

Fluorination of Alkylidenecyclopropanes and Alkylidenecyclobutanes: Divergent Synthesis of Fluorinated Cyclopropanes and Cyclobutanes

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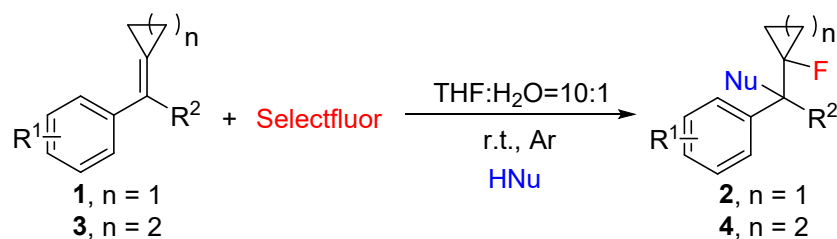
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Supporting Information

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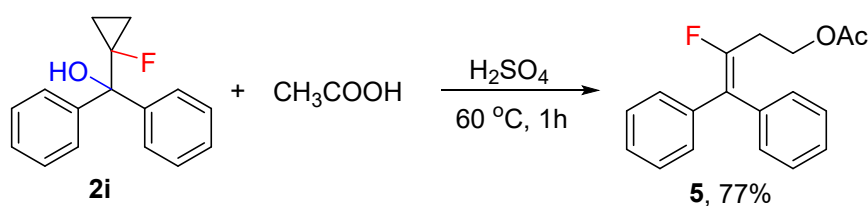
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2.2.2 General procedure for the synthesis of compounds 2m-2q and 4o-4q



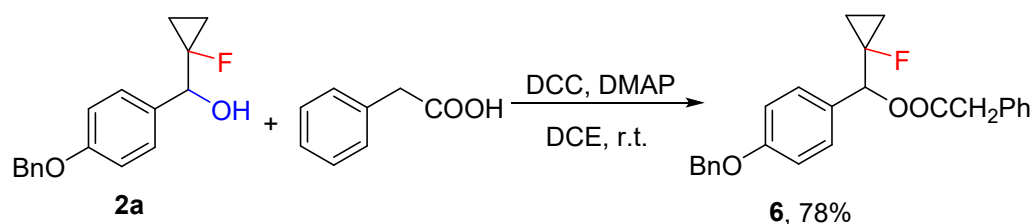
To a Schlenk tube were added **1** or **3** (0.2 mmol, 1.0 equiv.), selectfluor (0.4 mmol, 2.0 equiv.), nucleophilic reagent such as alcohol or carboxylic acid (1.0 mL), THF (2.0 mL), H₂O (0.2 mL). Then the mixture was stirred at room temperature under argon atmosphere for 3-6 h. Upon completion as indicated by TLC, the solution was concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products **2** or **4**.

2.3 The experimental procedure for the synthesis of product 5



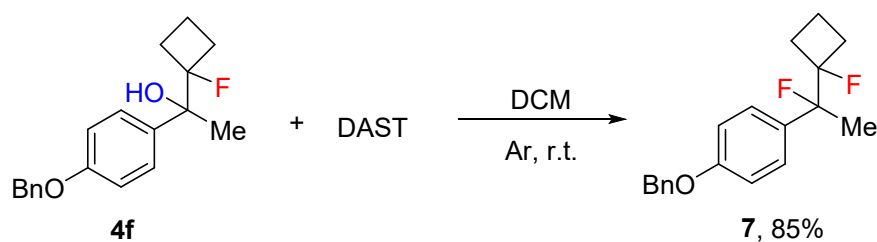
To a Schlenk tube were added **2i** (0.1 mmol, 1.0 equiv.), CH₃COOH (1.0 mL), two drops of H₂SO₄. The mixture was stirred at 60 °C for 1 h. Upon completion as monitored by TLC, adjusting the pH of the reaction mixture to 7 with NaHCO₃ solution. The aqueous phase was extracted with EtOAc for three times. The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **5**.

2.4 The experimental procedure for the synthesis of product 6



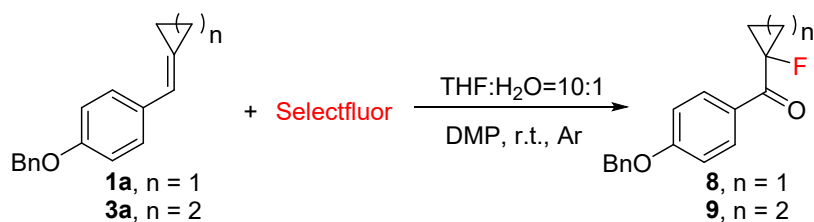
To a Schlenk tube were added **2a** (0.2 mmol, 1.0 equiv.), phenylacetic acid (0.2 mmol, 1.0 equiv.), DCC (0.22 mmol, 1.1 equiv.), DMAP (0.02 mmol, 0.1 equiv.), DCE (2.0 mL). The mixture was stirred at room temperature for 5 h. Upon completion as indicated by TLC, the solution was concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **6**.

2.5 The experimental procedure for the synthesis of product 7



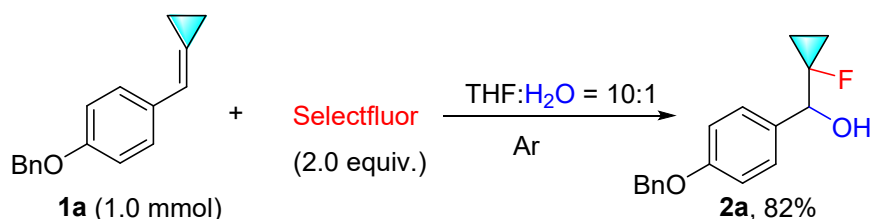
To a Schlenk tube were added **4f** (0.2 mmol, 1.0 equiv.), DAST (0.22 mmol, 1.1 equiv.), DCM (2.0 mL). Then the mixture was stirred at room temperature under argon atmosphere for 6 h. Upon completion as indicated by TLC, NaHCO_3 solution was added to quench the reaction. The aqueous phase was extracted with EtOAc for three times. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **7**.

2.6 The experimental procedure for the synthesis of product 8 and 9



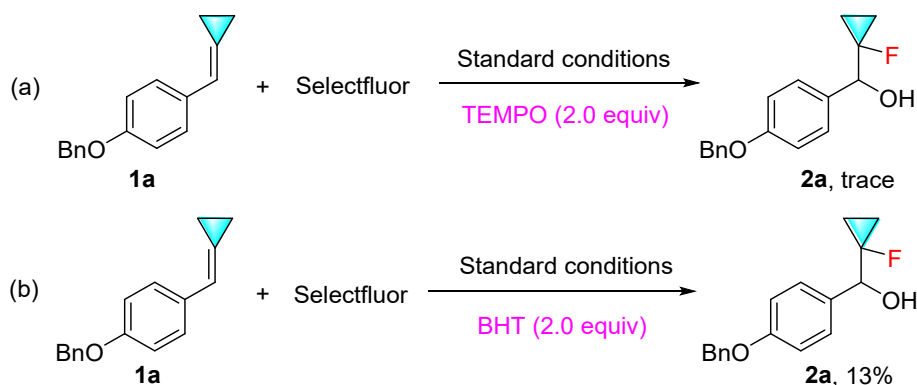
To a Schlenk tube were added **1a** or **3a** (0.2 mmol, 1.0 equiv.), selectfluor (0.4 mmol, 2.0 equiv.), DMP (0.4 mmol, 2.0 equiv.), THF (2.0 mL), H₂O (0.2 mL). Then the mixture was stirred at room temperature under argon atmosphere for 5 h. Upon completion as indicated by TLC, the solution was concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **8** or **9**.

2.7 Fluorohydroxylation of ACP **1a** at 1.0 mmol scale



To a Schlenk tube were added **1a** (1.0 mmol, 1.0 equiv.), selectfluor (2.0 mmol, 2.0 equiv.), THF (10.0 mL), H₂O (1.0 mL). Then the mixture was stirred at room temperature under argon atmosphere for 5 h. Upon completion as indicated by TLC, the solution was concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products **2a**.

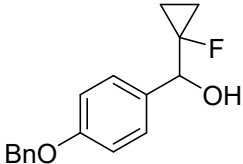
2.8 Radical trapping experiments

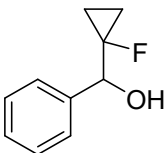


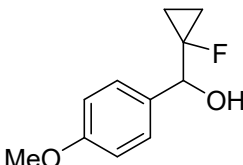
To a Schlenk tube were added **1a** (0.2 mmol, 1.0 equiv.), selectfluor (0.4 mmol, 2.0 equiv.), TEMPO or BHT (0.4 mmol, 2.0 equiv.), THF (2.0 mL) and H₂O (0.2 mL). Then the mixture was stirred at room temperature under argon atmosphere

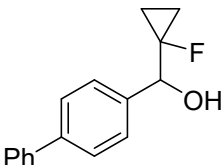
for 5 h. The reaction was monitored by TLC, and the yield was obtained by ^1H NMR analysis using 4-methyl benzophenone as the internal standard.

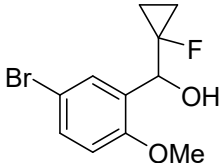
3. Characterization data of products

 **(4-(benzyloxy)phenyl)(1-fluorocyclopropyl)methanol (2a):** White solid (47.3 mg, 87% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 7.4$ Hz, 2H), 7.42-7.31 (m, 5H), 6.98 (d, $J = 8.2$ Hz, 2H), 5.07 (s, 2H), 4.81 (d, $J = 16.6$ Hz, 1H), 2.37 (s, 1H), 1.16-0.98 (m, 2H), 0.84-0.73 (m, 1H), 0.72-0.65 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.7, 136.9, 131.9 (d, $J = 3.1$ Hz), 128.6, 128.1, 128.0, 127.5, 114.7, 81.9 (d, $J = 219.3$ Hz), 75.0 (d, $J = 22.9$ Hz), 70.1, 9.2 (d, $J = 11.9$ Hz), 8.1 (d, $J = 11.8$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -192.48. **ESI-MS:** calcd for $\text{C}_{17}\text{H}_{17}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 295.1110, Found: 295.1112.

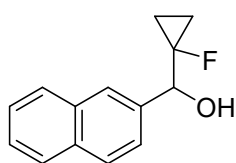
 **(1-fluorocyclopropyl)(phenyl)methanol (2b):** Colorless oil (13.8 mg, 41% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.4$ Hz, 2H), 7.32 (t, $J = 7.1$ Hz, 1H), 4.85 (d, $J = 17.0$ Hz, 1H), 2.49 (brs, 1H), 1.15-1.01 (m, 2H), 0.82-0.76 (m, 1H), 0.72-0.66 (m, 1H); ^{19}F NMR (471 MHz, CDCl_3) δ -192.56. ^{13}C NMR (126 MHz, CDCl_3) δ 139.5 (d, $J = 3.3$ Hz), 128.4, 128.2, 126.8, 81.8 (d, $J = 219.6$ Hz), 75.5 (d, $J = 22.9$ Hz), 9.3 (d, $J = 11.9$ Hz), 8.2 (d, $J = 11.6$ Hz). **ESI-MS:** calcd for $\text{C}_{10}\text{H}_{11}\text{OFNa}$ [$\text{M} + \text{Na}$] $^+$: 189.0692, Found: 189.0694.

 **(1-fluorocyclopropyl)(4-methoxyphenyl)methanol (2c):** Colorless oil (29.9 mg, 76% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.35 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 4.79 (d, $J = 16.5$ Hz, 1H), 3.80 (s, 3H), 2.48 (d, $J = 3.6$ Hz, 1H), 1.12-0.99 (m, 2H), 0.79-0.73 (m, 1H), 0.70-0.64 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.4, 131.7 (d, $J = 3.3$ Hz), 128.1, 113.7, 81.9 (d, $J = 219.5$ Hz), 75.0 (d, $J = 22.9$ Hz), 55.3, 9.2 (d, $J = 11.8$ Hz), 8.0 (d, $J = 11.7$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -192.38. **ESI-MS:** calcd for $\text{C}_{11}\text{H}_{13}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 219.0797, Found: 219.0791.

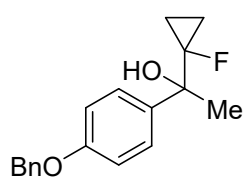
 **[1,1'-biphenyl]-4-yl(1-fluorocyclopropyl)methanol (2d):** White solid (41.1 mg, 85% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.61-7.59 (m, 4H), 7.52 (d, $J = 8.1$ Hz, 2H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.3$ Hz, 1H), 4.89 (d, $J = 17.1$ Hz, 1H), 2.43 (s, 1H), 1.19-1.05 (m, 2H), 0.87-0.81 (m, 1H), 0.78-0.72 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.1, 140.7, 138.5, 138.4, 128.8, 127.4, 127.3, 127.1, 81.8 (d, $J = 219.8$ Hz), 75.3 (d, $J = 22.8$ Hz), 9.3 (d, $J = 11.9$ Hz), 8.3 (d, $J = 11.7$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -192.72. **ESI-MS:** calcd for $\text{C}_{16}\text{H}_{15}\text{OFNa}$ [$\text{M} + \text{Na}$] $^+$: 265.1005, Found: 265.1009.

 **(5-bromo-2-methoxyphenyl)(1-fluorocyclopropyl)methanol (2f):** Colorless oil (21.9 mg, 40% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.62 (d, $J = 2.2$ Hz, 1H), 7.38 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.76 (d, $J = 8.7$ Hz, 1H), 5.14 (dd, $J = 17.8, 4.6$ Hz, 1H), 3.83 (s, 3H), 2.79 (d, $J = 4.9$ Hz, 1H), 1.17-1.06 (m, 1H), 1.06-0.95 (m, 1H), 0.83-0.76 (m, 1H), 0.69-0.60 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.7, 131.7, 130.9 (d, $J = 1.5$ Hz), 129.8 (d, $J = 3.0$ Hz),

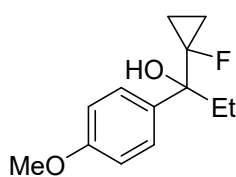
113.2, 112.3, 81.3 (d, $J = 220.4$ Hz), 70.3 (d, $J = 22.9$ Hz), 55.7, 9.7 (d, $J = 11.9$ Hz), 8.1 (d, $J = 11.6$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -192.23. **ESI-MS**: calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{FNaBr}$ [$\text{M} + \text{Na}$] $^+$: 296.9902, Found: 296.9902.



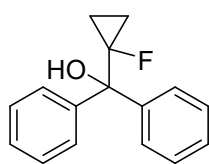
(1-fluorocyclopropyl)(naphthalen-2-yl)methanol (2g): White solid (32.4 mg, 75% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.90 (s, 1H), 7.86-7.84 (m, 3H), 7.56 (d, $J = 8.4$ Hz, 1H), 7.51-7.48 (m, 2H), 5.04 (dd, $J = 16.8, 3.8$ Hz, 1H), 2.54 (d, $J = 4.1$ Hz, 1H), 1.18-1.04 (m, 2H), 0.88-0.81 (m, 1H), 0.76-0.70 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 136.89 (d, $J = 3.4$ Hz), 133.2, 133.1, 128.1, 128.0, 127.7, 126.2, 126.2, 125.8, 124.8, 82.0 (d, $J = 219.8$ Hz), 75.6 (d, $J = 22.9$ Hz), 9.4 (d, $J = 11.9$ Hz), 8.3 (d, $J = 11.4$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -191.96. **ESI-MS**: calcd for $\text{C}_{14}\text{H}_{13}\text{OFNa}$ [$\text{M} + \text{Na}$] $^+$: 239.0848, Found: 239.0842.



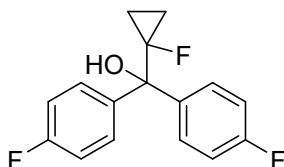
1-(4-(benzyloxy)phenyl)-1-(1-fluorocyclopropyl)ethan-1-ol (2h): White solid (46.9 mg, 82% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, $J = 8.7$ Hz, 2H), 7.43 (d, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.1$ Hz, 1H), 6.96 (d, $J = 8.7$ Hz, 2H), 5.06 (s, 2H), 2.18 (s, 1H), 1.62 (s, 3H), 1.10-0.91 (m, 2H), 0.89-0.82 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.2, 137.0, 136.7 (d, $J = 1.1$ Hz), 128.6, 128.0, 127.5, 127.2, 114.4, 84.6 (d, $J = 218.2$ Hz), 73.9 (d, $J = 23.0$ Hz), 70.0, 26.2 (d, $J = 2.0$ Hz), 8.7 (d, $J = 12.0$ Hz), 7.9 (d, $J = 11.9$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -187.79. **ESI-MS**: calcd for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 309.1267, Found: 309.1261.



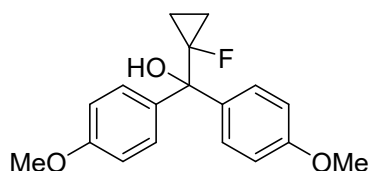
1-(1-fluorocyclopropyl)-1-(4-methoxyphenyl)propan-1-ol (2i): Colorless oil (38.6 mg, 86% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.42 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 3.81 (s, 3H), 2.07 (s, 1H), 2.06-1.98 (m, 2H), 1.05-0.95 (m, 1H), 0.93-0.89 (m, 1H), 0.86 (t, $J = 7.3$ Hz, 3H), 0.84-0.79 (m, 1H), 0.78-0.72 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.7, 134.4, 127.5, 113.3, 84.7 (d, $J = 218.4$ Hz), 76.2 (d, $J = 22.3$ Hz), 55.2, 30.3 (d, $J = 1.9$ Hz), 8.8 (d, $J = 12.3$ Hz), 7.5 (d, $J = 3.7$ Hz), 7.4; ^{19}F NMR (471 MHz, CDCl_3) δ -187.51. **ESI-MS**: calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 247.1110, Found: 247.1107.



(1-fluorocyclopropyl)diphenylmethanol (2j)^[3]: Colorless oil (34.8 mg, 72% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.52 (d, $J = 7.6$ Hz, 4H), 7.36-7.28 (m, 6H), 2.84 (s, 1H), 1.18-1.11 (m, 2H), 0.86-0.81 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.6, 128.0, 127.7, 127.7, 83.1 (d, $J = 220.3$ Hz), 79.0 (d, $J = 22.7$ Hz), 8.2 (d, $J = 11.7$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -185.09.

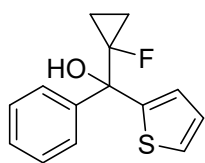


(1-fluorocyclopropyl)bis(4-fluorophenyl)methanol (2k): Colorless oil (47.8 mg, 86% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.47-7.44 (m, 4H), 7.02 (t, $J = 8.7$ Hz, 4H), 2.79 (s, 1H), 1.17-1.11 (m, 2H), 0.82-0.77 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.3 (d, $J = 246.8$ Hz), 139.2 (d, $J = 3.1$ Hz), 129.5 (d, $J = 8.2$ Hz), 114.9 (d, $J = 21.2$ Hz), 83.1 (d, $J = 220.4$ Hz), 78.2 (d, $J = 23.0$ Hz), 8.1 (d, $J = 11.7$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -114.54, -185.29. **ESI-MS**: calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NaO}$ [$\text{M} + \text{Na}$] $^+$: 301.0816, Found: 301.0813.

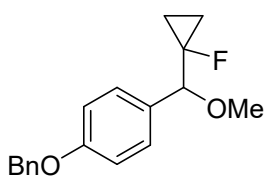


(1-fluorocyclopropyl)bis(4-methoxyphenyl)methanol (2l)^[3]: Colorless oil (50.1 mg, 83% yield); ^1H NMR (500 MHz,

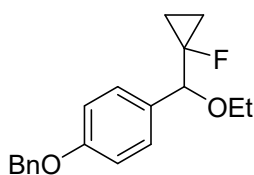
CDCl₃) δ 7.40 (d, *J* = 8.7 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 3.80 (s, 6H), 2.76 (d, *J* = 1.4 Hz, 1H), 1.14-1.07 (m, 2H), 0.83-0.78 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 158.9, 136.1, 128.9, 113.2, 83.3 (d, *J* = 220.2 Hz), 78.4 (d, *J* = 22.8 Hz), 55.2, 8.1 (d, *J* = 11.7 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -184.81.



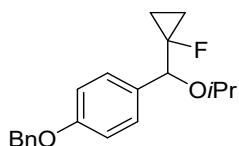
(1-fluorocyclopropyl)(phenyl)(thiophen-2-yl)methanol (2m): Colorless oil (43.6 mg, 88% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, *J* = 7.3 Hz, 2H), 7.34-7.27(m, 4H), 7.03 (d, *J* = 2.7 Hz, 1H), 6.98-6.92 (m, 1H), 2.98 (s, 1H), 1.21-1.05 (m, 2H), 0.95-0.91 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 148.3, 142.7, 128.1, 128.0, 127.2, 126.5, 126.4, 125.6, 83.9 (d, *J* = 220.8 Hz), 77.5, 8.9 (d, *J* = 11.8 Hz), 8.4 (d, *J* = 11.3 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -185.25. **ESI-MS:** calcd for C₁₄H₁₃OFNa [M + Na]⁺: 271.0569, Found: 271.0562.



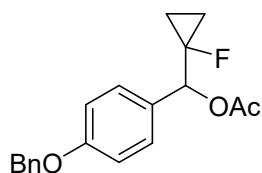
1-(benzyloxy)-4-((1-fluorocyclopropyl)(methoxy)methyl)benzene (2n): White solid (41.2 mg, 72% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 5.08 (s, 2H), 4.39 (d, *J* = 15.2 Hz, 1H), 3.36 (s, 3H), 1.09-0.94 (m, 2H), 0.81-0.71 (m, 1H), 0.67-0.57 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 158.8, 137.0, 129.9 (d, *J* = 3.5 Hz), 128.8, 128.6, 128.0, 127.5, 114.7, 83.9 (d, *J* = 22.3 Hz), 80.7 (d, *J* = 219.9 Hz), 70.1, 57.2, 9.4 (d, *J* = 11.8 Hz), 7.6 (d, *J* = 11.7 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -189.34. **ESI-MS:** calcd for C₁₈H₁₉O₂FNa [M + Na]⁺: 309.1267, Found: 309.1264.



1-(benzyloxy)-4-(ethoxy(1-fluorocyclopropyl)methyl)benzene (2o): White solid (40.2 mg, 67% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 5.07 (s, 2H), 4.48 (d, *J* = 15.1 Hz, 1H), 3.53-3.44 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H), 1.07-0.93 (m, 2H), 0.80-0.73 (m, 1H), 0.66-0.60 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 158.7, 137.0, 130.8 (d, *J* = 3.7 Hz), 128.7, 128.6, 128.0, 127.5, 114.6, 81.8 (d, *J* = 22.7 Hz), 79.9, 70.0, 64.7, 15.3, 9.3 (d, *J* = 11.3 Hz), 7.8 (d, *J* = 11.3 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -189.45. **ESI-MS:** calcd for C₁₉H₂₁O₂FNa [M + Na]⁺: 323.1423, Found: 323.1427.

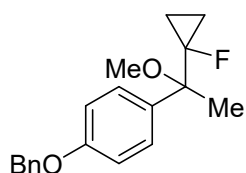


1-(benzyloxy)-4-((1-fluorocyclopropyl)(isopropoxy)methyl)benzene (2p): White solid (25.1 mg, 40% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.06 (s, 2H), 4.57 (d, *J* = 14.6 Hz, 1H), 3.63-3.54 (m, 1H), 1.17 (d, *J* = 6.0 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.05-0.90 (m, 2H), 0.79-0.73 (m, 1H), 0.63-0.57 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 158.6, 137.0, 131.5 (d, *J* = 3.4 Hz), 128.7, 128.6, 128.0, 127.5, 114.5, 81.1 (d, *J* = 219.7 Hz), 78.9 (d, *J* = 22.8 Hz), 70.0, 69.5, 23.2, 21.2, 9.0 (d, *J* = 11.8 Hz), 7.9 (d, *J* = 11.8 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -189.58. **ESI-MS:** calcd for C₂₀H₂₃O₂FNa [M + Na]⁺: 337.1580, Found: 337.1578.



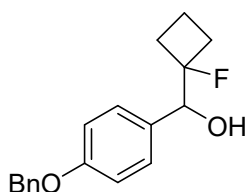
(benzyloxy)phenyl(1-fluorocyclopropyl)methyl acetate (2q): White solid (30.1 mg, 48% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.44-7.34 (m, 7H), 6.97 (d, *J* = 8.2 Hz, 2H), 5.76 (d, *J* = 20.9 Hz, 1H), 5.06 (s, 2H),

2.16 (s, 3H), 1.17-1.04 (m, 2H), 0.87-0.72 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.2, 158.9, 136.9, 128.8 (d, $J = 2.6$ Hz), 128.6, 128.0, 127.5, 114.7, 80.0 (d, $J = 222.5$ Hz), 76.5 (d, $J = 20.6$ Hz), 70.0, 21.2, 10.1 (d, $J = 12.0$ Hz), 9.2 (d, $J = 11.4$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -193.03. **ESI-MS:** calcd for $\text{C}_{19}\text{H}_{19}\text{O}_3\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 337.1216, Found: 337.1215.



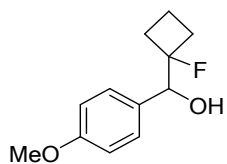
1-(benzyloxy)-4-(1-(1-fluorocyclopropyl)-1-methoxyethyl)benzene (2r):

White solid (43.8 mg, 73% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, $J = 7.5$ Hz, 2H), 7.42-7.36 (m, 4H), 7.34 (t, $J = 7.1$ Hz, 1H), 6.98 (d, $J = 8.6$ Hz, 2H), 5.07 (s, 2H), 3.13 (s, 3H), 1.69 (s, 3H), 0.98-0.89 (m, 2H), 0.88-0.82 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.3, 137.0, 133.7, 128.6, 128.6, 128.0, 127.5, 114.3, 84.4 (d, $J = 217.9$ Hz), 77.9 (d, $J = 23.1$ Hz), 70.0, 50.4, 20.1 (d, $J = 1.7$ Hz), 8.2 (d, $J = 11.9$ Hz), 8.1 (d, $J = 11.9$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -186.80. **ESI-MS:** calcd for $\text{C}_{19}\text{H}_{21}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 323.1423, Found: 323.1429.



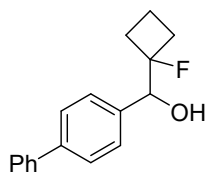
(4-(benzyloxy)phenyl)(1-fluorocyclobutyl)methanol (4a):

White solid (42.1 mg, 73% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 7.3$ Hz, 2H), 7.39 (dd, $J = 12.4, 7.9$ Hz, 4H), 7.33 (t, $J = 7.2$ Hz, 1H), 6.98 (d, $J = 8.7$ Hz, 2H), 5.07 (s, 2H), 4.71 (d, $J = 18.8$ Hz, 1H), 2.42-2.35 (m, 1H), 2.36-2.15 (m, 4H), 1.81-1.71 (m, 1H), 1.27-1.14 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.7, 136.9, 131.0 (d, $J = 3.8$ Hz), 128.7 (d, $J = 1.3$ Hz), 128.6, 128.0, 127.5, 114.6, 98.3 (d, $J = 215.5$ Hz), 75.8 (d, $J = 23.9$ Hz), 70.0, 31.0 (d, $J = 21.4$ Hz), 30.3 (d, $J = 21.4$ Hz), 11.5 (d, $J = 11.3$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -142.90. **ESI-MS:** calcd for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 309.1267, Found: 309.1262.



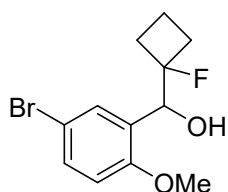
(1-fluorocyclobutyl)(4-methoxyphenyl)methanol (4b):

White solid (37.0 mg, 88% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.37 (d, $J = 8.3$ Hz, 2H), 6.89 (d, $J = 8.4$ Hz, 2H), 4.70 (dd, $J = 18.8, 4.0$ Hz, 1H), 3.81 (s, 3H), 2.38-2.30 (m, 3H), 2.27-2.14 (m, 2H), 1.80-1.68 (m, 1H), 1.29-1.15 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.5, 130.6 (d, $J = 3.7$ Hz), 128.6, 113.6, 98.3 (d, $J = 215.1$ Hz), 75.8 (d, $J = 23.3$ Hz), 55.3, 31.0 (d, $J = 21.4$ Hz), 30.2 (d, $J = 21.1$ Hz), 11.5 (d, $J = 12.7$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -142.56. **ESI-MS:** calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 233.0954, Found: 233.0948.



[1,1'-biphenyl]-4-yl(1-fluorocyclobutyl)methanol (4c):

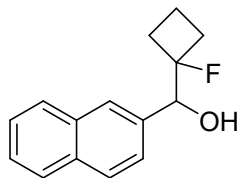
White solid (42.4 mg, 83% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.60 (d, $J = 8.0$ Hz, 4H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.3$ Hz, 1H), 4.81 (d, $J = 18.8$ Hz, 1H), 2.49-2.41 (m, 1H), 2.42-2.17 (m, 4H), 1.85-1.74 (m, 1H), 1.30-1.22 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.1, 140.7, 137.5 (d, $J = 3.8$ Hz), 128.8, 127.9, 127.4, 127.1, 126.9, 98.3 (d, $J = 215.5$ Hz), 76.0 (d, $J = 23.9$ Hz), 31.0 (d, $J = 21.4$ Hz), 30.4 (d, $J = 21.4$ Hz), 11.6 (d, $J = 12.6$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -142.70. **ESI-MS:** calcd for $\text{C}_{17}\text{H}_{17}\text{OFNa}$ [$\text{M} + \text{Na}$] $^+$: 279.1161, Found: 279.1157.



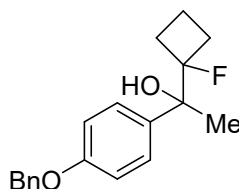
(5-bromo-2-methoxyphenyl)(1-fluorocyclobutyl)methanol (4d):

Colorless oil (25.0 mg, 43% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.58 (s, 1H), 7.38 (d, $J = 8.7$ Hz, 1H), 6.78 (d, $J = 8.7$ Hz, 1H), 5.17 (dd, $J = 21.5, 5.5$ Hz, 1H), 3.83 (s, 3H), 2.69 (d, $J = 5.8$ Hz, 1H), 2.46-2.40 (m, 1H), 2.38-2.28 (m, 1H), 2.28-2.11 (m, 2H), 1.84-1.77 (m, 1H), 1.40-1.31 (m, 1H); ^{13}C

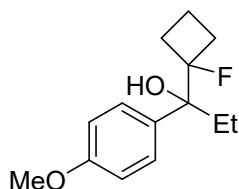
NMR (126 MHz, CDCl₃) δ 156.1, 131.7, 131.4 (d, $J = 2.9$ Hz), 129.2 (d, $J = 2.8$ Hz), 113.2, 112.4, 98.6 (d, $J = 216.4$ Hz), 69.9 (d, $J = 23.1$ Hz), 55.7, 31.3 (d, $J = 21.5$ Hz), 30.4 (d, $J = 21.1$ Hz), 11.8 (d, $J = 12.6$ Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -144.68. **ESI-MS**: calcd for C₁₂H₁₄O₂FNaBr [M + Na]⁺: 311.0059, Found: 311.0063.



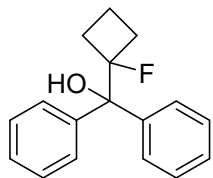
(1-fluorocyclobutyl)(naphthalen-2-yl)methanol (4e): White solid (36.0 mg, 78% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.90 (s, 1H), 7.88-7.82 (m, 3H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.52-7.46 (m, 2H), 4.93 (d, $J = 18.7$ Hz, 1H), 2.54-2.40 (m, 2H), 2.40-2.31 (m, 2H), 2.29-2.18 (m, 1H), 1.82-1.71 (m, 1H), 1.27-1.15 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 136.0 (d, $J = 3.5$ Hz), 133.2, 133.0, 128.1, 127.9, 127.7, 126.6, 126.2, 126.1, 125.3 (d, $J = 1.5$ Hz), 98.5 (d, $J = 215.3$ Hz), 76.4 (d, $J = 23.8$ Hz), 31.1 (d, $J = 21.8$ Hz), 30.3 (d, $J = 21.2$ Hz), 11.6 (d, $J = 12.2$ Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -187.51. **ESI-MS**: calcd for C₁₅H₁₅OFNa [M + Na]⁺: 253.1005, Found: 253.1001.



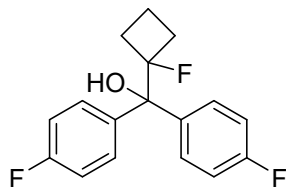
1-(4-(benzyloxy)phenyl)-1-(1-fluorocyclobutyl)ethan-1-ol (4f): White solid (36.6 mg, 61% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, $J = 8.7$ Hz, 2H), 7.44 (d, $J = 7.4$ Hz, 2H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 1H), 6.96 (d, $J = 8.7$ Hz, 2H), 5.07 (s, 2H), 2.52-2.44 (m, 1H), 2.41-2.32 (m, 1H), 2.28-2.10 (m, 2H), 2.08 (s, 1H), 1.80-1.70 (m, 1H), 1.59 (s, 3H), 1.19-1.09 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 158.0, 137.0, 135.3 (d, $J = 1.8$ Hz), 128.6, 128.0, 127.5, 127.5, 114.1, 101.9 (d, $J = 210.9$ Hz), 75.2 (d, $J = 24.7$ Hz), 70.0, 29.9 (d, $J = 7.1$ Hz), 29.8 (d, $J = 7.5$ Hz), 23.4 (d, $J = 3.7$ Hz), 11.9 (d, $J = 8.9$ Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -141.20. **ESI-MS**: calcd for C₁₉H₂₁O₂FNa [M + Na]⁺: 323.1423, Found: 323.1418.



1-(1-fluorocyclobutyl)-1-(4-methoxyphenyl)propan-1-ol (4g): Colorless oil (41.9 mg, 88% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H), 2.50-2.40 (m, 1H), 2.8-2.29 (m, 1H), 2.26-2.17 (m, 1H), 2.15-2.04 (m, 2H), 2.04 (s, 1H), 1.89-1.81 (m, 1H), 1.78-1.69 (m, 1H), 1.20-1.10 (m, 1H), 0.76 (t, $J = 7.4$ Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 158.6, 132.2 (d, $J = 1.4$ Hz), 128.0 (d, $J = 1.6$ Hz), 113.2, 102.3 (d, $J = 210.5$ Hz), 77.9 (d, $J = 23.9$ Hz), 55.2, 29.9 (d, $J = 9.5$ Hz), 29.8 (d, $J = 8.9$ Hz), 26.4 (d, $J = 3.2$ Hz), 12.2 (d, $J = 8.3$ Hz), 7.21; ¹⁹F NMR (471 MHz, CDCl₃) δ -142.39. **ESI-MS**: calcd for C₁₄H₁₉O₂FNa [M + Na]⁺: 261.1267, Found: 261.1263.

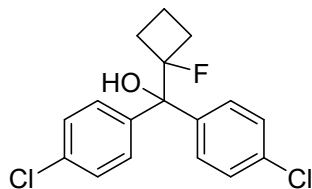


(1-fluorocyclobutyl)diphenylmethanol (4h): Colorless oil (34.3 mg, 67% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, $J = 7.5$ Hz, 4H), 7.34-7.27 (m, 6H), 2.74-2.62 (m, 2H), 2.66 (s, 1H), 2.51-2.40 (m, 2H), 1.81-1.69 (m, 1H), 1.01-0.96 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 143.2, 128.0 (d, $J = 1.8$ Hz), 127.8, 127.4, 101.3 (d, $J = 214.7$ Hz), 79.9 (d, $J = 24.3$ Hz), 31.7 (d, $J = 21.4$ Hz), 12.4 (d, $J = 8.8$ Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -134.15. **ESI-MS**: calcd for C₁₇H₁₇OFNa [M + Na]⁺: 279.1161, Found: 279.1165.

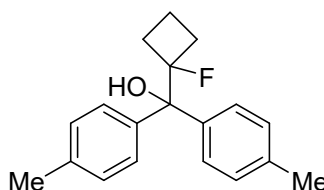


(1-fluorocyclobutyl)bis(4-fluorophenyl)methanol (4i): Colorless oil (50.8 mg, 87% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.39 (dd, $J = 8.3, 5.6$ Hz, 4H), 6.99 (t, $J = 8.7$ Hz, 4H), 2.63 (d, $J = 6.8$ Hz, 1H), 2.61-2.54 (m, 2H), 2.50-2.37 (m, 2H), 1.82-1.71 (m, 1H), 1.04-0.99

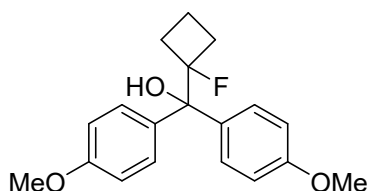
(m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.1 (d, $J = 246.7$ Hz), 138.8 (d, $J = 3.1$ Hz), 129.8 (dd, $J = 8.0, 2.1$ Hz), 114.7 (d, $J = 21.2$ Hz), 101.1 (d, $J = 214.7$ Hz), 79.2 (d, $J = 24.4$ Hz), 31.5 (d, $J = 21.4$ Hz), 12.4 (d, $J = 8.9$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -114.86, -134.29. **ESI-MS**: calcd for $\text{C}_{17}\text{H}_{15}\text{OF}_3\text{Na}$ $[\text{M} + \text{Na}]^+$: 315.0973, Found: 315.0962.



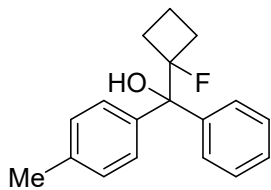
bis(4-chlorophenyl)(1-fluorocyclobutyl)methanol (4j): Colorless oil (55.8 mg, 86% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.35 (d, $J = 8.5$ Hz, 4H), 7.28 (d, $J = 8.6$ Hz, 4H), 2.67 (s, 1H), 2.63-2.52 (m, 2H), 2.50-2.35 (m, 2H), 1.85-1.73 (m, 1H), 1.08-1.03 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.3, 133.6, 129.4 (d, $J = 1.3$ Hz), 128.1, 101.0 (d, $J = 215.5$ Hz), 79.2 (d, $J = 25.2$ Hz), 31.4 (d, $J = 21.4$ Hz), 12.4 (d, $J = 8.8$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -134.53. **ESI-MS**: calcd for $\text{C}_{17}\text{H}_{15}\text{OF}_3\text{NaCl}_2$ $[\text{M} + \text{Na}]^+$: 347.0382, Found: 347.0388.



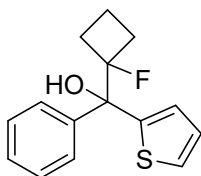
(1-fluorocyclobutyl)di-p-tolylmethanol (4k): Colorless oil (48.3 mg, 85% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.32 (d, $J = 8.0$ Hz, 4H), 7.12 (d, $J = 8.1$ Hz, 4H), 2.70-2.59 (m, 2H), 2.58 (s, 1H), 2.49-2.37 (m, 2H), 2.34 (s, 6H), 1.79-1.69 (m, 1H), 1.03-0.98 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 140.5, 136.9, 128.4, 127.9 (d, $J = 2.5$ Hz), 101.4 (d, $J = 215.4$ Hz), 79.7 (d, $J = 23.9$ Hz), 31.6 (d, $J = 22.7$ Hz), 21.1, 12.5 (d, $J = 8.8$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -134.10. **ESI-MS**: calcd for $\text{C}_{19}\text{H}_{21}\text{OFNa}$ $[\text{M} + \text{Na}]^+$: 307.1474, Found: 307.1478.



(1-fluorocyclobutyl)bis(4-methoxyphenyl)methanol (4l): Colorless oil (51.7 mg, 82% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.34 (d, $J = 8.7$ Hz, 4H), 6.83 (d, $J = 8.7$ Hz, 4H), 3.80 (s, 6H), 2.67-2.59 (m, 2H), 2.58 (s, 1H), 2.49-2.35 (m, 2H), 1.80-1.68 (m, 1H), 1.01-0.96 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.7, 135.7, 129.2 (d, $J = 1.3$ Hz), 113.0, 101.5 (d, $J = 215.5$ Hz), 79.4 (d, $J = 23.9$ Hz), 55.2, 31.6 (d, $J = 21.4$ Hz), 12.4 (d, $J = 8.8$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -133.74. **ESI-MS**: calcd for $\text{C}_{19}\text{H}_{21}\text{O}_3\text{FNa}$ $[\text{M} + \text{Na}]^+$: 339.1372, Found: 339.1373.

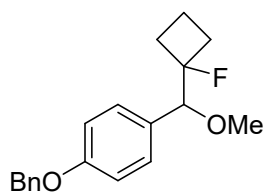


(1-fluorocyclobutyl)(phenyl)(p-tolyl)methanol (4m): Colorless oil (40.2 mg, 74% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.44 (d, $J = 7.6$ Hz, 2H), 7.35-7.27 (m, 5H), 7.12 (d, $J = 8.0$ Hz, 2H), 2.70-2.63 (m, 2H), 2.61 (s, 1H), 2.52-2.37 (m, 2H), 2.34 (s, 3H), 1.81-1.69 (m, 1H), 1.02-0.97 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.4, 140.3, 137.0, 128.5, 128.0 (d, $J = 1.3$ Hz), 127.9 (d, $J = 1.3$ Hz), 127.7, 127.3, 101.3 (d, $J = 215.5$ Hz), 79.8 (d, $J = 23.9$ Hz), 31.7 (d, $J = 5.0$ Hz), 31.6 (d, $J = 5.0$ Hz), 21.1, 12.5 (d, $J = 8.8$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -134.16. **ESI-MS**: calcd for $\text{C}_{18}\text{H}_{19}\text{OFNa}$ $[\text{M} + \text{Na}]^+$: 293.1318, Found: 293.1318.



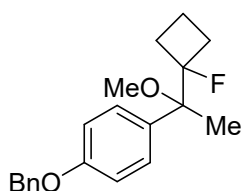
(1-fluorocyclobutyl)(phenyl)(thiophen-2-yl)methanol (4n): Colorless oil (44.5 mg, 85% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, $J = 7.5$ Hz, 2H), 7.37-7.31 (m, 3H), 7.30-7.27 (m, 1H), 7.05 (d, $J = 3.5$ Hz, 1H), 6.98-6.96 (m, 1H), 2.90 (s, 1H), 2.74-2.60 (m, 2H), 2.51-2.29 (m, 2H), 1.86-1.75 (m, 1H), 1.20-1.08 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ

147.6, 141.8, 127.8, 127.8, 127.4 (d, $J = 1.9$ Hz), 126.3, 126.3, 125.4, 101.6 (d, $J = 214.4$ Hz), 78.7 (d, $J = 25.0$ Hz), 31.2 (d, $J = 19.4$ Hz), 31.0 (d, $J = 18.8$ Hz), 12.4 (d, $J = 8.3$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -136.15. **ESI-MS**: calcd for $\text{C}_{15}\text{H}_{15}\text{OFNaS}$ [$\text{M} + \text{Na}$] $^+$: 285.0725, Found: 285.0728.



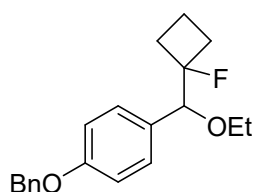
1-(benzyloxy)-4-((1-fluorocyclobutyl)(methoxy)methyl)benzene (4o):

White solid (43.8 mg, 73% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, $J = 7.4$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.35 (d, $J = 7.2$ Hz, 1H), 7.32 (d, $J = 8.3$ Hz, 2H), 6.99 (d, $J = 8.5$ Hz, 2H), 5.07 (s, 2H), 4.16 (d, $J = 18.9$ Hz, 1H), 3.30 (s, 3H), 2.43-2.36 (m, 1H), 2.31-2.22 (m, 2H), 2.19-2.13 (m, 1H), 1.84-1.74 (m, 1H), 1.45-1.34 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.8, 136.0, 128.5, 127.7 (d, $J = 2.4$ Hz), 127.6, 127.0, 126.5, 113.4, 96.5 (d, $J = 216.1$ Hz), 83.8 (d, $J = 23.0$ Hz), 69.0, 56.3, 29.9 (d, $J = 4.7$ Hz), 29.7 (d, $J = 4.1$ Hz), 10.7 (d, $J = 11.8$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -142.59. **ESI-MS**: calcd for $\text{C}_{19}\text{H}_{21}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 323.1423, Found: 323.1426.



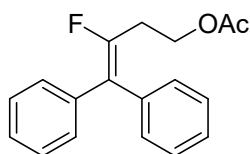
1-(benzyloxy)-4-(1-(1-fluorocyclobutyl)-1-methoxyethyl)benzene (4p):

White solid (33.9 mg, 54% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, $J = 7.4$ Hz, 2H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.1$ Hz, 3H), 6.97 (d, $J = 8.7$ Hz, 2H), 5.07 (s, 2H), 3.17 (s, 3H), 2.62-2.40 (m, 2H), 2.22-2.08 (m, 1H), 1.96-1.84 (m, 1H), 1.84-1.72 (m, 1H), 1.31 (dd, $J = 9.7, 4.8$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.1, 137.1, 132.2, 128.9, 128.6, 128.0, 127.6, 114.0, 101.9 (d, $J = 208.9$ Hz), 79.8 (d, $J = 24.9$ Hz), 70.0, 50.4, 29.5 (d, $J = 22.2$ Hz), 29.3 (d, $J = 21.8$ Hz), 16.6 (d, $J = 4.2$ Hz), 12.3 (d, $J = 6.5$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -144.15. **ESI-MS**: calcd for $\text{C}_{20}\text{H}_{23}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 337.1580, Found: 337.1579.



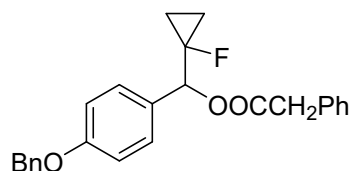
1-(benzyloxy)-4-(ethoxy(1-fluorocyclobutyl)methyl)benzene (4q):

White solid (43.8 mg, 73% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, $J = 7.4$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.34 (d, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 8.2$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 5.07 (s, 2H), 4.25 (d, $J = 18.9$ Hz, 1H), 3.52-3.46 (m, 1H), 3.41-3.32 (m, 1H), 2.45-2.36 (m, 1H), 2.32-2.11 (m, 3H), 1.83-1.76 (m, 1H), 1.48-1.39 (m, 1H), 1.21 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.7, 137.1, 129.6 (d, $J = 2.5$ Hz), 129.4, 128.6, 128, 127.5, 114.3, 97.5 (d, $J = 216.7$ Hz), 82.7 (d, $J = 22.7$ Hz), 70.0, 64.8, 31.0 (d, $J = 21.4$ Hz), 30.8 (d, $J = 21.4$ Hz), 15.2, 11.8 (d, $J = 12.6$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -142.52. **ESI-MS**: calcd for $\text{C}_{20}\text{H}_{23}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 337.1580, Found: 337.1580.

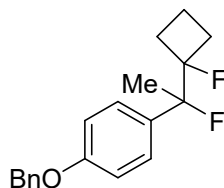


3-fluoro-4,4-diphenylbut-3-en-1-yl acetate (5):

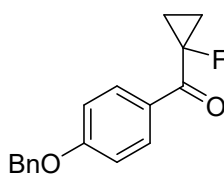
Colorless oil (43.7 mg, 77% yield); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.40 (t, $J = 7.4$ Hz, 2H), 7.33 (dd, $J = 14.4, 7.2$ Hz, 3H), 7.27-7.16 (m, 5H), 4.19 (t, $J = 6.3$ Hz, 2H), 2.63 (t, $J = 6.2$ Hz, 1H), 2.58 (t, $J = 6.2$ Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 170.6, 154.6 (d, $J = 258.9$ Hz), 138.4 (d, $J = 7.7$ Hz), 137.4, 130.3 (d, $J = 2.7$ Hz), 129.5 (d, $J = 4.4$ Hz), 129.1, 128.6, 128.0, 127.6, 122.5 (d, $J = 14.6$ Hz), 60.5, 30.2 (d, $J = 27.2$ Hz), 21.1; ^{19}F NMR (471 MHz, $\text{DMSO}-d_6$) δ -107.91. **ESI-MS**: calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{FNa}$ [$\text{M} + \text{Na}$] $^+$: 307.1110, Found: 307.1109.



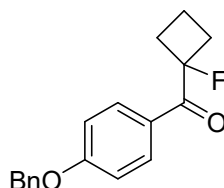
1-(benzyloxy)-4-((1-fluorocyclopropyl)((1-phenylvinyl)peroxy)methyl)benzene (6): White solid (61.3 mg, 78% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.46-7.36 (m, 4H), 7.34-7.25 (m, 8H), 6.92 (d, $J = 8.2$ Hz, 2H), 5.77 (d, $J = 20.1$ Hz, 1H), 5.04 (s, 2H), 3.82-3.65 (m, 2H), 1.10-1.01 (m, 2H), 0.80-0.64 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.7, 158.9, 136.9, 133.8, 129.3, 128.6, 128.6, 128.1, 127.5, 127.2, 114.7, 79.9 (d, $J = 222.5$ Hz), 76.6, 70.0, 41.5, 9.9 (d, $J = 11.9$ Hz), 9.1 (d, $J = 11.4$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -192.77. **ESI-MS:** calcd for $\text{C}_{25}\text{H}_{23}\text{O}_3\text{FNa}$ $[\text{M} + \text{Na}]^+$: 413.1529, Found: 413.1530.



1-(benzyloxy)-4-(1-fluoro-1-(1-fluorocyclobutyl)ethyl)benzene (7): White solid (51.4 mg, 85% yield); ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, $J = 7.2$ Hz, 2H), 7.42-7.33 (m, 5H), 6.98 (d, $J = 8.7$ Hz, 2H), 5.08 (s, 2H), 2.65-2.53 (m, 1H), 2.38-2.24 (m, 2H), 2.11-1.97 (m, 1H), 1.91-1.79 (m, 1H), 1.68 (dd, $J = 23.3$, 2.1 Hz, 3H), 1.53-1.43 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.4, 136.9, 132.6 (d, $J = 22.4$ Hz), 128.6, 128.0, 127.5, 126.7 (dd, $J = 10.0$, 2.5 Hz), 114.2, 99.7 (dd, $J = 211.3$, 34.0 Hz), 96.0 (dd, $J = 173.3$, 28.1 Hz), 70.0, 29.7 (dd, $J = 22.5$, 2.0 Hz), 29.5 (dd, $J = 23.9$, 1.3 Hz), 20.9 (dd, $J = 23.1$, 2.6 Hz), 11.90 (d, $J = 7.6$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -144.77, -159.07. **ESI-MS:** calcd for $\text{C}_{19}\text{H}_{20}\text{OF}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 325.1380, Found: 325.1379.



(4-(benzyloxy)phenyl)(1-fluorocyclopropyl)methanone (8): White solid (38.8 mg, 72% yield); ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, $J = 7.8$ Hz, 2H), 7.47-7.38 (m, 4H), 7.35 (t, $J = 7.1$ Hz, 1H), 7.04 (d, $J = 8.8$ Hz, 2H), 5.15 (s, 2H), 1.58-1.54 (m, 2H), 1.48-1.41 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 196.2 (d, $J = 21.7$ Hz), 162.7, 136.2, 131.9, 131.8, 128.7, 128.3, 127.5, 114.5, 83.3 (d, $J = 233.6$ Hz), 70.1, 16.5 (d, $J = 10.8$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -189.90. **ESI-MS:** calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2\text{FNa}$ $[\text{M} + \text{Na}]^+$: 293.0954, Found: 293.0948.



(4-(benzyloxy)phenyl)(1-fluorocyclobutyl)methanone (9): White solid (33.9 mg, 60% yield); ^1H NMR (500 MHz, CDCl_3) δ 8.00-7.98 (m, 2H), 7.44-7.39 (m, 4H), 7.36-7.34 (m, 1H), 7.01 (d, $J = 8.9$ Hz, 2H), 5.14 (s, 2H), 2.81-2.74 (m, 2H), 2.58-2.47 (m, 2H), 2.02-1.92 (m, 1H), 1.76-1.64 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 194.7 (d, $J = 27.3$ Hz), 162.8, 136.1, 132.2 (d, $J = 5.6$ Hz), 128.7, 128.3, 127.5, 126.3 (d, $J = 3.8$ Hz), 114.5, 98.5 (d, $J = 222.8$ Hz), 70.1, 32.2 (d, $J = 21.9$ Hz), 12.0 (d, $J = 11.9$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -134.59. **ESI-MS:** calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{FNa}$ $[\text{M} + \text{Na}]^+$: 307.1110, Found: 307.1104.

4. Reference

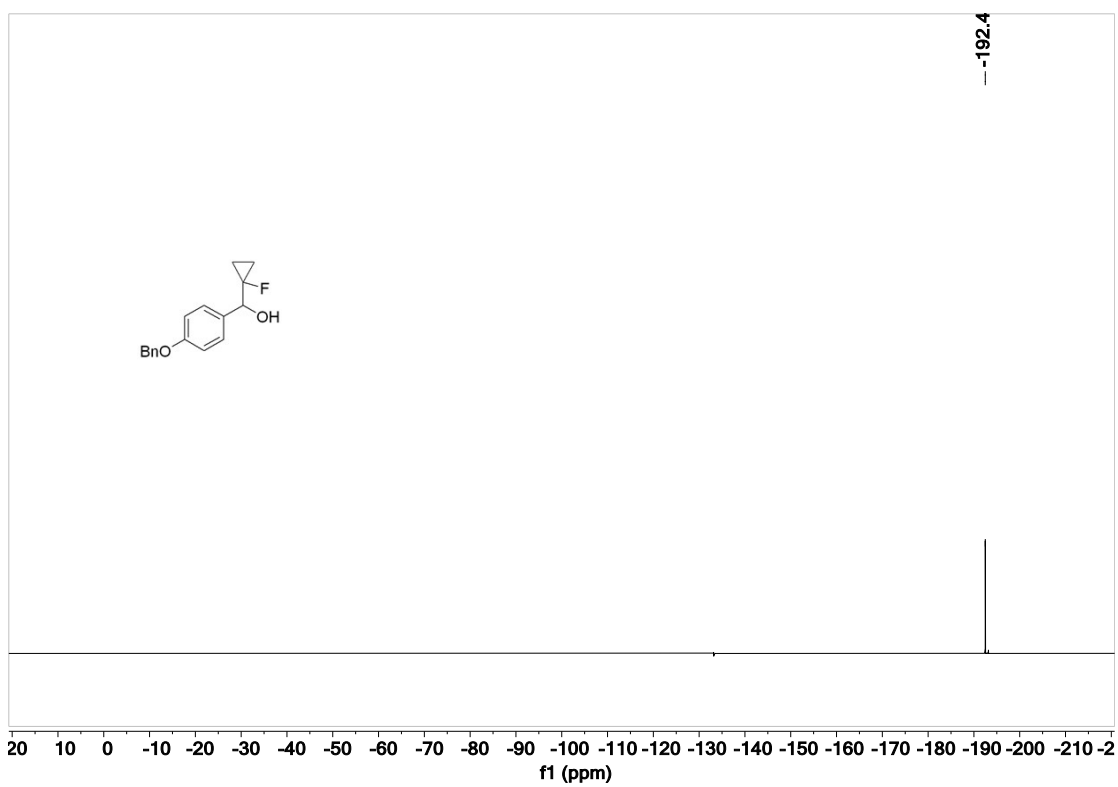
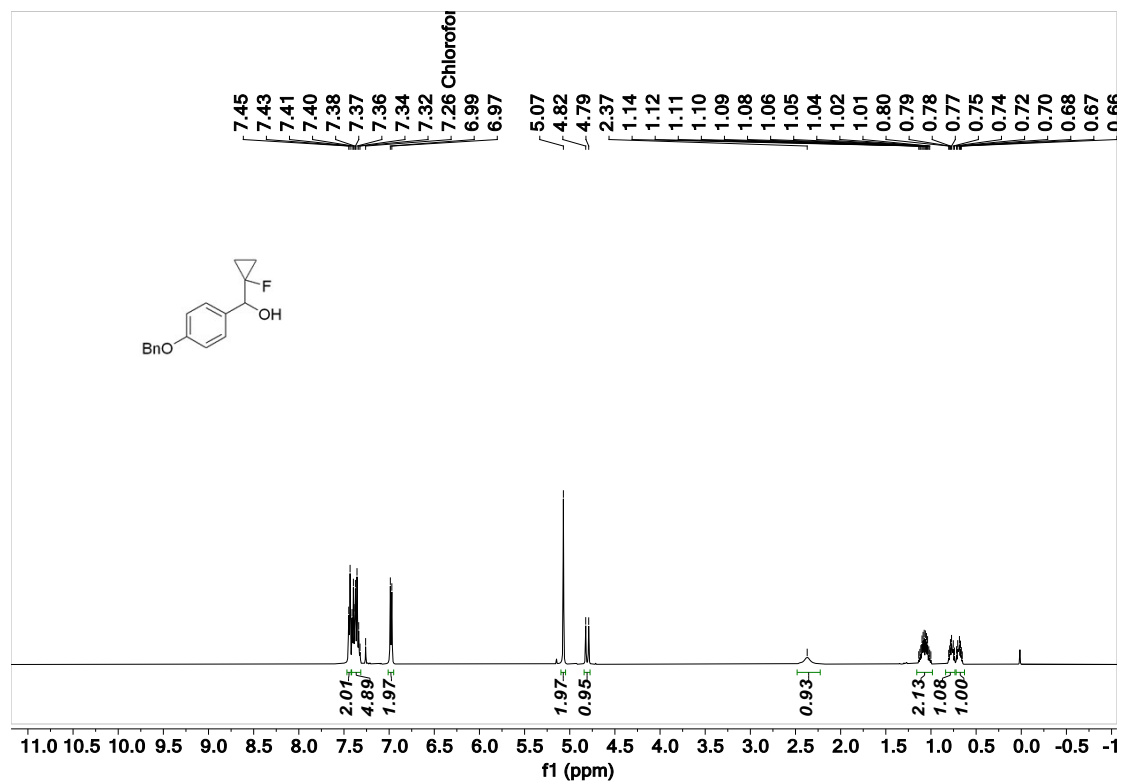
[1] Z.-Z. Zhu, K. Chen, L.-Z. Yu, X.-Y. Tang, and M. Shi, *Org. Lett.* **2015**, 17, 5994.

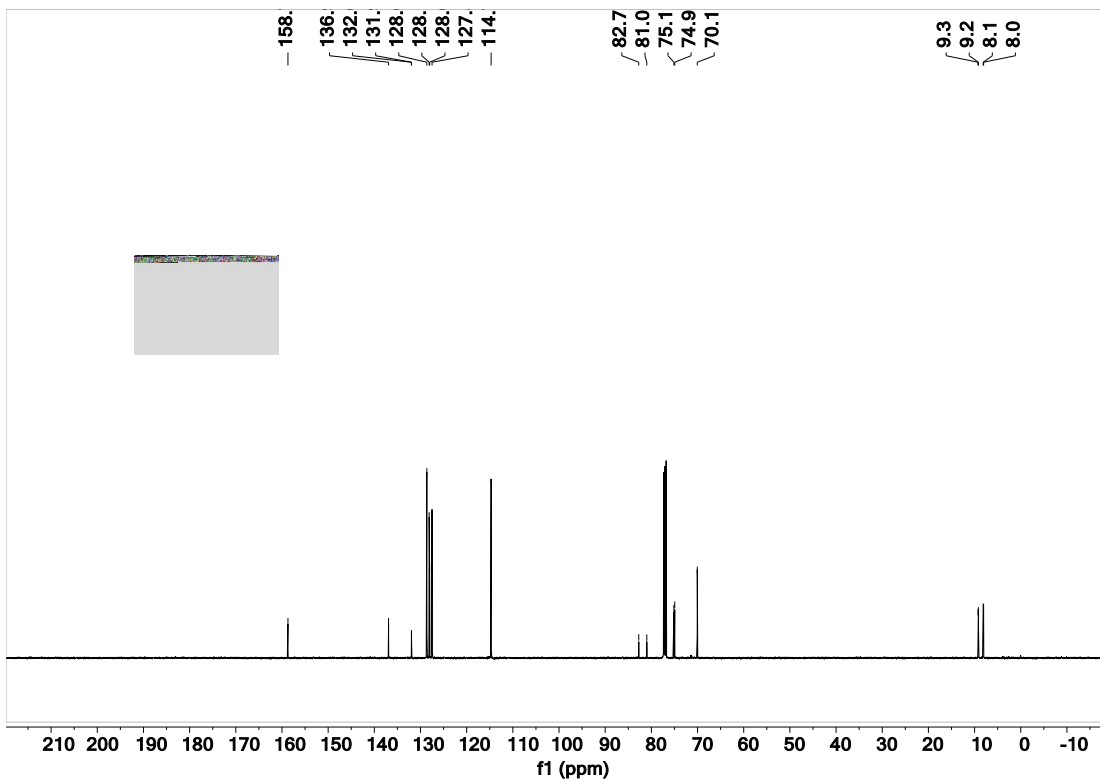
[2] T. Kang, T.-G. Erbay, K.-L. Xu, G.-M. Gallego, A.-Burtea, S.-K. Nair, R.-L. Patman, R. Zhou, S.-C. Sutton, I.- J. Mc Alpine, P. Liu, and K.-M. Engle, *ACS Catal.* **2020**, 10, 13075.

[3] Y. Yang, C. Su, X. Huang, Q. Liu, *Tetrahedron Lett.* **2009**, 50, 5754.

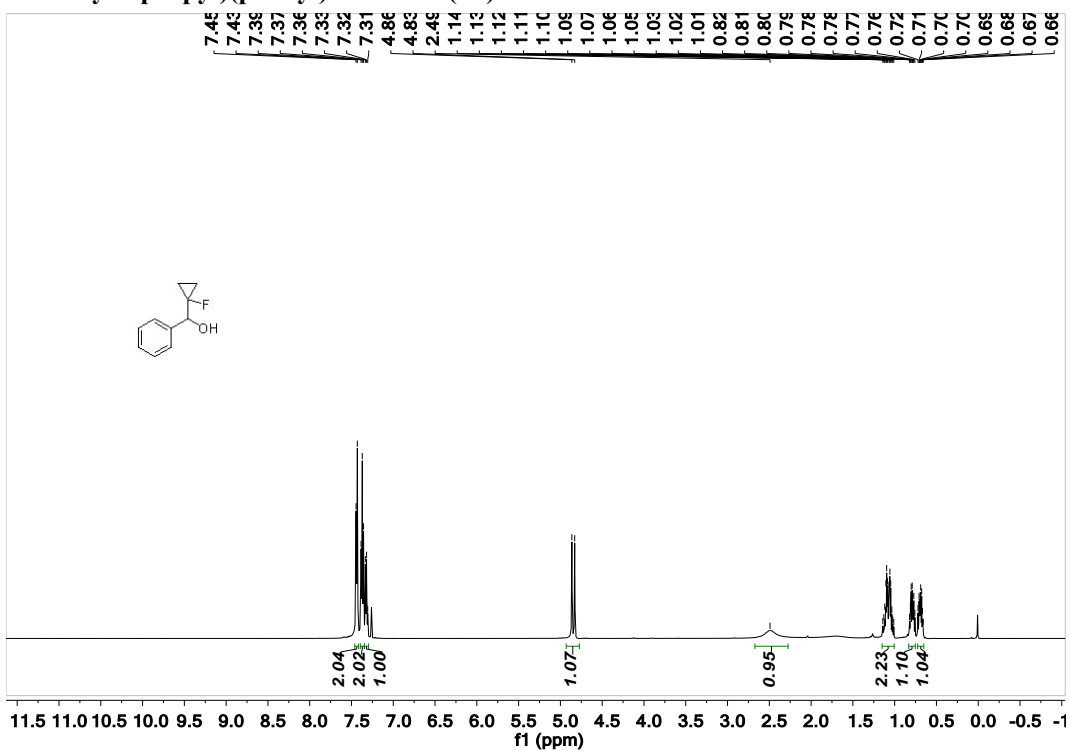
5. NMR spectra of products

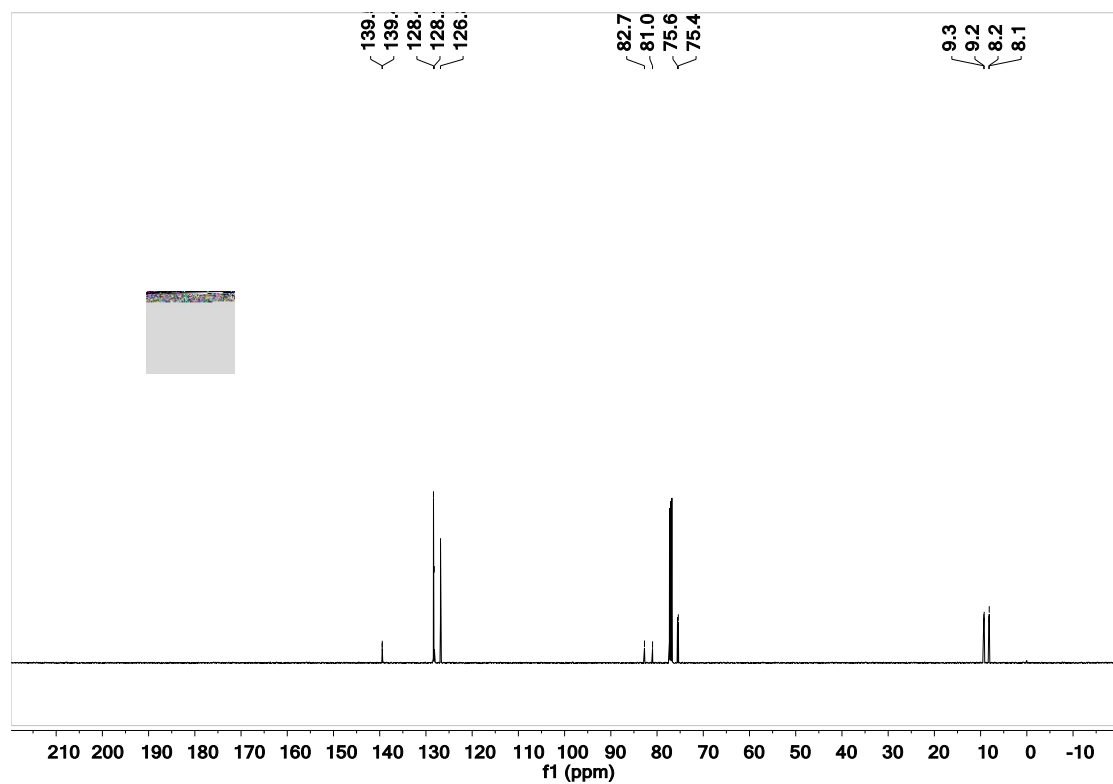
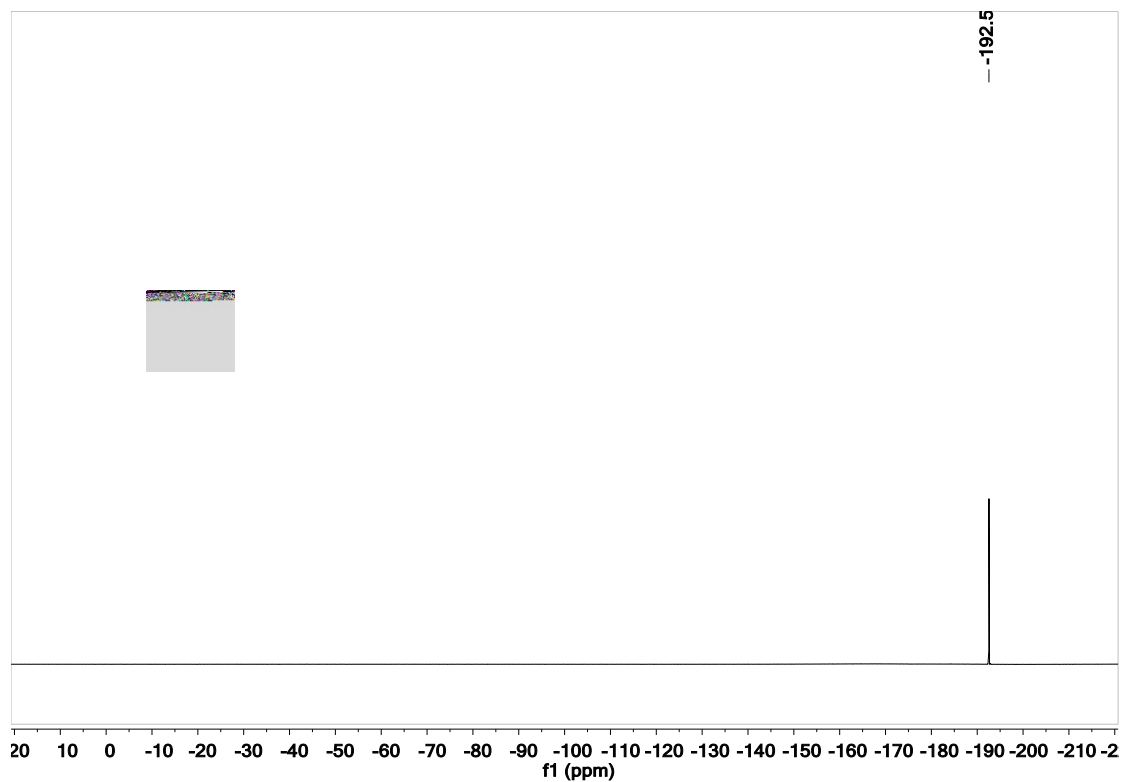
(4-(benzyloxy)phenyl)(1-fluorocyclopropyl)methanol (2a)



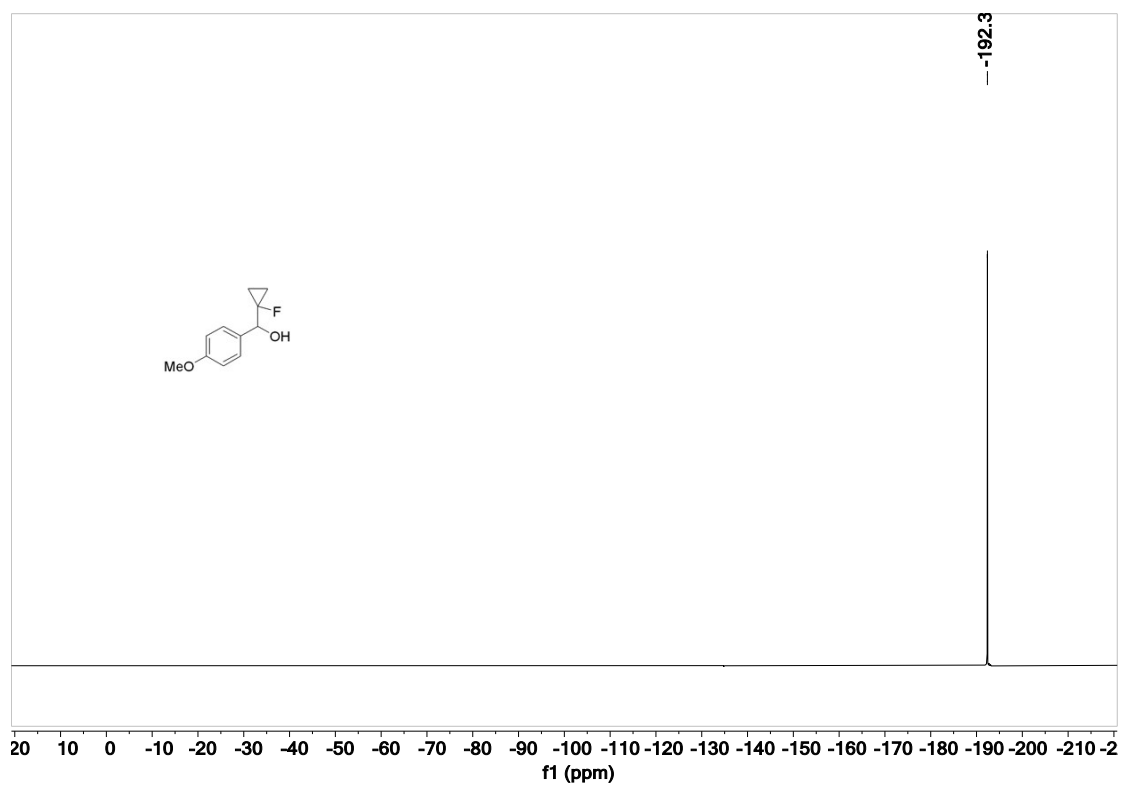
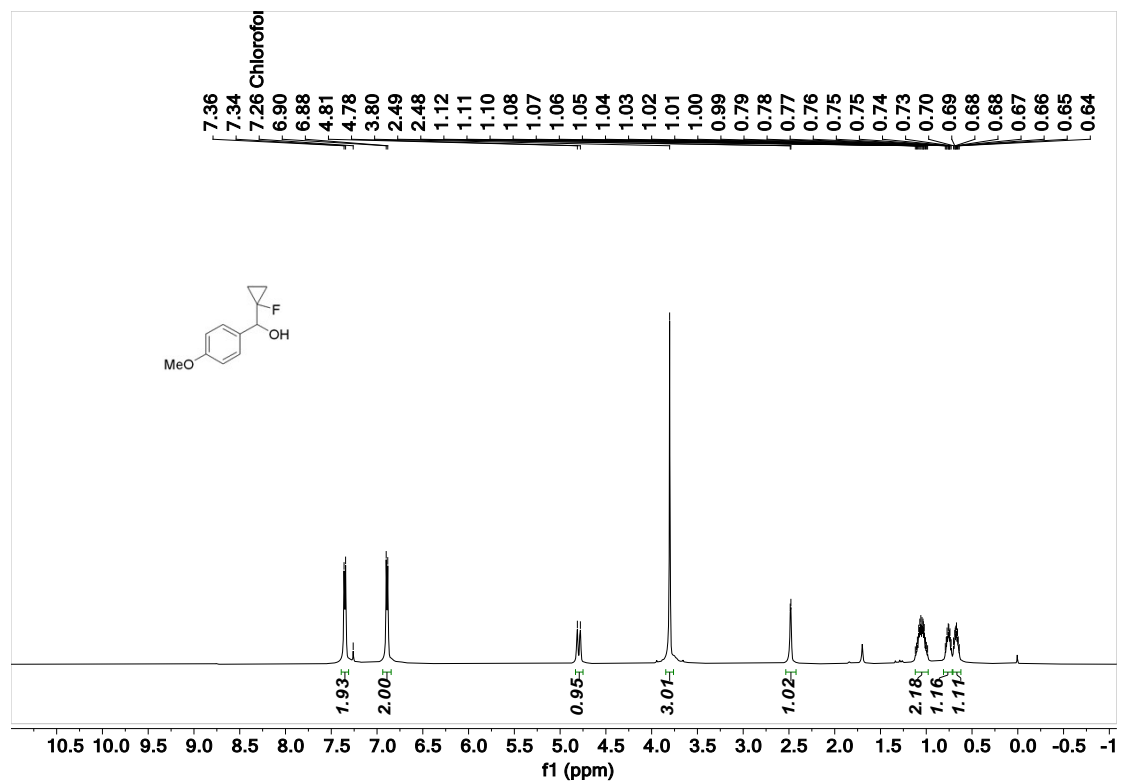


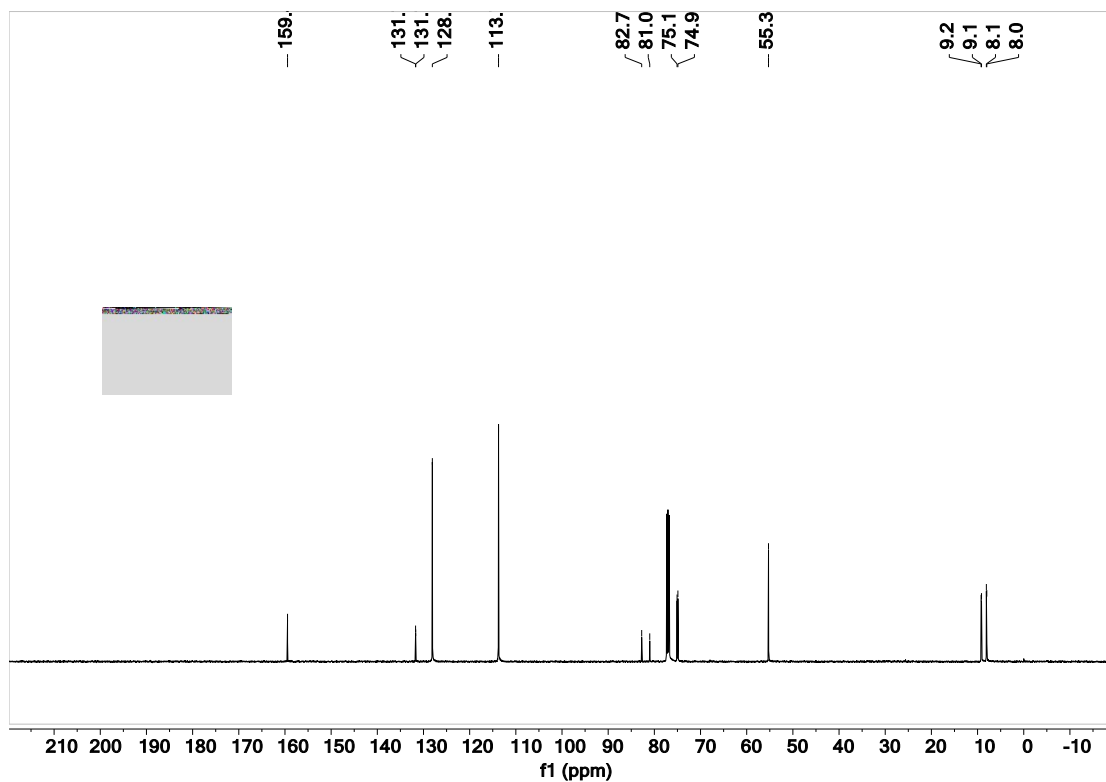
(1-fluorocyclopropyl)(phenyl)methanol (2b)



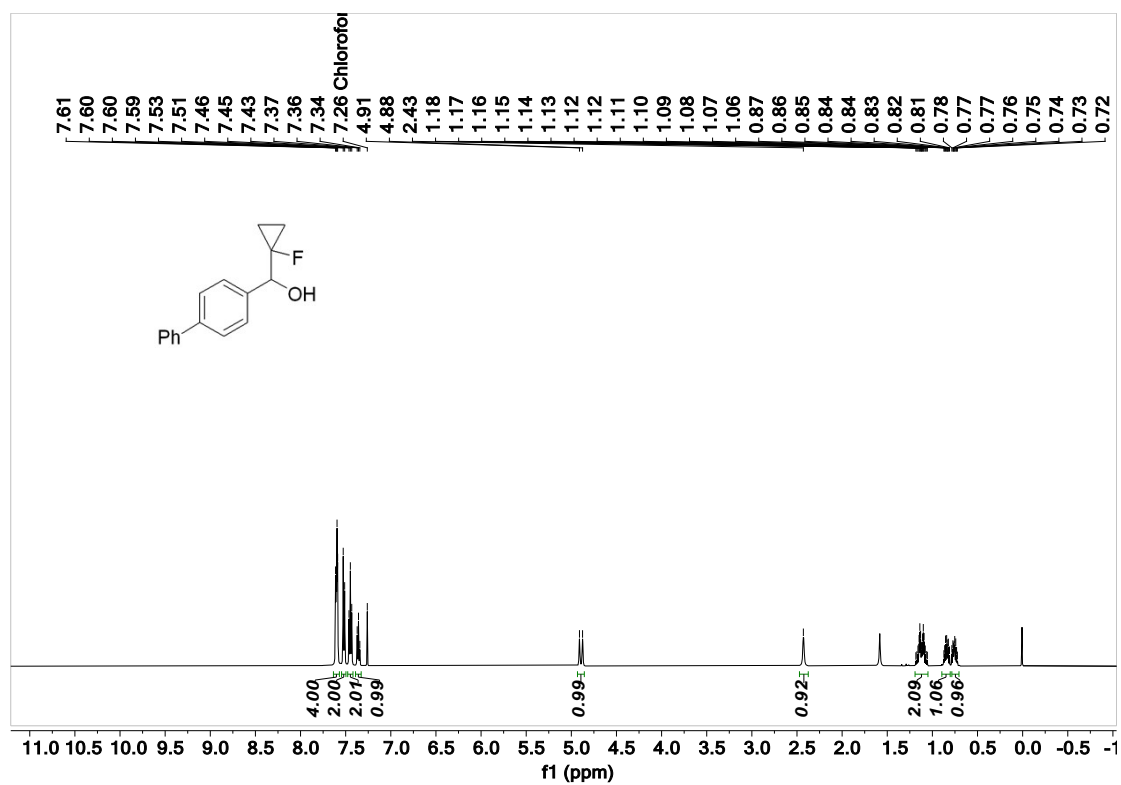


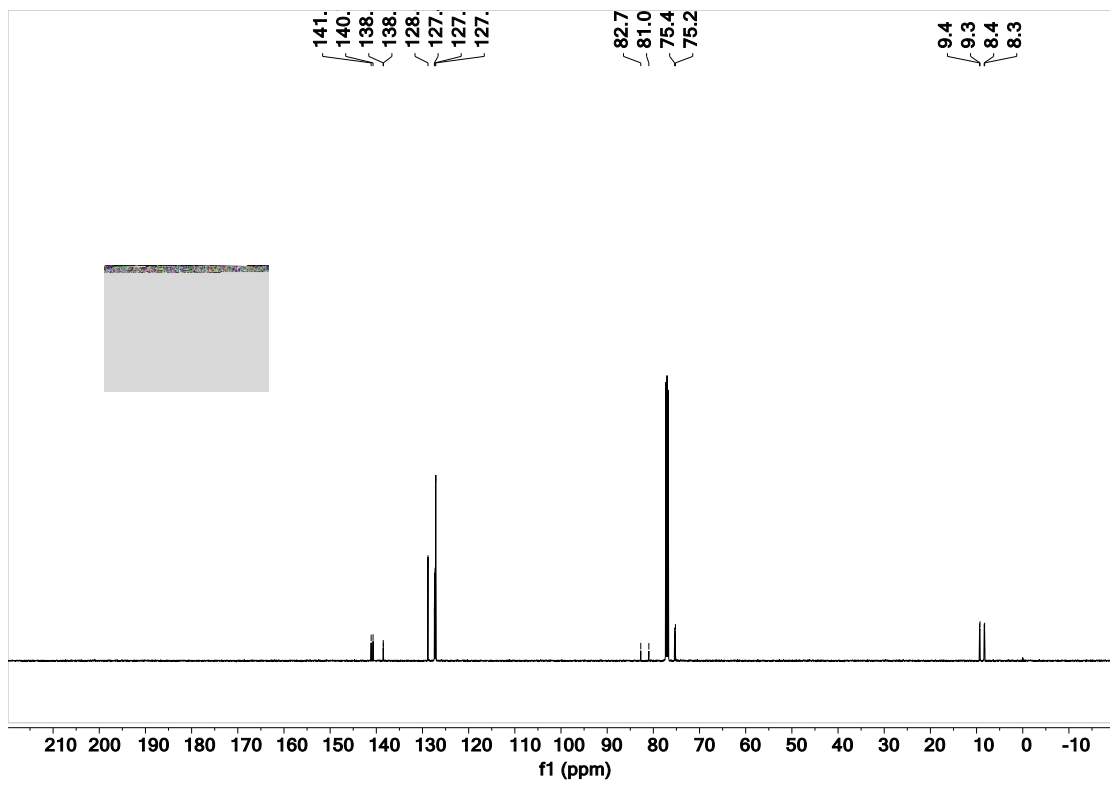
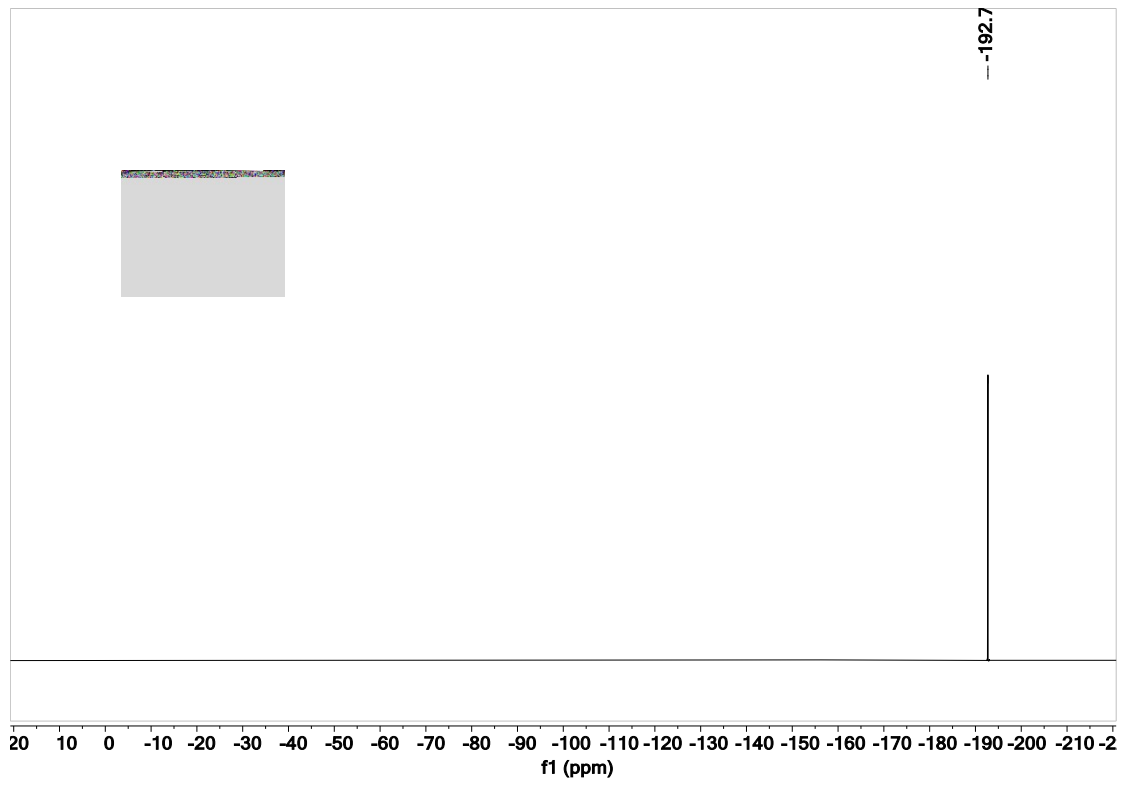
(1-fluorocyclopropyl)(4-methoxyphenyl)methanol (2c)



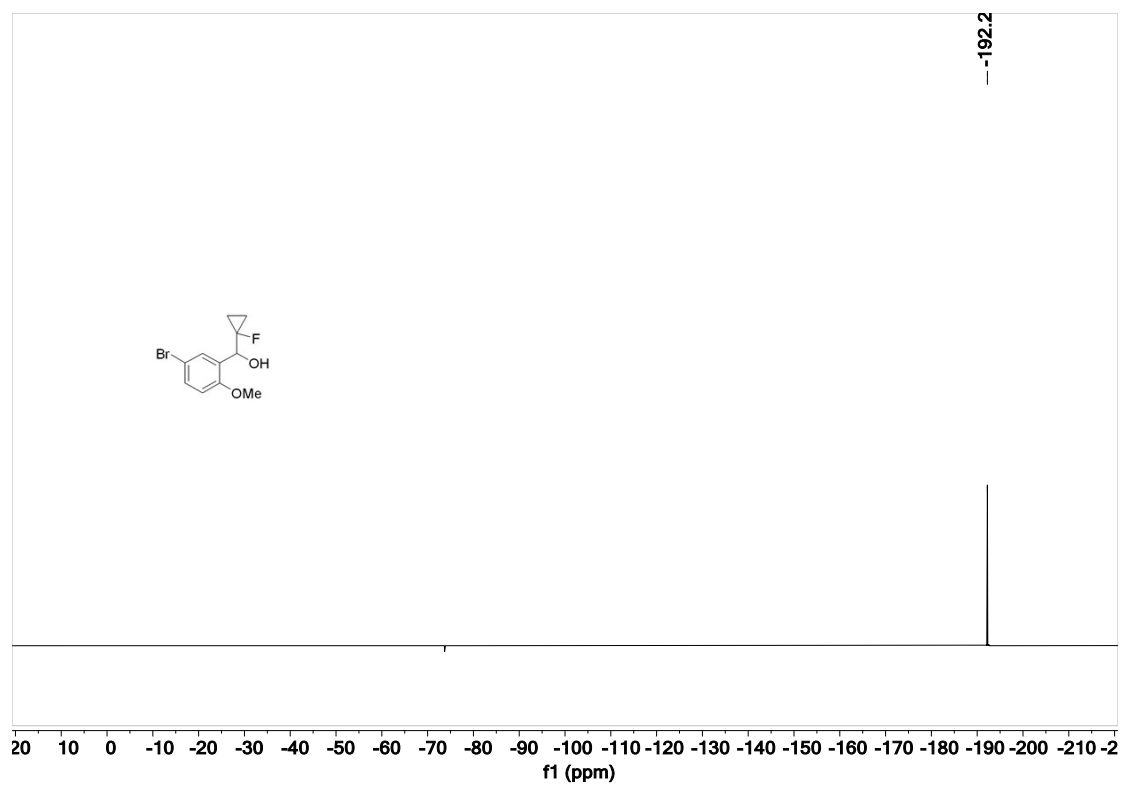
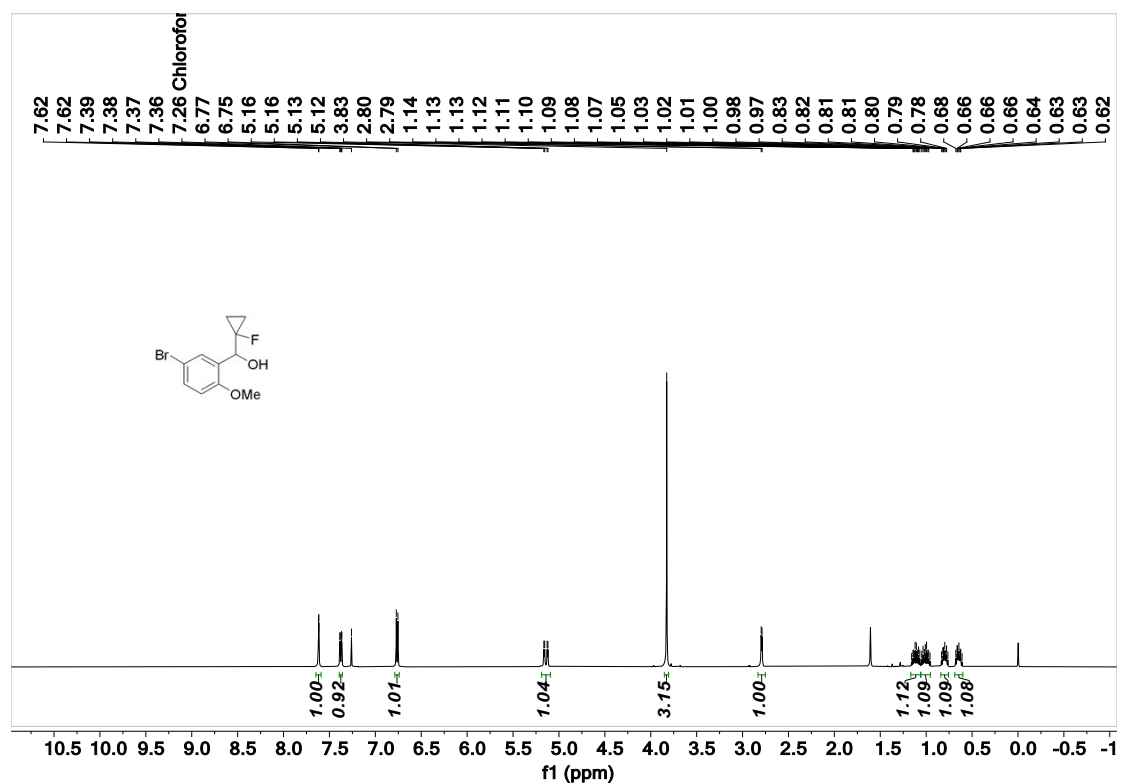


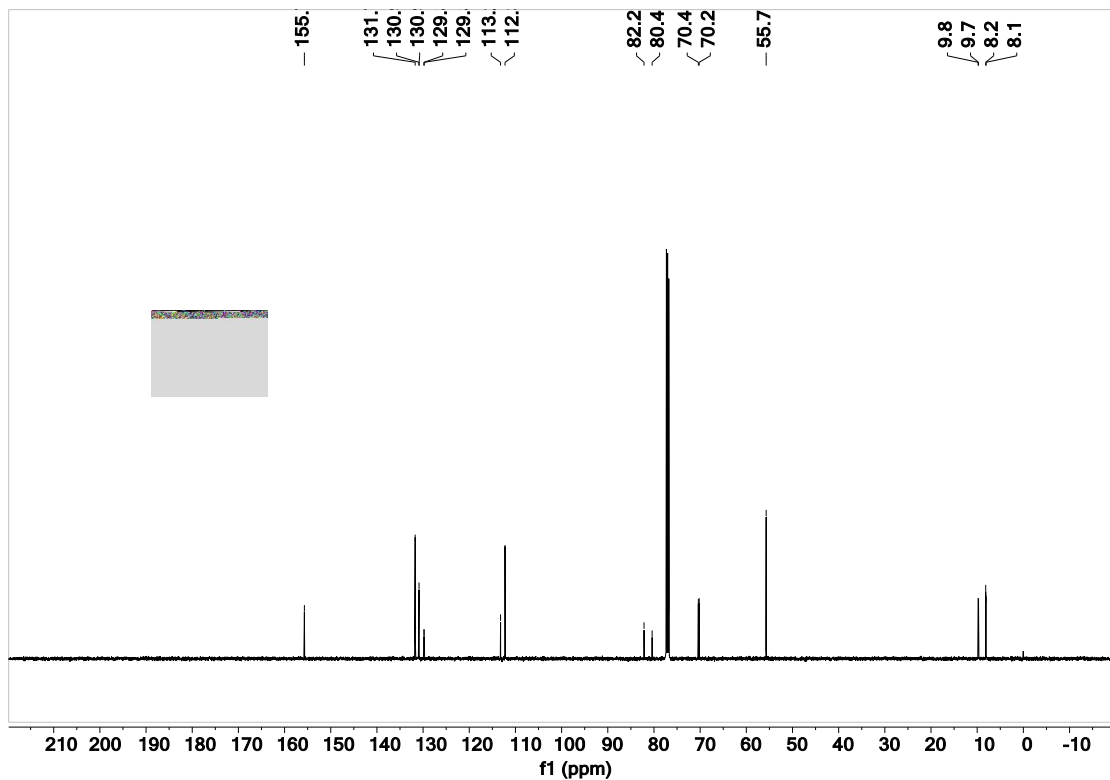
[1,1'-biphenyl]-4-yl(1-fluorocyclopropyl)methanol (2d)



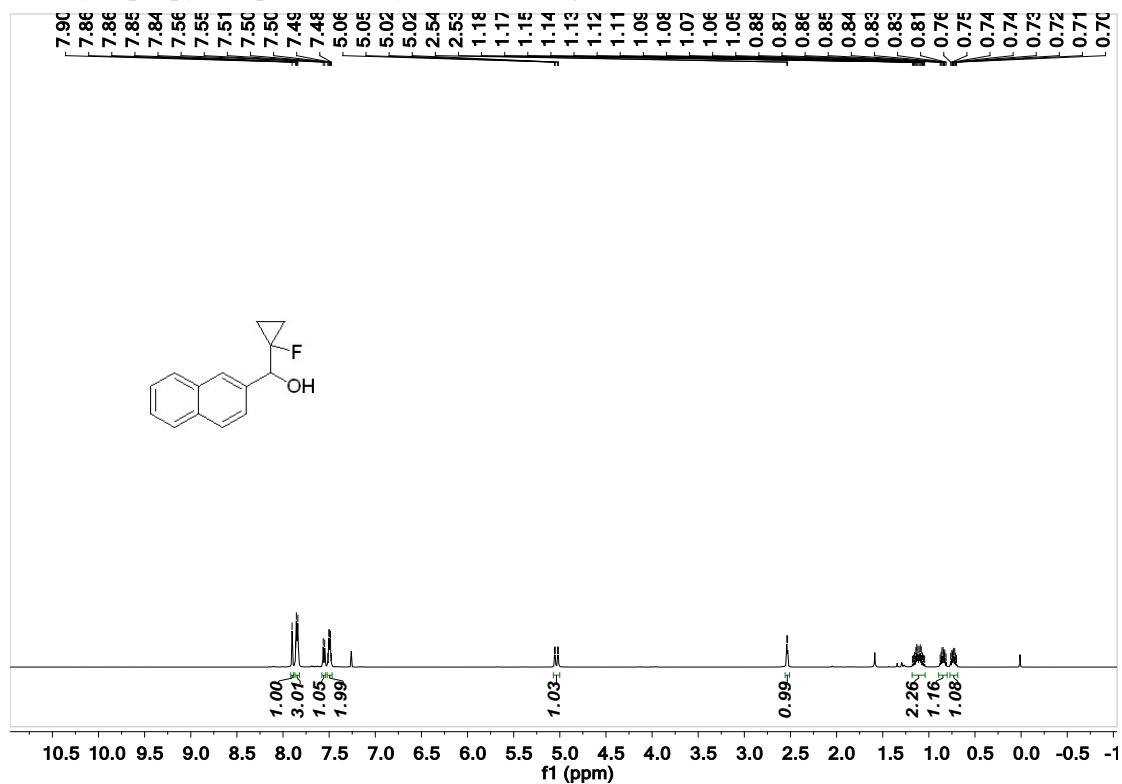


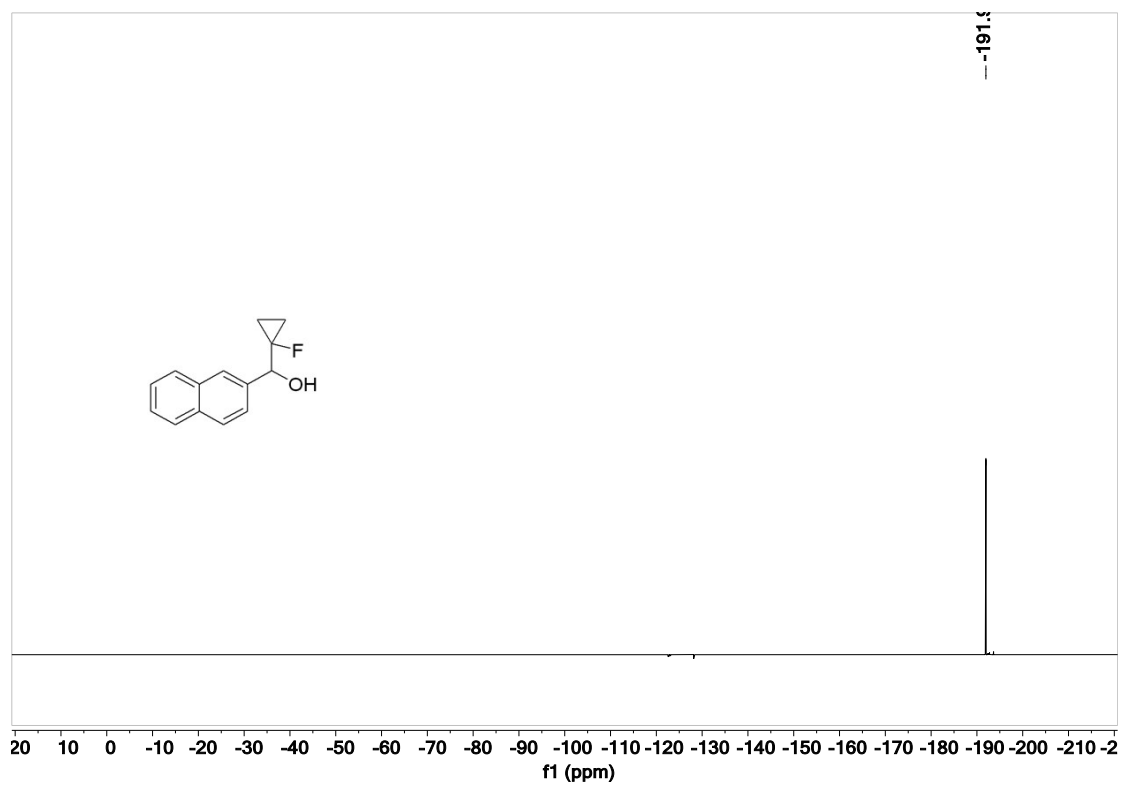
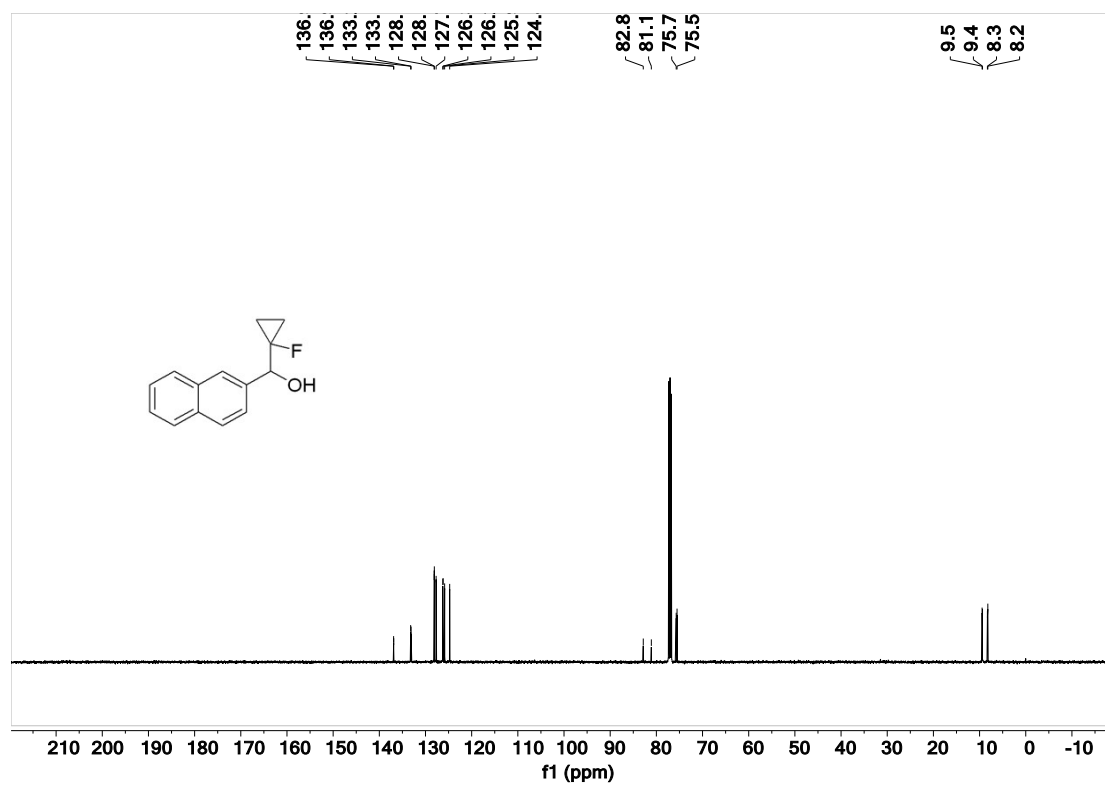
(5-bromo-2-methoxyphenyl)(1-fluorocyclopropyl)methanol (2f)



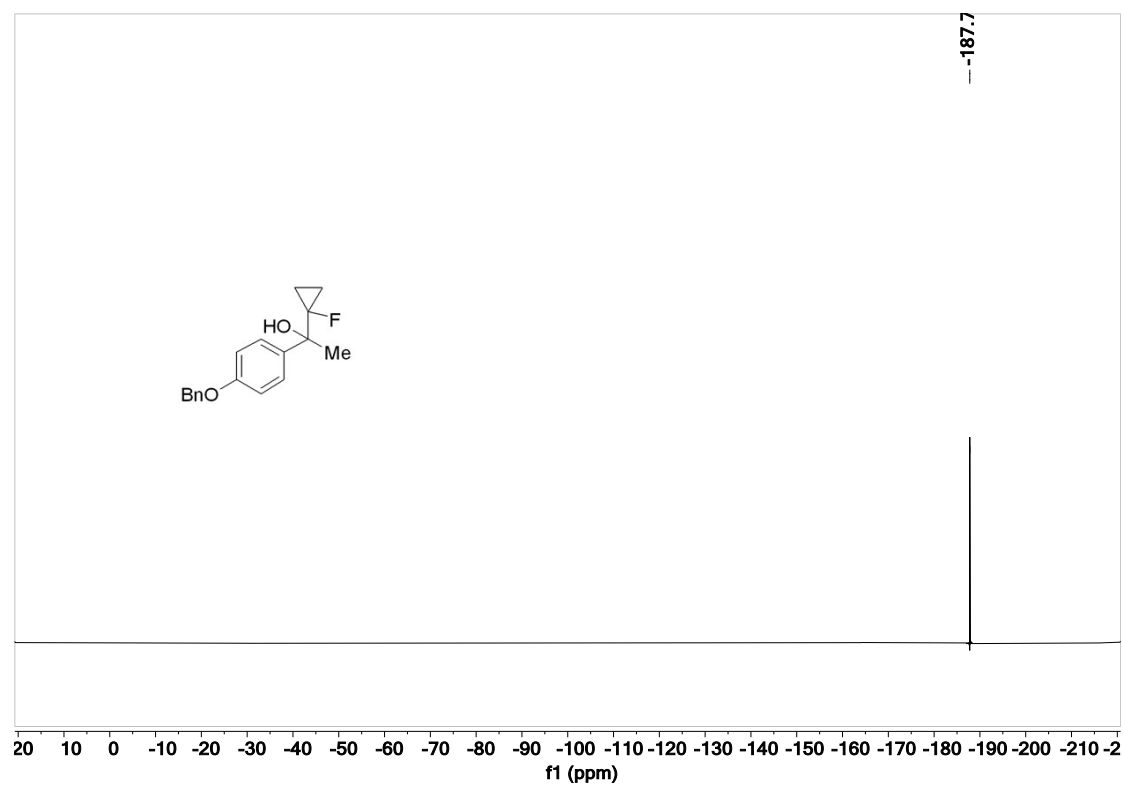
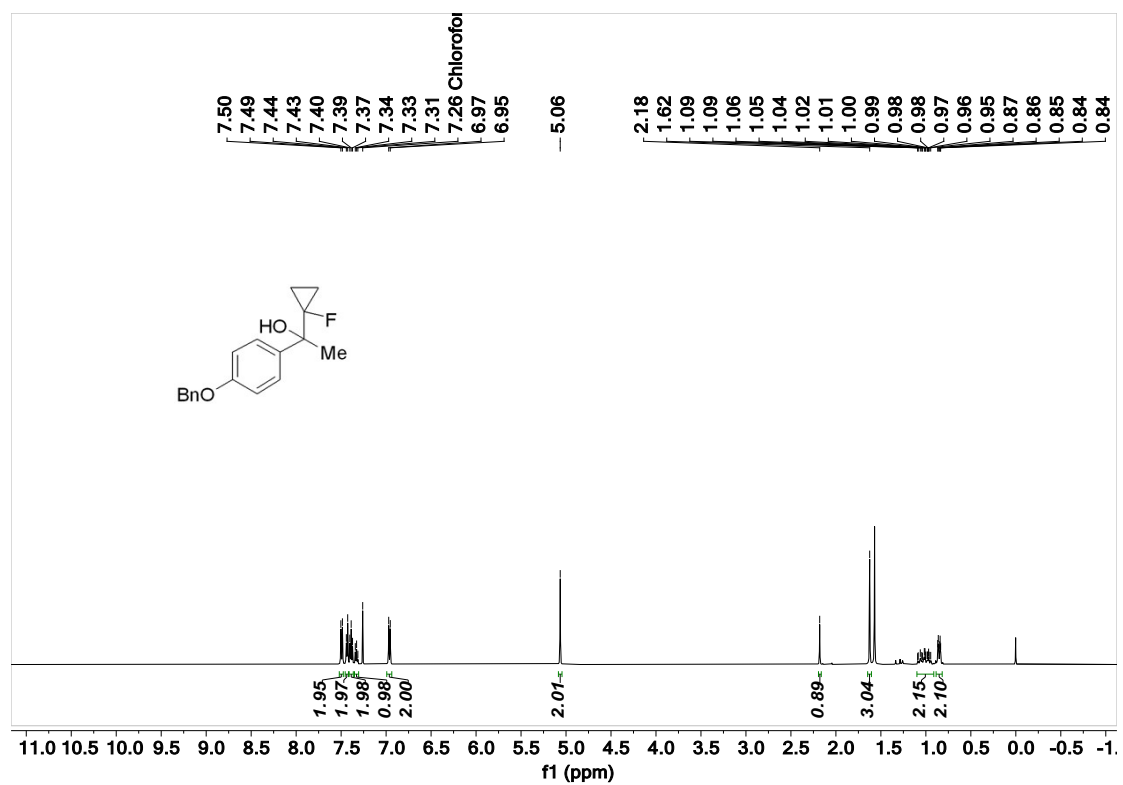


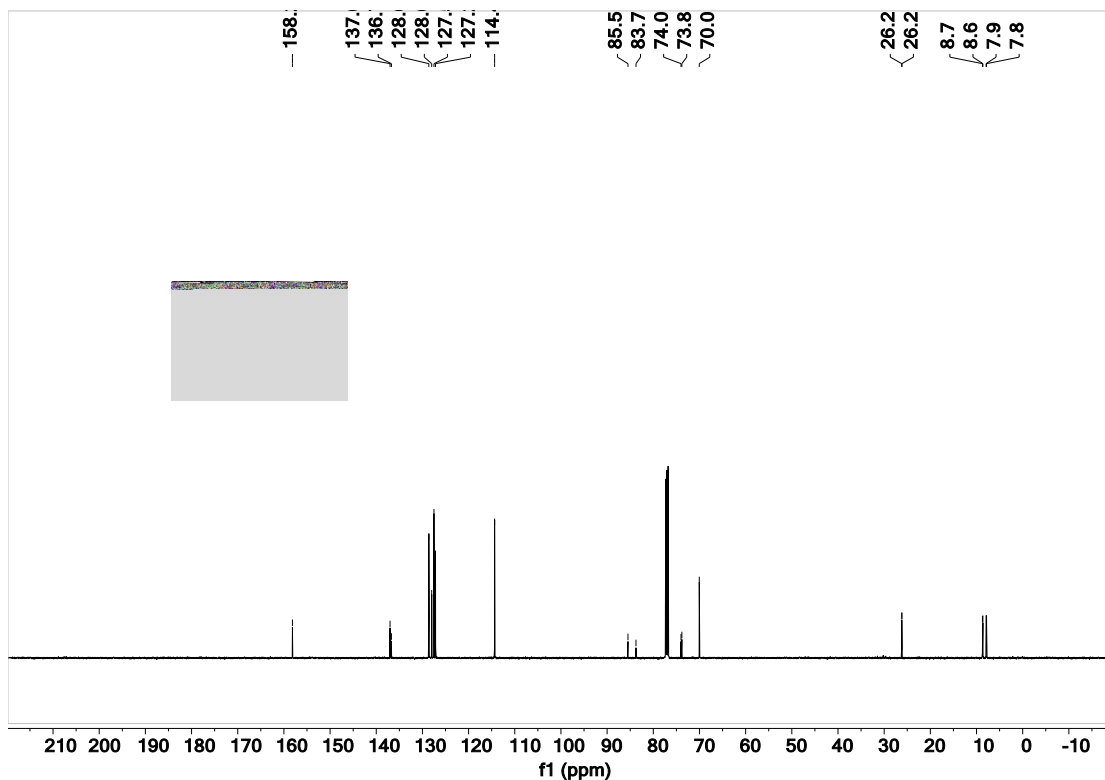
(1-fluorocyclopropyl)(naphthalen-2-yl)methanol (2g)



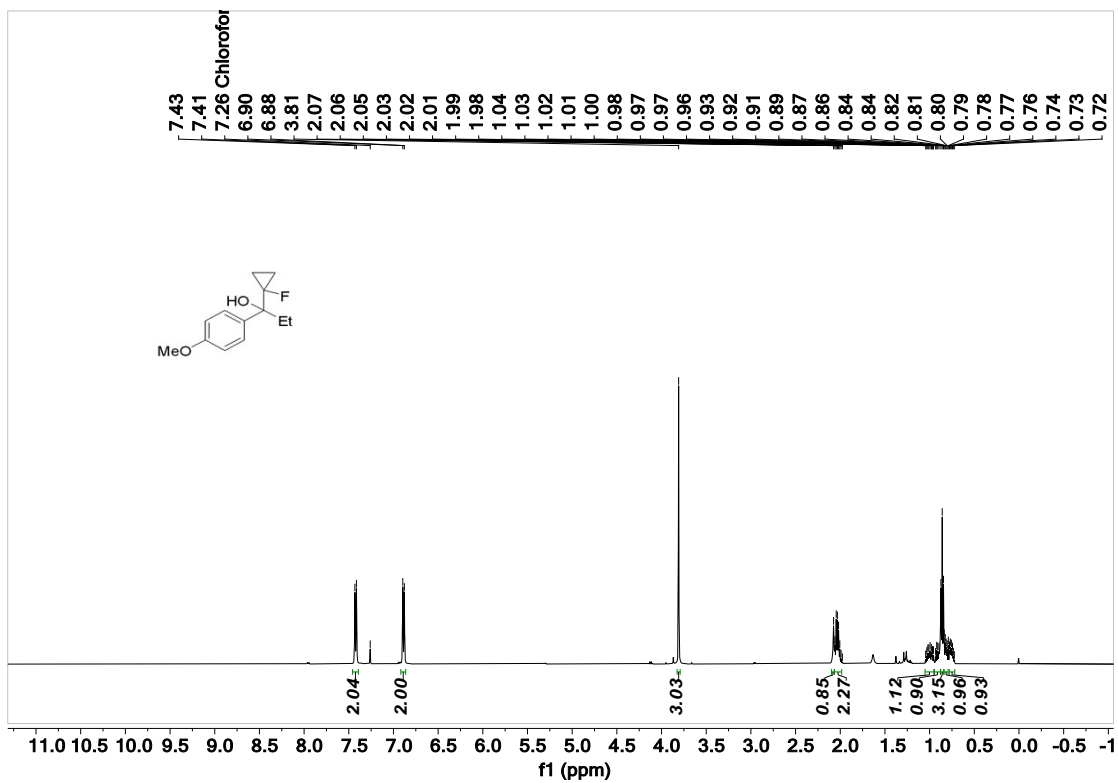


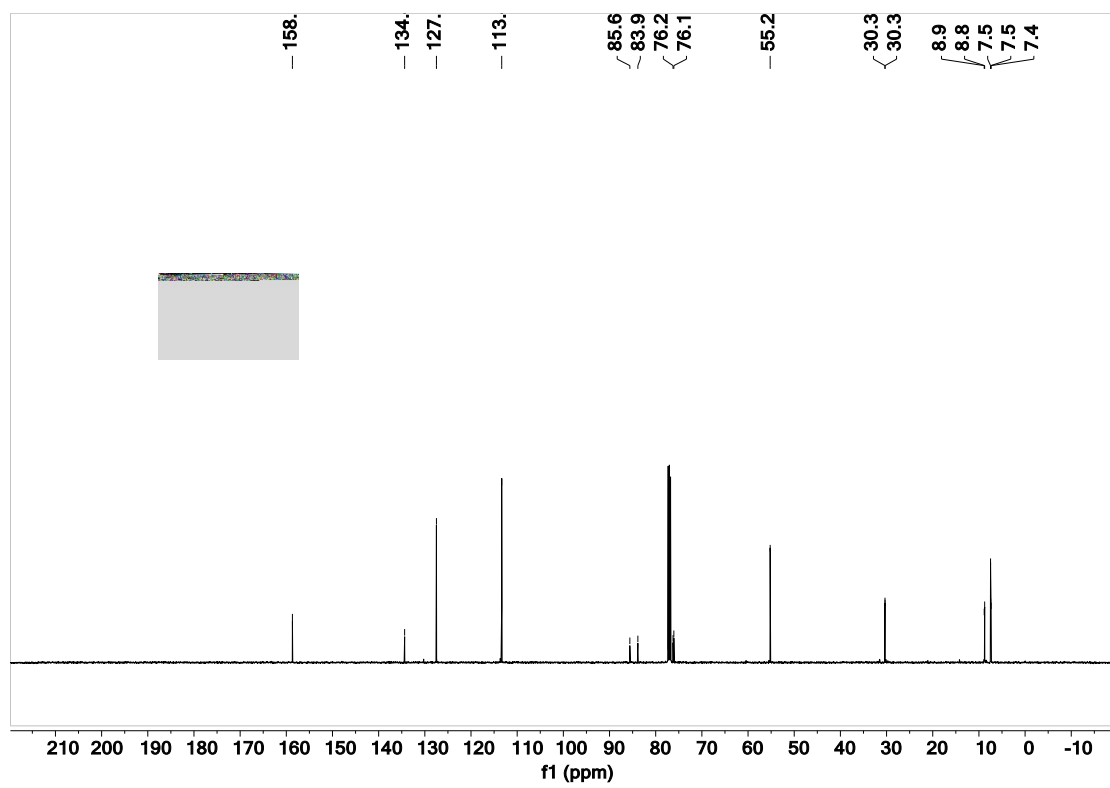
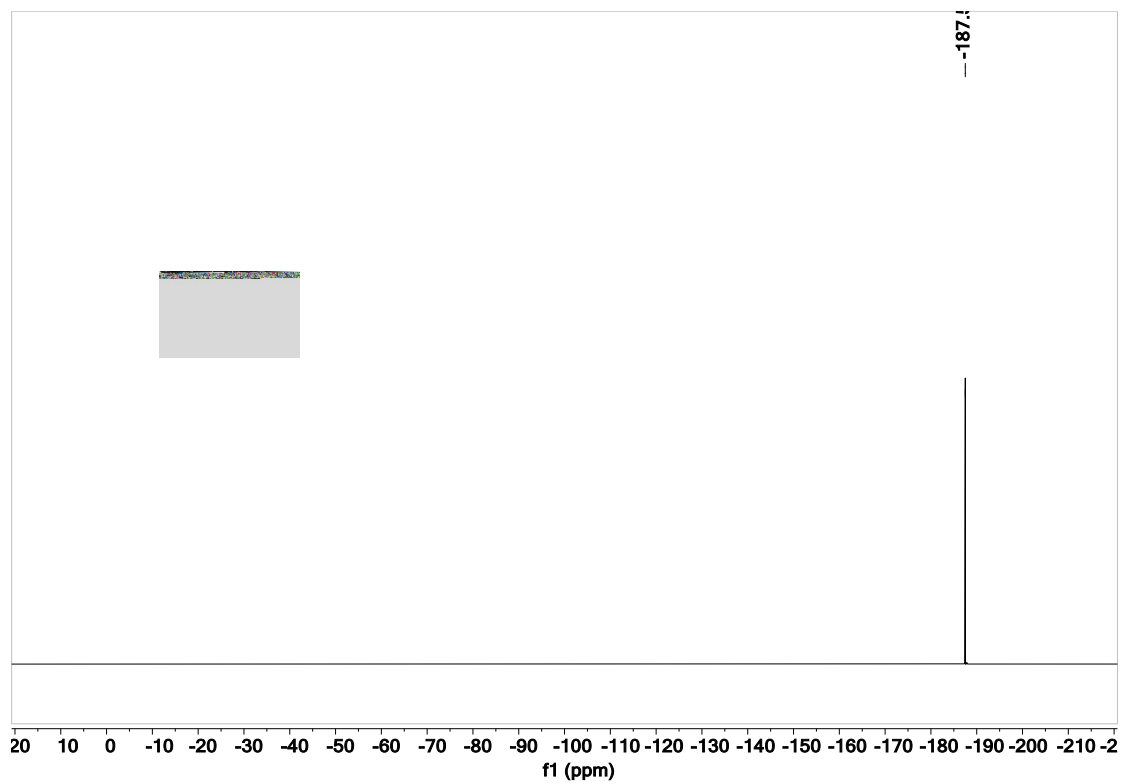
1-(4-(benzyloxy)phenyl)-1-(1-fluorocyclopropyl)ethan-1-ol (2h)



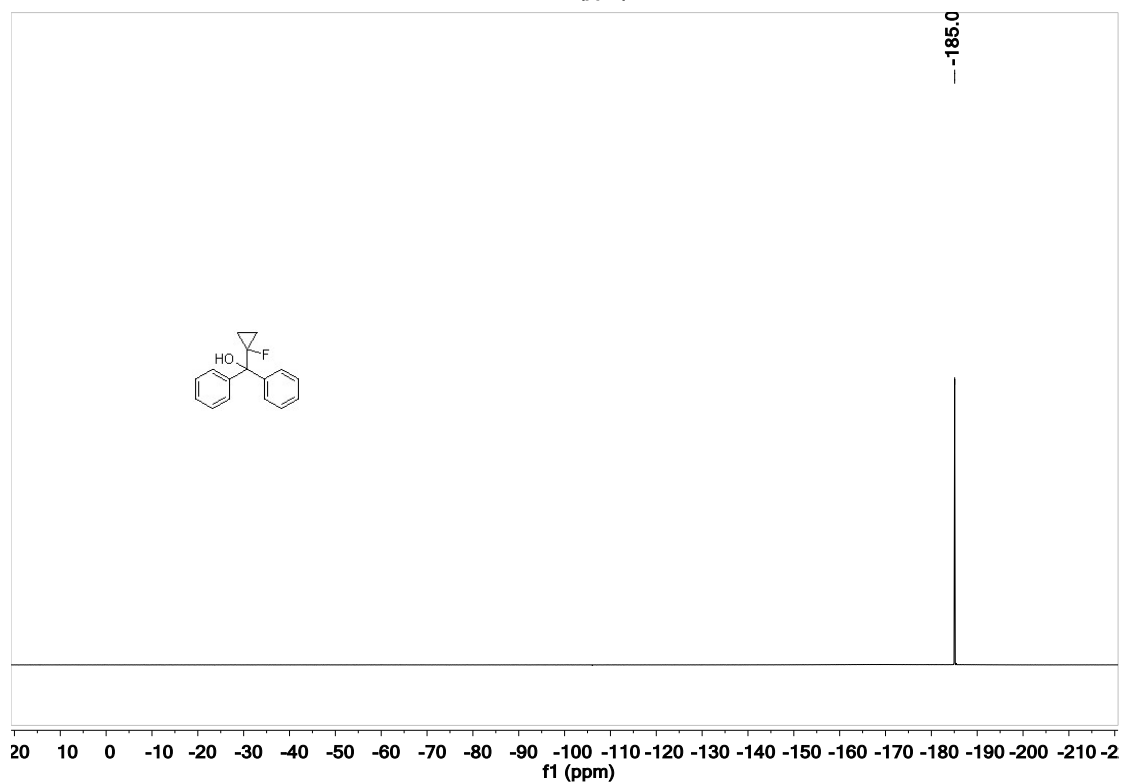
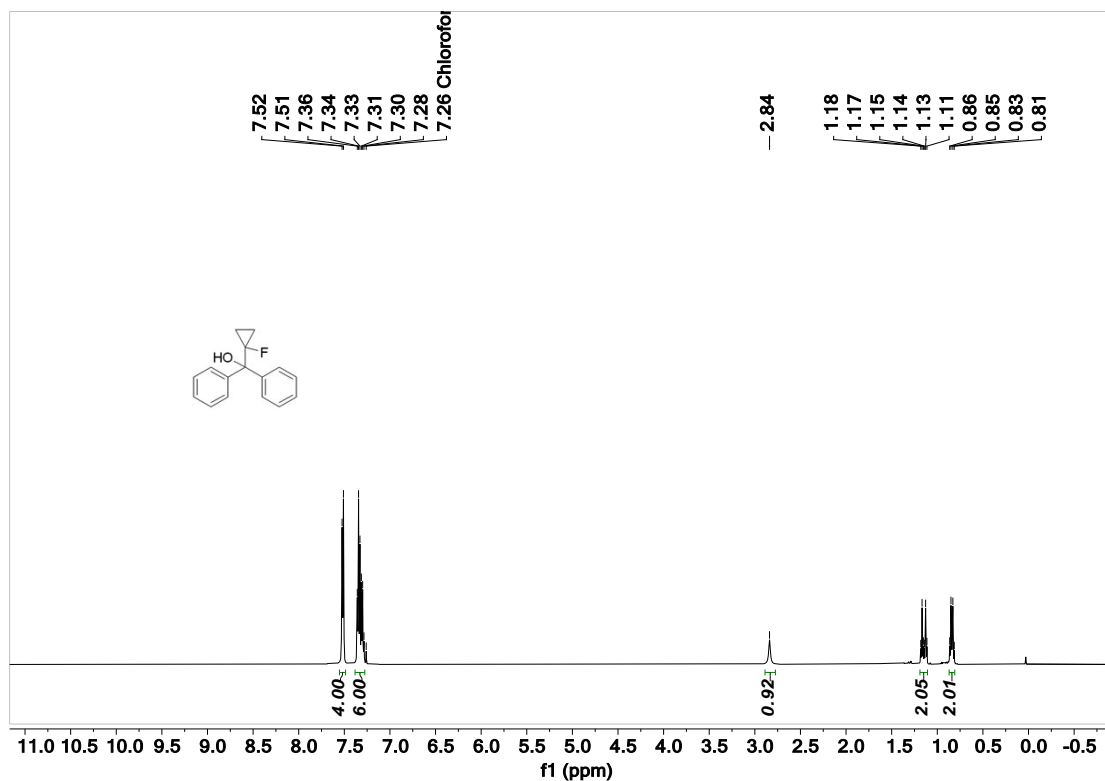


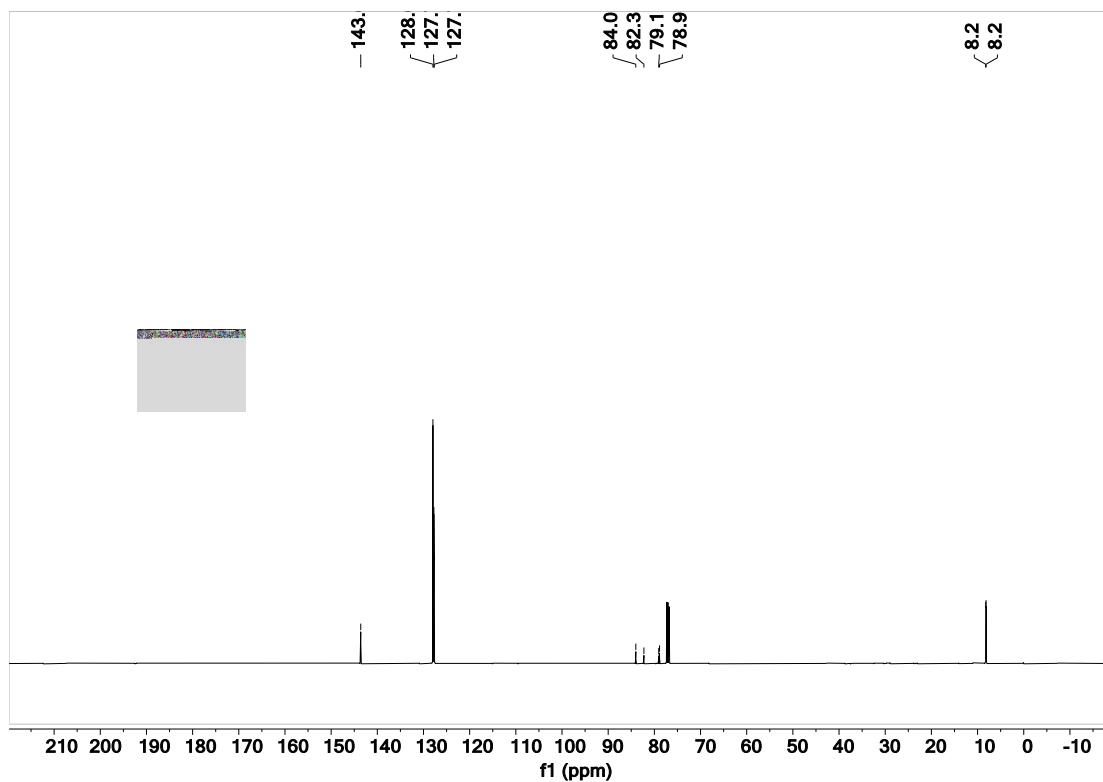
1-(1-fluorocyclopropyl)-1-(4-methoxyphenyl)propan-1-ol (2i)



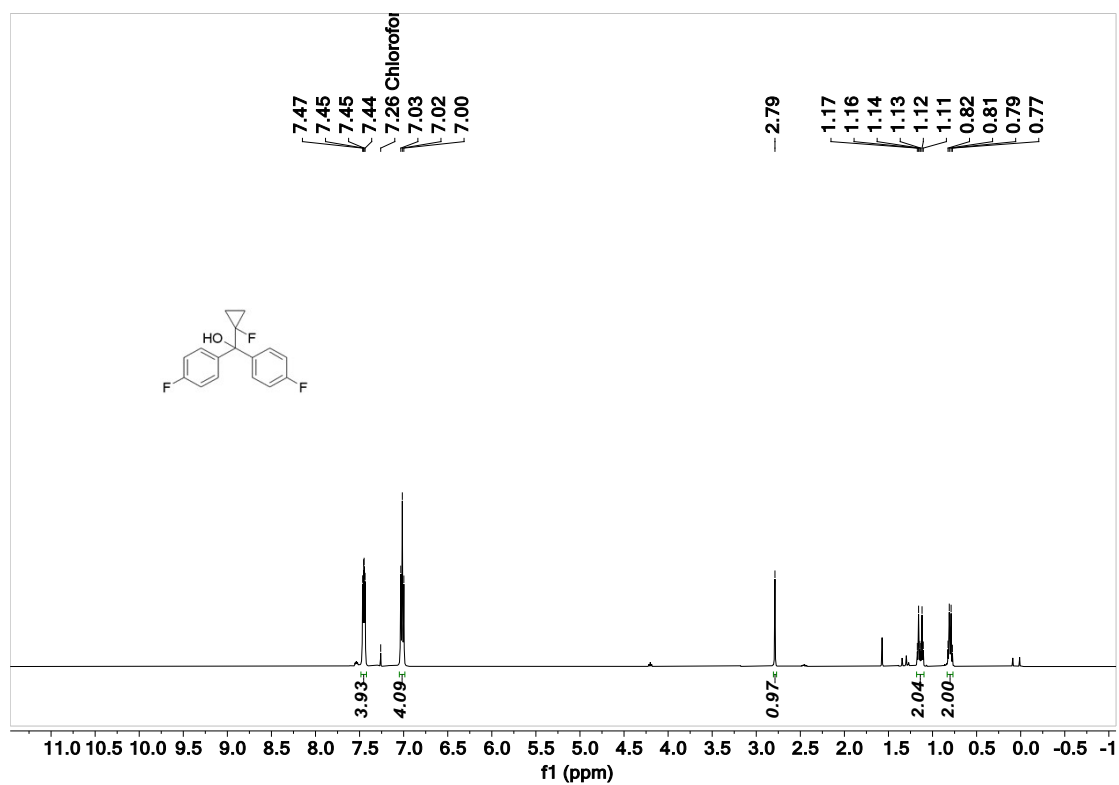


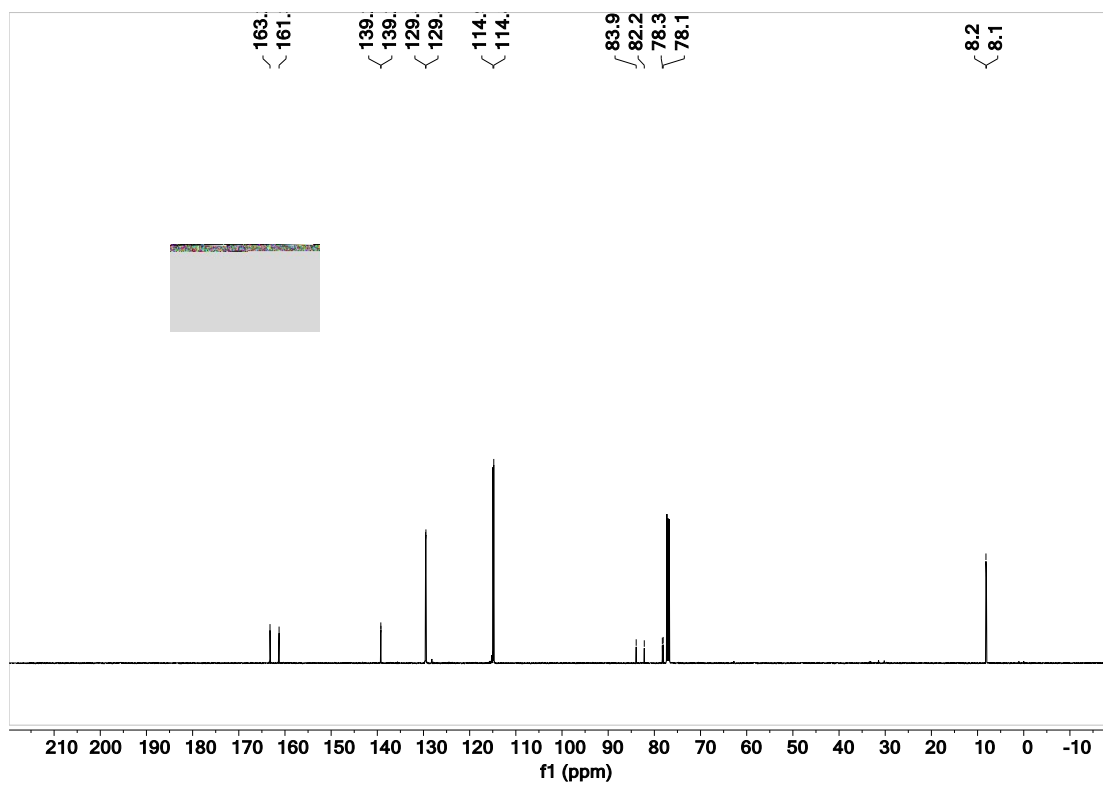
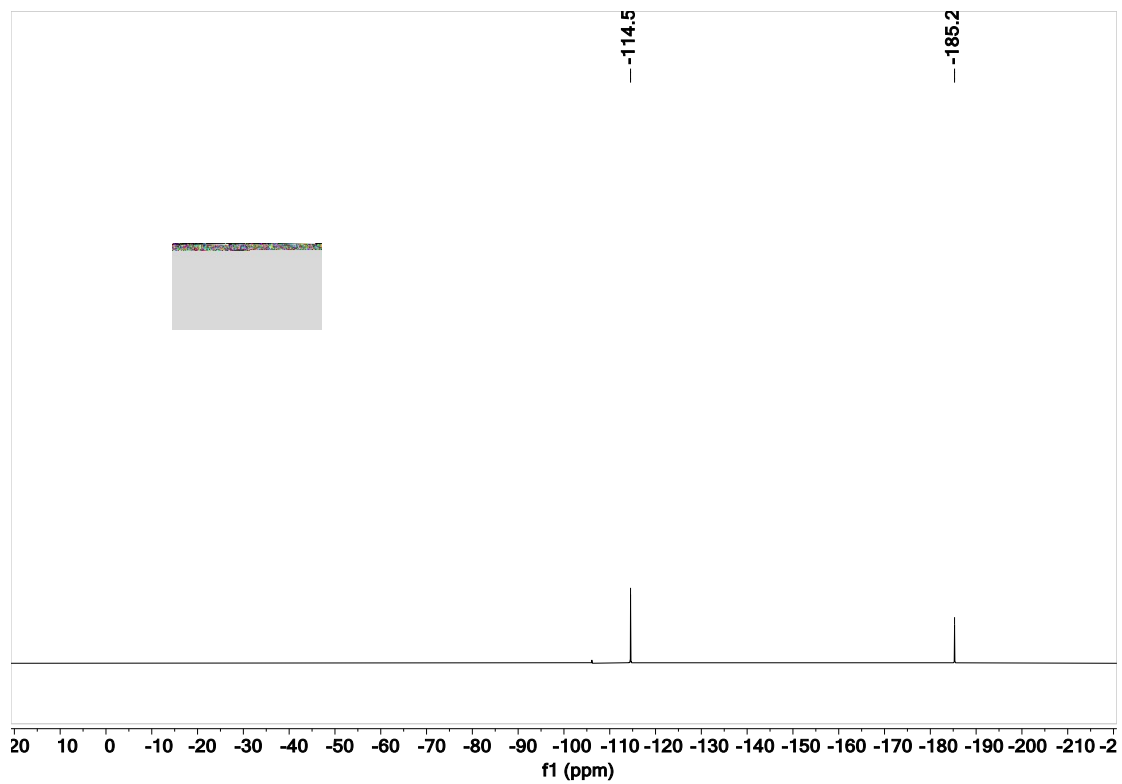
(1-fluorocyclopropyl)diphenylmethanol (2j)



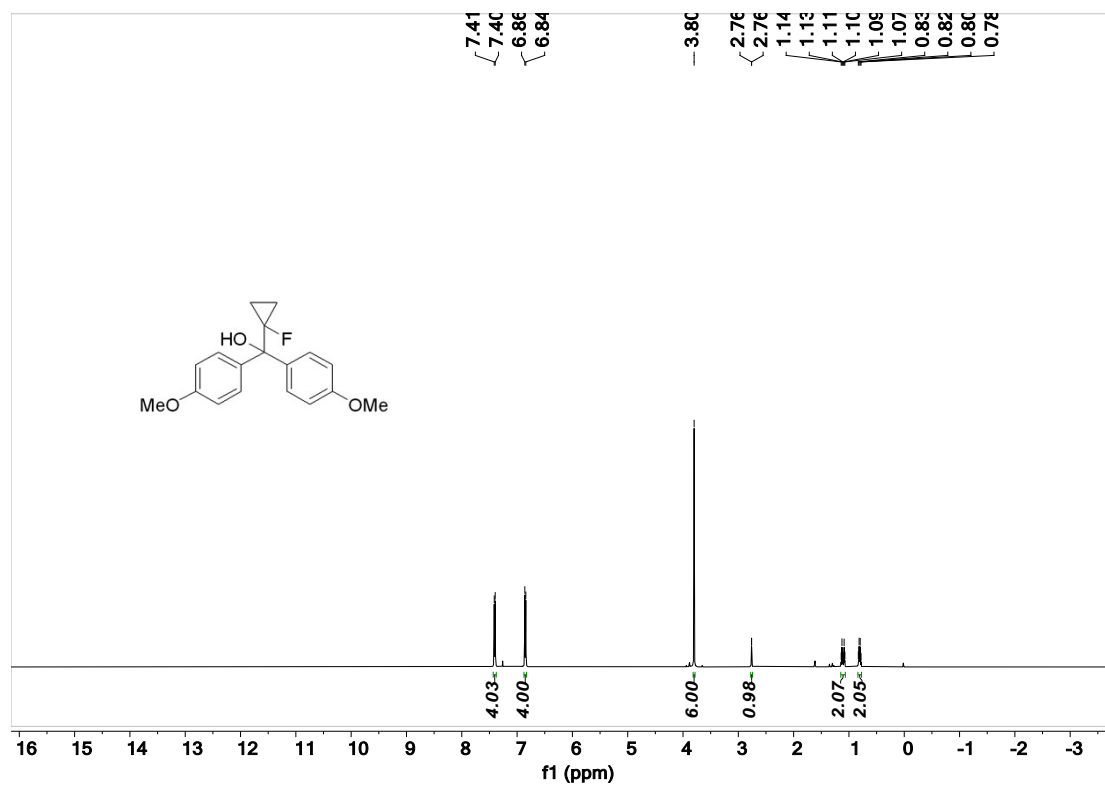


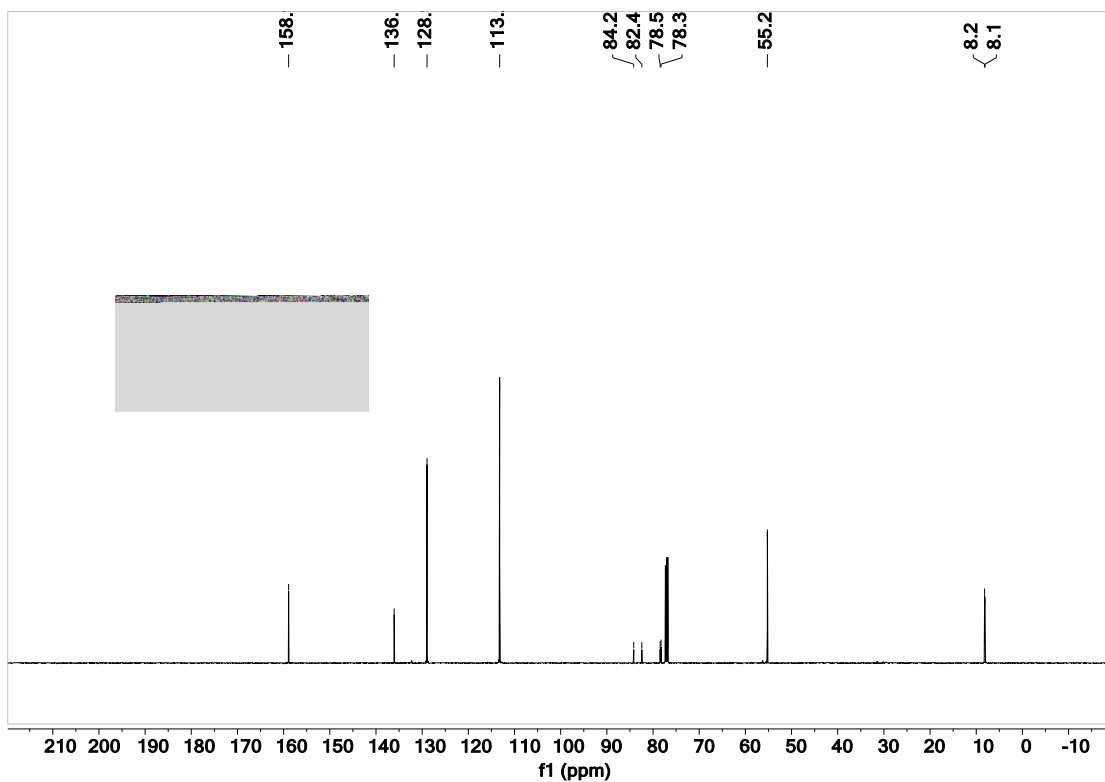
(1-fluorocyclopropyl)bis(4-fluorophenyl)methanol (2k)



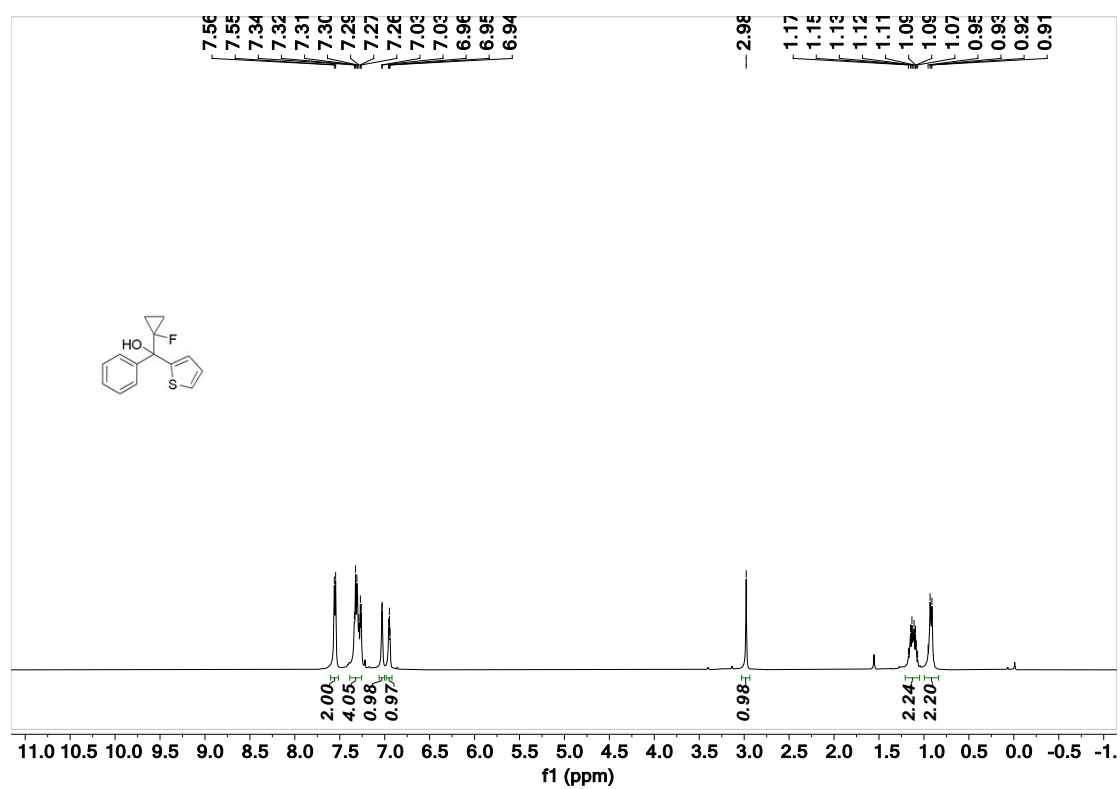


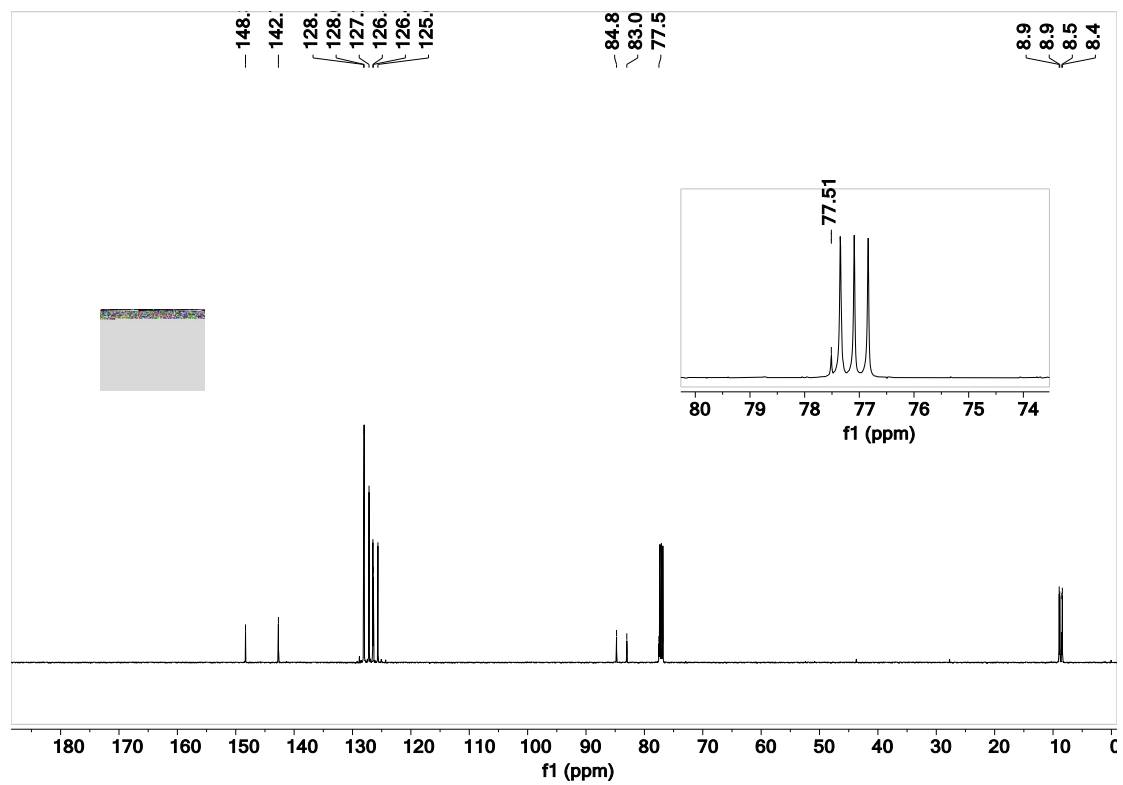
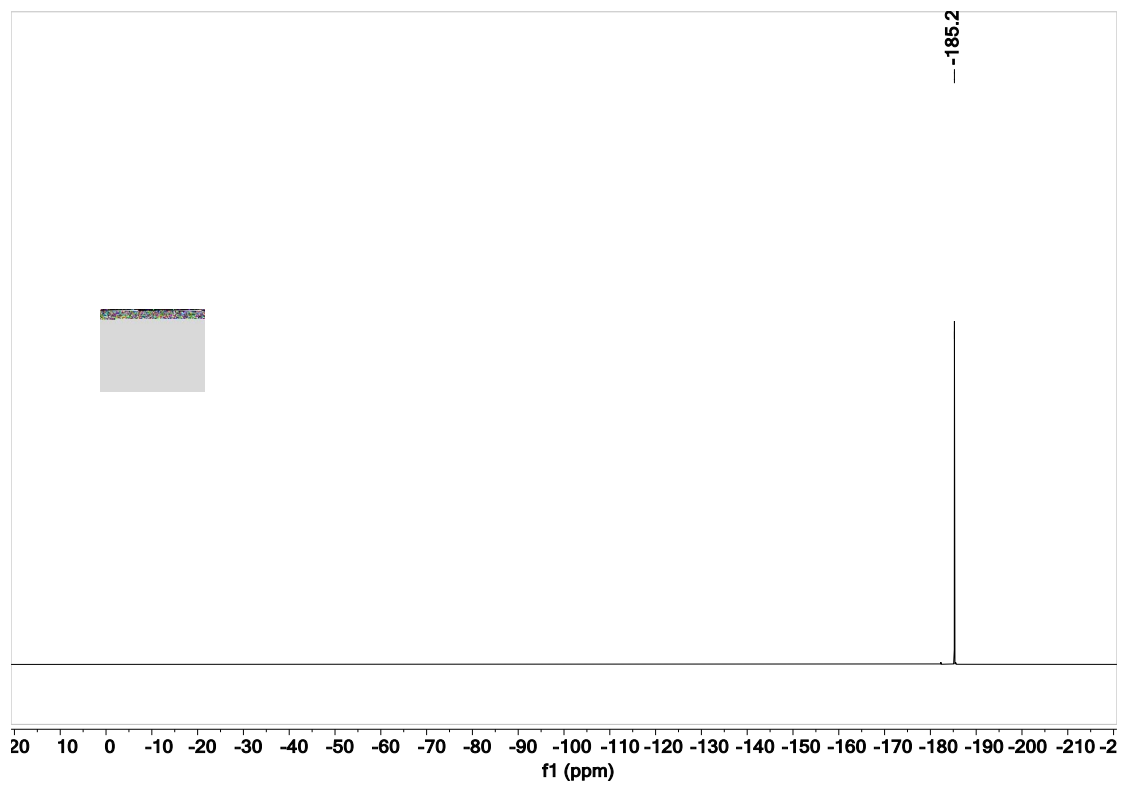
(1-fluorocyclopropyl)bis(4-methoxyphenyl)methanol (21)



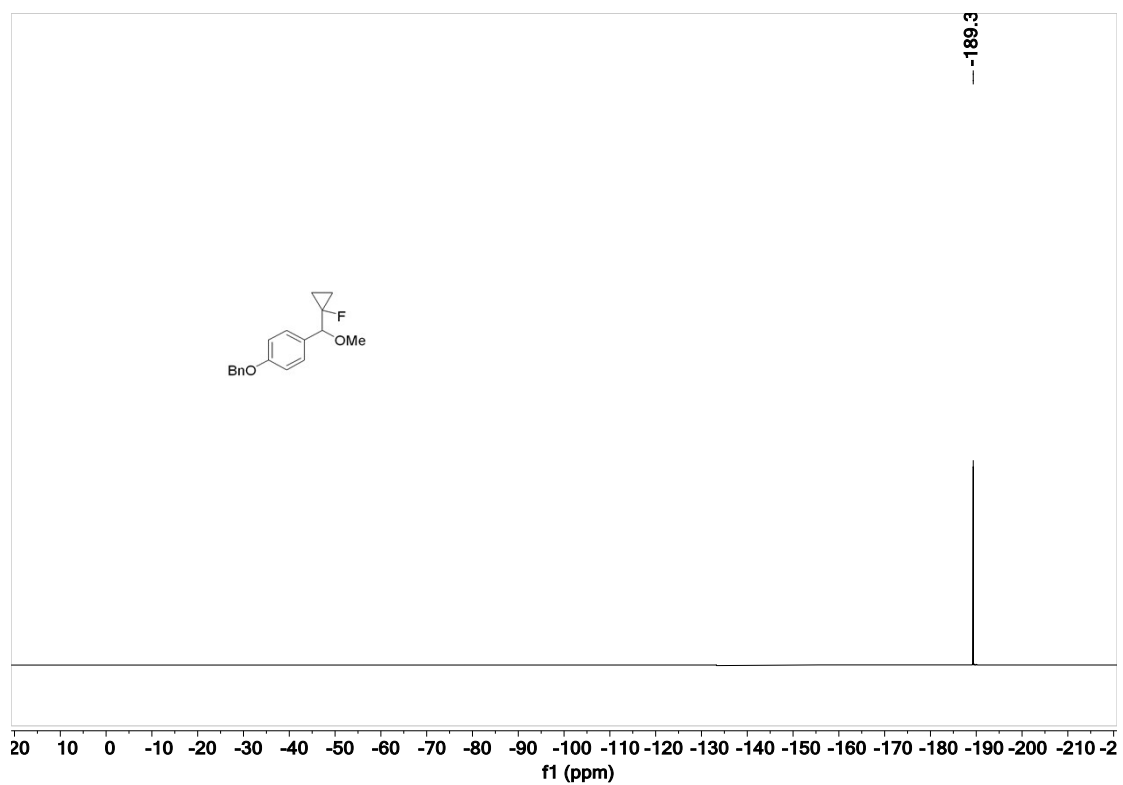
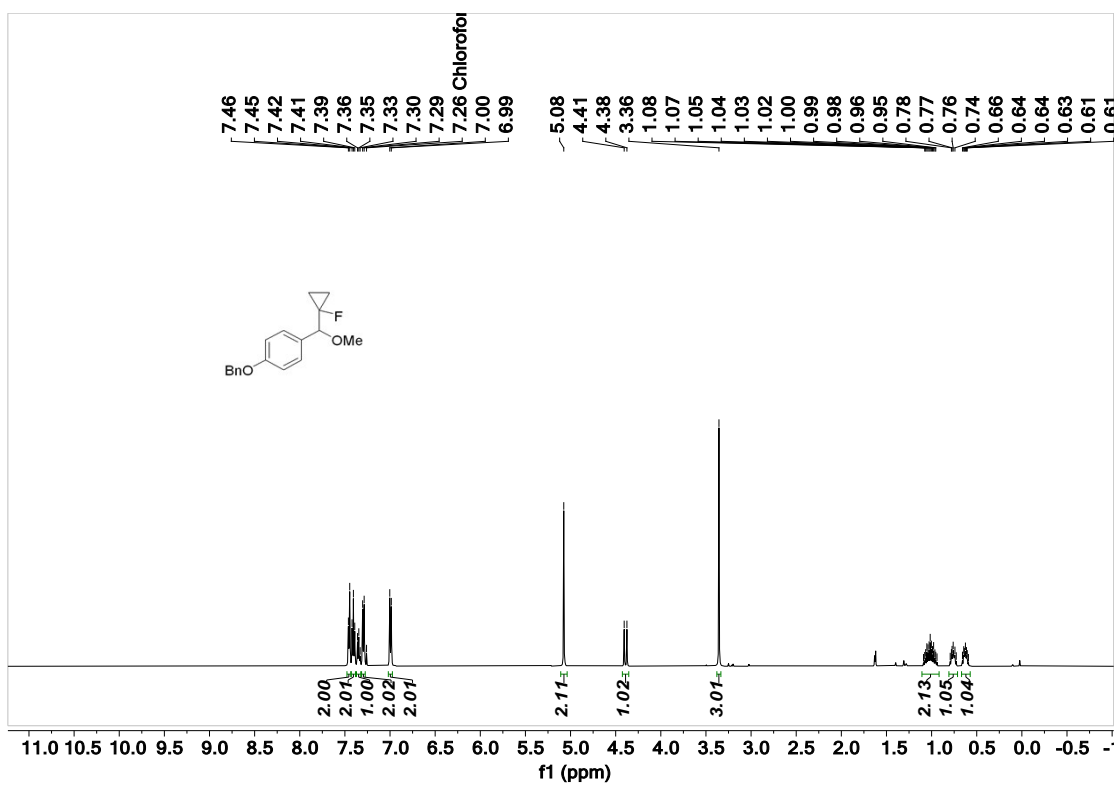


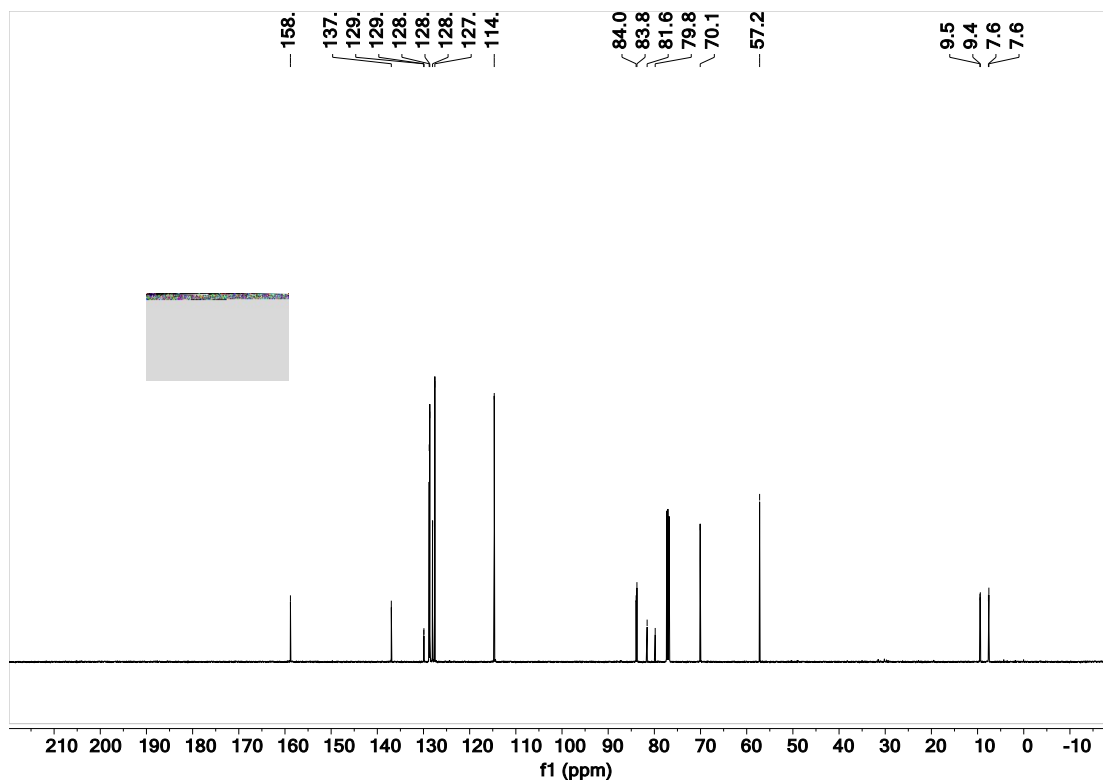
(1-fluorocyclopropyl)(phenyl)(thiophen-2-yl)methanol (2m)



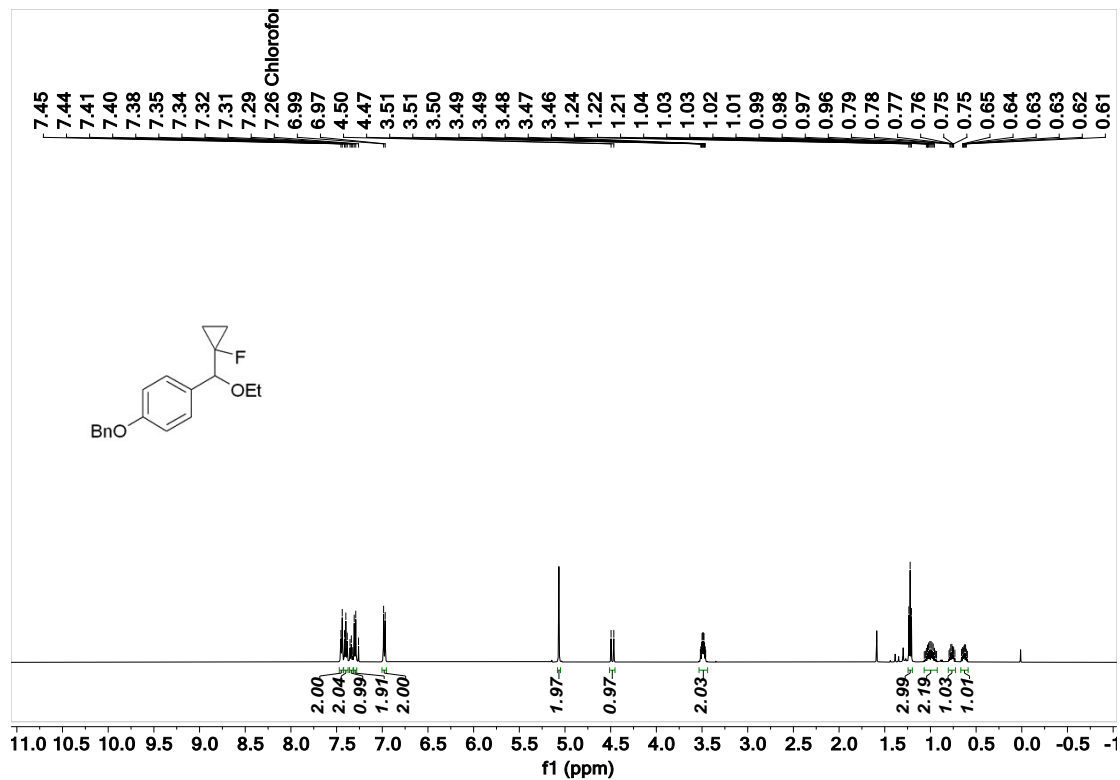


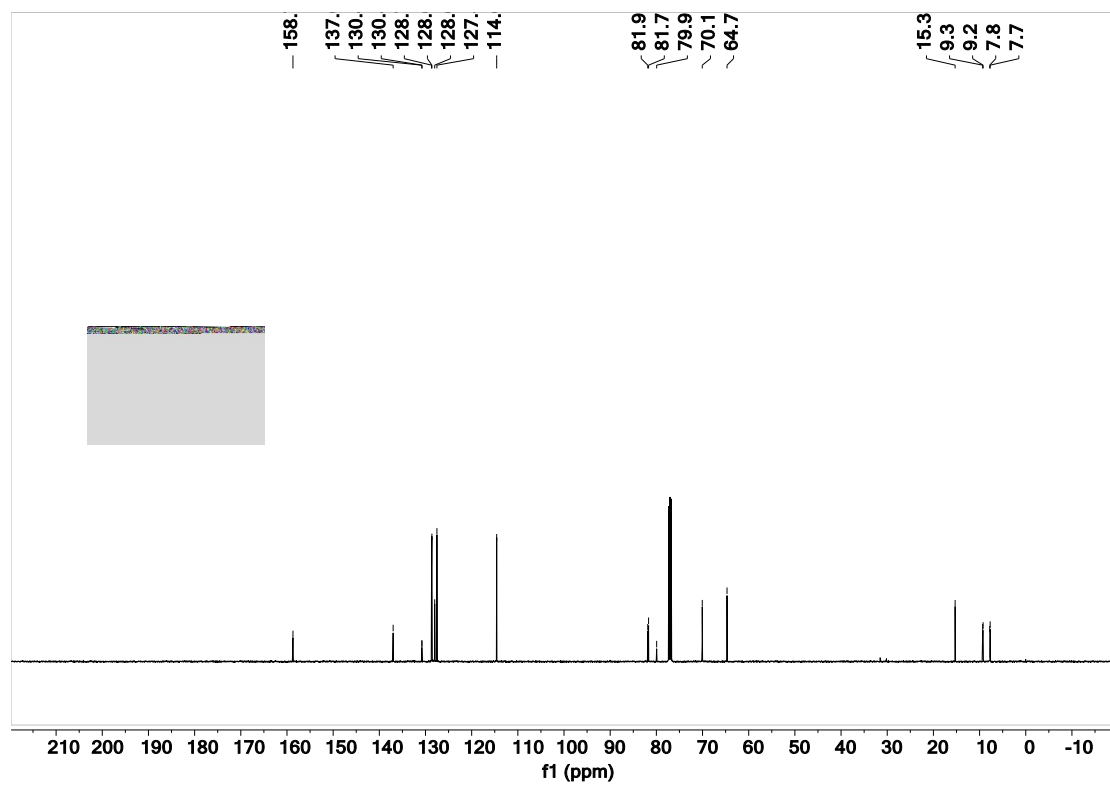
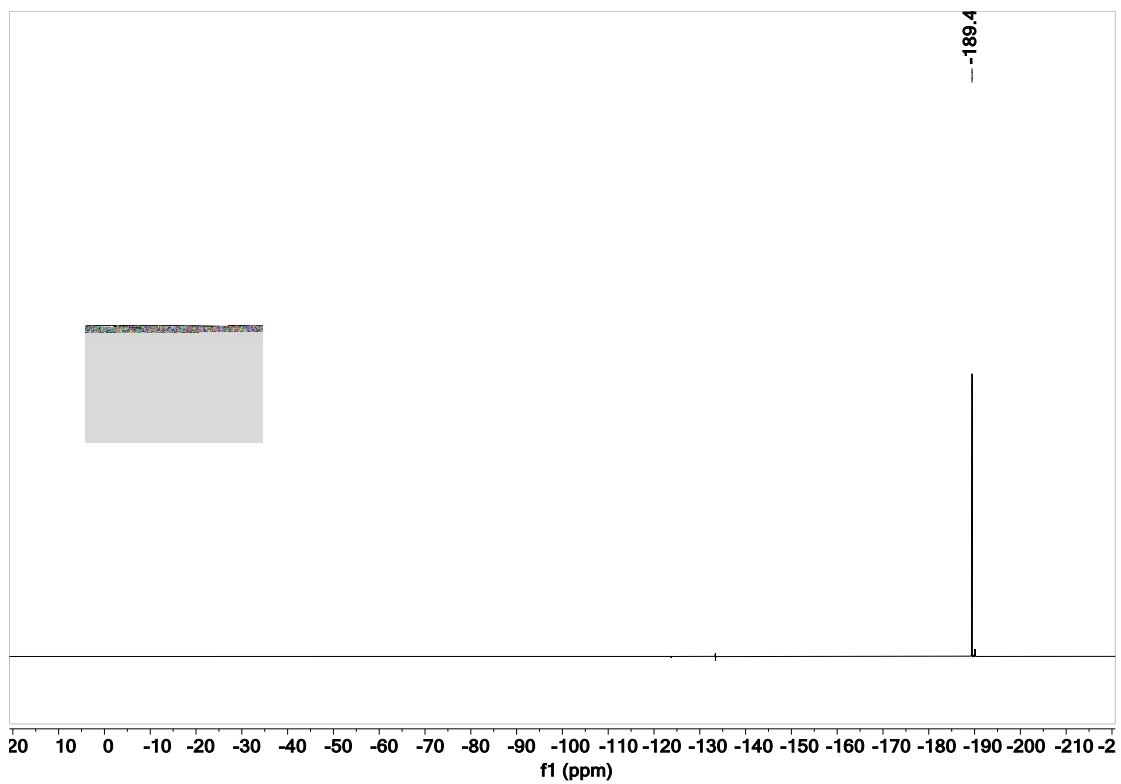
1-(benzyloxy)-4-((1-fluorocyclopropyl)methoxy)methyl)benzene (2n)



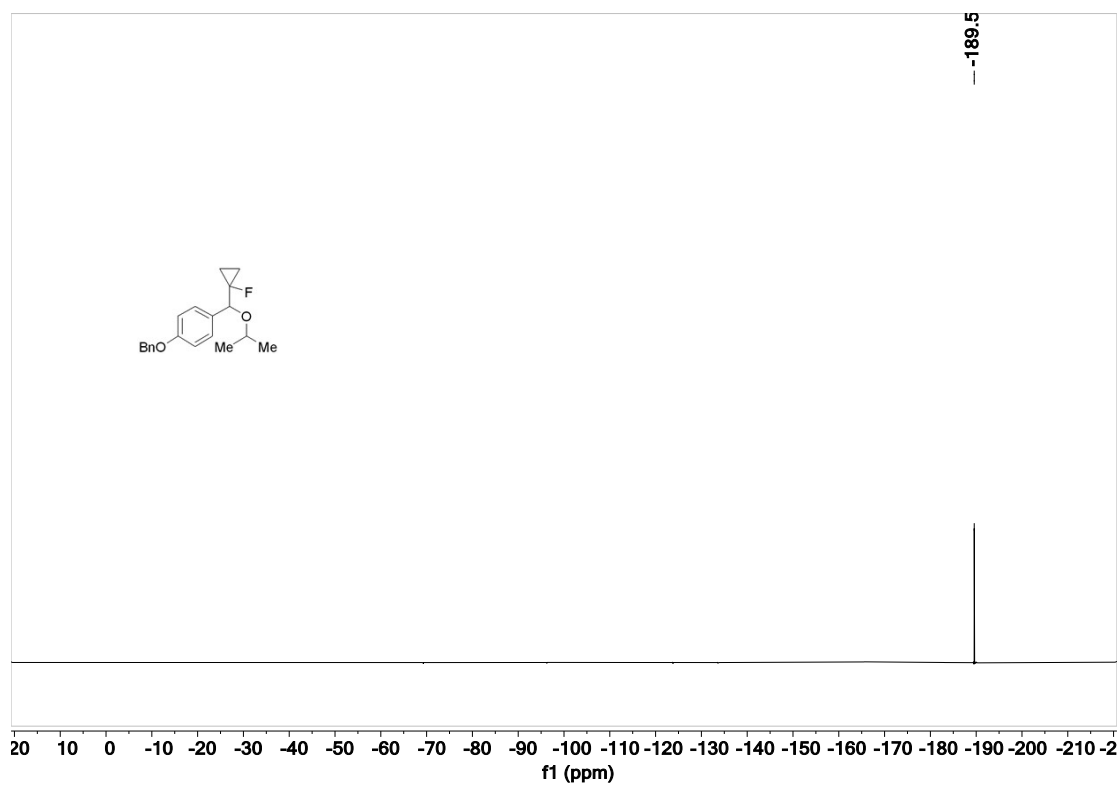
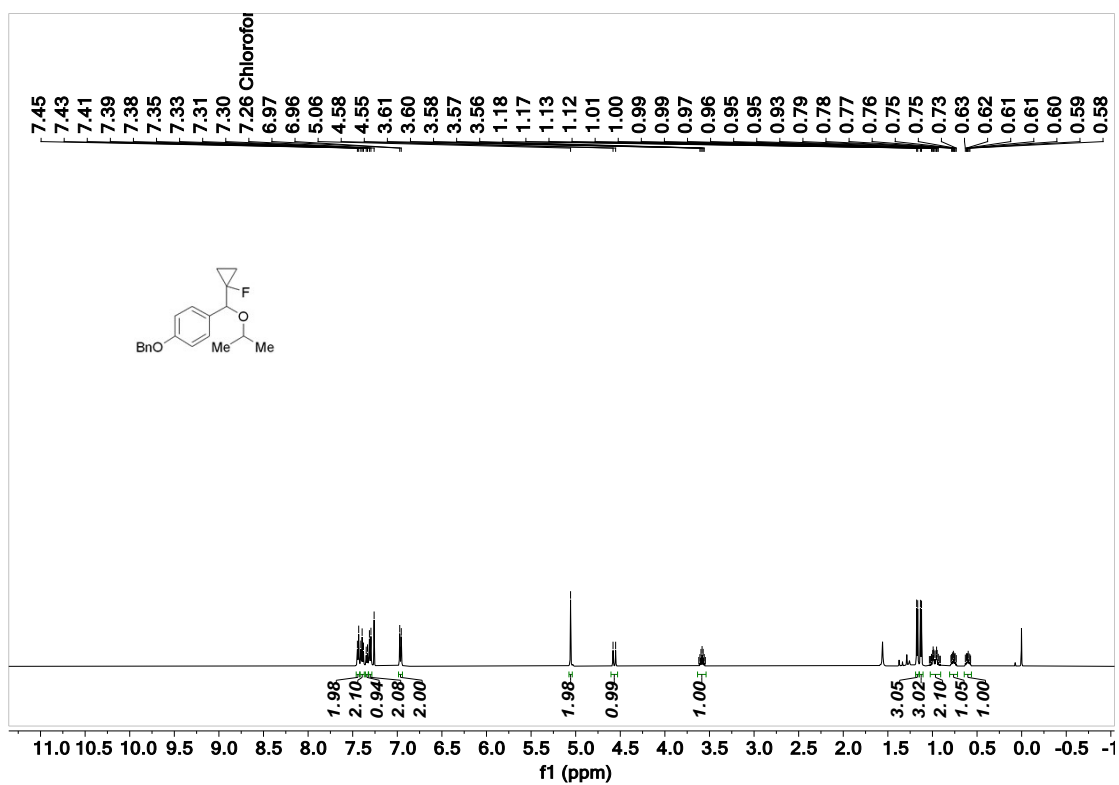


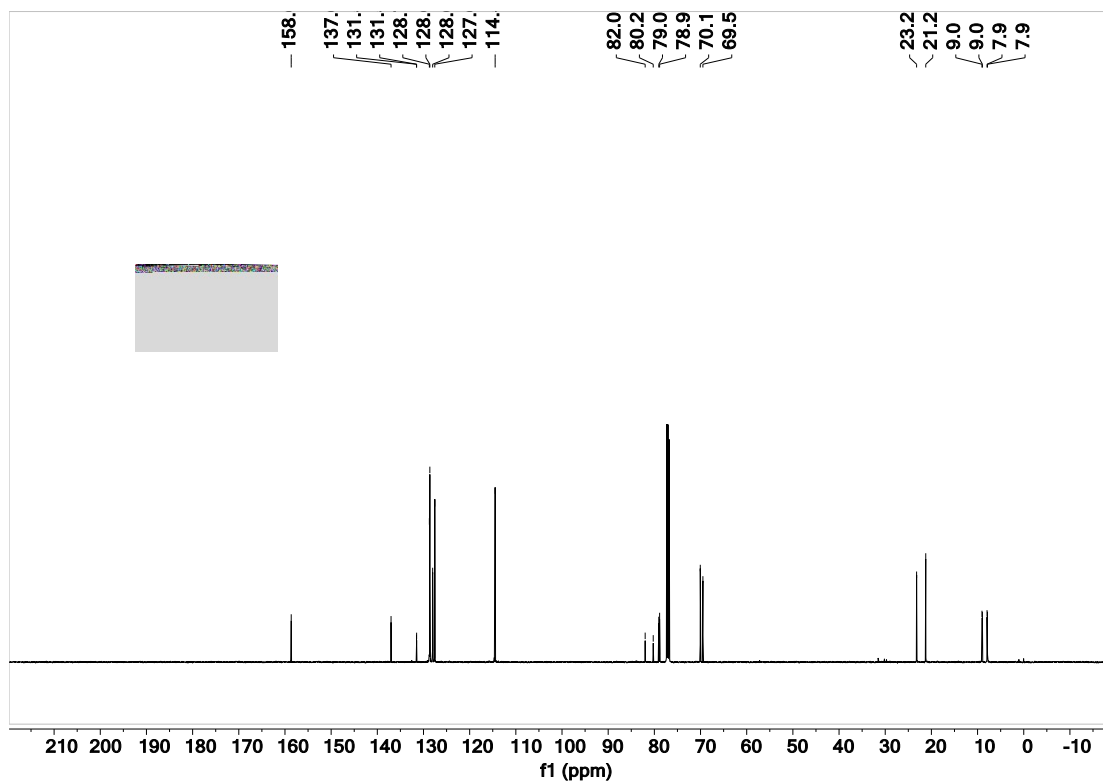
1-(benzyloxy)-4-(ethoxy(1-fluorocyclopropyl)methyl)benzene (2o)



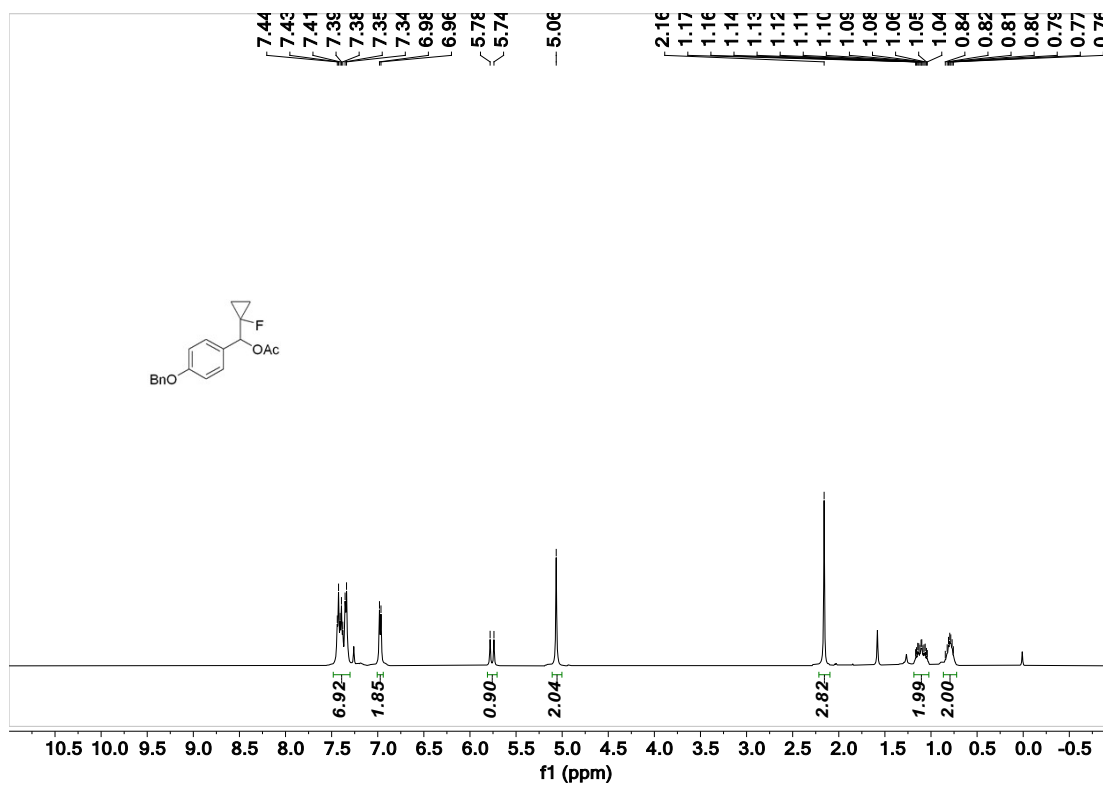


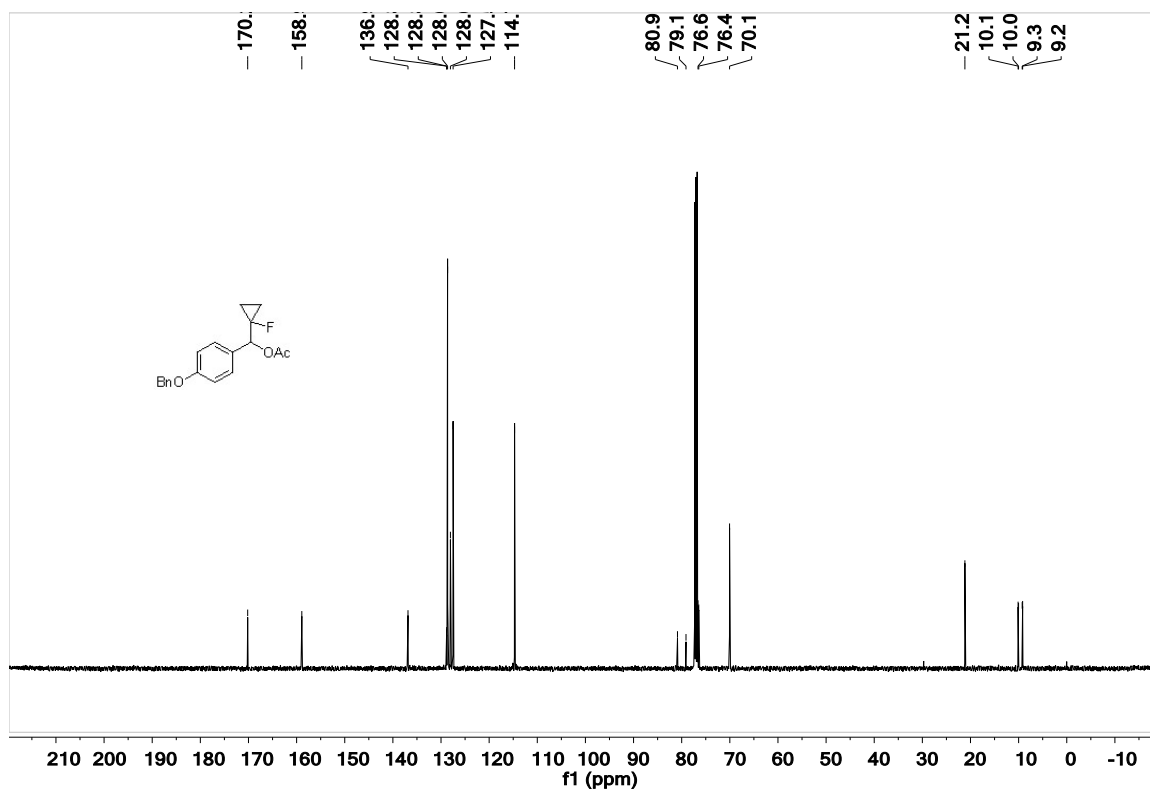
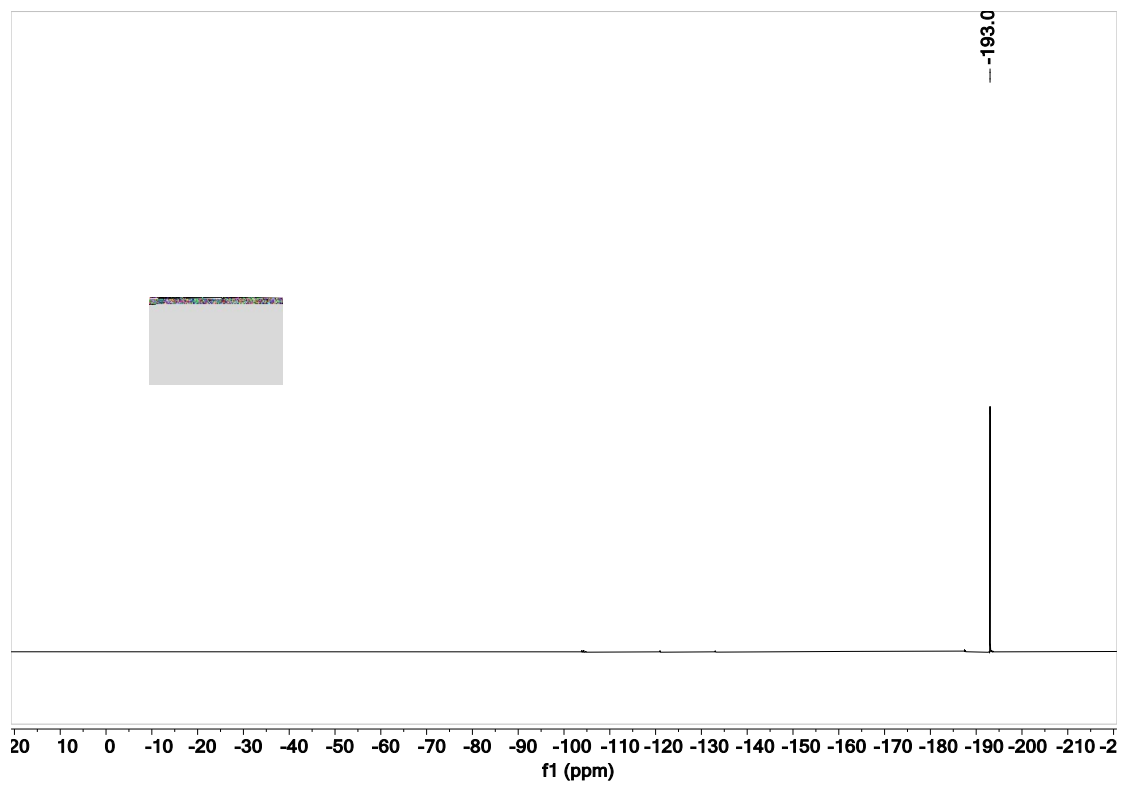
1-(benzyloxy)-4-((1-fluorocyclopropyl)isopropoxy)methylbenzene (2p)



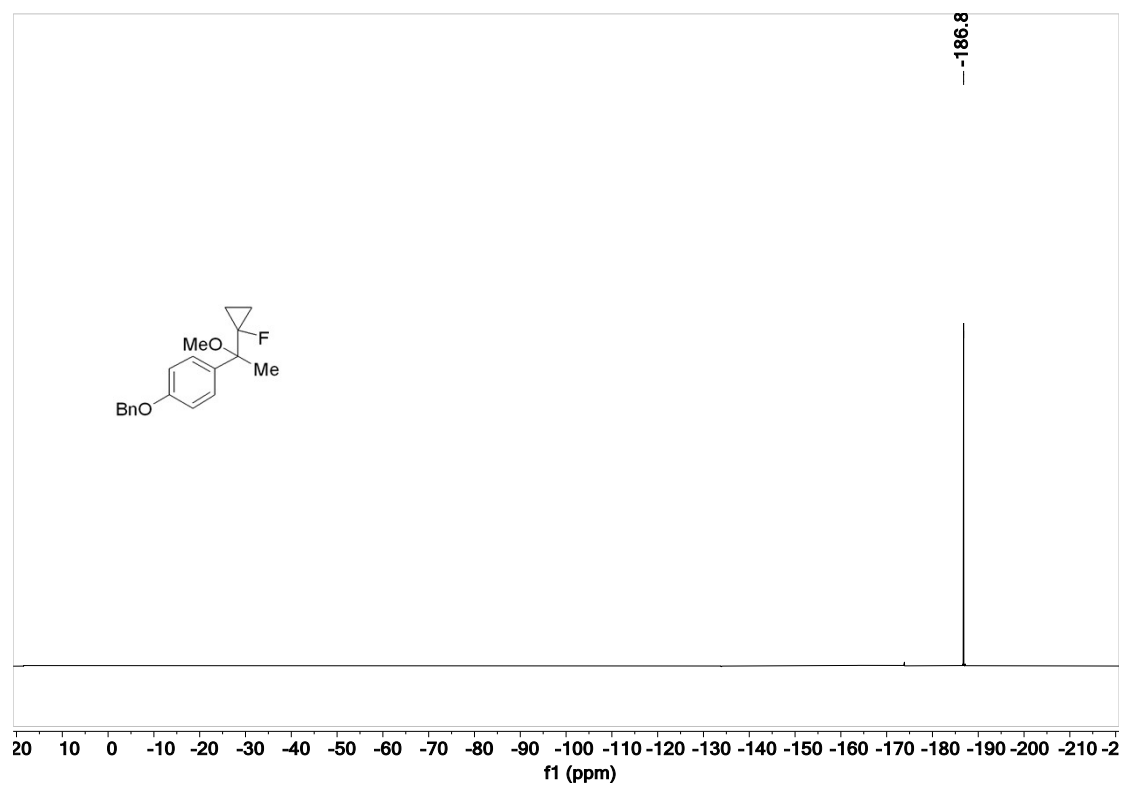
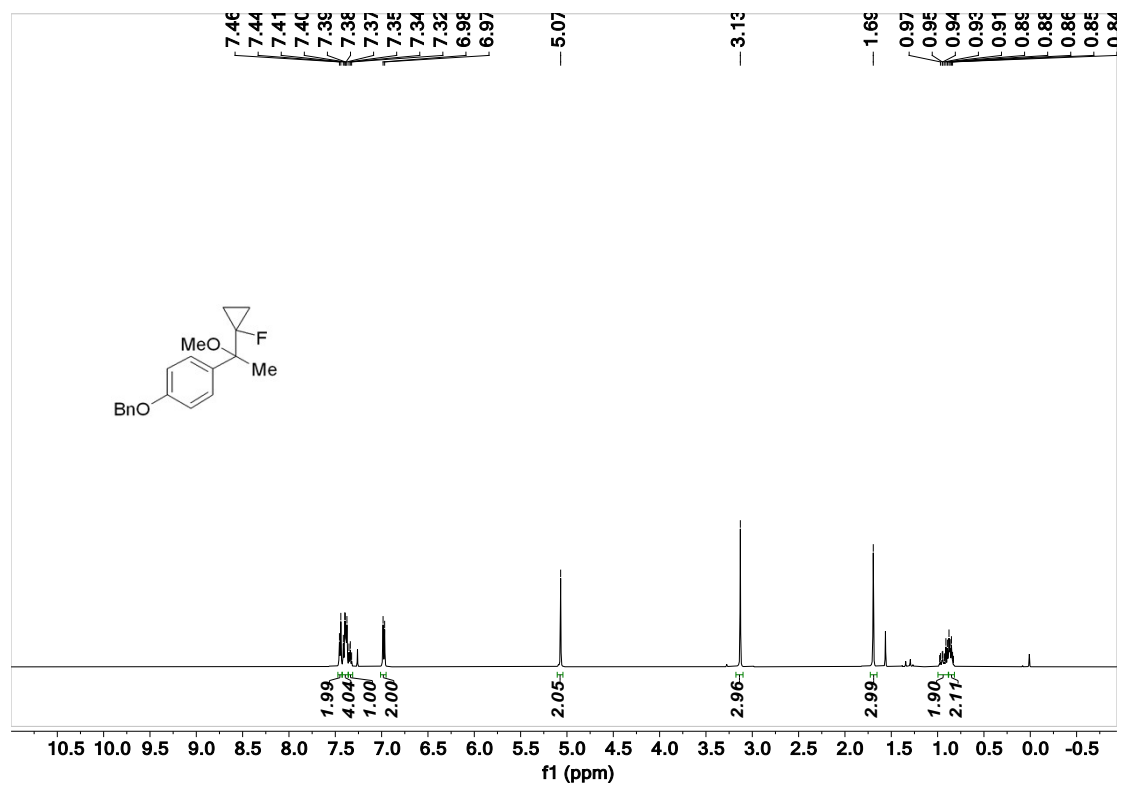


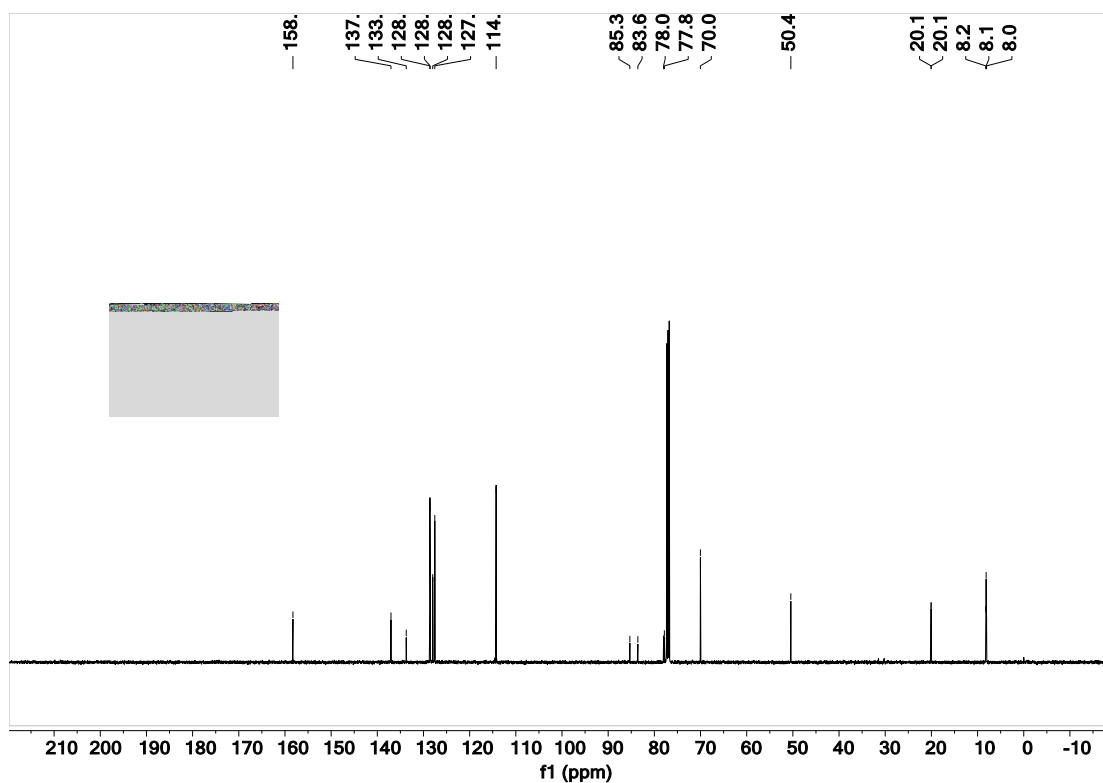
(benzyloxy)phenyl(1-fluorocyclopropyl)methyl acetate (2q)



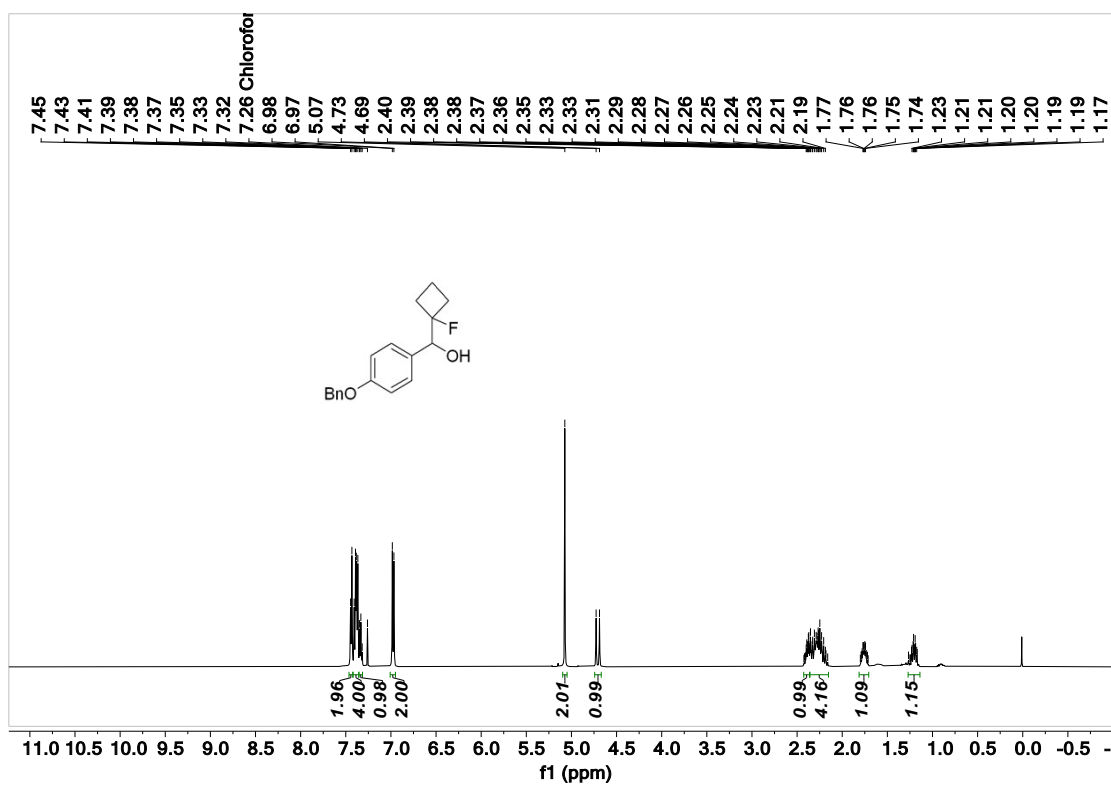


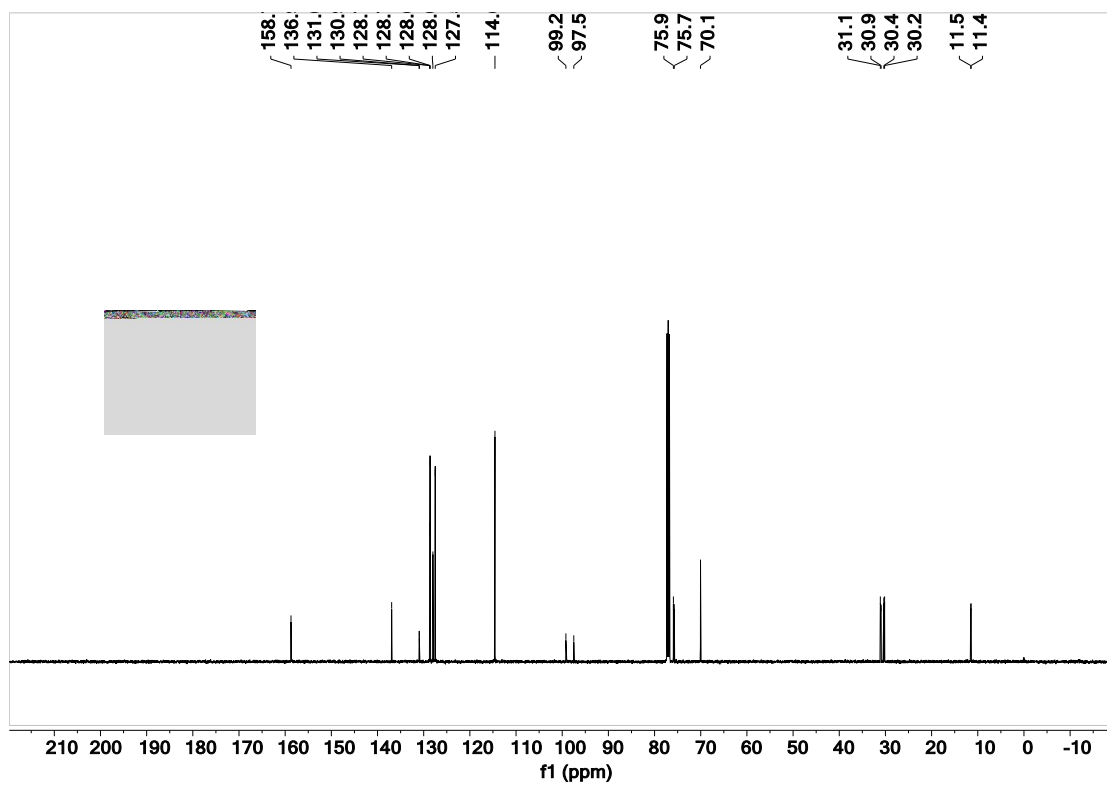
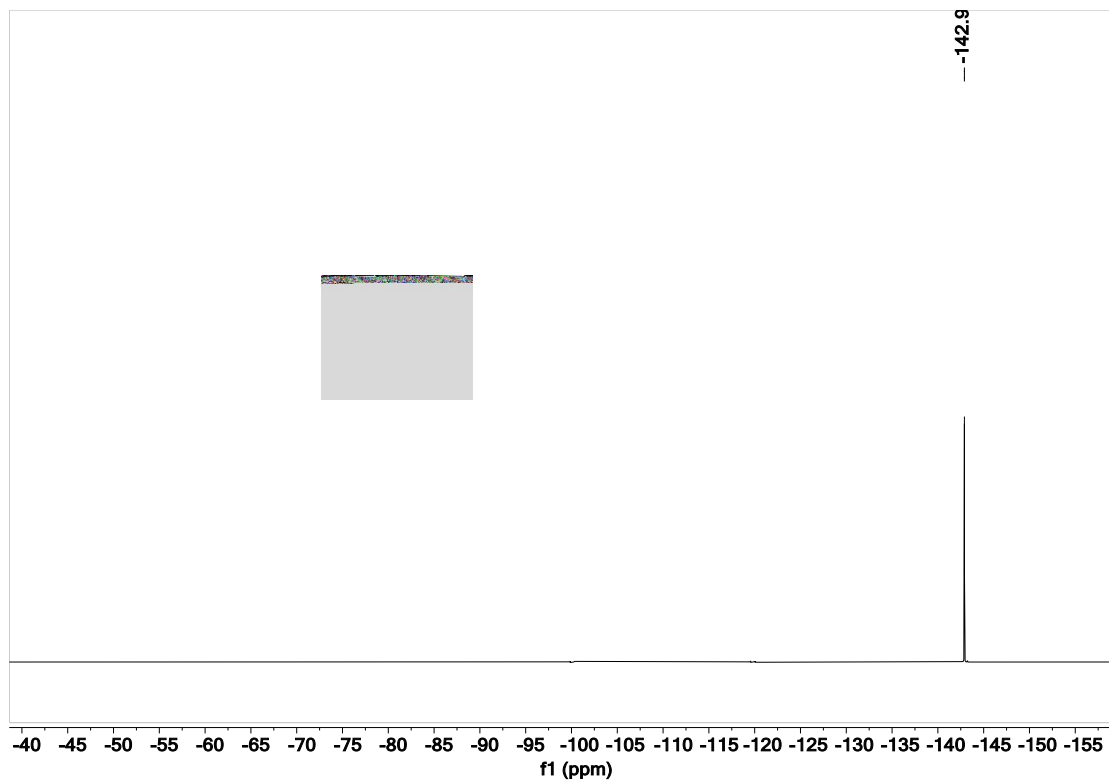
1-(benzyloxy)-4-(1-(1-fluorocyclopropyl)-1-methoxyethyl)benzene (2r)



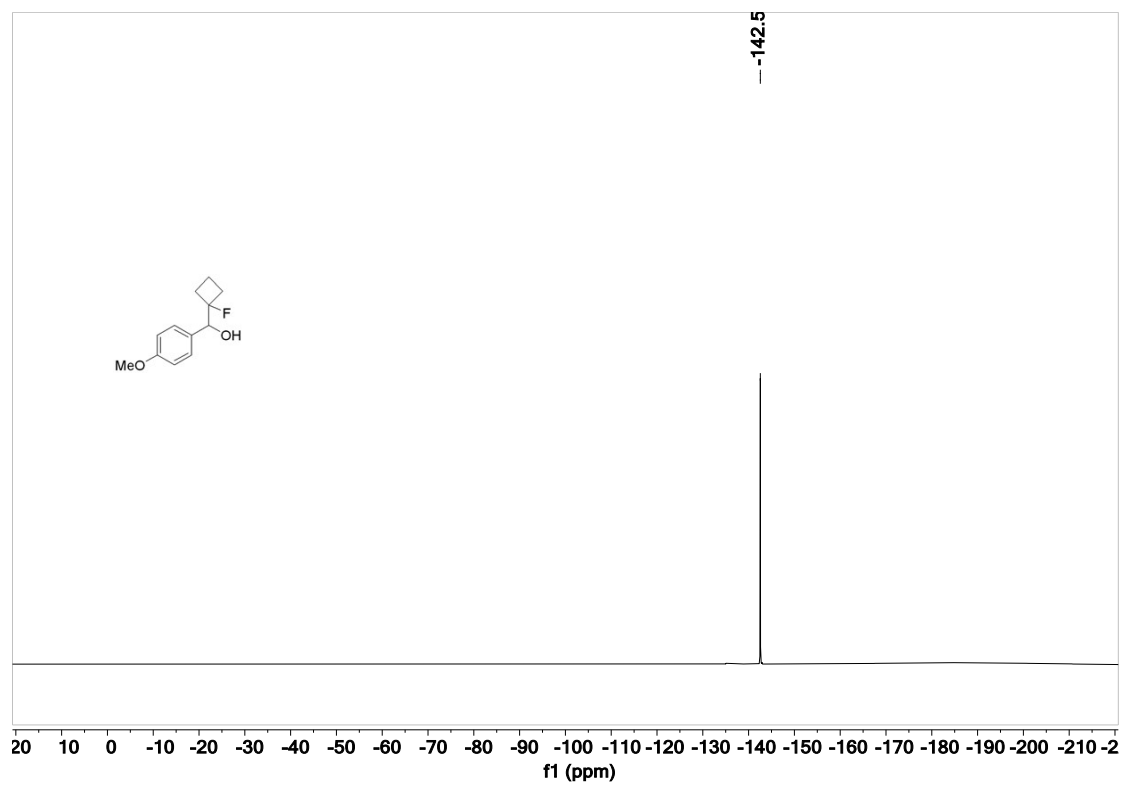
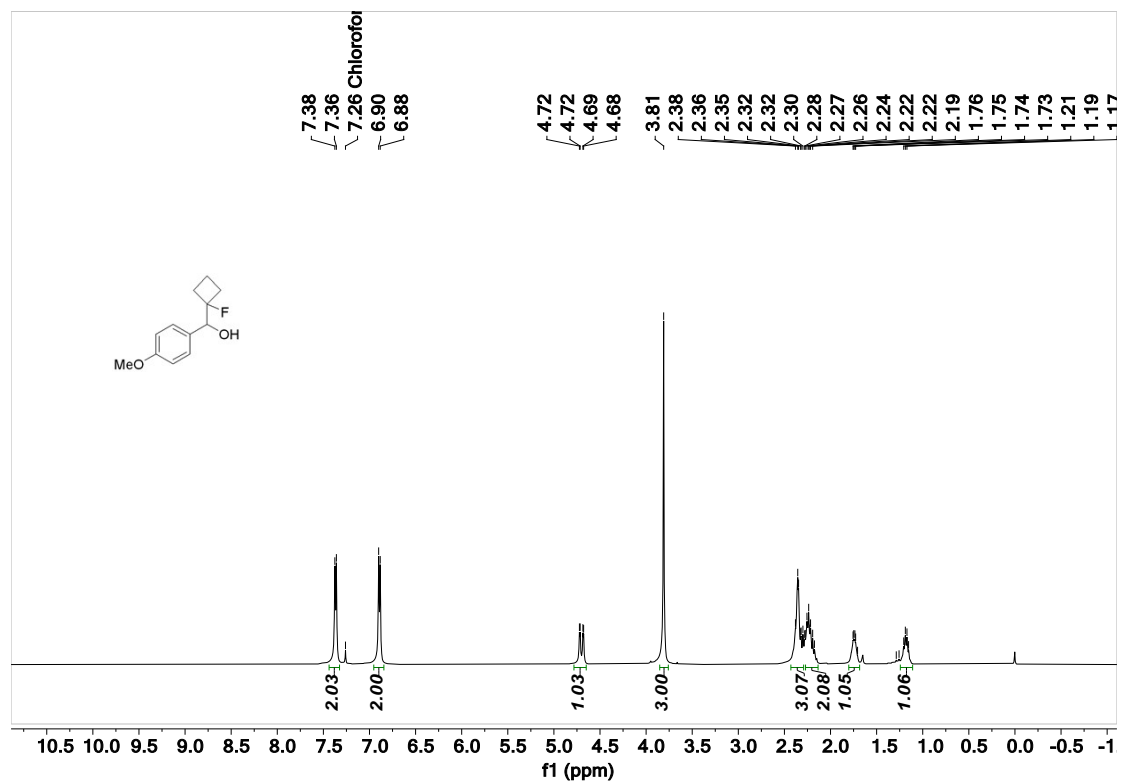


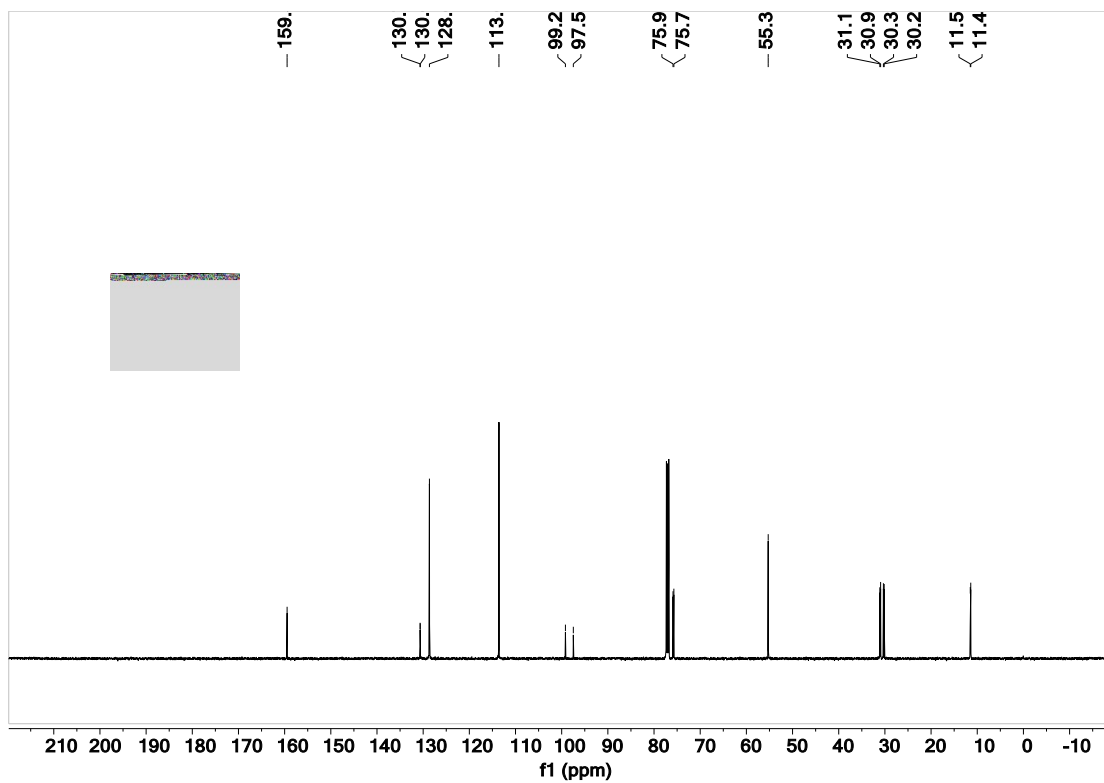
(4-(benzyloxy)phenyl)(1-fluorocyclobutyl)methanol (4a)



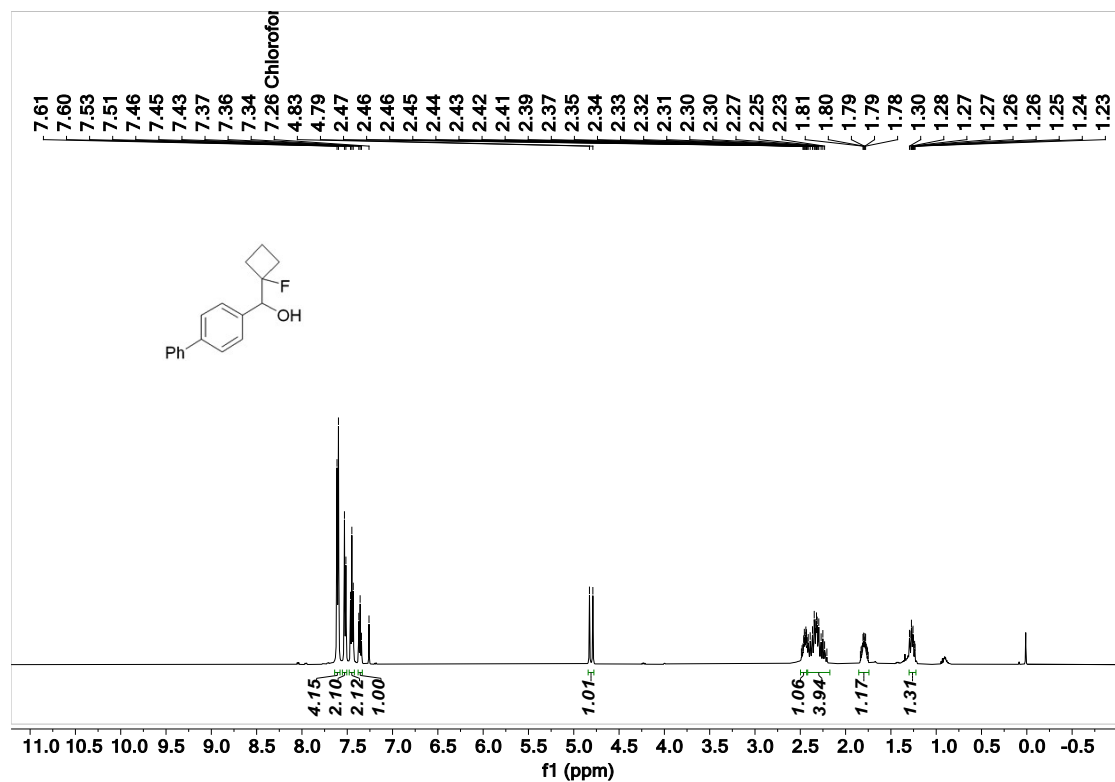


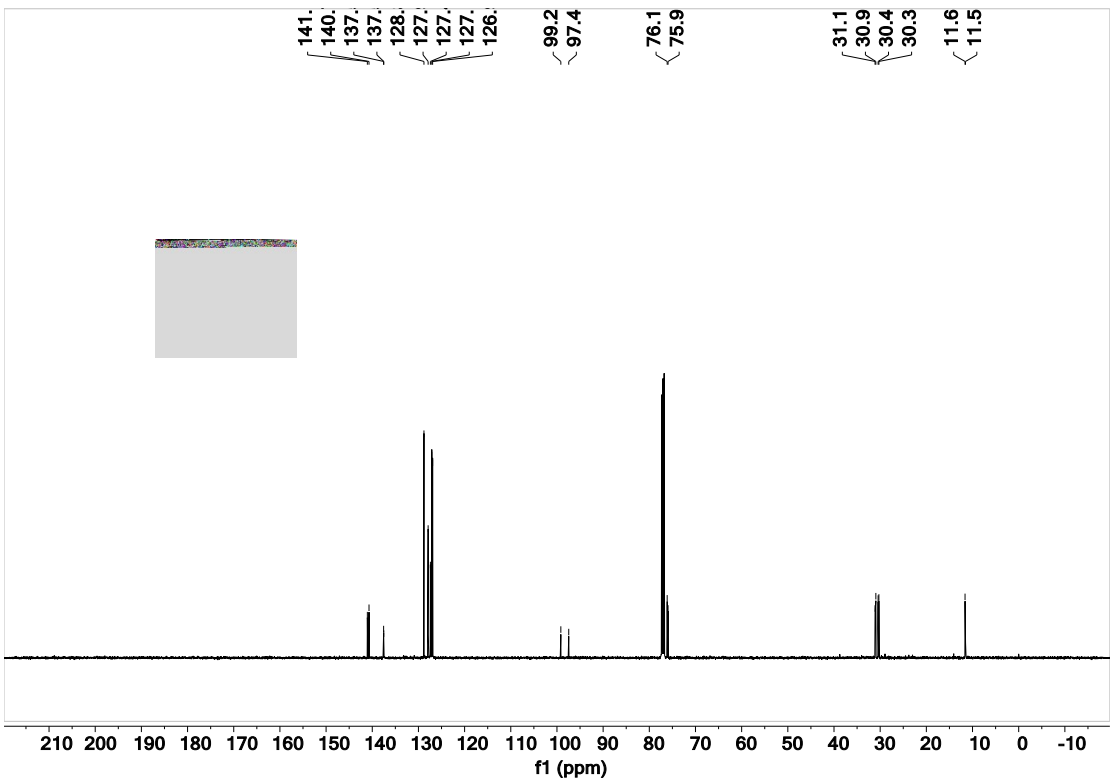
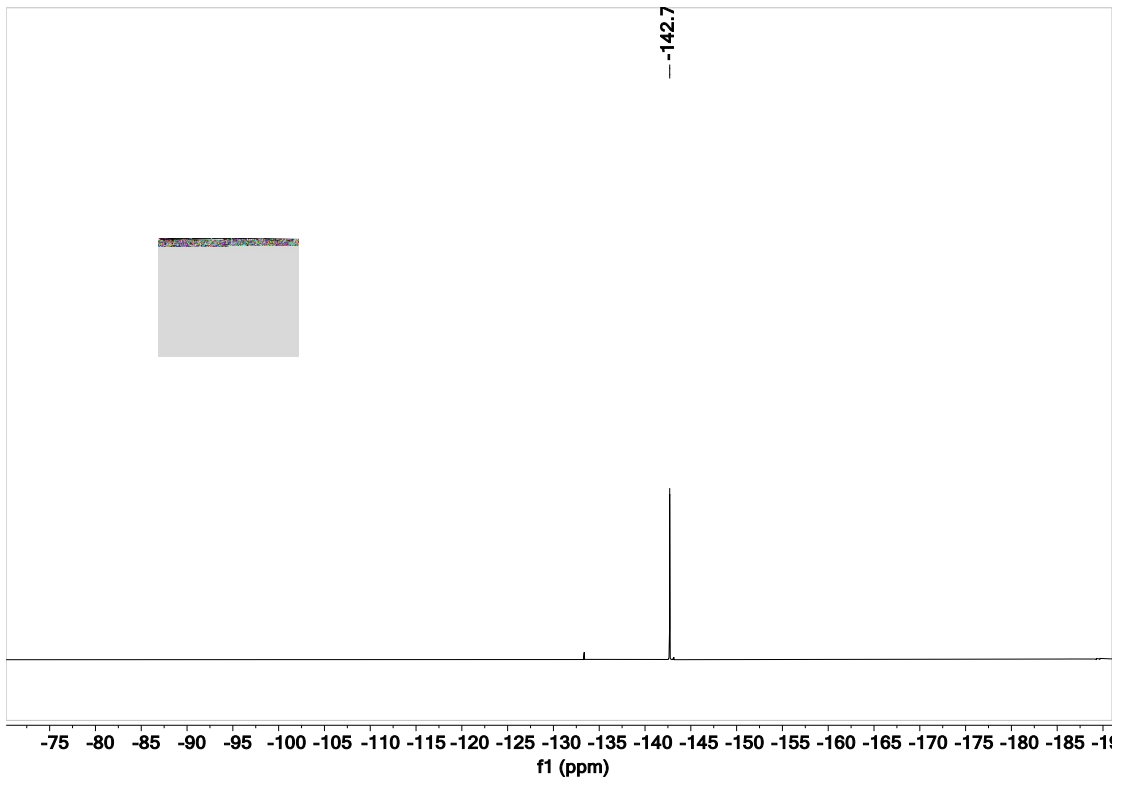
(1-fluorocyclobutyl)(4-methoxyphenyl)methanol (4b)



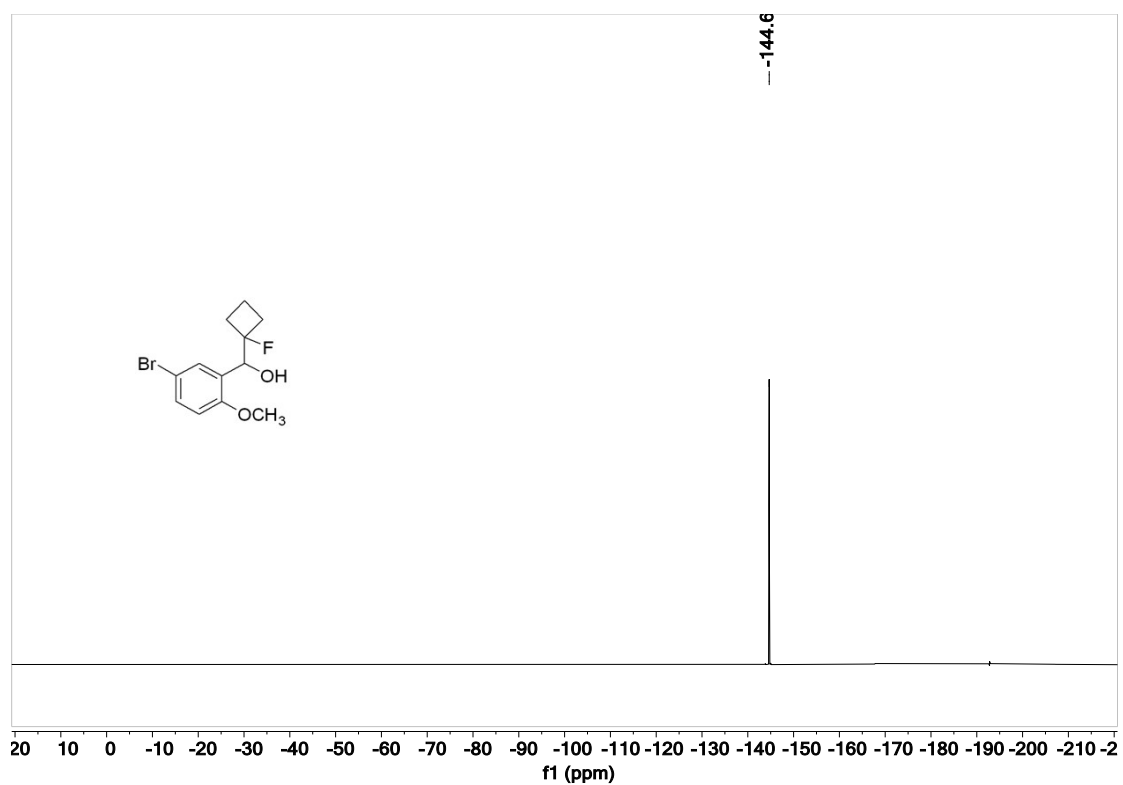
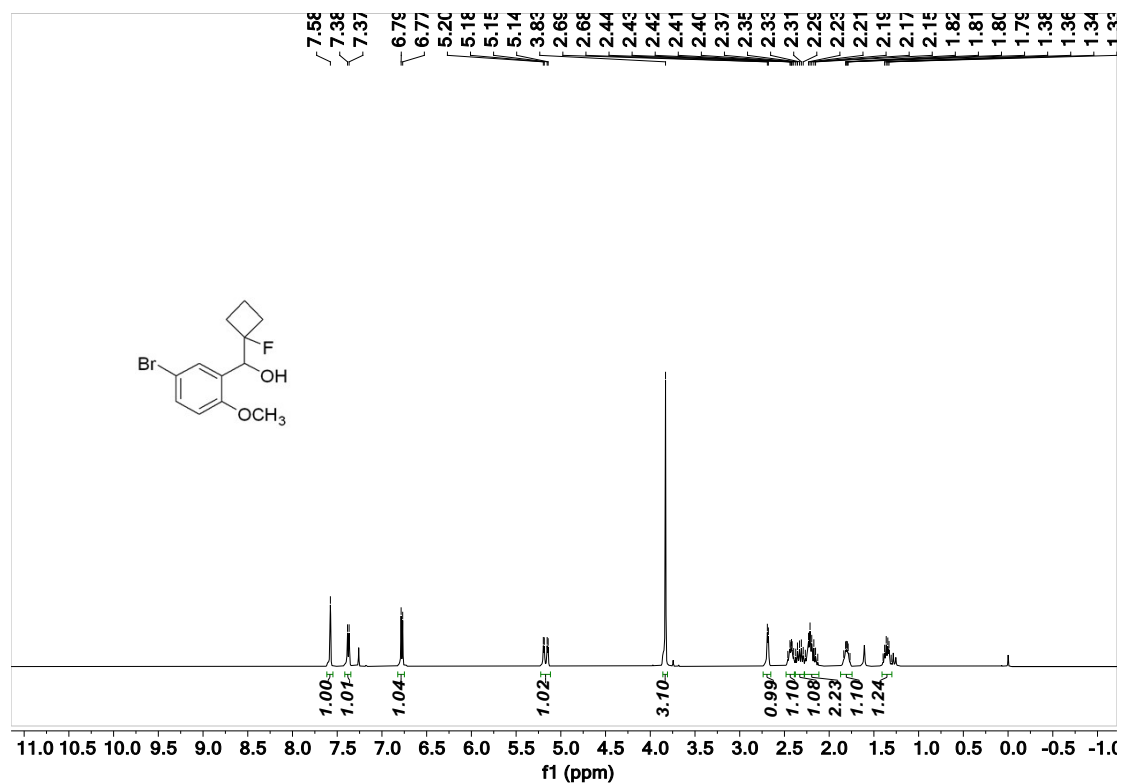


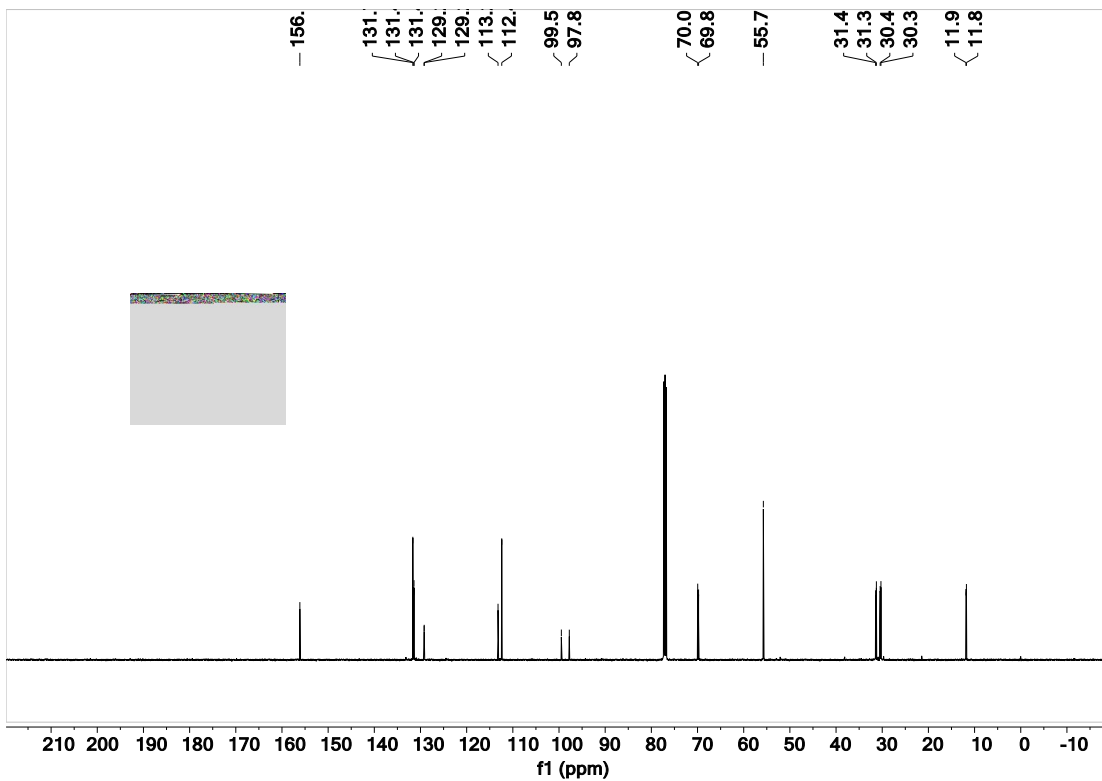
[1,1'-biphenyl]-4-yl(1-fluorocyclobutyl)methanol (4c)



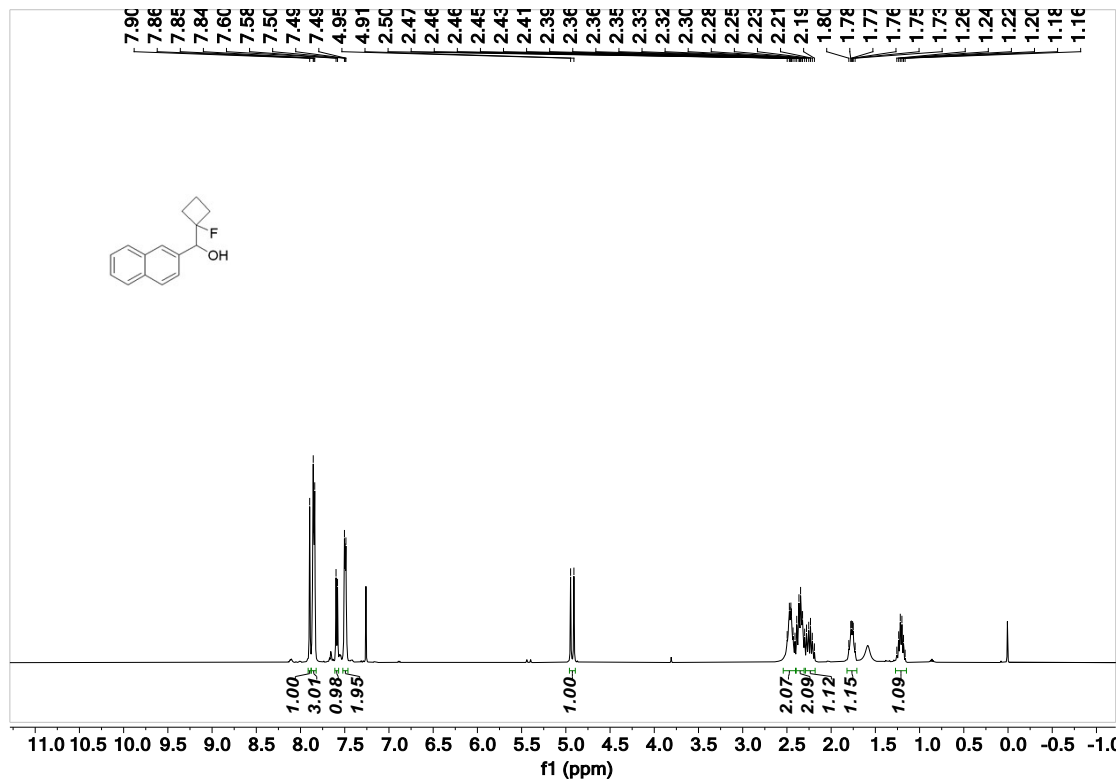


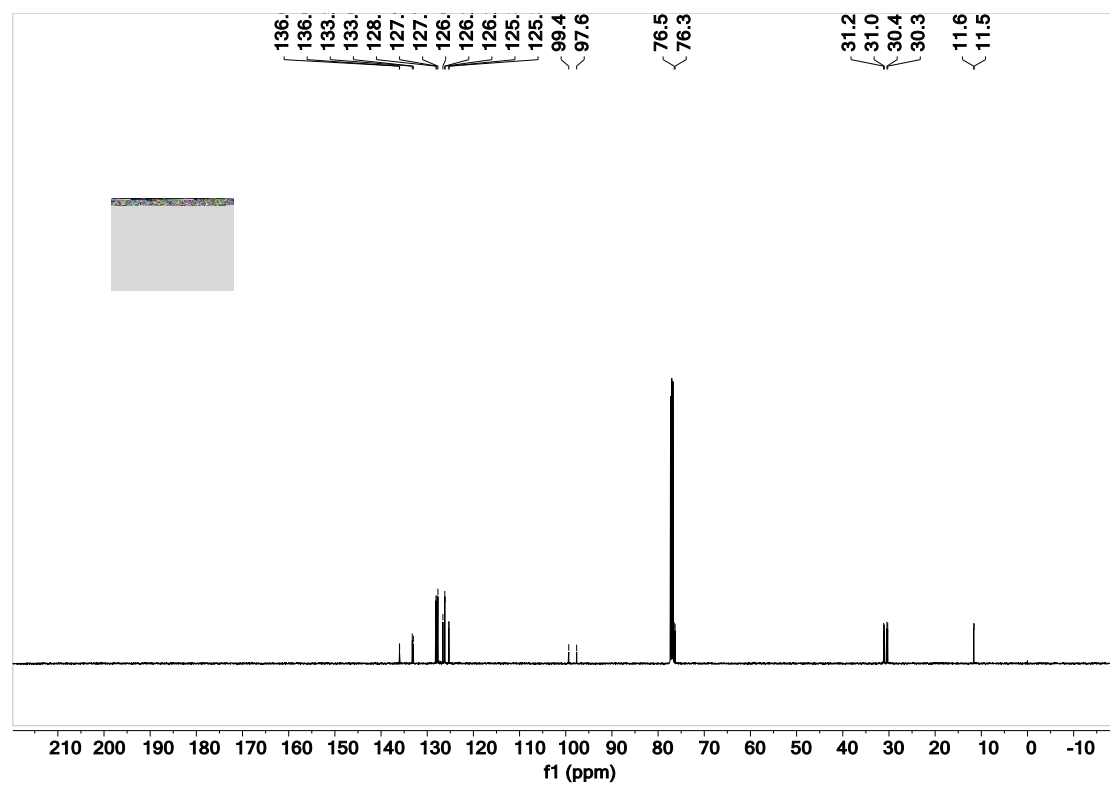
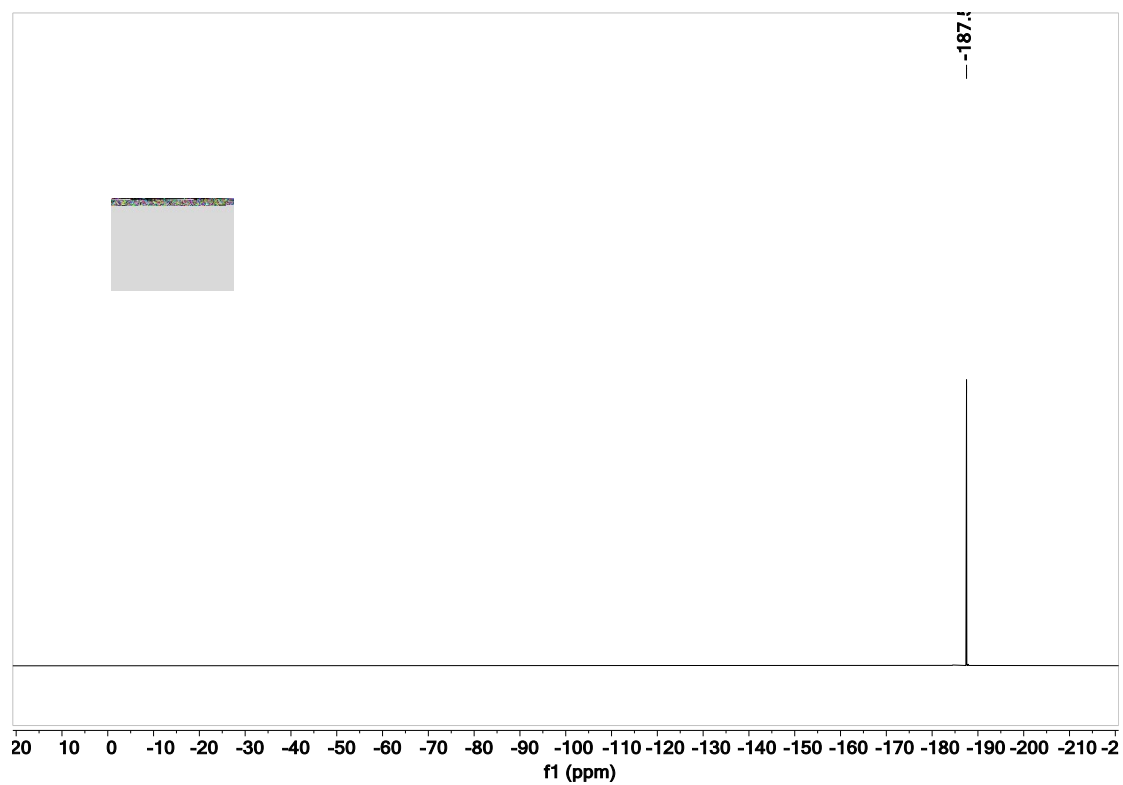
(5-bromo-2-methoxyphenyl)(1-fluorocyclobutyl)methanol (4d)



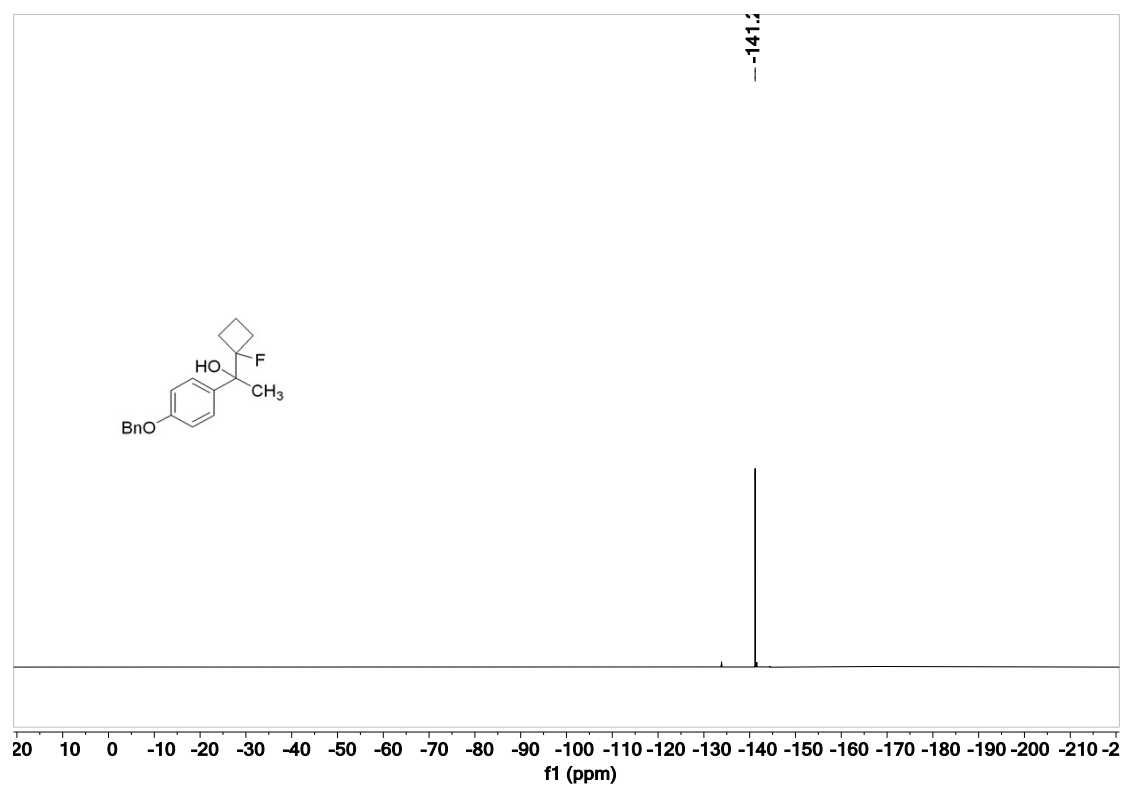
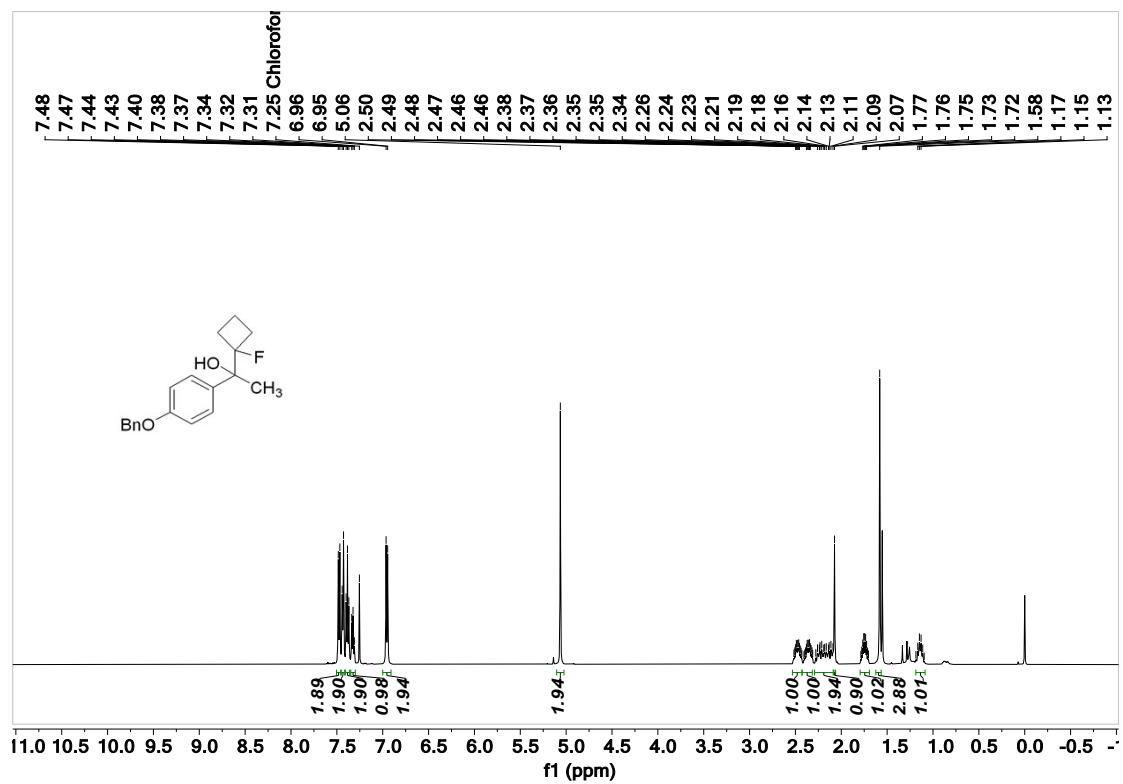


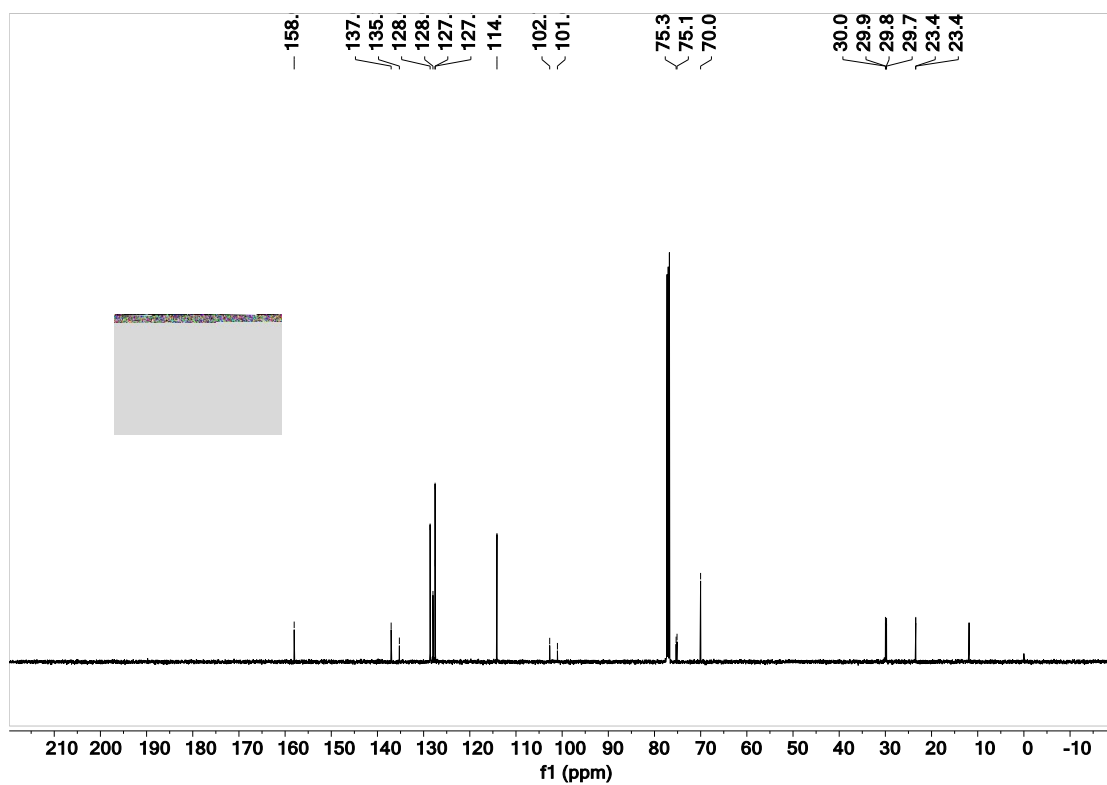
(1-fluorocyclobutyl)(naphthalen-2-yl)methanol (4e)



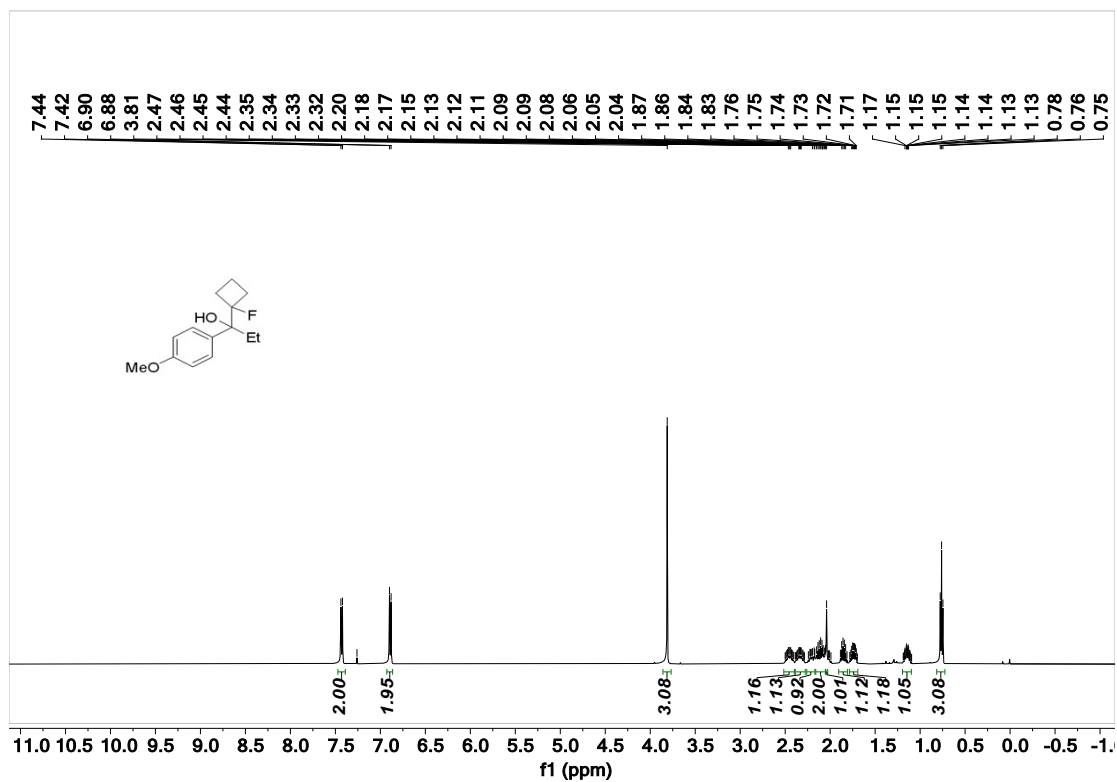


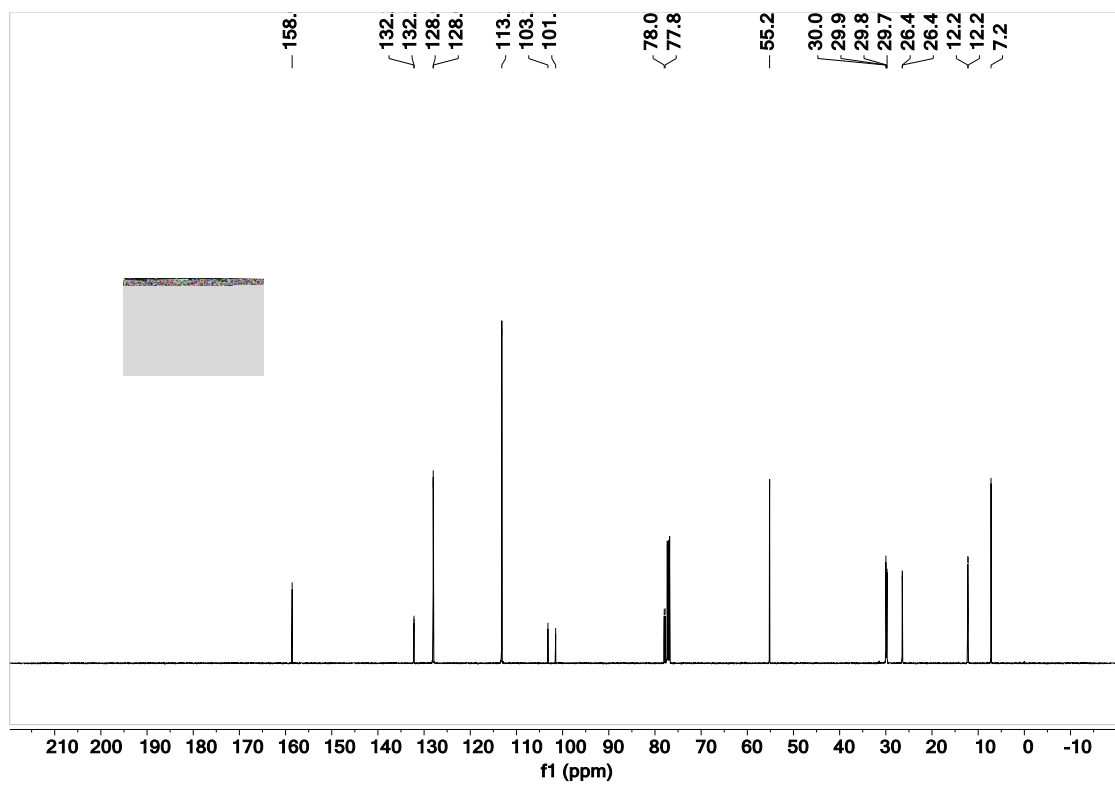
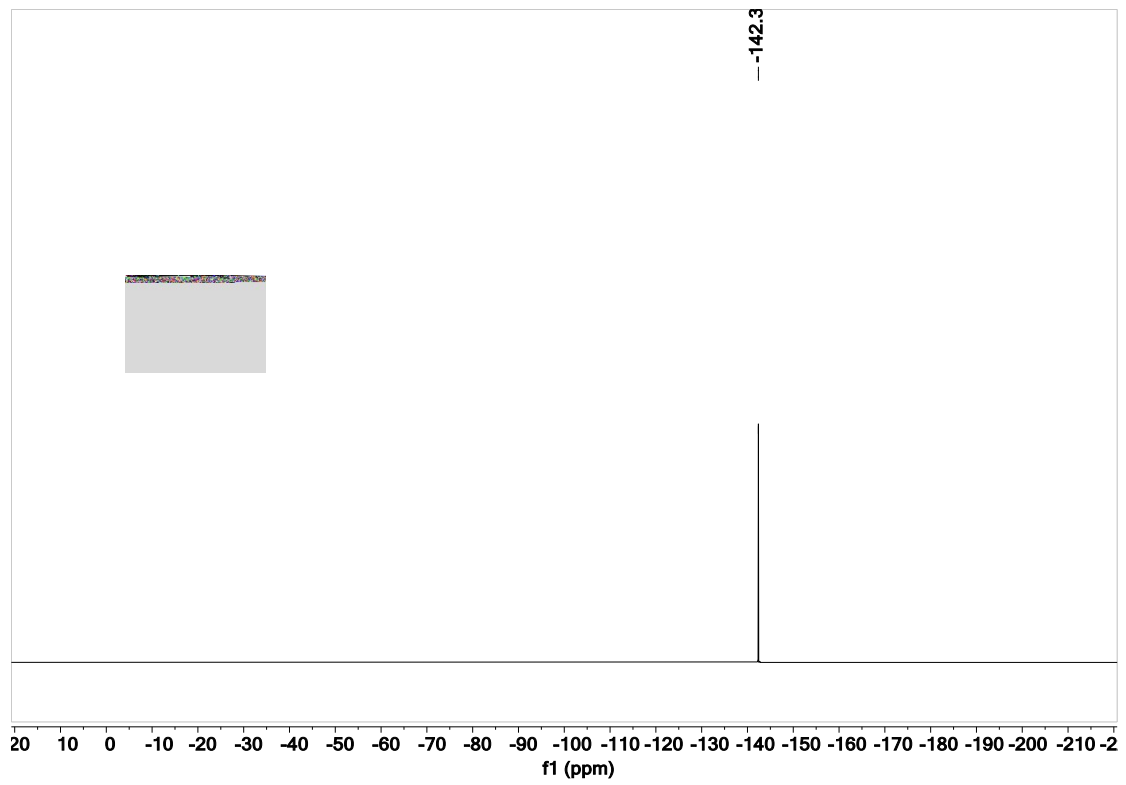
1-(4-(benzyloxy)phenyl)-1-(1-fluorocyclobutyl)ethan-1-ol (4f)



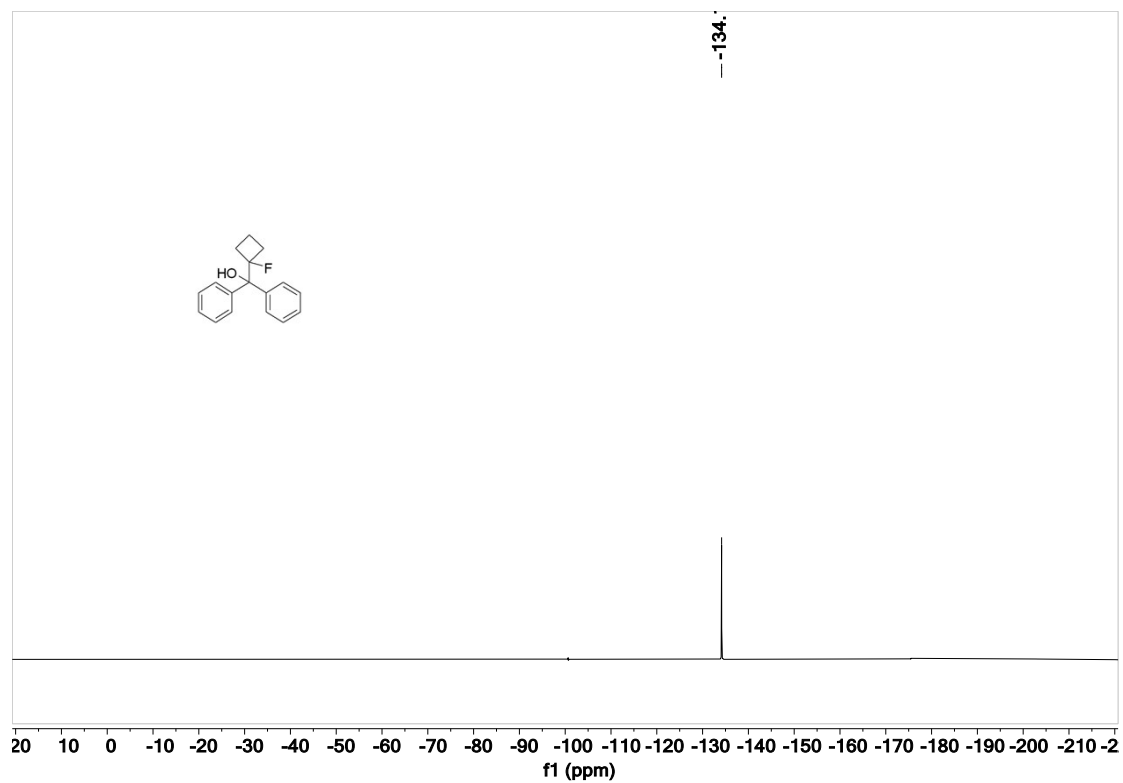
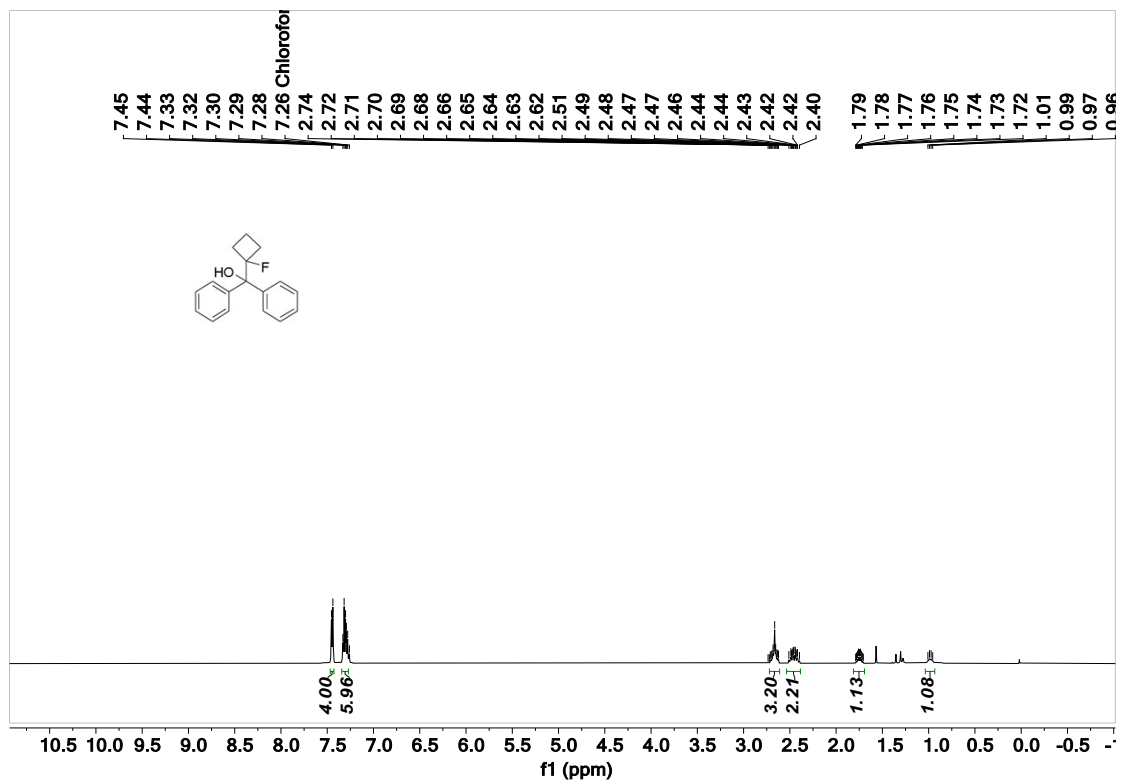


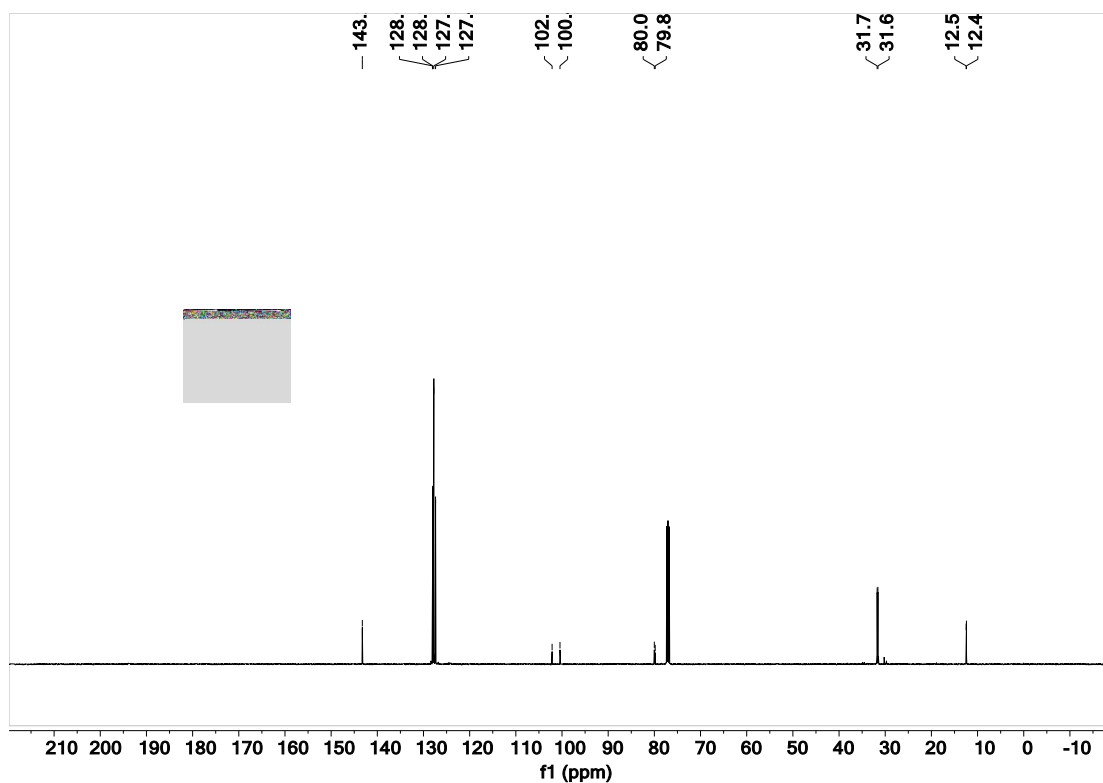
1-(1-fluorocyclobutyl)-1-(4-methoxyphenyl)propan-1-ol (4g)



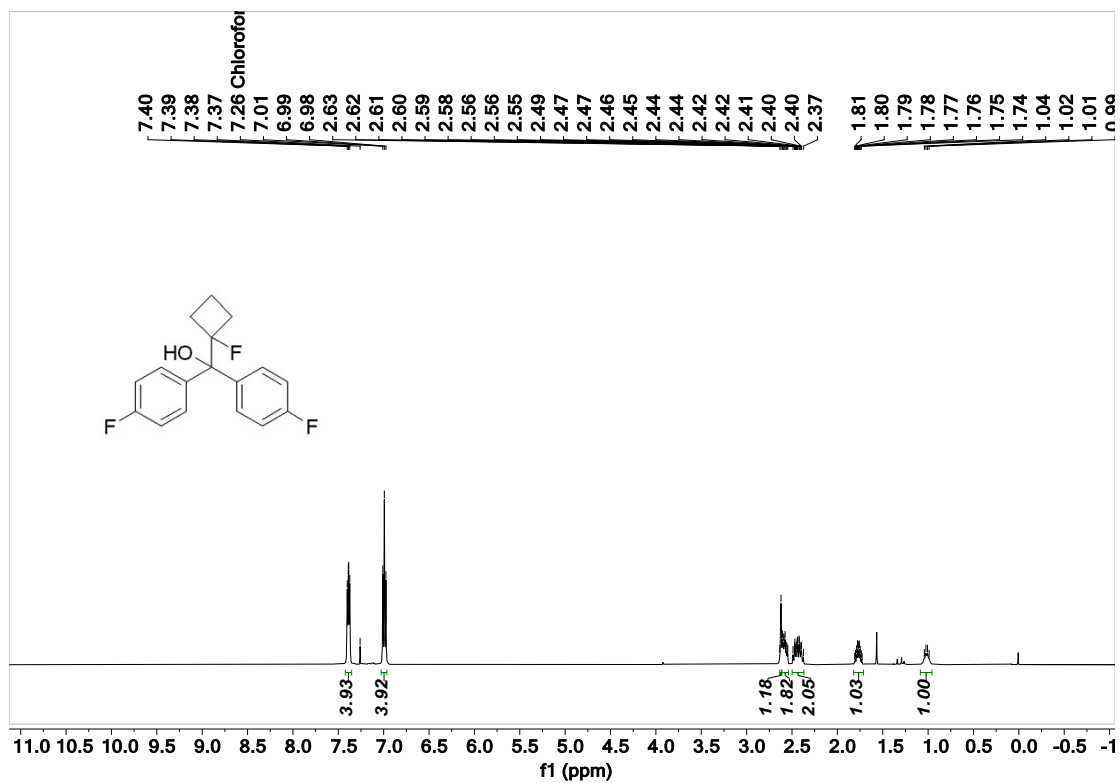


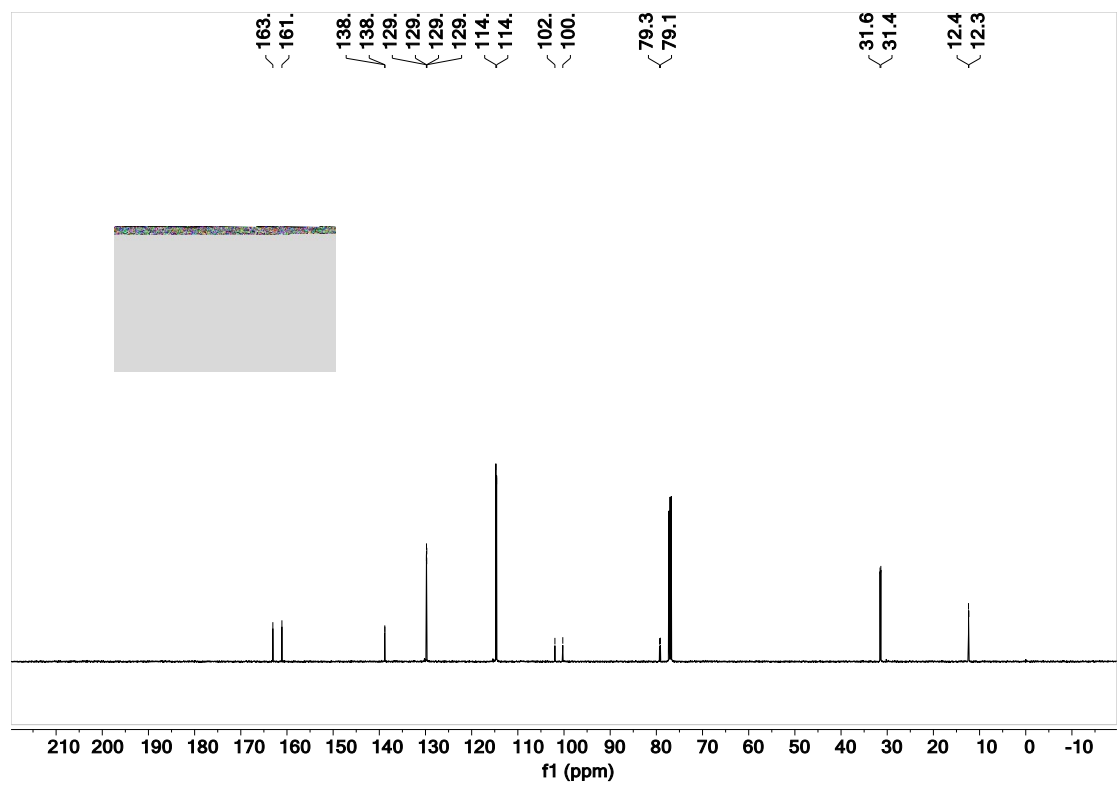
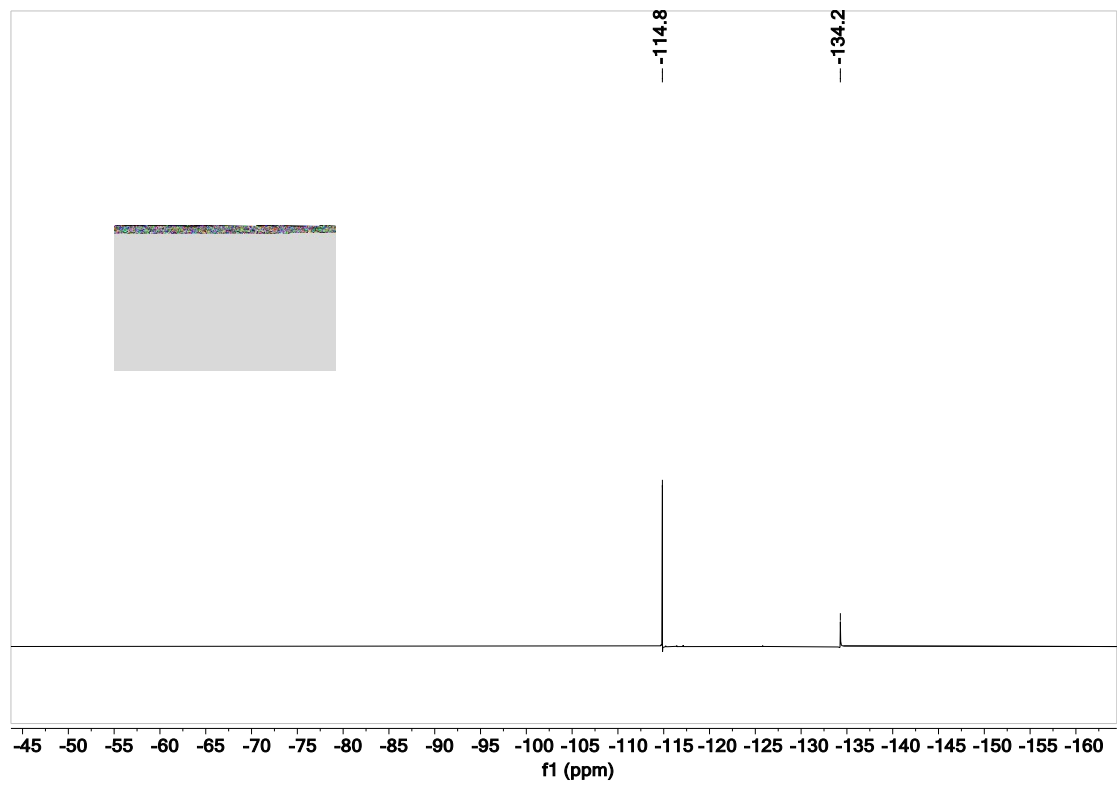
(1-fluorocyclobutyl)diphenylmethanol (4h)



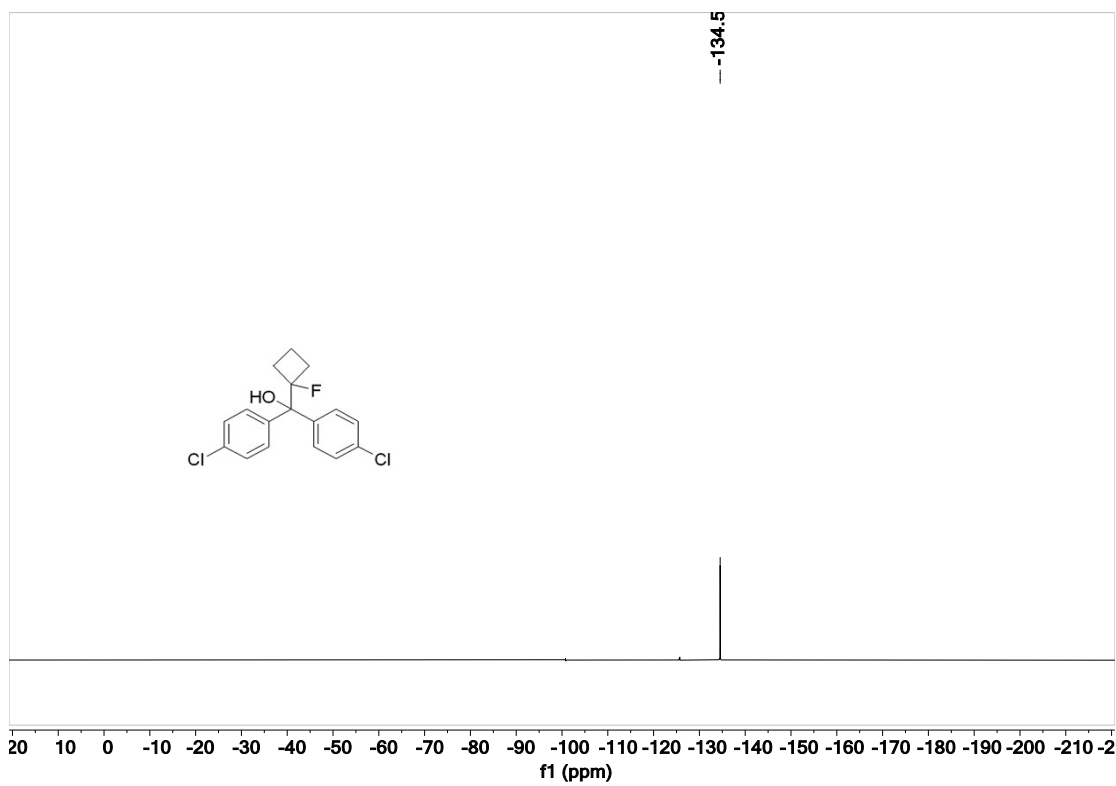
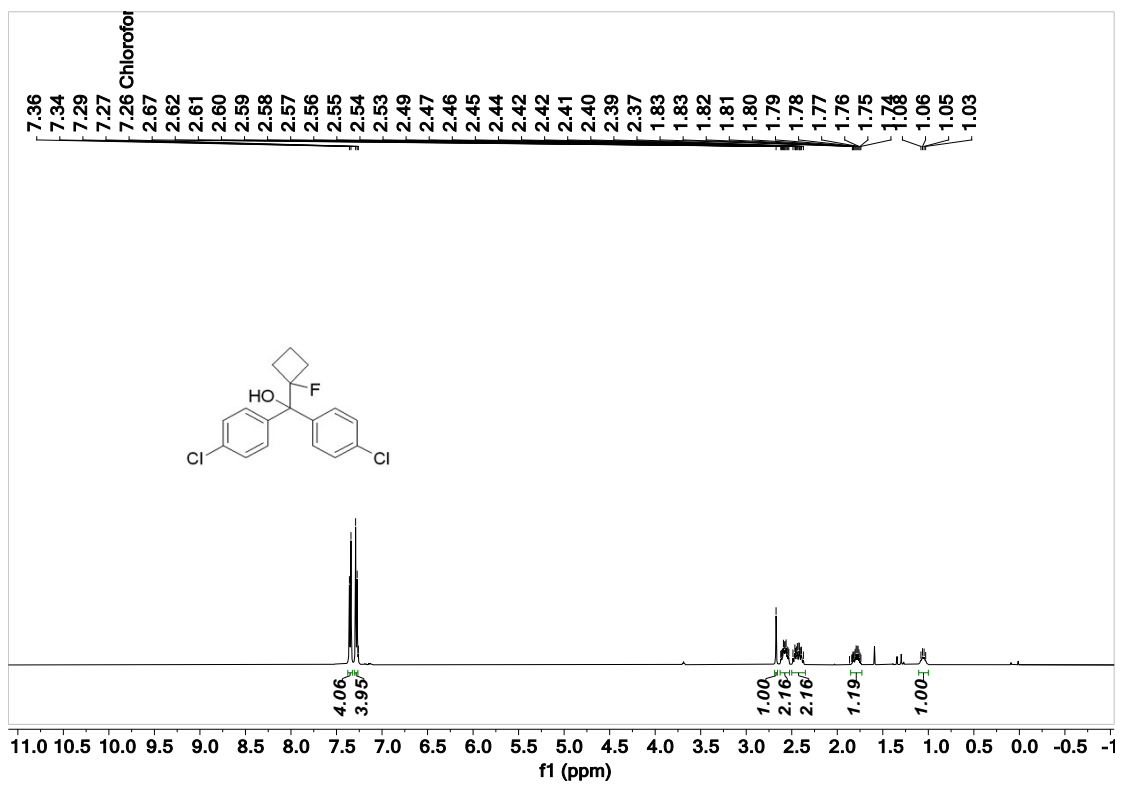


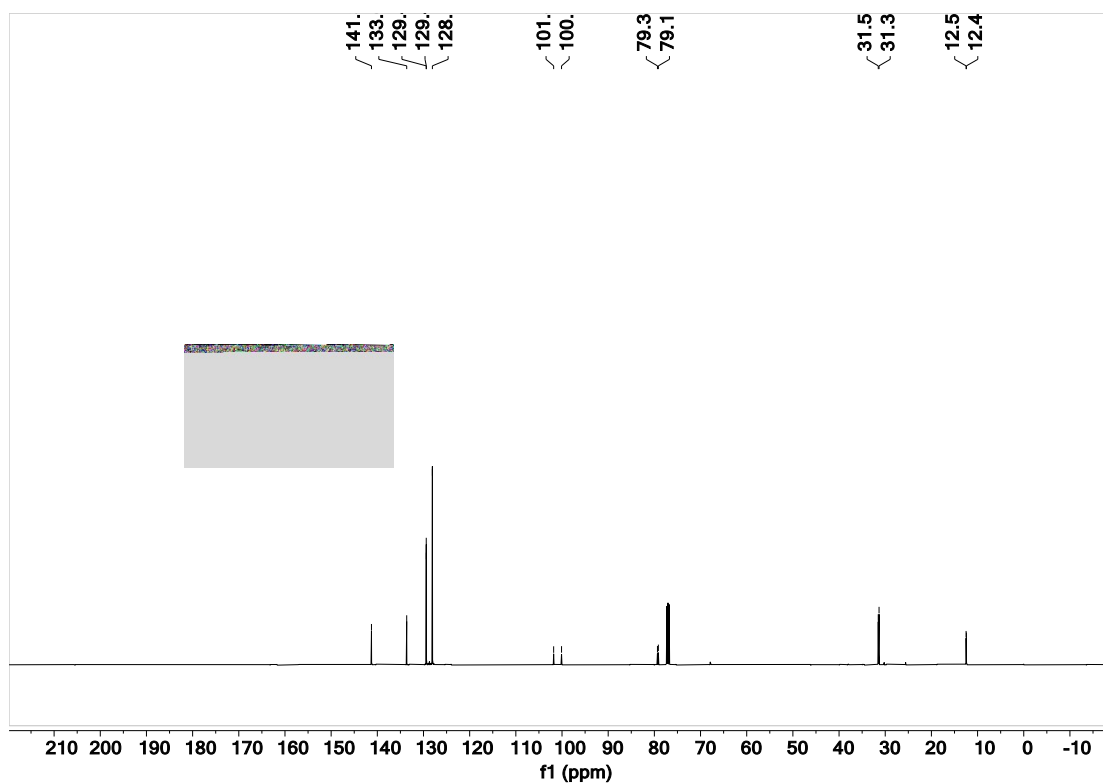
(1-fluorocyclobutyl)bis(4-fluorophenyl)methanol (4i)



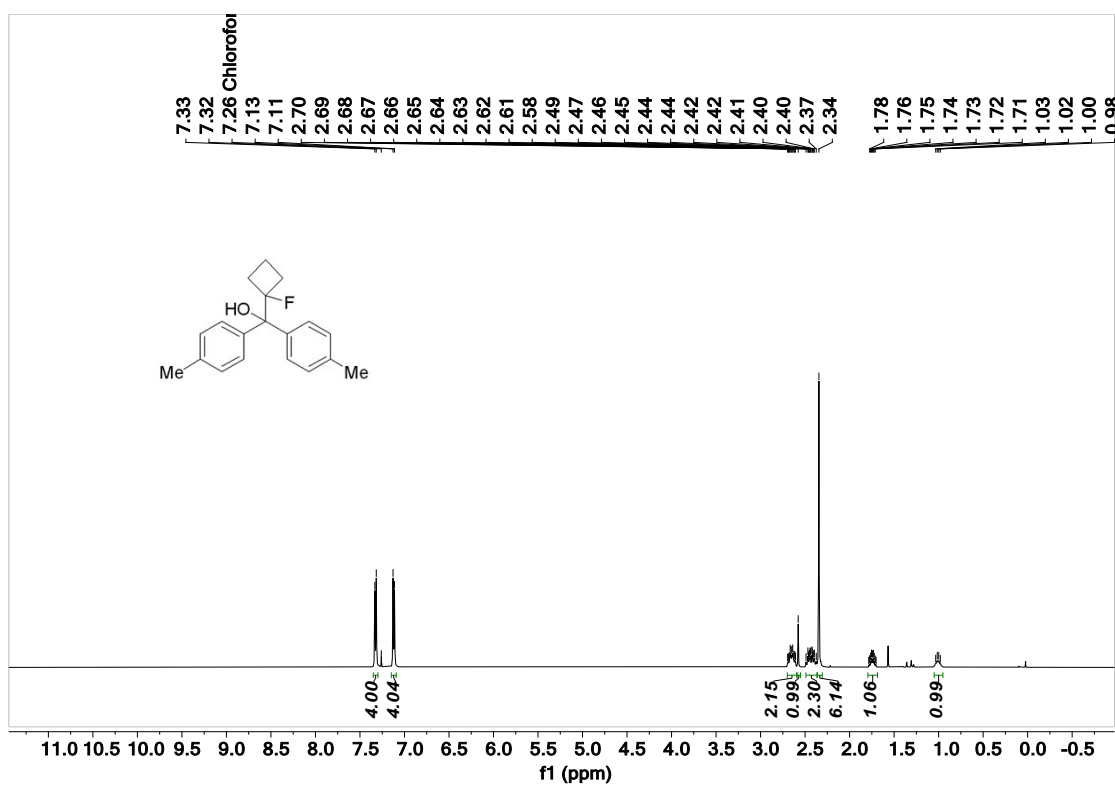


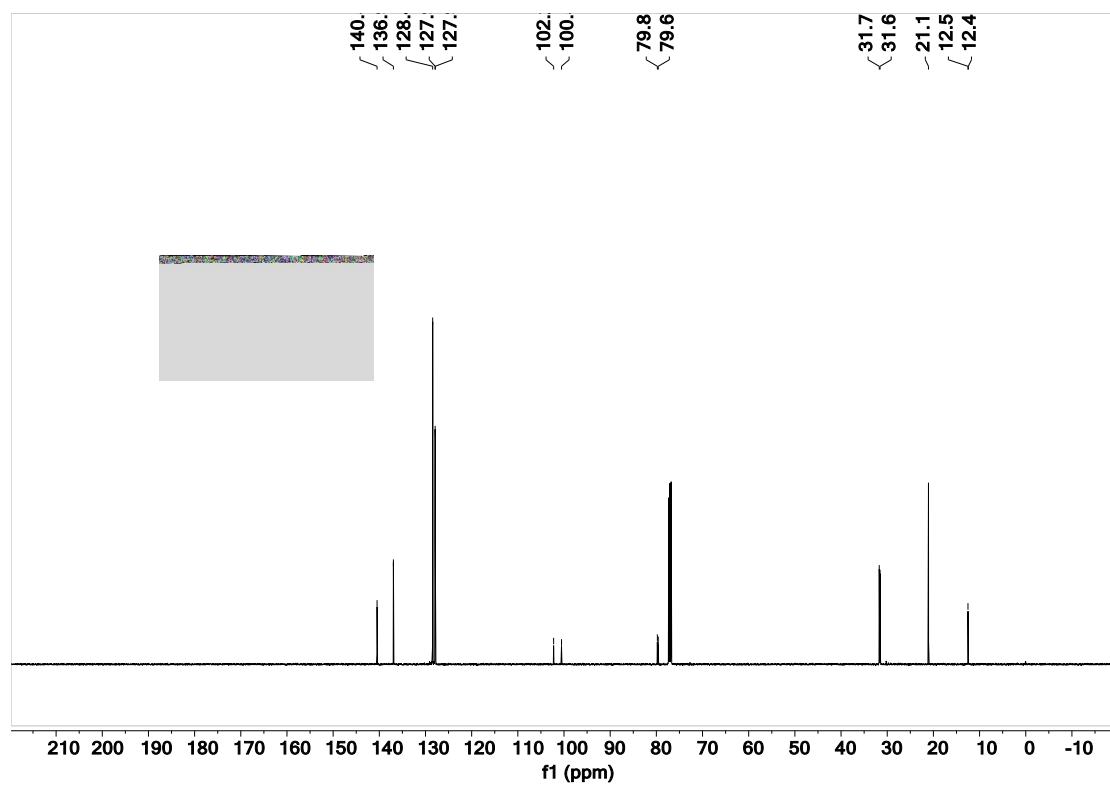
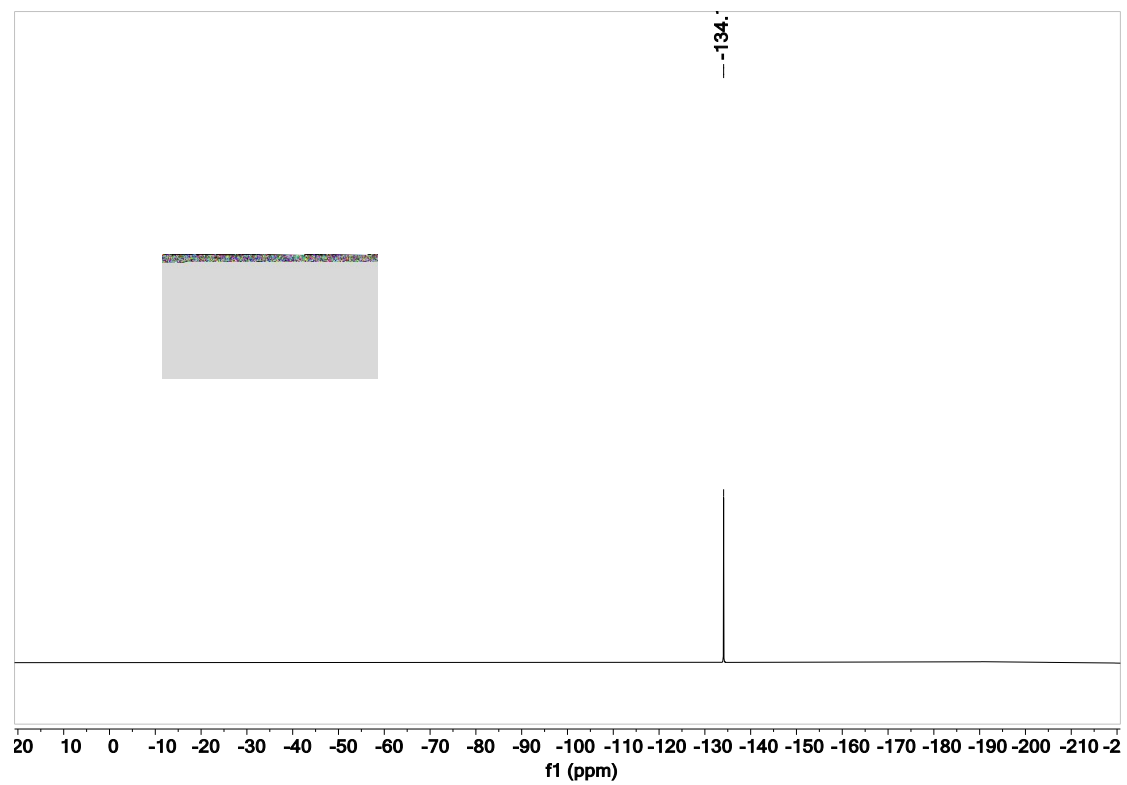
bis(4-chlorophenyl)(1-fluorocyclobutyl)methanol (4j)



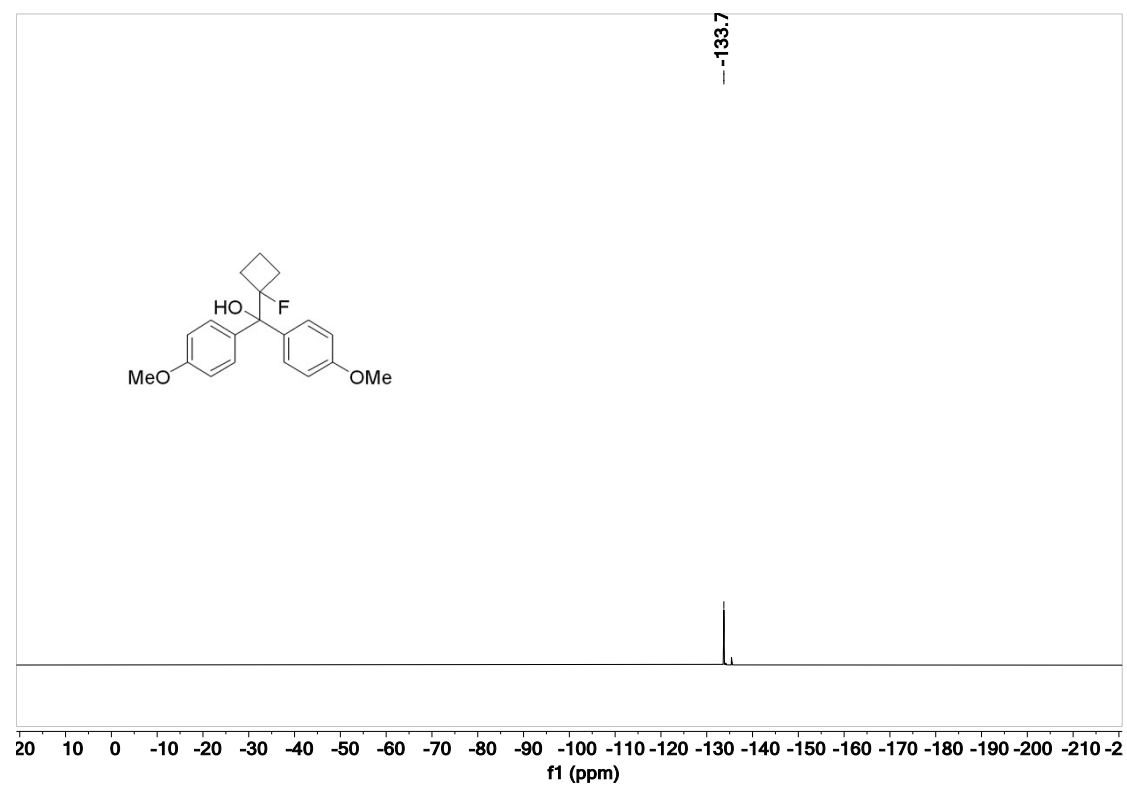
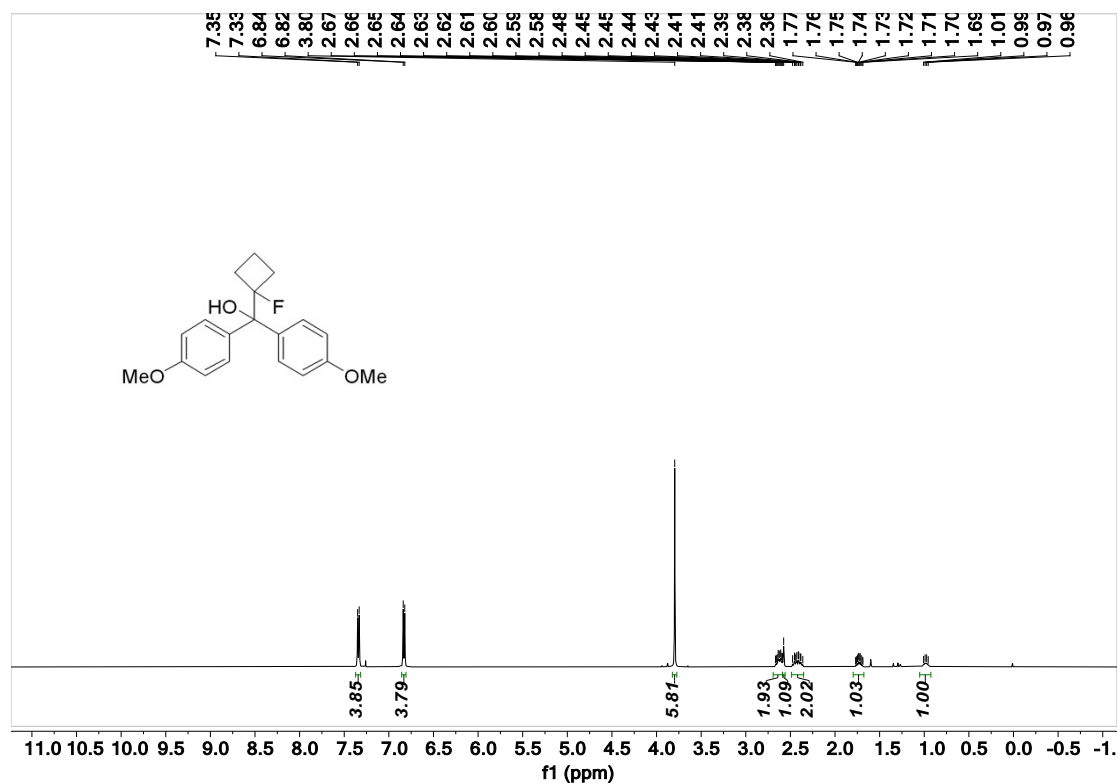


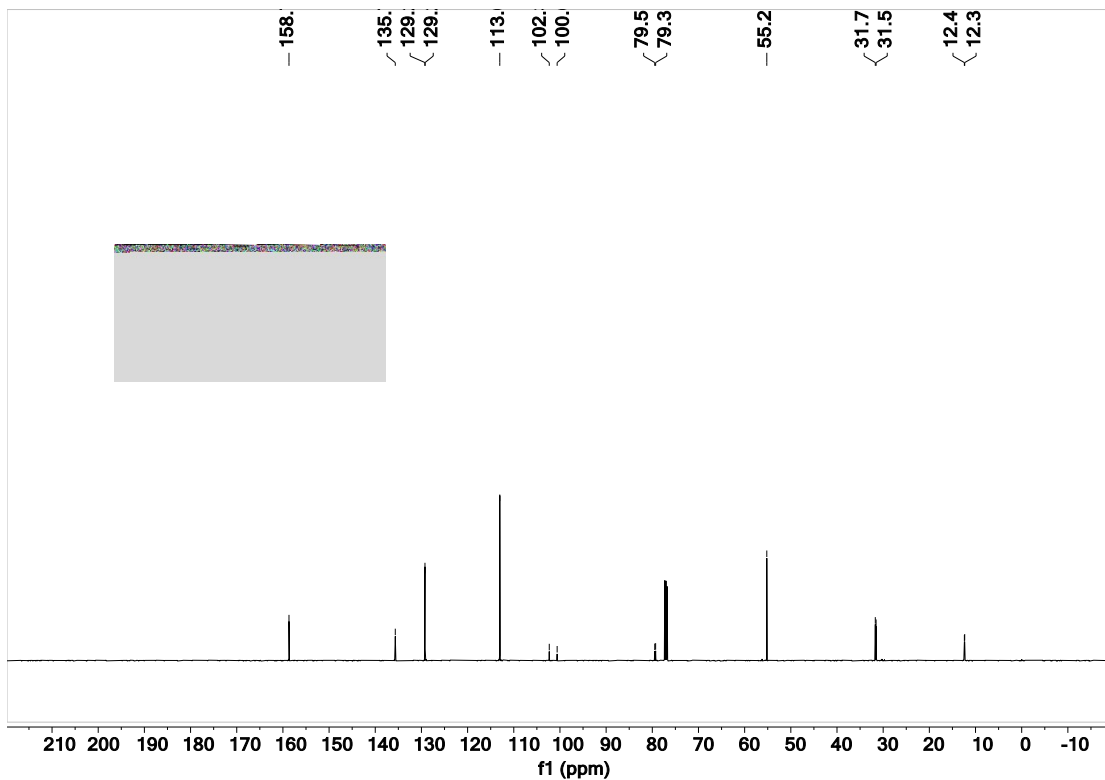
(1-fluorocyclobutyl)di-p-tolylmethanol (4k)



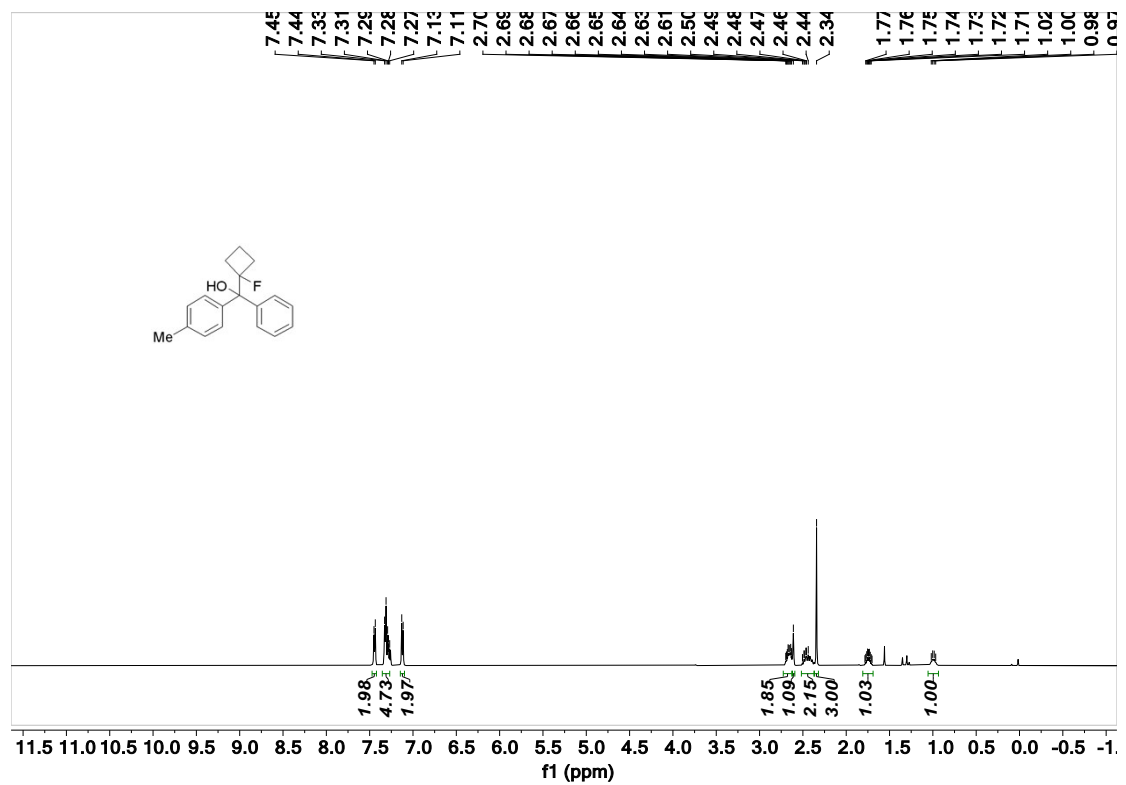


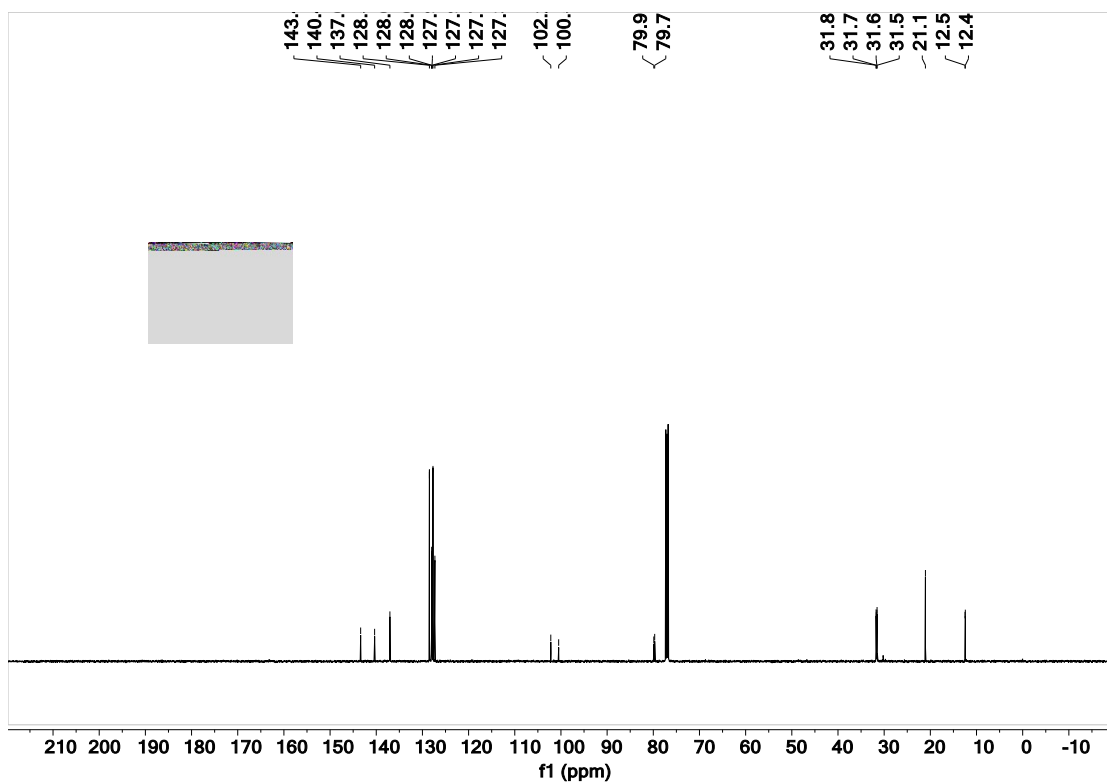
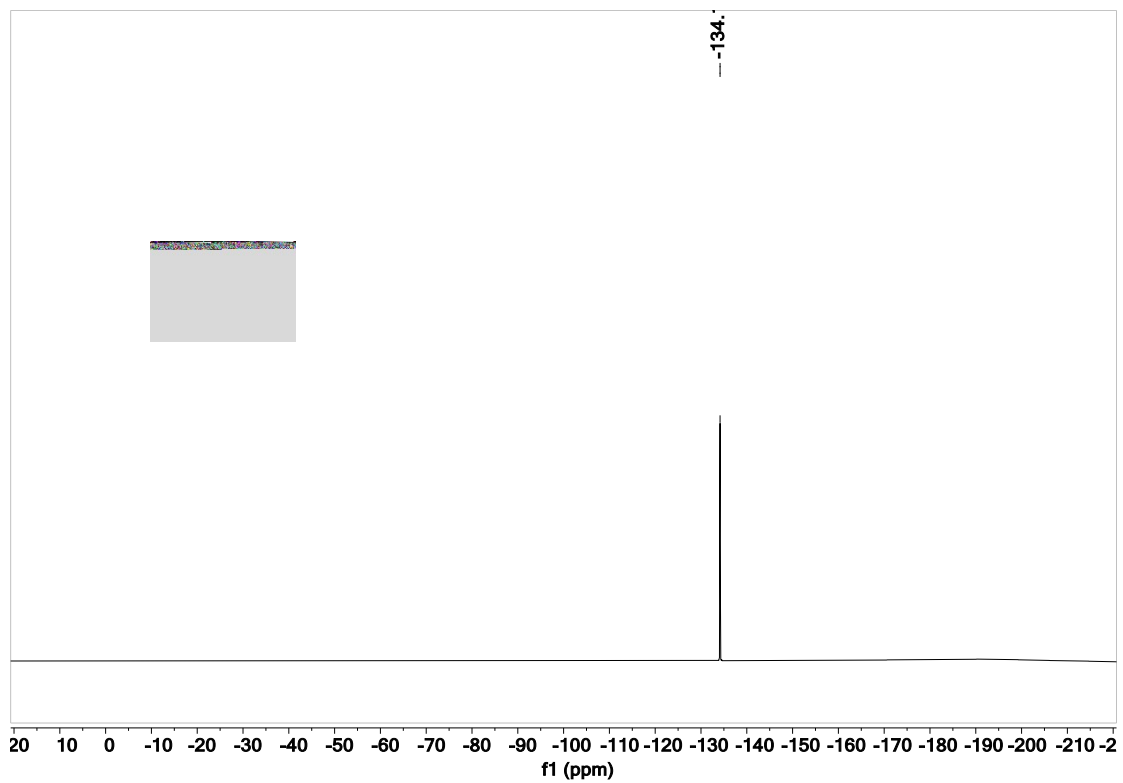
(1-fluorocyclobutyl)bis(4-methoxyphenyl)methanol (4I)



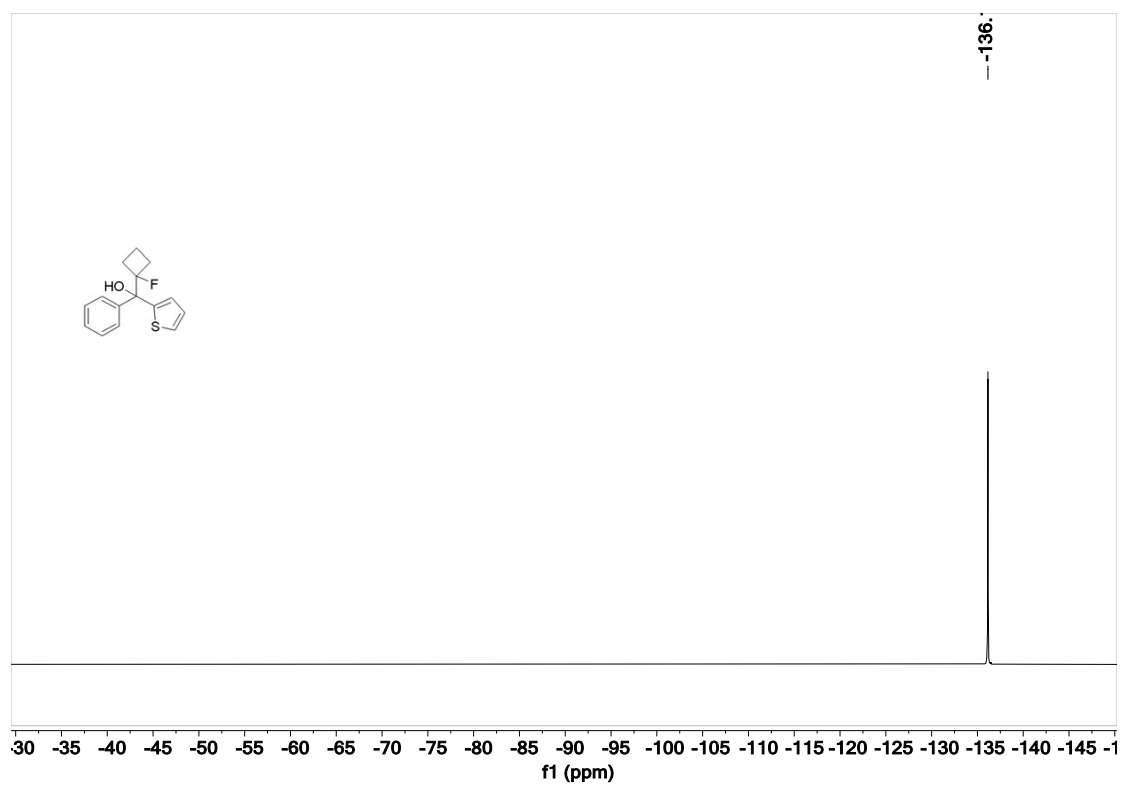
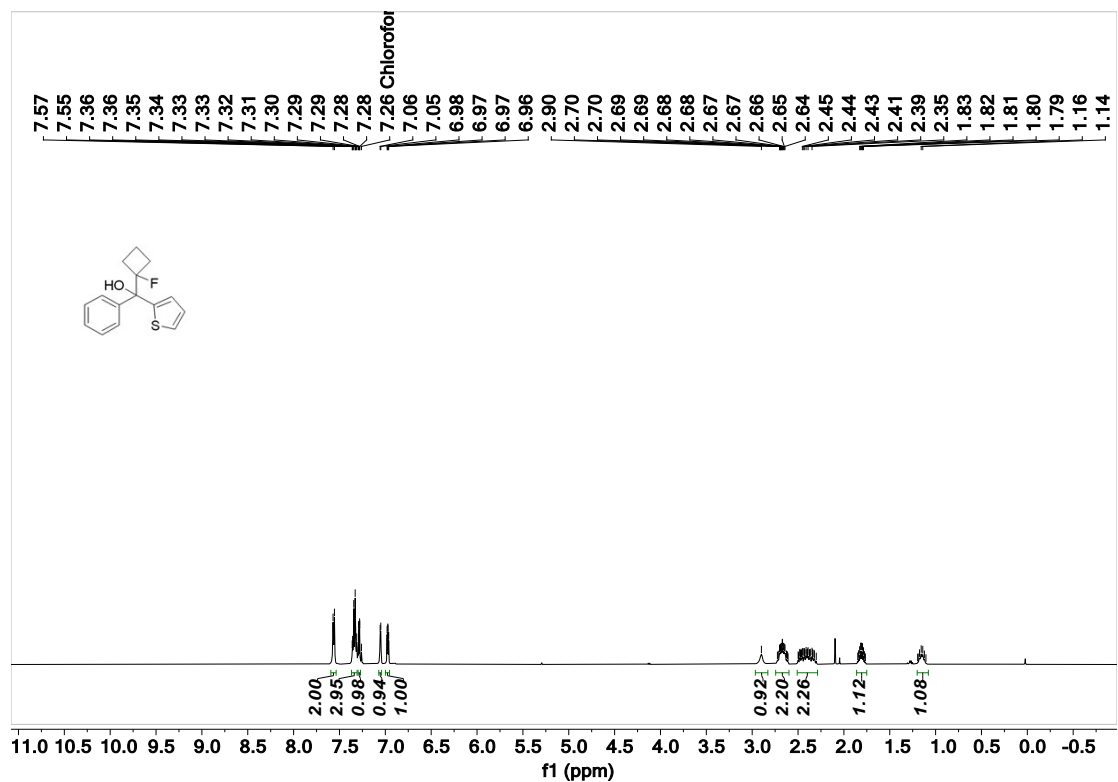


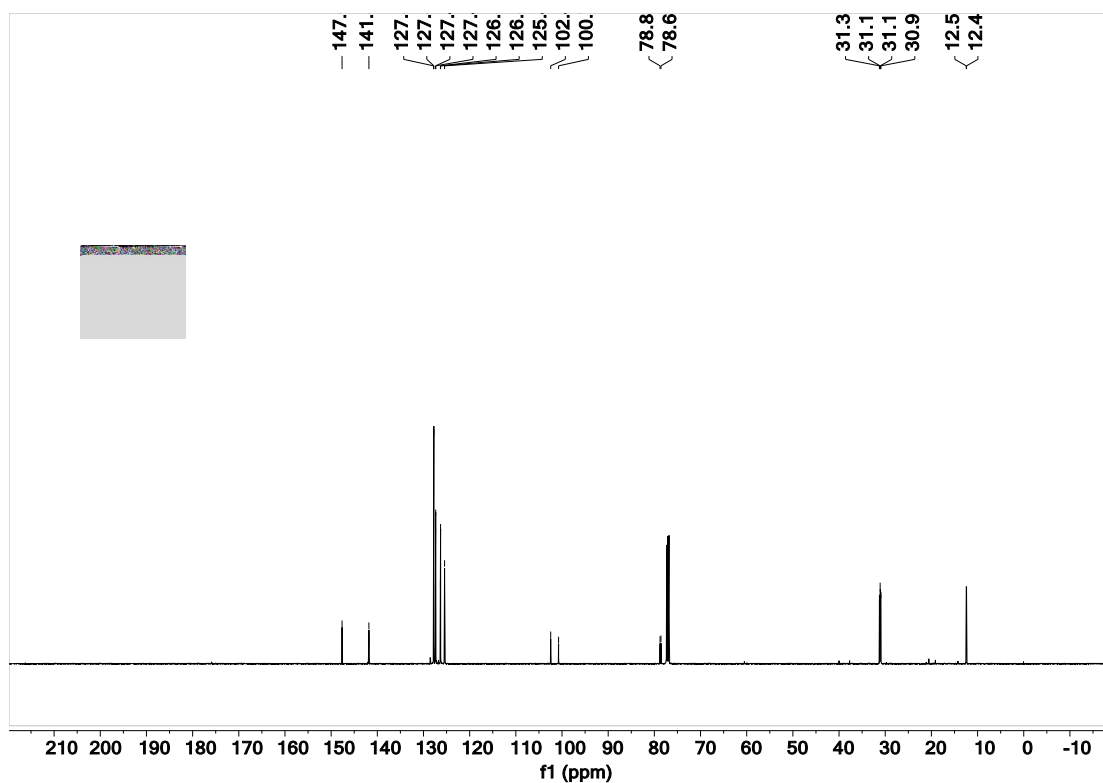
(1-fluorocyclobutyl)(phenyl)(p-tolyl)methanol (4m)



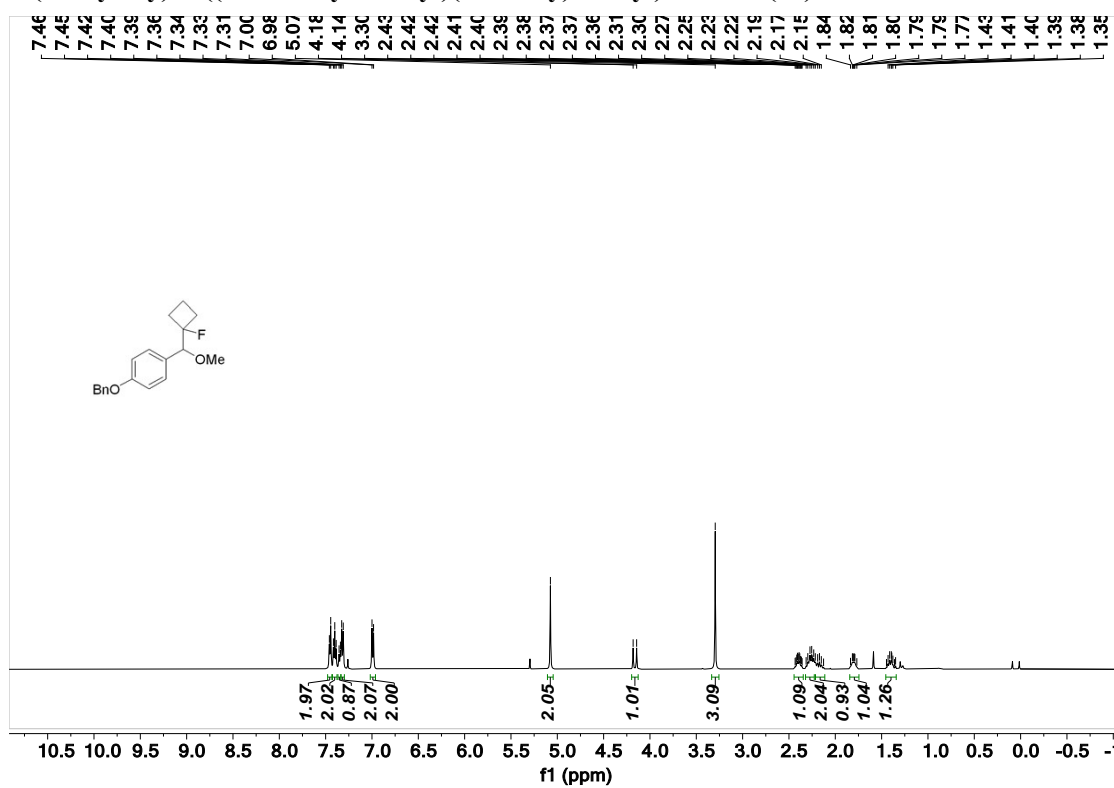


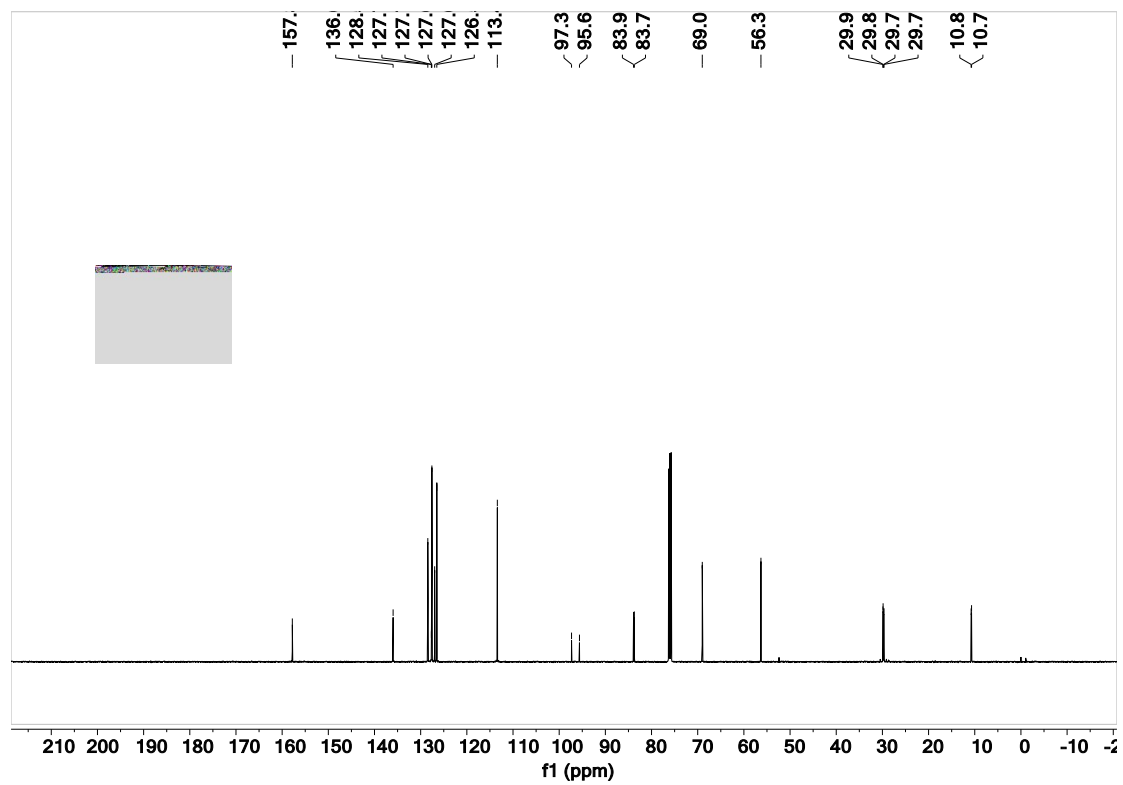
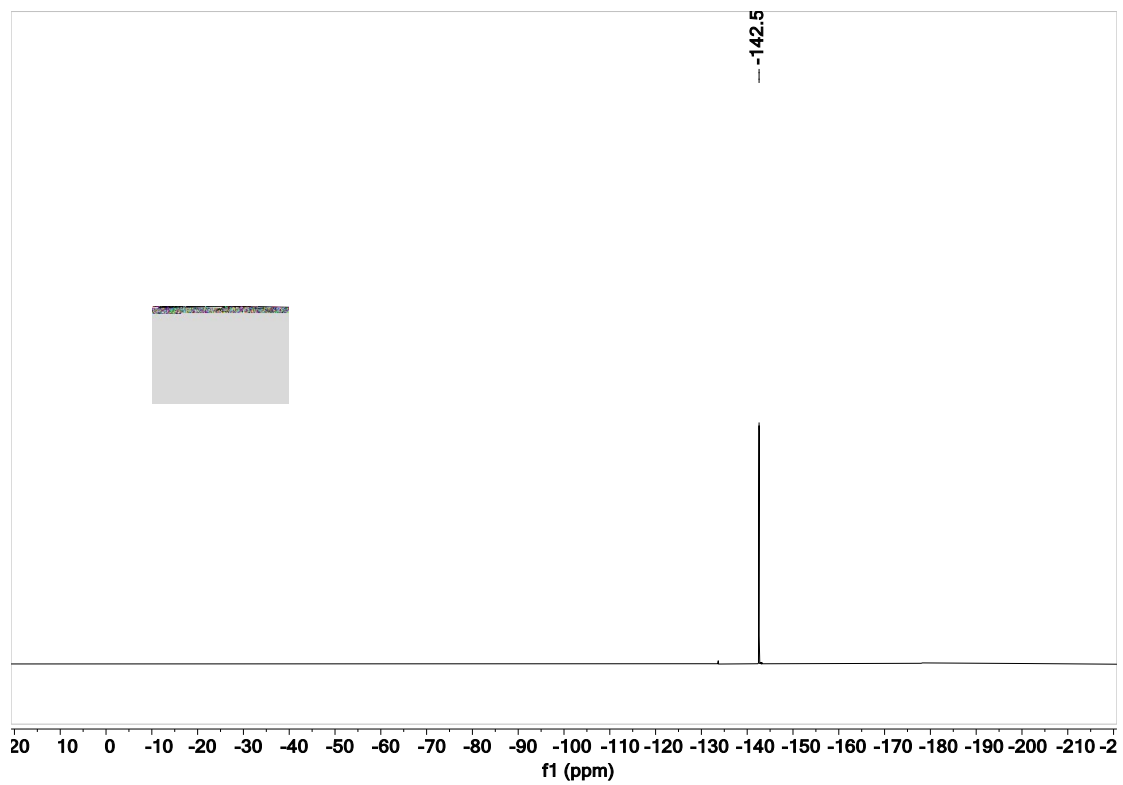
(1-fluorocyclobutyl)(phenyl)(thiophen-2-yl)methanol (4n)



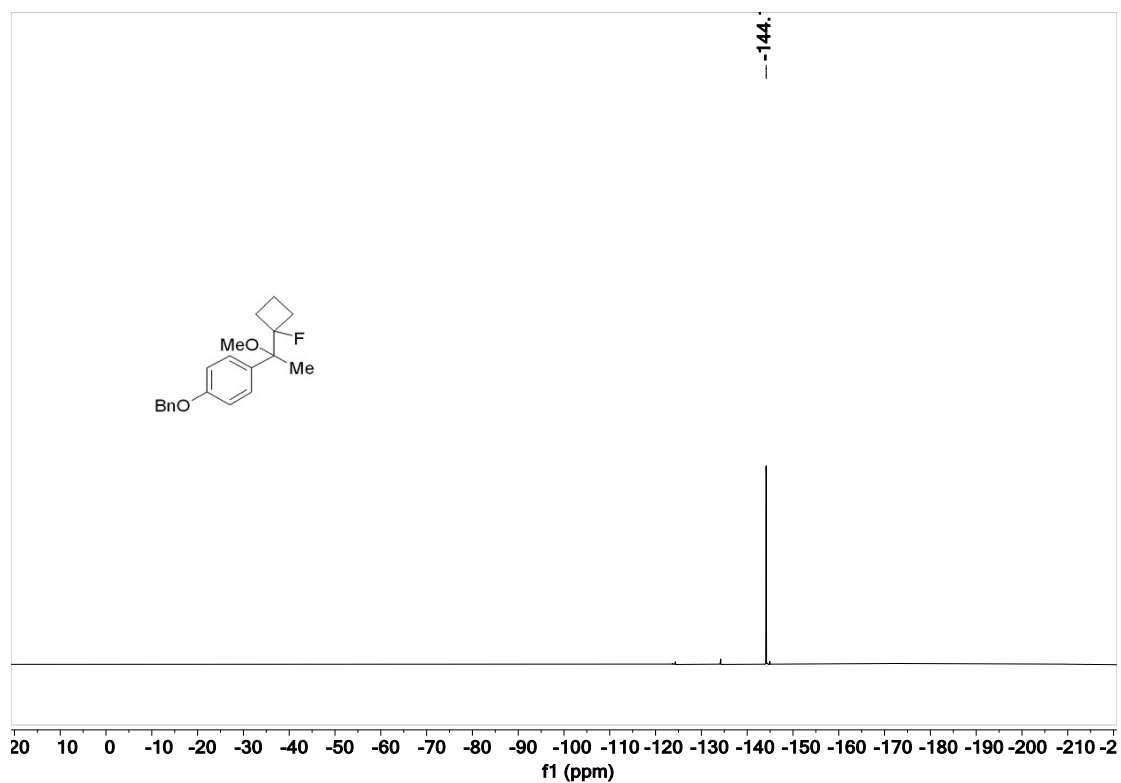
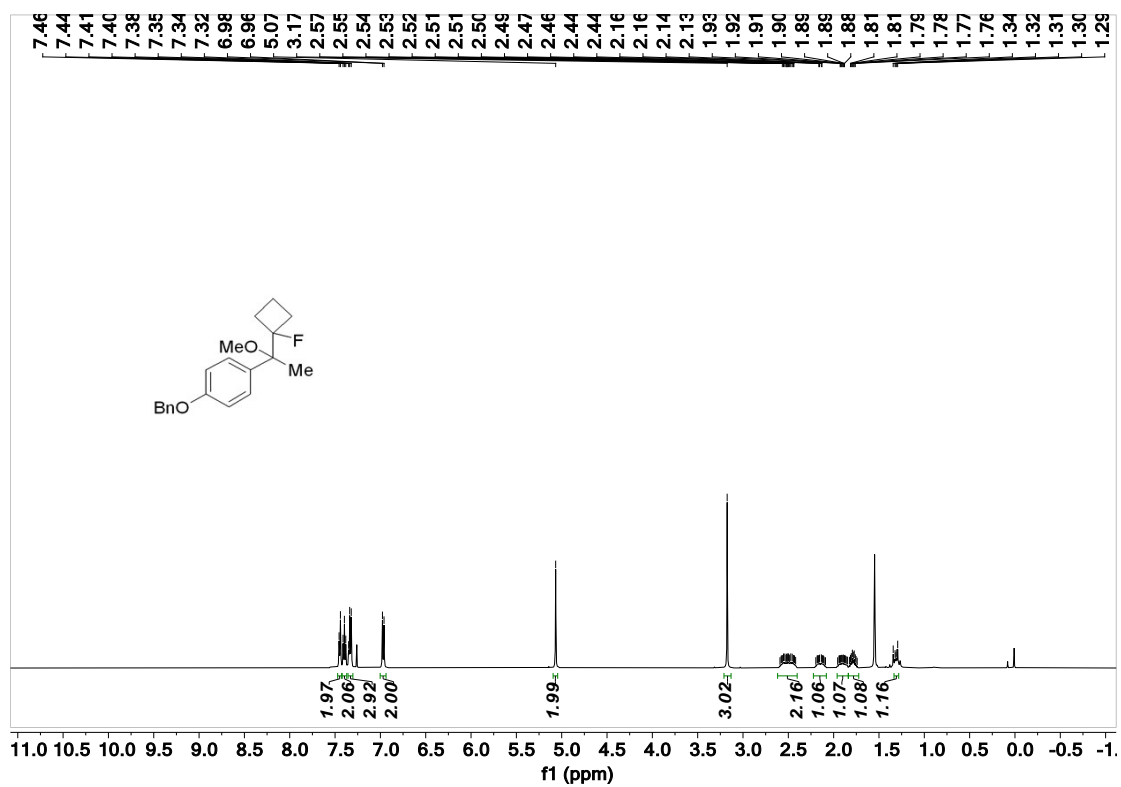


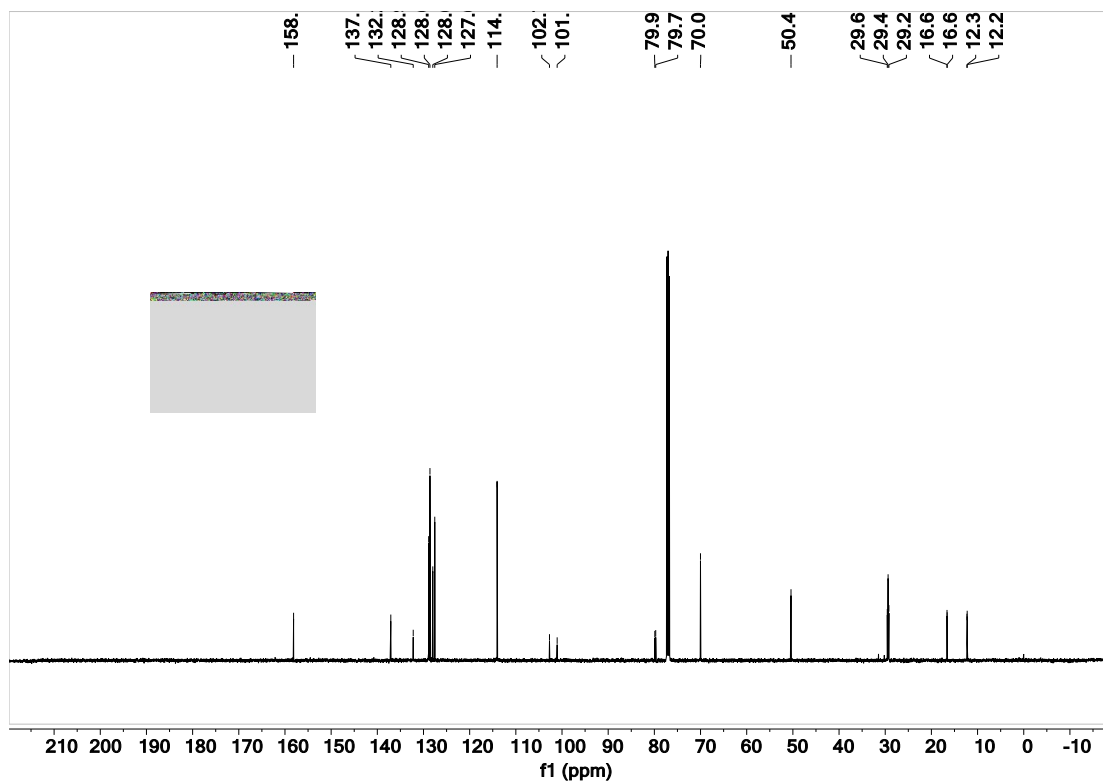
1-(benzyloxy)-4-((1-fluorocyclobutyl)(methoxy)methyl)benzene (4o)



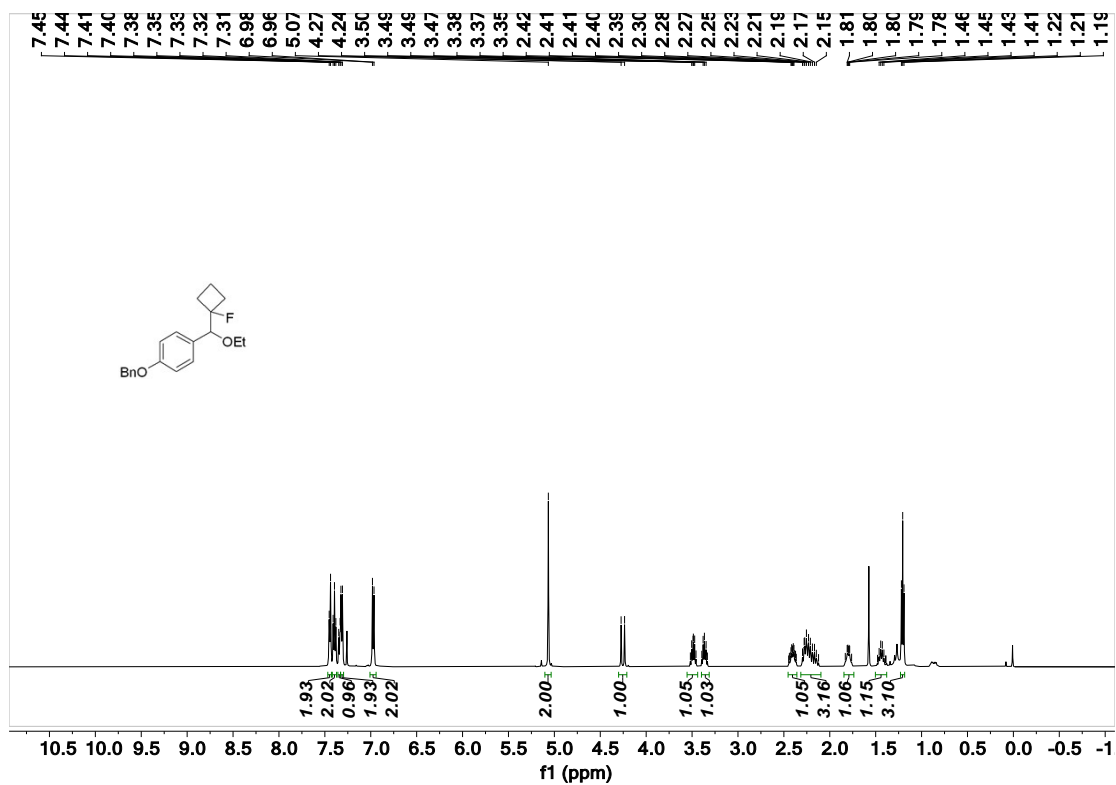


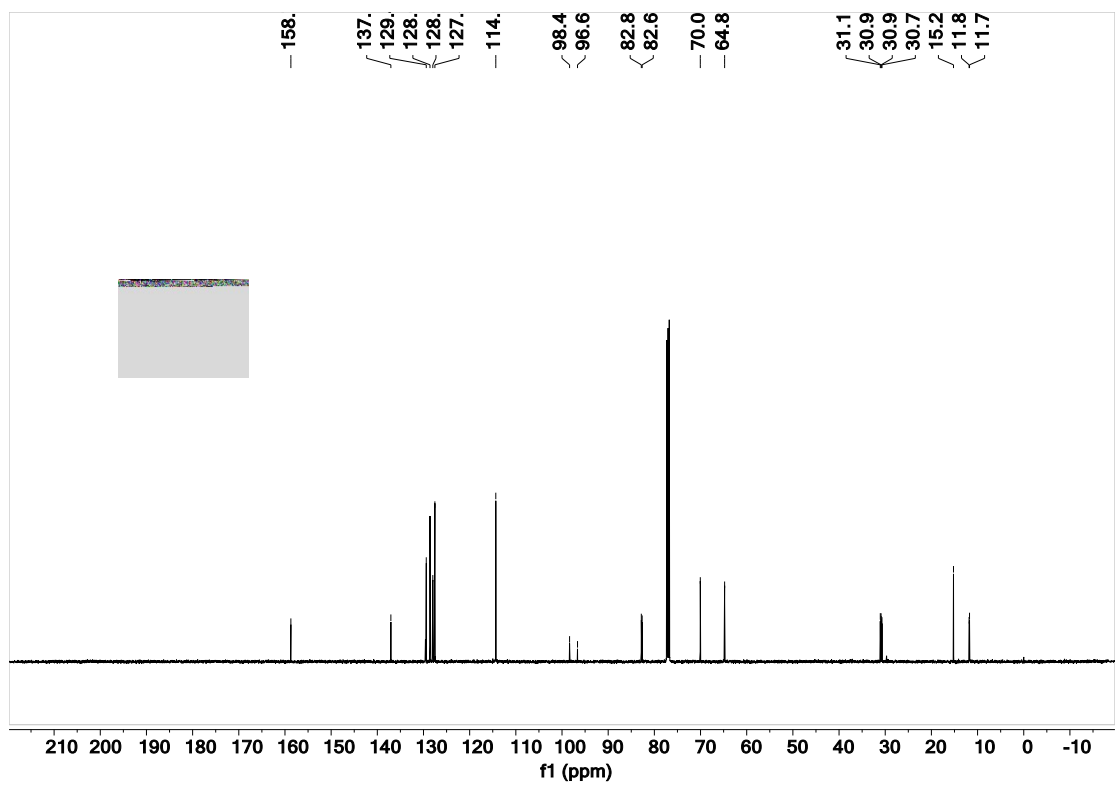
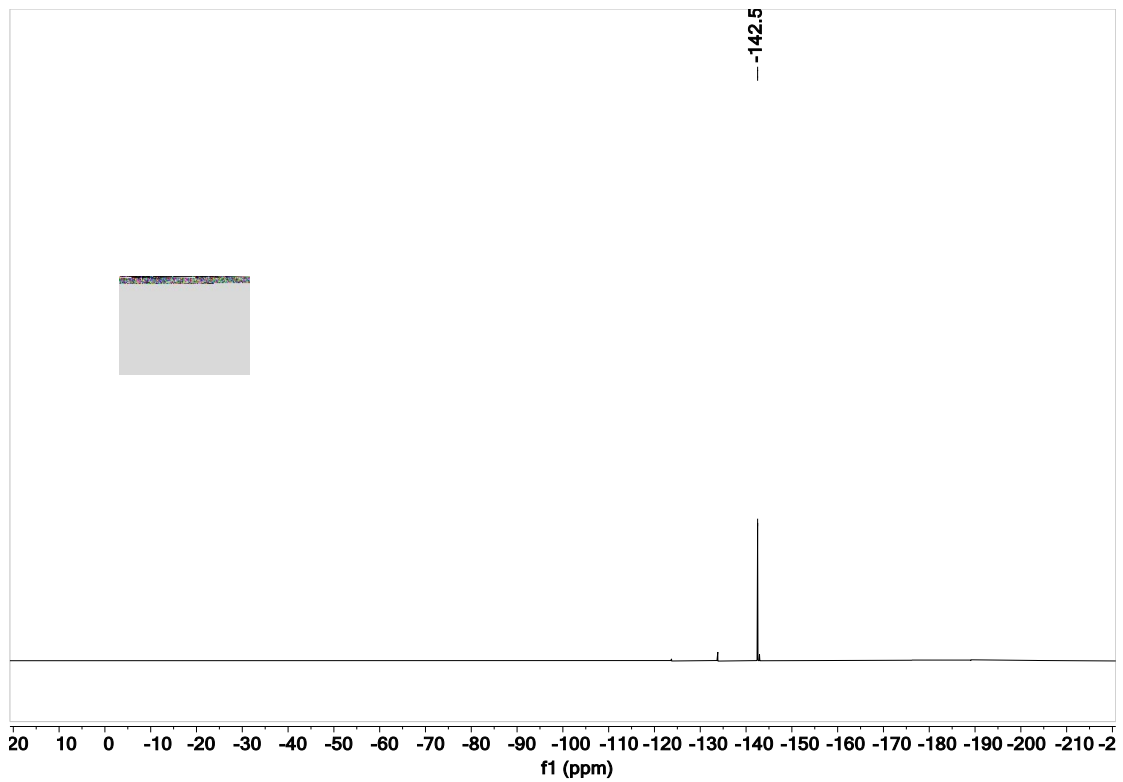
1-(benzyloxy)-4-(1-(1-fluorocyclobutyl)-1-methoxyethyl)benzene (4p)



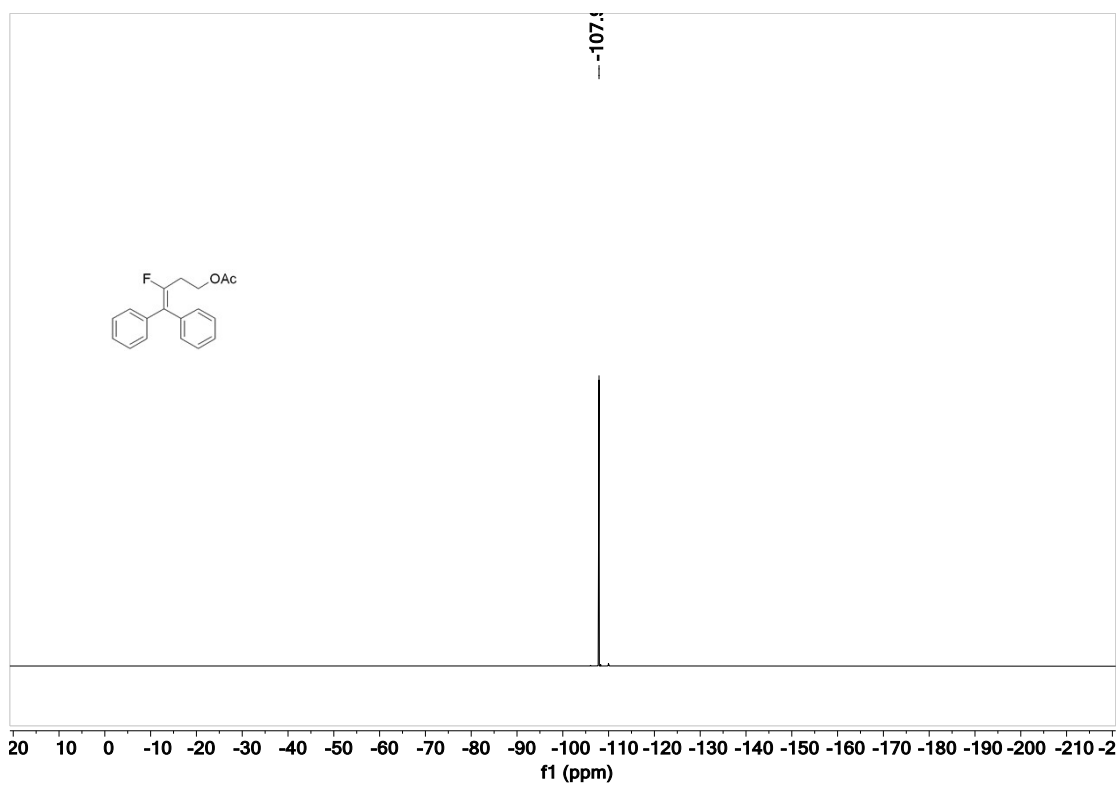
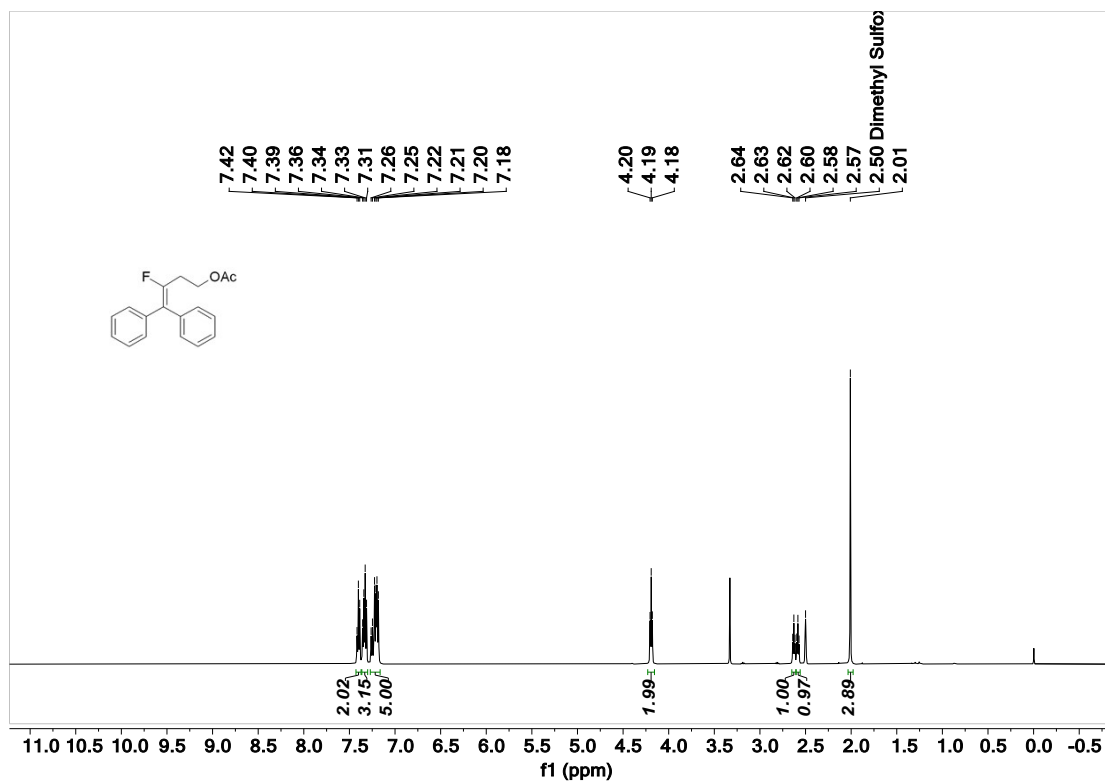


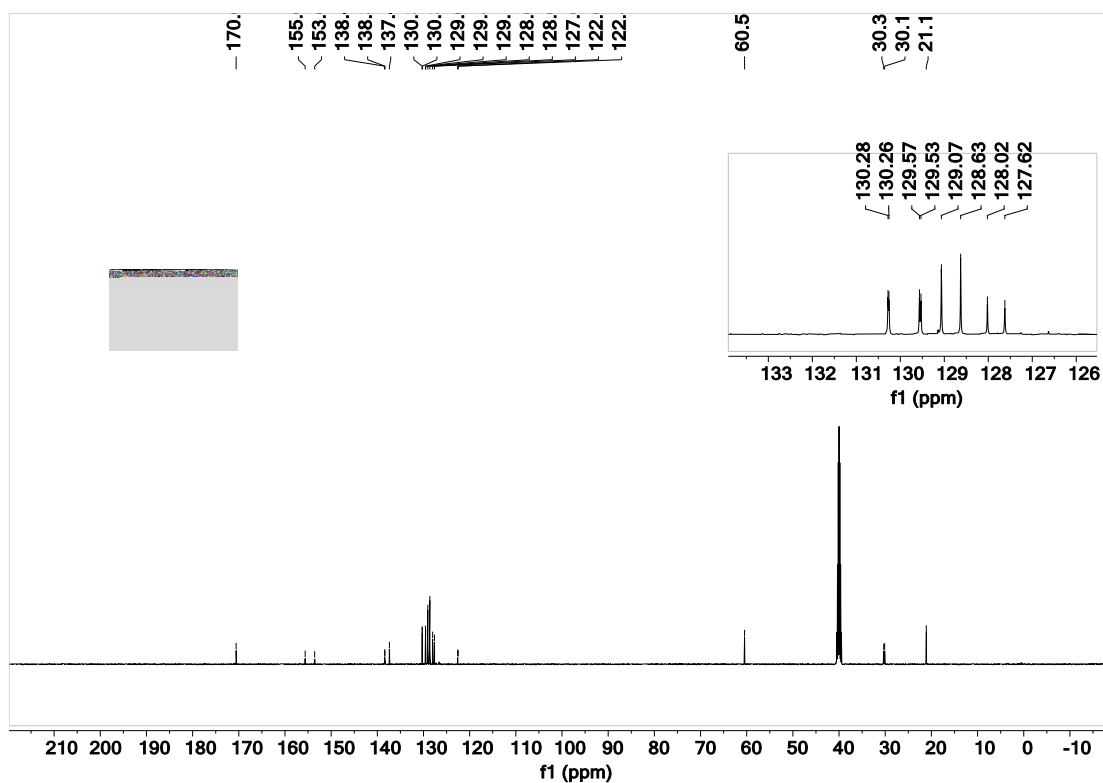
1-(benzyloxy)-4-(ethoxy(1-fluorocyclobutyl)methyl)benzene (4q)



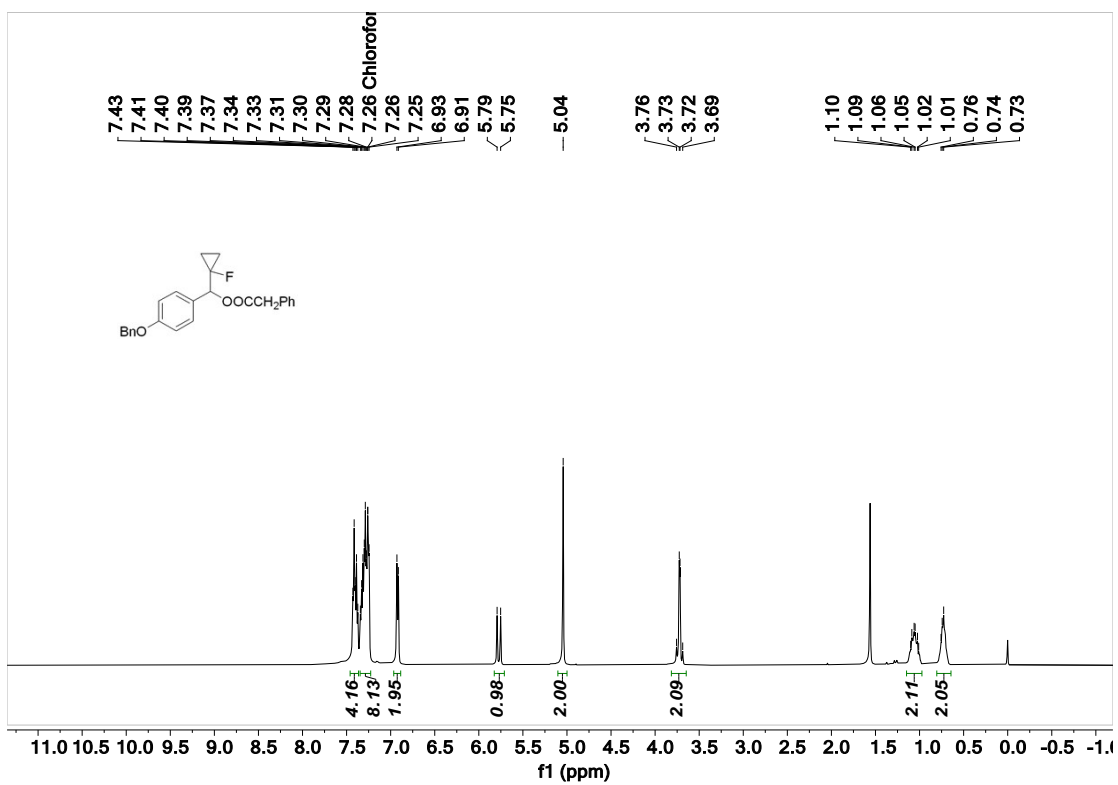


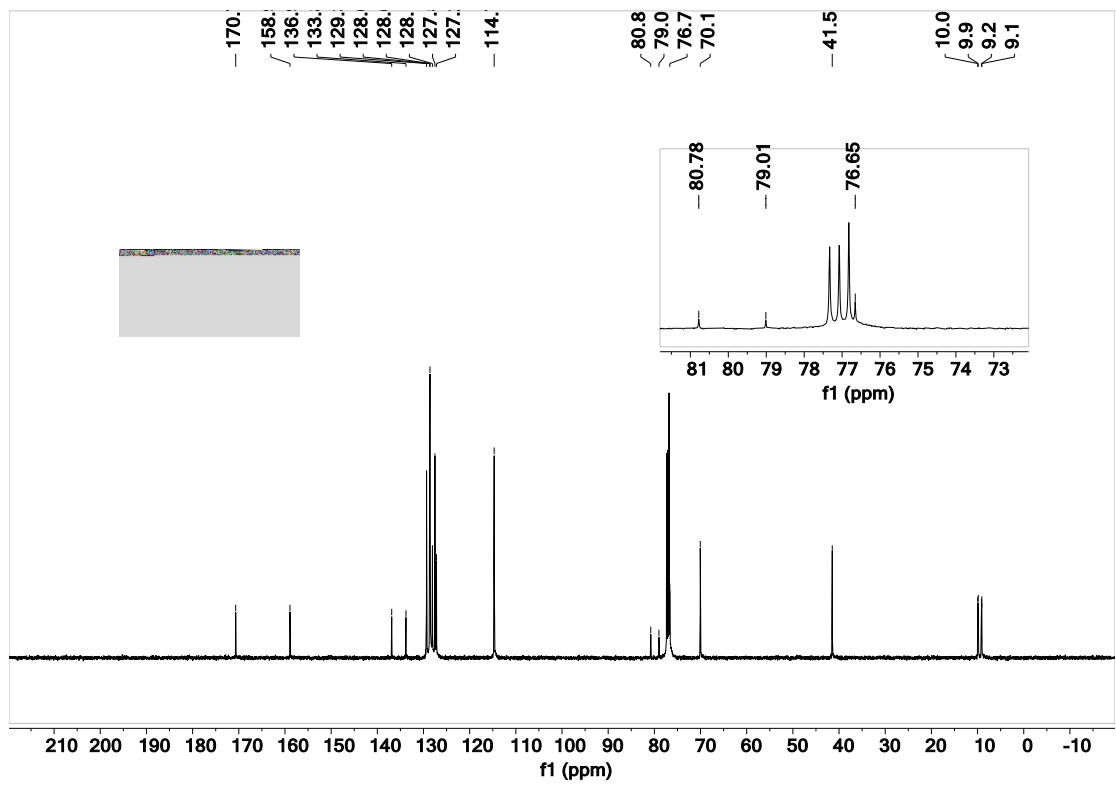
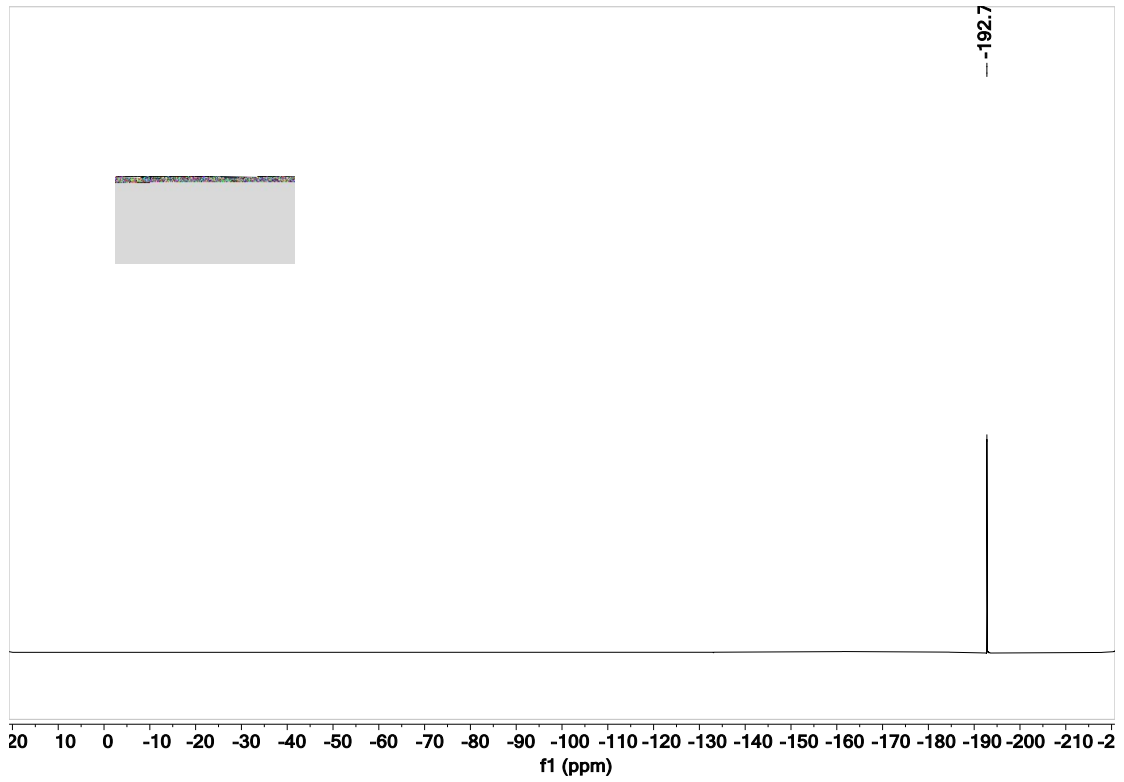
3-fluoro-4,4-diphenylbut-3-en-1-yl acetate (5)



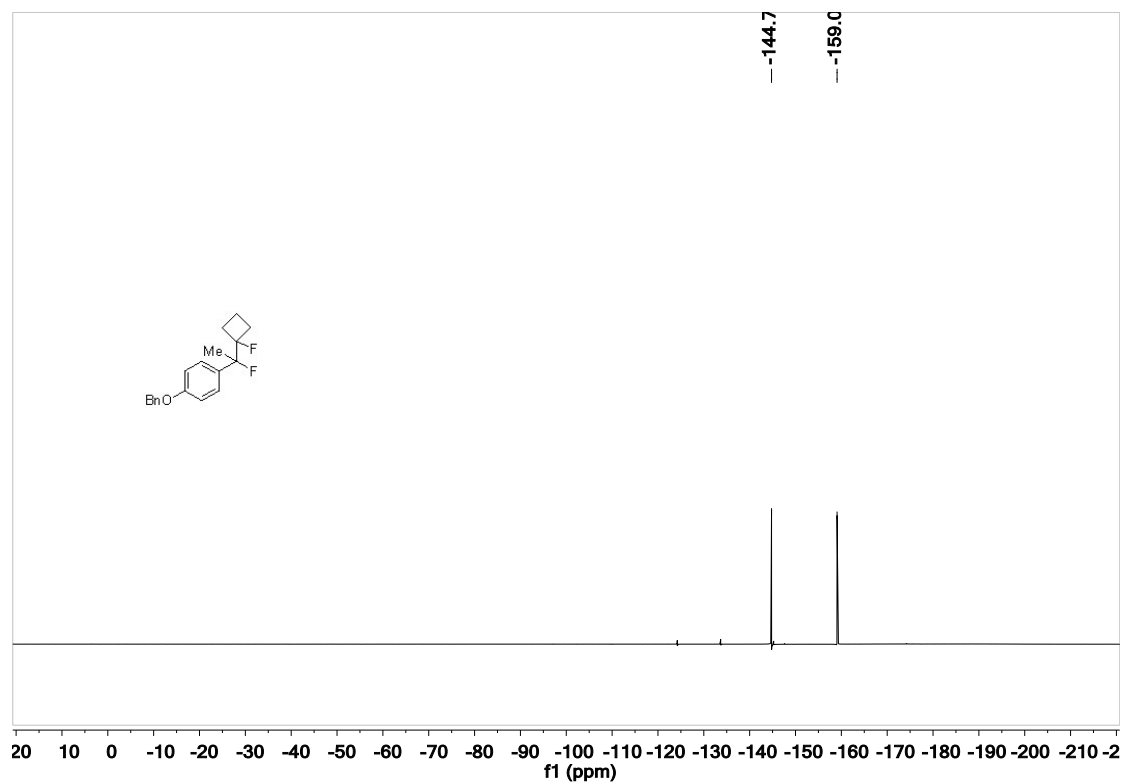
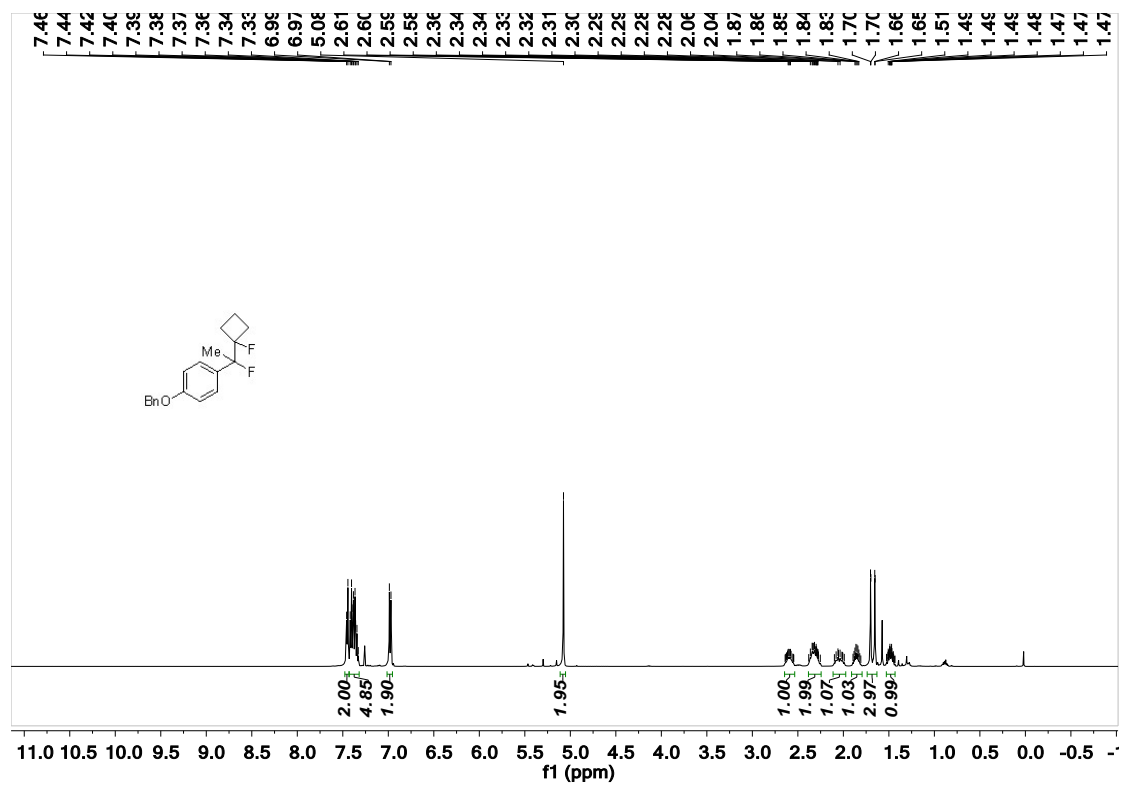


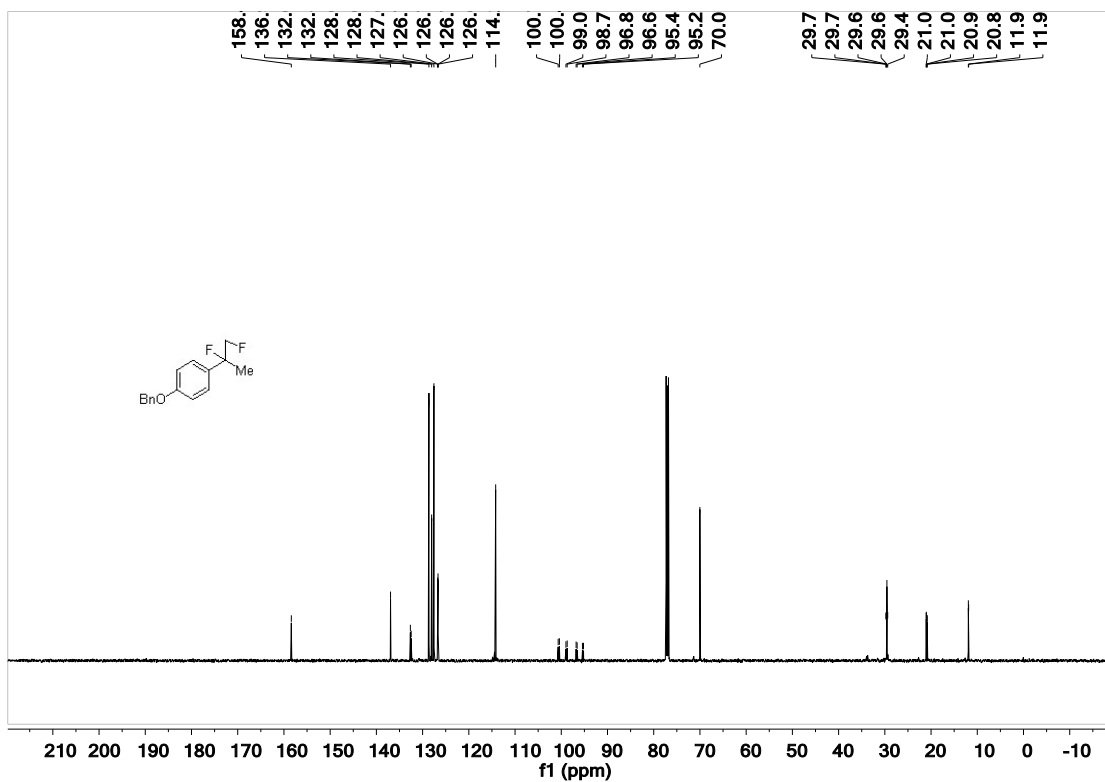
1-(benzyloxy)-4-((1-fluorocyclopropyl)((1-phenylvinyl)peroxy)methyl)benzene (6)



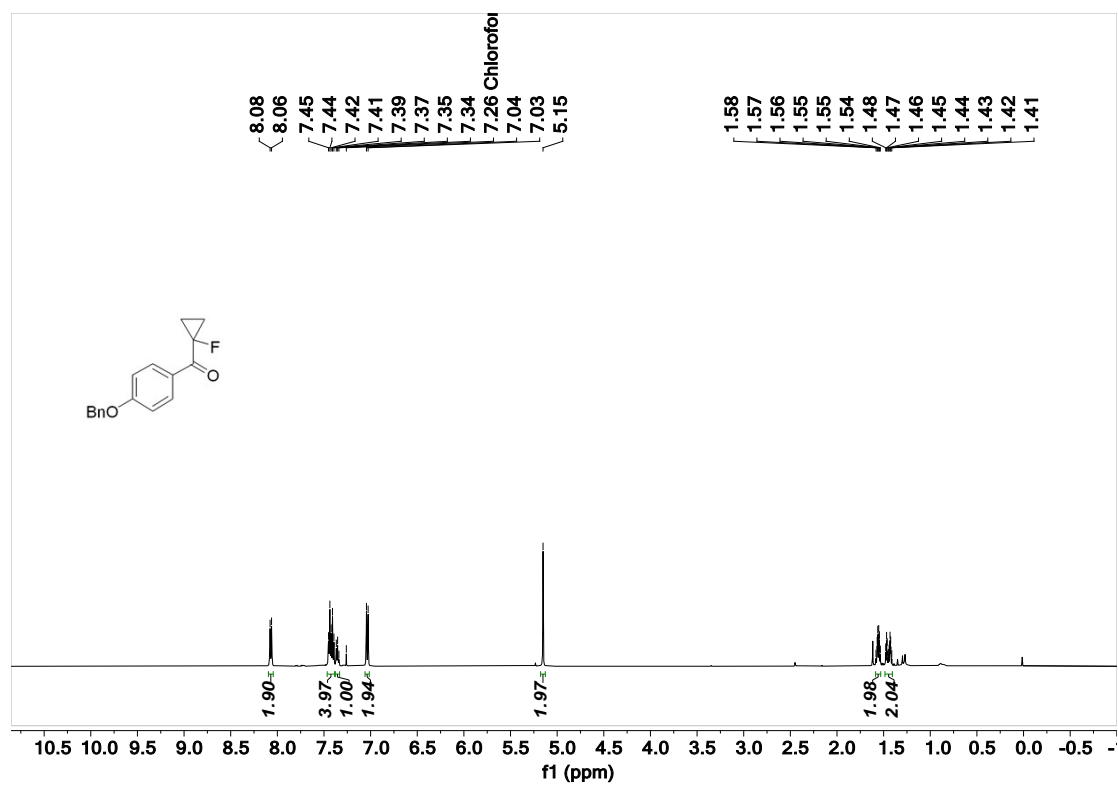


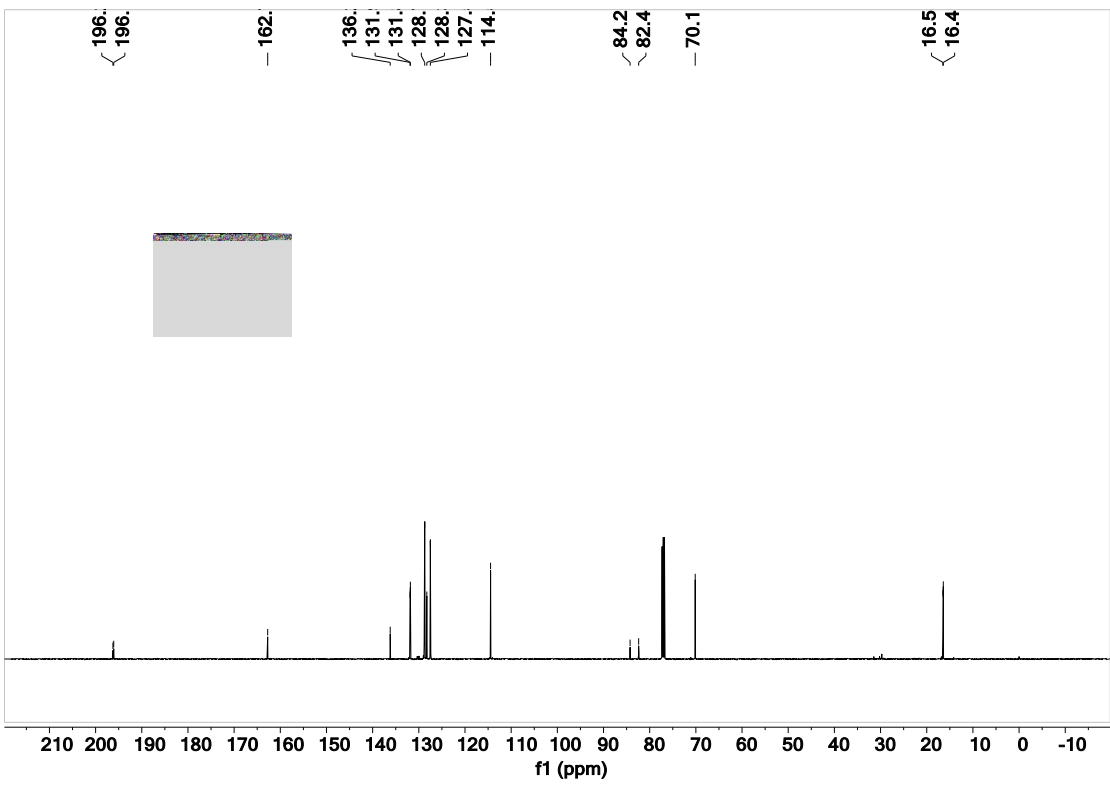
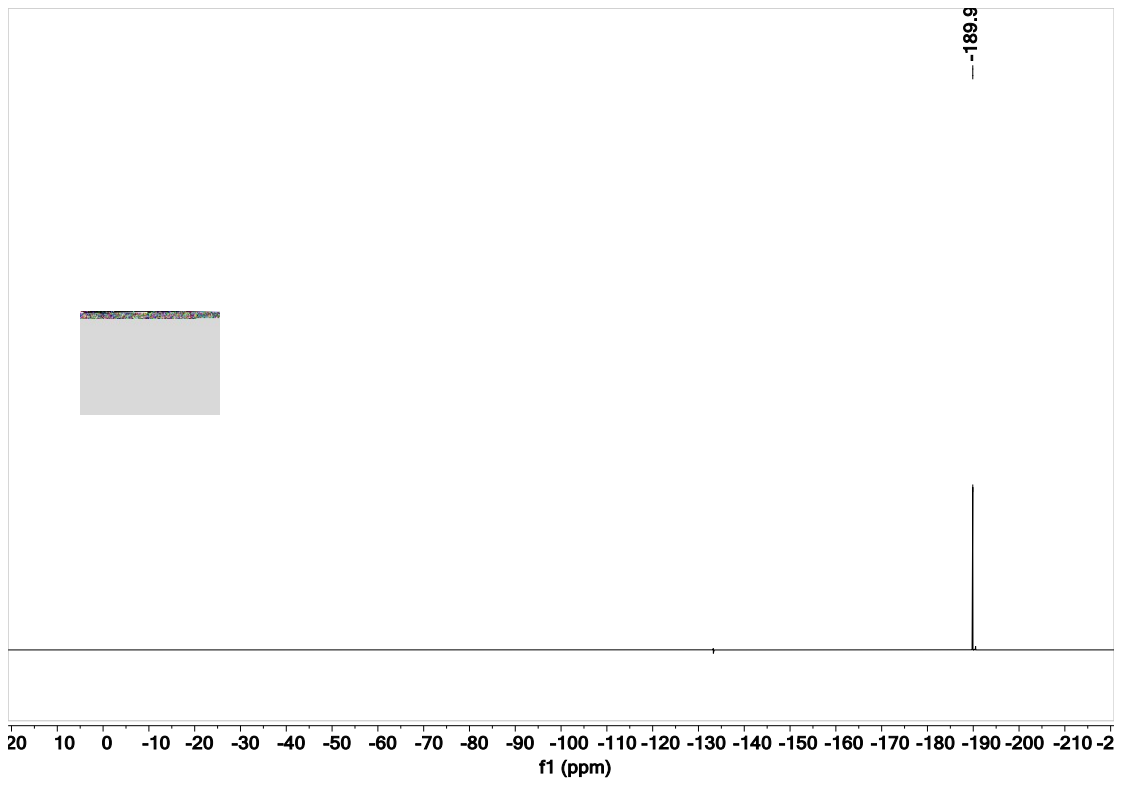
1-(benzyloxy)-4-(1-fluoro-1-(1-fluorocyclobutyl)ethyl)benzene (7)





(4-(benzyloxy)phenyl)(1-fluorocyclopropyl)methanone (8)





(4-(benzyloxy)phenyl)(1-fluorocyclobutyl)methanone (9)

