8.9 Hz, 1H), 4.38 – 3.88 (m, 1H), 2.75 – 2.56 (m, 2H), 1.64 – 1.52 (m, 1H), 1.52 – 1.42 (m, 1H), 1.36 – 1.19 (m, 6H), 0.87 – 0.82 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.39 (d, J = 41.2 Hz), -90.58 (d, J = 41.1 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.44, 154.52 (dd, J = 291.1, 287.3 Hz), 139.14, 133.59 (d, J = 6.0 Hz), 129.84, 128.86, 128.47 (t, J = 3.0 Hz), 127.69, 127.54, 89.92 (dd, J = 20.8, 15.3 Hz), 49.15 (t, J = 2.8 Hz), 34.50, 33.25 (d, J = 1.4 Hz), 31.74, 25.64, 22.60, 14.10. **HRMS** calcd. for ($C_{20}H_{23}F_2NNaOS$) $[M+Na]^+$: 386.1361, found 386.1345. **IR (neat):** 3250, 3081, 2928, 2855, 1705, 1613, 1544, 1227, 693.

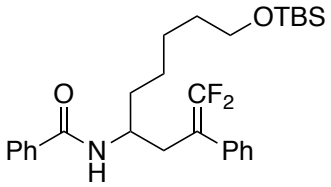


N-(1,1-difluoro-9-hydroxy-2-phenylnon-1-en-4-yl)benzamide (**3m**) Following General Procedure A, N-(6-hydroxyhexyl)benzamide (**1m**) (88.5 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (2a) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (59.2 mg, 79% yield) by using Hexane/EtOAc (1:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 3H), 7.39 – 7.33 (m, 6H), 7.31 – 7.28 (m, 1H), 5.75 (d, J = 9.0 Hz, 1H), 4.31 – 4.19 (m, 1H), 3.59 (t, J = 6.4 Hz, 2H), 2.78 – 2.66 (m, 2H), 1.67 – 1.58 (m, 1H), 1.60 – 1.46 (m, 3H), 1.43 – 1.31 (m, 4H). **^{19}F**

NMR (376 MHz, $CDCl_3$) δ -89.99 (d, *J* = 41.4 Hz), δ -90.12 (d, *J* = 41.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.15, 154.48 (dd, *J* = 290.2, 288.0 Hz), 134.55, 133.67 (d, *J* = 2.9 Hz), 131.45, 128.90, 128.54, 128.48 (t, *J* = 3.0 Hz), 127.69, 126.78, 89.92 (dd, *J* = 20.1, 16.0 Hz), 62.54, 48.79 (t, *J* = 2.7 Hz), 34.62, 33.39, 32.52, 29.80, 25.54. **HRMS** calcd. for ($C_{22}H_{26}F_2NO_2$) $[M+H]^+$: 374.1926, found 374.1934. **IR (neat):** 3308, 2927, 2857, 1736, 1635, 1541, 1233, 695.

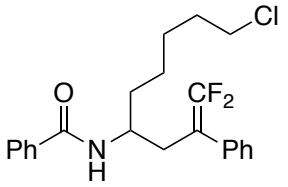


6-benzamido-9,9-difluoro-8-phenylnon-8-en-1-yl benzoate (**3n**) Following General Procedure A, 6-benzamidohexyl benzoate (**1n**) (130.2 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as an oil (58.0 mg, 60% yield) by using Hexane/EtOAc (6:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.59 – 7.50 (m, 1H), 7.49 – 7.39 (m, 5H), 7.38 – 7.29 (m, 6H), 7.27 – 7.21 (m, 1H), 5.80 (d, *J* = 8.8 Hz, 1H), 4.34 – 4.14 (m, 3H), 2.78 – 2.65 (m, 2H), 1.77 – 1.66 (m, 2H), 1.68 – 1.57 (m, 1H), 1.59 – 1.47 (m, 1H), 1.49 – 1.33 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.95 (d, J = 41.0 Hz), -90.09 (d, J = 41.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.02, 166.74, 154.46 (dd, J = 290.7, 287.7 Hz), 134.60, 133.61 (t, J = 2.4 Hz), 132.93, 131.39, 130.50, 129.61, 128.87, 128.50, 128.45, 128.42, 127.67, 126.77, 89.92 (dd, J = 20.2, 15.9 Hz), 64.94, 48.94 (t, J = 2.8 Hz), 34.47, 33.26, 28.67, 26.00, 25.70. **HRMS** calcd. for ($C_{29}H_{30}F_2NO_3$) $[M+H]^+$: 478.2188, found 478.2197. **IR (neat):** 3305, 3063, 2933, 2855, 1731, 1629, 1539, 1230, 693.

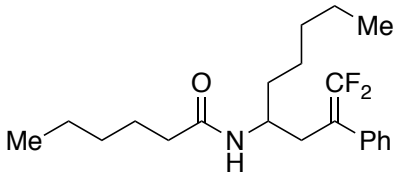


N-(9-((tert-butyldimethylsilyl)oxy)-1,1-difluoro-2-phenylnon-1-en-4-yl)benzamide (**3o**) Following General Procedure A, N-(6-((tert-butyldimethylsilyl)oxy)hexyl)benzamide (**1o**) (134.2 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (49.0 mg, 50% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 3H), 7.39 – 7.30 (m, 6H), 7.30 – 7.21 (m, 1H), 5.67 (d, *J* = 8.8 Hz, 1H), 4.29 – 4.13 (m, 1H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.77

– 2.63 (m, 2H), 1.68 – 1.56 (m, 1H), 1.54 – 1.41 (m, 3H), 1.41 – 1.28 (m, 4H), 0.88 (s, 9H), 0.03 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.03 (d, J = 41.2 Hz), -90.17 (d, J = 42.1 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.98, 154.47 (dd, *J* = 290.2, 288.0 Hz), 134.68, 133.69 (d, *J* = 2.5 Hz), 131.36, 128.86, 128.49, 128.44 (t, *J* = 3.0 Hz), 127.63, 126.76, 89.94 (dd, *J* = 20.0, 16.1 Hz), 63.17, 49.06 (t, *J* = 2.8 Hz), 34.62, 33.25, 32.77, 26.06, 25.85, 25.83, 18.44, -5.19. **HRMS** calcd. for ($C_{28}H_{40}F_2NO_2Si$) $[M+H]^+$: 488.2791, found 488.2779. **IR (neat):** 3302, 2929, 2856, 1728, 1636, 1540, 1236, 694.

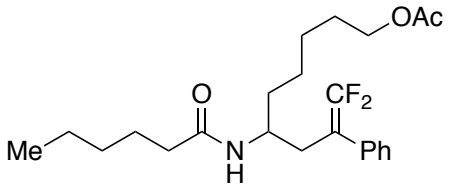


N-(9-chloro-1,1-difluoro-2-phenylnon-1-en-4-yl)benzamide (**3p**) Following General Procedure A, N-(6-chlorohexyl)benzamide (**1p**) (95.9 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (41.0 mg, 52% yield) by using Hexane/EtOAc (8:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 3H), 7.38 – 7.32 (m, 6H), 7.30 – 7.26 (m, 1H), 5.65 (d, *J* = 9.0 Hz, 1H), 4.29 – 4.16 (m, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.75 – 2.66 (m, 2H), 1.77 – 1.68 (m, 2H), 1.66 – 1.57 (m, 1H), 1.56 – 1.47 (m, 1H), 1.45 – 1.32 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.93 (d, *J* = 41.0 Hz), -90.10 (d, *J* = 41.0 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.01, 154.51 (dd, *J* = 290.2, 288.0 Hz), 134.61, 133.66 (d, *J* = 2.5 Hz), 131.48, 128.95, 128.58, 128.49 (t, *J* = 2.9 Hz), 127.74, 126.77, 89.90 (dd, *J* = 20.7, 15.5 Hz), 48.94 (d, *J* = 2.8 Hz), 45.05, 34.55, 33.35, 32.52, 26.82, 25.39. **HRMS** calcd. for ($C_{22}H_{25}ClF_2NO$) $[M+H]^+$: 392.1587, found 392.1593. **IR (neat):** 3305, 3063, 2933, 2855, 1731, 1629, 1539, 1230, 693.

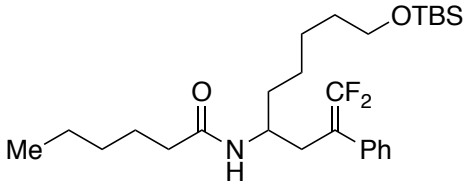


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)hexanamide (**3q**) Following General Procedure A, N-hexylhexanamide (**1q**) (79.7 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (2a) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (67.7 mg, 96% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 5.02 (d, *J* = 9.0 Hz, 1H),

4.27 – 3.74 (m, 1H), 2.83 – 2.38 (m, 2H), 1.99 – 1.90 (m, 2H), 1.56 – 1.40 (m, 3H), 1.37 – 1.16 (m, 11H), 0.91 – 0.80 (m, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.67 (d, *J* = 41.8 Hz), -90.87 (d, *J* = 41.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.69, 154.46 (dd, *J* = 290.8, 287.0 Hz), 133.70 (dd, *J* = 3.8, 2.3 Hz), 128.72, 128.47 (t, *J* = 3.0 Hz), 127.62, 90.05 (dd, *J* = 20.7, 15.0 Hz), 48.31 (t, *J* = 2.7 Hz), 36.90, 34.49, 33.34 (d, *J* = 1.5 Hz), 31.71, 31.53, 25.59, 25.40, 22.61, 22.50, 14.07, 14.03. **HRMS** calcd. for ($C_{21}H_{32}F_2NO$) $[M+H]^+$: 352.2446, found 352.2459. **IR (neat):** 3276, 2929, 2859, 1736, 1642, 1543, 1223, 696.

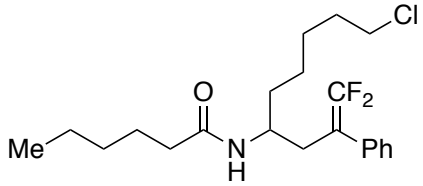


9,9-difluoro-6-hexanamido-8-phenylnon-8-en-1-yl acetate (**3r**) Following General Procedure A, 6-hexanamidohexyl acetate (**1r**) (102.9 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (56.0 mg, 68% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.29 – 7.23 (m, 1H), 5.04 (d, *J* = 9.0 Hz, 1H), 4.27 – 3.80 (m, 3H), 2.68 – 2.44 (m, 2H), 2.02 (s, 3H), 1.97 – 1.92 (m, 2H), 1.60 – 1.42 (m, 5H), 1.39 – 1.17 (m, 9H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.56 (d, *J* = 41.5 Hz), -90.79 (d, *J* = 41.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.71, 171.28, 154.44 (dd, *J* = 291.1, 287.0 Hz), 133.59 (dd, *J* = 4.0, 2.5 Hz), 128.73, 128.43 (t, *J* = 3.0 Hz), 127.66, 89.98 (dd, *J* = 21.0, 14.9 Hz), 64.43, 48.16 (t, *J* = 2.8 Hz), 36.85, 34.41, 33.34 (d, *J* = 1.4 Hz), 31.52, 28.54, 25.80, 25.56, 25.35, 22.47, 21.08, 14.02. **HRMS** calcd. for ($C_{23}H_{33}F_2NNaO_3$) $[M+Na]^+$: 432.2321, found 432.2321. **IR (neat):** 3284, 2933, 2860, 1737, 1644, 1542, 1232, 697.

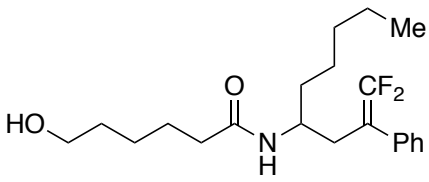


N-(9-((tert-butyldimethylsilyl)oxy)-1,1-difluoro-2-phenylnon-1-en-4-yl)hexanamide (**3s**) Following General Procedure A, N-(6-(tert-butyldimethylsilyl)hexyl)hexanamide (**1s**) (131.8 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (50.9 mg, 53%

yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 4.98 (d, *J* = 8.5 Hz, 1H), 4.07 – 3.87 (m, 1H), 3.55 (t, *J* = 6.5 Hz, 2H), 2.65 – 2.45 (m, 2H), 1.95 (t, *J* = 7.4 Hz, 2H), 1.55 – 1.40 (m, 5H), 1.37 – 1.17 (m, 9H), 0.93 – 0.80 (m, 12H), 0.03 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.22 (d, *J* = 41.6 Hz), -90.42 (d, *J* = 41.8 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.66, 154.43 (dd, *J* = 290.2, 288.0 Hz), 133.63, 128.71, 128.44 (t, *J* = 3.0 Hz), 127.61, 90.01 (dd, *J* = 19.7, 16.3 Hz), 63.18, 48.30, 36.89, 34.56, 33.33, 32.80, 31.52, 29.81, 26.07, 25.80, 25.37, 22.48, 18.45, 14.03, -5.18. **HRMS** calcd. for ($C_{27}H_{46}F_2NO_2Si$) $[M+H]^+$: 482.3260, found 482.3255. **IR (neat):** 3283, 2928, 2857, 1729, 1642, 1548, 1235, 696.

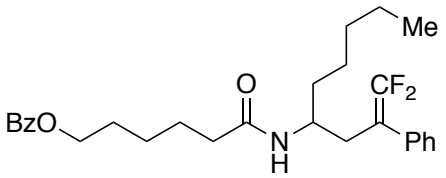


N-(9-chloro-1,1-difluoro-2-phenylnon-1-en-4-yl)hexanamide (**3t**) Following General Procedure A, N-(6-chlorohexyl)hexanamide (**1ae**) (93.5 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (50.2 mg, 65% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.29 – 7.26 (m, 1H), 5.11 – 4.75 (m, 1H), 4.04 – 3.89 (m, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.59 – 2.52 (m, 2H), 2.00 – 1.93 (m, 2H), 1.76 – 1.64 (m, 2H), 1.57 – 1.49 (m, 2H), 1.48 – 1.43 (m, 3H), 1.41 – 1.19 (m, 7H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.12 (d, *J* = 41.5 Hz), -90.36 (d, *J* = 41.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.74, 154.47 (dd, *J* = 291.1, 286.9 Hz), 133.58 (d, *J* = 6.6 Hz), 128.77, 128.45 (t, *J* = 3.0 Hz), 127.70, 89.97 (dd, *J* = 21.0, 14.9 Hz), 48.18 (t, *J* = 2.8 Hz), 45.00, 36.87, 34.46, 33.40 (d, *J* = 1.4 Hz), 32.51, 31.54, 26.75, 25.38, 25.29, 22.49, 14.04. **HRMS** calcd. for ($C_{21}H_{31}ClF_2NO$) $[M+H]^+$: 386.2057, found 386.2048. **IR (neat):** 3274, 2930, 2859, 1728, 1640, 1546, 1234, 696.

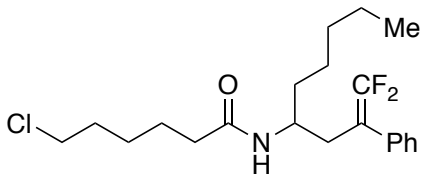


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-6-hydroxyhexanamide (**3u**) Following General Procedure A, N-hexyl-6-hydroxyhexanamide (**1u**) (86.1 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording

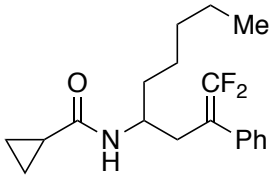
the title compound as a colorless oil (64.3 mg, 87% yield) by using Hexane/EtOAc (1:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 5.07 (d, *J* = 9.0 Hz, 1H), 4.02 – 3.90 (m, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.59 – 2.47 (m, 2H), 1.97 (td, *J* = 7.3, 2.1 Hz, 2H), 1.85 (s, 1H), 1.61 – 1.43 (m, 5H), 1.38 – 1.15 (m, 9H), 0.84 (t, *J* = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.62 (d, *J* = 41.5 Hz), -90.79 (d, *J* = 41.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.54, 154.45 (dd, *J* = 290.2, 288.0 Hz), 133.69 (d, *J* = 5.7 Hz), 128.73, 128.45 (t, *J* = 3.0 Hz), 127.64, 90.03 (dd, *J* = 20.6, 15.2 Hz), 62.66, 48.42 (t, *J* = 2.8 Hz), 36.65, 34.46, 33.31, 32.38, 31.70, 25.60, 25.41, 25.21, 22.61, 14.09. **HRMS** calcd. for ($C_{21}H_{32}F_2NO_2$) $[M+H]^+$: 368.2396, found 368.2404. **IR (neat):** 3284, 2930, 2859, 1735, 1641, 1547, 1366, 1233, 696.



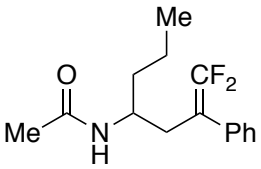
6-((1,1-difluoro-2-phenylnon-1-en-4-yl)amino)-6-oxohexyl benzoate (**3v**) Following General Procedure A, 6-(hexylamino)-6-oxohexyl benzoate (**1v**) (127.8 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (48.3 mg, 51% yield) by using Hexane/EtOAc (2:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 2H), 7.60 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 7.39 – 7.29 (m, 4H), 7.29 – 7.20 (m, 1H), 4.99 (d, *J* = 9.0 Hz, 1H), 4.30 (t, *J* = 6.6 Hz, 2H), 4.04 – 3.91 (m, 1H), 2.59 – 2.51 (m, 2H), 2.04 – 1.92 (m, 2H), 1.81 – 1.70 (m, 2H), 1.64 – 1.54 (m, 2H), 1.51 – 1.37 (m, 3H), 1.32 – 1.14 (m, 7H), 0.90 – 0.78 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.59 (d, *J* = 41.7 Hz), -90.76 (d, *J* = 41.7 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.24, 166.77, 154.45 (dd, *J* = 290.2, 288.0 Hz), 133.70 (d, *J* = 4.2 Hz), 133.00, 130.53, 129.66, 128.73, 128.47, 128.45(t, *J* = 3.0 Hz), 127.63, 90.02 (dd, *J* = 20.4, 15.3 Hz), 64.90, 48.41 (t, *J* = 2.8 Hz), 36.66, 34.44, 33.29, 31.68, 28.63, 25.84, 25.60, 25.29, 22.59, 14.09. **HRMS** calcd. for ($C_{28}H_{35}F_2NNaO_3$) $[M+Na]^+$: 494.2477, found 494.2492. **IR (neat):** 3291, 2930, 2859, 1719, 1641, 1542, 1272, 1233, 710.



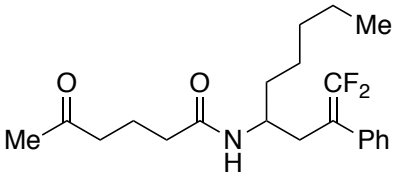
6-chloro-N-(1,1-difluoro-2-phenylnon-1-en-4-yl)hexanamide (**3w**) Following General Procedure A, 6-chloro-N-hexylhexanamide (**1w**) (93.5 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (40.0 mg, 52% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.30 – 7.25 (m, 1H), 4.97 (d, *J* = 9.0 Hz, 1H), 4.04 – 3.91 (m, 1H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.60 – 2.50 (m, 2H), 2.04 – 1.88 (m, 2H), 1.82 – 1.70 (m, 2H), 1.59 – 1.45 (m, 3H), 1.45 – 1.35 (m, 2H), 1.33 – 1.17 (m, 7H), 0.90 – 0.79 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.59 (d, *J* = 41.6 Hz), -90.76 (d, *J* = 41.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.19, 154.44 (dd, *J* = 290.2, 288.0 Hz), 133.70 (t, *J* = 2.8 Hz), 128.74, 128.45 (t, *J* = 3.1 Hz), 127.64, 90.01 (dd, *J* = 20.6, 15.3 Hz), 48.44 (t, *J* = 2.8 Hz), 44.93, 36.55, 34.47, 33.30, 32.38, 31.69, 26.55, 25.61, 24.84, 22.60, 14.09. **HRMS** calcd. for ($C_{21}H_{31}ClF_2NO$) $[M+H]^+$: 386.2057, found 386.2049. **IR (neat):** 3276, 2930, 2859, 1736, 1640, 1546, 1336, 1232, 696.



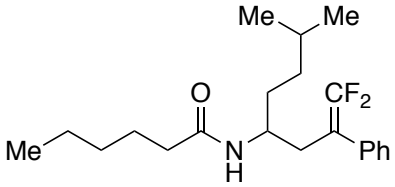
N-(1,1-difluoro-2-phenylnon-1-en-4-yl)cyclopropanecarboxamide (**3x**) Following General Procedure A, with double catalyst loading, N-hexylcyclopropanecarboxamide (**1x**) (67.7 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (42.0 mg, 65% yield) by using Hexane/EtOAc (3:1) as eluent. M.P.: 86-87 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 4H), 7.28 – 7.23 (m, 1H), 5.16 (d, *J* = 8.9 Hz, 1H), 4.03 – 3.88 (m, 1H), 2.66 – 2.50 (m, 2H), 1.53 – 1.43 (m, 1H), 1.39 – 1.15 (m, 7H), 1.13 – 1.02 (m, 1H), 0.90 – 0.80 (m, 5H), 0.68 – 0.59 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.72 (d, *J* = 41.8 Hz), -90.88 (d, *J* = 41.9 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.04, 154.44 (dd, *J* = 290.5, 287.2 Hz), 133.69 (d, *J* = 5.2 Hz), 128.68, 128.46 (t, *J* = 3.0 Hz), 127.55, 90.05 (dd, *J* = 20.6, 15.2 Hz), 48.59, 34.33, 33.28, 31.73, 25.56, 22.59, 14.79, 14.09, 7.11, 6.93. **HRMS** calcd. for ($C_{19}H_{26}F_2NO$) $[M+H]^+$: 322.1977, found 322.1981. **IR (neat):** 3282, 3031, 2929, 1720, 1635, 1549, 1230, 694.



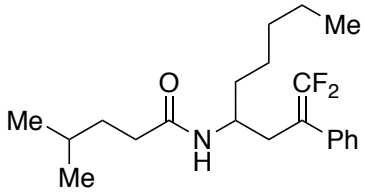
N-(1,1-difluoro-2-phenylhept-1-en-4-yl)acetamide (**3y**) Following General Procedure A, N-butylacetamide (**1y**) (46.1 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (45.8 mg, 86% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 4.97 (d, *J* = 9.0 Hz, 1H), 4.09 – 3.89 (m, 1H), 2.74 – 2.45 (m, 2H), 1.75 (s, 3H), 1.52 – 1.40 (m, 1H), 1.39 – 1.21 (m, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.26 (d, *J* = 41.4 Hz), -90.49 (d, *J* = 41.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.75, 154.47 (dd, *J* = 290.2, 288.0 Hz), 133.76 (d, *J* = 6.4 Hz), 128.74, 128.44 (t, *J* = 3.0 Hz), 127.64, 89.99 (dd, *J* = 21.0, 15.0 Hz), 48.47 (t, *J* = 2.8 Hz), 36.63, 33.20 (d, *J* = 1.5 Hz), 23.29, 19.19, 14.00. **HRMS** calcd. for ($C_{15}H_{20}F_2NO$) $[M+H]^+$: 268.1507, found 268.1506. **IR (neat):** 3273, 2969, 1737, 1647, 1557, 1373, 1232.



N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-5-oxohexanamide (**3z**) Following General Procedure A, N-hexyl-5-oxohexanamide (**1z**) (89.2 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as an oil (45.0 mg, 55% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.28 – 7.23 (m, 1H), 5.16 (d, *J* = 9.0 Hz, 1H), 4.02 – 3.82 (m, 1H), 2.58 – 2.51 (m, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.11 (s, 3H), 2.02 – 1.92 (m, 2H), 1.84 – 1.71 (m, 2H), 1.53 – 1.39 (m, 1H), 1.37 – 1.09 (m, 7H), 0.89 – 0.78 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.22 (d, *J* = 41.6 Hz), -90.38 (d, *J* = 41.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.65, 171.92, 154.45 (dd, *J* = 290.2, 288.0 Hz), 133.66 (t, *J* = 3.0 Hz), 128.73, 128.44 (t, *J* = 3.0 Hz), 127.64, 90.03 (dd, *J* = 20.5, 15.3 Hz), 48.45, 42.57, 35.48, 34.43, 33.32, 31.68, 30.05, 25.62, 22.61, 19.62, 14.09. **HRMS** calcd. for ($C_{21}H_{30}F_2NO_2$) $[M+H]^+$: 366.2239, found 366.2230. **IR (neat):** 3291, 2929, 2858, 1718, 1643, 1543, 1366, 1233, 697.

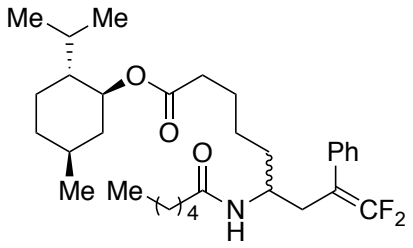


N-(1,1-difluoro-7-methyl-2-phenyloct-1-en-4-yl)hexanamide (**3aa**) Following General Procedure A, N-(4-methylpentyl)hexanamide (**1aa**) (79.7 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (41.0 mg, 58% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.29 – 7.26 (m, 1H), 4.97 (d, *J* = 9.0 Hz, 1H), 4.03 – 3.87 (m, 1H), 2.56 (dt, *J* = 6.6, 2.3 Hz, 2H), 2.00 – 1.93 (m, 2H), 1.55 – 1.40 (m, 4H), 1.38 – 1.19 (m, 5H), 1.17 – 1.08 (m, 2H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 3.8 Hz, 3H), 0.81 (d, *J* = 3.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.67 (d, *J* = 41.8 Hz), -90.85 (d, *J* = 41.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.66, 154.46 (dd, *J* = 290.8, 286.9 Hz), 133.69 (d, *J* = 6.4 Hz), 128.74, 128.48 (t, *J* = 3.1 Hz), 127.65, 90.06 (dd, *J* = 20.9, 15.0 Hz), 48.49, 36.92, 34.94, 33.35, 32.36, 31.55, 28.00, 25.42, 22.73, 22.52, 22.49, 14.06. **HRMS** calcd. for ($C_{21}H_{32}F_2NO$) $[M+H]^+$: 352.2446, found 352.2433. **IR (neat):** 3277, 2955, 2870, 1729, 1639, 1548, 1236, 696.

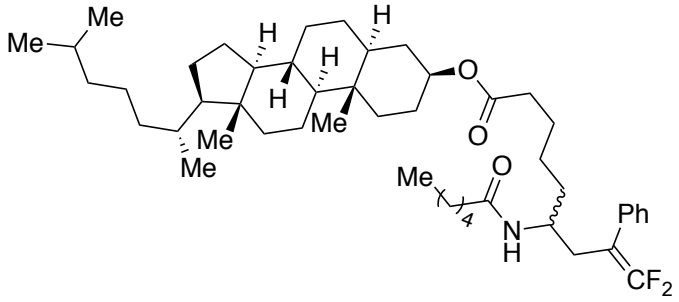


N-(1,1-difluoro-2-phenylnon-1-en-4-yl)-4-methylpentanamide (**3ab**) Following General Procedure A, N-hexyl-4-methylpentanamide (**1ab**) (79.7 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (51.4 mg, 73% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.31 – 7.22 (m, 1H), 5.05 (d, *J* = 9.0 Hz, 1H), 4.02 – 3.91 (m, 1H), 2.55 (dt, *J* = 6.5, 2.3 Hz, 2H), 2.00 – 1.91 (m, 2H), 1.55 – 1.43 (m, 2H), 1.40 – 1.32 (m, 3H), 1.29 – 1.16 (m, 6H), 0.89 – 0.80 (m, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.31 (d, *J* = 41.4 Hz), δ -90.42 (d, *J* = 41.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.86, 154.45 (dd, *J* = 290.2, 288.0 Hz), 133.73, 128.74, 128.46 (t, *J* = 3.0 Hz), 127.64, 90.03 (dd, *J* = 20.1, 15.7 Hz), 48.37, 34.89, 34.52, 34.47, 33.29, 31.71, 27.88, 25.59, 22.61, 22.41, 22.37, 14.08. **HRMS** calcd. for ($C_{21}H_{32}F_2NO$)

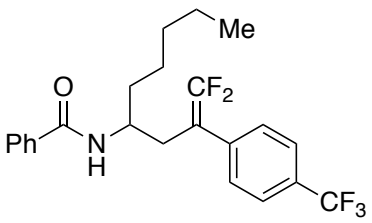
$[M+H]^+$: 352.2446, found 352.2432. **IR (neat):** 3283, 2956, 2859, 1728, 1639, 1546, 1234, 695.



(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 9,9-difluoro-8-phenyl-6-propionamidonon-8-enoate (**3ac**) Following General Procedure A and using 1,4-dioxane/DCM (3/1) as solvent, (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 6-propionamidohexanoate (**1ac**) (147.0 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the mixture of diastereomers (dr = 1:1) as a colorless oil (55.1 mg, 53% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.30 – 7.21 (m, 1H), 5.03 (d, *J* = 8.9 Hz, 1H), 4.66 (dt, *J* = 10.9, 5.5 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 1H), 2.60 – 2.49 (m, 2H), 2.22 (t, *J* = 7.5 Hz, 2H), 2.00 – 1.89 (m, 3H), 1.87 – 1.78 (m, 1H), 1.72 – 1.60 (m, 2H), 1.58 – 1.44 (m, 6H), 1.37 – 1.20 (m, 9H), 1.09 – 0.98 (m, 1H), 0.94 – 0.82 (m, 10H), 0.77 – 0.69 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.51 (d, *J* = 41.5 Hz) (*diastereomer 1*), -90.52 (d, *J* = 41.7 Hz) (*diastereomer 2*), -90.73 (d, *J* = 41.5 Hz) (*diastereomer 1*), -90.74 (d, *J* = 41.7 Hz) (*diastereomer 2*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.20, 172.67, 154.44 (dd, *J* = 291.1, 286.9 Hz), 133.57 (t, *J* = 3.2 Hz), 128.73, 128.43 (t, *J* = 3.1 Hz), 127.65, 89.96 (dd, *J* = 20.9, 14.9 Hz), 74.13, 48.19, 47.12, 41.07, 36.85, 34.50, 34.37, 34.13, 33.30, 31.53, 31.49, 29.80, 26.40, 25.45, 25.33, 24.93, 23.56, 22.47, 22.12, 20.84, 16.43, 14.02. **HRMS** calcd. for ($C_{31}H_{48}F_2NO_3$) $[M+H]^+$: 520.3597, found 520.3592. **IR (neat):** 3284, 2928, 2867, 1729, 1642, 1543, 1223, 697.

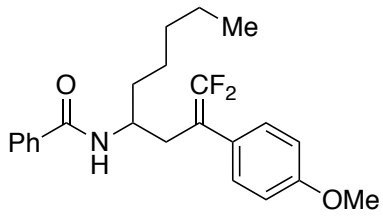


(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 9,9-difluoro-8-phenyl-6-propionamidonon-8-enoate (**3ad**) Following General Procedure A, (3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 6-propionamidohexanoate (**1ad**) (240.0 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the mixture of diastereomers (dr = 1:1) as a colorless oil (77.5 mg, 52% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 5H), 5.04 (d, *J* = 8.8 Hz, 1H), 4.85 – 4.45 (m, 1H), 4.23 – 3.73 (m, 1H), 2.60 – 2.45 (m, 2H), 2.20 (t, *J* = 7.3 Hz, 2H), 2.00 – 1.85 (m, 3H), 1.84 – 1.62 (m, 5H), 1.60 – 1.44 (m, 9H), 1.40 – 1.18 (m, 16H), 1.18 – 0.94 (m, 12H), 0.93 – 0.82 (m, 12H), 0.81 (s, 3H), 0.64 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.10 (d, *J* = 41.5 Hz), -90.30 (d, *J* = 41.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.25, 172.81, 154.47 (dd, *J* = 291.1, 286.9 Hz), 133.56, 128.75, 128.44 (t, *J* = 3.0 Hz), 127.67, 89.95 (dd, *J* = 20.9, 14.9 Hz), 73.76, 56.54 (*diastereomer 1*), 56.39 (*diastereomer 2*), 54.35, 48.22, 44.79, 42.71, 40.11, 39.64, 36.87, 36.29, 35.92, 35.59, 34.54, 34.18, 34.13, 33.32, 32.11, 31.54, 28.74, 28.36, 28.13, 27.63, 25.44, 25.35, 24.86, 24.33, 23.96, 22.94, 22.68, 22.49, 21.32, 18.79, 14.06, 12.35, 12.19. **HRMS** calcd. for ($C_{48}H_{75}F_2NNaO_3$) $[M+Na]^+$: 774.5607, found 774.5588 **IR (neat):** 2930, 2866, 1730, 1449, 1379, 1173, 700.

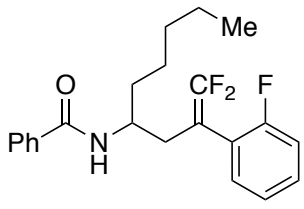


N-(1,1-difluoro-2-(4-(trifluoromethyl)phenyl)non-1-en-4-yl)benzamide (**3ae**) Following General Procedure A, N-hexylbenzamide (1a) (82.1 mg, 0.40 mmol) and 1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (48.0 mg, 0.20 mmol) were used, affording the title compound as a white solid (82.0 mg, 96% yield) by using

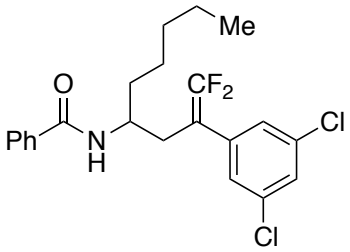
Hexane/EtOAc (10:1) as eluent. M.P.: 83-84 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.42 (m, 5H), 7.36 (t, *J* = 7.6 Hz, 2H), 5.61 (d, *J* = 8.8 Hz, 1H), 4.31 – 4.02 (m, 1H), 2.76 – 2.68 (m, 2H), 1.67 – 1.54 (m, 1H), 1.54 – 1.41 (m, 1H), 1.38 – 1.18 (m, 6H), 0.88 – 0.80 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.80, -88.54 (d, *J* = 37.2 Hz), -88.78 (d, *J* = 37.1 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.15, 154.62 (dd, *J* = 290.2, 288.0 Hz), 137.31, 134.56, 131.61, 129.72 (d, *J* = 32.3 Hz), 128.84 (t, *J* = 3.2 Hz), 128.66, 126.64, 125.76 (q, *J* = 3.7 Hz), 124.08 (q, *J* = 272.2 Hz), 89.62 (dd, *J* = 19.7, 16.3 Hz), 49.04 (t, *J* = 2.8 Hz), 34.61, 33.31, 31.72, 25.71, 22.60, 14.08. **HRMS** calcd. for ($C_{23}H_{25}F_5NO$) $[M+H]^+$: 426.1851, found 426.1833. **IR (neat):** 3294, 2928, 2857, 1721, 1634, 1547, 1324, 696.



N-(1,1-difluoro-2-(4-methoxyphenyl)non-1-en-4-yl)benzamide (**3af**) Following General Procedure A and using 2x catalyst loading, N-hexylbenzamide (**1a**) (82.1 mg, 0.40 mmol) and 1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (40.4 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (41.0 mg, 53% yield) by using Hexane/EtOAc (6:1) as eluent. M.P.: 96-97 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.65 (d, *J* = 8.9 Hz, 1H), 4.28 – 4.07 (m, 1H), 3.77 (s, 3H), 2.73 – 2.59 (m, 2H), 1.66 – 1.53 (m, 1H), 1.54 – 1.39 (m, 1H), 1.38 – 1.18 (m, 6H), 0.88 – 0.83 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.32 (d, *J* = 43.9 Hz), -91.56 (d, *J* = 43.8 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.93, 159.05, 154.39 (dd, *J* = 290.2, 288.0 Hz), 134.77, 131.41, 129.65 (t, *J* = 3.1 Hz), 128.54, 126.80, 125.77, 114.36, 89.40 (dd, *J* = 22.0, 15.3 Hz), 55.39, 49.04 (t, *J* = 2.8 Hz), 34.53, 33.31, 31.78, 25.70, 22.63, 14.12. **HRMS** calcd. for ($C_{23}H_{28}F_2NO_2$) $[M+H]^+$: 388.2083, found 388.2065. **IR (neat):** 3331, 2928, 2857, 1735, 1631, 1513, 1223, 696.

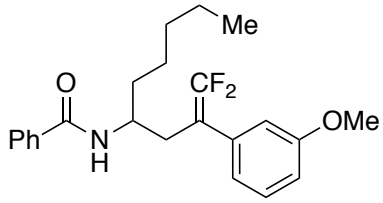


N-(1,1-difluoro-2-(2-fluorophenyl)non-1-en-4-yl)benzamide (**3ag**) Following General Procedure A, N-hexylbenzamide (1a) (82.1 mg, 0.40 mmol) and 1-fluoro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (38.0 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (71.0 mg, 94% yield) by using Hexane/EtOAc (10:1) as eluent. M.P.: 79-80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.20 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (dd, *J* = 10.2, 8.2 Hz, 1H), 5.74 (d, *J* = 8.8 Hz, 1H), 4.25 – 3.98 (m, 1H), 2.79 – 2.57 (m, 2H), 1.64 – 1.52 (m, 1H), 1.55 – 1.41 (m, 1H), 1.36 – 1.16 (m, 6H), 0.87 – 0.81 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -86.43 (dd, *J* = 36.5, 11.8 Hz), -90.12 (dd, *J* = 36.4, 1.9 Hz), -113.67 (dd, *J* = 11.9, 1.9 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.02, 160.05 (d, *J* = 247.9 Hz), 154.26 (dd, *J* = 290.8, 288.2 Hz), 134.78, 131.42, 131.21, 129.85 (d, *J* = 8.3 Hz), 128.57, 126.78, 124.56 (d, *J* = 3.5 Hz), 121.36 (d, *J* = 10.1 Hz), 116.03 (d, *J* = 22.1 Hz), 84.50 (dd, *J* = 24.8, 17.1 Hz), 48.89 (t, *J* = 2.8 Hz), 34.56, 33.16, 31.72, 25.69, 22.59, 14.09. **HRMS** calcd. for ($C_{22}H_{25}F_3NO$) $[M+H]^+$: 376.1883, found 376.1886. **IR (neat):** 3307, 2933, 2855, 1741, 1636, 1541, 1251, 693.

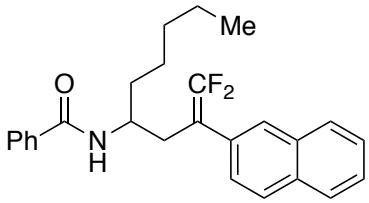


N-(2-(3,5-dichlorophenyl)-1,1-difluorononon-1-en-4-yl)benzamide (**3ah**) Following General Procedure A, N-hexylbenzamide (1a) (82.1 mg, 0.40 mmol) and 1,3-dichloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzene (48.2 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (58.1 mg, 68% yield) by using Hexane/EtOAc (10:1) as eluent. M.P.: 89-90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.52 – 7.44 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.19 (t, *J* = 1.8 Hz, 1H), 5.66 (d, *J* = 8.8 Hz, 1H), 4.27 – 4.09 (m, 1H), 2.73 – 2.55 (m, 2H), 1.66 – 1.55 (m, 1H), 1.54 – 1.44 (m, 1H), 1.38 – 1.23 (m, 6H), 0.93 – 0.81 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.15 (d, *J* = 35.4 Hz), -87.45 (d, *J* = 35.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.16, 154.78 (dd, *J* = 290.2, 288.0 Hz), 136.87, 135.35, 134.49 (d, *J* = 2.5 Hz), 131.61, 128.66, 127.75, 126.92 (t, *J* = 3.3 Hz), 126.74, 88.89 (dd, *J* = 23.3, 13.8 Hz), 49.00 (t, *J* = 2.8 Hz), 34.72, 33.35, 31.72, 25.72, 22.63, 14.10. **HRMS** calcd. for

($C_{22}H_{24}Cl_2F_2NO$) $[M+H]^+$: 426.1198, found 426.1185. **IR (neat):** 3291, 2928, 2855, 1736, 1634, 1536, 1246, 692.

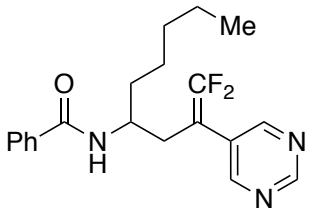


N-(1,1-difluoro-2-(3-methoxyphenyl)non-1-en-4-yl)benzamide (**3ai**) Following General Procedure A, N-hexylbenzamide (**1a**) (82.1 mg, 0.40 mmol) and 1-methoxy-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (40.4 mg, 0.20 mmol) were used, affording the title compound as an white solid (49.4 mg, 64% yield) by using Hexane/EtOAc (6:1) as eluent. M.P.: 81-82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 3H), 7.38 – 7.31 (m, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 6.98 – 6.90 (m, 1H), 6.91 – 6.85 (m, 1H), 6.83 – 6.75 (m, 1H), 5.67 (d, *J* = 8.9 Hz, 1H), 4.30 – 4.16 (m, 1H), 3.74 (s, 3H), 2.76 – 2.61 (m, 2H), 1.65 – 1.53 (m, 1H), 1.53 – 1.43 (m, 1H), 1.39 – 1.19 (m, 6H), 0.89 – 0.81 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.73 (d, *J* = 40.6 Hz), -90.32 (d, *J* = 40.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.93, 159.92, 154.50 (dd, *J* = 291.7, 286.9 Hz), 135.19 (dd, *J* = 4.5, 2.9 Hz), 134.75, 131.37, 129.88, 128.51, 126.77, 120.83 (t, *J* = 3.0 Hz), 114.30 (t, *J* = 3.1 Hz), 113.21, 89.95 (dd, *J* = 21.6, 14.6 Hz), 55.35, 49.16 (t, *J* = 2.8 Hz), 34.58, 33.23 (d, *J* = 1.5 Hz), 31.78, 25.70, 22.62, 14.11. **HRMS** calcd. for ($C_{23}H_{27}F_2NNaO_2$) $[M+Na]^+$: 410.1902, found 410.1906. **IR (neat):** 3298, 2930, 2858, 1728, 1634, 1537, 1246, 693.

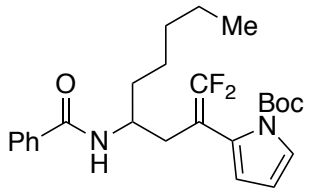


N-(1,1-difluoro-2-(naphthalen-2-yl)non-1-en-4-yl)benzamide (**3aj**) Following General Procedure A, 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (82.1 mg, 0.40 mmol) and 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (44.4 mg, 0.20 mmol) were used, affording the title compound as an oil (76.5 mg, 94% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.73 (m, 5H), 7.57 – 7.40 (m, 3H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 2H), 5.63 (d, *J* = 8.8 Hz, 1H), 4.35 – 4.19 (m, 1H), 2.87 – 2.75 (m, 2H), 1.68 – 1.57 (m, 1H), 1.57 – 1.44 (m, 1H), 1.38 – 1.19 (m, 6H), 0.88 – 0.81 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -89.50 (d, *J* = 40.1 Hz), -89.71 (d, *J* = 40.1 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.98, 154.72 (dd,

J = 290.2, 288.0 Hz), 134.52, 133.49, 132.69, 131.34, 131.29, 128.68, 128.38, 128.11, 127.71, 127.63 (t, *J* = 3.0 Hz), 126.62, 126.55, 126.42, 126.16 (t, *J* = 2.9 Hz), 90.05 (dd, *J* = 21.2, 14.9 Hz), 49.27 (t, *J* = 2.8 Hz), 34.56, 33.25, 31.77, 25.73, 22.62, 14.10. **HRMS** calcd. for ($C_{26}H_{28}F_2NO$) $[M+H]^+$: 408.2133, found 408.2121. **IR (neat):** 3298, 2928, 2858, 1726, 1635, 1537, 1228, 695.

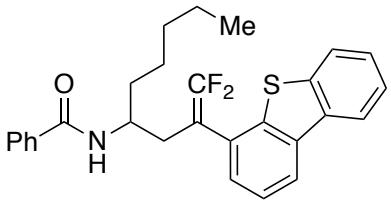


N-(1,1-difluoro-2-(pyrimidin-5-yl)non-1-en-4-yl)benzamide (**3ak**) Following General Procedure A, N-hexylbenzamide (**1a**) (82.1 mg, 0.40 mmol) and N-(1,1-difluoro-2-(pyrimidin-5-yl)non-1-en-4-yl)benzamide (34.8 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (53.2 mg, 74% yield) by using Hexane/EtOAc (5:1) as eluent. M.P.: 89-90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.77 (s, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 5.88 (s, 1H), 4.29 – 3.95 (m, 1H), 2.85 – 2.51 (m, 2H), 1.69 – 1.45 (m, 2H), 1.41 – 1.17 (m, 6H), 0.89 – 0.80 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -85.95 (d, *J* = 33.6 Hz), -86.84 (d, *J* = 33.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.39, 156.83 (d, *J* = 115.0 Hz), 155.07 (dd, *J* = 290.2, 288.0 Hz), 134.38, 131.72, 128.76, 128.10, 126.80, 85.30 (dd, *J* = 24.5, 14.2 Hz), 48.73 (t, *J* = 2.8 Hz), 34.89, 33.26, 31.65, 25.80, 22.57, 14.05. **HRMS** calcd. for ($C_{20}H_{24}F_2N_3O$) $[M+H]^+$: 360.1882, found 360.1867. **IR (neat):** 3295, 3062, 2927, 2857, 1706, 1637, 1538, 1253, 691.

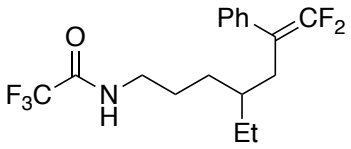


tert-butyl 2-(4-benzamido-1,1-difluorononon-1-en-2-yl)-1H-pyrrole-1-carboxylate (**3al**) Following General Procedure A, N-hexylbenzamide (**1a**) (82.1 mg, 0.40 mmol) and tert-butyl 2-(3,3,3-trifluoroprop-1-en-2-yl)-1H-pyrrole-1-carboxylate (52.2 mg, 0.20 mmol) were used, affording the title compound as an amorphous white solid (50.0 mg, 56% yield) by using Hexane/EtOAc (6:1) as eluent. M.P.: 90-91 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 2H), 7.51 – 7.43 (m, 1H), 7.42 – 7.35 (m, 2H), 7.19 (dd, *J* =

3.4, 1.7 Hz, 1H), 6.32 (d, *J* = 9.0 Hz, 1H), 6.22 (dd, *J* = 3.4, 1.7 Hz, 1H), 6.15 (t, *J* = 3.4 Hz, 1H), 4.42 – 4.14 (m, 1H), 2.72 – 2.62 (m, 1H), 2.55 – 2.44 (m, 1H), 1.56 (s, 9H), 1.50 – 1.42 (m, 2H), 1.36 – 1.19 (m, 6H), 0.88 – 0.82 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -86.34 (d, *J* = 35.6 Hz), -90.66 (d, *J* = 35.9 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.72, 164.60, 164.16 (dd, *J* = 290.2, 288.0 Hz), 133.96, 127.27, 126.34, 125.62, 108.60, 107.68, 100.90, 99.46, 85.83 (dd, *J* = 19.7, 16.3 Hz), 53.32, 53.14, 52.17, 30.35, 18.72, 18.68, 11.39, 11.33. **HRMS** calcd. for ($C_{25}H_{32}F_2N_2NaO_3$) $[M+Na]^+$: 469.2273, found 469.2260. **IR (neat):** 3343, 2970, 2929, 2857, 1739, 1637, 1370, 1146, 712.

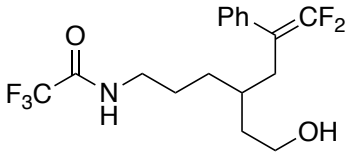


N-(2-(dibenzo[b,d]thiophen-4-yl)-1,1-difluorononon-1-en-4-yl)benzamide (**3am**)
Following General Procedure A, N-hexylbenzamide (1a) (82.1 mg, 0.40 mmol) and *N*-(2-(dibenzo[b,d]thiophen-4-yl)-1,1-difluorononon-1-en-4-yl)benzamide (55.7 mg, 0.20 mmol) were used, affording the title compound as an oil (84.0 mg, 91% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 7.96 (dd, *J* = 6.7, 2.1 Hz, 1H), 7.90 – 7.81 (m, 1H), 7.51 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 5.76 (d, *J* = 8.7 Hz, 1H), 4.33 – 4.18 (m, 1H), 3.04 – 2.88 (m, 1H), 2.87 – 2.73 (m, 1H), 1.72 – 1.55 (m, 2H), 1.39 – 1.22 (m, 6H), 0.92 – 0.81 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -84.11 (d, *J* = 34.6 Hz), -89.08 (d, *J* = 34.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.81, 154.17 (dd, *J* = 290.2, 288.0 Hz), 139.07, 138.89, 136.27, 135.97, 134.16, 131.15, 129.10 (d, *J* = 4.5 Hz), 128.16, 127.83 (d, *J* = 3.1 Hz), 127.16, 126.45, 125.31, 124.75, 122.89, 121.93, 121.10, 88.78 (dd, *J* = 23.1, 16.9 Hz), 49.40 (t, *J* = 2.7 Hz), 34.36, 32.86, 31.74, 25.85, 22.60, 14.09. **HRMS** calcd. for ($C_{28}H_{28}F_2NOS$) $[M+H]^+$: 464.1854, found 464.1838. **IR (neat):** 3307, 2928, 2857, 1729, 1635, 1537, 1246, 694.

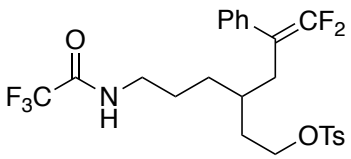


N-(4-ethyl-7,7-difluoro-6-phenylhept-6-en-1-yl)-2,2,2-trifluoroacetamide (**6a**)
Following General Procedure B, 2,2,2-trifluoro-N-hexylacetamide (**5a**) (77.08 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used,

affording the title compound as a colorless oil (54.6 mg, 78% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.31 – 7.24 (m, 3H), 6.29 (s, 1H), 3.44 – 3.13 (m, 2H), 2.45 – 2.34 (m, 1H), 2.34 – 2.26 (m, 1H), 1.55 – 1.42 (m, 2H), 1.35 – 1.23 (m, 5H), 0.82 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.69, -91.09 (d, *J* = 44.2 Hz), -91.27 (d, *J* = 44.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.29 (q, *J* = 36.8 Hz), 154.06 (dd, *J* = 289.9, 286.5 Hz), 133.78 (dd, *J* = 3.7, 2.1 Hz), 128.63, 128.37 (t, *J* = 3.0 Hz), 127.49, 115.99 (q, *J* = 287.8 Hz), 91.43 (dd, *J* = 20.7, 14.1 Hz), 40.32, 36.70 (t, *J* = 2.3 Hz), 31.54, 29.32, 25.81, 25.35, 10.53. **HRMS** calcd. for ($C_{17}H_{20}F_5NNaO$) $[M+Na]^+$: 372.1357, found 372.1346. **IR (neat):** 3308, 2969, 1702, 1558, 1367, 1161, 697.

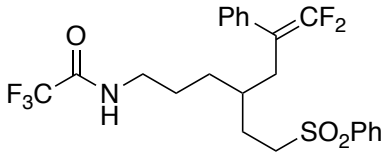


N-(7,7-difluoro-4-(2-hydroxyethyl)-6-phenylhept-6-en-1-yl)-2,2,2-trifluoroacetamide (**6b**) Following General Procedure B and using toluene/1,4-dioxane (4/1) as solvent, 2,2,2-trifluoro-N-(6-hydroxyhexyl)acetamide (**5b**) (85.3 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (61.0 mg, 83% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.25 (m, 3H), 6.61 (s, 1H), 3.67 – 3.58 (m, 2H), 3.30 – 3.19 (m, 2H), 2.43 – 2.34 (m, 2H), 1.56 – 1.44 (m, 5H), 1.36 – 1.28 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.91, -90.99 (d, *J* = 43.8 Hz), -91.18 (d, *J* = 42.9 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.40 (q, *J* = 36.7 Hz), 154.12 (dd, *J* = 290.6, 286.5 Hz), 133.56 (dd, *J* = 4.1, 2.4 Hz), 128.72, 128.34 (t, *J* = 3.0 Hz), 127.62, 115.99 (q, *J* = 288.0 Hz), 91.19 (dd, *J* = 21.1, 13.8 Hz), 60.72, 40.04, 35.76, 32.48, 32.20, 29.86, 25.37. **HRMS** calcd. for ($C_{17}H_{20}F_5NNaO_2$) $[M+Na]^+$: 388.1306, found 388.1290. **IR (neat):** 3301, 2942, 1704, 1560, 1367, 1153, 699.

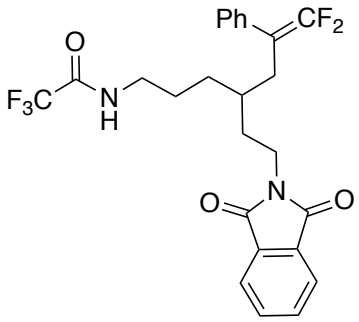


6,6-difluoro-5-phenyl-3-(3-(2,2,2-trifluoroacetamido)propyl)hex-5-en-1-yl 4-methylbenzenesulfonate (**6c**) Following General Procedure B, 6-(2,2,2-

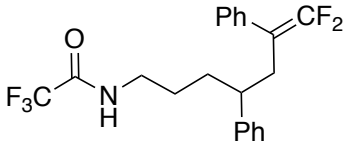
trifluoroacetamido)hexyl 4-methylbenzenesulfonate (**5c**) (147.0 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (54.6 mg, 53% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 2H), 7.39 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 6.51 (s, 1H), 3.99 (t, *J* = 6.3 Hz, 2H), 3.28 – 3.11 (m, 2H), 2.45 (s, 3H), 2.39 – 2.28 (m, 2H), 1.70 – 1.60 (m, 1H), 1.59 – 1.41 (m, 4H), 1.28 – 1.19 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.87, -90.63 (d, *J* = 42.7 Hz), -90.90 (d, *J* = 42.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.39 (q, *J* = 36.8 Hz), 154.09 (dd, *J* = 291.0, 286.7 Hz), 145.10, 133.17 (d, *J* = 3.1 Hz), 132.99, 130.03, 128.78, 128.31 (t, *J* = 3.0 Hz), 127.91, 127.73, 115.97 (q, *J* = 287.9 Hz), 90.79 (dd, *J* = 21.2, 13.9 Hz), 68.44, 32.37, 32.13, 31.73, 29.64, 25.49, 21.73. **HRMS** calcd. for ($C_{24}H_{26}F_2NNaO_4S$) $[M+Na]^+$: 542.1395, found 542.1376. **IR (neat):** 3346, 2944, 1722, 1556, 1356, 1171, 694.



N-(7,7-difluoro-6-phenyl-4-(2-(phenylsulfonyl)ethyl)hept-6-en-1-yl)-2,2,2-trifluoroacetamide (**6d**) Following General Procedure B, 2,2,2-trifluoro-N-(6-(phenylsulfonyl)hexyl)acetamide (**5d**) (134.94 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (61.0 mg, 62% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.75 – 7.66 (m, 1H), 7.64 – 7.55 (m, 2H), 7.37 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 7.19 – 7.11 (m, 2H), 6.44 (s, 1H), 3.29 – 3.17 (m, 2H), 3.03 – 2.92 (m, 2H), 2.41 – 2.33 (m, 1H), 2.30 – 2.21 (m, 1H), 1.75 – 1.65 (m, 1H), 1.66 – 1.58 (m, 1H), 1.54 – 1.42 (m, 3H), 1.28 – 1.21 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.86, -90.40 (d, *J* = 42.5 Hz), -90.64 (d, *J* = 42.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.38 (q, *J* = 37.0 Hz), 154.02 (dd, *J* = 291.5, 286.7 Hz), 138.96, 133.97, 132.96 (d, *J* = 3.7 Hz), 129.51, 128.84, 128.24 (t, *J* = 2.9 Hz), 128.14, 127.83, 115.95 (q, *J* = 287.8 Hz), 90.58 (dd, *J* = 21.2, 14.2 Hz), 53.29, 39.81, 34.30 (t, *J* = 2.6 Hz), 31.54, 29.43, 25.63, 25.39. **HRMS** calcd. for ($C_{23}H_{24}F_5NNaO_3S$) $[M+Na]^+$: 512.1295, found 512.1282. **IR (neat):** 3325, 2940, 1718, 1558, 1447, 1304, 1141, 689.

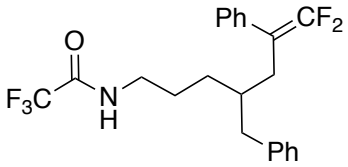


N-(4-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-7,7-difluoro-6-phenylhept-6-en-1-yl)-2,2,2-trifluoroacetamide (**6e**) Following General Procedure B, N-(6-(1,3-dioxoisoindolin-2-yl)hexyl)-2,2,2-trifluoroacetamide (**5e**) (136.9 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (56.0 mg, 57% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.76 – 7.69 (m, 2H), 7.15 – 7.09 (m, 2H), 7.10 – 7.03 (m, 2H), 7.01 – 6.93 (m, 2H), 3.62 (dd, *J* = 8.0, 5.5 Hz, 2H), 3.40 (dt, *J* = 12.3, 6.2 Hz, 1H), 3.14 (dt, *J* = 13.1, 6.4 Hz, 1H), 2.51 – 2.42 (m, 1H), 2.32 – 2.23 (m, 1H), 1.81 – 1.72 (m, 1H), 1.72 – 1.66 (m, 1H), 1.62 – 1.58 (m, 1H), 1.57 – 1.50 (m, 1H), 1.48 – 1.41 (m, 1H), 1.31 – 1.24 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.85, -90.76 (d, *J* = 43.1 Hz), -91.29 (d, *J* = 43.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.60, 157.52 (d, *J* = 36.6 Hz), 154.13 (dd, *J* = 290.2, 288.0 Hz), 134.10, 133.01 (dd, *J* = 4.5, 2.9 Hz), 132.05, 128.47, 128.14 (t, *J* = 2.9 Hz), 127.28, 123.38, 116.08 (q, *J* = 288.1 Hz), 90.80 (dd, *J* = 21.6, 13.9 Hz), 39.30, 35.36, 31.95, 31.81 (t, *J* = 2.3 Hz), 31.40, 29.10, 25.19. **HRMS** calcd. for ($C_{25}H_{23}F_5N_2NaO_3$) $[M+Na]^+$: 517.1521, found 517.1525. **IR (neat):** 3334, 2943, 1703, 1397, 1372, 1153, 719, 696.

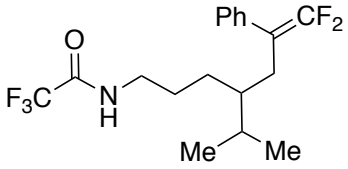


N-(7,7-difluoro-4,6-diphenylhept-6-en-1-yl)-2,2,2-trifluoroacetamide (**6f**) Following General Procedure B, 2,2,2-trifluoro-N-(4-phenylbutyl)acetamide (**5f**) (98.0 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (45.3 mg, 57% yield) by using Hexane/EtOAc (15:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 3H), 7.24 – 7.15 (m, 2H), 7.08 – 7.00 (m, 3H), 6.05 (s, 1H), 3.30 – 3.08 (m, 2H), 2.73 – 2.65 (m, 2H), 2.56 – 2.46 (m, 1H), 1.76 – 1.65 (m, 1H), 1.64 – 1.57 (m, 1H), 1.41 – 1.28 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.07, -91.05 (d, *J* = 42.0 Hz), -

91.69 (d, J = 42.0 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.19 (q, J = 36.1 Hz), 154.08 (dd, J = 290.6, 286.5 Hz), 143.39, 133.40 (d, J = 4.3 Hz), 128.67, 128.64, 128.48 (t, J = 3.0 Hz), 127.68, 127.55, 126.85, 115.92 (q, J = 289.8 Hz), 91.07 (dd, J = 21.6, 13.9 Hz), 43.48, 39.89, 35.15, 32.58, 27.06. **HRMS** calcd. for ($C_{21}H_{20}F_5NNaO$) $[M+Na]^+$: 420.1357, found 420.1343. **IR (neat):** 3310, 3028, 2942, 1703, 1557, 1367, 1161, 697.

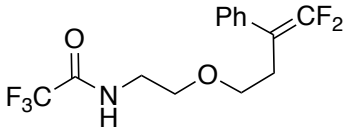


N-(4-benzyl-7,7-difluoro-6-phenylhept-6-en-1-yl)-2,2,2-trifluoroacetamide (**6g**) Following General Procedure B, 2,2,2-trifluoro-N-(5-phenylpentyl)acetamide (**5g**) (103.7 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (51.1 mg, 62% yield) by using Hexane/EtOAc (15:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.30 – 7.22 (m, 3H), 7.22 – 7.15 (m, 3H), 7.04 – 6.97 (m, 2H), 6.06 (s, 1H), 3.34 – 3.02 (m, 2H), 2.59 (dd, J = 13.7, 6.8 Hz, 1H), 2.48 (dd, J = 13.7, 7.8 Hz, 1H), 2.38 (dt, J = 7.2, 2.4 Hz, 2H), 1.71 – 1.59 (m, 1H), 1.55 – 1.42 (m, 2H), 1.32 – 1.21 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.04, -90.95 (d, J = 43.2 Hz), -91.12 (d, J = 43.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.05 (q, J = 36.1 Hz), 154.04(dd, J = 290.6, 286.5 Hz), 140.39, 133.35, 129.11, 128.68, 128.50, 128.33 (t, J = 3.1 Hz), 127.58, 126.25, 117.36 (q, J = 289.8 Hz), 91.36 (dd, J = 21.6, 13.9 Hz), 40.14, 40.08, 37.53 (d, J = 2.5 Hz), 31.76, 29.65, 25.77. **HRMS** calcd. for ($C_{22}H_{22}F_5NNaO$) $[M+Na]^+$: 434.1514, found 434.1512. **IR (neat):** 3306, 3027, 2927, 1702, 1557, 1367, 1160, 697.

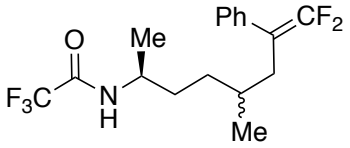


N-(7,7-difluoro-4-isopropyl-6-phenylhept-6-en-1-yl)-2,2,2-trifluoroacetamide (**6h**) Following General Procedure B, 2,2,2-trifluoro-N-(5-methylhexyl)acetamide (**5h**) (84.5 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (41.0 mg, 56% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 6.27 (s, 1H), 3.31 – 3.16 (m, 2H), 2.49 – 2.38 (m, 1H), 2.30 – 2.19 (m, 1H), 1.77 – 1.64 (m, 1H), 1.54 – 1.42 (m, 2H), 1.33 – 1.14 (m, 3H), 0.84 (d, J = 7.3 Hz,

3H), 0.79 (d, J = 13.6 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.69, -90.92 (d, J = 43.3 Hz), -91.48 (dt, J = 44.2, 2.8 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.13 (q, J = 36.8 Hz), 153.86 (dd, J = 290.3, 285.9 Hz), 133.48 (d, J = 7.4 Hz), 128.51, 128.24 (t, J = 3.0 Hz), 127.37, 115.85 (q, J = 288.0 Hz), 91.54 (dd, J = 21.5, 13.2 Hz), 40.91 (t, J = 2.3 Hz), 40.16, 28.56, 28.43, 26.64, 26.55, 18.76, 18.68. **HRMS** calcd. for ($C_{18}H_{22}F_5NNaO$) $[M+Na]^+$: 386.1514, found 386.1501. **IR (neat):** 3309, 2957, 1703, 1558, 1369, 1208, 1168, 697.

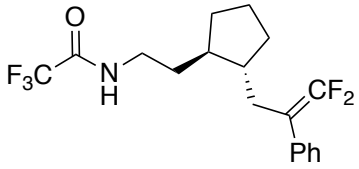


N-(2-((4,4-difluoro-3-phenylbut-3-en-1-yl)oxy)ethyl)-2,2,2-trifluoroacetamide (6i) Following General Procedure B and doubling the catalyst loading, 2,2,2-trifluoro-N-(2-methoxyethyl)acetamide (**5i**) (68.4 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (38.1 mg, 59% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 6.54 (s, 1H), 3.52 – 3.44 (m, 6H), 2.73 – 2.63 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.69, -89.82 (d, J = 41.2 Hz), -90.46 (d, J = 41.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.08 (q, J = 36.7 Hz), 151.37 (dd, J = 290.6, 286.5 Hz), 133.37, 128.70, 128.31 (t, J = 3.3 Hz), 127.68, 117.39 (q, J = 288.1 Hz), 89.70 (dd, J = 21.6, 13.9 Hz), 68.85, 68.26, 39.76, 28.40. **HRMS** calcd. for ($C_{14}H_{14}F_5NNaO_2$) $[M+Na]^+$: 346.0837, found 346.0829. **IR (neat):** 3317, 2970, 1736, 1558, 1446, 1365, 1216.

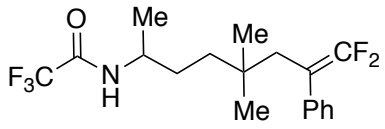


N-((2S)-8,8-difluoro-5-methyl-7-phenyloct-7-en-2-yl)-2,2,2-trifluoroacetamide (6j) Following General Procedure B, (S)-2,2,2-trifluoro-N-(hexan-2-yl)acetamide (**5j**) (78.9 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the mixture of diastereomers (dr = 1:1) as a colorless oil (47.8 mg, 68% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 5.96 (s, 1H), 4.06 – 3.59 (m, 1H), 2.40 – 2.29 (m, 1H), 2.28 – 2.17 (m, 1H), 1.50 – 1.36 (m, 3H), 1.35 – 1.27 (m, 1H), 1.17 – 1.07 (m,

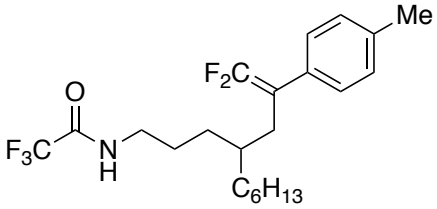
4H), 0.90 – 0.80 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.09 (*diastereomer 1*), -76.10 (*diastereomer 2*), -91.43 (d, *J* = 43.5 Hz) (*diastereomer 1*), -91.47 (d, *J* = 42.8 Hz) (*diastereomer 2*), -91.70 (d, *J* = 43.7 Hz). **^{13}C NMR** (126 MHz, CDCl3) δ 156.75 (q, *J* = 32.4 Hz), 154.19 (dd, *J* = 290.3, 285.9 Hz), 133.90, 128.63, 128.41 (t, *J* = 3.2 Hz), 127.47, 116.03 (q, *J* = 288.0 Hz), 91.46 (dd, *J* = 21.5, 13.2 Hz) (*diastereomer 1*), 91.29 (dd, *J* = 21.5, 13.2 Hz) (*diastereomer 2*), 46.87 (*diastereomer 1*), 46.82 (*diastereomer 2*), 34.94 (*diastereomer 1*), 34.82 (*diastereomer 2*), 33.75 (*diastereomer 1*), 33.60 (*diastereomer 2*), 32.39 (*diastereomer 1*), 32.36 (*diastereomer 2*), 31.17 (t, *J* = 2.4 Hz) (*diastereomer 1*), 31.12 (d, *J* = 2.5 Hz) (*diastereomer 2*), 20.50 (*diastereomer 1*), 20.29 (*diastereomer 2*), 19.14 (*diastereomer 1*), 19.12 (*diastereomer 2*). **HRMS** calcd. for ($C_{17}H_{20}F_5NNaO$) $[M+Na]^+$: 372.1357, found 372.1352. **IR (neat):** 3298, 2935, 1698, 1557, 1372, 1185, 698.



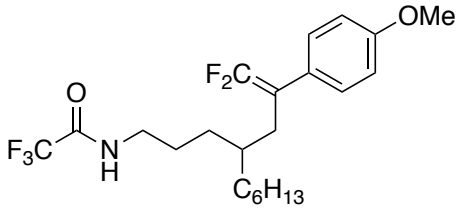
N-(2-((1R,2R)-2-(3,3-difluoro-2-phenylallyl)cyclopentyl)ethyl)-2,2,2-trifluoroacetamide (**6k**) Following General Procedure A, N-(2-cyclopentylethyl)-2,2,2-trifluoroacetamide (**5k**) (83.7 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the mixture of diastereomers (dr = 13:1) as a colorless oil as a colorless oil (45.0 mg, 62% yield) by using Hexane/EtOAc (20:1) as eluent. The major was interred to be a *trans* product according to a reported literature.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.25 (m, 3H), 6.25 (s, 1H), 3.58 – 3.14 (m, 2H), 2.59 – 2.45 (m, 1H), 2.37 – 2.24 (m, 1H), 1.93 – 1.80 (m, 1H), 1.77 – 1.63 (m, 2H), 1.64 – 1.48 (m, 2H), 1.49 – 1.39 (m, 2H), 1.35 – 1.12 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.65 (*diastereomer 1, minor*), -75.67 (*diastereomer 2, major*), -91.30 (d, *J* = 44.1 Hz), -91.49 (d, *J* = 45.3 Hz) (*diastereomer 1, minor*), -91.58 (d, *J* = 44.1 Hz) (*diastereomer 2, major*), -91.86 (d, *J* = 45.3 Hz) (*diastereomer 1, minor*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.25 (q, *J* = 36.8 Hz), 154.07 (dd, *J* = 290.3, 286.2 Hz), 133.87 (d, *J* = 3.8 Hz), 128.63, 128.38 (t, *J* = 3.1 Hz), 127.47, 115.99 (q, *J* = 288.0 Hz), 91.94 (dd, *J* = 21.3, 13.2 Hz), 44.11 (t, *J* = 2.3 Hz), 42.90, 39.28, 34.26, 32.67, 32.05, 31.69, 23.65. **HRMS** calcd. for ($C_{18}H_{20}F_5NNaO$) $[M+Na]^+$: 384.1357, found 384.1346. **IR (neat):** 3308, 2947, 2869, 1702, 1559, 1156, 697.



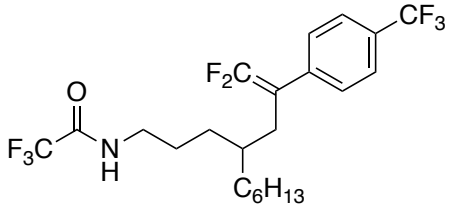
N-(8,8-difluoro-5,5-dimethyl-7-phenyloct-7-en-2-yl)-2,2,2-trifluoroacetamide (**6l**) Following General Procedure B, 2,2,2-trifluoro-N-(5-methylhexan-2-yl)acetamide (**5l**) (84.5 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (69.0 mg, 95% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 3H), 7.29 – 7.23 (m, 2H), 5.83 (s, 1H), 3.84 – 3.59 (m, 1H), 2.33 (dd, *J* = 2.8, 2.0 Hz, 2H), 1.36 – 1.25 (m, 2H), 1.10 – 1.06 (m, 2H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.79 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.60, -89.27 (d, *J* = 40.7 Hz), -91.53 (d, *J* = 40.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.54 (q, *J* = 36.6 Hz), 154.53 (dd, *J* = 290.3, 286.2 Hz), 135.55 (dd, *J* = 4.9, 2.5 Hz), 128.69 (t, *J* = 2.7 Hz), 128.51, 127.36, 115.99 (q, *J* = 288.2 Hz), 90.71 (dd, *J* = 21.4, 13.7 Hz), 47.12, 39.25, 37.83, 35.05 (d, *J* = 2.6 Hz), 30.79, 27.52, 27.44, 20.38. **HRMS** calcd. for ($C_{18}H_{22}F_5NNaO$) $[M+Na]^+$: 386.1510, found 386.1514. **IR (neat):** 3300, 2969, 1722, 1698, 1557, 1368, 1159, 698.



N-(4-(3,3-difluoro-2-(p-tolyl)allyl)decyl)-2,2,2-trifluoroacetamide (**6m**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 1-methyl-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (37.2 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (58.9 mg, 70% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.10 (m, 4H), 6.39 (s, 1H), 3.42 – 3.08 (m, 2H), 2.46 – 2.16 (m, 5H), 1.63 – 1.44 (m, 2H), 1.35 – 1.15 (m, 13H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.10, -91.91 (d, *J* = 45.4 Hz), -92.15 (d, *J* = 45.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.30 (q, *J* = 36.8 Hz), 153.98 (dd, *J* = 289.6, 285.9 Hz), 137.23, 130.69 (dd, *J* = 4.1, 2.4 Hz), 129.32, 128.20 (t, *J* = 3.1 Hz), 116.00 (q, *J* = 287.9 Hz), 91.26 (dd, *J* = 21.0, 13.7 Hz), 40.34, 35.30 (t, *J* = 2.3 Hz), 32.98, 31.90 (d, *J* = 1.9 Hz), 29.86, 29.66, 26.30, 25.74, 22.74, 21.21, 14.16. **HRMS** calcd. for ($C_{22}H_{30}F_5NNaO$) $[M+Na]^+$: 442.2140, found 442.2132. **IR (neat):** 3308, 2927, 2858, 1703, 1559, 1377, 1164.

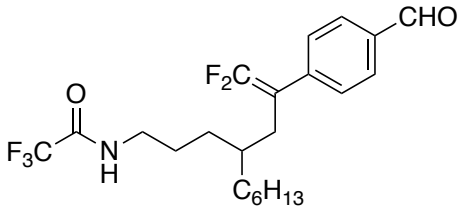


N-(4-(3,3-difluoro-2-(4-methoxyphenyl)allyl)decyl)-2,2,2-trifluoroacetamide (**6n**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 1-methoxy-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (40.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (53.5 mg, 61% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 6.93 – 6.84 (m, 2H), 6.29 (s, 1H), 3.81 (s, 3H), 3.37 – 3.18 (m, 2H), 2.40 – 2.29 (m, 1H), 2.31 – 2.19 (m, 1H), 1.57 – 1.44 (m, 2H), 1.38 – 1.14 (m, 13H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.08, -92.37 (d, *J* = 46.5 Hz), -92.57 (d, *J* = 46.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.84, 157.29 (q, *J* = 36.7 Hz), 153.94 (dd, *J* = 288.9, 285.7 Hz), 129.45 (t, *J* = 3.1 Hz), 125.82 (dd, *J* = 3.9, 2.2 Hz), 116.00 (q, *J* = 287.8 Hz), 114.06, 90.90 (dd, *J* = 20.9, 14.2 Hz), 55.33, 40.34, 35.27 (t, *J* = 2.3 Hz), 32.97, 32.00, 31.89, 29.86, 29.66, 26.31, 25.77, 22.74, 14.17. **HRMS** calcd. for ($C_{22}H_{30}F_5NNaO_2$) $[M+Na]^+$: 458.2089, found 458.2085. **IR (neat):** 3309, 2928, 2857, 1725, 1611, 1514, 1208, 832.

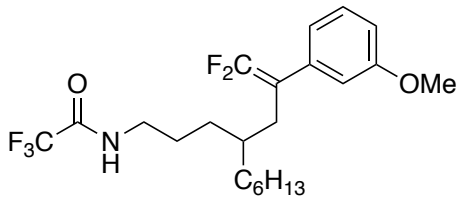


N-(4-(3,3-difluoro-2-(4-(trifluoromethyl)phenyl)allyl)decyl)-2,2,2-trifluoroacetamide (**6o**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 1-(trifluoromethyl)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzene (48.0 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (68.2 mg, 72% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.25 (s, 1H), 3.44 – 3.07 (m, 2H), 2.64 – 2.21 (m, 2H), 1.64 – 1.43 (m, 2H), 1.35 – 1.12 (m, 13H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.80, -76.08, -89.38 (d, *J* = 39.6 Hz), -89.65 (d, *J* = 39.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) 157.13 (q, *J* = 36.7 Hz), 154.75 (dd, *J* = 288.9, 285.7 Hz), 137.27, 129.56 (d, *J* = 14.9 Hz), 128.70 (t, *J* = 3.3 Hz), 125.89 (q, *J* = 287.9 Hz), 125.61 (t, *J* = 3.9 Hz), 115.85 (q, *J* = 317.3 Hz), 90.90 (dd, *J* = 20.9, 14.2 Hz), 40.34, 35.48, 32.88, 31.87, 31.80, 29.97, 29.64, 26.25,

25.95, 22.73, 14.15. **HRMS** calcd. for ($C_{22}H_{27}F_8NNaO$) $[M+Na]^+$: 496.1857, found 496.1867. **IR (neat):** 3310, 2929, 2859, 1704, 1619, 1559, 1325, 1161, 722.

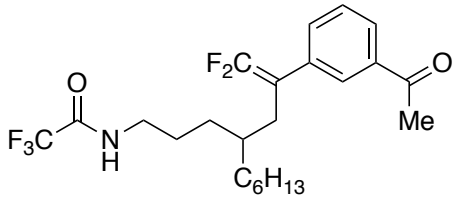


N-(4-(3,3-difluoro-2-(4-formylphenyl)allyl)decyl)-2,2,2-trifluoroacetamide (**6p**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (93.5 mg, 0.40 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)benzaldehyde (40.0 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (64.2 mg, 74% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 6.25 (s, 1H), 3.28 (q, *J* = 6.8 Hz, 2H), 2.49 – 2.23 (m, 2H), 1.59 – 1.43 (m, 2H), 1.36 – 1.14 (m, 13H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.04, -88.37 (d, *J* = 37.2 Hz), -88.60 (d, *J* = 37.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 191.70, 157.28 (q, *J* = 36.7 Hz), 154.43 (dd, *J* = 288.9, 285.7 Hz), 140.36, 135.40, 130.01, 128.95 (t, *J* = 3.3 Hz), 117.41 (q, *J* = 287.8 Hz), 91.17 (dd, *J* = 20.9, 14.2 Hz), 40.32, 35.60, 32.92, 31.87, 31.70, 29.97, 29.63, 26.28, 25.97, 22.73, 14.18. **HRMS** calcd. for ($C_{22}H_{28}F_5NNaO_2$) $[M+Na]^+$: 456.1932, found 456.1942. **IR (neat):** 3312, 2928, 2857, 1704, 1606, 1560, 1456, 1215, 831.

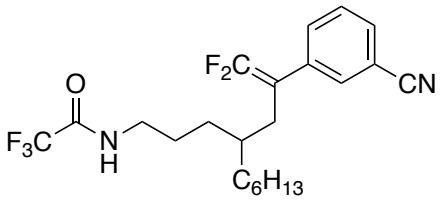


N-(4-(3,3-difluoro-2-(3-methoxyphenyl)allyl)decyl)-2,2,2-trifluoroacetamide (**6q**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.35 mg, 0.40 mmol) and 1-methoxy-3-(3,3,3-trifluoroprop-1-en-2-yl)benzene (40.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (70.2 mg, 81% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 6.91 – 6.77 (m, 3H), 6.23 (s, 1H), 3.81 (s, 3H), 3.34 – 3.17 (m, 2H), 2.41 – 2.22 (m, 2H), 1.54 – 1.45 (m, 2H), 1.38 – 1.17 (m, 13H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.08, -90.72 (d, *J* = 43.5 Hz), -91.32 (d, *J* = 43.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.75, 157.26 (q, *J* = 36.8 Hz), 154.65 (dd, *J* = 292.7, 288.3 Hz), 135.21, 129.61, 120.84 (t, *J* = 3.1 Hz), 117.43 (q, *J* = 287.8 Hz), 114.51 (t, *J* = 3.2 Hz), 112.62,

91.43 (dd, J = 21.9, 12.9 Hz), 55.37, 40.35, 35.40 (t, J = 2.3 Hz), 33.04, 31.98, 31.92, 29.92, 29.68, 26.35, 25.84, 22.76, 14.19. **HRMS** calcd. for ($C_{22}H_{30}F_5NNaO_2$) $[M+Na]^+$: 458.2089, found 458.2102. **IR (neat):** 3309, 2927, 2857, 1703, 1579, 1456, 1247, 1160, 720.

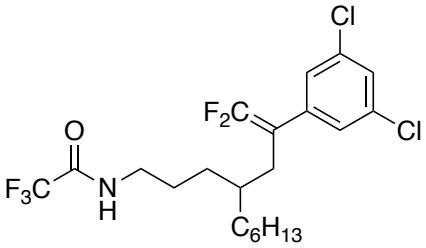


N-(4-(2-(3-acetylphenyl)-3,3-difluoroallyl)decyl)-2,2,2-trifluoroacetamide (**6r**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 1-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)ethan-1-one (42.8 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (80.1 mg, 89% yield) by using Hexane/EtOAc (8:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.57 – 7.42 (m, 2H), 6.47 (s, 1H), 3.38 – 3.15 (m, 2H), 2.61 (s, 3H), 2.43 – 2.32 (m, 2H), 1.57 – 1.46 (m, 2H), 1.35 – 1.13 (m, 13H), 0.85 (t, J = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.06, -90.15 (d, J = 41.5 Hz), -90.30 (d, J = 41.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.13, 157.33 (q, J = 36.4 Hz), 154.30 (dd, J = 290.2, 288.0 Hz), 137.51, 134.46, 133.10 (t, J = 3.3 Hz), 129.00, 127.83 (t, J = 3.1 Hz), 127.59, 116.00 (q, J = 287.9 Hz), 91.00 (dd, J = 21.0, 14.1 Hz), 40.28, 35.39 (t, J = 2.4 Hz), 33.03, 31.87, 31.77, 29.95, 29.62, 26.77, 26.29, 25.90, 22.73, 14.16. **HRMS** calcd. for ($C_{23}H_{30}F_5NNaO_2$) $[M+Na]^+$: 470.2089, found 470.2099. **IR (neat):** 3317, 2928, 2858, 1719, 1558, 1363, 1208, 1156, 702.

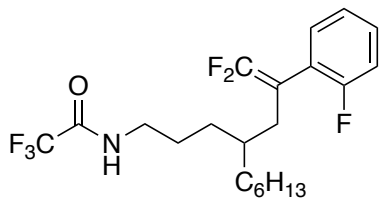


N-(4-(2-(3-cyanophenyl)-3,3-difluoroallyl)decyl)-2,2,2-trifluoroacetamide (**6s**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 3-(3,3,3-trifluoroprop-1-en-2-yl)benzonitrile (39.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (60.5 mg, 70% yield) by using Hexane/EtOAc (6:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 3H), 7.53 – 7.43 (m, 1H), 6.43 (s, 1H), 3.28 (q, J = 6.9 Hz, 2H), 2.39 – 2.30 (m, 2H), 1.58 – 1.45 (m, 2H), 1.31 – 1.13 (m, 13H), 0.86 (t, J = 7.0 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -

76.06, -88.90 (d, J = 38.9 Hz), -89.38 (d, J = 38.7 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.34 (q, J = 36.9 Hz), 154.39 (dd, J = 292.4, 288.3 Hz), 135.33 (dd, J = 5.1, 3.1 Hz), 132.76, 131.83, 131.04, 129.61, 118.59, 115.98 (q, J = 287.8 Hz), 113.00, 90.35 (dd, J = 23.4, 12.4 Hz), 40.26, 35.43 (t, J = 2.4 Hz), 32.75, 31.84, 31.67, 29.89, 29.61, 26.16, 25.87, 22.71, 14.15. **HRMS** calcd. for ($C_{22}H_{27}F_5N_2NaO$) $[M+Na]^+$: 453.1936, found 453.1943. **IR (neat):** 3317, 2928, 2858, 2232, 1719, 1558, 1456, 1160, 772.

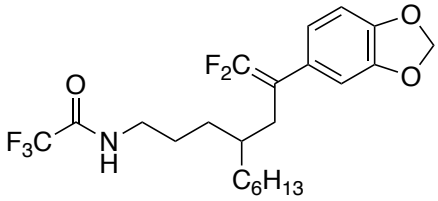


N-(4-(2-(3,5-dichlorophenyl)-3,3-difluoroallyl)decyl)-2,2,2-trifluoroacetamide (6t) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 1,3-dichloro-5-(3,3,3-trifluoroprop-1-en-2-yl)benzene (48.2 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (77.2 mg, 81% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (t, J = 1.9 Hz, 1H), 7.17 – 7.16 (m, 2H), 6.35 (s, 1H), 3.38 – 3.21 (m, 2H), 2.38 – 2.22 (m, 2H), 1.58 – 1.43 (m, 2H), 1.37 – 1.13 (m, 13H), 0.87 (t, J = 7.0 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.08, -88.44 (d, J = 37.9 Hz), -88.70 (d, J = 37.7 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.36 (q, J = 36.8 Hz), 154.38 (dd, J = 292.7, 288.3 Hz), 136.92 (dd, J = 4.8, 3.0 Hz), 135.26, 127.68, 126.80 (t, J = 3.4 Hz), 115.99 (q, J = 287.8 Hz), 90.21 (dd, J = 23.3, 12.7 Hz), 40.33, 35.42, 32.74, 31.88, 31.66, 29.94, 29.61, 26.16, 25.87, 22.74, 14.17. **HRMS** calcd. for ($C_{21}H_{26}Cl_2F_5NNaO$) $[M+Na]^+$: 496.1204, found 496.1228. **IR (neat):** 3308, 2927, 2857, 1702, 1559, 1457, 1161, 803.

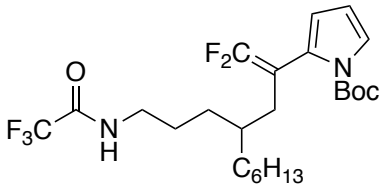


N-(4-(3,3-difluoro-2-(2-fluorophenyl)allyl)decyl)-2,2,2-trifluoroacetamide (6u) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 1-fluoro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzene (38.0 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (72.3 mg, 85% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 1H),

7.21 (td, J = 7.5, 2.0 Hz, 1H), 7.14 (td, J = 7.5, 1.2 Hz, 1H), 7.08 (ddd, J = 9.7, 8.2, 1.2 Hz, 1H), 6.28 (s, 1H), 3.55 – 3.01 (m, 2H), 2.39 – 2.24 (m, 2H), 1.55 – 1.40 (m, 2H), 1.33 – 1.15 (m, 13H), 0.86 (t, J = 7.0 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.11, -87.73 (dd, J = 39.2, 12.9 Hz), -91.64 (dd, J = 39.1, 2.1 Hz), -114.15 (d, J = 12.8 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.29 (d, J = 247.5 Hz), 157.30 (q, J = 36.8 Hz), 153.76 (dd, J = 288.9, 285.7 Hz), 130.80, 129.71 (d, J = 8.3 Hz), 124.31 (d, J = 3.5 Hz), 121.51 (d, J = 15.2 Hz), 116.05 (d, J = 22.4 Hz), 116.01 (q, J = 288.0 Hz), 86.07 (dd, J = 25.2, 15.7 Hz), 40.29, 35.64, 32.99, 32.07, 31.88, 29.85, 29.60, 26.32, 25.87, 22.74, 14.18. **HRMS** calcd. for ($C_{21}H_{27}F_6NNaO$) $[M+Na]^+$: 446.1889, found 446.1907. **IR (neat):** 3307, 2928, 2857, 1702, 1559, 1454, 1161, 757.

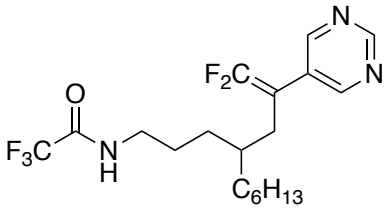


N-(4-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)decyl)-2,2,2-trifluoroacetamide (**6v**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 5-(3,3,3-trifluoroprop-1-en-2-yl)benzo[d][1,3]dioxole (43.2 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (55.2 mg, 61% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.84 – 6.60 (m, 3H), 6.31 (s, 1H), 5.96 (s, 2H), 3.27 (q, J = 7.2 Hz, 2H), 2.39 – 2.14 (m, 2H), 1.61 – 1.43 (m, 2H), 1.43 – 1.07 (m, 13H), 0.87 (t, J = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.69, -91.24 (d, J = 45.4 Hz), -91.79 (d, J = 45.4 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.29 (q, J = 36.7 Hz), 154.00 (dd, J = 289.5, 285.8 Hz), 147.90, 146.90, 127.34 (d, J = 7.3 Hz), 121.89 (t, J = 3.0 Hz), 115.99 (q, J = 288.0 Hz), 108.81 (t, J = 3.2 Hz), 108.45, 101.29, 91.20 (dd, J = 22.1, 13.2 Hz), 40.37, 35.26, 32.91, 32.22, 31.88, 29.88, 29.66, 26.27, 25.82, 22.73, 14.15. **HRMS** calcd. for ($C_{22}H_{28}F_5NNaO_3$) $[M+Na]^+$: 472.1882, found 472.1878. **IR (neat):** 3310, 2928, 2857, 1703, 1558, 1492, 1239, 1161, 1040.

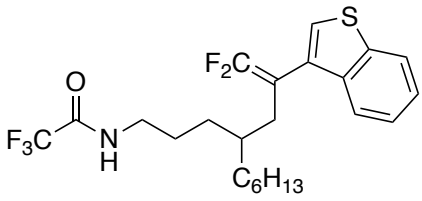


***tert*-butyl 2-(1,1-difluoro-4-(3-(2,2,2-trifluoroacetamido)propyl)dec-1-en-2-yl)-1H-pyrrole-1-carboxylate** (**6w**) Following General Procedure B, N-decyl-2,2,2-

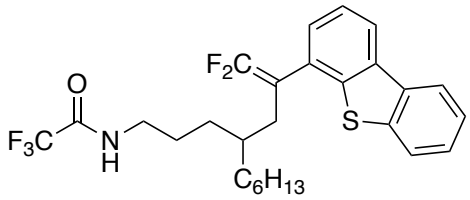
trifluoroacetamide (101.3 mg, 0.40 mmol) and *tert*-butyl 2-(3,3,3-trifluoroprop-1-en-2-yl)-1H-pyrrole-1-carboxylate (52.1 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (64.9 mg, 66% yield) by using Hexane/EtOAc (15:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 3.5, 1.9 Hz, 1H), 6.40 (s, 1H), 6.15 (t, *J* = 3.3 Hz, 1H), 6.08 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.44 – 3.14 (m, 2H), 2.29 – 2.02 (m, 2H), 1.57 (s, 9H), 1.55 – 1.40 (m, 2H), 1.37 – 1.15 (m, 13H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.06, -87.66 (d, *J* = 39.4 Hz), -92.09 (d, *J* = 39.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.31 (q, *J* = 36.6 Hz), 154.23 (dd, *J* = 289.5, 285.8 Hz), 148.88, 125.83 (d, *J* = 6.9 Hz), 122.65, 116.06 (q, *J* = 288.0 Hz), 115.36 (t, *J* = 2.1 Hz), 110.58, 85.34 (dd, *J* = 27.9, 15.0 Hz), 84.08, 40.32, 35.64 (t, *J* = 2.4 Hz), 33.16, 32.60, 31.94, 29.95, 29.67, 28.00, 26.50, 25.78, 22.75, 14.18. **HRMS** calcd. for ($C_{24}H_{35}F_5N_2NaO_3$) $[M+Na]^+$: 517.2460, found 517.2450. **IR (neat):** 3225, 2928, 2857, 1704, 1650, 1558, 1455, 1154, 726.



N-(4-(3,3-difluoro-2-(pyrimidin-5-yl)allyl)decyl)-2,2,2-trifluoroacetamide (**6x**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 5-(3,3,3-trifluoroprop-1-en-2-yl)pyrimidine (34.8 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (57.2 mg, 70% yield) by using Hexane/EtOAc (3:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.69 (d, *J* = 1.2 Hz, 2H), 6.48 (s, 1H), 3.30 (q, *J* = 6.9 Hz, 2H), 2.47 – 2.22 (m, 2H), 1.60 – 1.46 (m, 2H), 1.38 – 1.09 (m, 13H), 0.85 (t, *J* = 6.9 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.05, -86.57 (d, *J* = 35.1 Hz), -87.66 (d, *J* = 35.3 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.56 (q, *J* = 36.6 Hz), 157.39, 155.94, 154.67 (dd, *J* = 289.5, 285.8 Hz), 128.25, 115.98 (q, *J* = 287.9 Hz), 86.35 (dd, *J* = 25.0, 12.8 Hz), 40.25, 35.63 (t, *J* = 2.3 Hz), 32.78, 31.83, 31.02, 29.93, 29.62, 26.22, 25.98, 22.69, 14.14. **HRMS** calcd. for ($C_{19}H_{27}F_5N_3O$) $[M+H]^+$: 408.2069, found 408.2062. **IR (neat):** 3299, 2928, 2858, 1709, 1558, 1420, 1372, 1156, 732.

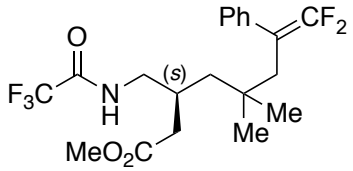


N-(4-(2-(benzo[b]thiophen-3-yl)-3,3-difluoroallyl)decyl)-2,2,2-trifluoroacetamide (**6y**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 3-(3,3,3-trifluoroprop-1-en-2-yl)benzo[b]thiophene (45.6 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (56.1 mg, 61% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 1H), 7.74 – 7.61 (m, 1H), 7.48 – 7.34 (m, 2H), 7.28 (s, 1H), 6.20 (s, 1H), 3.28 – 3.10 (m, 2H), 2.49 – 2.30 (m, 2H), 1.49 – 1.38 (m, 2H), 1.35 – 1.13 (m, 13H), 0.85 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.66, -85.66 (d, *J* = 39.9 Hz), -90.77 (d, *J* = 39.8 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.06 (q, *J* = 36.4 Hz), 152.67 (dd, *J* = 289.5, 285.8 Hz), 140.10, 137.83, 129.32, 126.76, 125.13, 124.61 (d, *J* = 23.8 Hz), 123.07, 122.58 (d, *J* = 2.3 Hz), 115.97 (q, *J* = 288.3 Hz), 86.06 (dd, *J* = 24.4, 15.9 Hz), 40.32, 35.83, 33.02, 32.90, 31.87, 30.05, 29.64, 26.31, 25.92, 22.72, 14.17. **HRMS** calcd. for ($C_{23}H_{28}F_5NNaOS$) $[M+Na]^+$: 484.1704, found 484.1694 **IR (neat):** 3306, 2926, 2856, 1703, 1558, 1457, 1367, 1272, 1160, 733.

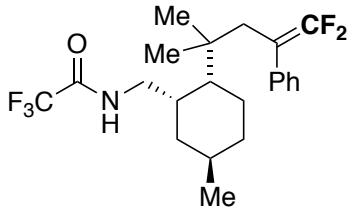


N-(4-(2-(dibenzo[b,d]thiophen-4-yl)-3,3-difluoroallyl)decyl)-2,2,2-trifluoroacetamide (**6z**) Following General Procedure B, N-decyl-2,2,2-trifluoroacetamide (101.3 mg, 0.40 mmol) and 4-(3,3,3-trifluoroprop-1-en-2-yl)dibenzo[b,d]thiophene (55.6 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (55.7 mg, 96% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 – 8.09 (m, 2H), 7.90 – 7.81 (m, 1H), 7.52 – 7.42 (m, 3H), 7.32 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.30 (s, 1H), 3.36 – 2.95 (m, 2H), 2.76 – 2.29 (m, 2H), 1.51 – 1.15 (m, 15H), 0.84 (t, *J* = 6.8 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.62, -85.43 (d, *J* = 38.4 Hz), -90.87 (d, *J* = 38.5 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.24 (q, *J* = 36.4 Hz), 153.68 (dd, *J* = 289.5, 285.8 Hz), 139.68, 139.15, 136.22, 135.77, 128.96 (d, *J* = 4.2 Hz), 127.46 (d, *J* = 2.9 Hz), 127.17, 124.85, 124.67, 122.84, 121.88,

121.16, 115.98 (q, J = 288.0 Hz), 90.63 (dd, J = 23.3, 15.3 Hz), 40.34, 35.82 (t, J = 2.4 Hz), 33.03, 32.16, 31.85, 30.08, 29.60, 26.28, 25.87, 22.70, 14.14. **HRMS** calcd. for ($C_{27}H_{30}F_5NNaOS$) $[M+Na]^+$: 534.1860, found 534.1856. **IR (neat):** 3311, 2927, 2856, 1726, 1558, 1206, 1160, 750.

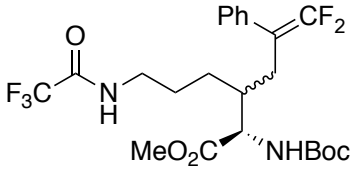


Methyl (S)-8,8-difluoro-5,5-dimethyl-7-phenyl-3-((2,2,2-trifluoroacetamido)methyl)oct-7-enoate (**6aa**) Following General Procedure B, methyl (S)-5-methyl-3-((2,2,2-trifluoroacetamido)methyl)hexanoate (**5aa**) (107.7 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (80.1 mg, 95% yield) by using Hexane/EtOAc (10:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 5H), 7.03 (s, 1H), 3.67 (s, 3H), 3.28 – 3.09 (m, 2H), 2.36 (t, J = 2.4 Hz, 2H), 2.33 – 2.16 (m, 2H), 2.16 – 2.06 (m, 1H), 1.13 (d, J = 4.9 Hz, 2H), 0.81 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.08, -89.19 (d, J = 39.6 Hz), -91.59 (d, J = 39.6 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.91, 157.54 (q, J = 36.1 Hz), 154.59 (dd, J = 290.6, 286.5 Hz), 135.38 (d, J = 4.4 Hz), 128.60, 128.57, 127.40, 116.00 (q, J = 287.7 Hz), 90.46 (dd, J = 21.2, 13.8 Hz), 52.06, 45.67, 44.33, 40.42, 39.56, 36.00 (t, J = 2.6 Hz), 30.60, 27.11 (d, J = 3.5 Hz). **HRMS** calcd. for ($C_{20}H_{24}F_5NNaO$) $[M+Na]^+$: 444.1569, found 444.1559. **IR (neat):** 3325, 2957, 1718, 1556, 1440, 1153, 698.

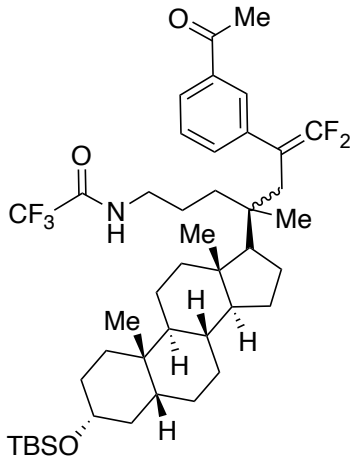


N-(((1S,2R,5R)-2-(5,5-difluoro-2-methyl-4-phenylpent-4-en-2-yl)-5-methylcyclohexyl)methyl)-2,2,2-trifluoroacetamide (**6ab**) Following General Procedure B, 2,2,2-trifluoro-N-(((1S,2S,5R)-2-isopropyl-5-methylcyclohexyl)methyl)acetamide (**5ab**) (106.1 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the title compound as a colorless oil (53.0 mg, 64% yield) by using Hexane/EtOAc (20:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.18 (m, 5H), 6.24 (s, 1H), 3.71 – 3.26 (m,

2H), 2.58 – 2.23 (m, 2H), 2.07 (d, *J* = 11.5 Hz, 1H), 1.74 – 1.64 (m, 1H), 1.60 – 1.48 (m, 3H), 1.33 – 1.19 (m, 3H), 0.99 – 0.70 (m, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.56 – -81.16 (m), -89.13 (d, *J* = 40.2 Hz), -91.23 (d, *J* = 40.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.38 (q, *J* = 36.6 Hz), 154.64 (dd, *J* = 290.6, 286.5 Hz), 135.68 (d, *J* = 3.2 Hz), 128.60 (t, *J* = 2.8 Hz), 128.53, 127.24, 116.04 (q, *J* = 288.2 Hz), 90.87 (dd, *J* = 21.2, 13.6 Hz), 47.77, 39.28, 38.35, 37.76, 37.71, 35.73, 35.66, 29.84, 26.50, 25.97, 25.40, 22.58. **HRMS** calcd. for ($C_{22}H_{28}F_5NNaO$) $[M+Na]^+$: 440.1983, found 440.1969. **IR (neat):** 3264, 2924, 2855, 1722, 1698, 1373, 1156, 697.



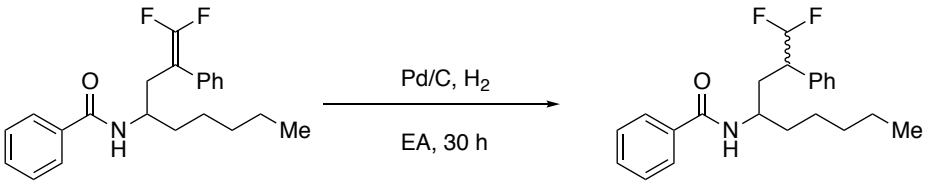
methyl 2-((tert-butoxycarbonyl)amino)-6,6-difluoro-5-phenyl-3-(3-(2,2,2-trifluoroacetamido)propyl)hex-5-enoate (**6ac**) Following General Procedure B, methyl N2-(tert-butoxycarbonyl)-N6-(2,2,2-trifluoroacetyl)lysinate (**5ac**) (142.5 mg, 0.40 mmol) and (3,3,3-trifluoroprop-1-en-2-yl)benzene (**2a**) (34.4 mg, 0.20 mmol) were used, affording the mixture of diastereomers (dr = 2/1) as a colorless oil (54.1 mg, 53% yield) by using Hexane/EtOAc (5:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.12 (m, 2H), 7.02 (s, 1H), 5.23 (d, *J* = 8.5 Hz, 1H), 4.43 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.64 (s, 3H), 3.44 – 3.32 (m, 1H), 3.29 – 3.14 (m, 1H), 2.34 – 2.19 (m, 2H), 1.84 – 1.69 (m, 2H), 1.61 – 1.52 (m, 1H), 1.45 (s, 9H), 1.42 – 1.32 (m, 2H). (*diastereomer 1*) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.25 (m, 3H), 6.47 (s, 1H), 5.08 (d, *J* = 8.7 Hz, 1H), 4.36 (d, *J* = 6.2 Hz, 1H), 3.71 (s, 3H), 3.32 (dd, *J* = 13.5, 6.8 Hz, 1H), 3.17 (dd, *J* = 13.9, 7.0 Hz, 1H), 2.50 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.41 – 2.28 (m, 1H), 1.90 (d, *J* = 4.4 Hz, 1H), 1.59 (t, *J* = 7.5 Hz, 2H), 1.42 (s, 9H), 1.37 – 1.24 (m, 2H). (*diastereomer 2*) **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.65, -89.79 (d, *J* = 41.2 Hz), -90.07 (d, *J* = 41.1 Hz).(*diastereomer 1*) **^{19}F NMR** (376 MHz, $CDCl_3$) δ -75.97, -89.82 (d, *J* = 40.7 Hz), -90.11 (d, *J* = 40.6 Hz). (*diastereomer 2*) **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.55, 157.52 (q, *J* = 36.9 Hz), 156.46, 153.96 (dd, *J* = 290.6, 286.5 Hz), 132.72 (t, *J* = 3.5 Hz), 128.61, 128.03 (t, *J* = 3.1 Hz), 127.70, 115.88 (q, *J* = 287.7 Hz), 90.13 (dd, *J* = 21.1, 14.6 Hz), 80.65, 54.37, 52.41, 39.93, 39.87, 28.14, 28.01, 27.49, 25.82. **HRMS** calcd. for ($C_{23}H_{29}F_5N_2NaO_5$) $[M+Na]^+$: 531.1889, found 531.1871. **IR (neat):** 3325, 2970, 1720, 1500, 1367, 1155, 699.



N-(6-(4-acetylphenyl)-4-((3R,5R,8R,9S,10S,13S,14S,17S)-3-((tert-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-7,7-difluoro-4-methylhept-6-en-1-yl)-2,2,2-trifluoroacetamide (**6ad**) Following General Procedure B, *N*-((*R*)-4-((3R,5R,8R,9S,10S,13R,14S,17S)-3-((tert-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentyl)-2,2,2-trifluoroacetamide (**5ad**) (229.0 mg, 0.40 mmol) and 1-(3-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)ethan-1-one (42.8 mg, 0.20 mmol) were used, affording the mixture of diastereomers (dr = 1/1) as a colorless oil (130.2 mg, 85% yield) by using Hexane/EtOAc (8:1) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 5.6 Hz, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.59 – 7.41 (m, 2H), 6.20 – 6.08 (m, 1H), 3.64 – 3.51 (m, 1H), 3.02 – 2.88 (m, 1H), 2.87 – 2.75 (m, 0.52H) (*diastereomer 1*), 2.77 – 2.69 (m, 0.48H) (*diastereomer 2*), 2.62 (s, 3H), 2.59 – 2.54 (m, 1H), 2.42 (d, *J* = 14.0 Hz, 1H), 2.05 – 1.99 (m, 0.52H) (*diastereomer 1*), 1.87 – 1.67 (m, 3.48H), 1.62 – 1.52 (m, 3H), 1.45 – 1.32 (m, 10H), 1.28 – 1.19 (m, 3H), 1.14 – 0.96 (m, 7H), 0.93 – 0.88 (m, 12H), 0.86 – 0.80 (m, 2H), 0.78 – 0.74 (m, 4H), 0.05 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -76.04 (*diastereomer 1*), -76.05 (*diastereomer 2*), -88.27 (d, *J* = 38.6 Hz) (*diastereomer 1*), -88.34 (d, *J* = 38.4 Hz) (*diastereomer 2*), -90.04 (d, *J* = 38.6 Hz) (*diastereomer 1*), -90.50 (d, *J* = 38.4 Hz) (*diastereomer 2*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.44, 198.34, 157.03 (q, *J* = 36.8 Hz), 154.58 (dd, *J* = 290.6, 286.5 Hz), 137.49 (d, *J* = 6.0 Hz), 136.50, 133.51, 128.91, 127.89, 127.51 (d, *J* = 4.5 Hz), 115.96 (q, *J* = 288.2 Hz), 90.44 (dd, *J* = 21.6, 13.9 Hz), 72.84, 72.82, 56.79, 56.77, 56.64, 44.10, 43.97, 42.31, 41.67, 41.52, 41.38, 41.07, 40.46, 40.34, 40.31, 37.04, 36.53, 36.30, 35.94, 35.79, 35.66, 35.44, 34.67, 31.15, 27.37, 26.84, 26.35, 26.09, 23.90, 23.81, 23.75, 23.68, 23.48, 23.45, 22.94, 22.70, 20.90, 20.76, 18.42,

15.19, 15.15, -4.46, -4.48. **HRMS** calcd. for ($C_{43}H_{64}F_5NNaO_3Si$) $[M+Na]^+$: 788.4468, found 788.4440. **IR (neat):** 3325, 2929, 2859, 1722, 1557, 1361, 1218, 776.

Transformation of 3a



3a **12**

Procedure: A mixture of Pd/C (10 mg, 0.01 mmol) and **3a** (35.7mg, 0.1 mmol) in 2 ml of EtOAc was stirred under 1 atm H_2 atmosphere at room temperature for 30 h. The reaction mixture was filtered and the filtrate was concentrated. The residue was purified with silica gel chromatography (Pentane/EtOAc = 10/1) to give a mixture of diastereomers (dr = 1.5/1) as a colorless oil (30.6 mg, 85% yield).

N-(1,1-difluoro-2-phenylnonan-4-yl)benzamide (**12**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.56 – 7.48 (m, 1H), 7.47 – 7.39 (m, 2H), 7.41 – 7.34 (m, 2H), 7.35 – 7.30 (m,3H), 6.06 – 5.73 (m, 1H), 5.73 – 5.55 (m, 1H), 4.27 – 3.98 (m, 1H), 3.32 – 3.02 (m, 1H), 2.26 – 1.94 (m, 2H), 1.71 – 1.45 (m, 2H), 1.34 – 1.24 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H).

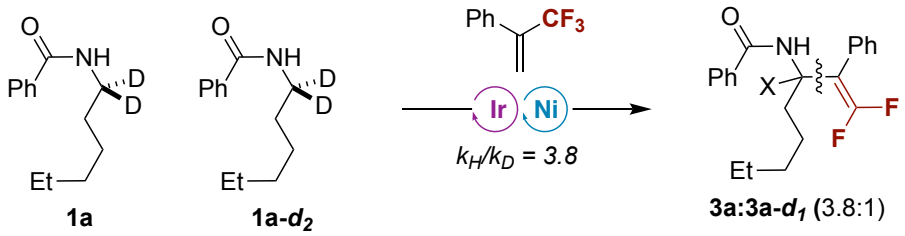
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.59 (d, *J* = 276.4 Hz) (*diastereomer 1*), -119.51 (d, *J* = 276.0 Hz) (*diastereomer 2*), -123.26 (d, *J* = 276.0 Hz) (*diastereomer 2*), -123.32 (d, *J* = 276.4 Hz) (*diastereomer 1*).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.10, 136.95, 134.84, 134.64, 131.55, 131.44, 129.18, 129.10, 129.01, 128.94, 128.68, 128.51, 128.03, 127.81, 126.89, 126.80, 117.92 (t, *J* = 244.6 Hz), 68.31, 48.95, 47.62, 35.86, 35.38, 31.75 (d, *J* = 2.6 Hz), 29.84, 25.68, 25.41, 22.62, 14.11.

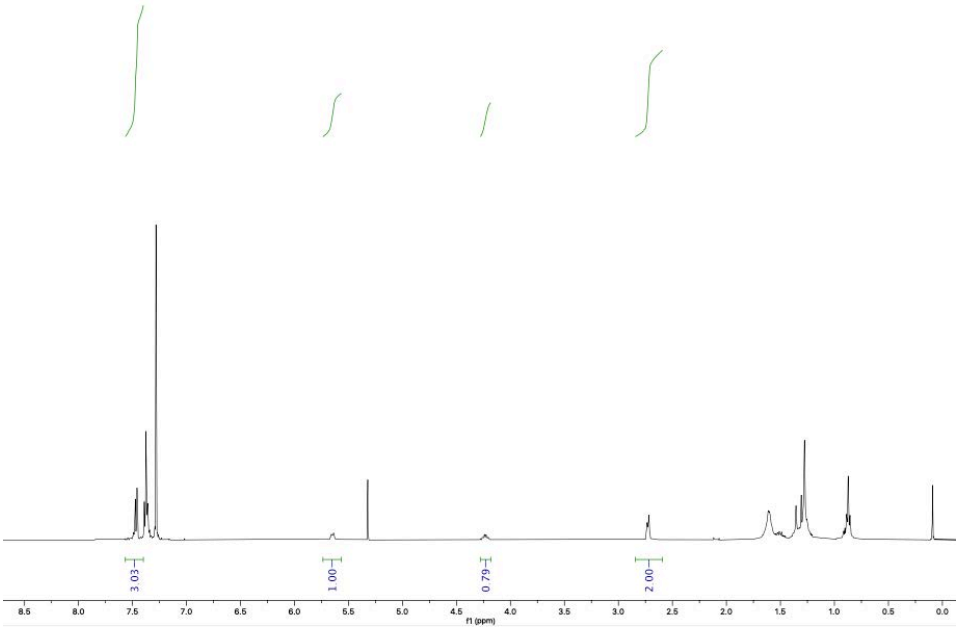
Mechanistic Studies

Mechanistic experiments for the α sp^3 C–H defluorinative alkylation

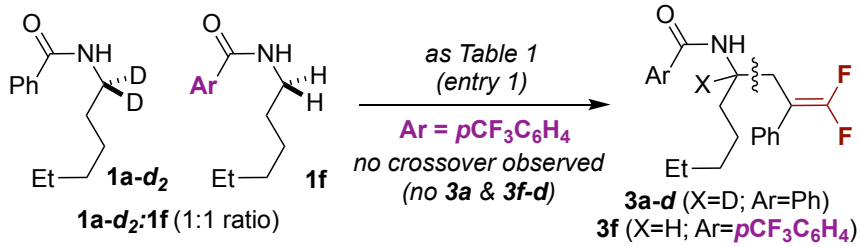
1. KIE Experiment



An oven-dried 8 mL Schlenk tube containing a stirring bar was charged with **1a** (20.5 mg, 0.10 mmol, 1.0 equiv), **1a-*d*$_2$** (20.7 mg, 0.10 mmol, 1.0 equiv), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (1.1 mg, 0.01 equiv), 5,5'-dimethyl-2,2'-dipyridyl (1.1 mg, 0.06 equiv), and $NiBr_2$·diglyme (1.8 mg, 0.05 equiv). The tube was then introduced in the nitrogen-filled glovebox where K_3PO_4 (32 mg, 0.15 mmol, 1.5 equiv) was added followed by 0.5 mL 1,4-dioxane. Then the tube was brought outside the glovebox, and **2a** (0.10 mmol, 1 equiv) was added to the reaction mixture under N_2 atmosphere. Then the tube was stirred at 15 °C under blue LED irradiation with a cooling system for 2 hours. The reaction was quenched by addition of EtOAc (5 mL), and the reaction mixture was concentrated under vacuum. The product was purified by flash column chromatography by using hexane/ethyl acetate (8/1) as eluent, affording the mixture as a white solid (3.9 mg, 11% yield). The K_H/K_D was calculated directly from ^{1}H NMR spectroscopy.

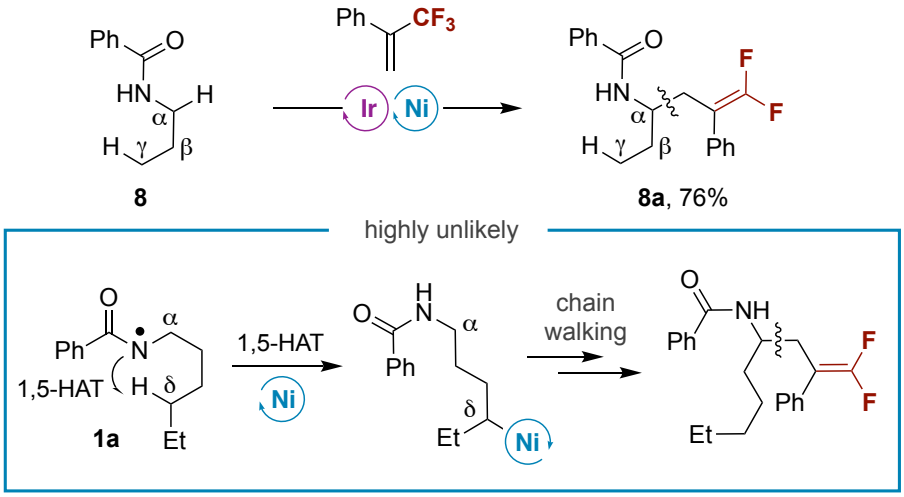


2. Crossover Experiment



An oven-dried 8 mL Schlenk tube containing a stirring bar was charged with **1a-*d*$_2$** (20.7 mg, 0.10 mmol, 1.0 equiv), **1f** (27.3 mg, 0.10 mmol, 1.0 equiv), (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (1.1 mg, 0.01 equiv), 5,5'-dimethyl-2,2'-dipyridyl (1.1 mg, 0.06 equiv), and NiBr$_2$·diglyme (1.8 mg, 0.05 equiv). The tube was then introduced in the nitrogen-filled glovebox where K$_3$PO$_4$ (32 mg, 0.15 mmol, 1.5 equiv) was added followed by 0.5 mL 1,4-dioxane. Then the tube was brought outside the glovebox, and **2a** (0.10 mmol, 1 equiv) was added to the reaction mixture under N$_2$ atmosphere. Then the tube was stirred at 15 °C under blue LED irradiation with a cooling system for 24 hours. The reaction was quenched by addition of EtOAc (5 mL) and the reaction mixture was concentrated under vacuum. The product was directly purified by flash column chromatography by using hexane/ethyl acetate (8/1) as eluent, affording **3f** as a white solid (3.1 mg, 7% yield) and **3a-*d*$_1$** as a white solid (3.0 mg, 8% yield). No deuterium exchange was observed.

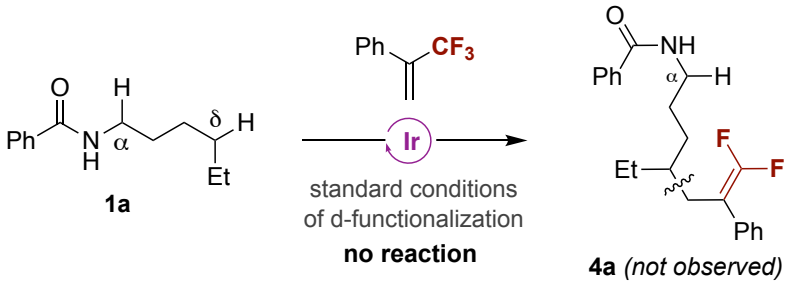
3. Arguing against the involvement of Ni chain-walking scenarios



An oven-dried 8 mL Schlenk tube containing a stirring bar was charged with **8** (65.3 mg, 0.40 mmol, 2.0 equiv), (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$ (1.1 mg, 0.01 equiv), 5,5'-dimethyl-2,2'-dipyridyl (2.2 mg, 0.06 equiv), and NiBr$_2$·diglyme (3.6 mg, 0.05 equiv). The tube

was then introduced in the nitrogen-filled glovebox where K_3PO_4 (64 mg, 0.30 mmol, 1.5 equiv) was added followed by 1 mL 1,4-dioxane. Then the tube was brought outside the glovebox, and **2a** (0.20 mmol, 1 equiv) was added to the reaction mixture under N_2 atmosphere. Then the tube was stirred at 15 °C under blue LED irradiation with a cooling system for 48 hours. The reaction was quenched by addition of EtOAc (5 mL) and the reaction mixture was concentrated under vacuum. The product was directly purified by flash column chromatography by using hexane/ethyl acetate (8/1) as eluent, affording **8a** as an amorphous solid (48.3 mg, 76% yield). M.P.: 81-82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 3H), 7.39 – 7.31 (m, 6H), 7.29 – 7.25 (m, 1H), 5.68 (d, *J* = 8.8 Hz, 1H), 4.31 – 3.88 (m, 1H), 2.90 – 2.43 (m, 2H), 1.75 – 1.60 (m, 1H), 1.58 – 1.44 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -90.04 (d, *J* = 41.3 Hz), -90.19 (d, *J* = 41.2 Hz). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.12, 154.51 (dd, *J* = 289.2, 287.5 Hz), 134.76, 133.73, 131.41, 128.91, 128.55, 128.50 (t, *J* = 3.1 Hz), 127.69, 126.78, 89.96 (dd, *J* = 20.4, 15.6 Hz), 50.44 (t, *J* = 2.8 Hz), 32.92, 27.50, 10.44. **HRMS** calcd. for ($C_{19}H_{20}F_2NO$) $[M+H]^+$: 316.1507, found 316.1508. **IR (neat):** 3265, 3062, 2961, 1736, 1636, 1539, 1233, 696.

4. Control Experiments



To an 8 mL vial equipped with a stirring bar was added **1a** (0.20 mmol, 2.0 equiv), $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (1.1 mg, 0.01 equiv). The vial was then introduced in the nitrogen-filled glovebox where K_3PO_4 (64 mg, 0.30 mmol, 3.0 equiv) was added followed by 0.5 mL toluene. Then the tube was brought outside the glovebox, and **2a** (0.20 mmol, 1 equiv) was added to the reaction mixture under N_2 atmosphere. The reaction was stirred and irradiated using 451 nm Kessil light (40 W), equipped with a fan cooling system for 72 hours. The reaction was quenched by the addition of EtOAc (5 mL). The mixture was filtered through a silica plug, the filtrate was then removed under vacuum and nitromethane (5.4 μL, 0.10 mmol) was added as internal standard. The reaction mixture was analyzed by ^{1}H NMR, showing that no reaction occurred.

5. Interactions of Ni(II) with the secondary amide by ^{1}H NMR

Two experiments were conducted to test whether a ^{1}H NMR chemical shift occurs by interaction of Ni(II) and the secondary amide. (**a**) In a glovebox, *N*-hexylbenzamide **1a** (4.8 mg, 0.02 mmol) and TMB (2.1 mg) were added to a 3 mL vial and dissolved in 1 mL THF-d_8. This solution was transferred to a J. Young NMR tube, and the chemical shifts were measured by ^{1}H-NMR. The solution was then brought back into the glovebox and added to $NiBr_2$diglyme (8.2 mg, 0.02 mmol). This solution was transferred into the J. Young NMR tube and measured by ^{1}H and paramagnetic ^{1}H NMR. **(b)** An analogous procedure was used by adding **1a** (1.3 mg, 0.01 mmol) at the very end. The ^{1}H and paramagnetic ^{1}H NMR of a mixture containing $NiBr_2$diglyme (8.2 mg, 0.02 mmol), 5,5-dimethyl-2,2-bipyridine (3.7 mg, 0.02 mmol), *N*-hexylbenzamide **1a** (4.8 mg, 0.02 mmol) and TMB (2.1 mg) was also measured, and the spectrum recorded was identical to that shown by mixing the amide with TMB, likely due to the insolubility of the formed Ni(II)-**L1** complex. *Conclusion*; A significant chemical shift is evident by looking at the diamagnetic ^{1}H NMR spectra, thus suggesting a molecular interaction between Ni(II) and *N*-hexylbenzamide **1a**.

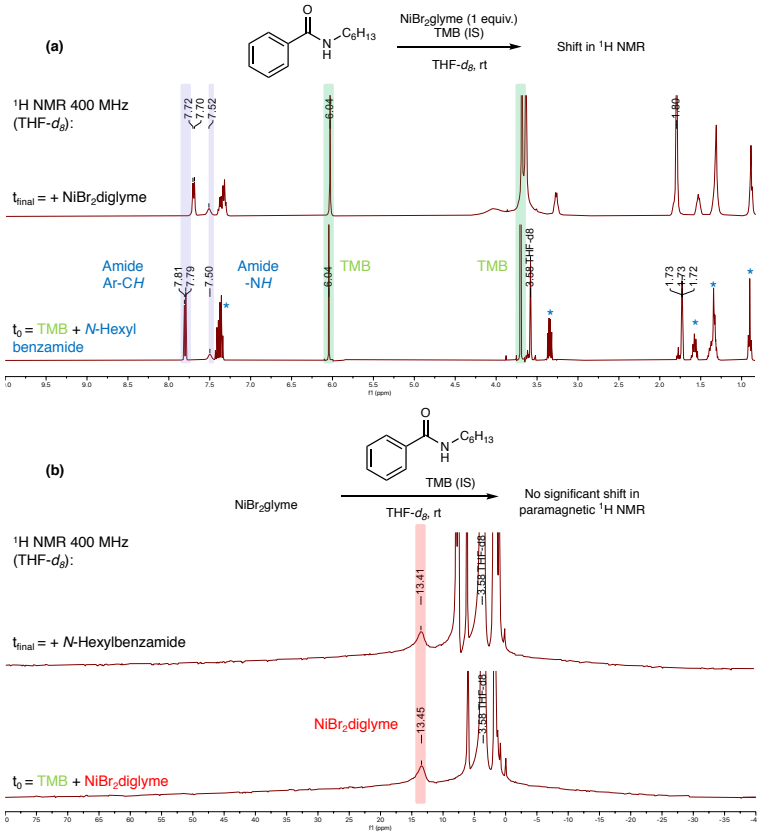


Figure SI ^{1}H spectra (THF-d_8, 400 MHz) of the *N*-hexylbenzamide (blue) and $NiBr_2$diglyme (red) (internal standard = TMB (green)).

6. Interactions of Ni(II) with the secondary amide by UV-VIS

Two additional experiments were conducted to identify interactions between Ni species and the corresponding secondary amide. **(a)** To a quartz cuvette containing (dtbbpy)$Ni^{I}Cl$ (0.2 mM) in THF was added a solution of *N*-hexylbenzamide **1a** (Figure S2). **(b)** To a quartz cuvette containing (dtbbpy)$Ni^{II}Cl_2$ (1.2 mM) in THF was added a solution of *N*-hexylbenzamide **1a** (Figure S3.). *Conclusion*; A significant decrease in the corresponding UV absorption by addition of the secondary amide suggests an interaction between amide and Ni.

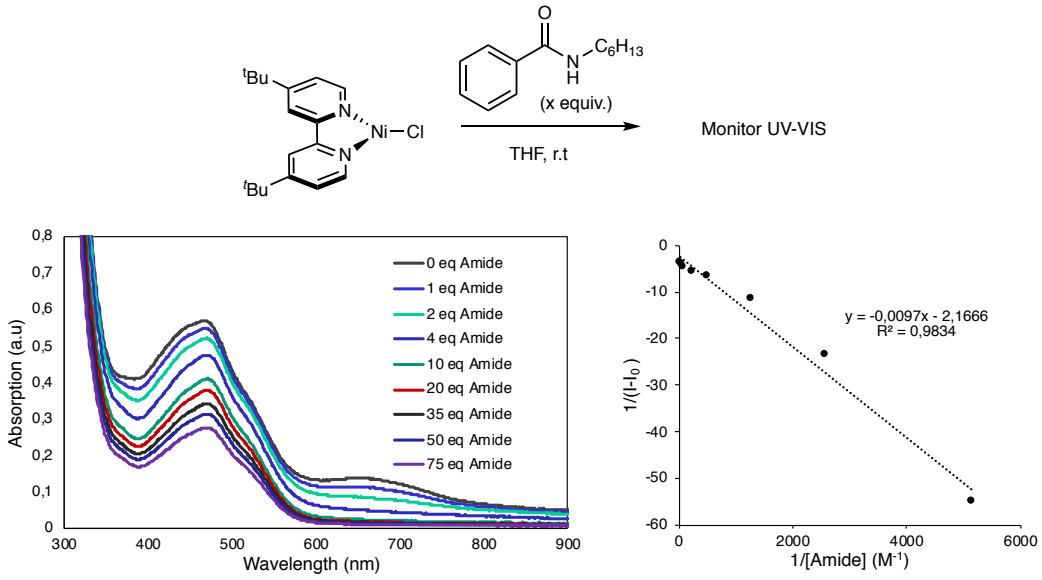


Figure S2 Monitoring UV-VIS of (dtbbpy)$Ni^{I}Cl$ with addition of *N*-hexylbenzamide

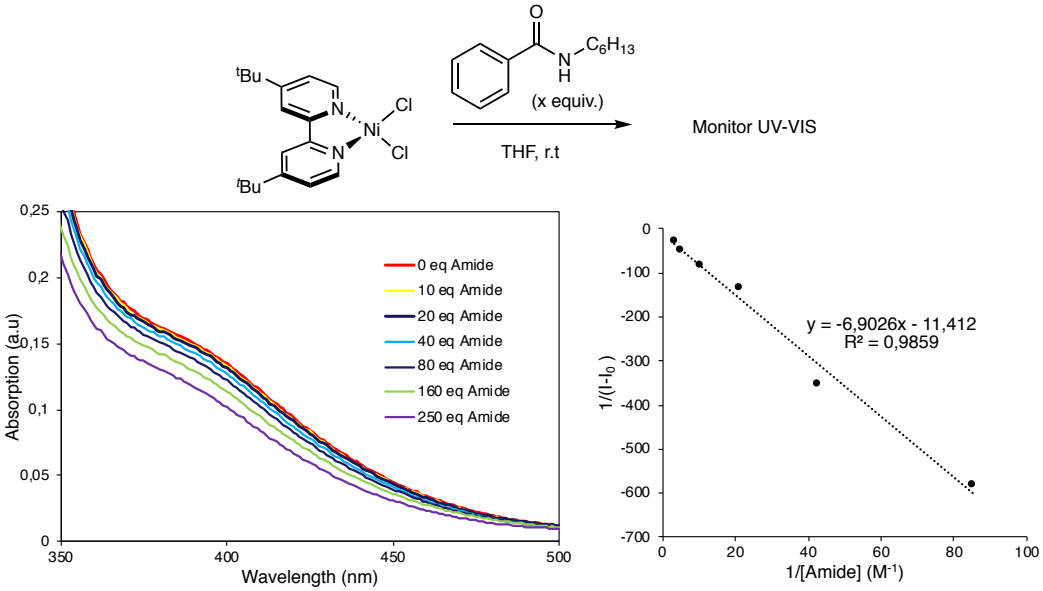


Figure S3. Monitoring UV-VIS of (dtbbpy)$Ni^{II}Cl_2$ with addition of *N*-hexylbenzamide

7. Quenching Experiments of Ir-1 with Ni Species or the Secondary Amide

Two experiments were conducted to identify whether quenching of the photocatalyst occurred with either the Ni species or the secondary amide. **(a)** To a quartz cuvette containing **Ir-1** (0.18 mM) in THF was added a solution of $NiBr_2$glyme and the emission spectra was recorded. (Figure S4); **(b)** Plot of the quenching experiment of **Ir-1** with $NiBr_2$glyme in the absence of the secondary amide; **(c)** To a quartz cuvette containing **Ir-1** (0.18 mM) and *N*-hexylbenzamide (17.1 mM, 95 eq) in THF was added a solution of $NiBr_2$glyme (Figure S4.). **(d)** Plot of the quenching experiment of **Ir-1** with $NiBr_2$glyme in the presence of the secondary amide. **(e)** Overlayed graphs of (b) and (c) showing no significant difference. We also tried to run an otherwise similar experiment to (a) and (c) with a solution of $NiBr_2$glyme and 5,5-dimethyl-2,2-bipyridine. Unfortunately, the Ni(II)-**L1** complex was rather insoluble, thus now allowing to obtain conclusive evidence about the role exerted for understanding the potential interaction with the Ni(II)-**L1** complex. *Conclusion*: the addition of secondary amide does not promote the quenching of **Ir-1** with $NiBr_2$digyme.

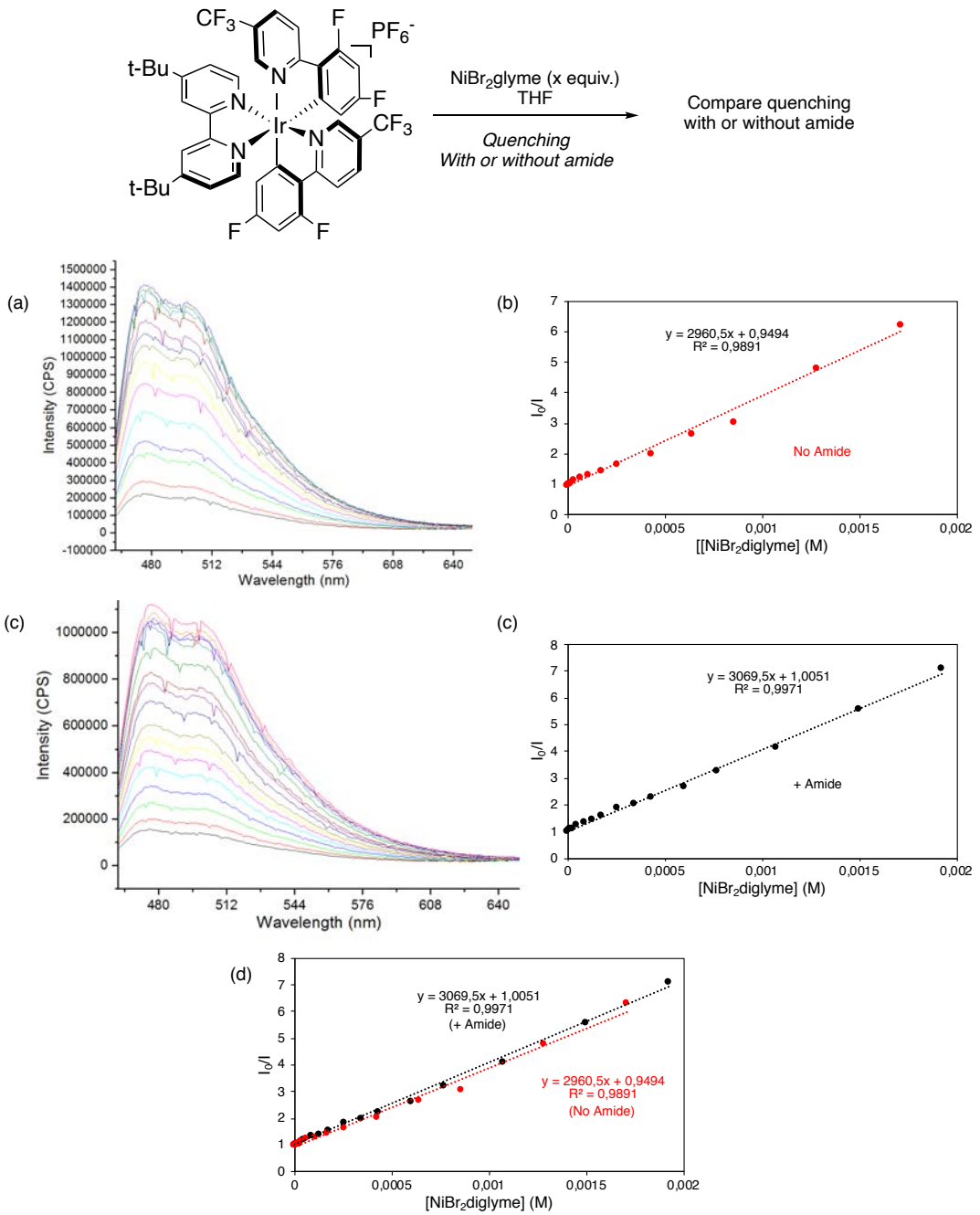


Figure S4 Quenching experiments aimed at identifying whether the presence of secondary amide promotes the quenching of **Ir-1** with the Ni complex.

8. Quenching experiments of Ir-1 with both Ni species and Secondary Amide

Experiments were conducted to identify whether quenching of the photocatalyst occurred with both Ni species and the secondary amide. **(a)** To a quartz cuvette containing **Ir-1** (0.18 mM) and $NiBr_2$·glyme (0.18mM) in THF was added a solution of **1a** and the emission spectra was recorded (Figure S5); **(b)** Plot of the quenching experiment of **Ir-1** with $NiBr_2$glyme and increased concentrations of secondary amide; **(c)** To a quartz cuvette containing **Ir-1** (0.18 mM) in THF was added a solution of **1a. (d)** Plot of the quenching experiment of **Ir-1** with increased concentrations of secondary amide in the absence of Ni catalyst. **(e)** To a quartz cuvette containing **Ir-1** (0.0125 mM), $NiBr_2$·glyme (0.0125mM) in THF was added a solution of **1a** and the emission spectra was recorded (Figure S5); **(f)** Plot of the quenching experiment of **Ir-1** (0.0125 mM) with $NiBr_2$glyme (0.0125 mM) and increased concentrations of secondary amide; **(g)** To a quartz cuvette containing **Ir-1** (0.0125 mM), $NiBr_2$·glyme (0.0125mM) and 5,5-dimethyl-2,2-bipyridine (0.0125mM) in THF was added a solution of **1a** and the emission spectra was recorded (Figure S5). **(h)** Plot of the quenching experiment of **Ir-1** (0.0125 mM), $NiBr_2$glyme (0.0125 mM) with 5,5-dimethyl-2,2-bipyridine (0.0125mM) and increased concentrations of secondary amide. *Conclusion*: the presence of Ni salts slightly improve the ability of the secondary amide to promote the quenching of **Ir-1** and the presence of Ni with ligand can further improve the ability of the secondary amide to promote the quenching of **Ir-1**.

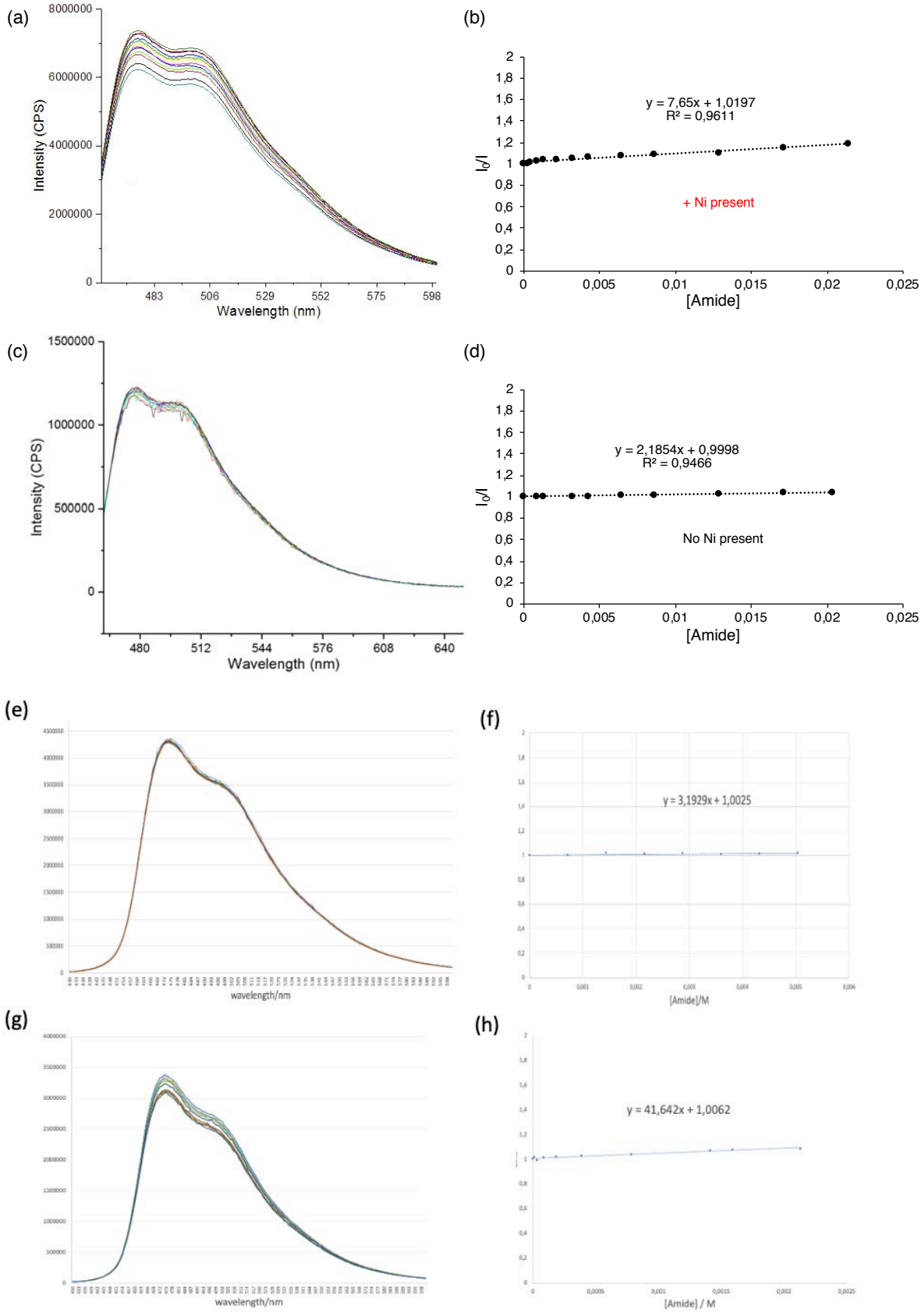


Figure S5. Quenching experiments of **Ir-1** by varying the concentration of the secondary amide **1a**.

9. Cyclic voltammogram of 1a

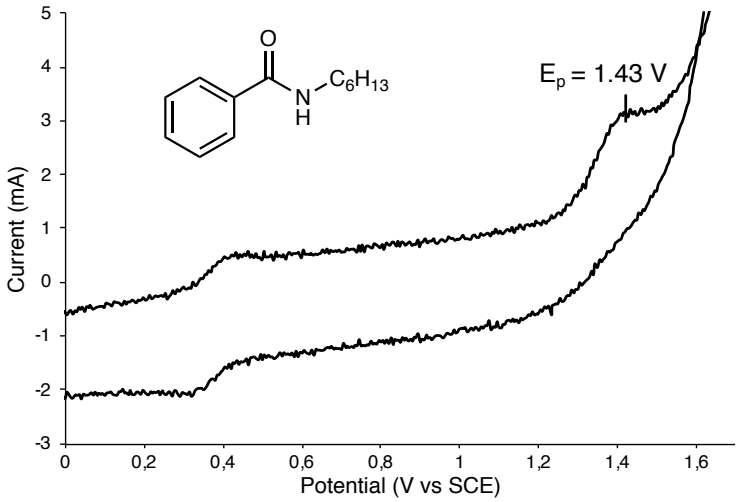
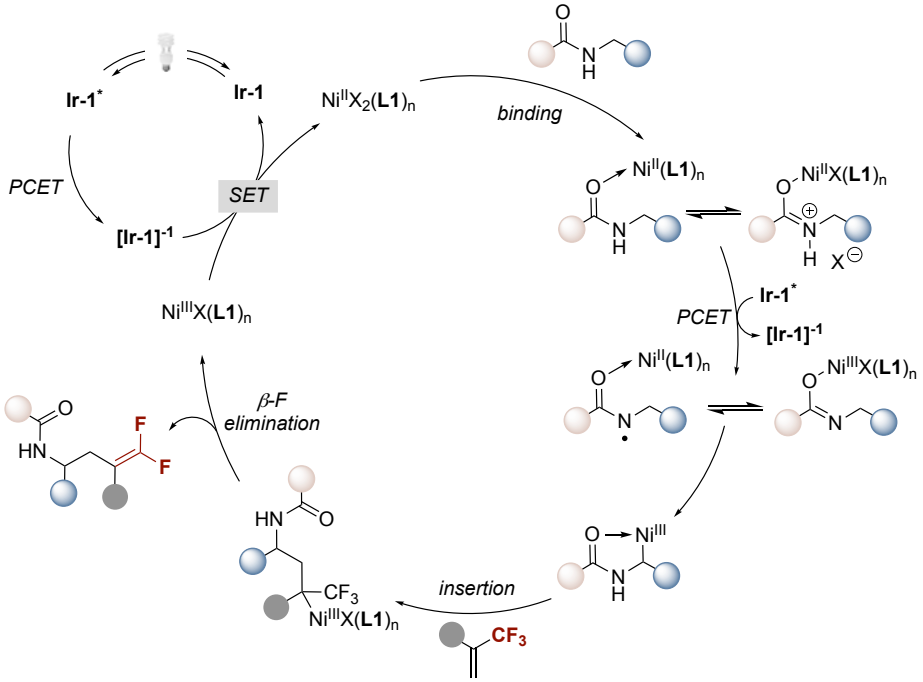


Figure S6 Cyclic voltammogram of **1a**. Voltammograms were taken using a glassy carbon working electrode in a 0.1 M [$^{n}Bu_4N$][PF_6] supporting electrolyte THF solution with a 100 mV/s scan rate and 0.01 M of sample referenced to Fc (+380 vs SCE, external). Scans were started at the open-circuit potential and scanned in the cathod direction first; the second cycle is shown here. E_p values for *N*-hexylbenzamide are 1.43 V.

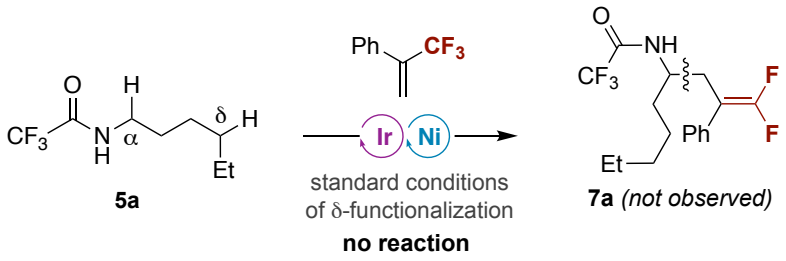
10. Proposed catalytic cycle for α *sp*^{3} C–H defluorinative alkylation.



At present, it is unclear whether the reaction operates via beta-F elimination at Ni(III) or Ni(II) (for an elegant disclosure, see Norton, J. et al., *J. Am. Chem. Soc* **2020**, *142*, 4793).

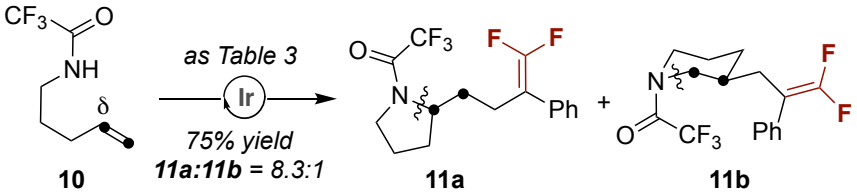
Mechanistic experiments for the δ *sp*^{3} C–H defluorinative alkylation

1. Control Experiments

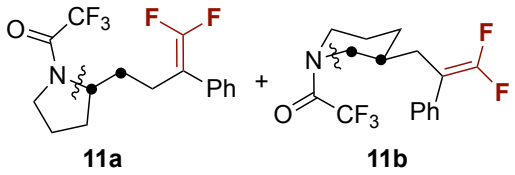


An oven-dried 8 mL Schlenk tube containing a stirring bar was charged with **5a** (0.20 mmol, 2 equiv), **Ir-1** (1.1 mg, 0.01 equiv), 5,5'-dimethyl-2,2'-dipyridyl (1.1 mg, 0.06 equiv), and $NiBr_2$·diglyme (1.8 mg, 0.05 equiv). The tube was introduced in the nitrogen-filled glovebox where K_3PO_4 (32 mg, 0.15 mmol, 1.5 equiv) was added followed by 0.5 mL 1,4-dioxane. Then the tube was brought outside the glovebox, and **2a** (0.10 mmol, 1 equiv) was added to the mixture under N_2 atmosphere. Then, the tube was stirred at 15 °C under blue LED irradiation with a cooling system for 72 hours. The reaction was quenched by addition of EtOAc (5 mL) and the mixture was filtered through a silica plug. The filtrate was removed under vacuum and $MeNO_3$ (5.4 μL, 0.10 mmol) was added as standard. The mixture was analyzed by ^{1}H NMR, showing that no reaction occurred.

2. Control experiments with secondary amides possessing a pending olefin



To an 8 mL vial equipped with a stirring bar was added **10** (0.40 mmol, 2.0 equiv) and **Ir-1** (2.2 mg, 0.01 equiv). The vial was then introduced in the nitrogen-filled glovebox where K_3PO_4 (128 mg, 0.60 mmol, 3.0 equiv) was added followed by 1.0 mL toluene. Then the tube was brought outside the glovebox, and **2a** (0.20 mmol, 1 equiv) was added to the reaction mixture under N_2 atmosphere. The reaction was stirred and irradiated using 451 nm Kessil light (40 W), equipped with a fan cooling system for 72 hours. The reaction was quenched by the addition of EtOAc (5 mL), and the reaction was quenched by addition of EtOAc (5 mL). The reaction mixture was concentrated under vacuum and purified by flash chromatography column on silica gel (Hexane/EA = 15: 1) to give a mixture of **11a** and **11b** (50.1 mg, 75% yield, **11a**/**11b** = 8.3/1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H$_{major+minor}$), 7.33 – 7.26 (m, 3H$_{major+minor}$), 4.43 – 4.27 (m, 0.11H $_{minor}$), 4.24 – 4.03 (m, 0.90H$_{major}$), 3.90 – 3.78 (m, 0.11H $_{minor}$), 3.73 – 3.51 (m, 1.80H$_{major}$), 3.53 – 3.38 (m, 0.11H $_{minor}$), 2.85 – 2.67 (m, 0.11H $_{minor}$), 2.61 – 2.27 (m, 2.0H$_{major+minor}$), 2.10 – 1.85 (m, 4H$_{major+minor}$), 1.81 – 1.67 (m, 1H$_{major+minor}$), 1.48 – 1.32 (m, 1H$_{major+minor}$).

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.94 (s, 0.33F$_{minor}$), -72.54 (s, 2.67F$_{major}$), -90.82 (d, j = 45.1 Hz, 0.33F$_{minor}$), -90.92 (d, j = 45.1 Hz, 0.33F$_{minor}$),, -91.26 (d, j = 41.4 Hz, 1.78F$_{major}$), -91.28(d, j = 41.4 Hz, 1.78F$_{major}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.59, 153.67, 133.35, 128.71, 128.32 (t, J = 3.3 Hz), 127.59, 116.45 (q, J = 287.9 Hz), 91.98 (dd, J = 20.1, 15.8 Hz), 58.94, 46.68 (d, J = 3.5 Hz), 31.01, 28.88, 24.82, 24.48.

HRMS calcd. for ($C_{16}H_{16}F_5NNaO$) $[M+Na]^+$: 356.1044, found 356.1052.

IR (neat): 2970, 1738, 1688, 1366, 1232, 1204, 1142, 698.

3. Identification of interactions between secondary amide and base via ^{1}H NMR

Two experiments were conducted to test whether a ^{1}H NMR chemical shift occurs between CF_3-amides and K_3PO_4. **(a)** N-decyl-2,2,2-trifluoroacetamide (9.7 mg, 0.04 mmol) and TMB (2.1 mg) were added to a 3 mL vial and dissolved in 1 mL THF-d_8. This solution was then transferred to an NMR tube, and the chemical shifts were measured by ^{1}H NMR. This solution was then added to K_3PO_4 (12.3 mg, 0.06 mmol) and stirred for 20 min, filtered through a celite plug and measured again by ^{1}H NMR. This solution was added to K_3PO_4 (155 mg, 0.73 mmol) and stirred for 20 min, filtered through celite and measured again by ^{1}H NMR. **(b)** An analogous procedure was used with **1a** (10.5 mg, 0.05 mmol) and TMB (3.0 mg). *Conclusion*; A minor chemical shift changes upon reaction of N-decyl-2,2,2-trifluoroacetamide with K_3PO_4, suggesting an interaction of these species, an observation that is in contrast with the analogous experiment using **1a**.

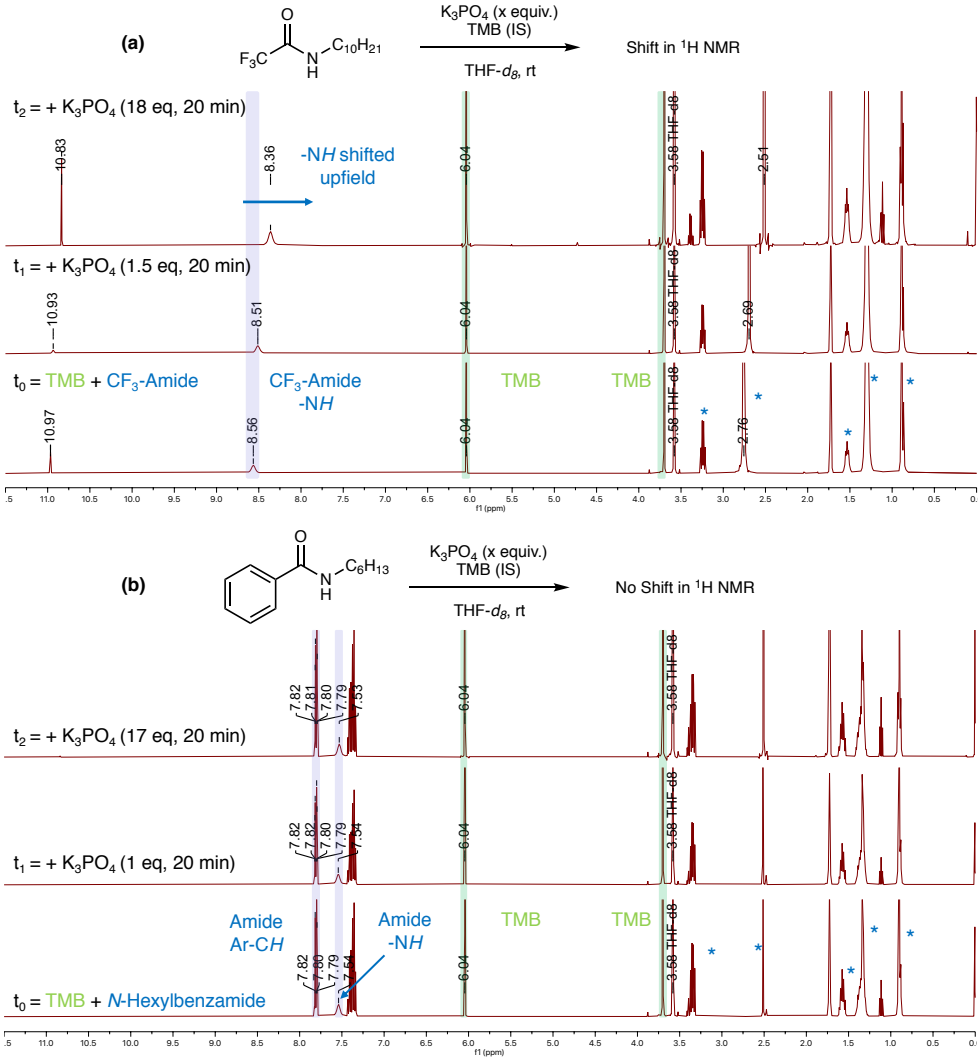


Figure S7. Interactions of the corresponding secondary amides with the base

4. Quenching of Ir-1 with both N-decyl-2,2,2-trifluoroacetamide and deprotonated N-decyl-2,2,2-trifluoroacetamide

Two experiments were conducted to test whether quenching of the photoexcited state of **Ir-1** was observed by the secondary amide or its deprotonated form. **(a)** To a quartz cuvette containing **Ir-1** (0.18 mM) in THF was added a solution of N-decyl-2,2,2-trifluoroacetamide and the emission spectra was recorded. (Figure S8) **(b)** Plot of the quenching of **Ir-1** with the secondary amide, indicating a virtually inexistent quenching. **(c)** To a quartz cuvette containing **Ir-1** (0.18 mM) in THF was added a solution of the Li salt of N-decyl-2,2,2-trifluoroacetamide (Figure S8). **(d)** Plot of the quenching of **Ir-1** with the secondary amide, indicating significant quenching of **Ir-1** (ca. 2000x more than just the amide) *Conclusion*; Deprotonation of the secondary amide causes a significant quenching of the photoexcited state of **Ir-1**.

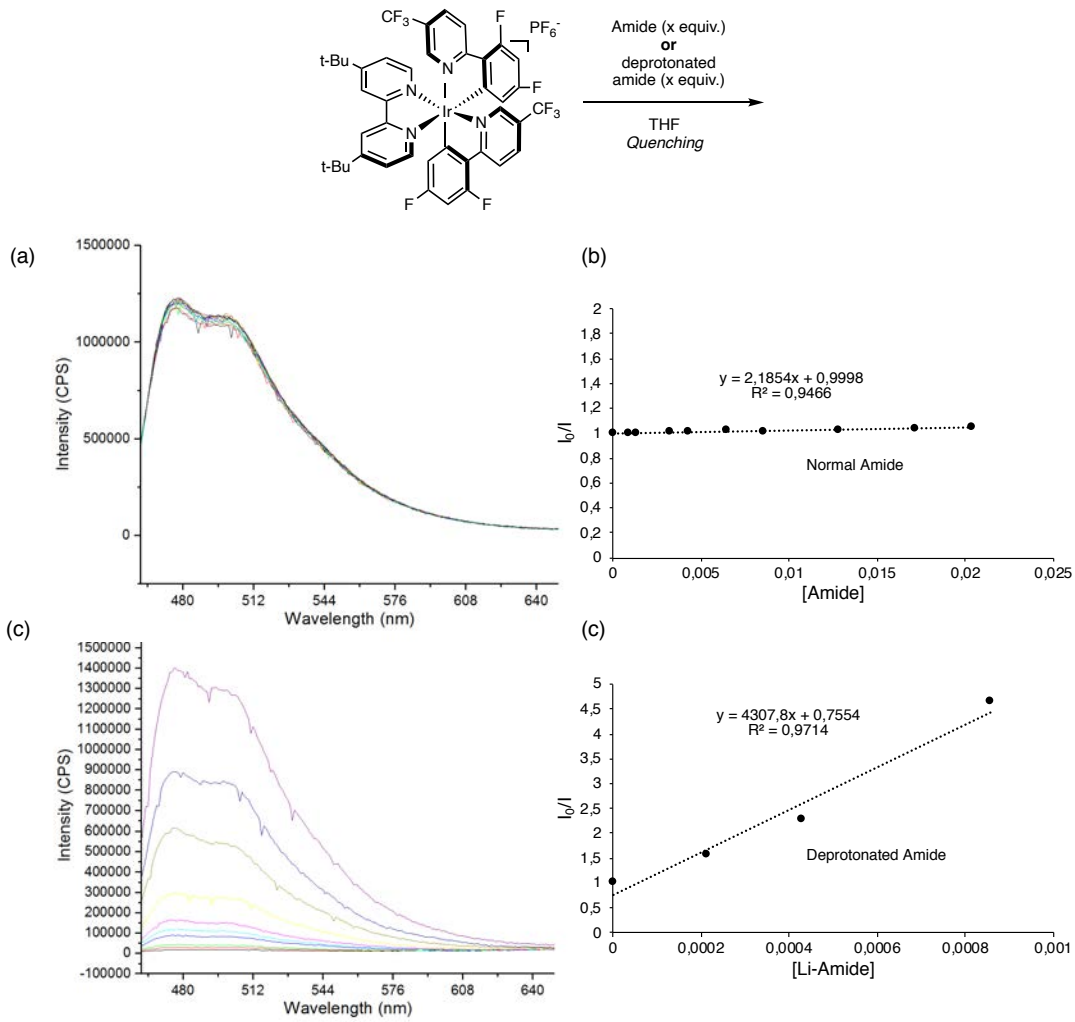


Figure S8. Quenching experiment of **Ir-1** with CF_3-amide and its Li salt.

5. Cyclic voltammogram of N-decyl-2,2,2-trifluoroacetamide and Deprotonated N-decyl-2,2,2-trifluoroacetamide

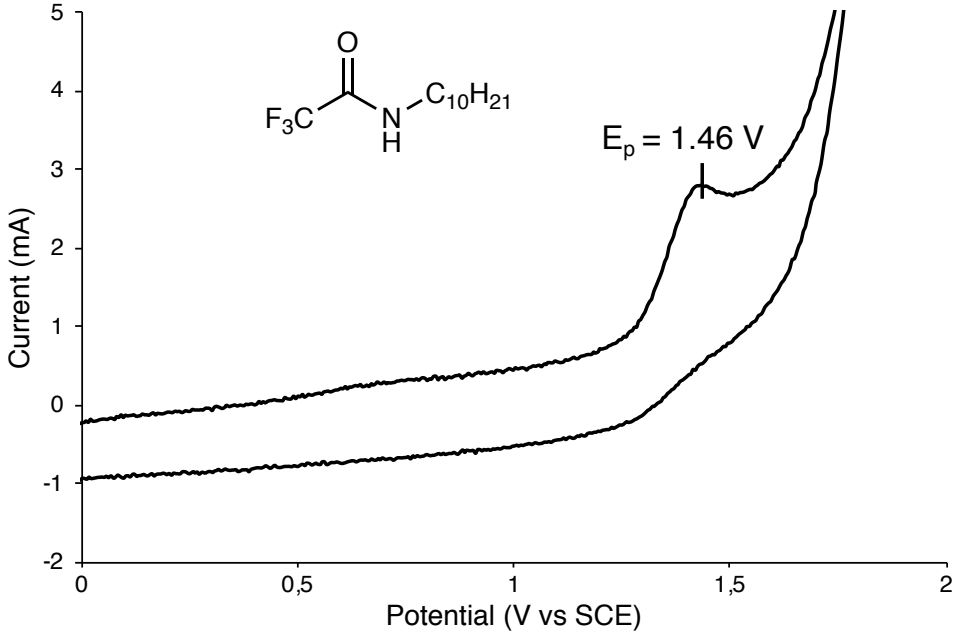


Figure S9. Cyclic voltammogram of N-decyl-2,2,2-trifluoroacetamide. Voltammograms were taken using a glassy carbon working electrode in a 0.1 M [$^{n}Bu_4N$][PF_6] supporting electrolyte THF solution with a 50 mV/s scan rate and 0.01 M of sample referenced to Fc (+380 vs SCE, external). Scans were started at the open-circuit potential and scanned in the cathod direction first; the second cycle is shown here. E_p values for N-decyl-2,2,2-trifluoroacetamide are 1.46 V.

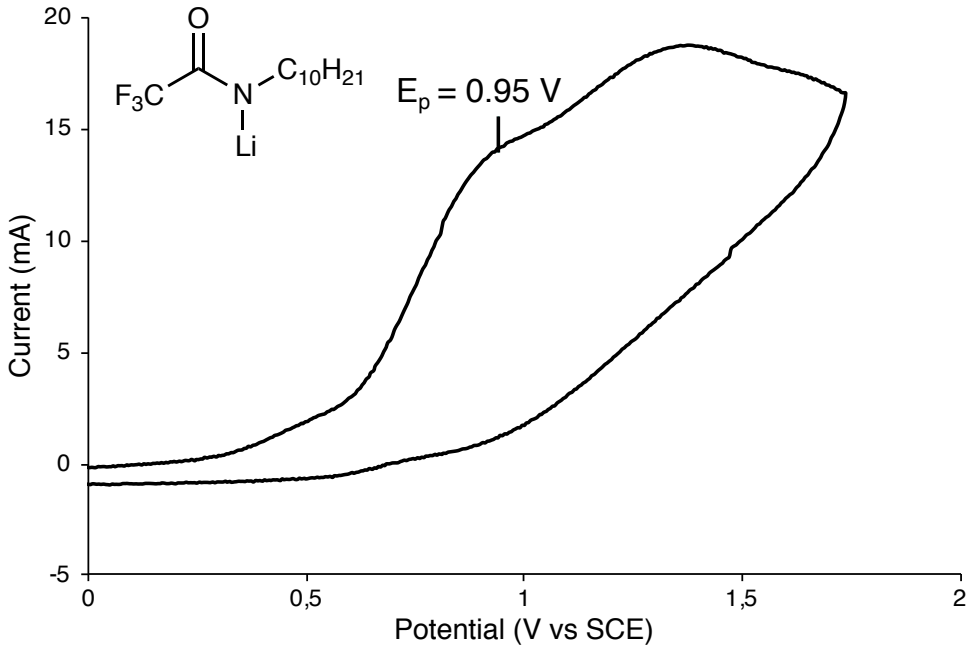
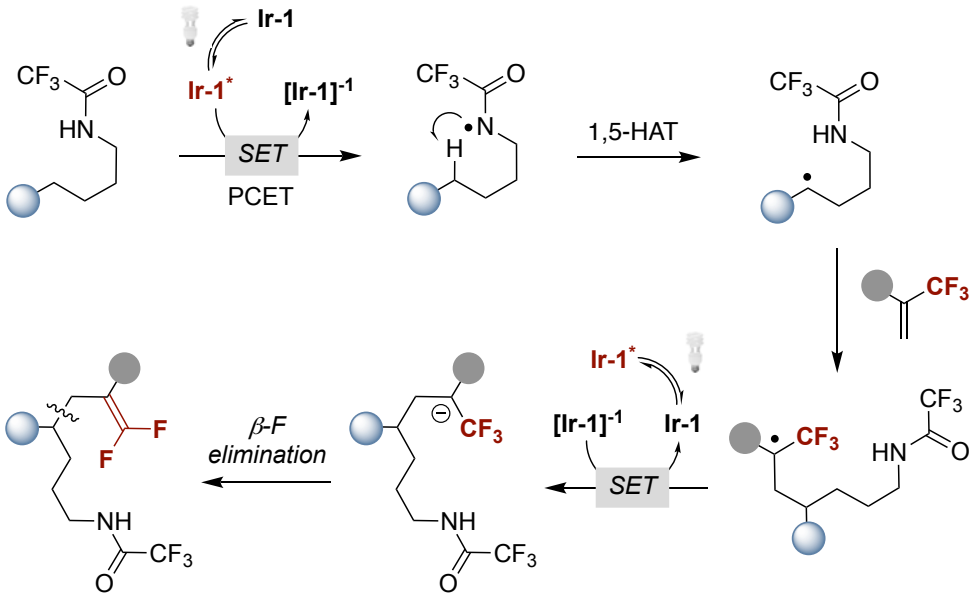


Figure S10. Cyclic voltammogram of deprotonated N-decyl-2,2,2-trifluoroacetamide. Voltammograms were taken using a glassy carbon working electrode in a 0.1 M [^{n}Bu$_4$N][PF$_6$] supporting electrolyte THF solution with a 100 mV/s scan rate and 0.01 M of sample referenced to Fc (+380 vs SCE, external). Scans were started at the open-circuit potential and scanned in the cathod direction first; the second cycle is shown here. E_p values for deprotonated N-decyl-2,2,2-trifluoroacetamide are 0.95 V.

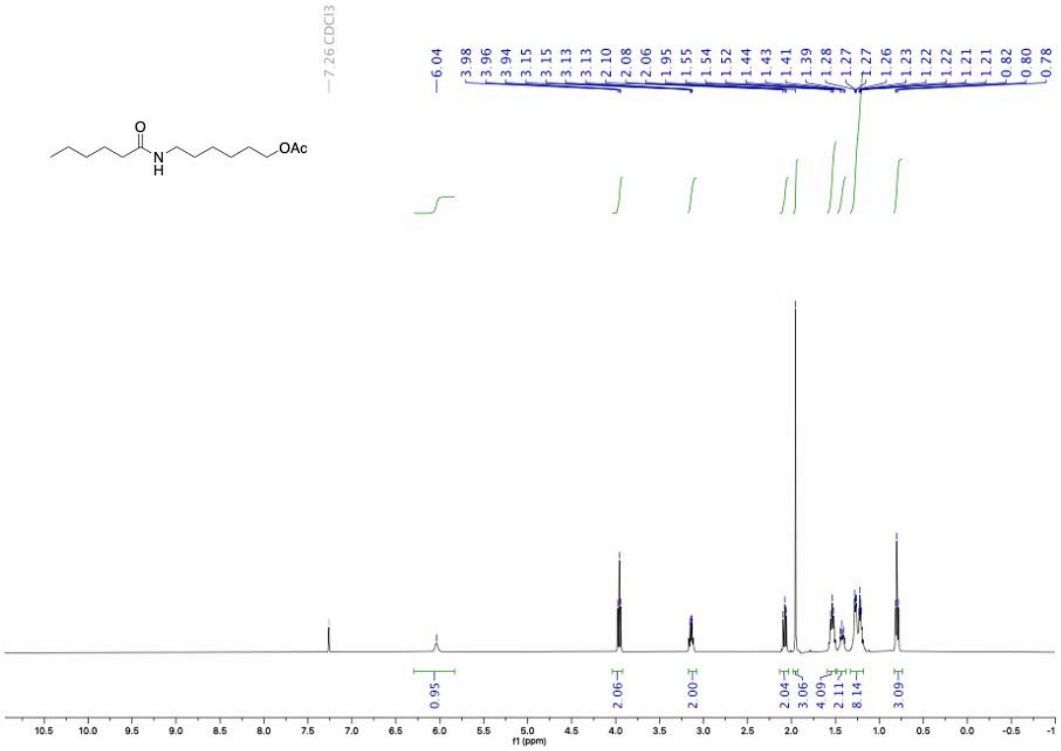
6. Proposed mechanistic rationale for the δ sp^3 C–H defluorinative alkylation



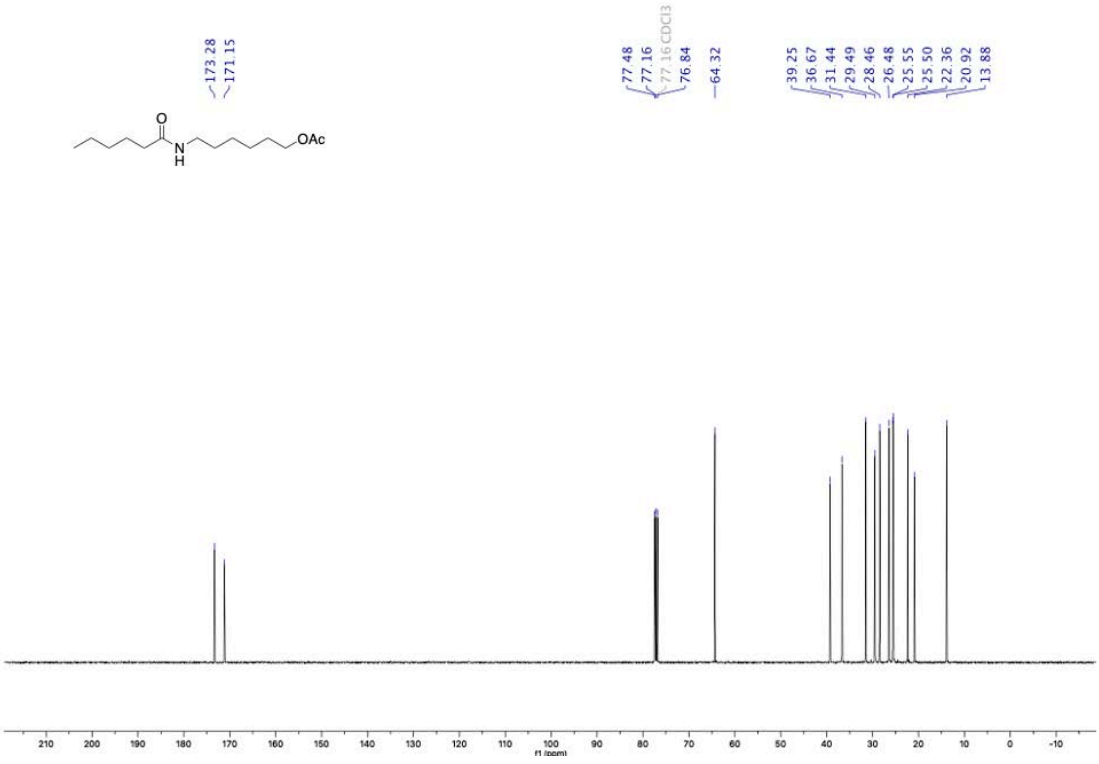
References

1. Choi, G. J.; Zhu, Q.; Miller, D. C.; Gu, C. J.; Knowles, R. R. *Nature* **2016**, *539*, 268.
2. Thullen, S. M.; Treacy, S. M.; Rovis, T. *J. Am. Chem. Soc.* **2019**, *141*, 14062.
3. Ichitsuka, T.; Fujita, T.; Ichikawa, J. *ACS Catal*. **2015,** *5*, 5947.
4. This complex was prepared according to M. Mohadjer Beromi, G. W. Brudvig, N. Hazari, H. M. C. Lant, B. Q. Mercado, *Angew. Chem. Int. Ed.* **2019**, *58*, 6094.

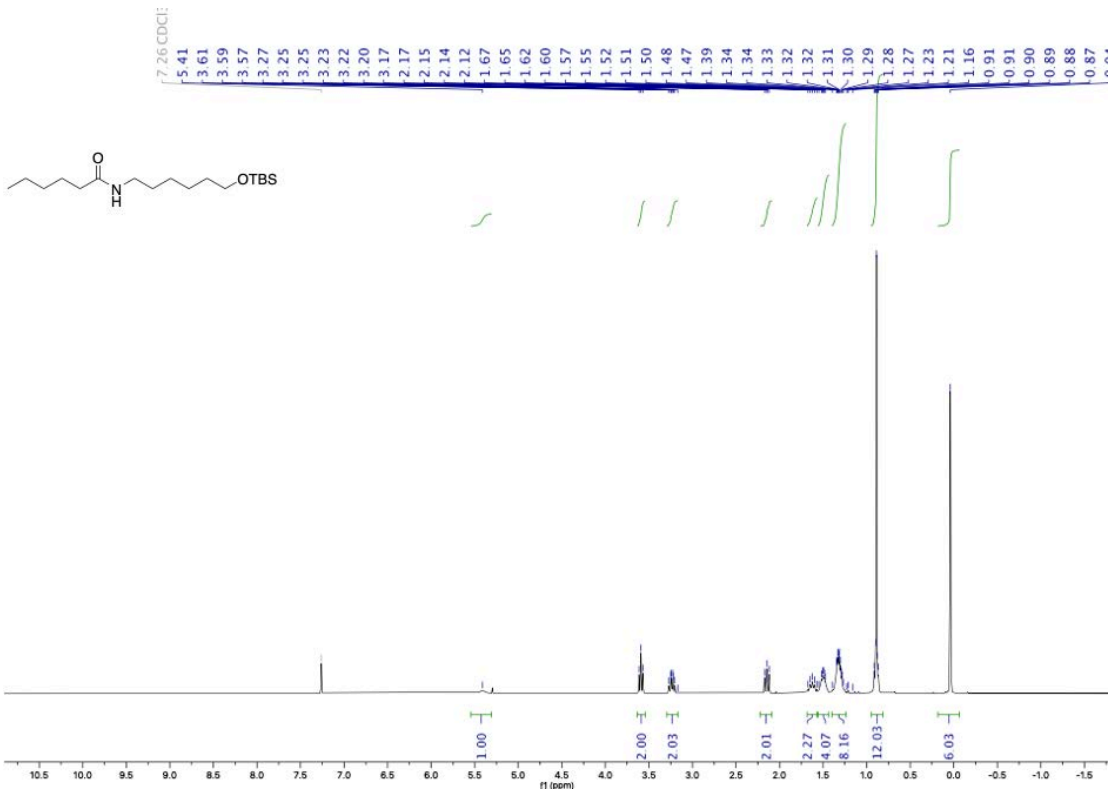
^{1}H NMR, ^{19}F NMR & ^{13}C NMR spectra



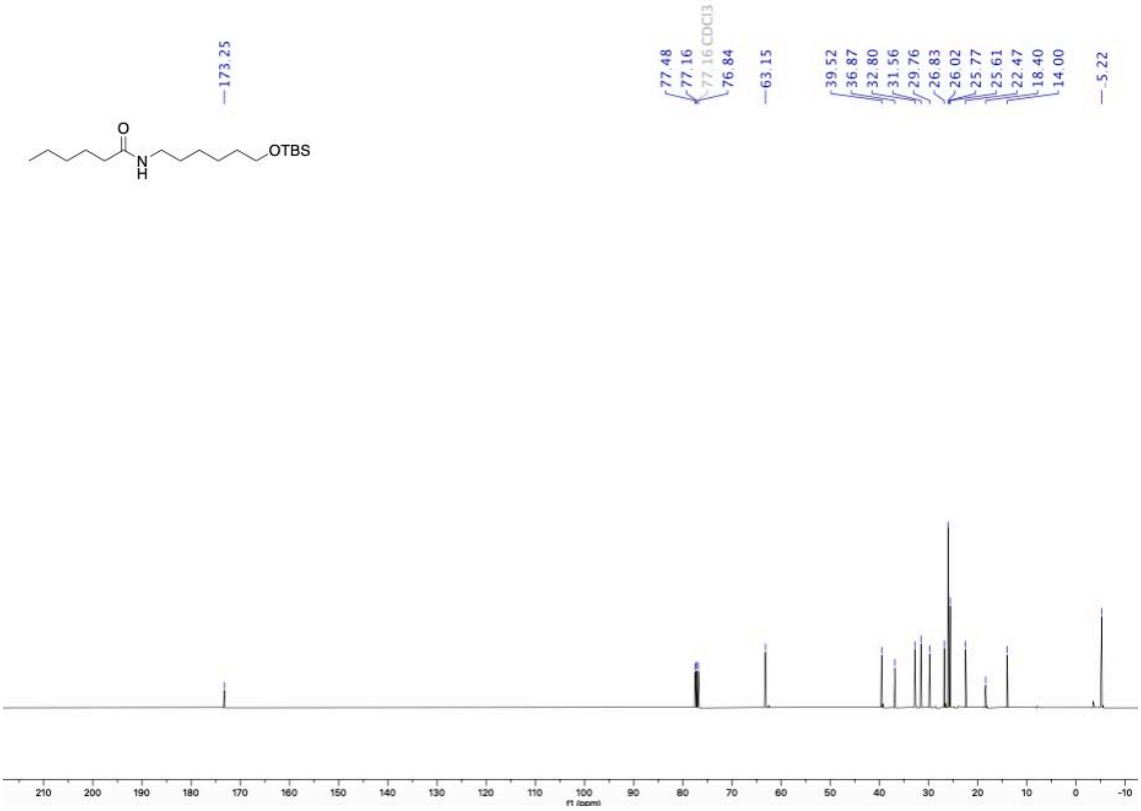
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1r**



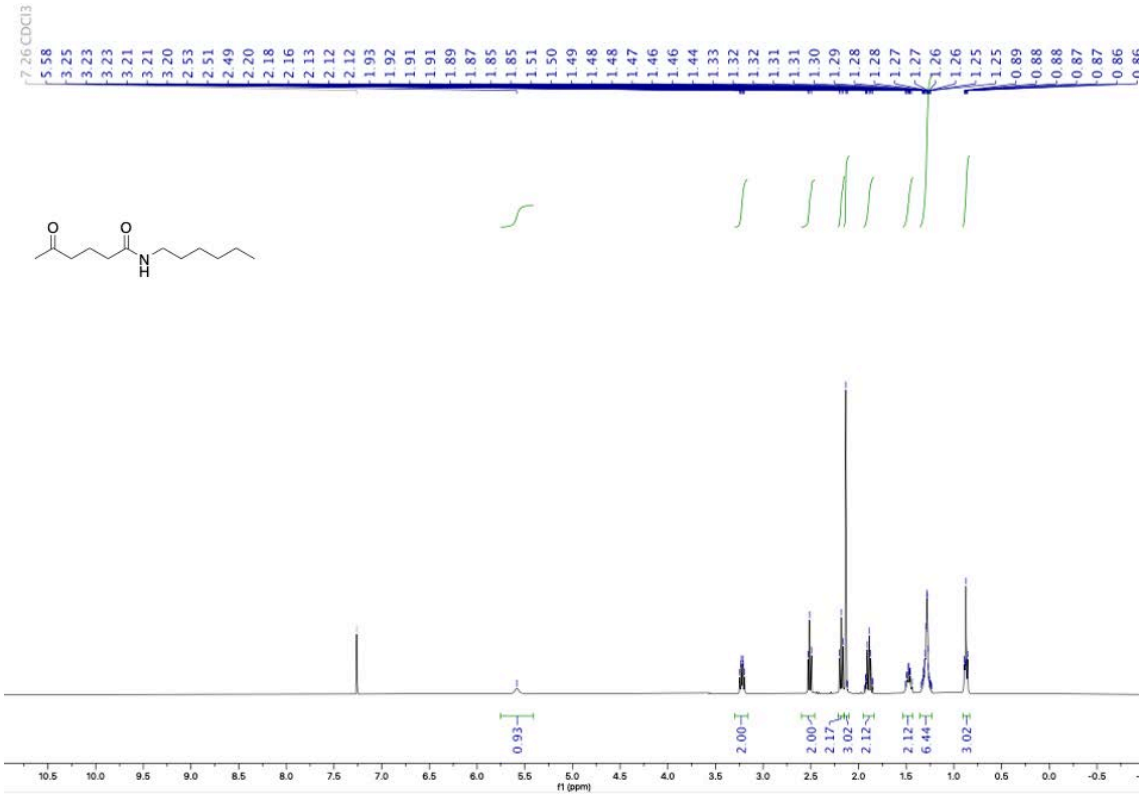
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1r**



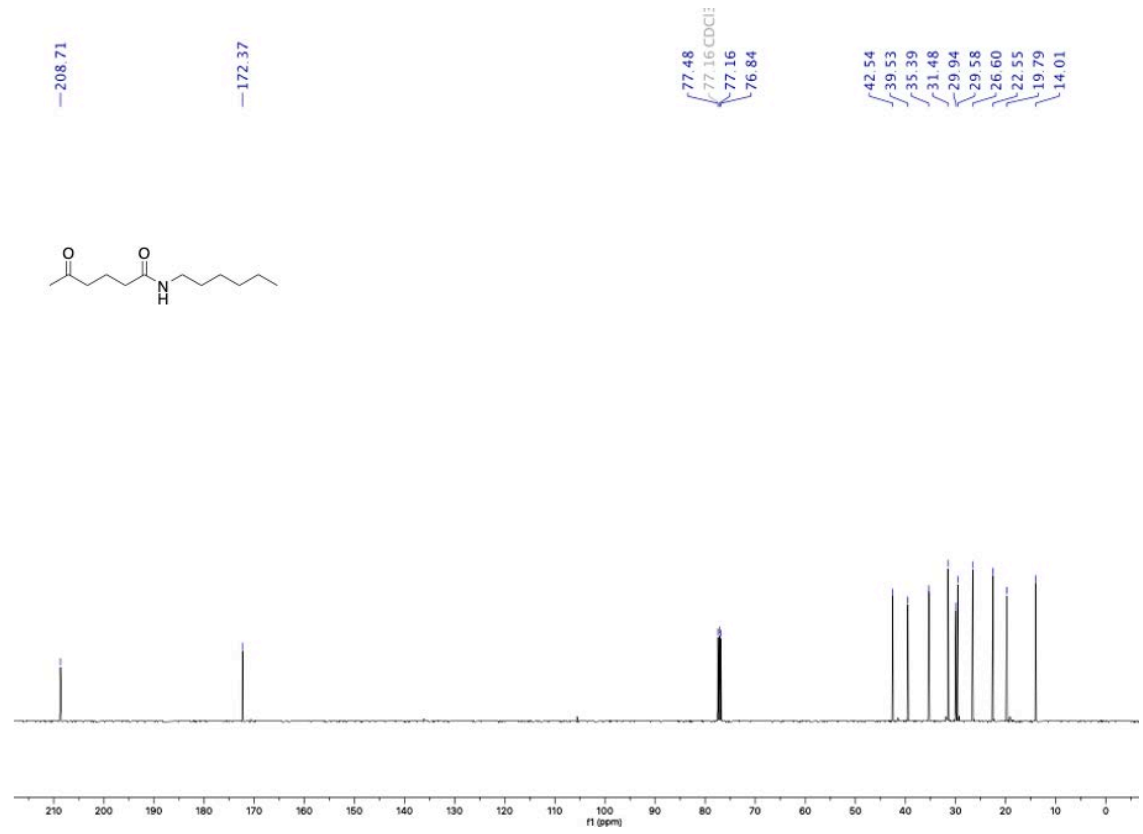
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1s**



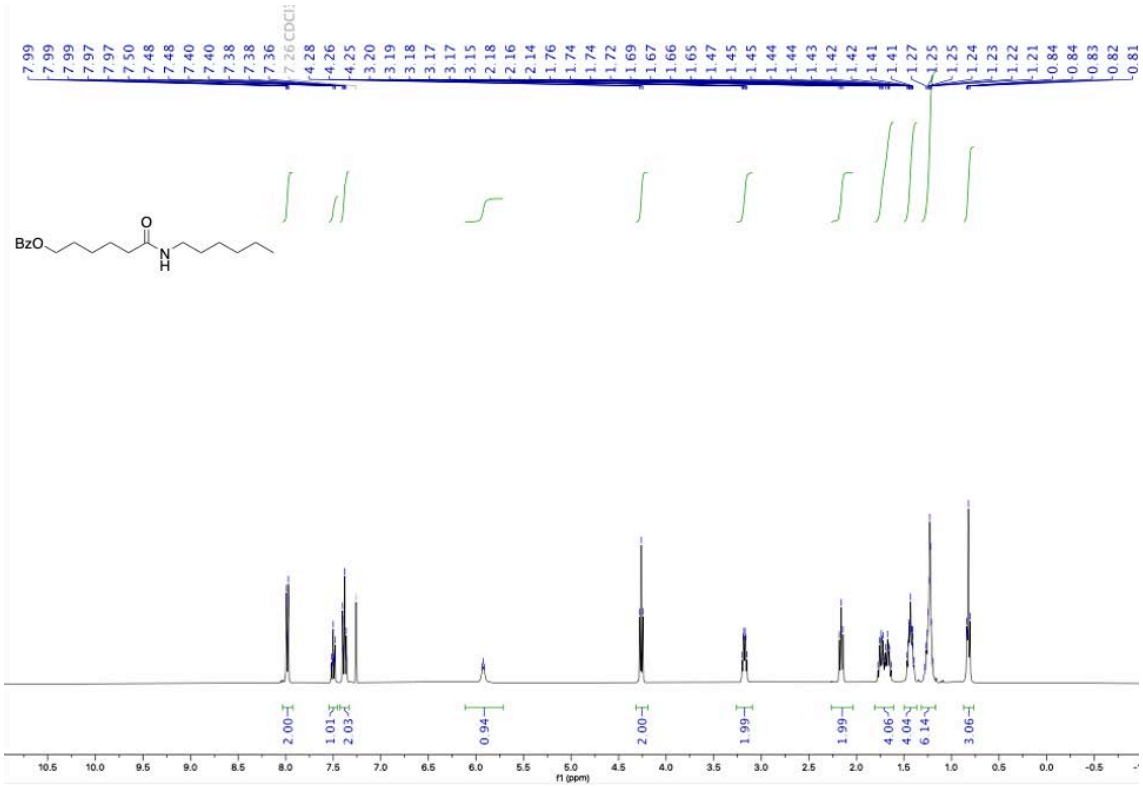
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1s**



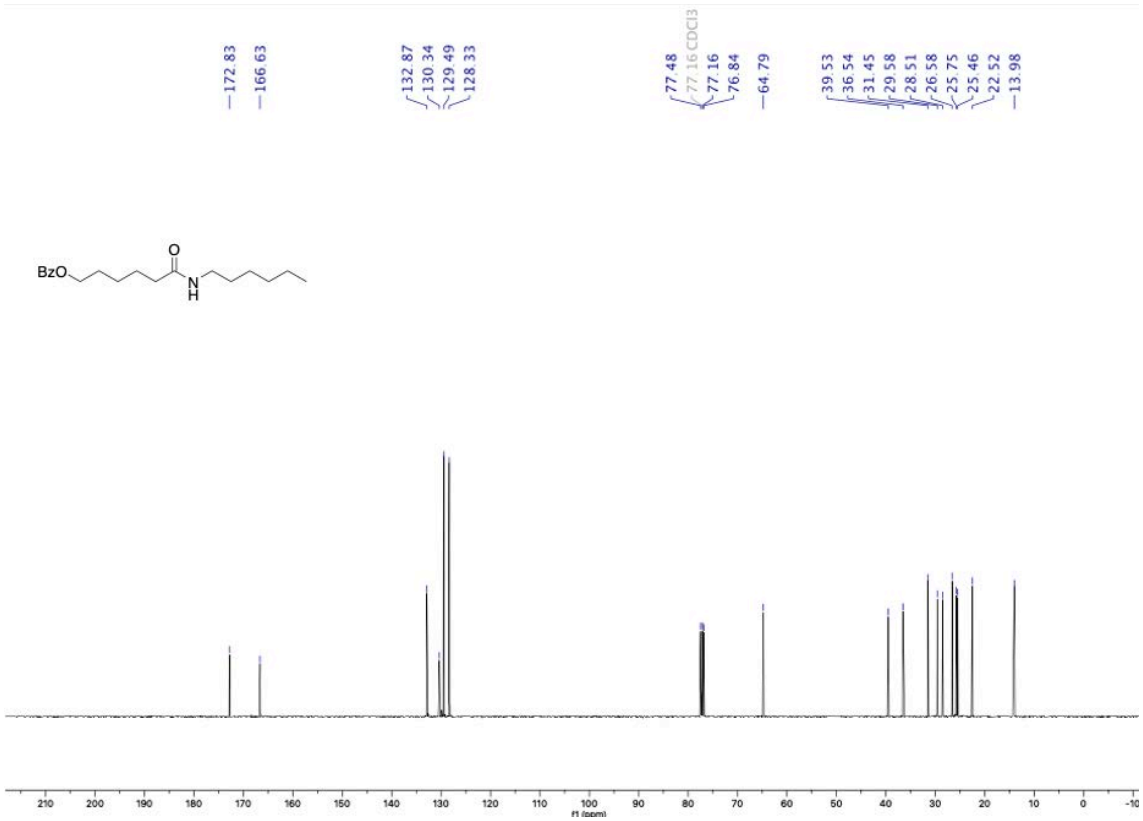
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1z**



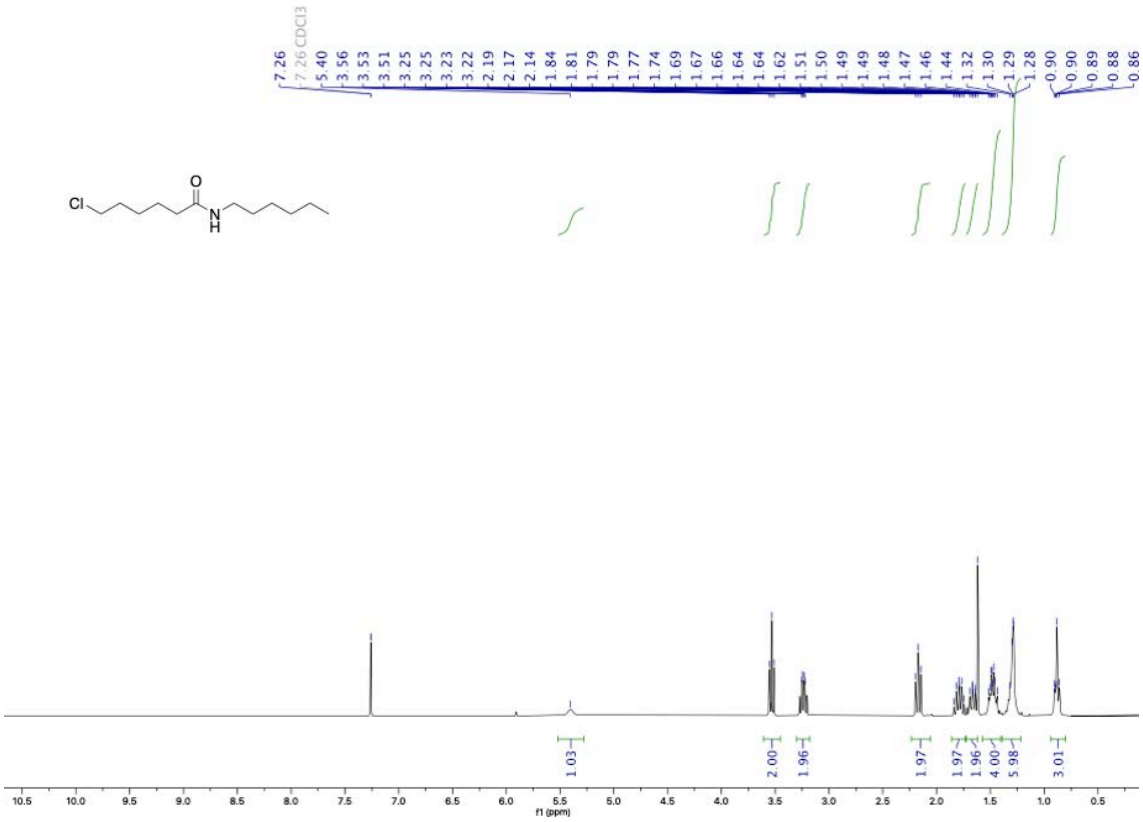
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1z**



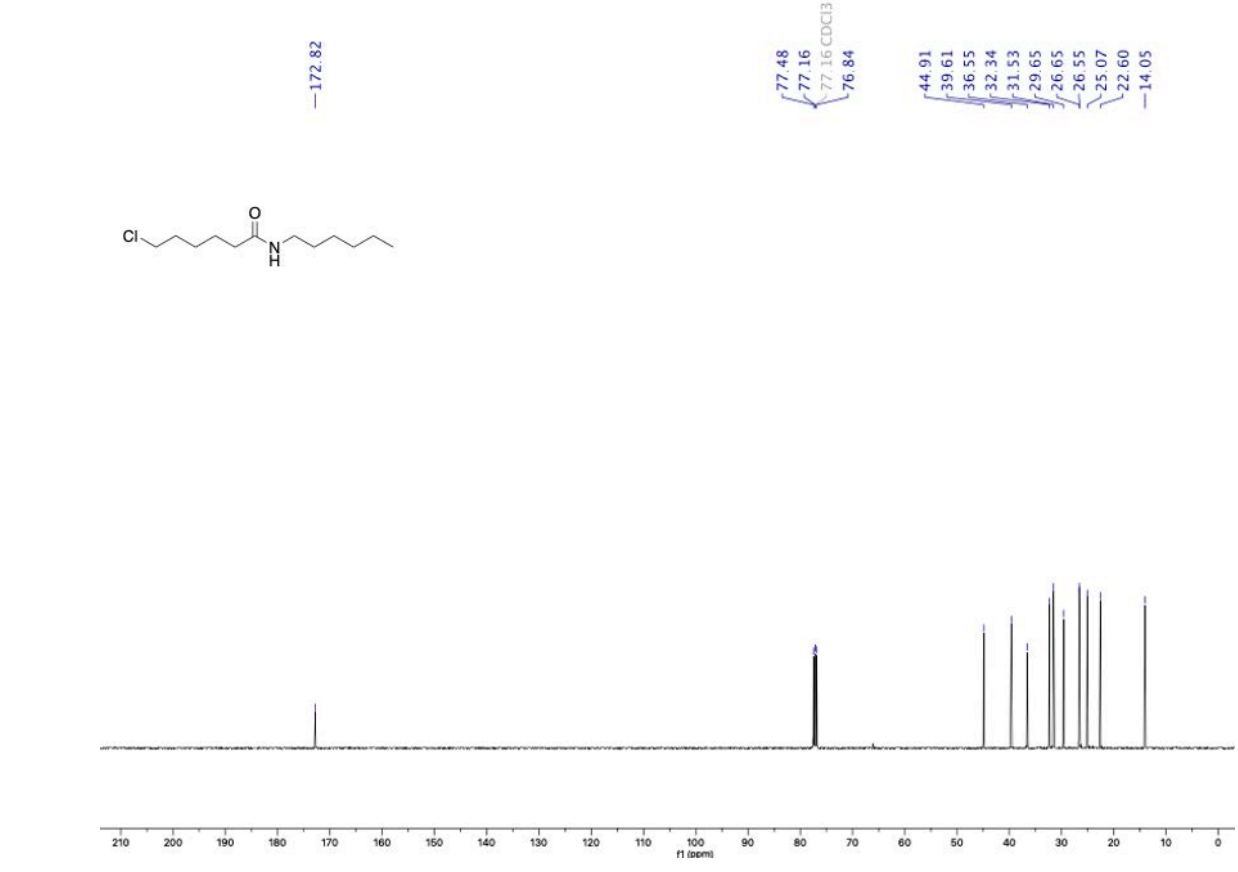
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1v**



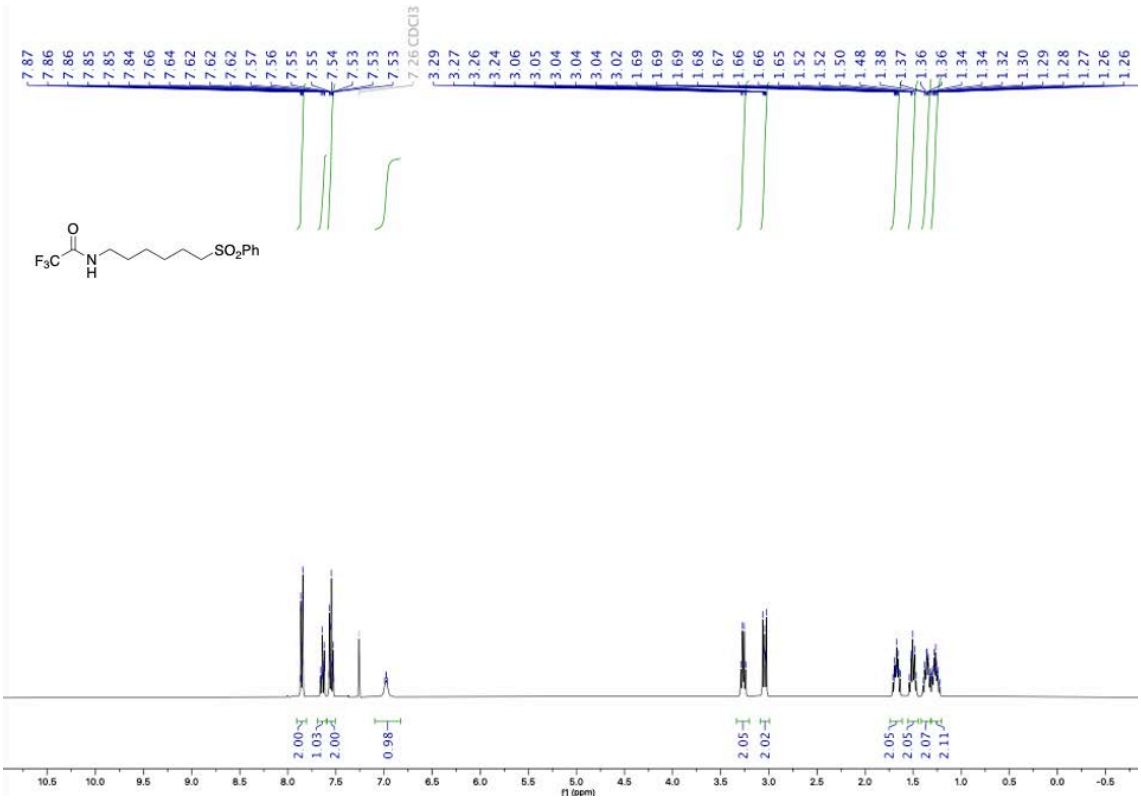
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1v**



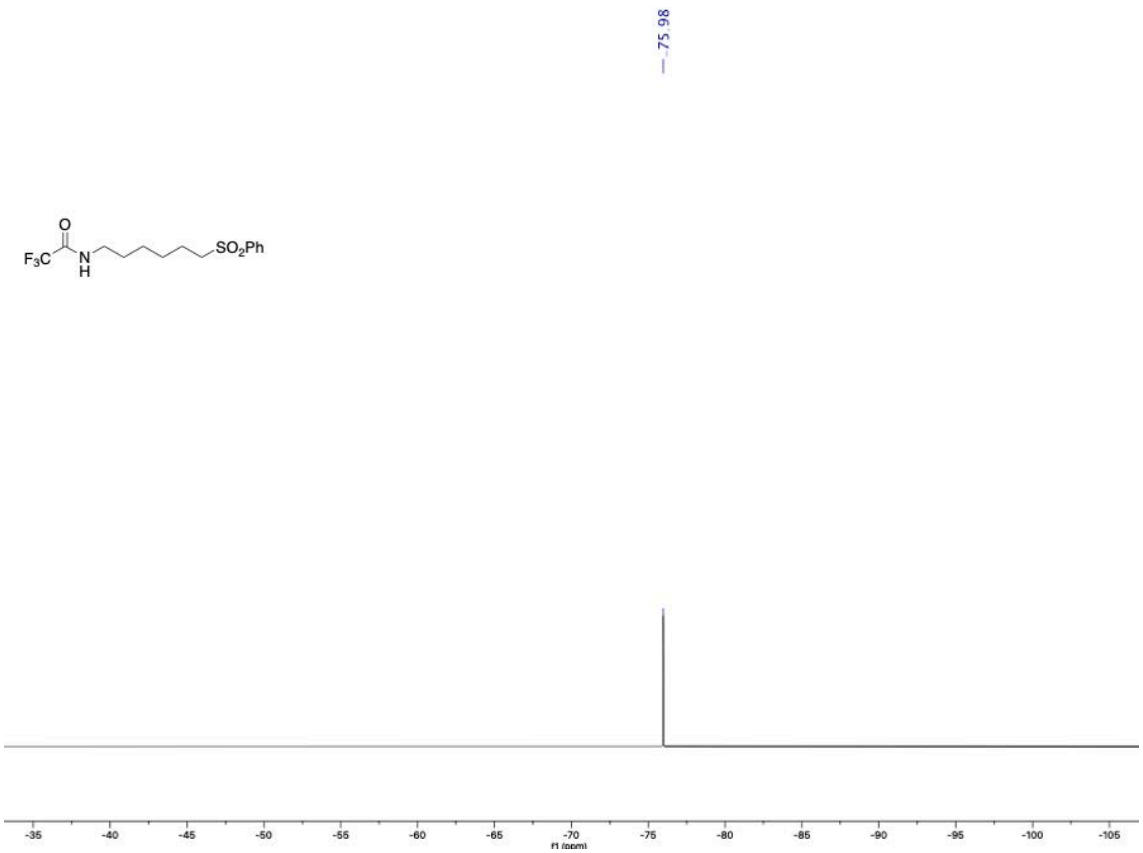
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1w**



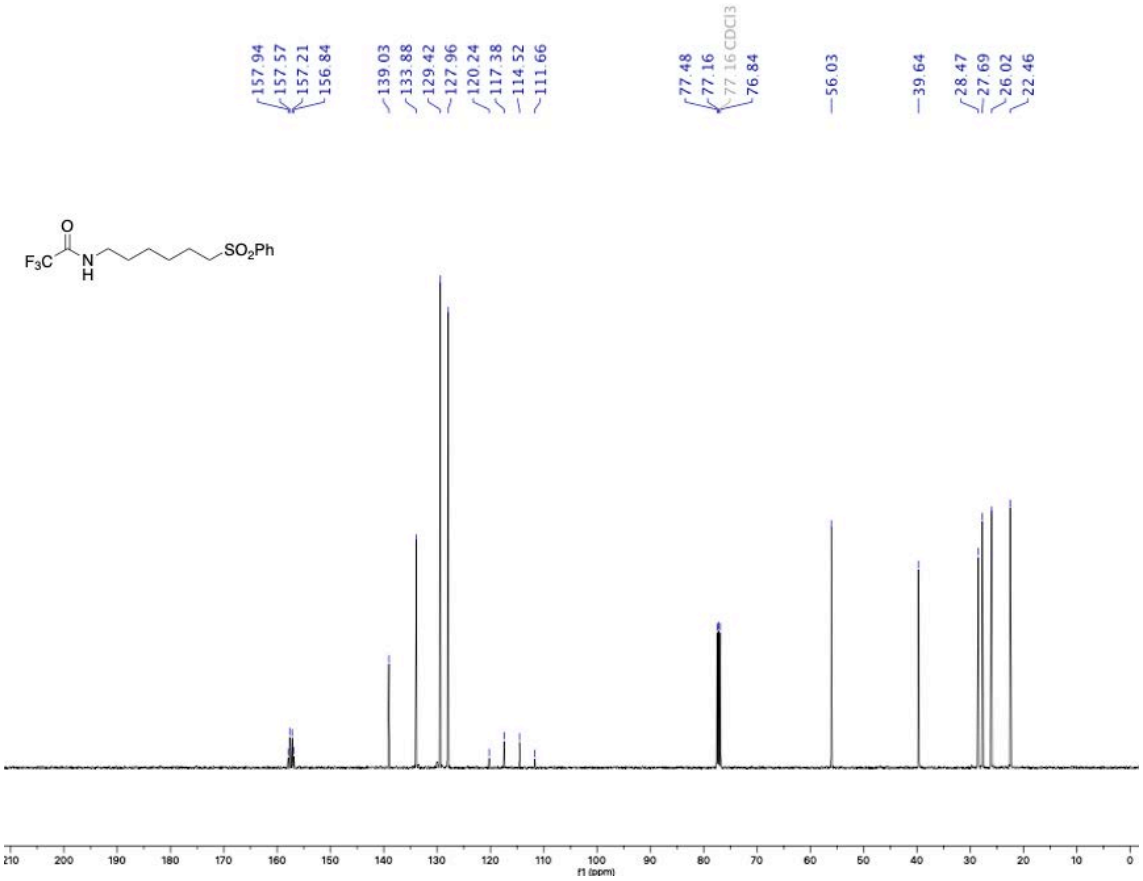
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1w**



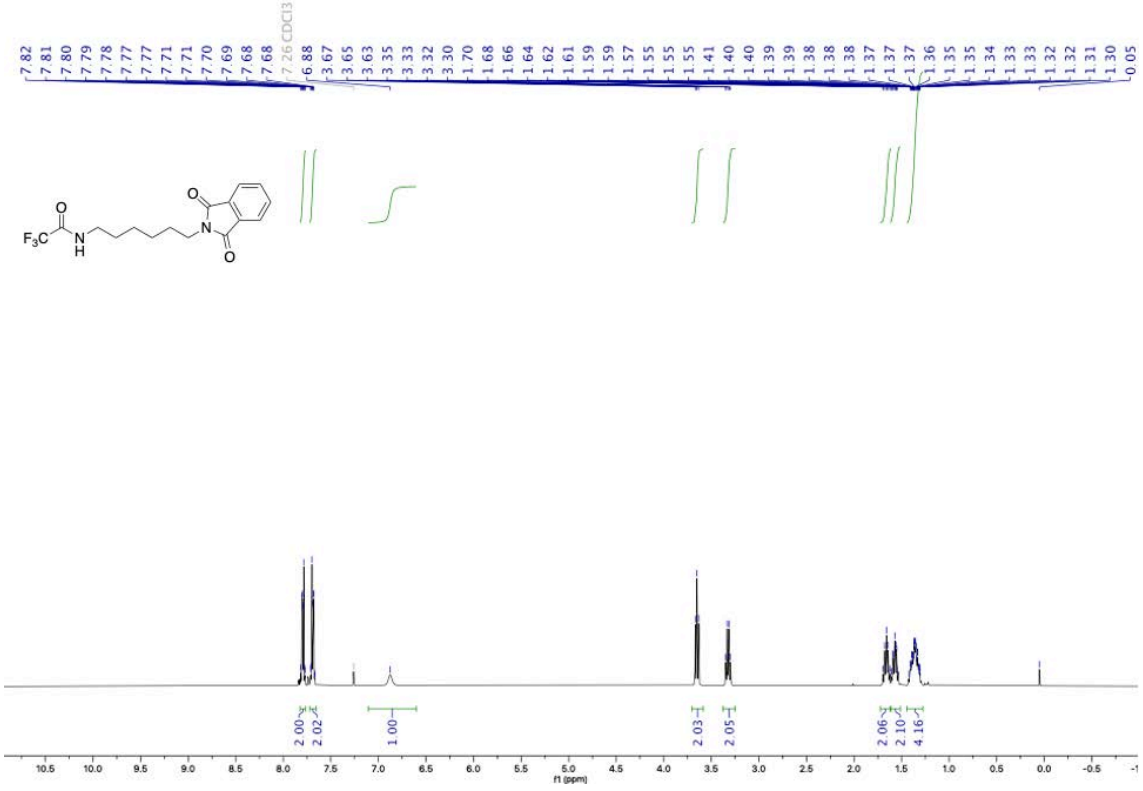
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5d**



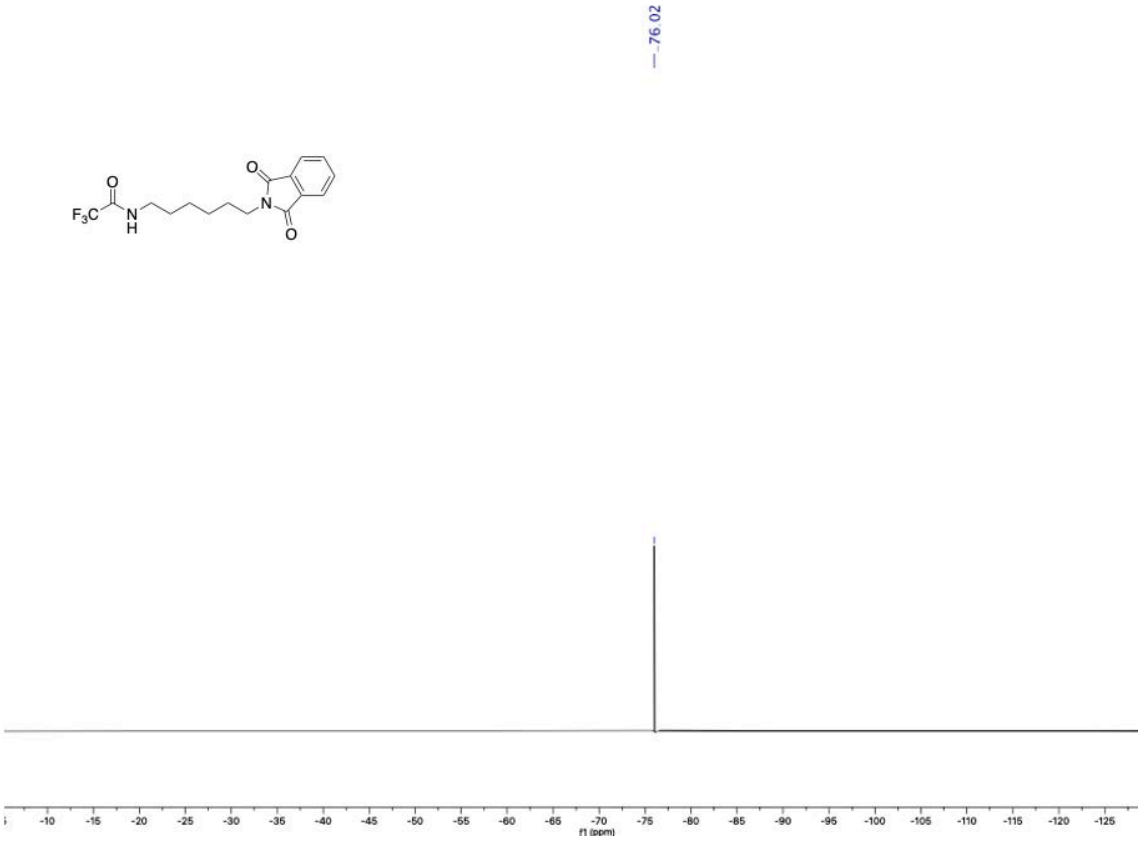
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **5d**



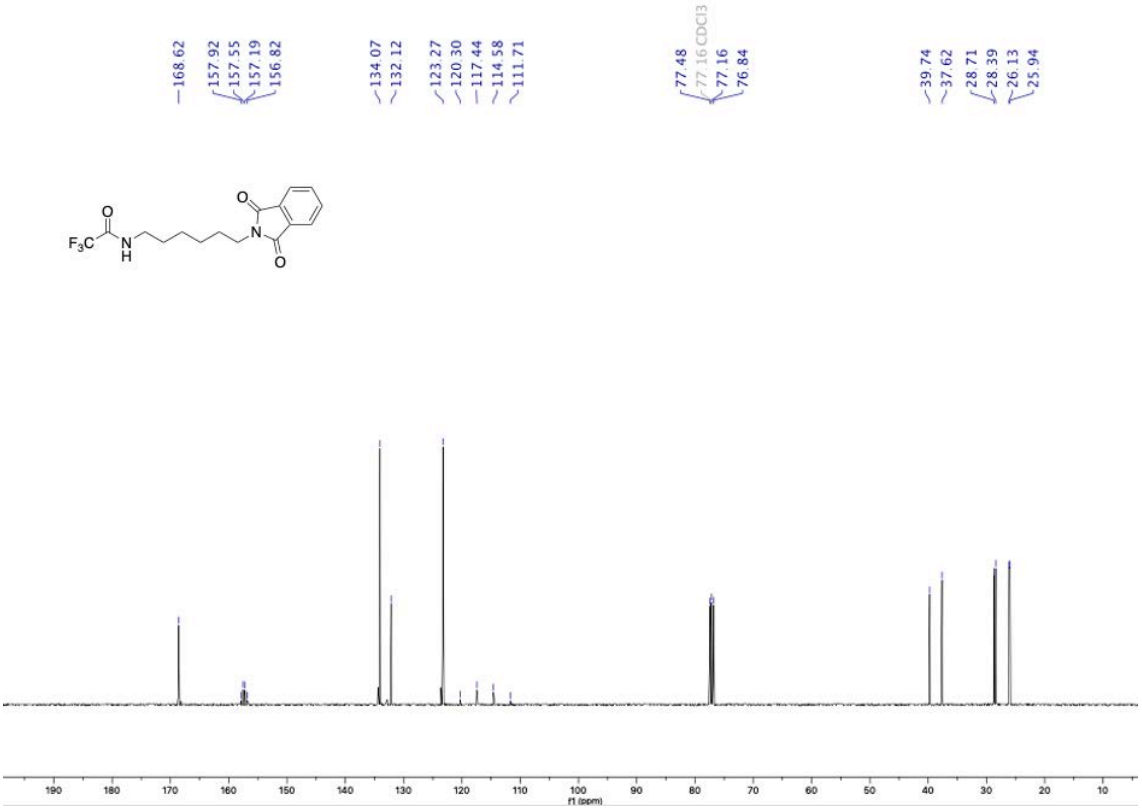
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5d**



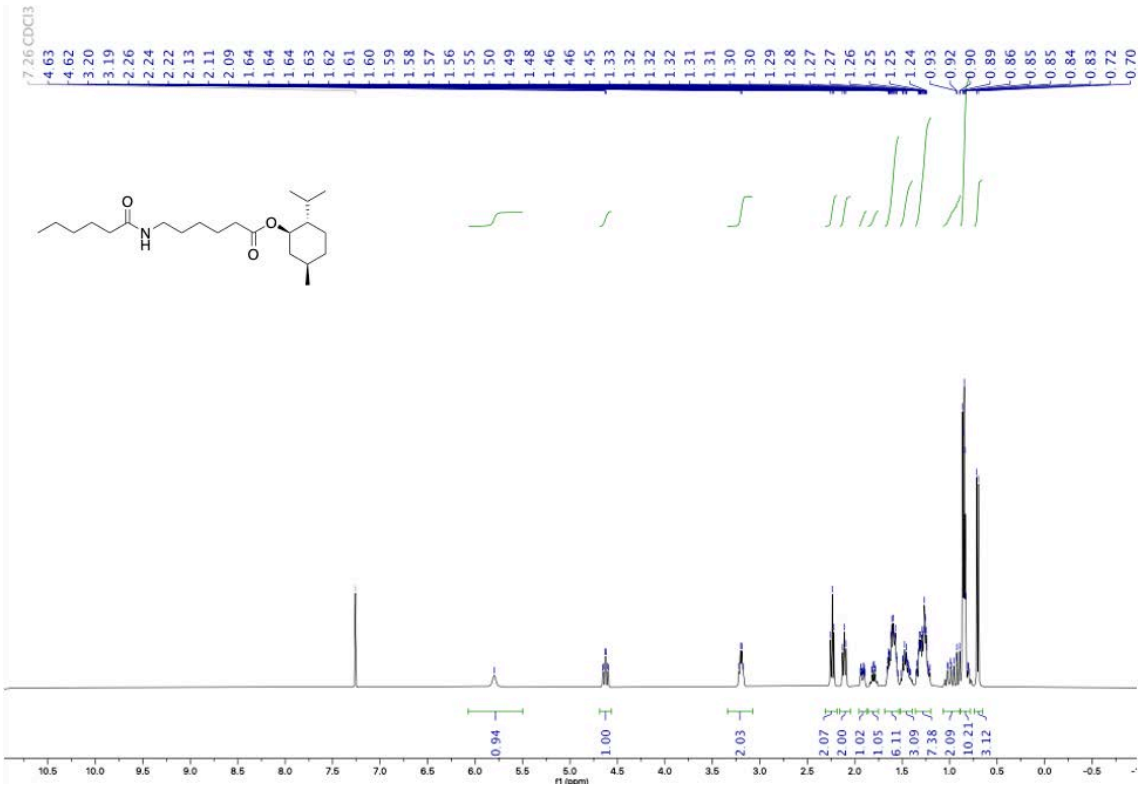
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5e**



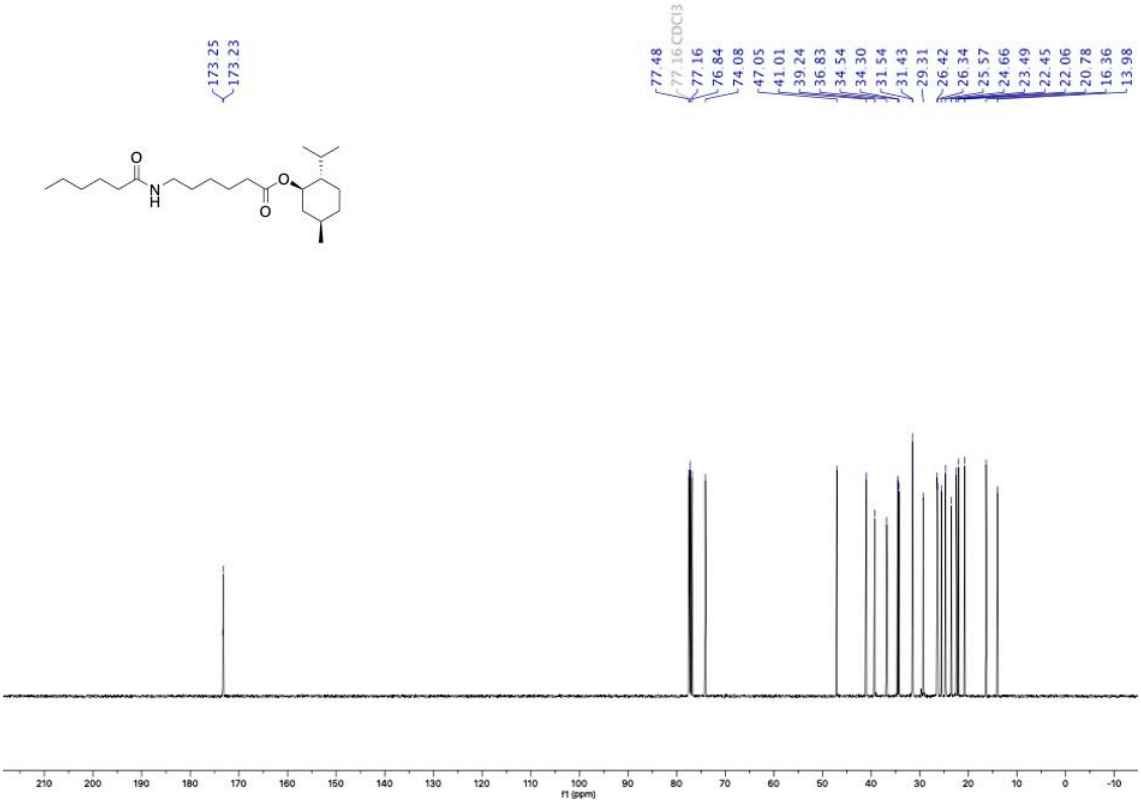
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **5e**



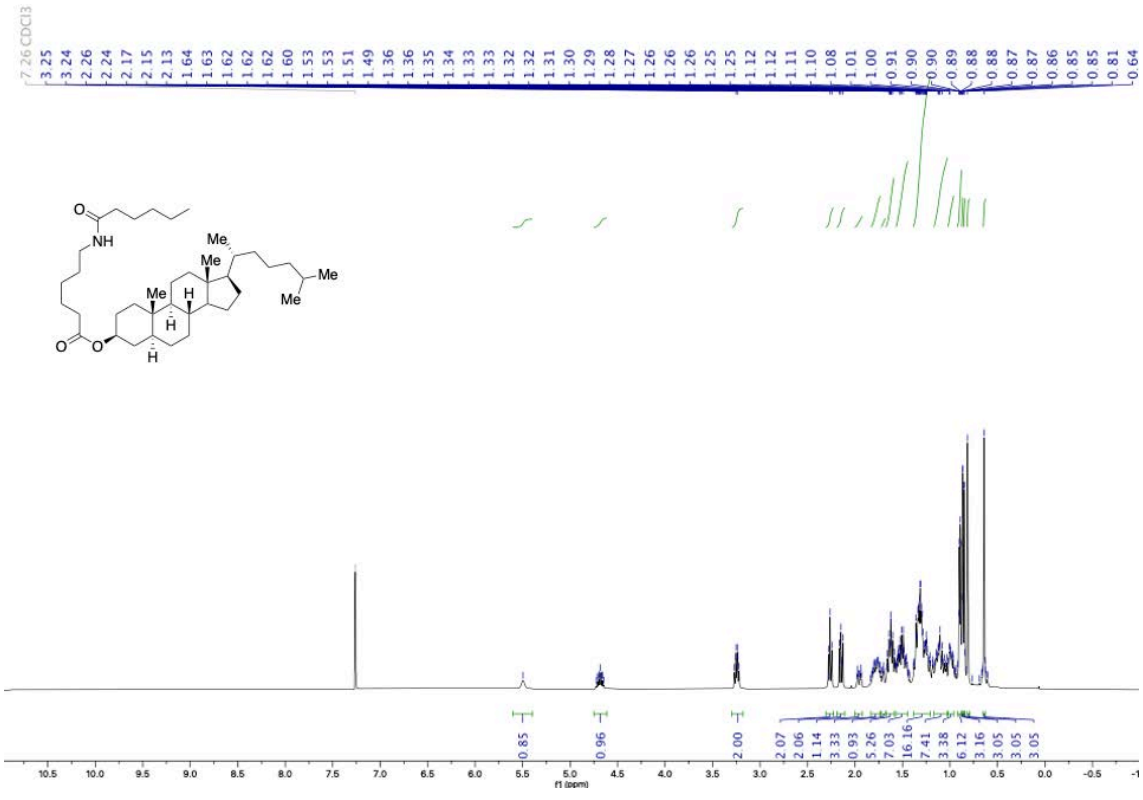
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5e**



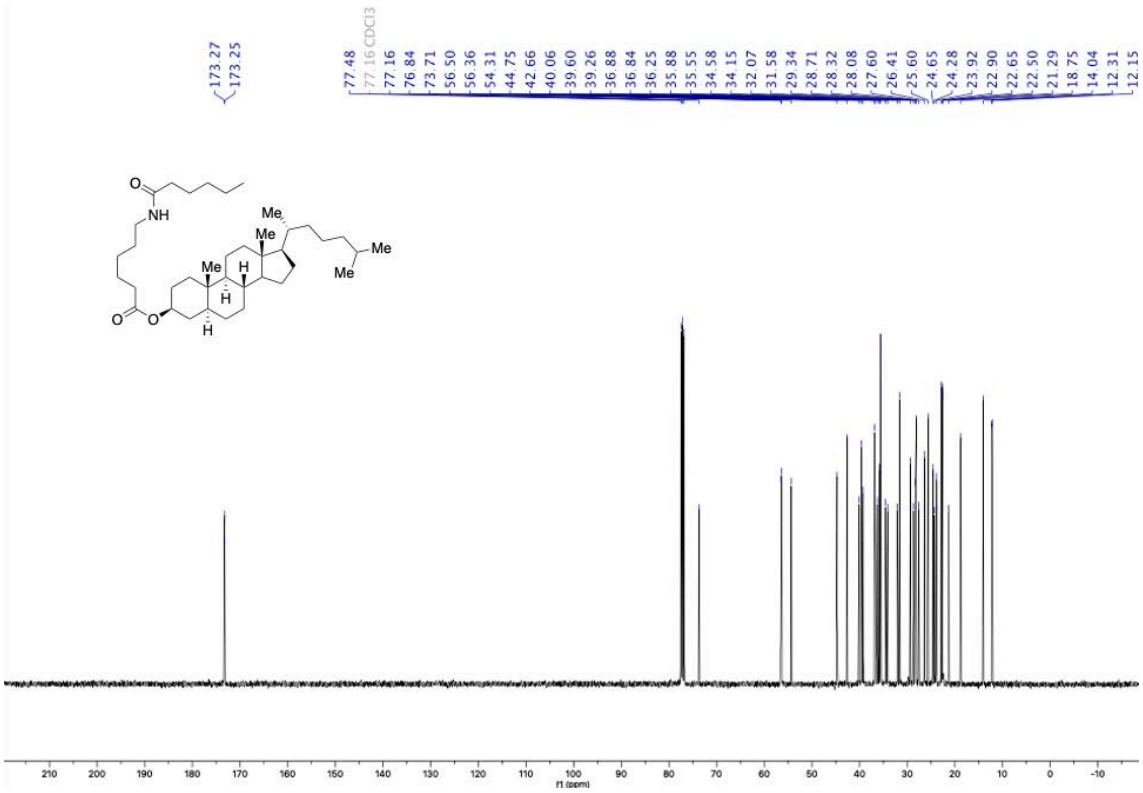
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1ac**



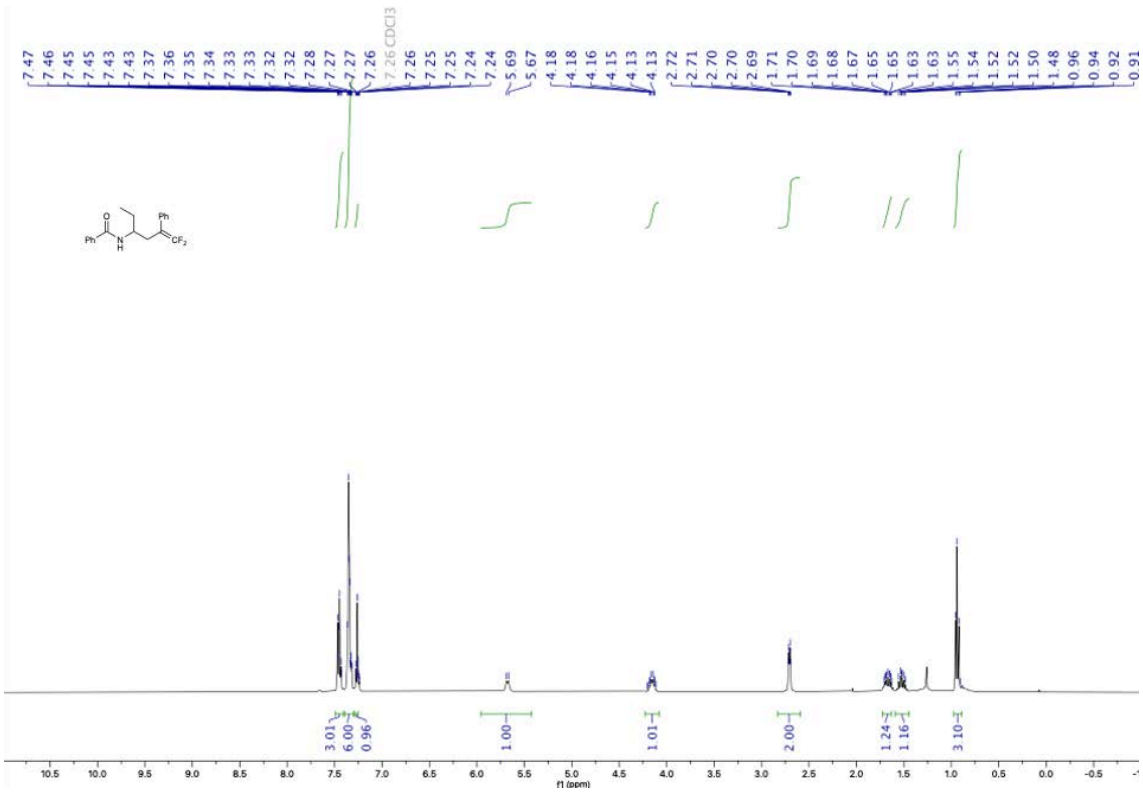
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1ac**



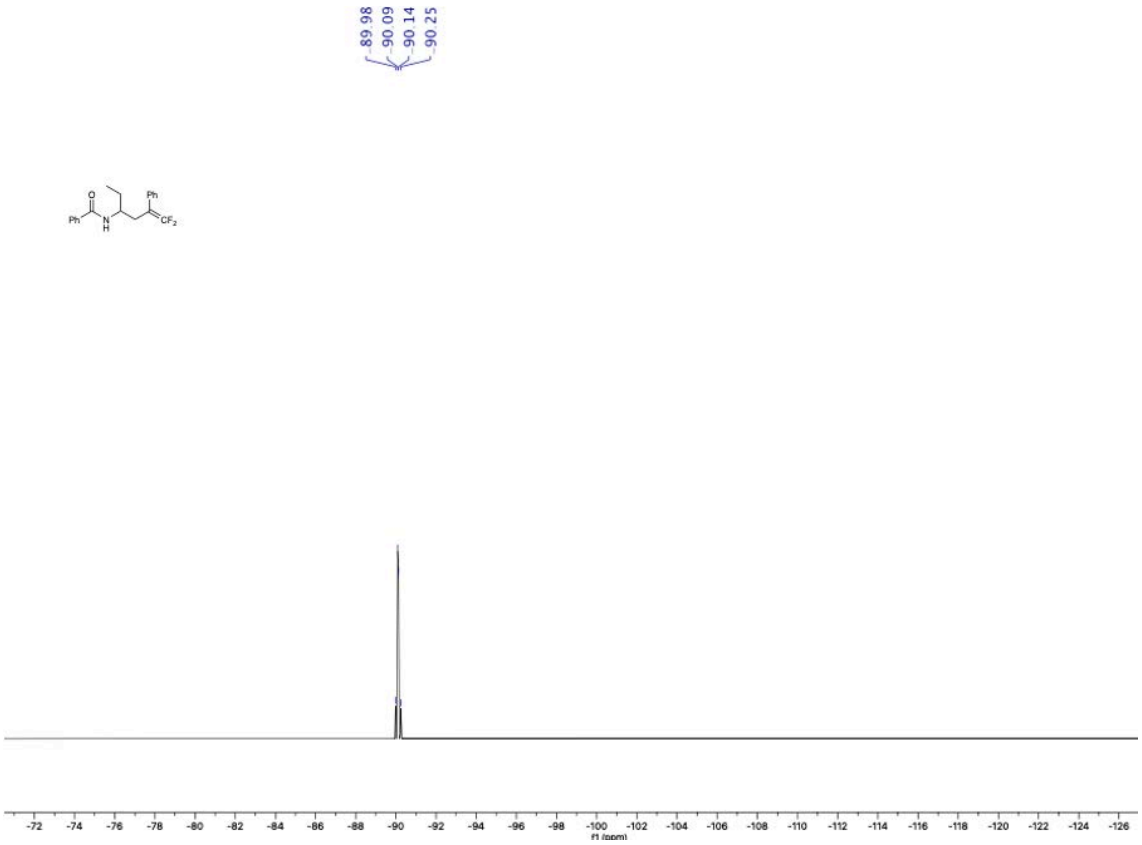
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1ad**



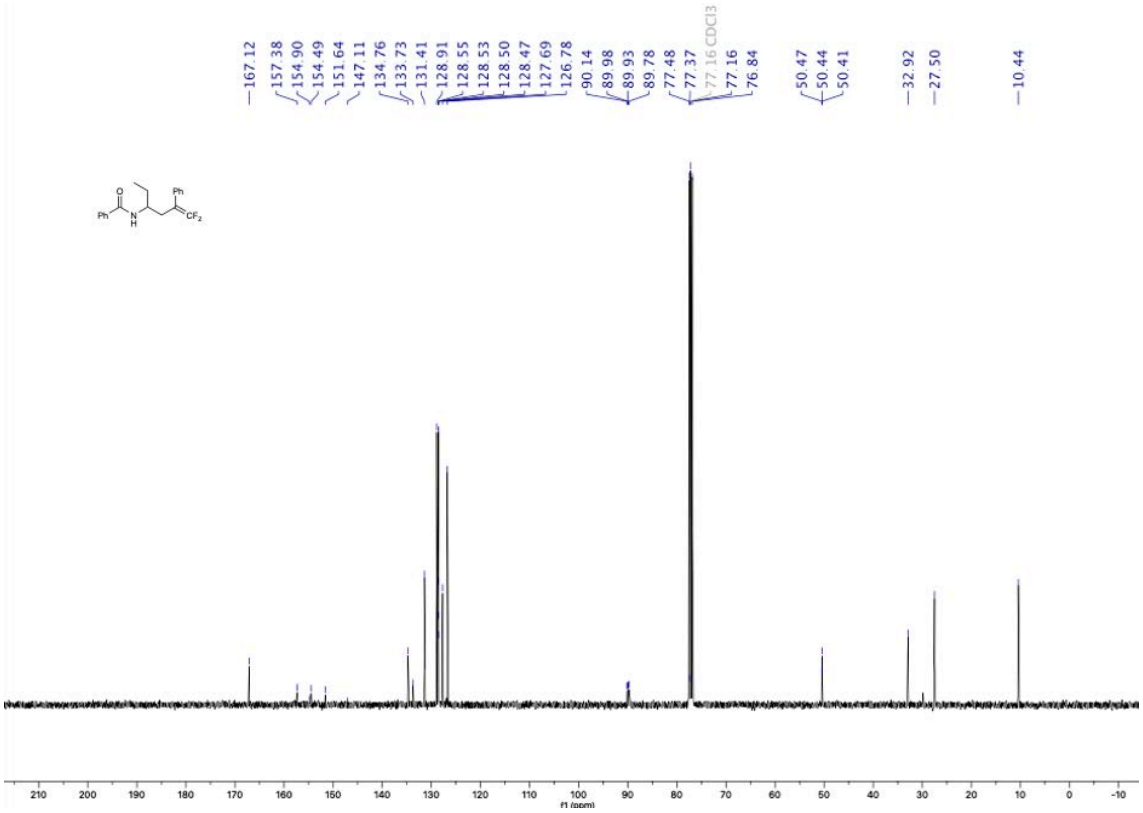
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1ad**



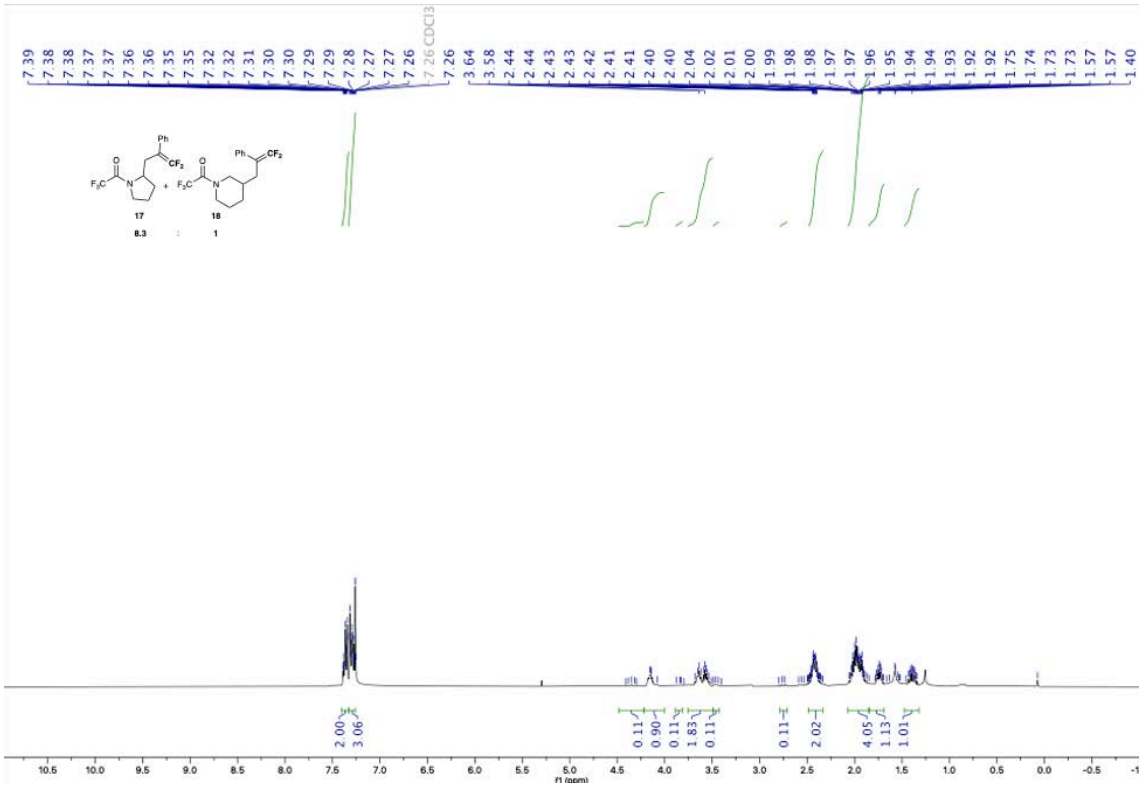
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8a**



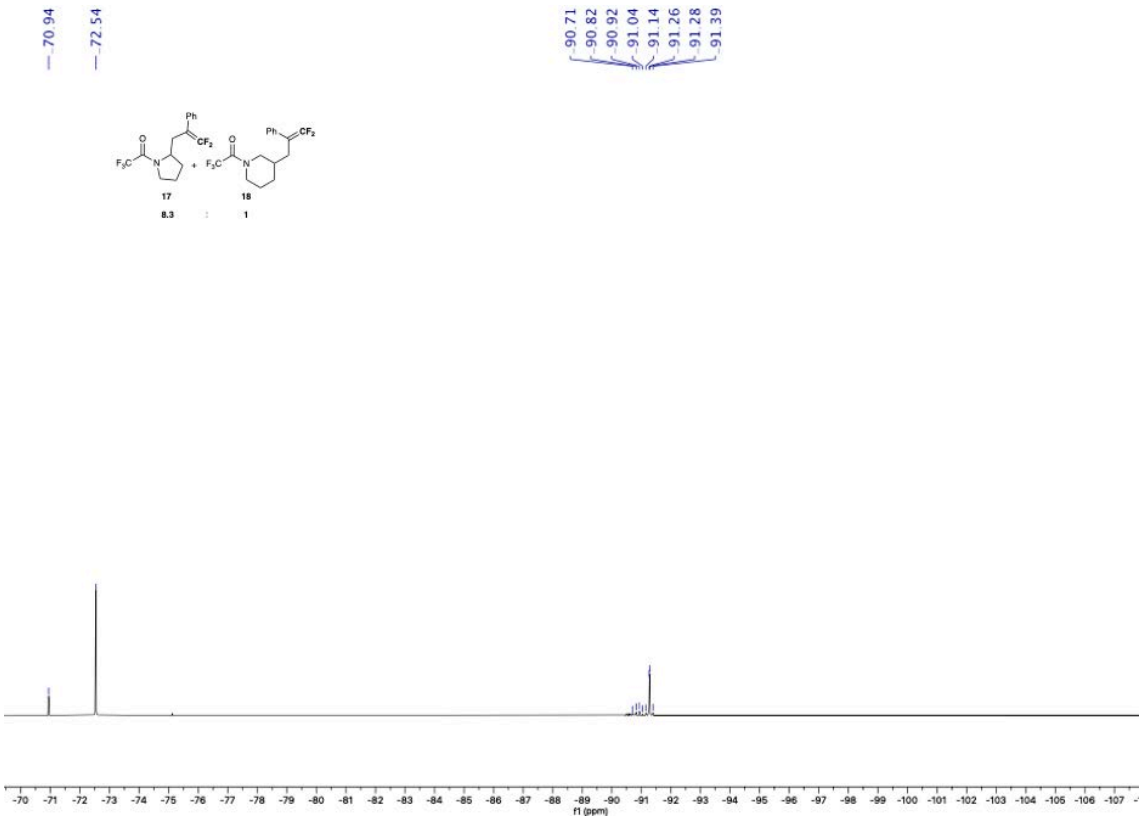
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **8a**



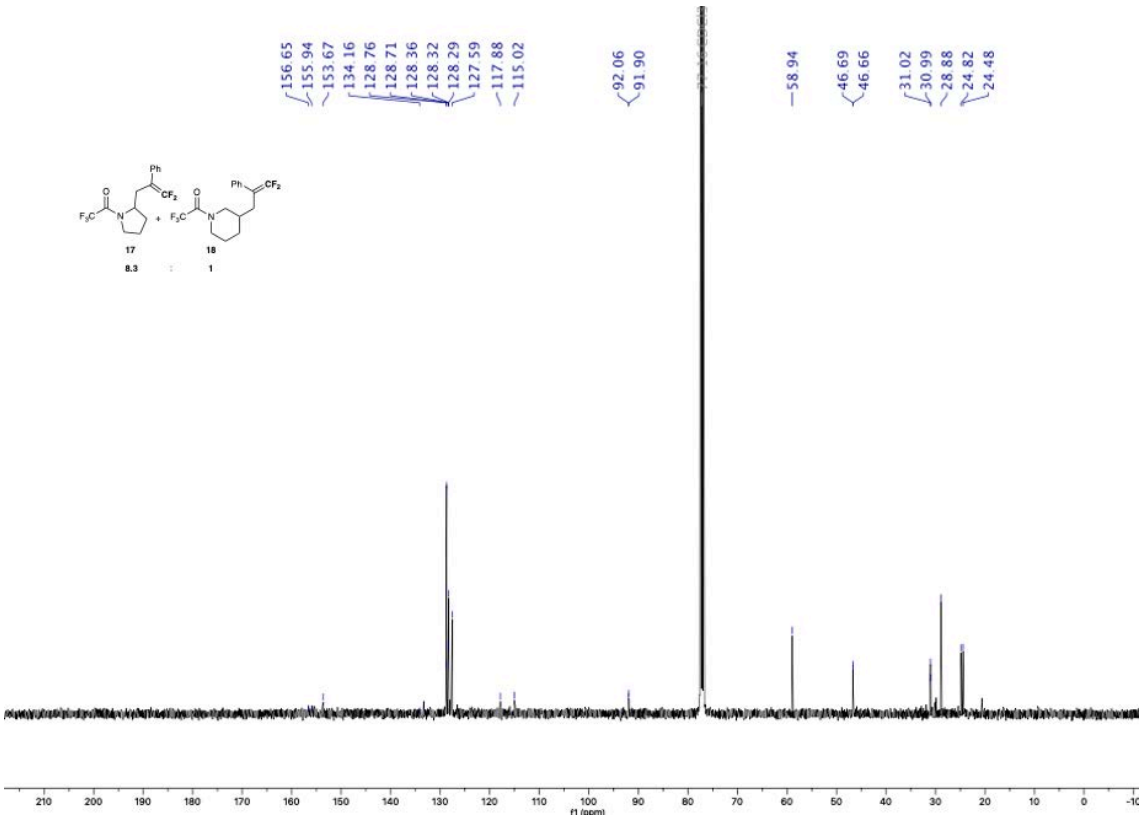
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **8a**



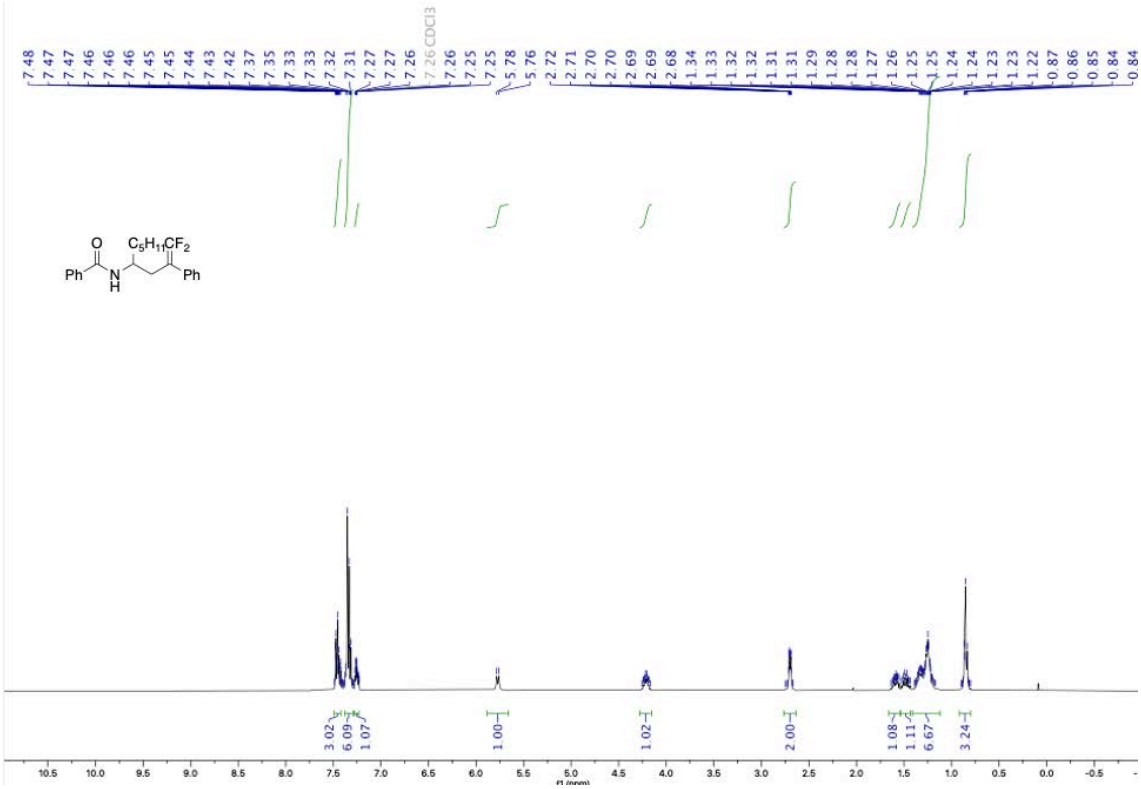
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11a** and **11b**



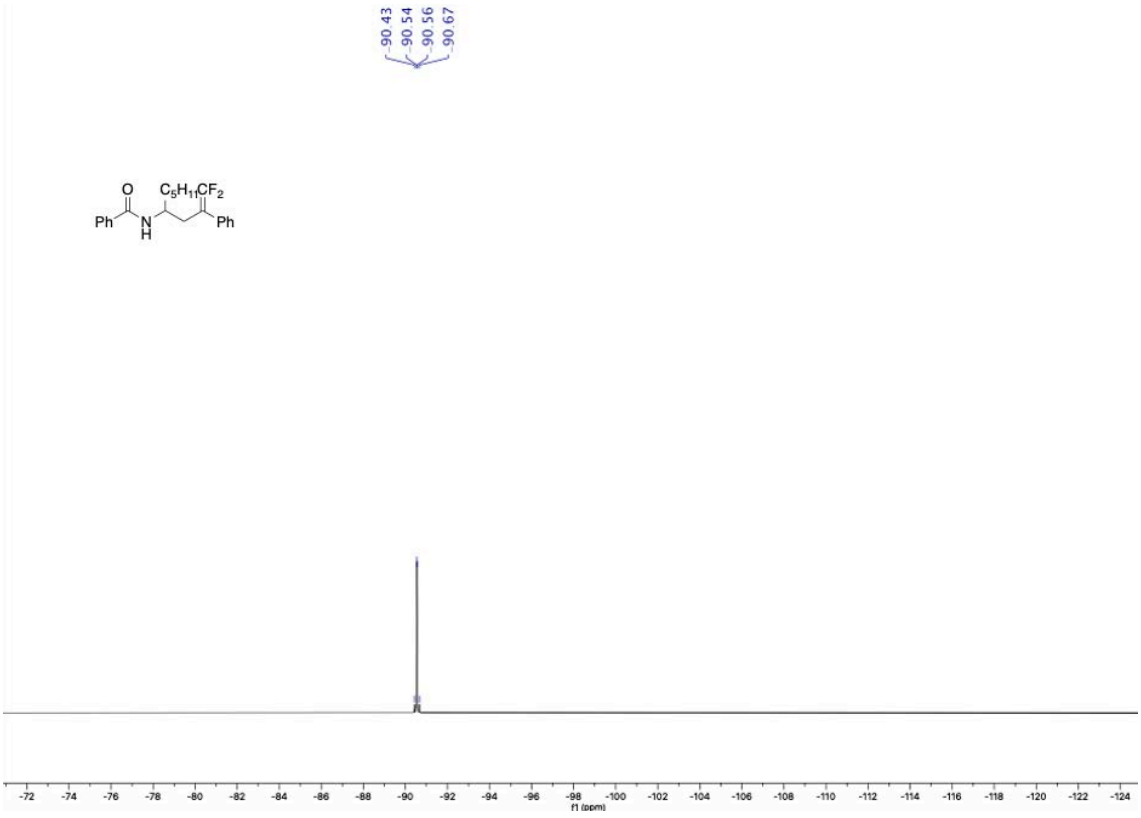
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **11a** and **11b**



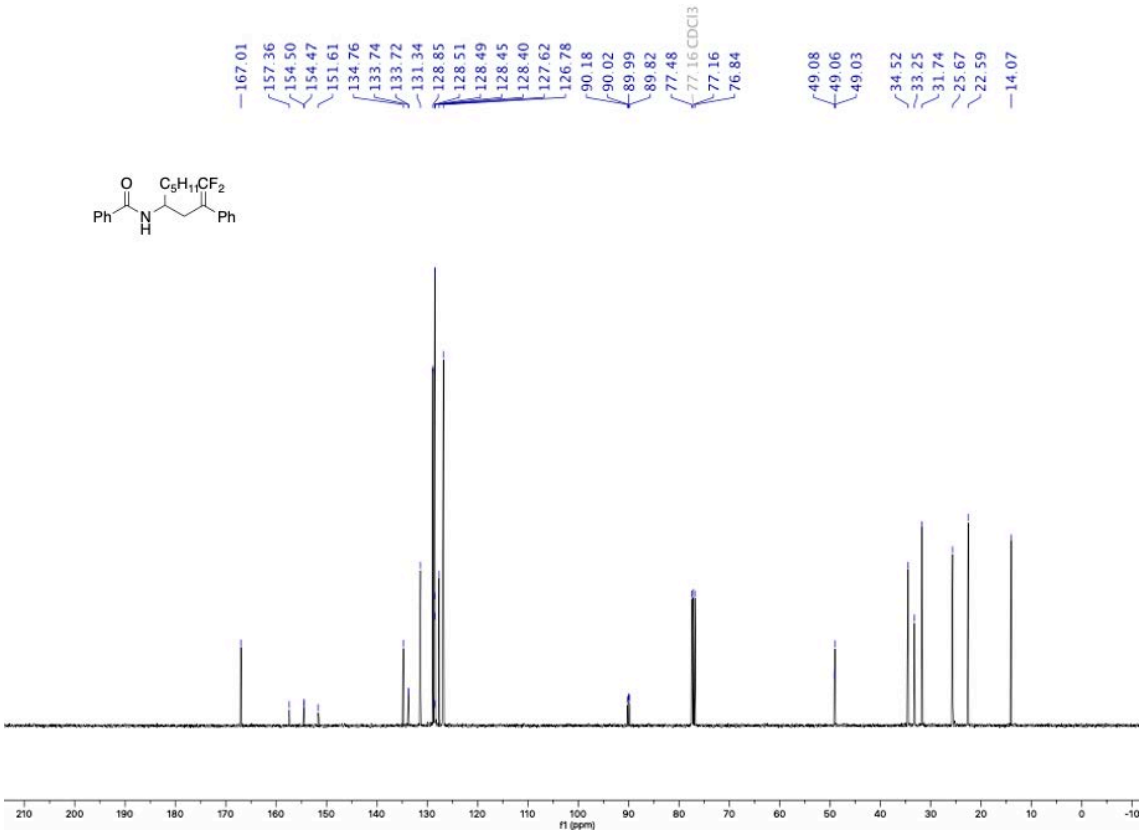
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **11a** and **11b**



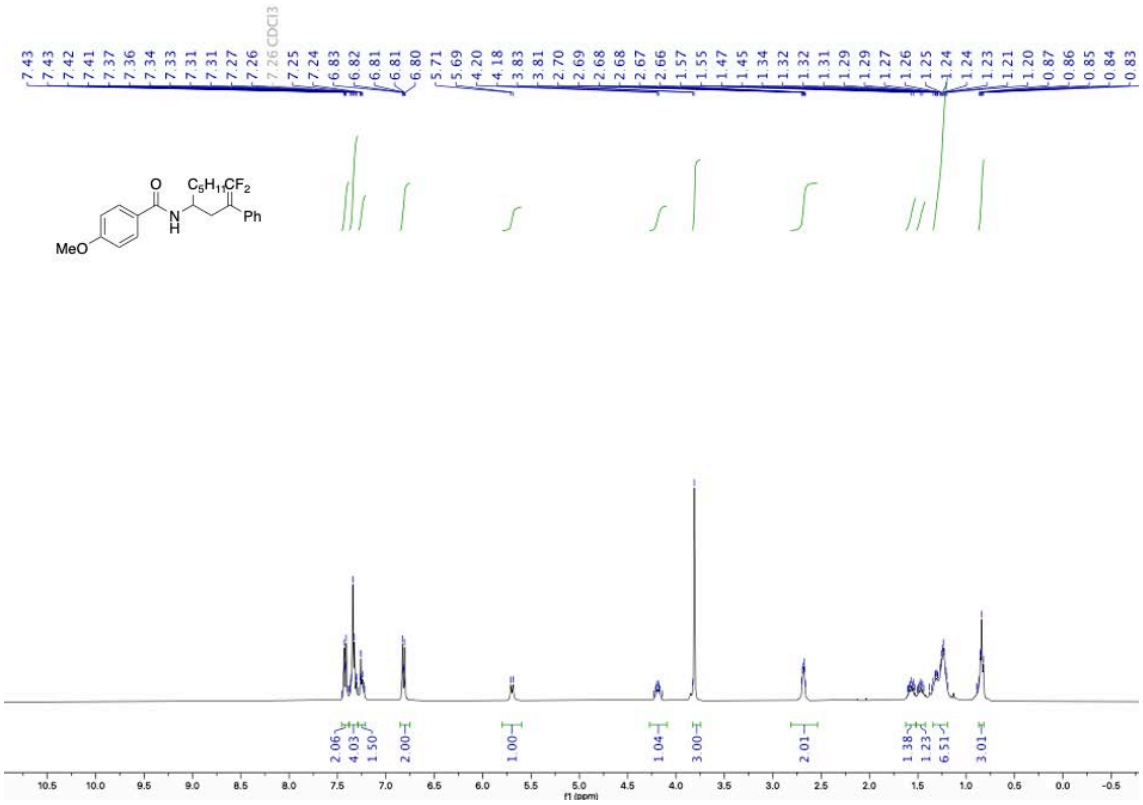
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**



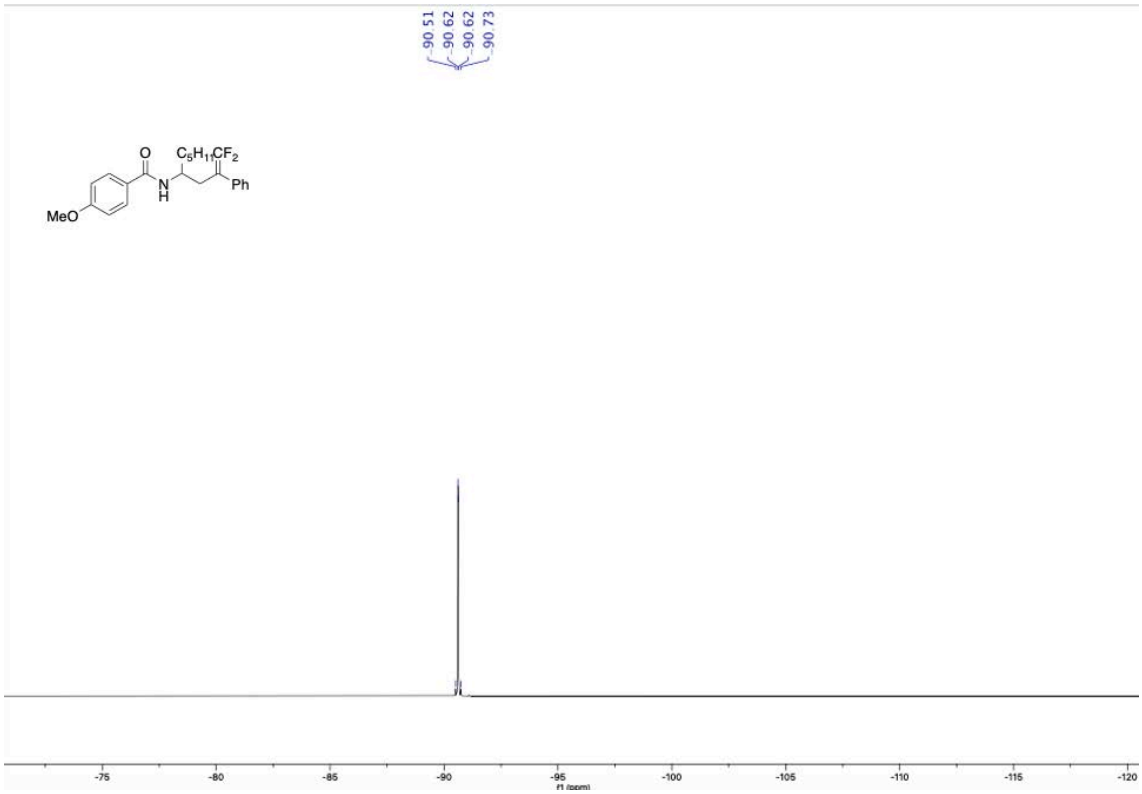
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3a**



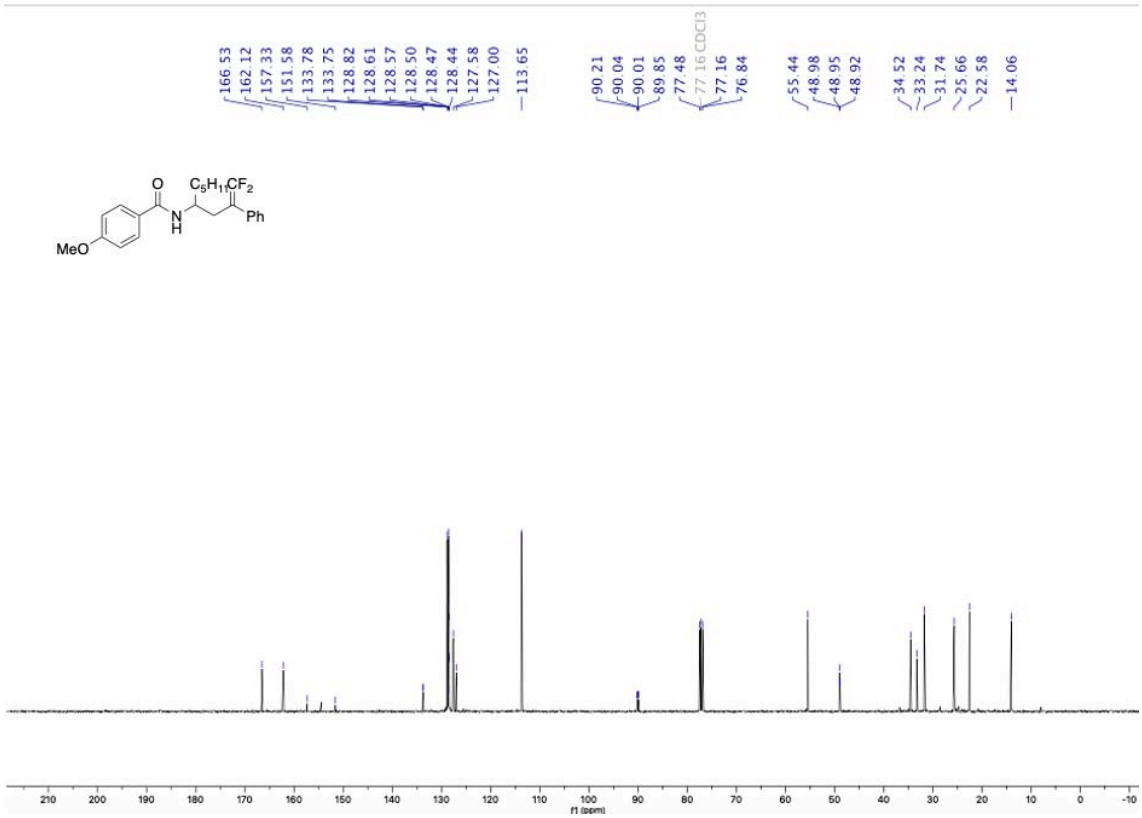
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3a**



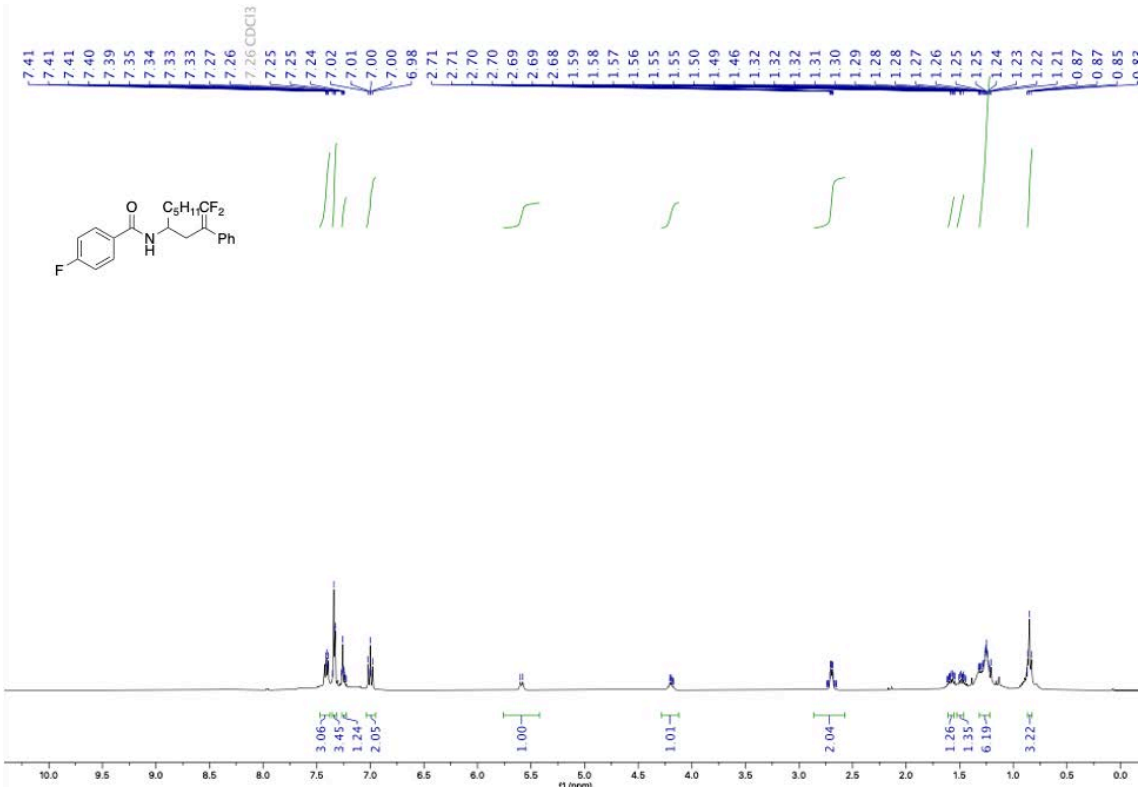
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**



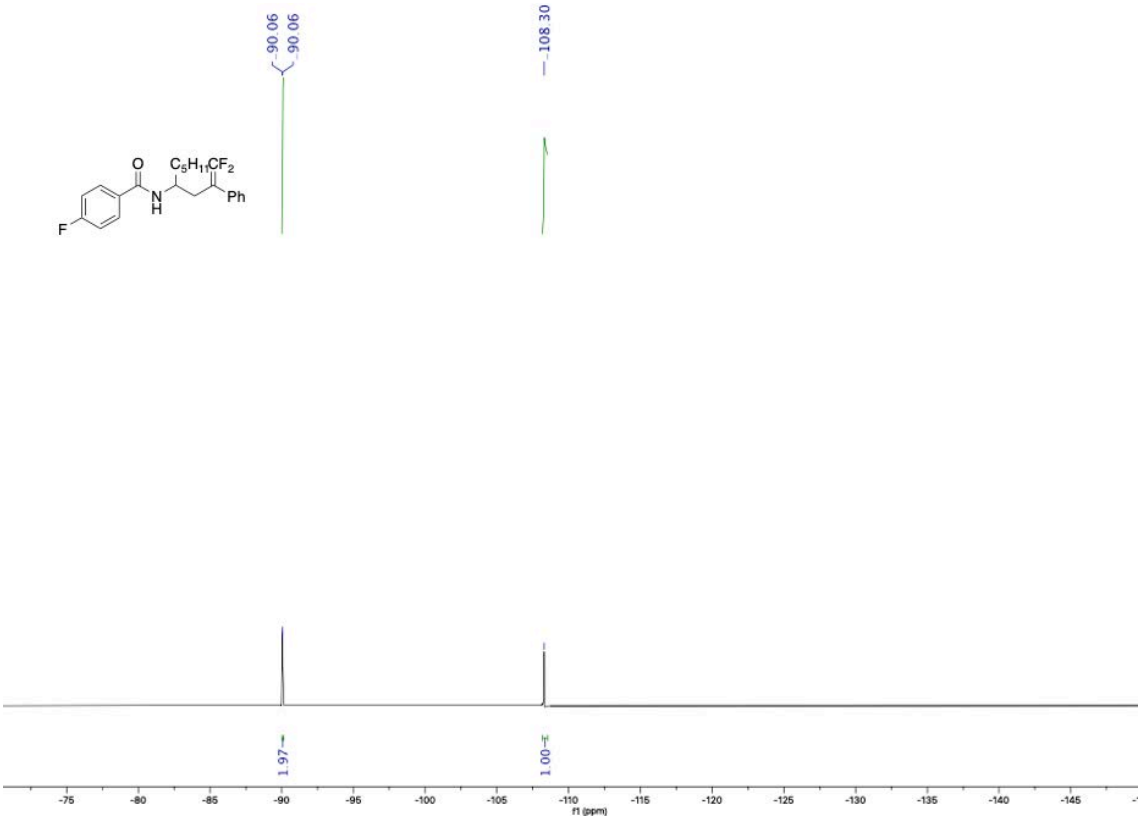
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3b**



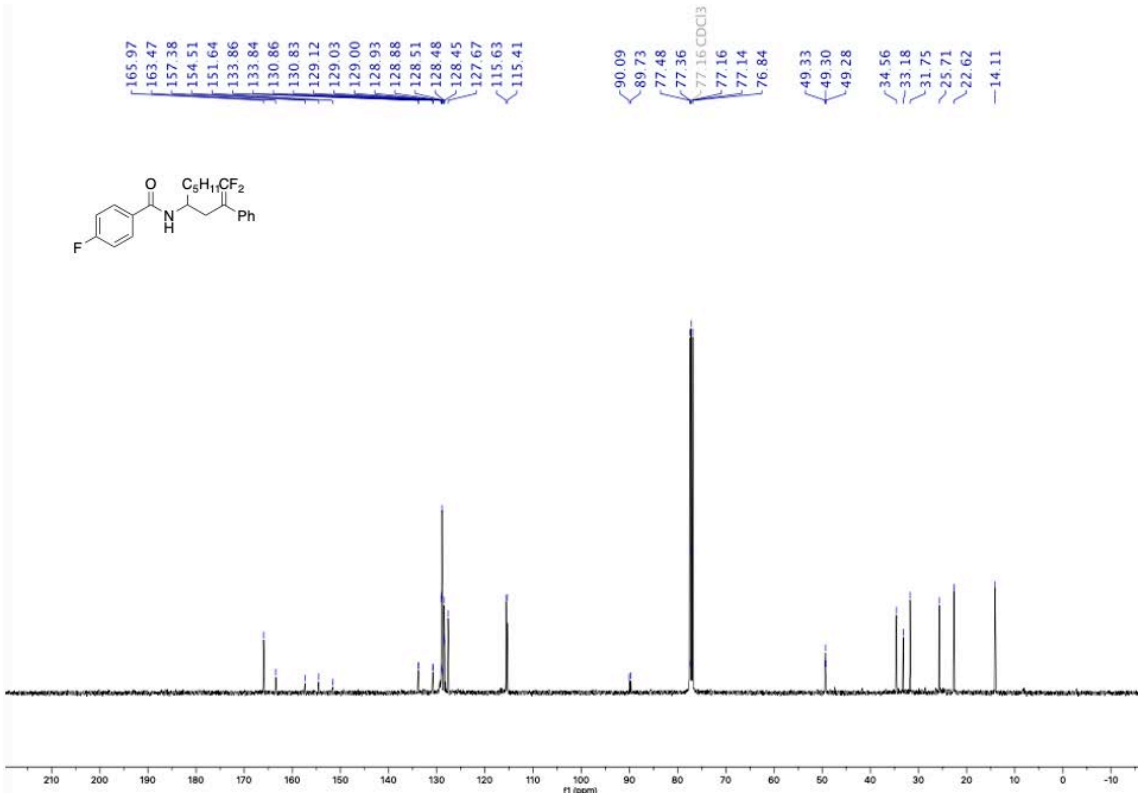
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3b**



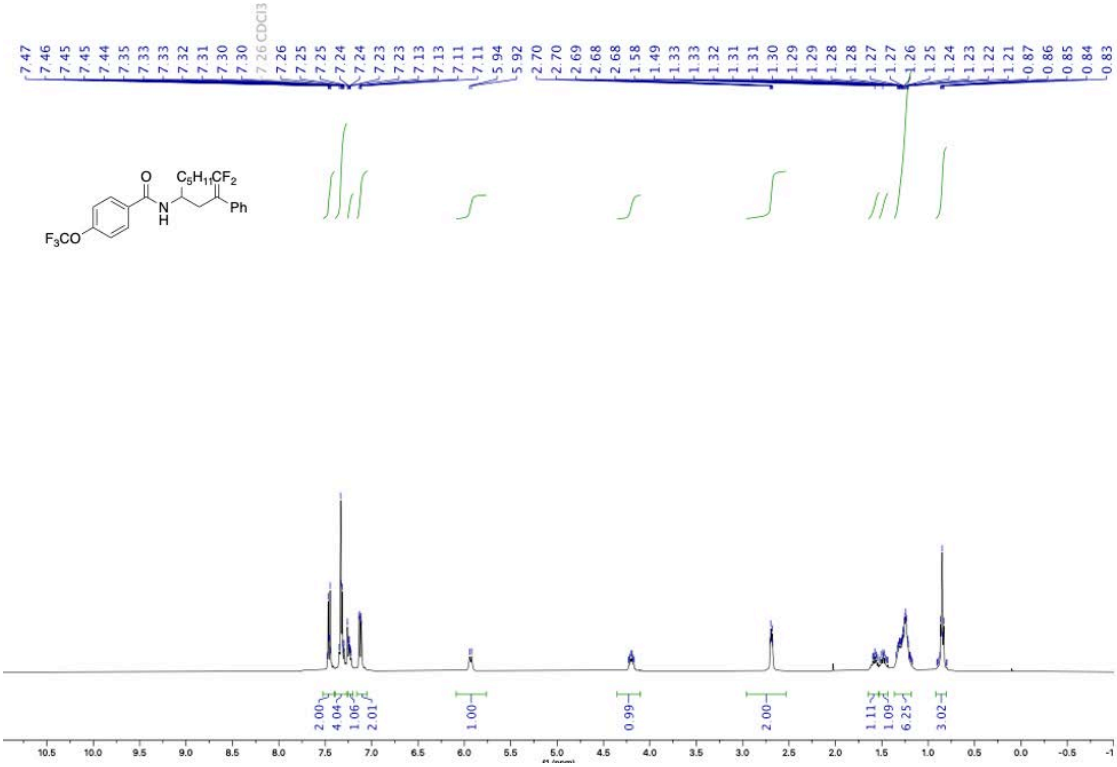
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3c**



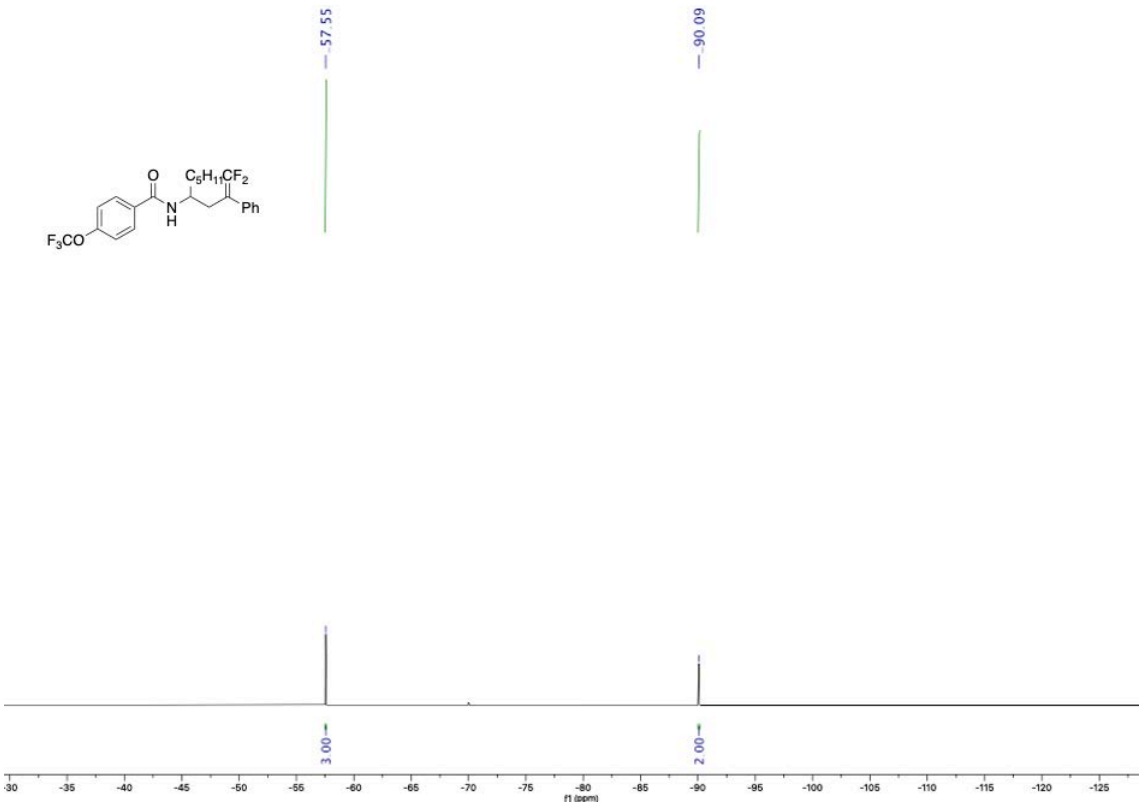
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3c**



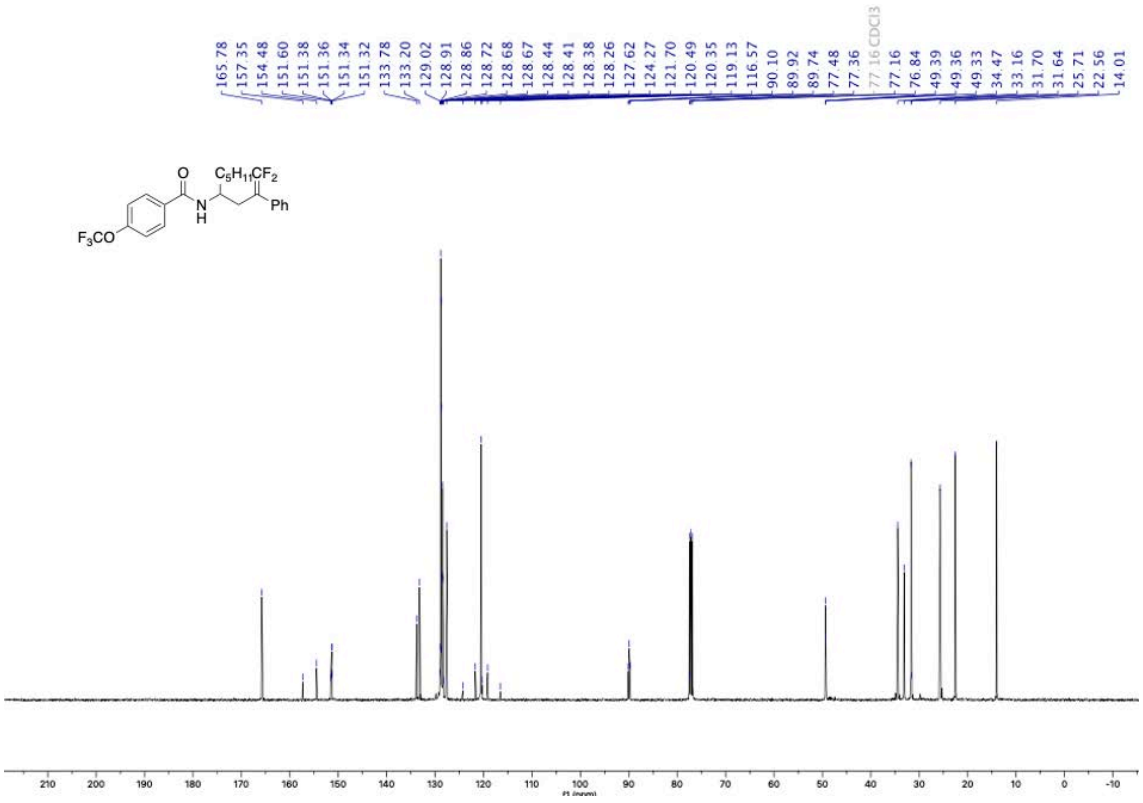
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3c**



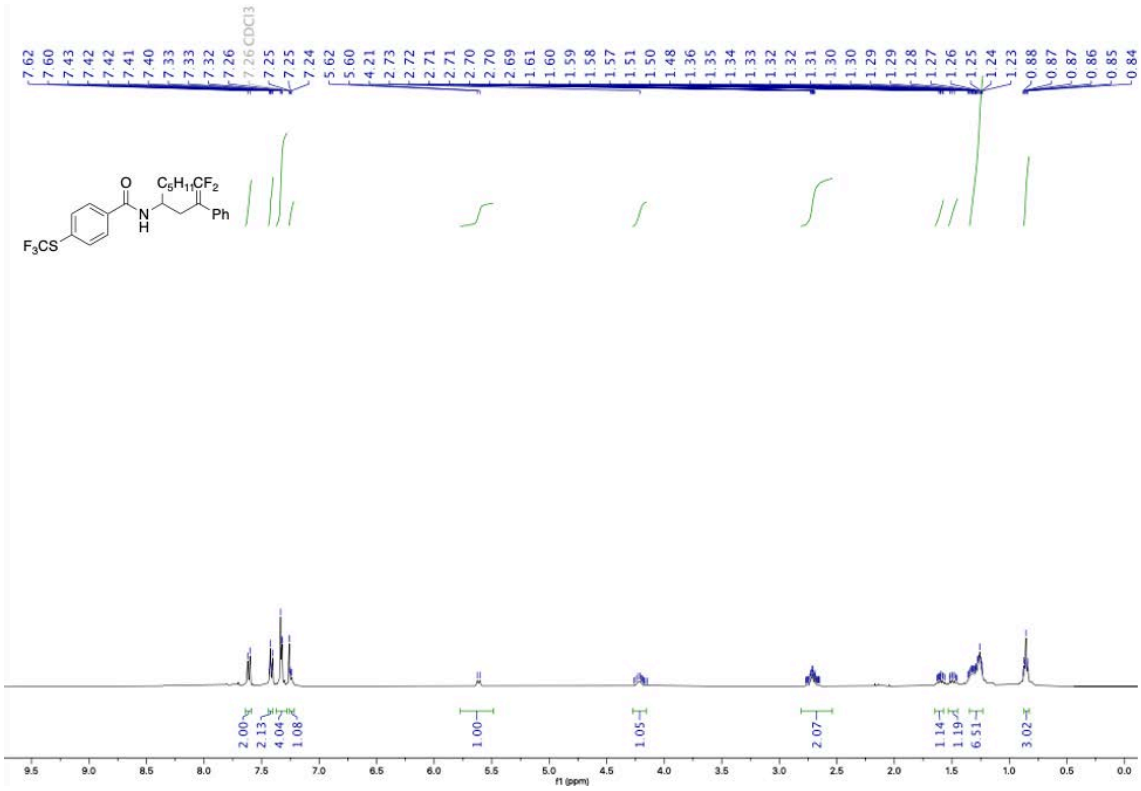
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3d**



^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3d**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3d**



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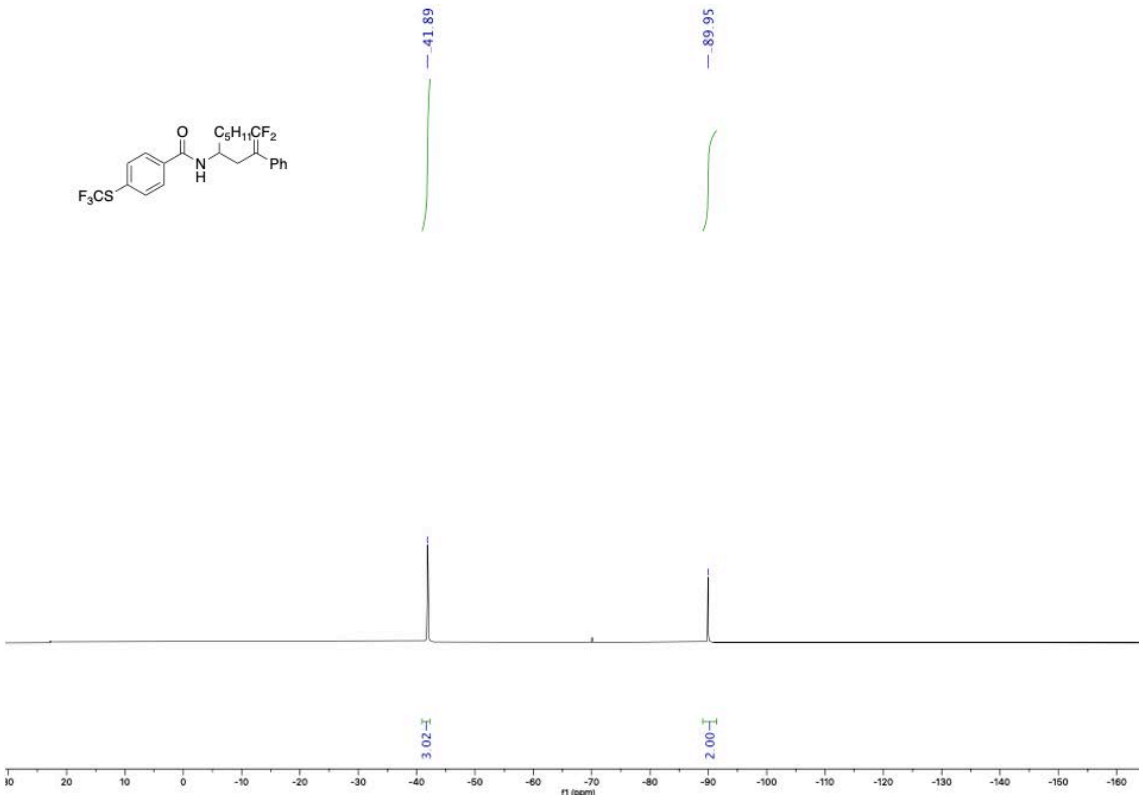
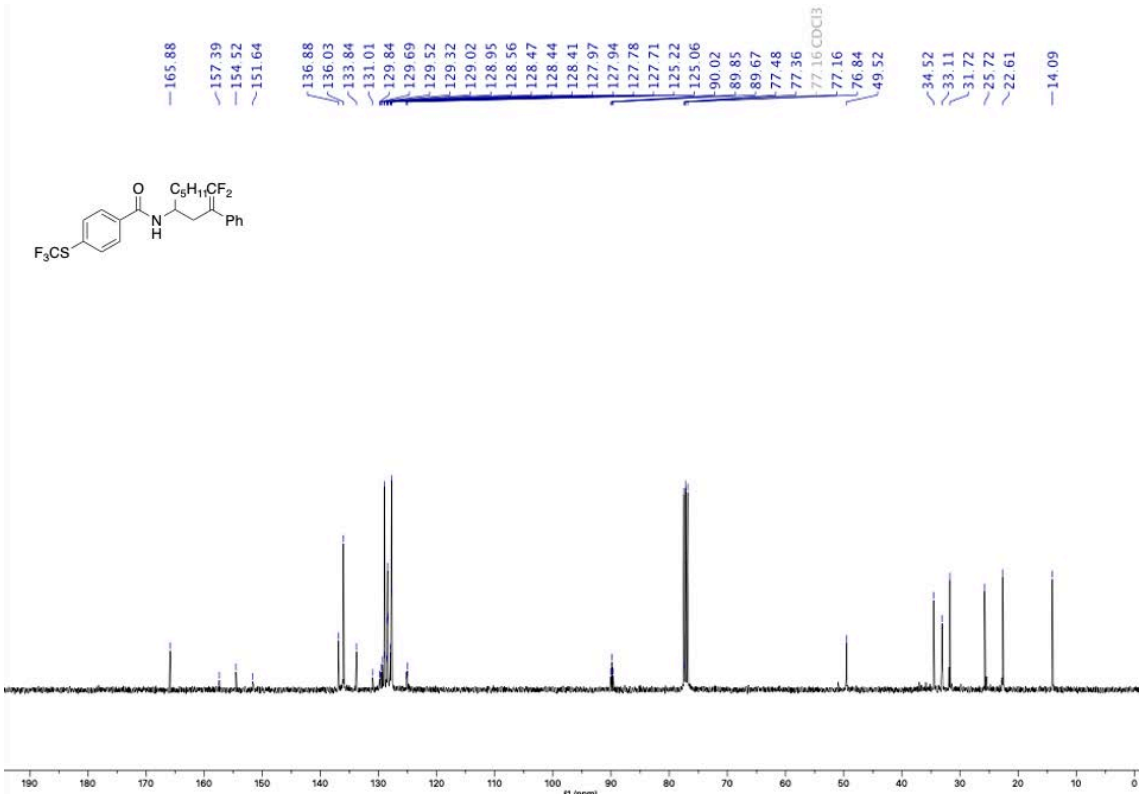
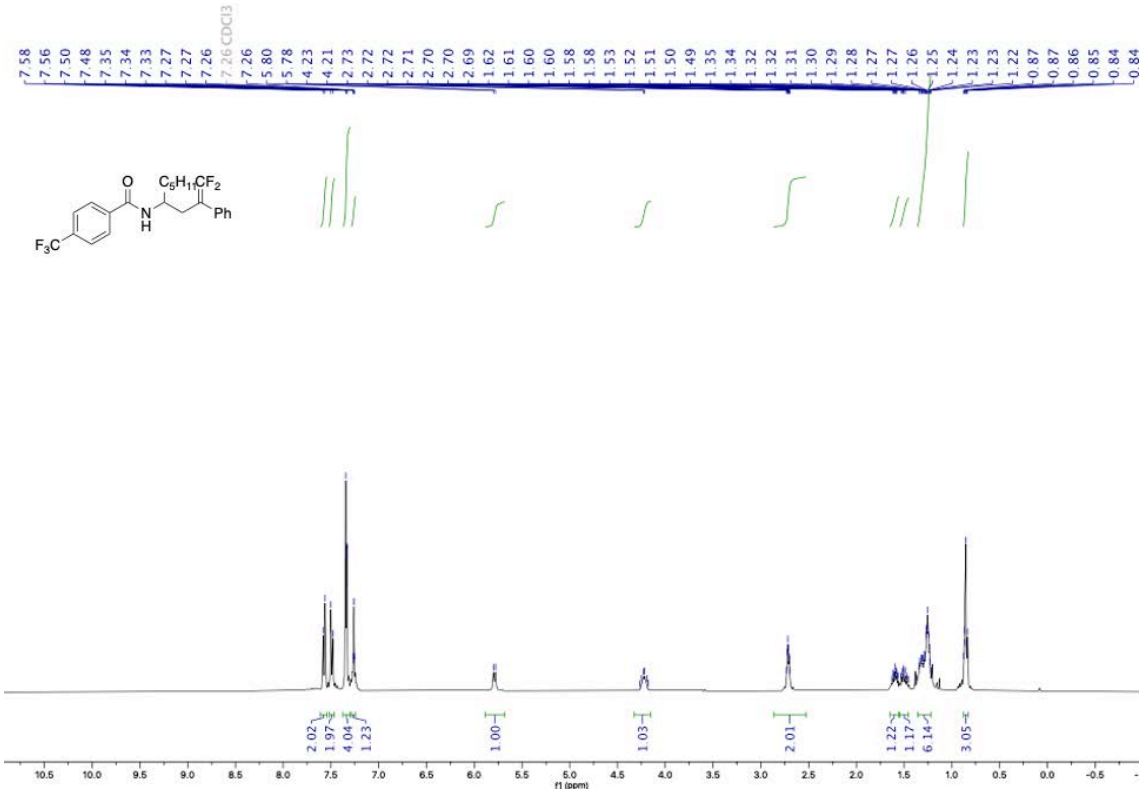


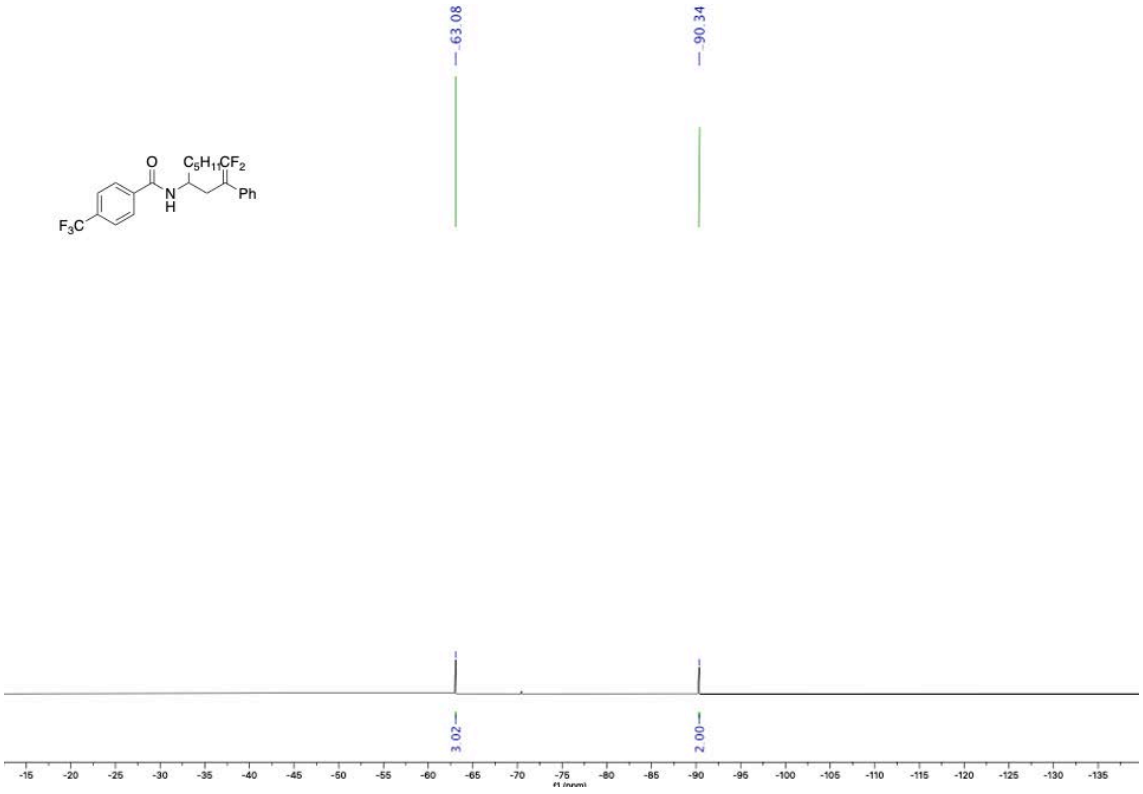
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3e**



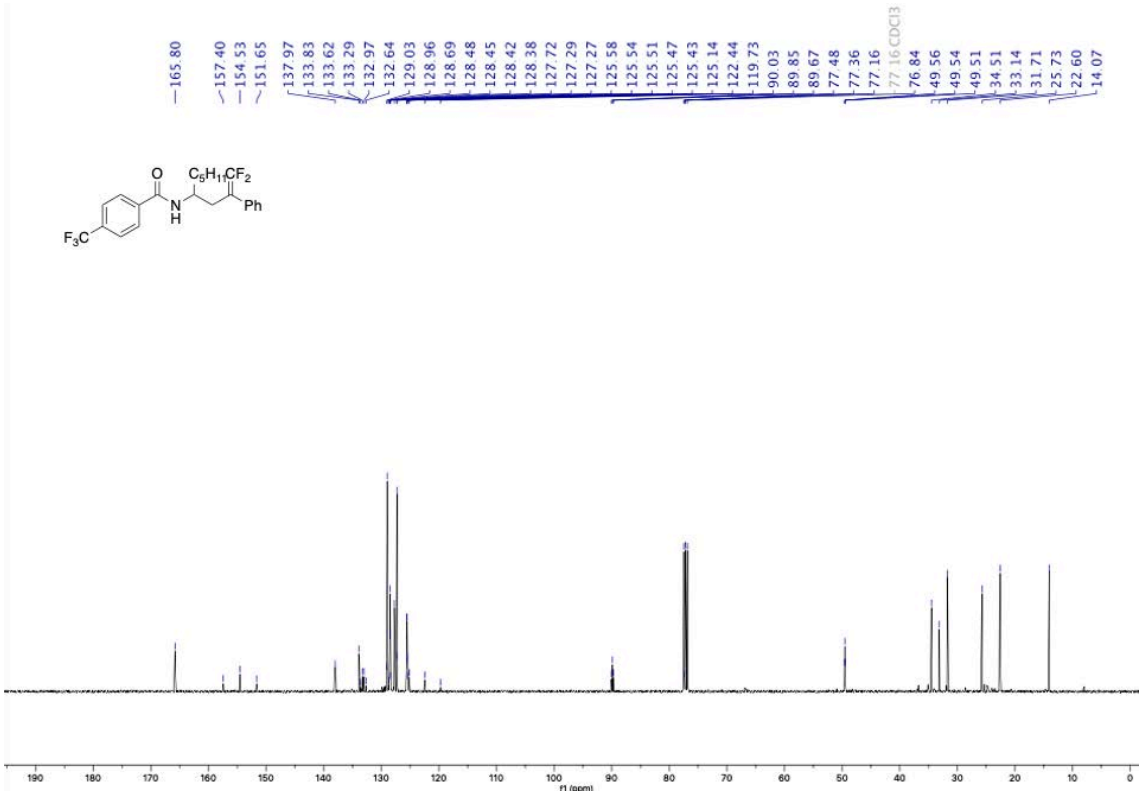
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3e**



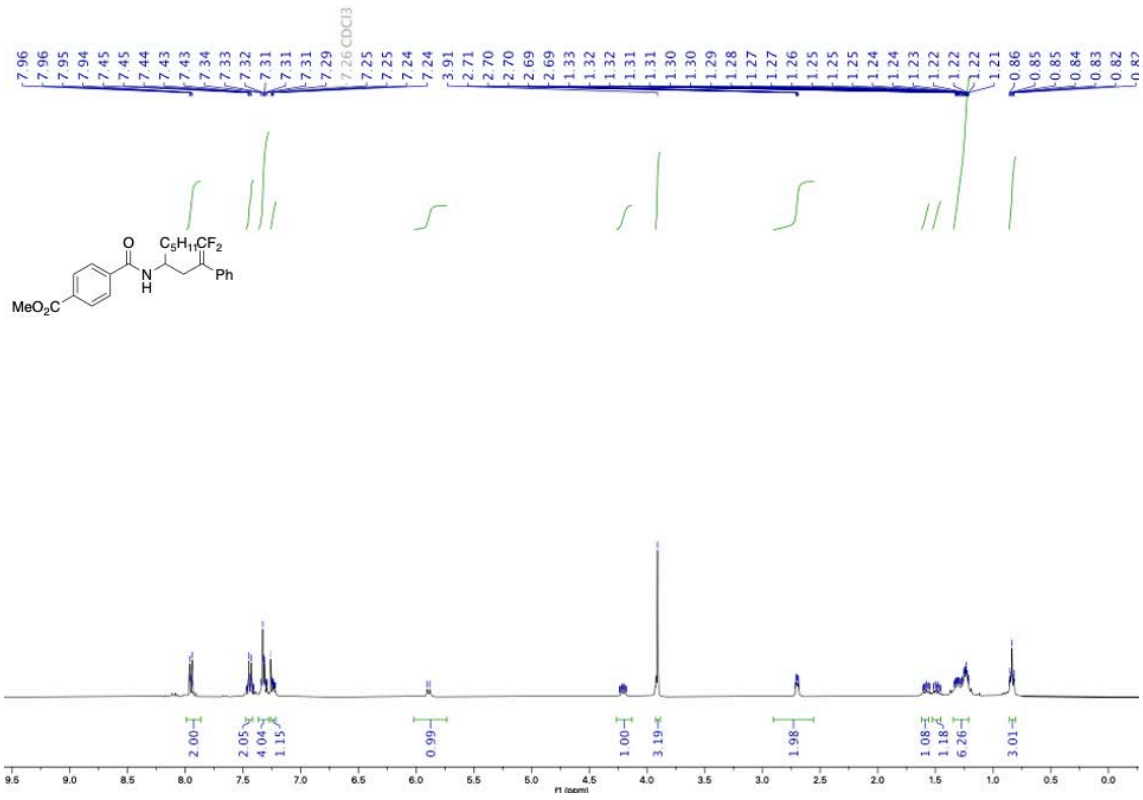
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3f**



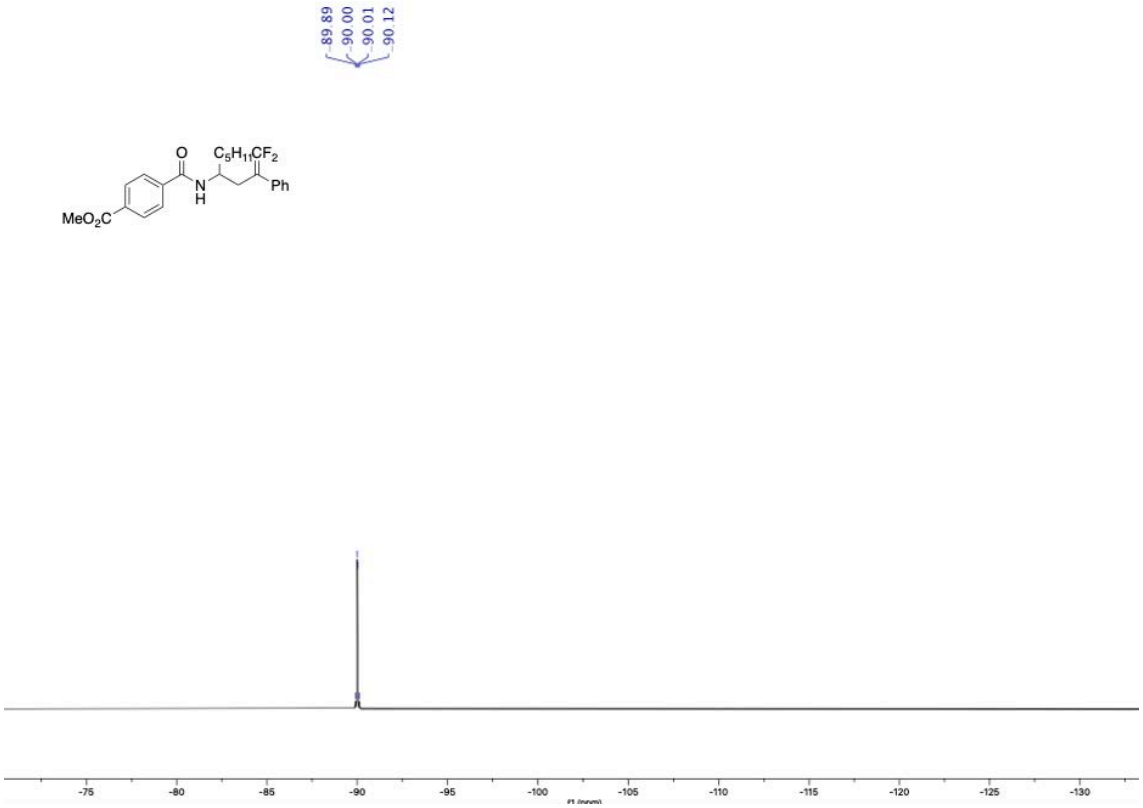
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3f**



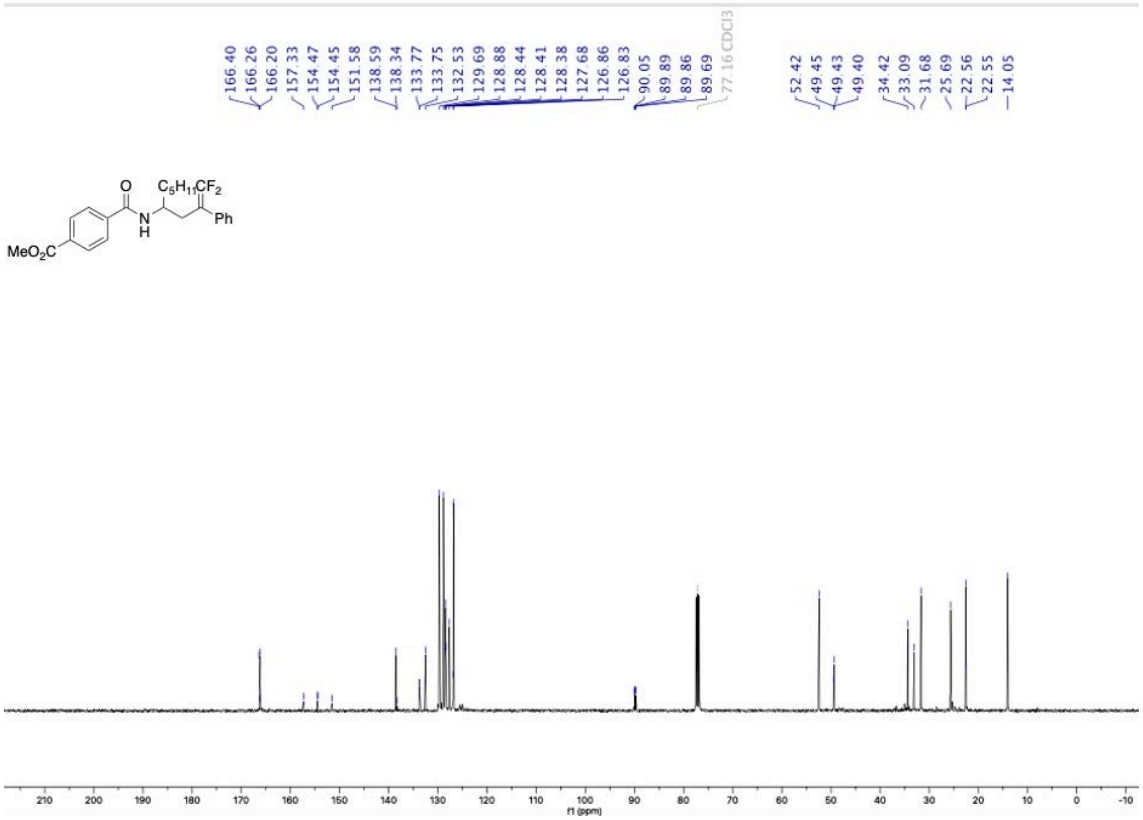
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3f**



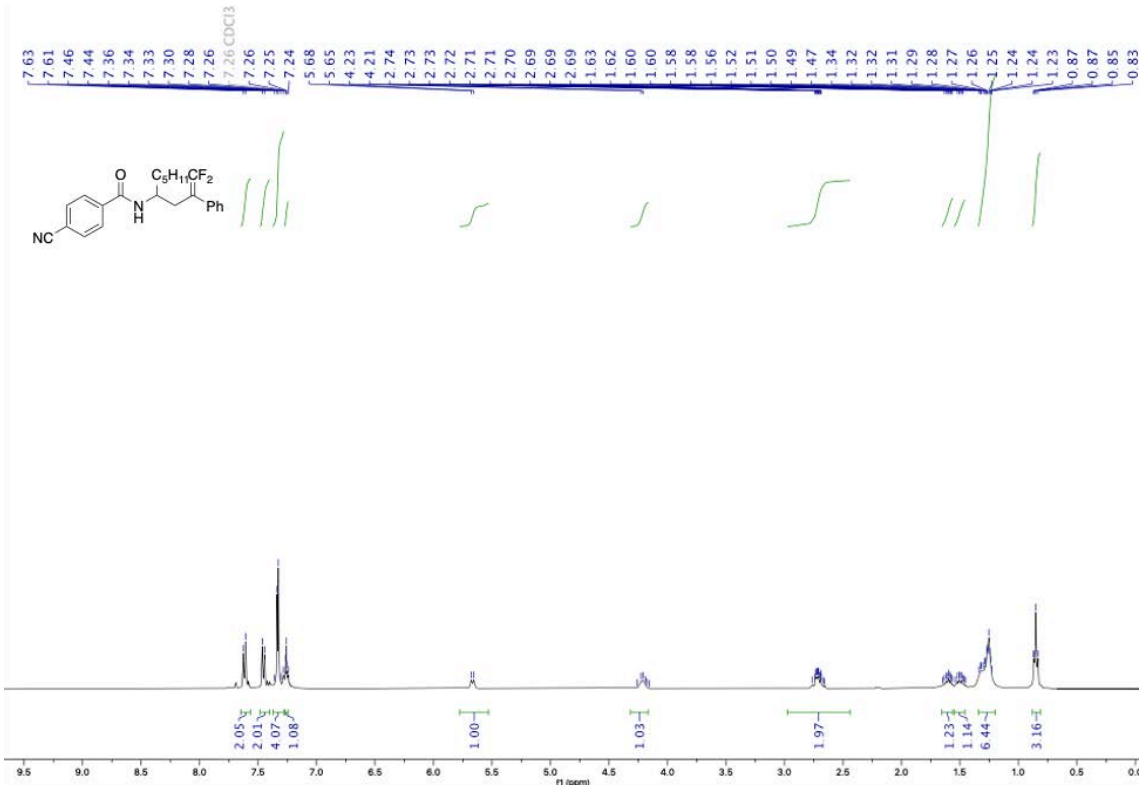
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3g**



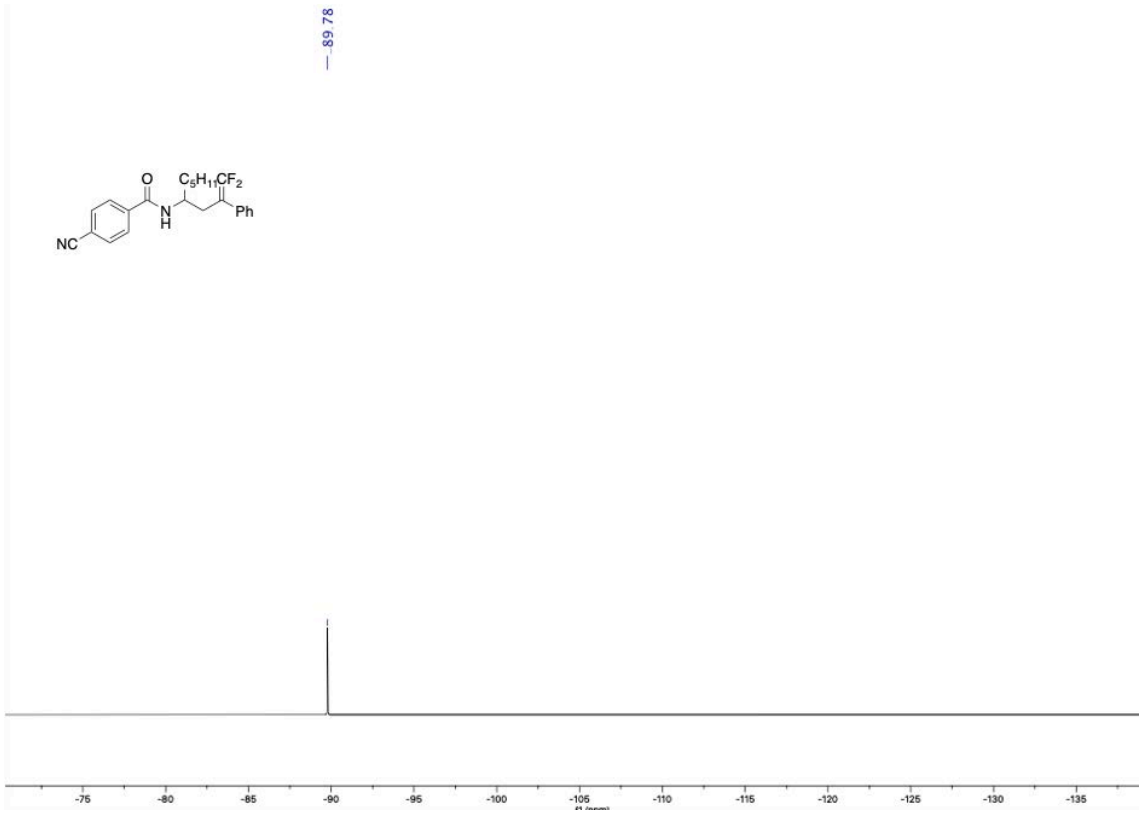
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3g**



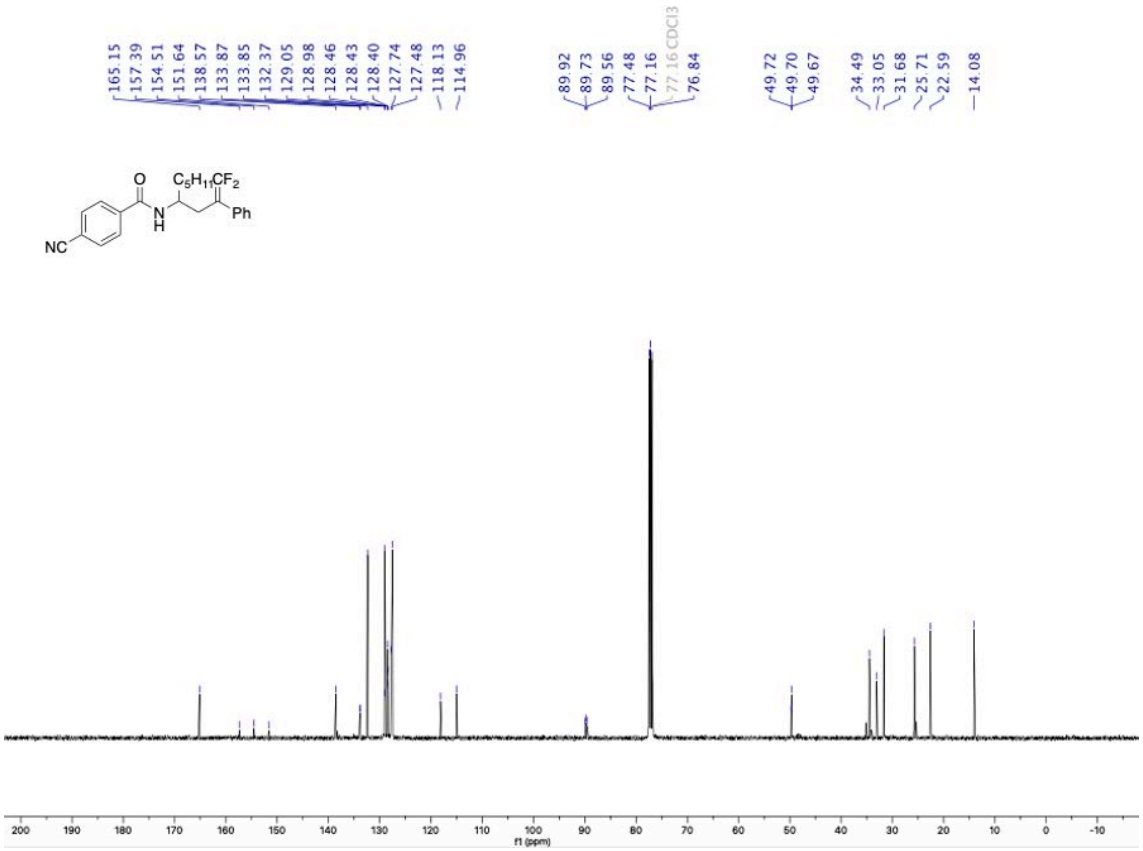
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3g**



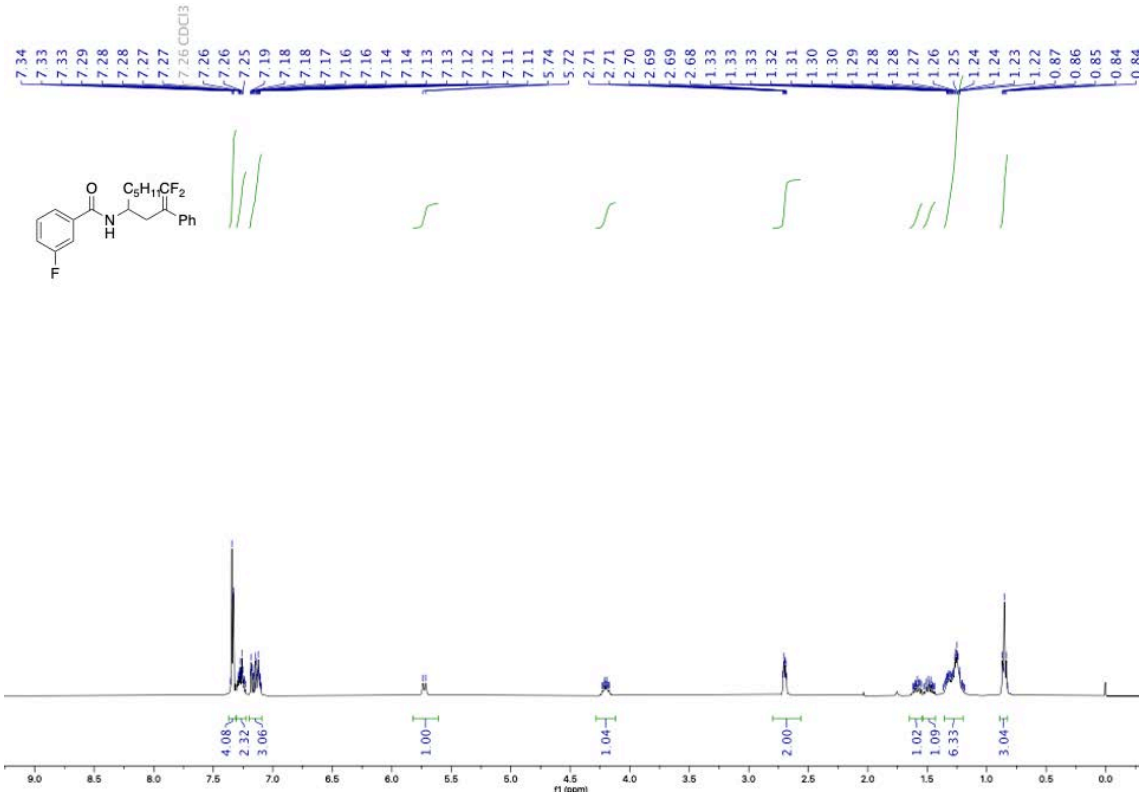
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3h**



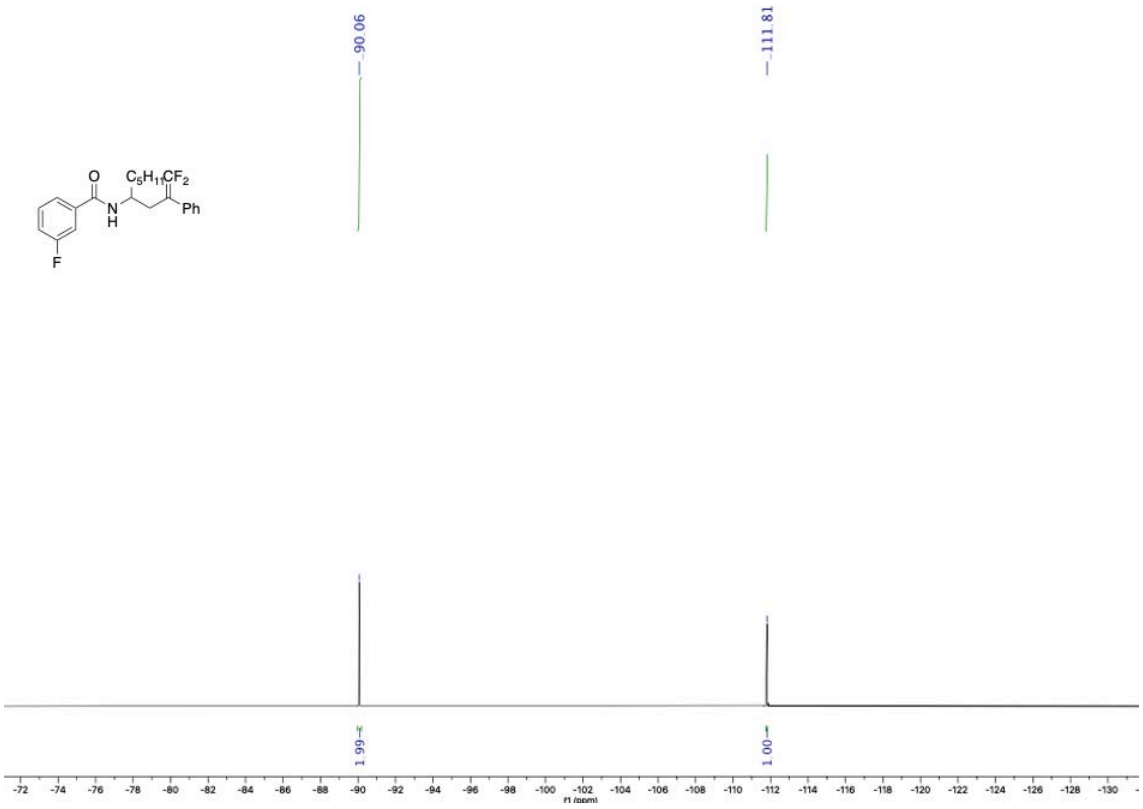
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3h**



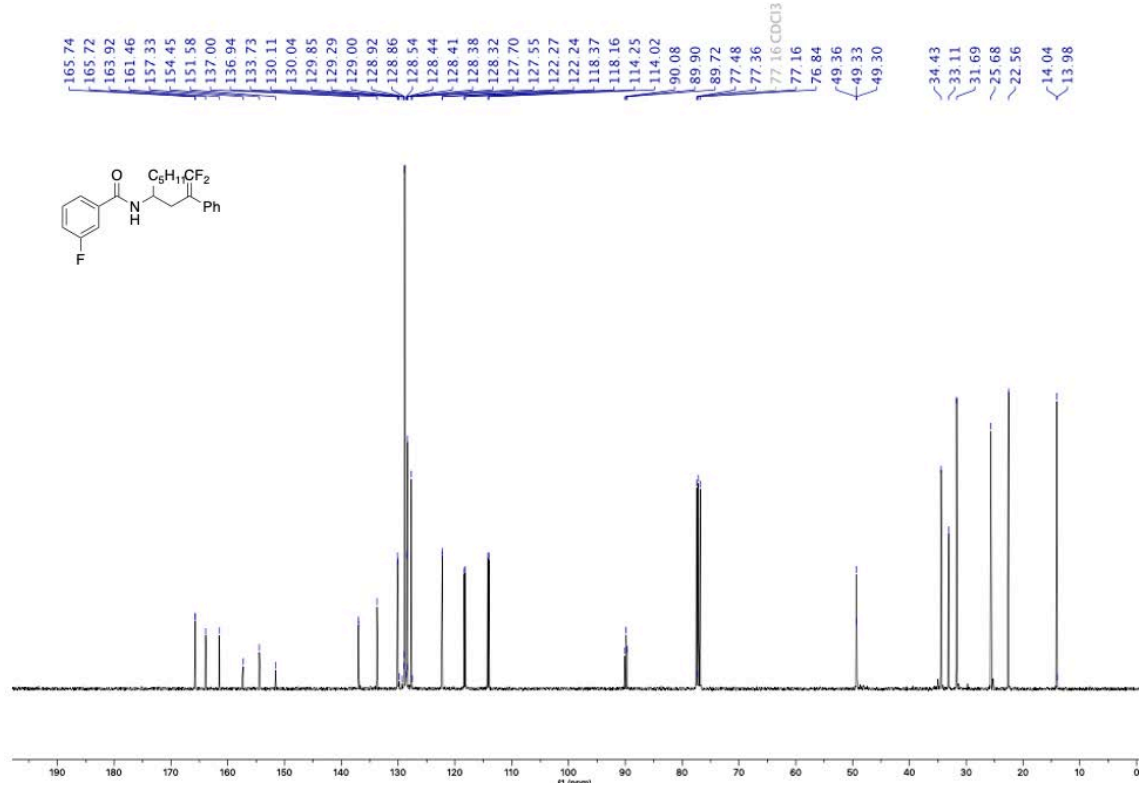
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3h**



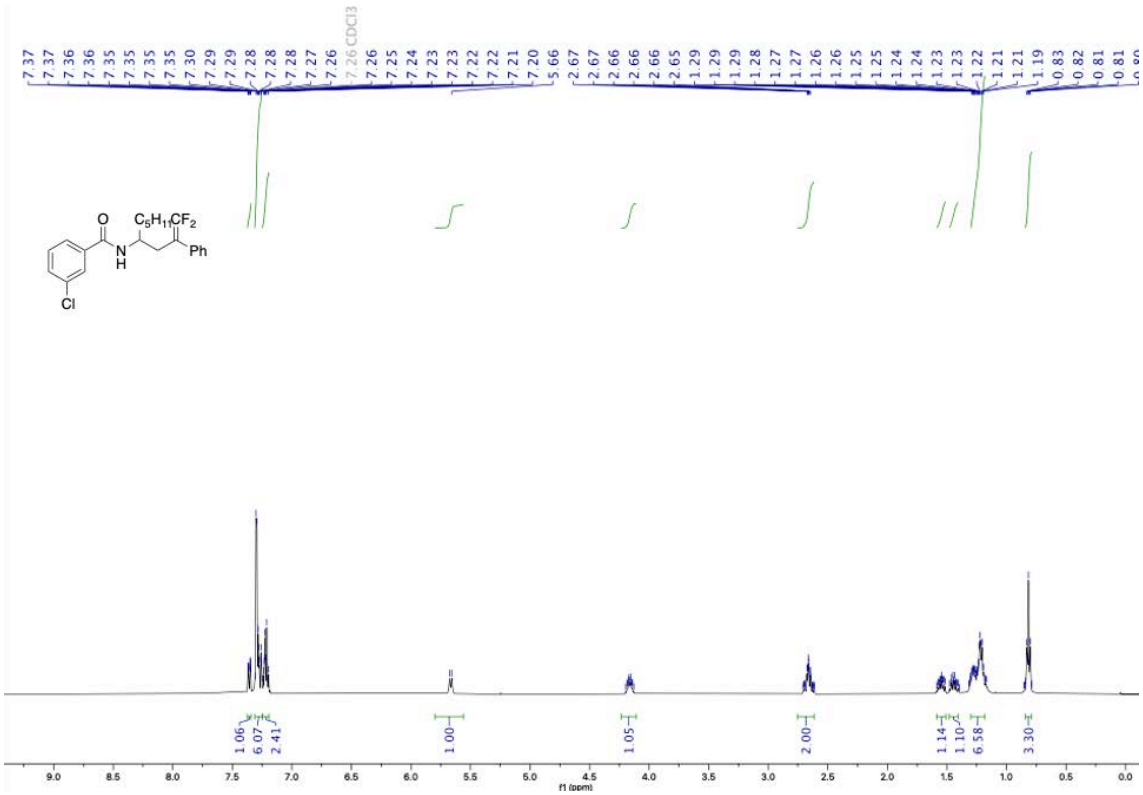
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3i**



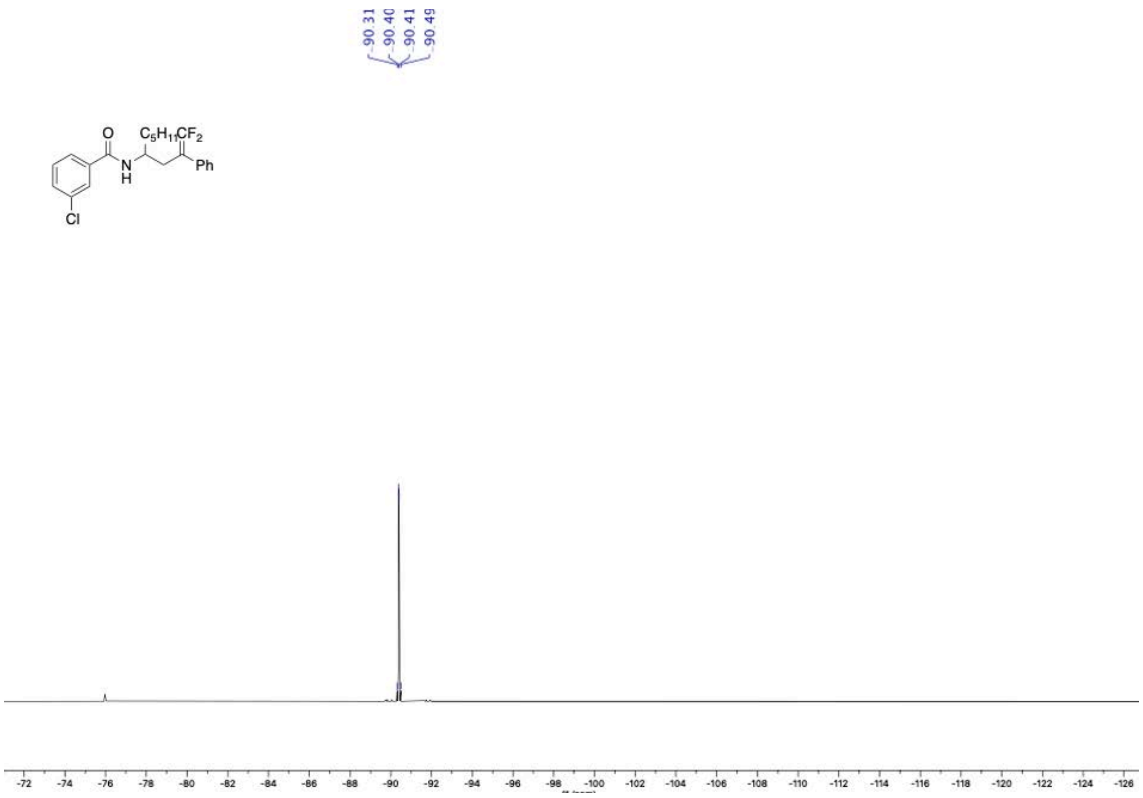
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3i**



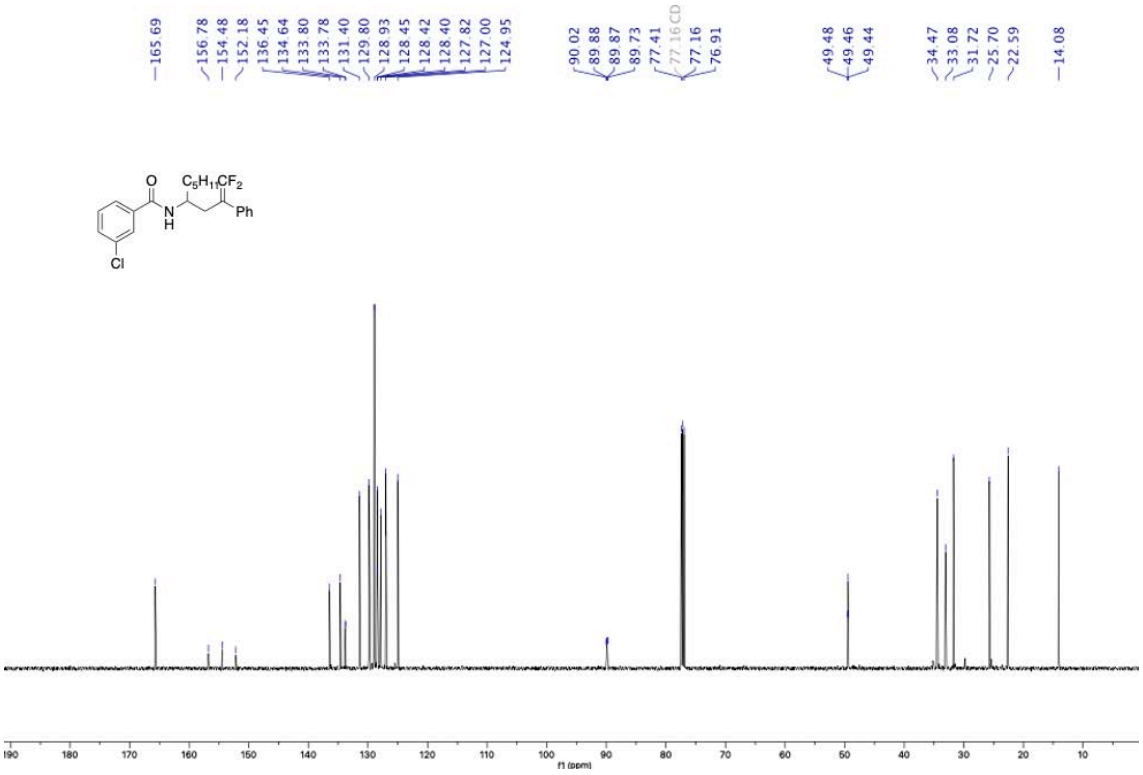
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3i**



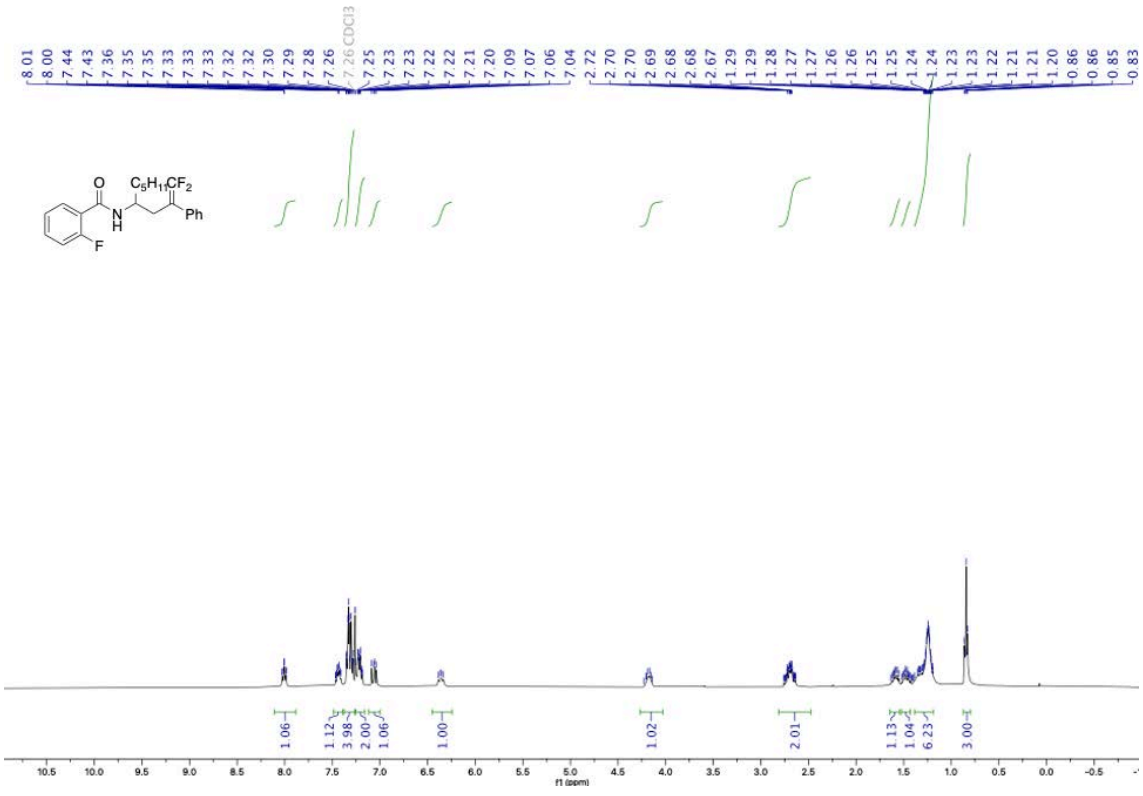
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3j**



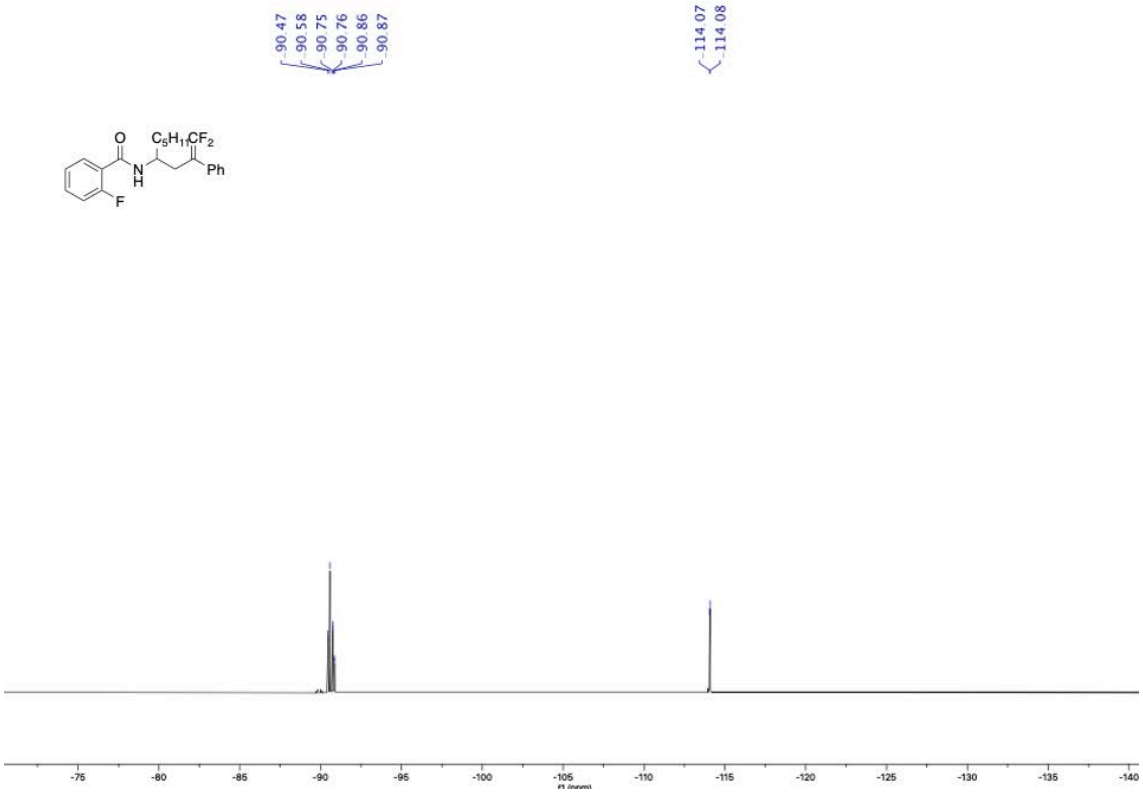
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3j**



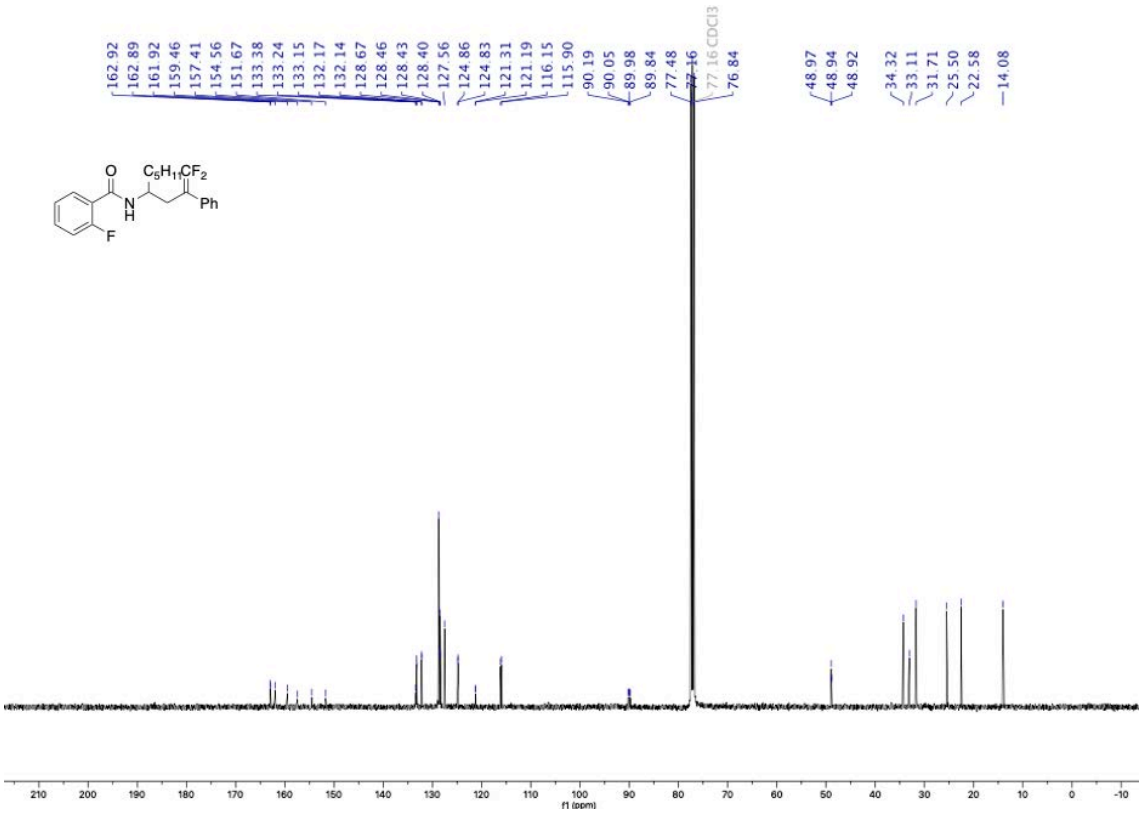
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3j**



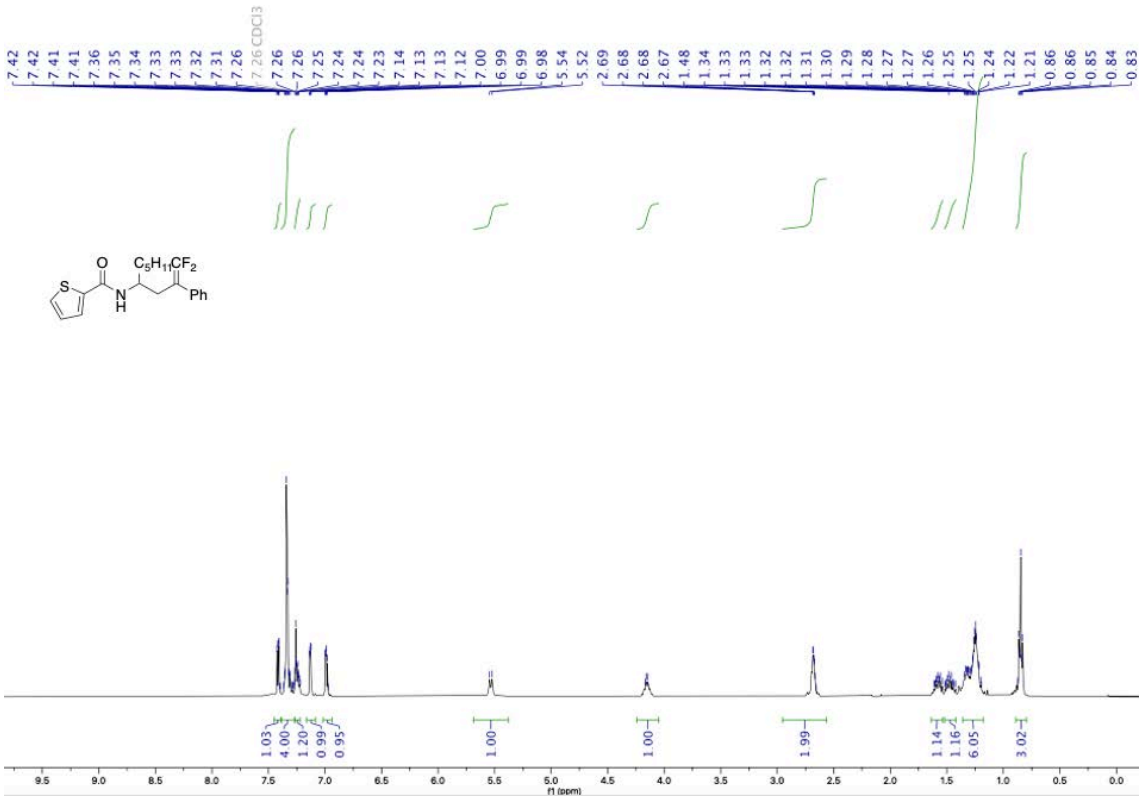
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3k**



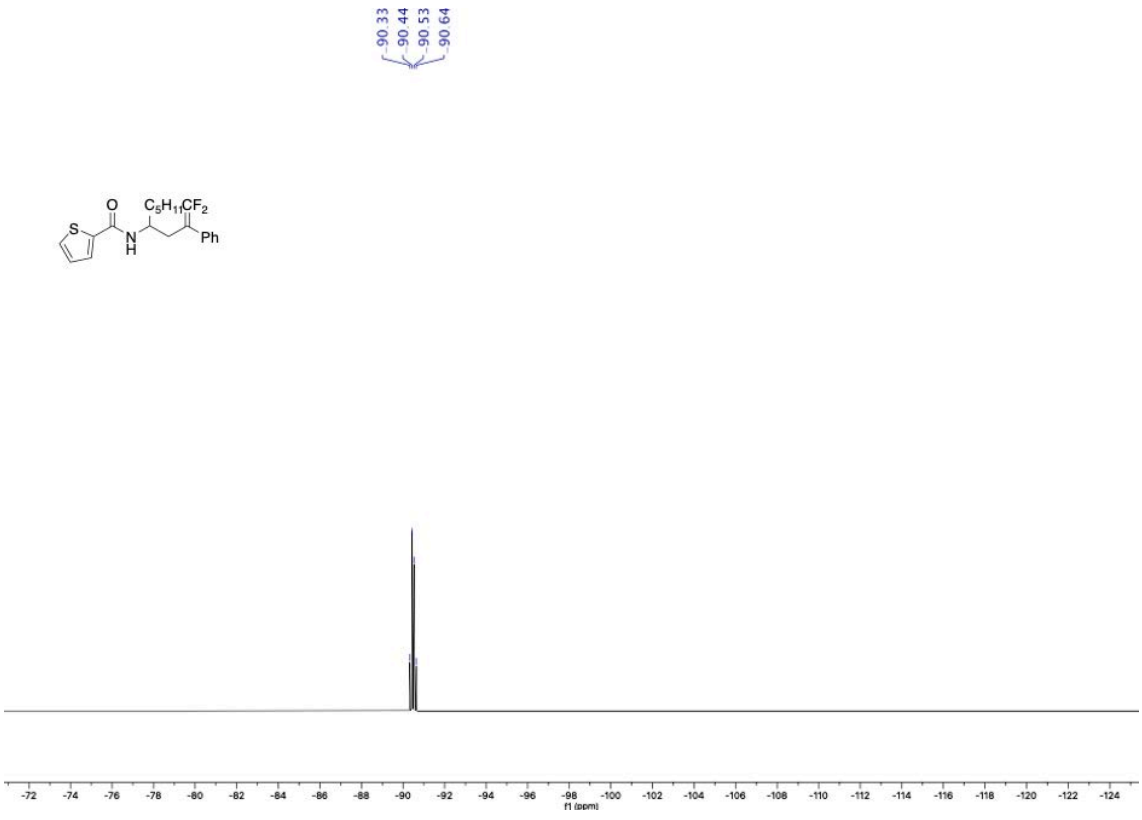
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3k**



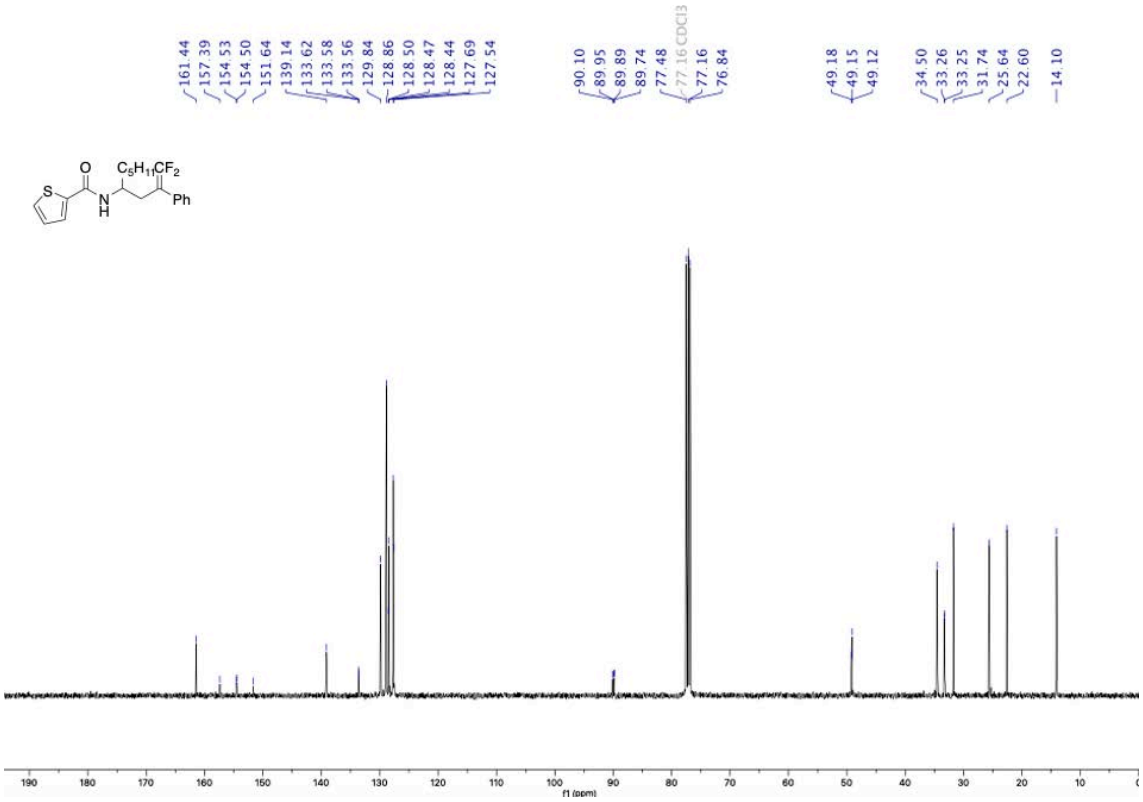
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3k**



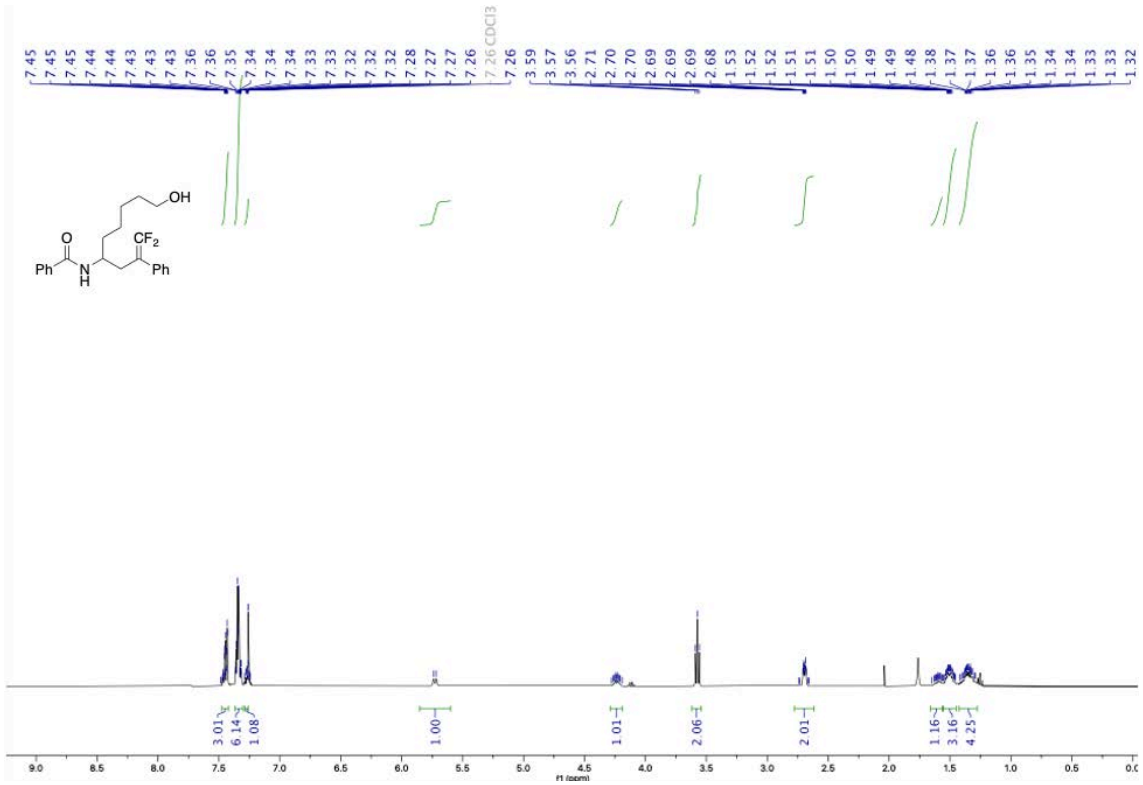
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3l**



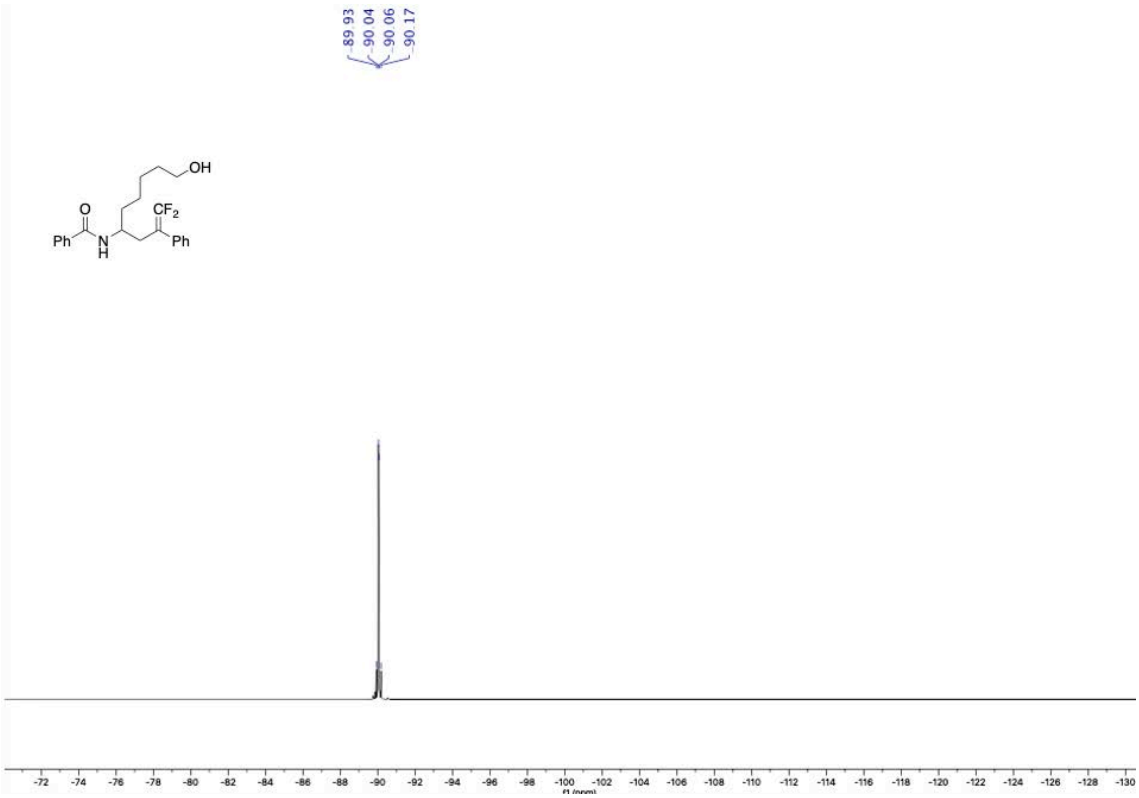
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3l**



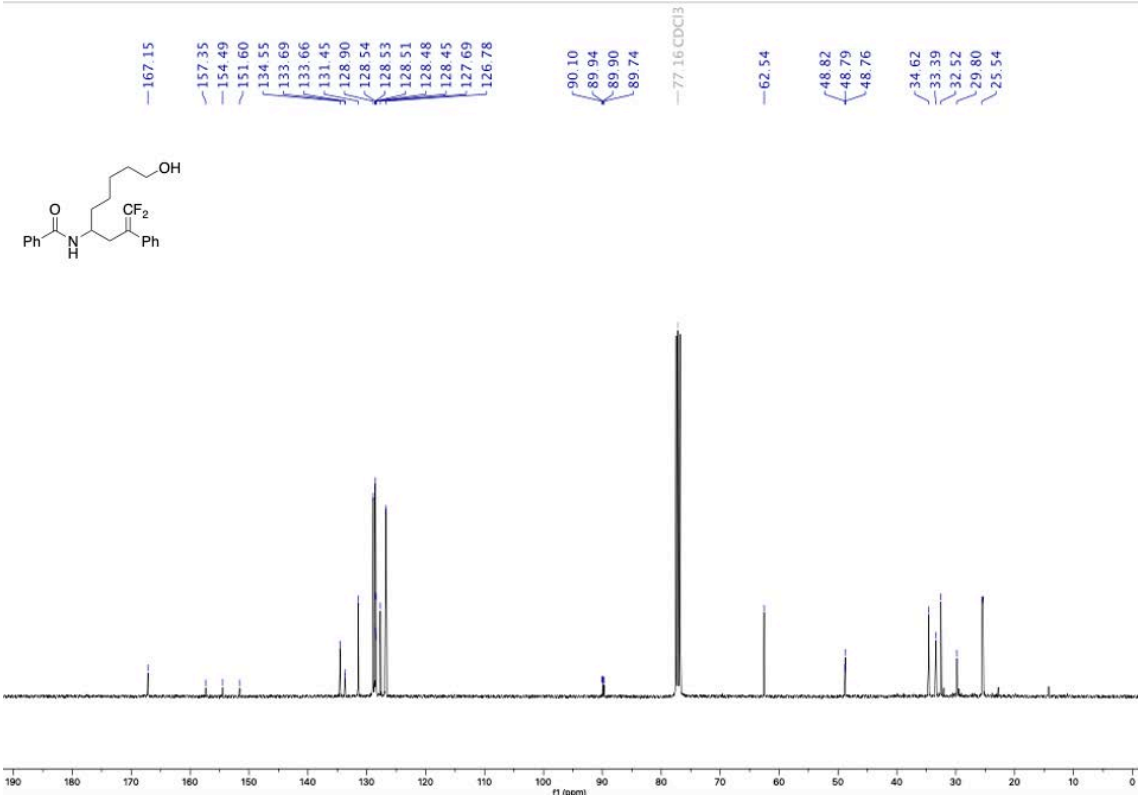
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3l**



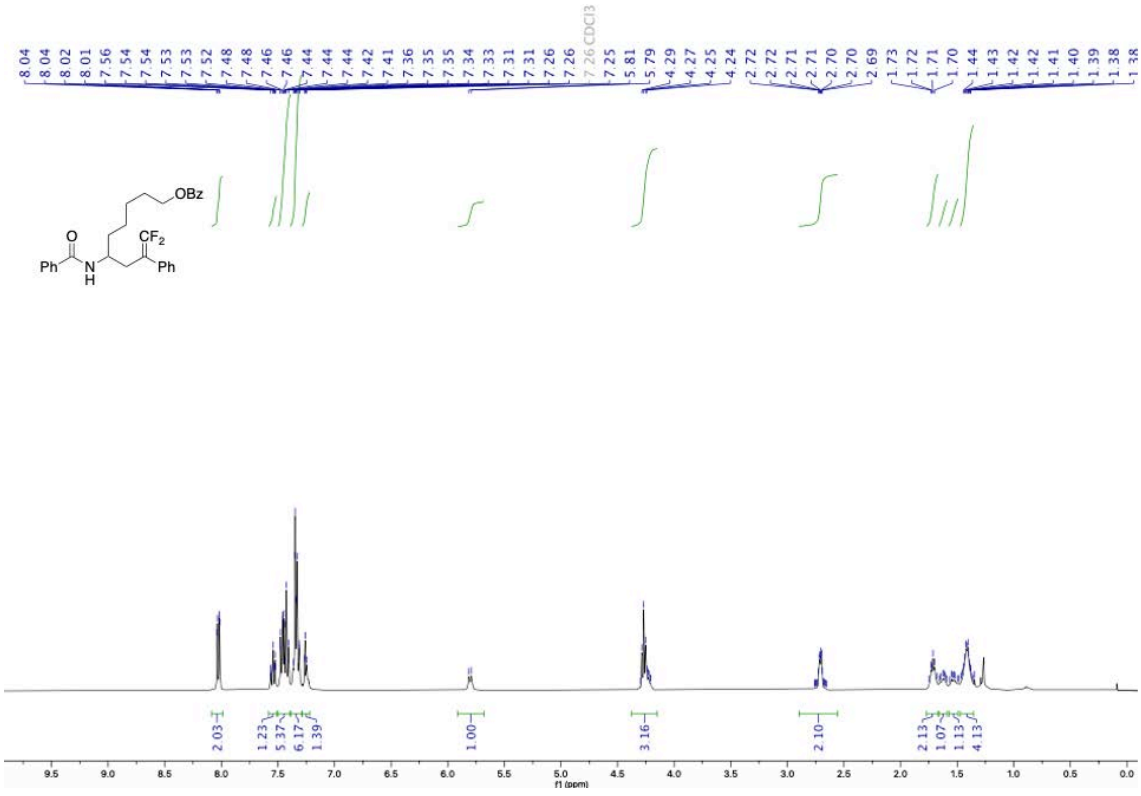
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3m**



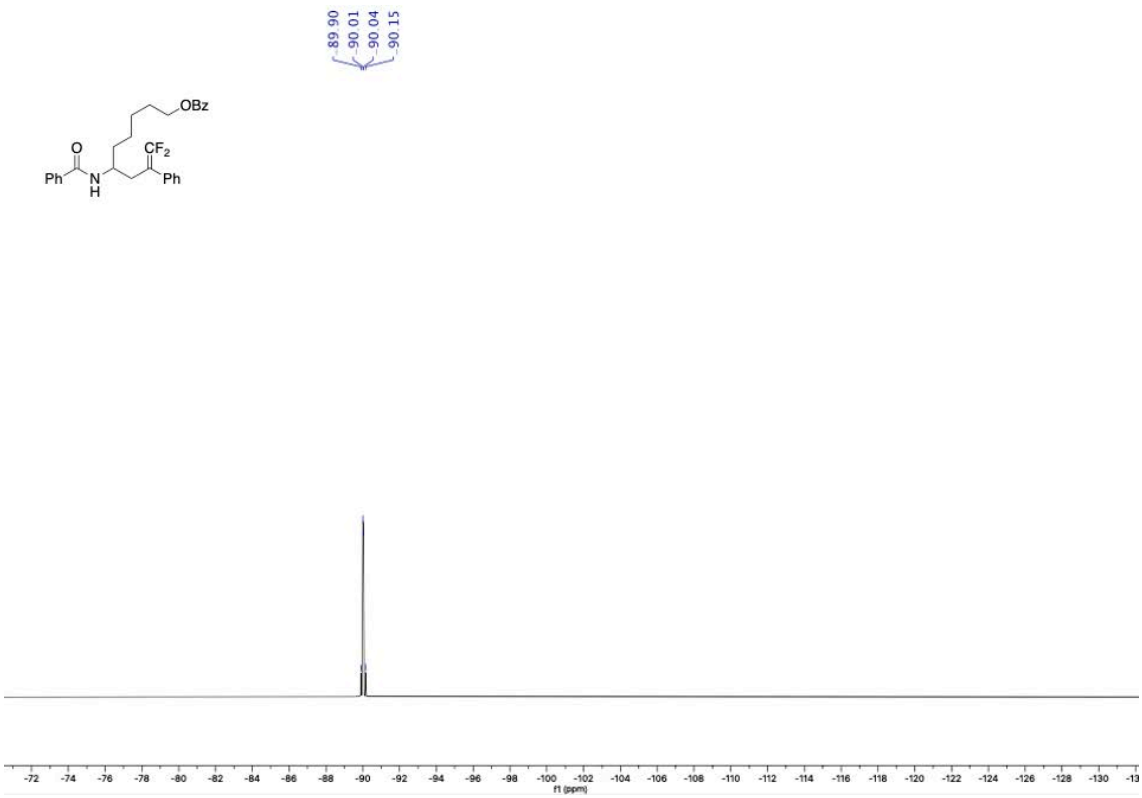
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3m**



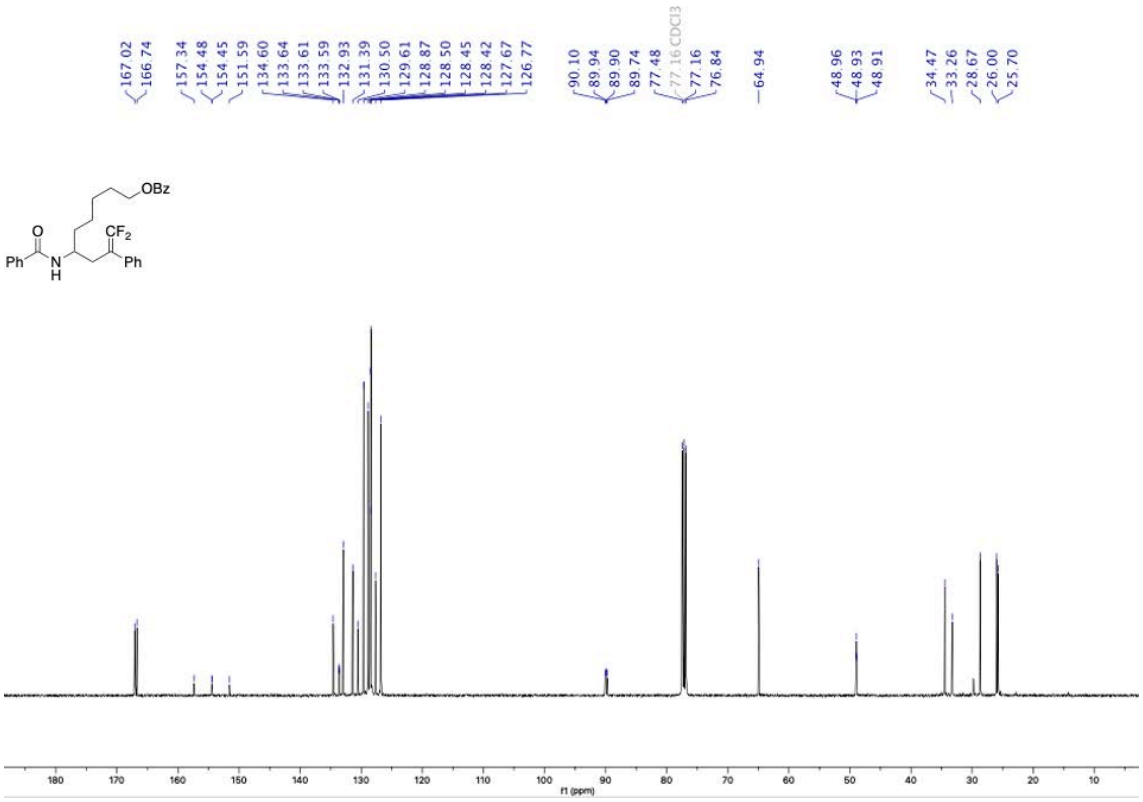
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3m**



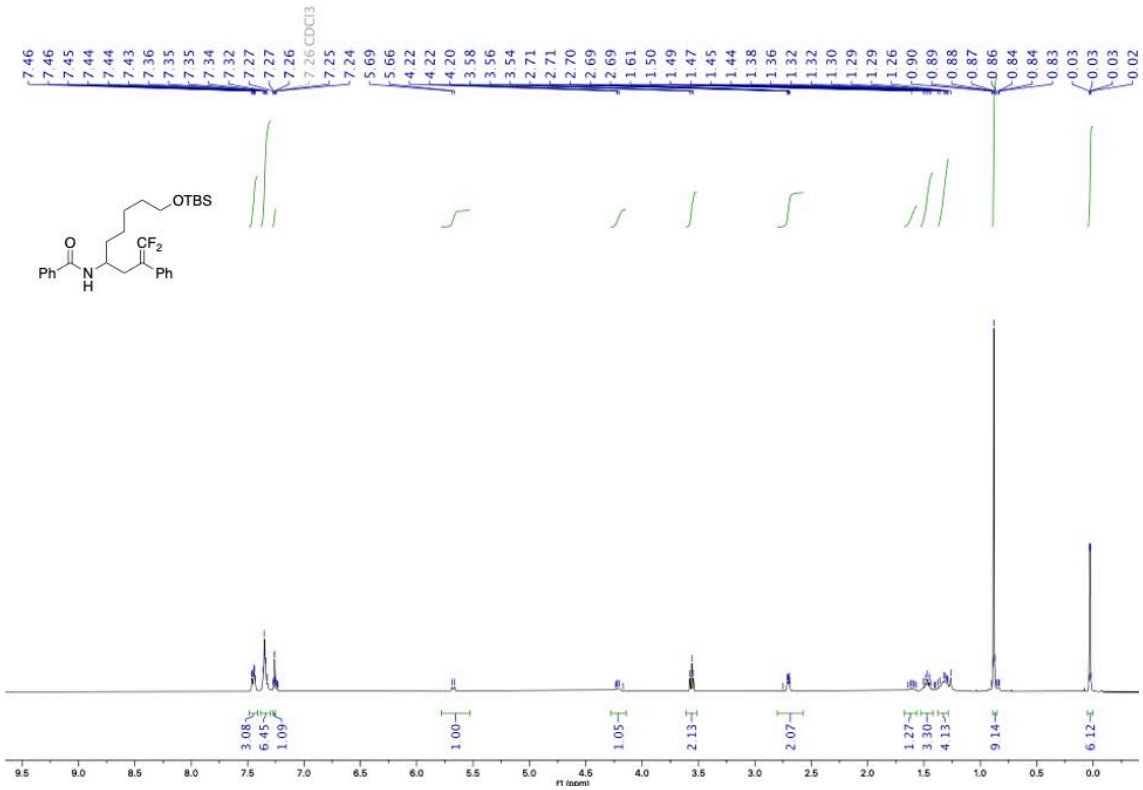
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3n**



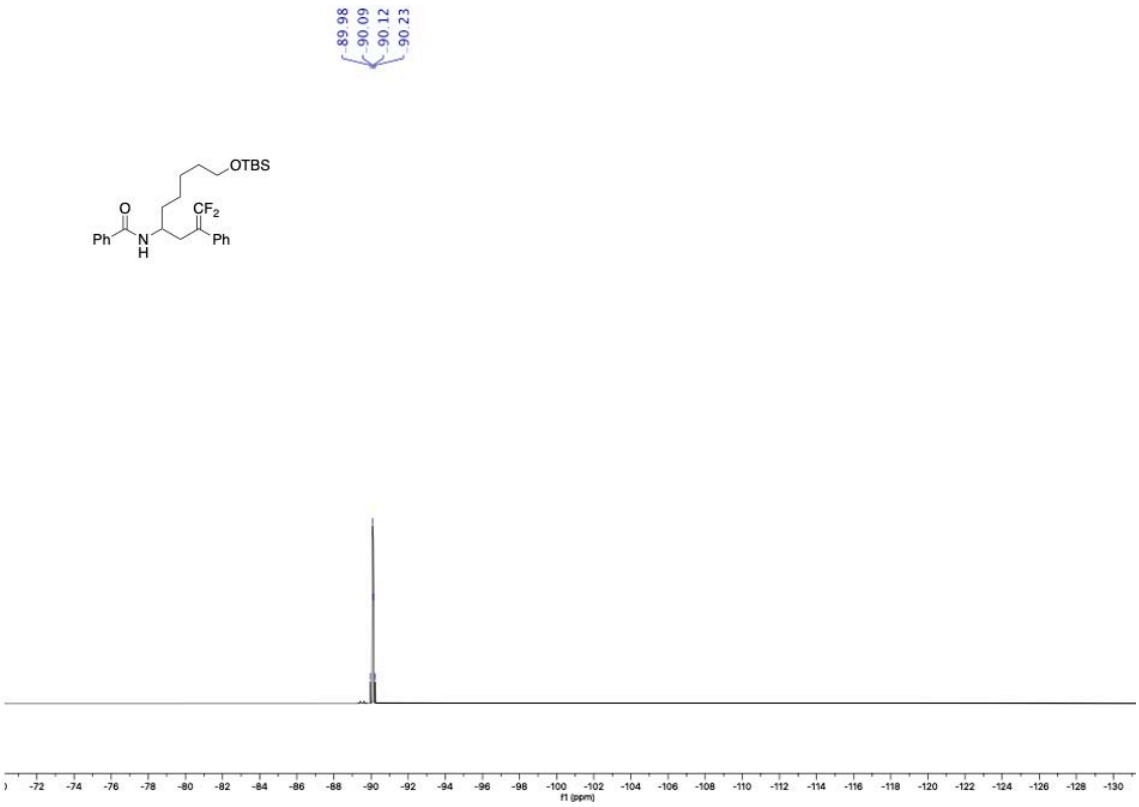
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3n**



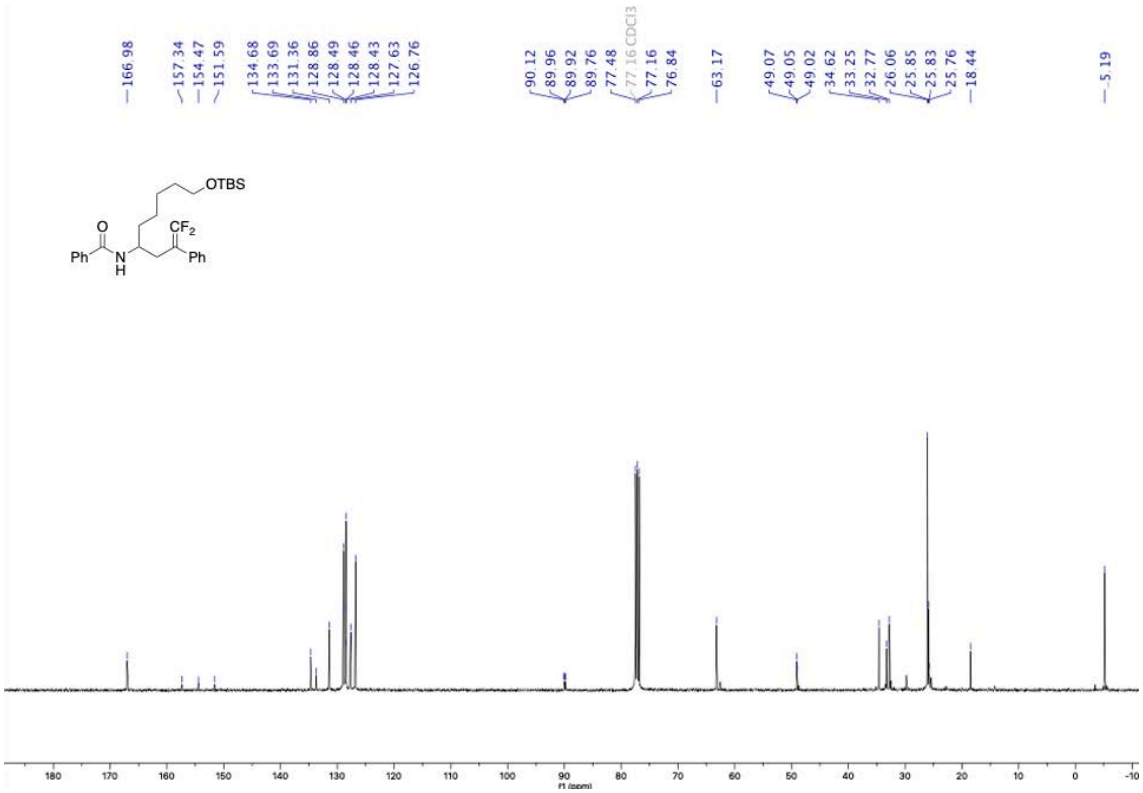
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3n**



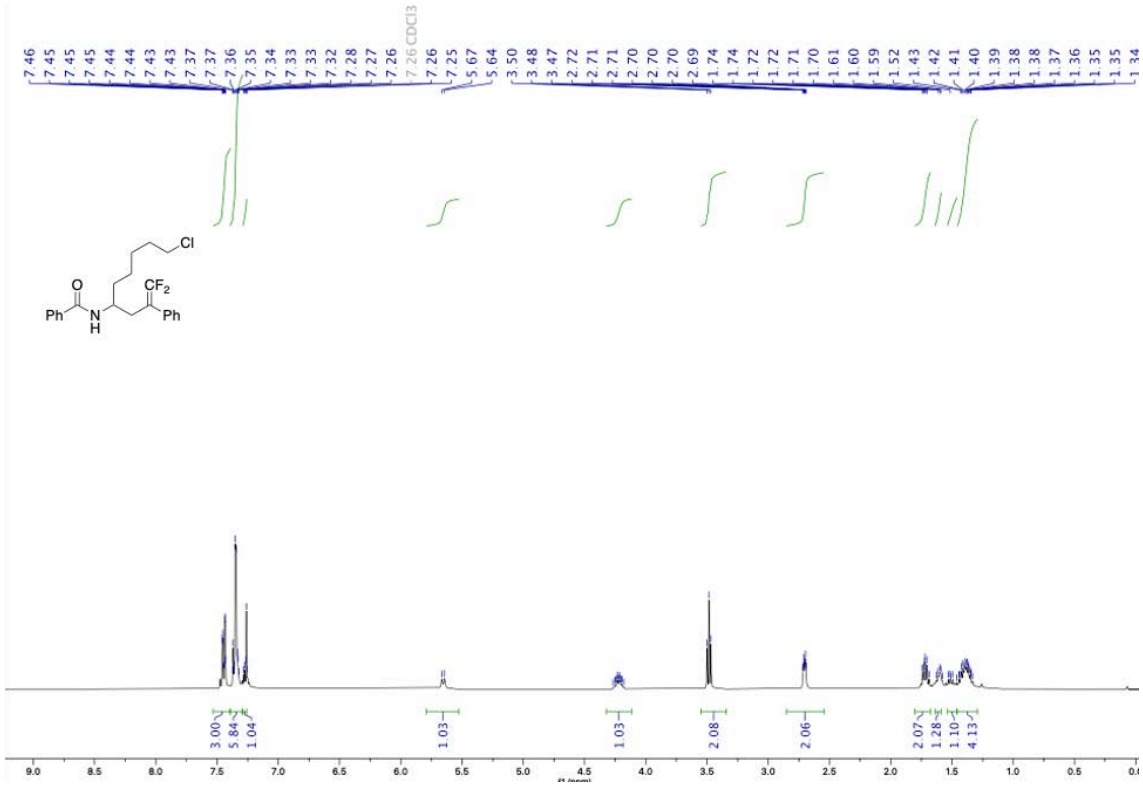
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3o**



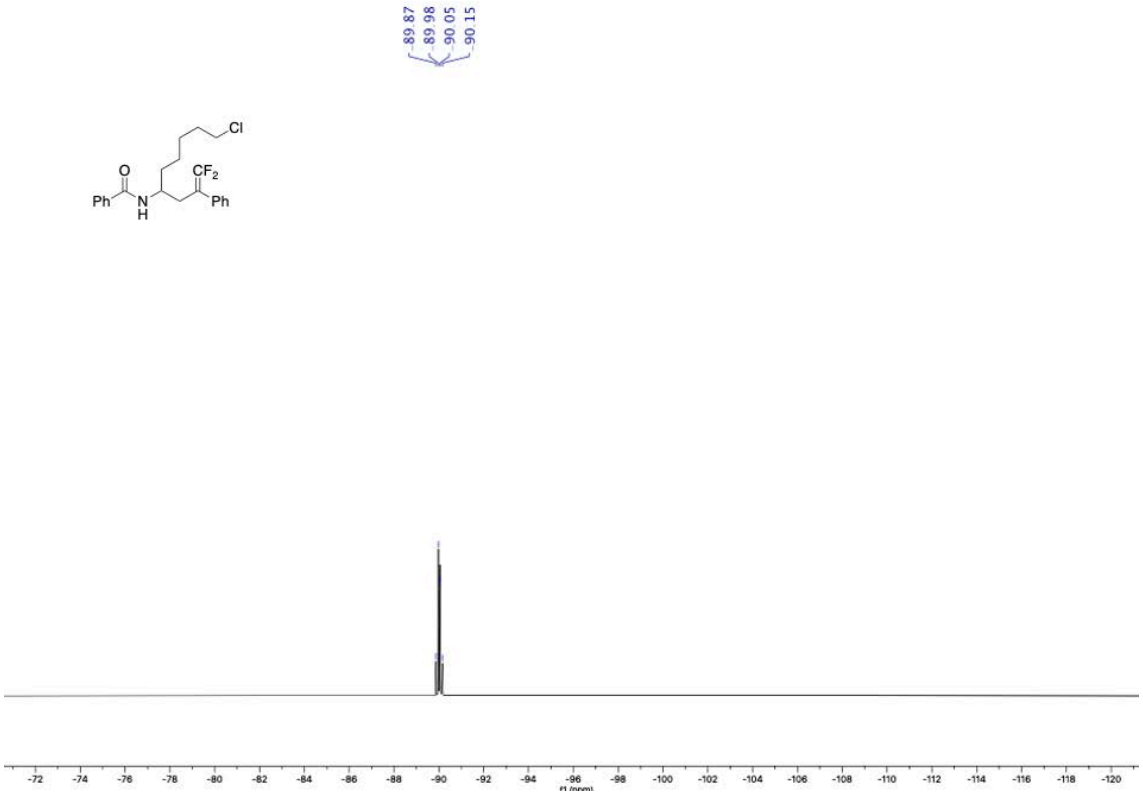
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3o**



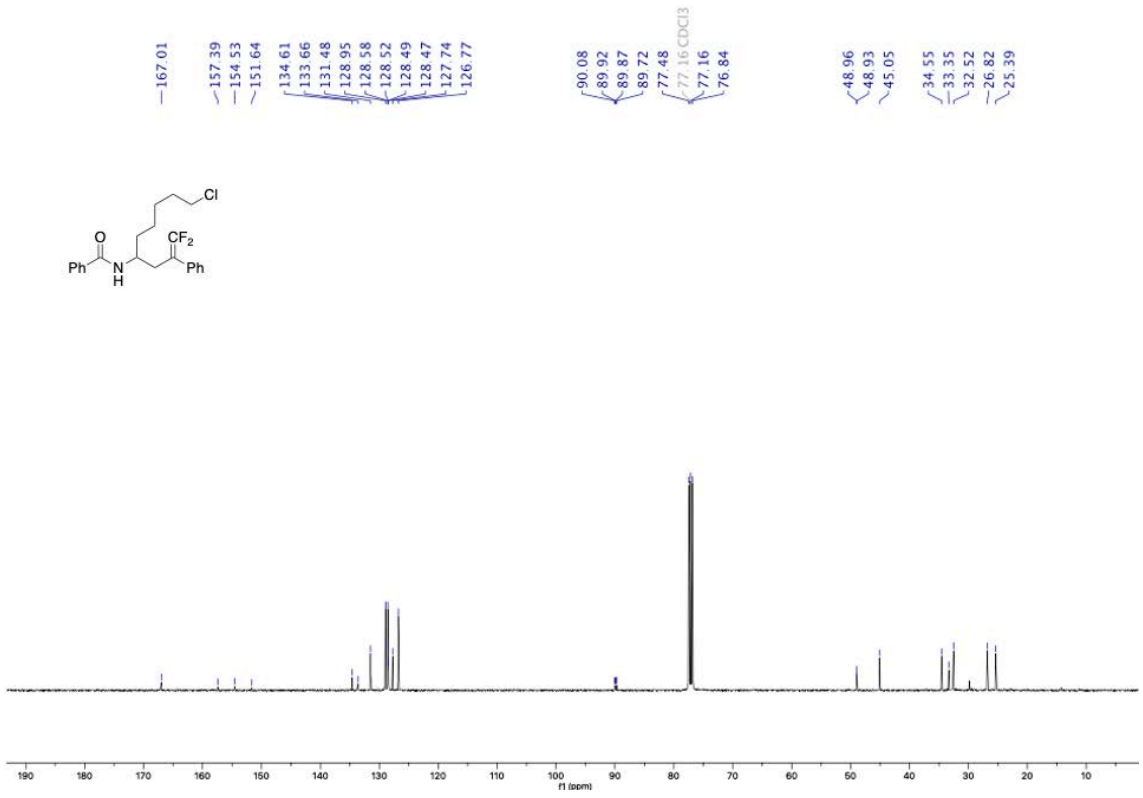
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3o**



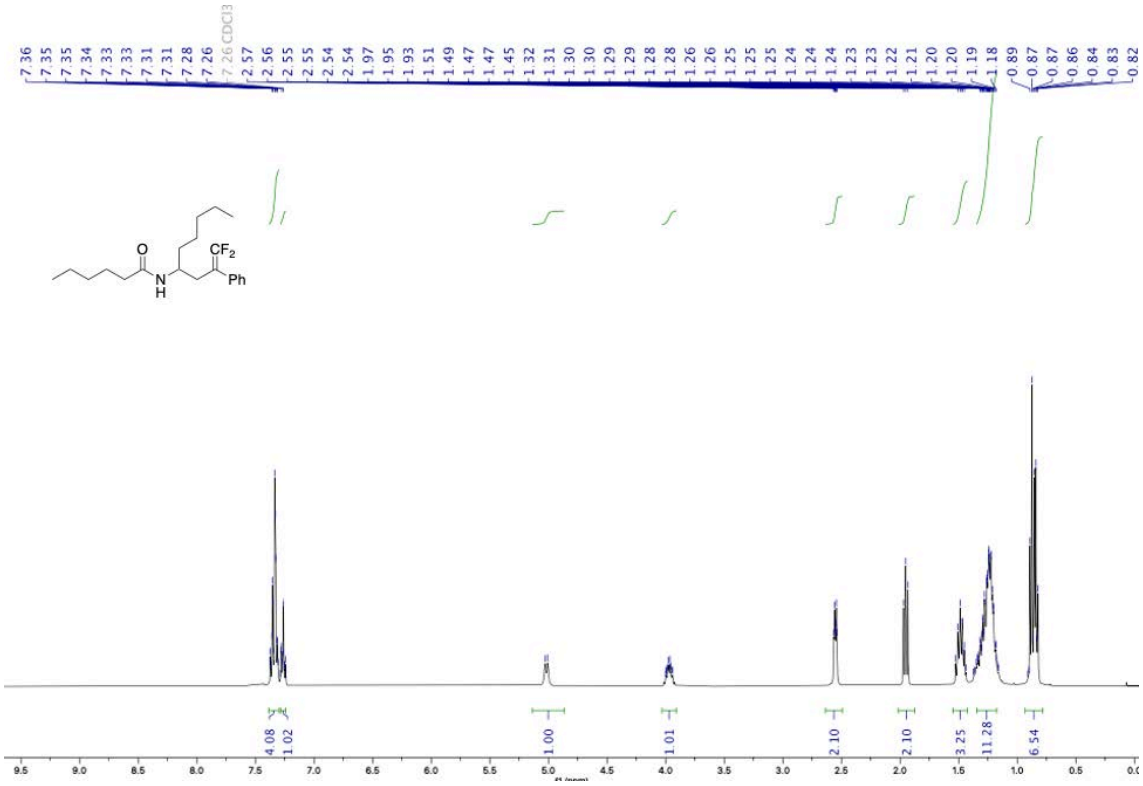
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3p**



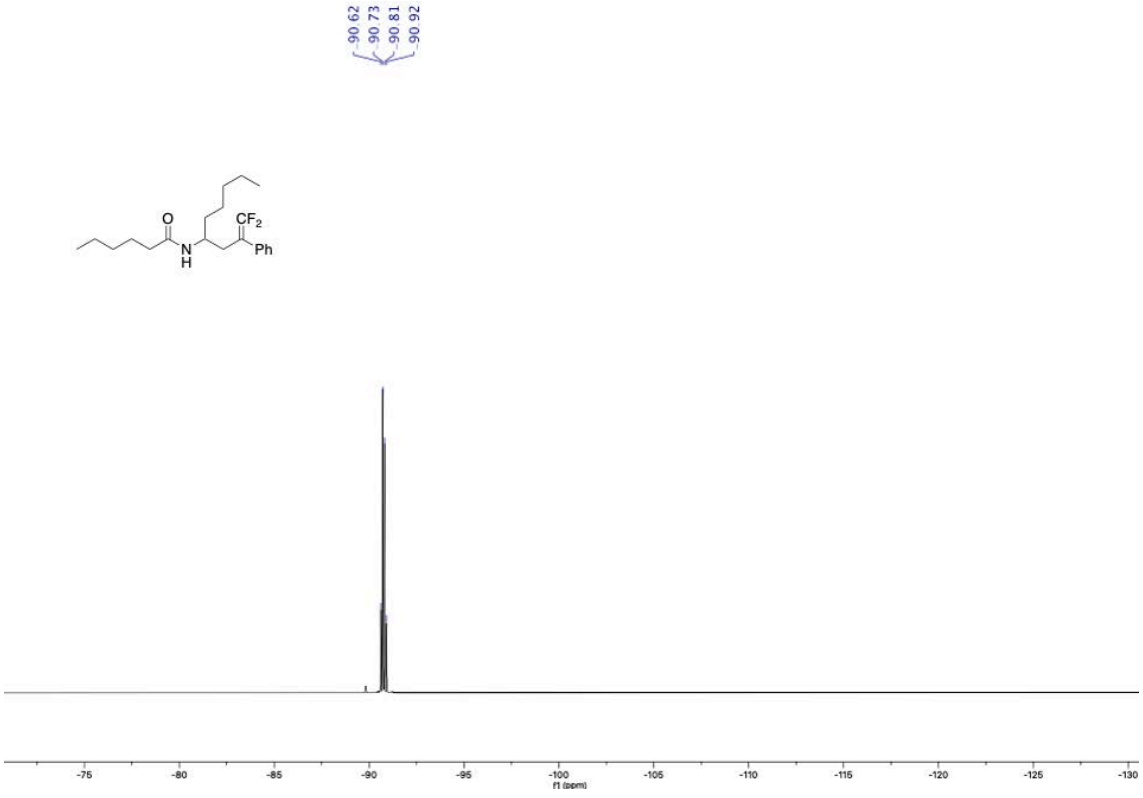
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3p**



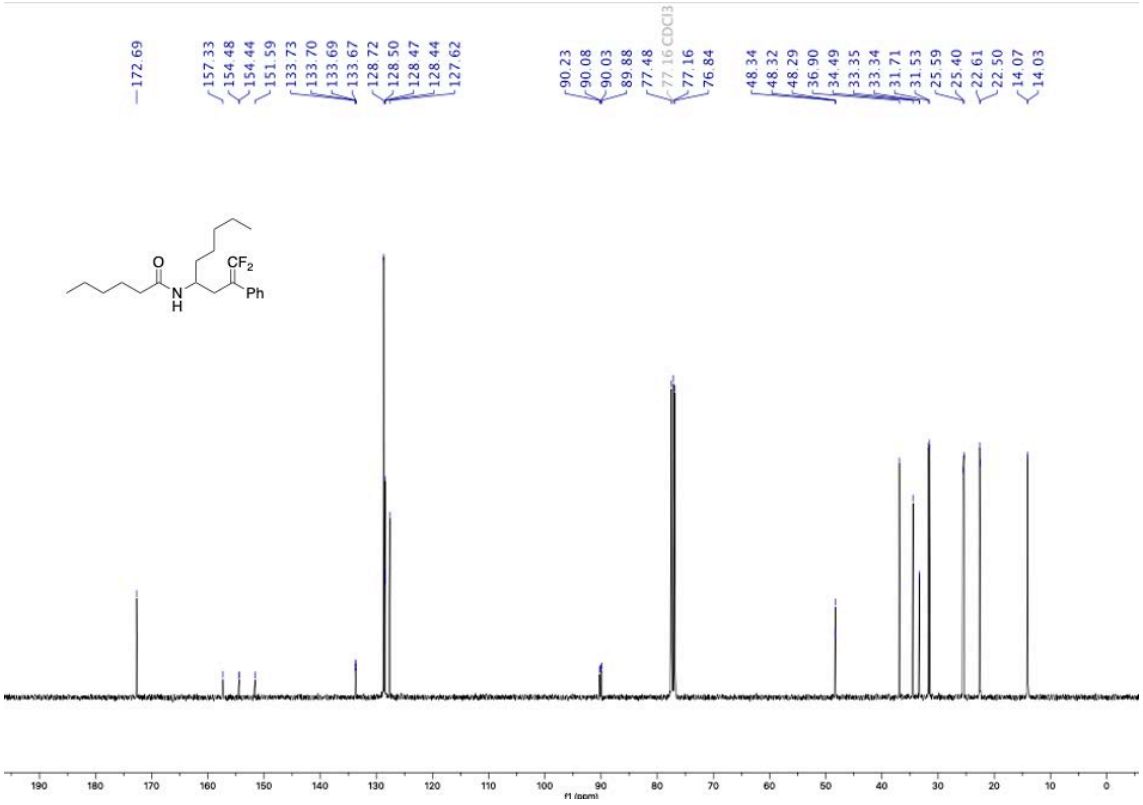
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3p**



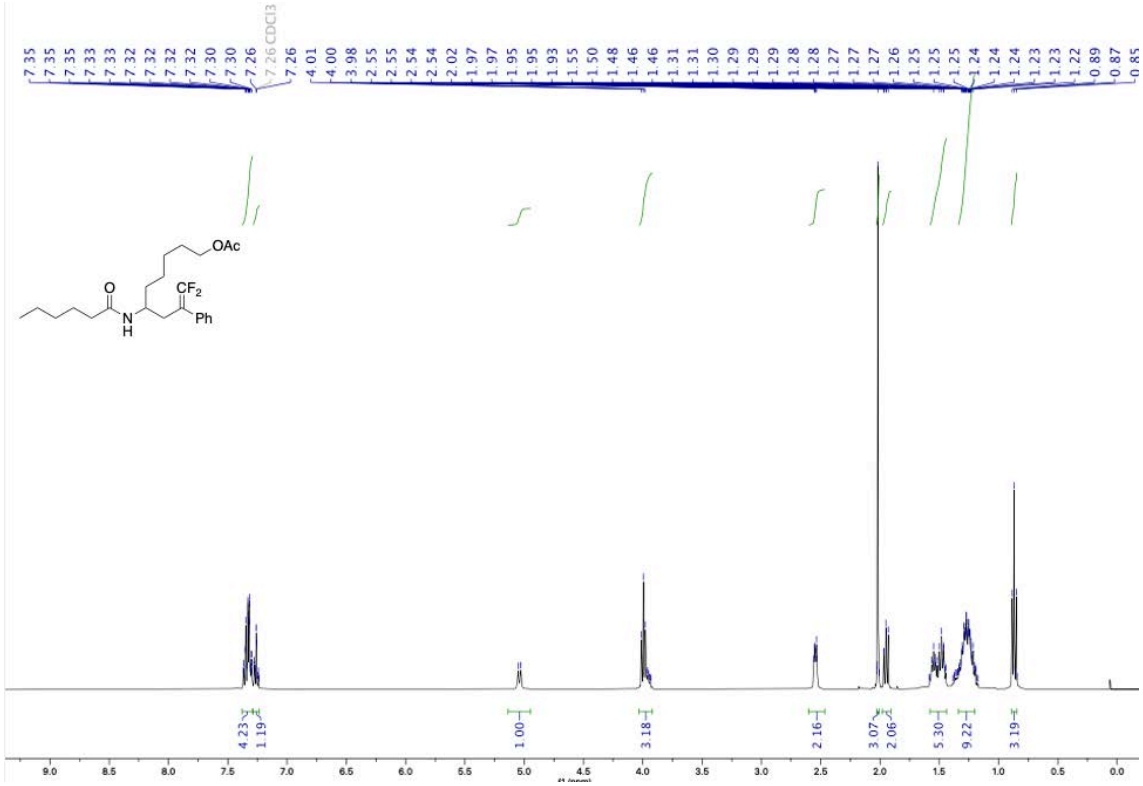
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3q**



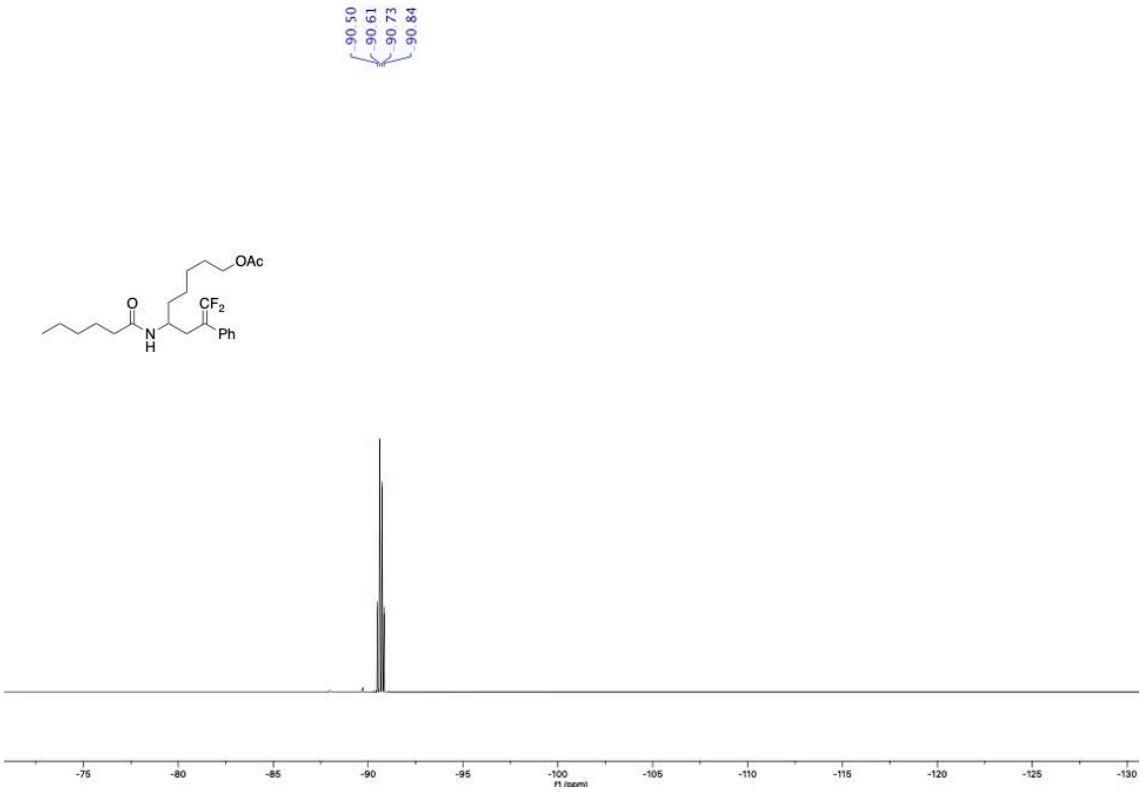
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3q**



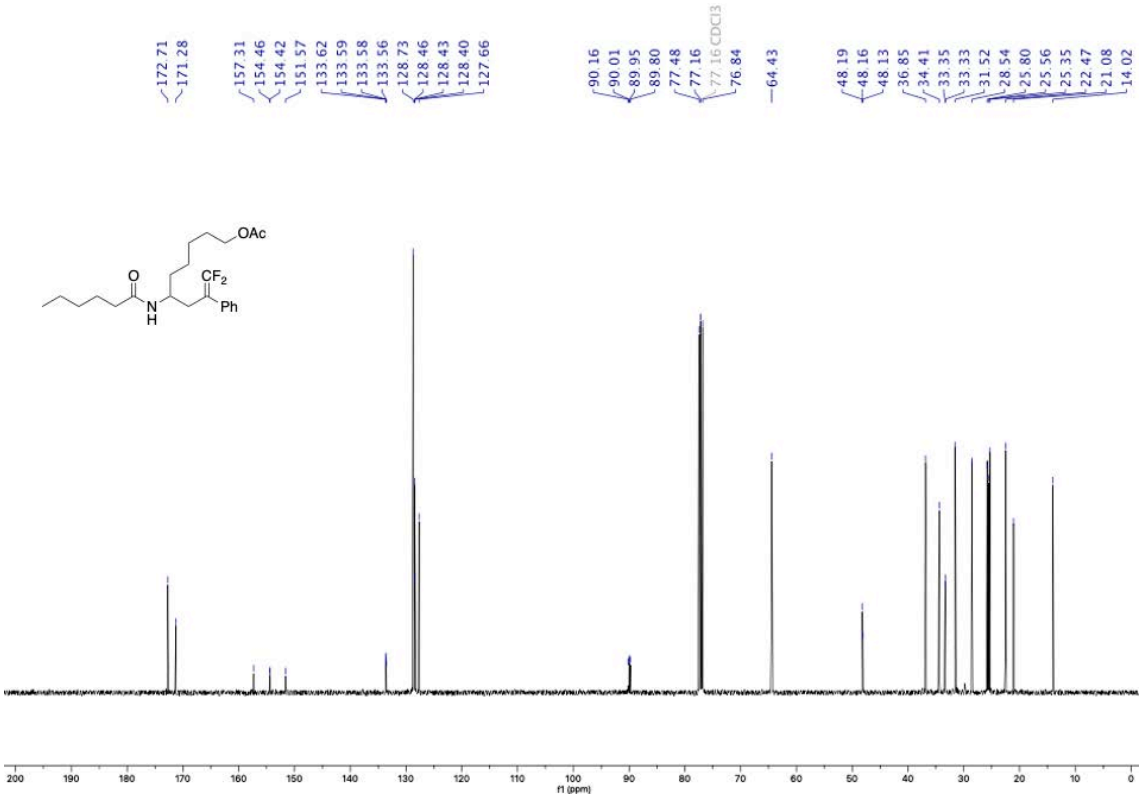
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3q**



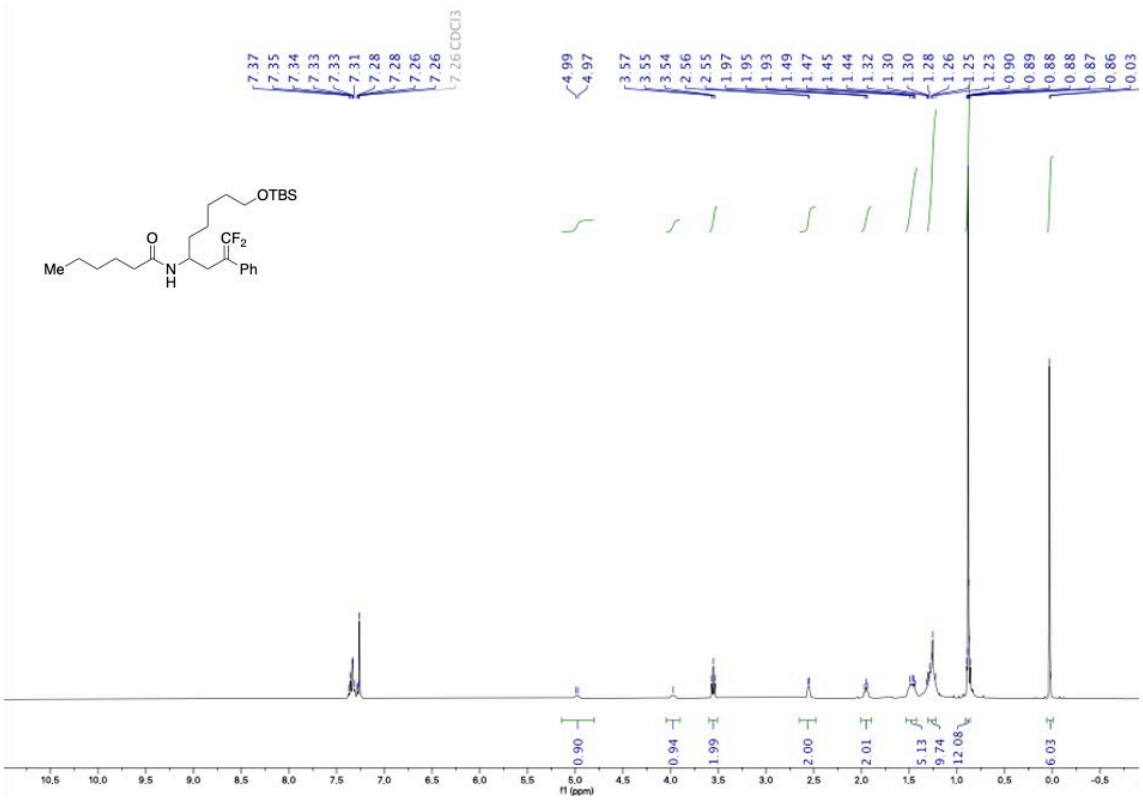
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3r**



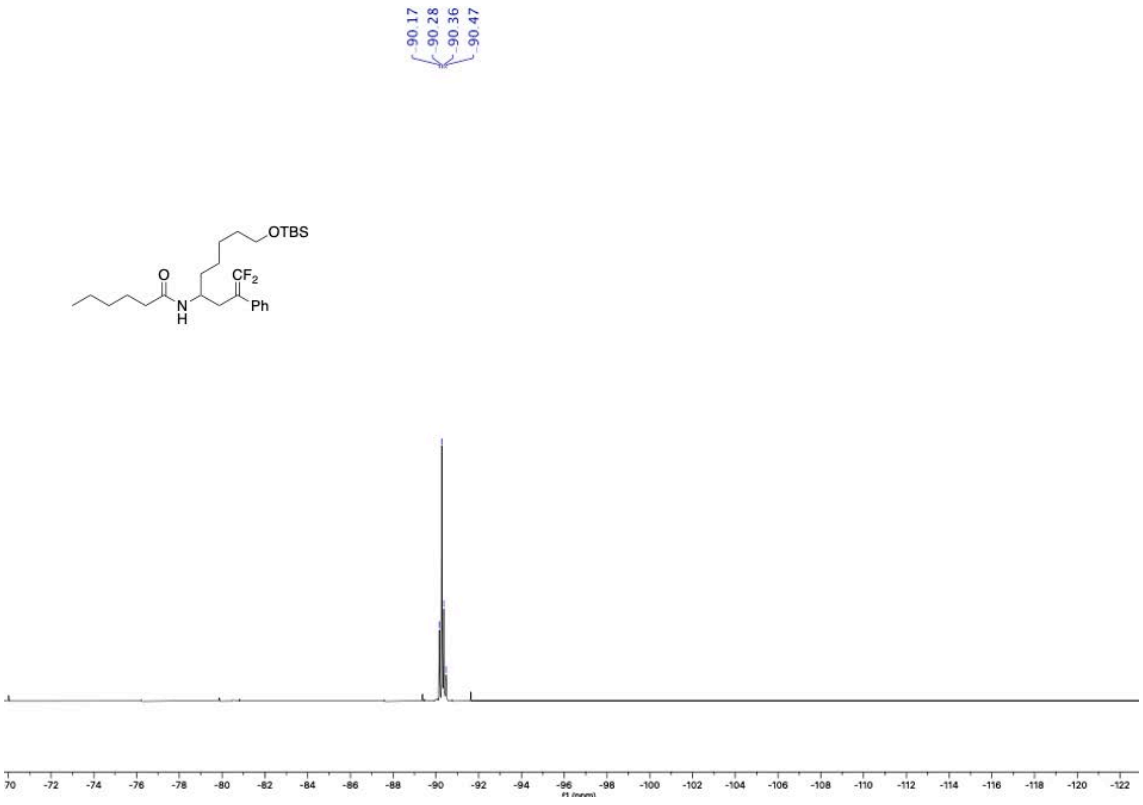
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3r**



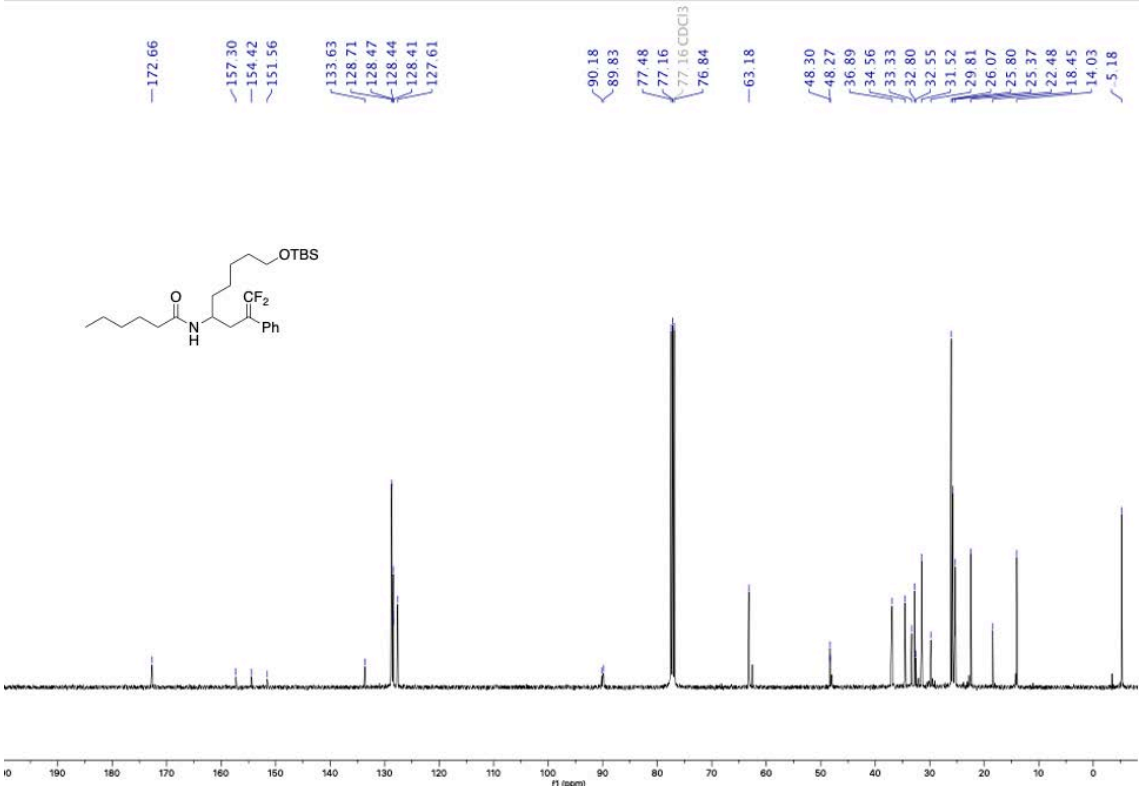
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3r**



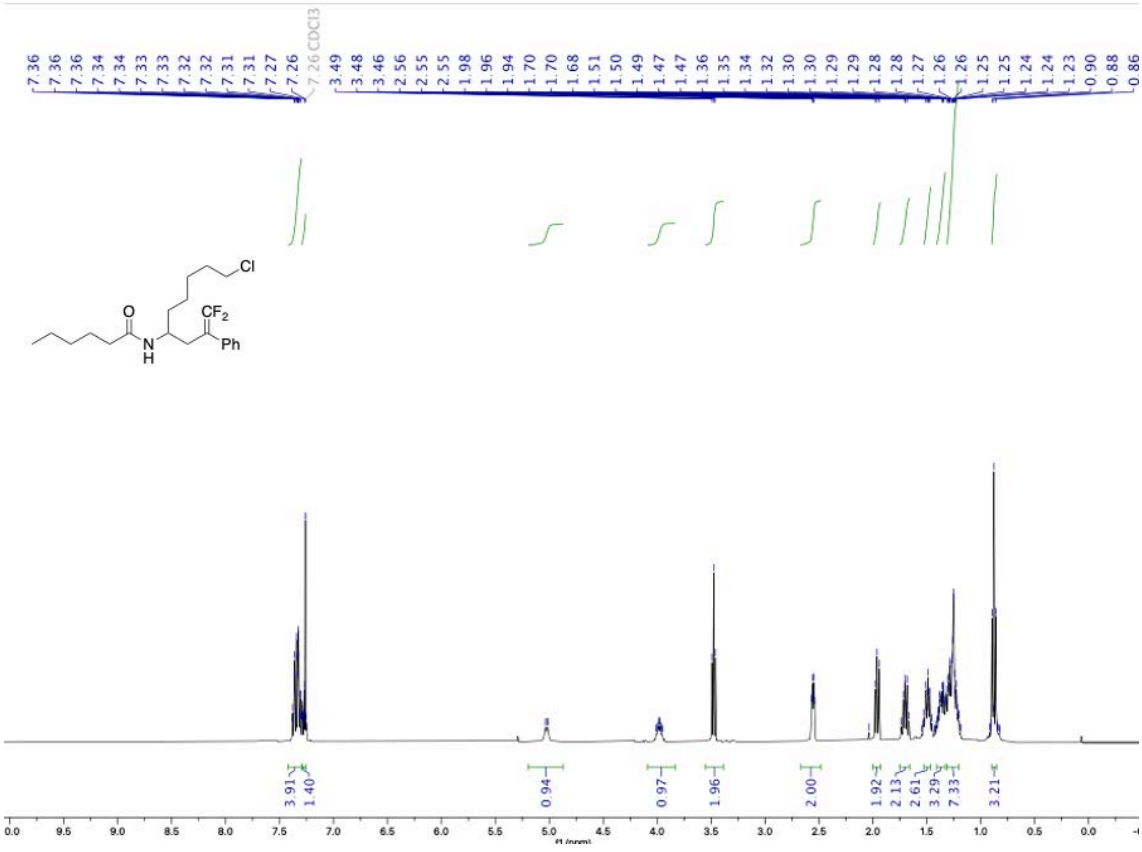
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3s**



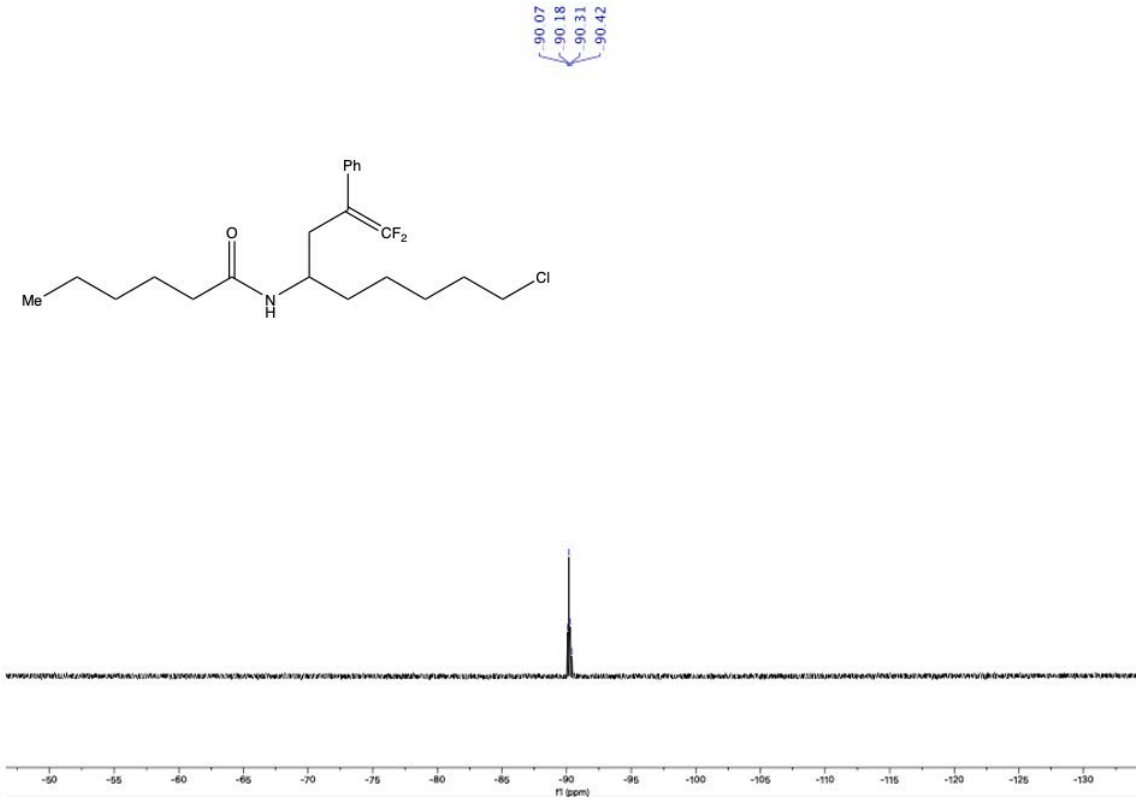
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3s**



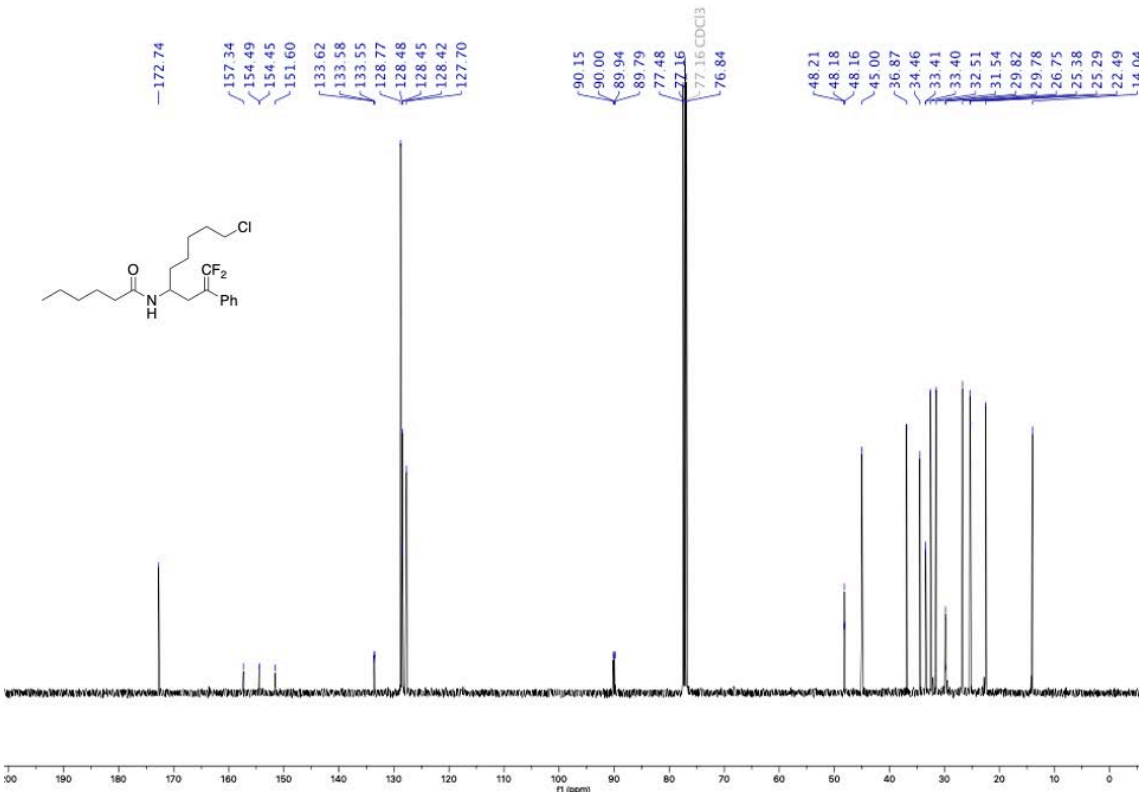
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3s**



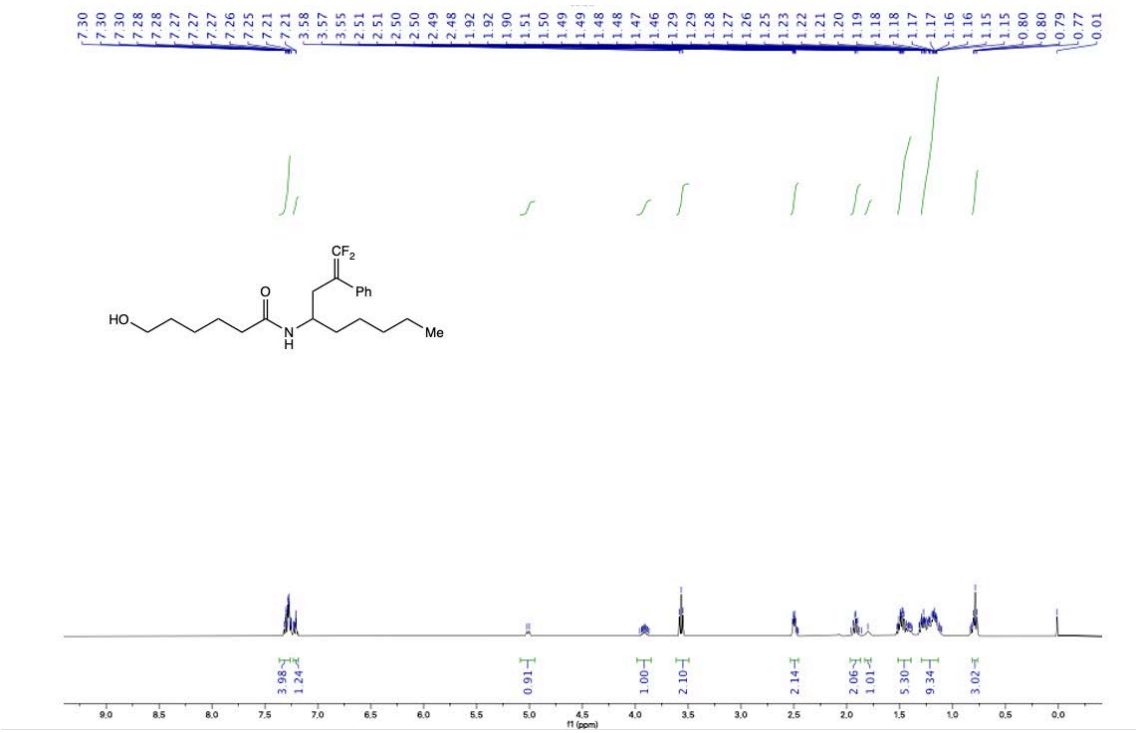
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3t**



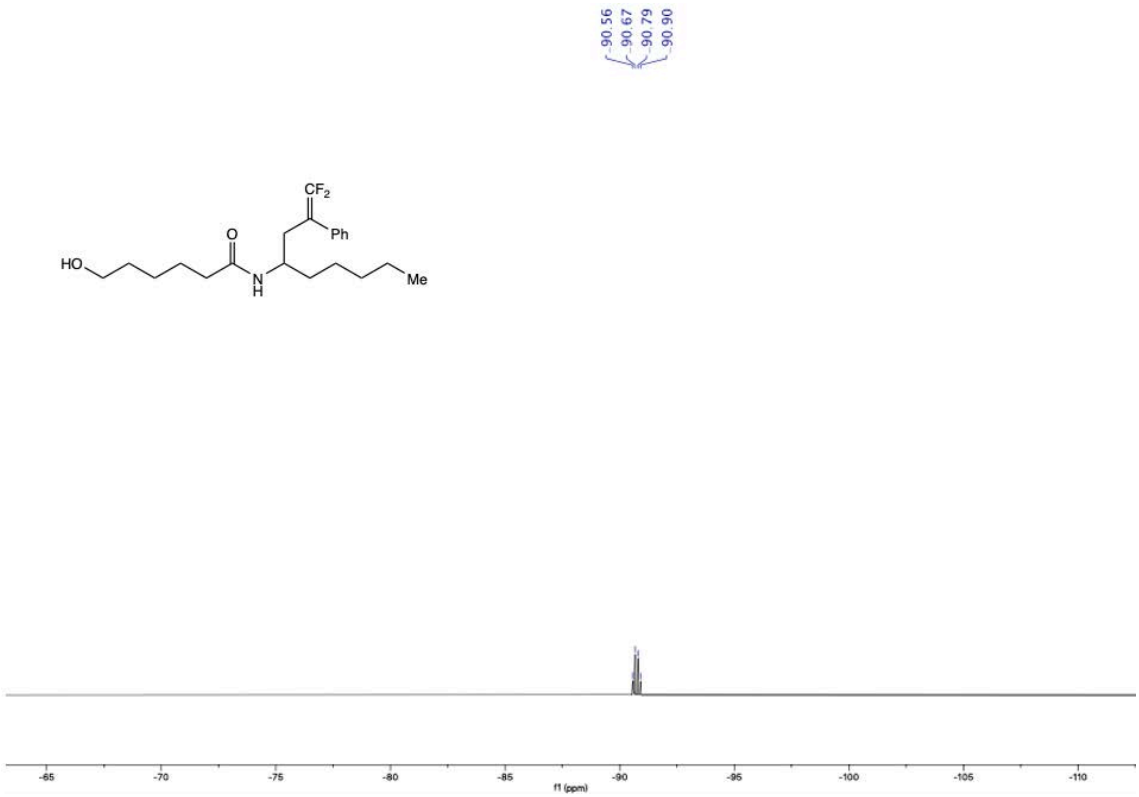
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3t**



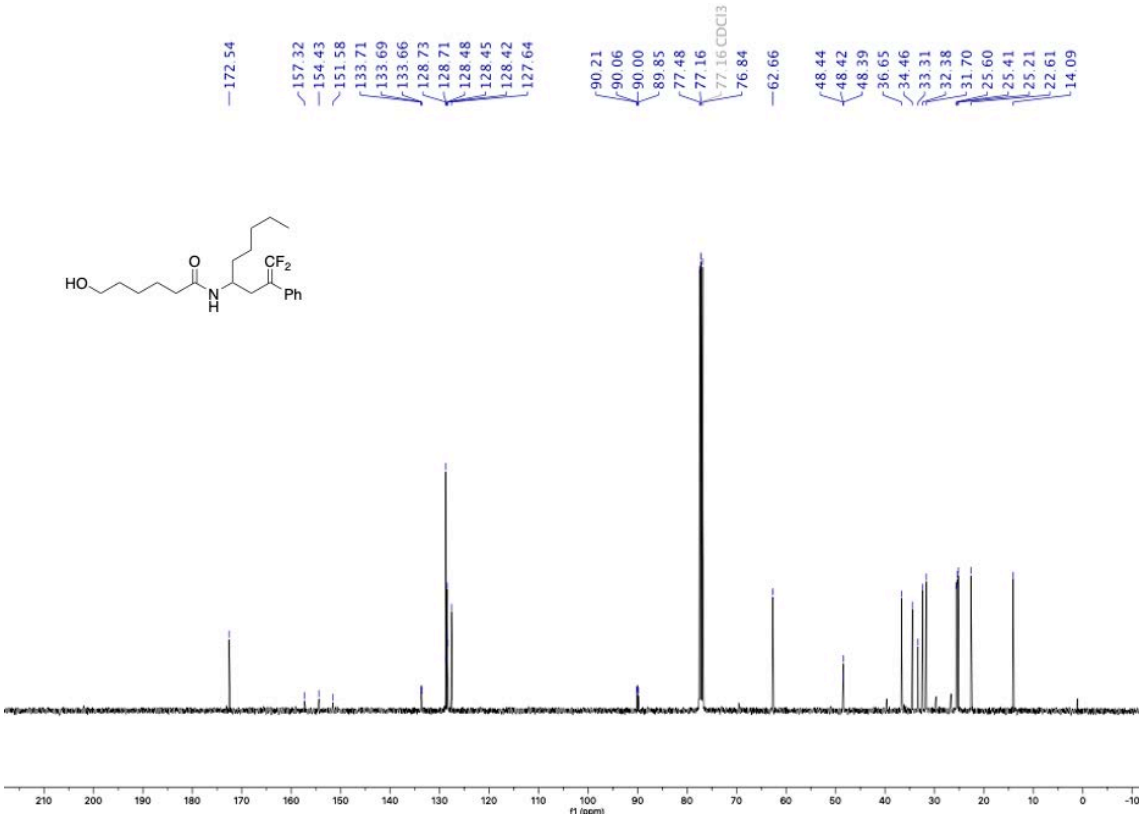
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3t**



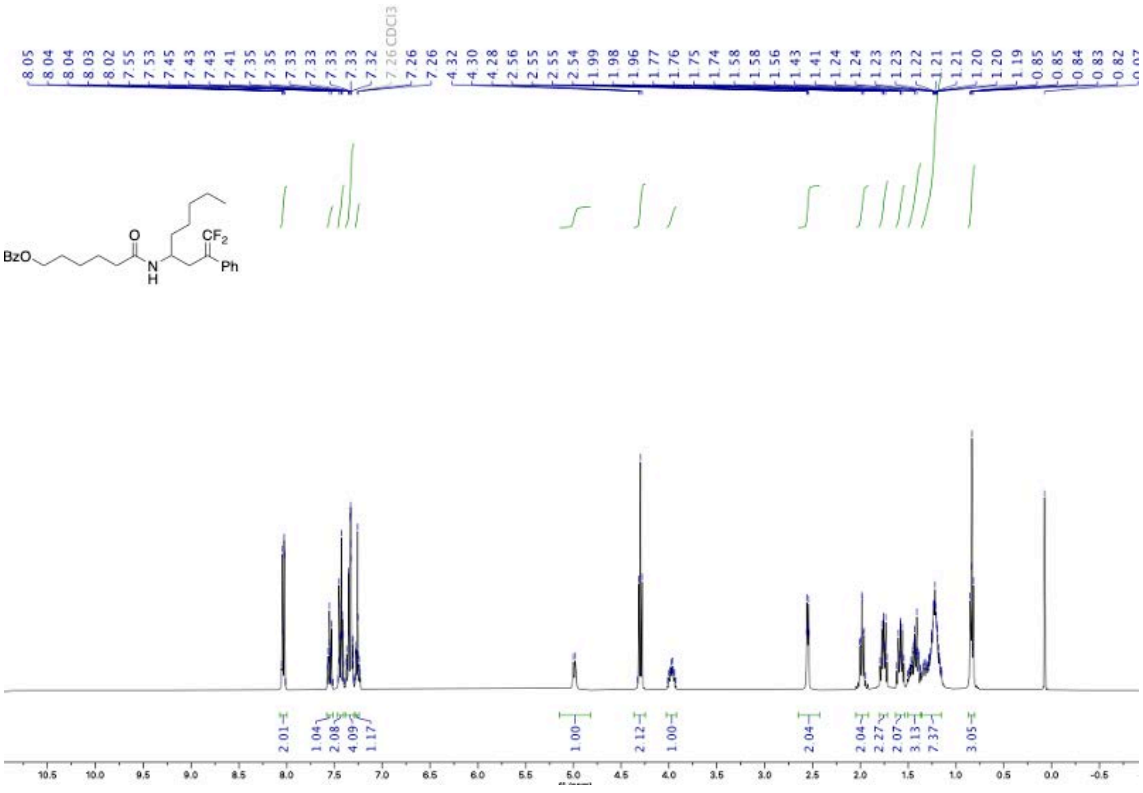
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3u**



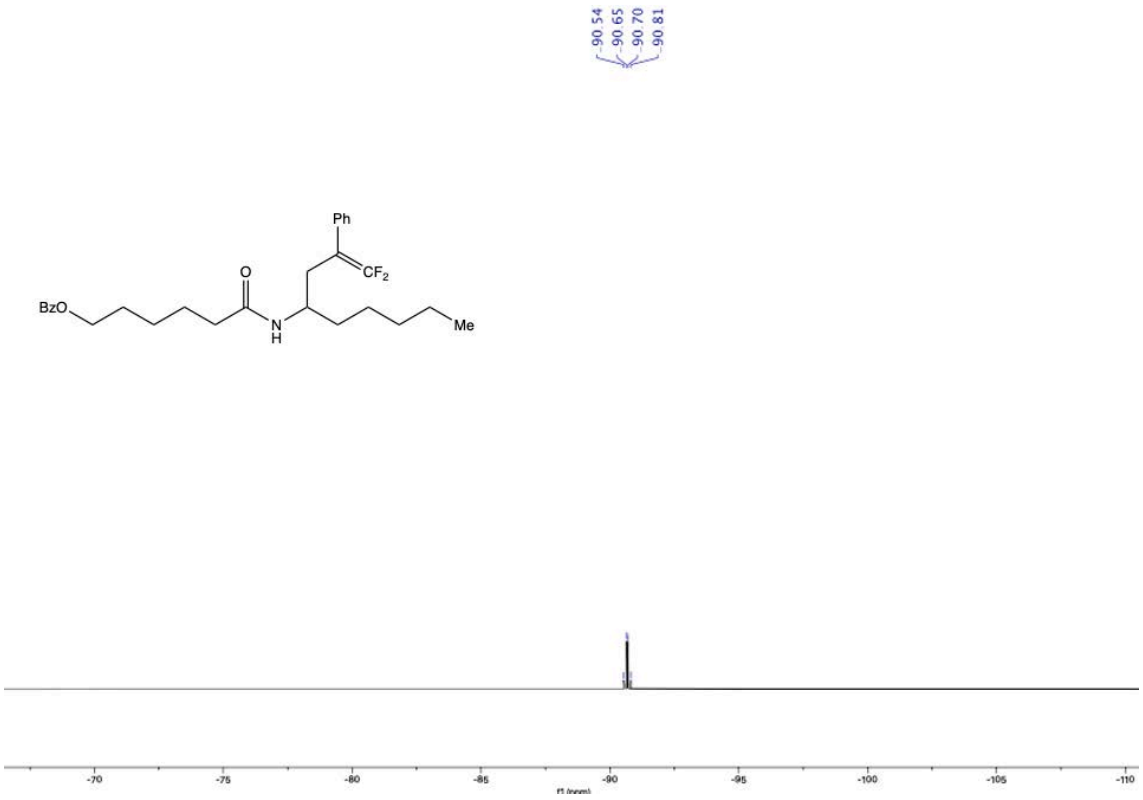
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3u**



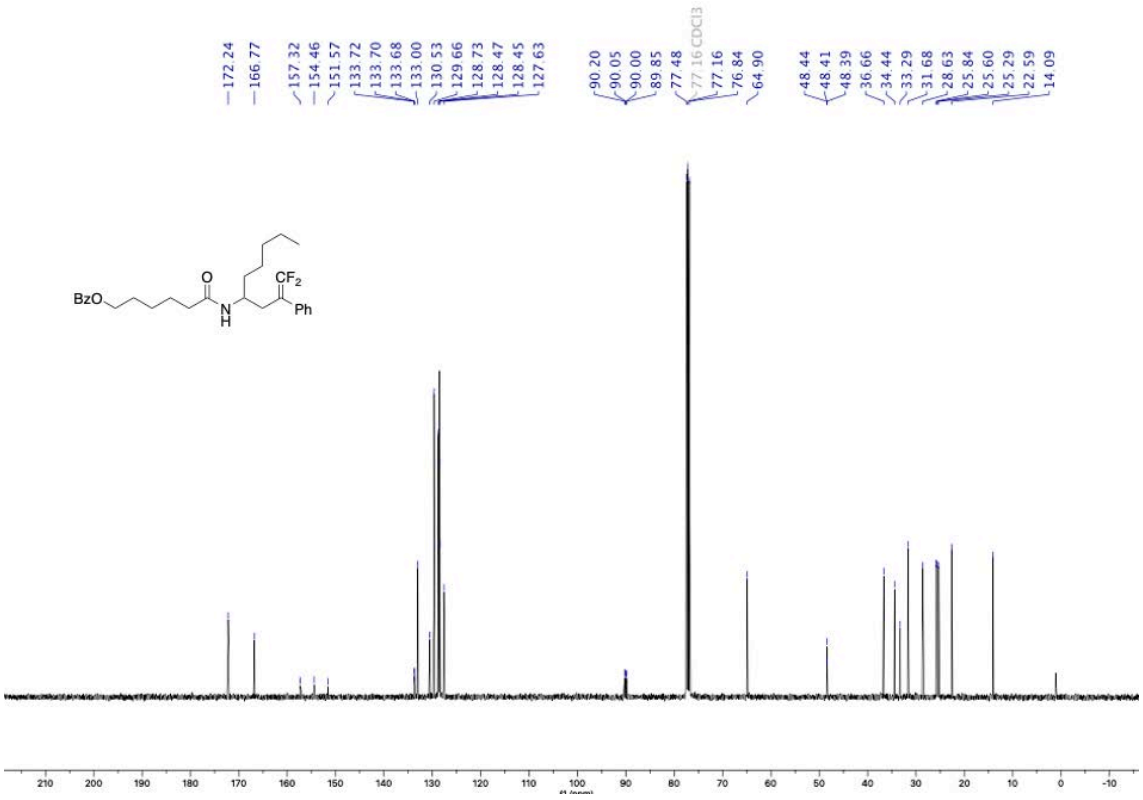
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3u**



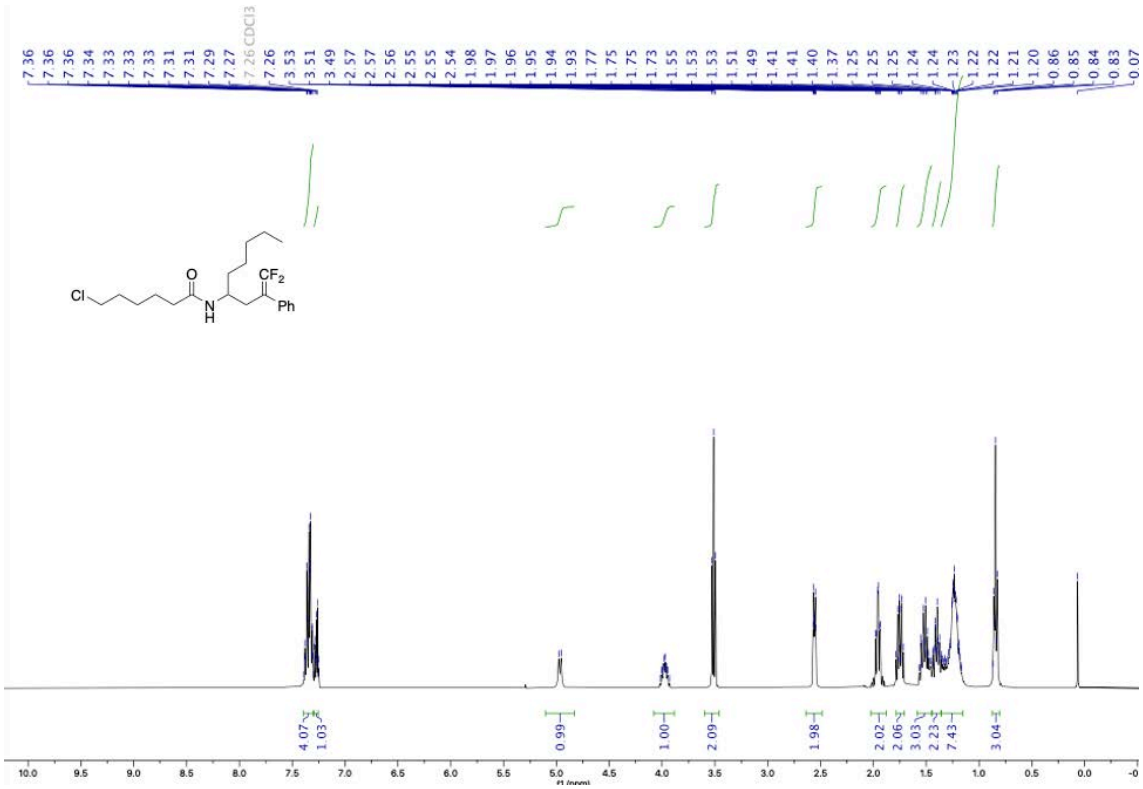
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3v**



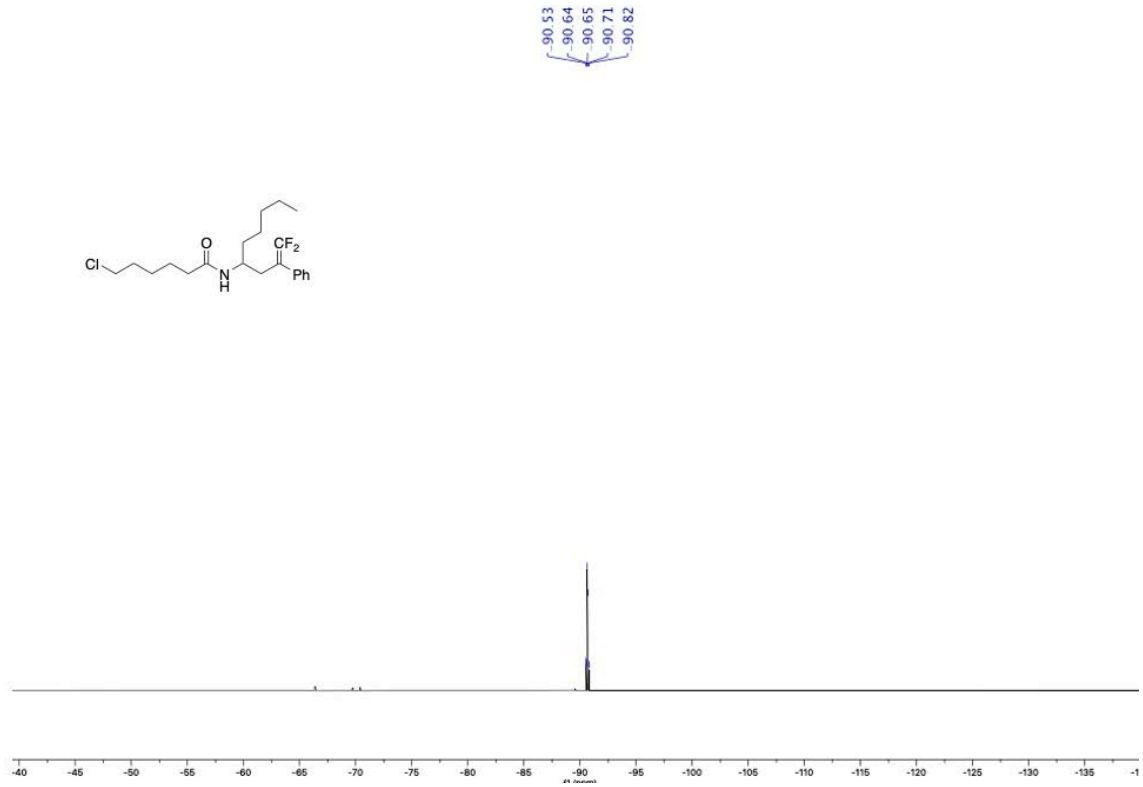
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3v**



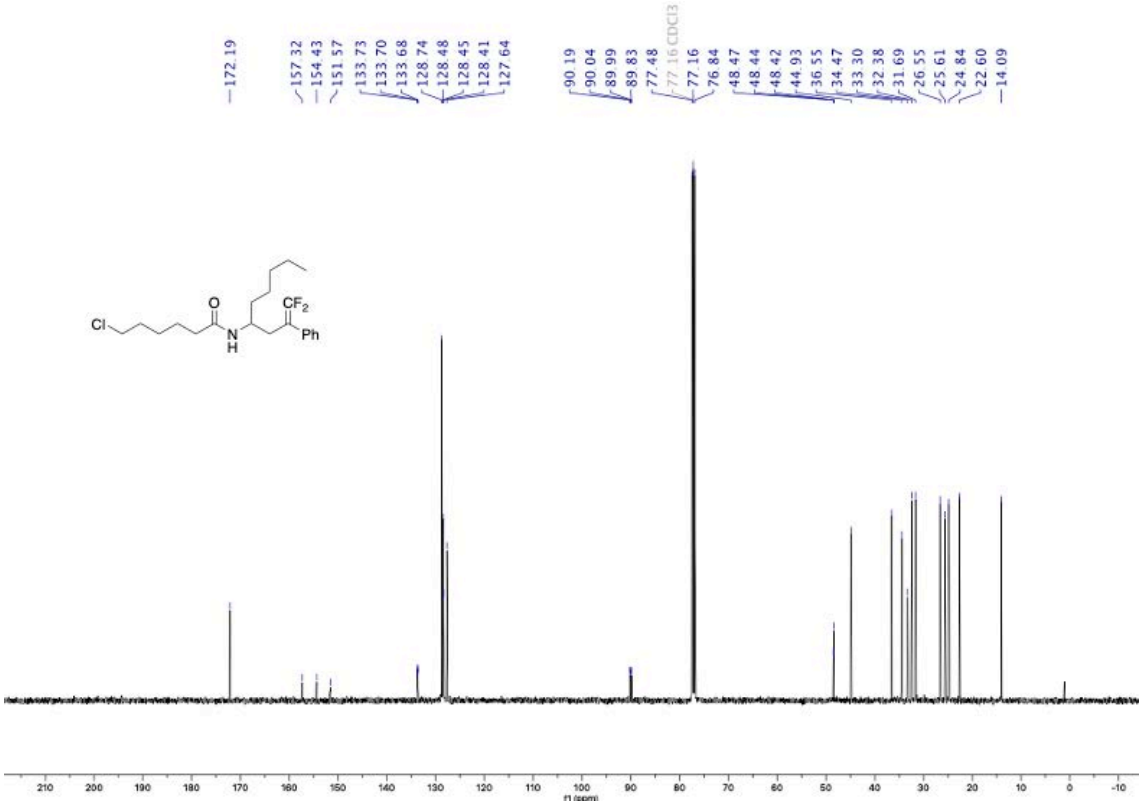
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3v**



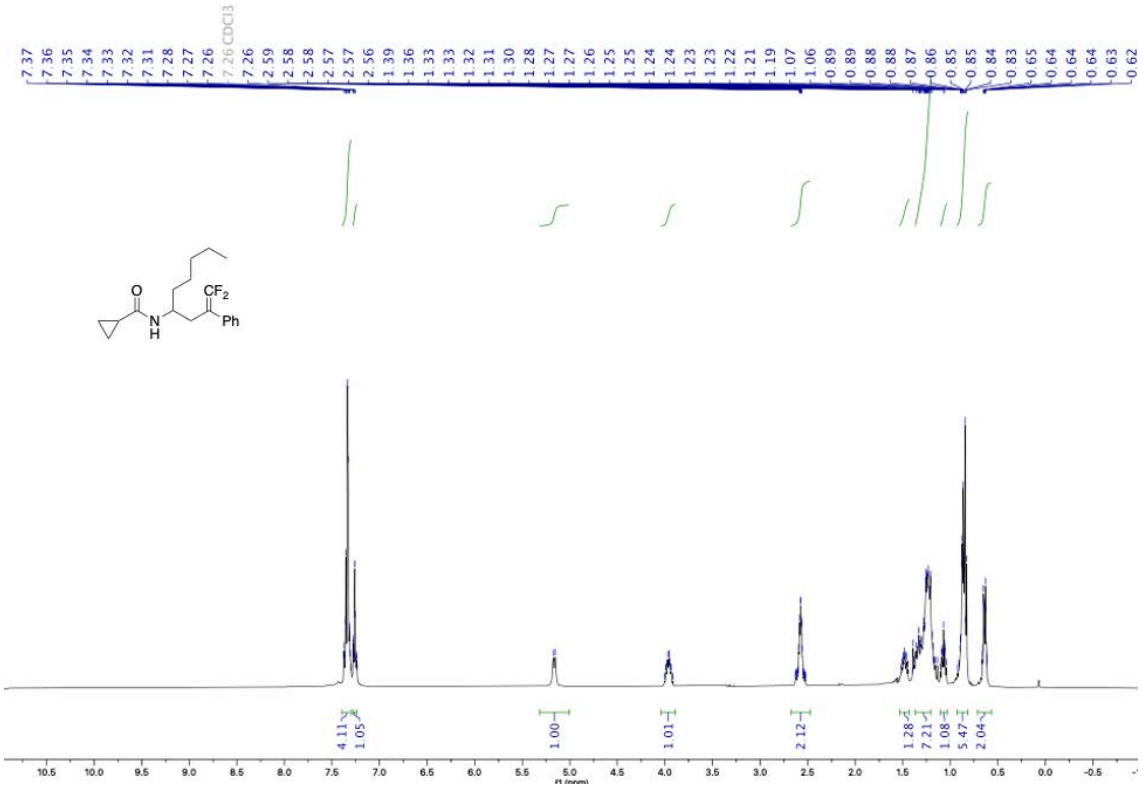
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3w**



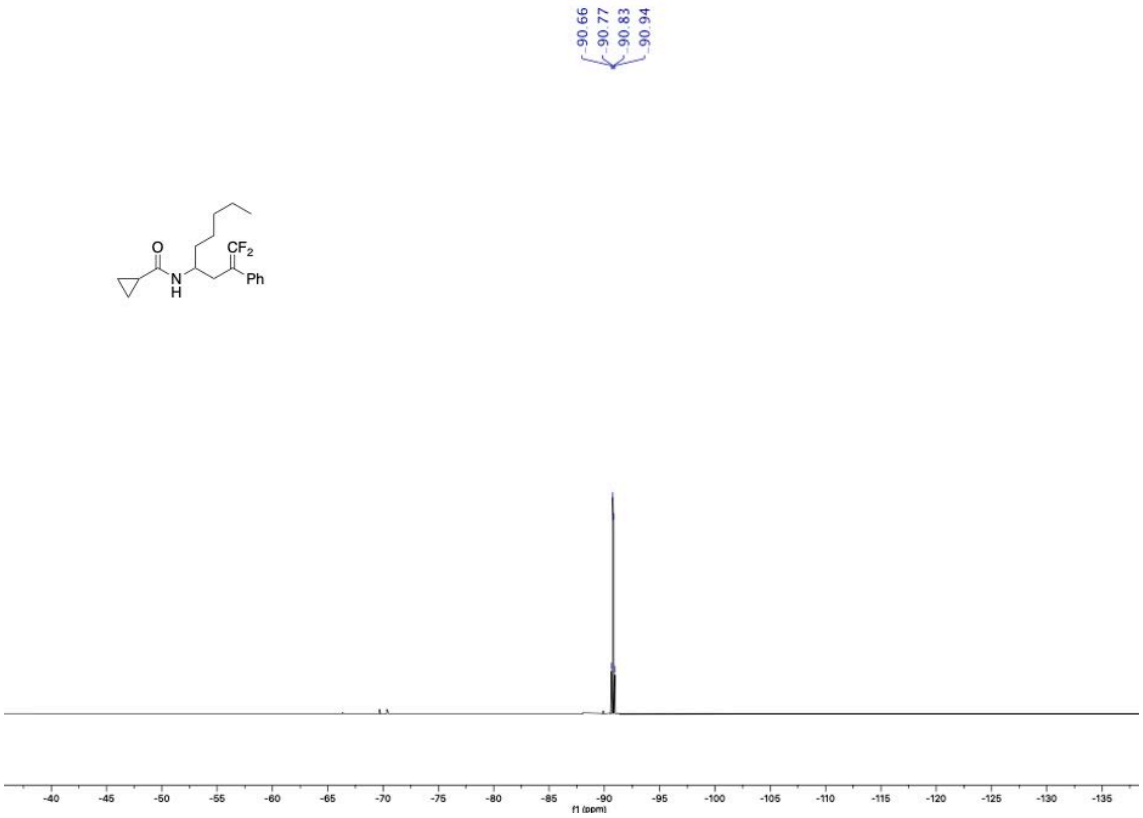
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3w**



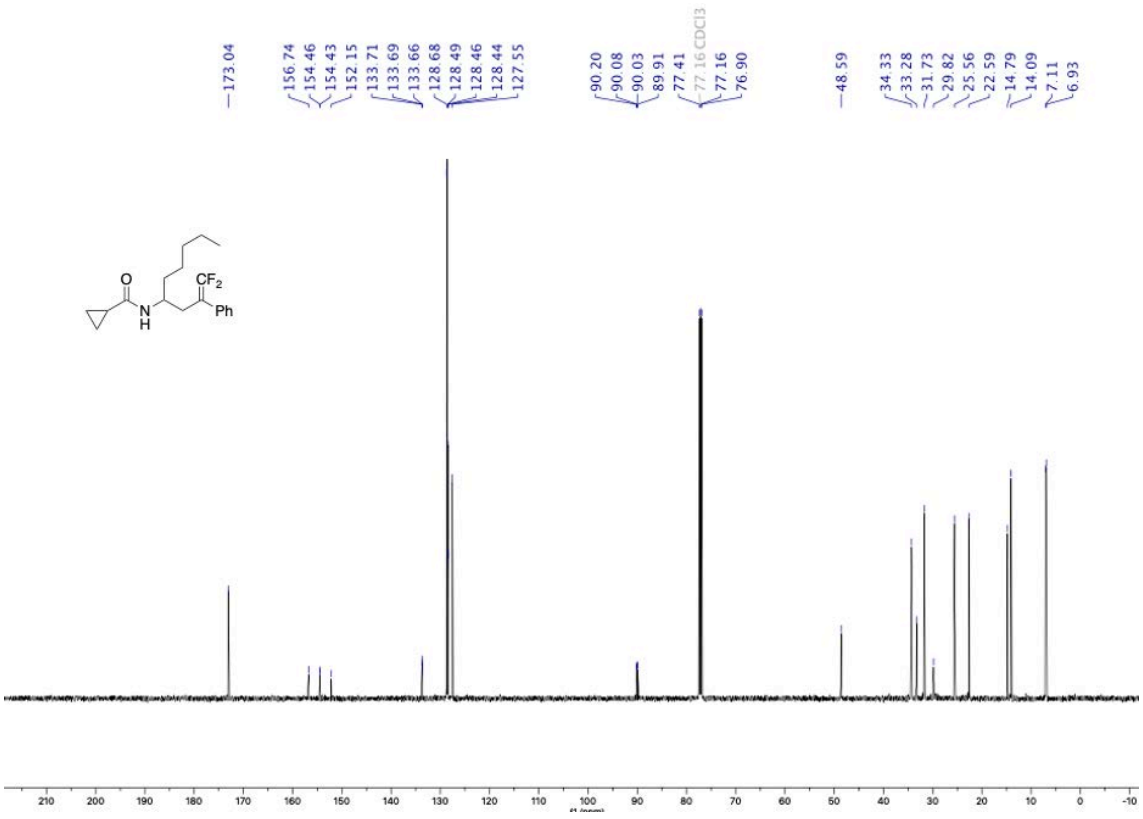
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3w**



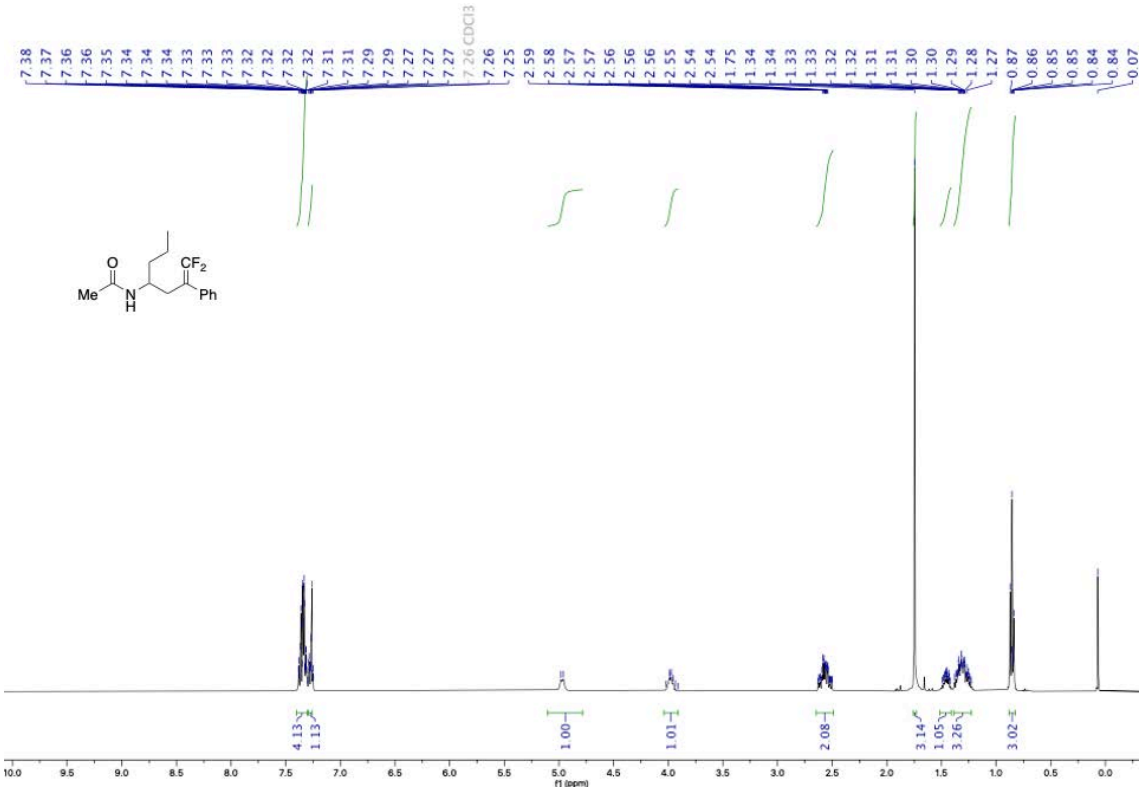
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3x**



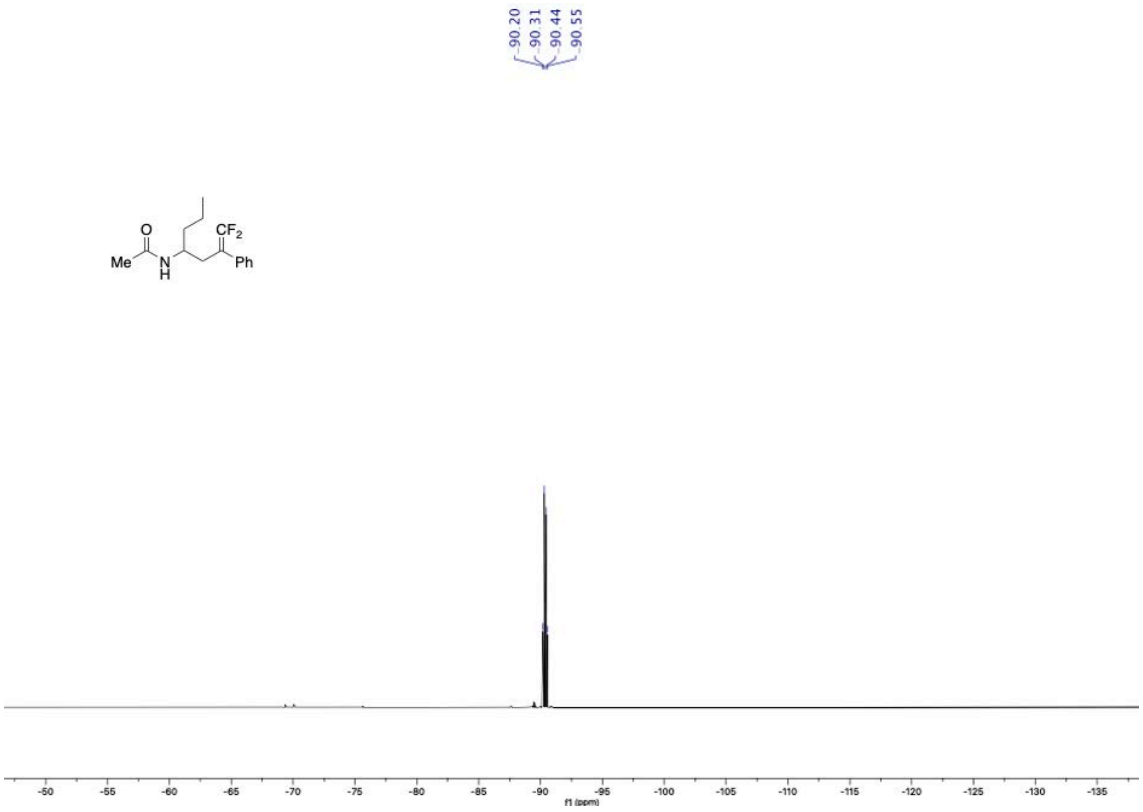
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3x**



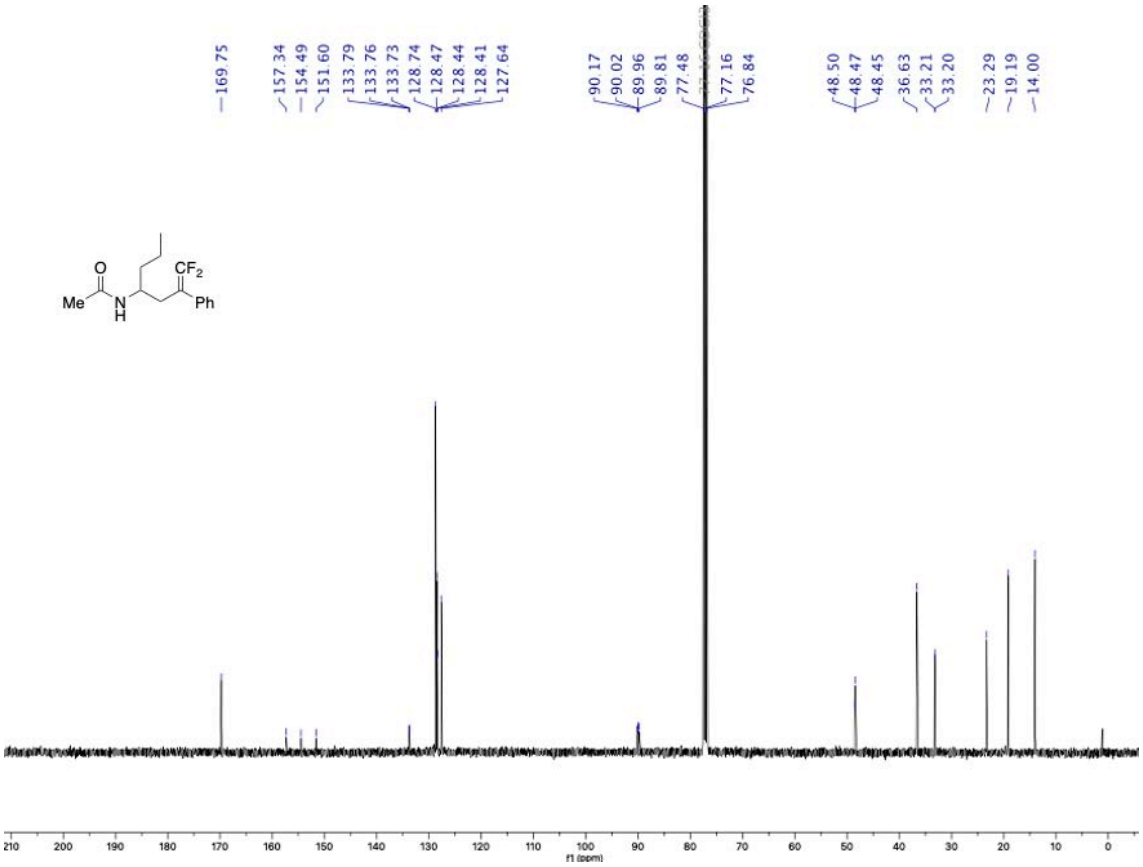
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3x**



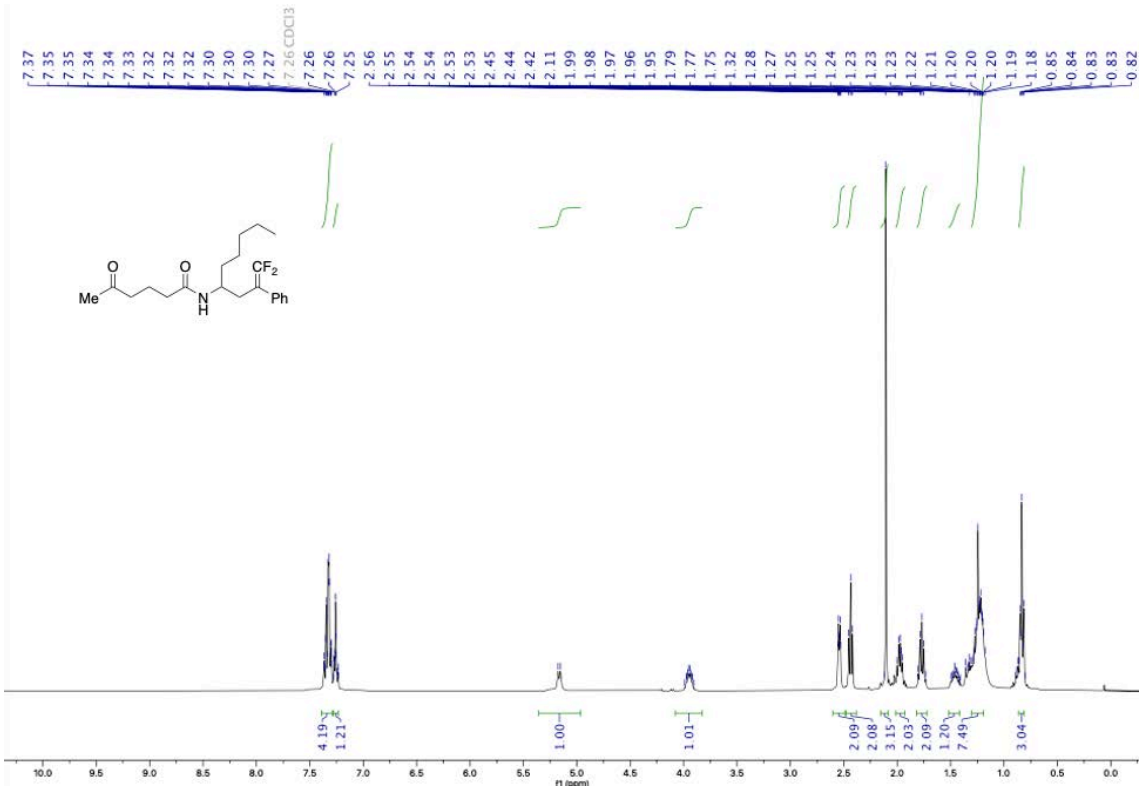
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3y**



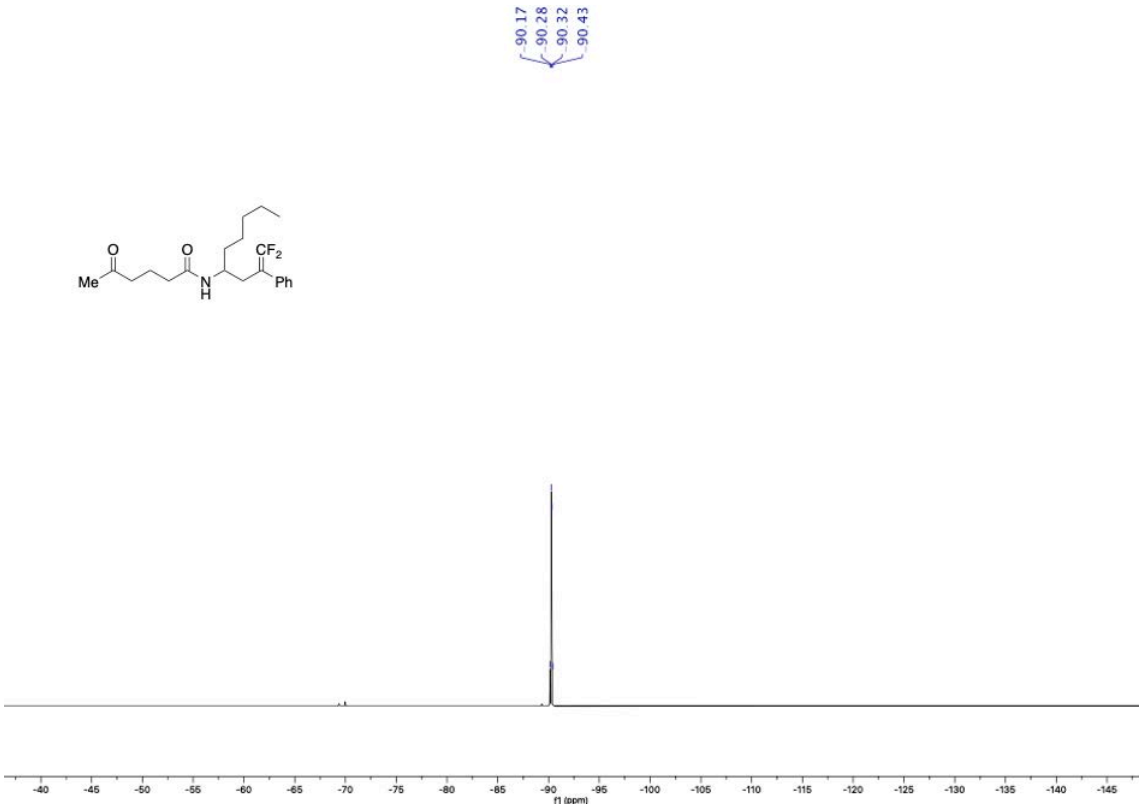
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3y**



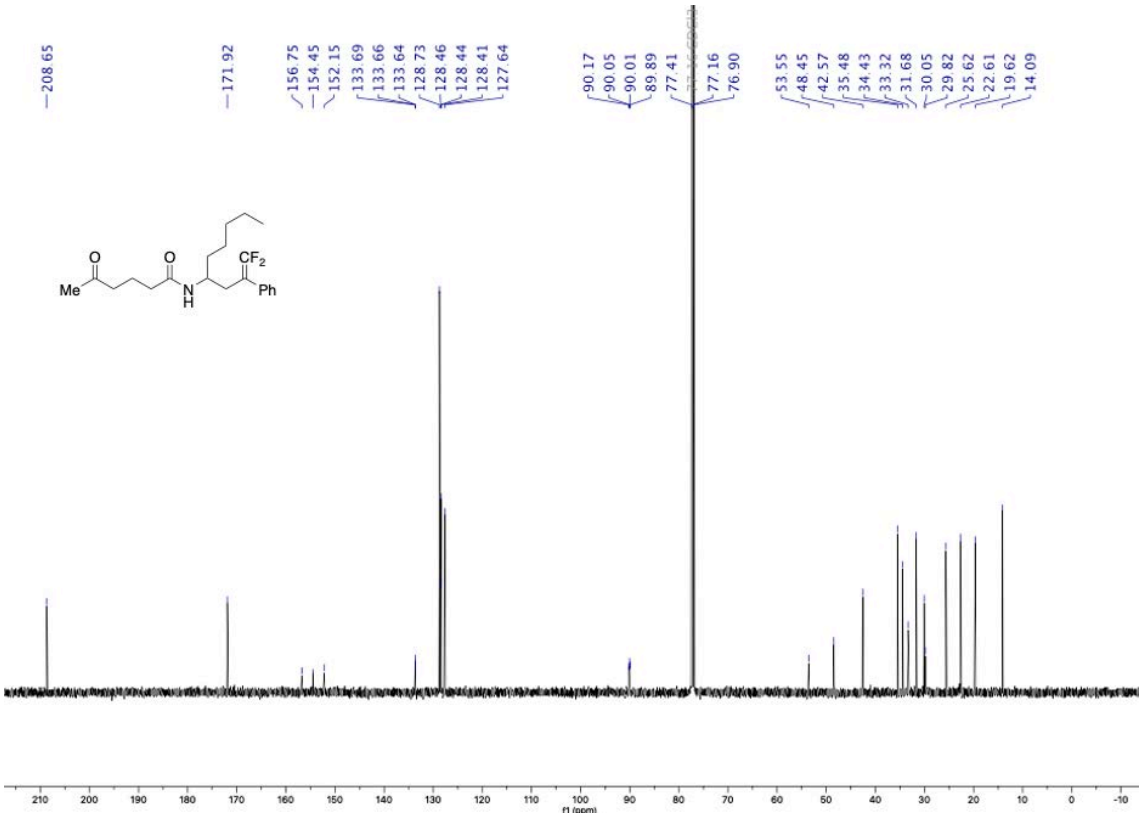
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3y**



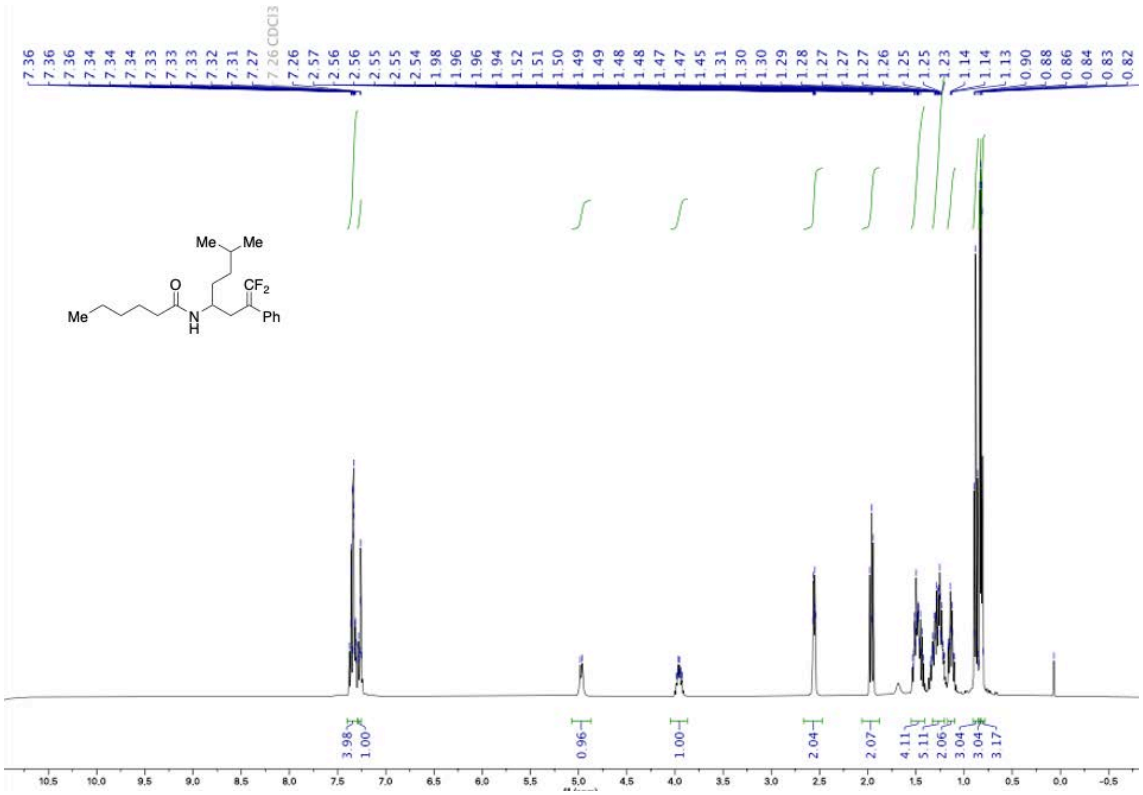
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3z**



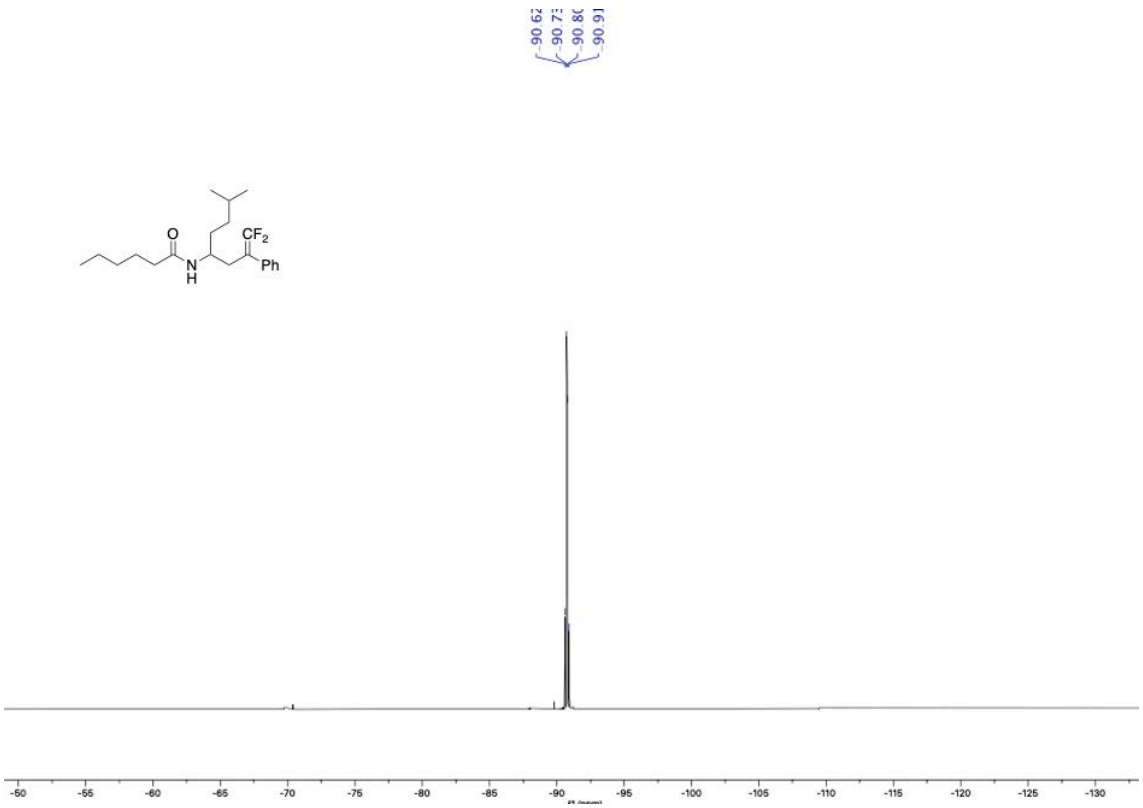
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3z**



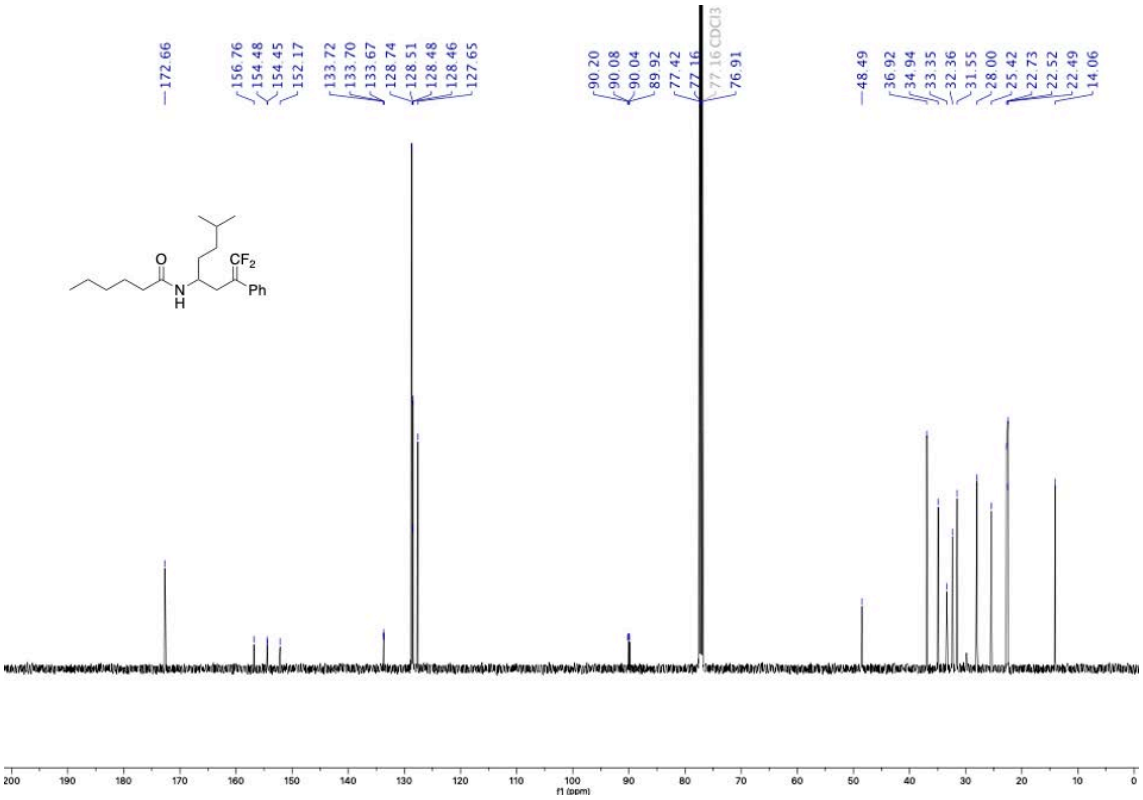
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3z**



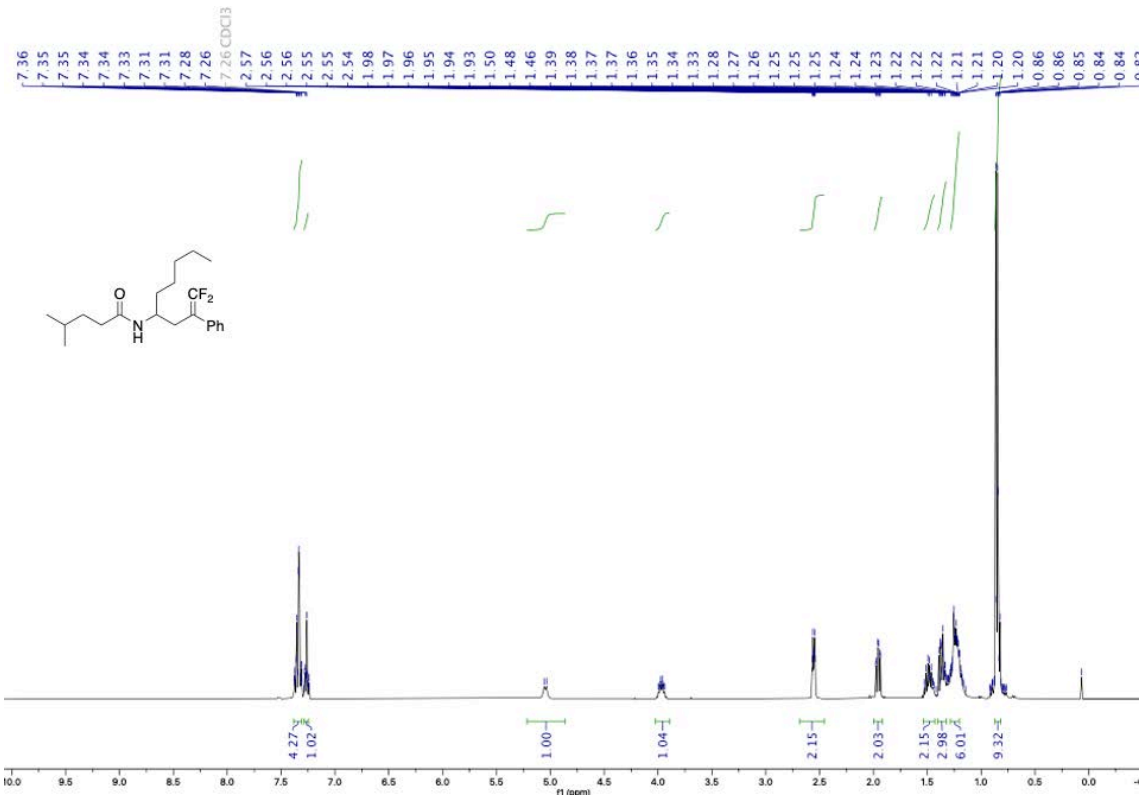
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3aa**



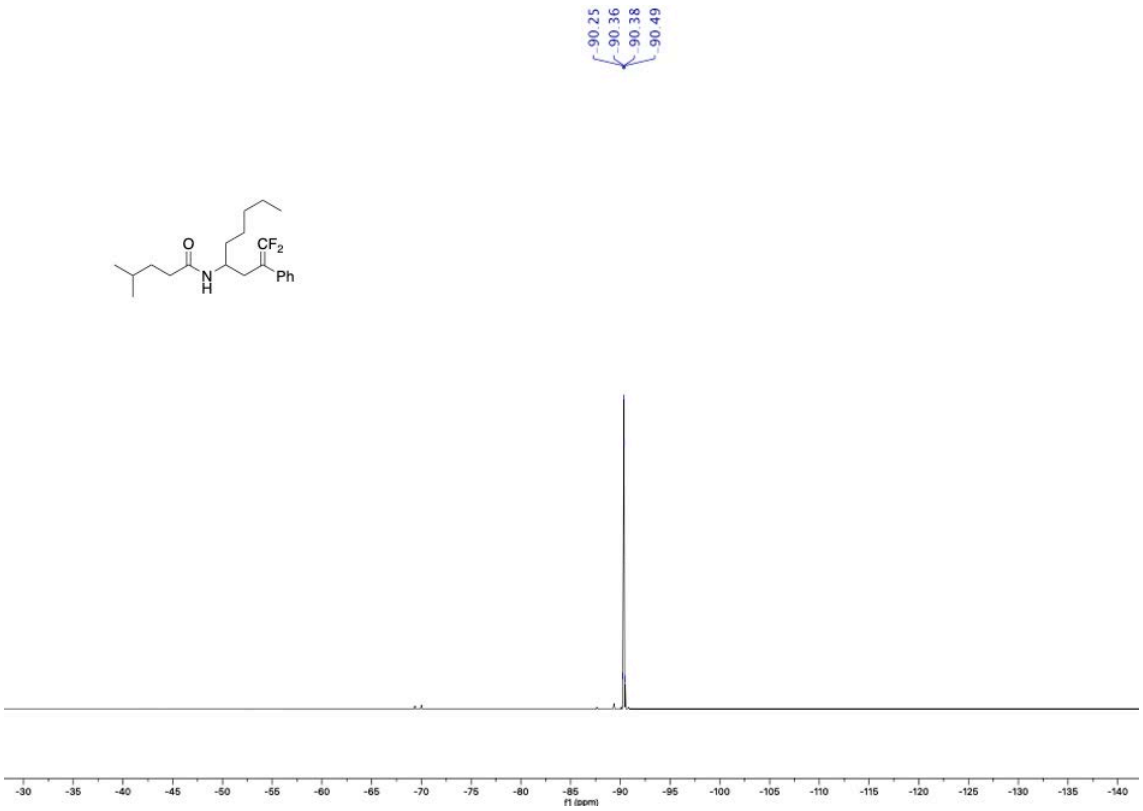
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3aa**



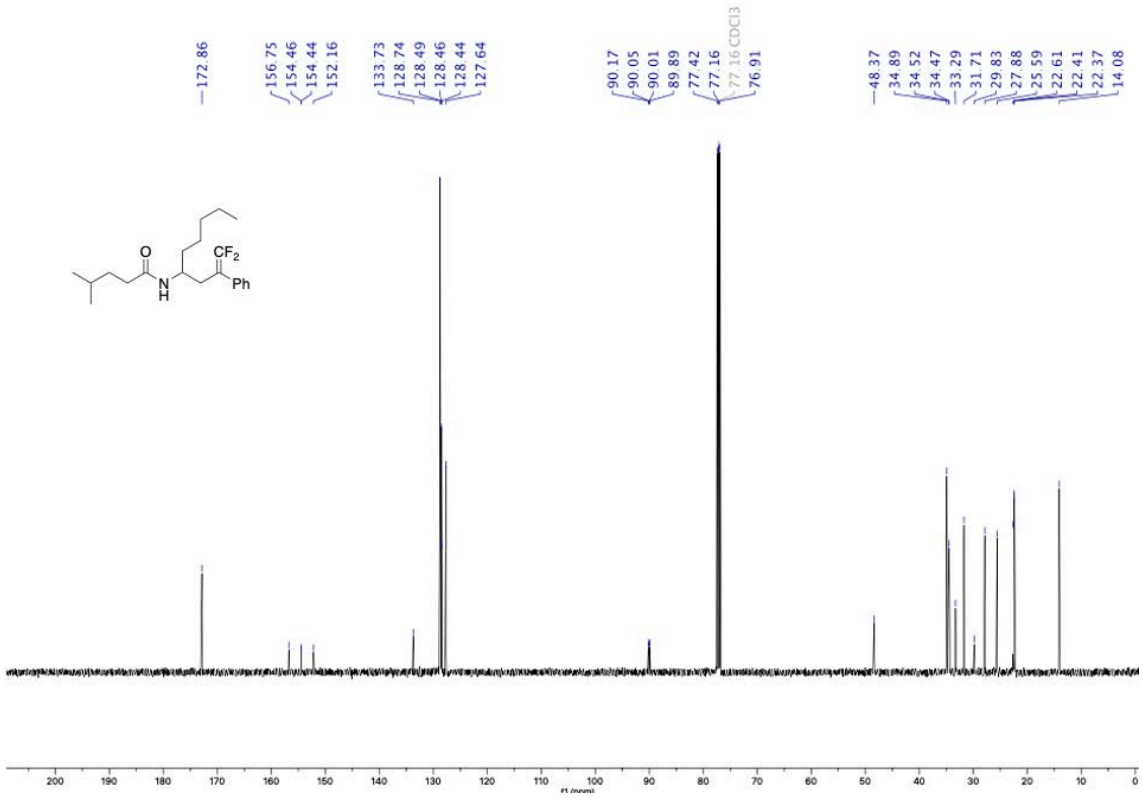
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3aa**



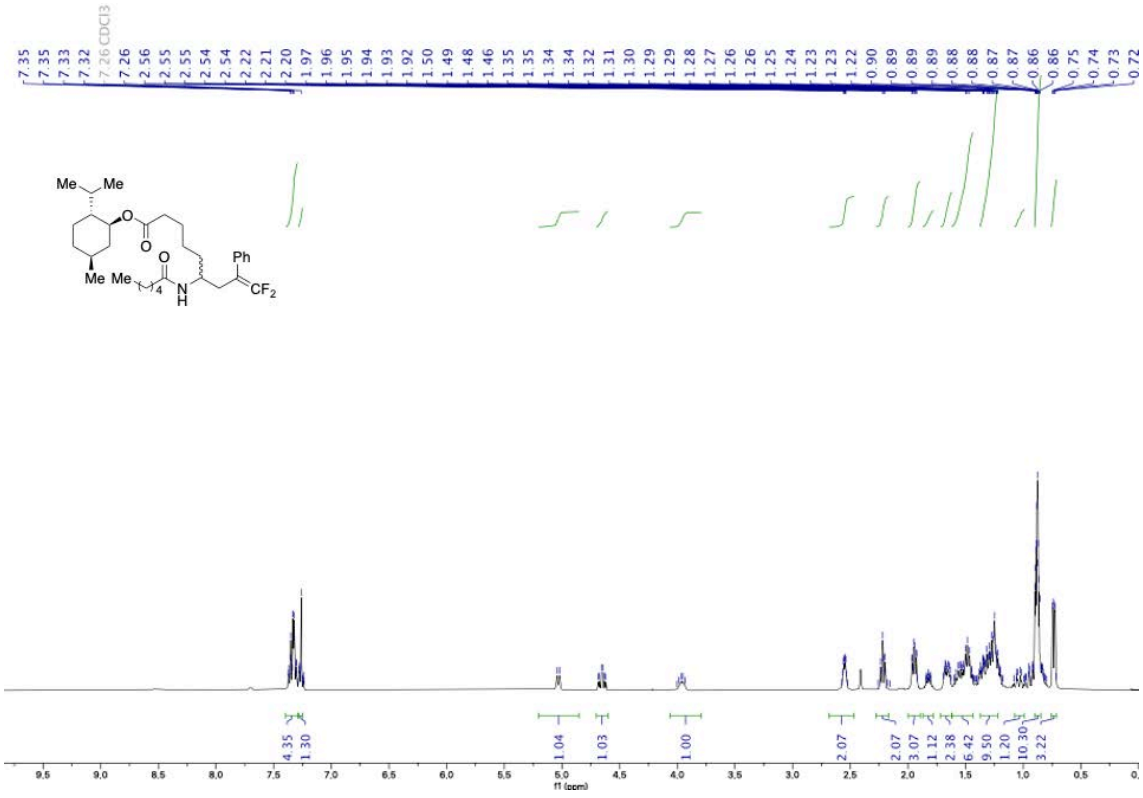
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ab**



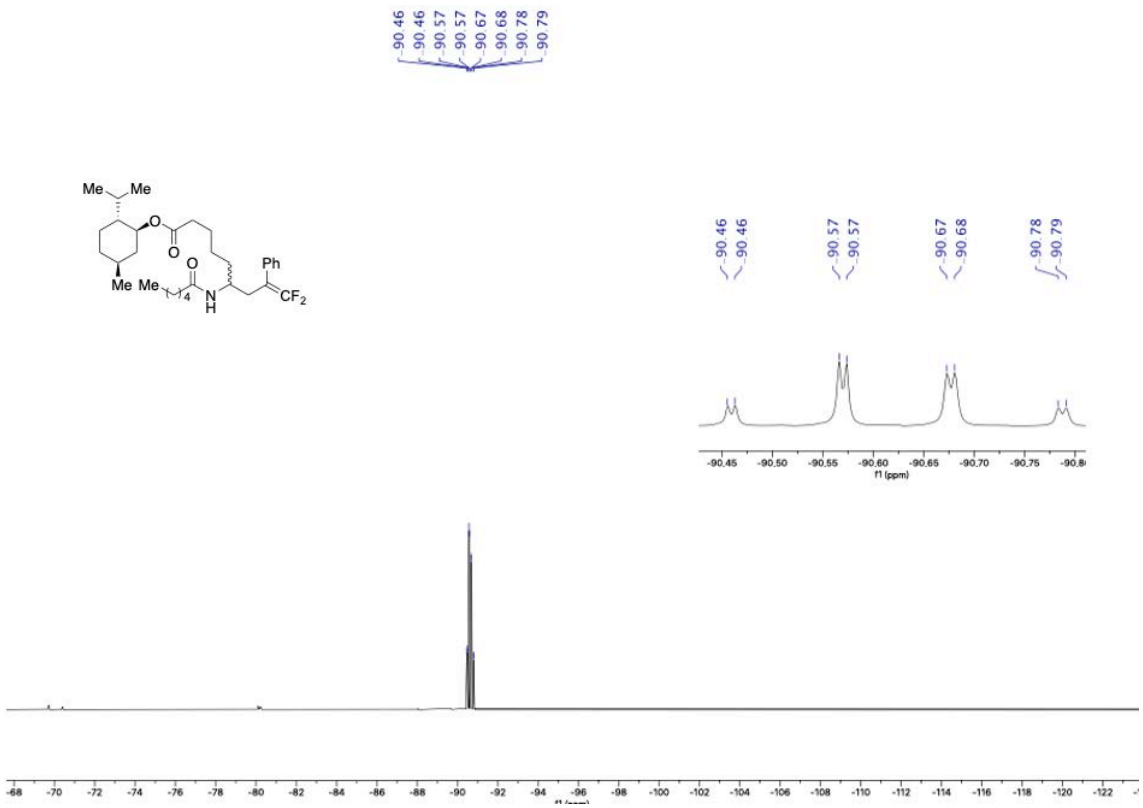
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3ab**



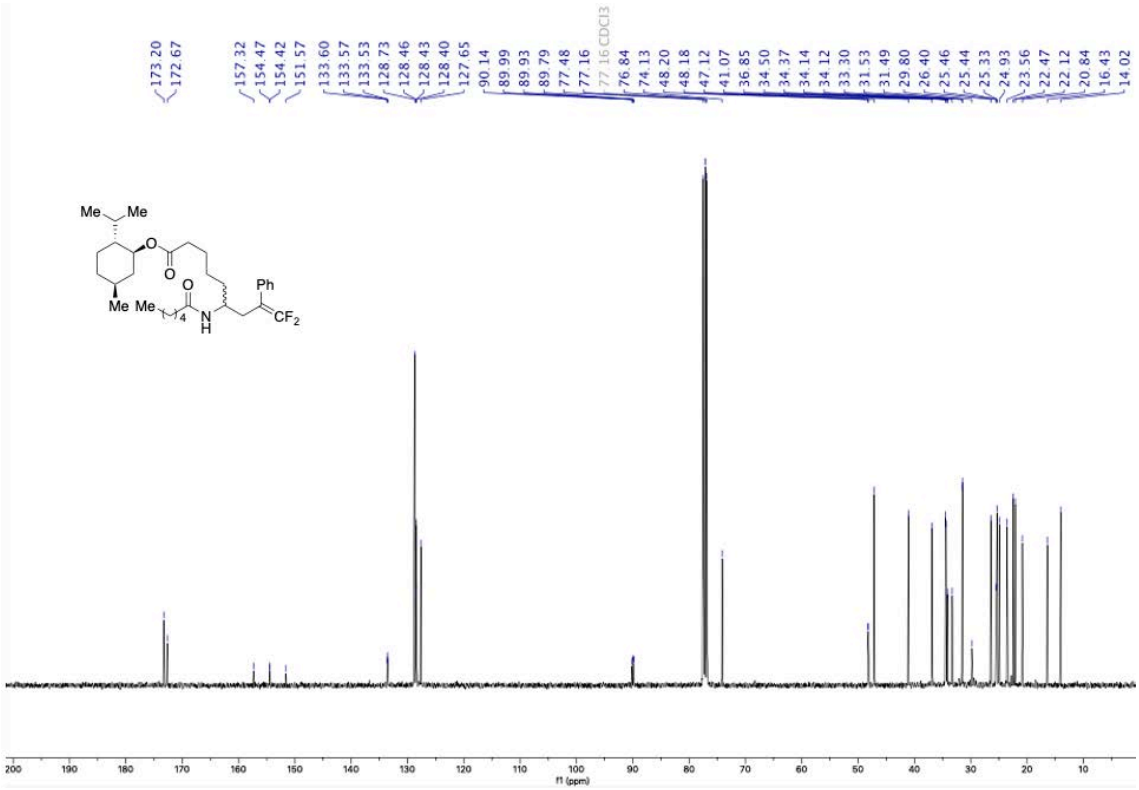
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ab**



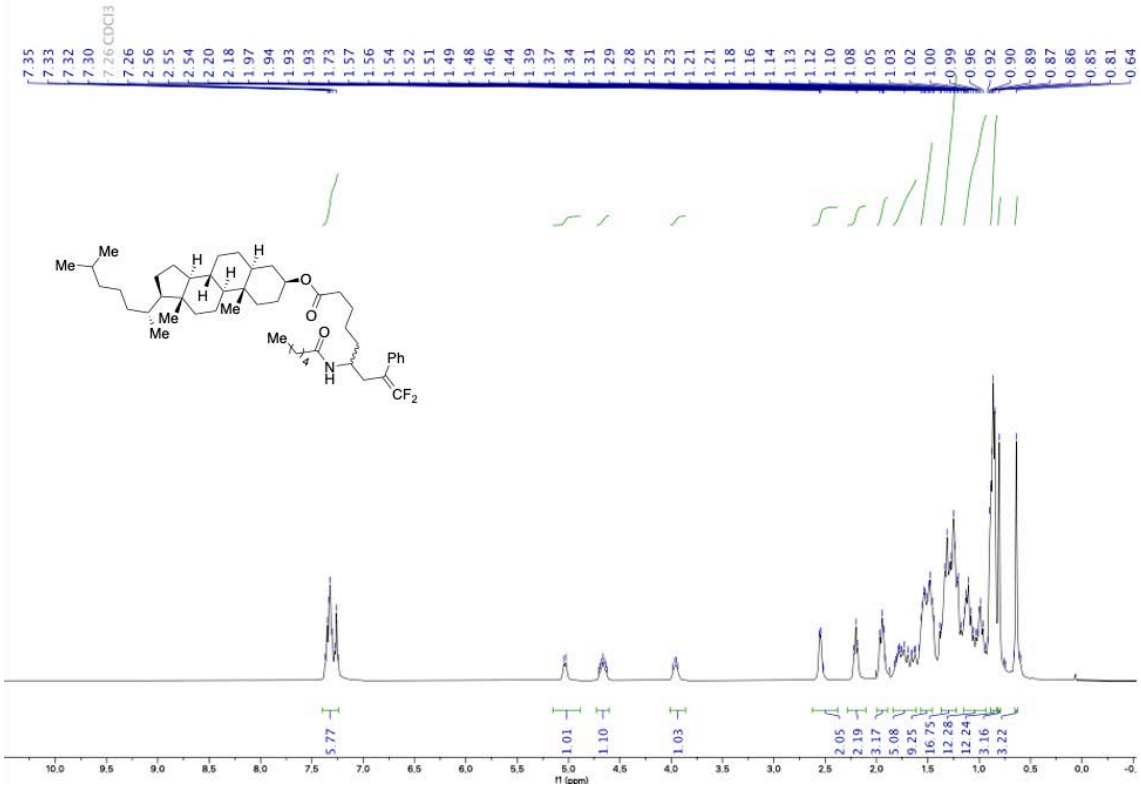
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ac**



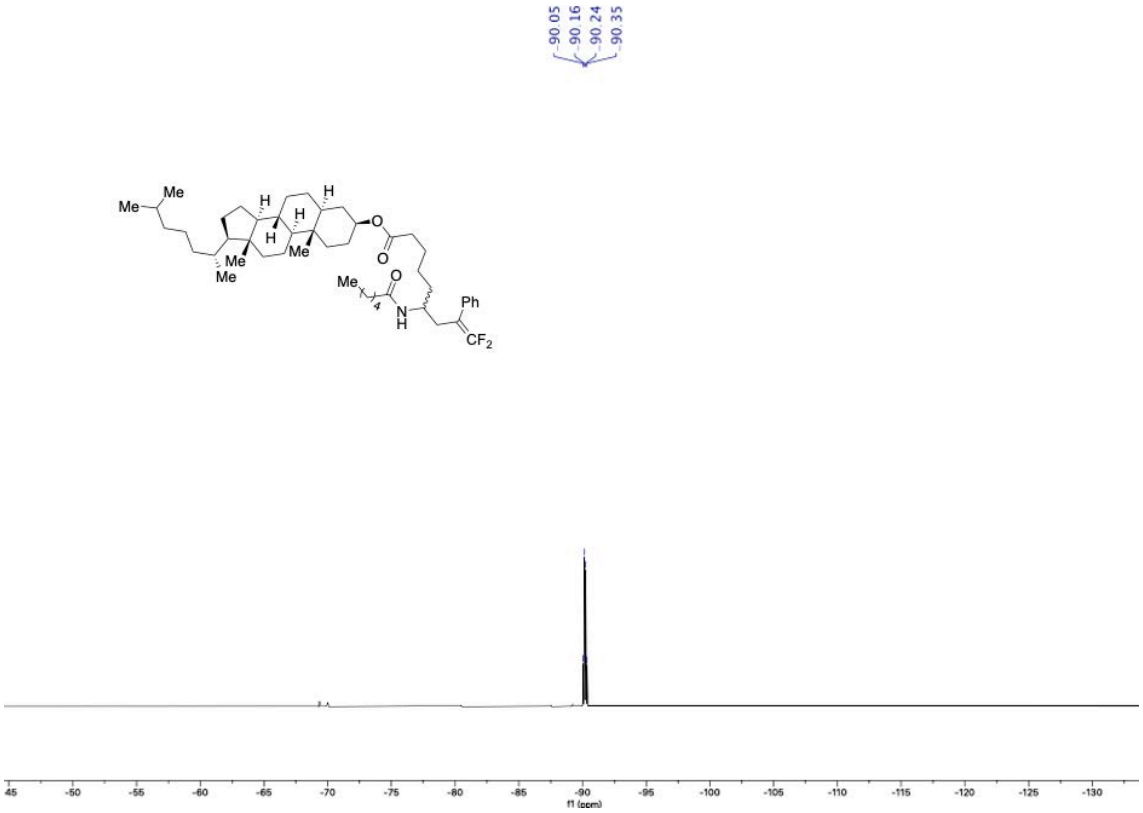
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3ac**



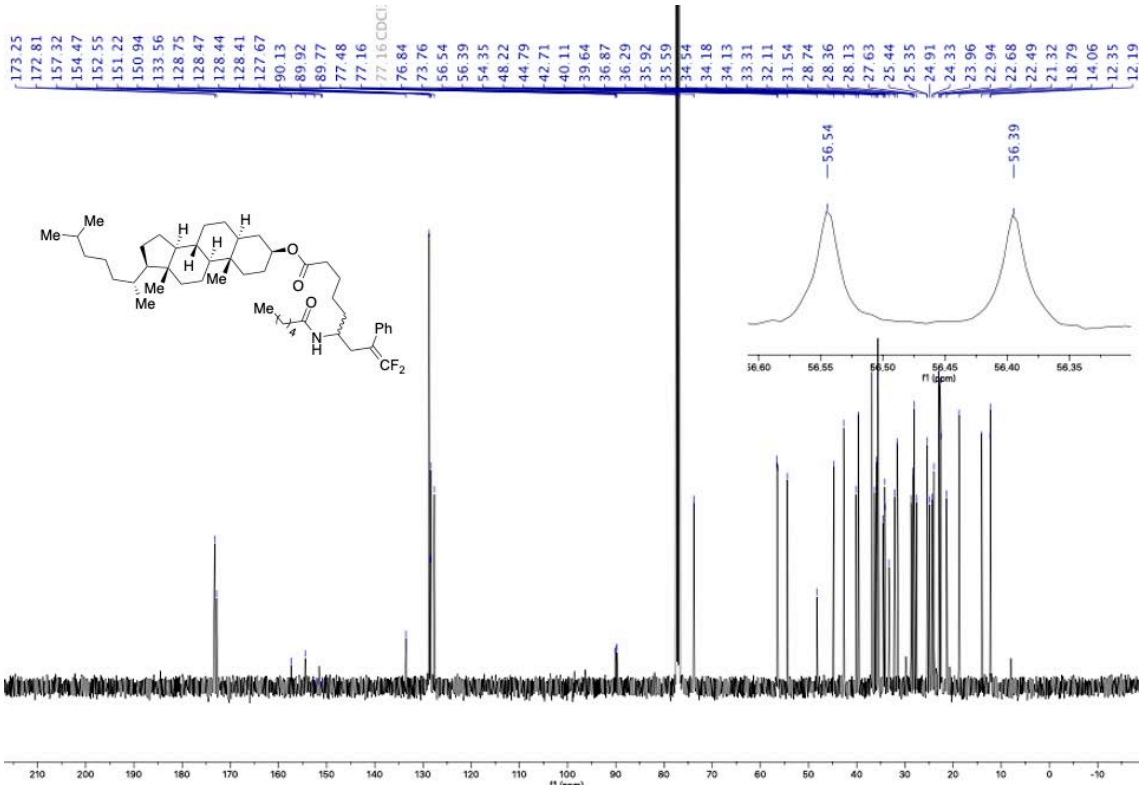
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ac**



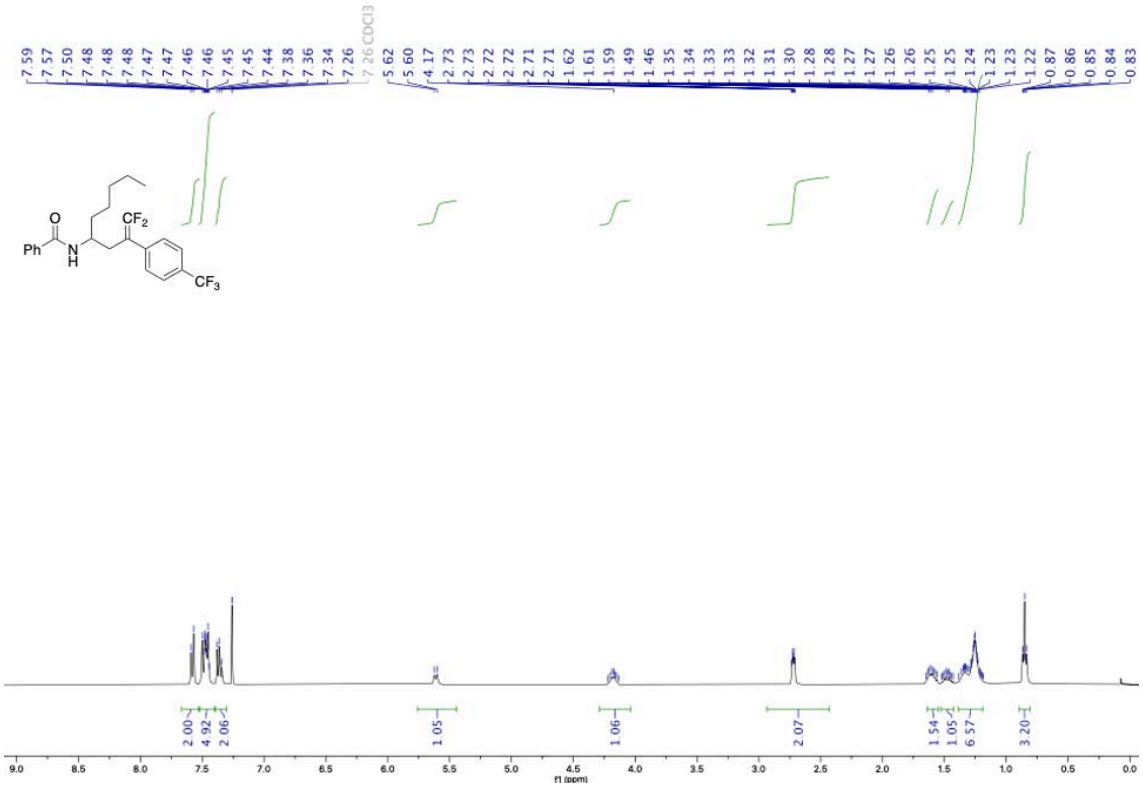
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ad**



^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3ad**

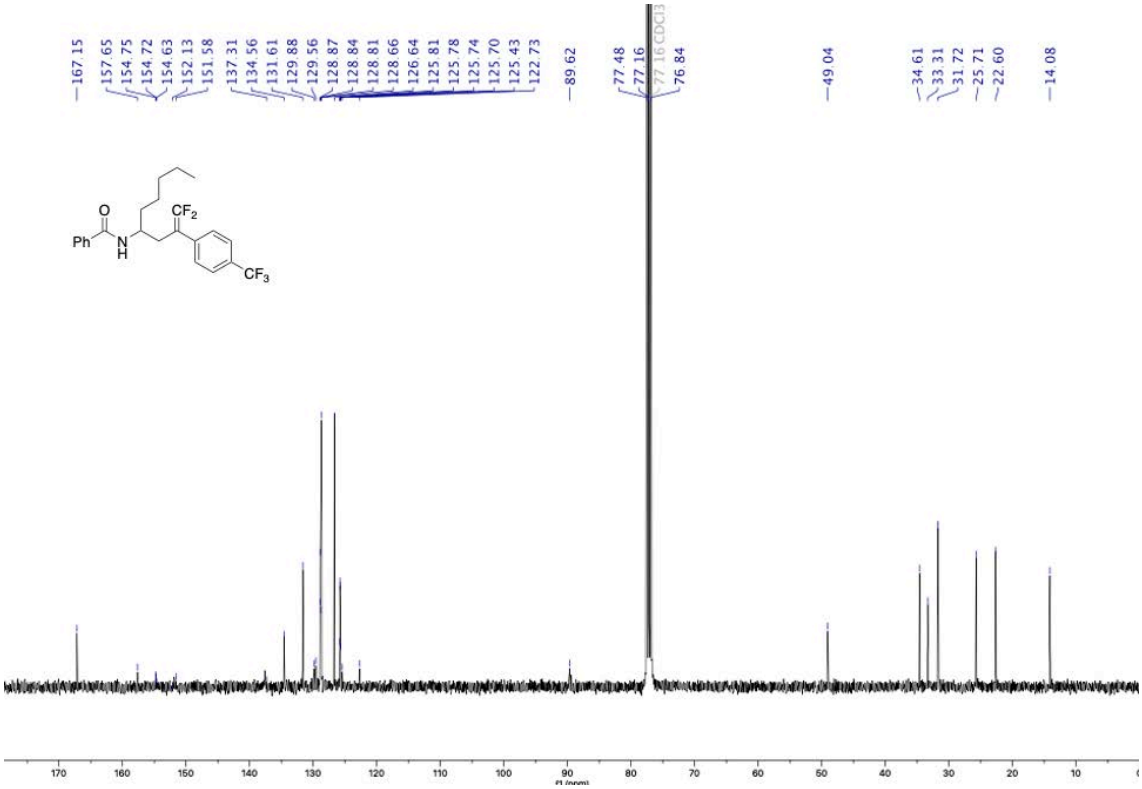


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ad**

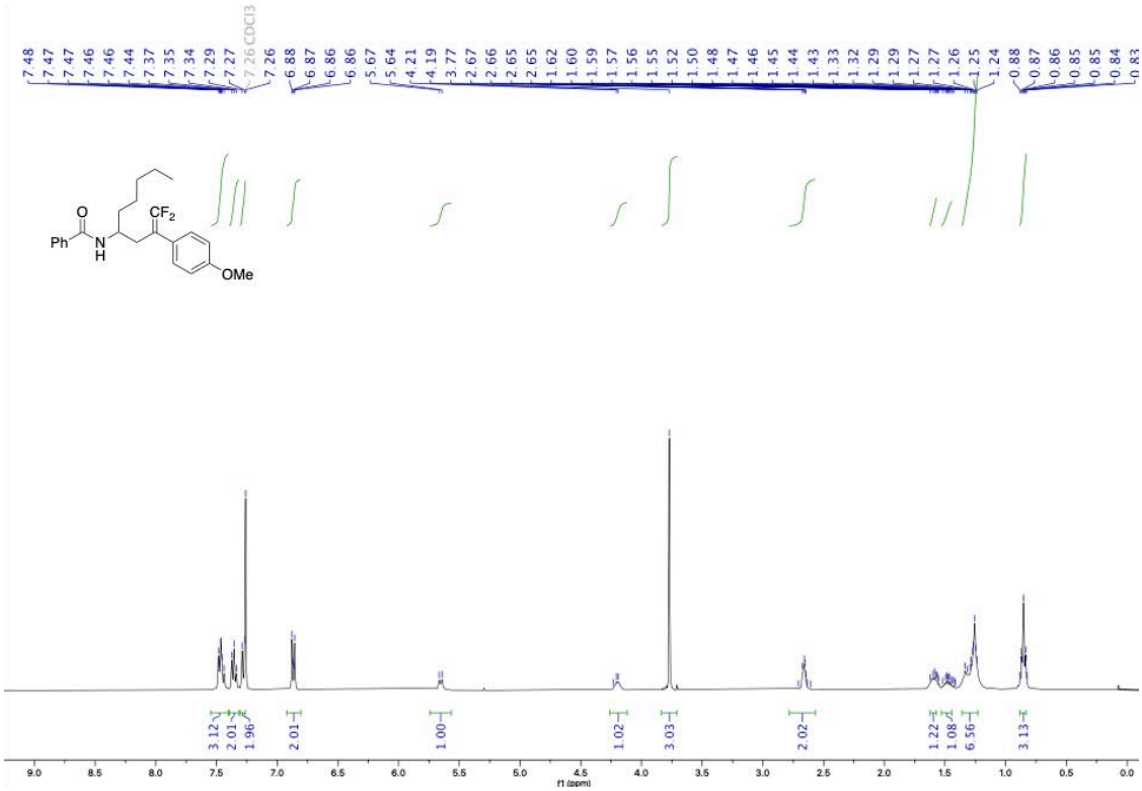


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ae**

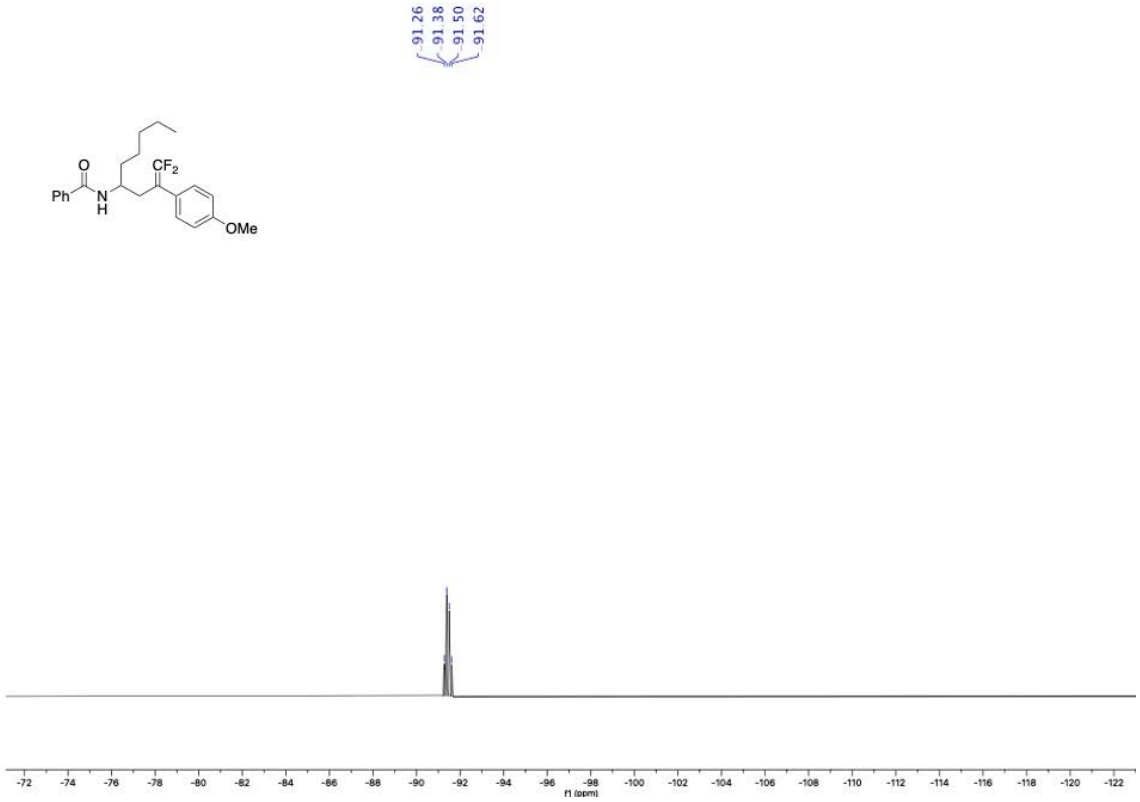
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3ae**



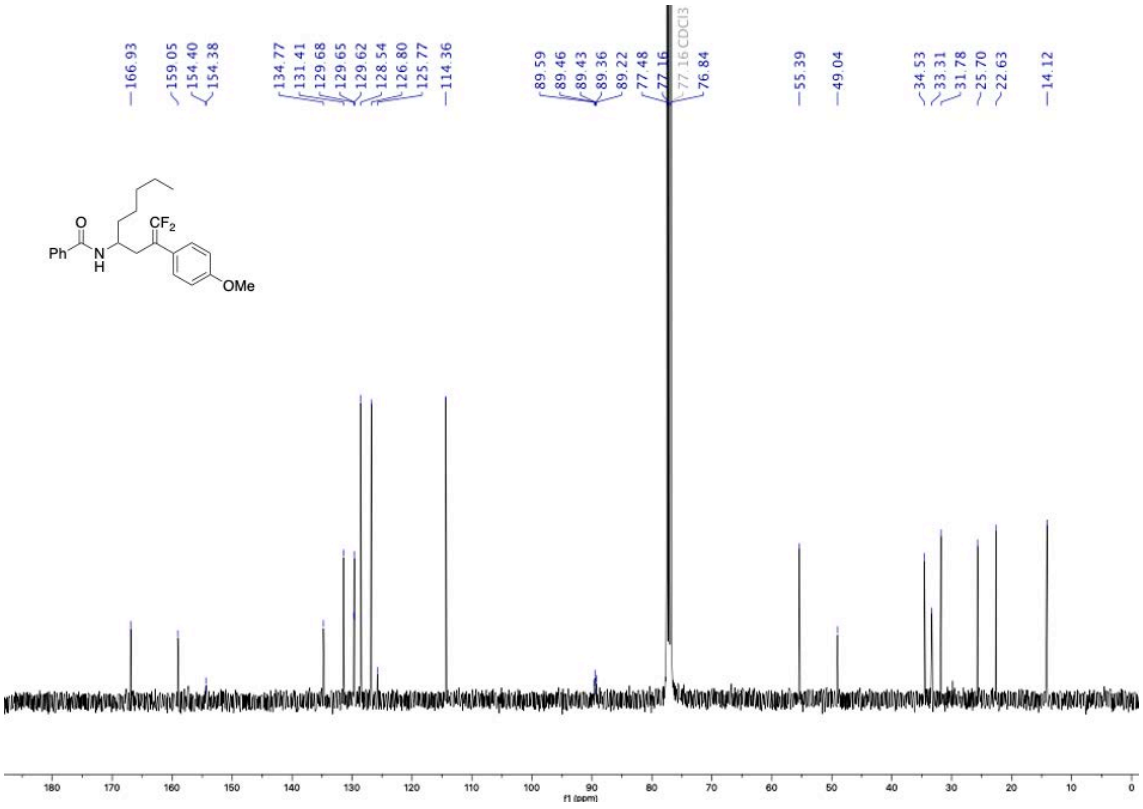
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ae**



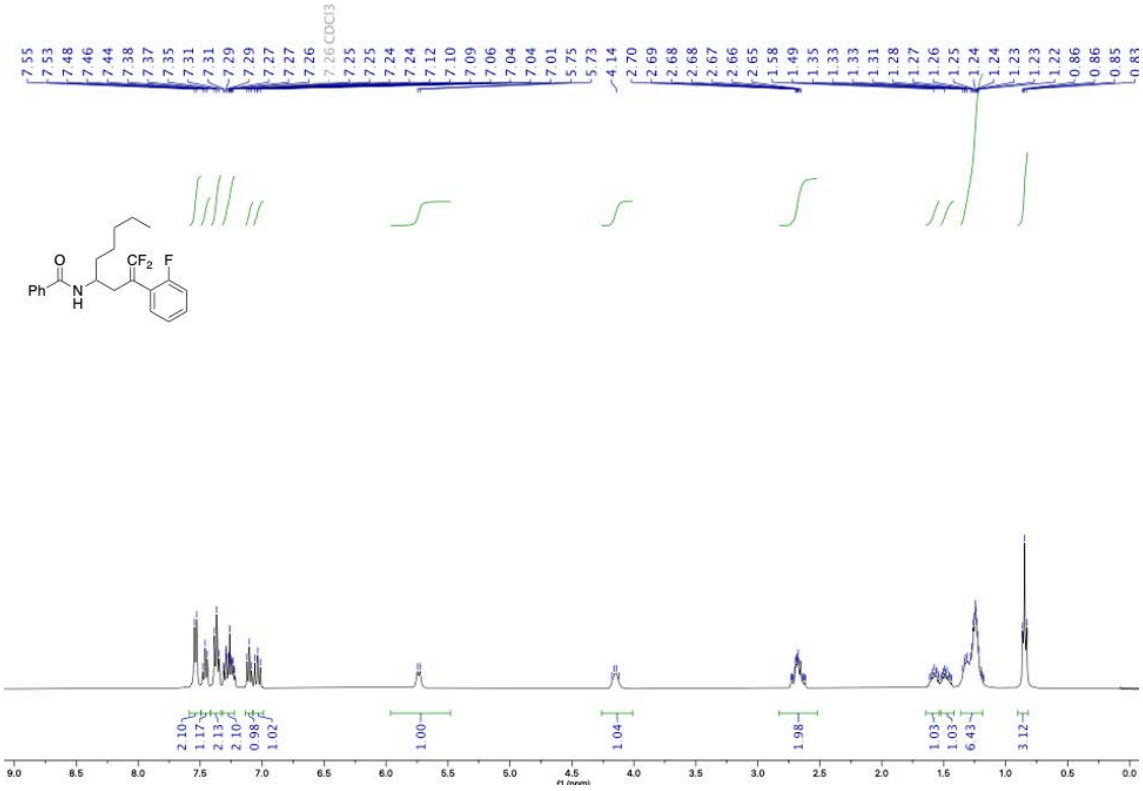
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3af**



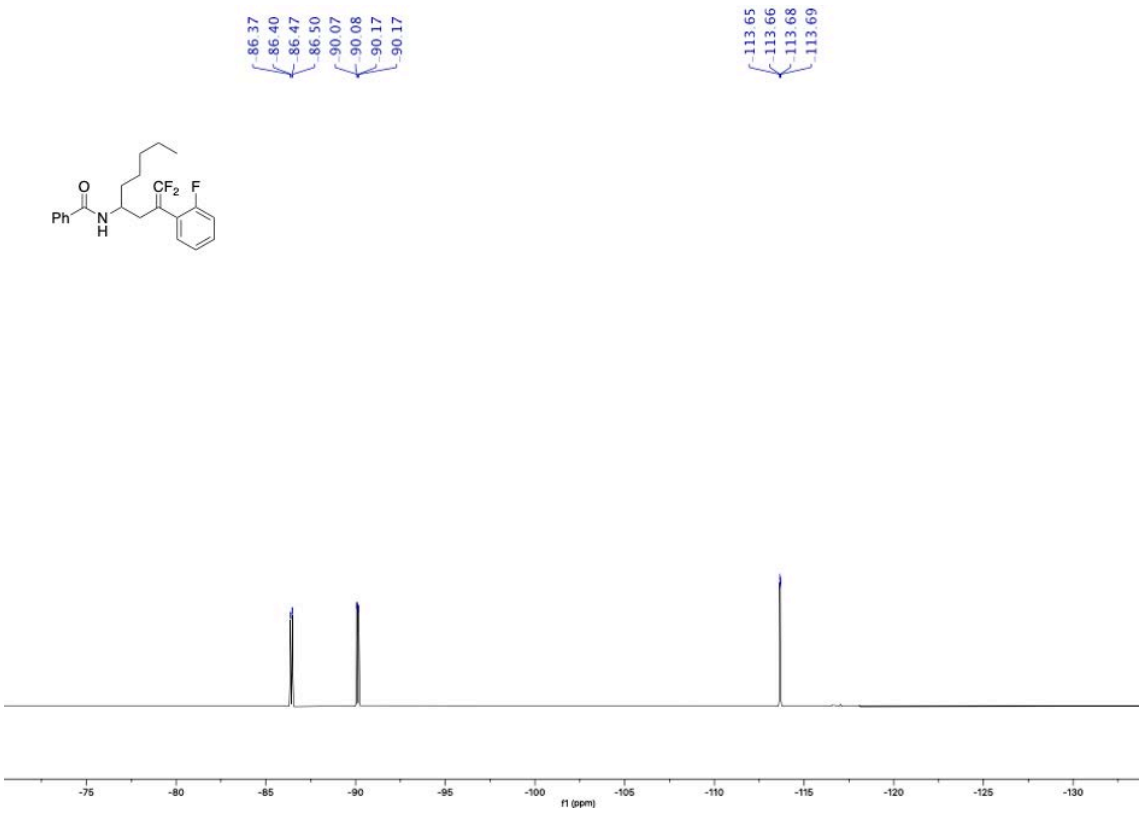
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3af**



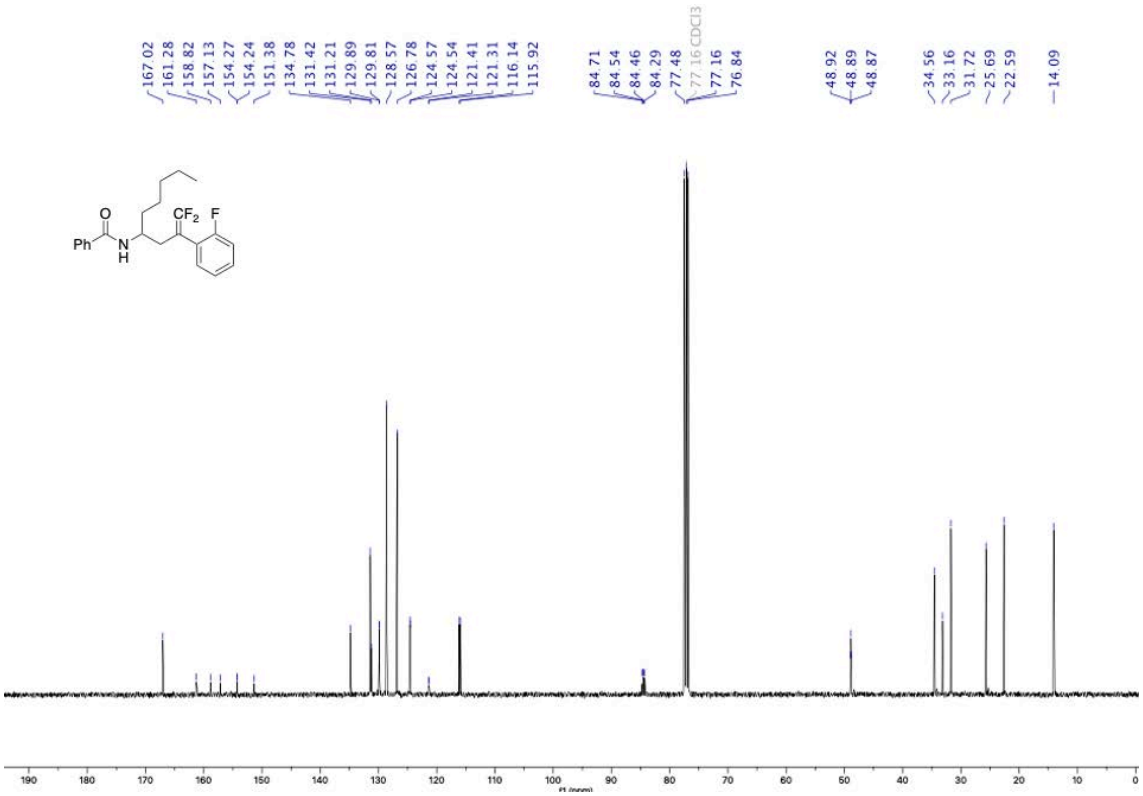
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3af**



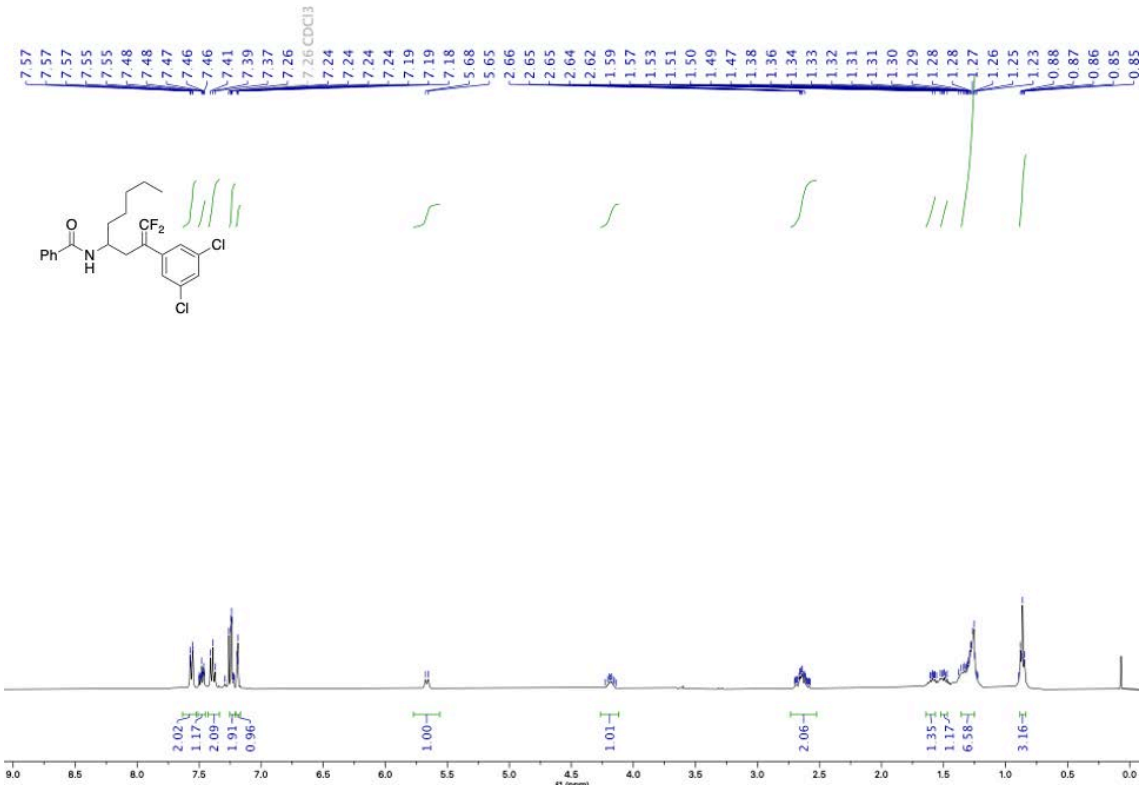
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ag**



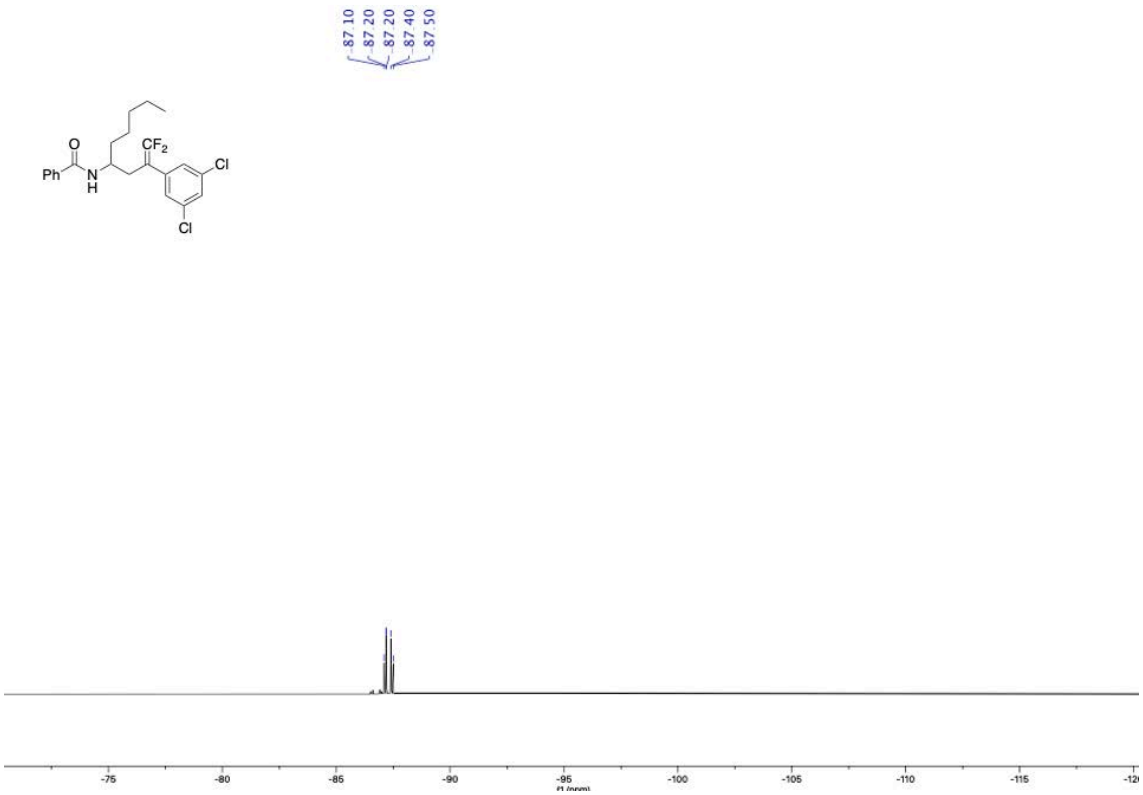
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3ag**



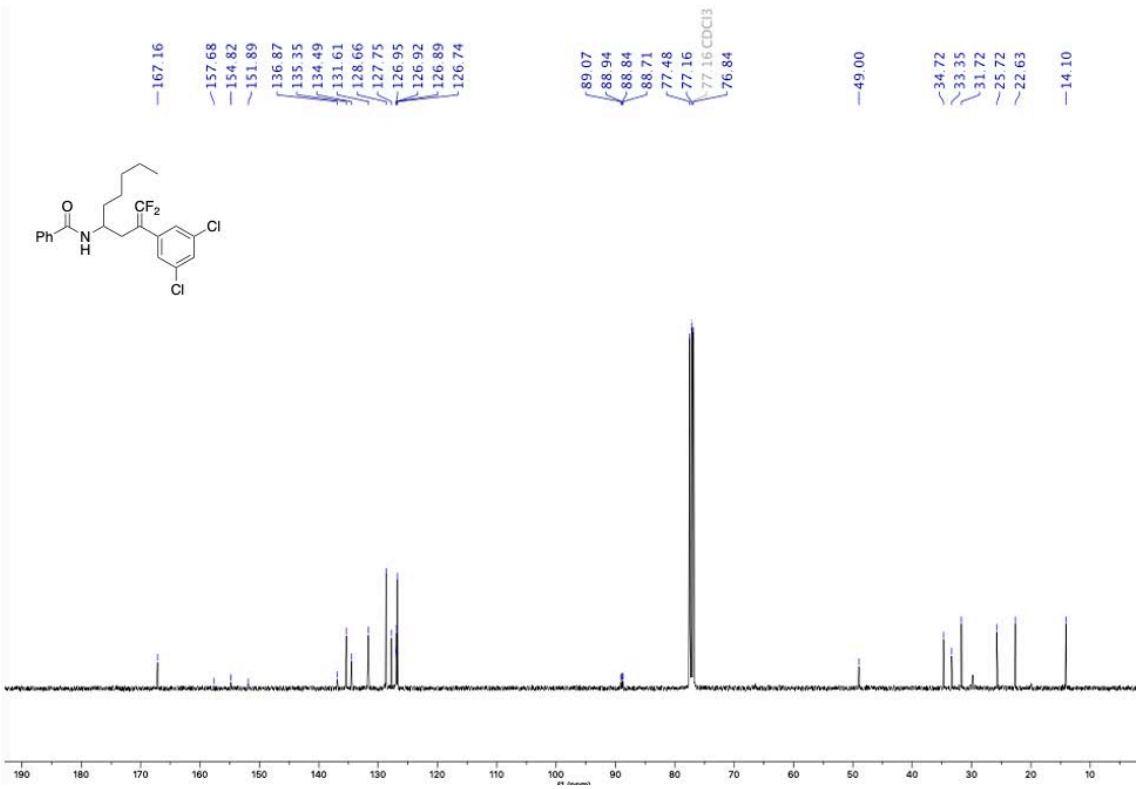
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ag**



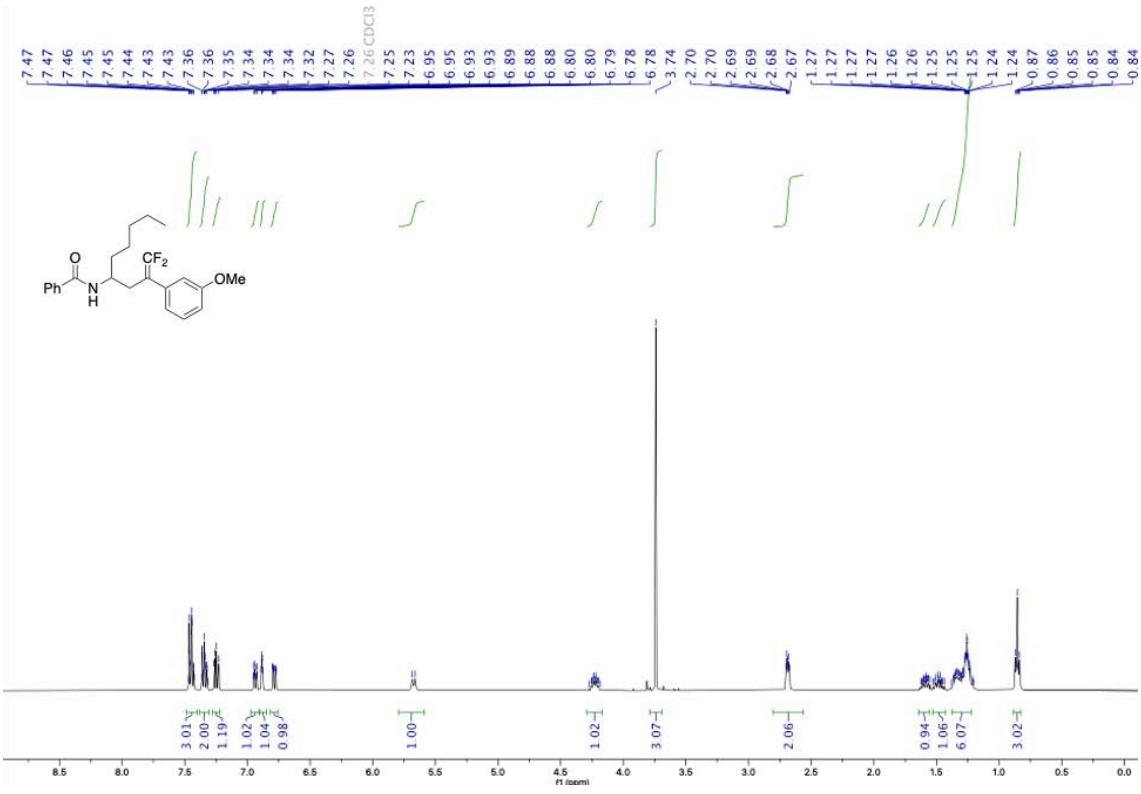
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ah**



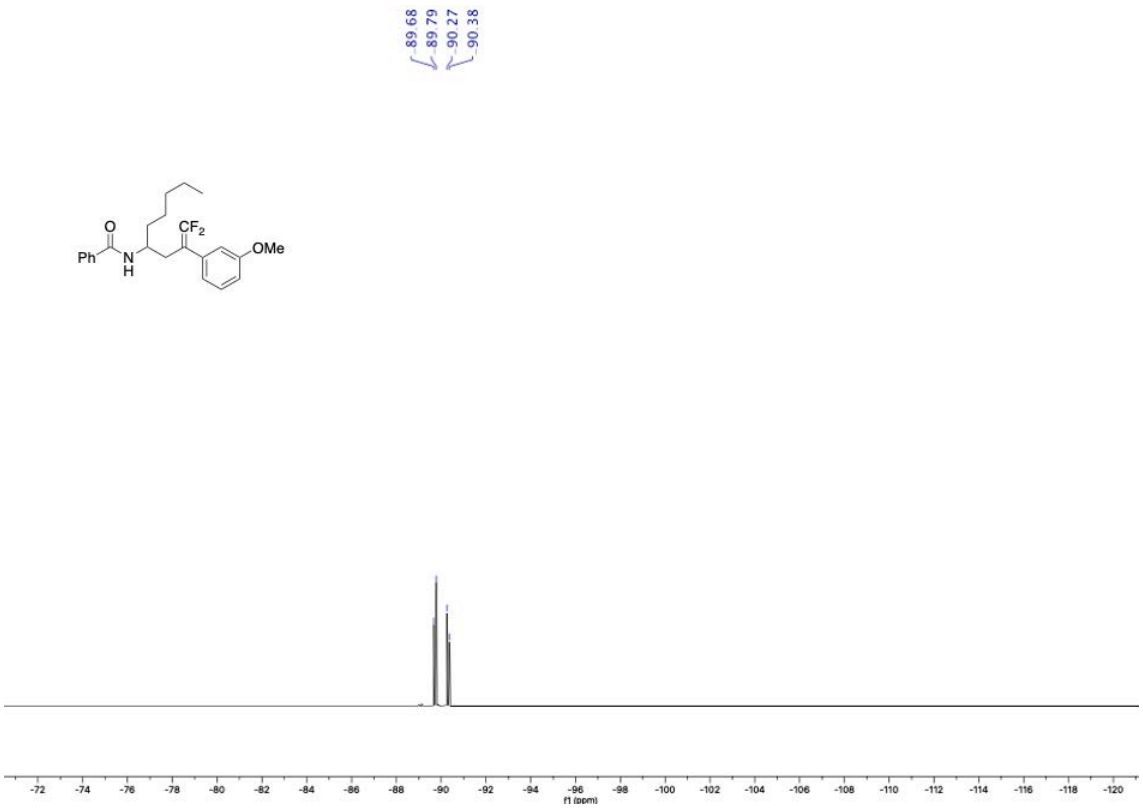
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3ah**



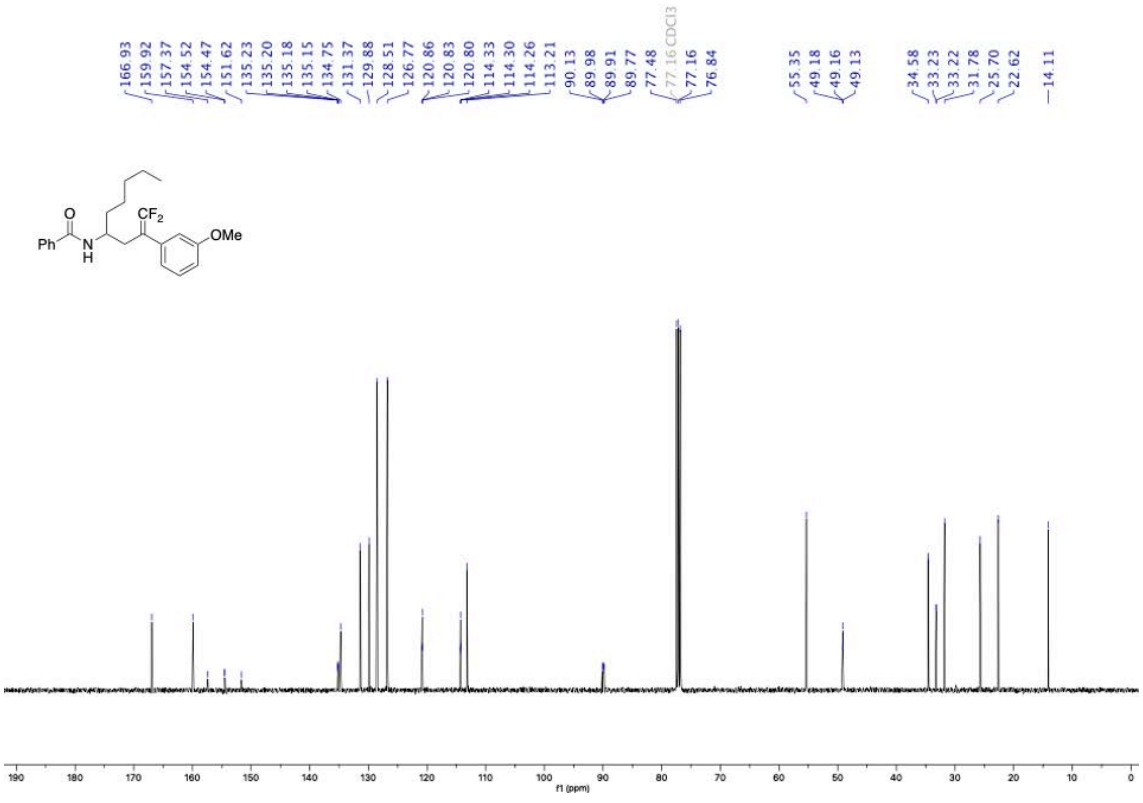
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ah**



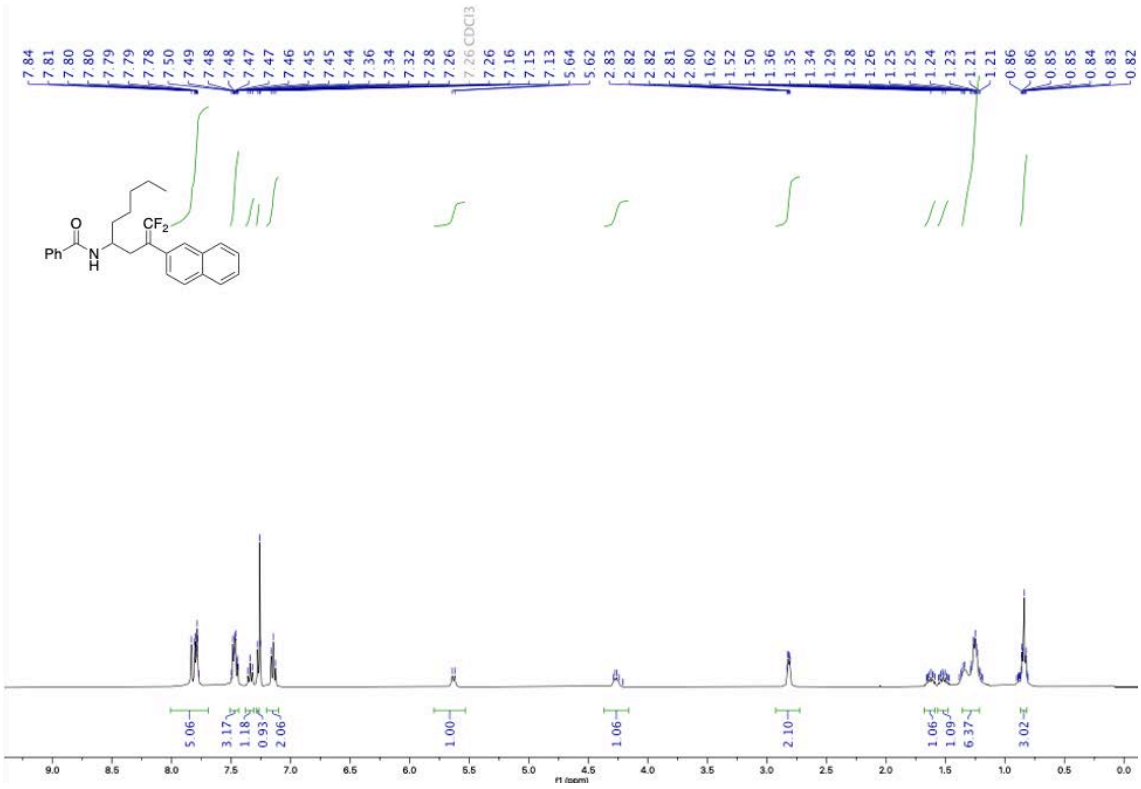
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ai**



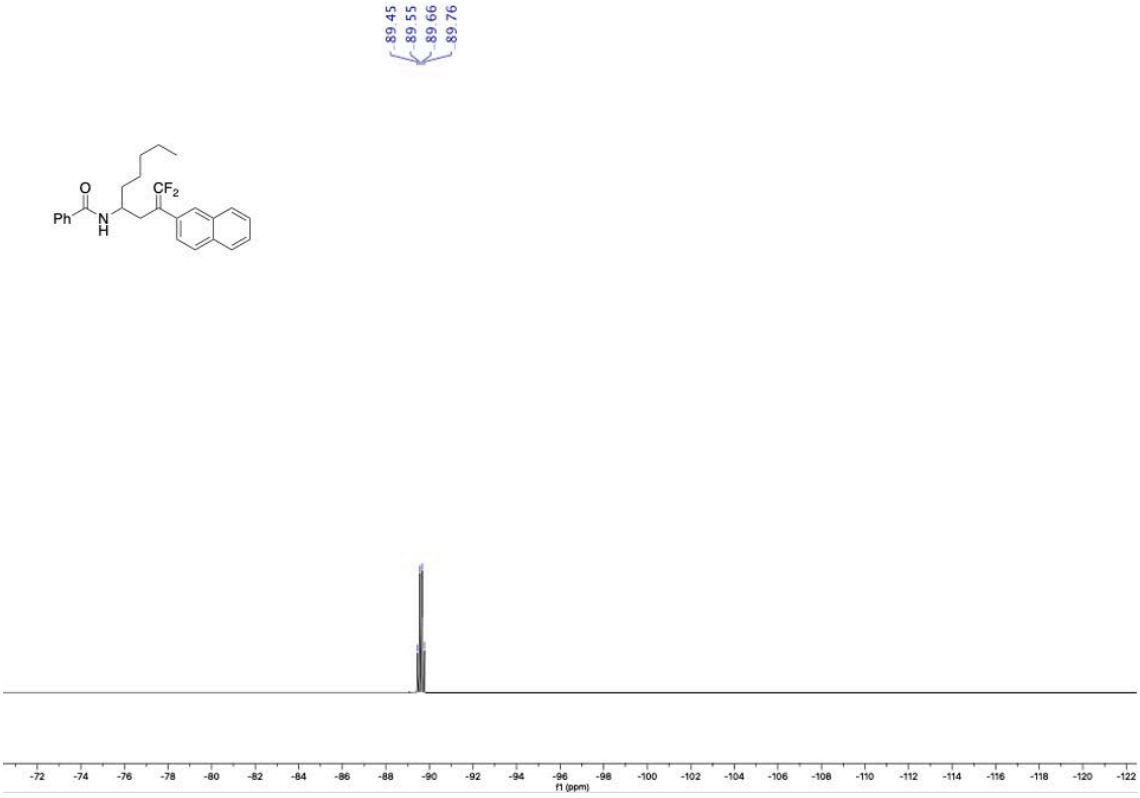
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3ai**



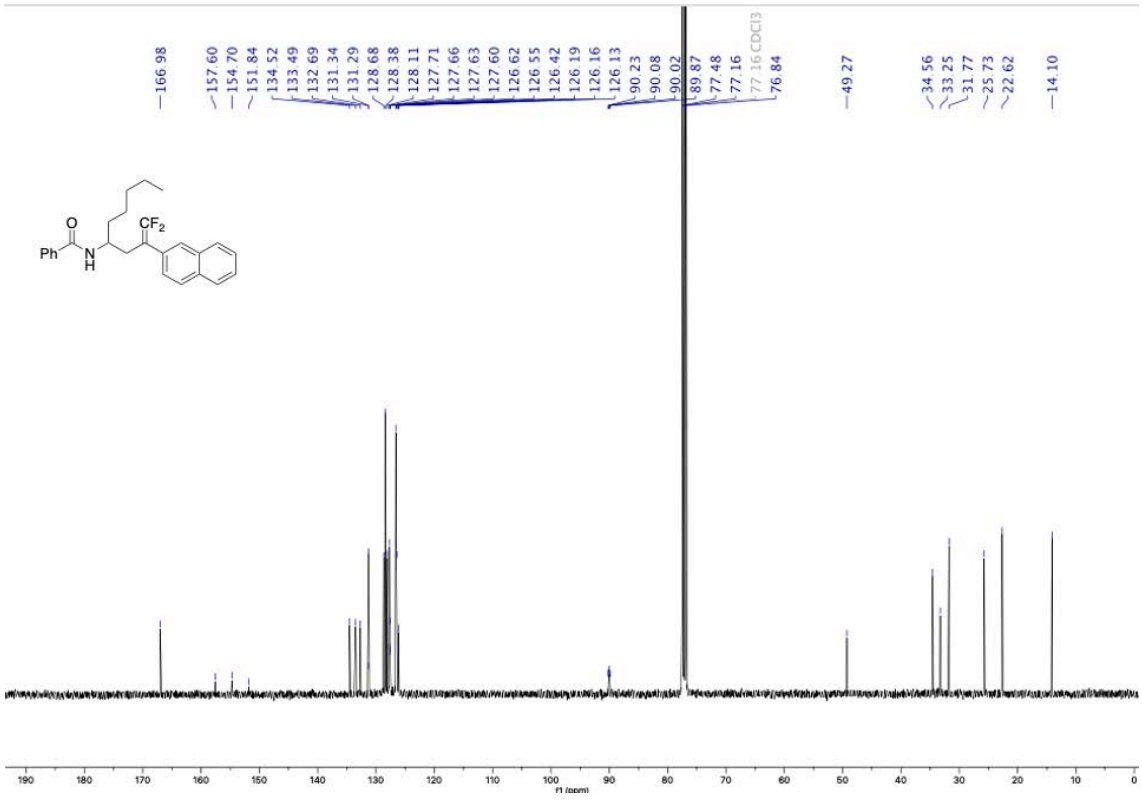
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ai**



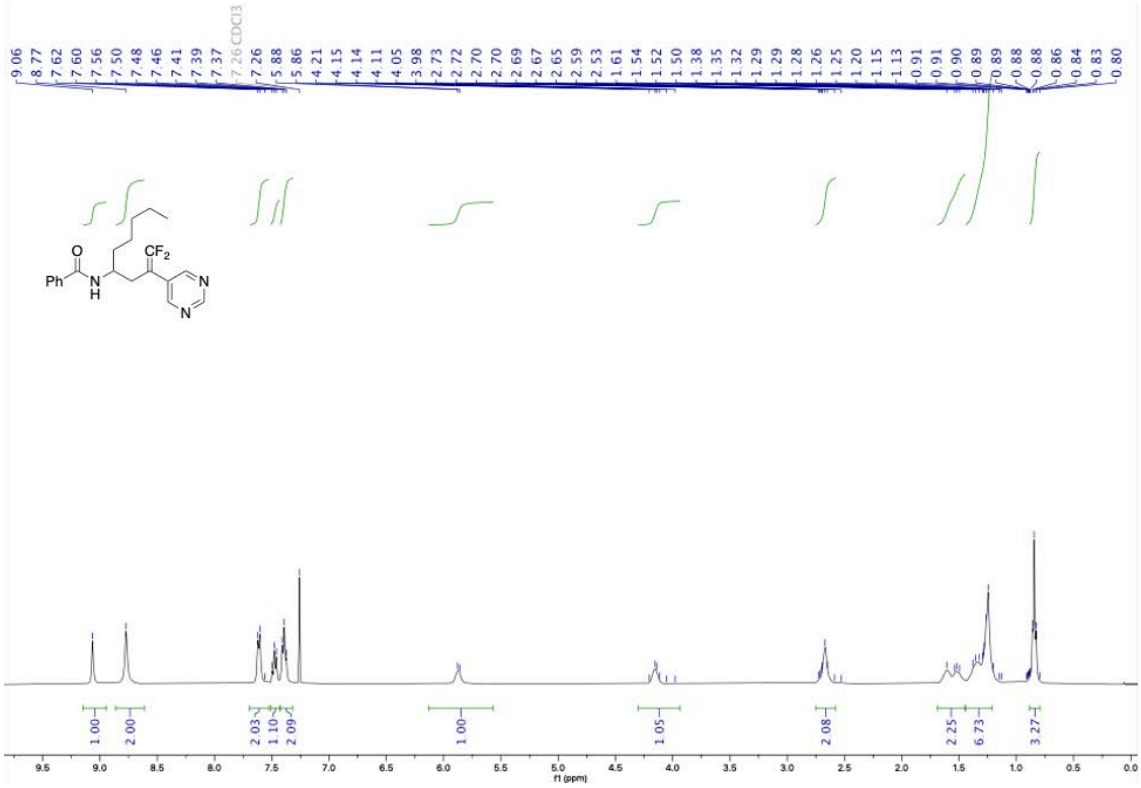
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3aj**



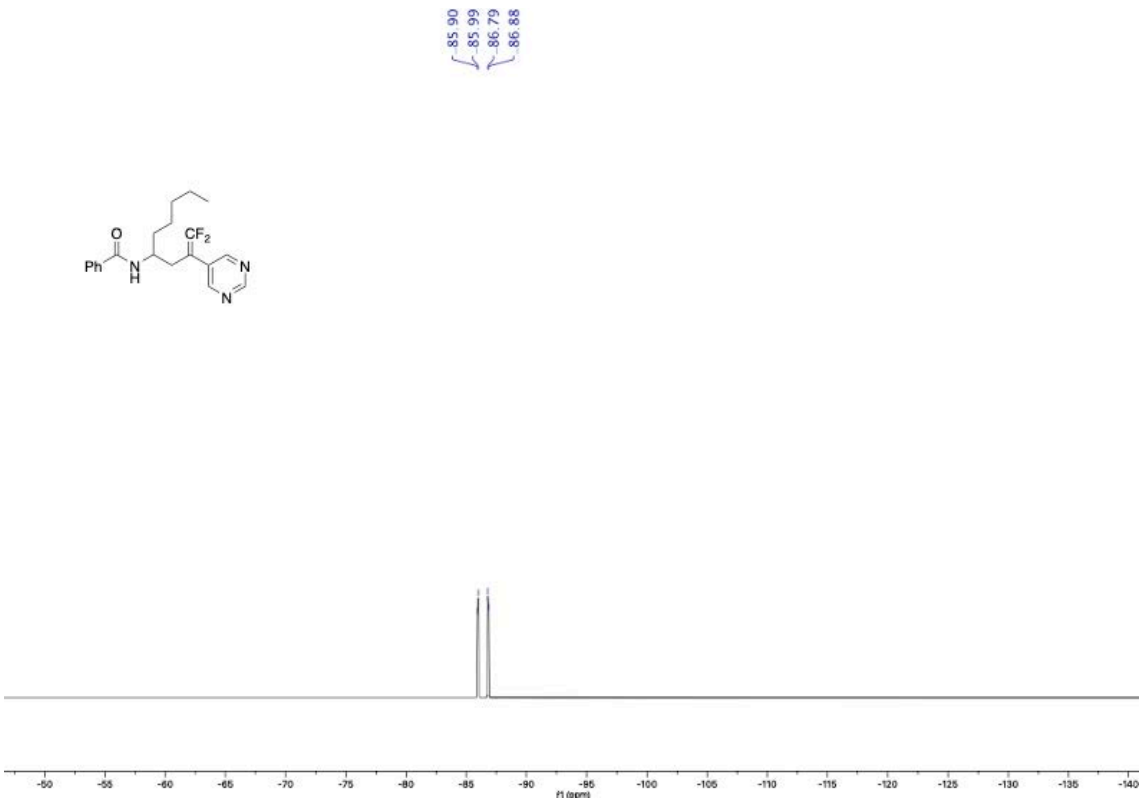
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3aj**



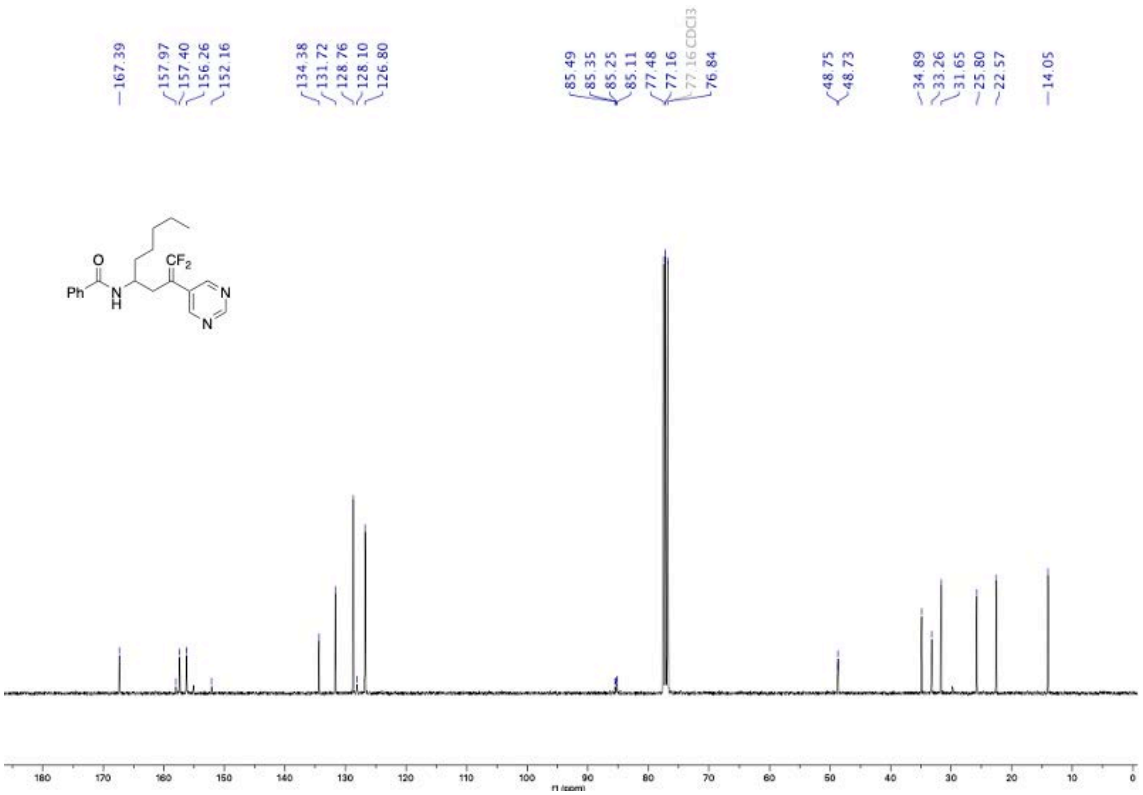
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3aj**



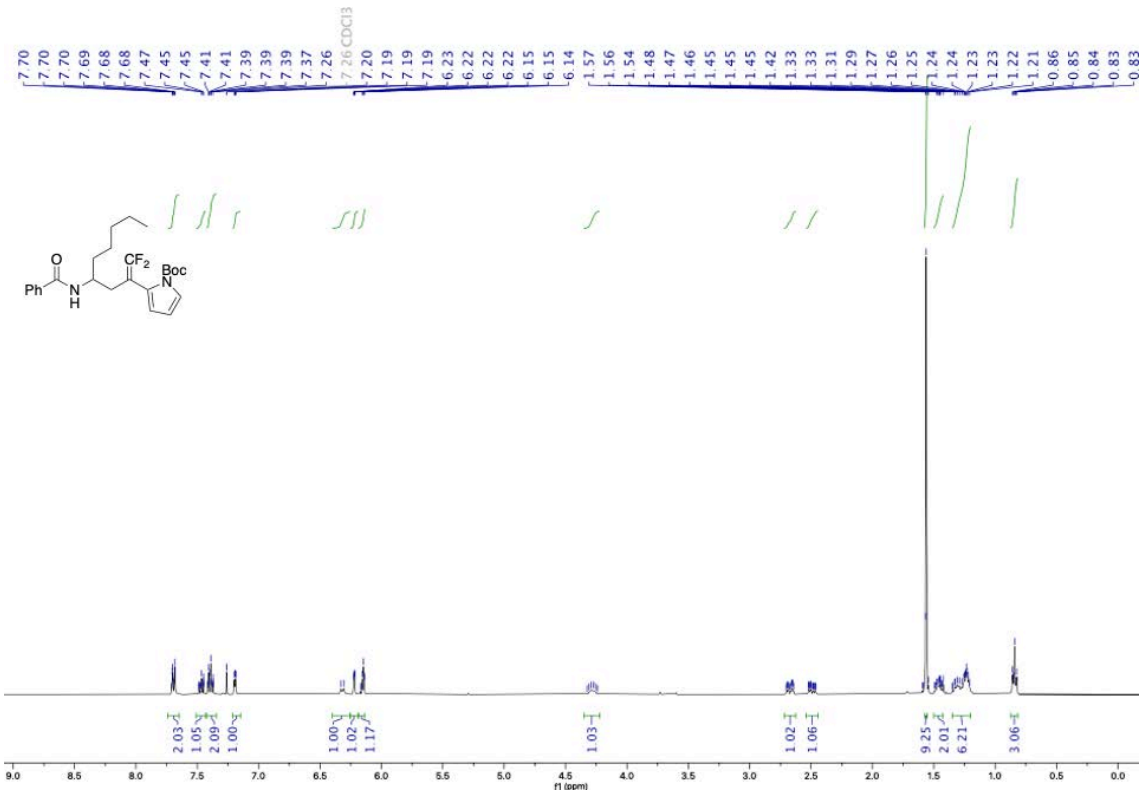
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3ak**



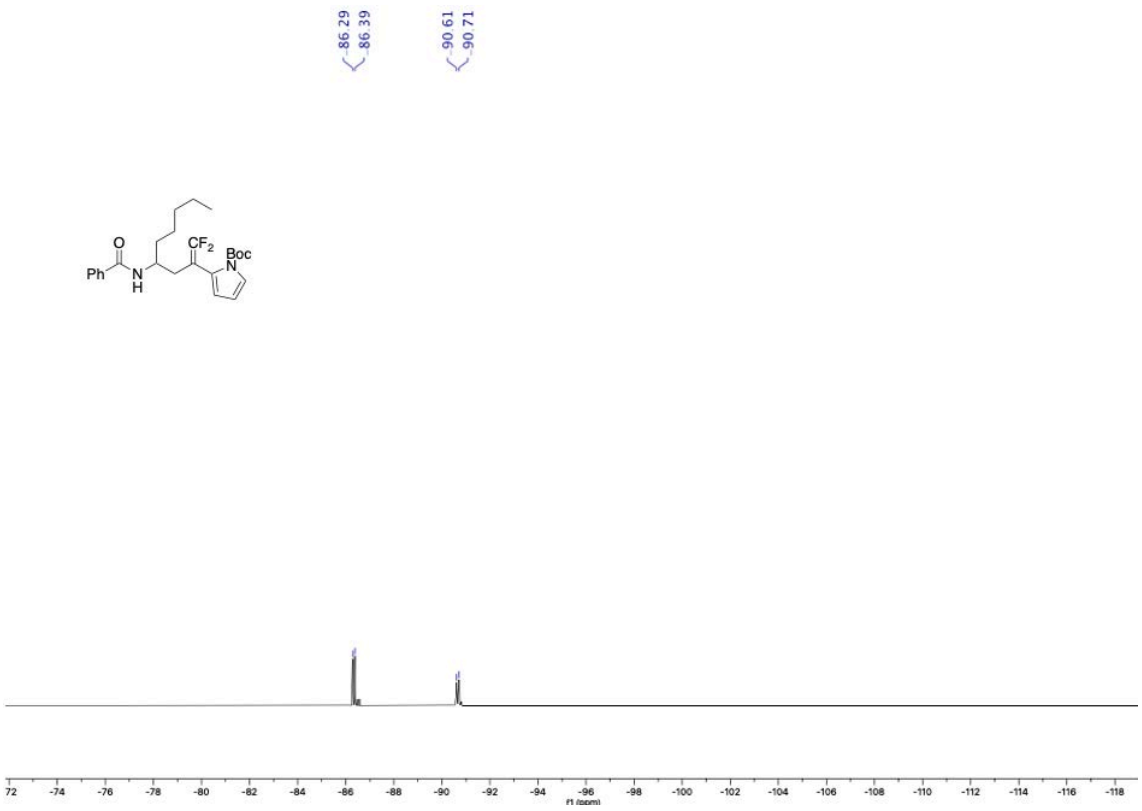
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3ak**



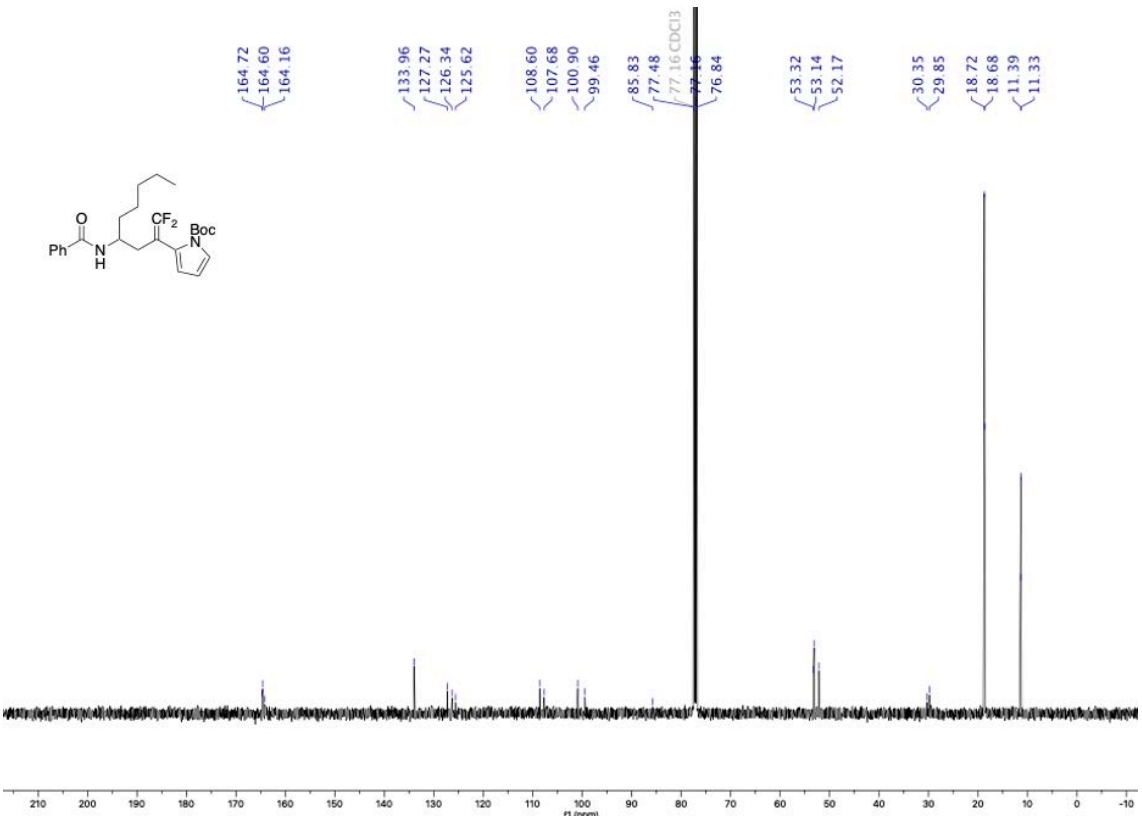
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3ak**



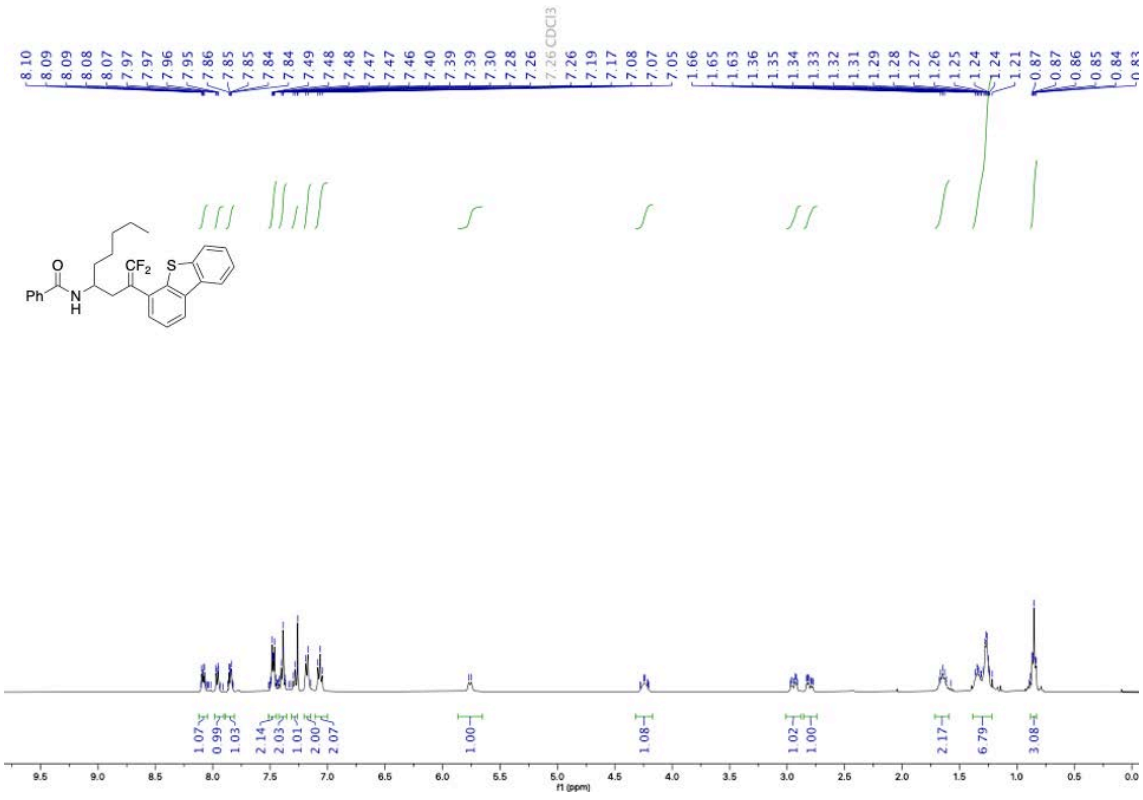
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3al**



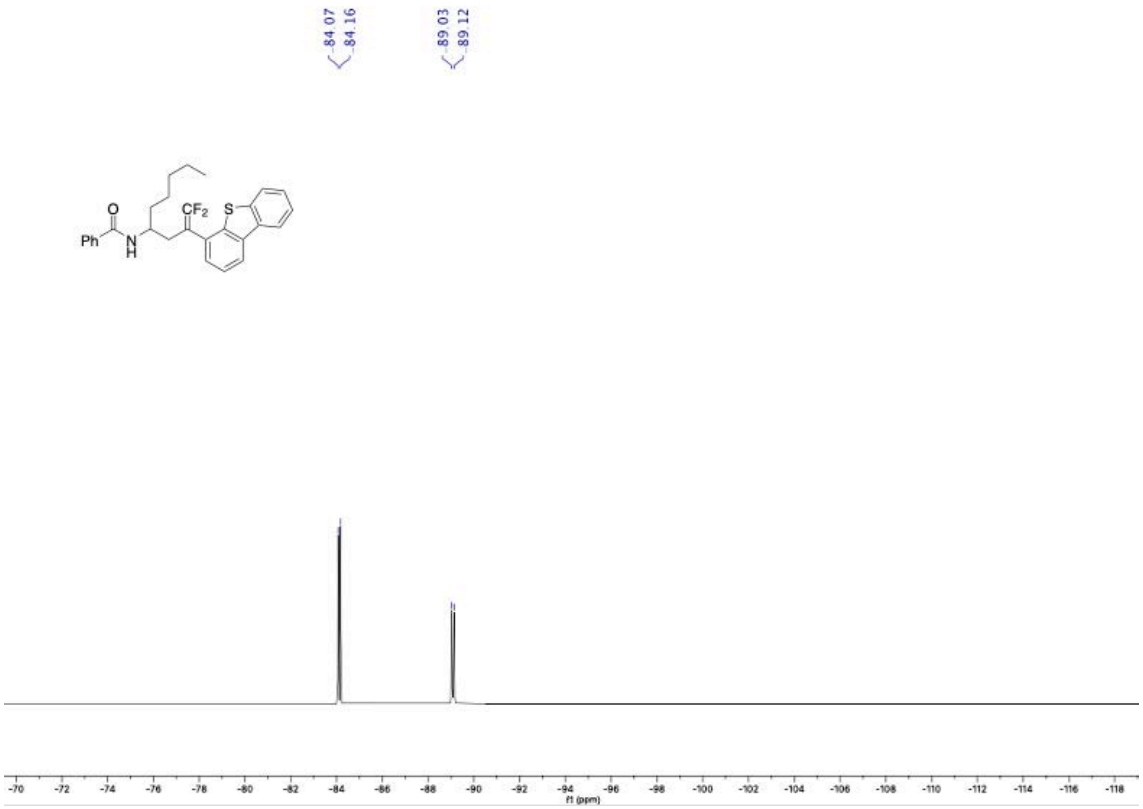
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3al**



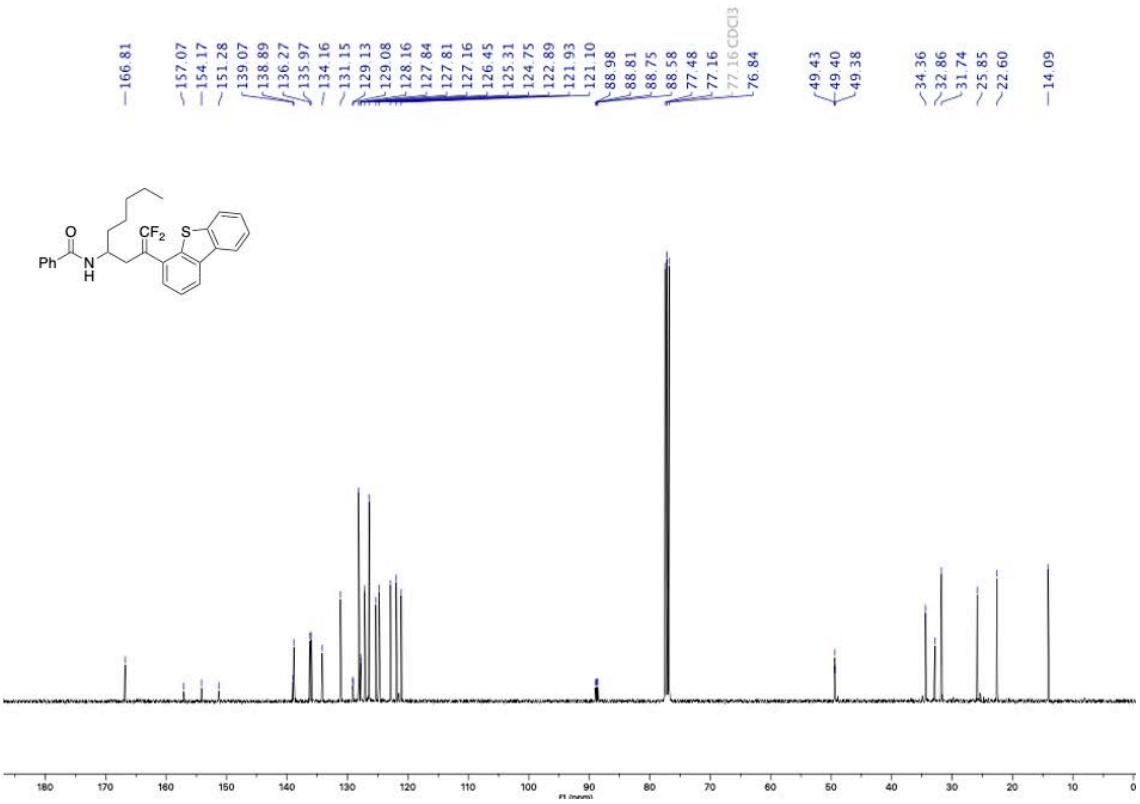
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3al**



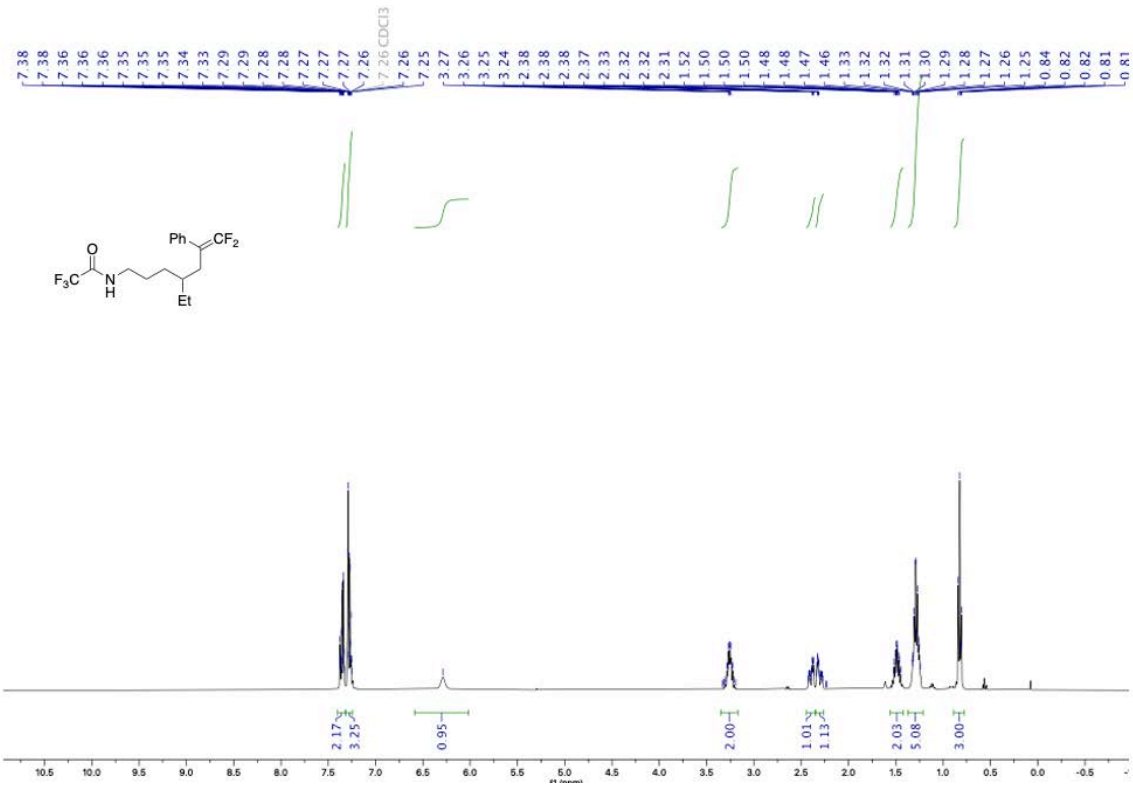
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3am**



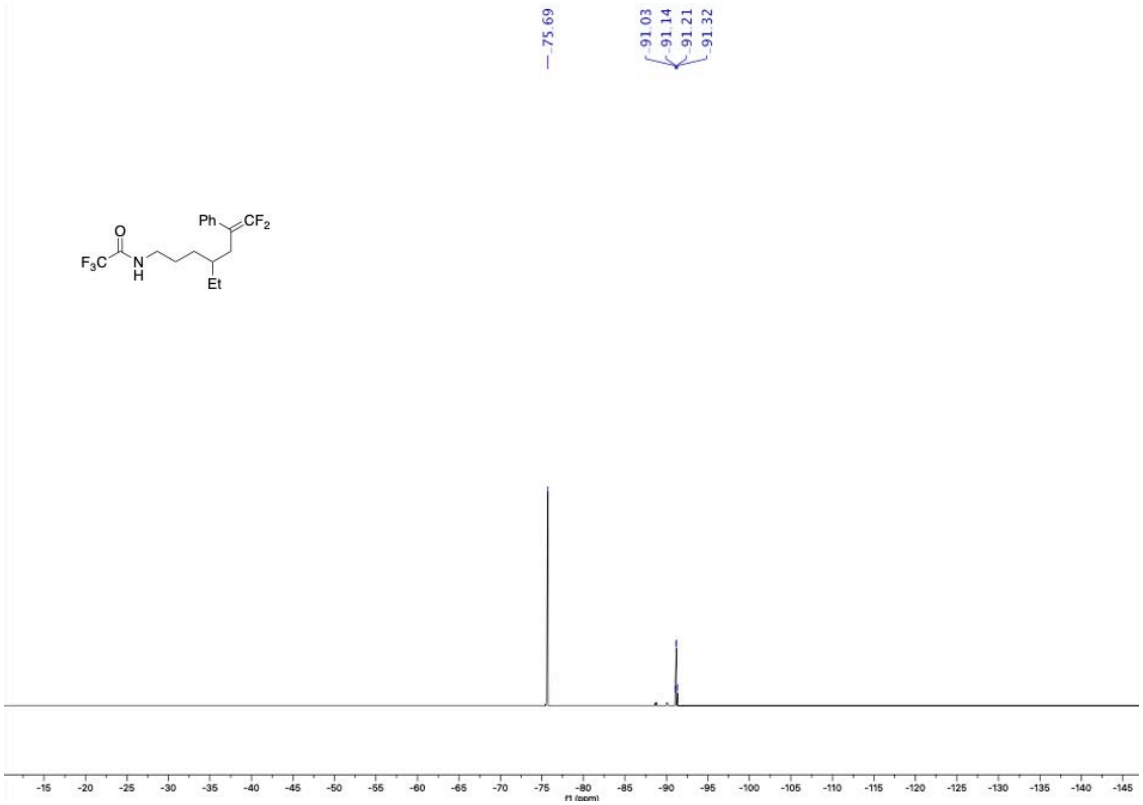
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3am**



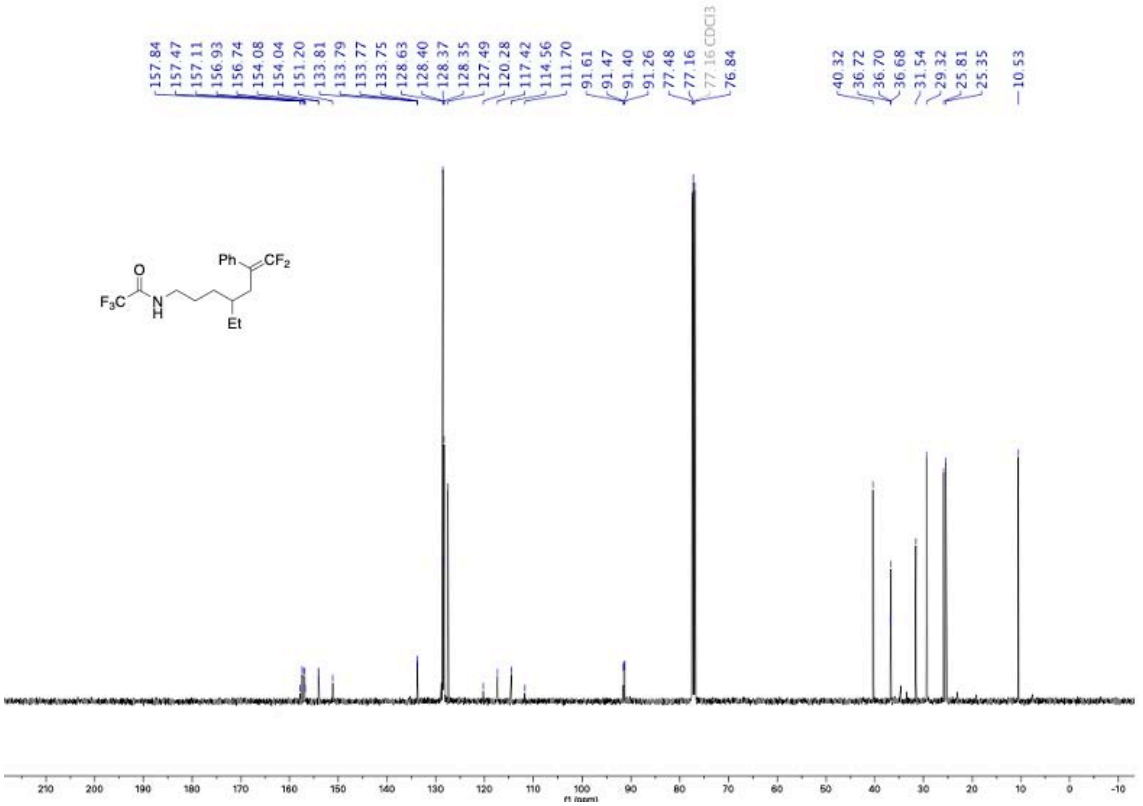
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3am**



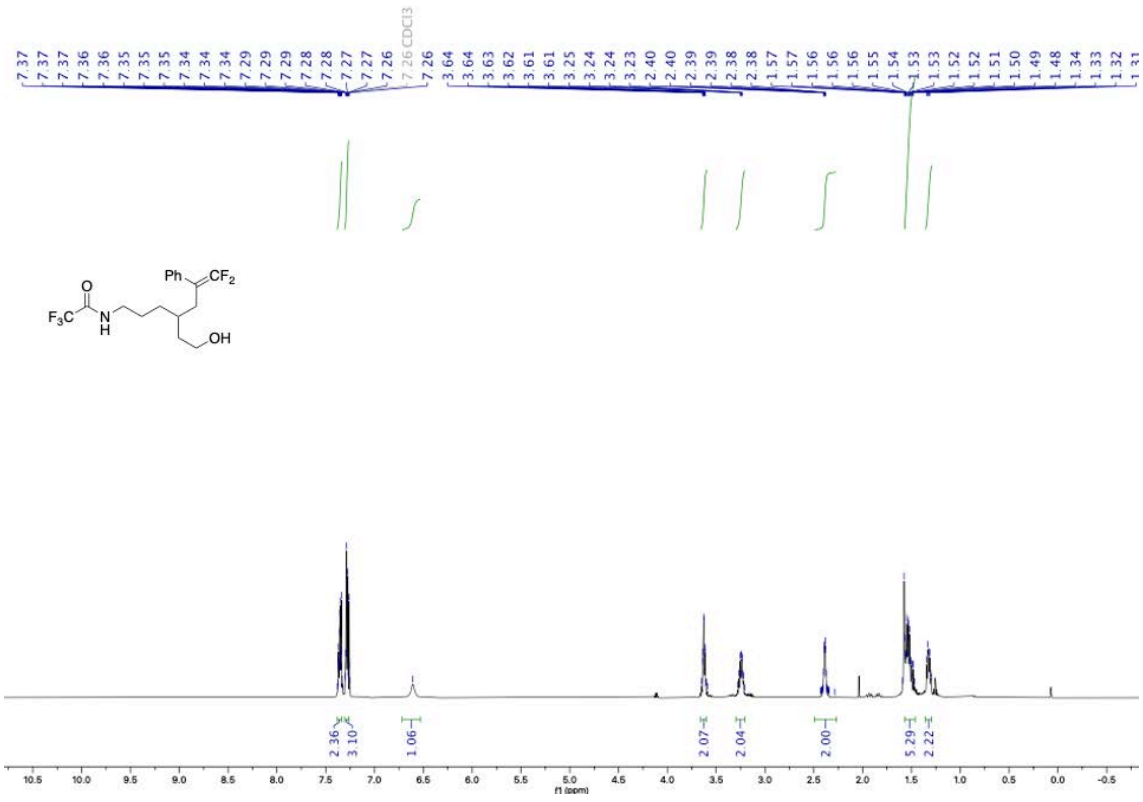
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6a**



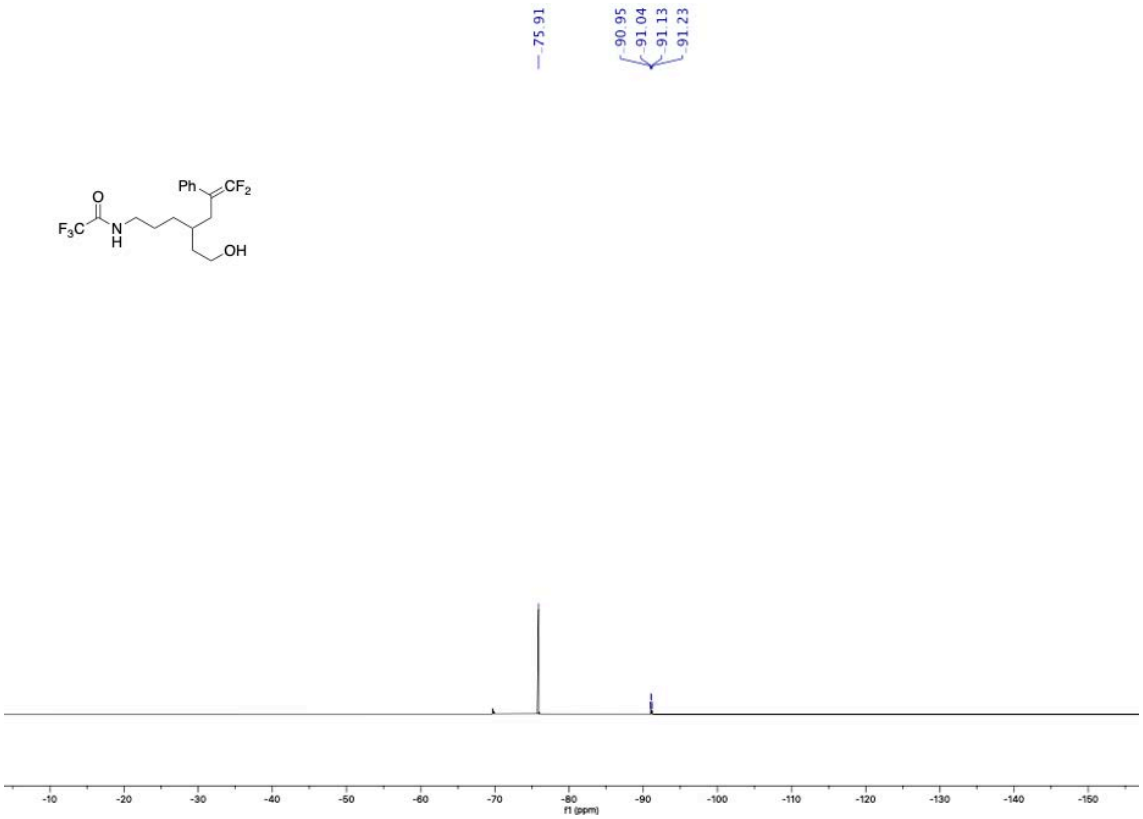
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6a**



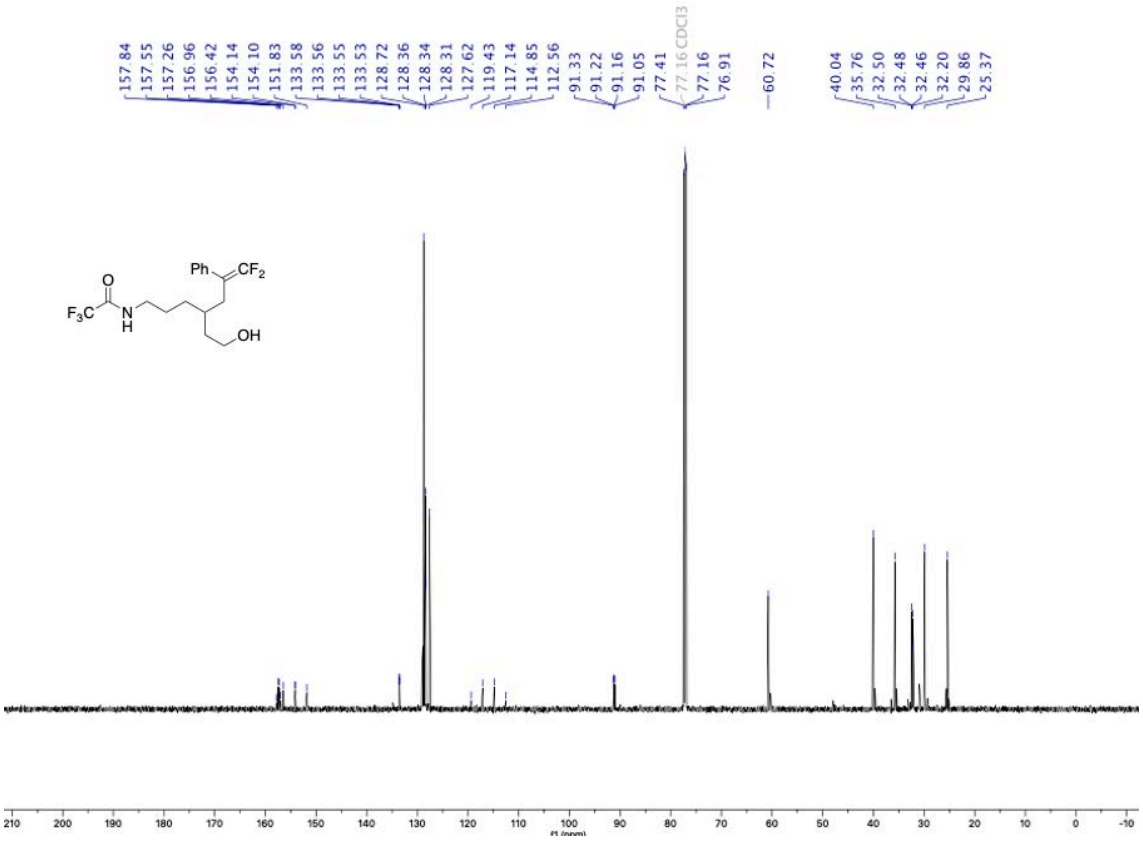
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6a**



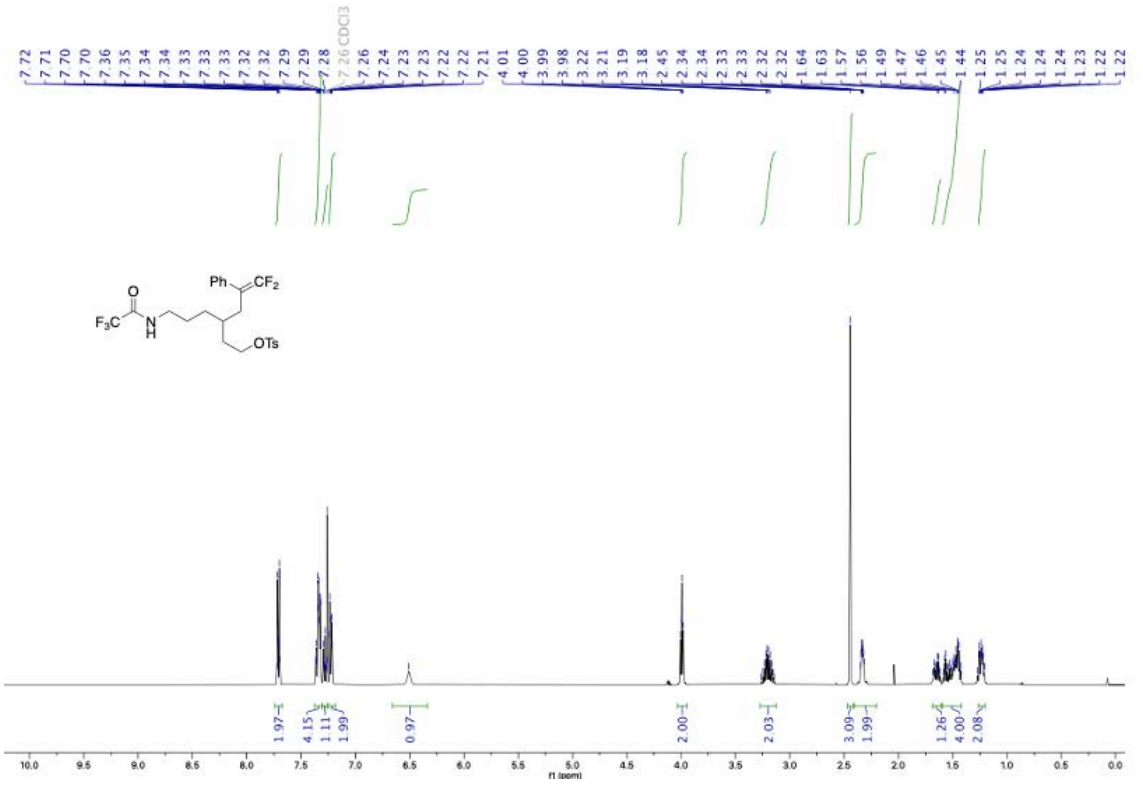
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6b**



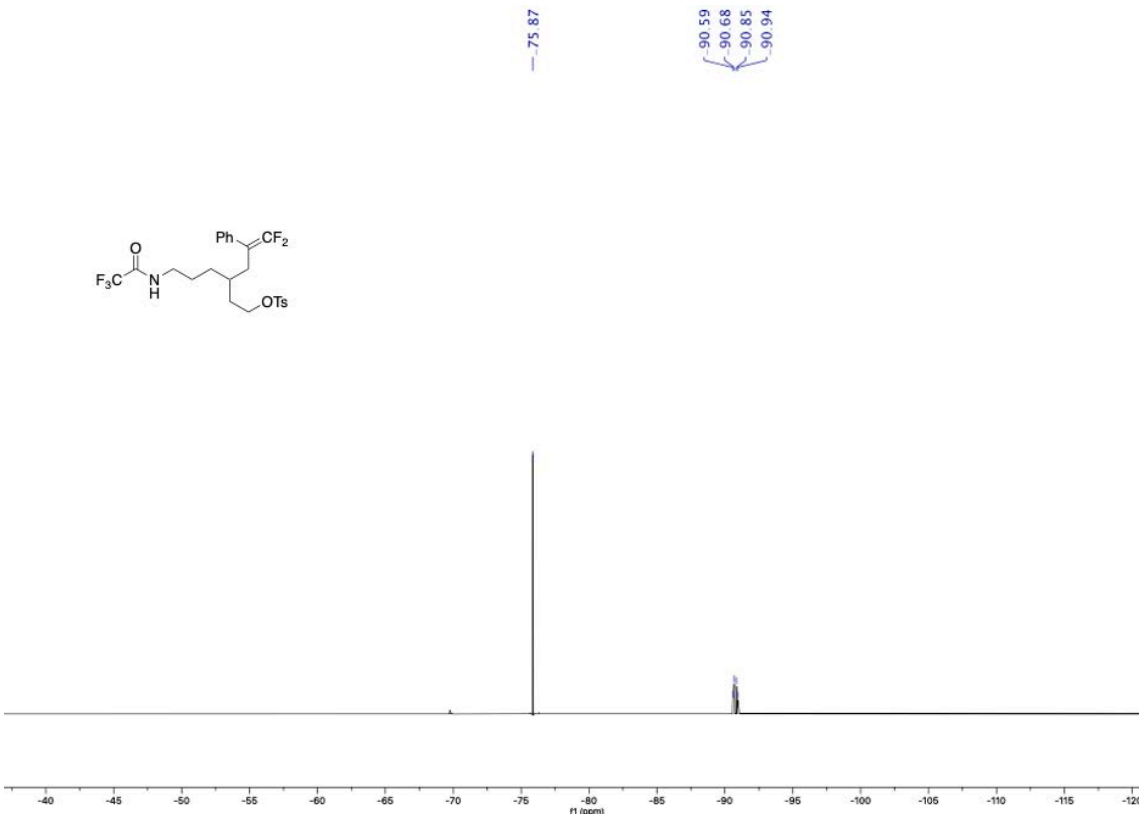
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6b**



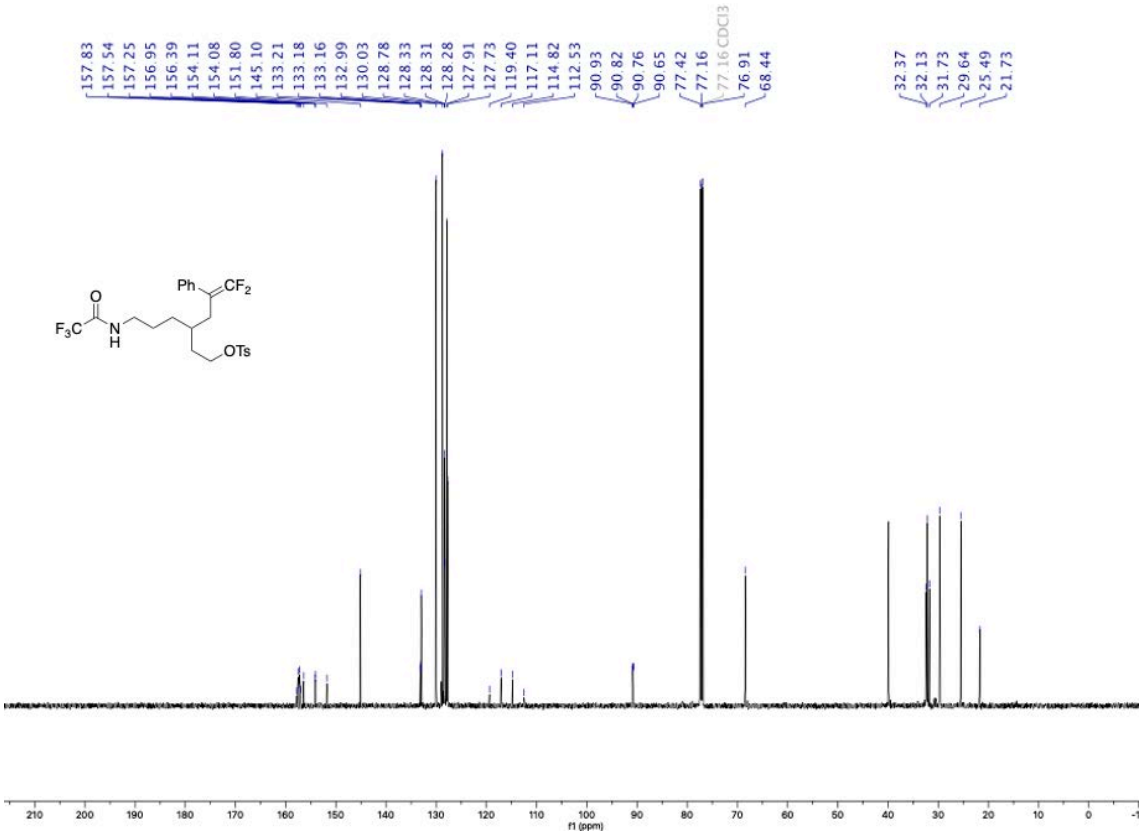
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6b**



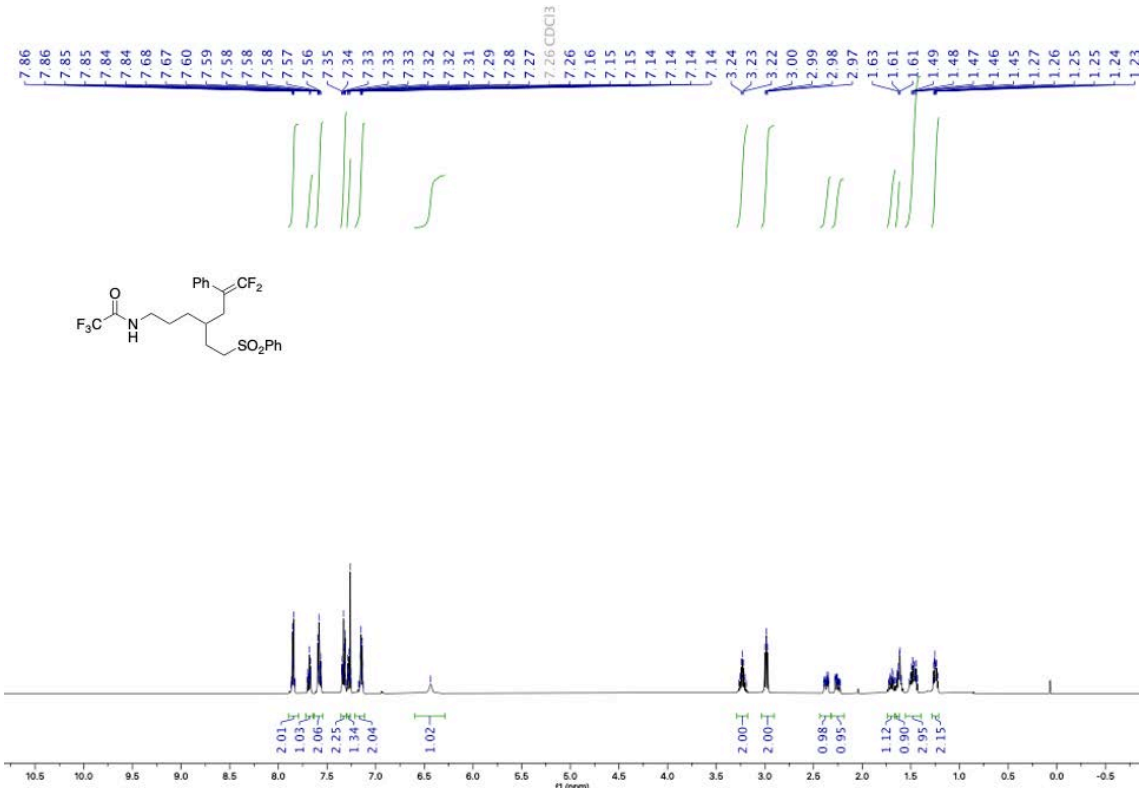
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6c**



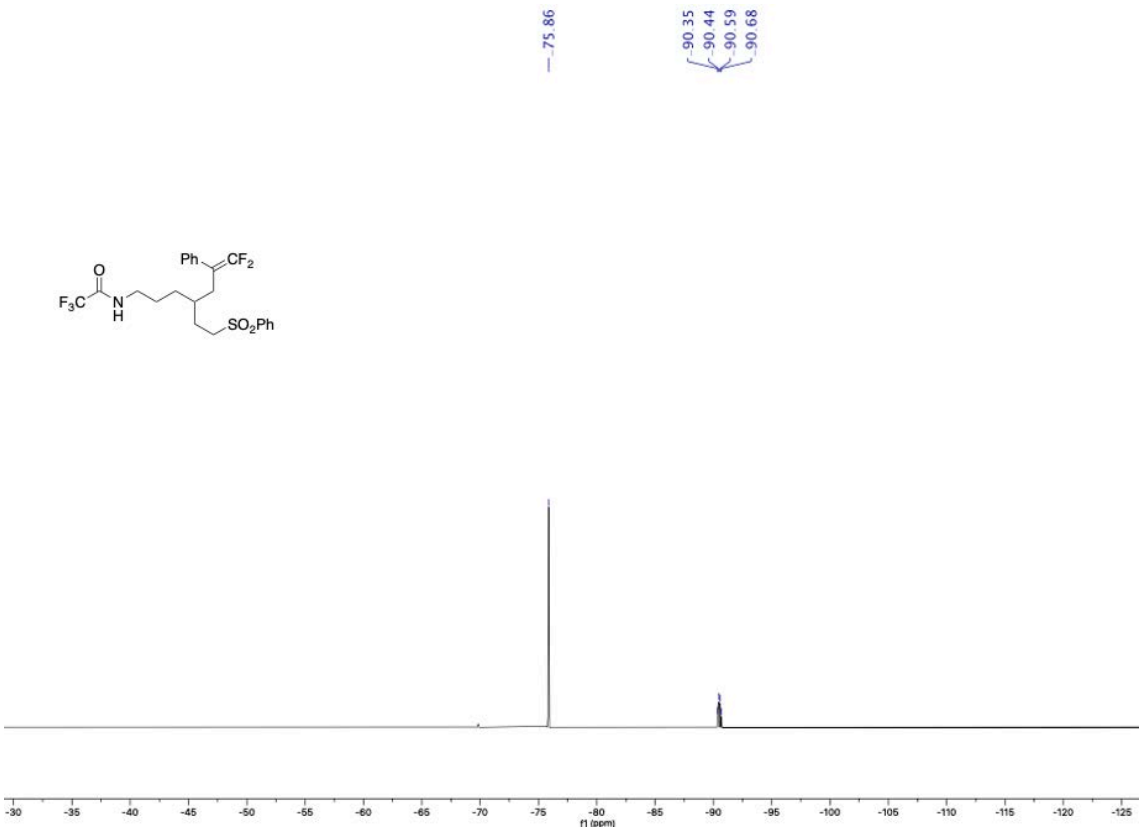
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6c**



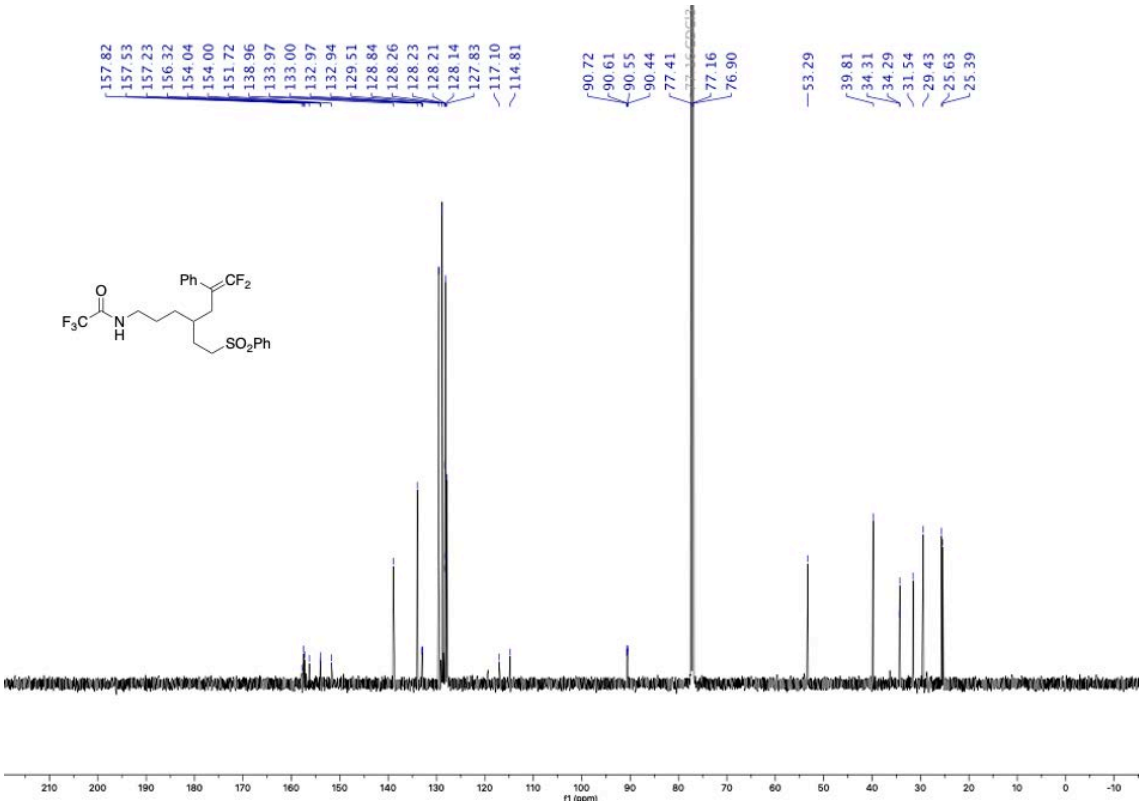
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6c**



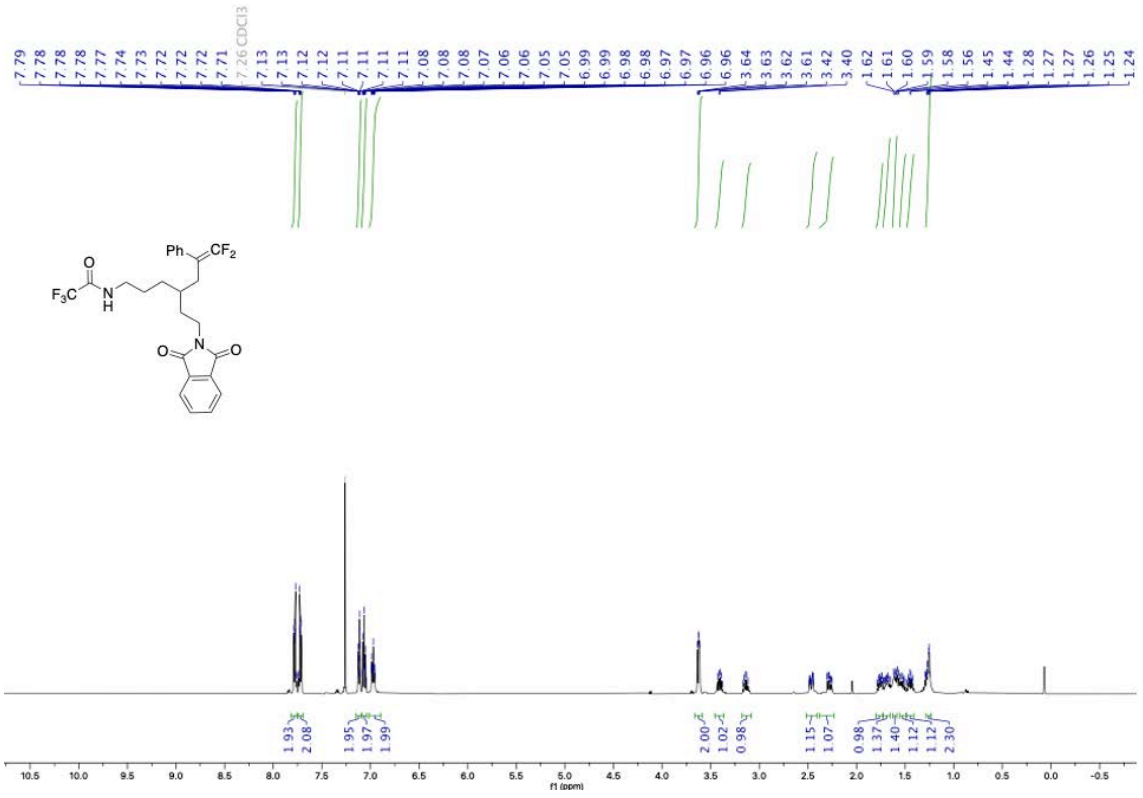
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6d**



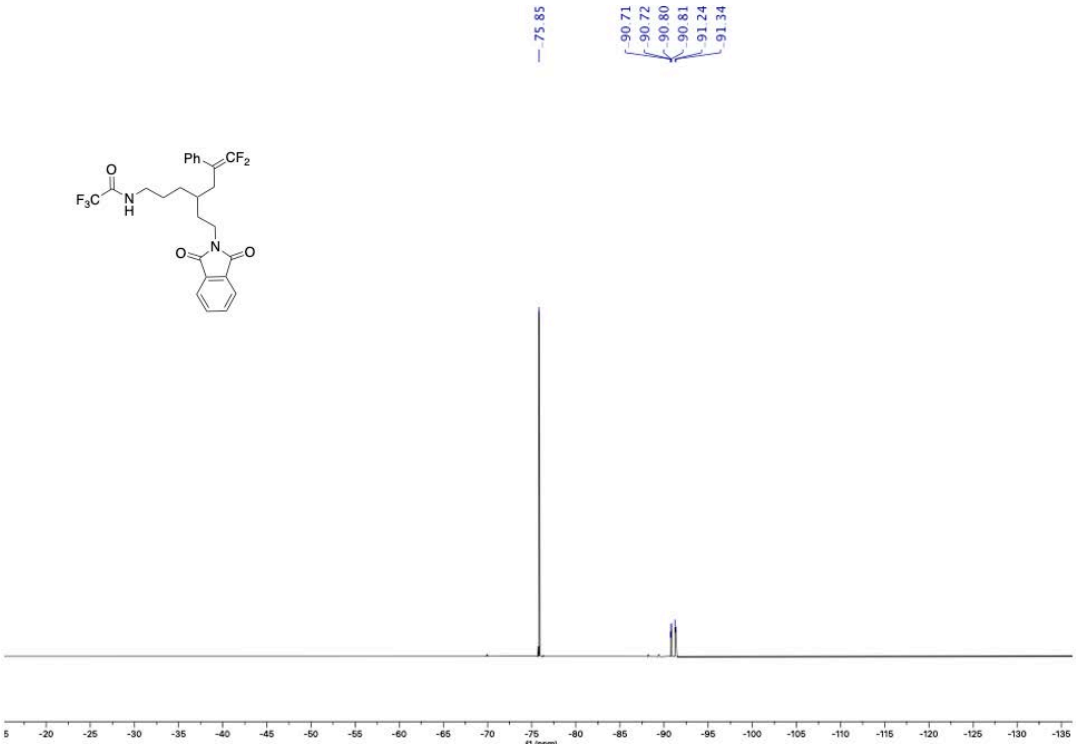
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6d**



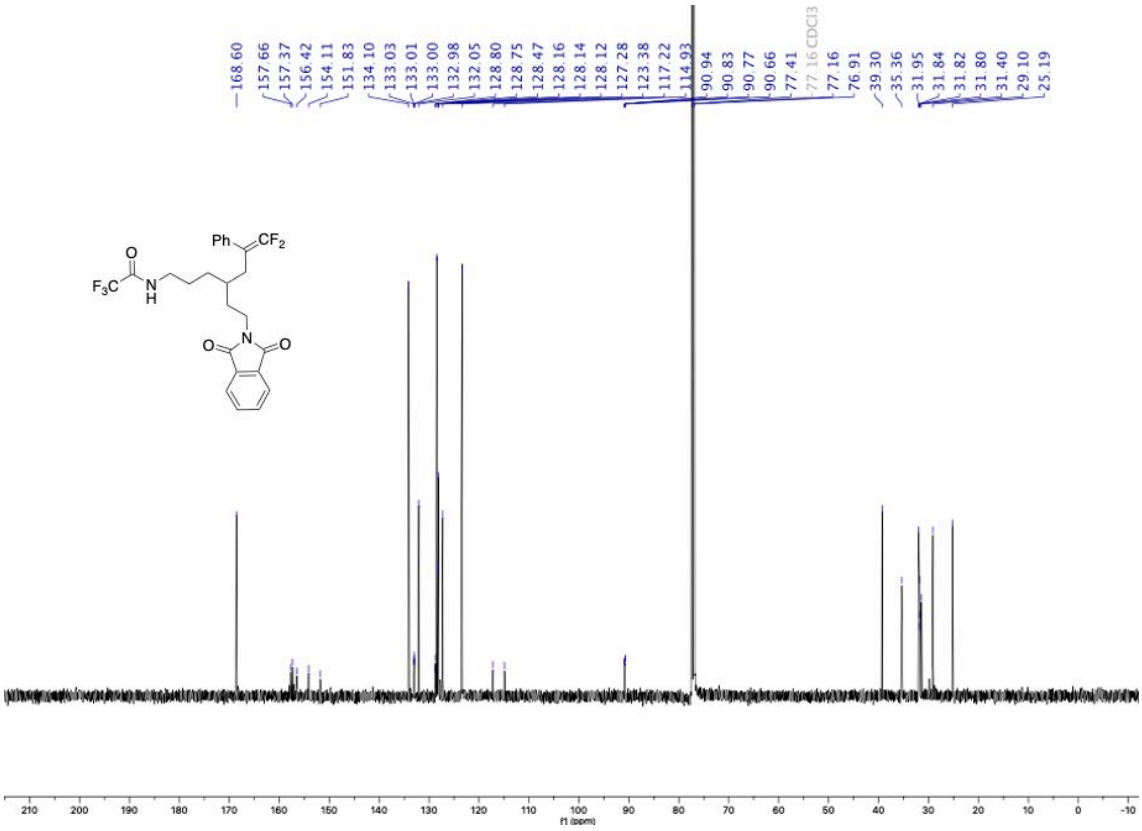
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6d**



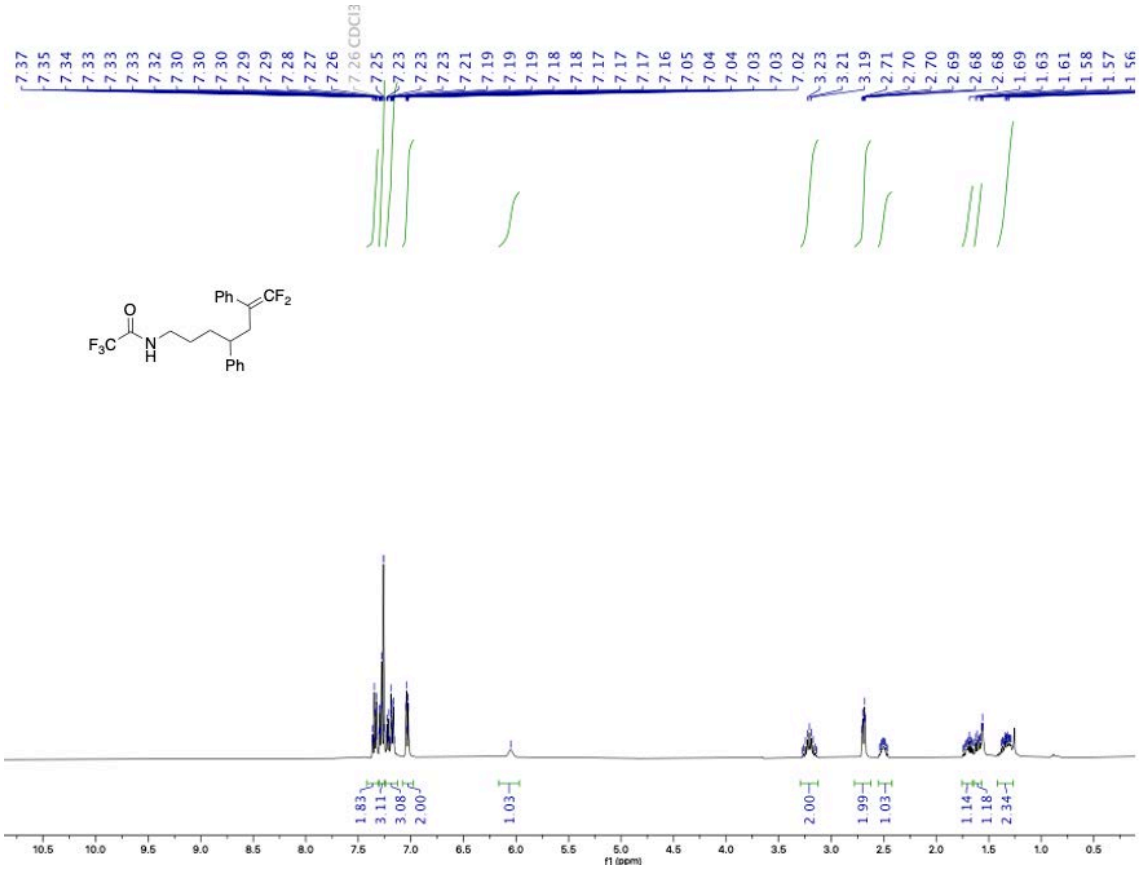
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6e**



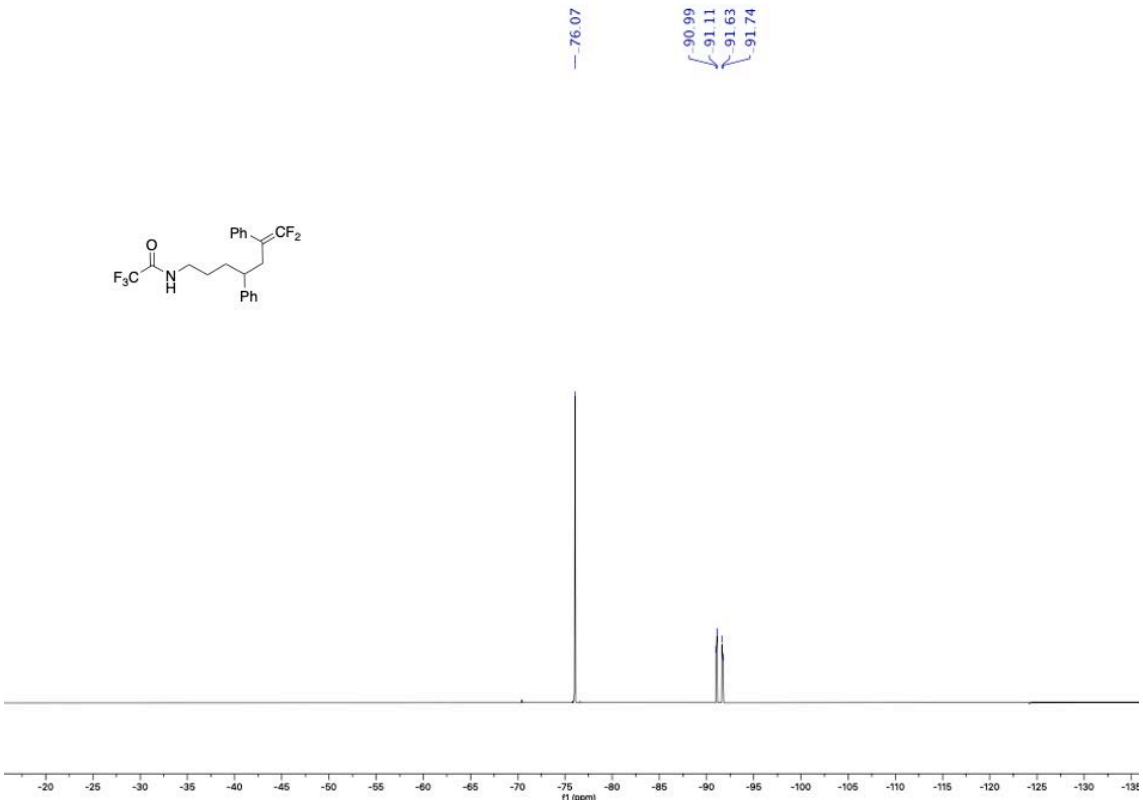
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6e**



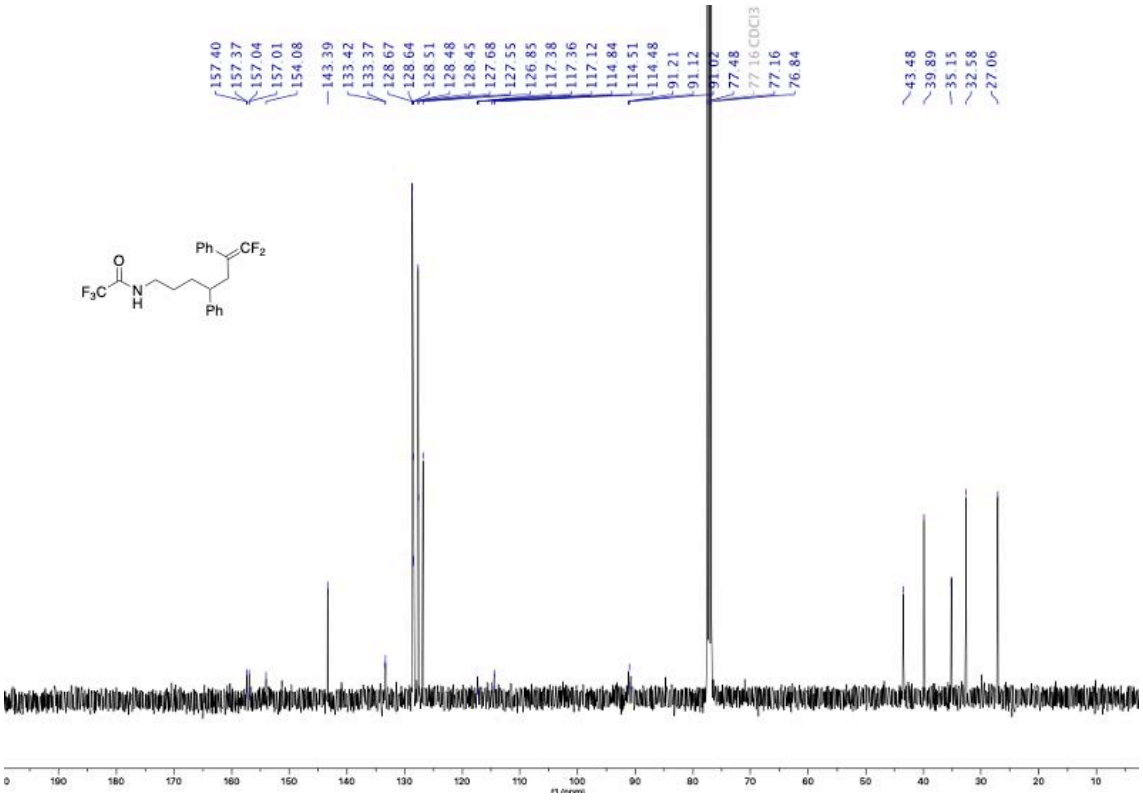
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6e**



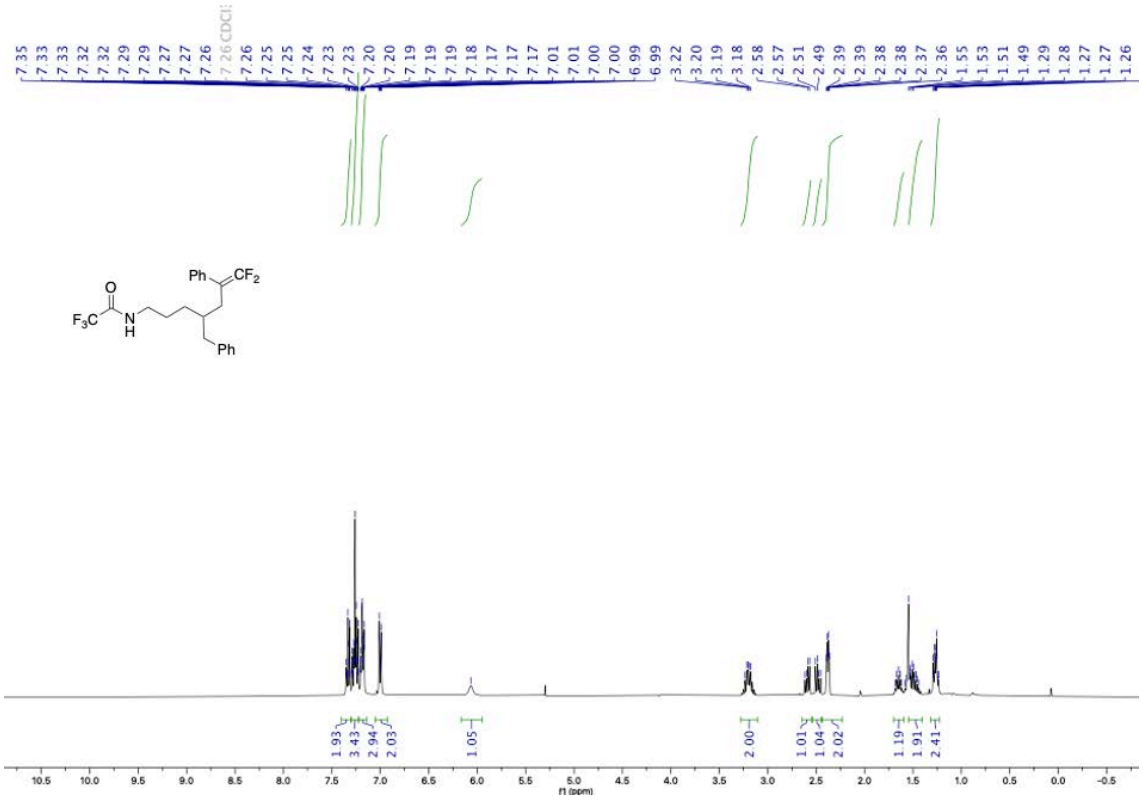
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6f**



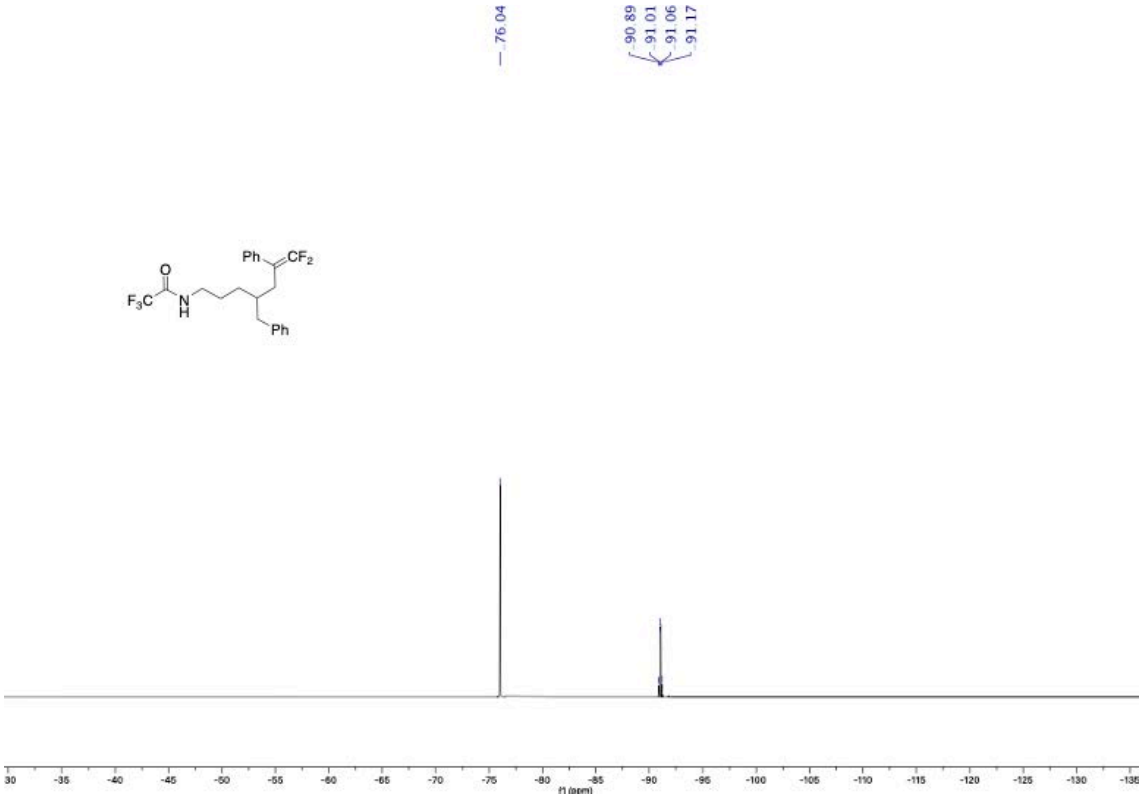
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6f**



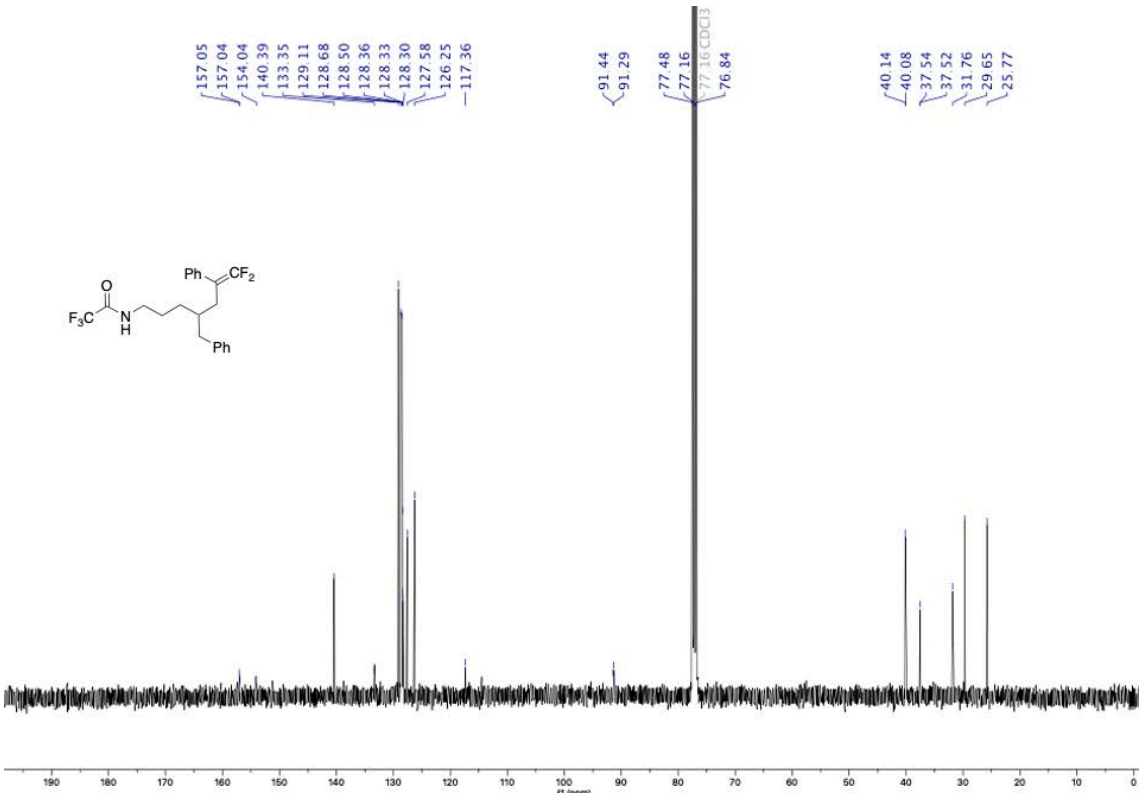
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6f**



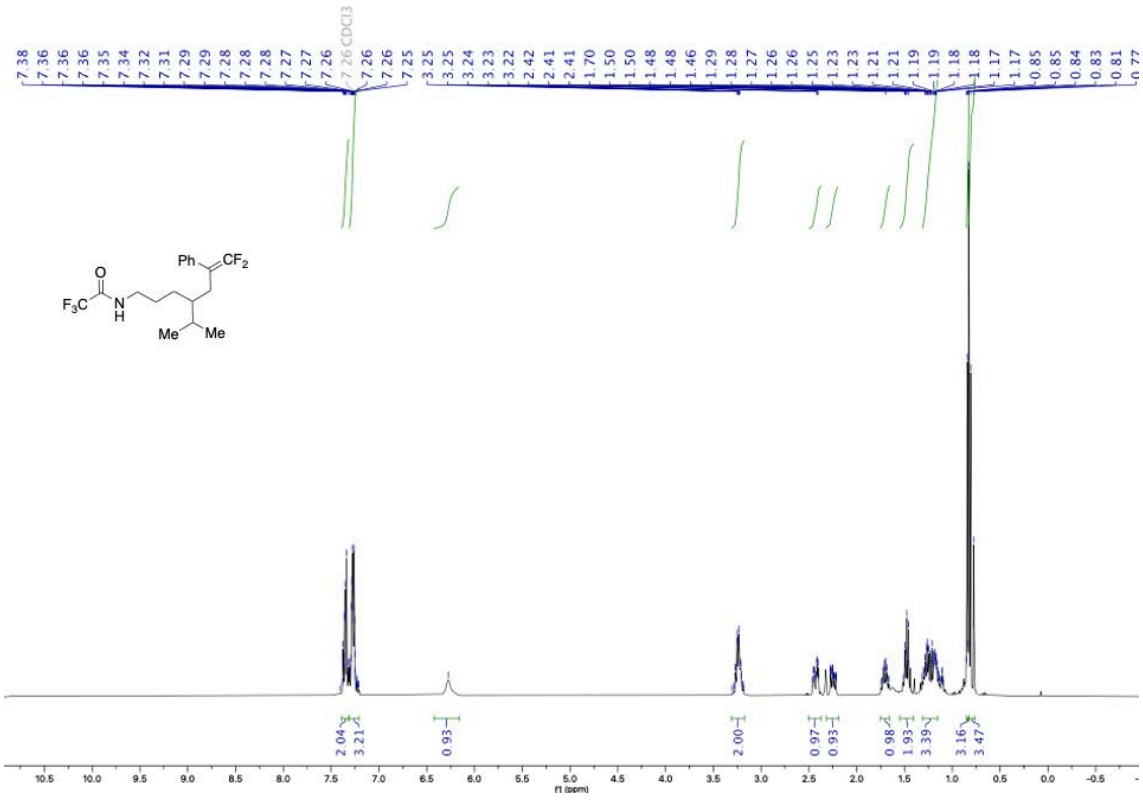
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6g**



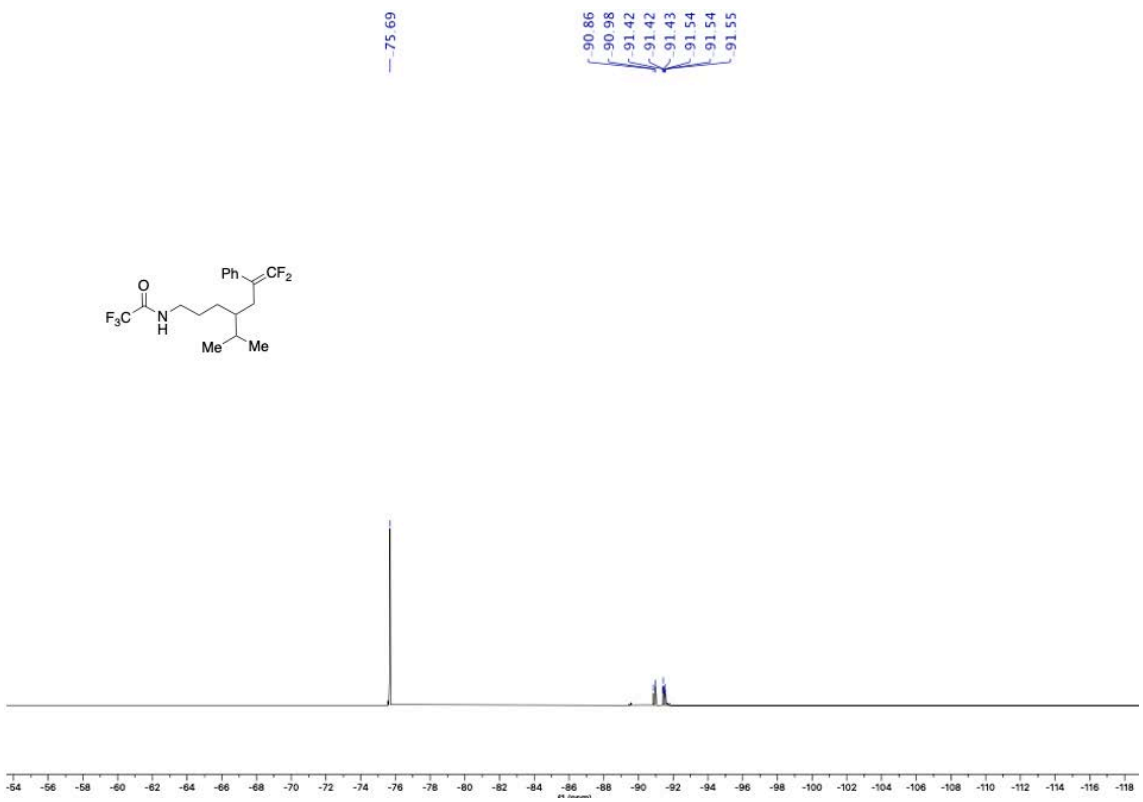
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6g**



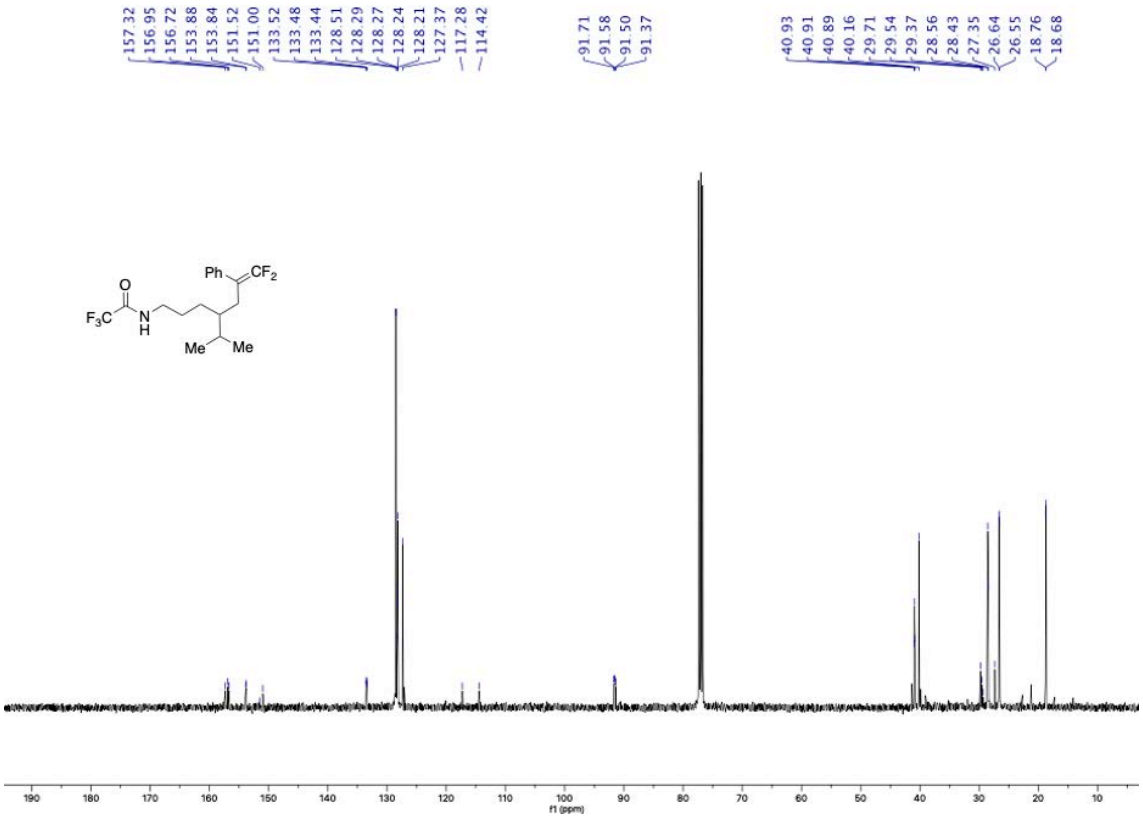
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6g**



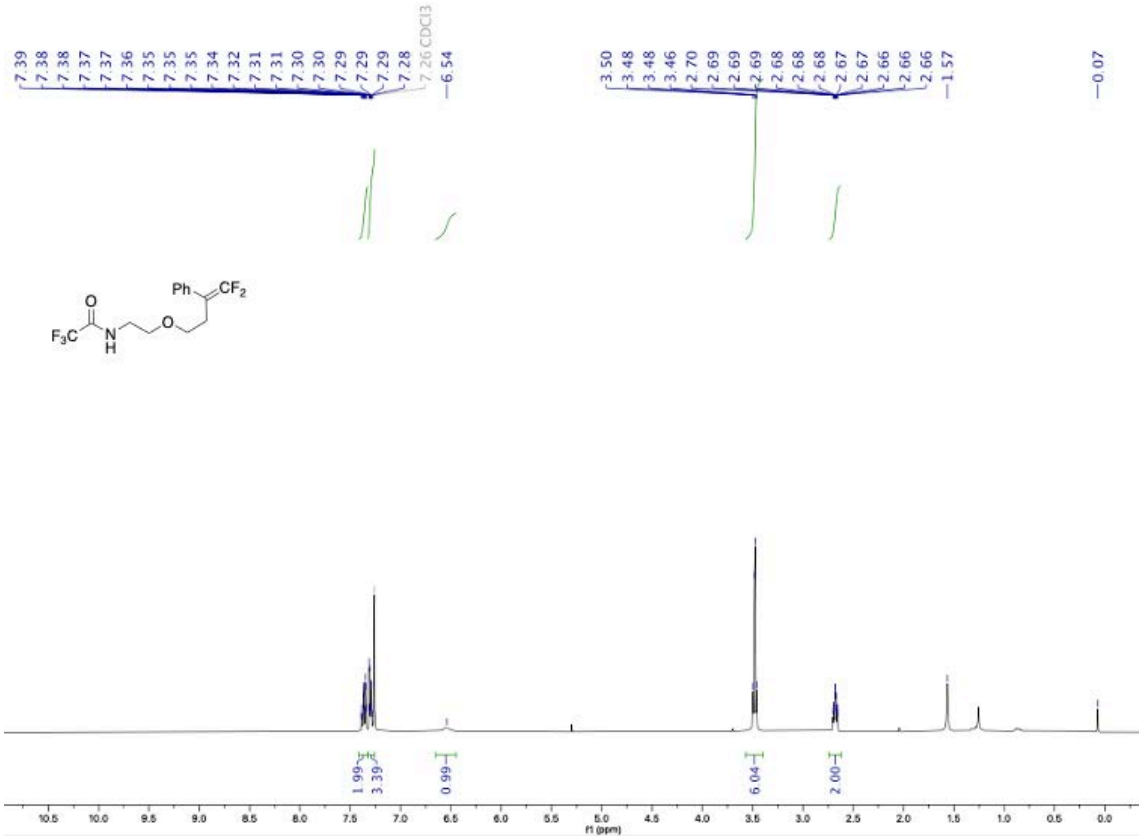
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6h**



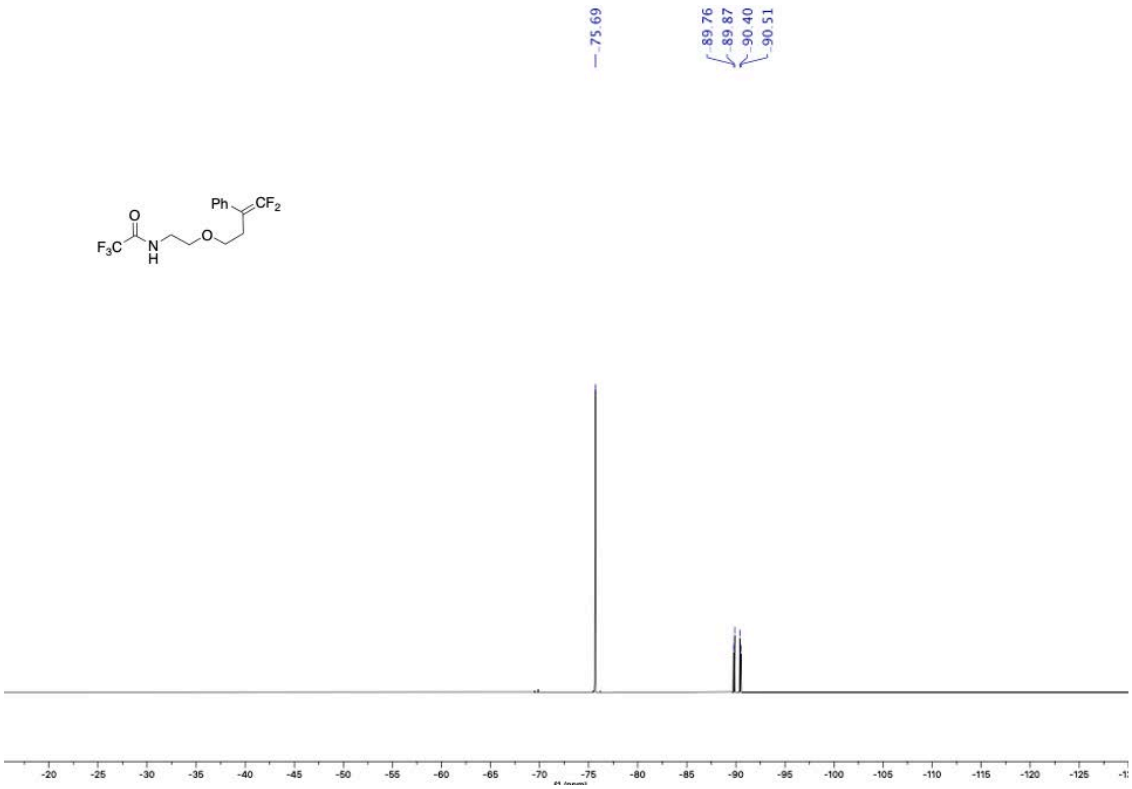
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6h**



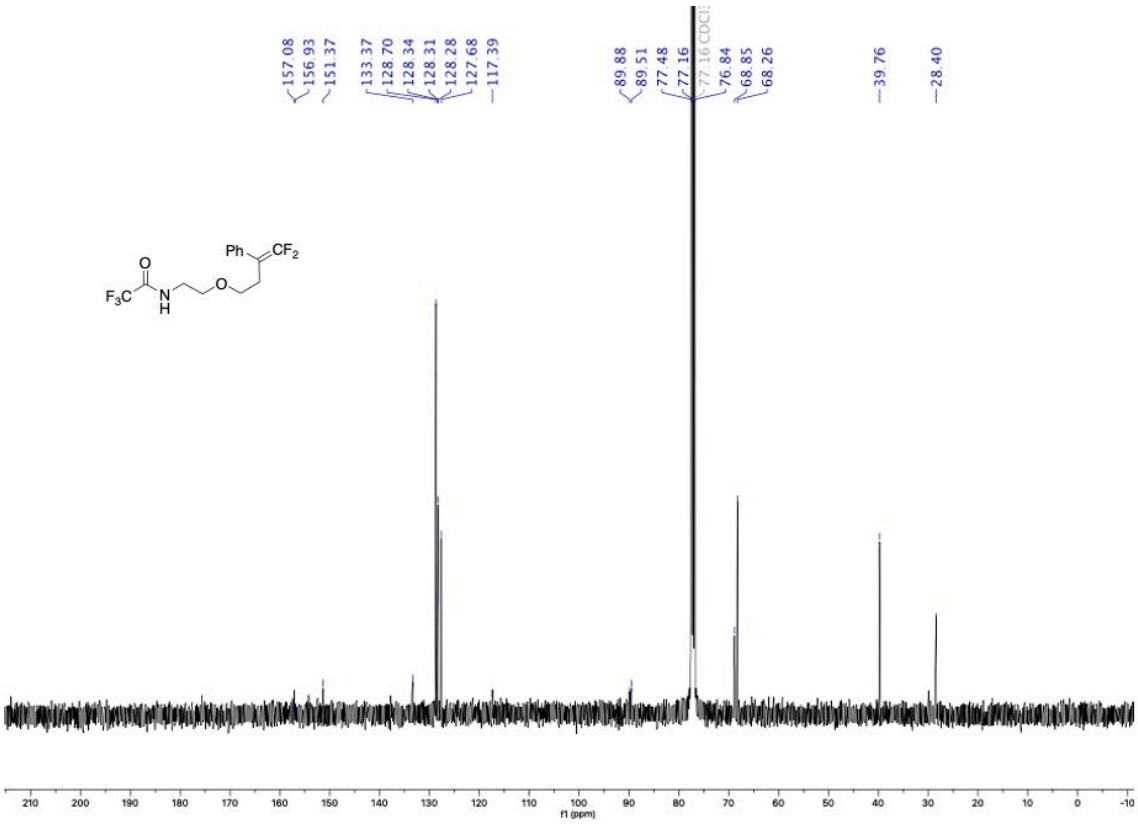
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6h**



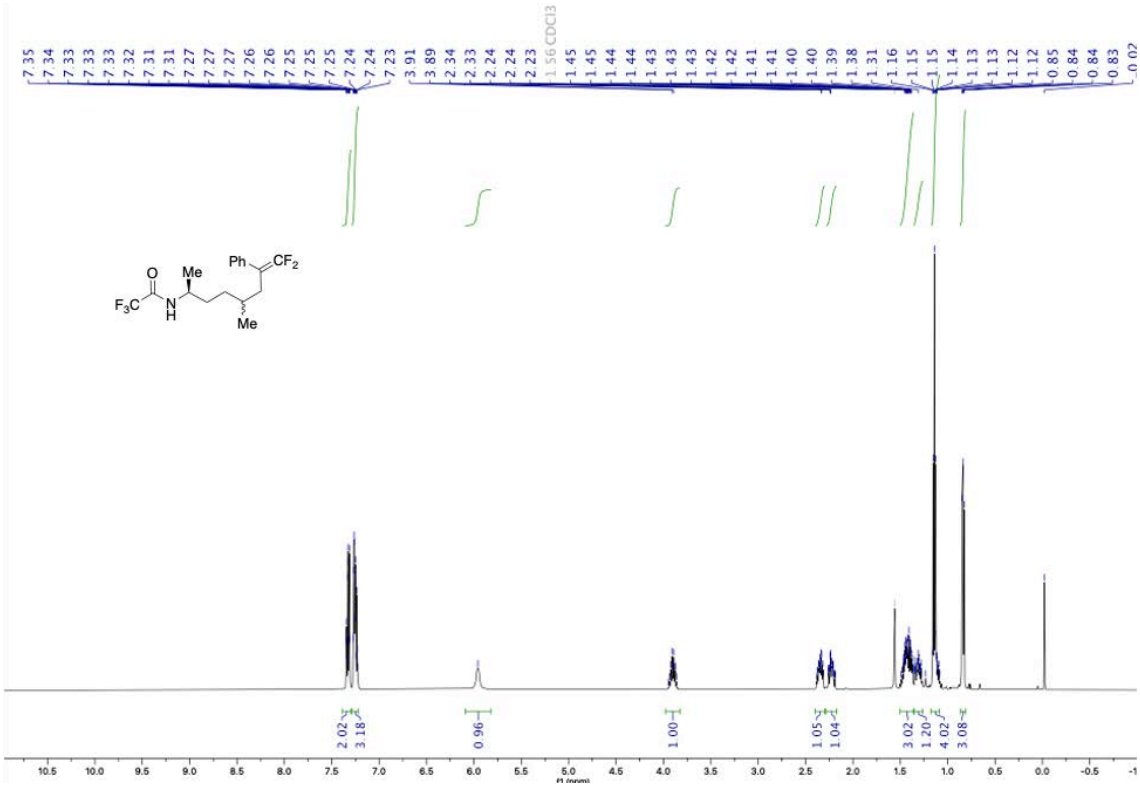
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6i**



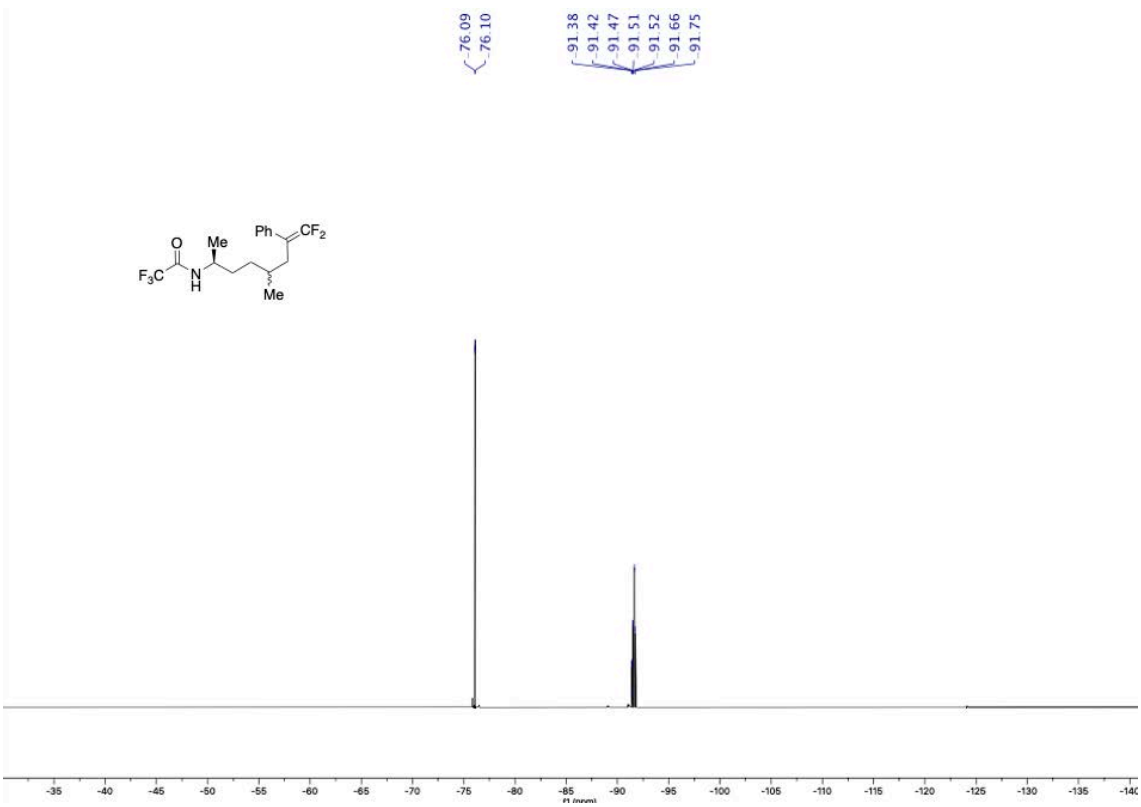
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6i**



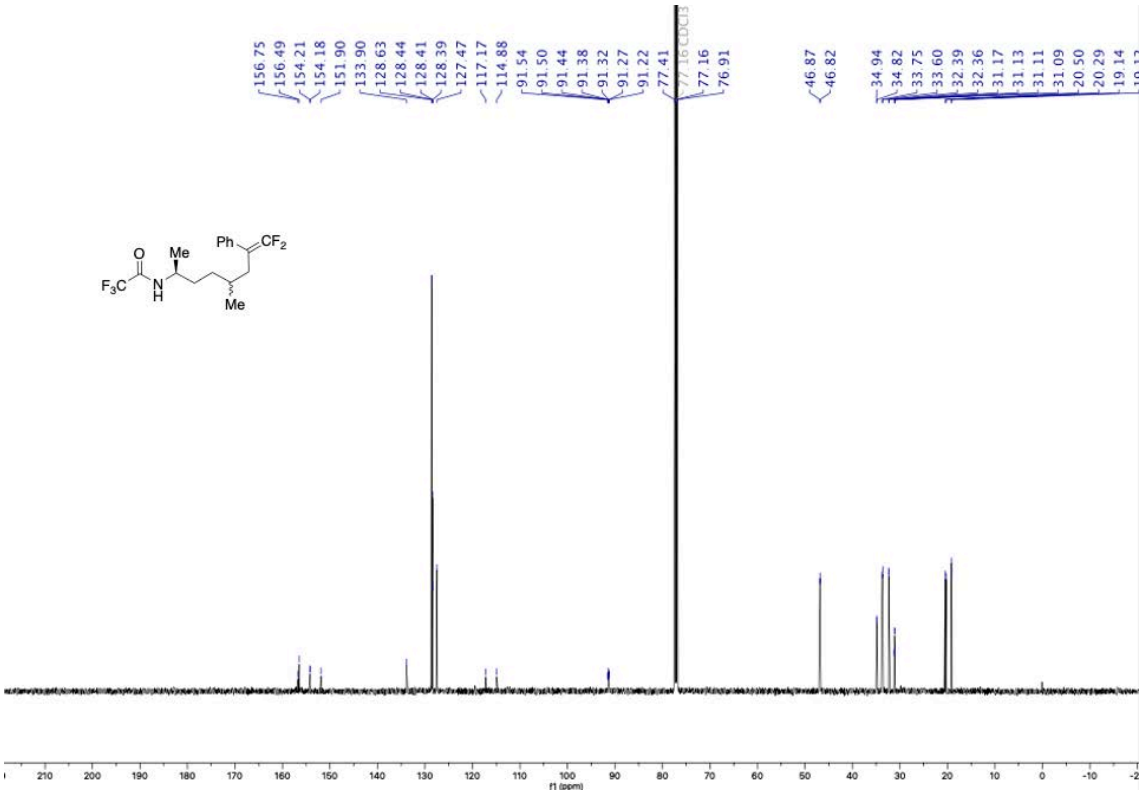
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6i**



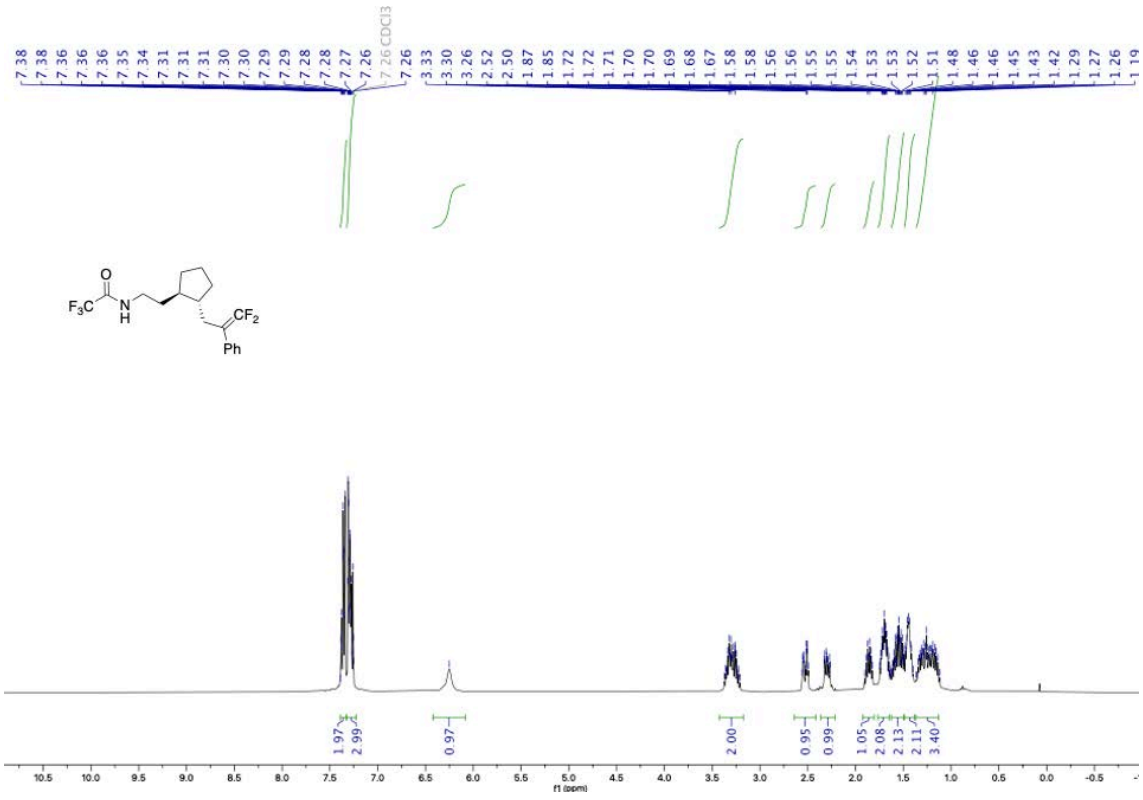
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6j**



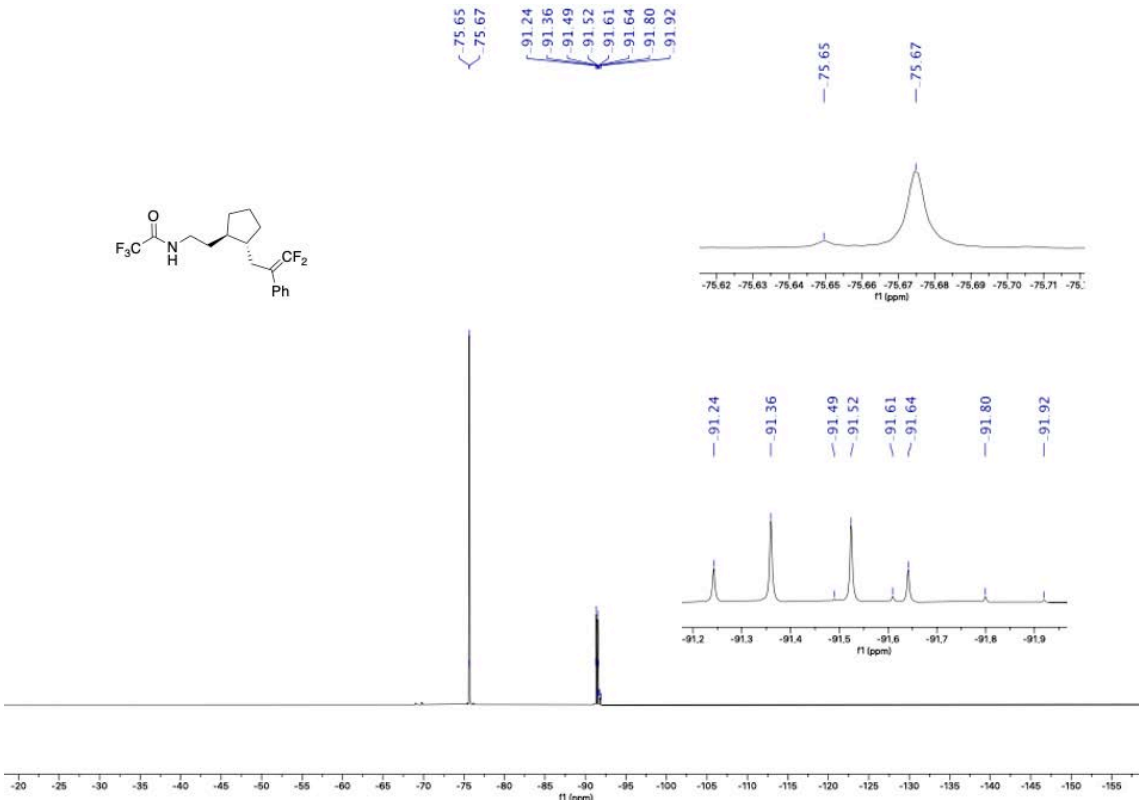
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6j**



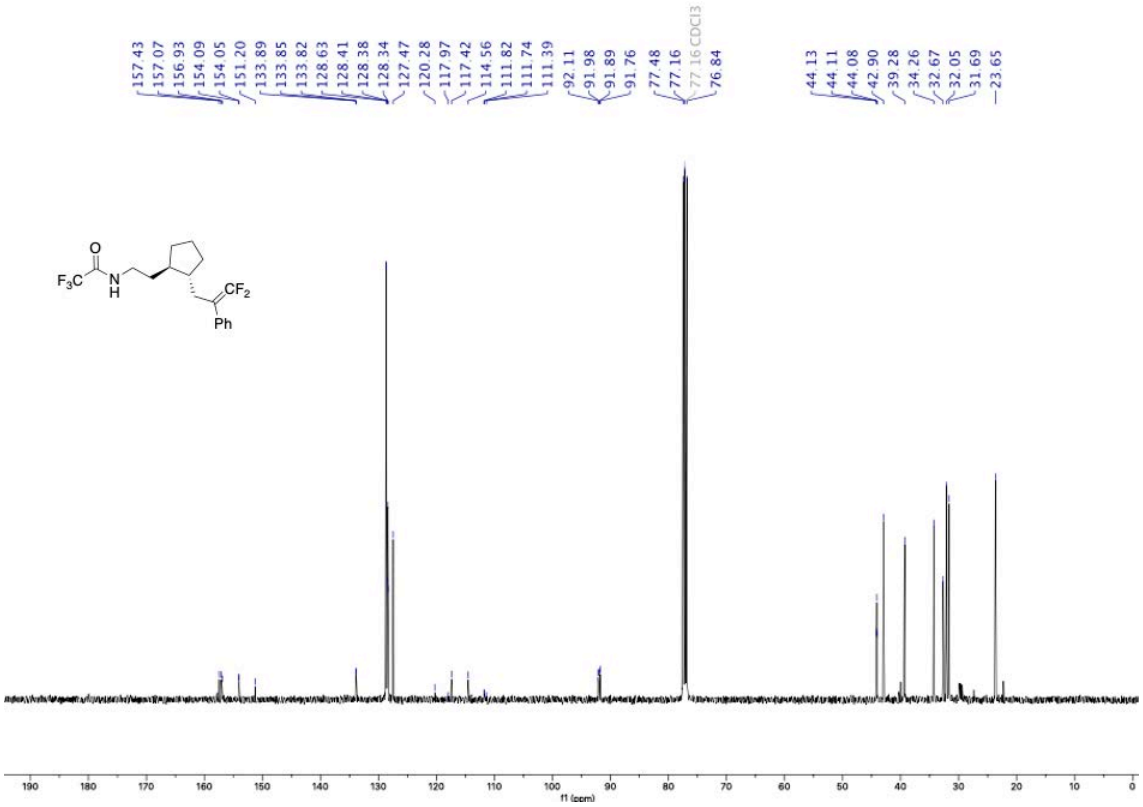
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6j**



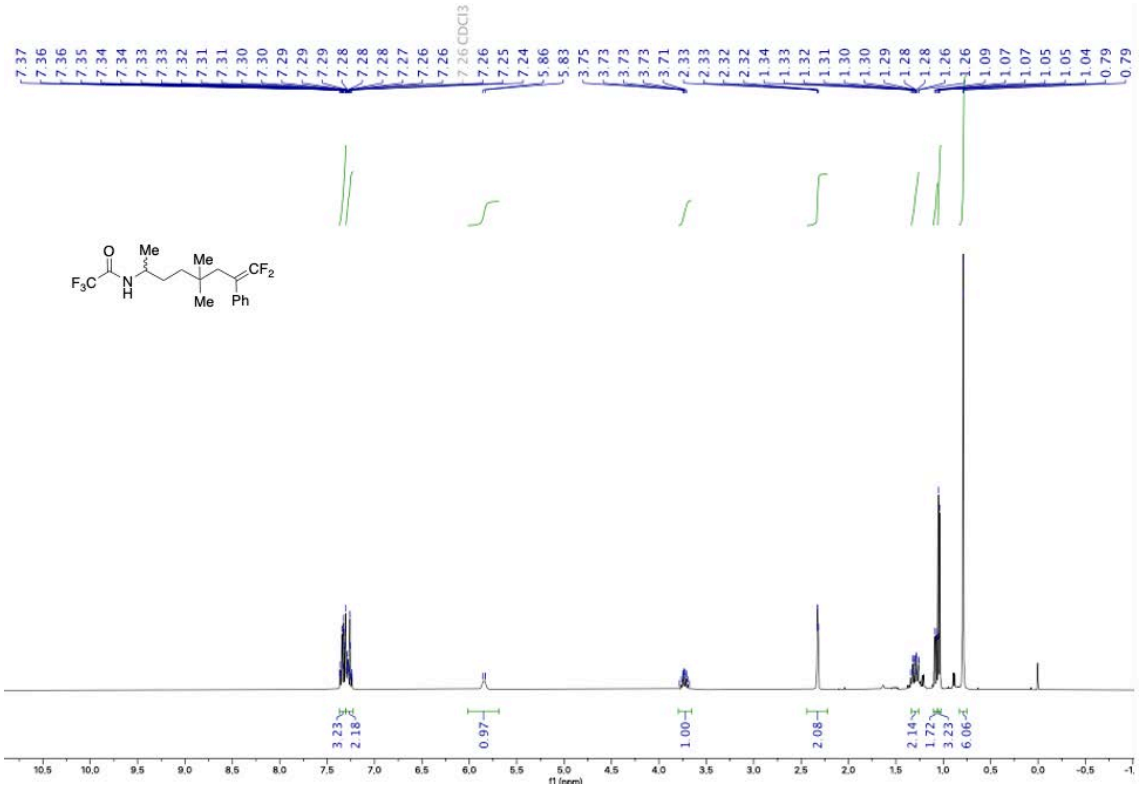
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6k**



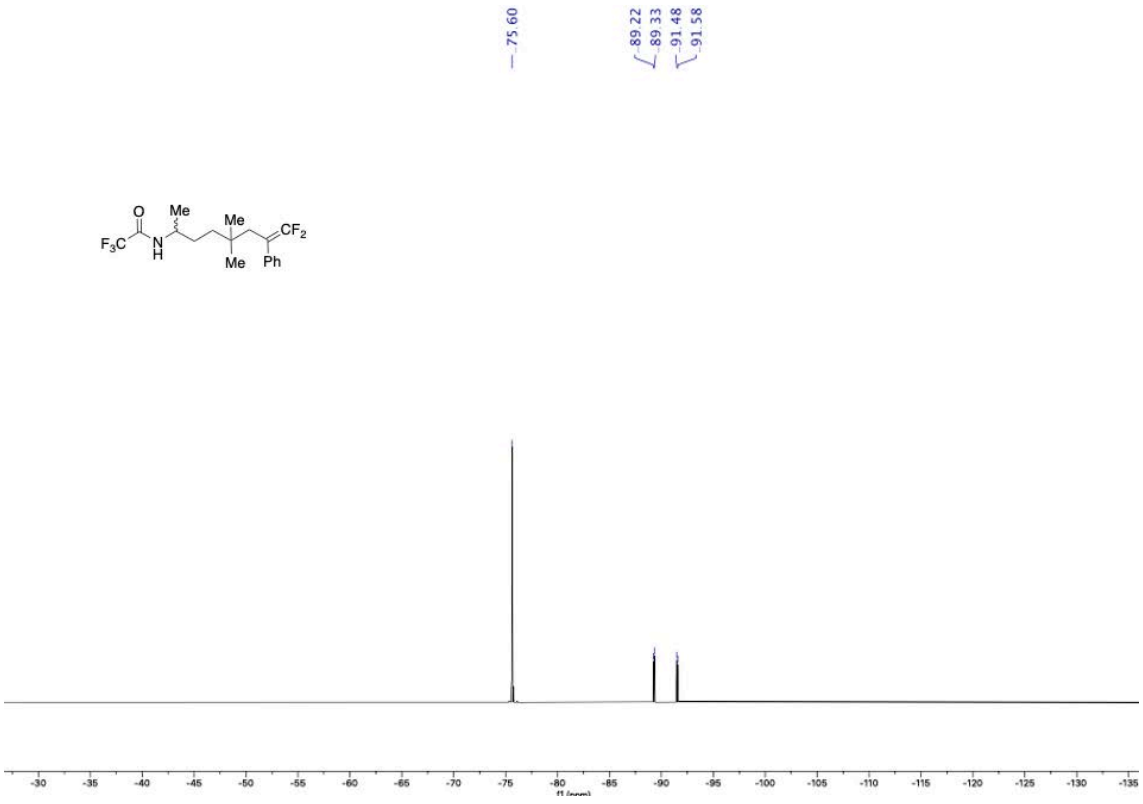
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6k**



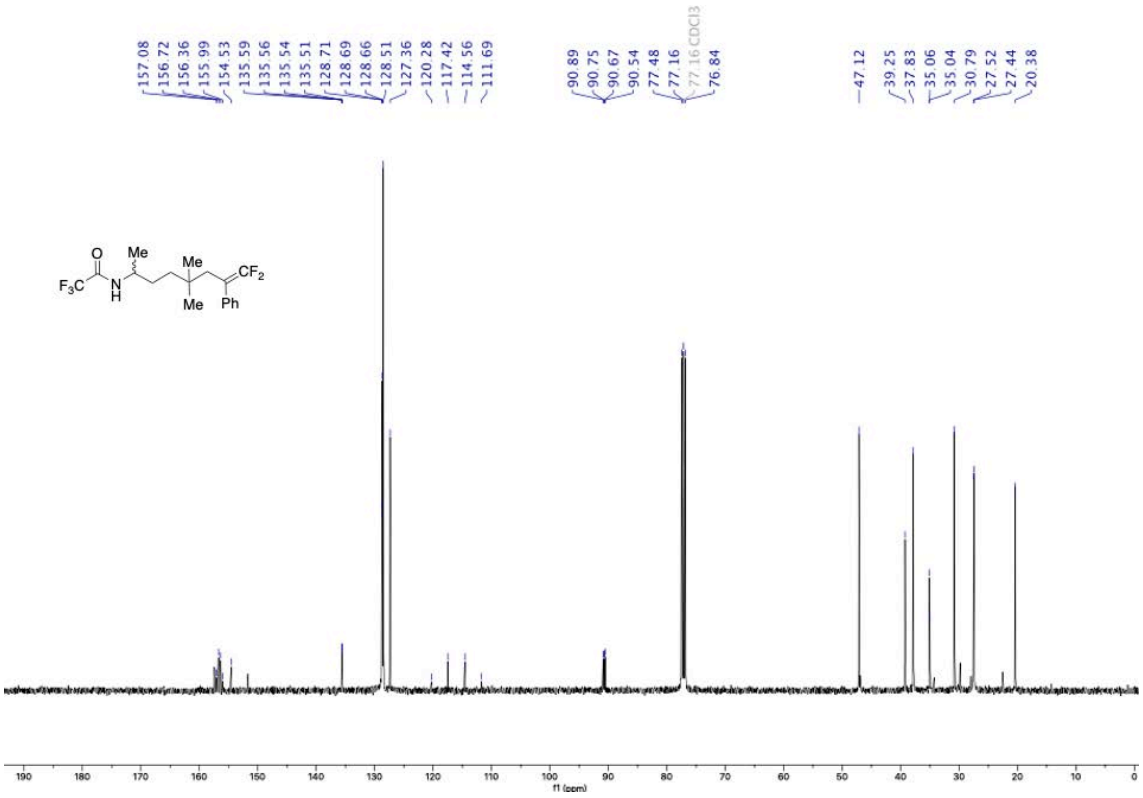
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6k**



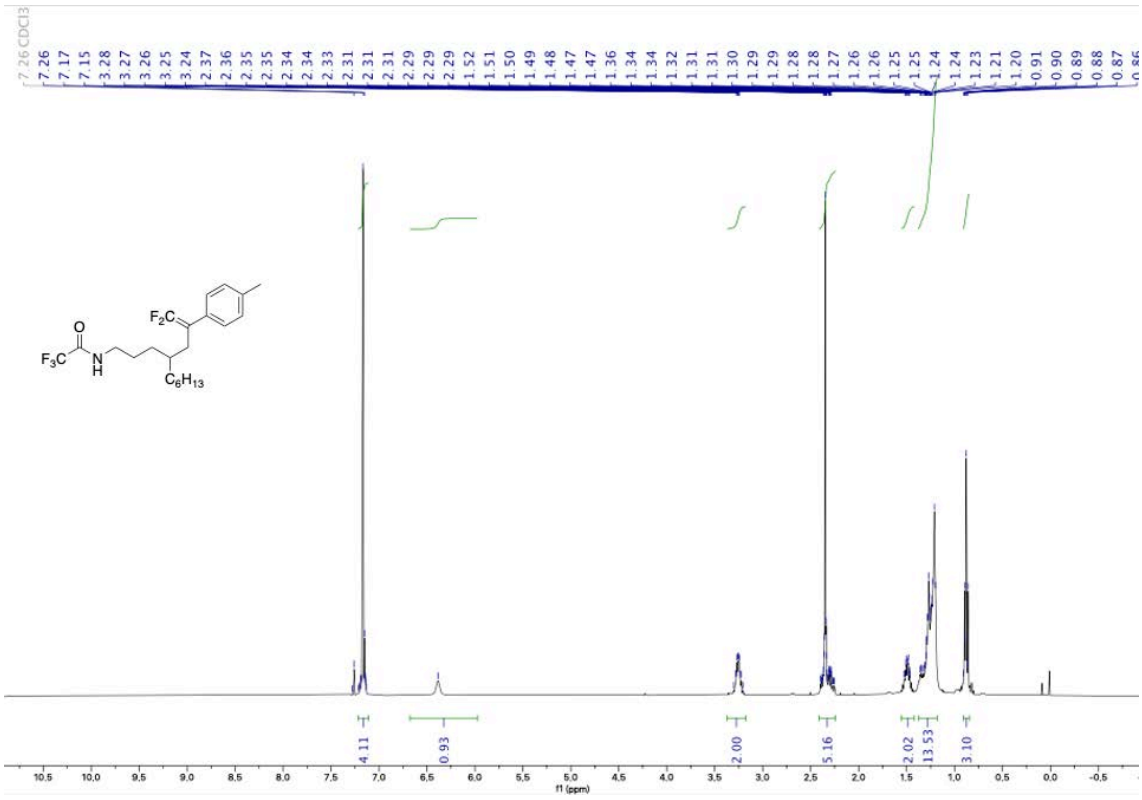
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6l**



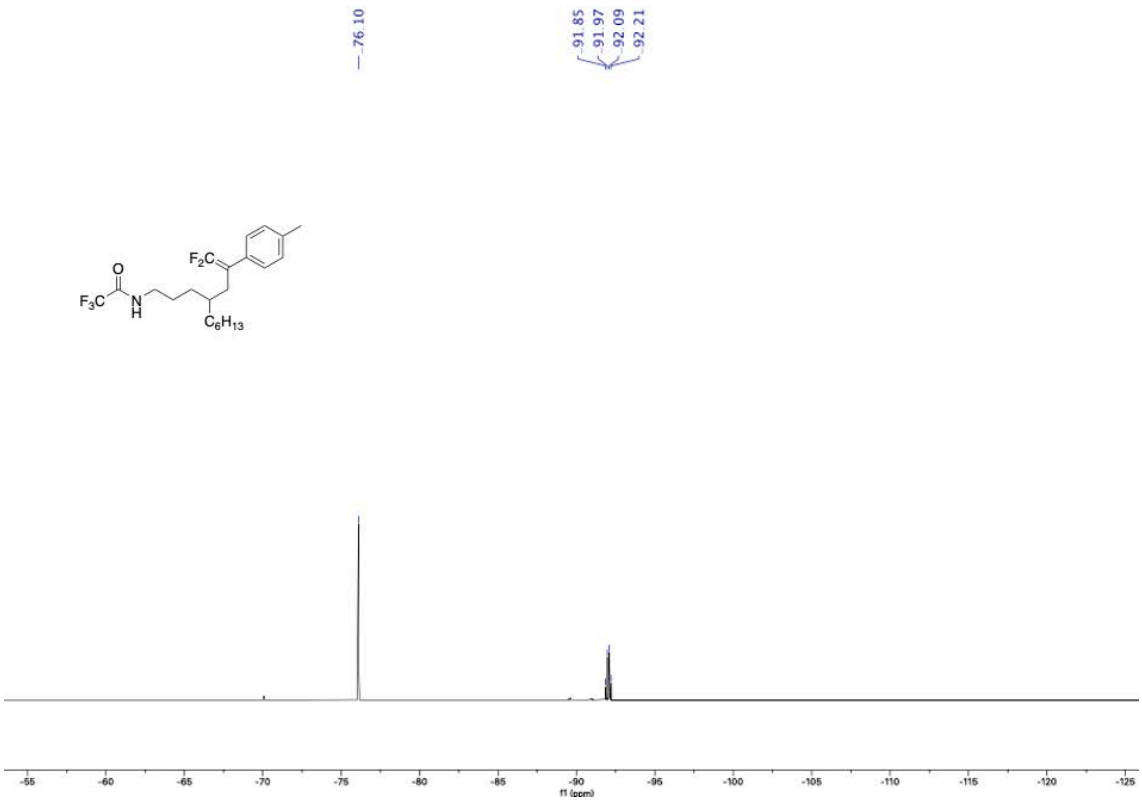
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6l**



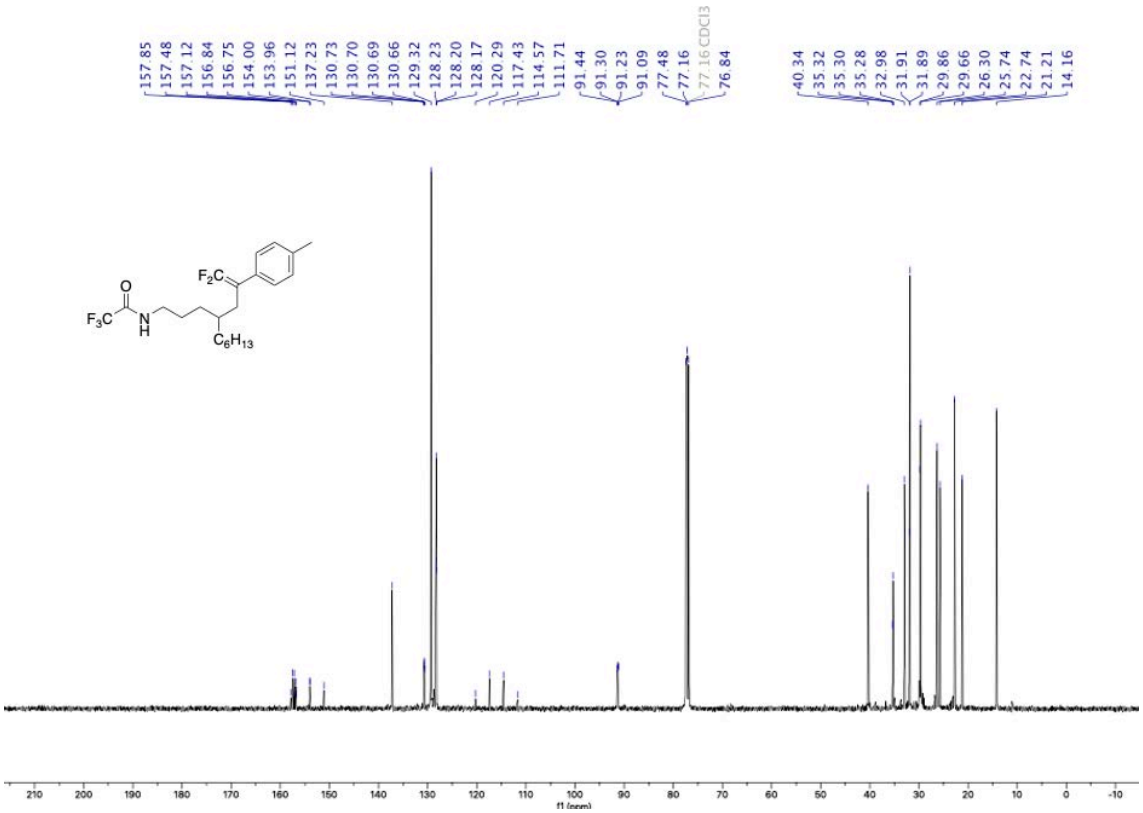
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6l**



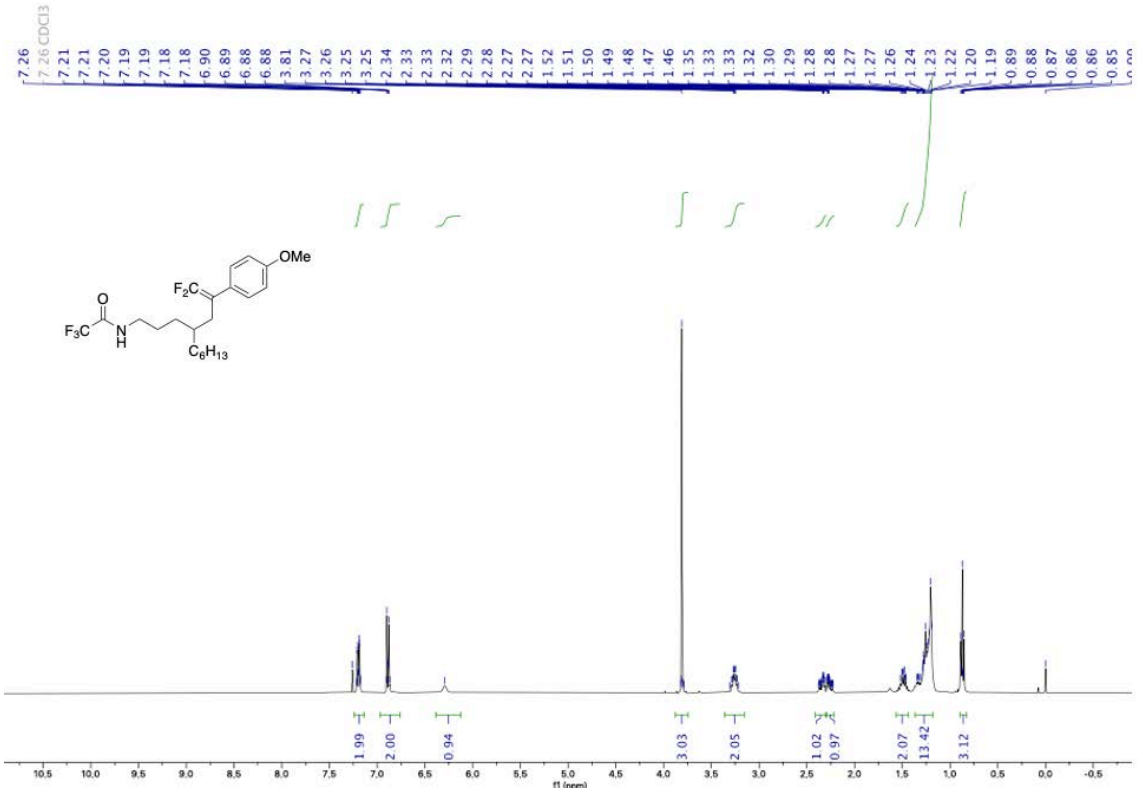
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6m**



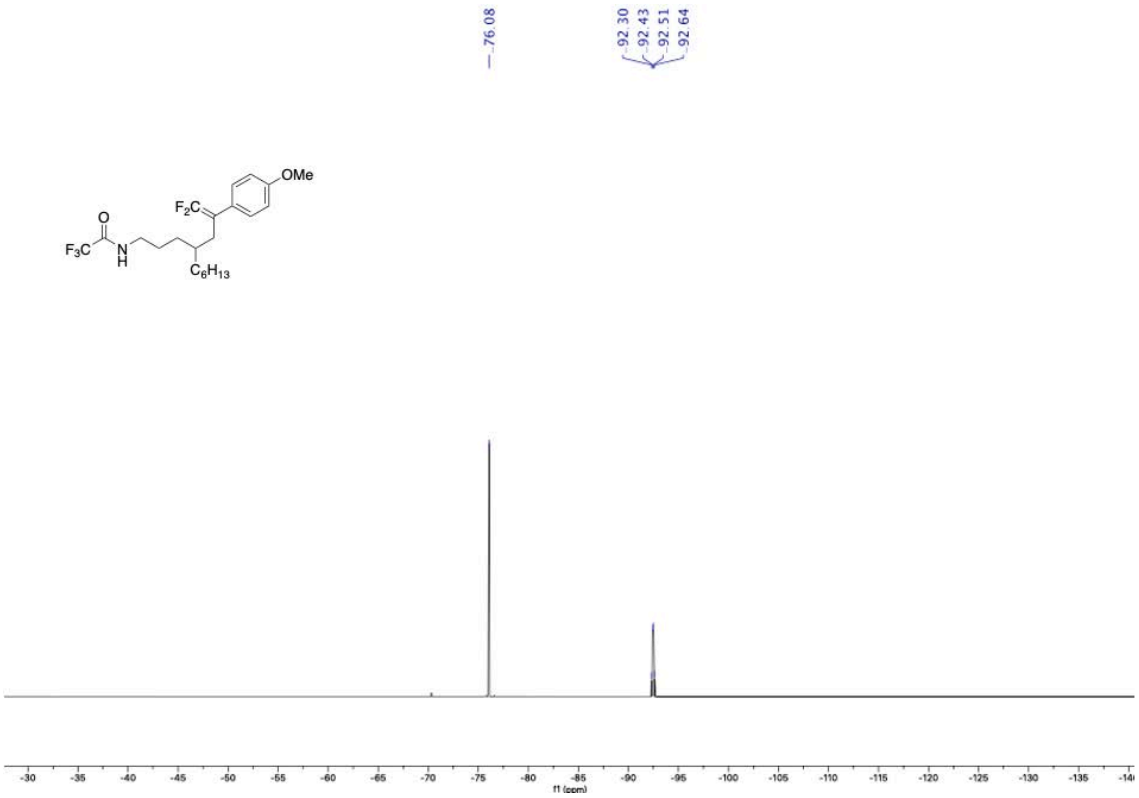
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6m**



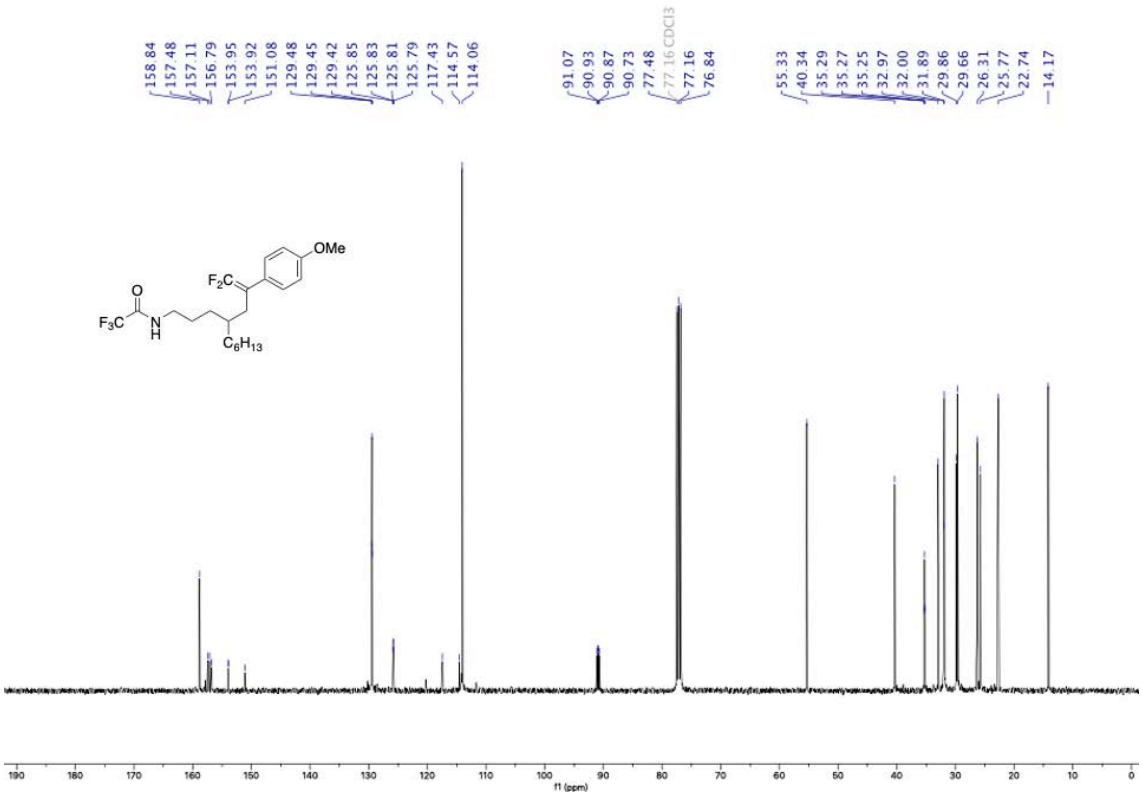
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6m**



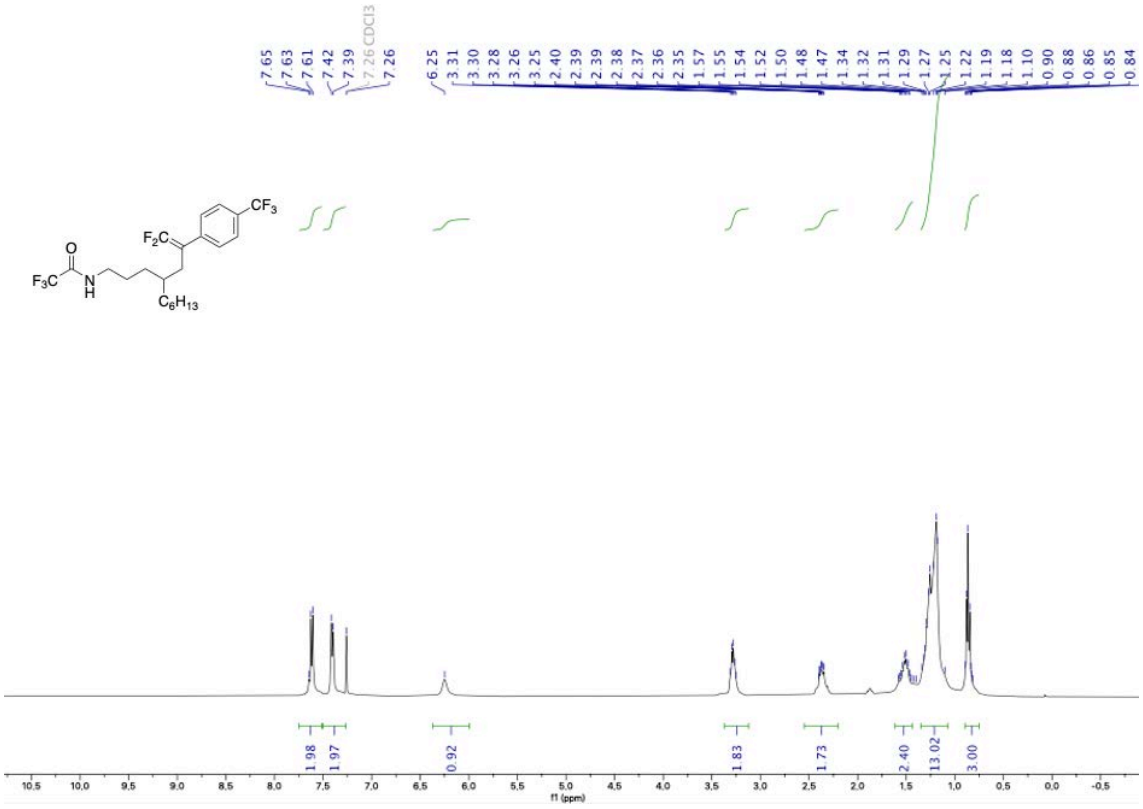
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6n**



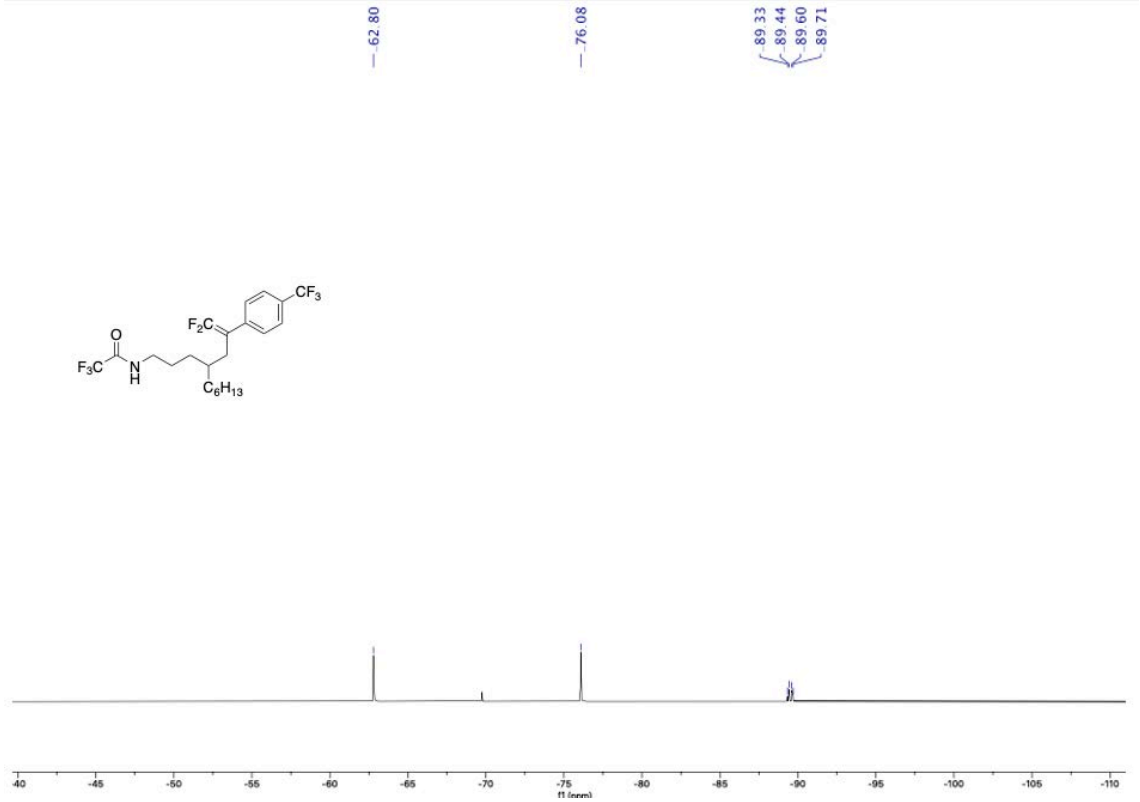
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6n**



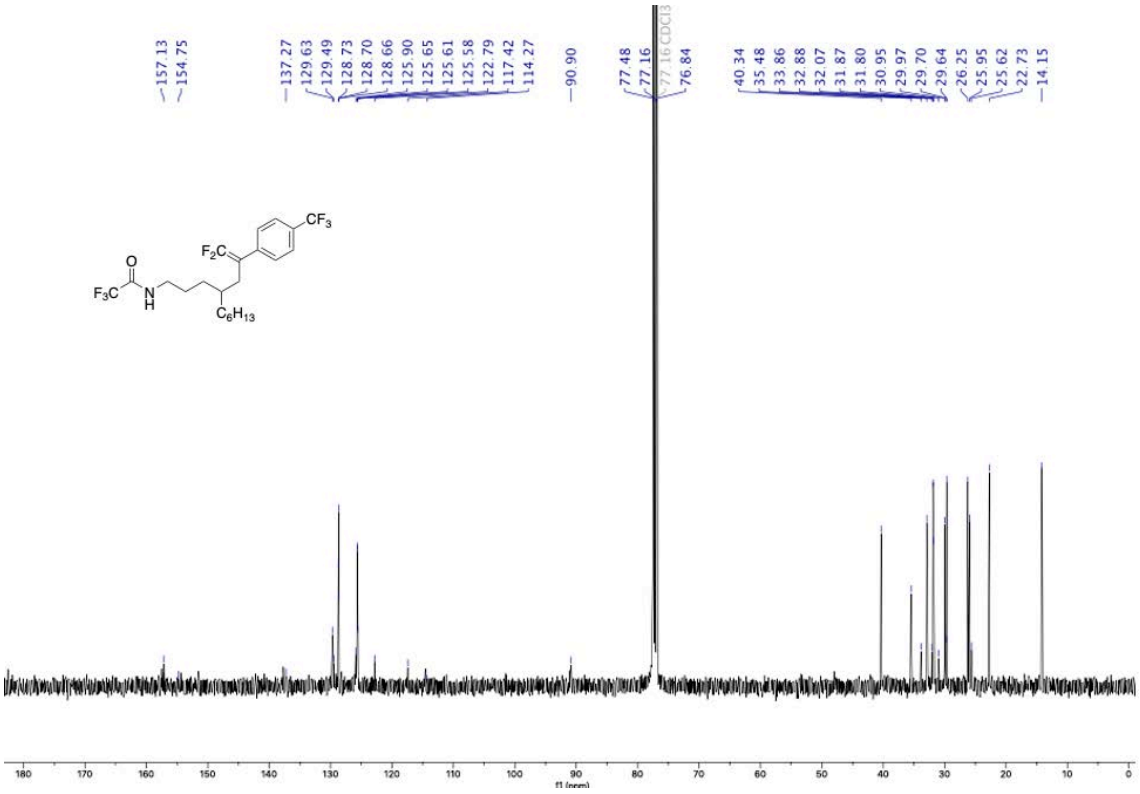
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6n**



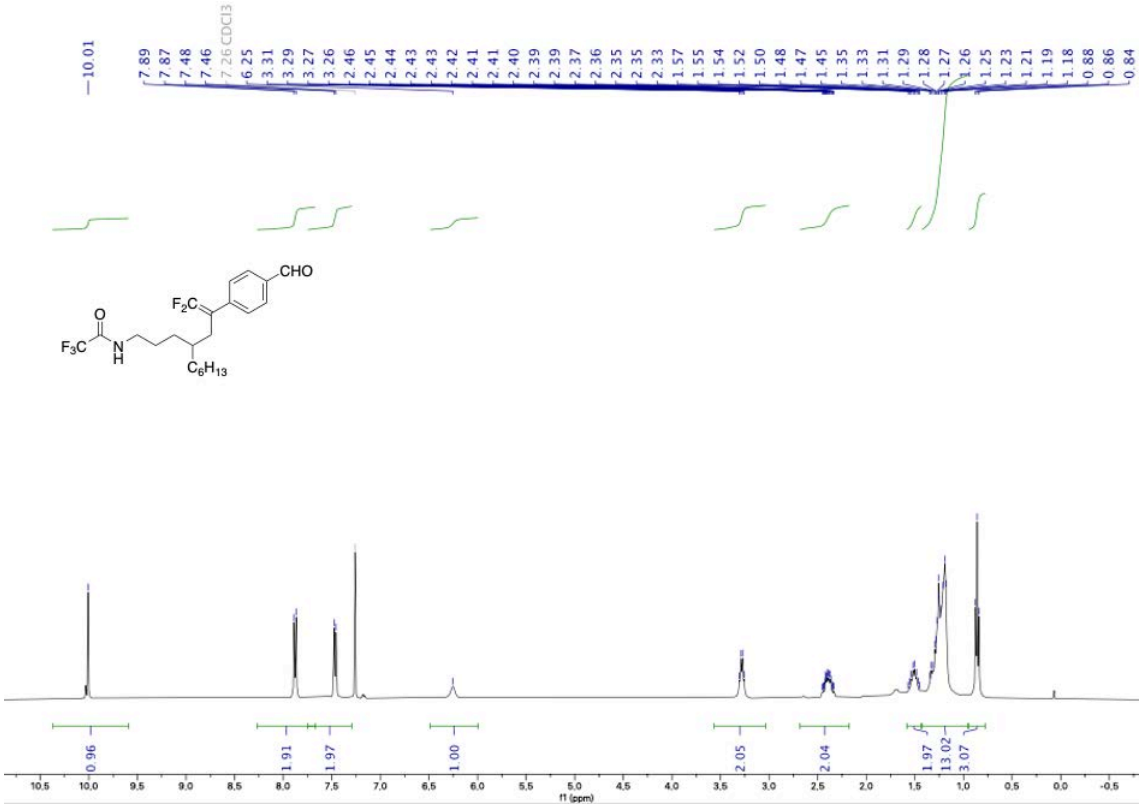
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6o**



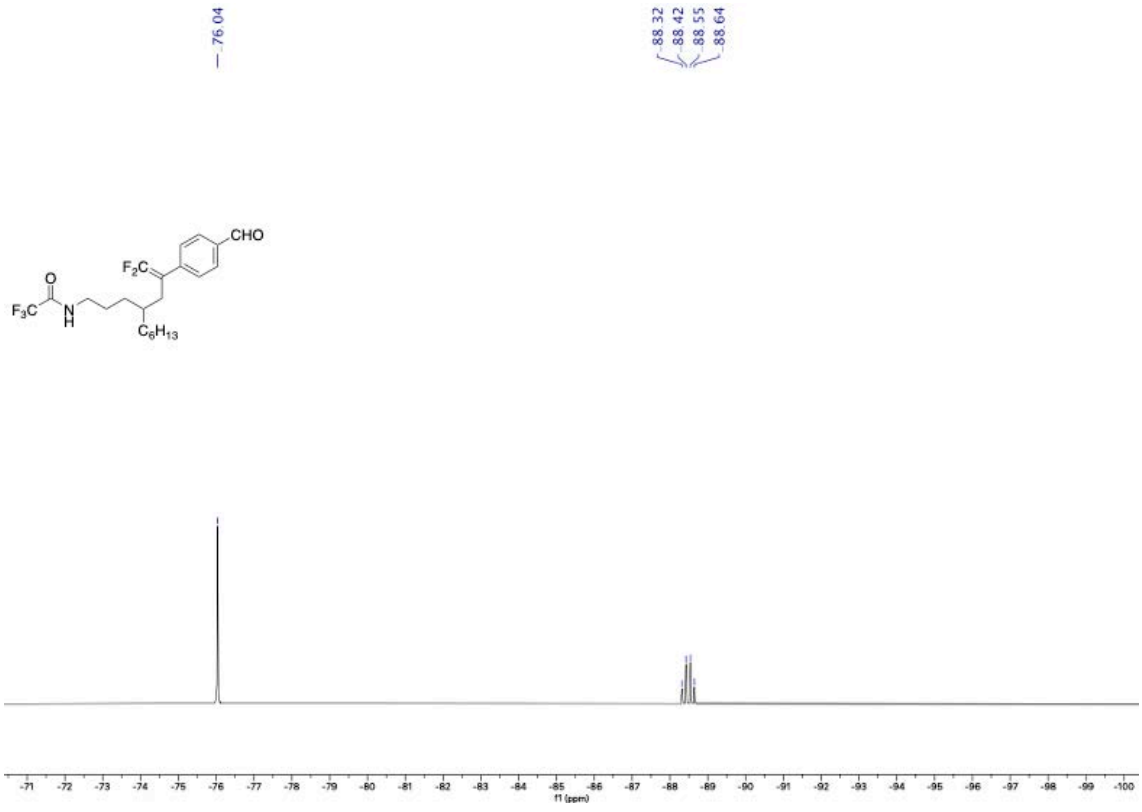
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6o**



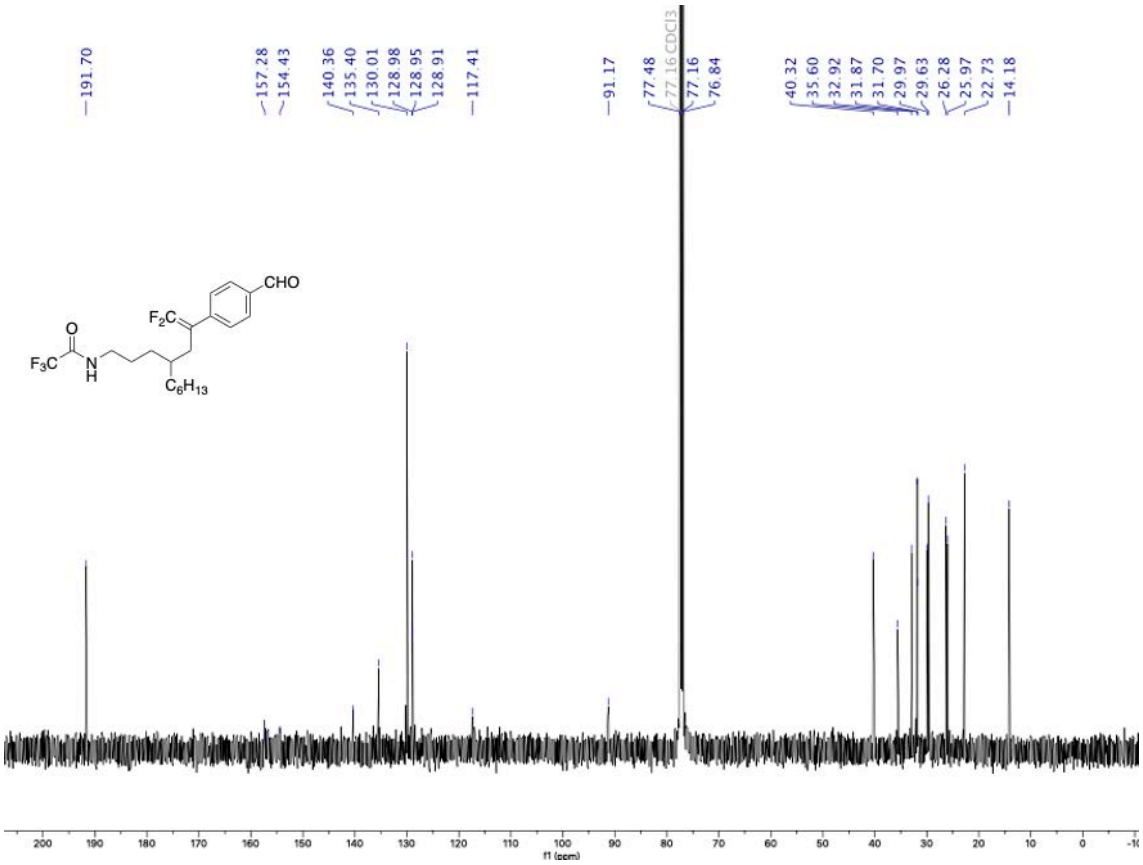
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6o**



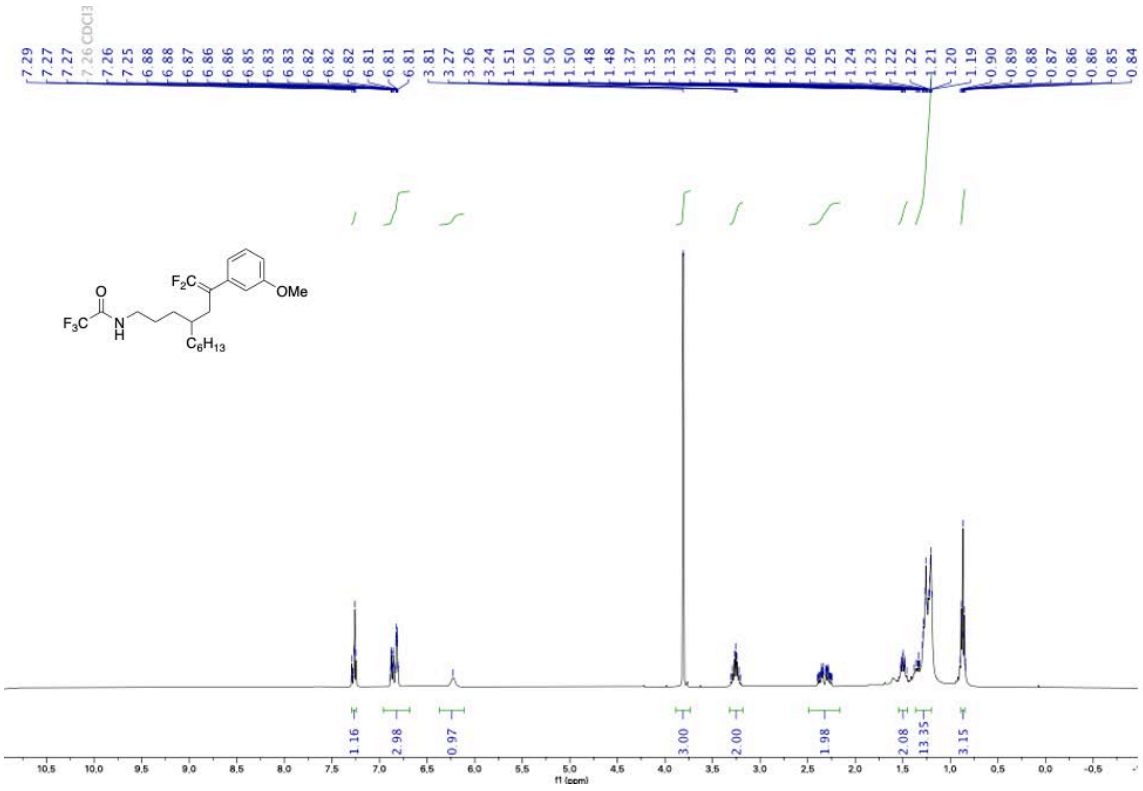
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6p**



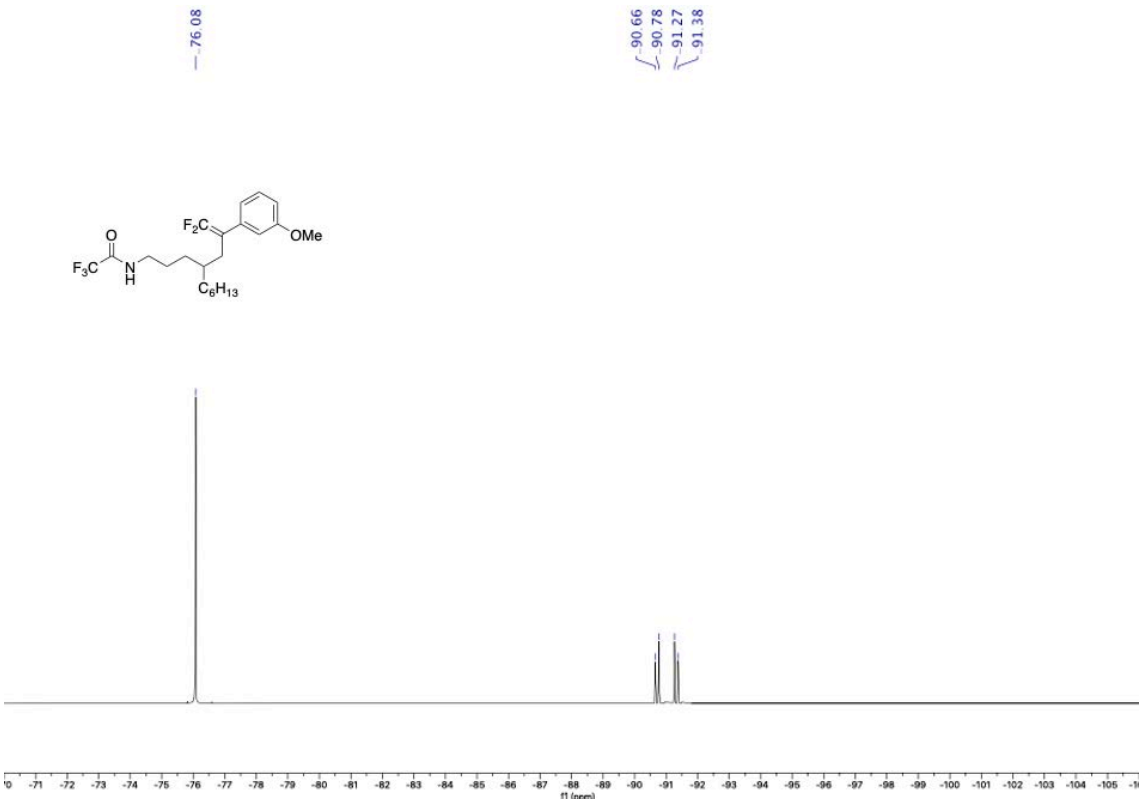
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6p**



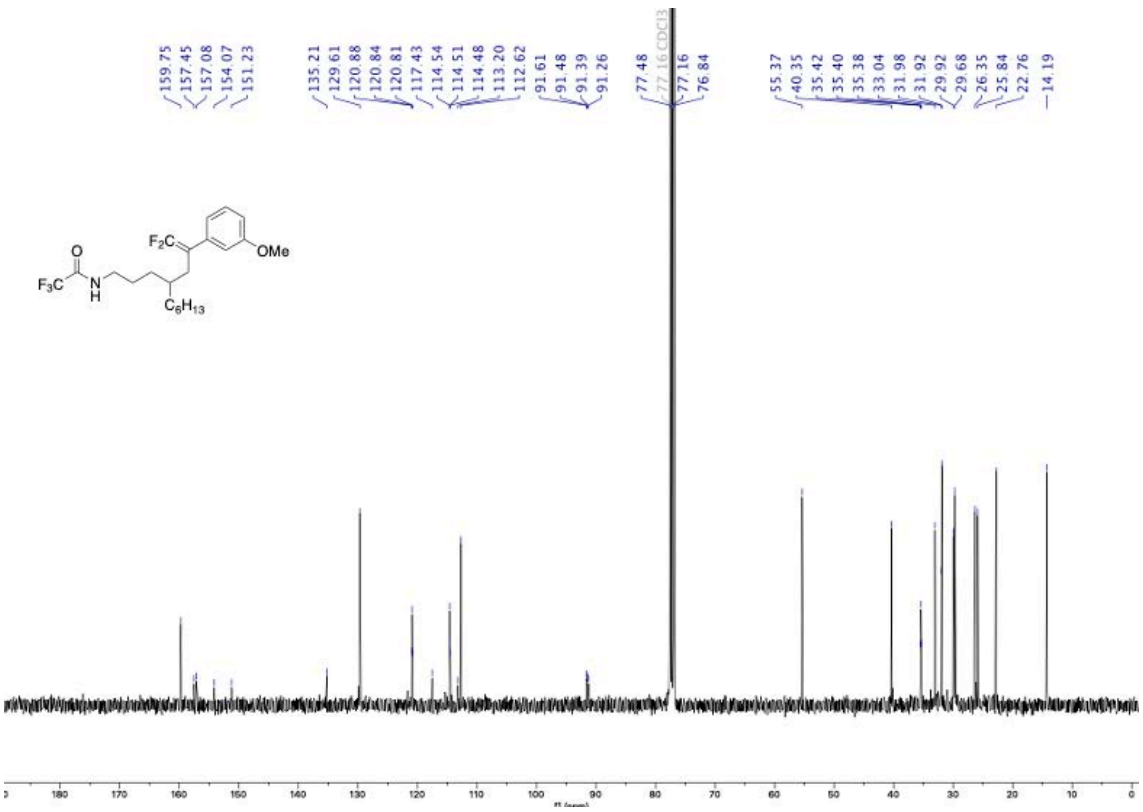
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6p**



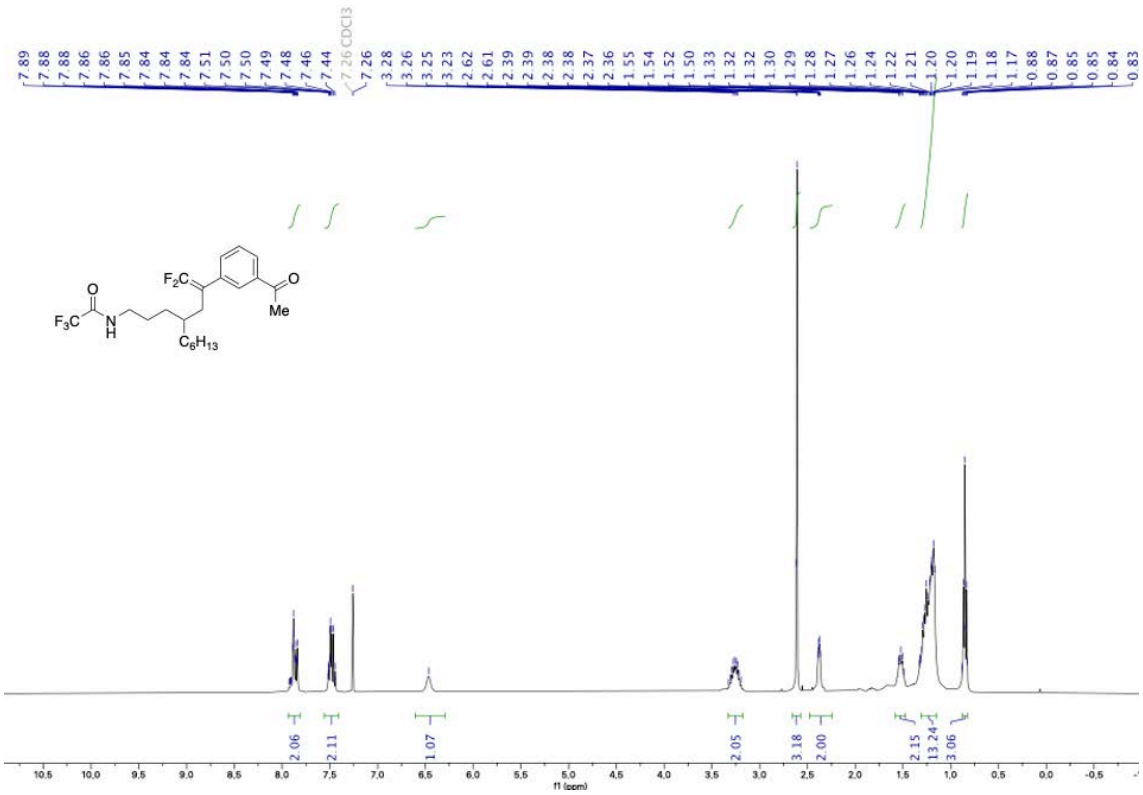
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6q**



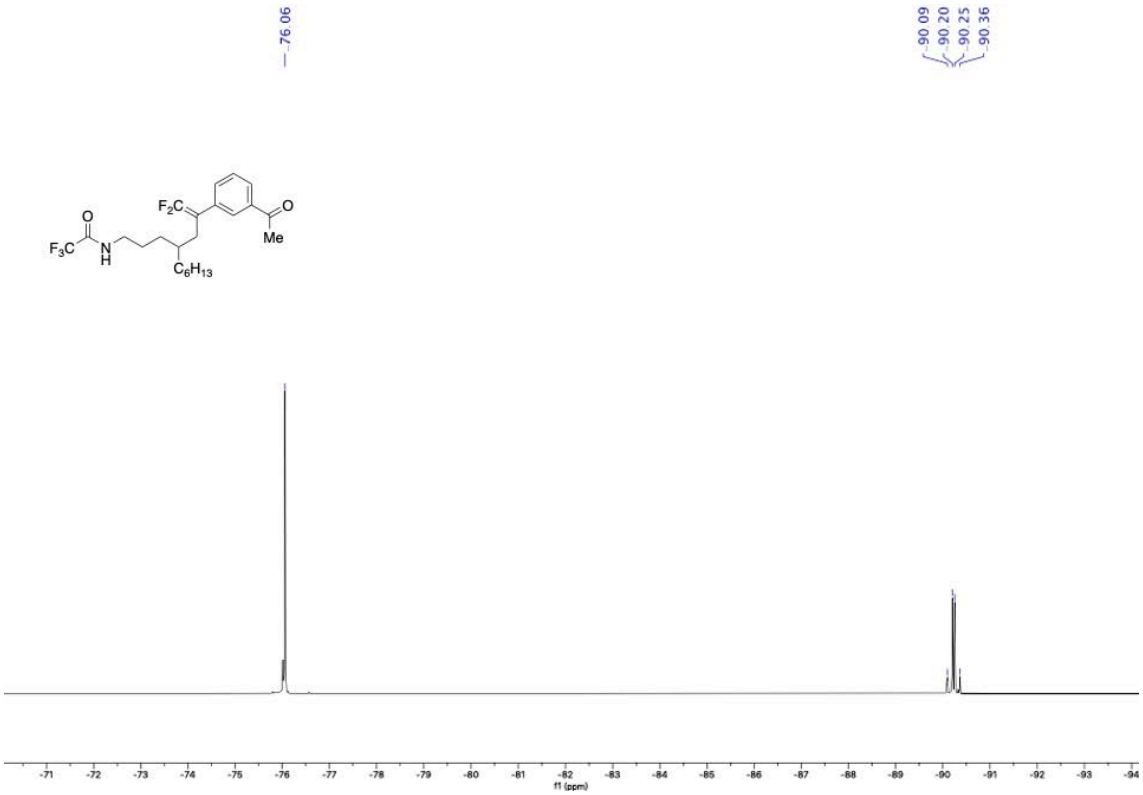
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6q**



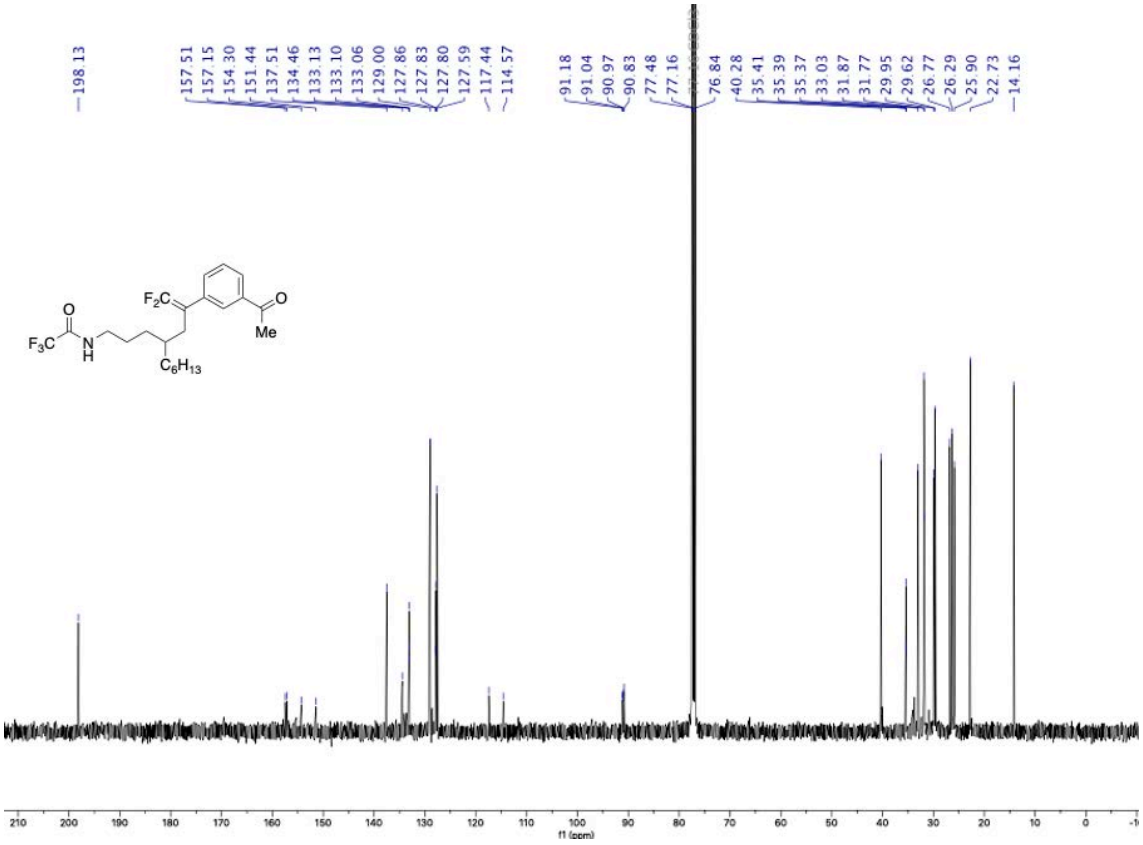
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6q**



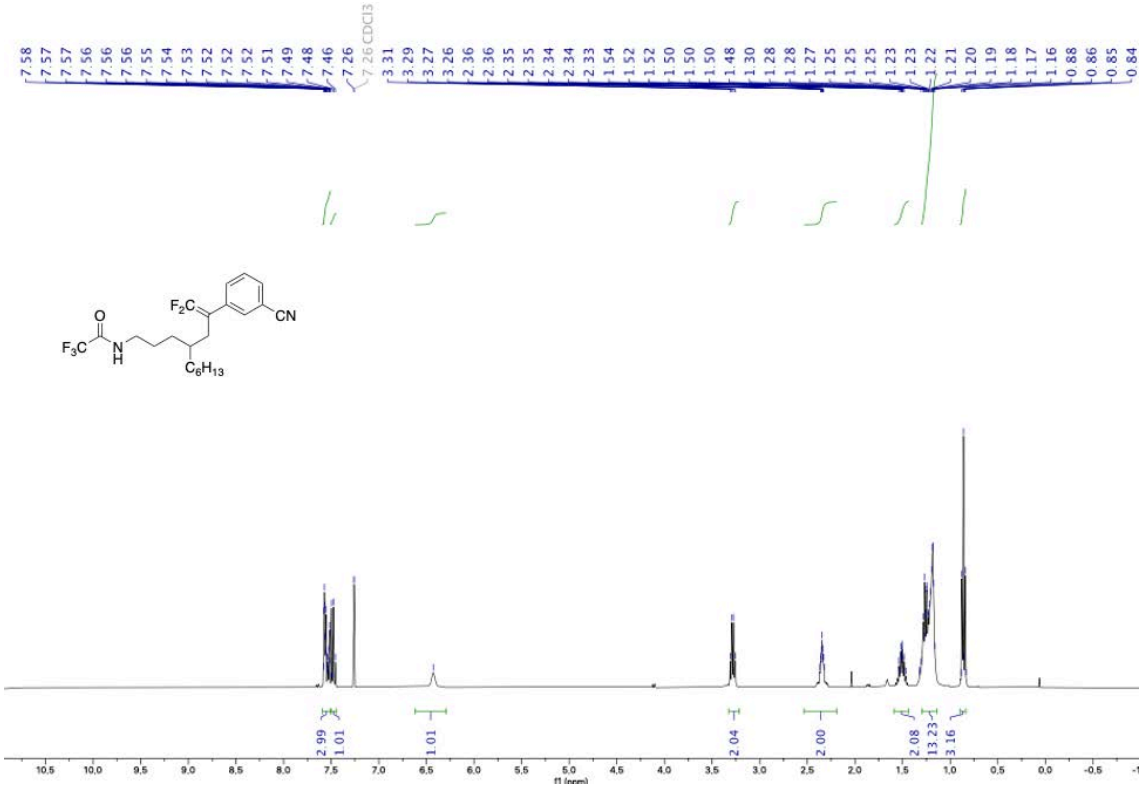
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6r**



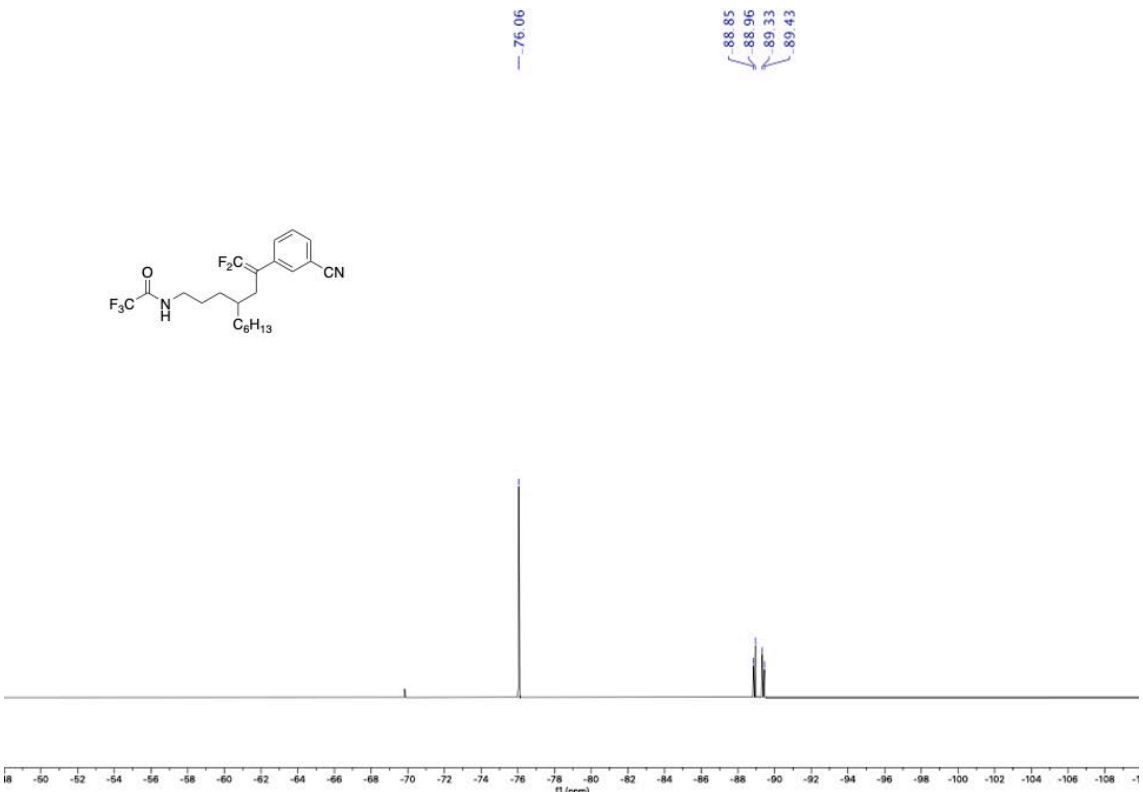
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6r**



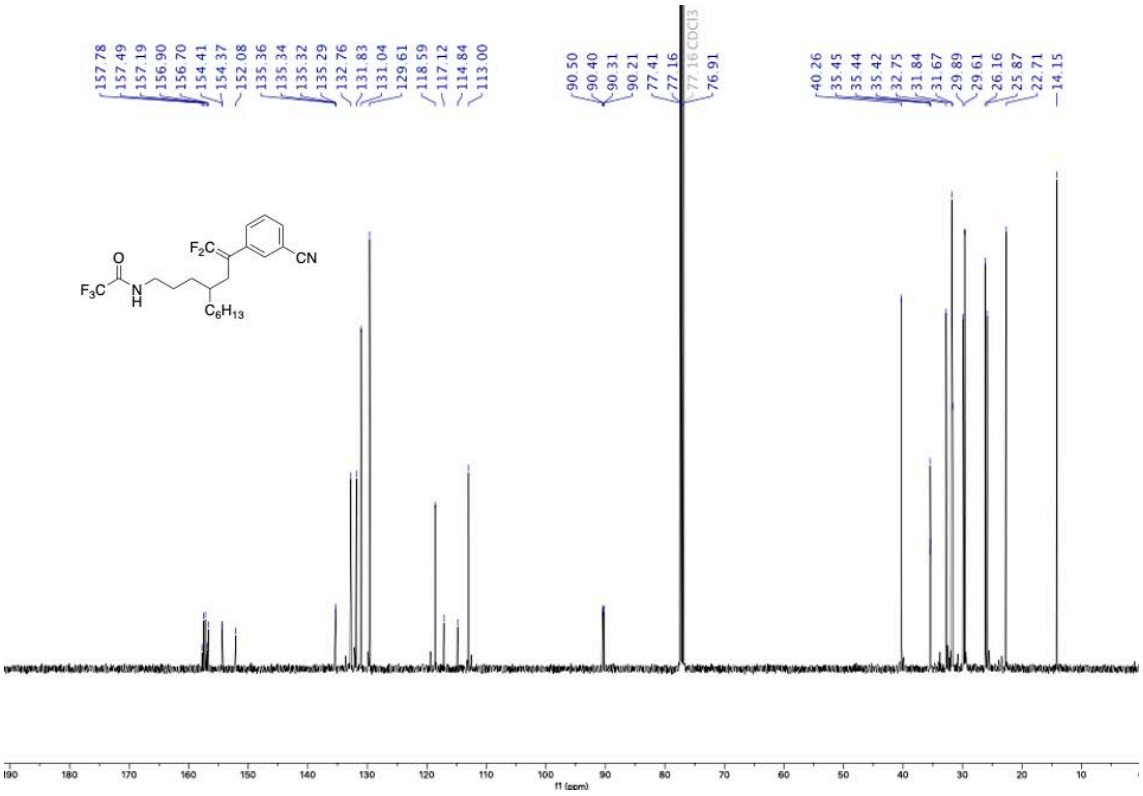
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6r**



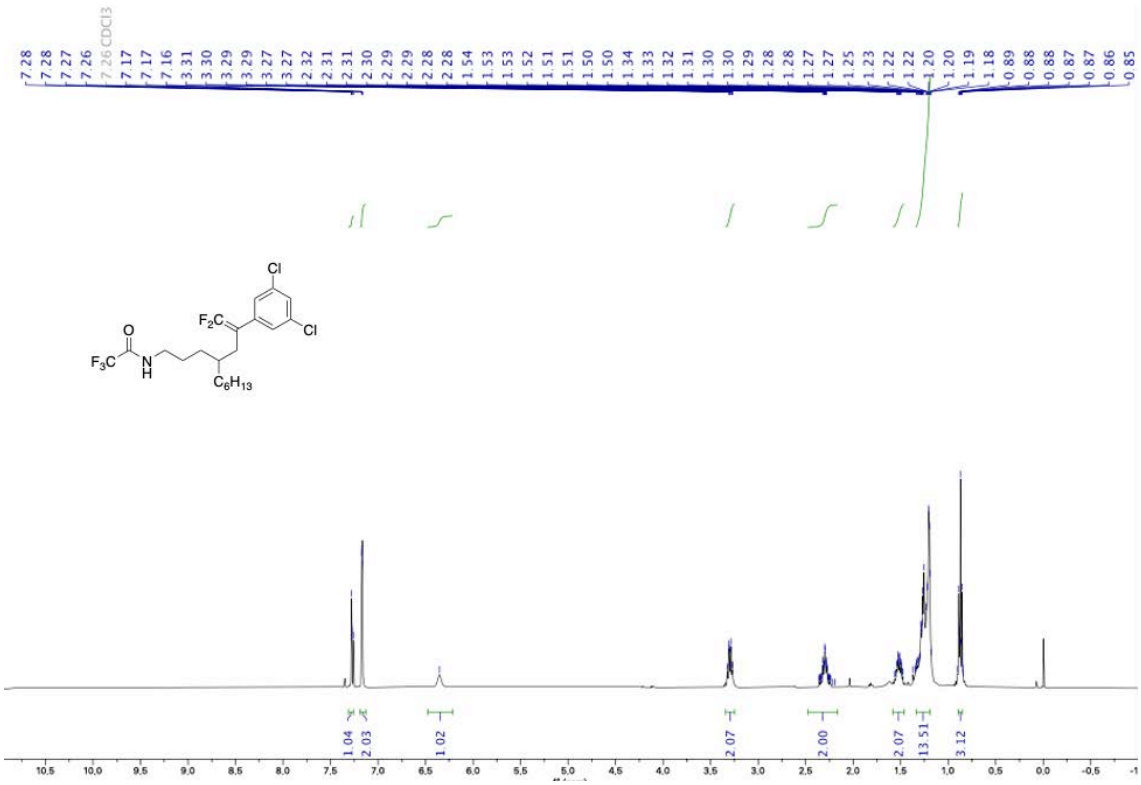
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6s**



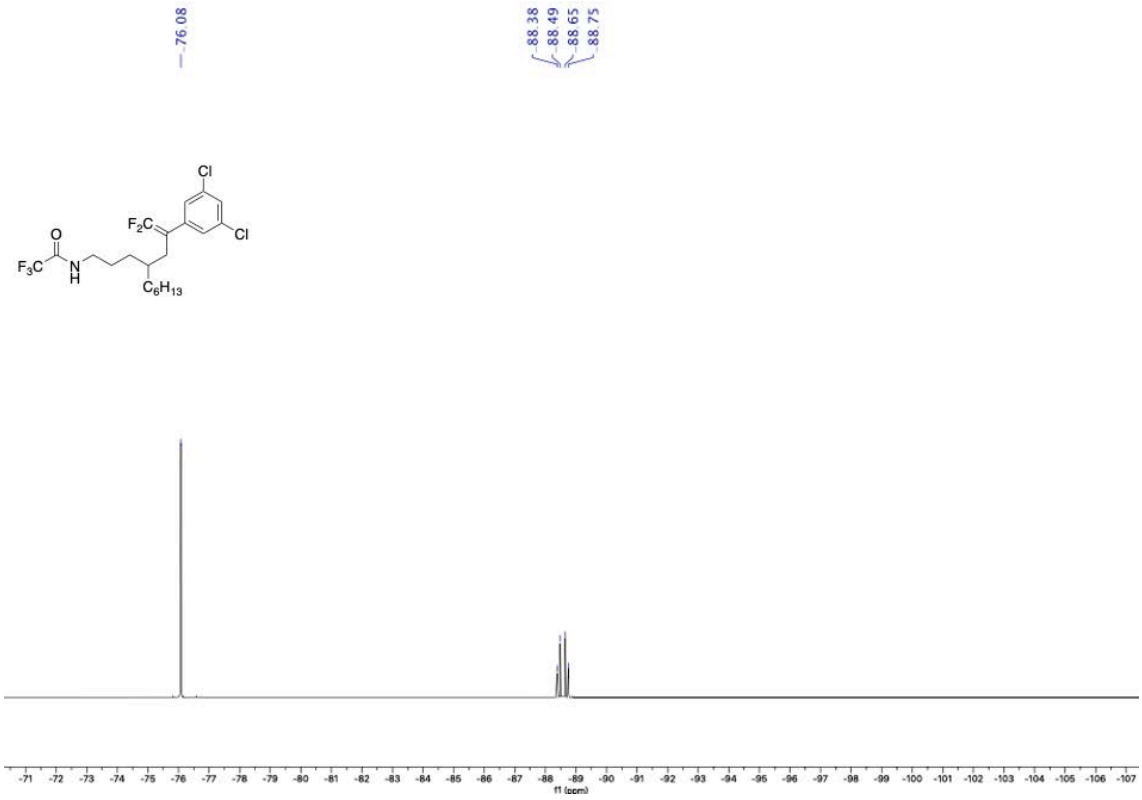
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6s**



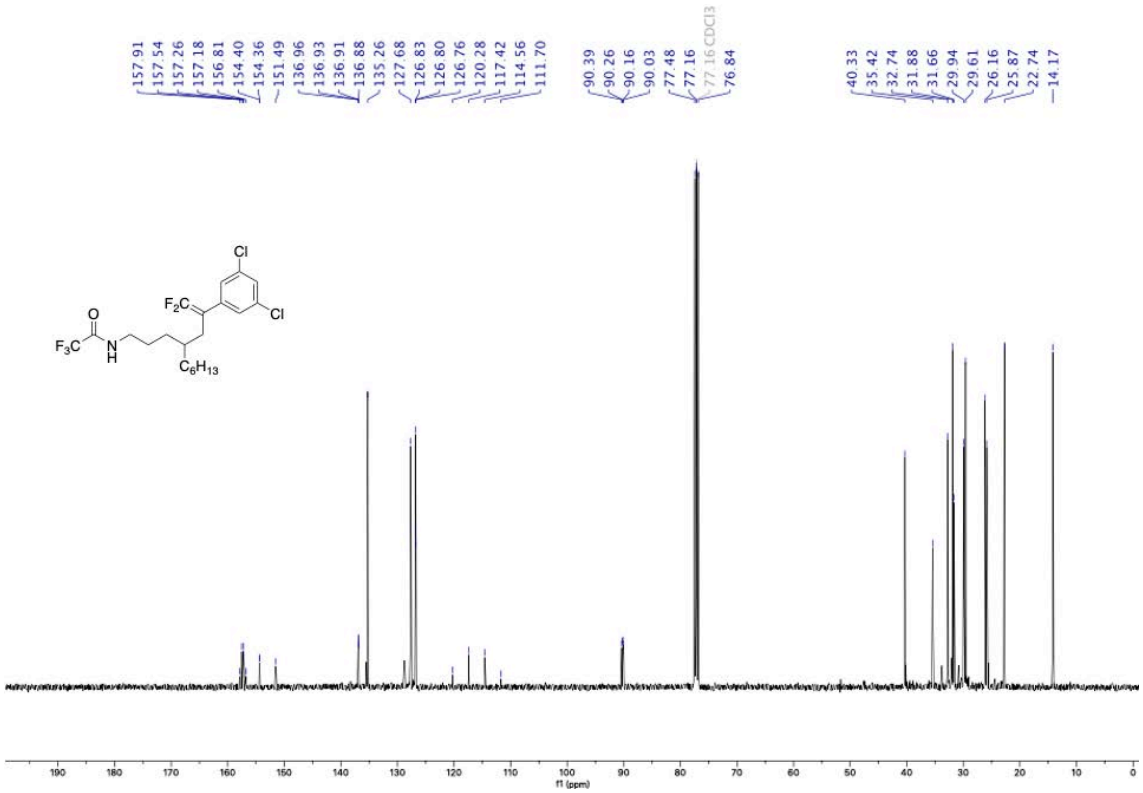
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6s**



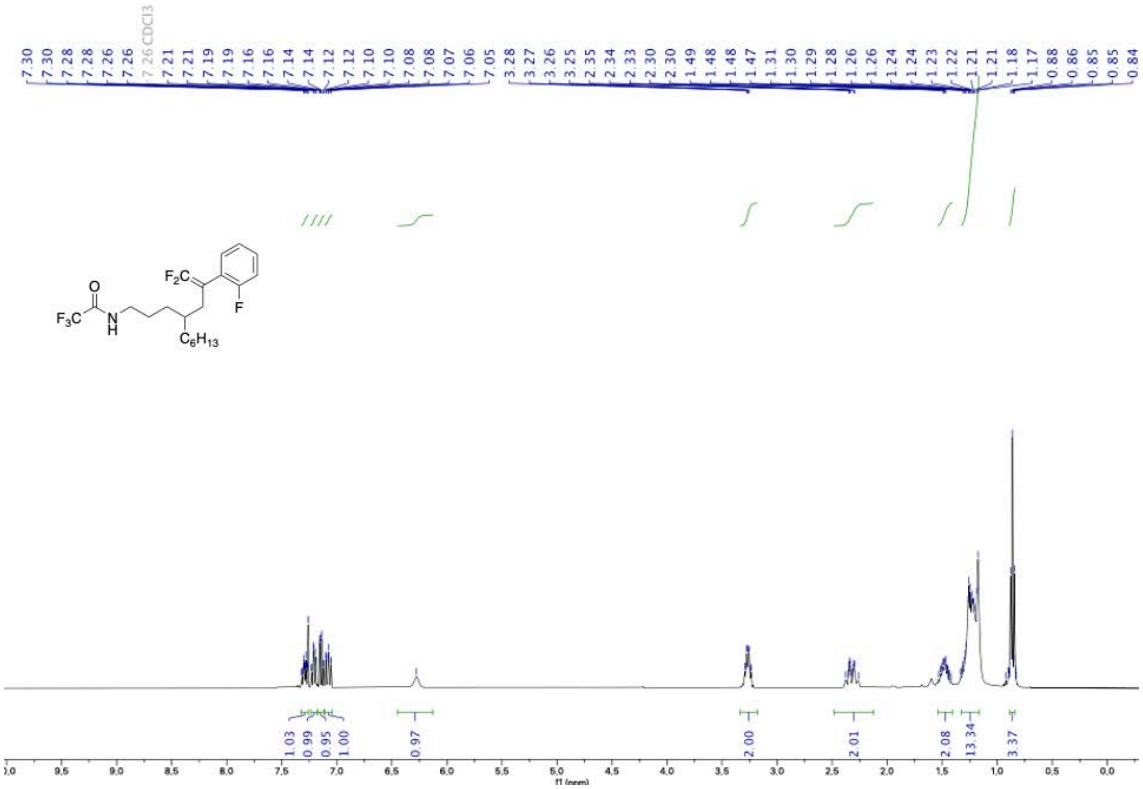
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6t**



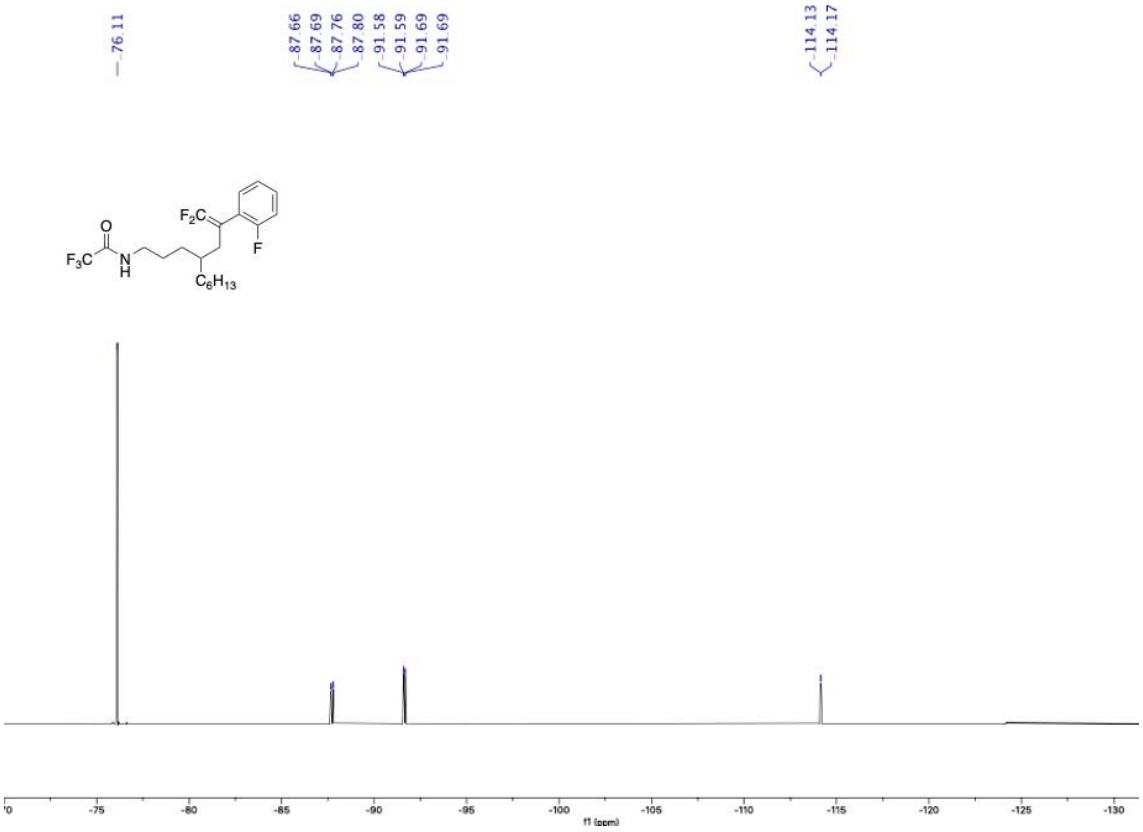
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6t**



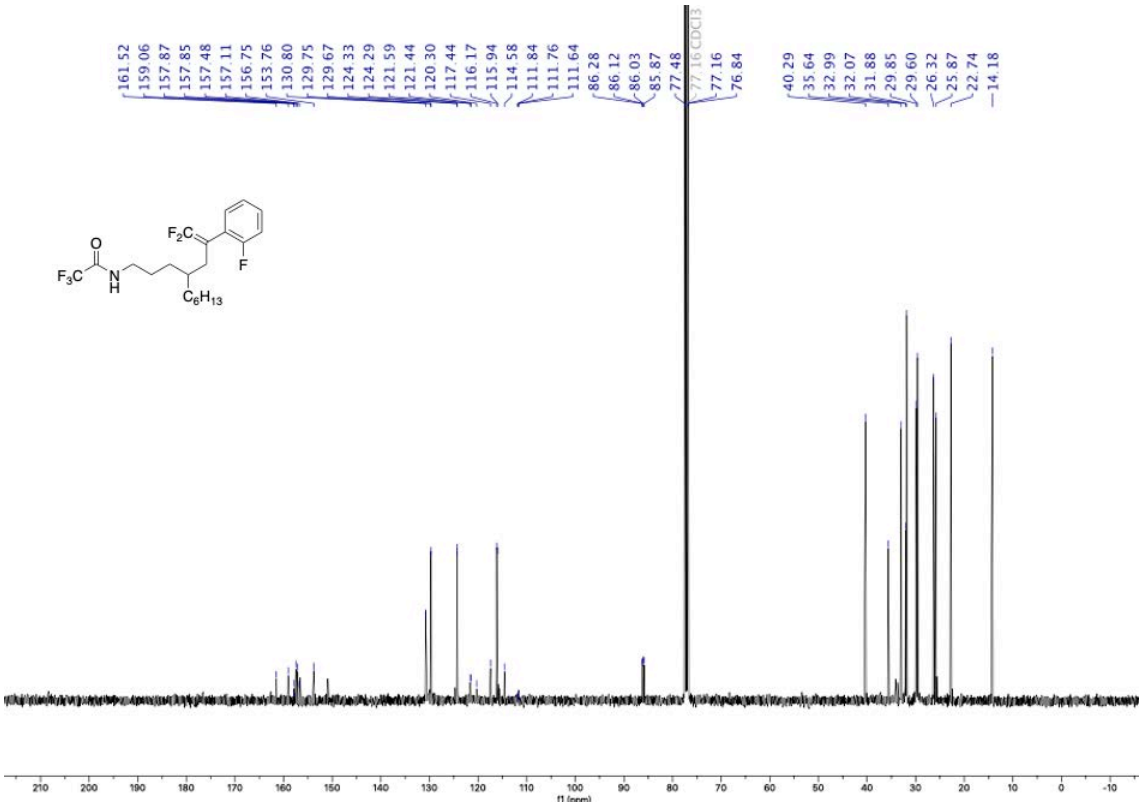
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6t**



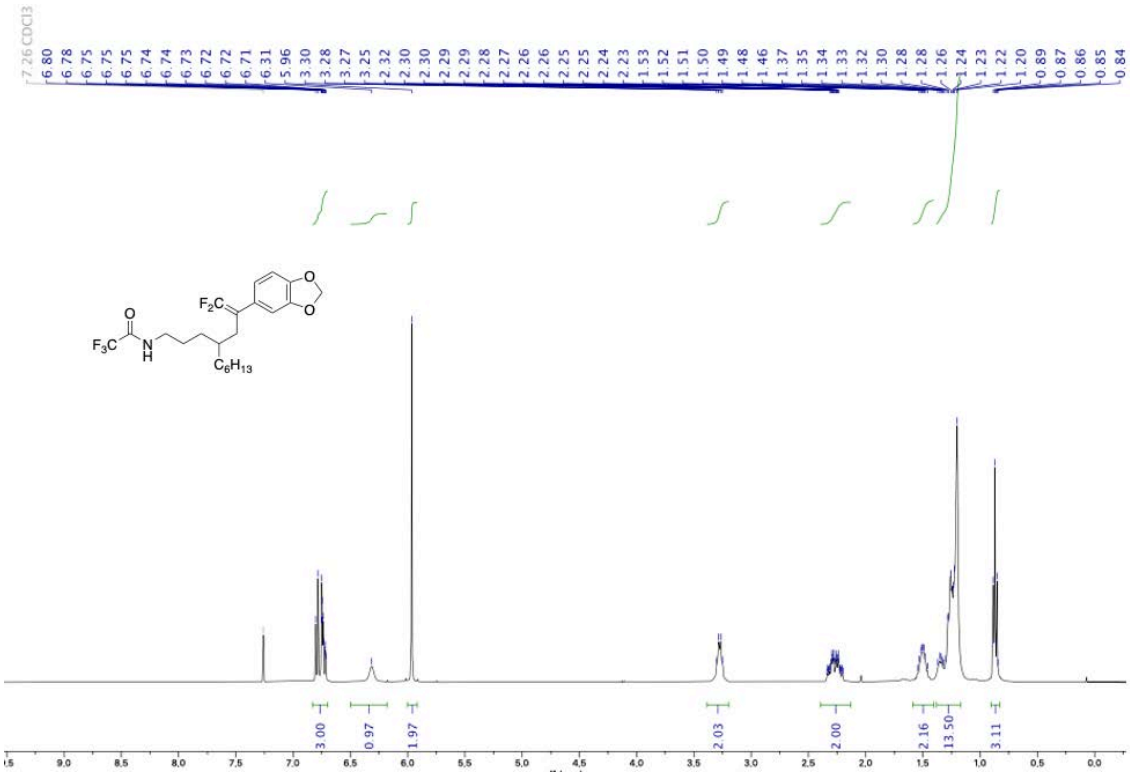
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6u**



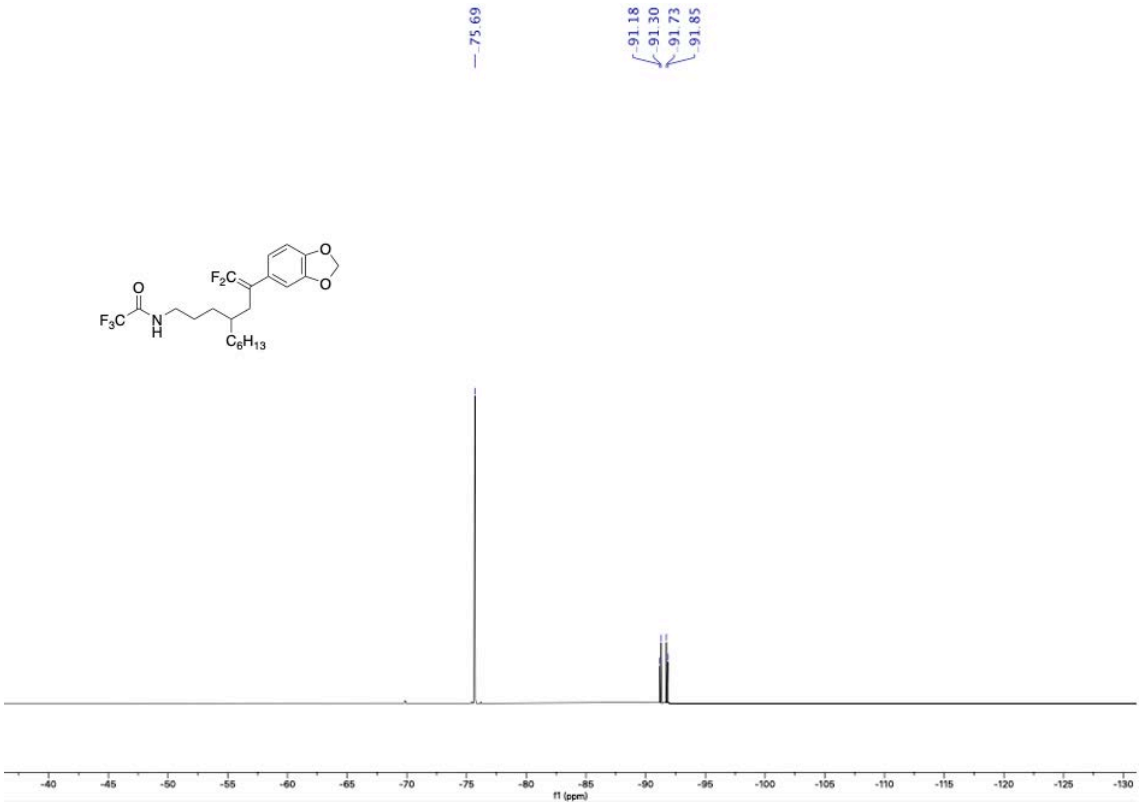
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6u**



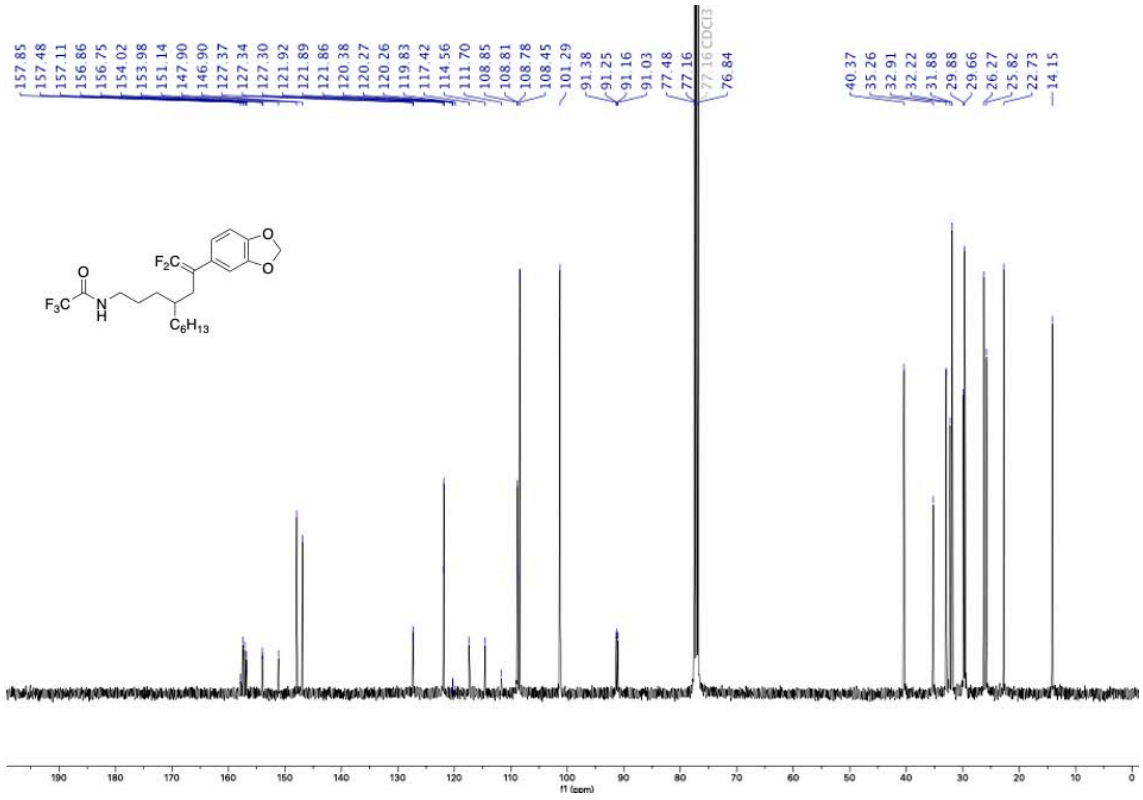
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6u**



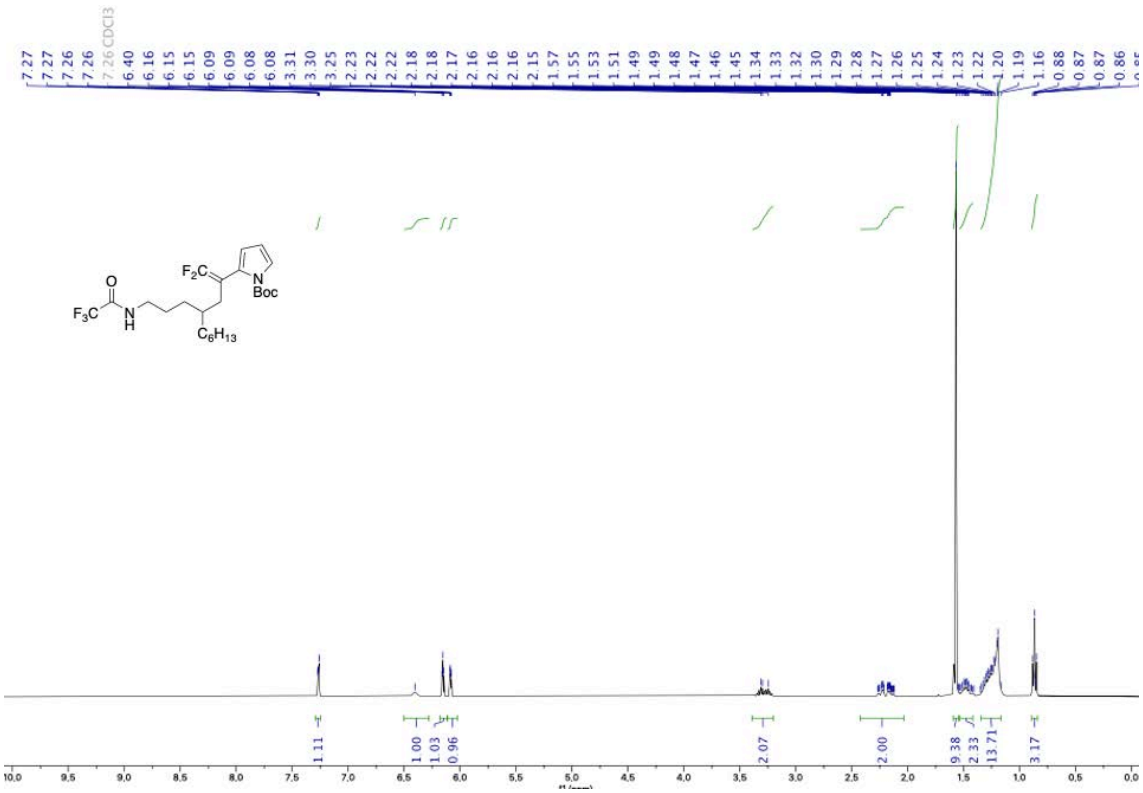
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6v**



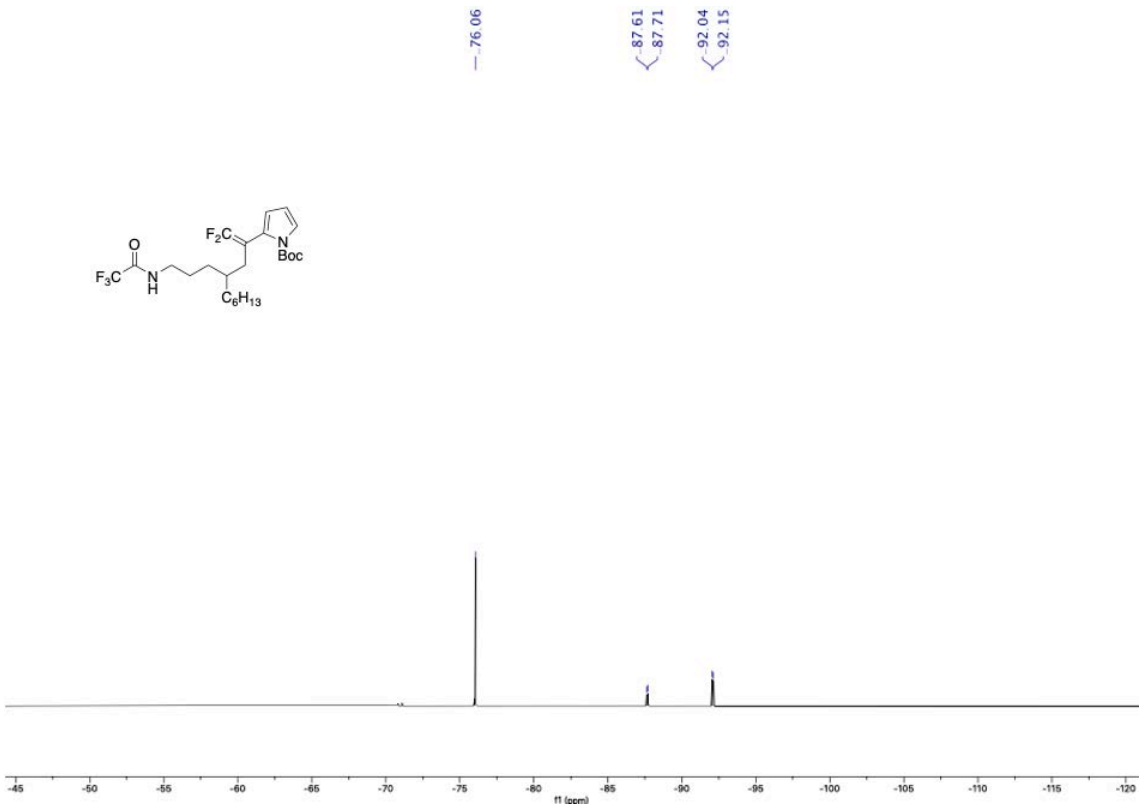
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6v**



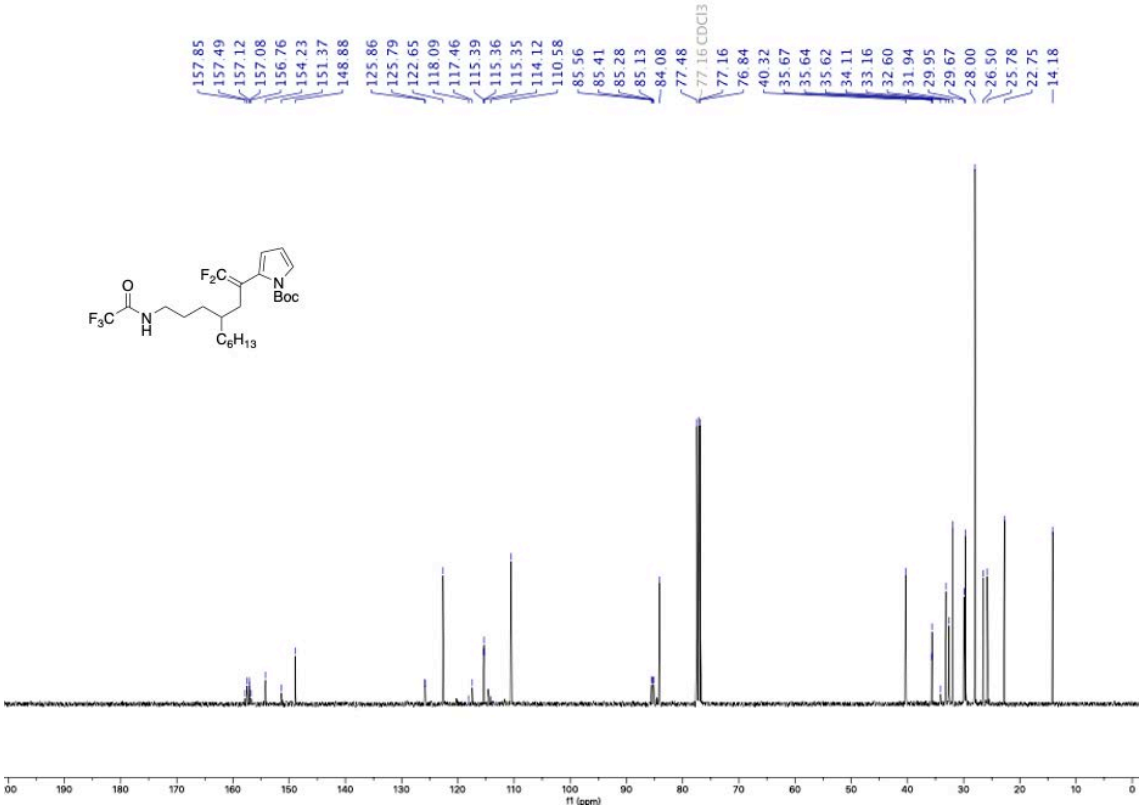
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6v**



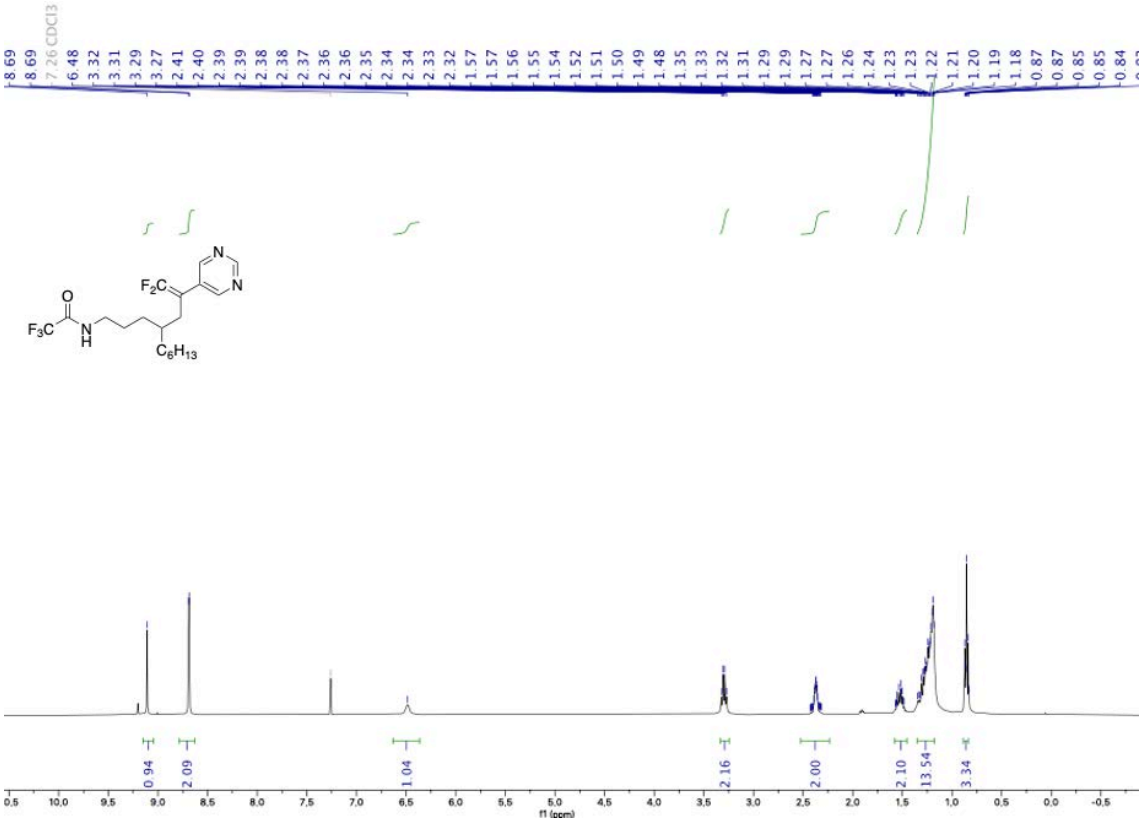
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6w**



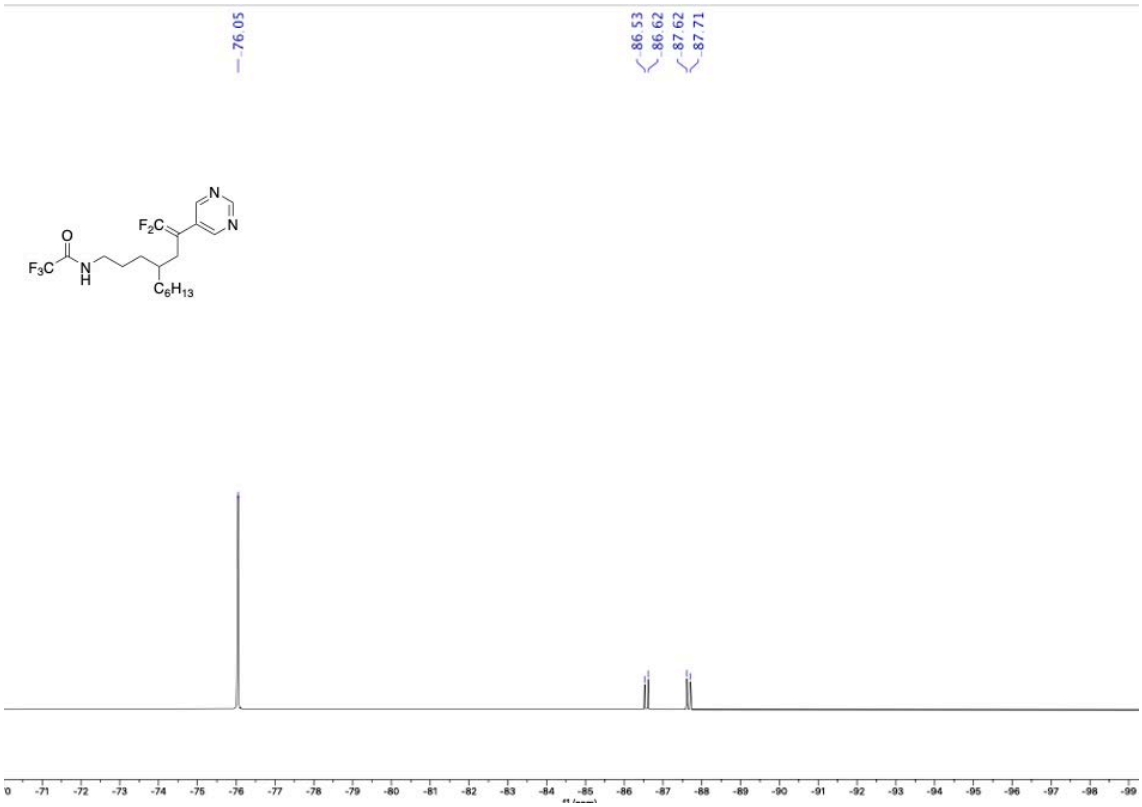
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6w**



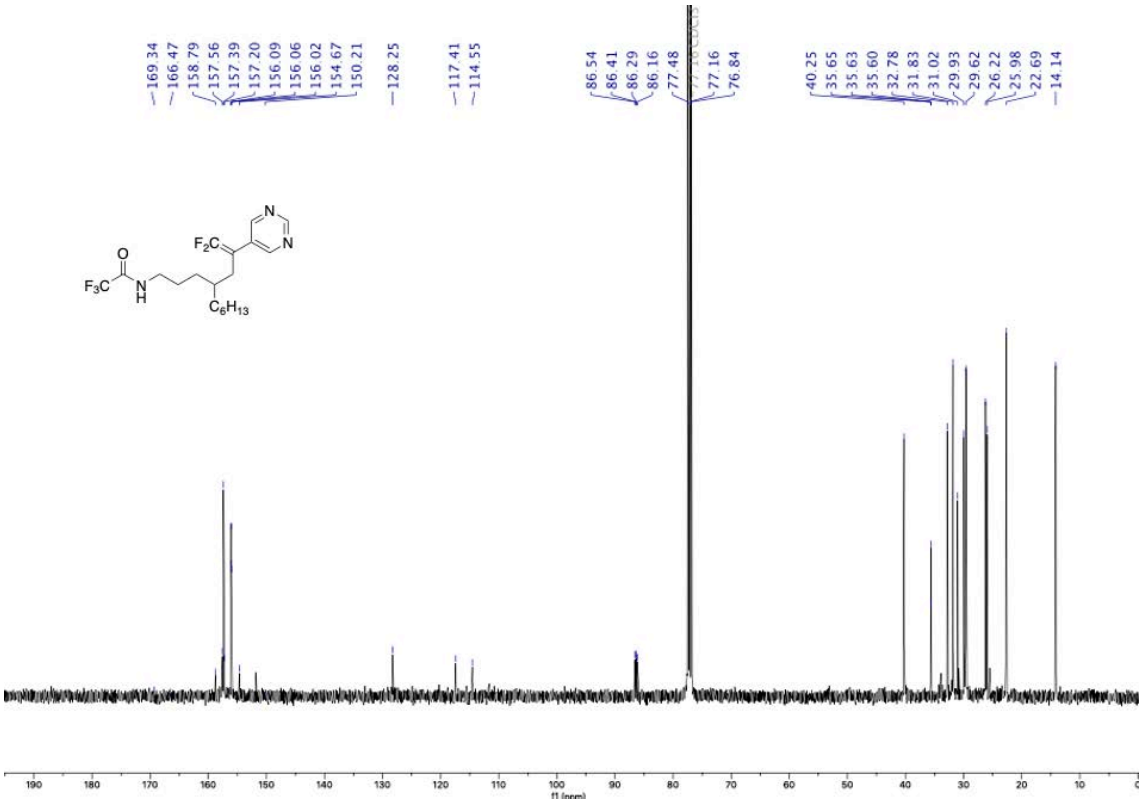
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6w**



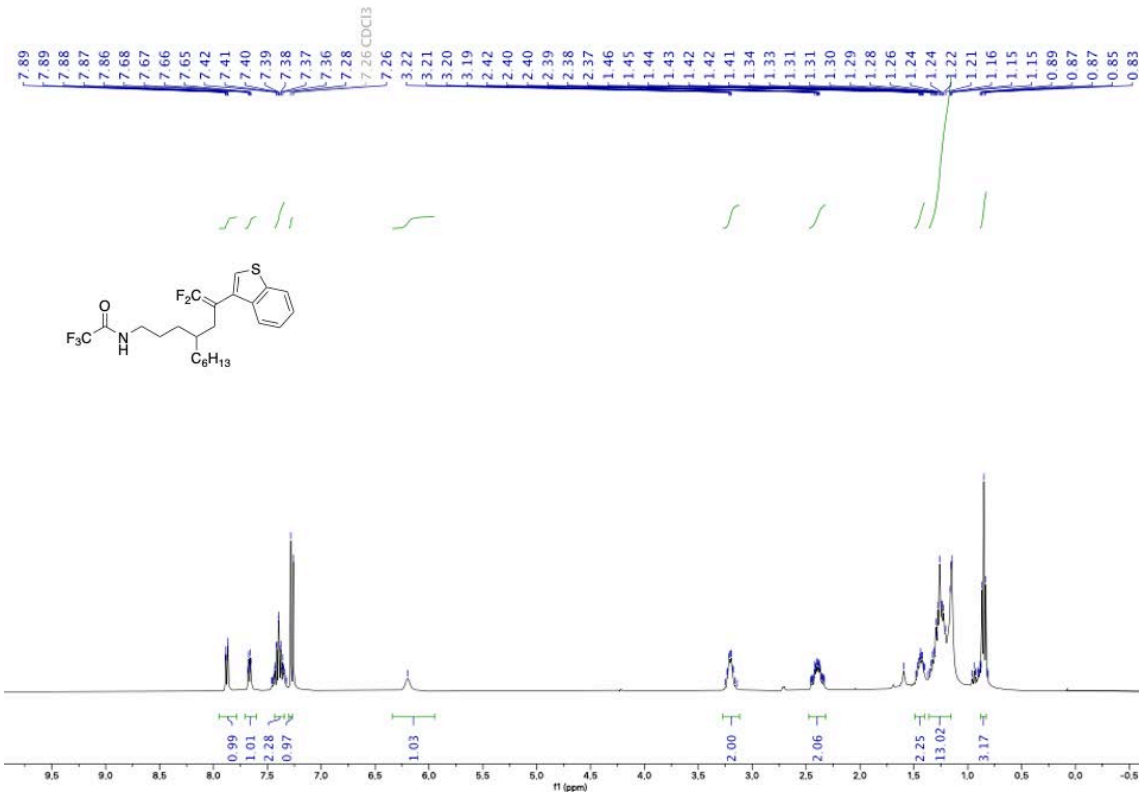
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6x**



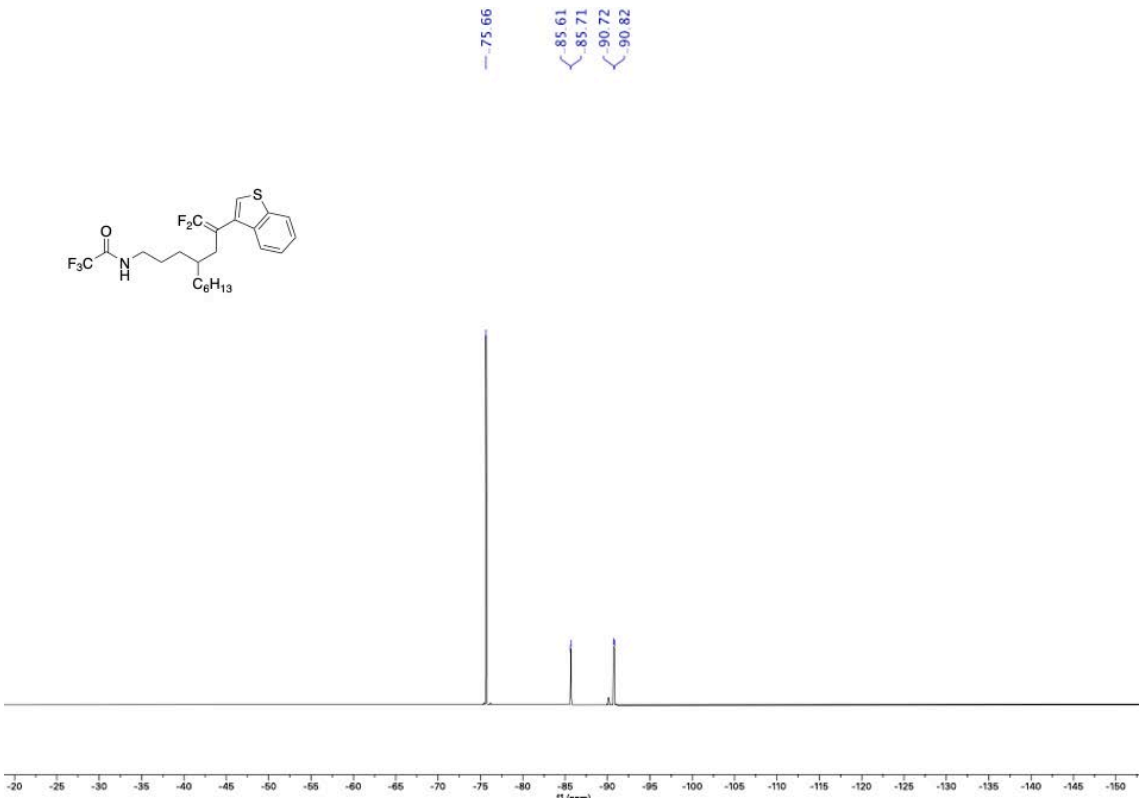
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6x**



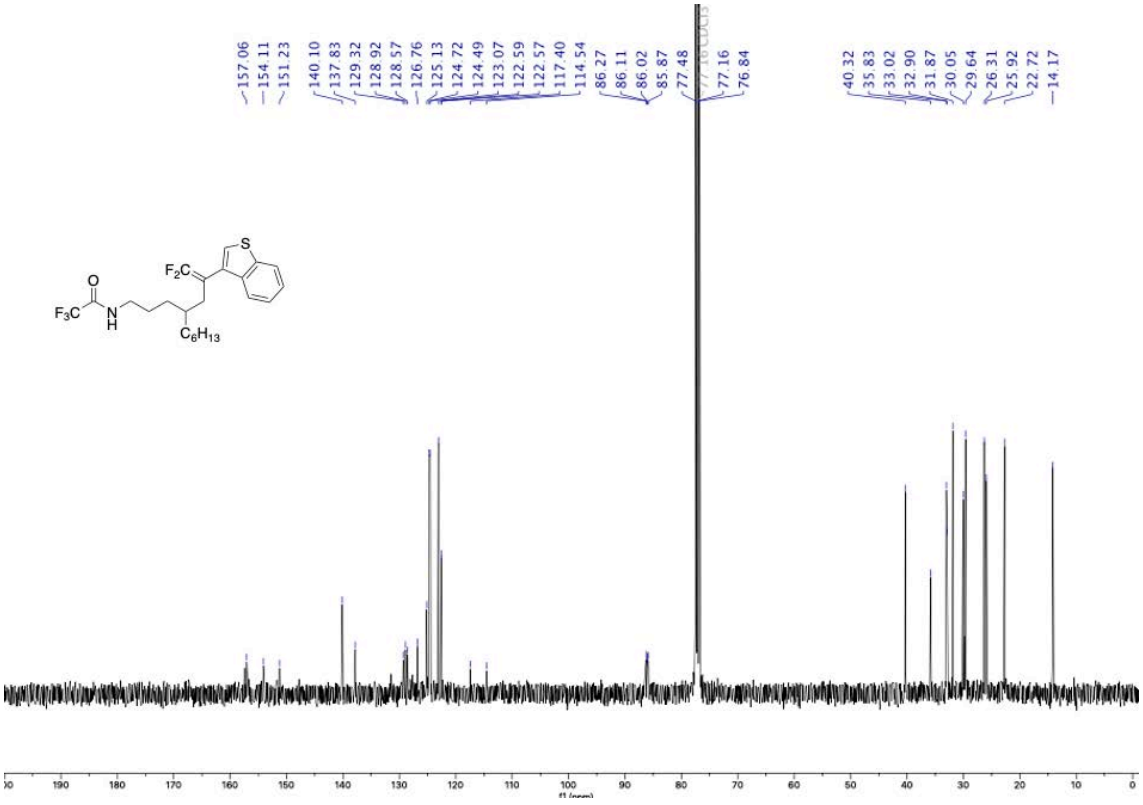
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6x**



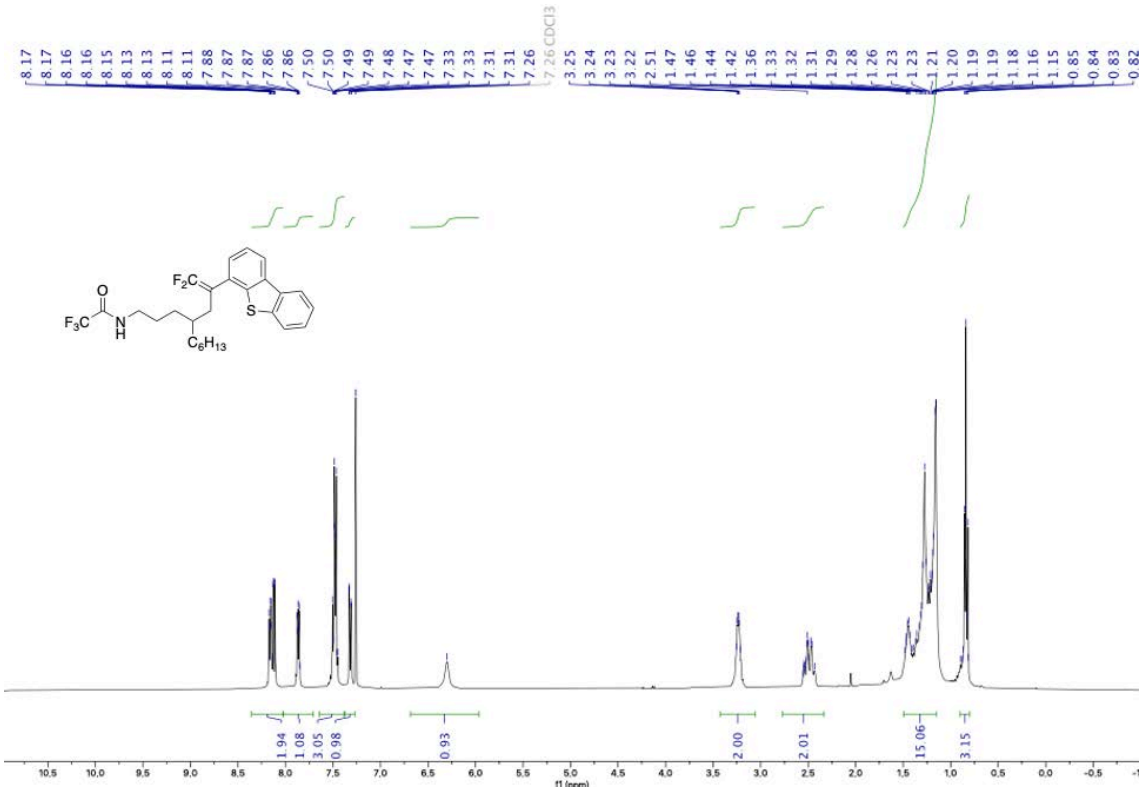
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6y**



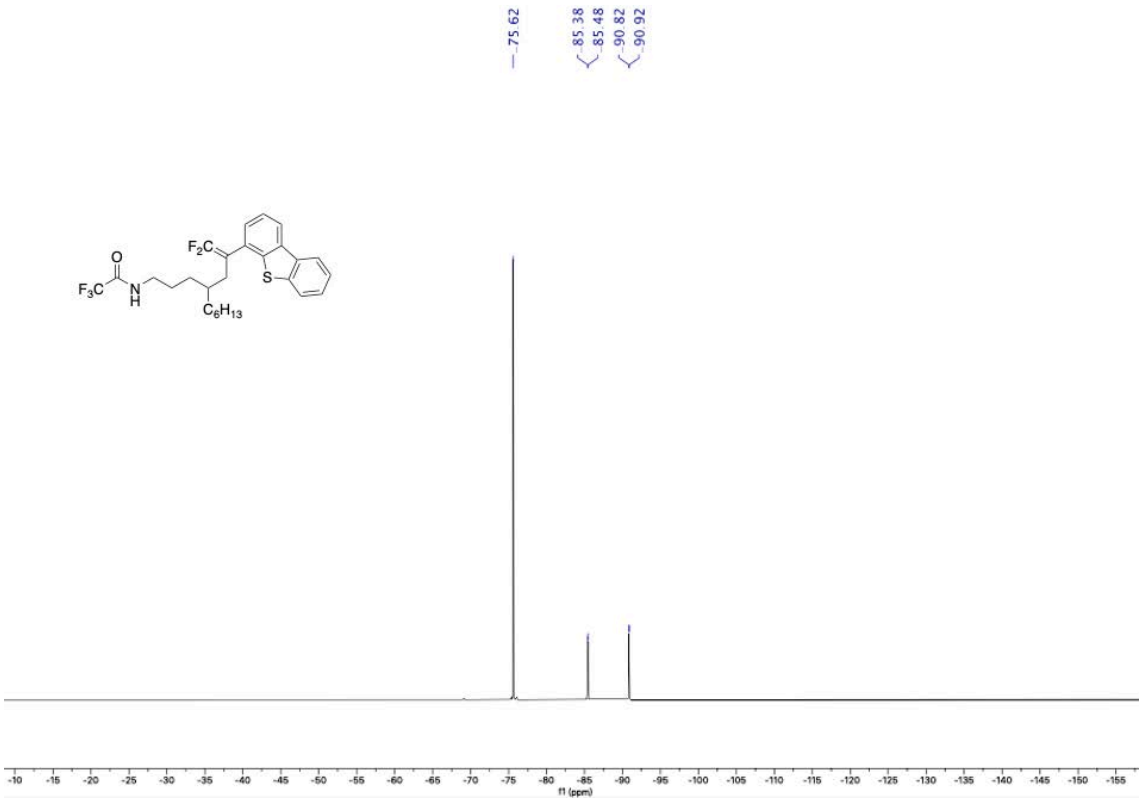
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6y**



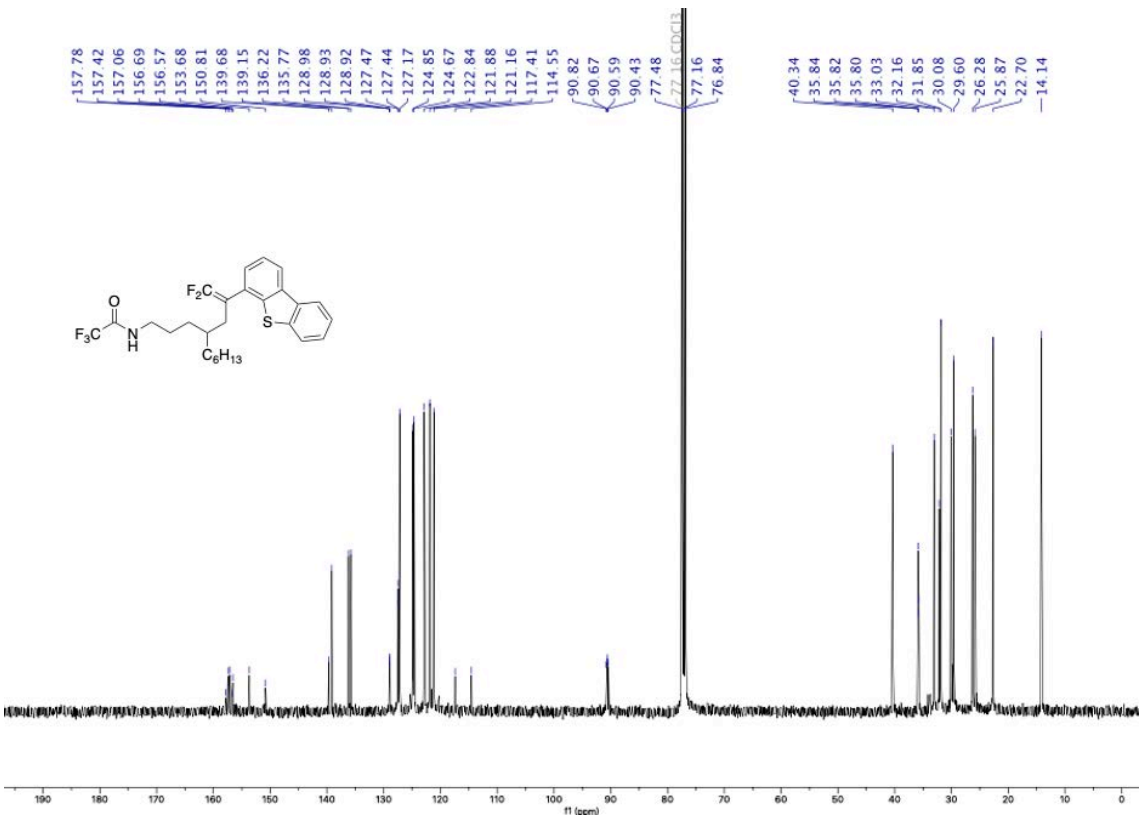
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6y**



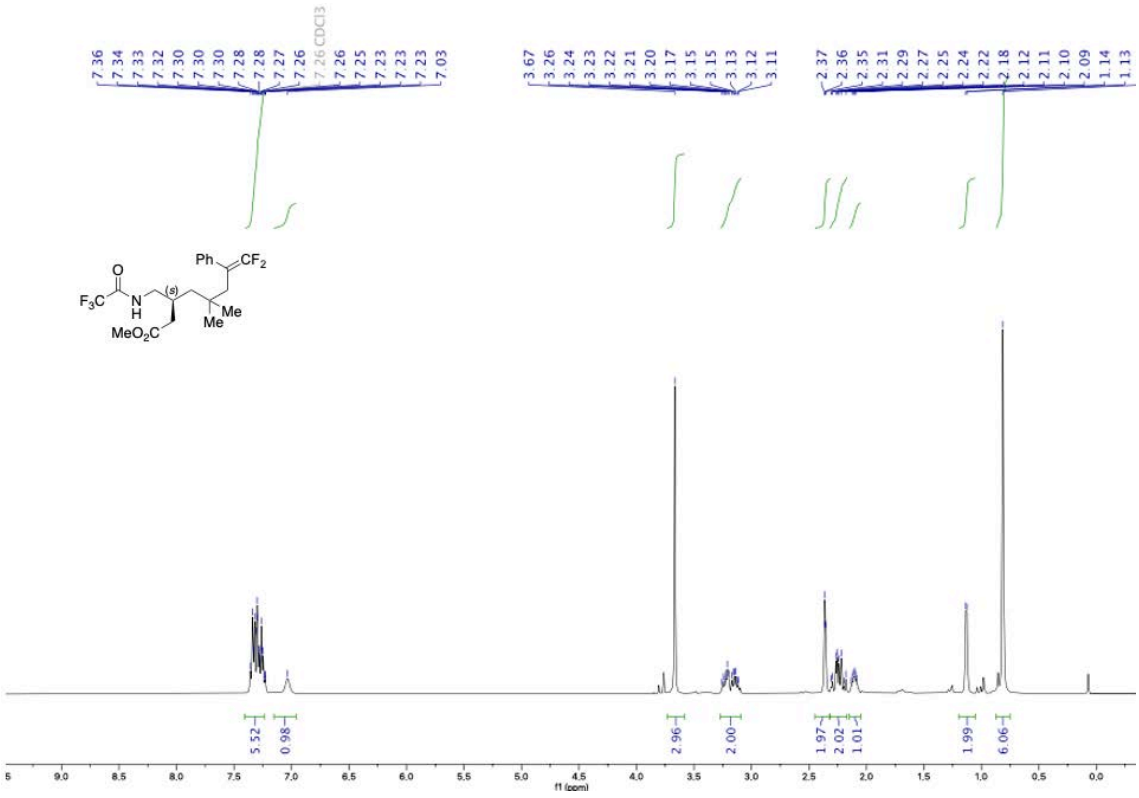
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6z**



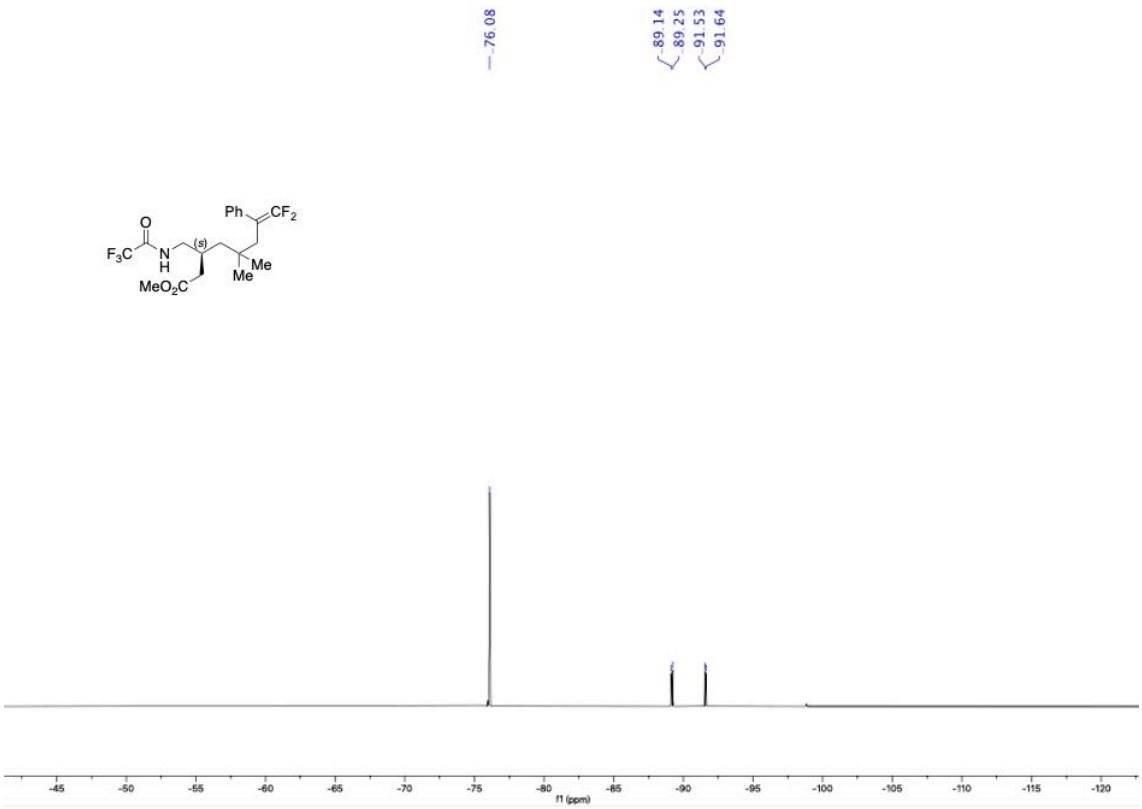
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6z**



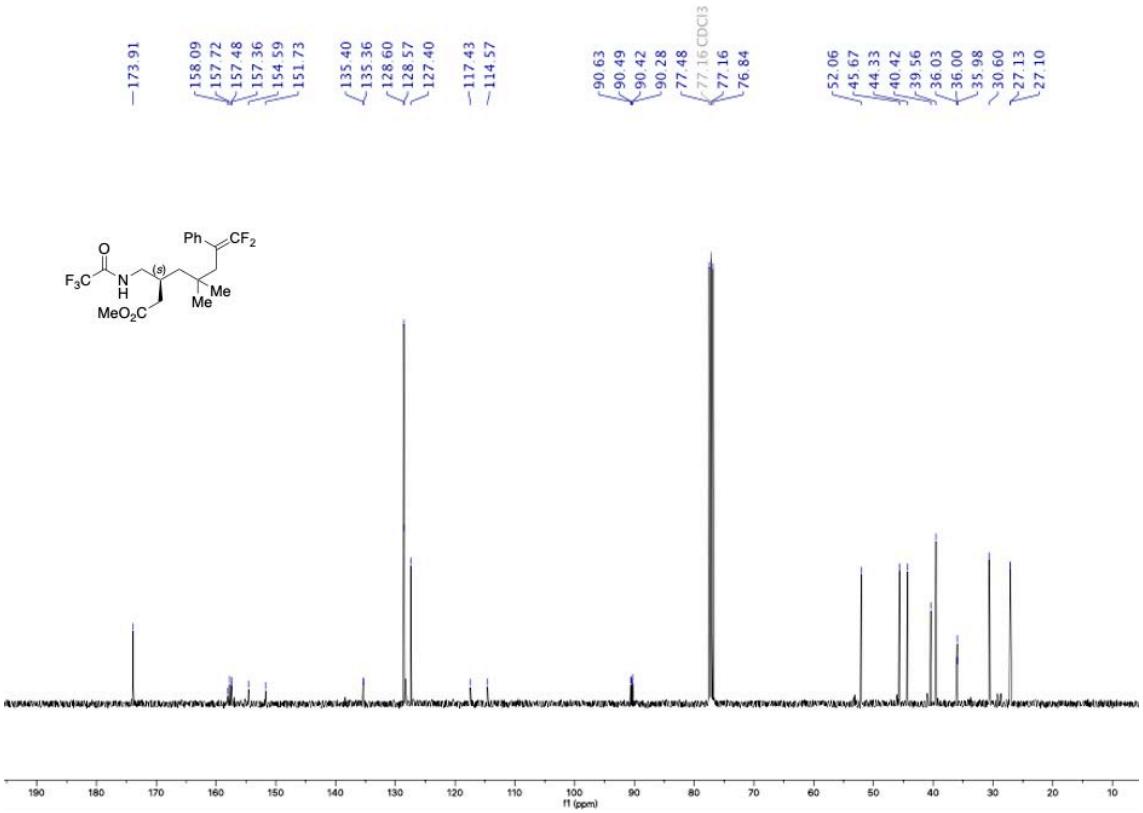
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6z**



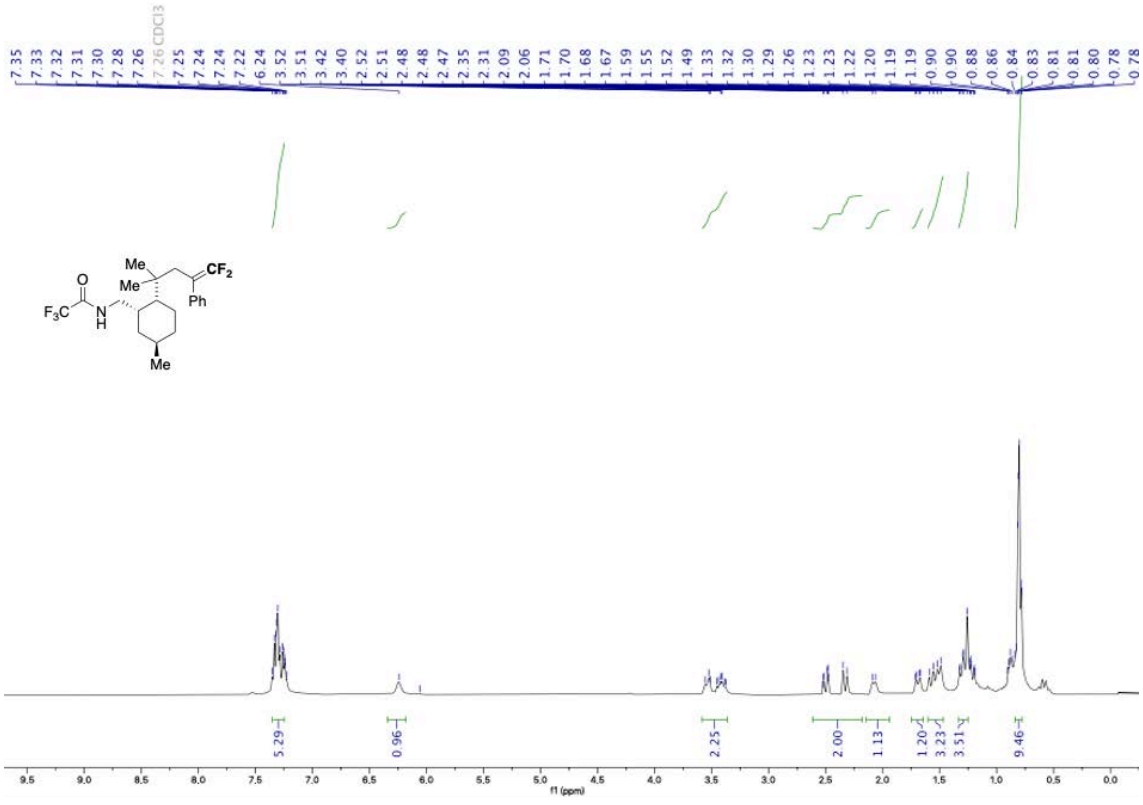
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6aa**



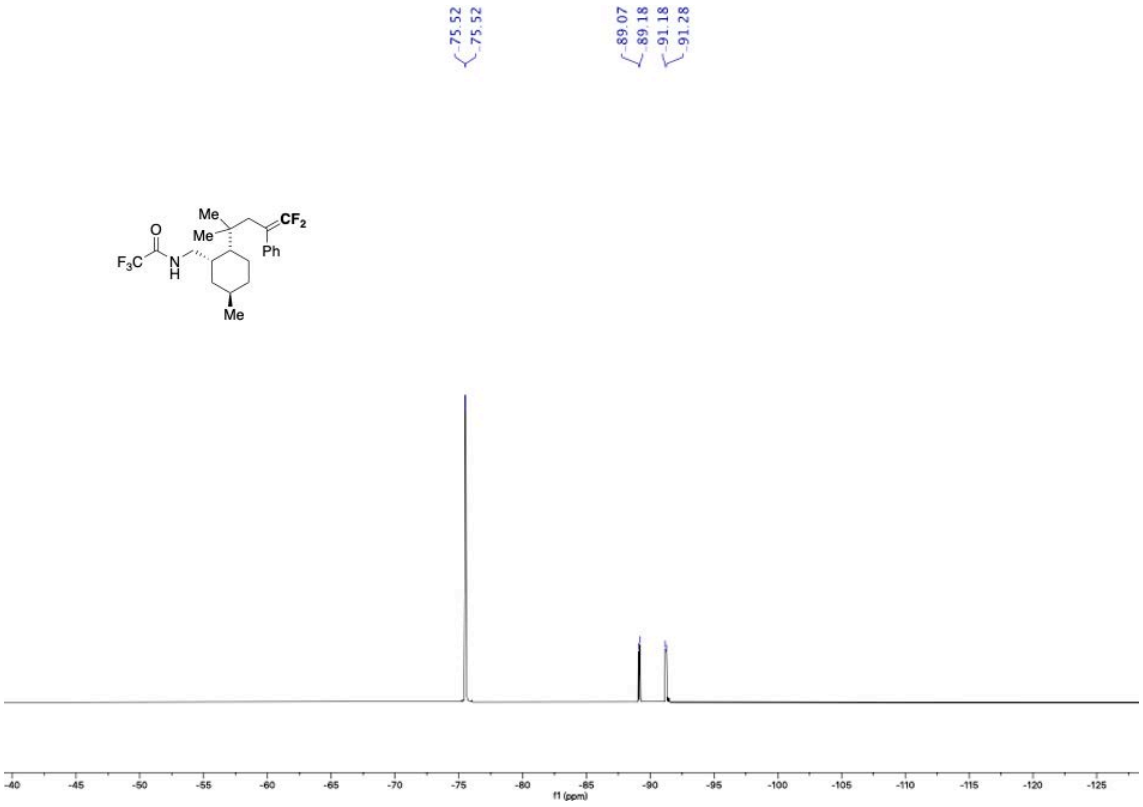
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 6**aa**



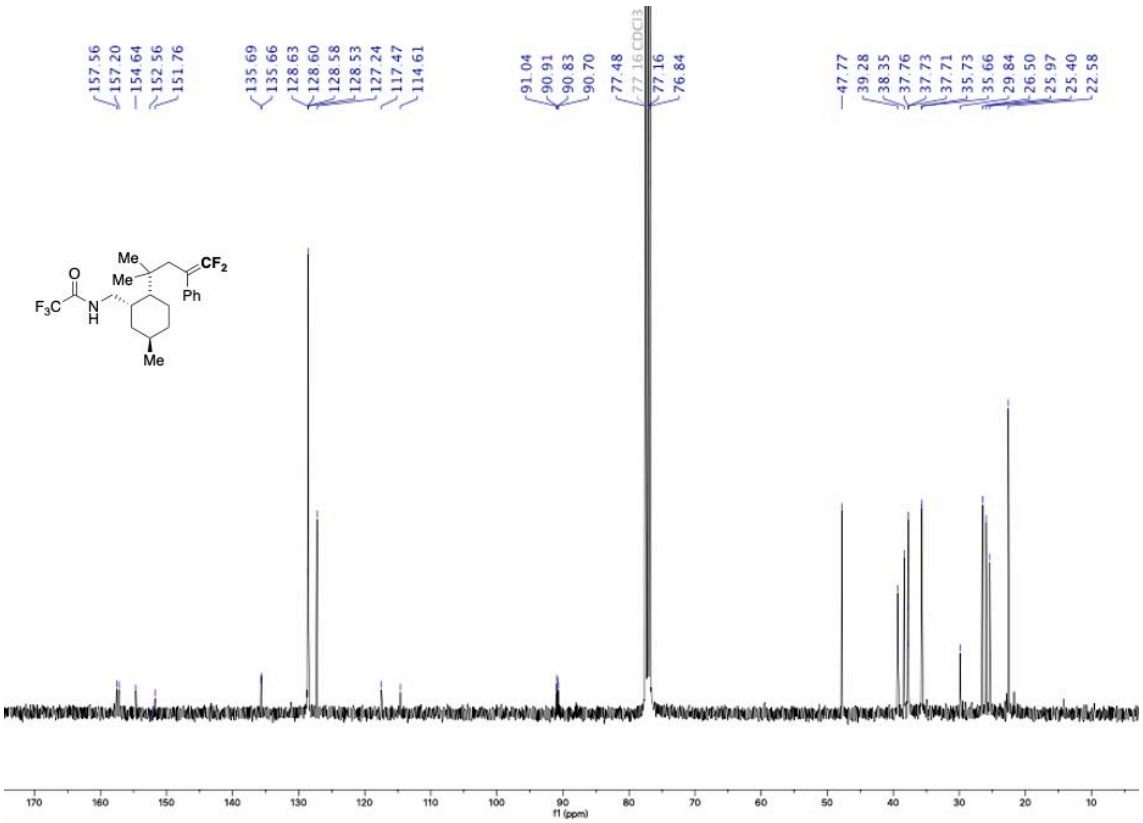
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6aa**



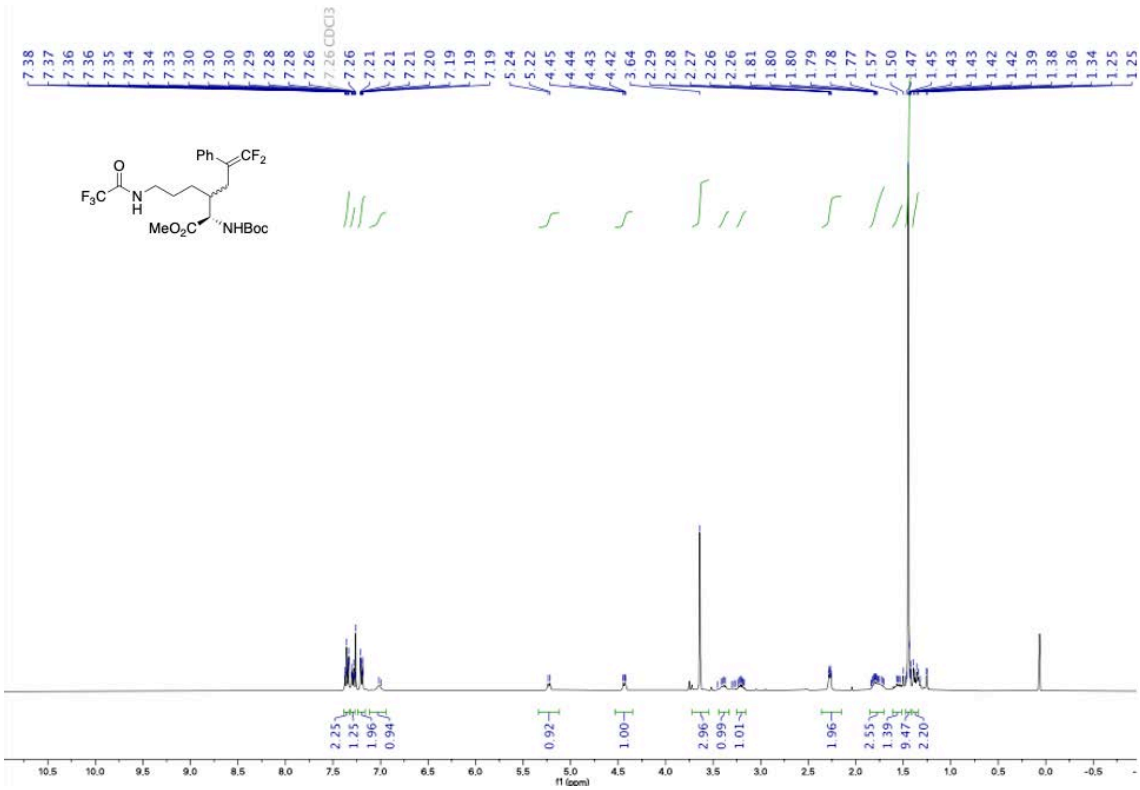
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6ab**



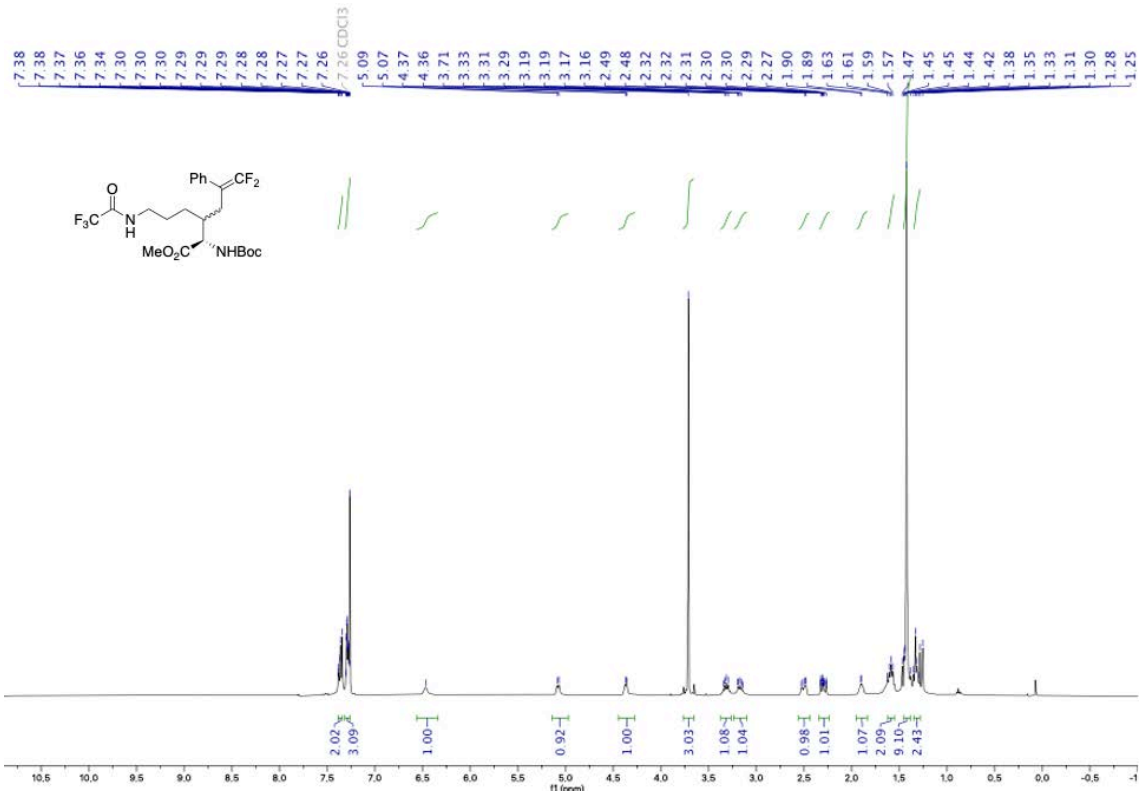
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6ab**



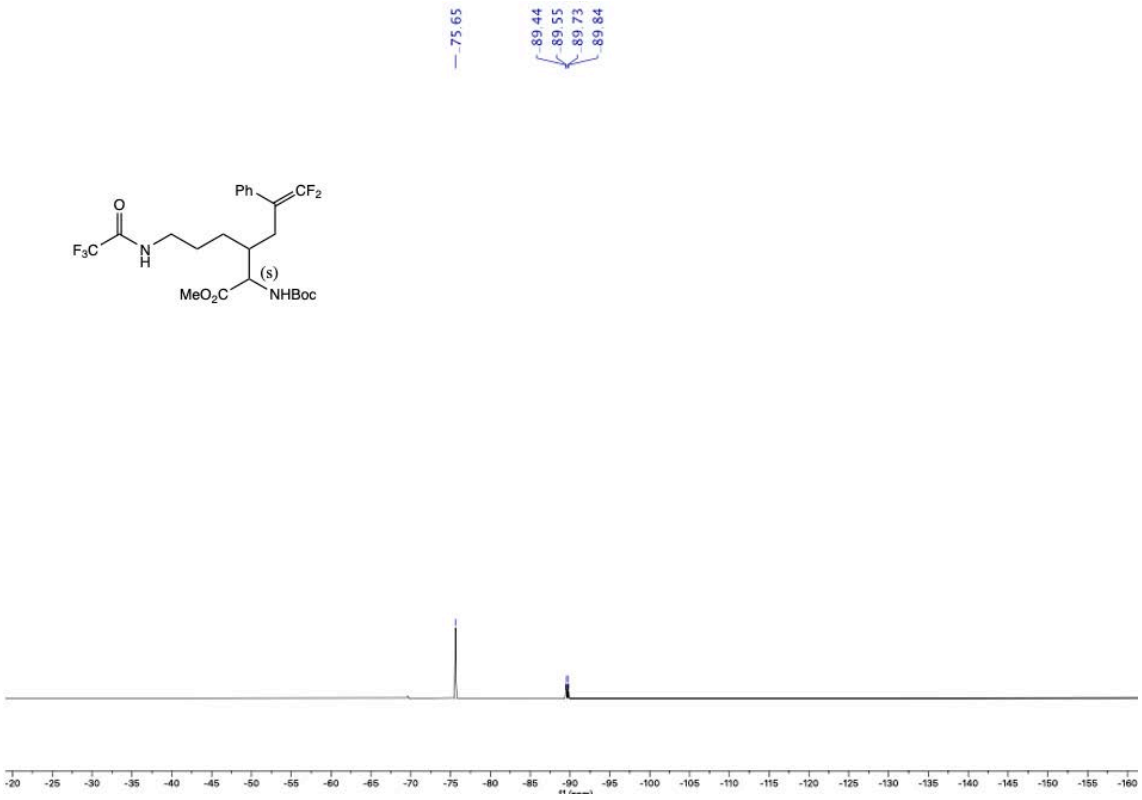
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6ab**



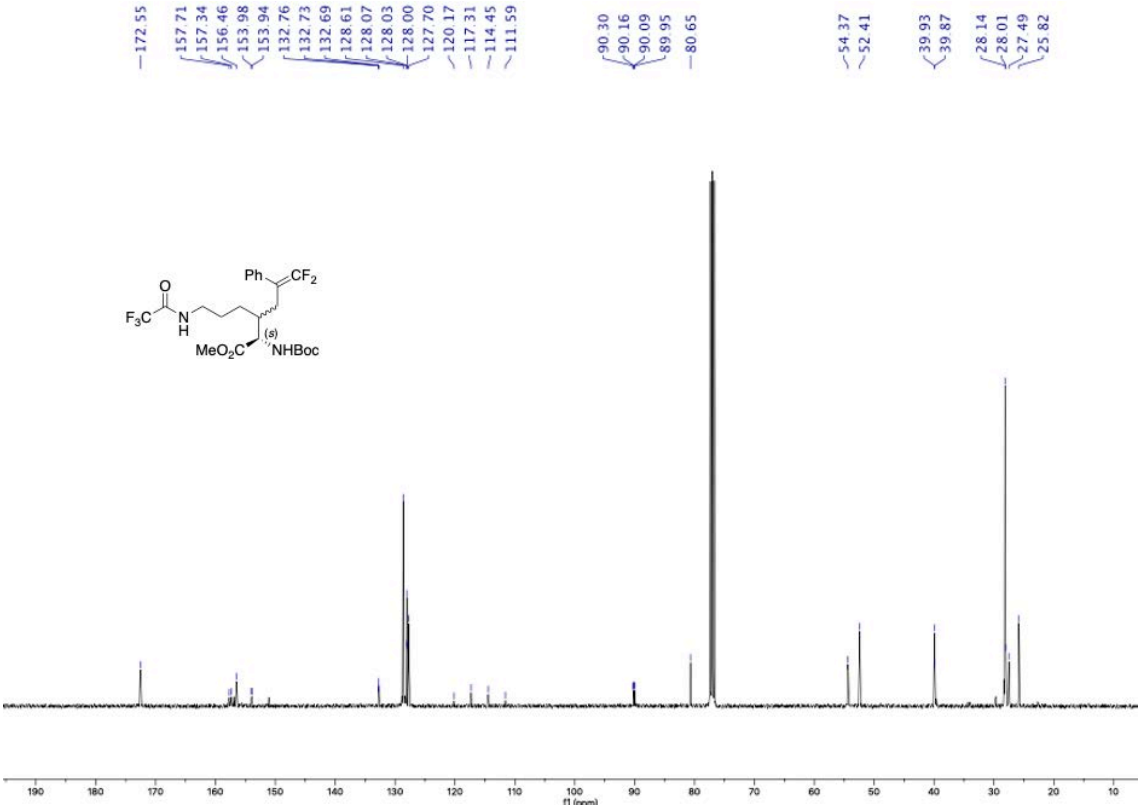
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6ac** (*diastereomer 1*)



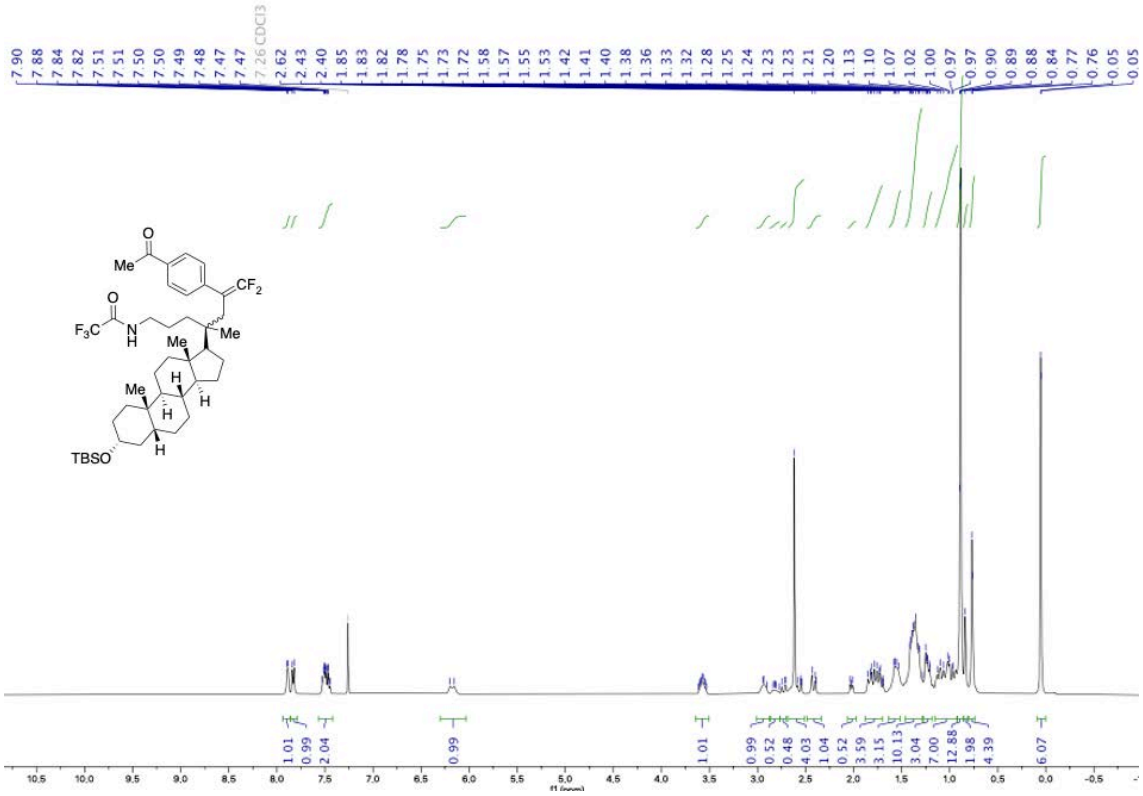
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6ac** (*diastereomer 2*)



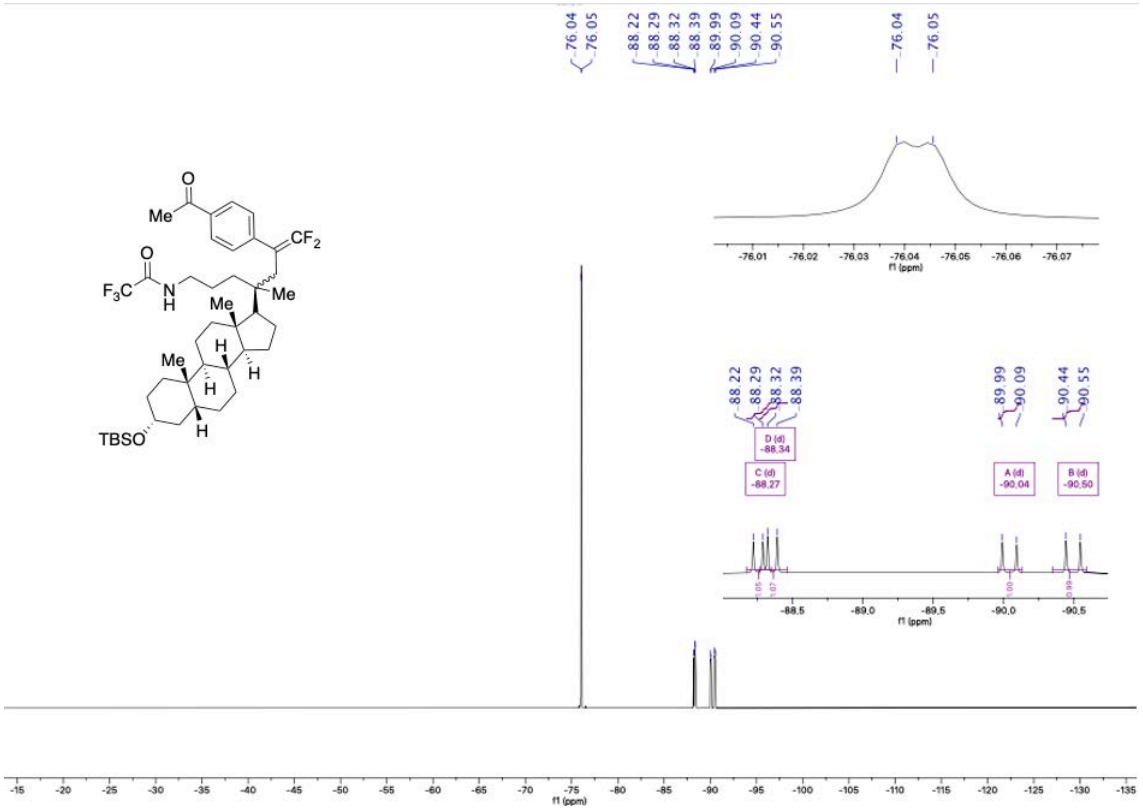
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6ac**



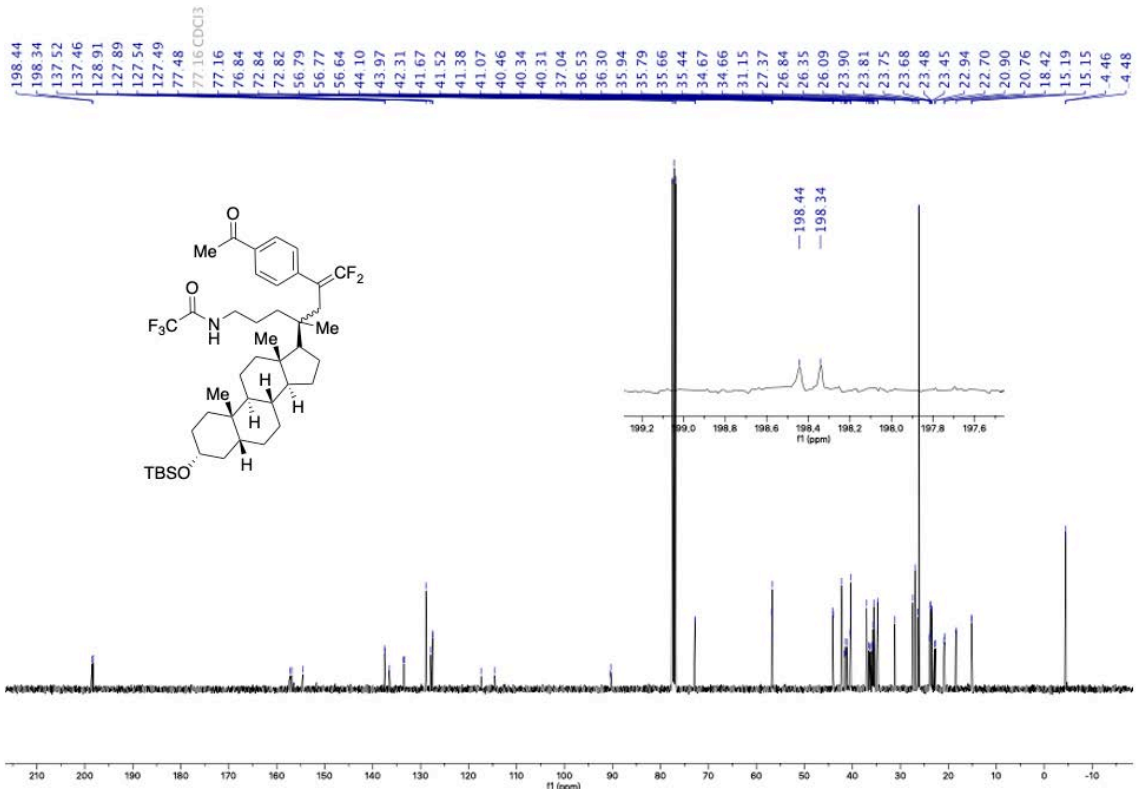
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6ac**



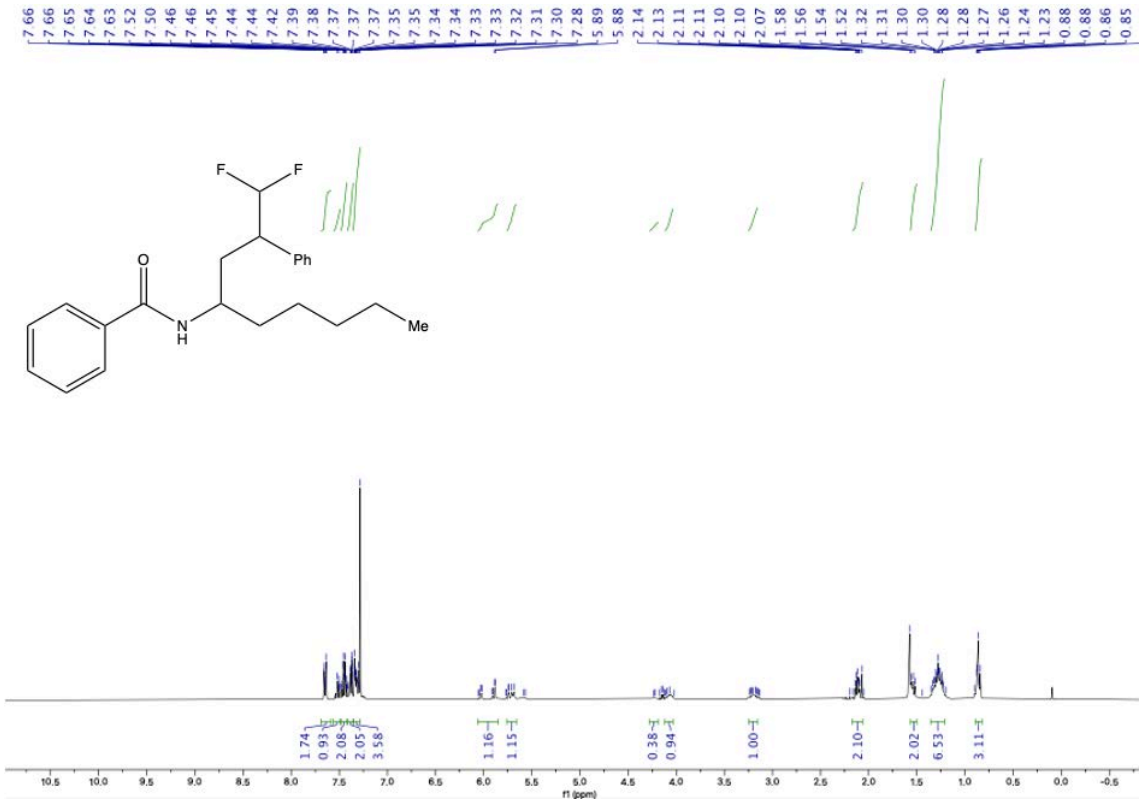
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6ad**



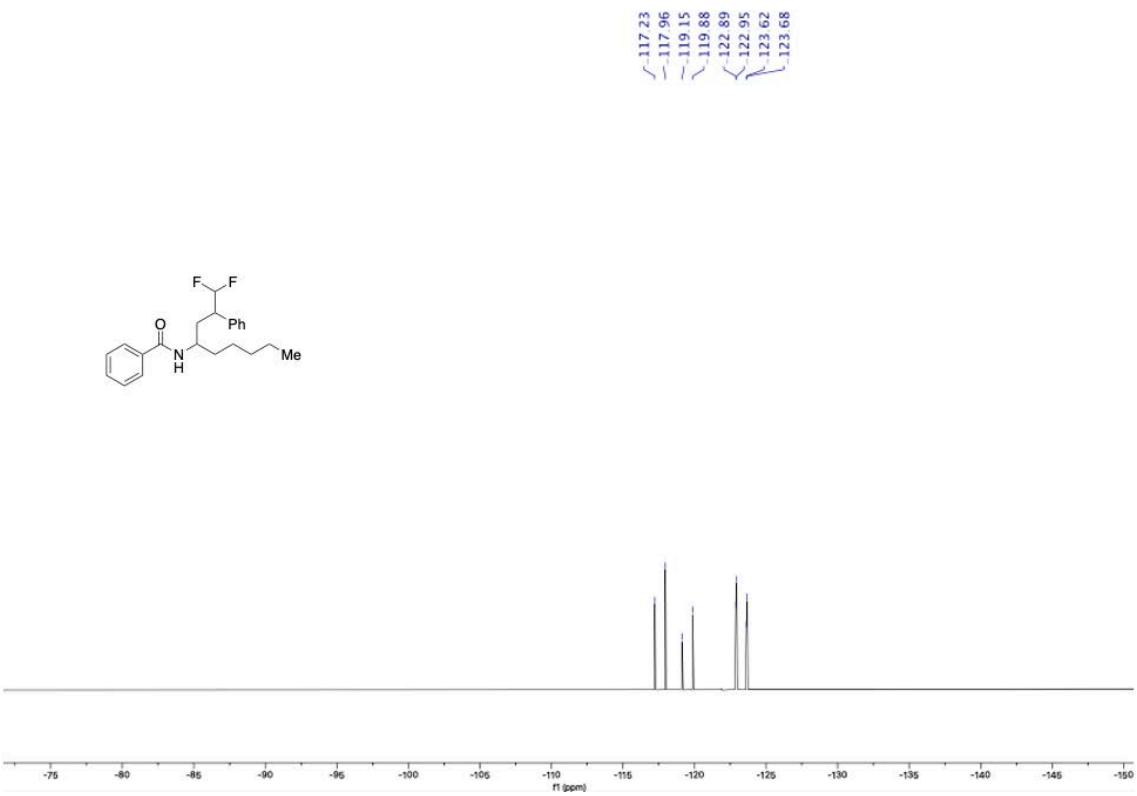
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6ad**



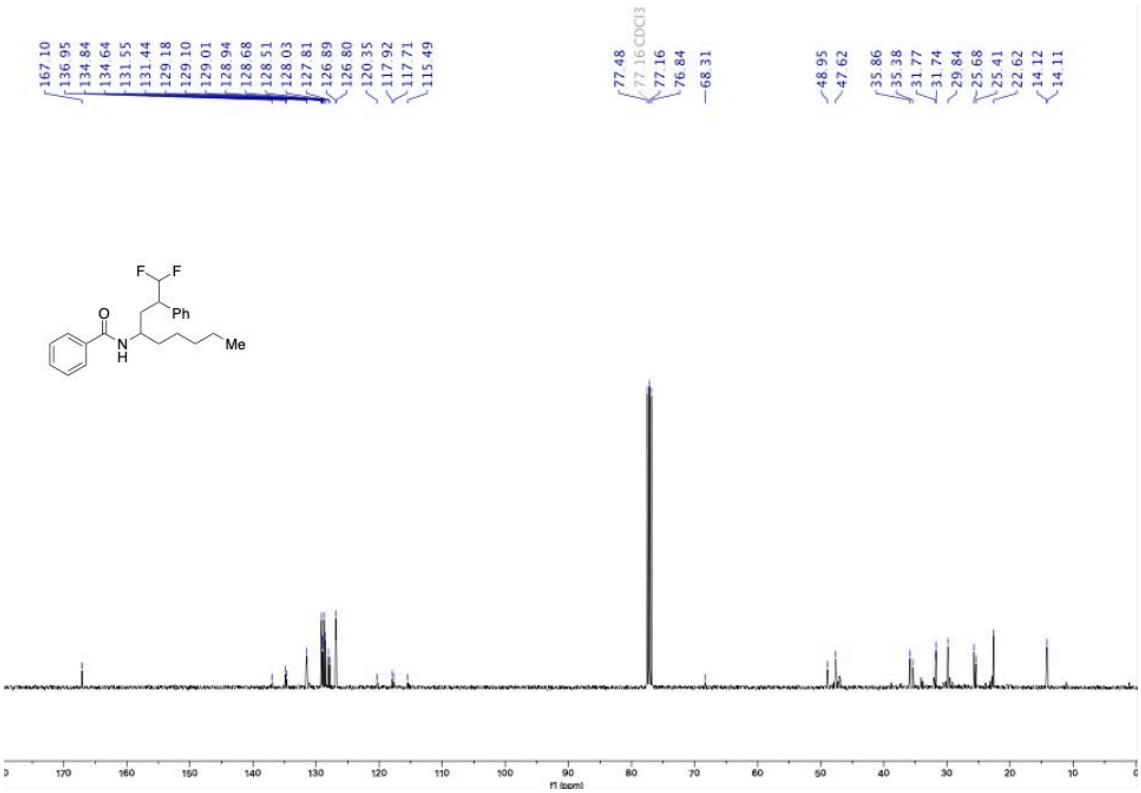
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6ad**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **12**



^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **12**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **12**