

Supporting Information

Photoinduced Difunctionalization of Unactivated Olefins Enabled by Ligand-to-Iron Charge Transfer and Functional Group Migration Strategies

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1. General Information

1.1 General information

All commercially available reagents were directly used as received without further purification. All experiments were monitored by analytical thin layer chromatography (TLC). Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. All yields of products refer to the isolated yields after chromatography.

^1H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Quantum-I Plus 400 spectrometer in CDCl_3 . For ^1H NMR, CDCl_3 ($\delta = 7.26$ ppm), or tetramethylsilane (TMS, $\delta = 0$ ppm) serves as the internal standard; for ^{13}C NMR, CDCl_3 ($\delta = 77.16$ ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, hept = heptet, m = multiplet, br = broad), coupling constant (in Hz), and integration. HR-MS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using TOF as the mass analyzer type.

1.2 Reaction setup for visible-light reaction

The photoreaction instrument (WP-TEC-1020SL) was purchased from WATTCAS, China. The distance from the light source to the irradiation vessel is 7 mm.

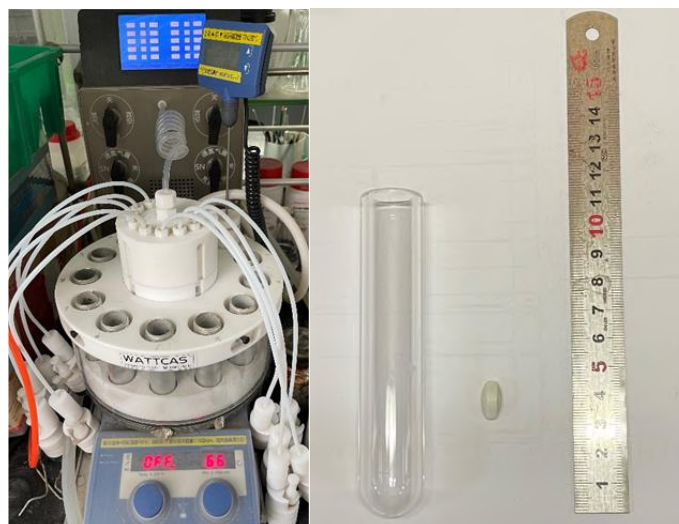


Figure S1. Reaction setup for general photoreactions

SPECTROPHOTOCOLORMETER ANALYSIS REPORT

Color Parameters:

CIE(1931:) $x = 0.1776$ $y = 0.0296$

CIE(1960:) $u = 0.2367$ $v = 0.0592$

CIE(1976:) $u' = 0.2367$ $v' = 0.0888$

Color Temperature: $T_c = 25000K$ Dominant Wave: $WL.D = 435.20nm$ Purity: $PUR = 93.54$

Peak Wave: $WL.P = 392.5nm$ Delta Wave: $WL.H = 18.0nm$

Color Tolerance: $SDCM = 186.7$ $Ra:Ra = 15.0$

$CRI_1 = 56.1$ $CRI_2 = 16.3$ $CRI_3 = 0.0$ $CRI_4 = 0.0$ $CRI_5 = 47.6$

$CRI_6 = 0.0$ $CRI_7 = 0.0$ $CRI_8 = 0.0$ $CRI_9 = 0.0$ $CRI_{10} = 0.0$

$CRI_{11} = 0.0$ $CRI_{12} = 0.0$ $CRI_{13} = 42.0$ $CRI_{14} = 6.3$ $CRI_{15} = 66.7$

Photology Parameters:

Lum Flux: $\Phi(lm) = 4.75lm$ Optical Power: $\Phi_e(mW) = 2769.6mW$ $\eta(lm/W) = 0.4lm/W$

Electric Parameters:

Forward Voltage: $V_F = 22.68V$ Forward Current: $I_F = 498.9mA$ Power = $11.32W$

Status:

Wavelength Range: $380nm \text{---} 780nm$ Intergration Time : $1000ms$

Test Project: LED COB TESTING **Test Equipment: ZP OPTO SYSTEM**

Product Model: HIGH POWER COB **Manufacturer: LEARNEW OPTO**

Temperature: 25 °C **Humidity: 40%**

Tester: MESSI LAN **Time: 2019-02-20 15:01**

Test Mechanism: ZP OPTO LAB

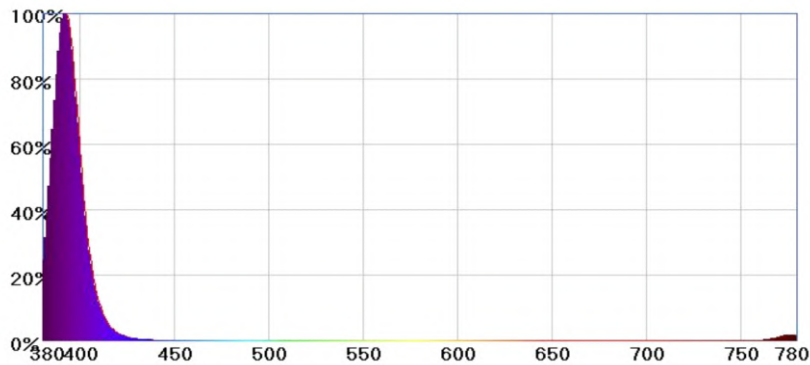
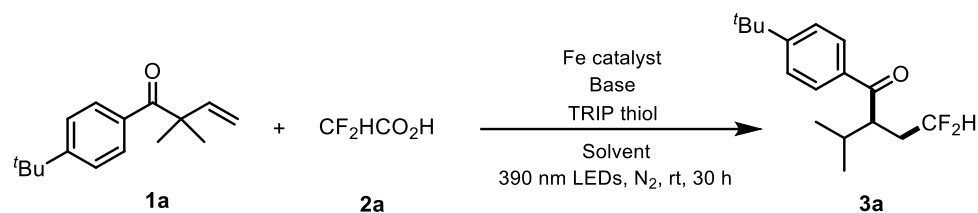


Figure S2. Wavelength of peak and intensity of light source

2. Optimization of the Reaction Conditions

(1) 1,2-fluoroalkylacylation of unactivated olefins ^{a, k}

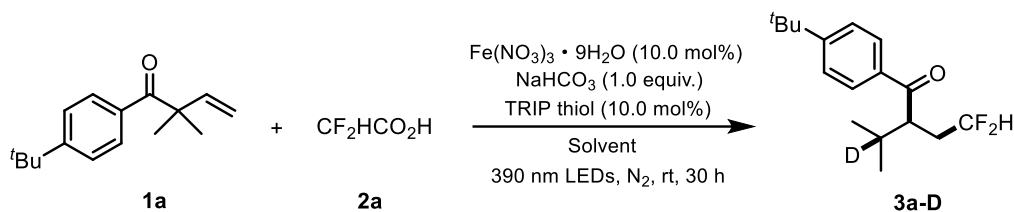


Entry	Fe catalyst	Base	Solvent	Yield ^b (%)
1	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (15 μL H ₂ O)	22
2	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	MeCN (AR)	n.d.
3	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (25 μL H ₂ O)	trace
4 ^c	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (15 μL H ₂ O)	trace
5 ^d	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (15 μL H ₂ O)	n.d.
6 ^e	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (15 μL H ₂ O)	17
7 ^f	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (15 μL H ₂ O)	trace
8 ^g	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (15 μL H ₂ O)	14
9 ^h	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (15 μL H ₂ O)	trace
10 ⁱ	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry MeCN (15 μL H ₂ O)	trace
11	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry DMSO (15 μL H ₂ O)	49
12	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry DMF (15 μL H ₂ O)	31
13	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry DCM (15 μL H ₂ O)	trace
14	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry THF (15 μL H ₂ O)	trace
15	Fe(acac) ₃	K ₂ CO ₃	Dry DMSO (15 μL H ₂ O)	37
16	Fe ₂ (SO ₄) ₃	K ₂ CO ₃	Dry DMSO (15 μL H ₂ O)	29
17	FeCl ₃	K ₂ CO ₃	Dry DMSO (15 μL H ₂ O)	27
18	Fe(OAc) ₂	K ₂ CO ₃	Dry DMSO (15 μL H ₂ O)	46
19	Fe(NO ₃) ₃ ·9H ₂ O	K ₂ CO ₃	Dry DMSO	59
20	Fe(NO₃)₃·9H₂O	NaHCO₃	Dry DMSO	69
21	Fe(NO ₃) ₃ ·9H ₂ O	DABCO	Dry DMSO	64
22	Fe(NO ₃) ₃ ·9H ₂ O	Et ₃ N	Dry DMSO	trace
23	Fe(NO ₃) ₃ ·9H ₂ O	2,6-lutidine	Dry DMSO	23
24	Fe(NO ₃) ₃ ·9H ₂ O	K ₃ PO ₄	Dry DMSO	27
25	Fe(NO ₃) ₃ ·9H ₂ O	Li ₂ CO ₃	Dry DMSO	trace
26	-	NaHCO ₃	Dry DMSO	n.d.
27	Fe(NO ₃) ₃ ·9H ₂ O	-	Dry DMSO	n.d.
28 ^j	Fe(NO ₃) ₃ ·9H ₂ O	NaHCO ₃	Dry DMSO	n.d.

^a Reaction condition: **1a** (0.20 mmol, 1.0 equiv.), **2a** (0.80 mmol, 4.0 equiv.), Fe catalyst (0.02 mmol, 10.0 mol%), Base (0.20 mmol, 1.0 equiv.), TRIP thiol (0.02 mmol, 5.0 μL, 10.0 mol%), anhydrous MeCN (0.1 M, 2.0 mL), H₂O (15 μL), 10 W 390 nm LEDs under N₂ atmosphere at room temperature

for 30 h. ^b Isolated yield. ^c **2a** (1.2 mmol, 6.0 equiv.). ^d K₂CO₃ (0.10 mmol, 0.5 equiv.). ^e Fe(NO₃)₃·9H₂O (0.04 mmol, 20.0 mol%). ^f TRIP thiol (0.03 mmol, 7.5 μL, 15.0 mol%). ^g PhSSPh (0.02 mmol, 4.4 mg, 10.0 mol%). ^h p-Toluenethiol (0.02 mmol, 2.5 mg, 10.0 mol%). ⁱ (TMS)₃SiH (0.02 mmol, 5.0 mg, 10.0 mol%). ^j no TRIP thiol. ^k n.d. = not detected.

(2) Deuteration reaction ^a

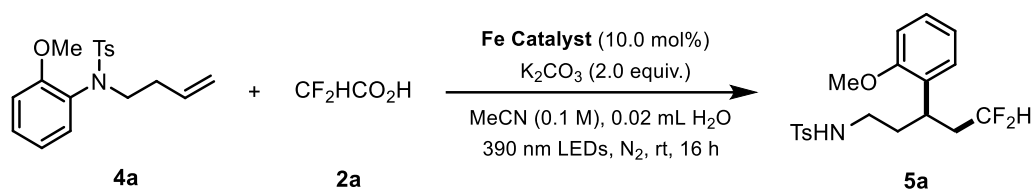


Entry	Solvent	Yield ^b (%)
1	Dry DMSO (0.1 M, no D ₂ O)	69 (0% D)
2	Dry DMSO (0.1 M) + 30 μL D ₂ O	64 (36% D)
3	Dry DMSO (0.1 M) + 50 μL D ₂ O	64 (42% D)
4	Dry DMSO (0.1 M) + 100 μL D ₂ O	62 (72% D)
5	Dry DMSO : D₂O (0.1 M, 4 : 1)	59 (82% D)
6	Dry DMSO : D ₂ O (0.1 M, 3 : 1)	31 (80% D)
7	Dry DMSO : D ₂ O (0.1 M, 2 : 1)	trace
8 ^c	Dry DMSO : D ₂ O (0.1 M, 4 : 1)	28 (72% D)
9 ^d	Dry DMSO : D ₂ O (0.1 M, 4 : 1)	17 (77% D)
10 ^e	Dry DMSO : D ₂ O (0.1 M, 4 : 1)	33 (81% D)

^a Reaction condition: **1a** (0.20 mmol, 1.0 equiv.), **2a** (0.80 mmol, 4.0 equiv.), Fe catalyst (0.02 mmol, 10.0 mol%), NaHCO₃ (0.20 mmol, 1.0 equiv.), TRIP thiol (0.02 mmol, 5.0 μL, 10.0 mol%), anhydrous DMSO (0.1 M, 2.0 mL), D₂O, 10 W 390 nm LEDs under N₂ atmosphere at room temperature for 30 h. ^b Isolated yield (the D-incorporation ratio of the product was determined by ¹H NMR). ^c Fe(acac)₃ (0.02 mmol, 10.0 mol%). ^d Fe₂(SO₄)₃ (0.02 mmol, 10.0 mol%). ^e Fe(OAc)₂ (0.02 mmol, 10.0 mol%)

(3) 1,2-fluoroalkylarylation of unactivated olefins

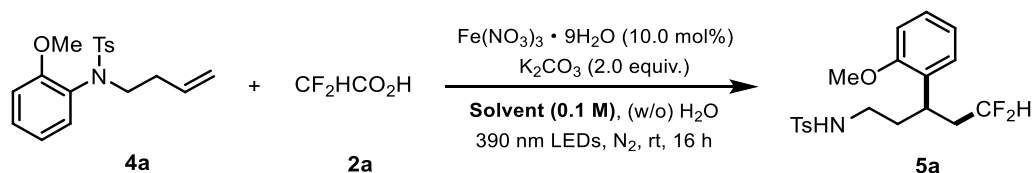
a. Screening of catalysts ^{a, c}



Entry	Fe Catalyst	Yield ^b (%)
1	Fe ₂ (SO ₄) ₃	14
2	Fe(NO₃)₃·9H₂O	25
3	Fe(OAc) ₂	trace
4	Fe(acac) ₃	15
5	FeBr ₃	trace
6	FeCl ₃ ·6H ₂ O	trace
7	FeCl ₃	trace
8	Fe(acac) ₂	23
9	FeSO ₄ ·7H ₂ O	21
10	Cu(OTf) ₂	n.d.
11	CuCl ₂	n.d.
12	CeCl ₃ ·7H ₂ O	trace

^a Reaction condition: **4a** (0.10 mmol, 1.0 equiv.), **2a** (0.60 mmol, 6.0 equiv.), **Fe Catalyst** (0.01 mmol, 10.0 mol%), K₂CO₃ (0.20 mmol, 2.0 equiv.), anhydrous MeCN (0.1 M, 1.0 mL), H₂O (20 μL), 10 W 390 nm LEDs under N₂ atmosphere at room temperature for 16 h. ^b Isolated yield. ^c n.d. = not detected.

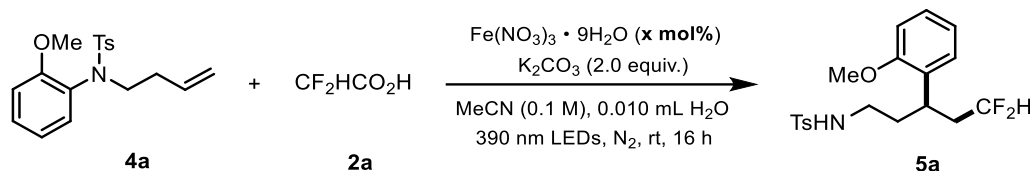
b. Screening of solvents ^{a, c}



Entry	Solvent	Yield ^b (%)
1	MeCN (20 μL H ₂ O)	25
2	H ₂ O	n.d.
3	MeCN (50 μL H ₂ O)	trace
4	MeCN (100 μL H ₂ O)	trace
5	Dry MeCN	trace
6	MeCN (15 μL H ₂ O)	35
7	MeCN (10 μL H₂O)	42
8	MeCN (5 μL H ₂ O)	trace
9	DCM (10 μL H ₂ O)	trace
10	Acetone (10 μL H ₂ O)	36
11	PhCF ₃ (10 μL H ₂ O)	n.d.

^a Reaction condition: **4a** (0.10 mmol, 1.0 equiv.), **2a** (0.60 mmol, 6.0 equiv.), Fe(NO₃)₃·9H₂O (0.01 mmol, 10.0 mol%), K₂CO₃ (0.20 mmol, 2.0 equiv.), anhydrous **Solvent** (0.1 M, 1.0 mL), (w/o) H₂O, 10 W 390 nm LEDs under N₂ atmosphere at room temperature for 16 h. ^b Isolated yield. ^c n.d. = not detected.

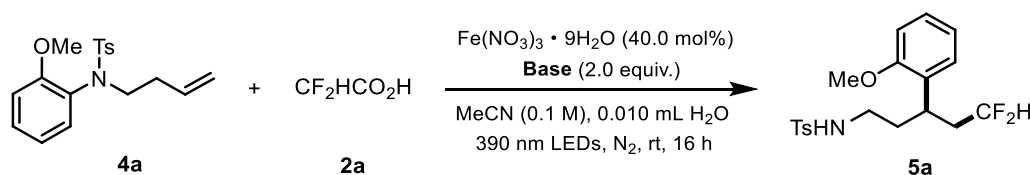
c. Screening of photocatalyst loadings ^a



Entry	Loadings of Fe catalyst	Yield ^b (%)
1	10.0	42
2	15.0	50
3	30.0	63
4	40.0	71
5	50.0	59

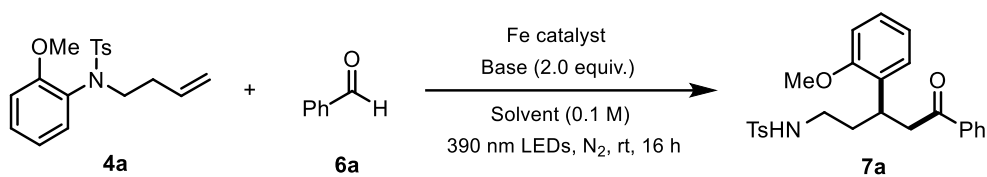
^a Reaction condition: **4a** (0.10 mmol, 1.0 equiv.), **2a** (0.60 mmol, 6.0 equiv.), Fe(NO₃)₃·9H₂O (**x mol%**), K₂CO₃ (0.20 mmol, 2.0 equiv.), anhydrous MeCN (0.1 M, 1.0 mL), H₂O (10 μL), 10 W 390 nm LEDs under N₂ atmosphere at room temperature for 16 h. ^b Isolated yield.

d. Screening of bases ^a



Entry	Base	Yield ^b (%)
1	K₂CO₃	71
2	DABCO	trace
3	CsF	trace
4	NaHCO ₃	48
5	HCO ₂ Na	trace
6	DMAP	15
7	NaOAc	trace
8	K ₂ HPO ₄	33

^a Reaction condition: **4a** (0.10 mmol, 1.0 equiv.), **2a** (0.60 mmol, 6.0 equiv.), Fe(NO₃)₃·9H₂O (0.04 mmol, 40.0 mol%), **Base** (0.20 mmol, 2.0 equiv.), anhydrous MeCN (0.1 M, 1.0 mL), H₂O (10 μL), 10 W 390 nm LEDs under N₂ atmosphere at room temperature for 16 h. ^b Isolated yield.

(4) 1,2-acylarylation of unactivated olefins ^{a,f}

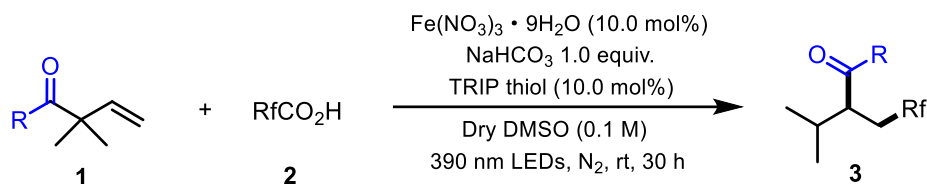
Entry	Fe catalyst	Base	Solvent	Yield ^b (%)
1	FeCl ₂	/	H ₂ O	trace
2	Fe ₂ (SO ₄) ₃	/	H ₂ O	trace
3	FeCl ₃	/	H ₂ O	30
4	Fe(NO ₃) ₃ ·9H ₂ O	/	H ₂ O	trace
5	Fe(acac) ₂	/	H ₂ O	n.d.
6	FeBr ₃	/	H ₂ O	n.d.
7	Fe(OAc) ₂	/	H ₂ O	trace
8	Fe(acac) ₃	/	H ₂ O	trace
9	FeCl ₃	DABCO	H ₂ O	trace
10	FeCl ₃	Et ₃ N	H ₂ O	n.d.
11	FeCl ₃	DBU	H ₂ O	19
12	FeCl ₃	K ₂ CO ₃	H ₂ O	35
13	FeCl ₃	Na ₃ PO ₄	H ₂ O	21
14	FeCl ₃	Cs ₂ CO ₃	H ₂ O	23
15	FeCl ₃	LiOH	H ₂ O	trace
16	FeCl ₃	KF	H ₂ O	20
17 ^c	FeCl ₃	K ₂ CO ₃	H ₂ O	16
18	FeCl ₃	K ₂ CO ₃	MeCN (20 μL H ₂ O)	20
19	FeCl ₃	K ₂ CO ₃	MeCN : H ₂ O = 9:1	trace
20	FeCl ₃	K ₂ CO ₃	MeCN : H ₂ O = 1:1	n.d.
21	FeCl ₃	K ₂ CO ₃	MeCN : H ₂ O = 1:4	18
22 ^d	FeCl₃	K₂CO₃	H₂O	55
23 ^e	FeCl ₃	K ₂ CO ₃	H ₂ O	trace

^a Reaction condition: **4a** (0.10 mmol, 1.0 equiv.), **6a** (0.30 mmol, 3.0 equiv.), **Fe Catalyst** (0.008 mmol, 8.0 mol%), Base (0.20 mmol, 2.0 equiv.), Solvent (0.1 M, 1.0 mL), 10 W 390 nm LEDs under N₂ atmosphere at room temperature for 16 h. ^b Isolated yield. ^c FeCl₃ (15.0 mol%). ^d **6a** (0.50 mmol, 5.0 equiv.). ^e **6a** (0.20 mmol, 2.0 equiv.). ^f n.d. = not detected.

3. General Procedures

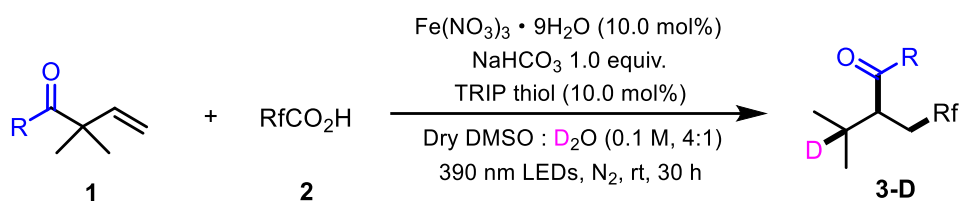
3.1 General procedure for the photoreactions

General Procedure A1



β,γ -unsaturated ketone **1** (0.20 mmol, 1.0 equiv.), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.02 mmol, 10.0 mol%) and NaHCO_3 (0.20 mmol, 1.0 equiv.) were added in an oven-dried 20 mL quartz tube containing a magnetic stirrer bar. To this was added dry dimethyl sulfoxide (2.0 mL, 0.1 M) followed by addition of TRIP thiol (0.02 mmol, 10.0 mol%) and fluorocarboxylic acid **2** (0.80 mmol, 4.0 equiv.) via pipettor. The reaction vial was sealed, evacuated and backfilled ten times with 1 atm of N_2 . The reaction mixture was stirred for 30 hours at room temperature in the presence of 10W 390 nm LED lamp (WATTCAS: WP-TEC-1020SL). After the reaction was completed (monitored by TLC), the mixture was diluted with EtOAc, and organic phase was washed with saturated NaCl solution. The combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by PTLC (Preparative Thin-Layer Chromatography) with a gradient eluent of petroleum ether and ethyl acetate to give the desired product **3**.

General Procedure A2



β,γ -unsaturated ketone **1** (0.20 mmol, 1.0 equiv.), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.02 mmol, 10.0 mol%) and NaHCO_3 (0.20 mmol, 1.0 equiv.) were added in an oven-dried 20 mL quartz tube containing a magnetic stirrer bar. To this was added dry dimethyl sulfoxide and deuterium oxide (0.1 M, 4:1) followed by addition of TRIP thiol (0.02 mmol, 10.0 mol%) and fluorocarboxylic acid **2** (0.80 mmol, 4.0 equiv.) via pipettor. The reaction vial was sealed, evacuated and backfilled ten times with 1 atm of N_2 . The reaction mixture was stirred for 30 hours at room temperature in the presence of 10W 390 nm LED lamp (WATTCAS: WP-TEC-1020SL). After the reaction was completed

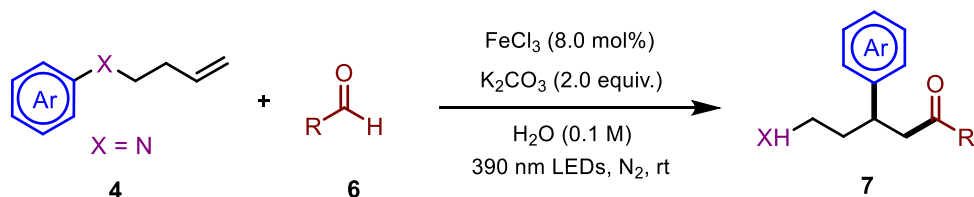
(monitored by TLC), the mixture was diluted with EtOAc, and organic phase was washed with saturated NaCl solution. The combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was purified by PTLC (Preparative Thin-Layer Chromatography) with a gradient eluent of petroleum ether and ethyl acetate to give the desired product **3-D**.

General Procedure B



Unactivated olefin **4** (0.10 mmol, 1.0 equiv.), $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.04 mmol, 40.0 mol%) and K_2CO_3 (0.20 mmol, 2.0 equiv.) were added in an oven-dried 20 mL quartz tube containing a magnetic stirrer bar. To this was added dry MeCN (0.1 M) and 10.0 μL H_2O followed by addition of fluorocarboxylic acid **2** (0.60 mmol, 6.0 equiv.) via pipettor. The reaction vial was sealed, evacuated and backfilled ten times with 1 atm of N_2 . The reaction mixture was stirred for 16 hours at room temperature in the presence of 10W 390 nm LED lamp (WATTCAS: WP-TEC-1020SL). After the reaction was completed (monitored by TLC), the solvent was removed by rotary evaporation and the residue was purified by PTLC (Preparative Thin-Layer Chromatography) with a gradient eluent of petroleum ether and ethyl acetate to give the desired product **5**.

General Procedure C



Unactivated olefin **4** (0.10 mmol, 1.0 equiv.), FeCl_3 (0.008 mmol, 8.0 mol%) and K_2CO_3 (0.20 mmol, 2.0 equiv.) were added in an oven-dried 20 mL quartz tube containing a magnetic stirrer bar. To this was added aldehyde **6** (0.50 mmol, 5.0 equiv.) via pipettor followed by addition of H_2O (0.1 M). The reaction vial was sealed, evacuated and backfilled ten times with 1 atm of N_2 . The reaction mixture was stirred for 16 - 30 hours at room temperature in the presence of 10W 390 nm LED lamp (WATTCAS: WP-TEC-1020SL). After the reaction was completed (monitored by

TLC), the mixture was diluted with EtOAc, and organic phase was washed with saturated NaCl solution. The combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure. and the residue was purified by PTLC (Preparative Thin-Layer Chromatography) with a gradient eluent of petroleum ether and ethyl acetate to give the desired product **7**.

3.2 General procedure for the gram-scale reaction

To an oven-dried 50 mL double-necked flask (charged with a stir bar) was added distal olefinic aryl ether (**4i**, 1.0 mmol, 206 mg, 1.0 equiv.), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (40 mol%, 162 mg, 0.4 mmol) and K_2CO_3 (2.0 mmol, 276 mg, 2.0 equiv.). The reaction vial was evacuated and back-filled with nitrogen under -78°C (this process was repeated three times), difluoroacetic acid (**2a**, liquid, 6.0 mmol, 377 μL , 6.0 equiv.), 100 μL H_2O and MeCN (10.0 mL, 0.1M) was added subsequently via syringe. The resulting mixture was stirred at room temperature with four 10 W 390 nm LED lamps until the reaction completion. The mixture was filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (PE : EA = 5:1, v/v). to give the desired product **5i** (175 mg, 68%).

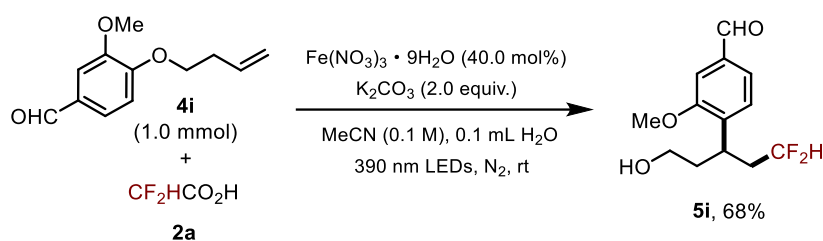
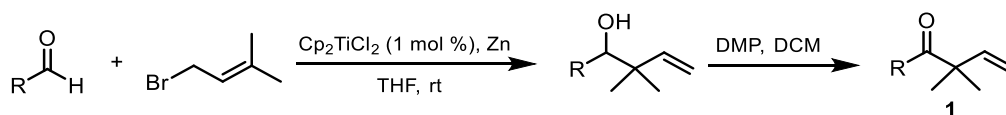


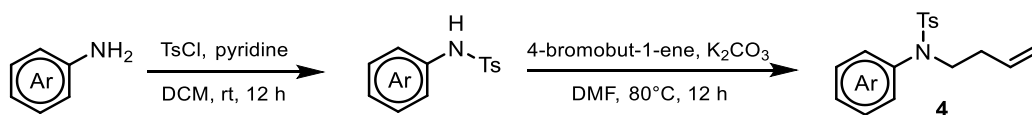
Figure S3. Reaction setup for the gram-scale reaction

3.3 General procedure for the synthesis of unactivated olefins¹⁻³



To an oven-dried 50 mL double-necked flask (charged with a stir bar) was charged with Cp_2TiCl_2 (1.0 mol%, 12.5 mg, 0.05 mmol) and zinc dust (12.5 mmol, 825 mg, 2.5 equiv.) under an atmosphere of N_2 at room temperature. THF (10.0 mL) was added via syringe and the reaction stirred until the solution had turned from red to green. A solution of aldehyde (5.0 mmol, 1.0 equiv.) and 3,3-dimethylallyl bromide (12.5 mmol, 2.5 equiv.) in THF (10.0 mL) was then added via syringe. The reaction was stirred until all starting material was consumed as monitored by TLC. The crude residue was purified by flash chromatography, eluting with hexanes/EtOAc to give the homoallylic alcohol.

The solution of the homoallylic alcohol (1.0 equiv) in DCM (0.5 M) was added to a mixture of Dess-Martin periodinane (1.5 equiv) and DCM (0.5 M). The reaction mixture was stirred until the homoallylic alcohol was consumed. The solvent was removed in vacuo. Purify the residue by silica gel column chromatography (petroleum ether-EtOAc 100:1) to give the β,γ -unsaturated ketones **1**.

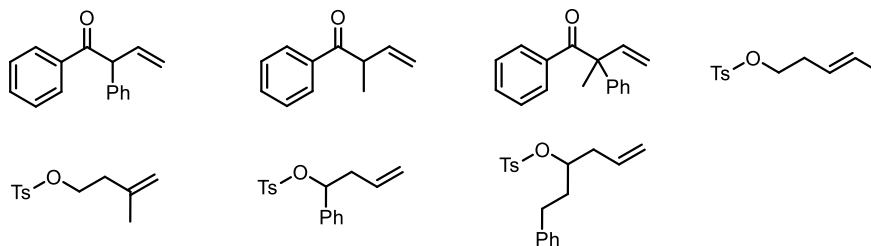


To an oven-dried 100 mL round-bottom flask (charged with a stir bar) was added aromatic amine (10.0 mmol), tosyl chloride (2.28 g, 12 mmol, 1.2 equiv), pyridine (2.42 mL, 30.0 mmol, 3.0 equiv), and 30 mL DCM. The mixture was stirred at room temperature until starting material was consumed. This organic solution was washed with 1N HCl and brine. The combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure.

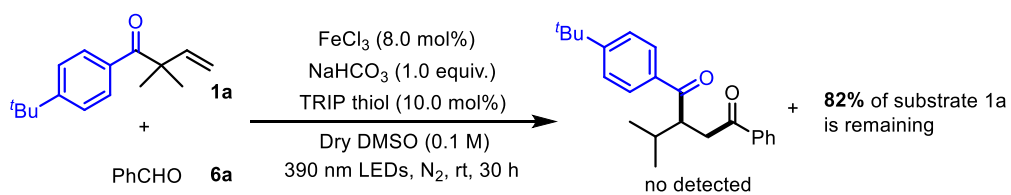
The crude product that the product of the first step, 4-bromobut-1-ene (2 mL, 20 mmol), and K_2CO_3 (2.7 g, 20 mmol) were dispersed in DMF (20 mL). The mixture was stirred for 12 h at 80 °C and quenched with H_2O and EtOAc. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate as the eluent to give unactivated olefin **4**.

3.4 Unreacted substrates

Unreacted alkene substrates :

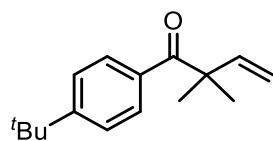


1,2-acyl migration using aldehyde as radical precursor :



4. Characterization Data of Substrates and Products

4.1 Characterization data of substrates



1-(4-(*tert*-butyl)phenyl)-2,2-dimethylbut-3-en-1-one (1a)

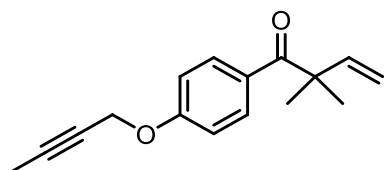
Yellow oil liquid.

Compound **1a** was purified by flash chromatography eluted with PE/EA = 100:1.

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 6.20 (dd, J = 17.6, 10.6 Hz, 1H), 5.27 – 5.16 (m, 2H), 1.40 (s, 6H), 1.32 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 203.9, 155.4, 144.3, 134.1, 129.6, 125.0, 113.9, 50.1, 35.1, 31.2, 26.3.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₆H₂₃O⁺ 231.1743; found 231.1745.



1-(4-(but-2-yn-1-yloxy)phenyl)-2,2-dimethylbut-3-en-1-one (1d)

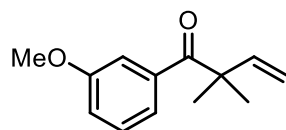
Yellow oil liquid.

Compound **1d** was purified by flash chromatography eluted with PE/EA = 100:1.

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 6.20 (dd, J = 17.6, 10.6 Hz, 1H), 5.27 – 5.15 (m, 2H), 4.71 – 4.64 (m, 2H), 1.85 (t, J = 2.2 Hz, 3H), 1.39 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 202.4, 160.7, 144.4, 132.0, 129.6, 114.0, 113.7, 84.3, 73.5, 56.5, 49.9, 26.4, 3.7.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₆H₁₉O₂⁺ 243.1380; found 243.1376.



1-(3-methoxyphenyl)-2,2-dimethylbut-3-en-1-one (1i)

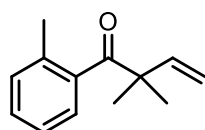
Yellow oil liquid.

Compound **1i** was purified by flash chromatography eluted with PE/EA = 100:1.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 7.7 Hz, 1H), 7.41 (s, 1H), 7.30 – 7.26 (m, 1H), 7.01 (dd, J = 8.2, 2.1 Hz, 1H), 6.19 (dd, J = 17.5, 10.6 Hz, 1H), 5.28 – 5.19 (m, 2H), 3.81 (s, 3H), 1.39 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 204.5, 159.3, 144.0, 138.5, 129.0, 121.9, 117.9, 114.2, 114.1, 55.4, 50.3, 26.1.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₃H₁₇O₂⁺ 205.1223; found 205.1219.



2,2-dimethyl-1-(o-tolyl)but-3-en-1-one (**1j**)

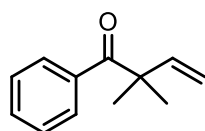
Yellow oil liquid.

Compound **1j** was purified by flash chromatography eluted with PE/EA = 100:1.

¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.12 (m, 4H), 6.03 (dd, J = 17.4, 10.6 Hz, 1H), 5.22 – 5.12 (m, 2H), 2.23 (s, 3H), 1.33 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 211.1, 142.8, 140.6, 134.6, 130.9, 129.1, 125.6, 124.8, 114.3, 51.5, 24.6, 20.1.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₃H₁₇O⁺ 189.1274; found 189.1276.



2,2-dimethyl-1-phenylbut-3-en-1-one (**1l**)

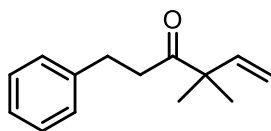
Yellow oil liquid.

Compound **1l** was purified by flash chromatography eluted with PE/EA = 100:1.

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.85 (m, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 6.18 (dd, J = 17.6, 10.6 Hz, 1H), 5.27 – 5.17 (m, 2H), 1.39 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 204.8, 144.0, 137.2, 131.8, 129.4, 128.1, 114.2, 50.3, 26.2.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₂H₁₅O⁺ 175.1117; found 175.1120.



4,4-dimethyl-1-phenylhex-5-en-3-one (1o)

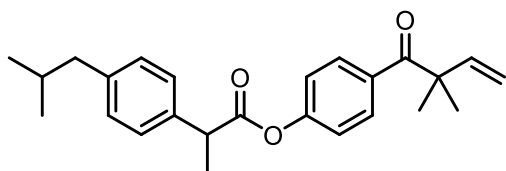
Yellow oil liquid.

Compound **1o** was purified by flash chromatography eluted with PE/EA = 100:1.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.28 – 7.24 (m, 2H), 7.17 (t, J = 8.1 Hz, 3H), 5.86 (dd, J = 17.3, 10.7 Hz, 1H), 5.15 – 5.04 (m, 2H), 2.87 – 2.80 (m, 2H), 2.81 – 2.74 (m, 2H), 1.19 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 212.2, 142.5, 141.5, 128.5, 128.5, 126.1, 114.5, 50.9, 39.5, 30.3, 23.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{19}\text{O}^+$ 203.1430; found 203.1426.



4-(2,2-dimethylbut-3-enoyl)phenyl 2-(4-isobutylphenyl)propanoate (1p)

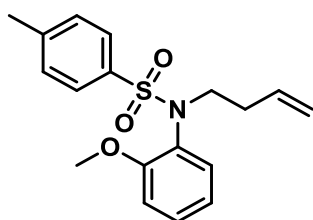
Yellow oil liquid.

Compound **1p** was purified by flash chromatography eluted with PE/EA = 100:1.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 6.15 (dd, J = 17.6, 10.6 Hz, 1H), 5.25 – 5.13 (m, 2H), 3.93 (q, J = 7.1 Hz, 1H), 2.46 (d, J = 7.2 Hz, 2H), 1.90 - 1.83 (m, 1H), 1.60 (d, J = 7.1 Hz, 3H), 1.37 (s, 6H), 0.90 (d, J = 6.6 Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 203.1, 172.8, 153.6, 143.9, 141.1, 137.0, 134.2, 131.2, 129.7, 127.3, 121.0, 114.2, 50.2, 45.4, 45.2, 30.3, 26.2, 22.5, 18.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{31}\text{O}_3^+$ 379.2268; found 379.2266.



N-(but-3-en-1-yl)-N-(2-methoxyphenyl)-4-methylbenzenesulfonamide (4a)

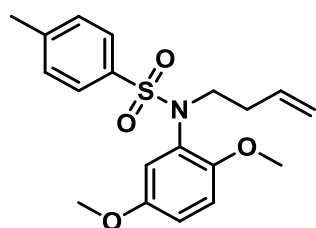
Colorless oil.

Compound **4a** was purified by flash chromatography eluted with PE/EA = 10:1.

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 8.1 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 5.74 (ddt, J = 17.1, 10.4, 6.7 Hz, 1H), 5.02 (d, J = 7.8 Hz, 1H), 4.98 (s, 1H), 3.63 (br, 2H), 3.36 (s, 3H), 2.40 (s, 3H), 2.20 (q, J = 7.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.7, 142.7, 137.6, 135.2, 133.5, 129.8, 129.0, 127.6, 126.5, 120.6, 116.8, 111.7, 54.9, 49.3, 33.5, 21.5.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₈H₂₂NO₃S⁺ 332.1315; found 332.1317.



***N*-(but-3-en-1-yl)-*N*-(2,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (**4c**)**

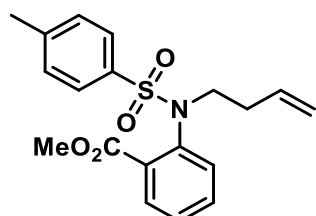
Colorless oil.

Compound **4c** was purified by flash chromatography eluted with PE/EA = 10:1.

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.85 – 6.81 (m, 2H), 6.70 (d, J = 8.5 Hz, 1H), 5.74 (ddt, J = 17.1, 10.3, 6.7 Hz, 1H), 5.05 – 5.01 (m, 1H), 4.99 (s, 1H), 3.74 (s, 3H), 3.63 (br, 2H), 3.32 (s, 3H), 2.40 (s, 3H), 2.20 (q, J = 7.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 153.1, 151.0, 142.8, 137.5, 135.2, 129.0, 127.6, 127.0, 118.9, 116.8, 115.0, 112.2, 55.8, 55.3, 49.3, 33.5, 21.5.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₉H₂₄NO₄S⁺ 362.1421; found 362.1419.



Methyl 2-((*N*-(but-3-en-1-yl)-4-methylphenyl)sulfonamido)benzoate (4f**)**

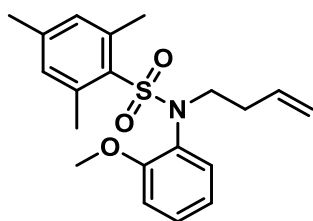
Colorless oil.

Compound **4f** was purified by flash chromatography eluted with PE/EA = 10:1.

¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, $J = 7.4, 2.0$ Hz, 1H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.44 – 7.38 (m, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 6.96 (dd, $J = 7.6, 1.4$ Hz, 1H), 5.73 (ddt, $J = 17.1, 10.3, 6.7$ Hz, 1H), 5.05 – 4.97 (m, 2H), 3.79 (s, 3H), 3.71 (br, 2H), 2.41 (s, 3H), 2.41 – 2.25 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 166.7, 143.3, 138.2, 136.5, 134.9, 132.9, 132.2, 131.5, 130.4, 129.5, 128.3, 127.6, 117.0, 52.3, 51.3, 33.3, 21.6.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₉H₂₂NO₄S⁺ 360.1264; found 360.1262.



***N*-(but-3-en-1-yl)-*N*-(2-methoxyphenyl)-2,4,6-trimethylbenzenesulfonamide (4m)**

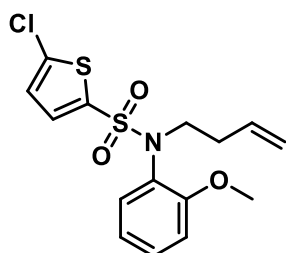
White solid.

Compound **4m** was purified by flash chromatography eluted with PE/EA = 10:1.

¹H NMR (400 MHz, CDCl₃) δ 7.44 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.26 – 7.20 (m, 1H), 6.91 (td, $J = 7.6, 1.1$ Hz, 1H), 6.80 (s, 2H), 6.70 (d, $J = 8.3$ Hz, 1H), 5.78 (ddt, $J = 17.1, 10.4, 6.8$ Hz, 1H), 5.08 – 5.00 (m, 2H), 3.82 (br, 2H), 3.35 (s, 3H), 2.37 (s, 6H), 2.27 – 2.22 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) δ 157.3, 141.6, 140.5, 135.3, 134.3, 133.9, 131.2, 129.9, 125.9, 120.6, 116.9, 111.7, 54.9, 49.3, 33.5, 23.2, 21.0.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₀H₂₆NO₃S⁺ 360.1628; found 360.1625.



***N*-(but-3-en-1-yl)-5-chloro-*N*-(2-methoxyphenyl)thiophene-2-sulfonamide (4n)**

Colorless oil.

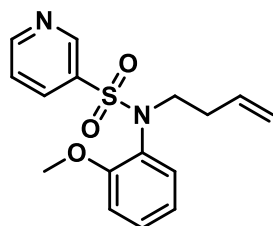
Compound **4n** was purified by flash chromatography eluted with PE/EA = 10:1.

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.27 (m, 2H), 7.16 (d, $J = 4.0$ Hz, 1H), 6.96 (td, $J = 7.6, 1.1$ Hz, 1H), 6.88 (d, $J = 4.0$ Hz, 1H), 6.85 (d, $J = 8.3$ Hz, 1H), 5.74 (ddt, $J =$

16.3, 11.0, 6.7 Hz, 1H), 5.07 – 5.03 (m, 1H), 5.01 (s, 1H), 3.69 (br, 2H), 3.54 (s, 3H), 2.23 (q, $J = 7.2$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.5, 139.2, 136.4, 134.9, 133.6, 131.1, 130.3, 126.4, 125.8, 120.9, 117.1, 111.8, 55.1, 49.6, 33.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{ClNO}_3\text{S}_2^+$ 358.0333; found 358.0337.



N-(but-3-en-1-yl)-*N*-(2-methoxyphenyl)pyridine-3-sulfonamide (**4o**)

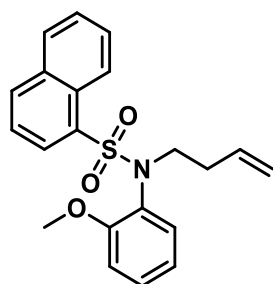
Yellow oil liquid.

Compound **4o** was purified by flash chromatography eluted with PE/EA = 8:1.

^1H NMR (400 MHz, CDCl_3) δ 8.85 (d, $J = 1.9$ Hz, 1H), 8.74 (dd, $J = 4.9, 1.6$ Hz, 1H), 7.93 (dt, $J = 8.0, 1.9$ Hz, 1H), 7.41 – 7.30 (m, 3H), 6.97 (td, $J = 7.6, 1.2$ Hz, 1H), 6.78 (dd, $J = 8.3, 1.0$ Hz, 1H), 5.75 (ddt, $J = 18.1, 9.6, 6.7$ Hz, 1H), 5.07 – 5.01 (m, 2H), 3.68 (br, 2H), 3.32 (s, 3H), 2.23 (q, $J = 7.2$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.0, 152.5, 148.3, 137.0, 135.0, 134.7, 133.9, 130.3, 125.4, 123.1, 120.9, 117.1, 111.7, 54.8, 49.3, 33.4.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_3\text{S}^+$ 319.1111; found 319.1106.



N-(but-3-en-1-yl)-*N*-(2-methoxyphenyl)naphthalene-1-sulfonamide (**4p**)

Yellow oil liquid.

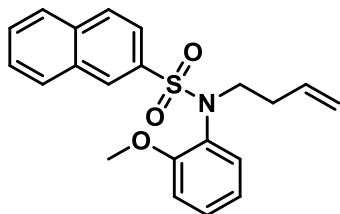
Compound **4p** was purified by flash chromatography eluted with PE/EA = 10:1.

^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 8.7$ Hz, 1H), 8.08 (dd, $J = 7.4, 1.1$ Hz, 1H), 7.93 (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.46 – 7.32 (m, 4H), 7.20 (td, $J = 8.2, 1.7$ Hz, 1H), 6.91 (td, $J = 7.6, 1.2$ Hz, 1H), 6.47 (dd, $J = 8.3, 1.0$ Hz, 1H), 5.72 (ddt, $J = 17.0, 10.2, 6.7$ Hz, 1H), 5.04 – 4.94 (m, 2H), 3.71 (br, 2H), 2.68 (s, 3H), 2.21 (q, $J =$

7.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.7, 136.0, 135.0, 134.0, 133.9, 133.5, 129.8, 129.6, 129.1, 128.2, 127.0, 126.3, 125.8, 125.7, 123.8, 120.2, 116.7, 111.2, 54.0, 49.0, 33.4.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₁H₂₂NO₃S⁺ 368.1315; found 368.1311.



***N*-(but-3-en-1-yl)-*N*-(2-methoxyphenyl)naphthalene-2-sulfonamide (4q)**

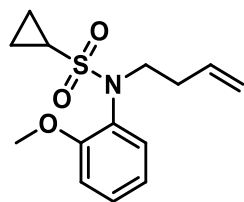
Yellow oil liquid.

Compound **4q** was purified by flash chromatography eluted with PE/EA = 10:1.

¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.16 (m, 1H), 7.88 – 7.81 (m, 3H), 7.68 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.33 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.96 – 6.89 (m, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 5.76 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.07 – 4.95 (m, 2H), 3.71 (br, 2H), 3.07 (s, 3H), 2.23 (q, *J* = 7.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.5, 137.3, 135.0, 134.5, 133.6, 131.9, 129.9, 129.0, 128.4, 128.3, 128.2, 127.7, 127.2, 126.2, 123.3, 120.5, 116.7, 111.6, 54.6, 49.3, 33.4.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₁H₂₂NO₃S⁺ 368.1315; found 368.1317.



***N*-(but-3-en-1-yl)-*N*-(2-methoxyphenyl)cyclopropanesulfonamide (4r)**

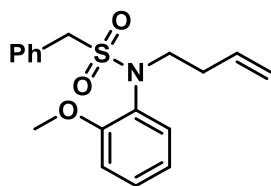
Colorless oil.

Compound **4r** was purified by flash chromatography eluted with PE/EA = 10:1.

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.29 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 2H), 5.76 (ddt, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.04 (d, *J* = 8.9 Hz, 1H), 5.01 (s, 1H), 3.87 (s, 3H), 3.71 (br, 2H), 2.49 (ddd, *J* = 12.9, 8.0, 4.9 Hz, 1H), 2.21 (q, *J* = 7.2 Hz, 2H), 1.09 – 1.00 (m, 2H), 0.88 (d, *J* = 7.7 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 156.8, 135.2, 133.8, 129.9, 127.1, 120.9, 116.9, 111.7, 55.5, 49.5, 33.7, 30.0, 5.2.

HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{14}H_{20}NO_3S^+$ 282.1158; found 282.1160.



***N*-(but-3-en-1-yl)-*N*-(2-methoxyphenyl)-1-phenylmethanesulfonamide (4s)**

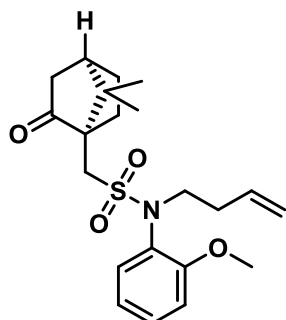
Yellow oil liquid.

Compound **4s** was purified by flash chromatography eluted with PE/EA = 10:1.

1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.35 – 7.30 (m, 4H), 7.25 (dd, J = 7.7, 1.7 Hz, 1H), 6.97 – 6.91 (m, 2H), 5.74 – 5.60 (m, 1H), 5.01 – 4.92 (m, 2H), 4.26 (s, 2H), 3.86 (s, 3H), 3.58 (t, J = 7.4 Hz, 2H), 2.14 (q, J = 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 134.8, 133.7, 130.9, 129.9, 129.4, 128.5, 128.3, 126.4, 120.8, 116.7, 111.9, 58.2, 55.4, 49.5, 33.4.

HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{18}H_{22}NO_3S^+$ 332.1315; found 332.1319.



***N*-(but-3-en-1-yl)-1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-(2-methoxyphenyl)methanesulfonamide (4t)**

White solid.

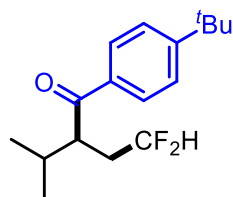
Compound **4t** was purified by flash chromatography eluted with PE/EA = 10:1.

1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 6.99 – 6.95 (m, 2H), 5.77 (ddt, J = 17.1, 10.4, 6.7 Hz, 1H), 5.08 – 5.03 (m, 1H), 5.02 (s, 1H), 3.89 (s, 3H), 3.84 – 3.63 (m, 2H), 3.60 (d, J = 14.9 Hz, 1H), 2.97 (d, J = 14.9 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.36 (dt, J = 18.4, 3.9 Hz, 1H), 2.22 (q, J = 7.1 Hz, 2H), 2.07 – 1.98 (m, 2H), 1.91 (d, J = 18.4 Hz, 1H), 1.61 – 1.55 (m, 1H), 1.40 – 1.35 (m, 1H), 1.12 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.6, 156.3, 135.1, 134.2, 130.0, 126.7, 121.0, 116.9, 112.0, 58.6, 55.4, 49.2, 48.5, 47.6, 43.0, 42.7, 33.7, 26.9, 25.2, 20.3, 19.8.

HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{21}H_{30}NO_4S^+$ 392.1890; found 392.1894.

4.2 Characterization data of products



1-(4-(tert-butyl)phenyl)-4,4-difluoro-2-isopropylbutan-1-one (3a)

Colorless liquid.

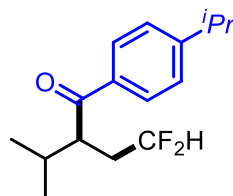
Compound **3a** was purified by PTLC with PE/EA = 35:1, 69% yield (38.9 mg) following the procedure A₁.

1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 5.90 - 5.60 (m, 1H), 3.57 - 3.48 (m, 1H), 2.61 - 2.43 (m, 1H), 2.16 - 2.05 (m, 1H), 2.02 - 1.89 (m, 1H), 1.35 (s, 9H), 1.01 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 157.2, 134.5, 128.4, 125.9, 116.7 (t, J = 238.8 Hz), 45.7 (dd, J = 6.6, 2.2 Hz), 35.3, 31.7 (t, J = 21.1 Hz), 31.2, 30.7, 21.2, 18.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.25 - -117.42 (m).

HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{17}H_{25}F_2O^+$ 283.1868; found 283.1870.



4,4-difluoro-2-isopropyl-1-(4-isopropylphenyl)butan-1-one (3b)

Colorless liquid.

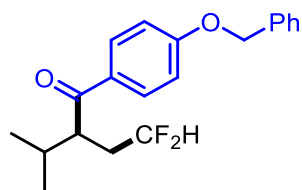
Compound **3b** was purified by PTLC with PE/EA = 35:1, 70% yield (37.5 mg) following the procedure A₁.

1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.91 - 5.59 (m, 1H), 3.55 - 3.49 (m, 1H), 2.97 (p, J = 6.9 Hz, 1H), 2.60 - 2.43 (m, 1H), 2.16 - 2.06 (m, 1H), 2.02 - 1.89 (m, 1H), 1.28 (d, J = 6.9 Hz, 6H), 1.01 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 154.9, 135.0, 128.7, 127.0, 116.7 (t, J = 238.8 Hz), 45.7 (dd, J = 6.6, 2.2 Hz), 34.4, 31.7 (t, J = 21.2 Hz), 30.7, 23.8, 21.2, 18.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.26 - -117.42 (m).

HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{16}H_{23}F_2O^+$ 269.1711; found 269.1714.



1-(4-(benzyloxy)phenyl)-4,4-difluoro-2-isopropylbutan-1-one (3c)

Colorless liquid.

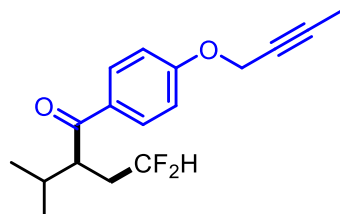
Compound **3c** was purified by PTLC with PE/EA = 35:1, 61% yield (40.5 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.8 Hz, 2H), 7.46 – 7.31 (m, 5H), 7.02 (d, J = 8.8 Hz, 2H), 5.90 – 5.58 (m, 1H), 5.13 (s, 2H), 3.56 – 3.38 (m, 1H), 2.60 – 2.41 (m, 1H), 2.12 – 1.89 (m, 2H), 0.99 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 200.8, 163.0, 136.2, 130.8, 130.3, 128.9, 128.4, 127.6, 116.7 (t, J = 238.8 Hz), 114.9, 70.3, 45.6 – 45.3 (m), 31.9 (t, J = 21.1 Hz), 30.9, 21.2, 18.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.29 – -117.39 (m).

HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{20}H_{23}F_2O_2^+$ 333.1661; found 333.1657.



1-(4-(but-2-yn-1-yloxy)phenyl)-4,4-difluoro-2-isopropylbutan-1-one (3d)

Colorless liquid.

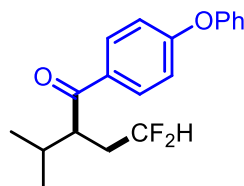
Compound **3d** was purified by PTLC with PE/EA = 35:1, 64% yield (37.6 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 5.94 – 5.56 (m, 1H), 4.77 – 4.66 (m, 2H), 3.55 – 3.42 (m, 1H), 2.60 – 2.41 (m, 1H), 2.15 – 1.90 (m, 2H), 1.87 (t, J = 2.2 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 200.8, 162.0, 130.7, 130.6, 116.7 (t, J = 239.4 Hz), 114.9, 84.7, 73.4, 56.7, 45.6 – 45.5 (m), 31.9 (t, J = 21.2 Hz), 30.9, 21.2, 18.6, 3.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.32 – -117.39 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₇H₂₁F₂O₂⁺ 295.1504; found 295.1502.



4,4-difluoro-2-isopropyl-1-(4-phenoxyphenyl)butan-1-one (3e)

Colorless liquid.

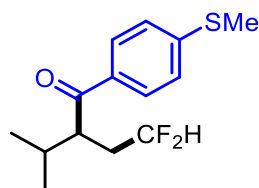
Compound **3e** was purified by PTLC with PE/EA = 35:1, 73% yield (46.4 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.94 – 5.58 (m, 1H), 3.53 – 3.44 (m, 1H), 2.60 – 2.42 (m, 1H), 2.13 – 1.90 (m, 2H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 200.9, 162.4, 155.5, 131.7, 130.7, 130.2, 124.9, 120.4, 117.5, 116.7 (t, *J* = 238.8 Hz), 45.6 (dd, *J* = 6.4, 2.2 Hz), 31.9 (t, *J* = 21.1 Hz), 30.9, 21.2, 18.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.41 – -117.34 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₉H₂₁F₂O₂⁺ 319.1504; found 319.1507.



4,4-difluoro-2-isopropyl-1-(4-(methylthio)phenyl)butan-1-one (3f)

Colorless liquid.

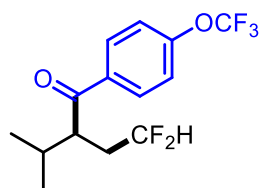
Compound **3f** was purified by PTLC with PE/EA = 35:1, 81% yield (44.1 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 5.91 – 5.59 (m, 1H), 3.51 – 3.45 (m, 1H), 2.57 – 2.45 (m, 4H), 2.12 – 2.03 (m, 1H), 2.02 – 1.90 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.3, 146.4, 133.4, 128.8, 125.2, 116.7 (t, *J* = 238.9 Hz), 45.6 (dd, *J* = 6.4, 2.3 Hz), 31.9 (t, *J* = 21.1 Hz), 30.9, 21.1, 18.6, 14.8.

^{19}F NMR (376 MHz, CDCl_3) δ -113.42 – -117.31 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{19}\text{F}_2\text{OS}^+$ 273.1119; found 273.1123.



4,4-difluoro-2-isopropyl-1-(4-(trifluoromethoxy)phenyl)butan-1-one (3g)

Colorless liquid.

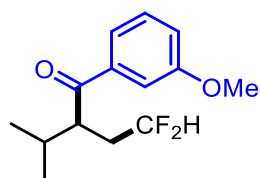
Compound **3g** was purified by PTLC with PE/EA = 35:1, 42% yield (26.0 mg) following the procedure A₁.

^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.94 – 5.62 (m, 1H), 3.55 – 3.48 (m, 1H), 2.61 – 2.45 (m, 1H), 2.13 – 2.04 (m, 1H), 2.03 – 1.91 (m, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 200.9, 152.9, 135.4, 130.5, 120.7, 120.4 (q, J = 260.6 Hz), 116.5 (t, J = 238.9 Hz), 45.8 (dd, J = 6.0, 2.5 Hz), 31.8 (t, J = 21.1 Hz), 30.8, 21.1, 18.5.

^{19}F NMR (376 MHz, CDCl_3) δ -57.58 (s), -113.82 – -117.21 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{F}_5\text{O}_2^+$ 311.1065; found 311.1070.



4,4-difluoro-2-isopropyl-1-(3-methoxyphenyl)butan-1-one (3i)

Colorless liquid.

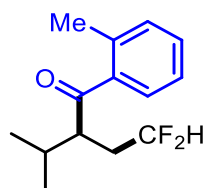
Compound **3i** was purified by PTLC with PE/EA = 35:1, 56% yield (28.7 mg) following the procedure A₁.

^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 7.6 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.13 (dd, J = 8.0, 2.3 Hz, 1H), 5.95 – 5.59 (m, 1H), 3.87 (s, 3H), 3.58 – 3.43 (m, 1H), 2.63 – 2.42 (m, 1H), 2.15 – 1.90 (m, 2H), 1.01 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 202.2, 160.1, 138.5, 129.9, 120.9, 119.7, 116.6 (t, J = 238.9 Hz), 112.8, 55.6, 46.1 – 45.8 (m), 31.7 (t, J = 20.2 Hz), 30.8, 21.1, 18.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.42 – -117.29 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₄H₁₉F₂O₂⁺ 257.1348; found 257.1349.



4,4-difluoro-2-isopropyl-1-(*o*-tolyl)butan-1-one (3j)

Colorless liquid.

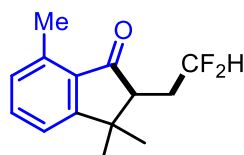
Compound **3j** was purified by PTLC with PE/EA = 35:1, 54% yield (25.9 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.02 – 5.70 (m, 1H), 3.49 – 3.37 (m, 1H), 2.62 – 2.43 (m, 4H), 2.07 – 1.84 (m, 2H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 206.0, 138.4, 132.2, 131.4, 128.2, 125.9, 116.9 (t, *J* = 238.7 Hz), 48.7 (dd, *J* = 6.4, 2.4 Hz), 30.8 (t, *J* = 21.2 Hz), 30.1, 21.2, 21.0, 18.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.23 – -117.60 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₄H₁₉F₂O⁺ 241.1398; found 241.1395.



2-(2,2-difluoroethyl)-3,3,7-trimethyl-2,3-dihydro-1H-inden-1-one (3k)

Colorless liquid.

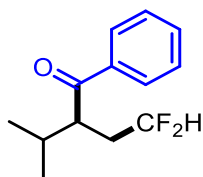
Compound **3k** was purified by PTLC with PE/EA = 35:1, 35% yield (16.7 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.40 (tdd, *J* = 57.5, 6.8, 2.8 Hz, 1H), 2.64 – 2.55 (m, 4H), 2.41 – 2.26 (m, 1H), 2.07 – 1.92 (m, 1H), 1.50 (s, 3H), 1.13 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 206.6, 163.1, 138.7, 134.5, 131.5, 129.6, 120.7, 116.7 (t, *J* = 238.8 Hz), 54.3 (dd, *J* = 6.8, 2.3 Hz), 41.2, 30.9 (t, *J* = 22.1 Hz), 28.0, 26.9, 18.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.04 – -118.98 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₄H₁₇F₂O⁺ 239.1242; found 239.1247.



4,4-difluoro-2-isopropyl-1-phenylbutan-1-one (3l)

Colorless liquid.

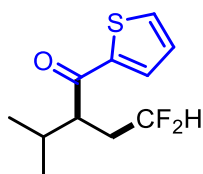
Compound **3l** was purified by PTLC with PE/EA = 35:1, 41% yield (18.5 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 5.96 – 5.59 (m, 1H), 3.68 – 3.42 (m, 1H), 2.64 – 2.44 (m, 1H), 2.16 – 1.89 (m, 2H), 1.01 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 202.4, 137.2, 133.4, 128.9, 128.4, 116.7 (t, J = 238.9 Hz), 45.8 (dd, J = 6.4, 2.3 Hz), 31.6 (t, J = 21.2 Hz), 30.7, 21.2, 18.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.40 – -117.40 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₃H₁₇F₂O⁺ 227.1242; found 227.1243.



4,4-difluoro-2-isopropyl-1-(thiophen-2-yl)butan-1-one (3m)

Colorless liquid.

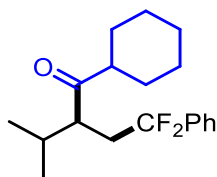
Compound **3m** was purified by PTLC with PE/EA = 35:1, 39% yield (18.1 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 3.8 Hz, 1H), 7.68 (d, J = 4.9 Hz, 1H), 7.17 – 7.13 (m, 1H), 5.92 – 5.61 (m, 1H), 3.35 – 3.28 (m, 1H), 2.54 – 2.42 (m, 1H), 2.17 – 2.09 (m, 1H), 2.04 – 1.94 (m, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.1, 144.8, 134.5, 132.3, 128.4, 116.4 (t, J = 239.0 Hz), 48.0 (dd, J = 6.3, 2.3 Hz), 32.6 (t, J = 21.3 Hz), 31.4, 21.1, 19.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.72 – -117.24 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₁H₁₅F₂OS⁺ 233.0806; found 233.0805.



1-cyclohexyl-4,4-difluoro-2-isopropyl-4-phenylbutan-1-one (3n)

Colorless liquid.

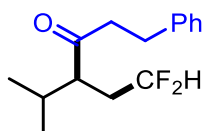
Compound **3n** was purified by PTLC with PE/EA = 35:1, 53% yield (32.6 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.39 (m, 5H), 2.97 (dd, J = 9.5, 3.7 Hz, 1H), 2.88 – 2.70 (m, 1H), 2.50 – 2.40 (m, 1H), 2.03 – 1.90 (m, 2H), 1.84 – 1.66 (m, 5H), 1.31 – 1.13 (m, 5H), 0.99 (d, J = 6.8 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 214.4, 137.5 (t, J = 26.5 Hz), 129.9, 128.5, 125.1 (t, J = 6.2 Hz), 122.8 (t, J = 243.4 Hz), 50.8, 49.5, 35.1 (t, J = 26.9 Hz), 29.4, 28.0, 26.3, 26.0, 25.7, 21.4, 17.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -94.33 – -97.22 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₉H₂₇F₂O⁺ 309.2024; found 309.2028.



6,6-difluoro-4-isopropyl-1,6-diphenylhexan-3-one (3o)

Colorless liquid.

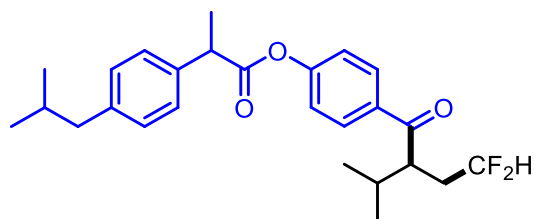
Compound **3o** was purified by PTLC with PE/EA = 35:1, 61% yield (31.0 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.31 - 7.25 (m, 2H), 7.23 - 7.14 (m, 3H), 5.69 (tdd, J = 57.1, 5.4, 3.2 Hz, 1H), 2.92 - 2.72 (m, 4H), 2.64 - 2.55 (m, 1H), 2.39 - 2.22 (m, 1H), 2.02 - 1.92 (m, 1H), 1.86 - 1.72 (m, 1H), 0.94 (d, J = 6.8 Hz, 3H), 0.78 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 211.6, 141.1, 128.6, 128.5, 126.3, 116.5 (t, J = 238.9 Hz), 51.4 (dd, J = 5.0, 3.0 Hz), 45.0, 31.5 (t, J = 21.2 Hz), 29.8, 29.7, 21.0, 18.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.93 - -117.03 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₅H₂₁F₂O⁺ 255.1555; found 255.1558.



4-(4,4-difluoro-2-isopropylbutanoyl)phenyl 2-(4-isobutylphenyl)propanoate (**3p**)

Colorless liquid.

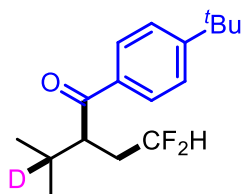
Compound **3p** was purified by PTLC with PE/EA = 35:1, 27% yield (23.2 mg) following the procedure A₁.

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.16 - 7.10 (m, 4H), 5.90 - 5.60 (m, 1H), 3.95 (q, J = 7.1 Hz, 1H), 3.52 - 3.44 (m, 1H), 2.69 - 2.33 (m, 4H), 2.11 - 1.80 (m, 4H), 1.61 (d, J = 7.1 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H), 0.82 (d, J = 6.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.1, 172.8, 154.8, 141.2, 136.9, 134.5, 130.0, 129.7, 127.3, 121.9, 116.6 (t, J = 238.8 Hz), 45.8 - 45.7 (m), 45.4, 45.2, 31.6 (t, J = 21.5 Hz), 30.7, 30.4, 29.9, 22.5, 21.1, 18.6, 18.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -113.53 - -117.34 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₆H₃₃F₂O₃⁺ 431.2392; found 431.2391.



1-(4-(tert-butyl)phenyl)-2-(2,2-difluoroethyl)-3-methylbutan-1-one-3-d (**3a-D**)

Colorless liquid.

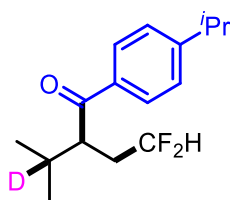
Compound **3a-D** was purified by PTLC with PE/EA = 35:1, 59% yield (82% D, 33.4 mg) following the procedure A₂.

¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 5.75 (tdd, J = 58.9, 6.4, 2.7 Hz, 1H), 3.52 (d, J = 10.4 Hz, 1H), 2.60 - 2.44 (m, 1H), 2.16 - 2.08 (m, 0H), 2.02 - 1.89 (m, 1H), 1.35 (s, 9H), 1.01 (d, J = 5.7 Hz, 3H), 0.84 (d, J = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 201.9, 157.2, 134.4, 128.4, 125.9, 116.8 (t, J = 238.7 Hz), 45.6 (dd, J = 6.7, 1.8 Hz), 35.3, 31.5 (t, J = 21.3 Hz), 31.2, 30.7 (t, J = 24.5 Hz, C-D), 21.1, 18.2.

^{19}F NMR (376 MHz, CDCl_3) δ -113.23 – -117.47 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{24}\text{DF}_2\text{O}^+$ 284.1931; found 284.1930.



2-(2,2-difluoroethyl)-1-(4-isopropylphenyl)-3-methylbutan-1-one-3-d (3b-D)

Colorless liquid.

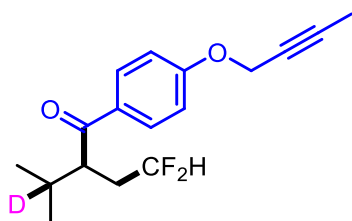
Compound **3b-D** was purified by PTLC with PE/EA = 35:1, 61% yield (80% D, 32.8 mg) following the procedure A₂.

^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.92 – 5.58 (m, 1H), 3.51 (d, J = 10.8 Hz, 1H), 2.97 (hept, J = 6.9 Hz, 1H), 2.60 – 2.43 (m, 1H), 2.15 – 2.07 (m, 0H), 2.02 – 1.89 (m, 1H), 1.28 (d, J = 6.9 Hz, 6H), 1.01 (d, J = 5.7 Hz, 3H), 0.84 (d, J = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 201.9, 154.9, 135.0, 128.7, 127.0, 116.8 (t, J = 238.9 Hz), 45.7 (dd, J = 6.8, 2.1 Hz), 34.4, 31.6 (t, J = 21.0 Hz), 30.3 (t, J = 19.6 Hz, C-D), 23.8, 21.1, 18.3.

^{19}F NMR (376 MHz, CDCl_3) δ -113.20 – -117.39 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{22}\text{DF}_2\text{O}^+$ 270.1774; found 270.1772.



1-(4-(but-2-yn-1-yloxy)phenyl)-2-(2,2-difluoroethyl)-3-methylbutan-1-one-3-d (3d-D)

Colorless liquid.

Compound **3d-D** was purified by PTLC with PE/EA = 35:1, 52% yield (77% D, 30.7 mg) following the procedure A₂.

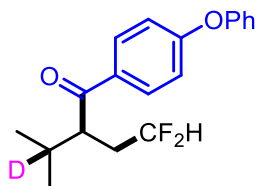
^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 8.9 Hz, 2H), 5.96 – 5.53 (m, 1H), 4.72 (q, J = 2.2 Hz, 2H), 3.48 (d, J = 10.0 Hz, 1H), 2.61 – 2.42 (m, 1H), 2.14 – 2.06 (m, 0H), 2.04 – 1.90 (m, 1H), 1.87 (t, J = 2.3 Hz, 3H), 1.00 (d, J = 5.7

Hz, 3H), 0.85 (d, $J = 7.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 200.8, 162.0, 130.7, 130.5, 116.7 (t, $J = 239.4$ Hz), 114.9, 84.7, 73.4, 56.7, 45.5 - 45.4 (m), 31.8 (t, $J = 21.1$ Hz), 30.4 (t, $J = 19.6$ Hz, C-D), 21.1, 18.4, 3.9.

^{19}F NMR (376 MHz, CDCl_3) δ -113.30 – -117.45 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{DF}_2\text{O}_2^+$ 296.1567; found 296.1568.



2-(2,2-difluoroethyl)-3-methyl-1-(4-phenoxyphenyl)butan-1-one-3-d (3e-D)

Colorless liquid.

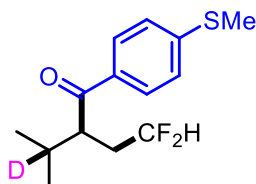
Compound **3e-D** was purified by PTLC with PE/EA = 35:1, 60% yield (82% D, 38.3 mg) following the procedure A₂.

^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.8$ Hz, 2H), 7.40 (t, $J = 7.9$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.08 (d, $J = 7.7$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 2H), 5.91 – 5.60 (m, 1H), 3.51 – 3.44 (m, 1H), 2.59 – 2.43 (m, 1H), 2.13 – 2.06 (m, 0H), 2.03 – 1.90 (m, 1H), 1.00 (d, $J = 5.8$ Hz, 3H), 0.86 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 200.9, 162.4, 155.5, 131.7, 130.7, 130.2, 124.9, 120.5, 117.5, 116.7 (t, $J = 238.9$ Hz), 45.86 – 44.98 (m), 31.9 (t, $J = 21.1$ Hz), 30.4 (t, $J = 19.6$ Hz, C-D), 21.1, 18.4.

^{19}F NMR (376 MHz, CDCl_3) δ -108.13 – -117.36 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{DF}_2\text{O}_2^+$ 320.1567; found 320.1567.



2-(2,2-difluoroethyl)-3-methyl-1-(4-(methylthio)phenyl)butan-1-one-3-d (3f-D)

Colorless liquid.

Compound **3f-D** was purified by PTLC with PE/EA = 35:1, 68% yield (83% D, 37.1 mg) following the procedure A₂.

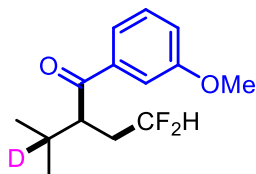
^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 5.91

– 5.60 (m, 1H), 3.48 (d, $J = 10.4$ Hz, 1H), 2.57 – 2.47 (m, 4H), 2.11 – 2.05 (m, 0H), 2.03 – 1.91 (m, 1H), 0.99 (d, $J = 5.7$ Hz, 3H), 0.85 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 201.3, 146.4, 133.4, 128.9, 125.2, 116.7 (t, $J = 238.9$ Hz), 46.0 – 44.9 (m), 31.9 (t, $J = 21.2$ Hz), 30.5 (t, $J = 19.6$ Hz, C-D), 21.0, 18.4, 14.9.

^{19}F NMR (376 MHz, CDCl_3) δ -113.29 – -117.22 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{DF}_2\text{OS}^+$ 274.1182; found 274.1187.



2-(2,2-difluoroethyl)-1-(3-methoxyphenyl)-3-methylbutan-1-one-3-d (3i-D)

Colorless liquid.

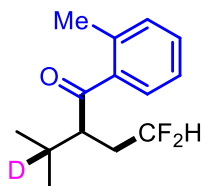
Compound **3i-D** was purified by PTLC with PE/EA = 35:1, 40% yield (81% D, 20.6 mg) following the procedure A₂.

^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 7.6$ Hz, 1H), 7.49 – 7.43 (m, 1H), 7.39 (t, $J = 7.9$ Hz, 1H), 7.13 (dd, $J = 8.2, 2.1$ Hz, 1H), 5.93 – 5.61 (m, 1H), 3.87 (s, 3H), 3.57 – 3.45 (m, 1H), 2.61 – 2.44 (m, 1H), 2.14 – 2.06 (m, 0H), 2.04 – 1.90 (m, 1H), 1.01 (d, $J = 5.8$ Hz, 3H), 0.84 (d, $J = 7.5$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 202.2, 160.1, 138.6, 129.9, 120.9, 119.7, 116.7 (t, $J = 238.9$ Hz), 112.8, 55.6, 45.9 (dd, $J = 6.5, 2.3$ Hz), 31.7 (t, $J = 21.2$ Hz), 30.3 (t, $J = 19.6$ Hz, C-D), 21.0, 18.3.

^{19}F NMR (376 MHz, CDCl_3) δ -113.42 – -117.31 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{DF}_2\text{O}_2^+$ 258.1410; found 258.1412.



2-(2,2-difluoroethyl)-3-methyl-1-(o-tolyl)butan-1-one-3-d (3j-D)

Colorless liquid.

Compound **3j-D** was purified by PTLC with PE/EA = 35:1, 43% yield (80% D, 20.7 mg) following the procedure A₂.

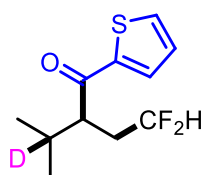
^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.7$ Hz, 1H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.27

(t, $J = 7.7$ Hz, 2H), 6.09 – 5.66 (m, 1H), 3.42 (d, $J = 10.7$ Hz, 1H), 2.72 – 2.32 (m, 4H), 2.08 – 1.99 (m, 0H), 1.97 – 1.83 (m, 1H), 0.98 (d, $J = 6.2$ Hz, 3H), 0.82 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 206.0, 138.4, 132.2, 131.4, 128.2, 125.9, 116.9 (t, $J = 238.7$ Hz), 48.7 - 48.5 (m), 30.8 (t, $J = 21.2$ Hz), 29.6 (t, $J = 19.6$ Hz, C-D), 21.1, 20.6, 18.1.

^{19}F NMR (376 MHz, CDCl_3) δ -113.23 – -117.62 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{DF}_2\text{O}^+$ 242.1461; found 242.1457.



2-(2,2-difluoroethyl)-3-methyl-1-(thiophen-2-yl)butan-1-one-3-d (3m-D)

Colorless liquid.

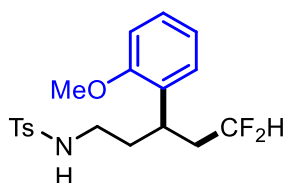
Compound **3m-D** was purified by PTLC with PE/EA = 35:1, 26% yield (76% D, 12.1 mg) following the procedure A₂.

^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 3.8$ Hz, 1H), 7.68 (d, $J = 4.9$ Hz, 1H), 7.15 (t, $J = 4.4$ Hz, 1H), 5.92 – 5.61 (m, 1H), 3.33 – 3.28 (m, 1H), 2.56 – 2.41 (m, 1H), 2.17 – 2.09 (m, 0H), 2.06 – 1.95 (m, 1H), 1.01 (d, $J = 6.0$ Hz, 3H), 0.93 (d, $J = 7.3$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.1, 144.8, 134.6, 132.3, 128.5, 116.5 (t, $J = 239.3$ Hz), 48.0 - 47.8 (m), 32.77 – 32.18 (m), 31.78 – 31.35 (m), 21.0, 19.0.

^{19}F NMR (376 MHz, CDCl_3) δ -113.72 – -117.30 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{DF}_2\text{OS}^+$ 234.0869; found 234.0871.



N-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)-4-methylbenzenesulfonamide (5a)

Yellow oil liquid.

Compound **5a** was purified by PTLC with PE/EA = 3:1, 71% yield (27.2 mg) following the procedure B.

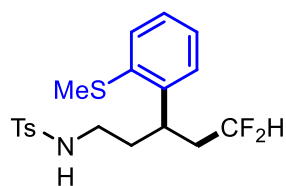
^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H), 7.23

- 7.18 (m, 1H), 7.03 - 7.01 (m, 1H), 6.91 (td, $J = 7.5, 0.8$ Hz, 1H), 6.85 (d, $J = 8.2$ Hz, 1H), 5.46 (tdd, $J = 56.8, 6.5, 3.2$ Hz, 1H), 4.85 - 4.56 (m, 1H), 3.81 (s, 3H), 3.28 - 3.21 (m, 1H), 2.93 - 2.85 (m, 1H), 2.67 - 2.57 (m, 1H), 2.41 (s, 3H), 2.26 - 2.10 (m, 1H), 2.06 - 1.94 (m, 1H), 1.87 - 1.70 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 157.2, 143.4, 137.2, 129.8, 129.3, 128.3, 128.0, 127.1, 121.5, 116.7 (t, $J = 238.9$ Hz), 111.3, 55.7, 41.1, 39.6 (t, $J = 20.8$ Hz), 35.3, 30.6, 21.6.

^{19}F NMR (376 MHz, CDCl_3) δ -114.13 – -117.23 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{F}_2\text{NO}_3\text{S}^+$ 384.1439; found 384.1441.



***N*-(5,5-difluoro-3-(2-(methylthio)phenyl)pentyl)-4-methylbenzenesulfonamide (5b)**

Yellow oil liquid.

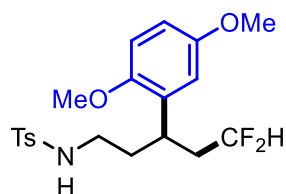
Compound **5b** was purified by PTLC with PE/EA = 3:1, 55% yield (21.9 mg) following the procedure B.

^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H), 7.25 – 7.18 (m, 2H), 7.18 – 7.13 (m, 1H), 7.07 (d, $J = 7.5$ Hz, 1H), 5.61 – 5.30 (m, 1H), 4.91 (br, 1H), 3.46 – 3.31 (m, 1H), 3.01 – 2.89 (m, 1H), 2.65 – 2.57 (m, 1H), 2.45 (s, 3H), 2.41 (s, 3H), 2.17 – 1.97 (m, 2H), 1.92 – 1.83 (m, 1H), 1.76 – 1.66 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.5, 139.6, 137.4, 129.8, 127.9, 127.1, 126.5, 126.1, 116.3 (t, $J = 239.4$ Hz), 40.8, 36.5, 32.4, 29.8, 21.6, 16.3.

^{19}F NMR (376 MHz, CDCl_3) δ -113.84 – -116.21 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{F}_2\text{NO}_2\text{S}_2^+$ 400.1211; found 400.1215.



***N*-(3-(2,5-dimethoxyphenyl)-5,5-difluoropentyl)-4-methylbenzenesulfonamide (5c)**

Yellow oil liquid.

Compound **5c** was purified by PTLC with PE/EA = 3:1, 54% yield (22.3 mg) following

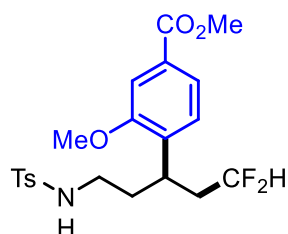
the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.2 Hz, 2H), 7.29 – 7.26 (m, 2H), 6.82 – 6.76 (m, 1H), 6.74 – 6.69 (m, 1H), 6.60 (d, J = 2.9 Hz, 1H), 5.47 (tdd, J = 56.8, 6.5, 3.2 Hz, 1H), 4.94 – 4.70 (m, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.28 – 3.17 (m, 1H), 2.96 – 2.85 (m, 1H), 2.65 – 2.55 (m, 1H), 2.41 (s, 3H), 2.23 – 2.09 (m, 1H), 2.06 – 1.91 (m, 1H), 1.87 – 1.77 (m, 1H), 1.74 – 1.67 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 154.2, 151.4, 143.4, 137.3, 130.7, 129.8, 127.1, 116.6 (t, J = 240.4 Hz), 114.4, 112.5, 112.0, 56.4, 55.7, 41.0, 39.6 (t, J = 20.9 Hz), 35.4, 30.5, 21.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.24 – -117.25 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₀H₂₆F₂NO₄S⁺ 414.1545; found 414.1548.



Methyl-4-(1,1-difluoro-5-((4-methylphenyl)sulfonamido)pentan-3-yl)-3-methoxybenzoate (5d)

Yellow oil liquid.

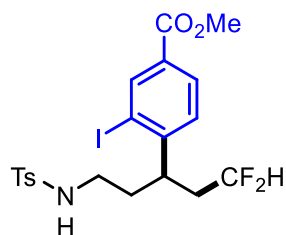
Compound **5d** was purified by PTLC with PE/EA = 3:1, 75% yield (33.1 mg) following the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.2 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.52 – 7.48 (m, 1H), 7.28 – 7.24 (m, 2H), 7.10 (d, J = 7.9 Hz, 1H), 5.64 – 5.34 (m, 1H), 4.73 (br, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 3.36 – 3.26 (m, 1H), 2.90 – 2.81 (m, 1H), 2.67 – 2.57 (m, 1H), 2.41 (s, 3H), 2.26 – 2.14 (m, 1H), 2.10 – 2.00 (m, 1H), 1.90 – 1.78 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 166.8, 157.2, 143.6, 137.0, 135.0, 130.2, 129.8, 128.2, 127.1, 122.7, 116.4 (t, J = 239.3 Hz), 111.9, 55.9, 52.4, 41.0, 39.2 (t, J = 21.0 Hz), 34.9, 31.1, 21.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.19 – -117.17 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₁H₂₆F₂NO₅S⁺ 442.1494; found 442.1493.



Methyl-4-(1,1-difluoro-5-((4-methylphenyl)sulfonamido)pentan-3-yl)-3-iodobenzoate (5e)

Yellow oil liquid.

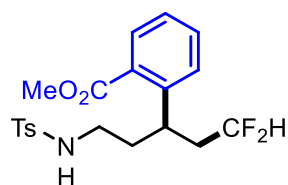
Compound **5e** was purified by PTLC with PE/EA = 3:1, 29% yield (15.6 mg) following the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 8.48 (s, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 8.2 Hz, 2H), 7.30 - 7.27 (m, 2H), 7.16 (d, J = 8.1 Hz, 1H), 5.71 - 5.39 (m, 1H), 4.55 (t, J = 6.2 Hz, 1H), 3.92 (s, 3H), 3.43 - 3.35 (m, 1H), 2.87 - 2.71 (m, 2H), 2.42 (s, 3H), 2.15 - 2.03 (m, 2H), 1.98 - 1.90 (m, 1H), 1.85 - 1.77 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 165.3, 149.6, 143.8, 141.2, 136.8, 130.7, 130.1, 129.9, 128.4, 127.2, 126.7, 115.7 (t, J = 240.0 Hz), 52.6, 41.1 (t, J = 5.0 Hz), 40.7, 36.5, 29.8, 21.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.33 - -114.75 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₀H₂₃F₂INO₄S⁺ 538.0355; found 538.0353.



Methyl-2-(1,1-difluoro-5-((4-methylphenyl)sulfonamido)pentan-3-yl)benzoate (5f)

Yellow oil liquid.

Compound **5f** was purified by PTLC with PE/EA = 3:1, 57% yield (23.4 mg) following the procedure B.

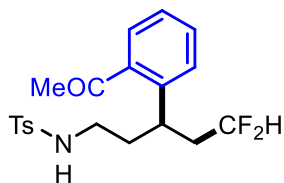
¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 8.2 Hz, 3H), 7.48 (t, J = 7.6 Hz, 1H), 7.29 - 7.22 (m, 4H), 5.98 (dd, J = 8.7, 3.5 Hz, 1H), 5.31 (tdd, J = 56.5, 6.3, 3.4 Hz, 1H), 3.95 (s, 3H), 3.82 - 3.72 (m, 1H), 3.09 - 3.00 (m, 1H), 2.56 - 2.46 (m, 1H), 2.39 (s, 3H), 2.06 - 1.86 (m, 3H), 1.79 - 1.73 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.4, 143.1, 142.4, 137.8, 132.5, 131.6, 130.1, 129.6, 127.1, 127.0, 126.9, 116.1 (t, J = 239.4 Hz), 53.0, 41.6 (t, J = 20.8 Hz), 40.4, 36.4, 31.2

- 31.1 (m), 21.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.75 – -117.68 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₀H₂₄F₂NO₄S⁺ 412.1389; found 412.1387.



***N*-(3-(2-acetylphenyl)-5,5-difluoropentyl)-4-methylbenzenesulfonamide (5g)**

Yellow oil liquid.

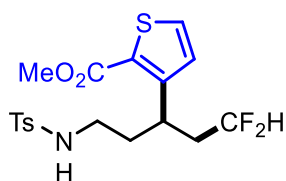
Compound **5g** was purified by PTLC with PE/EA = 3:1, 23% yield (9.1 mg) following the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 9.4 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.23 (d, *J* = 7.1 Hz, 2H), 6.36 (d, *J* = 8.8 Hz, 1H), 5.45 – 5.14 (m, 1H), 3.53 - 3.42 (m, 1H), 3.12 - 3.03 (m, 1H), 2.60 (s, 3H), 2.50 - 2.44 (m, 1H), 2.39 (s, 3H), 2.03 – 1.85 (m, 3H), 1.78 – 1.71 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 205.4, 143.0, 140.6, 140.3, 138.1, 132.0, 129.6, 128.1, 127.5, 127.0, 126.8, 116.2 (t, *J* = 239.4 Hz), 41.8 (t, *J* = 20.4 Hz), 40.2, 36.5, 30.6, 30.3, 21.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -115.29 – -117.72 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₀H₂₄F₂NO₃S⁺ 396.1439; found 396.1434.



Methyl-3-(1,1-difluoro-5-((4-methylphenyl)sulfonamido)pentan-3-yl)thiophene-2-carboxylate (5h)

Yellow oil liquid.

Compound **5h** was purified by PTLC with PE/EA = 3:1, 42% yield (17.5 mg) following the procedure B.

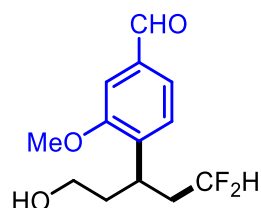
¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 5.2 Hz, 1H), 7.28 - 7.26 (m, 2H), 6.95 (d, *J* = 5.2 Hz, 1H), 5.59 – 5.30 (m, 2H), 4.09 - 4.01 (m, 1H), 3.90 (s, 3H), 3.08 - 2.99 (m, 1H), 2.56 - 2.47 (m, 1H), 2.42 (s, 3H), 2.09 – 1.85 (m, 3H),

1.68 - 1.62 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.6, 150.3, 143.4, 137.7, 132.2, 129.7, 127.9, 127.1, 127.0, 116.1 (t, $J = 239.7$ Hz), 52.6, 40.7, 40.5 (t, $J = 21.2$ Hz), 36.2, 29.8 - 29.7 (m), 21.6.

^{19}F NMR (376 MHz, CDCl_3) δ -114.04 – -117.02 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{F}_2\text{NO}_4\text{S}_2^+$ 418.0953; found 418.0952.



4-(1,1-difluoro-5-hydroxypentan-3-yl)-3-methoxybenzaldehyde (**5i**)

Yellow oil liquid.

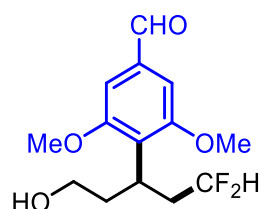
Compound **5i** was purified by PTLC with PE/EA = 3:1, 81% yield (20.9 mg) following the procedure B.

^1H NMR (400 MHz, CDCl_3) δ 9.96 (s, 1H), 7.49 - 7.45 (m, 1H), 7.41 (s, 1H), 7.35 (d, $J = 7.6$ Hz, 1H), 5.77 - 5.45 (m, 1H), 3.92 (s, 3H), 3.59 - 3.49 (m, 2H), 3.43 - 3.35 (m, 1H), 2.36 - 2.19 (m, 2H), 2.05 - 1.98 (m, 1H), 1.96 - 1.89 (m, 1H), 1.89 - 1.83 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 191.8, 158.1, 138.3, 136.5, 129.0, 124.8, 116.6 (t, $J = 240.4$ Hz), 109.4, 60.4, 55.9, 39.2 (t, $J = 20.8$ Hz), 37.9, 31.0 - 30.8 (m).

^{19}F NMR (376 MHz, CDCl_3) δ -114.13 – -117.11 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{17}\text{F}_2\text{O}_3^+$ 259.1140; found 259.1136.



4-(1,1-difluoro-5-hydroxypentan-3-yl)-3,5-dimethoxybenzaldehyde (**5j**)

Yellow oil liquid.

Compound **5j** was purified by PTLC with PE/EA = 3:1, 67% yield (19.3 mg) following the procedure B.

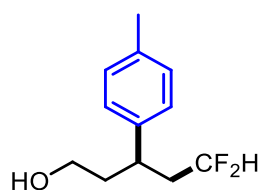
^1H NMR (400 MHz, CDCl_3) δ 9.92 (s, 1H), 7.09 (s, 2H), 5.58 (tdd, $J = 56.9, 5.9, 3.6$

Hz, 1H), 3.91 (s, 6H), 3.85 - 3.78 (m, 1H), 3.54 - 3.47 (m, 1H), 3.36 - 3.28 (m, 1H), 2.63 - 2.50 (m, 1H), 2.29 - 2.17 (m, 1H), 2.14 - 2.06 (m, 1H), 1.99 - 1.91 (m, 1H), 1.72 (br, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 191.7, 136.4, 125.0, 117.3 (t, $J = 238.9$ Hz), 105.5, 61.1, 37.5 (t, $J = 20.5$ Hz), 36.0, 29.8, 26.5 - 26.4 (m).

¹⁹F NMR (376 MHz, CDCl₃) δ -115.10 – -115.55 (m).

HRMS (ESI) m/z : $[M+H]^+$ calcd for C₁₄H₁₉F₂O₄⁺ 289.1246; found 289.1251.



5,5-difluoro-3-(p-tolyl)pentan-1-ol (5k)

Yellow oil liquid.

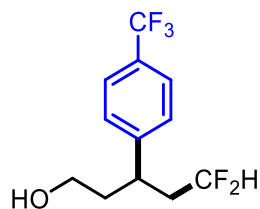
Compound **5k** was purified by PTLC with PE/EA = 3:1, 56% yield (12.0 mg) following the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 7.24 – 6.93 (m, 4H), 5.50 (tdd, $J = 56.8, 6.7, 3.3$ Hz, 1H), 3.58 - 3.49 (m, 1H), 3.49 - 3.39 (m, 1H), 3.01 - 2.92 (m, 1H), 2.33 (s, 3H), 2.20 – 2.06 (m, 2H), 1.99 – 1.78 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 139.4, 136.7, 129.7, 127.4, 116.7 (t, $J = 238.6$ Hz), 60.6, 41.1 (t, $J = 20.7$ Hz), 39.3, 36.6 - 36.5 (m), 21.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.87 – -118.27 (m).

HRMS (ESI) m/z : $[M+H]^+$ calcd for C₁₂H₁₇F₂O⁺ 215.1242; found 215.1245.



5,5-difluoro-3-(4-(trifluoromethyl)phenyl)pentan-1-ol (5l)

Yellow oil liquid.

Compound **5l** was purified by PTLC with PE/EA = 3:1, 43% yield (11.5 mg) following the procedure B.

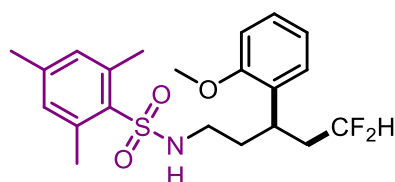
¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 5.53

(tdd, $J = 56.6, 6.4, 3.3$ Hz, 1H), 3.61 - 3.53 (m, 1H), 3.46 - 3.38 (m, 1H), 3.20 - 3.10 (m, 1H), 2.29 - 2.13 (m, 2H), 2.05 - 1.96 (m, 1H), 1.91 - 1.82 (m, 1H), 1.58 (br, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.0, 129.5 (q, $J = 32.9$ Hz), 128.0, 126.0 (q, $J = 3.6$ Hz), 124.2 (q, $J = 272.7$ Hz), 116.2 (t, $J = 239.1$ Hz), 60.1, 40.7 (t, $J = 21.0$ Hz), 39.0, 36.7 - 36.6 (m).

^{19}F NMR (376 MHz, CDCl_3) δ -62.47 (s), -114.76 - -117.88 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{14}\text{F}_5\text{O}^+$ 269.0959; found 269.0961.



***N*-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)-2,4,6-trimethylbenzenesulfonamide (5m)**

Yellow oil liquid.

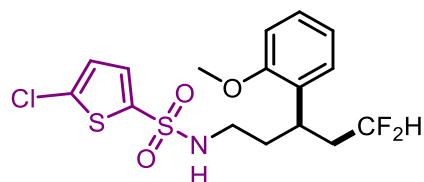
Compound **5m** was purified by PTLC with PE/EA = 3:1, 57% yield (23.4 mg) following the procedure B.

^1H NMR (400 MHz, CDCl_3) δ 7.24 - 7.18 (m, 1H), 7.01 - 6.98 (m, 1H), 6.96 - 6.83 (m, 4H), 5.42 (tdd, $J = 56.8, 6.6, 3.2$ Hz, 1H), 4.88 - 4.61 (m, 1H), 3.82 (s, 3H), 3.30 - 3.16 (m, 1H), 2.93 - 2.82 (m, 1H), 2.66 - 2.56 (m, 7H), 2.29 (s, 3H), 2.21 - 2.08 (m, 1H), 1.99 - 1.86 (m, 1H), 1.79 - 1.66 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 157.2, 142.2, 139.0, 134.3, 132.1, 129.4, 128.3, 127.9, 121.5, 116.7 (t, $J = 238.9$ Hz), 111.3, 55.7, 40.5, 39.6 (t, $J = 20.9$ Hz), 35.5, 30.5 - 30.4 (m), 23.0, 21.0.

^{19}F NMR (376 MHz, CDCl_3) δ -114.25 - -117.28 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{28}\text{F}_2\text{NO}_3\text{S}^+$ 412.1752; found 412.1757.



5-chloro-*N*-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)thiophene-2-sulfonamide (5n)

Yellow oil liquid.

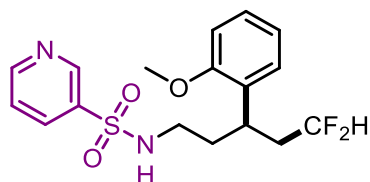
Compound **5n** was purified by PTLC with PE/EA = 3:1, 49% yield (20.0 mg) following the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, J = 4.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.07 (d, J = 7.4 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 6.91 – 6.86 (m, 2H), 5.68 – 5.36 (m, 1H), 5.01 – 4.65 (m, 1H), 3.84 (s, 3H), 3.37 - 3.25 (m, 1H), 3.04 - 2.93 (m, 1H), 2.75 – 2.64 (m, 1H), 2.31 – 2.18 (m, 1H), 2.14 – 2.03 (m, 1H), 1.98 - 1.88 (m, 1H), 1.85 – 1.75 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 139.1, 137.2, 131.4, 129.1, 128.5, 128.0, 126.8, 121.6, 116.6 (t, J = 239.0 Hz), 111.4, 55.8, 41.4, 39.7 (t, J = 20.9 Hz), 35.2, 30.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.27 – -117.35 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₆H₁₉ClF₂NO₃S₂⁺ 410.0457; found 410.0454.



***N*-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)pyridine-3-sulfonamide (**5o**)**

Yellow oil liquid.

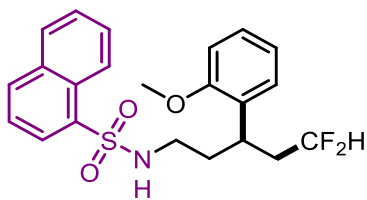
Compound **5o** was purified by PTLC with PE/EA = 3:1, 54% yield (20.0 mg) following the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 8.98 (s, 1H), 8.78 (d, J = 4.8 Hz, 1H), 8.04 (dt, J = 8.0, 1.9 Hz, 1H), 7.42 (dd, J = 8.0, 4.9 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 9.0 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 5.49 (tdd, J = 56.7, 6.5, 3.1 Hz, 1H), 5.02 – 4.94 (m, 1H), 3.83 (s, 3H), 3.32 - 3.24 (m, 1H), 2.99 – 2.91 (m, 1H), 2.72 - 2.62 (m, 1H), 2.26 - 2.16 (m, 1H), 2.11 – 1.99 (m, 1H), 1.93 - 1.85 (m, 1H), 1.84 - 1.77 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 153.2, 148.0, 136.9, 134.7, 129.1, 128.5, 127.9, 123.8, 121.6, 116.6 (t, J = 239.0 Hz), 111.4, 55.8, 41.2, 39.6 (t, J = 20.8 Hz), 35.3, 30.6 - 30.4 (m).

¹⁹F NMR (376 MHz, CDCl₃) δ -114.30 – -117.38 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₁₇H₂₁F₂N₂O₃S⁺ 371.1235; found 371.1235.



***N*-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)naphthalene-1-sulfonamide (5p)**

Yellow oil liquid.

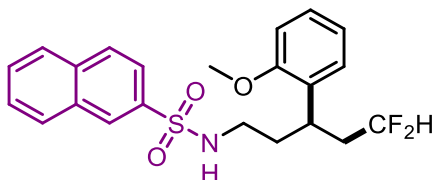
Compound **5p** was purified by PTLC with PE/EA = 3:1, 32% yield (13.4 mg) following the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, J = 8.6 Hz, 1H), 8.24 – 8.14 (m, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 7.7 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.20 – 7.14 (m, 1H), 6.90 – 6.80 (m, 3H), 5.46 – 5.14 (m, 1H), 5.04 – 4.93 (m, 1H), 3.79 (s, 3H), 3.14 - 3.06 (m, 1H), 2.94 - 2.86 (m, 1H), 2.64 - 2.55 (m, 1H), 2.12 – 2.00 (m, 1H), 1.85 – 1.75 (m, 1H), 1.67 – 1.61 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 135.1, 134.4, 134.3, 129.6, 129.3, 128.4, 128.2, 127.9, 127.0, 124.4, 124.3, 121.4, 116.6 (t, J = 239.1 Hz), 111.3, 55.7, 41.2, 39.4 (t, J = 20.8 Hz), 35.3, 30.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.20 – -117.02 (m).

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₂H₂₄F₂NO₃S⁺ 420.1439; found 420.1443.



***N*-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)naphthalene-2-sulfonamide (5q)**

Yellow oil liquid.

Compound **5q** was purified by PTLC with PE/EA = 3:1, 30% yield (12.6 mg) following the procedure B.

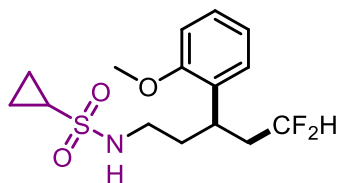
¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 7.92 (t, J = 9.3 Hz, 3H), 7.74 (d, J = 8.6 Hz, 1H), 7.63 (p, J = 6.9 Hz, 2H), 7.16 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.88 – 6.78 (m, 2H), 5.59 – 5.28 (m, 1H), 4.84 (t, J = 5.9 Hz, 1H), 3.77 (s, 3H), 3.31 - 3.21 (m, 1H), 2.99 - 2.88 (m, 1H), 2.71 - 2.61 (m, 1H), 2.23 - 2.10 (m, 1H), 2.04 - 1.94 (m, 1H), 1.87 - 1.79 (m, 1H), 1.77 – 1.72 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 136.9, 134.9, 132.2, 129.6, 129.3, 128.9, 128.4, 128.3, 128.0, 127.7, 122.3, 121.5, 116.6 (t, J = 238.8 Hz), 111.3, 55.7, 41.2, 39.6 (t, J =

20.6 Hz), 35.3, 30.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.30 – -117.28 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₄F₂NO₃S⁺ 420.1439; found 420.1440.



***N*-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)cyclopropanesulfonamide (5r)**

Yellow oil liquid.

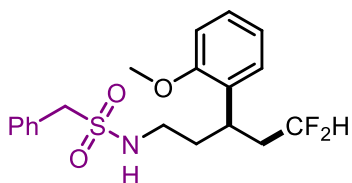
Compound **5r** was purified by PTLC with PE/EA = 3:1, 70% yield (23.3 mg) following the procedure B.

¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 5.72 - 5.40 (m, 1H), 4.53 (br, 1H), 3.85 (s, 3H), 3.45 - 3.34 (m, 1H), 3.12 - 3.02 (m, 1H), 2.92 - 2.80 (m, 1H), 2.33 - 2.10 (m, 3H), 2.04 - 1.96 (m, 1H), 1.95 - 1.84 (m, 1H), 1.14 - 1.05 (m, 2H), 0.92 (d, *J* = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.3, 129.5, 128.4, 128.1, 121.5, 116.7 (t, *J* = 239.4 Hz), 111.3, 55.7, 41.3, 39.7 (t, *J* = 20.7 Hz), 36.0, 30.8 - 30.6 (m), 30.1, 5.4, 5.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -114.21 – -117.29 (m).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₅H₂₂F₂NO₃S⁺ 334.1283; found 334.1288.



***N*-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)-1-phenylmethanesulfonamide (5s)**

Yellow oil liquid.

Compound **5s** was purified by PTLC with PE/EA = 3:1, 56% yield (21.4 mg) following the procedure B.

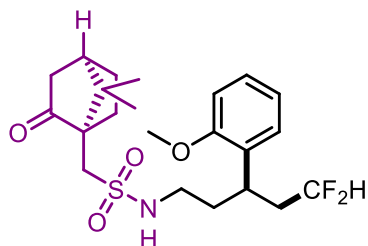
¹H NMR (400 MHz, CDCl₃) δ 7.37 - 7.28 (m, 5H), 7.26 - 7.20 (m, 1H), 7.07 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 5.72 - 5.32 (m, 1H), 4.48 - 4.36 (m, 1H), 4.16 (d, *J* = 1.7 Hz, 2H), 3.71 (s, 3H), 3.38 - 3.22 (m, 1H), 2.95 - 2.83 (m, 1H), 2.72 - 2.62 (m, 1H), 2.28 - 2.04 (m, 2H), 1.90 - 1.70 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 157.1, 130.7, 129.6, 129.3, 128.9, 128.8, 128.3, 127.9,

121.5, 116.7 (t, $J = 239.4$ Hz), 111.3, 58.8, 55.6, 41.5, 39.7 (t, $J = 20.8$ Hz), 36.3, 30.4.

^{19}F NMR (376 MHz, CDCl_3) δ -114.21 – -117.20 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{F}_2\text{NO}_3\text{S}^+$ 384.1439; found 384.1441.



***N*-(5,5-difluoro-3-(2-methoxyphenyl)pentyl)-1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonamide (5t)**

Yellow oil liquid.

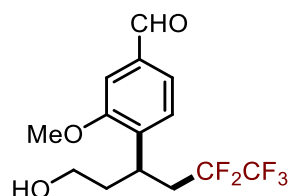
Compound **5t** was purified by PTLC with PE/EA = 3:1, 53% yield (23.5 mg) following the procedure B.

^1H NMR (400 MHz, CDCl_3) δ 7.22 (t, $J = 7.8$ Hz, 1H), 7.14 (d, $J = 7.5$ Hz, 1H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), 5.55 (tdd, $J = 56.8, 6.4, 3.3$ Hz, 1H), 5.16 (q, $J = 7.1, 6.6$ Hz, 1H), 3.84 (s, 3H), 3.40 - 3.27 (m, 2H), 3.11 - 3.00 (m, 1H), 2.98 - 2.87 (m, 1H), 2.83 (d, $J = 15.1$ Hz, 1H), 2.39 - 2.11 (m, 5H), 2.04 - 1.88 (m, 5H), 1.48 - 1.40 (m, 1H), 1.01 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 216.8, 157.4, 129.6, 128.3, 128.2, 121.2, 116.9 (t, $J = 238.8$ Hz), 111.2, 59.2, 55.6, 49.6, 49.4, 48.8, 42.8 (d, $J = 16.6$ Hz), 41.7, 39.5 (td, $J = 20.7, 4.7$ Hz), 35.6 (d, $J = 15.9$ Hz), 31.6, 27.1, 26.5, 20.0, 19.7.

^{19}F NMR (376 MHz, CDCl_3) δ -114.15 – -117.08 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{32}\text{F}_2\text{NO}_4\text{S}^+$ 444.2015; found 444.2019.



3-methoxy-4-(5,5,6,6,6-pentafluoro-1-hydroxyhexan-3-yl)benzaldehyde (5u)

Yellow oil liquid.

Compound **5u** was purified by PTLC with PE/EA = 3:1, 71% yield (23.1 mg) following the procedure B.

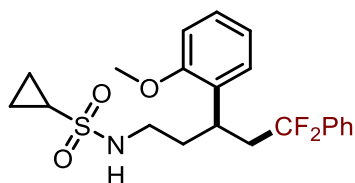
^1H NMR (400 MHz, CDCl_3) δ 9.96 (s, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.41 (s, 1H), 7.35

(d, $J = 7.6$ Hz, 1H), 3.93 (s, 3H), 3.78 - 3.66 (m, 1H), 3.57 - 3.50 (m, 1H), 3.41 - 3.32 (m, 1H), 2.69 - 2.54 (m, 1H), 2.48 - 2.36 (m, 1H), 2.14 - 1.98 (m, 2H), 1.65 (br, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 191.8, 158.0, 138.1, 136.6, 129.5, 124.8, 121.5 - 111.7 (m), 109.5, 60.4, 55.9, 37.9, 35.1 (t, $J = 20.6$ Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -85.85 (s), -116.86 - -117.35 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{F}_5\text{O}_3^+$ 327.1014; found 327.1015.



***N*-(5,5-difluoro-3-(2-methoxyphenyl)-5-phenylpentyl)cyclopropanesulfonamide (5v)**

Yellow oil liquid.

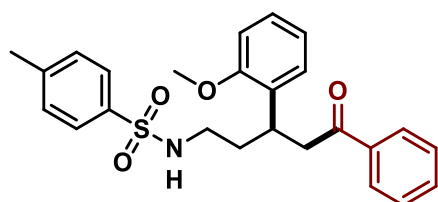
Compound **5v** was purified by PTLC with PE/EA = 3:1, 74% yield (30.3 mg) following the procedure B.

^1H NMR (400 MHz, CDCl_3) δ 7.39 - 7.32 (m, 5H), 7.17 (t, $J = 7.8$ Hz, 1H), 7.06 (d, $J = 7.5$ Hz, 1H), 6.89 (t, $J = 7.4$ Hz, 1H), 6.80 (d, $J = 8.2$ Hz, 1H), 4.57 - 4.41 (m, 1H), 3.77 (s, 3H), 3.49 - 3.35 (m, 1H), 3.07 - 2.96 (m, 1H), 2.80 - 2.70 (m, 1H), 2.66 - 2.41 (m, 2H), 2.28 - 2.18 (m, 1H), 2.13 - 2.02 (m, 1H), 1.92 - 1.82 (m, 1H), 1.09 - 1.03 (q, $J = 5.7, 4.8$ Hz, 2H), 0.91 - 0.85 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 156.8, 137.3 (t, $J = 26.4$ Hz), 130.9, 129.7, 128.3, 127.9, 125.0 (t, $J = 6.3$ Hz), 123.0 (t, $J = 244.4$ Hz), 121.3, 111.0, 55.6, 44.7 (t, $J = 26.7$ Hz), 41.4, 36.4, 30.9, 30.1, 5.4, 5.3.

^{19}F NMR (376 MHz, CDCl_3) δ -91.43 - -95.83 (m).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{26}\text{F}_2\text{NO}_3\text{S}^+$ 410.1596; found 410.1592.



***N*-(3-(2-methoxyphenyl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (7a)**

Yellow oil liquid.

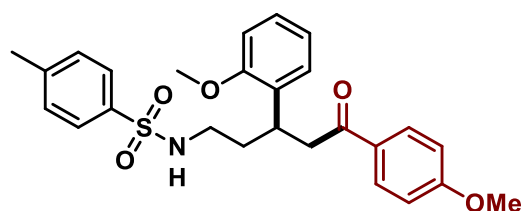
Compound **7a** was purified by PTLC with PE/EA = 3:1, 55% yield (24.0 mg) following

the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.85 (m, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.19 – 7.16 (m, 1H), 7.03 (d, J = 8.8 Hz, 1H), 6.89 – 6.82 (m, 2H), 4.90 (t, J = 6.1 Hz, 1H), 3.80 (s, 3H), 3.75 – 3.68 (m, 1H), 3.30 – 3.18 (m, 2H), 2.91 – 2.84 (m, 1H), 2.79 – 2.71 (m, 1H), 2.38 (s, 3H), 1.88 – 1.79 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 199.1, 157.1, 143.2, 137.2, 137.0, 133.2, 131.3, 129.7, 128.7, 128.2, 128.1, 127.9, 127.2, 121.1, 111.1, 55.6, 44.3, 41.5, 34.7, 32.0, 21.6.

HRMS (ESI) m/z : $[M+H]^+$ calcd for C₂₅H₂₈NO₄S⁺ 438.1734; found 438.1731.



***N*-(3-(2-methoxyphenyl)-5-(4-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7b)**

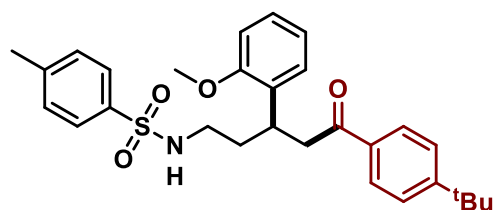
Yellow oil liquid.

Compound **7b** was purified by PTLC with PE/EA = 3:1, 41% yield (19.1 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.6 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.18 (t, J = 7.8 Hz, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 6.88 – 6.81 (m, 2H), 4.92 (t, J = 6.0 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.73 – 3.66 (m, 1H), 3.26 – 3.12 (m, 2H), 2.91 – 2.93 (m, 1H), 2.79 – 2.71 (m, 1H), 2.39 (s, 3H), 1.87 – 1.78 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 197.7, 163.6, 157.1, 143.2, 137.2, 131.5, 130.5, 130.1, 129.7, 128.0, 127.8, 127.2, 121.1, 113.8, 111.1, 55.6, 43.9, 41.5, 34.7, 32.0, 21.6.

HRMS (ESI) m/z : $[M+H]^+$ calcd for C₂₆H₃₀NO₅S⁺ 468.1839; found 468.1835.



***N*-(5-(4-(tert-butyl)phenyl)-3-(2-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7c)**

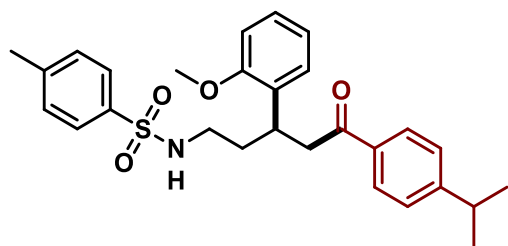
Yellow oil liquid.

Compound **7c** was purified by PTLC with PE/EA = 3:1, 48% yield (23.7 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.05 – 7.01 (m, 1H), 6.89 – 6.81 (m, 2H), 4.95 (t, J = 6.1 Hz, 1H), 3.79 (s, 3H), 3.75 – 3.66 (m, 1H), 3.30 – 3.16 (m, 2H), 2.91 – 2.82 (m, 1H), 2.79 – 2.70 (m, 1H), 2.38 (s, 3H), 1.87 – 1.77 (m, 2H), 1.33 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 198.8, 157.1, 156.9, 143.2, 137.2, 134.4, 131.4, 129.7, 128.1, 128.0, 127.8, 127.2, 125.6, 121.1, 111.1, 55.6, 44.2, 41.5, 35.2, 34.6, 31.9, 31.2, 21.6.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₉H₃₆NO₄S⁺ 494.2360; found 494.2358.



***N*-(5-(4-isopropylphenyl)-3-(2-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7d)**

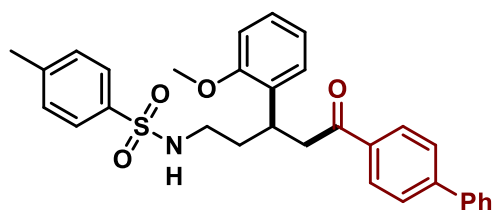
Yellow oil liquid.

Compound **7d** was purified by PTLC with PE/EA = 3:1, 41% yield (19.6 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 7.9 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 6.85 (dd, J = 18.3, 7.8 Hz, 2H), 4.94 (t, J = 5.8 Hz, 1H), 3.80 (s, 3H), 3.75 – 3.67 (m, 1H), 3.29 – 3.14 (m, 2H), 2.99 – 2.91 (m, 1H), 2.89 – 2.83 (m, 1H), 2.79 – 2.71 (m, 1H), 2.38 (s, 3H), 1.87 – 1.77 (m, 2H), 1.27 (s, 3H), 1.25 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 198.8, 157.1, 154.7, 143.2, 137.2, 134.9, 131.4, 129.7, 128.4, 128.0, 127.8, 127.2, 126.7, 121.1, 111.1, 55.6, 44.2, 41.5, 34.6, 34.4, 31.9, 23.8, 21.6.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₈H₃₄NO₄S⁺ 480.2203; found 480.2208.



***N*-(5-([1,1'-biphenyl]-4-yl)-3-(2-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7e)**

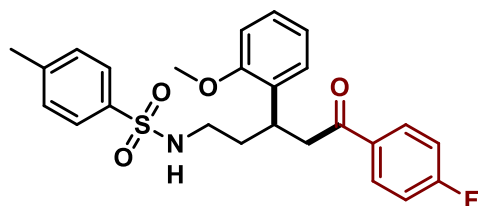
Yellow oil liquid.

Compound **7e** was purified by PTLC with PE/EA = 3:1, 40% yield (20.5 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.4 Hz, 2H), 7.69 – 7.60 (m, 6H), 7.47 (t, J = 7.4 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.20 – 7.16 (m, 1H), 7.07 – 7.03 (m, 1H), 6.91 – 6.82 (m, 2H), 4.90 (t, J = 6.1 Hz, 1H), 3.81 (s, 3H), 3.77 – 3.71 (m, 1H), 3.34 – 3.21 (m, 2H), 2.94 – 2.85 (m, 1H), 2.81 – 2.72 (m, 1H), 2.38 (s, 3H), 1.92 – 1.78 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 198.7, 157.2, 145.9, 143.2, 139.9, 137.2, 135.7, 131.3, 129.7, 129.1, 128.8, 128.4, 128.1, 127.9, 127.4, 127.3, 127.2, 121.2, 111.1, 55.6, 44.3, 41.5, 34.7, 32.0, 21.6.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₃₁H₃₂NO₄S⁺ 514.2047; found 514.2048.



***N*-(5-(4-fluorophenyl)-3-(2-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7f)**

Yellow oil liquid.

Compound **7f** was purified by PTLC with PE/EA = 3:1, 42% yield (19.1 mg) following the procedure C.

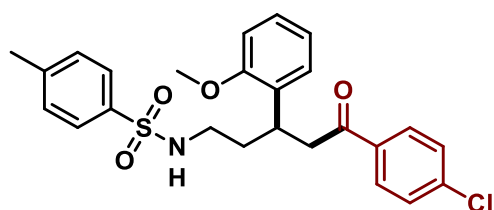
¹H NMR (400 MHz, CDCl₃) δ 7.90 (dd, J = 8.7, 5.5 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.20 – 7.15 (m, 1H), 7.09 (t, J = 8.6 Hz, 2H), 7.04 – 7.00 (m, 1H), 6.89 – 6.81 (m, 2H), 4.88 (t, J = 6.1 Hz, 1H), 3.79 (s, 3H), 3.73 – 3.65 (m, 1H),

3.22 (qd, $J = 17.0, 6.8$ Hz, 2H), 2.92 – 2.83 (m, 1H), 2.79 – 2.70 (m, 1H), 2.39 (s, 3H), 1.90 – 1.77 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 197.6, 165.8 (d, $J = 254.7$ Hz), 157.1, 143.2, 137.2, 133.5, 131.1, 130.8 (d, $J = 9.3$ Hz), 129.7, 128.0 (d, $J = 11.4$ Hz), 127.2, 121.1, 115.8, 115.6, 111.1, 55.6, 44.2, 41.5, 34.6, 32.2, 21.6.

^{19}F NMR (376 MHz, CDCl_3) δ -105.2 (p, $J = 8.1$ Hz).

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{27}\text{FNO}_4\text{S}^+$ 456.1639; found 456.1640.



***N*-(5-(4-chlorophenyl)-3-(2-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7g)**

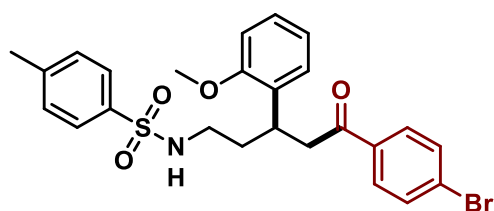
Yellow oil liquid.

Compound **7g** was purified by PTLC with PE/EA = 3:1, 43% yield (20.3 mg) following the procedure C.

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 8.1$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.19 – 7.15 (m, 1H), 7.02 (d, $J = 6.6$ Hz, 1H), 6.89 – 6.81 (m, 2H), 4.87 (t, $J = 5.7$ Hz, 1H), 3.79 (s, 3H), 3.73 – 3.64 (m, 1H), 3.28 – 3.14 (m, 2H), 2.92 – 2.82 (m, 1H), 2.78 – 2.68 (m, 1H), 2.39 (s, 3H), 1.90 – 1.77 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 197.9, 157.1, 143.2, 139.6, 137.1, 135.3, 131.0, 129.7, 129.6, 128.9, 128.1, 128.0, 127.2, 121.1, 111.1, 55.6, 44.2, 41.4, 34.6, 32.1, 21.6.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{27}\text{ClNO}_4\text{S}^+$ 472.1344; found 472.1343.



***N*-(5-(4-bromophenyl)-3-(2-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7h)**

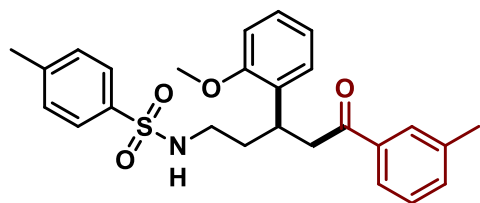
Yellow oil liquid.

Compound **7h** was purified by PTLC with PE/EA = 3:1, 47% yield (24.2 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.02 (dd, J = 7.5, 1.5 Hz, 1H), 6.89 – 6.79 (m, 2H), 4.93 (t, J = 5.8 Hz, 1H), 3.78 (s, 3H), 3.72 – 3.62 (m, 1H), 3.28 – 3.11 (m, 2H), 2.92 – 2.81 (m, 1H), 2.80 – 2.68 (m, 1H), 2.38 (s, 3H), 1.89 – 1.78 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 198.1, 157.1, 143.2, 137.1, 135.7, 131.9, 130.9, 129.7, 129.1, 128.3, 128.0, 127.9, 127.1, 121.1, 111.1, 55.5, 44.1, 41.4, 34.5, 32.1, 21.6.

HRMS (ESI) m/z : $[M+H]^+$ calcd for C₂₅H₂₇BrNO₄S⁺ 516.0839; found 516.0842.



***N*-(3-(2-methoxyphenyl)-5-oxo-5-(*m*-tolyl)pentyl)-4-methylbenzenesulfonamide
(**7i**)**

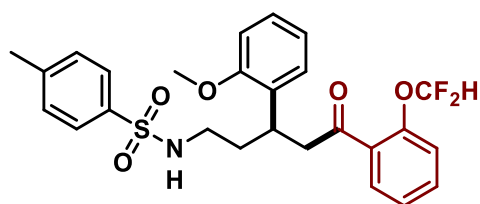
Yellow oil liquid.

Compound **7i** was purified by PTLC with PE/EA = 3:1, 51% yield (23.0 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.57 (m, 4H), 7.36 – 7.29 (m, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.17 (t, J = 7.1 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.89 – 6.81 (m, 2H), 4.94 (t, J = 6.0 Hz, 1H), 3.80 (s, 3H), 3.74 – 3.67 (m, 1H), 3.30 – 3.15 (m, 2H), 2.91 – 2.82 (m, 1H), 2.79 – 2.70 (m, 1H), 2.38 (s, 6H), 1.89 – 1.77 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 199.3, 157.1, 143.2, 138.4, 137.2, 137.0, 133.9, 131.4, 129.7, 128.7, 128.5, 128.0, 127.8, 127.2, 125.4, 121.1, 111.1, 55.6, 44.3, 41.5, 34.6, 31.9, 21.6, 21.5.

HRMS (ESI) m/z : $[M+H]^+$ calcd for C₂₆H₃₀NO₄S⁺ 452.1890; found 452.1894.



***N*-(5-(2-(difluoromethoxy)phenyl)-3-(2-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7j)**

Yellow oil liquid.

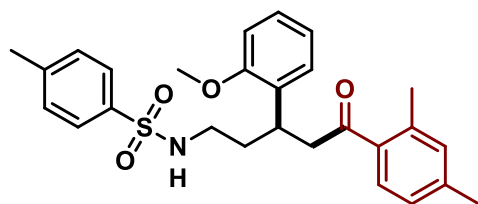
Compound **7j** was purified by PTLC with PE/EA = 3:1, 40% yield (20.1 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.41 (m, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.16 – 7.12 (m, 2H), 7.00 – 6.97 (m, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.50 (t, *J* = 73.5 Hz, 1H), 4.85 (t, *J* = 5.7 Hz, 1H), 3.74 (s, 3H), 3.69 – 3.62 (m, 1H), 3.25 (d, *J* = 7.1 Hz, 2H), 2.92 – 2.82 (m, 1H), 2.74 – 2.64 (m, 1H), 2.39 (s, 3H), 1.85 – 1.73 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 200.7, 157.1, 149.0, 143.2, 137.2, 133.0, 132.0, 130.8, 130.2, 129.7, 128.1, 127.9, 127.2, 125.7, 121.1, 119.7, 116.2 (t, *J* = 260.7 Hz), 111.0, 55.5, 48.8, 41.4, 35.0, 31.9, 21.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -80.62 (d, *J* = 4.5 Hz), -80.82 (d, *J* = 4.4 Hz).

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₈F₂NO₅S⁺ 504.1651; found 504.1649.



***N*-(5-(2,4-dimethylphenyl)-3-(2-methoxyphenyl)-5-oxopentyl)-4-methylbenzenesulfonamide (7k)**

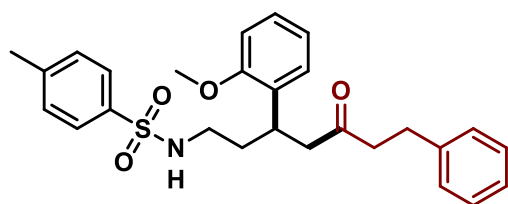
Yellow oil liquid.

Compound **7k** was purified by PTLC with PE/EA = 3:1, 40% yield (18.6 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.12 (m, 1H), 7.04 – 6.97 (m, 3H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 4.94 (t, *J* = 6.1 Hz, 1H), 3.73 (s, 3H), 3.70 – 3.62 (m, 1H), 3.21 – 3.07 (m, 2H), 2.92 – 2.82 (m, 1H), 2.76 – 2.66 (m, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H), 1.86 – 1.75 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 202.8, 157.1, 143.2, 141.8, 138.5, 137.2, 135.1, 132.8, 131.0, 129.7, 128.9, 128.1, 127.8, 127.1, 126.3, 121.1, 111.0, 55.5, 46.9, 41.4, 34.9, 32.2, 21.6, 21.4, 21.2.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₇H₃₂NO₄S⁺ 466.2047; found 466.2050.



***N*-(3-(2-methoxyphenyl)-5-oxo-7-phenylheptyl)-4-methylbenzenesulfonamide (7l)**

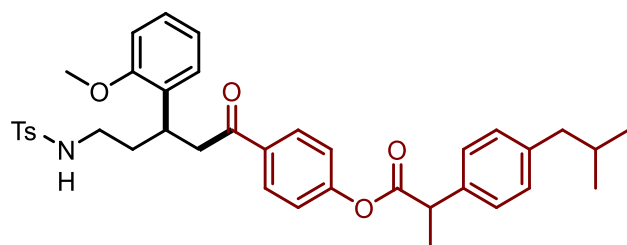
Yellow oil liquid.

Compound **7l** was purified by PTLC with PE/EA = 3:1, 23% yield (10.7 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.2 Hz, 2H), 7.25 – 7.22 (m, 4H), 7.18 – 7.14 (m, 2H), 7.08 (d, J = 7.1 Hz, 2H), 6.95 (dd, J = 7.5, 1.6 Hz, 1H), 6.88 – 6.80 (m, 2H), 4.88 (t, J = 6.2 Hz, 1H), 3.78 (s, 3H), 3.59 – 3.50 (m, 1H), 2.83 – 2.74 (m, 3H), 2.70 – 2.57 (m, 5H), 2.39 (s, 3H), 1.75 – 1.66 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 209.0, 157.0, 143.2, 141.0, 137.1, 130.8, 129.7, 128.5, 128.3, 127.9, 127.9, 127.1, 126.1, 121.1, 111.0, 55.5, 48.5, 44.5, 41.3, 34.8, 31.6, 29.6, 21.6.

HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₇H₃₂NO₄S⁺ 466.2047; found 466.2045.



4-(3-(2-methoxyphenyl)-5-((4-methylphenyl)sulfonamido)pentanoyl)phenyl 2-(4-isobutylphenyl)propanoate (7m)

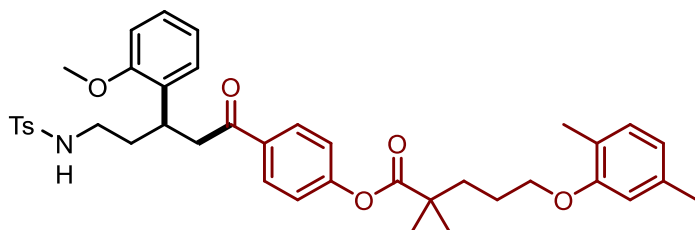
Yellow oil liquid.

Compound **7m** was purified by PTLC with PE/EA = 3:1, 43% yield (27.6 mg) following the procedure C.

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 3H), 7.05 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 6.5 Hz, 1H), 6.88 – 6.80 (m, 2H), 4.84 (t, J = 6.1 Hz, 1H), 3.96 – 3.91 (m, 1H), 3.78 (s, 3H), 3.68 (p, J = 7.9 Hz, 1H), 3.19 (qd, J = 17.0, 6.8 Hz, 2H), 2.91 – 2.82 (m, 1H), 2.79 – 2.70 (m, 1H), 2.47 (d, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.89 – 1.80 (m, 3H), 1.60 (d, J = 7.1 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 172.8, 157.1, 154.7, 143.2, 141.2, 137.2, 137.0, 134.5, 131.1, 129.7, 129.7, 128.0, 127.9, 127.3, 127.2, 121.7, 121.2, 111.1, 55.6, 45.4, 45.2, 44.2, 41.5, 34.6, 32.1, 30.3, 22.5, 21.6, 18.6.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₃₈H₄₄NO₆S⁺ 642.2884; found 642.2880.



4-(3-(2-methoxyphenyl)-5-((4-methylphenyl)sulfonamido)pentanoyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (7n)

Yellow oil liquid.

Compound **7n** was purified by PTLC with PE/EA = 3:1, 41% yield (28.1 mg) following the procedure C.

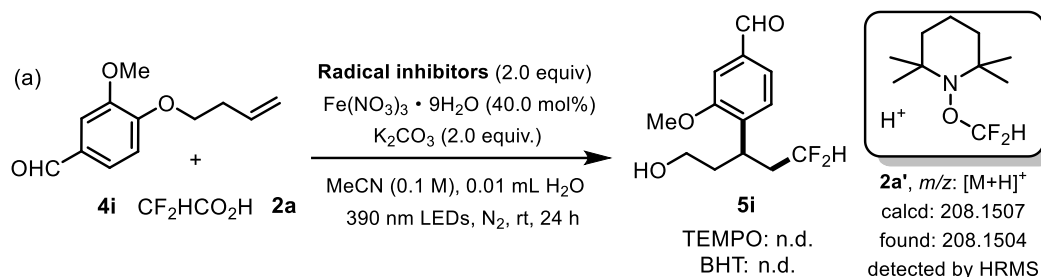
¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.20 - 7.15 (m, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.01 (dd, *J* = 10.4, 7.1 Hz, 2H), 6.90 - 6.81 (m, 2H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 4.85 (t, *J* = 5.8 Hz, 1H), 3.98 (t, *J* = 5.2 Hz, 2H), 3.79 (s, 3H), 3.74 - 3.66 (m, 1H), 3.22 (qd, *J* = 17.0, 6.8 Hz, 2H), 2.93 - 2.84 (m, 1H), 2.80 - 2.70 (m, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 2.16 (s, 3H), 1.90 - 1.81 (m, 6H), 1.37 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 176.0, 157.2, 156.9, 154.9, 143.2, 137.2, 136.7, 134.5, 131.2, 130.5, 129.8, 129.7, 128.1, 128.0, 127.2, 123.7, 121.9, 121.2, 121.0, 112.1, 111.2, 67.8, 55.6, 44.3, 42.7, 41.5, 37.2, 34.7, 32.1, 25.4, 25.2, 21.6, 21.6, 15.9.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₄₀H₄₈NO₇S⁺ 686.3146; found 686.3150.

5. Mechanistic Study

5.1 Radical trapping experiments



When 2.0 equivalents of TEMPO (2,2,6,6-Tetramethylpiperidoxyl) or BHT (Butylated Hydroxytoluene) were added to the 1,2-fluoroalkylarylation reaction of unactivated olefins under the standard conditions, the formation of product **5i** was completely inhibited. Meanwhile, the TEMPO- CF_2H adduct **2a'** was detected by HRMS. HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{20}\text{F}_2\text{NO}^+$ m/z $[\text{M} + \text{H}]^+$ 208.1507, found 208.1504, as Figure S4 shown. This result indicated that radical intermediate was probably involved in this transformation.

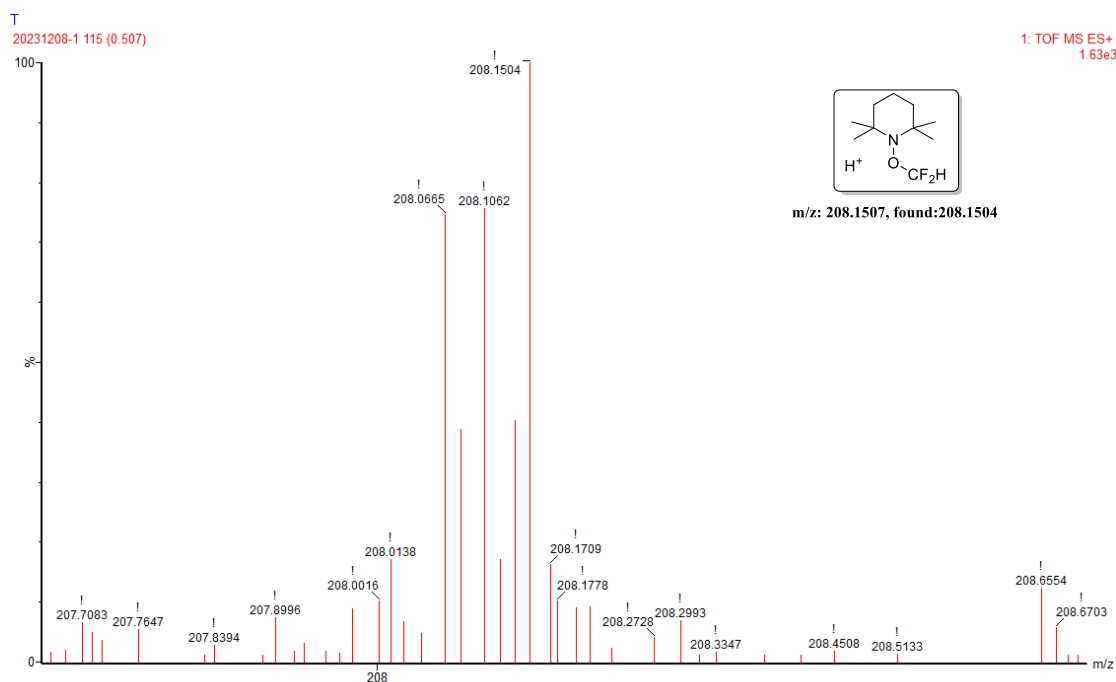
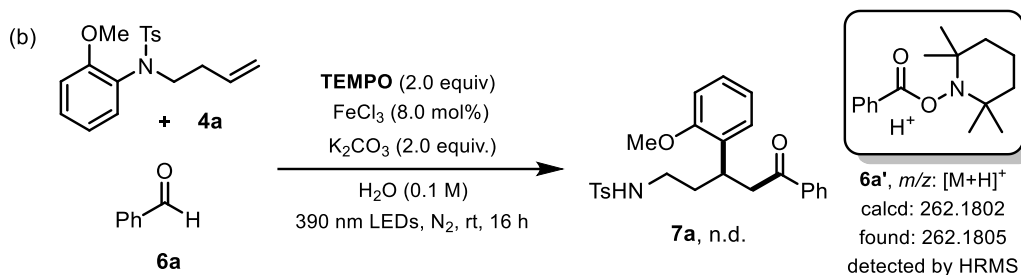


Figure S4. Detected HR-MS for compound **2a'**



When 2.0 equivalents of TEMPO were added to the 1,2-acylarylation reaction of unactivated olefins under the standard conditions, the formation of product **7a** was completely inhibited. Meanwhile, the TEMPO-adduct **6a'** was detected by HRMS. HRMS (ESI) calcd for C₁₆H₂₄NO₂⁺ *m/z* [M + H]⁺ 262.1802, found 262.1805, as Figure S5 shown. This result indicated that radical intermediate was probably involved in this transformation.

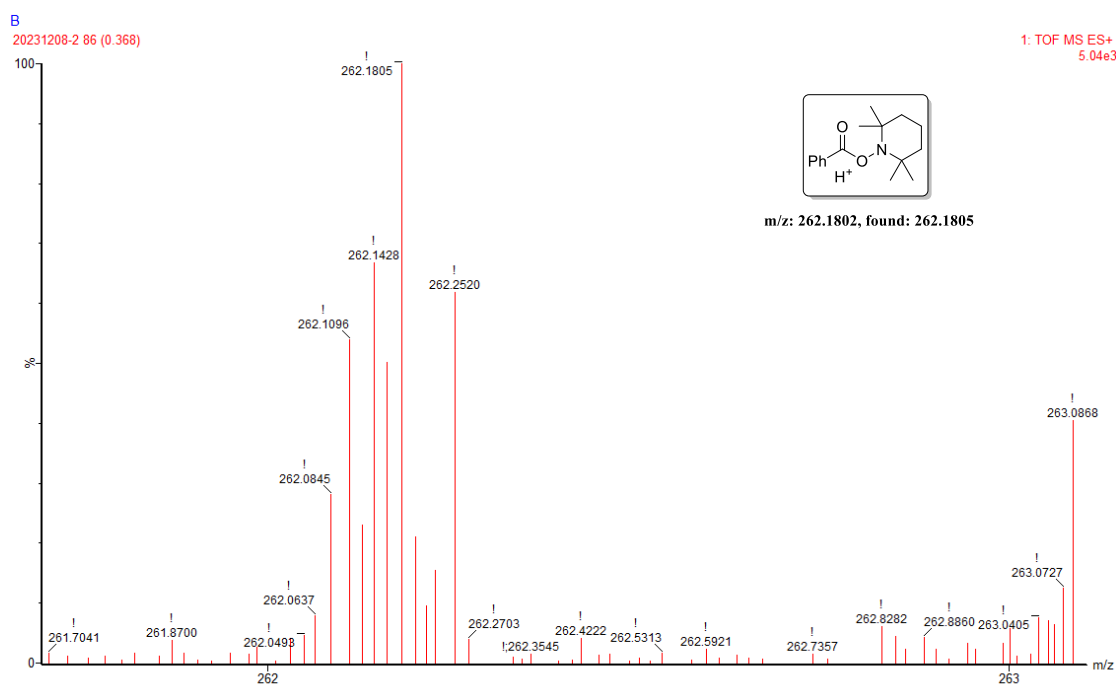
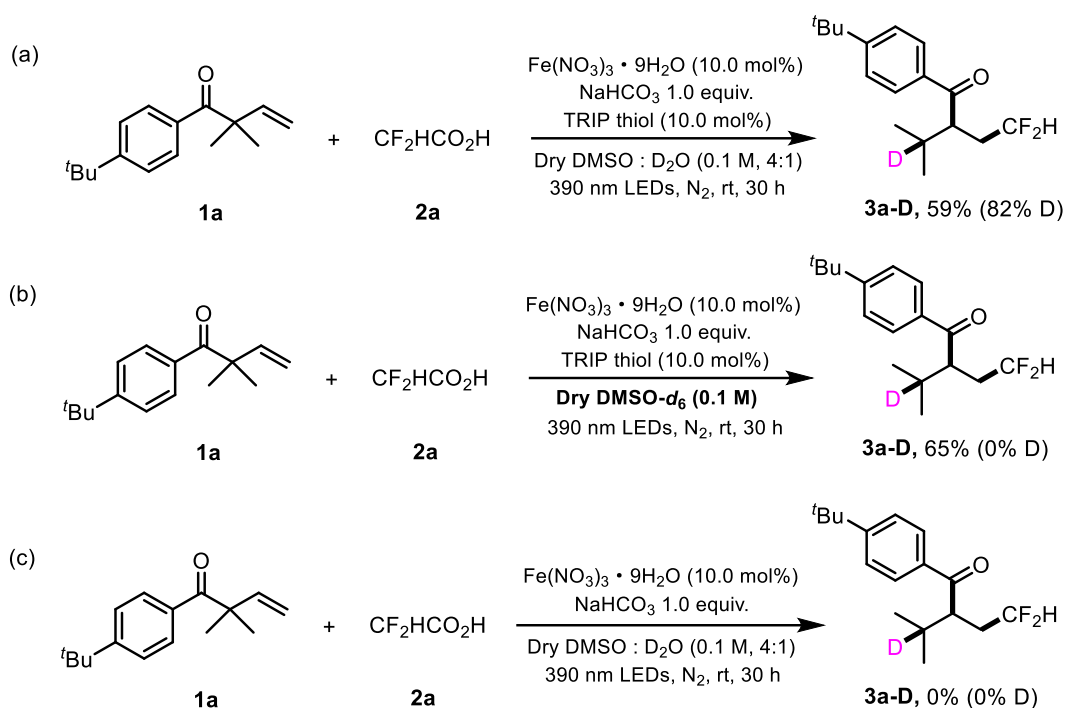


Figure S5. Detected HR-MS for compound **6a'**

5.2 Verification of deuteration mechanism

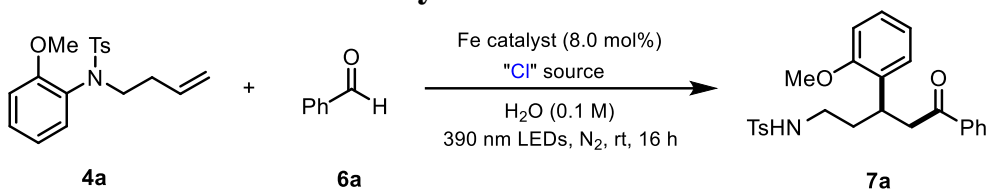


When 1,2-fluoroalkylation of **1a** was carried out in $\text{DMSO-}d_6$ (0.1 M) instead of the mixed solvent of anhydrous DMSO and deuterium oxide (0.1 M, 4:1), the product **3a** was obtained in 65% yield without deuterium incorporation, indicating that DMSO does not act as a hydrogen atom donor.

Moreover, the control experiment showed that the deuteration reaction could not proceed smoothly without the participation of 2,4,6-triisopropylbenzenethiol (TRIP thiol).

Based on the experimental results and literature investigation, it can be inferred that the deuterated TRIP thiol obtained by hydrogen-deuterium exchange between TRIP thiol and deuterium oxide is the key intermediate in this deuteration reaction.

5.3 Verification of the necessity of chlorine source



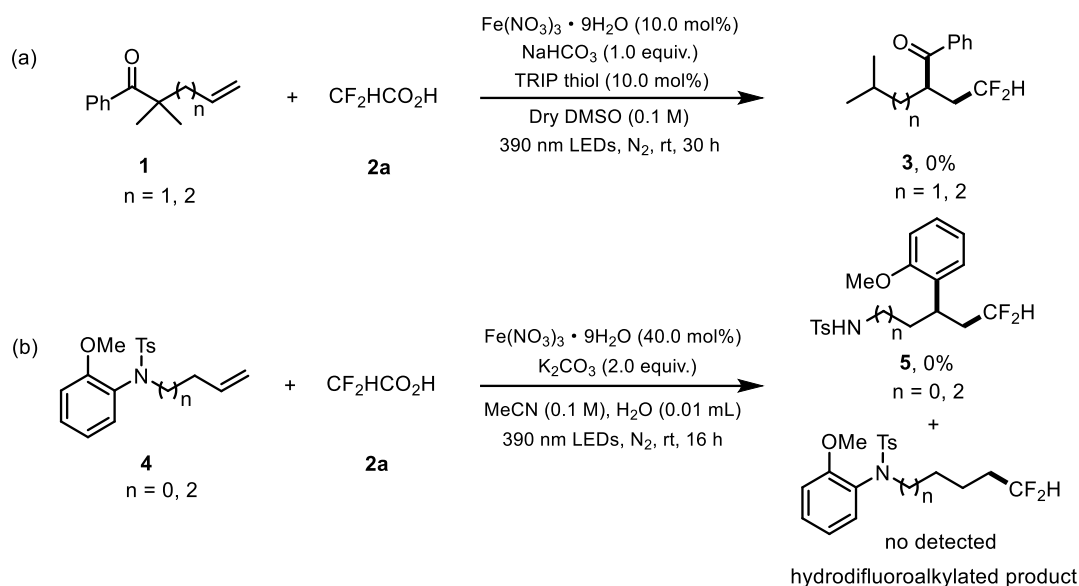
Entry	Fe catalyst	"Cl" source	Yield ^b (%)
1	Fe ₂ (SO ₄) ₃	/	trace
2	Fe(NO ₃) ₃ ·9H ₂ O	/	trace
3 ^c	Fe ₂ (SO ₄) ₃	HCl	27
4 ^c	Fe(NO ₃) ₃ ·9H ₂ O	HCl	19

^a Reaction condition: **4a** (0.10 mmol, 1.0 equiv.), **6a** (0.30 mmol, 3.0 equiv.), **Fe Catalyst** (0.008 mmol, 8.0 mol%), H₂O (0.1 M, 1.0 mL), 10 W 390 nm LEDs under N₂ atmosphere at room temperature for 16 h. ^b Isolated yield. ^c HCl (5.0 equiv.).

As shown in the above table, ferric salts such as Fe₂(SO₄)₃ and Fe(NO₃)₃·9H₂O have little catalytic effect on the acyl-arylation reaction (entries 1, 2). To further verify the necessity of chlorine source, HCl (5.0 equiv.) was added into the system with Fe₂(SO₄)₃ or Fe(NO₃)₃·9H₂O as the catalyst, affording the product **7a** in 27% or 19% yield respectively under the above conditions (entries 3, 4).

The above results suggested that the Fe(III)-chlorine complexes formed by the coordination of chloride-containing ferric salts or non-chloride ferric salts with chloride ion can be excited by visible light. Subsequently, high-activity chlorine radical and Fe(II) species can be generated through Fe-LMCT process. The hydrogen-atom-transfer (HAT) process between the chlorine radical and the aldehyde substrate produces the acyl radical intermediate.

5.4 Verification of reaction intermediates



In order to determine the rearrangement processes of 1,2-acyl migration and 1,4-aryl migration, unactivated olefins with different carbon chains were used as substrates to explore the range of cyclic transition states. When the carbon chain of β,γ -unsaturated ketone was extended, neither 1,3- nor 1,4-acyl migration products were obtained under the optimal reaction conditions. Moreover, when the carbon chain of the distal olefinic aromatic amine was shortened or extended, the 1,3- or 1,5-aryl migration reactions could not proceed.

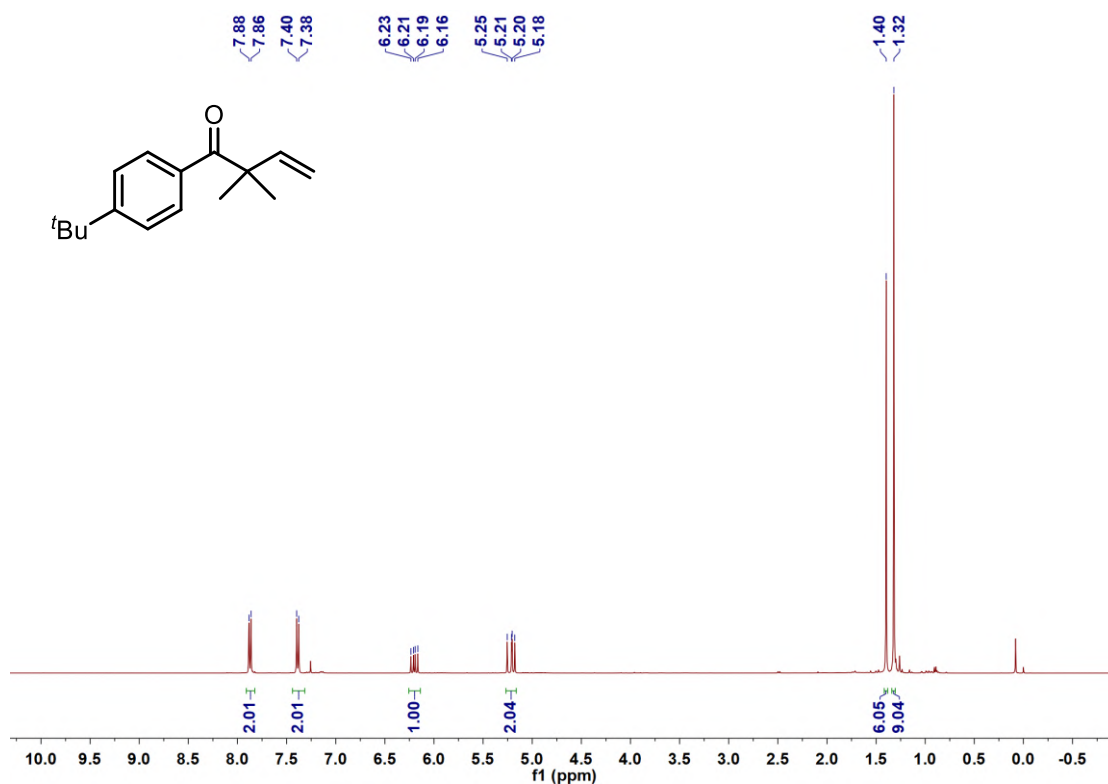
The above results showed that the 1,2-acyl migration reaction was rearranged through the three-membered ring transition state and the 1,4-aryl migration reaction was carried out through the five-membered ring transition state with lower energy.

6. References

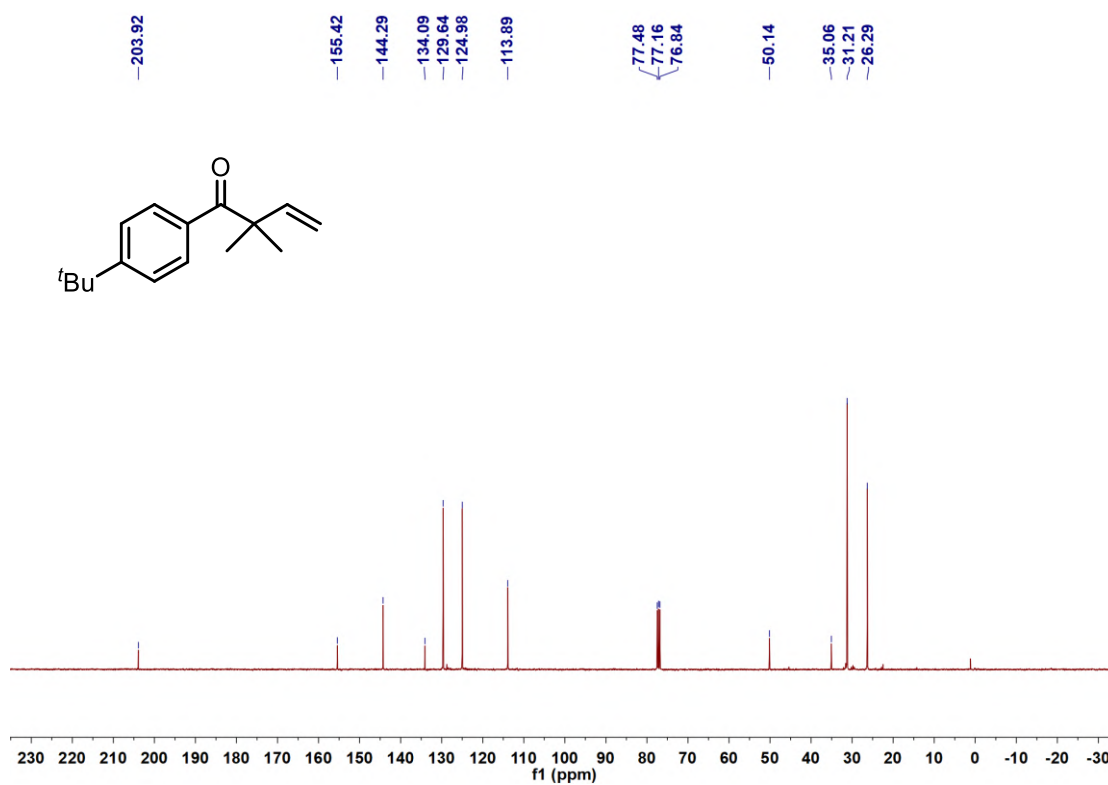
- (1) Fleury, L.; Kosal, A.; Masters, J.; Ashfeld, B. Cooperative Titanocene and Phosphine Catalysis: Accelerated C–X Activation for the Generation of Reactive Organometallics. *J. Org. Chem.* **2013**, *78*, 253-269.
- (2) Liu, R.; Tian, Y.; Wang, J.; Wang, Z.; Li, X.; Zhao, C.; Yao, R.; Li, S.; Yuan, L.; Yang, J.; Shi, D. Visible Light–Initiated Radical 1,3-Difunctionalization of β,γ -Unsaturated Ketones. *Sci. Adv.* **2022**, *8*, 1-13.
- (3) Cao, Y.; Shi, X.; Wang, X.; Zhang, M.; Song, H.; Liu, Y.; Wang, Q. Visible-Light-Induced Sulfonylarylation of Unactivated Alkenes via 1,4-(Hetero)aryl Migration from Oxygen or Nitrogen to Carbon. *Green Chem.* **2022**, *24*, 7869-7873.

7. ^1H , ^{13}C and ^{19}F NMR Spectra for Substrates and Products

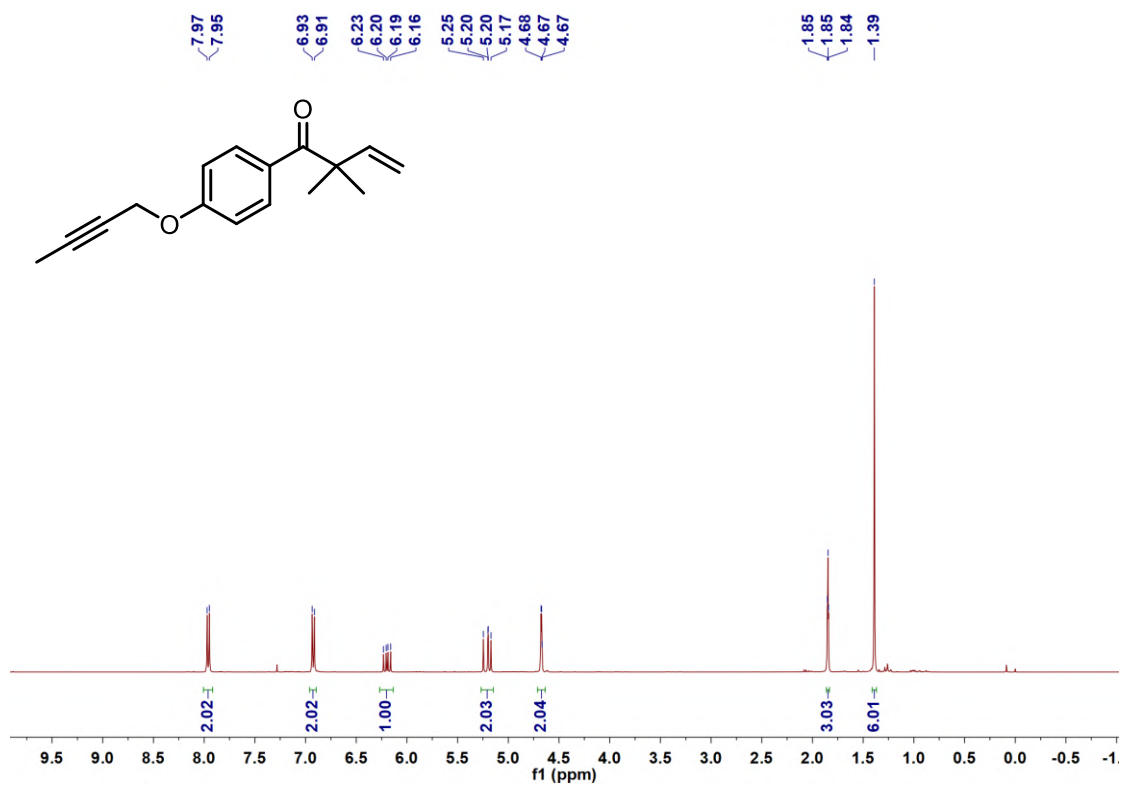
^1H NMR of Substrates **1a** (400 MHz, CDCl_3)



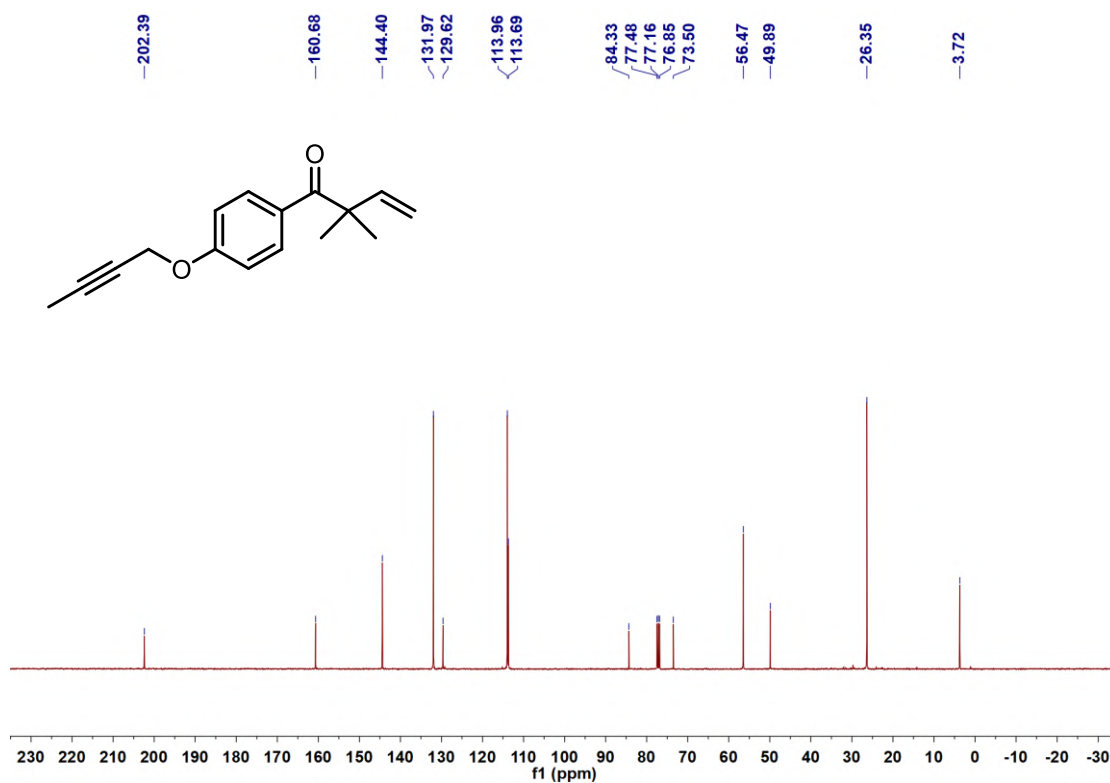
^{13}C NMR of Substrates **1a** (101 MHz, CDCl_3)



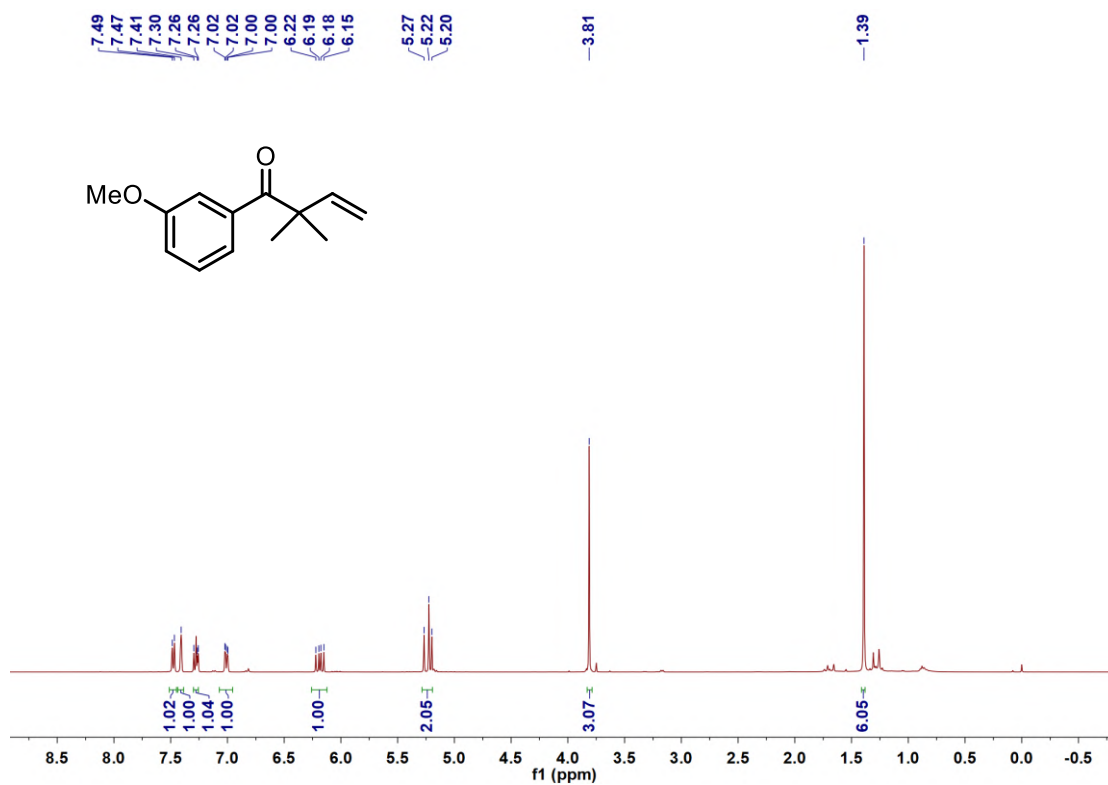
¹H NMR of Substrates **1d** (400 MHz, CDCl₃)



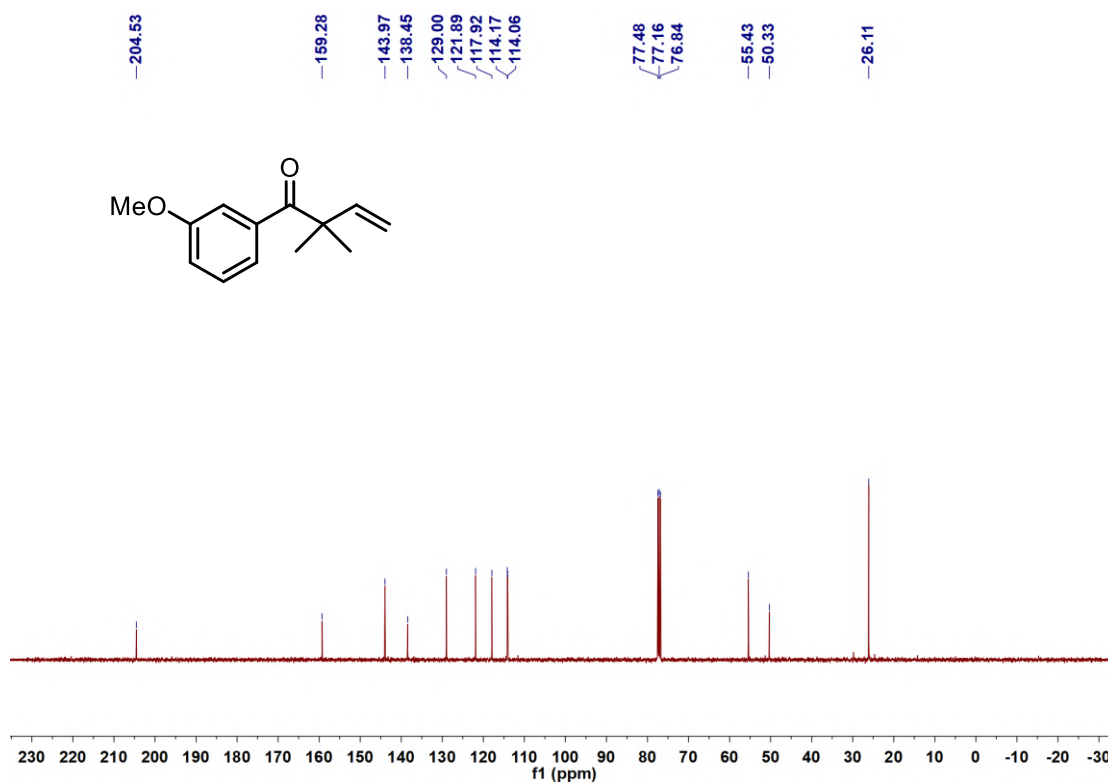
¹³C NMR of Substrates **1d** (101 MHz, CDCl₃)



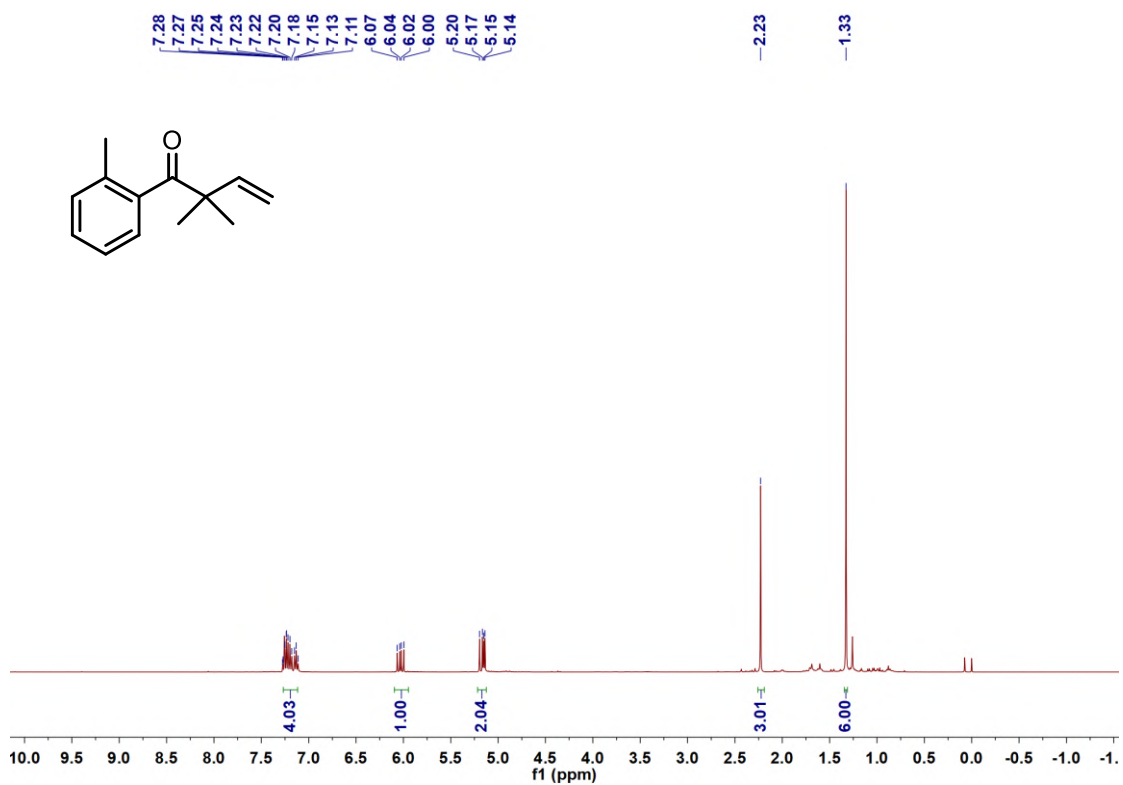
^1H NMR of Substrates **1i** (400 MHz, CDCl_3)



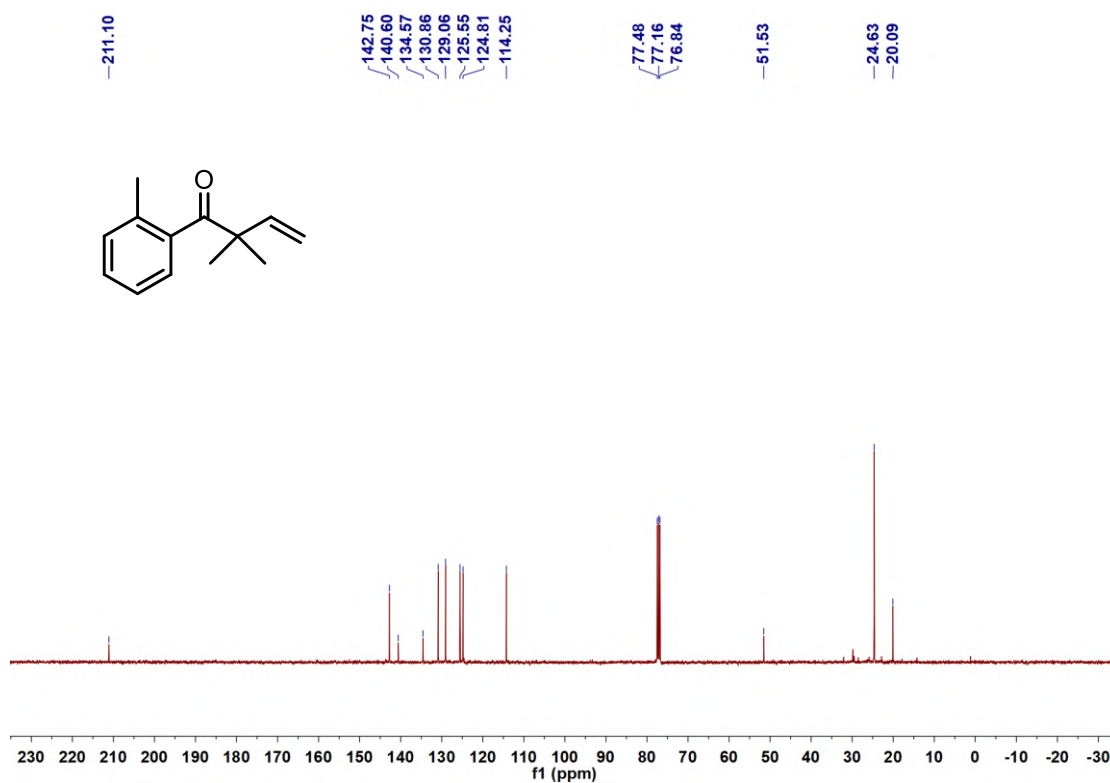
^{13}C NMR of Substrates **1i** (101 MHz, CDCl_3)



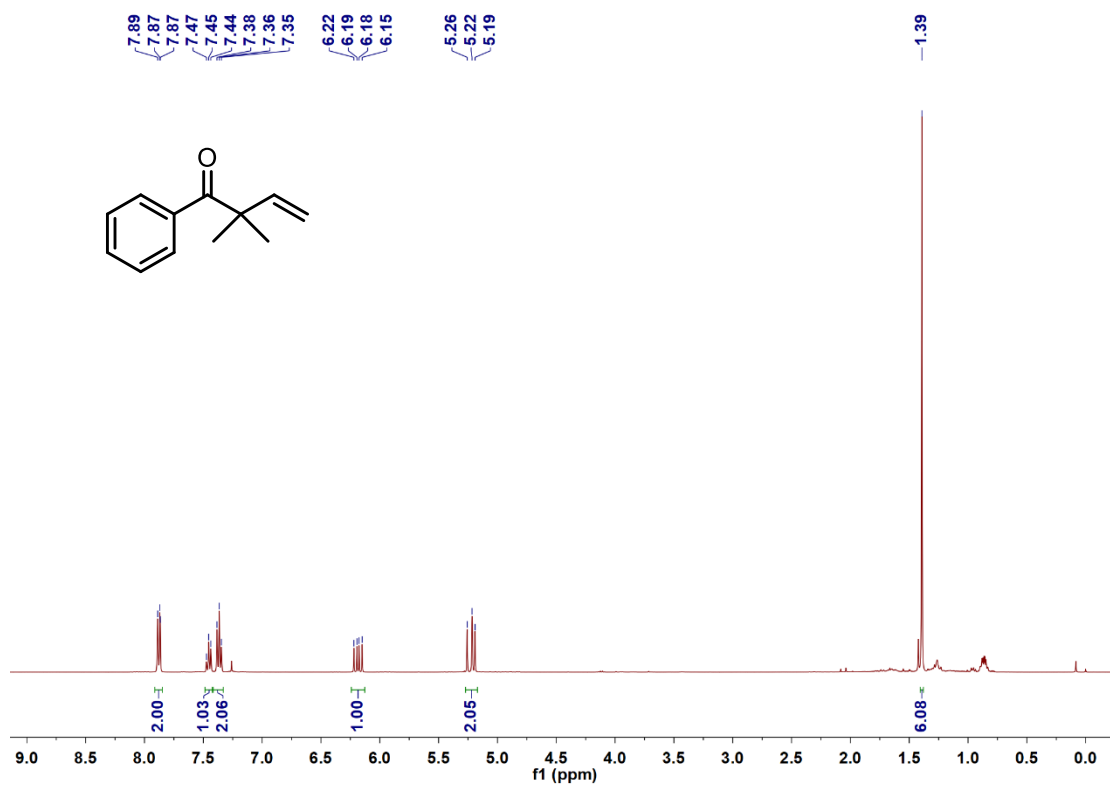
¹H NMR of Substrates **1j** (400 MHz, CDCl₃)



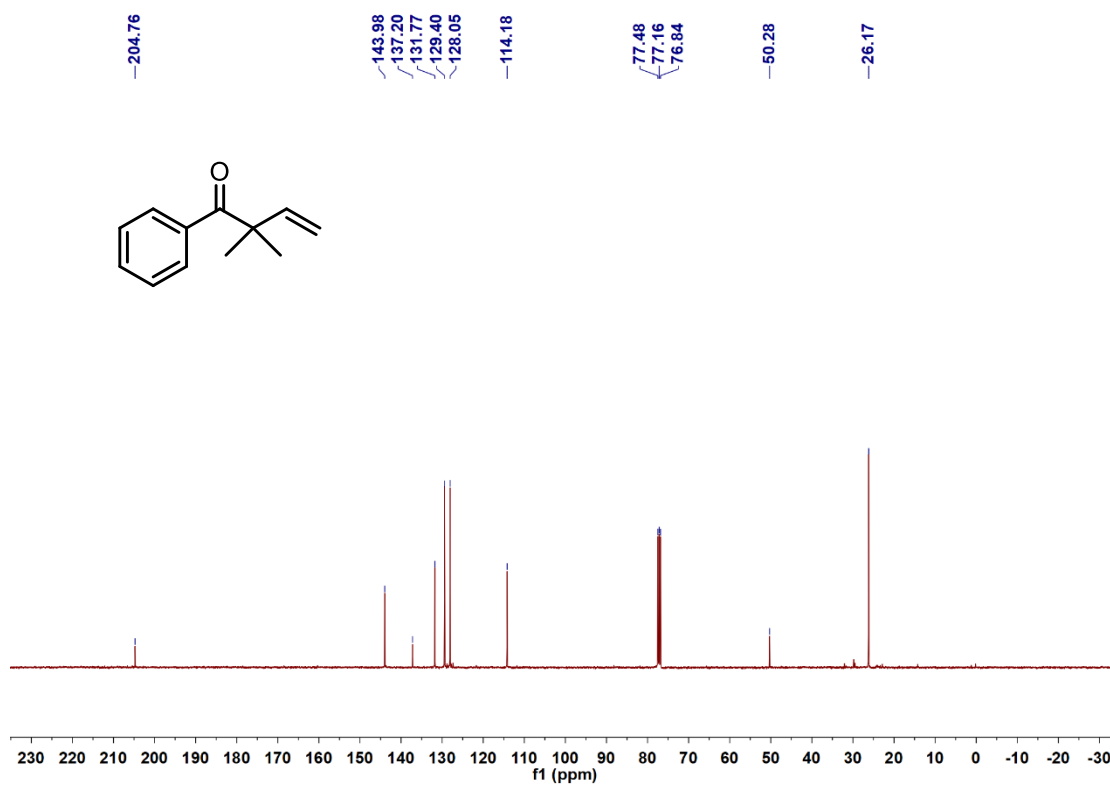
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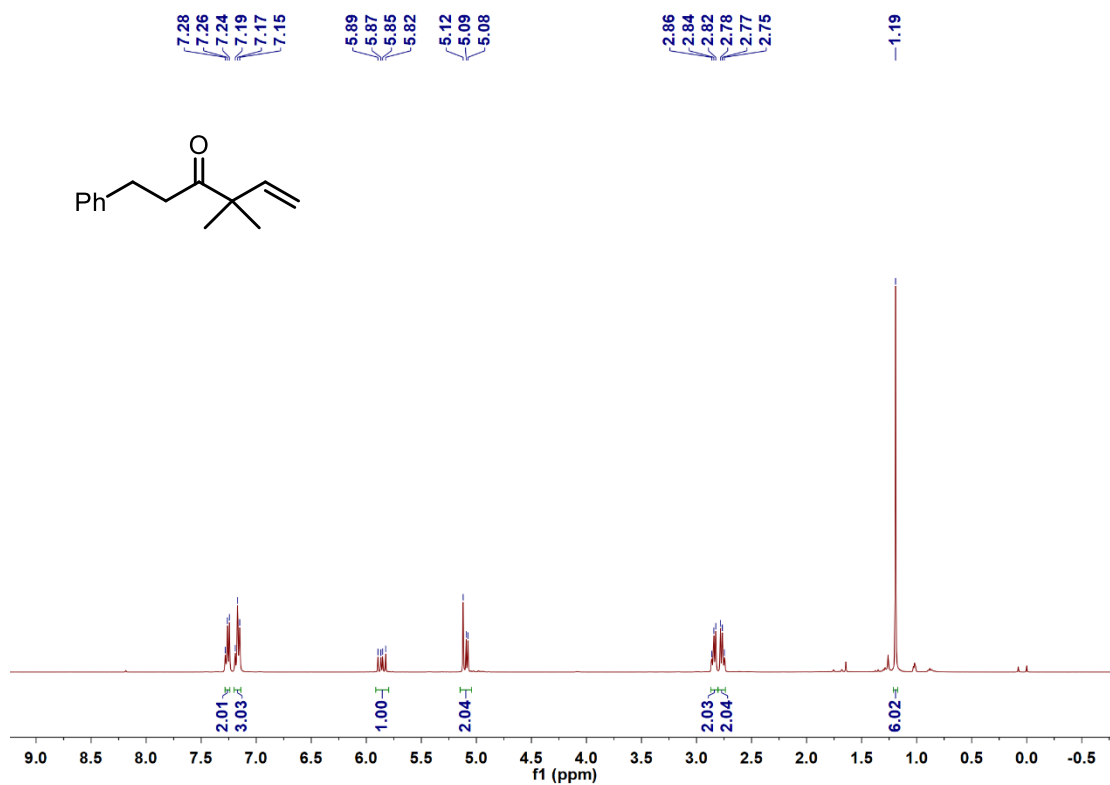
¹H NMR of Substrates **11** (400 MHz, CDCl₃)



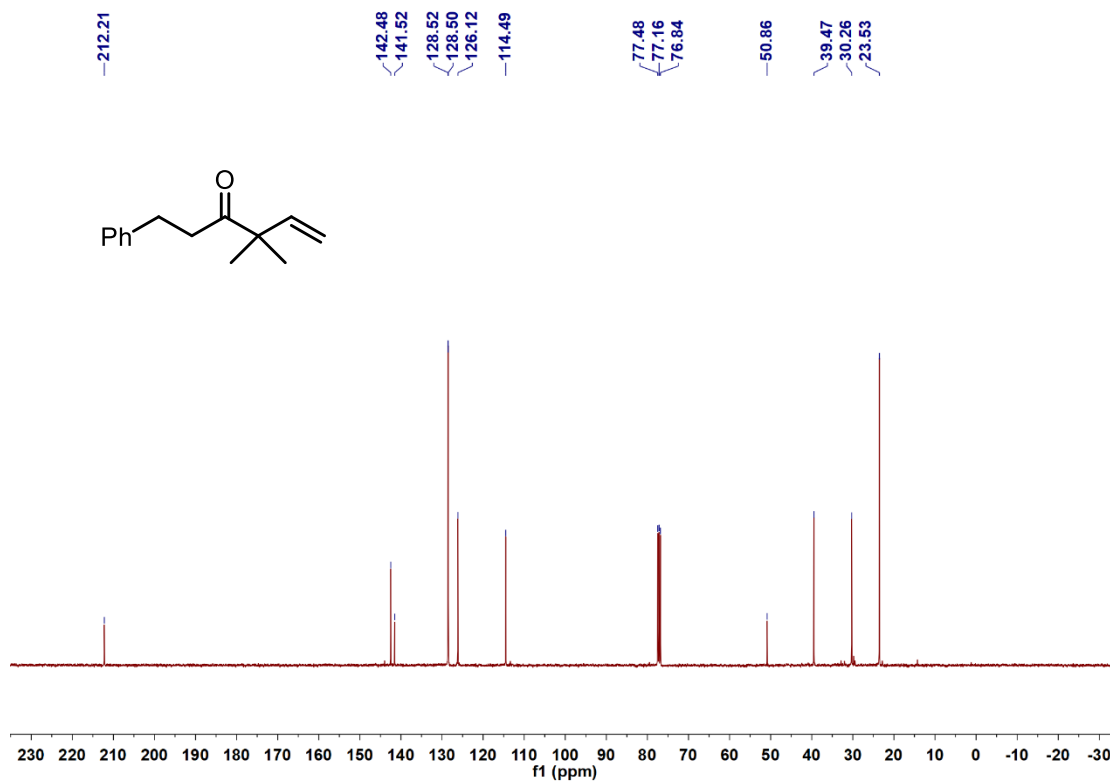
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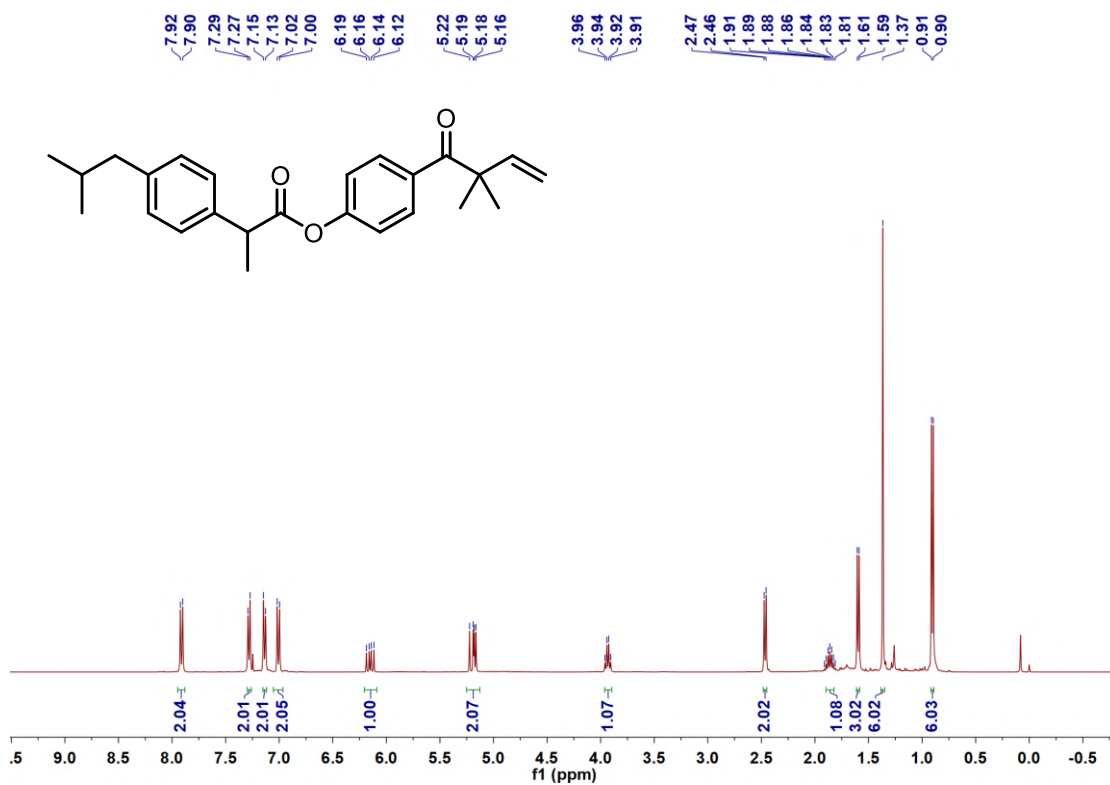
^1H NMR of Substrates **1o** (400 MHz, CDCl_3)



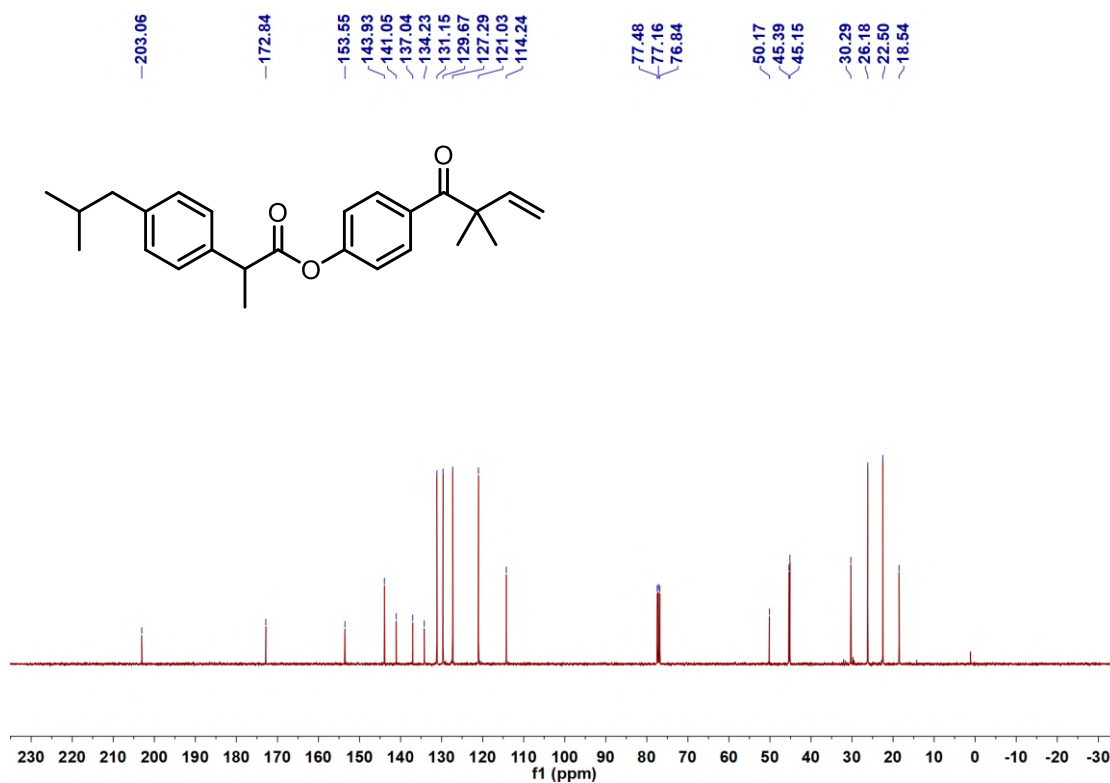
^{13}C NMR of Substrates **1o** (101 MHz, CDCl_3)



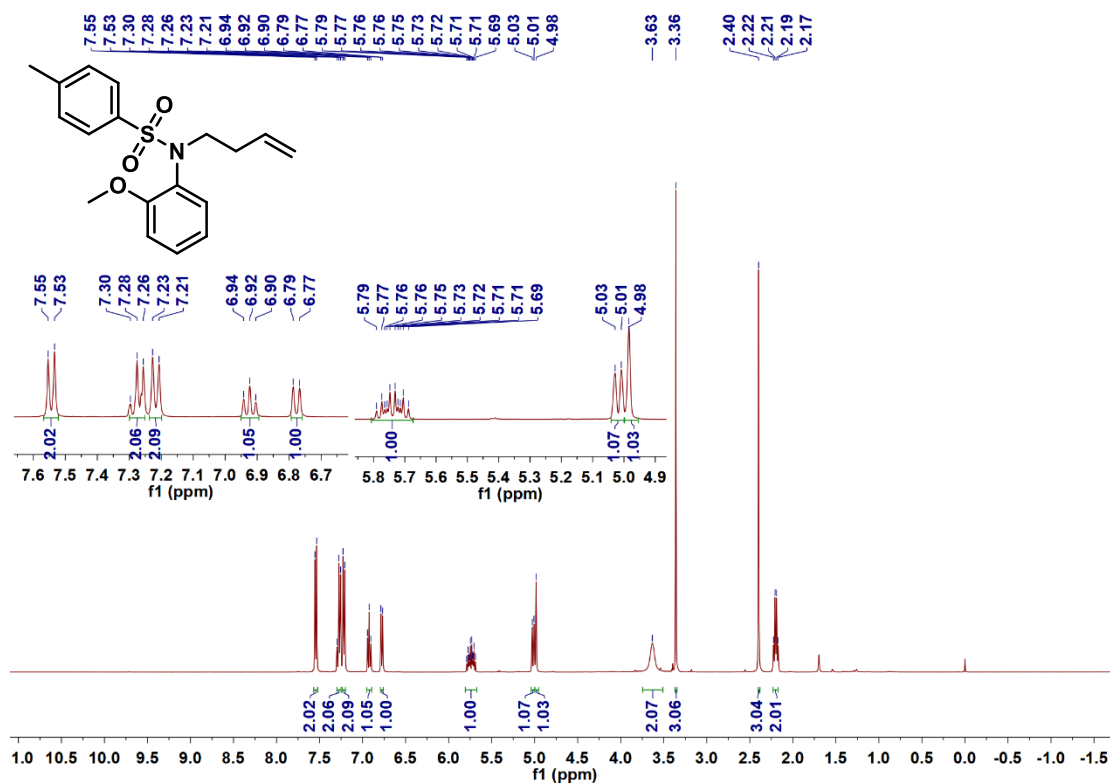
^1H NMR of Substrates **1p** (400 MHz, CDCl_3)



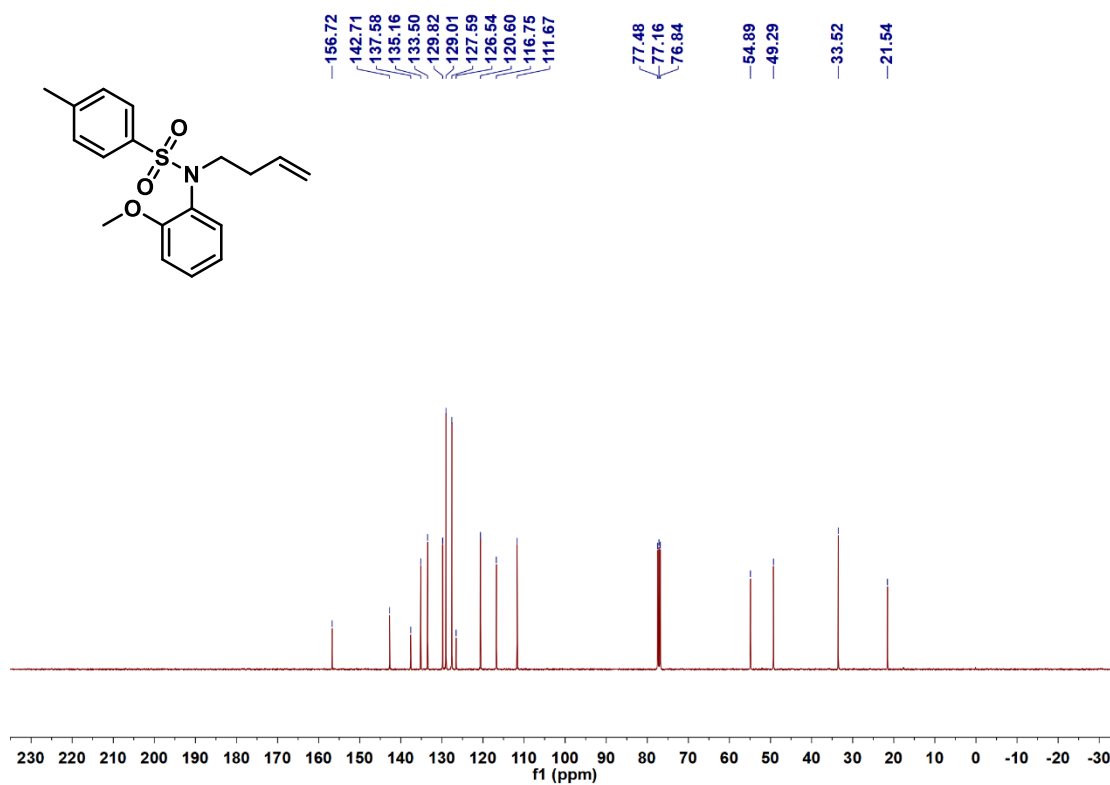
^{13}C NMR of Substrates **1p** (101 MHz, CDCl_3)



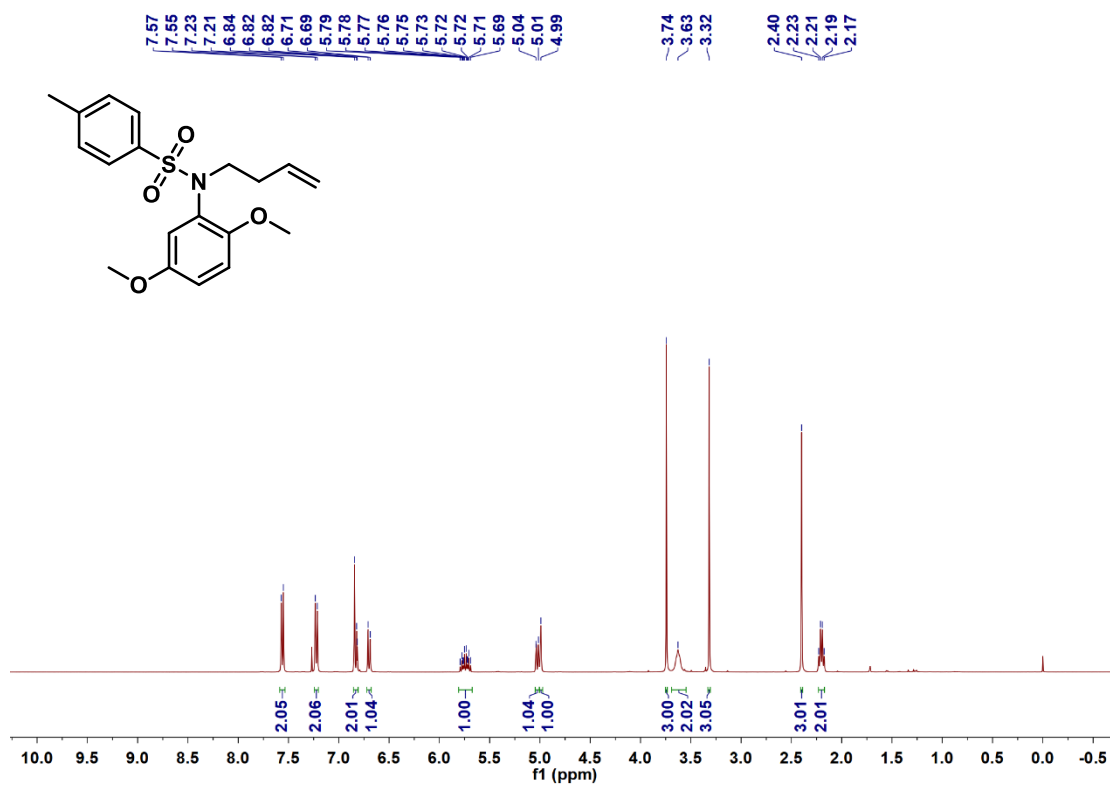
¹H NMR of Substrates **4a** (400 MHz, CDCl₃)



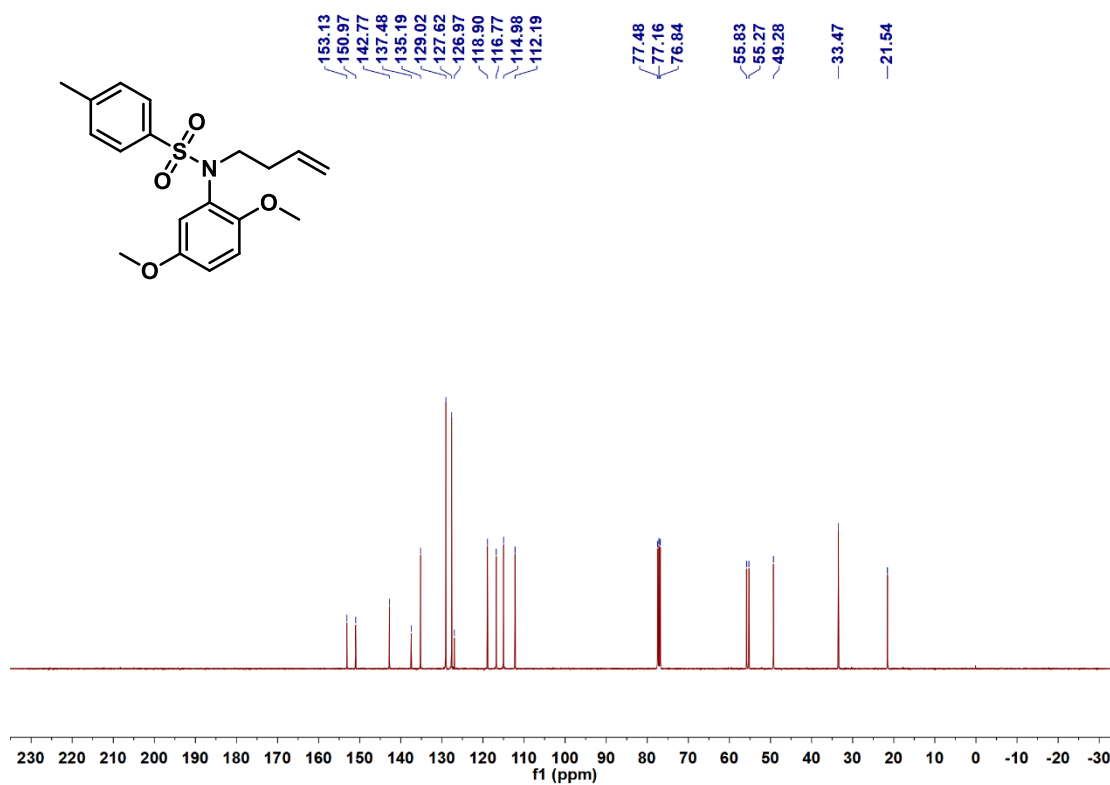
¹³C NMR of Substrates **4a** (101 MHz, CDCl₃)



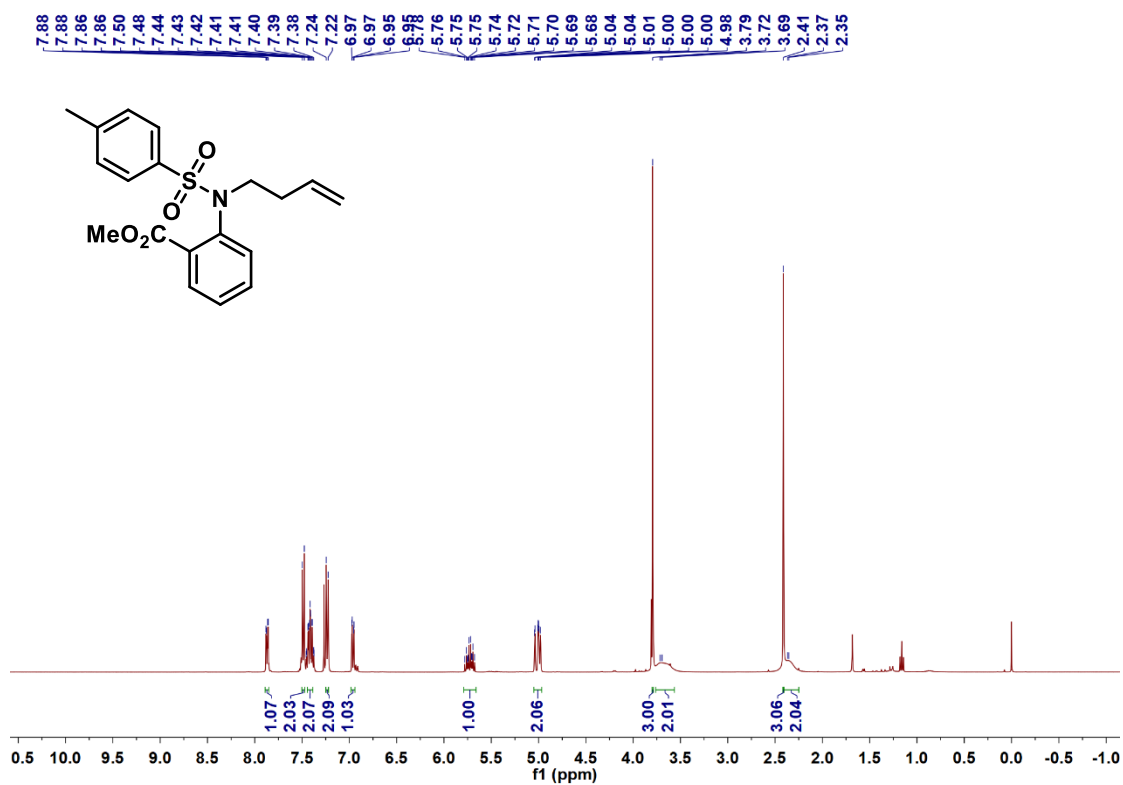
¹H NMR of Substrates **4c** (400 MHz, CDCl₃)



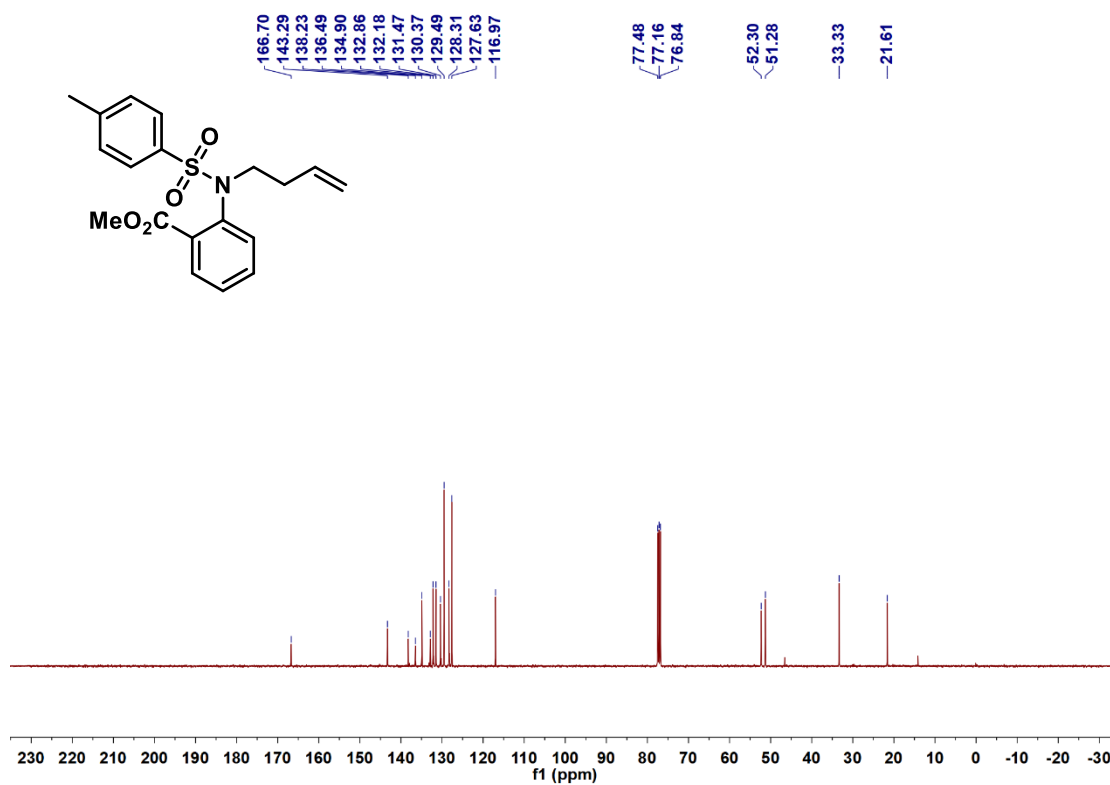
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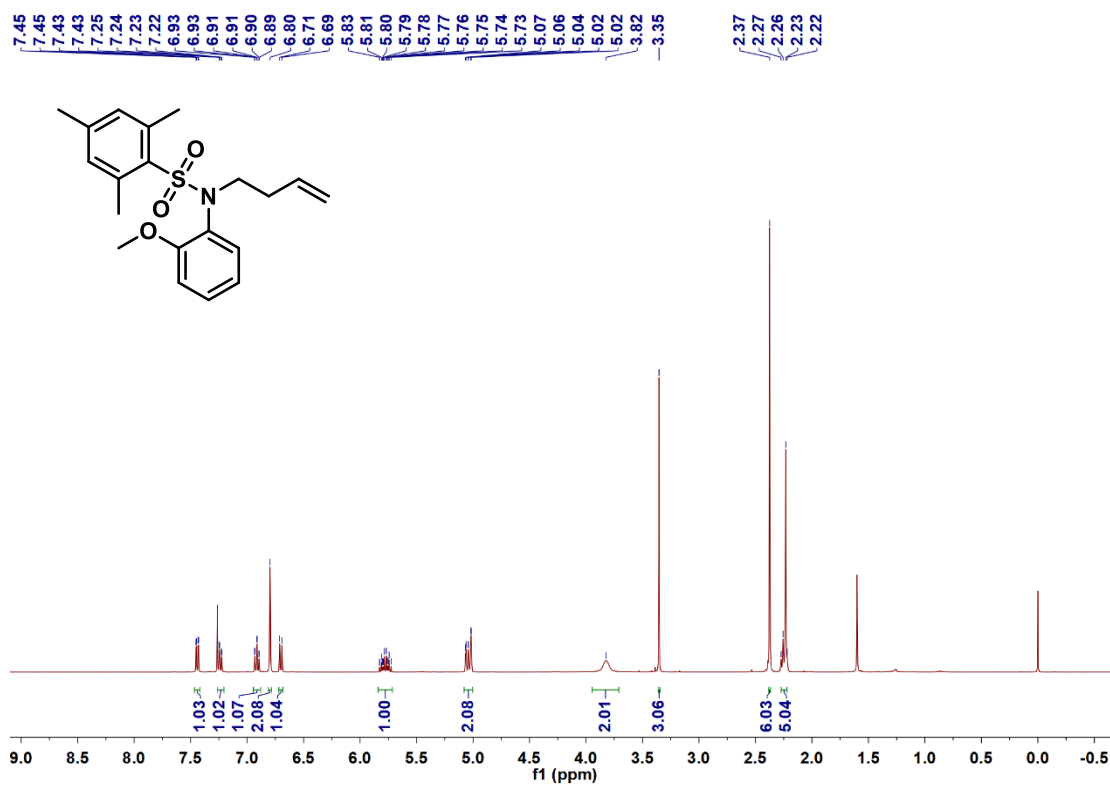
¹H NMR of Substrates **4f** (400 MHz, CDCl₃)



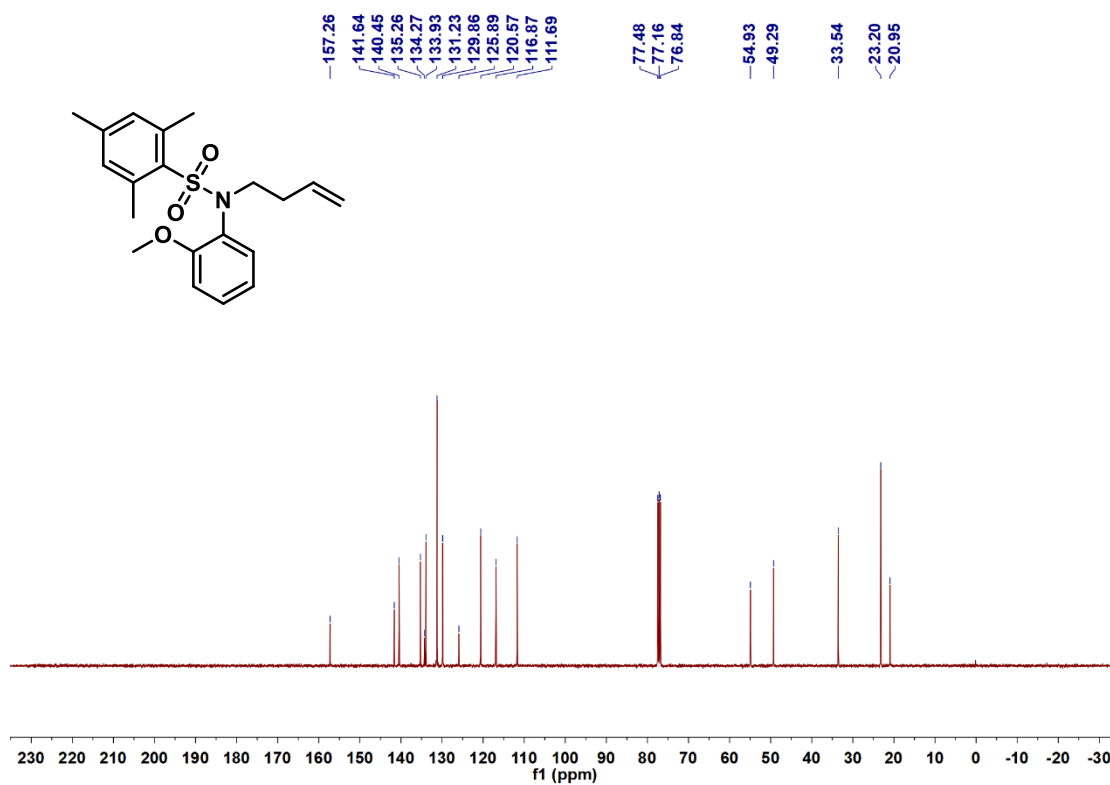
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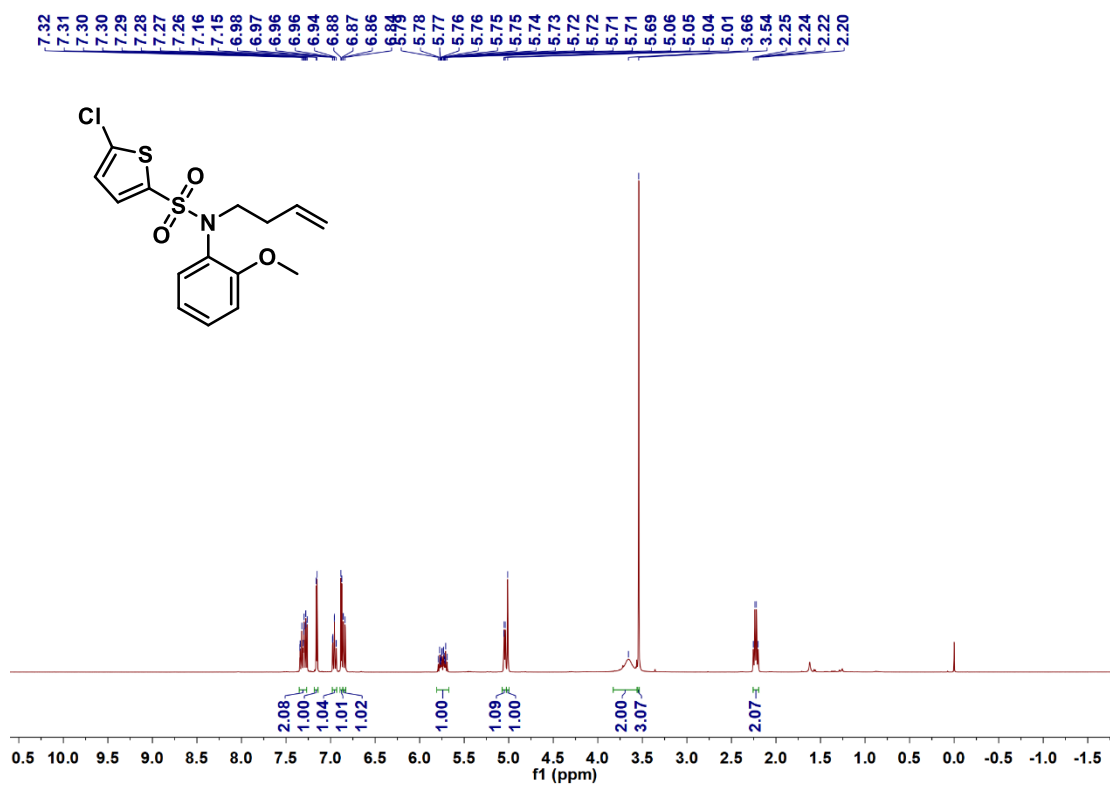
¹H NMR of Substrates **4m** (400 MHz, CDCl₃)



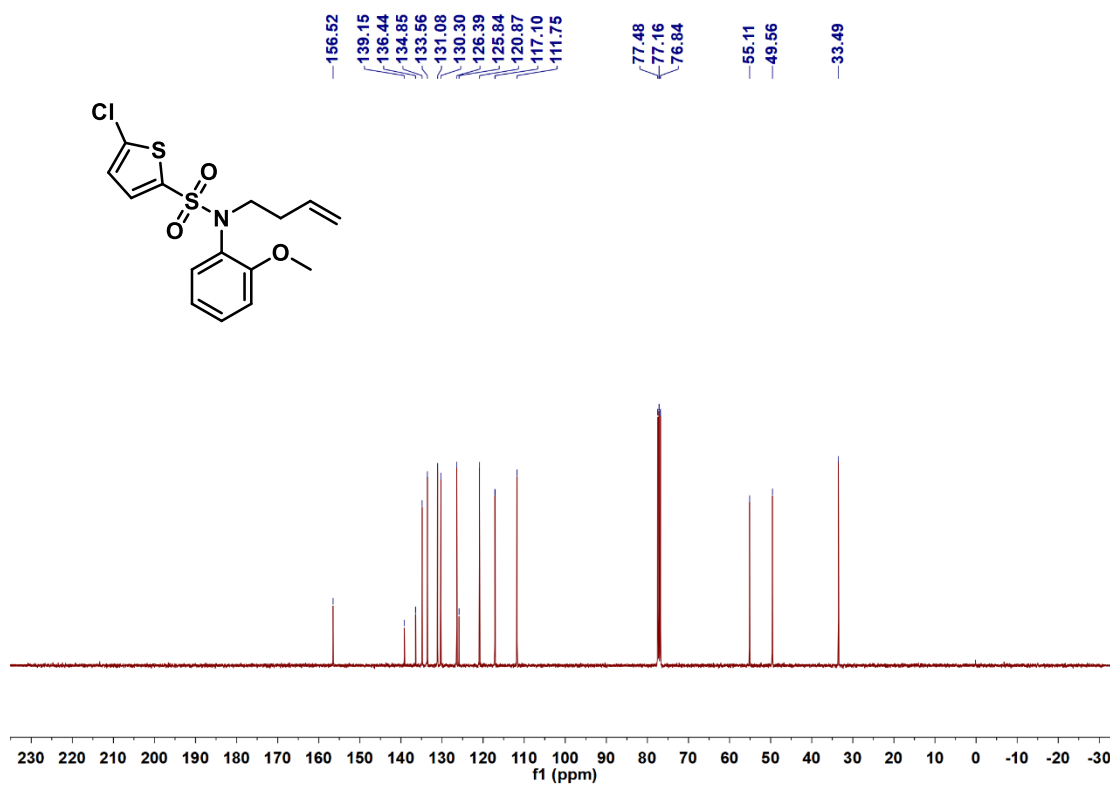
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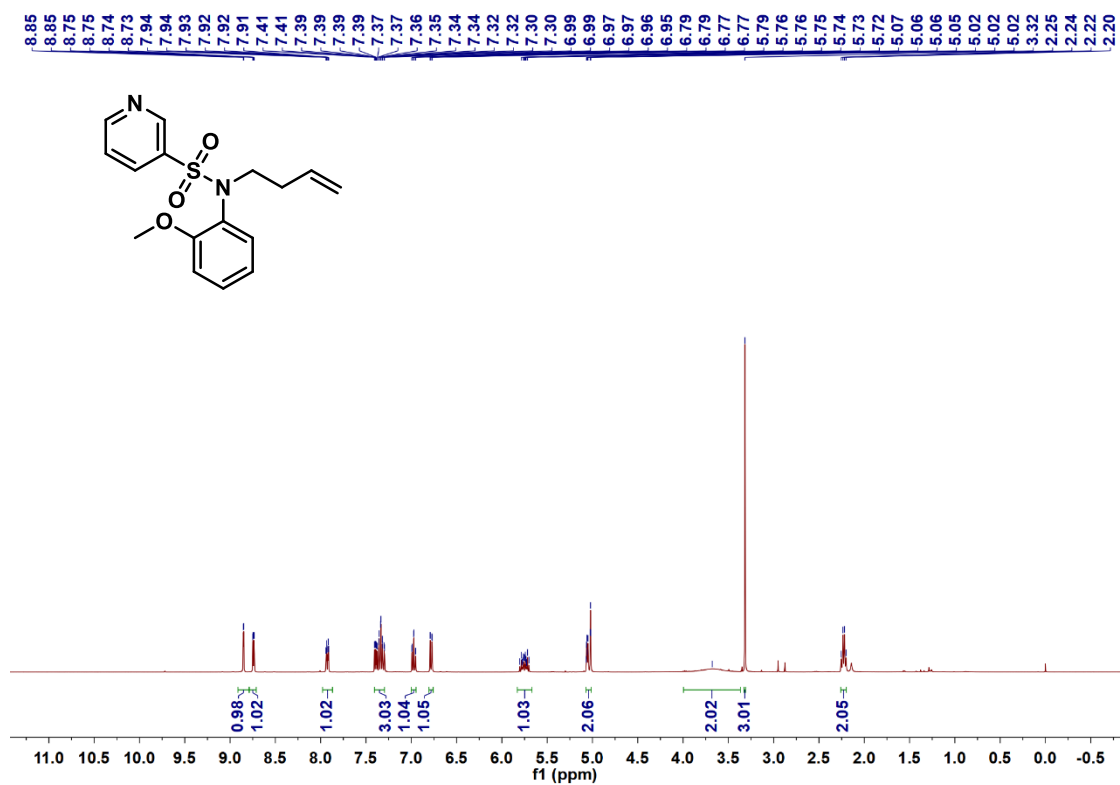
¹H NMR of Substrates **4n** (400 MHz, CDCl₃)



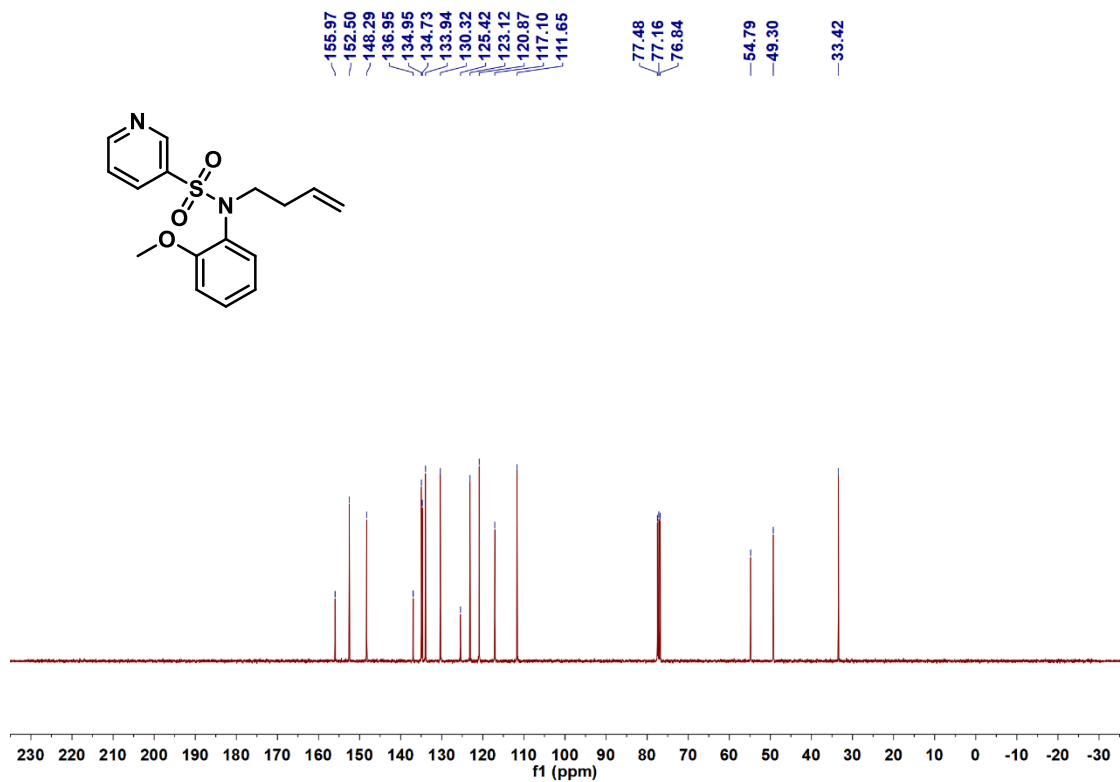
¹³C NMR of Substrates **4n** (101 MHz, CDCl₃)



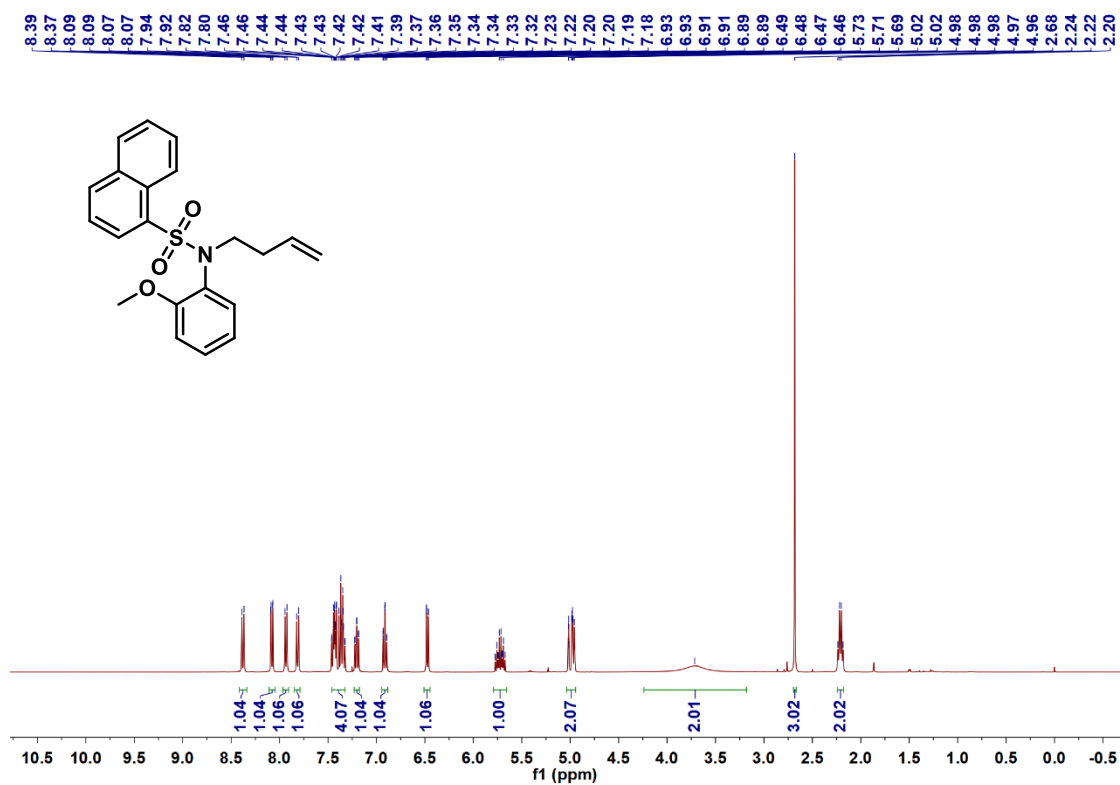
¹H NMR of Substrates **4o** (400 MHz, CDCl₃)



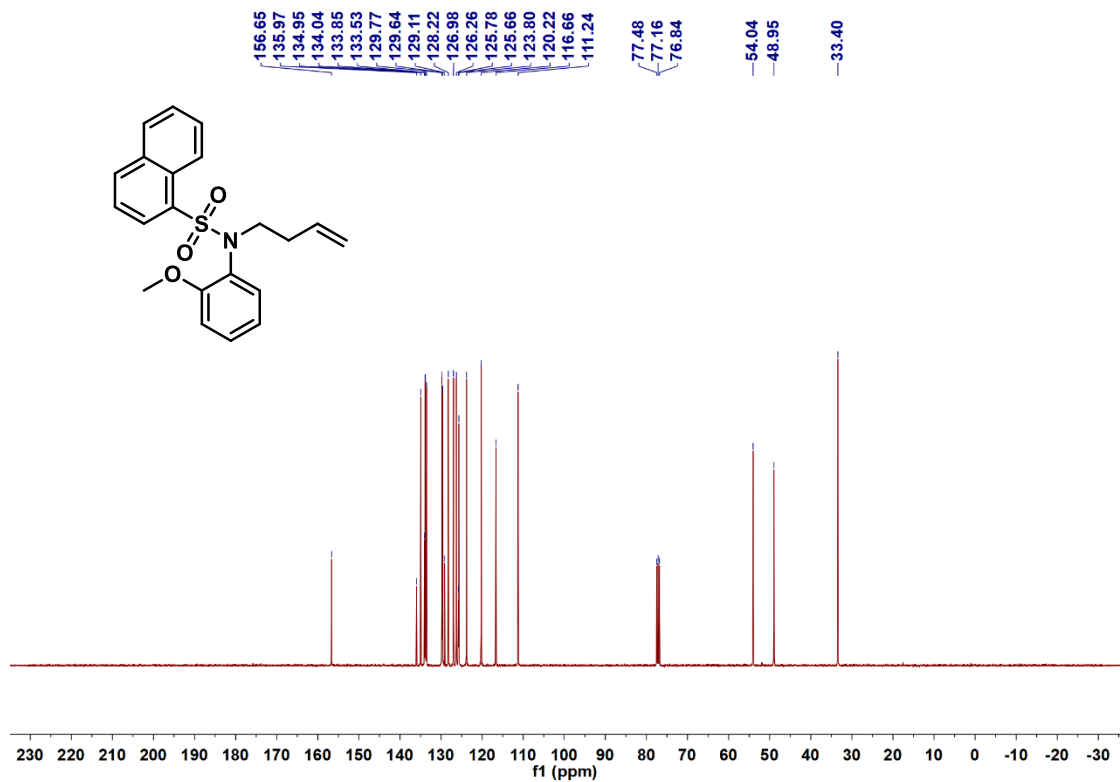
¹³C NMR of Substrates **4o** (101 MHz, CDCl₃)



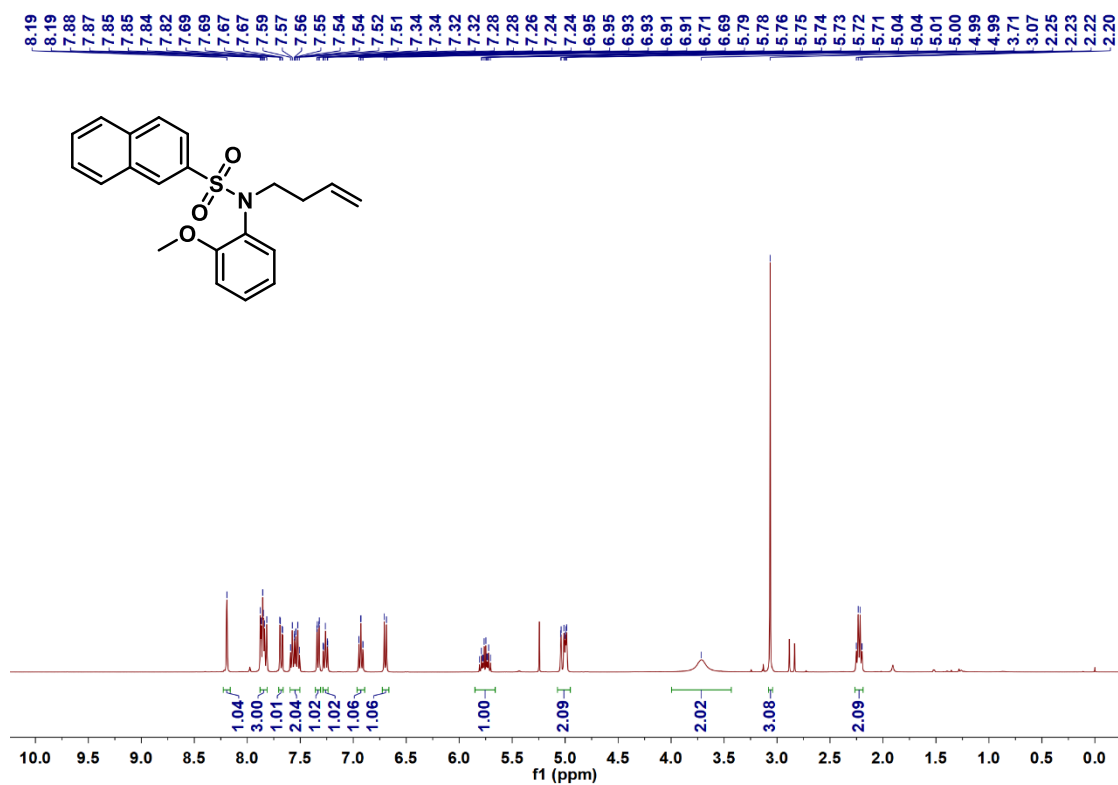
¹H NMR of Substrates **4p** (400 MHz, CDCl₃)



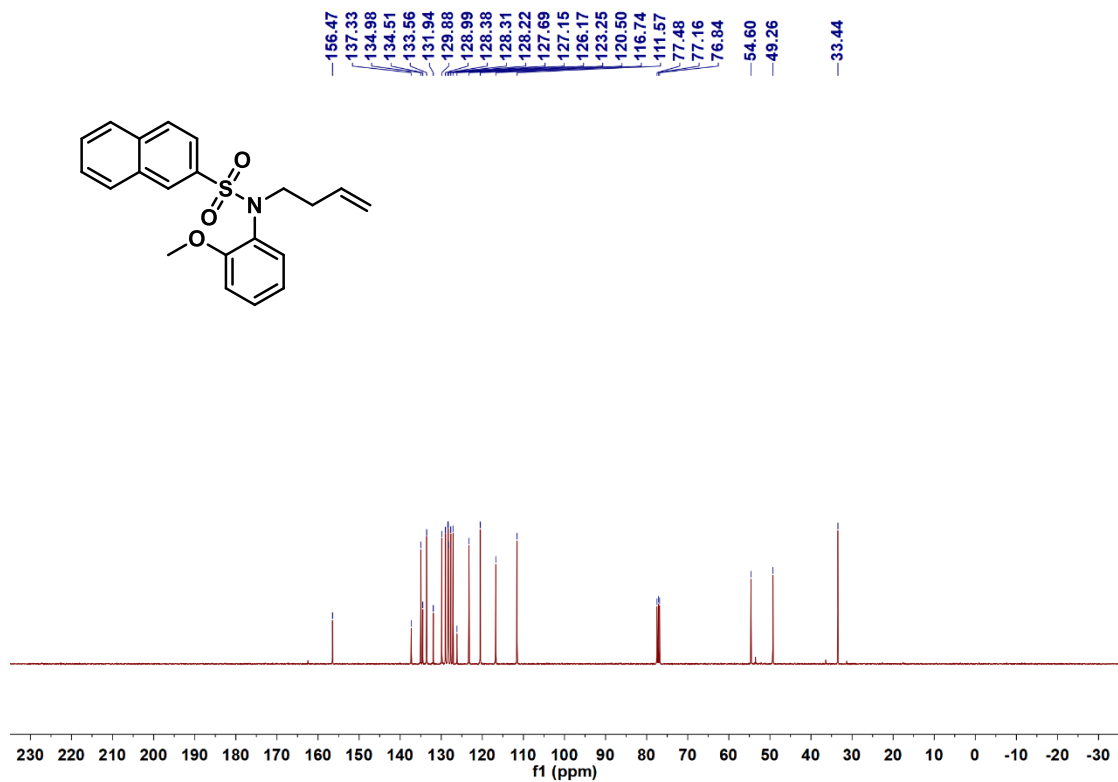
¹³C NMR of Substrates **4p** (101 MHz, CDCl₃)



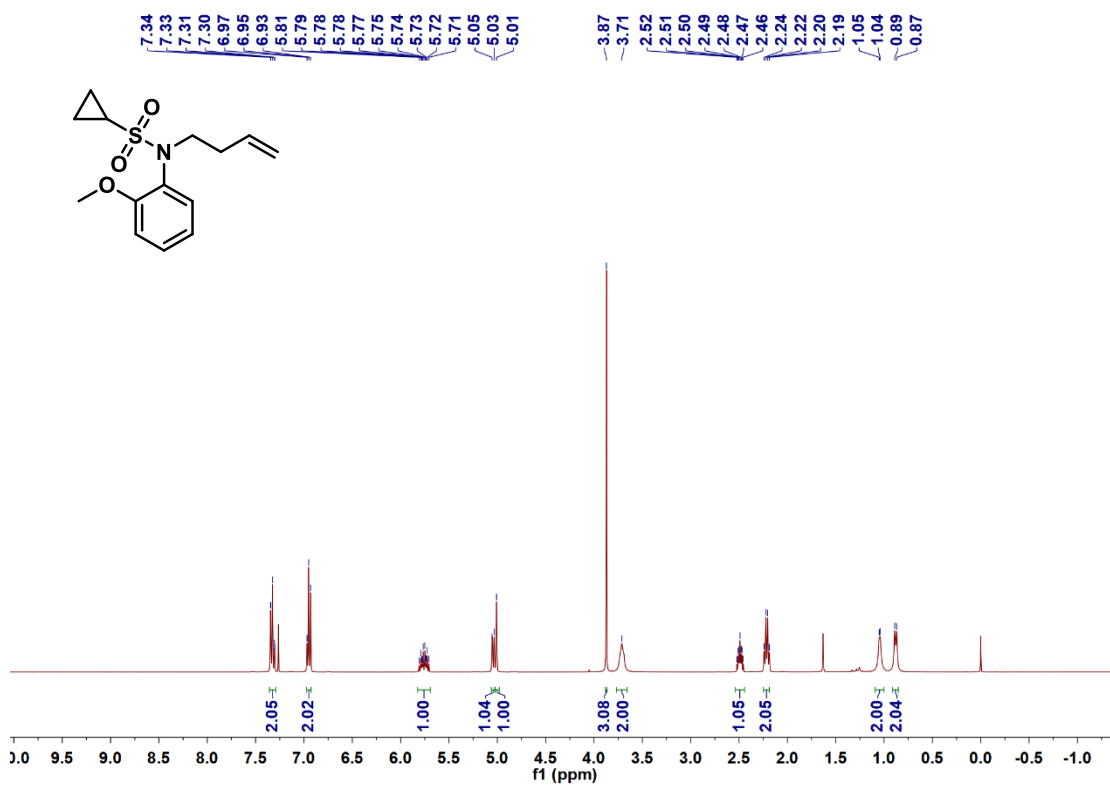
¹H NMR of Substrates **4q** (400 MHz, CDCl₃)



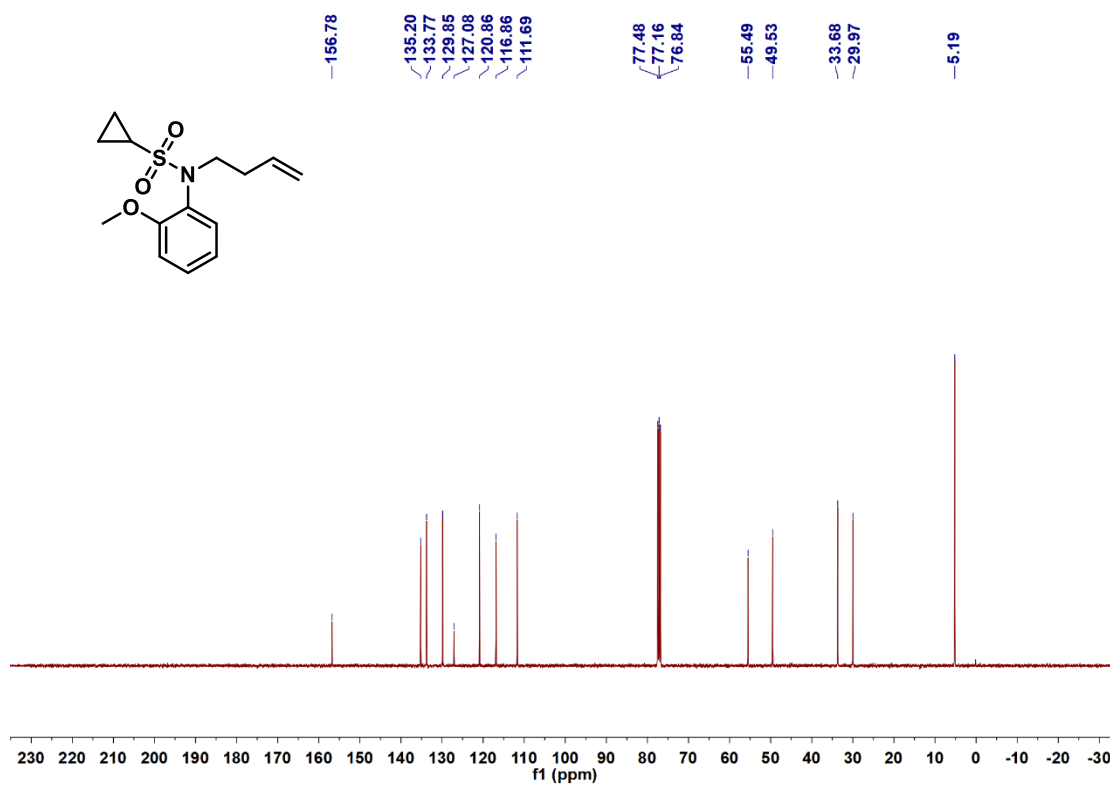
¹³C NMR of Substrates **4q** (101 MHz, CDCl₃)



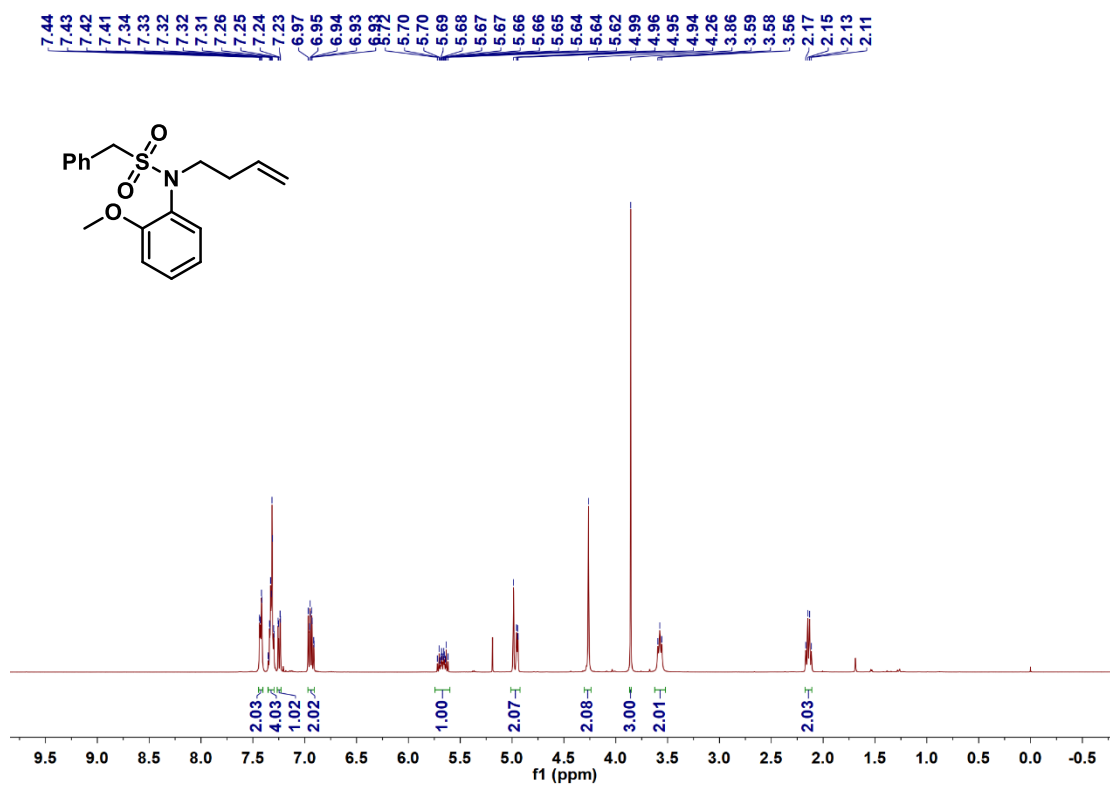
¹H NMR of Substrates **4r** (400 MHz, CDCl₃)



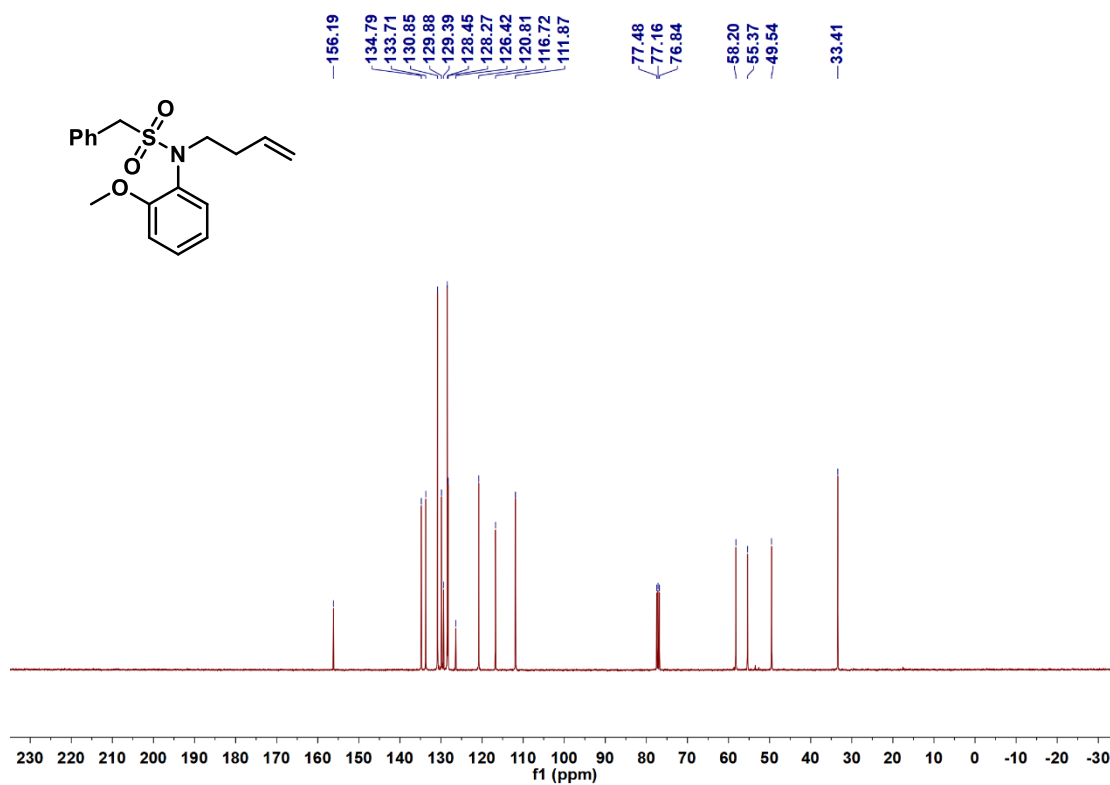
¹³C NMR of Substrates **4r** (101 MHz, CDCl₃)



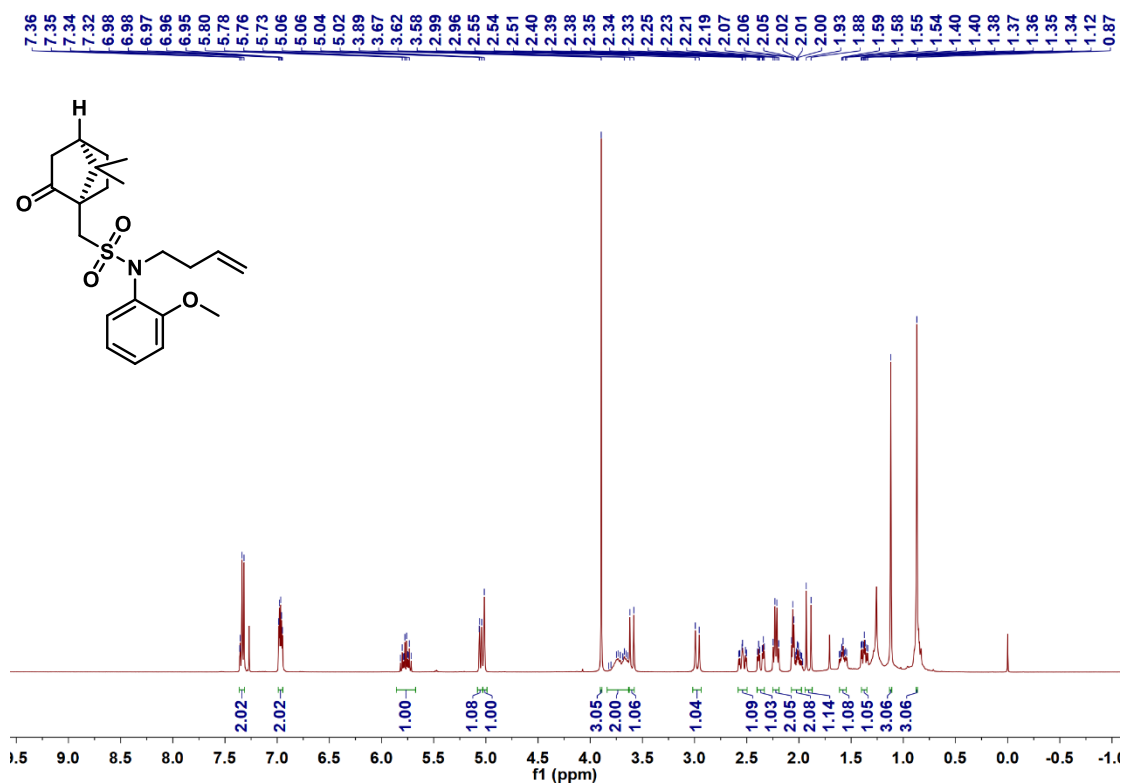
¹H NMR of Substrates **4s** (400 MHz, CDCl₃)



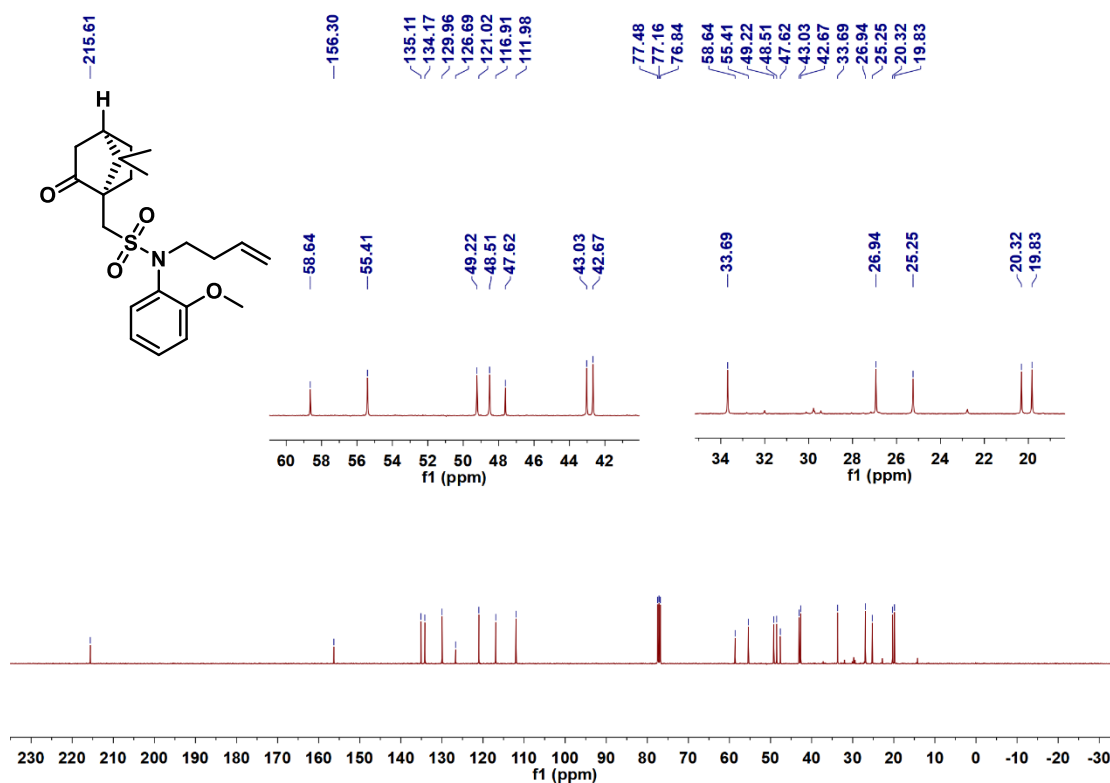
¹³C NMR of Substrates **4s** (101 MHz, CDCl₃)



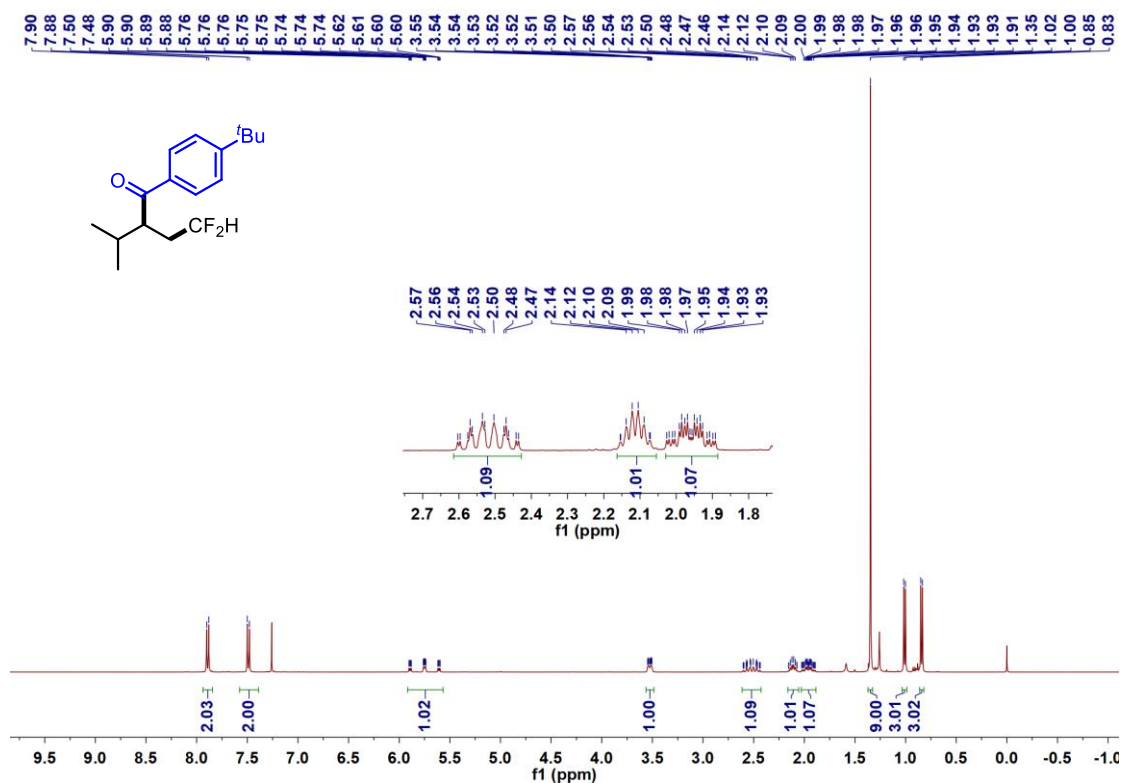
¹H NMR of Substrates **4t** (400 MHz, CDCl₃)



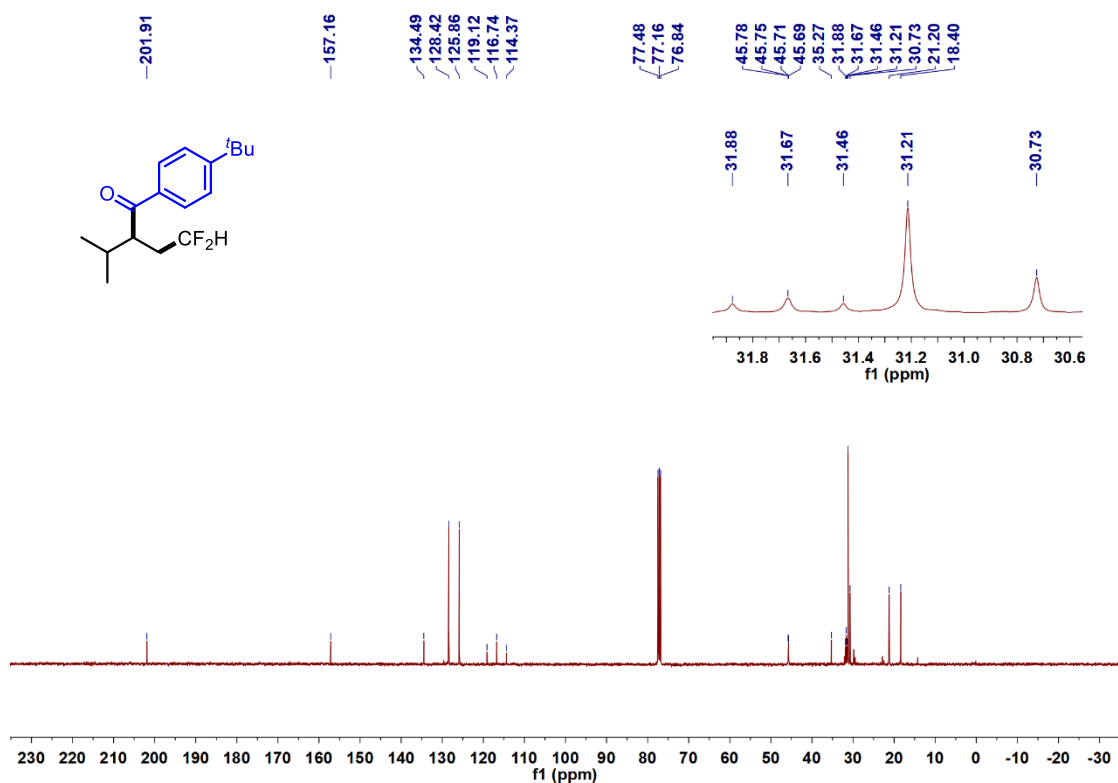
¹³C NMR of Substrates **4t** (101 MHz, CDCl₃)



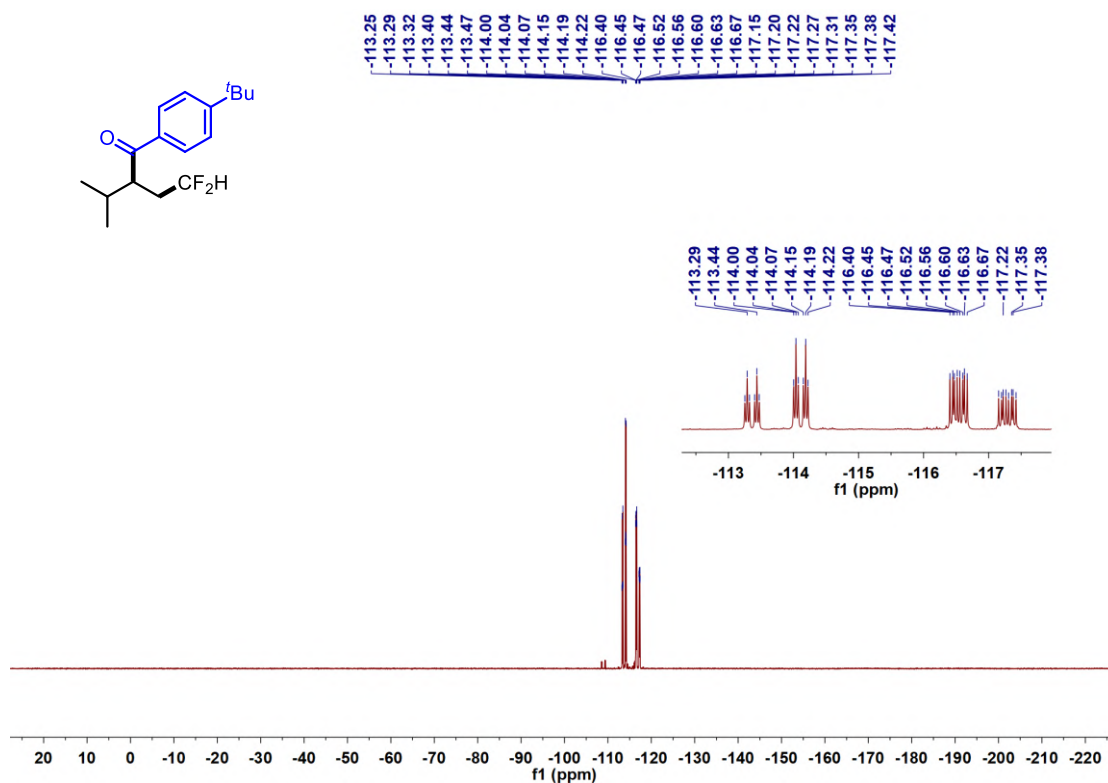
¹H NMR of Compound **3a** (400 MHz, CDCl₃)



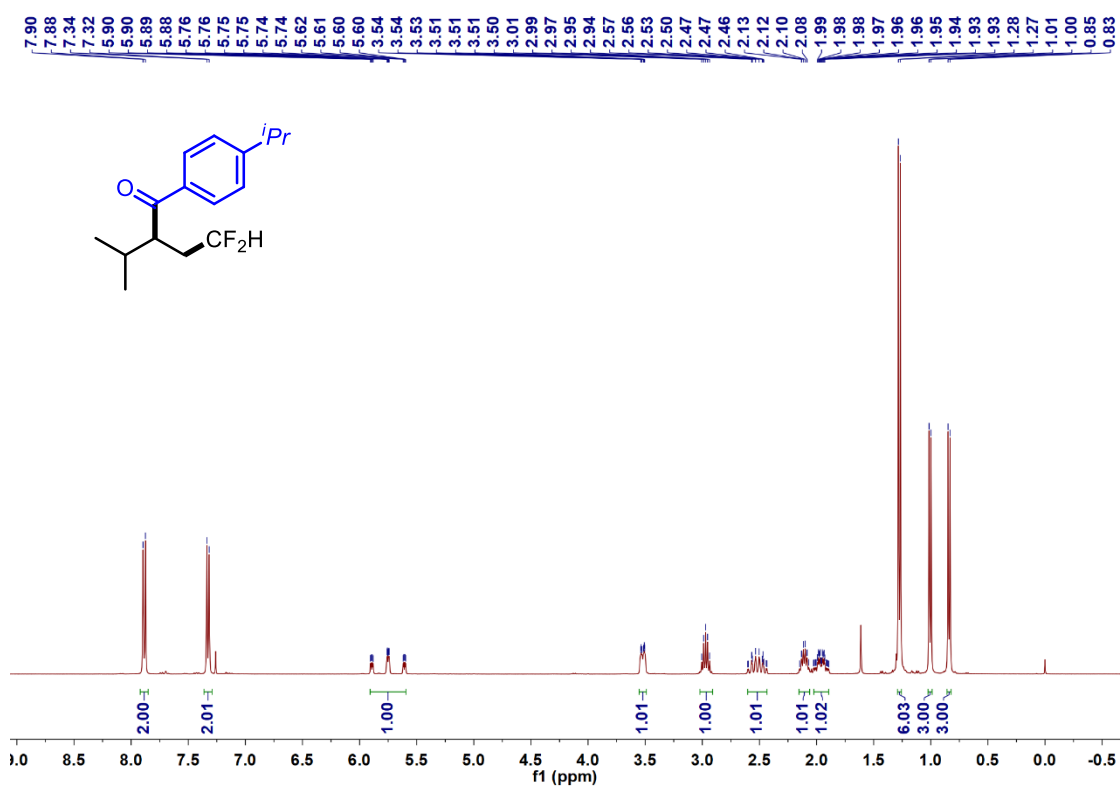
¹³C NMR of Compound **3a** (101 MHz, CDCl₃)



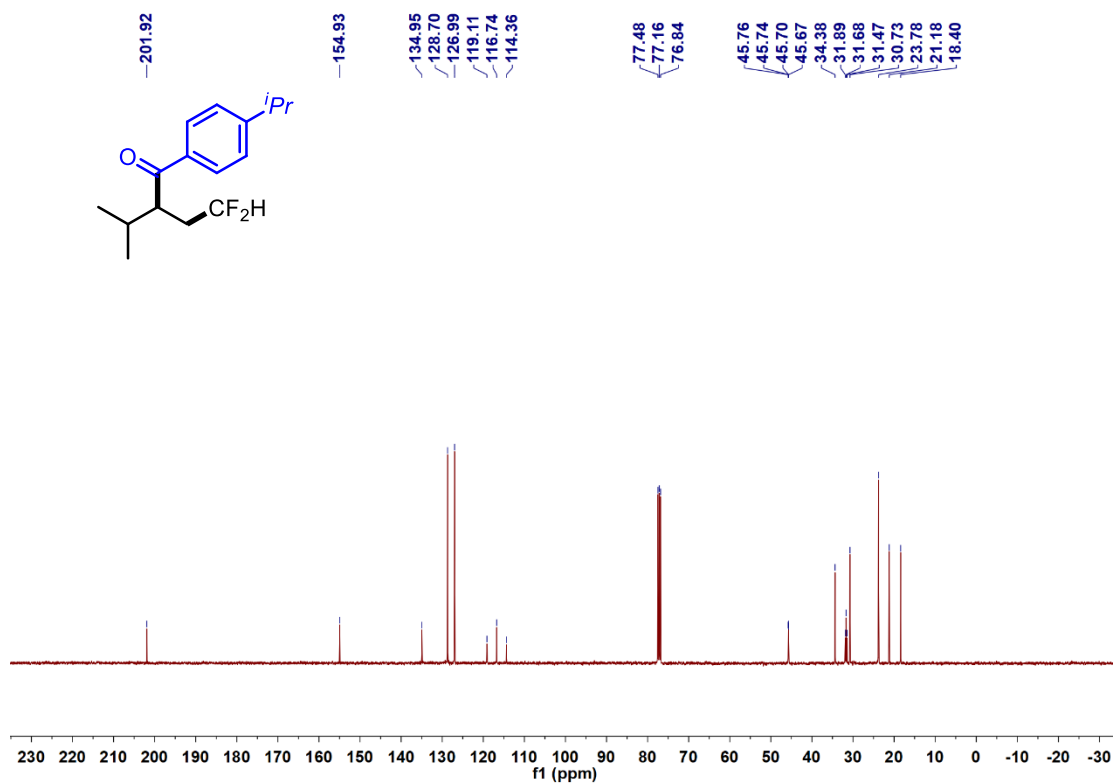
¹⁹F NMR of Compound **3a** (400 MHz, CDCl₃)



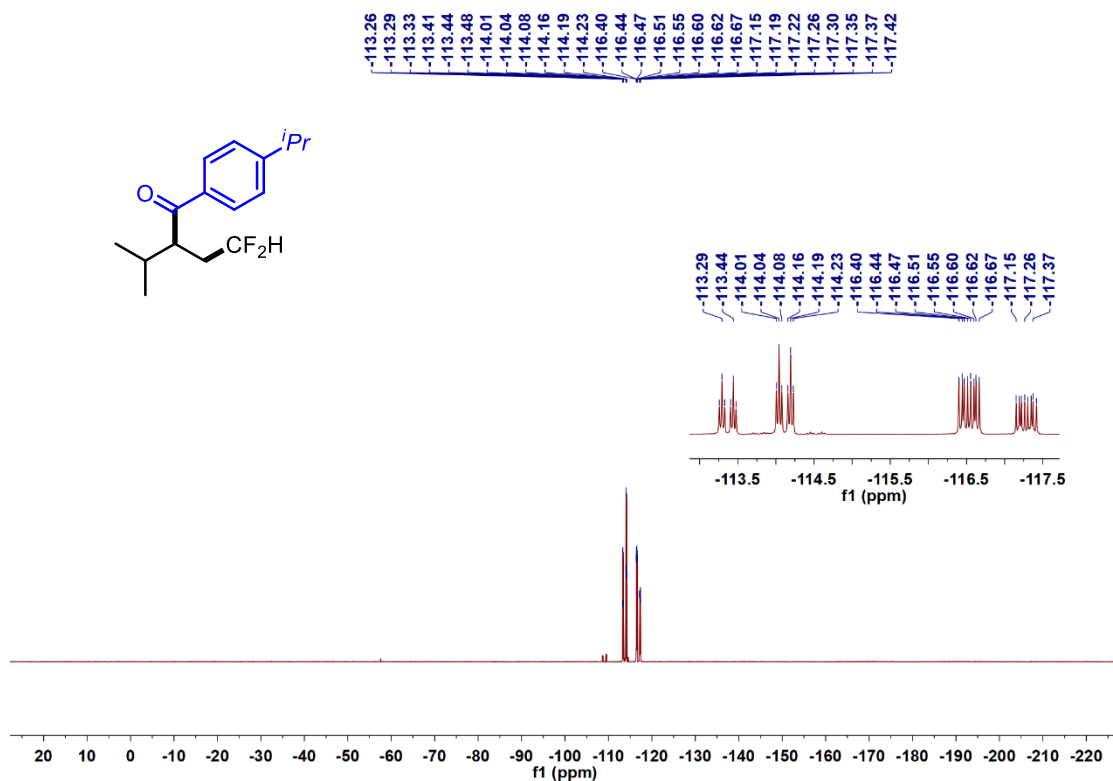
¹H NMR of Compound **3b** (400 MHz, CDCl₃)



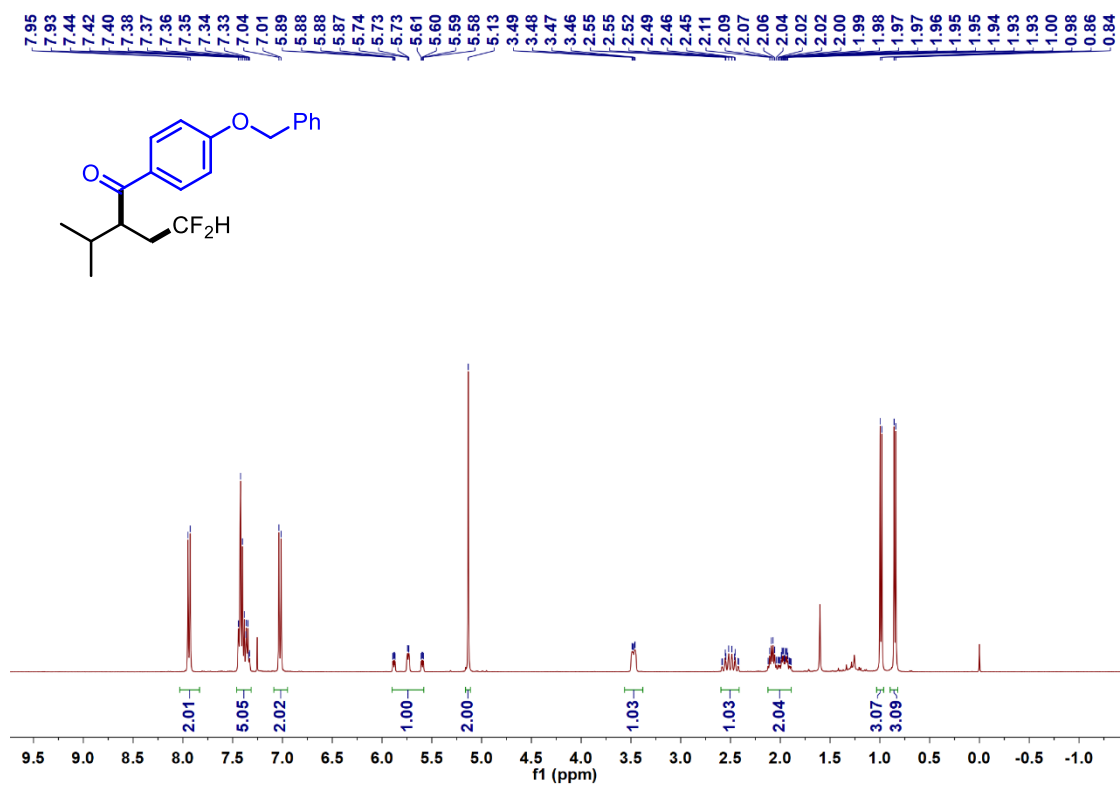
¹³C NMR of Compound **3b** (101 MHz, CDCl₃)



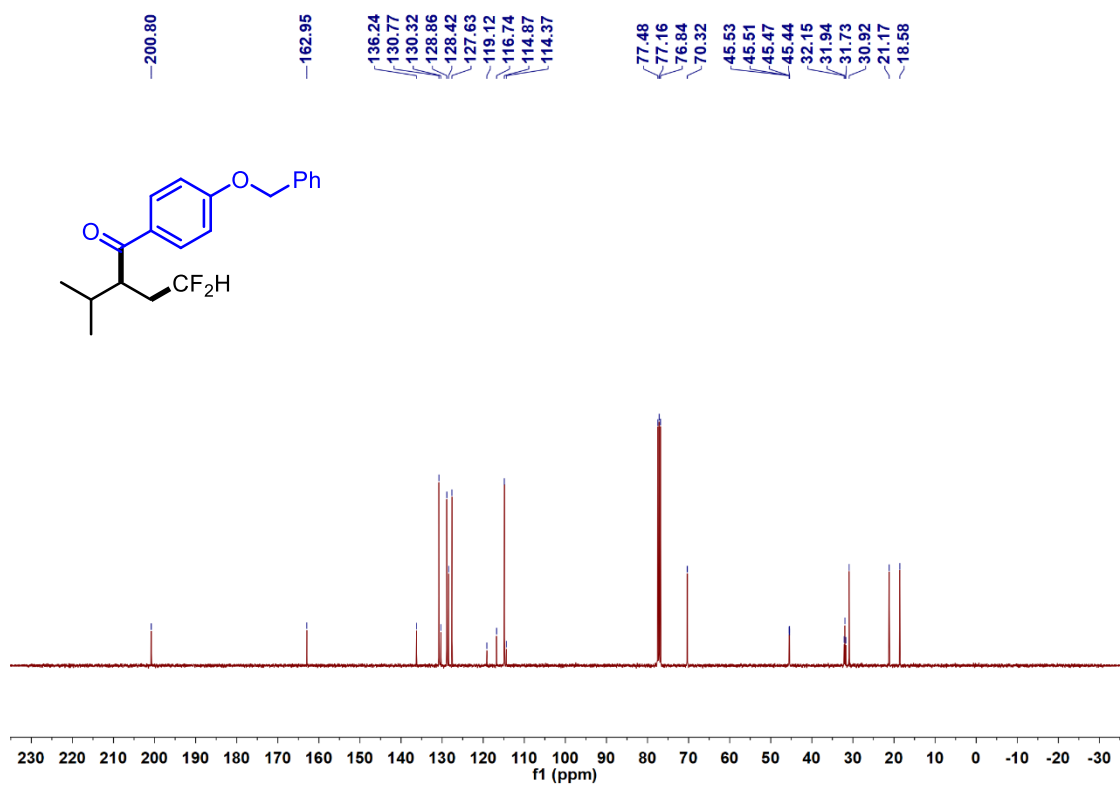
¹⁹F NMR of Compound **3b** (400 MHz, CDCl₃)



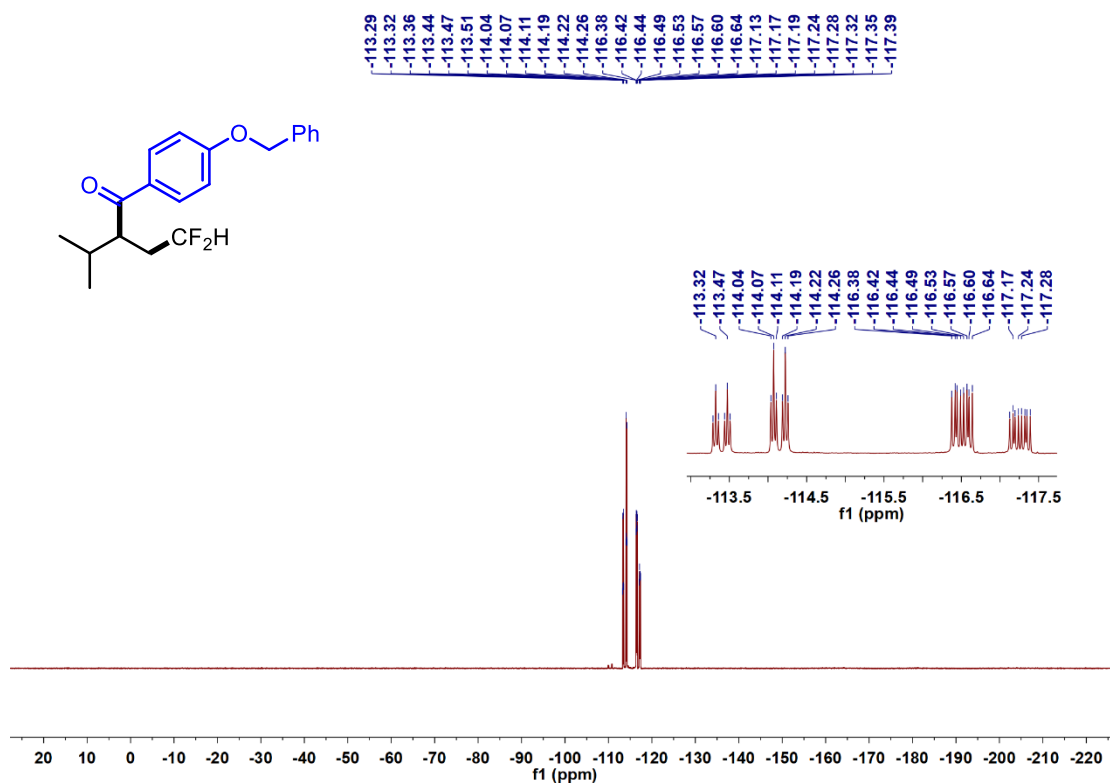
¹H NMR of Compound 3c (400 MHz, CDCl₃)



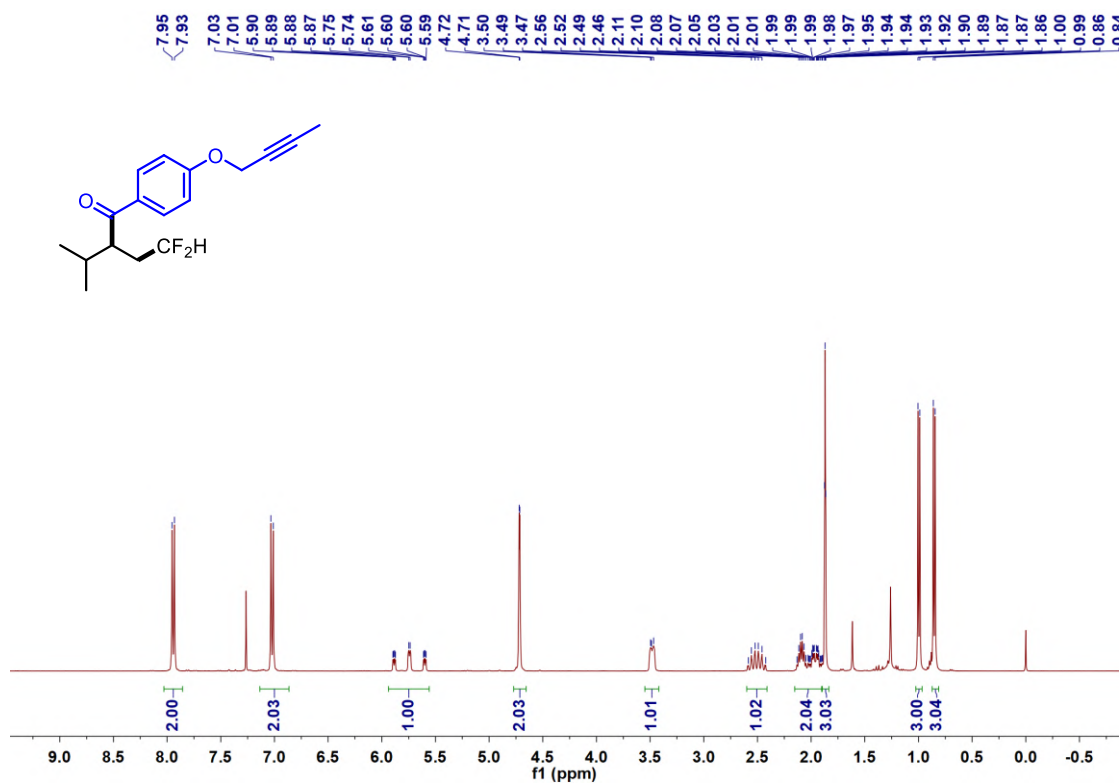
¹³C NMR of Compound 3c (101 MHz, CDCl₃)



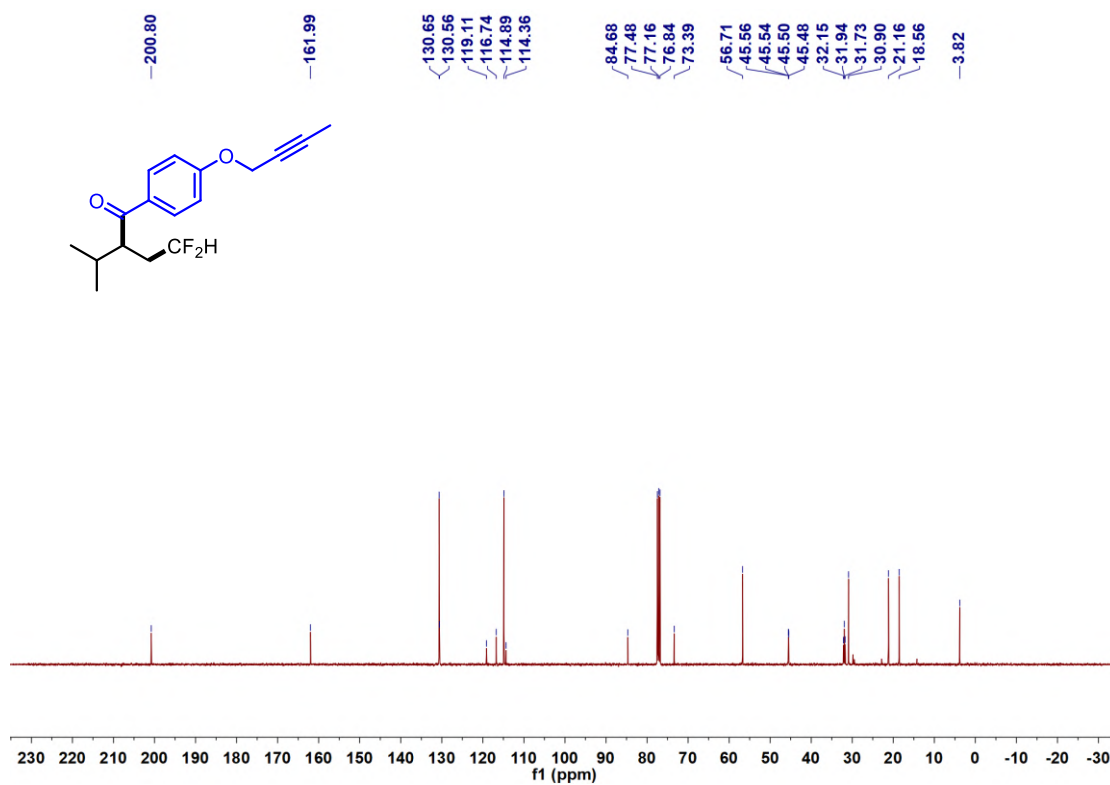
¹⁹F NMR of Compound **3c** (400 MHz, CDCl₃)



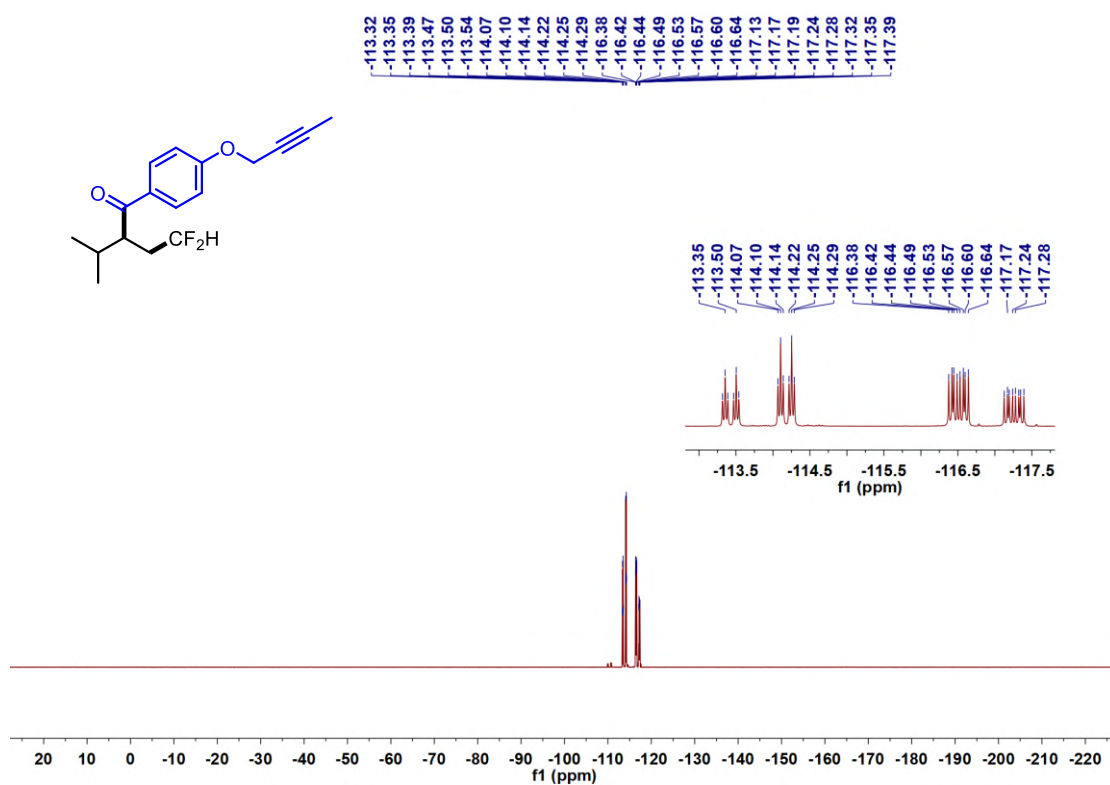
¹H NMR of Compound **3d** (400 MHz, CDCl₃)



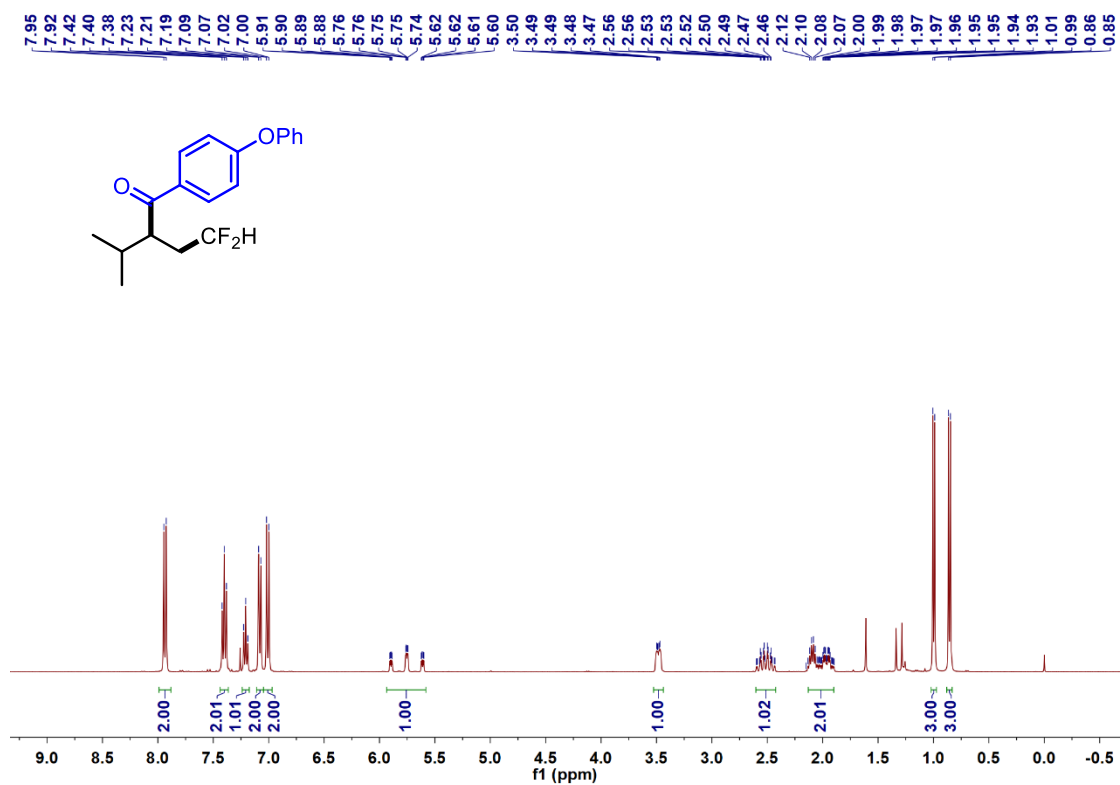
¹³C NMR of Compound **3d** (101 MHz, CDCl₃)



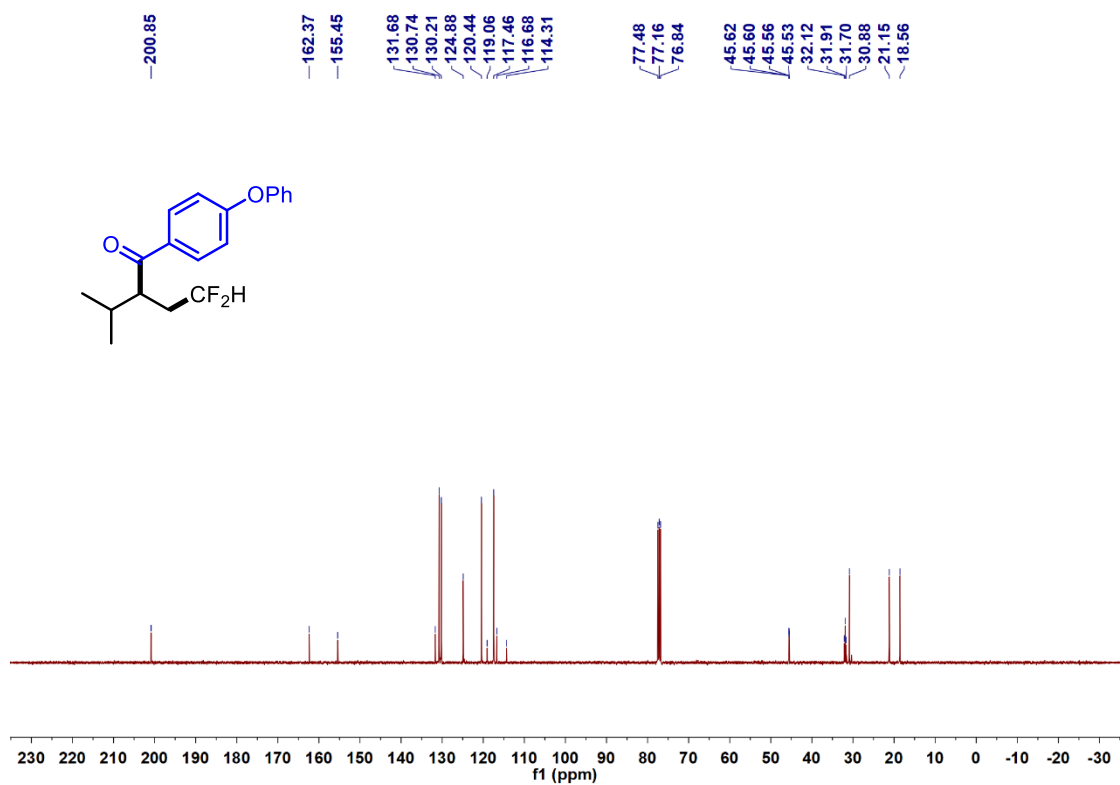
¹⁹F NMR of Compound **3d** (400 MHz, CDCl₃)



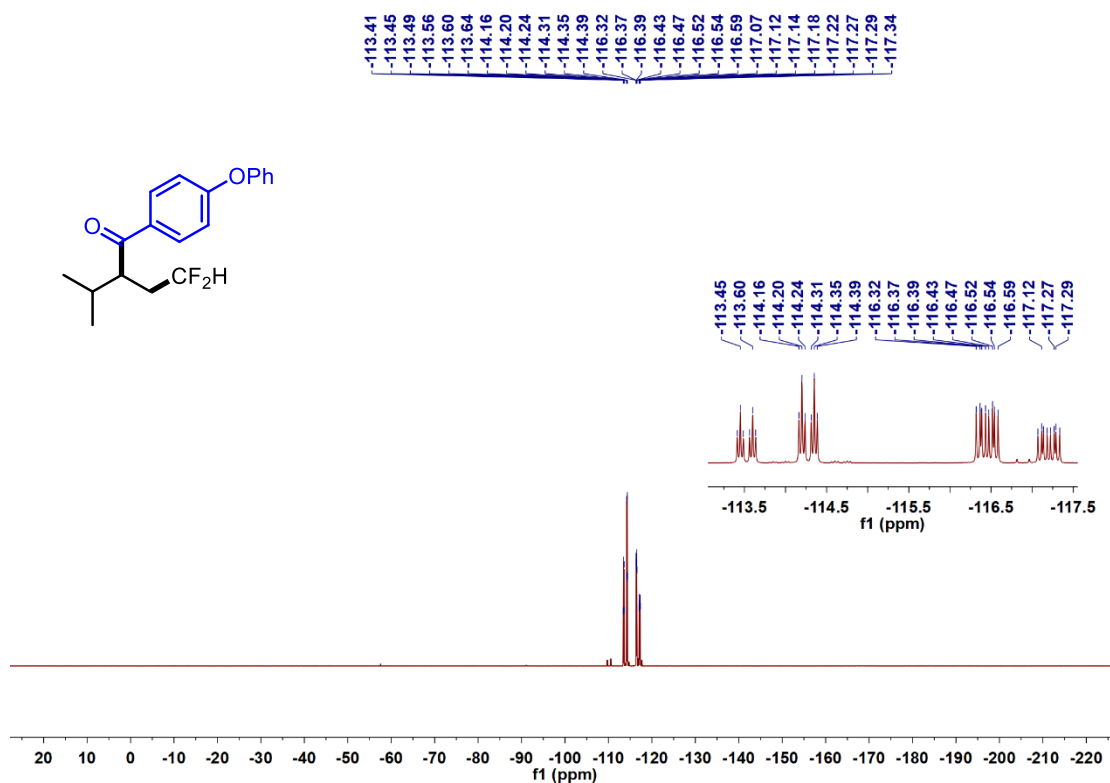
¹H NMR of Compound **3e** (400 MHz, CDCl₃)



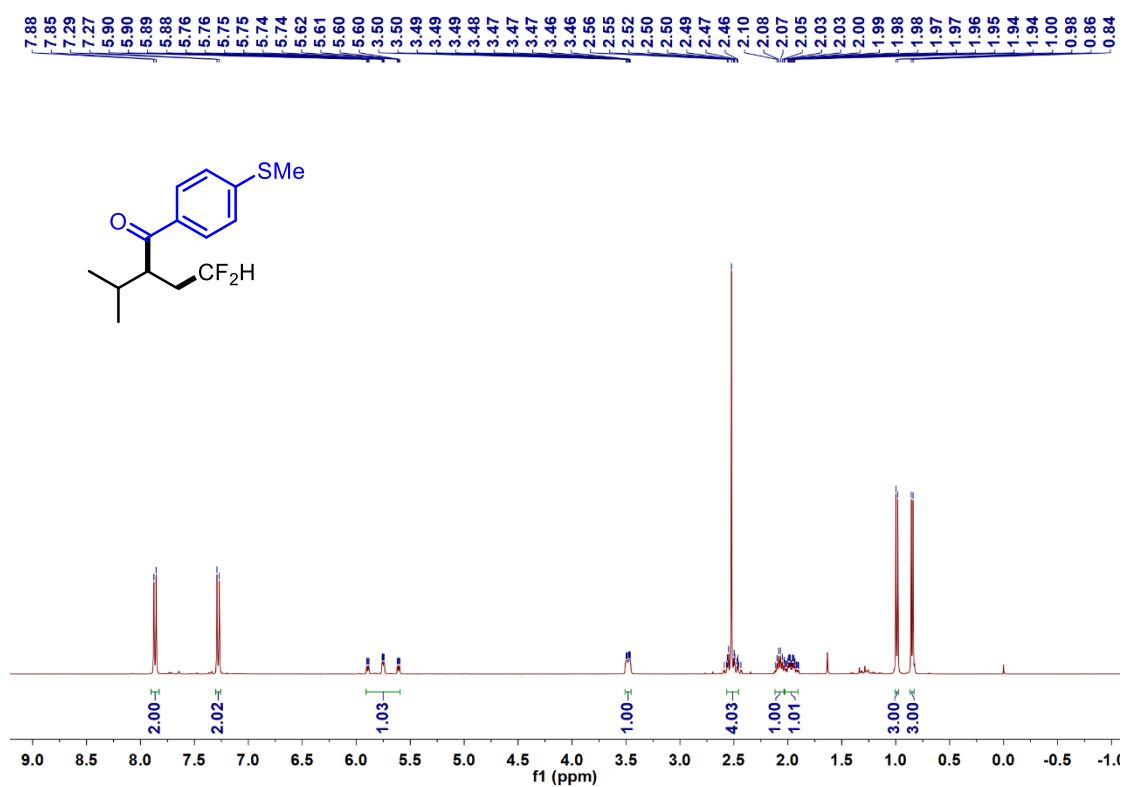
¹³C NMR of Compound **3e** (101 MHz, CDCl₃)



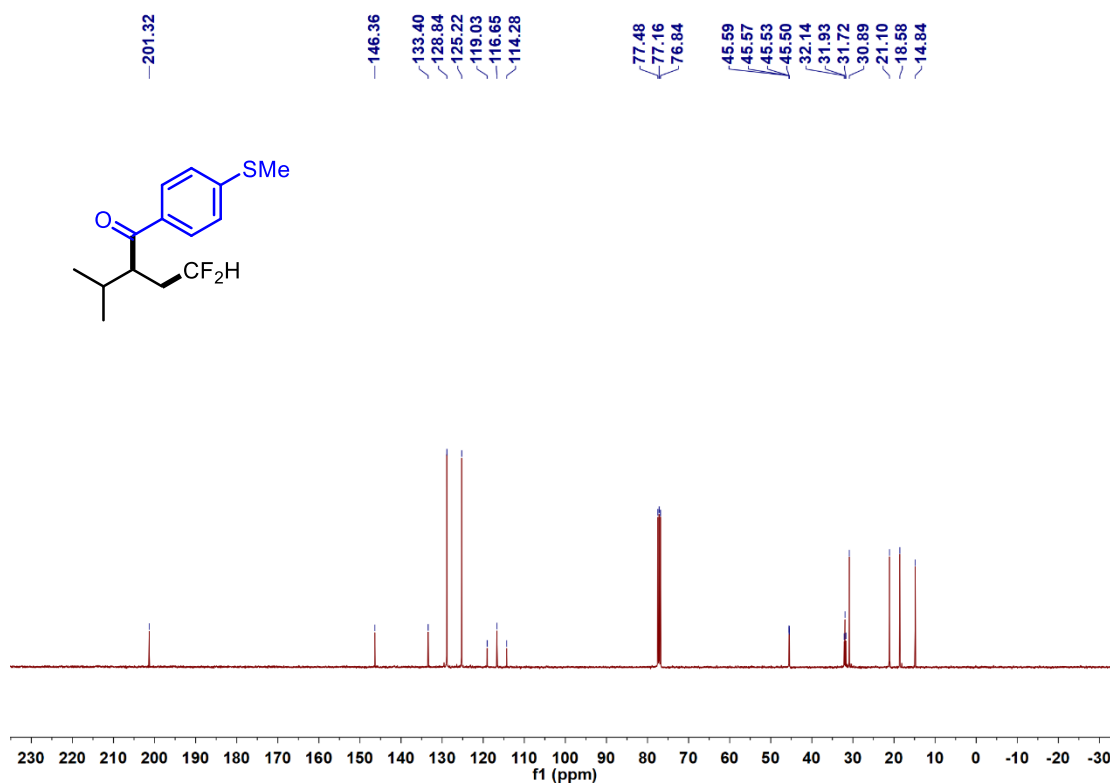
¹⁹F NMR of Compound **3e** (400 MHz, CDCl₃)



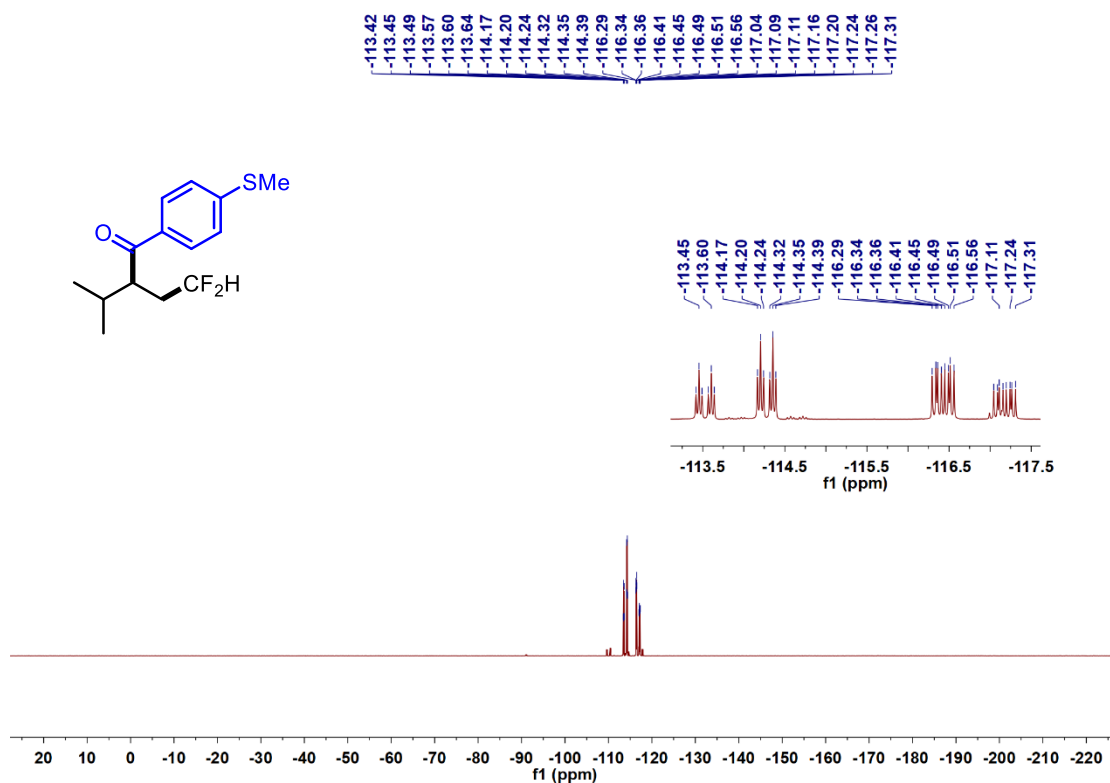
¹H NMR of Compound **3f** (400 MHz, CDCl₃)



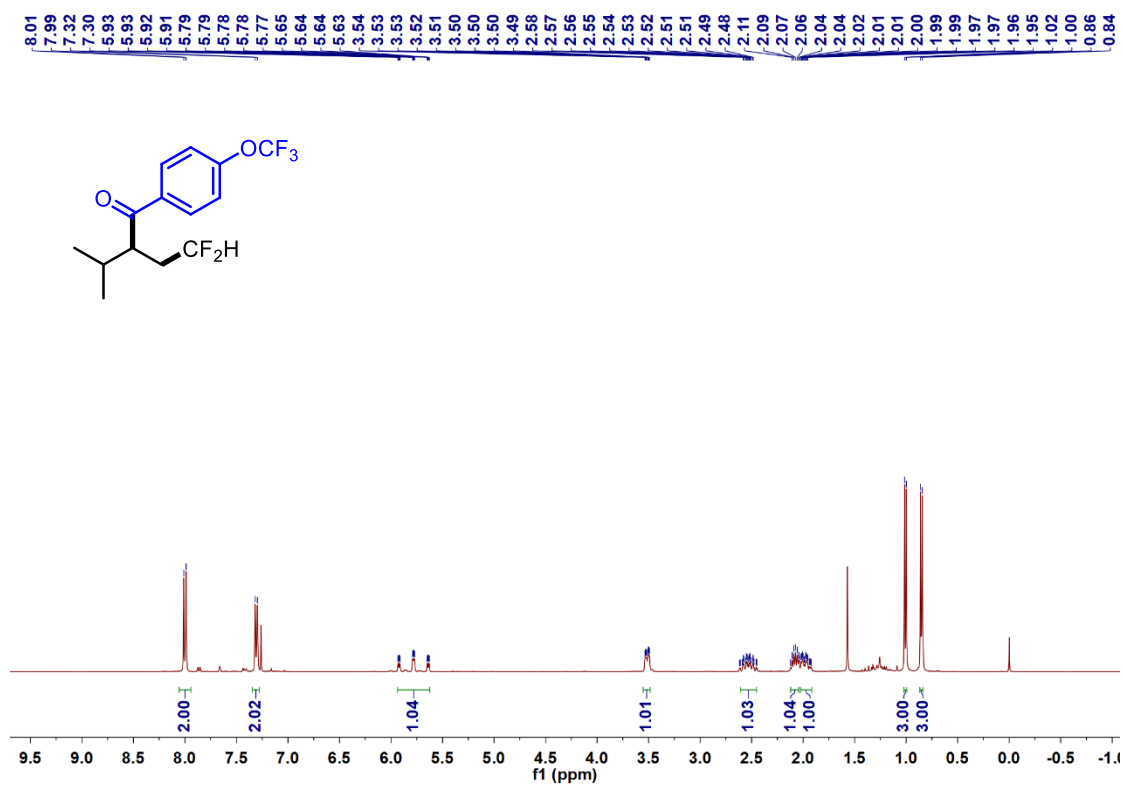
¹³C NMR of Compound **3f** (101 MHz, CDCl₃)



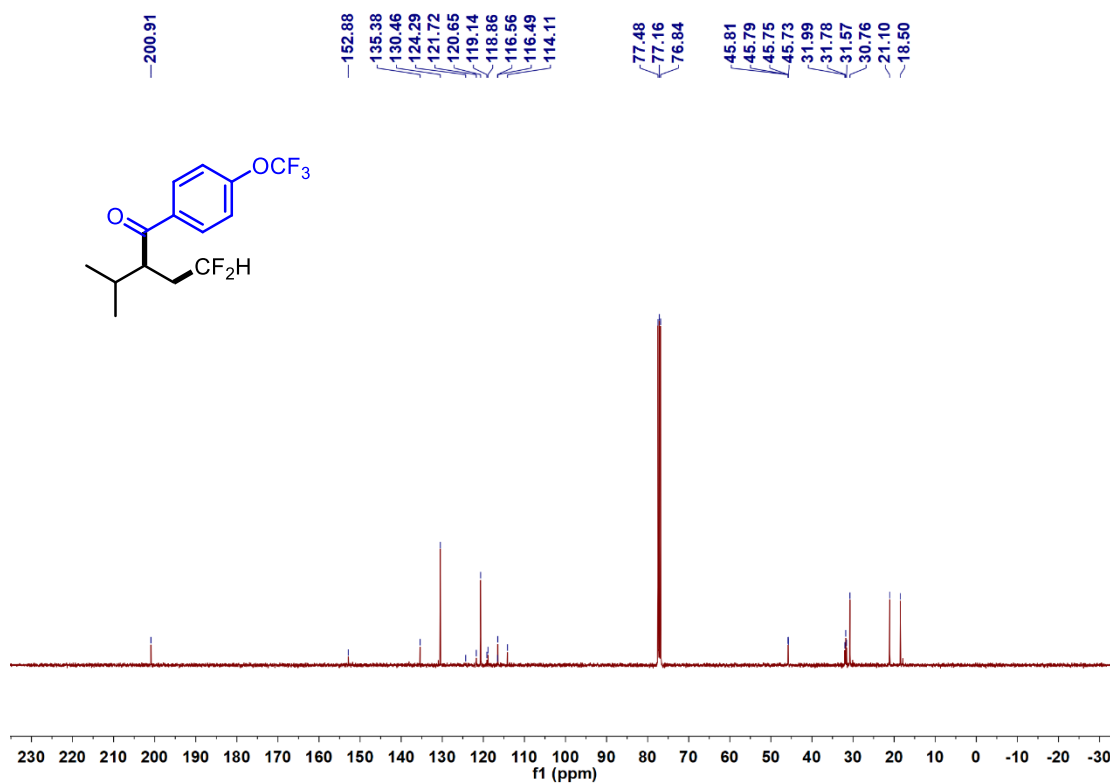
¹⁹F NMR of Compound **3f** (400 MHz, CDCl₃)



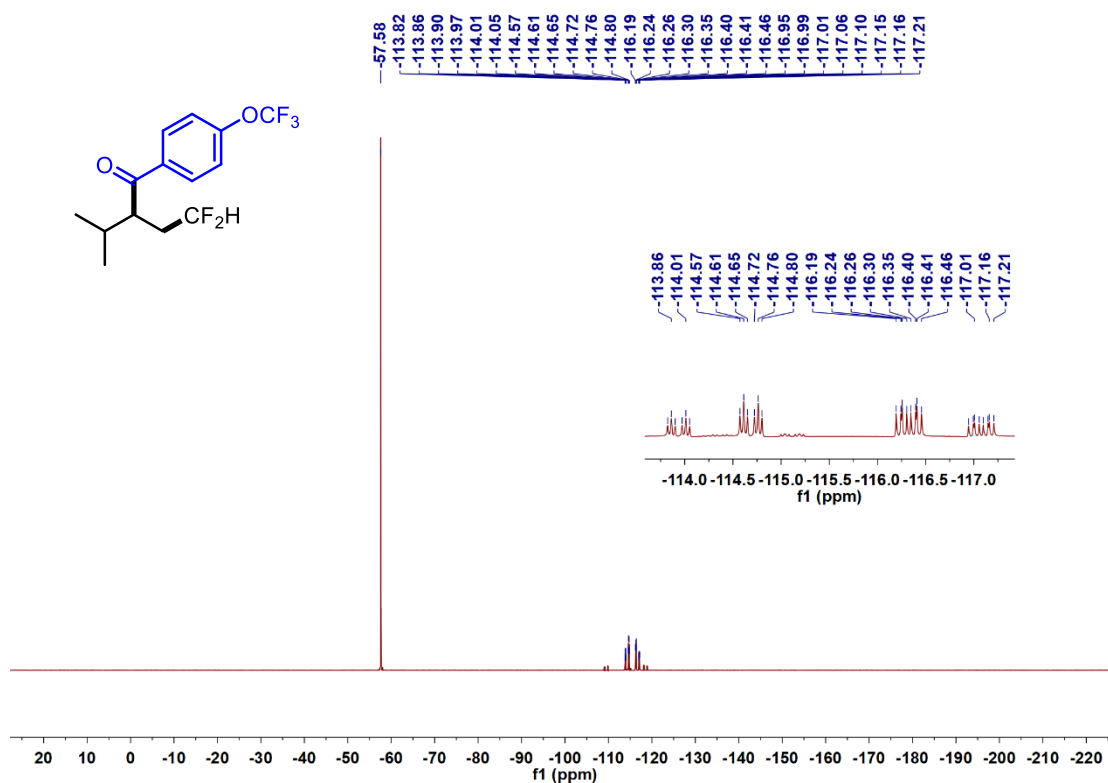
^1H NMR of Compound **3g** (400 MHz, CDCl_3)



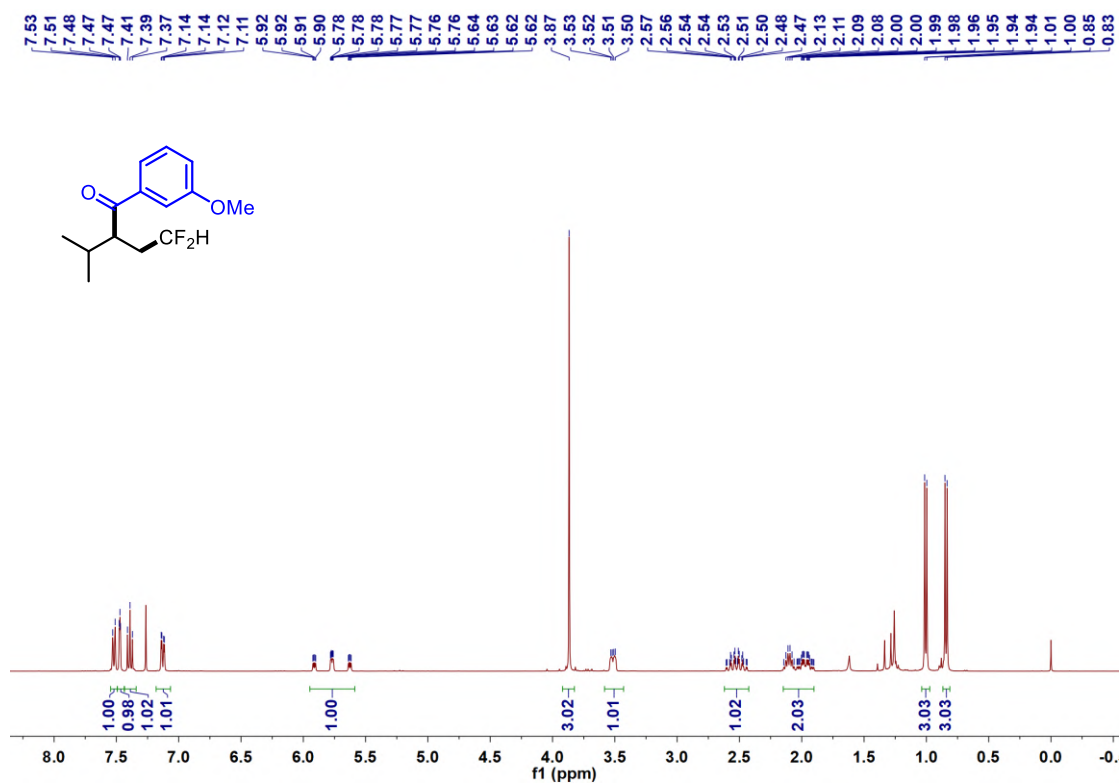
^{13}C NMR of Compound **3g** (101 MHz, CDCl_3)



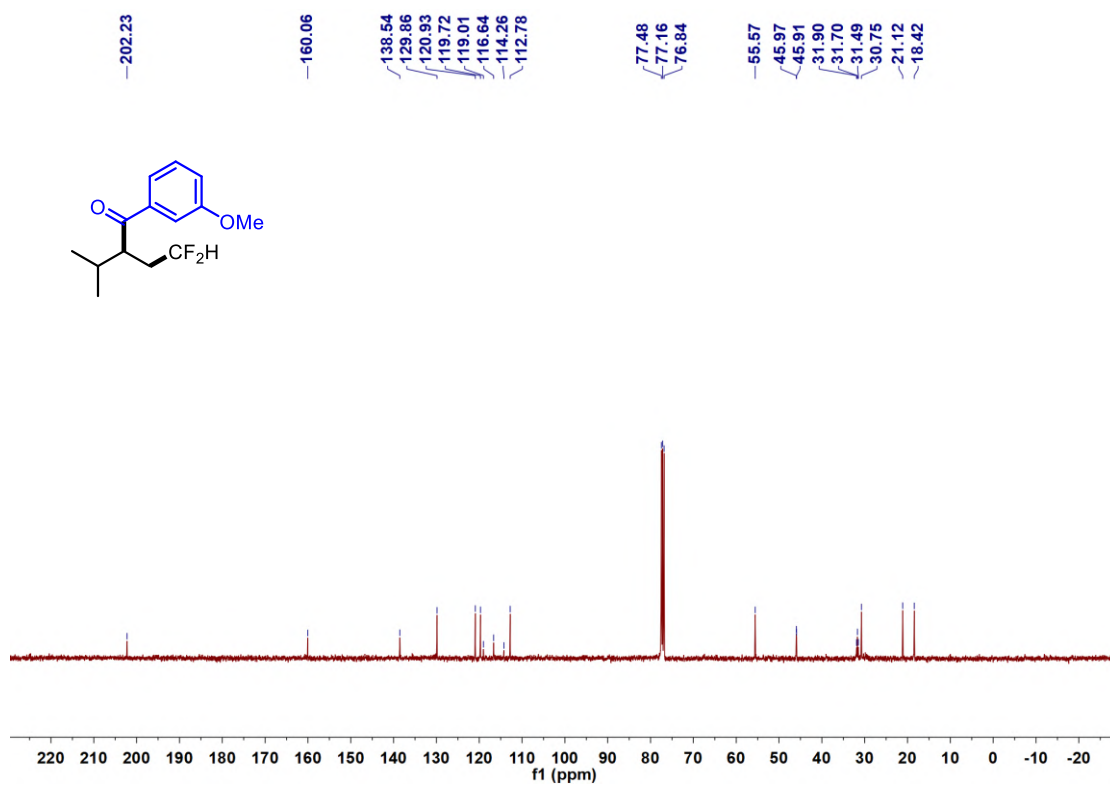
¹⁹F NMR of Compound **3g** (400 MHz, CDCl₃)



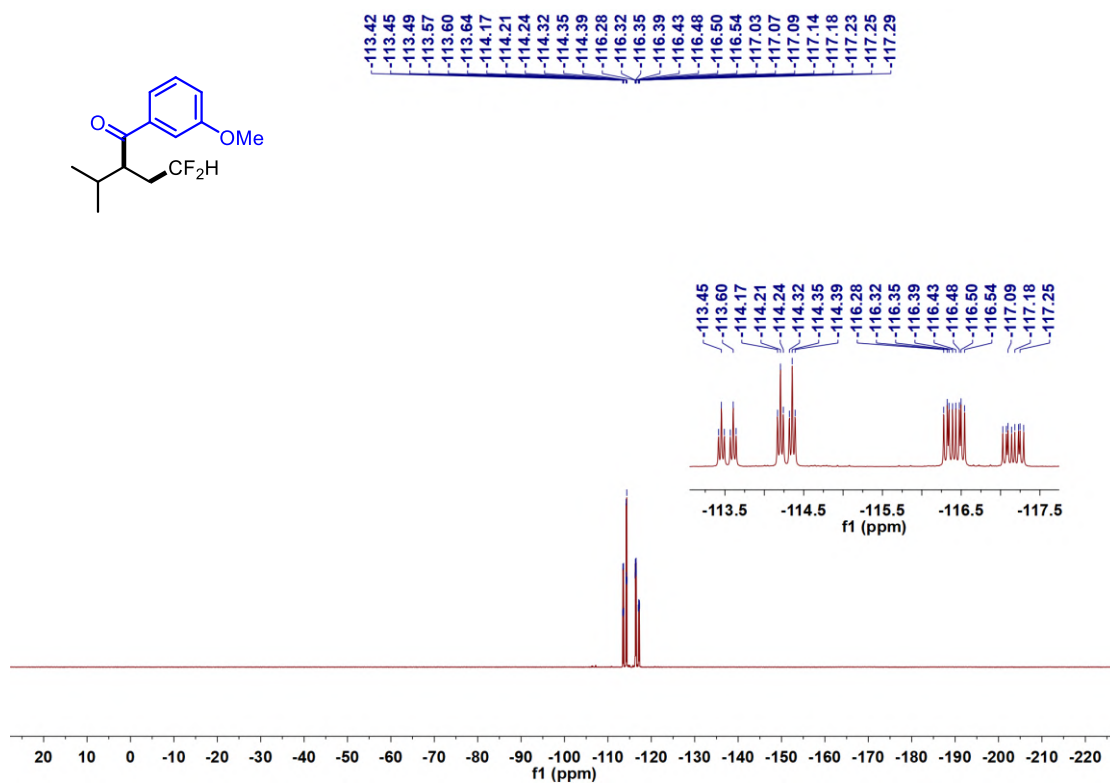
¹H NMR of Compound **3i** (400 MHz, CDCl₃)



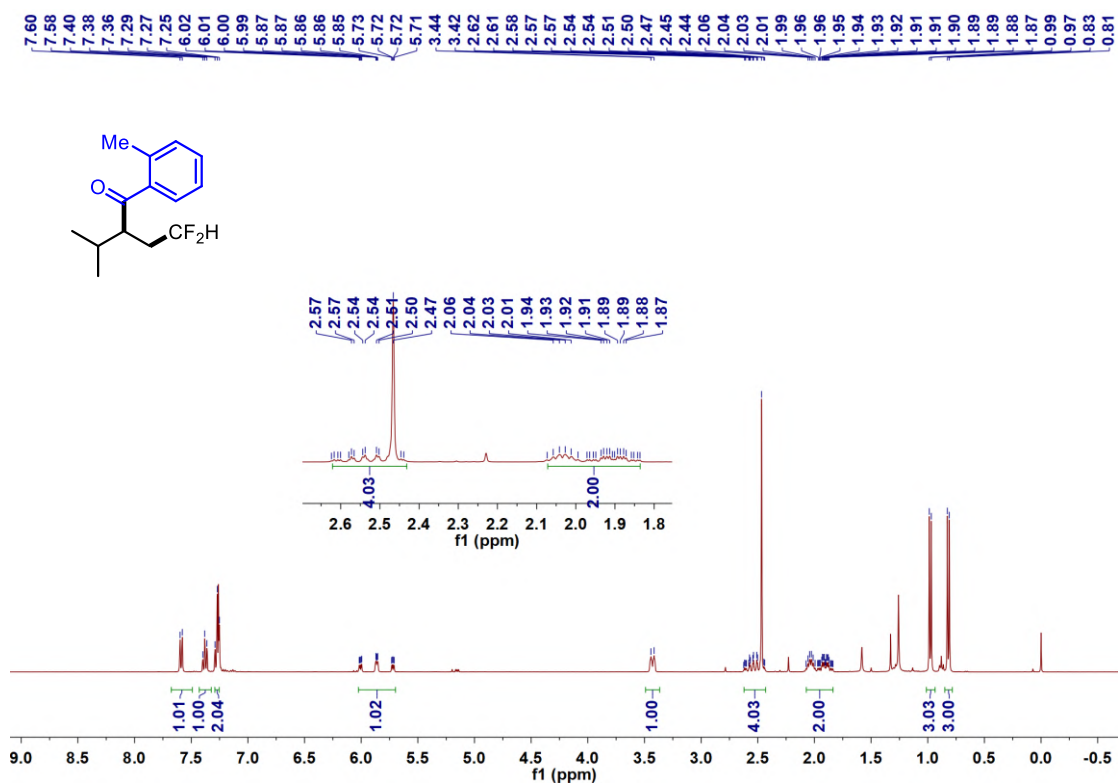
¹³C NMR of Compound **3i** (101 MHz, CDCl₃)



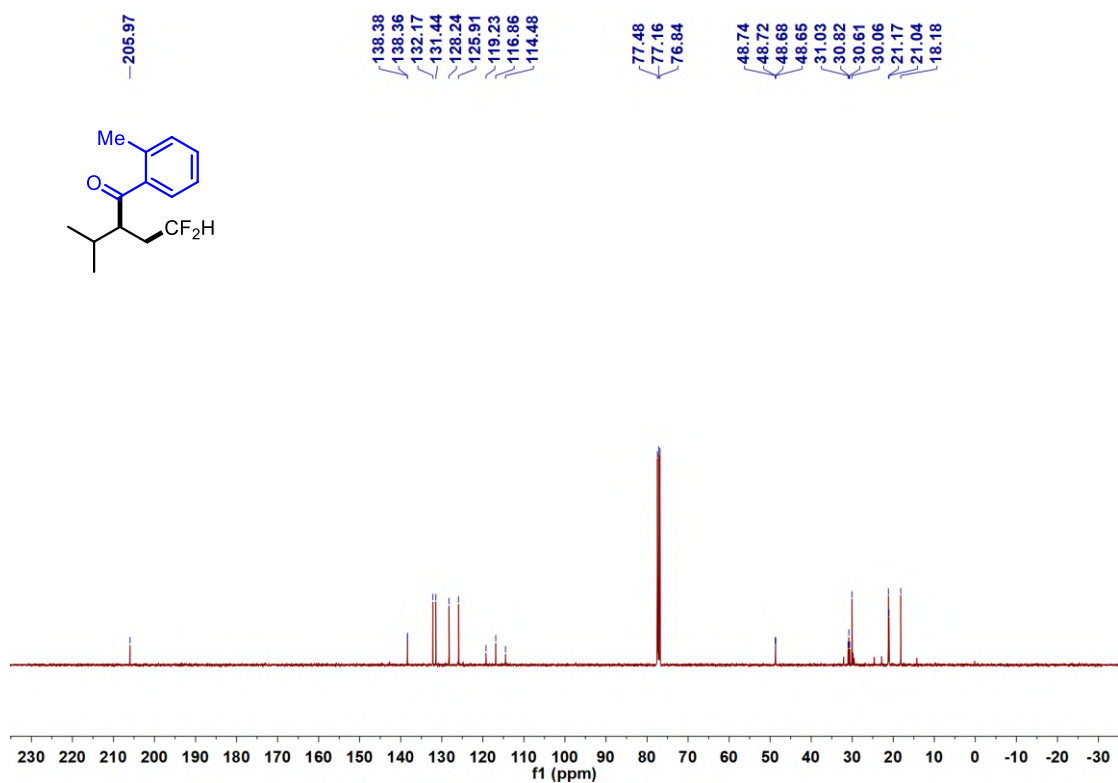
¹⁹F NMR of Compound **3i** (400 MHz, CDCl₃)



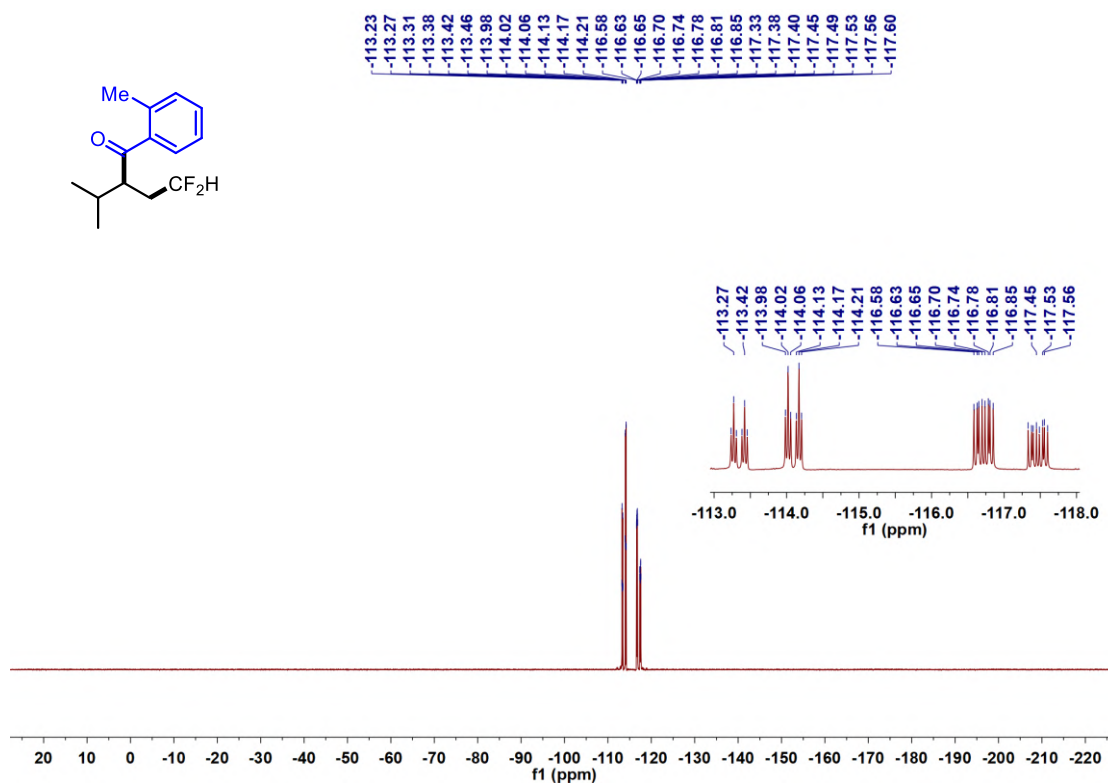
¹H NMR of Compound **3j** (400 MHz, CDCl₃)



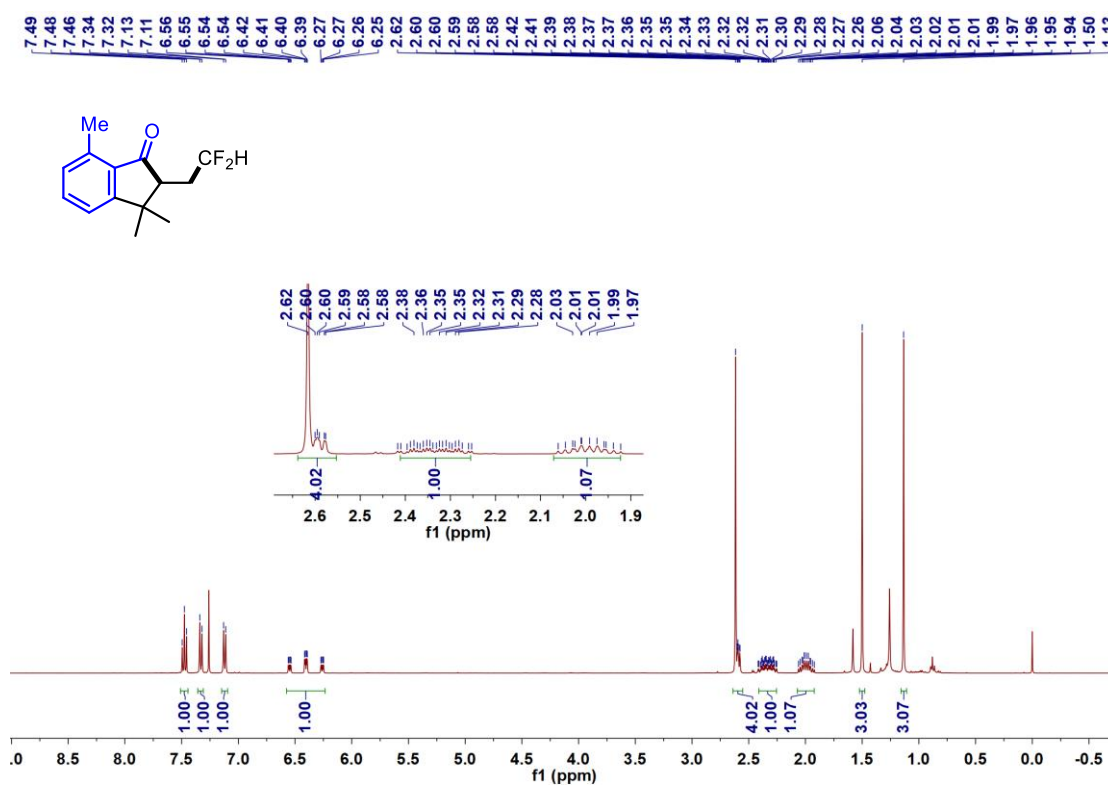
¹³C NMR of Compound **3j** (101 MHz, CDCl₃)



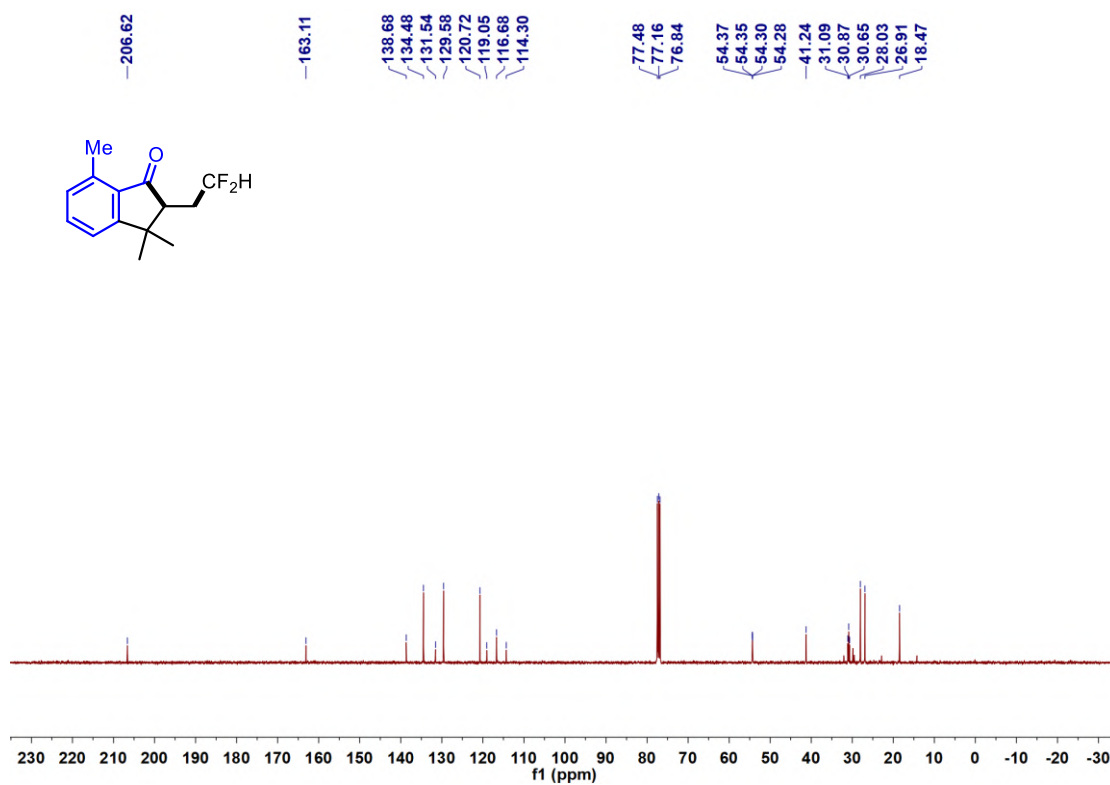
¹⁹F NMR of Compound **3j** (400 MHz, CDCl₃)



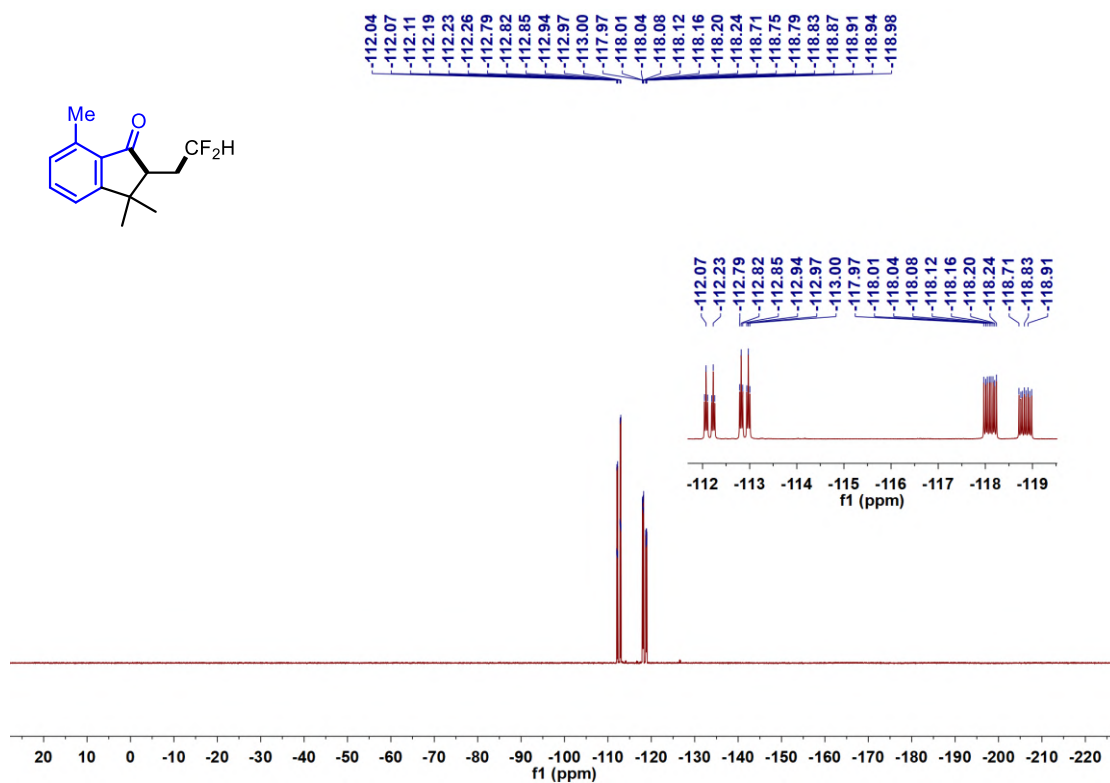
¹H NMR of Compound **3k** (400 MHz, CDCl₃)



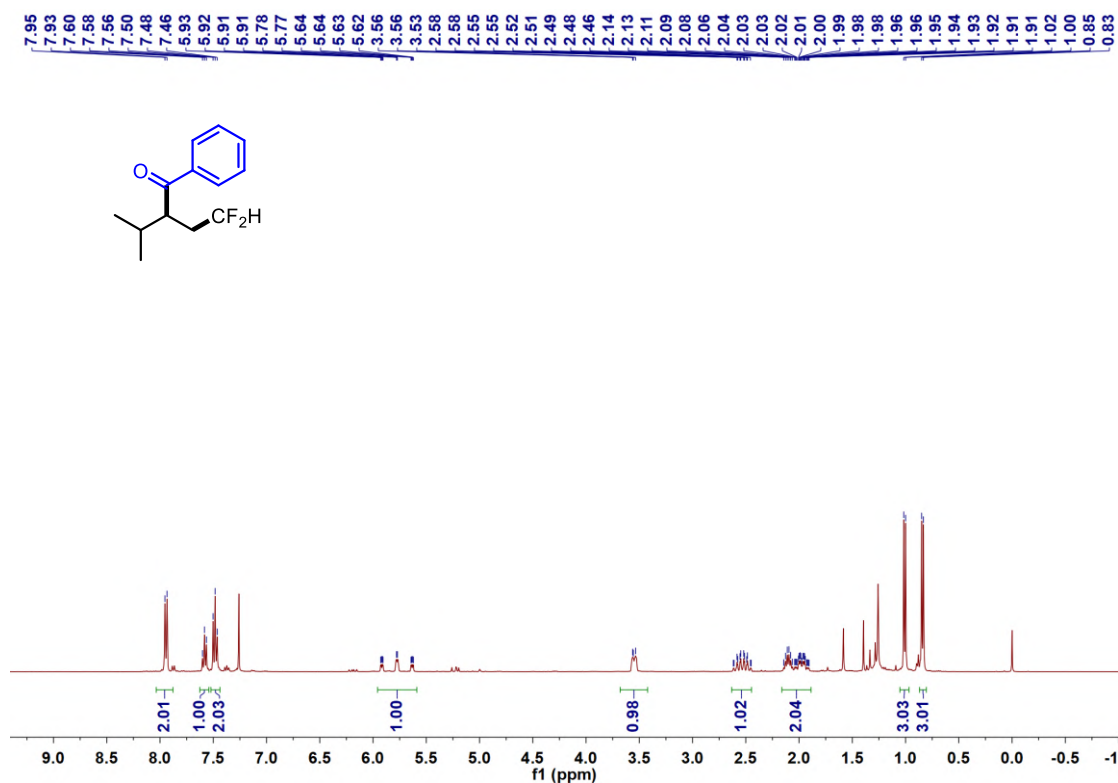
¹³C NMR of Compound **3k** (101 MHz, CDCl₃)



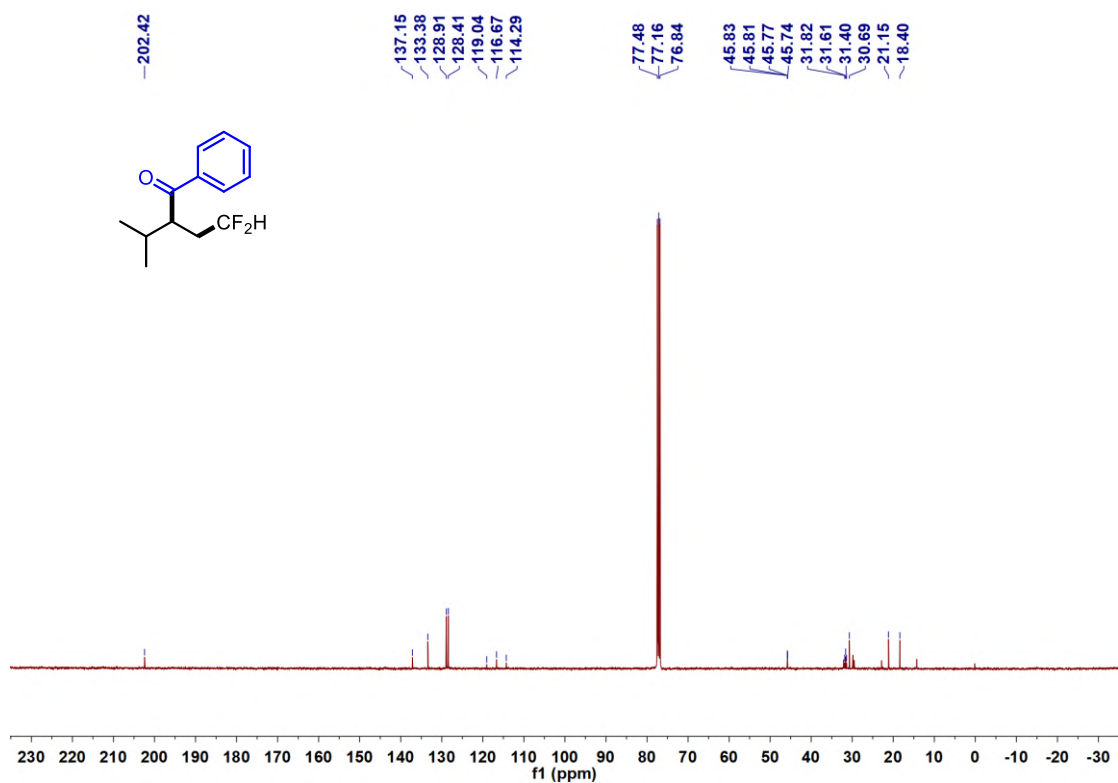
¹⁹F NMR of Compound **3k** (400 MHz, CDCl₃)



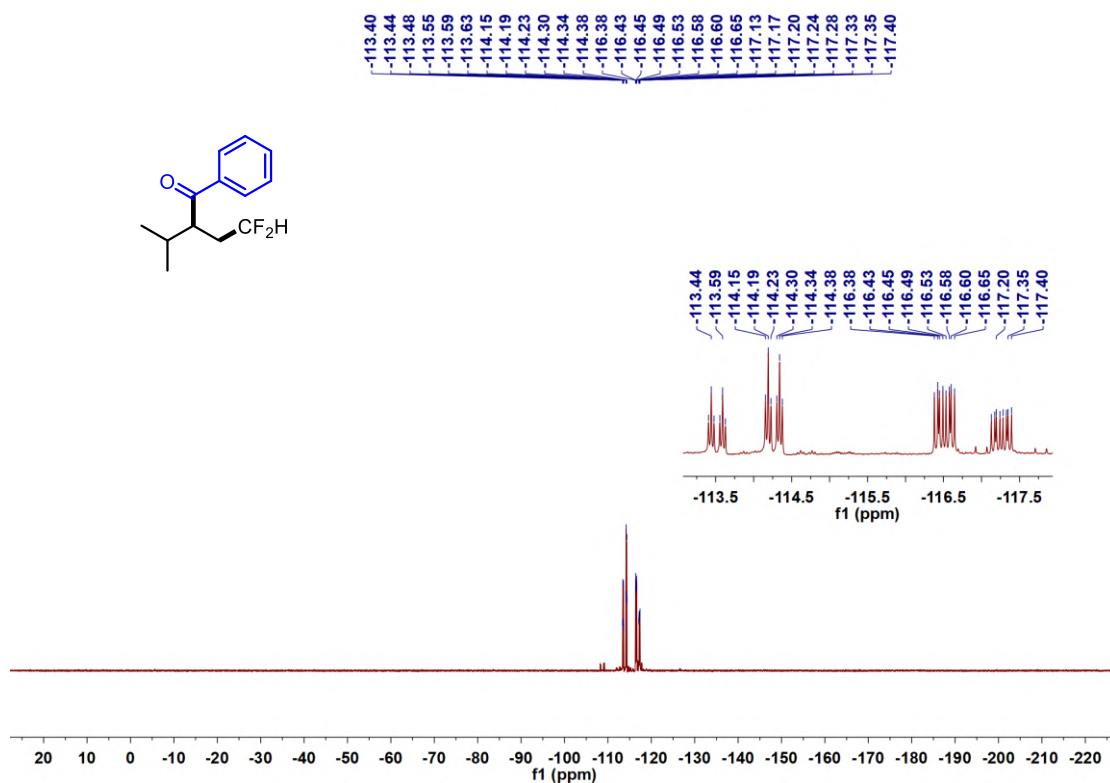
¹H NMR of Compound **31** (400 MHz, CDCl₃)



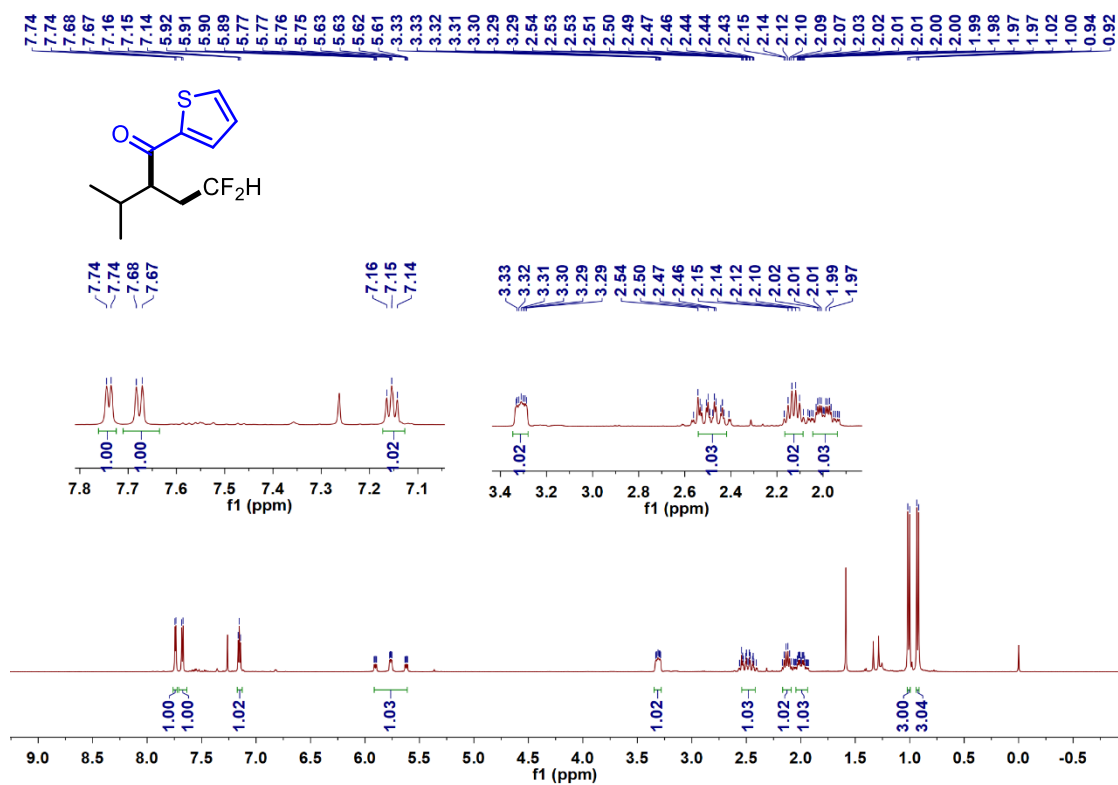
¹³C NMR of Compound **31** (101 MHz, CDCl₃)



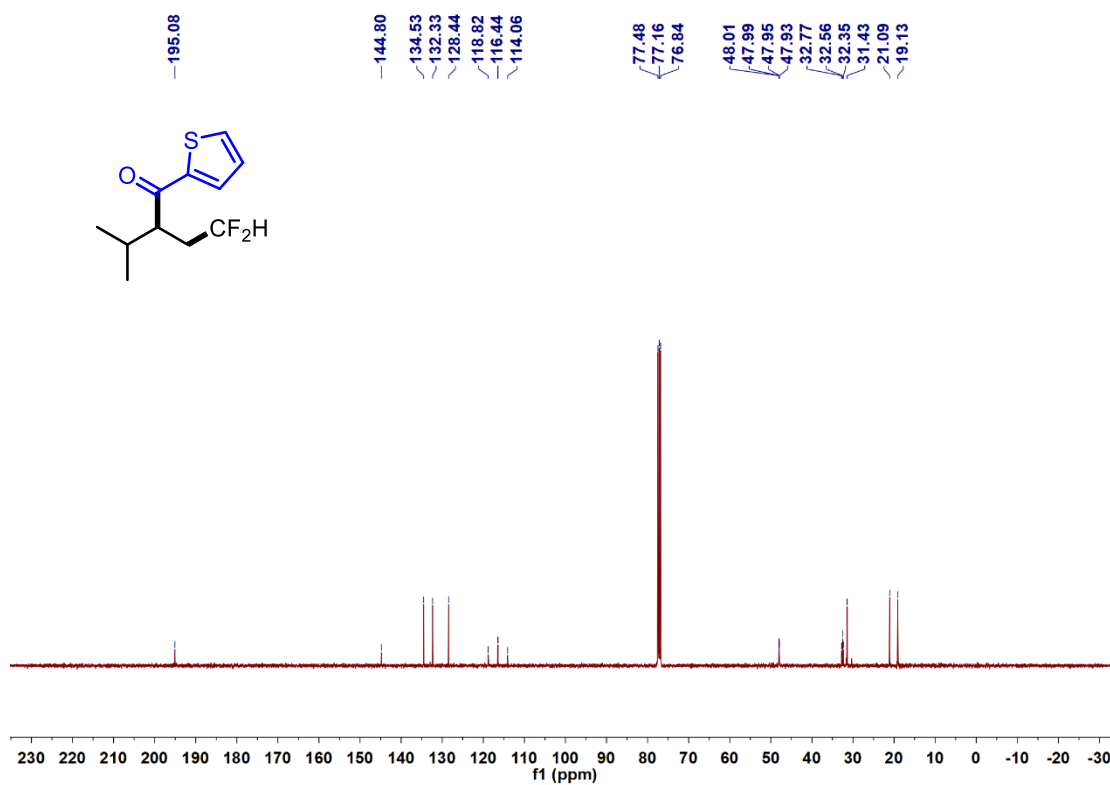
¹⁹F NMR of Compound **3l** (400 MHz, CDCl₃)



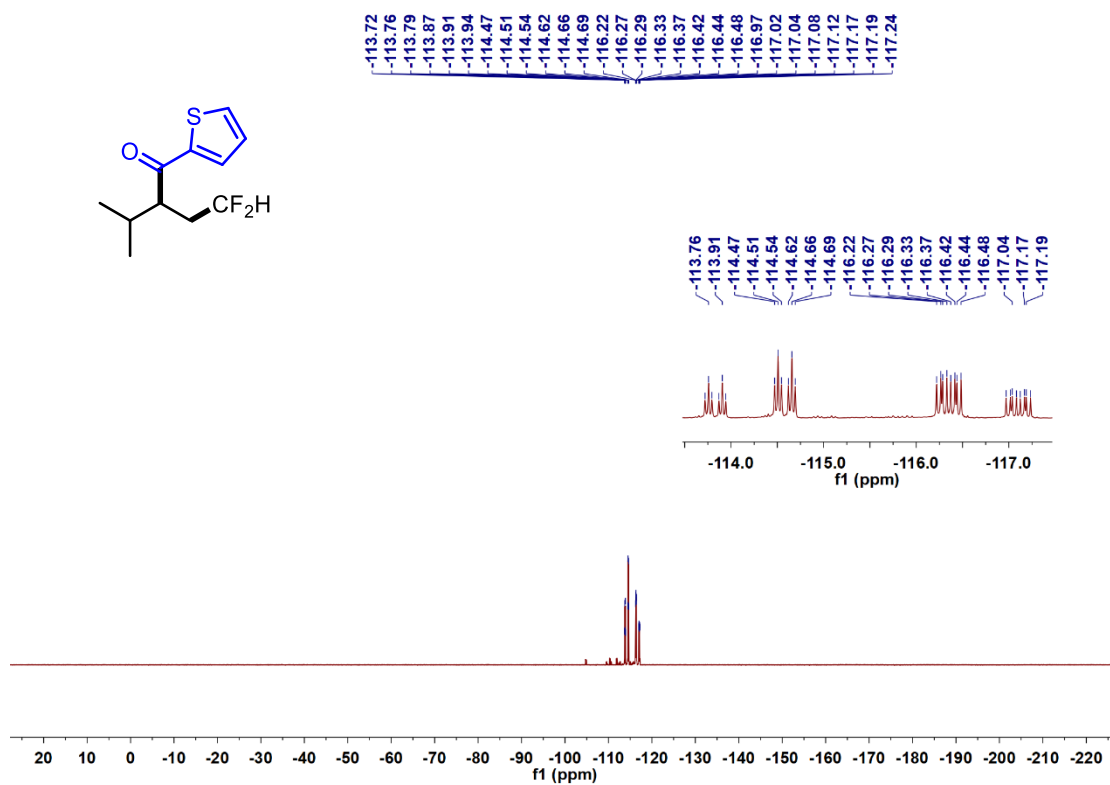
¹H NMR of Compound **3m** (400 MHz, CDCl₃)



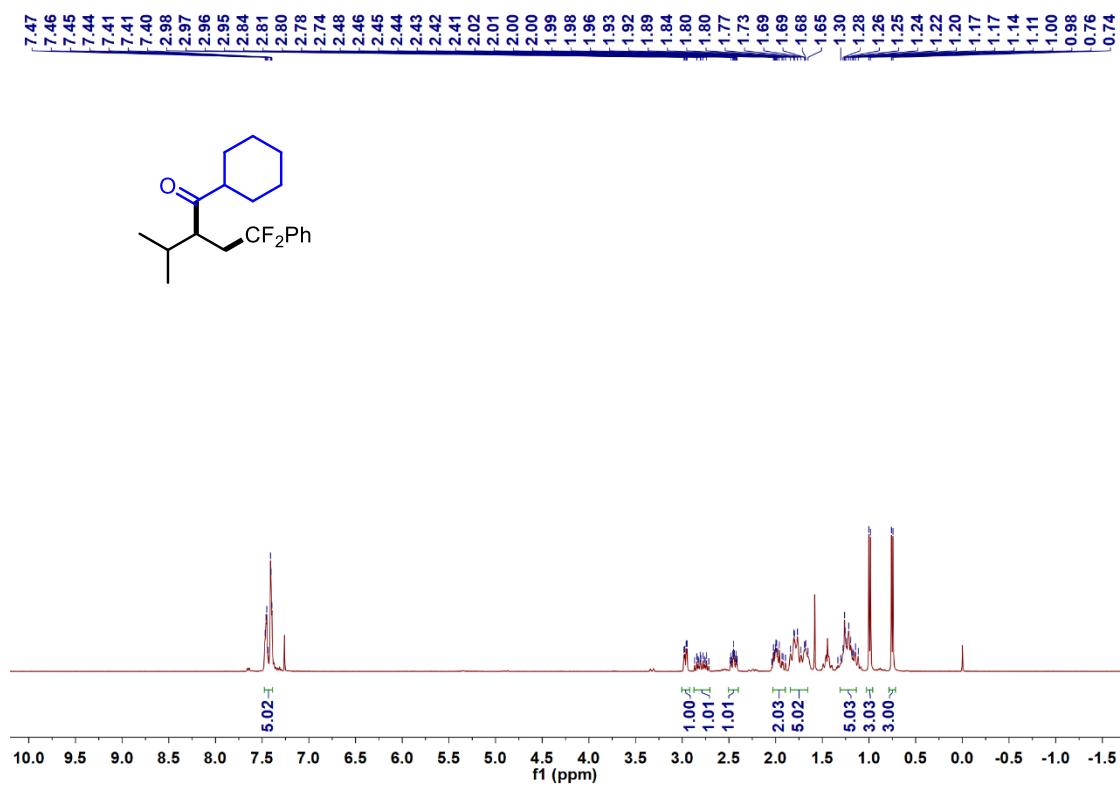
¹³C NMR of Compound **3m** (101 MHz, CDCl₃)



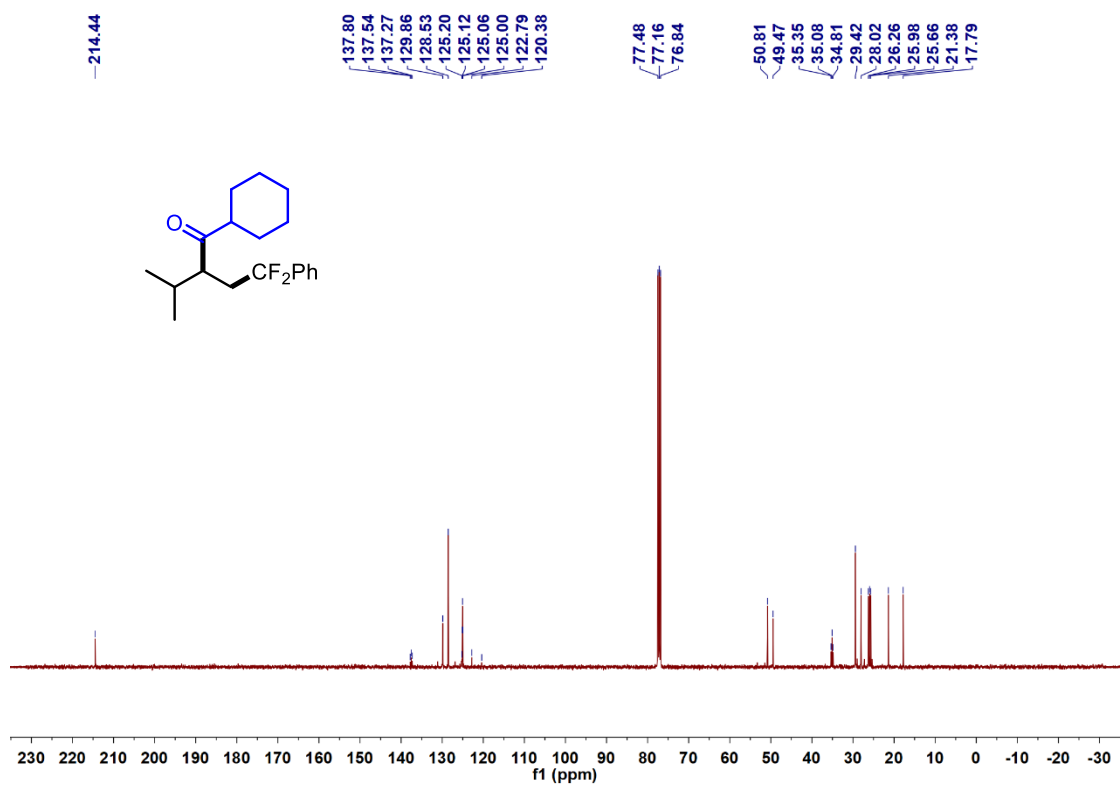
¹⁹F NMR of Compound **3m** (400 MHz, CDCl₃)



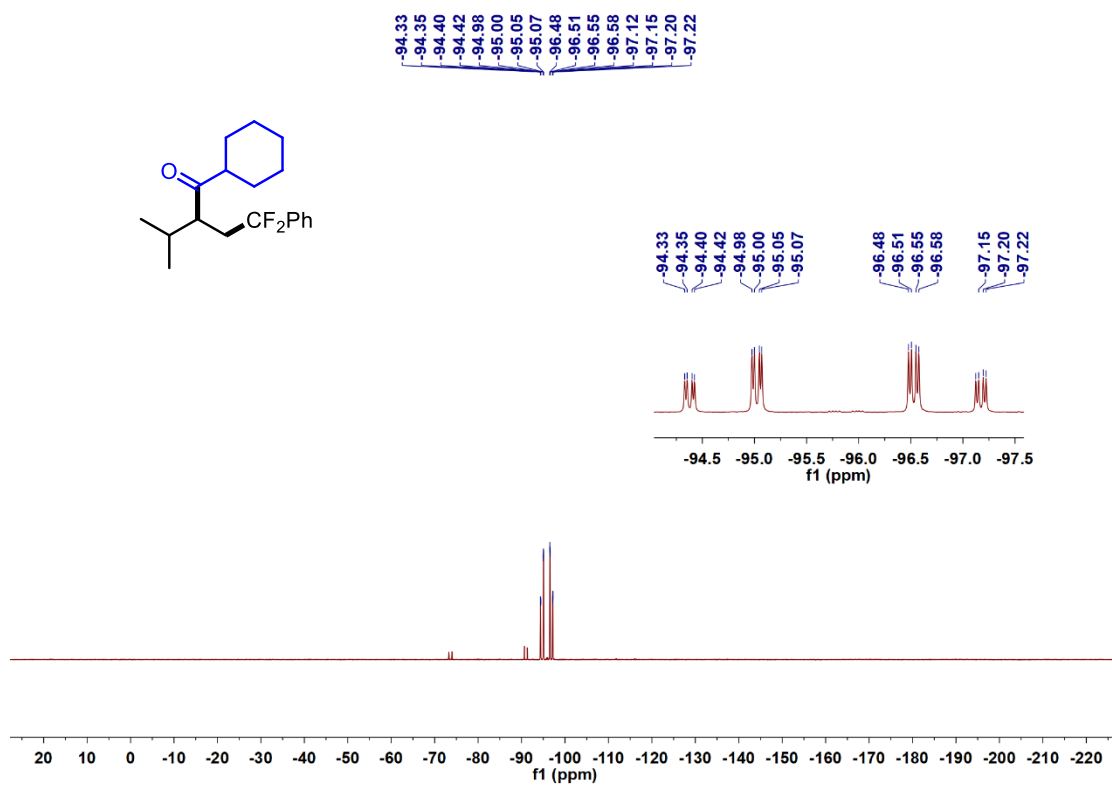
¹H NMR of Compound **3n** (400 MHz, CDCl₃)



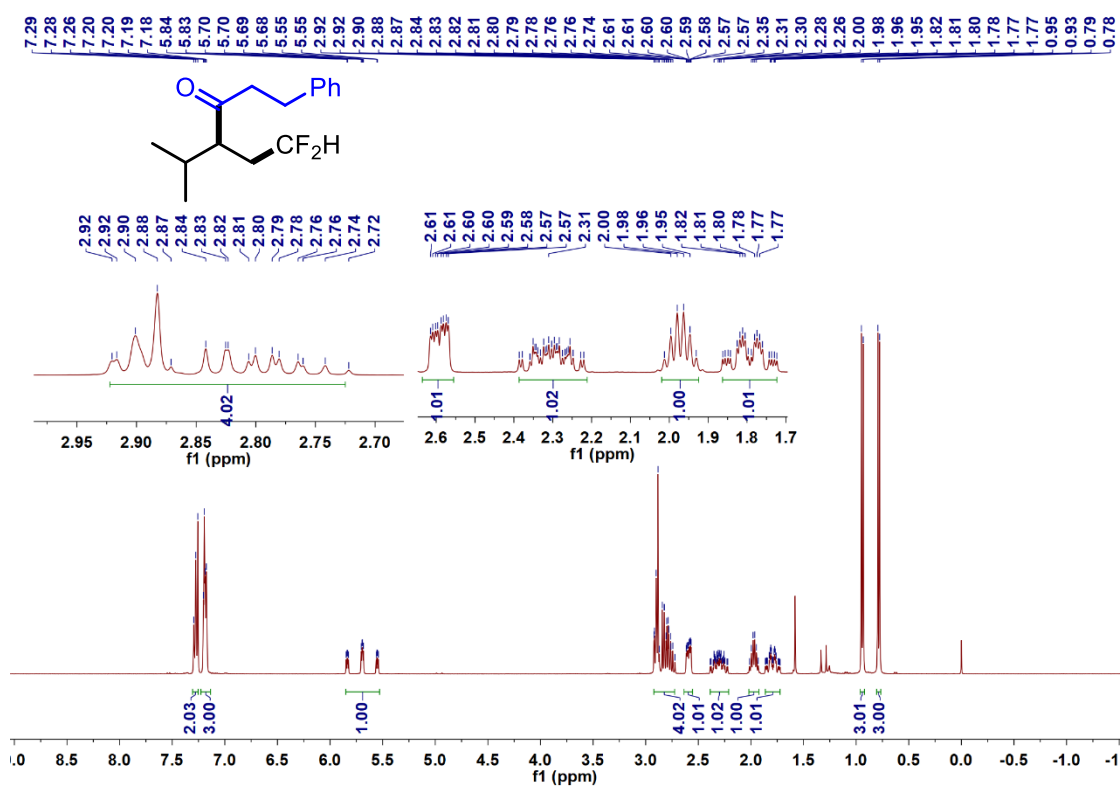
¹³C NMR of Compound **3n** (101 MHz, CDCl₃)



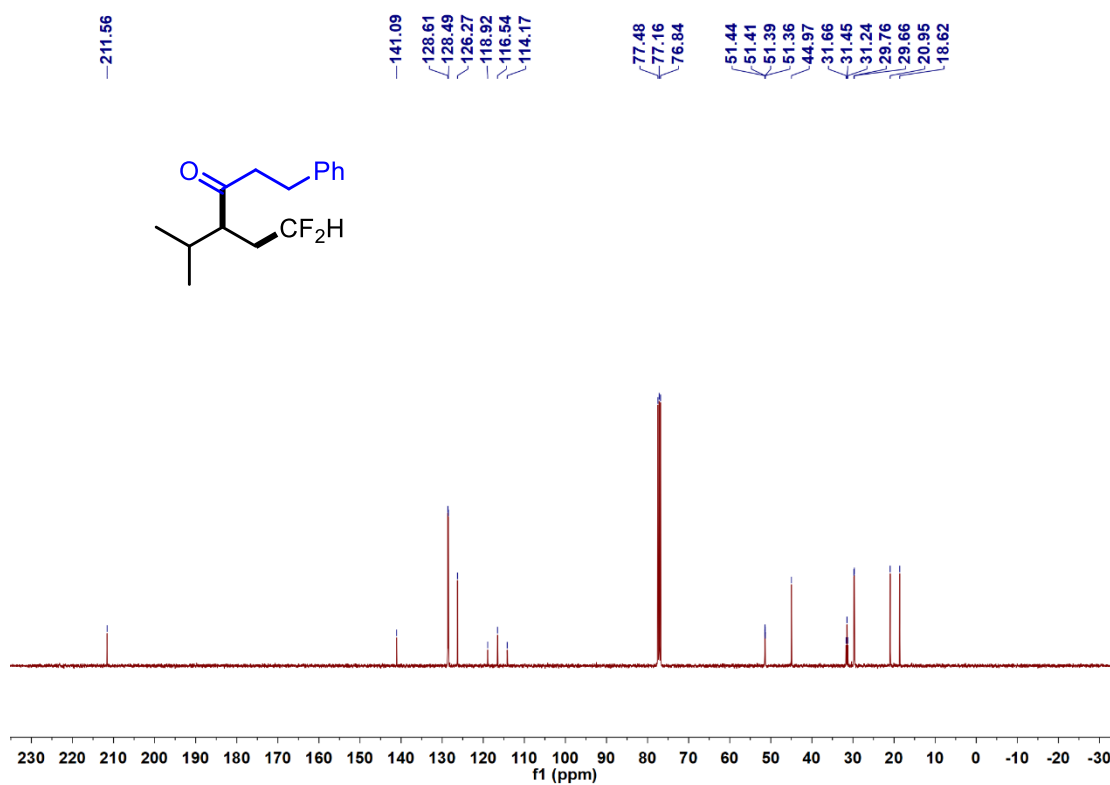
¹⁹F NMR of Compound **3n** (400 MHz, CDCl₃)



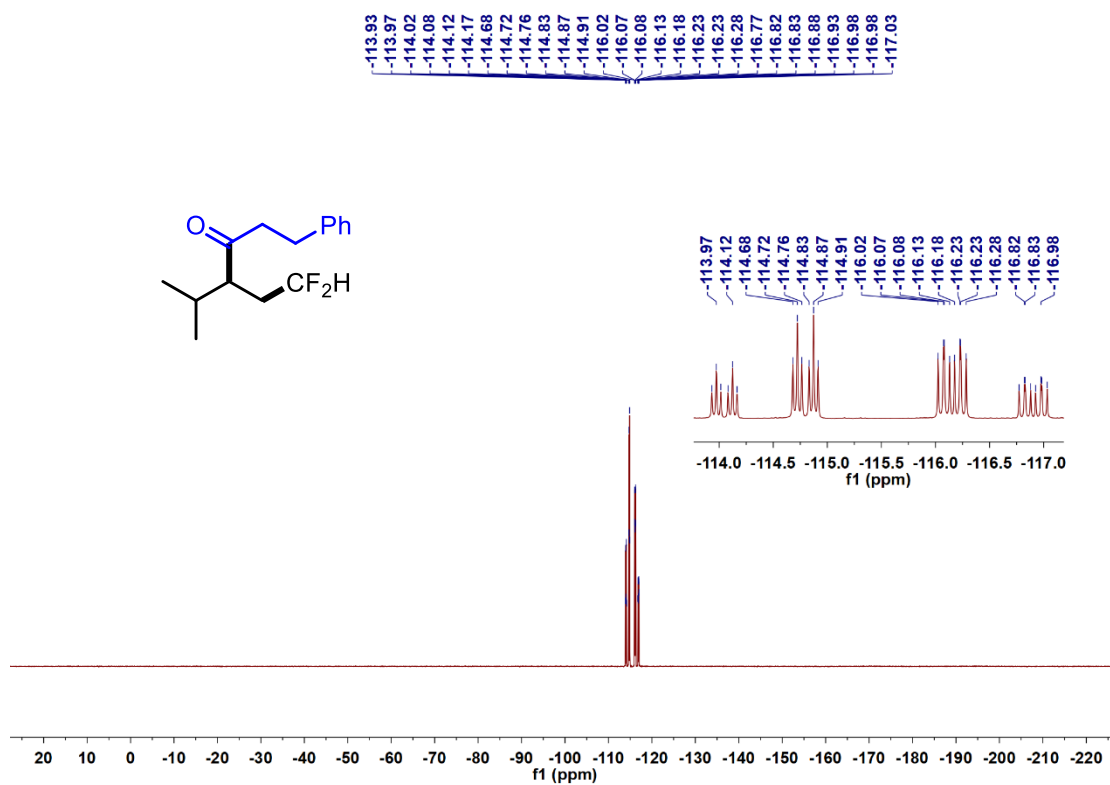
¹H NMR of Compound **3o** (400 MHz, CDCl₃)



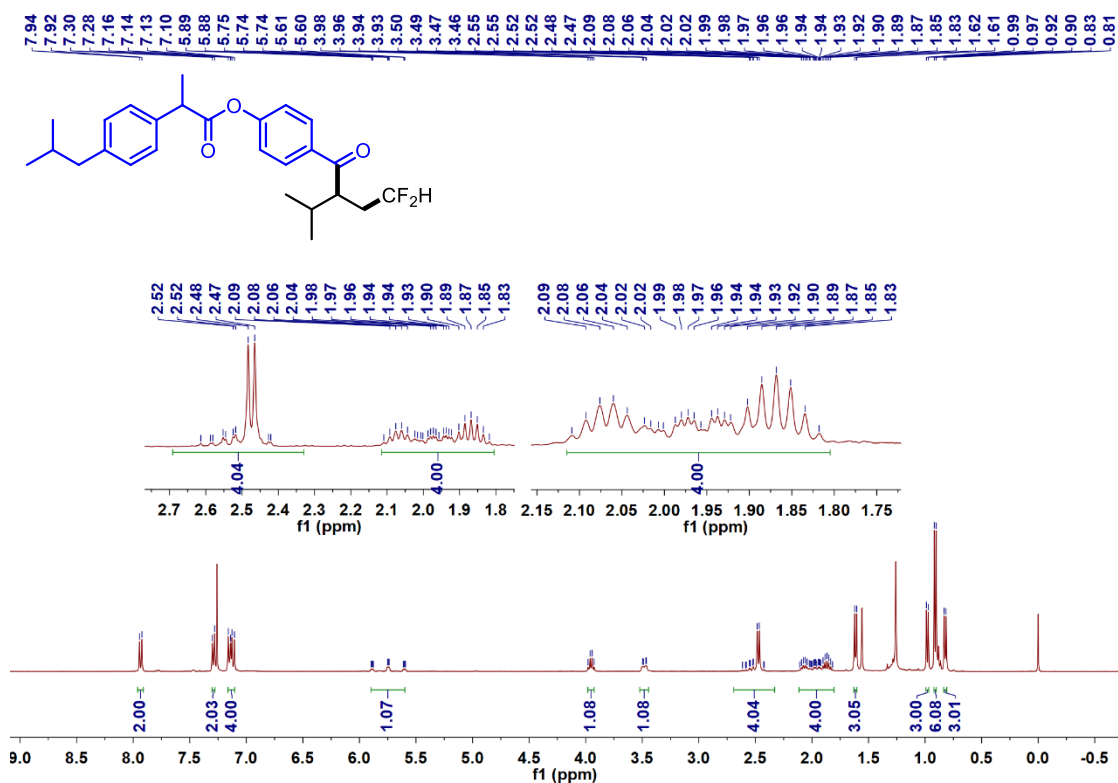
¹³C NMR of Compound **3o** (101 MHz, CDCl₃)



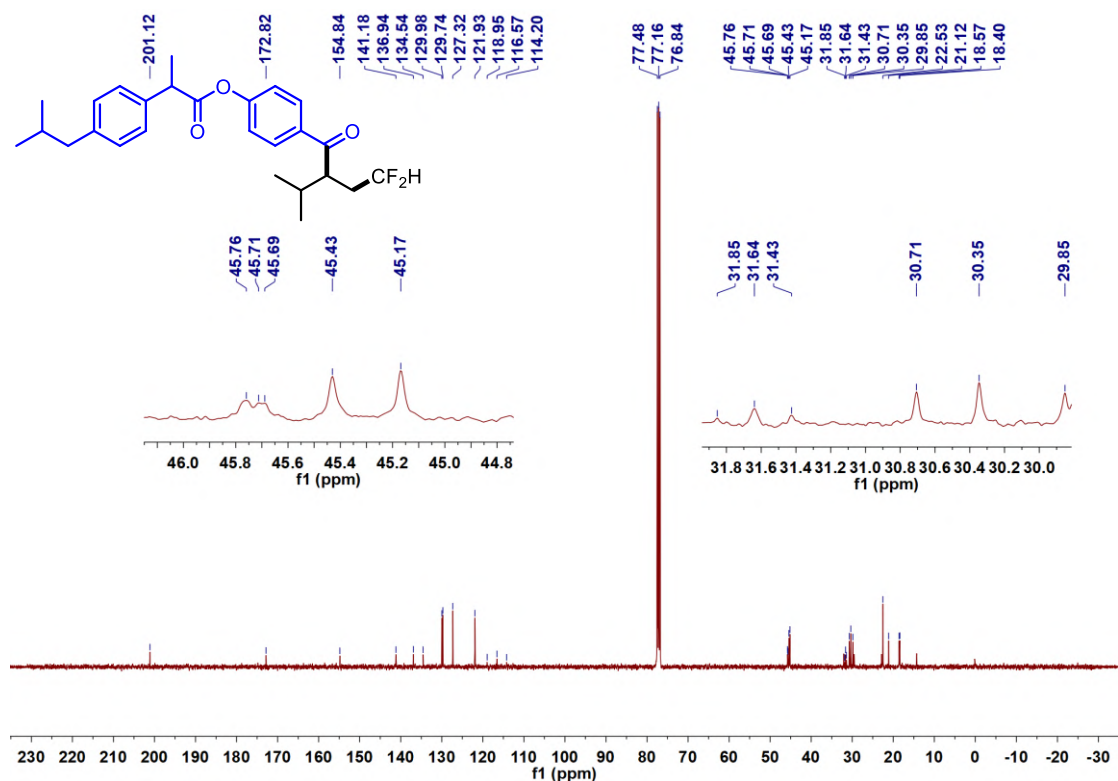
¹⁹F NMR of Compound **3o** (400 MHz, CDCl₃)



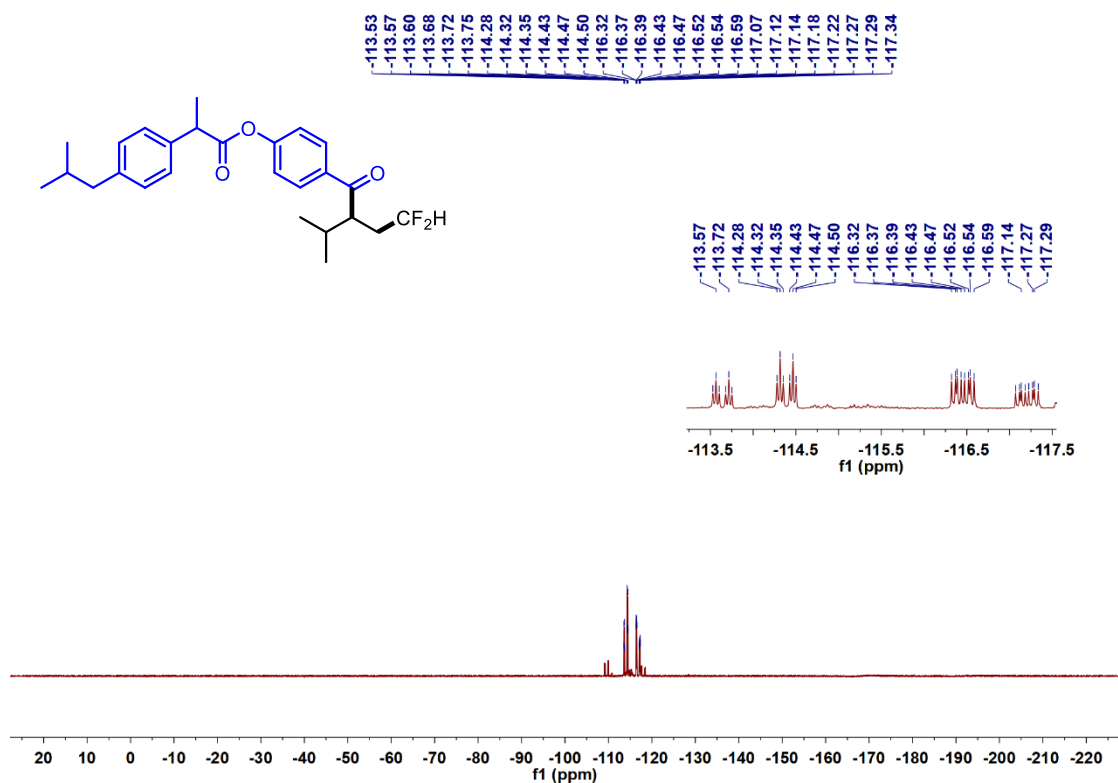
¹H NMR of Compound **3p** (400 MHz, CDCl₃)



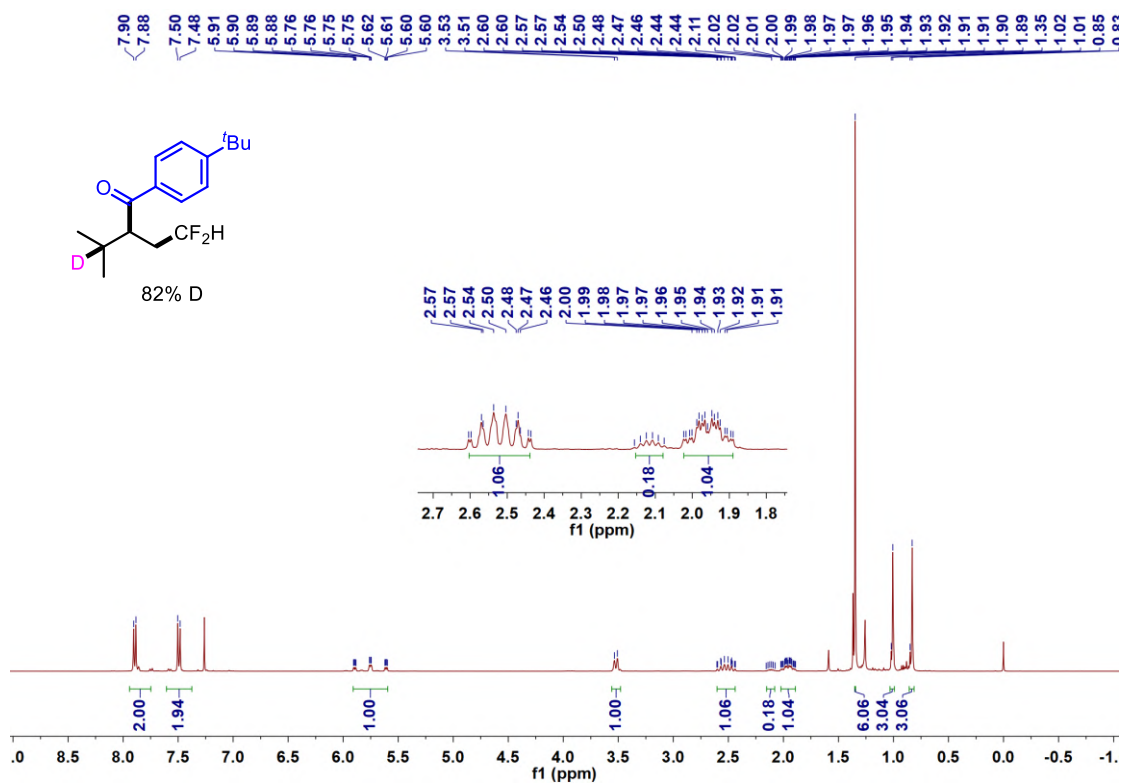
¹³C NMR of Compound **3p** (101 MHz, CDCl₃)



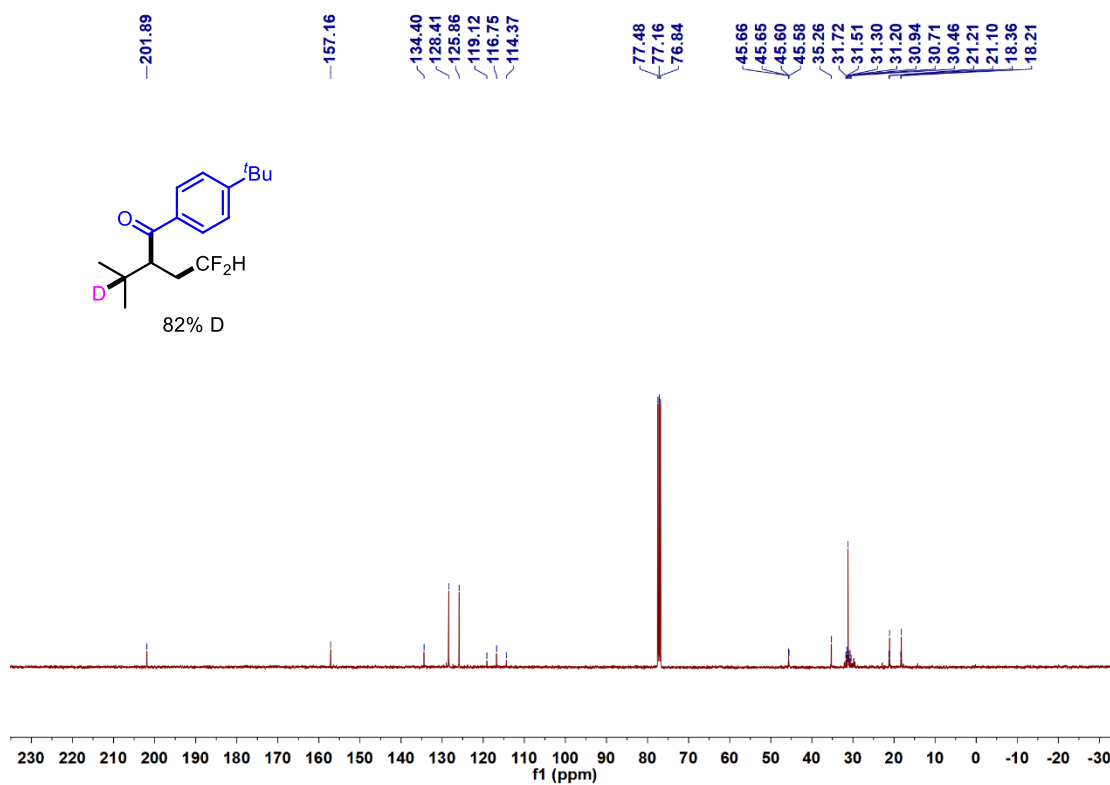
¹⁹F NMR of Compound **3p** (400 MHz, CDCl₃)



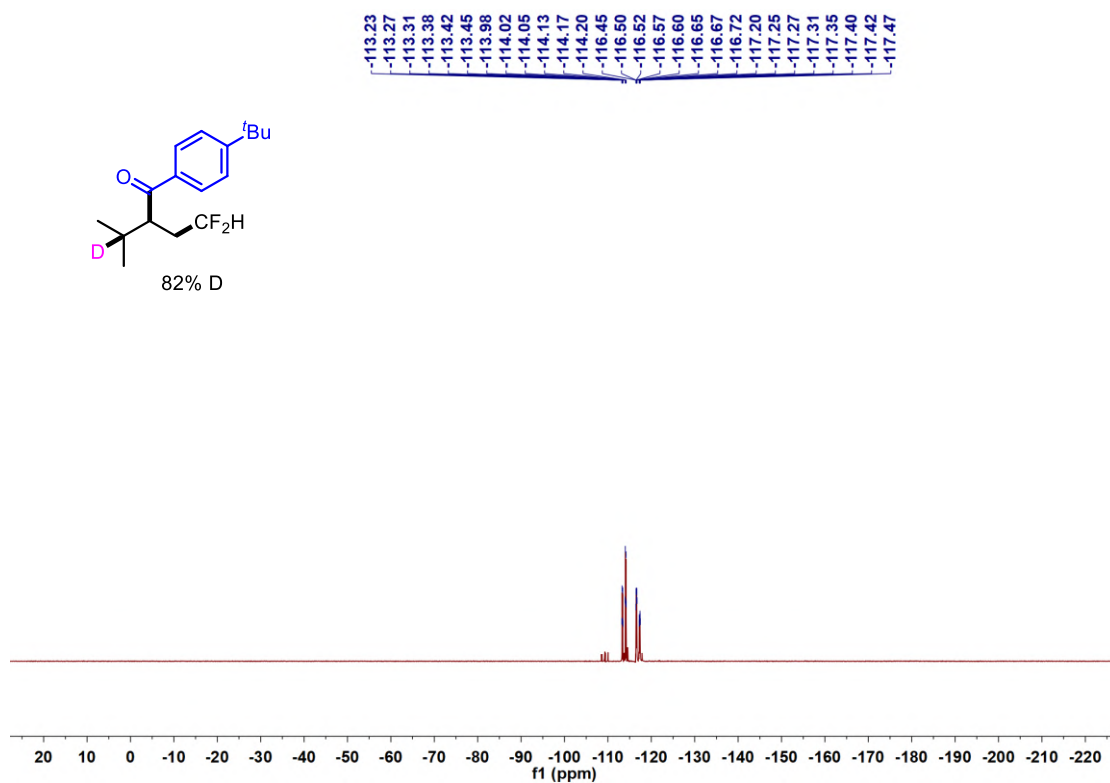
¹H NMR of Compound **3a-D** (400 MHz, CDCl₃)



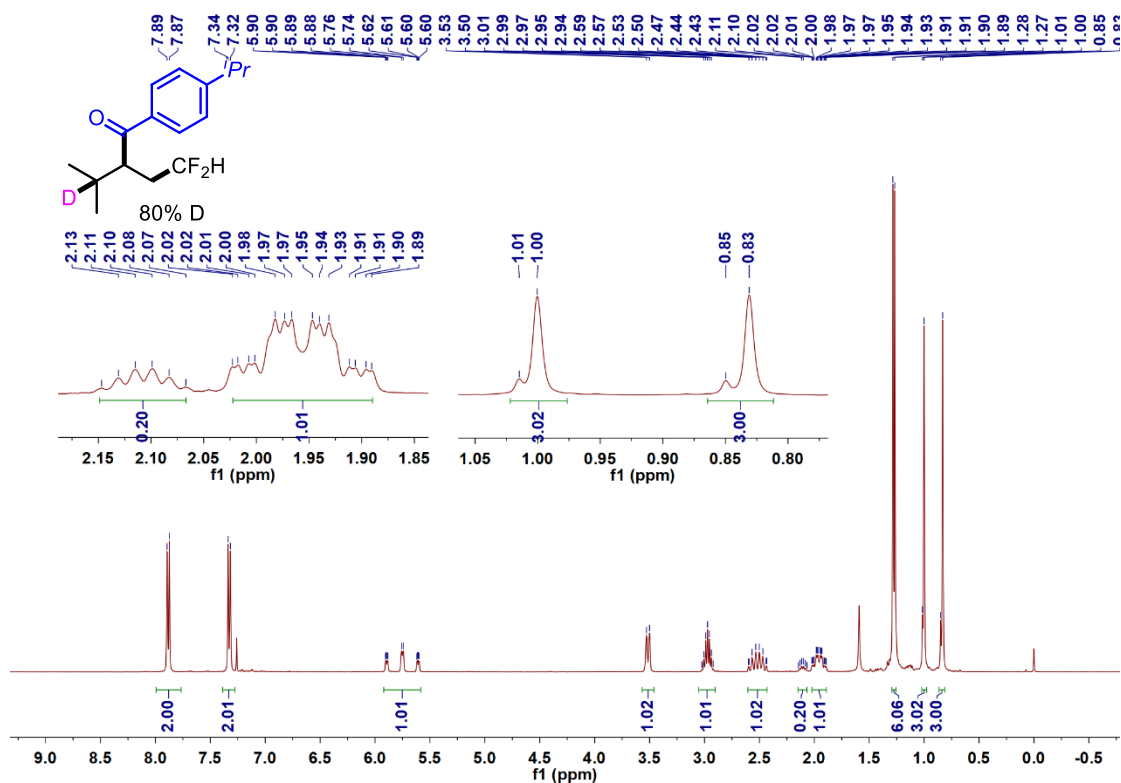
¹³C NMR of Compound **3a-D** (101 MHz, CDCl₃)



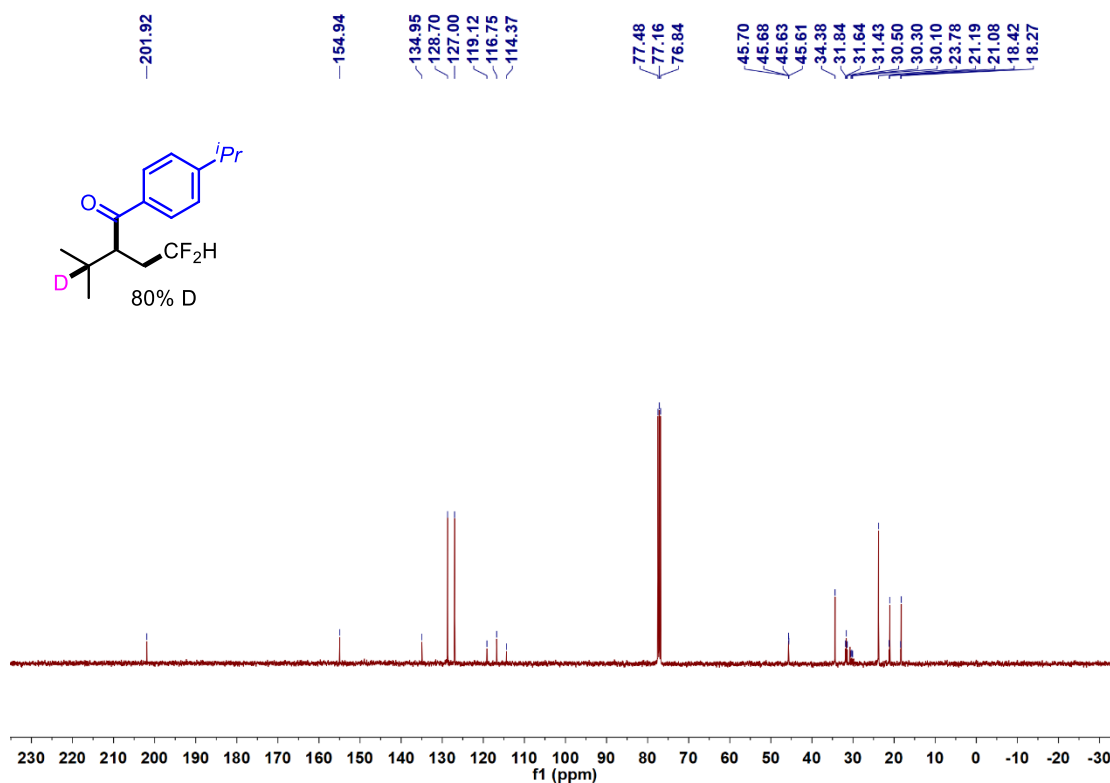
¹⁹F NMR of Compound **3a-D** (400 MHz, CDCl₃)



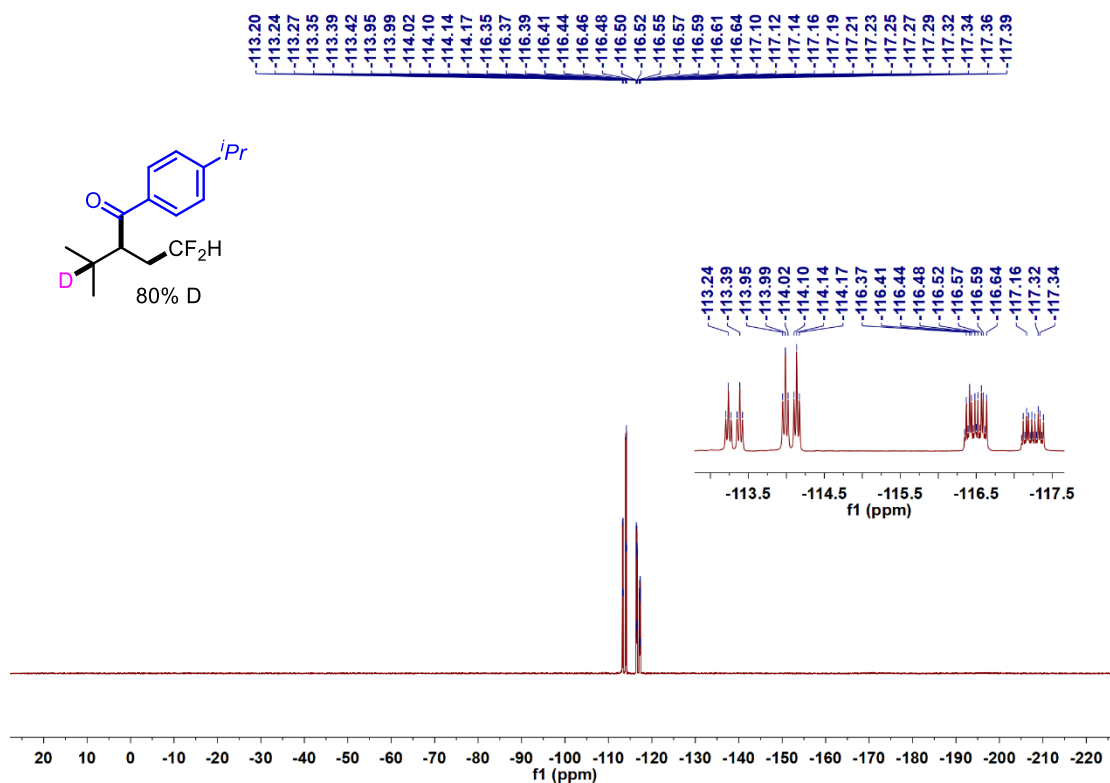
¹H NMR of Compound **3b-D** (400 MHz, CDCl₃)



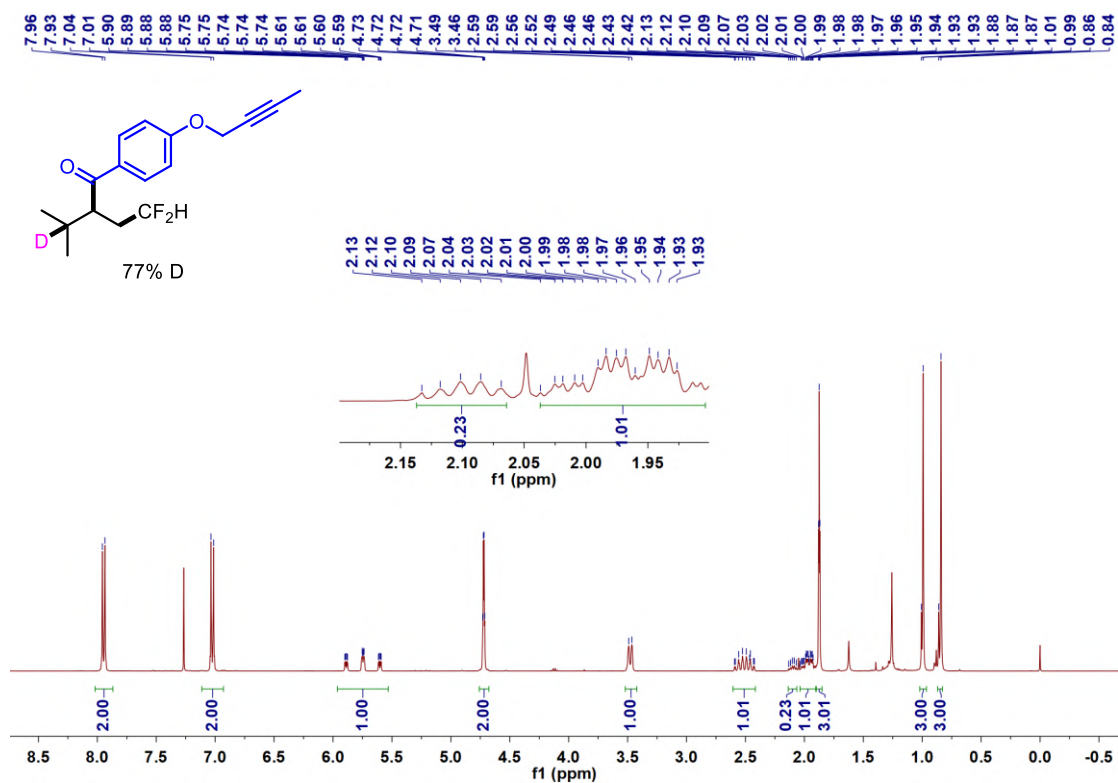
¹³C NMR of Compound **3b-D** (101 MHz, CDCl₃)



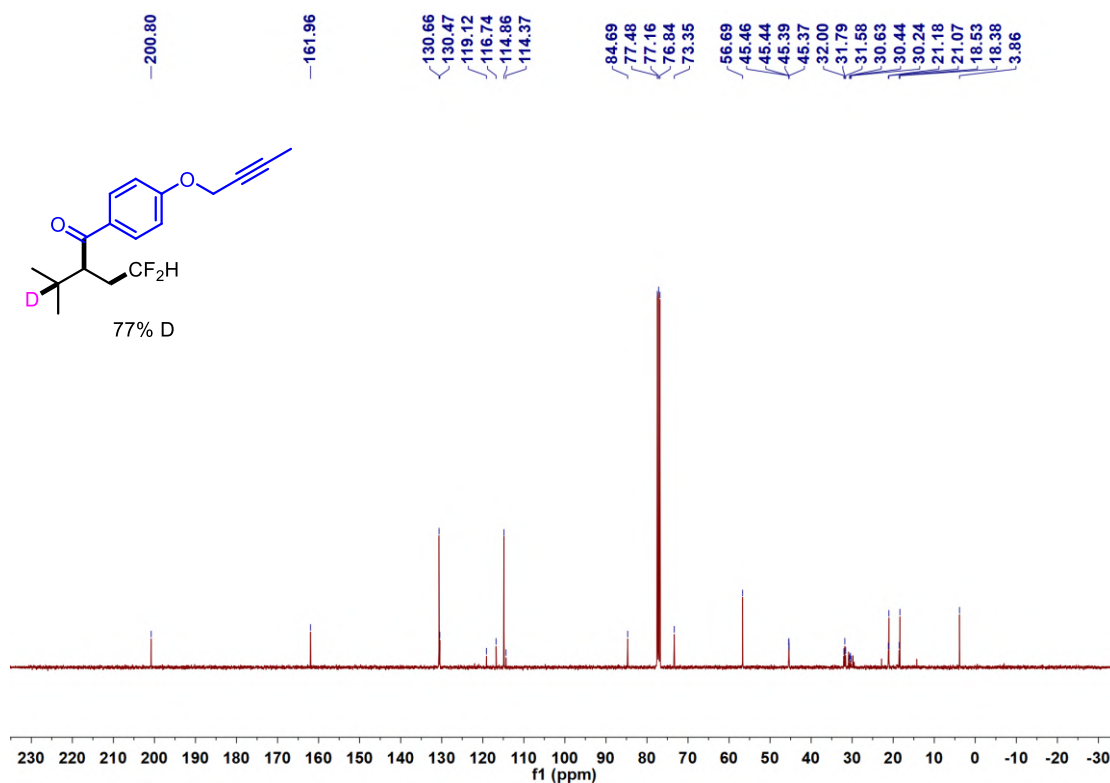
¹⁹F NMR of Compound **3b-D** (400 MHz, CDCl₃)



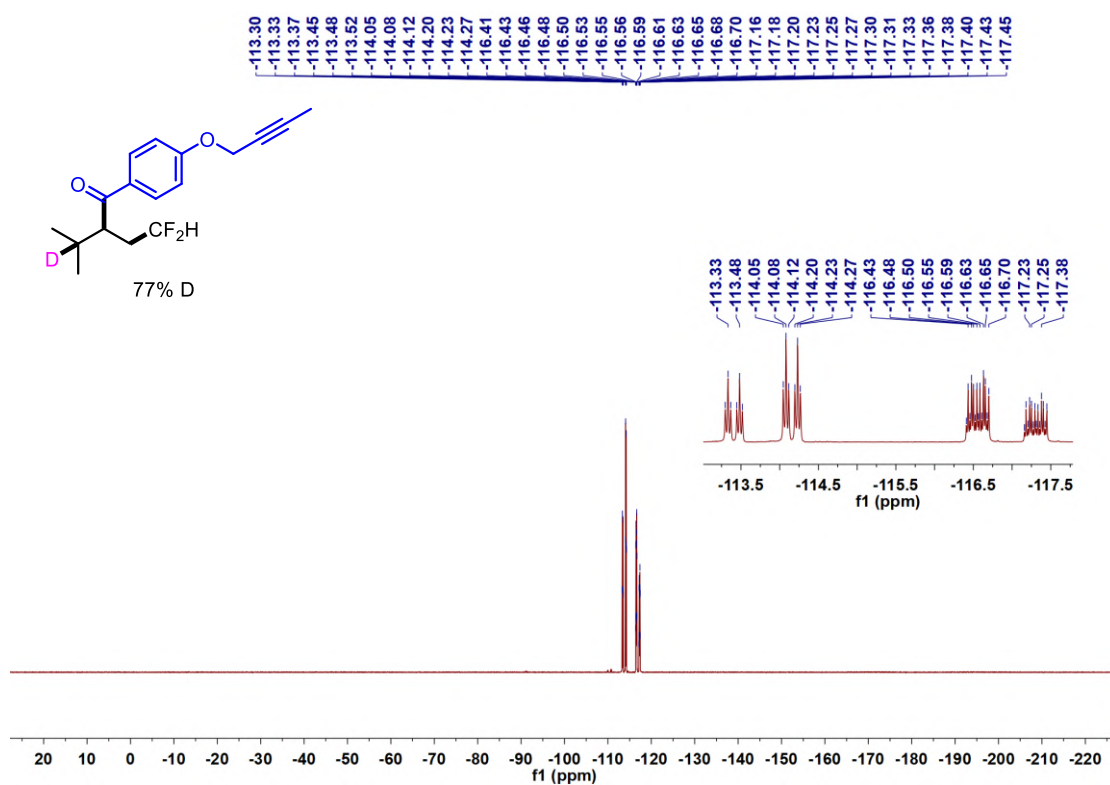
¹H NMR of Compound **3d-D** (400 MHz, CDCl₃)



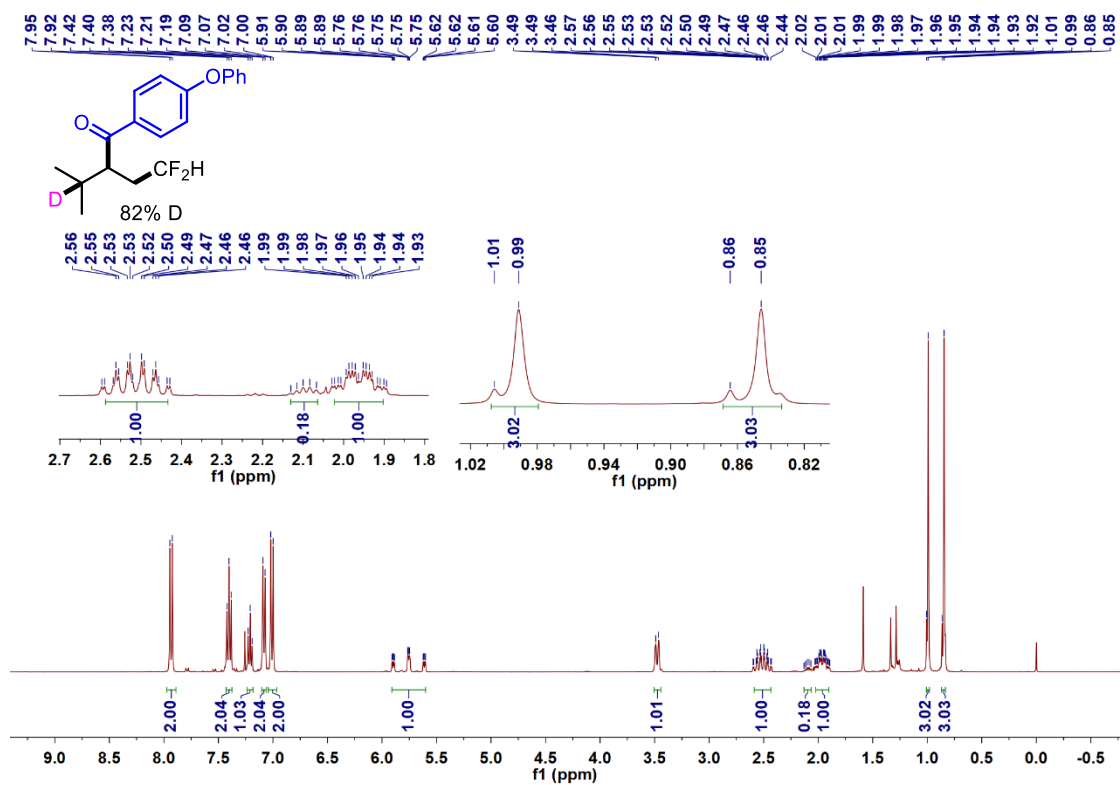
¹³C NMR of Compound **3d-D** (101 MHz, CDCl₃)



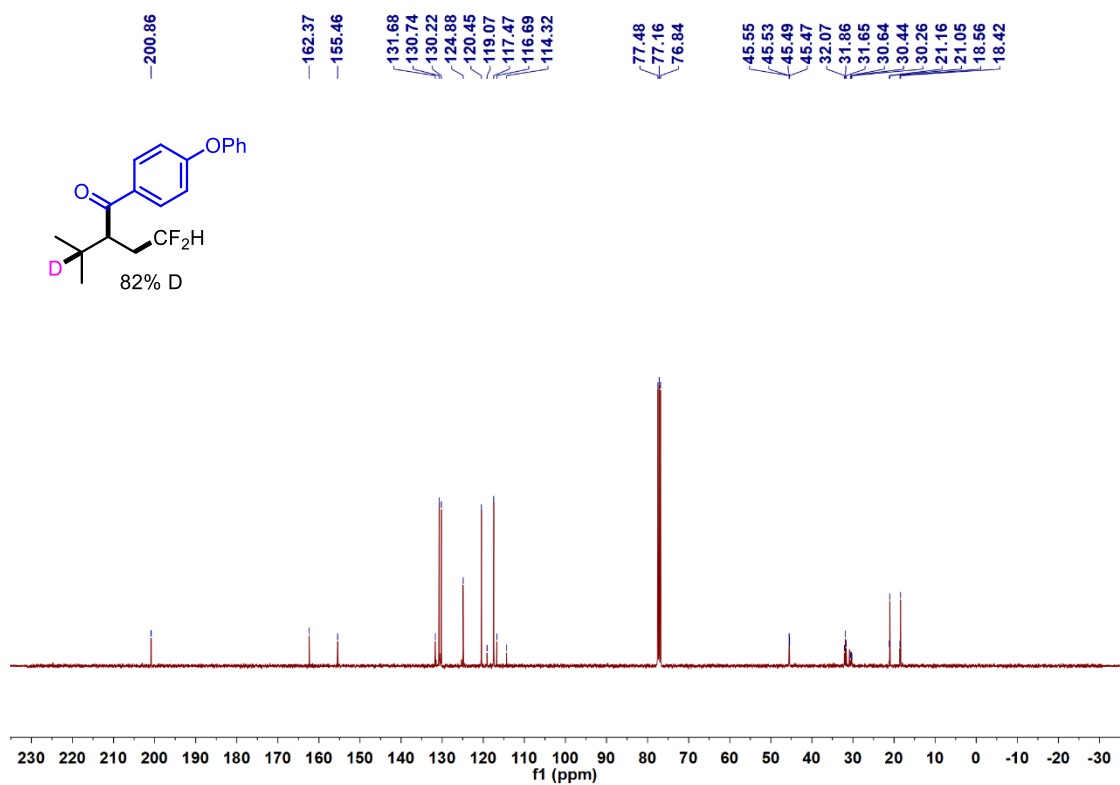
¹⁹F NMR of Compound **3d-D** (400 MHz, CDCl₃)



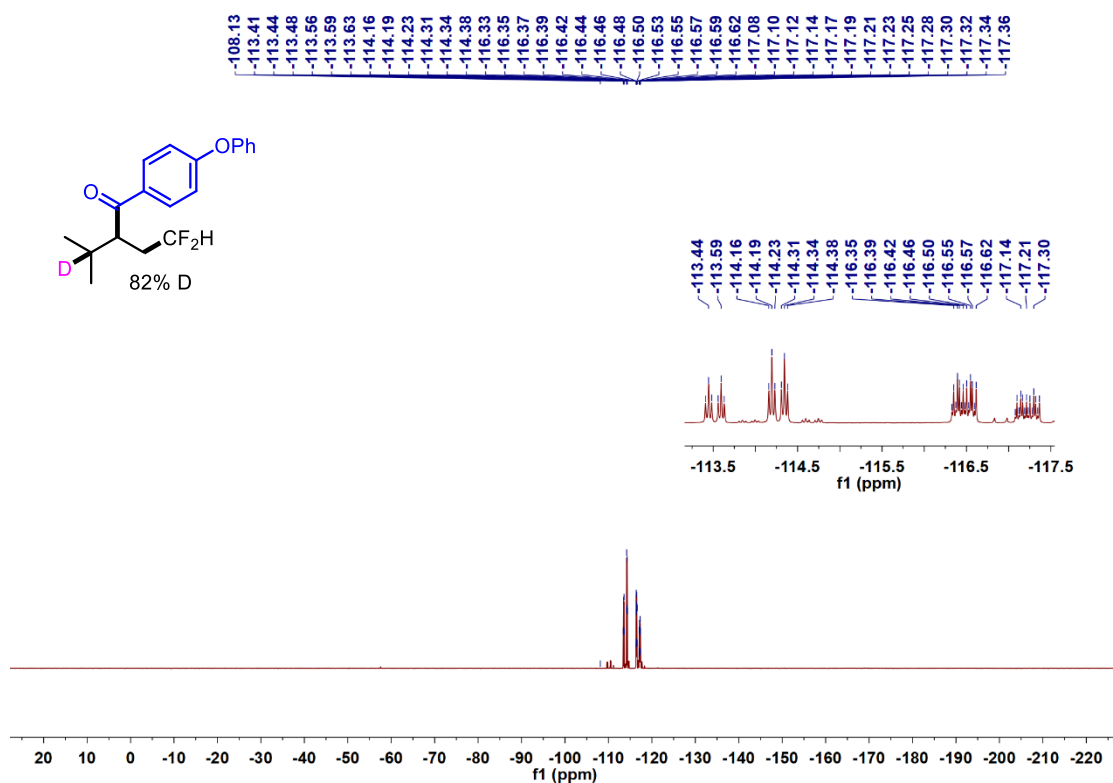
¹H NMR of Compound **3e-D** (400 MHz, CDCl₃)



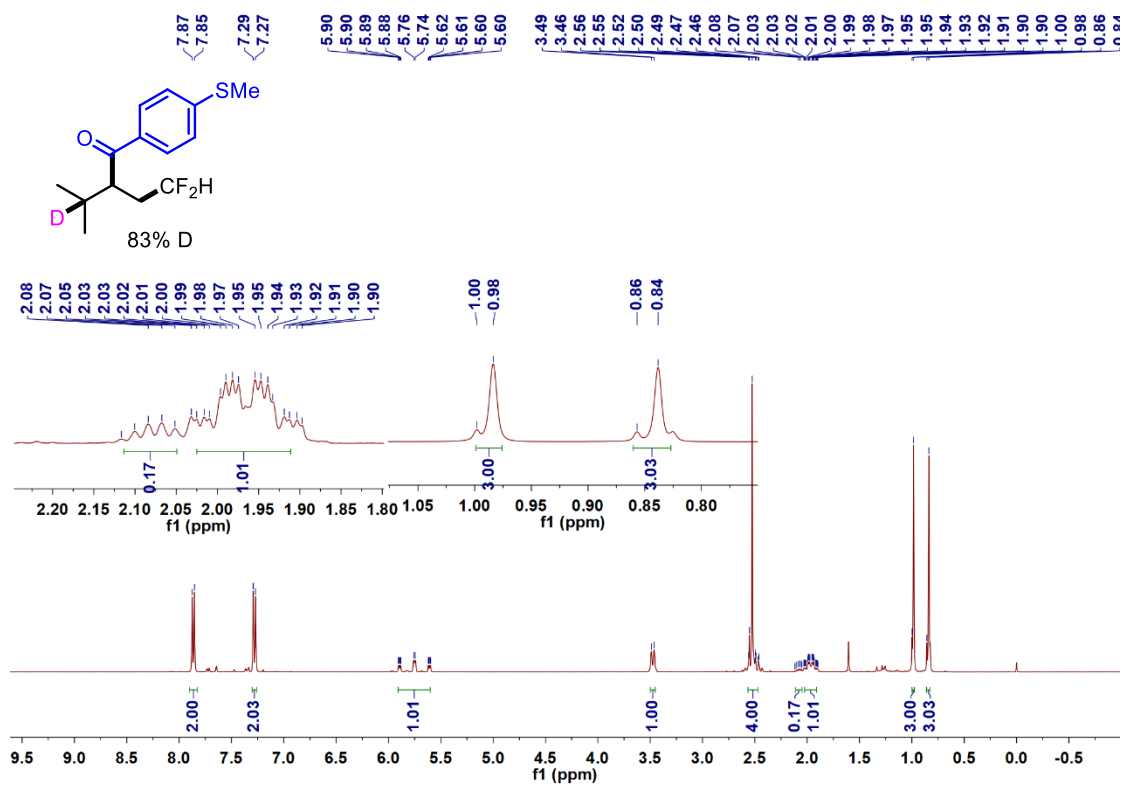
¹³C NMR of Compound **3e-D** (101 MHz, CDCl₃)



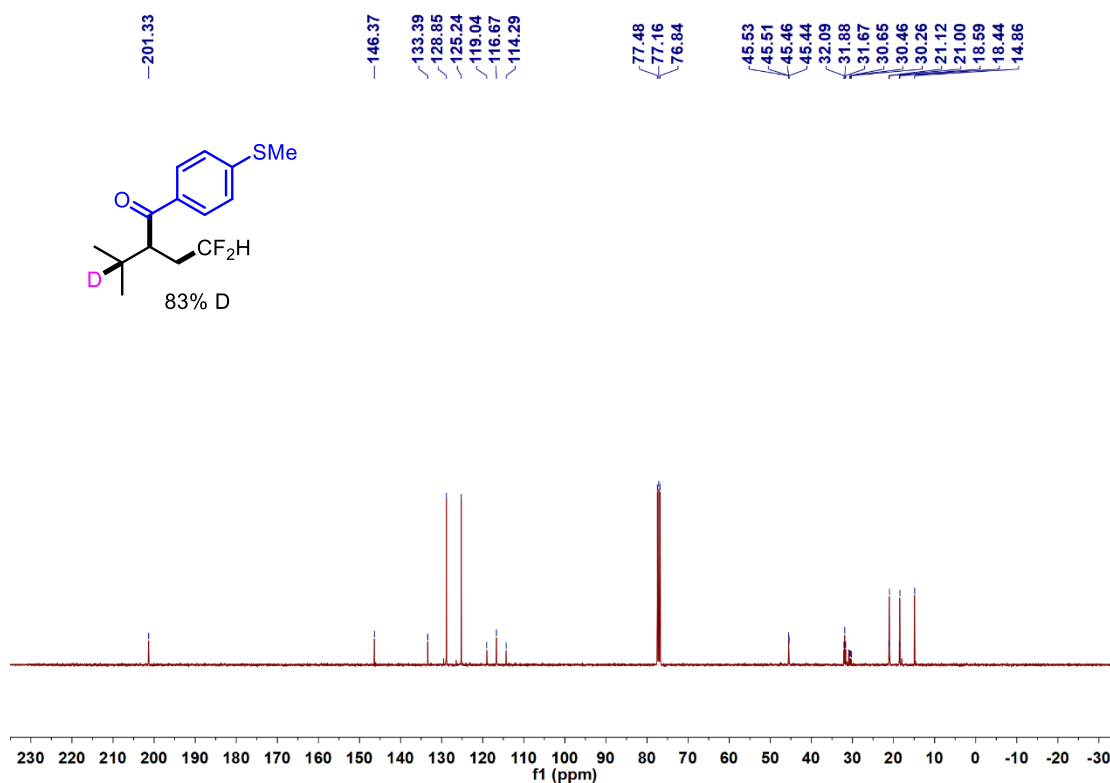
¹⁹F NMR of Compound **3e-D** (400 MHz, CDCl₃)



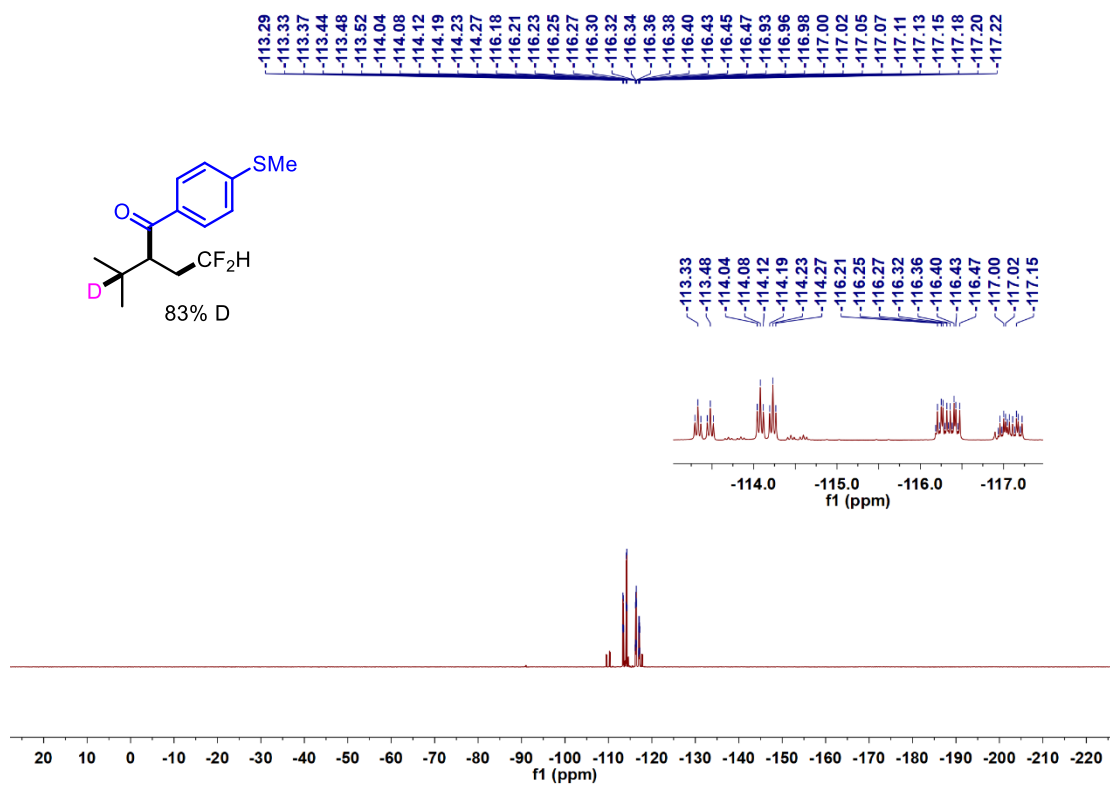
¹H NMR of Compound **3f-D** (400 MHz, CDCl₃)



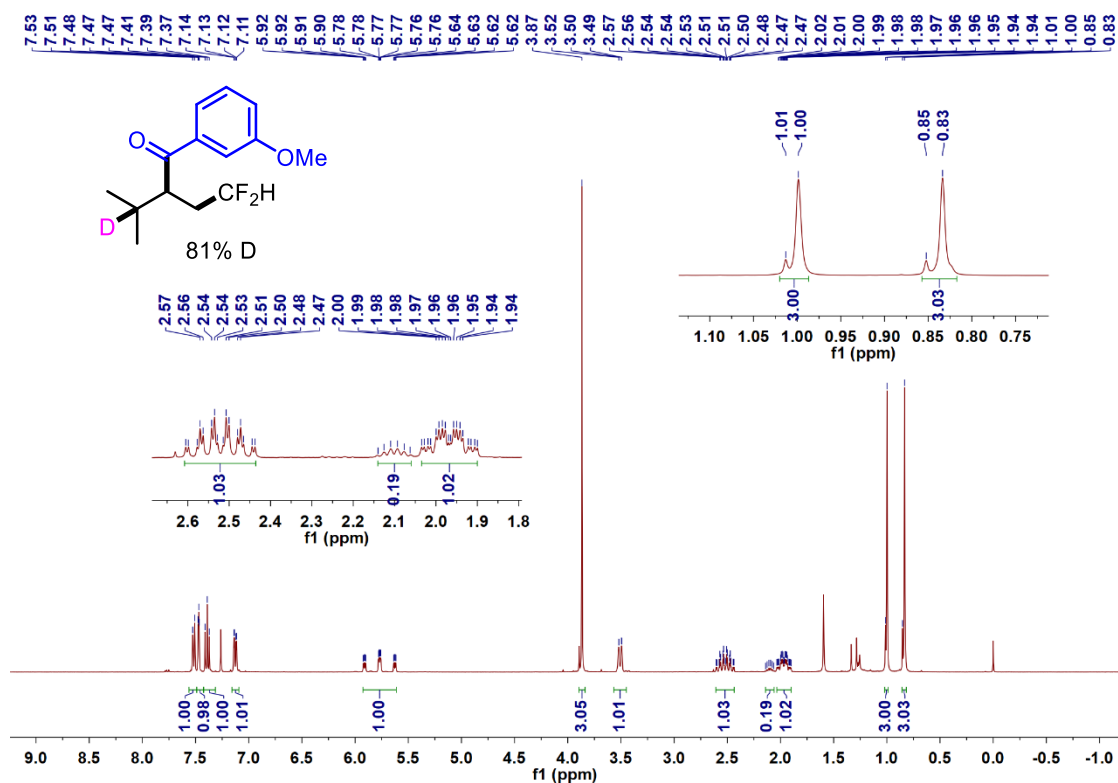
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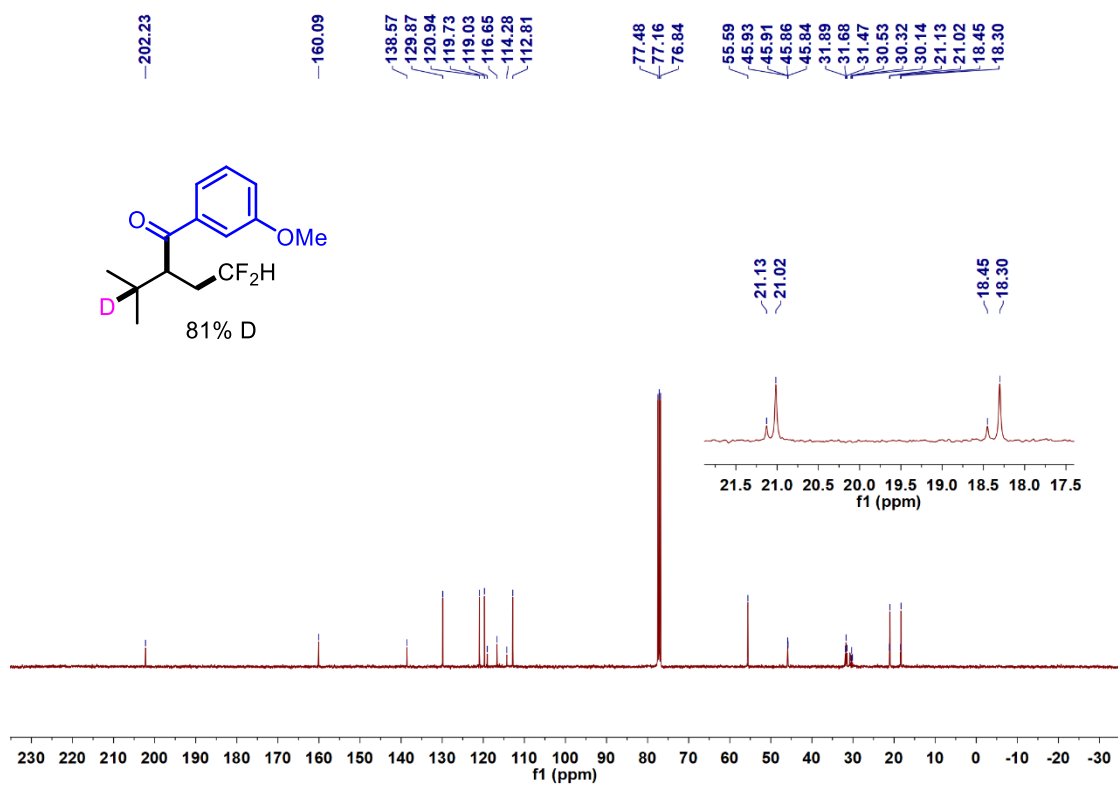
¹⁹F NMR of Compound **3f-D** (400 MHz, CDCl₃)



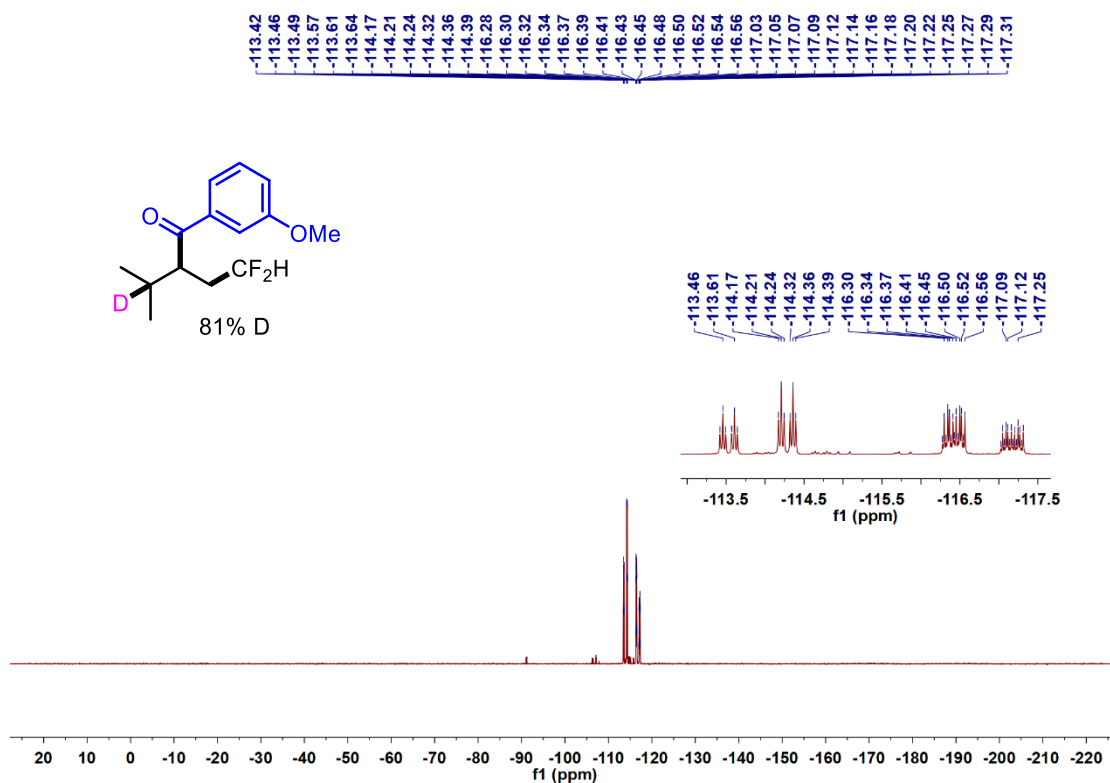
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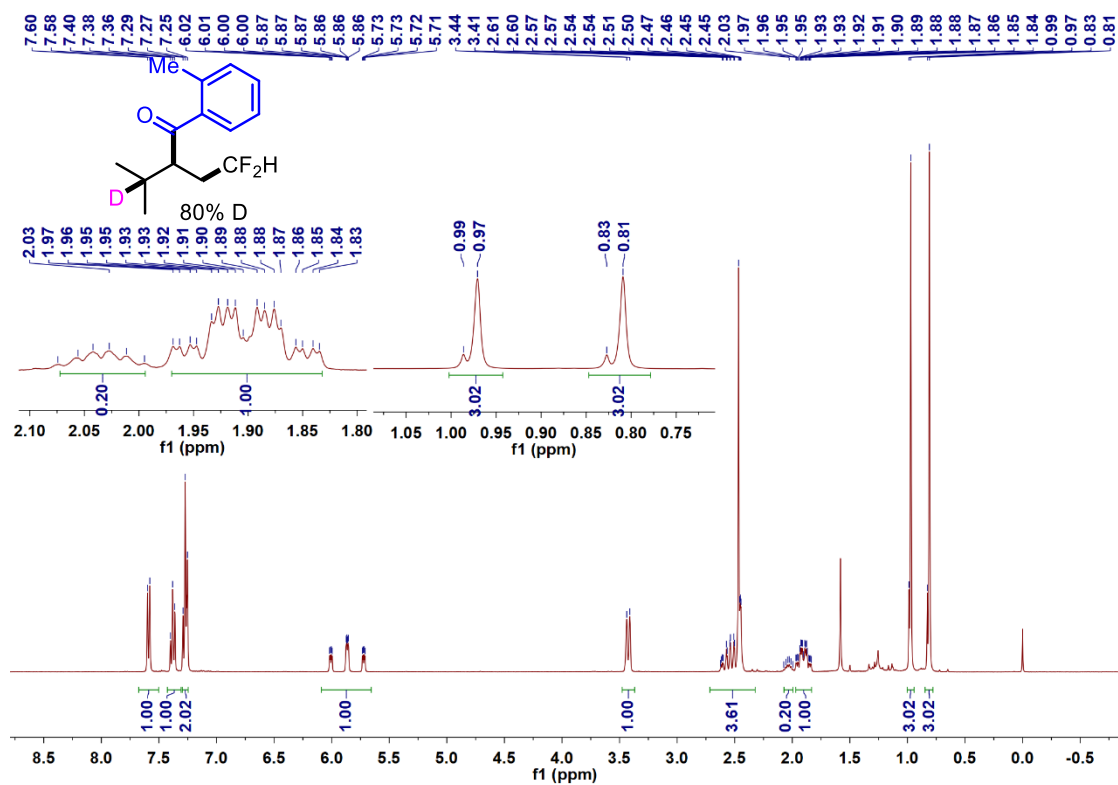
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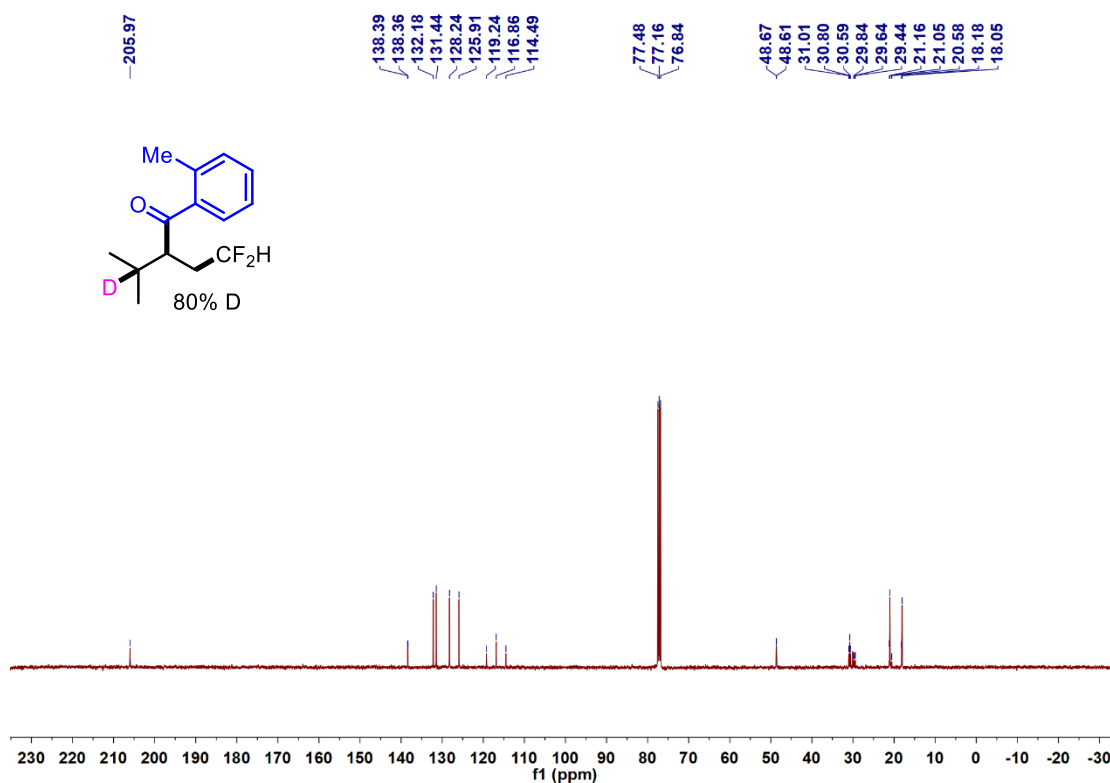
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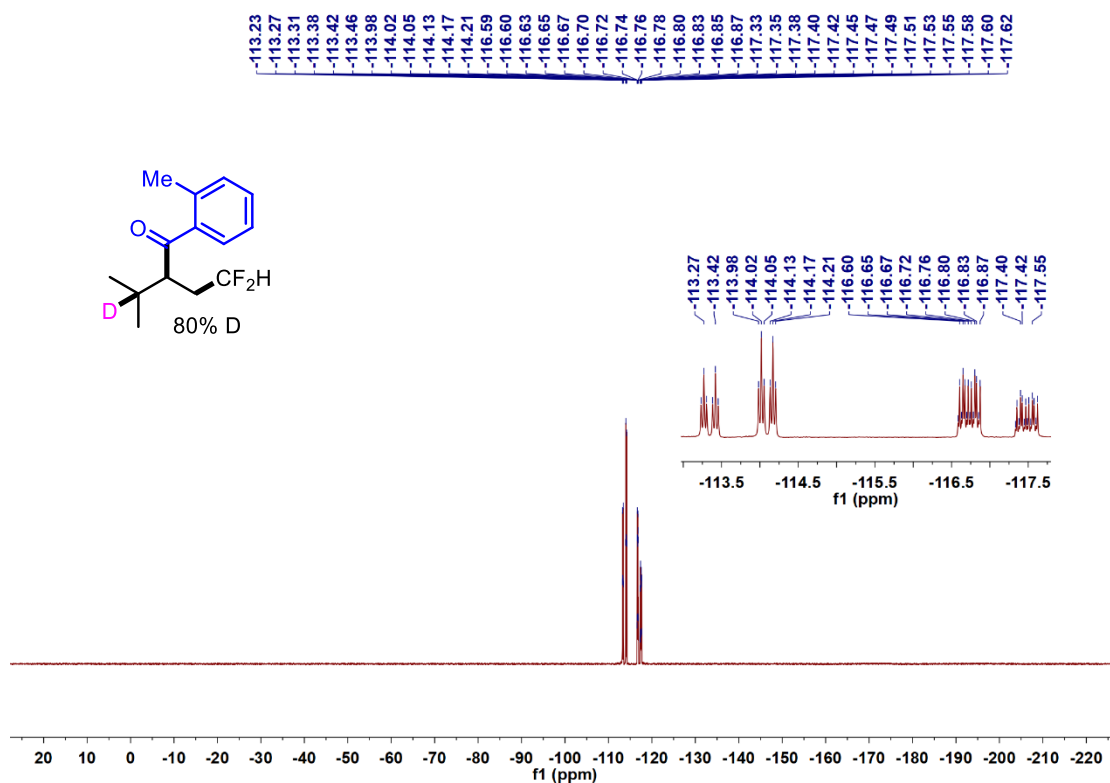
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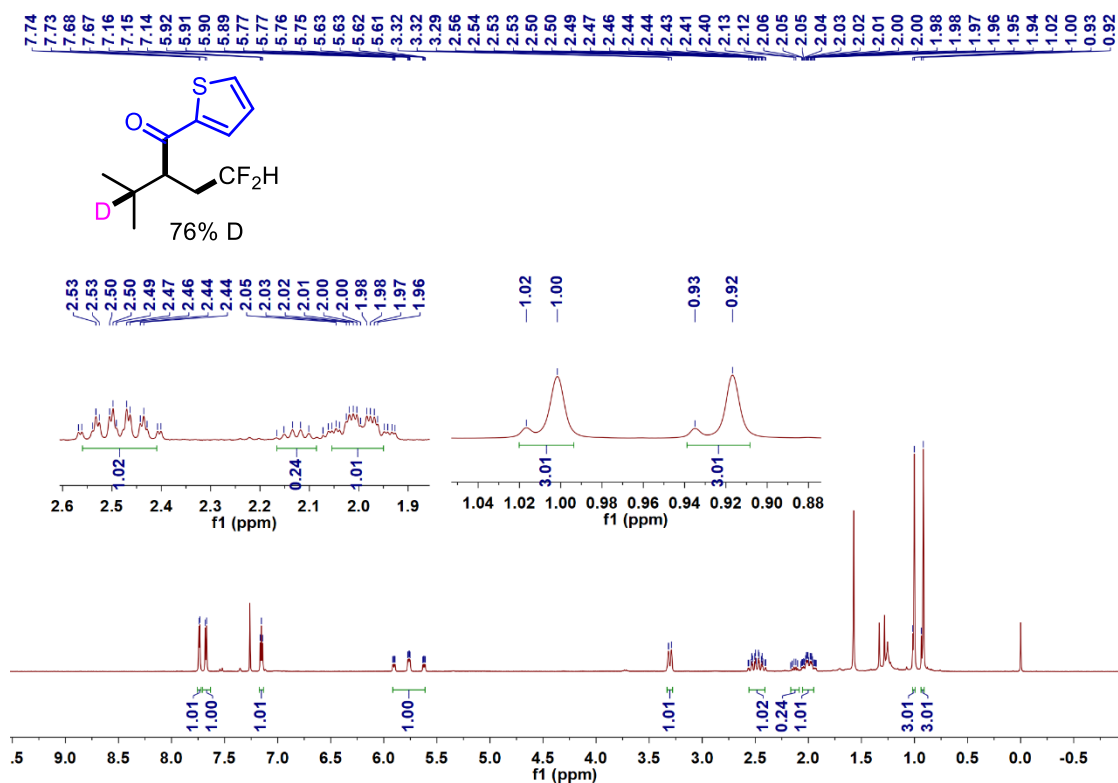
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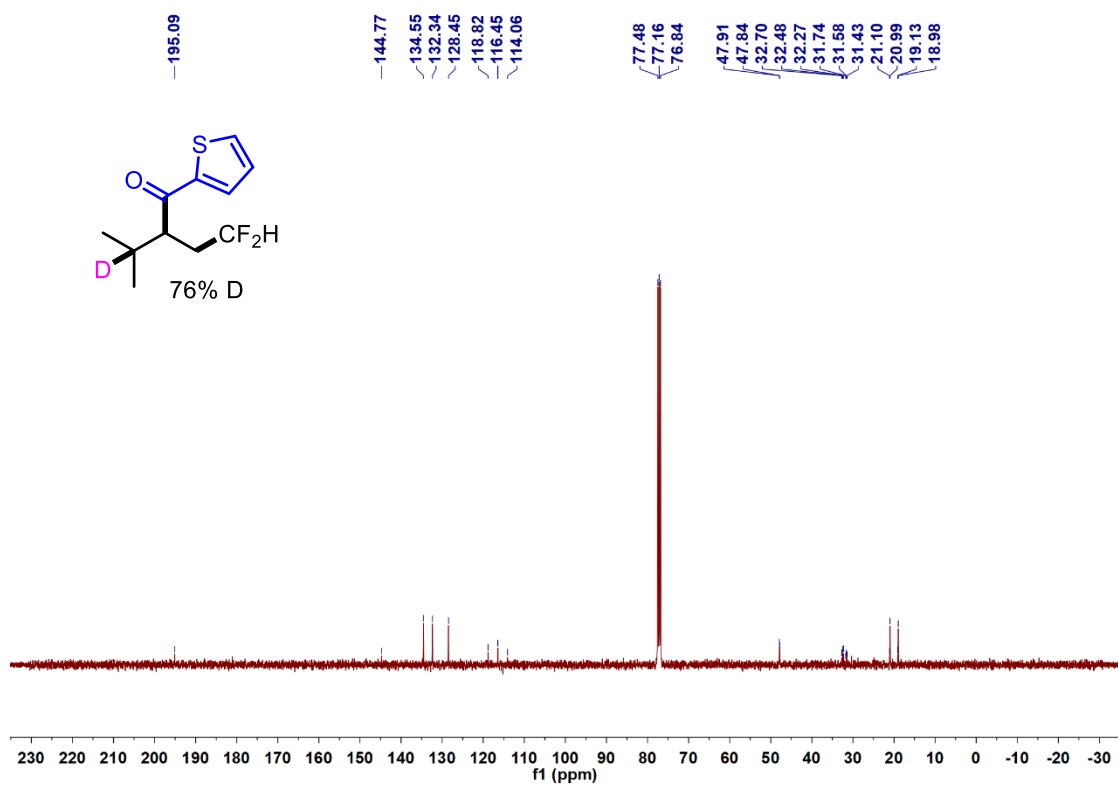
¹⁹F NMR of Compound **3j-D** (400 MHz, CDCl₃)



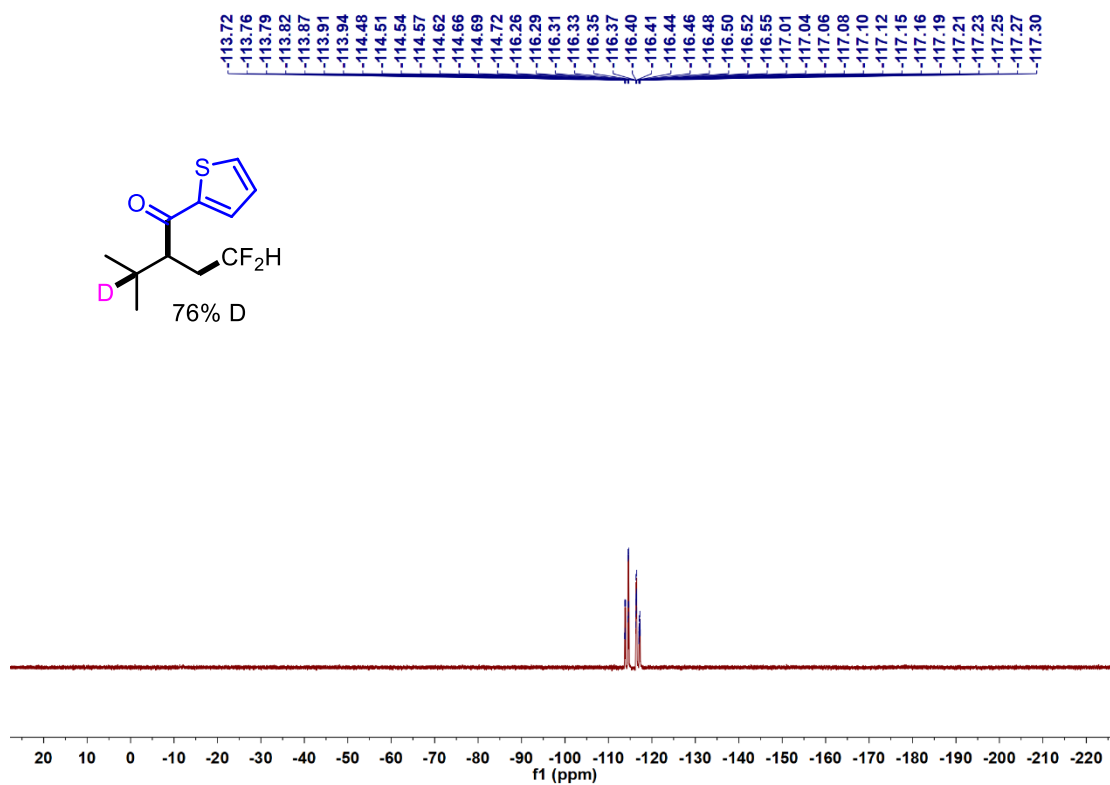
¹H NMR of Compound **3m-D** (400 MHz, CDCl₃)



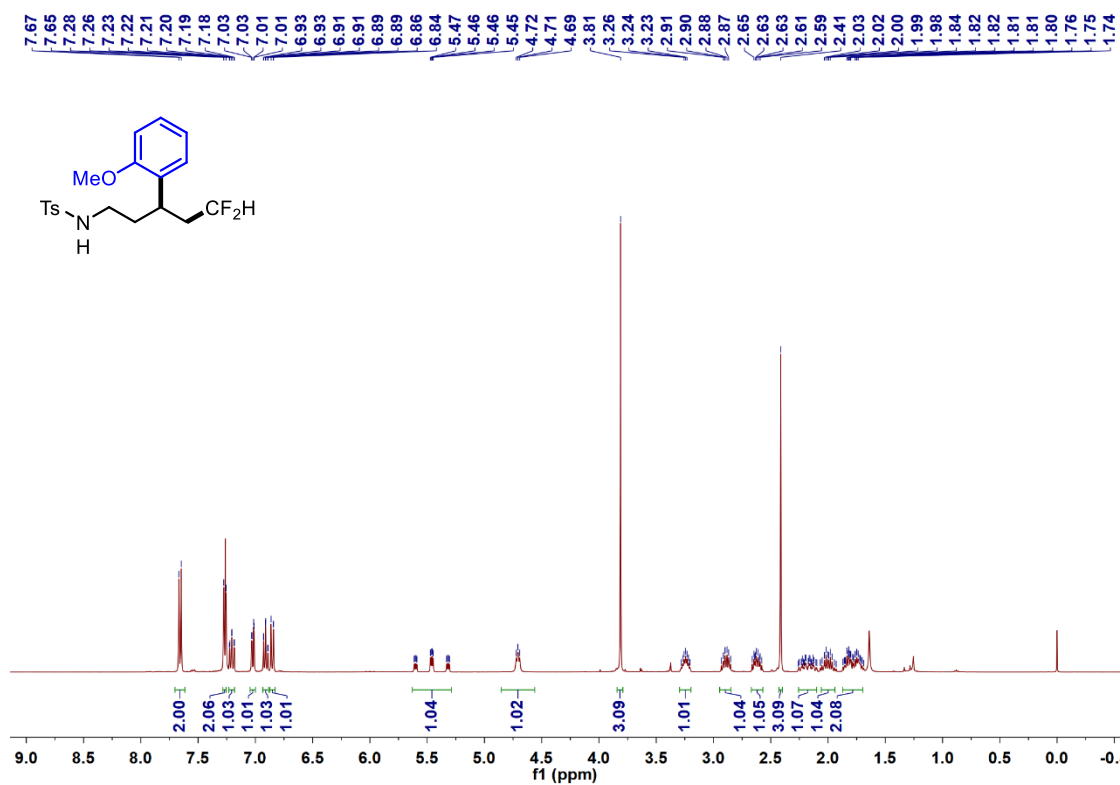
¹³C NMR of Compound **3m-D** (101 MHz, CDCl₃)



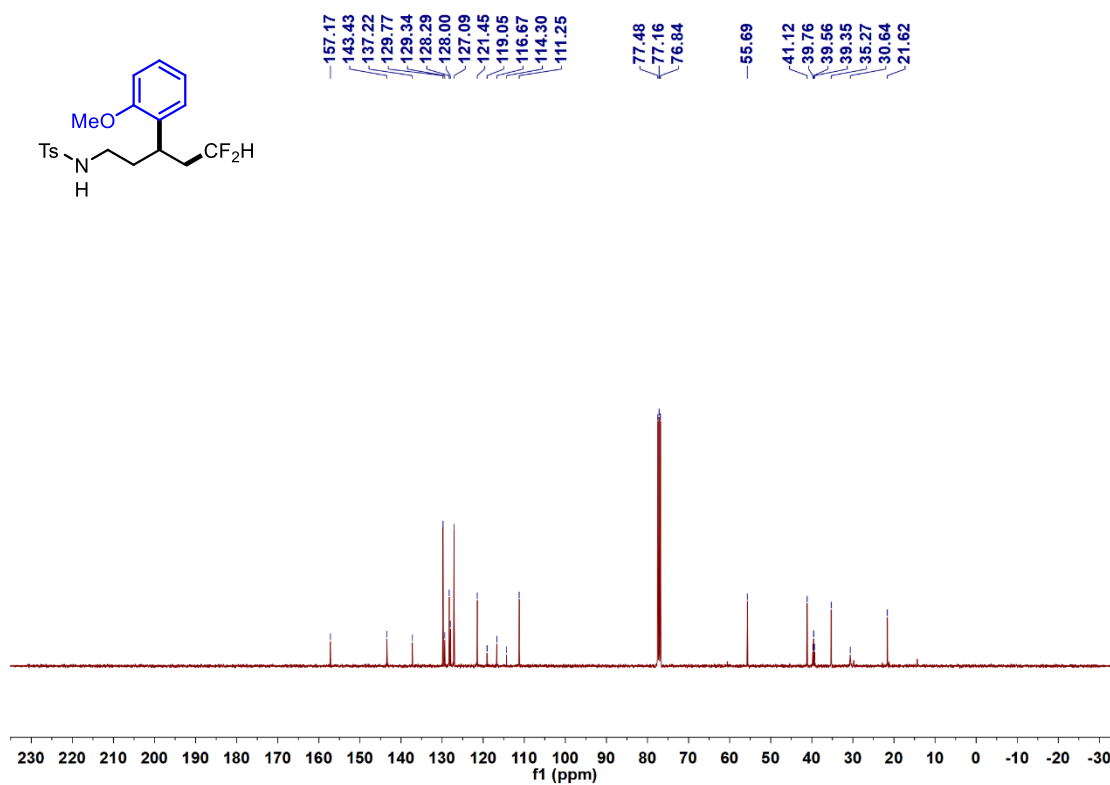
¹⁹F NMR of Compound **3m-D** (400 MHz, CDCl₃)



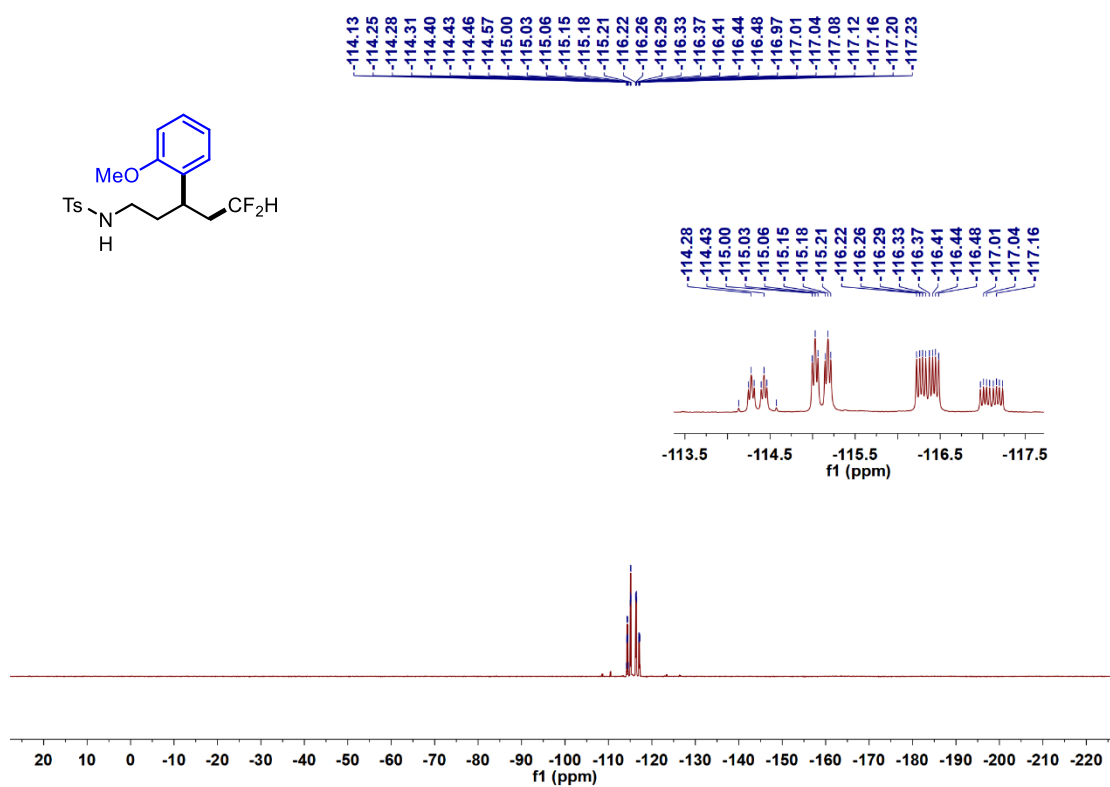
¹H NMR of Compound **5a** (400 MHz, CDCl₃)



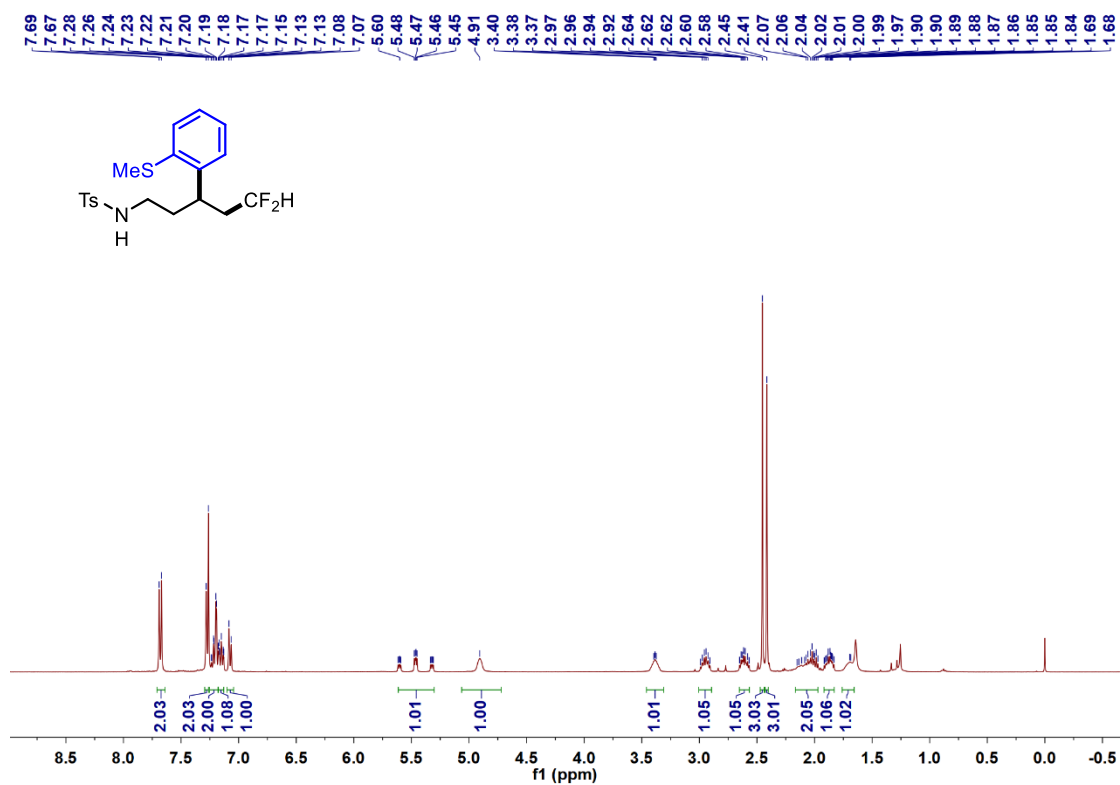
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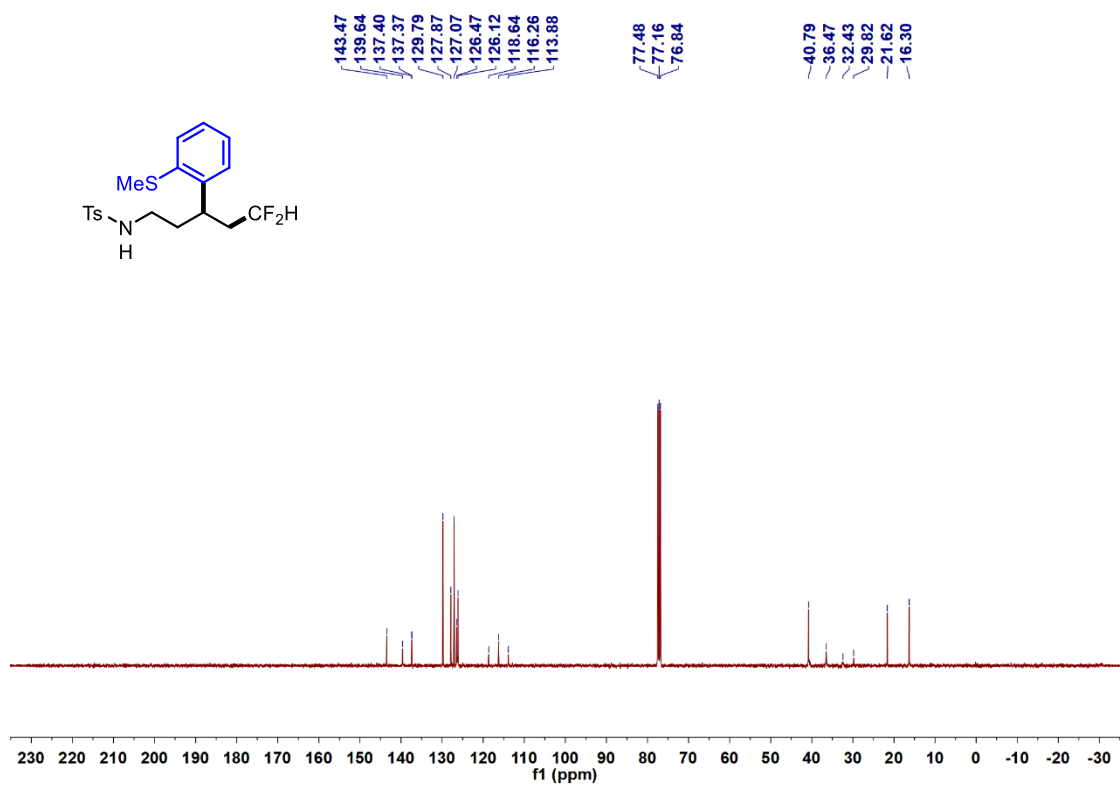
¹⁹F NMR of Compound **5a** (400 MHz, CDCl₃)



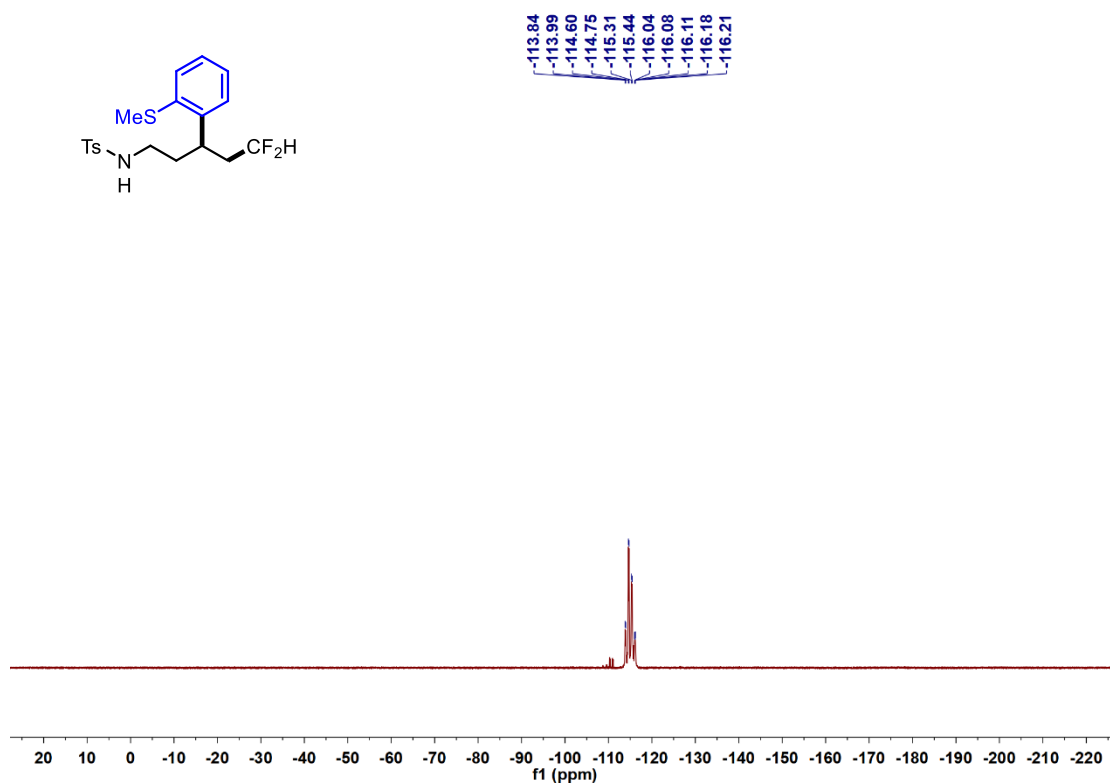
¹H NMR of Compound **5b** (400 MHz, CDCl₃)



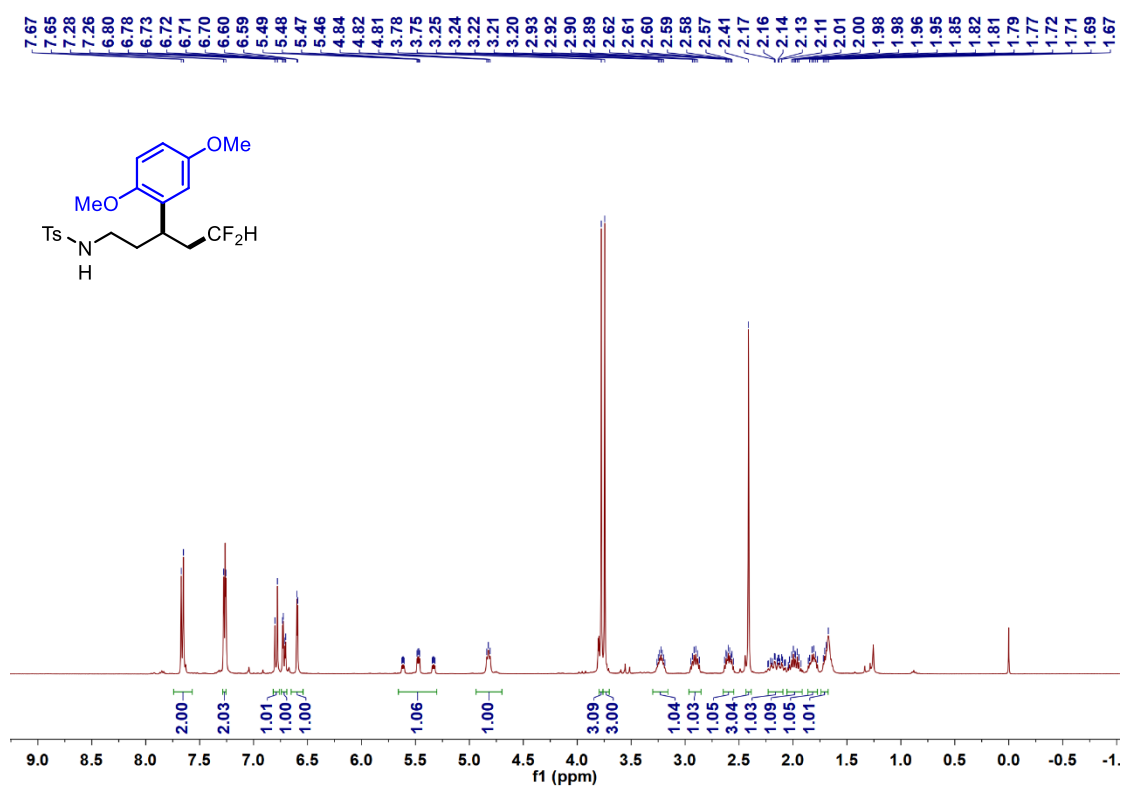
¹³C NMR of Compound **5b** (101 MHz, CDCl₃)



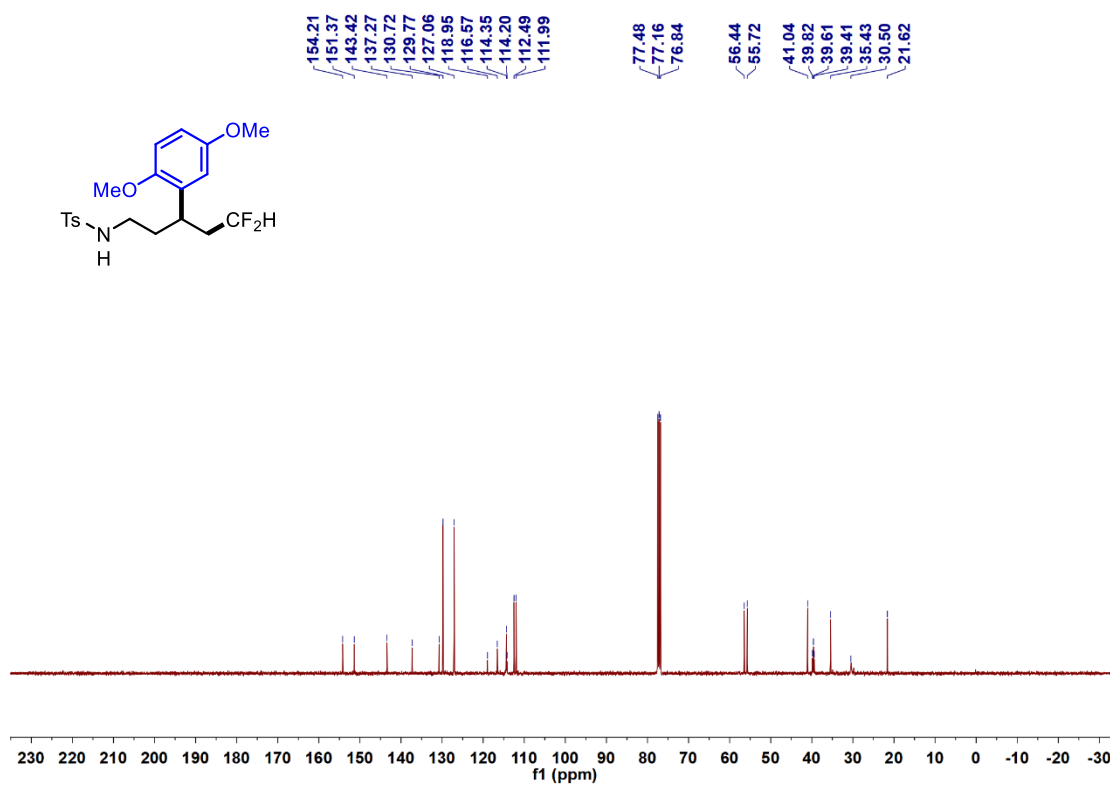
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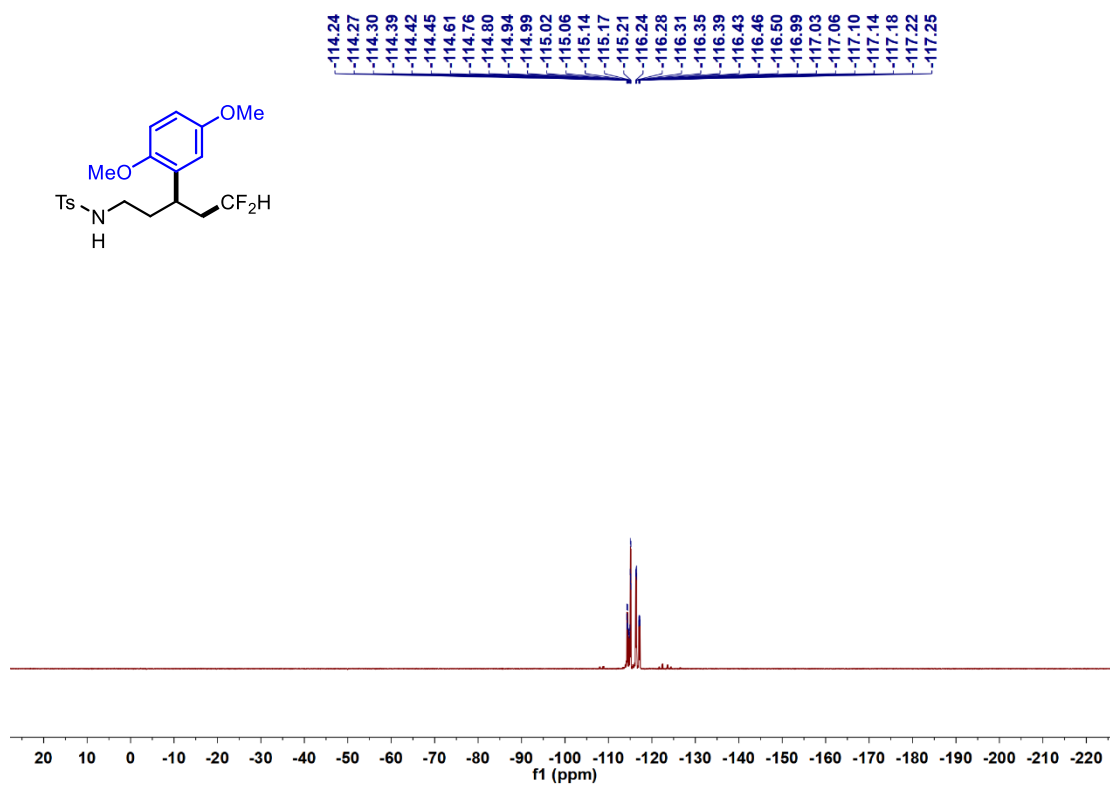
^1H NMR of Compound **5c** (400 MHz, CDCl_3)



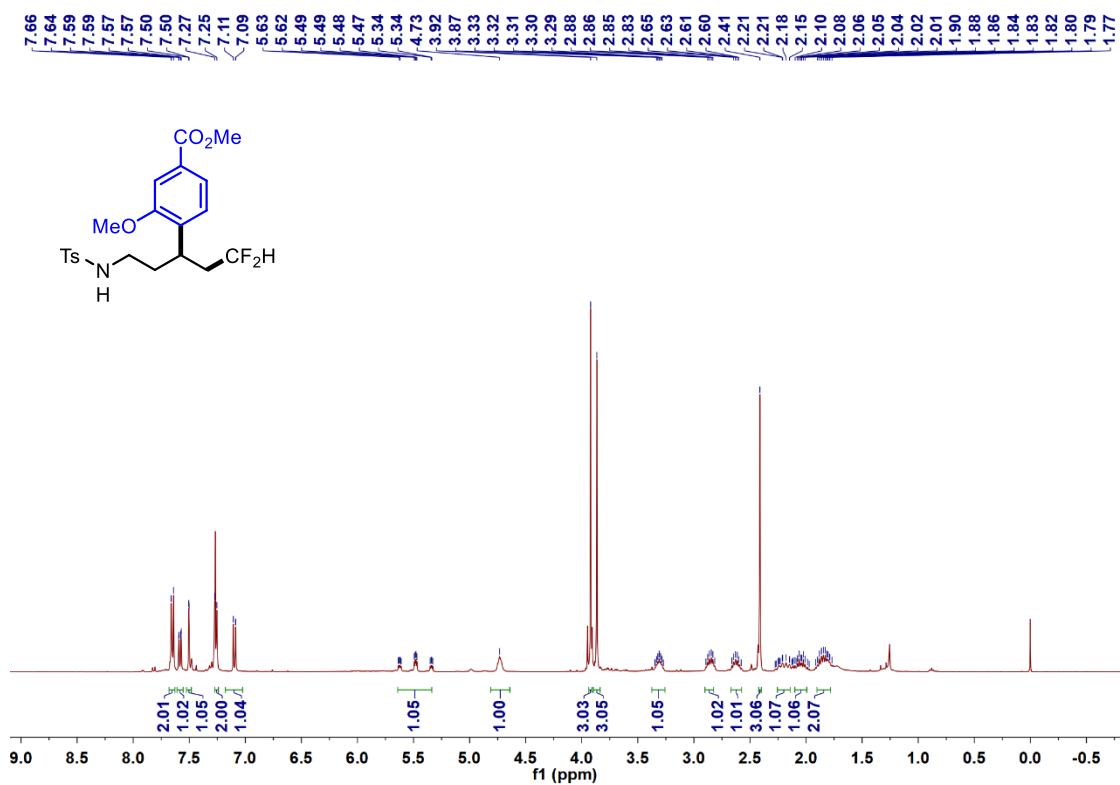
¹³C NMR of Compound **5c** (101 MHz, CDCl₃)



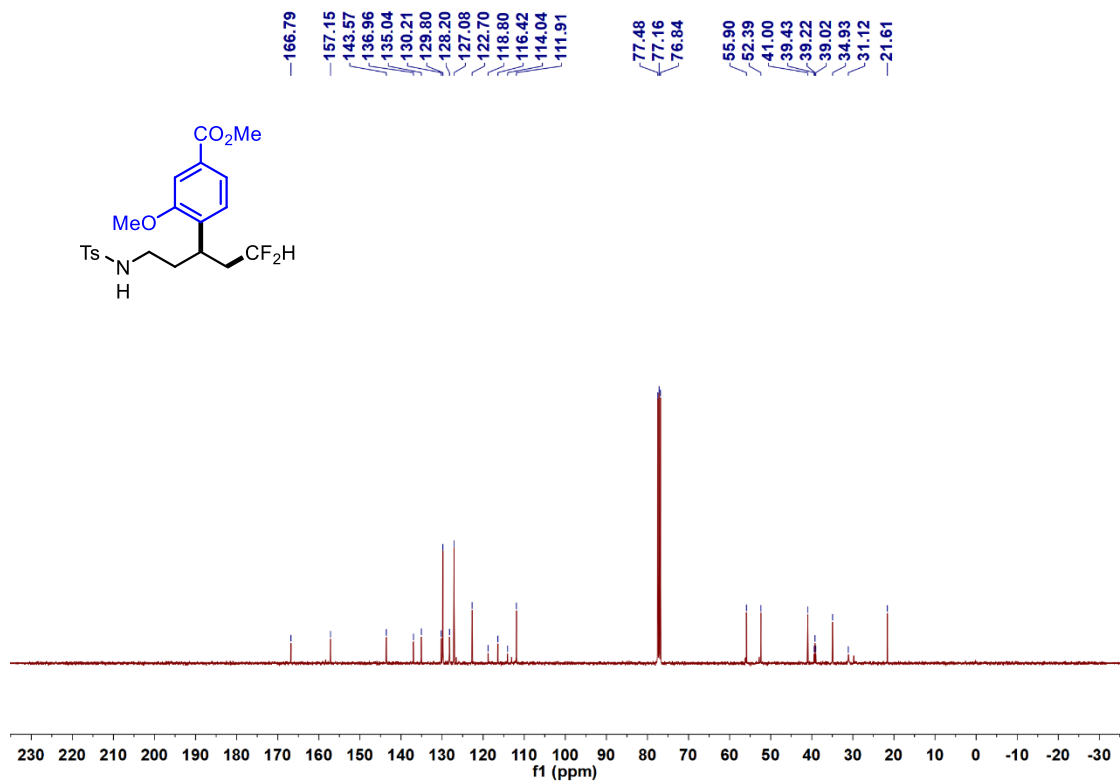
¹⁹F NMR of Compound **5c** (400 MHz, CDCl₃)



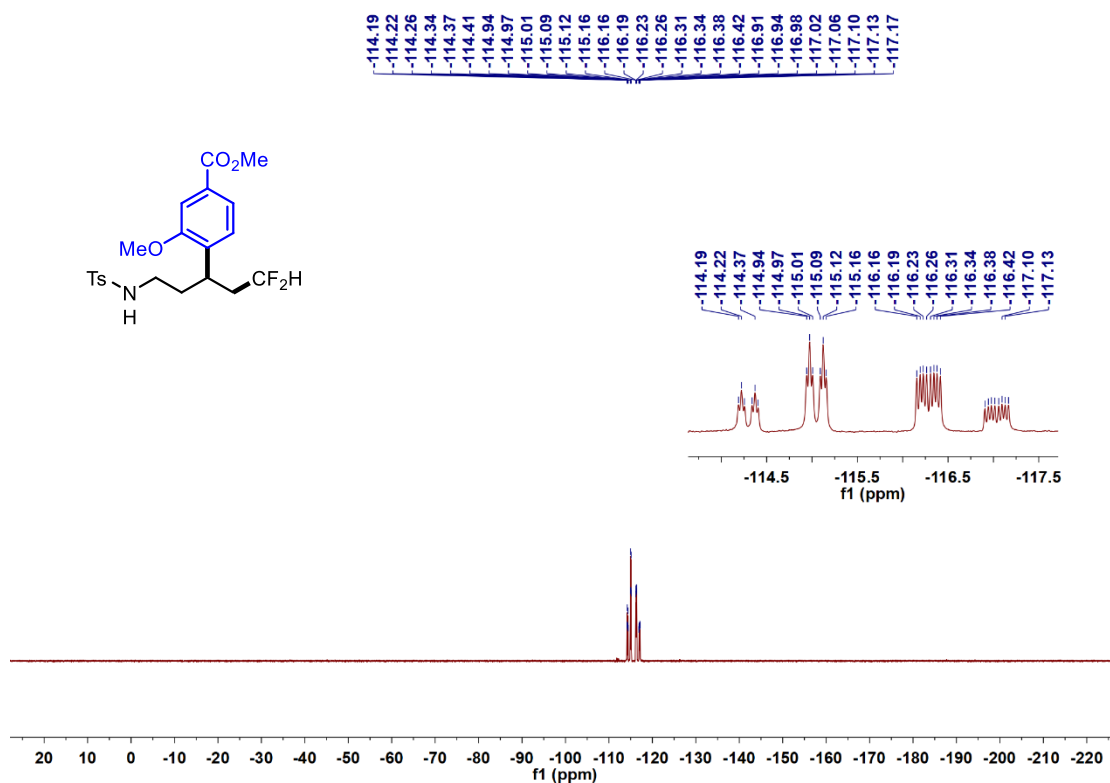
¹H NMR of Compound **5d** (400 MHz, CDCl₃)



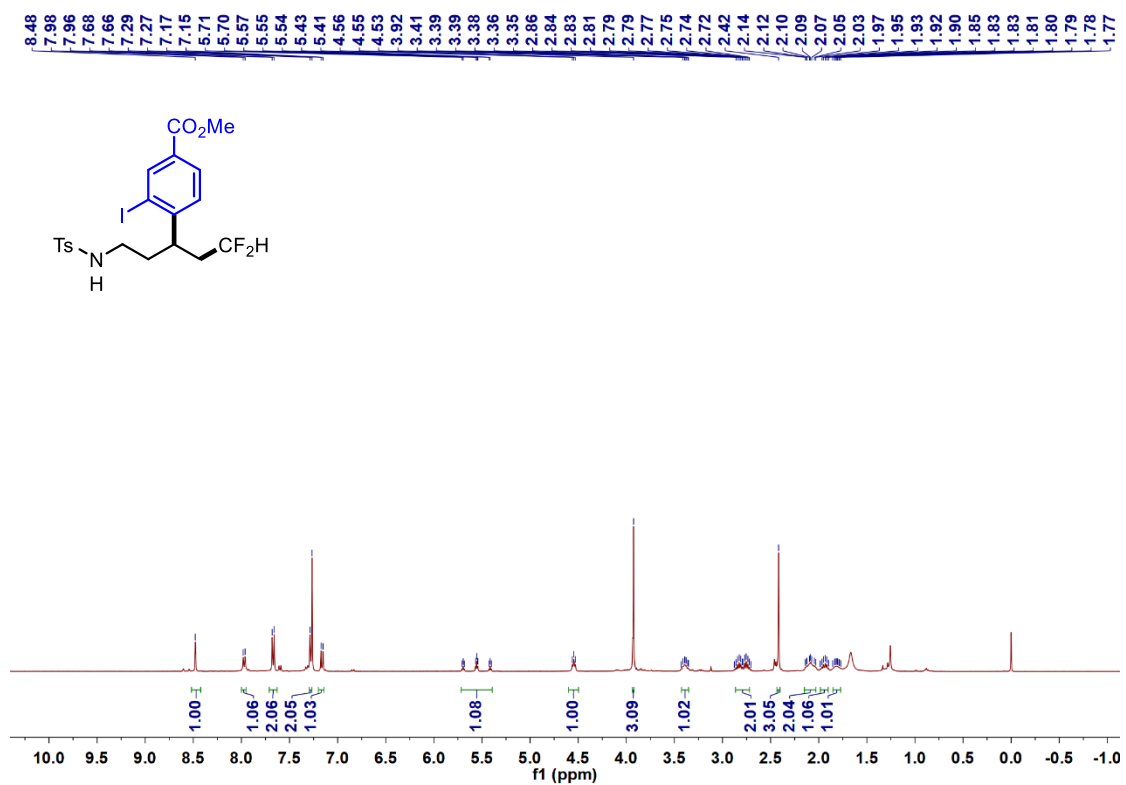
¹³C NMR of Compound **5d** (101 MHz, CDCl₃)



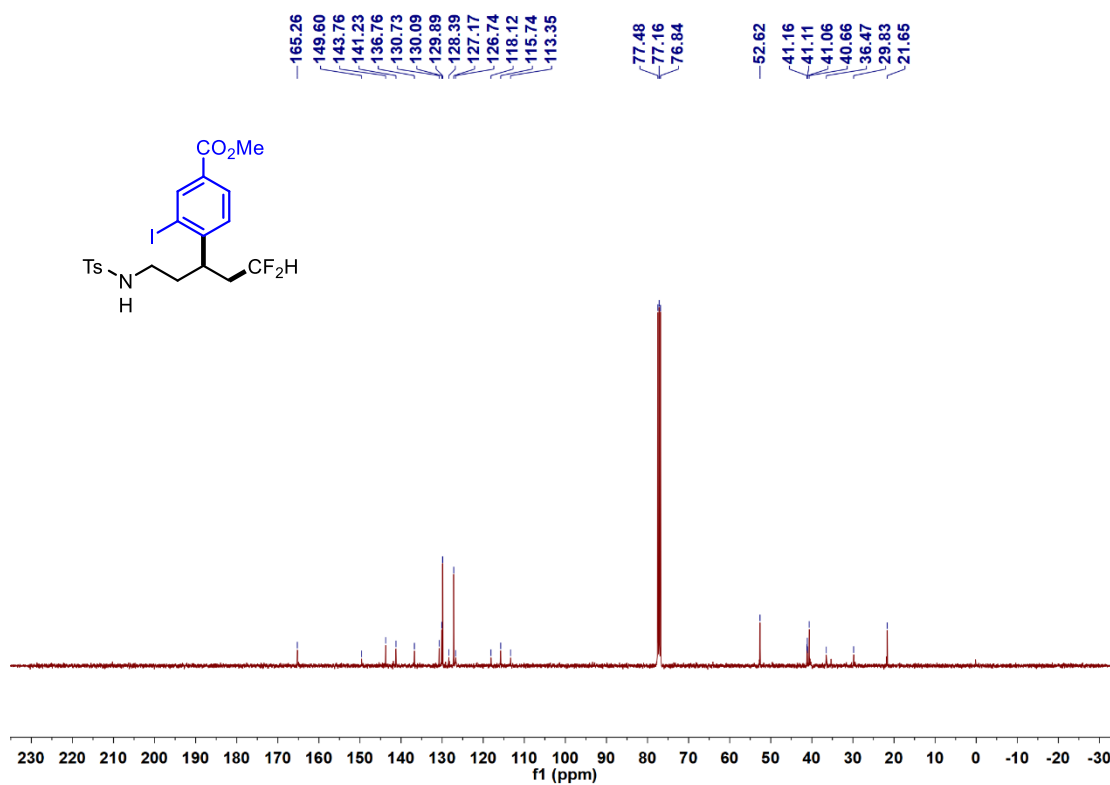
¹⁹F NMR of Compound **5d** (400 MHz, CDCl₃)



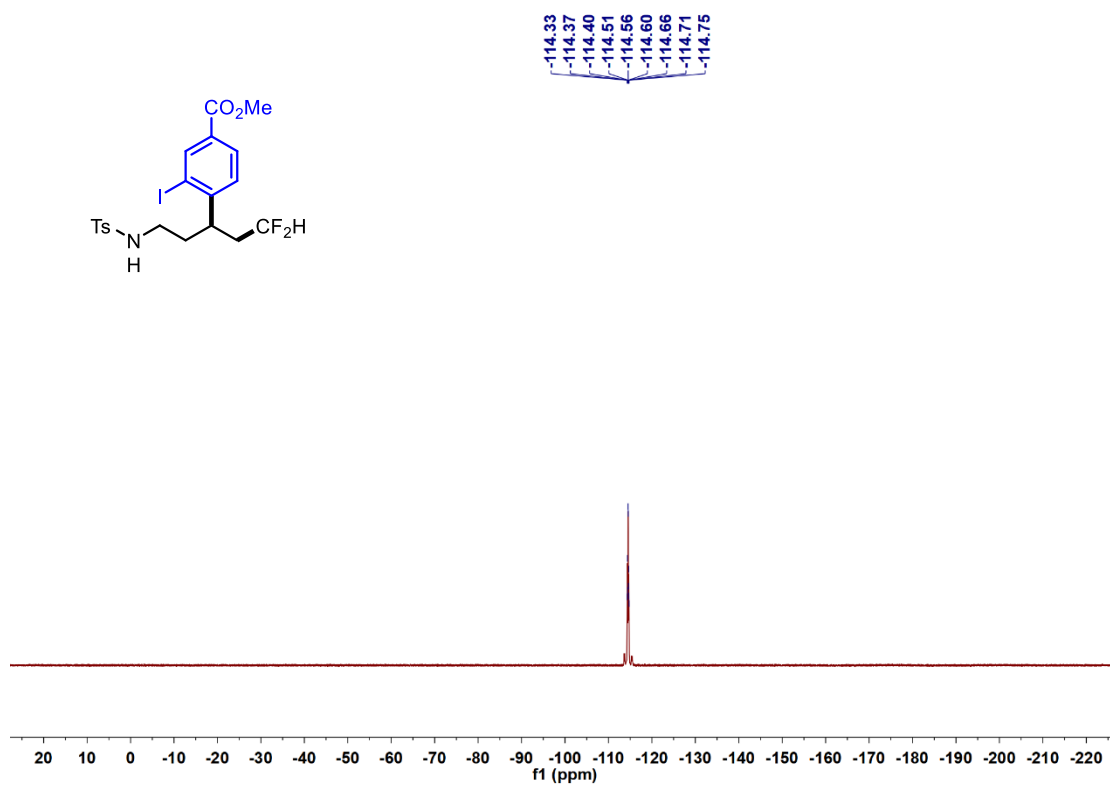
¹H NMR of Compound **5e** (400 MHz, CDCl₃)



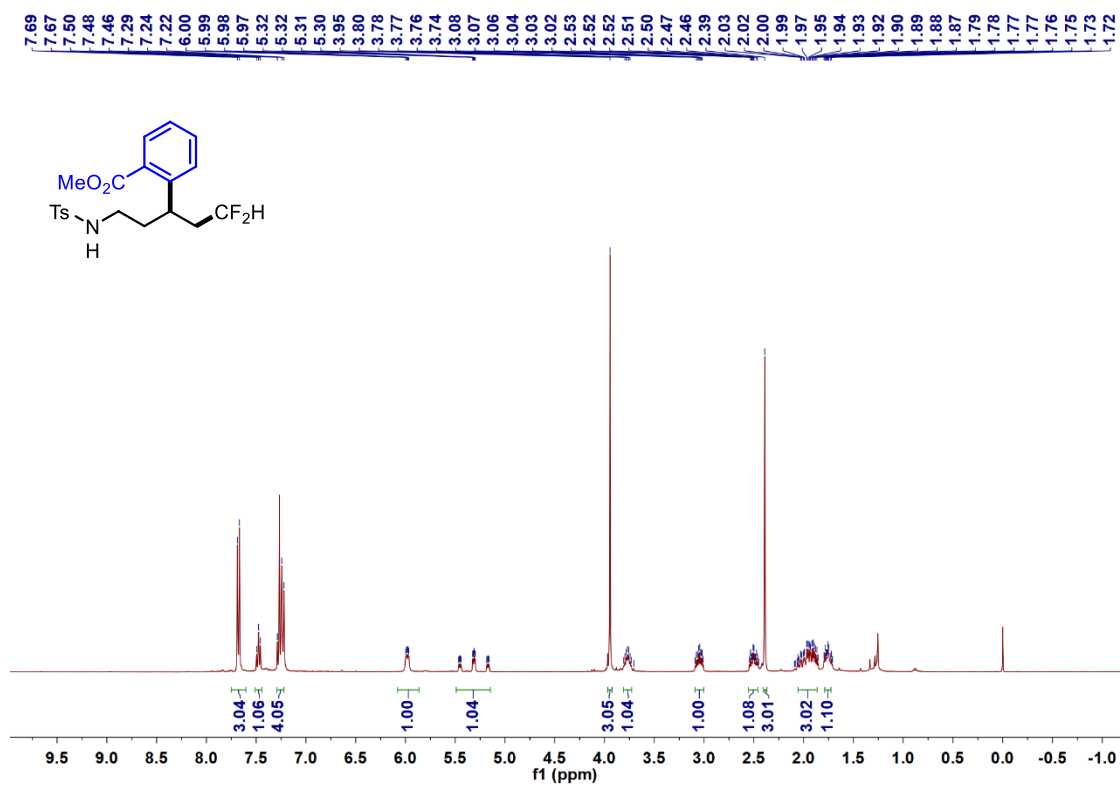
¹³C NMR of Compound **5e** (101 MHz, CDCl₃)



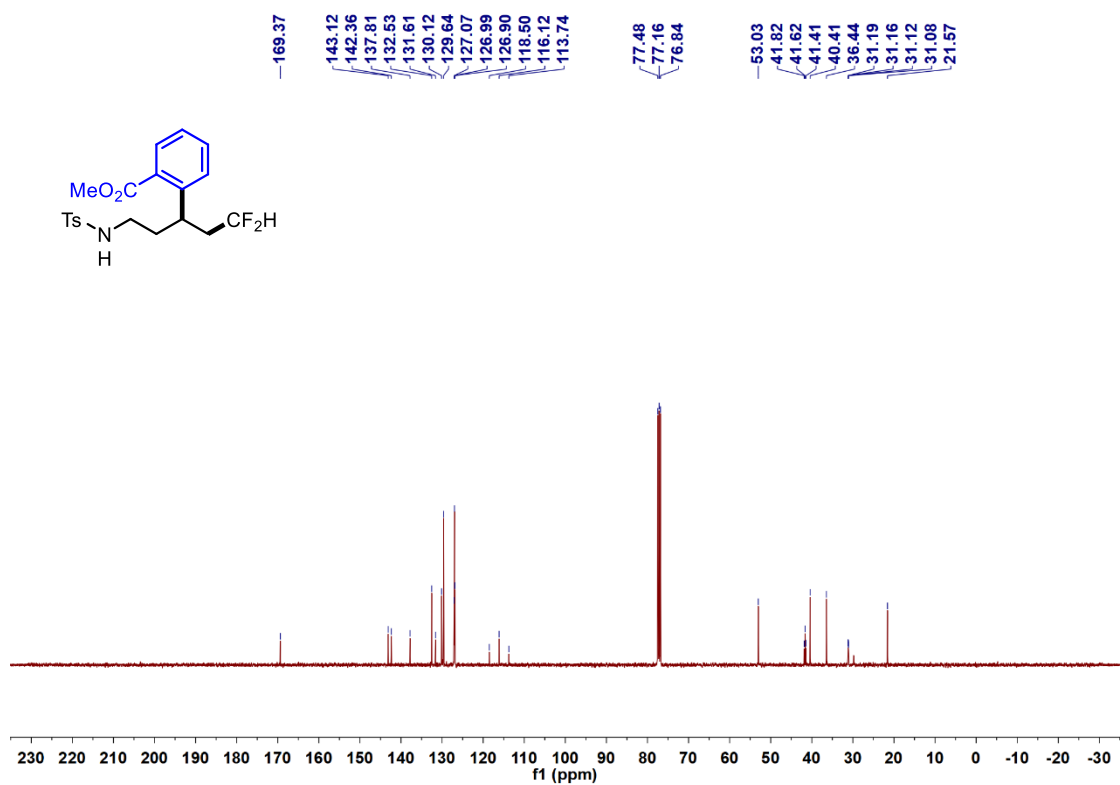
¹⁹F NMR of Compound **5e** (400 MHz, CDCl₃)



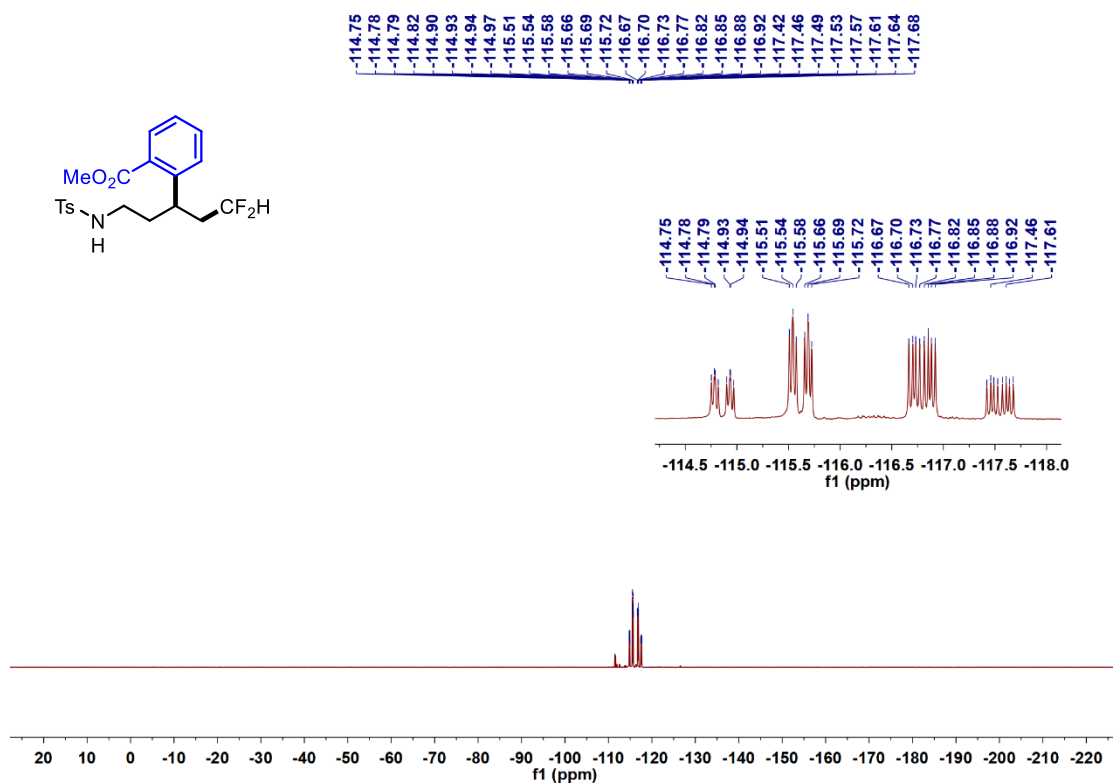
¹H NMR of Compound **5f** (400 MHz, CDCl₃)



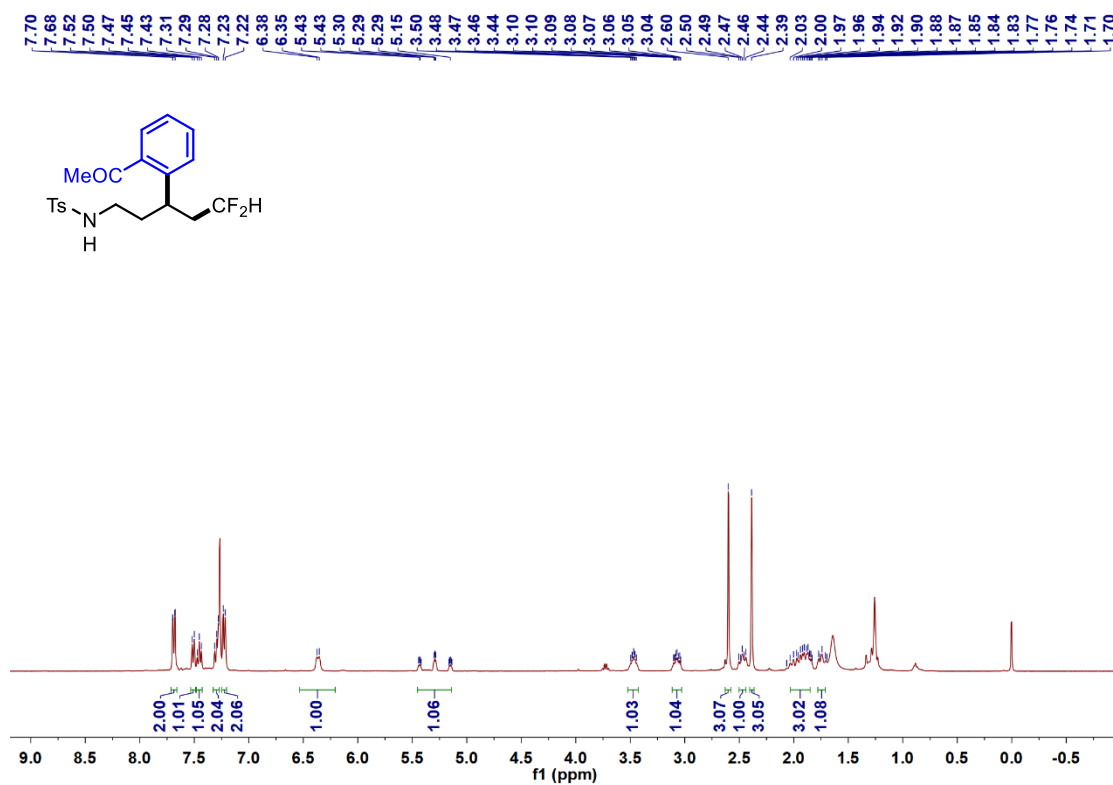
¹³C NMR of Compound **5f** (101 MHz, CDCl₃)



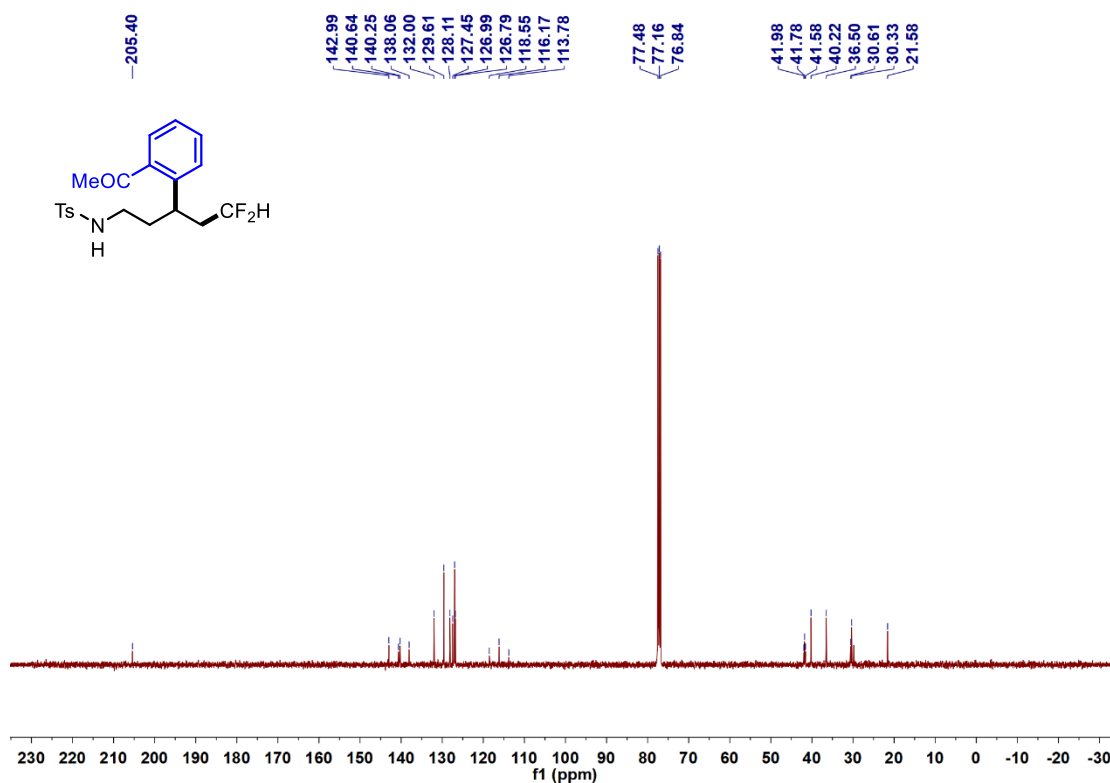
¹⁹F NMR of Compound **5f** (400 MHz, CDCl₃)



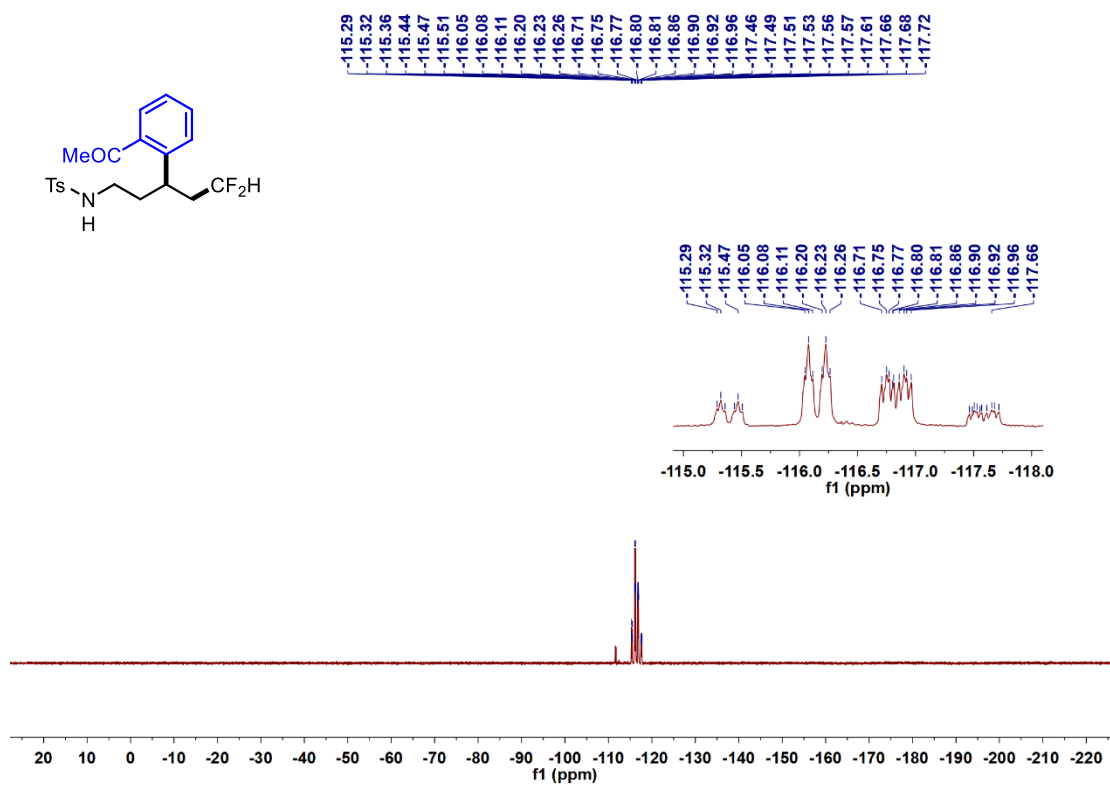
¹H NMR of Compound **5g** (400 MHz, CDCl₃)



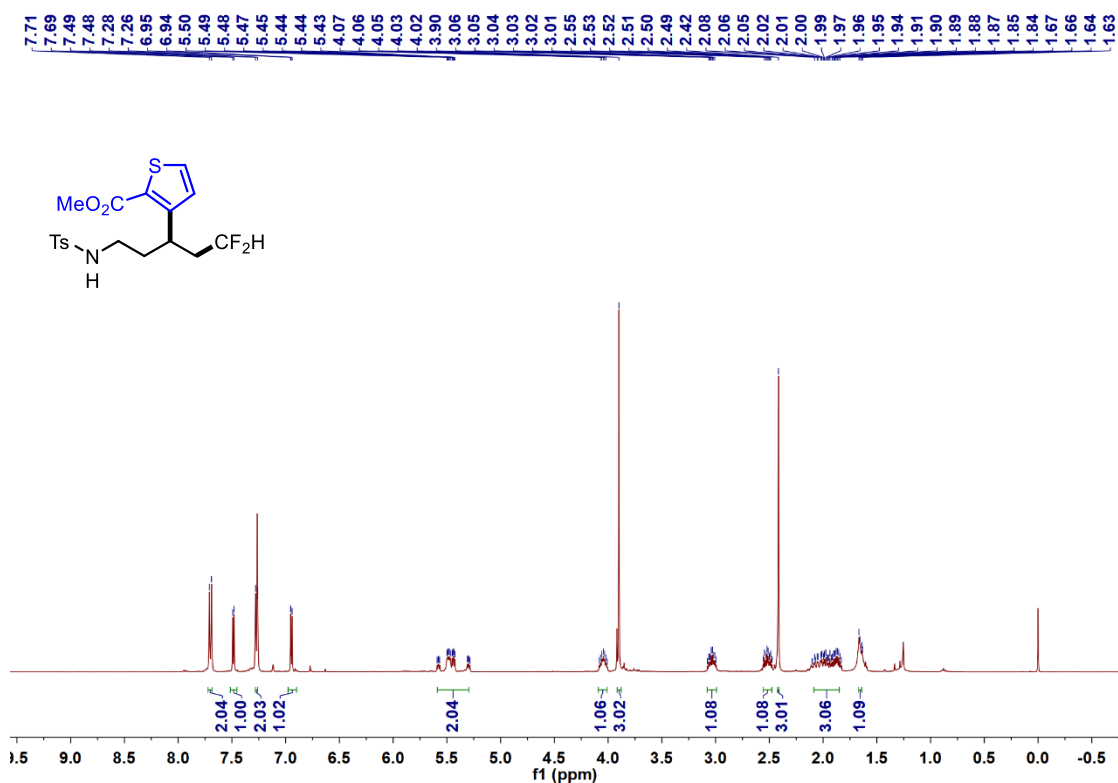
¹³C NMR of Compound **5g** (101 MHz, CDCl₃)



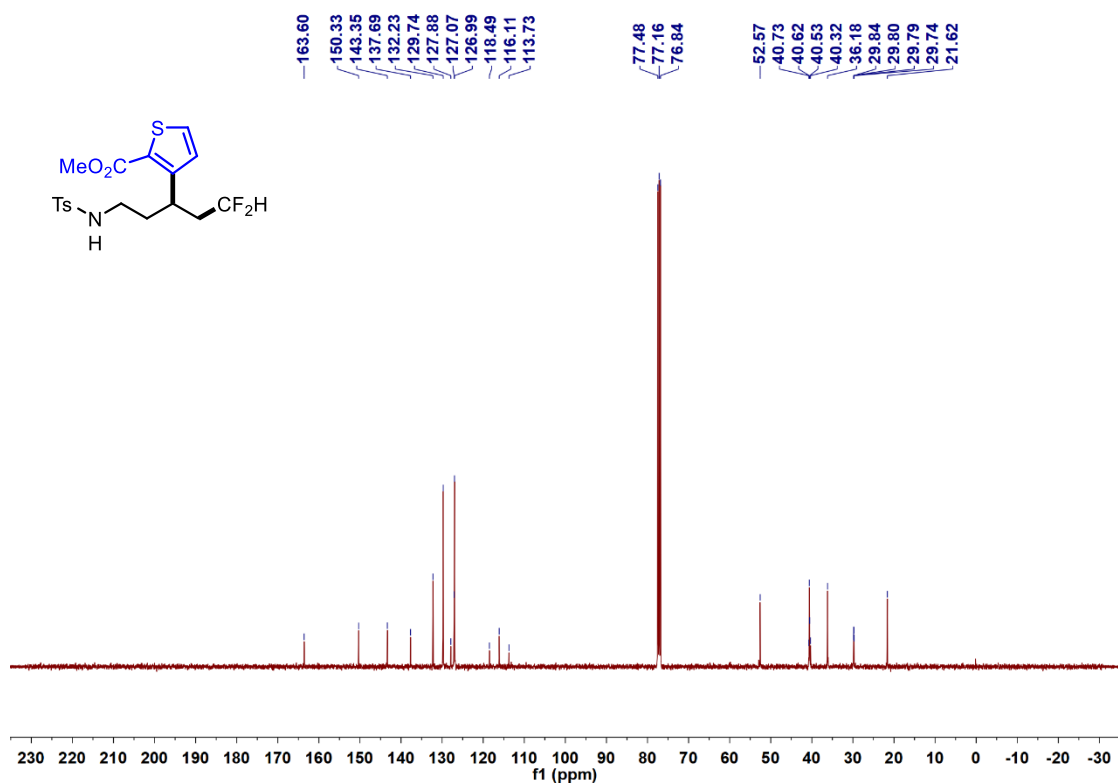
¹⁹F NMR of Compound **5g** (400 MHz, CDCl₃)



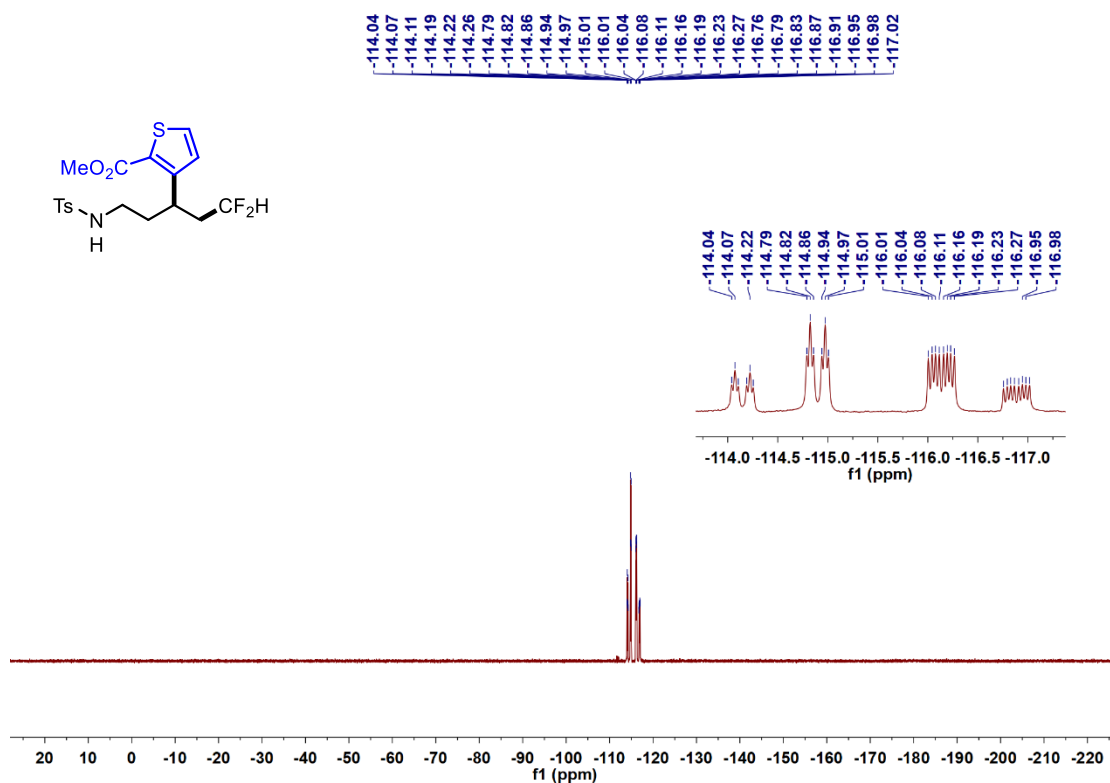
¹H NMR of Compound **5h** (400 MHz, CDCl₃)



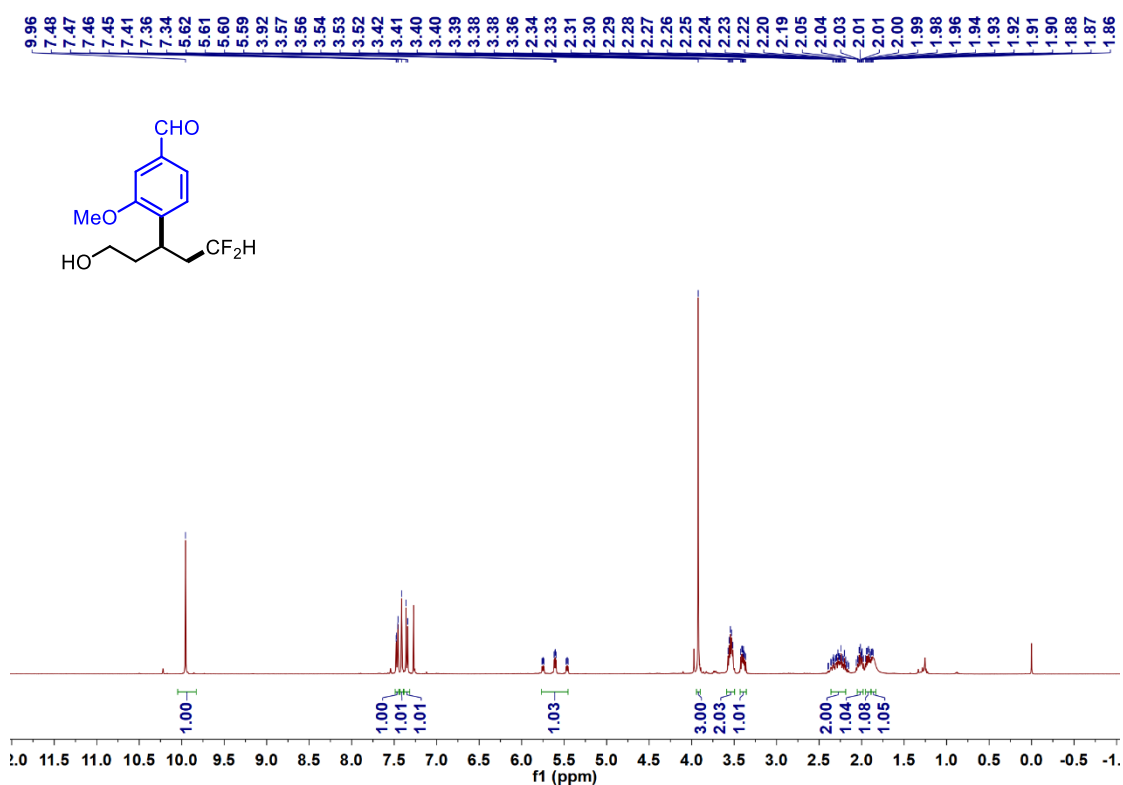
¹³C NMR of Compound **5h** (101 MHz, CDCl₃)



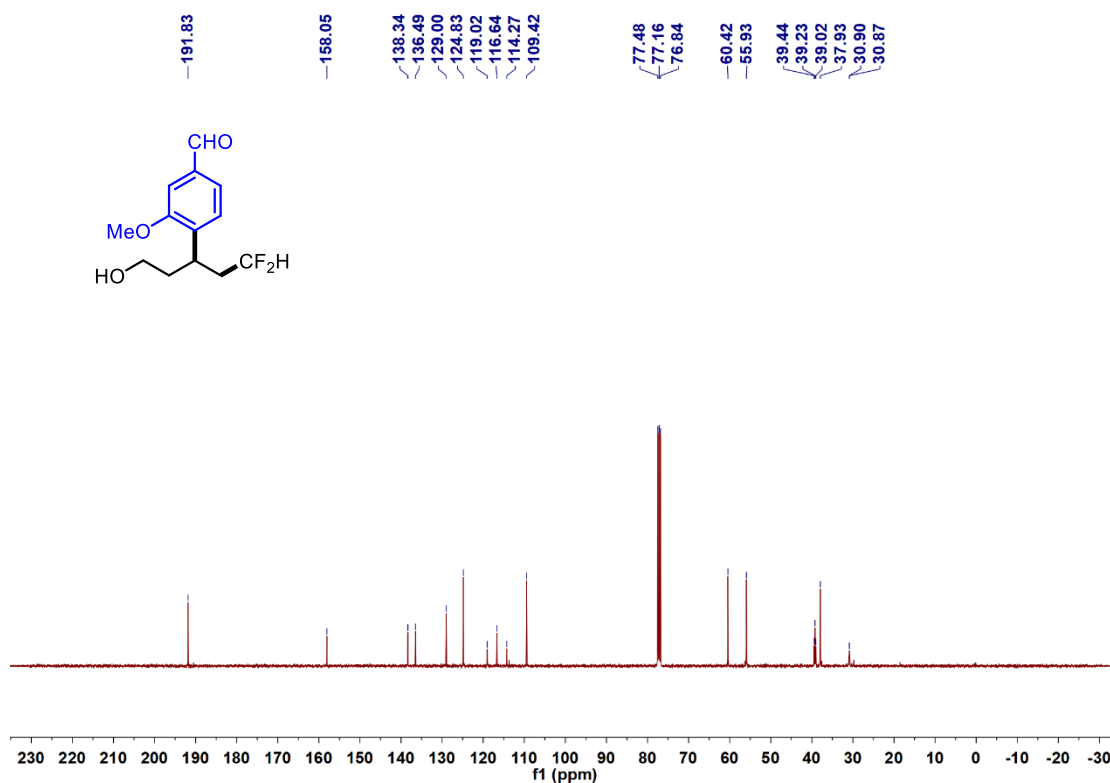
¹⁹F NMR of Compound **5h** (400 MHz, CDCl₃)



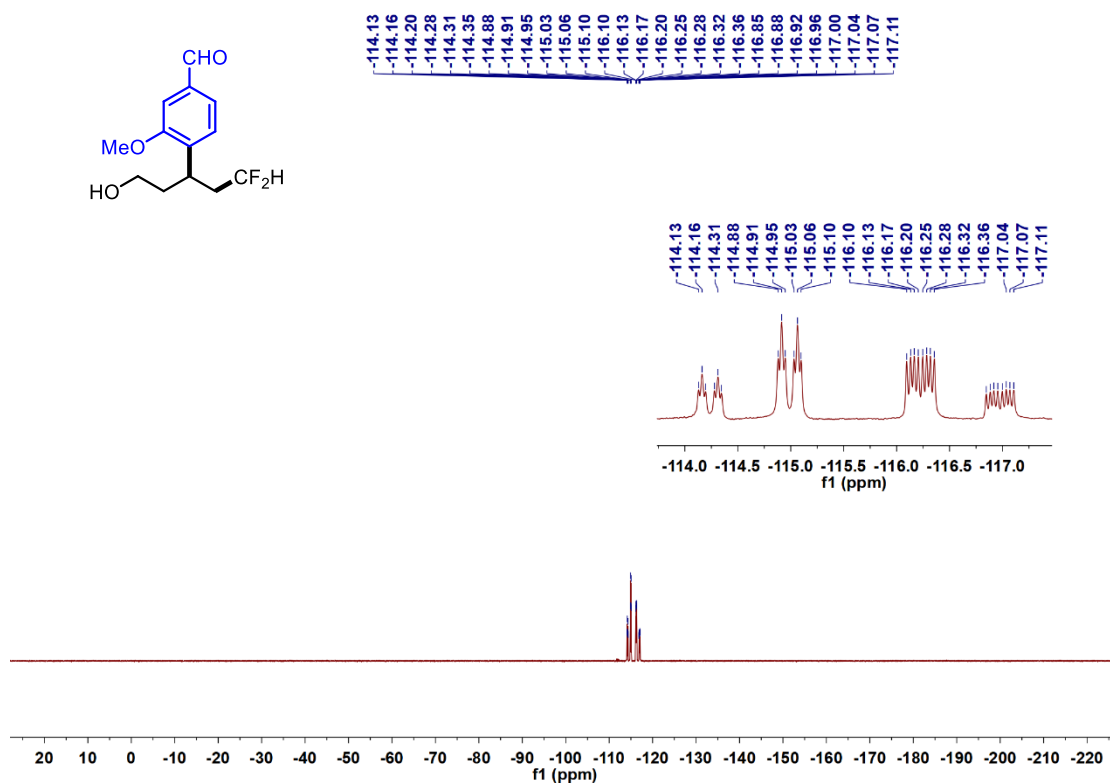
¹H NMR of Compound **5i** (400 MHz, CDCl₃)



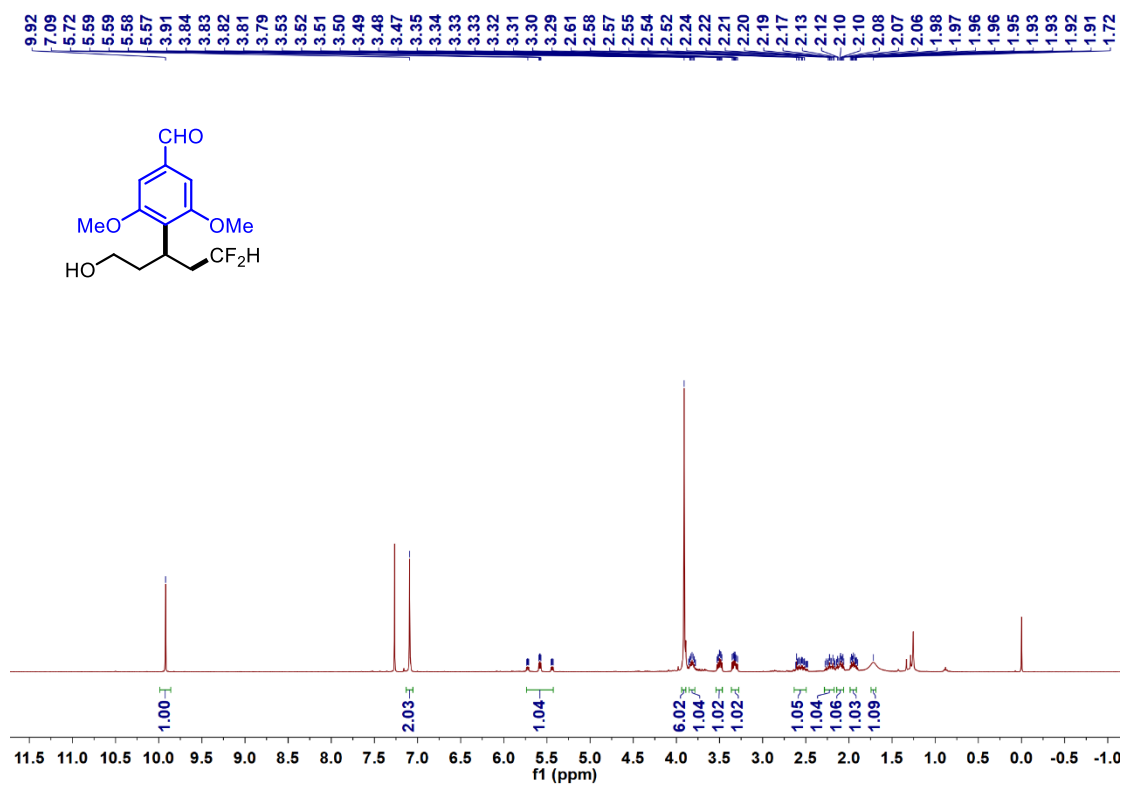
¹³C NMR of Compound **5i** (101 MHz, CDCl₃)



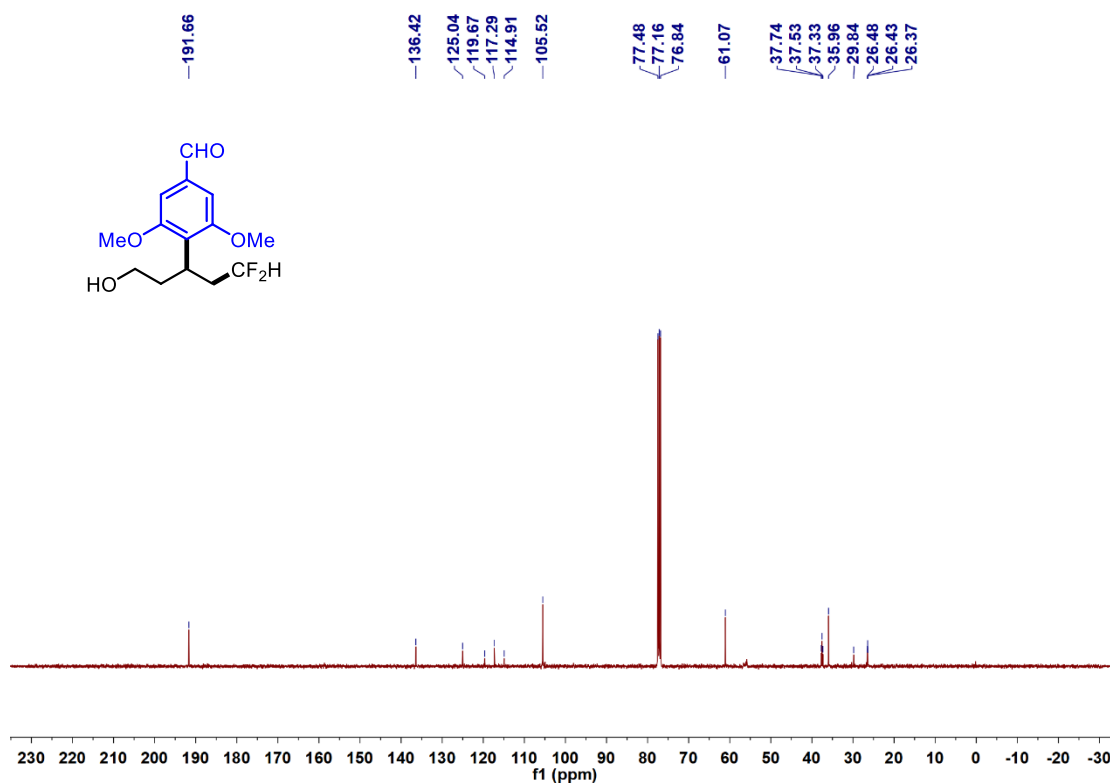
¹⁹F NMR of Compound **5i** (400 MHz, CDCl₃)



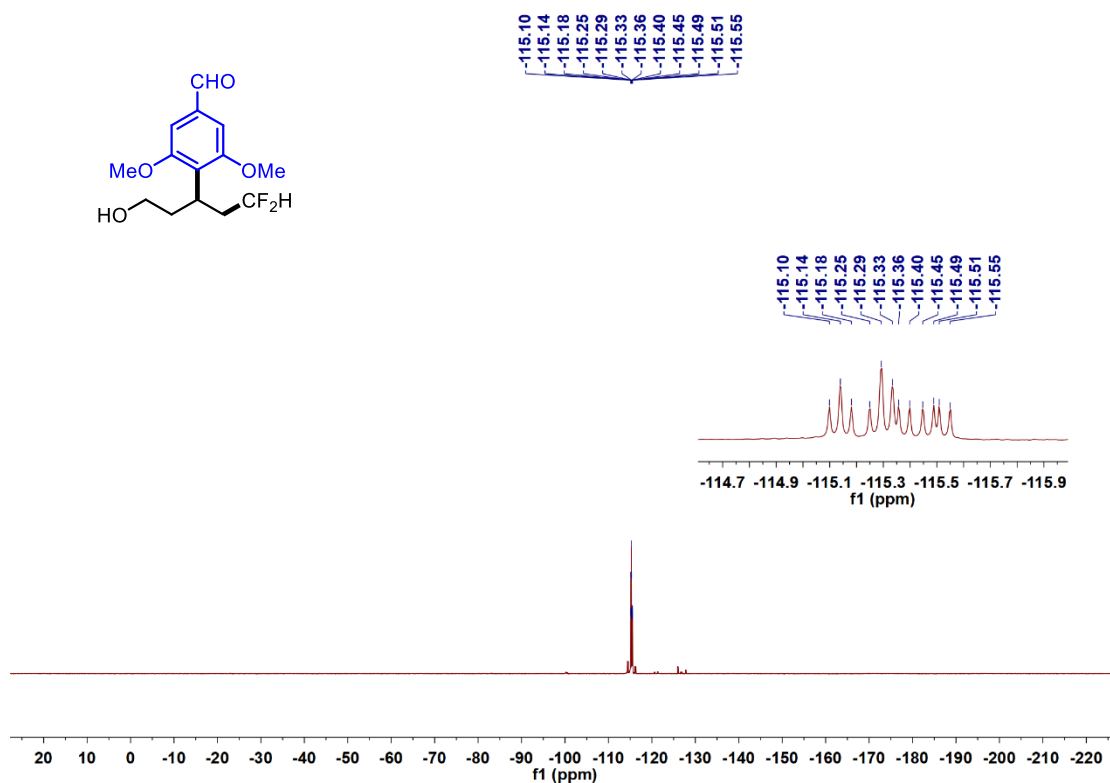
¹H NMR of Compound **5j** (400 MHz, CDCl₃)



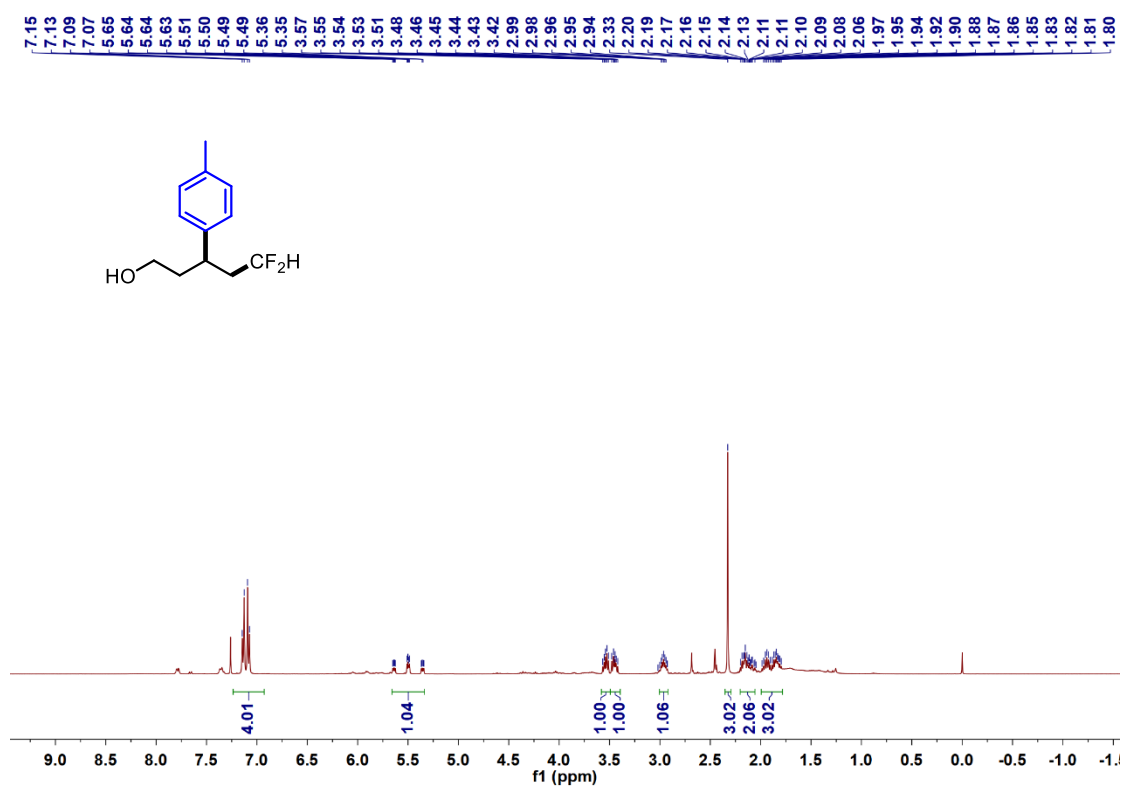
¹³C NMR of Compound **5j** (101 MHz, CDCl₃)



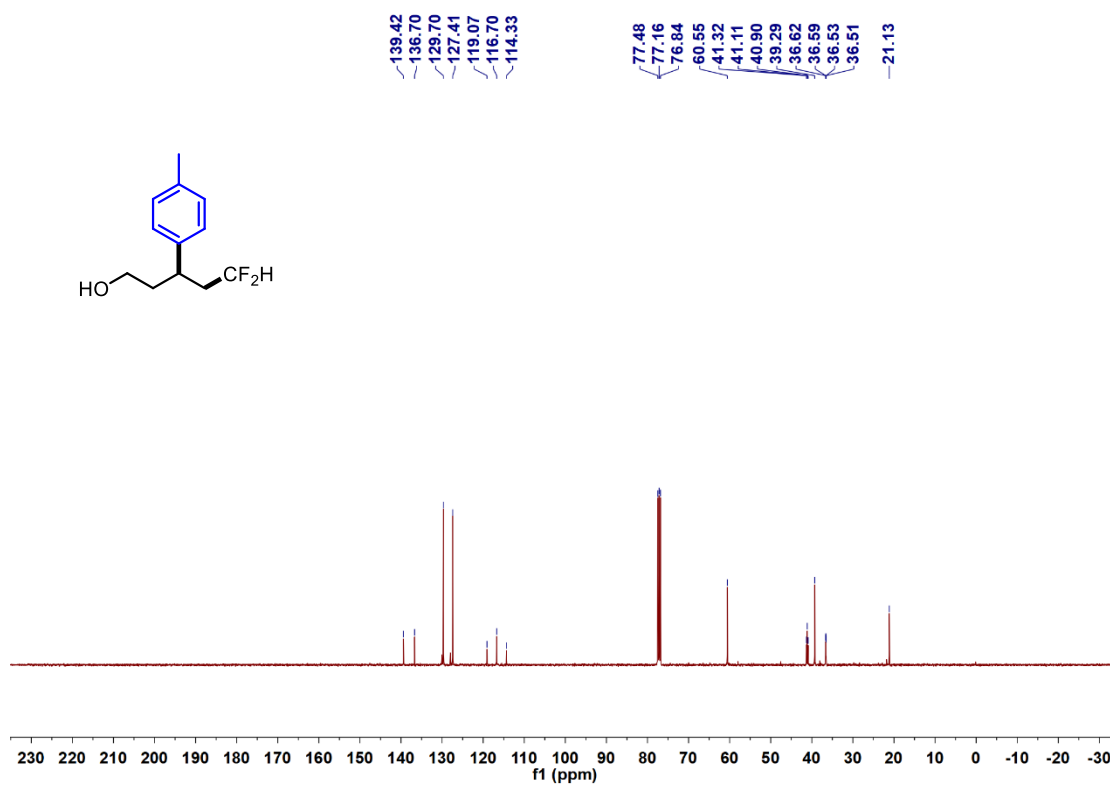
¹⁹F NMR of Compound **5j** (400 MHz, CDCl₃)



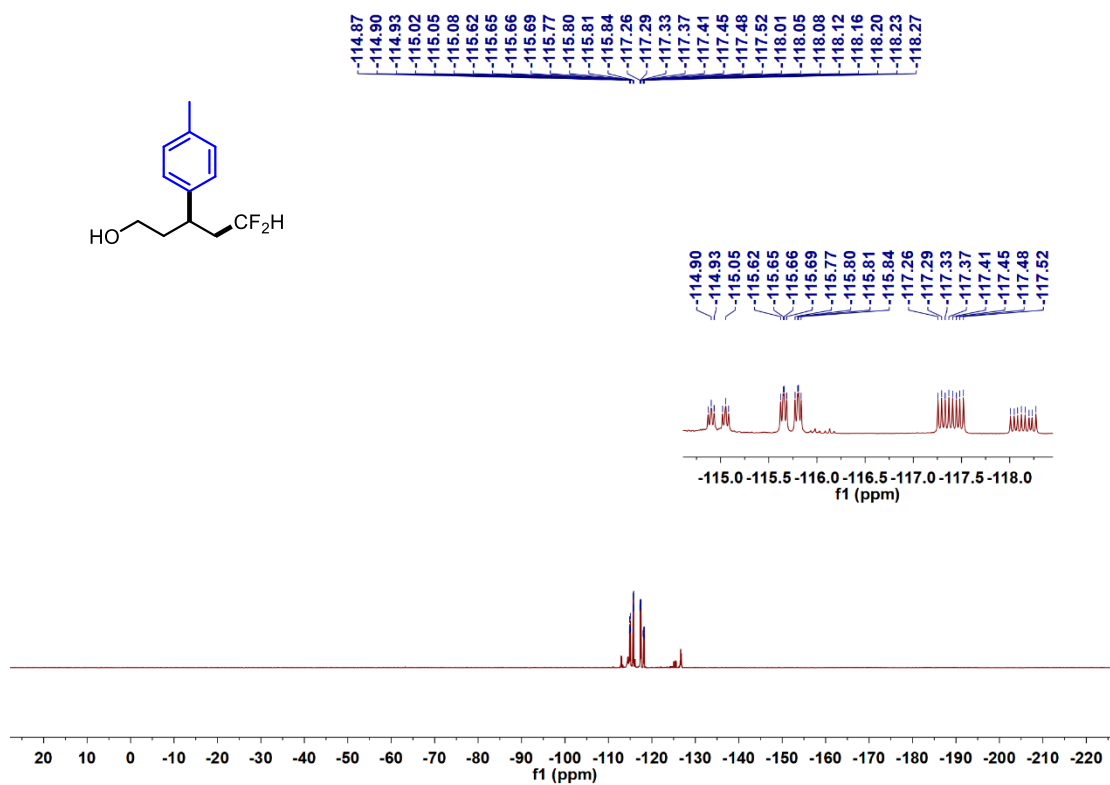
¹H NMR of Compound **5k** (400 MHz, CDCl₃)



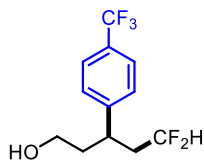
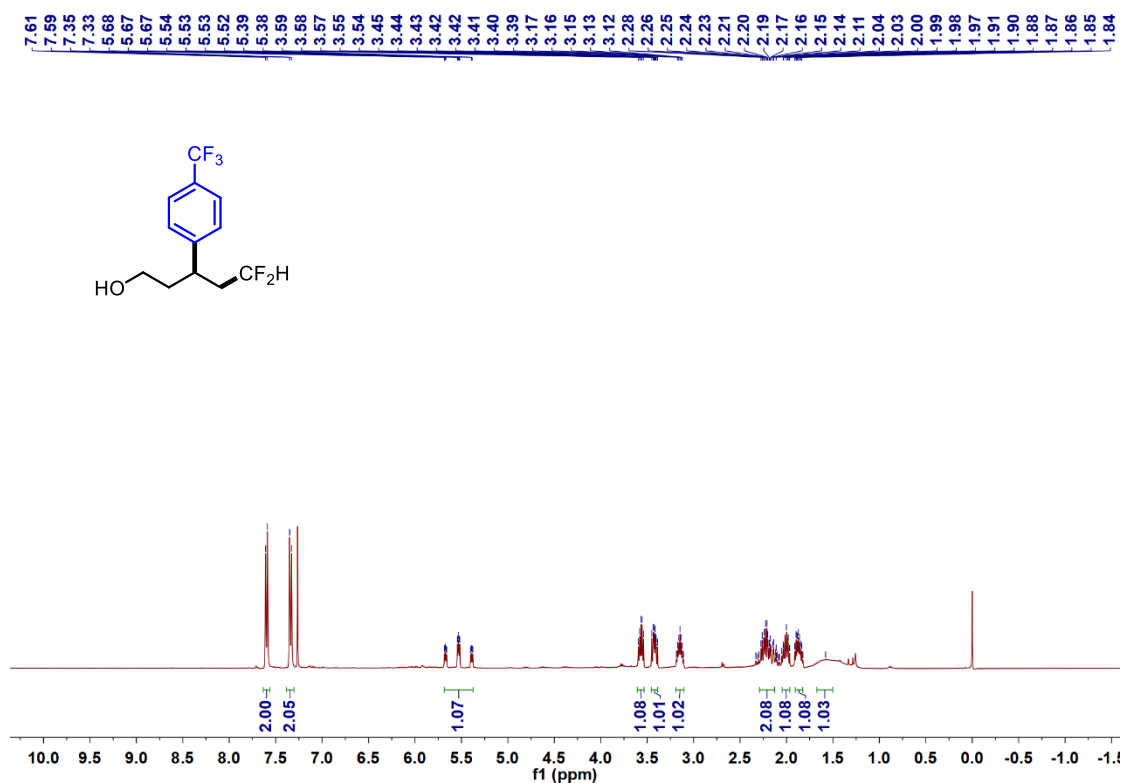
¹³C NMR of Compound **5k** (101 MHz, CDCl₃)



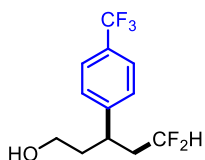
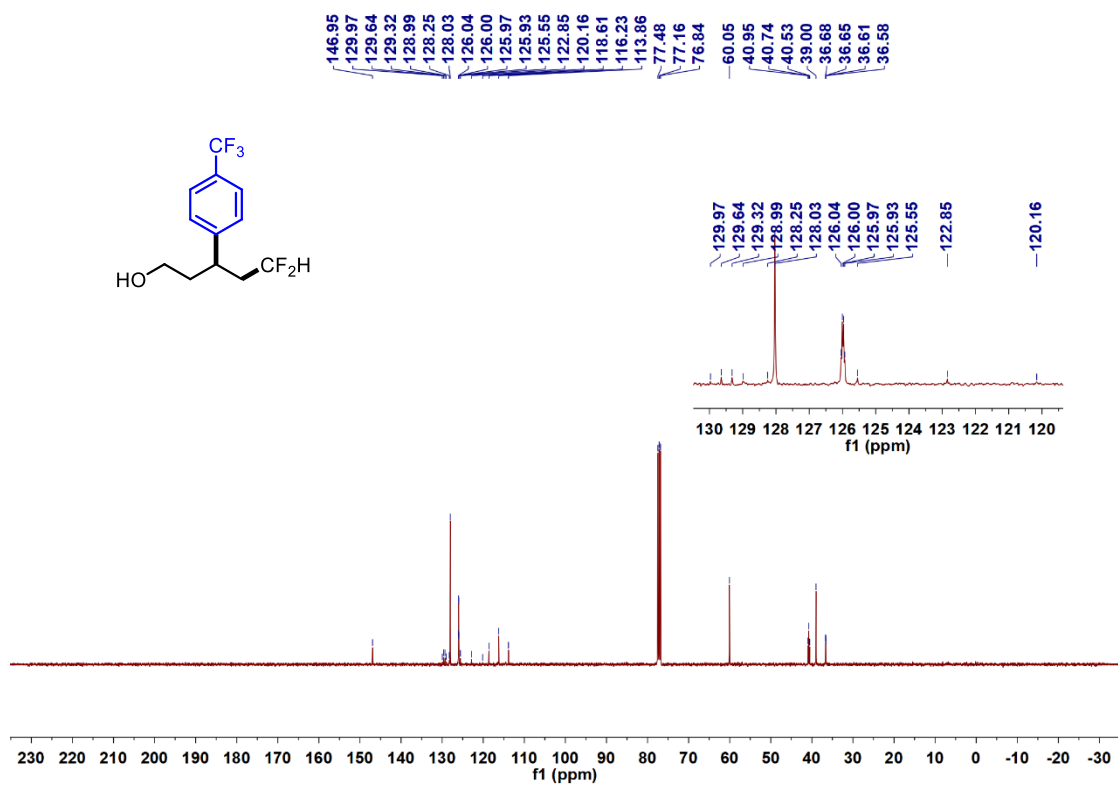
¹⁹F NMR of Compound **5k** (400 MHz, CDCl₃)



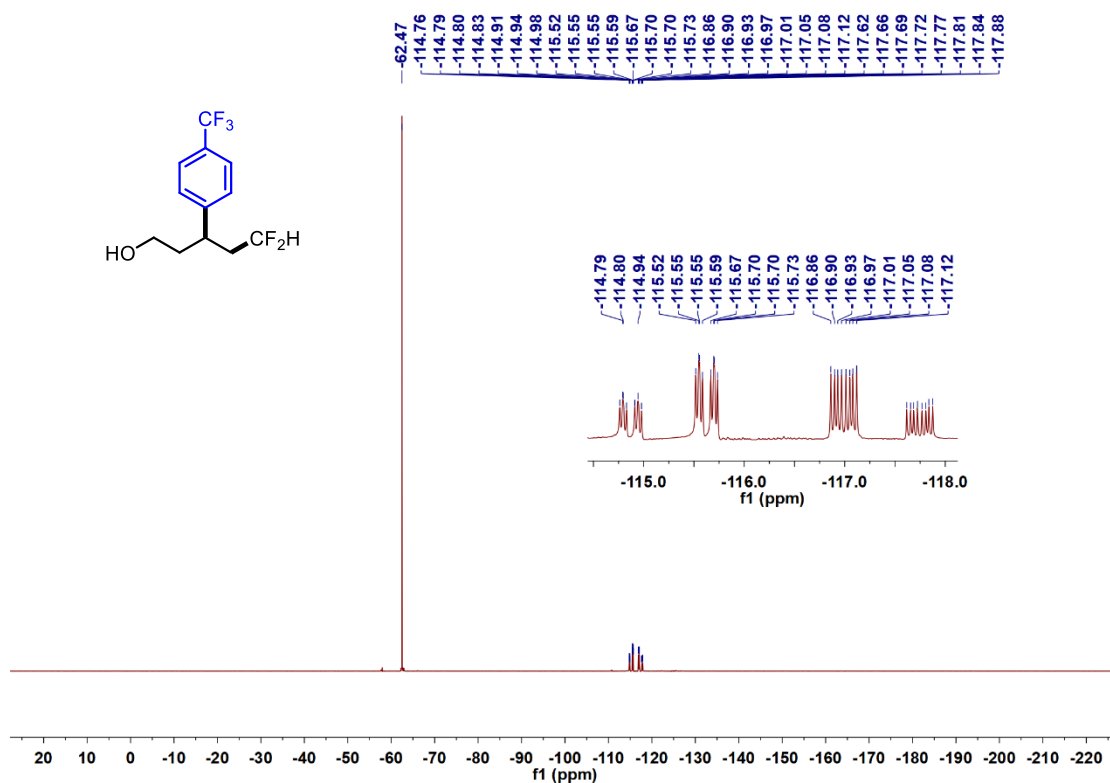
¹H NMR of Compound **5I** (400 MHz, CDCl₃)



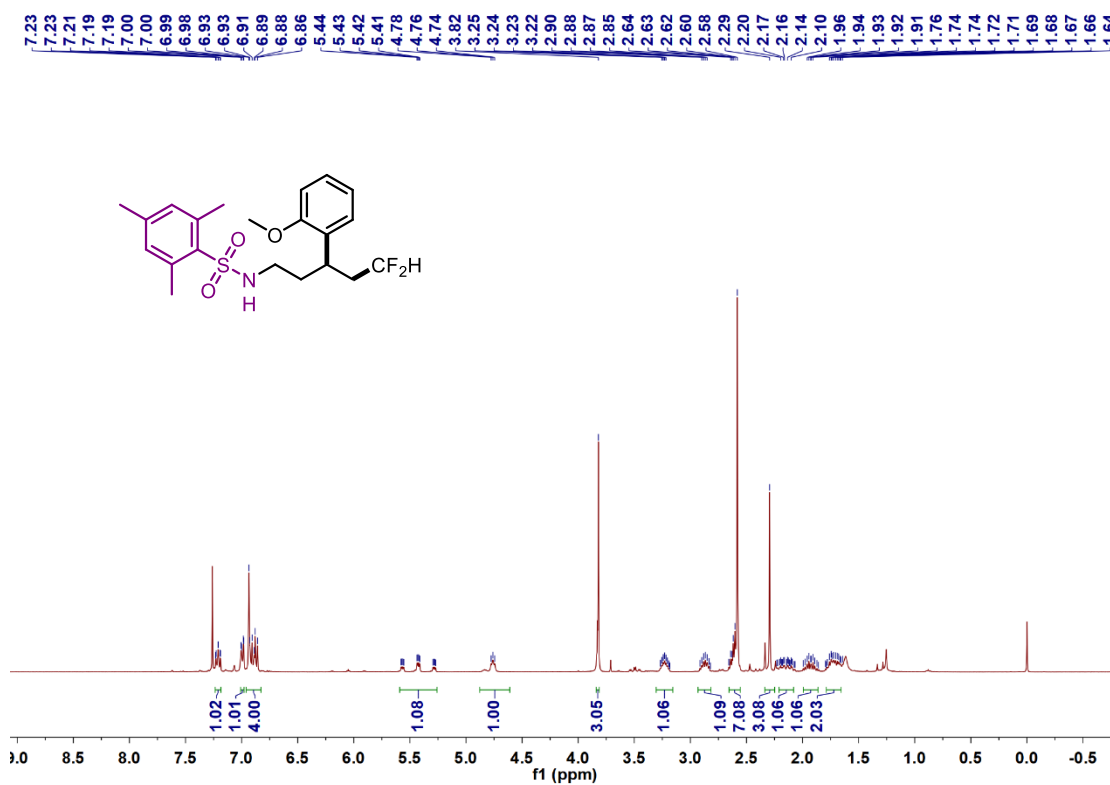
¹³C NMR of Compound **5I** (101 MHz, CDCl₃)



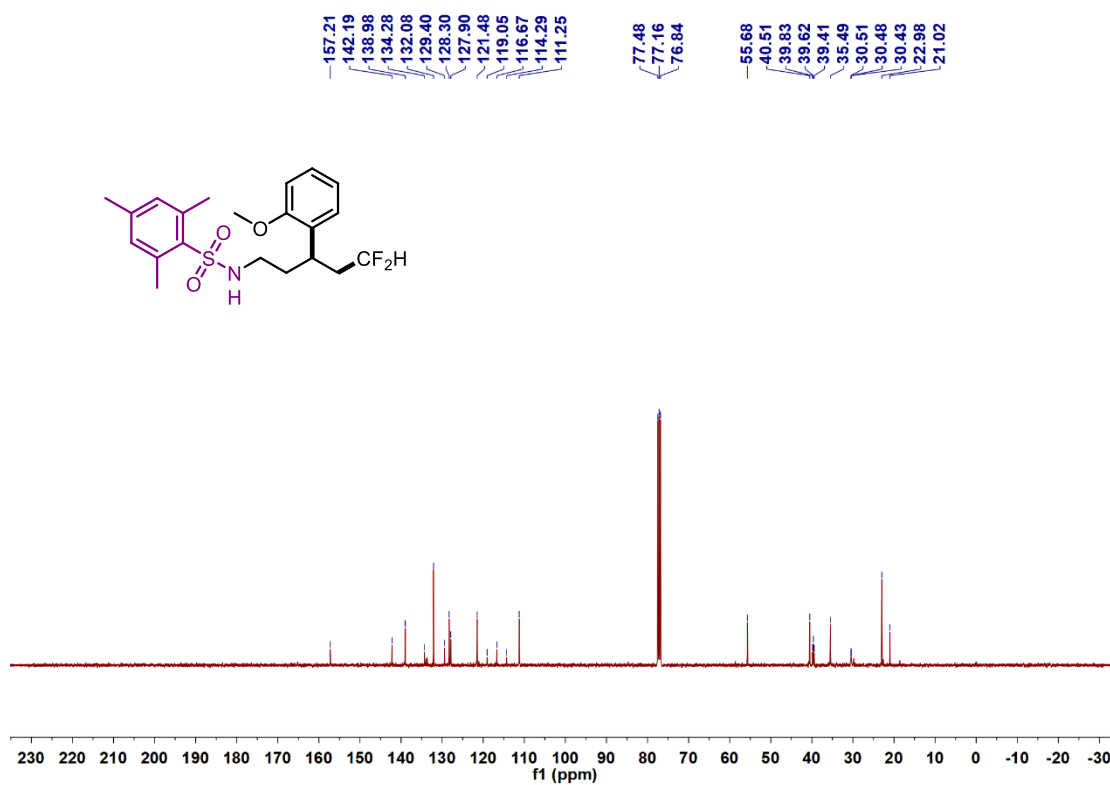
¹⁹F NMR of Compound **5l** (400 MHz, CDCl₃)



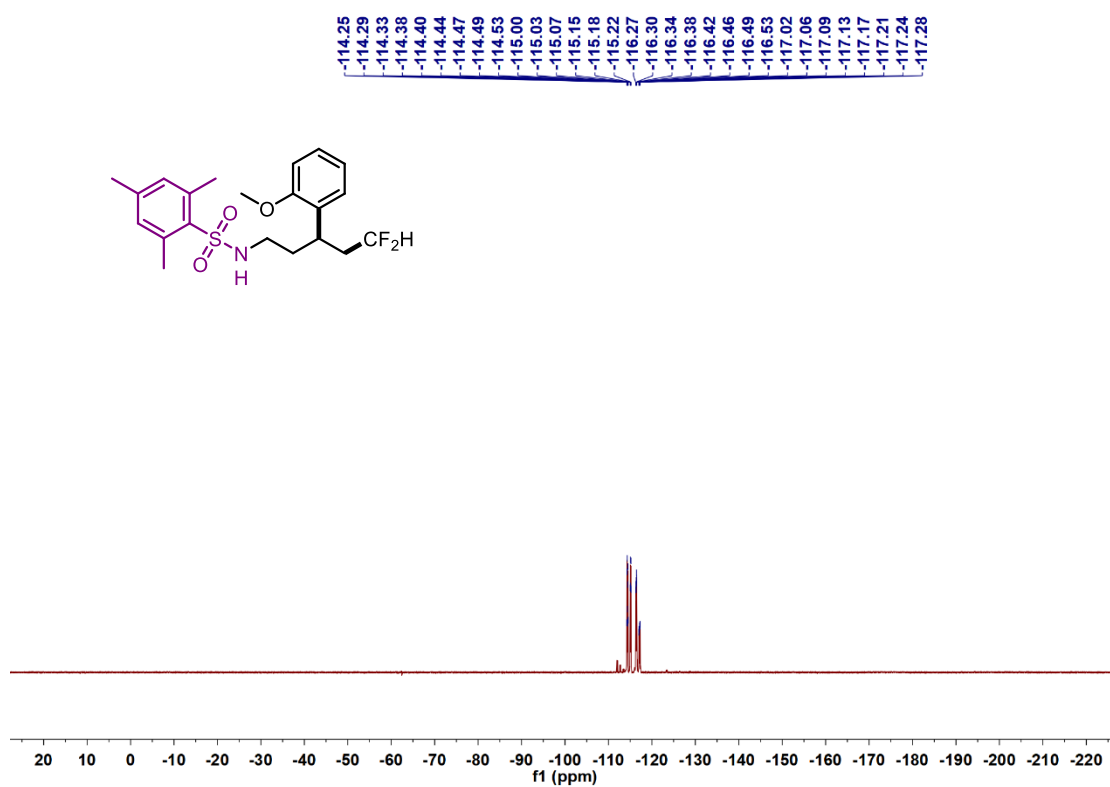
¹H NMR of Compound **5m** (400 MHz, CDCl₃)



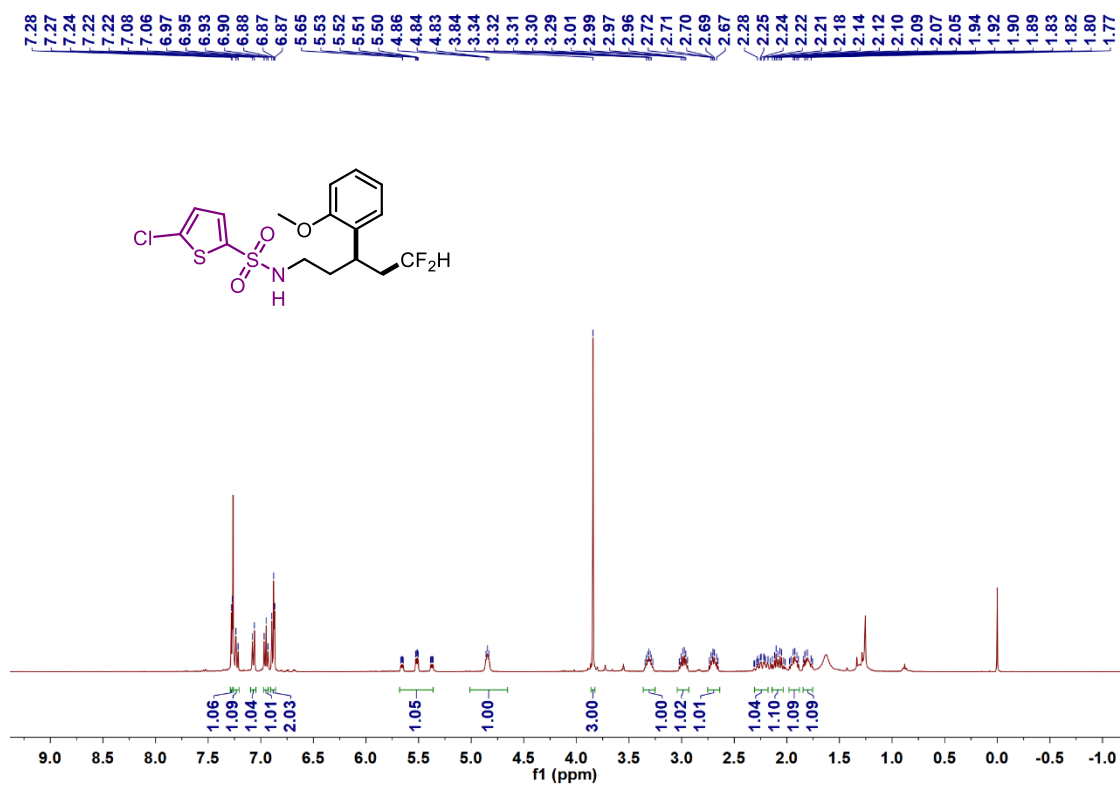
¹³C NMR of Compound **5m** (101 MHz, CDCl₃)



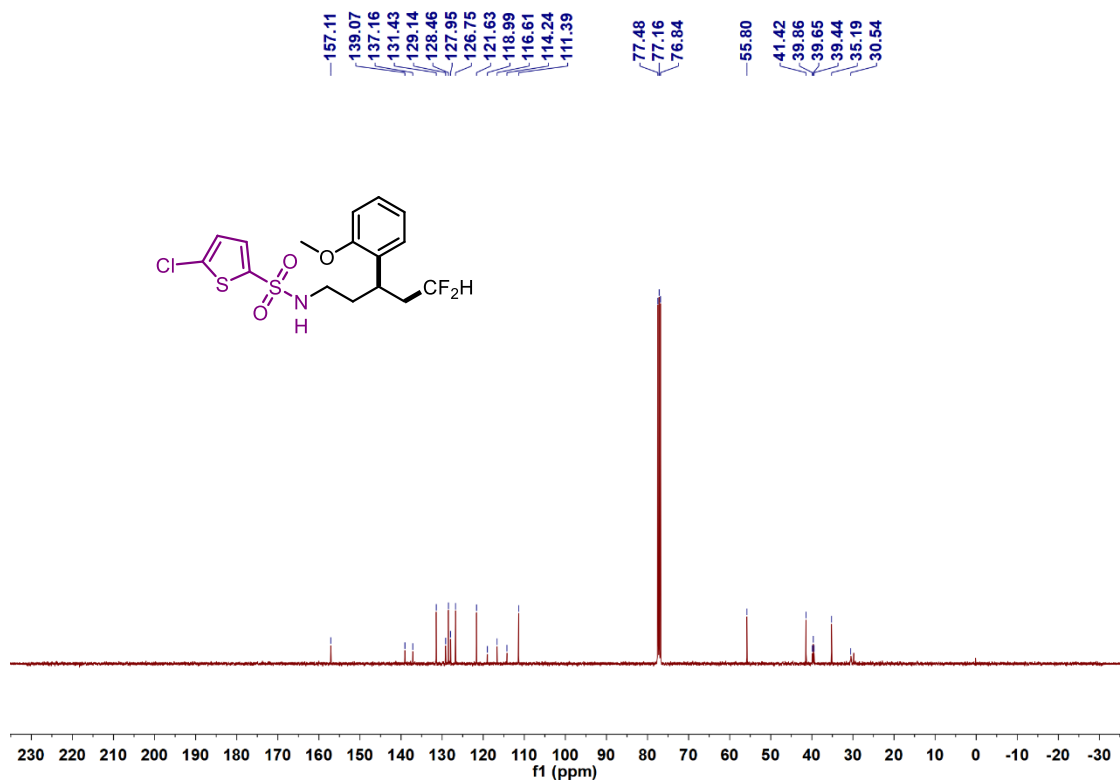
¹⁹F NMR of Compound **5m** (400 MHz, CDCl₃)



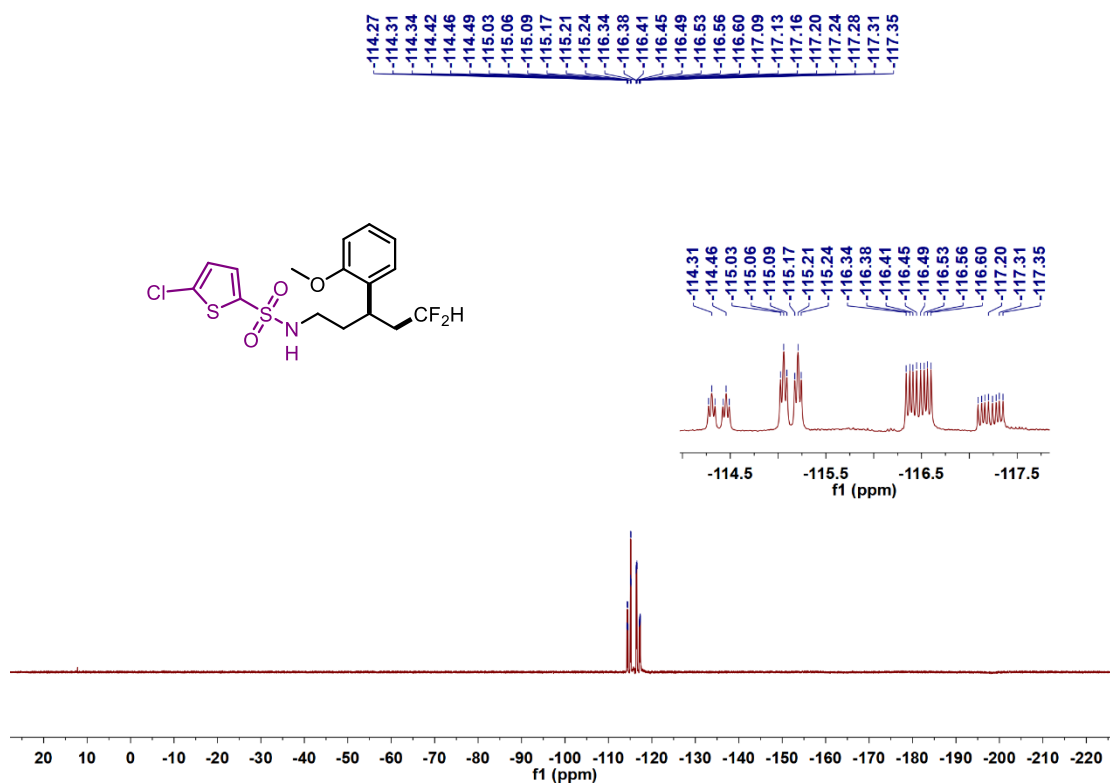
¹H NMR of Compound **5n** (400 MHz, CDCl₃)



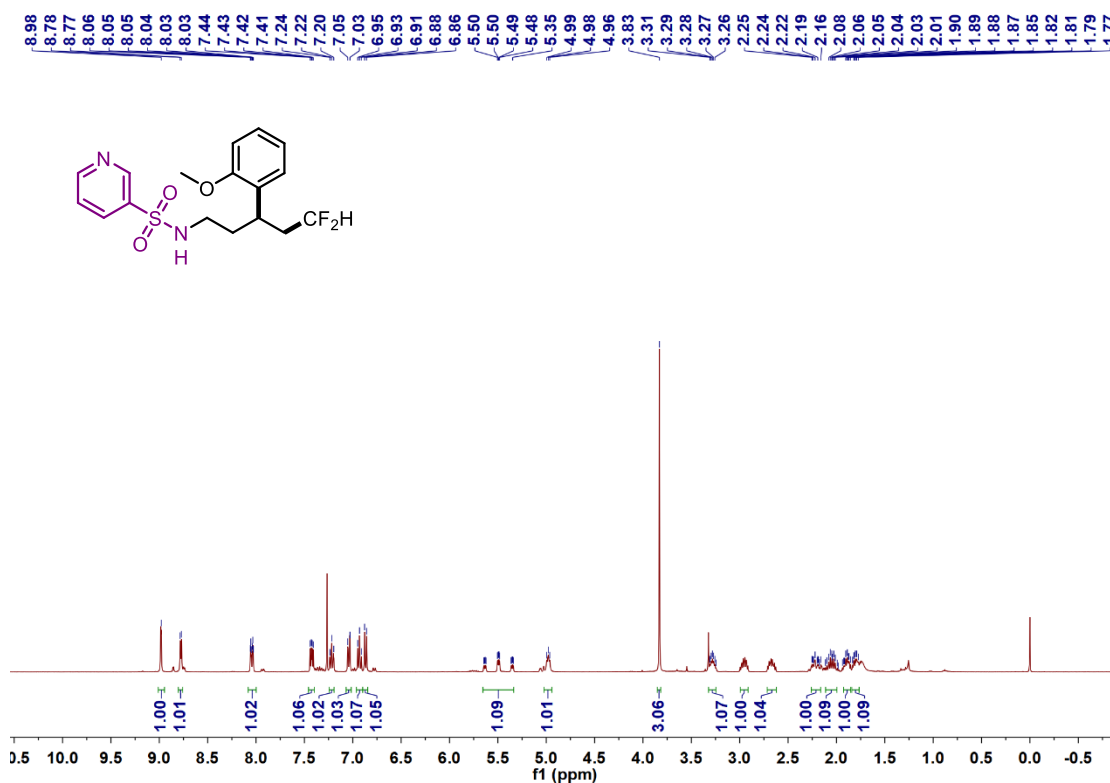
¹³C NMR of Compound **5n** (101 MHz, CDCl₃)



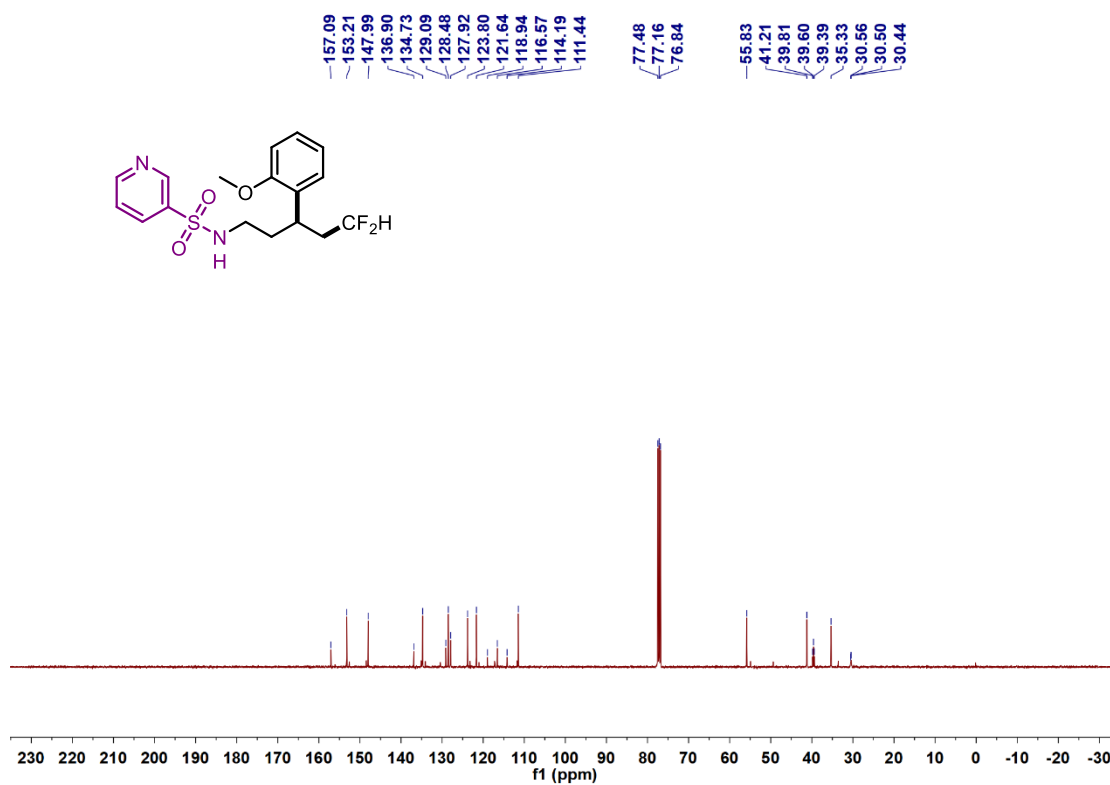
¹⁹F NMR of Compound **5n** (400 MHz, CDCl₃)



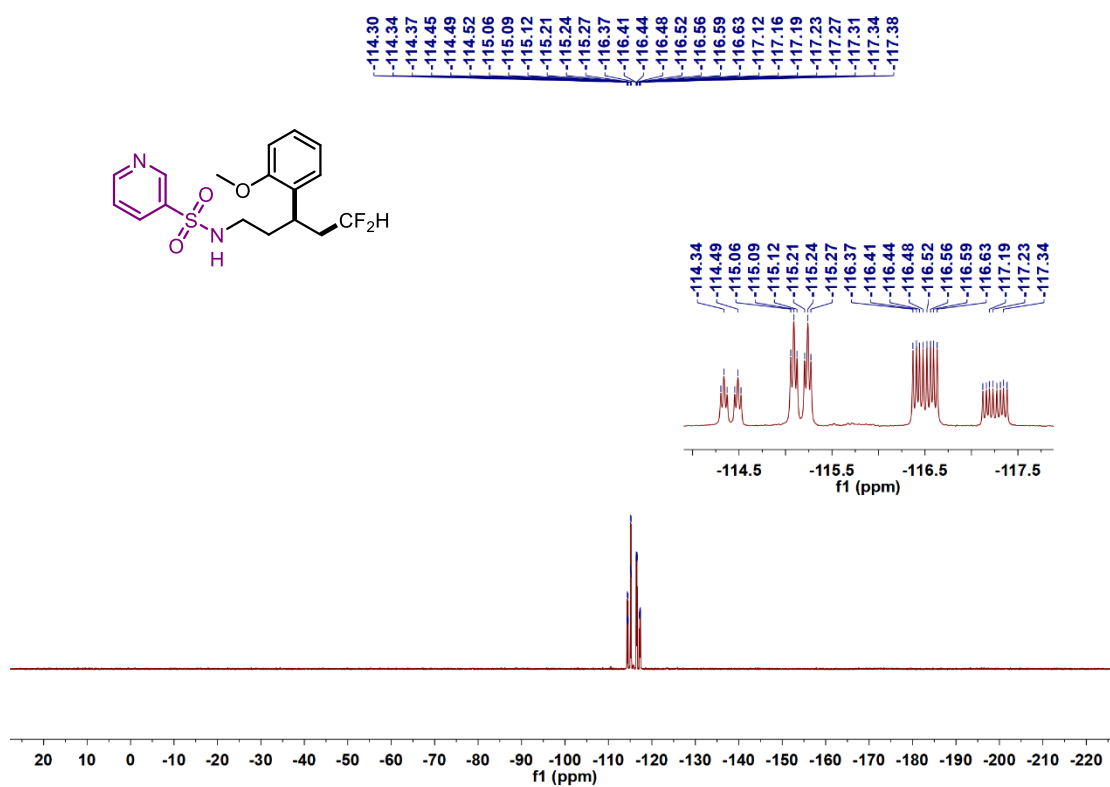
¹H NMR of Compound **5o** (400 MHz, CDCl₃)



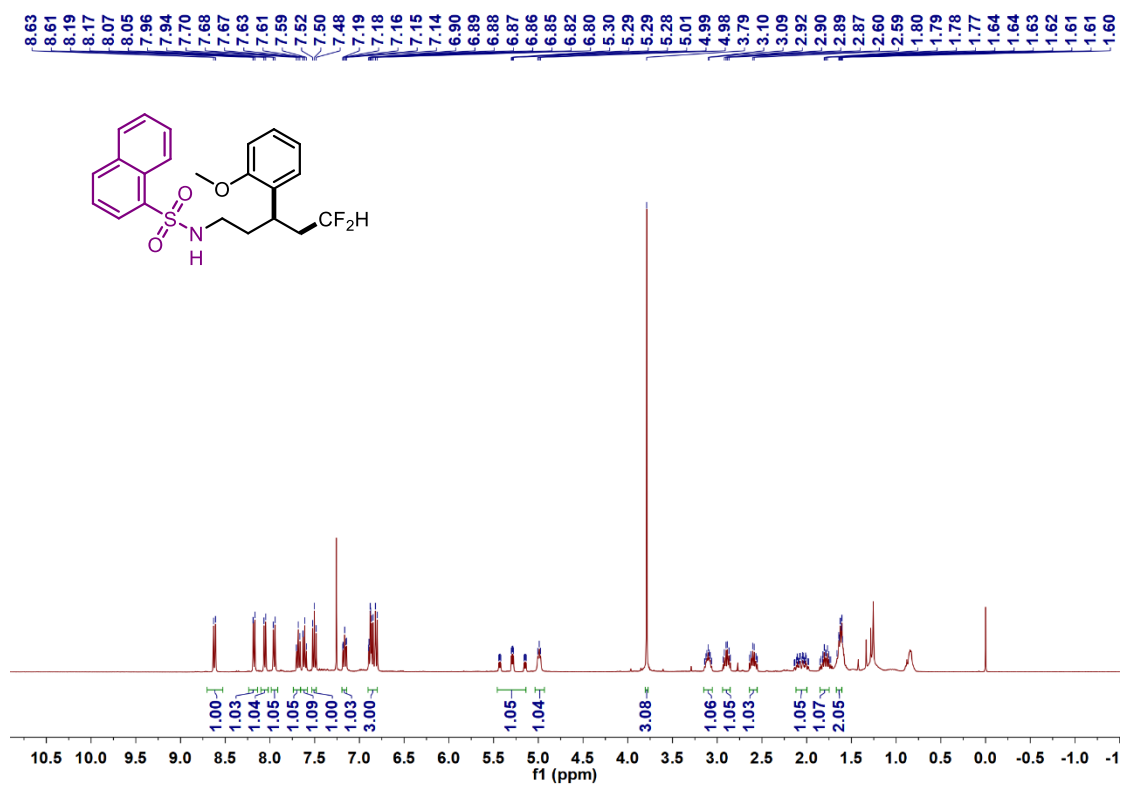
¹³C NMR of Compound **5o** (101 MHz, CDCl₃)



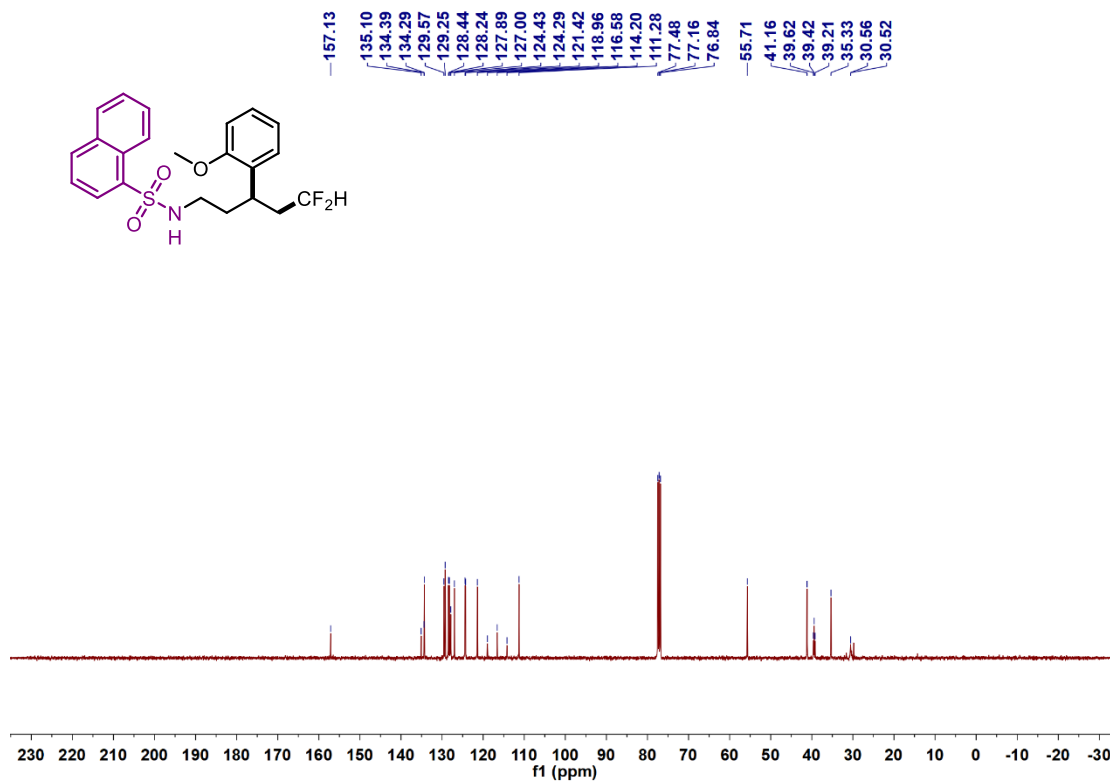
¹⁹F NMR of Compound **5o** (400 MHz, CDCl₃)



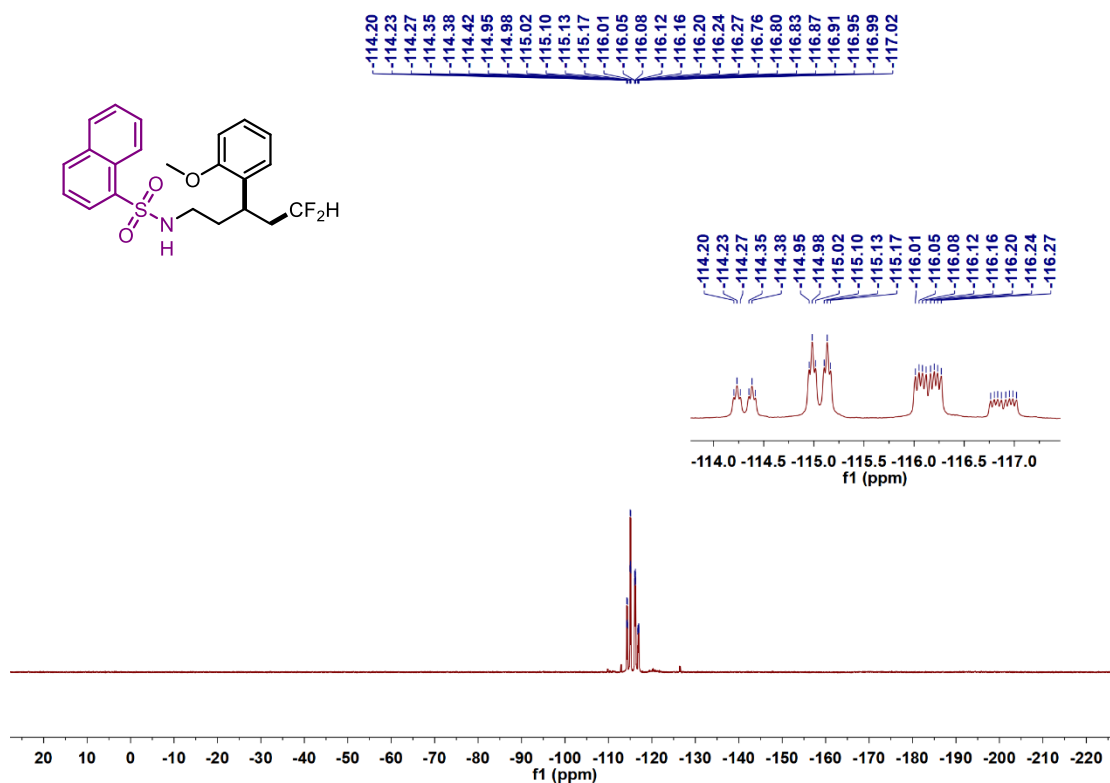
¹H NMR of Compound **5p** (400 MHz, CDCl₃)



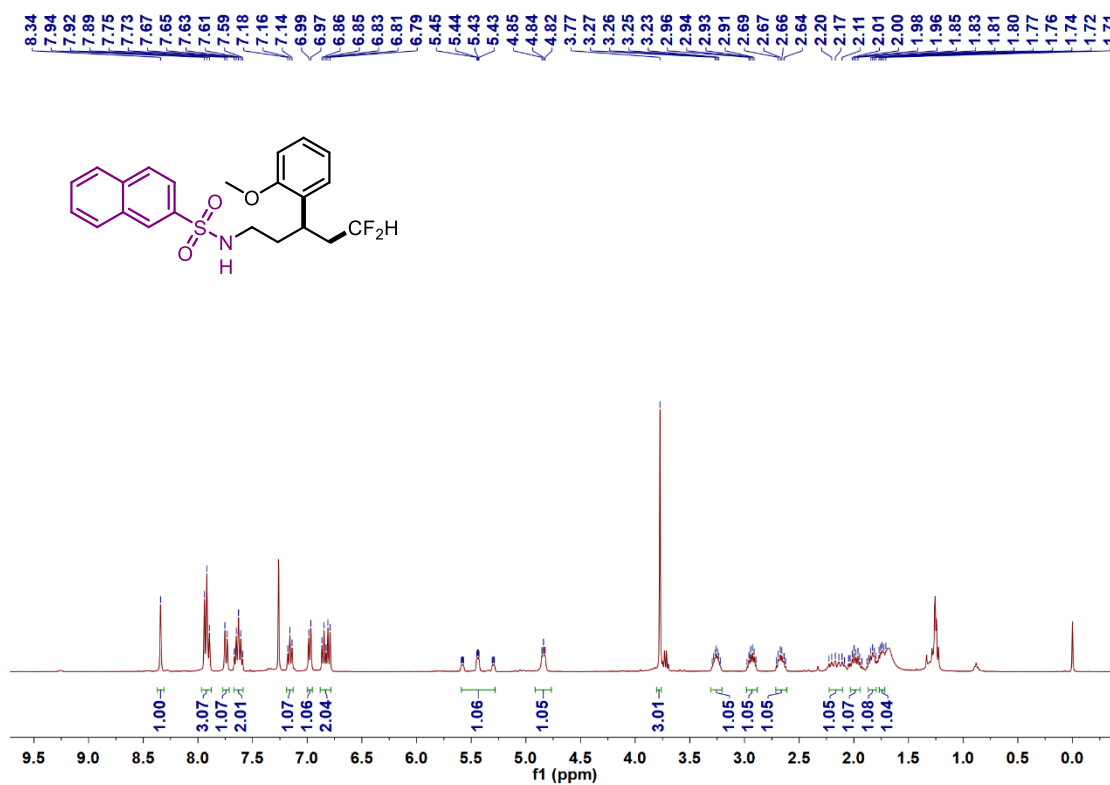
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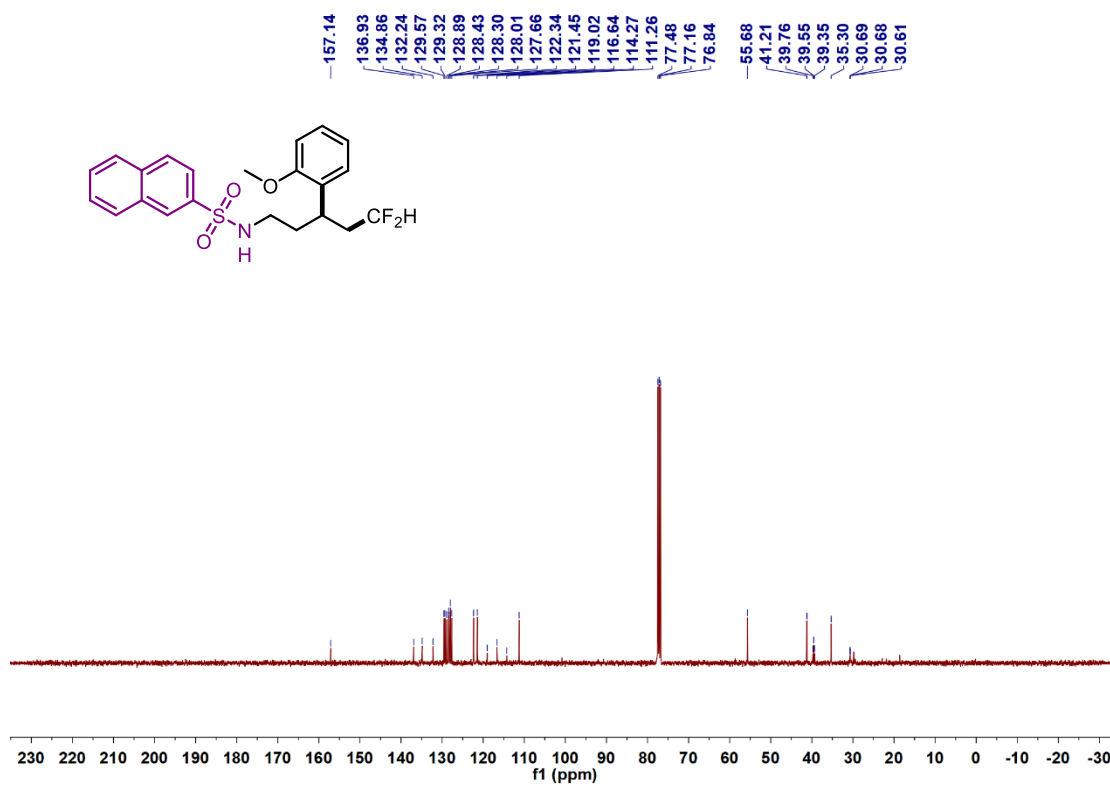
¹⁹F NMR of Compound **5p** (400 MHz, CDCl₃)



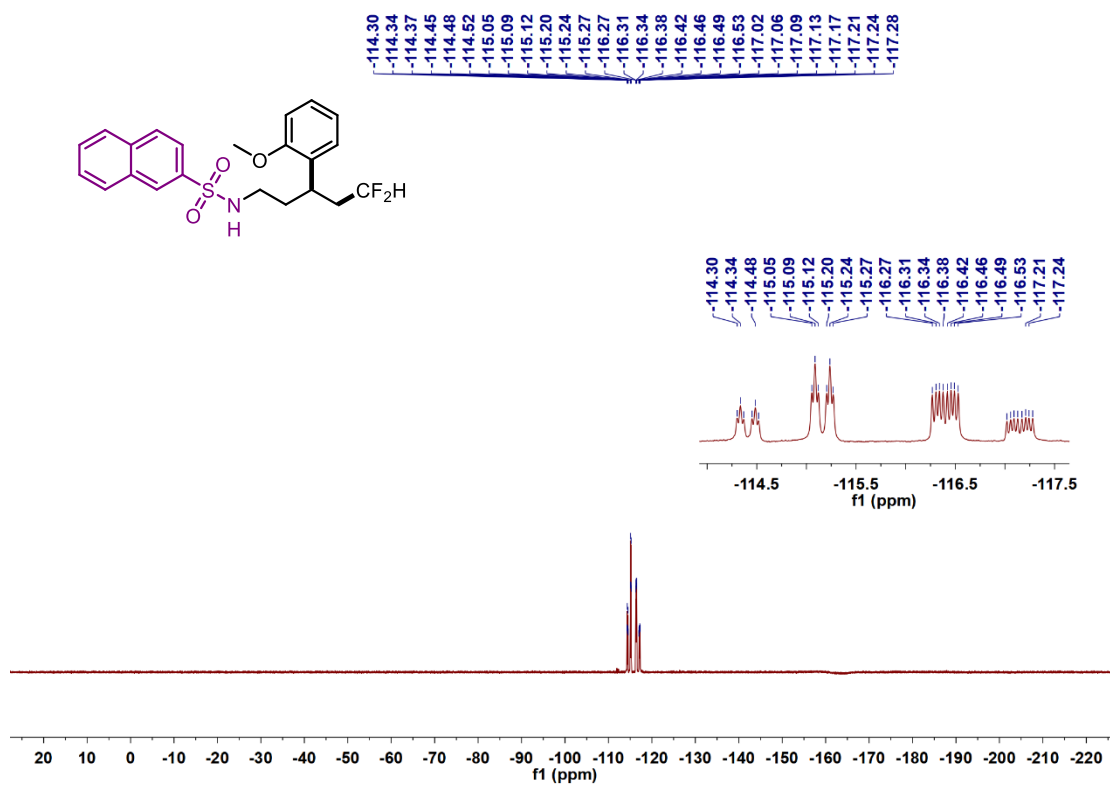
¹H NMR of Compound **5q** (400 MHz, CDCl₃)



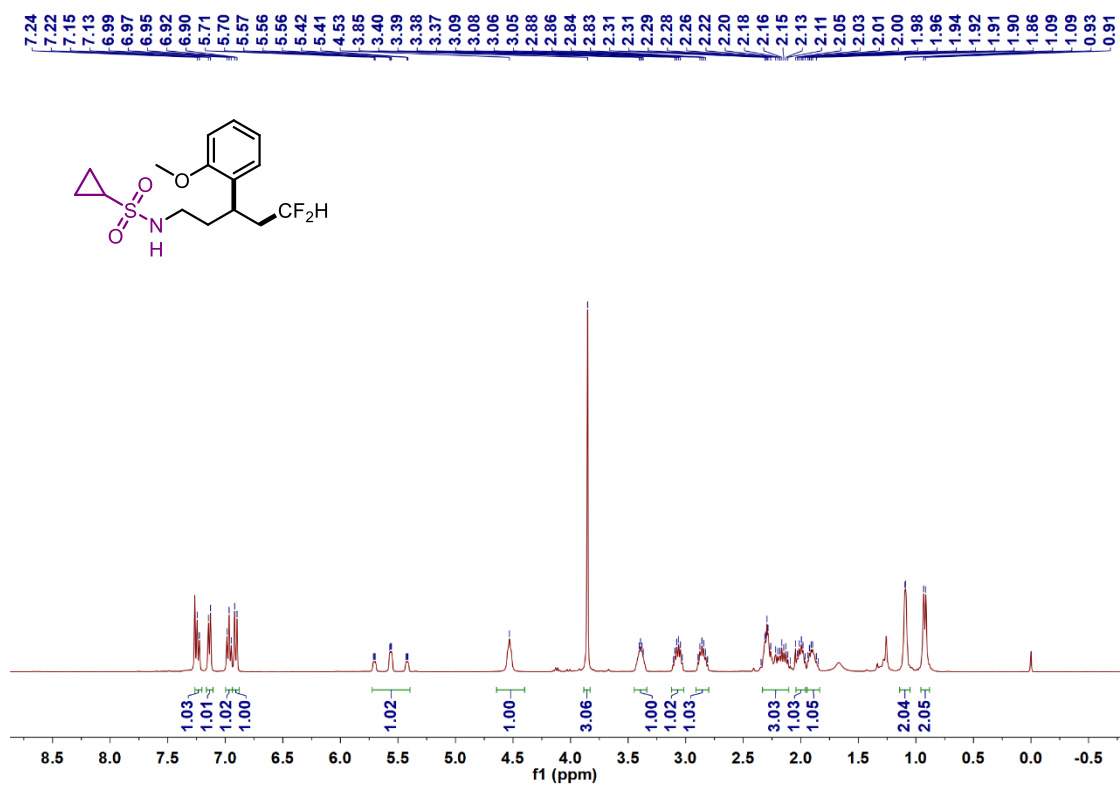
¹³C NMR of Compound **5q** (101 MHz, CDCl₃)



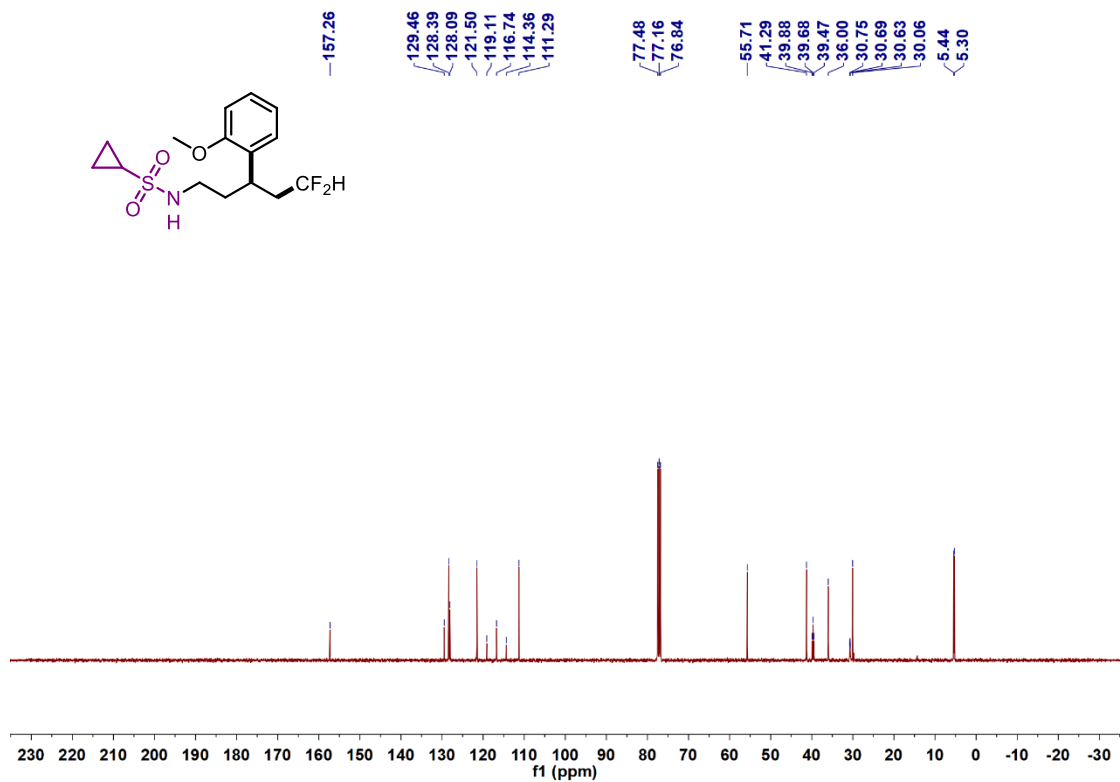
¹⁹F NMR of Compound **5q** (400 MHz, CDCl₃)



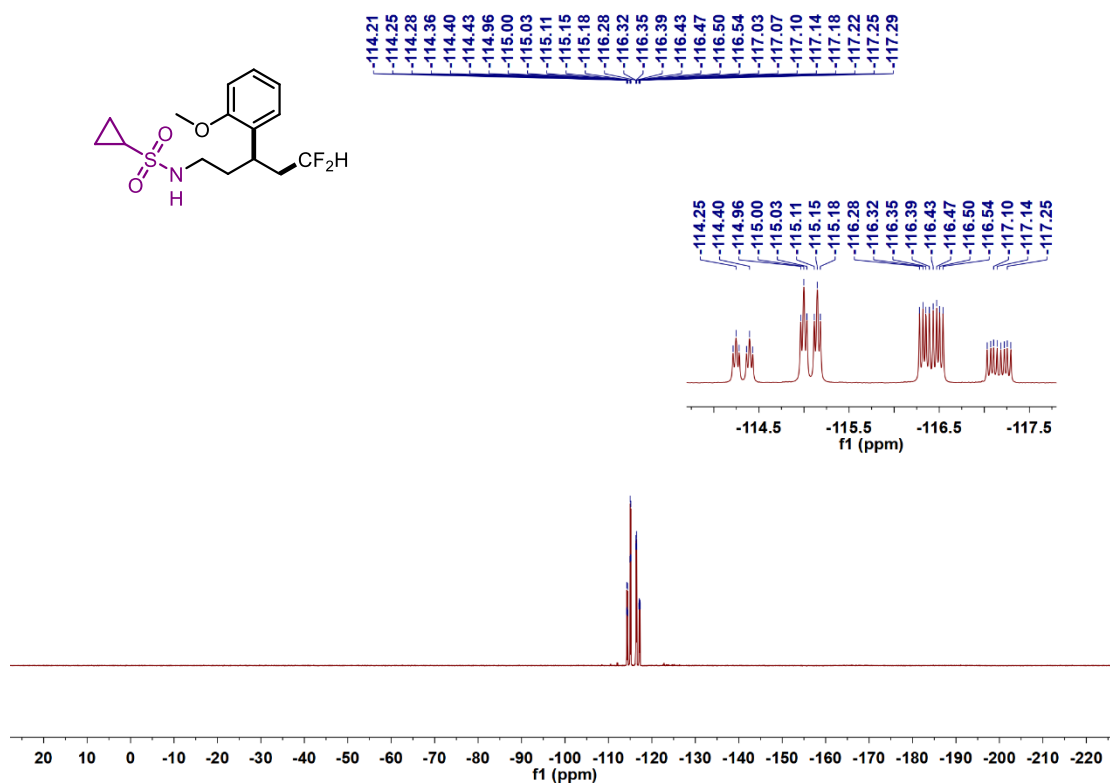
¹H NMR of Compound **5r** (400 MHz, CDCl₃)



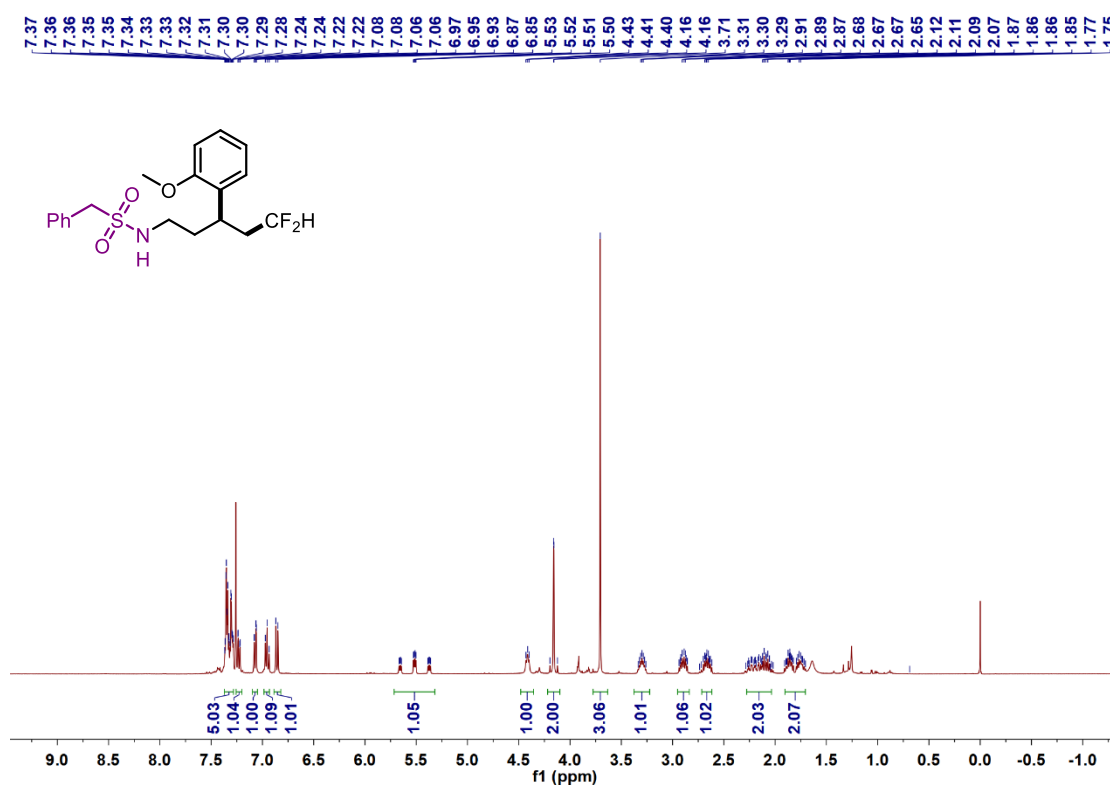
¹³C NMR of Compound **5r** (101 MHz, CDCl₃)



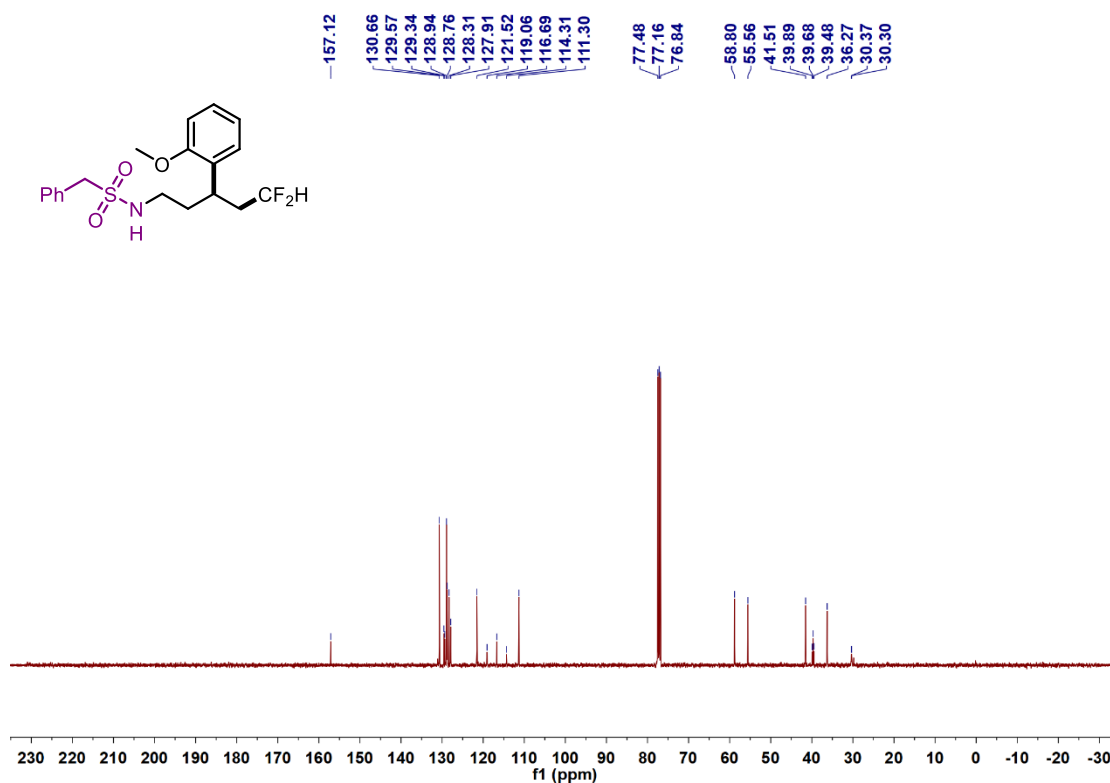
¹⁹F NMR of Compound **5r** (400 MHz, CDCl₃)



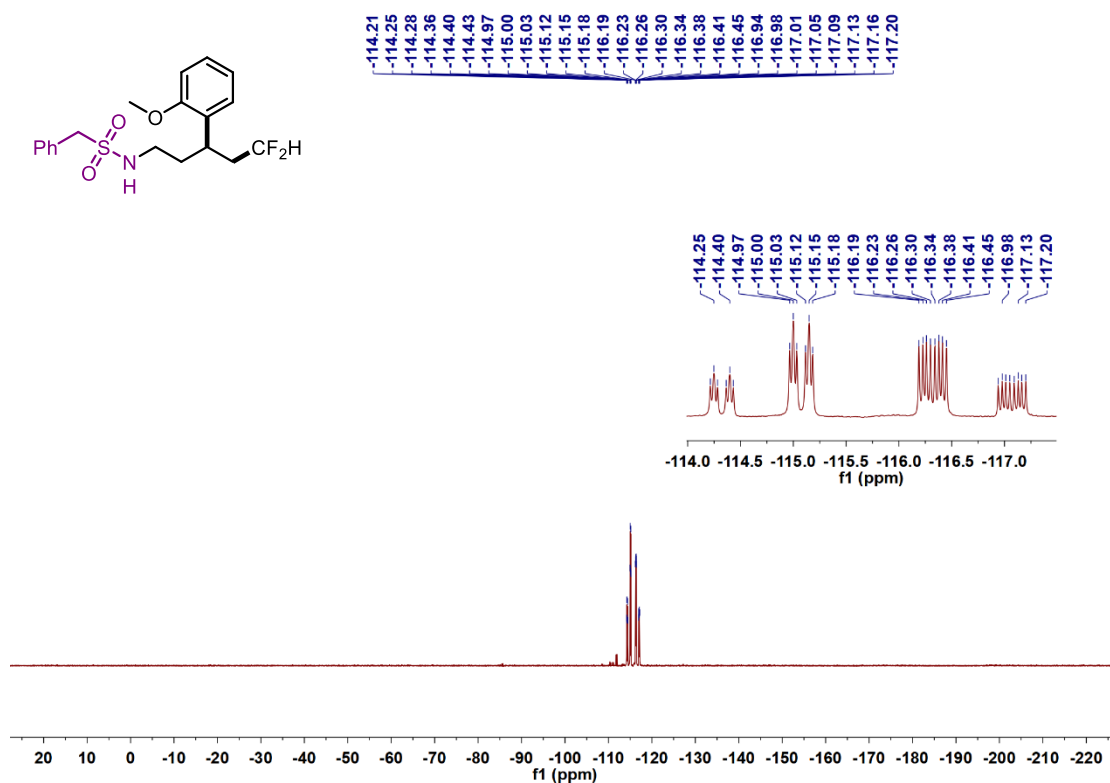
¹H NMR of Compound **5s** (400 MHz, CDCl₃)



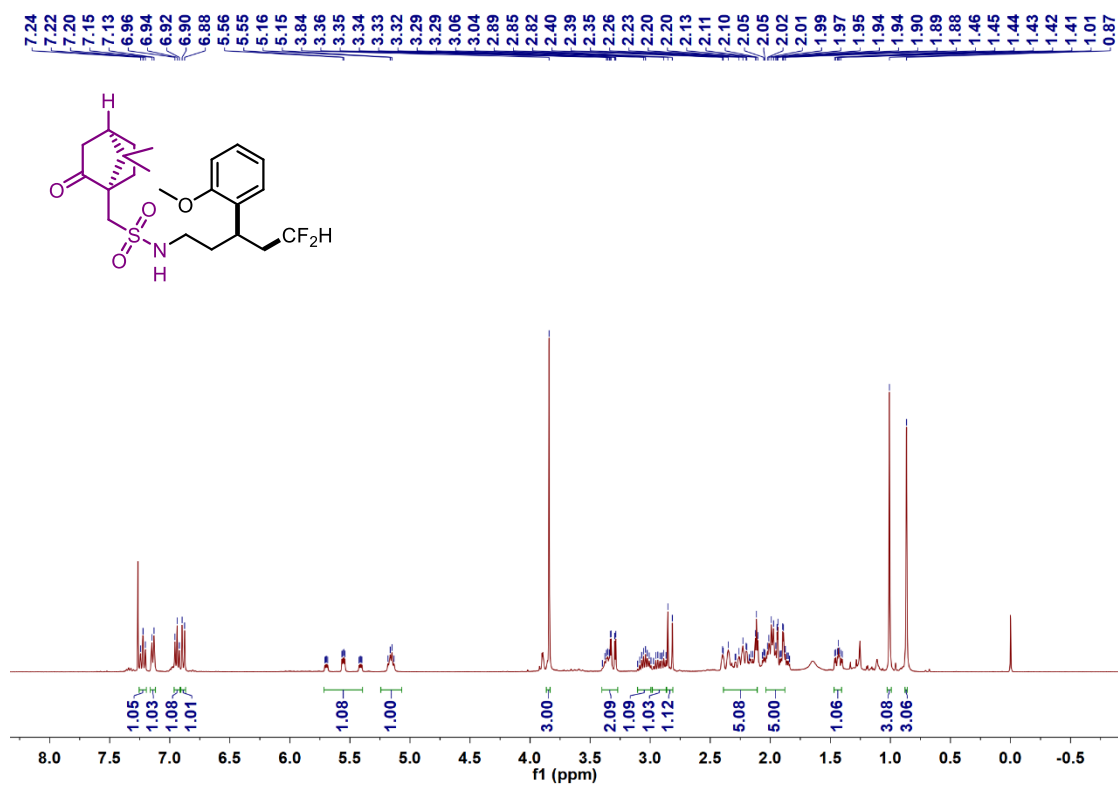
¹³C NMR of Compound 5s (101 MHz, CDCl₃)



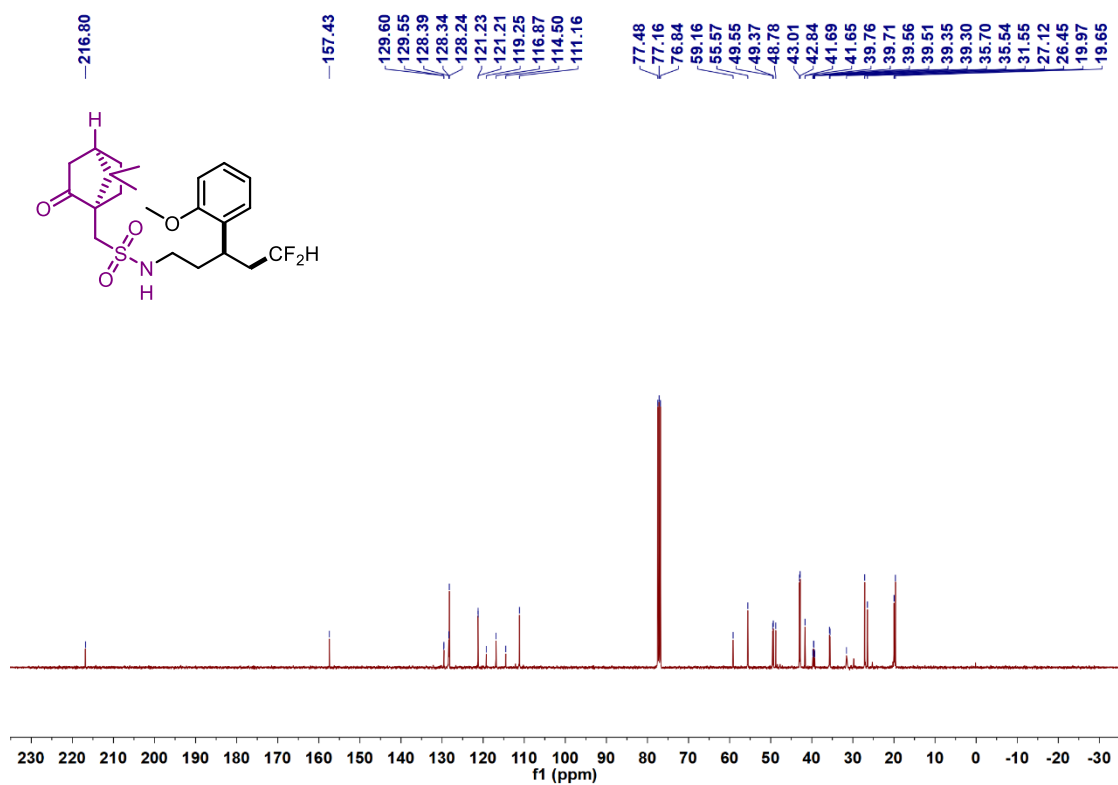
¹⁹F NMR of Compound 5s (400 MHz, CDCl₃)



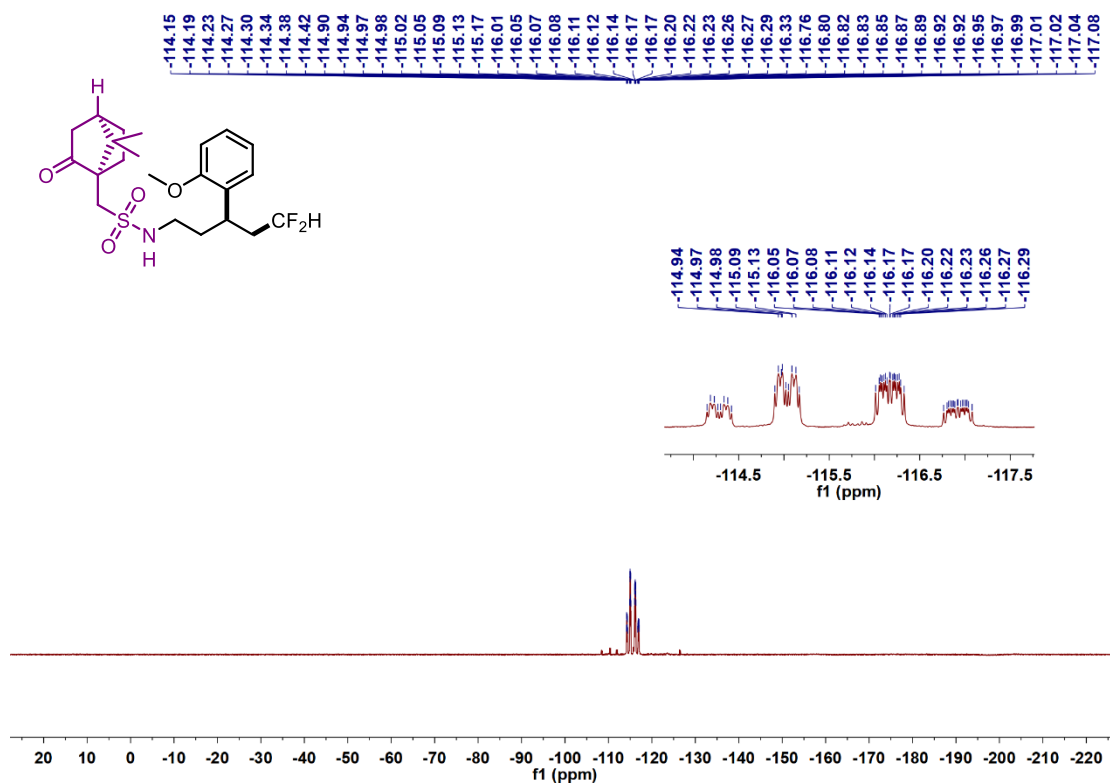
¹H NMR of Compound **5t** (400 MHz, CDCl₃)



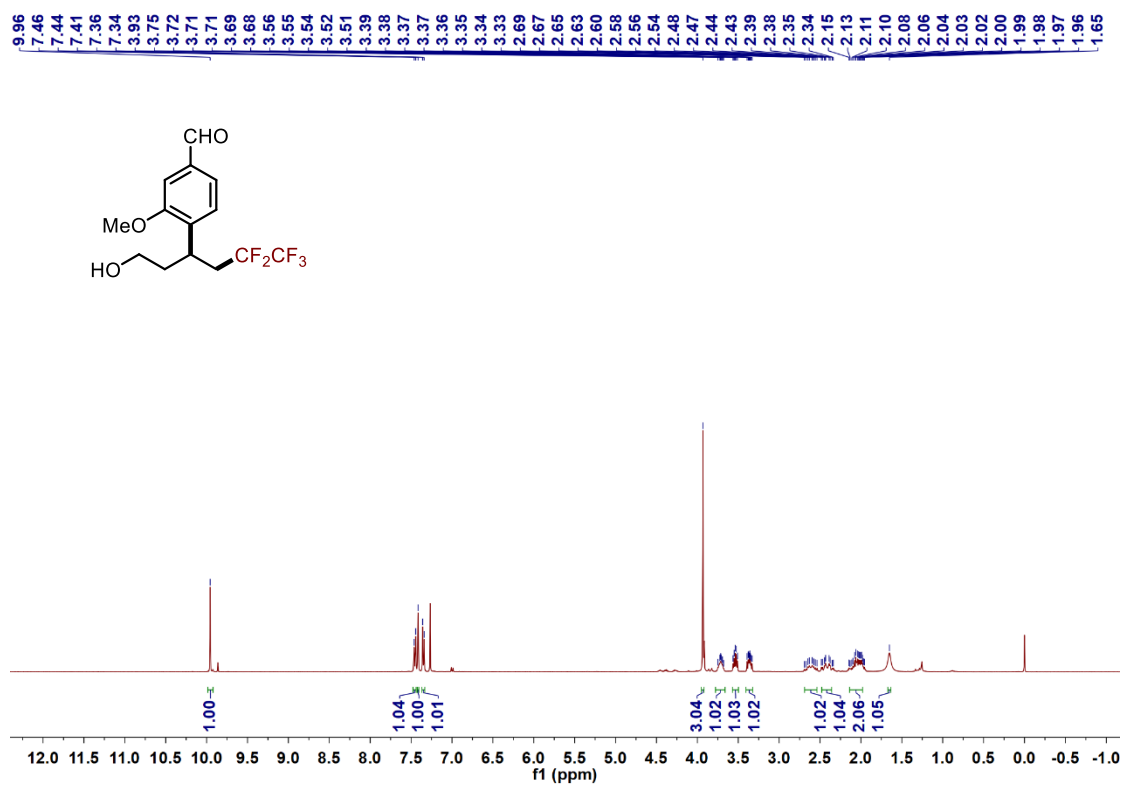
¹³C NMR of Compound **5t** (101 MHz, CDCl₃)



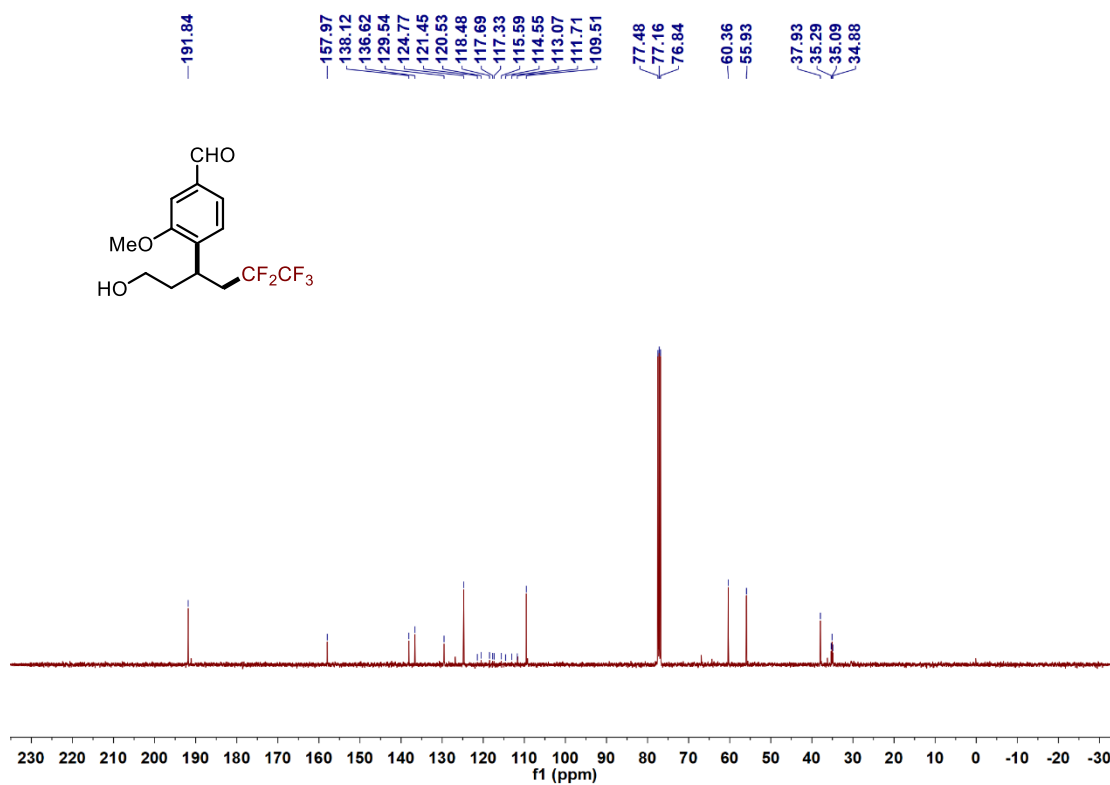
¹⁹F NMR of Compound **5t** (400 MHz, CDCl₃)



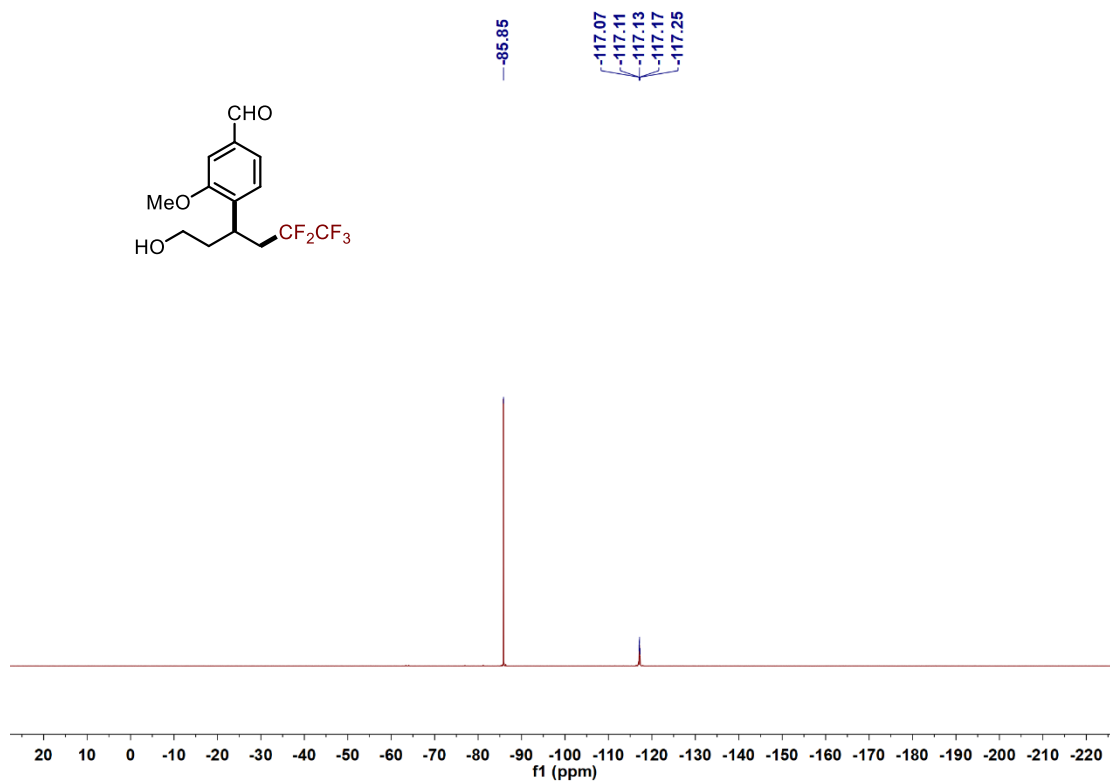
¹H NMR of Compound **5u** (400 MHz, CDCl₃)



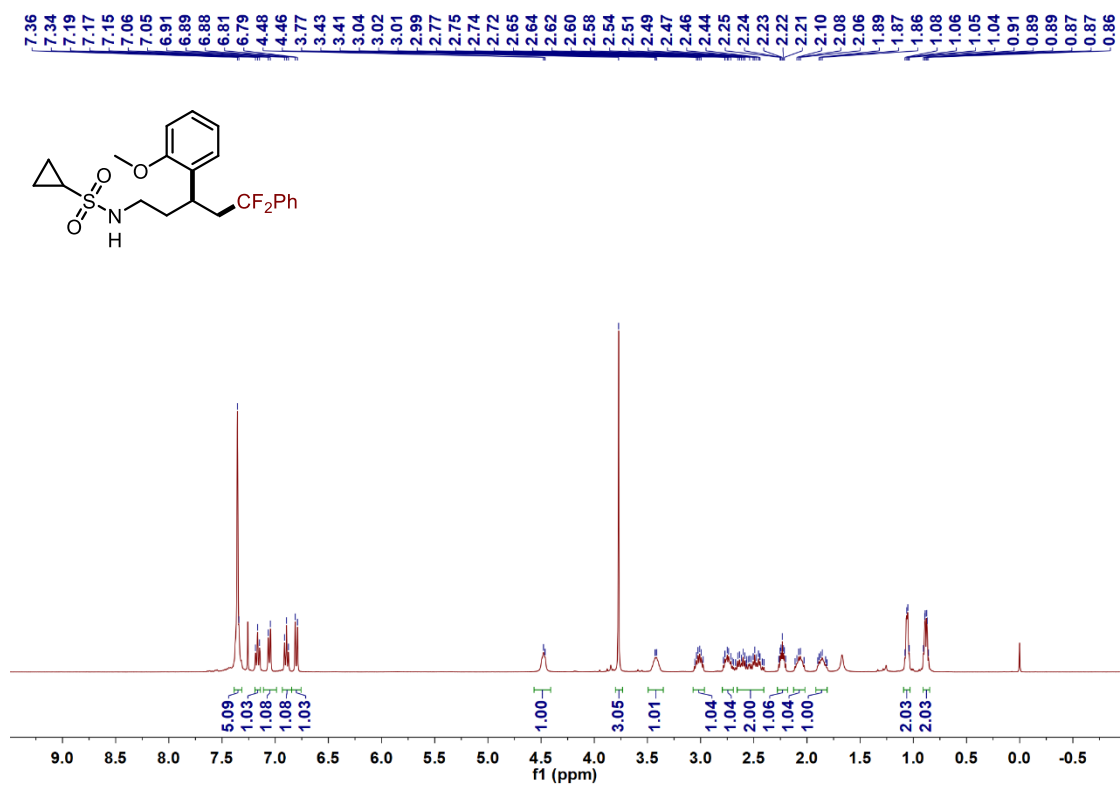
¹³C NMR of Compound **5u** (101 MHz, CDCl₃)



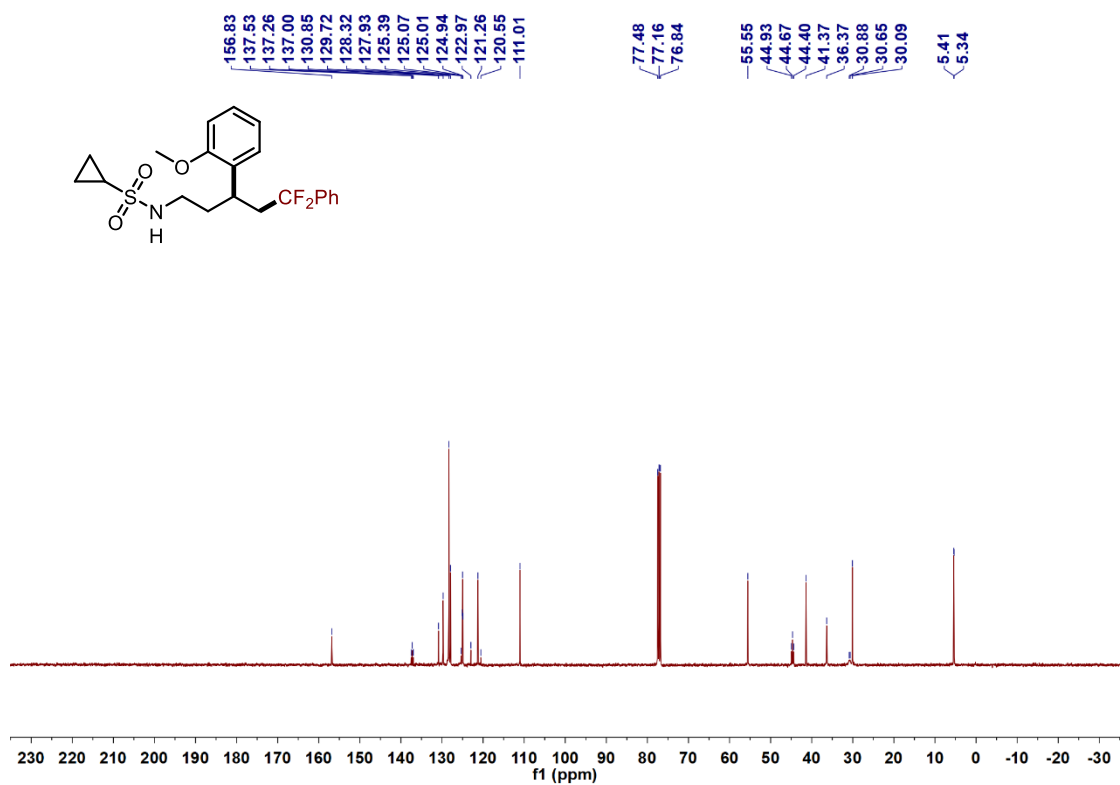
¹⁹F NMR of Compound **5u** (400 MHz, CDCl₃)



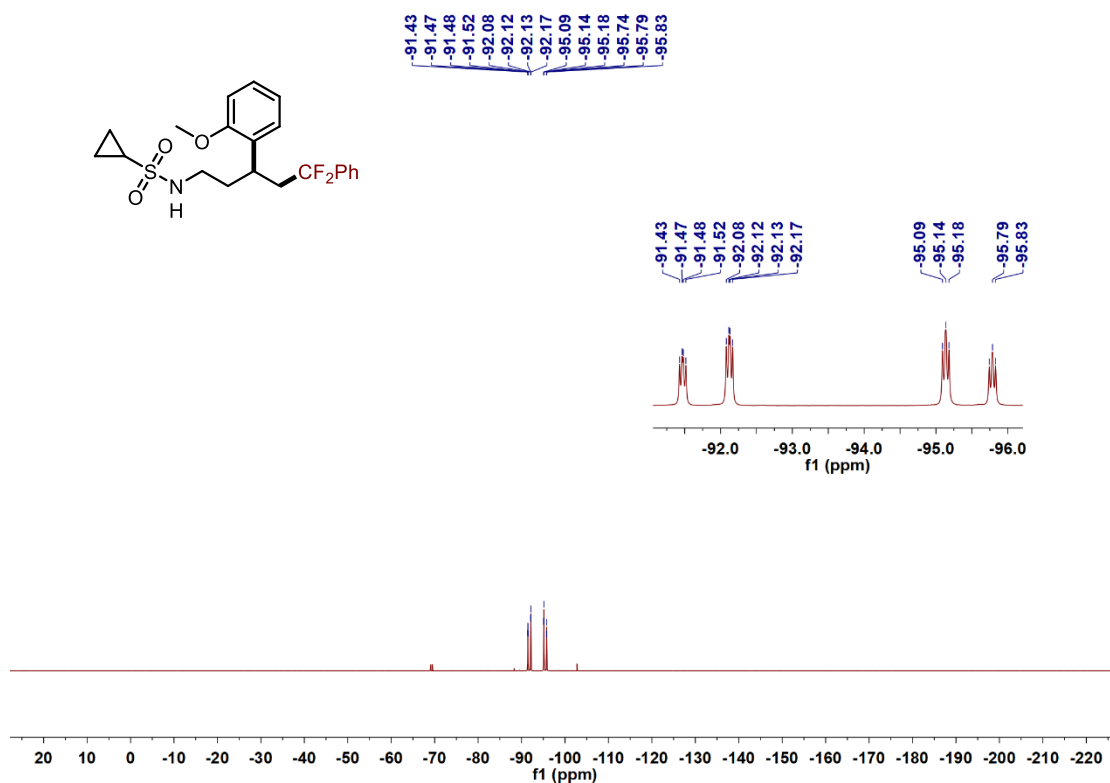
¹H NMR of Compound 5v (400 MHz, CDCl₃)



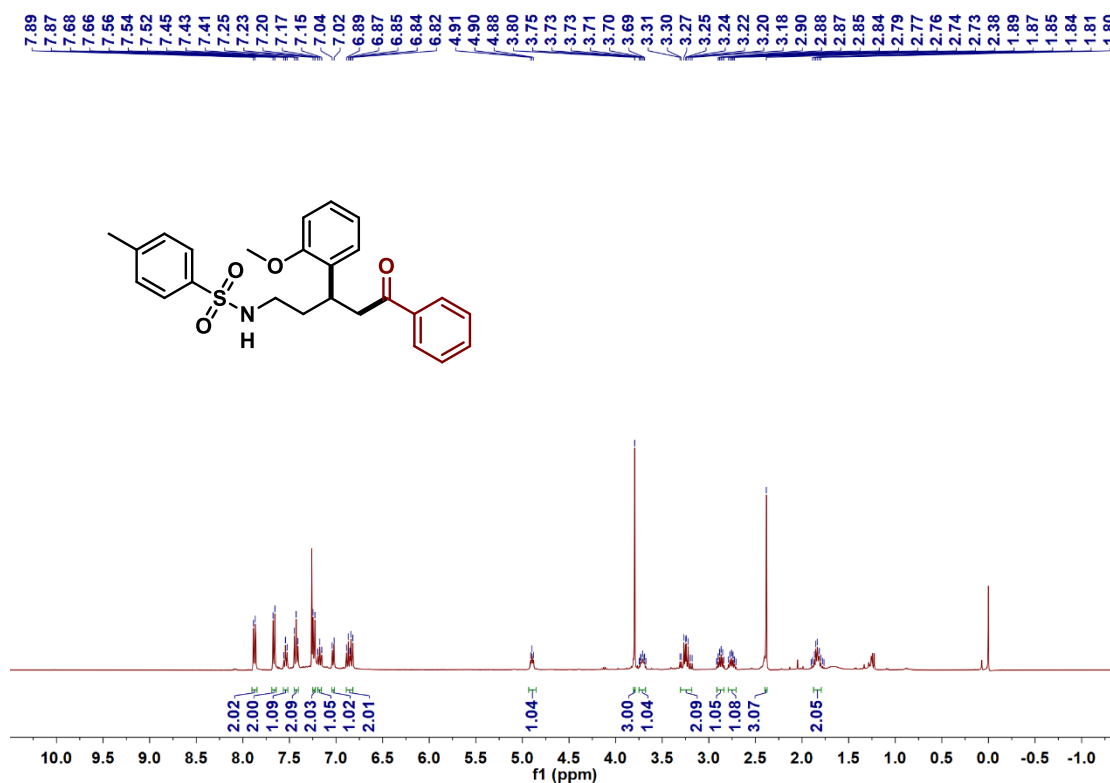
¹³C NMR of Compound 5v (101 MHz, CDCl₃)



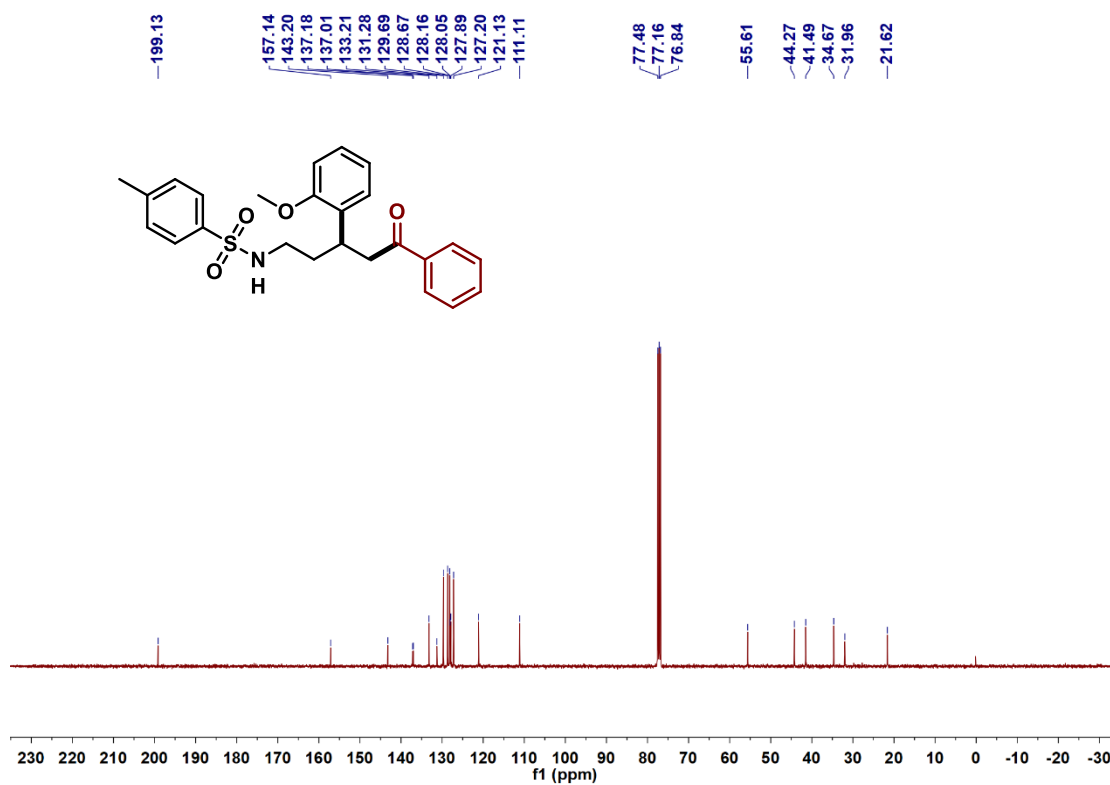
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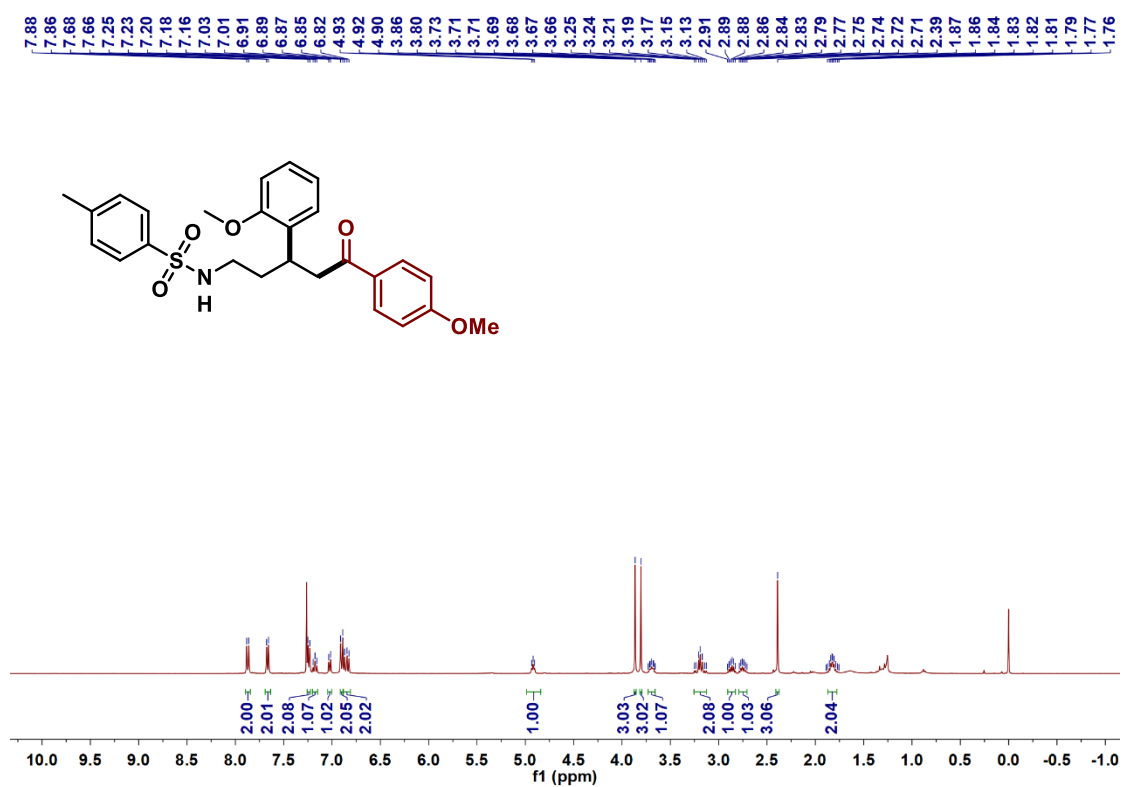
¹H NMR of Compound 7a (400 MHz, CDCl₃)



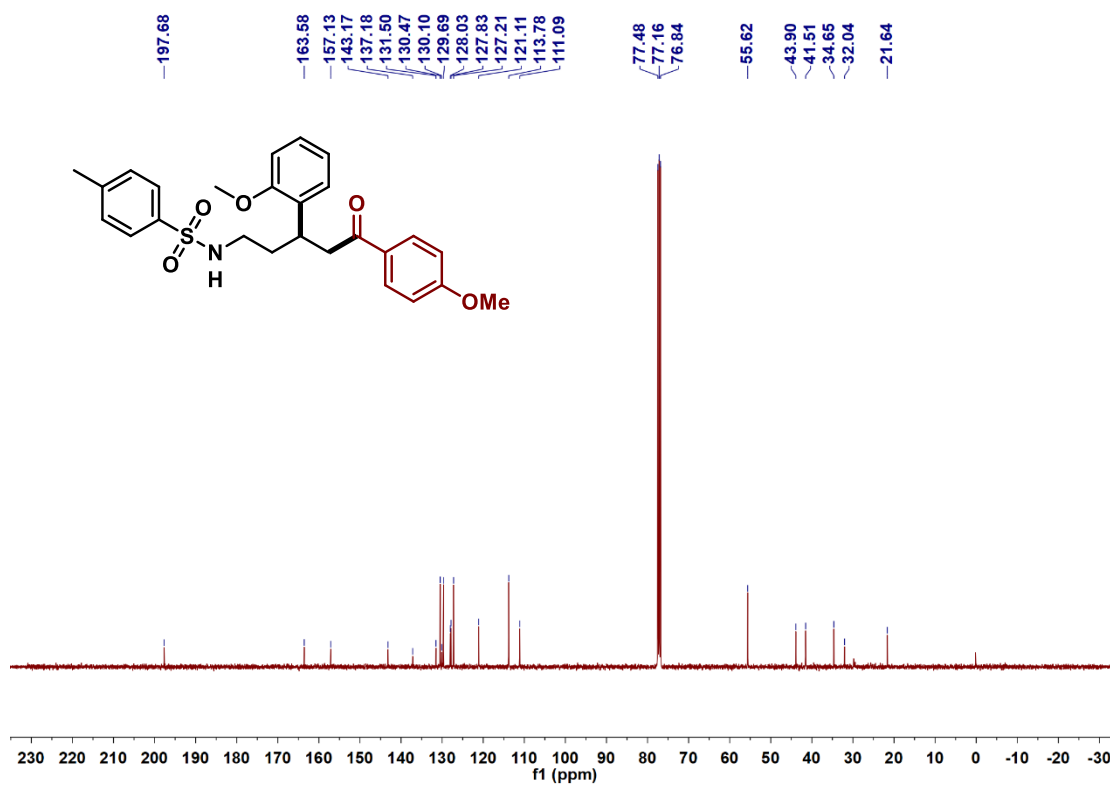
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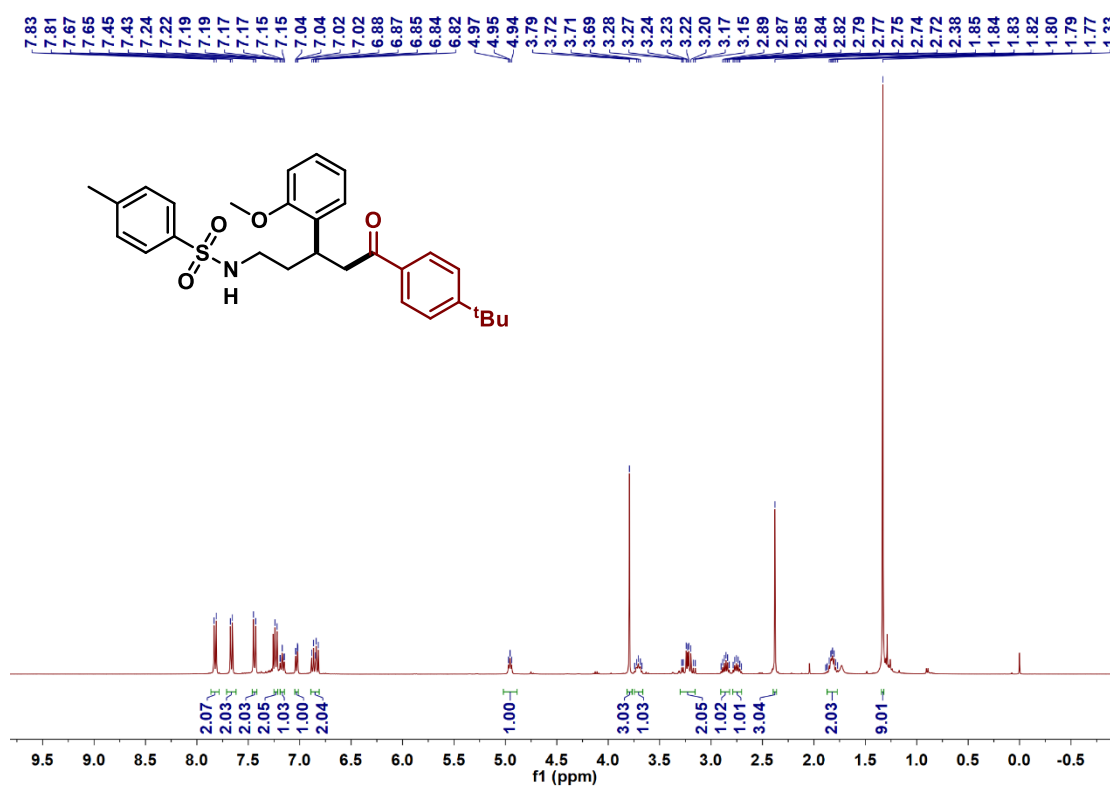
¹H NMR of Compound **7b** (400 MHz, CDCl₃)



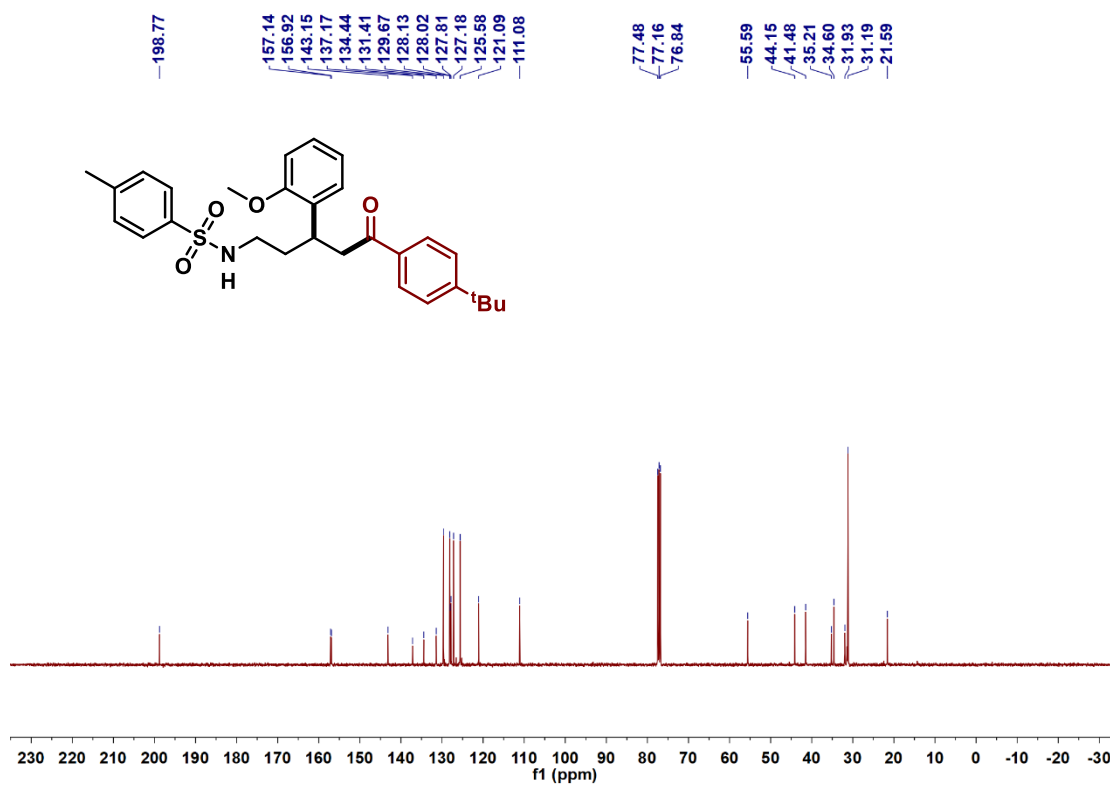
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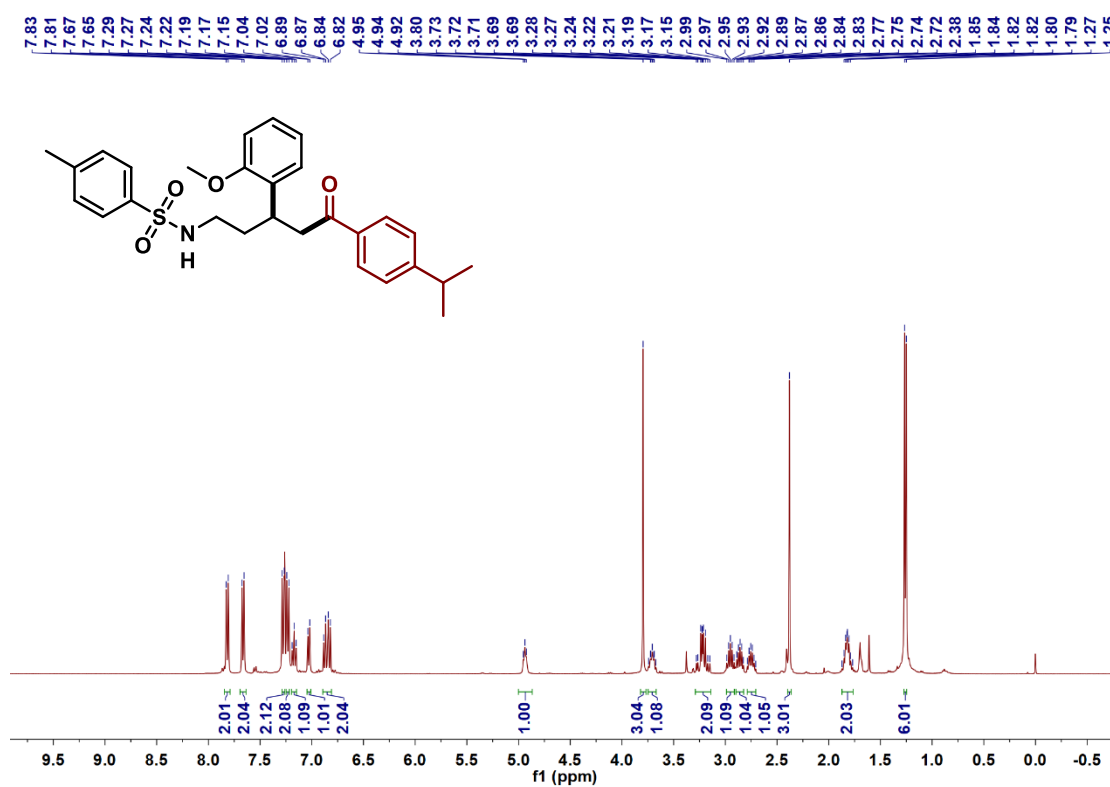
¹H NMR of Compound **7c** (400 MHz, CDCl₃)



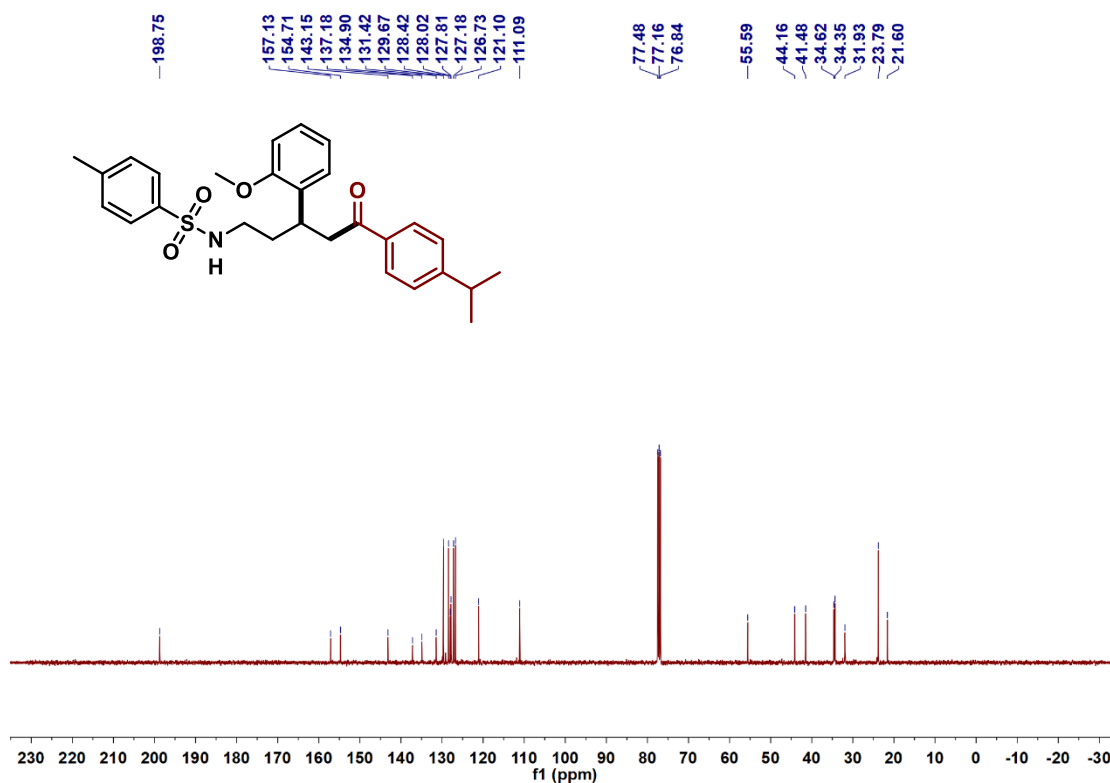
¹³C NMR of Compound **7c** (101 MHz, CDCl₃)



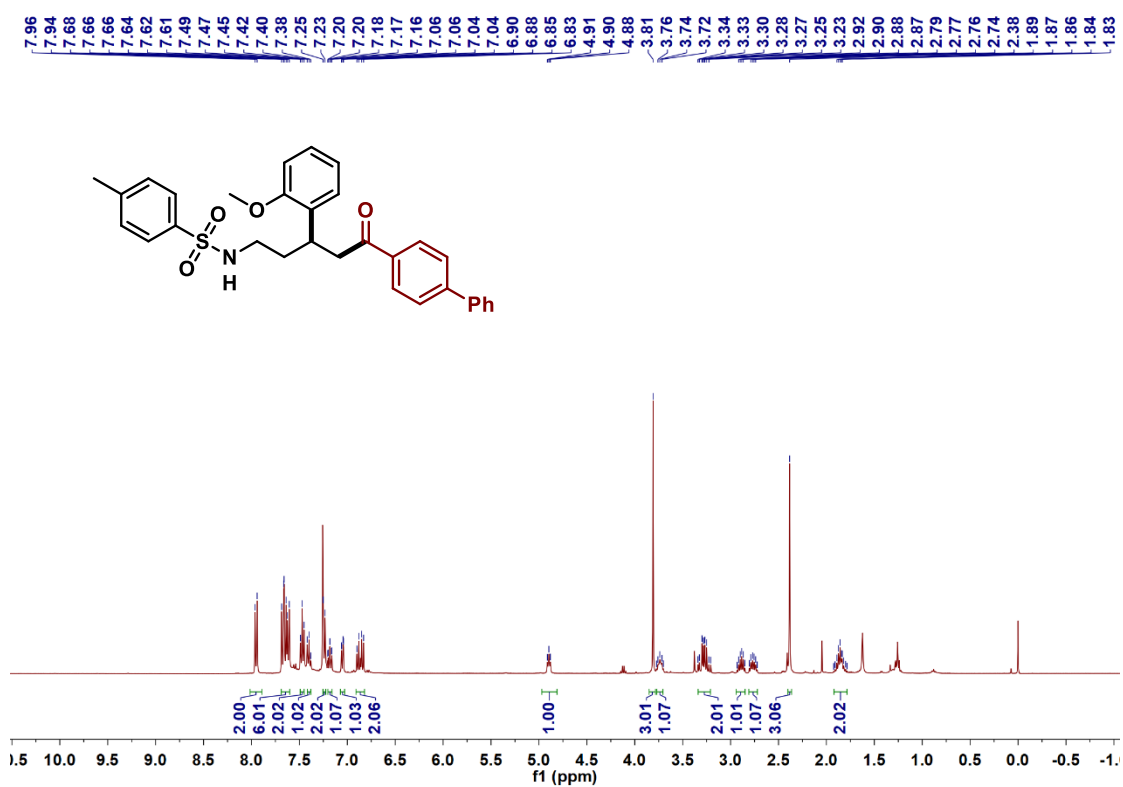
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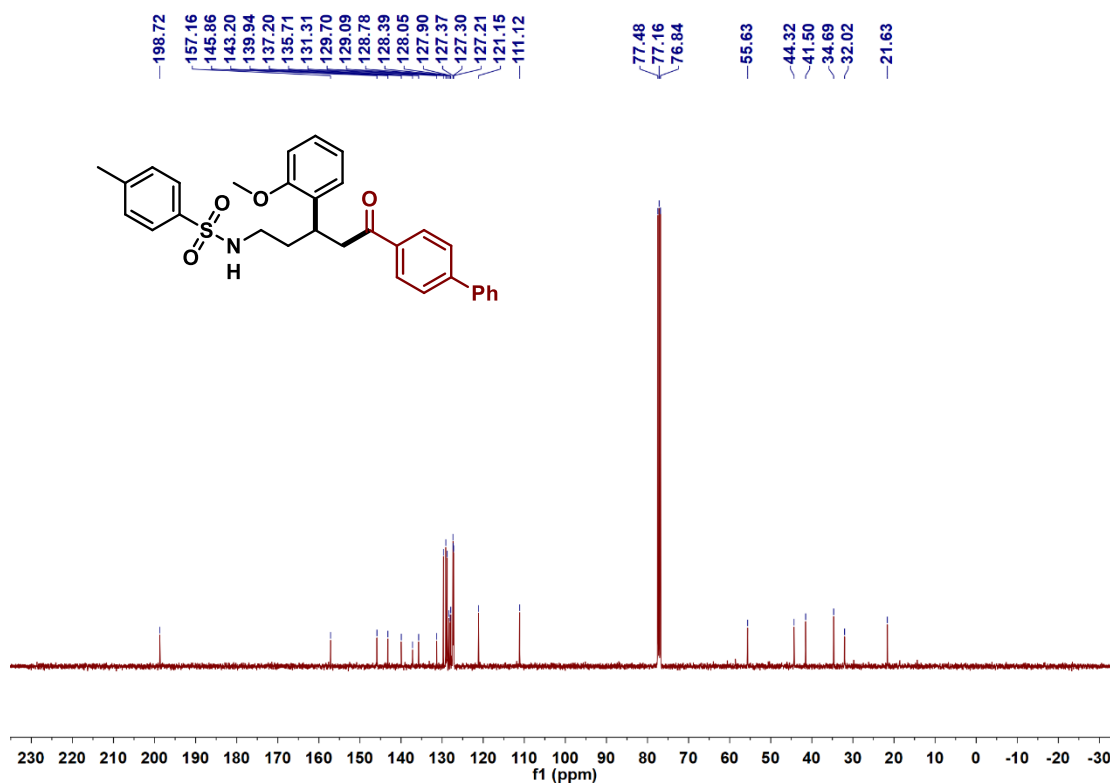
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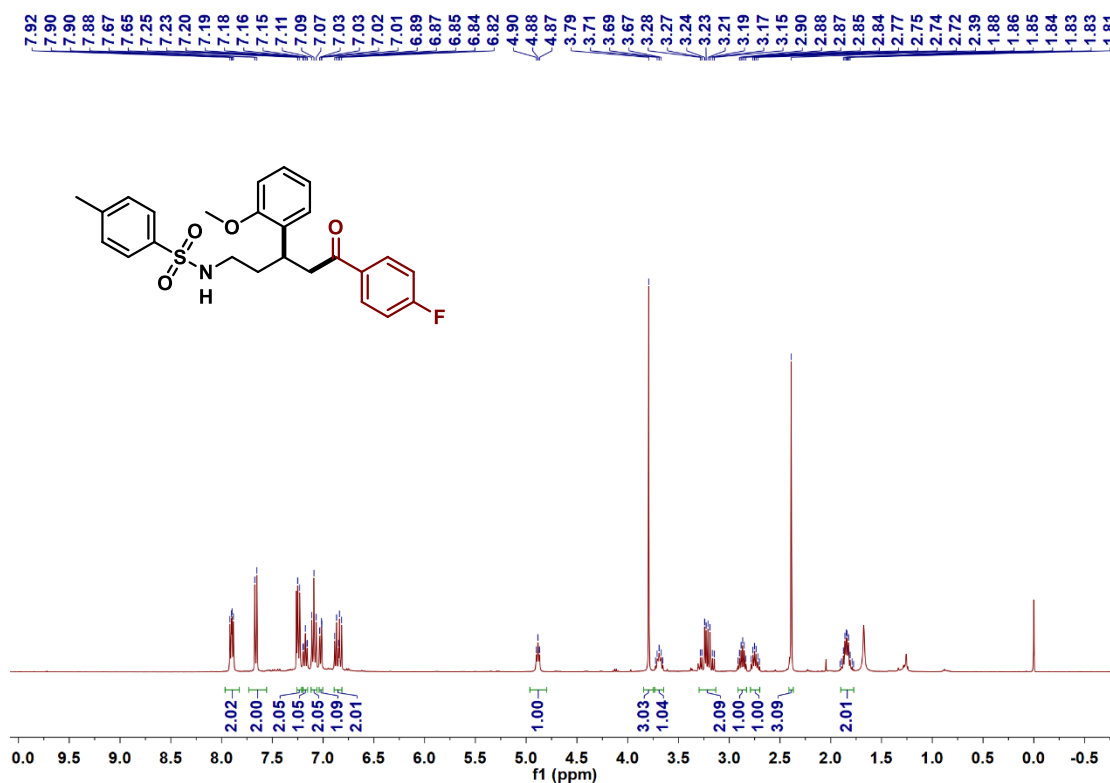
¹H NMR of Compound **7e** (400 MHz, CDCl₃)



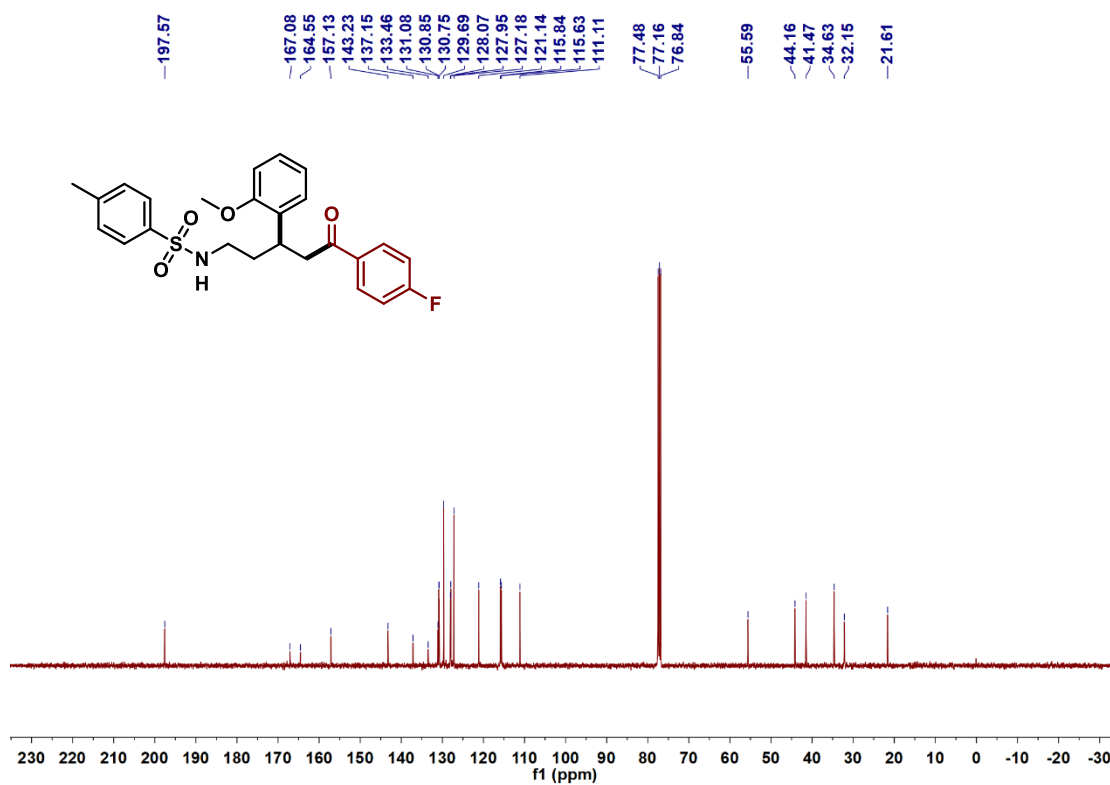
¹³C NMR of Compound **7e** (101 MHz, CDCl₃)



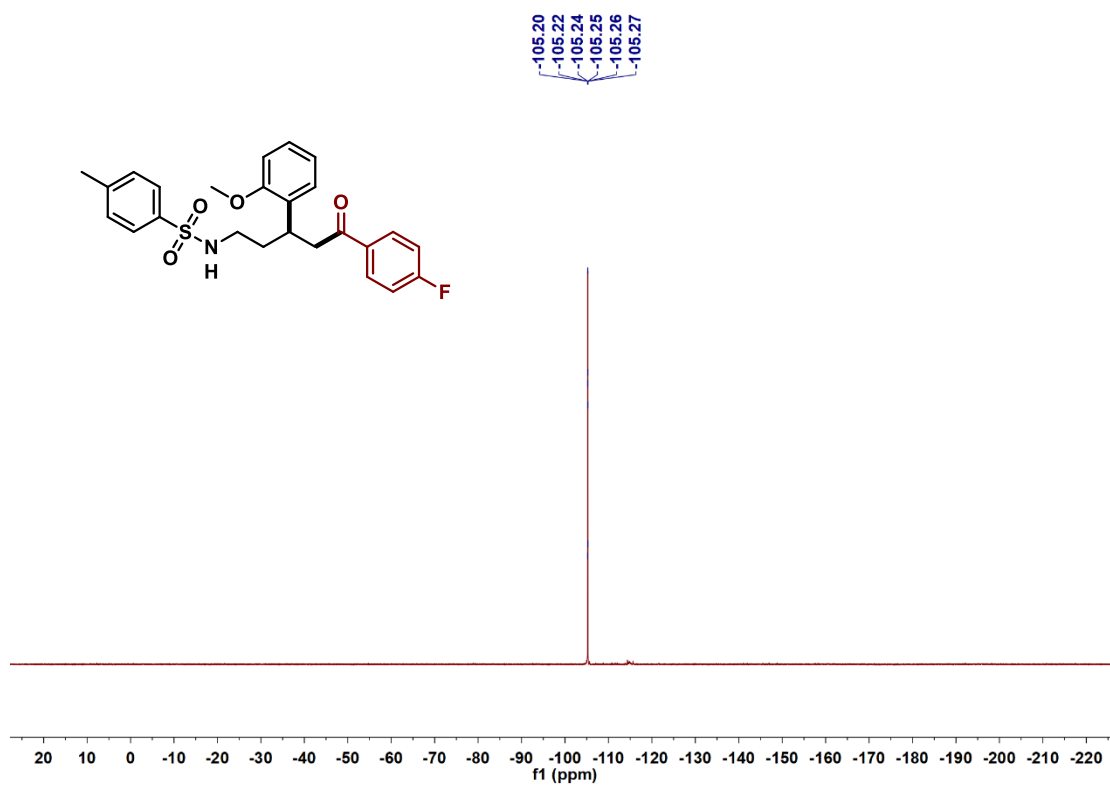
¹H NMR of Compound **7f** (400 MHz, CDCl₃)



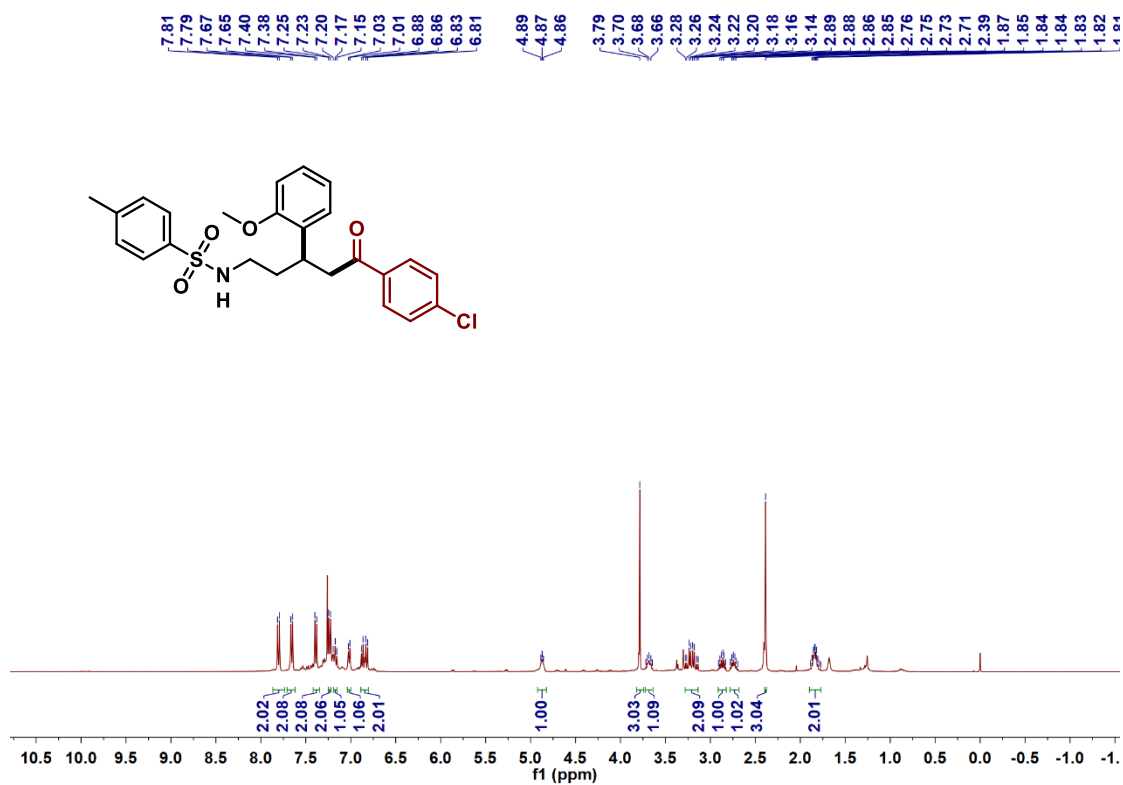
¹³C NMR of Compound **7f** (101 MHz, CDCl₃)



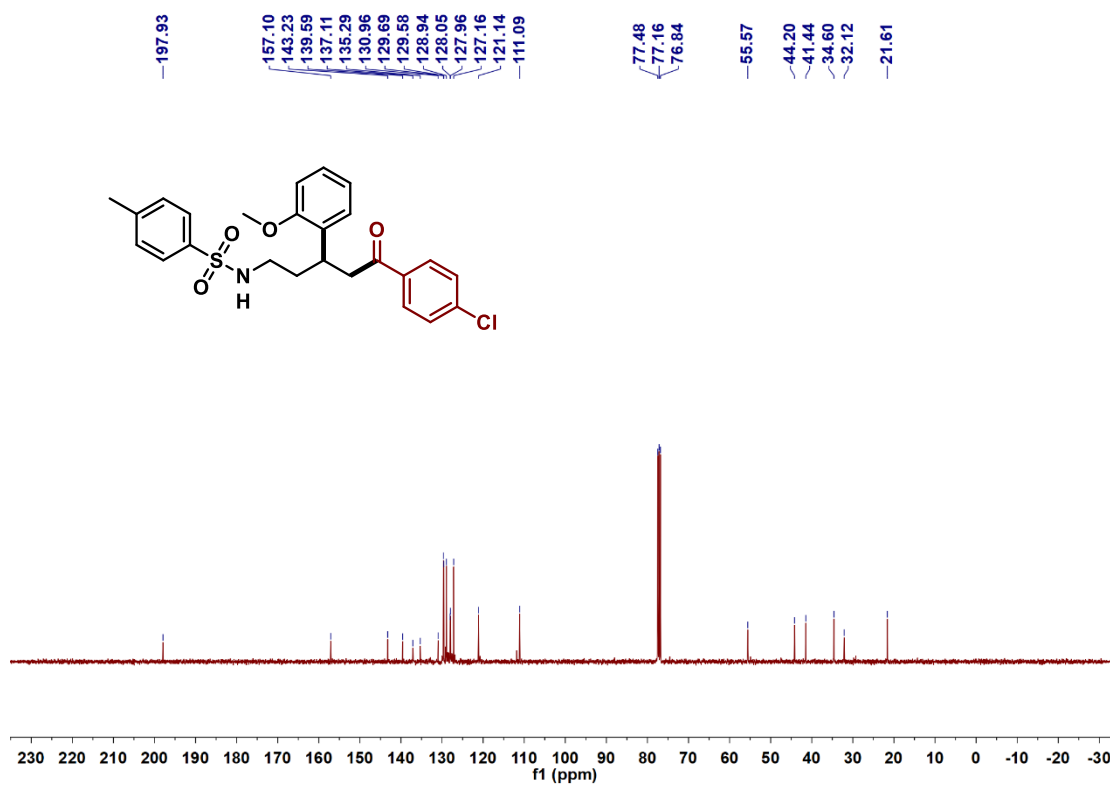
¹⁹F NMR of Compound **7f** (376 MHz, CDCl₃)



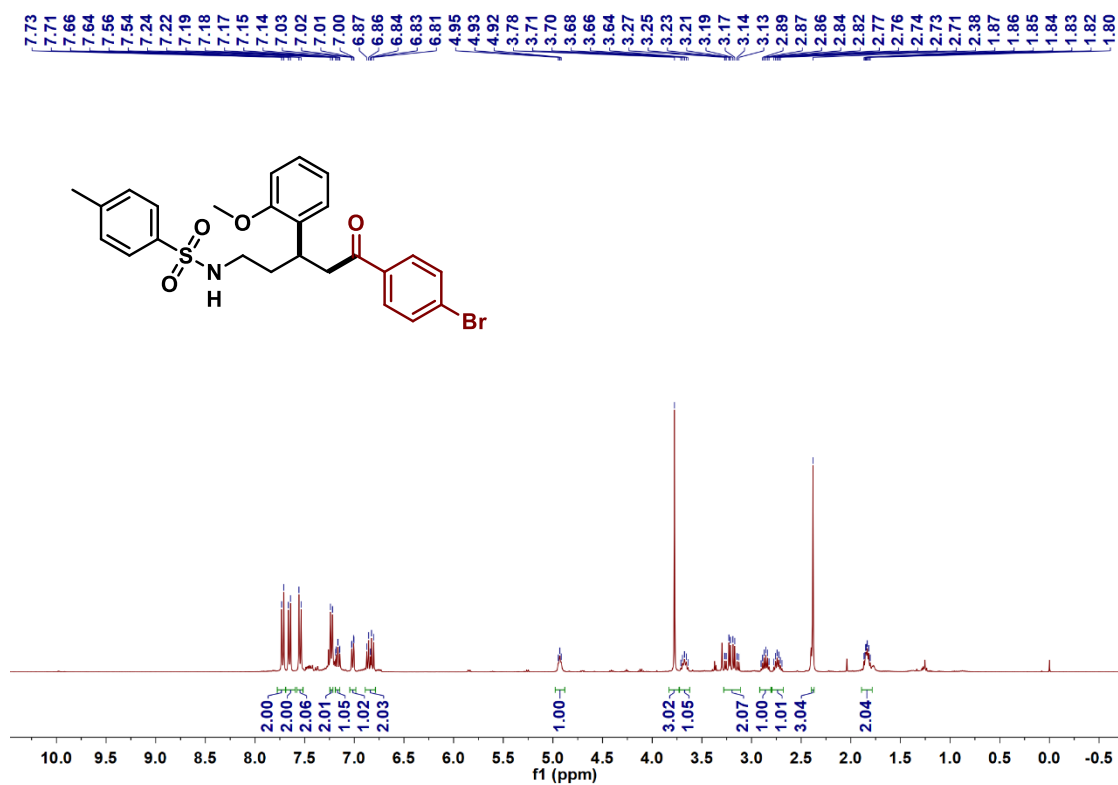
¹H NMR of Compound **7g** (400 MHz, CDCl₃)



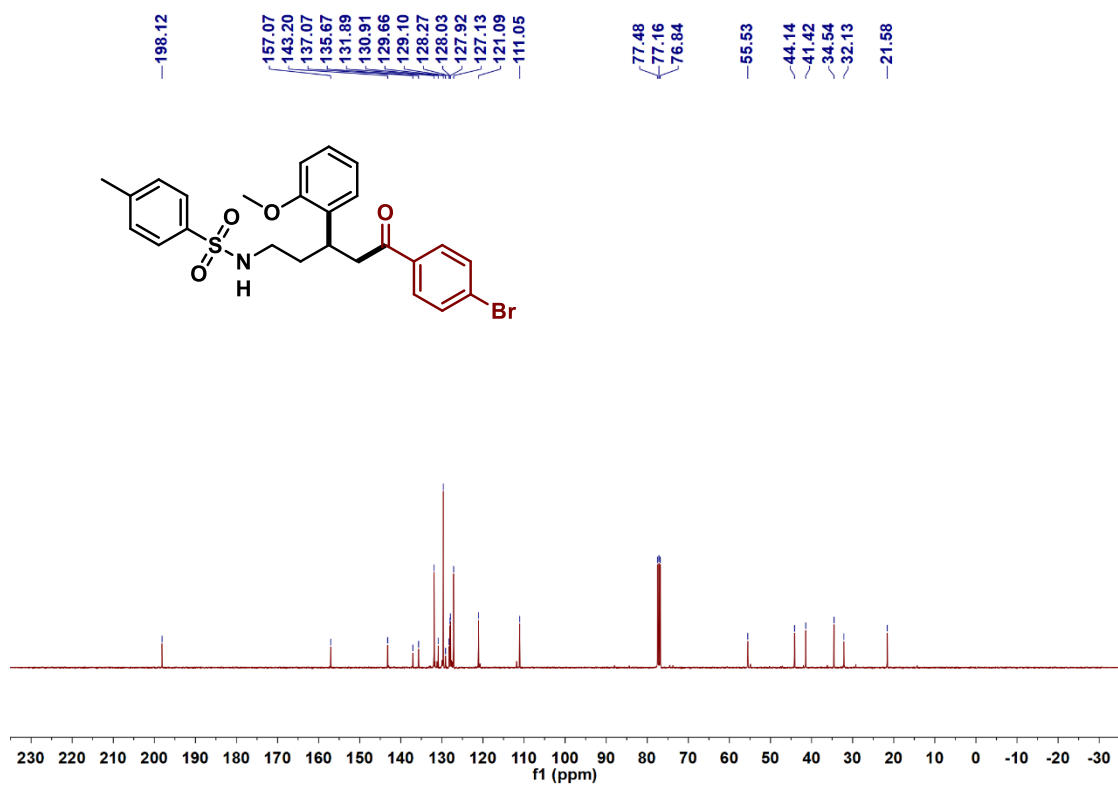
¹³C NMR of Compound **7g** (101 MHz, CDCl₃)



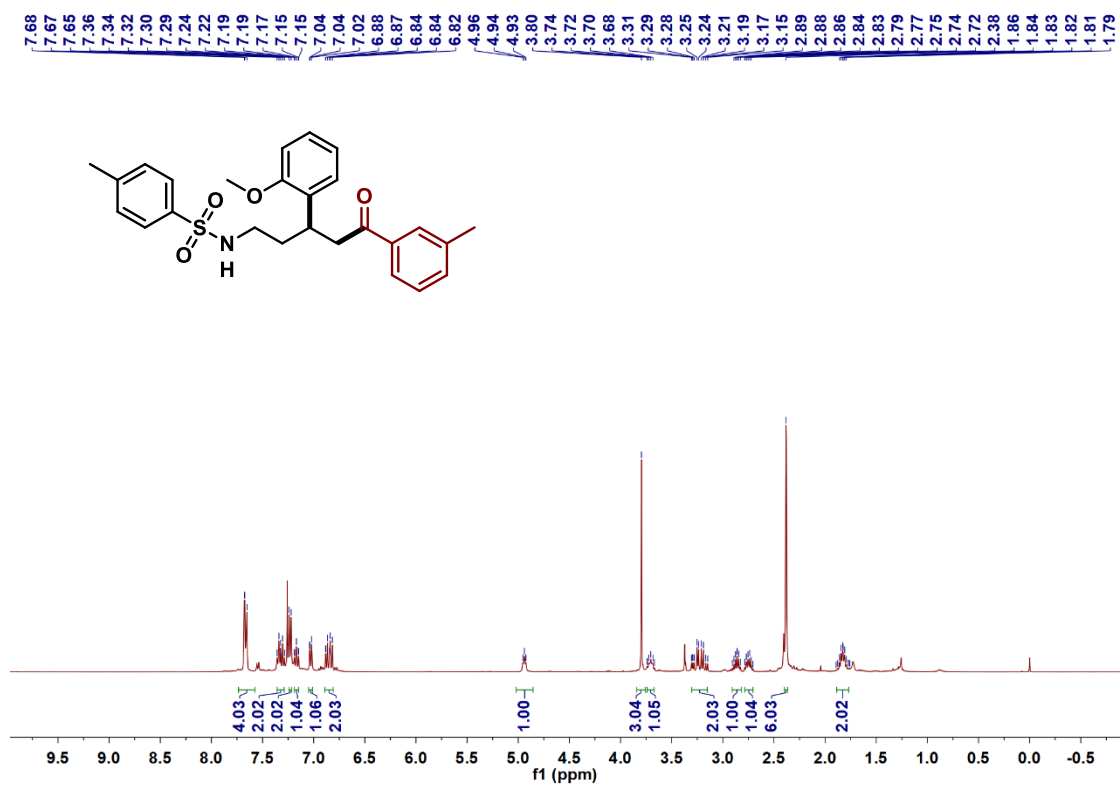
¹H NMR of Compound **7h** (400 MHz, CDCl₃)



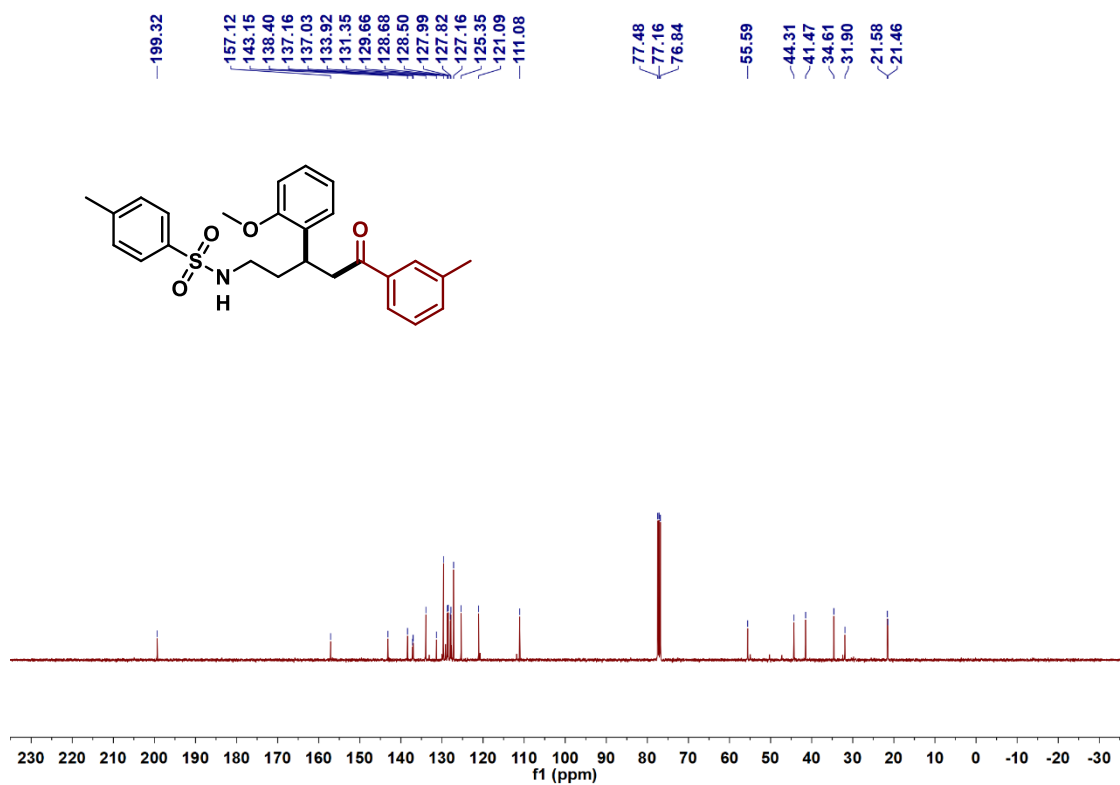
¹³C NMR of Compound **7h** (101 MHz, CDCl₃)



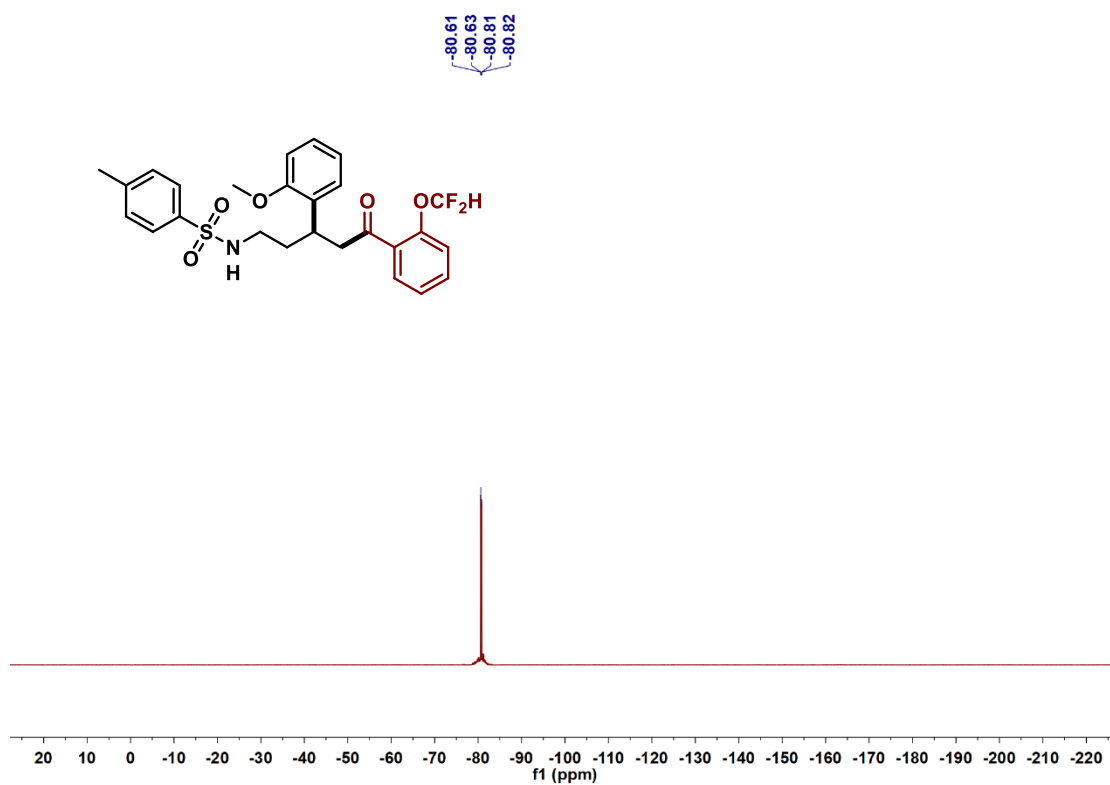
¹H NMR of Compound **7i** (400 MHz, CDCl₃)



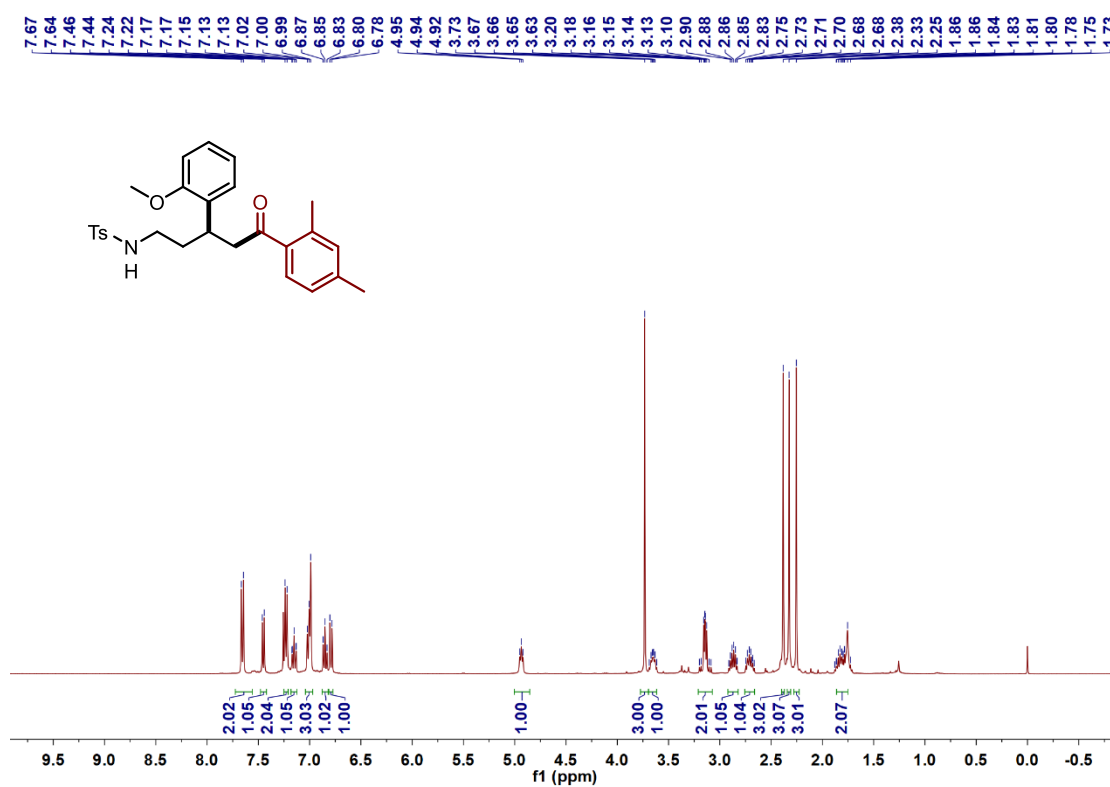
¹³C NMR of Compound **7i** (101 MHz, CDCl₃)



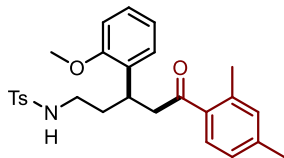
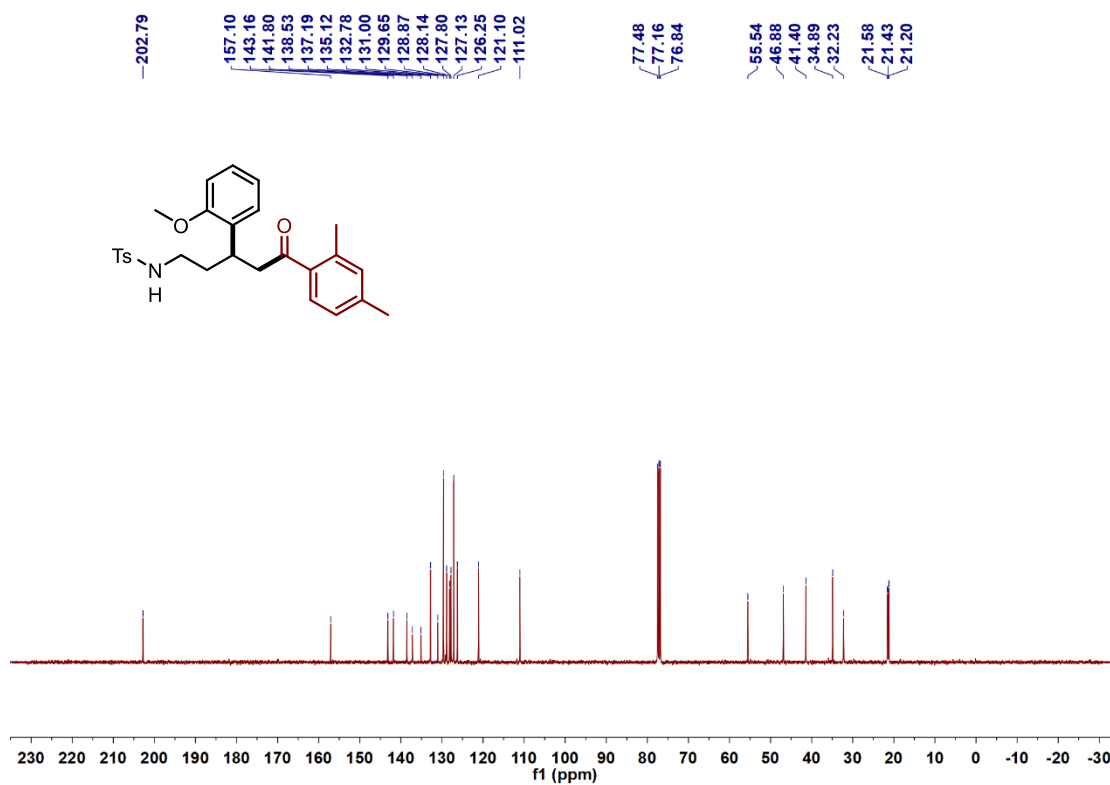
¹⁹F NMR of Compound **7j** (376 MHz, CDCl₃)



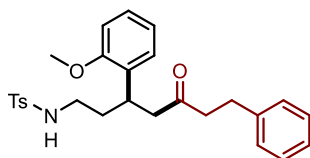
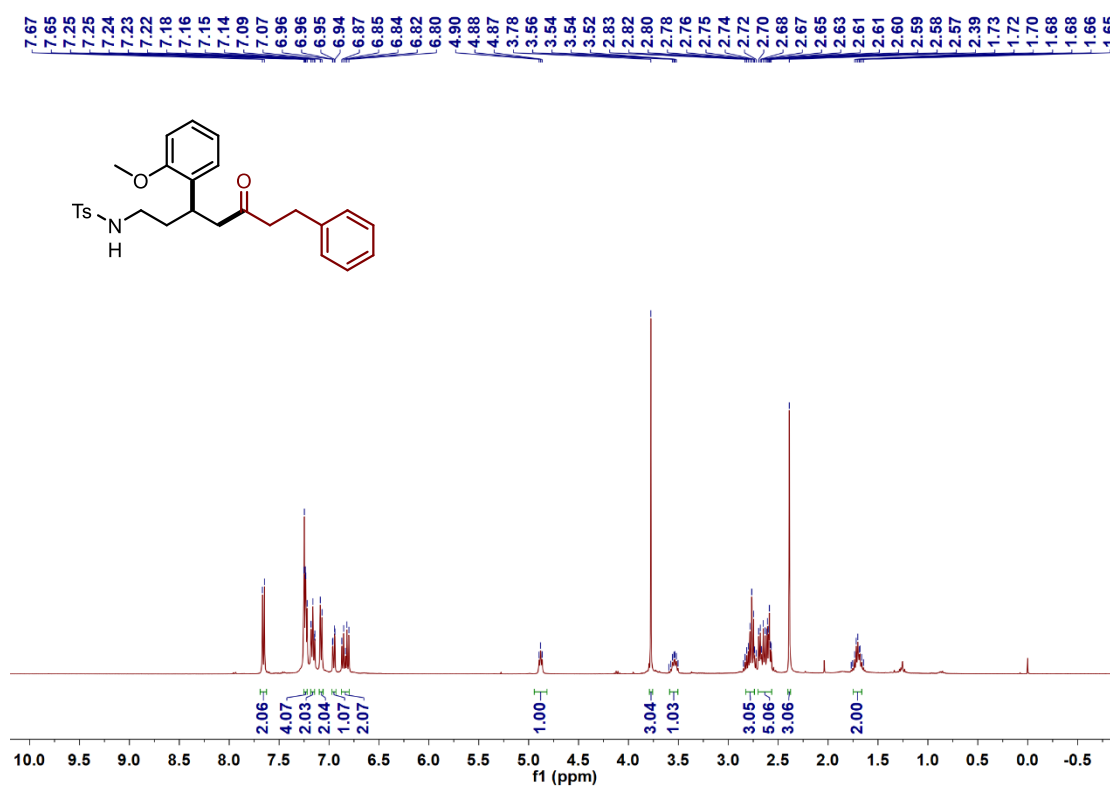
¹H NMR of Compound **7k** (400 MHz, CDCl₃)



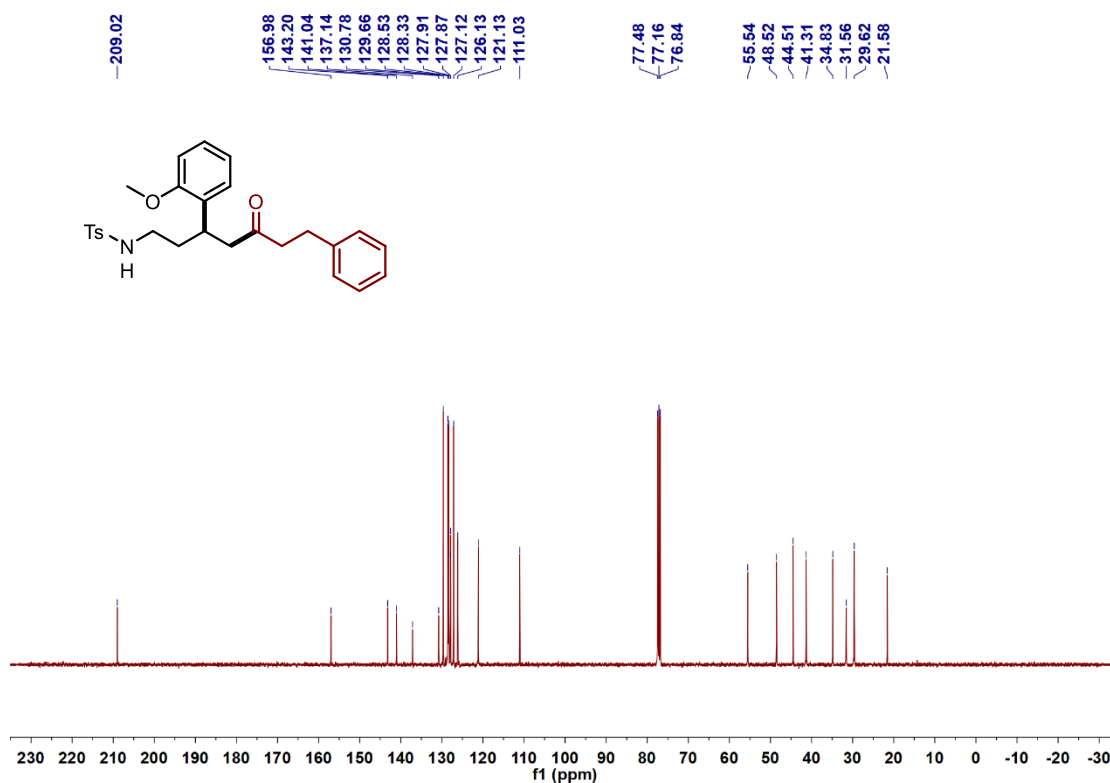
¹³C NMR of Compound **7k** (101 MHz, CDCl₃)



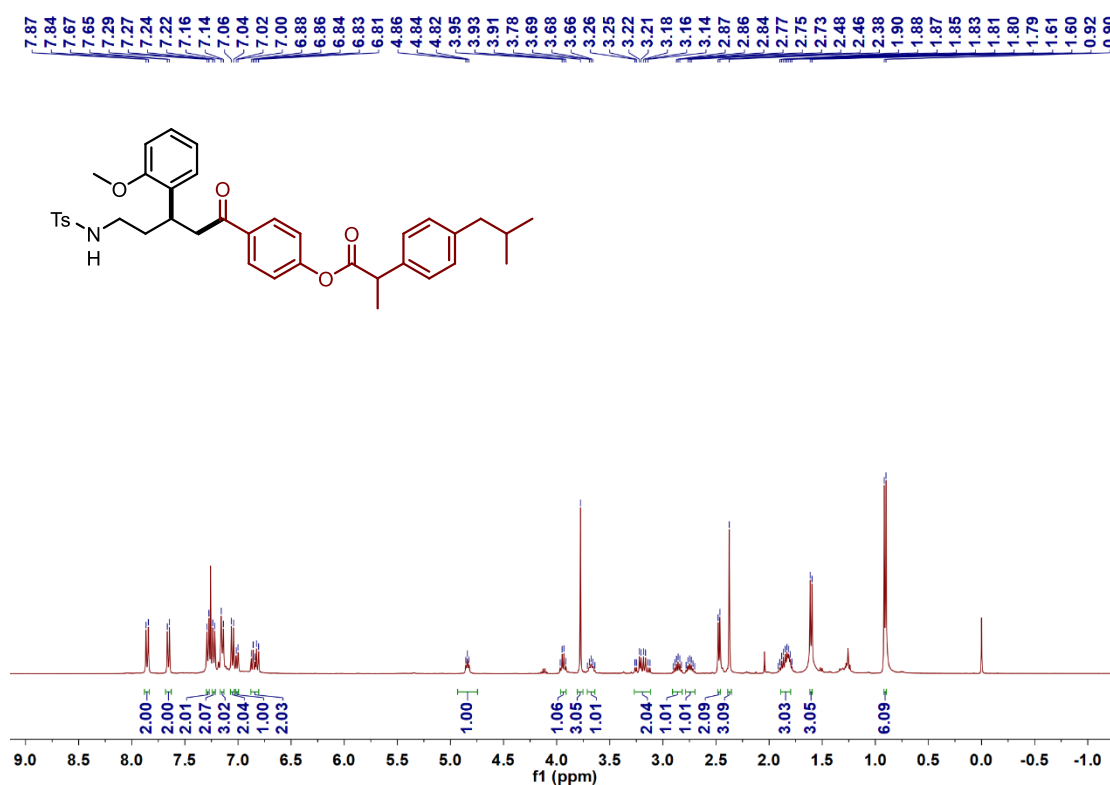
¹H NMR of Compound **7l** (400 MHz, CDCl₃)



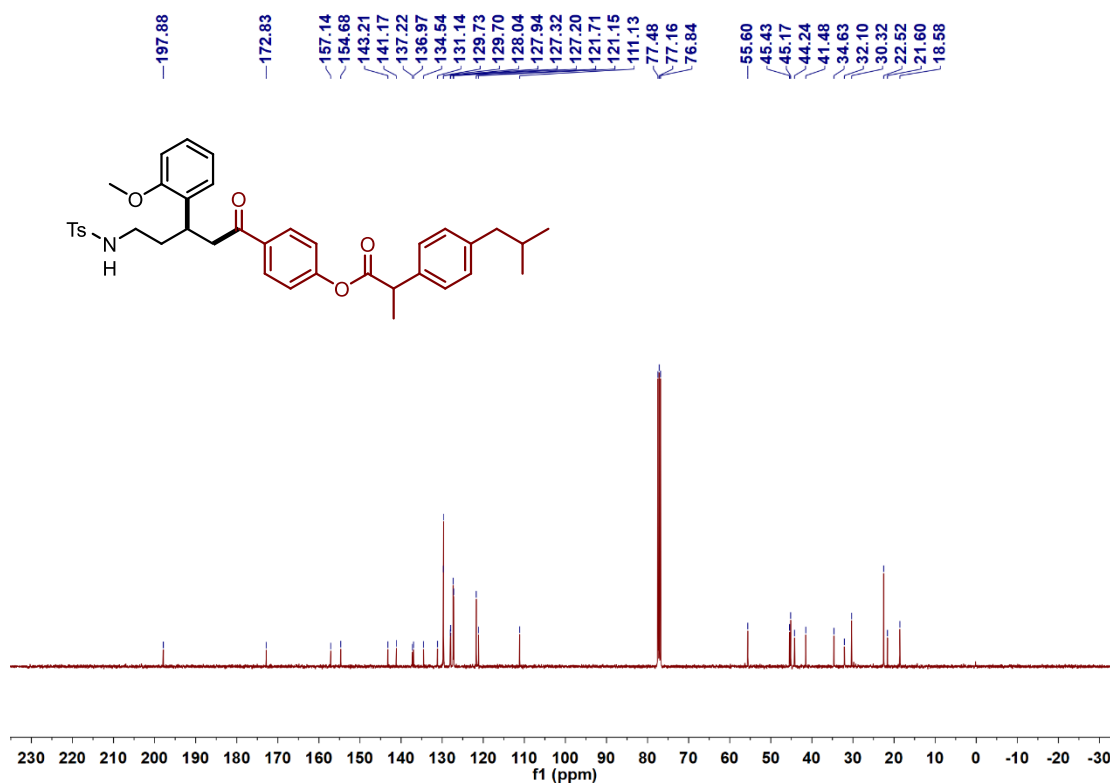
¹³C NMR of Compound **7l** (101 MHz, CDCl₃)



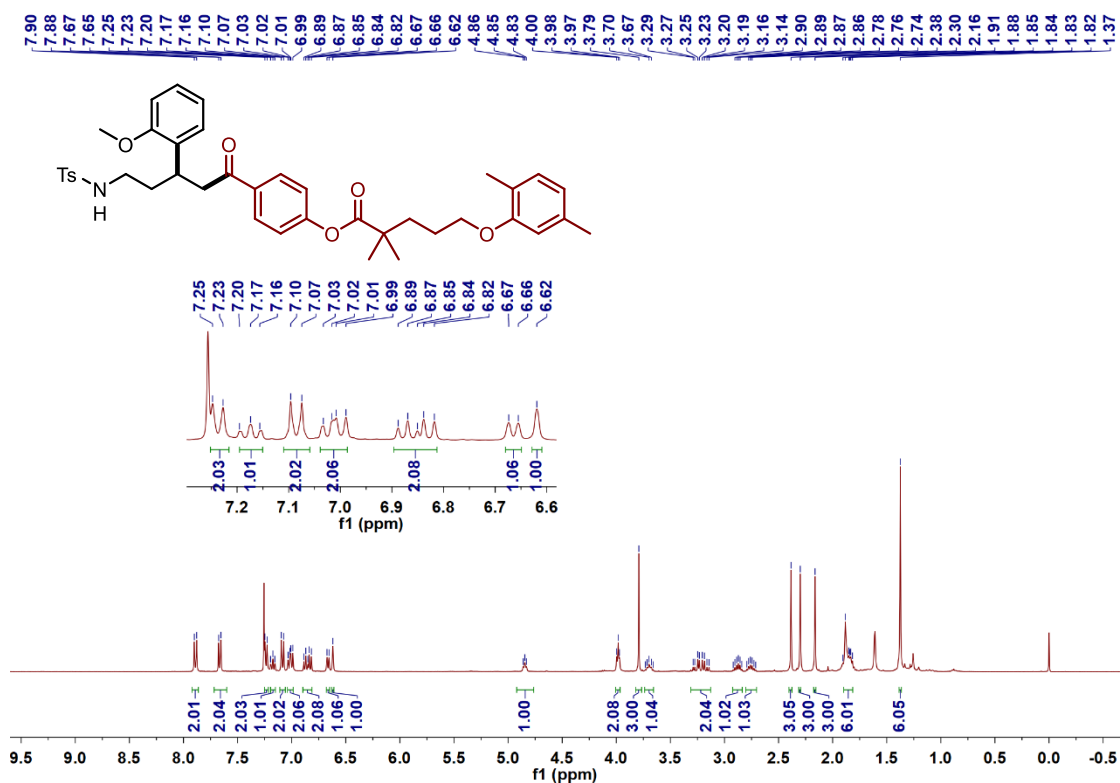
¹H NMR of Compound **7m** (400 MHz, CDCl₃)



¹³C NMR of Compound **7m** (101 MHz, CDCl₃)



¹H NMR of Compound **7n** (400 MHz, CDCl₃)



¹³C NMR of Compound **7n** (101 MHz, CDCl₃)

