Supporting Information

Accessing Structurally Diverse Aryl Difluoromethyl Ethers with Bromo(difluoro)acetic Acid

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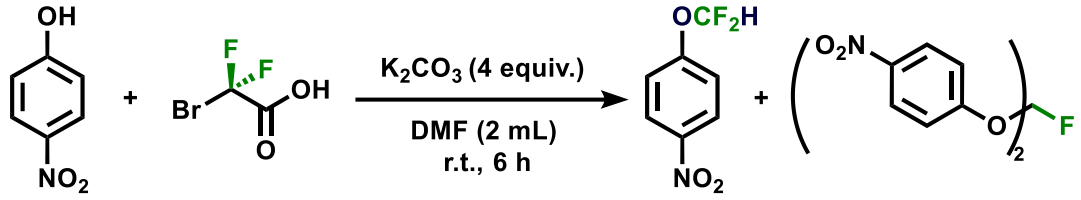
1. General information

Unless otherwise stated, all experiments were performed in a 15 mL borosilicate glass vial purchased from local glassware supplier. Gram scale synthesis was carried out in a 500 mL Schlenk flask. All chemicals obtained from BLD, TCI, and Merck (formerly called Sigma-Aldrich) were used directly without further purification. $BrCF_2CO_2H$ was purchased from BLD (Cat. No. BD41626, CAS No. 354-08-5) and used without further purification. To get the best reproducibility, it is advised to use the freshly purchased $BrCF_2CO_2H$ and store it in a refrigerator. DMF solvent was purchased from SRL (CAS No. 68-12-2, Product No. 79121) and used without further drying. Column chromatography was carried out using silica gel (60–120 mesh). Throughout the experiments, Merck precoated TLC plates (silica gel 60 F254, 0.25 mm) were used for analysis and visualized with UV light. All NMR spectra were recorded on Bruker Avance 400 MHz spectrometer (for ^{1}H NMR at 400 MHz, for $^{13}C\{1H\}$ NMR at 100 MHz, and for ^{19}F NMR at 376 MHz) at 298 K using DMSO-d_6 and $CDCl_3$ as solvents. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 ppm and C: δ = 77.0 ppm) and in DMSO-d_6 (H: δ = 2.5 ppm and C: δ = 39.5 ppm) as the internal standard, and coupling constants (J) are indicated in Hz. The multiplicity is represented by the letters s, d, t, q, dt, td, dd, and m, which stand for singlet, doublet, triplet, quadruplet, doublet of triplets, triplet of doublets, doublet of doublets, and multiplet, respectively. High-resolution mass spectra (HRMS) were recorded on an Agilent LCMS Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. The crystal structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 1.5-alpha (Dolomanov et al., 2009) as the graphical interface. The model was refined with XL (Sheldrick, 2008) using full matrix least squares minimisation on F^2.

2. Optimization table for the difluoromethylation of 4-Nitrophenol

Table S1. Optimization of difluoromethylation of 4-Nitrophenol[a]



1 1.5 equiv. 1a 1b

Entry	Deviation from the above	Yield 1a [%]	Yield 1b [%]
1	^{t}BuOK (7.0 equiv.)	82	<10
2	NaOH (7.0 equiv.)	80	16
3	KOH (7.0 equiv.)	89	<10
4	Na_2CO_3 (7.0 equiv.)	62	32
5	$NaHCO_3$ (7.0 equiv.)	42	29
6	NaOMe (7.0 equiv.)	84	<10
7	Et_3N (7.0 equiv.)	73	Trace
8	CH_3CN	43	15
9	Benzene	39	30
10	THF	30	0
11	H_2O	<10	Trace
12	MeOH	32	Trace
13	DMF/H_2O (8:2)	41	Trace

[a] ^{19}F NMR yield were determined using Hexafluorobenzene as an internal standard.

3. Plausible reaction mechanism for the difluoromethylation of phenols.

According to the plausible reaction mechanism, the first step of the reaction involves the abstraction of a proton from phenol **(43)** to generate a phenolate ion **(44)** in the presence of K_2CO_3 as a base. At the same time, bromo(difluoro)acetic acid also generates difluorocarbene precursor (:CF_2) with the release of CO_2 gas in the presence of K_2CO_3. Next, the generated nucleophilic phenolate ion immediately combines with electrophilic difluorocarbene precursor to generate intermediate **45**, which is also supported by the short half-life time of carbene intermediates. It is hypothesized that intermediate **45** generates a more stable aryloxyfluoromethane carbene intermediate (**46**) through the release of the KF molecule. Now, this intermediate **46** reacts with another phenolate ion **(44)** to generate a potassium salt of bis(aryloxy)fluoromethane anion **(47)** and then, by protonation, leads to the formation of bis(aryloxy)fluoromethane moiety (**48**). The intermediate **48** is an isolable and stable molecule, which was isolated as **1b** for 4-nitrophenol and characterized with NMR spectroscopy and HRMS. The final step of the reaction involves the release of phenolate ion from **48** to generate an oxonium intermediate (**49**), which upon a nucleophilic attack by *in situ* generated KF molecule leads to the formation of aryl difluroromethyl ether (**50**) as a final product (**Figure S1**).

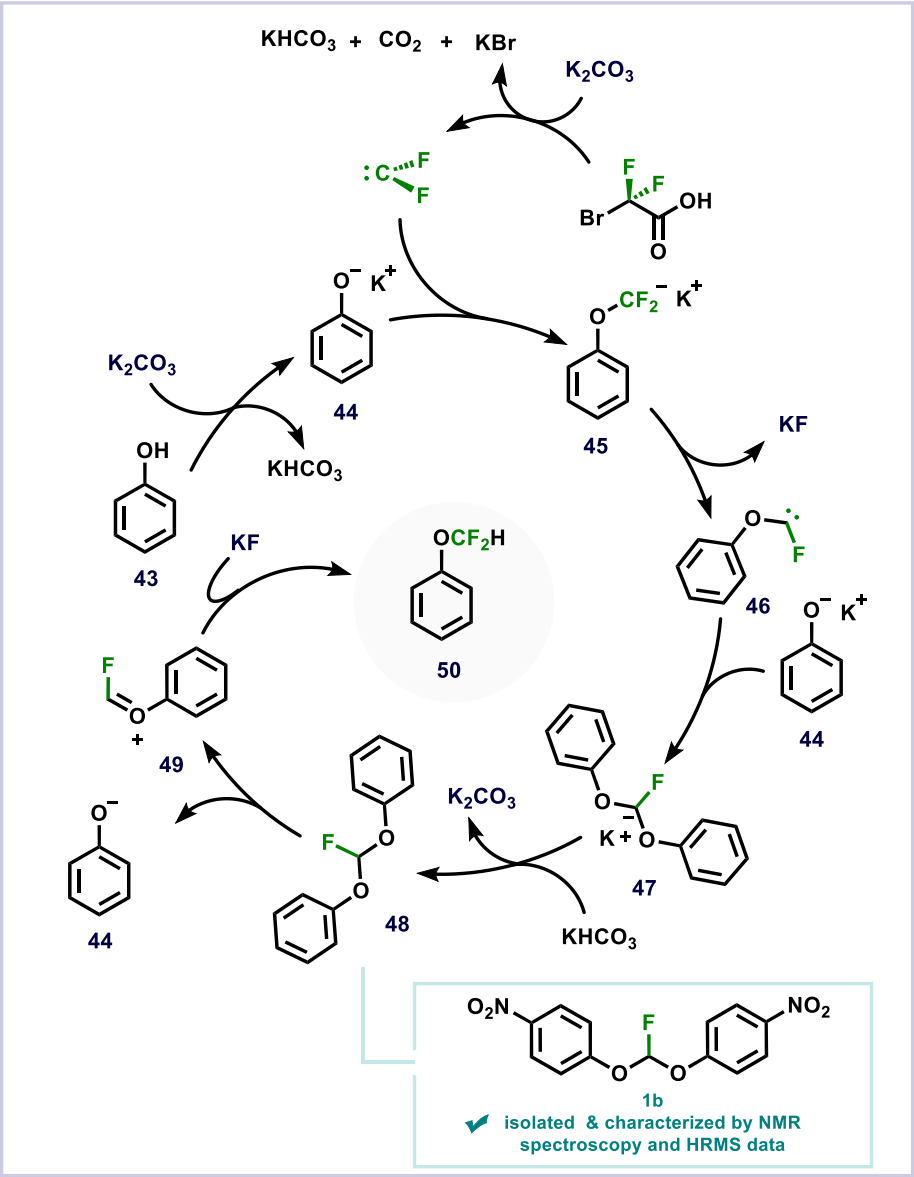


Figure S1. Plausible reaction mechanism for the difluoromethylation of phenols.

4. General procedure for the difluoromethylation of phenols using bromo(difluoro)acetic acid.

An oven-dried 15 mL borosilicate glass vial was charged with a magnetic stir bar, Phenol reactant (0.5 mmol), K_2CO_3 (4.0 equiv.), $BrCF_2CO_2H$ (1.5 equiv.), and DMF (2 mL). This borosilicate glass vial was then closed properly and sealed by applying a layer of Teflon tape (**Figure S2**). The reaction mixture was allowed to stir at room temperature for 6 to 24 h. After completion of the reaction, the crude reaction mixture was analysed through the Merck precoated TLC plates by using UV light. Then 20 mL of ice-cold water was added to the crude reaction mixture and the aqueous solution was extracted twice by ethyl acetate (2×20 mL). The combined organic phase was washed with saturated brine solution twice (2×10 mL), dried over anhydrous Na_2SO_4, then filtered and concentrated in vacuo. The residue was subjected to the silica-gel column chromatography using petroleum ether or petroleum ether /ethyl

acetate as the eluent to obtain a pure desired product, which was further analysed by NMR spectral data and HRMS data.

Figure S2. 15 mL borosilicate glass vial.

5. EcoScale calculation

For the calculation of EcoScale value, the model reaction from 4-Nitrophenol (**1**) to **1a** has been considered; the following website has been used: https://ecoscale.cheminfo.org/calculator

The data entered in the website are the following

- 0.5 mmol (1.0 equiv.) 4-Nitrophenol
- 0.75 mmol (1.5 equiv.) $BrCF_2CO_2H$
- 2.0 mmol (4.0 equiv.) K_2CO_3
- 0.489 mmol 1-(Difluoromethoxy)-4-nitrobenzene (98% Yield)
- Technical set-up = Common set-up
- Temperature / Time = Room temperature, < 24 h
- Workup and purification = Adding solvent, Liquid-liquid extraction or washing, removal of solvent with bp < 150 °C, Classical chromatography.

Final EcoScale value = 70

6. 25-gram scale synthesis of (4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene (33)

An oven-dried 500 mL Schlenk flask was charged with a magnetic stir bar, 2,4-Bis(phenylsulfonyl)phenol reactant (25 gram, 66.7 mmol), K_2CO_3 (4.0 equiv.), and $BrCF_2CO_2H$ (1.5 equiv.) (**Figure S3**). After that, an empty balloon was fixed on the Schlenk of the Schlenk flask so that released CO_2 could be captured to avoid any kind of pressure generation in the flask, as it can be dangerous. Now, 100 mL DMF was added to the flask, and the flask was closed and sealed properly as it immediately started releasing CO_2 gas. The reaction mixture was allowed to stir at room temperature for 12 h (**Figure S3**). After completion of the reaction, the crude reaction mixture was analyzed through the Merck precoated TLC plates by using UV light. Then 250 mL of ice-cold water was added to the crude reaction mixture and the aqueous solution was extracted twice by ethyl acetate (2×200 mL). The

combined organic phase was washed with saturated brine solution twice (2×100 mL), dried over anhydrous Na_2SO_4, then filtered and concentrated in vacuo. The residue was subjected to the silica-gel column chromatography (60-120 mesh silica gel) using petroleum ether /ethyl acetate (9:1) as the eluent to obtain 97% isolated yield of the targeted (4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene (**33**) as a light Brown solid.

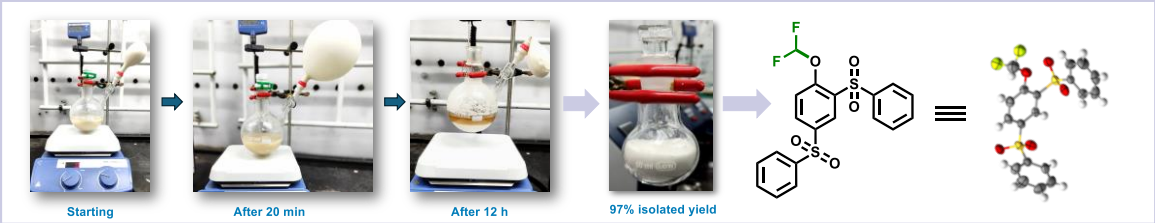
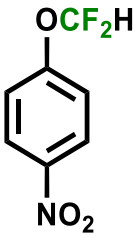


Figure S3. 25-gram scale synthesis of (4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene

7. Characterization data of products

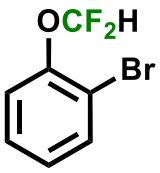
1-(Difluoromethoxy)-4-nitrobenzene (**1**)[1]



1

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (69.6 mg) of 4-Nitrophenol for 6 h to afford a 98% (92.7 mg) isolated yield of the desired product 1-(Difluoromethoxy)-4-nitrobenzene (**1**) as yellow oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 9.2 Hz, 2H), 7.25 (d, *J* = 9.1 Hz, 2H), 6.64 (t, *J* = 72.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.7 (t, *J* = 2 Hz), 144.9, 125.9, 119.4, 115.1 (t, *J* = 262 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.6 (d, *J* = 75.2 Hz, 2F).

1-Bromo-2-(difluoromethoxy)benzene (**2**)[6]

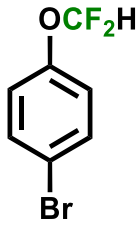


2

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (86.5 mg) of 2-Bromophenol for 12 h to afford a 69% (77.0 mg) isolated yield of the desired product 1-Bromo-2-(difluoromethoxy)benzene (**2**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether

as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.36 – 7.28 (m, 1H), 7.22 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.11 (td, *J* = 7.7, 1.5 Hz, 1H), 6.53 (t, *J* = 73.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.2, 134.0, 128.8, 127.1, 121.7, 116.0 (t, *J* = 260 Hz), 115.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.3 (d, *J* = 75.2 Hz, 2F).

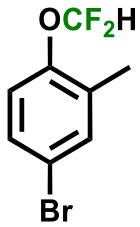
1-Bromo-4-(difluoromethoxy)benzene (**3**)[1]



3

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (86.5 mg) of 4-Bromophenol for 12 h to afford a 73% (81.4 mg) isolated yield of the desired product 1-Bromo-4-(difluoromethoxy)benzene (**3**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.48 (t, *J* = 73.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.2, 132.9, 121.7, 118.6, 115.7 (t, *J* = 260 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.2 (d, *J* = 71.4 Hz, 2F).

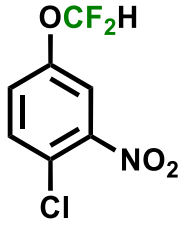
4-Bromo-1-(difluoromethoxy)-2-methylbenzene (**4**)



4

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (93.5 mg) of 4-Bromo-2-methylphenol for 12 h to afford a 67% (79.4 mg) isolated yield of the desired product 4-Bromo-1-(difluoromethoxy)-2-methylbenzene (**4**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 (s, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.50 (t, *J* = 73.7 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.7, 134.3, 132.6, 130.0, 120.9, 118.4, 116.1 (t, *J* = 260 Hz), 16.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.5 (d, *J* = 75.2 Hz, 2F). **HRMS (ESI)**: m/z: $[M]^+$ Calcd for $C_8H_7BrF_2O$: 235.9648; Found: 235.9618.

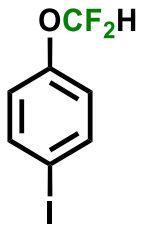
1-Chloro-4-(difluoromethoxy)-2-nitrobenzene (**5**)[2]



5

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (86.8 mg) of 4-Chloro-3-nitrophenol for 6 h to afford a 92% (103 mg) isolated yield of the desired product 1-Chloro-4-(difluoromethoxy)-2-nitrobenzene (**5**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 2.8 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.33 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.57 (t, *J* = 71.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.2 (t, *J* = 3 Hz), 148.2, 133.1, 125.1, 123.9, 117.5, 115.1 (t, *J* = 264 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.4 (d, *J* = 71.4 Hz, 2F).

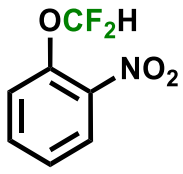
1-(Difluoromethoxy)-4-iodobenzene (**6**)[1]



6

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (110.0 mg) of 4-Iodophenol for 12 h to afford a 74% (100.0 mg) isolated yield of the desired product 1-(Difluoromethoxy)-4-iodobenzene (**6**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.49 (t, *J* = 73.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.0, 138.9, 121.9, 115.7 (t, *J* = 260 Hz), 89.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.2 (d, *J* = 75.2 Hz, 2F).

1-(Difluoromethoxy)-2-nitrobenzene (**7**)[1]

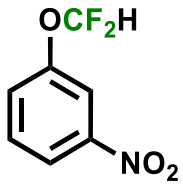


7

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (69.6 mg) of 2-Nitrophenol for 6 h to afford a 97% (91.7 mg) isolated yield of the desired product 1-(Difluoromethoxy)-2-nitrobenzene (**7**) as yellow

oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.70 – 7.53 (m, 1H), 7.39 (ddd, *J* = 5.9, 3.8, 1.5 Hz, 2H), 6.62 (t, *J* = 73.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.2 (t, *J* = 3 Hz), 142.9, 134.3, 126.5, 125.8, 123.6, 115.8 (t, *J* = 263 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.1 (d, *J* = -71.4 Hz, 2F).

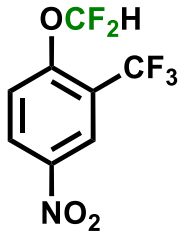
1-(Difluoromethoxy)-3-nitrobenzene (**8**)[3]



8

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (69.6 mg) of 3-Nitrophenol for 12 h to afford 51% (48.2 mg) isolated yield of the desired product 1-(Difluoromethoxy)-3-nitrobenzene (**8**) as light-yellow oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 – 8.05 (m, 1H), 7.99 (t, *J* = 2.0 Hz, 1H), 7.57 (t, *J* = 8.2 Hz, 1H), 7.48 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.61 (t, *J* = 72.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.2 (t, *J* = 3 Hz), 149.1, 130.7, 126.1, 120.5, 115.4 (t, *J* = 262 Hz), 115.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.1 (d, *J* = -71.4 Hz, 2F).

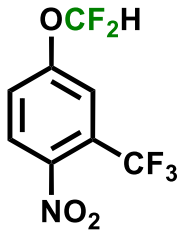
1-(Difluoromethoxy)-4-nitro-2-(trifluoromethyl)benzene (**9**)



9

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (103.6 mg) of 4-Nitro-2-(trifluoromethyl)phenol for 6 h to afford 94% (120.8 mg) isolated yield of the desired product 1-(Difluoromethoxy)-4-nitro-2-(trifluoromethyl)benzene (**9**) as yellow oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 1.9 Hz, 1H), 7.89 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 6.69 (t, *J* = 71.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.6, 142.5 (t, *J* = 2 Hz), 131.0 (q, *J* = 3 Hz), 128.9 (q, *J* = 35 Hz), 123.6, 123.5 (q, *J* = 3 Hz), 122.6 (q, *J* = 271 Hz), 115.3 (t, *J* = 266 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.8 (s, 3F), -82.6 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_8H_4F_5NO_3$: 258.0184; Found: 258.0170.

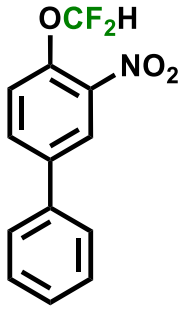
4-(Difluoromethoxy)-1-nitro-2-(trifluoromethyl)benzene (**10**)



10

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (103.6 mg) of 4-Nitro-3-(trifluoromethyl)phenol for 6 h to afford 92% (118.3 mg) isolated yield of the desired product 4-(Difluoromethoxy)-1-nitro-2-(trifluoromethyl)benzene (**10**) as yellow oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.9 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.67 (t, *J* = 71.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.4 (t, *J* = 2 Hz), 144.7, 127.7, 126.2 (q, *J* = 35 Hz), 122.9, 121.4 (q, *J* = 272 Hz), 119.4 (q, *J* = 5 Hz), 114.9 (t, *J* = 264 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -60.4 (s, 3F), -83.1 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_8H_4F_5NO_3$: 258.0184; Found: 258.0206.

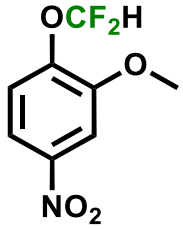
4-(Difluoromethoxy)-3-nitro-1,1'-biphenyl (**11**)



11

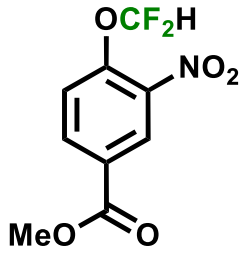
The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (107.6 mg) of 3-Nitro-[1,1'-biphenyl]-4-ol for 6 h to afford 98% (130.0 mg) isolated yield of the desired product 4-(Difluoromethoxy)-3-nitro-1,1'-biphenyl (**11**) as shine yellow solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (8:2) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 2.2 Hz, 1H), 7.81 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.71 – 7.38 (m, 6H), 6.66 (t, *J* = 73.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.9, 142.1 (t, *J* = 3 Hz), 140.0, 137.6, 132.4, 129.3, 128.8, 127.0, 123.9, 115.8 (t, *J* = 263 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.9 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+Na]^+$ Calcd for $C_{13}H_9F_2NO_3$: 288.0443; Found: 288.0448.

1-(Difluoromethoxy)-2-methoxy-4-nitrobenzene (**12**)



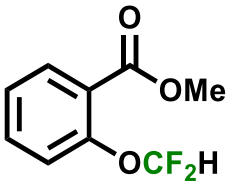
12 The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (84.6 mg) of 2-Methoxy-4-nitrophenol for 6 h to afford 93% (102.0 mg) isolated yield of the desired product 1-(Difluoromethoxy)-2-methoxy-4-nitrobenzene (**12**) as yellow oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.18 (d, *J* = 9.3 Hz, 1H), 6.60 (t, *J* = 73.8 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.2, 145.7, 144.9 (t, *J* = 3 Hz), 121.2, 116.7, 115.5 (t, *J* = 261 Hz), 107.9, 56.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.3 (d, *J* = 75.2 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_8H_7F_2NO_4$: 220.0416; Found: 220.0425.

Methyl 4-(difluoromethoxy)-3-nitrobenzoate (**13**)



13 The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (98.6 mg) of Methyl 4-hydroxy-3-nitrobenzoate for 6 h to afford 97% (119.9 mg) isolated yield of the desired product Methyl 4-(difluoromethoxy)-3-nitrobenzoate (**13**) as yellow oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 (s, 1H), 8.24 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 6.68 (t, *J* = 72.0 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.2, 146.4 (t, *J* = 3 Hz), 142.2, 135.0, 128.3, 127.1, 122.3, 115.4 (t, *J* = 266 Hz), 52.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.5 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_9H_7F_2NO_5$: 248.0365; Found: 248.0367.

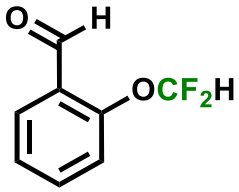
Methyl 2-(difluoromethoxy)benzoate (**14**)[4]



14

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (76.1 mg) of Methyl 2-hydroxybenzoate for 12 h to afford 92% (93.0 mg) isolated yield of the desired product Methyl 2-(difluoromethoxy)benzoate (**14**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65 – 7.47 (m, 1H), 7.44 – 7.19 (m, 2H), 6.57 (t, *J* = 74.8 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.7, 150.0 (t, *J* = 3 Hz), 133.7, 131.9, 126.2, 124.5, 123.1, 116.6 (t, *J* = 259 Hz), 52.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.7 (d, *J* = 75.2 Hz, 2F).

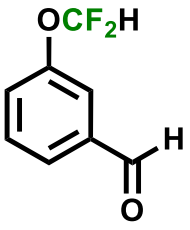
2-(Difluoromethoxy)benzaldehyde (**15**)[5]



15

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (61.1 mg) of 2-Hydroxybenzaldehyde for 12 h to afford 95% (81.8 mg) isolated yield of the desired product 2-(Difluoromethoxy)benzaldehyde (**15**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.37 (s, 1H), 7.90 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.69 – 7.43 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.67 (t, *J* = 72.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.6, 152.9 (t, *J* = 3 Hz), 135.8, 129.0, 127.7, 125.9, 119.8, 115.7 (t, *J* = 261 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.6 (d, *J* = 71.4 Hz, 2F).

3-(Difluoromethoxy)benzaldehyde (**16**)[2]

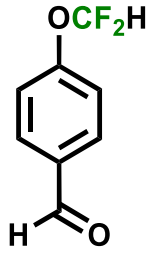


16

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (61.1 mg) of 3-Hydroxybenzaldehyde for 12 h to afford 52% (44.8 mg) isolated yield of the desired product 3-(Difluoromethoxy)benzaldehyde (**16**)

as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.97 (s, 1H), 7.79 – 7.66 (m, 1H), 7.60 (s, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.58 (t, *J* = 73.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.2, 151.7 (t, *J* = 3 Hz), 138.1, 130.7, 127.2, 125.8, 119.4, 115.62 (t, *J* = 260 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.6 (d, *J* = 71.4 Hz, 2F).

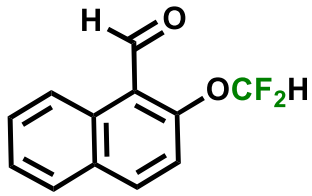
4-(Difluoromethoxy)benzaldehyde (**17**)[2]



17

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (61.1 mg) of 4-Hydroxybenzaldehyde for 12 h to afford 97% (83.5 mg) isolated yield of the desired product 4-(Difluoromethoxy)benzaldehyde (**17**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.94 (s, 1H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.63 (t, *J* = 72.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.8, 155.8 (t, *J* = 2 Hz), 133.4, 131.8, 119.2, 115.3 (t, *J* = 260 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.1 (d, *J* = 71.4 Hz, 2F).

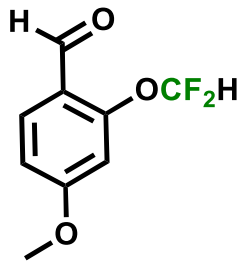
2-(Difluoromethoxy)-1-naphthaldehyde (**18**)



18

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (86.1 mg) of 2-hydroxy-1-Naphthaldehyde for 18 h to afford 78% (86.7 mg) isolated yield of the desired product 2-(Difluoromethoxy)-1-naphthaldehyde (**18**) as light brown solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.83 (s, 1H), 9.24 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 7.90 (t, *J* = 23.2 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 6.74 (t, *J* = 72.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.3, 154.7 (t, *J* = 3 Hz), 137.2, 131.4, 131.1, 130.3, 128.5, 126.9, 125.7, 121.5, 118.7, 115.9 (t, *J* = 261 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.8 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_{12}H_8F_2O_2$: 223.0565; Found: 223.0571.

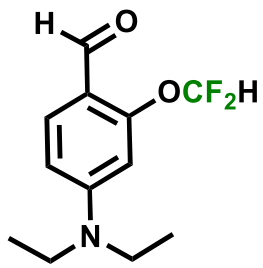
2-(Difluoromethoxy)-4-methoxybenzaldehyde (**19**)



19

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (76.1 mg) of 2-Hydroxy-4-methoxybenzaldehyde for 12 h to afford 92% (93.0 mg) isolated yield of the desired product 2-(difluoromethoxy)-4-methoxybenzaldehyde (**19**) as colourless liquid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.19 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 6.81 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.67 (d, *J* = 2.2 Hz, 1H), 6.64 (t, *J* = 72.9 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.3, 165.6, 154.6 (t, *J* = 3 Hz), 130.8, 121.3, 115.7 (t, *J* = 261 Hz), 111.4, 105.4, 55.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.6 (d, *J* = 75.2 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_9H_8F_2O_3$: 203.0514; Found: 203.0522.

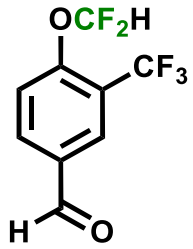
4-(Diethylamino)-2-(difluoromethoxy)benzaldehyde (**20**)



20

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (96.6 mg) of 4-(Diethylamino)-2-hydroxybenzaldehyde for 12 h to afford 79% (96.1 mg) isolated yield of the desired product 4-(Diethylamino)-2-(difluoromethoxy)benzaldehyde (**20**) as Blue Oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (19:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.01 (s, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 6.59 (t, *J* = 73.7 Hz, 1H), 6.50 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.26 (d, *J* = 1.9 Hz, 1H), 3.40 (q, *J* = 7.1 Hz, 4H), 1.20 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 186.5, 155.5 (t, *J* = 3 Hz), 153.4, 131.1, 116.2 (t, *J* = 259 Hz), 116.1, 108.6, 100.9, 44.9, 12.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.6 (d, *J* = 75.2 Hz, 2F). **HRMS (ESI)**: m/z: $[M+Na]^+$ Calcd for $C_{12}H_{15}F_2NO_2$: 266.0963; Found: 266.0963.

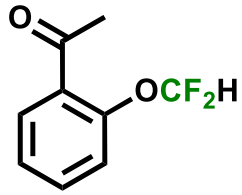
4-(Difluoromethoxy)-3-(trifluoromethyl)benzaldehyde (**21**)



21

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (95.1 mg) of 4-Hydroxy-3-(trifluoromethyl)benzaldehyde for 12 h to afford 90% (108.1 mg) isolated yield of the desired product 4-(Difluoromethoxy)-3-(trifluoromethyl)benzaldehyde (**21**) as light-yellow oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.01 (s, 1H), 8.20 (d, *J* = 1.8 Hz, 1H), 8.10 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 6.67 (t, *J* = 71.7 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.5, 153.0, 134.8, 132.9, 129.2 (q, *J* = 5 Hz), 122.9 (q, *J* = 33 Hz), 122.3 (q, *J* = 271 Hz), 119.8, 115.2 (t, *J* = 264 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.38 (s, 3F), -82.3 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_9H_5F_5O_2$: 241.0282; Found: 241.0279.

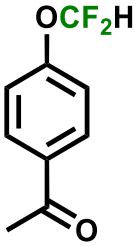
1-(2-(Difluoromethoxy)phenyl)ethan-1-one (**22**)[7]



22

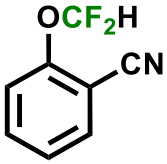
The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (68.1 mg) of 1-(2-Hydroxyphenyl)ethan-1-one for 12 h to afford 82% (76.3 mg) isolated yield of the desired product 1-(2-(Difluoromethoxy)phenyl)ethan-1-one (**22**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 6.62 (t, *J* = 73.4 Hz, 1H), 2.64 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.7, 149.6 (t, *J* = 3 Hz), 133.5, 131.6, 130.6, 125.8, 119.8, 116.2 (t, *J* = 259 Hz), 31.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.8 (d, *J* = 75.2 Hz, 2F).

1-(4-(Difluoromethoxy)phenyl)ethan-1-one (**23**)[2]



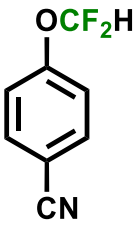
23 The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (68.1 mg) of 1-(4-Hydroxyphenyl)ethan-1-one for 12 h to afford 85% (79.1 mg) isolated yield of the desired product 1-(4-(Difluoromethoxy)phenyl)ethan-1-one (**23**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.59 (t, *J* = 73.1 Hz, 1H), 2.56 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.7, 154.8, 134.1, 130.5, 118.8, 115.4 (t, *J* = 259 Hz), 26.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.9 (d, *J* = 71.4 Hz, 2F).

2-(Difluoromethoxy)benzonitrile (**24**)[3]



24 The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (59.5 mg) of 2-Hydroxybenzonitrile for 12 h to afford 89% (75.3 mg) isolated yield of the desired product 2-(Difluoromethoxy)benzonitrile (**24**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (ddd, *J* = 9.6, 8.9, 1.3 Hz, 2H), 7.31 (dd, *J* = 12.7, 4.8 Hz, 2H), 6.68 (t, *J* = 72.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.9 (t, *J* = 2 Hz), 134.5, 133.9, 125.7, 119.6, 115.2 (t, *J* = 264 Hz), 115.0, 105.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.4 (d, *J* = 71.4 Hz, 2F).

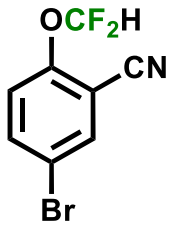
4-(Difluoromethoxy)benzonitrile (**25**)[3]



25 The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (59.5 mg) of 4-Hydroxybenzonitrile for 12 h to afford 90% (76.1 mg)

isolated yield of the desired product 4-(Difluoromethoxy)benzonitrile (**25**) as colourless solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 9.0 Hz, 2H), 7.21 (d, *J* = 8.9 Hz, 2H), 6.60 (t, *J* = 72.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.2, 134.3, 119.9, 118.2, 115.2 (t, *J* = 261 Hz), 109.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.3 (d, *J* = 71.4 Hz, 2F).

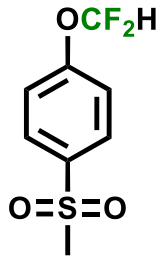
5-Bromo-2-(difluoromethoxy)benzonitrile (**26**)



26

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (99.0 mg) of 5-Bromo-2-hydroxybenzonitrile for 12 h to afford 91% (112.8 mg) isolated yield of the desired product 5-Bromo-2-(difluoromethoxy)benzonitrile (**26**) as white solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 2.4 Hz, 1H), 7.72 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.23 (d, *J* = 8.9 Hz, 1H), 6.64 (t, *J* = 71.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.8 (t, *J* = 3 Hz), 137.5, 136.3, 121.9, 118.5, 114.9 (t, *J* = 266 Hz), 113.4, 108.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.6 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_8H_4BrF_2NO$: 247.9517; Found: 247.9525.

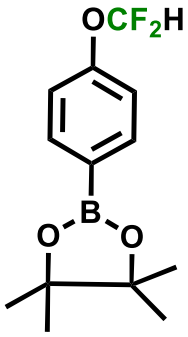
1-(Difluoromethoxy)-4-(methylsulfonyl)benzene (**27**)[2]



27

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (86.1 mg) of 4-(Methylsulfonyl)phenol for 12 h to afford 87% (96.7 mg) isolated yield of the desired product 1-(Difluoromethoxy)-4-(methylsulfonyl)benzene (**27**) as white solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (7:3) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.65 (t, *J* = 72.5 Hz, 1H), 3.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.0 (t, *J* = 2 Hz), 137.1, 129.7, 119.6, 115.2 (t, *J* = 261 Hz), 44.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.4 (d, *J* = 71.4 Hz, 2F).

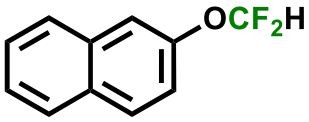
2-(4-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**)[8]



28

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (110.0 mg) of 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol for 18 h to afford 54% (73.0 mg) isolated yield of the desired product 2-(4-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**) as white solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (19:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.54 (t, *J* = 73.8 Hz, 1H), 1.34 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.9 (t, *J* = 2 Hz), 136.8, 118.4, 115.9 (t, *J* = 258 Hz), 84.1, 24.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.9 (d, *J* = 75.2 Hz, 2F).

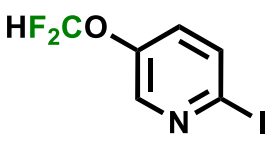
2-(Difluoromethoxy)naphthalene (**29**)[1]



29

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (71.1 mg) of Naphthalen-2-ol for 12 h to afford 77% (74.8 mg) isolated yield of the desired product 2-(Difluoromethoxy)naphthalene (**29**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (dd, *J* = 17.9, 8.5 Hz, 3H), 7.68 – 7.46 (m, 3H), 7.30 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.65 (t, *J* = 74.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.1 (t, *J* = 3 Hz), 133.9, 131.2, 130.2, 127.9, 127.6, 127.1, 125.8, 119.8, 116.2 (t, *J* = 258 Hz), 115.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.5 (d, *J* = 75.2 Hz, 2F).

5-(Difluoromethoxy)-2-iodopyridine (**30**)

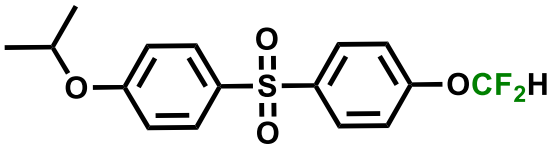


30

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (110.5 mg) of 6-Iodopyridin-3-ol for 12 h to

afford 85% (115.2 mg) isolated yield of the desired product 5-(Difluoromethoxy)-2-iodopyridine (**30**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (3:2) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.35 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.20 (dd, *J* = 8.1, 4.7 Hz, 1H), 6.52 (t, *J* = 72.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.1 (t, *J* = 2 Hz), 147.6, 127.2, 123.7, 115.5 (t, *J* = 264 Hz), 114.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.7 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_6H_4F_2INO$: 271.9378; Found: 271.9376.

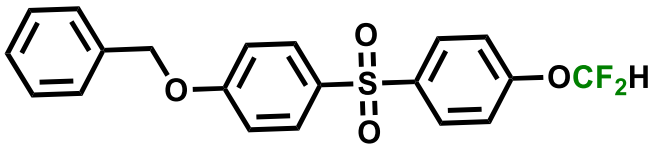
1-(Difluoromethoxy)-4-((4-isopropoxyphenyl)sulfonyl)benzene (**31**)



31

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (146.2 mg) of 4-((4-Isopropoxyphenyl)sulfonyl)phenol for 12 h to afford 97% (165.9 mg) isolated yield of the desired product 1-(Difluoromethoxy)-4-((4-isopropoxyphenyl)sulfonyl)benzene (**31**) as brown solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (8:2) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.57 (t, *J* = 72.7 Hz, 1H), 4.59 (dt, *J* = 12.1, 6.1 Hz, 1H), 1.31 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.1, 154.3 (t, *J* = 3 Hz), 139.2, 132.2, 129.9, 129.6, 119.5, 115.9, 115.3 (t, *J* = 261 Hz), 70.57, 21.80. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.2 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+NH_4]^+$ Calcd for $C_{16}H_{16}F_2O_4S$: 360.1076; Found: 360.1080.

1-(Benzyloxy)-4-((4-(difluoromethoxy)phenyl)sulfonyl)benzene (**32**)

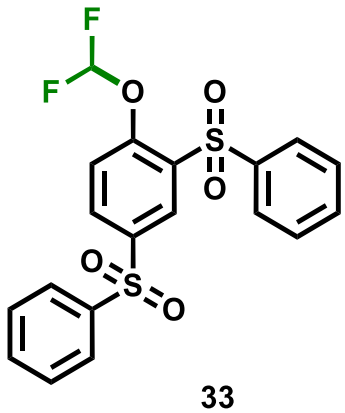


32

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (170.2 mg) of 4-((4-(Benzyloxy)phenyl)sulfonyl)phenol for 12 h to afford 98% (191.3 mg) isolated yield of the desired product 1-(Benzyloxy)-4-((4-(difluoromethoxy)phenyl)sulfonyl)benzene (**32**) as white solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (8:2) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (dd, *J* = 25.4, 8.8 Hz, 4H), 7.49 – 7.30 (m, 5H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.57 (t, *J* = 72.6 Hz,

1H), 5.10 (s, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.7, 154.4 (t, *J* = 2 Hz), 139.1, 135.8, 133.2, 129.9, 129.7, 128.9, 128.5, 127.6, 119.6, 115.5, 115.3 (t, *J* = 261 Hz), 70.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.1 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+NH_4]^+$ Calcd for $C_{20}H_{16}F_2O_4S$: 408.1076; Found: 408.1083.

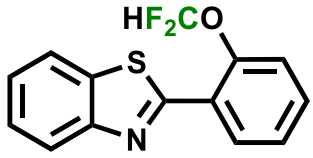
(4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene (**33**)



33

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (187.2 mg) of 2,4-Bis(phenylsulfonyl)phenol for 12 h to afford 98% (207.7 mg) isolated yield of the desired product (4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene (**33**) as light brown solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (8:2) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.76 (d, *J* = 2.3 Hz, 1H), 8.14 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.92 (dd, *J* = 12.2, 4.4 Hz, 4H), 7.64 – 7.56 (m, 2H), 7.55 – 7.41 (m, 4H), 7.29 (d, *J* = 8.7 Hz, 1H), 6.57 (t, *J* = 72.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.6 (t, *J* = 3 Hz), 140.2, 139.3, 139.0, 134.8, 134.2, 134.0, 133.7, 129.7, 129.7, 129.1, 128.6, 127.8, 120.5, 115.1 (t, *J* = 264 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -82.7 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}F_2O_5S_2$: 425.0323; Found: 425.0328.

2-(2-(Difluoromethoxy)phenyl)benzo[d]thiazole (**34**)

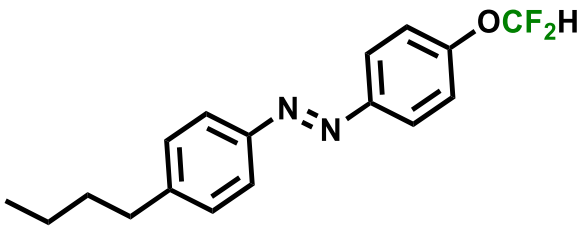


34

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (113.6 mg) of 2-(2-Hydroxyphenyl)benzothiazole for 12 h to afford 96% (133.0 mg) isolated yield of the desired product 2-(2-(Difluoromethoxy)phenyl)benzo[d]thiazole (**34**) as light brown solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.23 – 7.15 (m, 2H), 7.11 (td, *J* = 7.7, 1.1 Hz, 1H), 7.03 (dd, *J*

= 8.3, 0.7 Hz, 1H), 6.48 (t, *J* = 73.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.8, 152.3, 148.7 (t, *J* = 3 Hz), 136.0, 131.6, 130.5, 126.2, 125.8, 125.4, 125.3, 123.2, 121.4, 119.3, 116.2 (t, *J* = 260 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -80.3 (d, *J* = 75.2 Hz, 2F). **HRMS (ESI)**: m/z: $[M+Na]^+$ Calcd for $C_{14}H_9F_2NOS$: 300.0265; Found: 300.0260.

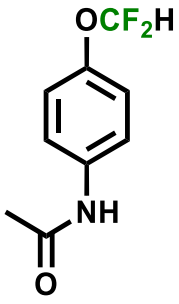
1-(4-butylphenyl)-2-(4-(difluoromethoxy)phenyl)diazene (**35**)



35

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (127.1 mg) of 4-(4-Butylphenylazo)phenol for 18 h to afford 79% (120.2 mg) isolated yield of the desired product 1-(4-butylphenyl)-2-(4-(difluoromethoxy)phenyl)diazene (**35**) as yellow solid. The product was purified with preparative TLC separation technique by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.50 (t, *J* = 73.5 Hz, 1H), 2.77 – 2.47 (m, 2H), 1.56 (dt, *J* = 15.4, 7.6 Hz, 2H), 1.31 (dt, *J* = 14.9, 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.9 (t, *J* = 3 Hz), 150.9, 150.1, 146.9, 129.3, 124.5, 123.0, 119.8, 115.8 (t, *J* = 259 Hz), 35.7, 33.6, 22.5, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.1 (d, *J* = 71.4 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}F_2N_2O$: 305.1460; Found: 305.1437.

N-(4-(Difluoromethoxy)phenyl)acetamide (**36**)[4]

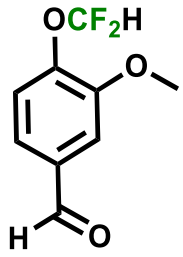


36

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (75.6 mg) of N-(4-Hydroxyphenyl)acetamide for 24 h to afford 69% (69.4 mg) isolated yield of the desired product N-(4-(Difluoromethoxy)phenyl)acetamide (**36**) as brown solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (8:2) as an eluent**. ^{1}H NMR (400 MHz, DMSO)** δ 10.13 (s, 1H), 7.63 (d, *J* = 9.0 Hz, 2H), 7.11 (t, *J* = 74.4 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 2.04 (s, 3H). **^{13}C NMR (100 MHz,**

DMSO) δ 168.4, 146.1 (t, *J* = 3 Hz), 136.8, 120.4, 119.5, 116.6 (t, *J* = 256 Hz), 23.9. **^{19}F NMR (376 MHz, DMSO)** δ -81.4 (d, *J* = 75.2 Hz, 2F).

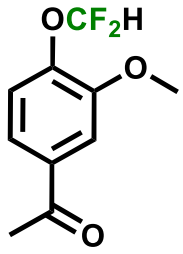
4-(Difluoromethoxy)-3-methoxybenzaldehyde (**37**)[4]



37

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (76.1 mg) of Vanillin for 12 h to afford 90% (91.0 mg) isolated yield of the desired product 4-(Difluoromethoxy)-3-methoxybenzaldehyde (**37**) as white solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent**. ^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.93 (s, 1H), 7.66 – 7.39 (m, 2H), 7.29 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.67 (t, *J* = 74.2 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 190.9, 151.6, 144.9, 134.6, 125.1, 121.5, 115.7 (t, *J* = 260 Hz), 111.0, 56.2. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -82.0 (d, *J* = 75.2 Hz, 2F).

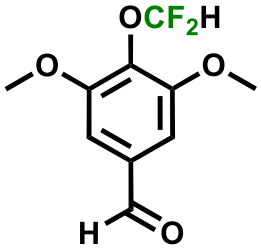
1-(4-(Difluoromethoxy)-3-methoxyphenyl)ethan-1-one (**38**)



38

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (83.0 mg) of Acetovanillone for 12 h to afford 86% (93.0 mg) isolated yield of the desired product 1-(4-(Difluoromethoxy)-3-methoxyphenyl)ethan-1-one (**38**) as white solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.56 (d, *J* = 1.8 Hz, 1H), 7.51 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 6.64 (t, *J* = 74.5 Hz, 1H), 3.91 (s, 3H), 2.57 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 196.8, 150.9, 143.9 (t, *J* = 3 Hz), 135.3, 122.2, 121.1, 115.8 (t, *J* = 259 Hz), 111.6, 56.1, 26.5. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -81.9 (d, *J* = 75.2 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_{10}H_{10}F_2O_3$: 217.0671; Found: 217.0678.

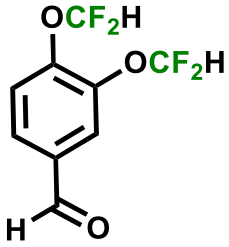
4-(Difluoromethoxy)-3,5-dimethoxybenzaldehyde (**39**)



39

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (91.1 mg) of Syringaldehyde for 12 h to afford 79% (91.7 mg) isolated yield of the desired product 4-(Difluoromethoxy)-3,5-dimethoxybenzaldehyde (**39**) as white solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (9:1) as an eluent. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.86 (s, 1H), 7.11 (s, 2H), 6.63 (t, *J* = 75.9 Hz, 1H), 3.91 (s, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 190.9, 153.5, 134.2, 133.9, 116.3 (t, *J* = 259 Hz), 106.3, 56.5. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -81.8 (d, *J* = 78.9 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_{10}H_{10}F_2O_4$: 233.0620; Found: 233.0627.

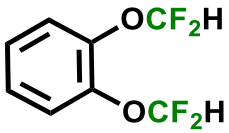
3,4-Bis(difluoromethoxy)benzaldehyde (**40**)



40

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (69.1 mg) of Protocatechuic aldehyde in the presence of 3.0 equivalent of $BrCF_2CO_2H$, and 8.0 equivalents of K_2CO_3 in 3 mL of DMF for 24 h to afford 82% (97.6 mg) isolated yield of the desired product 3,4-Bis(difluoromethoxy)benzaldehyde (**40**) as colourless liquid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether /ethyl acetate (8:2) as an eluent. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.93 (s, 1H), 7.93 – 7.56 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 1H), 6.62 (td, *J* = 72.7, 15.4 Hz, 2H from $2CF_2H$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 189.9, 147.1 (t, *J* = 3 Hz), 142.5, 134.4, 128.7, 122.3, 121.6, 115.6 (t, *J* = 263 Hz), 115.4 (t, *J* = 263 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -81.9 (d, *J* = 45.1 Hz, 2F), -82.2 (d, *J* = 45.2 Hz, 2F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_9H_6F_4O_3$: 239.0326; Found: 239.0335.

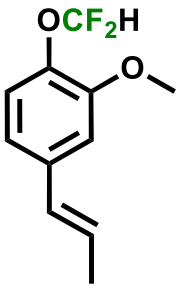
1,2-Bis(difluoromethoxy)benzene (**41**)



41

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (55.1 mg) of Catechol in the presence of 3.0 equivalent of $BrCF_2CO_2H$, and 8.0 equivalents of K_2CO_3 in 3 mL of DMF for 24 h to afford 62% (65.1 mg) isolated yield of the desired product 1,2-Bis(difluoromethoxy)benzene (**41**) as brownish oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 – 7.09 (m, 4H), 6.56 (t, *J* = 73.7 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.5, 126.8, 122.6, 116.0 (t, *J* = 260 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.4 (d, *J* = 71.4 Hz, 4F). **HRMS (ESI)**: m/z: $[M+H]^+$ Calcd for $C_8H_6F_4O_2$: 211.0377; Found: 211.0375.

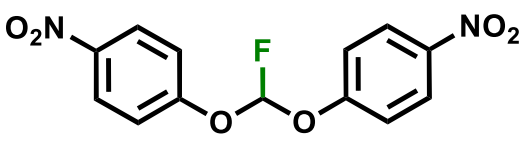
(E)-1-(Difluoromethoxy)-2-methoxy-4-(prop-1-en-1-yl)benzene (**42**)[2]



42

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (82.1 mg) of Isoeugenol for 12 h to afford 73% (78.2 mg) isolated yield of the desired product (E)-1-(Difluoromethoxy)-2-methoxy-4-(prop-1-en-1-yl)benzene (**42**) as colourless oil. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.08 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 6.88 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.52 (t, *J* = 75.3 Hz, 1H), 6.42 – 6.32 (m, 1H), 6.29 – 6.18 (m, 1H), 3.88 (s, 3H), 1.89 (dd, *J* = 6.6, 1.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.2, 138.9 (t, *J* = 3 Hz), 136.9, 130.3, 126.6, 122.4, 118.6, 116.4 (t, *J* = 258 Hz), 109.9, 55.9, 18.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -81.3 (d, *J* = 71.4 Hz, 2F).

4,4'-((Fluoromethylene)bis(oxy))bis(nitrobenzene) (**1b**)



1b

The general procedure of *O*-difluoromethylation of phenols using bromo(difluoro)acetic acid was followed with 0.5 mmol (69.5 mg) of 4-Nitrophenol and

1.0 equivalent of K_2CO_3 for 6 h to afford 35% (27.0 mg) isolated yield of the desired product 4,4'-((Fluoromethylene)bis(oxy))bis(nitrobenzene) (**1b**) as white solid. The product was purified with silica-gel (60-120 mesh) column chromatography by using petroleum ether as an eluent. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 9.2 Hz, 4H), 7.27 (d, *J* = 9.1 Hz, 4H), 6.81 (d, *J* = 72.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 156.9, 144.5, 126.0, 118.5, 113.0 (d, *J* = 251 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -85.2 (d, *J* = 71.4 Hz, 1F). **HRMS (ESI)**: m/z: $[M+NH_4]^+$ Calcd for $C_{13}H_9FN_2O_6$: 326.0783; Found: 326.0787.

8. References

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9. X-Ray crystallographic data of (4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene (33)

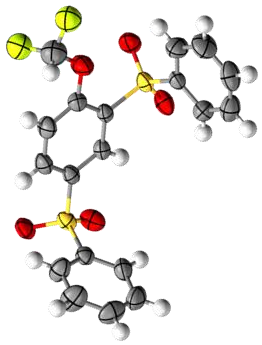

Figure S4. X-ray crystal structure of **33** displacement ellipsoid is drawn at 57% probability level. The title compound was recrystallized from $CHCl_3$/EtOAC, by slow evaporation of solvent. Slight disorder was found in the crystal structure.

Table S2. Crystal data and structure refinement of compound **33** (**CCDC: 2380891**)

Empirical formula	$C_{19}H_{14}F_2O_5S_2$
Formula weight	424.42
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	7.2477(2)
b/Å	9.2848(3)
c/Å	14.6674(4)
α/°	99.9870(10)
β/°	97.5440(10)
γ/°	105.3410(10)
Volume/Å^3	920.97(5)
Z	2
ρ_{calc}g/cm^3	1.530
μ/mm^{-1}	0.338
F(000)	436.0
Crystal size/mm^3	0.455 × 0.176 × 0.061
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.66 to 54.424
Index ranges	-8 ≤ h ≤ 9, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18
Reflections collected	21103

Independent reflections	4075 [R_{int} = 0.0461, R_{sigma} = 0.0330]
Data/restraints/parameters	4075/66/281
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0526, wR_2 = 0.1285
Final R indexes [all data]	R_1 = 0.0665, wR_2 = 0.1374
Largest diff. peak/hole / e $Å^{-3}$	0.84/-0.79

10. Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra of products

Figure S5: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-nitrobenzene (**1**).

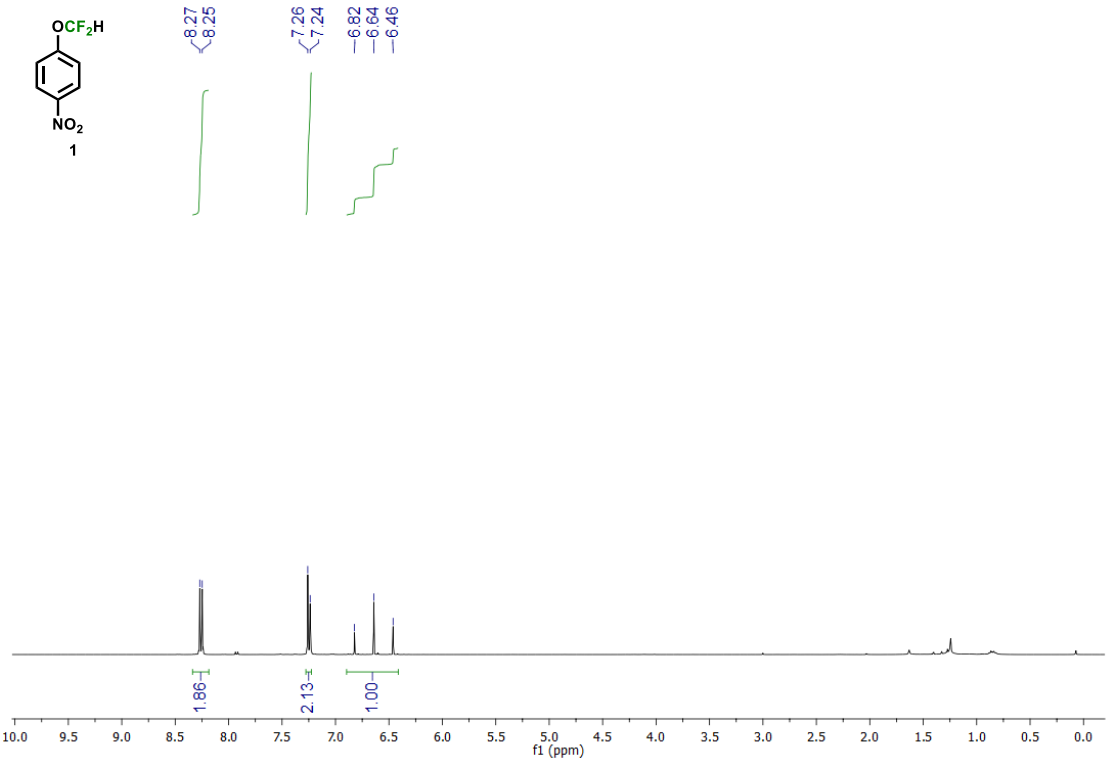

Figure S6: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-nitrobenzene (**1**).

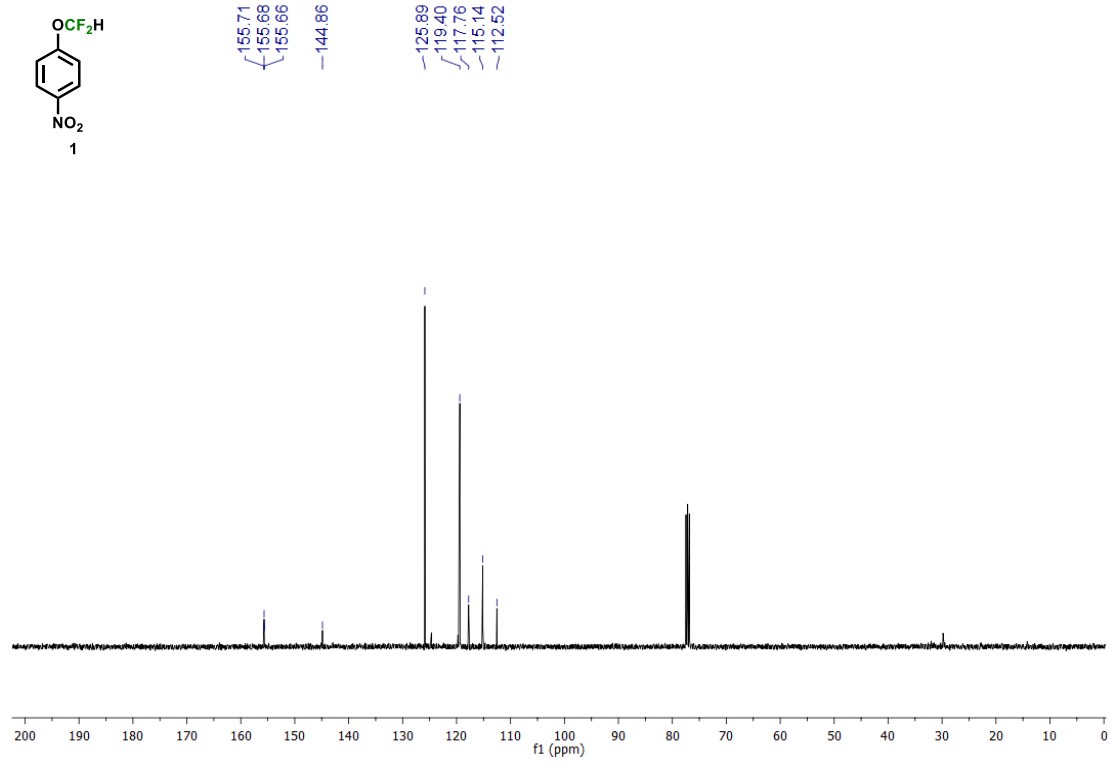

Figure S7: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-nitrobenzene (**1**).

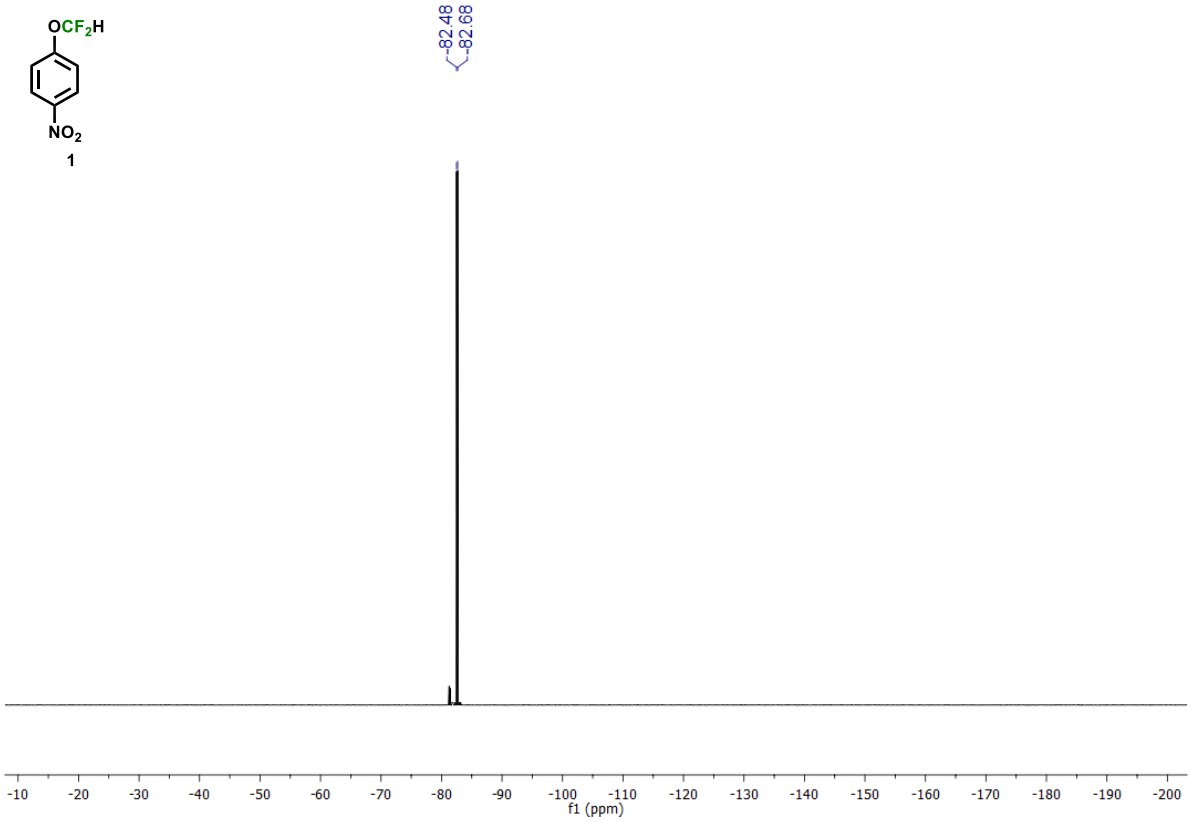

Figure S8: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-Bromo-2-(difluoromethoxy)benzene (**2**).

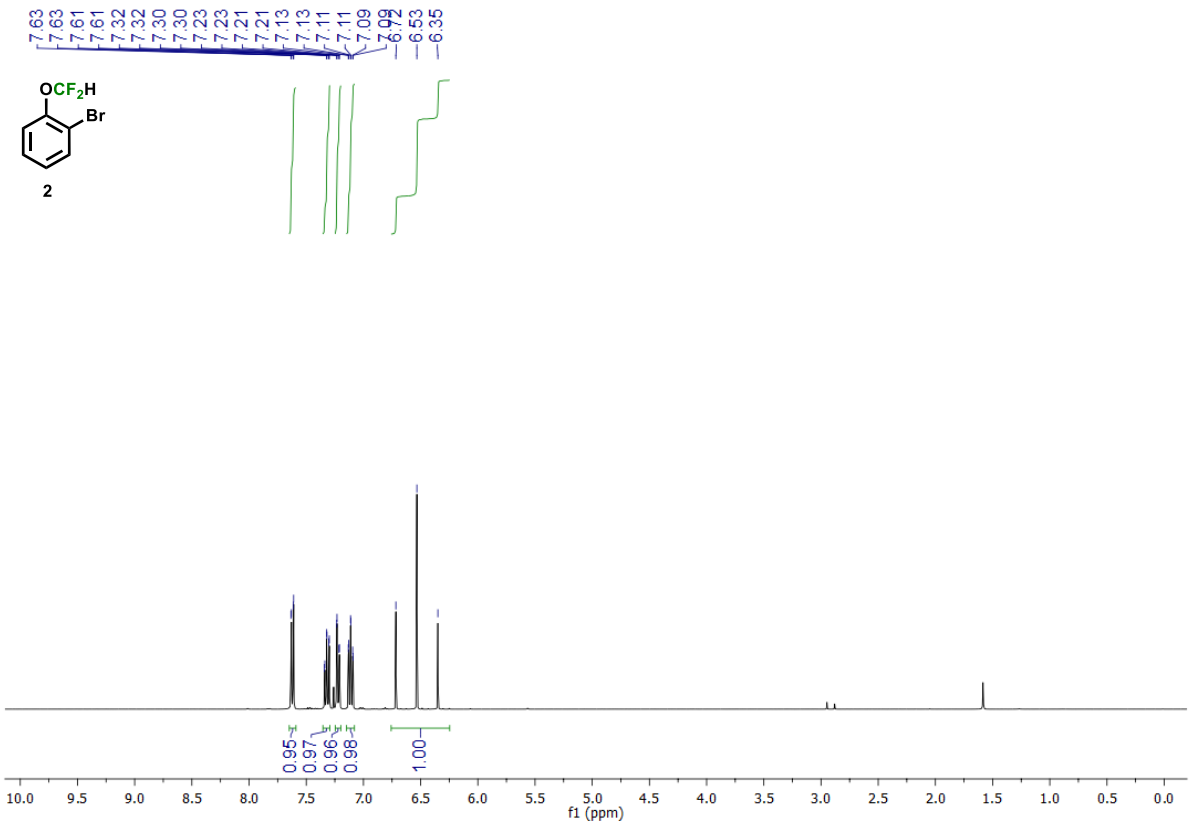

Figure S9: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-Bromo-2-(difluoromethoxy)benzene (**2**).

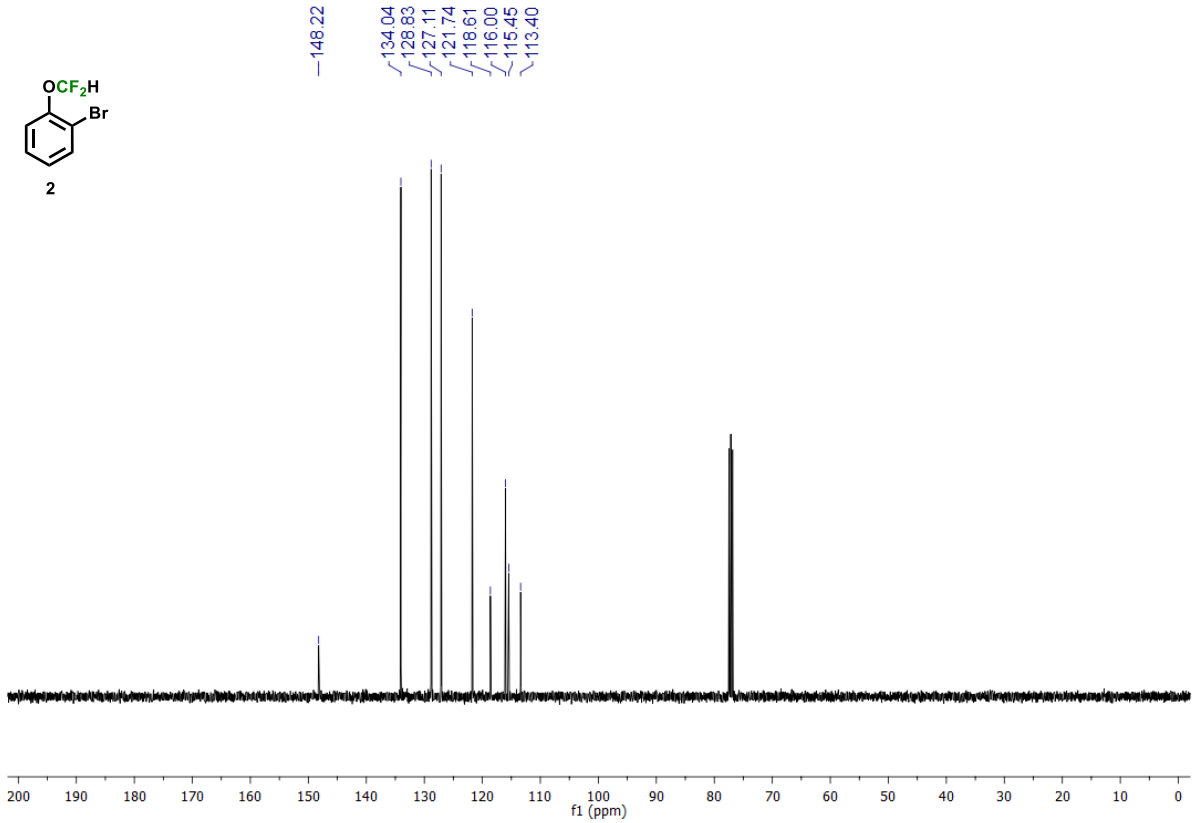

Figure S10: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-Bromo-2-(difluoromethoxy)benzene (**2**).

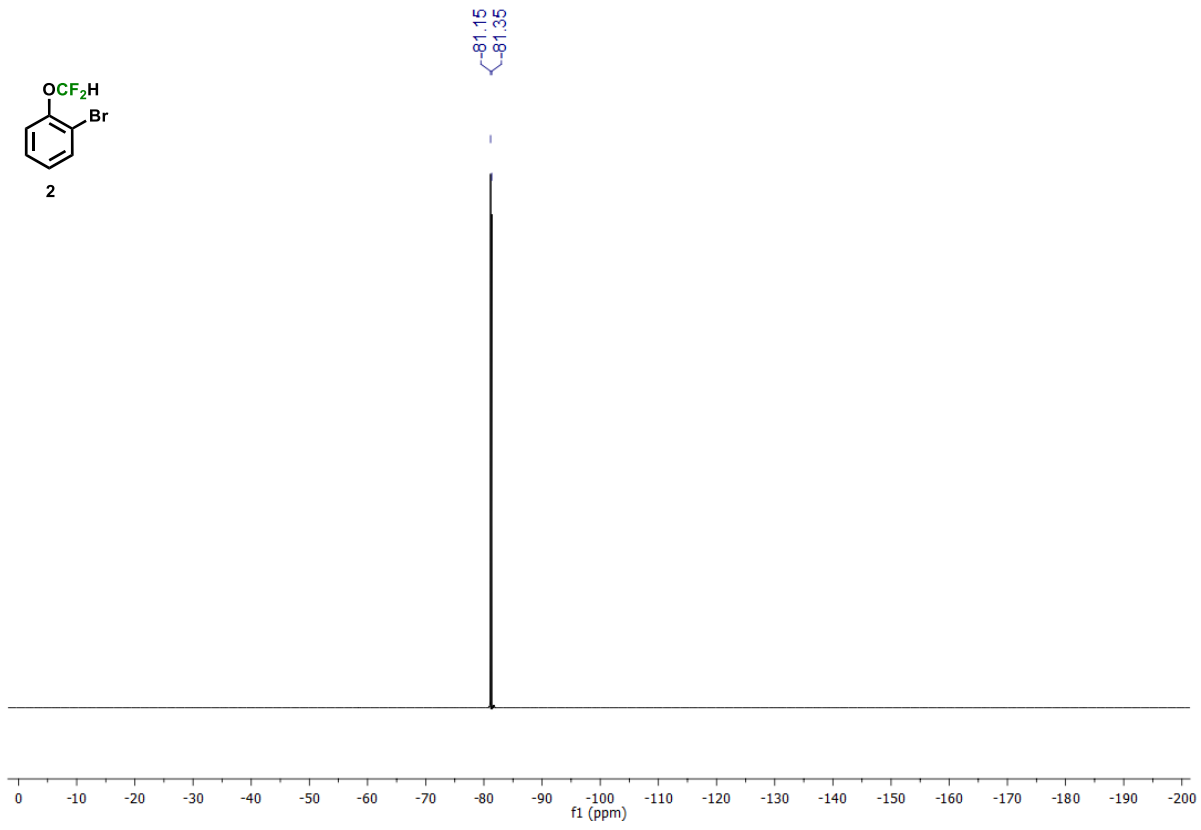

Figure S11: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-Bromo-4-(difluoromethoxy)benzene (**3**).

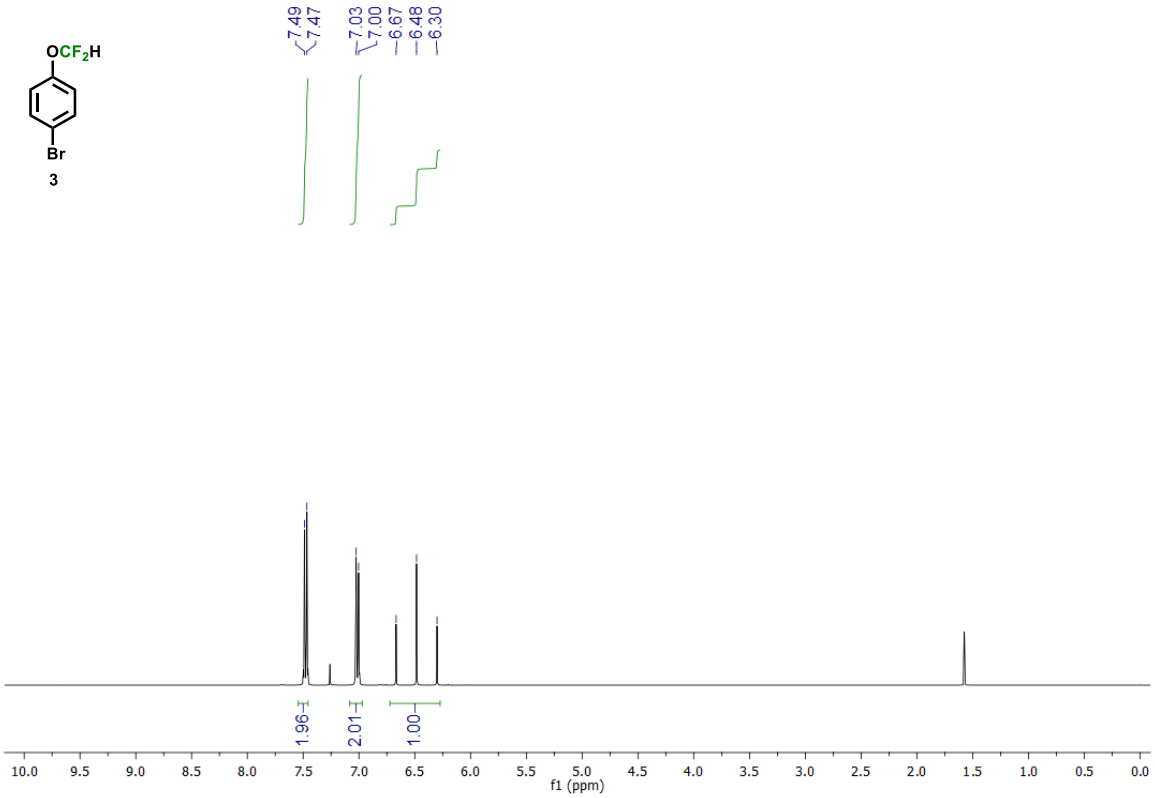

Figure S12: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-Bromo-4-(difluoromethoxy)benzene (**3**).

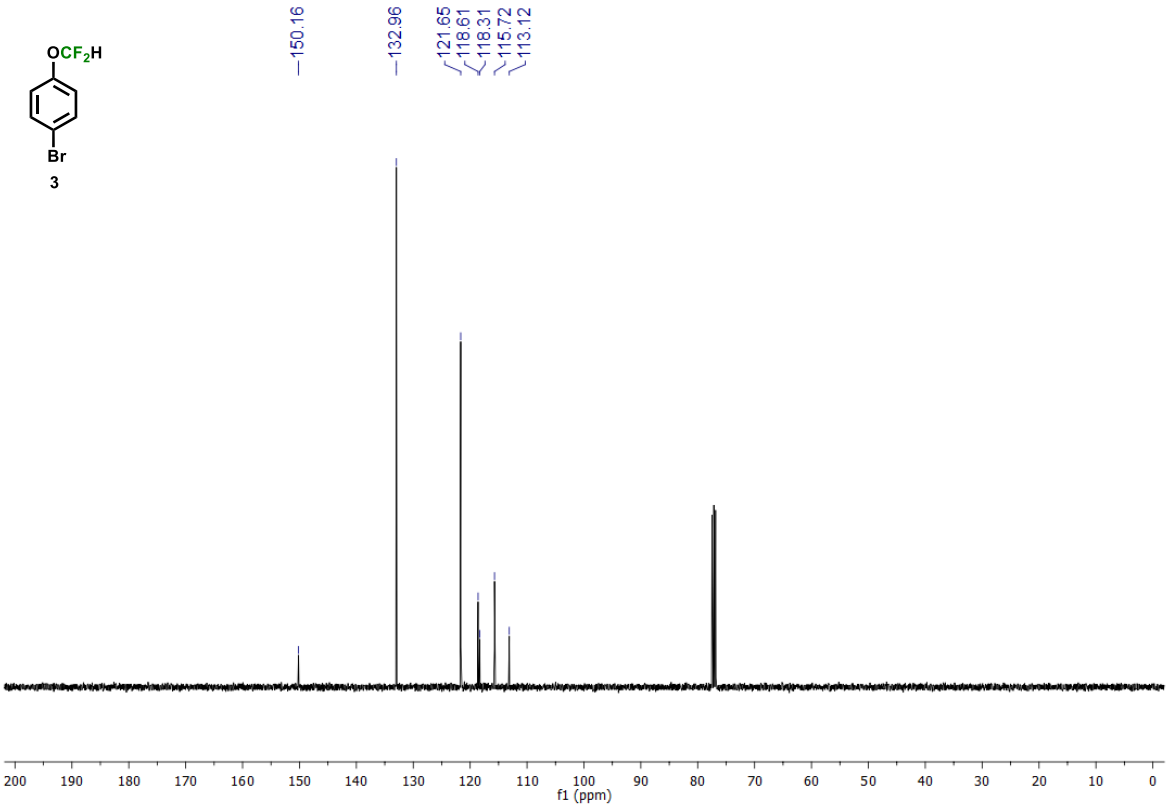

Figure S13: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-Bromo-4-(difluoromethoxy)benzene (**3**).

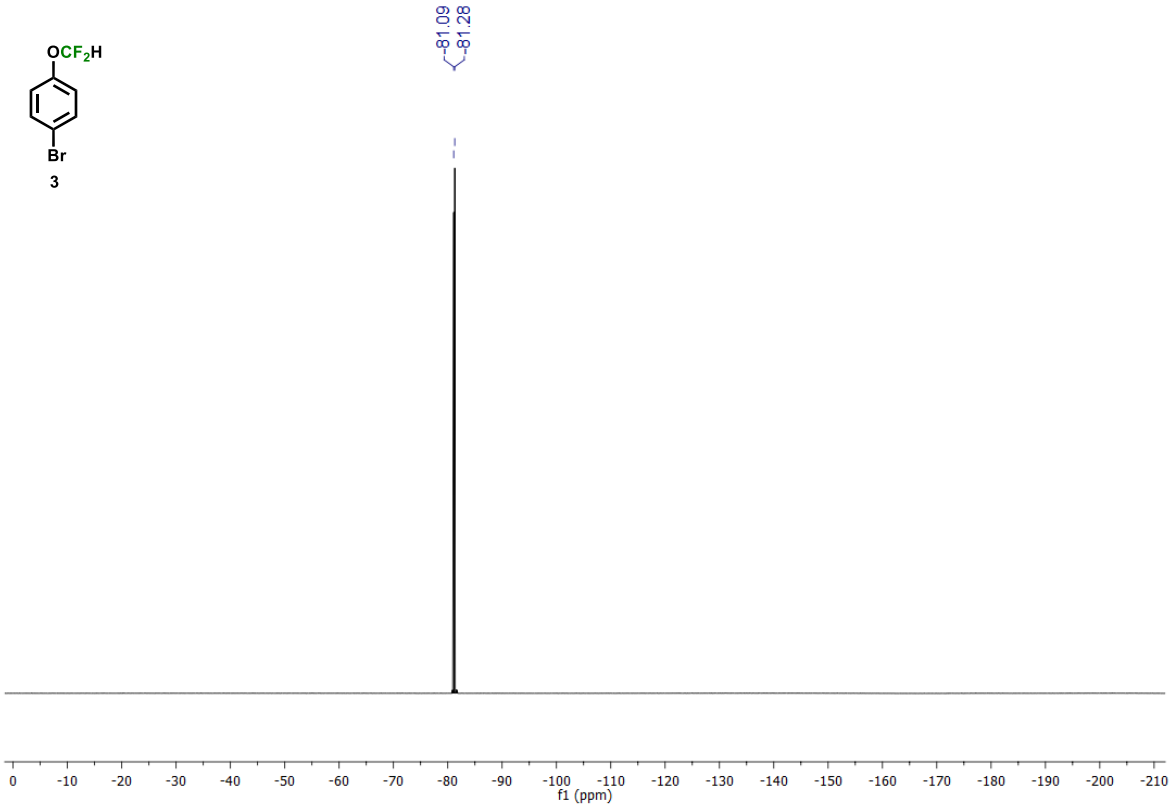

Figure S14: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-Bromo-1-(difluoromethoxy)-2-methylbenzene (**4**).

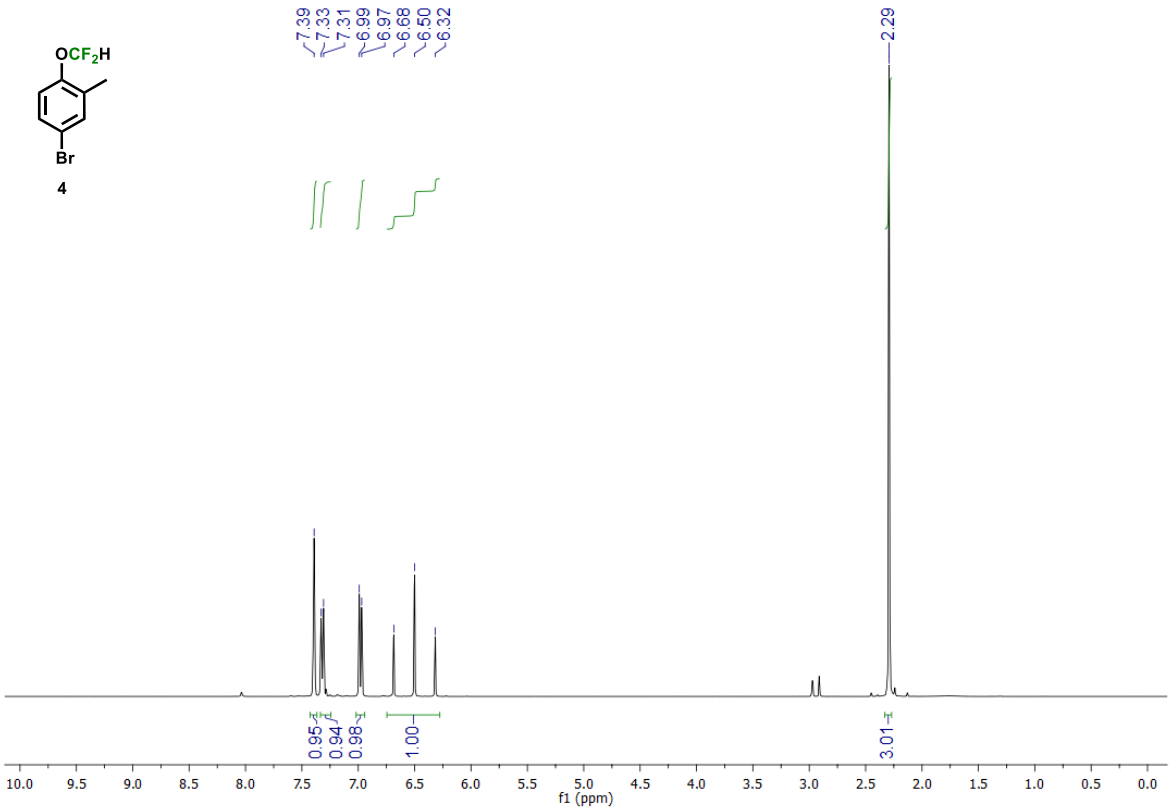

Figure S15: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-Bromo-1-(difluoromethoxy)-2-methylbenzene (**4**).

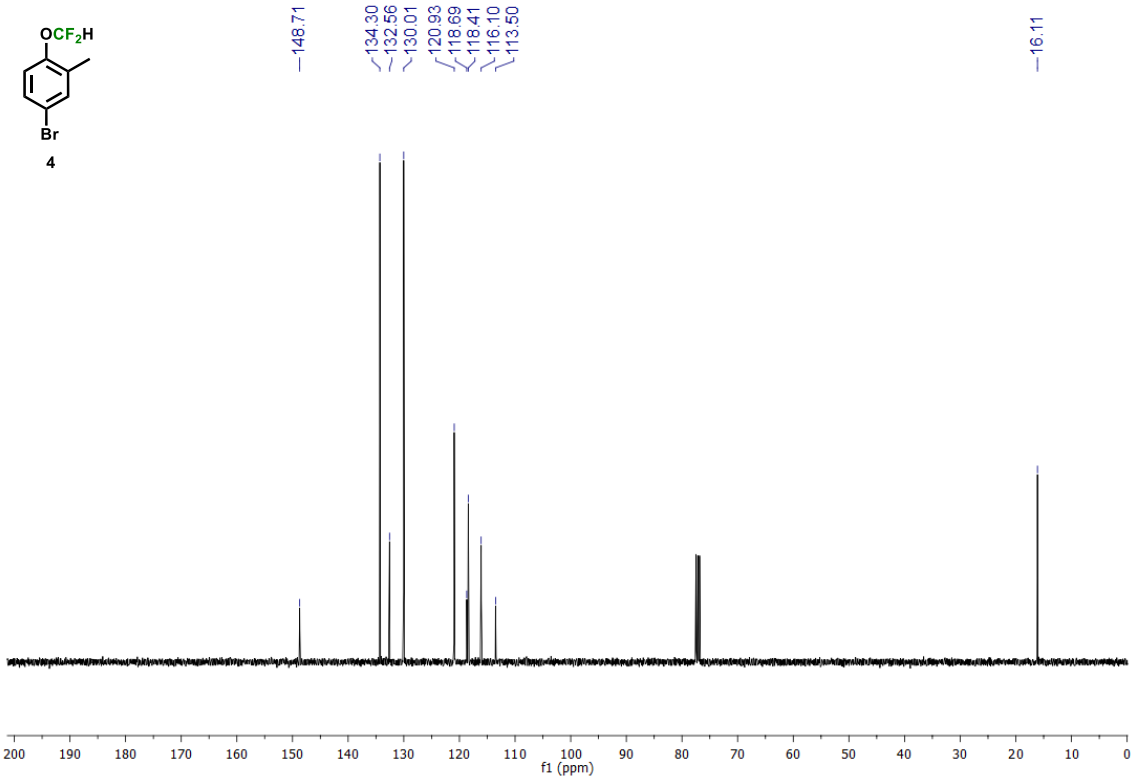

Figure S16: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-Bromo-1-(difluoromethoxy)-2-methylbenzene (**4**).

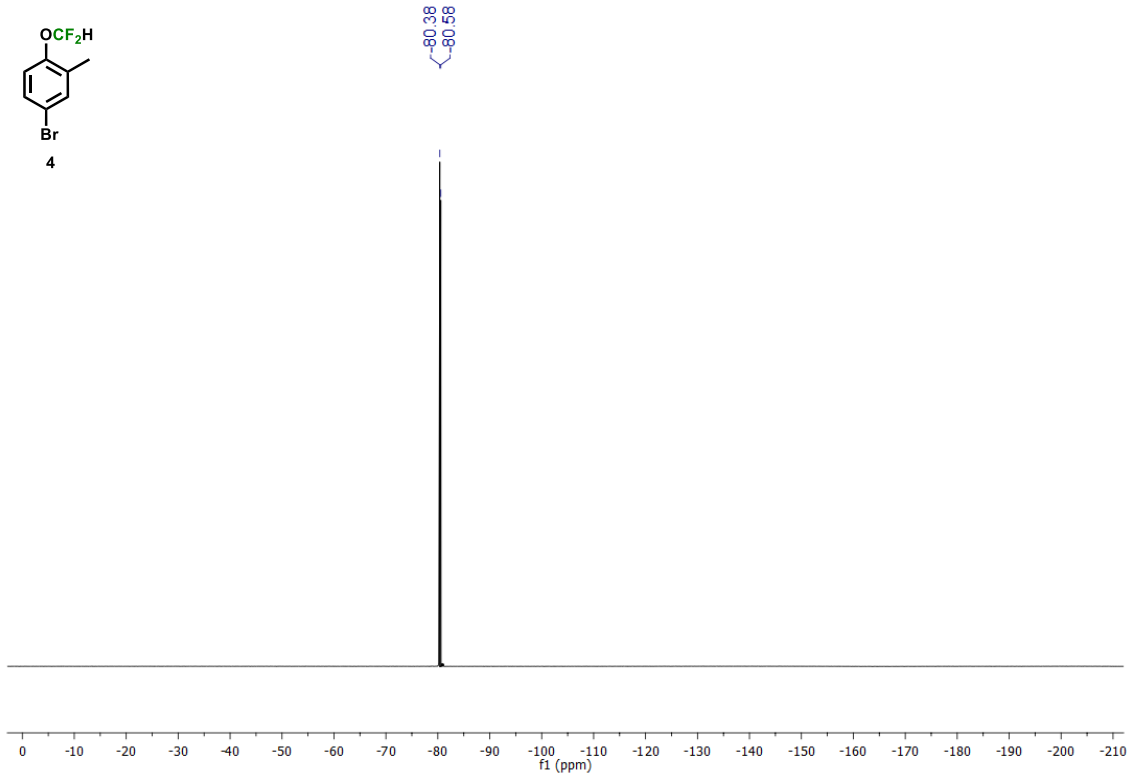

Figure S17: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-Chloro-4-(difluoromethoxy)-2-nitrobenzene (**5**).

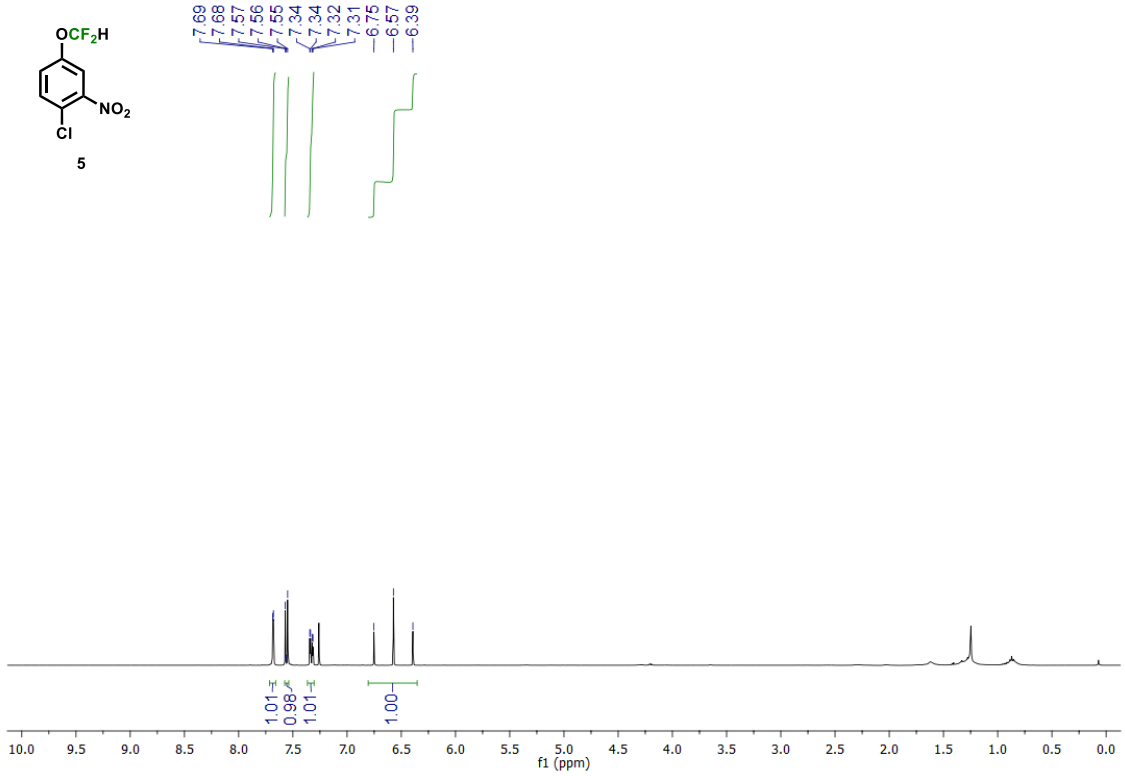

Figure S18: ^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of 1-Chloro-4-(difluoromethoxy)-2-nitrobenzene (**5**).

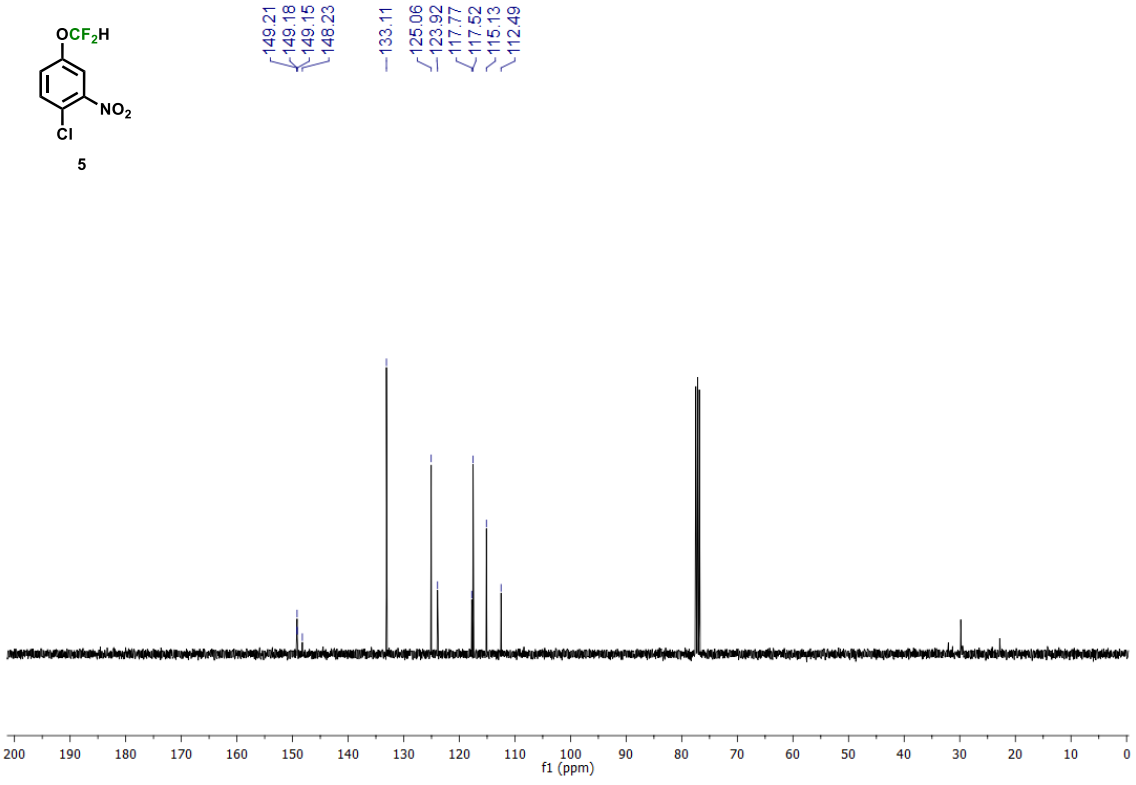

Figure S19: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-Chloro-4-(difluoromethoxy)-2-nitrobenzene (**5**).

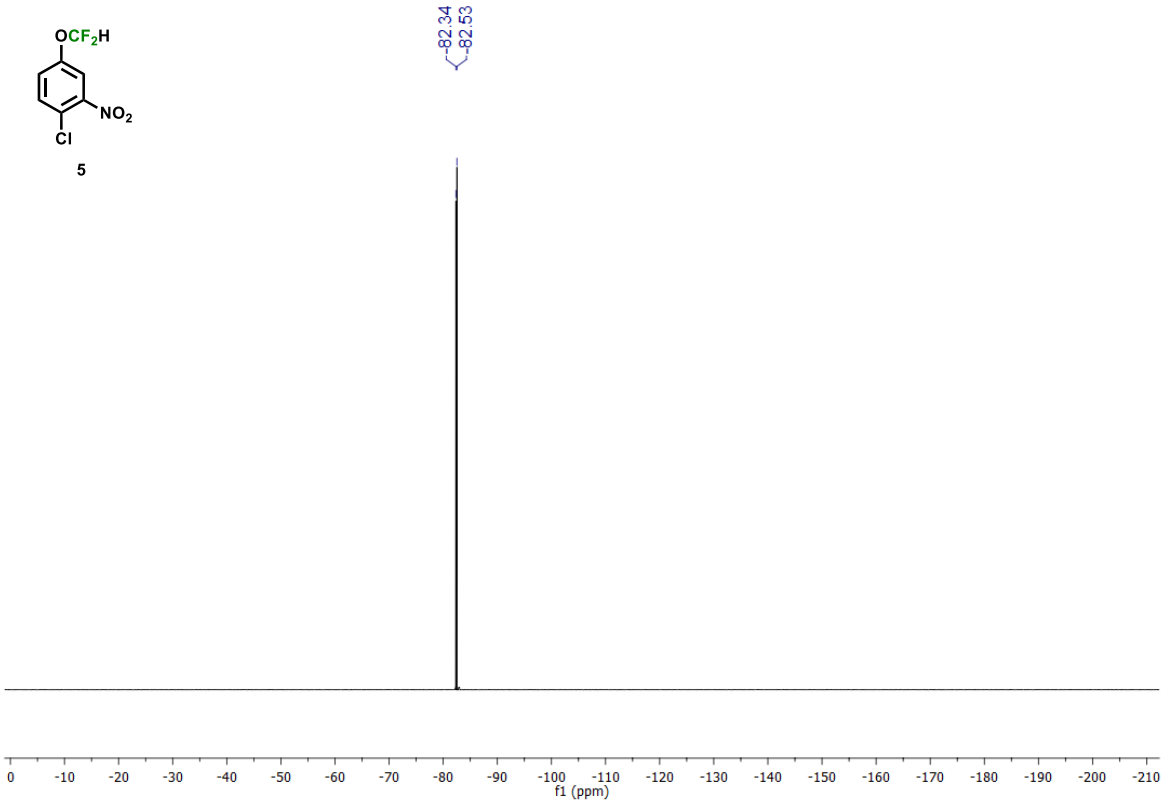

Figure S20: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-iodobenzene (**6**).

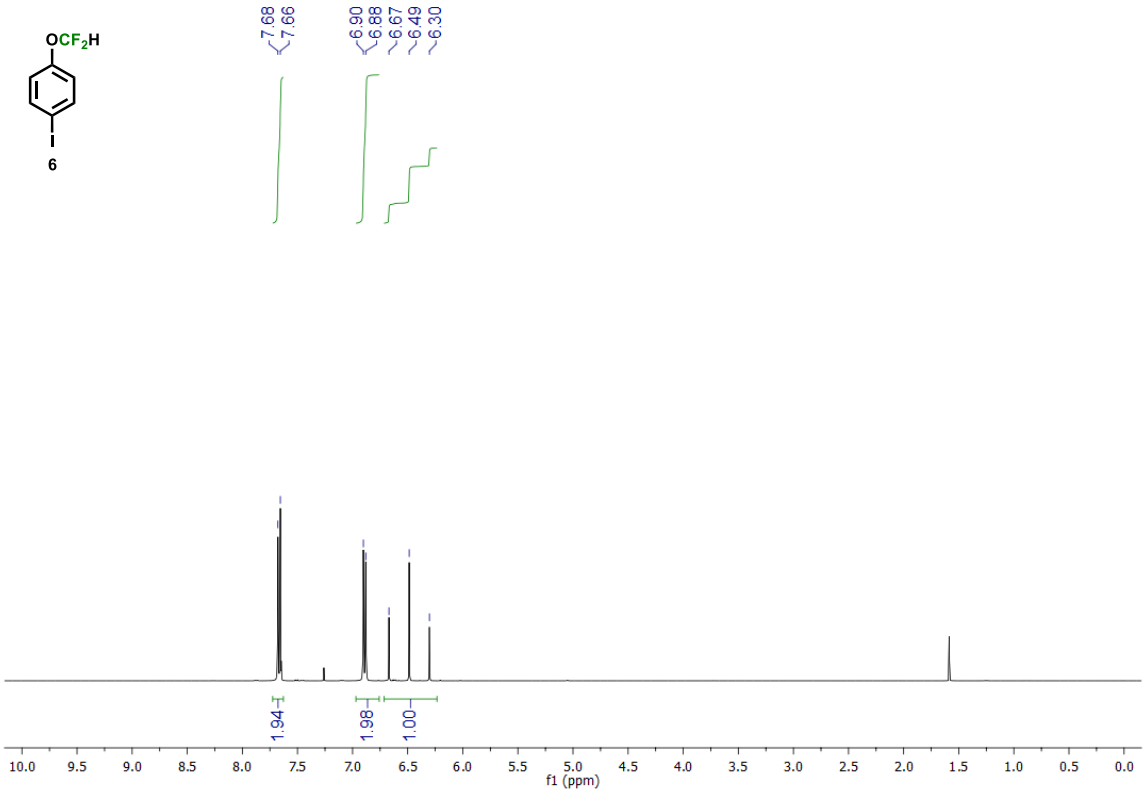

Figure S21: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-iodobenzene (**6**).

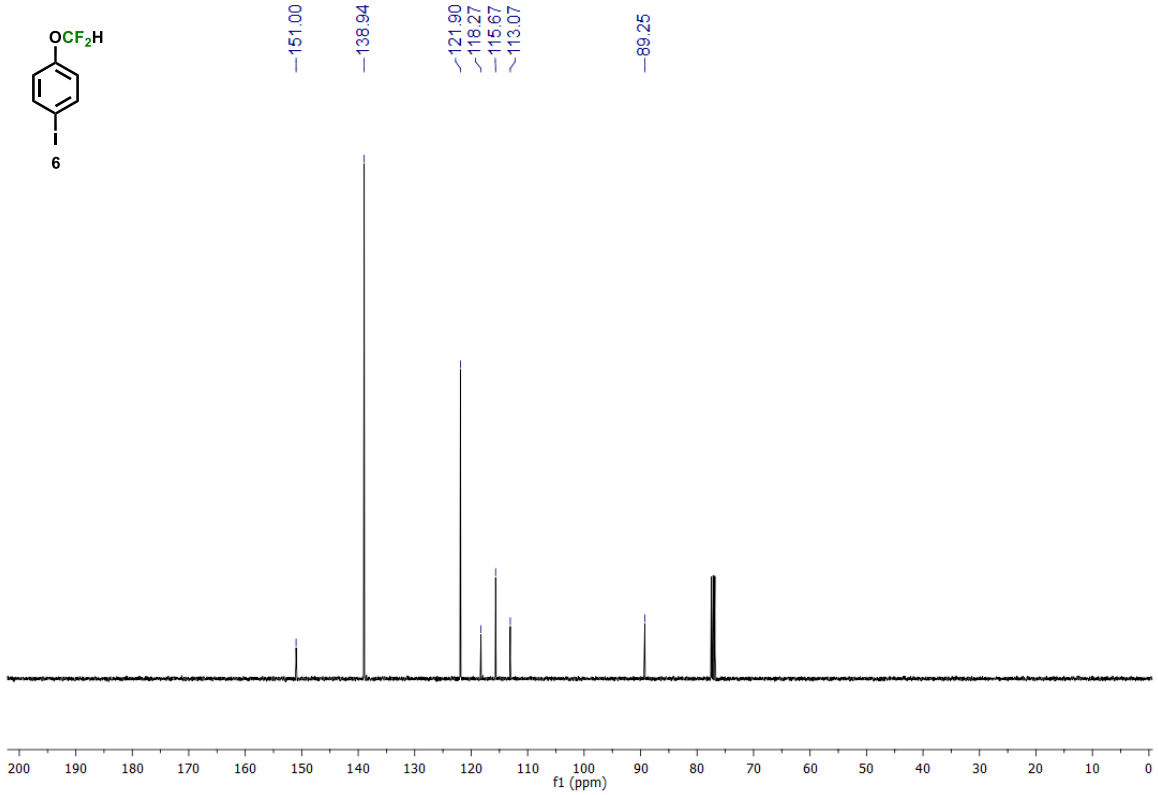

Figure S22: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-iodobenzene (**6**).

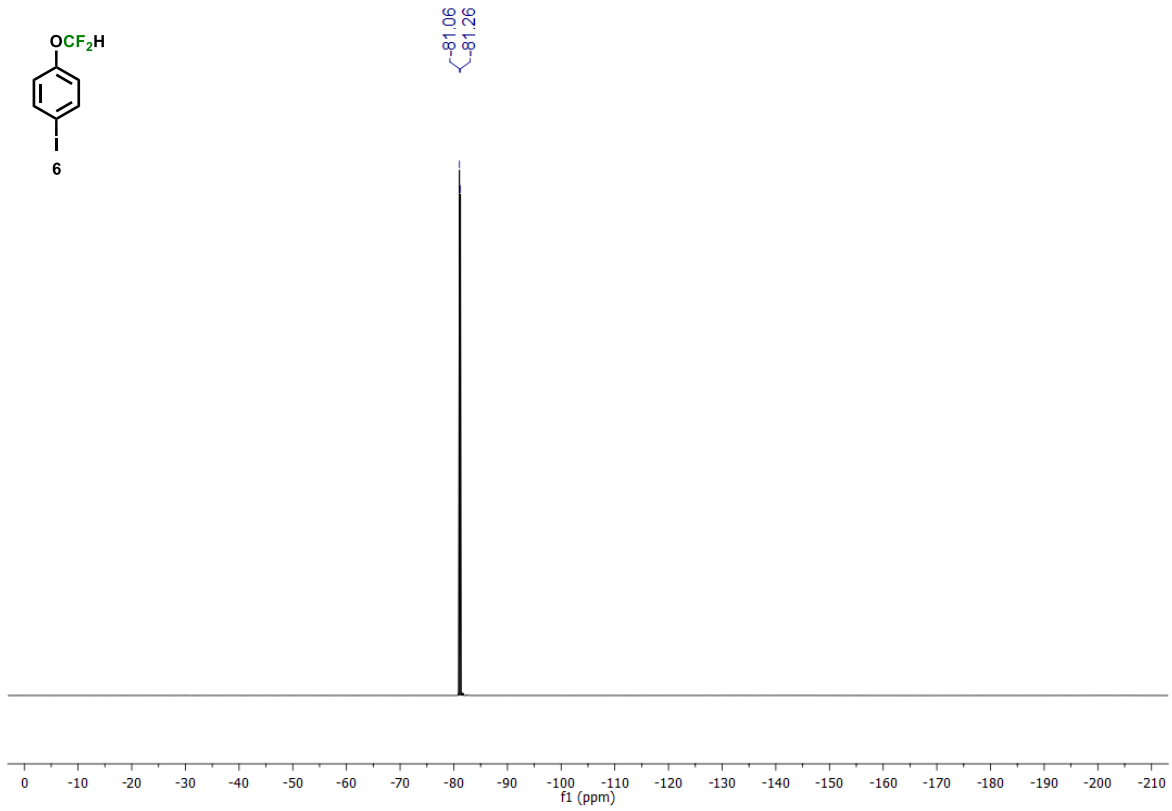

Figure S23: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-2-nitrobenzene (**7**).

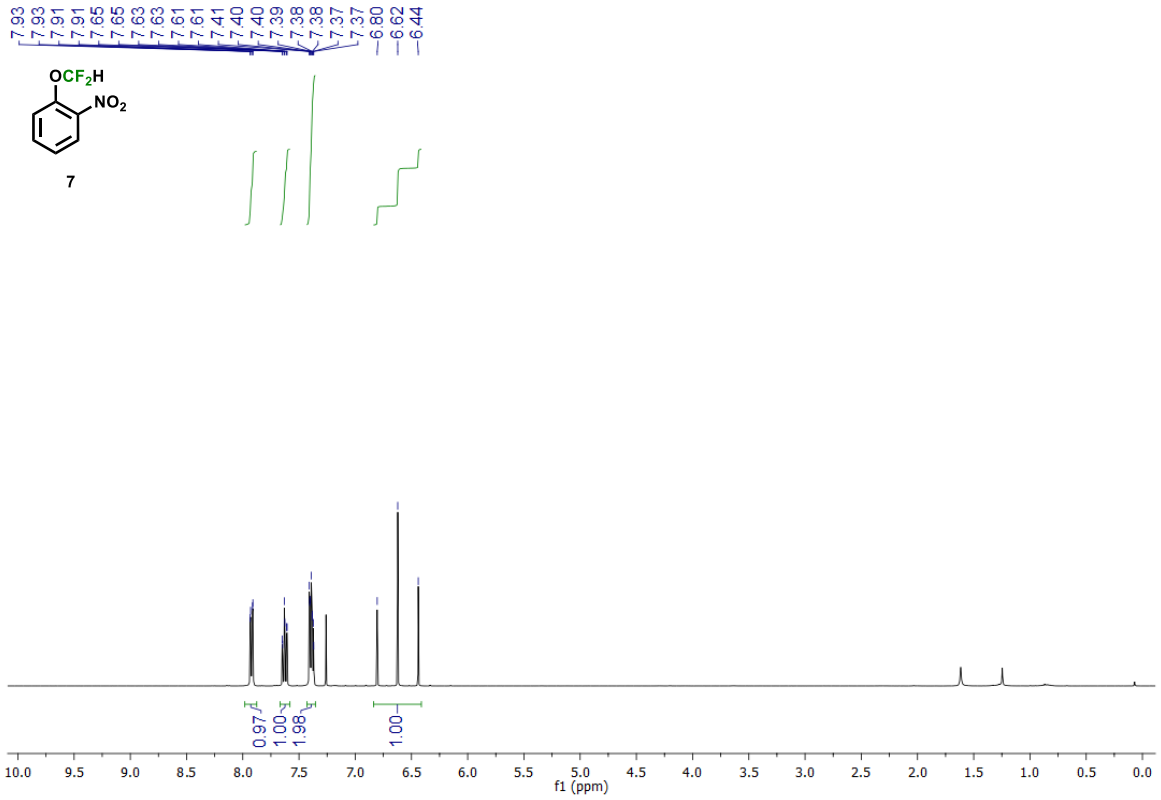

Figure S24: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-2-nitrobenzene (**7**).

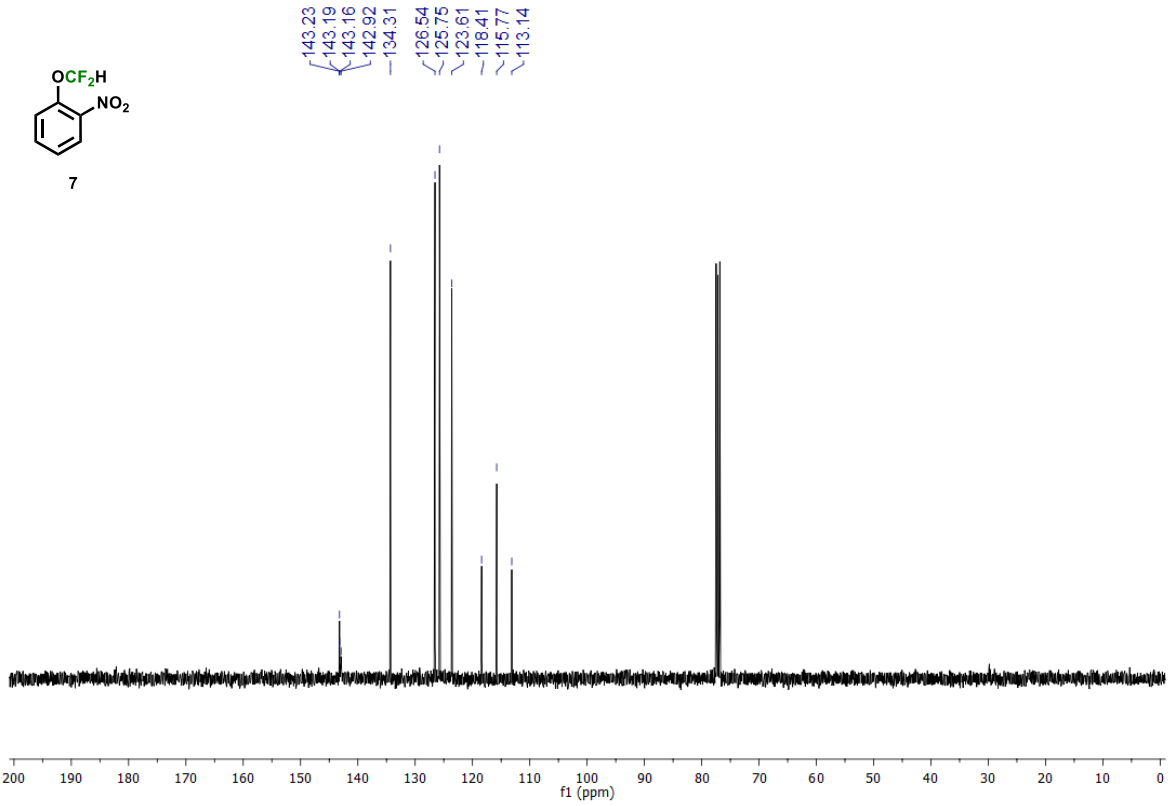

Figure S25: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-2-nitrobenzene (**7**).

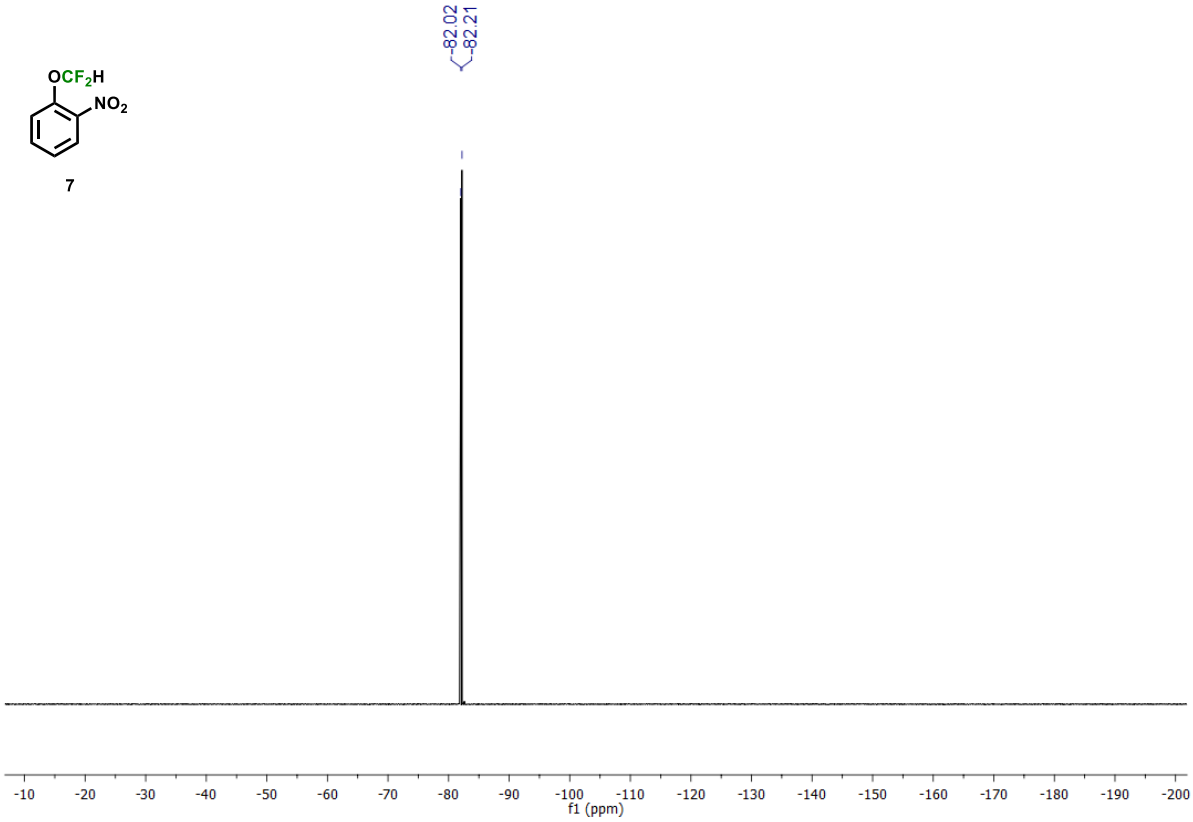

Figure S26: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-3-nitrobenzene (**8**).

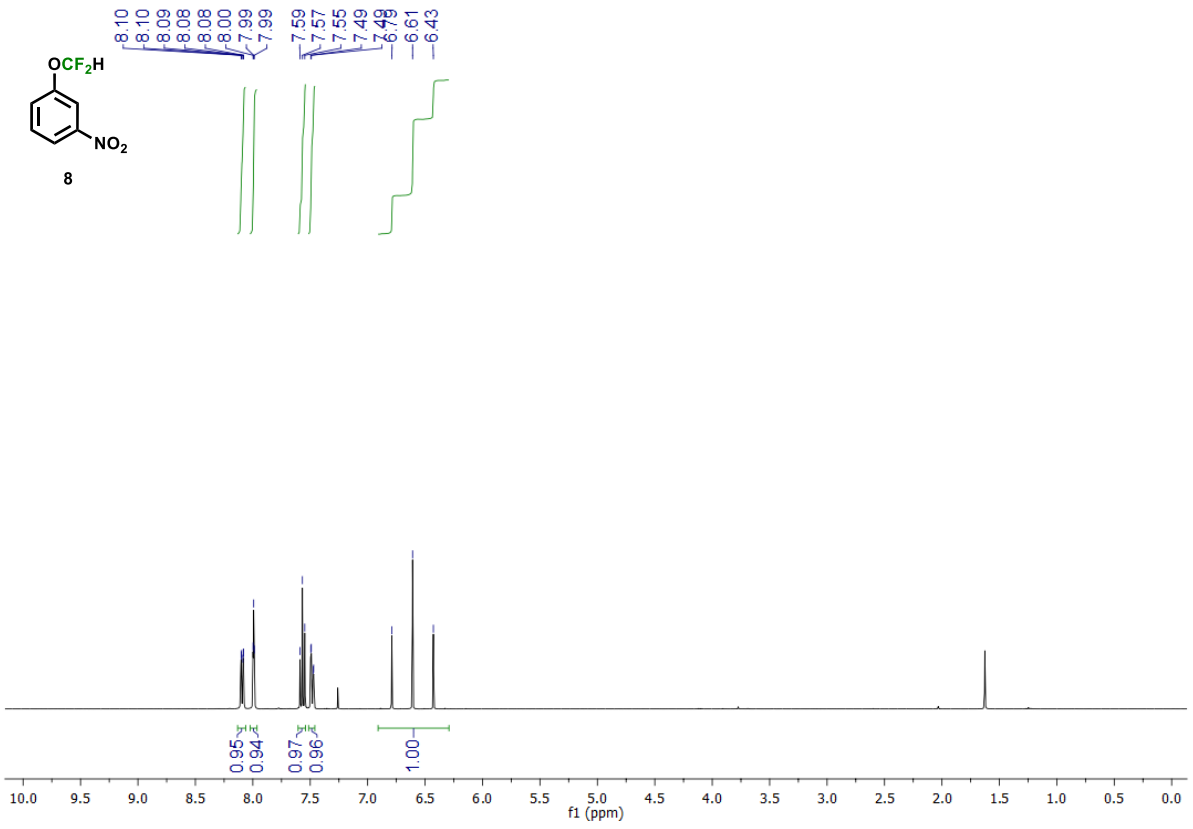

Figure S27: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-3-nitrobenzene (**8**).

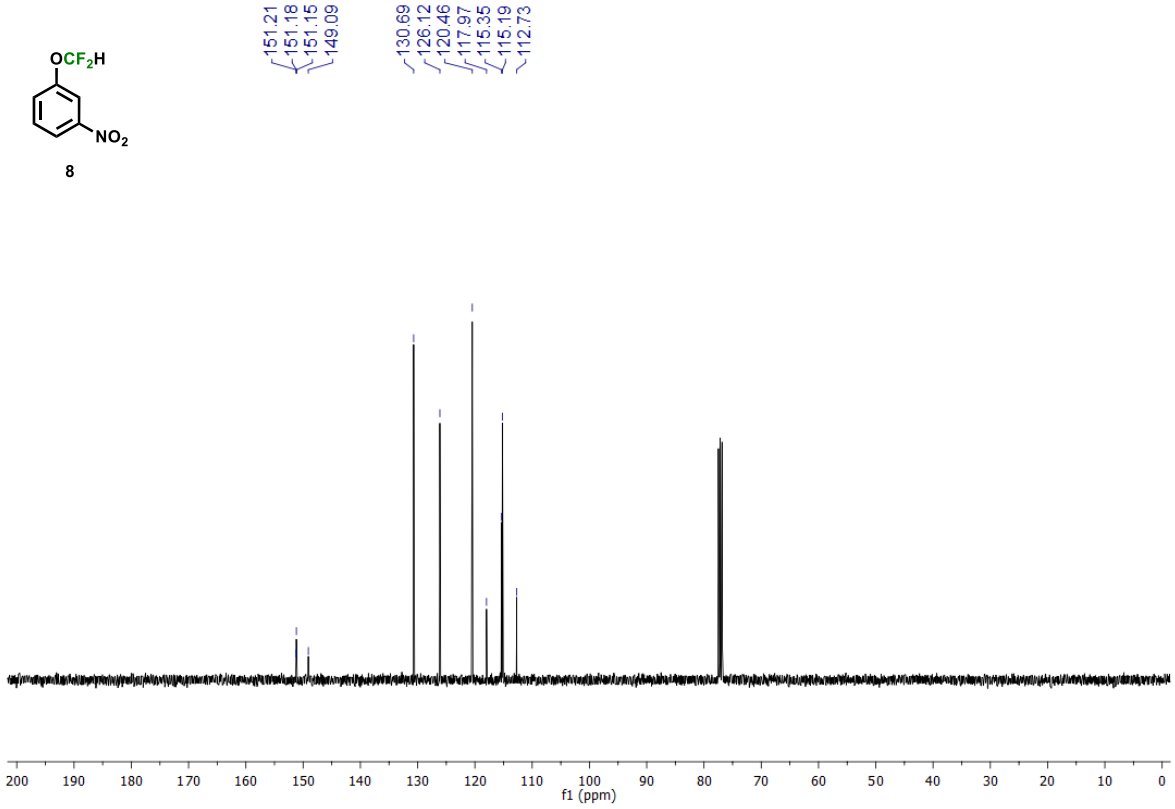

Figure S28: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-3-nitrobenzene (**8**).

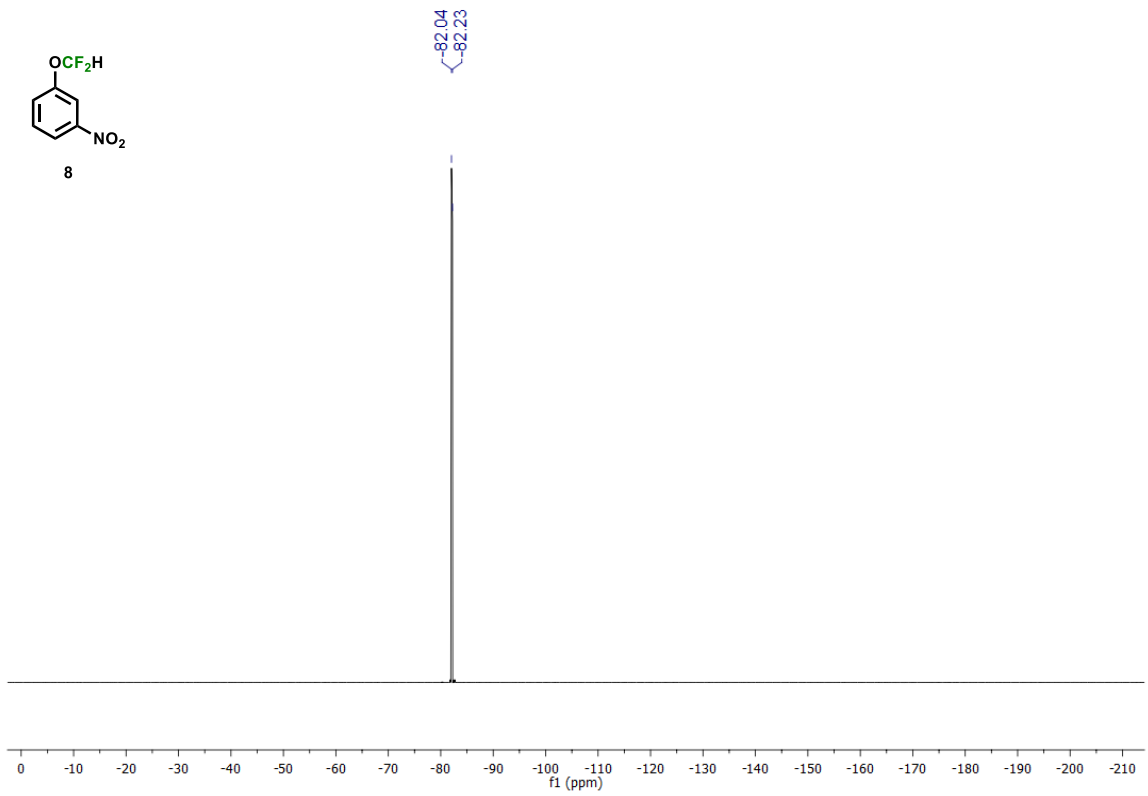

Figure S29: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-nitro-2-(trifluoromethyl)benzene (**9**).

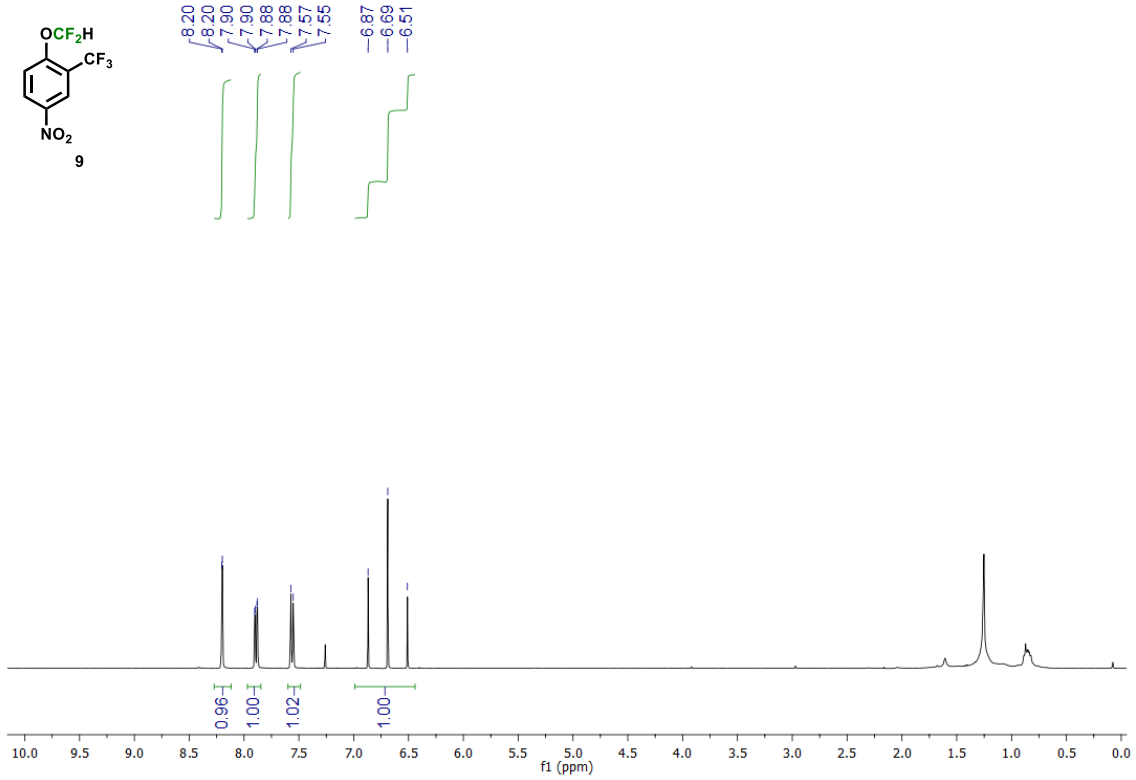

Figure S30: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-nitro-2-(trifluoromethyl)benzene (**9**).

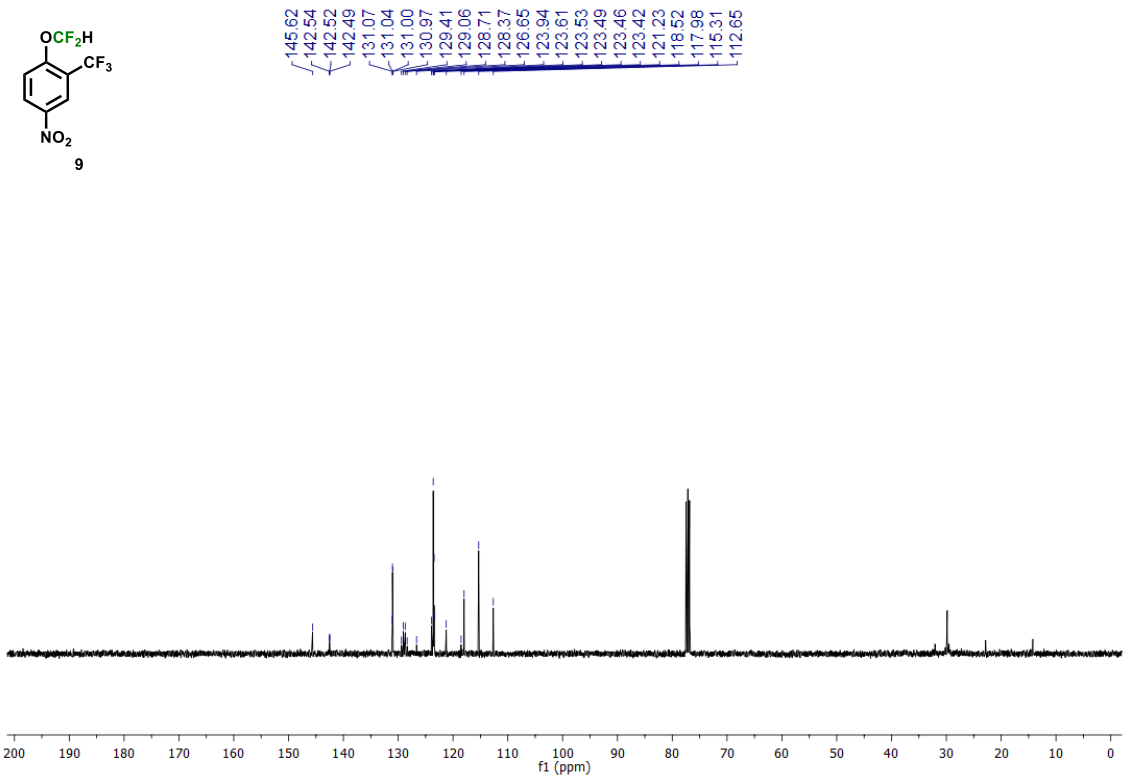

Figure S31: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-nitro-2-(trifluoromethyl)benzene (**9**).

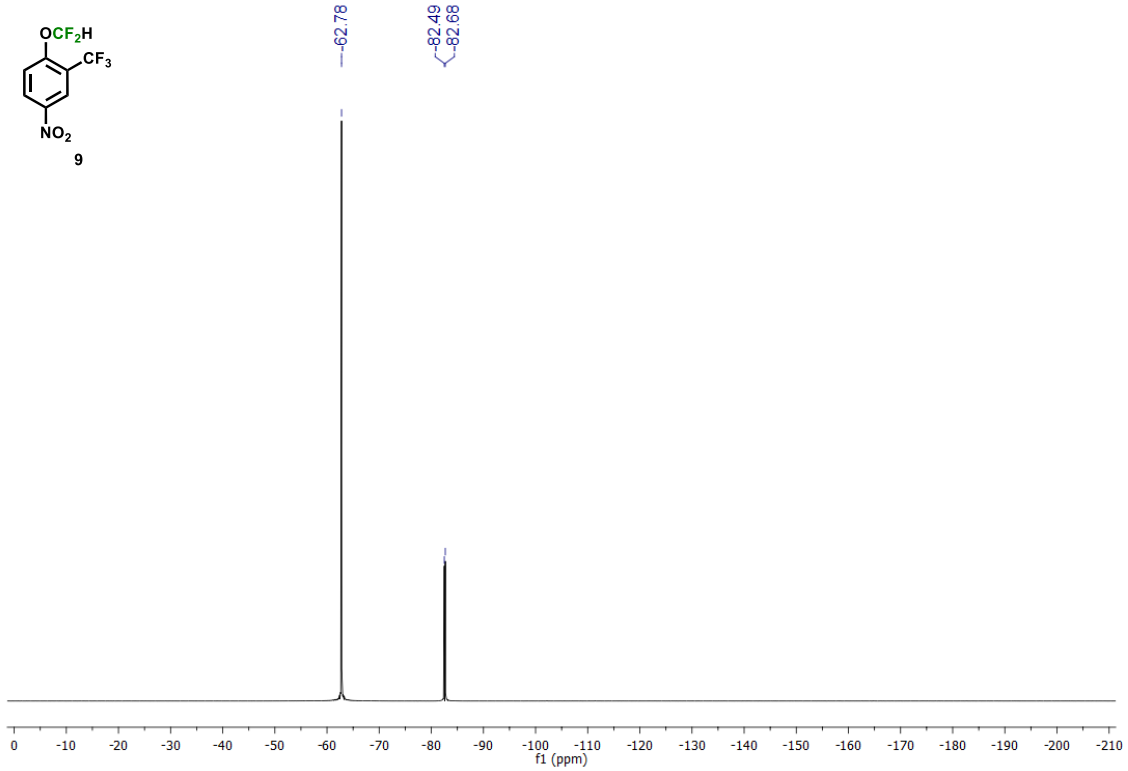

Figure S32: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-1-nitro-2-(trifluoromethyl)benzene (**10**).

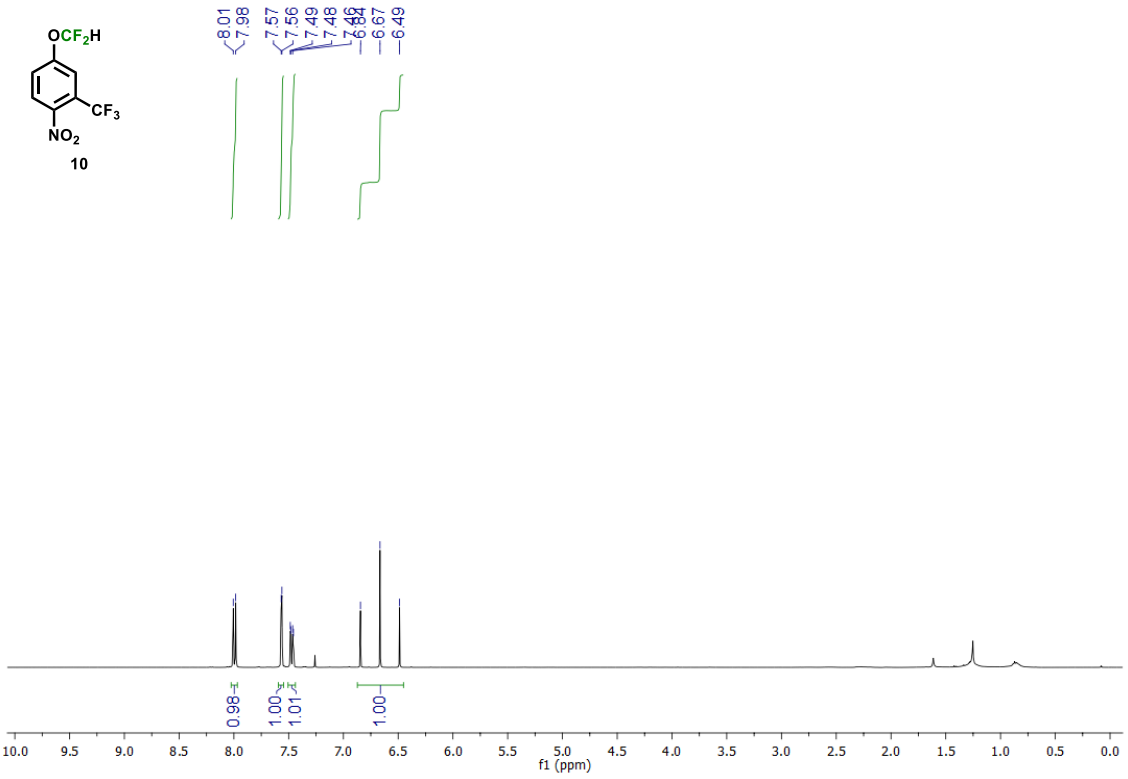

Figure S33: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-1-nitro-2-(trifluoromethyl)benzene (**10**).

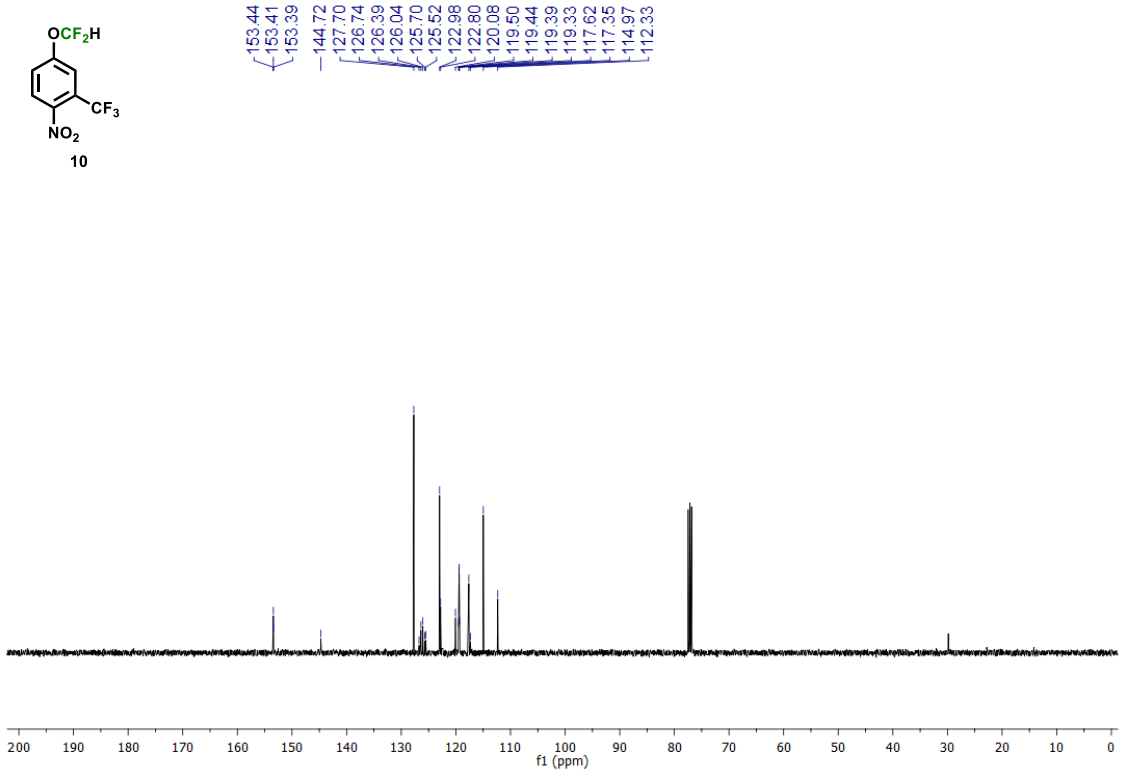

Figure S34: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-1-nitro-2-(trifluoromethyl)benzene (**10**).

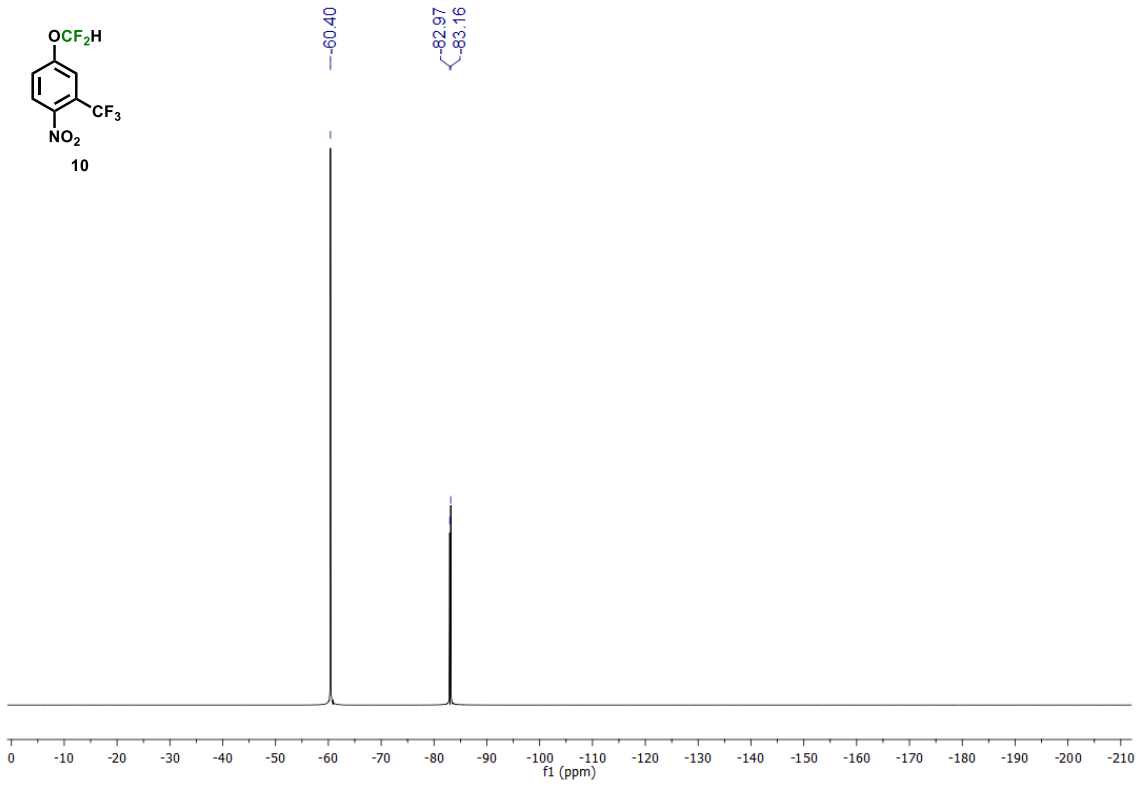

Figure S35: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-nitro-1,1'-biphenyl (**11**).

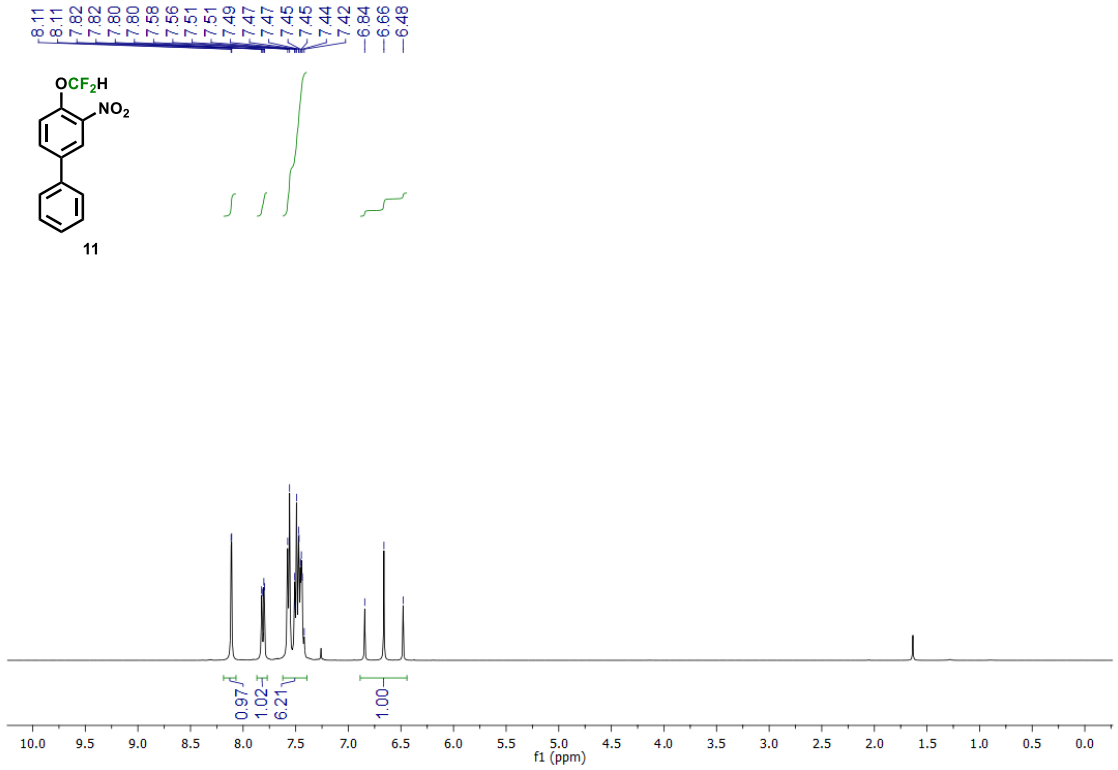

Figure S36: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-nitro-1,1'-biphenyl (**11**).

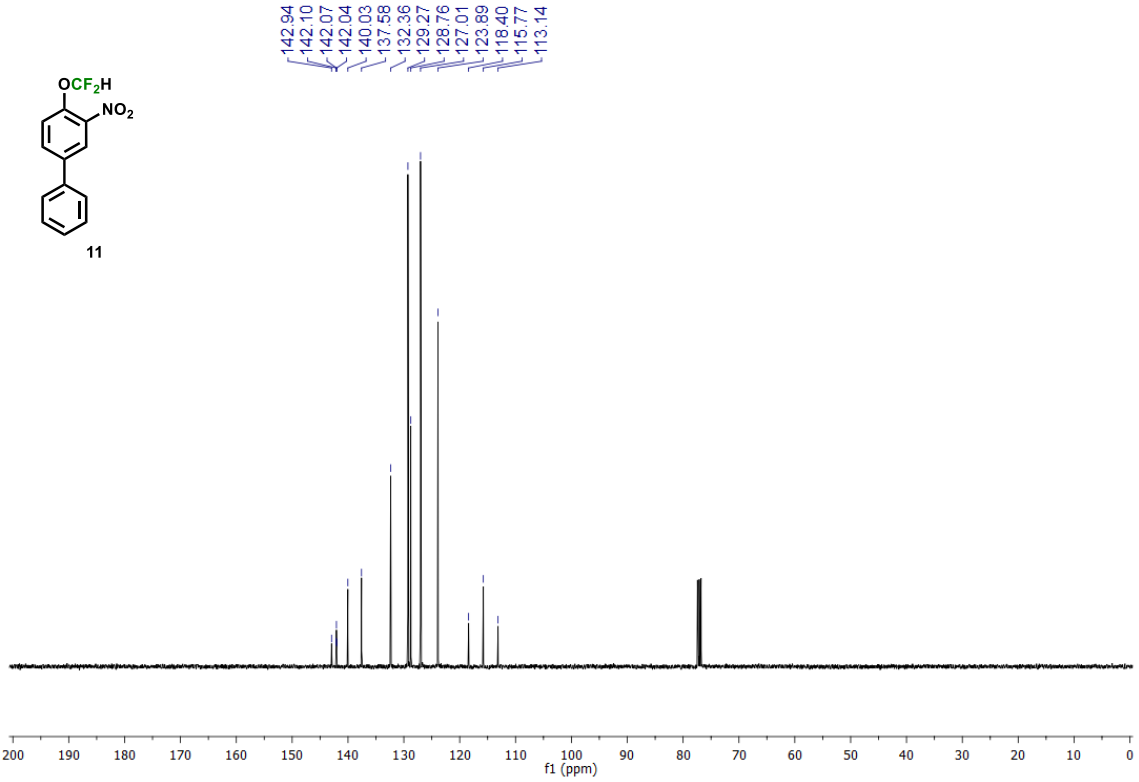

Figure S37: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-nitro-1,1'-biphenyl (**11**).

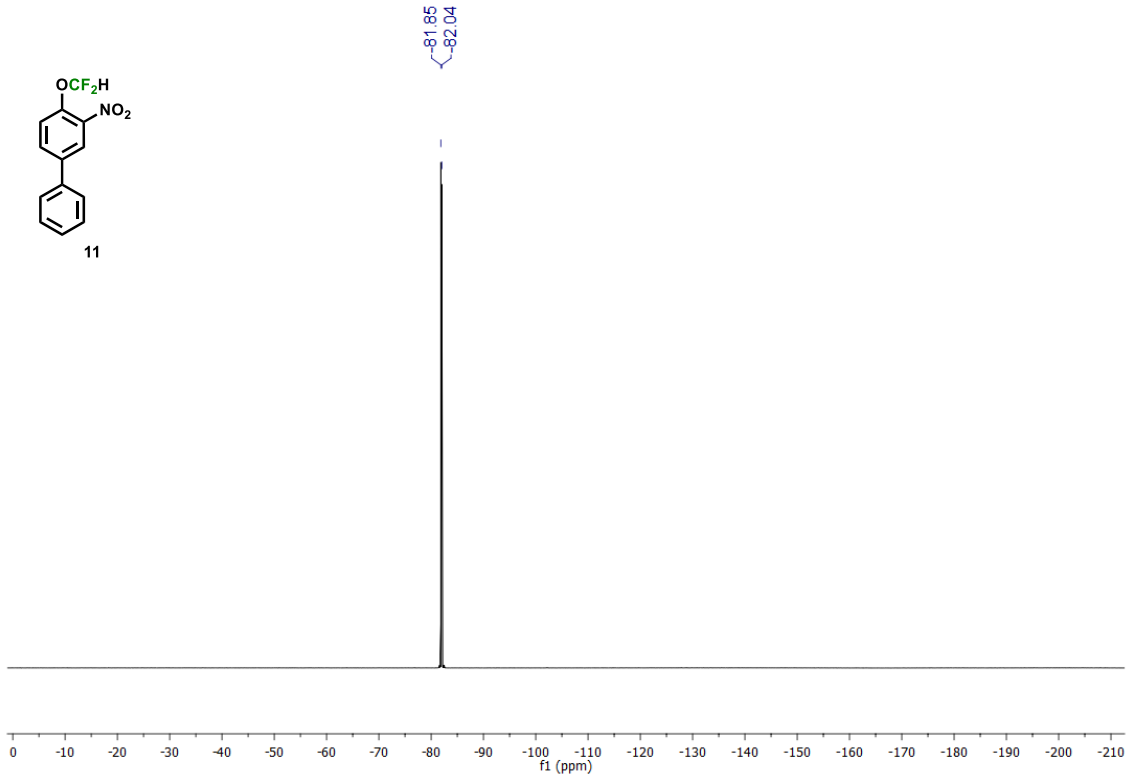

Figure S38: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-2-methoxy-4-nitrobenzene (**12**).

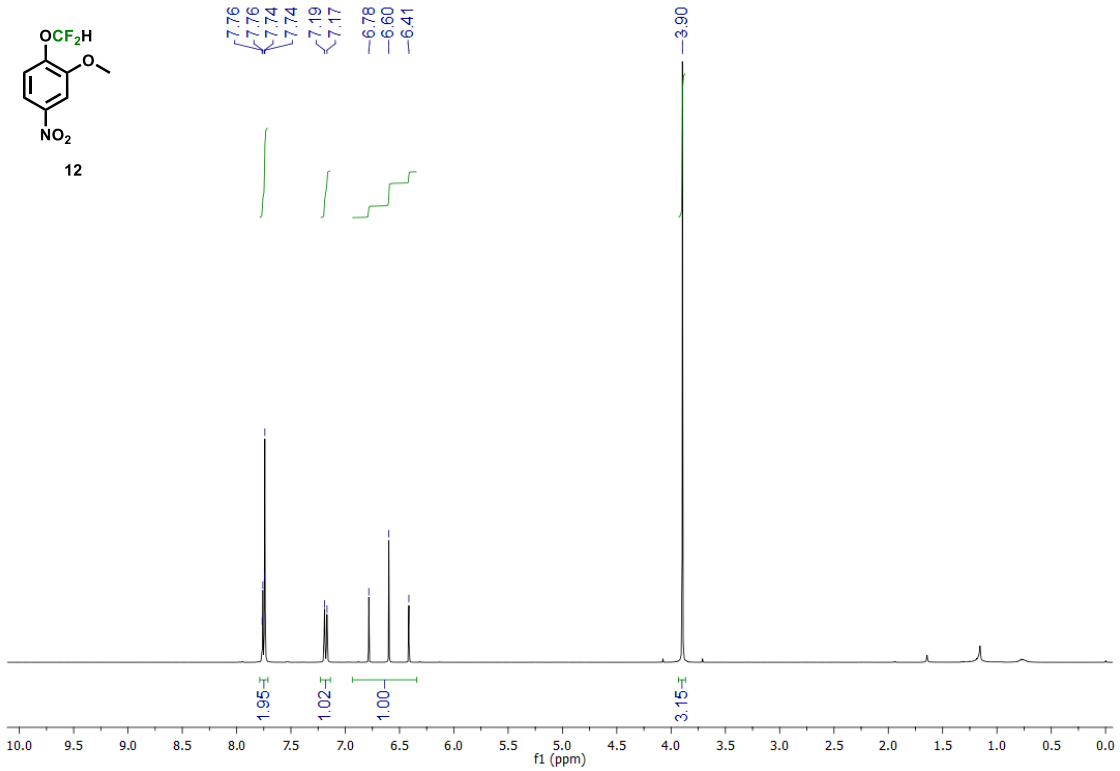

Figure S39: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-2-methoxy-4-nitrobenzene (**12**).

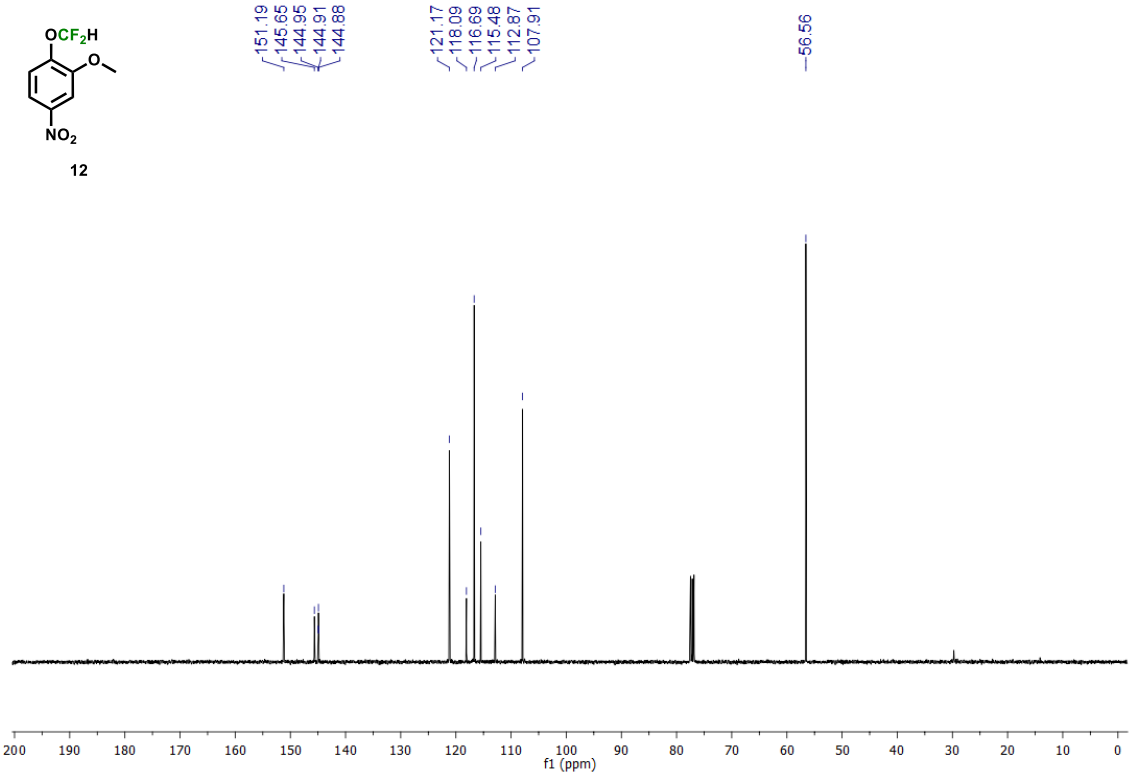

Figure S40: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-2-methoxy-4-nitrobenzene (**12**).

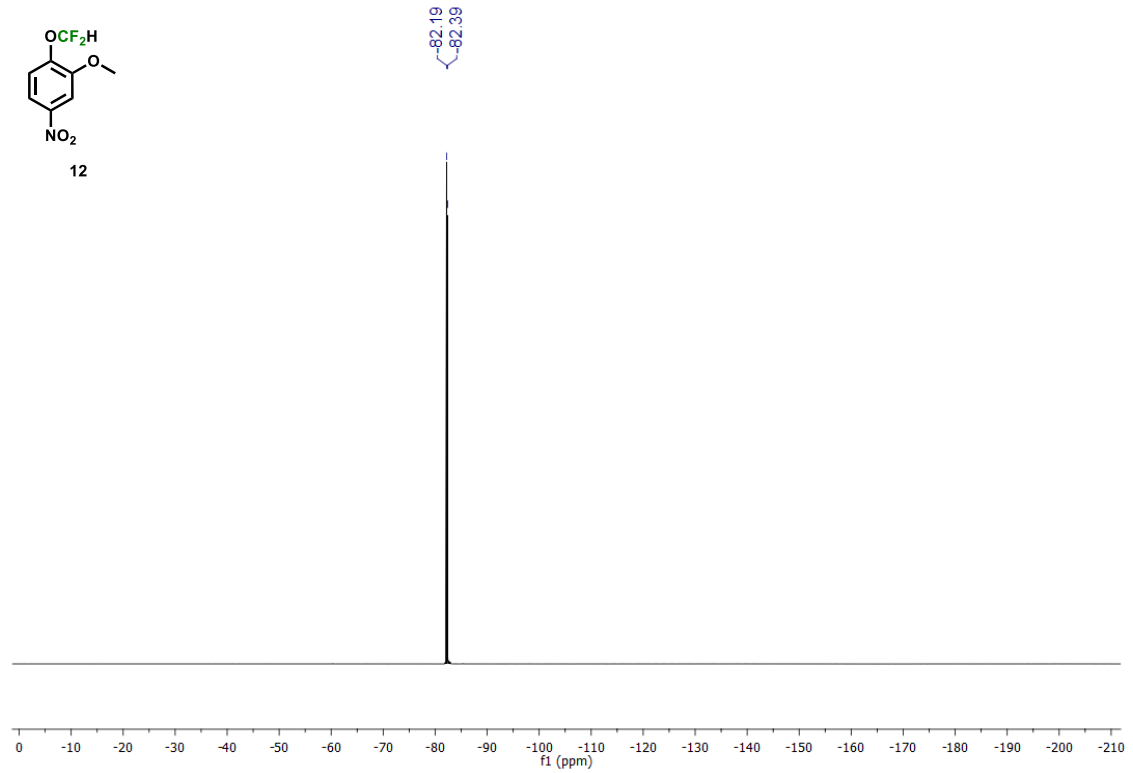

Figure S41: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Methyl 4-(difluoromethoxy)-3-nitrobenzoate (**13**).

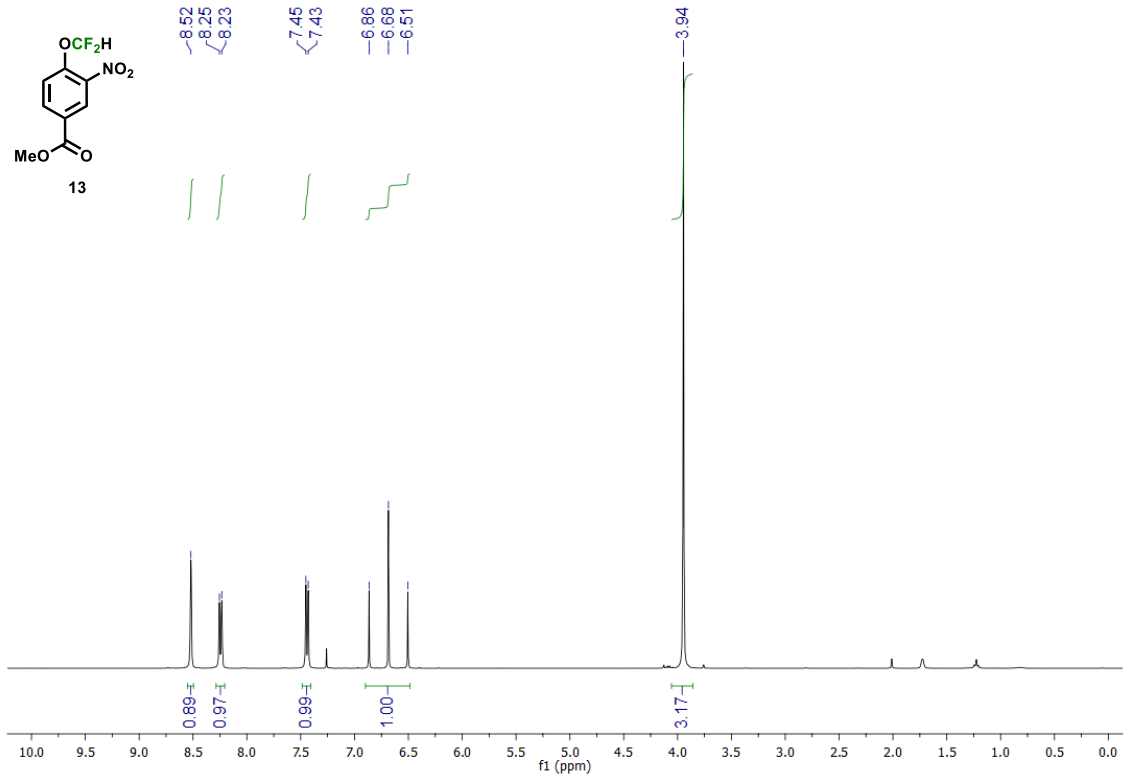

Figure S42: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of Methyl 4-(difluoromethoxy)-3-nitrobenzoate (**13**).

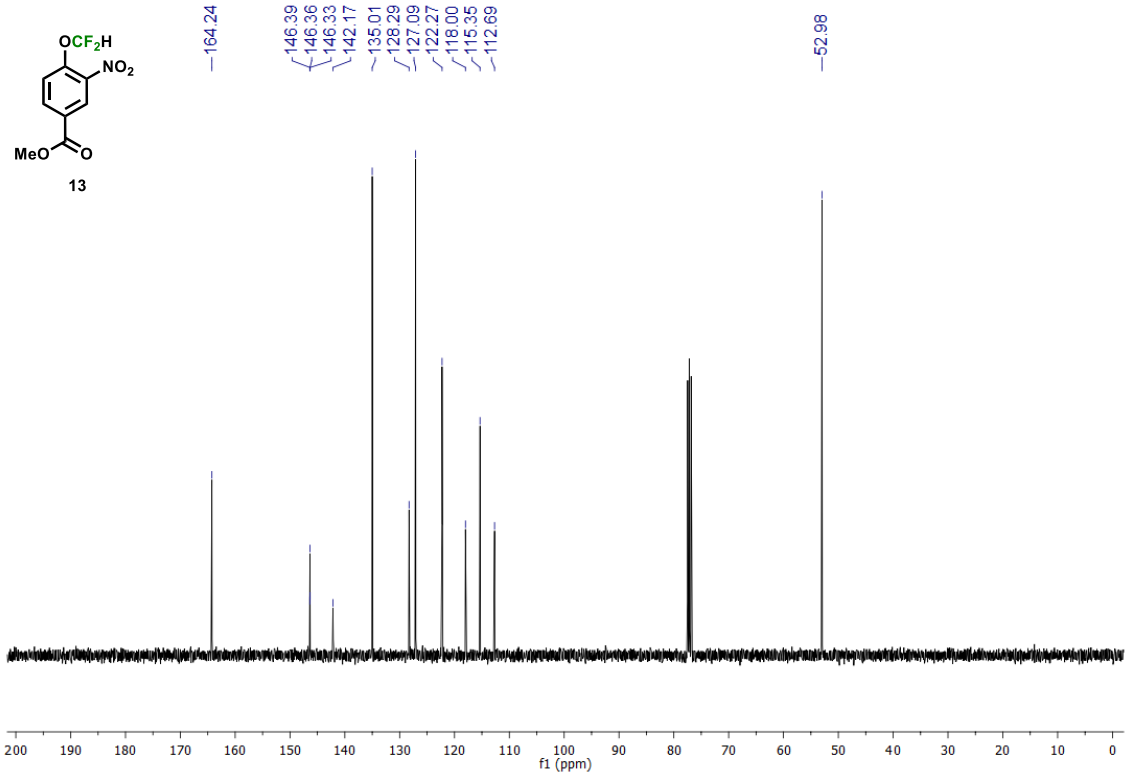

Figure S43: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of Methyl 4-(difluoromethoxy)-3-nitrobenzoate (**13**).

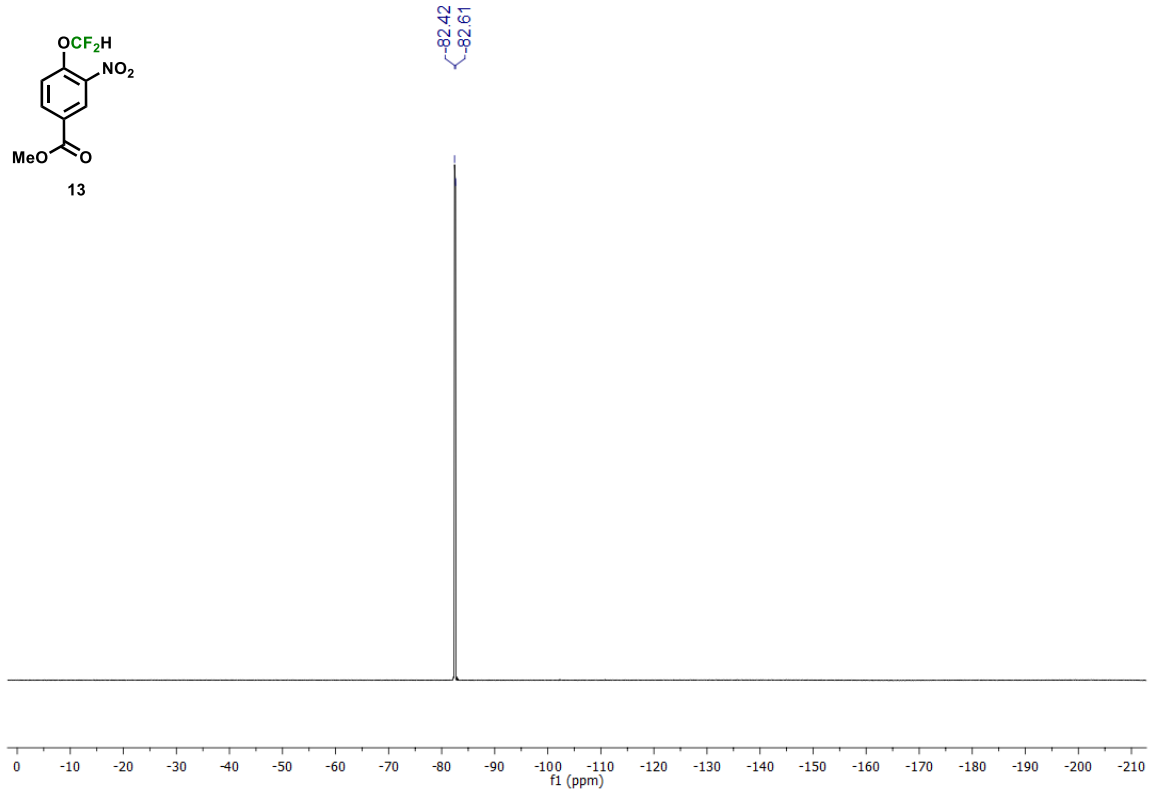

Figure S44: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Methyl 2-(difluoromethoxy)benzoate (**14**).

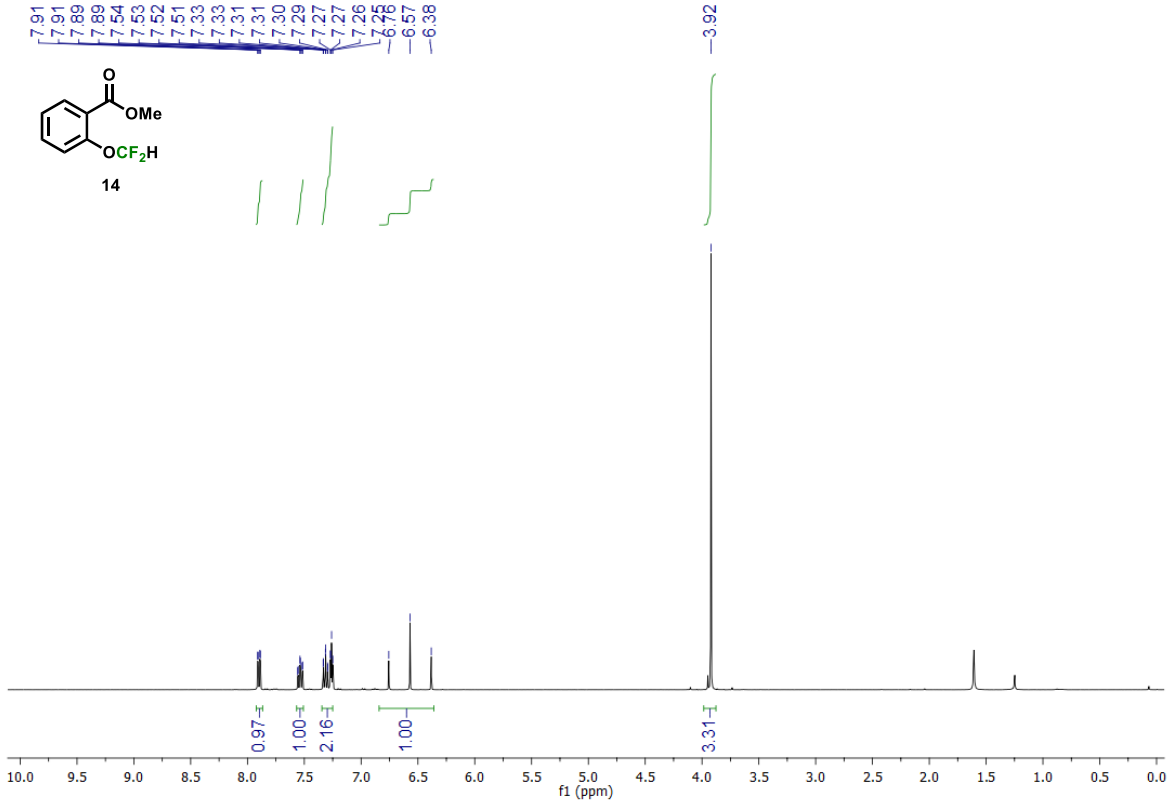

Figure S45: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of Methyl 2-(difluoromethoxy)benzoate (**14**).

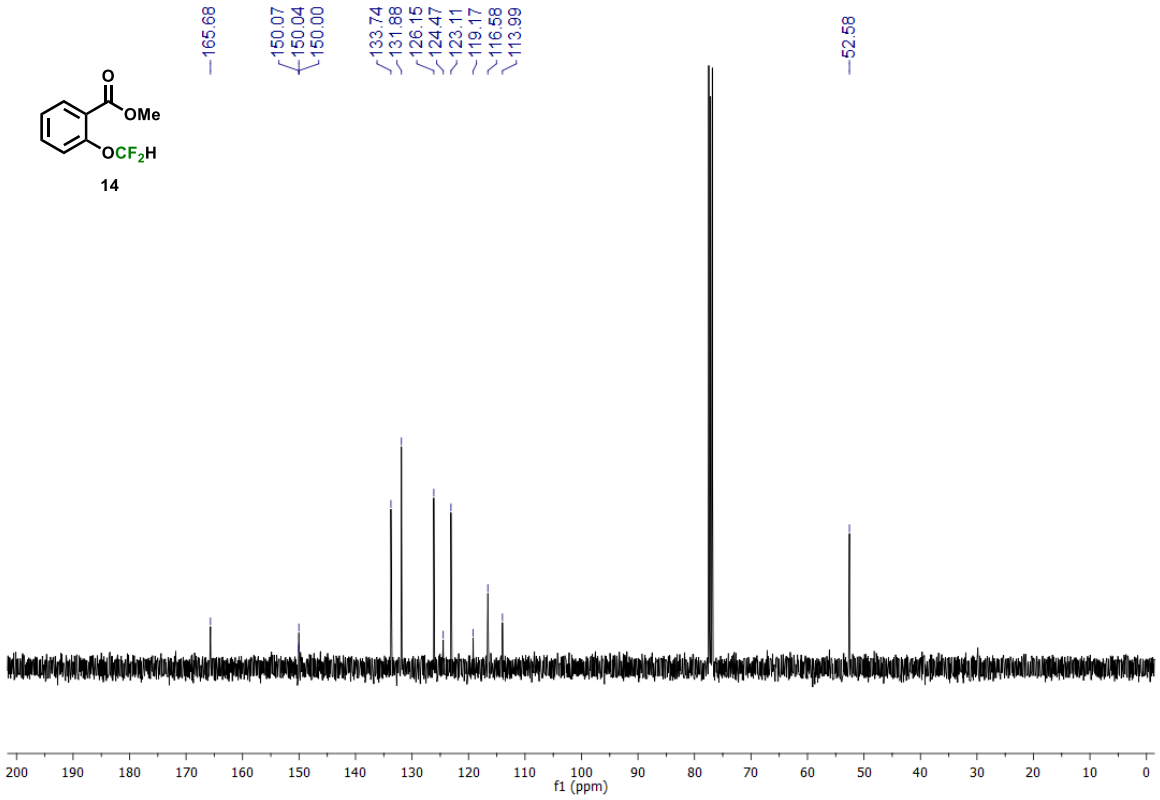

Figure S46: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of Methyl 2-(difluoromethoxy)benzoate (**14**).

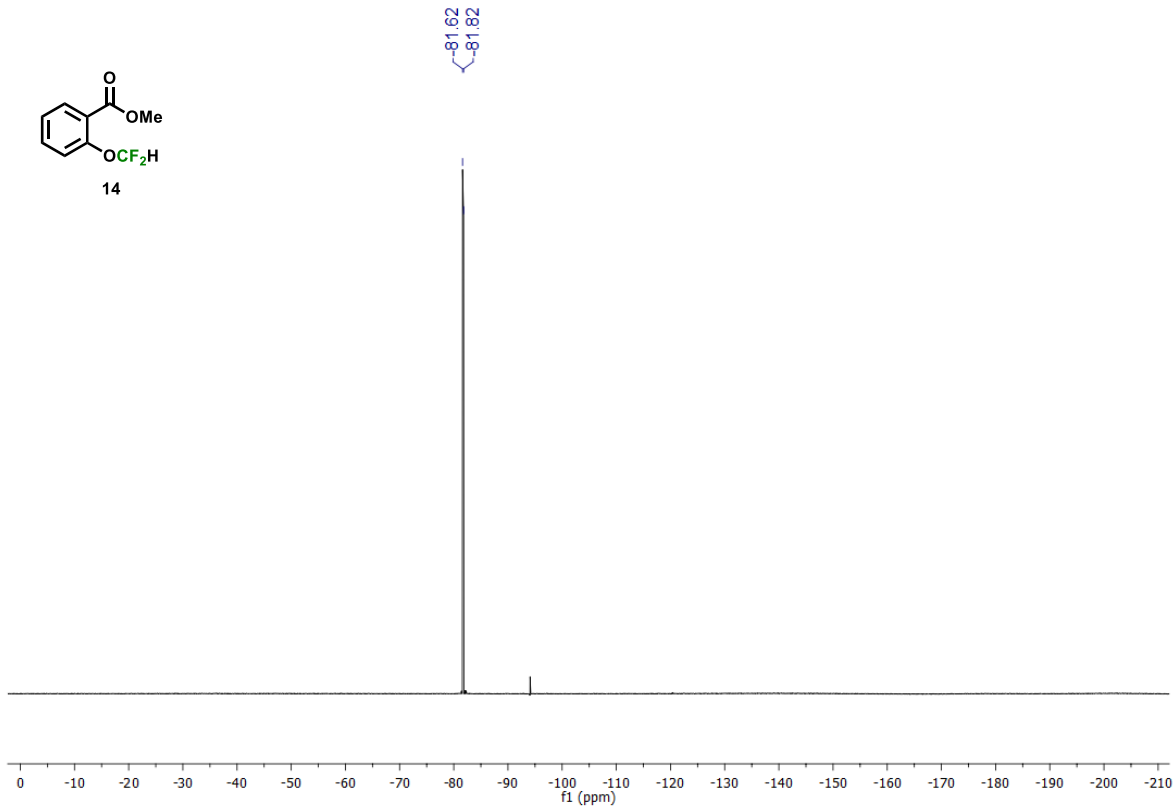

Figure S47: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)benzaldehyde (**15**).

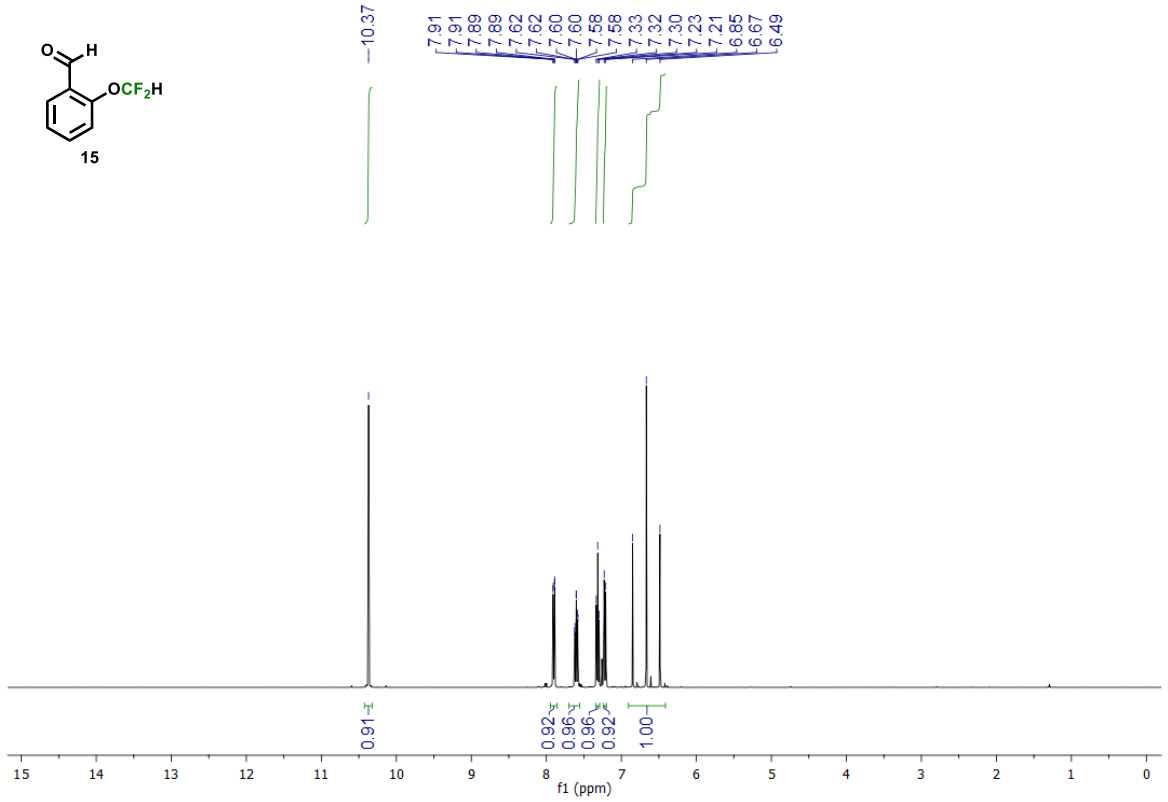

Figure S48: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)benzaldehyde (**15**).

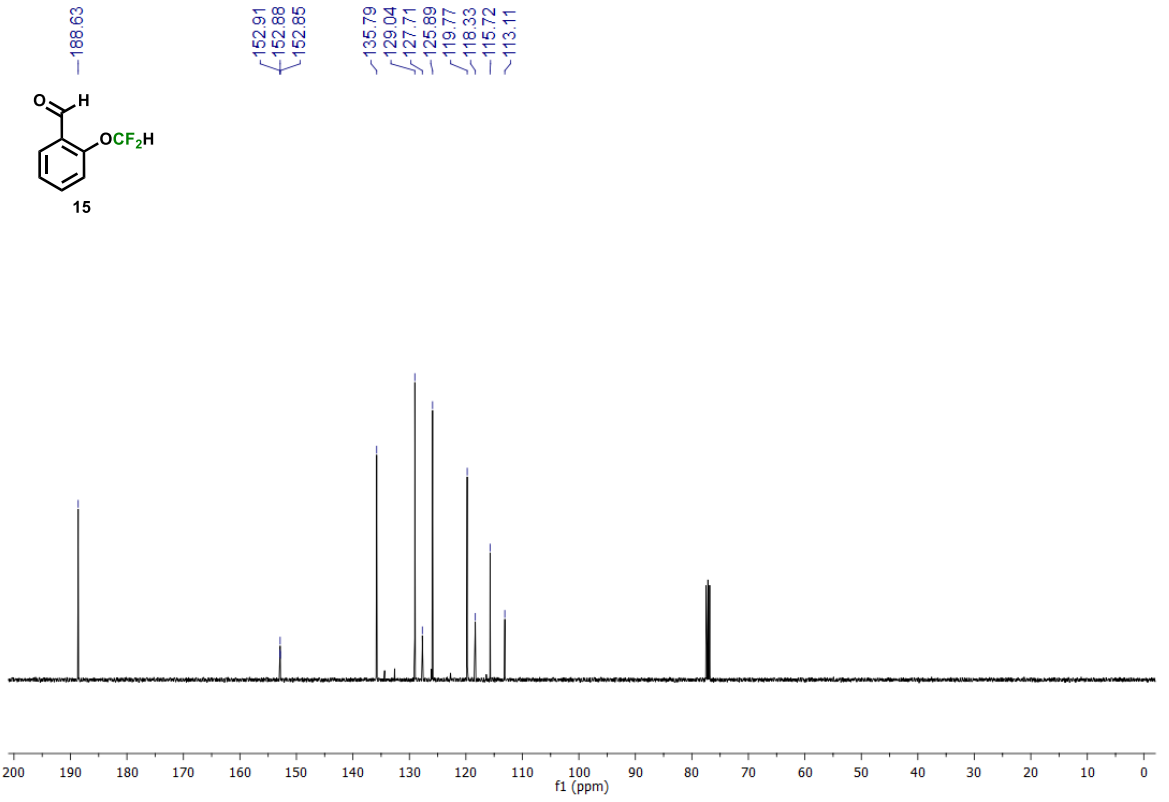

Figure S49: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)benzaldehyde (**15**).

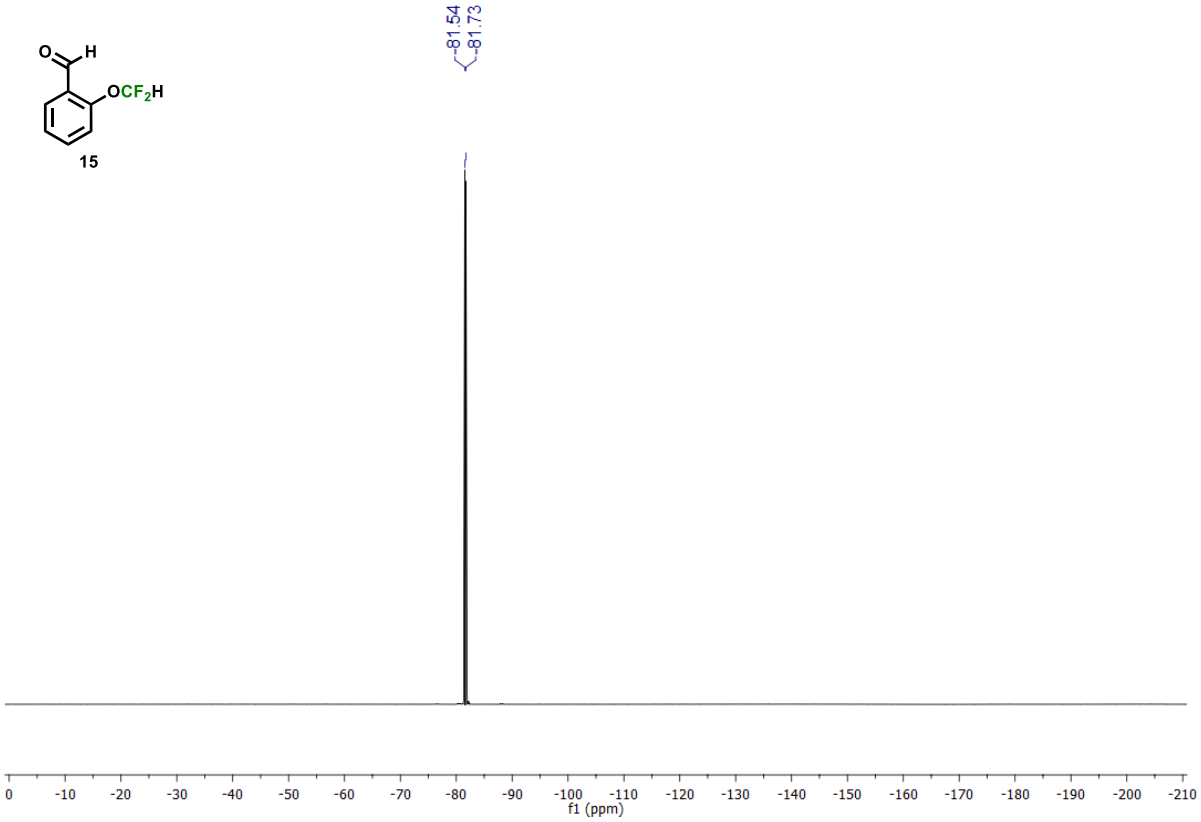

Figure S50: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(Difluoromethoxy)benzaldehyde (**16**).

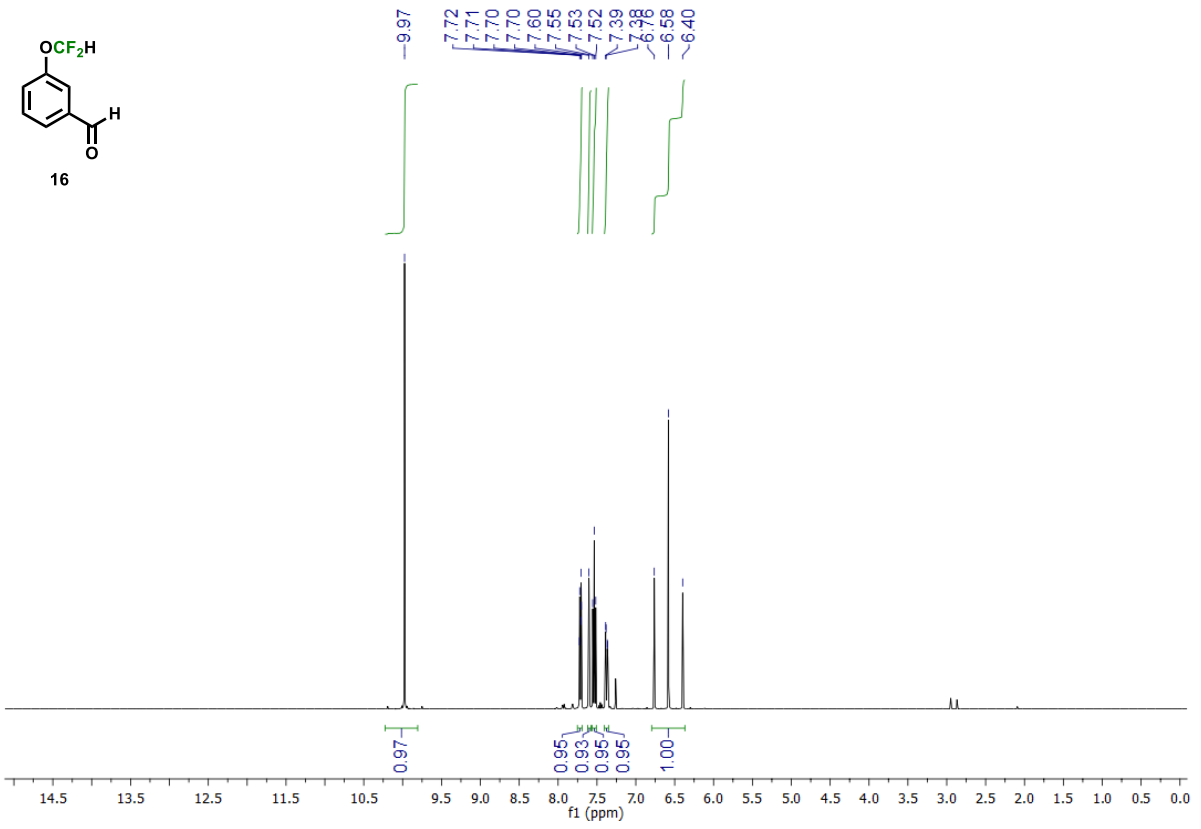

Figure S51: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 3-(Difluoromethoxy)benzaldehyde (**16**).

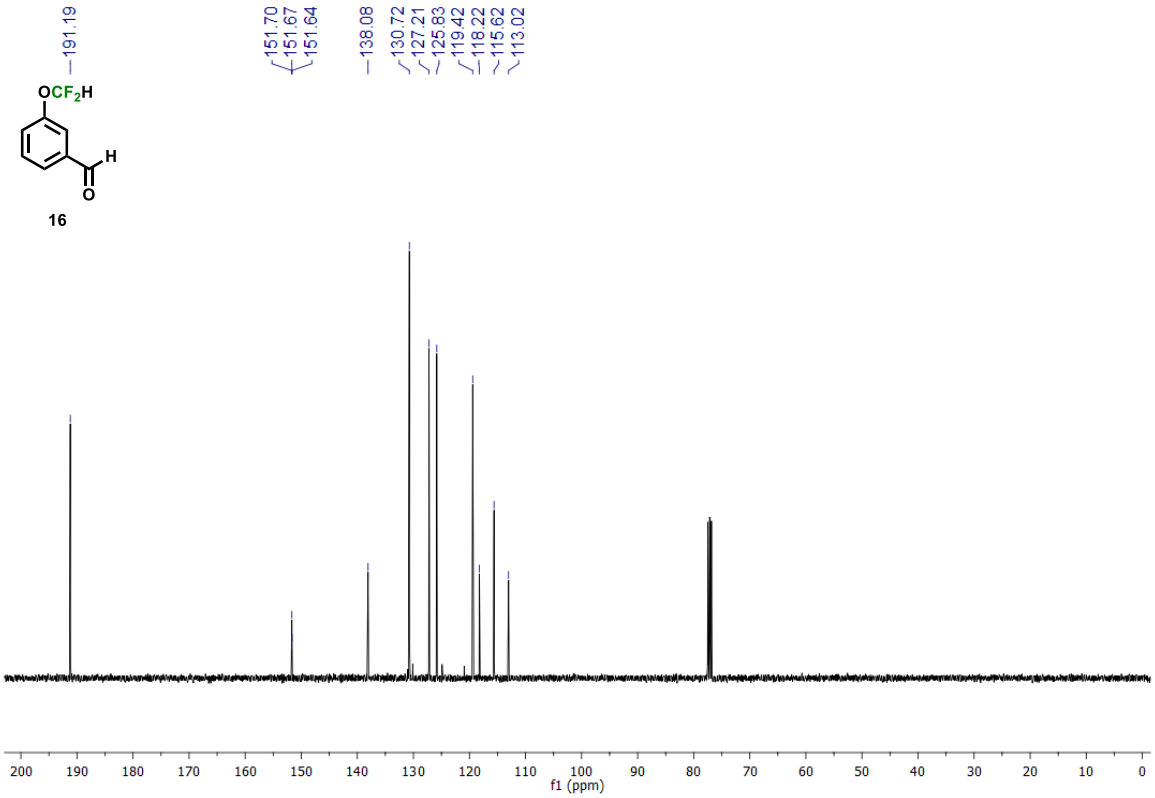

Figure S52: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3-(Difluoromethoxy)benzaldehyde (**16**).

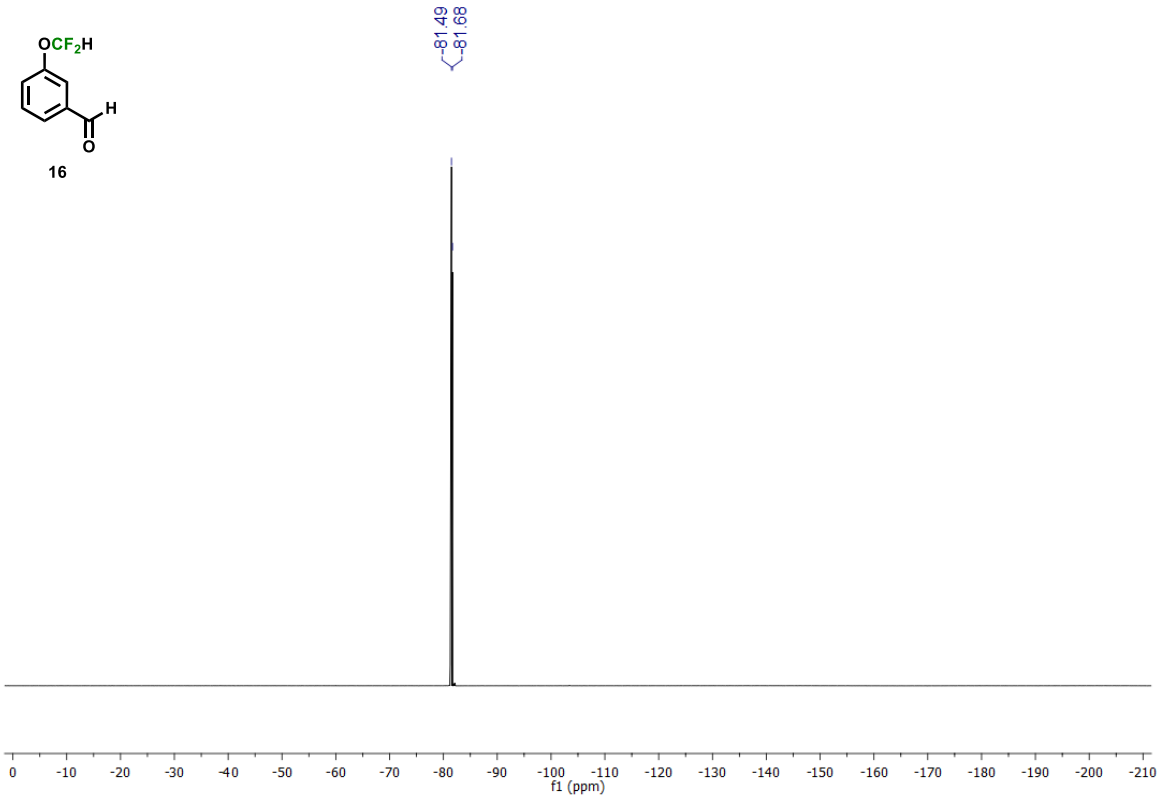

Figure S53: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)benzaldehyde (**17**).

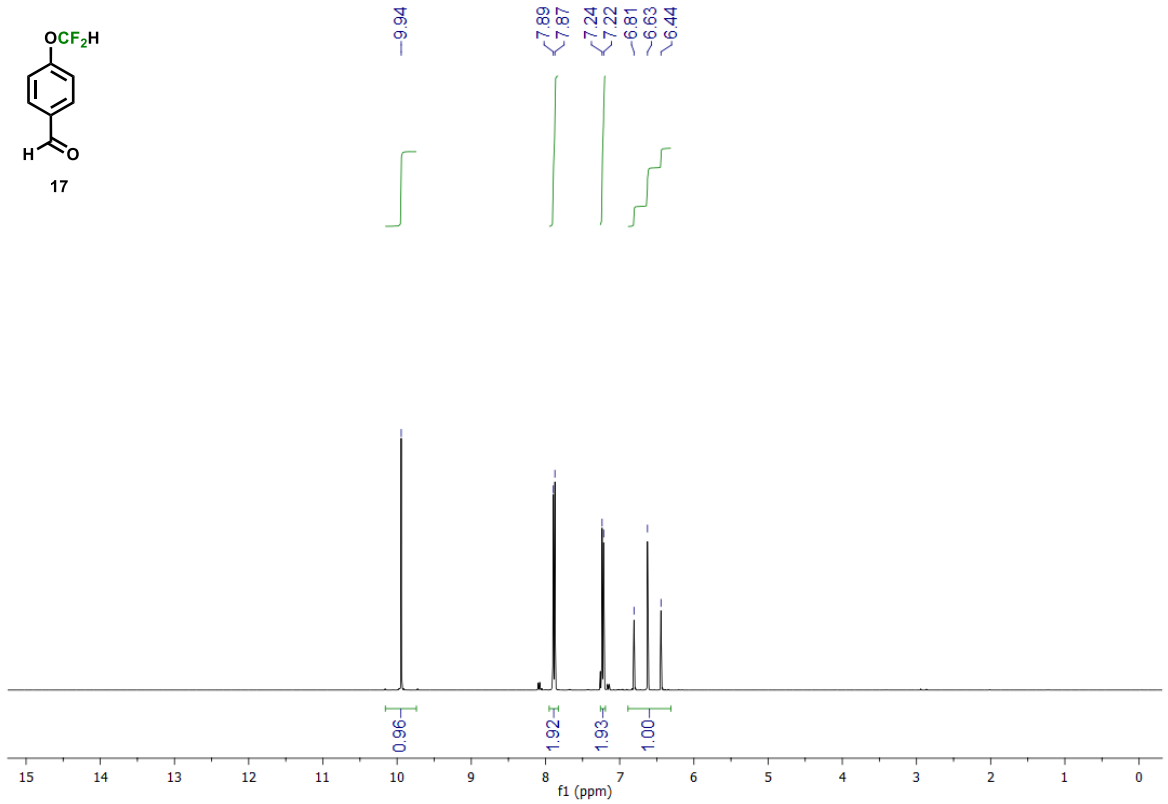

Figure S54: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)benzaldehyde (**17**).

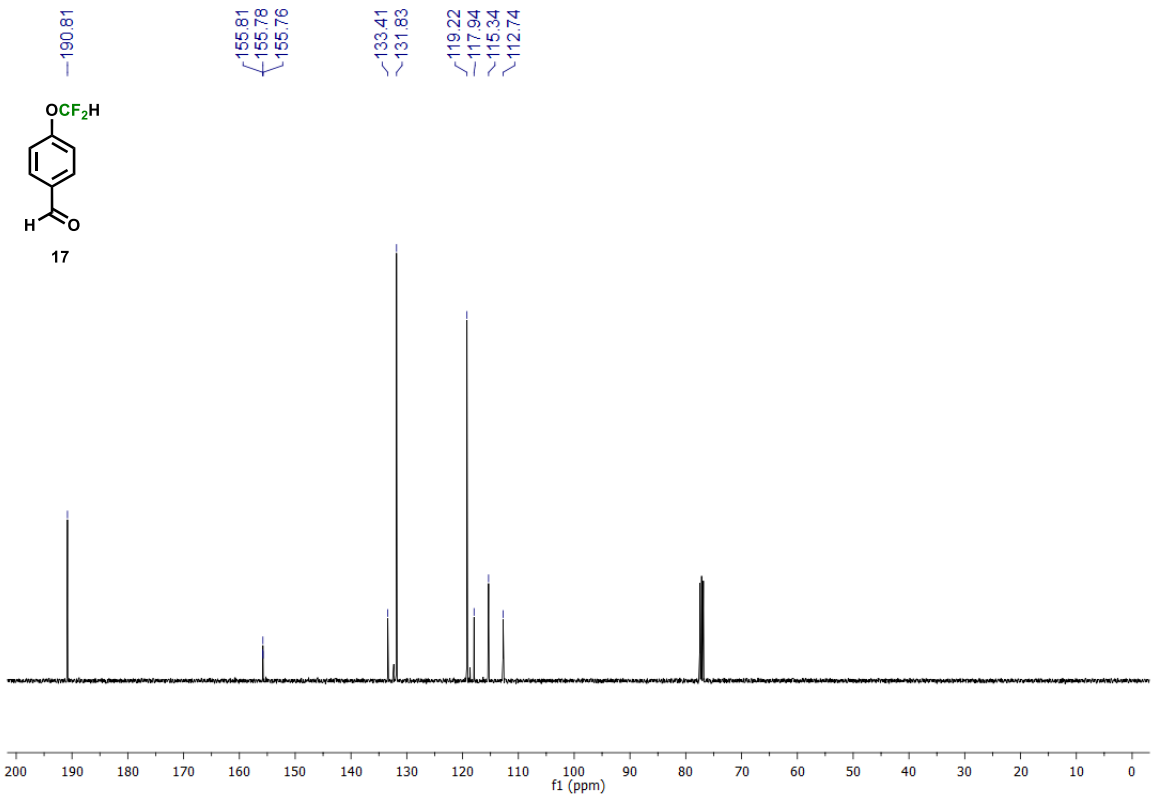

Figure S55: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)benzaldehyde (**17**).

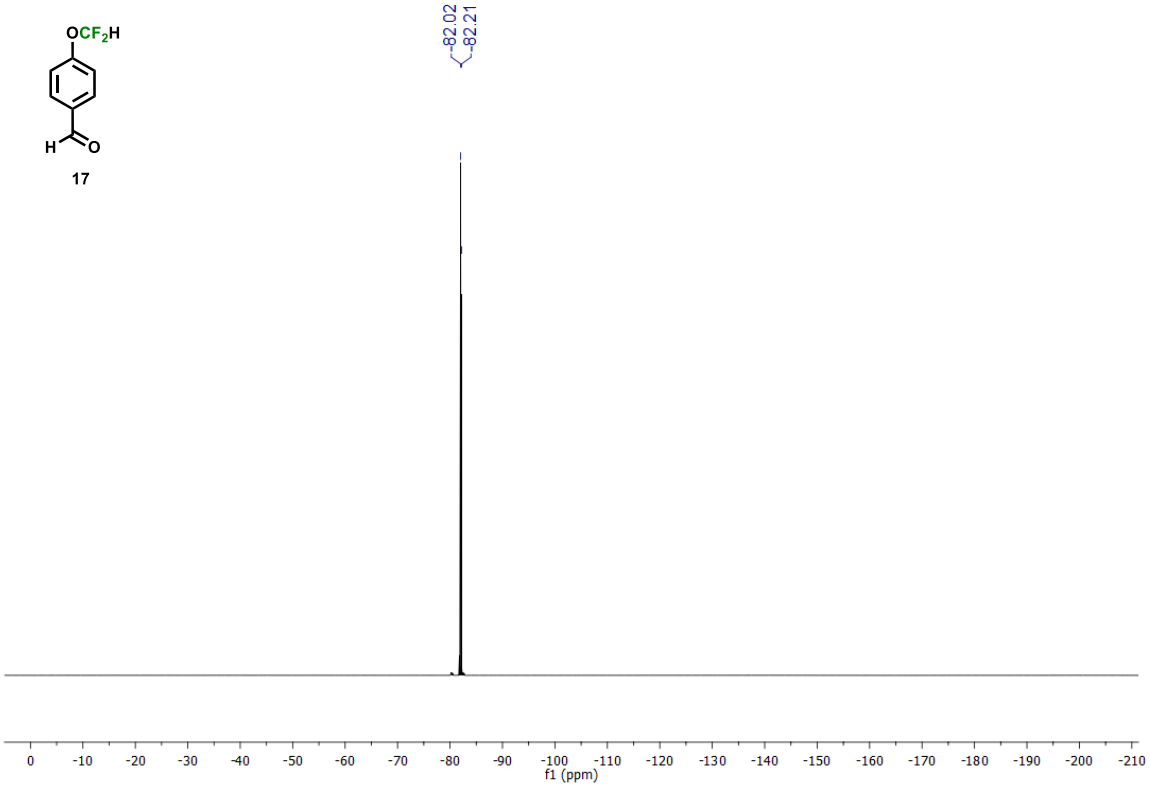

Figure S56: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)-1-naphthaldehyde (**18**).

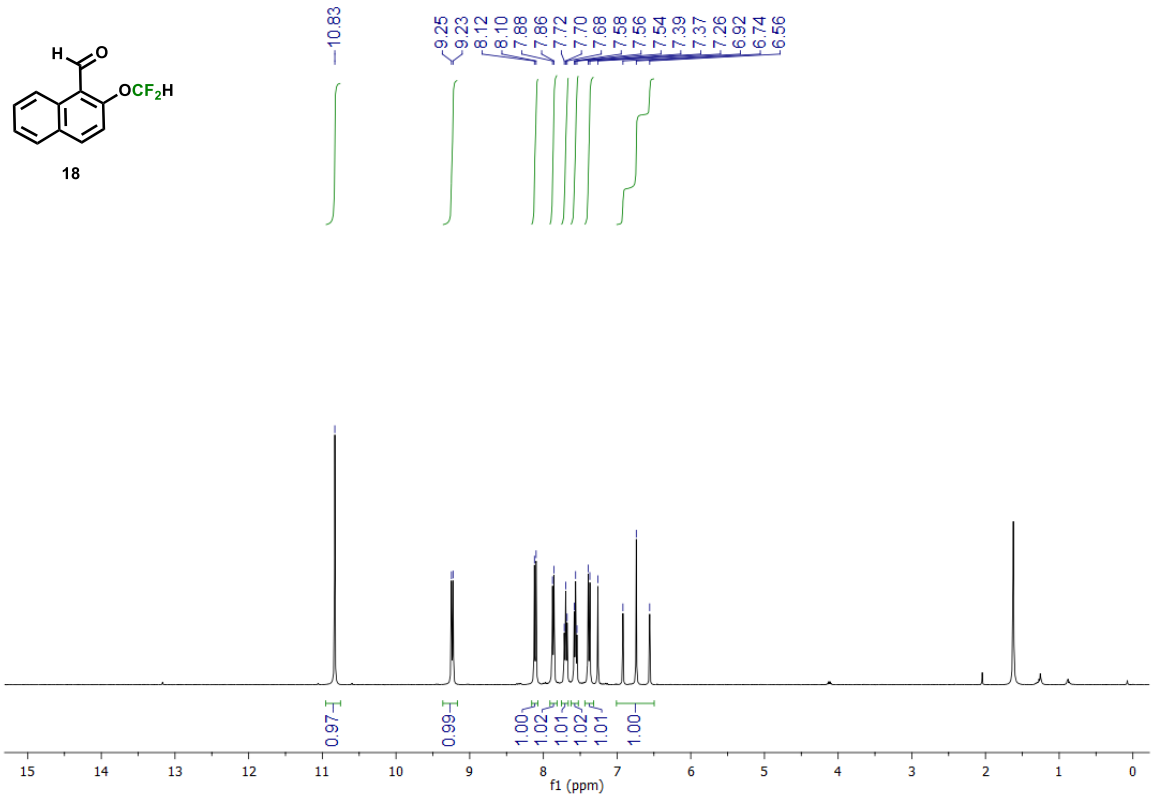

Figure S57: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)-1-naphthaldehyde (**18**).

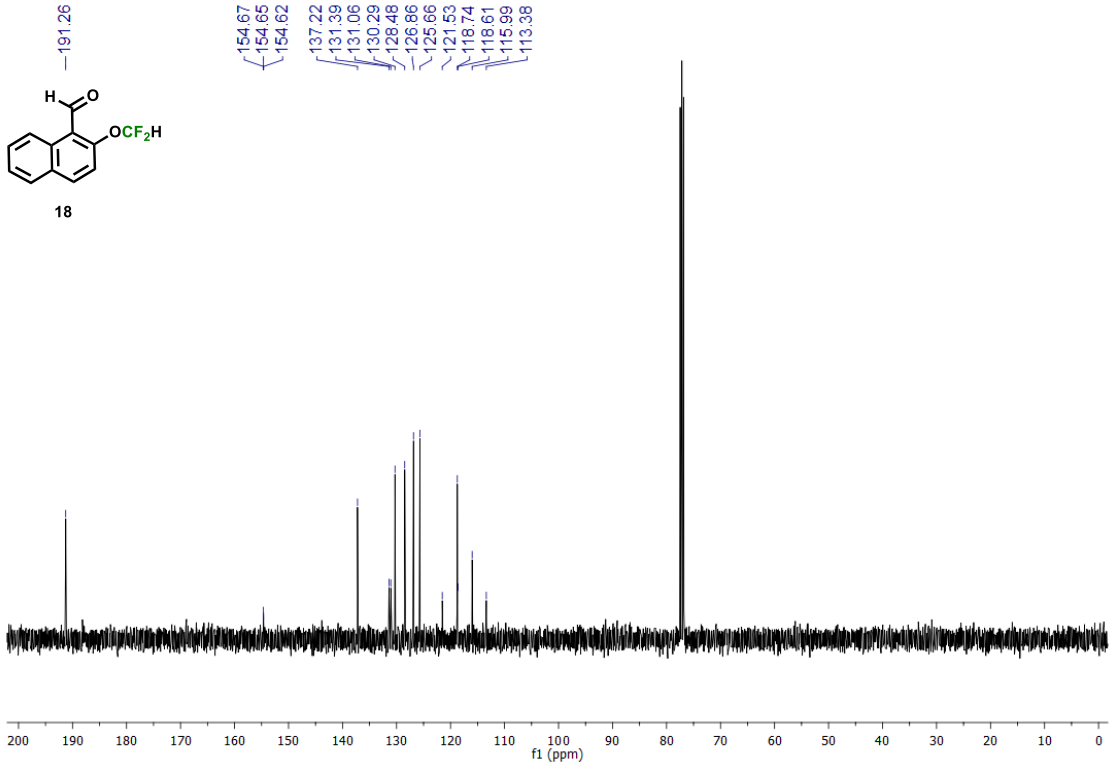

Figure S58: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)-1-naphthaldehyde (**18**).

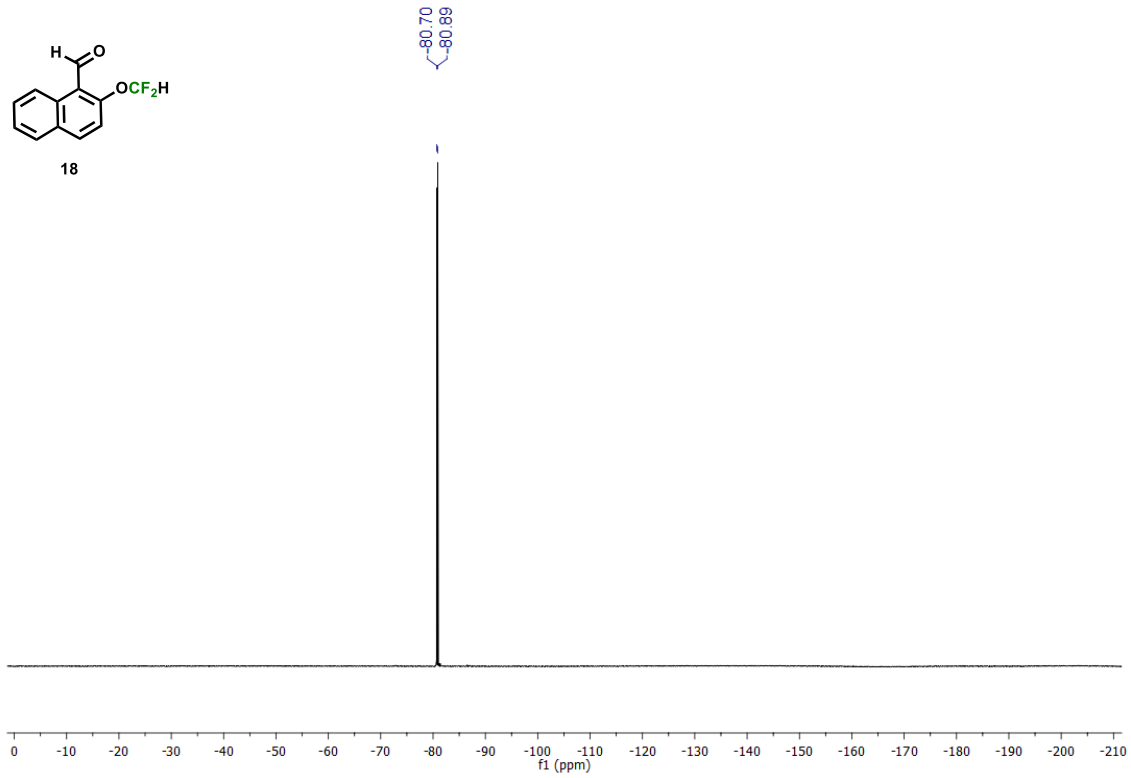

Figure S59: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)-4-methoxybenzaldehyde (**19**).

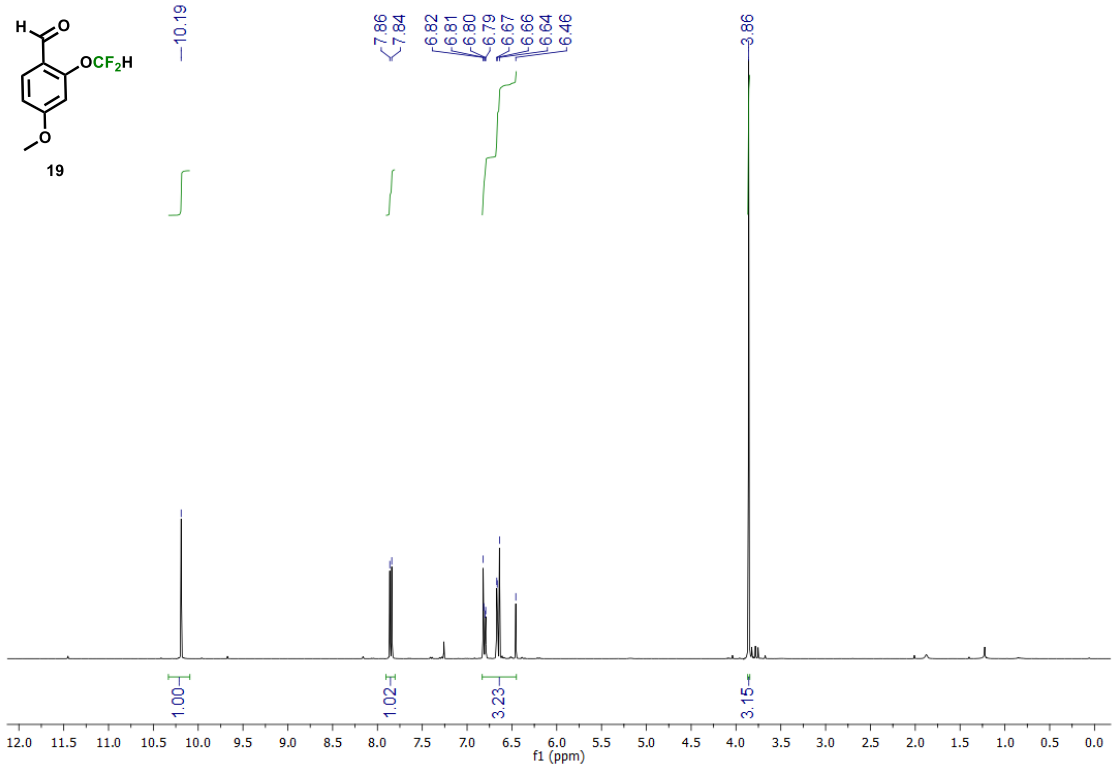

Figure S60: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)-4-methoxybenzaldehyde (**19**).

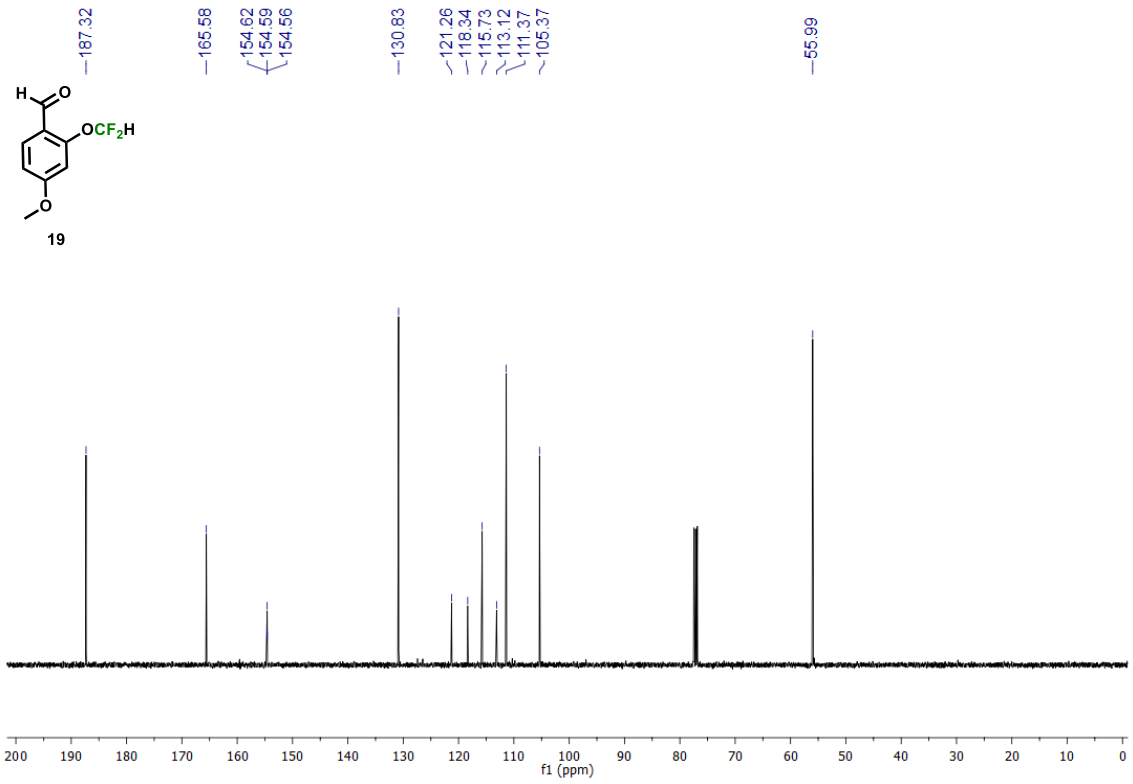

Figure S61: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)-4-methoxybenzaldehyde (**19**).

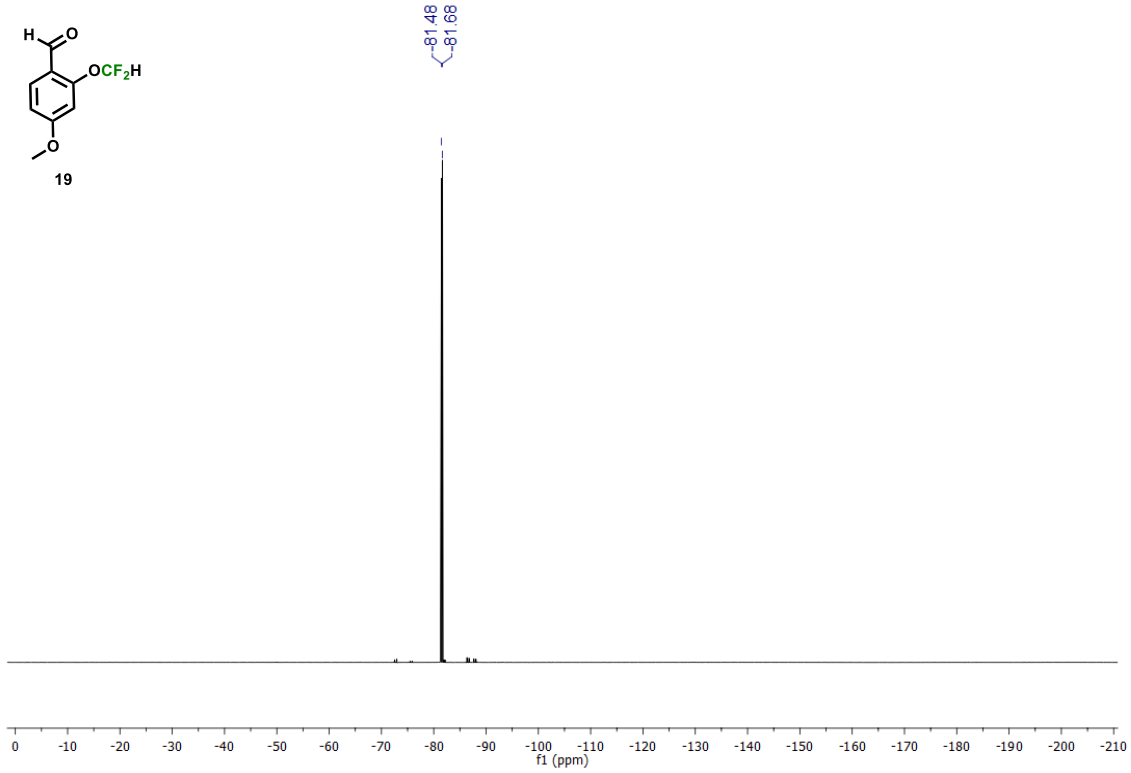

Figure S62: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(Diethylamino)-2-(difluoromethoxy)benzaldehyde (**20**).

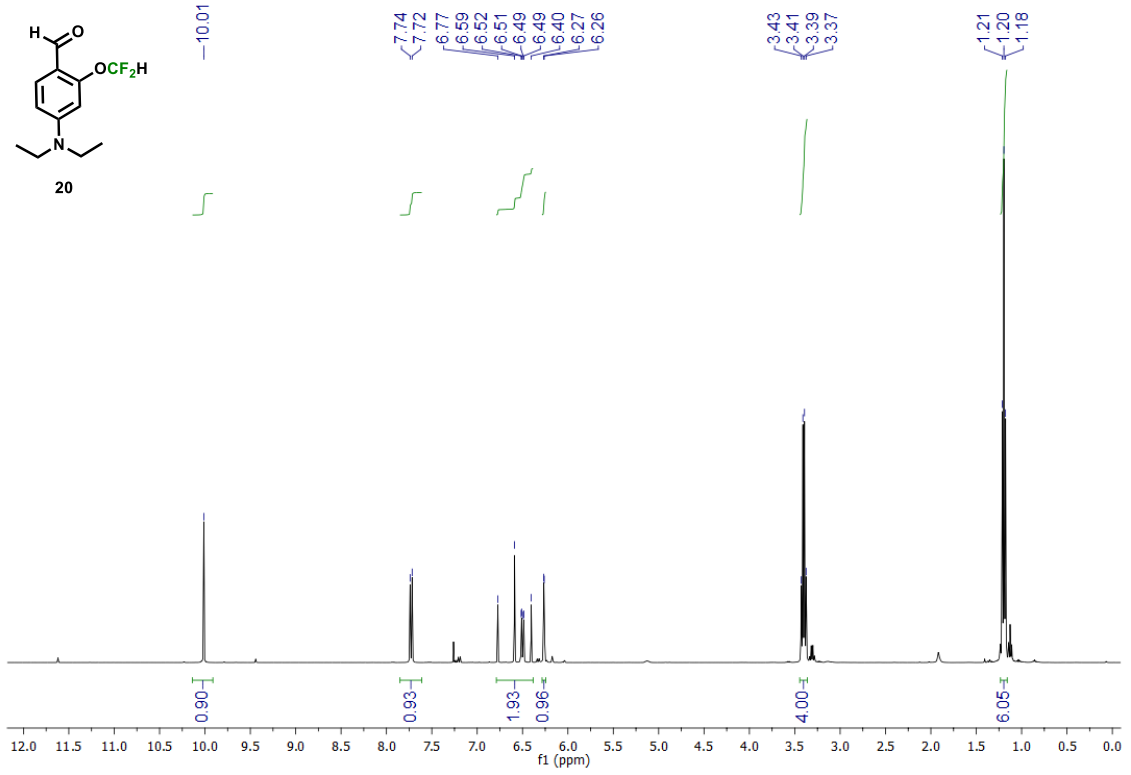

Figure S63: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-(Diethylamino)-2-(difluoromethoxy)benzaldehyde (**20**).

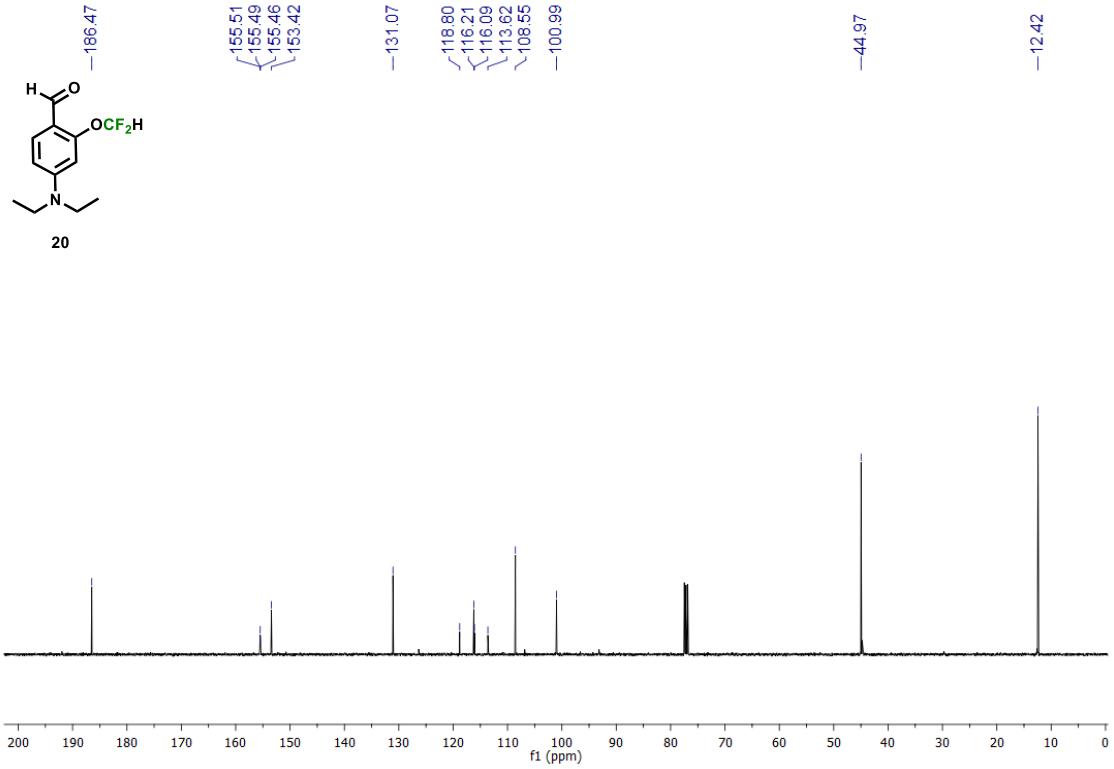

Figure S64: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(Diethylamino)-2-(difluoromethoxy)benzaldehyde (**20**).

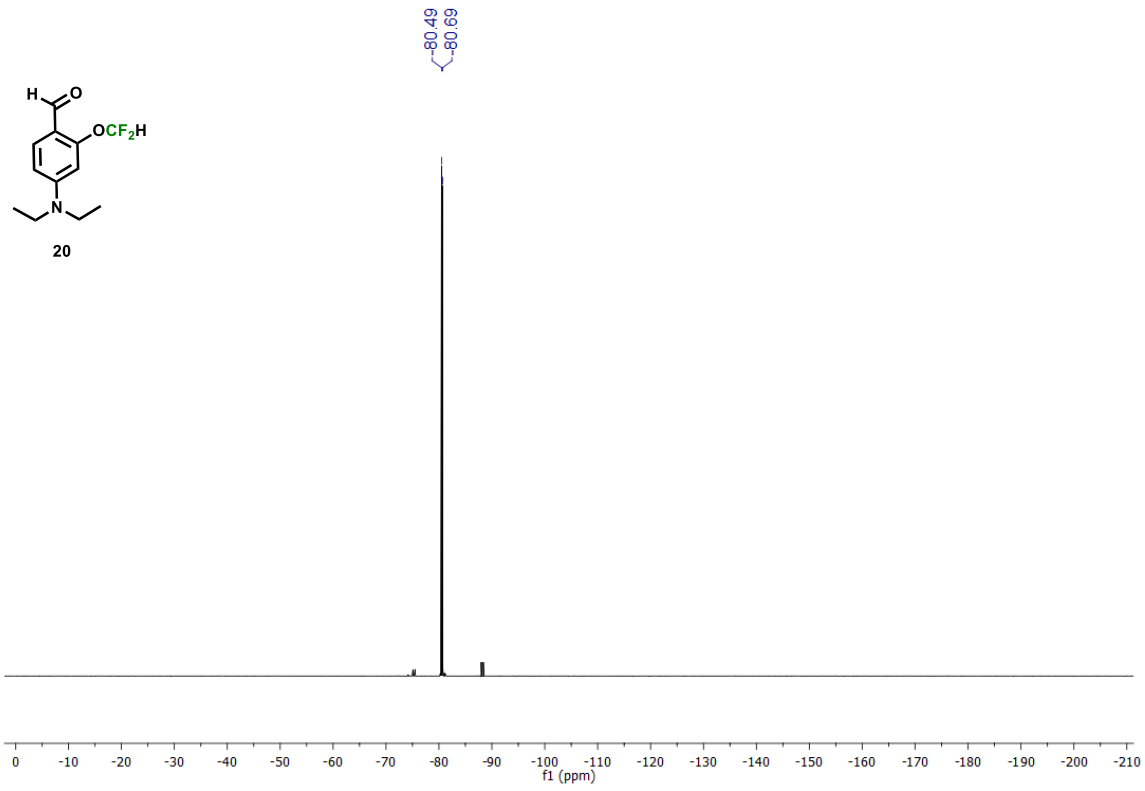

Figure S65: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-(trifluoromethyl)benzaldehyde (**21**).

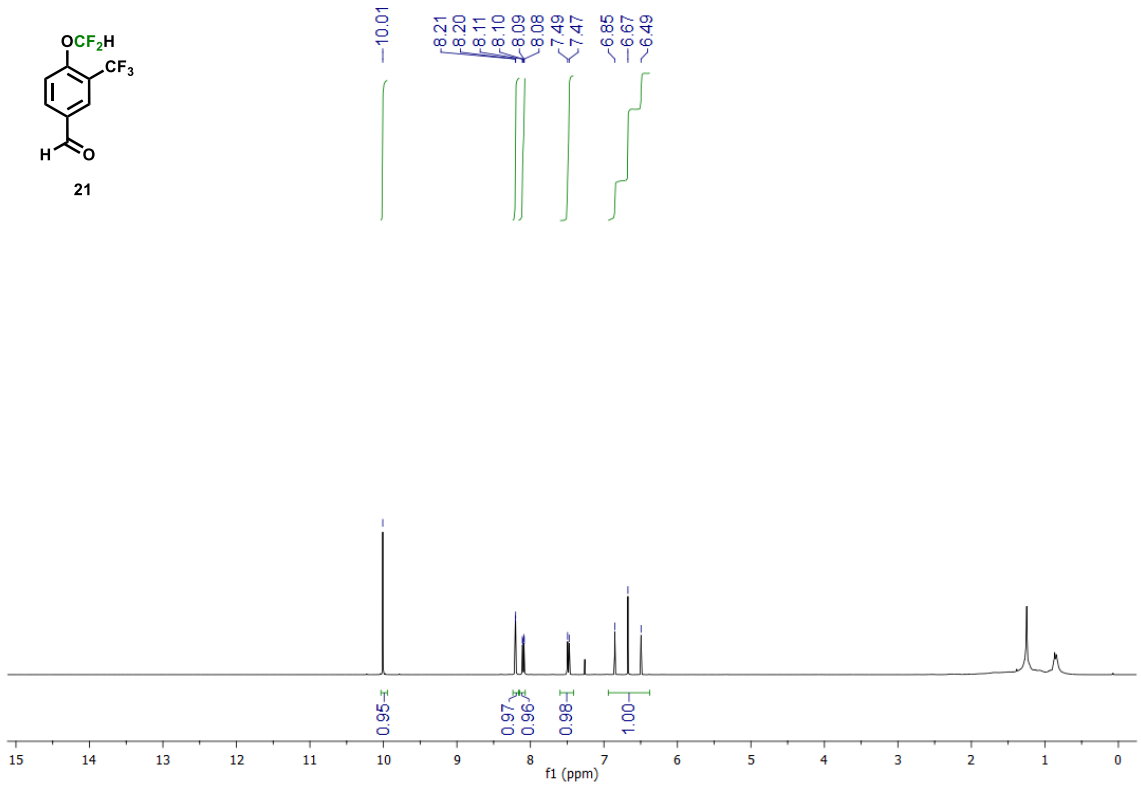

Figure S66: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-(trifluoromethyl)benzaldehyde (**21**).

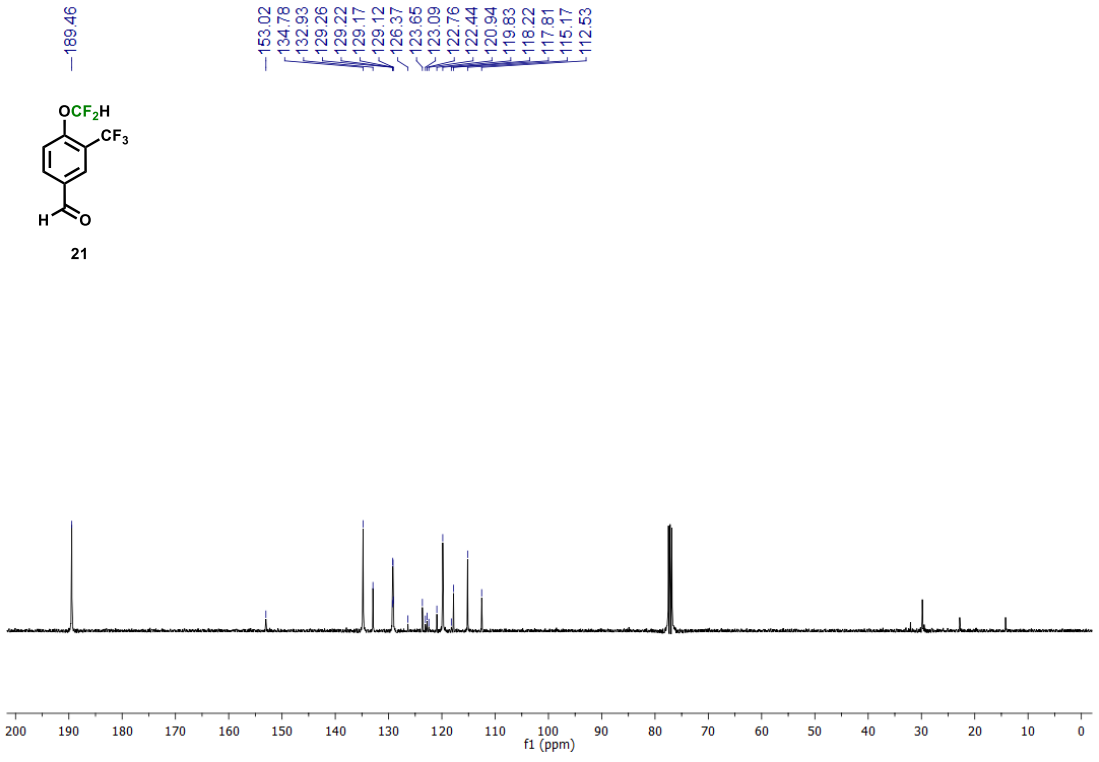

Figure S67: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-(trifluoromethyl)benzaldehyde (**21**).

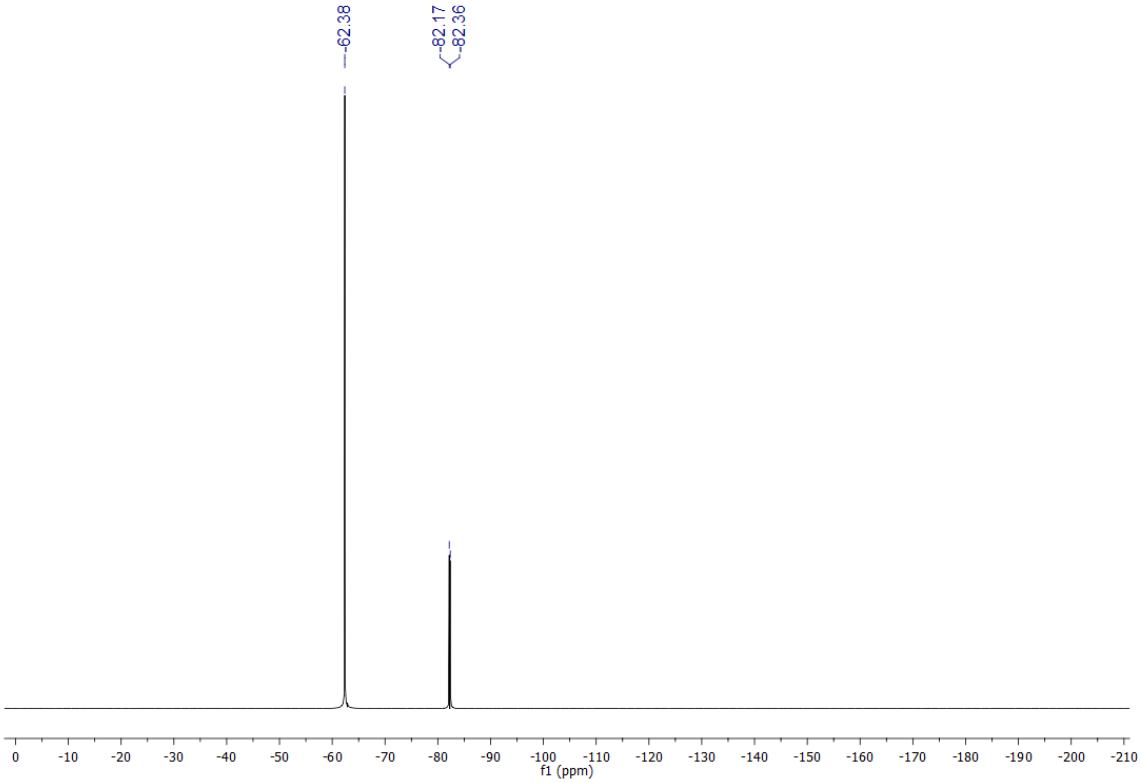

Figure S68: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(2-(Difluoromethoxy)phenyl)ethan-1-one (**22**).

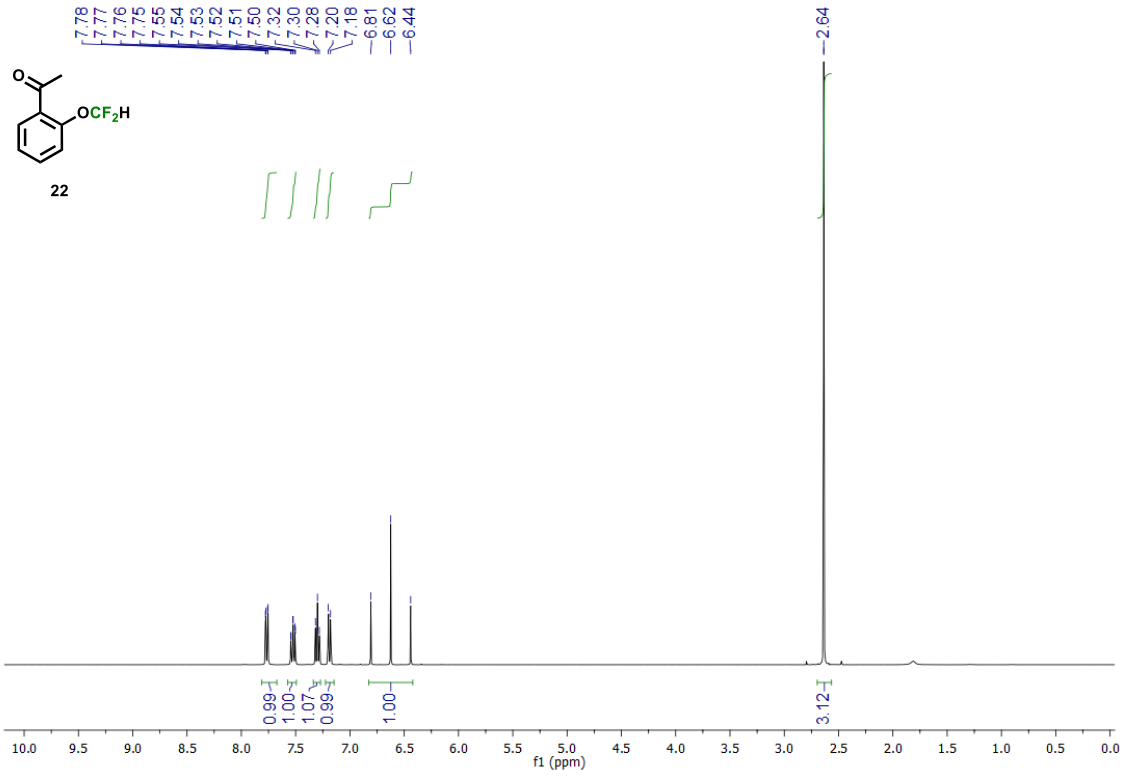

Figure S69: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(2-(Difluoromethoxy)phenyl)ethan-1-one (**22**).

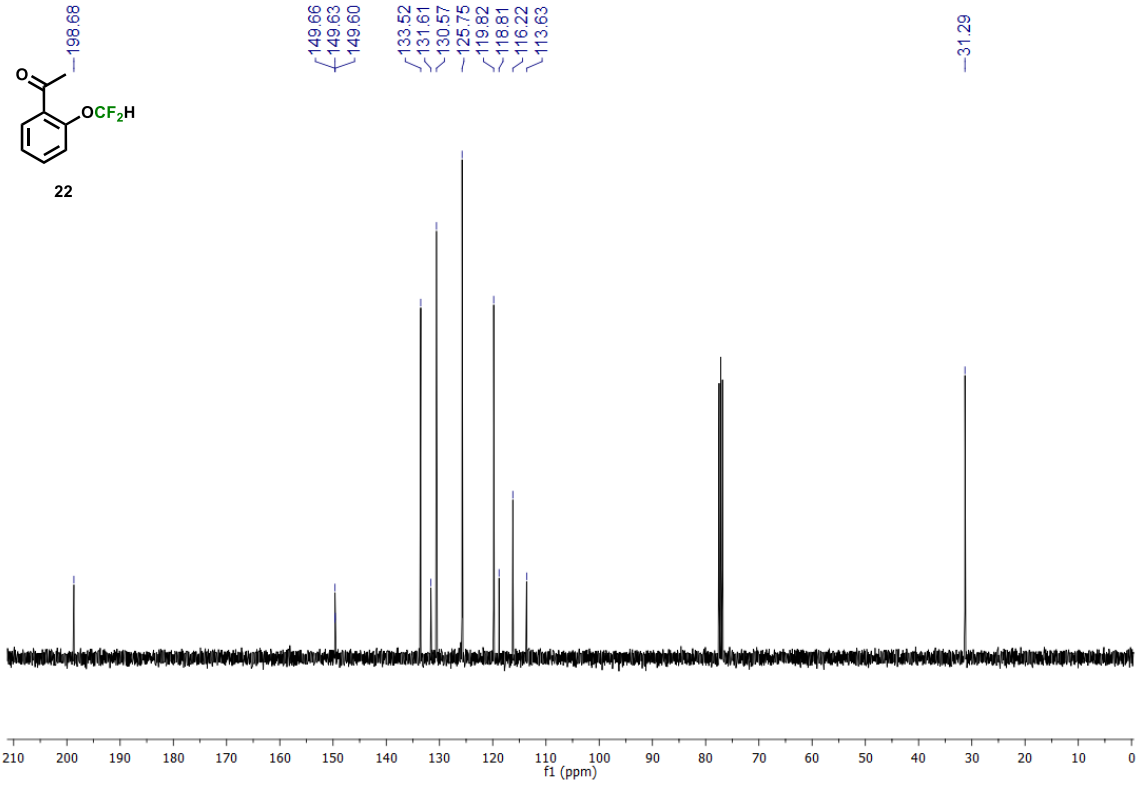

Figure S70: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(2-(Difluoromethoxy)phenyl)ethan-1-one (**22**).

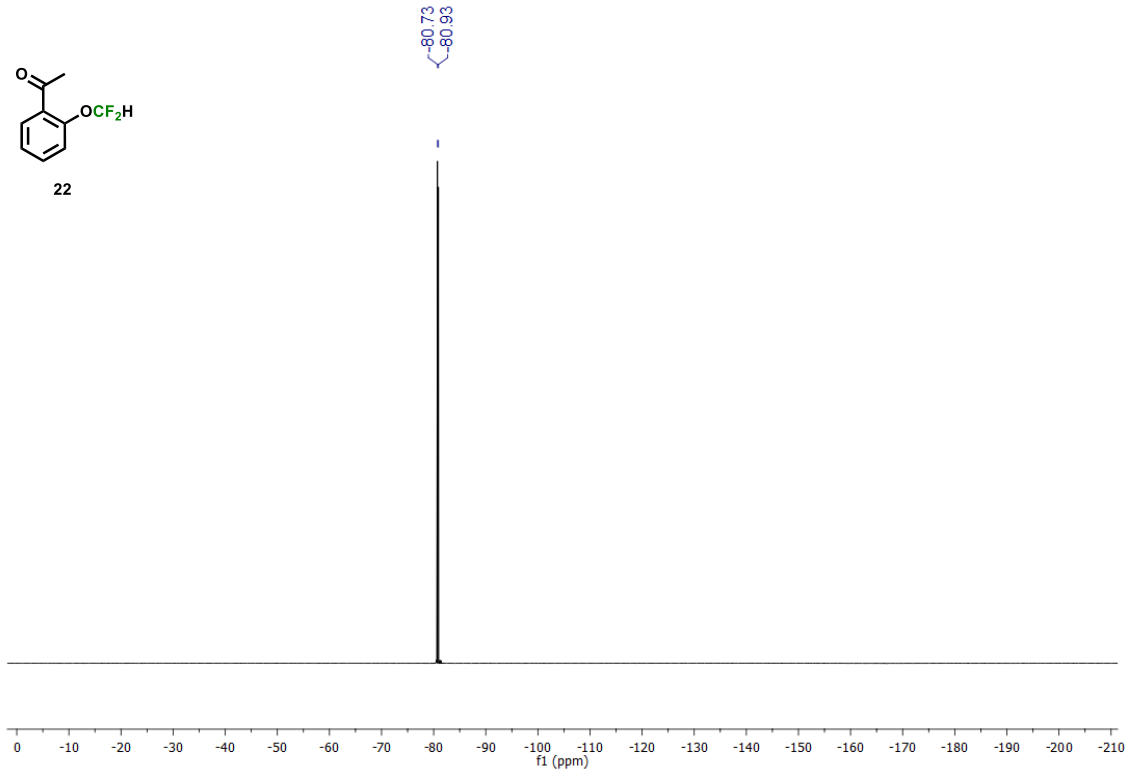

Figure S71: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(4-(Difluoromethoxy)phenyl)ethan-1-one (**23**).

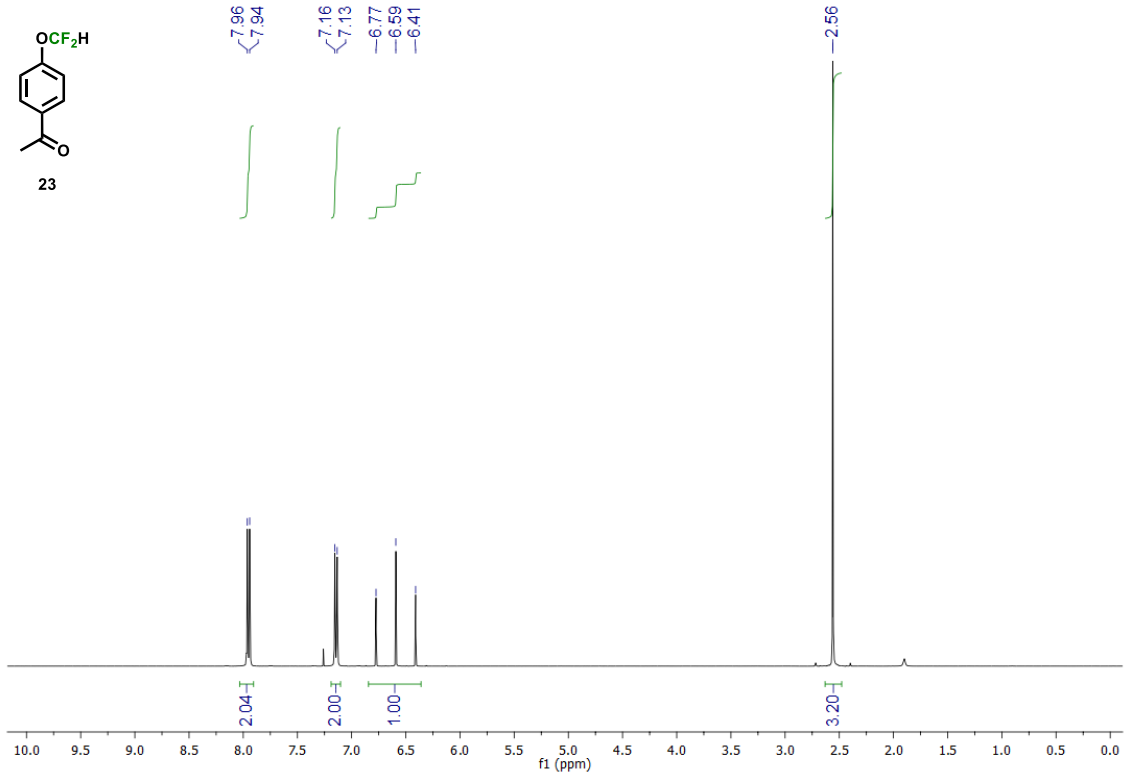

Figure S72: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(4-(Difluoromethoxy)phenyl)ethan-1-one (**23**).

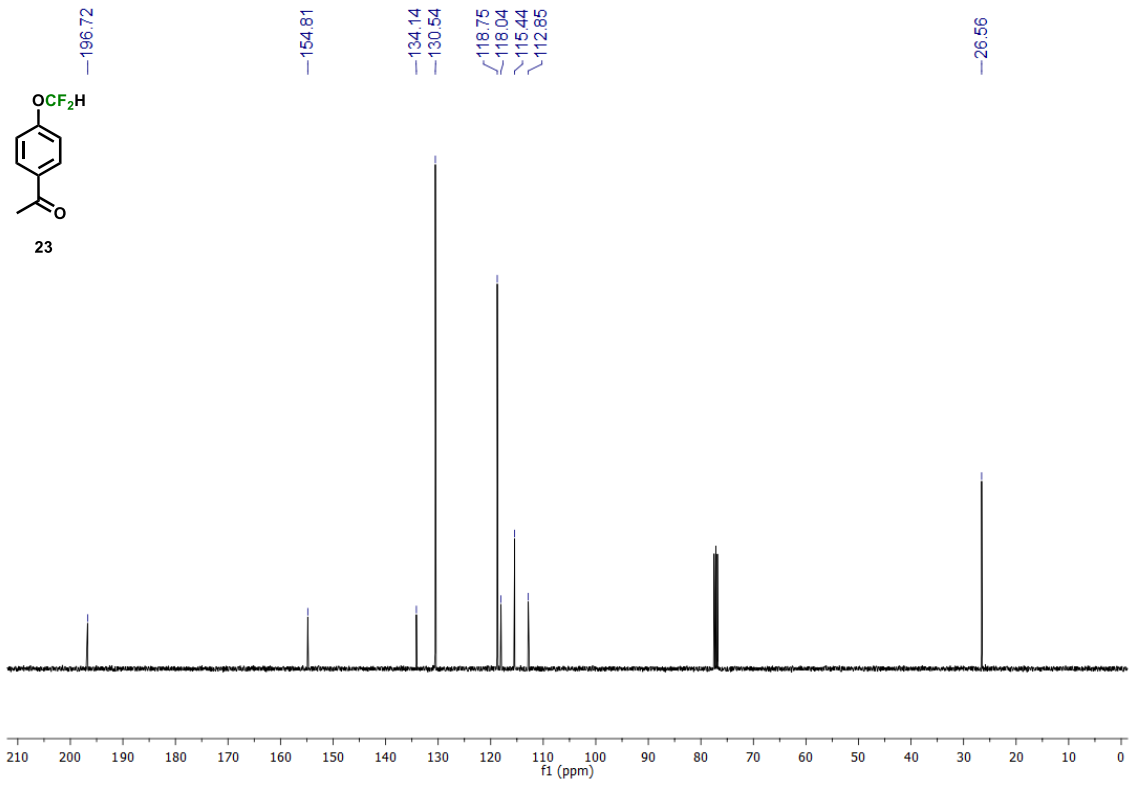

Figure S73: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(4-(Difluoromethoxy)phenyl)ethan-1-one (**23**).

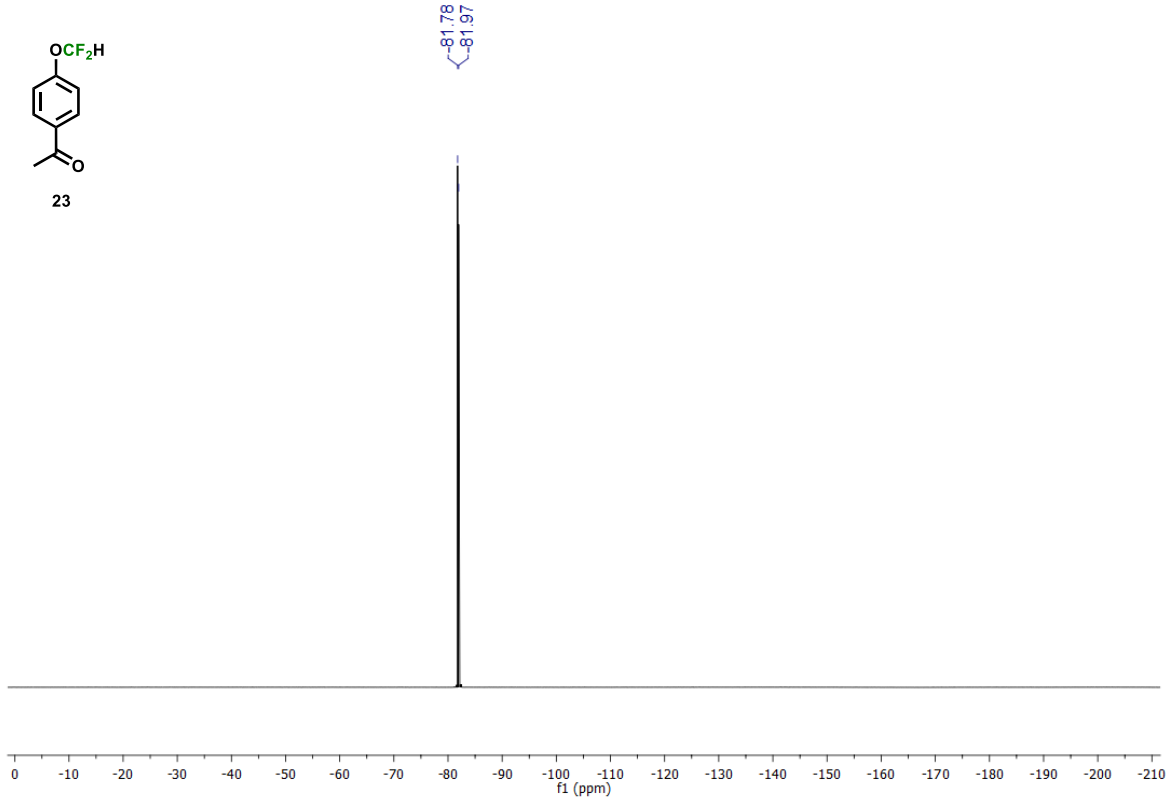

Figure S74: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)benzonitrile (**24**).

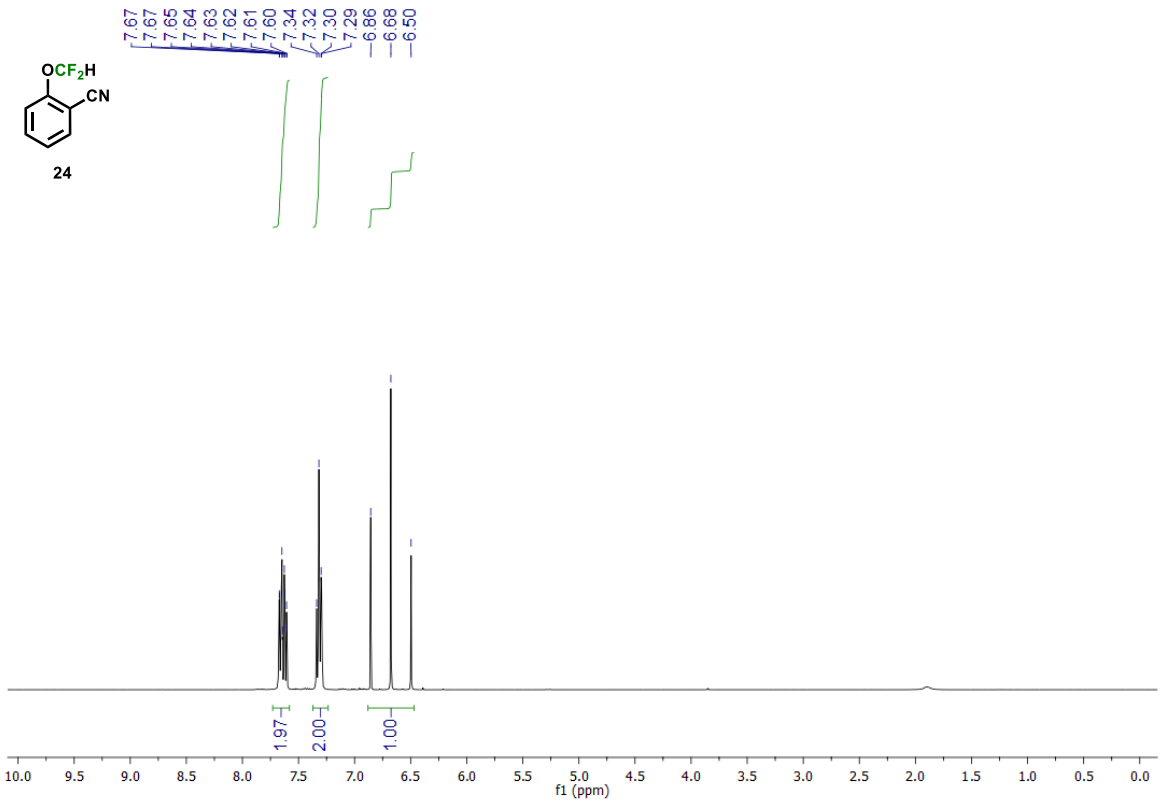

Figure S75: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)benzonitrile (**24**).

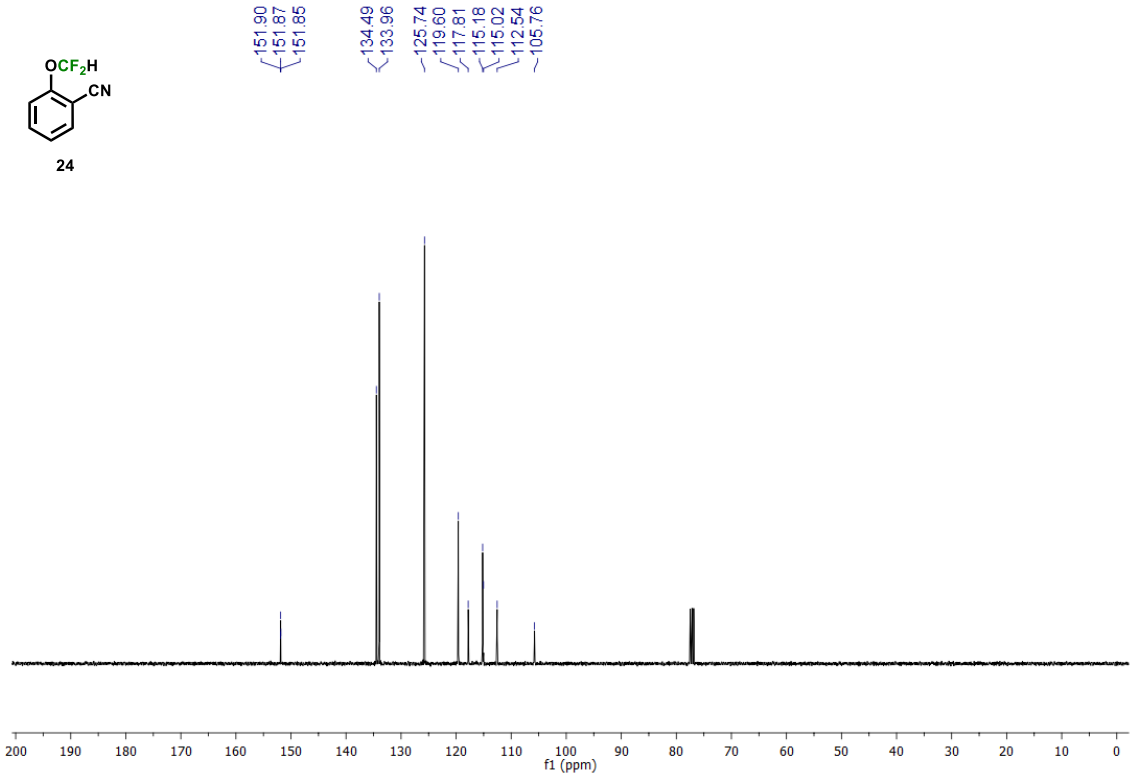

Figure S76: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)benzonitrile (**24**).

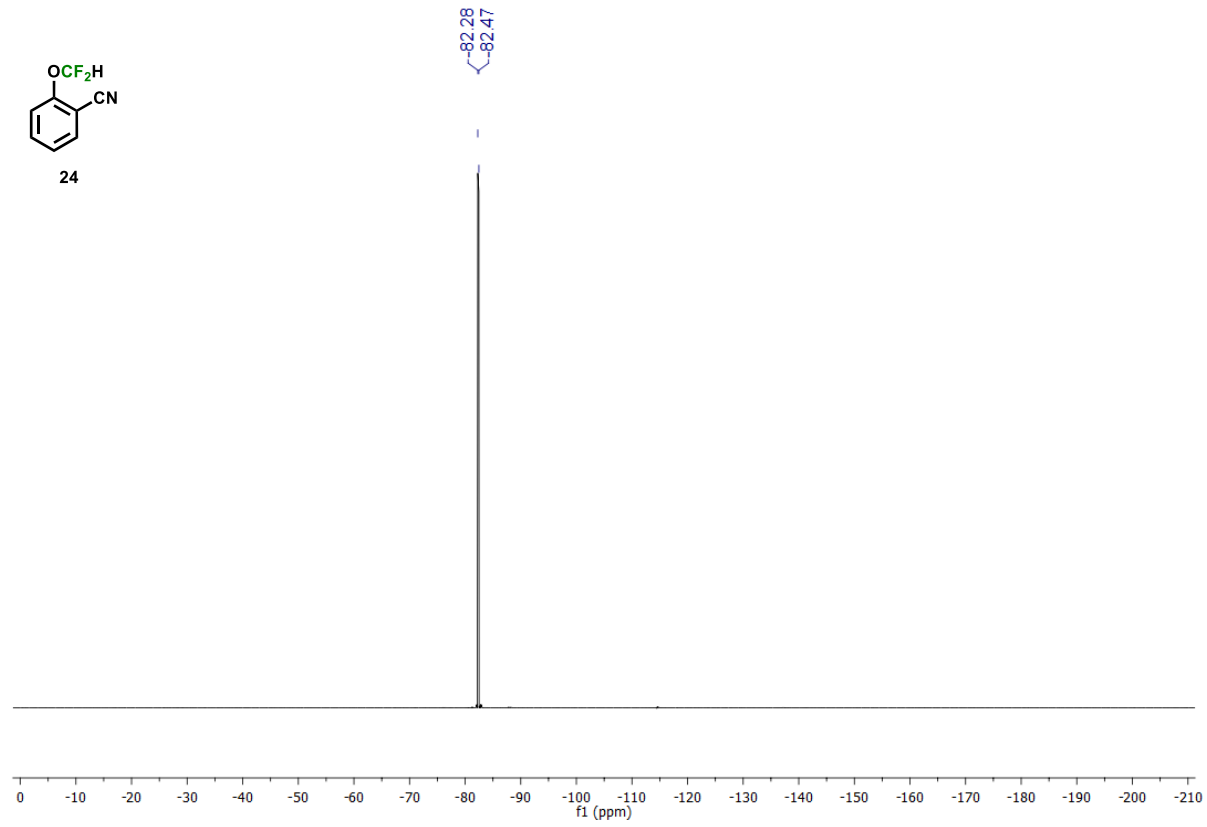

Figure S77: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)benzonitrile (**25**).

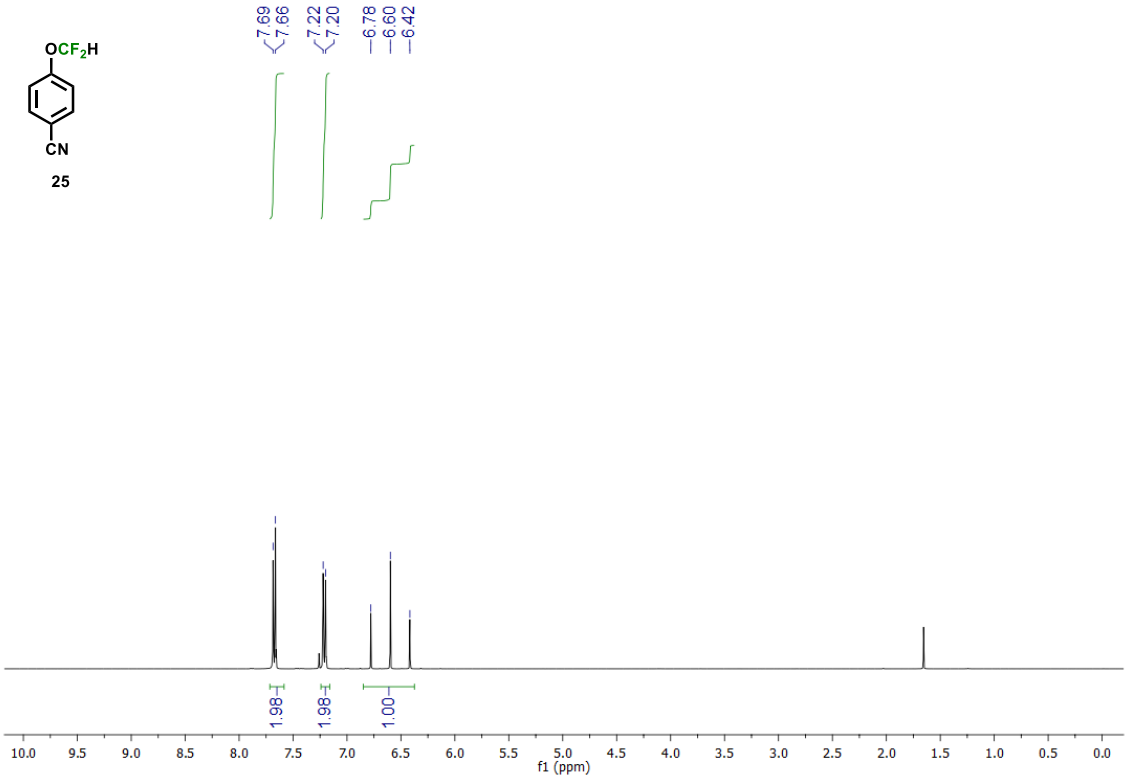

Figure S78: ^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)benzonitrile (**25**).

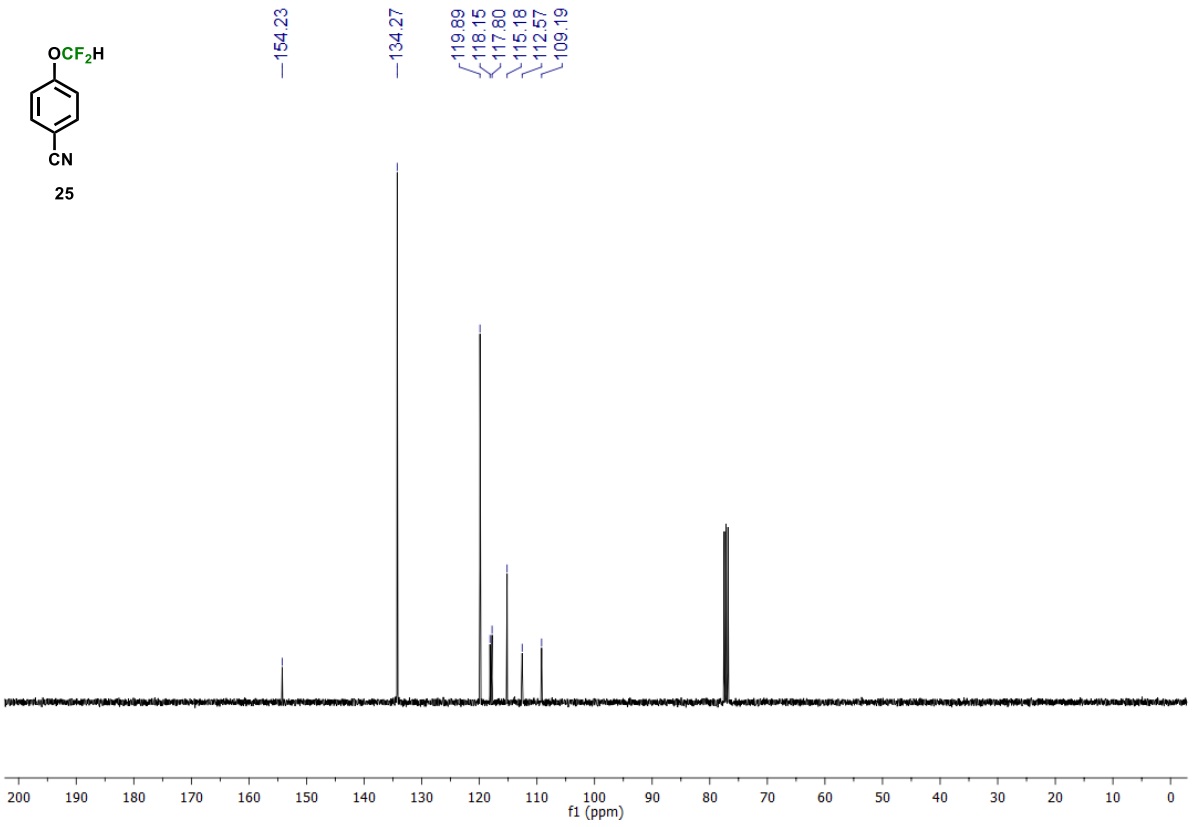

Figure S79: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)benzonitrile (**25**).

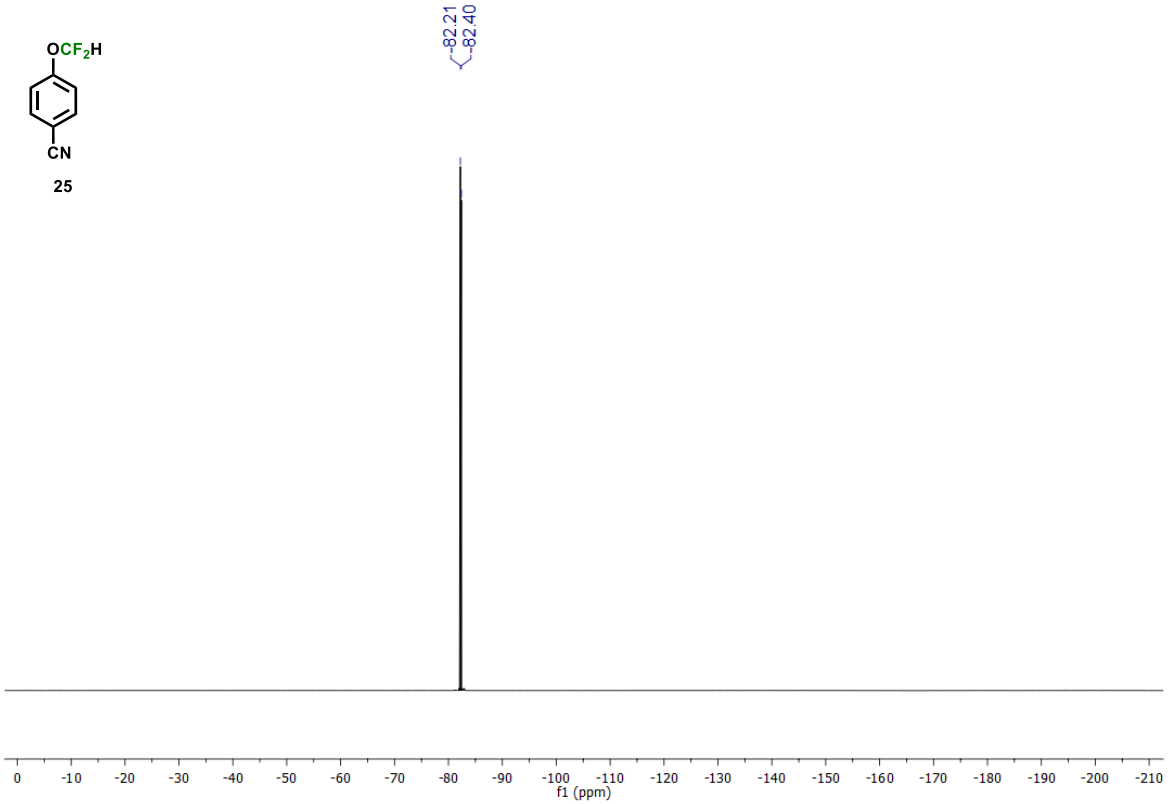

Figure S80: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5-Bromo-2-(difluoromethoxy)benzonitrile (**26**).

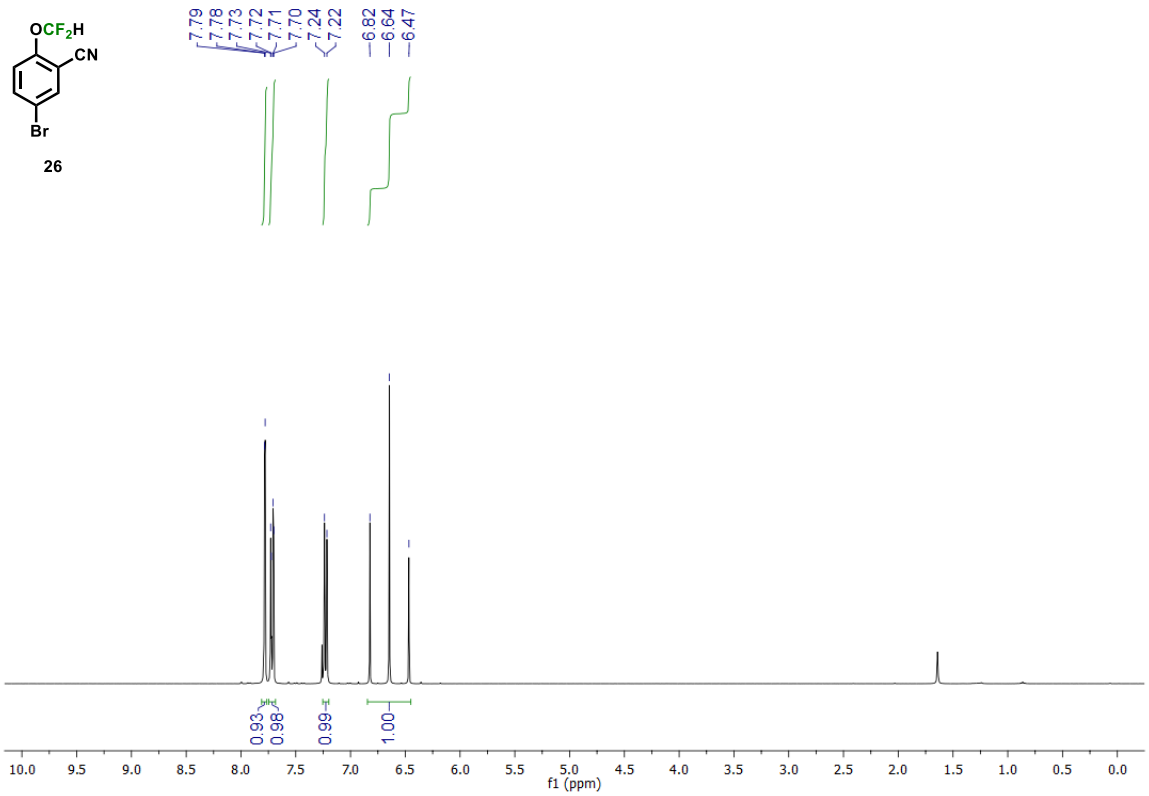

Figure S81: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 5-Bromo-2-(difluoromethoxy)benzonitrile (**26**).

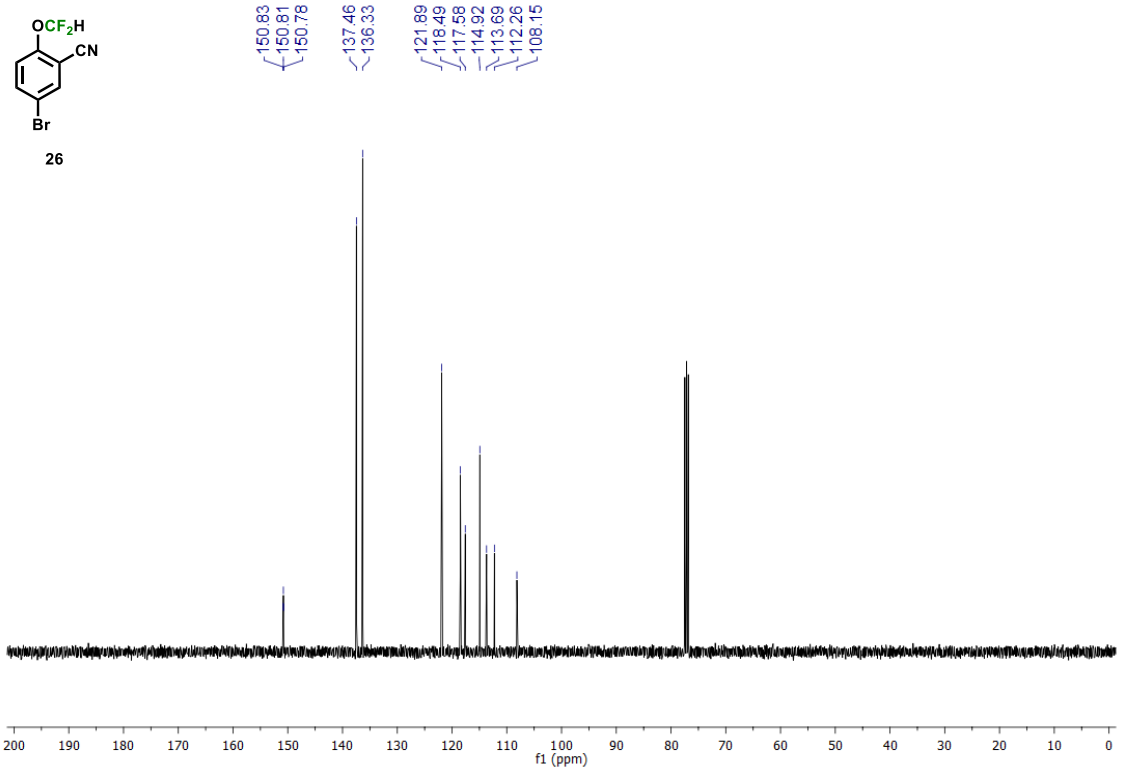

Figure S82: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5-Bromo-2-(difluoromethoxy)benzonitrile (**26**).

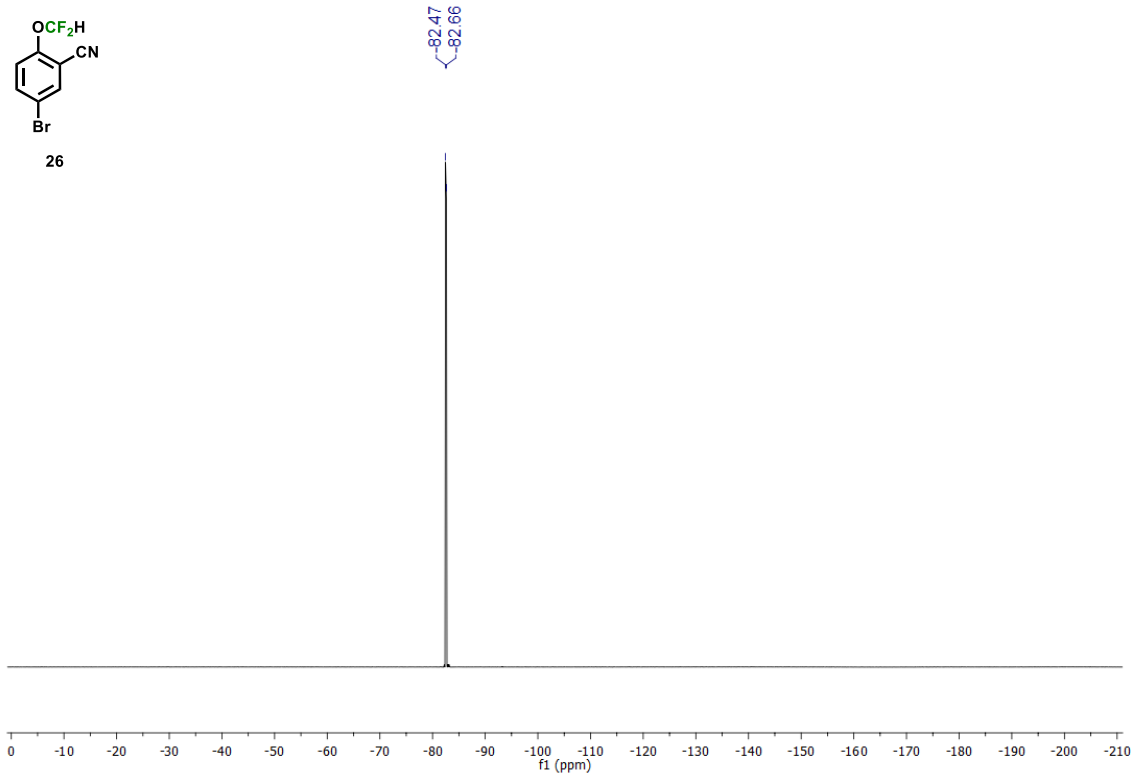

Figure S83: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-(methylsulfonyl)benzene (**27**).

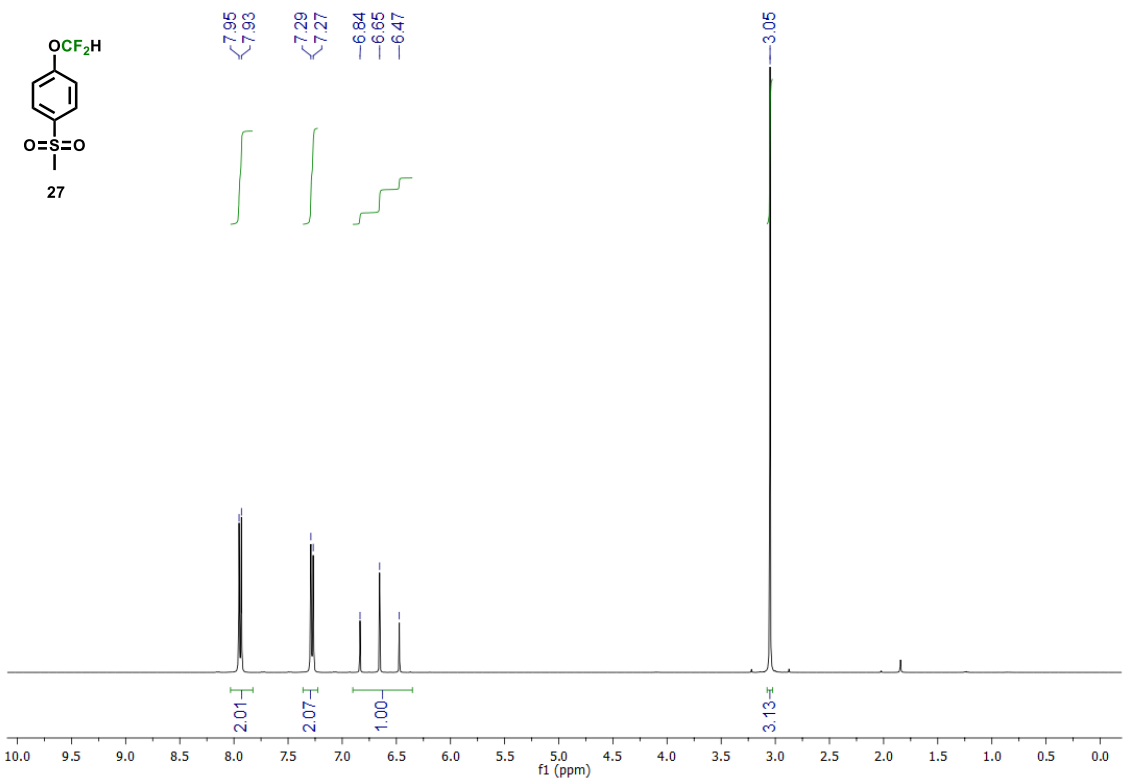

Figure S84: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-(methylsulfonyl)benzene (**27**).

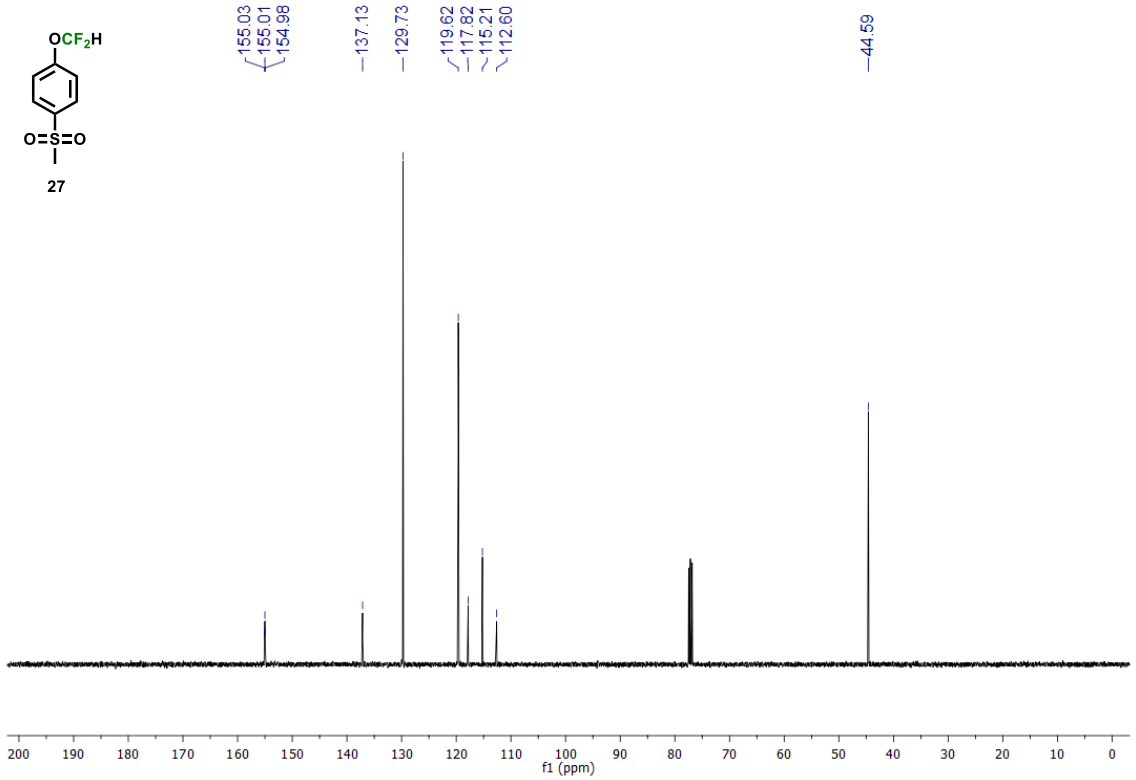

Figure S85: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-(methylsulfonyl)benzene (**27**).

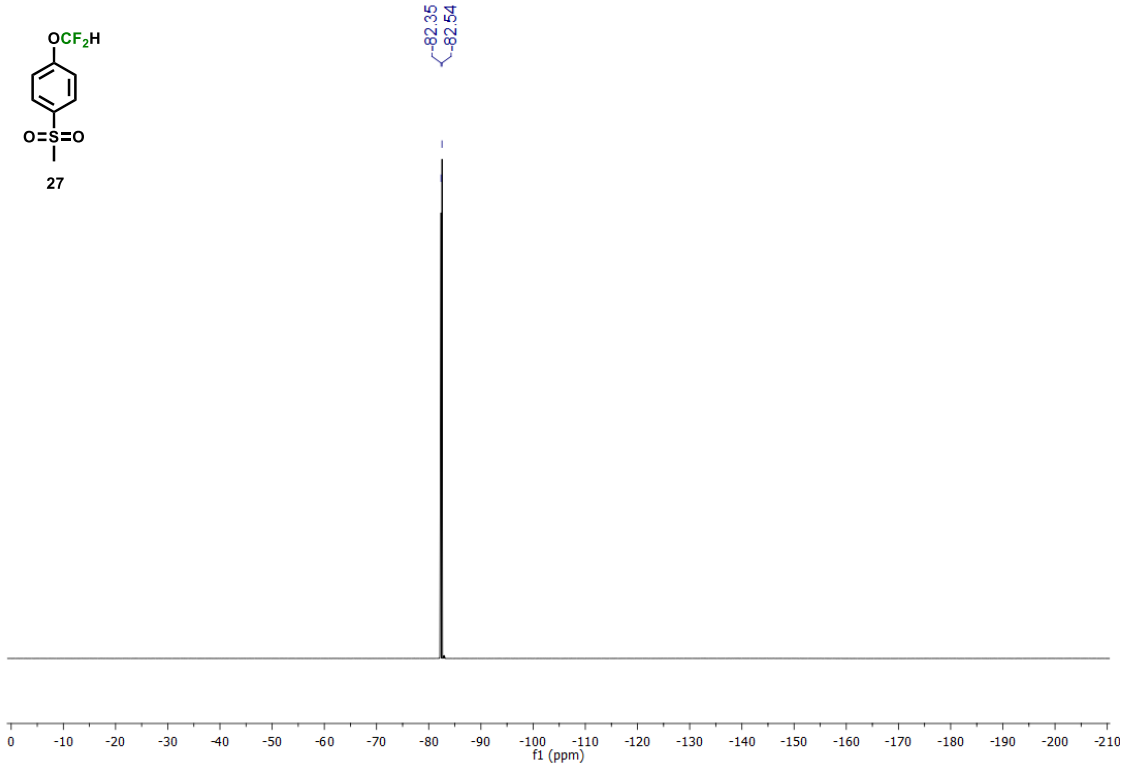

Figure S86: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**).

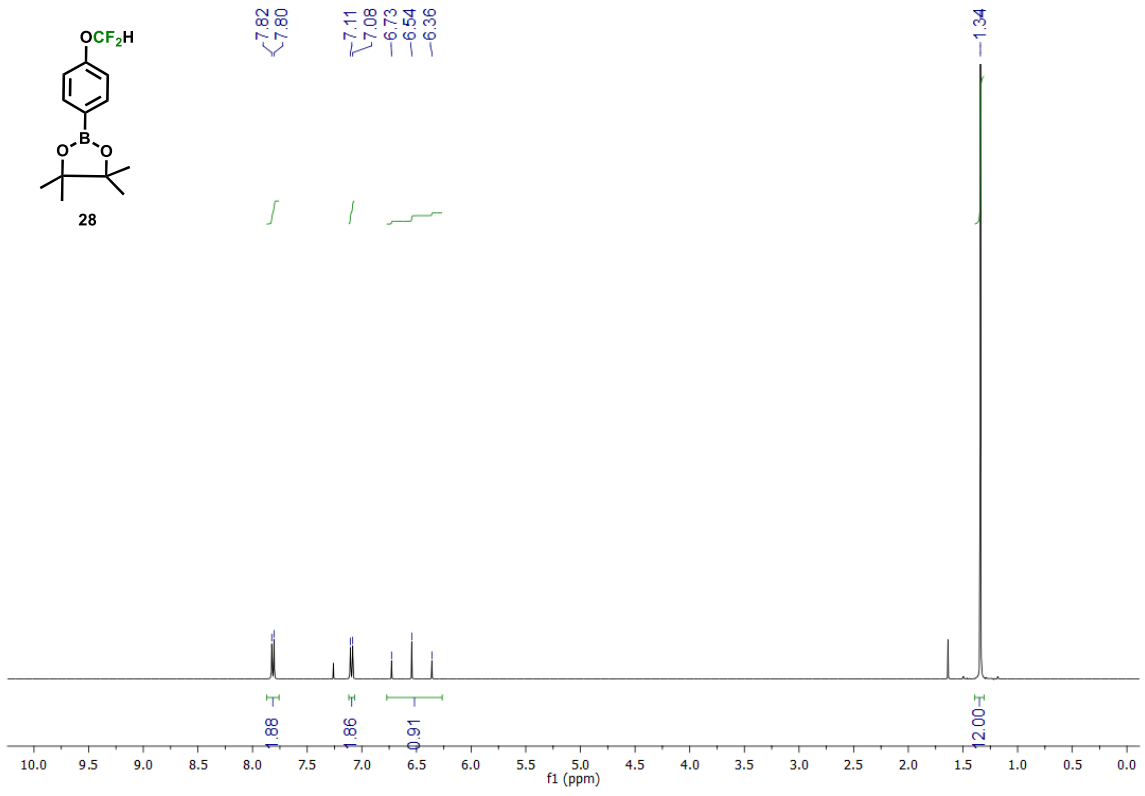

Figure S87: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**).

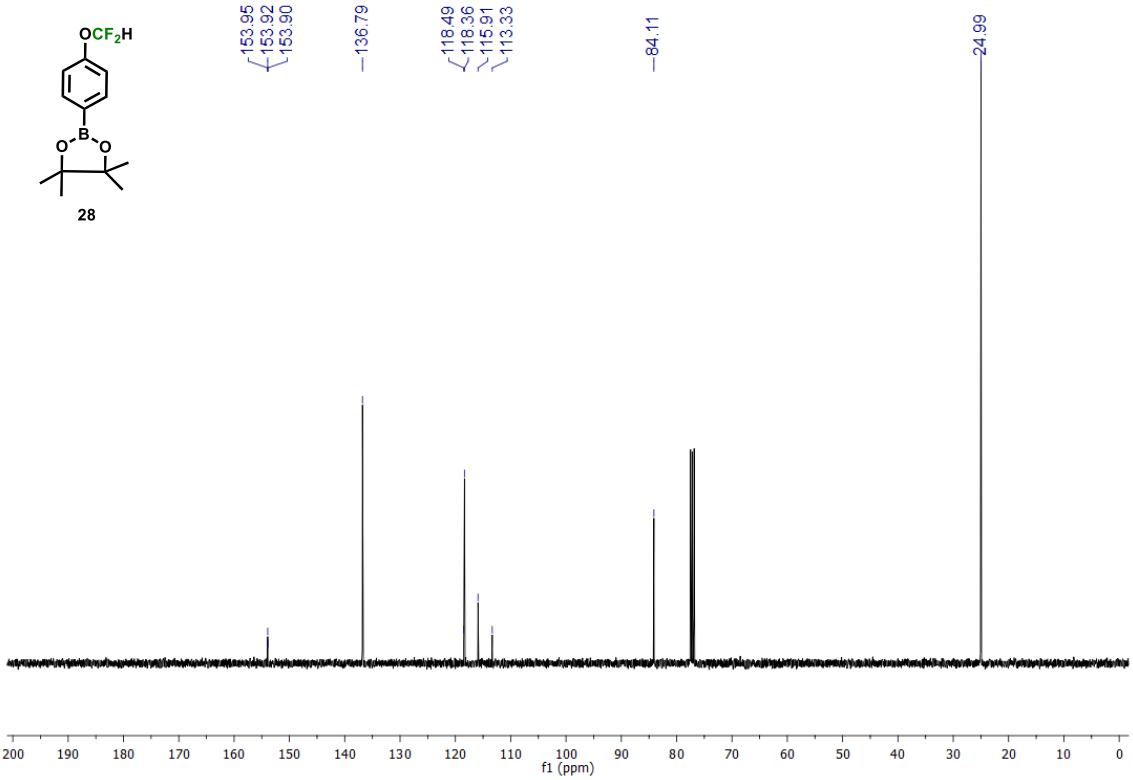

Figure S88: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(4-(Difluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**28**).

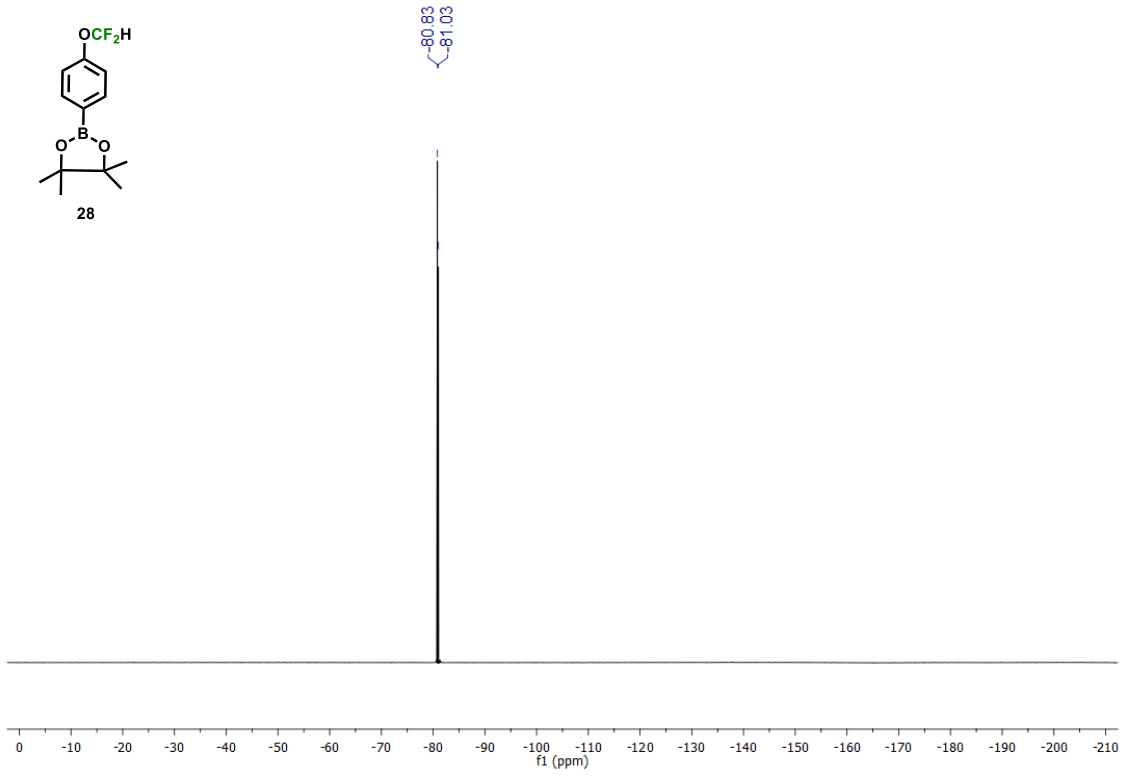

Figure S89: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)naphthalene (**29**).

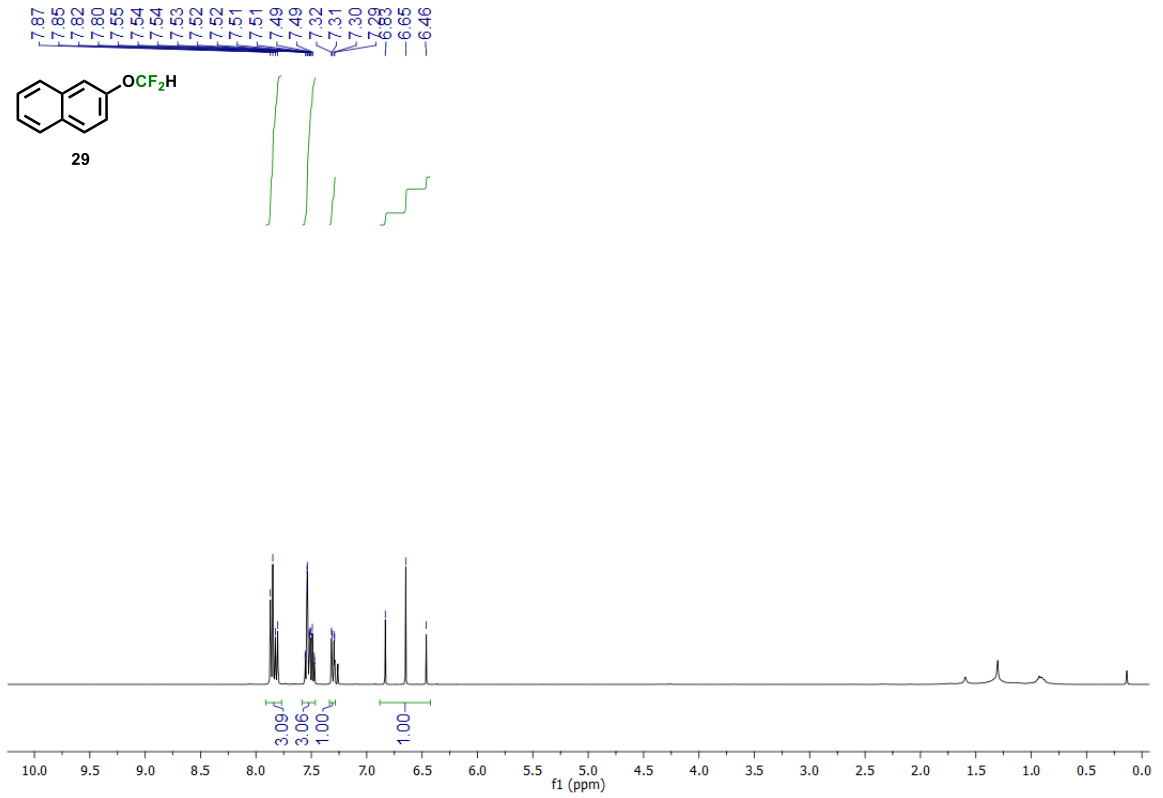

Figure S90: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)naphthalene (**29**).

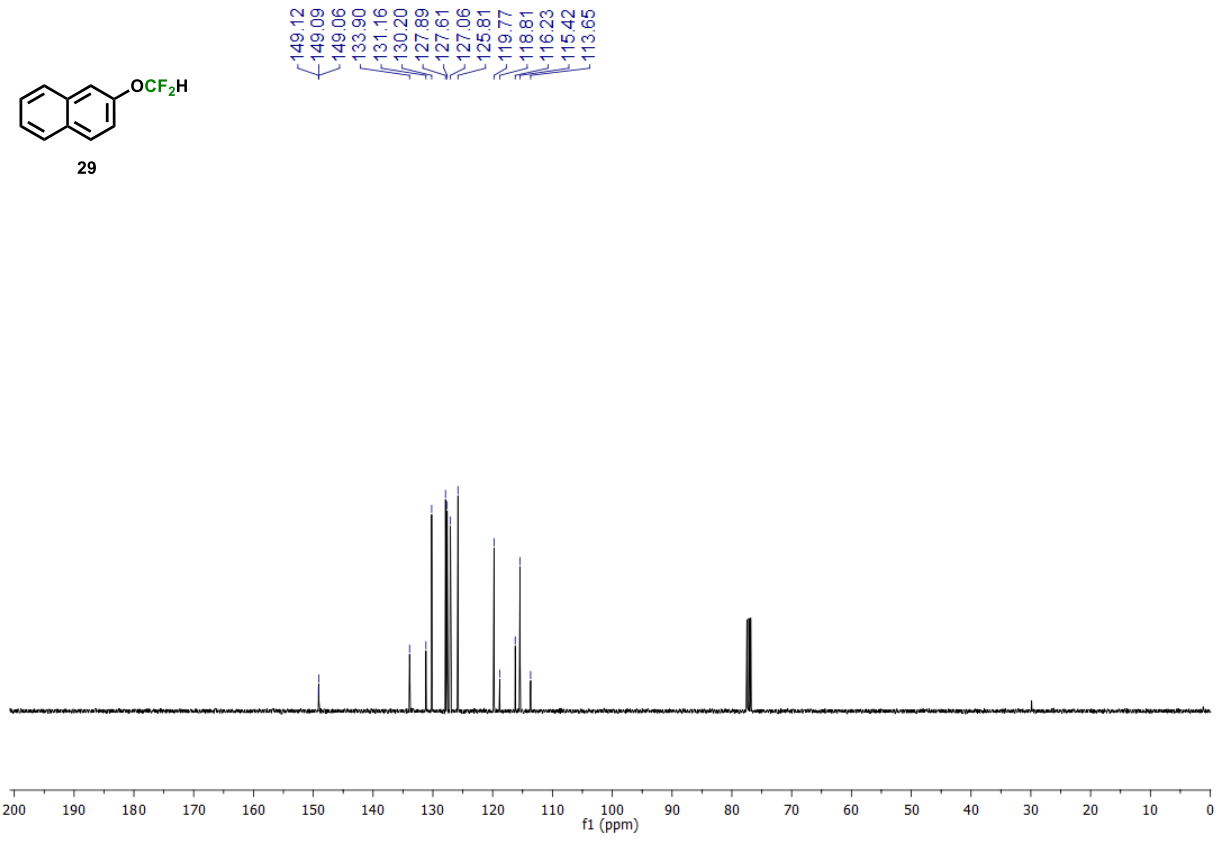

Figure S91: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(Difluoromethoxy)naphthalene (**29**).

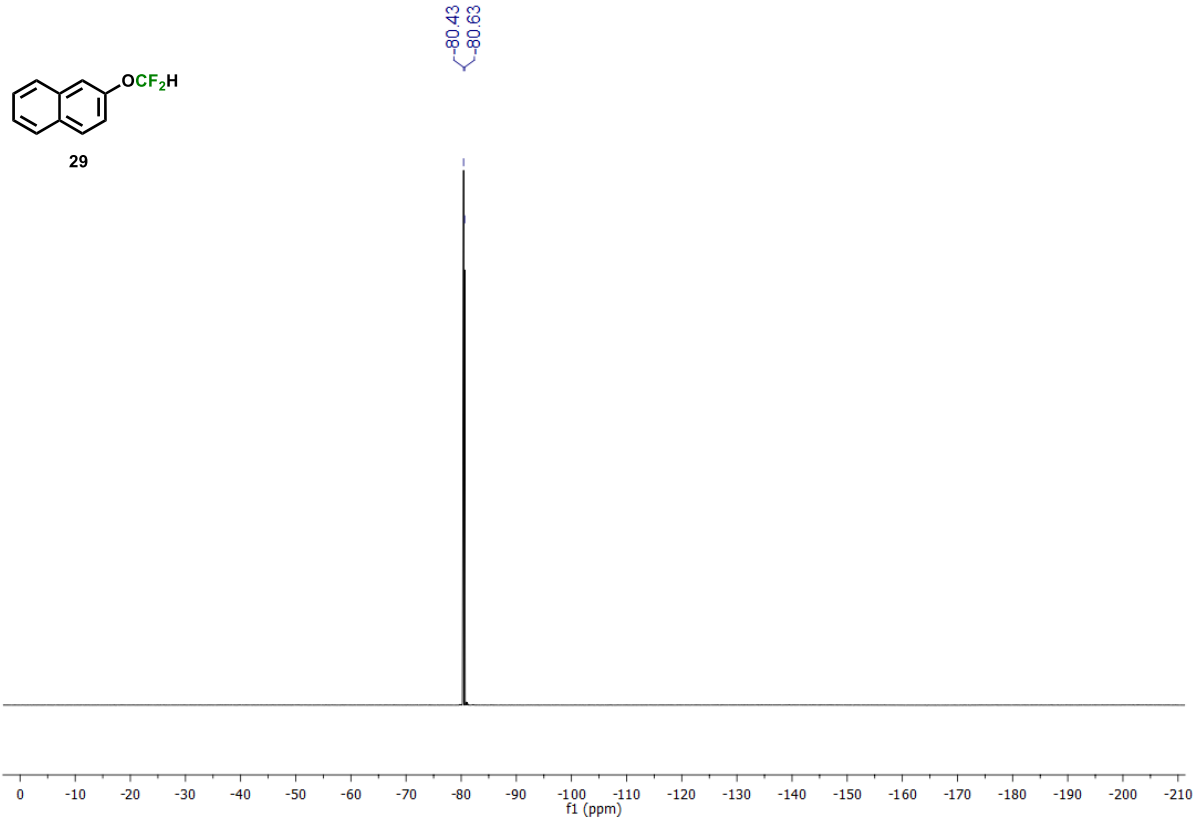

Figure S92: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5-(Difluoromethoxy)-2-iodopyridine (**30**).

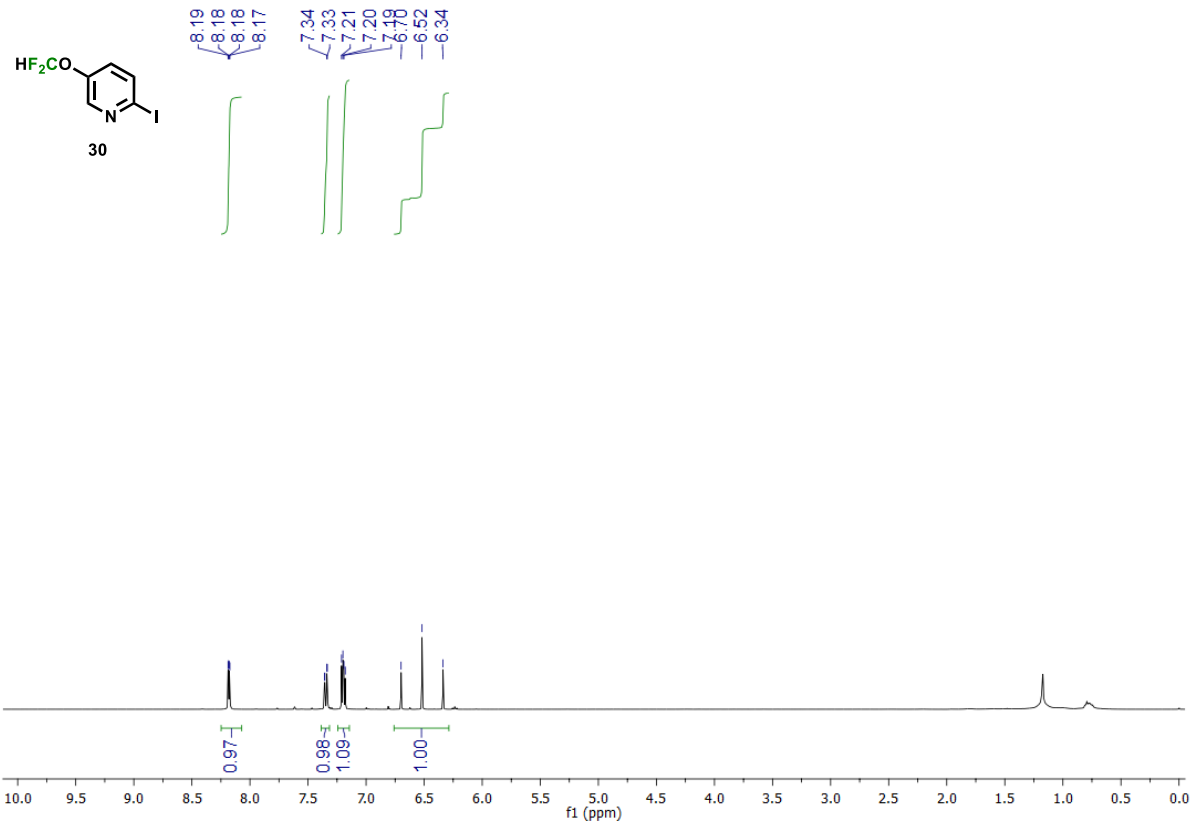

Figure S93: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 5-(Difluoromethoxy)-2-iodopyridine (**30**).

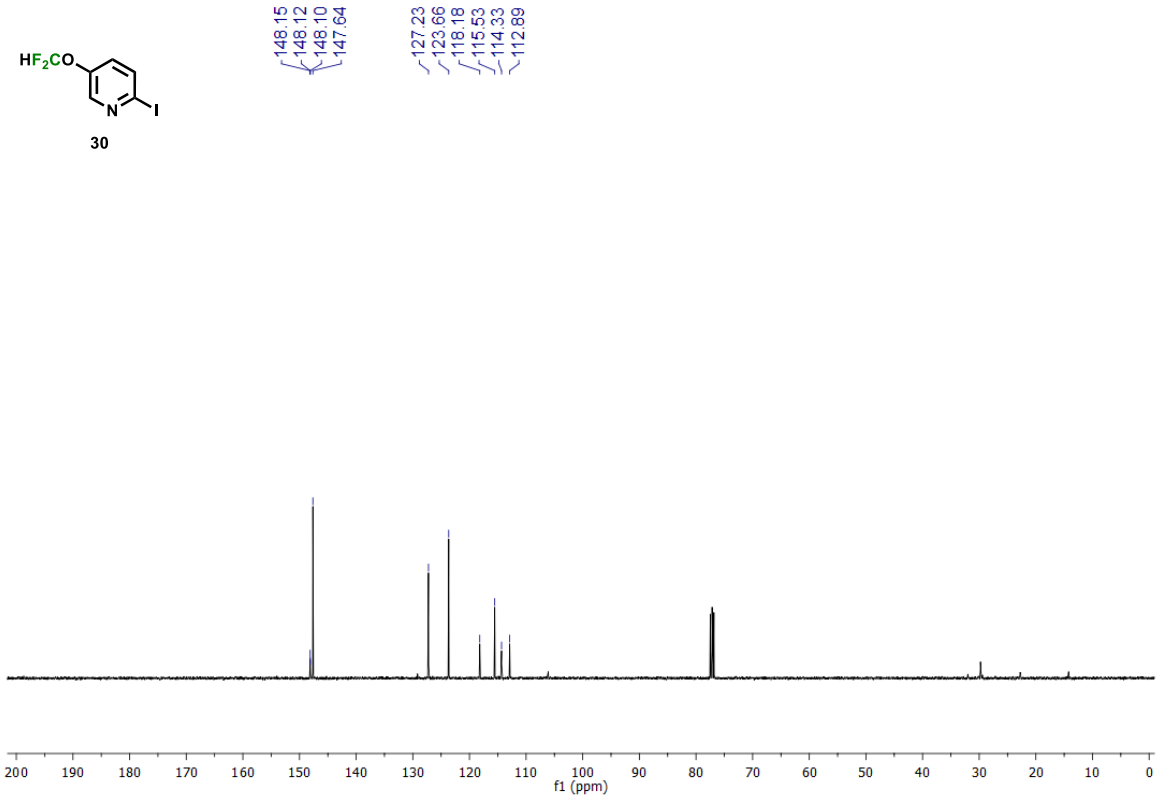

Figure S94: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5-(Difluoromethoxy)-2-iodopyridine (**30**).

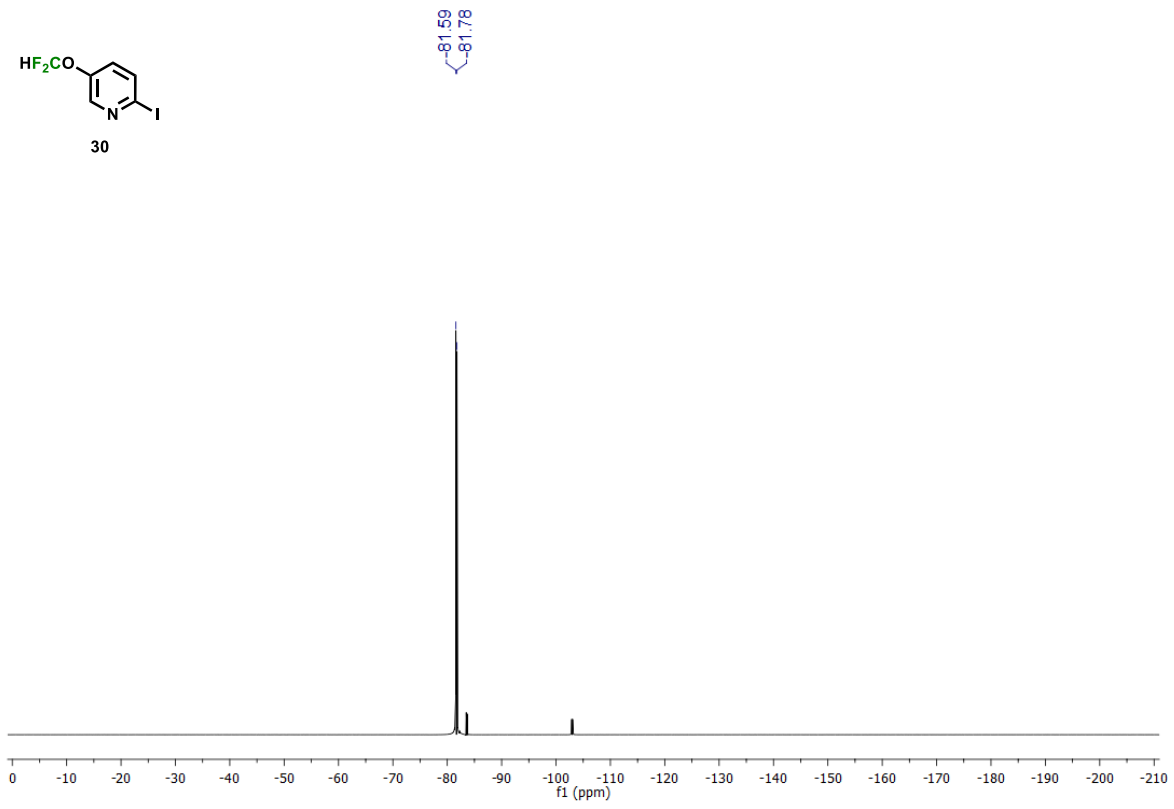

Figure S95: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-((4-isopropoxyphenyl)sulfonyl)benzene (**31**).

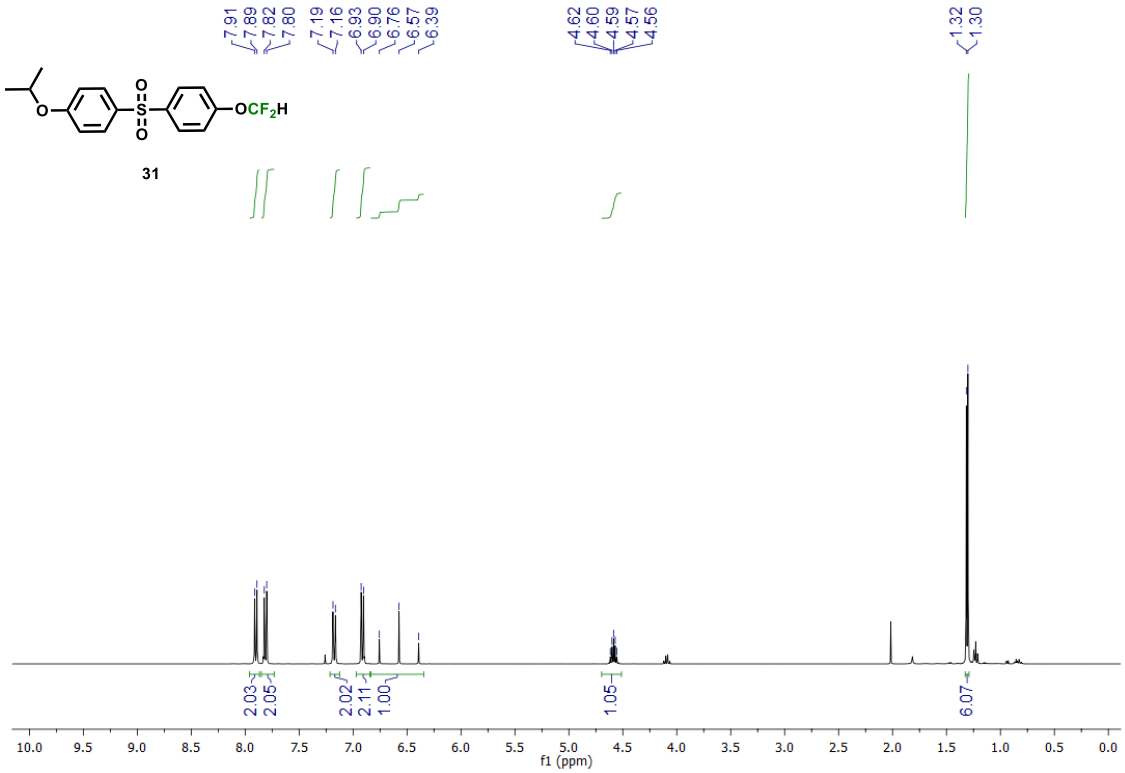

Figure S96: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-((4-isopropoxyphenyl)sulfonyl)benzene (**31**).

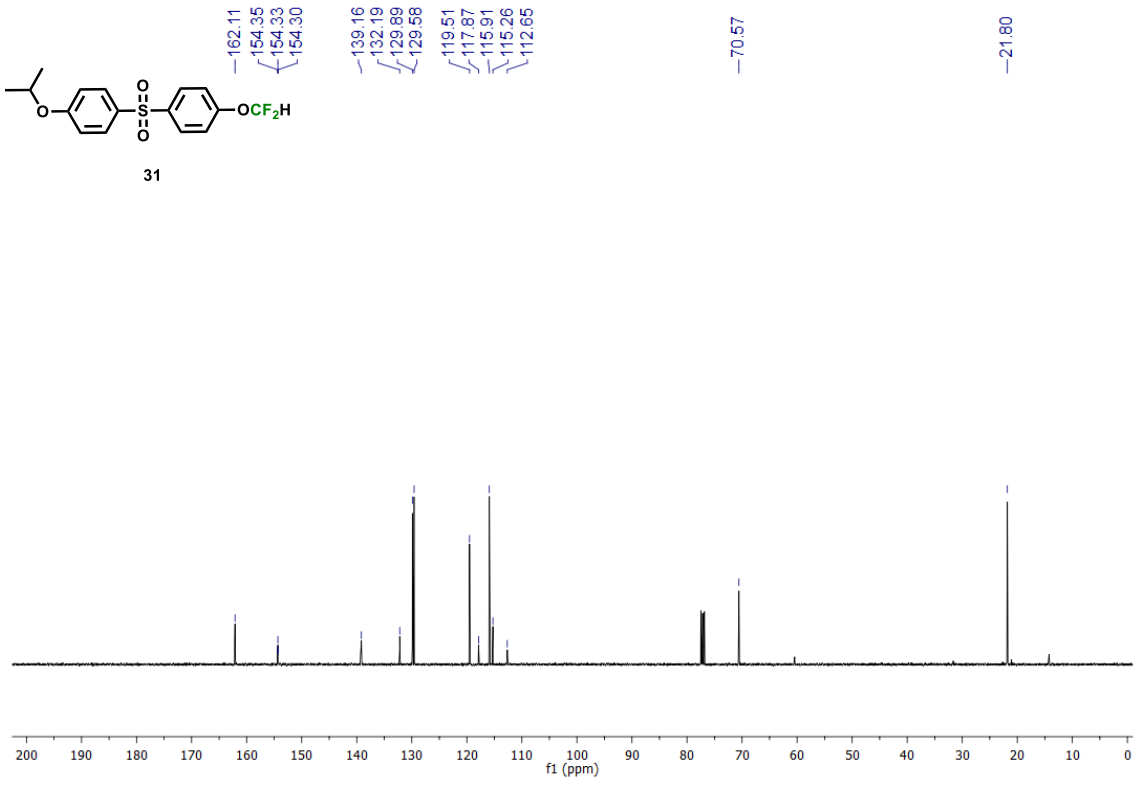

Figure S97: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Difluoromethoxy)-4-((4-isopropoxyphenyl)sulfonyl)benzene (**31**).

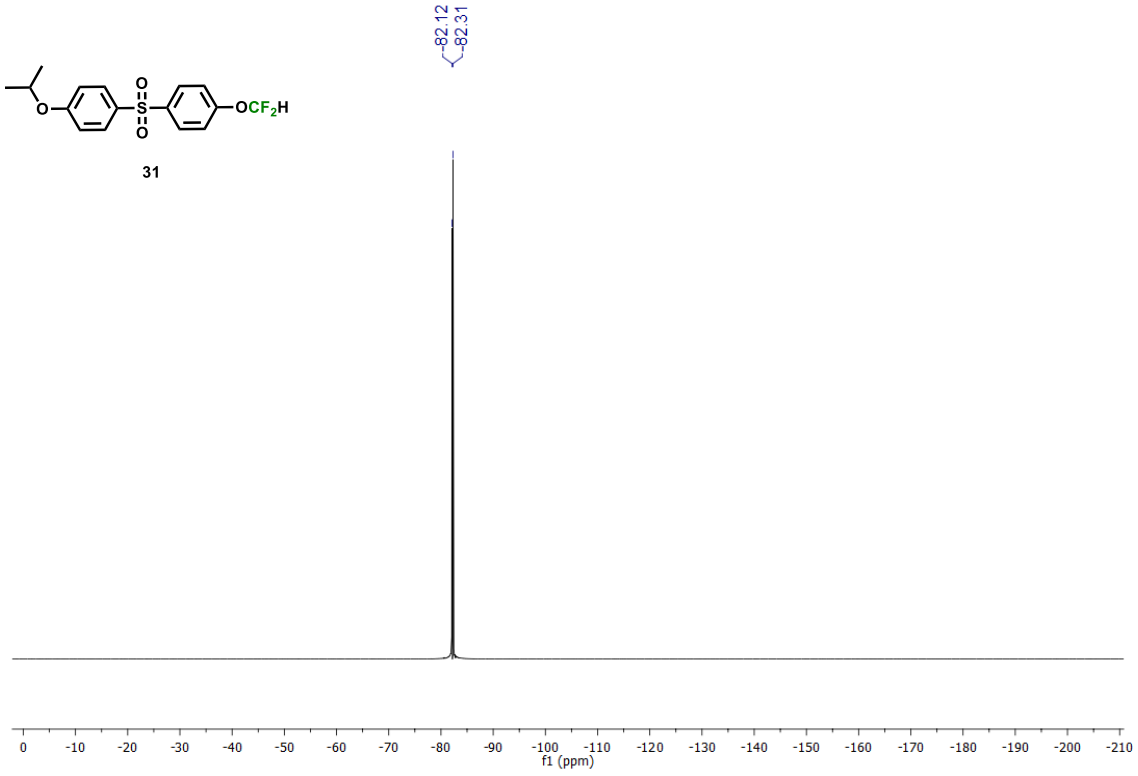

Figure S98: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Benzyloxy)-4-((4-(difluoromethoxy)phenyl)sulfonyl)benzene (**32**).

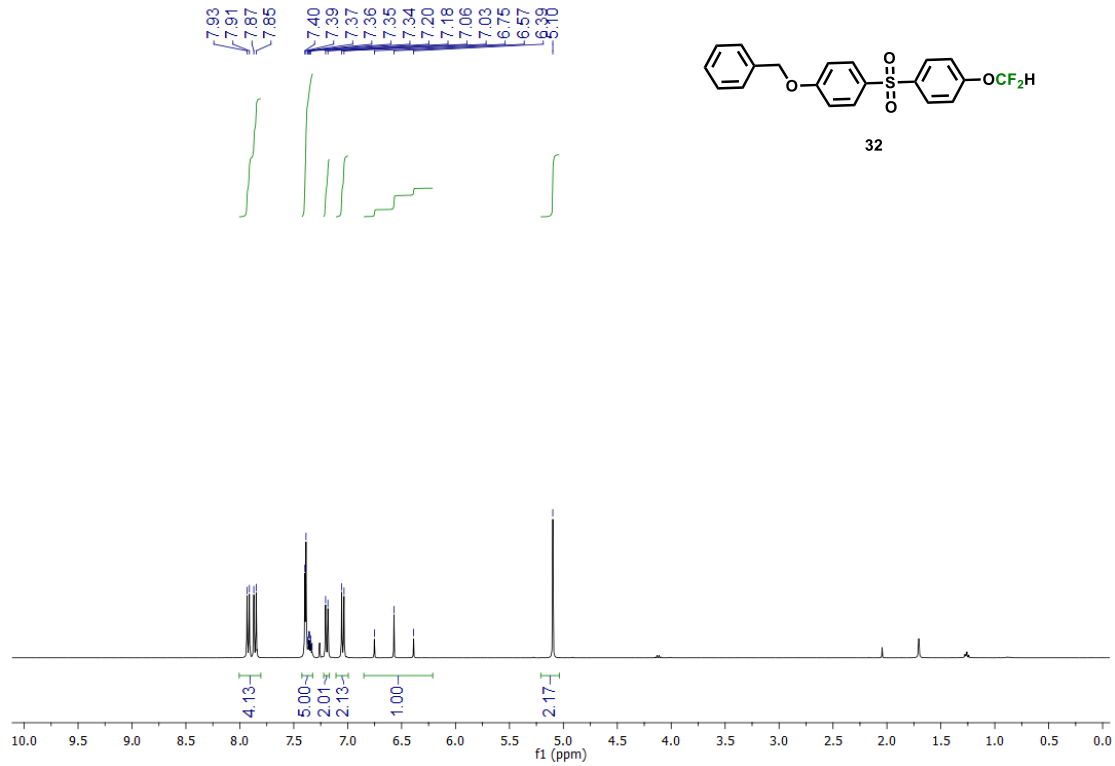

Figure S99: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(Benzyloxy)-4-((4-(difluoromethoxy)phenyl)sulfonyl)benzene (**32**).

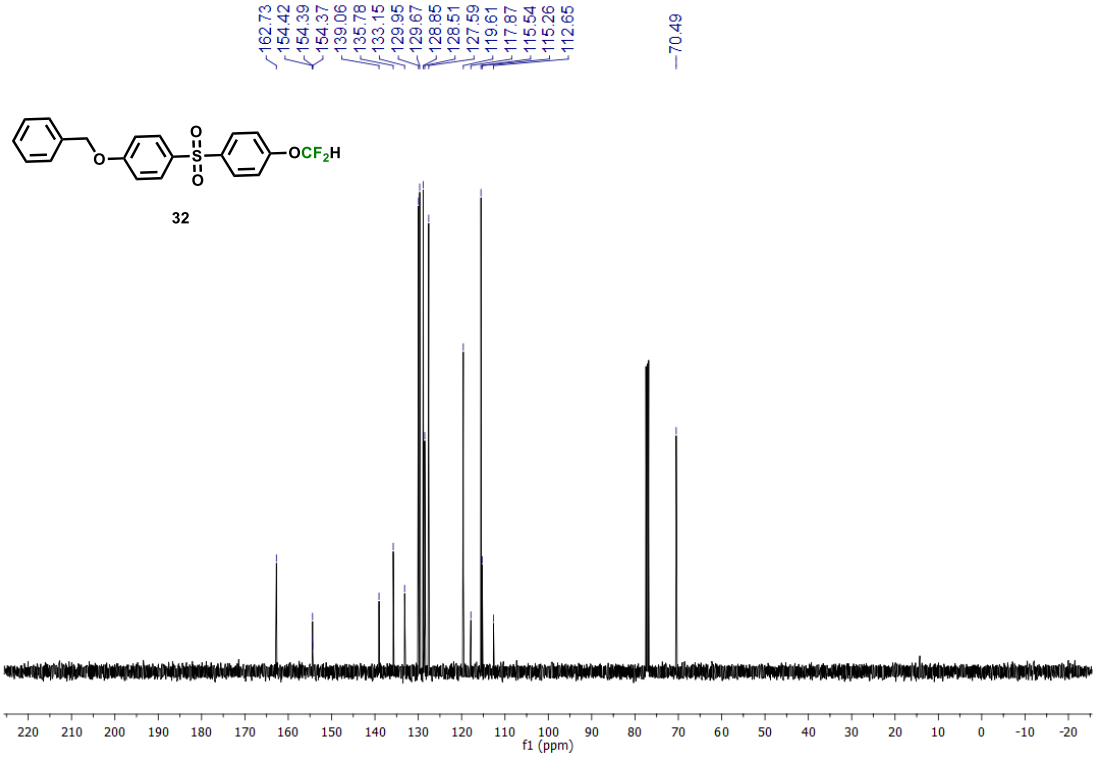

Figure S100: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(Benzyloxy)-4-((4-(difluoromethoxy)phenyl)sulfonyl)benzene (**32**).

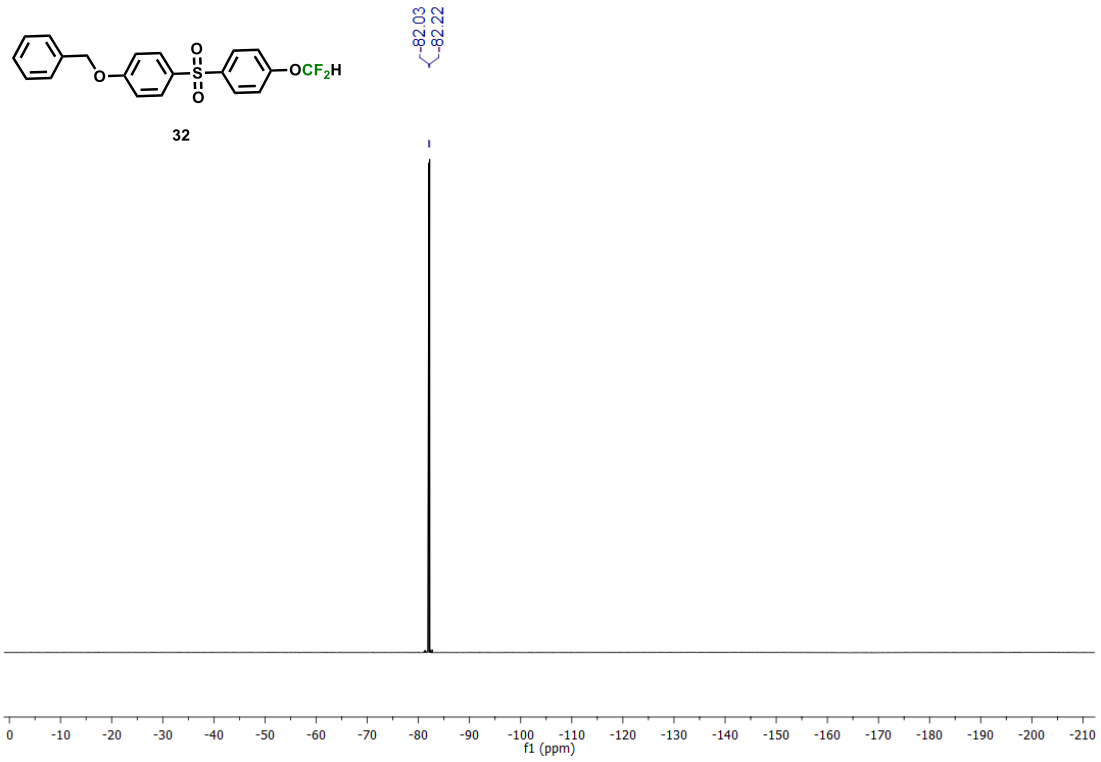

Figure S101: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene (**33**).

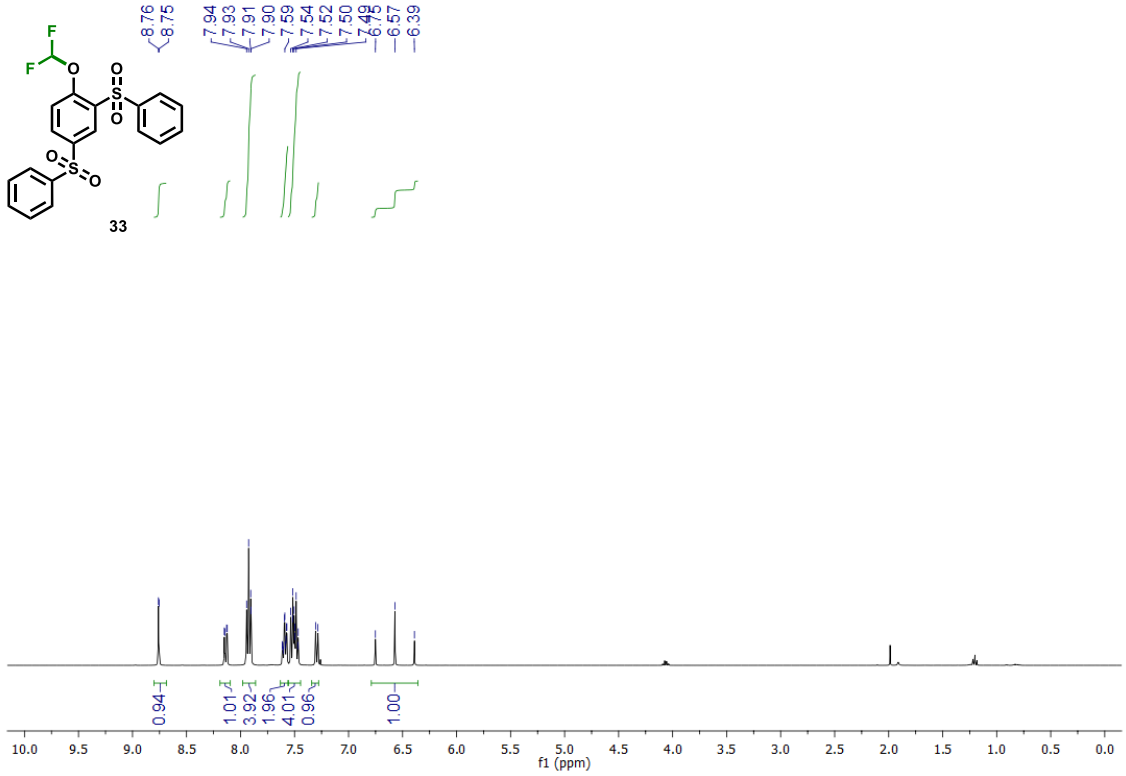

Figure S102: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene (**33**).

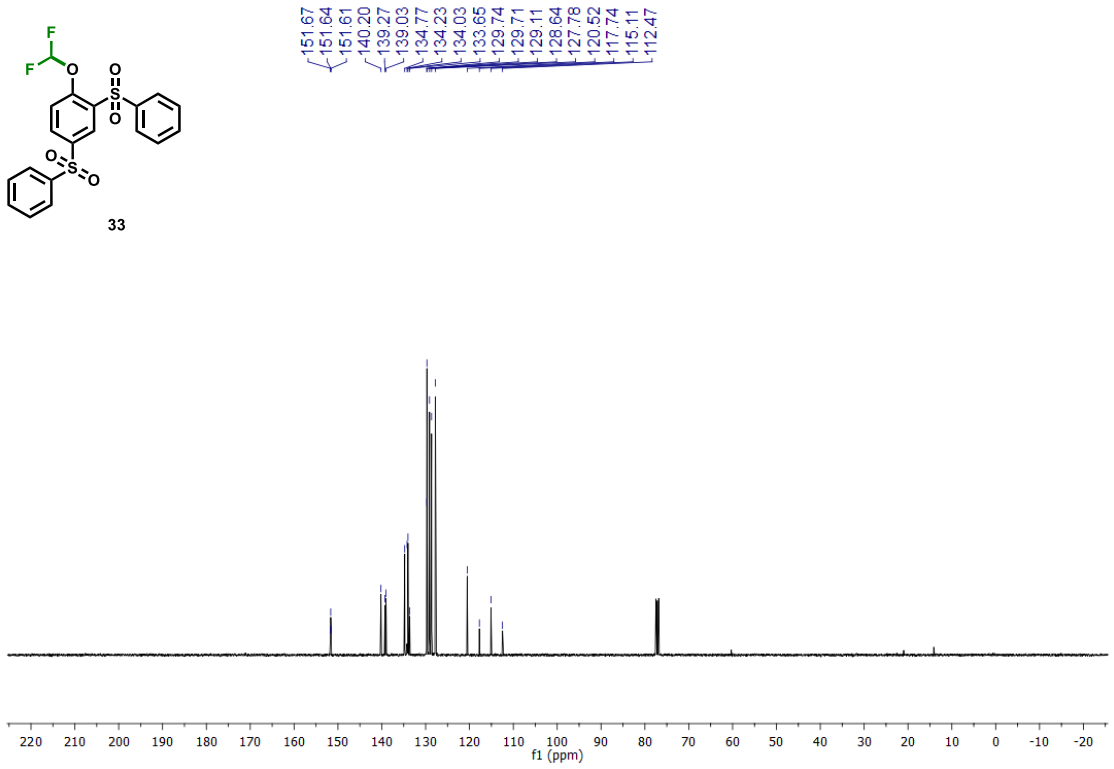

Figure S103: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (4-(Difluoromethoxy)-1,3-phenylenedisulfonyl)dibenzene (**33**).

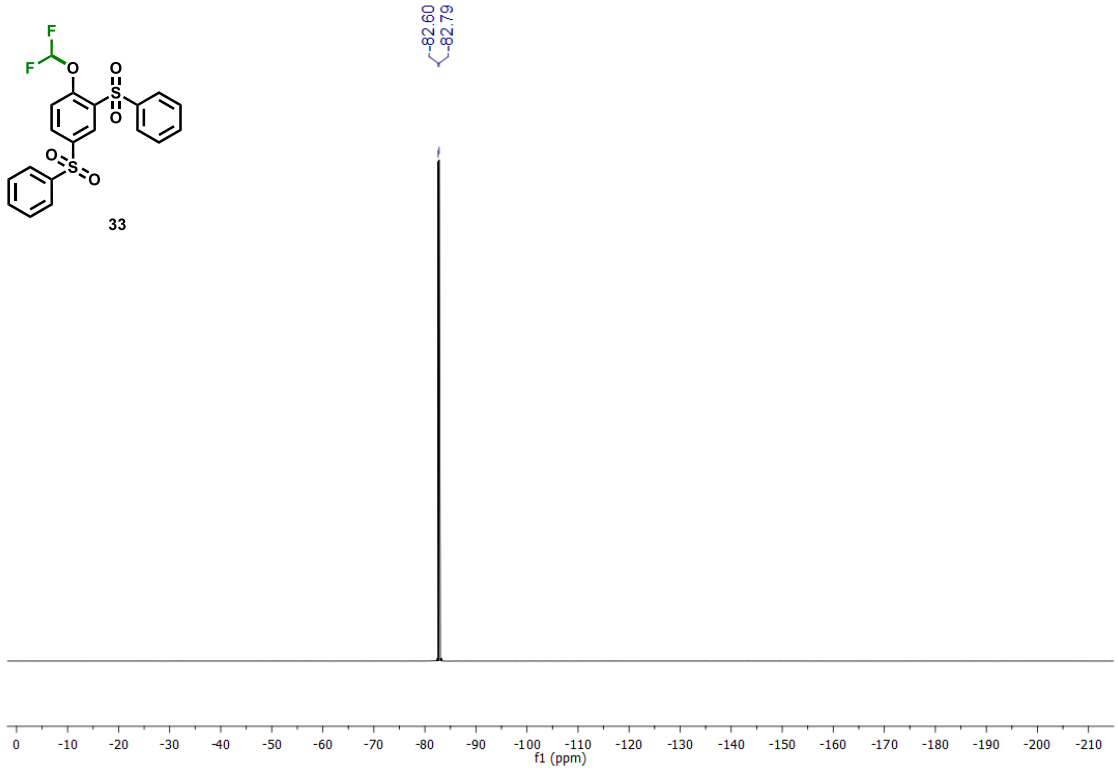

Figure S104: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(2-(Difluoromethoxy)phenyl)benzo[d]thiazole (**34**).

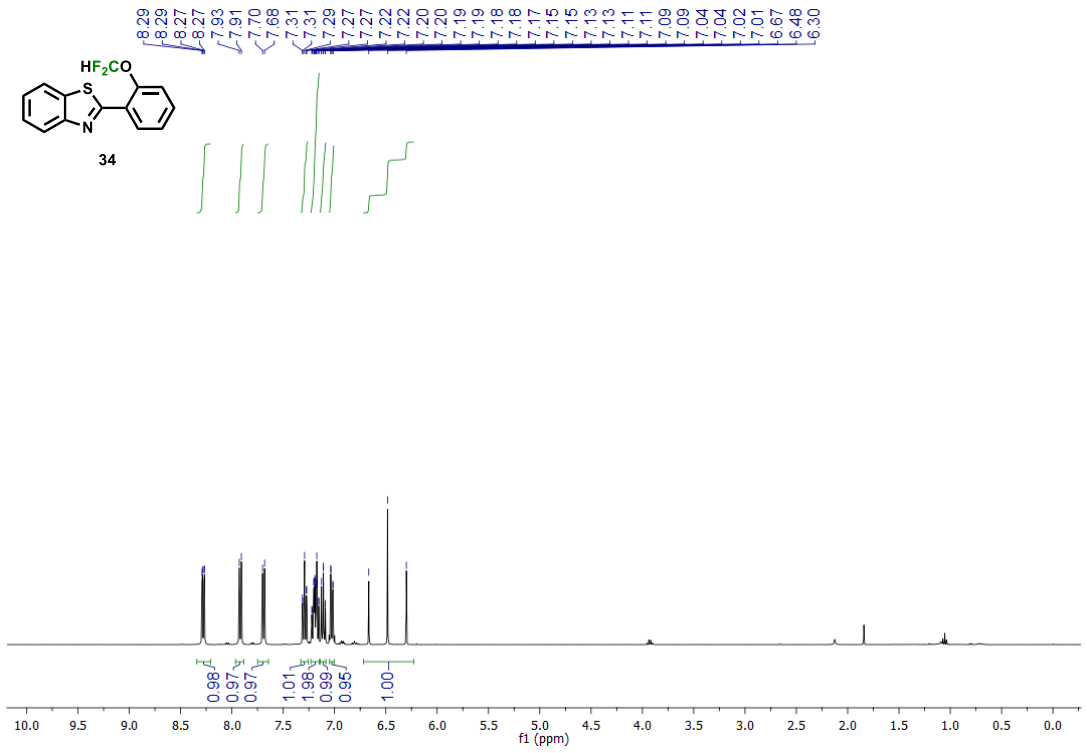

Figure S105: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 2-(2-(Difluoromethoxy)phenyl)benzo[d]thiazole (**34**).

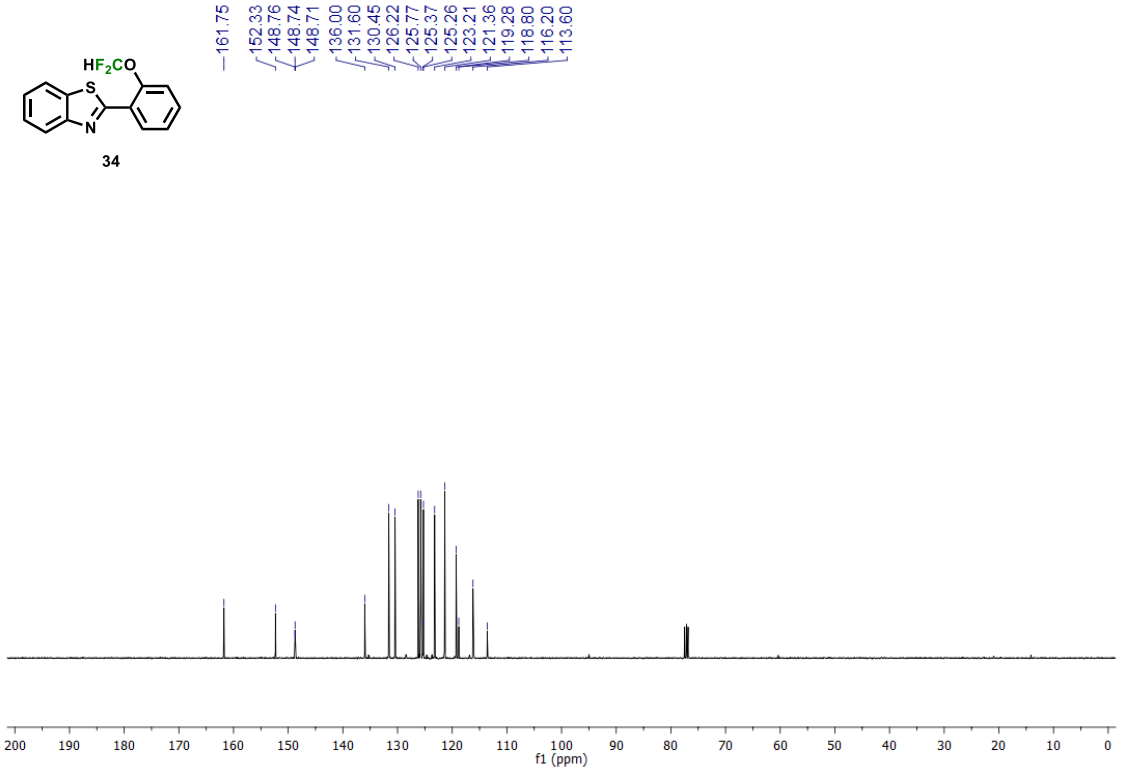

Figure S106: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(2-(Difluoromethoxy)phenyl)benzo[d]thiazole (**34**).

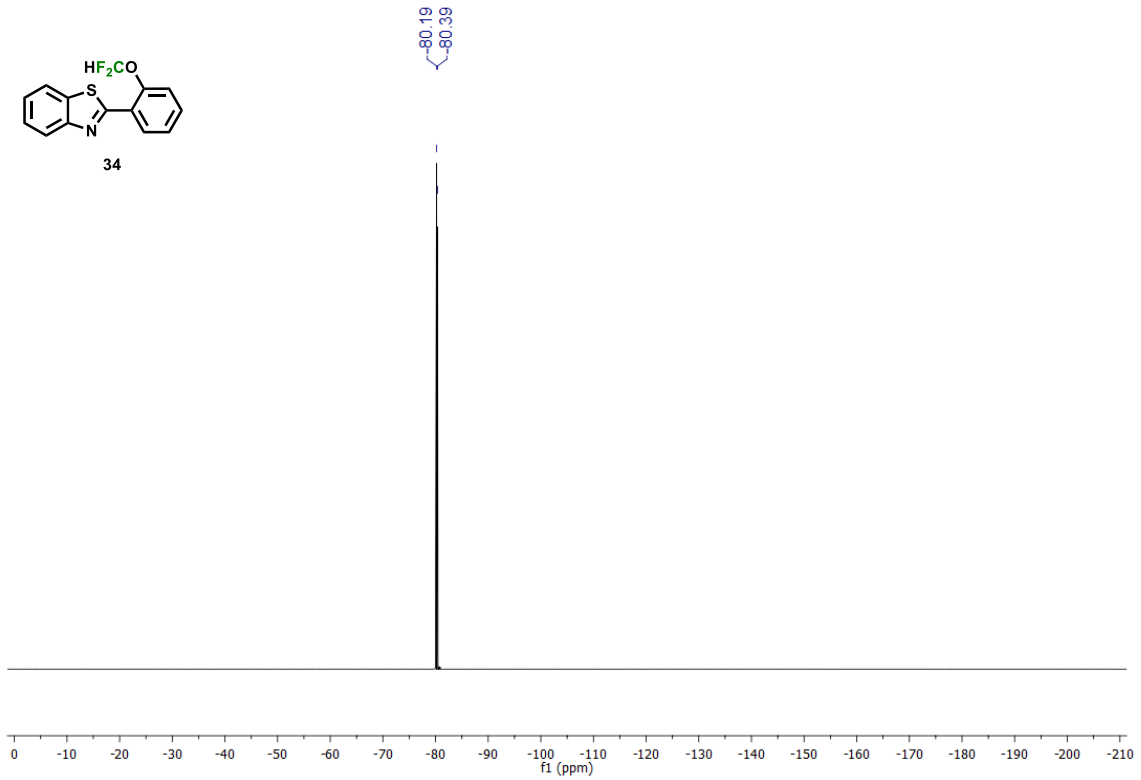

Figure S107: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(4-butylphenyl)-2-(4-(difluoromethoxy)phenyl)diazene (**35**).

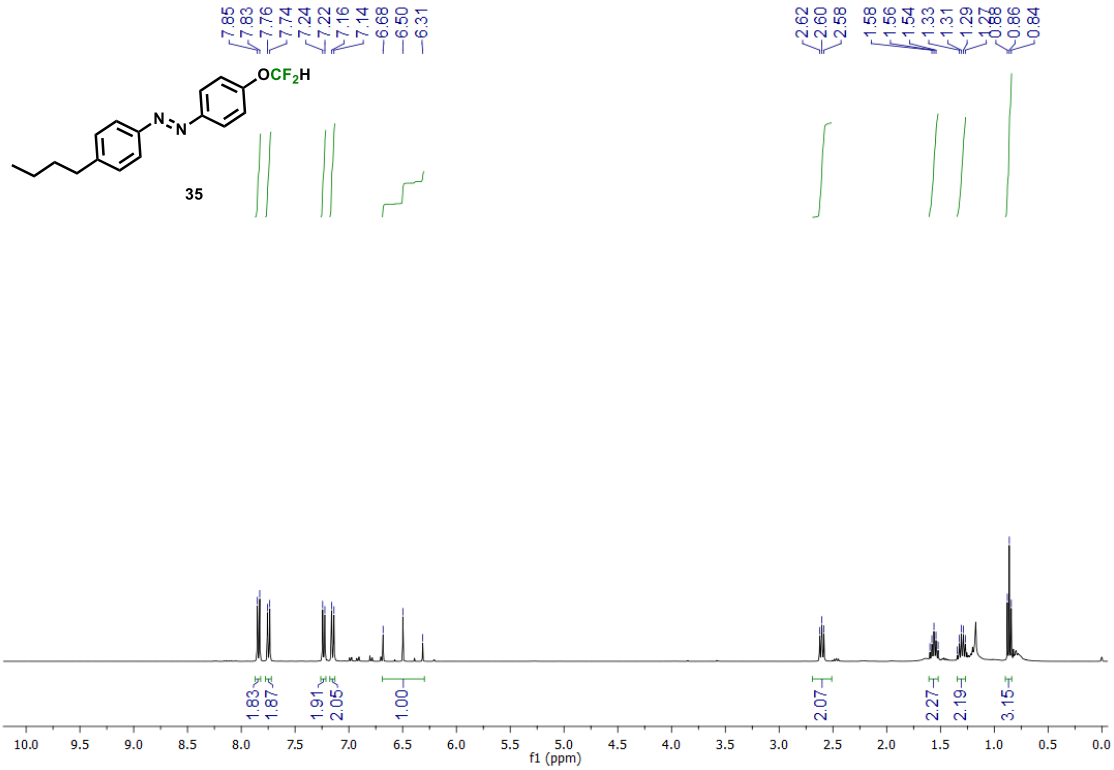

Figure S108: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(4-butylphenyl)-2-(4-(difluoromethoxy)phenyl)diazene (**35**).

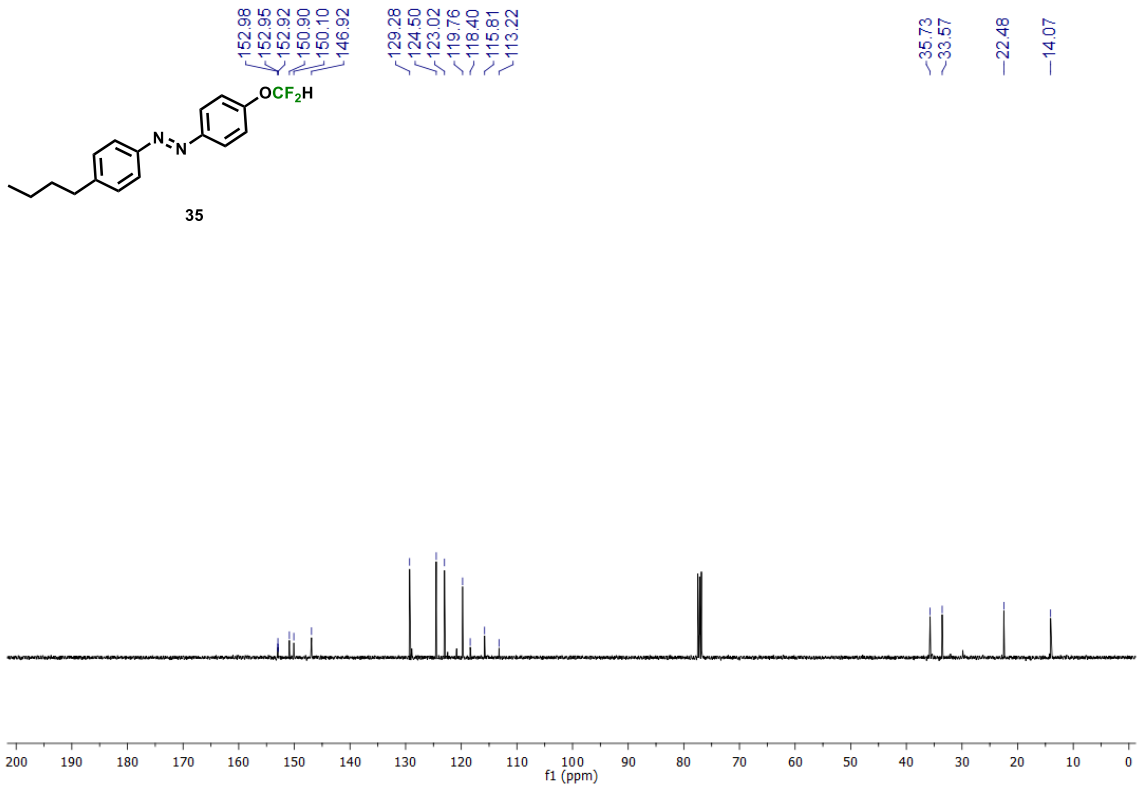

Figure S109: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(4-butylphenyl)-2-(4-(difluoromethoxy)phenyl)diazene (**35**).

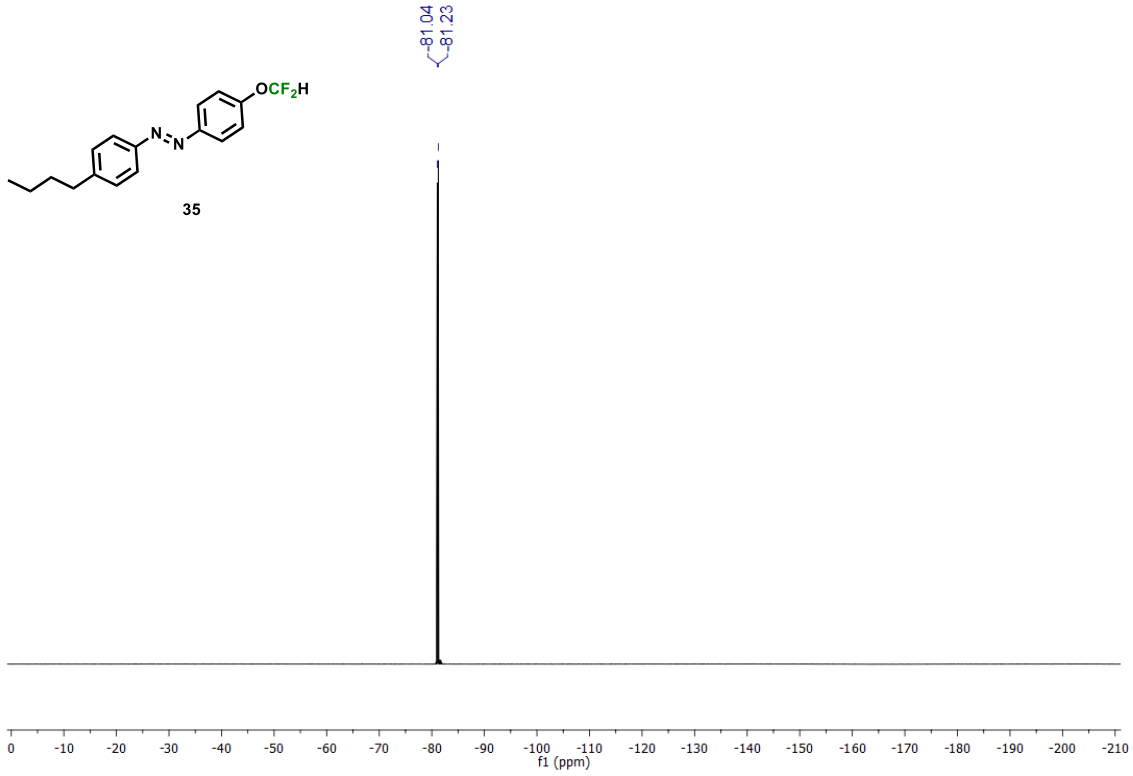

Figure S110: ^{1}H NMR (400 MHz, DMSO) spectrum of N-(4-(Difluoromethoxy)phenyl)acetamide (**36**).

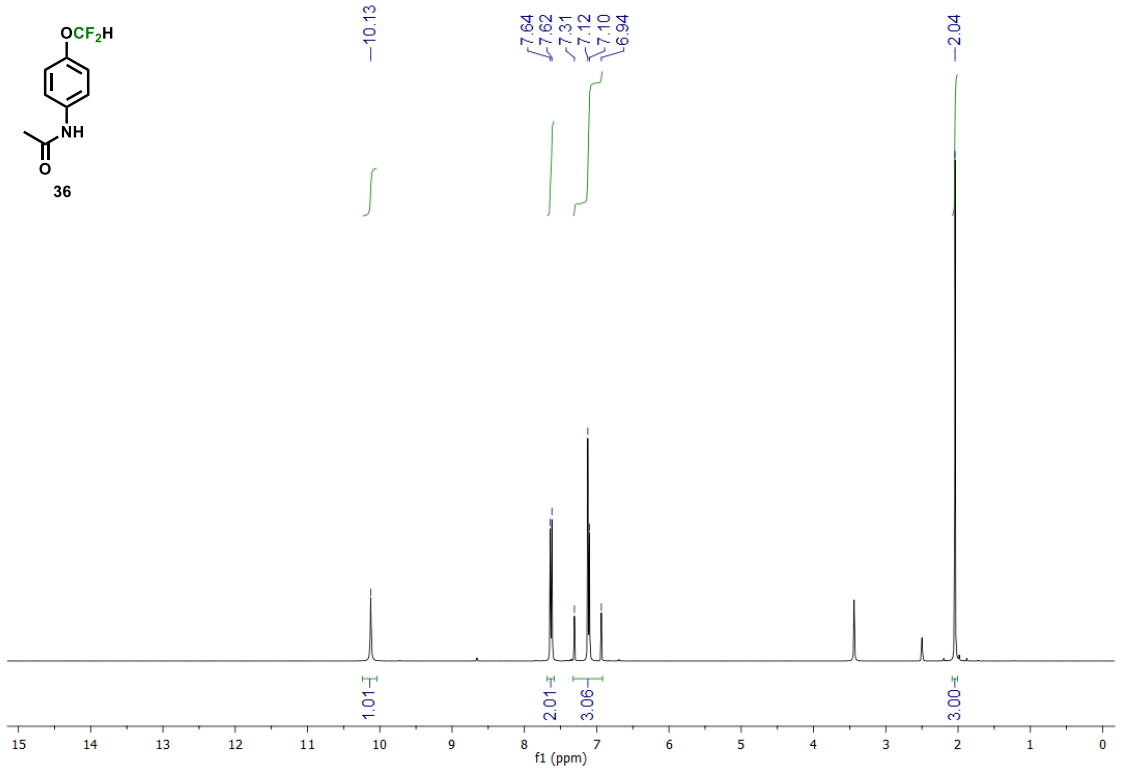

Figure S111: $^{13}C\{1H\}$ NMR (100 MHz, DMSO) spectrum of N-(4-(Difluoromethoxy)phenyl)acetamide (**36**).

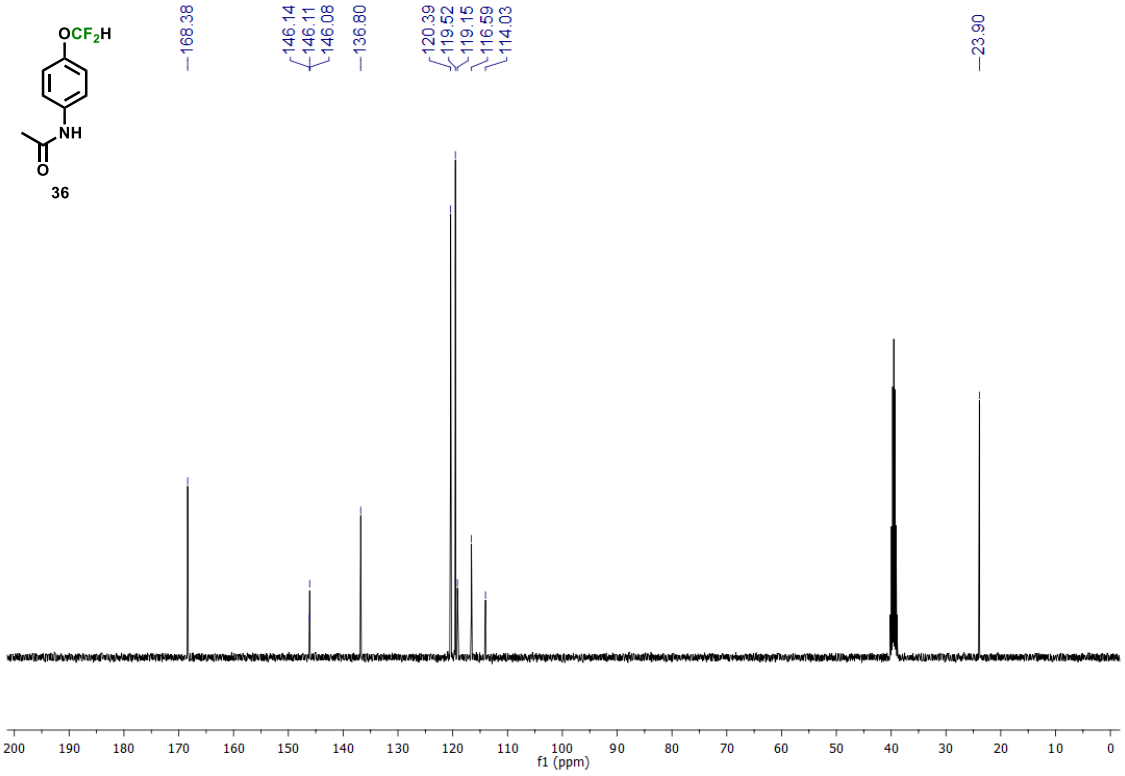

Figure S112: ^{19}F NMR (376 MHz, DMSO) spectrum of N-(4-(Difluoromethoxy)phenyl)acetamide (**36**).

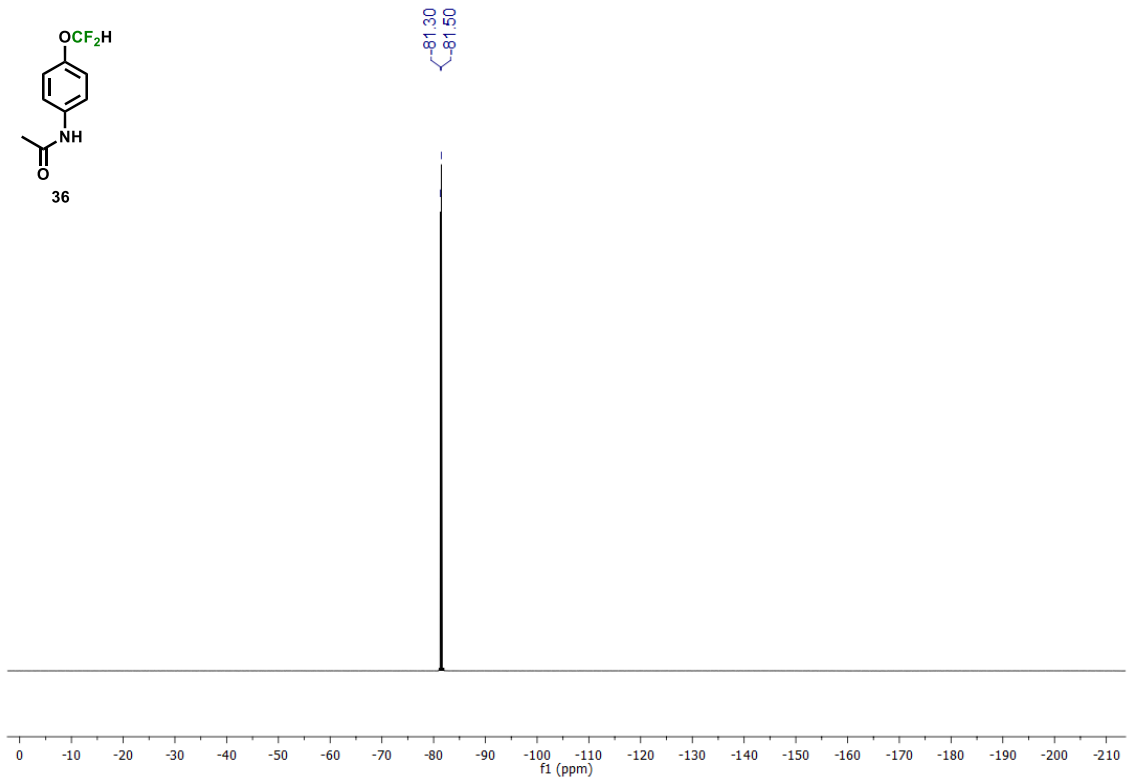

Figure S113: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-methoxybenzaldehyde (**37**).

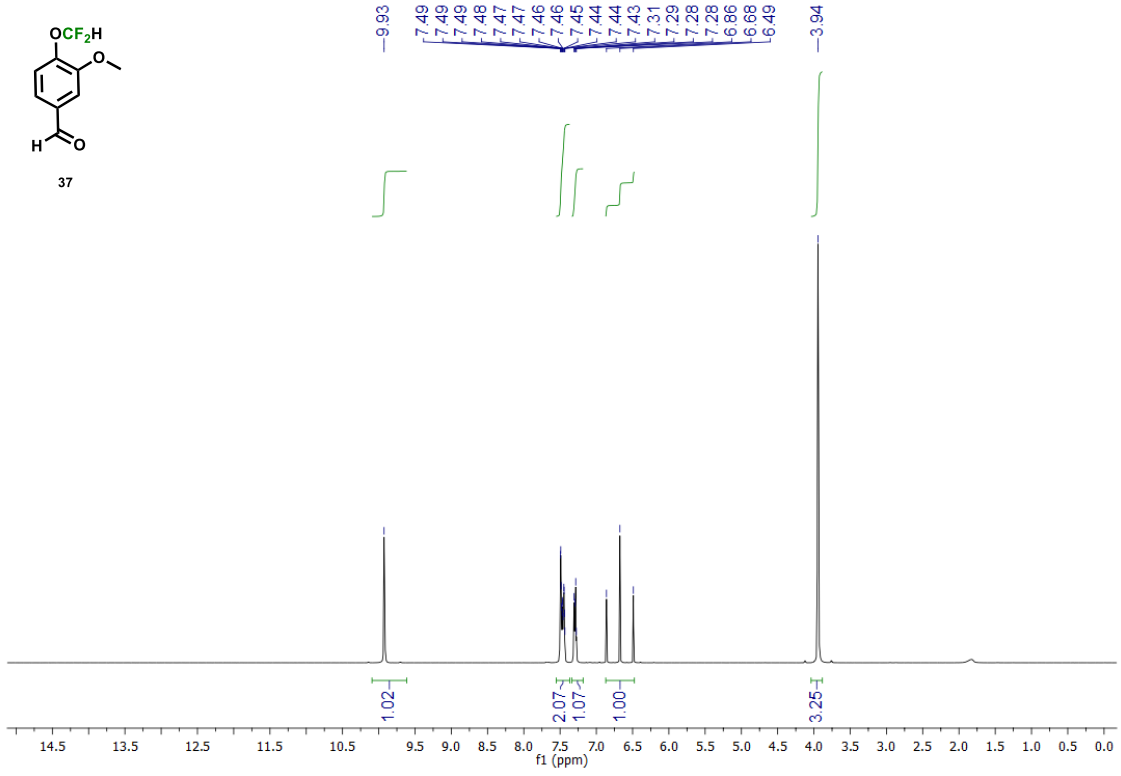

Figure S114: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-methoxybenzaldehyde (**37**).

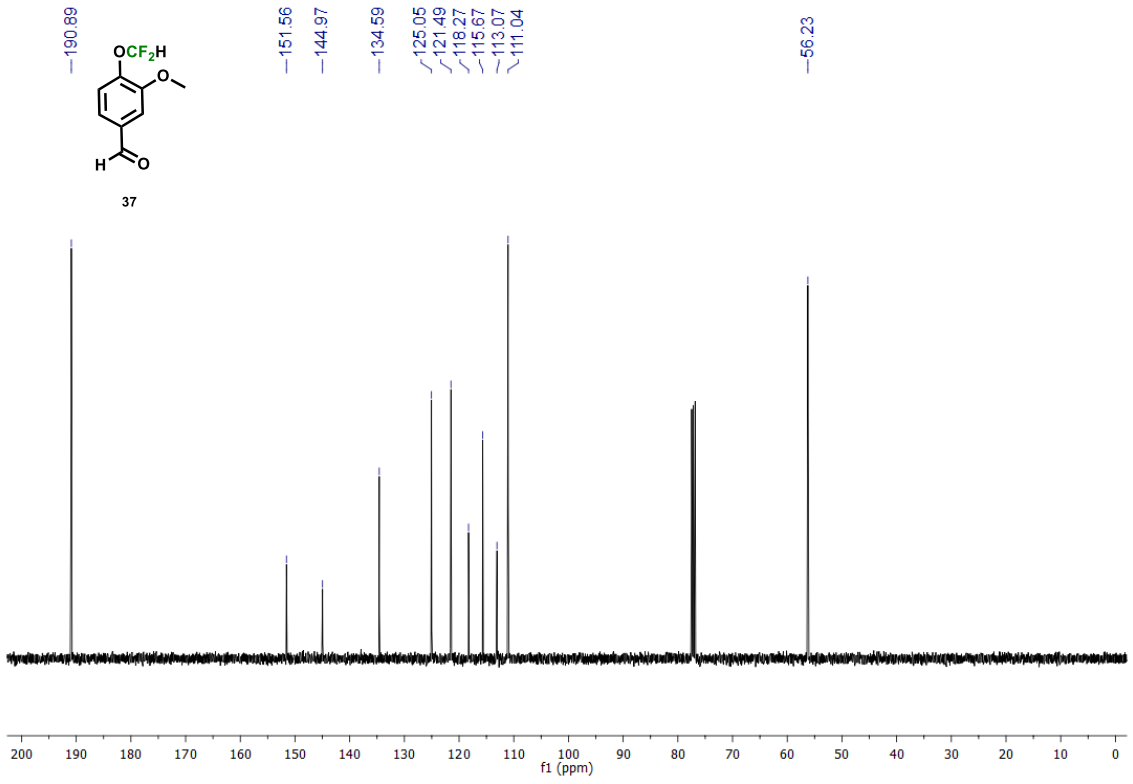

Figure S115: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3-methoxybenzaldehyde (**37**).

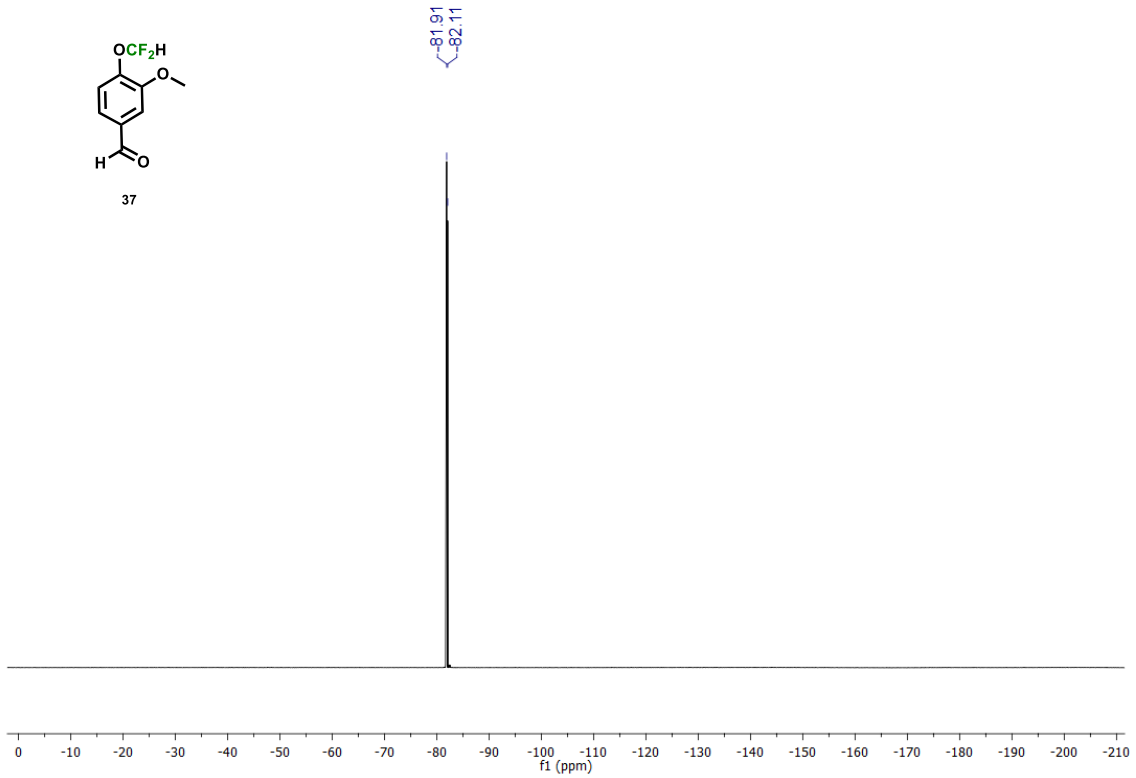

Figure S116: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(4-(Difluoromethoxy)-3-methoxyphenyl)ethan-1-one (**38**).

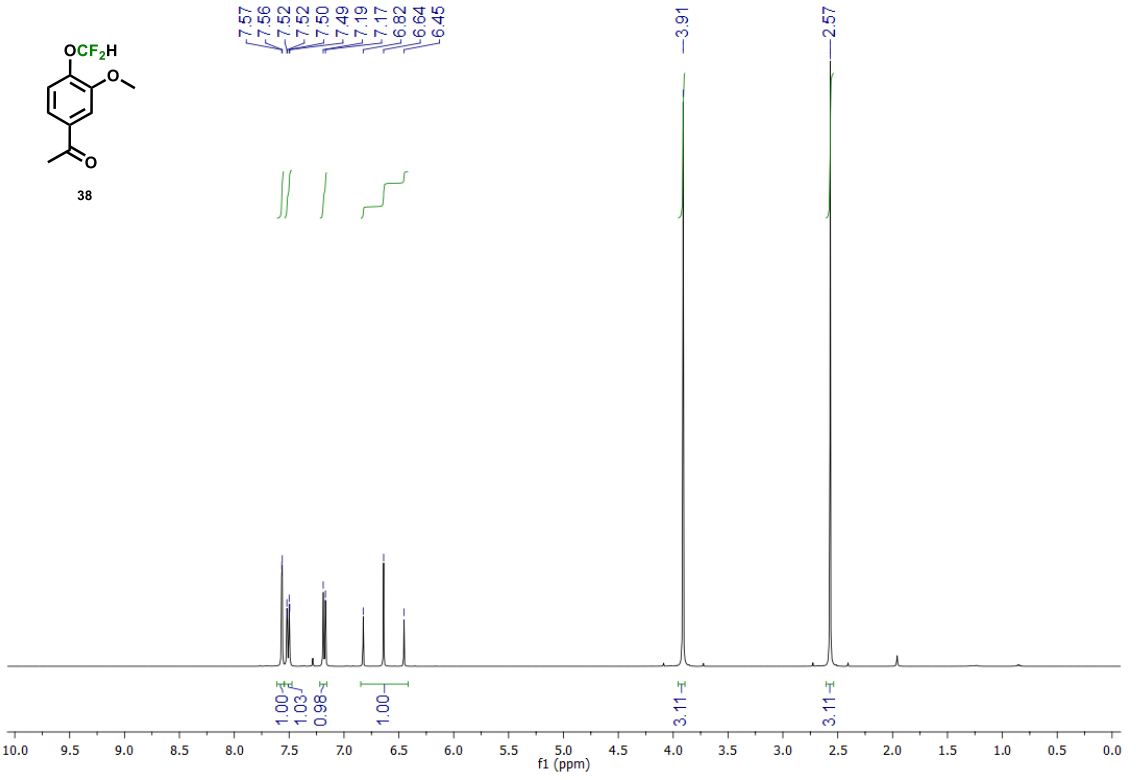

Figure S117: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1-(4-(Difluoromethoxy)-3-methoxyphenyl)ethan-1-one (**38**).

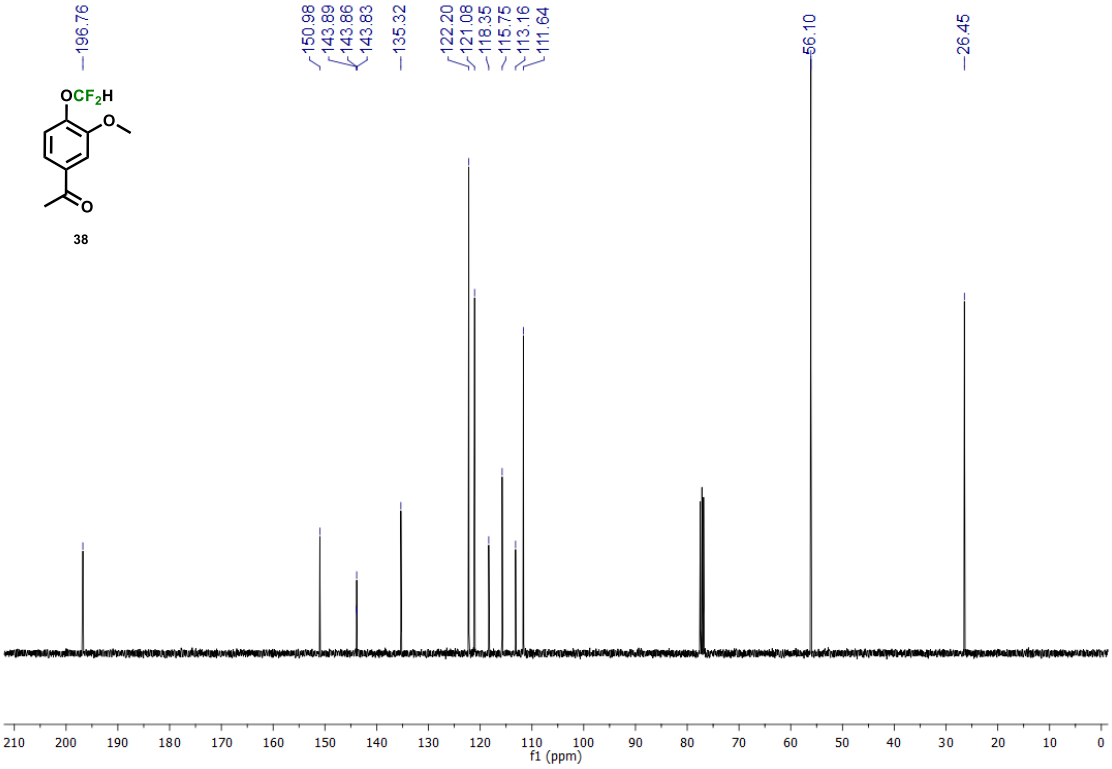

Figure S118: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(4-(Difluoromethoxy)-3-methoxyphenyl)ethan-1-one (**38**).

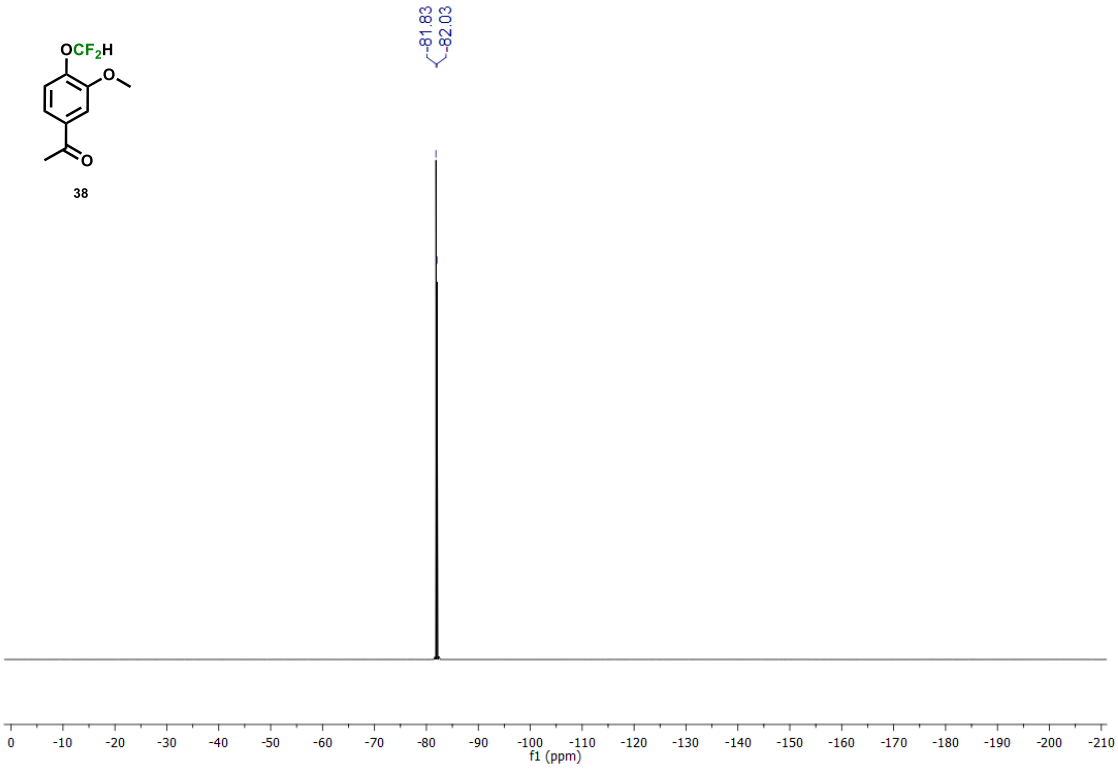

Figure S119: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3,5-dimethoxybenzaldehyde (**39**).

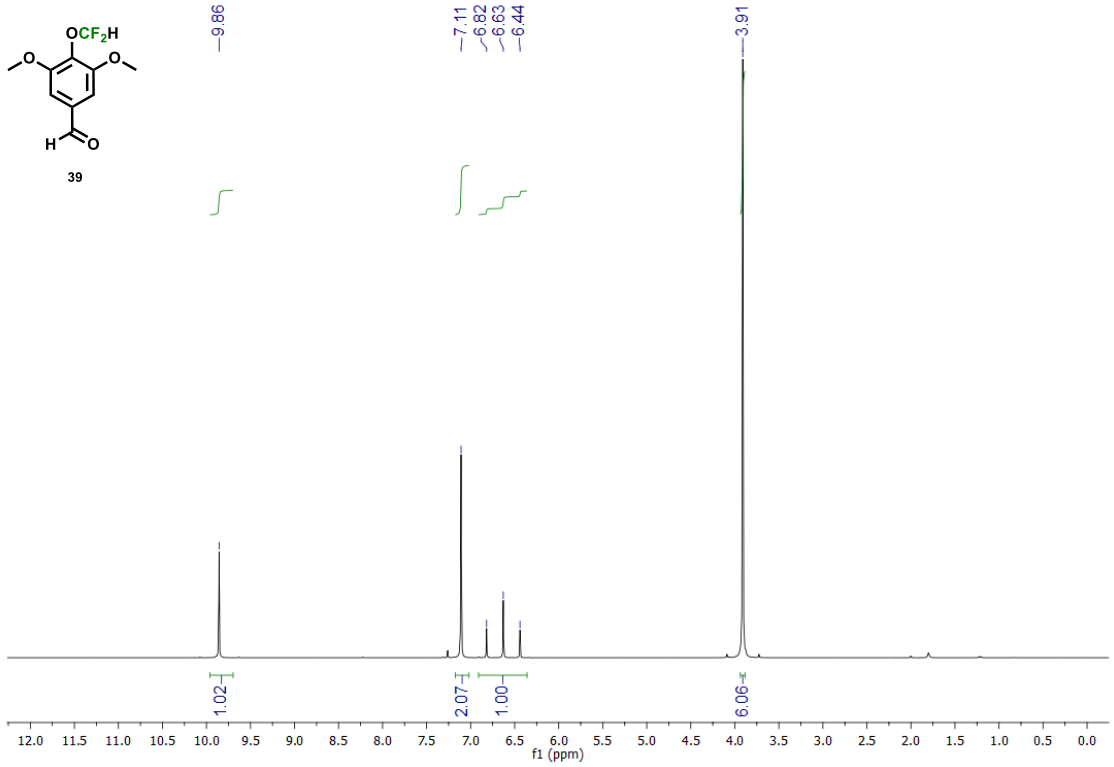

Figure S120: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3,5-dimethoxybenzaldehyde (**39**).

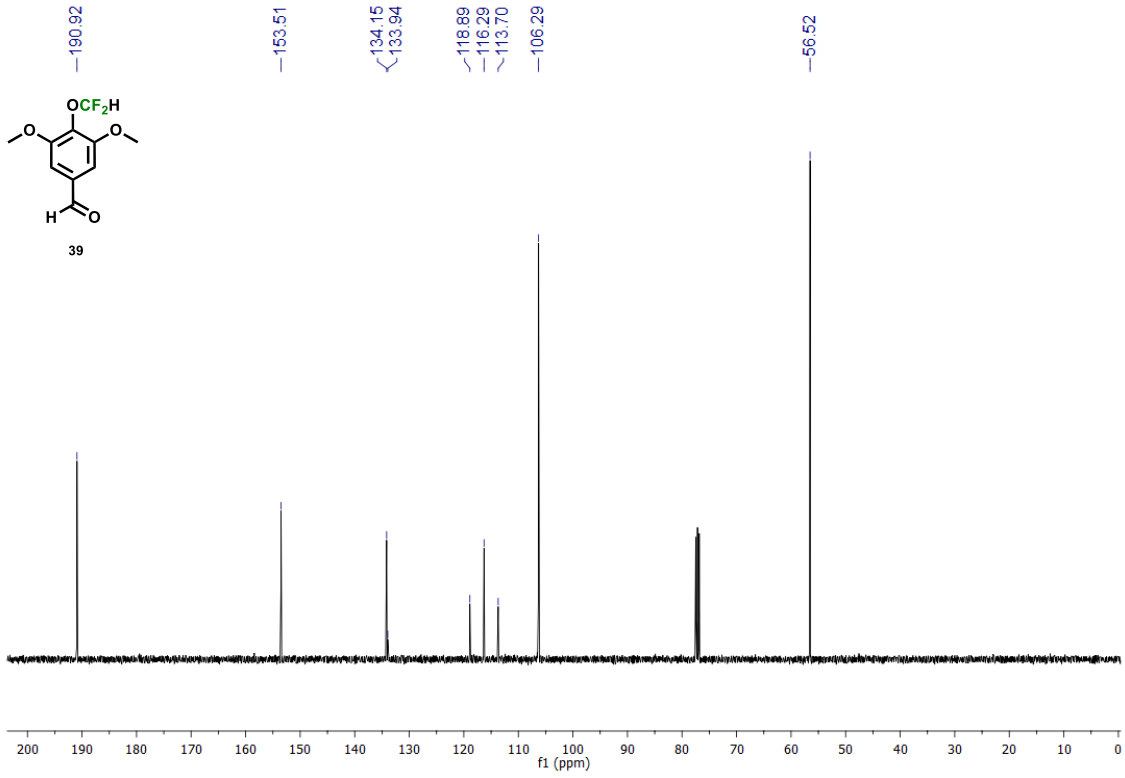

Figure S121: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(Difluoromethoxy)-3,5-dimethoxybenzaldehyde (**39**).

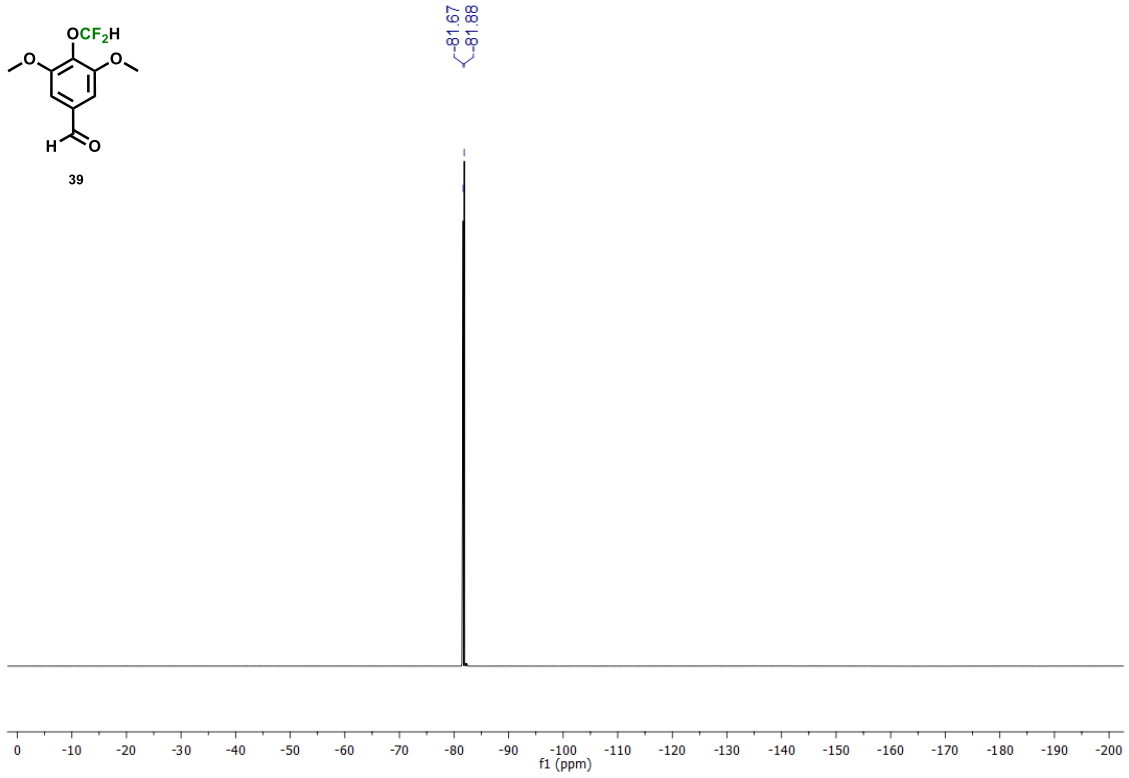

Figure S122: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3,4-Bis(difluoromethoxy)benzaldehyde (**40**).

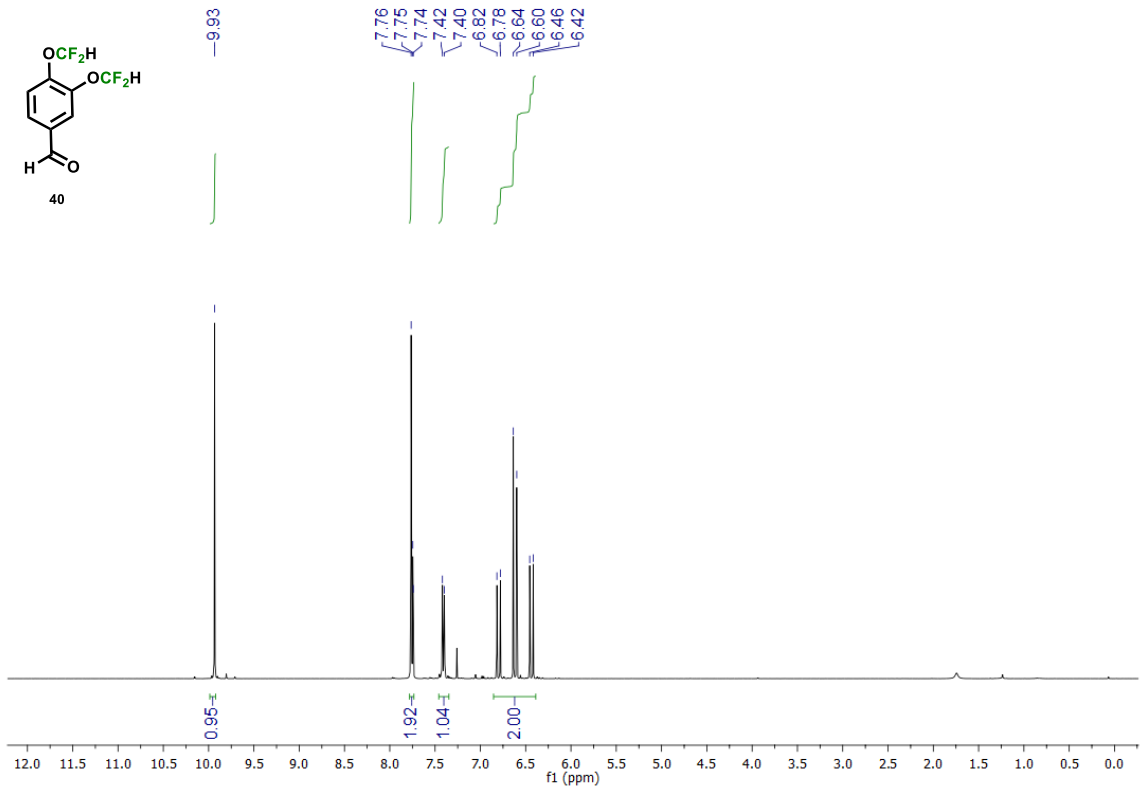

Figure S123: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 3,4-Bis(difluoromethoxy)benzaldehyde (**40**).

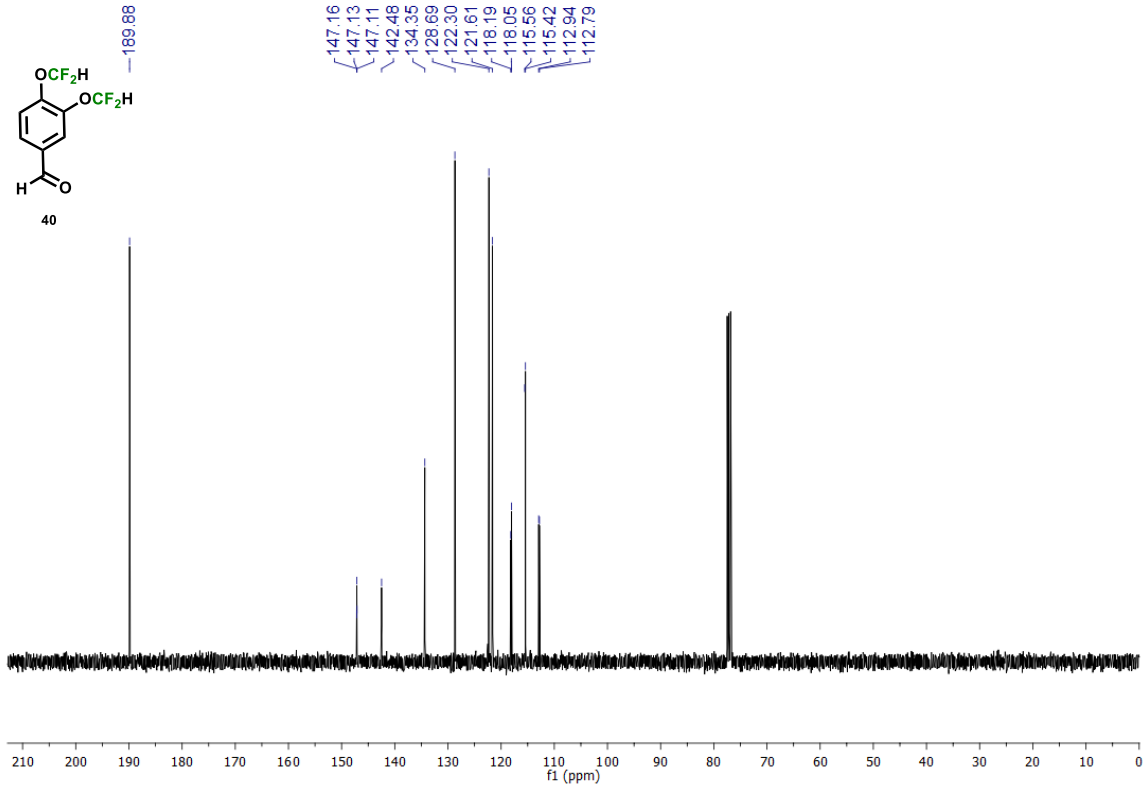

Figure S124: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3,4-Bis(difluoromethoxy)benzaldehyde (**40**).

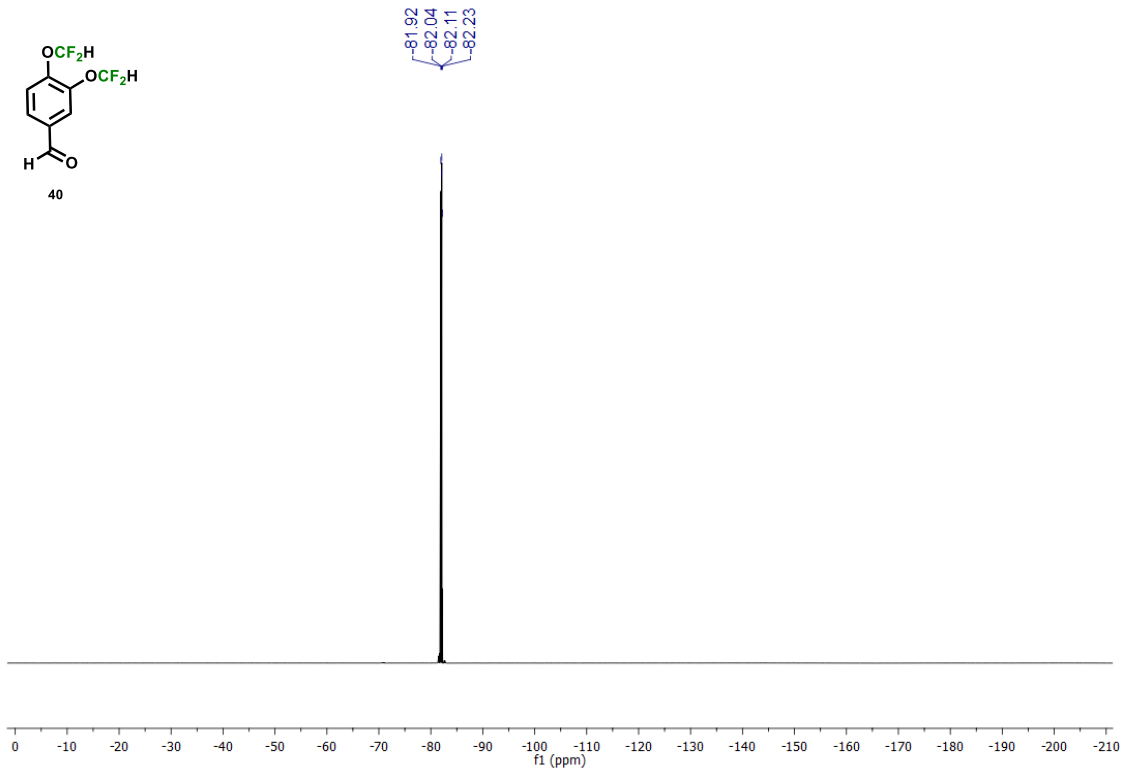

Figure S125: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1,2-Bis(difluoromethoxy)benzene (**41**).

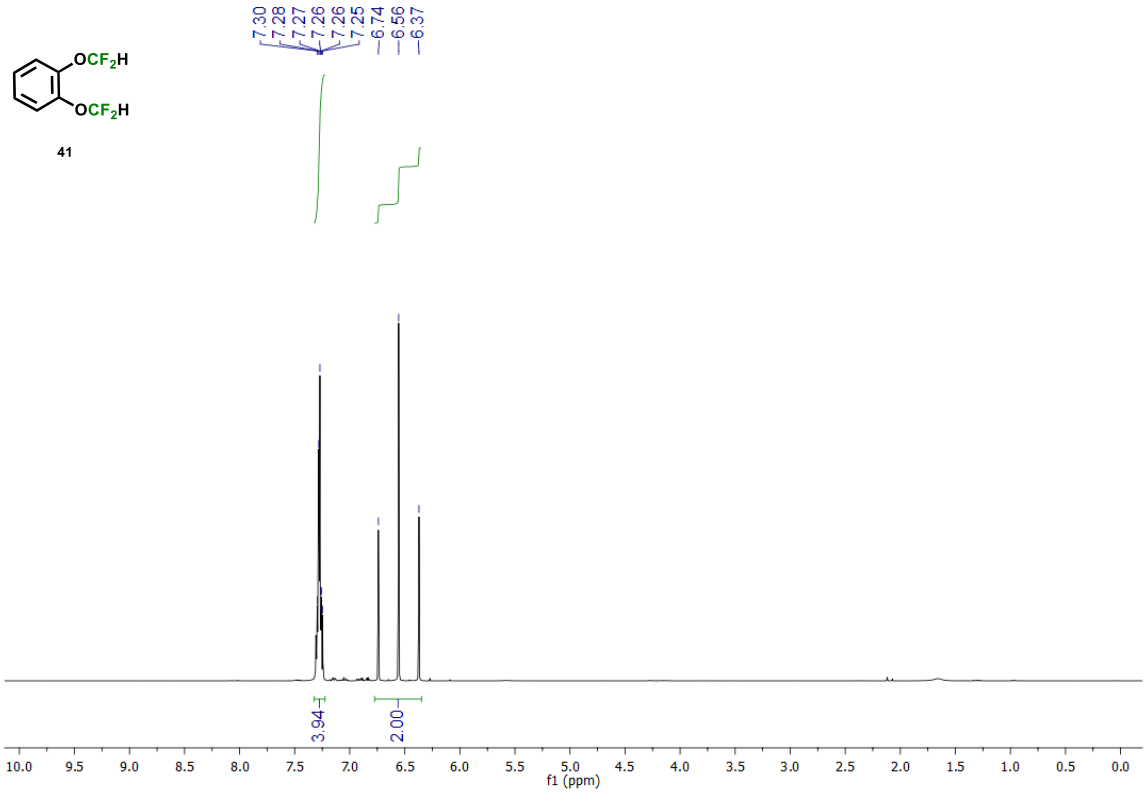

Figure S126: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 1,2-Bis(difluoromethoxy)benzene (**41**).

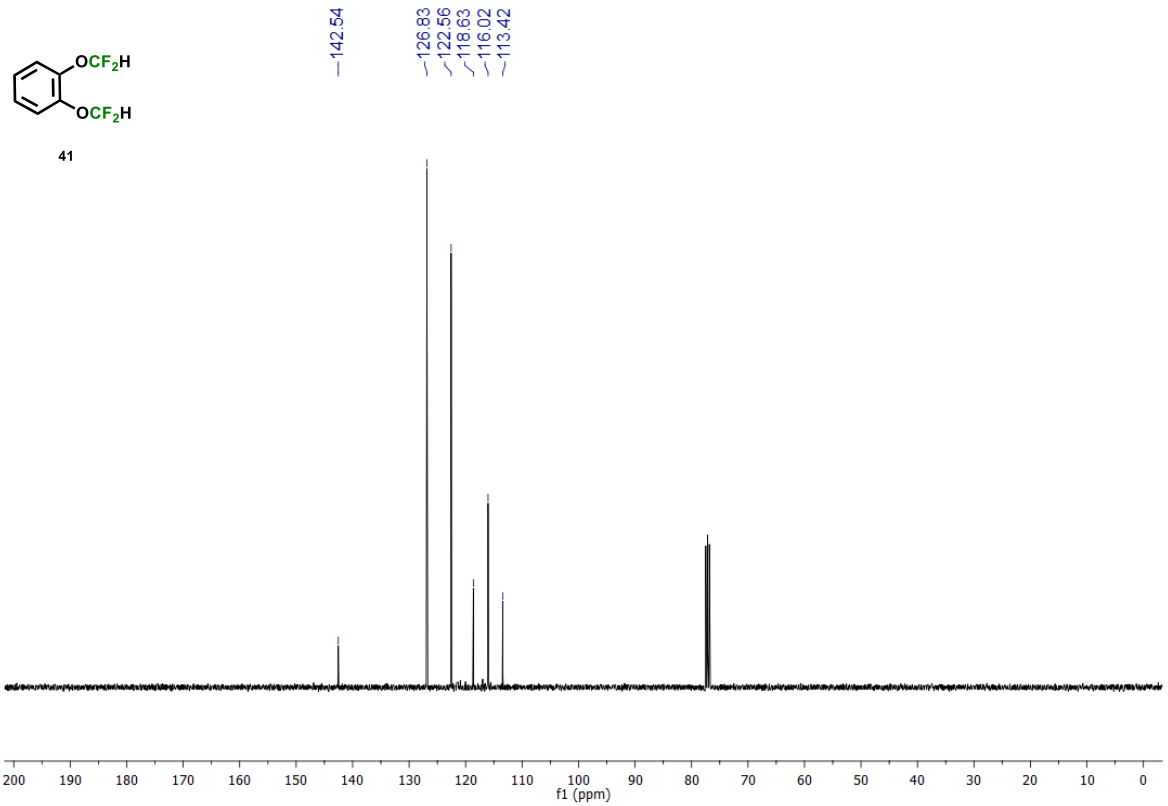

Figure S127: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1,2-Bis(difluoromethoxy)benzene (**41**).

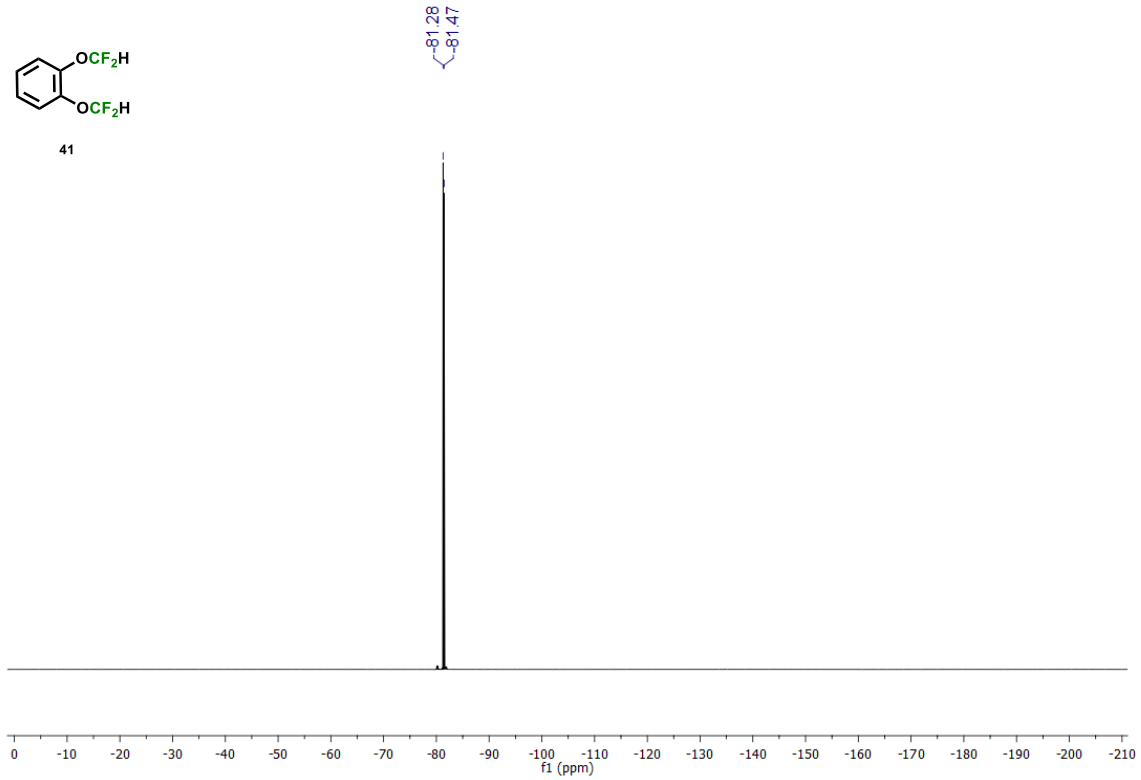

Figure S128: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (E)-1-(Difluoromethoxy)-2-methoxy-4-(prop-1-en-1-yl)benzene (**42**).

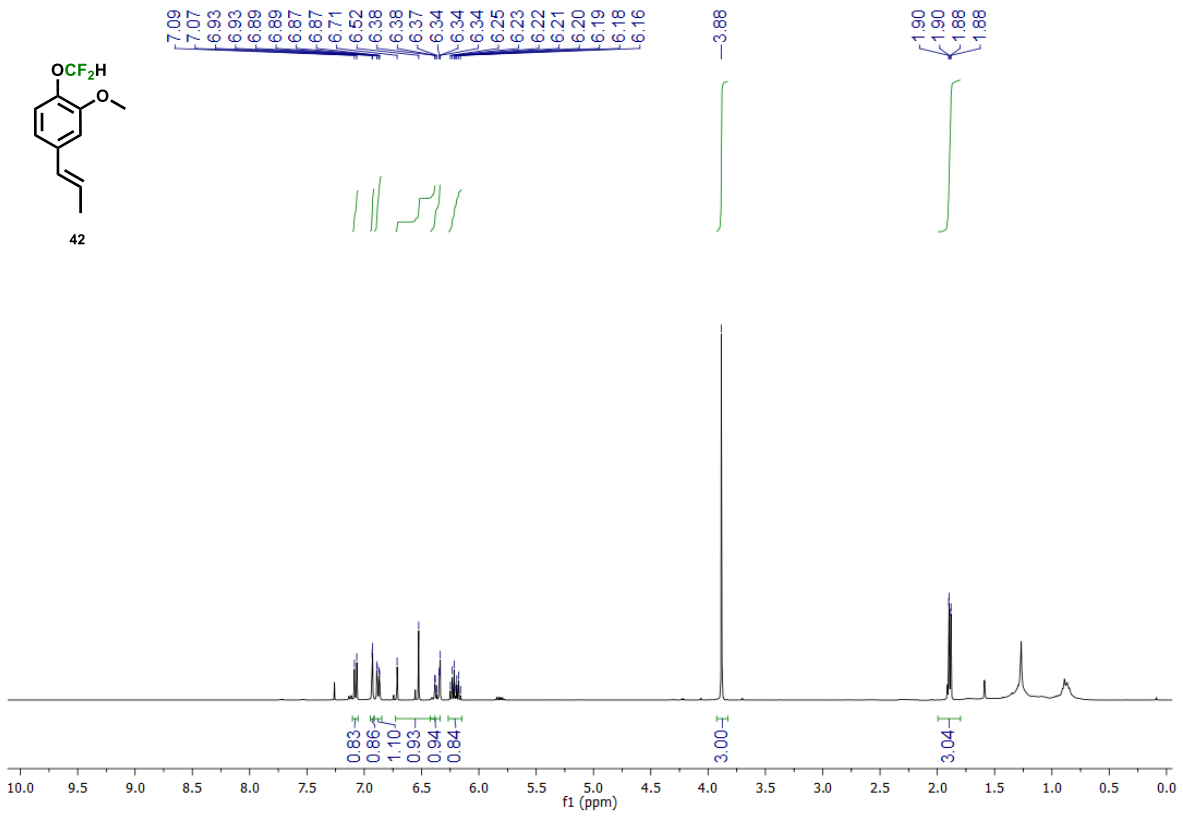

Figure S129: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (E)-1-(Difluoromethoxy)-2-methoxy-4-(prop-1-en-1-yl)benzene (**42**).

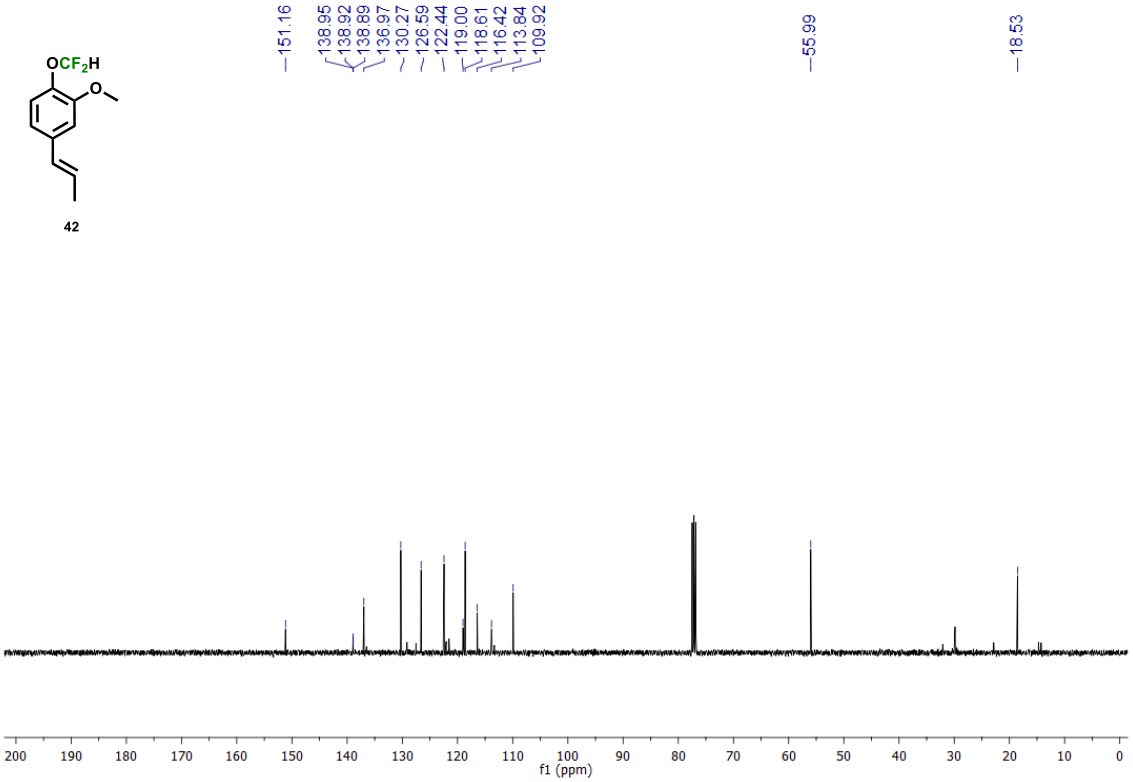

Figure S130: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (E)-1-(Difluoromethoxy)-2-methoxy-4-(prop-1-en-1-yl)benzene (**42**).

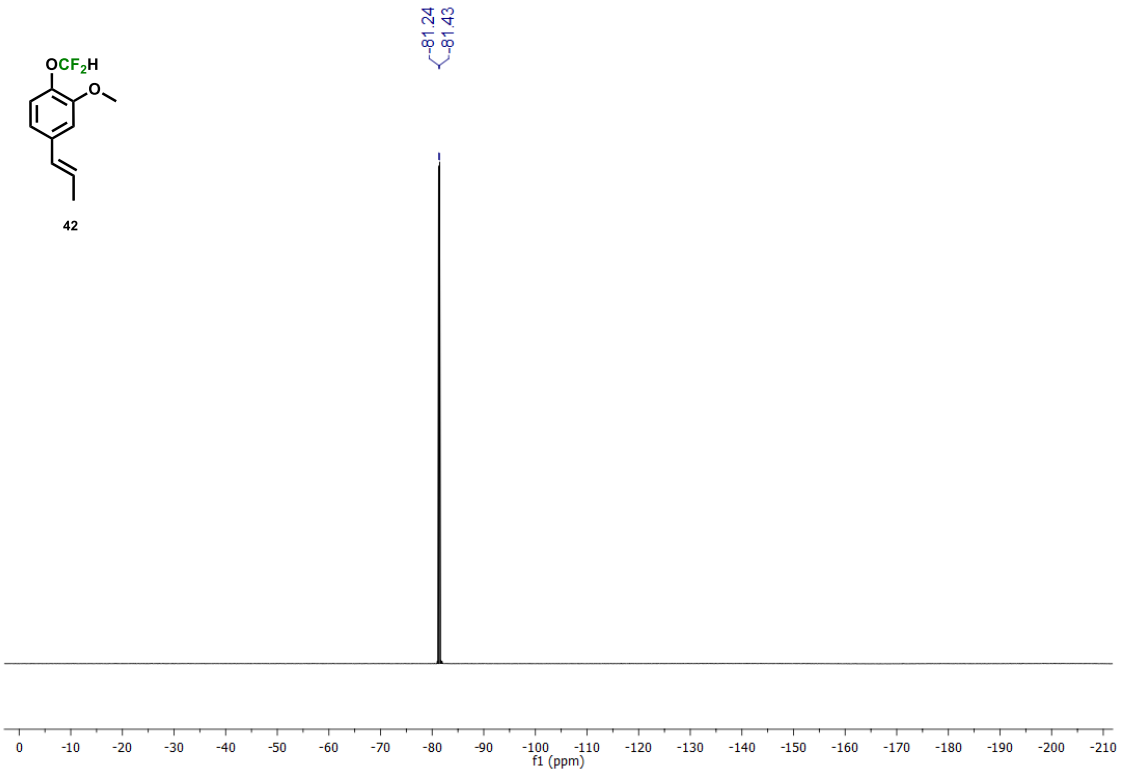

Figure S131: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4'-((Fluoromethylene)bis(oxy))bis(nitrobenzene) (**1b**).

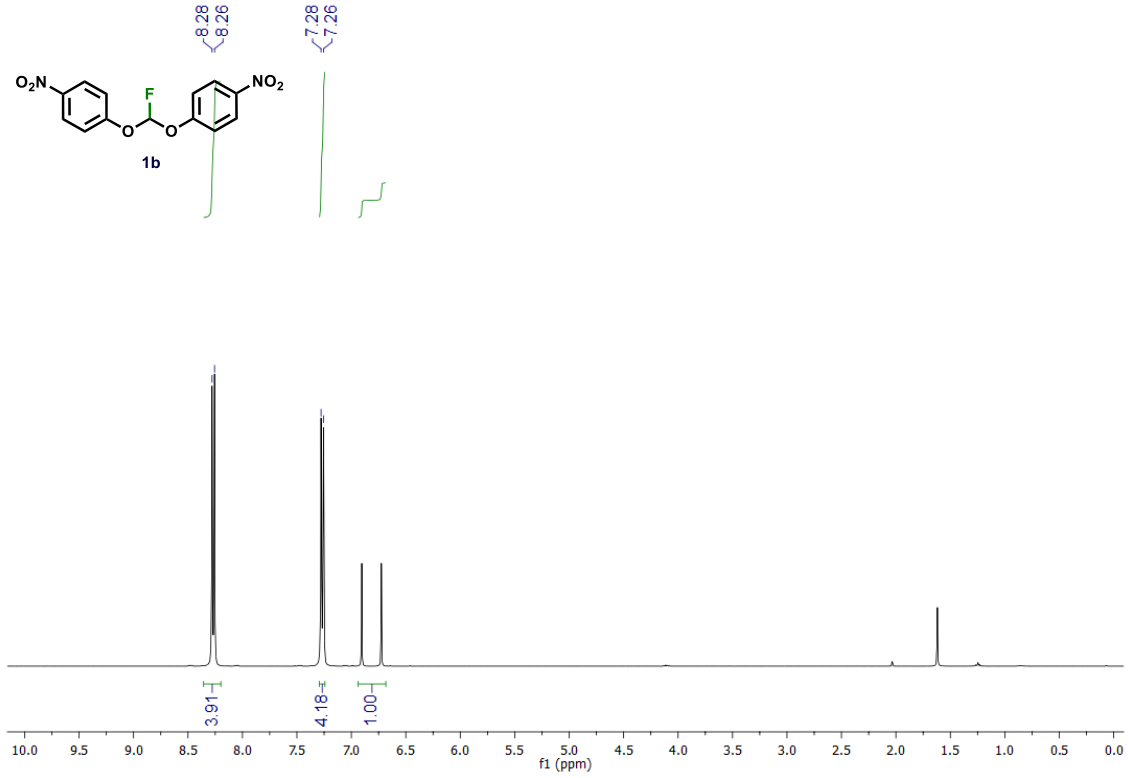

Figure S132: $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of 4,4'-((Fluoromethylene)bis(oxy))bis(nitrobenzene) (**1b**).

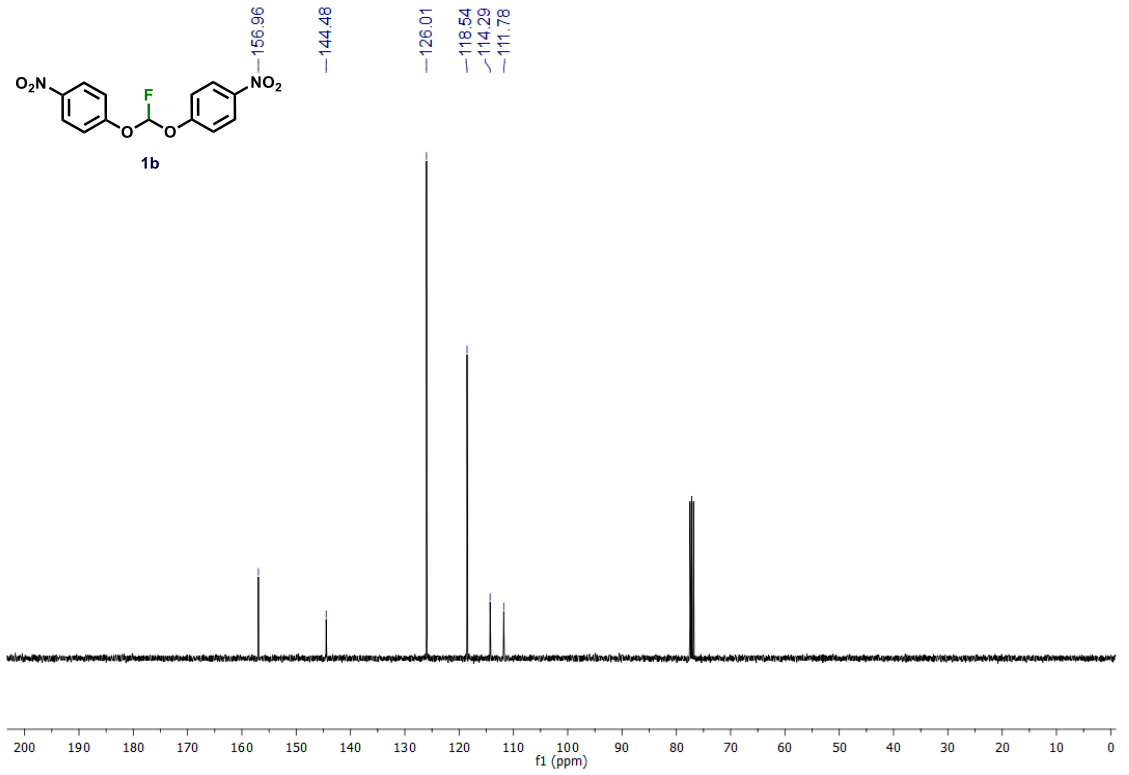

Figure S133: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4,4'-((Fluoromethylene)bis(oxy))bis(nitrobenzene) (**1b**).