Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Iodonium based regioselective double nucleophilic alkene functionalization of hydrofluoroolefin scaffold

by

János T. Csenki[1], Zoltán Novák[1*]

[1] MTA-ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Eötvös Loránd University, Institute of Chemistry, Pázmány Péter stny. 1/A, H-1117 Budapest, Hungary

Corresponding Author

* Zoltán Novák novakz@ttk.elte.hu

Table of contents

1. General conditions

Unless otherwise indicated, starting materials were obtained from commercial suppliers, and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on Merck DC pre-coated TLC plates with 0.25 mm Kieselgel 60 F_{254}. Visualization was performed with a 254 nm UV lamp and $KMnO_4$ stain.

All melting points were measured on Büchi 501 apparatus.

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance-400 and Bruker Avance-500 MHz spectrometer in $CDCl_3$, CD_3CN, DMSO-d6. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards ($CDCl_3$: δ 7.26 for ^{1}H, δ 77.16 for ^{13}C, CD_3CN: δ 1.94 for ^{1}H, δ 1.32 for ^{13}C, DMSO-d6: δ 2.50 for ^{1}H, δ 39.52 for ^{13}C). Coupling constants (J) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), dq (doublet quartet), qd (quartet doublet), m (multiplet).

Conversions determined by gas chromatography. This, and low-resolution mass spectrometry was obtained on an Agilent 6890N Gas Chromatograph (30 m x 0.25 mm column with 0.25 µm HP-5MS coating, He carrier gas) and Agilent 5973 Mass Spectrometer (Ion source: EI+, 70eV, 230°C interface 300°C). GC-MS conversion was calculated from the chromatogram using the integral of the peak belonging to the starting material (ISM) and the integral of the peak belonging to the products (IP):

$$conversion(\%) = \frac{IP_y}{\sum_{x=1}^{n} IP_x + ISM} \cdot 100$$

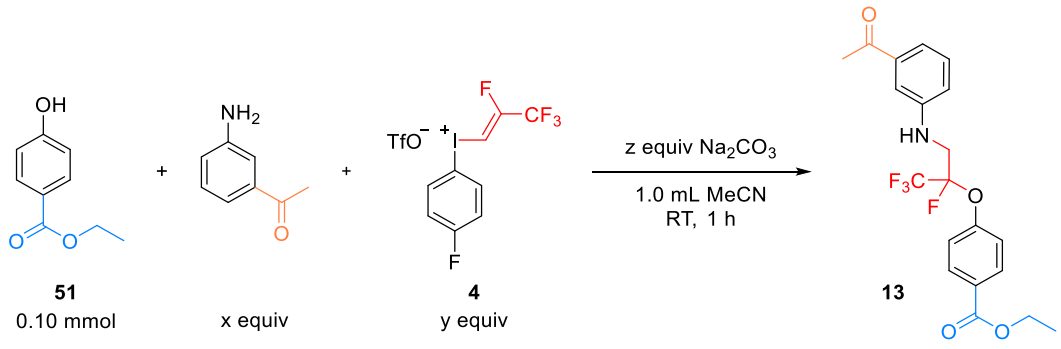
IR spectra were obtained on a Mettler Toledo ReactIR™ 15, AgX DiComp probe, 6 mm x 1.5 m Fiber (Silver Halide), MCT detector.

High-resolution mass spectra were acquired on an Agilent 6230 time-of-flight mass spectrometer equipped with a Jet Stream electrospray ion source in positive ion mode. Injections of 0.1-0.3 µl were directed to the mass spectrometer at a flow rate 0.5 ml/min (70% acetonitrile-water mixture, 0.1 % formic acid), using an Agilent 1260 Infinity HPLC system. Jet Stream parameters: drying gas (N_2) flow and temperature: 10.0 l/min and 325 °C, respectively; nebulizer gas (N_2) pressure: 10 psi; capillary voltage: 4000V; sheath gas flow and temperature: 325°C and 7.5 l/min; TOFMS parameters: fragmentor voltage: 120 V; skimmer potential: 120 V; OCT 1 RF Vpp:750 V. Full-scan mass spectra were acquired over the m/z range 100-2500 at an acquisition rate of 250 ms/spectrum and processed by Agilent MassHunter B.03.01 software.

2. Optimization of the reaction conditions

2.1 Examination of the reaction conditions of the alkene difunctionalization

Na_2CO_3, ethyl 4-hydroxybenzoate (16.6 mg, 0.10 mmol), 1-(3-Aminophenyl)ethan-1-one and MeCN (1 mL) were measured into a screw cap vial. (*Z*)-(4-fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate was added in one portion to the stirred reaction mixture after 5 minutes. The mixture was stirred for further 1 hour at RT, then analyzed by NMR spectroscopy using 1-chloro-2-(trifluoromethyl)benzene as internal standard.



51
0.10 mmol

x equiv

4
y equiv

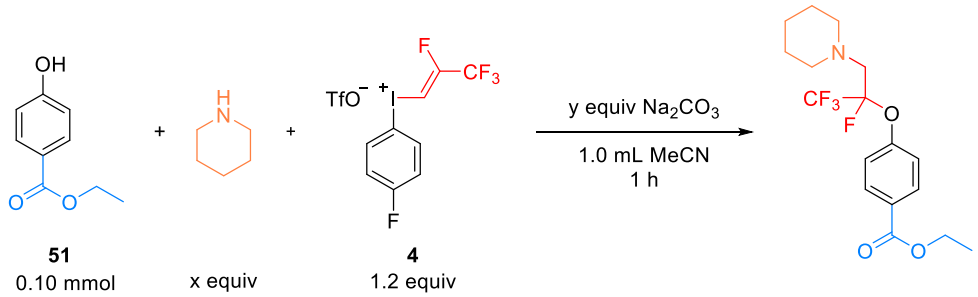
13

Entry	x	z	y	^{19}F NMR yield[a]
1	1.0	2.0	1.2	71%
2	2.0	2.0	1.2	78%
3	3.0	2.0	1.2	76%
4	2.0	0.0	1.2	0%
5	2.0	0.5	1.2	72%
6	**2.0**	**1.0**	**1.2**	**78%**
7	2.0	3.0	1.2	72%
8	2.0	1.0	1.0	68%
9	2.0	1.0	1.5	72%

[a]The yields were measured by NMR spectroscopy using 1-chloro-2-(trifluoromethyl)benzene as internal standard.

2.2 Further examination of the reaction conditions in the case of aliphatic amine

Na_2CO_3, ethyl 4-hydroxybenzoate (16.6 mg, 0.10 mmol), MeCN (1 mL) and piperidine were measured into a screw cap vial. (*Z*)-(4-fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate was added in one portion to the stirred reaction mixture after 5 minutes. The mixture was stirred for further 1 hour at the given temperature, then analyzed by NMR spectroscopy using 1-chloro-2-(trifluoromethyl)benzene as internal standard.



51
0.10 mmol

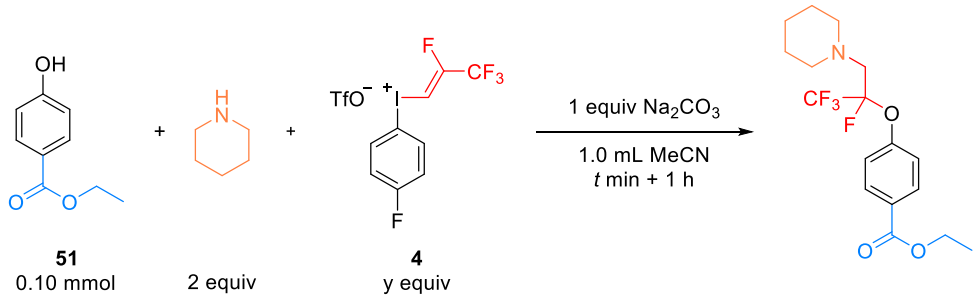
x equiv

4
1.2 equiv

Entry	*T*	y	x	NMR yield[a]
1	RT	1	2	29%
2	0 °C	1	2	32%
3	-20 °C	1	2	31%
4	RT	0	2	7%
5	RT	0.1	2	7%
6	RT	2	2	37%
7	RT	1	1	12%
8	RT	1	10	3%

[a]The yields were measured by NMR spectroscopy using 1-chloro-2-(trifluoromethyl)benzene as internal standard.

Na_2CO_3 (10.6 mg, 0.1 mmol), ethyl 4-hydroxybenzoate (16.6 mg, 0.10 mmol), MeCN (1 mL) were measured into a screw cap vial. (*Z*)-(4-fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate was added in one portion to the stirred reaction mixture after 5 minutes at the given temperature. After the given time (*t* min), the piperidine (20 µL, 17 mg, 0.20 mmol) was added to the reaction mixture and stirred for further 1 hour at the given temperature, then analyzed by NMR spectroscopy using 1-chloro-2-(trifluoromethyl)benzene as internal standard.



51
0.10 mmol

2 equiv

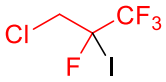
4
y equiv

Entry	*T*	*t* /min	NMR yield[a]
9	RT	15	37%
10	0 °C	15	46%
11	-20 °C	15	50%
12	-40 °C	15	34%
13	**-20 °C**	**60**	**58%**
14	-20 °C	180	45%

[a]The yields were measured by NMR spectroscopy using 1-chloro-2-(trifluoromethyl)benzene as internal standard.

3. Synthesis of starting materials

3-Chloro-1,1,1,2-tetrafluoro-2-iodopropane (2)

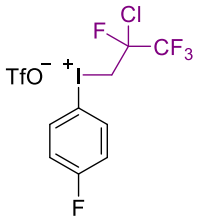


A 250 mL pressure flask was tared with the Teflon bottlecap and stirring bar. The flask was evacuated and refilled with HFO gas three times. 2,3,3,3-Tetrafluoroprop-1-ene (HFO-1234yf) gas was condensated and filled the flask about half (155.52 g, 1.364 mol) using liquid nitrogen bath then closed with the bottlecap. After the flask warmed up to room temperature the weight was measured and the required ICl amount was calculated. The flask was cooled down again using liquid nitrogen bath and the ICl (56.7 mL, 183.8 g, 1.132 mol) was added. The pressure flask was heated up to 50 °C using an oil bath for 3 hours. The reaction mixture cooled down until the next day to room temperature. The flask was cooled down again using liquid nitrogen bath then the bottlecap has been removed and the mixture was allowed to warm to room temperature. The dark oil was washed three times with 1:1 mixture of saturated $NaHCO_3$ and Na_2SO_3 (using no organic solvent). The organic phase was washed twice with 50 mL cc. NaCl and dried by pushing through a plug of $MgSO_4$ using positive pressure. The product was stored in a dark vial on copper shavings and refrigerated.[3-4]

The addition reaction produces 5-7% regioisomer.

Yield: 217.5 g (0.787 mol, 70%) colorless oil. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.55 (dd, *J* = 19.0, 13.5 Hz, 1H), 4.39 (dd, *J* = 19.5, 13.5 Hz, 1H). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -74.7 (d, *J* = 11.8 Hz), -139.0 (q, *J* = 11.8 Hz). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 121.5 (qd, *J* = 283.2, 29.2 Hz), 78.1 (dq, *J* = 255.6, 34.4 Hz), 48.4 (d, *J* = 22.1 Hz). **MS** (EI, 70 eV): m/z (%): 278 (13), 276 (41, [M^+]), 177 (10), 162 (12), 151 (32), 149 (100), 148 (12), 127 (33), 113 (9), 95 (15), 69 (41). Spectral data is in accordance with data given in literature. [3-4]

(2-chloro-2,3,3,3-tetrafluoropropyl)(4-fluorophenyl)iodonium trifluoromethanesulfonate (3)

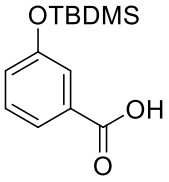


A screwed cap vial with a stirrer bar was evacuated and refilled with argon three times. Trifluoroacetic anhydride (49.42 g, 32.7 mL, 235 mmol) and catalytic amount of trifluoroacetic acid (0.75 g, 0.5 mL, 7 mmol) was added through syringe. The mixture was cooled to -10 °C, then hydrogen-peroxide (50 w/w% in water) (3.74 g, 3.2 mL, 55 mmol) was added dropwise within two minutes. 3-Chloro-1,1,1,2-tetrafluoro-2-iodopropane (13.82 g, 6.5 mL, 50 mmol) was added dropwise through syringe. The resulting reaction mixture was stirred for 16 hours at 35 °C. After that, the mixture was cooled to -20 °C, then freshly distilled dichloromethane (32.5 mL) was added to the mixture. Fluorobenzene (5.05 g, 5.0 mL, 52.5 mmol) was added dropwise to the reaction mixture, followed by the addition of trifluoromethanesulfonic acid (7.50 g, 4.5 mL, 50 mmol). The reaction mixture was kept between 0 °C and 4 °C for 16 hours. After that, all volatiles were removed under reduced pressure at 0 °C protected from light. The dark oil was shaken with cold (-20 °C) diethyl ether, getting white precipitate. The suspension was kept at -20 °C for 2 hours, then the white precipitate was filtered and washed with cold diethyl ether three times.[4]

Yield: 12.317 g (24 mmol, 47%) white solid. **Mp.** 129-130 °C. **MS** (EI, 70 eV): m/z (%): Compound decomposes in injector. **^{1}H NMR** (400 MHz, Acetonitrile-d_3) δ 8.22 (dd, *J* = 8.9, 4.8 Hz, 2H), 7.33 (t, *J* = 8.8 Hz, 2H), 5.09 (dd, *J* = 13.1, 8.7 Hz, 1H), 4.93 (dd, *J* = 28.1, 13.2 Hz, 1H). **^{19}F NMR** (376 MHz, Acetonitrile-d_3) δ -79.3, -80.9 (d, *J* = 6.2 Hz), -104.9, -118.3 (q, *J* = 6.2 Hz). **^{13}C NMR** (101 MHz, Acetonitrile-d_3) δ 166.6 (d, *J* = 254.8 Hz), 141.4 (d, *J* = 9.6 Hz), 121.7 (q, *J* = 320.0 Hz), 120.8 (d, *J* = 23.6

Hz), 119.9 (qd, *J* = 285.4, 31.2 Hz), 104.7 (dq, *J* = 254.7, 38.4 Hz), 103.8 (d, *J* = 3.3 Hz), 41.7 (d, *J* = 21.9 Hz). **IR** (solid, ATR) 1581, 1484, 1275, 1231, 1182, 1163, 1126, 1022, 1003, 929, 832, 813 cm^{-1}. **HRMS** (ESI) $[M - OTf]^+$ calculated for $C_9H_6ClF_5I^+$: 370.9123, found: 370.9120. Spectral data is in accordance with data given in literature. [4]

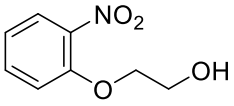
3-((*tert*-Butyldimethylsilyl)oxy)benzoic acid



A solution of 3-hydroxybenzoic acid (2.76 g, 20.0 mmol), *tert*-butyldimethylsilyl chloride (6.70 g, 44.4 mmol) and imidazole (3.03 g, 44.4 mmol) in dry *N*,*N*-dimethylformamide (28 mL) was stirred at ambient temperature for 16h. Acetone (140 mL) was added to the reaction mixture, filtered and the filtrate was evaporated. The residue was taken up in ethyl-acetate (130 mL), washed with water (3x80 mL) and dried over $MgSO_4$, then filtrated. The solvent was removed under reduced pressure. The crude product, *tert*-butyldimethylsilyl 3-((tert-butyldimethylsilyl)oxy)benzoate, was treated with a mixture of acetic acid (42 mL), tetrahydrofuran (14 mL), water (14 mL) and stirred at ambient temperature for 2 h. Ethyl-acetate (140 mL) and water (100 mL) were added and the organic phase was extracted, washed with cc. $NaHCO_3$ solution (4x80 mL) and dried over $MgSO_4$, then filtrated. The solvent was evaporated under reduced pressure to Celite and the crude product was purified by column chromatography using dichloromethane-methanol as eluent.[5]

Yield: 4.37 g (17.3 mmol, 87%) white solid. $\mathbf{R_f}$= 0.74 in dichloromethane: methanol 10:1. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.67 (bs, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 2.2 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.09 (dd, *J* = 8.0, 1.4 Hz, 1H), 1.01 (s, 9H), 0.23 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.2, 155.9, 130.8, 129.7, 125.9, 123.4, 121.6, 25.8, 18.4, -4.3. Spectral data is in accordance with data given in literature.[5]

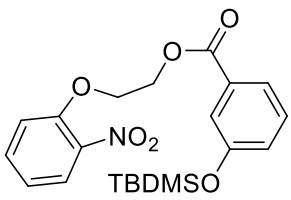
2-(2-Nitrophenoxy)ethan-1-ol



To a solution of 2-nitrophenol (1.11 g, 8 mmol) in acetone was added anhydrous K_2CO_3 (2.21 g, 16 mmol), NaI (80 mg, 0.53 mmol). 2-Bromoethanole (5.00 g, 40 mmol) was added to the reaction mixture and stirred under reflux for 7 h. After cooling to ambient temperature, the solid was filtered, washed with acetone and the filtrate was evaporated. The residue was dissolved in dichloromethane, washed with 1M NaOH solution and cc. NaCl solution, dried over Na_2SO_4, then filtrated and evaporated.[6]

Yield: 1.37 g (7.46 mmol, 93%) brown oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.54 (td, *J* = 8.1, 7.5, 1.9 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.05 (t, *J* = 8.2 Hz, 1H), 4.23 (t, *J* = 4.4 Hz, 2H), 3.98 (dt, *J* = 6.6, 4.3 Hz, 2H), 2.59 (t, *J* = 6.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.4, 140.0, 134.5, 125.9, 121.1, 115.3, 71.5, 61.1. Spectral data is in accordance with data given in literature.[6]

2-(2-Nitrophenoxy)ethyl 3-((tert-butyldimethylsilyl)oxy)benzoate



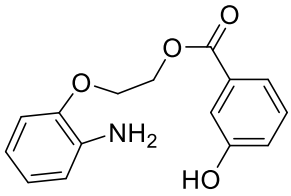
3-((tert-Butyldimethylsilyl)oxy)benzoic acid (1.67 g, 6.6 mmol) was dissolved in toluene (16 mL) then thionyl-chloride (2.9 mL, 4.71 g, 39.6 mmol) and 4 drops of *N*,*N*-dimethylformamide were added to the solution and heated at 80 °C for 3 h. The solvent was evaporated under

vacuum to give 3-((tert-butyldimethylsilyl)oxy)benzoyl chloride. The crude product was used in the next step without further purification.[7]

The previously isolated product was dissolved in freshly distilled THF (20 mL) under nitrogen atmosphere then 2-(2-nitrophenoxy)ethan-1-ol (6 mmol in 10 mL THF) and triethyl-amine (0.92 mL, 0.67 g, 6.6 mmol) were added to the reaction mixture and stirred overnight at ambient temperature. cc. $NaHCO_3$ was added, and the organic phase was separated. The remaining aqueous phase was extracted three times using ethyl-acetate. The organic phase was dried over Na_2SO_4, then filtrated. The solvent was evaporated under reduced pressure to Celite and the crude product was purified by column chromatography using hexane-ethyl acetate as eluent.[8]

Yield: 1.31 g (3.13 mmol, 52%) white solid. **Mp.** 72-74 °C. $\mathbf{R_f}$= 0.33 in hexane: ethyl-acetate 4:1. **MS** (EI, 70 eV): m/z (%): 362 (8), 361 (23), 360 (100), 316 (17), 239 (12), 235 (11), 223 (16), 196 (44), 195 (13), 193 (22), 179 (10), 151 (27), 150 (11), 136 (10), 135 (21), 121 (8), 120 (7), 92 (17), 91 (13), 78 (13), 75 (14), 73 (16). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.08 – 7.02 (m, 2H), 4.70 (d, *J* = 4.6 Hz, 2H), 4.44 (t, *J* = 4.8 Hz, 2H), 0.98 (s, 9H), 0.20 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.4, 155.9, 152.0, 140.6, 134.1, 131.1, 129.6, 125.8, 125.3, 122.9, 121.3, 121.2, 115.3, 68.0, 62.8, 25.8, 18.3, -4.3. **IR** (film, ATR) 2955, 2937, 2859, 1723, 1607, 1585, 1525, 1488, 1439, 1410, 1354, 1279, 1257, 1219, 1167, 1100, 1078, 1055, 1003, 962, 932, 888, 839, 809, 783, 757, 746, 671 cm^{-1}. **HRMS** (EI) $[M-C_4H_9]^+$ calculated for $C_{17}H_{18}NO_6Si^+$: 360.09034, found: 360.08809.

2-(2-Aminophenoxy)ethyl 3-hydroxybenzoate



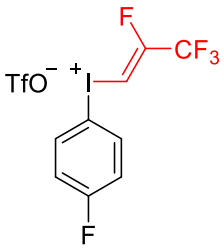
2-(2-nitrophenoxy)ethyl 3-((tert-butyldimethylsilyl)oxy)benzoate (1.14 g, 2.74 mmol) and iron powder (0.61 g, 11 mmol) were suspended in ethanol (10 mL) then cc. HCl (2 mL) was added dropwise within 30 min using Syringe Pump then the reaction mixture was stirred further 60 min at 80 °C. The pH of the reaction mixture was adjusted to 7 using NaOH and extracted three times with ethyl-acetate. The organic phase was dried over Na_2SO_4, filtered and evaporated. The crude product, mixture of 2-(2-aminophenoxy)ethyl 3-hydroxybenzoate and 2-(2-aminophenoxy)ethyl 3-((tert-butyldimethylsilyl)oxy)benzoate, was used in the next step without further purification.[9]

The previously isolated product (1.02 g) was dissolved in THF (7.5 mL) and cooled to 0°C. Tetra-*n*-butylammonium fluoride (TBAF) (2.6 mL, 1M in THF, 2.62 mmol) was added to the reaction mixture then stirred further 2 h at ambient temperature. The solvent was evaporated under reduced pressure to Celite and the crude product was purified by column chromatography using dichloromethane-methanol as eluent.[10]

Yield: 0.726 g (2.65 mmol, 97%) brown solid. **Mp.** 107-108 °C. $\mathbf{R_f}$= 0.71 in dichloromethane: methanol 4:1. **MS** (EI, 70 eV): m/z (%): Compound is not measurable using GC-MS. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.44 – 7.37 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 6.4 Hz, 1H), 6.51 (t, *J* = 6.8 Hz, 1H), 4.67 (s, 2H), 4.59 (t, *J* = 4.6 Hz, 2H), 4.26 (t, *J* = 4.6 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.9, 157.5, 145.2, 138.1, 130.9, 129.9, 121.6, 120.5, 120.0, 116.3, 115.7, 114.2, 112.6, 66.6, 63.5. **IR** (film, ATR) 1712, 1600, 1589, 1507, 1454, 1372, 1290, 1264, 1212, 1104, 1078, 999, 951, 929, 884, 805, 750, 682 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{15}H_{15}NO_4^+$: 273.10011, found: 273.09928.

4. HCl elimination from the fluoroalkyl(aryl)iodonium salt

(*Z*)-(4-Fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate (4)



Preparation using NaH: A 50 mL round bottom flask was evacuated and refilled with argon three times while it was heated. The (2-chloro-2,3,3,3-tetrafluoropropyl)(4-fluorophenyl)iodonium trifluoromethanesulfonate (2602.8 mg, 5 mmol) was added to the flask and solved in freshly distillated acetonitrile (33 mL). The mixture was cooled to 0 °C, then 60 w/w% NaH (220 mg, 5.50 mmol) was added in one portion. It was stirred at 0 °C for 3 hours then allowed to warm to ambient temperature. The reaction mixture was filtered throw Celite and washed with acetonitrile. The filtrate was concentrated under vacuum then diethyl ether was added to the semi crystal residue. The white precipitate was filtered and washed with cold diethyl ether three times.[1-2] Yield: 1.7421 g (3.60 mmol, 72%) white solid. (The product contains unknown quantity of chloride salt, which is disturbing during its subsequent use.)

Preparation using Ag_2O: The (2-chloro-2,3,3,3-tetrafluoropropyl)(4-fluorophenyl)iodonium trifluoromethanesulfonate (11.609 g, 22,3 mmol) was added to a 100 mL round bottom flask and solved in freshly distillated acetonitrile (85 mL). The mixture was stirred at ambient temerature until all the iodonium salt was dissolved, then Ag_2O (3.101 g, 13.4 mmol, 1.2 equiv Ag^+) was added in one portion. It was stirred for 2 hours (the brown Ag_2O turns into white AgCl) then the reaction mixture was filtered throw Celite and washed with freshly distilled acetonitrile. The filtrate was concentrated under vacuum then diethyl ether was added to the residue. The white precipitate was filtered and washed with cold diethyl ether three times. Yield: 9.076 g (18.7 mmol, 84%) white solid.

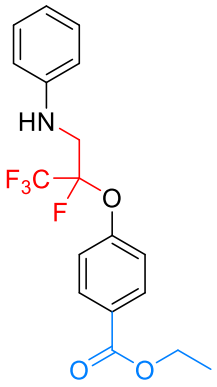
Mp. 99-105 °C. **MS** (EI, 70 eV): m/z (%): Compound decomposes in injector. **^{1}H NMR** (400 MHz, Acetonitrile-d_3) δ 8.14 (dd, *J* = 8.9, 4.9 Hz, 2H), 7.55 (d, *J* = 33.7 Hz, 1H), 7.30 (t, *J* = 8.6 Hz, 2H). **^{19}F NMR** (376 MHz, Acetonitrile-d_3) δ -72.4 (d, *J* = 10.4 Hz), -79.3, -102.1 (q, *J* = 10.5 Hz), -106.2. **^{13}C NMR** (101 MHz, Acetonitrile-d_3) δ 166.0 (d, *J* = 253.7 Hz), 153.3 (dq, *J* = 273.7, 41.8 Hz), 139.9 (d, *J* = 9.4 Hz), 121.7 (q, *J* = 319.8 Hz), 120.7 (d, *J* = 23.6 Hz), 117.1 (qd, *J* = 274.6, 42.7 Hz), 109.6 (d, *J* = 3.0 Hz), 91.9 (dd, *J* = 15.6, 3.6 Hz). **IR** (solid, ATR) 1581, 1484, 1342, 1272, 1249, 1231, 1167, 1044, 1026, 835, 768, 716 cm^{-1}. **HRMS** (ESI) $[M - OTf]^+$ calculated for $C_9H_5F_5I^+$: 334.9351, found: 334.9352.

5. Reactions of phenols and anilines using the alkenyliodonium salt

Method A

Na_2CO_3, phenol derivative (0.3 mmol), "second" nucleophile (0.6 mmol) and MeCN (3.0 mL) were measured into a screw cap vial. The mixture was stirred at ambient temperature for 5 minutes and (*Z*)-(4-fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate (174.3 mg, 0.36 mmol) was added in one portion. The mixture was stirred at ambient temperature for 1 hour. The solvent was evaporated under reduced pressure to Celite and the crude product was purified by column chromatography using hexanes-ethyl acetate as eluent.

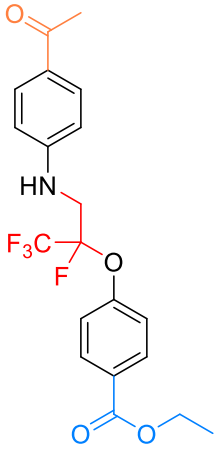
Ethyl 4-((1,1,1,2-tetrafluoro-3-(phenylamino)propan-2-yl)oxy)benzoate (8)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), aniline (55 µL, 55.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 75.6 mg (0.20 mmol, 68%) yellow oil. **R_f**= 0.57 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 371 (7, [M^+]), 236 (2), 151 (3), 121 (6), 107 (8), 106 (100), 104 (7), 77 (10), 65 (5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.79 – 3.61 (m, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.7 Hz), -125.7 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 155.4, 146.6, 131.4, 129.4, 128.2, 121.8 (d, *J* = 2.5 Hz), 120.6 (qd, *J* = 288.1, 37.8 Hz), 118.9, 113.3, 108.9 (dq, *J* = 241.5, 33.3 Hz), 61.3, 45.1 (d, *J* = 28.4 Hz), 14.4. **IR** (film, ATR) 1712, 1604, 1503, 1369, 1275, 1208, 1193, 1171, 1093, 1018, 943, 910, 861, 779, 750, 694 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{18}H_{17}F_4NO_3^+$: 371.11446, found: 371.11237.

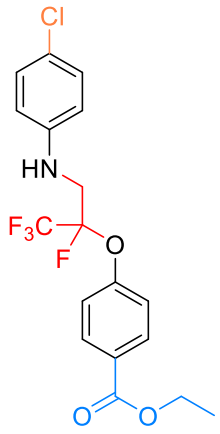
Ethyl 4-((3-((4-acetylphenyl)amino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (9)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 1-(4-aminophenyl)ethan-1-one (81.1 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 87.5 mg (0.21 mmol, 71%) yellow oil. **R_f**= 0.24 in hexane : ethyl acetate 2:1. **MS** (EI, 70 eV): m/z (%): 413 (11, [M^+]), 398 (2), 368 (2), 232 (2), 177 (7), 149 (10), 148 (100), 121 (6), 119 (4), 105 (8), 91 (3), 77 (3), 76 (3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 4.61 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.96 – 3.79 (m, 2H), 2.47 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.0 (d, *J* = 2.7 Hz), -126.2 (q, *J* = 2.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.6, 165.7, 155.3, 150.8, 131.4, 130.7, 128.3, 128.1, 121.7 (d, *J* = 2.5 Hz), 120.4 (qd, *J* = 288.2, 38.1 Hz), 112.0, 108.5 (dq, *J* = 242.0, 33.4 Hz), 61.3, 44.3 (d, *J* = 27.8 Hz), 26.1, 14.3. **IR** (film, ATR) 1715, 1663, 1600, 1536, 1503, 1421, 1361, 1331, 1309, 1275, 1208, 1171, 1096, 1018, 958, 865, 828, 779, 705 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{20}H_{19}F_4NO_4^+$: 413.12502, found: 413.12278.

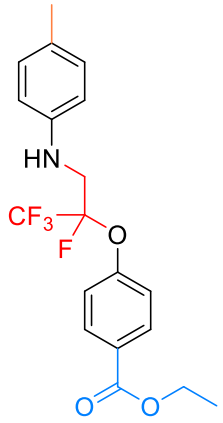
Ethyl 4-((3-((4-chlorophenyl)amino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (10)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 4-chloroaniline (76.5 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 92.8 mg (0.23 mmol, 76%) yellow oil. $\mathbf{R_f}$= 0.56 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 407 (3), 405 (8, [M^+]), 360 (2), 151 (5), 142 (32), 141 (8), 140 (100), 121 (8), 104 (9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.5 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 1H), 3.84 – 3.69 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.1 (d, *J* = 2.7 Hz), -125.8 (q, *J* = 2.6 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 155.4, 145.2, 131.4, 129.2, 128.3, 123.5, 121.8 (d, *J* = 2.7 Hz), 120.5 (qd, *J* = 287.9, 37.8 Hz), 114.4, 108.7 (dq, *J* = 241.2, 33.1 Hz), 61.3, 45.2 (d, *J* = 28.1 Hz), 14.4. **IR** (film, ATR) 1712, 1604, 1503, 1413, 1369, 1279, 1208, 1197, 1171, 1096, 1018, 865, 817, 779, 705 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{18}H_{16}ClF_4NO_3^+$: 405.07548, found: 405.07313.

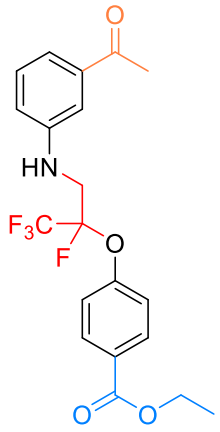
Ethyl 4-((1,1,1,2-tetrafluoro-3-(*p*-tolylamino)propan-2-yl)oxy)benzoate (11)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *p*-toluidine (64.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 29.6 mg (0.08 mmol, 26%) yellow oil. $\mathbf{R_f}$= 0.63 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 385 (8, [M^+]), 340 (2), 151 (2), 121 (14), 120 (100), 104 (6), 91 (13). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.86 – 3.70 (m, 2H), 3.68 (bs, 1H), 2.24 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ-80.2 (d, *J* = 3.0 Hz), -125.6 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 155.5, 144.3, 131.4, 129.9, 128.2, 128.2, 121.9 (d, *J* = 2.5 Hz), 120.6 (qd, *J* = 288.2, 37.4 Hz), 113.5, 108.9 (dq, *J* = 240.9, 33.2 Hz), 61.3, 45.4 (d, *J* = 28.4 Hz), 20.5, 14.4. **IR** (film, ATR) 1712, 1604, 1525, 1507, 1413, 1369, 1275, 1208, 1193, 1171, 1093, 1048, 1018, 943, 914, 861, 809, 779, 705 cm^{-1}. **IR** (film, ATR) 1712, 1604, 1525, 1507, 1413, 1369, 1275, 1208, 1193, 1171, 1093, 1048, 1018, 943, 914, 861, 809, 779, 705 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{19}H_{19}F_4NO_3^+$: 385.13011, found: 385.12798.

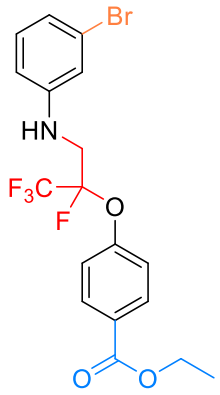
Ethyl 4-((3-((3-acetylphenyl)amino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (13)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 1-(3-aminophenyl)ethan-1-one (81.1 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 99.5 mg (0.24 mmol, 80%) yellow solid. **Mp.** 46-50 °C. **R_f**= 0.31 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 413 (8, [M^+]), 368 (2), 177 (3), 149 (11), 148 (100), 121 (7), 91 (4) . **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.27 (dd, *J* = 28.3, 7.9 Hz, 2H), 7.23 – 7.15 (m, 3H), 6.79 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.13 (bs, 1H), 3.90 – 3.76 (m, 2H), 2.52 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.1 (d, *J* = 2.7 Hz), -125.6 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 198.3, 165.7, 155.3, 146.9, 138.2, 131.4, 129.5, 128.2, 121.7 (d, *J* = 2.5 Hz), 120.5 (qd, *J* = 288.3, 37.8 Hz), 119.2, 117.8, 112.0, 108.7 (dq, *J* = 241.4, 33.2 Hz), 61.2, 44.8 (d, *J* = 28.5 Hz), 26.7, 14.3. **IR** (film, ATR) 1715, 1682, 1604, 1525, 1503, 1477, 1443, 1417, 1361, 1328, 1275, 1197, 1171, 1093, 1018, 973, 951, 917, 861, 779, 735, 705, 686 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{20}H_{19}F_4NO_4^+$: 413.12502, found: 413.12336.

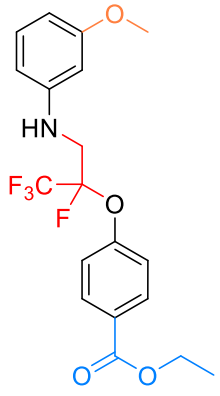
Ethyl 4-((3-((3-bromophenyl)amino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (14)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 3-bromoaniline (65 µL, 103.2 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 103.3 mg (0.23 mmol, 76%) yellow oil. **R_f**= 0.51 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 451 (2), 449 (2, [M^+]), 406 (2), 404 (2), 187 (8), 186 (94), 185 (10), 184 (100), 151 (8), 136 (4), 121 (15), 106 (12), 105 (22), 104 (21), 91 (6), 76 (12). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.70 (t, *J* = 2.2 Hz, 1H), 6.51 (dd, *J* = 8.1, 2.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 1H), 3.85 – 3.69 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ-80.1 (d, *J* = 2.7 Hz), -125.5 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 155.3, 147.9, 131.5, 130.6, 128.3, 123.3, 121.7 (d, *J* = 2.5 Hz), 121.7, 120.5 (qd, *J* = 288.3, 38.1 Hz), 116.0, 111.9, 108.7 (dq, *J* = 241.3, 33.1 Hz), 61.3, 44.7 (d, *J* = 28.5 Hz), 14.4. **IR** (film, ATR) 1708, 1596, 1503, 1480, 1369, 1324, 1275, 1193, 1171, 1093, 1018, 988, 947, 917, 861, 843, 761, 705, 679 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{18}H_{16}BrF_4NO_3^+$: 449.02497, found: 449.02366.

Ethyl 4-((1,1,1,2-tetrafluoro-3-((3-methoxyphenyl)amino)propan-2-yl)oxy)benzoate (15)

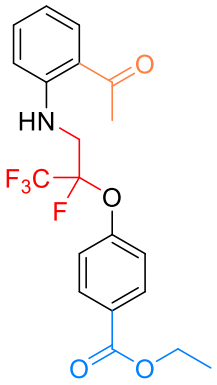


Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 3-methoxyaniline (67 µL, 73.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 89.0 mg (0.22 mmol, 74%) yellow oil. **R_f**= 0.42 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 401 (9, [M^+]), 356 (2), 151 (4), 137 (9), 136 (100), 121 (8), 108 (5), 104 (6), 92 (5), 77 (5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.34 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.22 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.15 (t, *J* = 2.4 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.88 – 3.69 (m, 6H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.9 Hz), -125.7 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 160.9,

155.4, 148.0, 131.4, 130.2, 128.2, 121.8 (d, *J* = 2.5 Hz), 120.6 (qd, *J* = 287.7, 37.6 Hz), 108.8 (dq, *J* = 241.2, 33.1 Hz), 106.2, 103.9, 99.5, 61.2, 55.1, 45.0 (d, *J* = 28.4 Hz), 14.4. **IR** (film, ATR) 1715, 1604, 1521, 1503, 1466, 1369, 1279, 1212, 1167, 1096, 1048, 1018, 861, 832, 761, 709, 686 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{19}H_{19}F_4NO_4^+$: 401.12502, found: 401.12458.

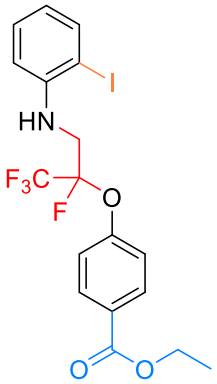
Ethyl 4-((3-((2-acetylphenyl)amino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (16)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 1-(2-aminophenyl)ethan-1-one (36 µL, 40.5 mg, 0.3 mmol, 1 equiv in this case, due to purification problems) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 79.0 mg (0.19 mmol, 64%) yellow oil. R_f= 0.50 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 413 (9, $[M^+]$), 368 (3), 247 (6), 149 (11), 148 (100), 130 (41), 121 (11), 106 (17), 104 (11), 103 (11), 92 (10), 77 (15). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.17 (t, *J* = 5.9 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.65 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.61 – 6.49 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.87 – 3.65 (m, 2H), 2.49 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.7 (d, *J* = 2.8 Hz), -123.9 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 201.3, 165.8, 155.2, 149.8, 135.1, 132.8, 131.4, 128.2, 121.9 (d, *J* = 2.5 Hz), 120.5 (qd, *J* = 287.7, 36.7 Hz), 118.6, 115.7, 111.4, 108.7 (dq, *J* = 240.5, 33.5 Hz), 61.2, 43.1 (d, *J* = 31.1 Hz), 28.0, 14.4. **IR** (film, ATR) 1719, 1645, 1607, 1581, 1525, 1507, 1462, 1432, 1365, 1328, 1275, 1238, 1212, 1167, 1096, 1044, 1022, 955, 865, 750, 709 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{20}H_{19}F_4NO_4^+$: 413.12502, found: 413.12277.

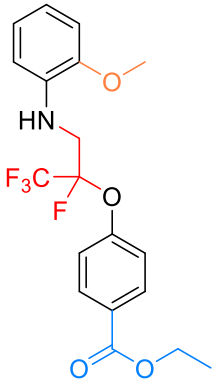
Ethyl 4-((1,1,1,2-tetrafluoro-3-((2-iodophenyl)amino)propan-2-yl)oxy)benzoate (17)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 2-iodoaniline (131.4 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 99.5 mg (0.20 mmol, 67%) orange oil. R_f= 0.39 in hexane : dichloromethane 4:1. **MS** (EI, 70 eV): m/z (%): 497 (13, $[M^+]$), 452 (2), 371 (1), 233 (9), 232 (100), 136 (4), 121 (8), 106 (11), 105 (25), 104 (25), 91 (7), 78 (7), 77 (9), 76 (8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.55 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.45 – 6.36 (m, 2H), 4.31 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.72 (dd, *J* = 10.5, 6.4 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.4 (d, *J* = 3.1 Hz), -124.7 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 155.2, 145.7, 139.3, 131.5, 129.5, 128.4, 121.9 (d, *J* = 2.4 Hz), 120.5 (qd, *J* = 287.9, 37.1 Hz), 120.2, 110.8, 108.6 (dq, *J* = 240.9, 33.4 Hz), 85.8, 61.3, 44.7 (d, *J* = 30.2 Hz), 14.4. **IR** (film, ATR) 1715, 1592, 1503, 1454, 1369, 1320, 1309, 1275, 1242, 1193, 1167, 1093, 1048, 1007, 943, 861, 779, 742, 705 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{18}H_{16}F_4INO_3^+$: 497.01110, found: 497.00907.

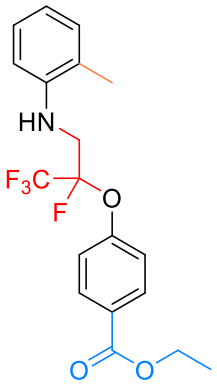
Ethyl 4-((1,1,1,2-tetrafluoro-3-((2-methoxyphenyl)amino)propan-2-yl)oxy)benzoate (18)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 2-methoxyaniline (68 µL, 73.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 83.6 mg (0.21 mmol, 69%) yellow oil. $\mathbf{R_f}$= 0.58 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 401 (15, [M^+]), 356 (2), 235 (1), 151 (4), 137 (8), 136 (100), 121 (32), 120 (22), 104 (8), 92 (9), 77 (6), 65 (7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.72 (td, *J* = 7.5, 1.6 Hz, 1H), 6.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.61 (td, *J* = 7.6, 1.6 Hz, 1H), 6.44 (d, *J* = 7.7 Hz, 1H), 4.39 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.70 (d, *J* = 17.5 Hz, 5H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.9 Hz), -125.2 (q, *J* = 2.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 155.4, 147.0, 136.6, 131.4, 128.1, 121.9 (d, *J* = 2.6 Hz), 121.2, 120.6 (qd, *J* = 287.9, 37.4 Hz), 118.0, 110.2, 109.9, 109.0 (dq, *J* = 240.9, 33.3 Hz), 61.2, 55.6, 44.7 (d, *J* = 29.1 Hz), 14.4. **IR** (film, ATR) 1715, 1604, 1521, 1507, 1462, 1275, 1249, 1219, 1193, 1171, 1093, 1048, 1018, 943, 861, 779, 735, 709 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{19}H_{19}F_4NO_4^+$: 401.12502, found: 401.12287.

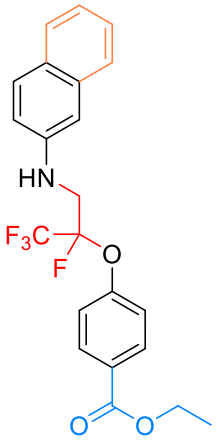
Ethyl 4-((1,1,1,2-tetrafluoro-3-(*o*-tolylamino)propan-2-yl)oxy)benzoate (19)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *o*-toluidine (64 µL, 64.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 82.5 mg (0.21 mmol, 71%) yellow oil. $\mathbf{R_f}$= 0.63 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 385 (9, [M^+]), 340 (2), 151 (3), 121 (13), 120 (100), 118 (7), 104 (7), 92 (5), 91 (15), 77 (4), 65 (5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.02 – 6.93 (m, 2H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 3H), 3.73 (d, *J* = 11.2 Hz, 2H), 3.57 (s, 1H), 2.01 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.8 Hz), -125.0 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 155.4, 144.5, 131.5, 130.5, 128.3, 127.2, 122.6, 121.8 (d, *J* = 2.4 Hz), 120.6 (qd, *J* = 287.8, 37.2 Hz), 118.5, 110.1, 108.9 (dq, *J* = 241.0, 33.2 Hz), 61.3, 44.6 (d, *J* = 29.2 Hz), 17.3, 14.4. **IR** (film, ATR) 1715, 1607, 1521, 1503, 1480, 1454, 1369, 1275, 1208, 1193, 1167, 1093, 1048, 1018, 943, 861, 776, 746, 709 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{19}H_{19}F_4NO_3^+$: 385.13011, found: 385.12918.

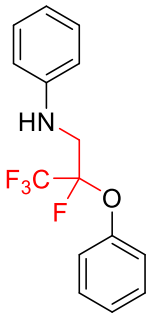
Ethyl 4-((1,1,1,2-tetrafluoro-3-(naphthalen-2-ylamino)propan-2-yl)oxy)benzoate (20)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), naphthalen-2-amine (85.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 92.0 mg (0.22 mmol, 73%) red/brown solid. **Mp.** 79-82 °C. $\mathbf{R_f}$= 0.48 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 421 (13, [M^+]), 157 (12), 156 (100), 151 (4), 129 (8) 128 (11), 127 (14), 121 (5), 115 (11), 104 (6), 76 (3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.05 (m, 3H), 6.72 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.90 (bs, 1H), 3.84 – 3.69 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.8 Hz), -125.2 (q, *J* = 2.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 155.4, 144.2, 134.9, 131.4, 129.3, 128.2, 128.2, 127.7, 126.6, 126.2, 122.8, 121.8 (d, *J* = 2.5 Hz), 120.6 (qd, *J* = 287.6, 37.5 Hz), 117.6, 108.9 (dq, *J* = 241.1, 33.3 Hz), 105.6, 61.2, 44.9 (d, *J* = 29.0 Hz), 14.4. **IR** (film, ATR) 1712, 1633, 1604, 1529, 1503, 1369, 1275, 1208, 1193, 1171, 1093, 1018, 958, 861, 832, 809, 779, 746, 705 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{22}H_{19}F_4NO_3^+$: 421.13011, found: 421.12765.

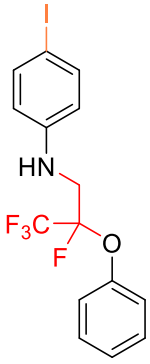
***N*-(2,3,3,3-tetrafluoro-2-phenoxypropyl)aniline (21)**



Method A. Using phenol (28.2 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), aniline (55 µL, 55.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 58.3 mg (0.19 mmol, 65%) yellow oil. $\mathbf{R_f}$= 0.49 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 299 (10, [M^+]), 166 (2), 136 (2), 107 (8), 106 (100), 104 (4), 79 (6), 77 (28), 65 (11). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.8 Hz, 2H), 7.15 – 7.02 (m, 5H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 2H), 3.81 – 3.56 (m, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 2.8 Hz), -124.7 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.7, 146.8, 129.8, 129.4, 126.1, 122.3 (d, *J* = 2.1 Hz), 120.7 (qd, *J* = 287.9, 37.7 Hz), 118.8, 113.3, 108.7 (dq, *J* = 239.1, 32.9 Hz), 44.9 (d, *J* = 29.6 Hz). **IR** (film, ATR) 1604, 1514, 1492, 1443, 1387, 1320, 1257, 1193, 1171, 1096, 1070, 1026, 943, 910, 873, 779, 750, 690 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{15}H_{13}F_4NO^+$: 299.09333, found: 299.09194.

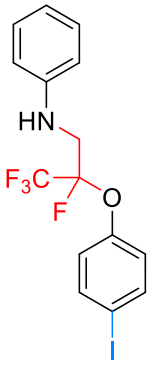
4-Iodo-*N*-(2,3,3,3-tetrafluoro-2-phenoxypropyl)aniline (22)



Method A. Using phenol (28.2 mg, 0.3 mmol) Na_2CO_3 (31.8 mg, 0.3 mmol), 4-iodoaniline (131.4 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 65.9 mg (0.15 mmol, 52%) orange/brown oil. $\mathbf{R_f}$= 0.47 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 425 (23, [M^+]), 131 (1), 298 (2), 272 (2), 233 (8), 232 (100), 136 (3), 106 (8), 105 (51), 104 (14) 91 (11), 78 (8), 77 (29), 76 (12), 65 (10). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.8 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.26 (d, *J* = 8.8 Hz, 2H), 3.78 – 3.54 (m, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 3.1 Hz), -124.8 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.6, 146.4, 138.0, 129.8, 126.2, 122.2 (d, *J* = 2.1 Hz), 120.6 (dd, *J* = 287.5, 37.9 Hz), 115.4, 108.5 (dq, *J* = 239.5, 33.1 Hz), 79.6, 44.7 (d, *J* = 29.3 Hz). **IR** (film, ATR) 1592, 1507, 1492, 1387, 1320, 1294, 1253, 1197, 1100, 1026, 1003, 943, 910, 809, 783, 753, 694 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{15}H_{12}F_4INO^+$: 424.98997, found: 424.98755.

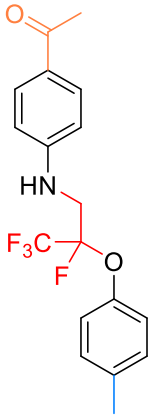
_N_-(2,3,3,3-Tetrafluoro-2-(4-iodophenoxy)propyl)aniline (23)



Method A. Using 4-iodophenol (66.0 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), aniline (55 µL, 55.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 87.2 mg (0.21 mmol, 68%) yellow solid. **Mp.** 43-46 °C. R_f= 0.55 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 425 (7, [M$^+$]), 219 (1), 203 (6), 191 (2), 136 (2), 107 (8), 106 (100), 92 (4), 77 (14), 65 (7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 2H), 3.88 – 3.71 (m, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.0 (d, *J* = 3.0 Hz), -125.7 (q, *J* = 2.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.6, 146.6, 138.8, 129.4, 124.4 (d, *J* = 2.1 Hz), 120.6 (qd, *J* = 288.1, 37.8 Hz), 118.9, 113.3, 108.7 (dq, *J* = 239.9, 33.1 Hz), 90.1, 45.0 (d, *J* = 28.9 Hz). **IR** (film, ATR) 1604, 1514, 1480, 1443, 1391, 1320, 1257, 1193, 1175, 1096, 1074, 1055, 1007, 943, 910, 873, 835, 750, 716, 690 cm^{-1}. **HRMS** (EI) [M]$^+$ calculated for $C_{15}H_{12}F_4INO^+$: 424.98997, found: 424.98730.

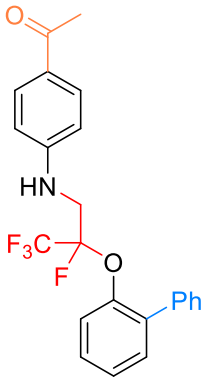
1-(4-((2,3,3,3-Tetrafluoro-2-(*p*-tolyloxy)propyl)amino)phenyl)ethan-1-one (24)



Method A. Using *p*-cresol (31 µL, 32.4 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 1-(4-aminophenyl)ethan-1-one (81.1 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 55.9 mg (0.16 mmol, 52%) yellow solid. **Mp.** 96-99 °C. R_f= 0.51 in hexane : ethyl acetate 2:1. **MS** (EI, 70 eV): m/z (%): 355 (14, [M$^+$]), 340 (1), 232 (2), 170 (2), 149 (9), 148 (100), 132 (3), 119 (8), 107 (5), 106 (5), 105 (10), 91 (12), 79 (5), 77 (10), 65 (5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.39 (s, 1H), 3.90 – 3.72 (m, 2H), 2.49 (s, 3H), 2.32 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 2.7 Hz), -125.0 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.5, 150.9, 149.2, 136.0, 130.8, 130.3, 128.0, 121.9 (d, *J* = 2.1 Hz), 120.6 (qd, *J* = 287.8, 38.3 Hz), 112.0, 108.3 (dq, *J* = 239.6, 33.0 Hz), 44.1 (d, *J* = 29.4 Hz), 26.1, 20.9. **IR** (film, ATR) 1659, 1600, 1536, 1507, 1424, 1361, 1331, 1275, 1178, 1156, 1100, 1070, 1022, 958, 828 cm^{-1}. **HRMS** (EI) [M]$^+$ calculated for $C_{18}H_{17}F_4NO_2^+$: 355.11954, found: 355.11801.

1-(4-((2-([1,1'-Biphenyl]-2-yloxy)-2,3,3,3-tetrafluoropropyl)amino)phenyl)ethan-1-one (25)

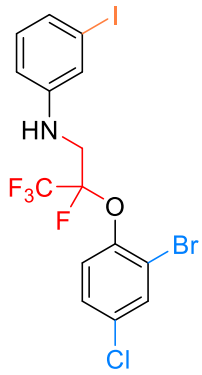


Method A. Using [1,1'-biphenyl]-2-ol (51.1 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 1-(4-aminophenyl)ethan-1-one (81.1 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 65.6 mg (0.16 mmol, 52%) yellow solid. **Mp.** 89-92 °C. R_f= 0.56 in hexane : ethyl acetate 2:1. **MS** (EI, 70 eV): m/z (%): 417 (12, [M$^+$]), 201 (3), 169 (6), 152 (10), 149 (10), 48 (100), 141 (6), 119 (9), 115 (7), 105 (8), 91 (6). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.55 – 7.30 (m, 9H), 6.17 (d, *J* = 8.8 Hz, 2H), 3.62 – 3.49 (m, 2H), 3.46 – 3.33 (m, 1H), 2.47 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -81.0 (d, *J* = 2.9 Hz), -121.1 (q, *J* = 3.1 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 196.4, 150.3, 148.1 (d, *J* = 1.7 Hz), 137.0, 135.2 (d, *J* = 1.8 Hz),

131.5, 130.6, 129.8, 129.0, 128.6, 128.1, 127.8, 126.8, 123.3 (d, *J* = 2.4 Hz), 120.3 (qd, *J* = 287.2, 35.6 Hz), 111.7, 108.6 (dq, *J* = 239.9, 33.6 Hz), 42.9 (d, *J* = 33.8 Hz), 26.1. **IR** (film, ATR) 1663, 1600, 1533, 1477, 1432, 1361, 1335, 1272, 1182, 1163, 1093, 1070, 1048, 1011, 955, 906, 824, 776, 761, 738, 701 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{23}H_{19}F_4NO_2^+$: 417.13519, found: 417.13291.

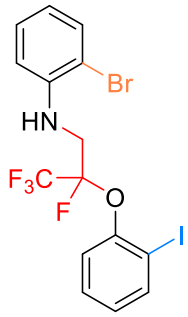
_N_-(2-(2-Bromo-4-chlorophenoxy)-2,3,3,3-tetrafluoropropyl)-3-iodoaniline (26)



Method A. Using 2-bromo-4-chlorophenol (62.2 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 3-iodoaniline (72 µL, 131.4 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 132.1 mg (0.25 mmol, 82%) yellow oil. R_f= 0.52 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 541 (2), 539 (9), 537 (6, $[M^+]$), 458 (2), 331 (1), 233 (8), 232 (100), 191 (4), 179 (3), 136 (5), 135 (4), 105 (25), 104 (12), 91 (9), 76 (10). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (t, *J* = 1.5 Hz, 1H), 7.16 (t, *J* = 1.5 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.80 – 6.69 (m, 2H), 6.39 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.77 – 3.63 (m, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.6 (d, *J* = 3.3 Hz), -123.0 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.8 (d, *J* = 1.9 Hz), 147.4, 133.5, 132.0, 130.8, 128.9, 127.8, 123.7 (d, *J* = 3.2 Hz), 121.6, 120.3 (qd, *J* = 287.3, 36.6 Hz), 116.8 (d, *J* = 2.9 Hz), 112.5, 109.2 (dq, *J* = 242.2, 33.9 Hz), 95.2, 44.0 (d, *J* = 29.1 Hz). **IR** (film, ATR) 1592, 1510, 1469, 1421, 1384, 1324, 1253, 1231, 1193, 1167, 1141, 1089, 1048, 1022, 984, 947, 917, 869, 847, 824, 764, 742, 682, 660 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{15}H_{10}BrClF_4INO^+$: 536.86151, found: 536.86097.

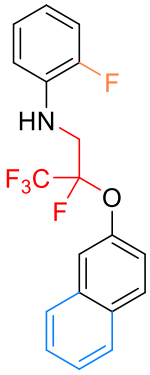
2-Bromo-_N_-(2,3,3,3-tetrafluoro-2-(2-iodophenoxy)propyl)aniline (27)



Method A. Using ethyl 2-iodophenol (66.0 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 2-bromoaniline (103.2 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 104.5 mg (0.21 mmol, 69%) yellow solid **Mp.** 54-57 °C. R_f= 0.59 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 505 (8), 503 (9, $[M^+]$), 378 (4), 376 (4), 358 (3), 356 (2), 203 (12), 186 (96), 184 (100), 157 (4), 155 (4), 136 (6), 135 (12), 109 (5), 105 (24), 104 (15), 92 (15), 91 (18), 78 (99, 77 (28), 76 (24). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.14 (td, *J* = 8.0, 1.6 Hz, 1H), 6.99 – 6.90 (m, 1H), 6.62 (td, *J* = 7.6, 1.5 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 4.51 (t, *J* = 6.5 Hz, 1H), 4.05 – 3.80 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.6 (d, *J* = 2.8 Hz), -122.3 (q, *J* = 2.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.9 (d, *J* = 2.3 Hz), 143.4, 140.3, 132.7, 129.8, 128.5, 127.4, 122.1 (d, *J* = 3.3 Hz), 120.4 (qd, *J* = 287.6, 36.3 Hz), 119.1, 111.3 (d, *J* = 1.6 Hz), 110.2, 109.0 (dq, *J* = 242.1, 33.6 Hz), 90.3 (d, *J* = 3.1 Hz), 44.3 (d, *J* = 28.5 Hz). **IR** (film, ATR) 1600, 1518, 1466, 1439, 1387, 1324, 1283, 1264, 1223, 1197, 1171, 1096, 1044, 1022, 943, 910, 858, 835, 772, 742 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{15}H_{11}BrF_4INO^+$: 502.90048, found: 502.89846.

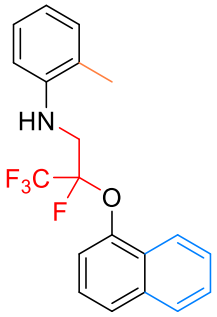
2-Fluoro-*N*-(2,3,3,3-tetrafluoro-2-(naphthalen-2-yloxy)propyl)aniline (28)



Method A. Using naphthalen-2-ol (43.3 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 2-fluoroaniline (58 µL, 66.7 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 71.3 mg (0.19 mmol, 65%) yellow oil. **R_f**= 0.42 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 367 (13, [M^+]), 250 (1), 223 (6), 184 (1), 144 (2), 127 (15), 125 (8), 124 (100), 115 (12), 83 (8), 77 (28). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (t, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.68 (s, 1H), 7.52 (pd, *J* = 7.0, 1.6 Hz, 2H), 7.37 (d, *J* = 9.4 Hz, 1H), 7.05 – 6.92 (m, 2H), 6.73 – 6.61 (m, 2H), 4.19 (s, 1H), 3.96 – 3.78 (m, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 2.9 Hz), -124.3 (q, *J* = 2.9 Hz), -136.4. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.8 (d, *J* = 238.7 Hz), 149.2, 135.2 (d, *J* = 11.2 Hz), 133.9, 131.6, 130.0, 127.9, 127.8, 127.0, 126.1, 124.6 (d, *J* = 3.6 Hz), 121.6 (d, *J* = 2.3 Hz), 120.8 (qd, *J* = 287.9, 37.6 Hz), 119.2 (d, *J* = 2.3 Hz), 118.2 (d, *J* = 7.0 Hz), 114.9 (d, *J* = 18.6 Hz), 112.6 (d, *J* = 2.9 Hz), 108.9 (dq, *J* = 239.3, 33.1 Hz), 44.5 (d, *J* = 30.1 Hz). **IR** (film, ATR) 1622, 1600, 1525, 1514, 1480, 1458, 1387, 1331, 1298, 1246, 1212, 1175, 1122, 1093, 1033, 966, 917, 888, 861, 817, 738, 690 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{19}H_{14}F_5NO^+$: 367.09956, found: 367.09813.

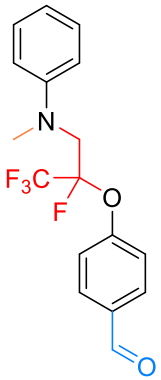
2-Methyl-*N*-(2,3,3,3-tetrafluoro-2-(naphthalen-1-yloxy)propyl)aniline (29)



Method A. Using naphthalen-1-ol (43.3 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *o*-toluidine (64 µL, 64.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 69.6 mg (0.19 mmol, 64%) yellow oil. **R_f**= 0.65 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 363 (15, [M^+]), 246 (1), 219 (2), 128 (4), 127 (12), 121 (8), 120 (100), 118 (9), 115 (23), 91 (22), 77 (13), 65 (8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.61 (qt, *J* = 6.8, 3.5 Hz, 2H), 7.52 – 7.41 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 4.03 – 3.84 (m, 2H), 3.46 (s, 1H), 1.90 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -81.1 (d, *J* = 2.4 Hz), -120.5 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.4 (d, *J* = 2.0 Hz), 144.4, 134.9, 130.4, 128.1, 127.5 (d, *J* = 2.1 Hz), 127.1, 127.1, 127.0, 126.0, 125.6, 122.6, 121.5, 121.0 (qd, *J* = 287.1, 36.3 Hz), 118.3, 117.1 (d, *J* = 2.7 Hz), 109.9, 109.5 (dq, *J* = 239.1, 33.4 Hz), 43.6 (d, *J* = 31.8 Hz), 17.1. **IR** (film, ATR) 1607, 1592, 1521, 1480, 1454, 1395, 1320, 1260, 1231, 1186, 1104, 1048, 1014, 865, 802, 776, 746, 712, 690 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{20}H_{17}F_4NO^+$: 363.12463, found: 363.12385.

4-((1,1,1,2-Tetrafluoro-3-(methyl(phenyl)amino)propan-2-yl)oxy)benzaldehyde (30)

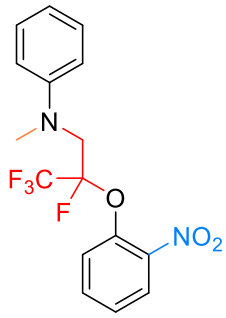


Method A. Using 4-hydroxybenzaldehyde (36.6 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *N*-methylaniline (65 µL, 64.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 58.3 mg (0.17 mmol, 57%) brown oil. **R_f**= 0.53 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 341 (4, [M^+]), 120 (1), 200 (1), 121 (2), 131 (1), 121 (9), 120 (100), 105 (10), 104 (12), 91 (4), 77 (18). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.20 – 7.09 (m, 4H), 6.76 – 6.64 (m, 3H), 3.94 – 3.81 (m, 2H), 2.94 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.9 (d, *J* = 2.7 Hz), -126.9 (q, *J* = 2.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 190.9, 157.1, 149.2, 133.7, 131.3, 129.2, 122.3 (d,

J = 2.9 Hz), 120.6 (qd, *J* = 289.2, 39.0 Hz), 118.1, 112.9, 109.9 (dq, *J* = 244.6, 32.5 Hz), 54.5 (d, *J* = 22.7 Hz), 40.1 (d, *J* = 1.4 Hz). **IR** (film, ATR) 1700, 1600, 1503, 1451, 1428, 1372, 1328, 1301, 1268, 1208, 1193, 1163, 1089, 1014, 996, 970, 917, 843, 750, 723, 694 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{17}H_{15}F_4NO_2^+$: 341.10389, found: 341.10240.

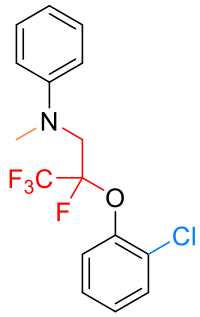
_N_-Methyl-_N_-(2,3,3,3-tetrafluoro-2-(2-nitrophenoxy)propyl)aniline (31)



Method A. Using 2-nitrophenol (41.4 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *N*-methylaniline (65 µL, 64.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 63.6 mg (0.18 mmol, 59%) yellow solid. **Mp.** 58-61 °C. **R_f**= 0.491 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 358 (5, $[M^+]$), 219 (1), 180 (1), 121 (9), 120 (100), 105 (7), 104 (8), 91 (4), 77 (15). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.59 (td, *J* = 8.4, 8.0, 1.7 Hz, 1H), 7.51 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.39 – 7.29 (m, 3H), 6.91 – 6.83 (m, 3H), 4.19 (dd, *J* = 16.2, 12.8 Hz, 1H), 4.09 (dd, *J* = 20.4, 16.2 Hz, 1H), 3.10 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.6 Hz), -124.8 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.1, 145.0, 143.0, 133.8, 129.2, 125.9, 125.5, 124.2 (d, *J* = 3.9 Hz), 120.3 (qd, *J* = 288.9, 38.5 Hz), 118.1, 112.9 (d, *J* = 1.4 Hz), 110.6 (dq, *J* = 246.5, 33.1 Hz), 54.1 (d, *J* = 21.8 Hz), 40.2 (d, *J* = 1.5 Hz). **IR** (film, ATR) 1600, 1533, 1507, 1484, 1451, 1428, 1354, 1268, 1197, 1156, 1085, 1033, 996, 970, 861, 828, 779, 750, 694, 664 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{16}H_{14}F_4N_2O_3^+$: 358.09406, found: 358.09211.

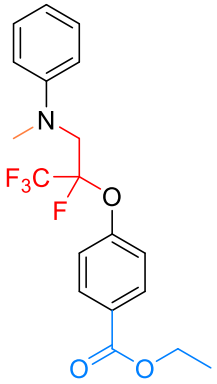
_N_-(2-(2-Chlorophenoxy)-2,3,3,3-tetrafluoropropyl)-_N_-methylaniline (32)



Method A. Using 2-chlorophenol (38.6 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *N*-methylaniline (65 µL, 64.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 61.6 mg (0.18 mmol, 59%) yellow solid. **Mp.** 33-35 °C. **R_f**= 0.64 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 349 (1), 347 (4, $[M^+]$), 218 (1), 200 (1), 180 (1), 150 (1), 121 (8), 120 (100), 111 (6), 105 (8), 104 (10), 77 (18). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.24 (dt, *J* = 8.2, 2.0 Hz, 1H), 7.17 – 7.09 (m, 3H), 7.03 (td, *J* = 7.7, 1.6 Hz, 1H), 6.74 – 6.64 (m, 3H), 3.96 (t, *J* = 15.8 Hz, 1H), 3.80 (t, *J* = 16.7 Hz, 1H), 2.93 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.6 Hz), -124.6 (q, *J* = 2.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.3, 148.3, 130.8, 129.2, 127.8, 127.2 (d, *J* = 2.2 Hz), 126.6, 123.8 (d, *J* = 3.2 Hz), 120.7 (qd, *J* = 288.8, 39.1 Hz), 117.9, 112.8 (d, *J* = 1.6 Hz), 110.1 (dq, *J* = 244.6, 33.0 Hz), 54.1 (d, *J* = 22.9 Hz), 40.1. **IR** (film, ATR) 1600, 1507, 1477, 1447, 1372, 1331, 1264, 1193, 1152, 1130, 1089, 1059, 1033, 996, 970, 839, 776, 750, 712, 690 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{16}H_{14}ClF_4NO^+$: 347.07000, found: 347.06849.

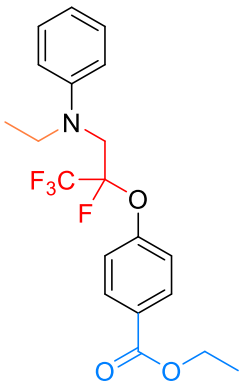
Ethyl 4-((1,1,1,2-tetrafluoro-3-(methyl(phenyl)amino)propan-2-yl)oxy)benzoate (33)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *N*-methylaniline (65 µL, 64.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 90.4 mg (0.23 mmol, 78%) yellow oil. **R_f**= 0.69 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 385 (3, [M^+]), 340 (1), 220 (2), 151 (3), 121 (10), 120 (100), 105 (5), 104 (8), 77 (8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.73 – 6.67 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.96 – 3.75 (m, 2H), 2.93 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.8 (d, *J* = 2.6 Hz), -126.7 (q, *J* = 2.6 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 155.8, 149.3, 131.2, 129.2, 127.8, 121.7 (d, *J* = 2.9 Hz), 120.7 (qd, *J* = 289.4, 39.3 Hz), 118.0, 112.9, 109.7 (dq, *J* = 243.9, 32.4 Hz), 61.2, 54.5 (d, *J* = 23.0 Hz), 40.0 (d, *J* = 1.5 Hz), 14.4. **IR** (film, ATR) 1719, 1600, 1507, 1369, 1328, 1305, 1275, 1193, 1167, 1152, 1126, 1089, 1018, 996, 970, 861, 832, 779, 750, 694 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{19}H_{19}F_4NO_3^+$: 385.13011, found: 385.12938.

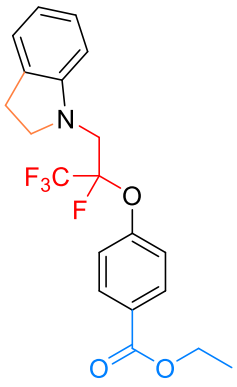
Ethyl 4-((3-(ethyl(phenyl)amino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (34)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *N*-ethylaniline (76 µL, 72.7 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 86.4 mg (0.22 mmol, 72%) yellow oil. **R_f**= 0.73 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 399 (3, [M^+]), 234 (3), 151 (4), 135 (10), 134 (100), 106 (18), 105 (5) 104 (11), 77 (10). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 – 7.82 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.93 – 3.76 (m, 2H), 3.39 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.6 (d, *J* = 2.6 Hz), -127.0 (q, *J* = 2.6 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 156.0, 147.9, 131.2, 129.3, 127.8, 121.7 (d, *J* = 2.7 Hz), 120.8 (qd, *J* = 289.9, 39.8 Hz), 117.8, 113.4 (d, *J* = 1.4 Hz), 109.7 (dq, *J* = 243.7, 32.3 Hz), 61.2, 52.5 (d, *J* = 22.5 Hz), 46.2, 14.4, 11.3. **IR** (film, ATR) 1719, 1600, 1503, 1275, 1193, 1167, 1093, 1018, 999, 861, 779, 746, 694 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{20}H_{21}F_4NO_3^+$: 399.14576, found: 399.14424.

Ethyl 4-((1,1,1,2-tetrafluoro-3-(indolin-1-yl)propan-2-yl)oxy)benzoate (35)

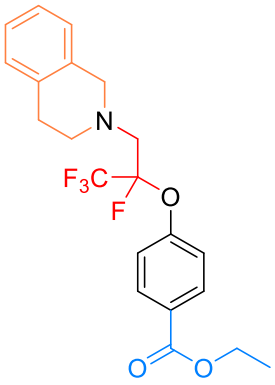


Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), indoline (67 µL, 71.5 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 73.9 mg (0.11 mmol, 37%) red oil. **R_f**= 0.62 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 397 (10, [M^+]), 352 (2), 232 (4), 151 (3), 133 (11), 132 (100), 130 (11), 117 (16), 104 (8), 91 (9), 77 (6). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.97 (t, *J* = 8.1 Hz, 2H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.76 – 3.50 (m, 2H), 3.46 – 3.31 (m, 2H), 2.89 (t, *J* = 8.5 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.9 (d, *J* = 2.6 Hz), -124.7 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 155.9, 151.6, 131.3, 129.1, 127.9, 127.5, 124.7, 121.7 (d, *J* = 2.7 Hz),

120.6 (qd, *J* = 288.7, 38.7 Hz), 118.7, 109.4 (dq, *J* = 241.8, 32.4 Hz), 106.8, 61.2, 55.5, 52.6 (d, *J* = 26.8 Hz), 28.9, 14.4. **IR** (film, ATR) 1719, 1600, 1503, 1275, 1193, 1167, 1093, 1018, 999, 861, 779, 746, 694 cm^{-1}. **HRMS** (EI) $[M\text{-}2H]^+$ calculated for $C_{20}H_{17}F_4NO_3^+$: 395.11446, found: 395.11362.

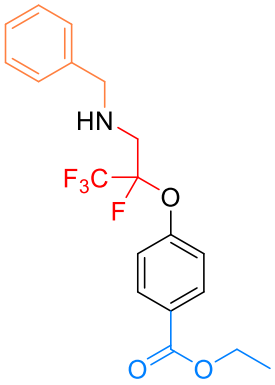
Ethyl 4-((3-(3,4-dihydroisoquinolin-2(1*H*)-yl)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (36)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 1,2,3,4-tetrahydroisoquinoline (75 µL, 79.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 55.0 mg (0.13 mmol, 45%) yellow oil. R_f= 0.59 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 411 (0, [M^+]), 366 (1), 262 (1), 246 (2), 183 (2), 147 (12), 146 (100), 131 (5), 130 (5), 117 (7), 115 (4), 105 (4), 104 (11), 103 (5), 91 (3), 78 (4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.08 – 6.93 (m, 2H), 6.87 – 6.82 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 3.07 (p, *J* = 14.7 Hz, 2H), 2.81 – 2.66 (m, 4H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.4 (d, *J* = 2.6 Hz), -122.5 (q, *J* = 2.1 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 156.1, 134.4, 134.0, 131.3, 128.8, 127.7, 126.5, 126.3, 125.8, 121.7 (d, *J* = 2.7 Hz), 120.6 (qd, *J* = 287.6, 37.1 Hz), 109.8 (dq, *J* = 240.5, 32.7 Hz), 61.2, 57.4 (d, *J* = 26.3 Hz), 56.7 (d, *J* = 1.5 Hz), 52.0, 28.9, 14.4. **IR** (film, ATR) 1715, 1604, 1503, 1466, 1451, 1369, 1275, 1197, 1171, 1089, 1018, 940, 861, 779, 746, 709, 682, 668 cm^{-1}. **HRMS** (EI) $[M\text{-}H]^+$ calculated for $C_{21}H_{20}F_4NO_3^+$: 410.13793, found: 410.13699.

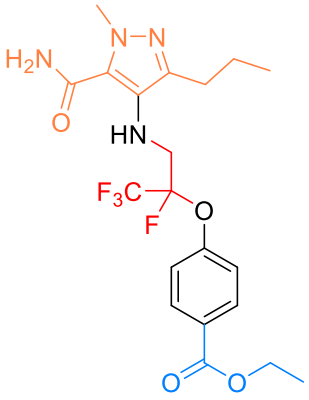
Ethyl 4-((3-(benzylamino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (37)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), phenylmethanamine (66 µL, 64.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 39.5 mg (0.10 mmol, 34%) yellow oil. R_f= 0.55 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 166 (18), 138 (25), 122 (10), 121 (100), 93 (33), 65 (25), 63 (10). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.23 – 7.08 (m, 7H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.62 (m, 2H), 3.18 – 3.03 (m, 2H), 1.54 (bs, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.8 Hz), -122.9 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 155.7, 139.3, 131.3, 128.6, 128.1, 127.9, 127.4, 121.8 (d, *J* = 2.6 Hz), 120.6 (qd, *J* = 287.4, 37.2 Hz), 109.5 (dq, *J* = 238.3, 33.0 Hz), 61.2, 53.7, 48.5 (d, *J* = 28.8 Hz), 14.4. **IR** (film, ATR) 1715, 1604, 1503, 1454, 1369, 1275, 1193, 1171, 1100, 1059, 1018, 973, 929, 861, 828, 779, 738, 697, 656 cm^{-1}. **HRMS** (EI) $[M\text{-}H]^+$ calculated for $C_{19}H_{18}F_4NO_3^+$: 384.12228, found: 384.12222.

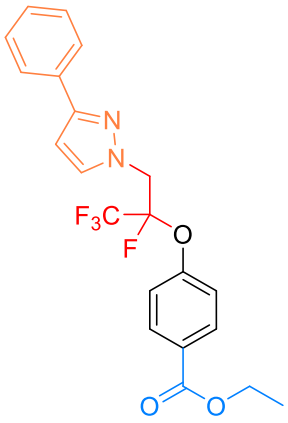
Ethyl 4-((3-((5-carbamoyl-1-methyl-3-propyl-1*H*-pyrazol-4-yl)amino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (38)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 4-amino-1-methyl-3-propyl-1*H*-pyrazole-5-carboxamide (109.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 83.3 mg (0.17 mmol, 58%) pink solid. **Mp.** 97-99 °C. **R_f**= 0.30 in hexane : ethyl acetate 1:1. **MS** (EI, 70 eV): m/z (%): 460 (14, [M^+]), 196 (11), 195 (100), 193 (9), 179 (9), 178 (77), 177 (8), 121 (8), 109 (7), 92 (7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (bs, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.94 (bs, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 3H), 3.62 – 3.34 (m, 2H), 2.97 (t, *J* = 7.4 Hz, 1H), 2.32 (t, *J* = 7.6 Hz, 2H), 1.54 (h, *J* = 7.5 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.8 (d, *J* = 1.7 Hz), -125.5. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.5, 161.2, 155.2, 146.6, 131.6, 128.7, 128.5, 126.5, 121.3 (d, *J* = 2.9 Hz), 120.4 (qd, *J* = 288.1, 38.1 Hz), 108.3 (dq, *J* = 240.4, 34.0 Hz), 61.3, 50.9 (d, *J* = 27.0 Hz), 40.1, 27.6, 22.5, 14.3, 14.0. **IR** (film, ATR) 1715, 1678, 1604, 1503, 1462, 1417, 1369, 1275, 1197, 1171, 1100, 1044, 1018, 962, 865, 776, 738, 705 cm^{-1}. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{20}H_{25}F_4N_4O_4^+$: 461.1806, found: 461.1808.

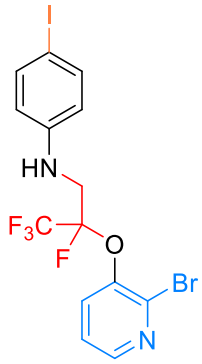
Ethyl 4-((1,1,1,2-tetrafluoro-3-(3-phenyl-1H-pyrazol-1-yl)propan-2-yl)oxy)benzoate (39)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 3-phenyl-1*H*-pyrazole (86.5 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 54.5 mg (0.13 mmol, 43%) yellow oil. **R_f**= 0.51 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 422 (5, [M^+]), 377 (8), 354 (5), 353 (22), 325 (4), 307 (11), 306 (64), 305 (100), 277 (13), 257 (8), 157 (46), 151 (7), 130 (17), 128 (12), 115 (12), 104 (21), 103 (14), 92 (7) 89 (10), 77 (42), 76 (13), 65 (8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.49 (d, *J* = 2.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 2.5 Hz, 1H), 4.85 (dd, *J* = 15.3, 10.0 Hz, 1H), 4.76 (t, *J* = 15.2 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.7 Hz), -125.2 (q, *J* = 2.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 155.1, 152.5, 133.0, 132.5, 131.3, 128.7, 128.3, 128.1, 125.9, 121.9 (d, *J* = 2.5 Hz), 120.1 (qd, *J* = 288.6, 37.5 Hz), 107.2 (dq, *J* = 243.0, 34.0 Hz), 104.4, 61.2, 52.3 (d, *J* = 28.3 Hz), 14.4. **IR** (film, ATR) 1715, 1604, 1503, 1458, 1413, 1365, 1275, 1205, 1167, 1096, 1018, 921, 861, 753, 694 cm^{-1}. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{21}H_{19}F_4N_2O_3^+$: 423.1326, found: 423.1333.

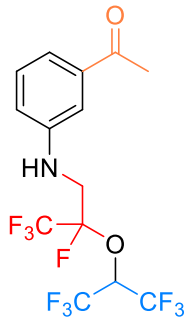
_N_-(2-((2-Bromopyridin-3-yl)oxy)-2,3,3,3-tetrafluoropropyl)-4-iodoaniline (40)



Method A. Using 2-bromopyridin-3-ol (52.2 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 4-iodoaniline (131.4 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 117.7 mg (0.23 mmol, 78%) brown oil. **R_f**= 0.58 in hexane : ethyl acetate 2:1. **MS** (EI, 70 eV): m/z (%): 506 (11), 504 (11, [M^+]), 425 (1), 423 (1), 231 (2), 297 (2), 233 (7), 232 (100), 181 (3), 156 (4), 135 (4), 109 (4), 106 (9), 105 (39), 104 (11), 91 (10), 78 (8), 77 (8), 76 (10). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 4.6, 1.9 Hz, 1H), 7.58 (dt, *J* = 8.3, 2.0 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.22 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.36 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 1H), 3.82 (d, *J* = 12.6 Hz, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 2.8 Hz), -124.6 (q, *J* = 2.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 146.5, 145.9, 137.9, 136.2 (d, *J* = 2.4 Hz), 130.6 (d, *J* = 3.3 Hz), 123.6, 120.2 (qd, *J* = 287.6, 36.5 Hz), 115.3, 109.3 (dq, *J* = 244.0, 34.1 Hz), 79.9, 44.6 (d, *J* = 27.2 Hz). **IR** (film, ATR) 1592, 1566, 1507, 1484, 1447, 1410, 1320, 1246, 1197, 1163, 1093, 1067, 1052, 1018, 943, 914, 809, 768, 738, 720, 694, 668 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{14}H_{10}BrF_4IN_2O^+$: 503.89573, found: 503.89239.

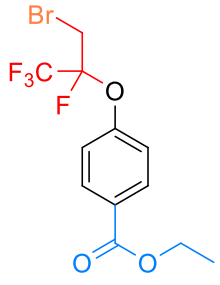
1-(3-((2,3,3,3-Tetrafluoro-2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)propyl)amino)phenyl)ethan-1-one (41)



Method A. Using 1,1,1,3,3,3-hexafluoropropan-2-ol (31 µL, 50.4 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 1-(3-aminophenyl)ethan-1-one (81.1 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 40.7 mg (0.10 mmol, 33%) yellow solid. **Mp.** 65-67 °C. **R_f**= 0.68 in hexane : ethyl acetate 2:1. **MS** (EI, 70 eV): m/z (%): 415 (14, [M^+]), 396 (2), 376 (2), 267 (1), 151 (2), 149 (9), 148 (100), 106 (9), 105 (10), 104 (10), 91 (12), 77 (7), 76 (7), 69 (10). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 1H), 7.32 – 7.26 (m, 2H), 6.88 (dd, *J* = 8.1, 2.7 Hz, 1H), 5.00 (hept, *J* = 5.1 Hz, 1H), 4.09 (s, 1H), 3.98 – 3.68 (m, 2H), 2.57 (s, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -73.3 (qq, *J* = 9.1, 4.6 Hz), -73.6 (p, *J* = 9.8 Hz), -81.6 (dp, *J* = 6.8, 2.7 Hz), -136.8 (q, *J* = 10.2 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 198.4, 146.8, 138.3, 129.7, 120.4 (q, *J* = 282.1 Hz), 120.2 (qd, *J* = 288.1, 38.1 Hz), 119.7, 118.1, 112.3, 108.0 (dq, *J* = 246.6, 33.9 Hz), 70.6 (pd, *J* = 34.5, 6.3 Hz), 45.3 (d, *J* = 21.6 Hz), 26.7. **IR** (film, ATR) 1678, 1607, 1592, 1521, 1492, 1436, 1361, 1331, 1294, 1197, 1178, 1145, 1108, 1011, 977, 940, 899, 880, 783, 738, 723, 686 cm^{-1}. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{14}H_{12}F_4NO_2^+$: 416.0703, found: 416.0700.

Ethyl 4-((3-bromo-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (42)

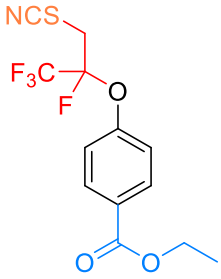


Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (63.6 mg, 0.6 mmol), NaBr (61.7 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 85.9 mg (0.24 mmol, 80%) colorless oil. **R_f**= 0.66 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 360 (22), 358 (19, [M^+]), 332 (46), 330 (45), 316 (14), 315 (100), 314 (14), 313 (97), 235 (9), 233 (16), 165 (11), 138 (17), 137 (20), 121 (76), 120 (22), 109 (27), 93 (27), 92 (56), 81 (19), 76 (19), 69 (14), 65 (33), 64 (36), 63 (38), 62 (12). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.53 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.7 (d, *J* = 2.4 Hz), -116.4 (q, *J* = 2.2 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 154.6, 131.4,

128.6, 122.1 (d, *J* = 2.5 Hz), 119.9 (qd, *J* = 288.1, 36.9 Hz), 107.2 (dq, *J* = 239.7, 34.3 Hz), 61.3, 25.3 (d, *J* = 34.6 Hz), 14.4. **IR** (film, ATR) 1719, 1607, 1507, 1417, 1369, 1324, 1279, 1212, 1190, 1104, 1063, 1040, 1022, 865, 783, 764, 701 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{12}H_{11}BrF_4O_3^+$: 357.98277, found: 357.98200.

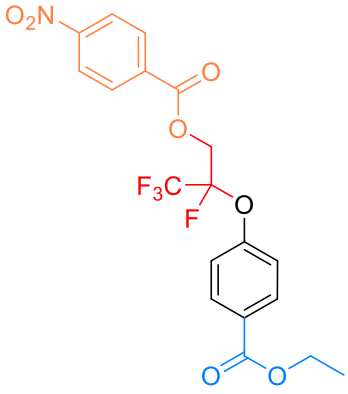
Ethyl 4-((1,1,1,2-tetrafluoro-3-thiocyanatopropan-2-yl)oxy)benzoate (43)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), sodium thiocyanate (48.6 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 50.4 mg (0.15 mmol, 50%) yellow oil. R_f= 0.43 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 337 (13, $[M^+]$), 310 (6), 309 (40), 293 (14), 292 (100), 233 (8), 138 (10), 122 (10), 121 (46), 120 (42), 109 (17), 93 (15), 92 (39), 91 (9), 76 (14), 69 (7), 65 (13), 64 (19), 63 (15). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.60 – 3.43 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.1 (d, *J* = 2.8 Hz), -122.0 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.6, 154.7, 131.6, 128.9, 121.9 (d, *J* = 2.5 Hz), 120.0 (qd, *J* = 289.5, 39.6 Hz), 110.3, 107.3 (dq, *J* = 243.0, 34.8 Hz), 61.4, 35.5 (d, *J* = 27.4 Hz), 14.4. **IR** (film, ATR) 1715, 1637, 1604, 1503, 1413, 1369, 1335, 1275, 1197, 1171, 1096, 1078, 1052, 1011, 861, 820, 768, 742, 697 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{13}H_{11}F_4NO_3S^+$: 337.03958, found: 337.03895.

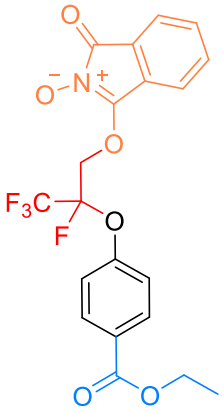
2-(4-(Ethoxycarbonyl)phenoxy)-2,3,3,3-tetrafluoropropyl 4-nitrobenzoate (44)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (95.4 mg, 0.9 mmol), 4-nitrobenzoic acid (100.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 81.6 mg (0.18 mmol, 61%) yellow oil. R_f= 0.54 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 445 (9, $[M^+]$), 417 (10), 401 (10), 400 (20), 281 (10), 280 (100), 264 (5), 251 (9), 234 (14), 222 (6), 150 (39), 134 (9), 121 (19), 120 (25), 104 (42), 93 (11), 92 (30), 76 (26), 75 (10), 65 (8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.72 (dd, *J* = 13.0, 6.2 Hz, 1H), 4.62 (t, *J* = 11.5 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -81.6 (d, *J* = 2.8 Hz), -125.5 (q, *J* = 3.0 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.5, 163.1, 154.7 (d, *J* = 1.4 Hz), 151.1, 133.8, 131.7, 131.1, 128.8, 123.9, 121.7 (d, *J* = 2.4 Hz), 120.0 (qd, *J* = 286.8, 34.8 Hz), 107.0 (dq, *J* = 239.8, 35.1 Hz), 61.4, 60.1 (d, *J* = 37.8 Hz), 14.4. **IR** (film, ATR) 1742, 1719, 1607, 1533, 1507, 1369, 1350, 1275, 1216, 1100, 1070, 1018, 873, 858, 783, 720 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{19}H_{15}F_4NO_7^+$: 445.07846, found: 445.07732.

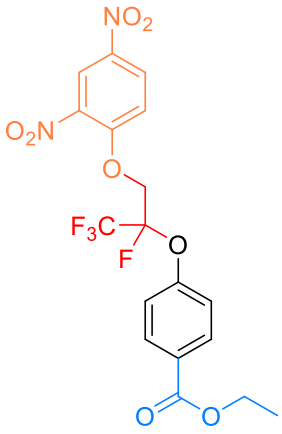
3-(2-(4-(Ethoxycarbonyl)phenoxy)-2,3,3,3-tetrafluoropropoxy)-1-oxo-1*H*-isoindole 2-oxide (45)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (63.6 mg, 0.6 mmol), 2-hydroxyisoindoline-1,3-dione (48.9 mg, 0.3 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 51.0 mg (0.12 mmol, 39%) white solid. **Mp.** 108-112 °C. **R_f**= 0.31 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): Compound is not measurable using GC-MS. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.71 (td, *J* = 7.5, 1.6 Hz, 1H), 7.67 (td, *J* = 7.6, 1.7 Hz, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 4.95 (s, 1H), 4.90 (s, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -85.7 (d, *J* = 2.8 Hz), -114.7 (q, *J* = 3.3 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.5, 165.9, 164.0, 154.3, 133.5, 133.5, 131.4, 131.4, 130.8, 128.8, 128.5, 128.4, 121.7, 118.6 (qd, *J* = 281.5, 44.3 Hz), 107.4 (dq, *J* = 271.6, 41.2 Hz), 61.3, 58.4 (d, *J* = 24.3 Hz), 14.4. **IR** (film, ATR) 1712, 1645, 1604, 1581, 1507, 1369, 1309, 1268, 1197, 1163, 1108, 1081, 1059, 1018, 895, 880, 858, 764, 753, 738, 712, 697, 656 cm^{-1}. **HRMS** (ESI) $[M+NH_4]^+$ calculated for $C_{20}H_{19}F_4N_2O_6^+$: 459.1174, found: 459.1179.

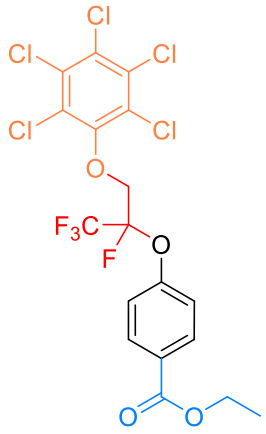
Ethyl 4-((3-(2,4-dinitrophenoxy)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (46)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (95.4 mg, 0.9 mmol), 2,4-dinitrophenol (110.5 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 101.0 mg (0.22 mmol, 73%) yellow solid. **Mp.** 72-80 °C. **R_f**= 0.48 in hexane : ethyl acetate 2:1. **MS** (EI, 70 eV): m/z (%): 462 (14, [M$^+$]), 434 (44), 418 (14), 417 (100), 402 (13), 401 (27), 371 (15), 355 (8), 269 (11), 253 (10), 249 (25), 208 (10), 207 (24), 205 (16), 168 (18), 139 (14), 138 (33), 121 (58), 120 (79), 110 (21), 109 (32), 93 (40), 92 (82). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 2.8 Hz, 1H), 8.31 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 9.3 Hz, 1H), 4.54 (dd, *J* = 11.3, 3.9 Hz, 1H), 4.44 (dd, *J* = 11.3, 6.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -81.2 (d, *J* = 3.4 Hz), -124.3 (q, *J* = 3.4 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.5, 154.3, 141.5, 139.4, 131.6, 129.1, 129.0, 122.1 (d, *J* = 2.2 Hz), 122.0, 119.7 (qd, *J* = 287.0, 34.2 Hz), 114.5, 106.7 (dq, *J* = 237.1, 35.3 Hz), 65.0 (d, *J* = 42.4 Hz), 61.4, 14.3. **IR** (film, ATR) 1715, 1607, 1536, 1503, 1462, 1417, 1346, 1279, 1249, 1208, 1182, 1108, 1074, 1044, 1018, 955, 925, 869, 835, 791, 768, 742, 716 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{18}H_{14}F_4N_2O_8^+$: 462.06863, found: 462.06808.

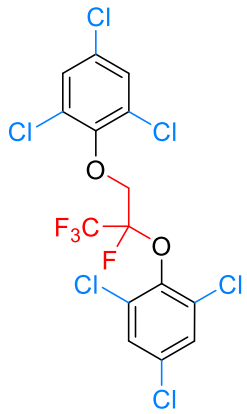
Ethyl 4-((1,1,1,2-tetrafluoro-3-(perchlorophenoxy)propan-2-yl)oxy)benzoate (47)



Method A. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (95.4 mg, 0.9 mmol), 2,3,4,5,6-pentachlorophenol (159.8 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 123.5 mg (0.23 mmol, 76%) yellow oil. **R_f**= 0.71 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 550 (1), 548 (4), 546 (14), 544 (17), 542 (11, [M^+]), 520 (2), 518 (7), 516 (10), 514 (6), 503 (6), 501 (18), 499 (29), 497 (18), 267 (10), 265 (15), 263 (11), 251 (11), 249 (11), 239 (21), 237 (32), 235 (22), 233 (14), 207 (24), 187 (17), 167 (16), 165 (26), 149 (13), 137 (14), 121 (36), 120 (100), 109 (41), 93 (20), 92 (58). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 4.43 (t, *J* = 10.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.22 (dd, *J* = 10.6, 5.2 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.9 (d, *J* = 3.3 Hz), -124.9 (q, *J* = 3.4 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 155.2 (d, *J* = 1.5 Hz), 149.4, 132.3, 131.5, 130.8, 128.3, 128.1, 121.5 (d, *J* = 2.7 Hz), 120.0 (qd, *J* = 286.5, 35.0 Hz), 106.8 (dq, *J* = 238.9, 35.4 Hz), 67.2 (d, *J* = 37.8 Hz), 61.3, 14.4. **IR** (film, ATR) 1715, 1641, 1607, 1507, 1410, 1357, 1305, 1275, 1249, 1208, 1178, 1137, 1100, 1048, 1018, 966, 943, 917, 861, 798, 761, 735, 712, 682 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{18}H_{11}Cl_5F_4O_4^+$: 541.90361, found: 541.90039.

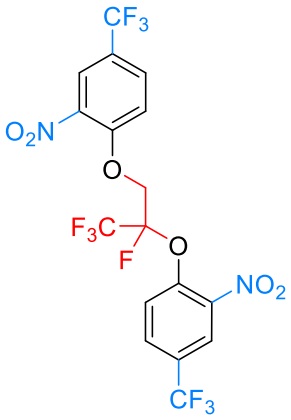
2,2'-((2,3,3,3-Tetrafluoropropane-1,2-diyl)bis(oxy))bis(1,3,5-trichlorobenzene) (48)



Method A. Using 2,4,6-trichlorophenol (118.5 mg, 0.6 mmol), Na_2CO_3 (63.6 mg, 0.6 mmol) and iodonium salt (145.2 mg, 0.30 mmol) in MeCN (3.0 mL).

Yield: 107.7 mg (0.21 mmol, 71%) white solid. **Mp.** 89-92 °C. **R_f**= 0.73 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 510 (9), 508 (13), 506 (14), 504 (7, [M^+]), 313 (8), 311 (25), 309 (30), 276 (6), 274 (8), 231 (4), 229 (8), 227 (10), 211 (10), 201 (7), 200 (22), 199 (33), 198 (70), 197 (100), 196 (78), 194 (99), 181 (13), 179 (14), 171 (29), 169 (90), 167 (91), 145 (11), 143 (15), 111 (10), 109 (40), 107 (34), 99 (20), 97 (67), 96 (12), 86 (11), 83 (14), 74 (16). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 (s, 2H), 7.17 (s, 2H), 4.40 (dd, *J* = 14.4, 10.9 Hz, 1H), 4.30 (t, *J* = 11.0 Hz, 1H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.8, -120.2. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.7, 144.3, 132.4, 131.3 (d, *J* = 1.8 Hz), 131.1, 129.9, 129.5, 129.2, 120.1 (qd, *J* = 287.3, 36.4 Hz), 107.9 (dq, *J* = 248.8, 35.7 Hz), 68.7 (d, *J* = 27.1 Hz). **IR** (film, ATR) 1574, 1559, 1443, 1387, 1339, 1246, 1219, 1197, 1178, 1141, 1108, 1093, 1044, 1003, 947, 925, 858, 817, 802, 776, 727, 709, 694, 660 cm^{-1}. **HRMS** (EI) [$M]^+$ calculated for $C_{15}H_6Cl_6F_4O_2^+$: 503.84351, found: 503.84371.

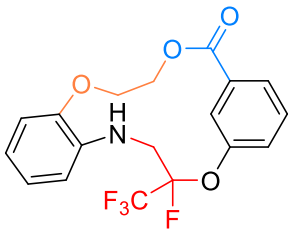
4,4'-((2,3,3,3-Tetrafluoropropane-1,2-diyl)bis(oxy))bis(3-nitro-1-(trifluoromethyl)benzene) (49)



Method A. Using 2-nitro-4-(trifluoromethyl)phenol (84.4 µL, 124.3 mg, 0.6 mmol), Na_2CO_3 (63.6 mg, 0.6 mmol) and iodonium salt (145.2 mg, 0.30 mmol) in MeCN (3.0 mL).

Yield: 132.2 mg (0.25 mmol, 84%) yellow solid. **Mp.** 85-87 °C. **R_f**= 0.26 in hexane : ethyl acetate 10:1. **MS** (EI, 70 eV): m/z (%): 526 (2, [M^+]), 507 (11), 436 (1), 320 (18), 319 (11), 290 (6), 207 (89), 204 (9), 191 (43), 190 (70), 177 (22), 174 (22), 163 (17), 162 (28), 160 (41), 148 (22), 147 (81), 146 (50), 141 (17), 132 (51), 127 (23), 126 (100), 125 (11), 120 (18), 113 (21), 107 (23), 101 (13), 95 (15), 81 (10), 75 (27). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 8.05 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 4.84 (dd, *J* = 15.7, 11.4 Hz, 1H), 4.71 (dd, *J* = 11.3, 7.9 Hz, 1H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.5, -63.0, -81.5 (d, *J* = 2.8 Hz), -128.2 (q, *J* = 2.8 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.3, 146.7, 142.9, 139.9, 131.3 (q, *J* = 3.5 Hz), 129.4 (q, *J* = 34.9 Hz), 125.7, 125.6, 125.4 (q, *J* = 34.8 Hz), 123.7 (q, *J* = 3.8 Hz), 123.4 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 272.1 Hz), 122.5 (q, *J* = 272.8 Hz), 119.5 (qd, *J* = 287.2, 33.4 Hz), 115.3, 107.7 (dq, *J* = 248.8, 35.5 Hz), 66.8 (d, *J* = 27.9 Hz). **IR** (film, ATR) 1630, 1544, 1507, 1357, 1324, 1290, 1272, 1238, 1178, 1130, 1093, 1074, 1052, 1014, 955, 899, 847, 820, 682 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{17}H_8F_{10}N_2O_6^+$: 526.02227, found: 526.02225.

3-Fluoro-3-(trifluoromethyl)-2,7,10-trioxa-5-aza-1(1,3),6(1,2)-dibenzenacycloundecaphan-11-one (50)



Method A. Using 2-(2-aminophenoxy)ethyl 3-hydroxybenzoate (82.0 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (15.0 mL).

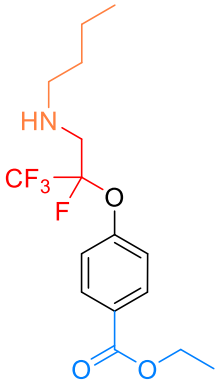
Yield: 44.8 mg (0.12 mmol, 39%) white solid. **Mp.** 165-168 °C. **R_f**= 0.37 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 386 (11), 385 (52, [M^+]), 316 (16), 296 (17), 269 (11), 198 (16), 197 (100), 196 (26), 195 (20), 177 (17), 168 (10), 162 (36), 151 (14), 148 (29), 221 (22), 120 (61), 118 (15), 105 (11), 104 (52), 93 (26), 92 (45), 91 (13), 90 (19), 78 (13), 77 (21), 76 (50), 65 (17), 64 (17), 63 (11). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.54 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.41 (dd, *J* = 8.3, 2.7 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.68 – 6.57 (m, 2H), 5.42 (t, *J* = 6.9 Hz, 1H), 4.70 – 4.52 (m, 2H), 4.45 (dt, *J* = 11.8, 3.6 Hz, 1H), 4.18 – 4.02 (m, 2H), 3.80 (td, *J* = 16.4, 6.8 Hz, 1H). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -83.8 (d, *J* = 4.2 Hz), -125.6 (q, *J* = 4.3 Hz). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.9, 151.0, 145.8, 137.4, 131.2, 130.6, 125.2, 124.6, 122.4, 121.4 (d, *J* = 2.7 Hz), 120.5 (dd, *J* = 286.7, 33.7 Hz), 116.8, 115.4, 109.5, 108.8 (dd, *J* = 247.8, 32.5 Hz), 68.3, 63.1, 42.1 (d, *J* = 22.2 Hz). **IR** (film, ATR) 1730, 1637, 1604, 1518, 1492, 1451, 1272, 1257, 1216, 1149, 1100, 1078, 1048, 1026, 910, 809, 742 cm^{-1}. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{18}H_{16}F_4NO_4^+$: 386.10100, found: 526.02225.

6. Reactions of phenols with aliphatic amines

Method B (incorporating aliphatic amines as nucleophile)

Na_2CO_3 (31.8 mg, 0.3 mmol), phenol (0.3 mmol) and MeCN (3.0 mL) were measured into a screw cap vial. The mixture was stirred at -20°C for 5 minutes and (*Z*)-(4-fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate (174.3 mg, 0.36 mmol) was added in one portion. The mixture was stirred at -20°C for 60 minutes then the amine derivative (0.6 mmol) was added. The mixture was stirred at -20°C for further 60 minutes then warmed up to ambient temperature. The solvent was evaporated under reduced pressure to Celite and the crude product was purified by column chromatography using hexanes-ethyl acetate as eluent.

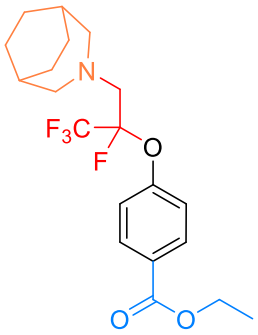
Ethyl 4-((3-(butylamino)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (52)



Method B. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), butan-1-amine (59 µL, 43.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 68.1 mg (0.19 mmol, 65%) yellow oil. **R_f**= 0.63 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 351 (<1, [M^+]), 308 (8), 306 (8), 259 (3), 231 (2), 216 (3), 215 (4), 187 (27), 167 (4), 159 (6), 132 (14), 124 (9), 121 (29), 109 (9), 104 (9), 87 (20), 86 (100), 76 (10), 65 (11), 57 (10). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.24 – 3.01 (m, 2H), 2.57 – 2.36 (m, 2H), 1.36 – 1.11 (m, 8H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.8 Hz), -123.5 (q, *J* = 2.7 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 155.7, 131.3, 127.9, 121.9 (d, *J* = 2.5 Hz), 120.6 (dd, *J* = 287.5, 37.3 Hz), 109.4 (dq, *J* = 239.0, 33.1 Hz), 61.2, 49.7, 49.4 (d, *J* = 28.0 Hz), 32.1, 20.2, 14.4, 14.0. **IR** (film, ATR) 1719, 1607, 1507, 1466, 1413, 1369, 1275, 1223, 1193, 1171, 1085, 1018, 929, 865, 779, 768, 709, 682 cm^{-1}. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{16}H_{22}F_4NO_3^+$: 352.1530, found: 352.1533.

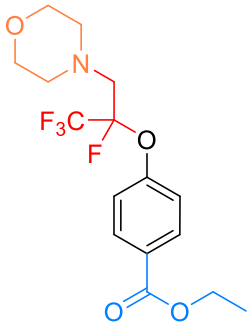
Ethyl 4-((3-(3-azabicyclo[3.2.2]nonan-3-yl)-1,1,1,2-tetrafluoropropan-2-yl)oxy)benzoate (53)



Method B. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 3-azabicyclo[3.2.2]nonane (53.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 53.9 mg (0.13 mmol, 45%) white solid. **Mp.** 56-59 °C. **R_f**= 0.75 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 403 (<1, [M^+]), 358 (2), 322 (1), 238 (2), 151 (1), 139 (11) 138 (100), 67 (5), 58 (14). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.13 –2.92 (m, 2H), 2.75 – 2.60 (m, 4H), 1.80 (s, 2H), 1.76 – 1.64 (m, 4H), 1.57 – 1.48 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.7 Hz), -122.9 (q, *J* = 2.5 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 156.1, 131.3, 127.5, 121.4 (d, *J* = 2.9 Hz), 120.7 (qd, *J* = 287.9, 37.3 Hz), 110.1 (dq, *J* = 241.8, 32.5 Hz), 64.5 (d, *J* = 1.6 Hz), 61.2, 58.0 (d, *J* = 26.3 Hz), 30.7, 25.6, 25.5, 14.4. **IR** (film, ATR) 1723, 1607, 1507, 1462, 1417, 1369, 1305, 1275, 1227, 1201, 1171, 1108, 1089, 1052, 1022, 984, 858, 779, 709 cm^{-1}. **HRMS** (EI) $[M-H]^+$ calculated for $C_{20}H_{24}F_4NO_3^+$: 402.16923, found: 402.16679.

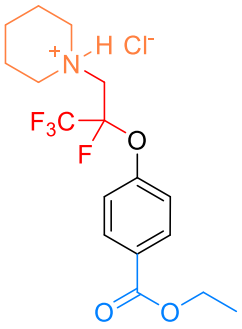
Ethyl 4-((1,1,1,2-tetrafluoro-3-morpholinopropan-2-yl)oxy)benzoate (54)



Method B. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), morpholine (53 µL, 52.3 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 70.3 mg (0.19 mmol, 64%) yellow oil. **R_f**= 0.30 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 365 (<1, [M^+]), 320 (3), 262 (1), 238 (1), 210 (1), 200 (7), 151 (5), 121 (3), 104 (9), 101 (18), 100 (100), 92 (5), 76 (5), 72 (5), 70 (10), 56 (11). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.55 (d, *J* = 3.3 Hz, 4H), 3.06 – 2.73 (m, 2H), 2.47 (t, *J* = 4.6 Hz, 4H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.8 (d, *J* = 2.7 Hz), -122.0 (q, *J* = 2.2 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.8, 156.1, 131.2, 127.7, 121.6 (d, *J* = 2.8 Hz), 120.5 (qd, *J* = 287.5, 36.7 Hz), 109.6 (dq, *J* = 241.1, 32.8 Hz), 67.0, 61.2, 58.2 (d, *J* = 26.2 Hz), 54.5, 14.4. **IR** (film, ATR) 1719, 1604, 1507, 1454, 1413, 1369, 1275, 1223, 1197, 1171, 1115, 1085, 1037, 1014, 940, 861, 779, 761, 709 cm^{-1}. **HRMS** (EI) [M-2H]$^+$ calculated for $C_{16}H_{17}F_4NO_4^+$: 363.10937, found: 363.10913.

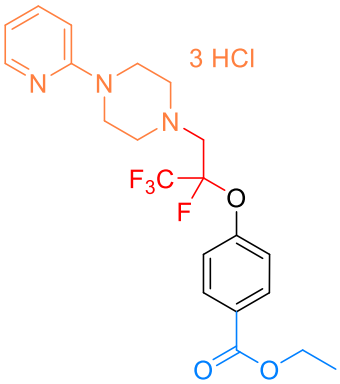
1-(2-(4-(Ethoxycarbonyl)phenoxy)-2,3,3,3-tetrafluoropropyl)piperidin-1-ium chloride (55)



Method B. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), piperidine (59 µL, 51.1 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL). The product was strongly contaminated after column chromatography. The product was dissolved in dichloromethane and washed with 2M HCl solution. The organic phase was dried over Na_2SO_4 then filtrated and evaporated. The solid residue was washed three times using pentane. The chloride salt of the pure product was isolated.

Yield: 46.7 mg (0.12 mmol, 39%) brown solid. **Mp.** 210-215 °C sublimate and decomposed. **R_f**= 0.71 in hexane : ethyl acetate 4:1 for the free amine. **MS** (EI, 70 eV): m/z (%): 363 (<1, [M^+]), 362 (1), 334 (1), 319 (1), 318 (4), 215 (2), 198 (9), 151 (6), 128 (2), 121 (3), 104 (11), 99 (30), 98 (100), 96 (9), 83 (8), 70 (13), 69 (11), 65 (6), 55 (14). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 12.92 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.81 – 3.54 (m, 4H), 3.28 (s, 2H), 2.38 (s, 1H), 2.29 (s, 1H), 1.83 (s, 3H), 1.46 (s, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -78.0, -119.1. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.4, 154.6, 131.4, 128.9, 121.7, 119.3 (dq, *J* = 291.7, 41.7 Hz), 107.4 (qd, *J* = 243.9, 35.0 Hz), 61.3, 56.0 (d, *J* = 21.8 Hz), 54.8 (d, *J* = 14.7 Hz), 22.7, 21.6, 14.3. **IR** (film, ATR) 1719, 1604, 1507, 1458, 1413, 1369, 1279, 1205, 1175, 1104, 1089, 1052, 1022, 1003, 966, 955, 932, 861, 779, 761, 701 cm^{-1}. **HRMS** (ESI) [M+H]$^+$ calculated for $C_{17}H_{22}F_4NO_3^+$: 364.15303, found: 364.1528.

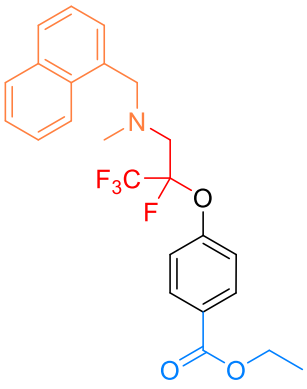
1-(2-(4-(Ethoxycarbonyl)phenoxy)-2,3,3,3-tetrafluoropropyl)-4-(pyridin-1-ium-2-yl)piperazine-1,4-diium trichloride (56)



Method B. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), 1-(pyridin-2-yl)piperazine (91 µL, 97.9 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL). After column chromatography, the product was dissolved in dichloromethane and washed with 2M HCl solution. The organic phase was dried over Na_2SO_4 then filtrated and evaporated. The chloride salt of the pure product was isolated.

Yield: 104.7 mg (0.19 mmol, 63%) brown oil. **R_f**= 0.38 in hexane : ethyl acetate 4:1 for the free amine. **MS** (EI, 70 eV): m/z (%): 441 (1, [M^+]) 421 (2), 396 (2), 276 (4), 270 (4), 258 (3), 176 (9), 164 (12), 147 (11), 133 (11), 121 (30), 120 (14), 119 (18), 108 (12), 107 (100), 95 (10), 94 (15), 79 (20), 78 (17). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 4.8 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.79 (t, *J* = 6.5 Hz, 1H), 5.24 (s, 3H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.73 – 3.70 (m, 4H), 2.99 (p, *J* = 14.7 Hz, 2H), 2.69 (s, 4H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.3, -122.5. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.6, 155.7, 152.2, 143.6, 138.5, 131.2, 127.7, 121.4 (d, *J* = 2.6 Hz), 120.2 (qd, *J* = 288.2, 36.9 Hz), 112.6, 111.3, 109.2 (dq, *J* = 241.3, 33.0 Hz), 61.1, 57.3 (d, *J* = 26.2 Hz), 53.5, 53.0, 47.0, 14.2. **IR** (film, ATR) 1715, 1637, 1604, 1540, 1503, 1466, 1439, 1369, 1309, 1275, 1193, 1171, 1085, 1052, 1018, 996, 936, 861, 764, 709 cm^{-1}. **HRMS** (EI) $[M]^+$ calculated for $C_{21}H_{23}F_4N_3O_3^+$: 441.16755, found: 441.16573.

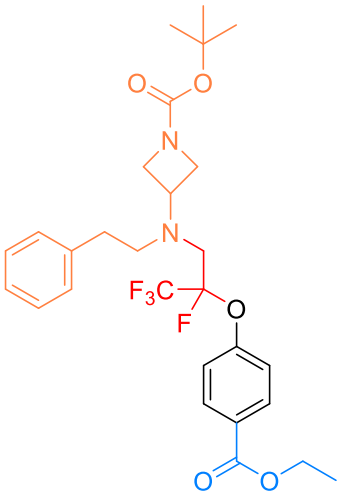
Ethyl 4-((1,1,1,2-tetrafluoro-3-(methyl(naphthalen-1-ylmethyl)amino)propan-2-yl)oxy)benzoate (57)



Method B. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *N*-methyl-1-(naphthalen-1-yl)methanamine (99 µL, 102.7 mg, 0.6 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 84.0 mg (0.19 mmol, 62%) yellow oil. **R_f**= 0.57 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): 449 (<1, [M^+]), 404 (2), 262 (1), 244 (1), 215 (1), 185 (17), 184 (100), 168 (6) 142 (37), 141 (100), 139 (10), 115 (50), 104 (10), 76 (7), 65 (6). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.32 – 8.25 (m, 1H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.89 – 7.76 (m, 2H), 7.49 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 3.32 – 3.10 (m, 2H), 2.36 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -79.9 (d, *J* = 2.0 Hz), -123.4 (q, *J* = 2.1 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 155.9, 134.0, 133.9, 132.4, 131.3, 128.5, 128.4, 127.6, 127.5, 125.9, 125.8, 125.2, 124.7, 121.6 (d, *J* = 2.7 Hz), 120.6 (qd, *J* = 288.5, 38.1 Hz), 110.0 (dq, *J* = 241.3, 32.3 Hz), 61.8, 61.2, 57.6 (d, *J* = 25.1 Hz), 43.6 (d, *J* = 1.9 Hz), 14.4. **IR** (film, ATR) 1715, 1604, 1507, 1462, 1413, 1369, 1275, 1193, 1167, 1085, 1055, 1018, 973, 858, 794, 776, 735, 709 cm^{-1}. **HRMS** (EI) $[M-C_2H_5O]^+$ calculated for $C_{22}H_{18}F_4NO_2^+$: 404.12737, found: 404.12493.

***tert*-Butyl 3-((2-(4-(ethoxycarbonyl)phenoxy)-2,3,3,3-tetrafluoropropyl)(phenethyl)amino)azetidine -1-carboxylate (58)**



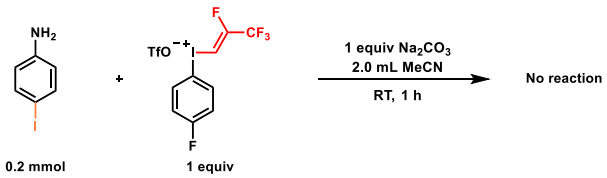
Method B. Using ethyl 4-hydroxybenzoate (49.9 mg, 0.3 mmol), Na_2CO_3 (31.8 mg, 0.3 mmol), *tert*-butyl 3-(phenethylamino)azetidine-1-carboxylate (131.9 mg, 0.48 mmol) and iodonium salt (174.3 mg, 0.36 mmol) in MeCN (3.0 mL).

Yield: 58.7 mg (0.11 mmol, 35%) yellow oil. $\mathbf{R_f}$= 0.36 in hexane : ethyl acetate 4:1. **MS** (EI, 70 eV): m/z (%): Compound is not measurable using GC-MS. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.15 – 7.09 (m, 3H), 7.08 – 7.00 (m, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.88 (q, *J* = 7.9 Hz, 2H), 3.82 – 3.68 (m, 3H), 3.29 – 3.12 (m, 2H), 3.00 – 2.85 (m, 2H), 2.72 – 2.60 (m, 2H), 1.35 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.8 Hz), -122.9 (q, *J* = 2.9 Hz). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 155.6, 139.2, 131.3, 128.6, 128.0, 127.9, 127.4, 121.8 (d, *J* = 2.6 Hz), 120.6 (qd, *J* = 287.4, 37.1 Hz), 109.5 (dq, *J* = 238.7, 33.3 Hz), 61.2, 53.6, 48.4 (d, *J* = 28.9 Hz), 14.4. **IR** (film, ATR) 1700, 1604, 1503, 1480, 1410, 1391, 1369, 1275, 1193, 1167, 1126, 1089, 1018, 929, 861, 776, 753, 701 cm $^{-1}$. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{28}H_{35}F_4N_2O_5^+$: 555.2477, found: 555.2478.

7. Unsuccessful attempts and selectivity

7.1 Reaction of amine and iodonium salt

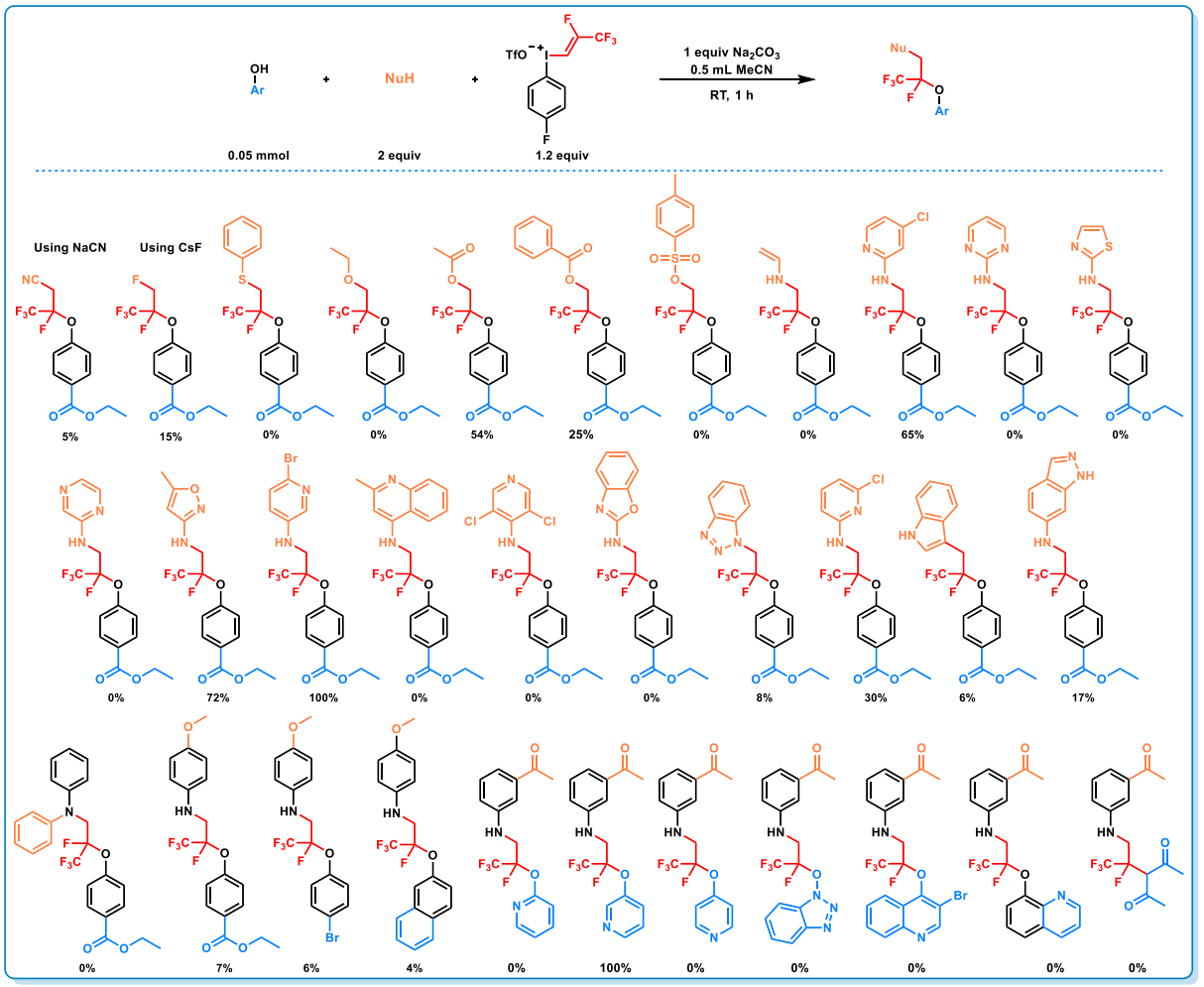
4-iodoaniline (43.8 mg, 0.2 mmol), Na_2CO_3 (21.2 mg, 1 equiv, 0.2 mmol), and (*Z*)-(4-fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate (96.8 mg, 1 equiv, 0.2 mmol) were measured into a screw cap vial and diossolved in MeCN (2 mL). The mixture was stirred at ambient temperature for 1 hour then analyzed by GC-MS and ^{19}F NMR. No reaction occurred. Based on the GC-MS measurement, the aniline derivative remained in the reaction mixture. Based on ^{19}F NMR measurement, the iodonium salt was decomposed.



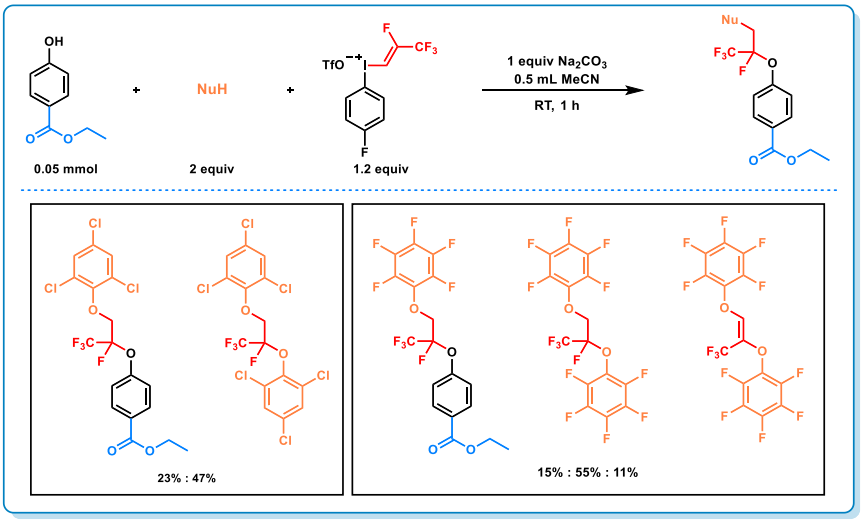
7.2 Heterodisubstitution

Phenol derivative (0.05 mmol), Na_2CO_3 (1 equiv, 0.05 mmol), “second” nucleophile (2 equiv, 0.1 mmol) and MeCN (0.5 mL) were measured into a screw cap vial. The mixture was stirred at ambient temperature for 5 minutes and (*Z*)-(4-fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate (1.2 equiv, 0.06 mmol) was added in one portion. The mixture was stirred at ambient temperature for 1 hour then analyzed by GC-MS and TLC.

In the following cases, the desired products formed in low conversions or not detected at all. The product formed in low amount in the cases of heteroaromatic compounds despite the high GC-MS conversions (ionization problems).



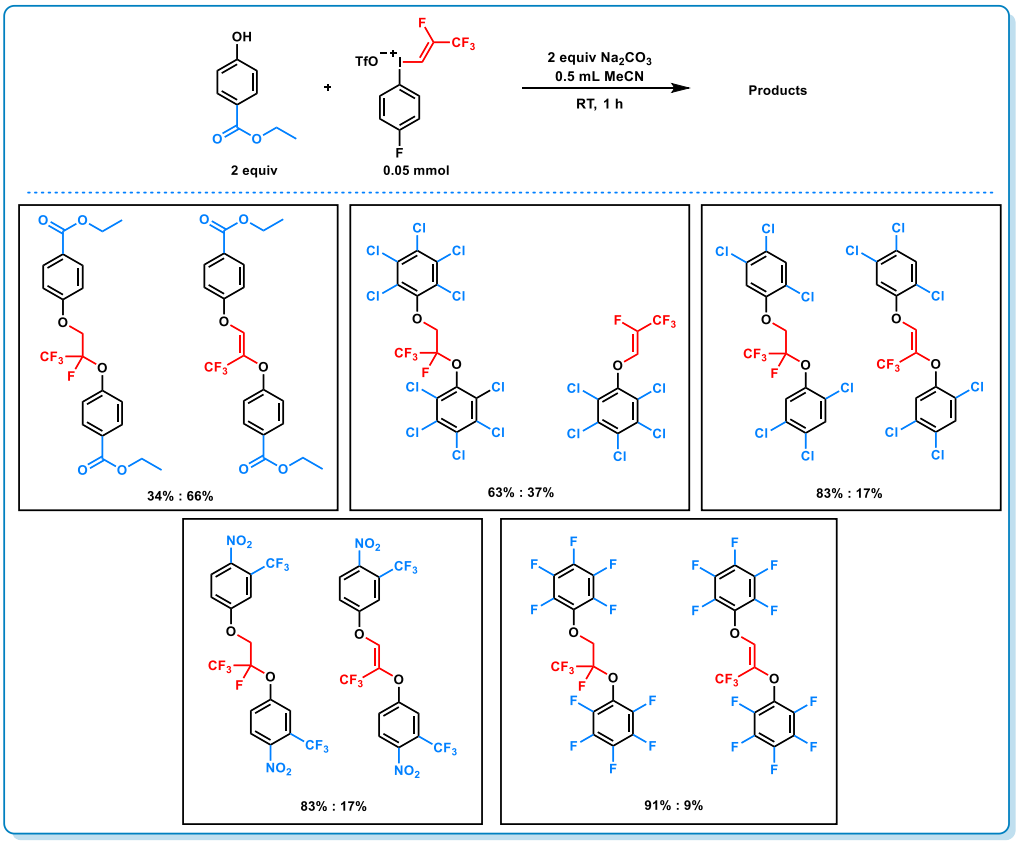
In the following cases, homodifunctionalized products were identified by GC-MS.



7.3 Homodisubstitution

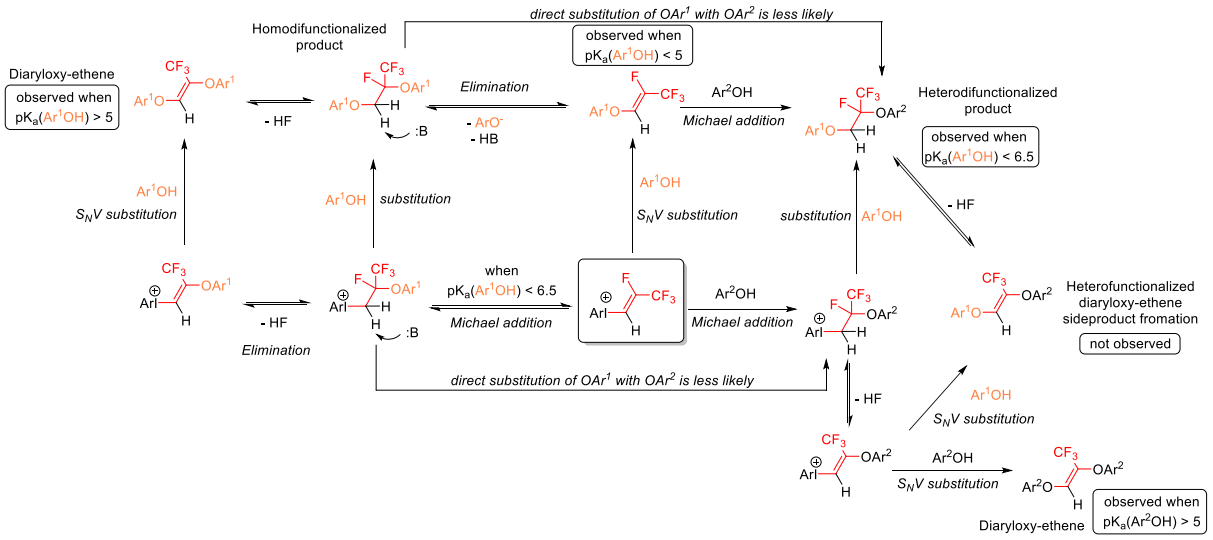
Phenol derivative (2 equiv, 0.1 mmol), Na_2CO_3 (2 equiv, 0.1 mmol) and MeCN (0.5 mL) were measured into a screw cap vial. The mixture was stirred at ambient temperature for 5 minutes and (*Z*)-(4-fluorophenyl)(2,3,3,3-tetrafluoroprop-1-en-1-yl)iodonium trifluoromethanesulfonate (1 equiv, 0.05 mmol) was added in one portion. The mixture was stirred at ambient temperature for 1 hour then analyzed by GC-MS and TLC.

In the following cases, several side products were identified by GC-MS and the ratio of the two products is shown.



8. Proposed mechanism

Reasonable pathways for the formation of identified products and side products



9. References

[1] Umemoto, T.; Gotoh, Y., Synthesis, Properties, and Reactivity of (1*H*,1*H*-Perfluoroalkyl)- and (1*H*-Perfluoro-1-alkenyl)aryliodonium Triflates and Their Analogs. *Bulletin of the Chemical Society of Japan* **1987,** *60* (9), 3307-3313.

[2] Tóth, B. L.; Sályi, G.; Domján, A.; Egyed, O.; Bényei, A.; Gonda, Z.; Novák, Z., Z-Selective Fluoroalkenylation of (Hetero)Aromatic Systems by Iodonium Reagents in Palladium-Catalyzed Directed C−H Activation. *Advanced Synthesis & Catalysis* **2022,** *364* (2), 348-354.

[3] Varga, B.; Tóth, B. L.; Béke, F.; Csenki, J. T.; Kotschy, A.; Novák, Z., Synthesis and Photochemical Application of Hydrofluoroolefin (HFO) Based Fluoroalkyl Building Block. *Organic Letters* **2021,** *23* (12), 4925-4929.

[4] Csenki, J. T.; Tóth, B. L.; Béke, F.; Varga, B.; P. Fehér, P.; Stirling, A.; Czégény, Z.; Bényei, A.; Novák, Z., Synthesis of Hydrofluoroolefin-Based Iodonium Reagent via Dyotropic Rearrangement and Its Utilization in Fluoroalkylation. *Angewandte Chemie International Edition* **2022,** *61* (37), e202208420.

[5] Jung, M. E.; Koch, P., Mild, selective deprotection of PMB ethers with triflic acid/1,3-dimethoxybenzene. *Tetrahedron Letters* **2011,** *52* (46), 6051-6054.

[6] Papageorgiou, G.; Corrie, J. E. T. Synthesis and Photolytic Assessment of Nitroindolinyl-Caged Calcium Ion Chelators *Molecules* [Online], 2022.

[7] Misal Castro, L. C.; Obata, A.; Aihara, Y.; Chatani, N., Chelation-Assisted Nickel-Catalyzed Oxidative Annulation via Double C−H Activation/Alkyne Insertion Reaction. *Chemistry – A European Journal* **2016,** *22* (4), 1362-1367.

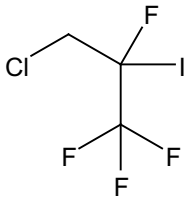
[8] Turrado, C.; Puig, T.; García-Cárceles, J.; Artola, M.; Benhamú, B.; Ortega-Gutiérrez, S.; Relat, J.; Oliveras, G.; Blancafort, A.; Haro, D.; Marrero, P. F.; Colomer, R.; López-Rodríguez, M. L., New Synthetic Inhibitors of Fatty Acid Synthase with Anticancer Activity. *Journal of Medicinal Chemistry* **2012,** *55* (11), 5013-5023.

[9] Béchamp, A., Bechamp reduction. *Annales de Chimie et de Phisique* **1854,** *42*, 186.

[10] Zhang, W.-W.; Gao, T.-T.; Xu, L.-J.; Li, B.-J., Macrolactonization of Alkynyl Alcohol through Rh(I)/Yb(III) Catalysis. *Organic Letters* **2018,** *20* (20), 6534-6538.

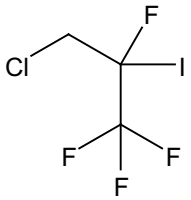
10. NMR spectra

^{1}H NMR (400 MHz, DMSO-d_6) δ 4.55 (dd, J = 19.0, 13.5 Hz, 1H), 4.39 (dd, J = 19.5, 13.5 Hz, 1H).



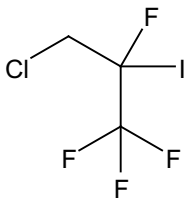
(2)

^{19}F NMR (376 MHz, DMSO-d_6) δ -74.7 (d, J = 11.8 Hz), -139.0 (q, J = 11.8 Hz).



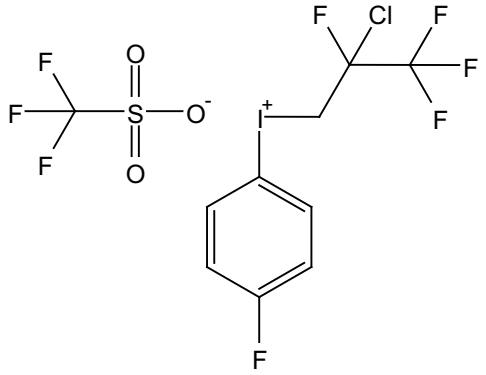
(2)

^{13}C NMR (101 MHz, DMSO-d_6) δ 121.5 (qd, J = 283.2, 29.2 Hz), 78.1 (dq, J = 255.6, 34.4 Hz), 48.4 (d, J = 22.1 Hz).



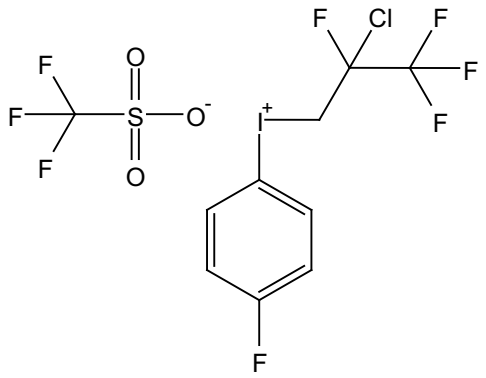
(2)

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.22 (dd, J = 8.9, 4.8 Hz, 2H), 7.33 (t, J = 8.8 Hz, 2H), 5.09 (dd, J = 13.1, 8.7 Hz, 1H), 4.93 (dd, J = 28.1, 13.2 Hz, 1H).



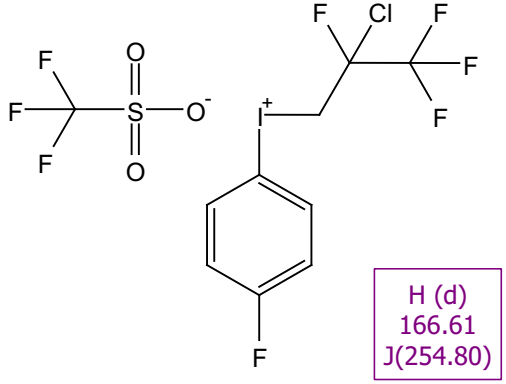
(3)

^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -79.3, -80.9 (d, J = 6.2 Hz), -104.9, -118.3 (q, J = 6.2 Hz).



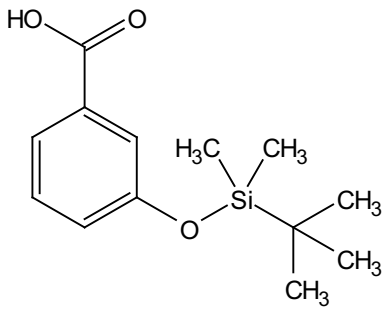
(3)

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 166.6 (d, J = 254.8 Hz), 141.4 (d, J = 9.6 Hz), 121.7 (q, J = 320.0 Hz), 120.8 (d, J = 23.6 Hz), 119.9 (qd, J = 285.4, 31.2 Hz), 104.7 (dq, J = 254.7, 38.4 Hz), 103.8 (d, J = 3.3 Hz), 41.7 (d, J = 21.9 Hz).

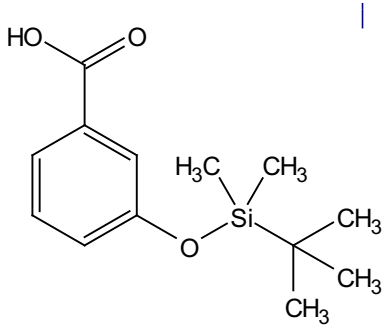


(3)

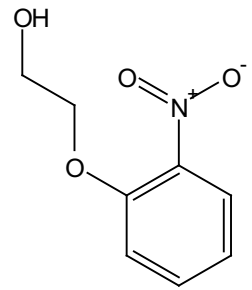
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.67 (bs, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 2.2 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.09 (dd, *J* = 8.0, 1.4 Hz, 1H), 1.01 (s, 9H), 0.23 (s, 6H).



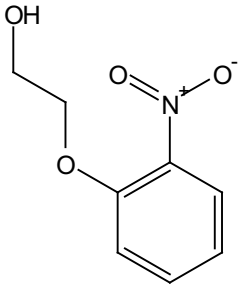
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 155.9, 130.8, 129.7, 125.9, 123.4, 121.6, 25.8, 18.4, -4.3.



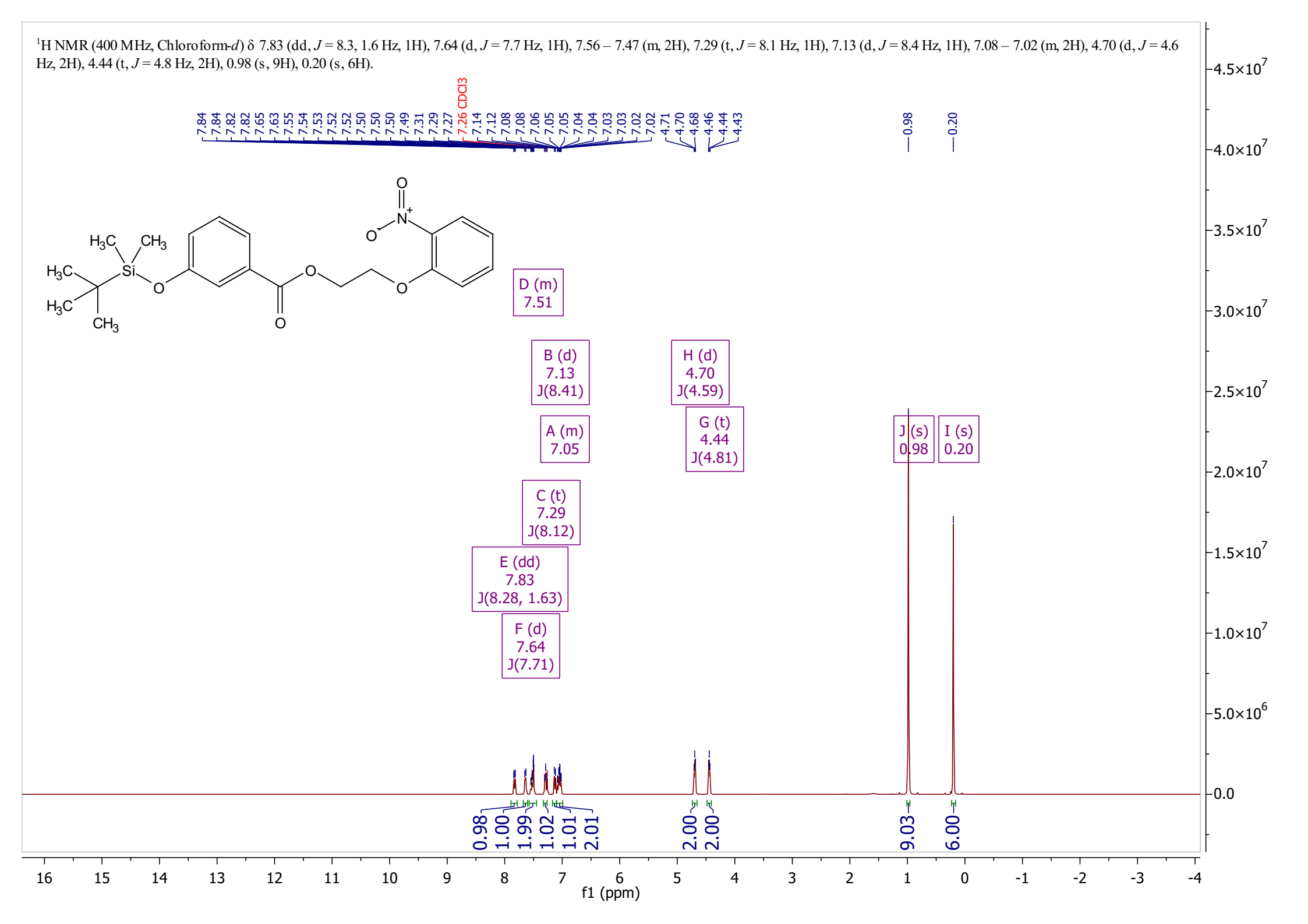
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.54 (td, *J* = 8.1, 7.5, 1.9 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.05 (t, *J* = 8.2 Hz, 1H), 4.23 (t, *J* = 4.4 Hz, 2H), 3.98 (dt, *J* = 6.6, 4.3 Hz, 2H), 2.59 (t, *J* = 6.6 Hz, 1H).



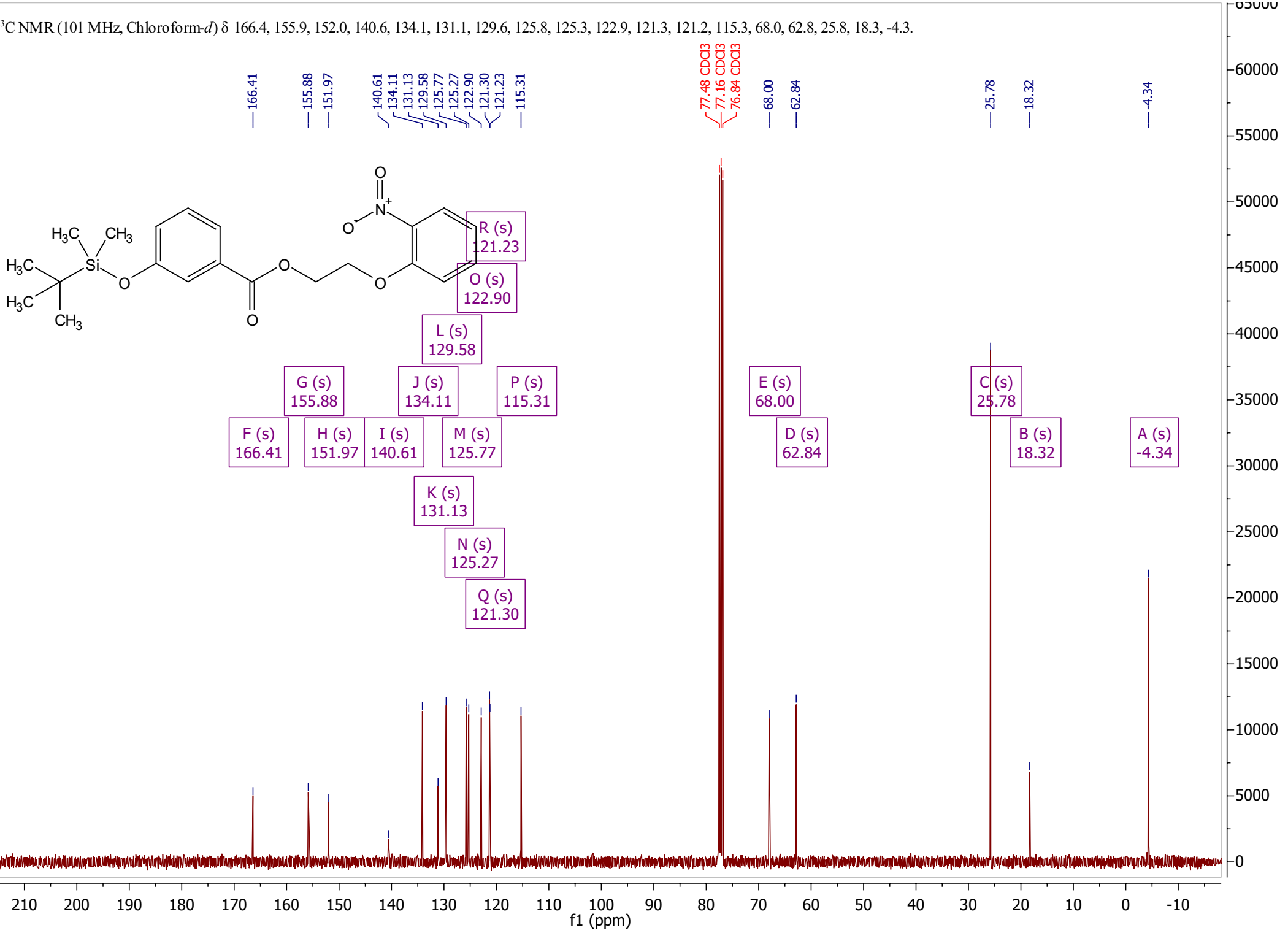
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.4, 140.0, 134.5, 125.9, 121.1, 115.3, 71.5, 61.1.



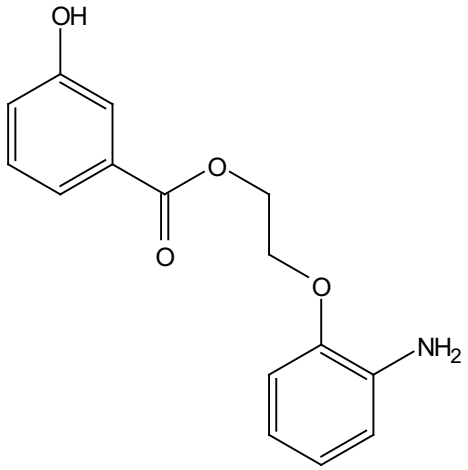
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.08 – 7.02 (m, 2H), 4.70 (d, *J* = 4.6 Hz, 2H), 4.44 (t, *J* = 4.8 Hz, 2H), 0.98 (s, 9H), 0.20 (s, 6H).



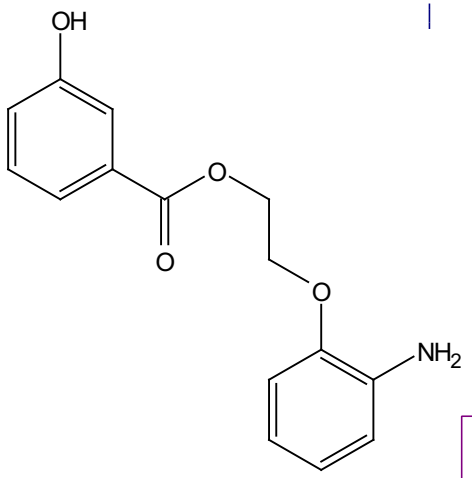
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 155.9, 152.0, 140.6, 134.1, 131.1, 129.6, 125.8, 125.3, 122.9, 121.3, 121.2, 115.3, 68.0, 62.8, 25.8, 18.3, -4.3.



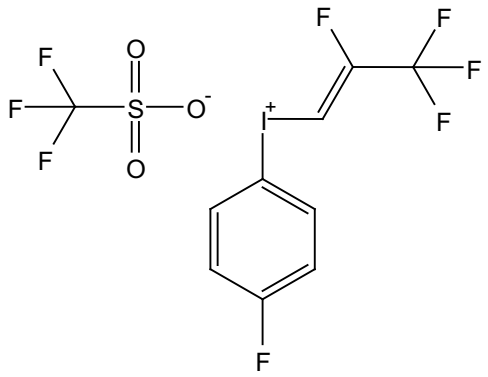
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.44 – 7.37 (m, 2H), 7.32 (t, J = 7.9 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 6.64 (d, J = 6.4 Hz, 1H), 6.51 (t, J = 6.8 Hz, 1H), 4.67 (s, 2H), 4.59 (t, J = 4.6 Hz, 2H), 4.26 (t, J = 4.6 Hz, 2H).



^{13}C NMR (101 MHz, DMSO-d_6) δ 165.9, 157.5, 145.2, 138.1, 130.9, 129.9, 121.6, 120.5, 120.0, 116.3, 115.7, 114.2, 112.6, 66.6, 63.5.

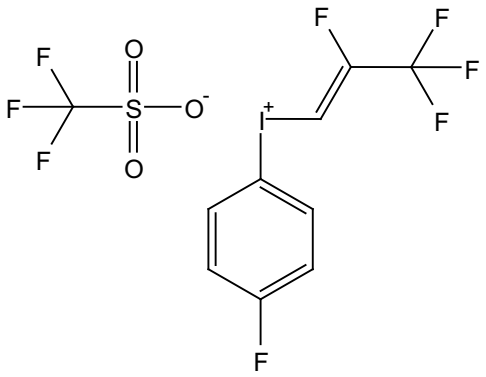


^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.14 (dd, J = 8.9, 4.9 Hz, 2H), 7.55 (d, J = 33.7 Hz, 1H), 7.30 (t, J = 8.6 Hz, 2H).



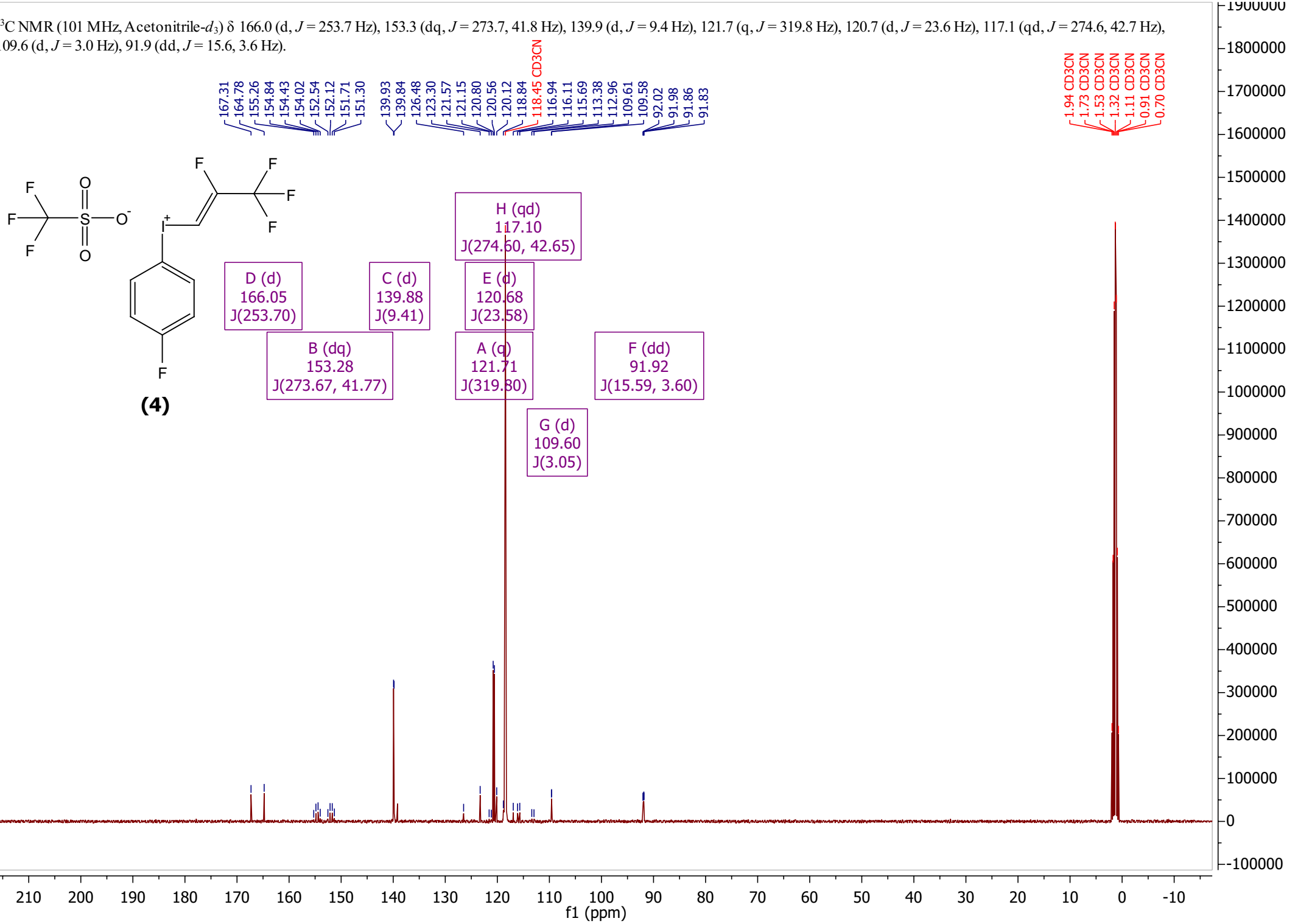
(4)

^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -72.4 (d, J = 10.4 Hz), -79.3, -102.1 (q, J = 10.5 Hz), -106.2.

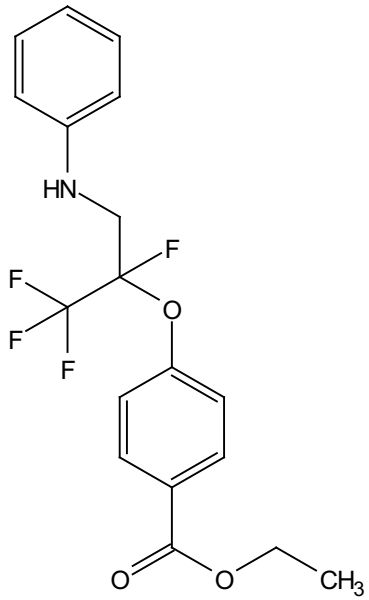


(4)

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 166.0 (d, J = 253.7 Hz), 153.3 (dq, J = 273.7, 41.8 Hz), 139.9 (d, J = 9.4 Hz), 121.7 (q, J = 319.8 Hz), 120.7 (d, J = 23.6 Hz), 117.1 (qd, J = 274.6, 42.7 Hz), 109.6 (d, J = 3.0 Hz), 91.9 (dd, J = 15.6, 3.6 Hz).

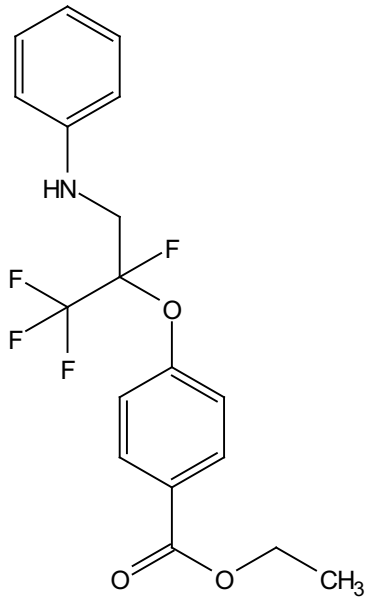


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.79 – 3.61 (m, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).



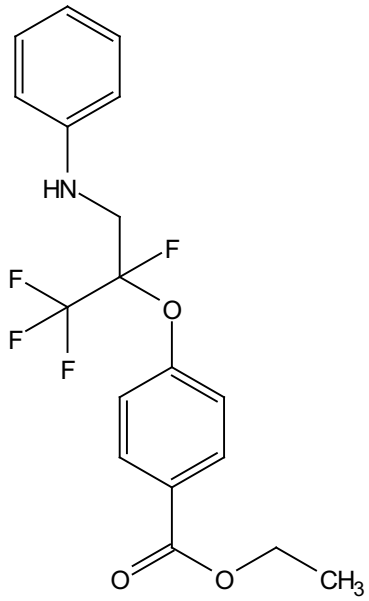
(8)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.7 Hz), -125.7 (q, *J* = 2.8 Hz).



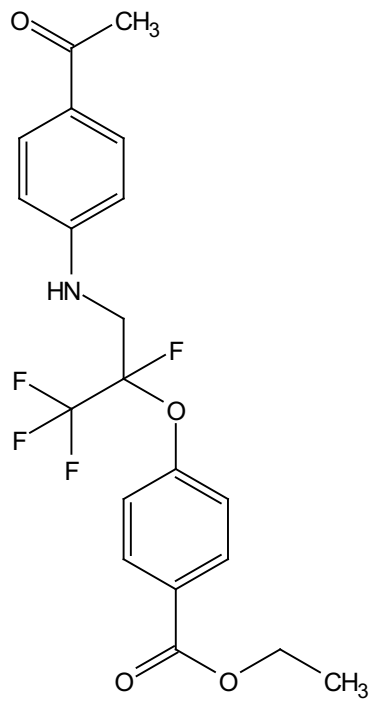
(8)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 155.4, 146.6, 131.4, 129.4, 128.2, 121.8 (d, *J* = 2.5 Hz), 120.6 (qd, *J* = 288.1, 37.8 Hz), 118.9, 113.3, 108.9 (dq, *J* = 241.5, 33.3 Hz), 61.3, 45.1 (d, *J* = 28.4 Hz), 14.4.



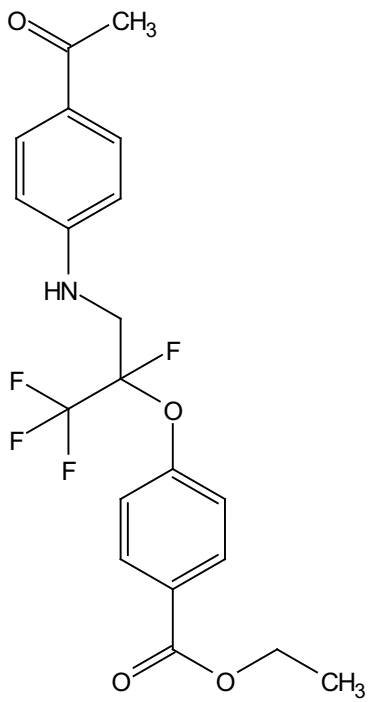
(8)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 4.61 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.96 – 3.79 (m, 2H), 2.47 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H).



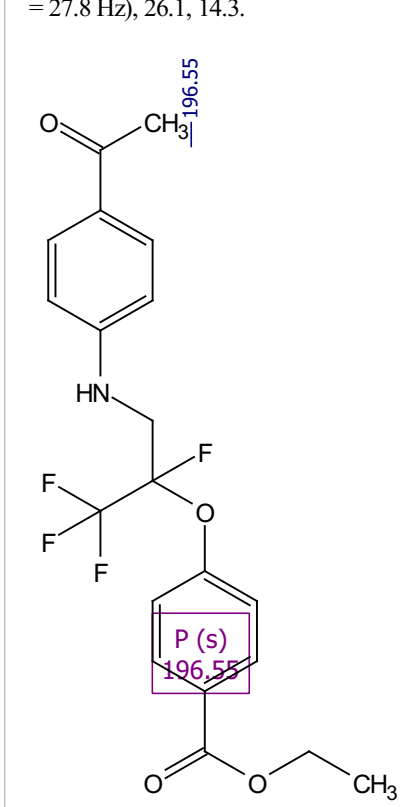
(9)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.0 (d, *J* = 2.7 Hz), -126.2 (q, *J* = 2.9 Hz).



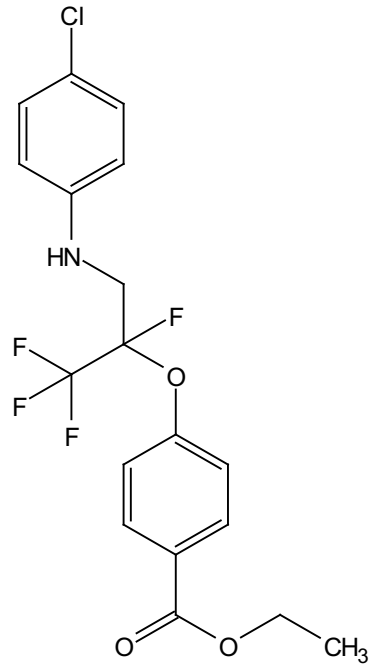
(9)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.6, 165.7, 155.3, 150.8, 131.4, 130.7, 128.3, 128.1, 121.7 (d, *J* = 2.5 Hz), 120.4 (qd, *J* = 288.2, 38.1 Hz), 112.0, 108.5 (dq, *J* = 242.0, 33.4 Hz), 61.3, 44.3 (d, *J* = 27.8 Hz), 26.1, 14.3.



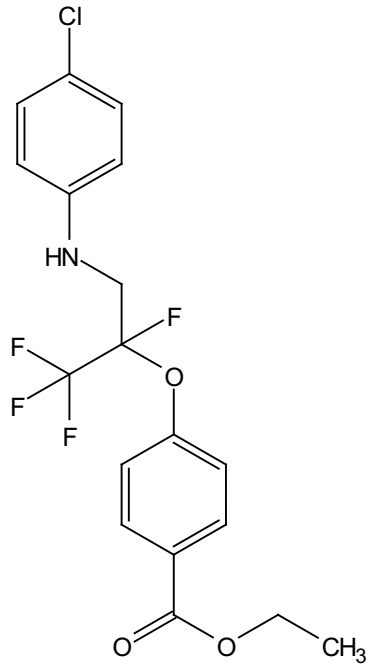
(9)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.5 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 1H), 3.84 – 3.69 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).



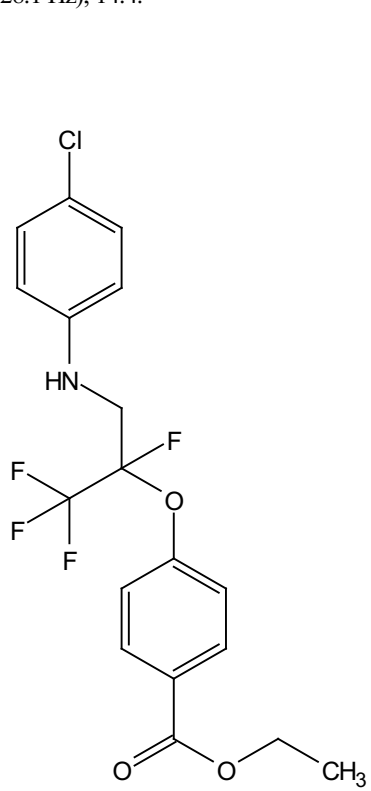
(10)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.1 (d, *J* = 2.7 Hz), -125.8 (q, *J* = 2.6 Hz).



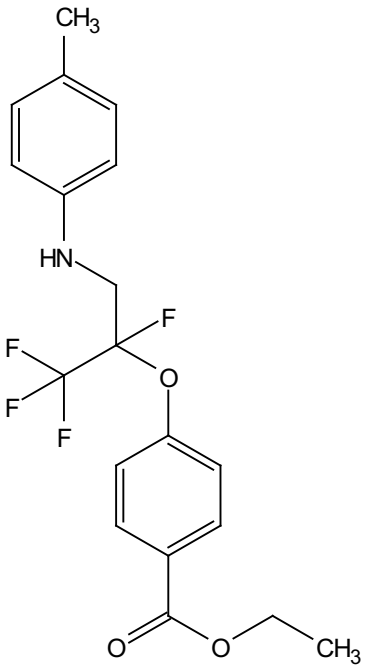
(10)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 155.4, 145.2, 131.4, 129.2, 128.3, 123.5, 121.8 (d, *J* = 2.7 Hz), 120.5 (qd, *J* = 287.9, 37.8 Hz), 114.4, 108.7 (dq, *J* = 241.2, 33.1 Hz), 61.3, 45.2 (d, *J* = 28.1 Hz), 14.4.



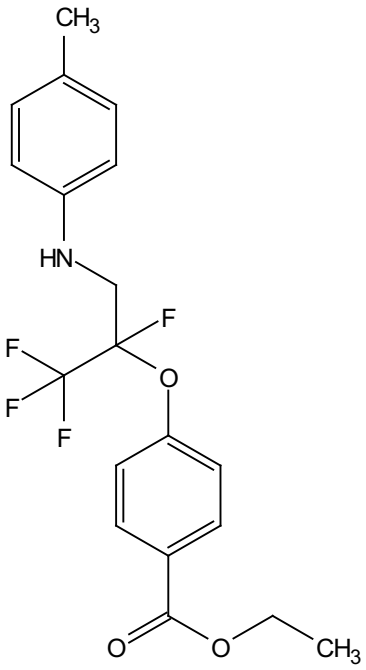
(10)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.86 – 3.70 (m, 2H), 3.68 (bs, 1H), 2.24 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).



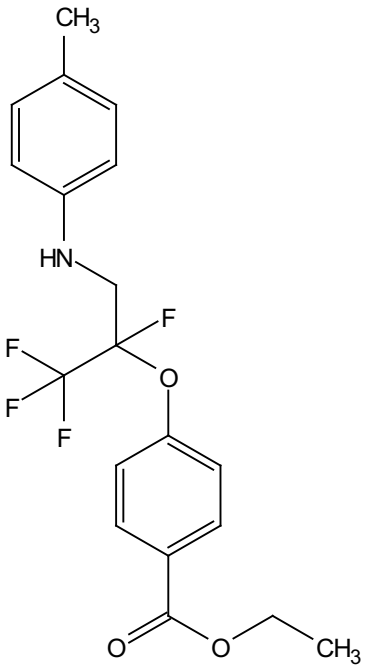
(11)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 3.0 Hz), -125.6 (q, *J* = 3.0 Hz).



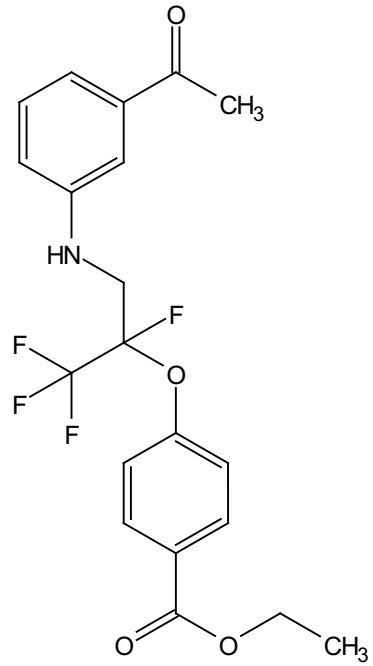
(11)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 155.5, 144.3, 131.4, 129.9, 128.2, 128.2, 121.9 (d, *J* = 2.5 Hz), 120.6 (qd, *J* = 288.2, 37.4 Hz), 113.5, 108.9 (dq, *J* = 240.9, 33.2 Hz), 61.3, 45.4 (d, *J* = 28.4 Hz), 20.5, 14.4.



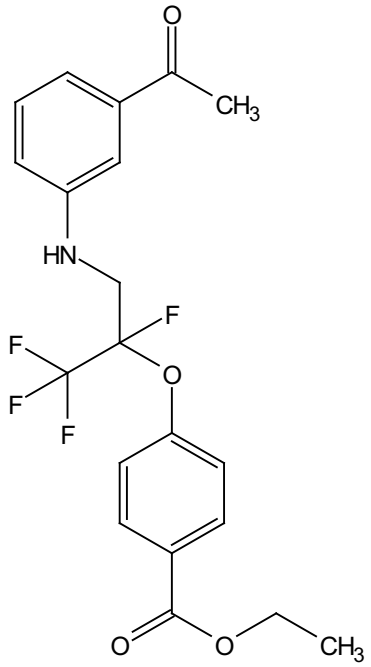
(11)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.27 (dd, *J* = 28.3, 7.9 Hz, 2H), 7.23 – 7.15 (m, 3H), 6.79 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.13 (bs, 1H), 3.90 – 3.76 (m, 2H), 2.52 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H).



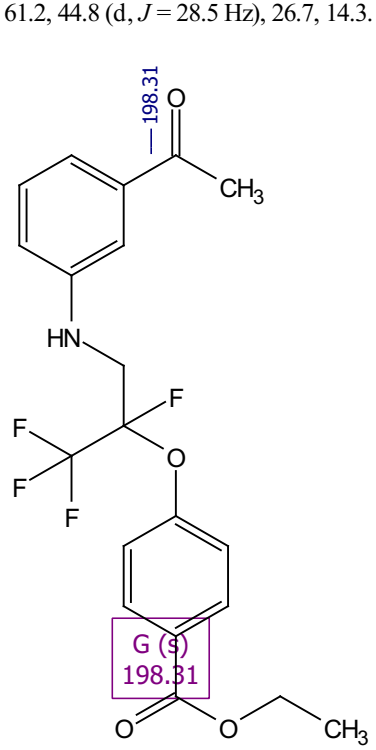
(13)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.1 (d, *J* = 2.7 Hz), -125.6 (q, *J* = 2.8 Hz).



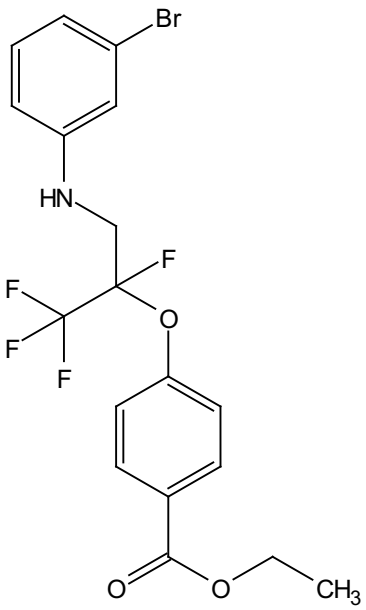
(13)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.3, 165.7, 155.3, 146.9, 138.2, 131.4, 129.5, 128.2, 121.7 (d, *J* = 2.5 Hz), 120.5 (qd, *J* = 288.3, 37.8 Hz), 119.2, 117.8, 112.0, 108.7 (dq, *J* = 241.4, 33.2 Hz), 61.2, 44.8 (d, *J* = 28.5 Hz), 26.7, 14.3.



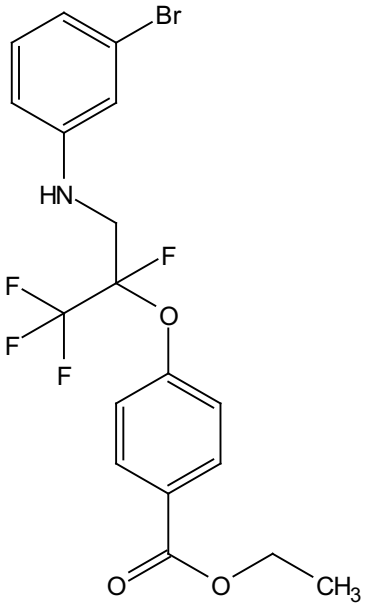
(13)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.70 (t, *J* = 2.2 Hz, 1H), 6.51 (dd, *J* = 8.1, 2.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 1H), 3.85 – 3.69 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).



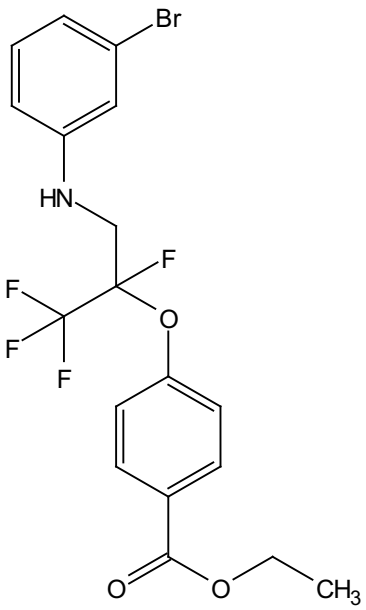
(14)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.1 (d, *J* = 2.7 Hz), -125.5 (q, *J* = 2.8 Hz).



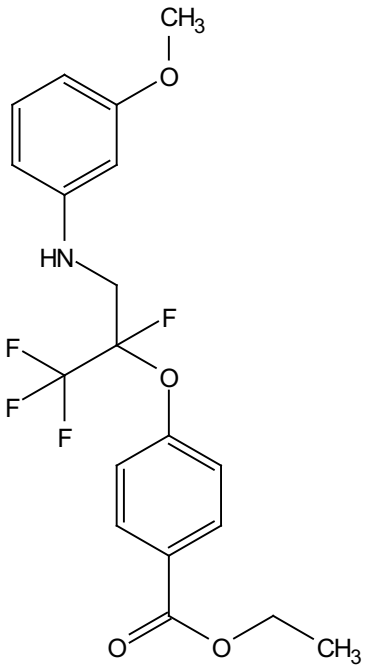
(14)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 155.3, 147.9, 131.5, 130.6, 128.3, 123.3, 121.7 (d, *J* = 2.5 Hz), 121.7, 120.5 (qd, *J* = 288.3, 38.1 Hz), 116.0, 111.9, 108.7 (dq, *J* = 241.3, 33.1 Hz), 61.3, 44.7 (d, *J* = 28.5 Hz), 14.4.



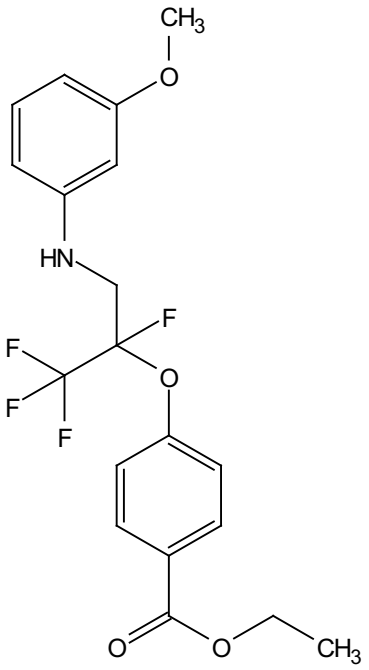
(14)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.34 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.22 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.15 (t, *J* = 2.4 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.88 – 3.69 (m, 6H), 1.40 (t, *J* = 7.2 Hz, 3H).



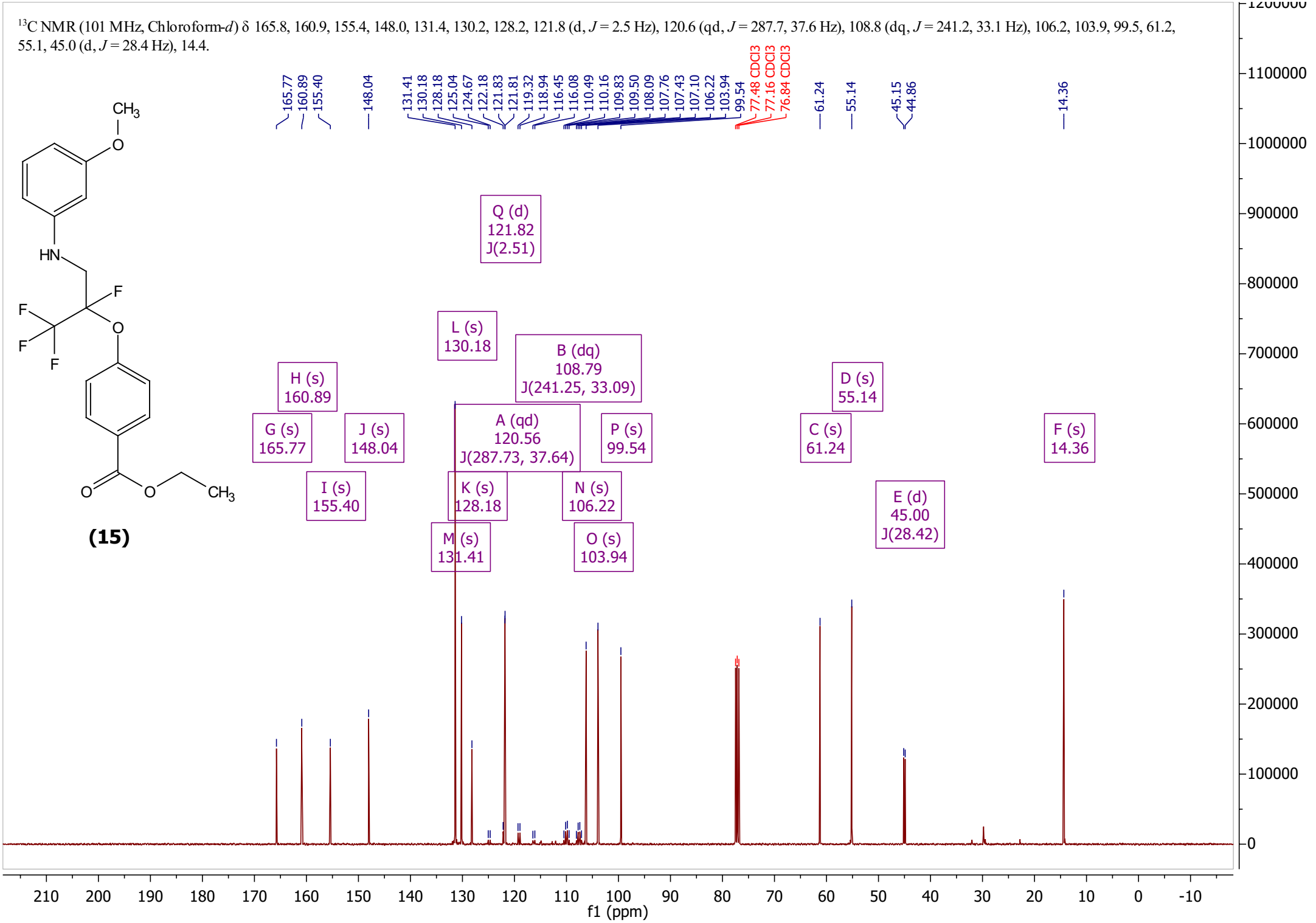
(15)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.9 Hz), -125.7 (q, *J* = 2.8 Hz).

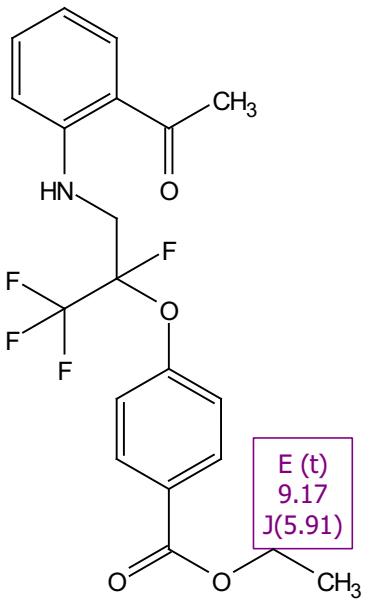


(15)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 160.9, 155.4, 148.0, 131.4, 130.2, 128.2, 121.8 (d, *J* = 2.5 Hz), 120.6 (qd, *J* = 287.7, 37.6 Hz), 108.8 (dq, *J* = 241.2, 33.1 Hz), 106.2, 103.9, 99.5, 61.2, 55.1, 45.0 (d, *J* = 28.4 Hz), 14.4.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.17 (t, *J* = 5.9 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.65 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.61 – 6.49 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.87 – 3.65 (m, 2H), 2.49 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).



(16)

E (t) 9.17 J(5.91)

F (d) 7.90 J(8.92)

G (dd) 7.65 J(8.03, 1.66)

H (t) 7.23 J(7.69)

I (d) 7.18 J(8.09)

J (m) 6.55

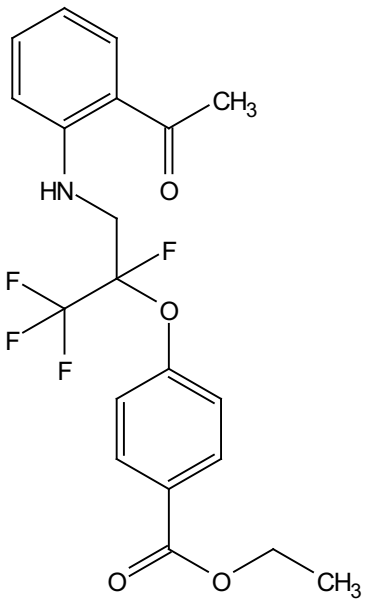
C (q) 4.26 J(7.14)

D (m) 3.76

B (s) 2.49

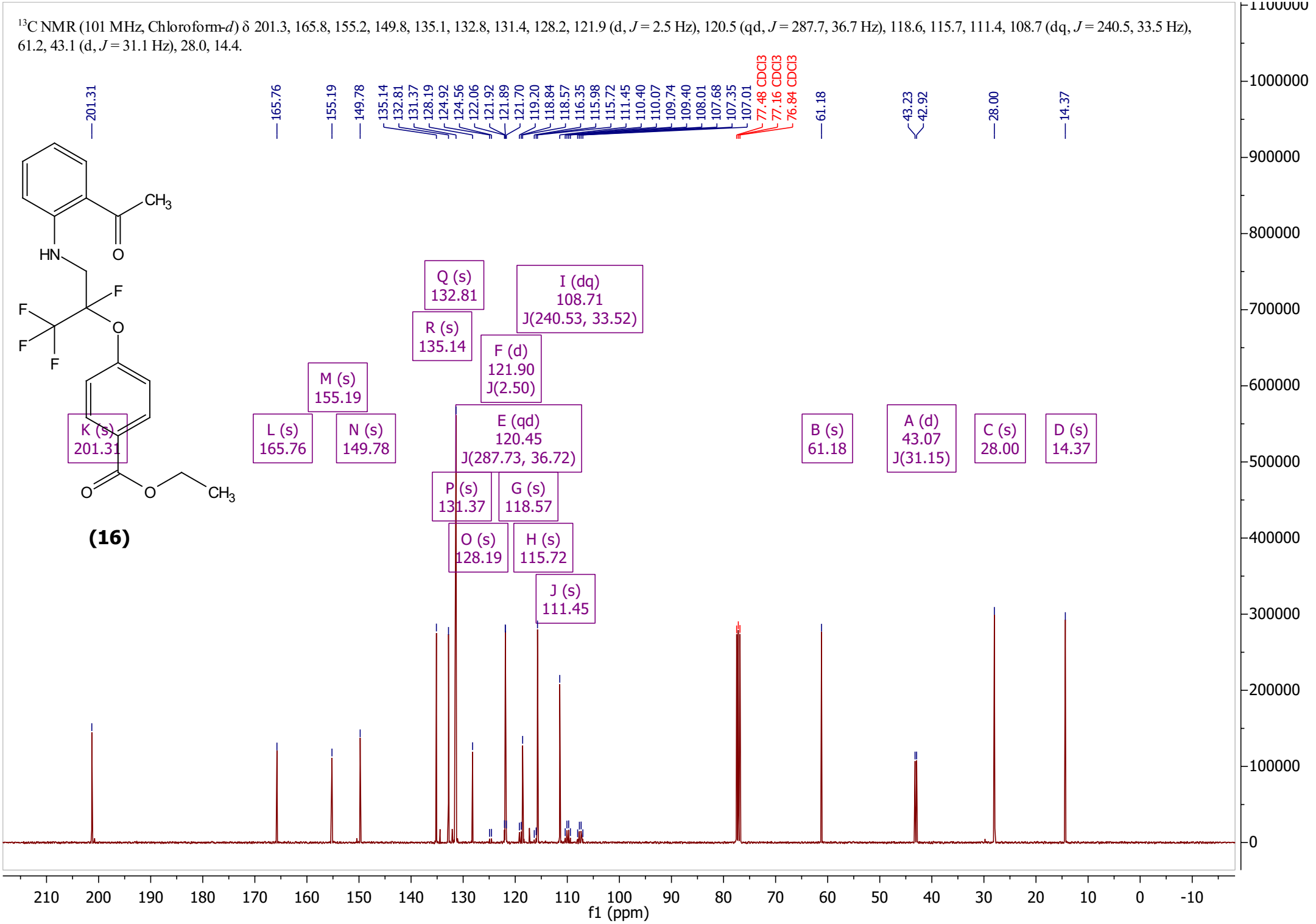
A (t) 1.28 J(7.16)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.7 (d, *J* = 2.8 Hz), -123.9 (q, *J* = 3.0 Hz).

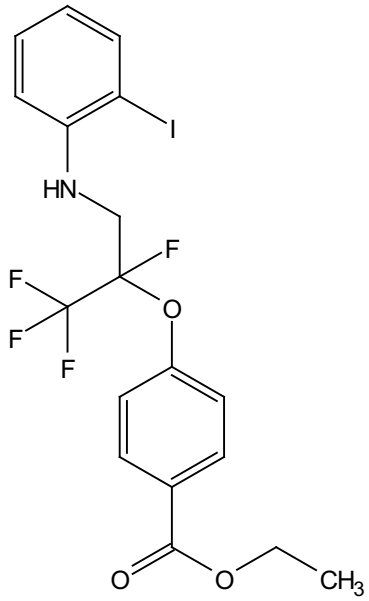


(16)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.3, 165.8, 155.2, 149.8, 135.1, 132.8, 131.4, 128.2, 121.9 (d, *J* = 2.5 Hz), 120.5 (qd, *J* = 287.7, 36.7 Hz), 118.6, 115.7, 111.4, 108.7 (dq, *J* = 240.5, 33.5 Hz), 61.2, 43.1 (d, *J* = 31.1 Hz), 28.0, 14.4.

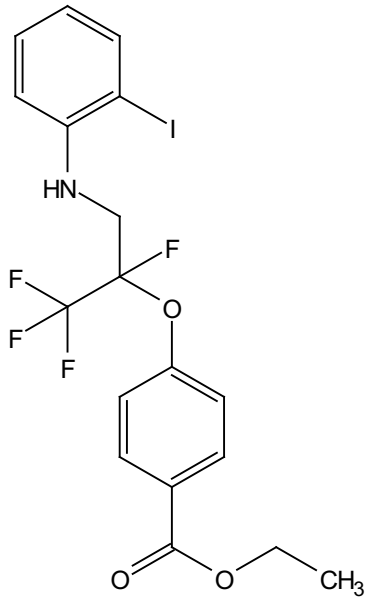


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.55 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.45 – 6.36 (m, 2H), 4.31 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.72 (dd, *J* = 10.5, 6.4 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).



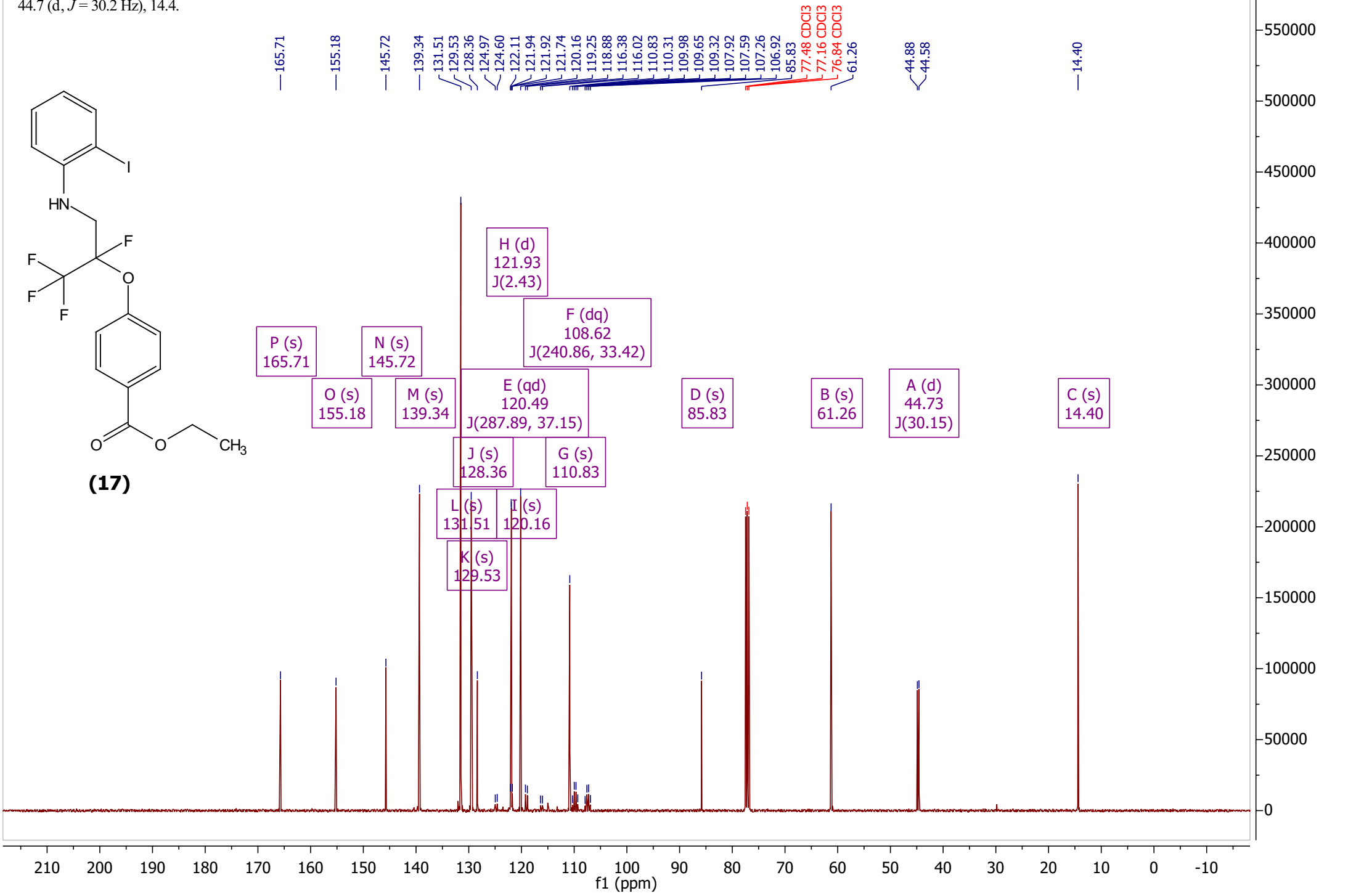
(17)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.4 (d, *J* = 3.1 Hz), -124.7 (q, *J* = 3.0 Hz).

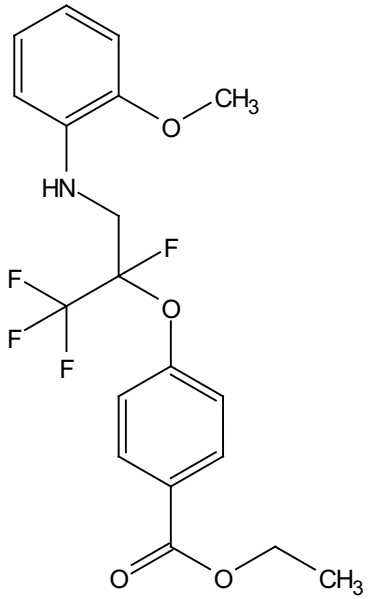


(17)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 155.2, 145.7, 139.3, 131.5, 129.5, 128.4, 121.9 (d, *J* = 2.4 Hz), 120.5 (qd, *J* = 287.9, 37.1 Hz), 120.2, 110.8, 108.6 (dq, *J* = 240.9, 33.4 Hz), 85.8, 61.3, 44.7 (d, *J* = 30.2 Hz), 14.4.

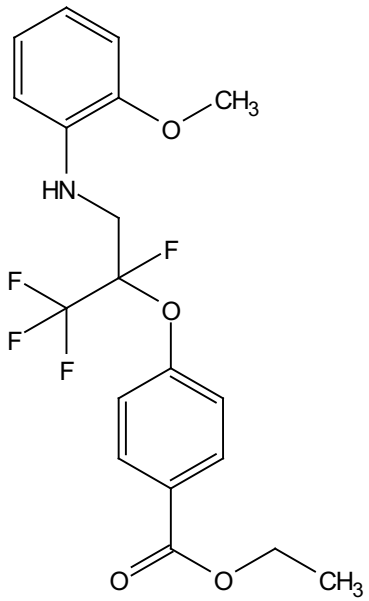


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.72 (td, *J* = 7.5, 1.6 Hz, 1H), 6.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.61 (td, *J* = 7.6, 1.6 Hz, 1H), 6.44 (d, *J* = 7.7 Hz, 1H), 4.39 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.70 (d, *J* = 17.5 Hz, 5H), 1.29 (t, *J* = 7.2 Hz, 3H).



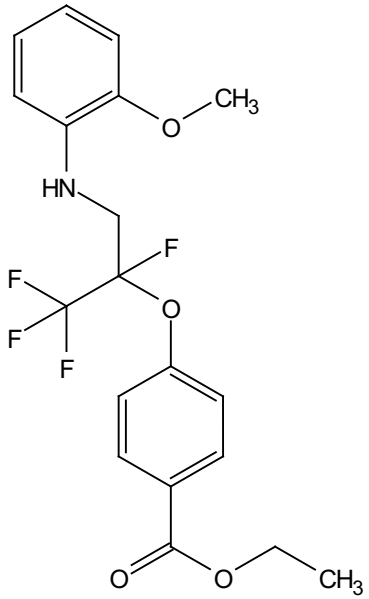
(18)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.9 Hz), -125.2 (q, *J* = 2.9 Hz).



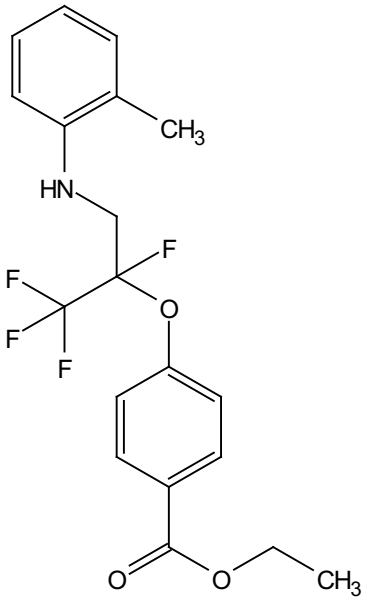
(18)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 155.4, 147.0, 136.6, 131.4, 128.1, 121.9 (d, *J* = 2.6 Hz), 121.2, 120.6 (qd, *J* = 287.9, 37.4 Hz), 118.0, 110.2, 109.9, 109.0 (dq, *J* = 240.9, 33.3 Hz), 61.2, 55.6, 44.7 (d, *J* = 29.1 Hz), 14.4.



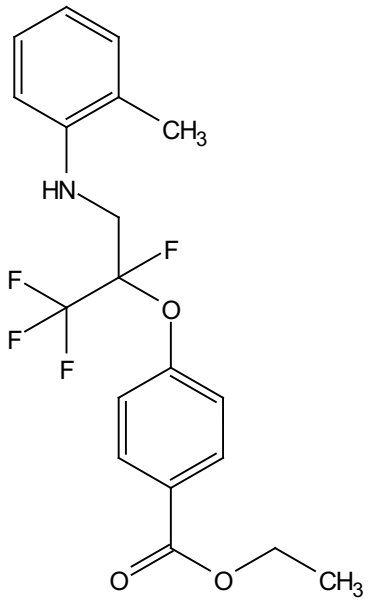
(18)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.02 – 6.93 (m, 2H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 3H), 3.73 (d, *J* = 11.2 Hz, 2H), 3.57 (s, 1H), 2.01 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).



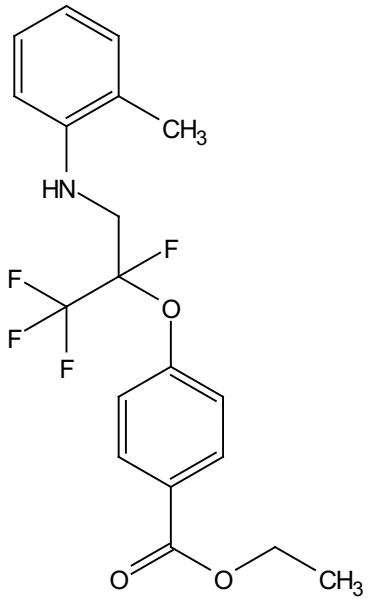
(19)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.8 Hz), -125.0 (q, *J* = 2.8 Hz).



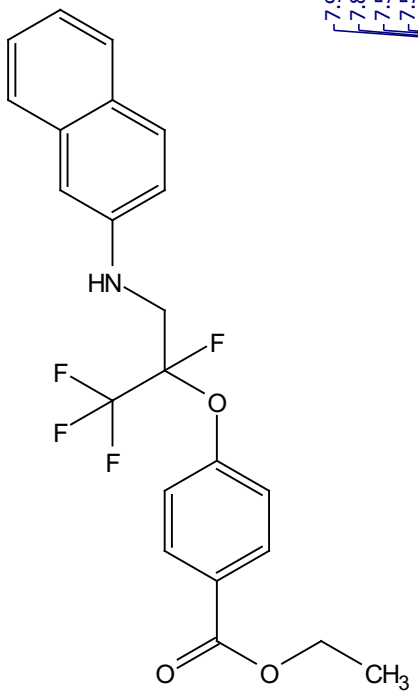
(19)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 155.4, 144.5, 131.5, 130.5, 128.3, 127.2, 122.6, 121.8 (d, *J* = 2.4 Hz), 120.6 (qd, *J* = 287.8, 37.2 Hz), 118.5, 110.1, 108.9 (dq, *J* = 241.0, 33.2 Hz), 61.3, 44.6 (d, *J* = 29.2 Hz), 17.3, 14.4.



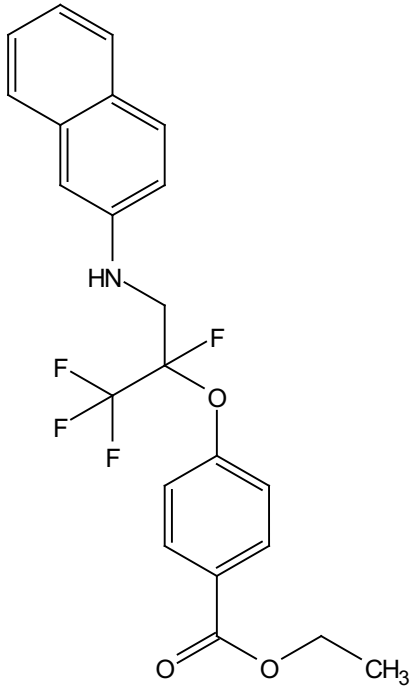
(19)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.05 (m, 3H), 6.72 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.90 (bs, 1H), 3.84 – 3.69 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H).



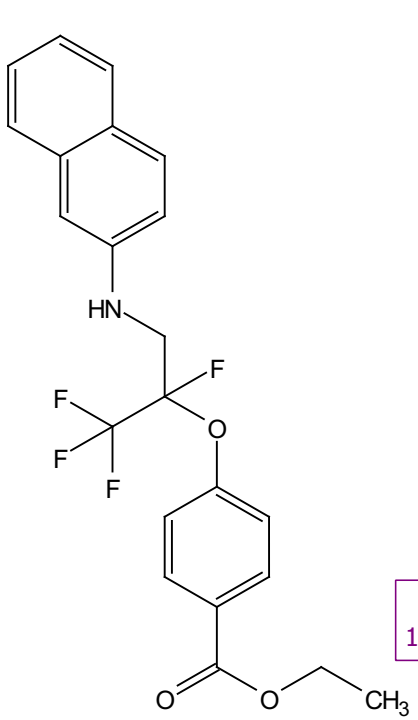
(20)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.8 Hz), -125.2 (q, *J* = 2.7 Hz).



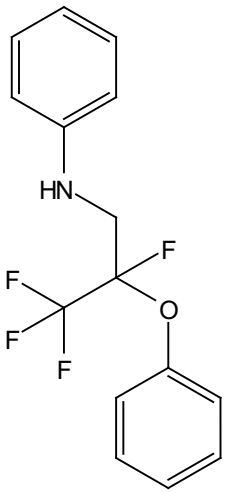
(20)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 155.4, 144.2, 134.9, 131.4, 129.3, 128.2, 128.2, 127.7, 126.6, 126.2, 122.8, 121.8 (d, *J* = 2.5 Hz), 120.6 (qd, *J* = 287.6, 37.5 Hz), 117.6, 108.9 (dq, *J* = 241.1, 33.3 Hz), 105.6, 61.2, 44.9 (d, *J* = 29.0 Hz), 14.4.



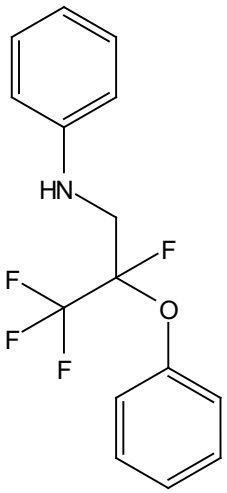
(20)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.8 Hz, 2H), 7.15 – 7.02 (m, 5H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 2H), 3.81 – 3.56 (m, 3H).



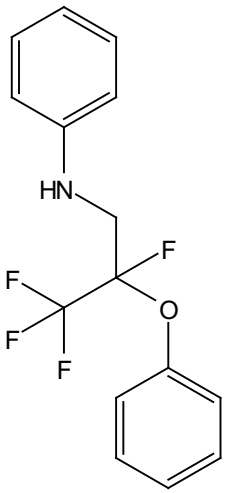
(21)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 2.8 Hz), -124.7 (q, *J* = 2.8 Hz).



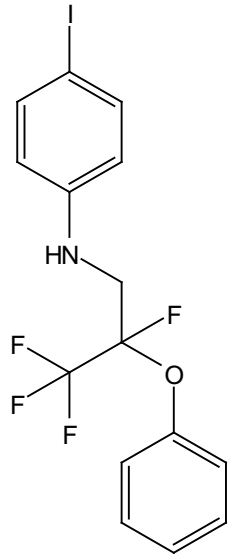
(21)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.7, 146.8, 129.8, 129.4, 126.1, 122.3 (d, *J* = 2.1 Hz), 120.7 (qd, *J* = 287.9, 37.7 Hz), 118.8, 113.3, 108.7 (dq, *J* = 239.1, 32.9 Hz), 44.9 (d, *J* = 29.6 Hz).



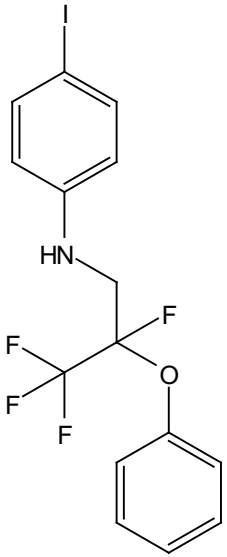
(21)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.8 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.26 (d, *J* = 8.8 Hz, 2H), 3.78 – 3.54 (m, 3H).



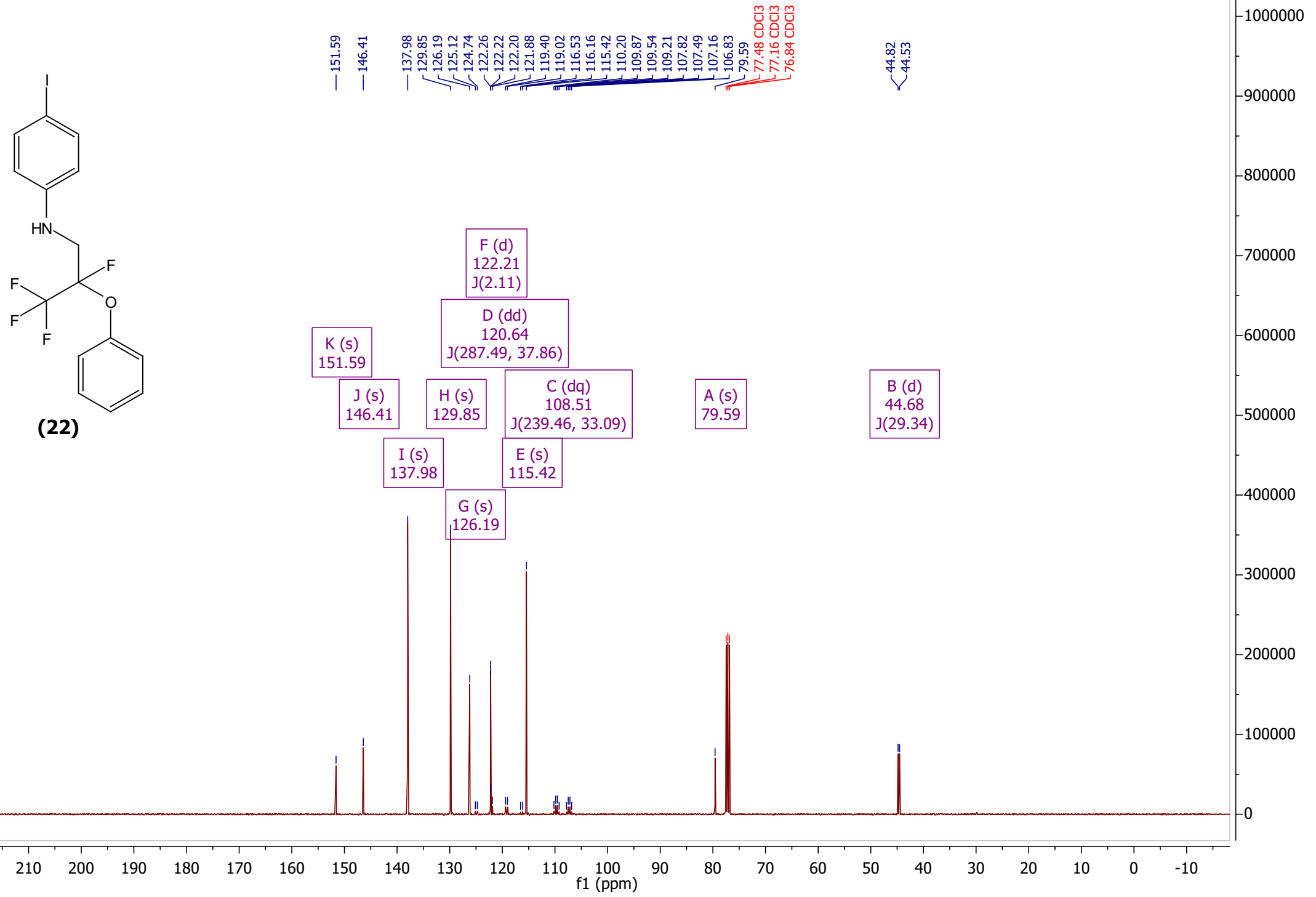
(22)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 3.1 Hz), -124.8 (q, *J* = 2.8 Hz).

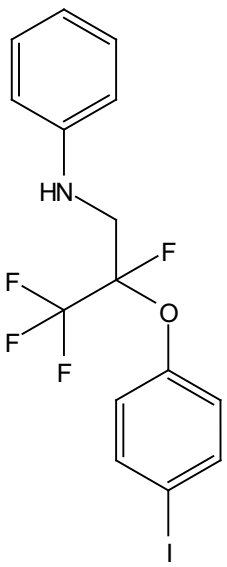


(22)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.6, 146.4, 138.0, 129.8, 126.2, 122.2 (d, *J* = 2.1 Hz), 120.6 (dd, *J* = 287.5, 37.9 Hz), 115.4, 108.5 (dq, *J* = 239.5, 33.1 Hz), 79.6, 44.7 (d, *J* = 29.3 Hz).

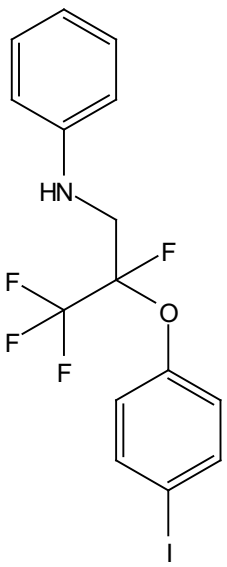


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 2H), 3.88 – 3.71 (m, 3H).



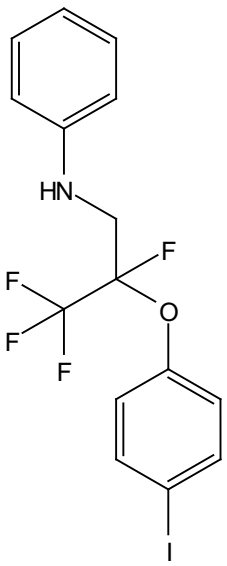
(23)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.0 (d, *J* = 3.0 Hz), -125.7 (q, *J* = 2.9 Hz).



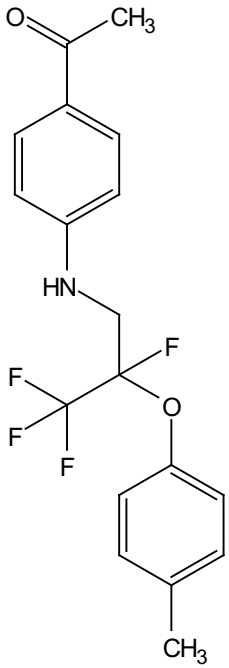
(23)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.6, 146.6, 138.8, 129.4, 124.4 (d, *J* = 2.1 Hz), 120.6 (qd, *J* = 288.1, 37.8 Hz), 118.9, 113.3, 108.7 (dq, *J* = 239.9, 33.1 Hz), 90.1, 45.0 (d, *J* = 28.9 Hz).



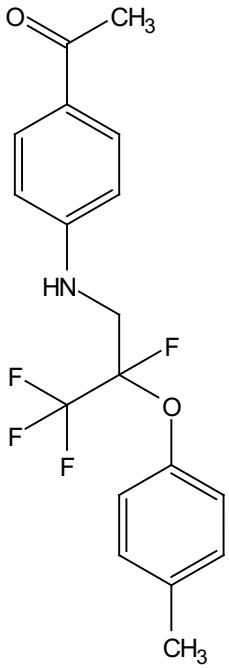
(23)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.39 (s, 1H), 3.90 – 3.72 (m, 2H), 2.49 (s, 3H), 2.32 (s, 3H).



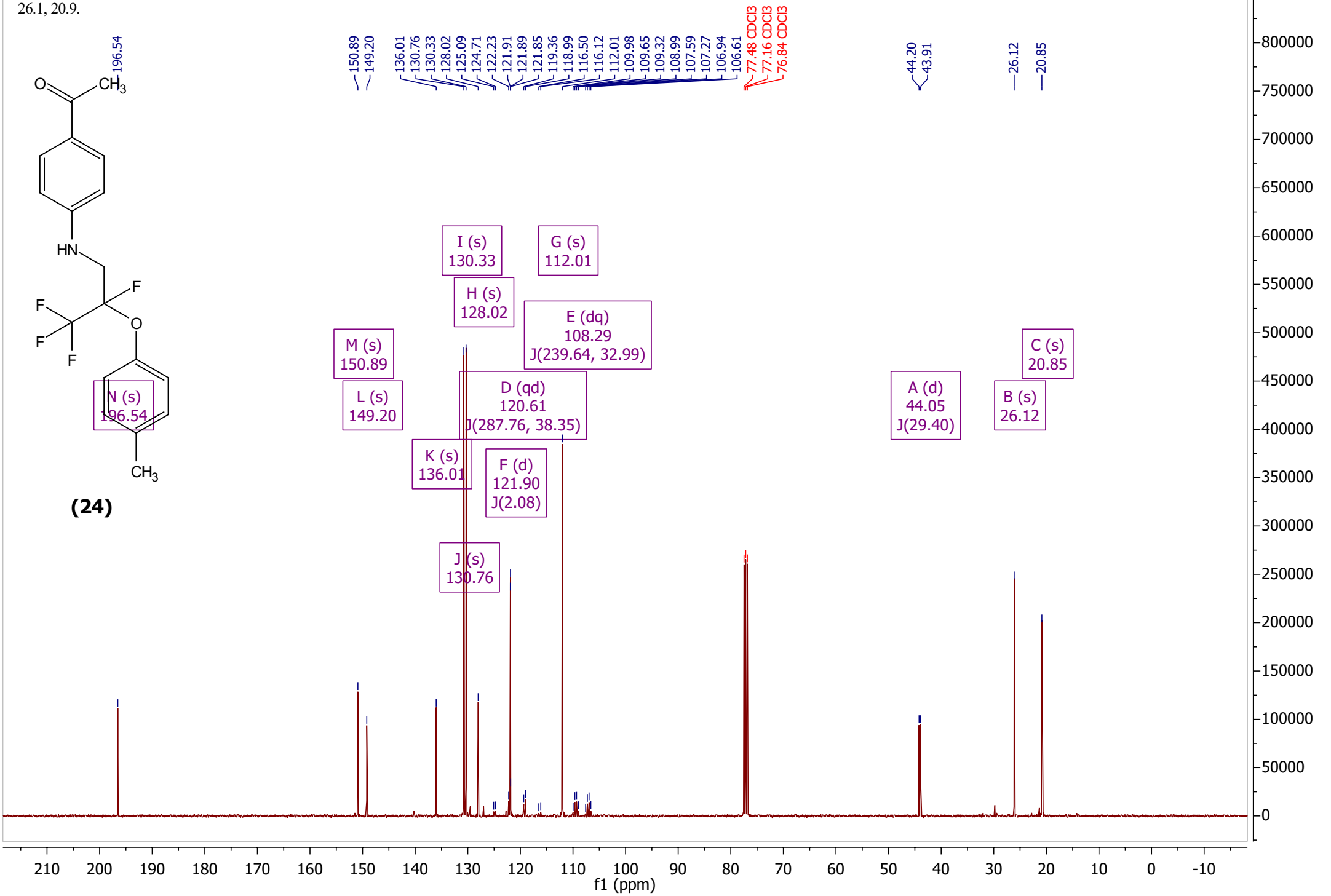
(24)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 2.7 Hz), -125.0 (q, *J* = 3.0 Hz).



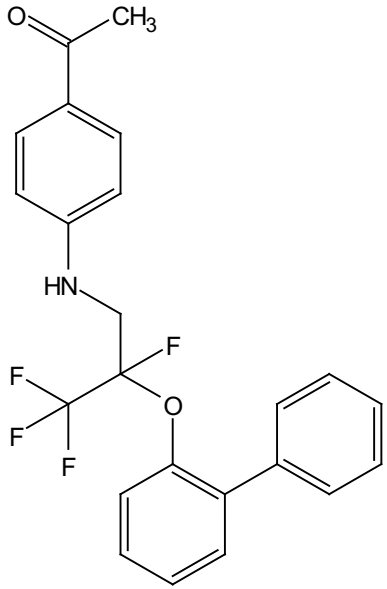
(24)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.5, 150.9, 149.2, 136.0, 130.8, 130.3, 128.0, 121.9 (d, *J* = 2.1 Hz), 120.6 (qd, *J* = 287.8, 38.3 Hz), 112.0, 108.3 (dq, *J* = 239.6, 33.0 Hz), 44.1 (d, *J* = 29.4 Hz), 26.1, 20.9.



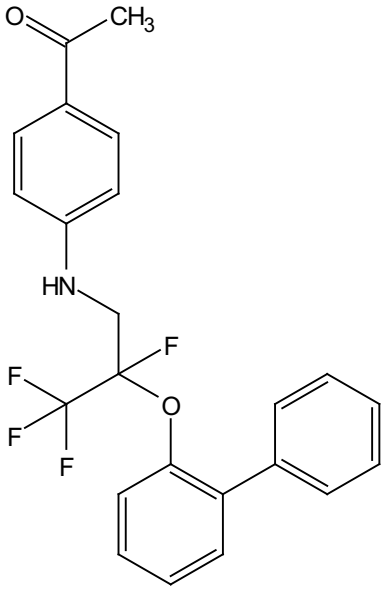
(24)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.55 – 7.30 (m, 9H), 6.17 (d, *J* = 8.8 Hz, 2H), 3.62 – 3.49 (m, 2H), 3.46 – 3.33 (m, 1H), 2.47 (s, 3H).



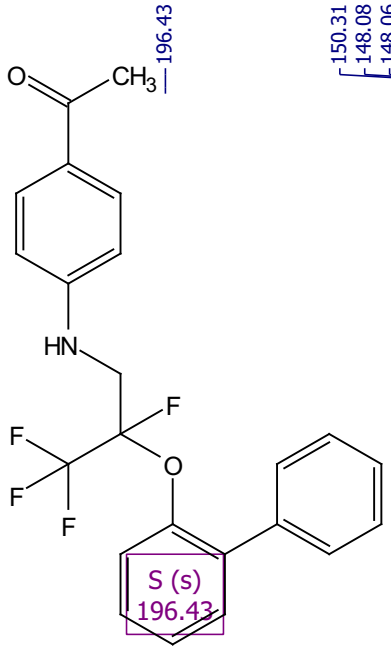
(25)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 (d, *J* = 2.9 Hz), -121.1 (q, *J* = 3.1 Hz).



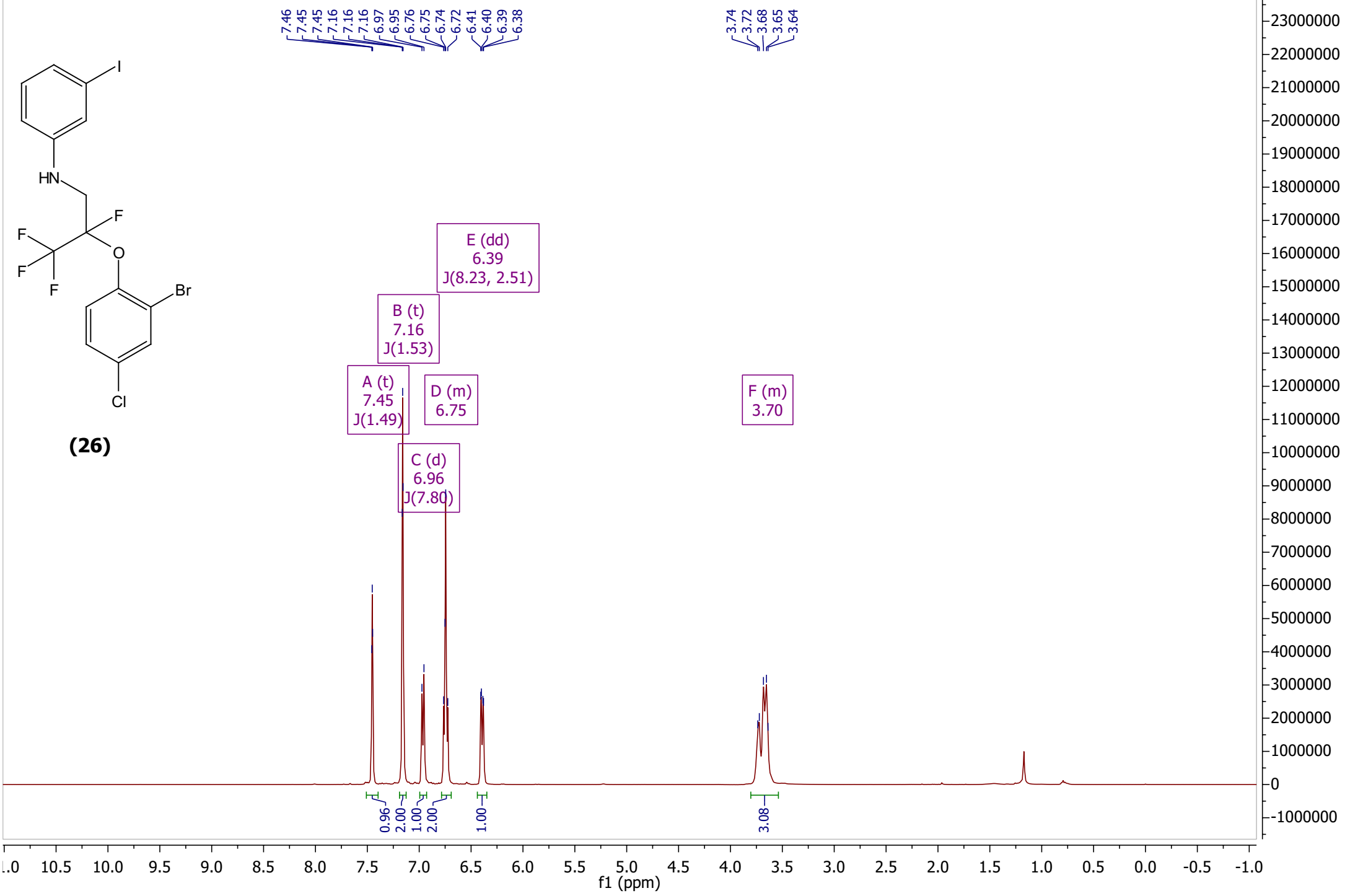
(25)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.4, 150.3, 148.1 (d, *J* = 1.7 Hz), 137.0, 135.2 (d, *J* = 1.8 Hz), 131.5, 130.6, 129.8, 129.0, 128.6, 128.1, 127.8, 126.8, 123.3 (d, *J* = 2.4 Hz), 120.3 (qd, *J* = 287.2, 35.6 Hz), 111.7, 108.6 (dq, *J* = 239.9, 33.6 Hz), 42.9 (d, *J* = 33.8 Hz), 26.1.

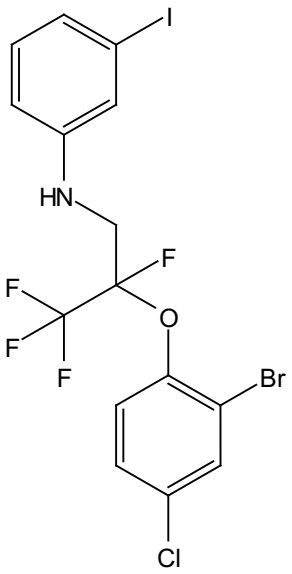


(25)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (t, *J* = 1.5 Hz, 1H), 7.16 (t, *J* = 1.5 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.80 – 6.69 (m, 2H), 6.39 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.77 – 3.63 (m, 3H).

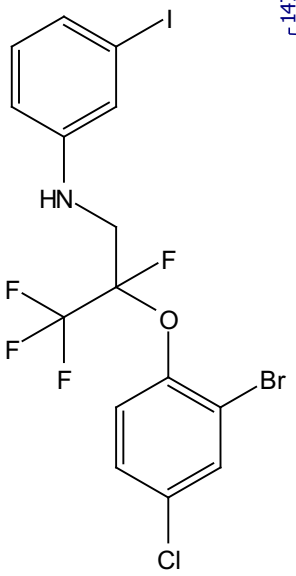


^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.6 (d, *J* = 3.3 Hz), -123.0 (q, *J* = 3.0 Hz).



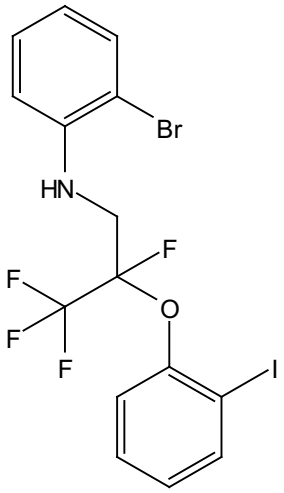
(26)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.8 (d, *J* = 1.9 Hz), 147.4, 133.5, 132.0, 130.8, 128.9, 127.8, 123.7 (d, *J* = 3.2 Hz), 121.6, 120.3 (qd, *J* = 287.3, 36.6 Hz), 116.8 (d, *J* = 2.9 Hz), 112.5, 109.2 (dq, *J* = 242.2, 33.9 Hz), 95.2, 44.0 (d, *J* = 29.1 Hz).



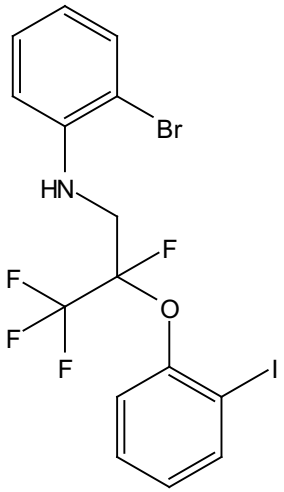
(26)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.14 (td, *J* = 8.0, 1.6 Hz, 1H), 6.99 – 6.90 (m, 1H), 6.62 (td, *J* = 7.6, 1.5 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 4.51 (t, *J* = 6.5 Hz, 1H), 4.05 – 3.80 (m, 2H).



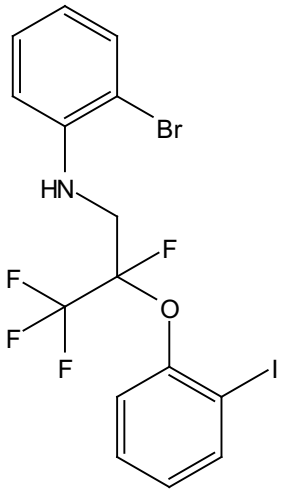
(27)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.6 (d, *J* = 2.8 Hz), -122.3 (q, *J* = 2.7 Hz).



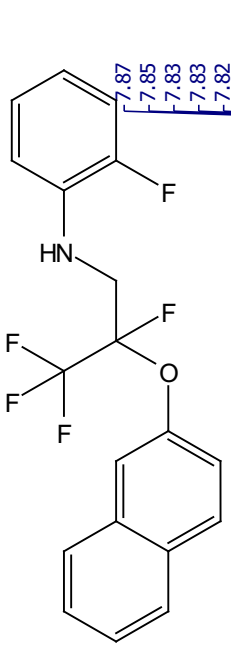
(27)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.9 (d, *J* = 2.3 Hz), 143.4, 140.3, 132.7, 129.8, 128.5, 127.4, 122.1 (d, *J* = 3.3 Hz), 120.4 (qd, *J* = 287.6, 36.3 Hz), 119.1, 111.3 (d, *J* = 1.6 Hz), 110.2, 109.0 (dq, *J* = 242.1, 33.6 Hz), 90.3 (d, *J* = 3.1 Hz), 44.3 (d, *J* = 28.5 Hz).



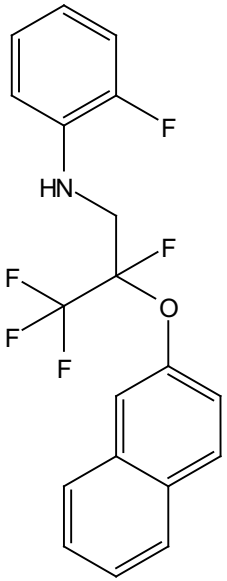
(27)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (t, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.68 (s, 1H), 7.52 (pd, *J* = 7.0, 1.6 Hz, 2H), 7.37 (d, *J* = 9.4 Hz, 1H), 7.05 – 6.92 (m, 2H), 6.73 – 6.61 (m, 2H), 4.19 (s, 1H), 3.96 – 3.78 (m, 2H).



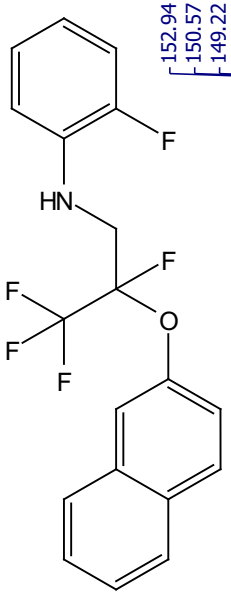
(28)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 2.9 Hz), -124.3 (q, *J* = 2.9 Hz), -136.4.



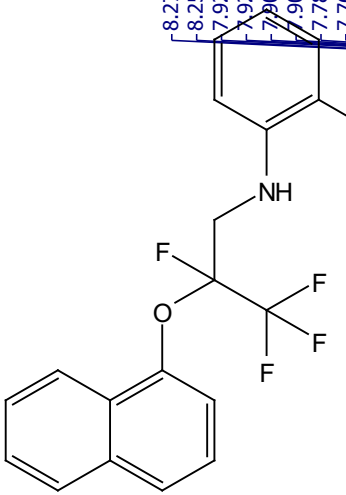
(28)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.8 (d, *J* = 238.7 Hz), 149.2, 135.2 (d, *J* = 11.2 Hz), 133.9, 131.6, 130.0, 127.9, 127.8, 127.0, 126.1, 124.6 (d, *J* = 3.6 Hz), 121.6 (d, *J* = 2.3 Hz), 120.8 (qd, *J* = 287.9, 37.6 Hz), 119.2 (d, *J* = 2.3 Hz), 118.2 (d, *J* = 7.0 Hz), 114.9 (d, *J* = 18.6 Hz), 112.6 (d, *J* = 2.9 Hz), 108.9 (dq, *J* = 239.3, 33.1 Hz), 44.5 (d, *J* = 30.1 Hz).



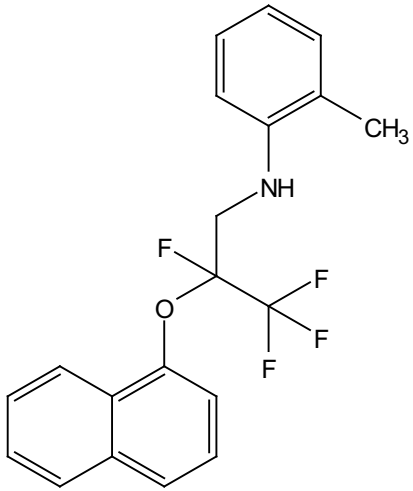
(28)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.61 (qt, *J* = 6.8, 3.5 Hz, 2H), 7.52 – 7.41 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 4.03 – 3.84 (m, 2H), 3.46 (s, 1H), 1.90 (s, 3H).



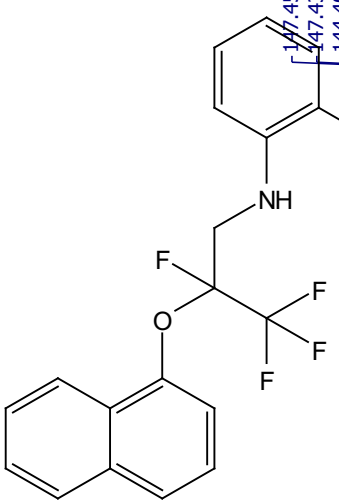
(29)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.1 (d, *J* = 2.4 Hz), -120.5 (q, *J* = 3.0 Hz).



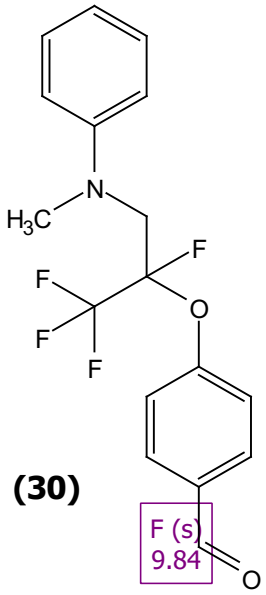
(29)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4 (d, *J* = 2.0 Hz), 144.4, 134.9, 130.4, 128.1, 127.5 (d, *J* = 2.1 Hz), 127.1, 127.1, 127.0, 126.0, 125.6, 122.6, 121.5, 121.0 (qd, *J* = 287.1, 36.3 Hz), 118.3, 117.1 (d, *J* = 2.7 Hz), 109.9, 109.5 (dq, *J* = 239.1, 33.4 Hz), 43.6 (d, *J* = 31.8 Hz), 17.1.



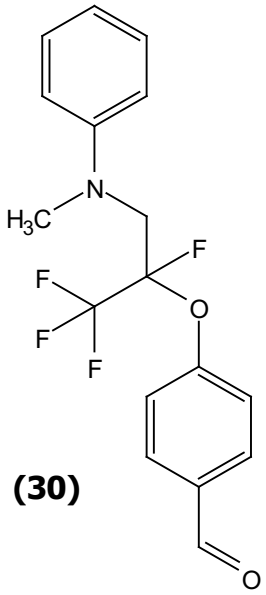
(29)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.20 – 7.09 (m, 4H), 6.76 – 6.64 (m, 3H), 3.94 – 3.81 (m, 2H), 2.94 (s, 3H).



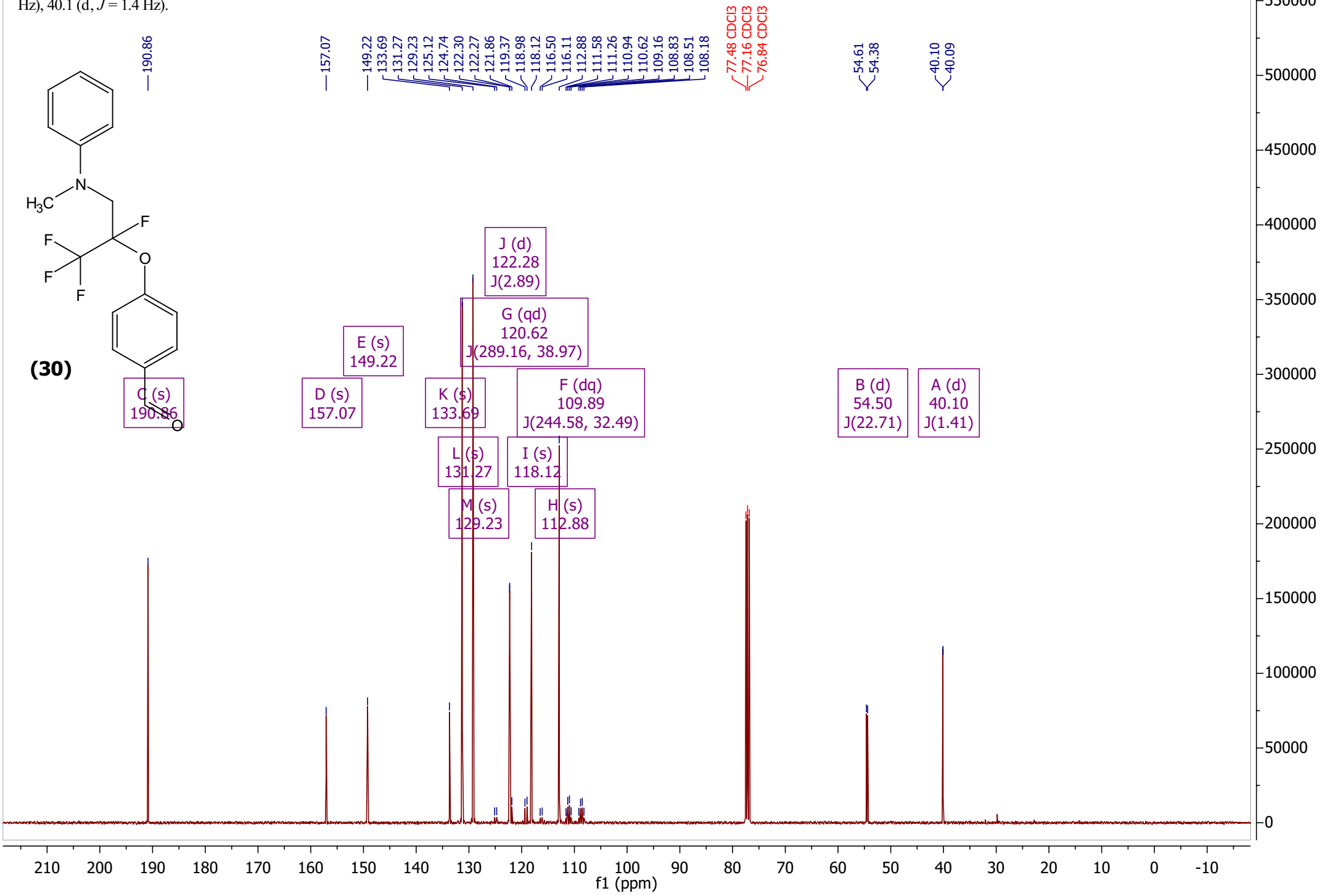
(30)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.9 (d, *J* = 2.7 Hz), -126.9 (q, *J* = 2.9 Hz).

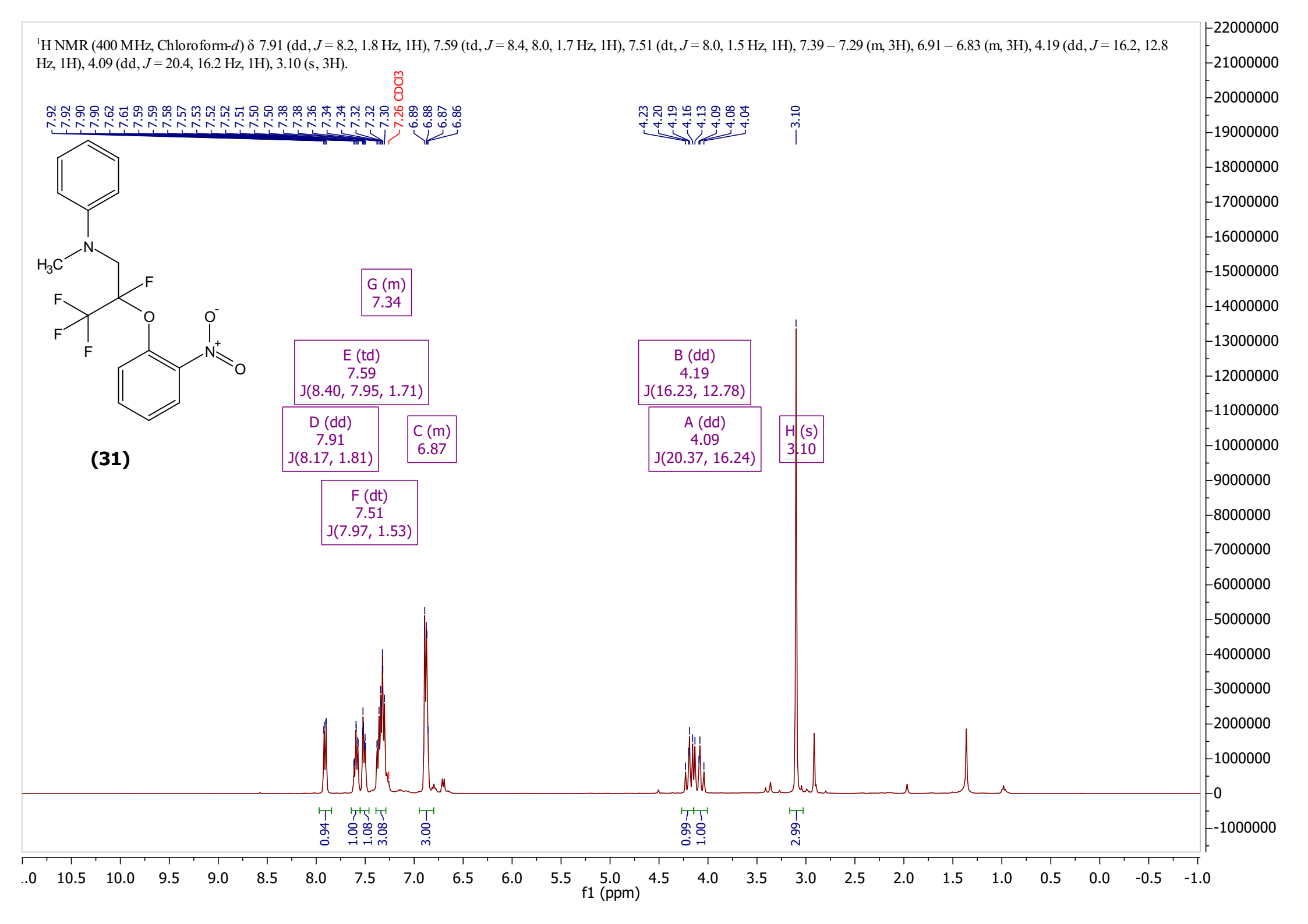


(30)

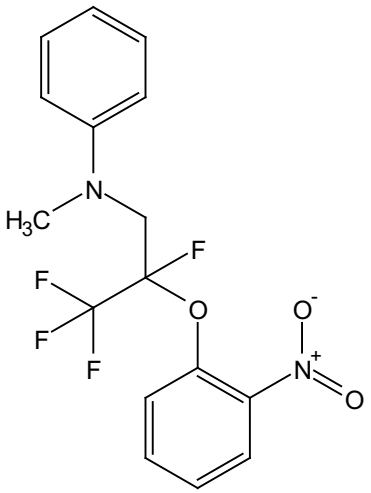
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.9, 157.1, 149.2, 133.7, 131.3, 129.2, 122.3 (d, *J* = 2.9 Hz), 120.6 (qd, *J* = 289.2, 39.0 Hz), 118.1, 112.9, 109.9 (dq, *J* = 244.6, 32.5 Hz), 54.5 (d, *J* = 22.7 Hz), 40.1 (d, *J* = 1.4 Hz).



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.59 (td, *J* = 8.4, 8.0, 1.7 Hz, 1H), 7.51 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.39 – 7.29 (m, 3H), 6.91 – 6.83 (m, 3H), 4.19 (dd, *J* = 16.2, 12.8 Hz, 1H), 4.09 (dd, *J* = 20.4, 16.2 Hz, 1H), 3.10 (s, 3H).

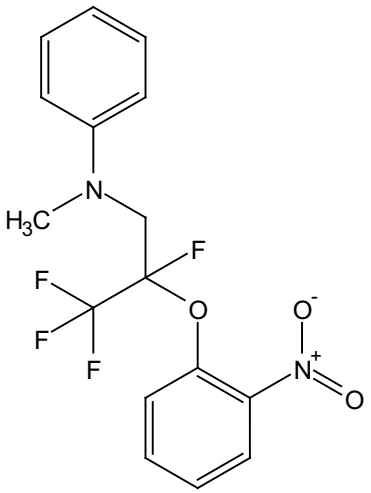


^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.6 Hz), -124.8 (q, *J* = 2.8 Hz).



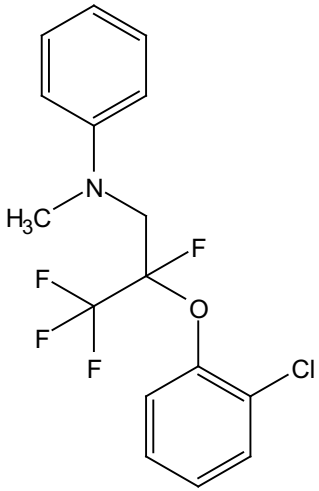
(31)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.1, 145.0, 143.0, 133.8, 129.2, 125.9, 125.5, 124.2 (d, *J* = 3.9 Hz), 120.3 (qd, *J* = 288.9, 38.5 Hz), 118.1, 112.9 (d, *J* = 1.4 Hz), 110.6 (dq, *J* = 246.5, 33.1 Hz), 54.1 (d, *J* = 21.8 Hz), 40.2 (d, *J* = 1.5 Hz).



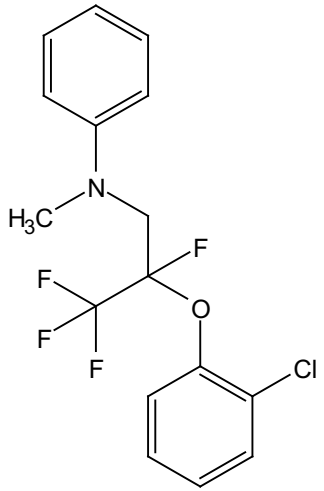
(31)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.24 (dt, *J* = 8.2, 2.0 Hz, 1H), 7.17 – 7.09 (m, 3H), 7.03 (td, *J* = 7.7, 1.6 Hz, 1H), 6.74 – 6.64 (m, 3H), 3.96 (t, *J* = 15.8 Hz, 1H), 3.80 (t, *J* = 16.7 Hz, 1H), 2.93 (s, 3H).



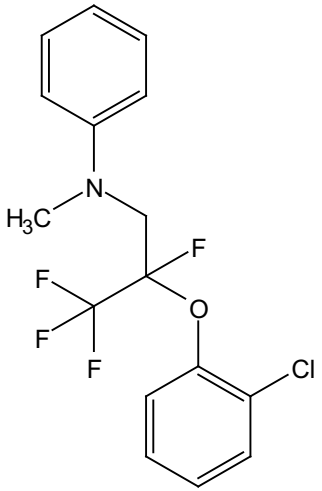
(32)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.6 Hz), -124.6 (q, *J* = 2.7 Hz).



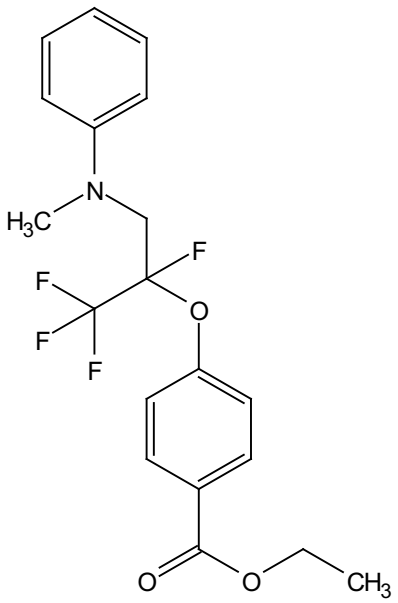
(32)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 148.3, 130.8, 129.2, 127.8, 127.2 (d, *J* = 2.2 Hz), 126.6, 123.8 (d, *J* = 3.2 Hz), 120.7 (qd, *J* = 288.8, 39.1 Hz), 117.9, 112.8 (d, *J* = 1.6 Hz), 110.1 (dq, *J* = 244.6, 33.0 Hz), 54.1 (d, *J* = 22.9 Hz), 40.1.



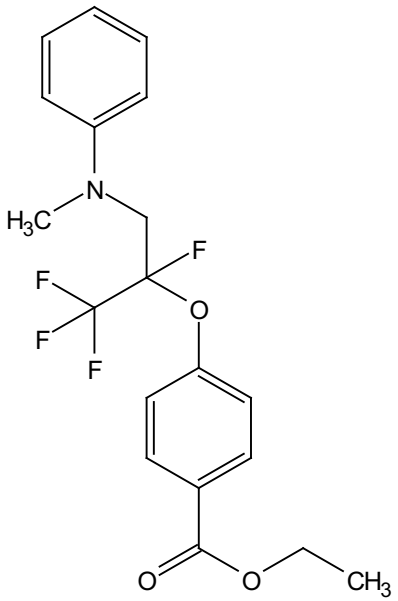
(32)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.73 – 6.67 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.96 – 3.75 (m, 2H), 2.93 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).



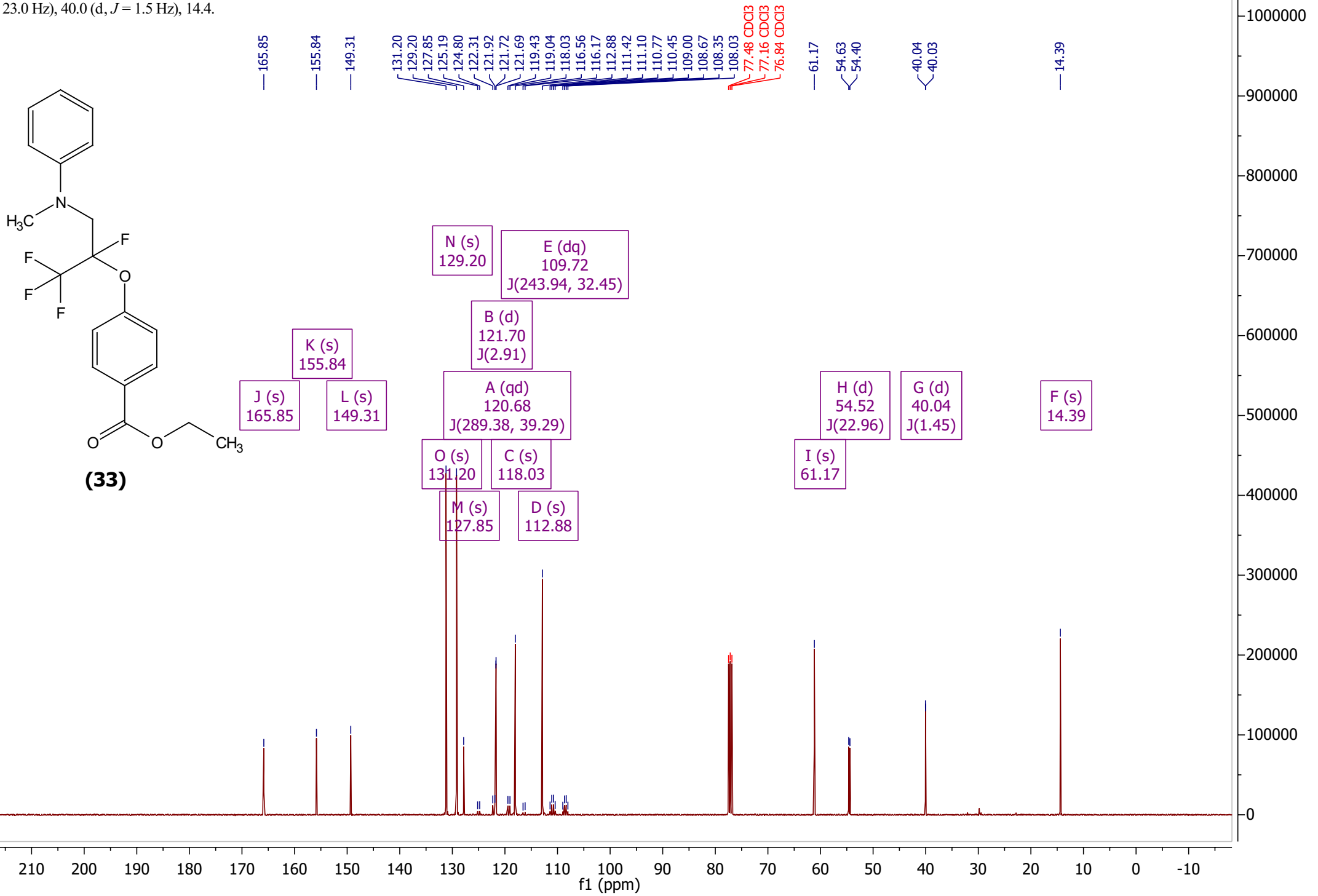
(33)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.8 (d, *J* = 2.6 Hz), -126.7 (q, *J* = 2.6 Hz).

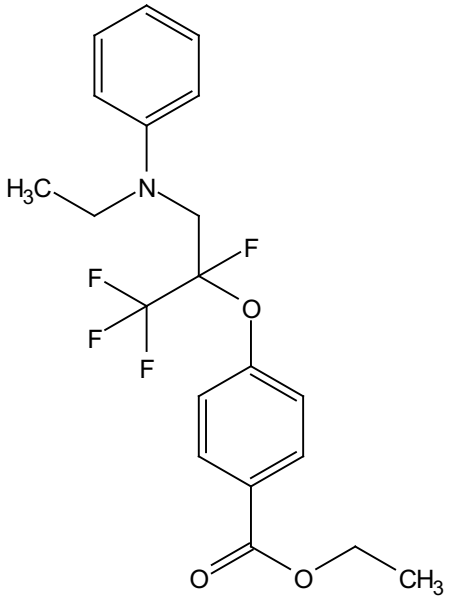


(33)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 155.8, 149.3, 131.2, 129.2, 127.8, 121.7 (d, *J* = 2.9 Hz), 120.7 (qd, *J* = 289.4, 39.3 Hz), 118.0, 112.9, 109.7 (dq, *J* = 243.9, 32.4 Hz), 61.2, 54.5 (d, *J* = 23.0 Hz), 40.0 (d, *J* = 1.5 Hz), 14.4.

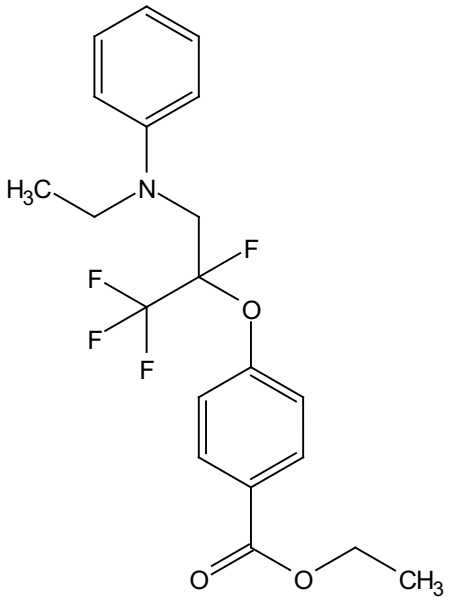


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.82 (m, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.93 – 3.76 (m, 2H), 3.39 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H).



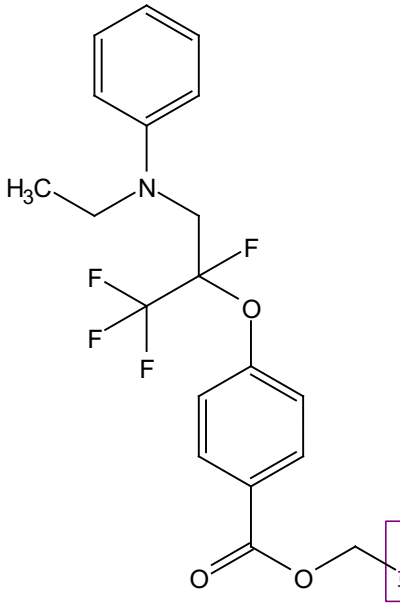
(34)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.6 (d, *J* = 2.6 Hz), -127.0 (q, *J* = 2.6 Hz).



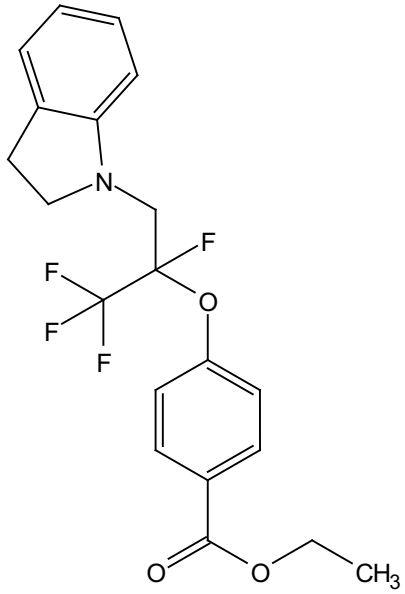
(34)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 156.0, 147.9, 131.2, 129.3, 127.8, 121.7 (d, *J* = 2.7 Hz), 120.8 (qd, *J* = 289.9, 39.8 Hz), 117.8, 113.4 (d, *J* = 1.4 Hz), 109.7 (dq, *J* = 243.7, 32.3 Hz), 61.2, 52.5 (d, *J* = 22.5 Hz), 46.2, 14.4, 11.3.



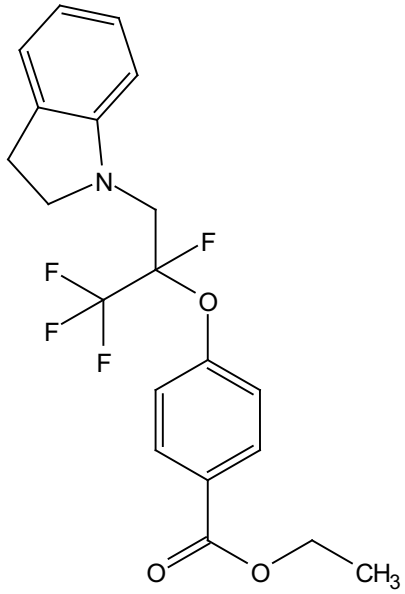
(34)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.97 (t, *J* = 8.1 Hz, 2H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.76 – 3.50 (m, 2H), 3.46 – 3.31 (m, 2H), 2.89 (t, *J* = 8.5 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).



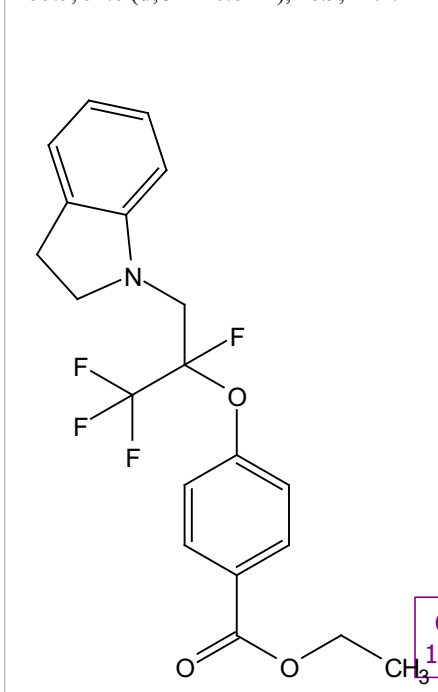
(35)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.9 (d, *J* = 2.6 Hz), -124.7 (q, *J* = 3.0 Hz).



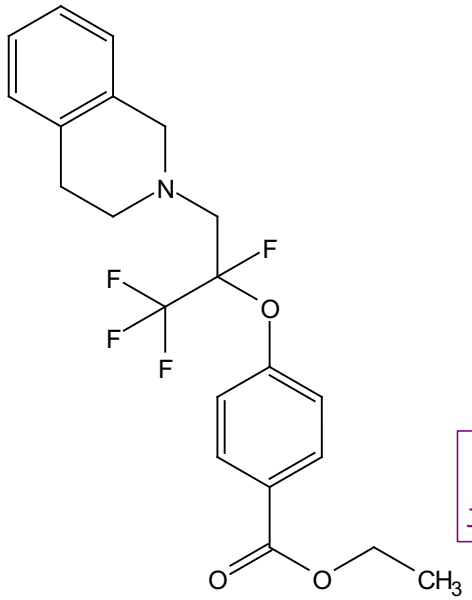
(35)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 155.9, 151.6, 131.3, 129.1, 127.9, 127.5, 124.7, 121.7 (d, *J* = 2.7 Hz), 120.6 (qd, *J* = 288.7, 38.7 Hz), 118.7, 109.4 (dq, *J* = 241.8, 32.4 Hz), 106.8, 61.2, 55.5, 52.6 (d, *J* = 26.8 Hz), 28.9, 14.4.



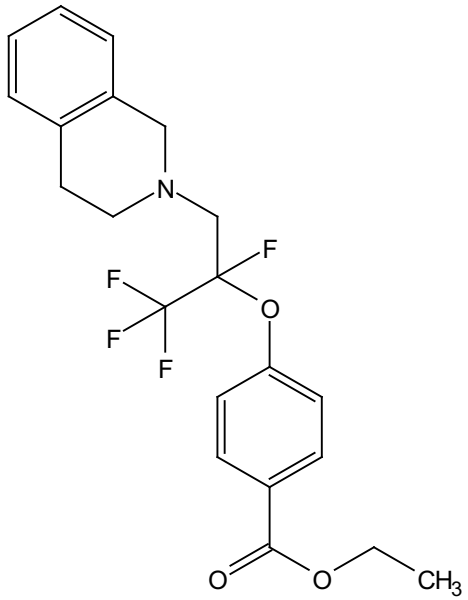
(35)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.08 – 6.93 (m, 2H), 6.87 – 6.82 (m, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 3.07 (p, *J* = 14.7 Hz, 2H), 2.81 – 2.66 (m, 4H), 1.30 (t, *J* = 7.2 Hz, 3H).



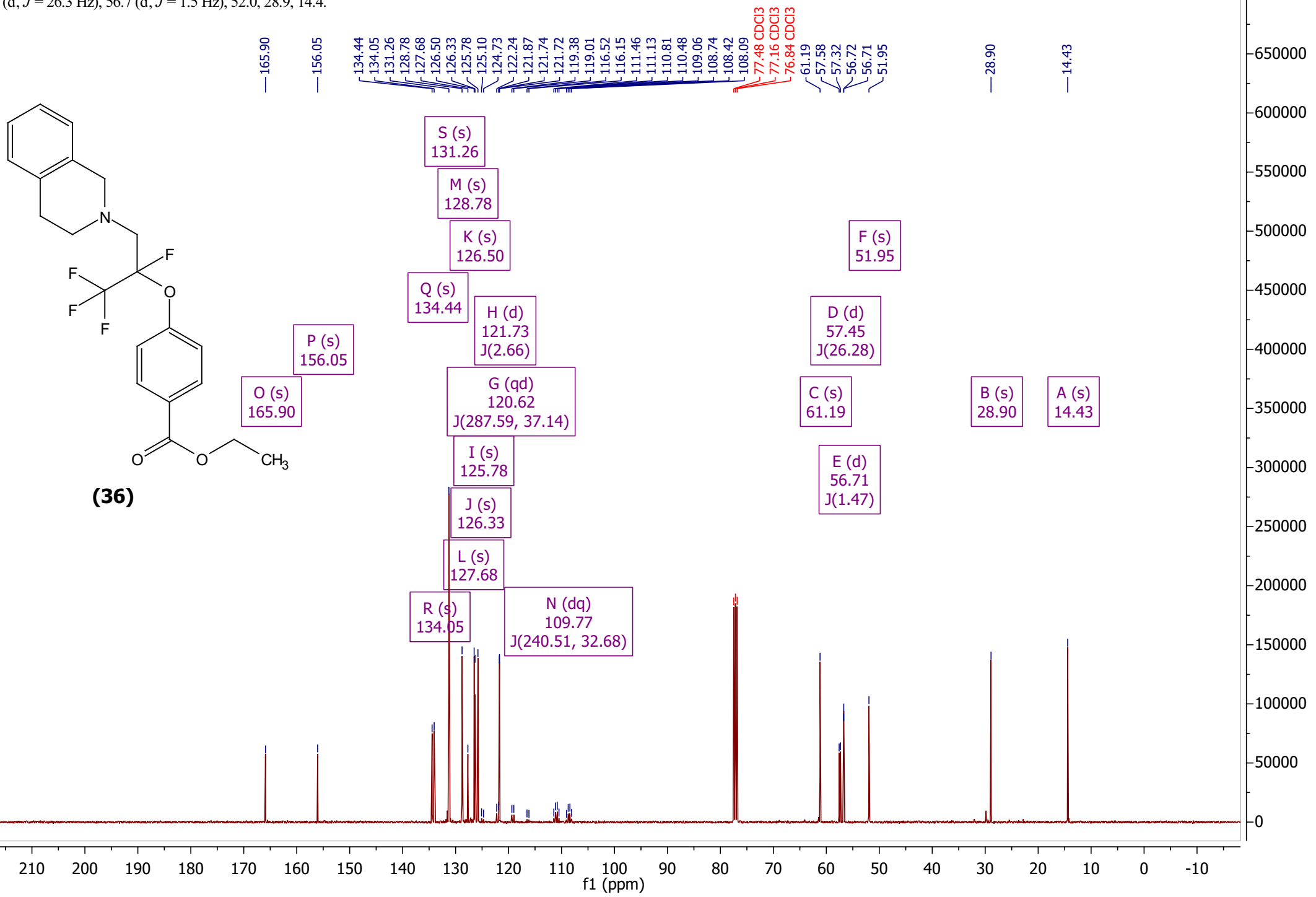
(36)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.4 (d, *J* = 2.6 Hz), -122.5 (q, *J* = 2.1 Hz).

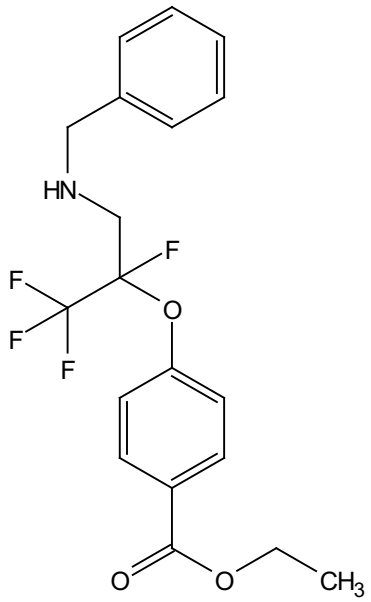


(36)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 156.1, 134.4, 134.0, 131.3, 128.8, 127.7, 126.5, 126.3, 125.8, 121.7 (d, *J* = 2.7 Hz), 120.6 (qd, *J* = 287.6, 37.1 Hz), 109.8 (dq, *J* = 240.5, 32.7 Hz), 61.2, 57.4 (d, *J* = 26.3 Hz), 56.7 (d, *J* = 1.5 Hz), 52.0, 28.9, 14.4.

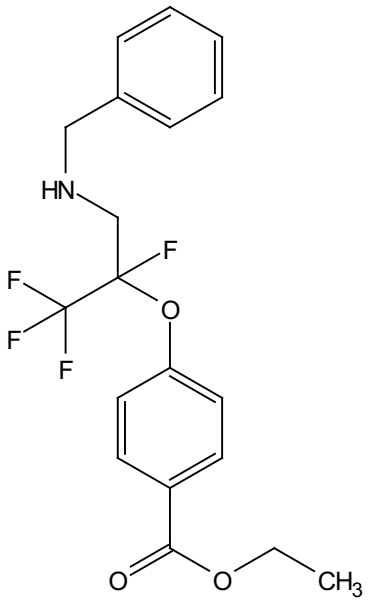


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.23 – 7.08 (m, 7H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.62 (m, 2H), 3.18 – 3.03 (m, 2H), 1.54 (bs, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).



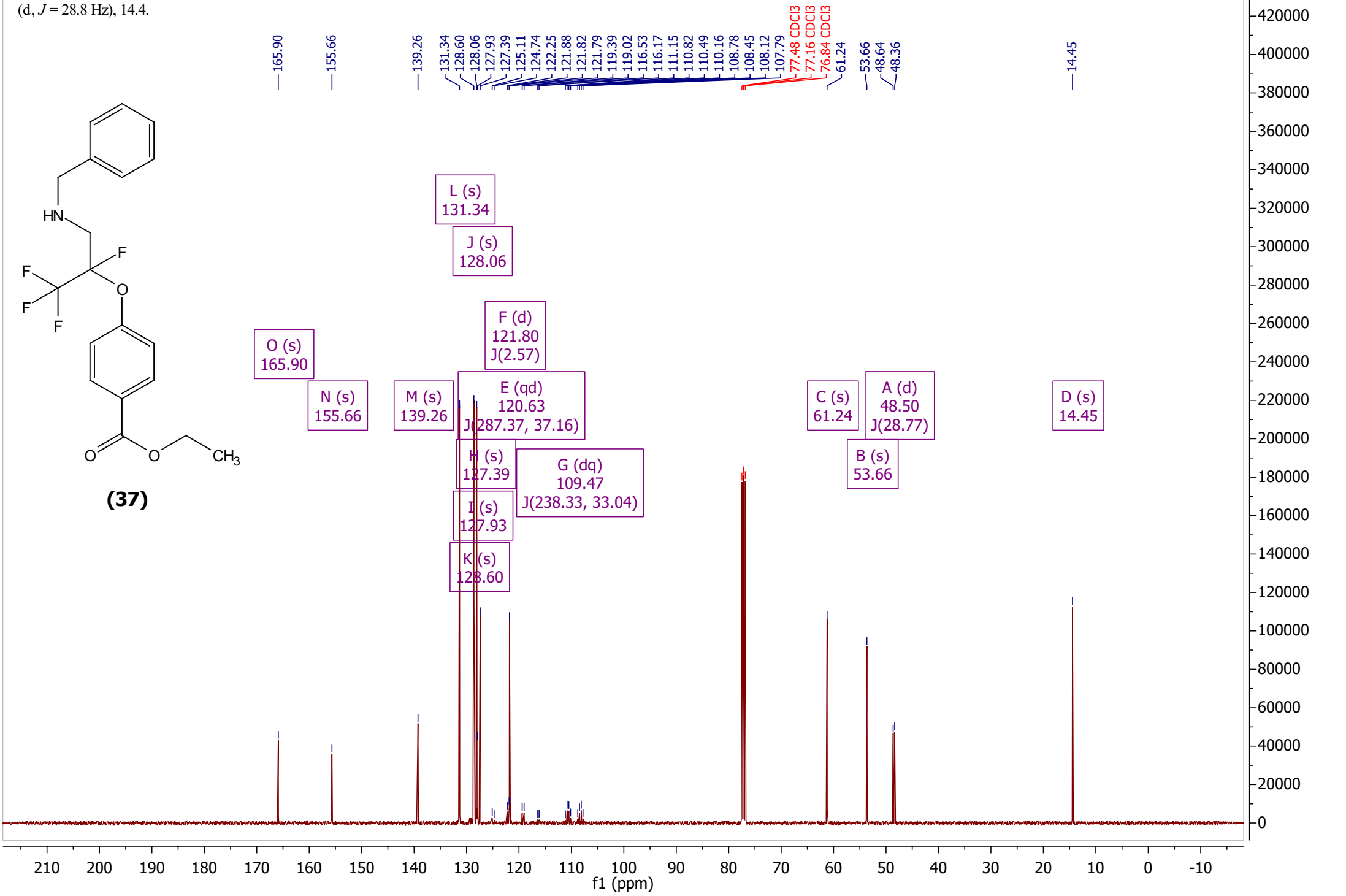
(37)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.8 Hz), -122.9 (q, *J* = 3.0 Hz).

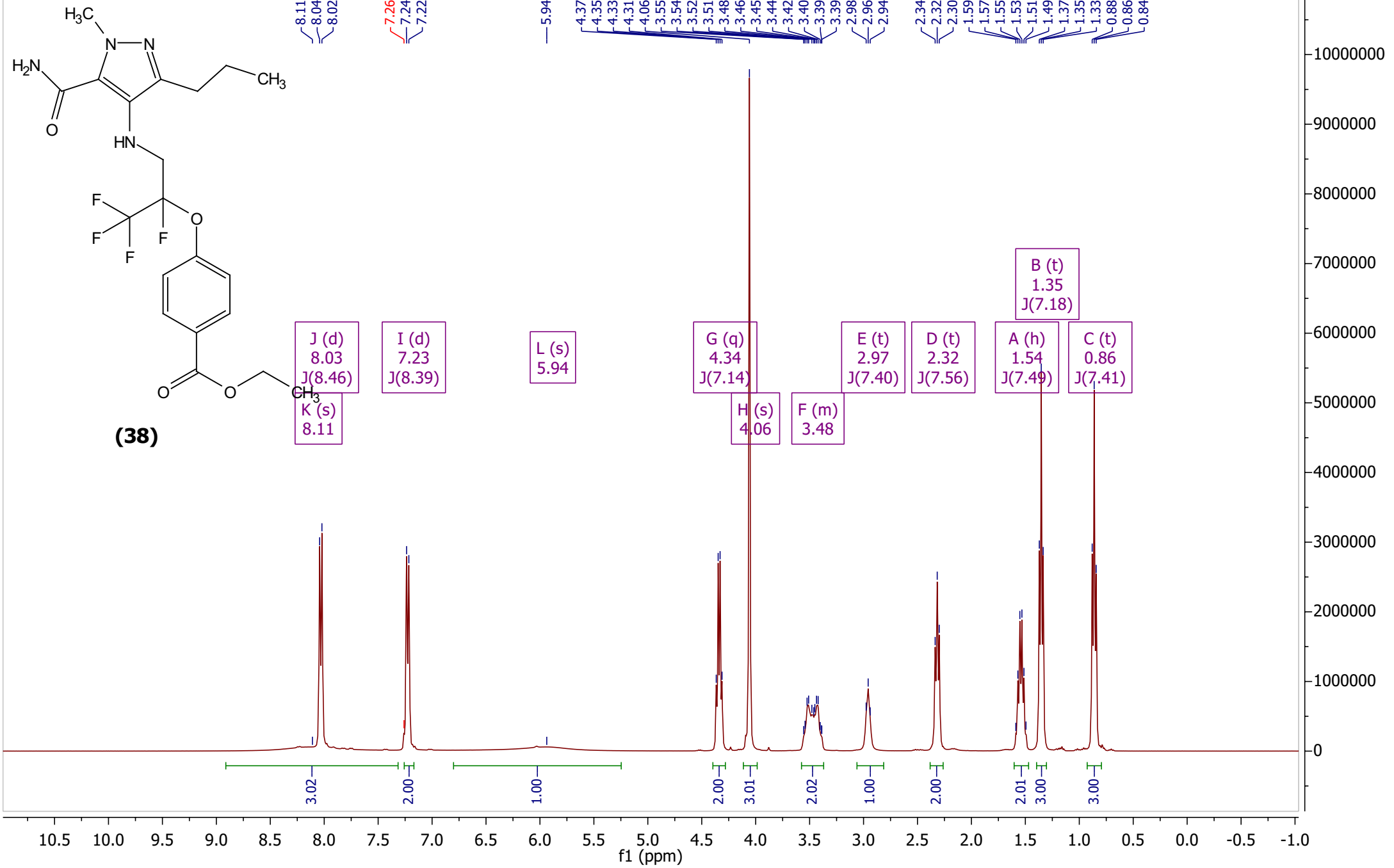


(37)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 155.7, 139.3, 131.3, 128.6, 128.1, 127.9, 127.4, 121.8 (d, *J* = 2.6 Hz), 120.6 (qd, *J* = 287.4, 37.2 Hz), 109.5 (dq, *J* = 238.3, 33.0 Hz), 61.2, 53.7, 48.5 (d, *J* = 28.8 Hz), 14.4.

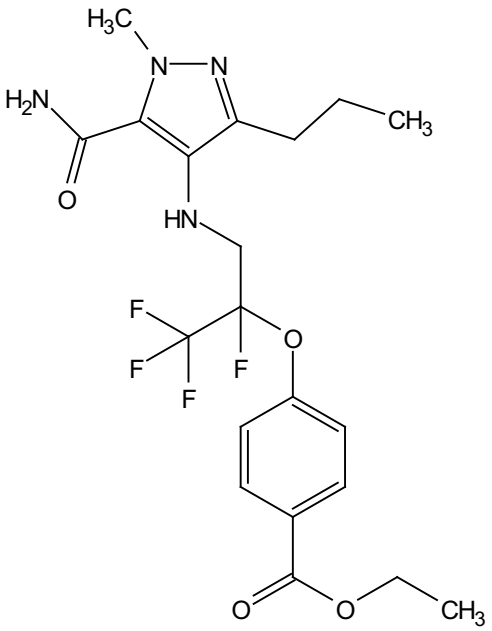


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (bs, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.94 (bs, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 3H), 3.62 – 3.34 (m, 2H), 2.97 (t, *J* = 7.4 Hz, 1H), 2.32 (t, *J* = 7.6 Hz, 2H), 1.54 (h, *J* = 7.5 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).



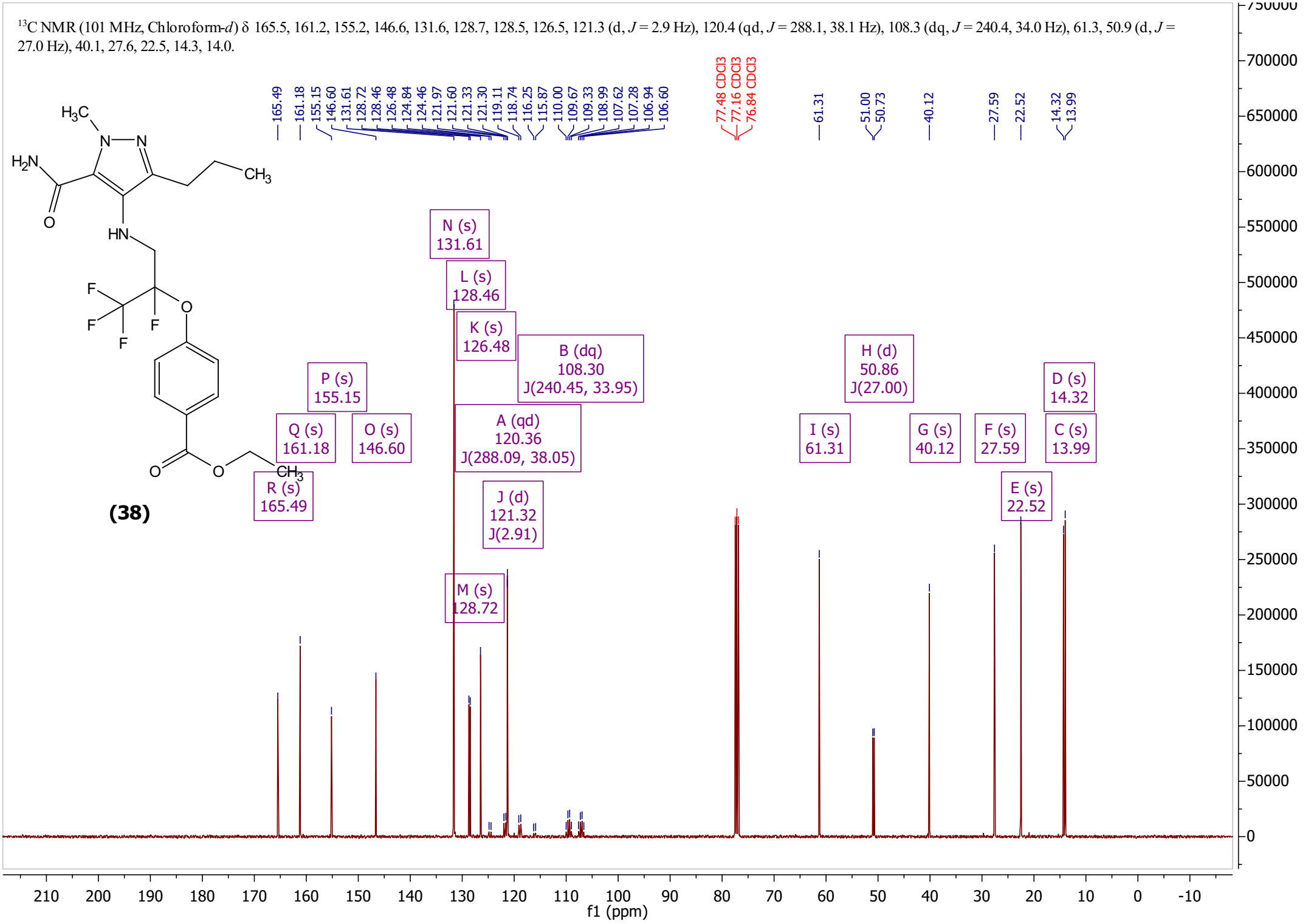
(38)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.8 (d, *J* = 1.7 Hz), -125.5.

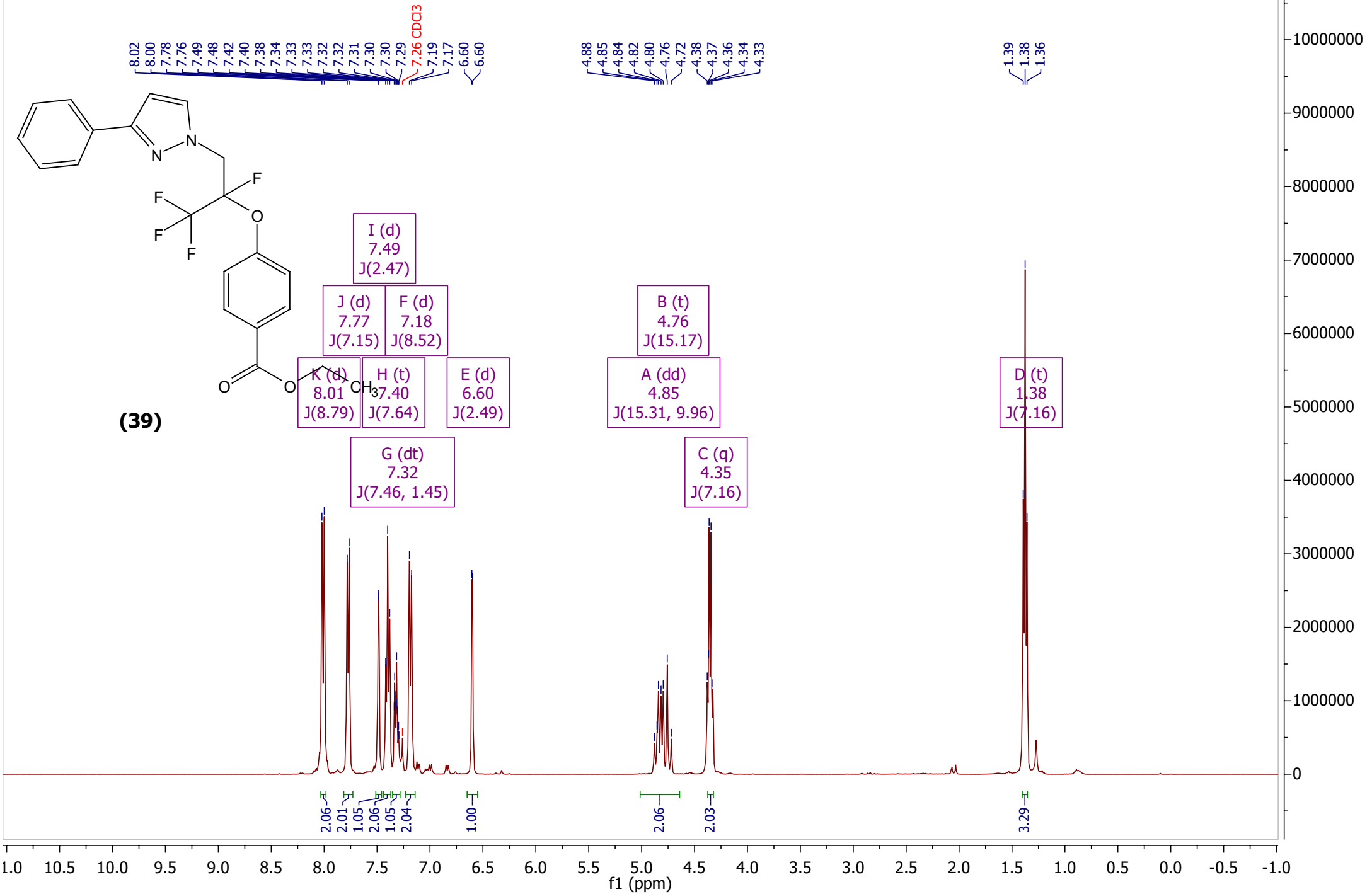


(38)

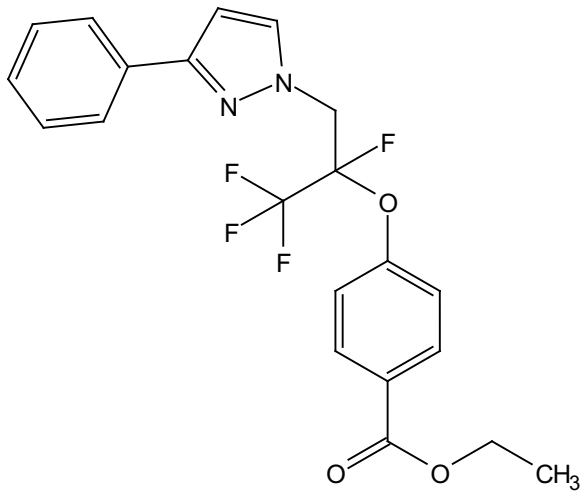
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 161.2, 155.2, 146.6, 131.6, 128.7, 128.5, 126.5, 121.3 (d, *J* = 2.9 Hz), 120.4 (qd, *J* = 288.1, 38.1 Hz), 108.3 (dq, *J* = 240.4, 34.0 Hz), 61.3, 50.9 (d, *J* = 27.0 Hz), 40.1, 27.6, 22.5, 14.3, 14.0.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.49 (d, *J* = 2.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 2.5 Hz, 1H), 4.85 (dd, *J* = 15.3, 10.0 Hz, 1H), 4.76 (t, *J* = 15.2 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H).

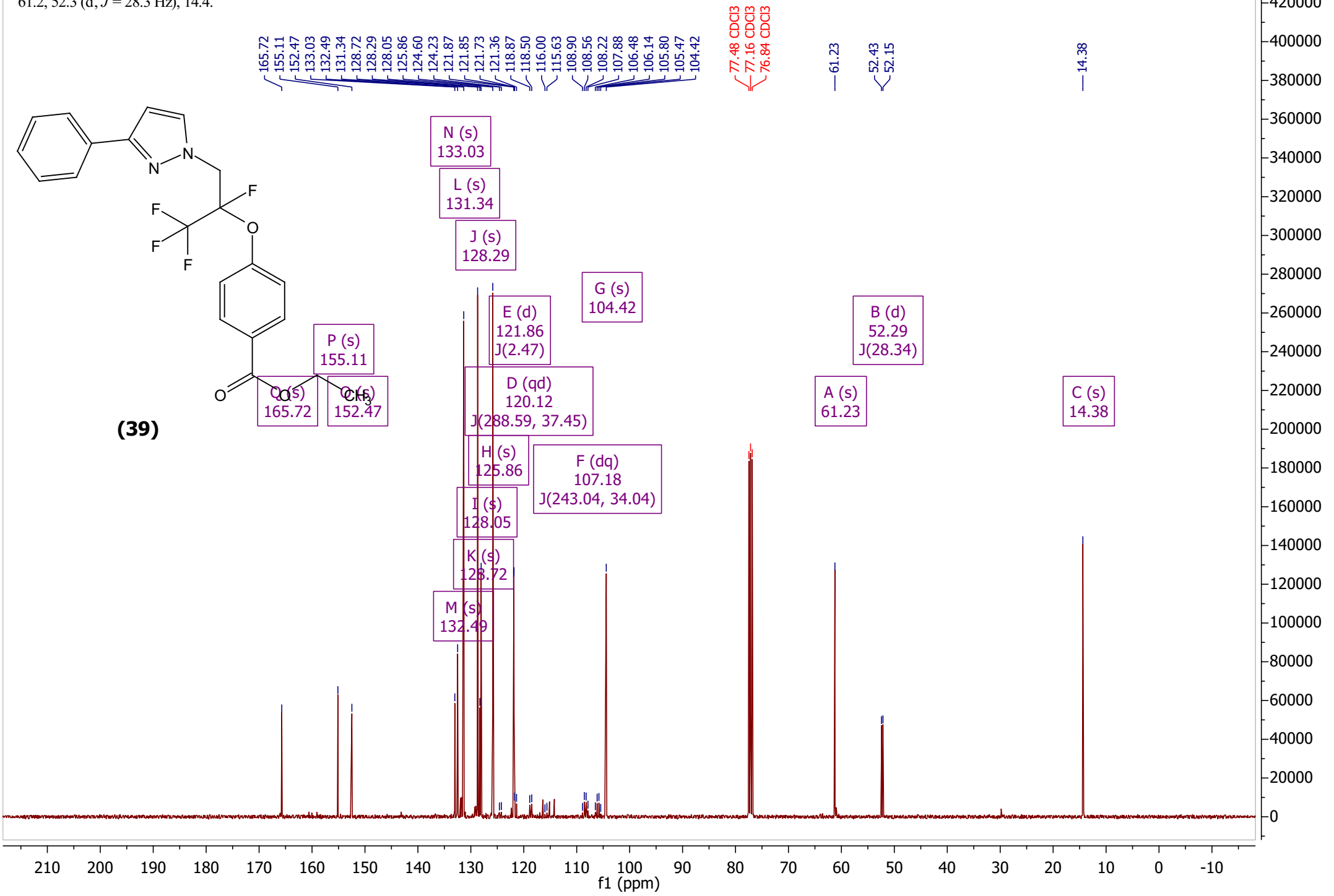


^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.7 Hz), -125.2 (q, *J* = 2.9 Hz).

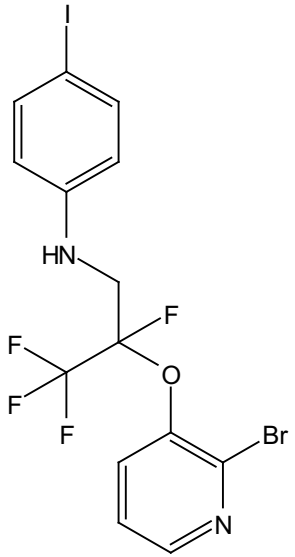


(39)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 155.1, 152.5, 133.0, 132.5, 131.3, 128.7, 128.3, 128.1, 125.9, 121.9 (d, *J* = 2.5 Hz), 120.1 (qd, *J* = 288.6, 37.5 Hz), 107.2 (dq, *J* = 243.0, 34.0 Hz), 104.4, 61.2, 52.3 (d, *J* = 28.3 Hz), 14.4.

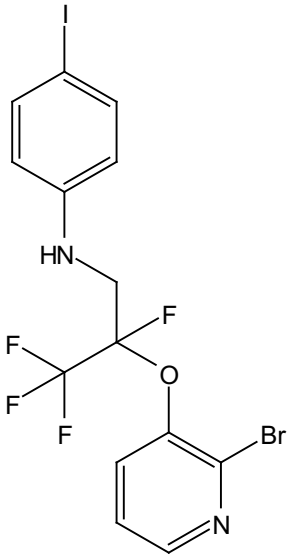


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 4.6, 1.9 Hz, 1H), 7.58 (dt, *J* = 8.3, 2.0 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.22 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.36 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 1H), 3.82 (d, *J* = 12.6 Hz, 2H).



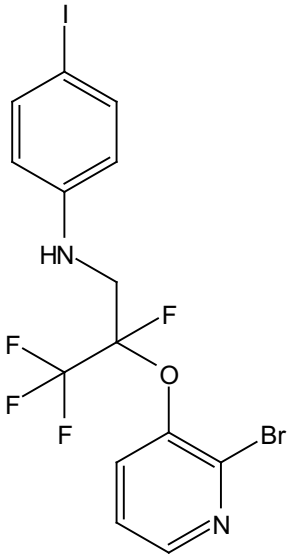
(40)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.3 (d, *J* = 2.8 Hz), -124.6 (q, *J* = 2.9 Hz).



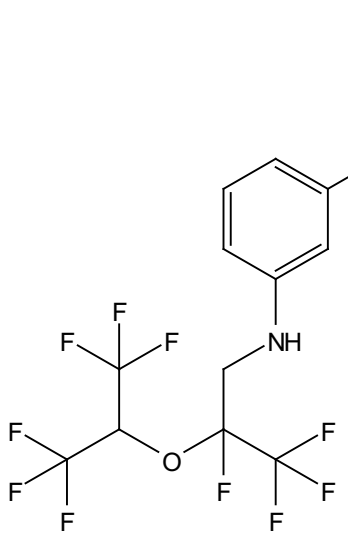
(40)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.8, 146.5, 145.9, 137.9, 136.2 (d, *J* = 2.4 Hz), 130.6 (d, *J* = 3.3 Hz), 123.6, 120.2 (qd, *J* = 287.6, 36.5 Hz), 115.3, 109.3 (dq, *J* = 244.0, 34.1 Hz), 79.9, 44.6 (d, *J* = 27.2 Hz).



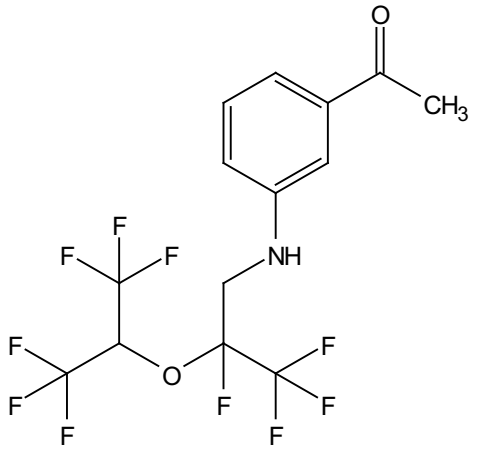
(40)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 1H), 7.32 – 7.26 (m, 2H), 6.88 (dd, *J* = 8.1, 2.7 Hz, 1H), 5.00 (hept, *J* = 5.1 Hz, 1H), 4.09 (s, 1H), 3.98 – 3.68 (m, 2H), 2.57 (s, 3H).



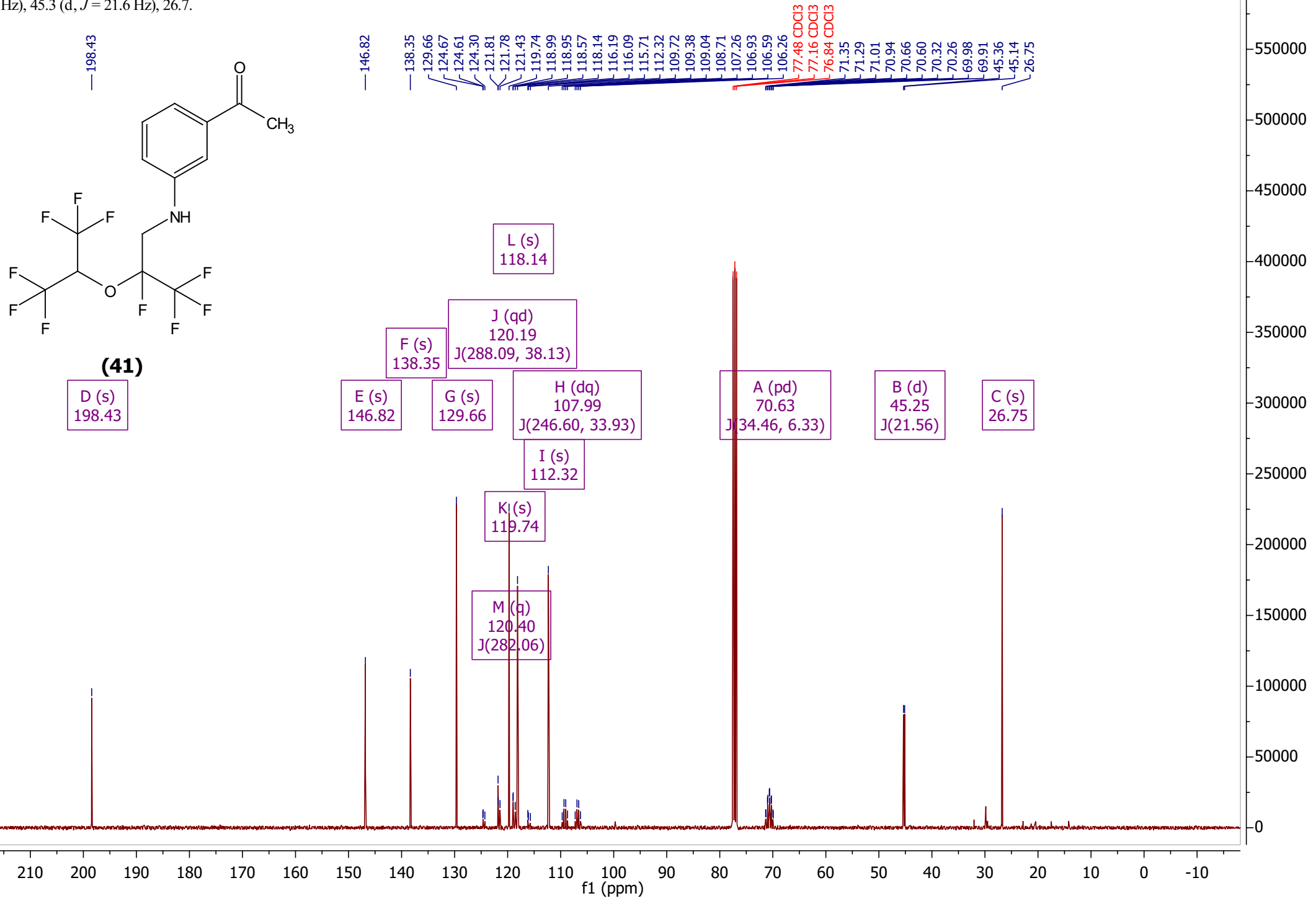
(41)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.3 (qq, *J* = 9.1, 4.6 Hz), -73.6 (p, *J* = 9.8 Hz), -81.6 (dp, *J* = 6.8, 2.7 Hz), -136.8 (q, *J* = 10.2 Hz).

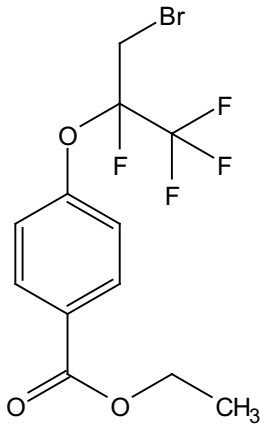


(41)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4, 146.8, 138.3, 129.7, 120.4 (q, *J* = 282.1 Hz), 120.2 (qd, *J* = 288.1, 38.1 Hz), 119.7, 118.1, 112.3, 108.0 (dq, *J* = 246.6, 33.9 Hz), 70.6 (pd, *J* = 34.5, 6.3 Hz), 45.3 (d, *J* = 21.6 Hz), 26.7.

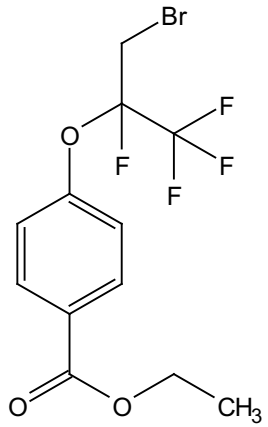


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.53 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).



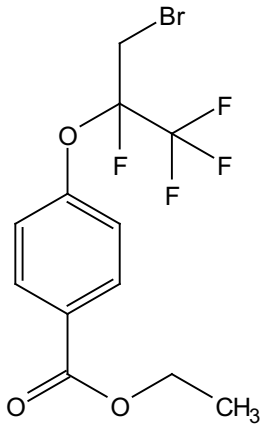
(42)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.7 (d, *J* = 2.4 Hz), -116.4 (q, *J* = 2.2 Hz).



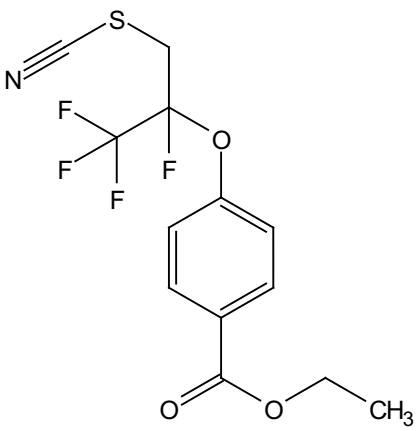
(42)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 154.6, 131.4, 128.6, 122.1 (d, *J* = 2.5 Hz), 119.9 (qd, *J* = 288.1, 36.9 Hz), 107.2 (dq, *J* = 239.7, 34.3 Hz), 61.3, 25.3 (d, *J* = 34.6 Hz), 14.4.



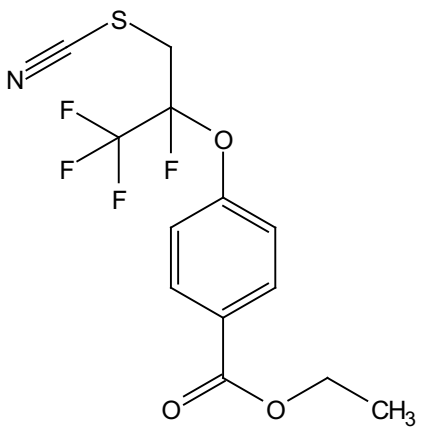
(42)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.60 – 3.43 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).



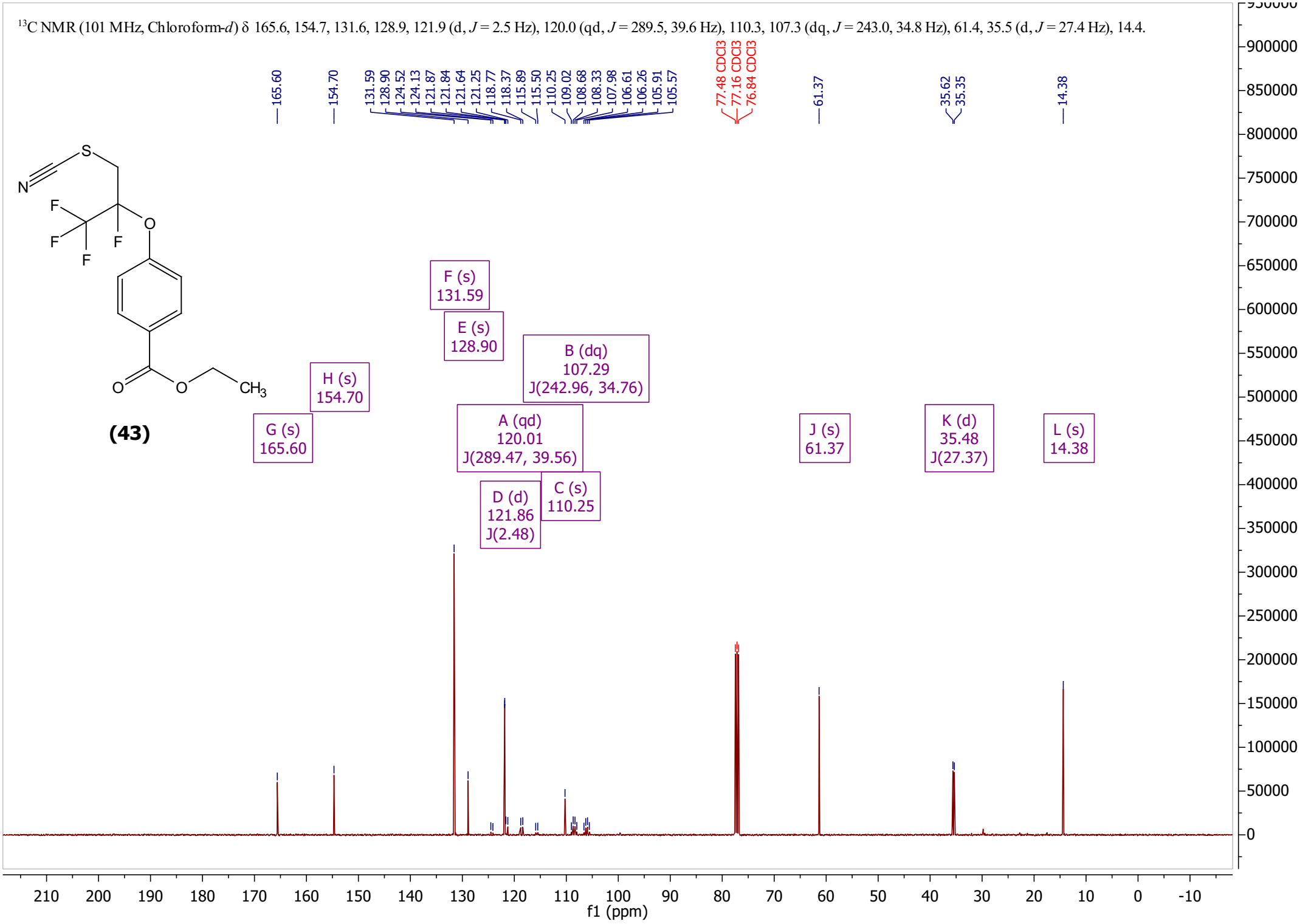
(43)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.1 (d, *J* = 2.8 Hz), -122.0 (q, *J* = 3.0 Hz).

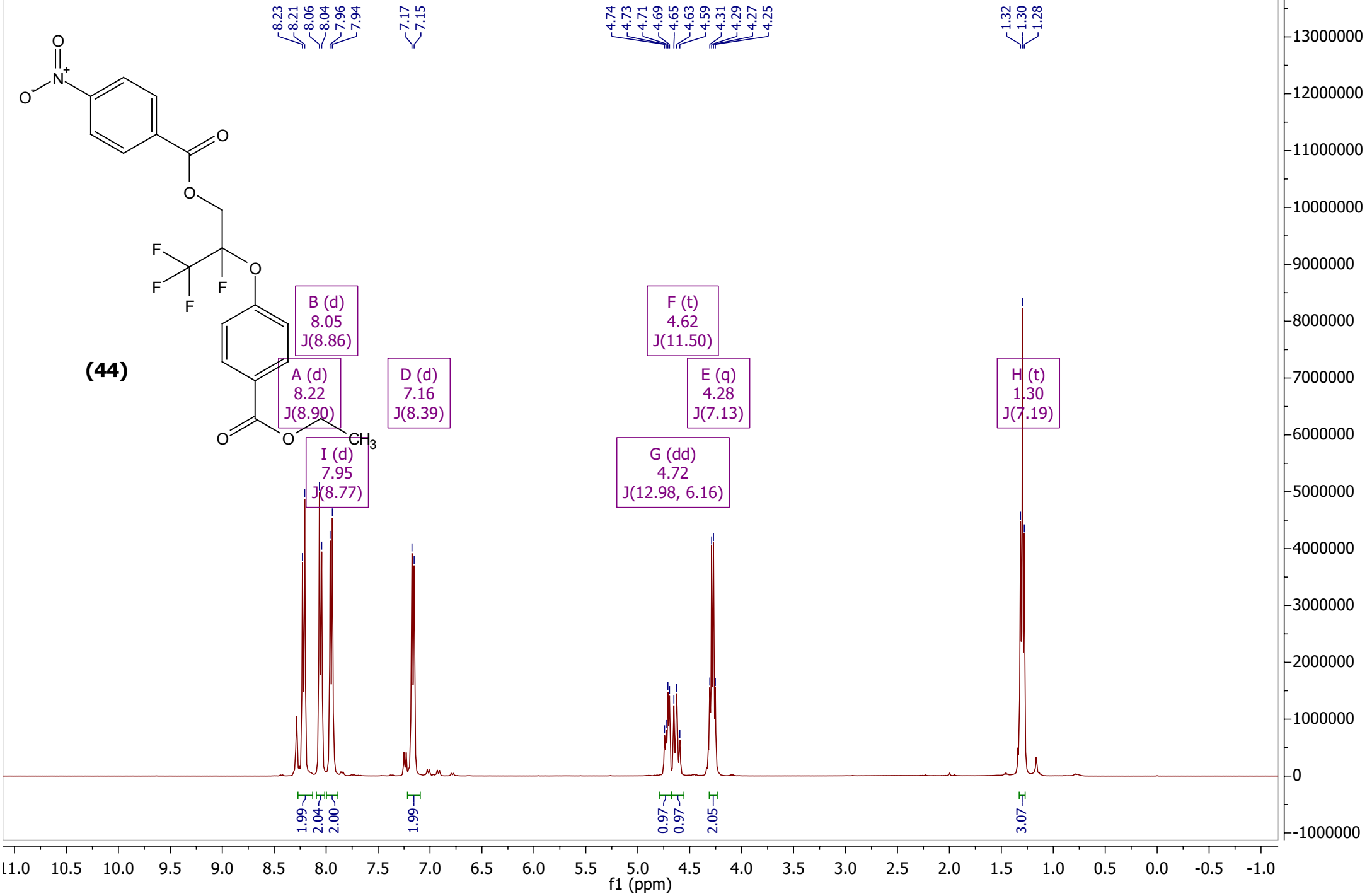


(43)

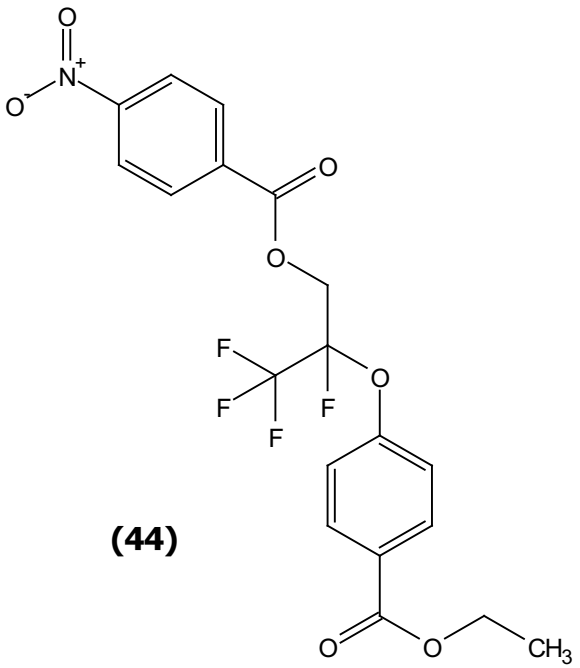
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 154.7, 131.6, 128.9, 121.9 (d, *J* = 2.5 Hz), 120.0 (qd, *J* = 289.5, 39.6 Hz), 110.3, 107.3 (dq, *J* = 243.0, 34.8 Hz), 61.4, 35.5 (d, *J* = 27.4 Hz), 14.4.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.72 (dd, *J* = 13.0, 6.2 Hz, 1H), 4.62 (t, *J* = 11.5 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).

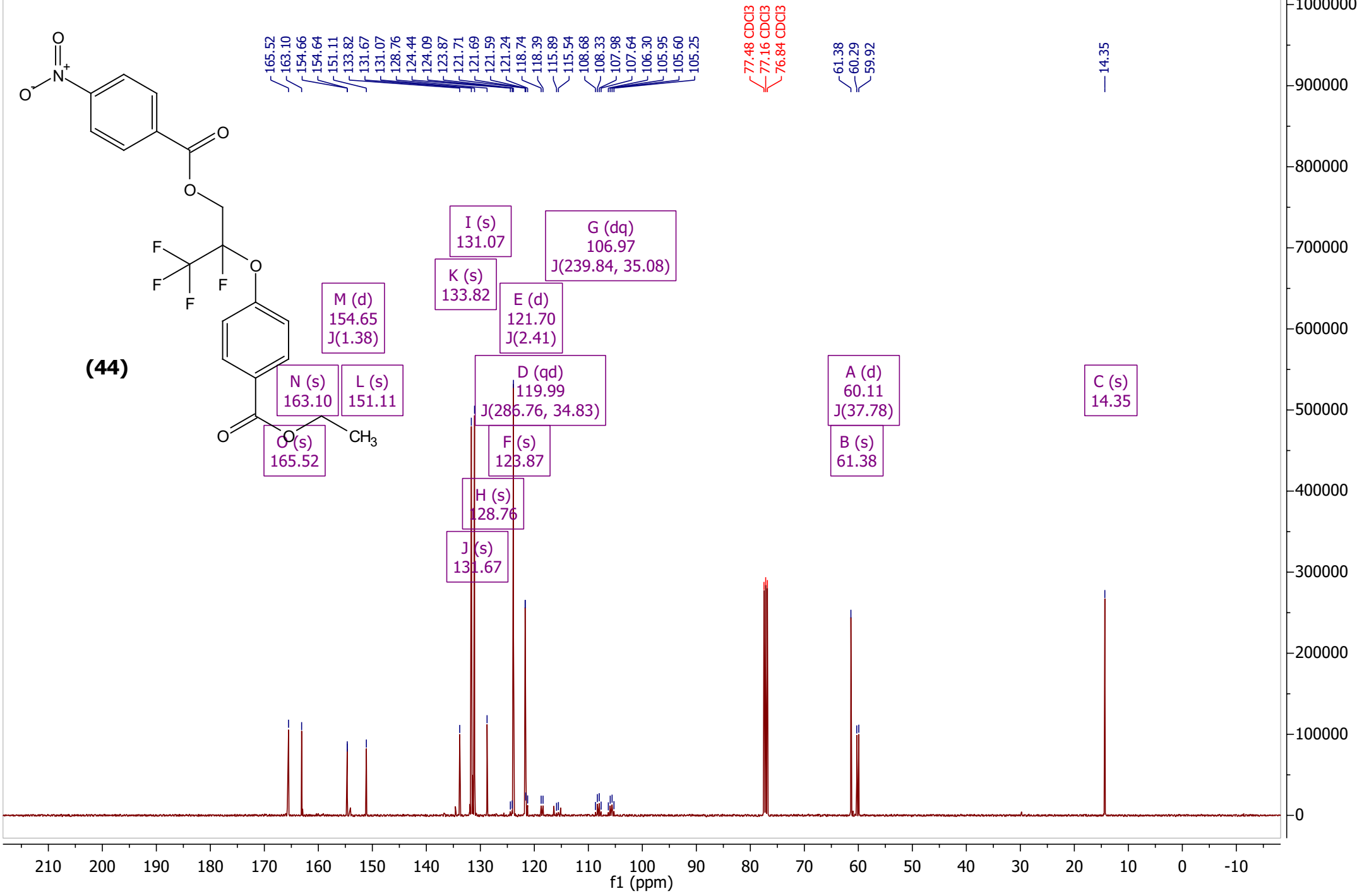


^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.6 (d, *J* = 2.8 Hz), -125.5 (q, *J* = 3.0 Hz).

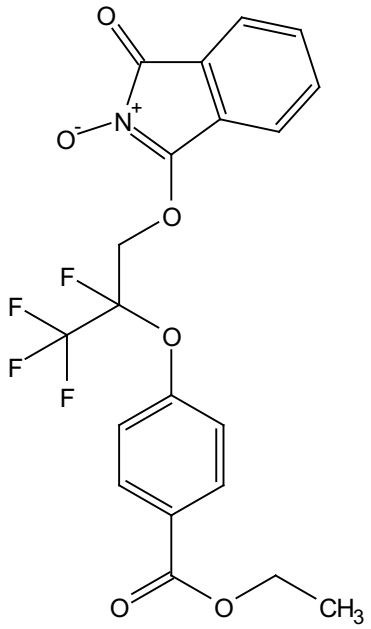


(44)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 163.1, 154.7 (d, *J* = 1.4 Hz), 151.1, 133.8, 131.7, 131.1, 128.8, 123.9, 121.7 (d, *J* = 2.4 Hz), 120.0 (qd, *J* = 286.8, 34.8 Hz), 107.0 (dq, *J* = 239.8, 35.1 Hz), 61.4, 60.1 (d, *J* = 37.8 Hz), 14.4.

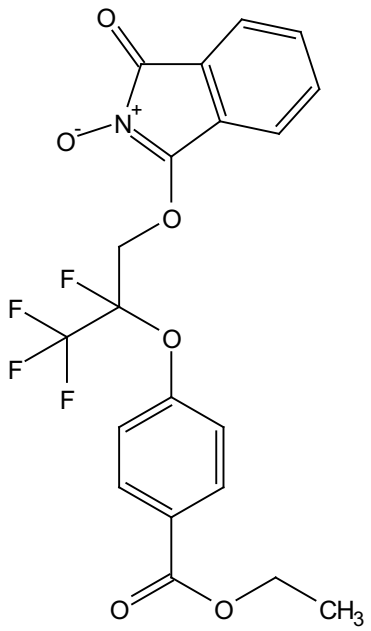


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.71 (td, *J* = 7.5, 1.6 Hz, 1H), 7.67 (td, *J* = 7.6, 1.7 Hz, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 4.95 (s, 1H), 4.90 (s, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H).



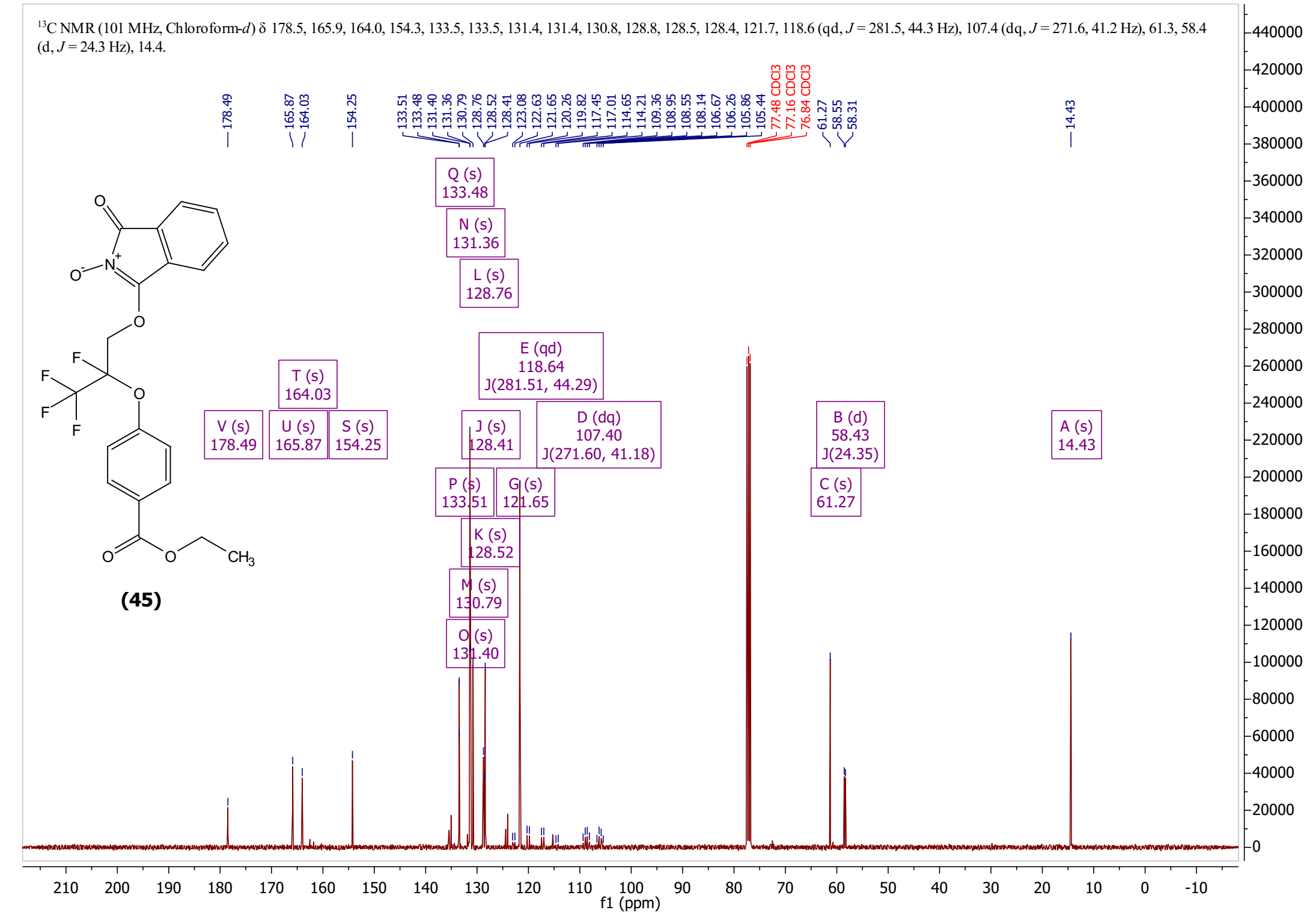
(45)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -85.7 (d, *J* = 2.8 Hz), -114.7 (q, *J* = 3.3 Hz).

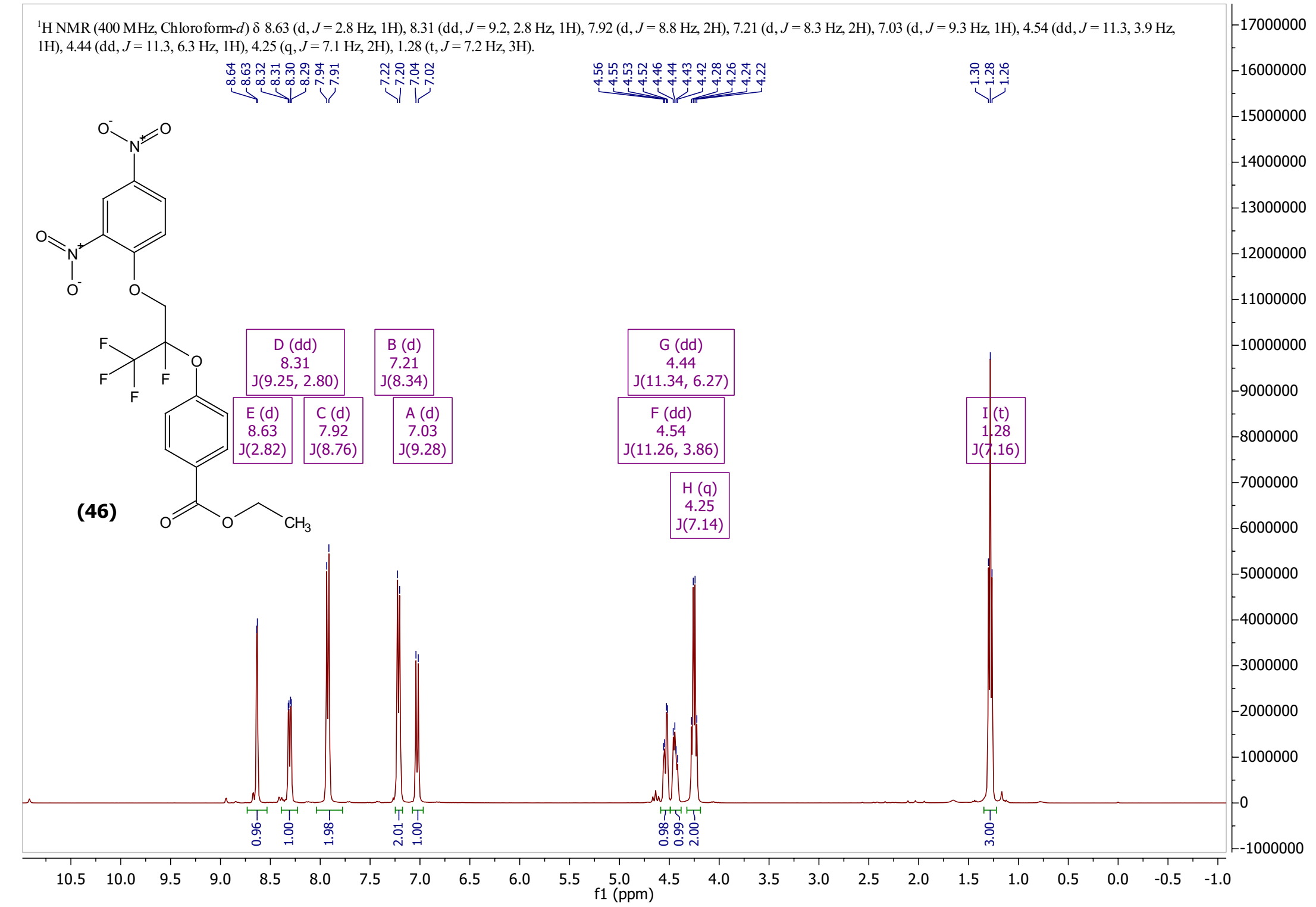


(45)

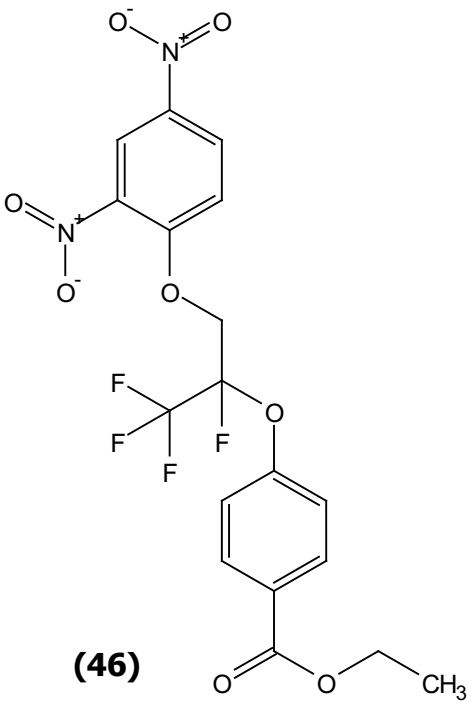
^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.5, 165.9, 164.0, 154.3, 133.5, 133.5, 131.4, 131.4, 130.8, 128.8, 128.5, 128.4, 121.7, 118.6 (qd, *J* = 281.5, 44.3 Hz), 107.4 (dq, *J* = 271.6, 41.2 Hz), 61.3, 58.4 (d, *J* = 24.3 Hz), 14.4.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 2.8 Hz, 1H), 8.31 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 9.3 Hz, 1H), 4.54 (dd, *J* = 11.3, 3.9 Hz, 1H), 4.44 (dd, *J* = 11.3, 6.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

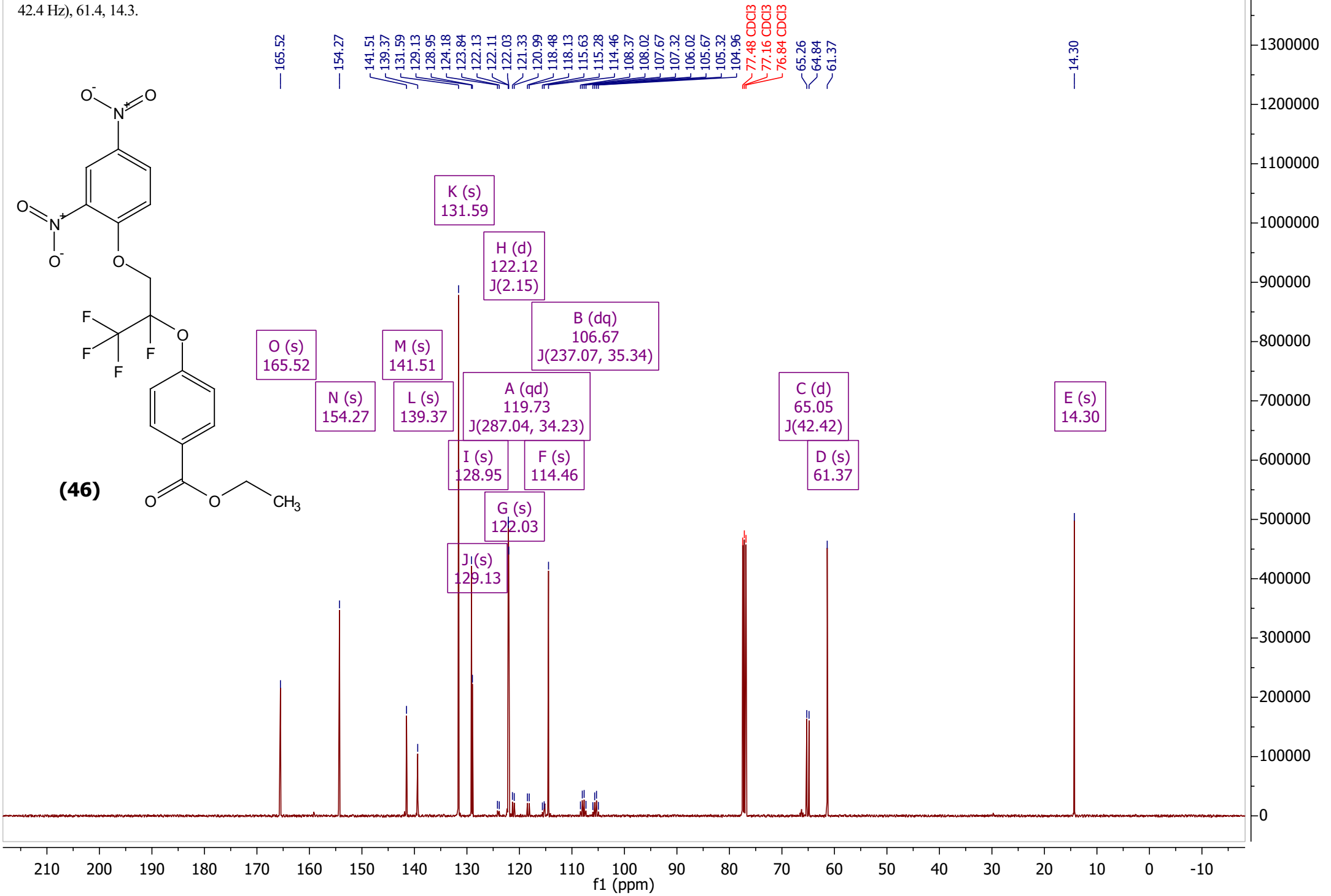


^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.2 (d, *J* = 3.4 Hz), -124.3 (q, *J* = 3.4 Hz).

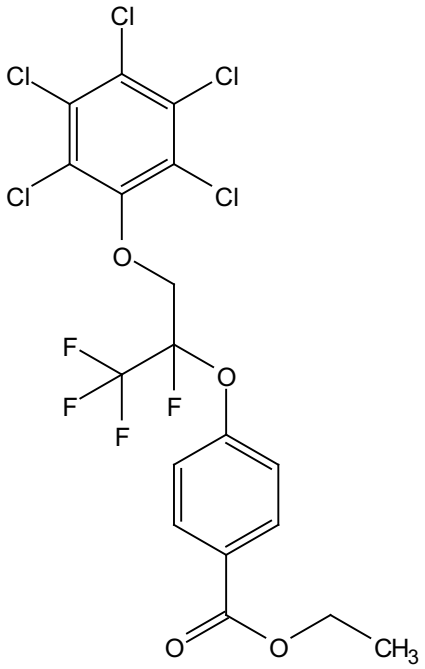


(46)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.5, 154.3, 141.5, 139.4, 131.6, 129.1, 129.0, 122.1 (d, *J* = 2.2 Hz), 122.0, 119.7 (qd, *J* = 287.0, 34.2 Hz), 114.5, 106.7 (dq, *J* = 237.1, 35.3 Hz), 65.0 (d, *J* = 42.4 Hz), 61.4, 14.3.

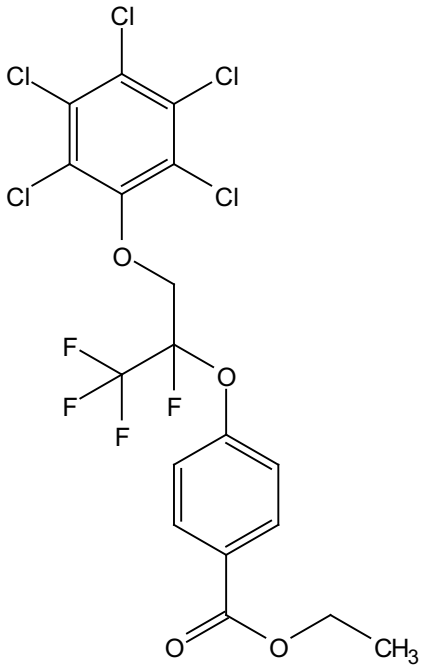


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 4.43 (t, *J* = 10.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.22 (dd, *J* = 10.6, 5.2 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H).



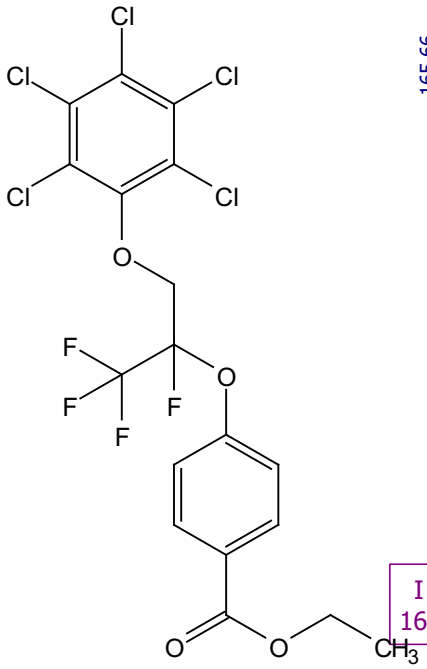
(47)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 (d, *J* = 3.3 Hz), -124.9 (q, *J* = 3.4 Hz).



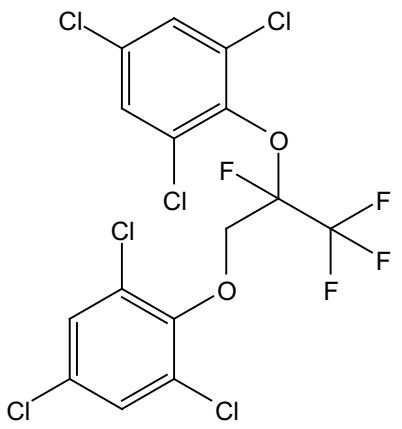
(47)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 155.2 (d, *J* = 1.5 Hz), 149.4, 132.3, 131.5, 130.8, 128.3, 128.1, 121.5 (d, *J* = 2.7 Hz), 120.0 (qd, *J* = 286.5, 35.0 Hz), 106.8 (dq, *J* = 238.9, 35.4 Hz), 67.2 (d, *J* = 37.8 Hz), 61.3, 14.4.



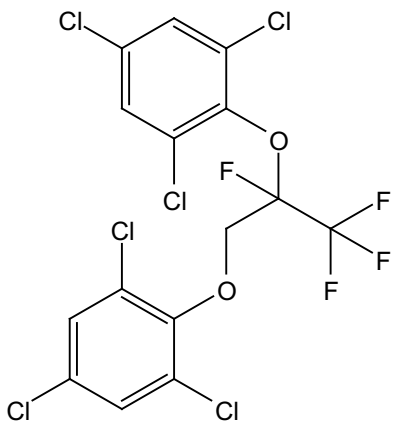
(47)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (s, 2H), 7.17 (s, 2H), 4.40 (dd, *J* = 14.4, 10.9 Hz, 1H), 4.30 (t, *J* = 11.0 Hz, 1H).



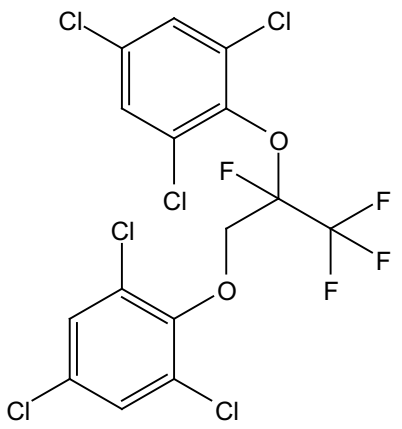
(48)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.8, -120.2.



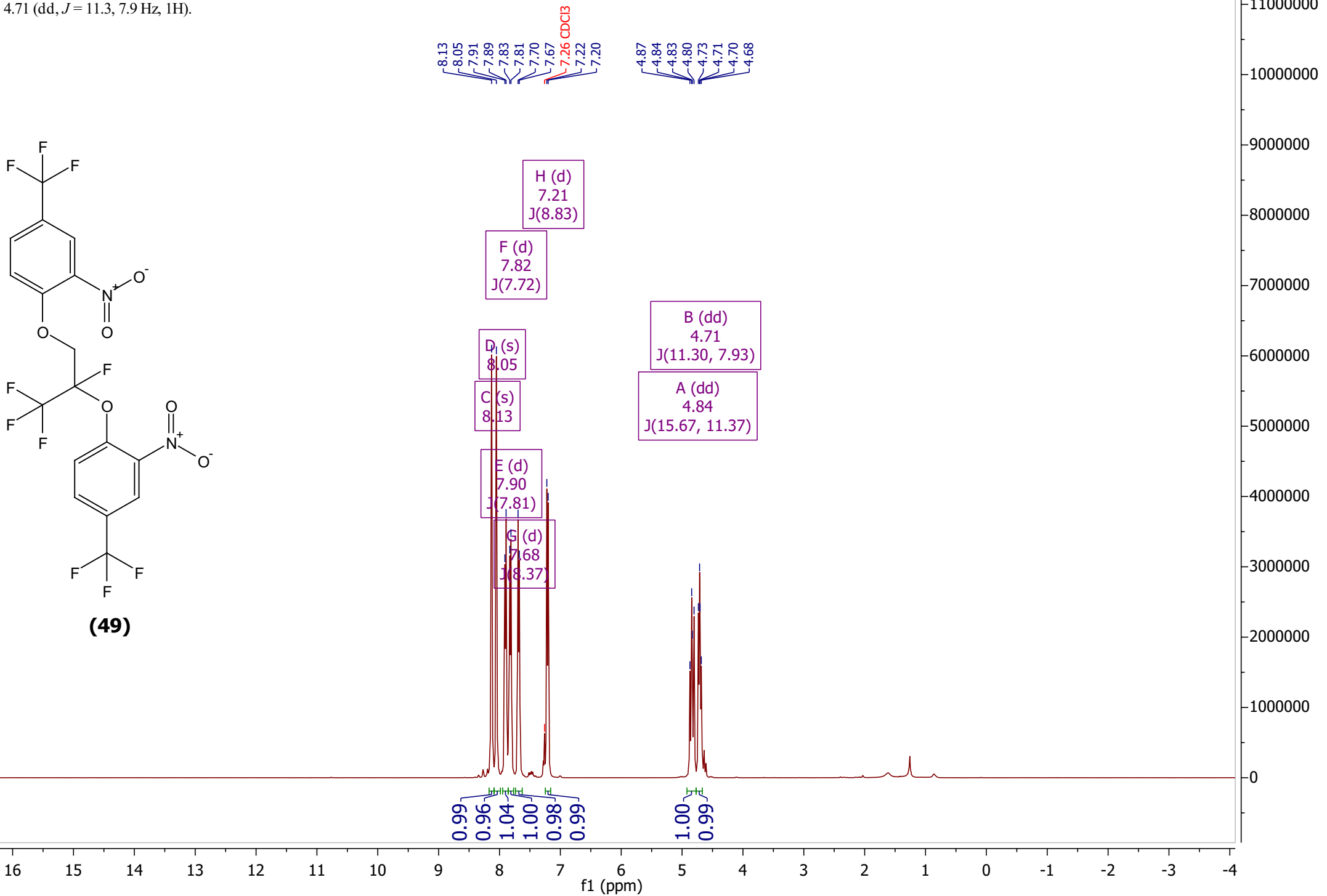
(48)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 144.3, 132.4, 131.3 (d, *J* = 1.8 Hz), 131.1, 129.9, 129.5, 129.2, 120.1 (qd, *J* = 287.3, 36.4 Hz), 107.9 (dq, *J* = 248.8, 35.7 Hz), 68.7 (d, *J* = 27.1 Hz).



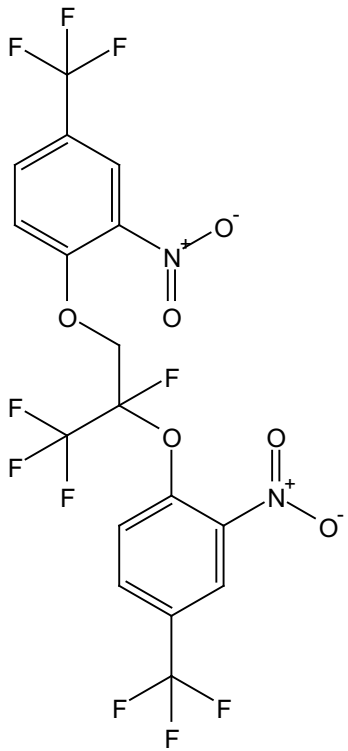
(48)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 8.05 (s, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 4.84 (dd, *J* = 15.7, 11.4 Hz, 1H), 4.71 (dd, *J* = 11.3, 7.9 Hz, 1H).



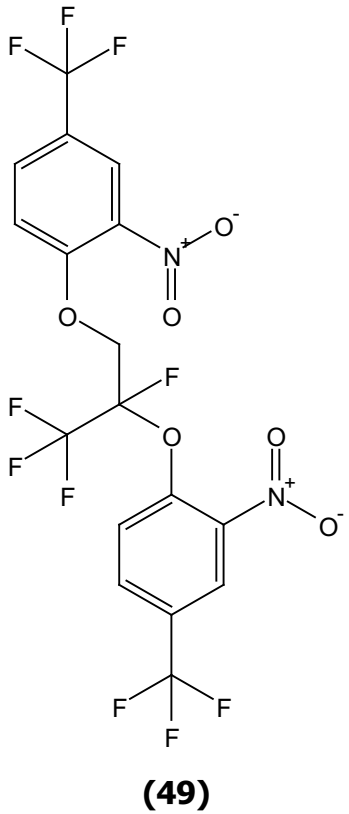
(49)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.5, -63.0, -81.5 (d, *J* = 2.8 Hz), -128.2 (q, *J* = 2.8 Hz).



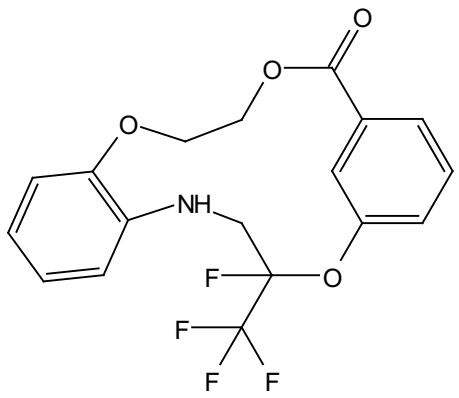
(49)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.3, 146.7, 142.9, 139.9, 131.3 (q, *J* = 3.5 Hz), 129.4 (q, *J* = 34.9 Hz), 125.7, 125.6, 125.4 (q, *J* = 34.8 Hz), 123.7 (q, *J* = 3.8 Hz), 123.4 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 272.1 Hz), 122.5 (q, *J* = 272.8 Hz), 119.5 (qd, *J* = 287.2, 33.4 Hz), 115.3, 107.7 (dq, *J* = 248.8, 35.5 Hz), 66.8 (d, *J* = 27.9 Hz).



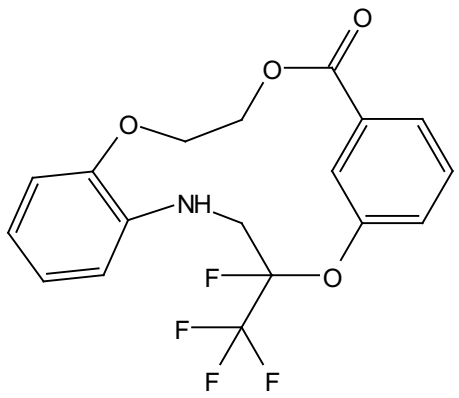
(49)

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.9 Hz, 1H), 7.41 (dd, J = 8.3, 2.7 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 7.7 Hz, 1H), 6.68 – 6.57 (m, 2H), 5.42 (t, J = 6.9 Hz, 1H), 4.70 – 4.52 (m, 2H), 4.45 (dt, J = 11.8, 3.6 Hz, 1H), 4.18 – 4.02 (m, 2H), 3.80 (td, J = 16.4, 6.8 Hz, 1H).



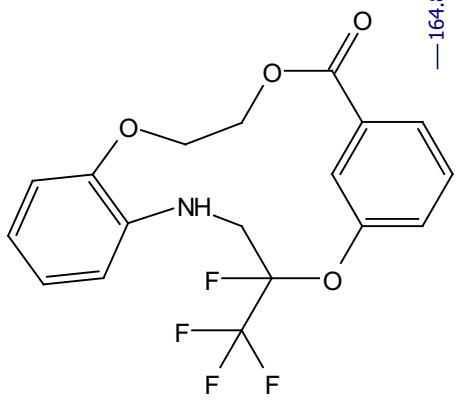
(50)

^{19}F NMR (376 MHz, DMSO-d_6) δ -83.8 (d, J = 4.2 Hz), -125.6 (q, J = 4.3 Hz).



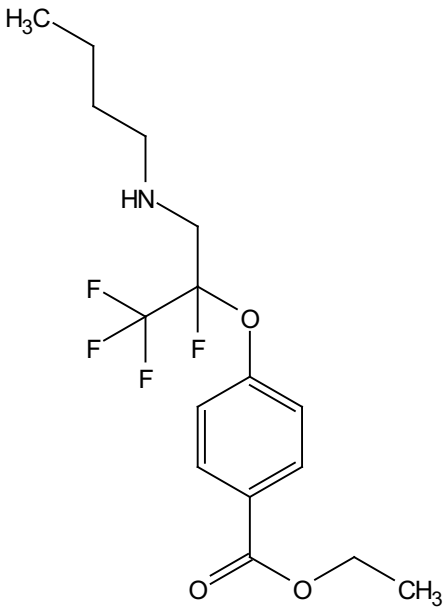
(50)

^{13}C NMR (101 MHz, DMSO-d_6) δ 164.9, 151.0, 145.8, 137.4, 131.2, 130.6, 125.2, 124.6, 122.4, 121.4 (d, J = 2.7 Hz), 120.5 (dd, J = 286.7, 33.7 Hz), 116.8, 115.4, 109.5, 108.8 (dd, J = 247.8, 32.5 Hz), 68.3, 63.1, 42.1 (d, J = 22.2 Hz).



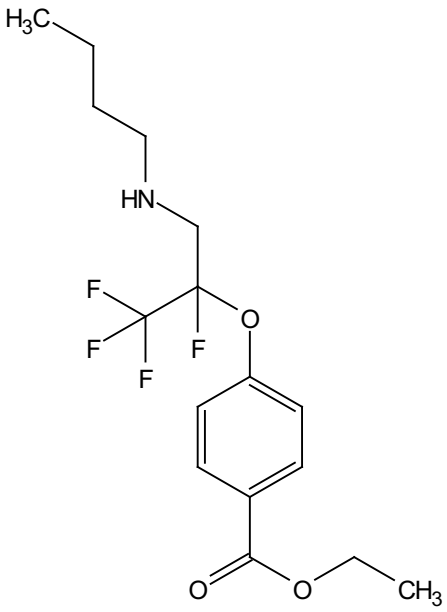
(50)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.24 – 3.01 (m, 2H), 2.57 – 2.36 (m, 2H), 1.36 – 1.11 (m, 8H), 0.79 (t, *J* = 7.3 Hz, 3H).



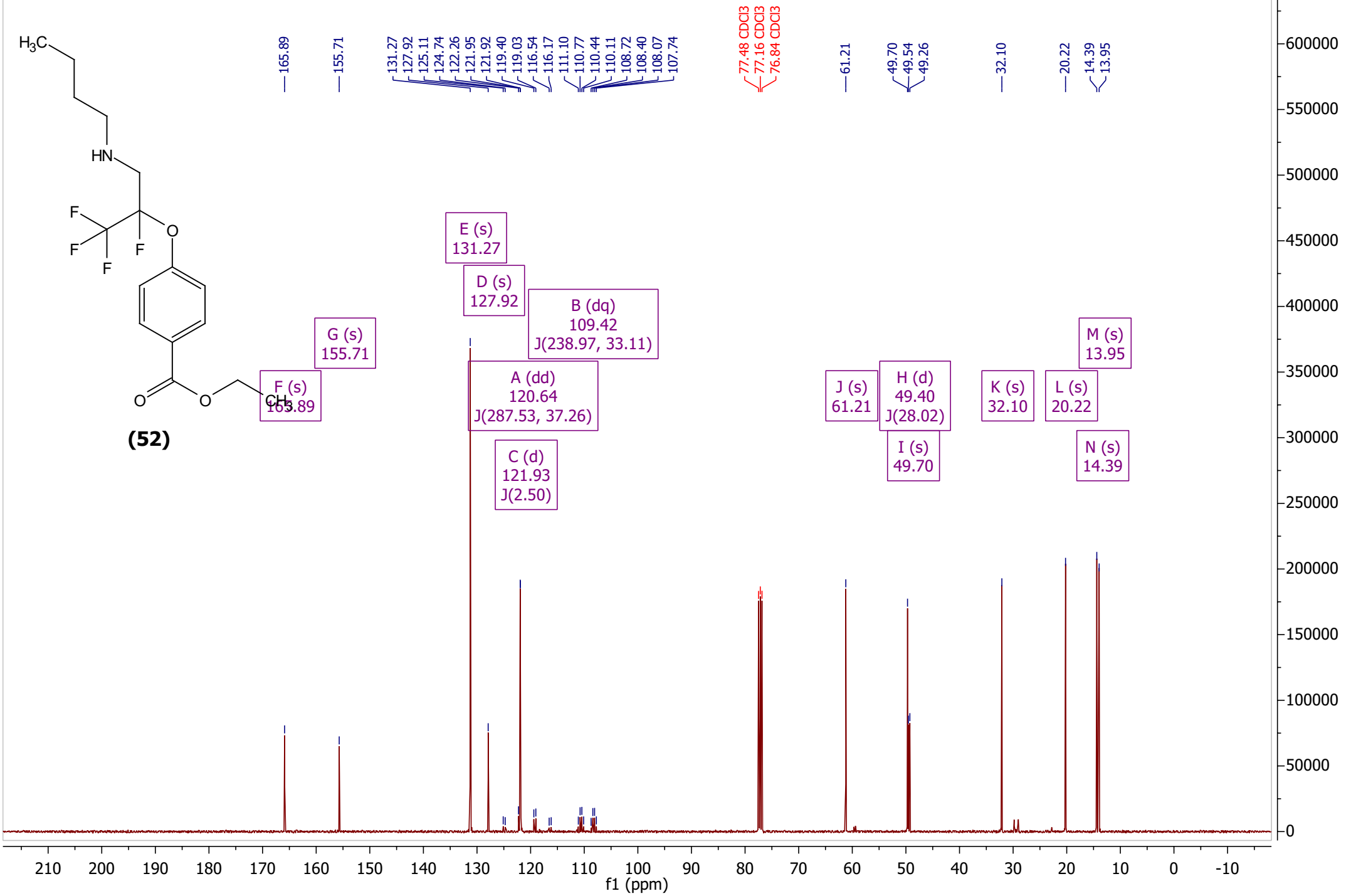
(52)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.5 (d, *J* = 2.8 Hz), -123.5 (q, *J* = 2.7 Hz).

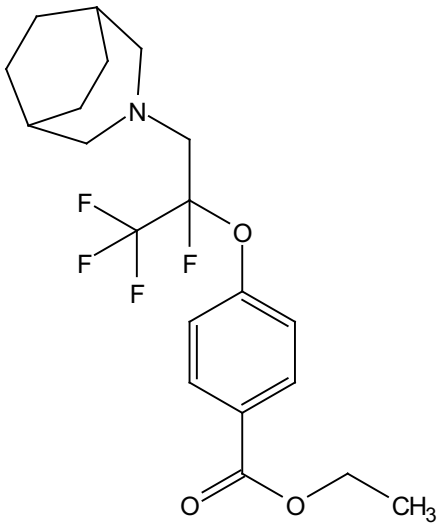


(52)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 155.7, 131.3, 127.9, 121.9 (d, *J* = 2.5 Hz), 120.6 (dd, *J* = 287.5, 37.3 Hz), 109.4 (dq, *J* = 239.0, 33.1 Hz), 61.2, 49.7, 49.4 (d, *J* = 28.0 Hz), 32.1, 20.2, 14.4, 14.0.

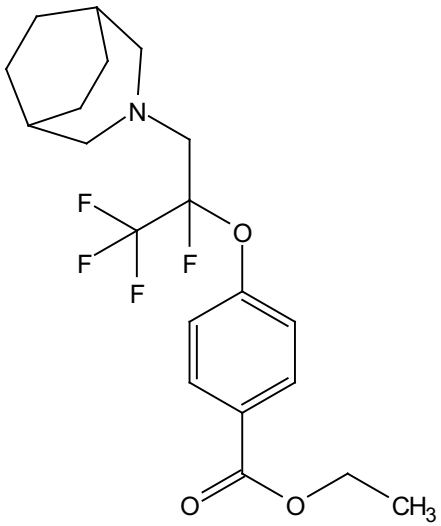


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.13 – 2.92 (m, 2H), 2.75 – 2.60 (m, 4H), 1.80 (s, 2H), 1.76 – 1.64 (m, 4H), 1.57 – 1.48 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H).



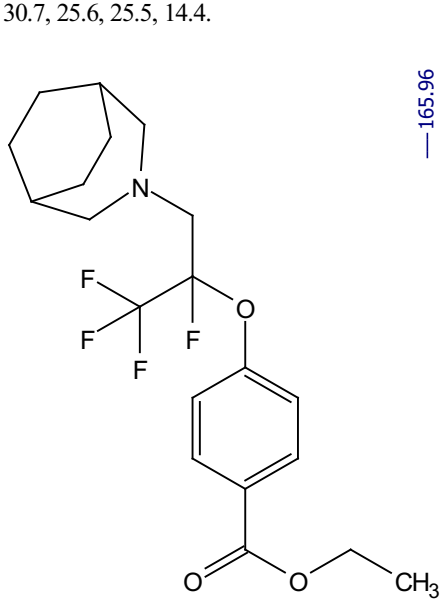
(53)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.2 (d, *J* = 2.7 Hz), -122.9 (q, *J* = 2.5 Hz).



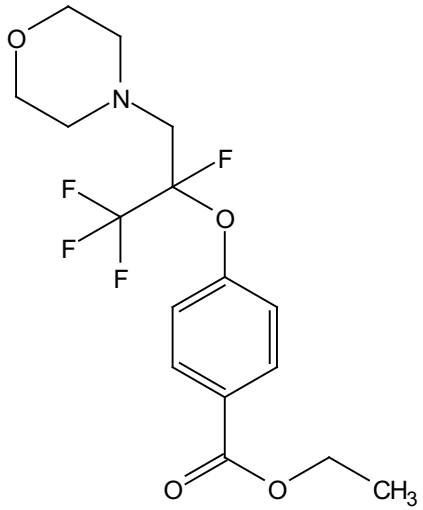
(53)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 156.1, 131.3, 127.5, 121.4 (d, *J* = 2.9 Hz), 120.7 (qd, *J* = 287.9, 37.3 Hz), 110.1 (dq, *J* = 241.8, 32.5 Hz), 64.5 (d, *J* = 1.6 Hz), 61.2, 58.0 (d, *J* = 26.3 Hz), 30.7, 25.6, 25.5, 14.4.



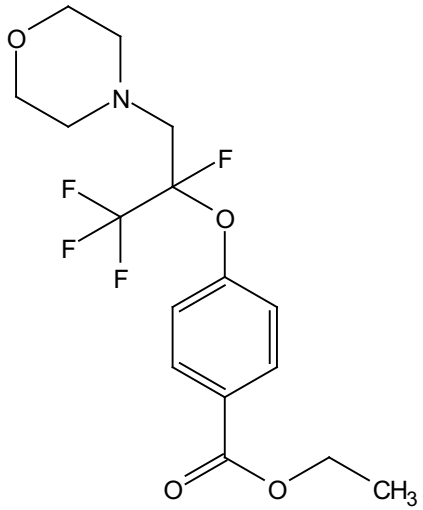
(53)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.55 (d, *J* = 3.3 Hz, 4H), 3.06 – 2.73 (m, 2H), 2.47 (t, *J* = 4.6 Hz, 4H), 1.37 (t, *J* = 7.1 Hz, 3H).



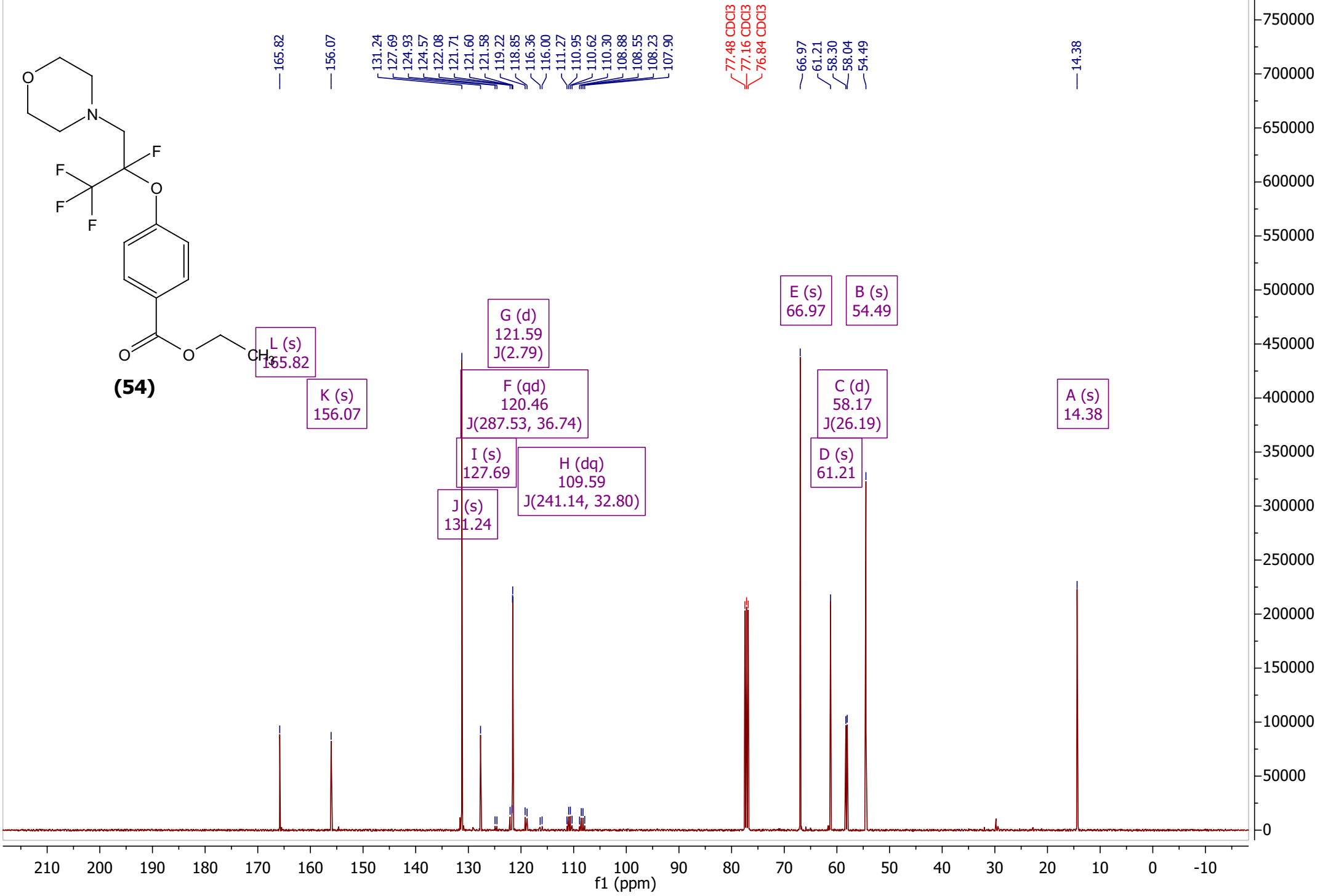
(54)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.8 (d, *J* = 2.7 Hz), -122.0 (q, *J* = 2.2 Hz).



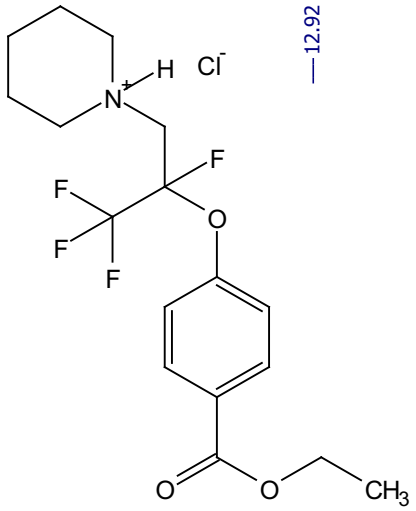
(54)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 156.1, 131.2, 127.7, 121.6 (d, *J* = 2.8 Hz), 120.5 (qd, *J* = 287.5, 36.7 Hz), 109.6 (dq, *J* = 241.1, 32.8 Hz), 67.0, 61.2, 58.2 (d, *J* = 26.2 Hz), 54.5, 14.4.



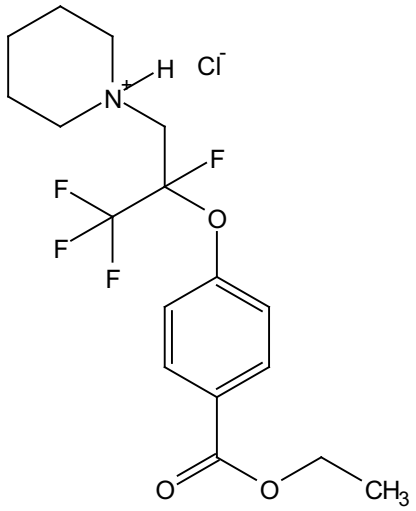
(54)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.92 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.81 – 3.54 (m, 4H), 3.28 (s, 2H), 2.38 (s, 1H), 2.29 (s, 1H), 1.83 (s, 3H), 1.46 (s, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).



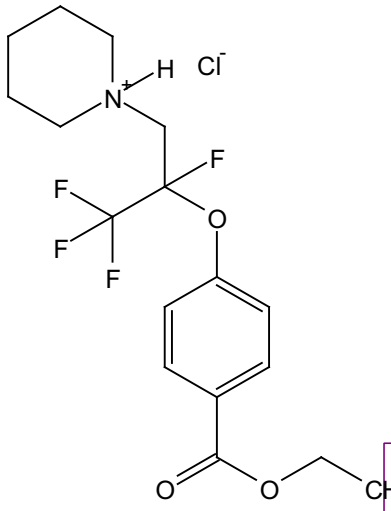
(55)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -78.0, -119.1.



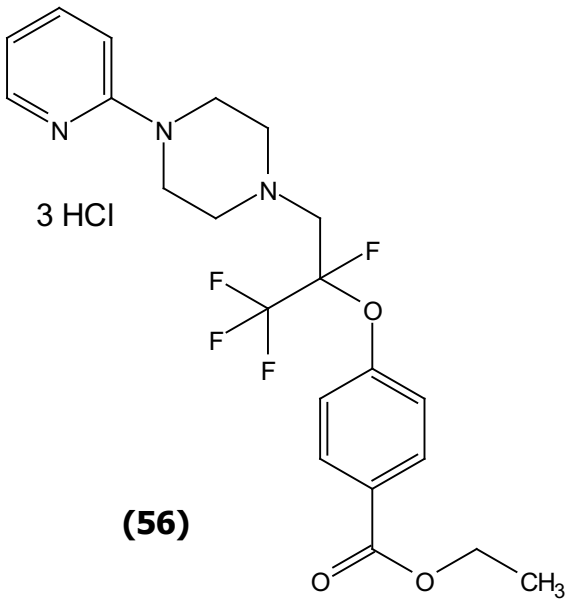
(55)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 154.6, 131.4, 128.9, 121.7, 119.3 (dq, *J* = 291.7, 41.7 Hz), 107.4 (qd, *J* = 243.9, 35.0 Hz), 61.3, 56.0 (d, *J* = 21.8 Hz), 54.8 (d, *J* = 14.7 Hz), 22.7, 21.6, 14.3.

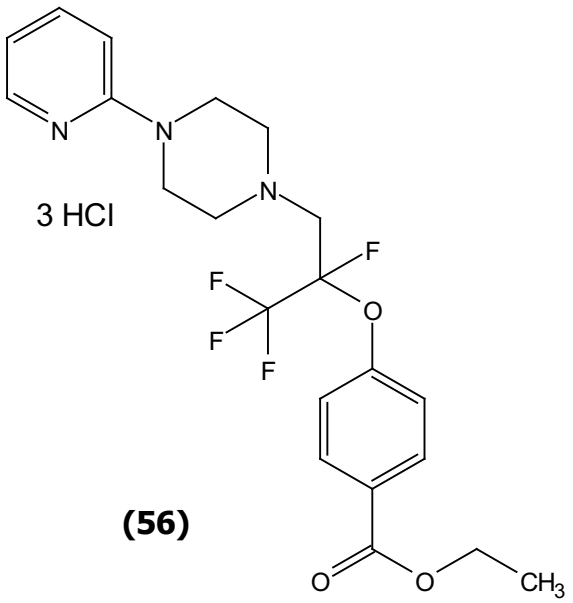


(55)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 4.8 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.79 (t, *J* = 6.5 Hz, 1H), 5.24 (s, 3H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.73 – 3.70 (m, 4H), 2.99 (p, *J* = 14.7 Hz, 2H), 2.69 (s, 4H), 1.32 (t, *J* = 7.1 Hz, 3H).

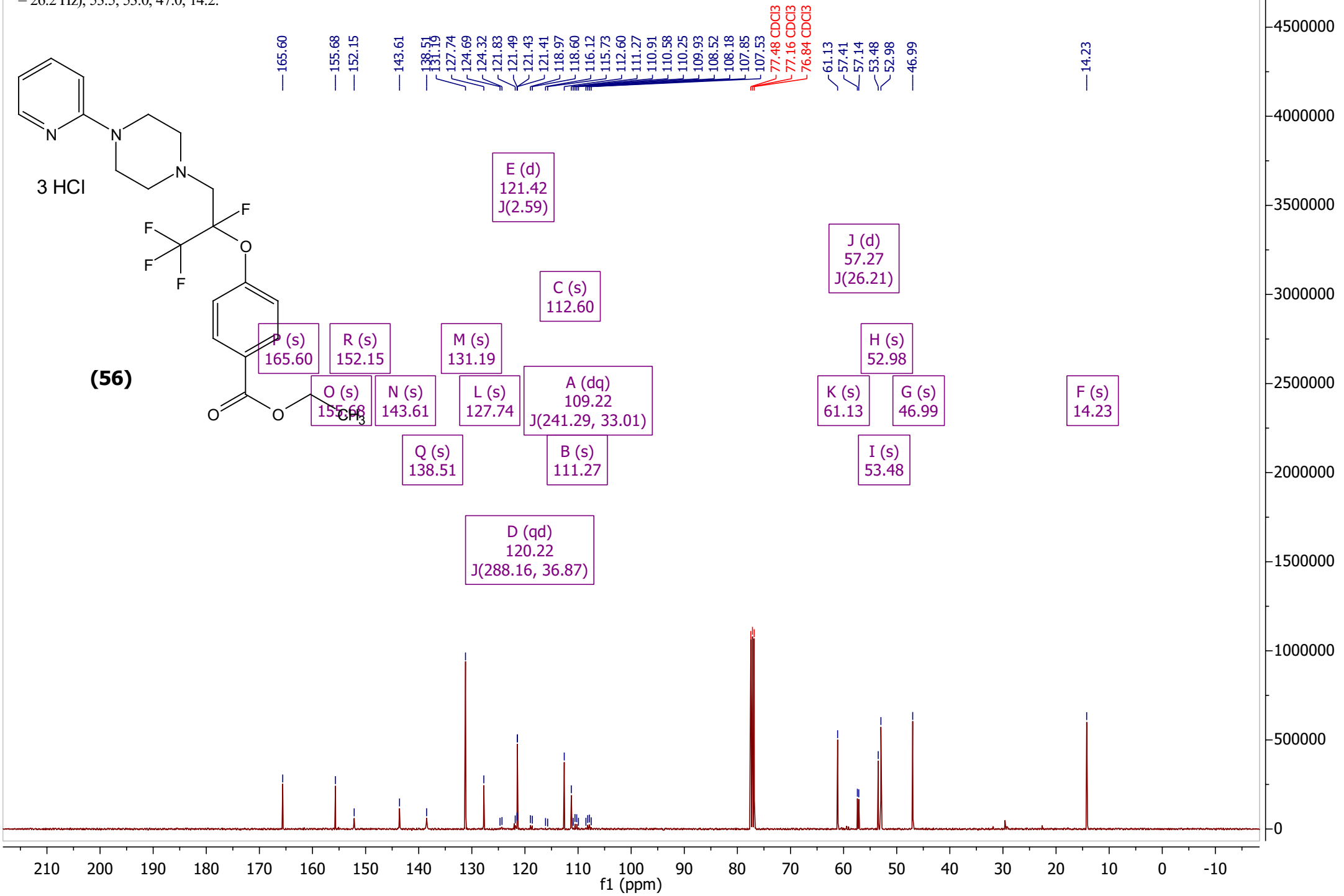


^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.3, -122.5.

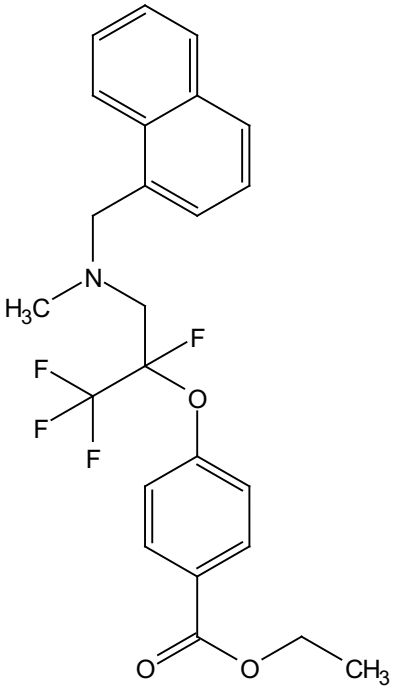


(56)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 155.7, 152.2, 143.6, 138.5, 131.2, 127.7, 121.4 (d, *J* = 2.6 Hz), 120.2 (qd, *J* = 288.2, 36.9 Hz), 112.6, 111.3, 109.2 (dq, *J* = 241.3, 33.0 Hz), 61.1, 57.3 (d, *J* = 26.2 Hz), 53.5, 53.0, 47.0, 14.2.

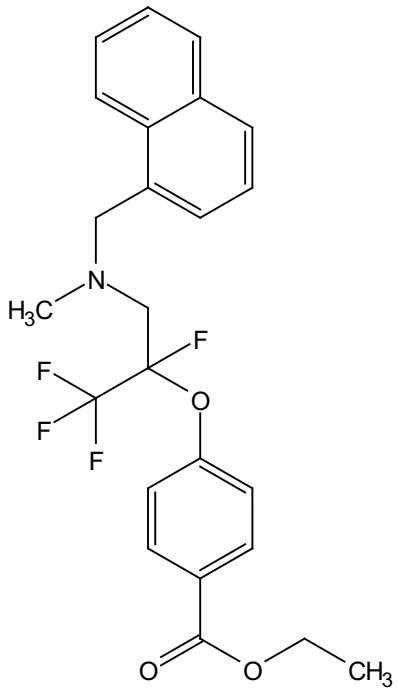


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 – 8.25 (m, 1H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.89 – 7.76 (m, 2H), 7.49 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 3.32 – 3.10 (m, 2H), 2.36 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H).



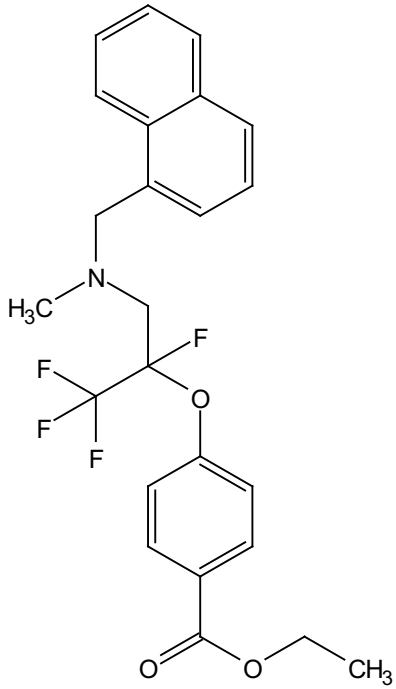
(57)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.9 (d, *J* = 2.0 Hz), -123.4 (q, *J* = 2.1 Hz).



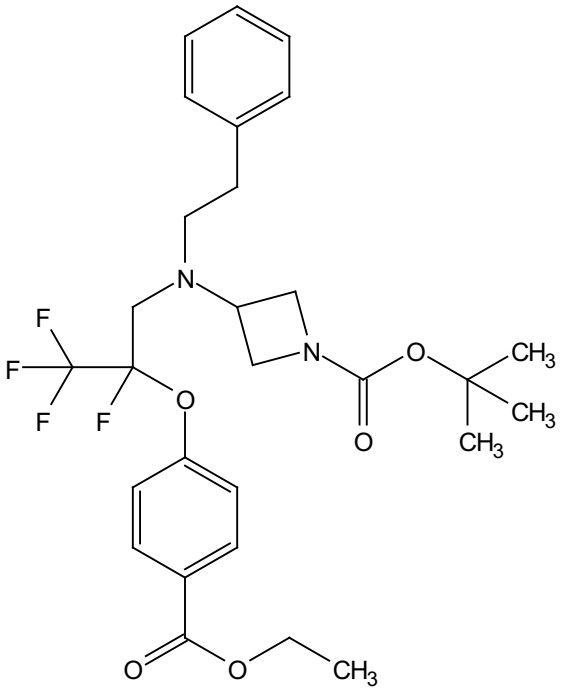
(57)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 155.9, 134.0, 133.9, 132.4, 131.3, 128.5, 128.4, 127.6, 127.5, 125.9, 125.8, 125.2, 124.7, 121.6 (d, *J* = 2.7 Hz), 120.6 (qd, *J* = 288.5, 38.1 Hz), 110.0 (dq, *J* = 241.3, 32.3 Hz), 61.8, 61.2, 57.6 (d, *J* = 25.1 Hz), 43.6 (d, *J* = 1.9 Hz), 14.4.



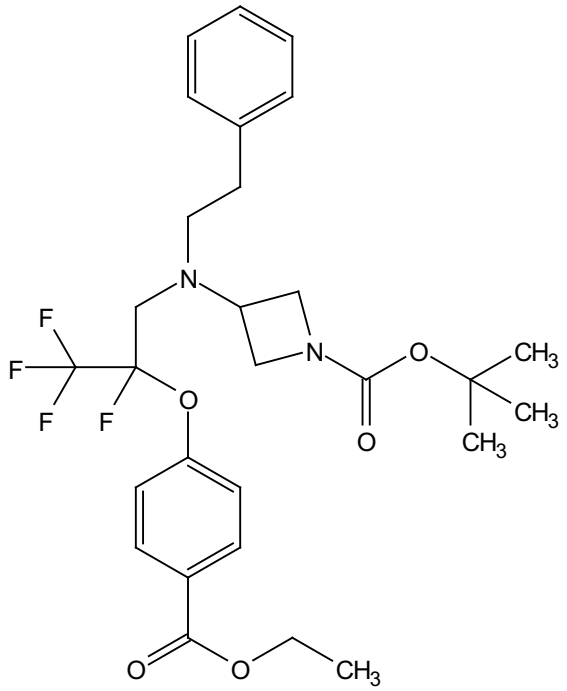
(57)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.15 – 7.09 (m, 3H), 7.08 – 7.00 (m, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.88 (q, *J* = 7.9 Hz, 2H), 3.82 – 3.68 (m, 3H), 3.29 – 3.12 (m, 2H), 3.00 – 2.85 (m, 2H), 2.72 – 2.60 (m, 2H), 1.35 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H).



(58)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -79.1, -126.2.



(58)

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 156.4, 155.9, 139.4, 131.3, 128.7, 128.6, 127.9, 126.4, 121.7 (d, *J* = 2.6 Hz), 120.5 (qd, *J* = 289.4, 40.0 Hz), 109.7 (dq, *J* = 242.5, 32.1 Hz), 79.8, 61.2, 53.8, 52.5, 51.2 (d, *J* = 22.8 Hz), 33.8, 28.4, 20.8, 14.4.