# Supporting Information

## Direct Synthesis of Pentafluoroethyl Copper from Pentafluoropropionate as an Economical $C_2F_5$ Source: Application to Pentafluoroethylation of Arylboronic Acids and Aryl Bromides

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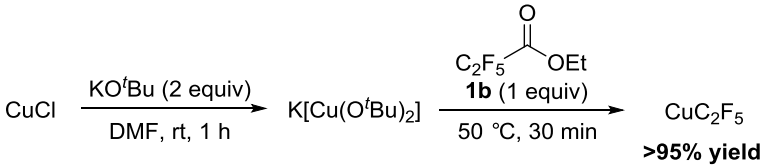
**General Information:**

$^{1}H$, $^{13}C$, and $^{19}F$ NMR spectra were measured on Bruker AV300M (300 MHz) spectrometers. Chemical shifts of $^{1}H$ NMR were expressed in parts per million relative to the singlet (δ = 7.26) for $CDCl_3$. Chemical shifts of $^{13}C$ NMR were expressed in parts per million relative to the central line of the triplet (δ = 77.0) for $CDCl_3$. Chemical shifts of $^{19}F$ NMR were expressed in parts per million relative to the singlet (δ = -63.24) for benzotrifluoride (BTF) as an external standard. IR spectra were measured on a JASCO FT/IR-4200 spectrometer. Mass spectra were measured on a JEOL JMS-T100CS (Accu-TOF) spectrometer. Optical rotations were measured on a JASCO P-1020. Potassium *tert*-butoxide (sublimed grade, 99.99% trace metals basis), sodium *tert*-butoxide (purification grade, 97%), lithium *tert*-butoxide (purification grade, 97%), and copper(I) chloride (anhydrous, beads, ≥99.99% trace basis) were purchased from Aldrich.

**Experimental Procedures:**

Ethyl pentafluoropropionate **1b** was purchased from TCI. Pentafluoropropionic anhydride **1f** and potassium pentafluoropropionate **1g** were purchased from Aldrich. Perfluoroalkyl ketones and **1a**,[1] **1c**,[1] **1d**,[2] and **1e**[3] were synthesized employing published procedures.

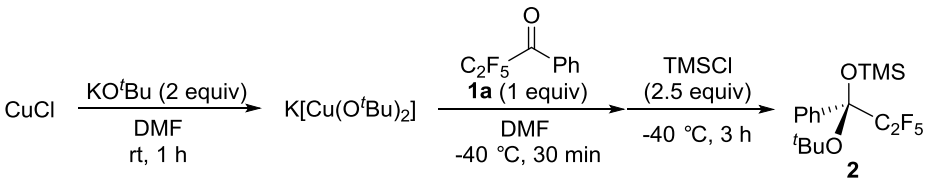
***Synthetic Procedure of $CuC_2F_5$ Reagent from Ethyl Pentafluoropropionate (Table 2, entry 3)***




A mixture of CuCl (50 mg, 0.50 mmol) and KO$^t$Bu (112 mg, 1.0 mmol) in DMF or DMF-$d_7$ (1 mL) was stirred for 1 hour at room temperature under argon atmosphere. To the mixture was added dropwise ethyl pentafluoropropionate **1b** (74 μL, 0.50 mmol) at 50 °C. After the reaction mixture was stirred for 30 min, $CuC_2F_5$ species was observed by $^{19}F$ NMR analysis using benzotrifluoride as an internal standard (>95% yield).

$^{13}C$ NMR (75 MHz, DMF-$d_7$) δ 124.6 (qt, $J_{CF}$ = 279.8, 30.2 Hz, $CF_3$), 140.8 (tq, $J_{CF}$ = 280.9, 49.3 Hz, $CF_2$); $^{19}F$ NMR (282 MHz, DMF-$d_7$) δ -84.4 (s, 3F), -111.7 (s, 2F).

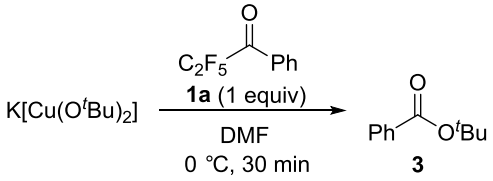
***Synthetic Procedure of (1-(tert-Butoxy)-2,2,3,3,3-pentafluoro-1-phenylpropoxy)trimethylsilane (2) (Scheme 1, Eq. 1)***




A mixture of CuCl (50 mg, 0.50 mmol) and KO$^t$Bu (112 mg, 1.0 mmol) in DMF (1 mL) was stirred for 1 hour at room temperature under argon atmosphere. To the mixture was added dropwise 2,2,3,3,3-pentafluoro-1-phenylpropan-1-one **1a** (112 mg, 0.50 mmol) at -40 °C. After the reaction mixture was stirred for 30 min, TMSCl (108 μL, 1.25 mmol) was added dropwise at the same temperature. After stirring for 3 hours, the reaction mixture was quenched by $H_2O$ (5 mL) at 0 °C. The organic layer was separated, and aqueous layer was extracted with $Et_2O$ (10 mL × 3). The

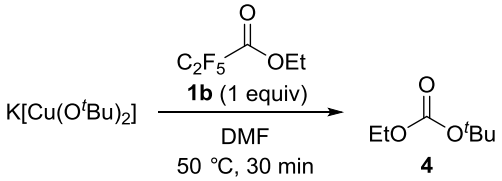
combined organic layer was washed with brine (10 mL), dried over $Na_2SO_4$, and evaporated. The resulting crude product was purified by silica-gel column chromatography (Hexane only) to give the product **2** (132 mg, 71% yield) as a colorless liquid.
$^1$H NMR (300 MHz, $CDCl_3$) δ 0.37 (s, 9H), 1.29 (s, 9H), 7.37-7.41 (m, 3H), 7.64-7.67 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 2.56-2.58 (m), 30.6, 77.9, 100.2 (dd, $J_{CF}$ = 26.2, 24.7 Hz), 112.1 (tq, $J_{CF}$ = 263.6, 33.8 Hz, *C*$F_2$), 119.2 (qt, $J_{CF}$ = 285.9, 35.9 Hz, *C*$F_3$), 127.4, 128.5, 129.1, 139.1; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -77.1 (s, 3F), -119.9 (d, $J_{FF}$ = 70.8 Hz, 1F), -119.9 (d, $J_{FF}$ = 71.0 Hz, 1F); HRMS (ESI-TOF) calcd for $C_{16}H_{23}F_5NaO_2Si$ $[M+Na]^+$: 393.1285, found: 393.1301; FT-IR (neat, $cm^{-1}$) 1180, 1227, 1257, 1653, 2979, 3065.

***Isolation of tert-Butyl Benzoate (3)***




A mixture of CuCl (50 mg, 0.50 mmol) and KO$^t$Bu (112 mg, 1.0 mmol) in DMF (1 mL) was stirred for 1 hour at room temperature under argon atmosphere. To the mixture was added dropwise 2,2,3,3,3-pentafluoro-1-phenylpropan-1-one **1a** (112 mg, 0.50 mmol) at 0 °C. After the reaction mixture was stirred for 30 min, and then quenched by 1M HCl aq. (5 mL) at 0 °C. The organic layer was separated, and aqueous layer was extracted with $Et_2O$ (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over $Na_2SO_4$, and evaporated. The resulting crude product was purified by silica-gel column chromatography (Hexane/AcOEt = 10/1) to give *tert*-butyl benzoate **3** (83.9 mg, 94% yield) as colorless liquid. *tert*-Butyl benzoate **3** is known compound, the following data is identical to those given in corresponding literature.[4]
$^1$H NMR (300 MHz, $CDCl_3$) δ 1.60 (s, 9H), 7.38-7.44 (m, 2H), 7.49-7.55 (m, 1H), 7.98-8.02 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 28.1, 80.89, 128.1, 129.4, 132.0, 132.4, 165.7.

***Isolation of tert-Butyl Ethyl Carbonate (4)***

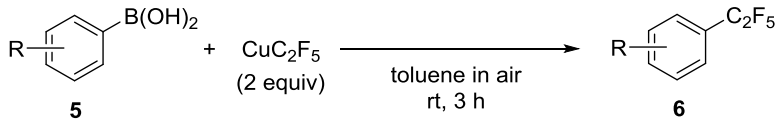



A mixture of CuCl (50 mg, 0.50 mmol) and KO$^t$Bu (112 mg, 1.0 mmol) in DMF (1 mL) was stirred for 1 hour at room temperature under argon atmosphere. To the mixture was added dropwise ethyl pentafluoropropionate **1b** (74 μL, 0.50 mmol) at 50 °C. After the reaction mixture was stirred for 30 min, and then quenched by 1M HCl aq. (5 mL) at 0 °C. The organic layer was separated, and aqueous layer was extracted with $Et_2O$ (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over $Na_2SO_4$, and evaporated. The resulting crude product was purified by silica-gel column chromatography (Pentane only) to give *tert*-butyl ethyl carbonate **4** (54.3 mg, 74% yield) as a colorless liquid. *tert*-Butyl ethyl carbonate **4** is known compound, the following data is identical to those given in corresponding literature.[5]
$^1$H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 9H), 4.07 (q, *J* = 7.1 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 14.2, 27.7, 62.8, 81.6, 153.5.

***Pentafluoroethylation of Arylboronic Acids***

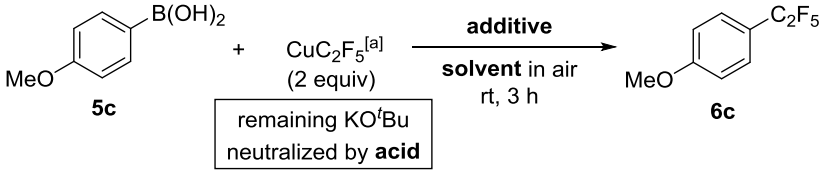
Boronic acid: **6a**, **6d-h,** and **6j** were purchased from Aldrich. **6b-6c** and **6i** were purchased from TCI. **6k** was synthesized employing published procedure.[6]

***Typical Procedure for Pentafluoroethylation of Arylboronic Acids with $CuC_2F_5$ Reagent (Scheme 2)***




To a solution of arylboronic acid **5** (0.1 mmol) in toluene (1 mL) was added $CuC_2F_5$ reagent (DMF solution 0.4-0.5 M, 400-500 μL, 0.2 mmol, prepared by CuCl, KO$^t$Bu, and ethyl pentafluoropropionate in DMF) neutralized by $Et_3N{\cdot}3HF$ (13 μL, 0.08 mmol) at room temperature in the air. After stirring for 3 hours, the reaction mixture was quenched by 1M HCl aq. (5 mL). The organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (5 mL × 3). The combined organic layer was washed with brine (10 mL), dried over $Na_2SO_4$, and evaporated. The resulting crude product was purified by silica-gel column chromatography to give the pentafluoroethylated products **6**.

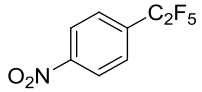
**Optimization of Reaction Conditions for Arylbronic Acid 5c Bearing Electron-Donating Substituent**




| entry | acid | additive | solvent | yield (%)[b] |
|---|---|---|---|---|
| 1 | $Et_3N{\cdot}HCl$ (2.4 equiv) | - | - | 71 |
| 2 | $Et_3N{\cdot}HCl$ (2.4 equiv) | - | DMF | 49 |
| 3 | $Et_3N{\cdot}HCl$ (2.4 equiv) | - | MeCN | 38 |
| 4 | $Et_3N{\cdot}HCl$ (2.4 equiv) | - | toluene | 63 |
| 5 | $Et_3N{\cdot}3HF$ (0.8 equiv) | - | toluene | 97(95[c]) |
| 6 | HCl in $Et_2O$ (2.4 equiv) | - | toluene | 54 |
| 7[d] | $Et_3N{\cdot}3HF$ (0.6 equiv) | - | toluene | 90 |
| 8[e] | $Et_3N{\cdot}3HF$ (0.5 equiv) | - | toluene | 80 |
| 9 | $Et_3N{\cdot}3HF$ (0.8 equiv) | $Et_3N$ (4 equiv) | toluene | 95 |
| 10 | $Et_3N{\cdot}3HF$ (0.8 equiv) | KCl (2 equiv) | toluene | 82 |
| 11 | $Et_3N{\cdot}3HF$ (0.8 equiv) | KCl (4 equiv) | toluene | 72 |
| 12 | $Et_3N{\cdot}3HF$ (0.8 equiv) | KF (2 equiv) | toluene | 89 |
| 13 | $Et_3N{\cdot}3HF$ (0.8 equiv) | KF (4 equiv) | toluene | 82 |

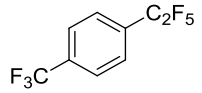
[a] $CuC_2F_5$ reagent neutralized by acid before being used in the reaction.
[b] Determined by $^{19}F$ NMR analysis using BTF as an internal standerd.
[c] Isolated yield. [d] $CuC_2F_5$ (1.5 equiv) was used. [e] $CuC_2F_5$ (1.2 equiv) was used.

**1-Nitro-4-(pentafluoroethyl)benzene (6a)**



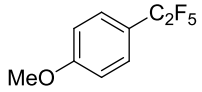
The title compound was obtained from 4-nitrophenylboronic acid **5a** following the procedure above. The yield of the compound (84% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (pentane/$Et_2O$ = 12/1) gave the compound (19.6 mg, 81% yield) as a yellow liquid.
$^1$H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, $J$ = 8.8 Hz, 2H), 8.38 (d, $J$ = 9.0 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 112.6 (tq, $J_{CF}$ = 253.7, 38.6 Hz, $CF_2$), 118.7 (qt, $J_{CF}$ = 284.4, 38.0 Hz, $CF_3$), 124.0, 128.0 (t, $J_{CF}$ = 5.8 Hz), 134.6 (t, $J_{CF}$ = 24.2 Hz), 150.2; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -84.5 (s, 3F), -115.4 (s, 2F); HRMS (ESI-TOF) calcd for $C_8H_3F_5NO_2$ $[M-H]^-$: 240.0084, found: 240.0096; FT-IR (neat, $cm^{-1}$) 1098, 1153, 1208, 1536, 1617, 3091.

**1-(Pentafluoroethyl)-4-(trifluoromethyl)benzene (6b)**



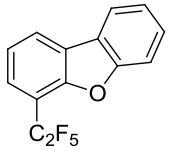
The title compound was obtained from 4-trifluoromethylphenylboronic acid **5b** following the procedure above. The yield (97% yield) was determined by $^{19}$F NMR analysis using (trifluoromethoxy)benzene as an internal standard. Purification by silica-gel column chromatography (pentane only) gave the compound as a colorless liquid in moderate yield (15.0 mg, 57% yield), because of the low boiling point compound.
$^1$H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, $J$ = 8.8 Hz, 2H), 7.79 (d, $J$ = 8.8 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 112.9 (tq, $J_{CF}$ = 254.4, 38.5 Hz, $CF_2$), 118.9 (qt, $J_{CF}$ = 286.0, 38.6 Hz, $CF_3$), 123.4 (q, $J_{CF}$ = 272.7 Hz, Ar-$CF_3$), 125.9 (q, $J_{CF}$ = 3.7 Hz), 127.2 (t, $J_{CF}$ = 6.2 Hz), 132.3 (t, $J_{CF}$ = 24.1 Hz), 134.2 (q, $J_{CF}$ = 33.1 Hz); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -63.4 (s, 3F), -84.8 (s, 3F), -115.5 (s, 2F); HRMS (ESI-TOF) calcd for $C_9H_3F_8$ $[M-H]^-$: 263.0107, found: 263.0107; FT-IR (neat, $cm^{-1}$) 910, 1213, 1635, 3154.

**1-Methoxy-4-(pentafluoroethyl)benzene (6c)**



The title compound was obtained from 4-methoxyphenylboronic acid **5c** following the procedure above. The yield (97% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (pentane only) gave the compound (21.6 mg, 95% yield) as a pale yellow liquid.
$^1$H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.99 (d, $J$ = 9.0 Hz, 2H), 7.52 (d, $J$ = 8.8 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 55.4, 113.6 (tq, $J_{CF}$ = 251.6, 38.0 Hz, $CF_2$), 114.1, 119.2 (qt, $J_{CF}$ = 284.0, 40.0 Hz, $CF_3$), 120.7 (t, $J_{CF}$ = 24.5 Hz), 128.0 (t, $J_{CF}$ = 5.9 Hz), 162.2; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -85.0 (s, 3F), -113.9 (s, 2F); HRMS (ESI-TOF) calcd for $C_9H_6F_5O$ $[M-H]^-$: 225.0339, found: 225.0347; FT-IR (neat, $cm^{-1}$) 1093, 1206, 1263, 1618, 2844, 3012.

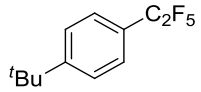
**4-(Pentafluoroethyl)dibenzo[b,d]furan (6d)**




The title compound was obtained from dibenzo[b,d]furan-4-ylboronic acid **5d** following the procedure above. The yield (93% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (hexane only) gave the compound (26.9 mg, 94% yield) as a white solid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.37-7.46 (m, 2H), 7.50-7.56 (m, 1H), 7.64-7.69 (m, 2H), 7.93-7.96 (m, 1H), 8.10 (d, $J$ = 7.8 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 112.1, 113.1 (t, $J_{CF}$ = 25.1 Hz), 113.3 (tq, $J_{CF}$ = 253.4, 39.2 Hz, $CF_2$), 119.4 (qt, $J_{CF}$ = 284.7, 38.6 Hz, $CF_3$), 120.7, 122.5, 122.8, 123.4, 124.5, 125.4 (t, $J_{CF}$ = 7.5 Hz), 126.2, 128.2, 152.9 (t, $J_{CF}$ = 3.0 Hz), 156.4; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -84.5 (s, 3F), -113.3 (s, 2F); HRMS (ESI-TOF) calcd for $C_{14}H_7F_5NaO$ $[M+Na]^+$: 309.0315, found: 309.0310; FT-IR (neat, $cm^{-1}$) 1184, 1200, 1425, 1610, 3077.

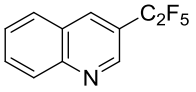
**1-(*tert*-Butyl)-4-(pentafluoroethyl)benzene (6e)**




The title compound was obtained from 4-*tert*-butylphenylboronic acid **5e** following the procedure above. The yield (96% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (pentane only) gave the compound (23.4 mg, 93% yield) as a colorless liquid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 9H), 7.53-7.59 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 31.1, 34.9, 113.7 (tq, $J_{CF}$ = 251.5, 38.0 Hz, $CF_2$), 119.3 (qt, $J_{CF}$ = 283.9, 39.5 Hz, $CF_3$), 125.7, 125.9, 126.2 (t, $J_{CF}$ = 5.9 Hz), 155.4 (t, $J_{CF}$ = 1.5 Hz); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -84.9 (s, 3F), -114.6 (s, 2F); HRMS (ESI-TOF) calcd for $C_{12}H_{14}F_5$ $[M+H]^+$: 253.1016, found: 253.1012; FT-IR (neat, $cm^{-1}$) 1113, 1207, 1616, 2968, 3064.

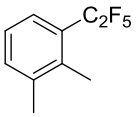
**3-(Pentafluoroethyl)quinoline (6f)**




The title compound was obtained from quinolin-3-ylboronic acid **5f** following the procedure above. The yield of the compound (83% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (hexane/AcOEt = 9/1) gave the compound (21.1 mg, 85% yield) as a pale yellow liquid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.64-7.69 (m, 1H), 7.84-7.94 (m, 1H), 7.93 (d, $J$ = 8.2 Hz, 1H), 8.20 (d, $J$ = 8.5 Hz, 1H), 8.44 (s, 1H), 9.06 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 113.3 (tq, $J_{CF}$ = 253.2, 38.8 Hz, $CF_2$), 119.0 (qt, $J_{CF}$ = 284.2, 38.6 Hz, $CF_3$), 121.8 (t, $J_{CF}$ = 24.0 Hz), 126.3, 128.0, 128.6, 129.6, 131.9, 135.6 (t, $J_{CF}$ = 6.8 Hz), 146.5 (t, $J_{CF}$ = 5.3 Hz), 149.4; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -84.7 (s, 3F), -114.7 (s, 2F); HRMS (ESI-TOF) calcd for $C_{11}H_7F_5N$ $[M+H]^+$: 248.0499, found: 248.0506; FT-IR (neat, $cm^{-1}$) 1092, 1207, 1498, 1574, 1607, 1626, 3063.

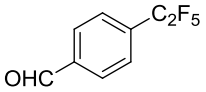
**1,2-Dimethyl-3-(pentafluoroethyl)benzene (6g)**




The title compound was obtained from 2,3-dimethylphenylboronic acid **5g** following the procedure above. The yield (87% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (pentane only) gave the compound (20.3 mg, 83% yield) as a colorless liquid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.38 (s, 3H), 7.21 (dd, $J$ = 7.9, 7.7 Hz, 1H), 7.35 (d, $J$ = 7.4 Hz, 1H), 7.43 (d, $J$ = 8.0 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 16.0-16.1 (m, 1C), 20.8, 115.0 (tq, $J_{CF}$ = 252.8, 38.3 Hz, $CF_2$), 119.6 (qt, $J_{CF}$ = 284.7, 39.2 Hz, $CF_3$), 125.5, 125.8 (t, $J_{CF}$ = 9.0 Hz), 126.9 (t, $J_{CF}$ = 21.1 Hz), 133.4, 136.5 (t, $J_{CF}$ = 2.0 Hz), 138.9; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -83.8 (s, 3F), -108.2 (s, 2F); HRMS (ESI-TOF) calcd for $C_{10}H_9F_5Na$ $[M+Na]^+$: 247.0522, found: 247.0533; FT-IR (neat, $cm^{-1}$) 1126, 1210, 1463, 2927, 3069.

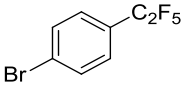
**4-(Pentafluoroethyl)benzaldehyde (6h)**




The title compound was obtained from 4-formylphenylboronic acid **5h** following the procedure above. The yield (91% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (pentane/$Et_2O$ = 9/1) gave the compound (20.0 mg, 89% yield) as a colorless liquid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, $J$ = 8.1 Hz, 2H), 8.02 (d, $J$ = 8.1 Hz, 2H), 10.1 (s, 1H); $^{13}$C NMR (282 MHz, $CDCl_3$) δ 112.9 (tq, $J_{CF}$ = 253.1, 38.3 Hz, $CF_2$), 118.8 (qt, $J_{CF}$ = 284.5, 38.3 Hz, $CF_3$), 127.3 (t, $J_{CF}$ = 6.3 Hz), 129.7, 134.0 (t, $J_{CF}$ = 23.8 Hz), 138.7, 191.1; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -84.6 (s, 3F), -115.5 (s, 2F); HRMS (APCI-TOF) calcd for $C_9H_6F_5O$ $[M+H]^+$: 225.0339, found: 225.0339; FT-IR (neat, $cm^{-1}$) 1097, 1265, 1653, 1705, 2987, 3055.

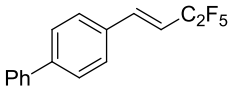
**1-Bromo-4-(pentafluoroethyl)benzene (6i)**




The title compound was obtained from 4-bromophenylboronic acid **5i** following the procedure above. The yield (98% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (pentane only) gave the compound (25.1 mg, 91% yield) as a pale yellow liquid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, $J$ = 8.4 Hz, 2H), 7.66 (d, $J$ = 8.3 Hz, 2H); $^{13}$C NMR (282 MHz, $CDCl_3$) δ 113.2 (tq, $J_{CF}$ = 252.5, 38.3 Hz, $CF_2$), 118.9 (qt, $J_{CF}$ = 284.1, 39.2 Hz, $CF_3$), 126.8 (t, $J_{CF}$ = 2.0 Hz), 127.7, 128.1 (t, $J_{CF}$ = 6.2 Hz), 132.1; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -84.9 (s, 3F), -115.2 (s, 2F); HRMS (ESI-TOF) calcd for $C_8H_3BrF_5$ $[M-H]^-$: 272.9338, found: 272.9335; FT-IR (neat, $cm^{-1}$) 1073, 1098, 1208, 1599, 3048.

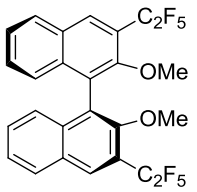
**(*E*)-4-(3,3,4,4,4-Pentafluorobut-1-en-1-yl)-1,1'-biphenyl (6j)**




The title compound was obtained from (*E*)-2-[1,1'-biphenyl]-4-ylvinylboronic acid **5j** following the procedure above. The yield (67% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (hexane only) gave the compound (21.1 mg, 71% yield) as a white solid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 6.25 (dt, $J$ = 16.2, $J_{HF}$ = 11.9 Hz, 1H), 7.26 (dt, $J$ = 16.2, $J_{HF}$ = 2.2 Hz, 1H), 7.38-7.68 (m, 9H); $^{13}$C NMR (282 MHz, $CDCl_3$) δ 112.8 (tq, $J_{CF}$ = 248.9, 38.3 Hz, $CF_2$), 113.8 (t, $J_{CF}$ = 23.0 Hz), 119.1 (qt, $J_{CF}$ = 283.8, 38.3 Hz, $CF_3$), 127.0, 127.6, 127.9, 128.1, 128.9, 132.4, 139.2 (t, $J_{CF}$ = 9.8 Hz), 140.0, 142.9; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -85.0 (s, 3F), -114.7 (d, $J_{FH}$ = 10.4 Hz, 2F); HRMS (ESI-TOF) calcd for $C_{16}H_{10}F_5$ $[M-H]^-$: 297.0703, found: 297.0699; FT-IR (neat, $cm^{-1}$) 1200, 1488, 1658, 3034.

**(*S*)-2,2'-Dimethoxy-3,3'-bis(pentafluoroethyl)-1,1'-binaphthalene (6k)**



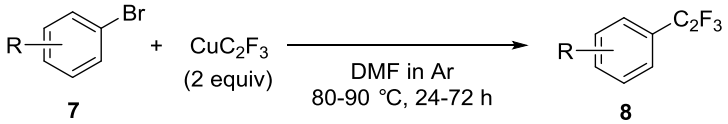

The title compound was obtained from (*S*)-(2,2'-dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)diboronic acid **5k** with $CuC_2F_5$ reagent (4 eq.) following the procedure above. The yield (90% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (hexane/AcOEt = 20/1) gave the compound (50.7 mg, 92% yield) as a white solid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 3.32 (s, 6H), 7.17 (d, $J$ = 8.4 Hz, 2H), 7.39-7.44 (m, 2H), 7.50-7.55 (m, 2H), 8.01 (d, $J$ = 8.2 Hz, 2H), 8.33 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 61.9, 113.9 (tq, $J_{CF}$ = 254.0, 39.2 Hz, $CF_2$), 119.4 (qt, $J_{CF}$ = 285.1, 38.5 Hz, $CF_3$), 122.1 (t, $J_{CF}$ = 22.1 Hz), 125.4, 125.8, 126.1, 129.0, 129.2, 129.4, 131.1 (t, $J_{CF}$ = 8.9 Hz), 135.8, 154.1; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -83.1 (s, 3F), -110.2 (d, $J_{FF}$ = 268.8 Hz, 1F), -111.21 (d, $J_{FF}$ = 268.8 Hz, 1F); HRMS (ESI-TOF) calcd for $C_{26}H_{16}F_{10}NaO_2$ $[M+Na]^+$: 573.0888, found: 573.0896; FT-IR (neat, $cm^{-1}$) 1154, 1200, 1625, 2853, 3065; $[\alpha]_D^{25}$ +68.5 (*c* 0.88, $CHCl_3$).

***Pentafluoroethylation of Aryl Bromides***

Aryl bromide substrates: **7b**, **7f-g**, **7i-j**, and **7l** were purchased from Aldrich. **7a**, **7c-e**, **7h**, and **7k** were purchased from TCI.

***Typical Procedure for Pentafluoroethylation of Aryl Bromides with $CuC_2F_5$ Reagent (Scheme 3)***

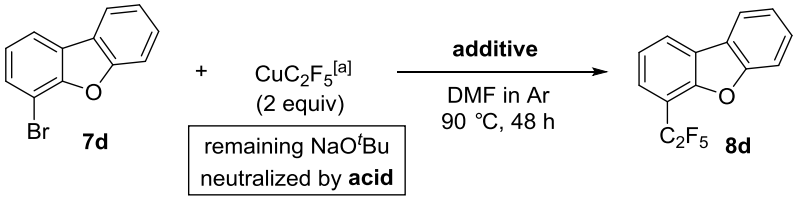



**7** **8**

A mixture of aryl bromide **7** (0.2 mmol) and $CuC_2F_5$ reagent (DMF solution 0.9-1.0 M, 400-444

μL, 0.4 mmol, prepared by CuCl, NaO$^t$Bu, and ethyl pentafluoropropionate in DMF) neutralized by $Et_3N{\cdot}3HF$ (26 μL, 0.16 mmol) was stirred for 24-72 hours at 80-90 °C under argon atmosphere. The reaction mixture was quenched by 1M HCl aq. (5 mL). The organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (5 mL × 3). The combined organic layer was washed with brine (10 ml), dried over $Na_2SO_4$, and evaporated. The resulting crude product was purified by silica-gel column chromatography to give the trifluoromethylated products **8**.

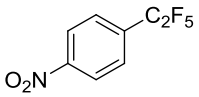
**Effect of Triethylamine in Pentafluoroethylation of Aryl Bromides**




| entry | acid | additive | yield (%)[b] |
|---|---|---|---|
| 1 | $Et_3N{\cdot}3HF$ (0.8 equiv) | $Et_3N$ (5 equiv) | 62 |
| 2 | $Et_3N{\cdot}3HF$ (0.8 equiv) | $Et_3N$ (2 equiv) | 70 |
| 3 | $Et_3N{\cdot}3HF$ (0.8 equiv) | - | 95 |

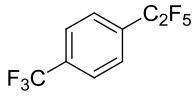
[a] $CuC_2F_5$ reagent neutralized by acid before being used in the reaction.
[b] Determined by $^{19}F$ NMR analysis using BTF as an internal standerd.

**1-Nitro-4-(pentafluoroethyl)benzene (8a) = (6a)**



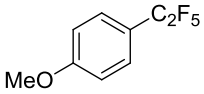

The title compound was obtained from 1-bromo-4-nitrobenzene **7a** at 80 °C for 24 hours following the procedure above. The yield (92% yield) was determined by $^{19}F$ NMR analysis using benzotrifluoride as an internal standard.

**1-(Pentafluoroethyl)-4-(trifluoromethyl)benzene (8b) = (6b)**



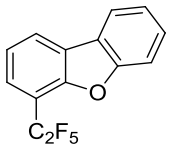

The title compound was obtained from 1-bromo-4-(trifluoromethyl)benzene **7b** at 80 °C for 48 hours following the procedure above. The yield (85% yield) was determined by $^{19}F$ NMR analysis using (trifluoromethoxy)benzene as an internal standard.

**1-Methoxy-4-(pentafluoroethyl)benzene (8c) = (6c)**



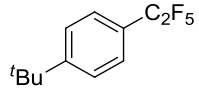

The title compound was obtained from 1-bromo-4-methoxybenzene **7c** at 90 °C for 72 hours following the procedure above. The yield (77% yield) was determined by $^{19}F$ NMR analysis using benzotrifluoride as an internal standard.

**4-(Pentafluoroethyl)dibenzo[*b,d*]furan (8d) = (6d)**



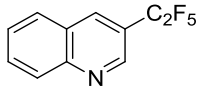

The title compound was obtained from 4-bromodibenzo[*b,d*]furan **7d** at 80 °C for 48 hours following the procedure above. The yield (98% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard.

**1-(*tert*-Butyl)-4-(pentafluoroethyl)benzene (8e) = (6e)**



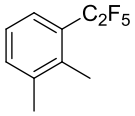

The title compound was obtained from 1-bromo-4-(*tert*-butyl)benzene **7e** at 90 °C for 72 hours following the procedure above. The yield (81% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard.

**3-(Pentafluoroethyl)quinoline (8f) = (6f)**



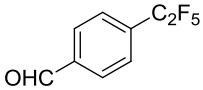

The title compound was obtained from 3-bromoquinoline **7f** at 90 °C for 48 hours following the procedure above. The yield (86% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard.

**1,2-Dimethyl-3-(pentafluoroethyl)benzene (8g) = (6g)**



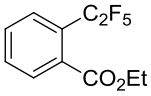

The title compound was obtained from 1-bromo-2,3-dimethylbenzene **7g** at 90 °C for 72 hours following the procedure above. The yield (60% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard.

**4-(Pentafluoroethyl)benzaldehyde (8h) = (6h)**



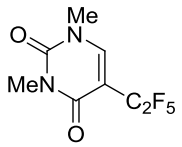

The title compound was obtained from 4-bromobenzaldehyde **7h** at 80 °C for 48 hours following the procedure above. The yield (92% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard.

**Ethyl 2-(pentafluoroethyl)benzoate (8i)**



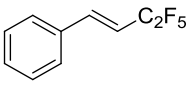
The title compound was obtained from ethyl 2-bromobenzoate **7i** at 80 °C for 24 hours following the procedure above. The yield (99% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (pentane/$Et_2O$ = 10/1) gave the compound (53.0 mg, 99% yield) as a pale yellow liquid. The compound **8i** is known compound, the following data is identical to those given in corresponding literature.[7]
$^1$H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H), 4.37 (q, *J* = 7.1 Hz, 2H), 7.53-7.64 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 13.8, 62.1, 113.6 (tq, $J_{CF}$ = 254.0, 38.9 Hz, *C*$F_2$), 119.0 (qt, $J_{CF}$ = 285.2, 38.5 Hz, *C*$F_3$), 125.9 (t, $J_{CF}$ = 23.4 Hz), 128.1 (t, $J_{CF}$ = 7.1 Hz), 129.0, 130.1, 131.8, 133.6 (t, $J_{CF}$ = 3.2 Hz), 167.8; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -83.2 (s, 3F), -108.5 (s, 2F).

**1,3-Dimethyl-5-(pentafluoroethyl)pyrimidine-2,4(1*H*,3*H*)-dione (8j)**



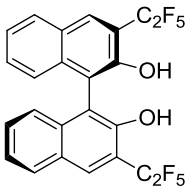

The title compound was obtained from 5-bromo-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione **7j** at 90 °C for 72 hours following the procedure above. The yield (90% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (hexane/AcOEt = 1/1) gave the compound (44.1 mg, 85% yield) as a yellow solid.
$^1$H NMR (300 MHz, $CDCl_3$) δ 3.33 (s, 3H), 3.49 (s, 3H), 7.64 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 28.0, 37.8, 101.8 (t, $J_{CF}$ = 23.9 Hz), 111.9 (tq, $J_{CF}$ = 254.2, 40.5 Hz, *C*$F_2$), 118.8 (qt, $J_{CF}$ = 284.9, 39.1 Hz, *C*$F_3$), 145.4 (t, $J_{CF}$ = 10.1 Hz), 150.8, 158.4 (t, $J_{CF}$ = 1.9 Hz); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -83.8 (s, 3F), -113.9 (s, 2F); HRMS (ESI-TOF) calcd for $C_8H_6F_5N_2O_2$ $[M-H]^-$: 257.0349, found: 257.03418; FT-IR (neat, $cm^{-1}$) 1120, 1195, 1462, 1680, 1715, 2963, 3069.

**(3,3,4,4,4-pentafluorobut-1-en-1-yl)benzene (8k)**




The title compound was obtained from (2-bromovinyl)benzene **7k** (*E*:*Z* = 12:1) at 90 °C for 60 hours following the procedure above. The yield (79% yield) was determined by $^{19}$F NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (pentane only) gave the compound (33.1 mg, 74% yield, *E*:*Z* = 12:1) as a colorless liquid.
$^1$H NMR (300 MHz, $CDCl_3$) δ 6.20 (dt, *J* = 16.2, 11.9 Hz, 1H), 7.20 (d, *J* = 16.2, 2.3 Hz, 1H), 7.38-7.50 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 112.8 (tq, $J_{CF}$ = 248.8, 38.3 Hz, *C*$F_2$), 114.1 (t, $J_{CF}$ = 23.0 Hz), 119.1 (qt, $J_{CF}$ = 283.7, 38.3 Hz, *C*$F_3$), 127.6, 129.0, 130.2, 133.5, 139.7 (t, $J_{CF}$ = 4.5 Hz); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -85.1 (s, 3F, *E* isomer), -85.6 (s, 3F, *Z* isomer), -109.3 (d, $J_{FH}$ = 15.1 Hz, 2F, *Z* isomer), -114.9 (d, $J_{FH}$ = 12.0 Hz, 2F, *E* isomer); HRMS (APCI-TOF) calcd for $C_{10}H_7F_5$ $[M+H]^+$: 223.0546, found: 223.0543; FT-IR (neat, $cm^{-1}$) 973, 1199, 1496, 1659, 2856, 2928.

**(*R*)-3,3'-Bis(pentafluoroethyl)-[1,1'-binaphthalene]-2,2'-diol (8l)**

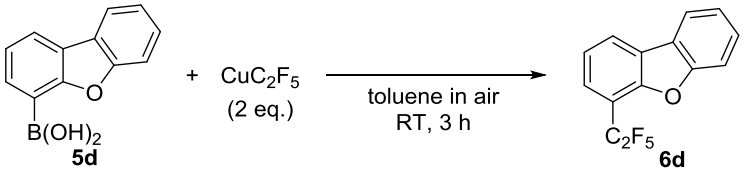



The title compound was obtained from (*R*)-3,3'-dibromo-1,1'-binaphthalene-2,2'-diol **7k** with $CuC_2F_5$ reagent (4 eq.) at 90 °C for 72 hours following the procedure above. The yield (66% yield) was determined by $^{19}F$ NMR analysis using benzotrifluoride as an internal standard. Purification by silica-gel column chromatography (hexane/AcOEt = 12/1) gave the compound (63.9 mg, 61% yield) as a white solid.

$^1H$ NMR (300 MHz, $CDCl_3$) δ 5.38 (s, 2H), 7.11 (d, $J$ = 8.2 Hz, 2H), 7.43-7.53 (m, 4H), 8.02 (d, $J$ = 7.4 Hz, 2H), 8.37 (s, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 112.6, 113.6 (tq, $J_{CF}$ = 254.3, 39.6 Hz, $CF_2$), 116.8 (t, $J_{CF}$ = 22.9 Hz), 119.3 (qt, $J_{CF}$ = 285.2, 38.6 Hz, $CF_3$), 123.8, 125.5, 128.0, 129.7, 130.2, 132.5 (t, $J_{CF}$ = 8.3 Hz), 134.8, 150.0; $^{19}F$ NMR (282 MHz, $CDCl_3$) δ -83.5 (s, 6F), -111.6 (s, 4F); HRMS (ESI-TOF) calcd for $C_{24}H_{11}F_{10}O_2$ $[M-H]^-$: 521.0599, found: 521.0596; FT-IR (neat, $cm^{-1}$) 1146, 1199, 1626, 3063, 3357, 3531; $[\alpha]_D^{25}$ +34.3 (*c* 1.25, $CHCl_3$).

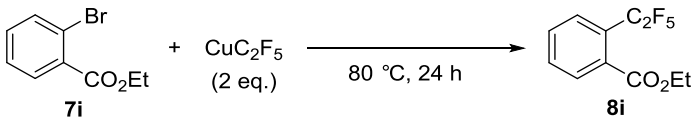
***Large Scale Operation of Pentafluoroethylation (Scheme 4)***

**Pentafluoroethylation of Arylboronic Acid 5d**




A mixture of CuCl (2.1 g, 21 mmol) and KO$^t$Bu (4.7 g, 42 mmol) in DMF (42 mL) was stirred for 1 hour at room temperature under argon atmosphere. To the mixture was added dropwise ethyl pentafluoropropionate **1b** (3.1 mL, 21 mmol) at 50 °C. After the reaction mixture was stirred for 30 min, $CuC_2F_5$ species was observed by $^{19}F$ NMR analysis using benzotrifluoride as an internal standard (>95% yield). To the mixture was added $Et_3N{\cdot}3HF$ (1.4 mL, 8.4 mmol) at 0 °C for the neutralization of $CuC_2F_5$ reagent. A solution of dibenzo[b,d]furan-4-ylboronic acid **5d** (2.1 g, 10 mmol) in toluene (100 mL) was added to the mixture at room temperature in the air. After stirring for 3 hours, the reaction mixture was quenched by 1M HCl aq. (50 mL). The organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (50 mL × 3). The combined organic layer was washed with brine (80 mL), dried over $Na_2SO_4$, and evaporated. The resulting crude product was purified by silica-gel column chromatography (hexane only) to give the pentafluoroethylated product **6d** (2.4 g, 84% yield) as a white solid.

**Pentafluoroethylation of Aryl Bromide 7i**




A mixture of CuCl (2.1 g, 21 mmol) and NaO$^t$Bu (4.0 g, 42 mmol) in DMF (10 mL) was stirred

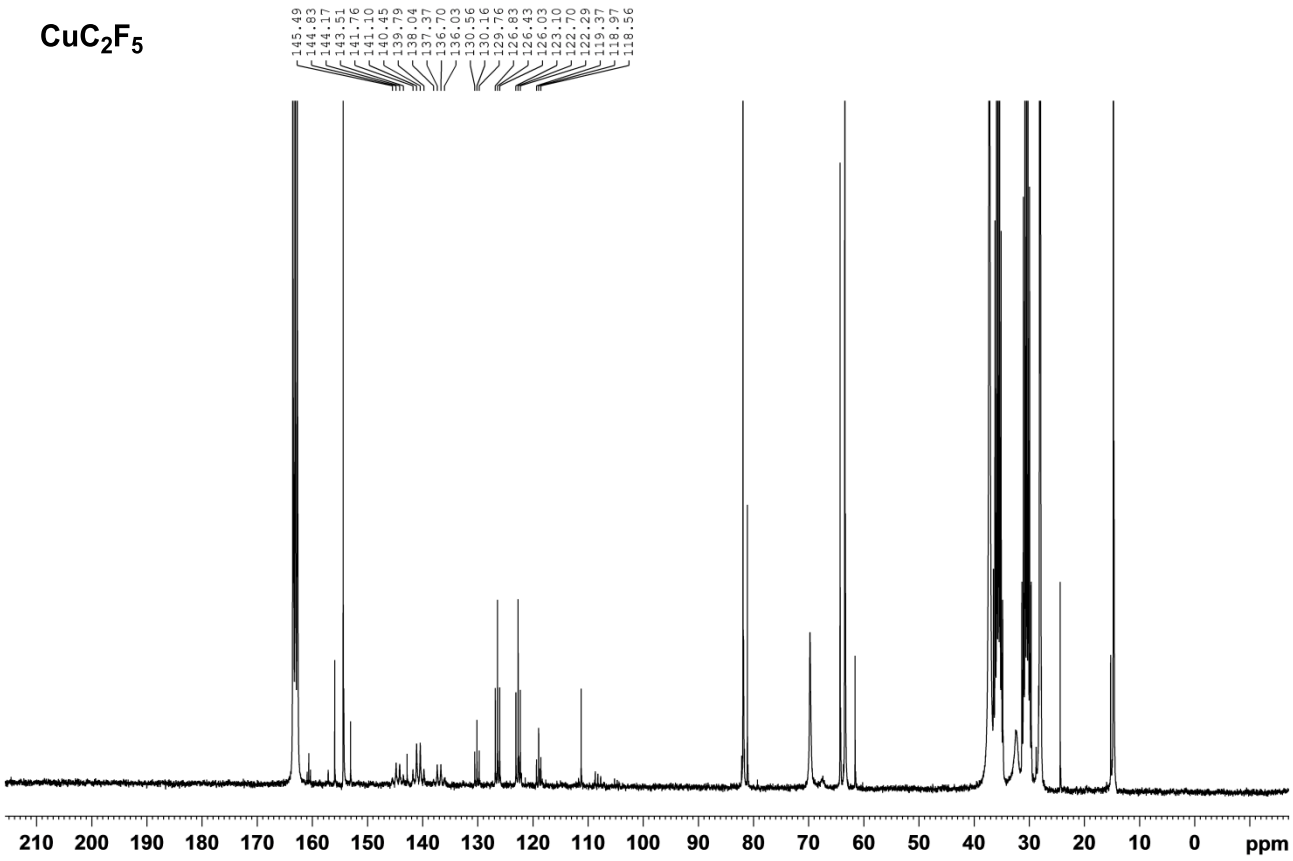
for 1 hour at room temperature under argon atmosphere. To the mixture was added dropwise ethyl pentafluoropropionate **1b** (3.1 mL, 21 mmol) at 50 °C. After the reaction mixture was stirred for 2 h, $CuC_2F_5$ species was observed by $^{19}F$ NMR analysis using benzotrifluoride as an internal standard (>95% yield). To the mixture was added $Et_3N{\cdot}3HF$ (1.4 mL, 8.4 mmol) at 0 °C for the neutralization of $CuC_2F_5$ reagent. Ethyl 2-bromobenzoate **7i** (2.2 g, 10 mmol) was added to the mixture at room temperature under argon atmosphere. After stirring at 80 °C for 24 hours, the reaction mixture was quenched by 1M HCl aq. (50 mL). The organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (50 mL × 3). The combined organic layer was washed with brine (80 mL), dried over $Na_2SO_4$, and evaporated. The resulting crude product was purified by silica-gel column chromatography (pentane/$Et_2O$ = 10/1) to give the pentafluoroethylated product **8i** (2.6 g, 98% yield) as a pale yellow liquid.

**References**


[1] Ramachandran, P. V.; Teodorovic, A. V.; Brown, H. C. *Tetrahedron* **1993**, *49*, 1725.
[2] Xue, C.; He, G.; Fu, C.; Xue, L.; Lin, Z.; Ma, S. *Eur. J. Org. Chem.* **2010**, 7012.
[3] Uno, H.; Shiraishi, Y.; Simokawa, K.; Suzuki, H. *Chem. Lett.* **1987**, 1153.
[4] Xin, Z.; Gogsig, T. M.; Lindhardt, A. T.; Skrydstrup, T. *Org. Lett.* **2012**, *14*, 284.
[5] White, E. H.; Field, K. W. *J. Am. Chem. Soc.* **1975**, *97*, 2148.
[6] Wipf, P.; Jung, J.-K. *J. Org. Chem.* **2000**, *65*, 6319.
[7] Popov, I.; Lindeman, S.; Daugulis, O. *J. Am. Chem. Soc.* **2011**, *133*, 9286.

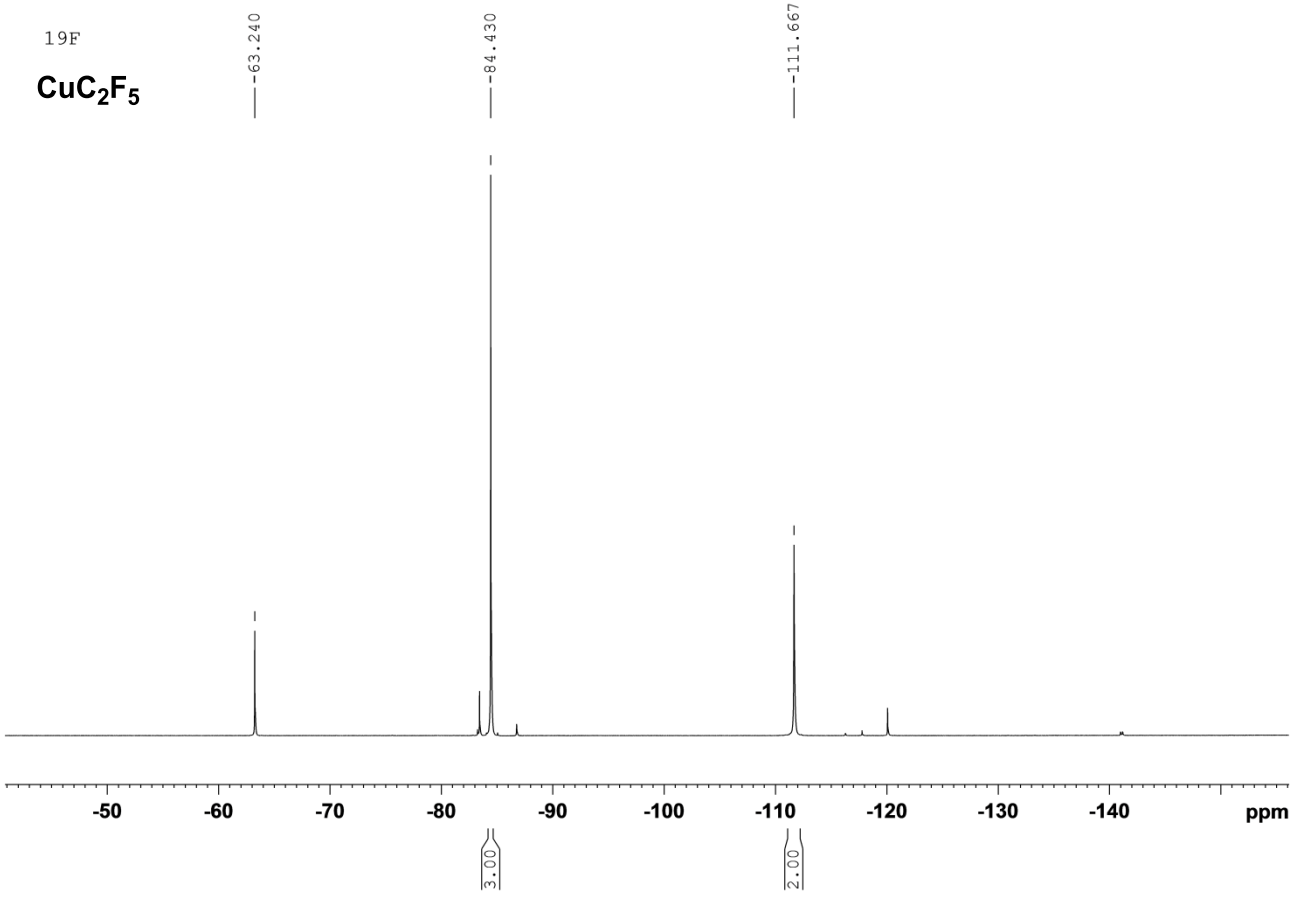
13C

$CuC_2F_5$

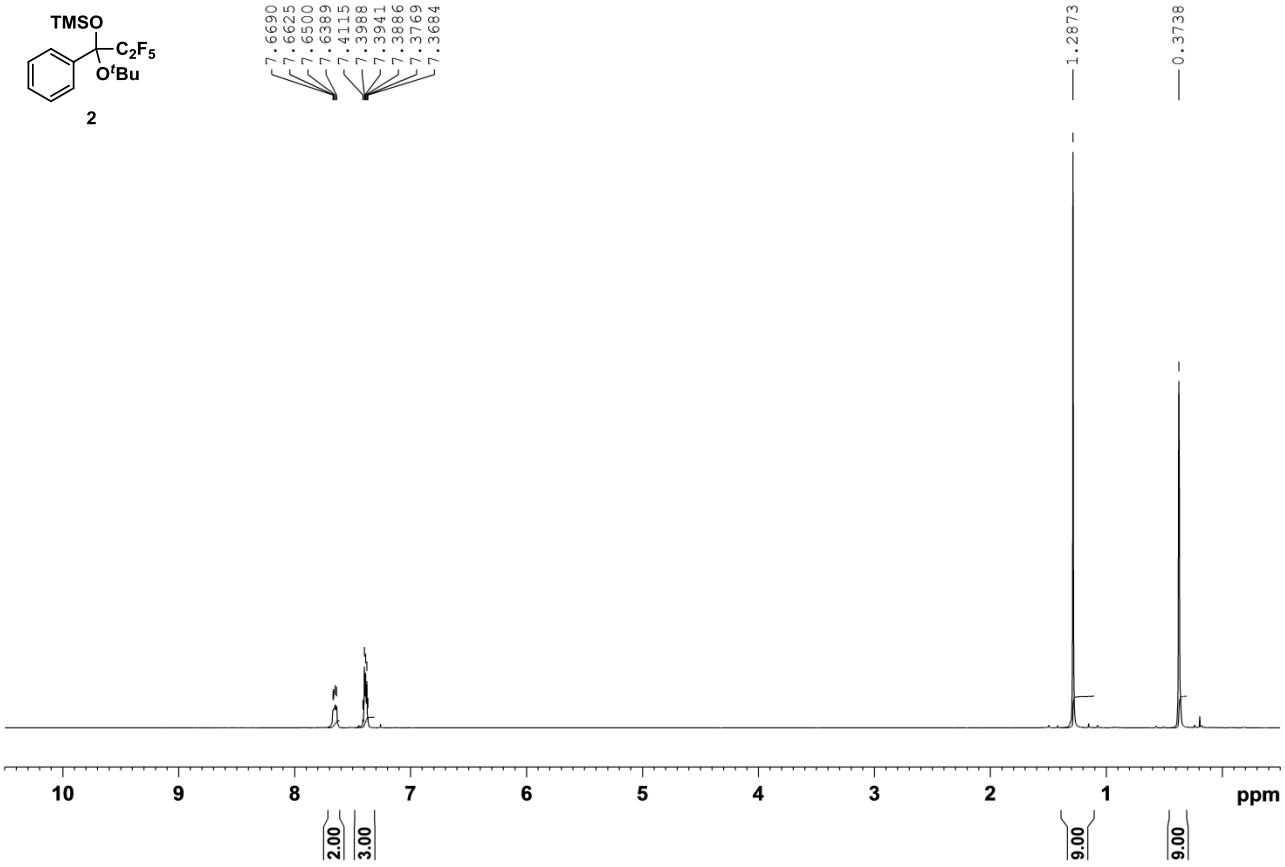



19F

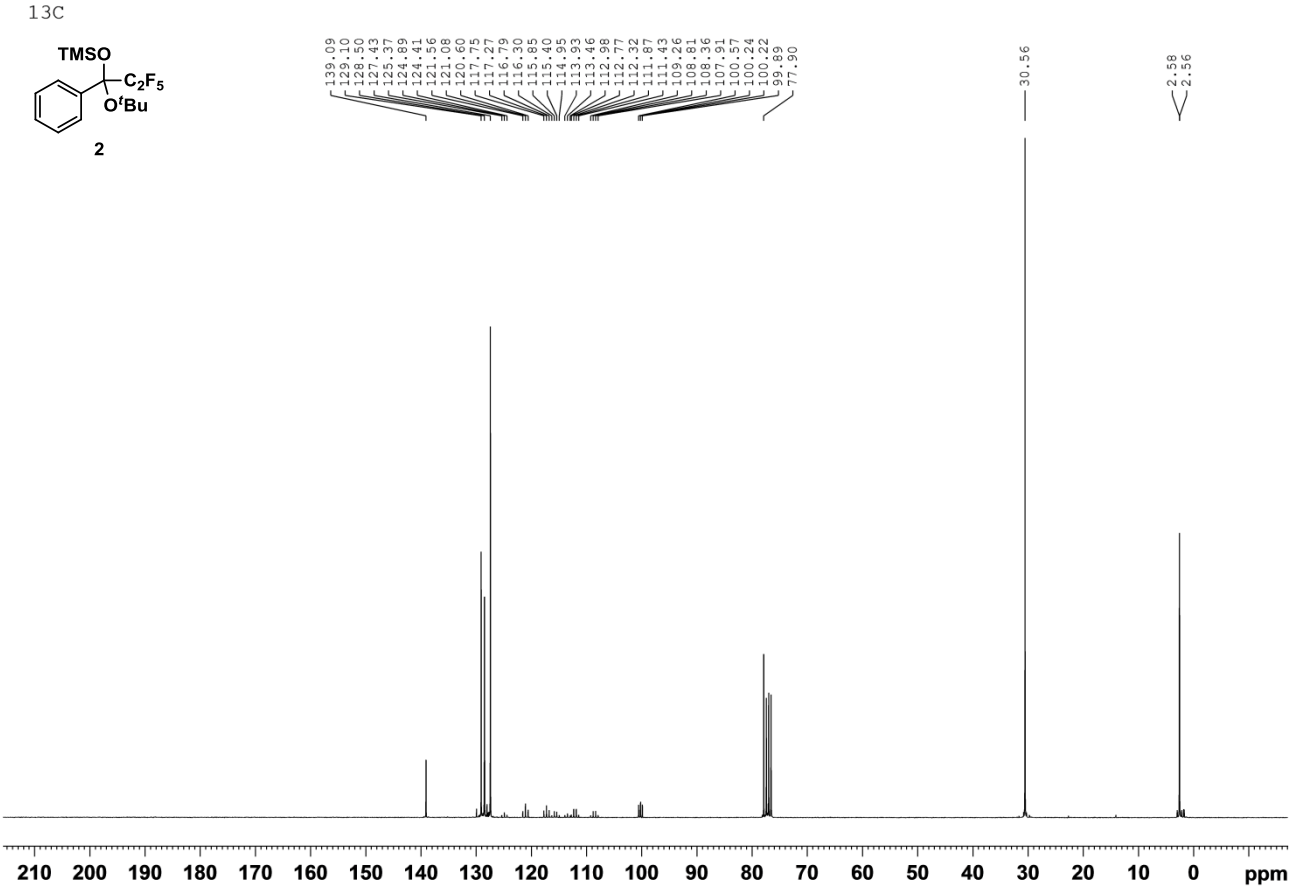
$CuC_2F_5$

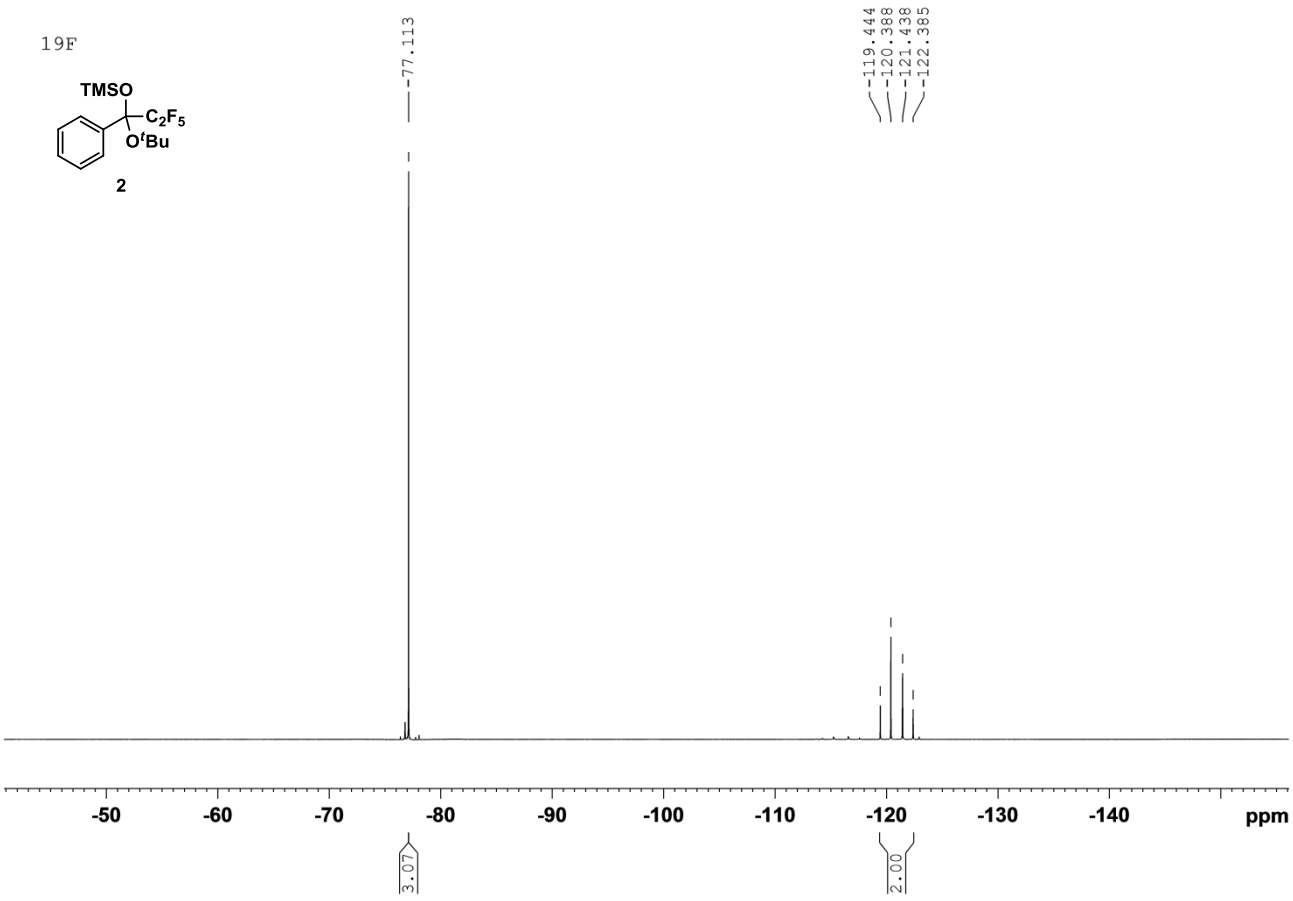


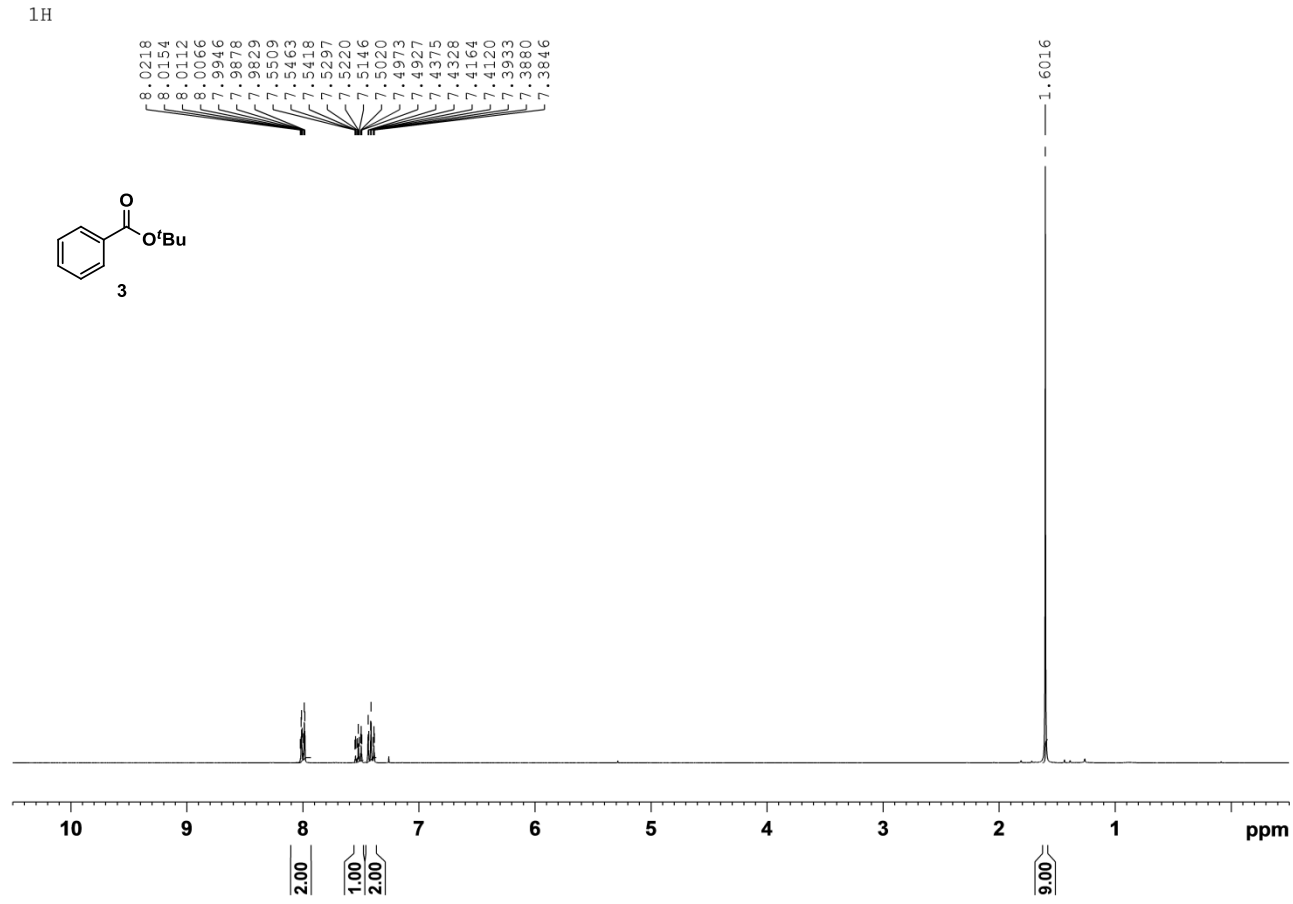
1H


TMSO
C2F5
OtBu
2
7.6690
7.6625
7.6500
7.6389
7.4115
7.3988
7.3941
7.3886
7.3769
7.3684
1.2873
0.3738
10
9
8
7
6
5
4
3
2
1
ppm
2.00
3.00
9.00
9.00

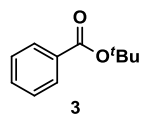
13C


TMSO
C2F5
OtBu
2
139.09
129.10
128.50
127.43
125.37
124.89
124.41
121.56
121.08
120.60
117.75
117.27
116.79
116.30
115.85
115.40
114.95
113.93
113.46
112.98
112.77
112.32
111.87
111.43
109.26
108.81
108.36
107.91
100.57
100.24
100.22
99.89
77.90
30.56
2.58
2.56
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


19F
TMSO
$C_2F_5$
O$^t$Bu
2
-77.113
-119.444
-120.388
-121.438
-122.385
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm
3.07
2.00


1H
8.0218
8.0154
8.0112
8.0066
7.9946
7.9878
7.9829
7.5509
7.5463
7.5418
7.5297
7.5220
7.5146
7.5020
7.4973
7.4927
7.4375
7.4328
7.4164
7.4120
7.3933
7.3880
7.3846
1.6016
O
O$^t$Bu
3
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.00
2.00
9.00

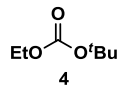
13C


O
O$^t$Bu

3


165.73
132.36
131.95
129.35
128.12
80.89
28.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

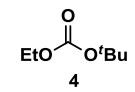
1H


O
EtO
O$^t$Bu

4


4.1070
4.0833
4.0595
4.0357
1.4385
1.2627
1.2389
1.2151
10 9 8 7 6 5 4 3 2 1 ppm
2.00
9.00
3.00

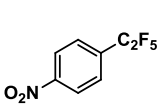
13C


O
EtO
O$^t$Bu

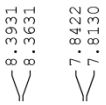
4

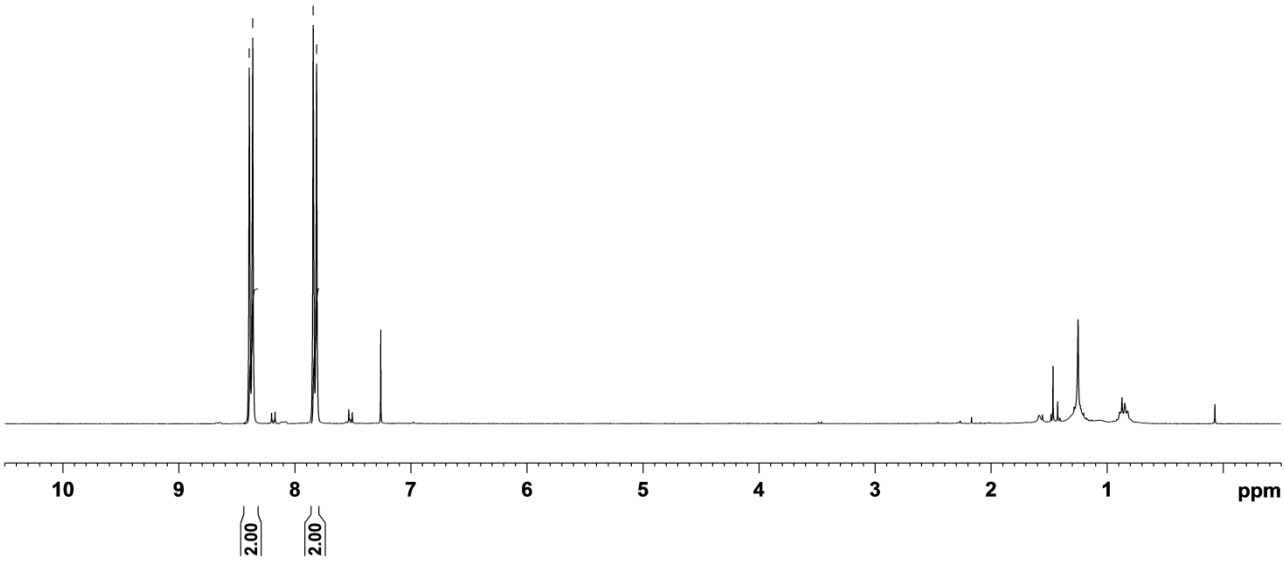

153.45
81.60
62.80
27.68
14.15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1H

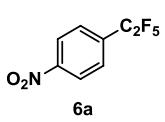

$C_2F_5$
$O_2N$

6a

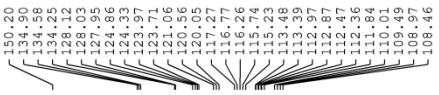

8.3931
8.3631
7.8422
7.8130


10 9 8 7 6 5 4 3 2 1 ppm
2.00
2.00

13C

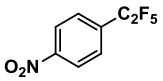

$C_2F_5$
$O_2N$

6a


150.20
134.90
134.58
134.25
128.12
128.03
127.95
124.86
124.33
123.97
123.71
121.06
120.56
120.05
117.27
116.77
116.26
115.74
115.23
113.48
113.39
112.97
112.87
112.47
112.36
111.84
110.01
109.49
108.97
108.46

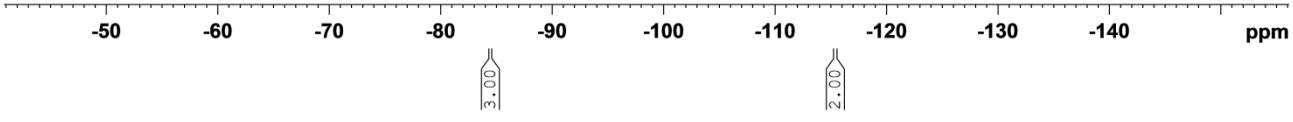

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

19F

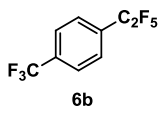

$C_2F_5$
$O_2N$

6a


-84.507
-115.384

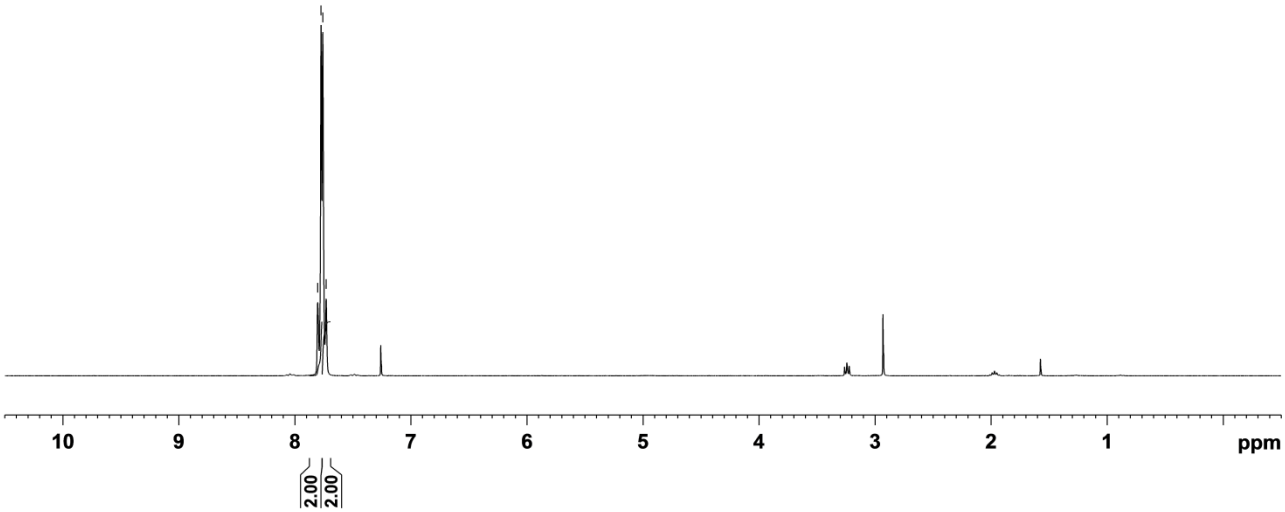

-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm
3.00
2.00

1H

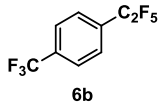

$C_2F_5$
$F_3C$

6b

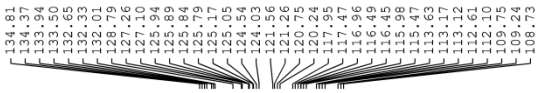

7.8034
7.7743
7.7598
7.7305


10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00

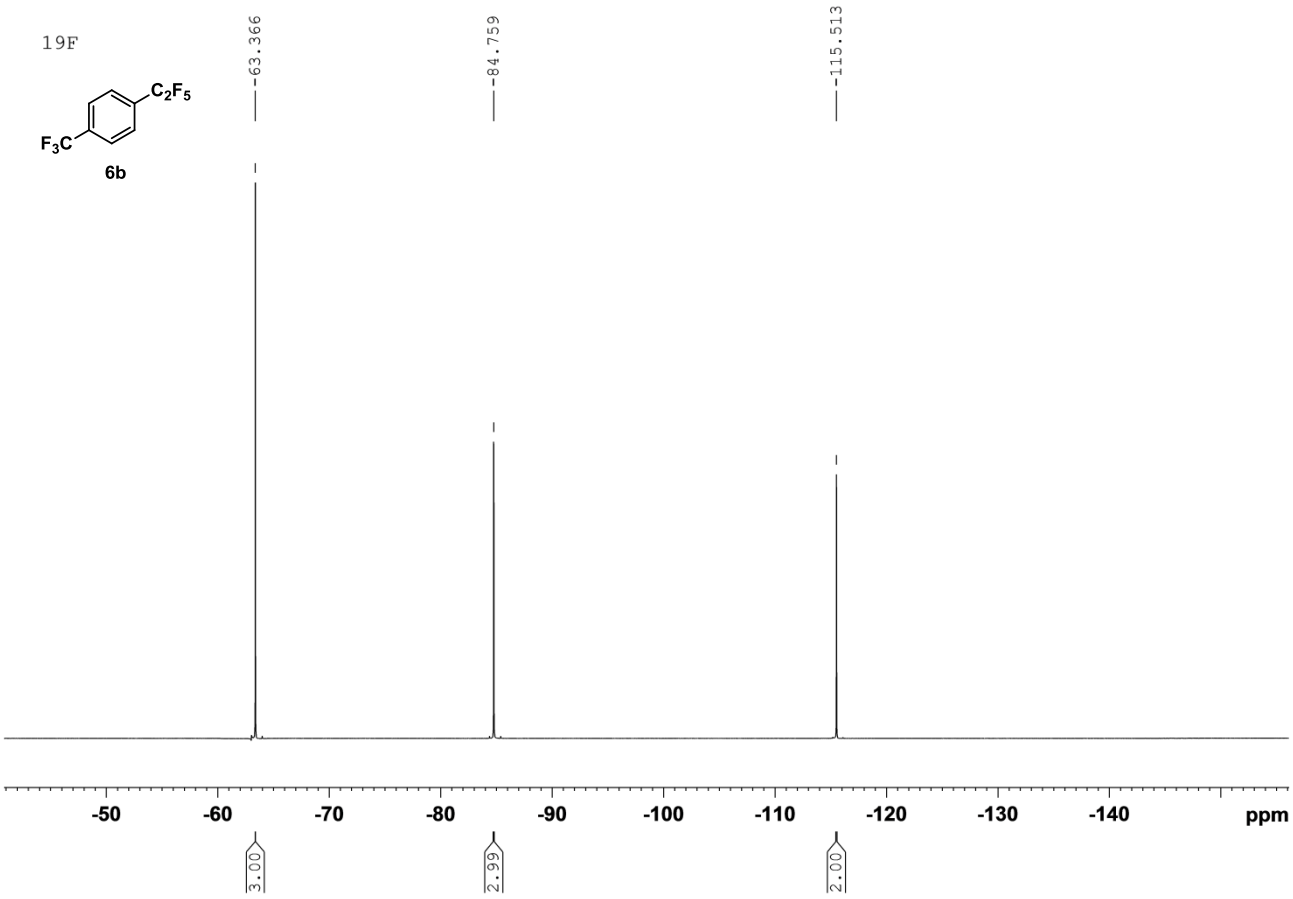
13C

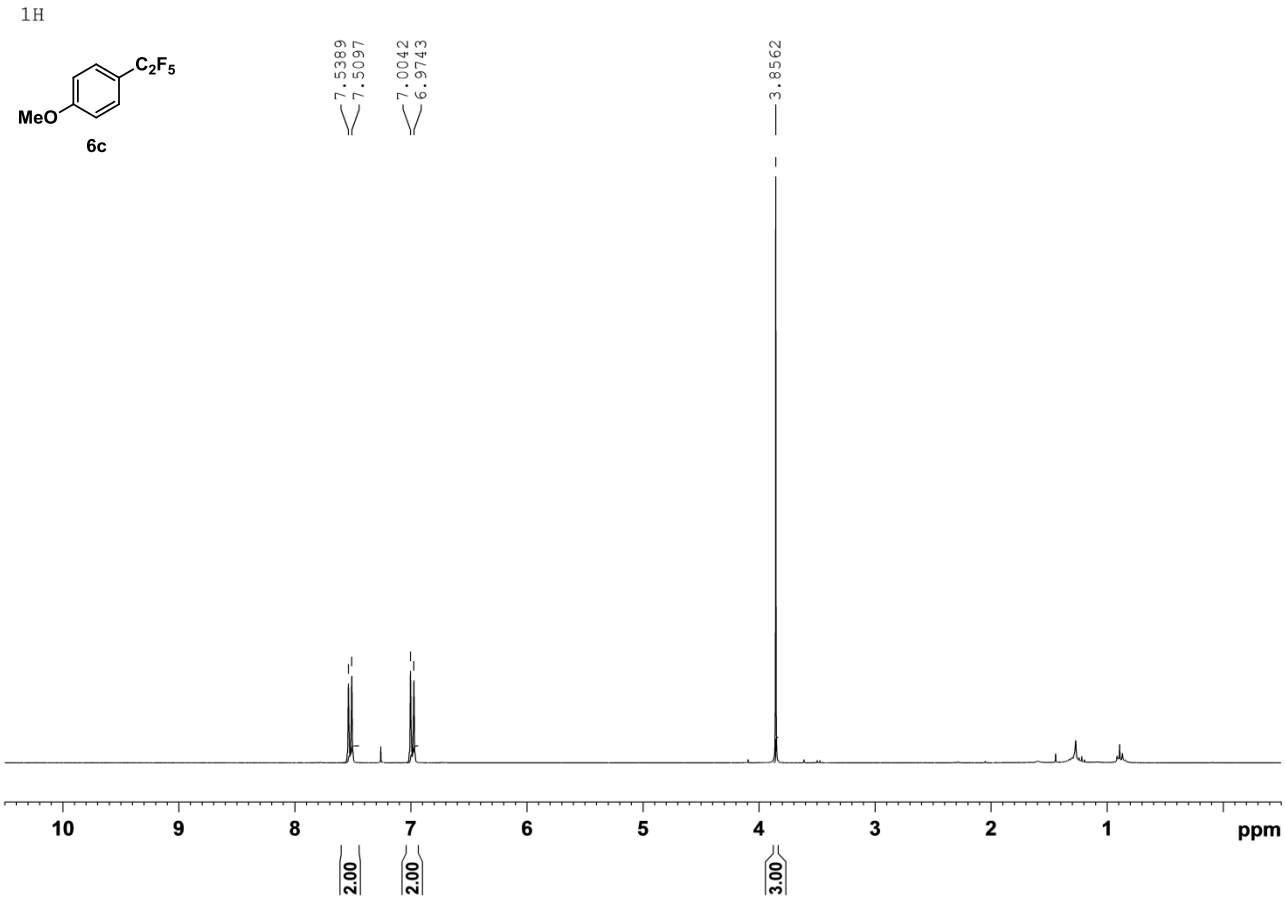

$C_2F_5$
$F_3C$

6b

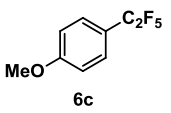

134.81
134.37
133.94
133.50
132.65
132.33
132.01
128.79
127.26
127.10
125.94
125.89
125.84
125.79
125.17
125.05
124.54
124.03
121.56
121.26
120.75
120.24
117.95
117.47
116.96
116.49
116.45
115.98
115.47
113.63
113.17
113.12
112.61
112.10
109.75
109.24
108.73


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


19F
-63.366
-84.759
-115.513
$C_2F_5$
$F_3C$
6b
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm
3.00
2.99
2.00


1H
7.5389
7.5097
7.0042
6.9743
3.8562
$C_2F_5$
MeO
6c
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
3.00

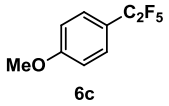
13C


$C_2F_5$
MeO

6c


162.23
128.12
128.03
127.95
125.43
124.89
124.36
121.64
121.11
120.98
120.65
120.57
120.33
117.86
117.73
117.32
117.23
116.79
116.72
116.22
114.38
114.06
113.87
113.37
112.86
111.02
110.52
110.01
109.51
55.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

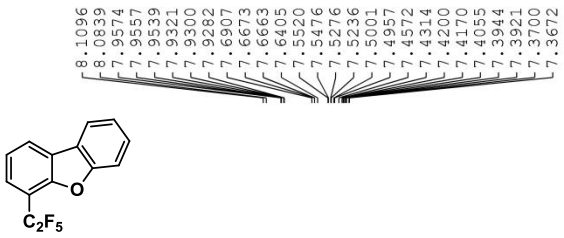
19F


$C_2F_5$
MeO

6c

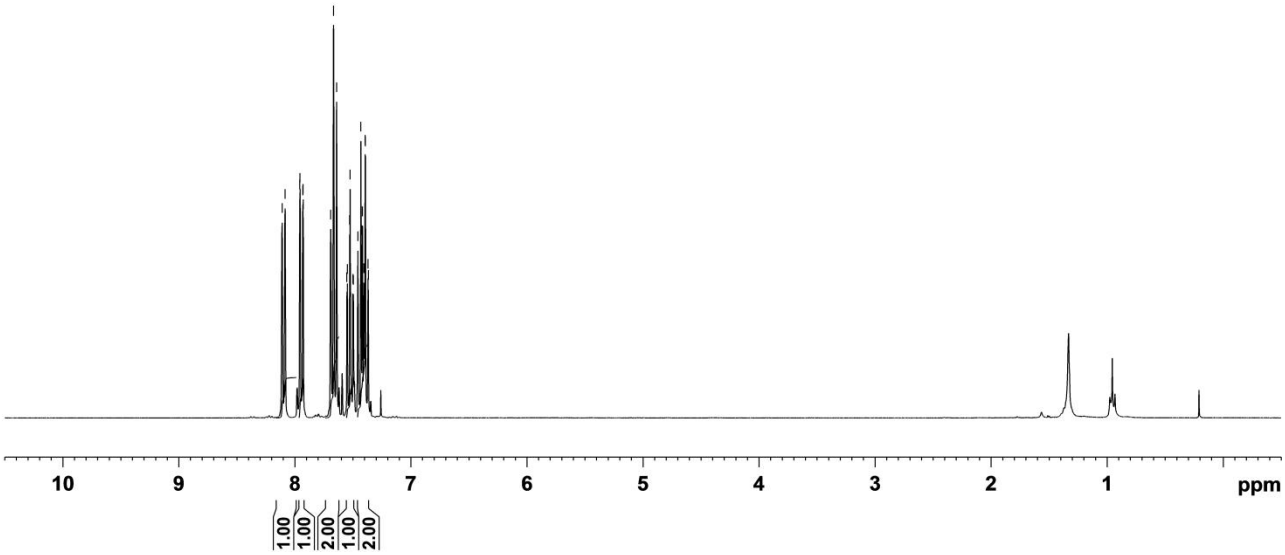

-85.045
-113.899
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm
3.00
2.00

1H

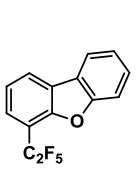

8.1096
8.0839
7.9574
7.9557
7.9539
7.9321
7.9300
7.9282
7.6907
7.6673
7.6663
7.6405
7.5520
7.5476
7.5276
7.5236
7.5001
7.4957
7.4572
7.4314
7.4200
7.4170
7.4055
7.3944
7.3921
7.3700
7.3672


O
$C_2F_5$

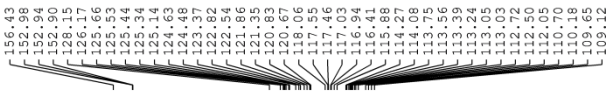
**6d**


10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
2.00
1.00
2.00

13C


O
$C_2F_5$

**6d**


156.43
152.98
152.94
152.90
128.15
126.17
125.66
125.53
125.44
125.34
125.14
124.63
124.48
123.37
122.82
122.54
121.86
121.35
120.83
120.67
118.06
117.55
117.46
117.03
116.94
116.41
115.88
114.27
114.08
113.75
113.56
113.39
113.24
113.05
113.03
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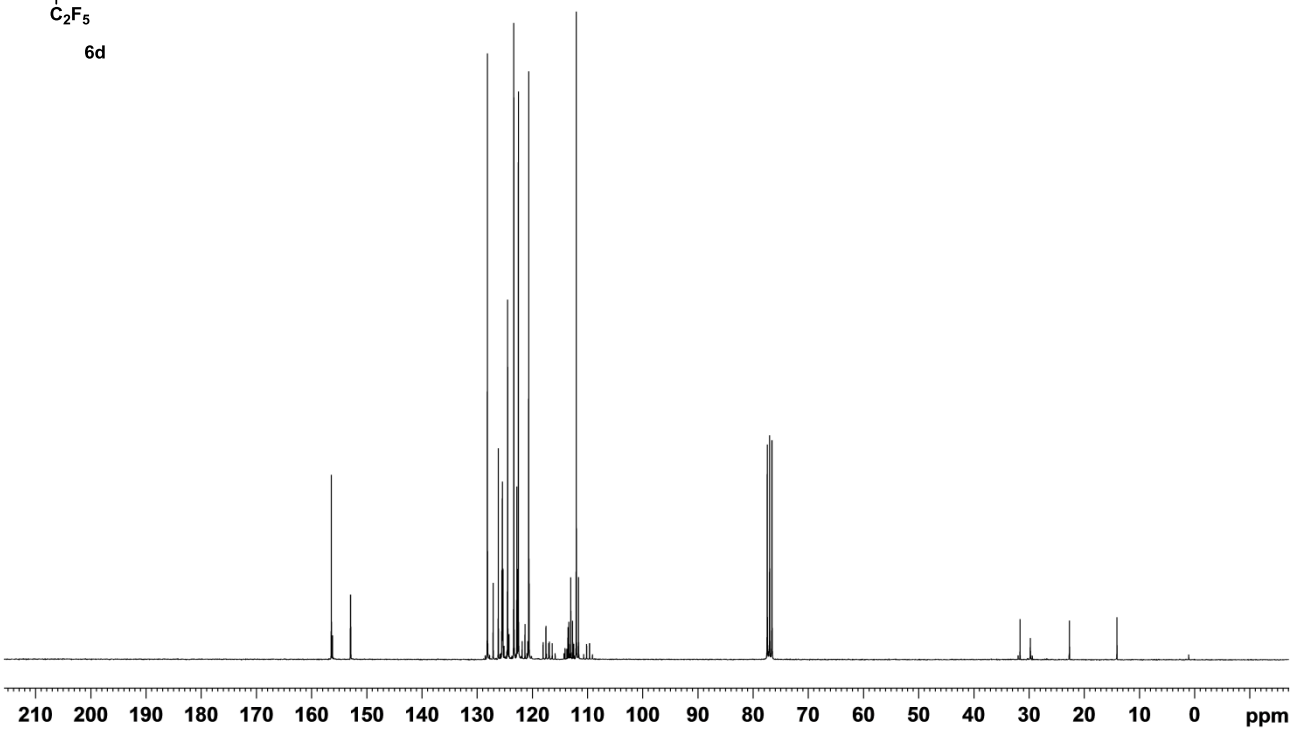
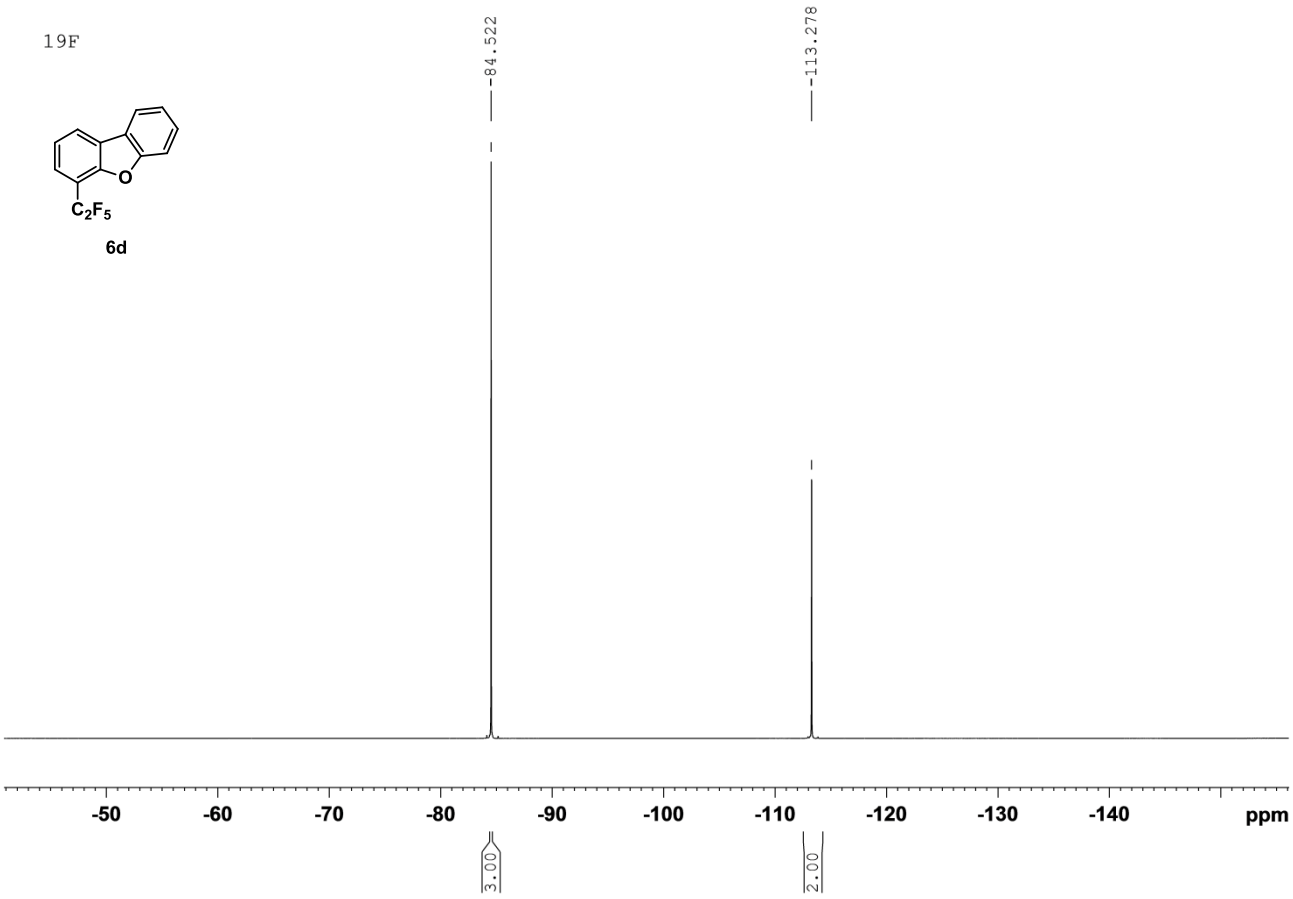
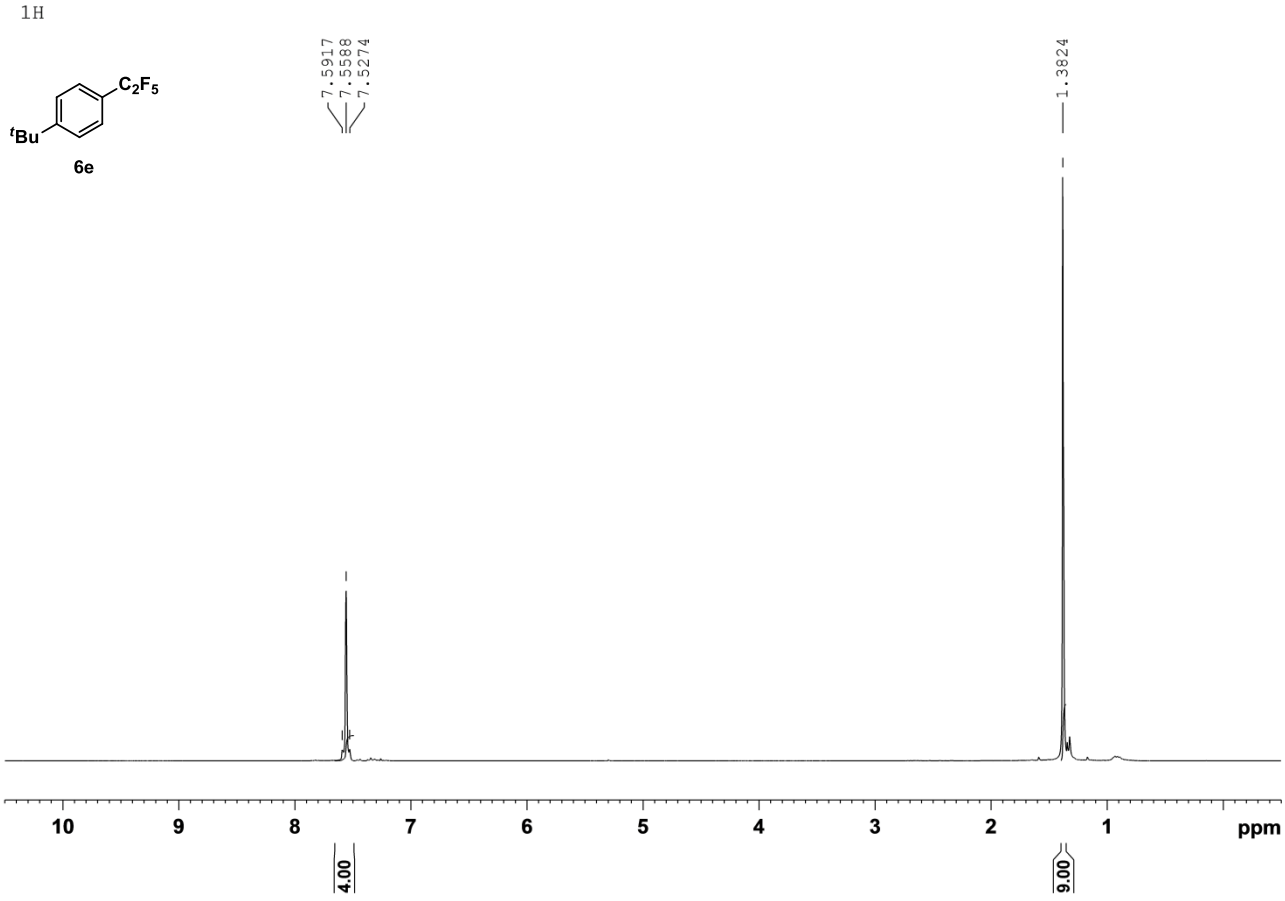
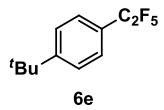
112.50
112.05
110.70
110.18
109.65
109.12


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


19F
-84.522
-113.278
C2F5
6d
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm
3.00
2.00


1H
7.5917
7.5588
7.5274
1.3824
C2F5
tBu
6e
10
9
8
7
6
5
4
3
2
1
ppm
4.00
9.00

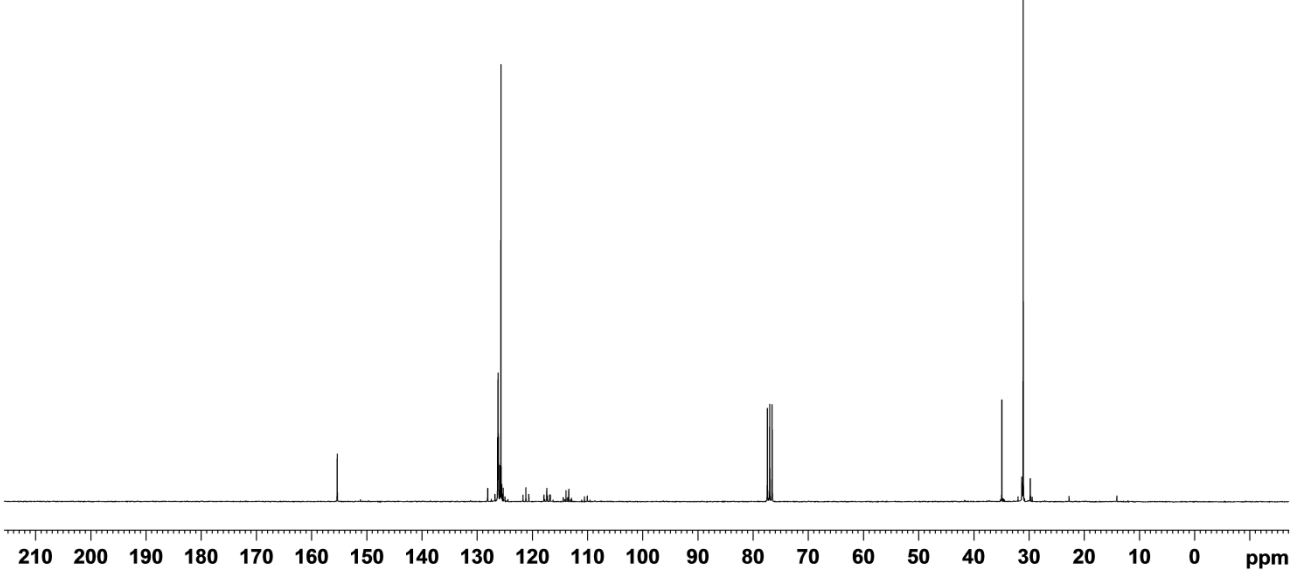
13C



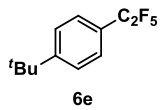

6e

155.38
155.36
155.34
126.31
126.22
126.15
125.88
125.71
125.50
124.97
124.44
121.71
121.18
120.66
117.92
117.78
117.40
117.27
116.87
116.77
116.26
114.42
114.14
113.92
113.61
113.41
113.08
112.91
111.07
110.57
110.06
109.56

34.94
31.08




19F

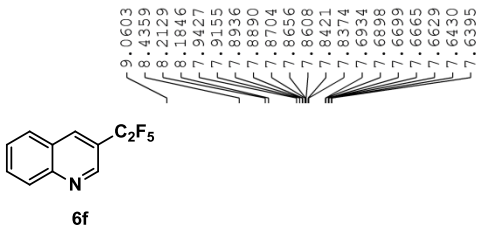



6e

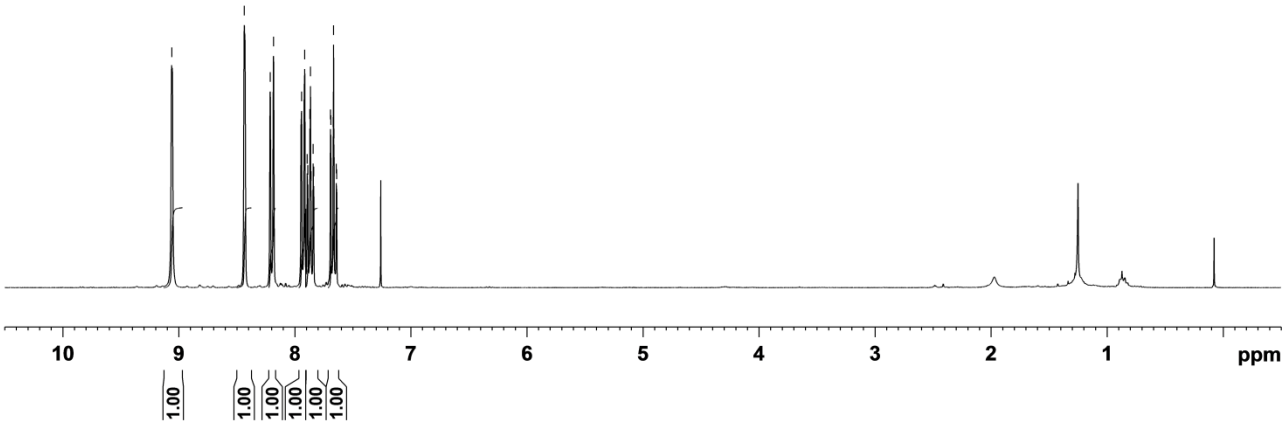
-84.897

-114.571

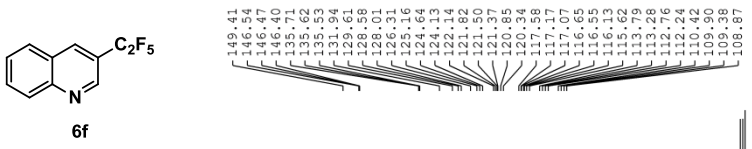
1H


9.0603
8.4359
8.2129
8.1846
7.9427
7.9155
7.8936
7.8890
7.8704
7.8656
7.8608
7.8421
7.8374
7.6934
7.6898
7.6699
7.6665
7.6629
7.6430
7.6395
$C_2F_5$
N

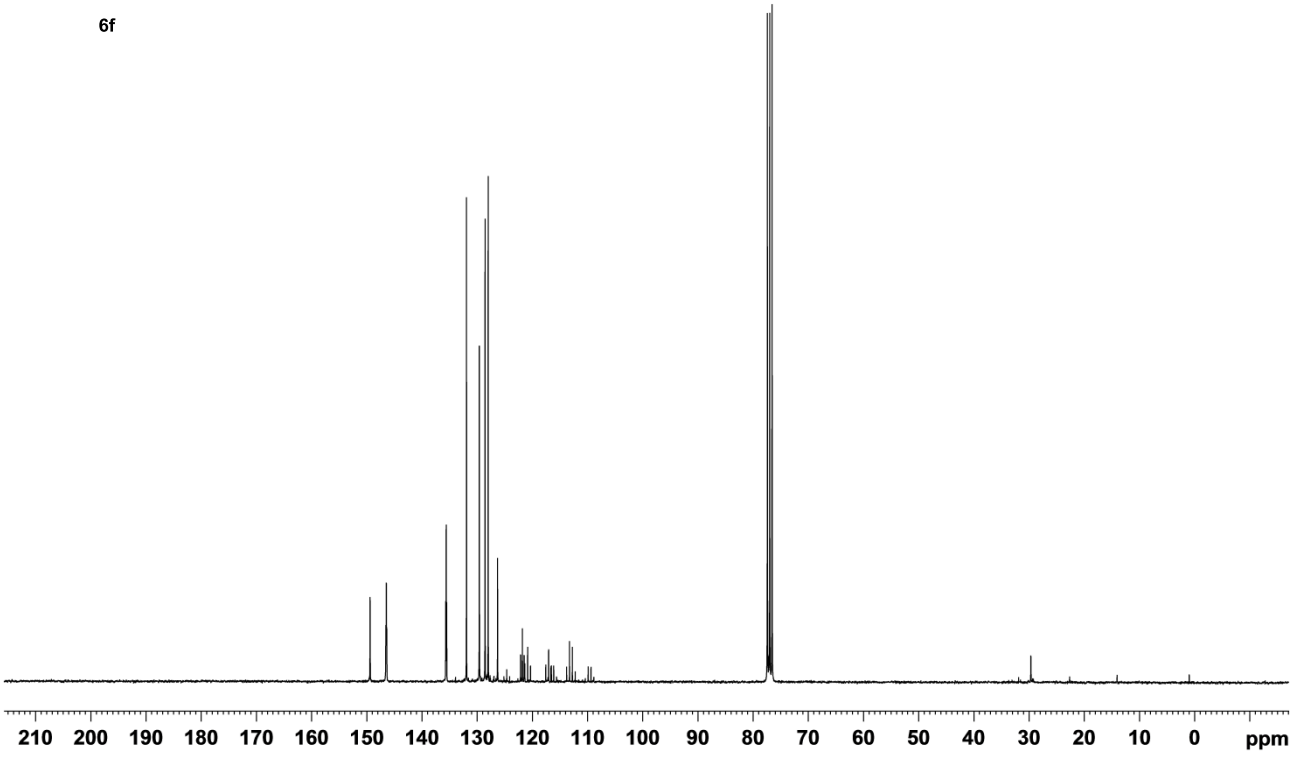
6f

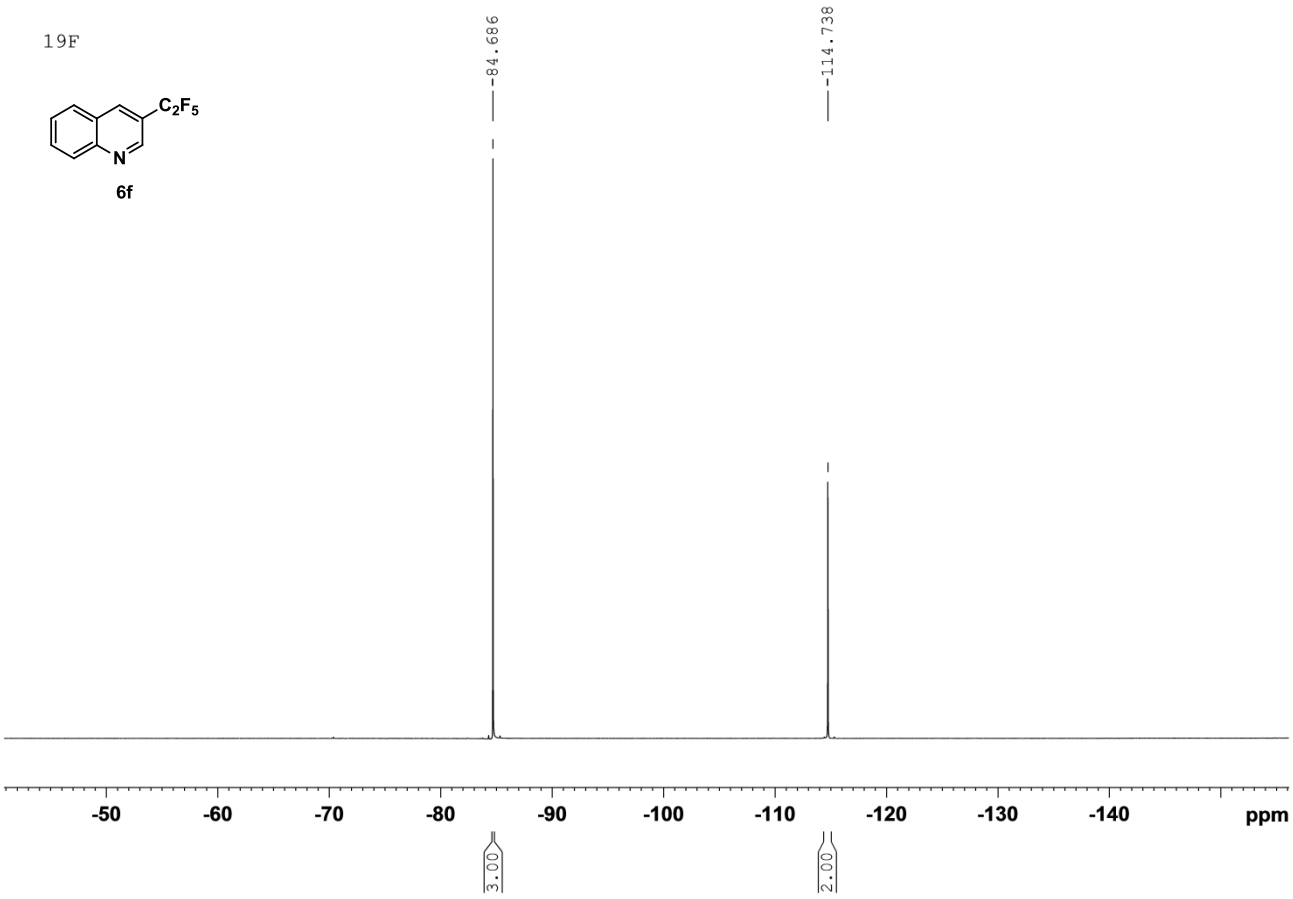

10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
1.00
1.00

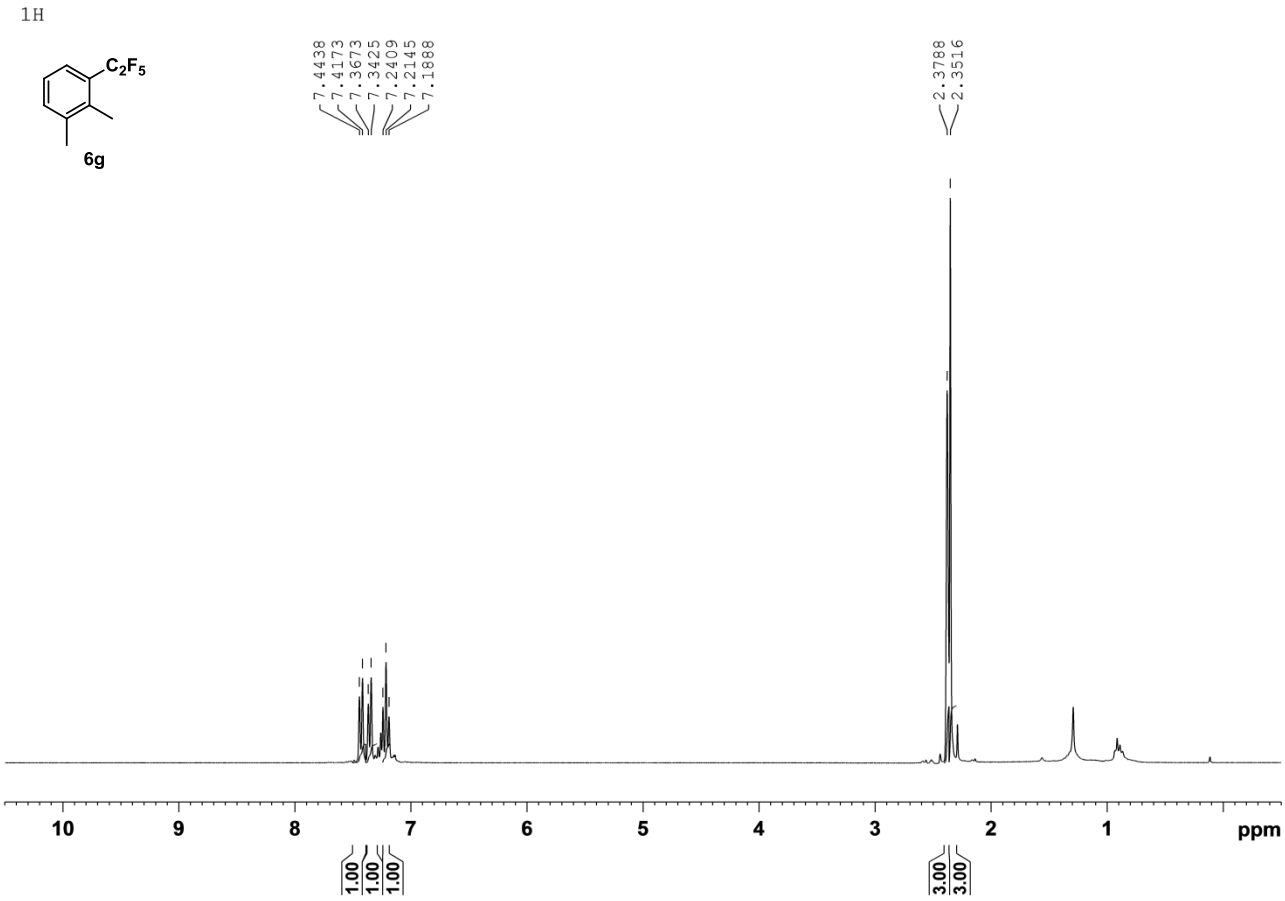
13C


149.41
146.54
146.47
146.40
135.71
135.62
135.53
131.94
129.61
128.58
128.01
126.31
125.16
124.64
124.13
122.14
121.82
121.50
121.37
120.85
120.34
117.58
117.17
117.07
116.65
116.55
116.13
115.62
113.79
113.28
112.76
112.24
110.42
109.90
109.38
108.87
$C_2F_5$
N

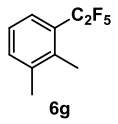
6f


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


19F
-84.686
-114.738
$C_2F_5$
N
6f
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm
3.00
2.00


1H
$C_2F_5$
6g
7.4438
7.4173
7.3673
7.3425
7.2409
7.2145
7.1888
2.3788
2.3516
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.00
1.00
3.00
3.00

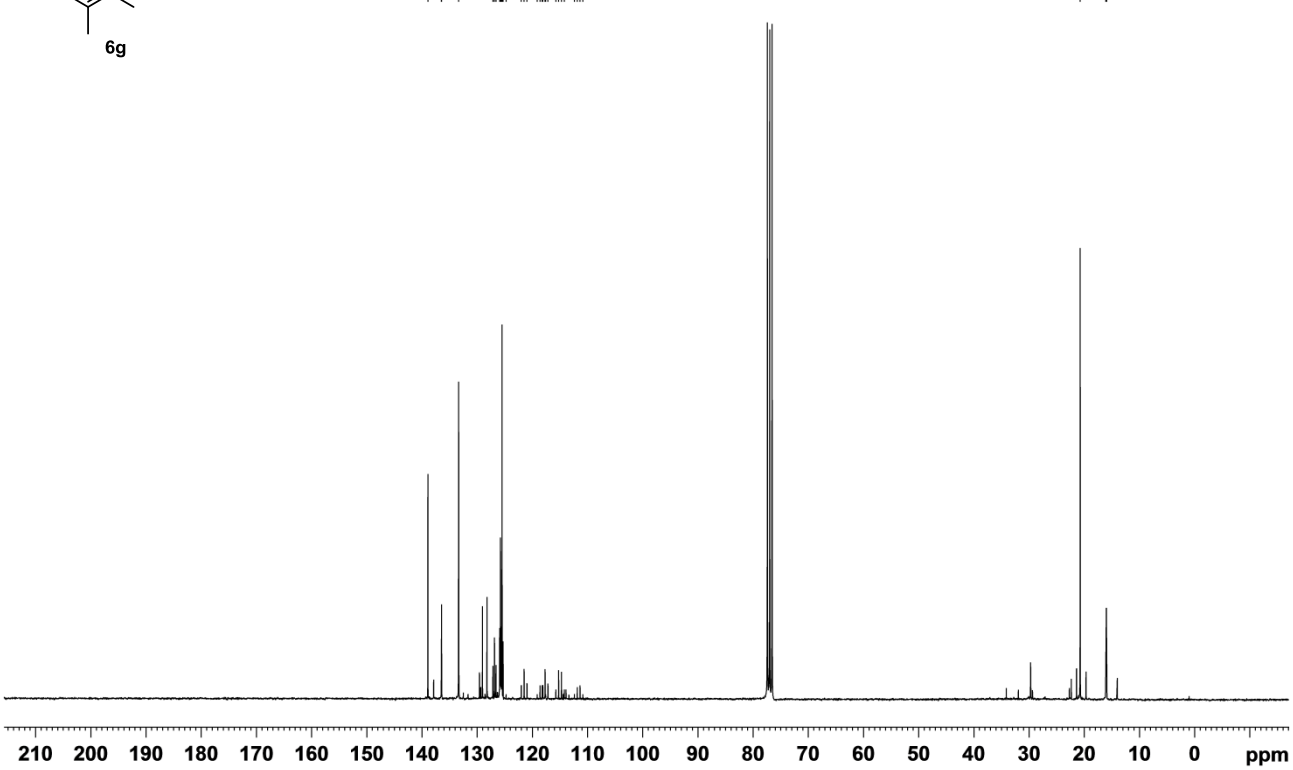
13C



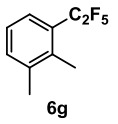

6g

138.93
136.49
136.47
136.44
133.35
127.15
126.87
126.59
126.32
125.79
125.67
125.50
125.30
124.77
122.02
121.50
120.97
119.13
118.62
118.22
118.10
117.70
117.59
117.18
115.76
115.25
114.73
114.22
112.39
111.87
111.36
110.85

20.76
16.11
16.08
16.05
16.01
15.98
15.95



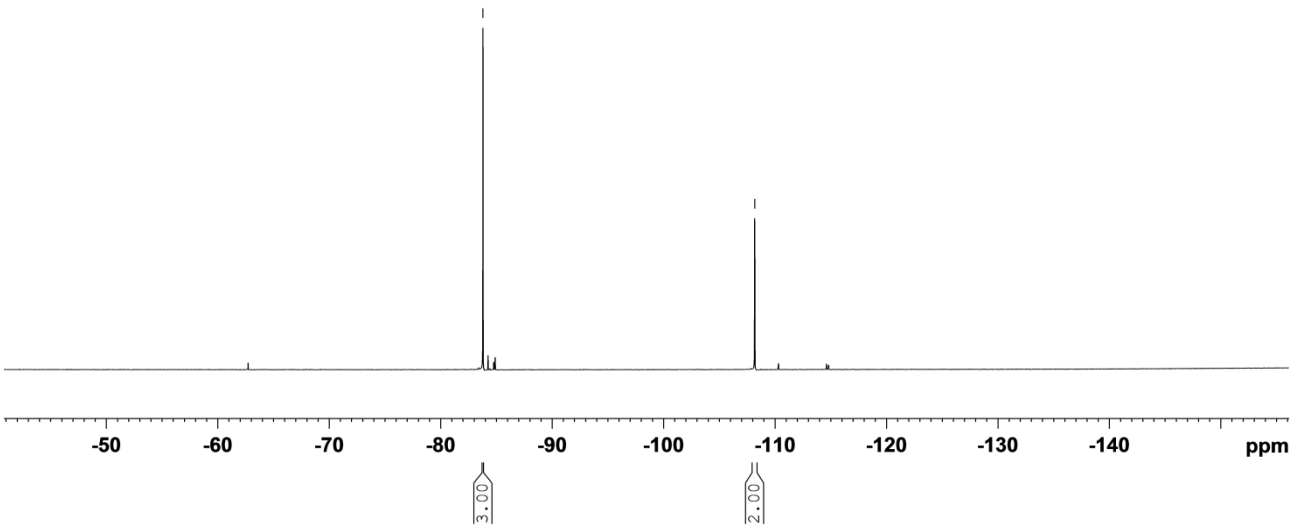

19F

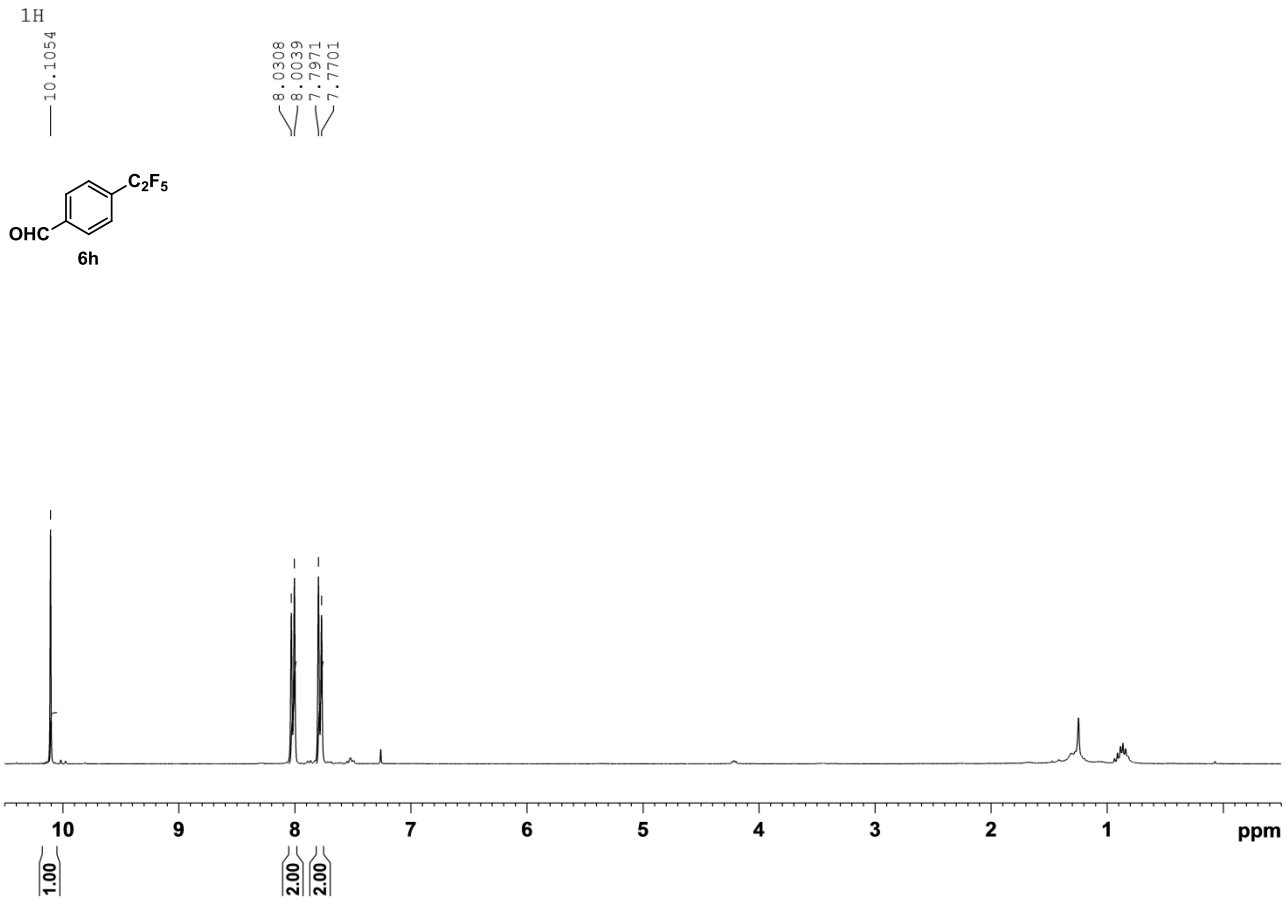


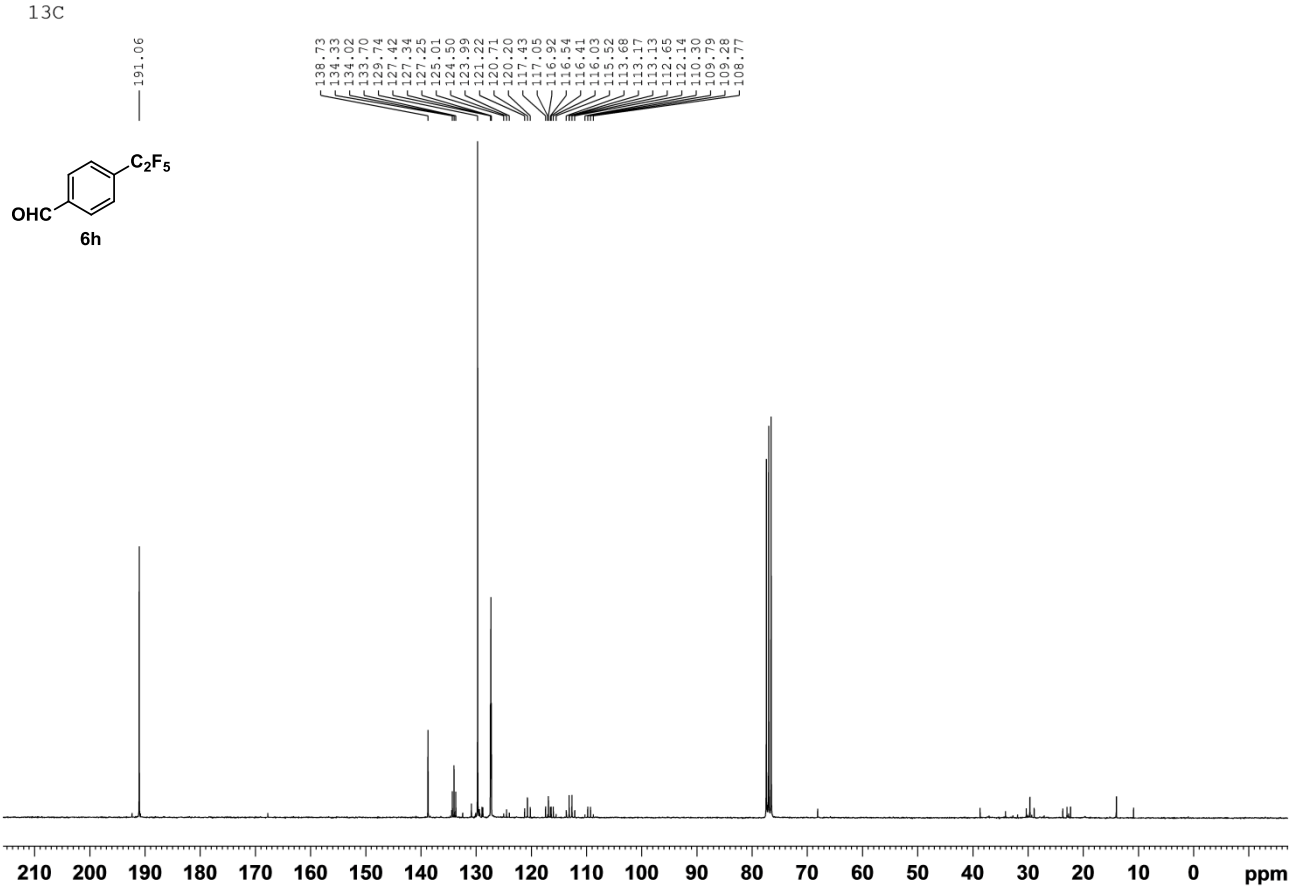

6g

-83.792

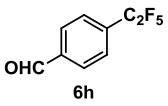
-108.173




1H
10.1054
8.0308
8.0039
7.7971
7.7701
C2F5
OHC
6h
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.00
2.00


13C
191.06
138.73
134.33
134.02
133.70
129.74
127.42
127.34
127.25
125.01
124.50
123.99
121.22
120.71
120.20
117.43
117.05
116.92
116.54
116.41
116.03
115.52
113.68
113.17
113.13
112.65
112.14
110.30
109.79
109.28
108.77
C2F5
OHC
6h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

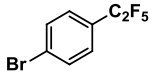
19F




6h

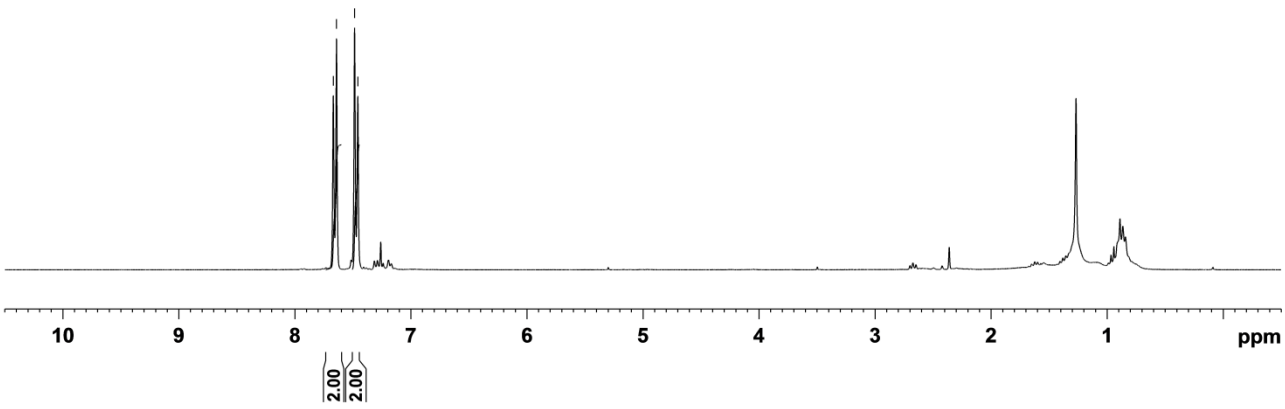



1H

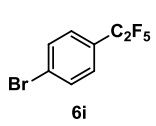



6i

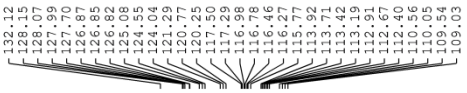
7.6690
7.6412
7.4854
7.4574

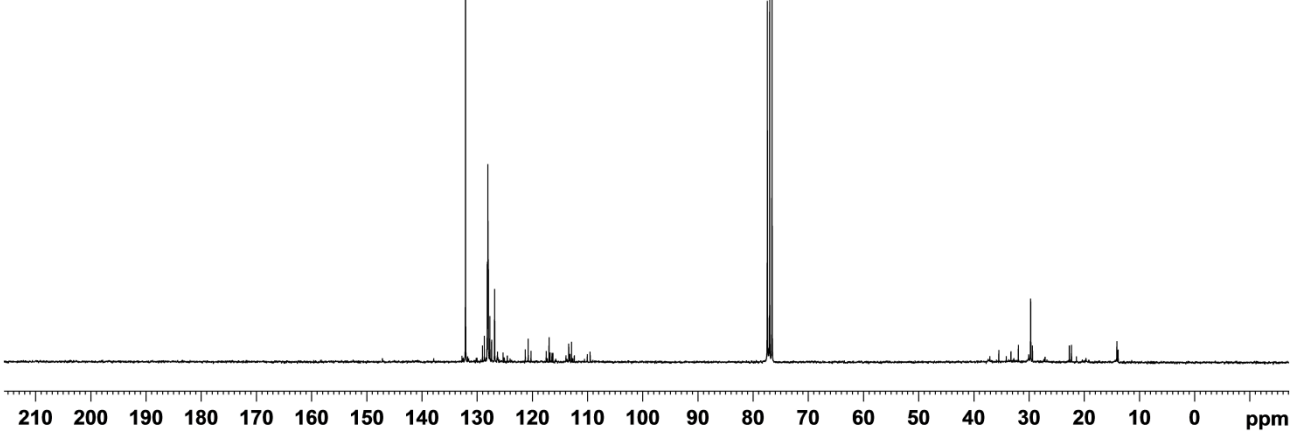


13C

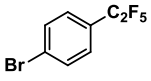

$C_2F_5$
Br

6i


132.12
128.15
128.07
127.99
127.70
126.87
126.85
126.82
125.08
124.55
124.04
121.29
120.77
120.25
117.50
117.29
116.98
116.78
116.46
116.27
115.77
113.92
113.71
113.42
113.19
112.91
112.67
112.40
110.56
110.05
109.54
109.03

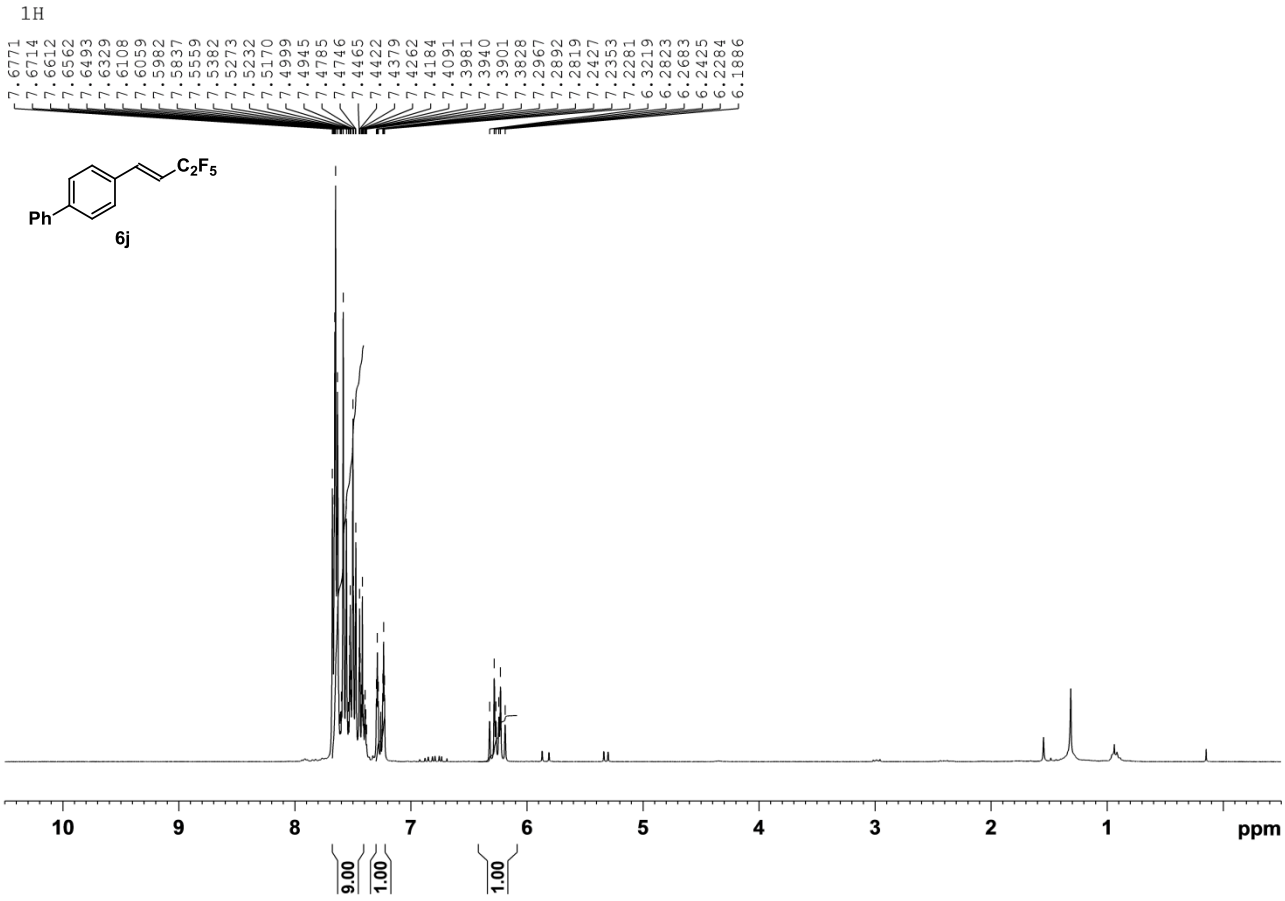

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

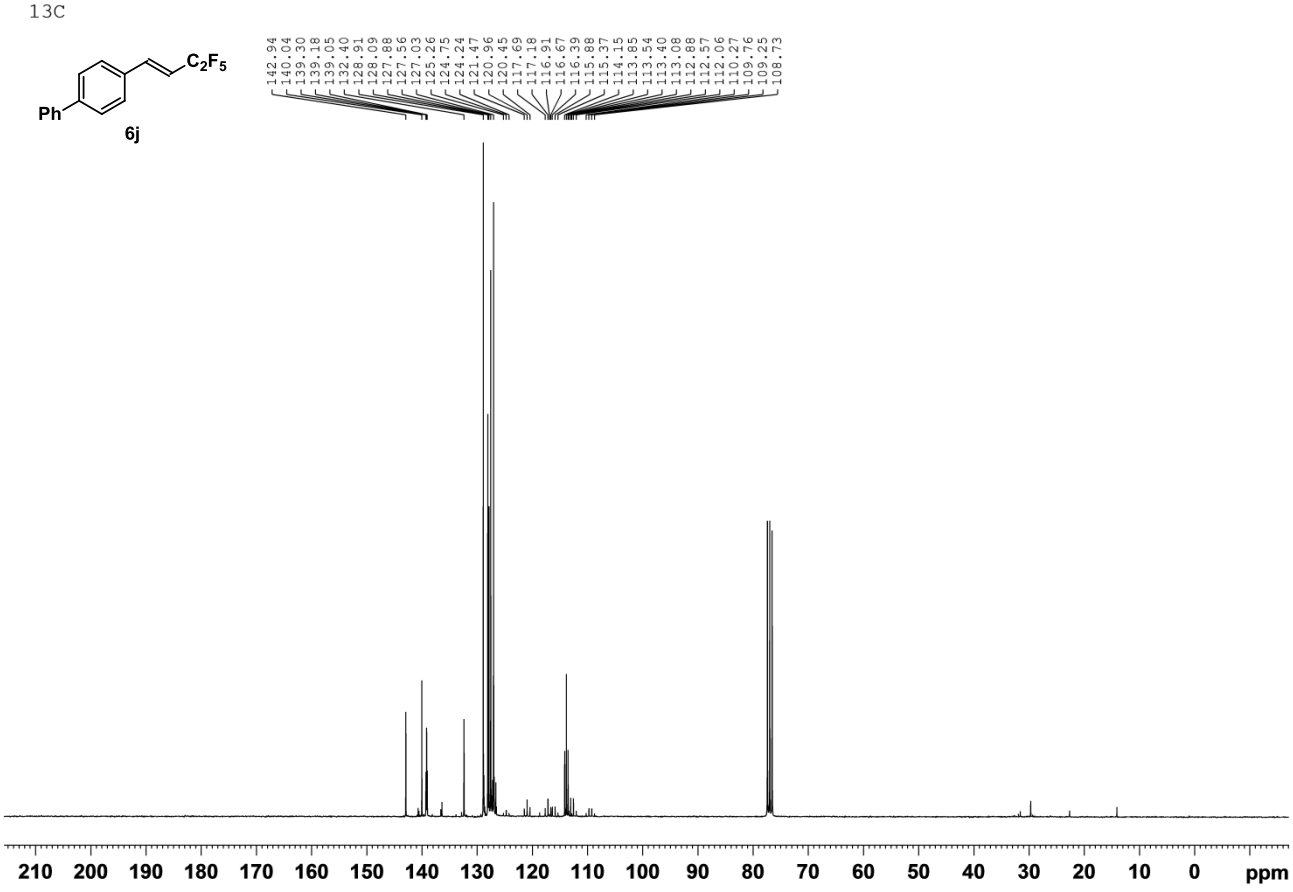
19F


$C_2F_5$
Br

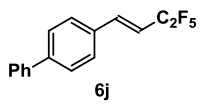
6i


-84.877
-115.155
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm
3.00
2.00


1H
7.6771
7.6714
7.6612
7.6562
7.6493
7.6329
7.6108
7.6059
7.5982
7.5837
7.5559
7.5382
7.5273
7.5232
7.5170
7.4999
7.4945
7.4785
7.4746
7.4465
7.4422
7.4379
7.4262
7.4184
7.4091
7.3981
7.3940
7.3901
7.3828
7.2967
7.2892
7.2819
7.2427
7.2353
7.2281
6.3219
6.2823
6.2683
6.2425
6.2284
6.1886
C2F5
Ph
6j
10
9
8
7
6
5
4
3
2
1
ppm
9.00
1.00
1.00


13C
142.94
140.04
139.30
139.18
139.05
132.40
128.91
128.09
127.88
127.56
127.03
125.26
124.75
124.24
121.47
120.96
120.45
117.69
117.18
116.91
116.67
116.39
115.88
115.37
114.15
113.85
113.54
113.40
113.08
112.88
112.57
112.06
110.27
109.76
109.25
108.73
C2F5
Ph
6j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

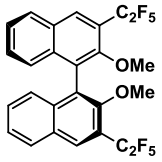
19F


$C_2F_5$
Ph

6j


-85.017
-114.728
-114.765
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm
3.00
2.00

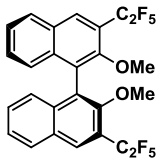
1H


$C_2F_5$
OMe
OMe
$C_2F_5$

6k


8.3270
8.0278
8.0006
7.5471
7.5240
7.5206
7.4972
7.4406
7.4129
7.3895
7.1878
7.1597
3.3228
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
2.00
2.00
2.00
6.00

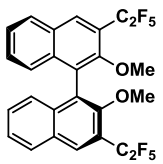
13C


$C_2F_5$
OMe
OMe
$C_2F_5$

6k


154.12
135.80
131.24
131.13
131.01
129.37
129.23
129.04
126.08
125.79
125.60
125.40
125.08
124.56
122.37
122.07
121.78
121.28
120.77
118.08
117.99
117.56
117.48
117.03
116.97
116.51
114.70
114.17
113.65
113.13
111.31
110.79
110.26
109.74
61.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

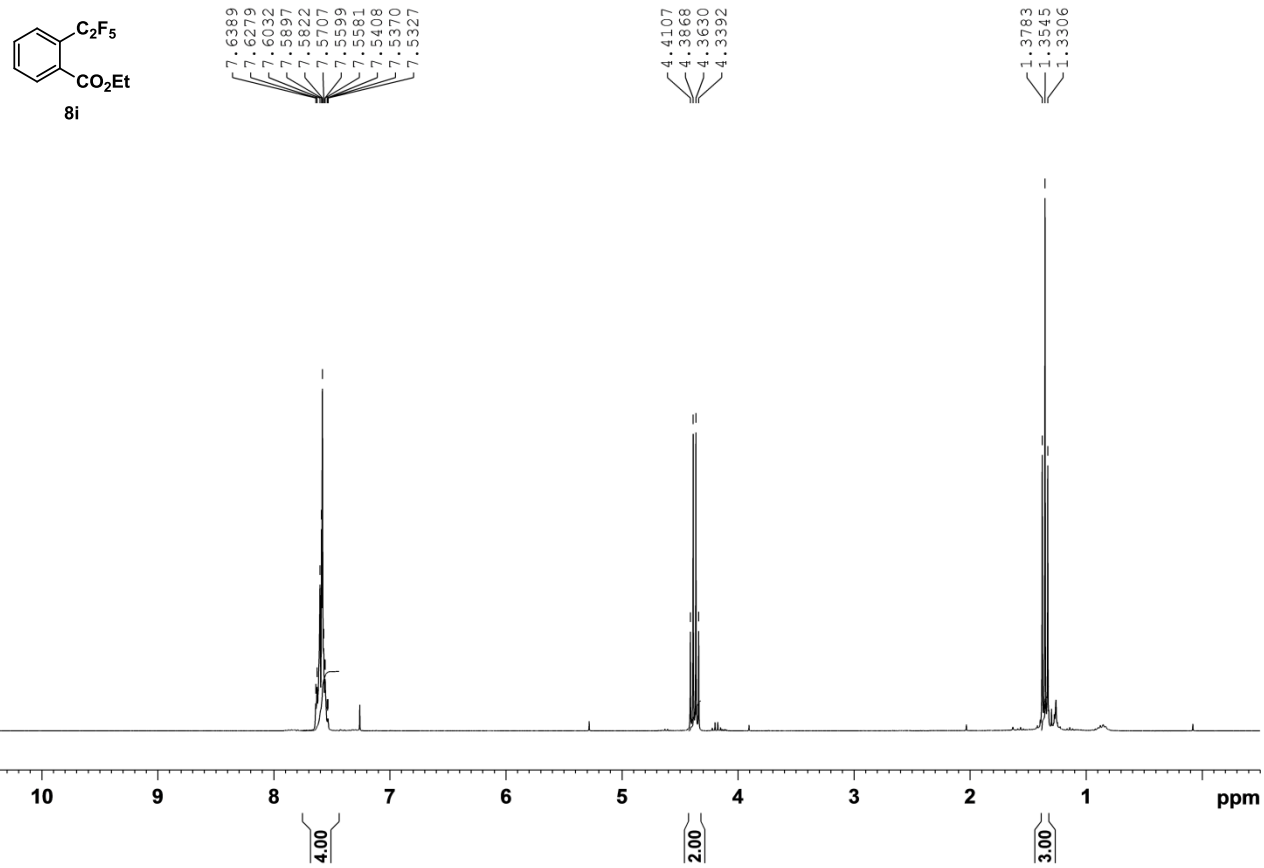
19F


$C_2F_5$
OMe
OMe
$C_2F_5$

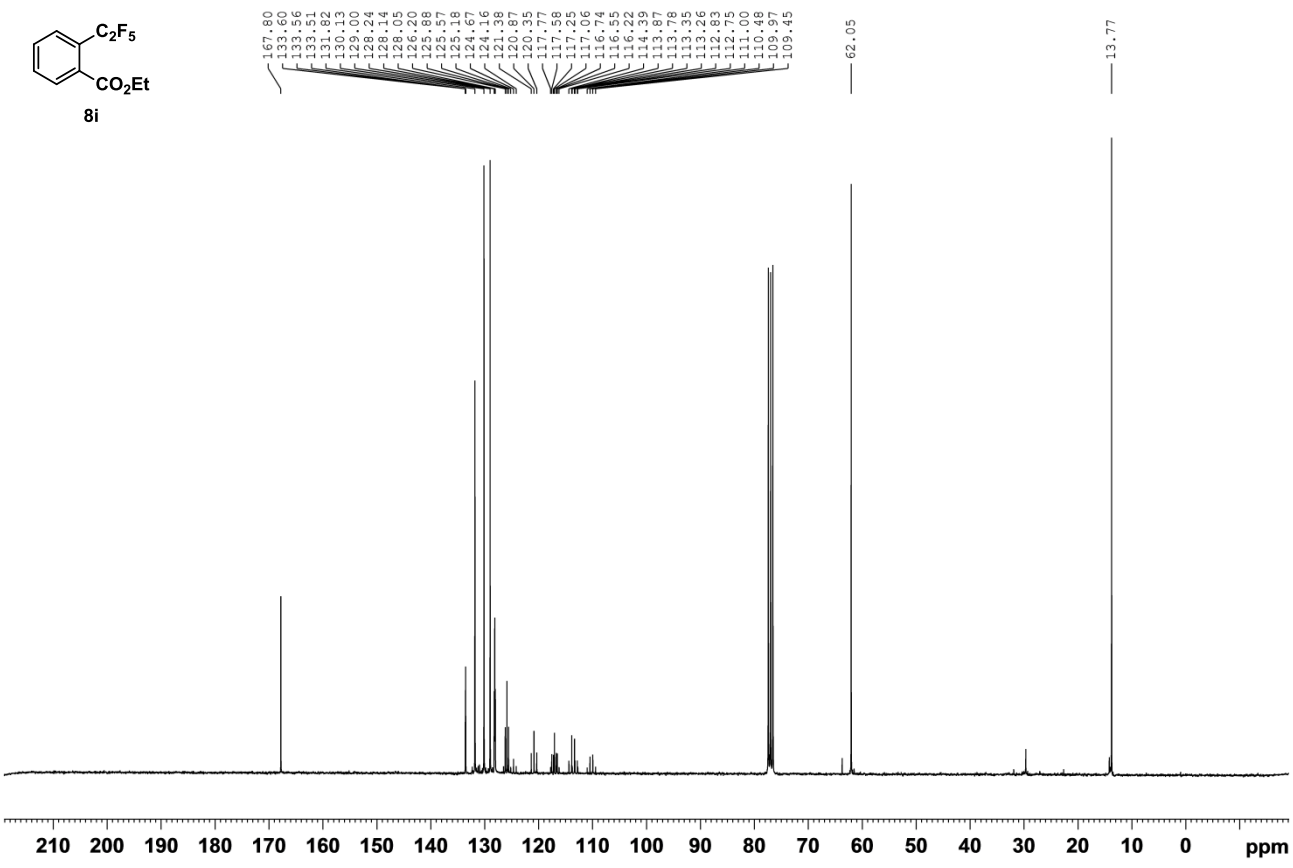
6k

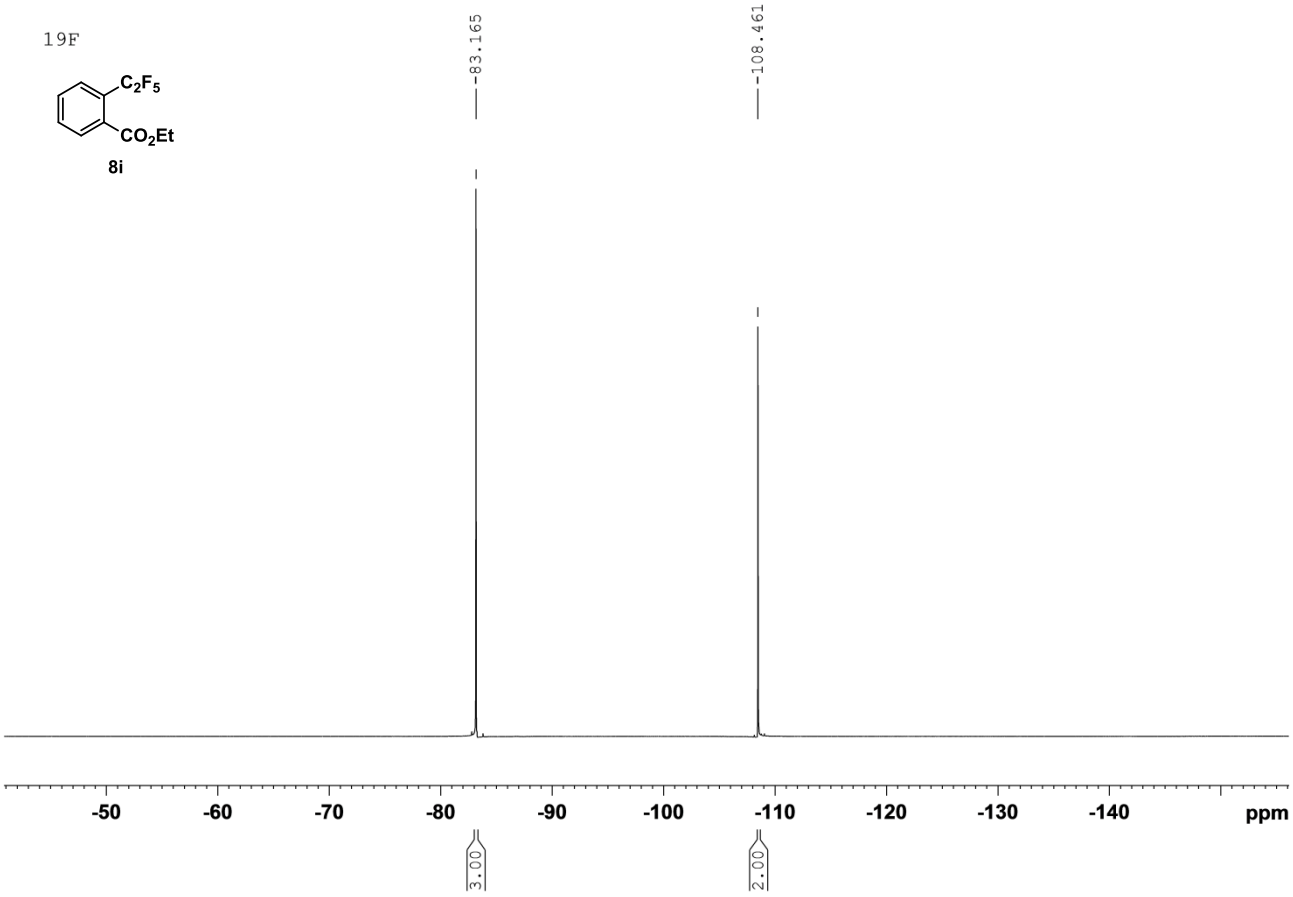

-83.062
-109.678
-110.638
-110.731
-111.691
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm
3.00
2.00

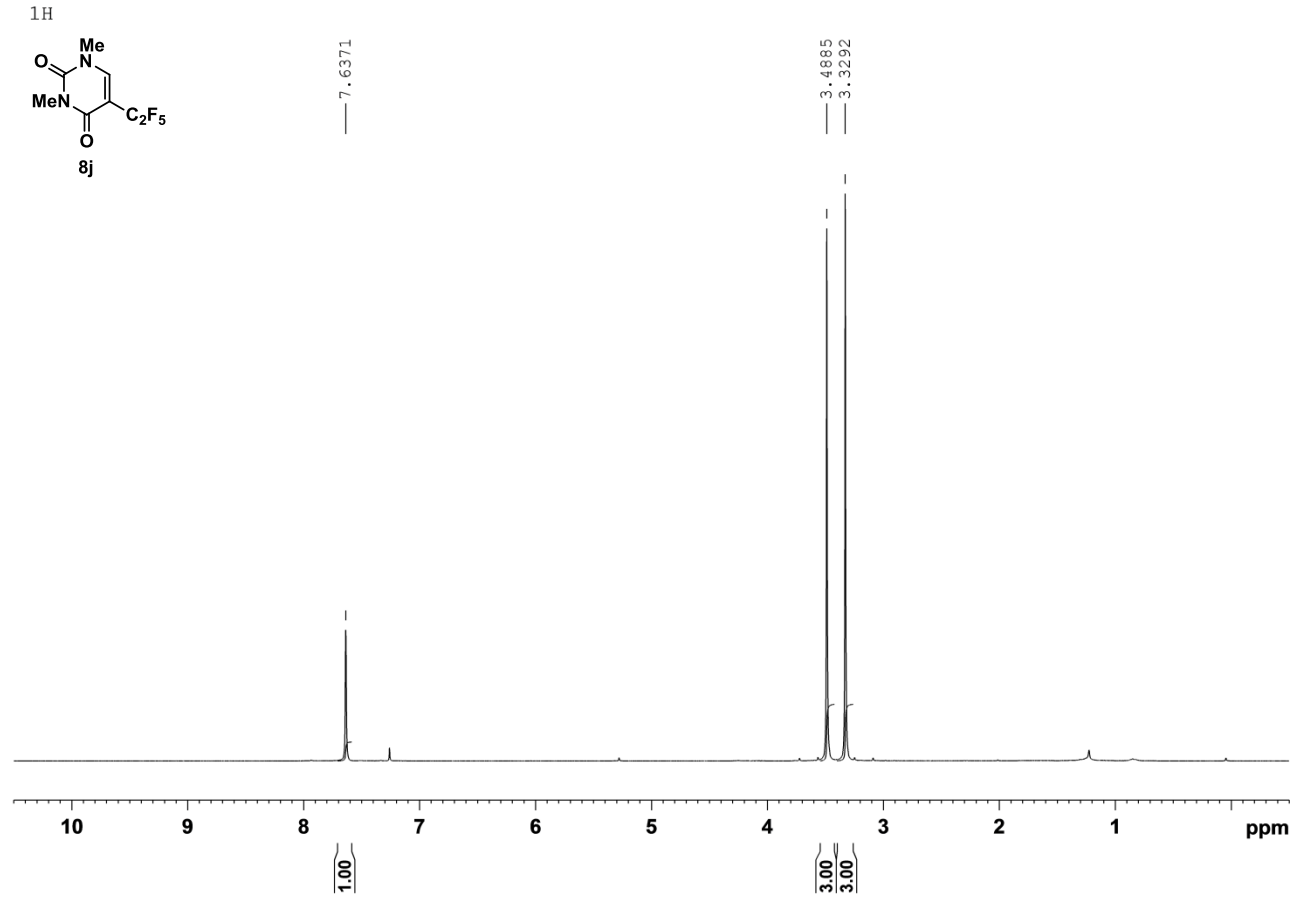
1H


C2F5
CO2Et
8i
7.6389
7.6279
7.6032
7.5897
7.5822
7.5707
7.5599
7.5581
7.5408
7.5370
7.5327
4.4107
4.3868
4.3630
4.3392
1.3783
1.3545
1.3306
10
9
8
7
6
5
4
3
2
1
ppm
4.00
2.00
3.00

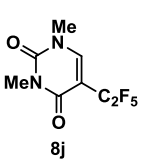
13C


C2F5
CO2Et
8i
167.80
133.60
133.56
133.51
131.82
130.13
129.00
128.24
128.14
128.05
126.20
125.88
125.57
125.18
124.67
124.16
121.38
120.87
120.35
117.77
117.58
117.25
117.06
116.74
116.55
116.22
114.39
113.87
113.78
113.35
113.26
112.83
112.75
111.00
110.48
109.97
109.45
62.05
13.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


19F
$C_2F_5$
$CO_2Et$
8i
-83.165
-108.461
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm
3.00
2.00


1H
Me
N
O
MeN
$C_2F_5$
O
8j
7.6371
3.4885
3.3292
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.00
3.00

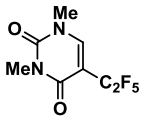
13C


Me
N
O
MeN
O
$C_2F_5$

8j


158.42
158.39
158.37
150.76
145.54
145.40
145.27
125.00
124.48
123.95
121.20
120.68
120.16
117.40
116.88
116.35
116.06
115.52
114.98
114.44
113.60
113.08
112.67
112.56
112.13
111.59
111.05
109.28
108.75
108.21
107.67
102.07
101.75
101.43
37.81
28.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

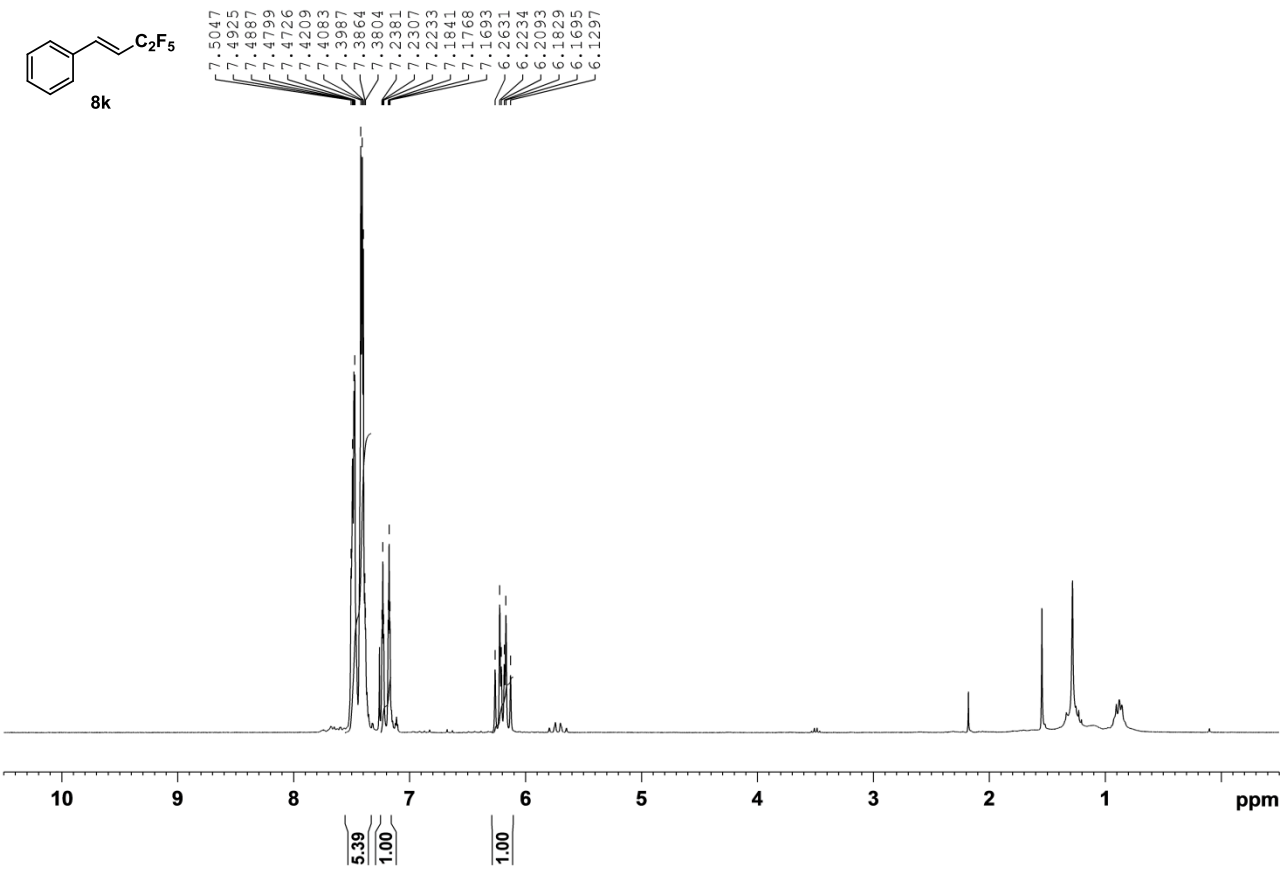
19F


Me
N
O
MeN
O
$C_2F_5$

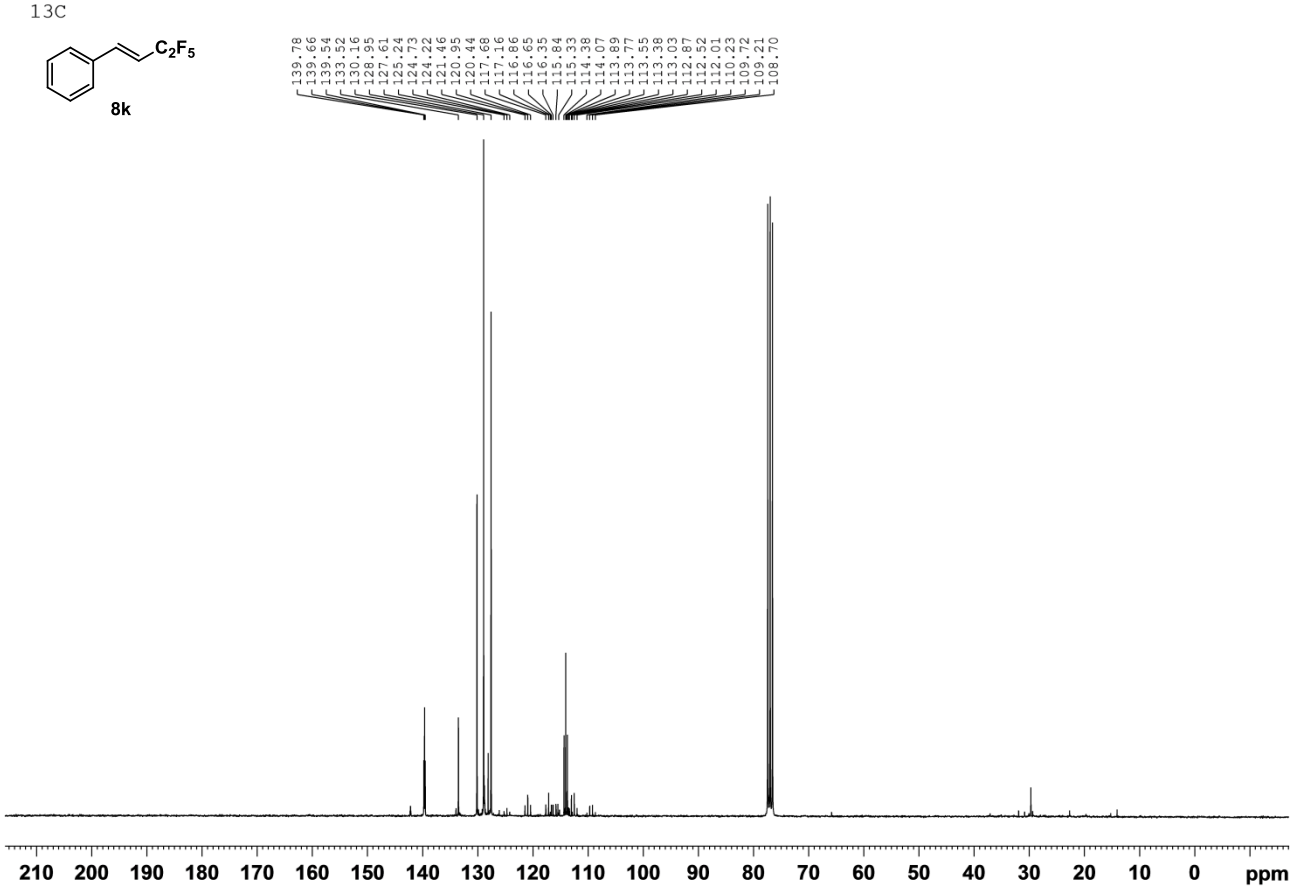
8j


-83.804
-113.874
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm
3.00
2.00

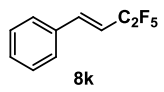
1H


8k
7.5047
7.4925
7.4887
7.4799
7.4726
7.4209
7.4083
7.3987
7.3864
7.3804
7.2381
7.2307
7.2233
7.1841
7.1768
7.1693
6.2631
6.2234
6.2093
6.1829
6.1695
6.1297
10
9
8
7
6
5
4
3
2
1
ppm
5.39
1.00
1.00

13C


8k
139.78
139.66
139.54
133.52
130.16
128.95
127.61
125.24
124.73
124.22
121.46
120.95
120.44
117.68
117.16
116.66
116.65
116.35
115.84
115.33
114.38
114.07
113.89
113.77
113.55
113.38
113.03
112.87
112.52
112.01
110.23
109.72
109.21
108.70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

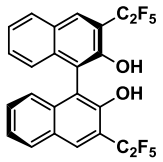
19F


$C_2F_5$

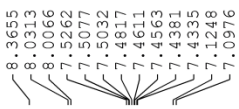
8k

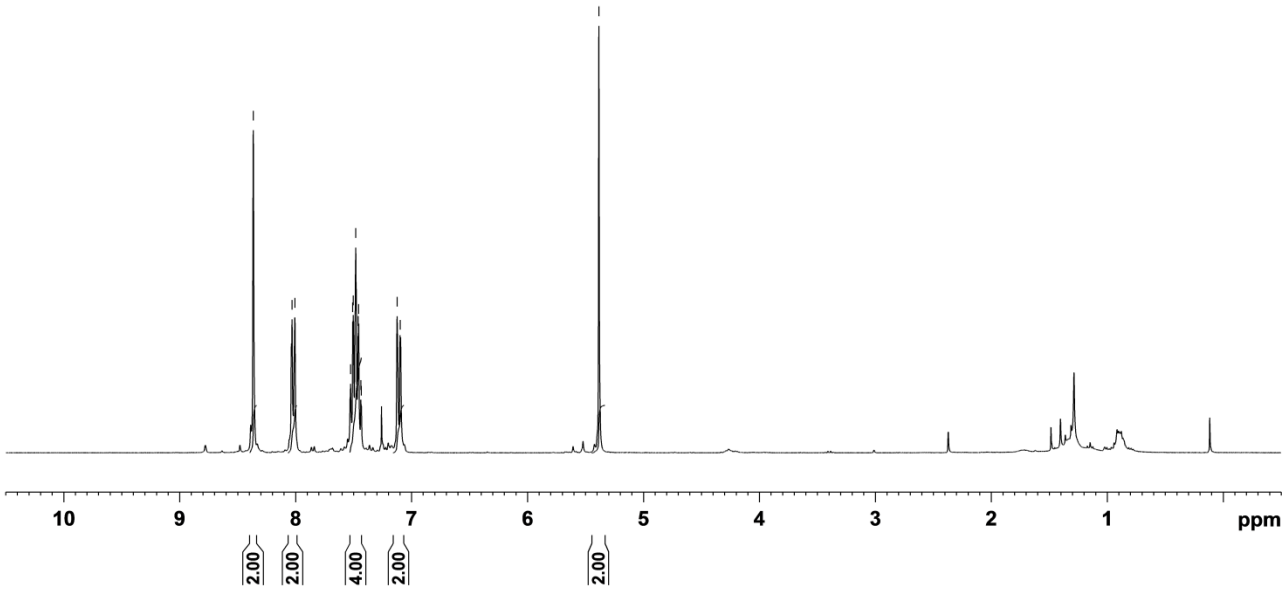

-85.124
-85.566
-109.251
-109.305
-114.885
-114.928
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm
3.00
0.25
0.15
2.00

1H

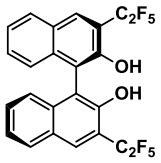

$C_2F_5$
OH
OH
$C_2F_5$

8l


8.3655
8.0313
8.0066
7.5262
7.5077
7.5032
7.4817
7.4611
7.4563
7.4381
7.4335
7.1248
7.0976
5.3849


10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
4.00
2.00
2.00

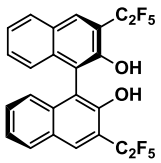
13C


$C_2F_5$
OH
OH
$C_2F_5$

8l


150.01
134.80
132.64
132.53
132.42
130.19
129.68
128.00
125.95
125.52
125.30
124.77
123.81
121.76
121.25
120.74
117.96
117.81
117.45
117.28
117.10
116.93
116.80
116.49
116.23
114.42
114.16
113.89
113.64
113.36
113.13
112.83
112.64
111.03
110.50
109.97
109.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

19F


$C_2F_5$
OH
OH
$C_2F_5$

8l


-83.510
-111.619
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 ppm
6.00
4.00