Supplementary Information

Borate-Mediated Aryl Polyfluoroalkoxylation under Transition-Metal-Free Conditions

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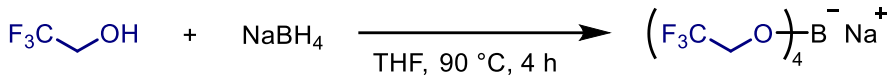
1. General information

Experiment and materials: All commercially available reagents were used as received unless otherwise noted. Sodium tetrakis(fluoroalkoxy)borate salts were synthesized according to previously reported methods in the literatures.[1,2] Diaryliodonium salts were employed as reported in our previous studies,[3] which were synthesized by the methods reported in the literature.[4] All reactions that required heating were performed using an oil bath or a metal block as a heating source. Flash column chromatography was carried out on Merck silica gel 60 (230-400 mesh).

Analysis: Melting points were measured using a Büchi B 545 apparatus and were uncorrected. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-AL400 spectrometer (^{1}H NMR: 400 MH, ^{19}F NMR: 376 MHz, and ^{13}C NMR: 100 MHz) at 25 °C. The chemical shifts in ^{1}H NMR spectra were recorded relative to residual solvent peaks ($CDCl_3$: δ 7.26, DMSO-d_6: δ 2.50). The chemical shifts in ^{19}F NMR spectrum were recorded relative to residual solvent peaks ($PhCF_3$: δ −63.0 ppm, 4-fluorotoluene: δ −121.0 ppm). The chemical shifts in ^{13}C NMR spectrum were recorded relative to residual solvent peaks ($CDCl_3$: δ 77.00 ppm, DMSO-d_6: δ 39.52 ppm). The data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, sept = septet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters (cm^{-1}) for strong and structurally important peaks. High-resolution mass spectra (HRMS) were obtained using a JMS-T100LP AccuTOF^{TM} LC-Express. Analytical TLC was performed on Merck Silica gel F_{254} plates (0.25 mm). The spots and bands were detected by UV irradiation (254 nm) or by staining with 3% *p*-anisaldehyde followed by heating.

2. Preparation of tetrakis(fluoroalkoxy)borate salts

2-1. Preparation of 1a



10 eq 20 mmol **1a**

The title compound was prepared according to the modified procedure previously described.[S1] A screw-capped test tube was charged with sodium borohydride (756 mg, 20 mmol) and THF (30 mL). 2,2,2-Trifluoroethyl alcohol (14.3 mL, 200 mmol, 10 eq) was added dropwise to the stirring mixture. After the mixture was stirred at 90 °C for 4 h, the solvent was evaporated under reduced pressure. The residue was dried by vacuum pump to afford the title compound in quantitative yield (8.583 g, 20.0 mmol) as a white solid.

Melting point: >450 °C

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.66 (q, *J* = 10.1 Hz, 8H) ppm.

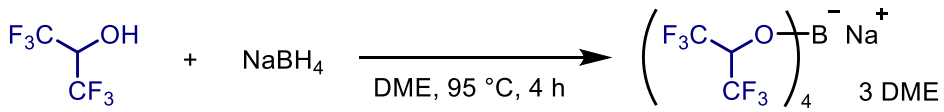
^{19}F NMR (376 MHz, DMSO-d$_6$): δ -76.9 (t, *J* = 9.8 Hz, 12 F) ppm.

^{13}C NMR (100 MHz, DMSO-d$_6$): δ 126.4 (q, *J* = 278.5 Hz), 59.8 (q, *J* = 32.4 Hz) ppm.

IR (KBr): 2953, 2900, 1425, 1277, 1173, 1120, 1054, 981, 835, 675 cm^{-1}.

Spectrum data of **1a** were matched with the product reported in the literature.[S1]

2-2. Preparation of 1b•(DME)$_3$



4.5 eq 20 mmol **1b•(DME)$_3$**

The title compound was prepared according to the modified procedure previously described.[S2] A screw-capped test tube was charged with sodium borohydride (756 mg, 20 mmol) and 1,2-dimethoxyethane (35 mL). 1,1,1,3,3,3-Hexafluoroisopropyl alcohol (10.0 mL, 90 mmol, 4.5 eq) was added dropwise to the stirring mixture. After the mixture was stirred at 95 °C for 4 h,

the solvent was evaporated under reduced pressure. The residue was azeotroped with ether at 45 °C several times and then dried by vacuum pump to generate a colorless solid. ^{1}H NMR analysis of the obtained product indicated that 3 equiv of DME remained. The title compound was afforded in 95% yield (18.476 g, 19.0 mmol) as a colorless solid.

Melting point: 98.5–100.4 ℃

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 4.66 (brs, 4H), 3.56 (s, 12H), 3.93 (s, 18H) ppm.

^{19}F NMR (376 MHz, DMSO-d$_6$): δ -76.0 (s, 24F) ppm.

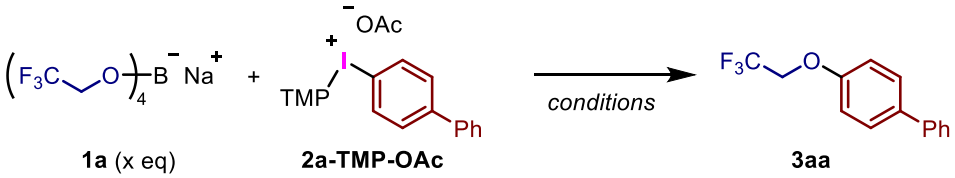
^{13}C NMR (100 MHz, DMSO-d$_6$): δ 122.4 (q, J = 282.4 Hz), 71.5, 69.3 (sept, J = 32.5 Hz), 59.1 ppm.

IR (KBr): 2943, 1457, 1380, 1192, 1101, 1027, 862, 743, 688, 656 cm^{-1}.

Spectrum data of **1b•(DME)$_3$** were matched with the product reported in the literature.[S2]

3. Optimization of reaction conditions

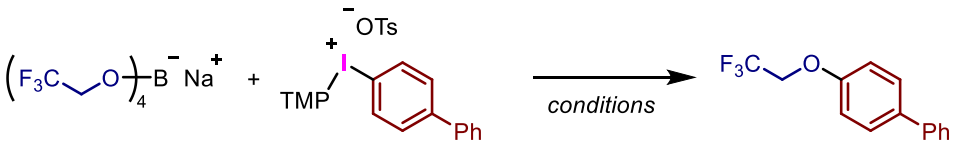
Table S1. Reaction of **1a** with **2a-TMP-OAc**



1a (x eq) **2a-TMP-OAc** **3aa**

entry	**1a** (eq)	solvent	time (h)	temp. (°C)	^{1}H NMR yield of **3aa** (%)
1	1	toluene	24	100	24%
2	1	toluene / H_2O (1:1)	24	100	86%
3	1	toluene / H_2O (1:1)	24	80	53%
4	1	toluene / H_2O (1:1)	24	60	53% (48% isol.)
5	1	DCE / H_2O (1:1)	24	60	18%
6	2	CH_3CN / H_2O (1:1)	24	80	18%
7	1	EtOAc/ H_2O (1:1)	65	80	14%
8	1	toluene / H_2O (1:4)	24	100	95%
9	1	toluene / H_2O (4:1)	24	100	88%
10	1	toluene / H_2O (1:4)	24	70	81%
11	1	toluene / H_2O (4:1)	24	70	96% (82% isol.)
12	1	H_2O	50	100	0%

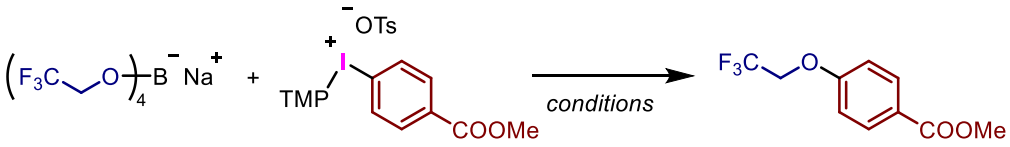
Table S2. Reaction of **1a** with **2a-TMP-OTs**



1a (1x eq) **2a-TMP-OTs** **3aa**

entry	**1a** (eq)	solvent	time (h)	temp. (°C)	^{1}H NMR yield of **3aa** (%)
1	1	toluene	24	100	35%
2	1	acetonitrile	24	100	76%
3	1	DME	24	100	16%
4	1	toluene / H_2O (1:1)	24	100	95%
5	1	toluene / H_2O (4:1)	24	100	>99% (80% isol.)
6	1	toluene / H_2O (1:4)	24	100	>99% (84% isol.)
7	1	hexane / H_2O (4:1)	24	100	70%
8	1	hexane / H_2O (1:4)	24	100	55% (54% isol.)
9	1	EtOAc / H_2O (4:1)	24	100	9%
10	1	EtOAc / H_2O (1:4)	24	100	7%
11	1	DME / H_2O (4:1)	24	100	20%
12	1	toluene / H_2O (4:1)	24	70	96% (88% isol.)
13	2	toluene / H_2O (4:1)	24	100	>99%
14	2	toluene / H_2O (4:1)	24	70	>99% (94% isol.)
15	2	toluene / H_2O (4:1)	2	70	>99% (94% isol.)

Table S3. Reaction of **1a** with **2b-TMP-OAc**

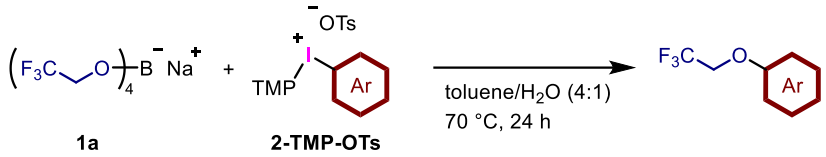


1a (x eq) **2b-TMP-OTs** **3ab**

entry	**1a** (eq)	solvent	time (h)	temp. (°C)	^{1}H NMR yield of **3ab** (%)
1	1	toluene	24	70	32%
2	1	toluene / H_2O (1:1)	24	70	70%
3	1	toluene / H_2O (1:4)	24	70	65%
4	1	toluene / H_2O (10:1)	24	70	75%
5	1	toluene / H_2O (4:1)	24	70	85%
6	1	toluene / H_2O (4:1)	24	100	69%
7	1	toluene / H_2O (4:1)	24	50	78%
8	2	toluene / H_2O (4:1)	24	70	90% (74% isol.)

4. Fluoroalkoxylation of 2-TMP-OTs

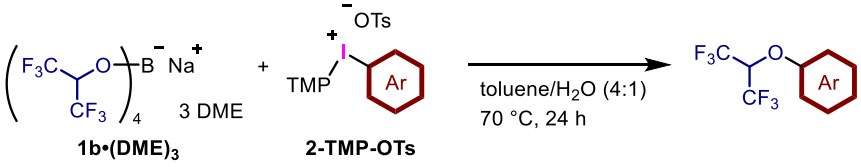
General procedure A



1a **2-TMP-OTs**

In a screw-capped test tube, sodium tetrakis(trifluoroethoxy)borate **1a** (171.7 mg, 0.40 mmol, 2.0 eq) and TMP-iodonium tosylate **2-TMP-OTs** (0.20 mmol) were dissolved in a mixed solvent of toluene and water (4:1, 4 mL). The mixture was stirred at 70 °C for 24 h using a metal block. After cooling to room temperature, the organic layer was decantated. The residual water layer was extracted with hexane (2 × 4 mL). The combined organic solution was washed with brine (2 × 4 mL), and then ^{19}F NMR analysis of the crude mixture was carried out with $CDCl_3$ and $PhCF_3$ (internal standard) to determine the NMR yield. After concentrating the organic solution under reduced pressure, the residue was purified by column chromatography (SiO_2) to afford the corresponding trifluoroethoxy arene.

General procedure B

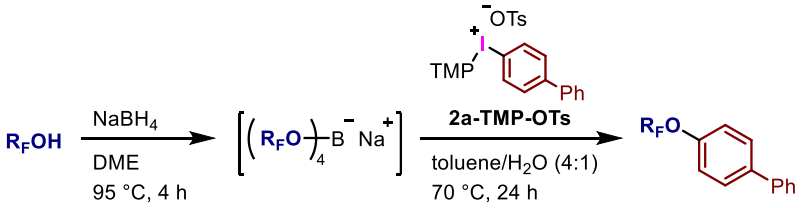


1b•(DME)$_3$ **2-TMP-OTs**

In a screw-capped test tube, sodium tetrakis(hexafluoroisopropoxy)borate **1b•(DME)$_3$** (280.0 mg, 0.288 mmol, 1.44 eq) and TMP-iodonium tosylate **2-TMP-OTs** (0.20 mmol) were dissolved in a mixed solvent of toluene and water (4:1, 4 mL). The mixture was stirred at 70 °C for 24 h using a metal block. After cooling to room temperature, the organic layer was decantated. The residual water layer was extracted with hexane (2 × 4 mL). The combined organic solution was washed with brine (2 × 4 mL), and then ^{19}F NMR analysis of the crude

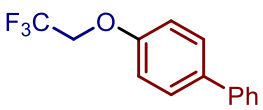
mixture was carried out with $CDCl_3$ and $PhCF_3$ (internal standard) to determine the NMR yield. After concentrating the organic solution under reduced pressure, the residue was purified by column chromatography (SiO_2) to afford the corresponding trifluoroethoxy arene.

General procedure C



A screw-capped test tube was charged with sodium borohydride (37.8 mg, 1.0 mmol, 2.0 eq) and 1,3-dimethoxyethane (1.5 mL). The polyfluoroalcohol (4.0 mmol, 8.0 eq) was added dropwise to the stirring mixture. After the mixture was stirred at 95 °C for 4 h, the solvent was evaporated under reduced pressure. The residual solid was dissolved in a mixed solvent of toluene and water (4:1, 10 mL), and then (4-phenylphenyl)(TMP)iodonium tosylate **2a-OTs** (301.2 mg, 0.50 mmol) was added to the mixture. The mixture was stirred at 70 °C for 24 h using a metal block. After cooling to room temperature, the organic layer was decantated. The residual water layer was extracted with hexane (2 × 10 mL). The combined organic solution was dried with Na_2SO. After filtration to remove the insoluble material followed by concentration of the filtrate, the residue was purified by column chromatography (SiO_2, hexane) to afford the corresponding polyfluoroalkoxy arene.

4-(2,2,2-Trifluoroethoxy)-1,1'-biphenyl (3aa)



The title compound (**3aa**) was synthesized by the general procedure A using (4-phenylphenyl)(TMP)iodonium tosylate (**2a-OTs**, 123.7 mg, 0.20 mmol). ^{19}F NMR analysis of

crude mixture indicated that **3aa** was generated in a quantitative yield. Purification by column chromatography (SiO_2, hexane) afforded **3aa** in 94% yield (47.2 mg, 0.187 mmol) as a colorless solid.

Melting Point: 96.6–98.3 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.8 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 4.40 (q, *J* = 8.0 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –76.3 (t, *J* = 8.5 Hz, 3F)

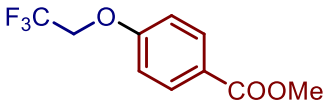
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.9, 140.3, 135.7, 128.8, 128.4, 127.0, 126.8, 123.3 (q, *J* = 276.6 Hz), 115.2, 65.9 (q, *J* = 35.4 Hz) ppm.

IR (KBr): 3019, 1602, 1523, 1427, 1224, 913, 722 cm^{-1}.

HRMS (DART) m/z: ($[M+H]^+$) Calcd for $C_{14}H_{12}OF_3^+$ 253.08348; Found 253.08333.

Spectrum data of **3aa** were matched with the product reported in the literature.[S5.6.7]

Methyl 4-(2,2,2-trifluoroethoxy)benzoate (3ab)



The title compound (**3ab**) was synthesized by the general procedure A using (4-methoxycarbonylphenyl)(TMP)iodonium tosylate (**2b-OTs**, 120.0 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3ab** was generated in 90% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:20) afforded **3ab** in 74% yield (34.7 mg, 0.148 mmol) as a colorless solid.

Melting Point: 54.5–56.0 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.40 (q, *J* = 8.0 Hz, 2H), 3.89 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –76.2 (t, *J* = 7.3 Hz, 3F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.4, 160.7, 131.8, 124.5, 123.4 (q, *J* = 276.6), 114.4,

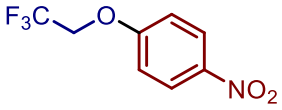
65.5 (q, *J* = 35.9 Hz), 52.0 ppm.

IR (KBr): 3021, 1718, 1605, 1520, 1427, 1230, 912, 795, 745 cm^{-1}.

HRMS (DART) m/z: ($[M+H]^+$) Calcd for $C_{10}H_{10}O_3F_3^+$ 235.05766; Found 235.05783.

Spectrum data of **3ab** were matched with the product reported in the literature.[S5,8]

1-Nitro-4-(2,2,2-trifluoroethoxy)benzene (3ac)



The title compound (**3ac**) was synthesized by the general procedure A using (4-nitrophenyl)(TMP)iodonium tosylate (**2c-OTs**, 117.5 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3ac** was generated in 91% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:20) afforded **3ac** in 56% yield (24.6 mg, 0.111 mmol) as a colorless solid.

Melting Point: 67.3–68.7 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 9.4 Hz, 2H), 7.04 (d, *J* = 9.4 Hz, 2H), 4.46 (q, *J* = 7.9 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –76.0 (t, *J* = 8.5 Hz, 3F) ppm.

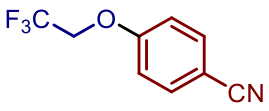
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.7, 143.0, 126.0, 122.8 (q, *J* = 276.6 Hz), 114.8, 65.8 (q, *J* = 36.5 Hz) ppm.

IR (KBr): 3021, 1793, 1602, 1520, 1477, 1380, 1349, 1237, 913, 745 cm^{-1}.

HRMS (DART) m/z: ($[M+H]^+$) Calcd for $C_8H_7NO_3F_3^+$ 222.03725; Found 222.03655.

Spectrum data of **3ac** were matched with the product reported in the literature.[S5,6,8,9]

4-(2,2,2-Trifluoroethoxy)benzonitrile (3ad)



The title compound (**3ad**) was synthesized by the general procedure A using (4-cyanophenyl)(TMP)iodonium tosylate (**2d-OTs**, 113.5 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3ad** was generated in 90% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:20) afforded **3ad** in 88% yield (35.4 mg, 0.176 mmol) as a colorless solid.

Melting Point: 49.8–51.5 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 9.4 Hz, 2H), 7.02 (d, *J* = 9.4 Hz, 2H), 4.41 (q, *J* = 8.0 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –76.1 (t, *J* = 8.6 Hz, 3F) ppm.

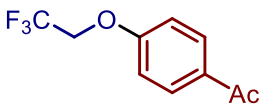
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.2, 134.2, 122.8 (q, *J* = 276.9 Hz), 118.5, 115.5, 106.2, 65.6 (q, *J* = 36.2 Hz) ppm.

IR (KBr): 3017, 2256, 1734, 1602, 1512, 1422, 1223, 1026, 913, 722 cm^{-1}.

HRMS (DART) m/z: ([M+H]$^+$) Calcd for $C_9H_7NOF_3^+$ 202.04742; Found 202.04678.

Spectrum data of **3ad** were matched with the product reported in the literature.[S5,6,7,8]

1-Acetyl-4-(2,2,2-trifluoroethoxy)benzene (3ae)



The title compound (**3ae**) was synthesized by the general procedure A using (4-acetylphenyl)(TMP)iodonium tosylate (**2e-OTs**, 116.9 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3ae** was generated in 60% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:20) afforded **3ad** in 60% yield (26.1 mg, 0.120 mmol) as a colorless solid.

Melting Point: 67.6–69.5 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.41 (q, *J* = 8.0 Hz, 2H), 2.57 (s, 3H) ppm.

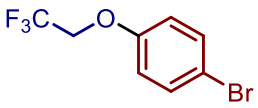
^{19}F NMR (376 MHz, $CDCl_3$): δ –76.2 (t, *J* = 8.6 Hz, 3F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.8, 131.8, 130.7, 123.0 (q, *J* = 276.6 Hz), 114.4, 65.5 (q, *J* = 36.0 Hz), 26.4 ppm.

IR (KBr): 3019, 1677, 1604, 1524, 1423, 1221, 1027, 929, 789, 765 cm^{-1}.

Spectrum data of **3ad** were matched with the product reported in the literature.[S5,8]

1-Bromo-4-(2,2,2-trifluoroethoxy)benzene (3af)



The title compound (**3af**) was synthesized by the general procedure A using (4-bromophenyl)(TMP)iodonium tosylate (**2f-OTs**, 124.3 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3af** was generated in 81% yield. Purification by column chromatography (SiO_2, hexane) afforded **3af** in 64% yield (32.8 mg, 0.129 mmol) as a colorless solid.

Melting Point: 40.1–40.9 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.32 (q, *J* = 7.9 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –76.3 (t, *J* = 7.1 Hz, 3F) ppm.

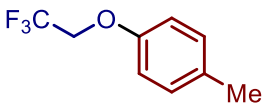
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.5, 132.6, 123.1 (q, *J* =276.6 Hz), 116.8, 115.0, 66.0 (q, *J* = 35.6 Hz) ppm.

IR (KBr): 3022, 1520, 1489, 1427, 1224, 913, 745, 679 cm^{-1}.

HRMS (DART) m/z: ([M]) Calcd for $C_8H_6OF_3Br$ 253.95486; Found 253.95453

Spectrum data of **3ae** were matched with the product reported in the literature.[S6,7]

1-Methyl-4-(2,2,2-trifluoroethoxy)benzene (3ag)



The title compound (**3ag**) was synthesized by the general procedure A using (4-methylphenyl)(TMP)iodonium tosylate (**2g-OTs**, 111.3 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3ag** was generated in 90% yield. Purification by column chromatography (SiO_2, hexane) afforded **3ag** in 70% yield (26.5 mg, 0.139 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.32 (q, *J* = 8.1 Hz, 2H), 2.31 (s, 3H) ppm.

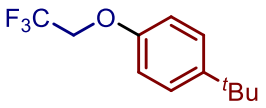
^{19}F NMR (376 MHz, $CDCl_3$): δ –76.4 (t, *J* = 8.6 Hz, 3F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.4, 131.9, 130.1, 123.4 (q, *J* = 276.6 Hz), 114.8, 66.1 (q, *J* = 34.9 Hz), 20.5 ppm.

IR (KBr): 3155, 2926, 1794, 1604, 1504, 1382, 1237, 1168, 1104, 913, 744 cm^{-1}.

Spectrum data of **3af** were matched with the product reported in the literature.[S7]

1-(*tert*-Butyl)-4-(2,2,2-trifluoroethoxy)benzene (3ah)



The title compound (**3ah**) was synthesized by the general procedure A using (4-*tet*-butylphenyl)(TMP)iodonium tosylate (**2h-OTs**, 119.7 mg, 0.20 mmol). Purification by column chromatography (SiO_2, hexane) afforded **3ah** in 75% yield (34.7 mg, 0.149 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.34 (q, *J* = 8.1 Hz, 2H), 1.32 (s, 9H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –76.4 (t, *J* = 7.3 Hz, 3F) ppm.

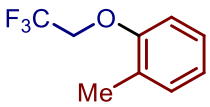
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.2, 145.3, 126.5, 123.4 (q, *J* = 276.6 Hz), 114.4, 66.0

(q, J = 35.1 Hz), 34.2, 31.4 ppm.

IR (KBr): 3021, 1734, 1602, 1152, 1427, 1223, 1018, 913, 792, 745 cm^{-1}.

Spectrum data of **3ag** were matched with the product reported in the literature.[S5,6]

1-Methyl-2-(2,2,2-trifluoroethoxy)benzene (3ai)



The title compound (**3ai**) was synthesized by the general procedure A using (4-methylphenyl)(TMP)iodonium tosylate (**2i-OTs**, 111.3 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3ai** was generated in 91% yield. Purification by column chromatography (SiO_2, hexane) afforded **3ai** in 59% yield (22.5 mg, 0.118 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.15 (m, 2H), 6.96 (dd, J = 7.6, 7.2 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 4.35 (q, J = 8.1 Hz, 2H), 2.27 (s, 3H) ppm.

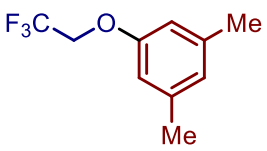
^{19}F NMR (376 MHz, $CDCl_3$): δ –74.5 (t, J = 9.8 Hz, 3F) ppm.

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 155.5, 131.2, 126.9, 123.5 (q, J = 276.7 Hz), 122.3, 117.6, 111.8, 66.2 (q, J = 35.7 Hz), 15.9 ppm.

IR (KBr): 2925, 1739, 1605, 1503, 1237, 1170, 976, 814, 660 cm^{-1}.

Spectrum data of **3ah** were matched with the product reported in the literature.[S5,7]

1,3-Dimethyl-5-(2,2,2-trifluoroethoxy)benzene (3aj)



The title compound (**3aj**) was synthesized by the general procedure A using (3,5-dimethylphenyl)(TMP)iodonium tosylate (**2j-OTs**, 114.1 mg, 0.20 mmol). ^{19}F NMR analysis

of crude mixture indicated that **3aj** was generated in 92% yield. Purification by column chromatography (SiO_2, hexane) afforded **3aj** in 69% yield (28.0 mg, 0.137 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (s, 1H), 6.58 (s, 2H), 4.32 (q, *J* = 8.1 Hz, 2H), 2.31 (s, 6H) ppm.

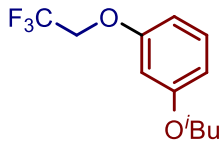
^{19}F NMR (376 MHz, $CDCl_3$): δ –76.4 (t, *J* = 8.5 Hz, 3F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.4, 139.6, 124.2, 123.4 (q, *J* = 276.6 Hz), 112.6, 65.7 (q, *J* = 35.1 Hz), 21.3 ppm.

IR (KBr): 3022, 1730, 1602, 1523, 1427, 1221, 1173, 1018, 911, 744 cm^{-1}.

HRMS (DART) m/z: ($[M+H]^+$) Calcd for $C_{10}H_{12}OF_3^+$ 205.08348; Found 205.08298.

1-Isobutoxy-3-(2,2,2-trifluoroethoxy)benzene (3ak)



The title compound (**3ak**) was synthesized by the general procedure A using (3-isobutoxyphenyl)(TMP)iodonium tosylate (**2k-OTs**, 122.9 mg, 0.20 mmol). Purification by column chromatography (SiO_2, hexane) afforded **3ak** in 85% yield (42.1 mg, 0.170 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, *J* = 8.8, 8.4 Hz, 1H), 6.62–6.59 (m, 1H), 6.53–6.49 (m, 2H), 4.33 (q, *J* = 8.1 Hz, 2H), 3.71 (d, *J* = 6.4 Hz, 2H), 2.08 (sept, *J* = 6.8 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 6H) ppm.

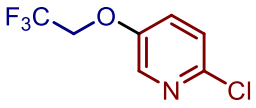
^{19}F NMR (376 MHz, $CDCl_3$): δ –76.4 (t, *J* = 8.5 Hz, 3F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.6, 158.5, 130.1, 123.3 (q, *J* = 276.6 Hz), 108.7, 106.4, 102.1, 74.5, 65.8 (q, *J* = 35.4 Hz), 28.2, 19.2 ppm.

IR (KBr): 3022, 1602, 1492, 1418, 1220, 928, 722 cm^{-1}.

HRMS (DART) m/z: ([M+H]$^+$) Calcd for $C_{12}H_{16}O_2F_3^+$ 249.10969; Found 249.10879.

2-Chloro-5-(2,2,2-trifluoroethoxy)pyridine (3al)



The title compound (**3al**) was synthesized by the general procedure A using (6-chloropyridin-3-yl)(TMP)iodonium tosylate (**2l-OTs**, 115.6 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3al** was generated in 77% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:20) afforded **3al** in 72% yield (30.5 mg, 0.144 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.25–7.21 (m, 2H), 4.35 (q, *J* = 7.9 Hz, 2H) ppm.

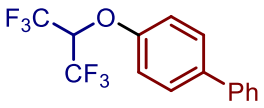
^{19}F NMR (376 MHz, $CDCl_3$): δ –76.2 (t, *J* = 7.3 Hz, 3F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.9, 144.7, 137.0, 125.8, 124.8, 122.8 (q, *J* = 276.6 Hz), 66.4 (q, *J* = 36.0 Hz) ppm.

IR (KBr): 2926, 1573, 1458, 1295, 1168, 1073, 975, 910, 831, 744 cm^{-1}.

HRMS (DART) m/z: ([M+H]$^+$) Calcd for $C_7H_6NOF_3Cl^+$ 212.00845; Found 212.00771.

4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-1,1'-biphenyl (3ba)



The title compound (**3ba**) was synthesized by the general procedure B using (4-phenylphenyl)(TMP)iodonium tosylate (**2a-OTs**, 123.7 mg, 0.20 mmol). Purification by column chromatography (SiO_2, hexane) afforded **3ba** in 91% yield (58.1 mg, 0.181 mmol) as a colorless solid.

Melting Point: 51.9–53.0 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 4.86 (sept, *J* = 5.7 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –75.9 (d, *J* = 4.9 Hz, 6F) ppm.

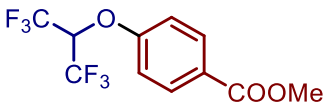
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.1, 140.0, 137.9, 128.9, 128.7, 127.4, 127.0, 121.1 (q, *J* = 283.2 Hz), 117.5, 76.3 (sept, *J* = 32.9 Hz) ppm.

IR (KBr): 3031, 2925, 1516, 1485, 1370, 1293, 1197, 1101, 899, 784, 744 cm^{-1}.

HRMS (DART) m/z: ([M]) Calcd for $C_{15}H_{10}OF_6$ 320.06304; Found 320.06232.

Spectrum data of **3ba** were matched with the product reported in the literature.[S10]

Methyl 4-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzoate (3bb)



The title compound (**3bb**) was synthesized by the general procedure B using (4-methoxycarbonylphenyl)(TMP)iodonium tosylate (**2b-OTs**, 120.0 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3bb** was generated in 99% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:14) afforded **3bb** in 82% yield (49.4 mg, 0.163 mmol) as a pale-yellow solid.

Melting Point: 51.7–52.9 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 4.94 (sept, *J* = 5.5 Hz, 1H), 3.91 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –75.8 (d, *J* = 4.9 Hz, 6F) ppm.

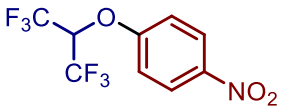
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.0, 160.5, 132.0, 126.5, 120.9 (q, *J* = 282.4 Hz), 116.4, 75.2 (sept, *J* = 33.5 Hz), 52.2 ppm.

IR (KBr): 3014, 1718, 1606, 1508, 1376, 1290, 1240, 1099, 917, 745 cm^{-1}.

HRMS (DART) m/z: ($[M+H]^+$) Calcd for $C_{11}H_9O_3F_6^+$ 303.04504; Found 303.04384.

Spectrum data of **3bb** were matched with the product reported in the literature.[S10]

1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-4-nitrobenzene (3bc)



The title compound (**3bc**) was synthesized by the general procedure B using (4-nitrophenyl)(TMP)iodonium tosylate (**2c-OTs**, 117.5 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3bc** was generated in 87% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:10) afforded **3bc** in 68% yield (39.4 mg, 0.136 mmol) as a pale-yellow solid.

Melting Point: 50.3–51.8 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 9.4 Hz, 2H), 7.20 (d, *J* = 9.4 Hz, 2H), 4.98 (sept, *J* = 5.5 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –75.6 (d, *J* = 7.3 Hz, 6F) ppm.

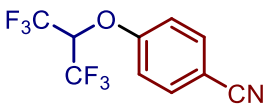
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.2, 144.2, 126.2, 120.6 (q, *J* = 283.2 Hz), 116.9, 75.1 (sept, *J* = 33.8 Hz) ppm.

IR (KBr): 3018, 1730, 1597, 1524, 1427, 1349, 1221, 1109, 911, 774, 744 cm^{-1}.

HRMS (DART) m/z: ([M+H]$^+$) Calcd for $C_9H_6NO_3F_6^+$ 290.02464; Found 290.02374.

Spectrum data of **3bc** were matched with the product reported in the literature.[S9]

4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)benzonitrile (3bd)



The title compound (**3bd**) was synthesized by the general procedure B using (4-cyanophenyl)(TMP)iodonium tosylate (**2d-OTs**, 113.5 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3bd** was generated in 87% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:30) afforded **3bd** in 62% yield (33.4 mg, 0.124

mmol) as a colorless solid.

Melting Point: 90.3–91.9 ℃

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 4.94 (sept, *J* = 5.5 Hz, 1H) ppm.

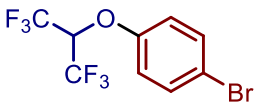
^{19}F NMR (376 MHz, $CDCl_3$): δ –75.7 (d, *J* = 4.9 Hz, 6F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.9, 134.5, 120.7 (q, *J* = 283.2 Hz), 117.9, 117.4, 108.5, 75.1 (sept, *J* = 33.8 Hz) ppm.

IR (KBr): 3021, 2251, 1732, 1602, 1511, 1422, 1227, 1019, 909, 722 cm^{-1}.

HRMS (DART) m/z: ([M+H]$^+$) Calcd for $C_{10}H_6NOF_6^+$ 270.03481; Found 270.03401.

1-Bromo-4-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzene (3bf)



The title compound (**3bf**) was synthesized by the general procedure B using (4-bromophenyl)(TMP)iodonium tosylate (**2f-OTs**, 124.3 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3bf** was generated in 91% yield. Purification by column chromatography (SiO_2, hexane) afforded **3bf** in 59% yield (37.8 mg, 0.117 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 4.73 (sept, *J* = 5.7 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ –75.9 (d, *J* = 7.3 Hz, 6F) ppm.

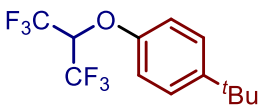
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.6, 133.1, 120.9 (q, *J* = 282.3 Hz), 119.1, 117.5, 76.4 (sept, *J* = 33.7 Hz) ppm.

IR (KBr): 3021, 1520, 1486, 1371, 1200, 1106, 1011, 911, 796, 741 cm^{-1}.

HRMS (DART) m/z: ([M]) Calcd for $C_9H_5OF_6Br^+$ 321.94225; Found 321.94214.

Spectrum data of **3be** were matched with the product reported in the literature.[S10]

1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-4-*tert*-butylbenzene (3bh)



The title compound (**3bh**) was synthesized by the general procedure B using (4-*tert*-butylphenyl)(TMP)iodonium tosylate (**2h-OTs**, 119.7 mg, 0.20 mmol). Purification by column chromatography (SiO_2, hexane) afforded **3bh** in 82% yield (49.3 mg, 0.164 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.77 (sept, *J* = 5.7 Hz, 1H), 1.32 (s, 9H) ppm.

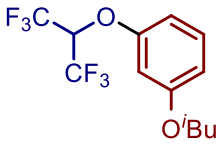
^{19}F NMR (376 MHz, $CDCl_3$): δ –76.0 (d. *J* = 4.5 Hz, 6F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.5, 147.6, 126.9, 121.2 (q, *J* = 283.3 Hz), 116.7, 76.7 (sept, *J* = 32.9 Hz), 34.4, 31.4 ppm.

IR (KBr): 2967, 1731, 1607, 1512, 1425, 1371, 1223, 1108, 907, 780, 765 cm^{-1}.

Spectrum data of **3bh** were matched with the product reported in the literature.[S10]

1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-3-isobutoxybenzene (3bk)



The title compound (**3bk**) was synthesized by the general procedure B using (3-isobutoxyphenyl)(TMP)iodonium tosylate (**2k-OTs**, 122.9 mg, 0.20 mmol). Purification by column chromatography (SiO_2, hexane) afforded **3bk** in 86% yield (54.7 mg, 0.173 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.6 Hz, 1H), 6.75–6.71 (m, 1H), 6.68–6.65 (m, 2H), 4.85 (sept, *J* = 5.8 Hz, 1H), 3.74 (d, *J* = 6.0 Hz, 2H), 2.11 (sept, *J* = 6.7 Hz, 1H), 1.06 (d, *J* =

6.8 Hz, 6H) ppm.

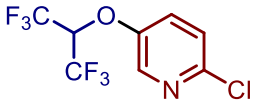
^{19}F NMR (376 MHz, $CDCl_3$): δ –75.9 (d. *J* = 4.9 Hz, 6F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.7, 158.6, 130.4, 121.1 (q, *J* = 279.1 Hz), 110.6, 108.4, 104.3, 76.0 (sept, *J* = 32.9 Hz), 74.6, 28.2, 19.2 ppm.

IR (KBr): 2964, 1605, 1492, 1370, 1230, 1197, 1106, 1035, 913, 744 cm^{-1}.

HRMS (DART) m/z: ([M+H]$^+$) Calcd for $C_{13}H_{15}O_2F_6^+$ 317.09708; Found 317.09588.

2-Chloro-5-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)pyridine (3bl)



The title compound (**3bl**) was synthesized by the general procedure B using (6-chloropyridin-3-yl)(TMP)iodonium tosylate (**2l-OTs**, 115.6 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that **3bl** was generated in 79% yield. Purification by column chromatography (SiO_2, AcOEt/hexane = 1:20) afforded **3bl** in 50% yield (27.7 mg, 0.099 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 3.2 Hz, 1H), 7.41 (dd, *J* = 8.8, 3.2 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 4.74 (sept, *J* = 5.5 Hz, 1H) ppm.

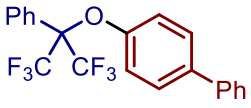
^{19}F NMR (376 MHz, $CDCl_3$): δ –75.8 (d, *J* = 4.9 Hz, 6F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.1, 147.0, 139.8, 128.0, 125.2, 120.7 (q, *J* = 282.9 Hz), 76.1 (sept, *J* = 33.6 Hz) ppm.

IR (KBr): 3018, 1578, 1460, 1369, 1298, 1232, 1107, 1018, 923, 831, 738, 690 cm^{-1}.

HRMS (DART) m/z: ([M+H]$^+$) Calcd for $C_8H_5NOF_6Cl^+$ 279.99584; Found 279.99484.

4-((1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-yl)oxy)-1,1'-biphenyl (3ca)



The title compound (**3ca**) was synthesized by the general procedure C using 1,1,1,3,3,3-hexafluoro-2-phenylpropan-2-ol (976.5 mg, 4.0 mmol). Purification by column chromatography (SiO_2, hexane) afforded **3ca** in 66% yield (129.9mg, 0.328 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.58-7.51 (m, 4H), 7.51 (t, *J* = 6.4 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H)6.93 (d, *J* = 8.8 Hz, 2H) ppm.

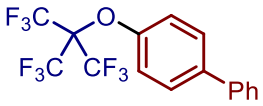
^{19}F NMR (376 MHz, $CDCl_3$): δ –70.4 (s, 6F) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.1, 140.1, 136.7, 130.5, 128.8, 128.6, 128.4–128.3 (m), 128.2, 127.2, 126.8, 126.6, 122.3 (q, *J* = 288.1 Hz), 119.8, 84.2 (sept, *J* = 28.8 Hz) ppm.

IR (KBr): 3020, 1605, 1516, 1477, 1423, 1220, 1112, 1030, 909, 768, 672 cm^{-1}.

HRMS (DART) m/z: ([M]) Calcd for $C_{21}H_{14}OF_6$ 396.09434; Found 396.09455.

4-((1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)-1,1'-biphenyl (3da)



The title compound (**3da**) was synthesized by the general procedure C using 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-ol (944.1 mg, 4.0 mmol). Purification by column chromatography (SiO_2, hexane) afforded **3da** in 38% yield (72.9 mg, 0.188 mmol) as a colorless solid.

Melting Point: 75.1–77.1 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H) ppm.

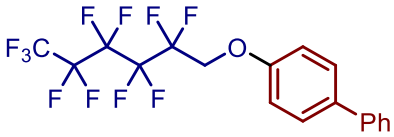
^{19}F NMR (376 MHz, $CDCl_3$): δ –69.3 (s, 9F) ppm.

^{13}C{^{1}H, ^{19}F} NMR (125 MHz, $CDCl_3$): δ 152.2, 139.8, 139.7, 128.9, 128.1, 127.7, 127.1, 123.0, 120.0, 81.3 ppm.

IR (KBr): 3022, 2925, 1731, 1604, 1516, 1486, 1297, 1221, 1110, 1001, 971, 849, 768 cm^{-1}.

Spectrum data of **3da** were matched with the product reported in the literature.[S11]

4-((2,2,3,3,4,4,5,5,6,6,6-Undecafluorohexyl)oxy)-1,1'-biphenyl (3ea)



The title compound (**3ea**) was synthesized by the general procedure C using 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-ol (1.20 g, 4.0 mmol). Purification by column chromatography (SiO_2, hexane) afforded **3ea** in 84% yield (189.8 mg, 0.420 mmol) as a colorless solid.

Melting Point: 90.4–92.4 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 4H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 4.54 (t, *J* = 12.8

Hz, 2H) ppm.

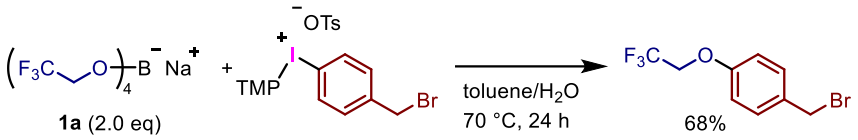
^{19}F NMR (376 MHz, $CDCl_3$): δ –83.1 (t, *J* = 9.8 Hz, 3F), –121.7– –121.9 (m, 2F), –125.1– –125.3 (m, 2F), –125.6– –125.7 (m, 2F), –128.4– –128.6 (m, 2F) ppm.

^{13}C{^{1}H, ^{19}F} NMR (125 MHz, $CDCl_3$): δ 156.9, 140.3, 135.8, 128.8, 128.4, 127.1, 126.8, 117.2, 115.2, 114.9, 111.0, 110.4, 108.5, 65.4 ppm.

IR (KBr): 3024, 1731, 1602, 1520, 1422, 1221, 1111, 1019, 929, 733, 673 cm^{-1}.

HRMS (DART) m/z: ($[M+H]^+$) Calcd for $C_{18}H_{12}OF_{11}^+$ 453.07070; Found 453.07030.

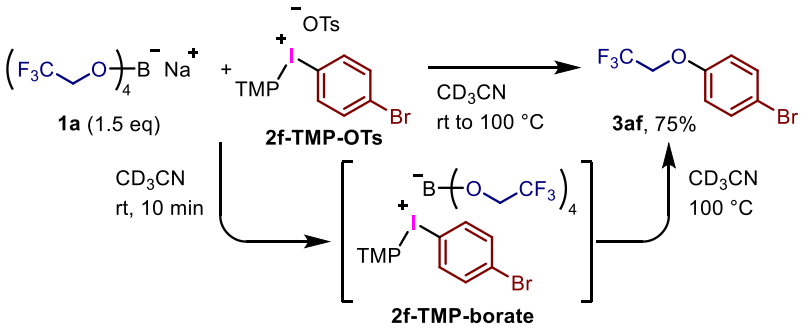
5. Trifluoroethoxylation of (4-bromomethylphenyl)(TMP)iodonium tosylate



Scheme S1. Reaction of **1a** with (4-bromomethylphenyl)(TMP)iodonium tosylate

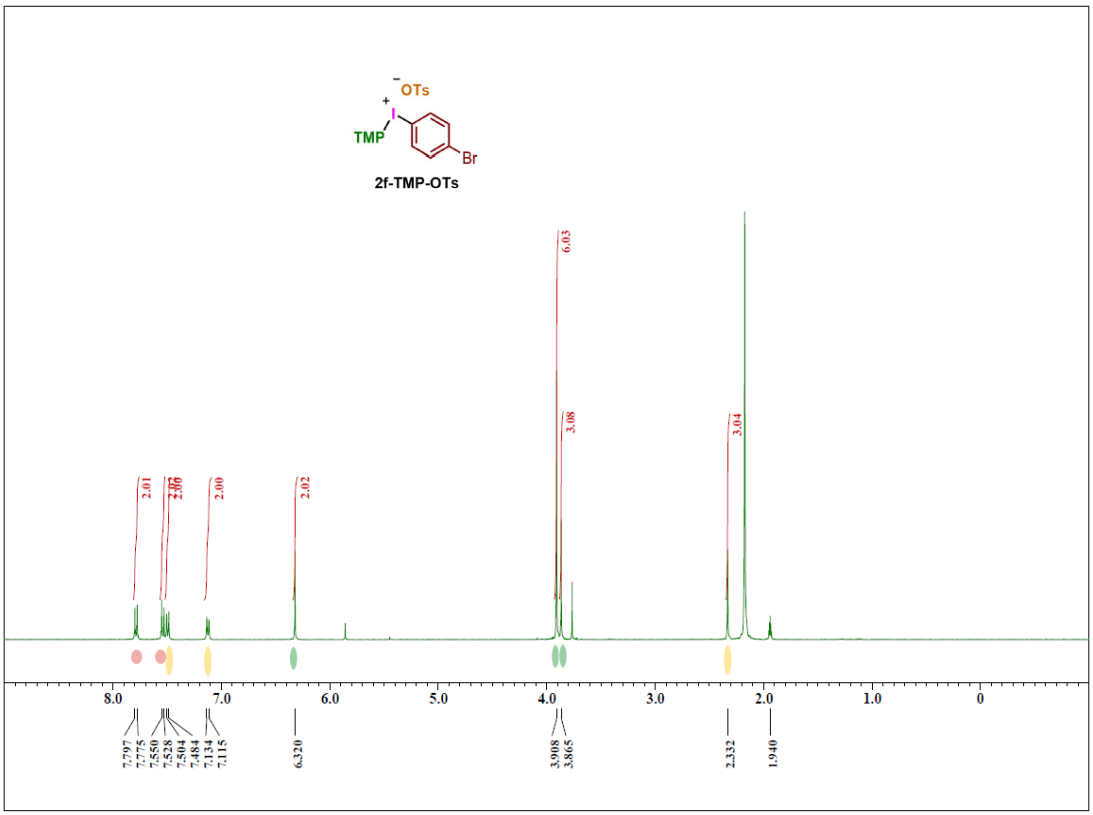
The reaction was carried out according to the general procedure A using (4-bromomethylphenyl)(TMP)iodonium tosylate (127.1 mg, 0.20 mmol). ^{19}F NMR analysis of crude mixture indicated that 4-(2,2,2-trifluoroethoxy)benzyl bromide was generated in 68% yield. In this reaction, SN2 reaction with the bromine atom did not proceed.

6. NMR monitoring of trifluroethoxylation of 2f-OTs-TMP (Fig. 5c)



A well-dried NMR tube with a J. Young valve was charged with sodium tetrakis(2,2,2-trifluoroethoxy)borate (**1a**, 12.8 mg, 0.030 mmol), (4-bromophenyl)(TMP)iodonium tosylate (**2f-TMP-OTs**, 12.8 mg, 0.020 mmol), and CD_3CN (0.75 mL). After stored at room temperature for 10 minutes, the reaction mixture was analyzed by ^{1}H NMR spectroscopy. The disappearance of the peak corresponding tosyl group was confirmed, which indicates the consumption of **2f-TMP-OTs** and the generation of **2f-TMP-borate** via ligand exchange (Fig. S1a vs b). The reaction mixture was stored at 100 °C using an oil bath. ^{1}H and ^{19}F NMR analysis of the reaction mixture indicated the generation of **3af** in 75%.

a)



b)

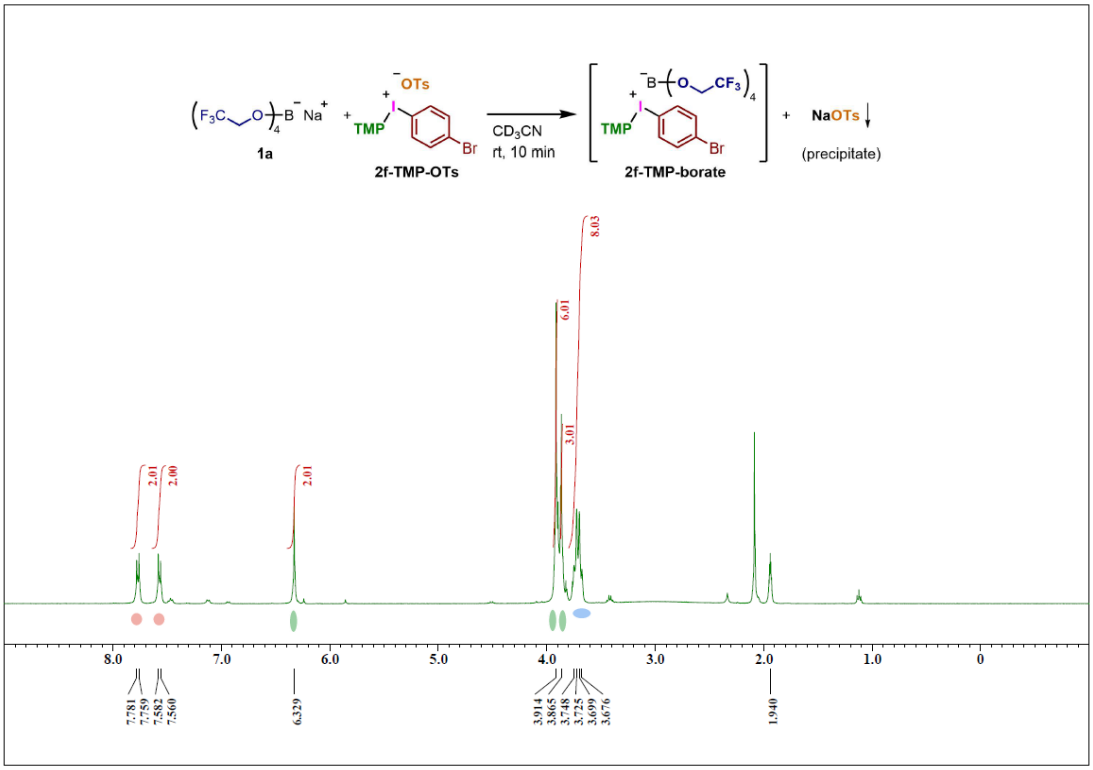


Fig. S1. a) ^{1}H NMR spectrum of **2f-TMP-OTs** in CD_3CN.

b) ^{1}H NMR spectrum of in situ generated **2f-TMP-borate** in CD_3CN.

7. References

S1. B. Pethő, M. Zwillinger, J. T. Csenki, A. E. Káncz, B. Krámos, J. Müller, G. T. Balogh and Z. Novák, *Chem. Eur. J*., 2017, **23**, 15628.

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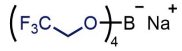
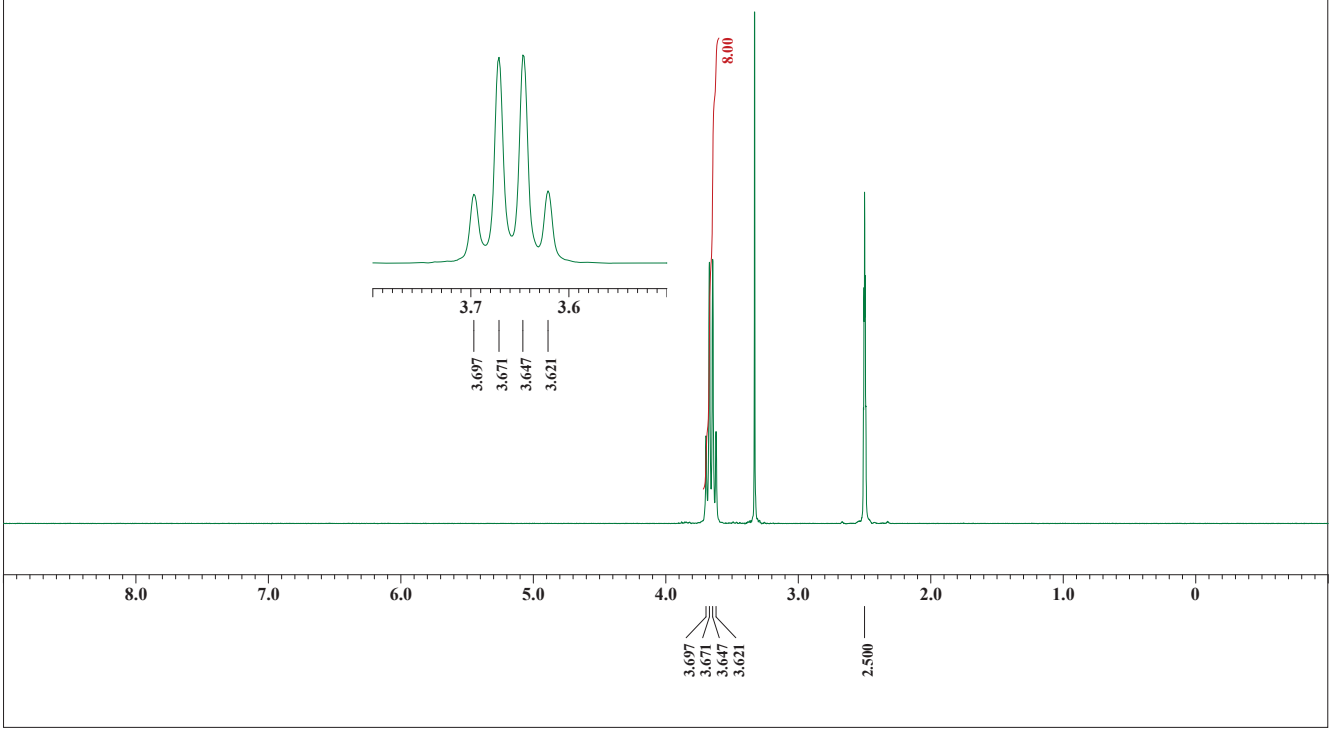
8. NMR spectra

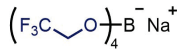
Sodium tetrakis(2,2,2-trifluoroethoxy)borate (1a)



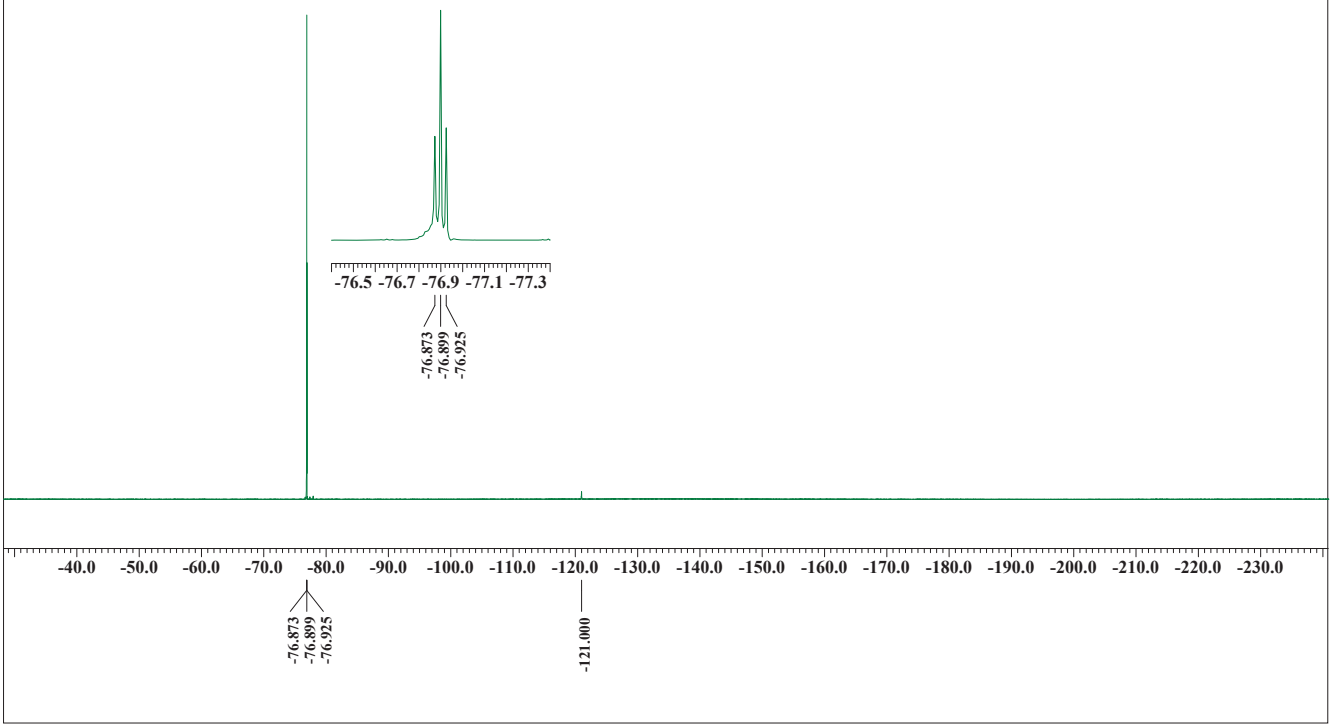
^{1}H NMR (400 MHz, $CDCl_3$)



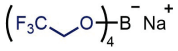
Sodium tetrakis(2,2,2-trifluoroethoxy)borate (1a)



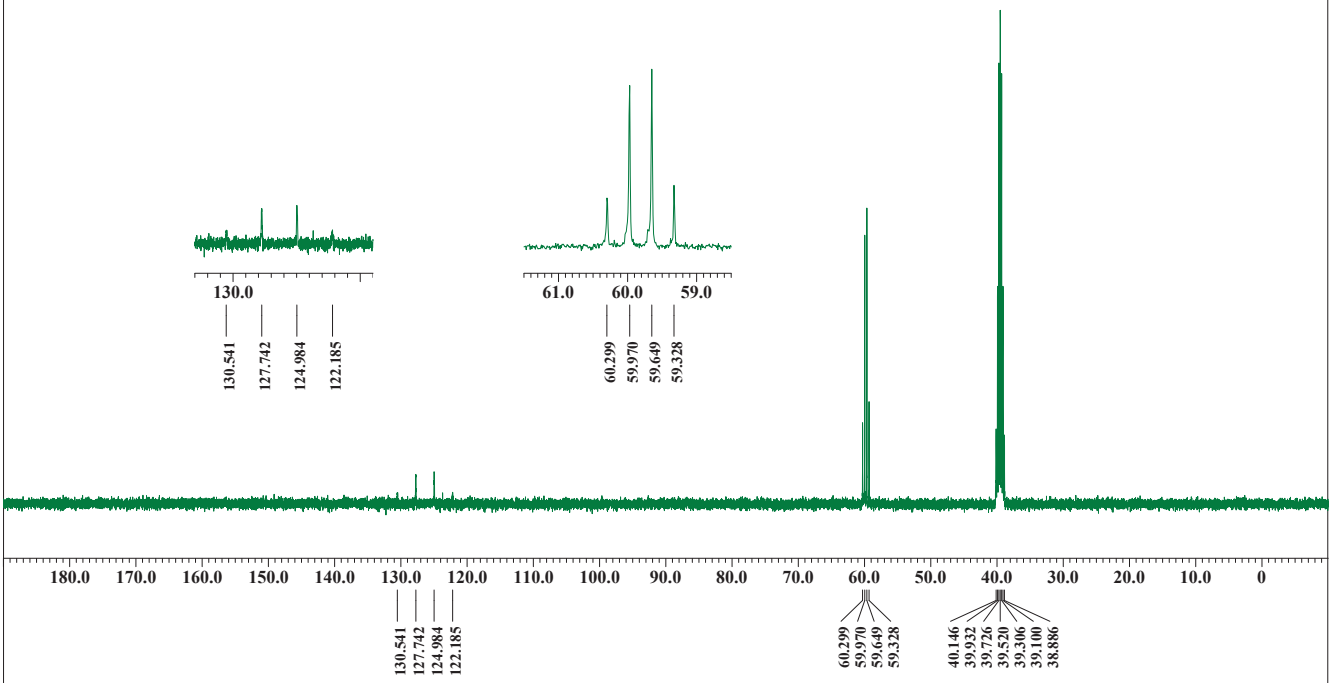
^{19}F NMR (376 MHz, $CDCl_3$)



Sodium tetrakis(2,2,2-trifluoroethoxy)borate (1a)

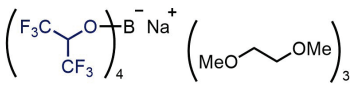


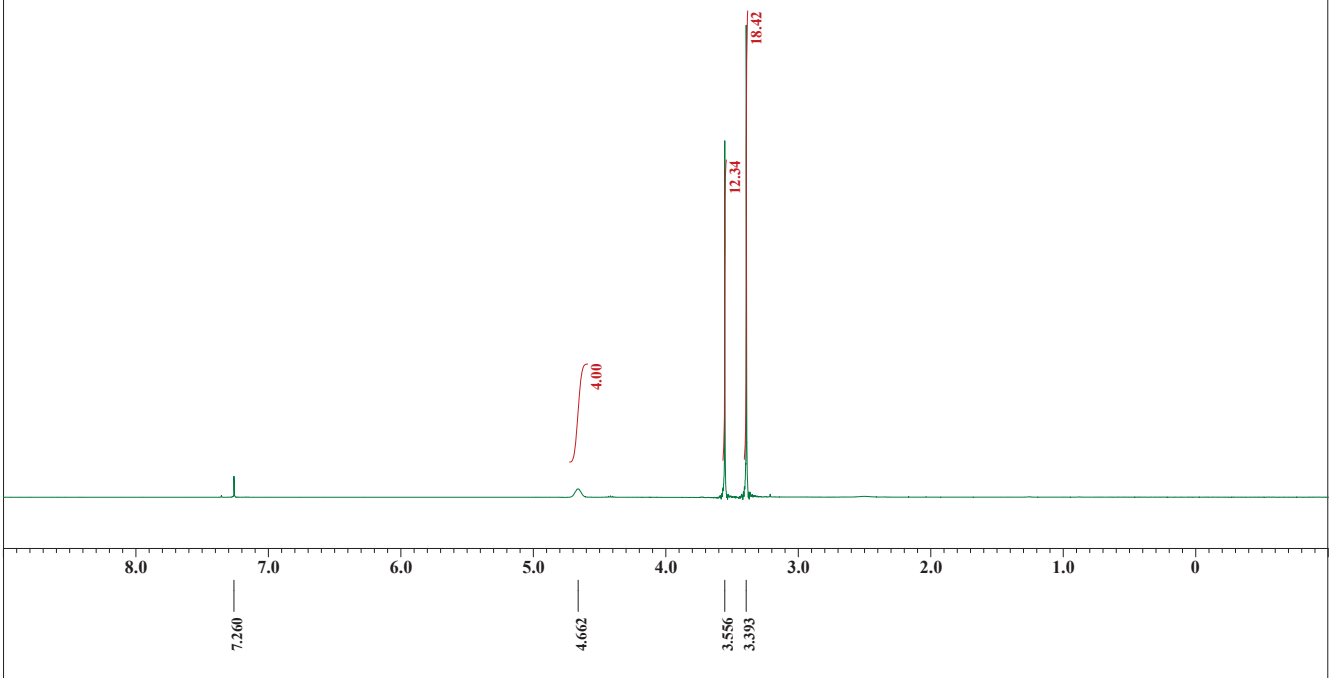
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



Sodium tetrakis(1,1,1,3,3,3,-hexafluoroisopropoxy)borate DME complex (1b•$(DME)_3$)

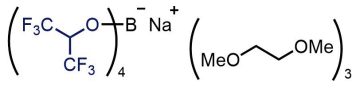
^{1}H NMR (400 MHz, $CDCl_3$)

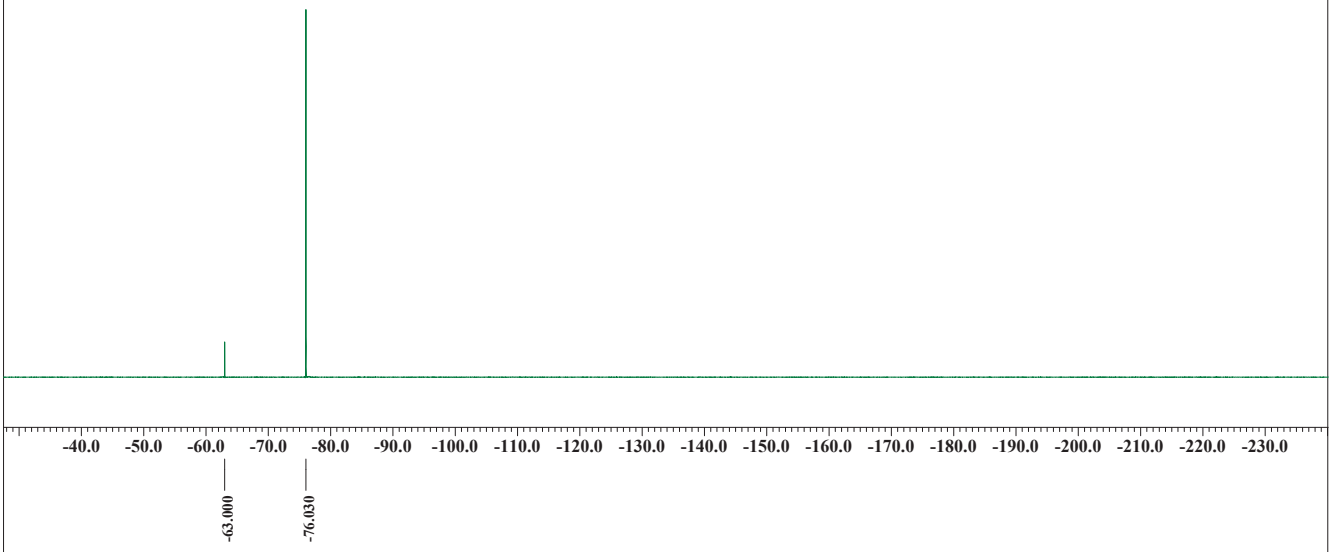




Sodium tetrakis(1,1,1,3,3,3,-hexafluoroisopropoxy)borate DME complex (1b•$(DME)_3$)

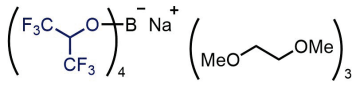
^{19}F NMR (376 MHz, $CDCl_3$)

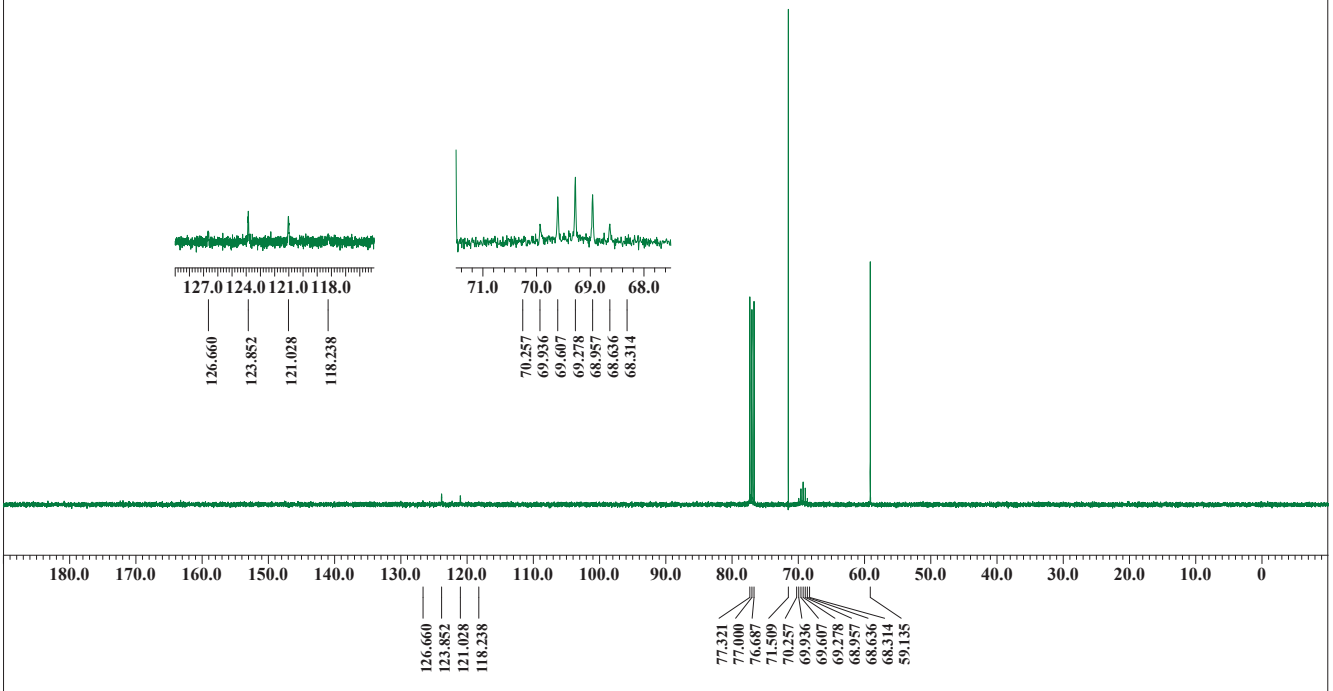




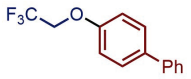
Sodium tetrakis(1,1,1,3,3,3,-hexafluoroisopropoxy)borate DME complex (1b•$(DME)_3$)

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)

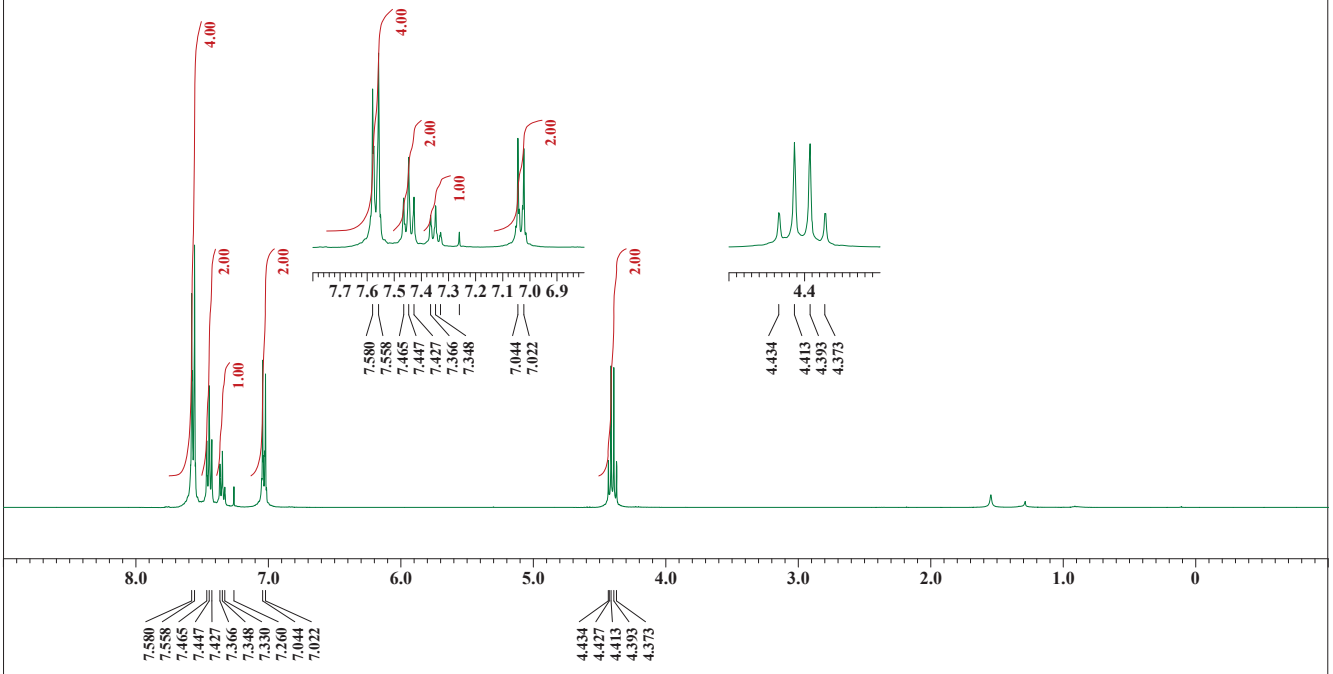




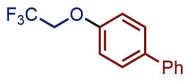
4-(2,2,2-Trifluoroethoxy)-1,1'-biphenyl (3aa)



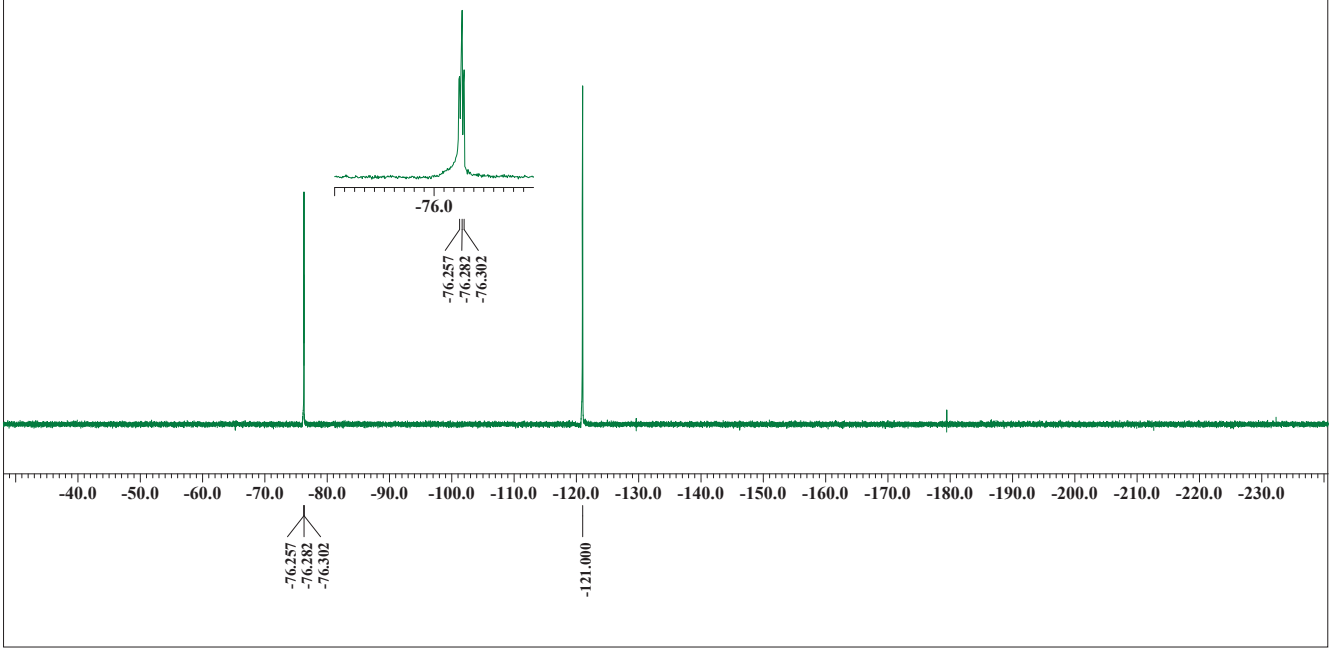
^{1}H NMR (400 MHz, $CDCl_3$)



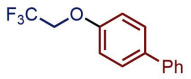
4-(2,2,2-Trifluoroethoxy)-1,1'-biphenyl (3aa)



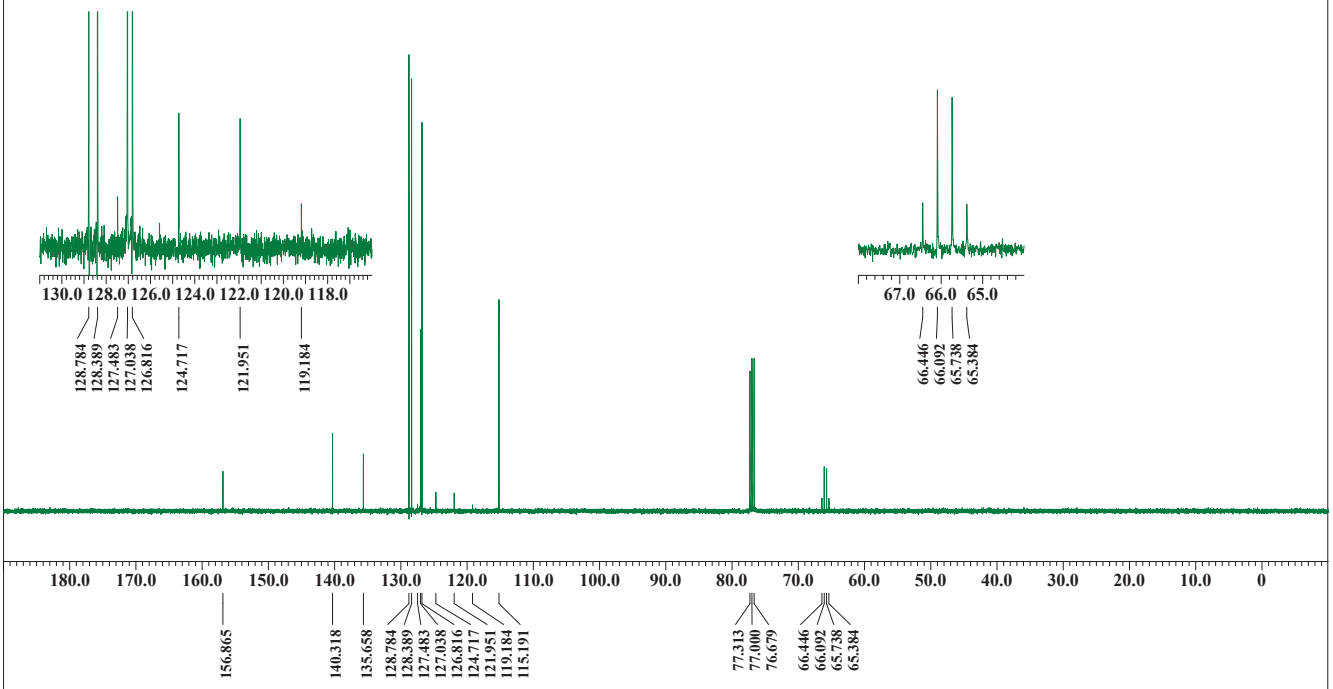
^{19}F NMR (376 MHz, $CDCl_3$)



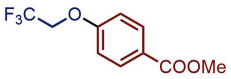
4-(2,2,2-Trifluoroethoxy)-1,1'-biphenyl (3aa)



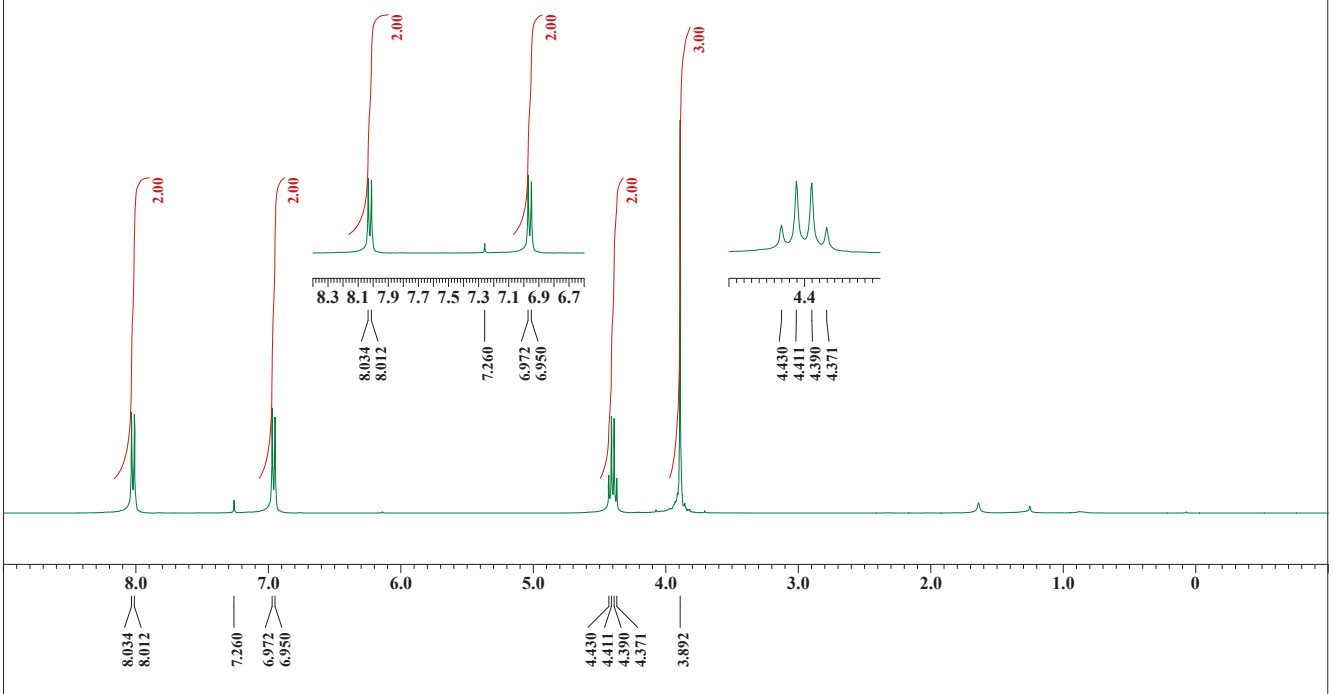
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



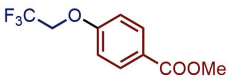
Methyl 4-(2,2,2-trifluoroethoxy)benzoate (3ab)



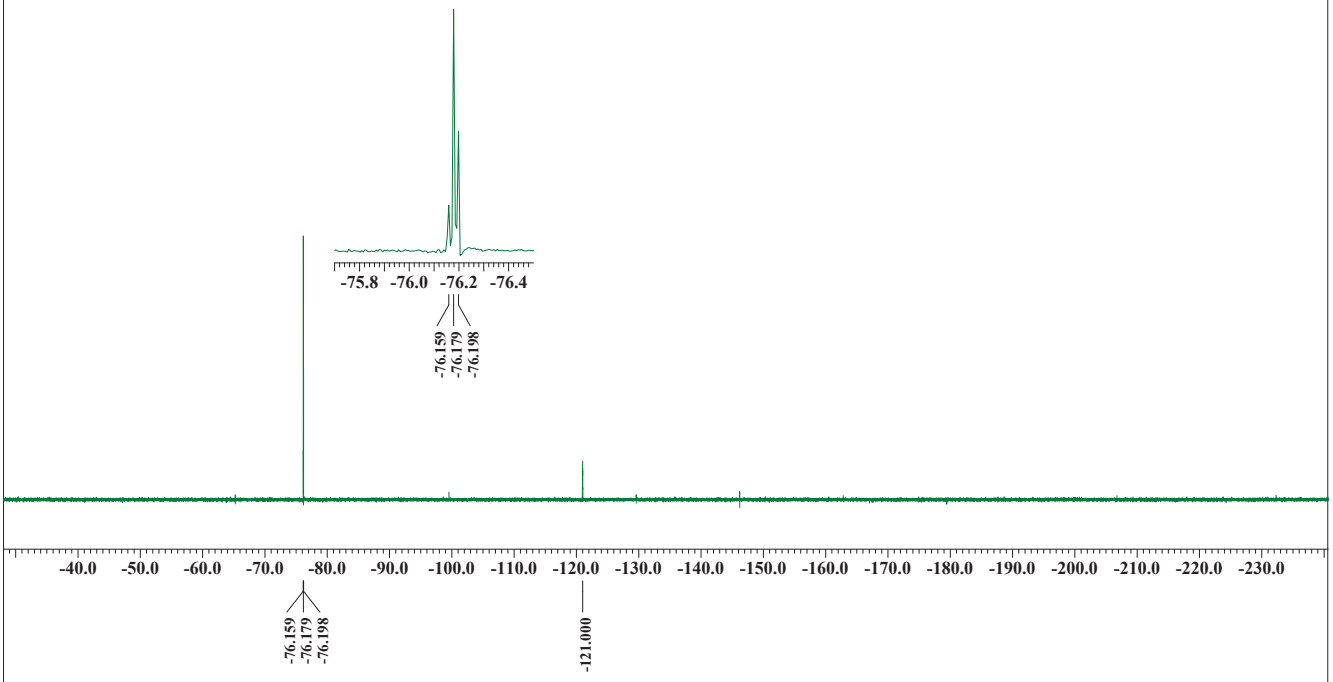
^{1}H NMR (400 MHz, $CDCl_3$)



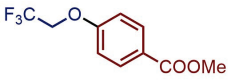
Methyl 4-(2,2,2-trifluoroethoxy)benzoate (3ab)



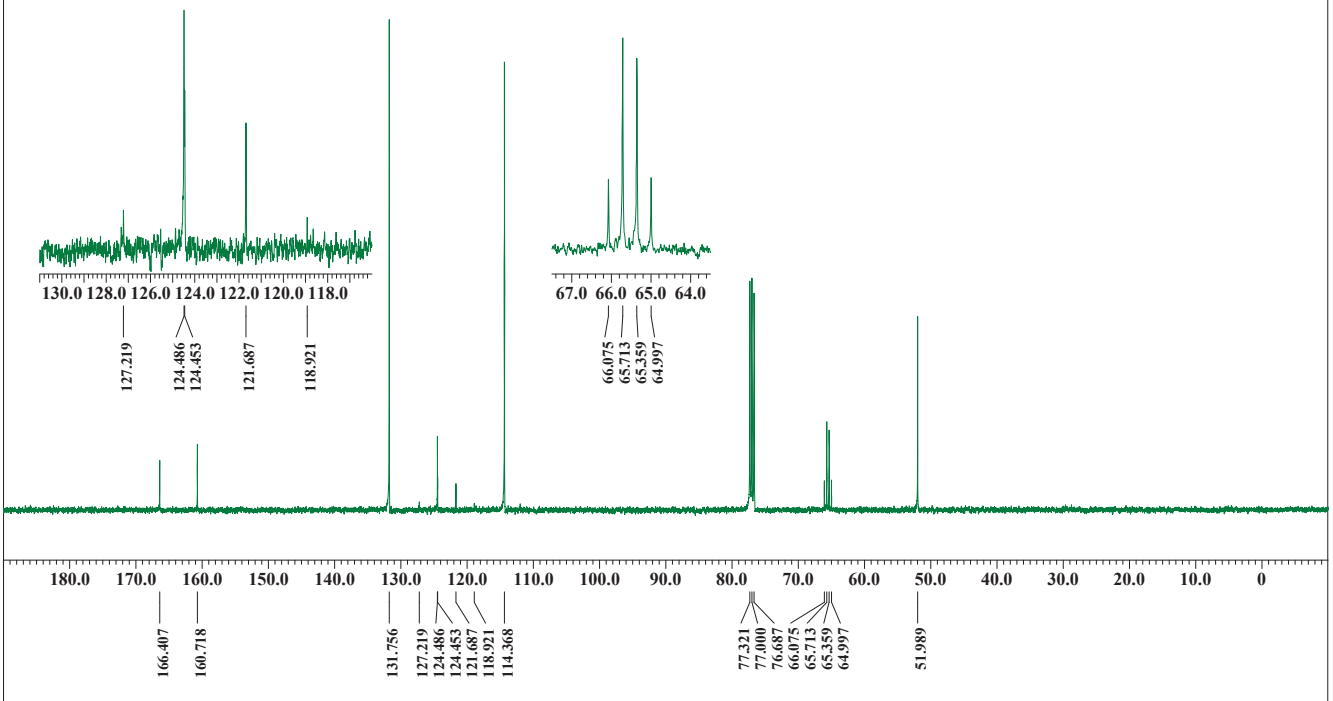
^{19}F NMR (376 MHz, $CDCl_3$)



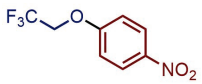
Methyl 4-(2,2,2-trifluoroethoxy)benzoate (3ab)



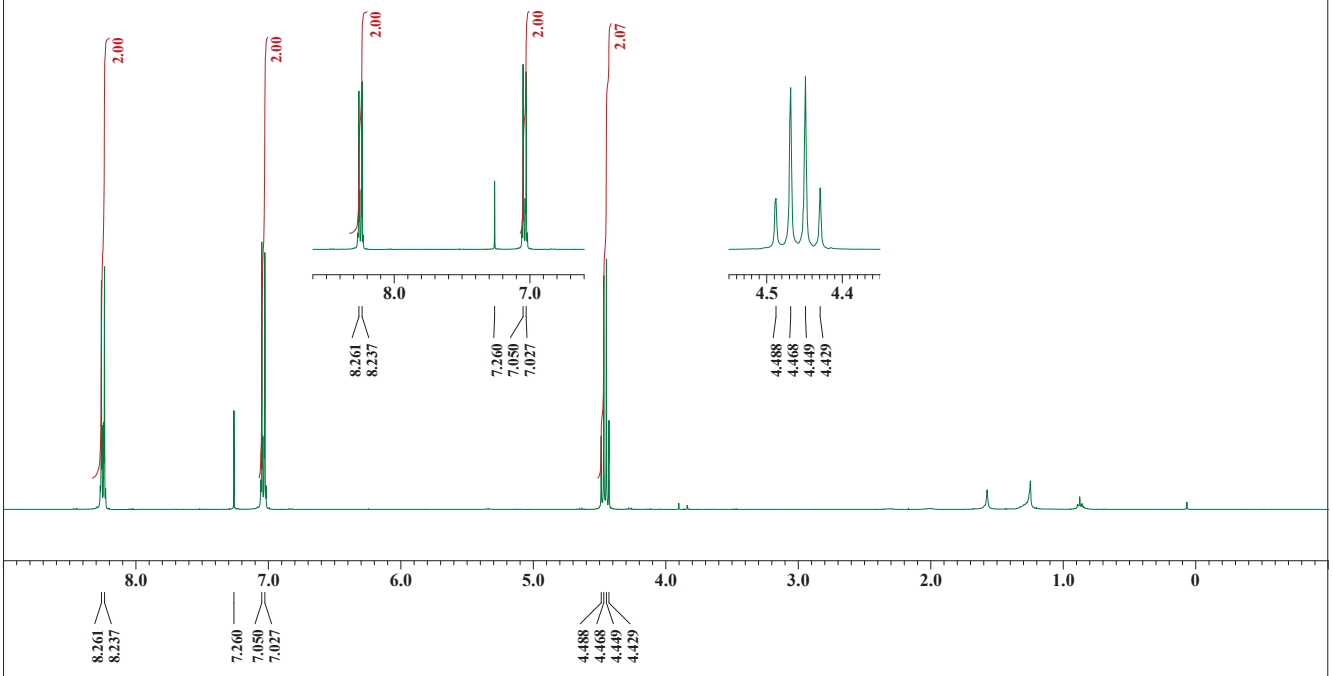
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



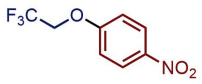
1-Nitro-4-(2,2,2-trifluoroethoxy)benzene (3ac)



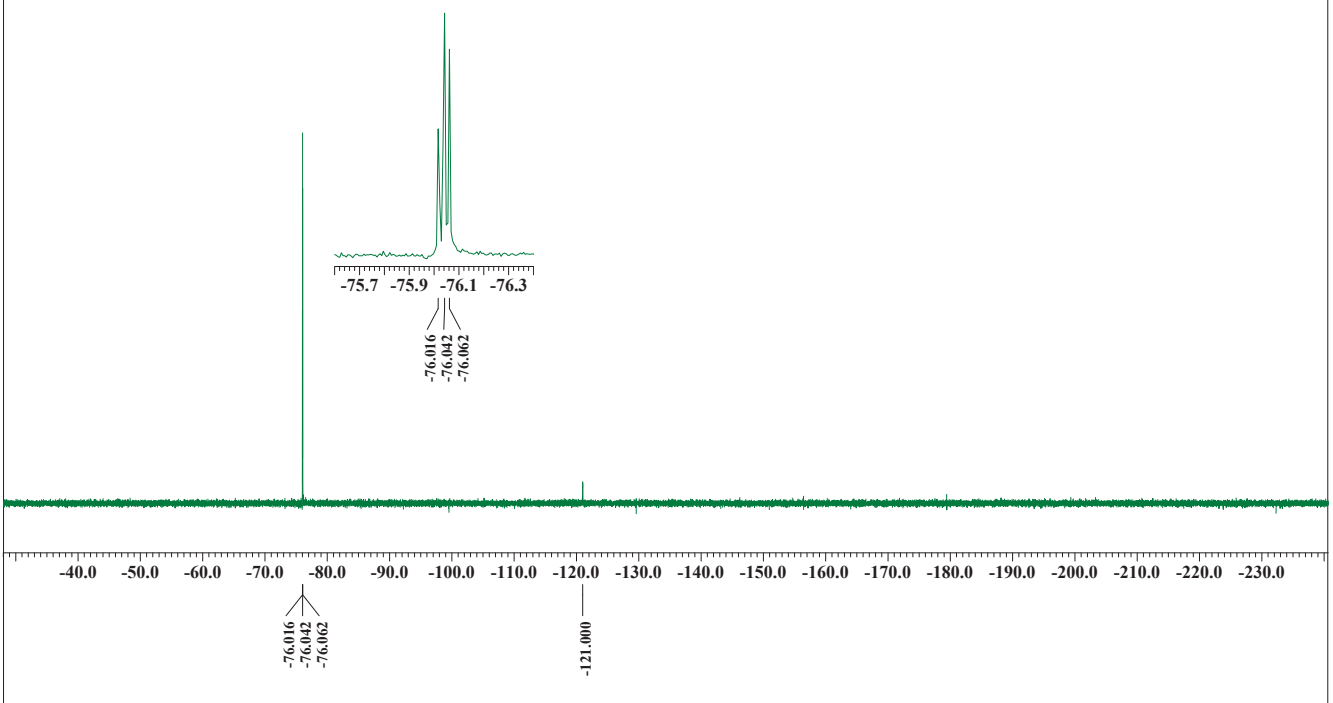
^{1}H NMR (400 MHz, $CDCl_3$)



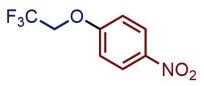
1-Nitro-4-(2,2,2-trifluoroethoxy)benzene (3ac)



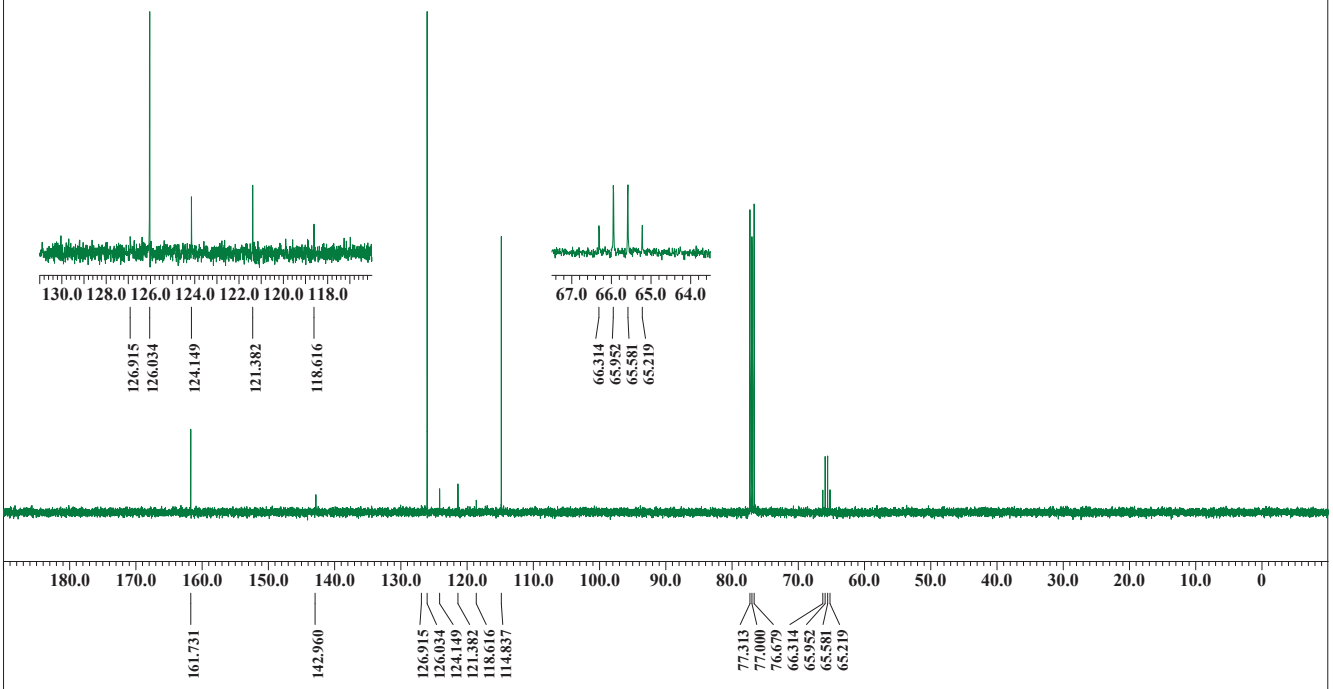
^{19}F NMR (376 MHz, $CDCl_3$)



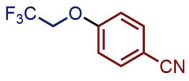
1-Nitro-4-(2,2,2-trifluoroethoxy)benzene (3ac)



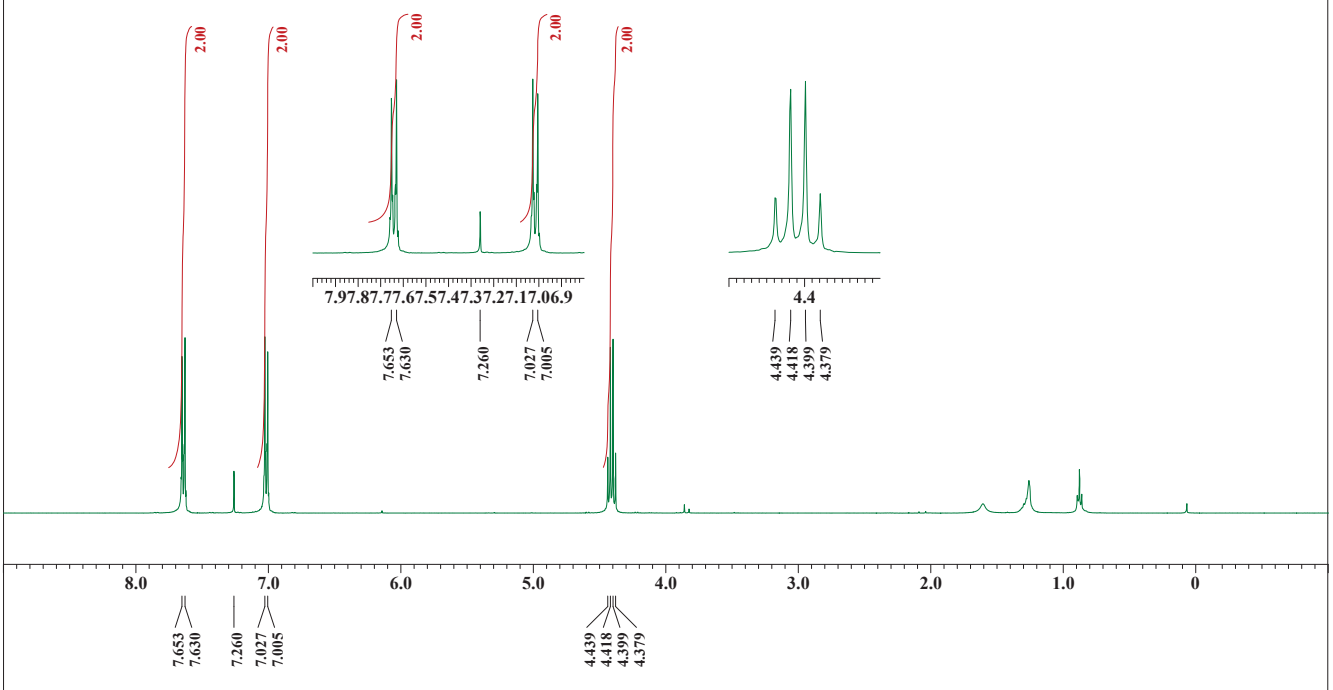
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



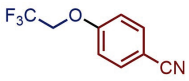
4-(2,2,2-Trifluoroethoxy)benzonitrile (3ad)



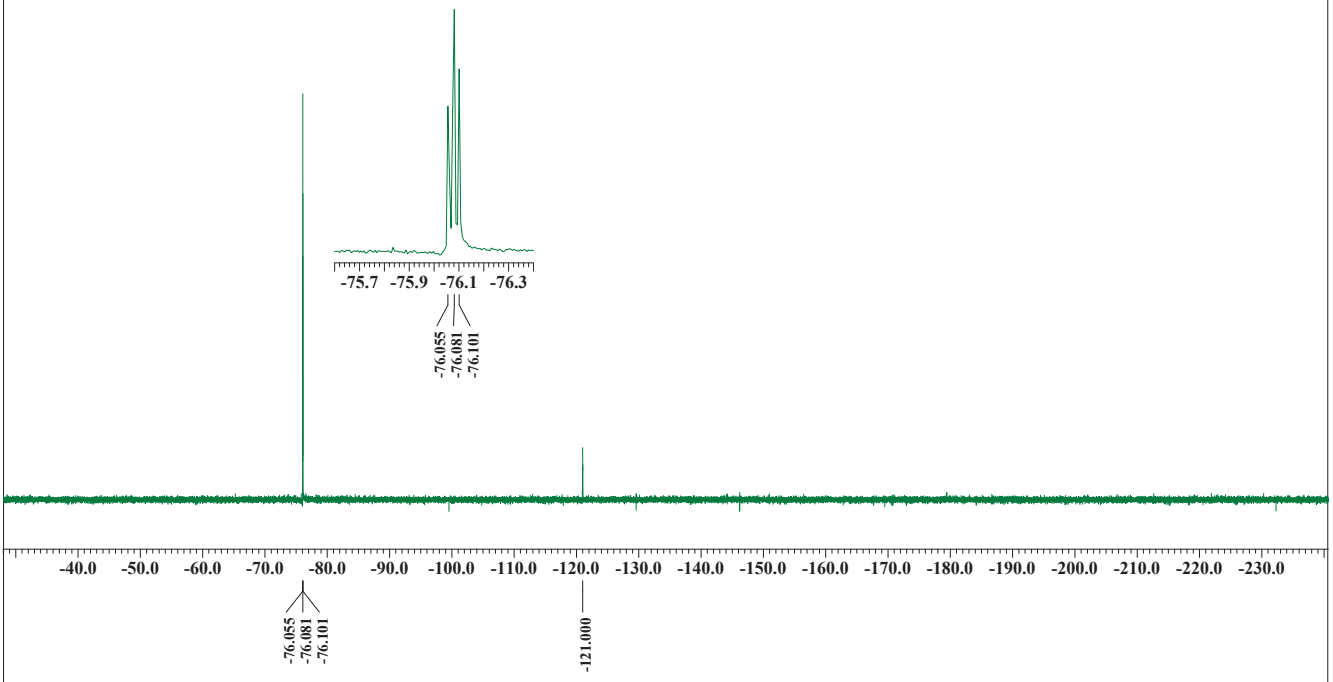
^{1}H NMR (400 MHz, $CDCl_3$)



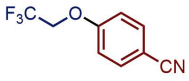
4-(2,2,2-Trifluoroethoxy)benzonitrile (3ad)



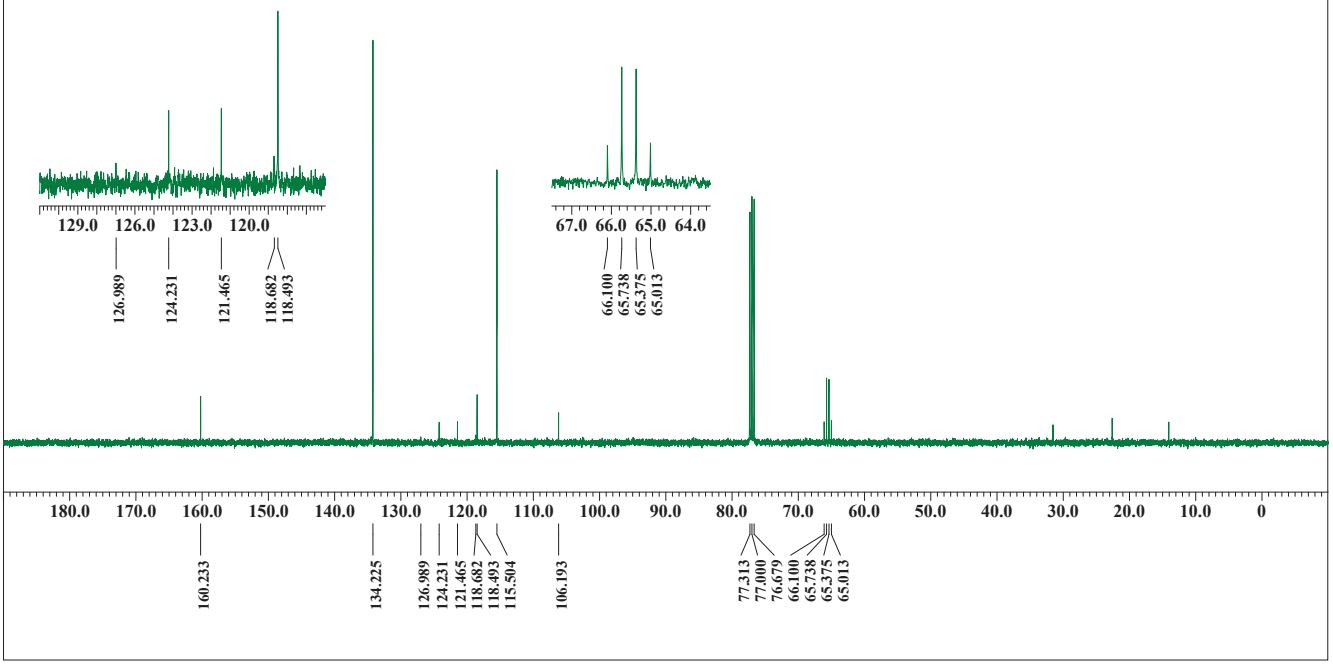
^{19}F NMR (376 MHz, $CDCl_3$)



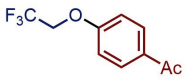
4-(2,2,2-Trifluoroethoxy)benzonitrile (3ad)



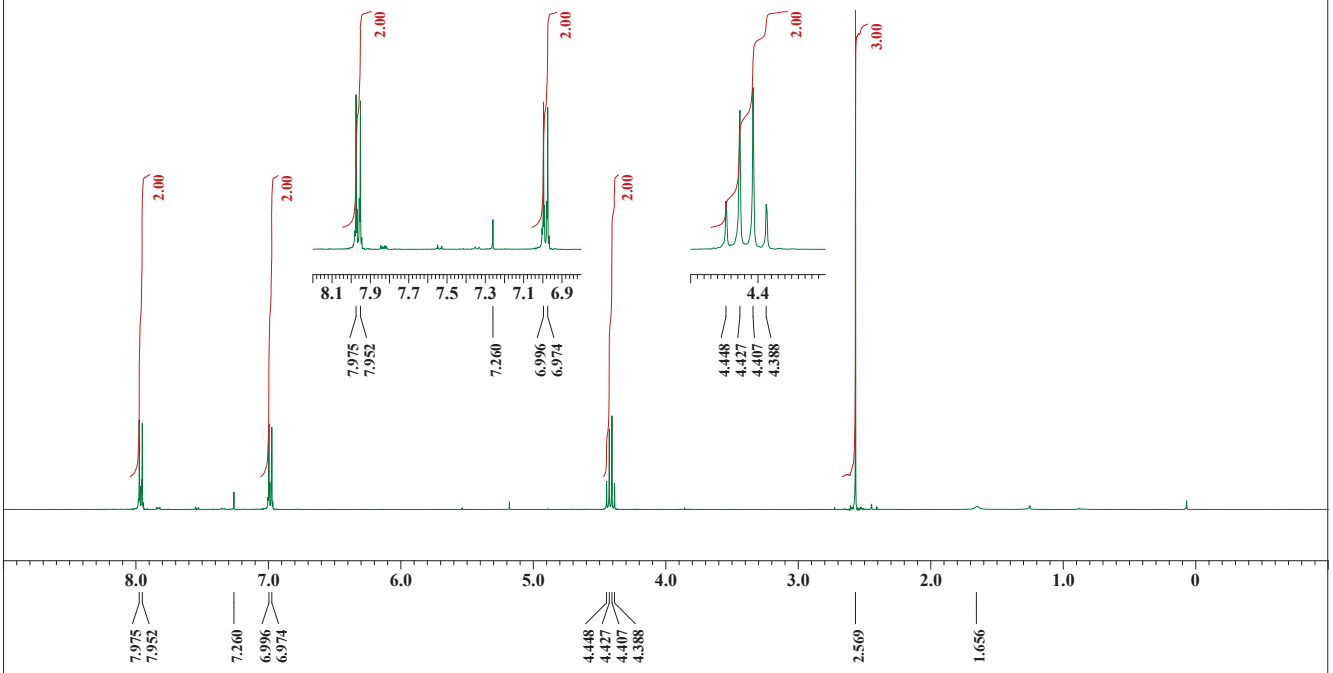
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



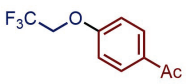
1-Acetyl-4-(2,2,2-trifluoroethoxy)benzene (3ae)



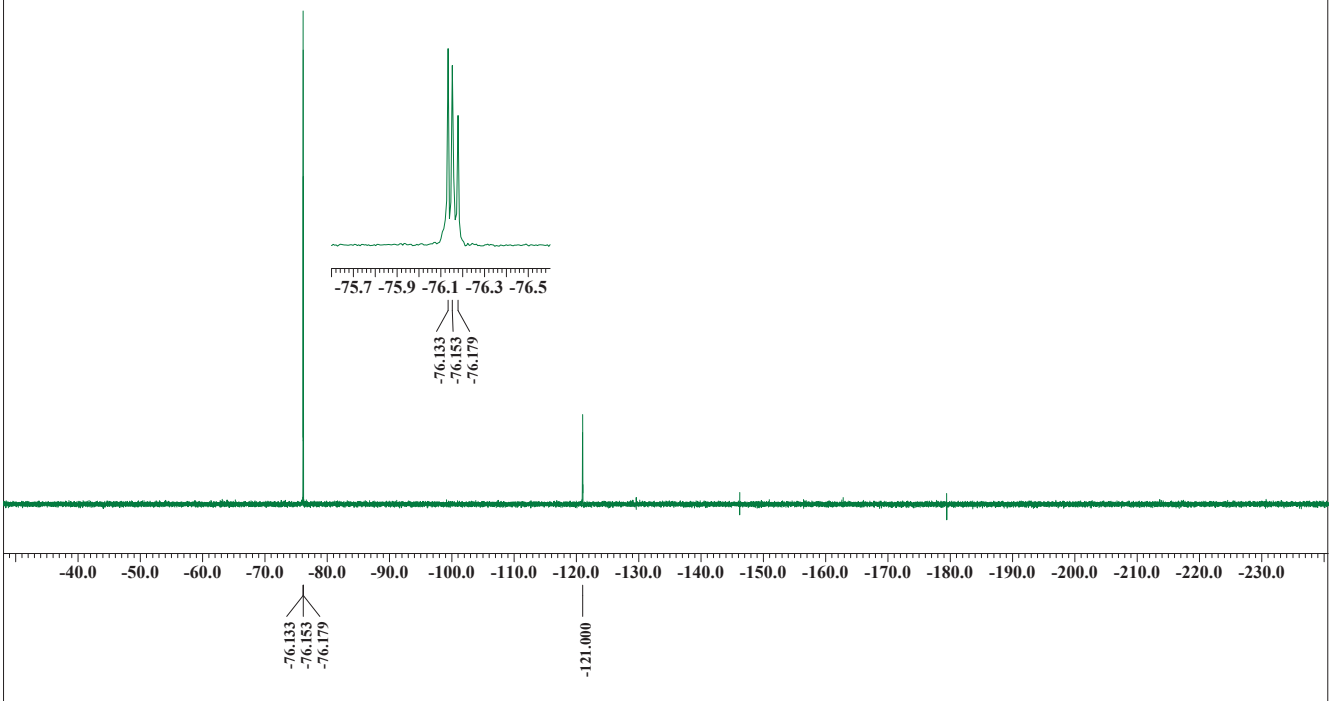
^{1}H NMR (400 MHz, $CDCl_3$)



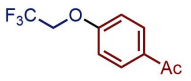
1-Acetyl-4-(2,2,2-trifluoroethoxy)benzene (3ae)



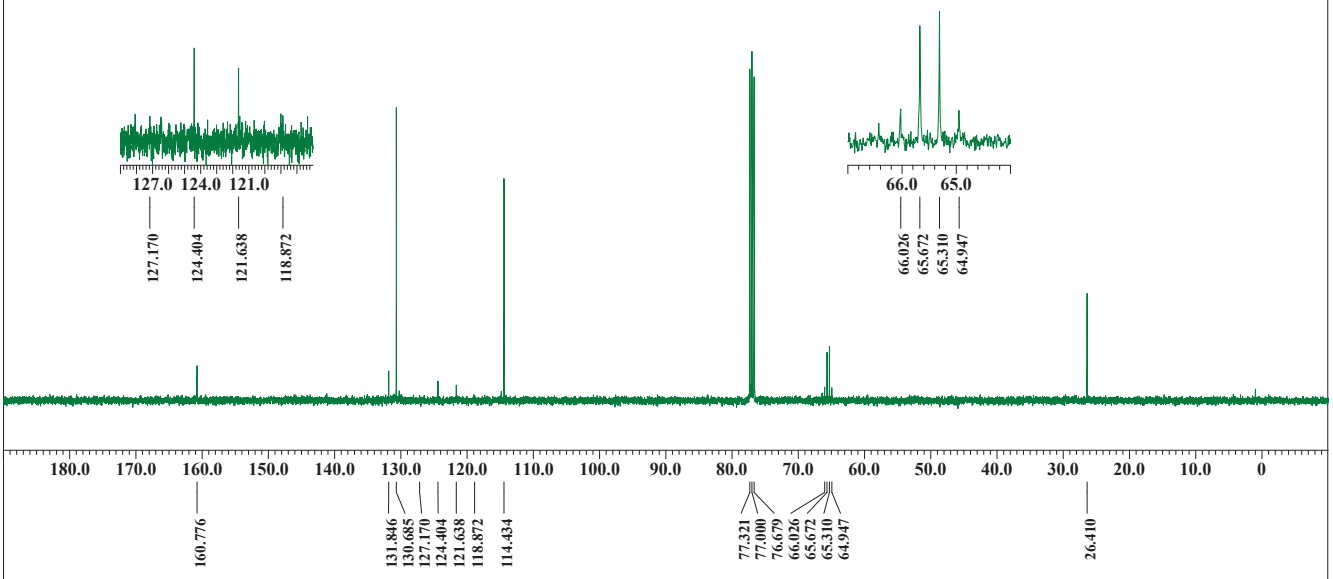
^{19}F NMR (376 MHz, $CDCl_3$)



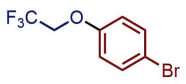
1-Acetyl-4-(2,2,2-trifluoroethoxy)benzene (3ae)



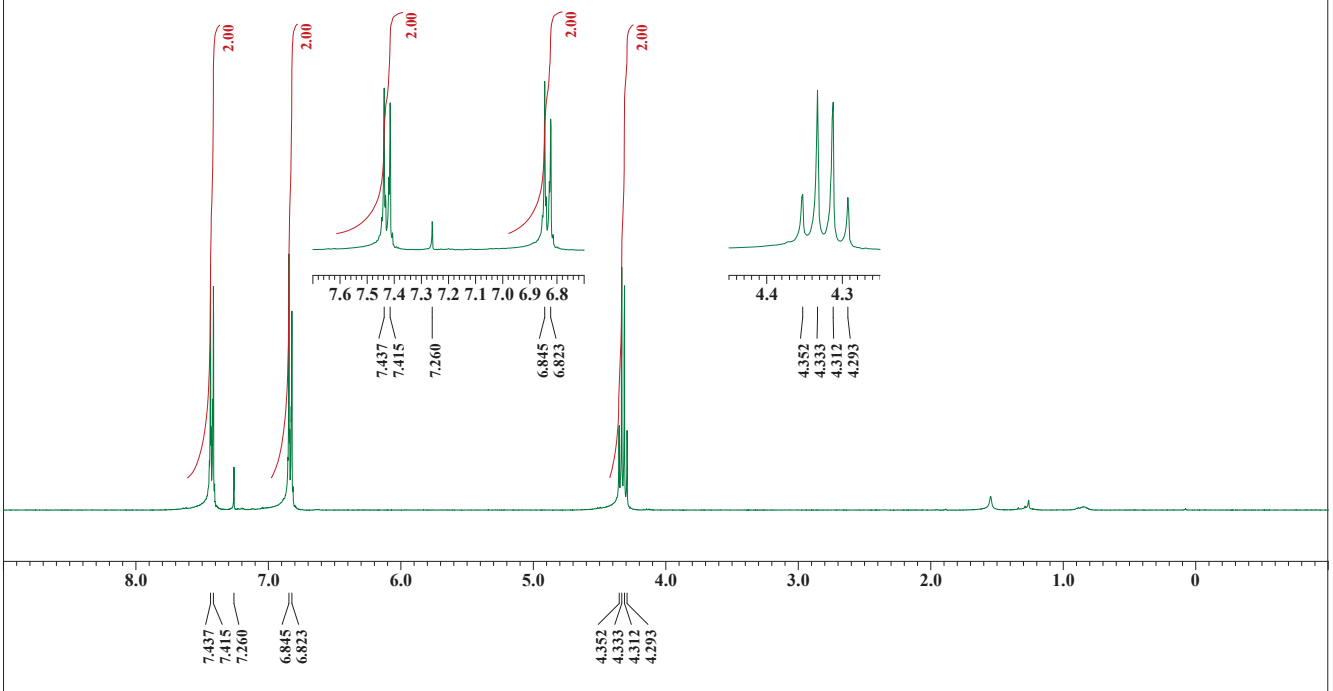
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



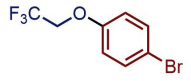
1-Bromo-4-(2,2,2-trifluoroethoxy)benzene (3af)



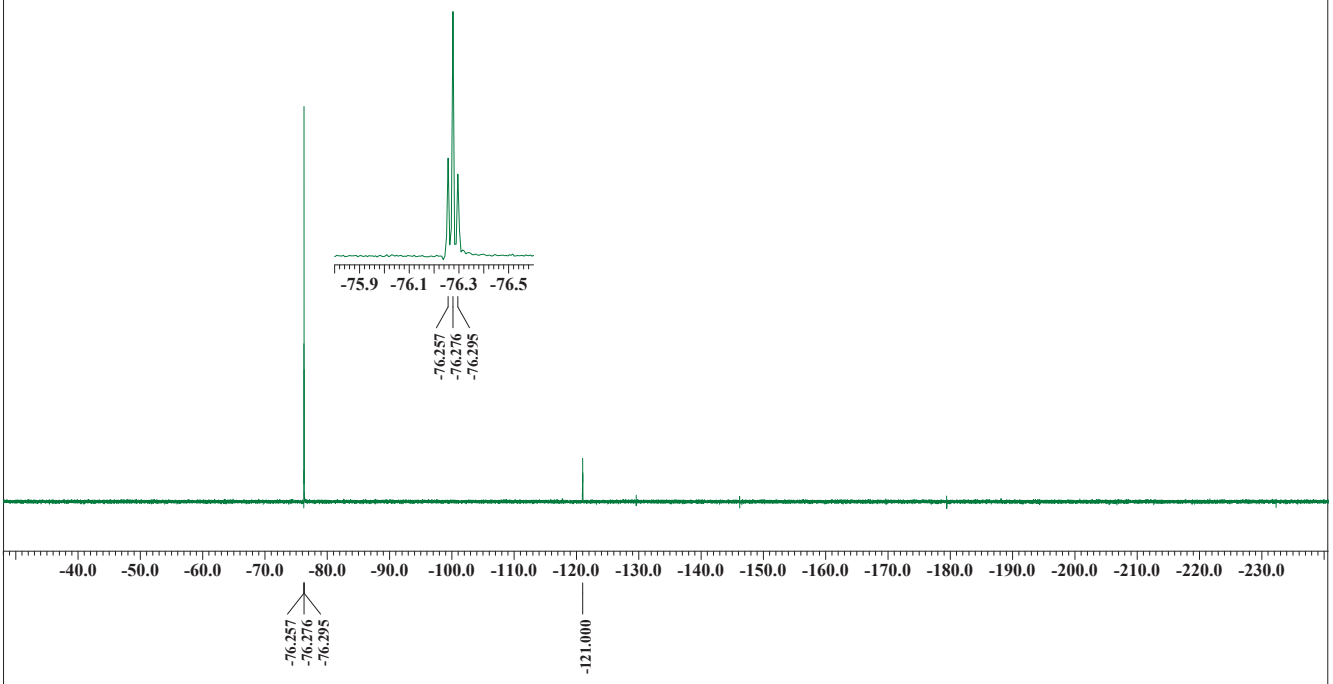
^{1}H NMR (400 MHz, $CDCl_3$)



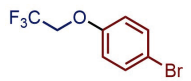
1-Bromo-4-(2,2,2-trifluoroethoxy)benzene (3af)



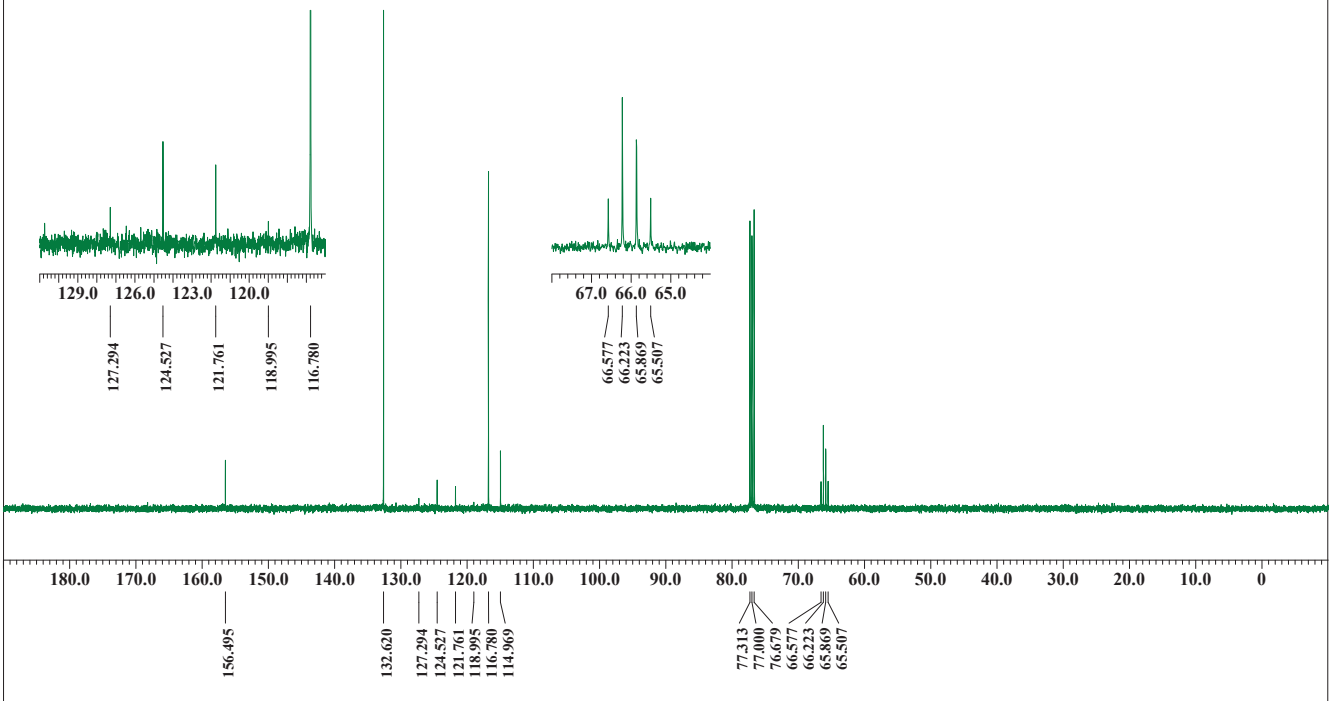
^{19}F NMR (376 MHz, $CDCl_3$)



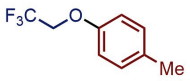
1-Bromo-4-(2,2,2-trifluoroethoxy)benzene (3af)



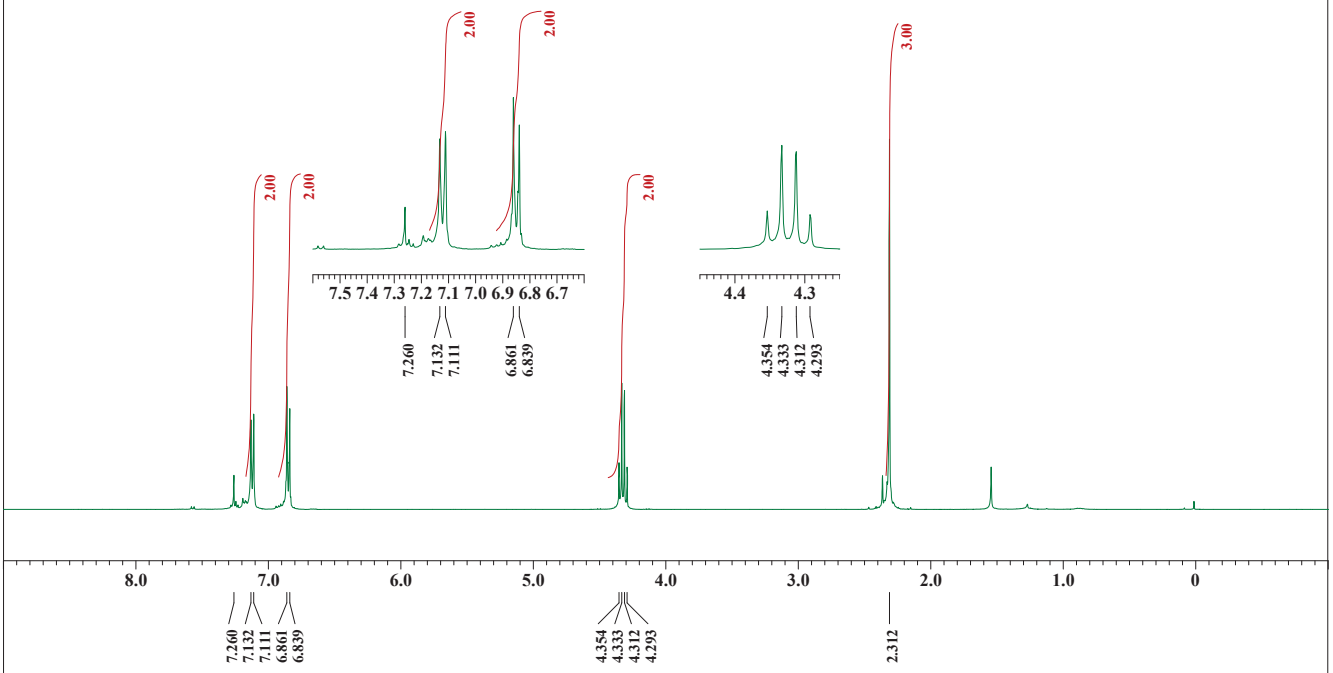
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



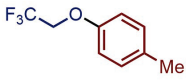
1-Methyl-4-(2,2,2-trifluoroethoxy)benzene (3ag)



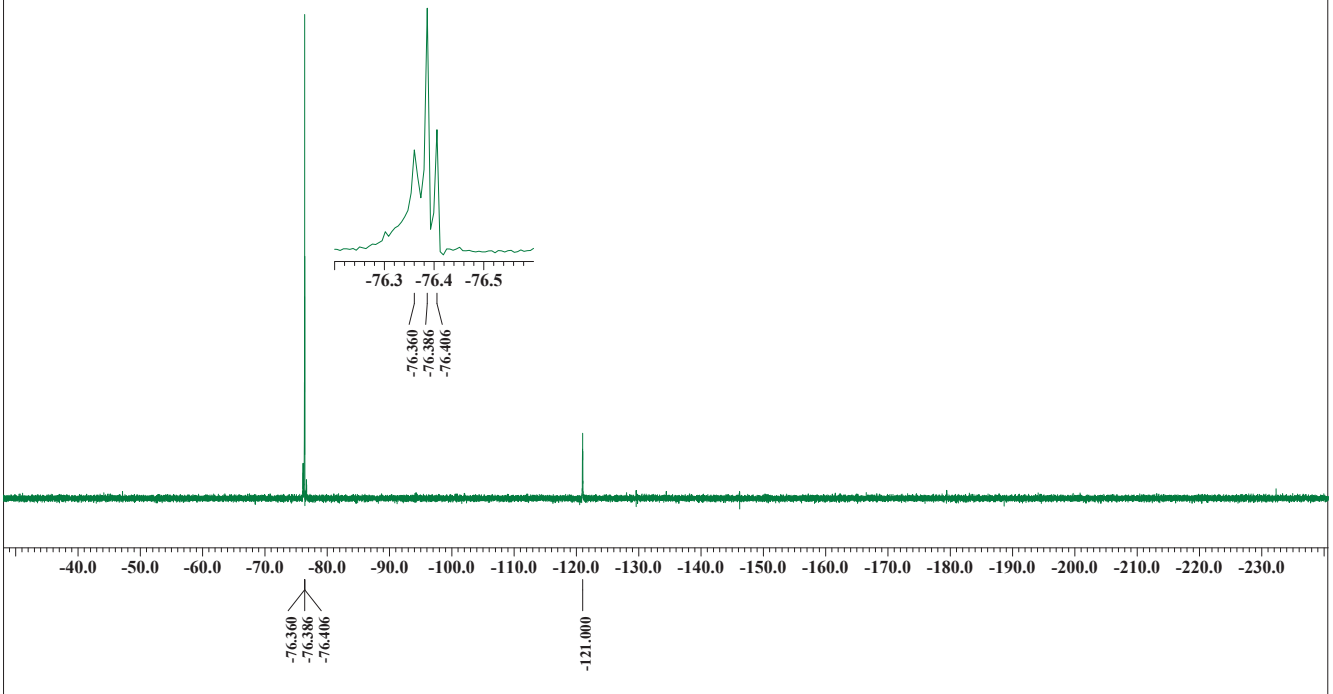
^{1}H NMR (400 MHz, $CDCl_3$)



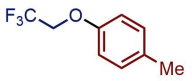
1-Methyl-4-(2,2,2-trifluoroethoxy)benzene (3ag)



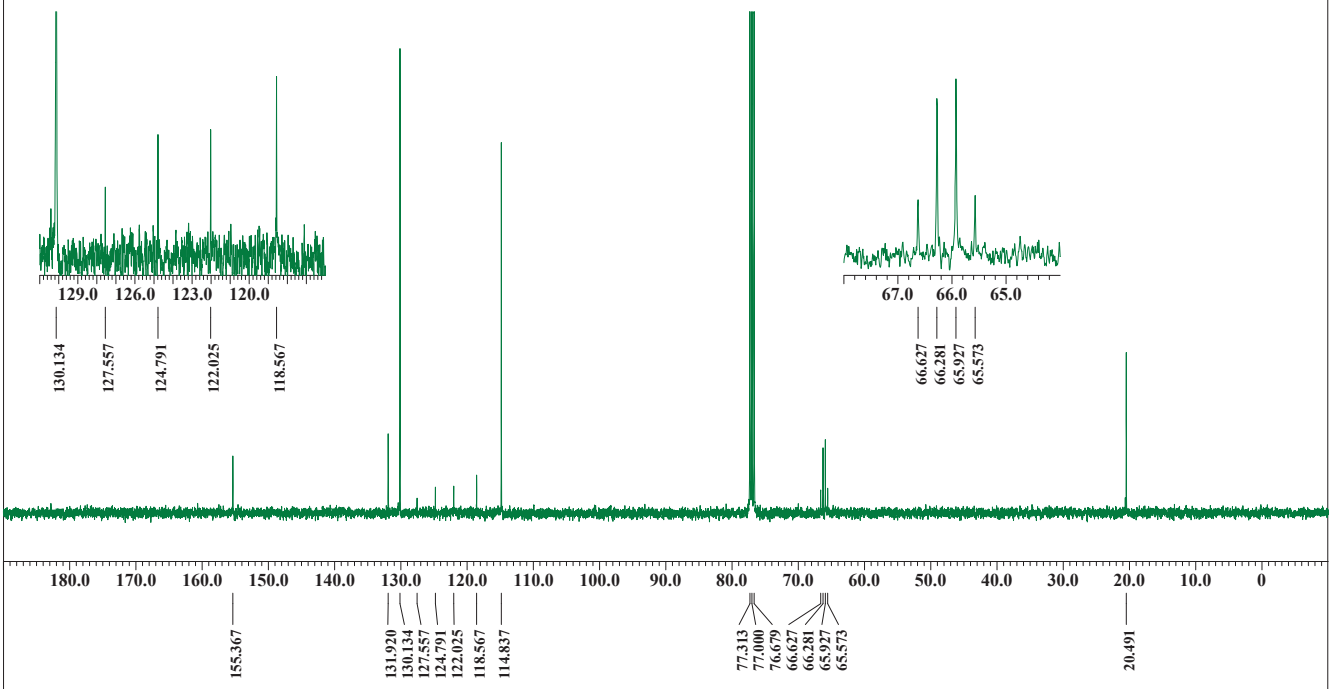
^{19}F NMR (376 MHz, $CDCl_3$)



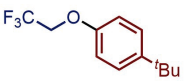
1-Methyl-4-(2,2,2-trifluoroethoxy)benzene (3ag)



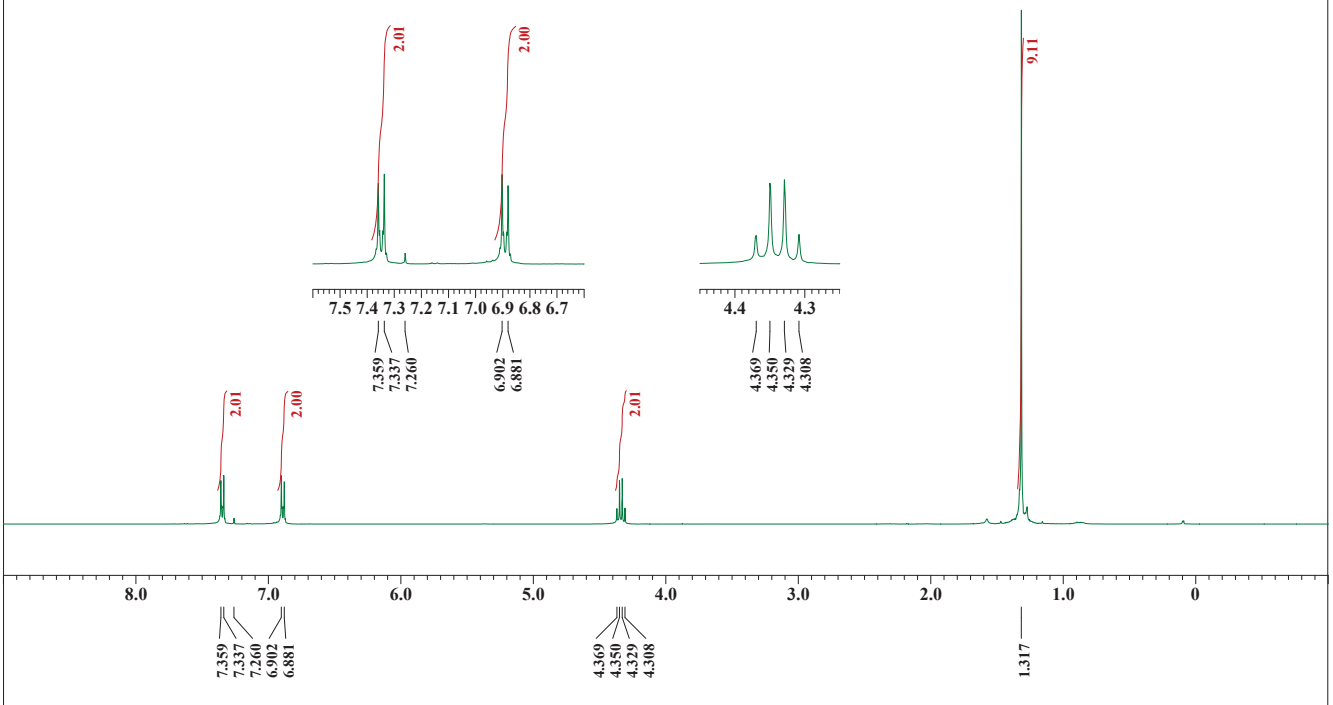
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



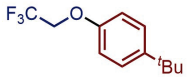
1-(*tert*-Butyl)-4-(2,2,2-trifluoroethoxy)benzene (3ah)



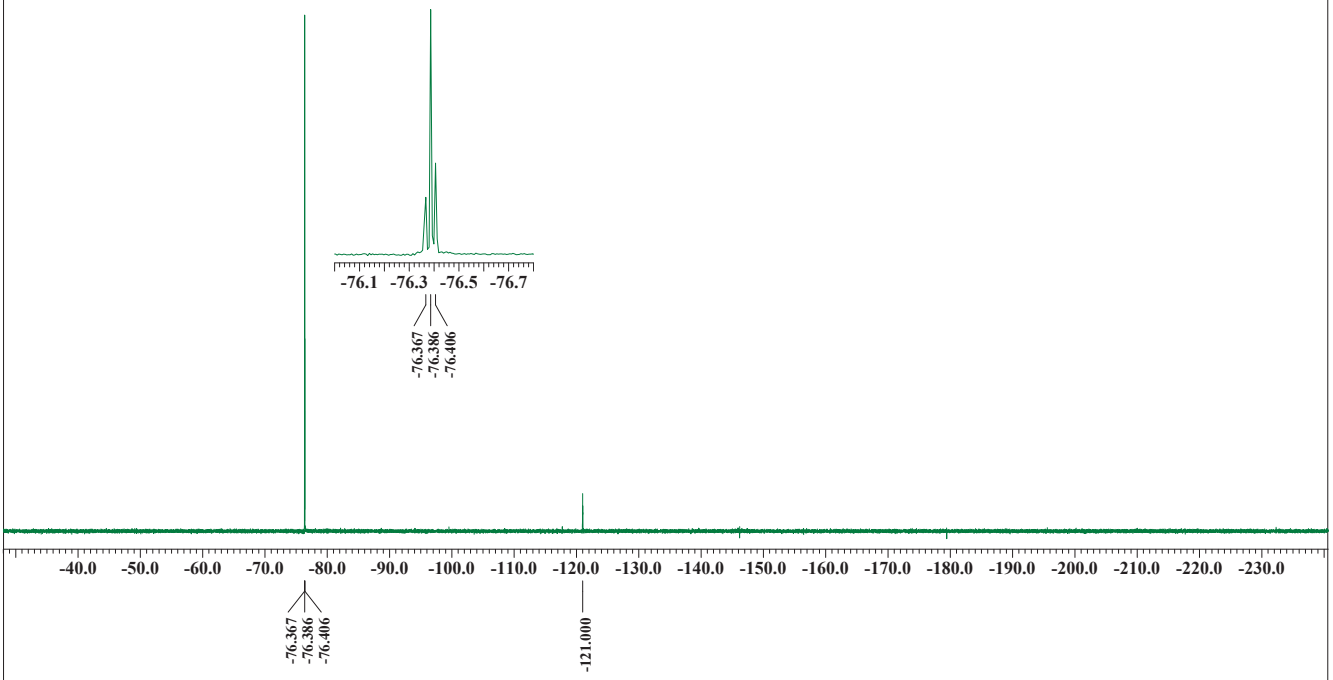
^{1}H NMR (400 MHz, $CDCl_3$)



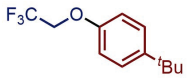
1-(*tert*-Butyl)-4-(2,2,2-trifluoroethoxy)benzene (3ah)



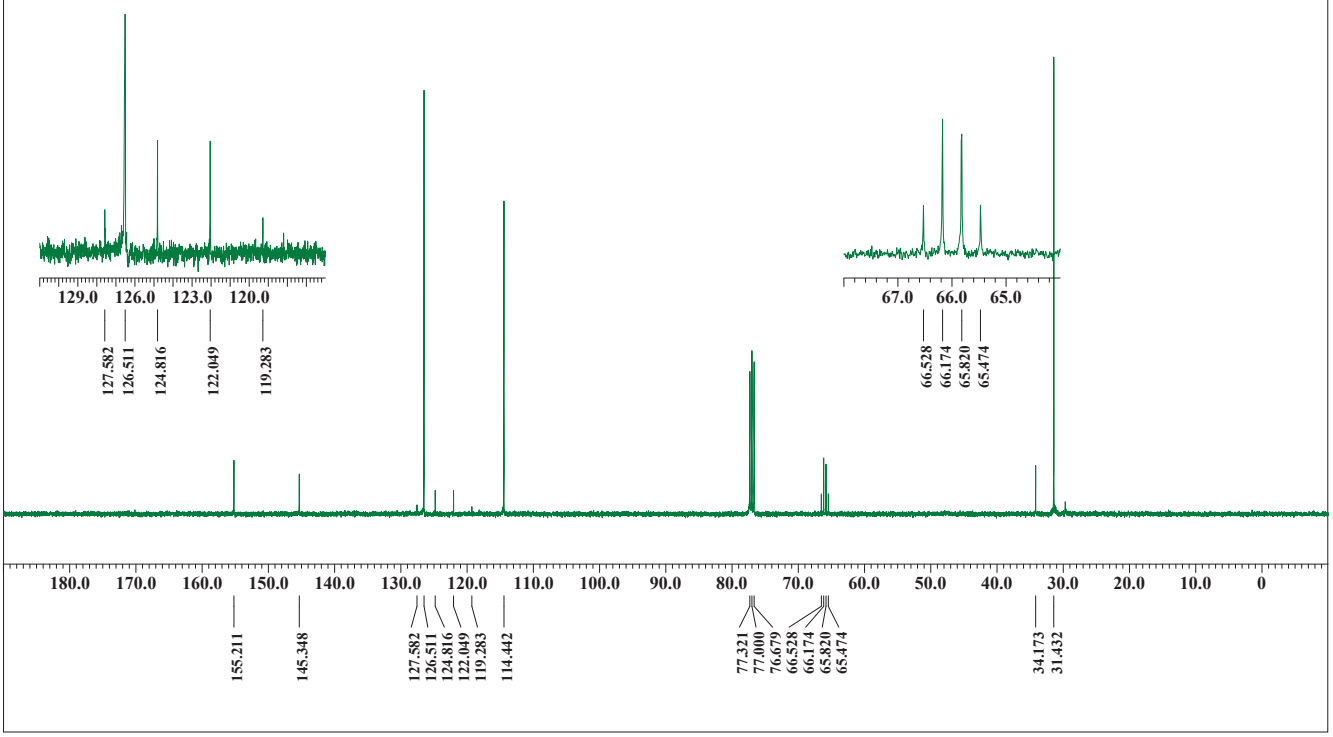
^{19}F NMR (376 MHz, $CDCl_3$)



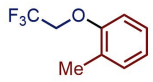
1-(*tert*-Butyl)-4-(2,2,2-trifluoroethoxy)benzene (3ah)



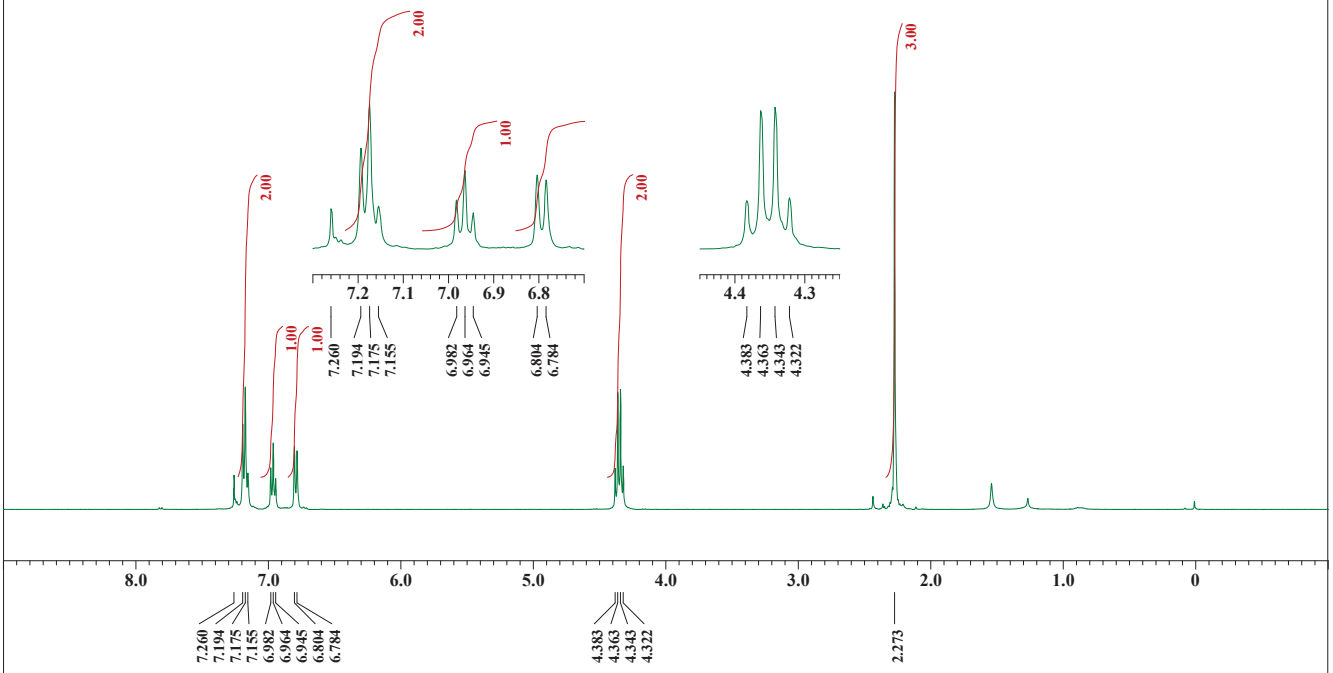
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



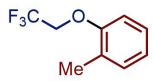
1-Methyl-2-(2,2,2-trifluoroethoxy)benzene (3ai)



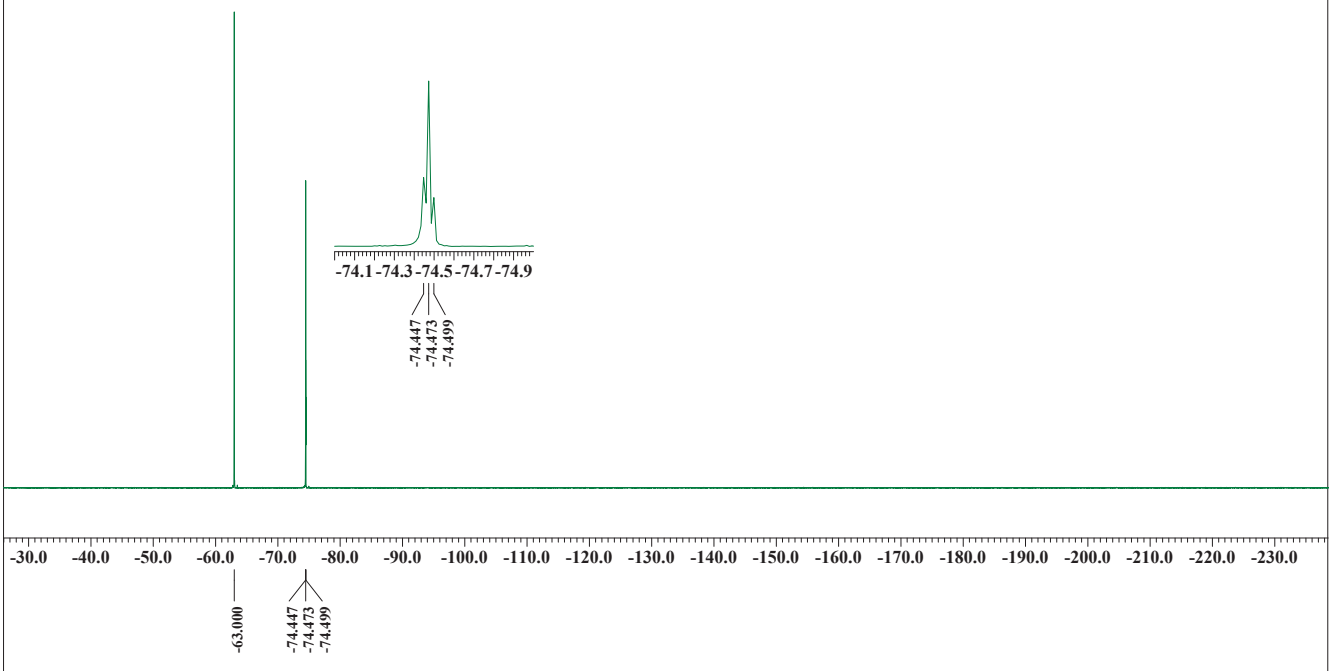
^{1}H NMR (400 MHz, $CDCl_3$)



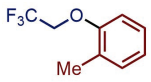
1-Methyl-2-(2,2,2-trifluoroethoxy)benzene (3ai)



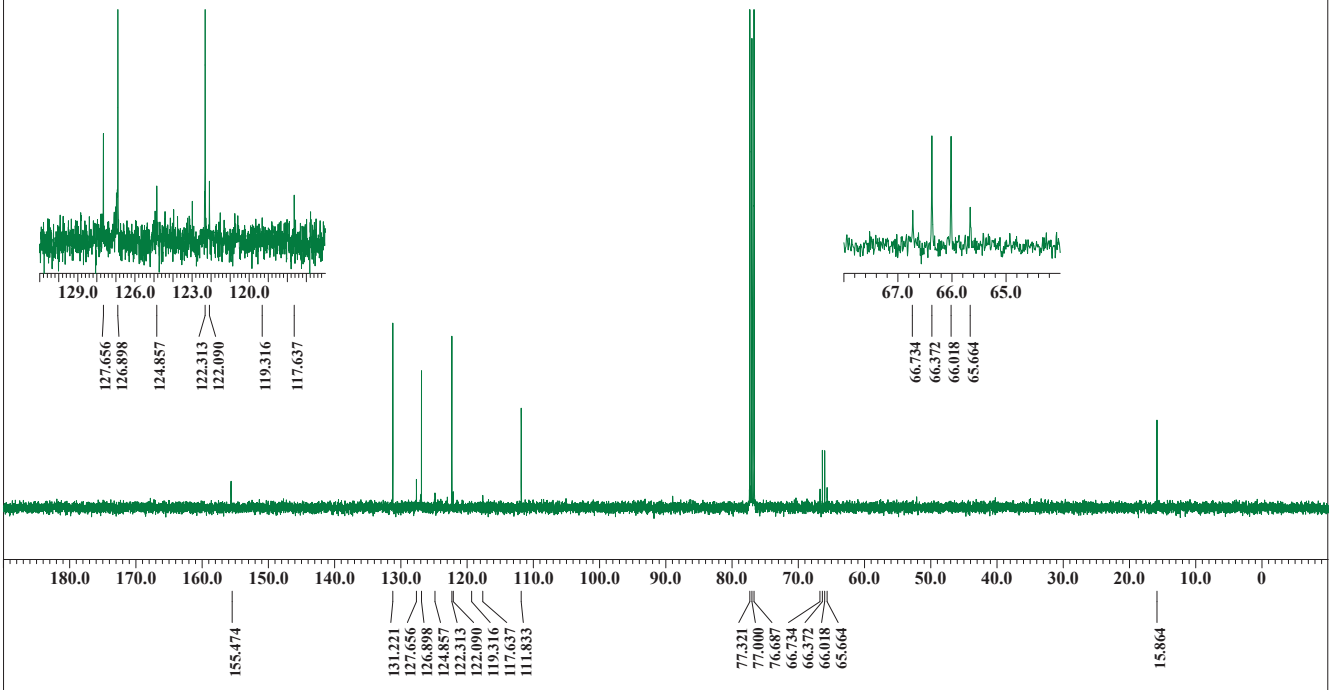
^{19}F NMR (376 MHz, $CDCl_3$)



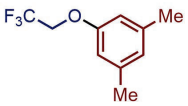
1-Methyl-2-(2,2,2-trifluoroethoxy)benzene (3ai)



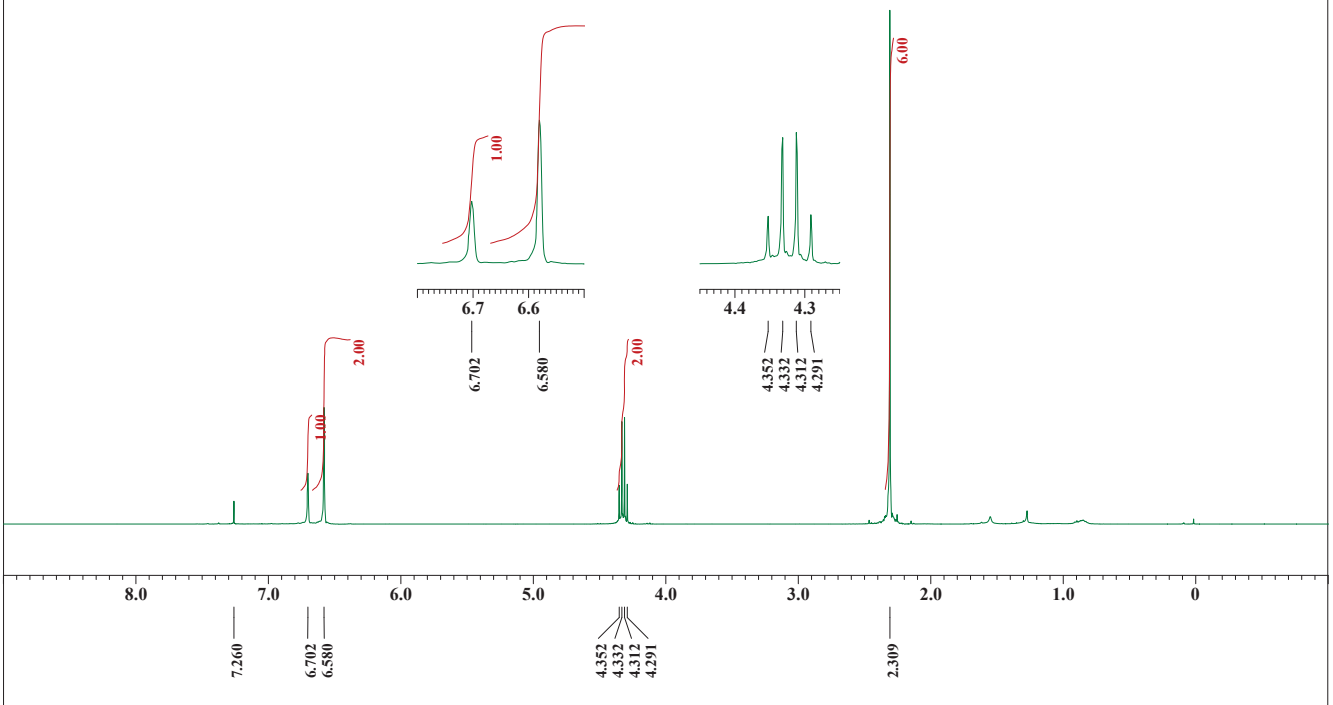
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



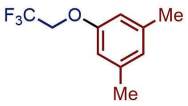
1,3-Dimethyl-5-(2,2,2-trifluoroethoxy)benzene (3aj)



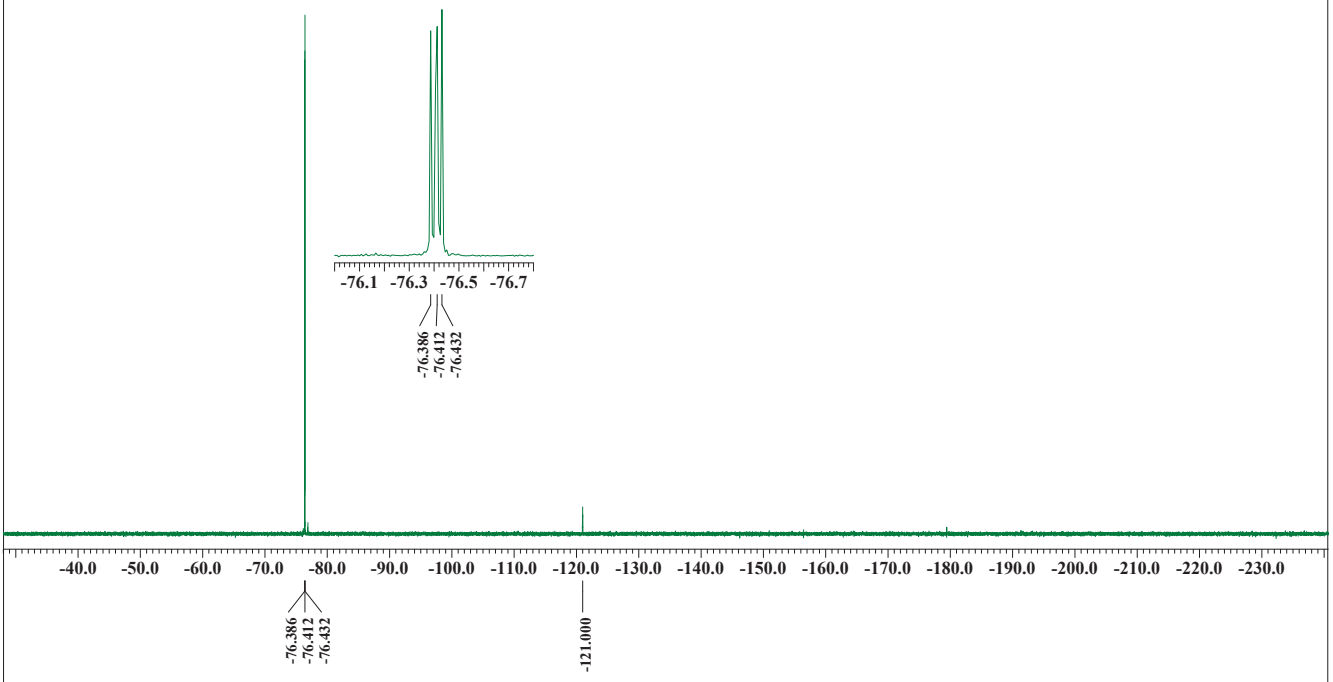
^{1}H NMR (400 MHz, $CDCl_3$)



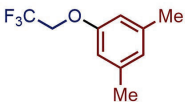
1,3-Dimethyl-5-(2,2,2-trifluoroethoxy)benzene (3aj)



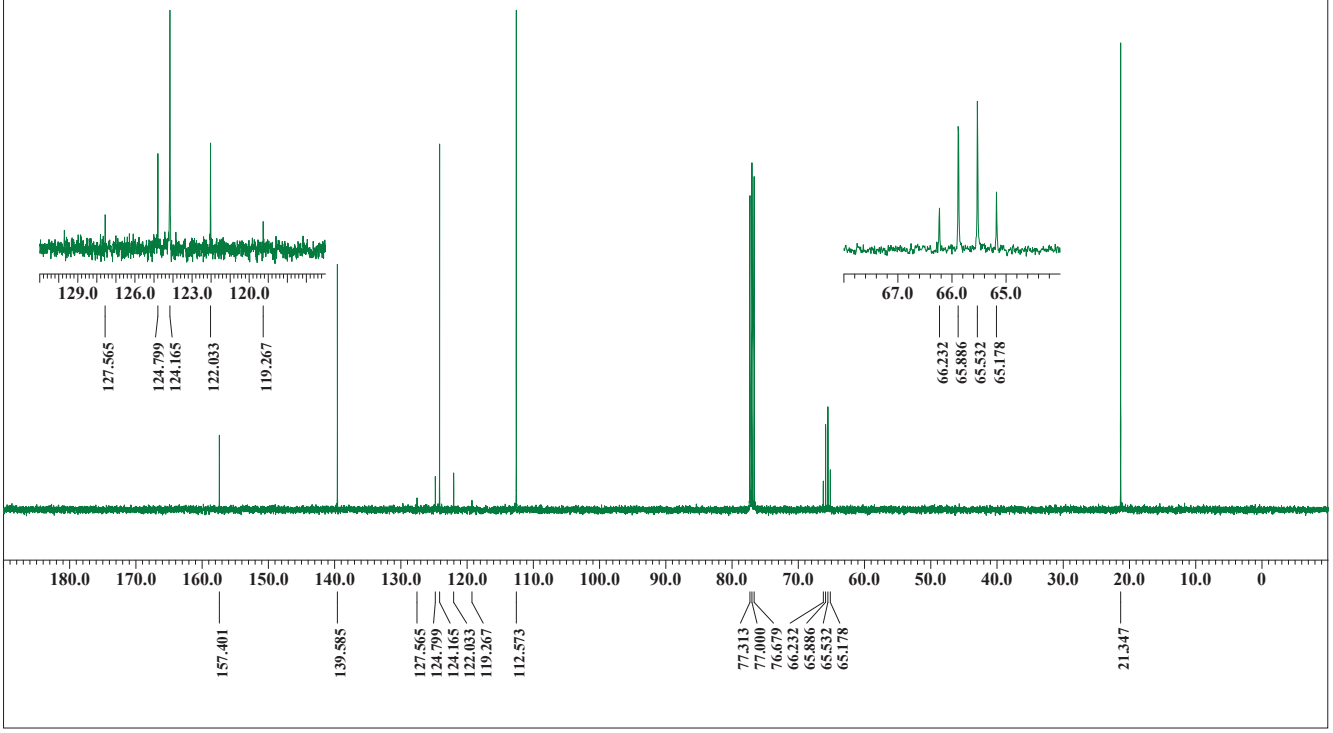
^{19}F NMR (376 MHz, $CDCl_3$)



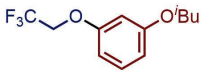
1,3-Dimethyl-5-(2,2,2-trifluoroethoxy)benzene (3aj)



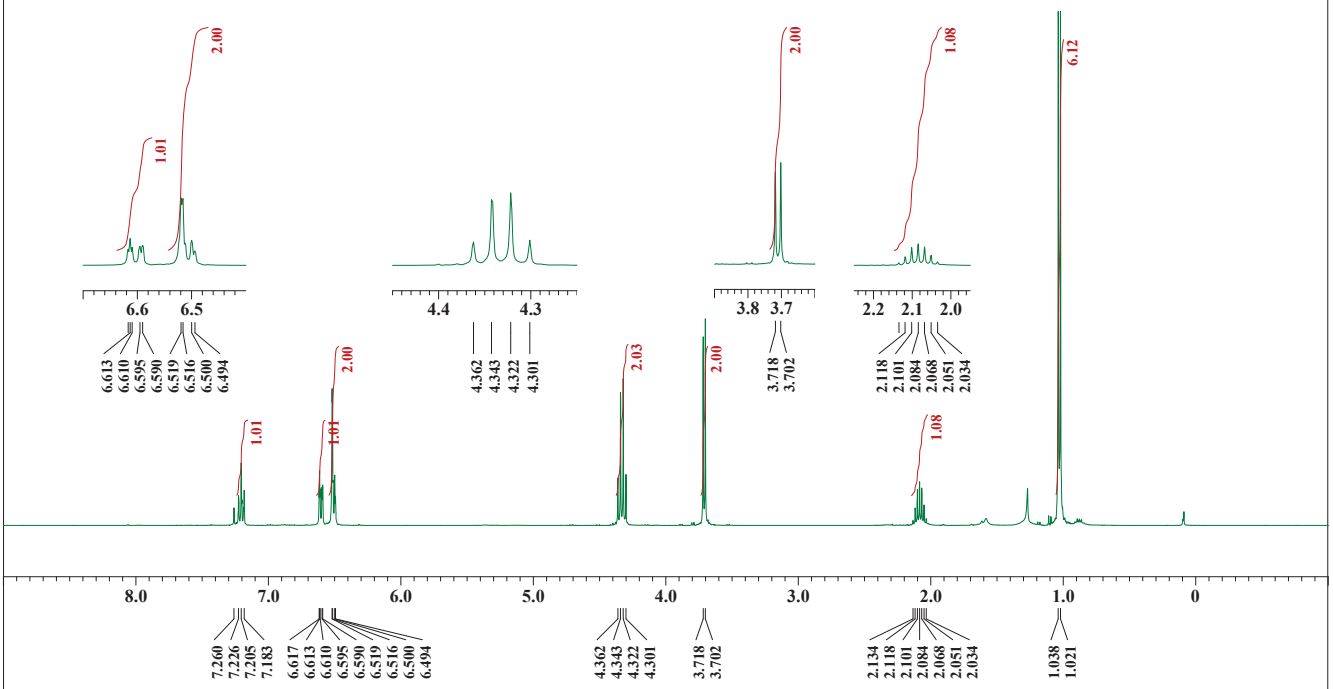
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



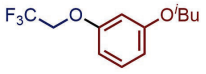
1-Isobutoxy-3-(2,2,2-trifluoroethoxy)benzene (3ak)



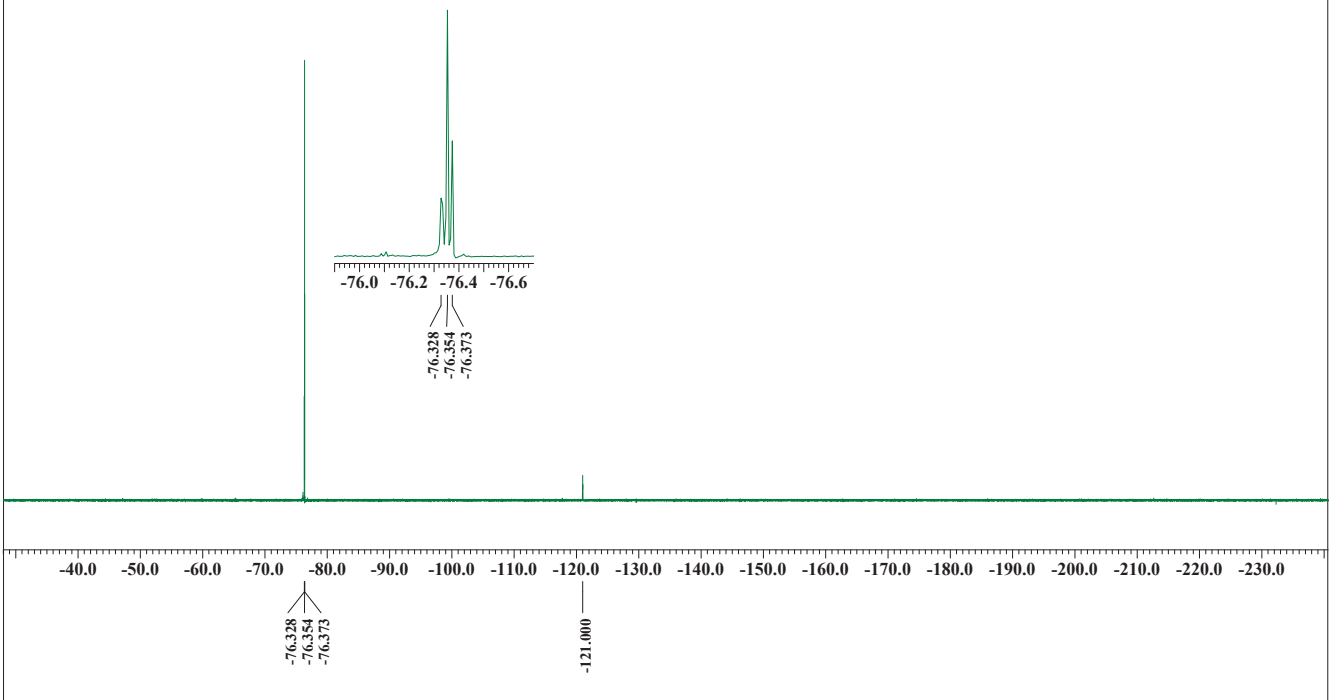
^{1}H NMR (400 MHz, $CDCl_3$)



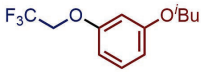
1-Isobutoxy-3-(2,2,2-trifluoroethoxy)benzene (3ak)



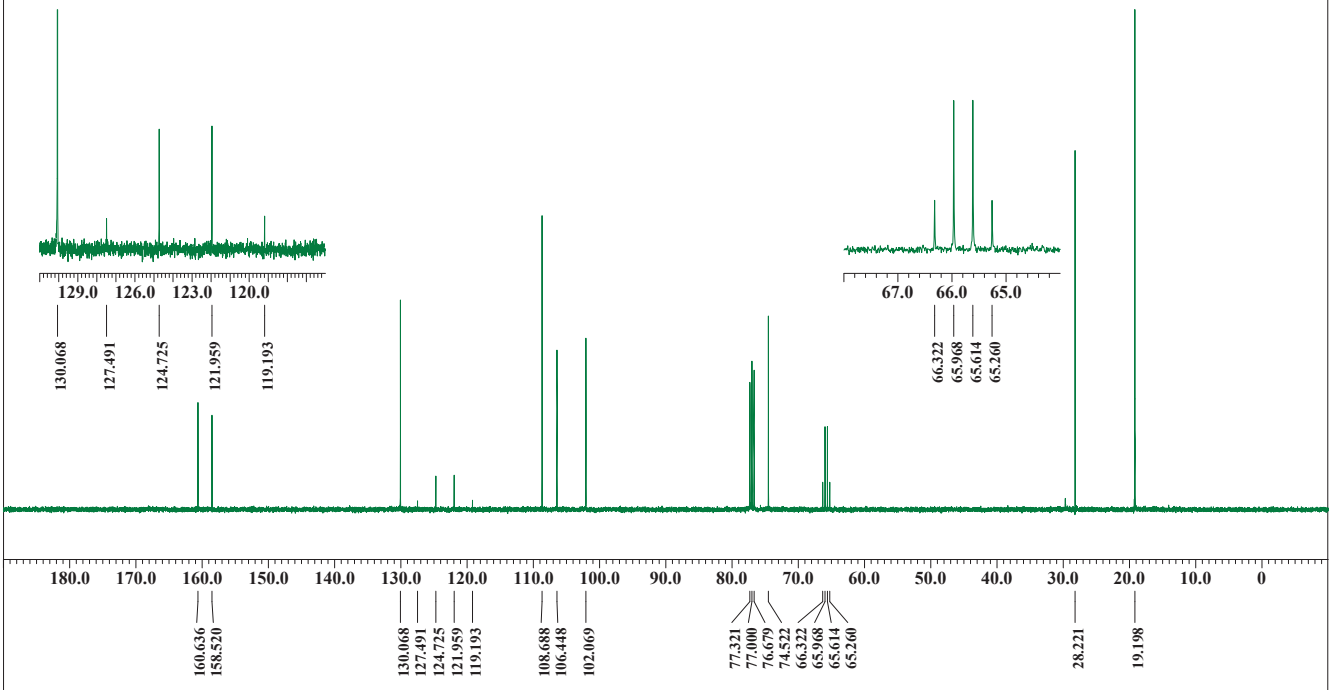
^{19}F NMR (376 MHz, $CDCl_3$)



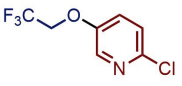
1-Isobutoxy-3-(2,2,2-trifluoroethoxy)benzene (3ak)



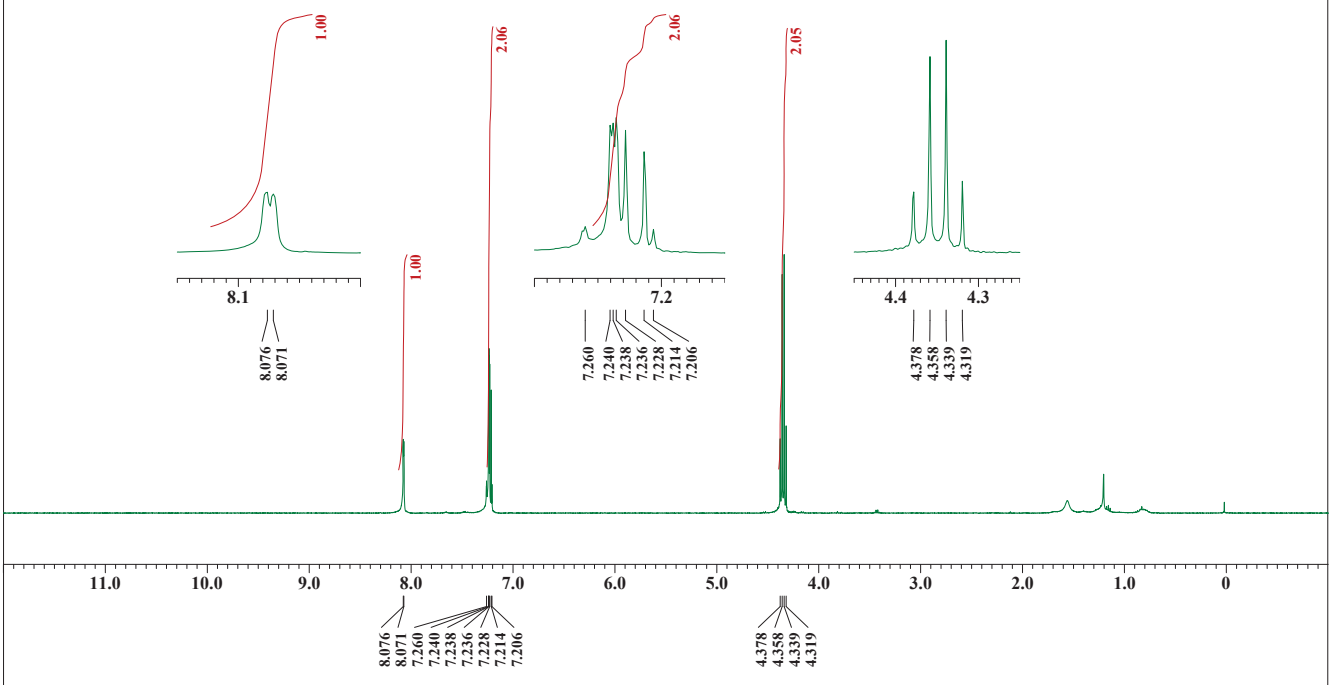
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



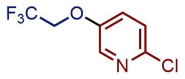
2-Chloro-5-(2,2,2-trifluoroethoxy)pyridine (3al)



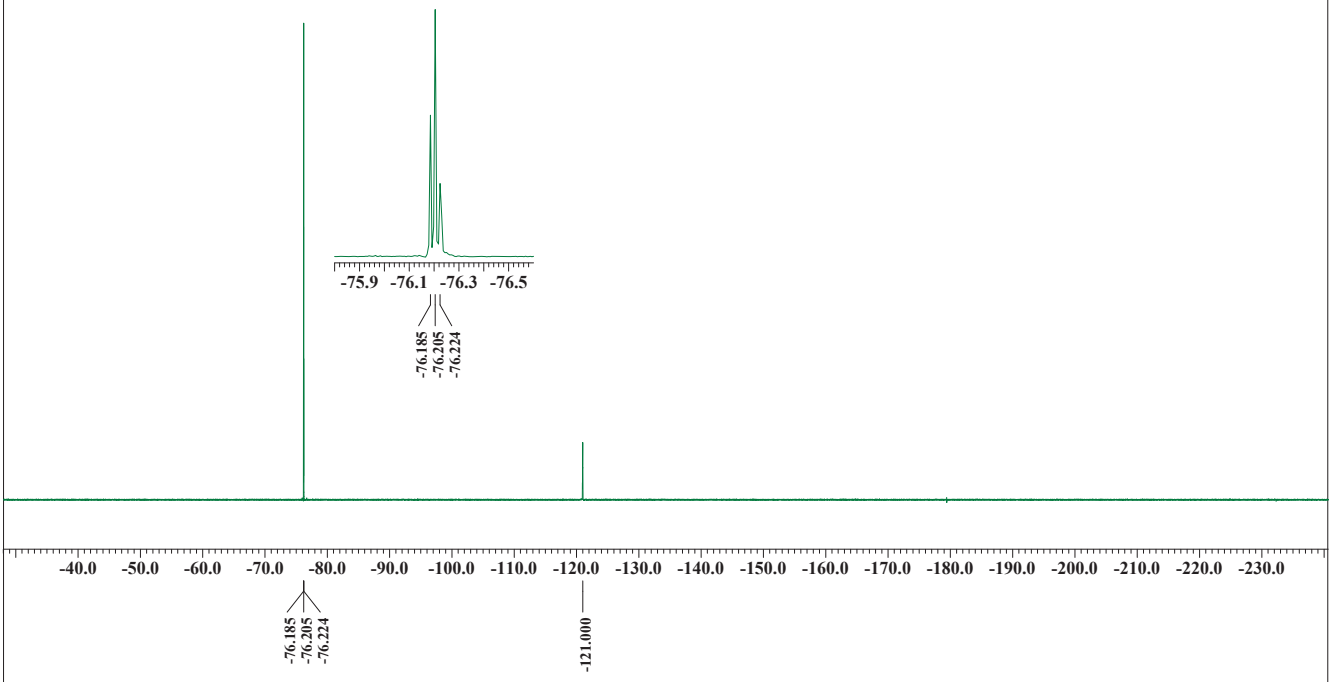
^{1}H NMR (400 MHz, $CDCl_3$)



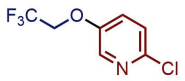
2-Chloro-5-(2,2,2-trifluoroethoxy)pyridine (3al)



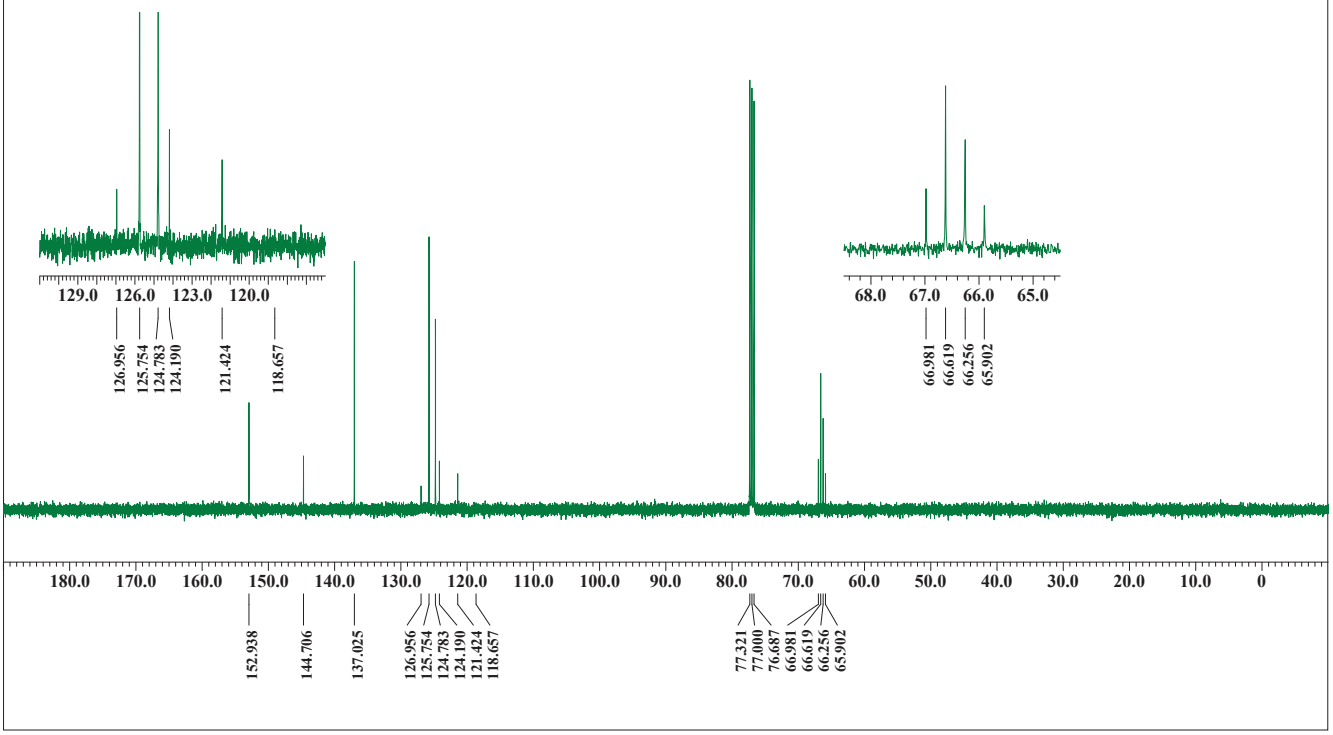
^{19}F NMR (376 MHz, $CDCl_3$)



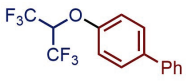
2-Chloro-5-(2,2,2-trifluoroethoxy)pyridine (3al)



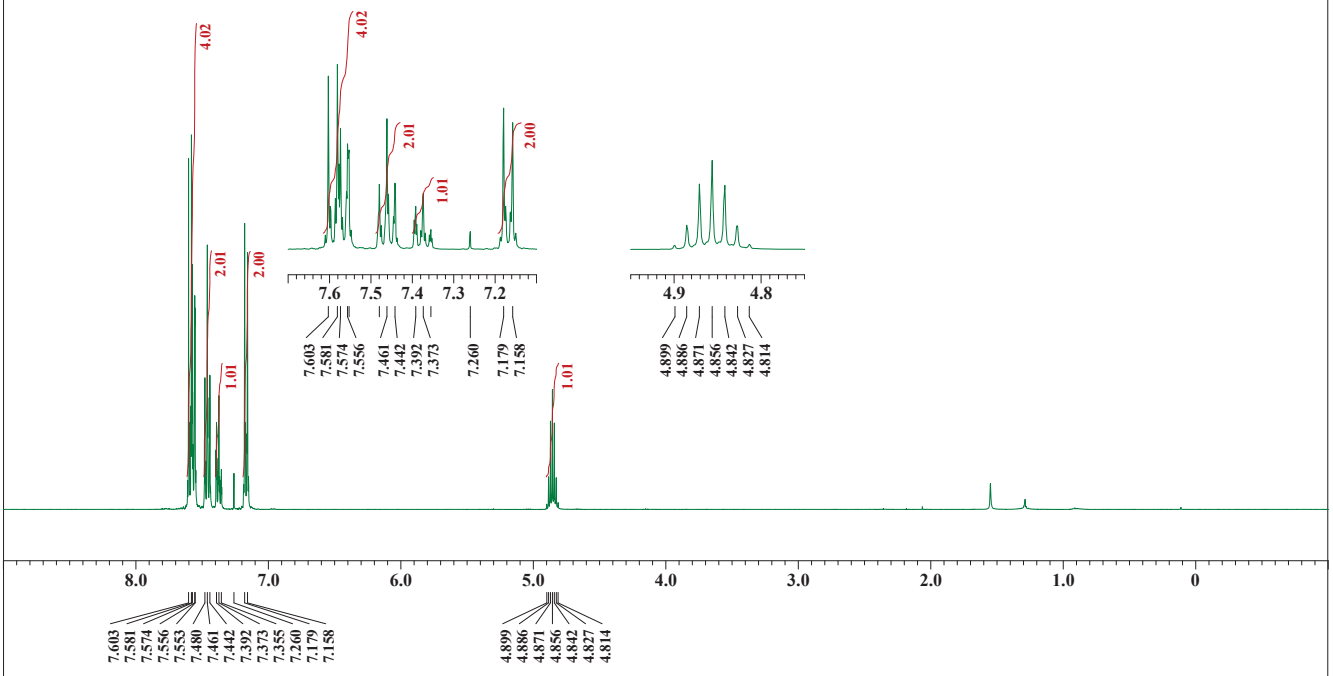
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



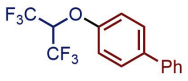
4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-1,1'-biphenyl (3ba)



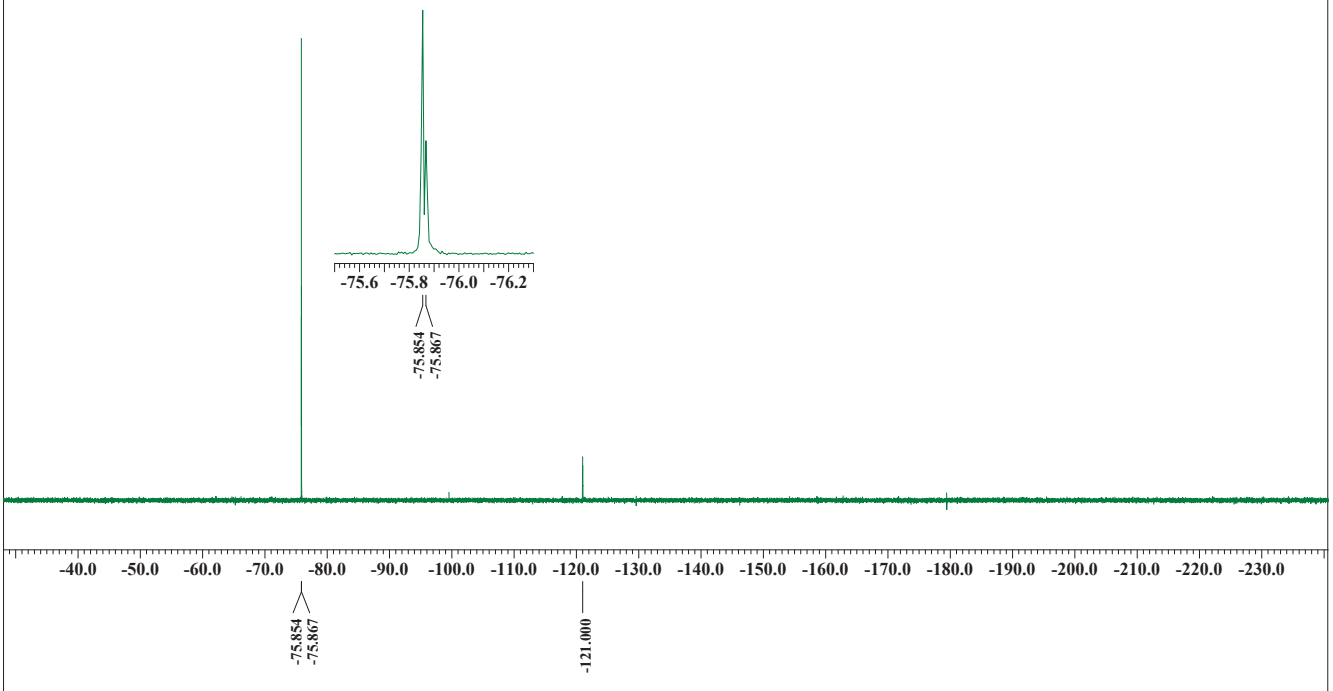
^{1}H NMR (400 MHz, $CDCl_3$)



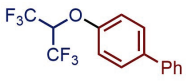
4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-1,1'-biphenyl (3ba)



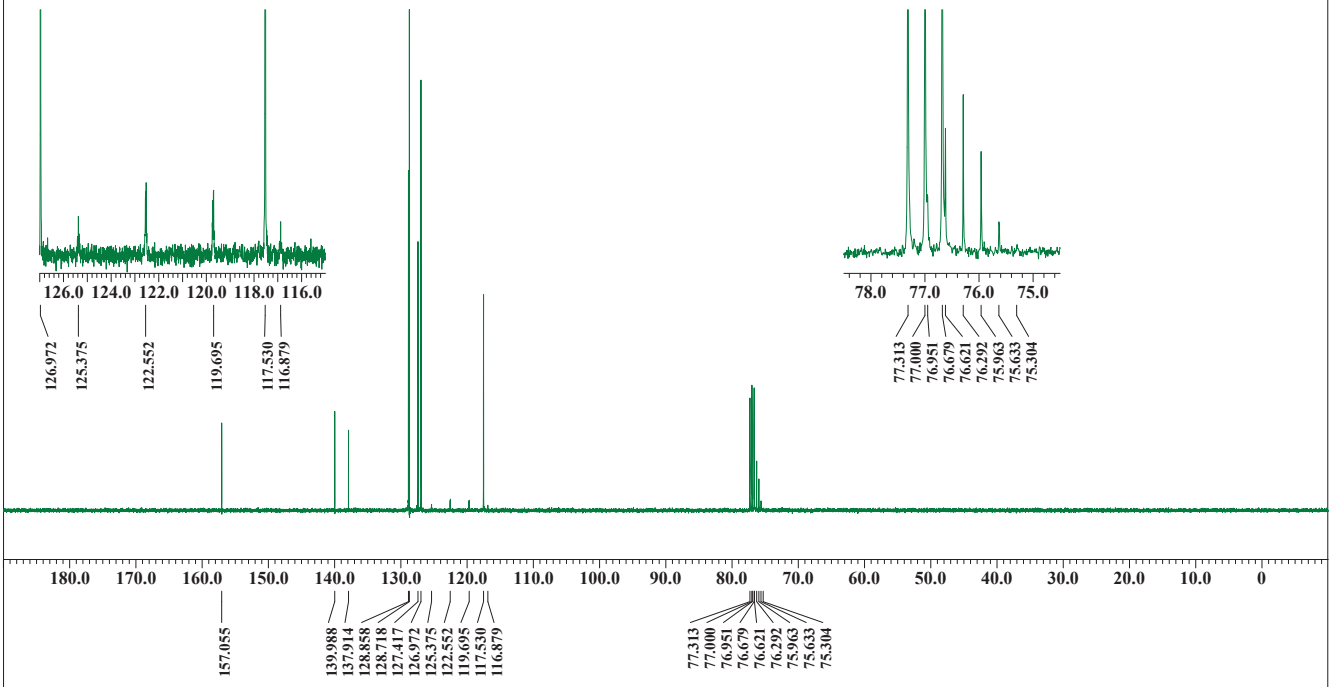
^{19}F NMR (376 MHz, $CDCl_3$)



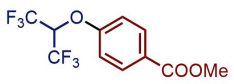
4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-1,1'-biphenyl (3ba)



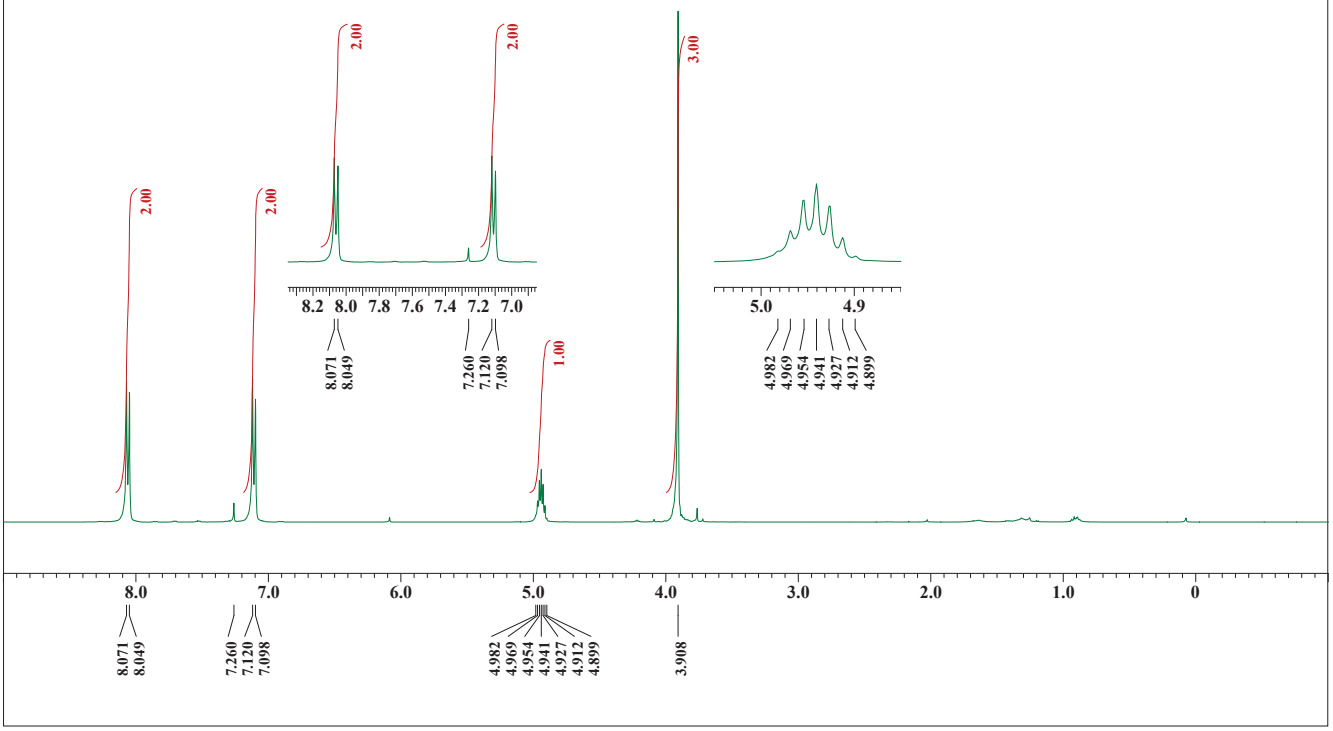
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



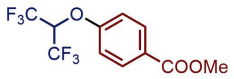
Methyl 4-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzoate (3bb)



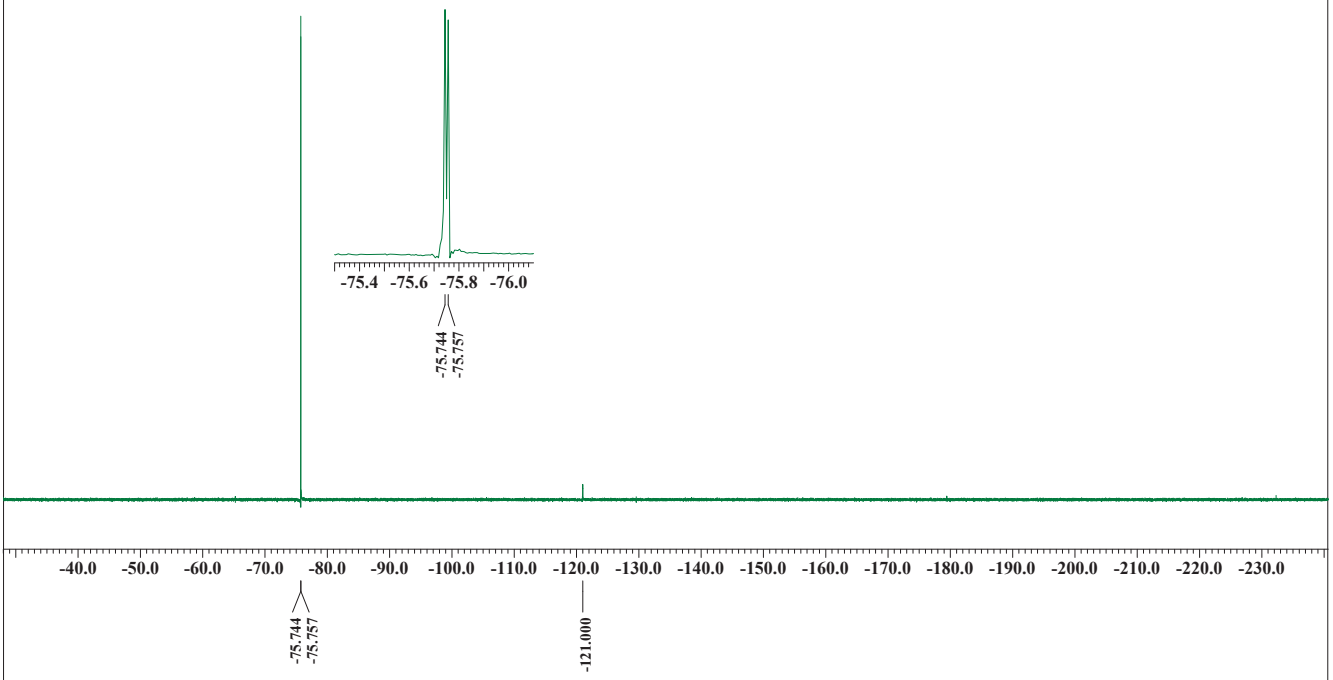
^{1}H NMR (400 MHz, $CDCl_3$)



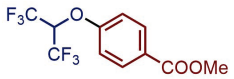
Methyl 4-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzoate (3bb)



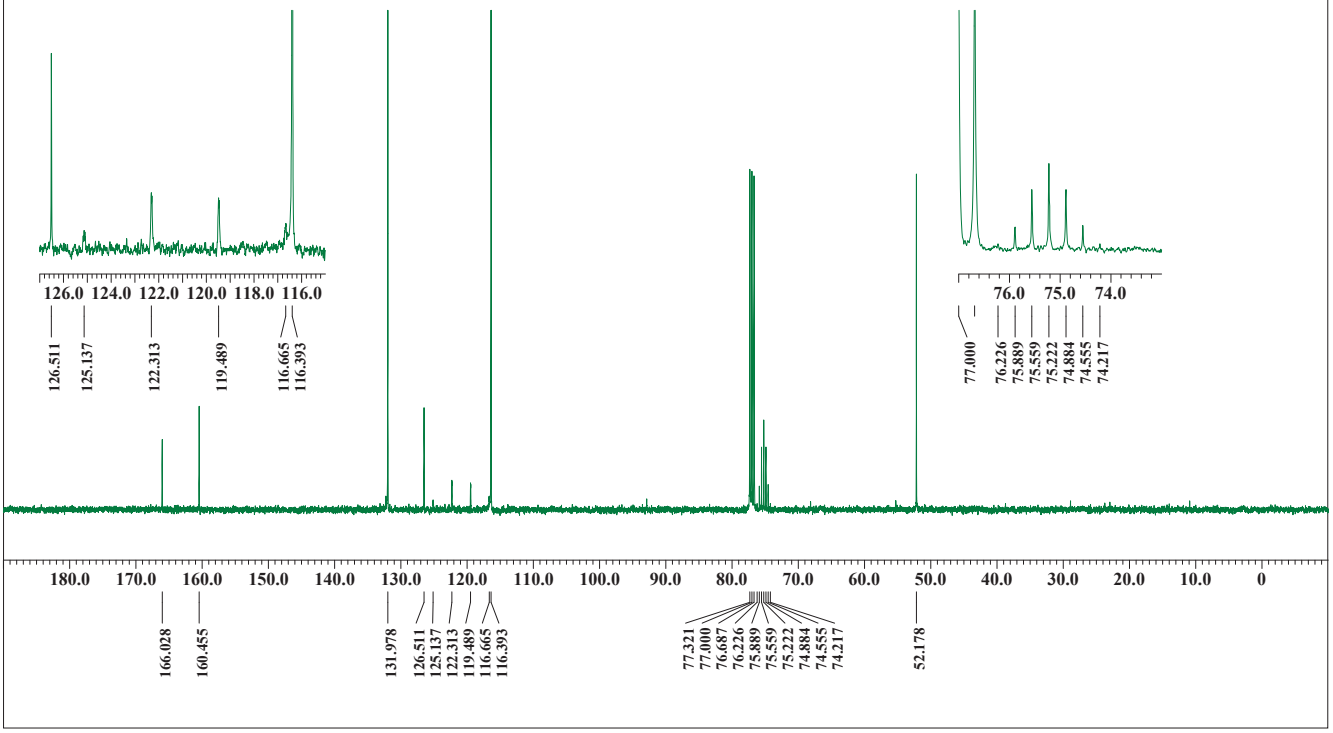
^{19}F NMR (376 MHz, $CDCl_3$)



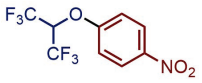
Methyl 4-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzoate (3bb)



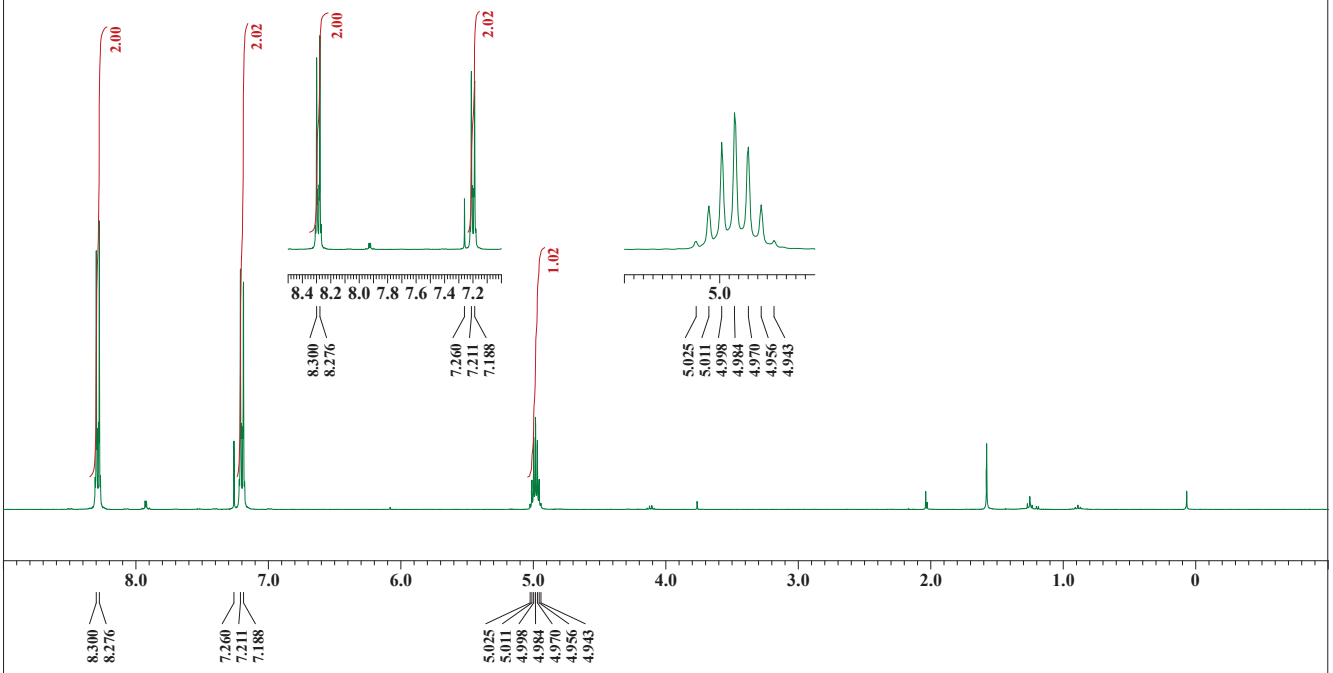
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



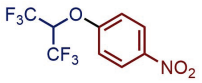
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-4-nitrobenzene (3bc)



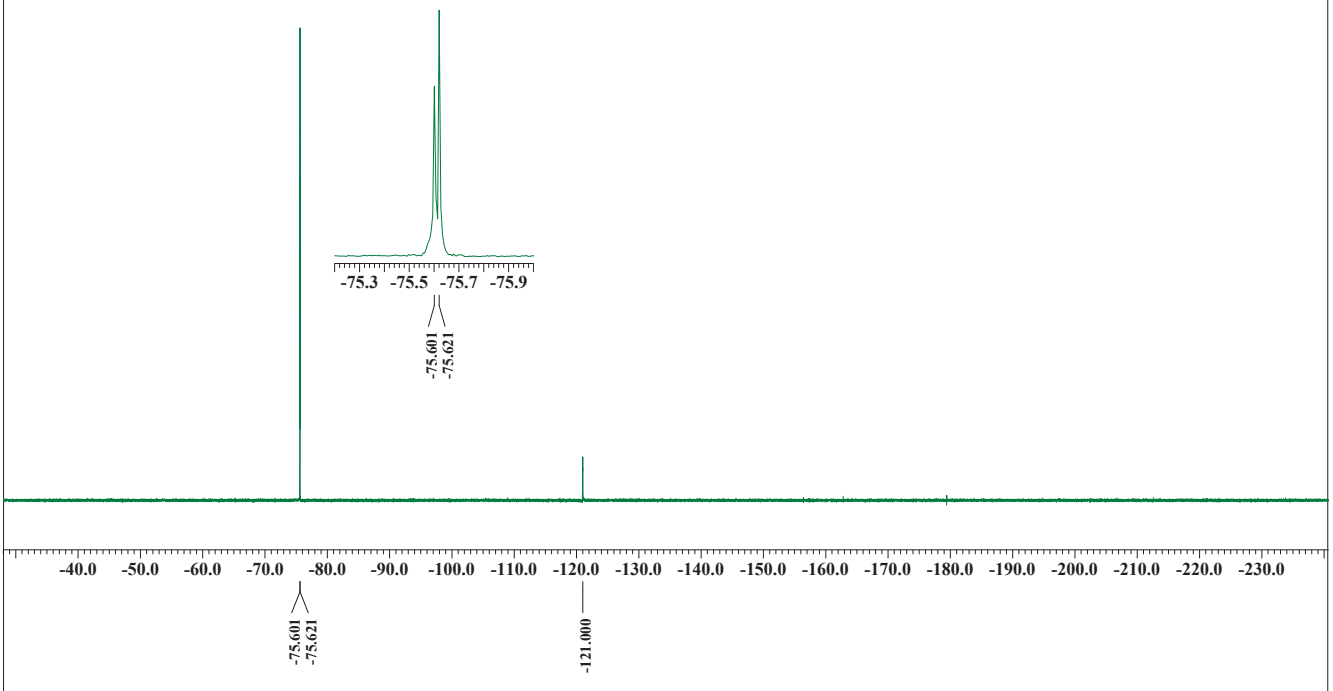
^{1}H NMR (400 MHz, $CDCl_3$)



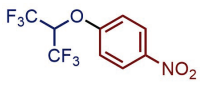
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-4-nitrobenzene (3bc)



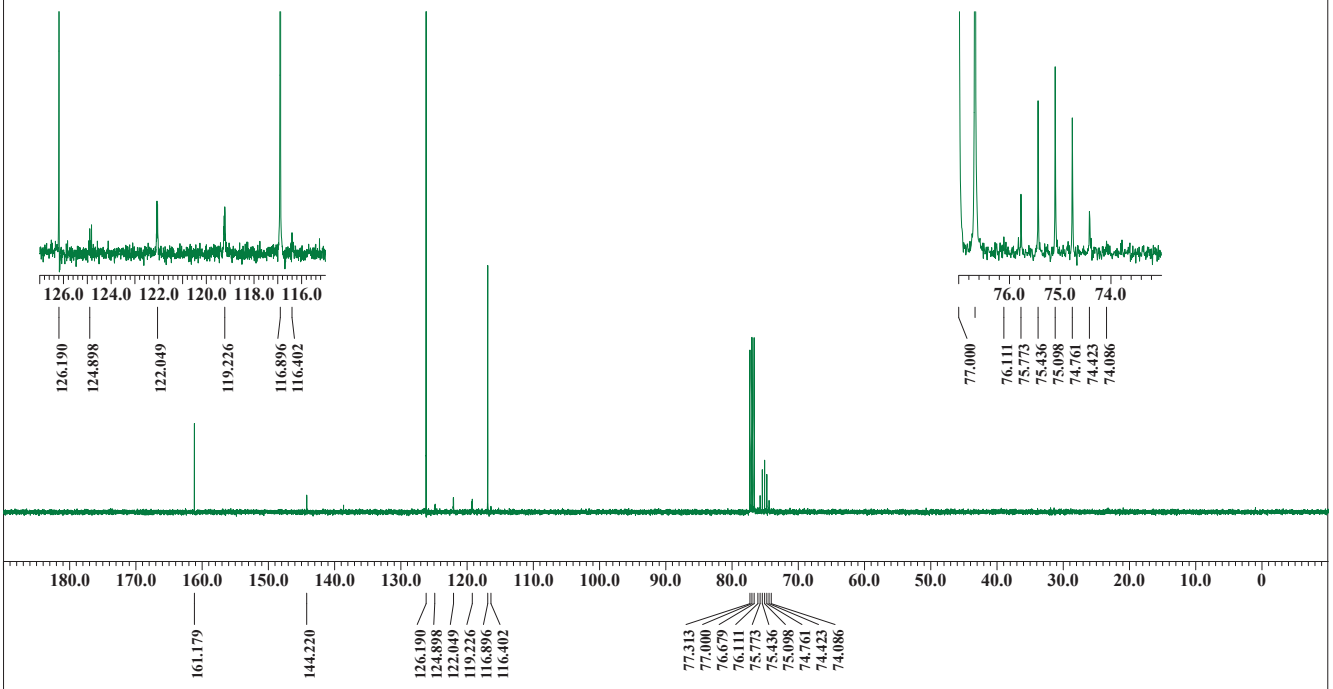
^{19}F NMR (376 MHz, $CDCl_3$)



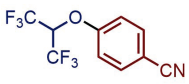
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-4-nitrobenzene (3bc)



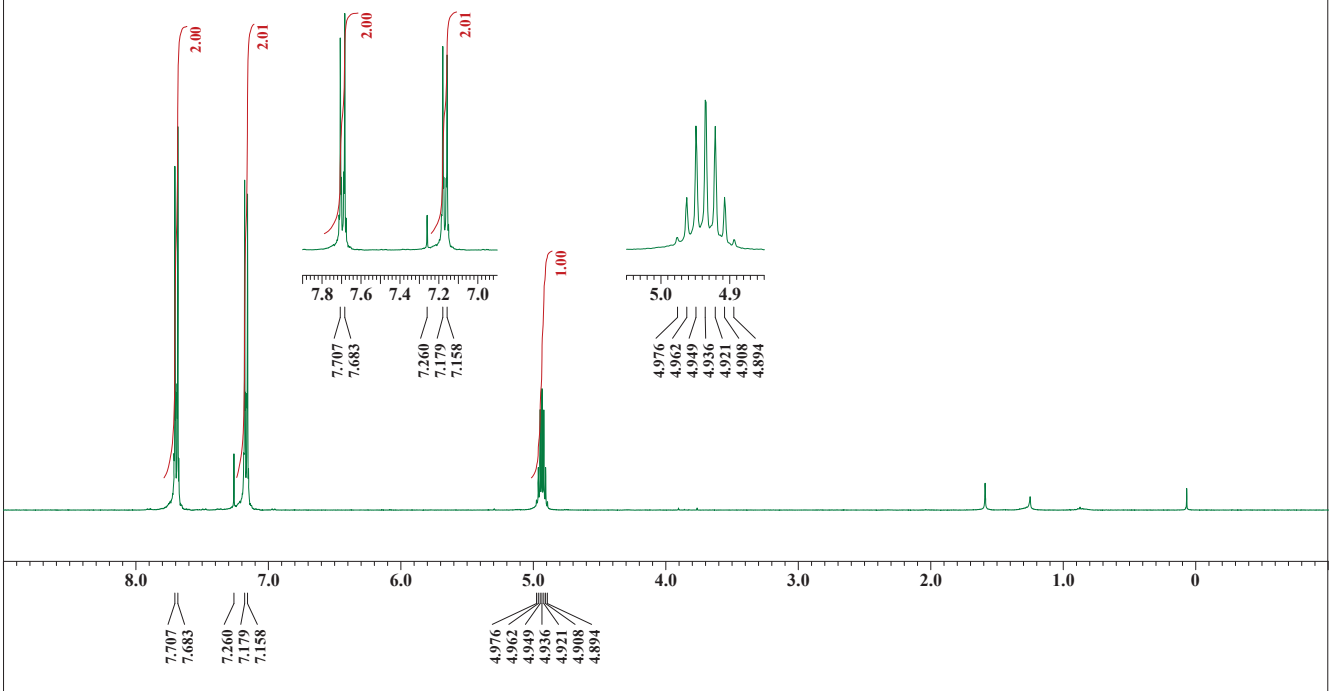
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



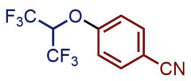
4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)benzonitrile (3bd)



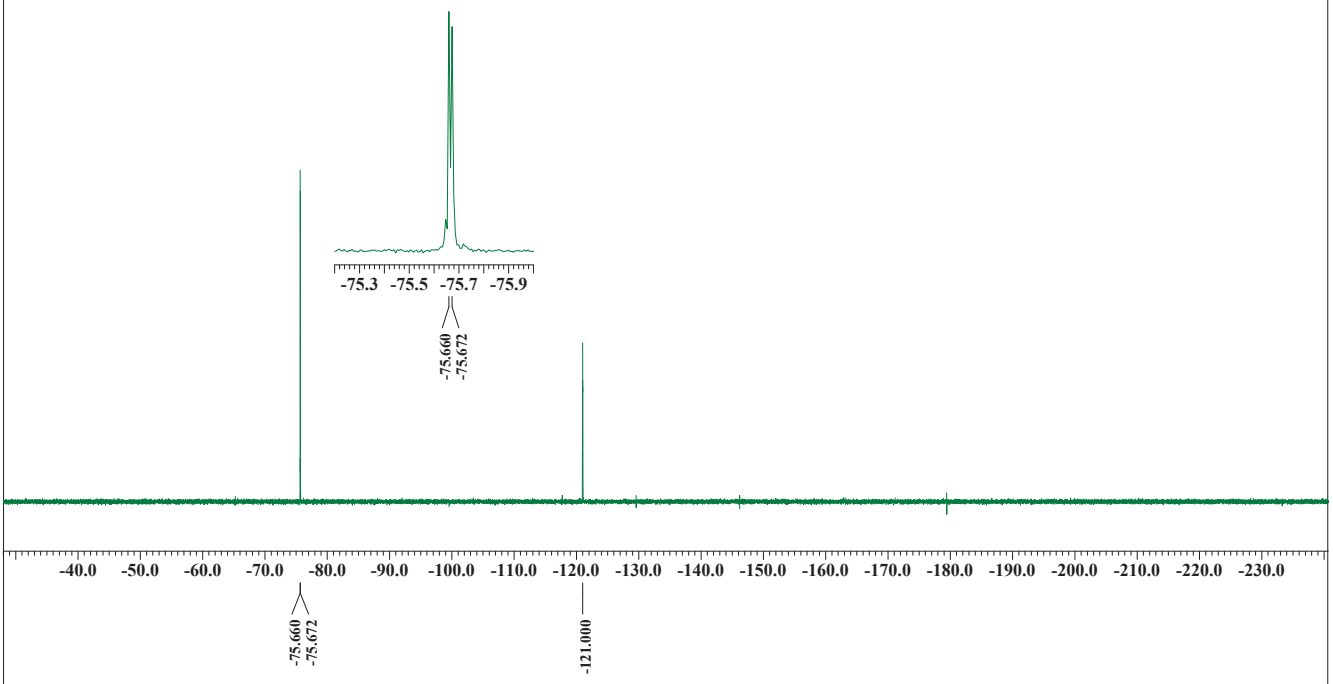
^{1}H NMR (400 MHz, $CDCl_3$)



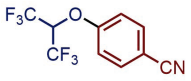
4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)benzonitrile (3bd)



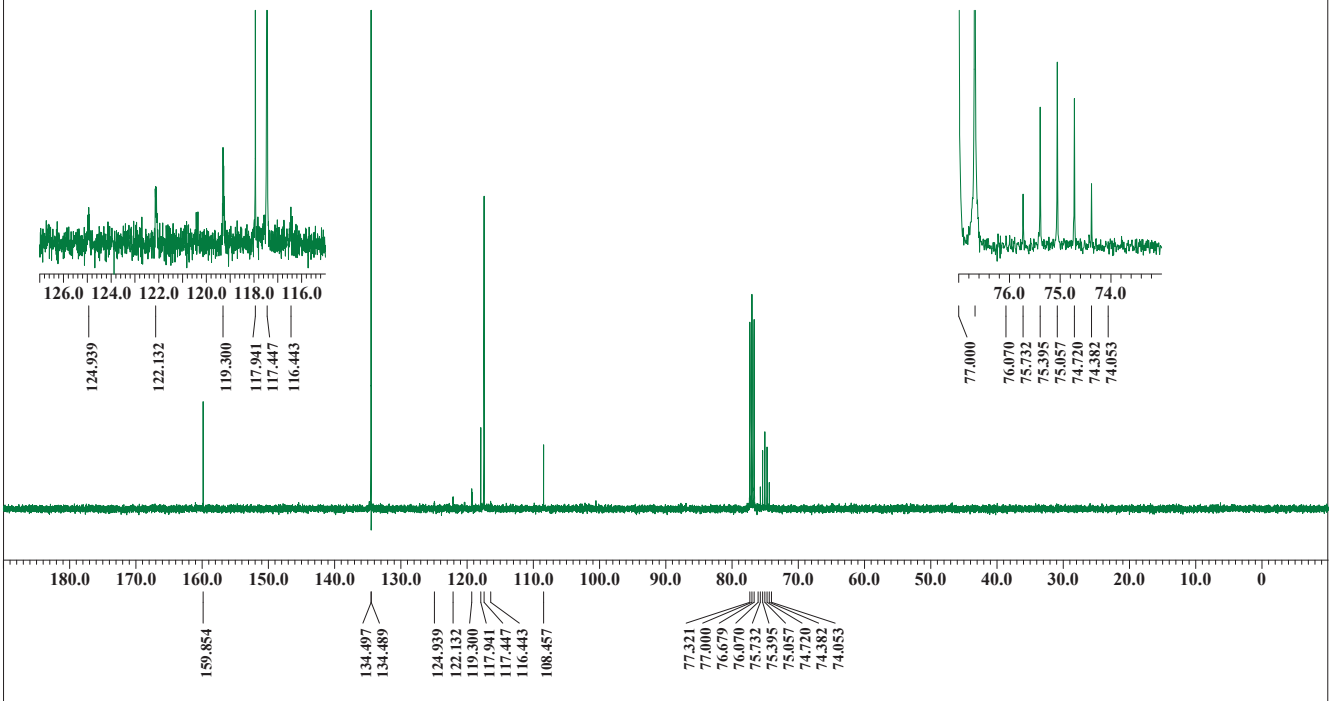
^{19}F NMR (376 MHz, $CDCl_3$)



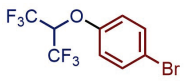
4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)benzonitrile (3bd)



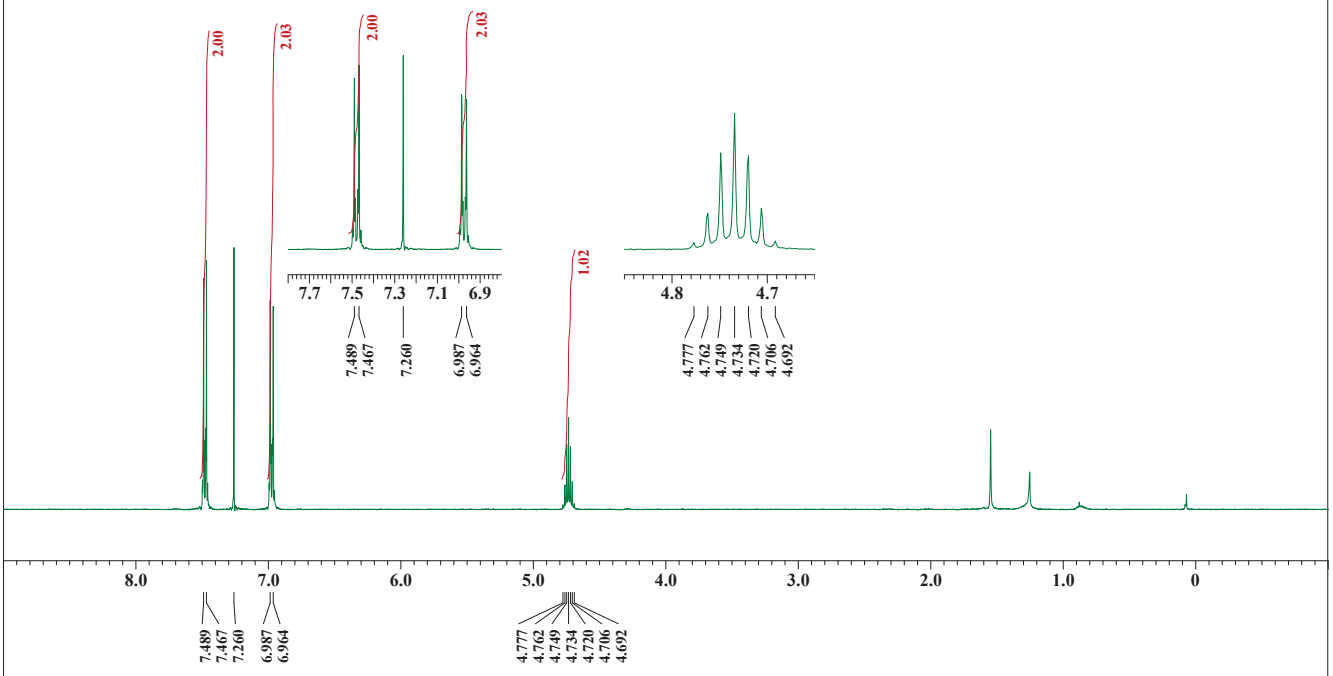
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



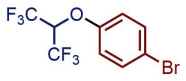
1-Bromo-4-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzene (3bf)



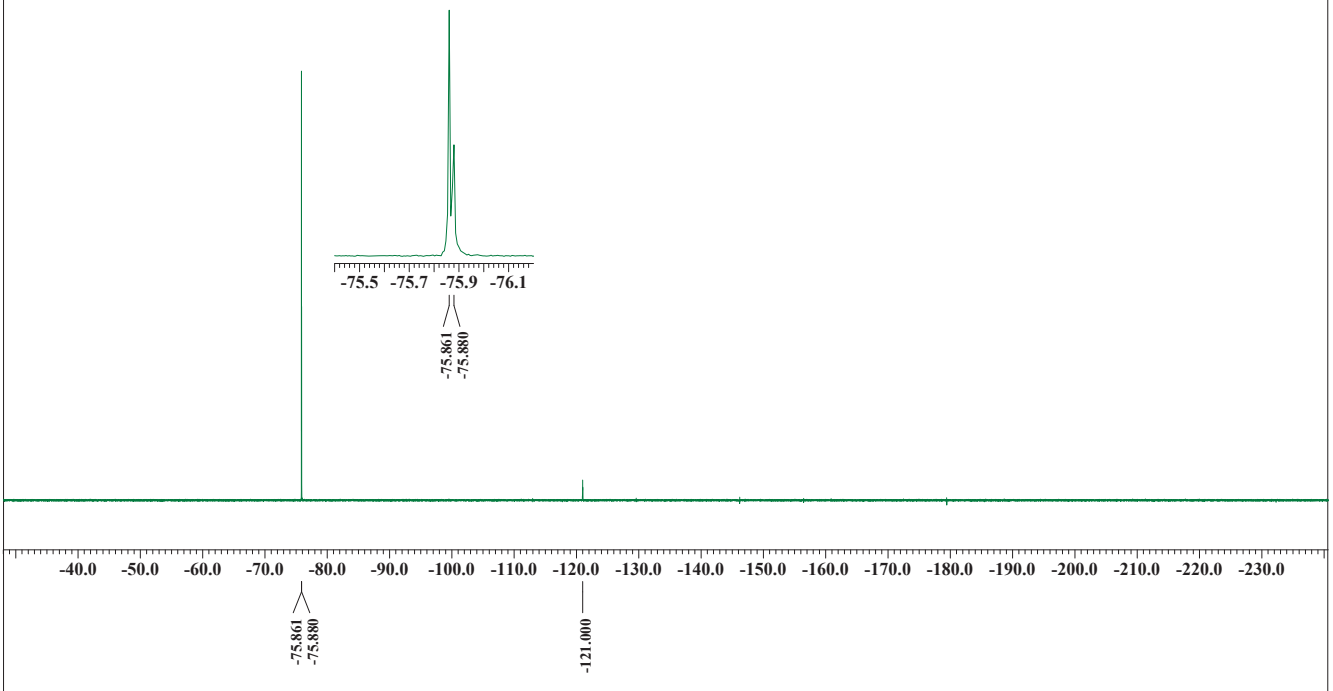
^{1}H NMR (400 MHz, $CDCl_3$)



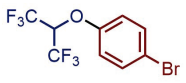
1-Bromo-4-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzene (3bf)



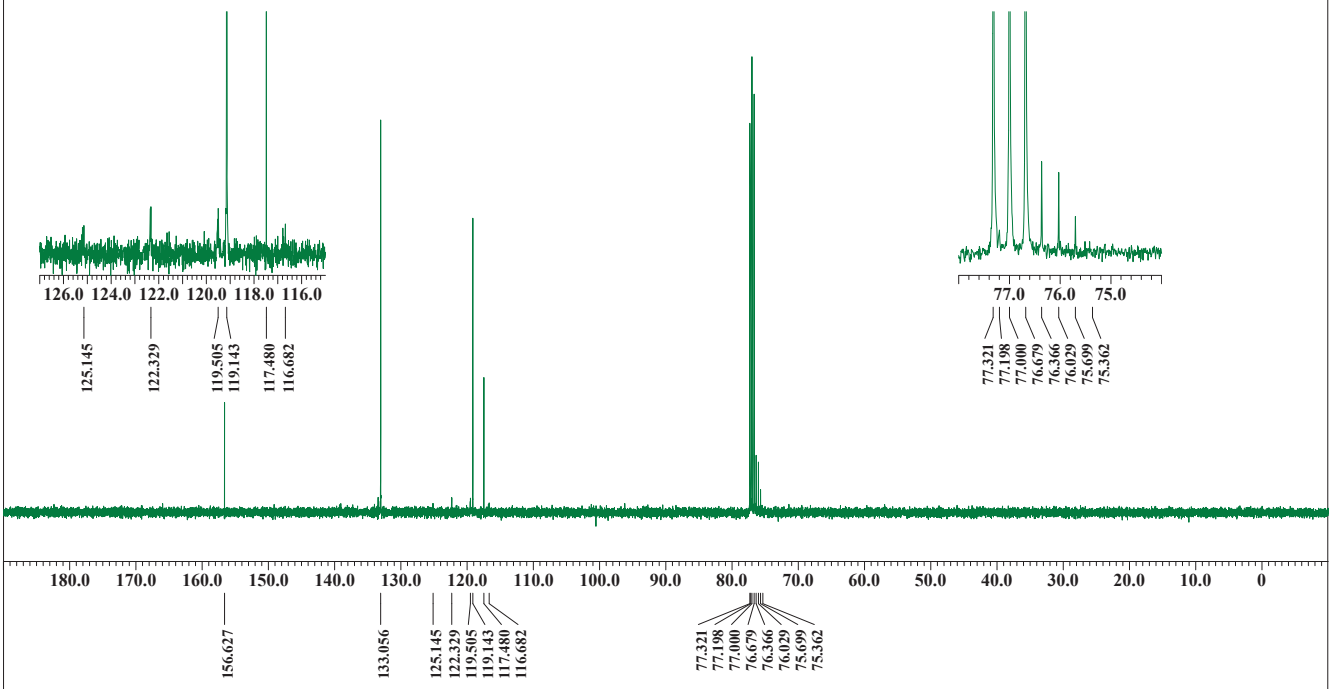
^{19}F NMR (376 MHz, $CDCl_3$)



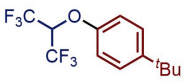
1-Bromo-4-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)benzene (3bf)



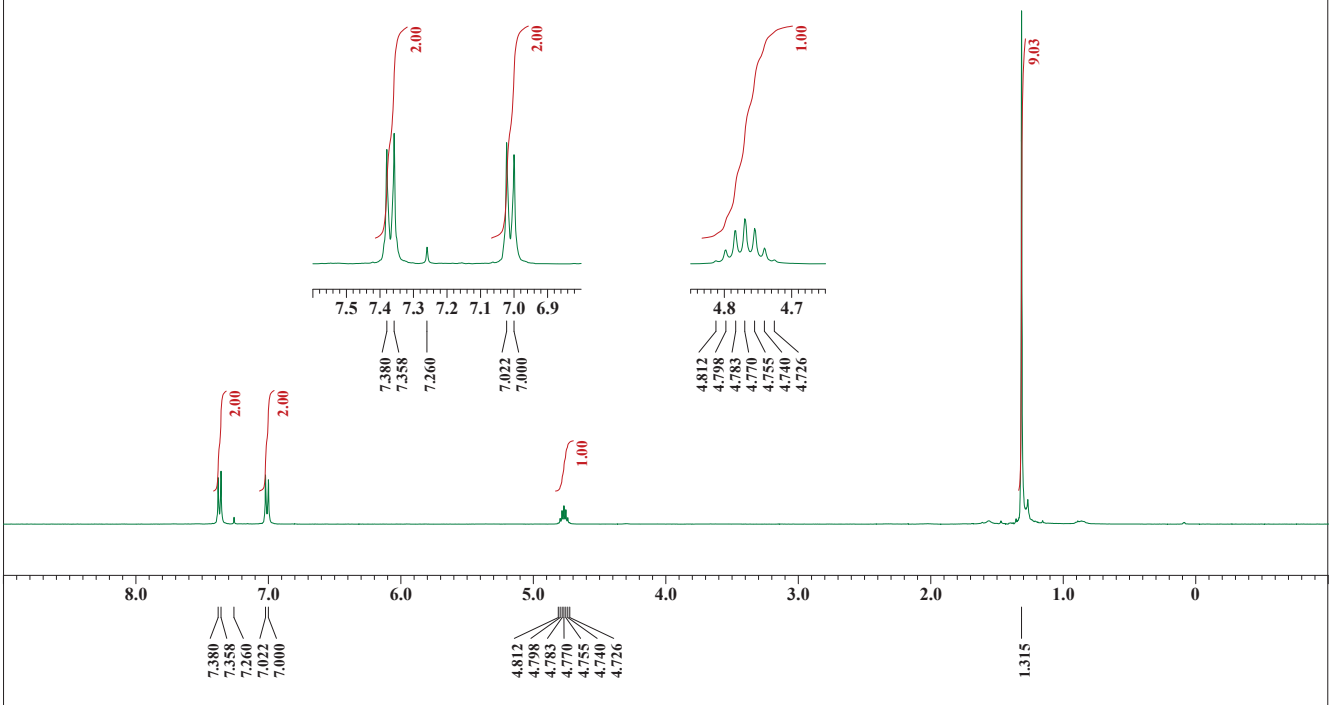
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



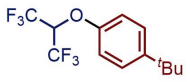
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-4-tert-butylbenzene (3bh)



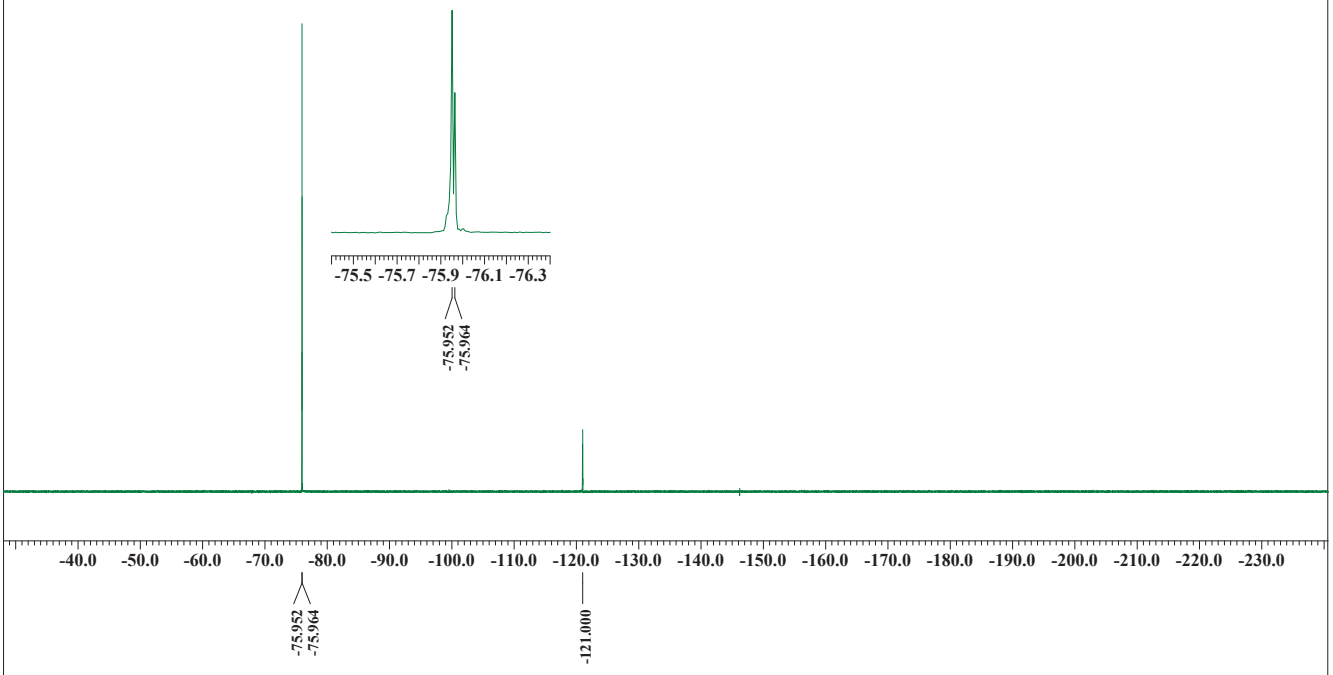
^{1}H NMR (400 MHz, $CDCl_3$)



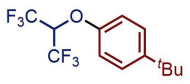
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-4-tert-butylbenzene (3bh)



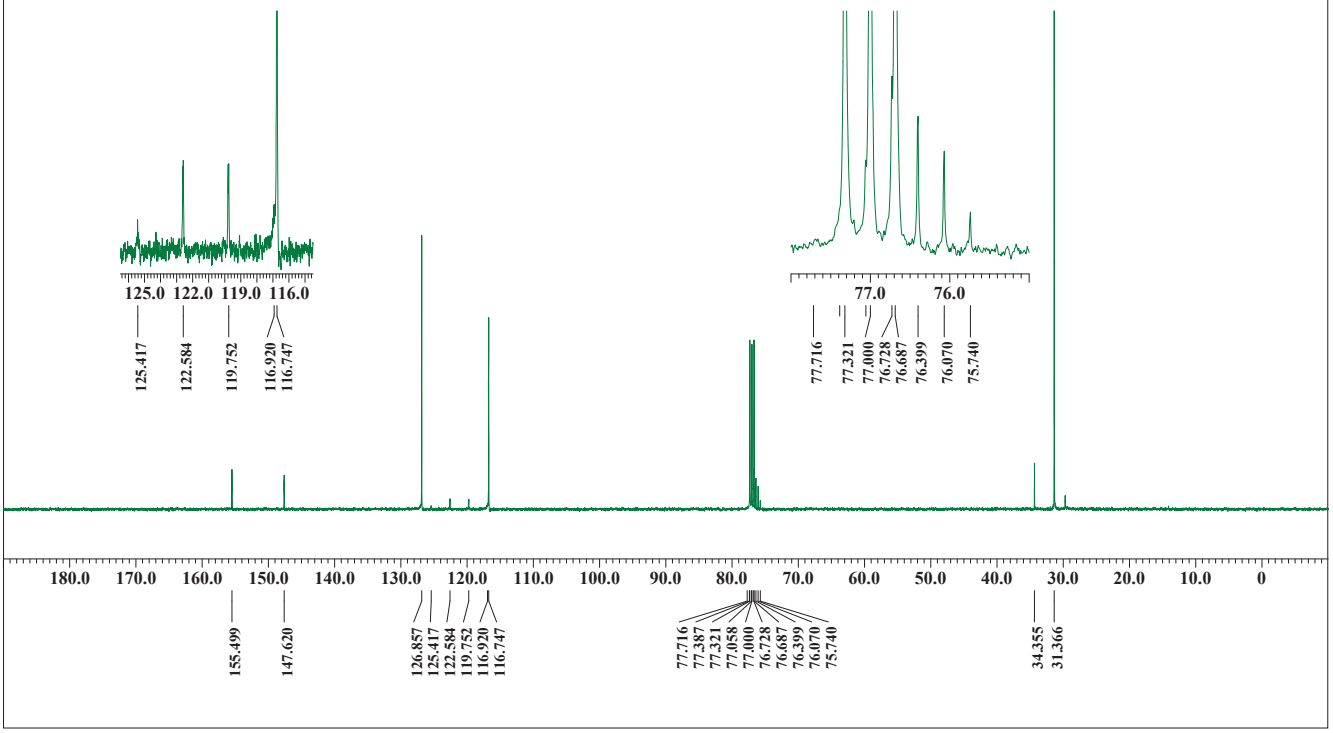
^{19}F NMR (376 MHz, $CDCl_3$)



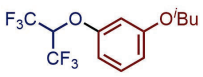
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-4-tert-butylbenzene (3bh)



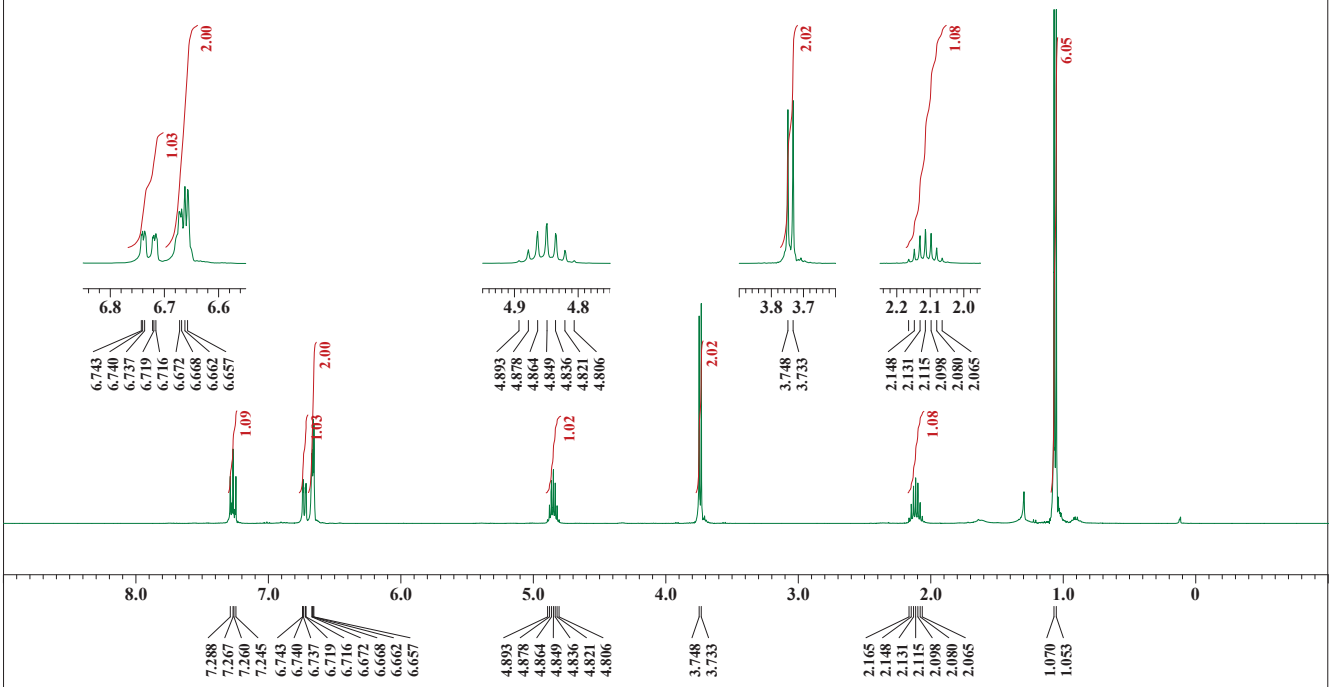
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



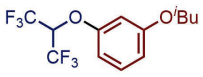
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-3-isobutoxybenzene (3bk)



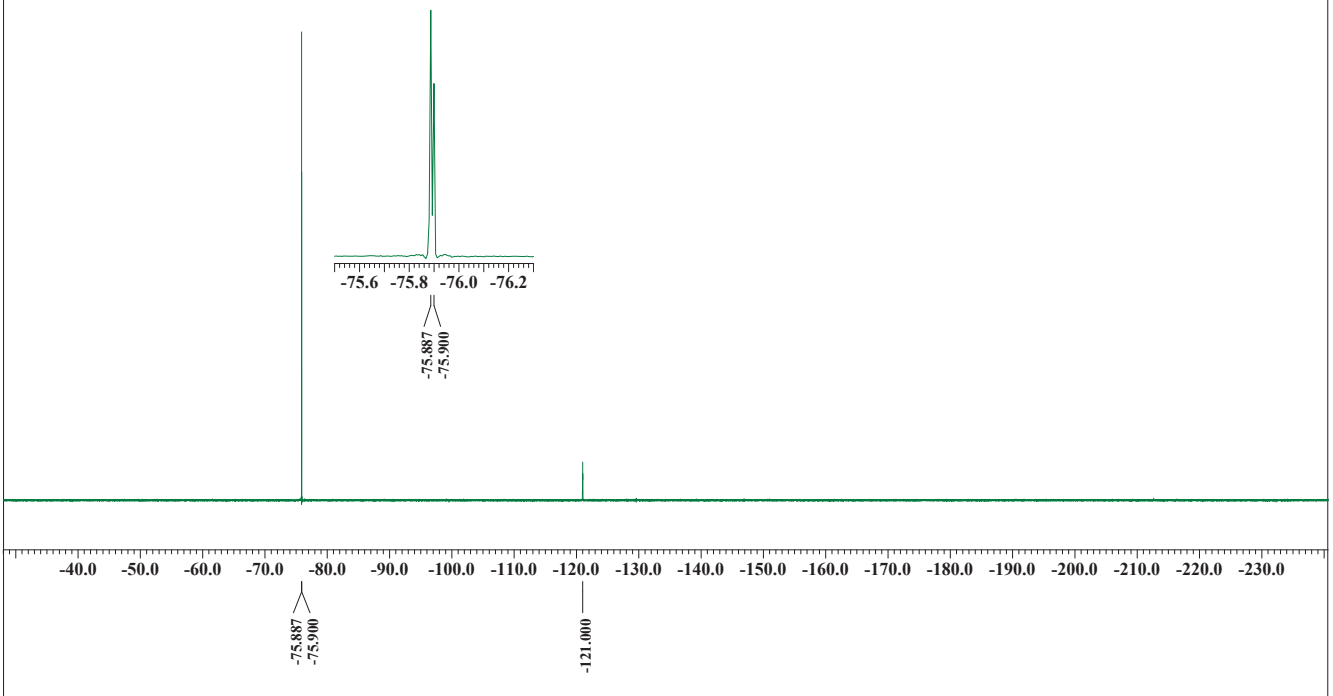
^{1}H NMR (400 MHz, $CDCl_3$)



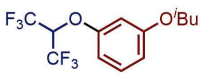
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-3-isobutoxybenzene (3bk)



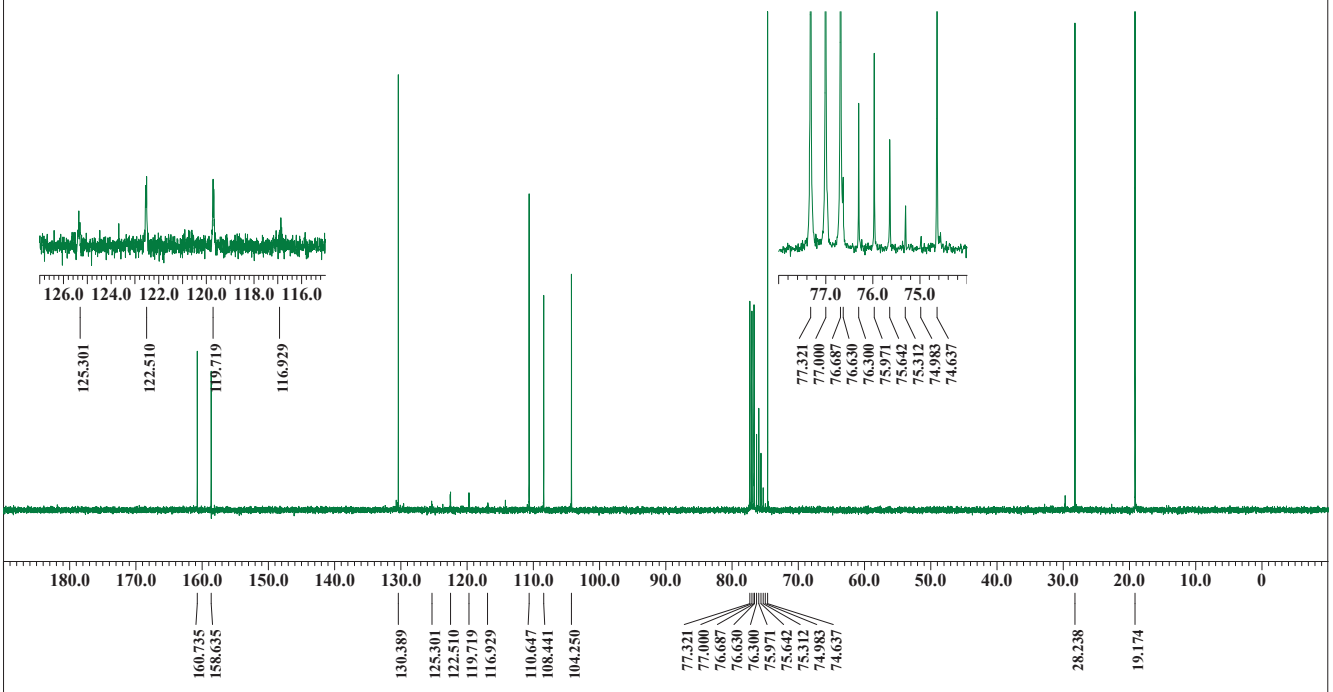
^{19}F NMR (376 MHz, $CDCl_3$)



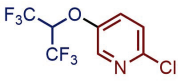
1-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-3-isobutoxybenzene (3bk)



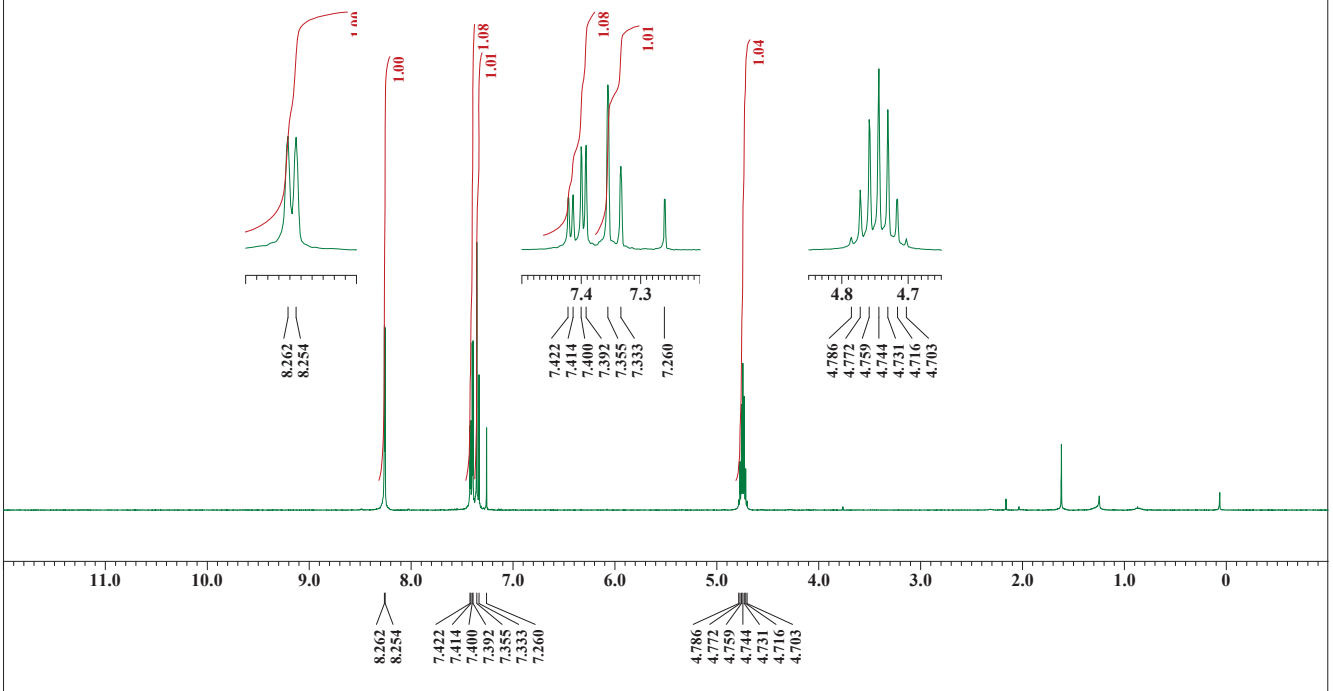
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



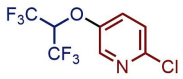
2-Chloro-5-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)pyridine (3bl)



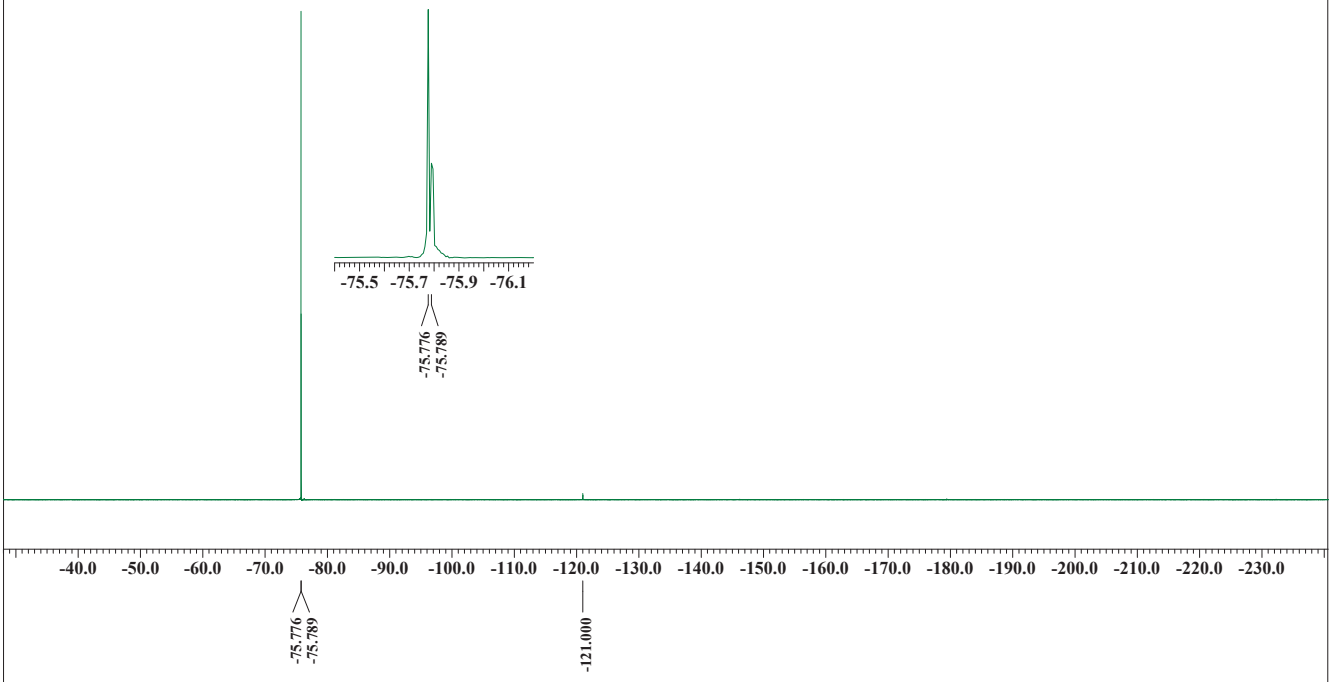
^{1}H NMR (400 MHz, $CDCl_3$)



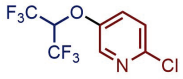
2-Chloro-5-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)pyridine (3bl)



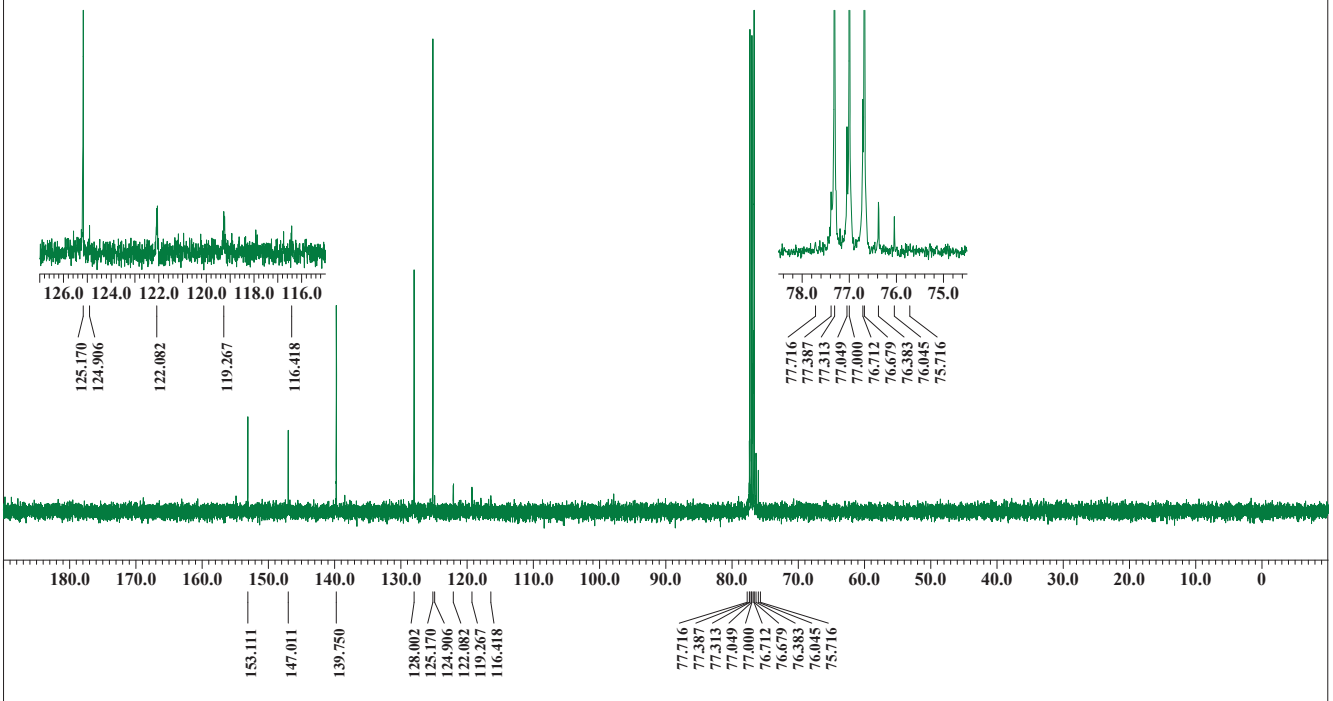
^{19}F NMR (376 MHz, $CDCl_3$)



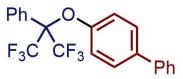
2-Chloro-5-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)pyridine (3bl)



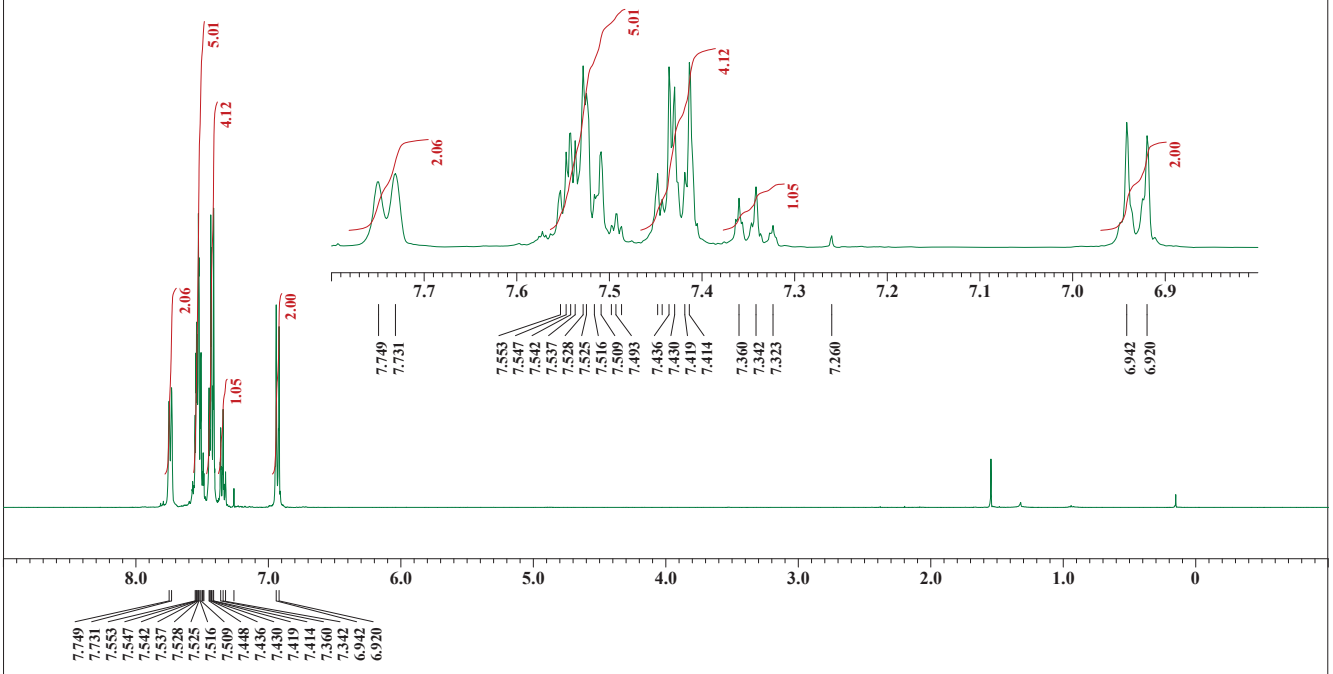
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)



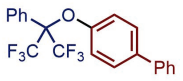
4-((1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-yl)oxy)-1,1'-biphenyl (3ca)



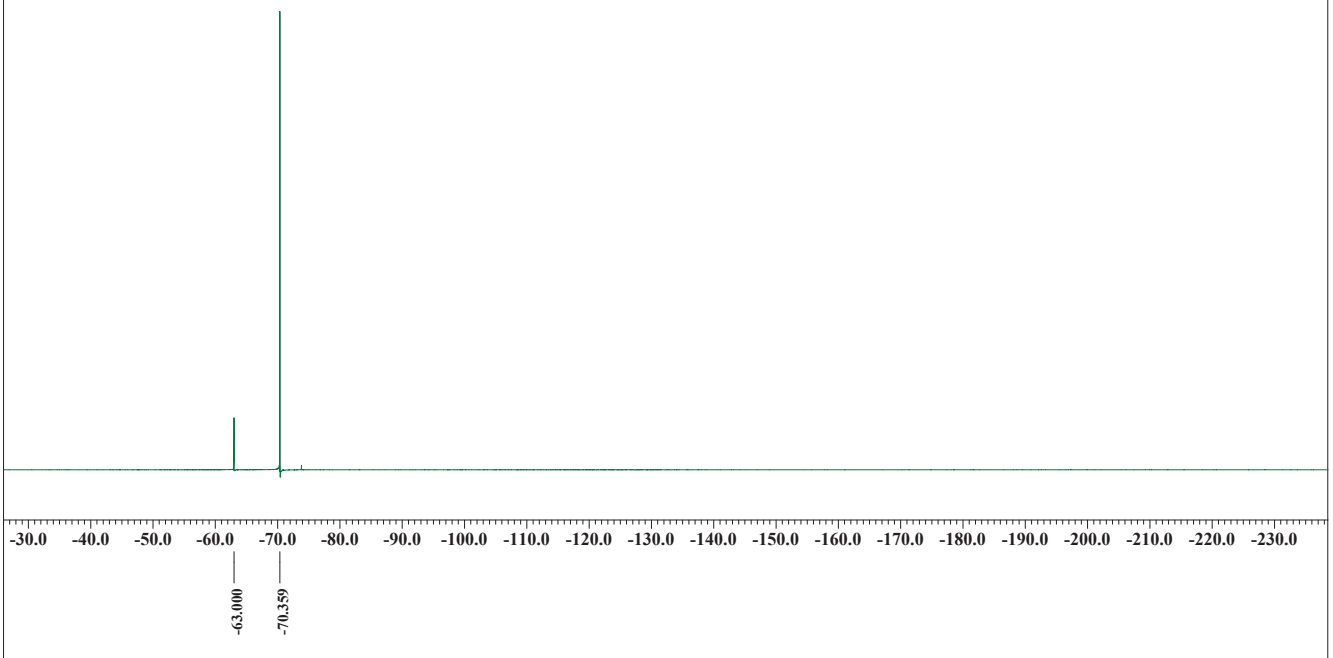
^{1}H NMR (400 MHz, $CDCl_3$)



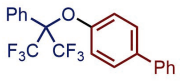
4-((1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-yl)oxy)-1,1'-biphenyl (3ca)



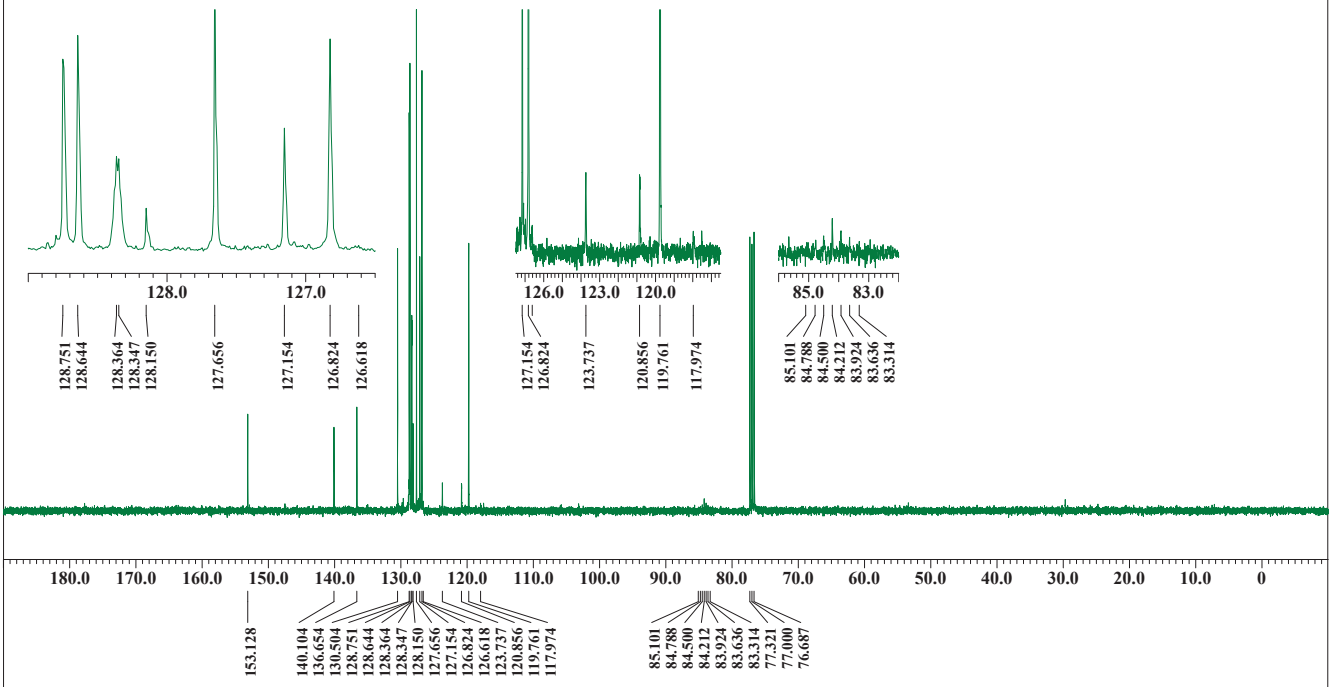
^{19}F NMR (376 MHz, $CDCl_3$)



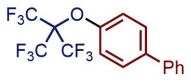
4-((1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-yl)oxy)-1,1'-biphenyl (3ca)



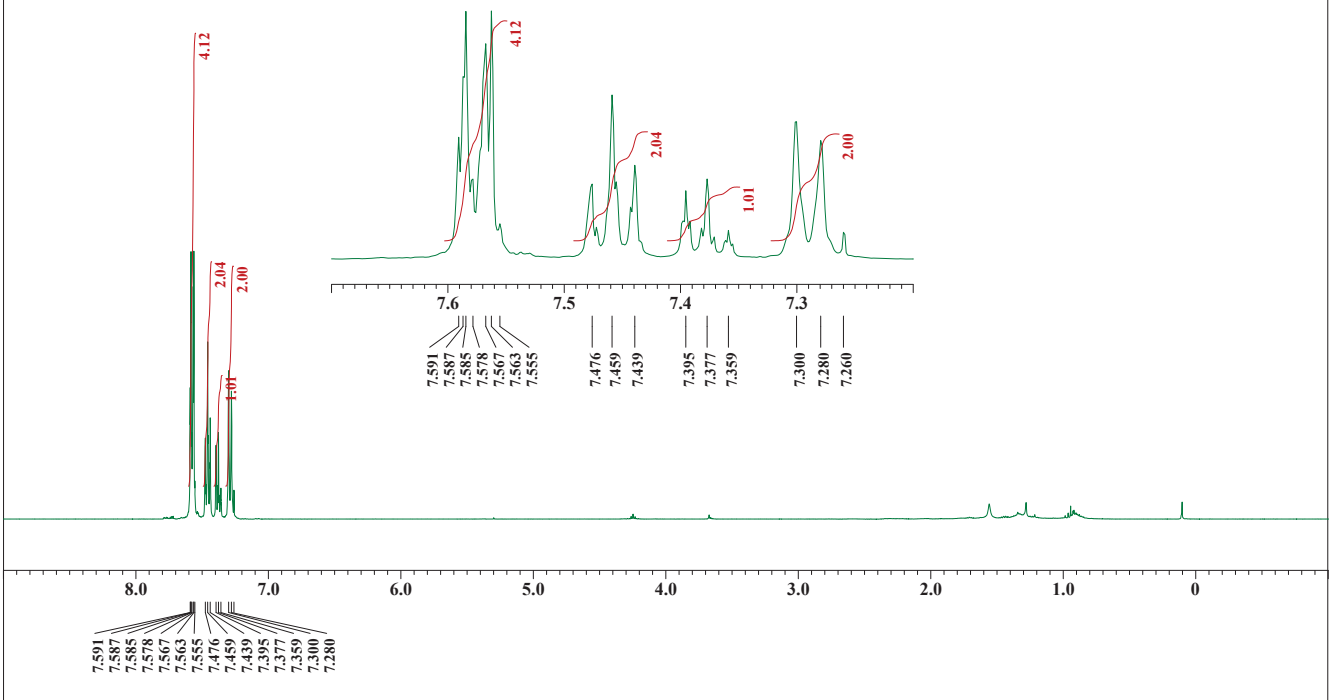
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



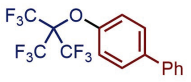
4-((1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)-1,1'-biphenyl (3da)



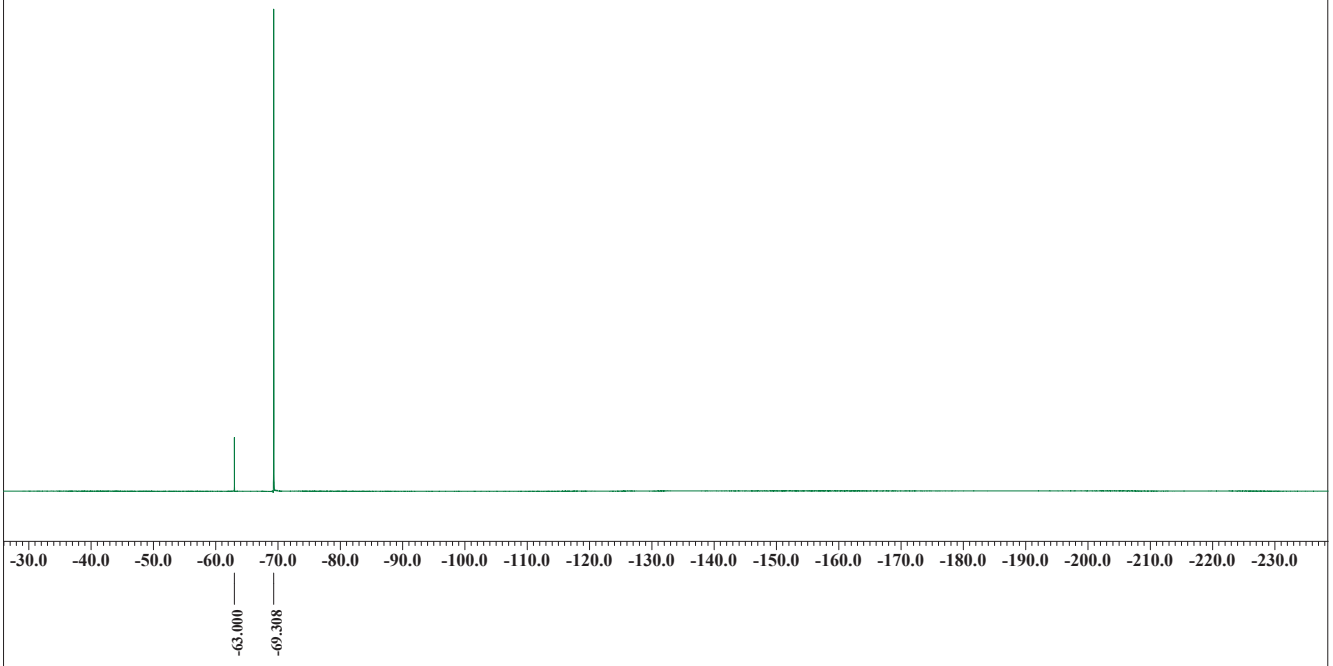
^{1}H NMR (400 MHz, $CDCl_3$)



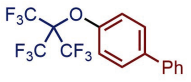
4-((1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)-1,1'-biphenyl (3da)



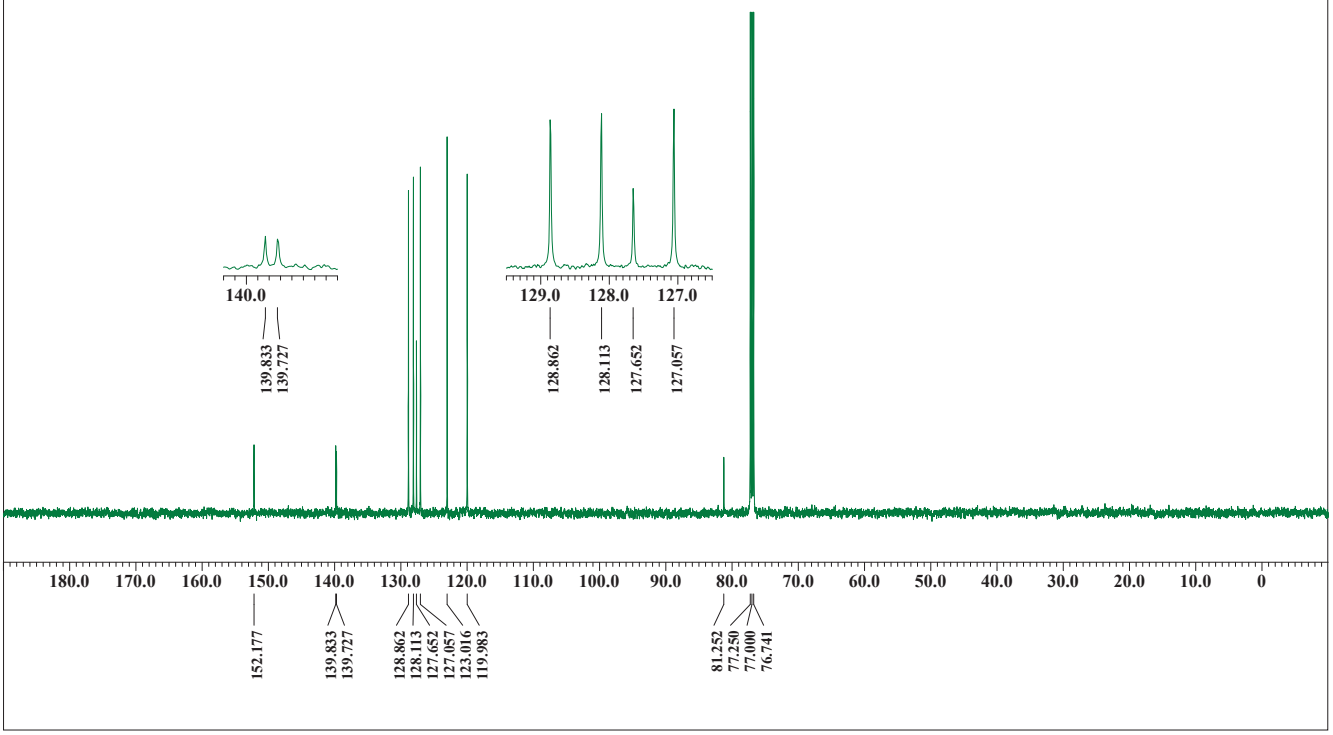
^{19}F NMR (376 MHz, $CDCl_3$)



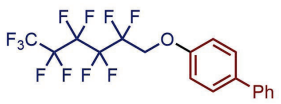
4-((1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl)oxy)-1,1'-biphenyl (3da)



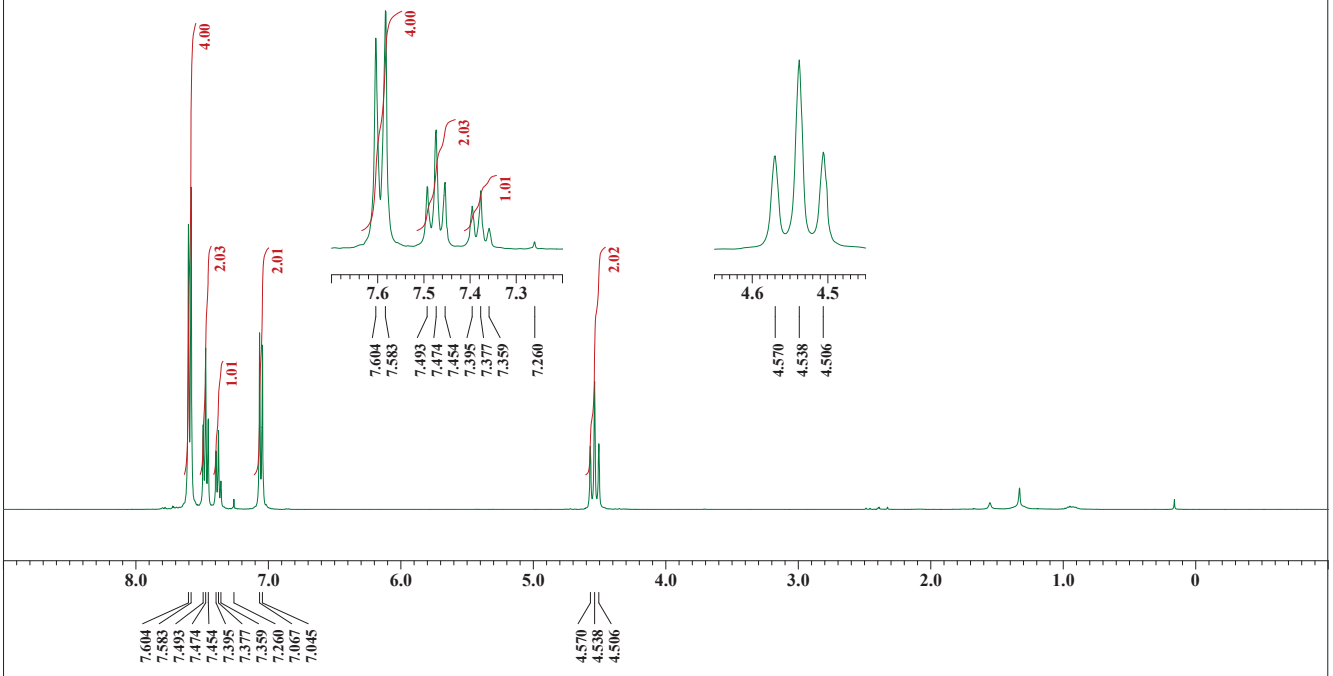
$^{13}C\{^{1}H,^{19}F\}$ NMR (125 MHz, $CDCl_3$)



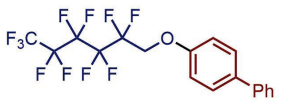
4-((2,2,3,3,4,4,5,5,6,6,6-Undecafluorohexyl)oxy)-1,1'-biphenyl (3ea)



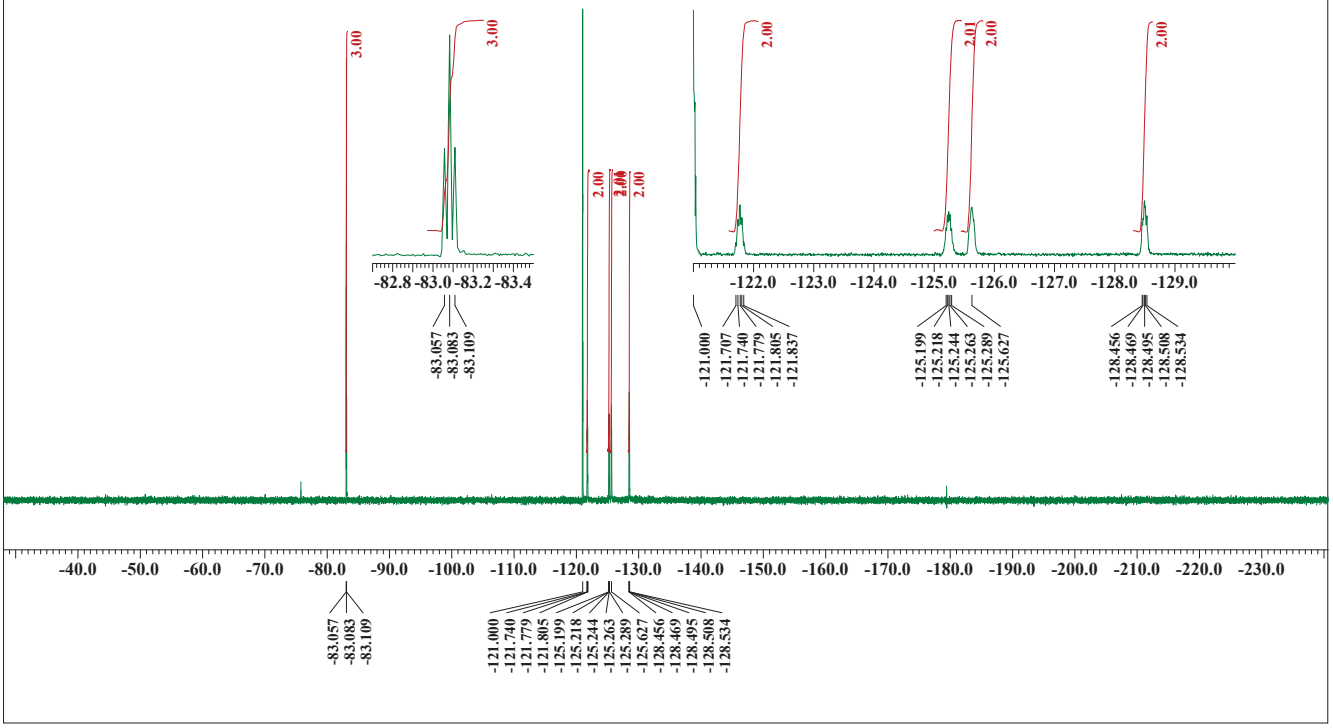
^{1}H NMR (400 MHz, $CDCl_3$)



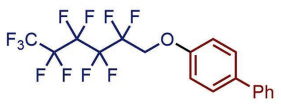
4-((2,2,3,3,4,4,5,5,6,6,6-Undecafluorohexyl)oxy)-1,1'-biphenyl (3ea)



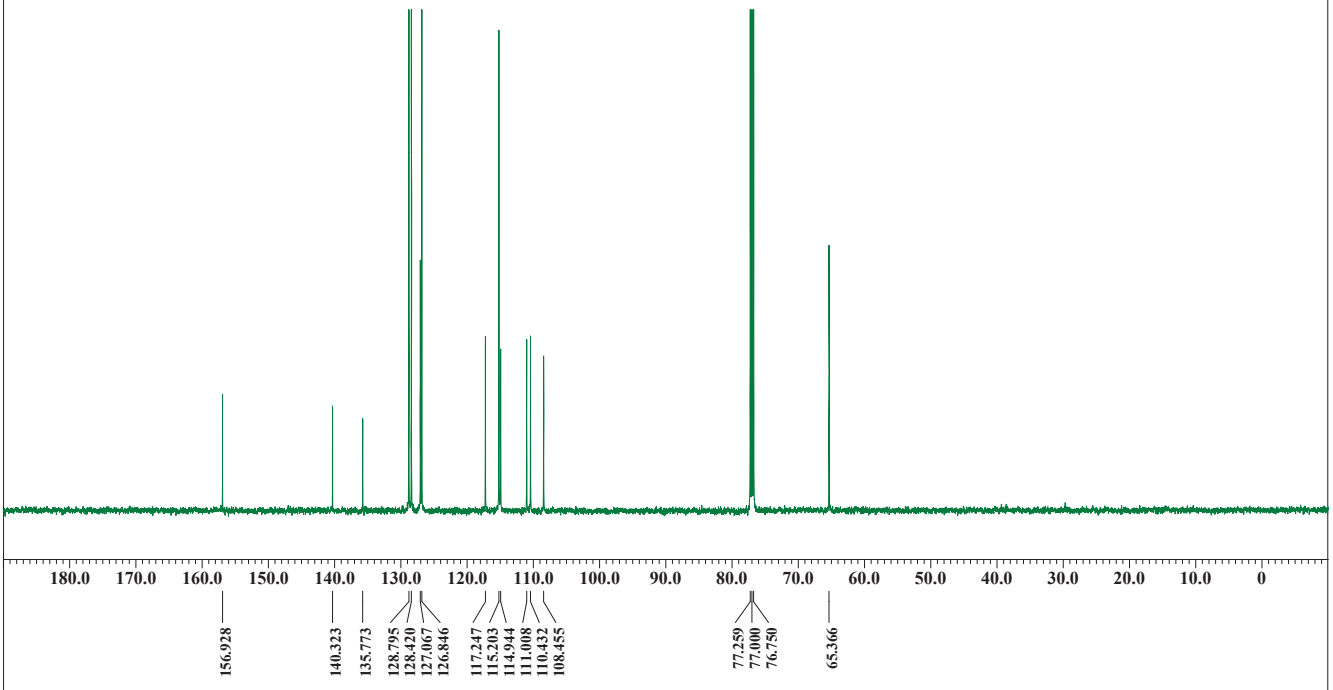
^{19}F NMR (376 MHz, $CDCl_3$)



4-((2,2,3,3,4,4,5,5,6,6,6-Undecafluorohexyl)oxy)-1,1'-biphenyl (3ea)



$^{13}C\{^{1}H,^{19}F\}$ NMR (125 MHz, $CDCl_3$)



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128.420
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111.008
110.432
108.455
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77.000
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65.366