Supporting Information

Photoredox Polyfluoroarylation of Alkyl Halides via Halogen-Atom-Transfer

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General Considerations

All reagents and solvents were purchased and used without further purification unless otherwise noted. All reactions were performed under an inert atmosphere unless otherwise stated. Room temperature refers to 26 °C. Moisture-sensitive reactions were performed using flame-dried glassware under an atmosphere of dry argon (Ar). Air- and water sensitive reactions were setup in a Vacuum Atmosphere GENESIS glovebox held under an atmosphere of argon gas (working pressure 2−6 mbar).

Flame-dried equipment was stored in a 130 °C oven before use and either allowed to cool in a cabinet desiccator or assembled hot and allowed to cool under an inert atmosphere. Chromatographic purification of products was accomplished using flash column chromatography Silicycle Silica flash F60 (particle size 40−63 μm, 230−400 mesh). Thin-layer chromatography was performed on EMD Millipore silica gel 60 F254 glass-backed plates (layer thickness 250 μm, particle size 10−12 μm, impregnated with a fluorescent indicator).

Visualization of the developed chromatogram was accomplished by fluorescence quenching under shortwave UV light and/or by staining with phosphomolybdic acid, p-anisaldehyde, or $KMnO_4$ stains.

A Kessil broadband Blue LED lamp (40 W) 440 nm (Model PR160) was used for this light-promoted reaction.

Instrumentation. For NMR spectrometry, NMR spectra were obtained on Bruker spectrometers operating at 400 or 500 MHz for 1 H NMR and 101 or 126 MHz for $^{13}C\{1\ H\}$ NMR. The data were reported in the following order: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant, (Hz), relative integral made in reference to NMR solvent signals.

For mass spectrometry, gas chromatograph−mass spectrometry was obtained using a Hewlett-Packard GC System HP 6890 Series coupled with a HP 5973 Mass Selective Detector. High-resolution mass spectra were obtained using an Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS with electrospray ionization (ESI).

Fluorescence quenching experiments were performed using an Agilent technologies Cary Eclipse Fluorescence Spectrophotometer G9800A, and UV fused quartz cuvettes from Thorlabs.

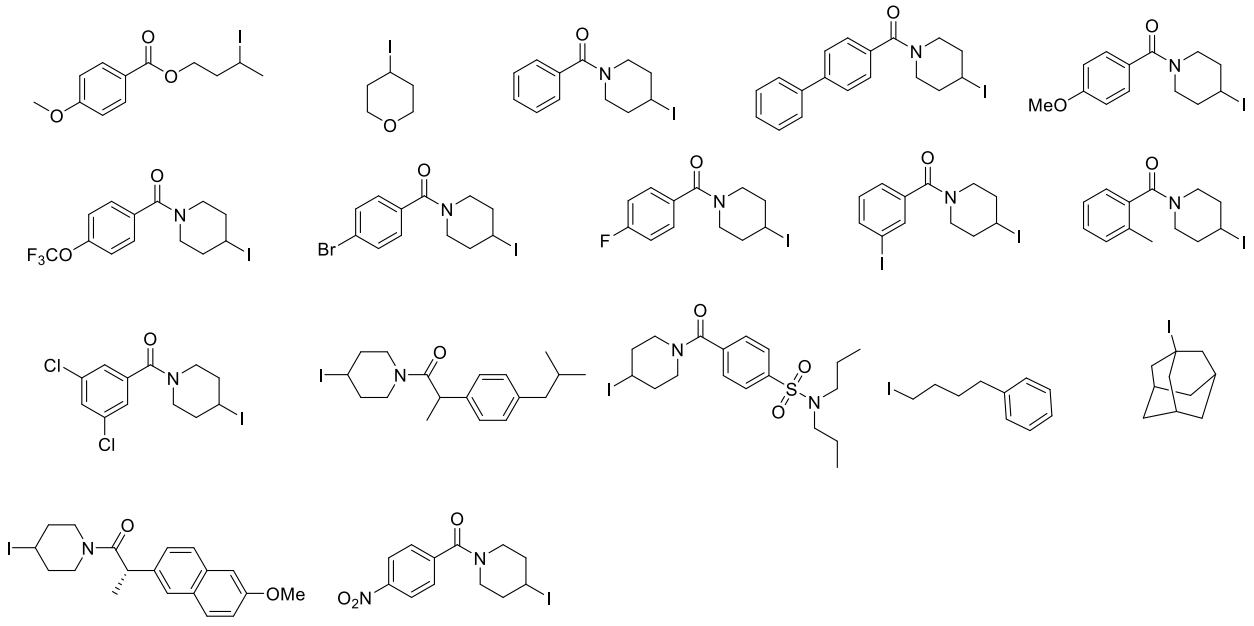
Hydrofluoric Acid Safety. During the reaction small amounts of hydrofluoric acid may be produced. Inhalation of hydrofluoric acid vapors may cause severe throat irritation, cough, dyspnea, cyanosis, lung injury and pulmonary edema resulting in death.

Our reactions were performed using disposable microwave vials (Chemglass, CG-4920-01) to minimize risk of glassware failure.

Materials. General procedure for the synthesis of alkyl iodide derivatives according to the reported procedure.[1-4]

Photocatalyst. 4CzIPN was synthesized according to the reported literature.[10]

Alkyl halides starting materials



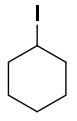
Alcohols	Corresponding iodides	references
3-Hydroxybutyl 4-methoxybenzoate	3-iodobutyl 4-methoxybenzoate	5
tetrahydro-2H-pyran-4-ol	4-iodotetrahydro-2H-pyran	7

(4-hydroxypiperidin-1-yl)(phenyl)methanone	(4-iodopiperidin-1-yl)(phenyl)methanone	4
[1,1'-biphenyl]-4-yl(4-hydroxypiperidin-1-yl)methanone	[1,1'-biphenyl]-4-yl(4-iodopiperidin-1-yl)methanone	4
(4-hydroxypiperidin-1-yl)(4-methoxyphenyl)methanone	(4-iodopiperidin-1-yl)(4-methoxyphenyl)methanone	4
(4-hydroxypiperidin-1-yl)(4-(trifluoromethoxy)phenyl)methanone	(4-iodopiperidin-1-yl)(4-(trifluoromethoxy)phenyl)methanone	3
(4-bromophenyl)(4-hydroxypiperidin-1-yl)methanone	(4-bromophenyl)(4-iodopiperidin-1-yl)methanone	3
(4-fluorophenyl)(4-hydroxypiperidin-1-yl)methanone	(4-fluorophenyl)(4-iodopiperidin-1-yl)methanone	4
(4-hydroxypiperidin-1-yl)(3-iodophenyl)methanone	(3-iodophenyl)(4-iodopiperidin-1-yl)methanone	4
(4-hydroxypiperidin-1-yl)(o-tolyl)methanone	(4-iodopiperidin-1-yl)(o-tolyl)methanone	3
(3,5-dichlorophenyl)(4-hydroxypiperidin-1-yl)methanone	(3,5-dichlorophenyl)(4-iodopiperidin-1-yl)methanone	3
4-phenylbutan-1-ol	(4-iodobutyl)benzene	8
(4-hydroxypiperidin-1-yl)(4-nitrophenyl)methanone	(4-iodopiperidin-1-yl)(4-nitrophenyl)methanone	3

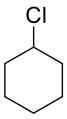
Procedure for Preparation of alkyl iodides

Note: The reactions and the yields to synthesize alkyl iodides are not optimized.

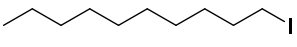
A. Following alkyl halides were purchased from Sigma-Aldrich, Oakwood chemicals and Fisher Chemical.



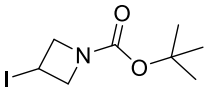
iodocyclohexane



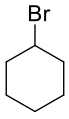
chlorocyclohexane



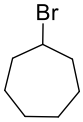
1-iododecane



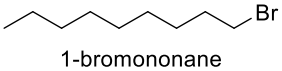
tert-butyl 3-iodoazetidine-1-carboxylate



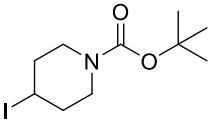
bromocyclohexane



bromocycloheptane

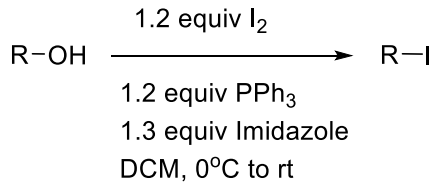


1-bromononane



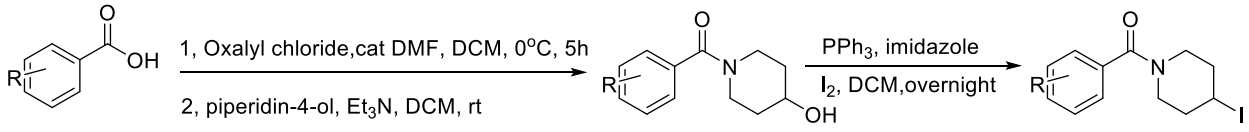
tert-butyl 4-iodopiperidine-1-carboxylate

B: General procedure for the synthesis of alkyl iodides[1]

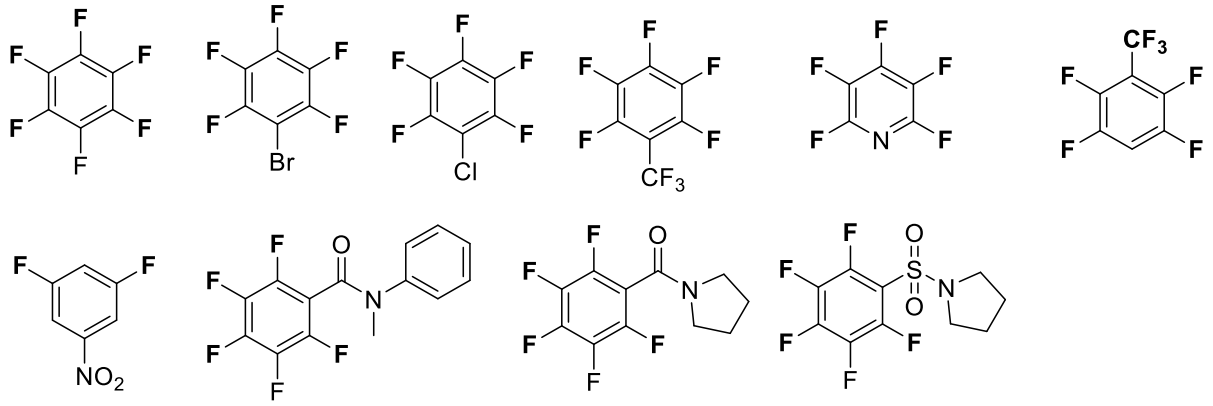


All the iodides were prepared from the corresponding alcohol using the following procedure:
According to general procedure: triphenylphosphine (12 mmol, 3.15g) and imidazole (13 mmol, 885 mg) were added to a 150 mL round bottom flask, followed by DCM (50 mL). The resulting mixture was placed in an ice bath. After 5 minutes of stirring, iodine (12 mmol, 3.04 g) was added in small portions and stirred for 15 minutes. Then the corresponding alcohol (10 mmol) was added dropwise. The reaction mixture was allowed to come to room temperature and stirred overnight at room temperature.
After overnight stirring, a saturated solution of Na_2SO_3 (15 mL) was added. The organic layer was separated, and the aqueous layer was extracted for (3x 15 mL DCM). The combined organic layers were dried with $MgSO_4$, filtered, and the solvent evaporated under reduced pressure. The resulting crude was purified by flash chromatography using hexane and ethyl acetate or through distillation.

C: Preparation of (R-phenyl) (4-I-piperidin-1-yl)methanone[2,3]

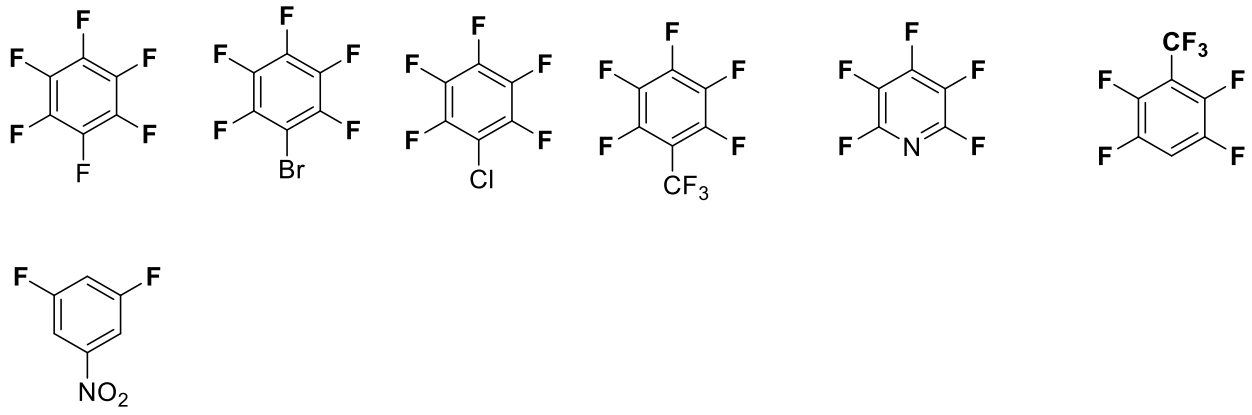


Polyfluoroarenes starting materials[5,6]

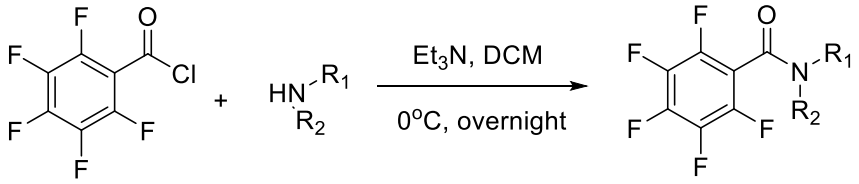


Note: The reactions and the yields to synthesize **Polyfluoroarenes** *are not optimized.*

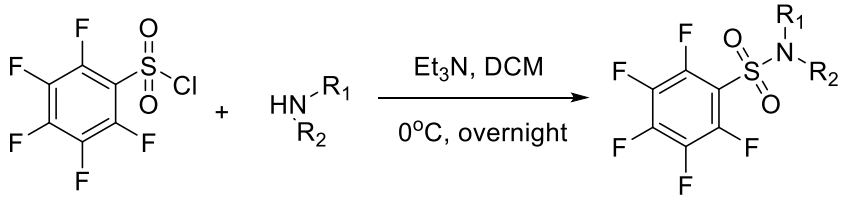
The following polyfuoroarenes were purchased from sigma-aldrich, oakwood chemicals and fisher chemical.



General Procedure for the Synthesis of Polyfluoroarenes.[5,6,11]



Pentafluorobenzoyl chloride (10 mmol) was added to a solution of the commercially available amines (12 mmol) and triethylamine (15.0 mmol, 2.1 mL) in dry DCM (50 mL) at 0 °C. The reaction mixture was then allowed to warm up to room temperature and stirred for 12h. The resulting mixture was quenched with water and then extracted with DCM. The organic layers were dried with $MgSO_4$, filtered and concentrated. The crude mixture was purified through column chromatography on silica gel using hexanes and ethyl acetate as eluents.



Pentafluoro sulfonyl chloride (10 mmol) was added to a solution of the commercially available amines (12 mmol) and triethylamine (15.0 mmol, 2.1 mL) in dry DCM (50 mL) at 0 °C. The reaction mixture was then allowed to warm up to room temperature and stirred for 12h. The resulting mixture was quenched with water and then extracted with DCM. The organic layers were dried with $MgSO_4$, filtered and concentrated. The crude mixture was purified through column chromatography on silica gel using hexanes and ethyl acetate as eluents.

Full Tables for Reaction Optimization

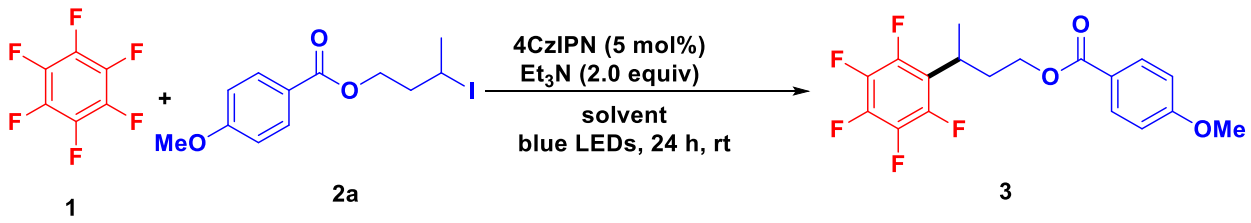
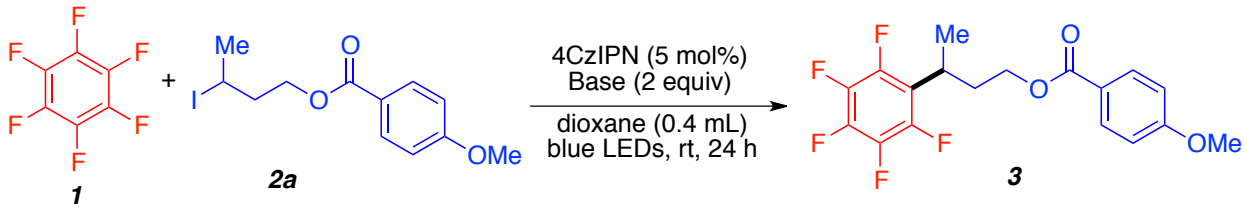


Table S1. Screening of the type and volume of solvents

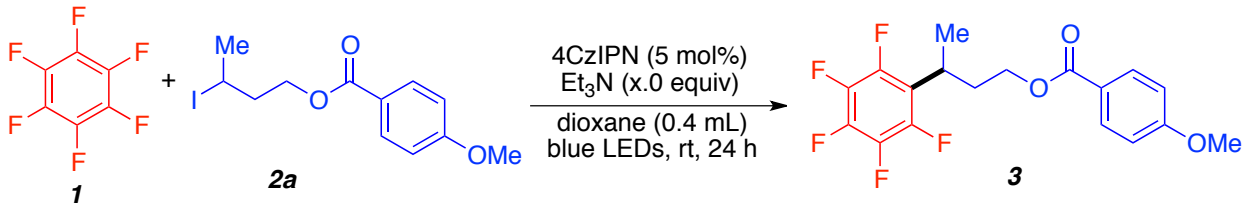
Entry	Solvent	Volume (mL)	Yield %
1	MeCN	1 mL	24%
2	DMF	1 mL	14%
3	DCM	1 mL	trace
4	1,4-dioxane	1 mL	26%
5	EtOAc	1 mL	14%
6	DMSO	1 mL	22%
7	1,4-Dioxane	0.5 mL	44%
8	DMSO	0.5 mL	40%
9	1,4-Dioxane	0.4 mL	46%
10	DMSO	0.4 mL	42%

Reaction conditions: 0.6 mmol hexafluorobenzene (**1**) , 0.2 mmol 3-iodobutyl 4-methoxybenzoate (**2a**) and other additives in the given solvent. Reaction under 440 nm Blue LED for 24 h.



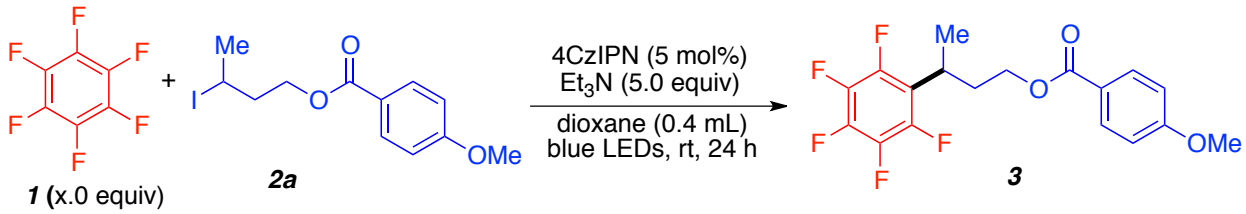
Entry	Base 2.0 equiv	Yield/%
1	Et_3N	46%
2	DIPEA	34%
3	DABCO	0%
4	1,2,2,6,6-Pentamethylpiperidine	28%

Reaction conditions: 0.6 mmol hexafluorobenzene (**1**), 0.2 mmol 3-iodobutyl 4-methoxybenzoate (**2a**) and 4CzIPN (5 mol%), in 1,4-dioxane (0.4 mL). Reaction under 440 nm Blue LED for 24 h.



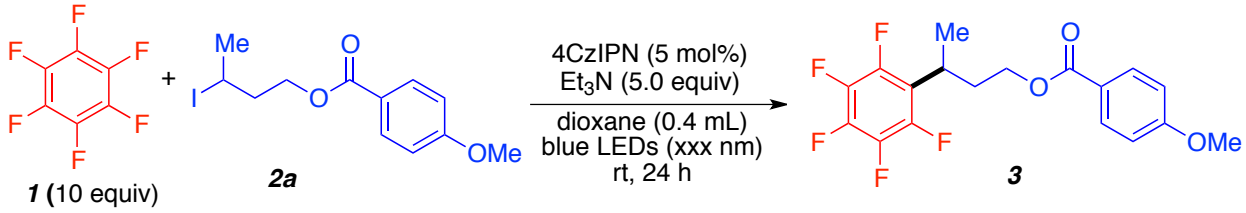
Entry	Amount of base (equiv)	Yield %
1	2	46%
2	3	48%
3	5	50%

Reaction conditions: 0.6 mmol hexafluorobenzene (**1**), 0.2 mmol 3-iodobutyl 4-methoxybenzoate (**2a**) and 4CzIPN (5 mol%), in 1,4-dioxane (0.4 mL). Reaction under 440 nm Blue LED for 24 h.



Entry	hexafluorobenzene (equiv)	Yield %
1	3	50%
2	5	55%
3	10	62 %(60%)

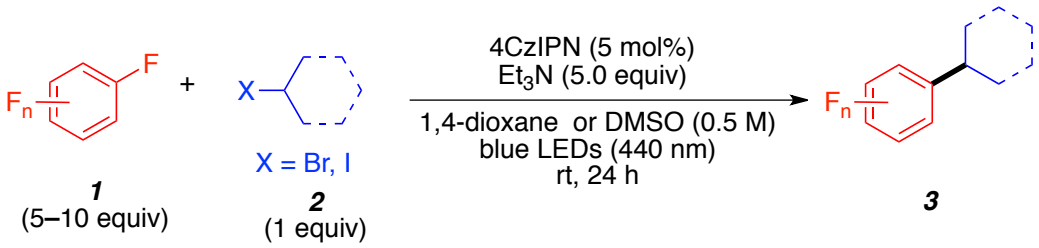
Reaction conditions: 1.0 mmol Et_3N, 4CzIPN (5mol%), 0.6 mmol hexafluorobenzene (**1**), 0.2 mmol 3-iodobutyl 4-methoxybenzoate (**2a**), in 1,4-dioxane (0.4 mL). Reaction under 440 nm Blue LED for 24 h.



Entry	LED wavelength range	Yield/%
1	427 nm	38%
2	390 nm	28%
3	440 nm	62%

Reaction conditions: 1.0 mmol Et_3N, 4CzIPN (5mol%), (2.0 mmol, 10 equiv) hexafluorobenzene (**1**), 0.2 mmol 3-iodobutyl 4-methoxybenzoate (**2a**) and 4CzIPN (5 mol%), in 1,4-dioxane (0.4 mL). Reaction under different Blue LED wavelengths for 24 h.

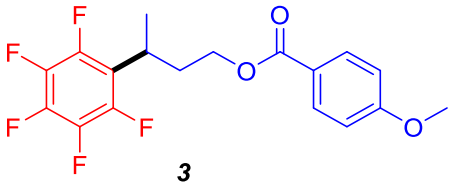
General Reaction Procedure and Characterizations Data.



General standard reaction procedure:

4CzIPN (7.88 mg, 0.01mol, 5 mol %) alkyl iodide (0.2 mmol, 1 equiv.), Et_3N (101 mg, 1 mmol, 5.0 equiv.), polyfluorobenzene (1-2 mmol, 5-10 equiv.), and dry 1,4-dioxane or DMSO (0.4 mL, c = 0.5 M) were mixed in a 10 mL microwave vial equipped with a stir bar under argon atmosphere. The vial was sealed with a septum-cap and placed 2 cm away from a 440 nm blue LED (40W). The temperature was kept at approximately 35 °C through cooling with a fan (heating caused by LED lamp). After being stirred for 24 hours, the reaction mixture was poured into 20 mL of water, and the resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic phase was dried over $MgSO_4$, filtered through celite, and concentrated under vacuum. The residue was further purified by flash column chromatography on silica gel.

3-(perfluorophenyl)butyl 4-methoxybenzoate, (3)



3

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv). After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/hexane=1/50 to 20/1 as a colourless solid. (44.8 mg, 60% yield)

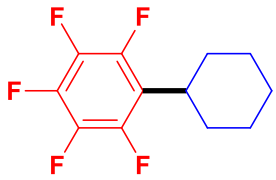
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.80 (m, 2H), 6.98- 6.82 (m, 2H), 4.39- 4.28 (m, 1H), 4.15 (ddt, *J* = 9.7, 7.1, 4.8 Hz, 1H), 3.86 (s, 3H), 3.47 (dp, *J* = 9.2, 7.0 Hz, 1H), 2.30- 2.09 (m, 2H), 1.41 (d, *J* = 7.1 Hz, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.9 (dd, *J* = 22.4, 8.0 Hz), -157.5 (d, *J* = 21.0 Hz), -157.5, -162.4 (td, *J* = 22.2, 8.0 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 163.5, 150.7(m), 146.5(m),143.1(m), 141.0(m),138.9(m),132.2, 131.5, 122.4, 113.6, 62.7, 55.4, 34.0, 27.5, 19.6.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for C18H15F5O3Na 397.0839, found 397.0844;

1-cyclohexyl-2,3,4,5,6-pentafluorobenzene, (4)

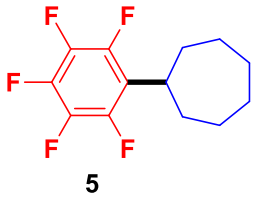


4

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv). This product was directly purified by flash column chromatography on silica gel, eluting with pentane to get colorless solid 34 mg, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (tt, *J* = 11.3, 4.7 Hz, 1H), 1.98-1.61 (m, 7H), 1.46- 1.15 (m, 3H).
^{19}F NMR (376 MHz, $CDCl_3$) -143.1 (dd, *J* = 22.3, 7.7 Hz), -158.7 (t, *J* = 21.0 Hz), -163.0, -163.2 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4(m), 143.9(m), 140.6(m),138.8(m), 138.1(m), 136.4(m),119.8, 35.3, 35.3, 31.0, 31.0, 31.0, 26.7, 25.6.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{12}H_{11}F_5Na$ 273.0679, found 273.0691;

(perfluorophenyl)cycloheptane, (5)

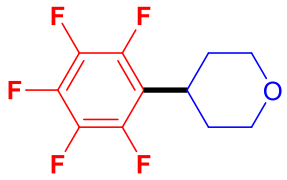


5

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv). This product was directly purified by flash column chromatography on silica gel, eluting with pentane to get colorless solid 34.3 mg, 65% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 3.12 (tt, *J* = 10.7, 3.3 Hz, 1H), 1.99- 1.76 (m, 6H), 1.75-1.54 (m, 6H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -143.1 (dd, *J* = 22.6, 7.7 Hz), -159.1 (t, *J* = 20.8 Hz), -163.0 – -163.2 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9(m), 143.5(m), 140.5(m), 138.9(m), 138.0(m), 136.4(m), 121.6(m), 36.9, 33.7, 27.9
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{13}H_{13}F_5$ 265.1016, found 265.1020;

4-(perfluorophenyl)tetrahydro-2H-pyran, (6)

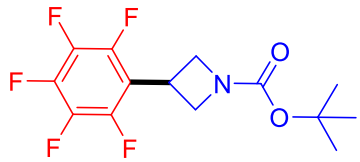


6

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
This product was directly purified by flash column chromatography on silica gel, eluting with ethyl acetate/hexane=1/60 to 30/1 to get colorless solid 35.3 mg, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06 (dd, *J* = 11.7, 4.5 Hz, 2H), 3.49 (td, *J* = 12.0, 2.0 Hz, 2H), 3.23 (tt, *J* = 12.5, 3.8 Hz, 1H), 2.17 (tddd, *J* = 12.3, 10.7, 4.6, 1.6 Hz, 2H), 1.66- 1.50 (m, 2H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -143.0 (dd, *J* = 22.1, 7.8 Hz), -157.2, -157.3, -157.4, -162.3 - 162.5 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7(m), 144.1(m), 139.0(m), 138.6(m), 136.5(m), 117.9(m), 68.4, 32.6, 30.8(m).
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{11}H_9F_5ONa$ 275.0471, found 275.0472;

tert-butyl 3-(perfluorophenyl)azetidine-1-carboxylate, (7)

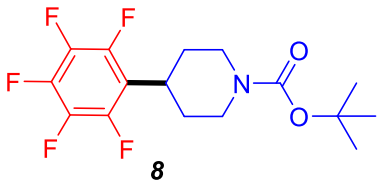


7

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (32 mg, 50% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (t, *J* = 8.7 Hz, 2H), 4.19 (dd, *J* = 8.5, 7.0 Hz, 2H), 4.08 (tt, *J* = 8.9, 6.5 Hz, 1H), 1.46 (s, 9H).
^{19}F NMR (376 MHz, $CDCl_3$) δ δ -142.8(m), -142.9 (m), -155.5(m), -155.5(m), -155.6(m), -161.8(m), -162.0 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2(m), 146.6(m), 144.1(m), 141.6(m), 139.0(m), 136.4, 114.2, 80.0, 29.70, 28.36, 24.10.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{14}H_{14}F_5NO_2Na$ 346.0843, found 346.0850;

tert-butyl 4-(perfluorophenyl)piperidine-1-carboxylate, (8)

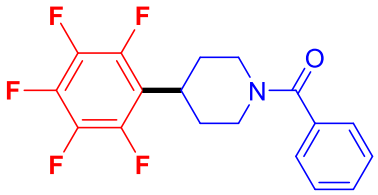


8

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (56 mg, 80% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (s, 2H), 3.11 (tt, *J* = 12.5, 3.7 Hz, 1H), 2.85-2.67 (m, 2H), 2.11-1.85 (m, 2H), 1.82-1.55 (m, 3H), 1.47 (s, 9H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.83 (dd, *J* = 22.2, 7.8 Hz), -157.28 (t, *J* = 20.9 Hz), -162.18 – -162.58 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 146.7, 143.9, 142.7, 141.0, 138.2, 136.4, 79.71, 33.53, 29.88, 28.40.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{16}H_{18}F5NO_2Na$ 374.1156, found 374.1160;

(4-(perfluorophenyl)piperidin-1-yl)(phenyl)methanone,(9)

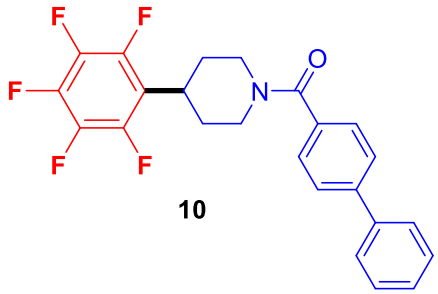


9

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv). After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (46 mg, 65% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 5H), 4.90 (s, 1H), 3.79 (d, *J* = 83.6 Hz, 1H), 3.25 (tt, *J* = 12.5, 3.7 Hz, 1H), 2.96 (d, *J* = 91.8 Hz, 2H), 2.02 (s, 2H), 1.89- 1.50 (m, 2H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.64 – -142.77 (m), -156.68, -156.73, -156.79, -161.96 – -162.15 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 146.0, 143.6, 138.6, 136.1, 135.7, 129.4, 128.2, 126.5, 117.0, 116.9, 33.2, 33.2.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{18}H_{14}F_5NONa$ 378.0893, found 378.0894;

[1,1'-biphenyl]-4-yl(4-(perfluorophenyl)piperidin-1-yl)methanone,(10)

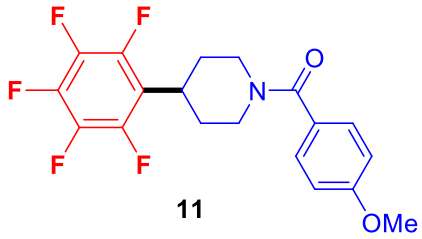


10

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (73 mg, 85% yield)

^{1}H NMR (400 MHz, Chloroform-d) δ 7.60-7.56 (m, 2H), 7.55-7.51 (m, 2H), 7.46- 7.43 (m, 2H), 7.42- 7.37 (m, 2H), 7.33- 7.28 (m, 1H), 4.85 (s, 1H), 3.94 (s, 1H), 3.21 (tt, *J* = 12.5, 3.7 Hz, 1H), 2.93 (d, *J* = 96.7 Hz, 2H), 2.01 (s, 2H), 1.73 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.36, 142.70, 140.27, 134.67, 128.92, 127.82, 127.49, 127.28, 127.17, 48.9, 43.3, 33.58, 29.7.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -142.65 (dd, *J* = 22.3, 7.9 Hz), -156.55 (t, *J* = 21.0 Hz), -161.90 (td, *J* = 21.9, 7.8 Hz).
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{24}H_{18}F_5NONa$ 454.1206, found 454.1210;

(4-methoxyphenyl)(4-(perfluorophenyl)piperidin-1-yl)methanone, (11)

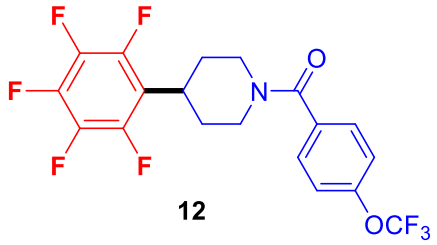


11

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (63 mg, 82% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 – 7.34 (m, 2H), 7.01 – 6.81 (m, 2H), 5.26 – 4.12 (m, 2H), 3.83 (s, 3H), 3.25 (tt, *J* = 12.5, 3.7 Hz, 1H), 2.96 (s, 2H), 2.05 (d, *J* = 14.6 Hz, 2H), 1.87 (s, 2H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.7 (dd, *J* = 22.3, 7.8 Hz), -156.7, -156.7, -156.8, -162.0 (td, *J* = 22.0, 7.7 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 160.8, 146.4, 136.4, 129.0, 128.0, 117.3, 113.798, 55.4, 33.6, 22.6.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{16}F_5O_2NNa$ 408.0999, found 408.1006;

(4-(perfluorophenyl)piperidin-1-yl)(4-(trifluoromethoxy)phenyl)methanone,(12)

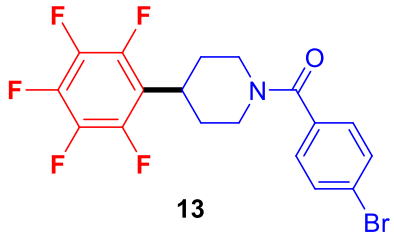


12

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (57 mg, 65% yield).

^{1}H NMR (400 MHz, Chloroform-d δ 7.57 – 7.31 (m, 2H), 7.27 – 7.08 (m, 2H), 4.81 (s, 1H), 3.96 – 3.61 (m, 1H), 3.20 (tt, *J* = 12.5, 3.7 Hz, 1H), 3.09 – 2.63 (m, 2H), 1.85 (d, *J* = 95.2 Hz, 4H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8, -142.7 (dd, *J* = 22.1, 7.9 Hz), -156.3, -156.4, -156.5, -161.7 – -162.0 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 150.1, 150.1, 134.5, 128.8, 121.7, 121.0, 121.0, 119.1, 119.1, 117.0, 117.0, 48.3, 33.5, 29.7.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{13}O_2NF_8Na$ 462.0716, found 462.0724;

(4-bromophenyl)(4-(perfluorophenyl)piperidin-1-yl)methanone,(13)

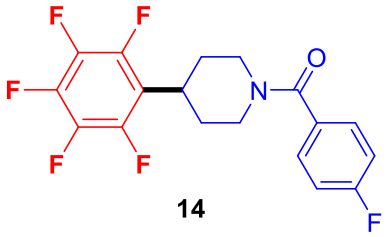


13

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (60 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 2H), 7.38 – 7.28 (m, 2H), 4.87 (s, 1H), 3.86 (s, 1H), 3.26 (tt, *J* = 12.5, 3.7 Hz, 1H), 2.97 (d, *J* = 88.0 Hz, 2H), 1.91 (d, *J* = 100.7 Hz, 4H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.6 – -142.8 (m), -156.4, -156.4, -156.5, -161.8 – -162.0 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 146.3, 144.0, 141.2, 139.0, 136.5, 134.7, 131.8, 128.6, 124.1, 117.1, 48.2, 33.5, 29.7.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{18}H_{13}OBrNF5Na$ 455.9999, found 456.0002;

(4-fluorophenyl)(4-(perfluorophenyl)piperidin-1-yl)methanone,(14)

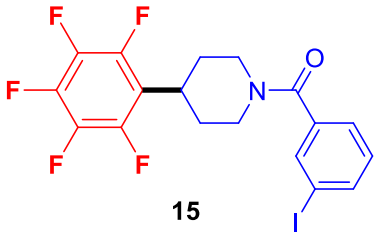


14

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv). After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (56 mg, 75% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.57-7.37 (m, 2H), 4.86 (s, 1H), 3.92 (s, 1H), 3.26 (tt, *J* = 12.5, 3.7 Hz, 1H), 2.95 (s, 2H), 2.16- 1.66 (m, 4H).
^{19}F NMR (400 MHz, $CDCl_3$) δ -110.2 – -110.3 (m), -142.6 – -142.8 (m), -156.4, -156.5, -156.5, -161.8 – -162.0 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 163.7, 161.2, 145.4, 143.0, 139.7, 138.7, 137.8, 130.9, 130.9, 128.2, 128.2, 116.1, 114.7, 114.5, 46.8, 32.5, 28.7.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{18}H_{13}ONF_6Na$ 396.0799, found 396.0812.

(3-iodophenyl)(4-(perfluorophenyl)piperidin-1-yl)methanone.(15)

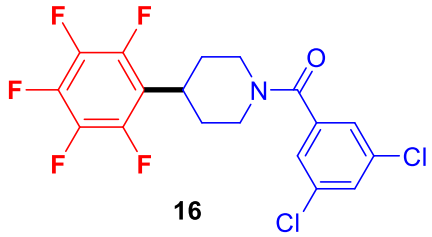


15

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (52 mg, 55% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.77 (dd, *J* = 7.5, 1.2 Hz, 2H), 7.39 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 4.87 (s, 1H), 3.85 (s, 1H), 3.26 (tt, *J* = 12.5, 3.7 Hz, 1H), 2.97 (d, *J* = 107.4 Hz, 2H), 1.89 (d, *J* = 116.7 Hz, 4H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.59 – -142.73 (m), -156.38, -156.43, -156.49, -161.84 (td, *J* = 22.0, 7.7 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 146.5, 144.0, 141.2, 140.6, 138.7, 138.0, 135.7, 130.2, 126.0, 94.3, 33.5, 29.7.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{18}H_{13}ONIF_5Na$ 503.9860, found 503.9872;

(3,5-dichlorophenyl)(4-(perfluorophenyl)piperidin-1-yl)methanone,(16)

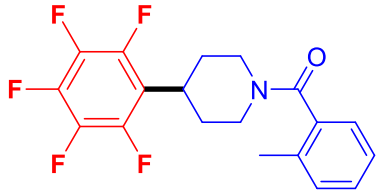


16

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (63 mg, 75% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.37-7.11 (m, 3H), 4.79 (s, 1H), 3.89-3.56 (m, 1H), 3.20 (tt, *J* = 12.5, 3.8 Hz, 1H), 2.92 (d, *J* = 120.9 Hz, 2H), 2.06-1.59 (m, 4H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.6 – -142.7 (m), -156.2, -156.3, -156.3, -161.7 – -161.8 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 145.9, 144.0, 141.4, 139.8, 138.7, 135.5, 129.8, 125.4, 116.9, 116.9, 48.5, 33.40, 29.7
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{18}H_{12}OF_5NNa$ 446.0114, found 446.0120;

(4-(perfluorophenyl)piperidin-1-yl)(o-tolyl)methanone.(17)

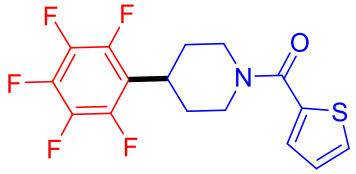


17

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (47 mg, 65% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.25 (dt, *J* = 13.2, 8.1 Hz, 4H), 5.02 (d, *J* = 12.4 Hz, 1H), 3.62 (t, *J* = 12.2 Hz, 1H), 3.26 (tt, *J* = 12.4, 3.6 Hz, 1H), 3.07 (td, *J* = 13.2, 2.9 Hz, 1H), 2.83 (td, *J* = 13.0, 3.0 Hz, 1H), 2.35 (d, *J* = 44.7 Hz, 3H), 2.18- 1.67 (m, 4H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.8 (ddd, *J* = 42.3, 22.3, 7.8 Hz), -156.6 (t, *J* = 21.0 Hz), -162.0 (td, *J* = 21.9, 7.5 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 143.9, 138.9, 136.2, 134.4, 134.0, 130.6, 130.4, 128.9, 126.1, 125.9, 125.6, 117.2, 117.0, 47.7, 47.1, 42.1, 33.5, 29.7.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{16}F_5ONNa$ 392.1050, found 392.1055.

(4-(perfluorophenyl)piperidin-1-yl)(thiophen-2-yl)methanone,(18)



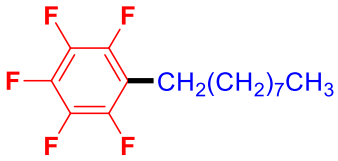
18

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv). After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (39 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.32 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.06 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.62 (s, 2H), 3.28 (tt, *J* = 12.5, 3.7 Hz, 1H), 3.03 (s, 2H), 2.20-2.02 (m, 2H), 1.93-1.74 (m, 2H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.65 (dd, *J* = 22.3, 7.9 Hz), -156.51, -156.57, -156.62, -161.82 – -162.02 (m), -162.42.
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 146.0, 145.2, 143.1, 142.5, 140.2, 138.0, 136.1, 127.7, 127.6, 125.7, 116.1, 44.8, 32.6, 28.7.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{16}H_{12}ONF_5SNa$ 384.0457, found 384.0458;

1,2,3,4,5-pentafluoro-6-nonylbenzene,(19)

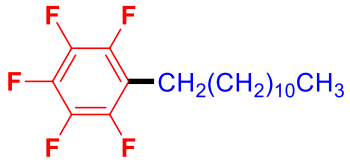


19

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (11.7 mg, 20% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73-2.65 (m, 2H), 1.59 (d, *J* = 7.9 Hz, 2H), 1.34-1.27 (m, 12H), 0.89 (s, 3H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -144.5 – -144.6 (m), -158.5, -158.5, -158.5, -158.6, -163.2 – -163.3 (m), -163.3.
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 144.2, 143.2, 140.2, 139.8, 138.7, 31.8, 29.7, 29.5, 29.5, 29.3, 29.2, 29.1, 22.7.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{15}H_{19}F_5Na$ 317.1305, found 317.1295.

1-dodecyl-2,3,4,5,6-pentafluorobenzene,(20)

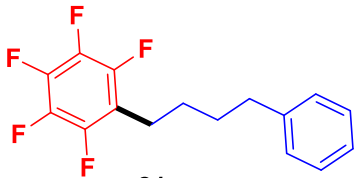


20

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (13.7 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71- 2.60 (m, 2H), 1.54 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.24 (s, 18H), 0.86 (t, *J* = 6.8 Hz, 3H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -144.48 – -144.60 (m), -158.48, -158.54, -158.59, -163.17 – -163.35 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 143.8, 141.2, 138.8, 138.5, 136.2, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 22.7, 14.1.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{18}H_{25}F_5Na$ 359.1774, found 359.1800.

1,2,3,4,5-pentafluoro-6-(4-phenylbutyl)benzene,(21)

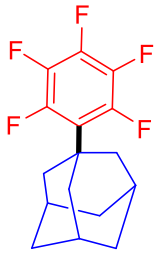


21

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (18 mg, 30% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.26 (m, 2H), 7.26 – 7.15 (m, 3H), 6.58 – 6.36 (m, 2H), 6.13 (d, *J* = 9.7 Hz, 1H), 4.26 – 4.05 (m, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 1.78 (dq, *J* = 6.9, 2.3, 1.5 Hz, 4H).
^{13}C NMR (400 MHz, $CDCl_3$) δ 141.54, 132.57, 130.01, 128.44, 128.41, 126.01, 70.75, 35.18, 28.50, 27.18.
^{19}F NMR (400 MHz, $CDCl_3$) δ -103.67.
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd. for $C_{16}H_{13}F_5$ 301.1016, found 301.1024,.

(3R,5R,7R)-1-(perfluorophenyl)adamantane,(22)

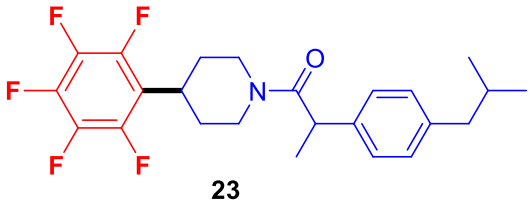


22

Reaction done in DMSO as solvent, using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with hexane as a colourless solid. (18 mg, 30% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 2.31- 2.17 (m, 6H), 2.07 (p, *J* = 3.3 Hz, 3H), 1.86- 1.71 (m, 6H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -138.07 (td, *J* = 4.0, 2.1 Hz), -138.13 (td, *J* = 4.0, 2.0 Hz), -158.43 (d, *J* = 2.6 Hz), -158.49 (t, *J* = 2.2 Hz), -158.55, -162.92 – -163.03 (m), -163.04 – -163.09 (m).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 145.2, 140.7, 139.4, 138.6, 137.3, 122.5, 122.4, 41.3 (t, *J* = 5.3 Hz), 40.7- 40.5 (m), 36.6, 28.9
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{16}H_{15}F_5Na$ 325.0992, found 325.0998.

2-(4-isobutylphenyl)-1-(4-(perfluorophenyl)piperidin-1-yl)propan-1-one,(23)

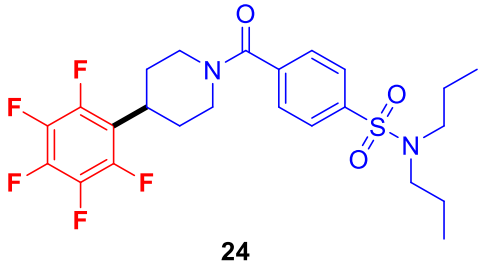


23

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (74 mg, 85% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.22-7.02 (m, 4H), 4.94-4.80 (m, 1H), 4.06-3.95 (m, 1H), 3.87 (dq, *J* = 13.5, 6.8 Hz, 1H), 3.19-2.88 (m, 2H), 2.79-2.63 (m, 1H), 2.56 (td, *J* = 12.9, 2.7 Hz, 1H), 2.43 (dd, *J* = 7.2, 3.1 Hz, 2H), 2.02-1.91 (m, 1H), 1.91-1.70 (m, 2H), 1.70-1.59 (m, 1H), 1.44 (d, *J* = 6.6 Hz, 3H), 1.29-1.19 (m, 1H), 1.02 (t, *J* = 7.1 Hz, 1H), 0.95-0.68 (m, 7H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.6 – -142.7 (m), -142.8 (dd, *J* = 22.0, 7.8 Hz), -156.6 (t, *J* = 20.9 Hz), -156.9 (t, *J* = 20.9 Hz), -157.2 (t, *J* = 20.8 Hz), -162.1 (td, *J* = 21.8, 7.8 Hz), -162.5 (td, *J* = 21.8, 7.8 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 140.3, 139.5, 129.8, 129.6, 127.0, 126.9, 117.3, 46.1, 45.0, 43.4, 43.2, 42.8, 42.6, 33.6, 33.3, 30.4, 30.2, 29.9, 29.3, 29.1, 22.4, 22.1, 20.7, 12.8.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{24}H_{26}ONF_5Na$ 462.1832, found 462.1833.

4-(4-(perfluorophenyl)piperidine-1-carbonyl)-N,N-dipropylbenzenesulfonamide,(24)

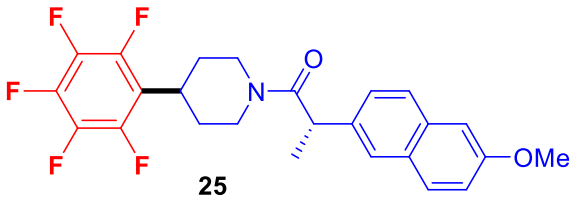


24

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (92 mg, 89% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.90 – 7.77 (m, 2H), 7.62 – 7.46 (m, 2H), 4.89 (s, 1H), 3.74 (s, 1H), 3.27 (tt, *J* = 12.6, 3.8 Hz, 1H), 3.21 – 2.75 (m, 6H), 2.18 – 1.64 (m, 4H), 1.56 (h, *J* = 7.4 Hz, 4H), 0.87 (t, *J* = 7.4 Hz, 7H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -142.64 – -142.78 (m), -156.35 (t, *J* = 20.9 Hz), -161.81 (td, *J* = 21.9, 7.8 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84, 146.33, 143.90, 141.45, 139.70, 127.44, 127.40, 116.93, 50.14, 48.15, 42.80, 33.38, 30.43, 29.69, 22.08, 11.15.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{24}H_{27}F_5SN_2O_3Na$ 541.1560, found 541.1561

(S)-2-(6-methoxynaphthalen-2-yl)-1-(4-(perfluorophenyl)piperidin-1-yl)propan-1-one,(25)

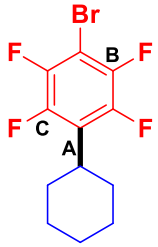


25

Reaction done in DMSO as solvent, using hexafluorobenzene (2.0 mmol, 10 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with ethyl acetate/DCM=1/50 to 20/1 as a colourless solid. (46 mg, 50% yield).

^{1}H NMR (400 MHz, Chloroform-d δ 7.80-7.55 (m, 3H), 7.36 (dt, *J* = 8.9, 3.1 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.5 Hz, 2H), 4.92 (t, *J* = 14.3 Hz, 1H), 4.06 (ddd, *J* = 27.2, 11.7, 6.4 Hz, 2H), 3.91 (s, 3H), 3.11- 2.99 (m, 1H), 2.62 (dq, *J* = 28.0, 14.4, 13.8 Hz, 1H), 2.03-1.62 (m, 3H), 1.53 (dd, *J* = 10.7, 6.8 Hz, 3H), 1.32-1.15 (m, 2H), 1.02-0.79 (m, 1H).
^{19}F NMR (101 MHz, $CDCl_3$) δ -142.78 (dd, *J* = 22.4, 7.8 Hz), -156.76 (t, *J* = 20.9 Hz), -157.12 (t, *J* = 21.0 Hz), -162.03 (td, *J* = 21.9, 7.7 Hz), -162.32 (td, *J* = 21.6, 7.7 Hz).
^{13}C NMR (376 MHz, $CDCl_3$) δ 157.63, 133.47, 129.15, 127.73, 127.59, 126.07, 125.90, 125.49, 125.41, 119.07, 105.65, 55.32, 46.04, 43.64, 43.23, 42.81, 42.70, 33.53, 33.22, 30.44, 29.88, 29.42, 20.96, 20.82.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{25}H_{22}O_2NF5Na$ 486.1468, found 486.1469.

1-bromo-4-cyclohexyl-2,3,5,6-tetrafluorobenzene,(26)



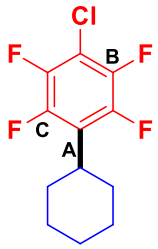
26

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv). After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (43 mg, 70% yield).

A:B:C=23:10:17

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.25 – 2.88 (m, 1H), 1.99 – 1.75 (m, 6H), 1.43 – 1.28 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.4, 146.1, 144.0, 143.6, 124.7, 124.5, 120.1, 103.2, 96.7, 39.6, 35.8, 35.6, 30.9, 30.8, 30.7, 30.7, 30.2, 29.7, 26.9, 26.8, 26.8, 26.7, 25.7, 25.7, 25.6, 25.2.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.05 (d, *J* = 9.1 Hz), -126.86 (dd, *J* = 22.4, 8.6 Hz), -129.39 (ddd, *J* = 21.8, 4.8, 2.1 Hz), -132.00 – -132.16 (m), -134.46 – -134.62 (m), -136.07 (dd, *J* = 21.7, 4.7 Hz), -139.39 – -139.51 (m), -140.07 (ddd, *J* = 21.9, 12.5, 9.7 Hz), -141.43 – -141.59 (m), -143.56 (ddd, *J* = 20.8, 12.3, 7.4 Hz), -153.88 (t, *J* = 20.8 Hz), -156.43 (t, *J* = 20.3 Hz), -157.17 (ddd, *J* = 22.2, 20.0, 2.3 Hz), -159.81 – -160.03 (m), -162.33 (td, *J* = 21.7, 9.3 Hz).
HRMS (ESI-TOF) m/z: $[M + Na]^{+}$ calcd. for $C_{12}H_{11}BrF_4Na$ 332.9878, found 332.9888.

1-chloro-4-cyclohexyl-2,3,5,6-tetrafluorobenzene,(27)



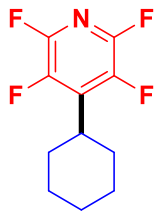
27

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (45 mg, 85% yield).
A:B:C=21:14:15

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.24 – 2.93 (m, 1H), 1.96 – 1.64 (m, 7H), 1.35 (td, *J* = 13.5, 12.5, 7.3 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.4,152.9, 150.9, 149.4, 148.0, 147.2, 146.4, 145.3, 144.7, 143.9, 142.9,147.8, 129.1,128.9, 123.8,123.6, 35.7, 35.5, 30.9, 30.9, 30.8, 30.8, 30. 8, 30.2, 30.2, 29.7, 26.8, 26.8, 26.7, 25.7, 25.7, 25.6, 14.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.2 (d, *J* = 8.9 Hz), -136.8 (dd, *J* = 21.1, 9.0 Hz), -137.3 (d, *J* = 21.6 Hz), -140.2 (dd, *J* = 20.7, 8.8 Hz), -142.0 – -142.3 (m), -157.5 – -157.9 (m), -162.8 (tdd, *J* = 21.4, 9.0, 3.0 Hz).
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{12}H_{11}ClF_4Na$ 289.0383, found 289.0388.

4-cyclohexyl-2,3,5,6-tetrafluoropyridine,(28)

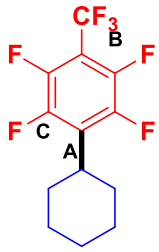


28

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv). After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (28 mg, 60% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.78 – 2.56 (m, 1H), 1.56 (dd, *J* = 14.7, 7.3 Hz, 1H), 1.26 (s, 10H), 0.88 (t, *J* = 6.8 Hz, 2H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -144.5 – -144.6 (m), -158.5, -158.6 (d, *J* = 21.0 Hz), -163.2 – -163.4 (m).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.7,146.3, 143.8, 143.1, 141.2, 138.8, 136.2, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 29.1, 22.7, 22.3, 14.1.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{11}H_{11}NF_4Na$ 256.0725, found 256.0730.

1-cyclohexyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene,(29)



29

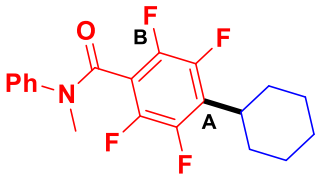
Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (51 mg, 85% yield).

Colourless liquid: 85% yield.

A:B:C=27:5:18

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.04 (dtt, *J* = 28.1, 11.9, 4.3 Hz, 1H), 2.02 – 1.66 (m, 7H), 1.36 (ddt, *J* = 21.8, 13.0, 4.7 Hz, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -53.3, -53.4, -56.0 – -56.4 (m), -118.0 – -118.1 (m), -128.3 (dt, *J* = 21.6, 7.7 Hz), -135.6, -137.0 – -137.3 (m), -141.2 (td, *J* = 15.8, 6.5 Hz), -141.5 – -141.8 (m), -149.4 (td, *J* = 20.7, 7.7 Hz), -156.9 (td, *J* = 20.8, 4.1 Hz), -163.0 (td, *J* = 21.6, 10.7 Hz).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.4, 145.3, 144.0, 142.9, 129.7, 122.3, 36.0, 36.0, 35.2, 30.8, 30.8, 30.7, 30.5, 30.5, 30.5, 29.7, 26.8, 26.7, 26.5, 25.6, 25.6.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{13}H_{11}F_7Na$ 323.0647, found 323.0648.

4-cyclohexyl-2,3,5,6-tetrafluoro-N-methyl-N-phenylbenzamide,(30)

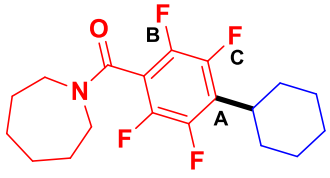


30

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (54 mg, 75% yield).
A:B=23:2

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.02 (m, 6H), 3.41 (s, 3H), 2.80 (tt, *J* = 11.9, 4.1 Hz, 1H), 1.77 – 1.56 (m, 6H), 1.29 – 1.13 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 142.3, 129.4, 128.3, 126.5, 126.1, 126.0, 37.3, 35.7, 30.7, 30.6, 30.6, 26.7, 26.6, 25.6.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -118.8 (d, *J* = 10.6 Hz), -134.2 (d, *J* = 21.7 Hz), -138.3 (dd, *J* = 22.5, 6.0 Hz), -141.5 (dd, *J* = 22.6, 12.5 Hz), -141.8 – -141.9 (m), -142.5 – -142.7 (m), -142.8 – -142.9 (m), -164.6 (td, *J* = 21.9, 10.9 Hz).
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{19}F_4NONa$ 388.1296, found 388.1293.

azepan-1-yl(4-cyclohexyl-2,3,5,6-tetrafluorophenyl)methanone,(31)

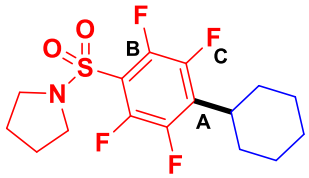


31

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (46 mg, 65% yield).
A:B:C=8:1:2

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.76 – 3.64 (m, 2H), 3.31 (dt, *J* = 16.0, 5.8 Hz, 2H), 3.10 – 2.83 (m, 1H), 1.91 – 1.54 (m, 16H), 1.47 – 1.17 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.6, 149.0,148.0, 146.1, 143.6, 143.5,125.9, 125.7, 114.6, 114.3, 49.2, 49.1, 46.0, 35.7, 35.2, 31.0, 30.8, 30.7, 30.7, 29.7, 28.9, 27.8, 27.6, 27.2, 26.8, 26.7, 26.2, 26.2, 25.7, 25.7.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.6 (d, *J* = 10.7 Hz), -134.4 (dd, *J* = 5.6, 2.4 Hz), -134.5 (dd, *J* = 5.4, 2.6 Hz), -139.0 – -139.1 (m), -139.1(d, *J* = 5.5 Hz), -141.8 – -141.9 (m), -142.8 – -142.9 (m), -164.0 (td, *J* = 21.8, 11.0 Hz).
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{23}ONF_4Na$ 380.1613, found 380.1619.

1-((4-cyclohexyl-2,3,5,6-tetrafluorophenyl)sulfonyl)pyrrolidine,(32)

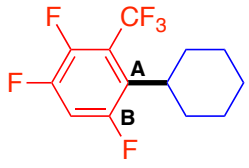


32

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (29 mg, 40% yield).
A: B: C =6:1:2

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.38 (q, *J* = 7.1 Hz, 4H), 2.97 (tdd, *J* = 20.4, 10.3, 6.1 Hz, 1H), 1.94 – 1.64 (m, 11H), 1.41 – 1.14 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.4,146.1, 144.0, 143.4, 143.2, 129.8, 129.6, 116.8, 47.8, 47.8, 47.8, 36.0, 35.4, 30.9, 30.8, 30.5, 30.5, 30.5, 26.7, 26.5, 25.7, 25.6, 25.6.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.3, -113.3 – -113.4 (m), -127.5 (dt, *J* = 21.7, 8.4 Hz), -133.1 (ddd, *J* = 23.3, 10.3, 4.9 Hz), -137.5 – -137.6 (m), -140.3 (td, *J* = 16.5, 7.6 Hz), -161.9 (td, *J* = 22.6, 10.6 Hz).
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{16}H_{19}O_2SNF_4Na$ 388.0970, found 388.0979.

2-cyclohexyl-1,4,5-trifluoro-3-(trifluoromethyl)benzene,(34)



33

Reaction in 1,4-dioxane (0.4 mL), using hexafluorobenzene (1.0 mmol, 5 equiv).
After workup, this product was isolated by flash column chromatography on silica gel, eluting with pentane as a colourless solid. (37 mg, 66% yield).
A:B=1.2:1

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.05 (ddd, *J* = 9.8, 5.2, 2.2 Hz, 1H), 3.19 – 2.83 (m, 1H), 1.97 – 1.67 (m, 7H), 1.37 (ddt, *J* = 17.3, 11.3, 6.4 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.0,156.9,151.0,151.0, 148.5,148.4,148.3, 129.0, 128.9, 128.8, 128.7, 123.0, 120.2, 108.8, 108.7, 108.7, 108.5, 108.4, 108.4, 39.5, 36.5, 36.0, 35.6, 35.6, 32.9, 31.9, 30.9, 30.6, 30.5, 30.5, 30.4, 30.4, 29.7, 26.8, 26.6, 26.5, 26.5, 25.8, 25.7, 25.7, 25.5, 22.7, 14.1.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -53.8, -53.9, -56.2 – -56.6 (m), -61.2 (d, *J* = 12.8 Hz), -116.2 (ddd, *J* = 14.4, 9.5, 4.1 Hz), -122.0 – -122.3 (m), -134.4 (dd, *J* = 20.1, 3.9 Hz).
HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd. for $C_{13}H_{12}F_6Na$ 305.0741, found 305.0749.

Fluorescence quenching measurements

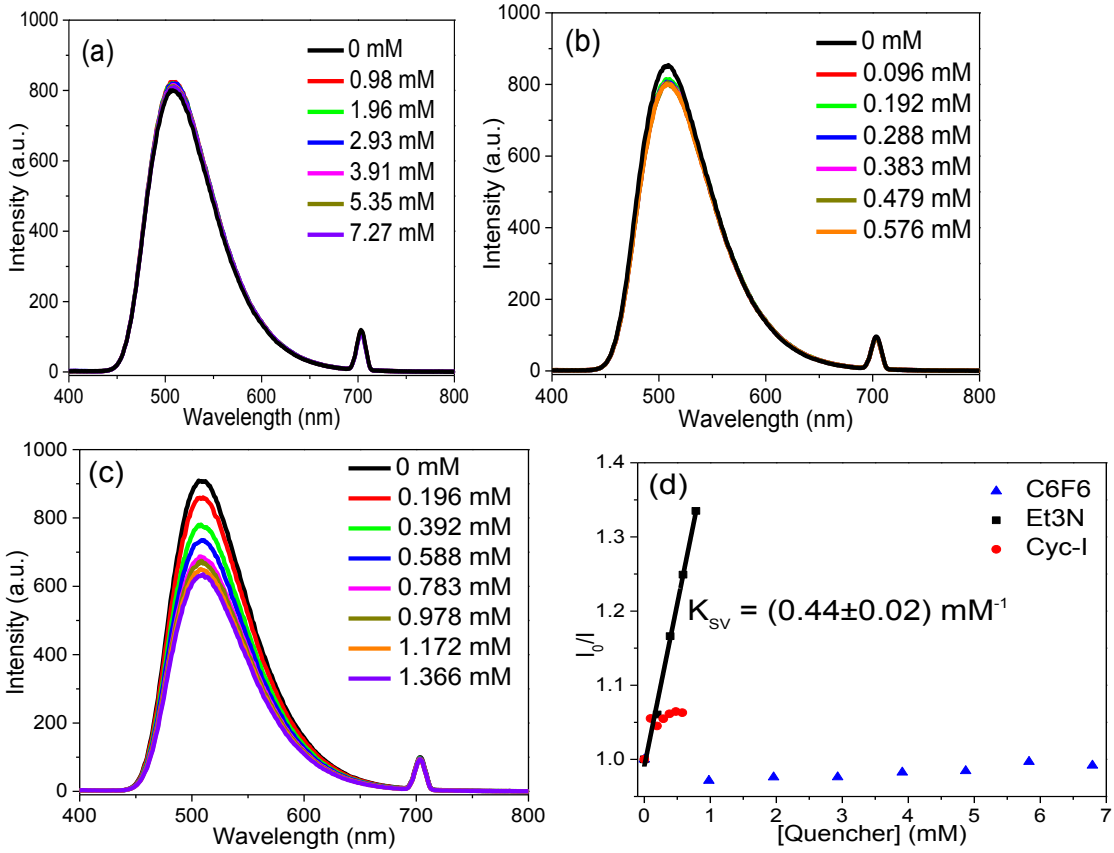
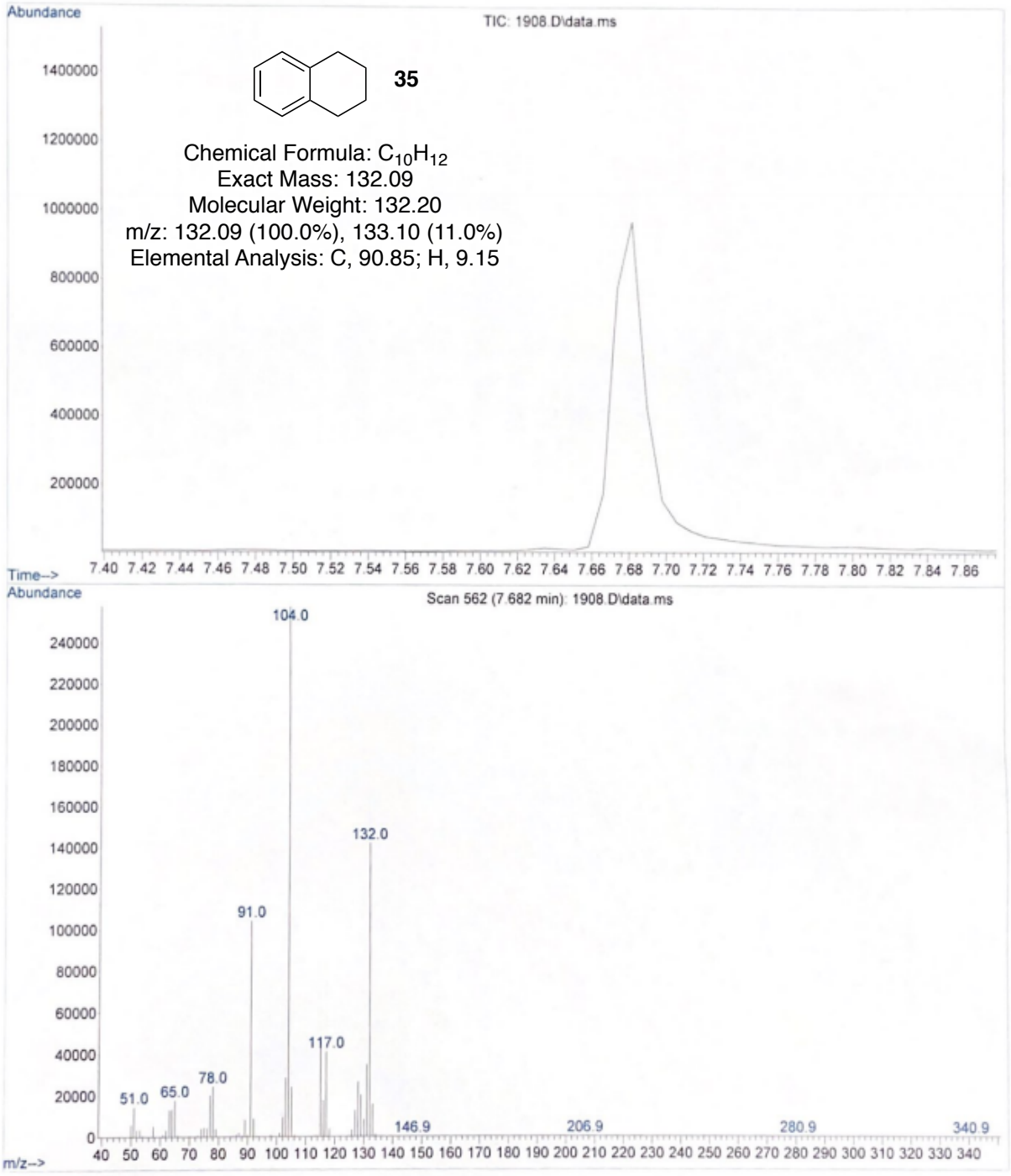
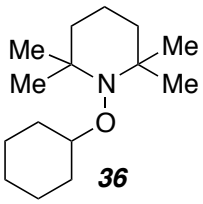


Figure 1 Fluorescence spectra of 4CzIPN in 1,4-dioxane (0.01 mM) before and after the addition of different amounts of C_6F_6 (a), iodocyclohexane (b), Et_3N (c) and stern-Volmer plot (d)

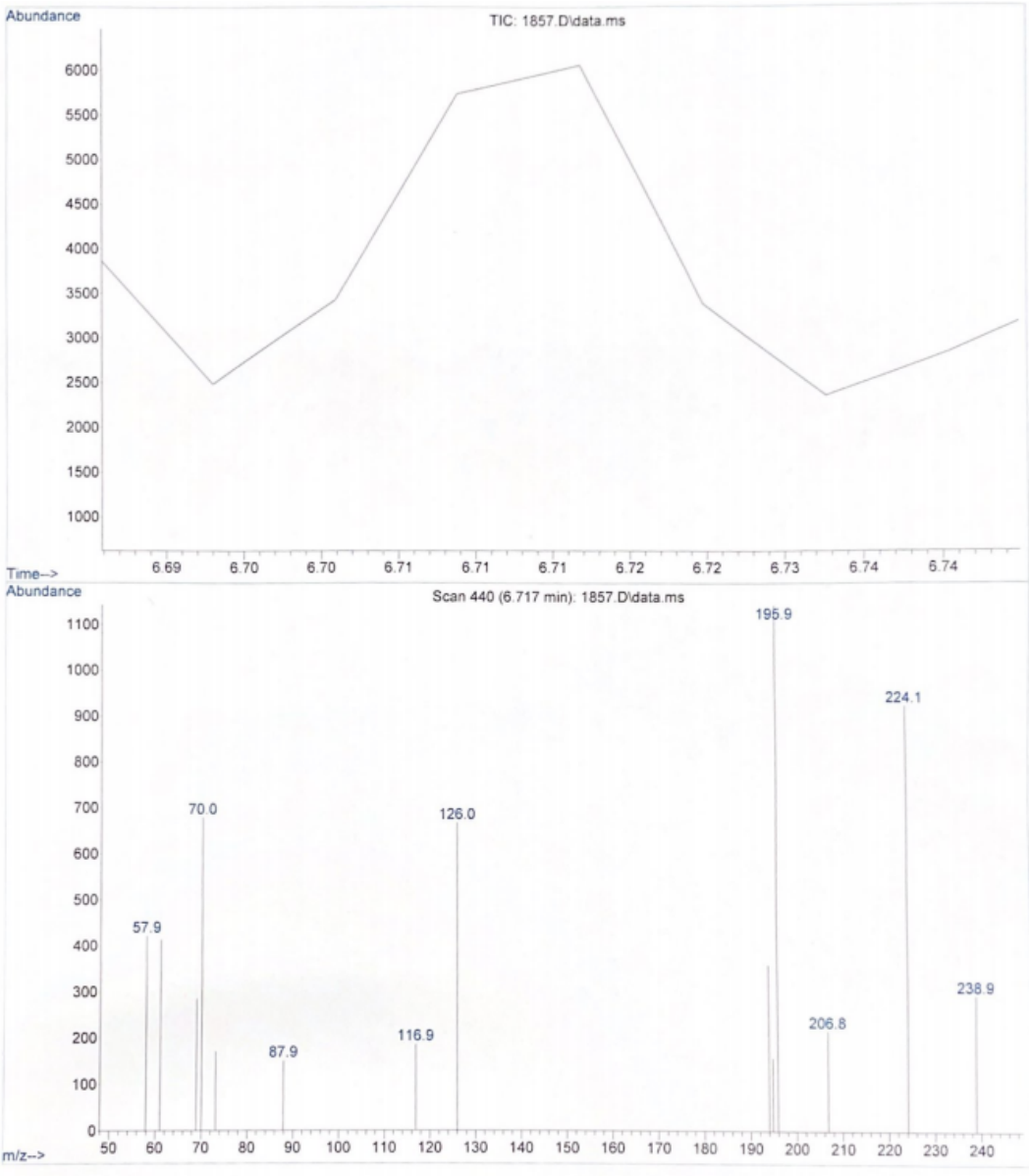
GC-MS spectrum for the radical addition trapping reaction

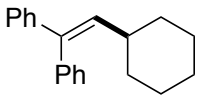




36

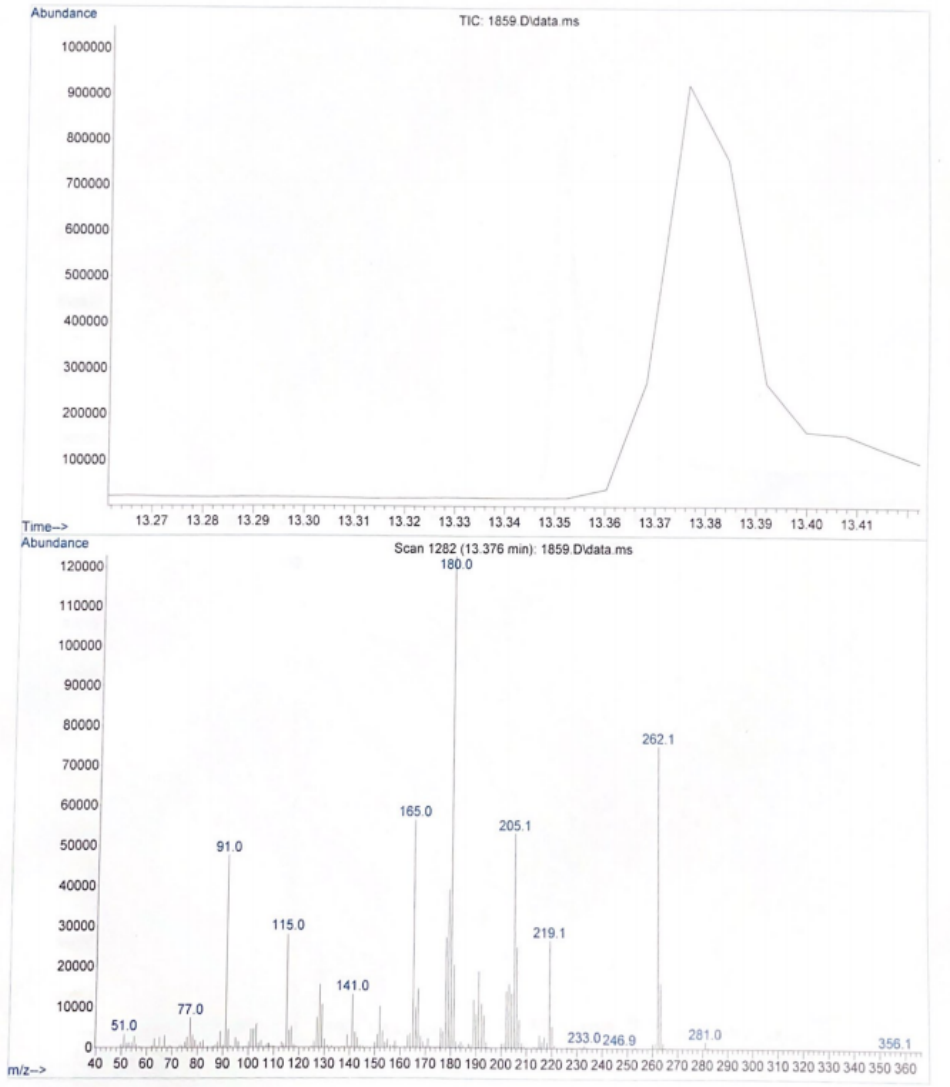
Chemical Formula: $C_{15}H_{29}NO$
Exact Mass: 239.22
Molecular Weight: 239.40
m/z: 239.22 (100.0%), 240.23 (16.6%), 241.23 (1.6%)
Elemental Analysis: C, 75.26; H, 12.21; N, 5.85; O, 6.68

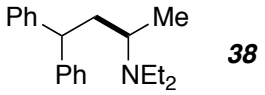




37

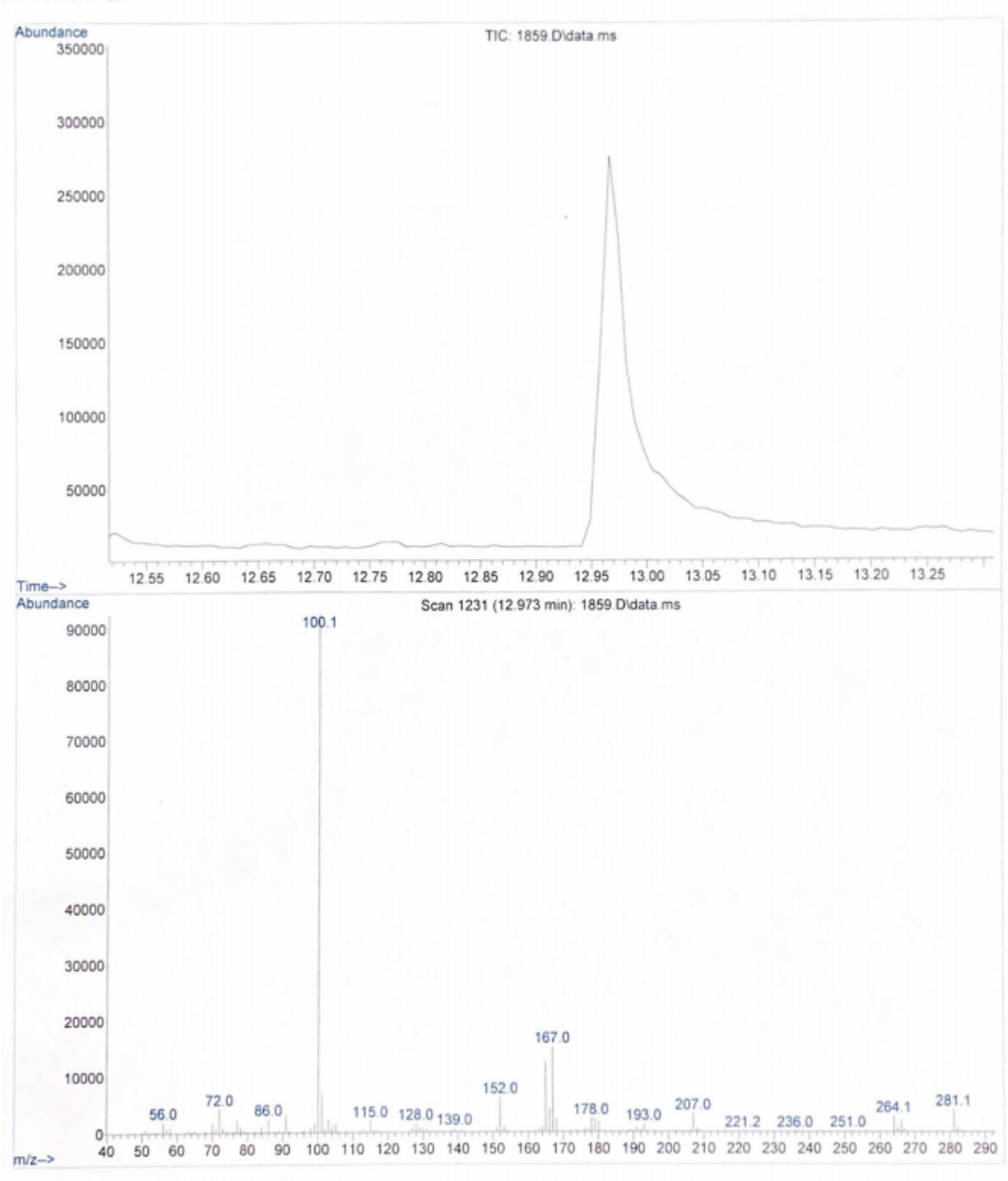
Chemical Formula: $C_{20}H_{22}$
Exact Mass: 262.17
Molecular Weight: 262.39
m/z: 262.17 (100.0%), 263.18 (21.9%), 264.18 (2.3%)
Elemental Analysis: C, 91.55; H, 8.45





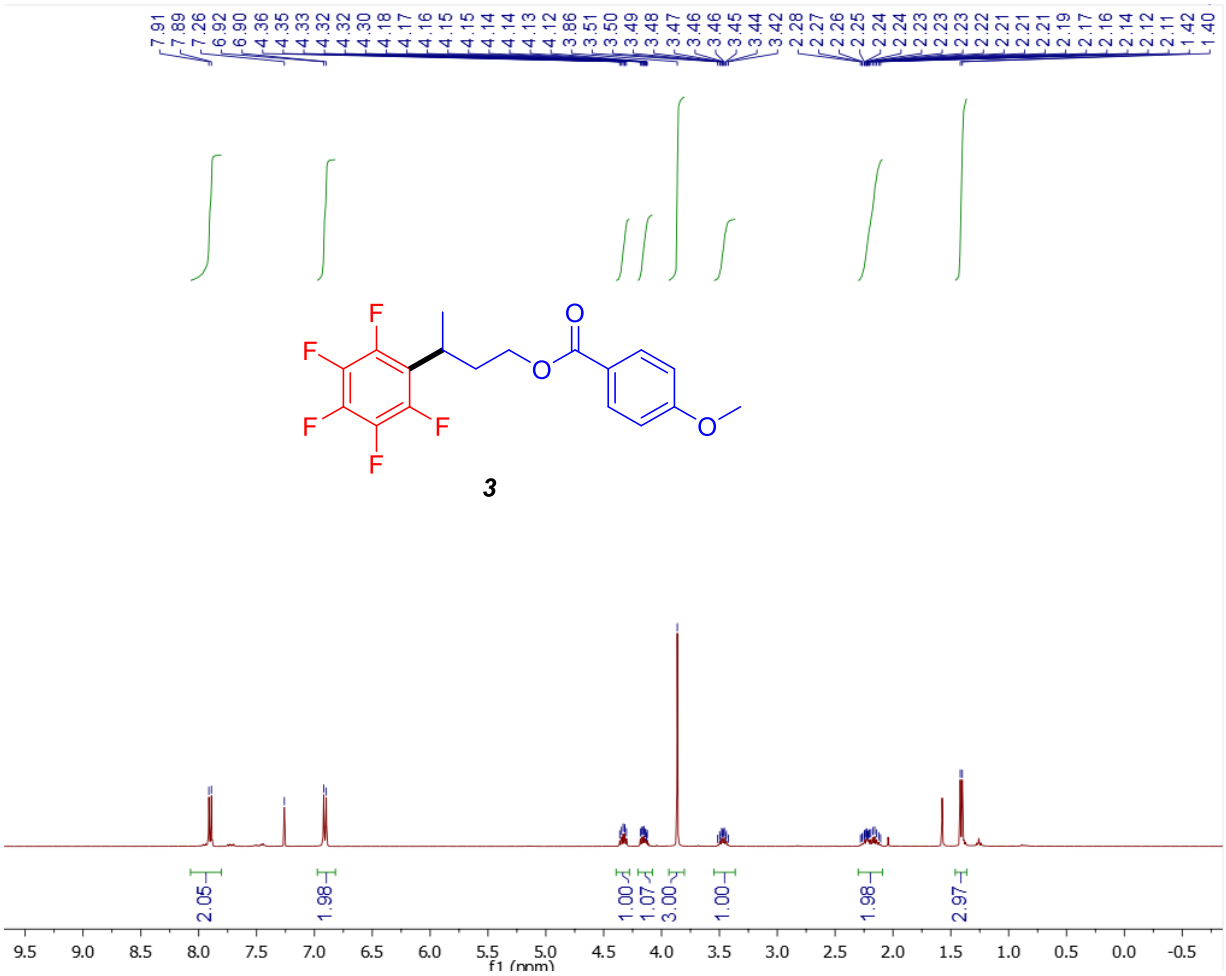
38

Chemical Formula: $C_{20}H_{27}N$
Exact Mass: 281.21
Molecular Weight: 281.44
m/z: 281.21 (100.0%), 282.22 (21.9%), 283.22 (2.3%)
Elemental Analysis: C, 85.35; H, 9.67; N, 4.98

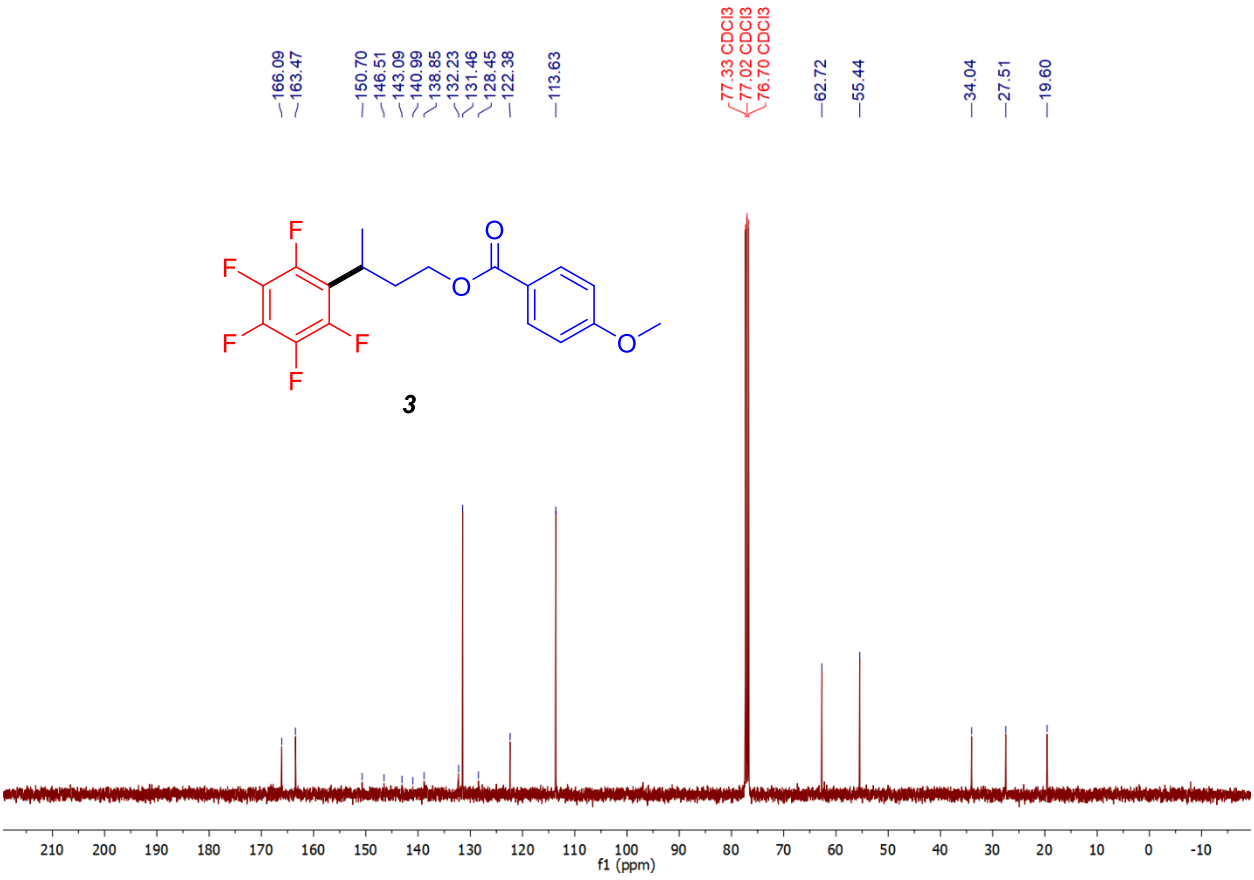


NMR Spectra

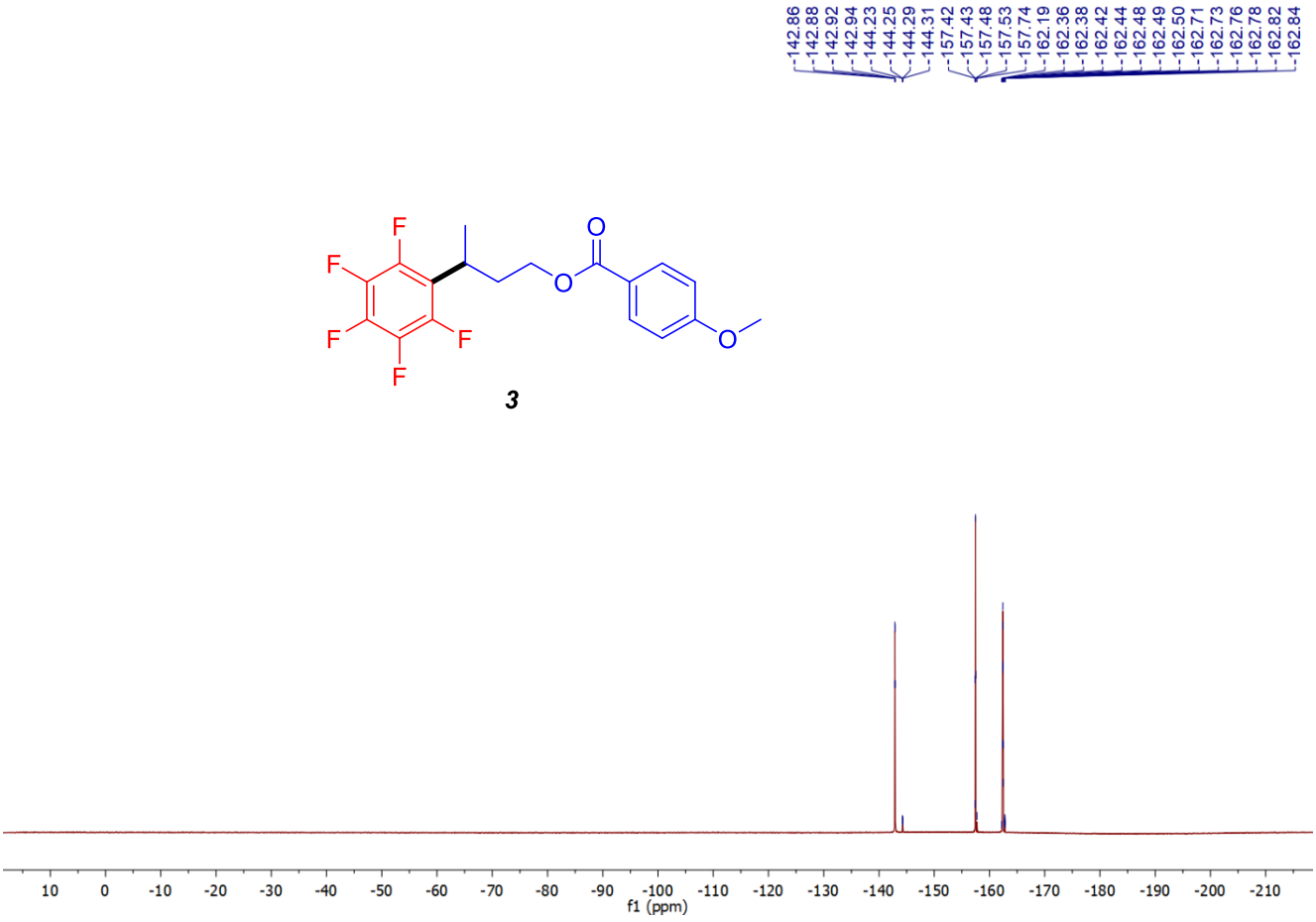
^{1}H-NMR (400 MHz, $CDCl_3$) of **3**



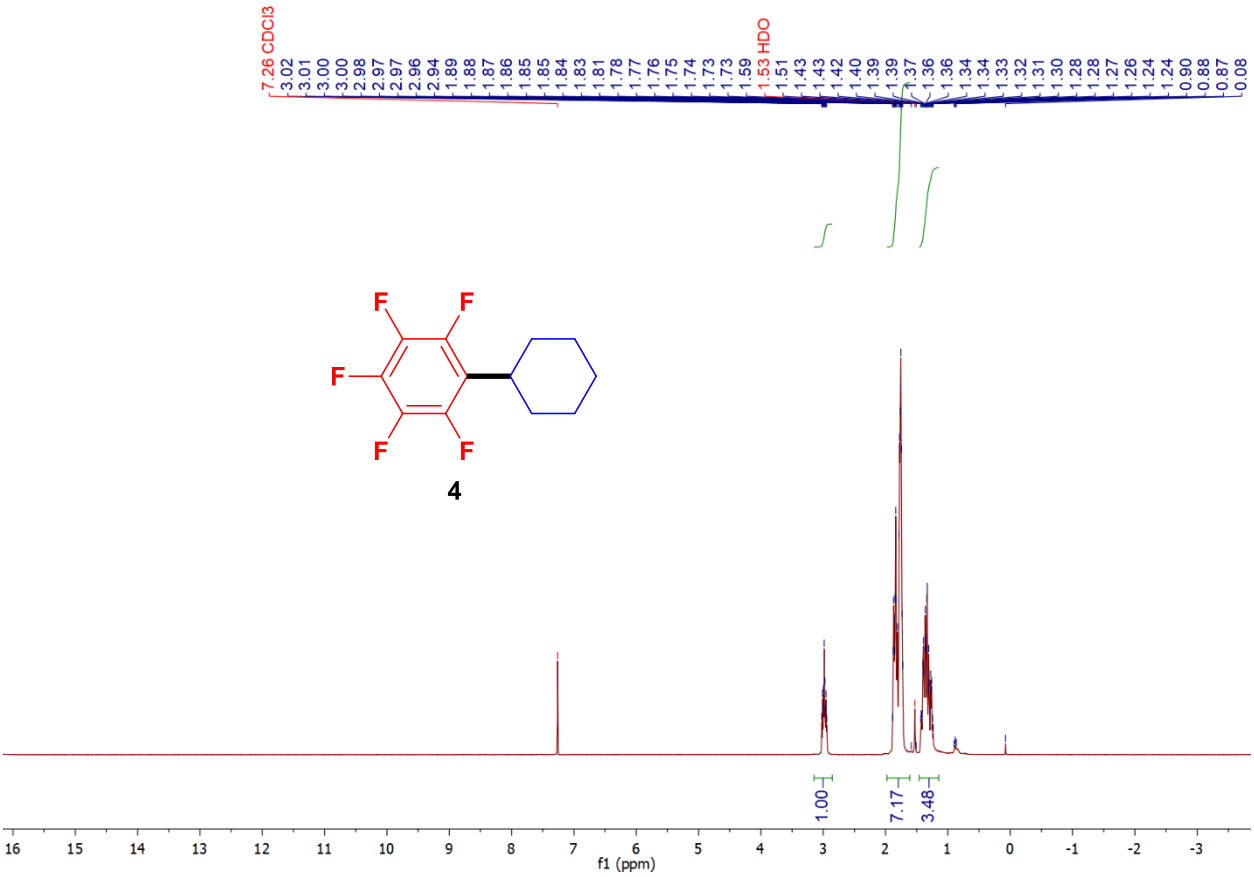
^{13}C-NMR (101 MHz, $CDCl_3$) of **3**



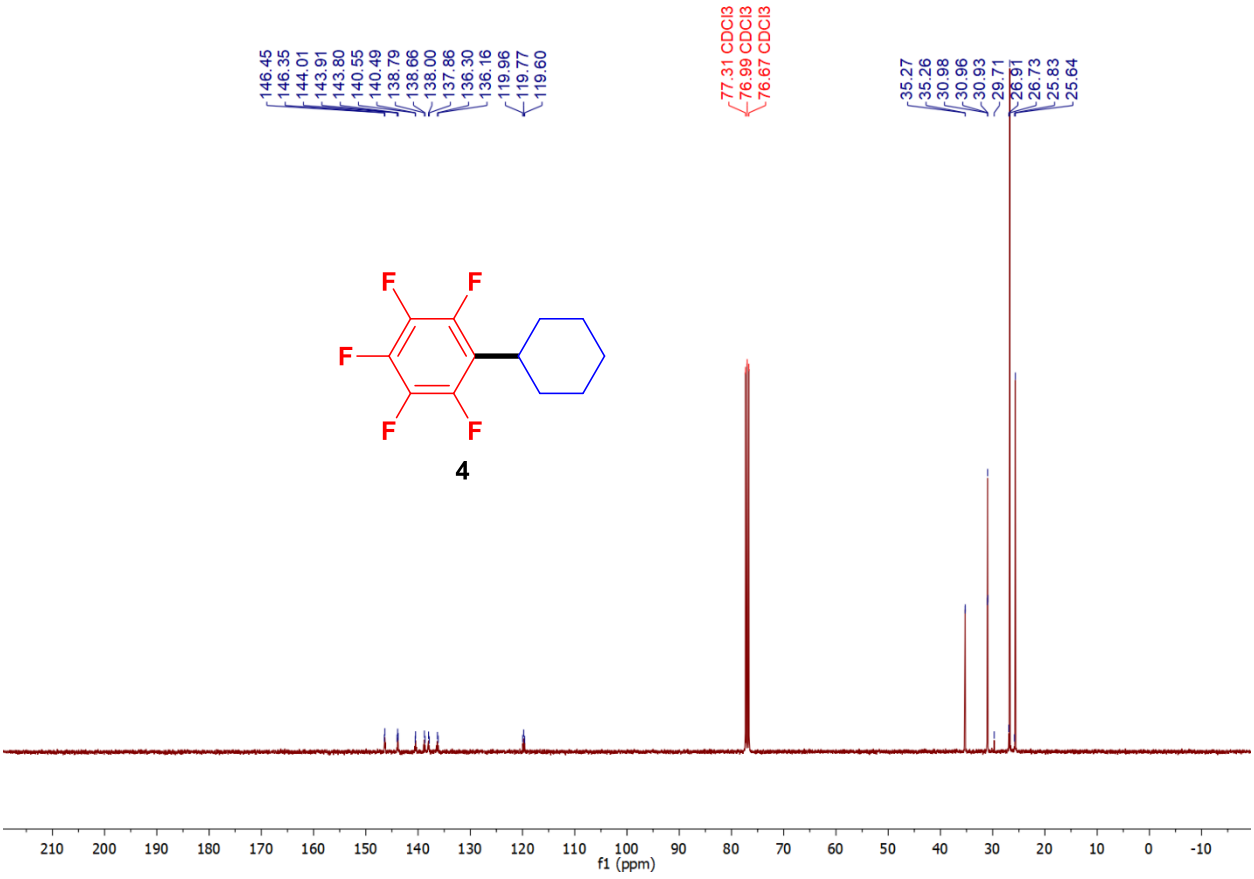
^{19}F-NMR (377 MHz, $CDCl_3$) of **3**



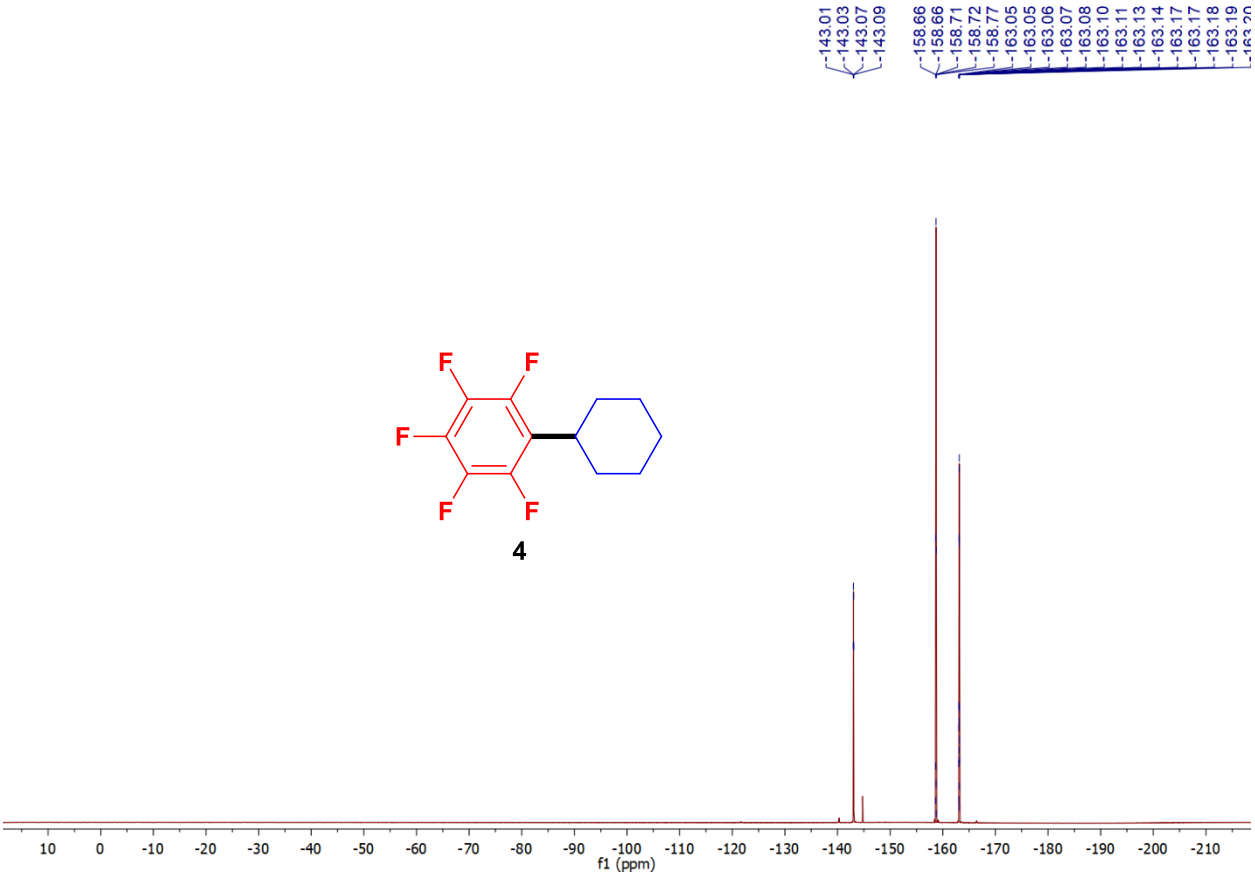
^{1}H-NMR (400 MHz, $CDCl_3$) of **4**



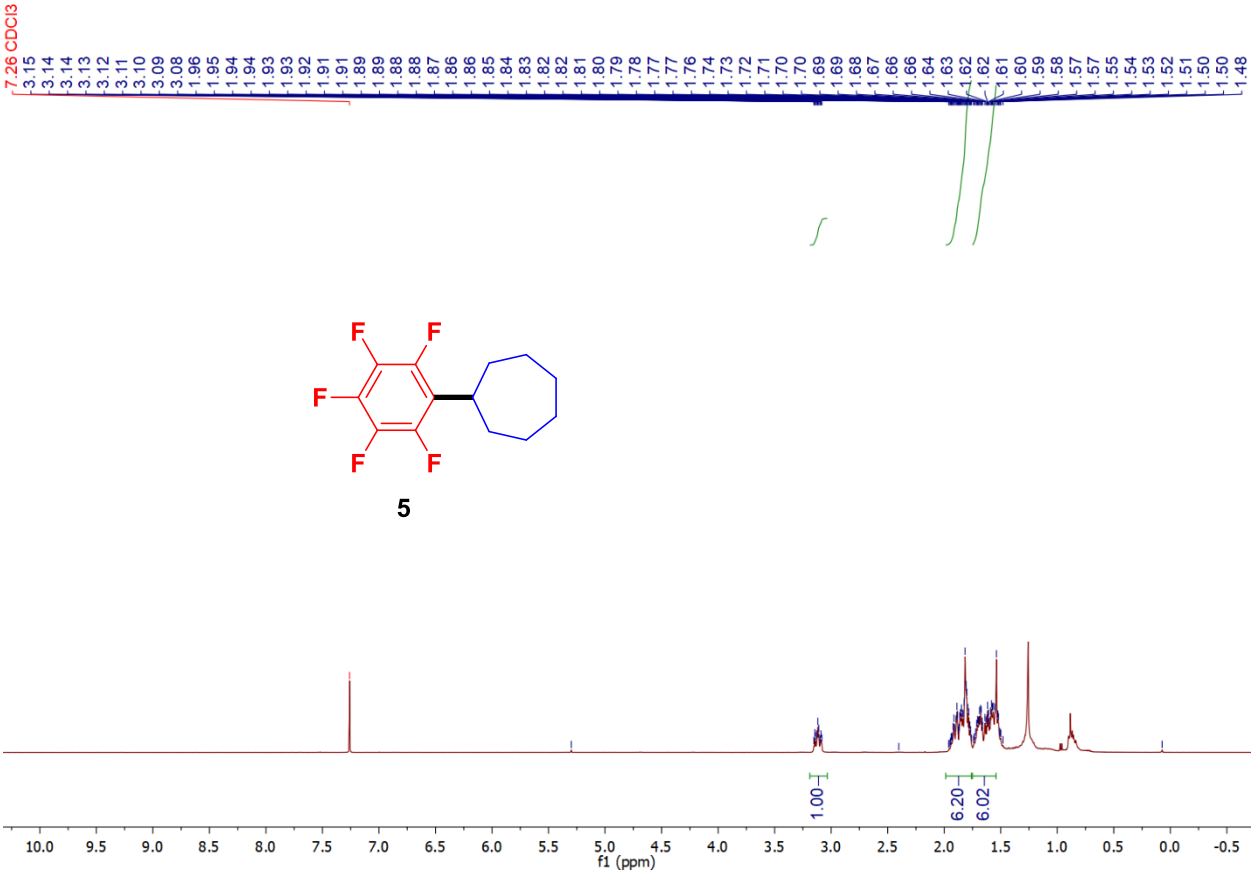
^{13}C-NMR (101 MHz, $CDCl_3$) of **4**



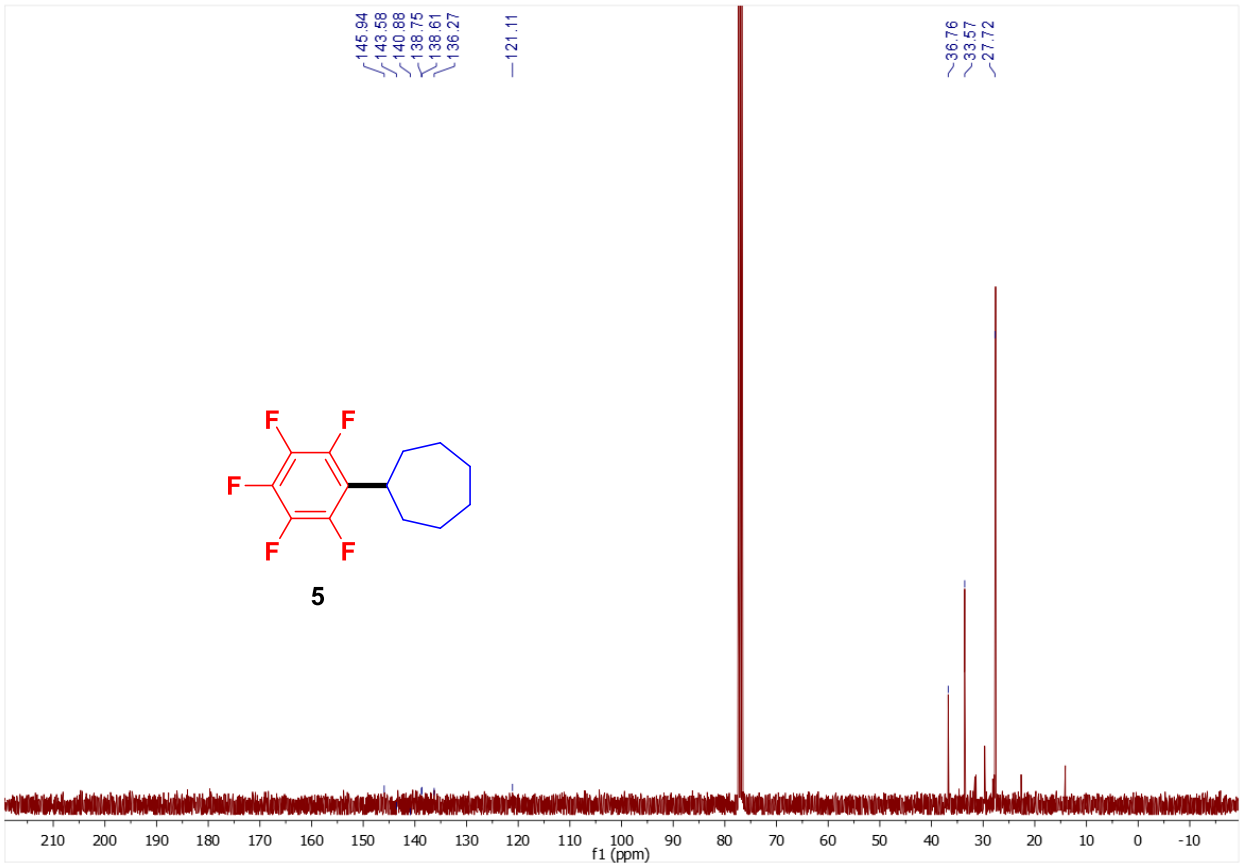
^{19}F-NMR (377 MHz, $CDCl_3$) of **4**



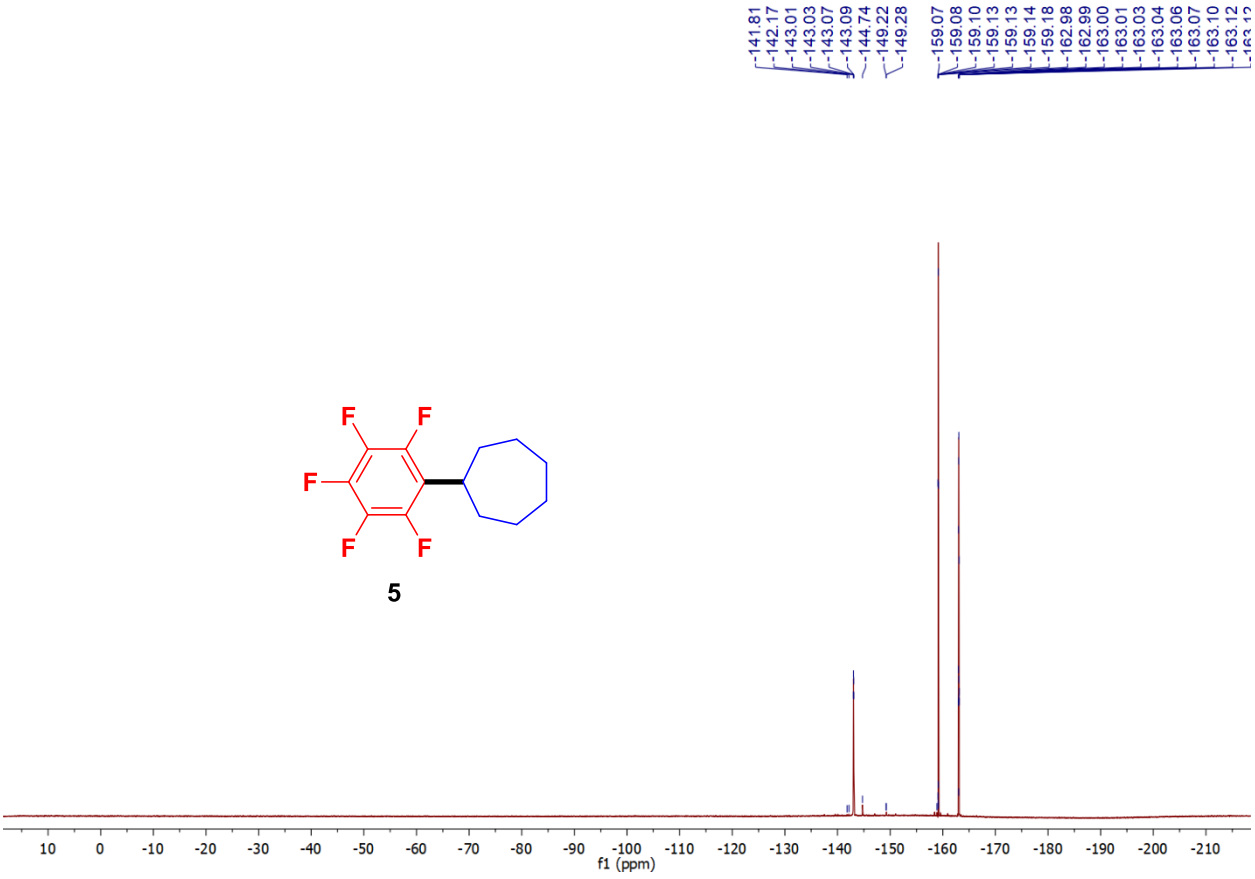
^{1}H-NMR (400 MHz, $CDCl_3$) of **5**



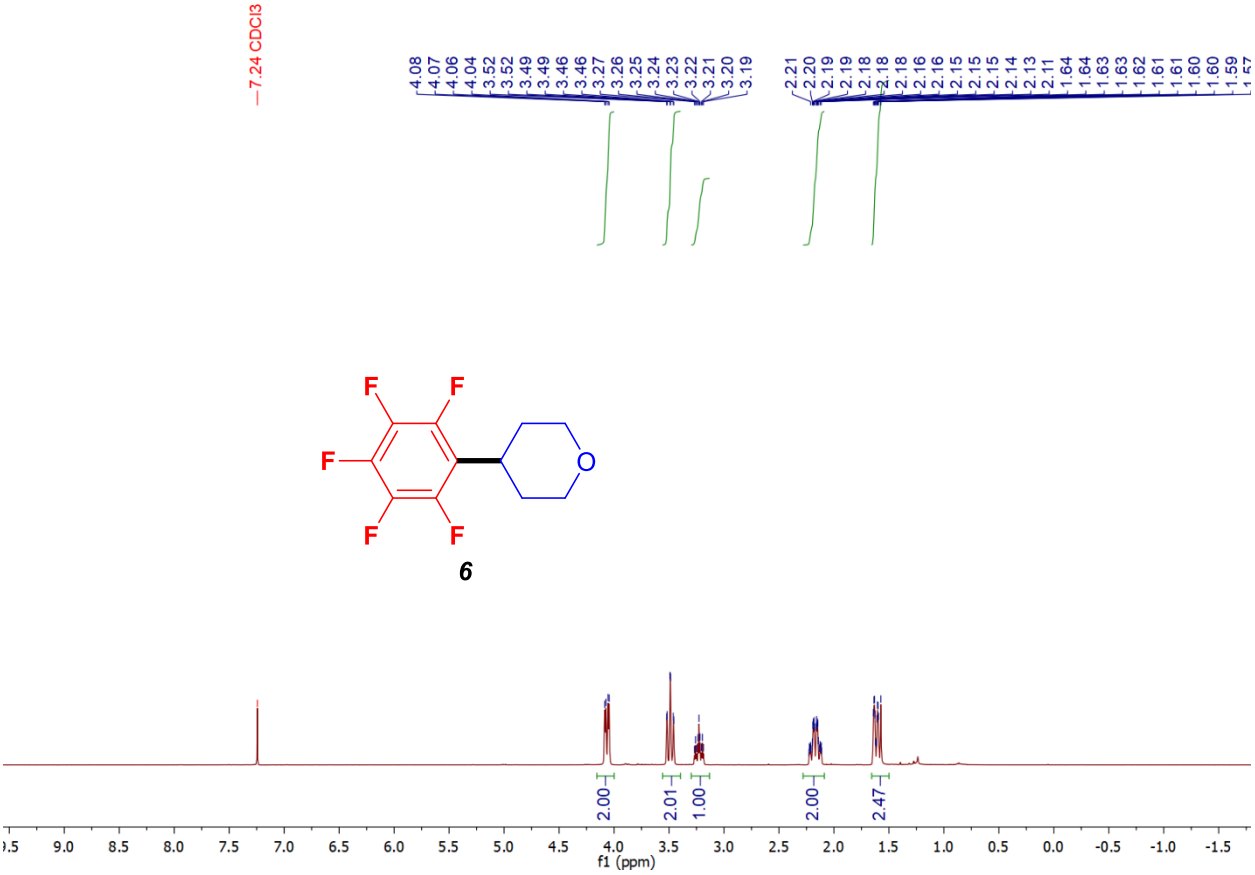
^{13}C-NMR (101 MHz, $CDCl_3$) of **5**



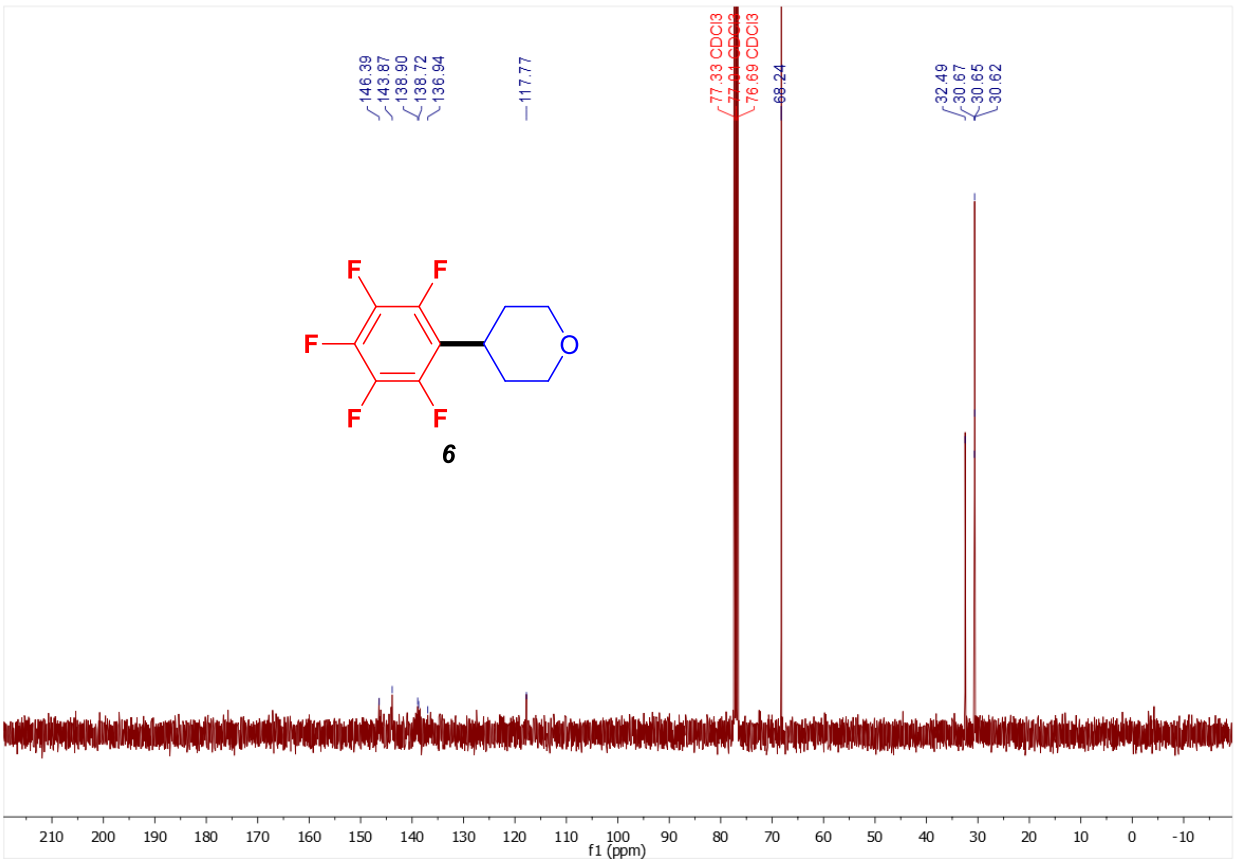
^{19}F-NMR (377 MHz, $CDCl_3$) of **5**



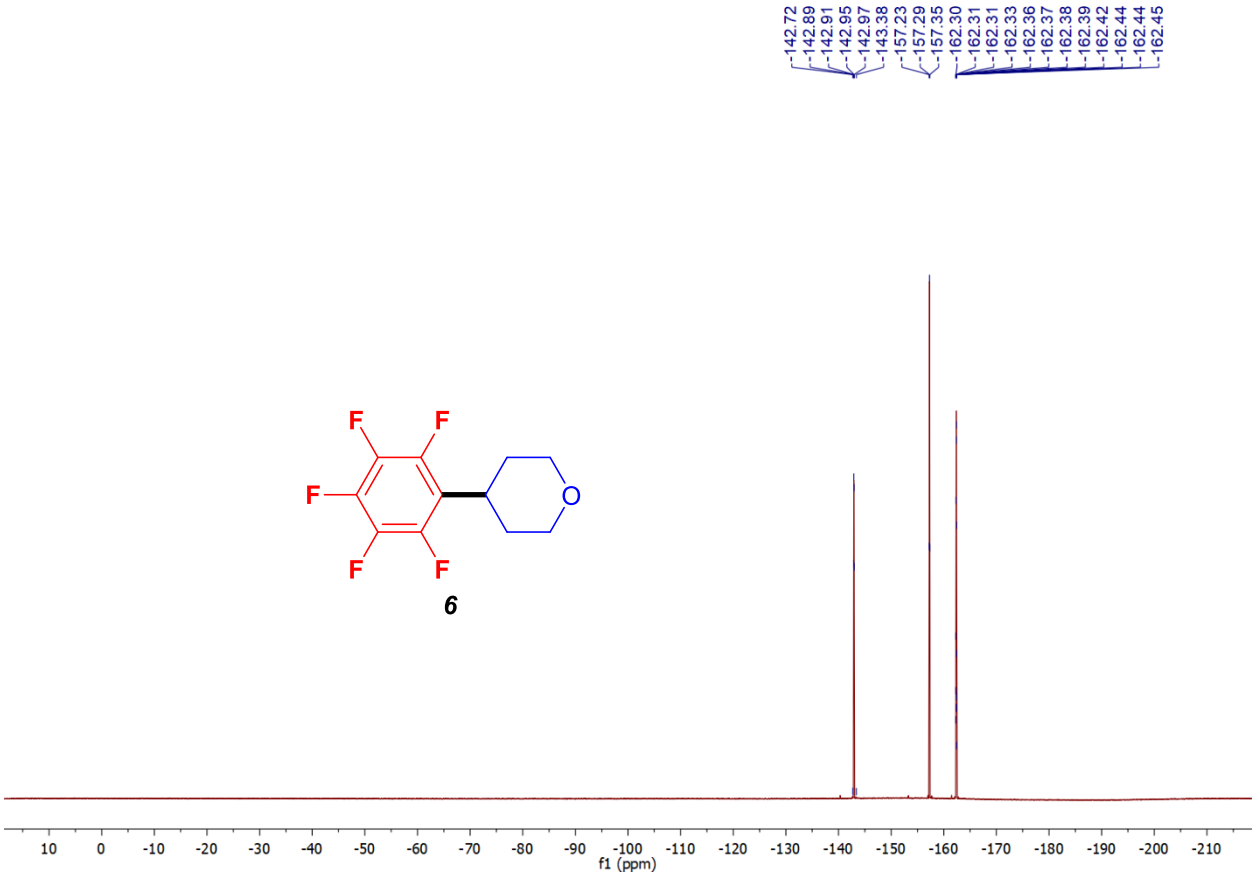
^{1}H-NMR (400 MHz, $CDCl_3$) of **6**



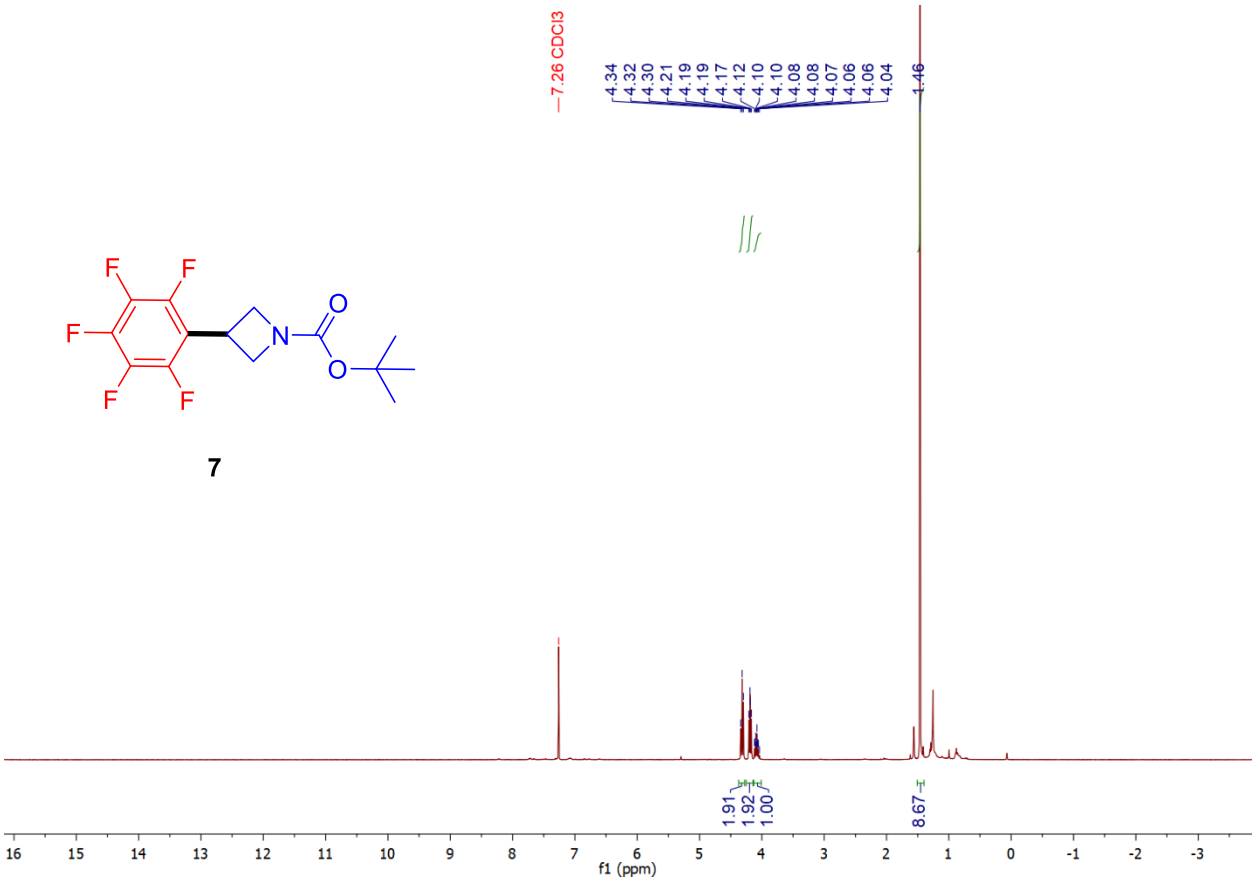
^{13}C-NMR (101 MHz, $CDCl_3$) of **6**



^{19}F-NMR (377 MHz, $CDCl_3$) of **6**

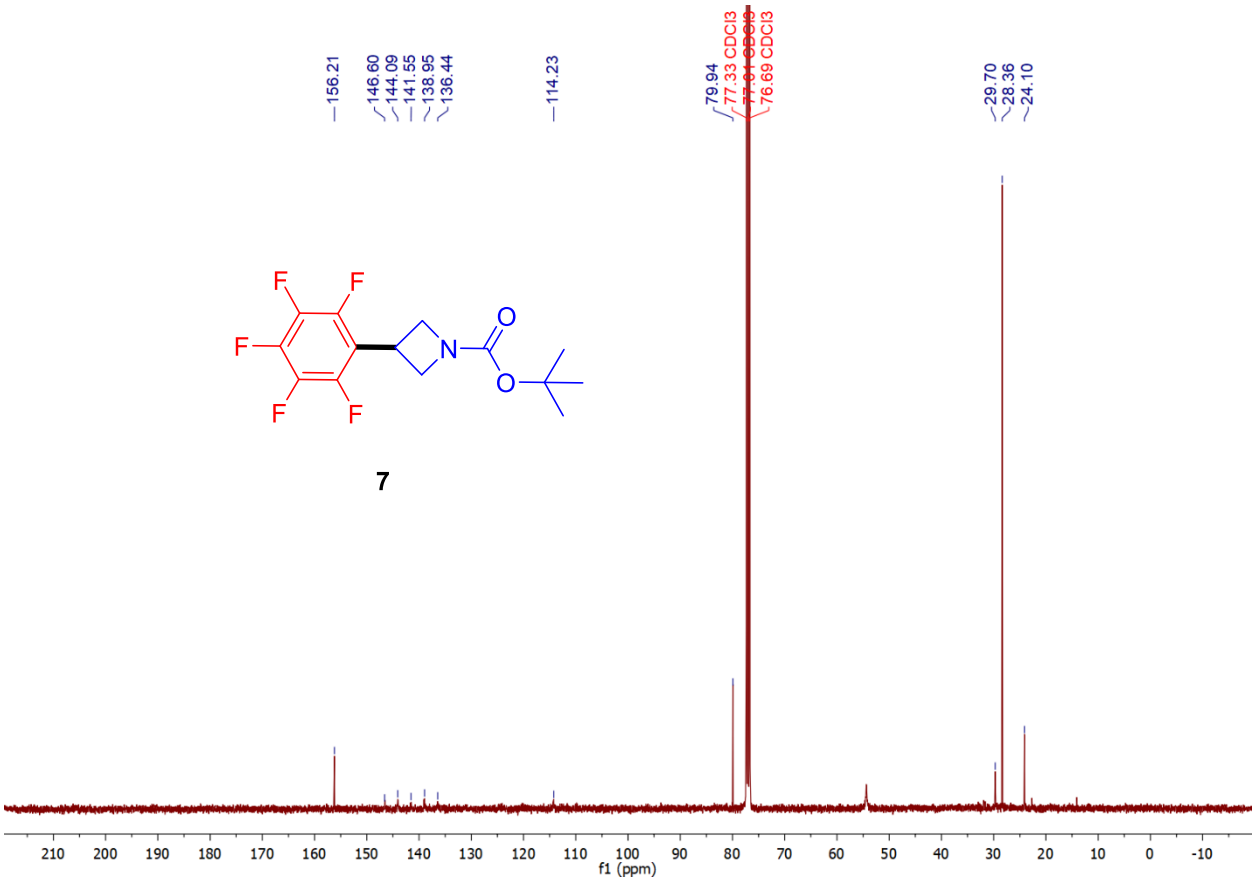


^{1}H-NMR (400 MHz, $CDCl_3$) of **7**

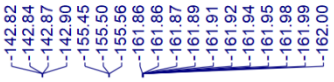


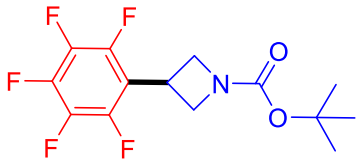
7

^{13}C-NMR (101 MHz, $CDCl_3$) of **7**

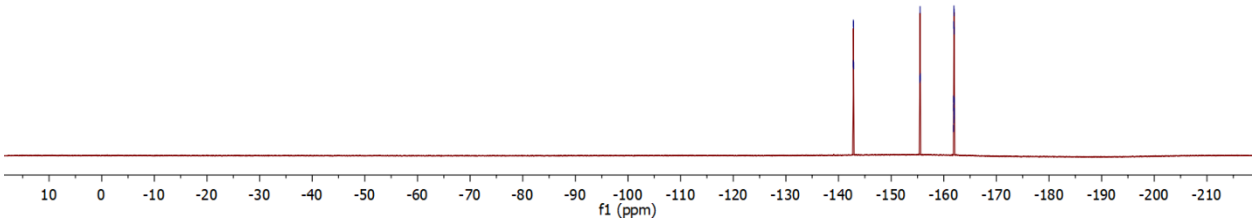


^{19}F-NMR (377 MHz, $CDCl_3$) of **7**

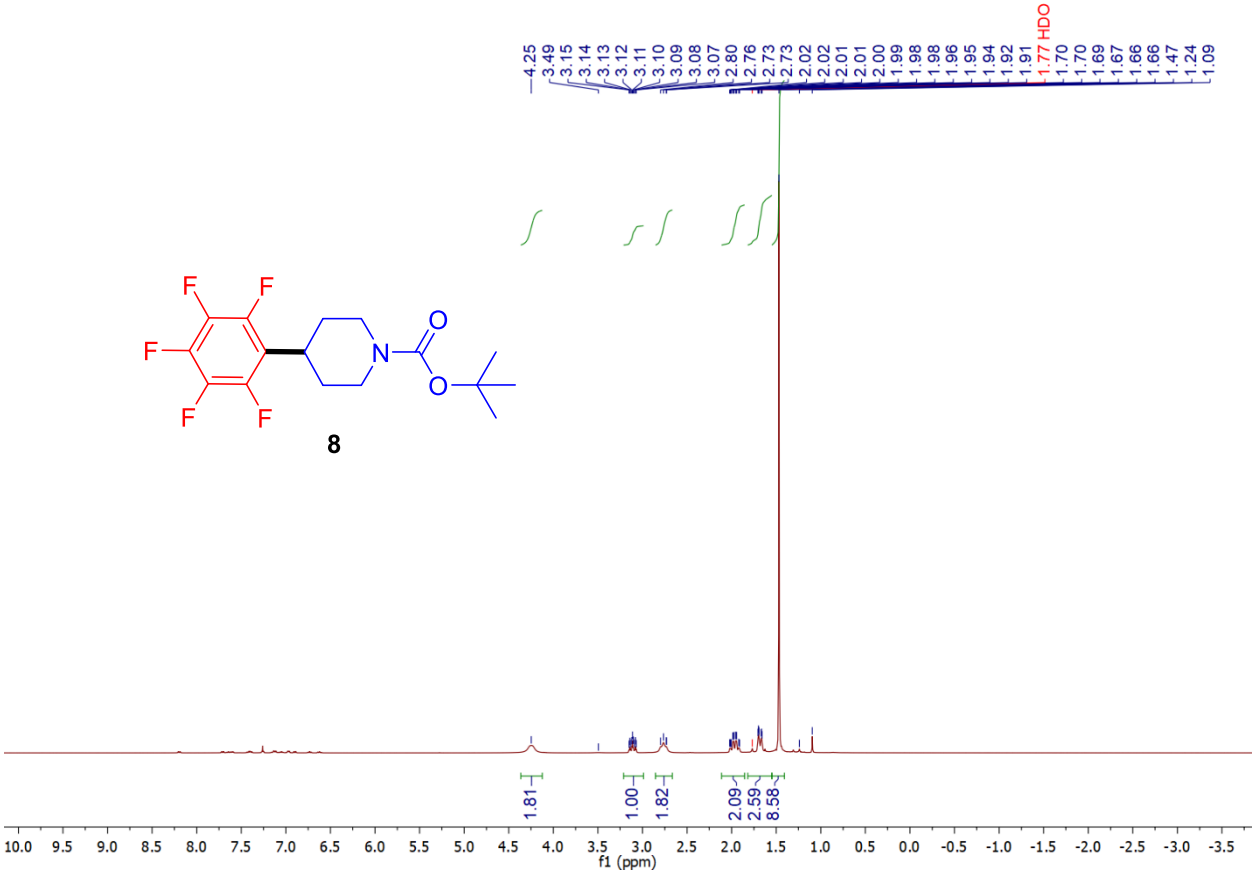




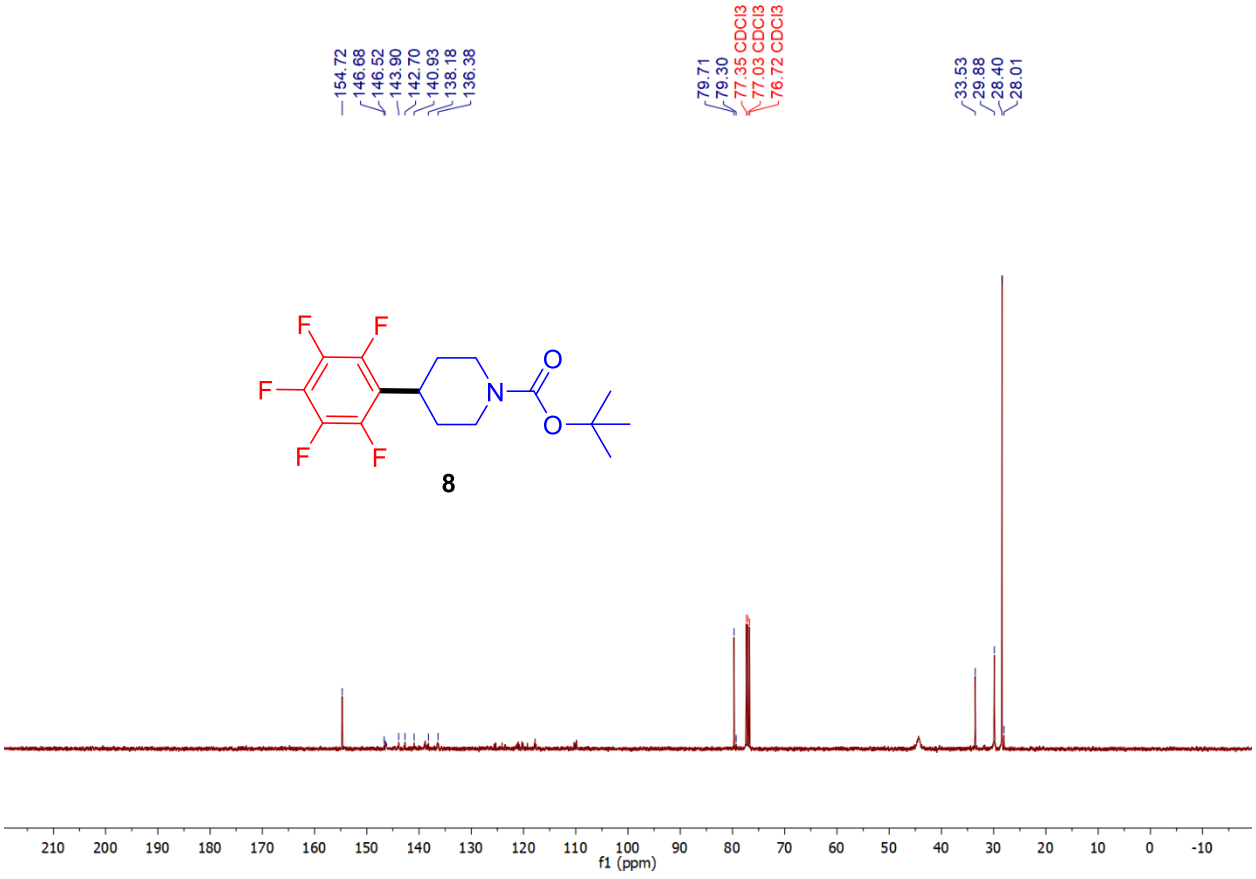
7



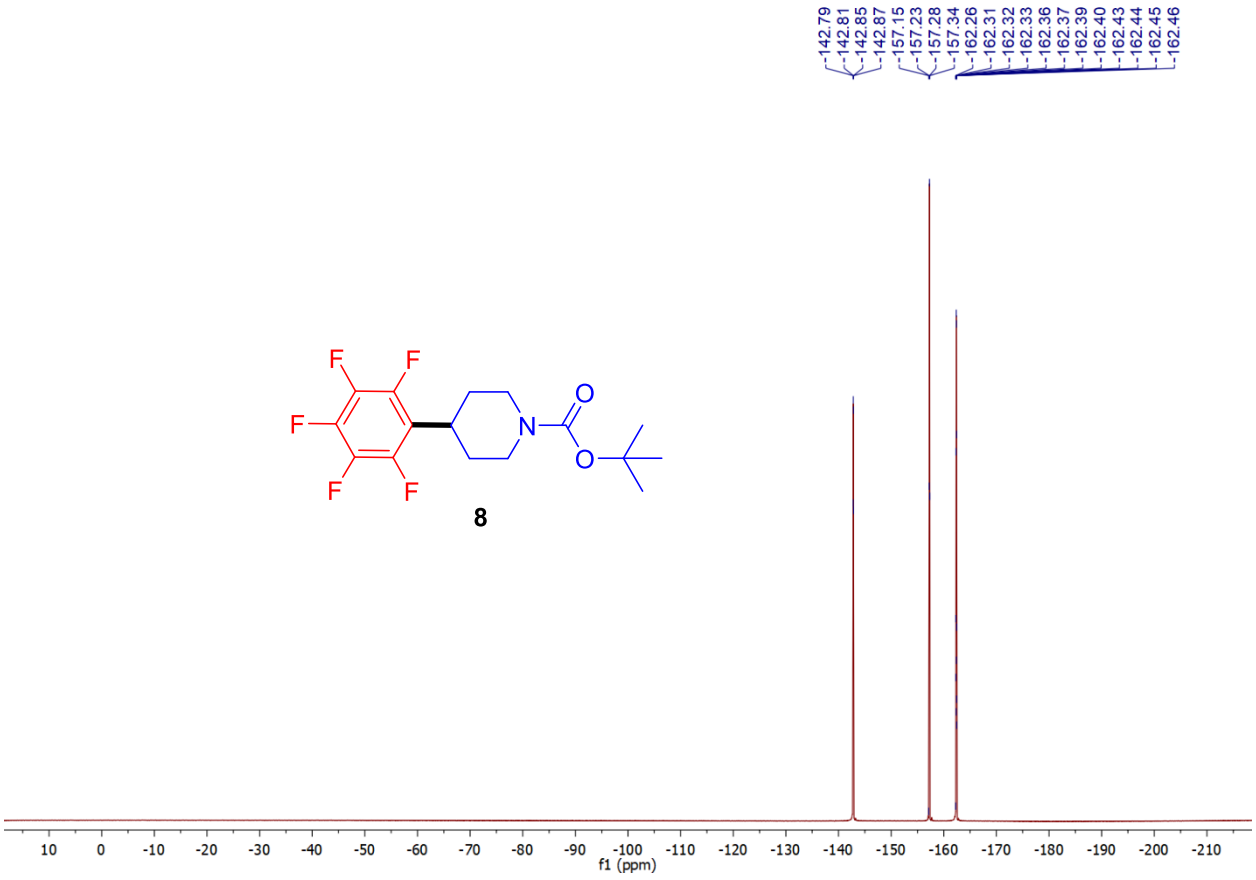
^{1}H-NMR (400 MHz, $CDCl_3$) of **8**



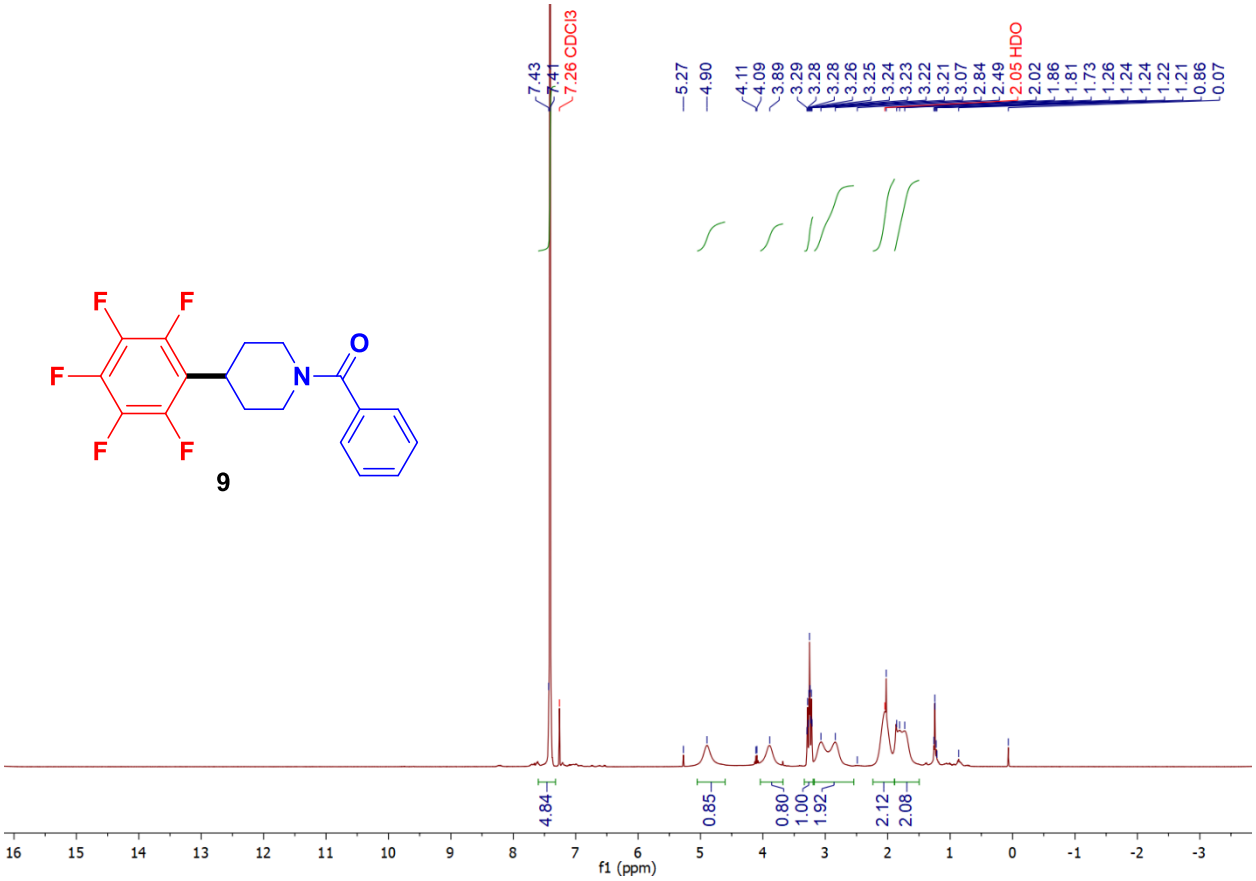
^{13}C-NMR (101 MHz, $CDCl_3$) of **8**



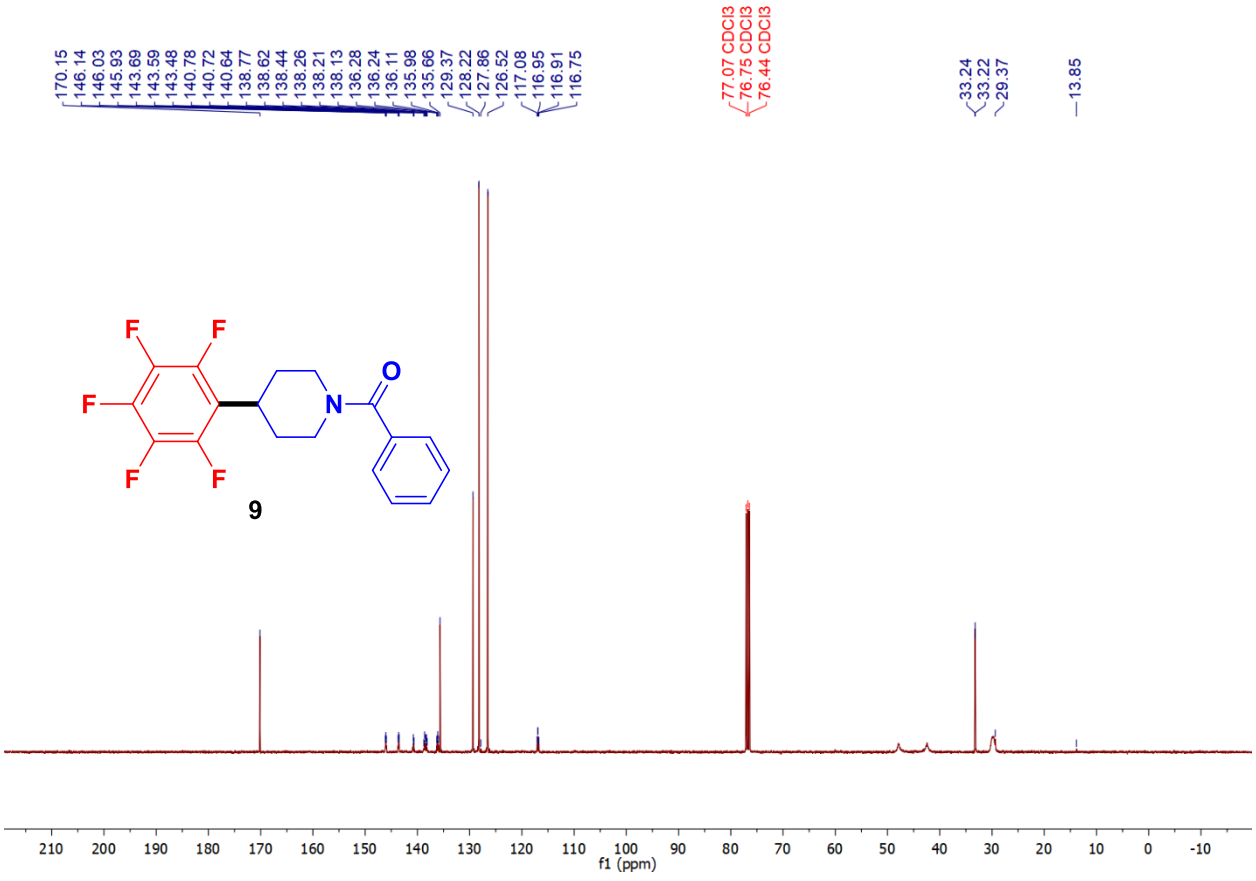
^{19}F-NMR (377 MHz, $CDCl_3$) of **8**



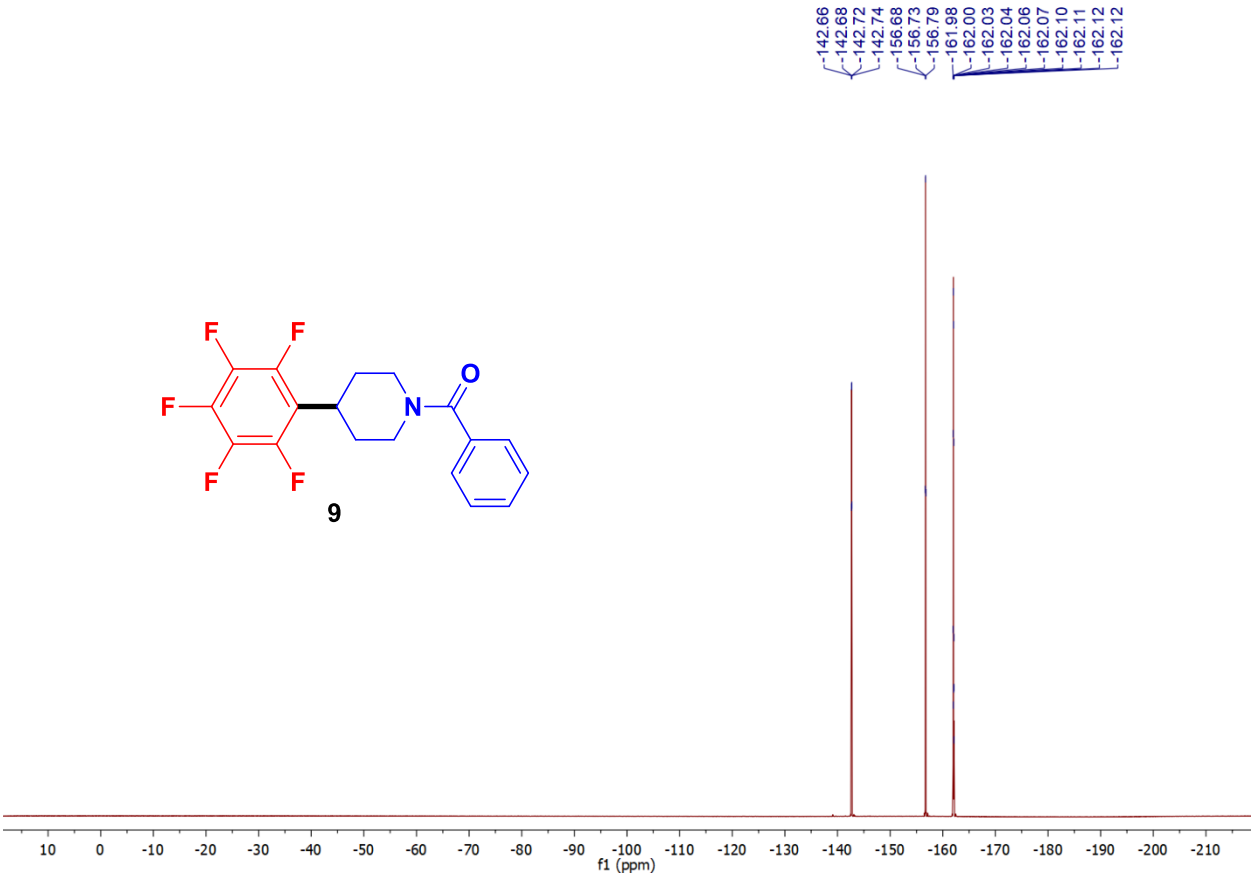
^{1}H-NMR (400 MHz, $CDCl_3$) of **9**



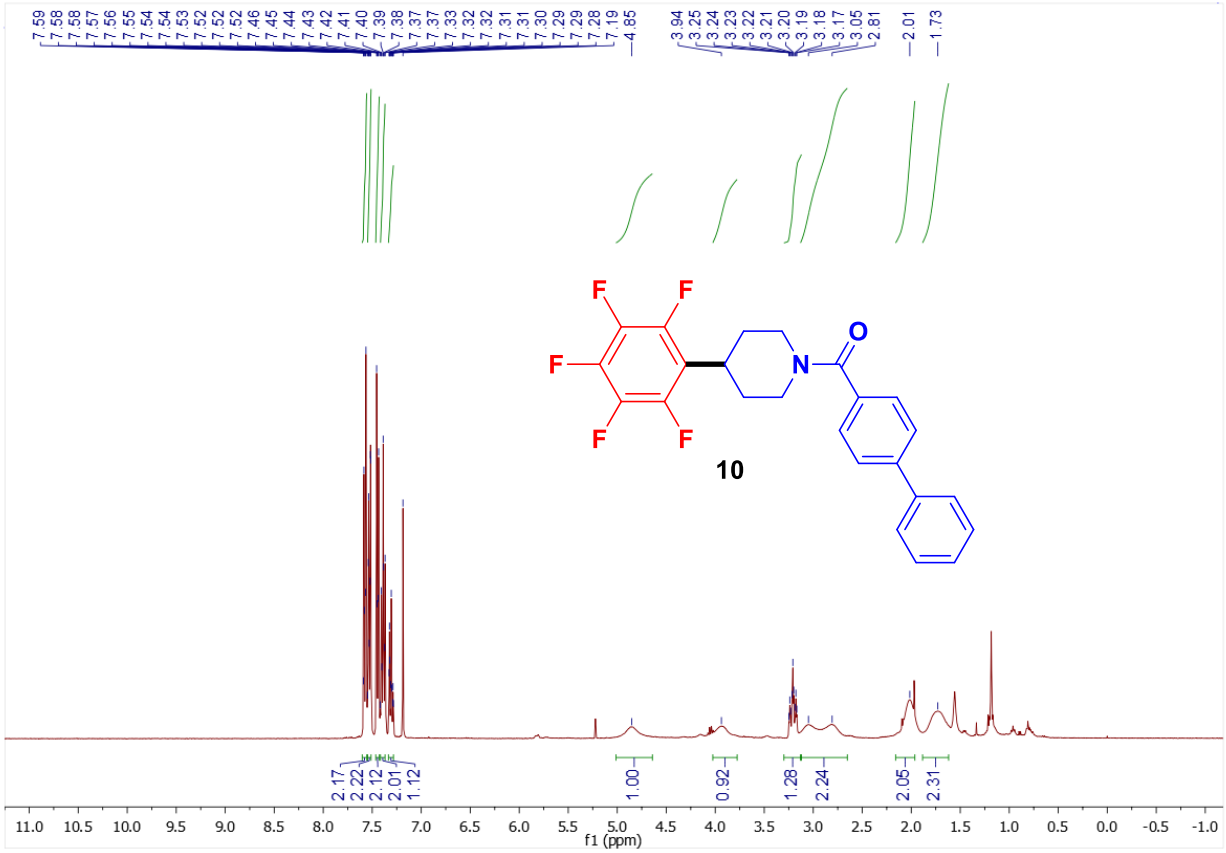
^{13}C-NMR (101 MHz, $CDCl_3$) of **9**



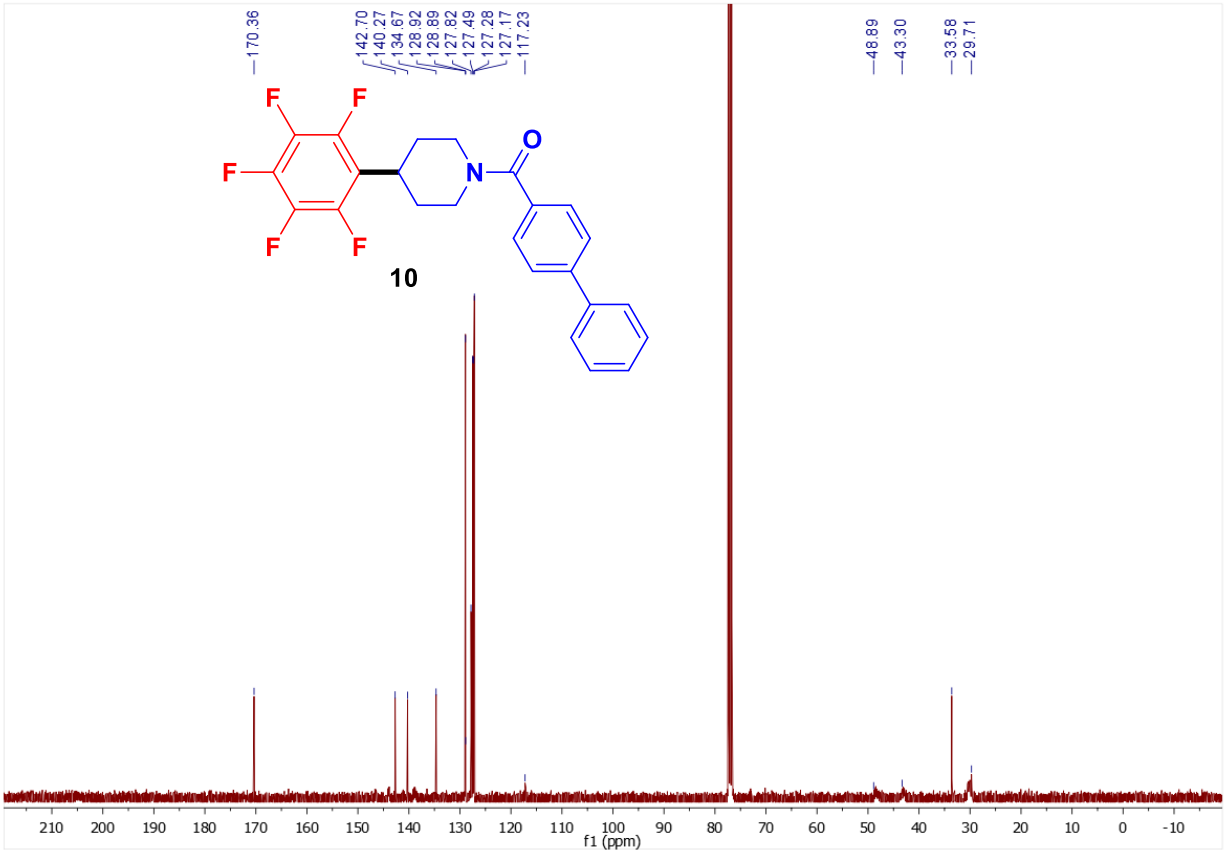
^{19}F-NMR (377 MHz, $CDCl_3$) of **9**



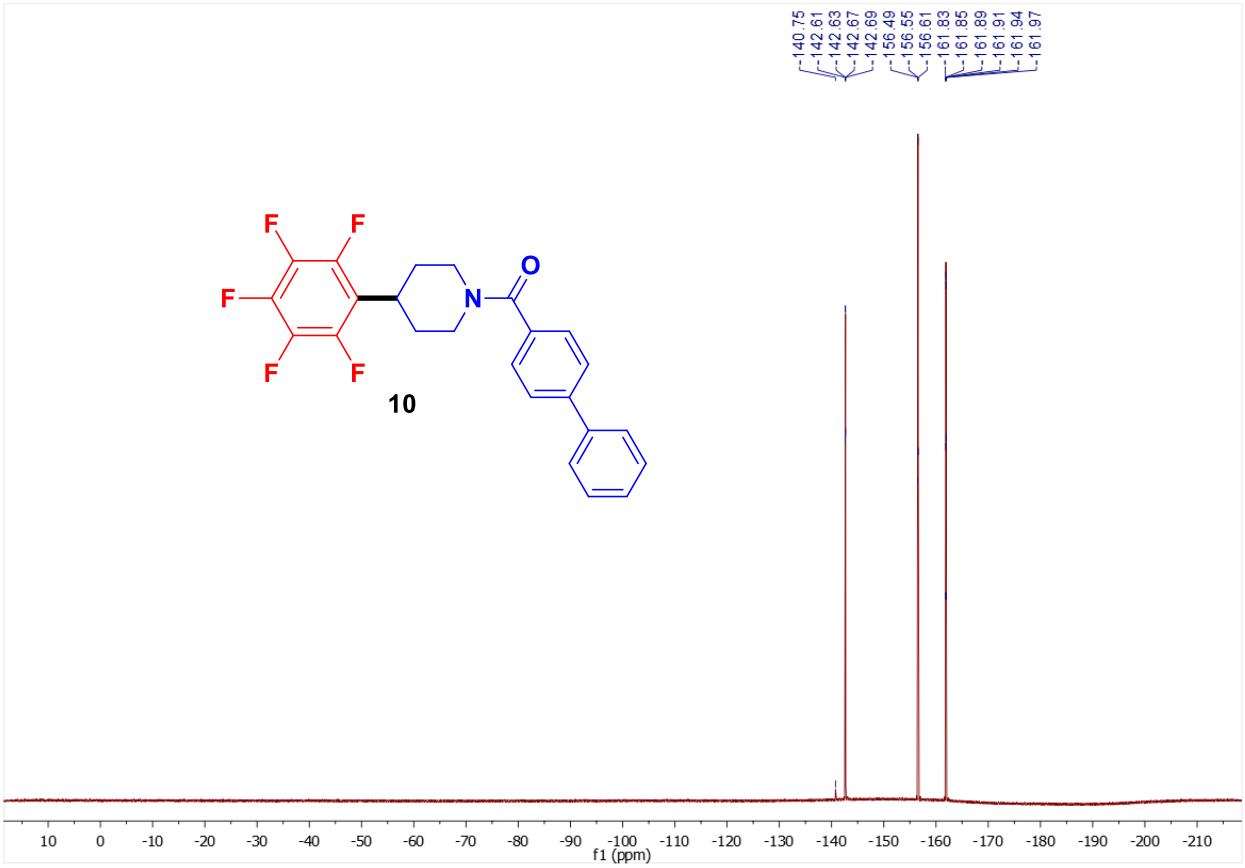
^{1}H-NMR (400 MHz, $CDCl_3$) of **10**



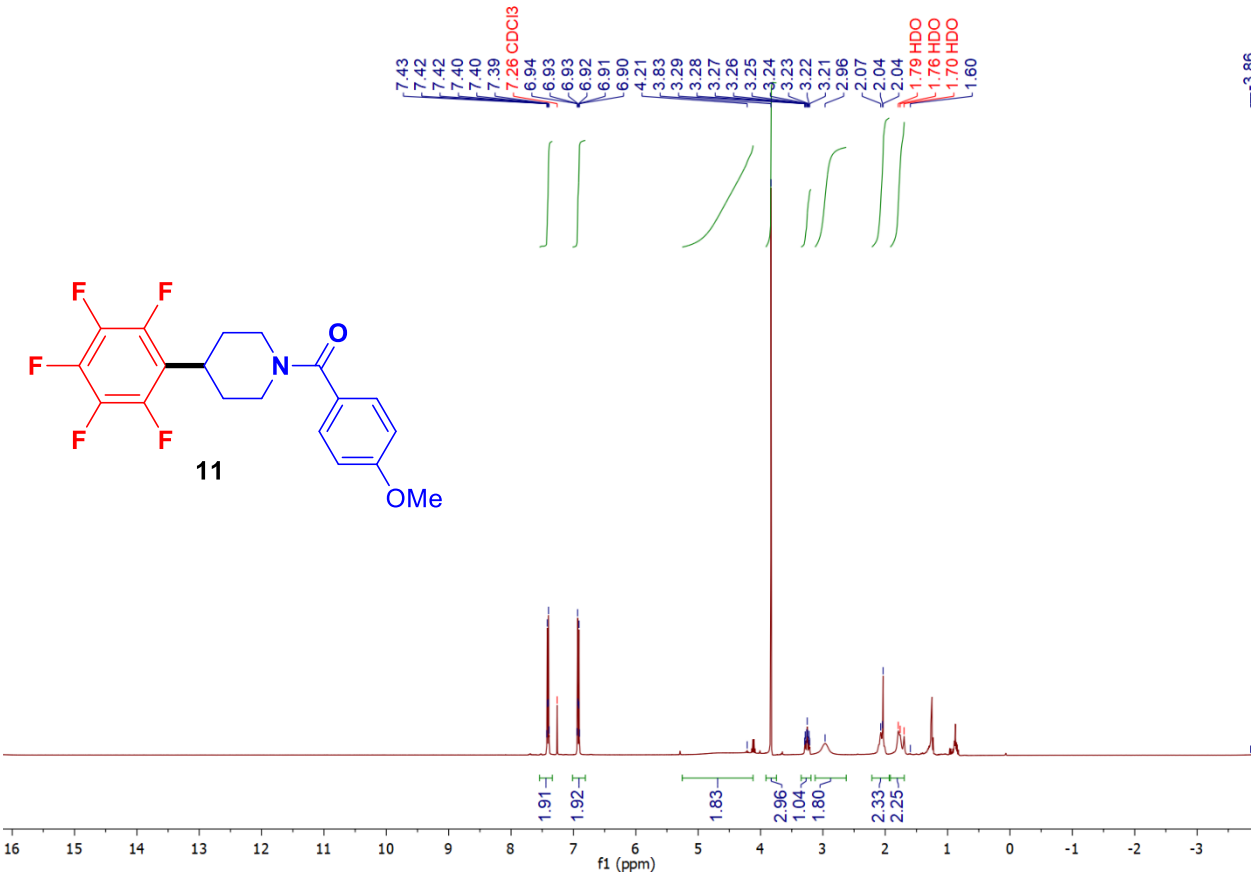
^{13}C-NMR (101 MHz, $CDCl_3$) of **10**



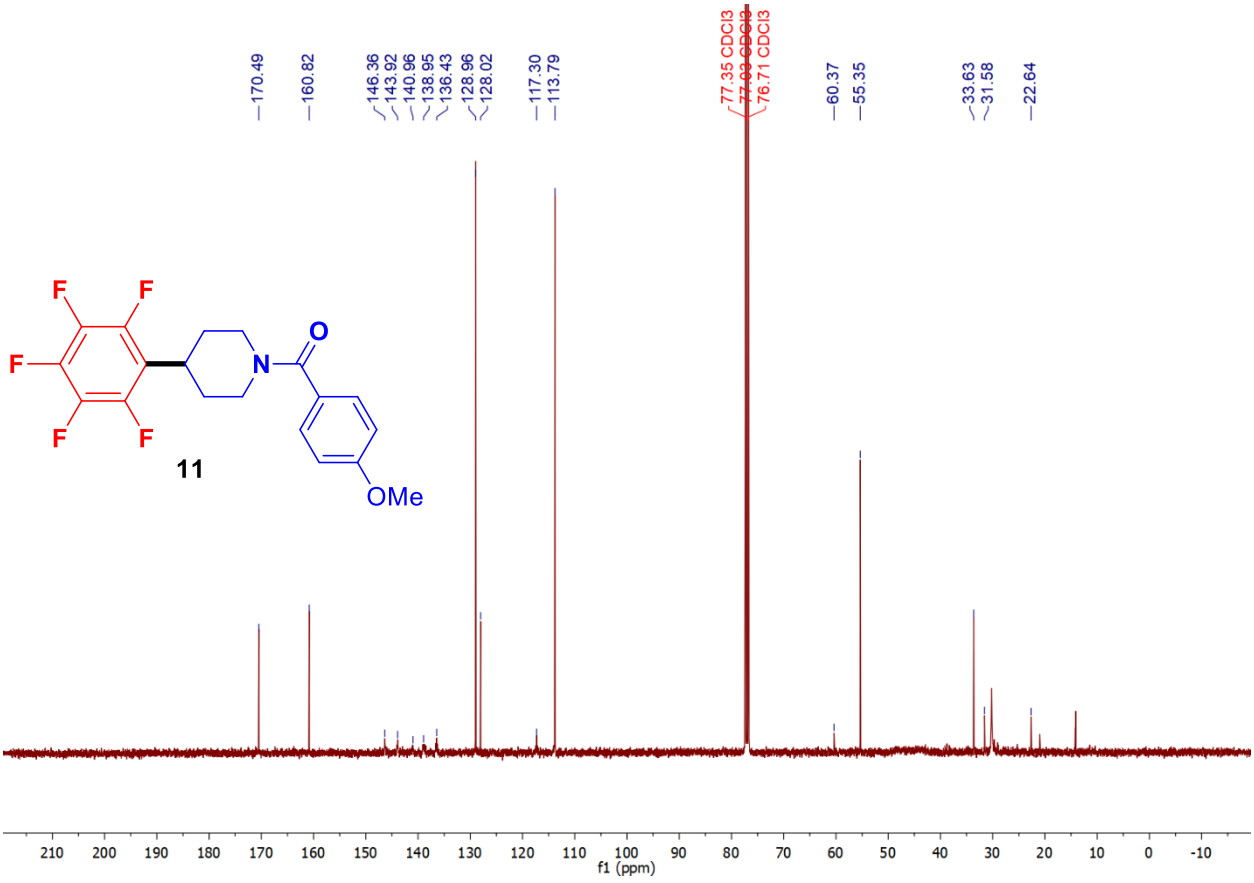
^{19}F-NMR (377 MHz, $CDCl_3$) of **10**



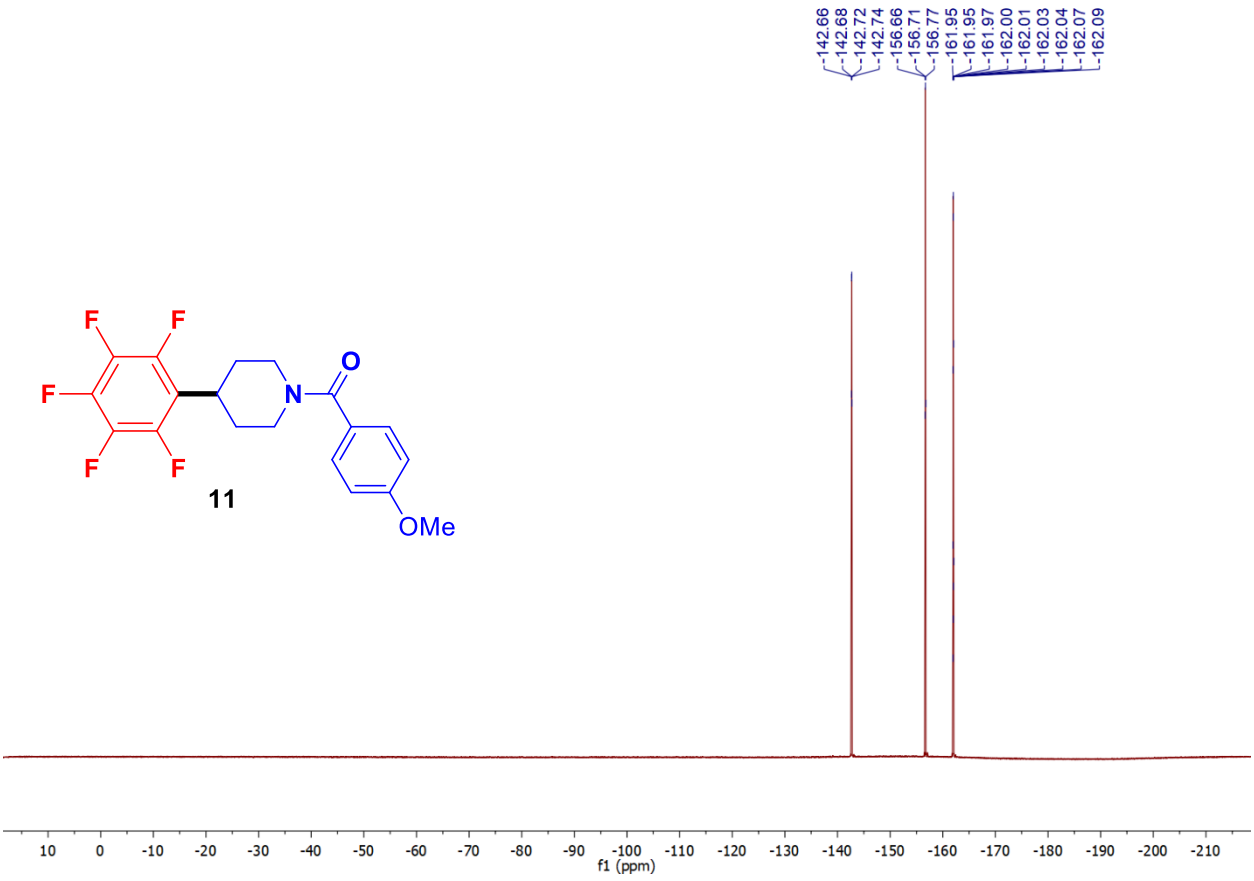
^{1}H-NMR (400 MHz, $CDCl_3$) of **11**



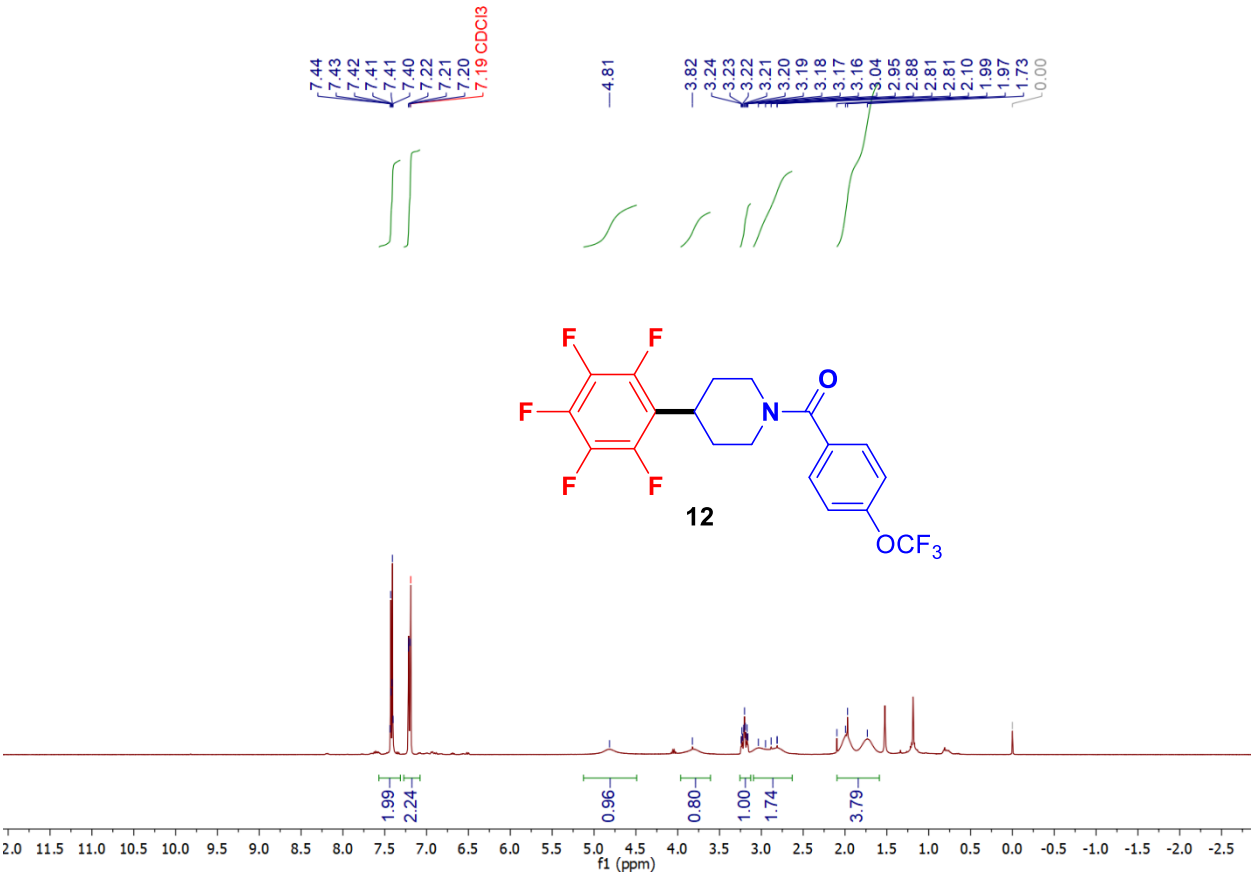
^{13}C-NMR (101 MHz, $CDCl_3$) of **11**



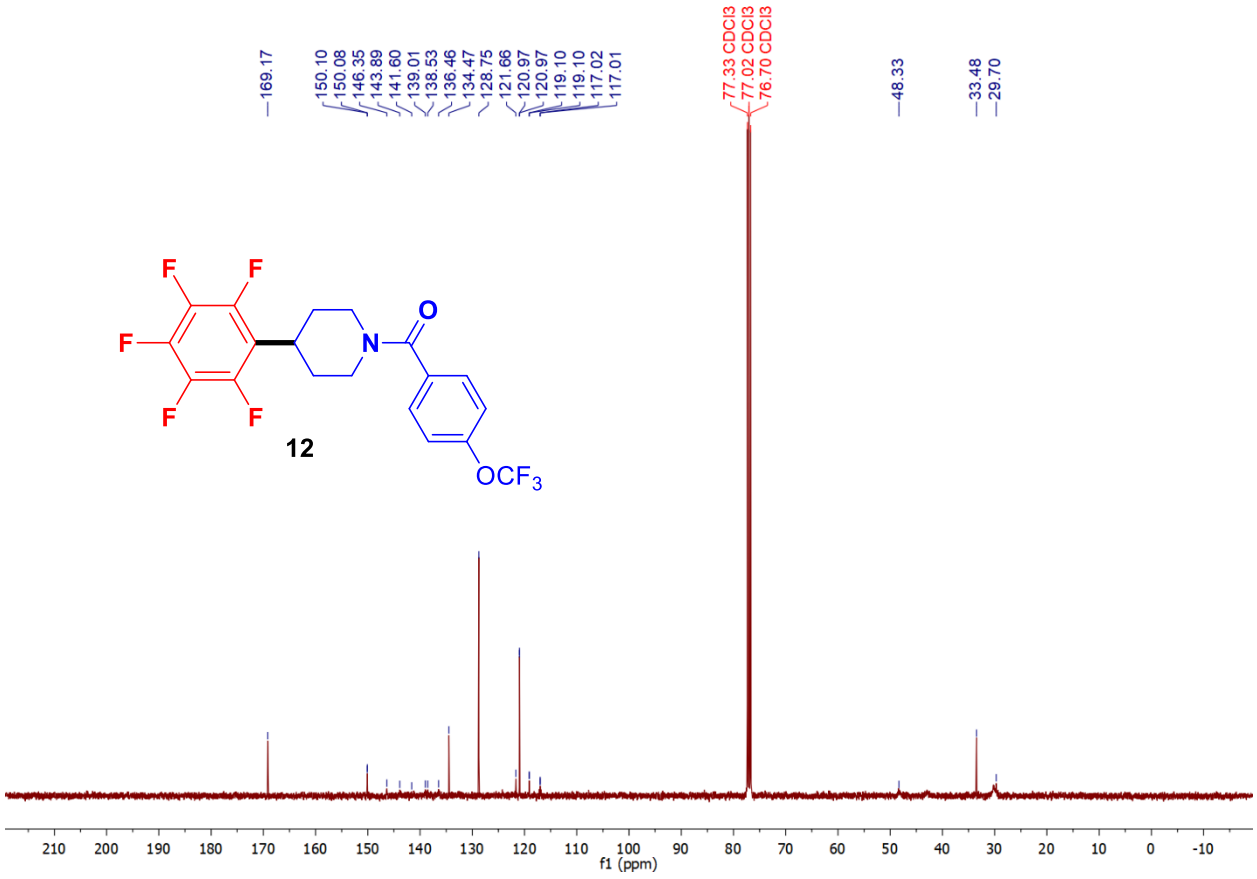
^{19}F-NMR (377 MHz, $CDCl_3$) of **11**



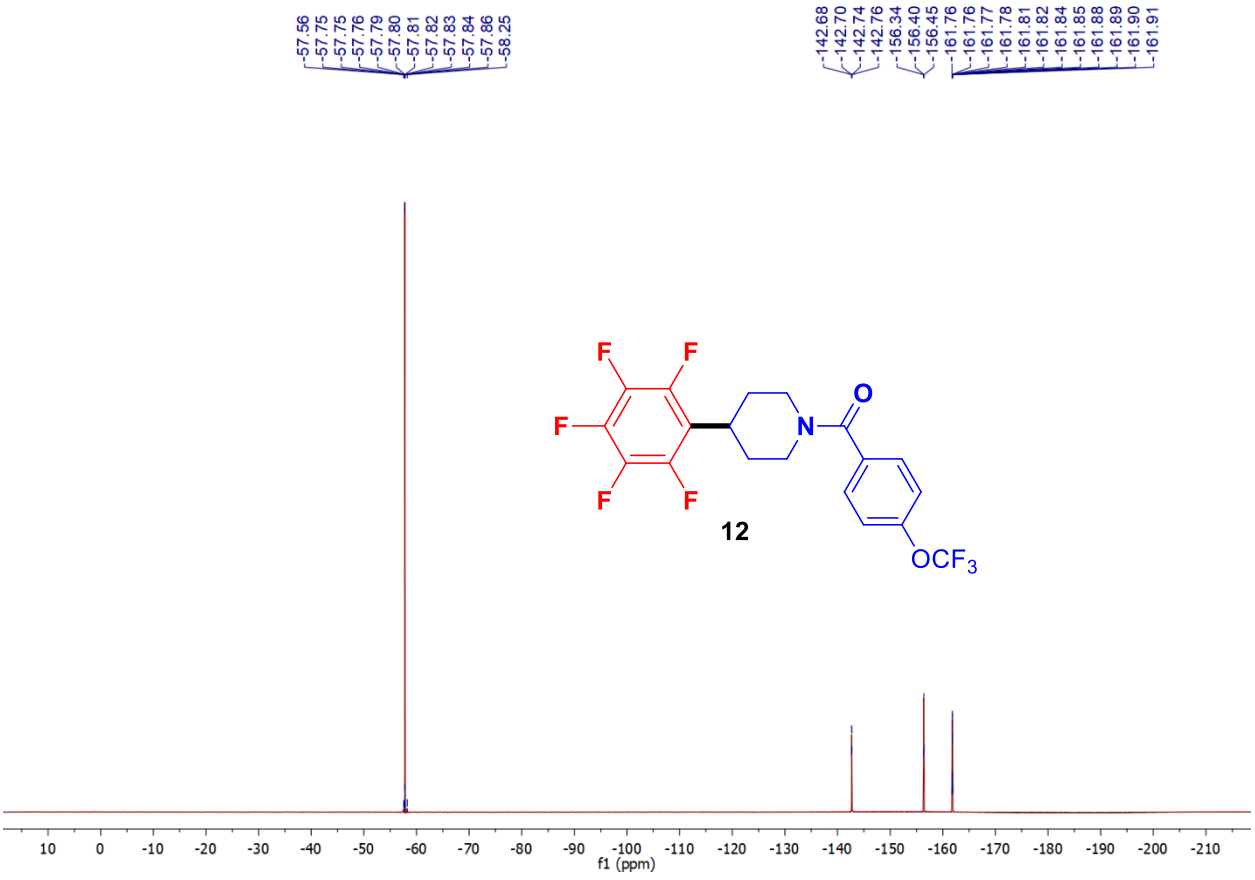
^{1}H-NMR (400 MHz, $CDCl_3$) of **12**



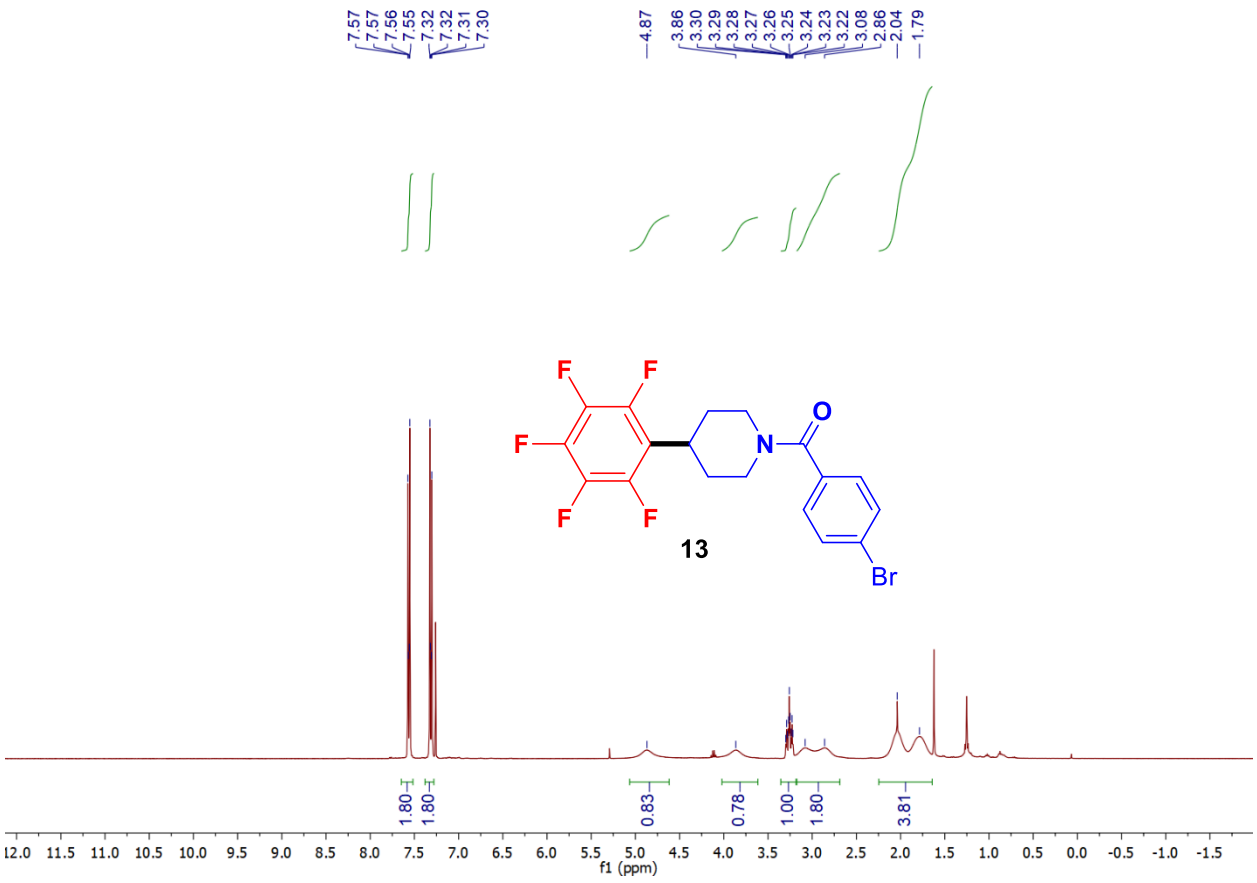
^{13}C-NMR (101 MHz, $CDCl_3$) of **12**



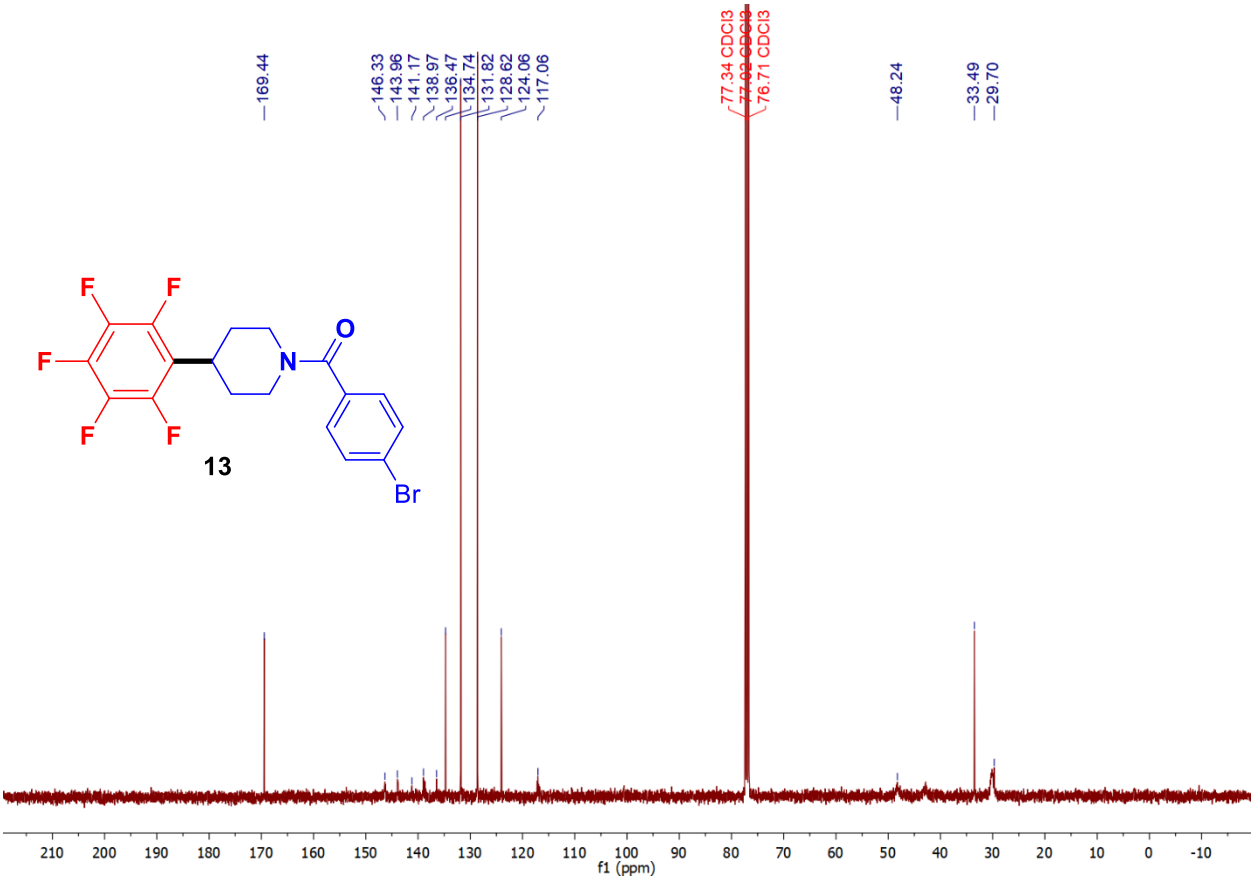
^{19}F-NMR (377 MHz, $CDCl_3$) of **12**



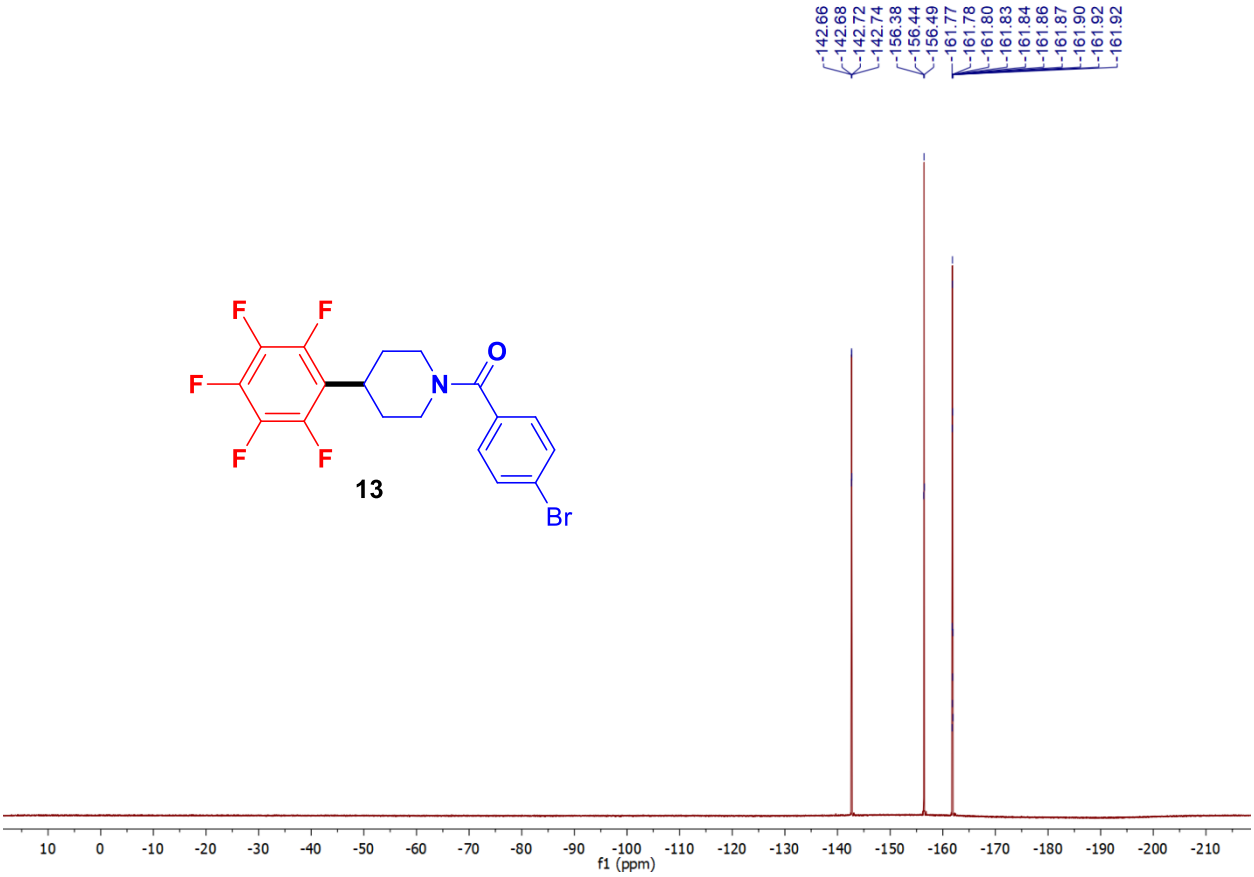
^{1}H-NMR (400 MHz, $CDCl_3$) of **13**



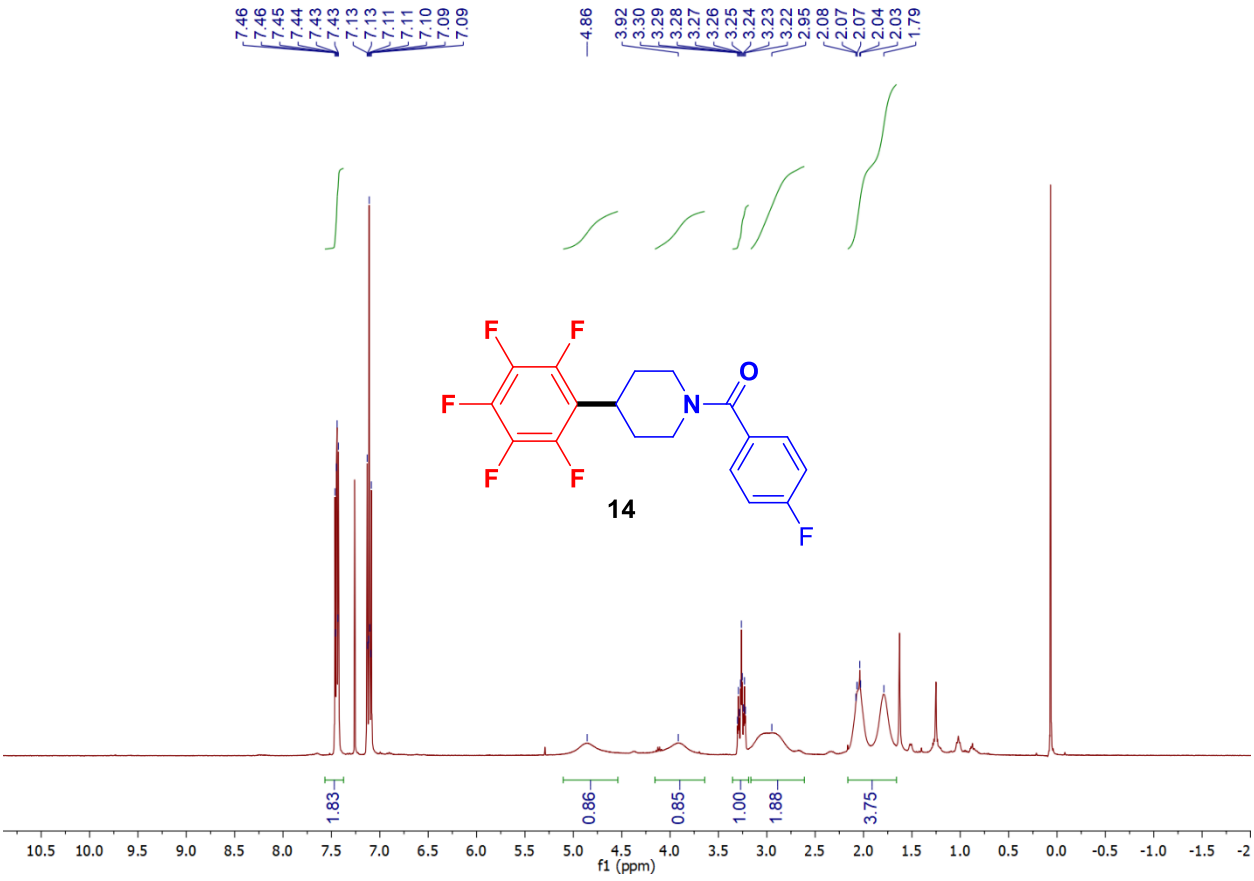
^{13}C-NMR (101 MHz, $CDCl_3$) of **13**



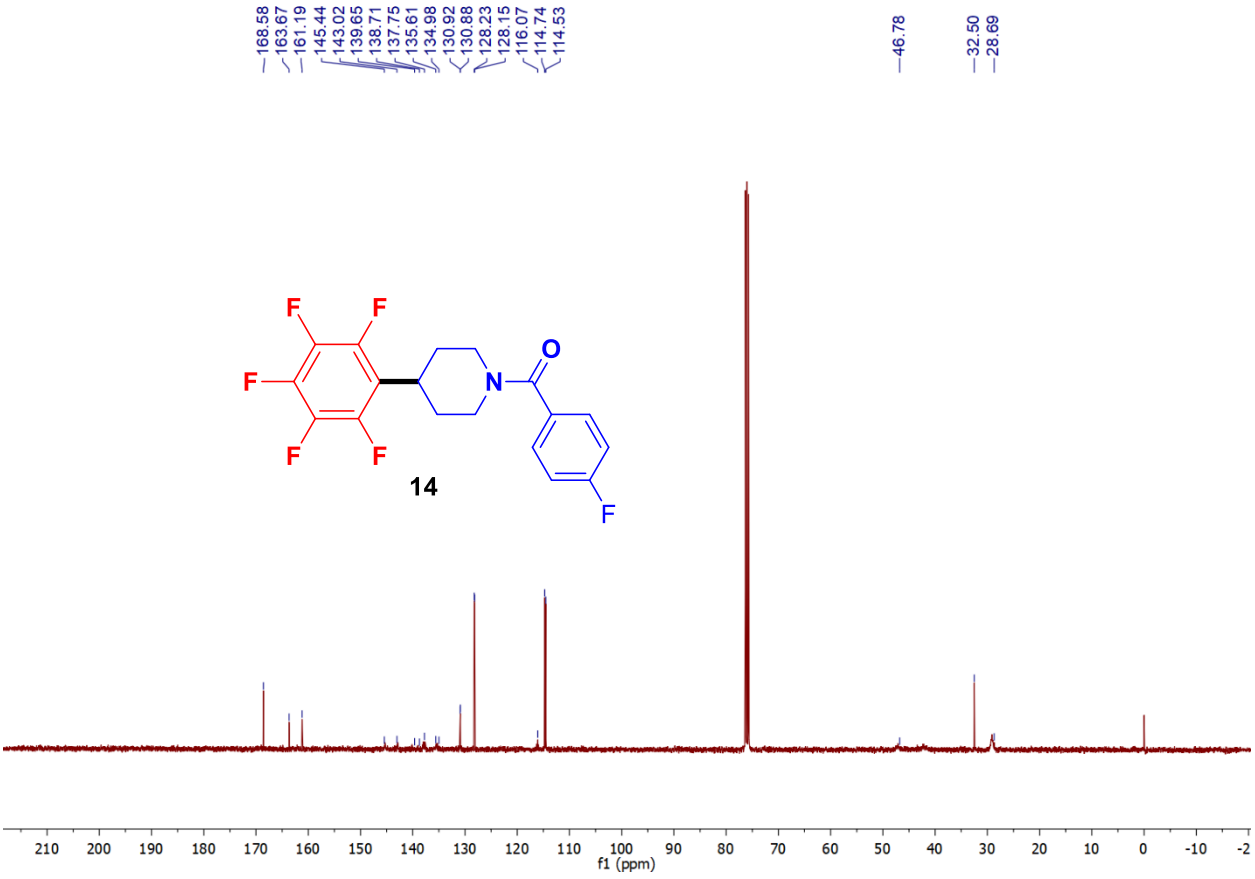
^{19}F-NMR (377 MHz, $CDCl_3$) of **13**



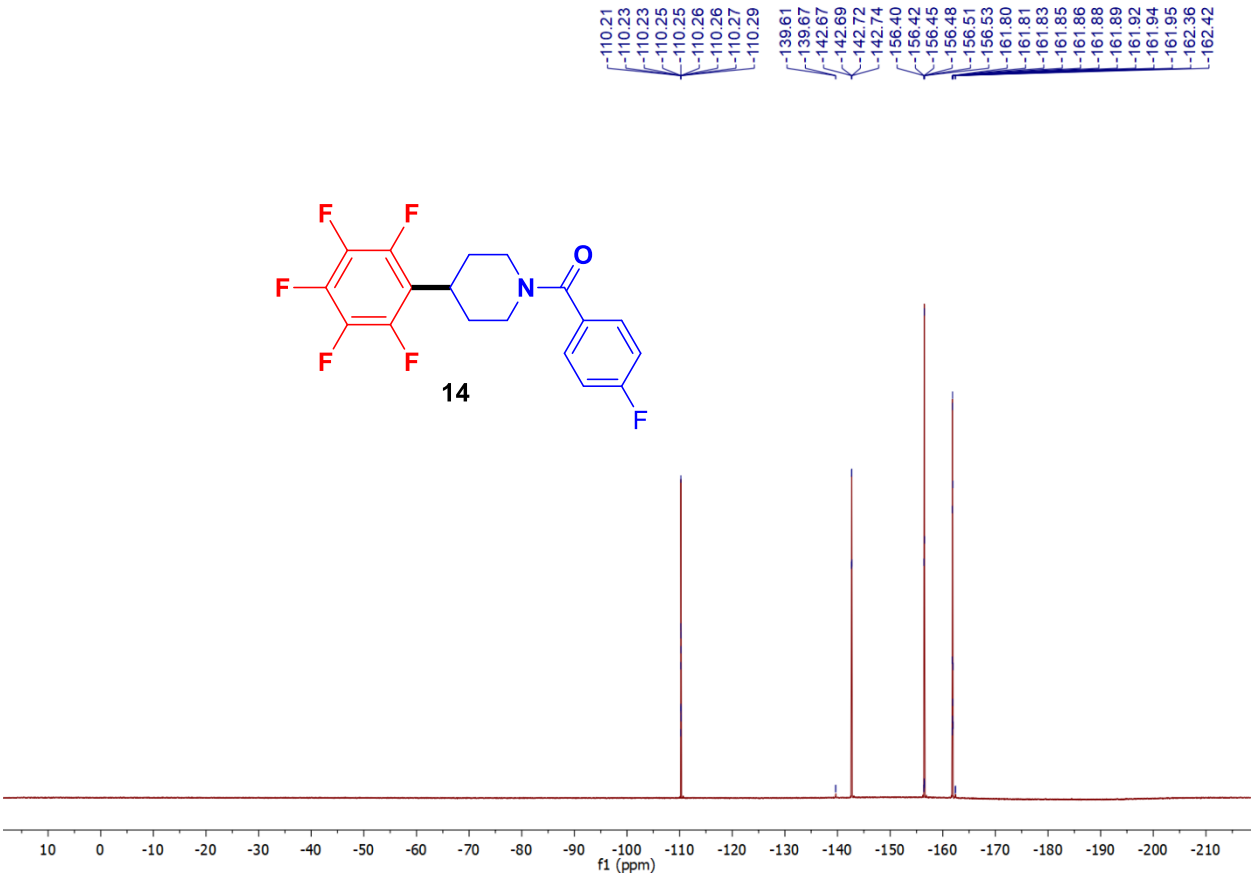
^{1}H-NMR (400 MHz, $CDCl_3$) of **14**



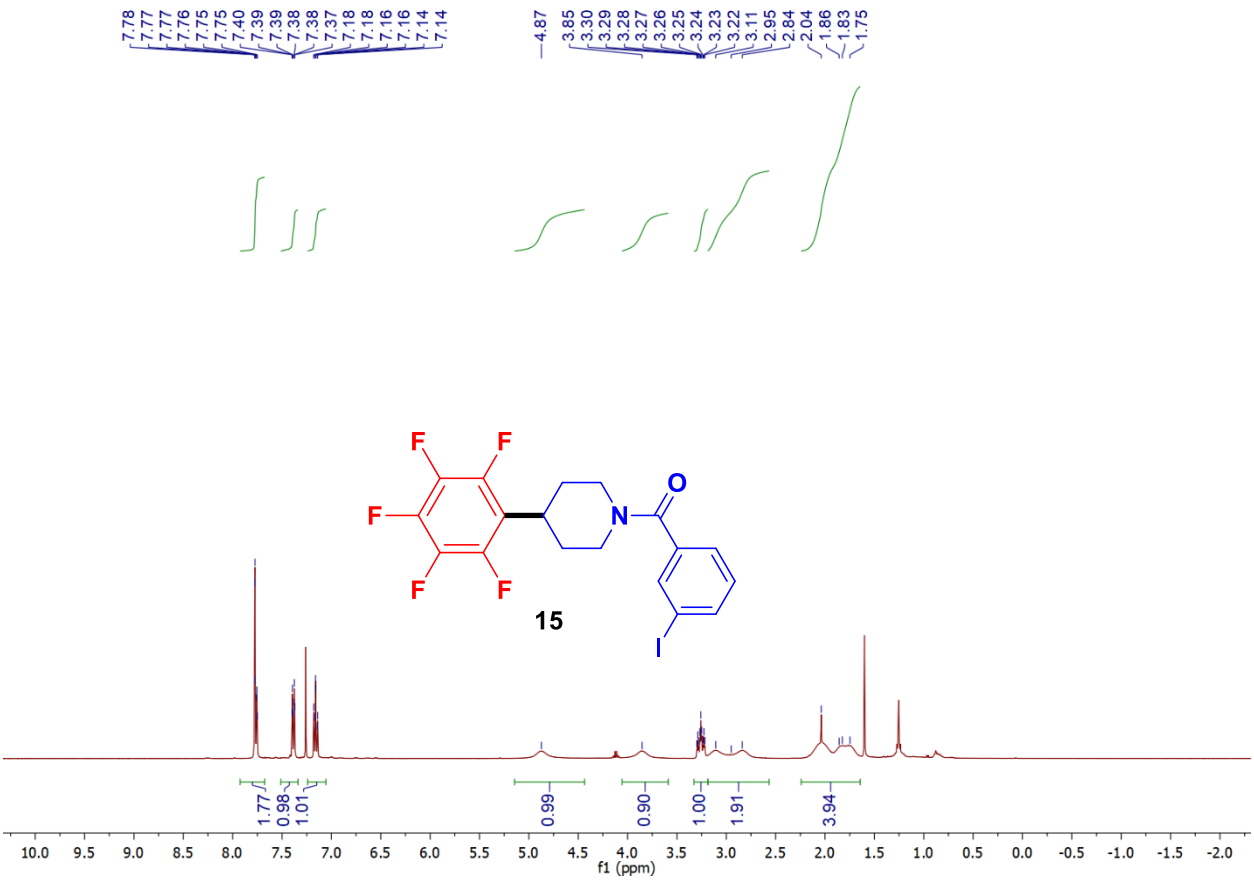
^{13}C-NMR (101 MHz, $CDCl_3$) of **14**



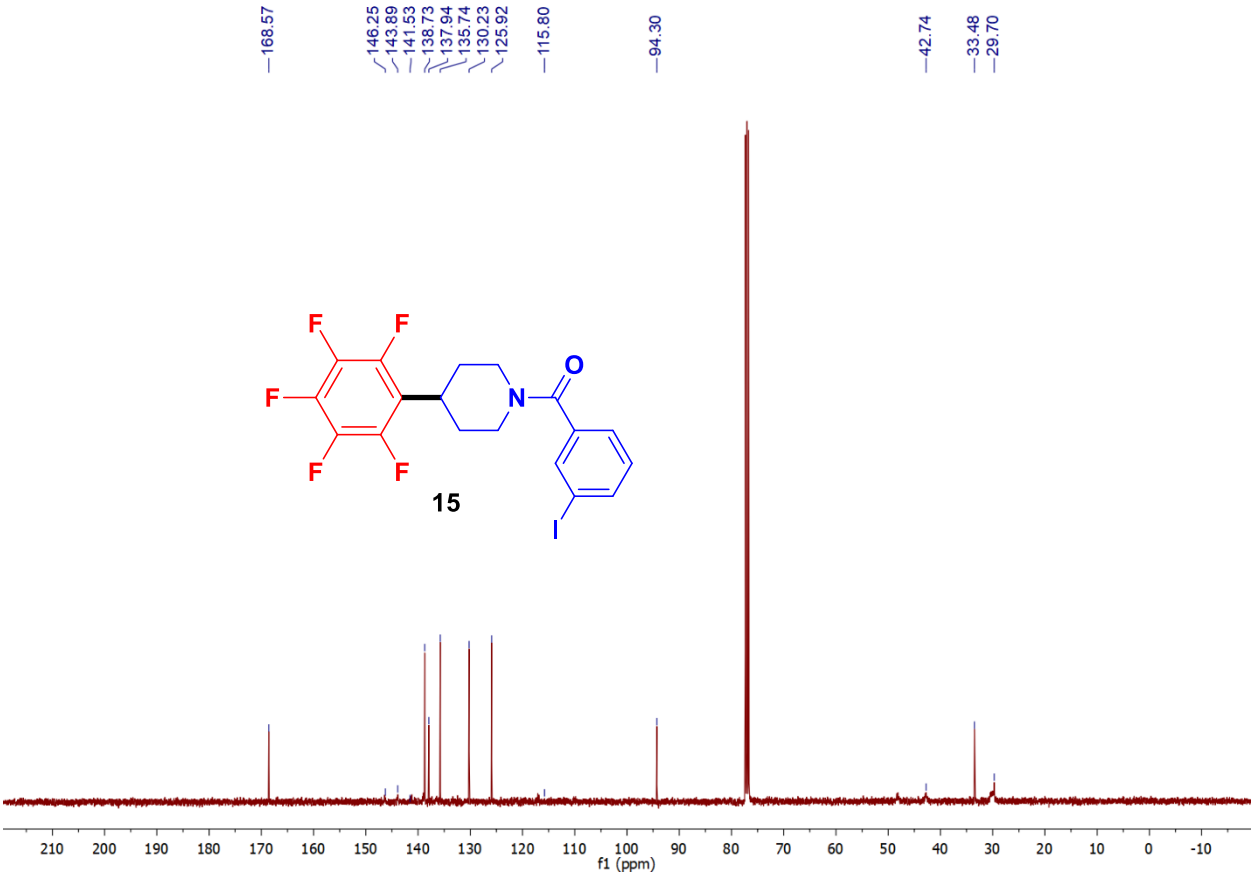
^{19}F-NMR (377 MHz, $CDCl_3$) of **14**



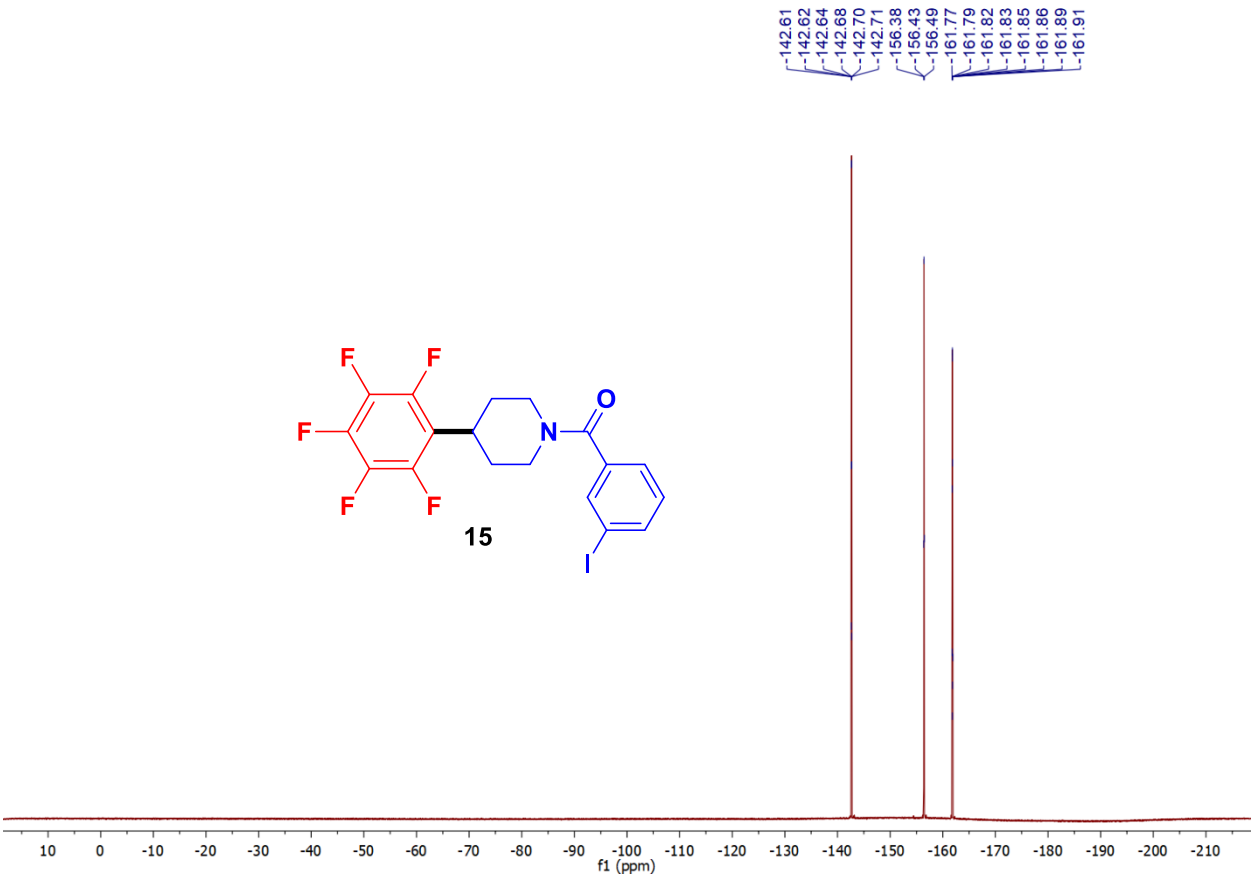
^{1}H-NMR (400 MHz, $CDCl_3$) of **15**



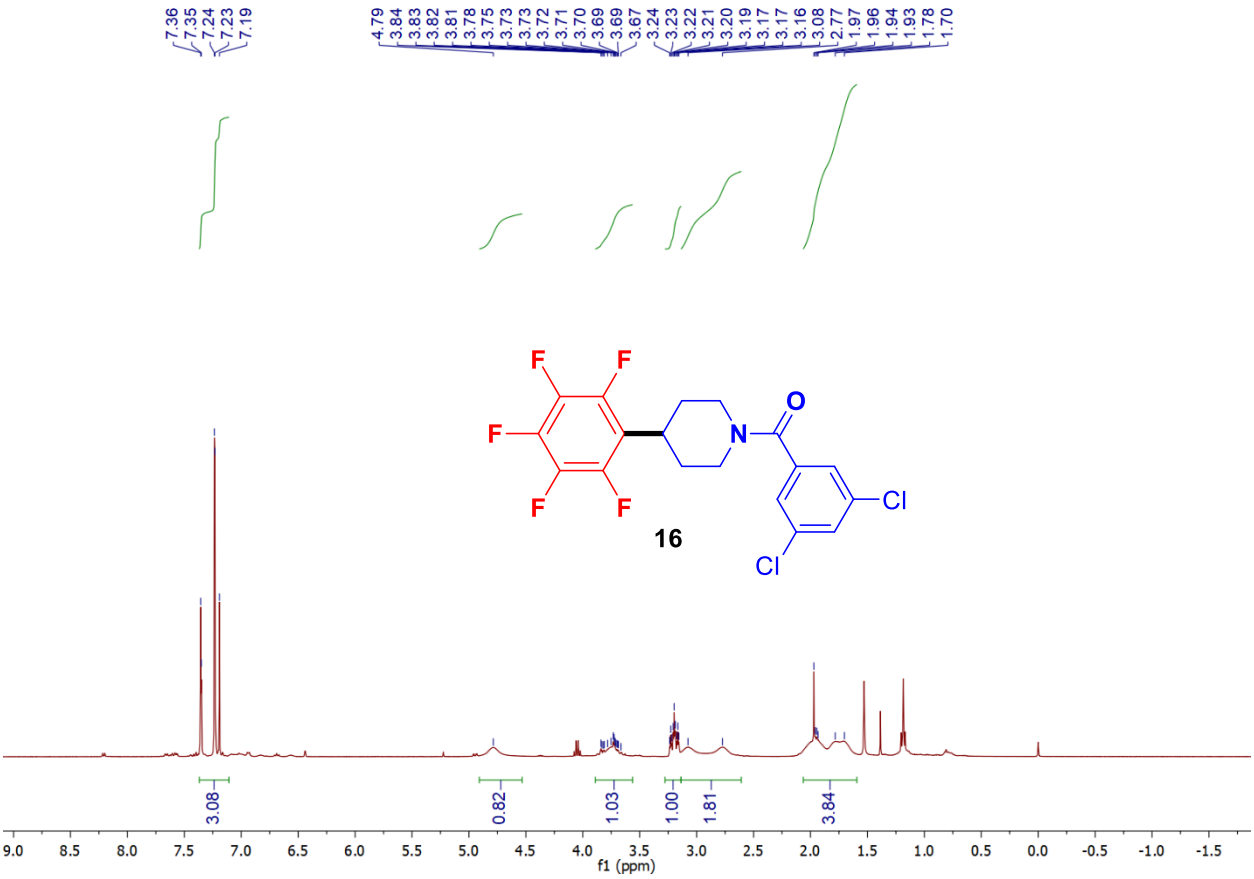
^{13}C-NMR (101 MHz, $CDCl_3$) of **15**



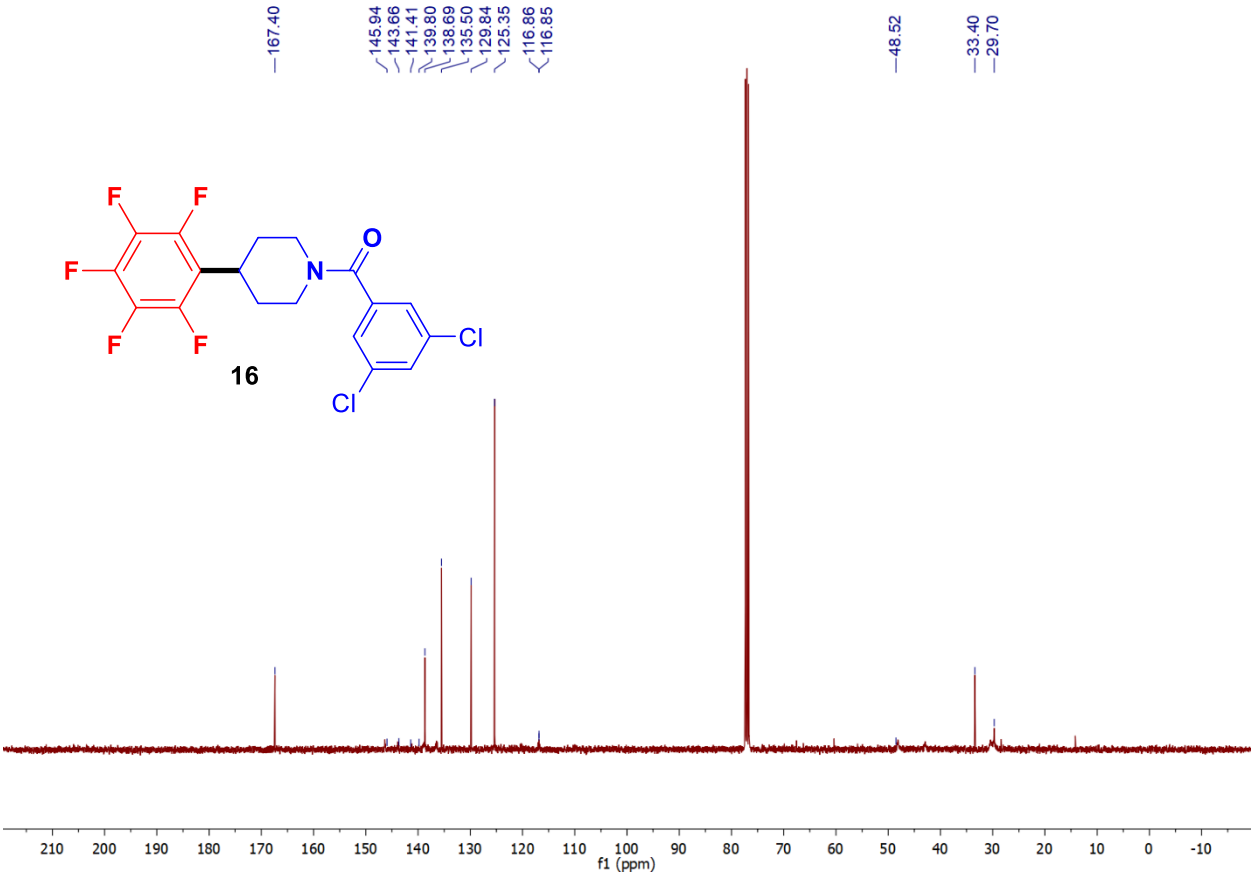
^{19}F-NMR (377 MHz, $CDCl_3$) of **15**



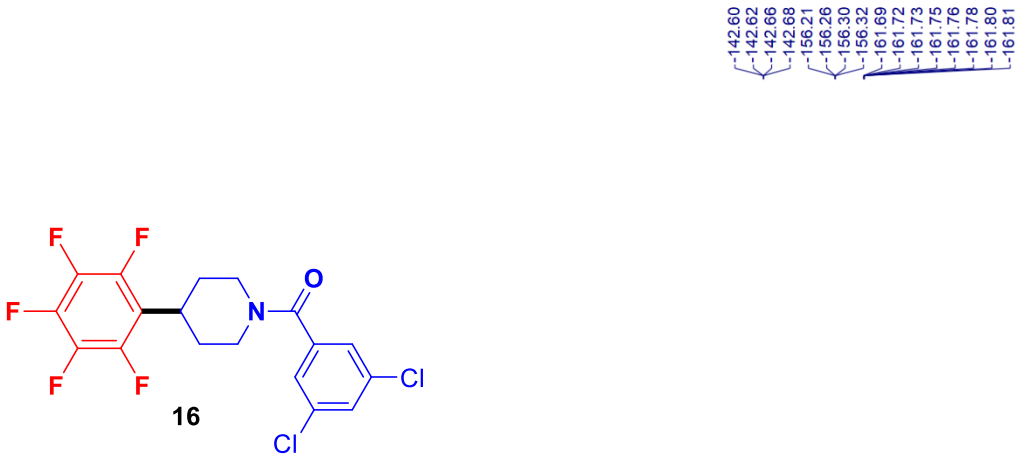
^{1}H-NMR (400 MHz, $CDCl_3$) of 1**6**



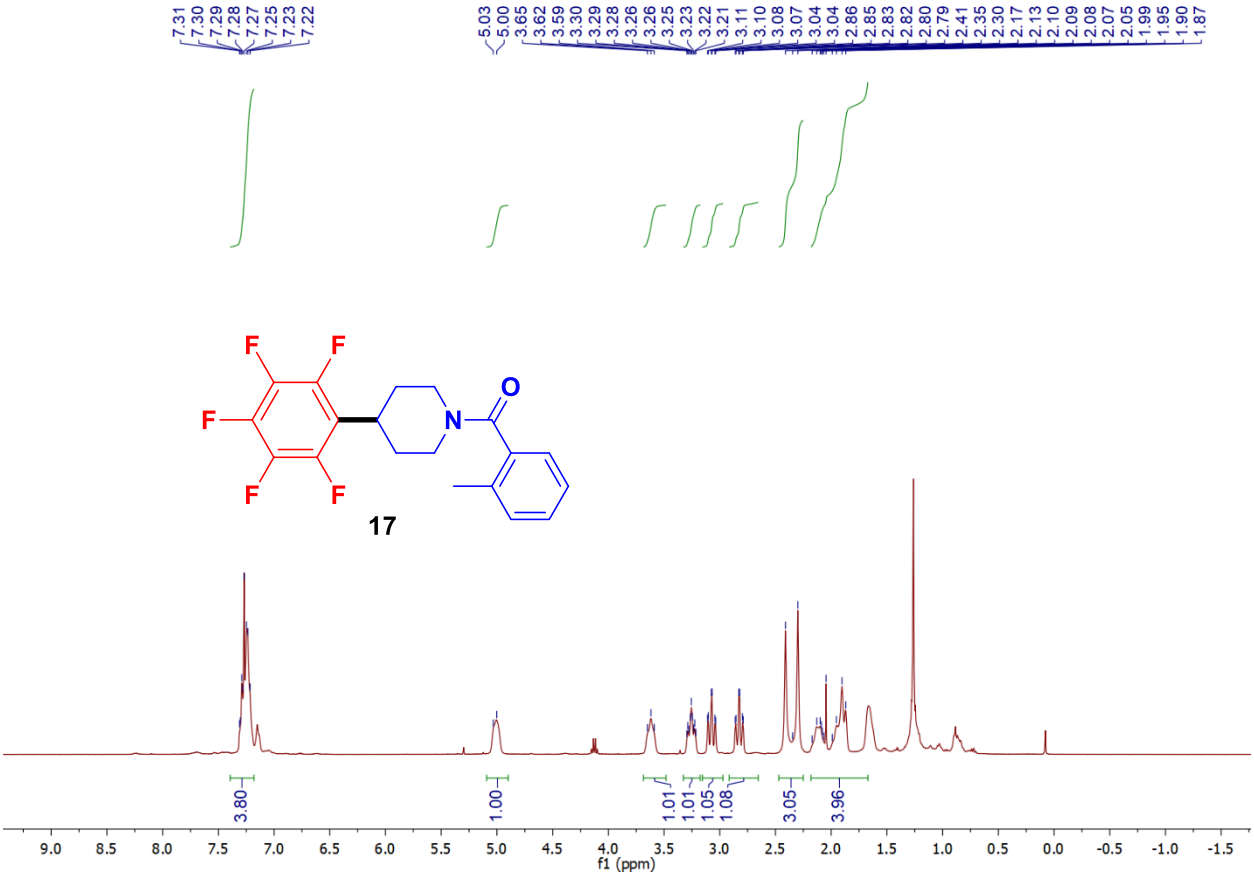
^{13}C-NMR (101 MHz, $CDCl_3$) of **16**



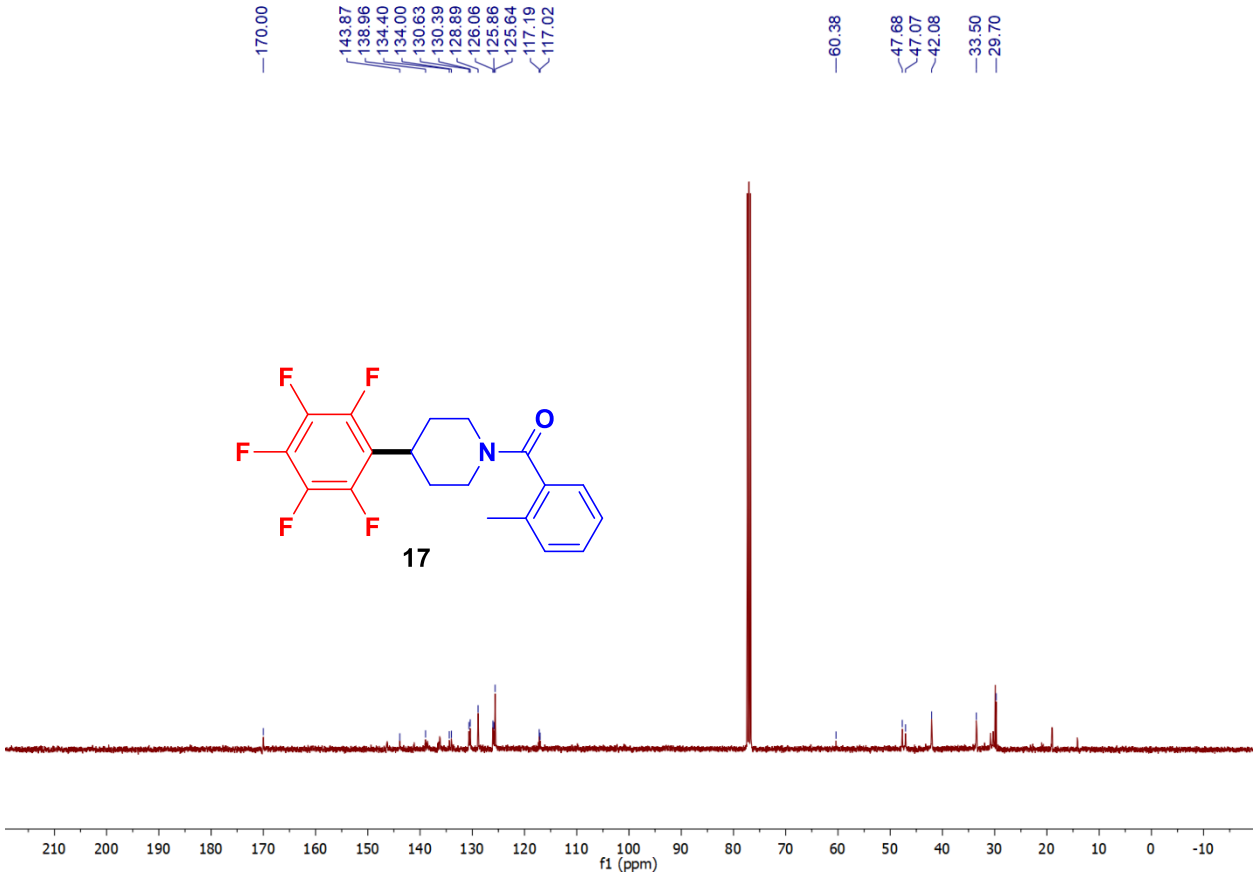
^{19}F-NMR (377 MHz, $CDCl_3$) of **16**



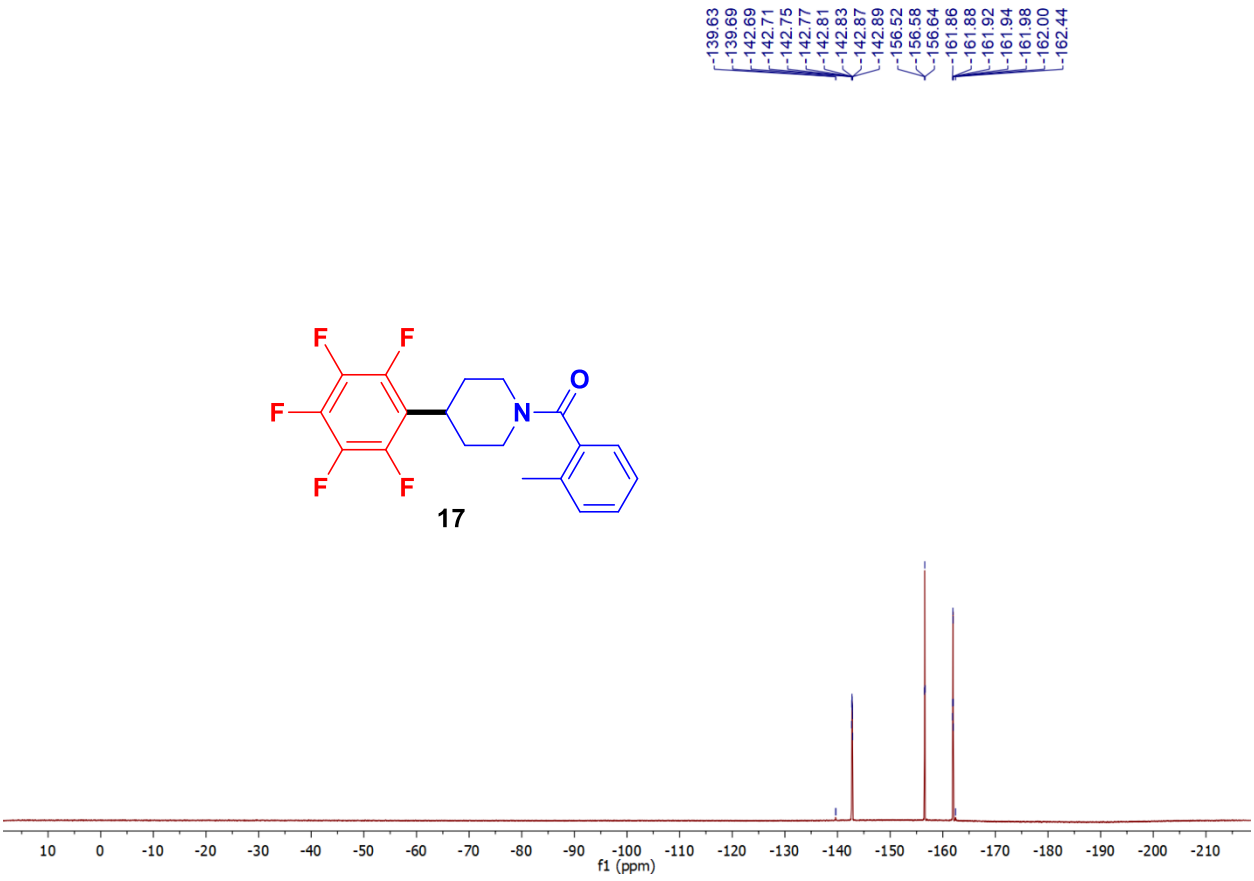
^{1}H-NMR (400 MHz, $CDCl_3$) of **17**



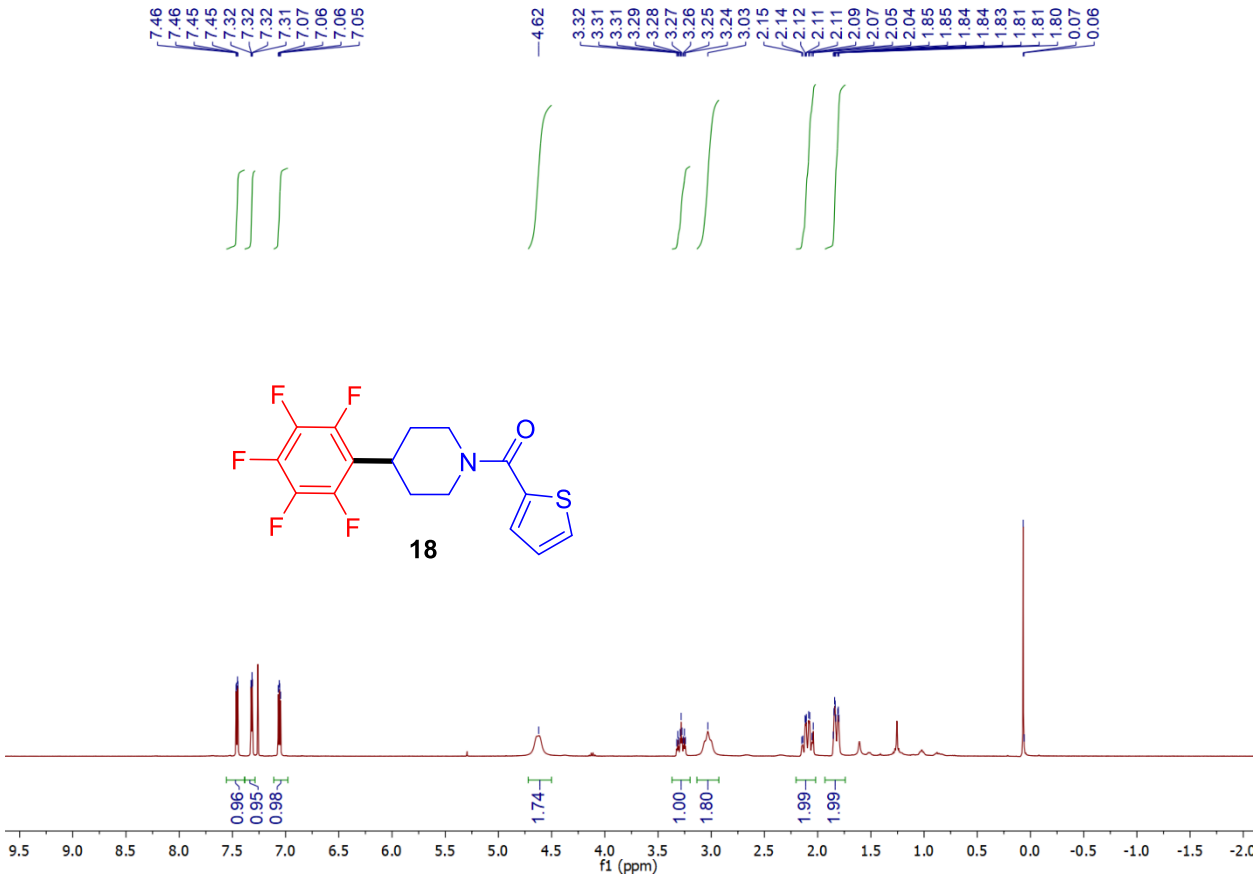
^{13}C-NMR (101 MHz, $CDCl_3$) of **17**



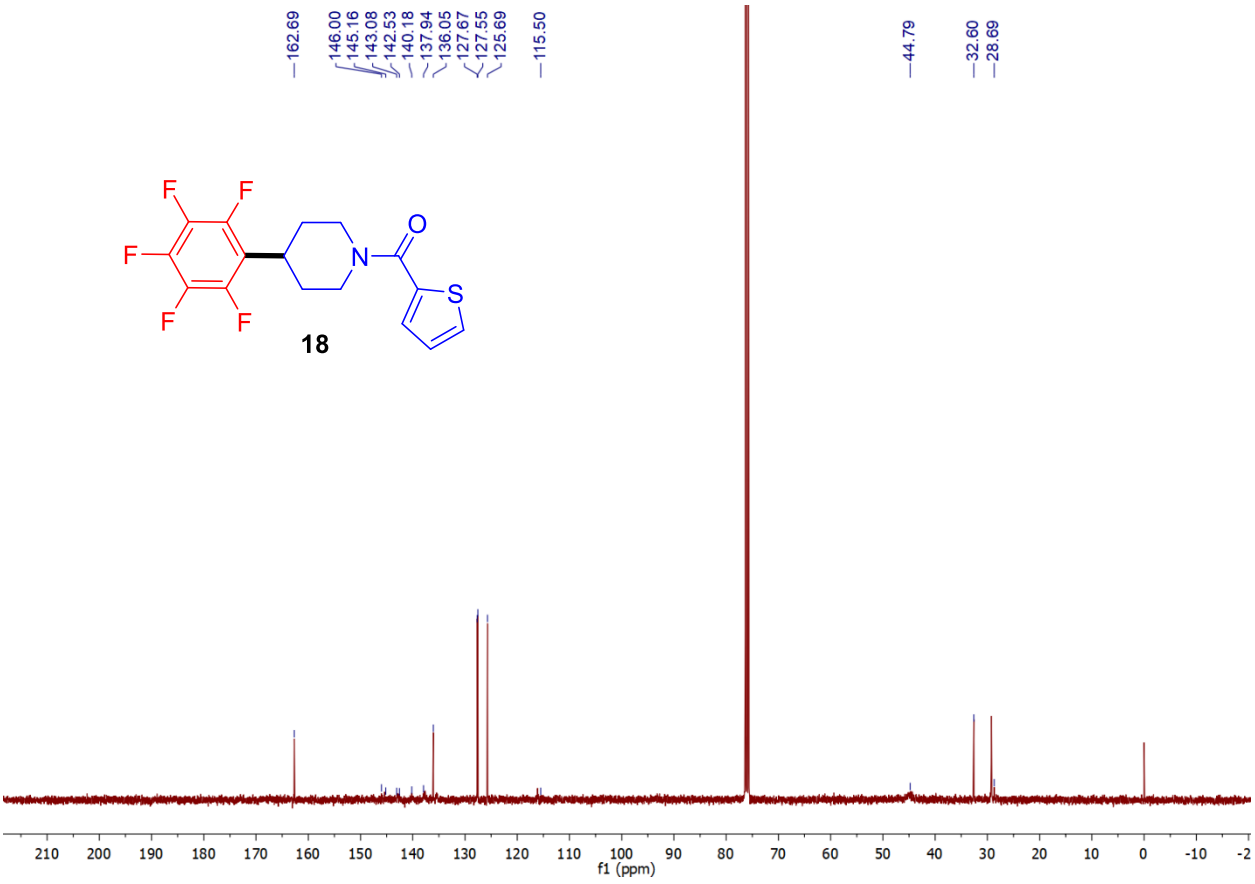
^{19}F-NMR (377 MHz, $CDCl_3$) of **17**



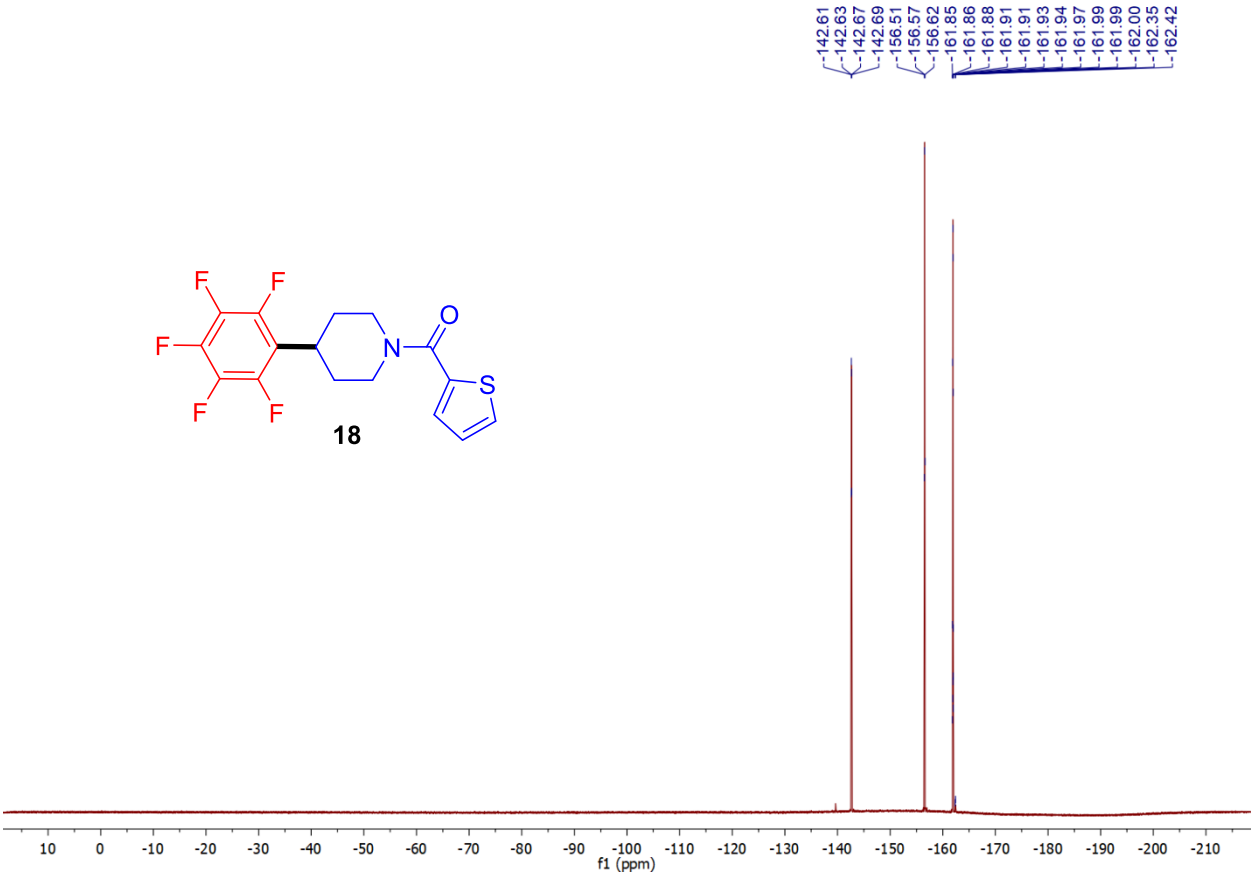
^{1}H-NMR (400 MHz, $CDCl_3$) of **18**



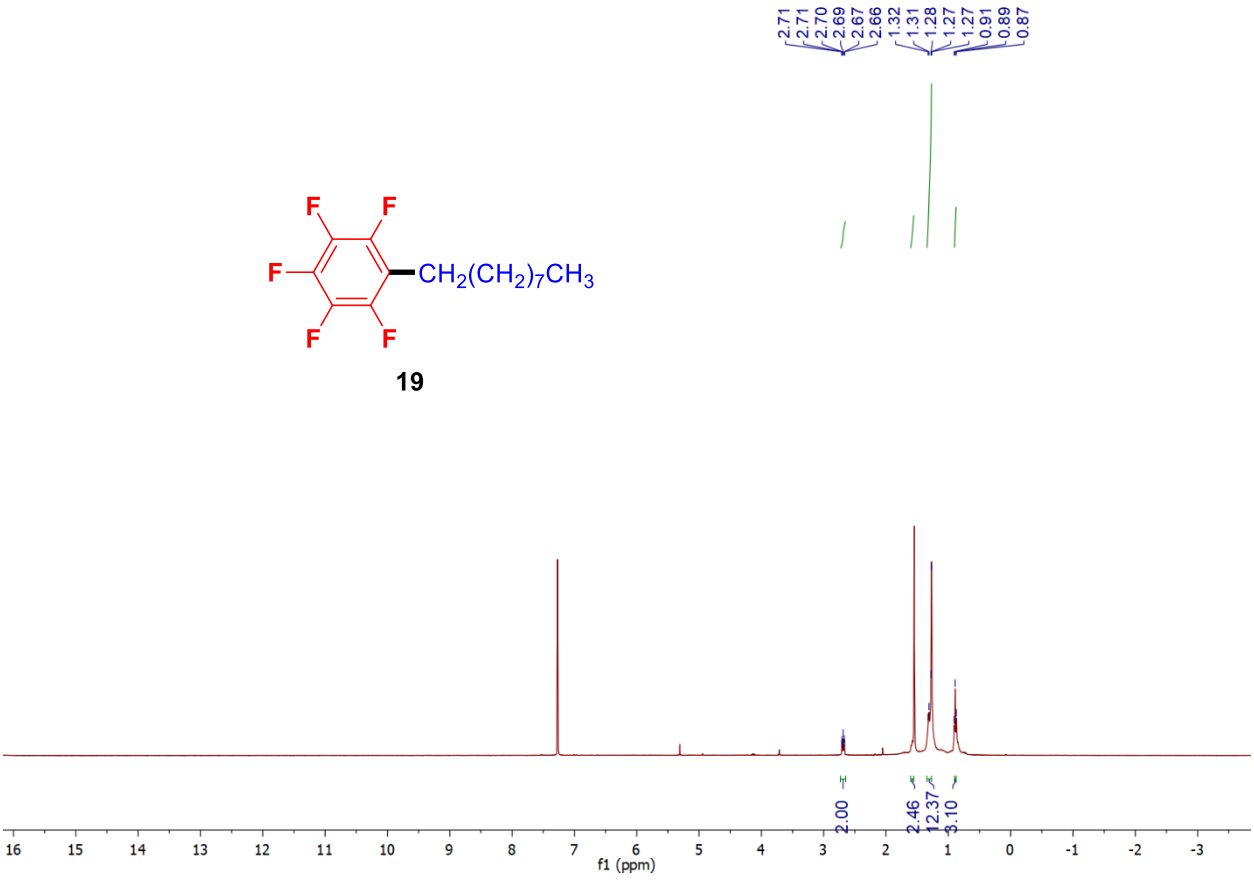
^{13}C-NMR (101 MHz, $CDCl_3$) of **18**



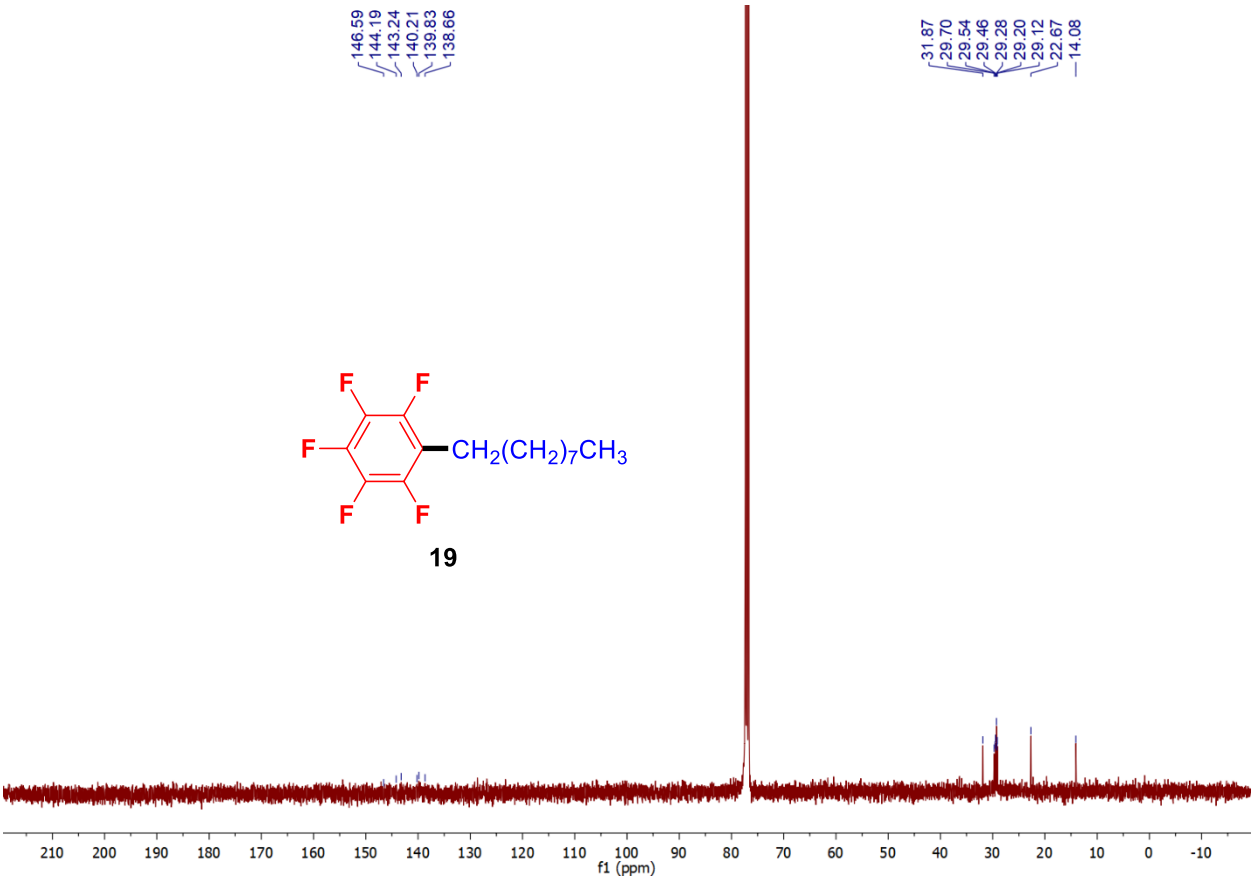
^{19}F-NMR (377 MHz, $CDCl_3$) of **18**



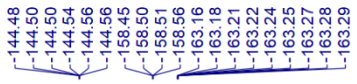
^{1}H-NMR (400 MHz, $CDCl_3$) of **19**

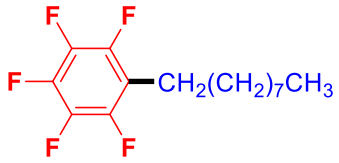


^{13}C-NMR (101 MHz, $CDCl_3$) of **19**



^{19}F-NMR (377 MHz, $CDCl_3$) of **19**





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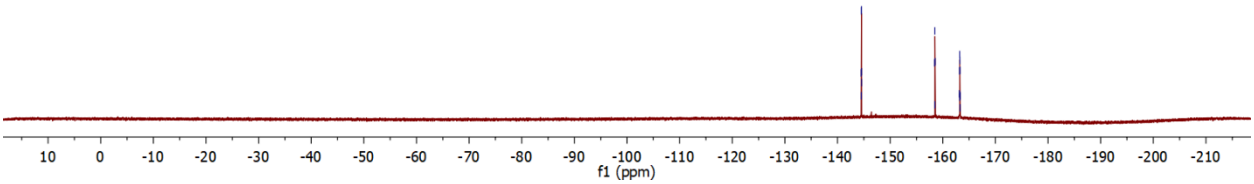
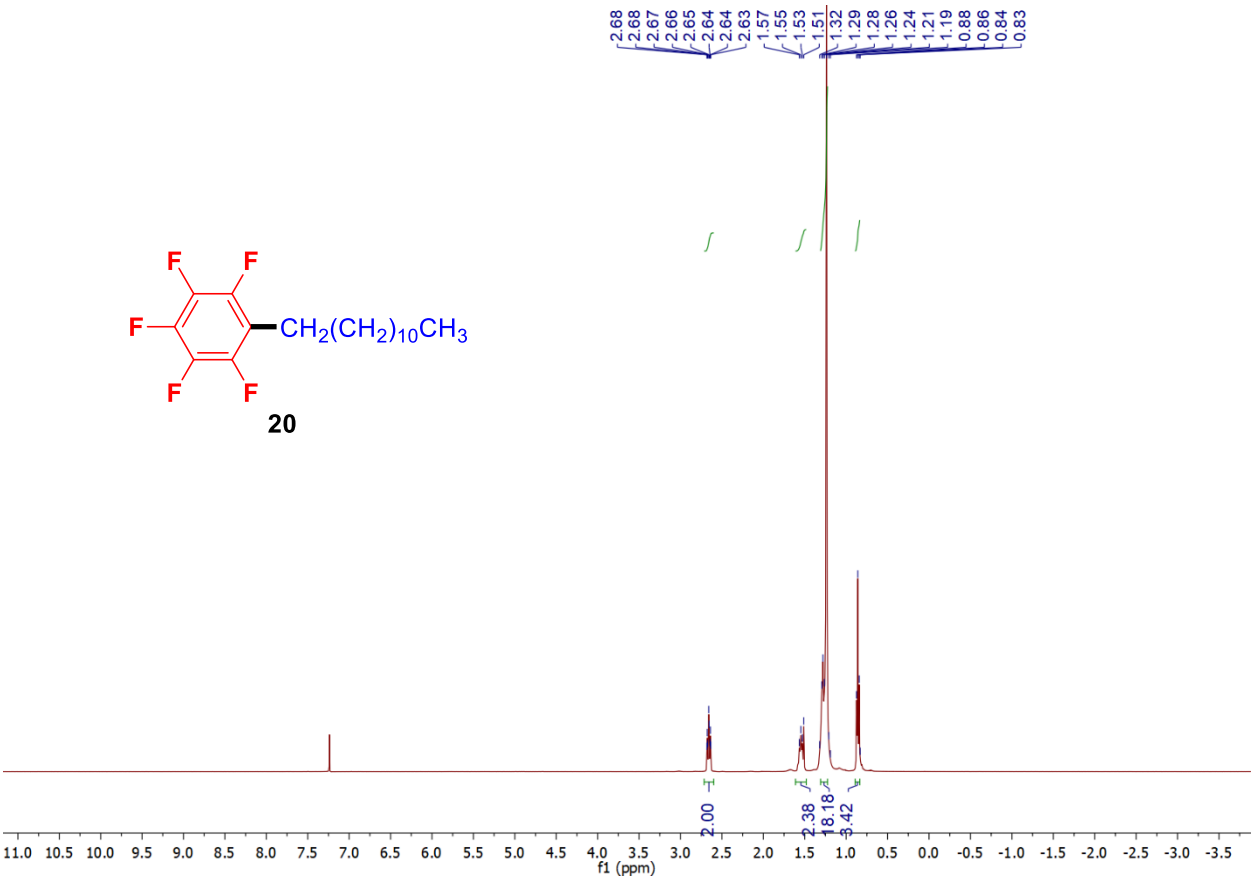
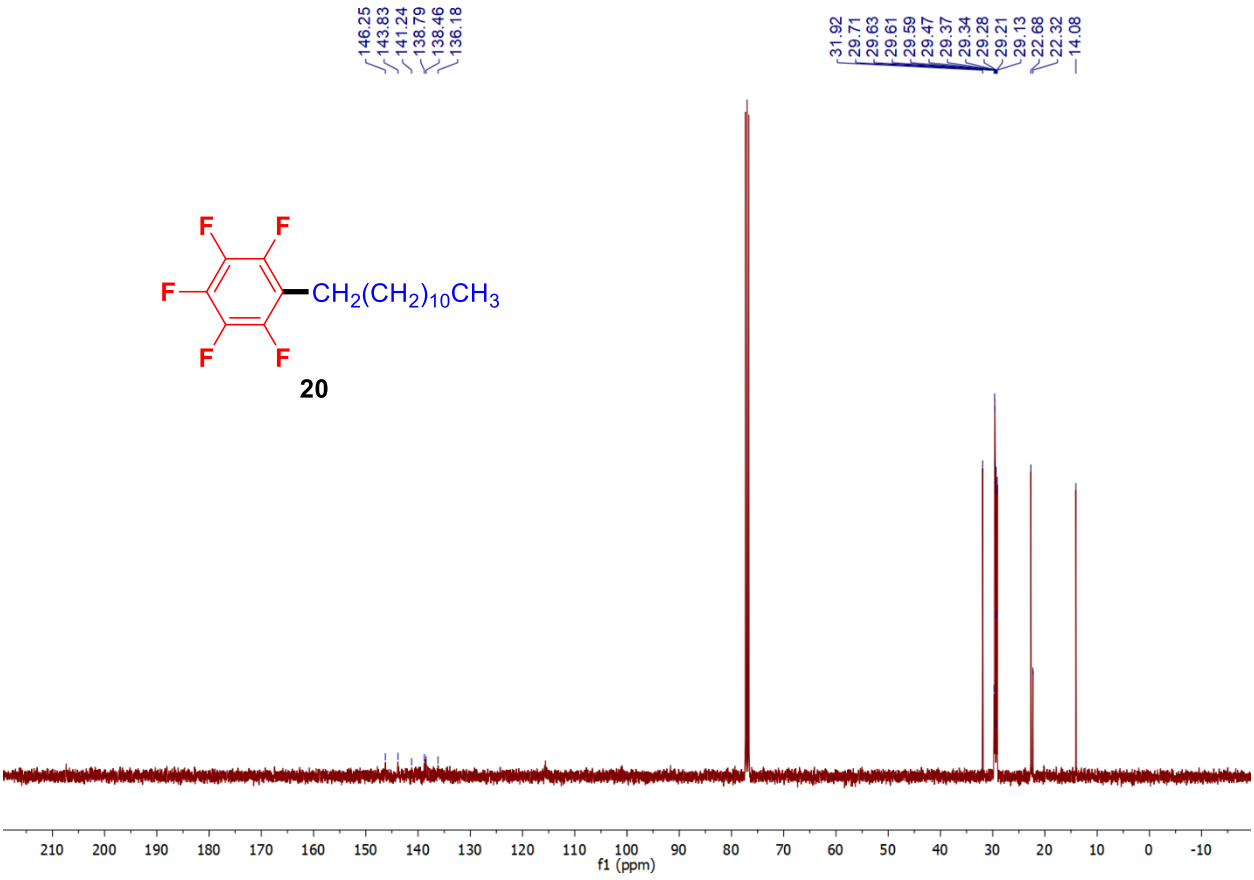


^{1}H-NMR (400 MHz, $CDCl_3$) of **20**



^{13}C-NMR (101 MHz, $CDCl_3$) of **20**



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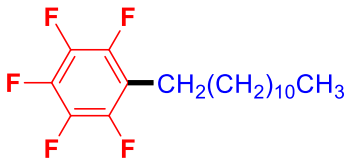

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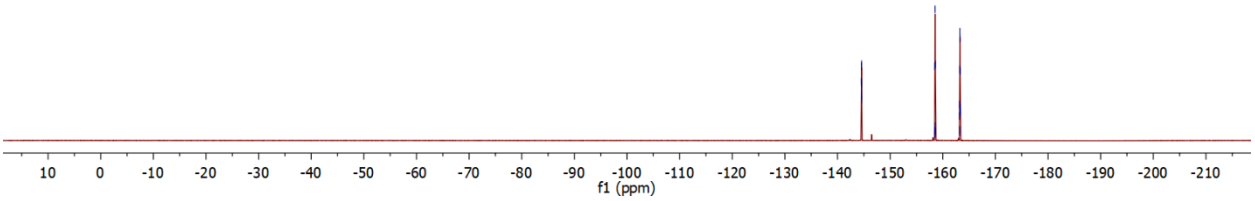
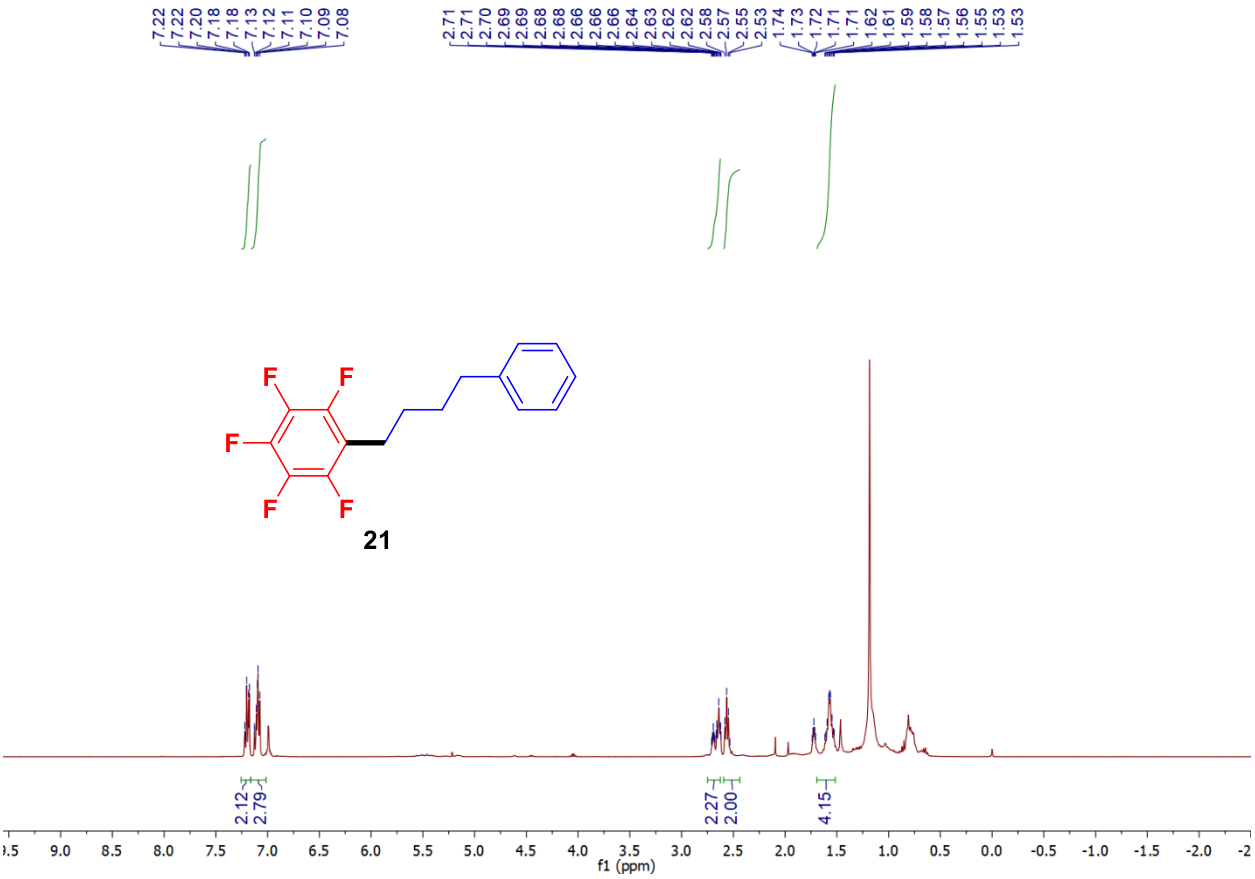
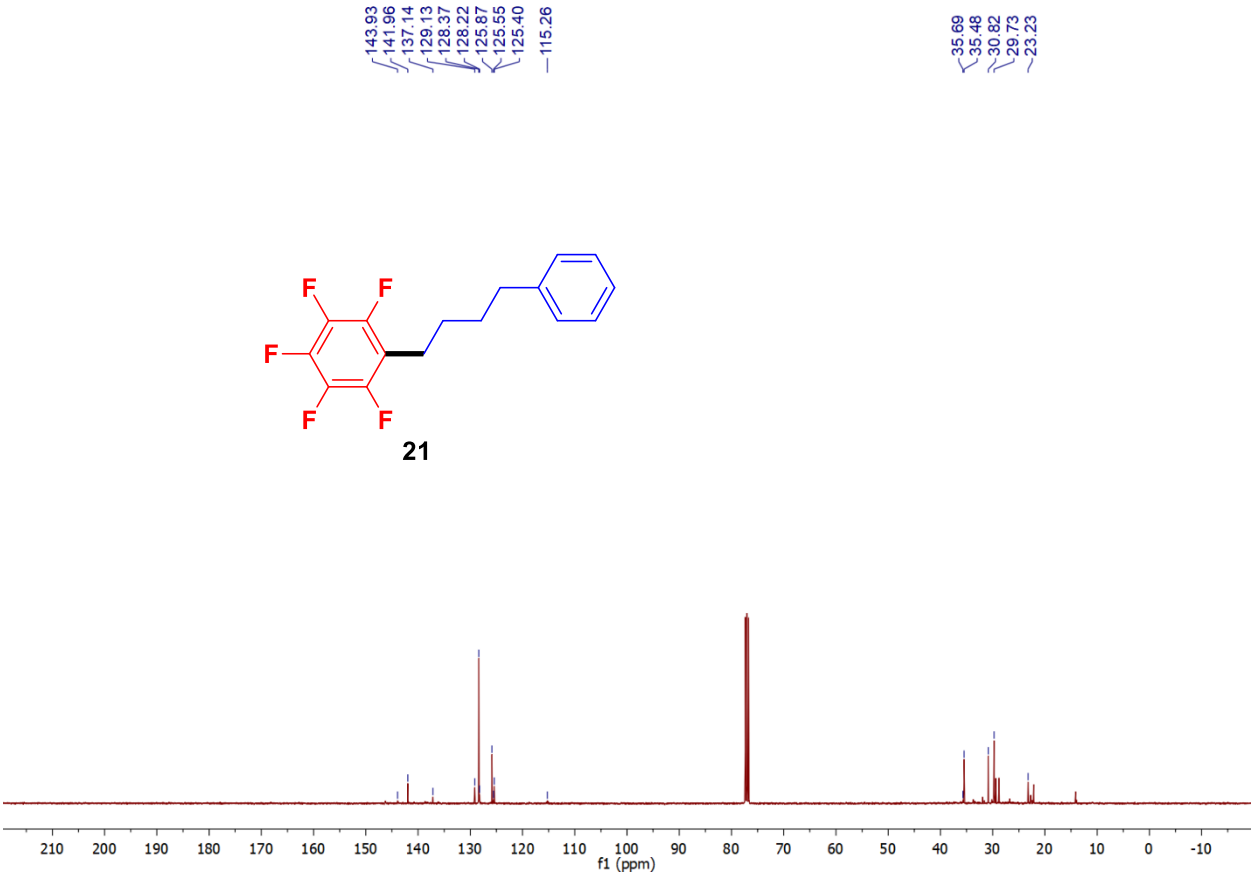


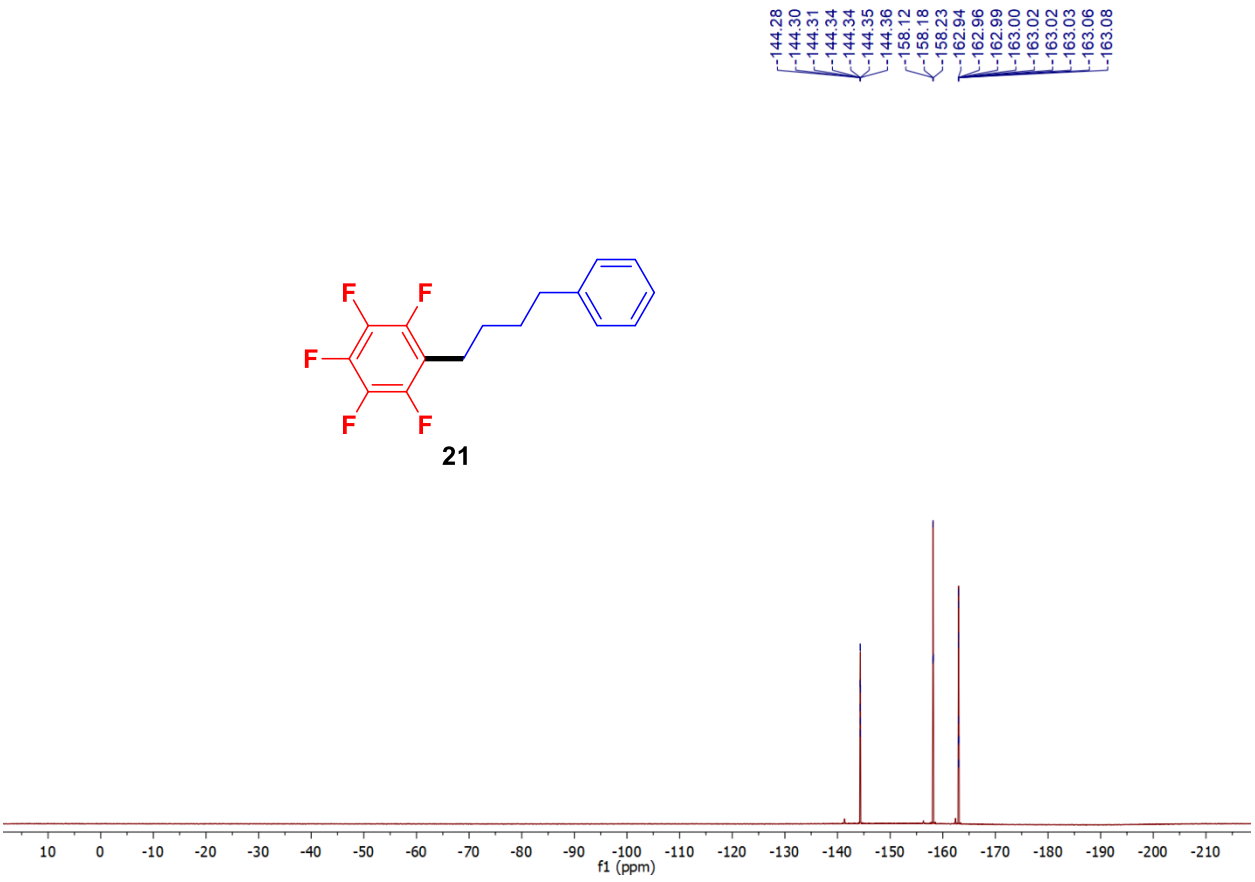
^{1}H-NMR (400 MHz, $CDCl_3$) of **21**



^{13}C-NMR (101 MHz, $CDCl_3$) of **21**



^{19}F-NMR (377 MHz, $CDCl_3$) of **21**



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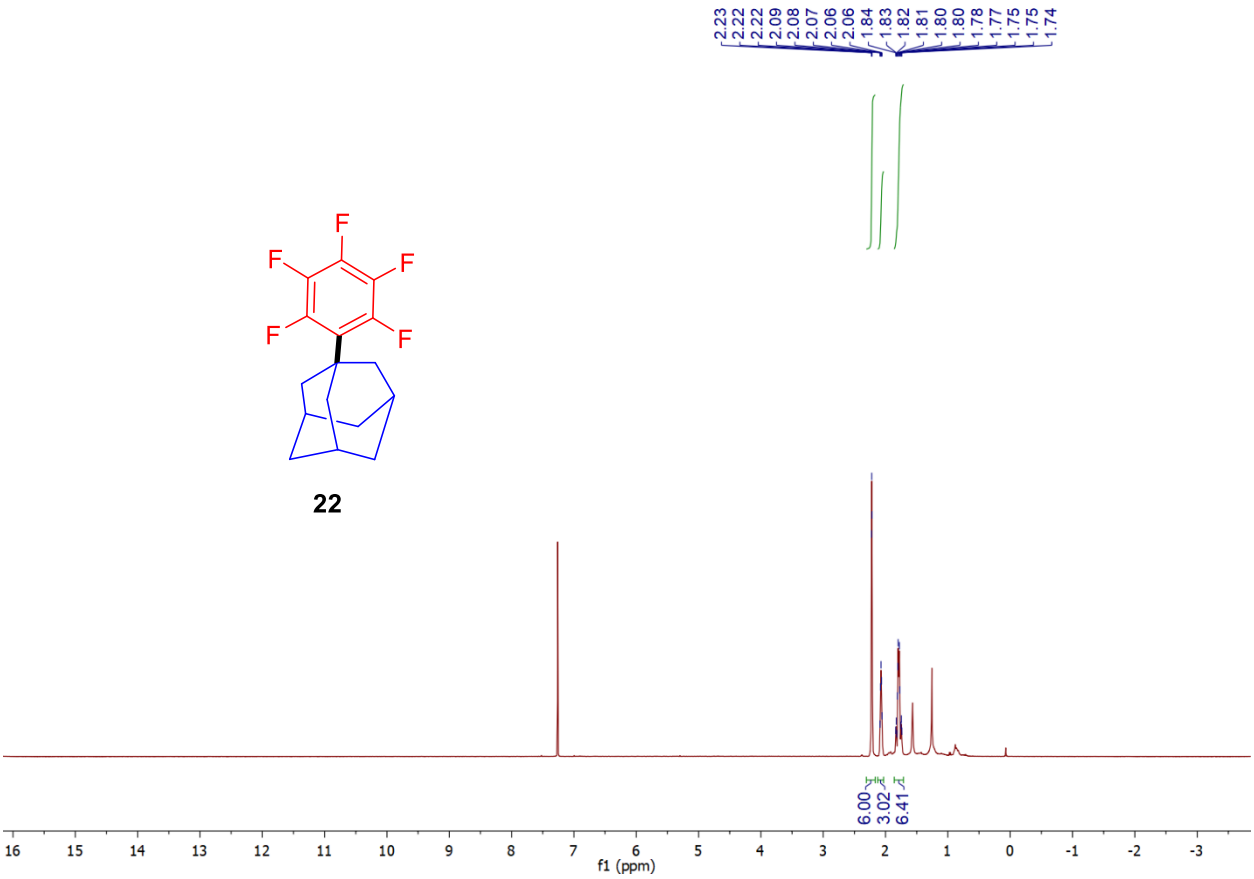

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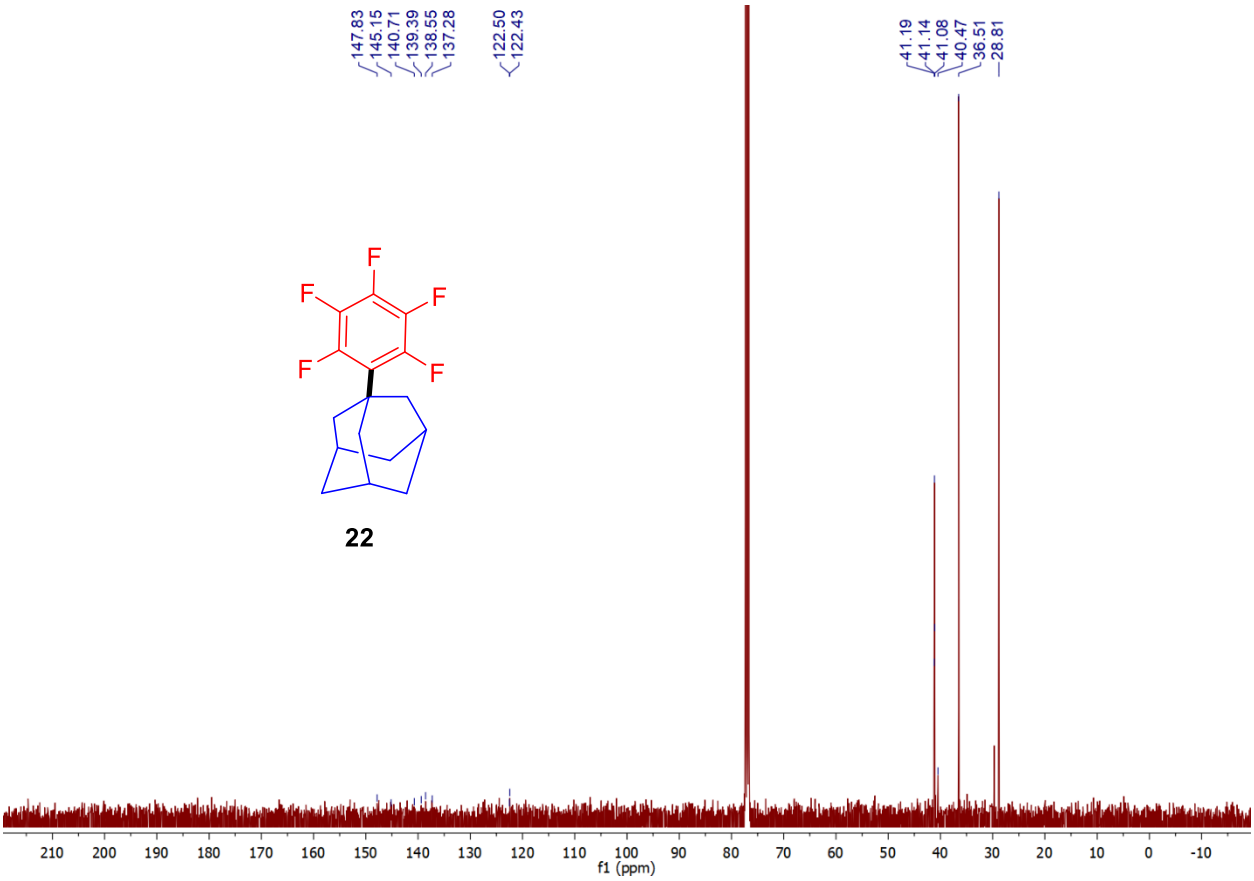

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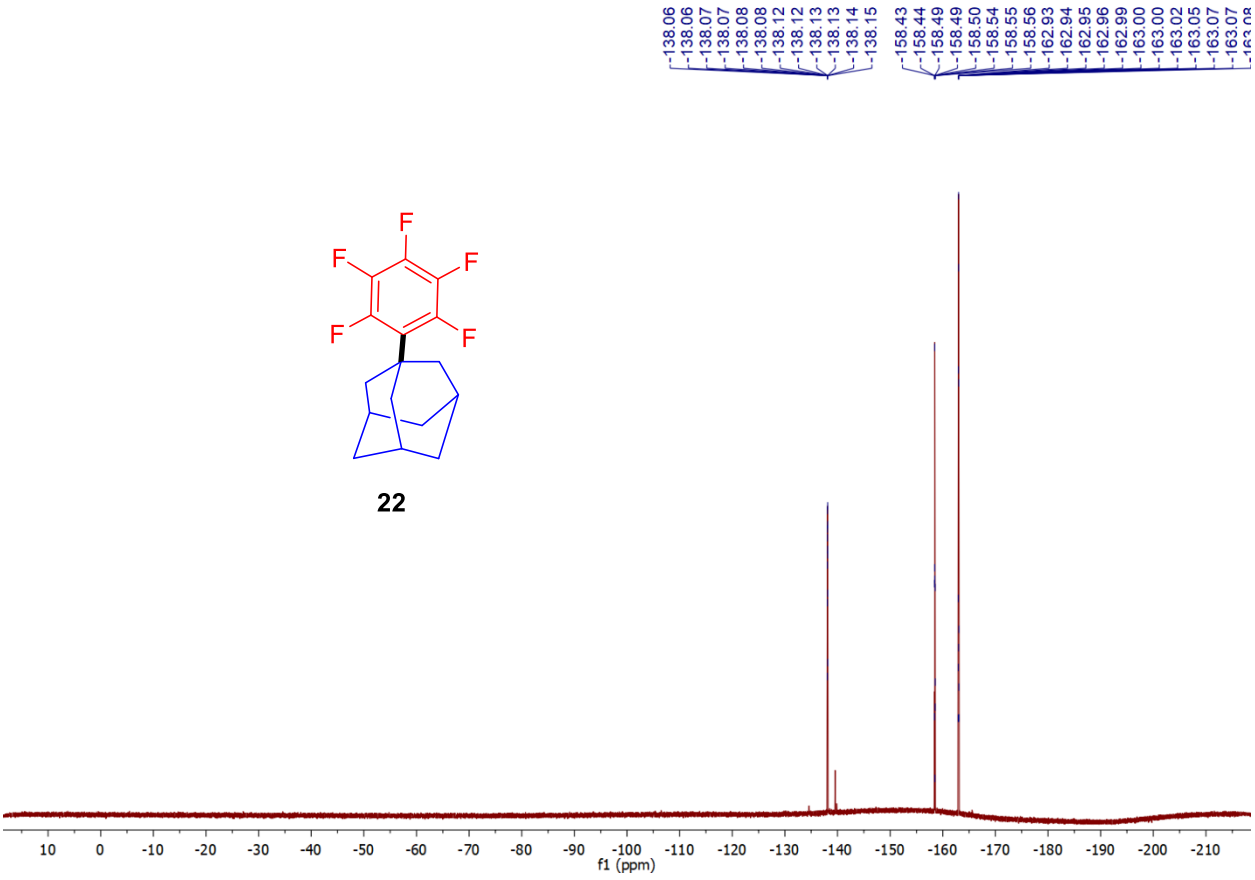

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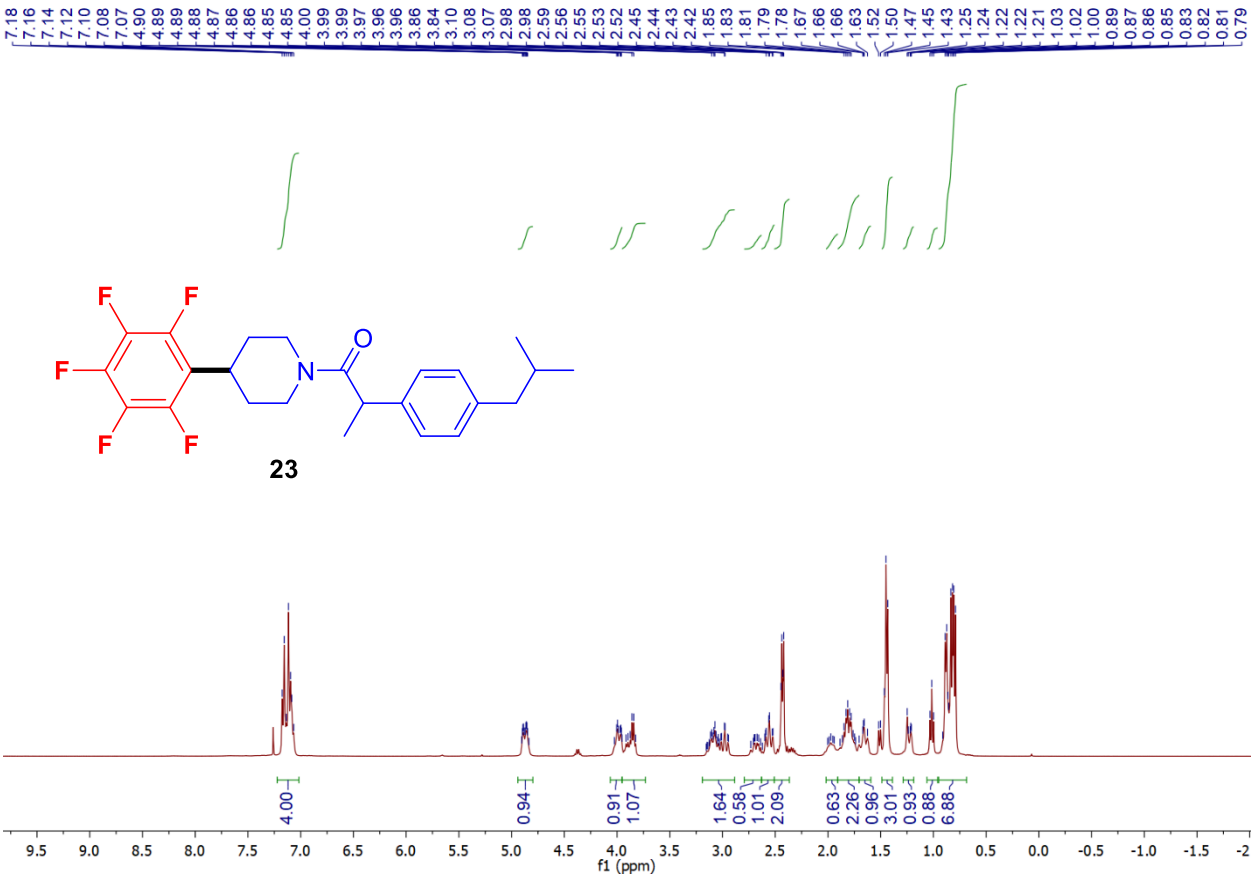

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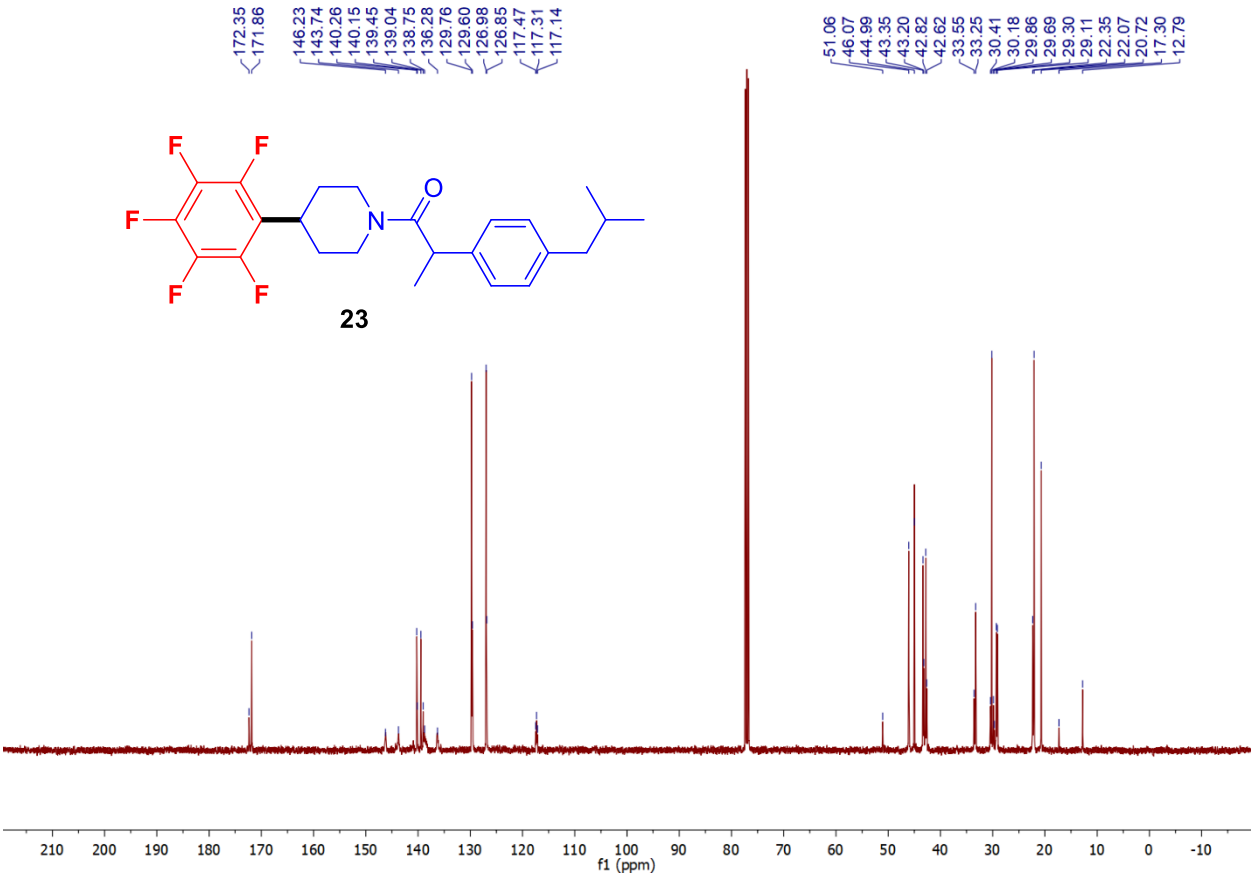

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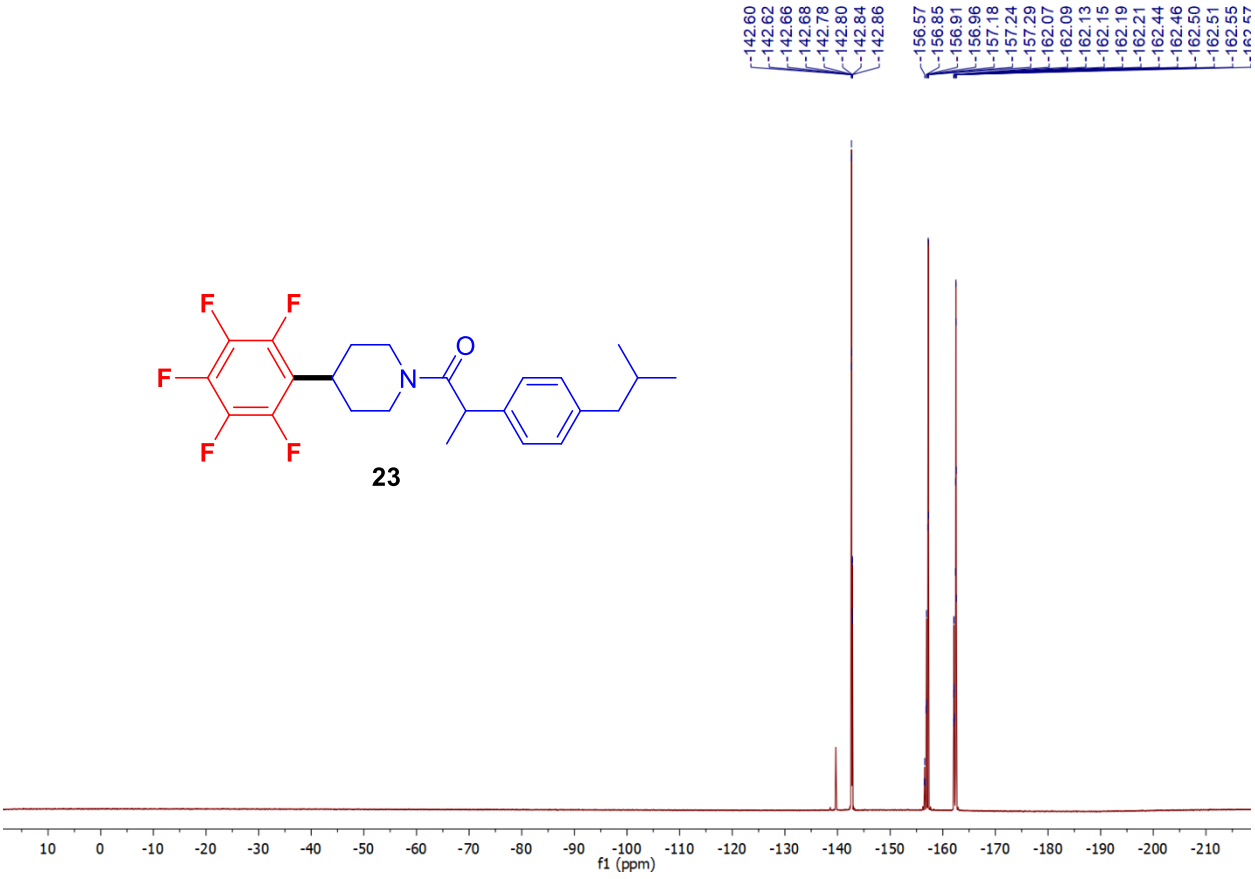
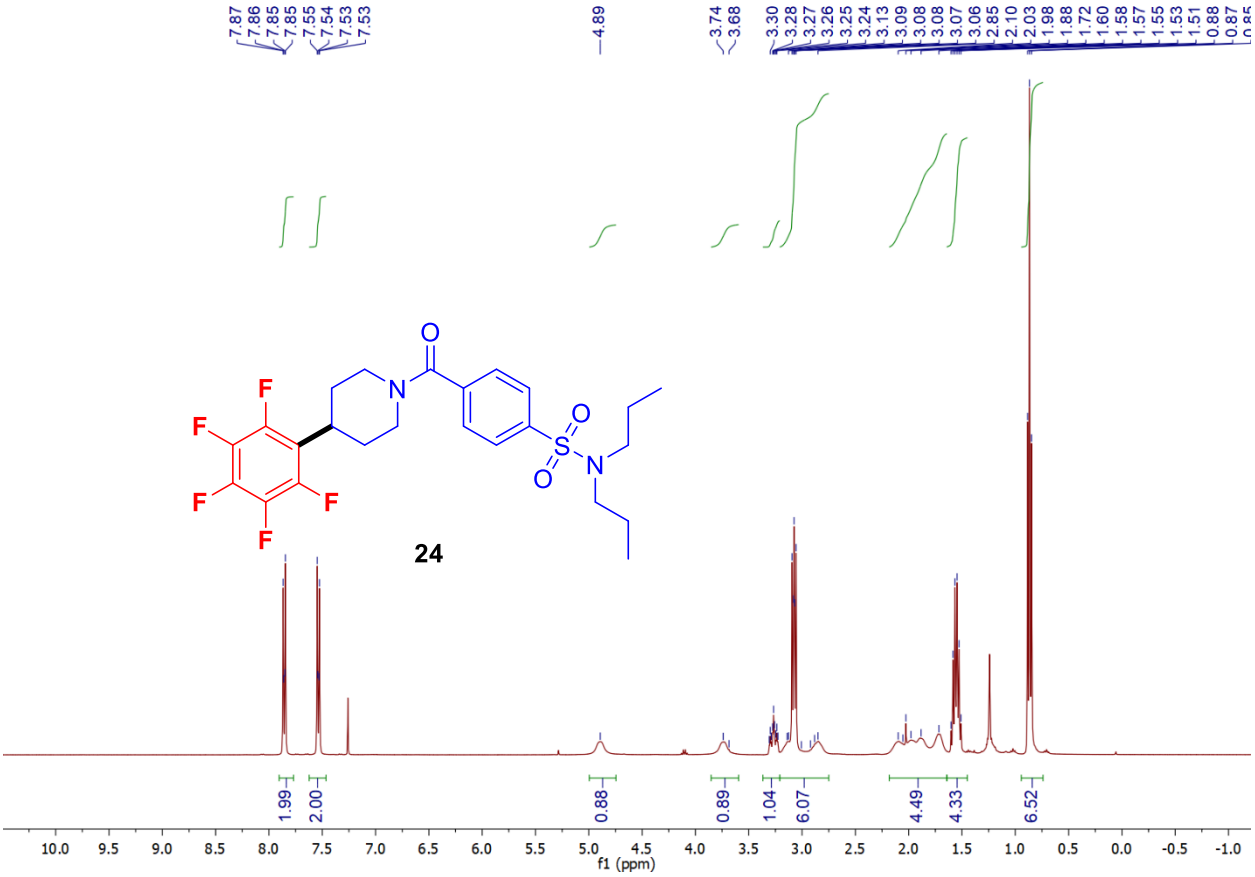


^{1}H-NMR (400 MHz, $CDCl_3$) of **24**



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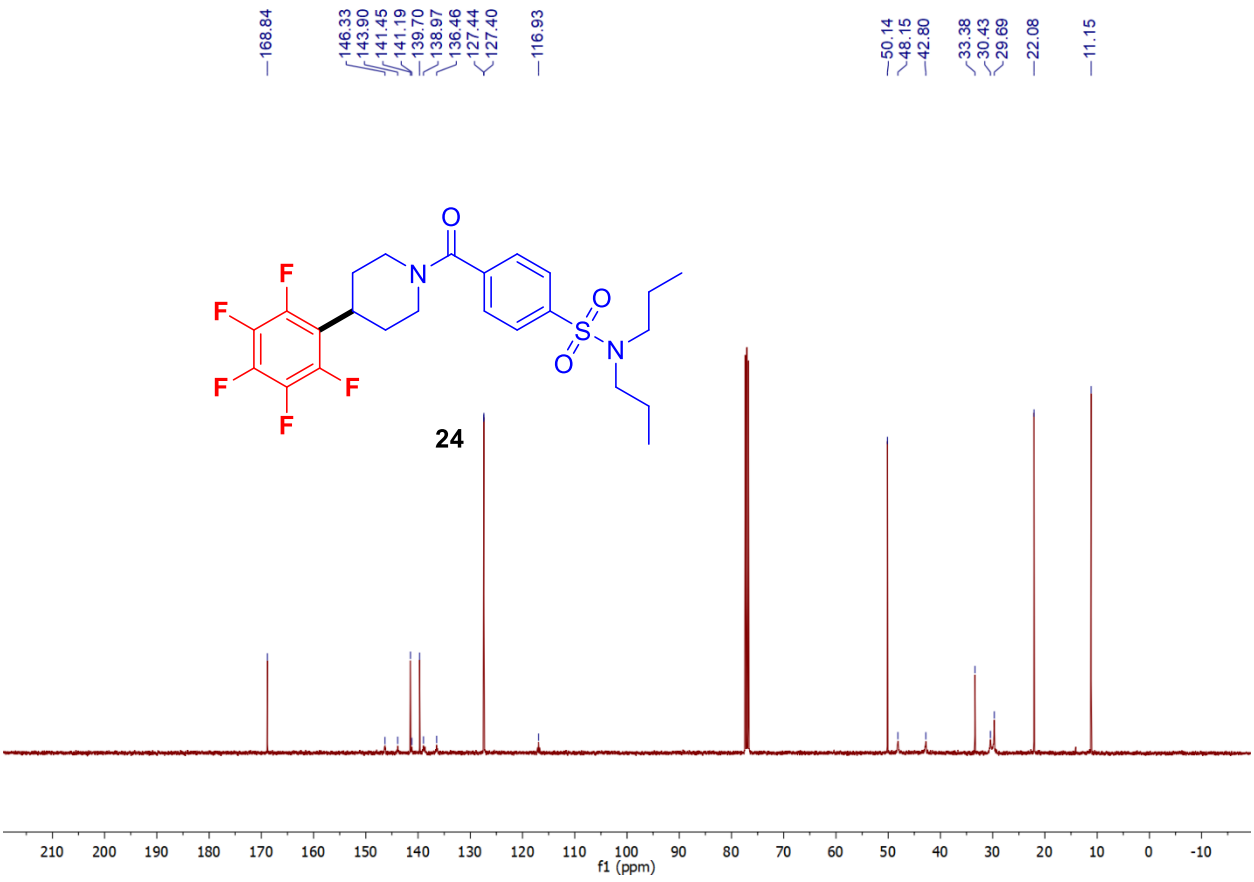

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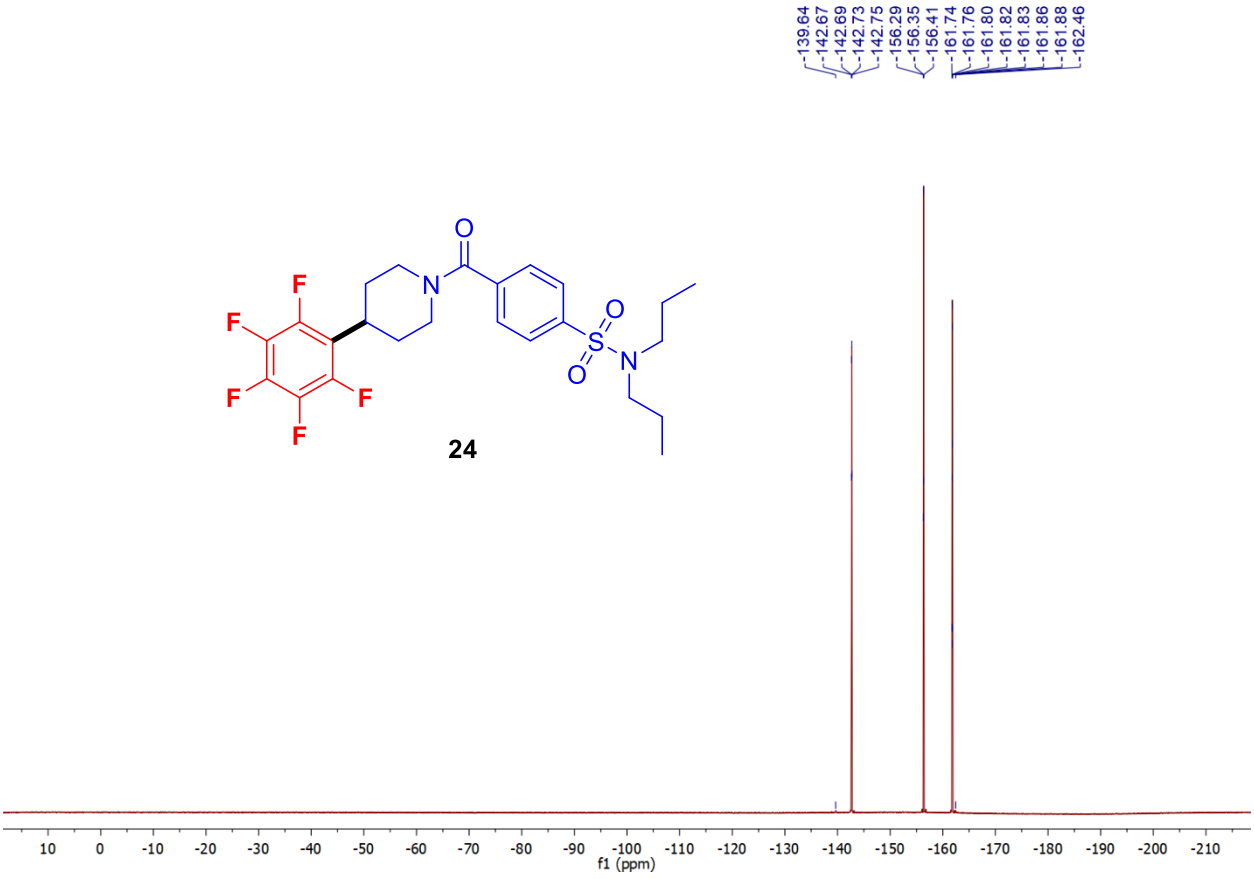
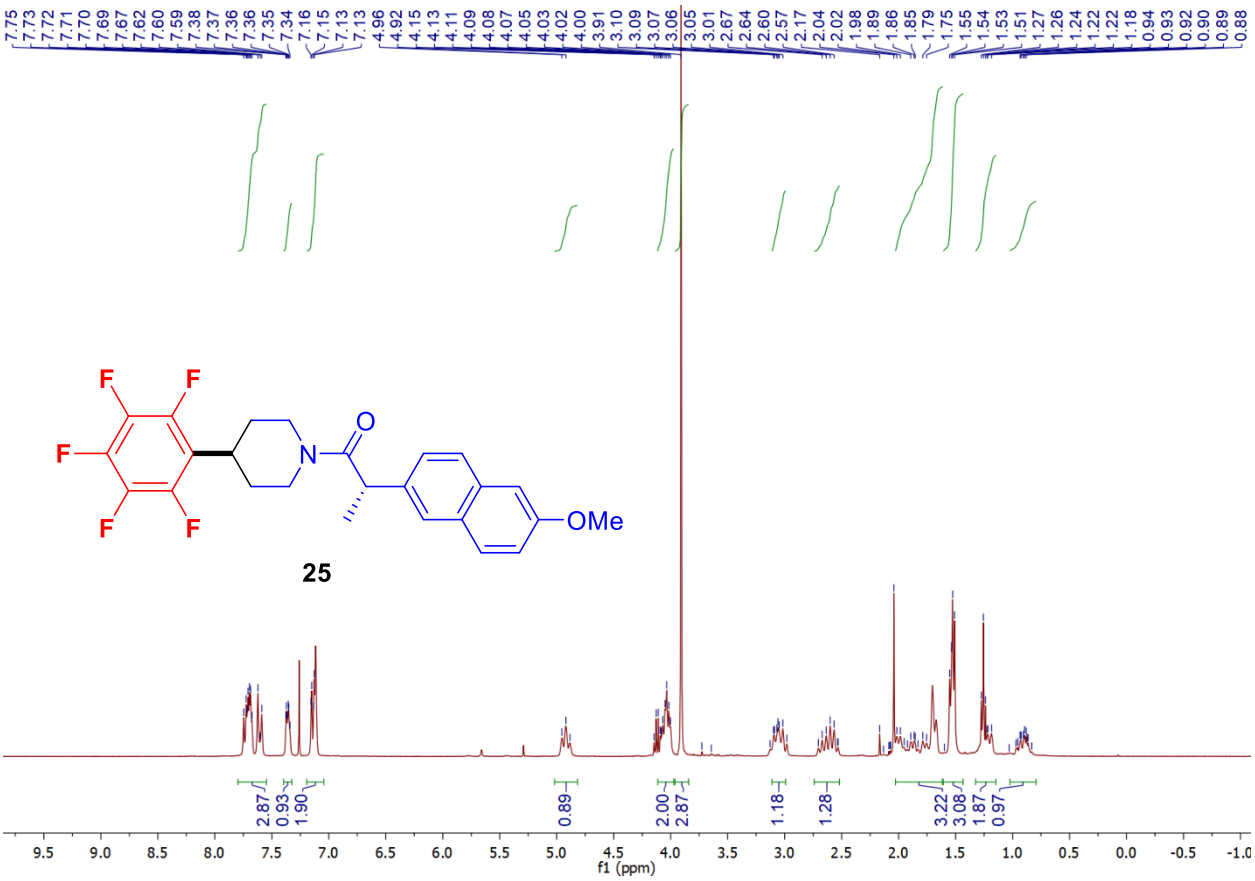
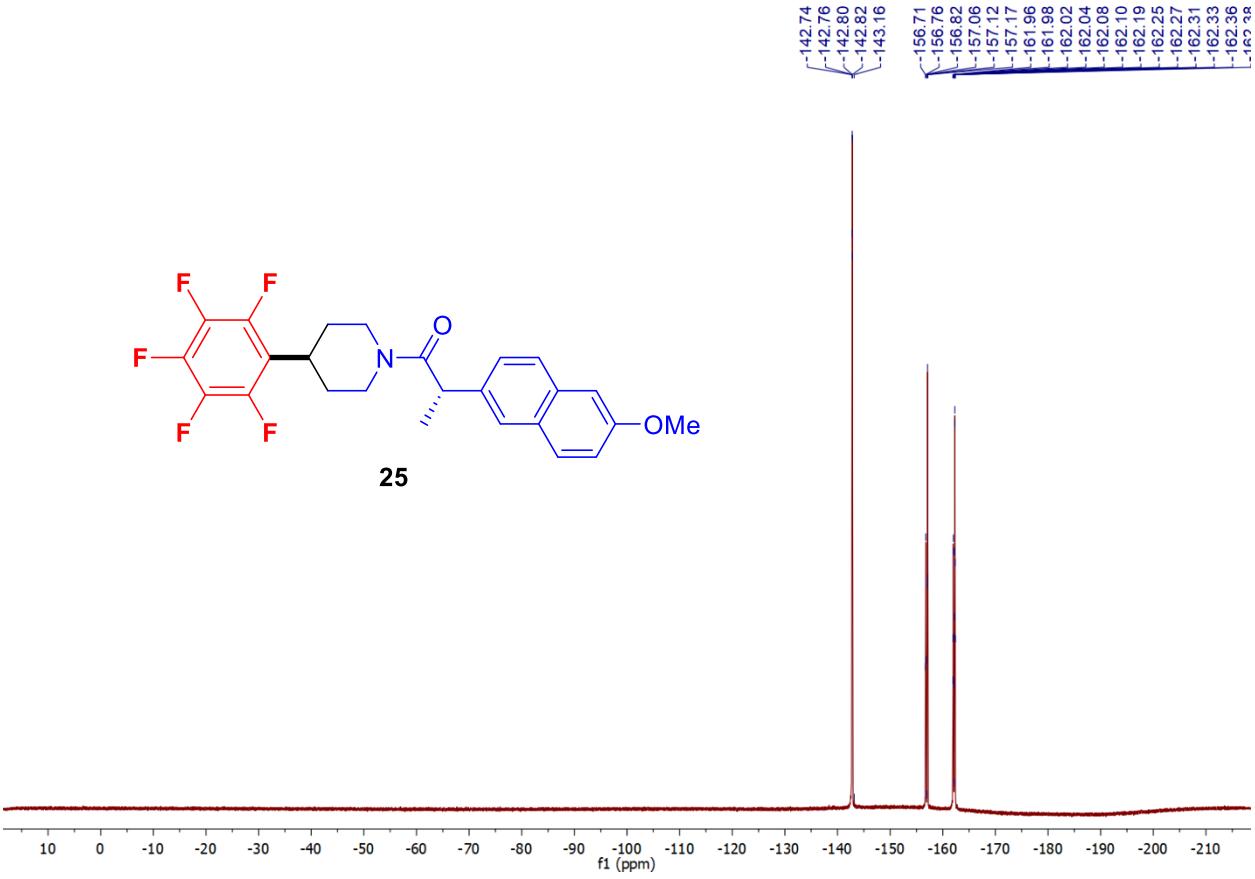


^{1}H-NMR (400 MHz, $CDCl_3$) of **25**



^{19}F-NMR (377 MHz, $CDCl_3$) of **25**



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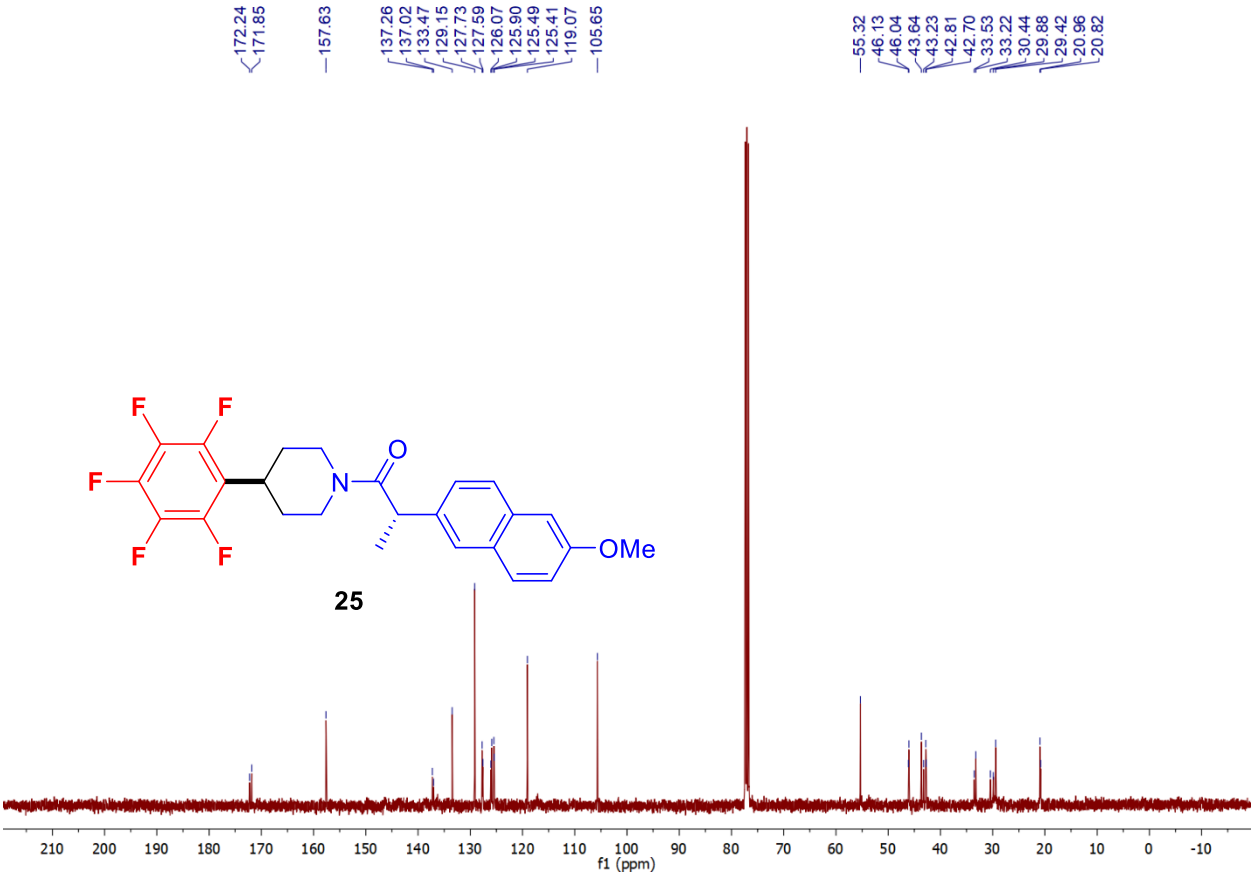
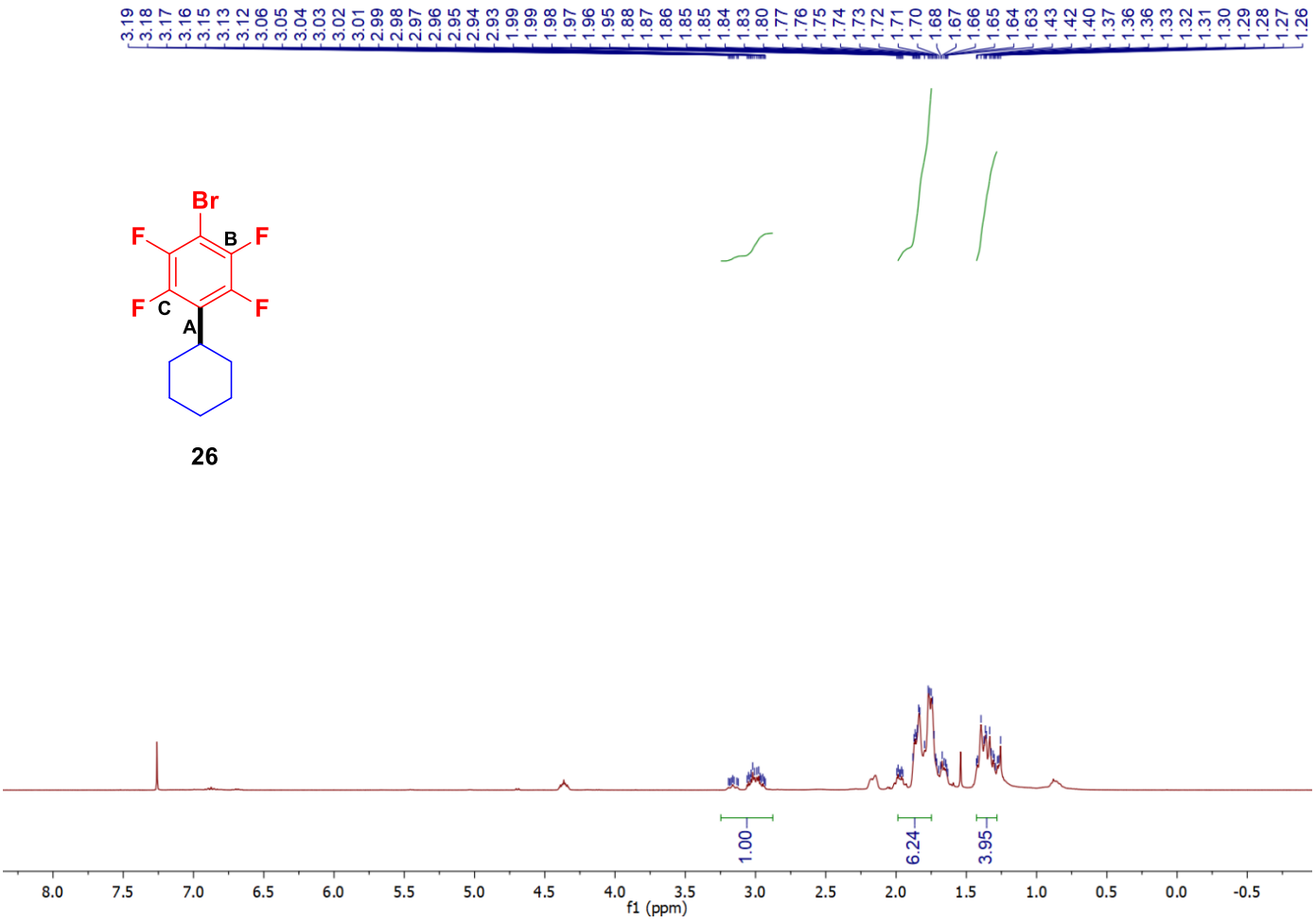
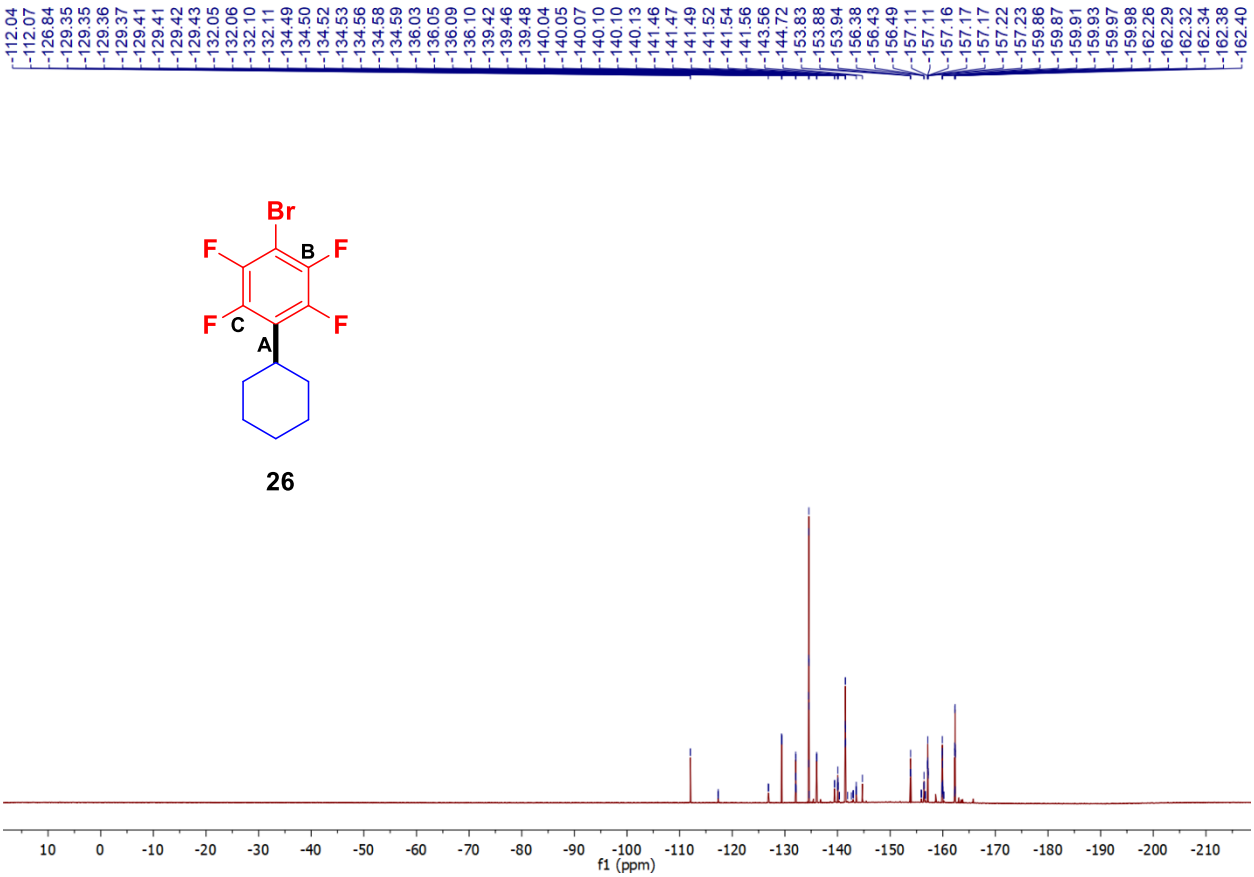


^{1}H-NMR (400 MHz, $CDCl_3$) of **26**

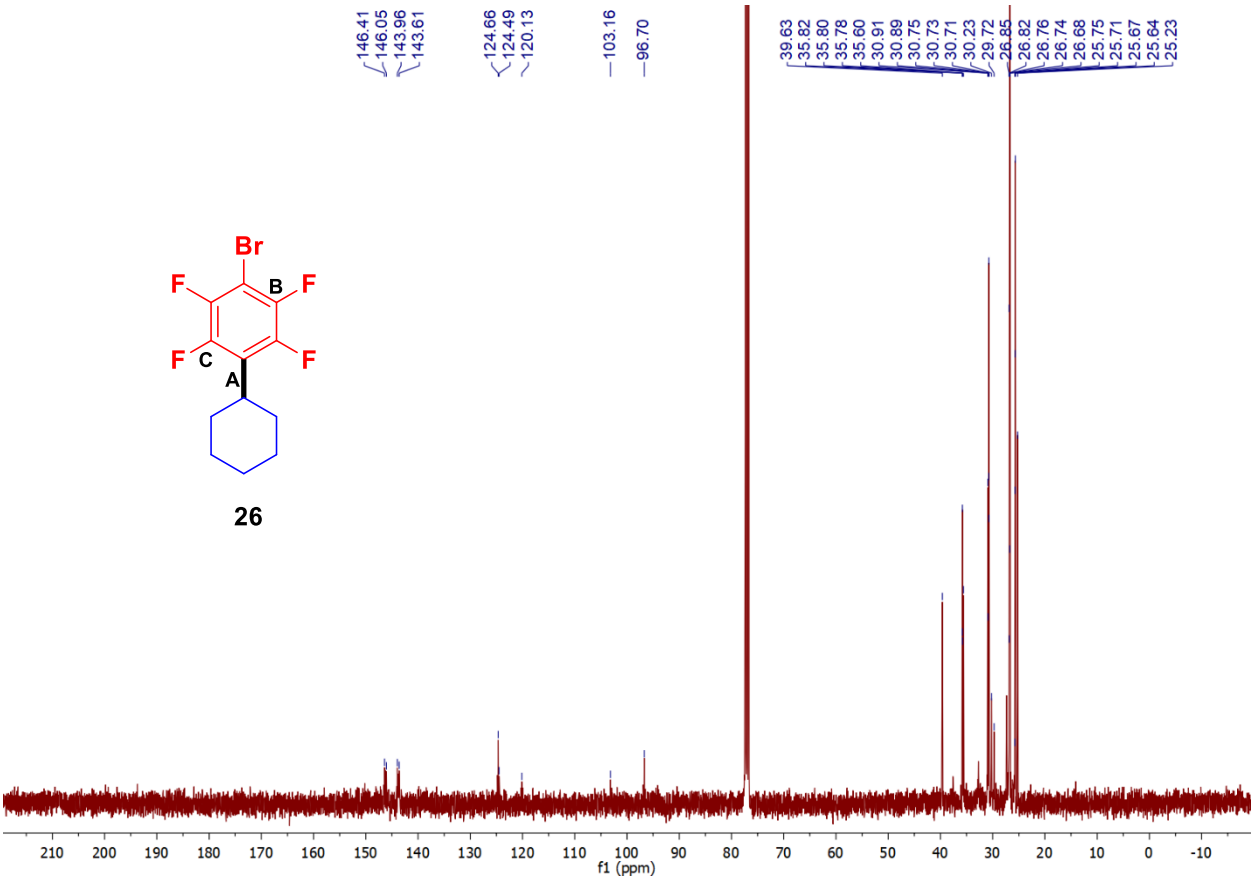


26

^{19}F-NMR (377 MHz, $CDCl_3$) of **26**



^{13}C-NMR (101 MHz, $CDCl_3$) of **26**



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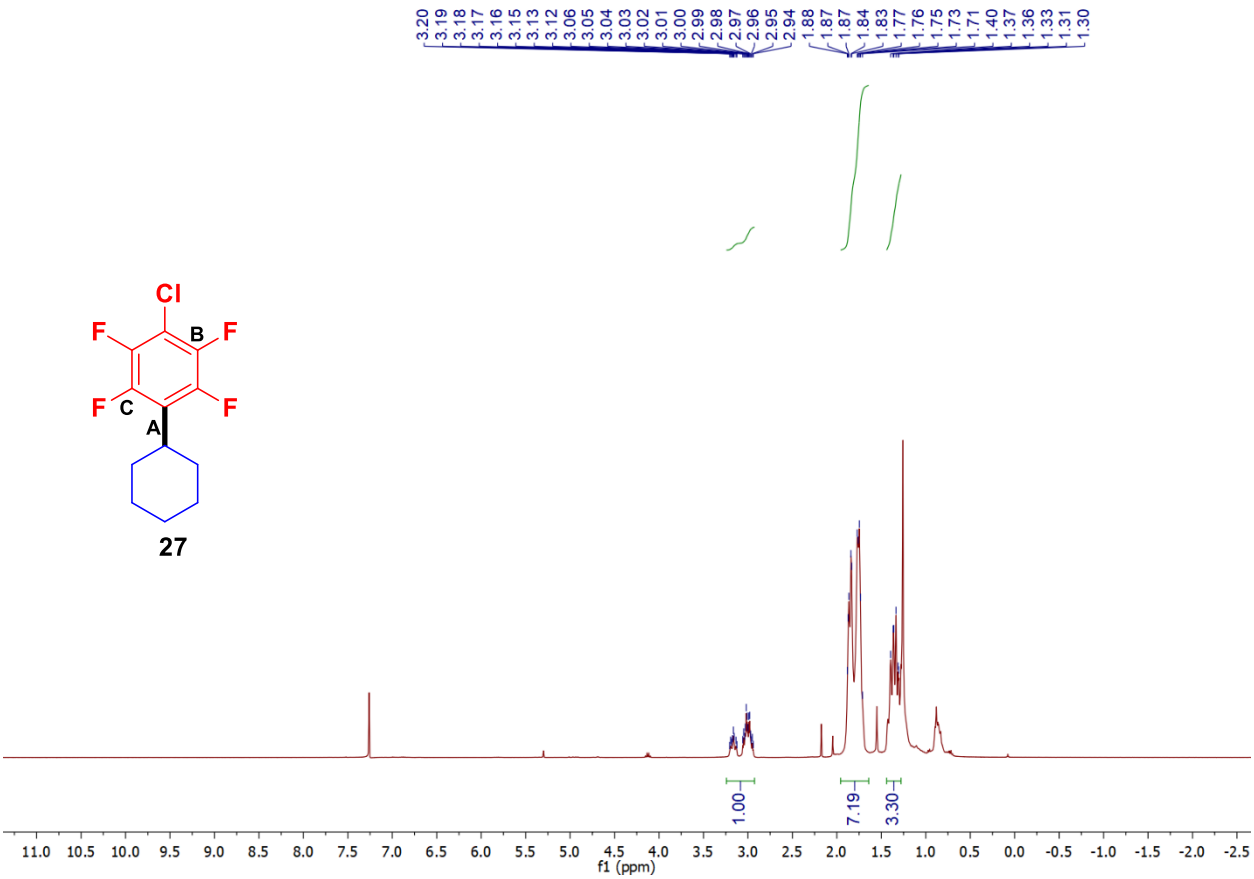

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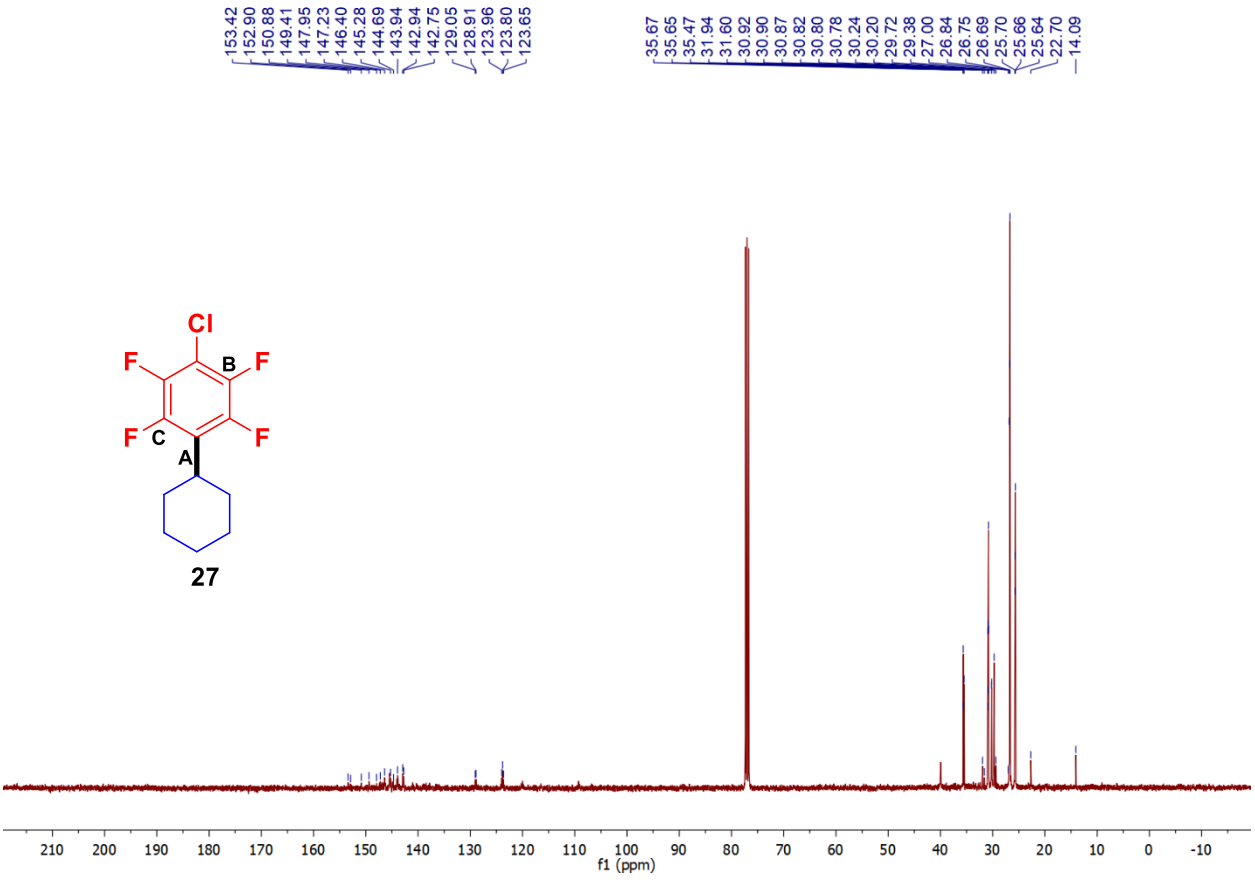
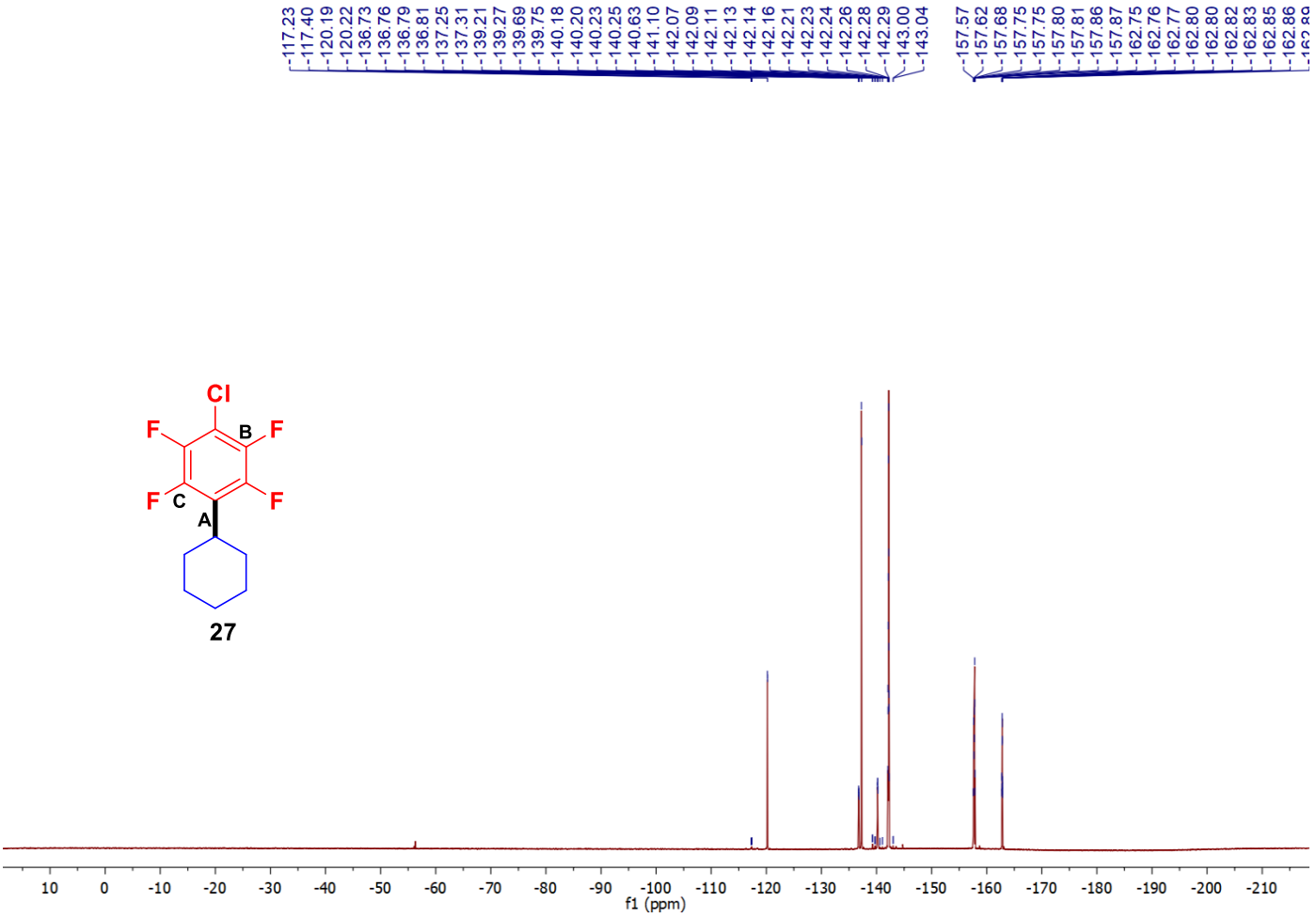
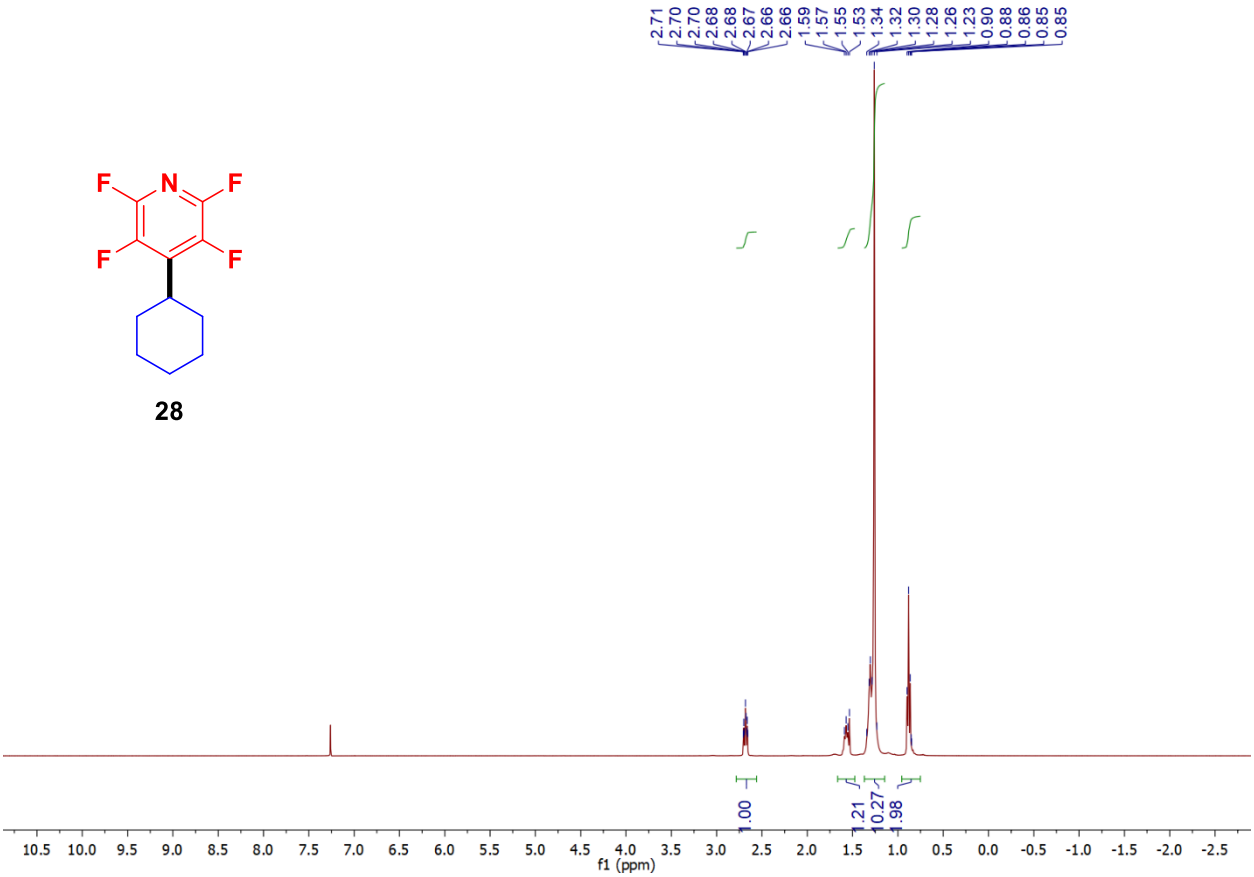


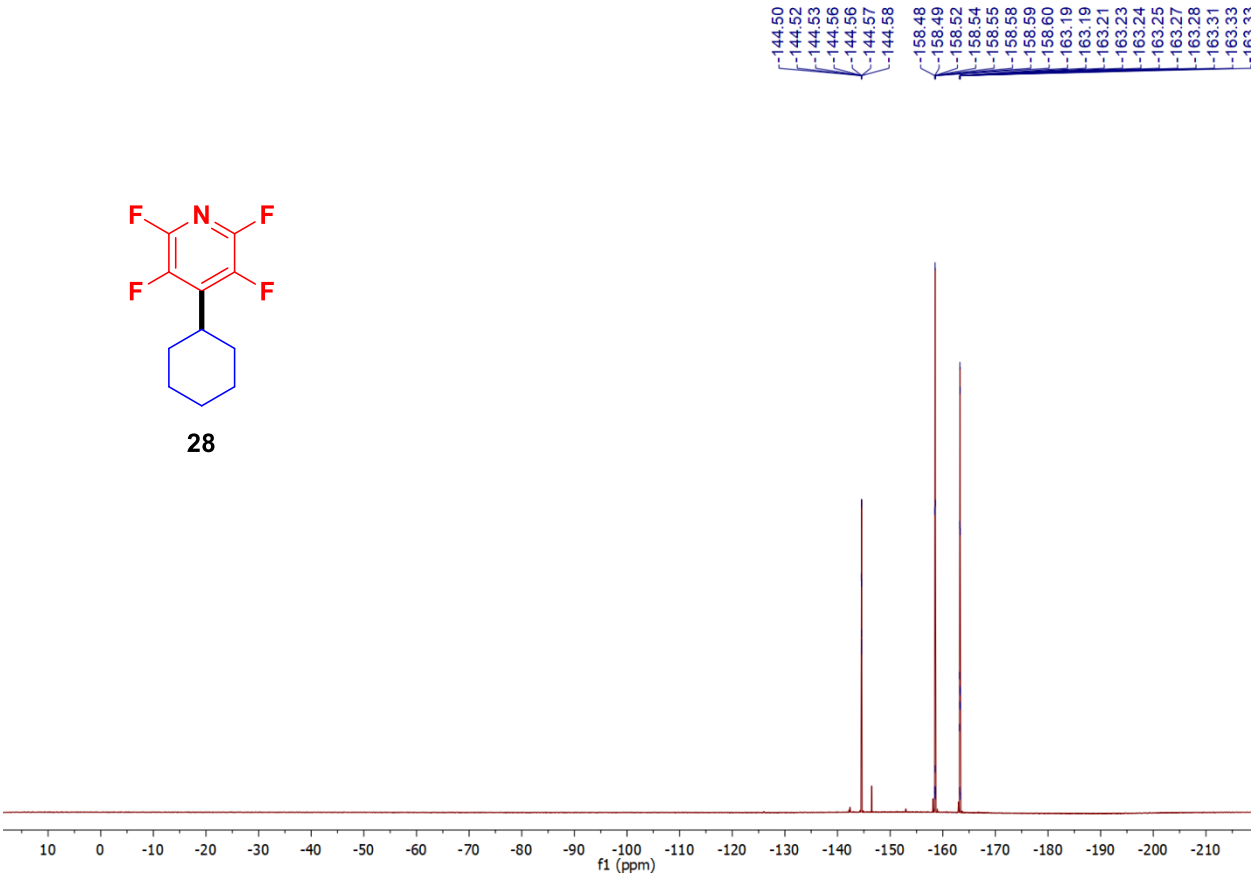
^{19}F-NMR (377 MHz, $CDCl_3$) of **27**



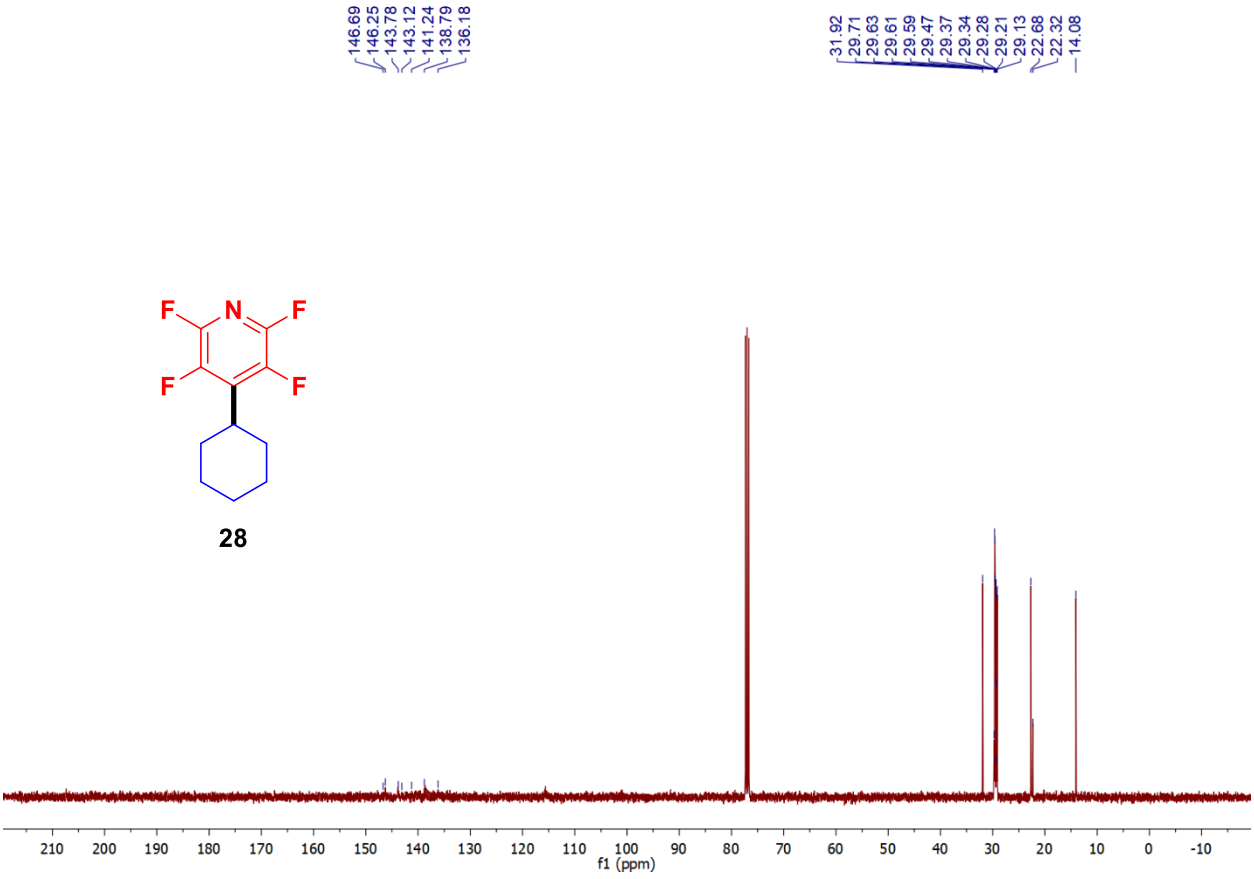
^{1}H-NMR (400 MHz, $CDCl_3$) of **28**



^{13}C-NMR (101 MHz, $CDCl_3$) of **28**



^{19}F-NMR (377 MHz, $CDCl_3$) of **28**



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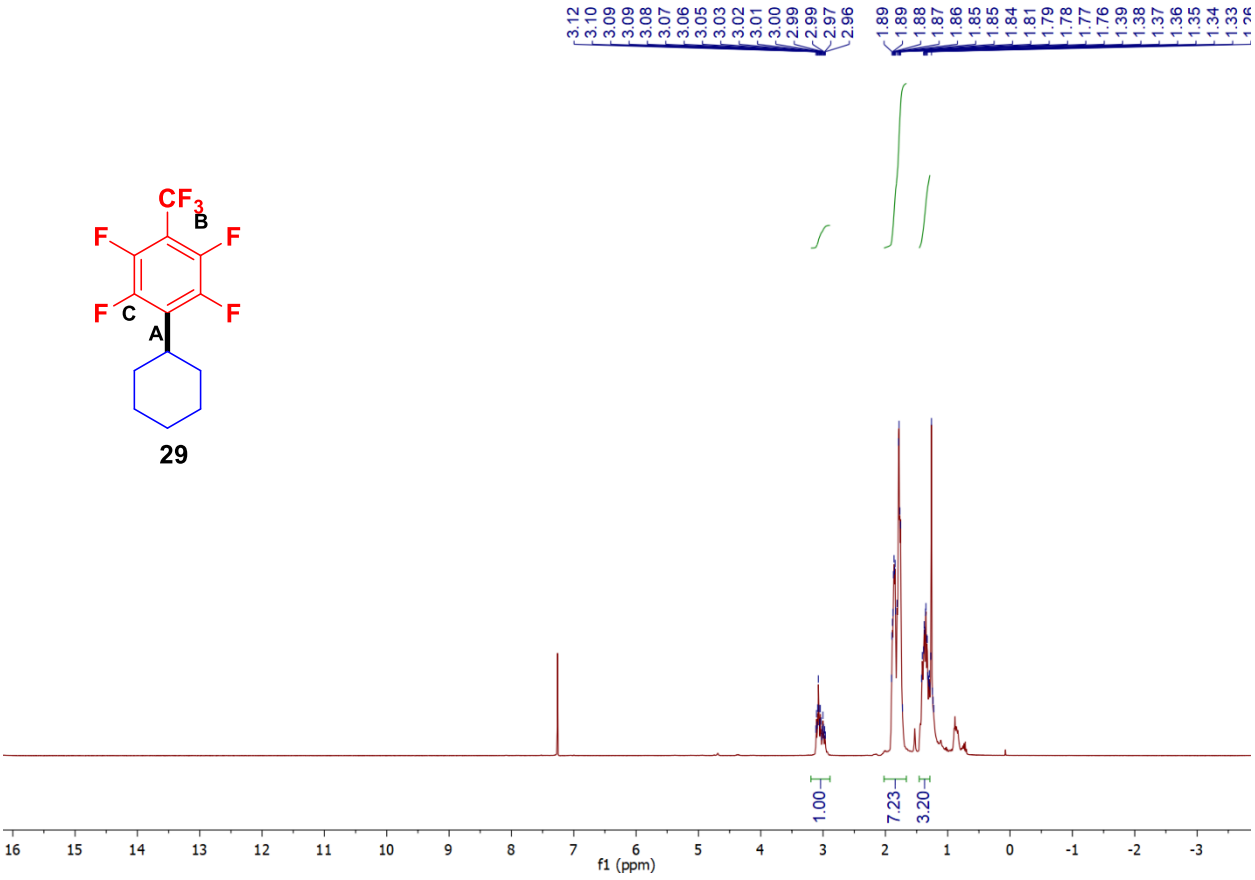
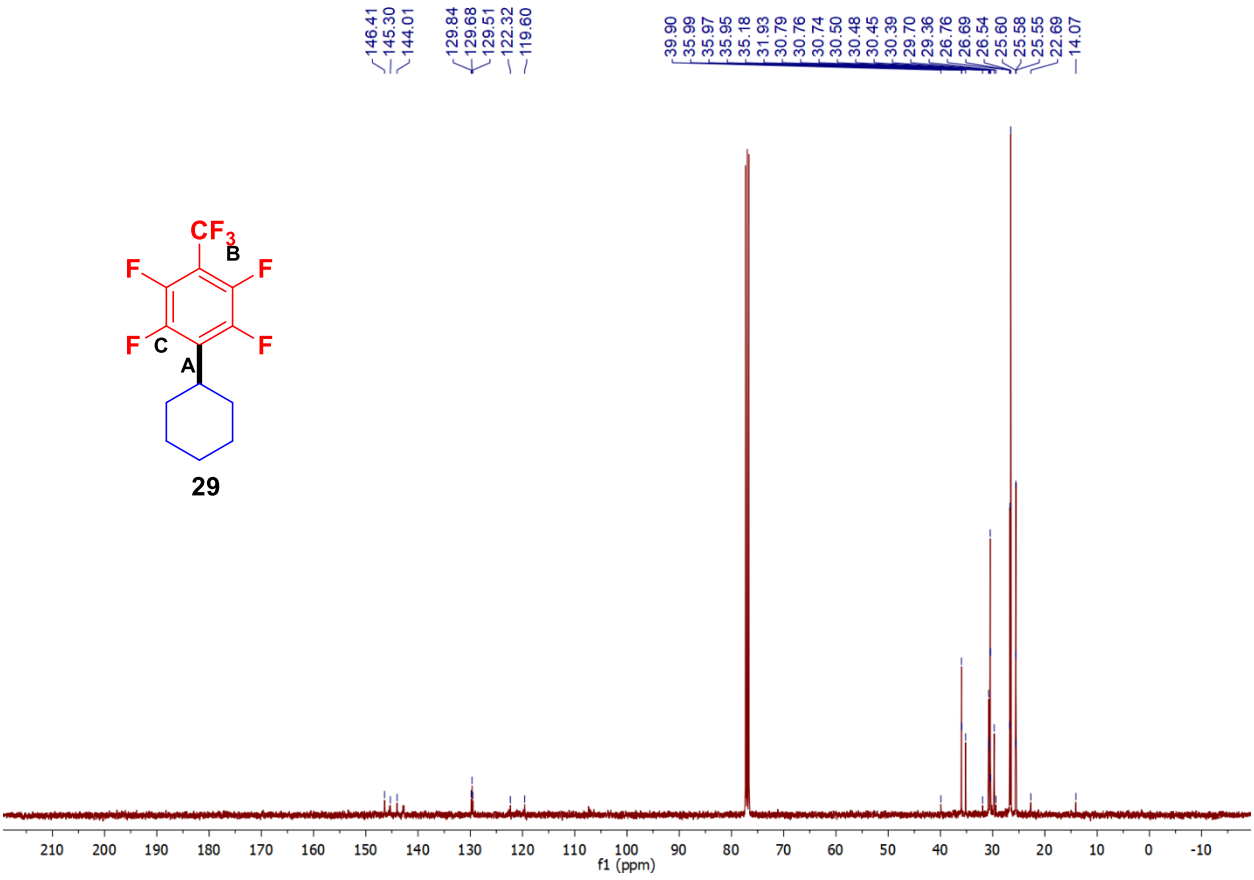
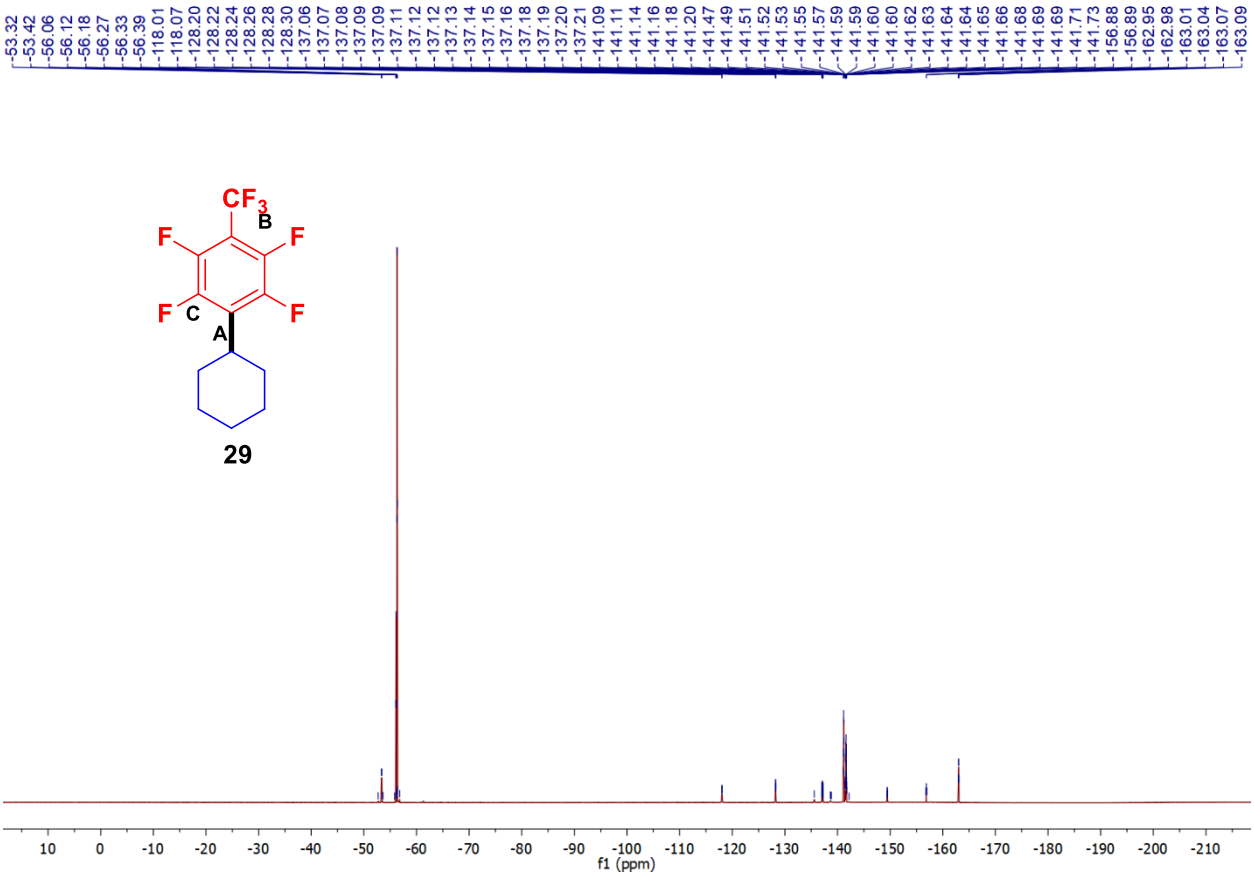


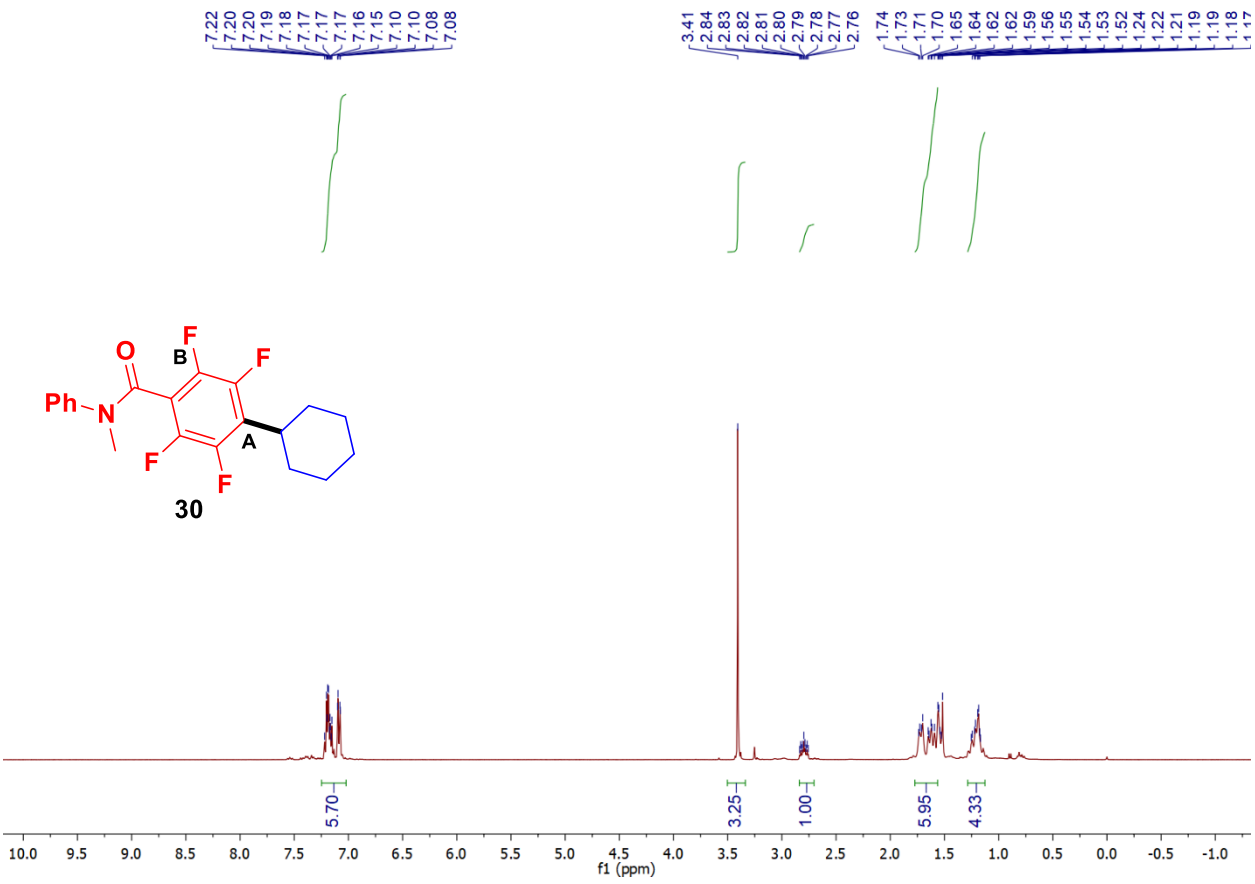
^{13}C-NMR (101 MHz, $CDCl_3$) of **29**



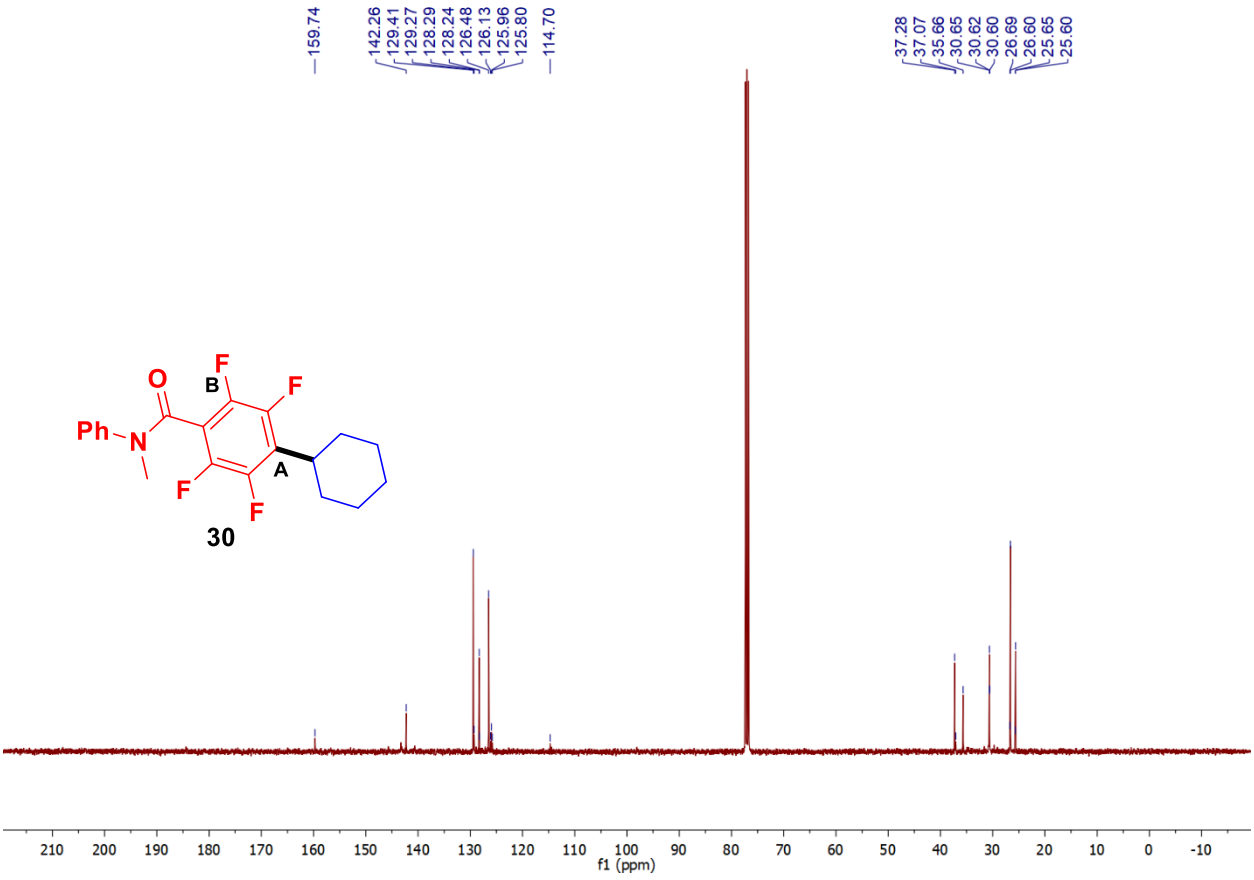
^{19}F-NMR (377 MHz, $CDCl_3$) of **29**



^{1}H-NMR (400 MHz, $CDCl_3$) of **30**



^{13}C-NMR (101 MHz, $CDCl_3$) of **30**



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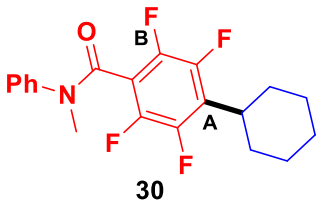

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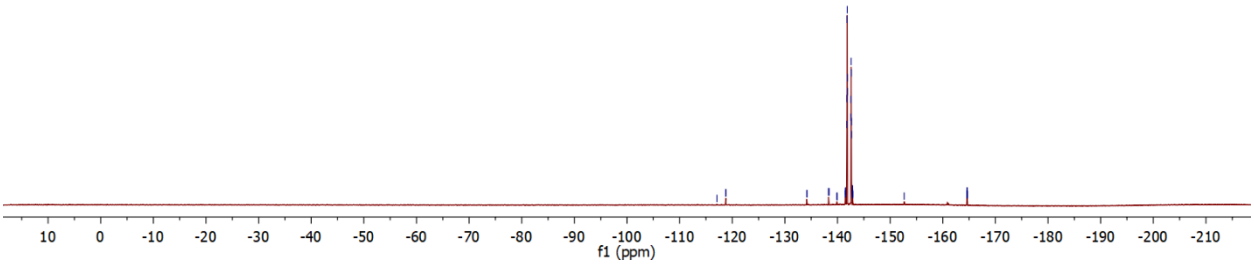
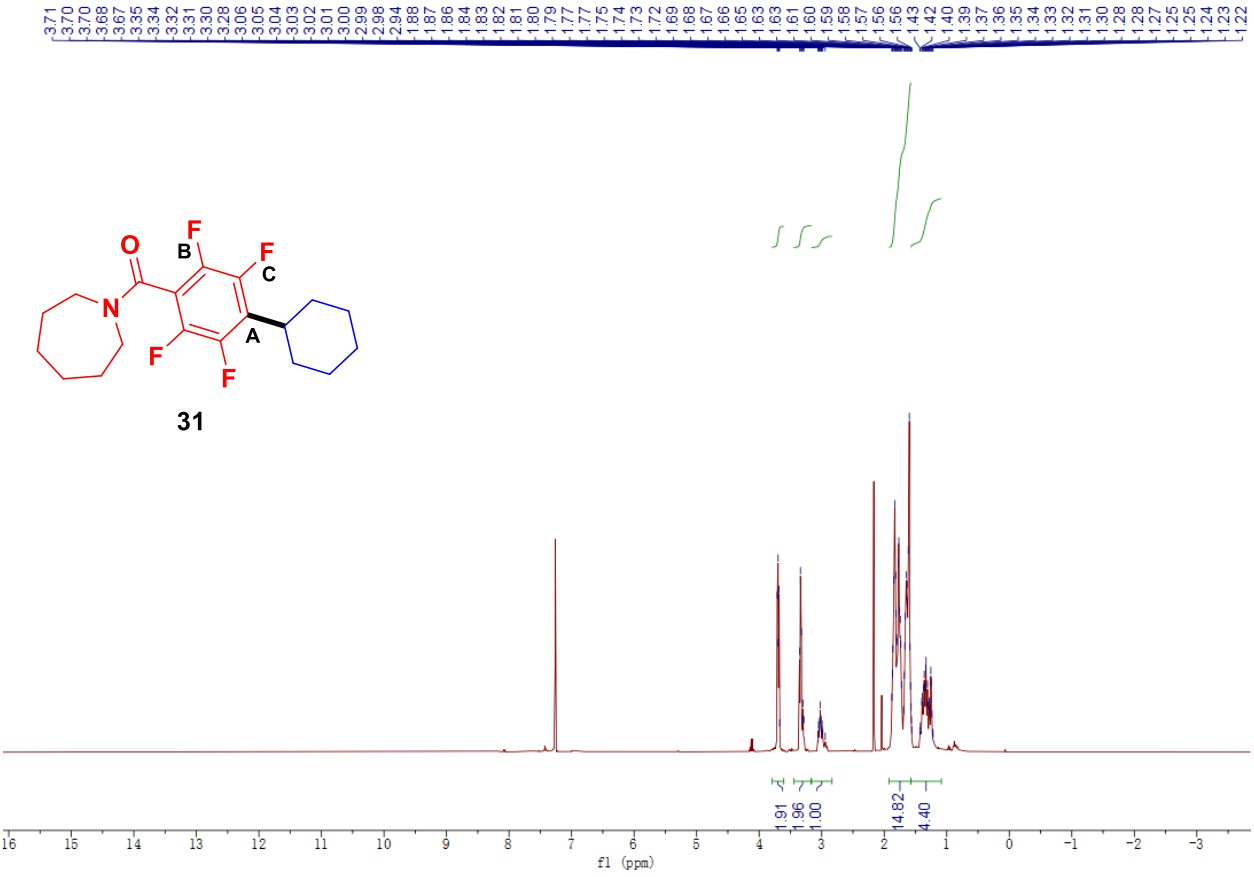
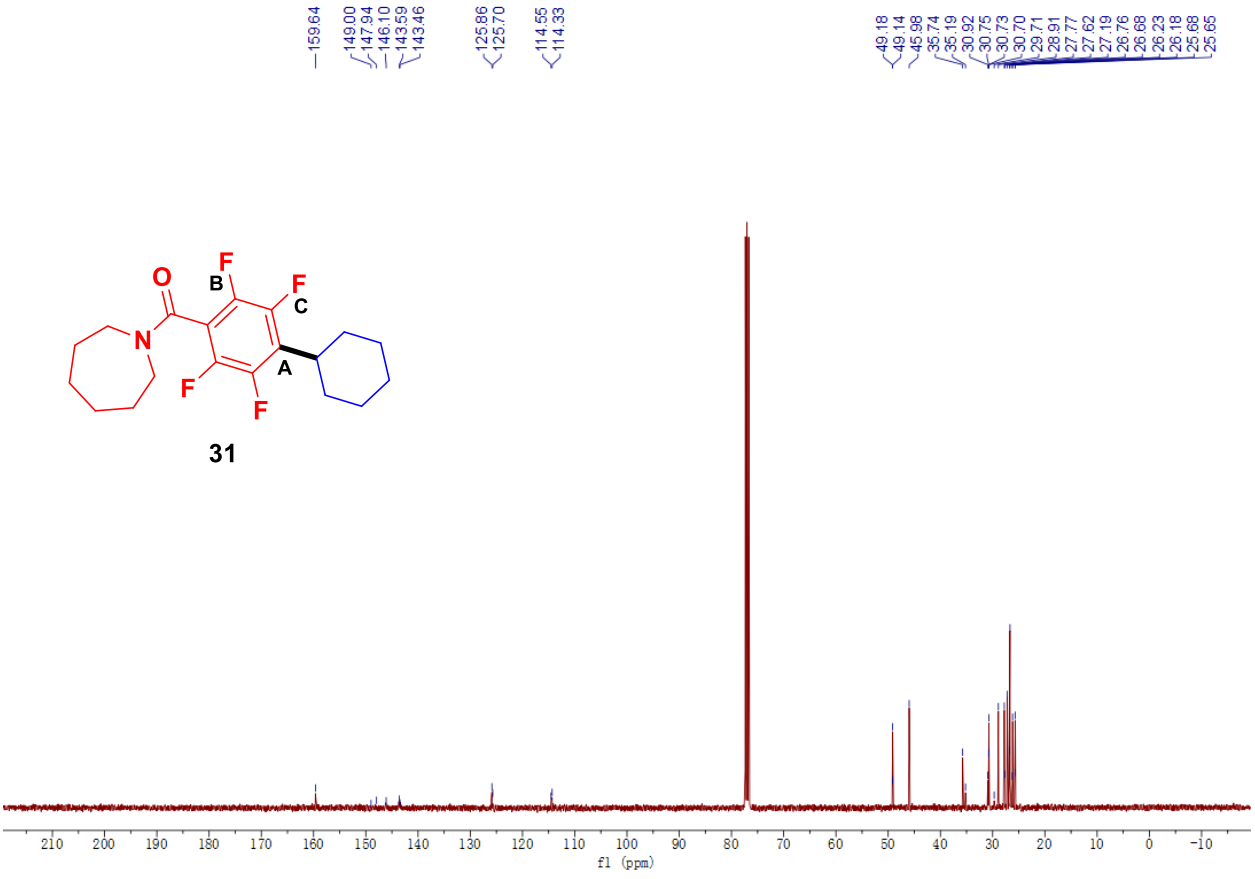


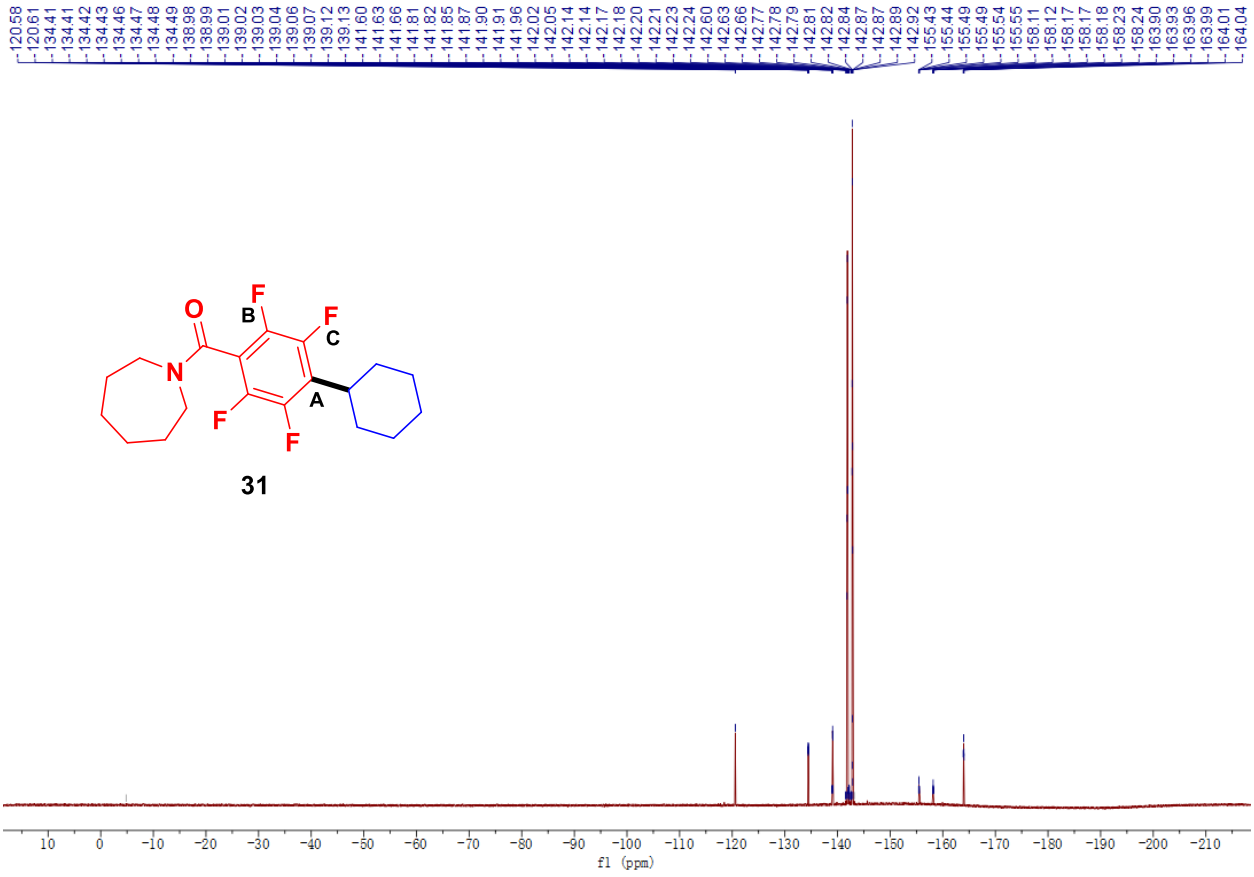
^{1}H-NMR (400 MHz, $CDCl_3$) of **31**



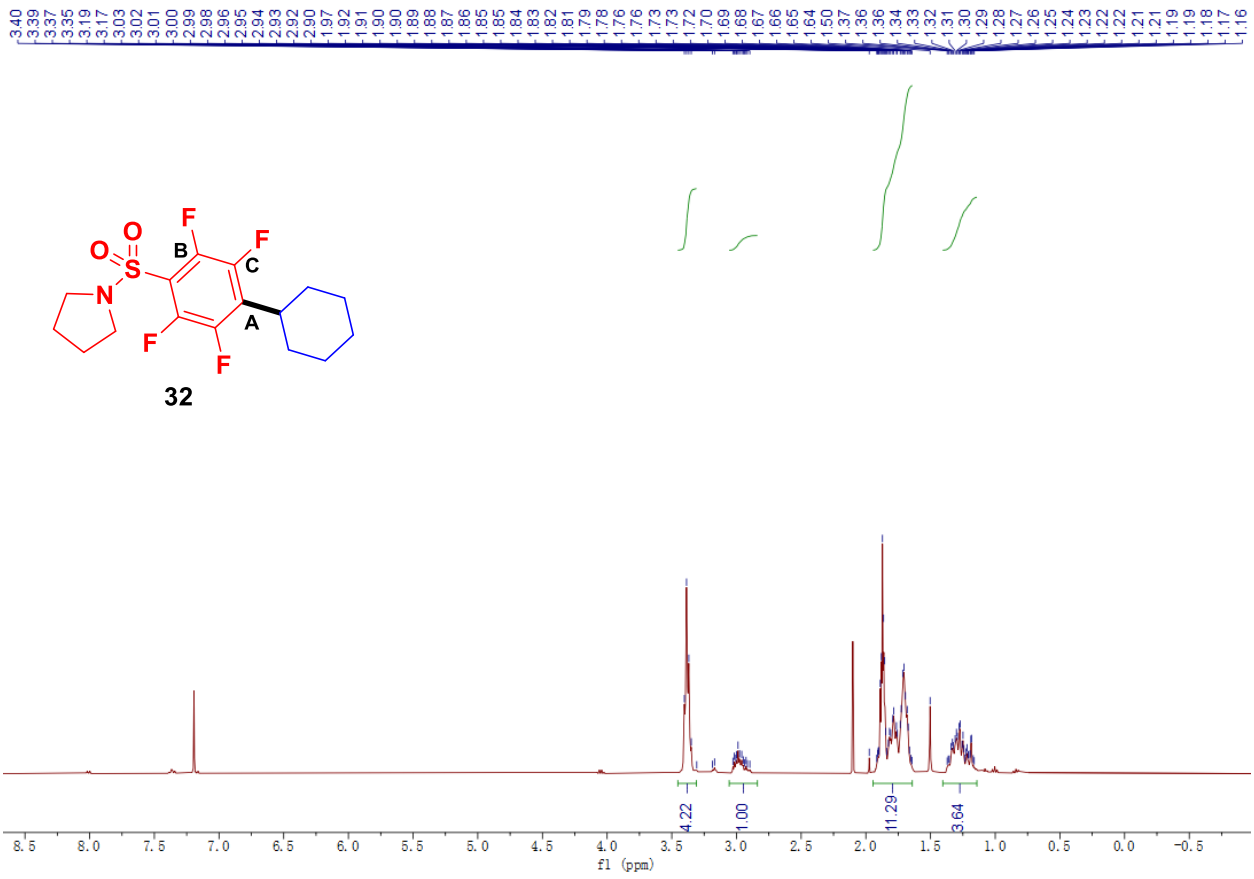
^{13}C-NMR (101 MHz, $CDCl_3$) of **31**



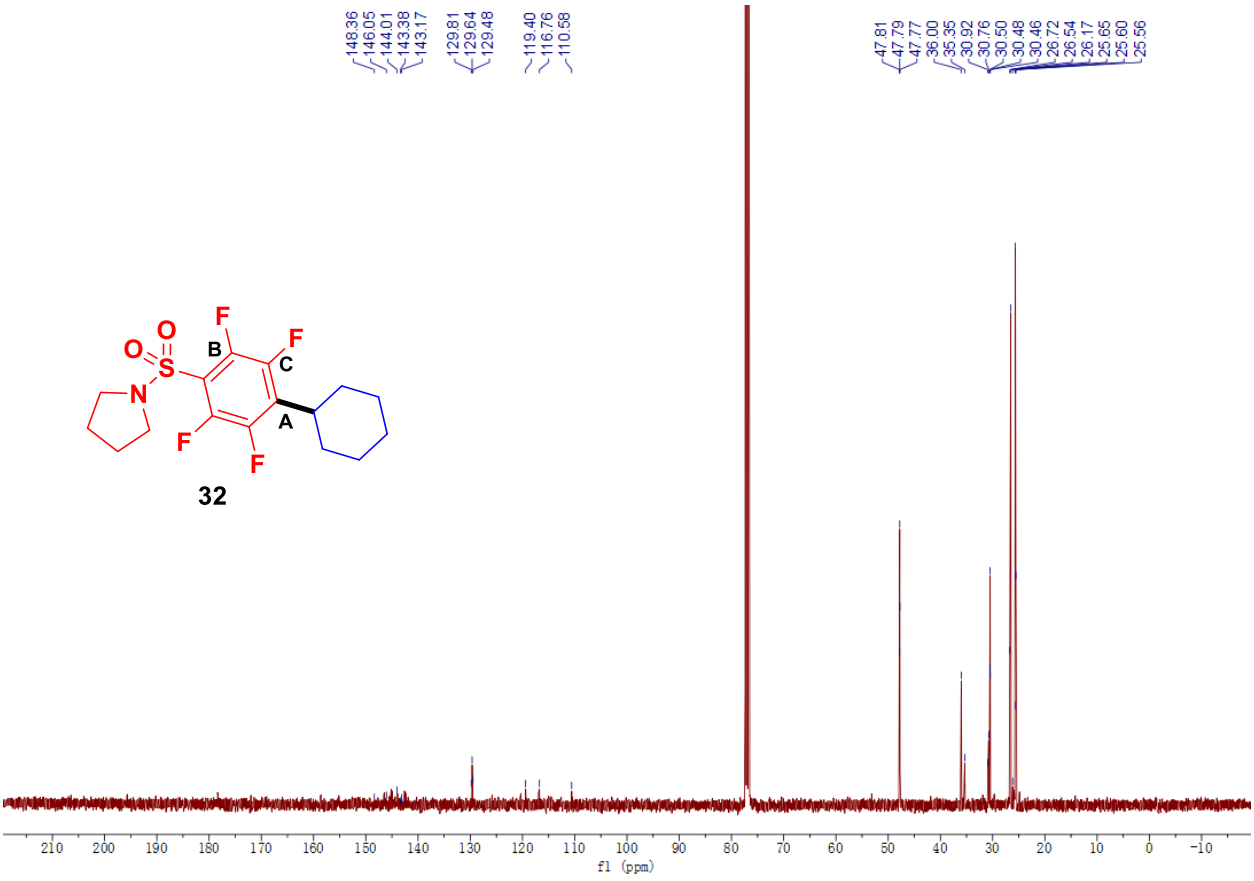
^{19}F-NMR (377 MHz, $CDCl_3$) of **31**



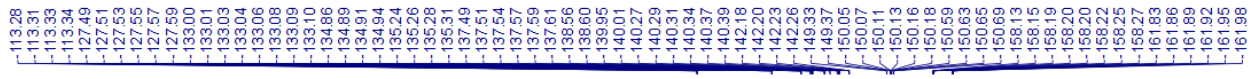
^{1}H-NMR (400 MHz, $CDCl_3$) of **32**

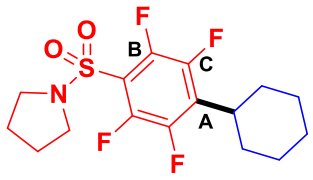


^{13}C-NMR (101 MHz, $CDCl_3$) of **32**



^{19}F-NMR (377 MHz, $CDCl_3$) of **32**





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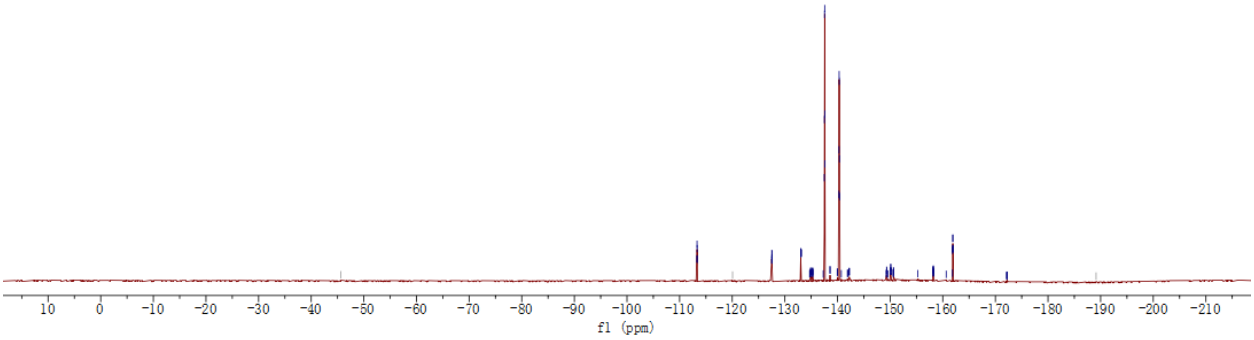
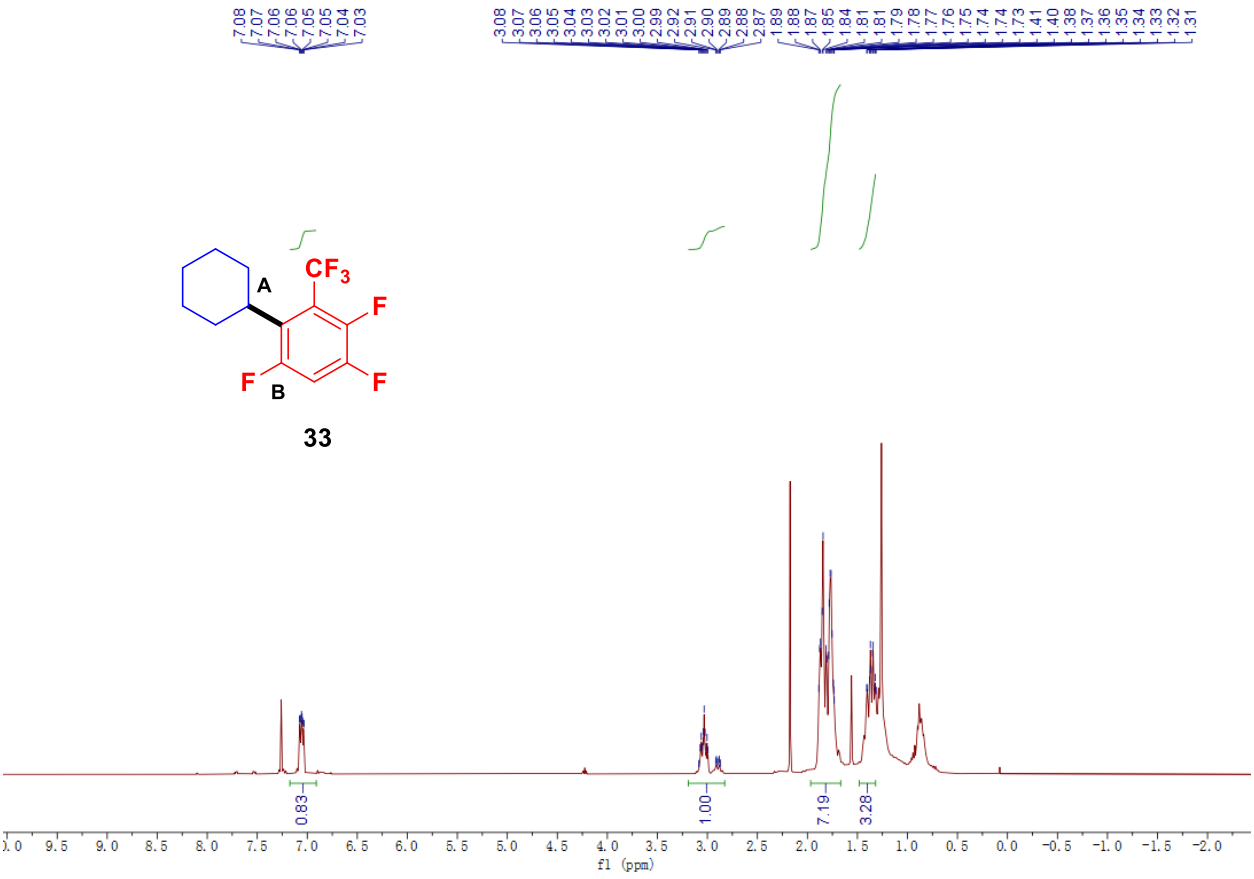
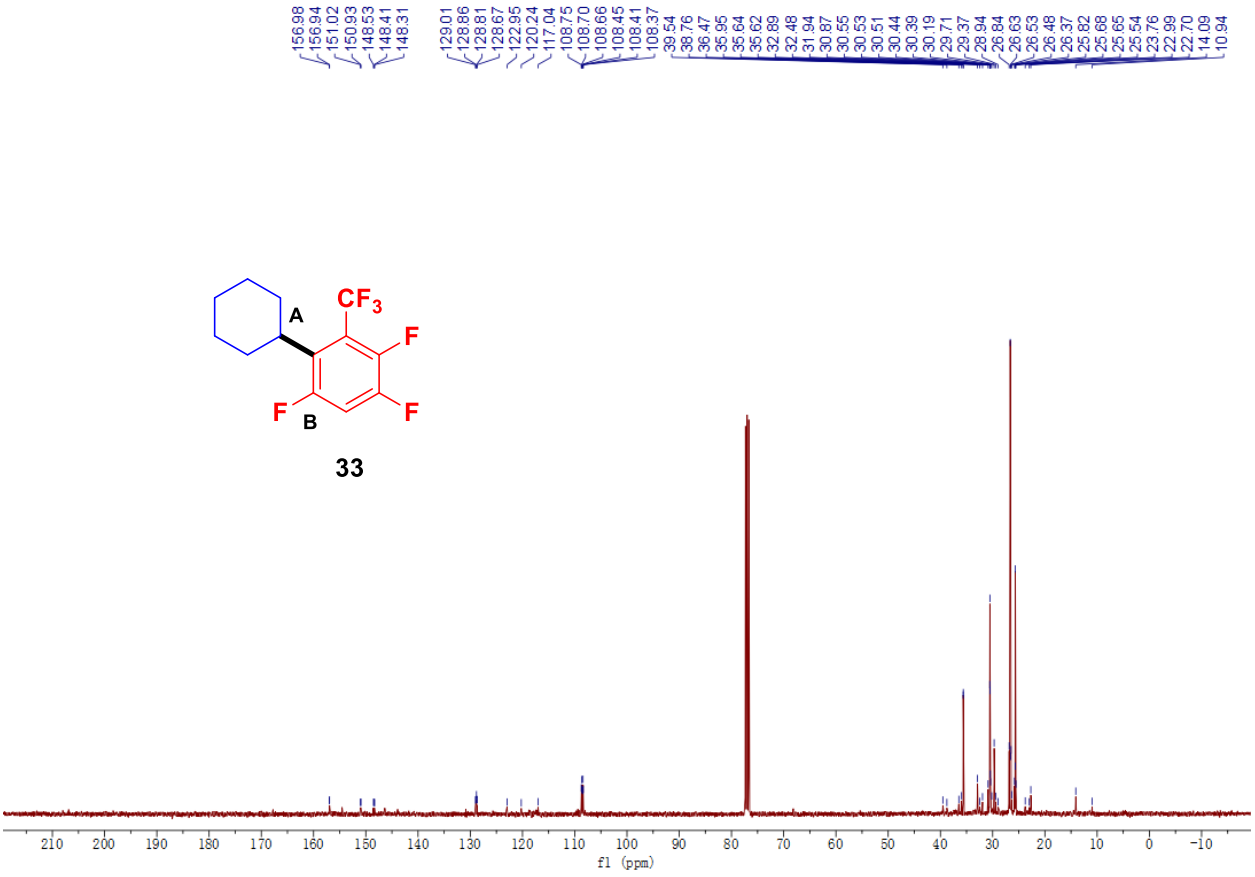


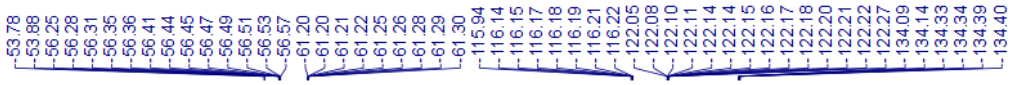
^{1}H-NMR (400 MHz, $CDCl_3$) of **33**

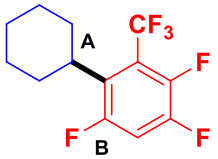


^{13}C-NMR (101 MHz, $CDCl_3$) of **33**

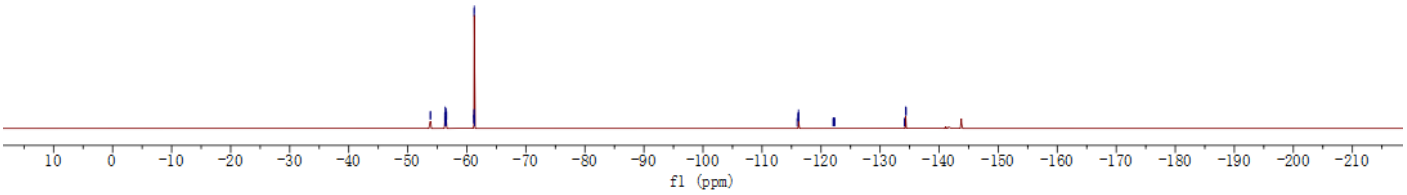


^{19}F-NMR (377 MHz, $CDCl_3$) of **33**





33



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