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Supporting Information

## **Deoxyfluorination of (Hetero)aryl Aldehydes Using Tetramethylammonium Fluoride and Perfluorobutane- sulfonyl Fluoride or Trifluoromethanesulfonic Anhydride**

Devin M. Ferguson, Patrick R. Melvin, and Melanie S. Sanford\*

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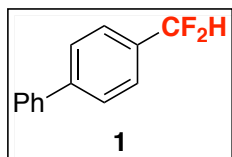
## 1. General Information

NMR spectra were obtained on a Varian MR400 (400.52 MHz for  $^1\text{H}$ , 376.87 MHz for  $^{19}\text{F}$ ), Varian VNMRS 500 (470.47 MHz for  $^{19}\text{F}$ ), Varian Inova 500 (499.91 MHz for  $^1\text{H}$ ), or a Varian VNMRS 700 (699.75 MHz for  $^1\text{H}$ , 175.97 MHz for  $^{13}\text{C}$ ) spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS), with the residual NMR solvent peak used as an internal reference.  $^{19}\text{F}$  NMR chemical shifts are reported in ppm and are referenced to the solvent lock. Abbreviations used to report the NMR data: app, apparent; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; ddd, doublet of doublets of doublets; m, multiplet.  $^{19}\text{F}$  NMR yields were obtained on a Varian MR400 spectrometer (376.87 MHz for  $^{19}\text{F}$ ) using (trifluoromethoxy)benzene ( $-58.3$  ppm) as an internal standard with a relaxation delay of 5 s. High-resolution mass spectra were recorded on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer. Melting points were obtained using a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected.

## 2. Materials and Methods

All commercial reagents were used as received unless stated otherwise. Black open-top caps (thread size: 13-425) and Teflon/silicone septa (for 13-425 open top caps) were purchased from Thermo Scientific. The solvents Et<sub>2</sub>O (Alfa Aesar), DCM (Fisher Scientific) and THF (Alfa Aesar) used in the glovebox were deaerated by sparging with N<sub>2</sub> and were dried using an Innovative Technology, Inc. (now rebranded to Inert) solvent purification system. EtOAc used in the glovebox was purchased from Fisher Scientific and distilled from CaH<sub>2</sub>. 5-bromo-2-pyridinecarboxaldehyde and 4-isoquinolinecarboxaldehyde were purchased from Alfa Aesar. 3-methoxy-pyridine-2-carbaldehyde was purchased from TCI America. Dibenzofuran-4-carboxaldehyde was purchased from Chem-Impex International, Inc. 4-cyanobenzaldehyde, *N*-methyl-2-pyrrolidone (NMP, extra dry over molecular sieves in an AcroSeal™ bottle), DMSO (anhydrous in an AcroSeal™ bottle, stored over activated 3Å molecular sieves) were purchased from Acros Organics. 1-naphthaldehyde was purchased from AK Scientific, Inc. 2-phenylbenzaldehyde was purchased from Ark Pharm. Perfluorobutanesulfonyl fluoride (stored in a nitrogen-filled glovebox), trifluoromethanesulfonic anhydride (stored in the freezer of a nitrogen-filled glovebox at -35 °C), and 4-phenylbenzaldehyde were purchased from Oakwood Chemical. Tetramethylammonium fluoride (anhydrous, 97%, stored in a nitrogen-filled glovebox), 4-bromobenzaldehyde, 4-nitrobenzaldehyde, 4-(2-pyridyl)benzaldehyde, 4-quinolinecarboxaldehyde (recrystallized from EtOAc/hexanes), and anhydrous *N,N*-DMF in a Sure/Seal™ bottle were purchased from Aldrich. CDCl<sub>3</sub> was purchased from Cambridge Isotope Laboratories, Inc. All glassware used in the glovebox was dried in an oven at 150 °C for at least 3 h and cooled under an inert atmosphere. DCM (Fisher Scientific), Et<sub>2</sub>O (EMD Millipore), and pentane (Fisher Scientific) used on the bench top were used as received. Silica (SiliaFlash F60) used on the bench top was purchased from SiliCycle, Inc. and used as received.

## 3. Characterization of Products Isolated from (Hetero)aryl Aldehydes using PBSF



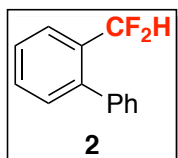
This reaction was performed with 4-phenylbenzaldehyde according to the general procedure using PBSF. Product **1** was obtained as a white solid (15 mg, 37% yield, *R<sub>f</sub>* = 0.26 in 100% pentane, mp = 76-77 °C). The NMR spectra are consistent with those reported in the literature.<sup>1</sup>

<sup>1</sup>H NMR (499.91 MHz, CDCl<sub>3</sub>): δ 7.68 (app d, *J* = 8.0 Hz, 2H), 7.61-7.58 (m, 4H), 7.48-7.45 (m, 2H), 7.41-7.37 (m, 1H), 6.70 (t, *J* = 56.4 Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -110.42 (d,  $J$  = 56.4 Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.85 (t,  $J$  = 2.0 Hz), 140.33, 133.35 (t,  $J$  = 22.4 Hz), 129.06, 128.04, 127.58, 127.39, 126.17 (t,  $J$  = 6.0 Hz), 114.88 (t,  $J$  = 238.5 Hz).

HRMS calcd. for  $\text{C}_{13}\text{H}_{10}\text{F}_2$ : 204.0751; Found: 204.0755



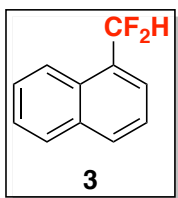
This reaction was performed with 2-phenylbenzaldehyde according to the general procedure using PBSF. Product **2** was obtained as a colorless oil (20 mg, 49% yield,  $R_f$  = 0.39 in 100% pentane). The NMR spectra are consistent with those reported in the literature.<sup>2</sup>

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (app d,  $J$  = 7.3 Hz, 1H), 7.54-7.35 (multiple peaks, 8H), 6.54 (t,  $J$  = 55.0 Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -107.44 (d,  $J$  = 55.0 Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  141.53 (t,  $J$  = 6.6 Hz), 138.80, 131.89 (t,  $J$  = 22.1 Hz), 130.59 (t,  $J$  = 2.0 Hz), 130.35, 129.59, 128.55, 128.01, 127.99, 125.74 (t,  $J$  = 5.2 Hz), 113.27 (t,  $J$  = 236.0).

HRMS calcd. for  $\text{C}_{13}\text{H}_{10}\text{F}_2$ : 204.0751; Found: 204.0758



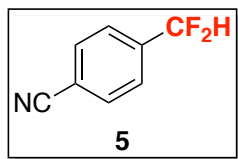
This reaction was performed with 1-naphthaldehyde according to the general procedure using PBSF. 1-naphthaldehyde is an oil and the order of addition of reagents changed to accommodate this: 1-naphthaldehyde was added to the vial first, followed by THF, TMAF, and finally PBSF. Product **3** was obtained as a colorless oil (13 mg, 37% yield,  $R_f$  = 0.31 in 100% pentane). The NMR spectra are consistent with those reported in the literature.<sup>1</sup>

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18 (d,  $J = 8.3$  Hz, 1H), 7.97 (d,  $J = 8.3$  Hz, 1H), 7.92 (app d,  $J = 8.0$  Hz, 1H), 7.70 (app d,  $J = 7.0$  Hz, 1H), 7.62-7.50 (multiple peaks, 3H), 7.14 (t,  $J = 55.2$  Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -110.95 (d,  $J = 55.2$  Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  133.93, 131.64 (t,  $J = 1.7$  Hz), 129.88 (t,  $J = 2.6$  Hz), 129.71 (t,  $J = 20.8$  Hz), 128.92, 127.31, 126.52, 124.94 (t,  $J = 8.7$  Hz), 124.82, 123.71 (t,  $J = 1.3$  Hz), 115.55 (t,  $J = 238.4$  Hz).

HRMS calcd. for  $\text{C}_{11}\text{H}_8\text{F}_2$ : 178.0594; Found: 178.0596



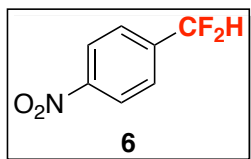
This reaction was performed with 4-cyanobenzaldehyde according to the general procedure using PBSF. Product **5** was obtained as a colorless oil (26 mg, 85% yield,  $R_f = 0.54$  in 20%  $\text{Et}_2\text{O}$  / 80% pentane). The NMR spectra are consistent with those reported in the literature.<sup>1</sup>

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77 (d,  $J = 8.0$  Hz, 2H), 7.64 (d,  $J = 8.0$  Hz, 2H), 6.69 (t,  $J = 55.8$  Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -113.19 (d,  $J = 55.8$  Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.71 (t,  $J = 22.8$  Hz), 132.74, 126.55 (t,  $J = 6.1$  Hz), 118.02, 114.97 (t,  $J = 2.1$  Hz), 113.45 (t,  $J = 240.7$ ).

HRMS calcd. for  $\text{C}_8\text{H}_5\text{F}_2\text{N}$ : 153.0390; Found: 153.0394



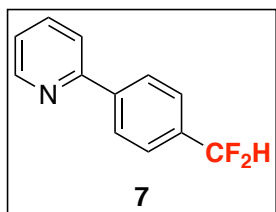
This reaction was performed with 4-nitrobenzaldehyde according to the general procedure using PBSF. Product **6** was obtained as a yellow oil and was pure after filtration through a silica plug using  $\text{Et}_2\text{O}$  (33 mg, 95% yield). The yield reported is an average of two independent runs (95% and 83%). The NMR spectra are consistent with those reported in the literature.<sup>1</sup>

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.33 (d,  $J = 8.2$  Hz, 2H), 7.72 (d,  $J = 8.2$  Hz, 2H), 6.74 (t,  $J = 55.8$  Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -113.00 (d,  $J$  = 55.8 Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.55, 140.34 (t,  $J$  = 22.9 Hz), 126.99 (t,  $J$  = 6.0 Hz), 124.15, 113.31 (t,  $J$  = 241.1 Hz).

HRMS calcd. for  $\text{C}_7\text{H}_5\text{F}_2\text{NO}_2$ : 173.0288; Found: 173.0290



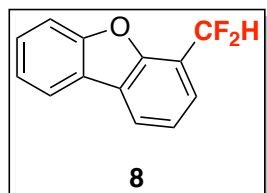
This reaction was performed with 4-(2-pyridyl)benzaldehyde according to the general procedure using PBSF. Product **7** was obtained as a white solid (21 mg, 51% yield,  $R_f$  = 0.48 in 30%  $\text{Et}_2\text{O}$  / 70% pentane, mp = 39-40  $^\circ\text{C}$ ). The NMR spectra are consistent with those reported in the literature.<sup>3</sup>

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.73-8.72 (m, 1H), 8.09 (d,  $J$  = 8.1 Hz, 2H), 7.81-7.75 (multiple peaks, 2H), 7.62 (d,  $J$  = 8.1 Hz, 2H), 7.28 (app ddd,  $J$  = 6.7, 4.8, 1.5 Hz, 1H), 6.71 (t,  $J$  = 56.5 Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -110.96 (d,  $J$  = 56.5 Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.51, 150.01, 141.86 (t,  $J$  = 1.9 Hz), 137.04, 134.88 (t,  $J$  = 22.3 Hz), 127.34, 126.14 (t,  $J$  = 6.1 Hz), 122.83, 120.92, 114.76 (t,  $J$  = 238.7 Hz).

HRMS calcd. for  $\text{C}_{12}\text{H}_9\text{F}_2\text{N}$   $[\text{M}+\text{H}]^+$ : 206.0776; Found: 206.0783



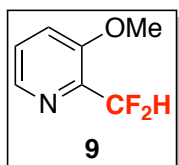
This reaction was performed with dibenzofuran-4-carboxaldehyde according to the general procedure using PBSF. Product **8** was obtained as a colorless oil (32 mg, 73% yield,  $R_f$  = 0.28 in 100% pentane). The yield reported is an average of two independent runs (73% and 52%). The NMR spectra are consistent with those reported in the literature.<sup>4</sup>

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (d,  $J = 7.7$  Hz, 1H), 7.98 (d,  $J = 7.7$  Hz, 1H), 7.67 (app d,  $J = 7.6$  Hz, 1H), 7.63 (app d,  $J = 8.3$  Hz, 1H), 7.53-7.49 (m, 1H), 7.44-7.37 (multiple peaks, 2H), 7.22 (t,  $J = 55.1$  Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -113.12 (d,  $J = 55.1$  Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.49, 153.19 (t,  $J = 5.1$  Hz), 127.97, 125.32, 123.87 (t,  $J = 5.8$  Hz), 123.53, 123.40, 123.24 (t,  $J = 1.5$  Hz), 122.88, 120.93, 118.64 (t,  $J = 23.8$  Hz), 112.10, 112.02 (t,  $J = 237.4$  Hz).

HRMS calcd. for  $\text{C}_{13}\text{H}_8\text{F}_2\text{O}$ : 218.0543; Found: 218.0544



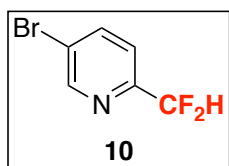
This reaction was performed with 3-methoxy-pyridine-2-carbaldehyde according to the general procedure using PBSF. Product **9** was obtained as a colorless oil (27 mg, 85% yield,  $R_f = 0.31$  in 40%  $\text{Et}_2\text{O}$  / 60% pentane).<sup>5</sup>

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.28 (app d,  $J = 4.4$  Hz, 1H), 7.40-7.39 (m, 1H), 7.31 (app d,  $J = 8.4$  Hz, 1H), 6.90 (t,  $J = 54.2$  Hz, 1H), 3.91 (s, 3H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -119.51 (d,  $J = 54.2$  Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.37 (t,  $J = 2.5$  Hz), 141.28, 141.11 (t,  $J = 22.7$  Hz), 126.53 (t,  $J = 1.7$  Hz), 119.15, 111.66 (t,  $J = 238.7$  Hz), 55.87.

HRMS calcd. for  $\text{C}_7\text{H}_7\text{F}_2\text{NO}$  [ $\text{M}+\text{H}$ ] $^+$ : 160.0568; Found: 160.0570



This reaction was performed with 5-bromo-2-pyridinecarboxaldehyde according to the general procedure using PBSF. Product **10** was obtained as a white solid (30 mg, 72% yield,  $R_f = 0.32$  in 2%  $\text{Et}_2\text{O}$  / 98% pentane, mp = 40-41 °C). The yield reported is an average of two independent runs (72% and 68%). The NMR spectra are consistent with those reported in the literature.<sup>6</sup>

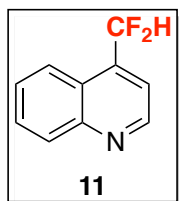
$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.72 (d,  $J = 2.0$  Hz, 1H), 7.98 (dd,  $J = 8.3, 2.0$  Hz, 1H), 7.55 (d,  $J = 8.3$  Hz, 1H), 6.61 (t,  $J = 55.3$  Hz, 1H).



$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -115.68 (d,  $J$  = 55.3 Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.46 (t,  $J$  = 26.4 Hz), 150.90, 140.10, 122.97 (t,  $J$  = 2.0 Hz), 121.57 (t,  $J$  = 2.7 Hz), 113.62 (t,  $J$  = 240.8).

HRMS calcd. for  $\text{C}_6\text{H}_4\text{BrF}_2\text{N}$   $[\text{M}+\text{H}]^+$ : 207.9568; Found: 207.9565



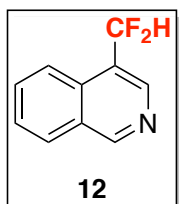
This reaction was performed with 4-quinolinecarboxaldehyde according to the general procedure using PBSF. Product **11** was obtained as a white solid and was pure after filtration through a silica plug using  $\text{Et}_2\text{O}$  (34 mg, 95% yield, mp = 55-56  $^\circ\text{C}$ ). The yield reported is an average of two independent runs (95% and 84%). The NMR spectra are consistent with those reported in the literature.<sup>5</sup>

$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.03 (d,  $J$  = 4.3 Hz, 1H), 8.21 (d,  $J$  = 8.5 Hz, 1H), 8.10 (d,  $J$  = 8.5 Hz, 1H), 7.82-7.79 (m, 1H), 7.69-7.65 (m, 1H), 7.60 (d,  $J$  = 4.3 Hz, 1H), 7.17 (t,  $J$  = 54.6 Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -115.13 (d,  $J$  = 54.6 Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.14, 148.79, 137.96 (t,  $J$  = 21.7 Hz), 130.60, 130.08, 127.97, 124.30 (t,  $J$  = 3.1 Hz), 123.45-123.43 (m), 118.09 (t,  $J$  = 7.7 Hz), 113.44 (t,  $J$  = 240.4 Hz).

HRMS calcd. for  $\text{C}_{10}\text{H}_7\text{F}_2\text{N}$   $[\text{M}+\text{H}]^+$ : 180.0619; Found: 180.0623



This reaction was performed with 4-isoquinolinecarboxaldehyde according to the general procedure using PBSF. Product **12** was obtained as a colorless oil (28 mg, 78% yield,  $R_f$  = 0.33 in 50%  $\text{Et}_2\text{O}$  / 50% pentane). The NMR spectra are consistent with those reported in the literature.<sup>5</sup>

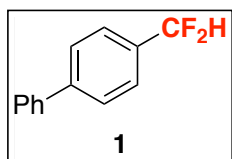
$^1\text{H}$  NMR (499.91 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.35 (s, 1H), 8.69 (s, 1H), 8.20 (app d,  $J$  = 8.5 Hz, 1H), 8.06 (app d,  $J$  = 8.2 Hz, 1H), 7.84-7.81 (m, 1H), 7.71 (app t,  $J$  = 7.6 Hz, 1H), 7.07 (t,  $J$  = 54.4 Hz, 1H).

$^{19}\text{F}$  NMR (470.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  -110.95 (d,  $J$  = 54.4 Hz, 2F).

$^{13}\text{C}$  NMR (175.97 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.21-156.19 (m), 141.88 (t,  $J$  = 9.4 Hz), 132.33 (t,  $J$  = 1.6 Hz), 131.80, 128.58, 128.07, 123.41 (t,  $J$  = 21.6 Hz), 123.32 (t,  $J$  = 1.7 Hz), 115.22 (t,  $J$  = 238.5 Hz).

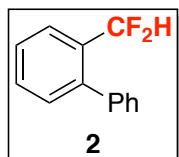
HRMS calcd. for  $\text{C}_{10}\text{H}_7\text{F}_2\text{N}$   $[\text{M}+\text{H}]^+$ : 180.0619; Found: 180.0621

#### 4. Characterization of Products Isolated from (Hetero)aryl Aldehydes using $\text{Tf}_2\text{O}$



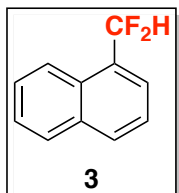
This reaction was performed with 4-phenylbenzaldehyde according to the general procedure using  $\text{Tf}_2\text{O}$ . Product **1** was obtained as a white solid (23 mg, 56% yield,  $R_f$  = 0.26 in 100% pentane). The yield reported is an average of two independent runs (56% and 59%).

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were consistent with the spectral data obtained for **1** isolated from the general procedure using PBSF.



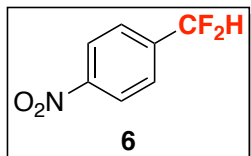
This reaction was performed with 2-phenylbenzaldehyde according to the general procedure using  $\text{Tf}_2\text{O}$ . Product **2** was obtained as a colorless oil (19 mg, 47% yield,  $R_f$  = 0.39 in 100% pentane).

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were consistent with the spectral data obtained for **2** isolated from the general procedure using PBSF.



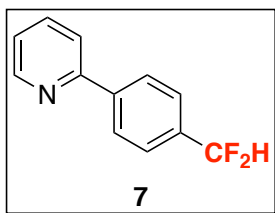
This reaction was performed with 1-naphthaldehyde according to the general procedure using  $\text{Tf}_2\text{O}$ . 1-naphthaldehyde is an oil and the order of addition of reagents changed to accommodate this: 1-naphthaldehyde was added to the vial first, followed by DCM, TMAF, and finally  $\text{Tf}_2\text{O}$ . Product **3** was obtained as a colorless oil (21 mg, 59% yield,  $R_f = 0.31$  in 100% pentane). The yield reported is an average of two independent runs (59% and 72%).

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were consistent with the spectral data obtained for **3** isolated from the general procedure using PBSF.



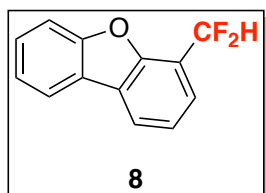
This reaction was performed with 4-nitrobenzaldehyde according to the general procedure using  $\text{Tf}_2\text{O}$ . Product **6** was obtained as a colorless oil (17 mg, 49% yield,  $R_f = 0.36$  in 6%  $\text{Et}_2\text{O}$  / 94% pentane).

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were consistent with the spectral data obtained for **6** isolated from the general procedure using PBSF.



This reaction was performed with 4-(2-pyridyl)benzaldehyde according to the general procedure using  $\text{Tf}_2\text{O}$ . Product **7** was obtained as a white solid (26 mg, 63% yield,  $R_f = 0.48$  in 30%  $\text{Et}_2\text{O}$  / 70% pentane).

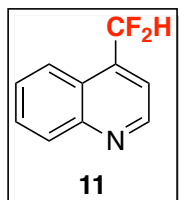
$^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were consistent with the spectral data obtained for **7** isolated from the general procedure using PBSF.



This reaction was performed with dibenzofuran-4-carboxaldehyde according to the general procedure using  $\text{Tf}_2\text{O}$ . Product **8** was obtained as a colorless oil (34 mg,

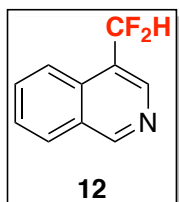
78% yield,  $R_f = 0.28$  in 100% pentane). The yield reported is an average of two independent runs (78% and 50%).

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were consistent with the spectral data obtained for **8** isolated from the general procedure using PBSF.



This reaction was performed with 4-quinolinecarboxaldehyde according to the general procedure using  $\text{Tf}_2\text{O}$ . Product **11** was obtained as an orange oil (14 mg, 39% yield  $R_f = 0.46$  in 50%  $\text{Et}_2\text{O}$  / 50% pentane).

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were consistent with the spectral data obtained for **11** isolated from the general procedure using PBSF.



This reaction was performed with 4-isoquinolinecarboxaldehyde according to the general procedure using  $\text{Tf}_2\text{O}$ . Product **12** was obtained as a colorless oil (25 mg, 70% yield,  $R_f = 0.33$  in 50%  $\text{Et}_2\text{O}$  / 50% pentane).

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were consistent with the spectral data obtained for **12** isolated from the general procedure using PBSF.

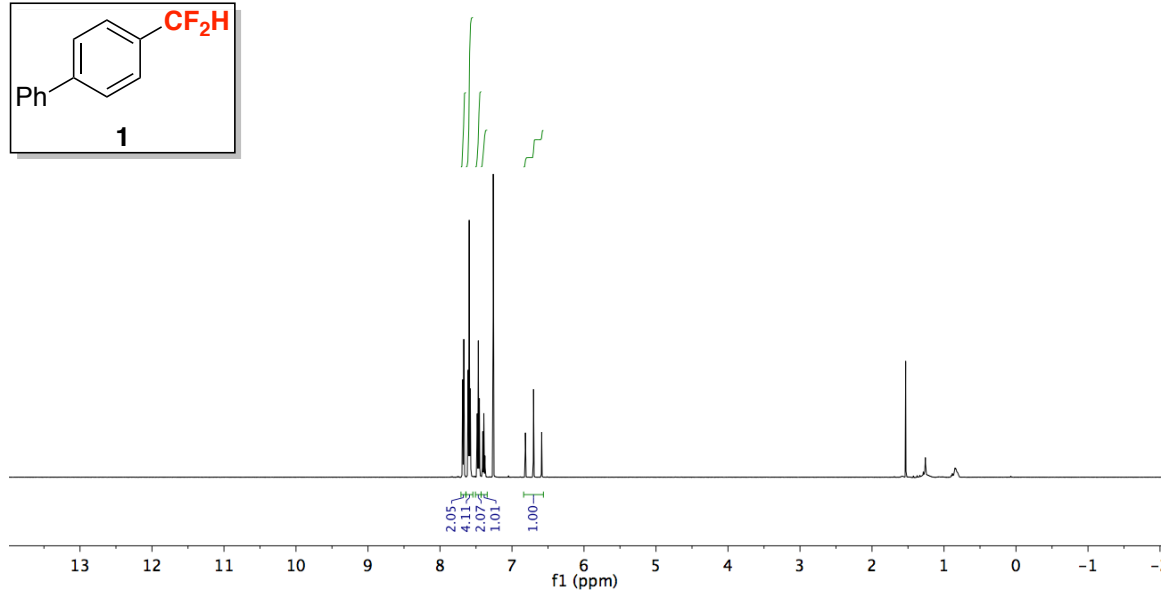
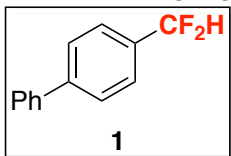
## 5. References

- <sup>1</sup> Motohashi, H.; Mikami, K. *Org. Lett.* **2018**, *20*, 5340.
- <sup>2</sup> Pan, F.; Boursalian, G. B.; Ritter, T. *Angew. Chem. Int. Ed.* **2018**, *57*, 16871.
- <sup>3</sup> Miao, W.; Zhao, Y.; Ni, C.; Gao, B.; Zhang, W.; Hu, J. *J. Am. Chem. Soc.* **2018**, *140*, 880.
- <sup>4</sup> Hori, K.; Motohashi, H.; Saito, D.; Mikami, K. *ACS Catal.* **2019**, *9*, 417.
- <sup>5</sup> Lu, C.; Gu, Y.; Wu, J.; Gu, Y.; Shen, Q. *Chem. Sci.* **2017**, *8*, 4848.
- <sup>6</sup> Zeng, X.; Wei, X.; Song, J. J.; Sarvestani, M.; Fandrick, D. R.; Qu, B.; Rodríguez, S.; Sieber, J. D.; Desrosiers, J.-N.; Yee, N. K.; Roschinger, F.; Senanayake, C. H. *Asian J. Org. Chem.* **2015**, *4*, 1262.

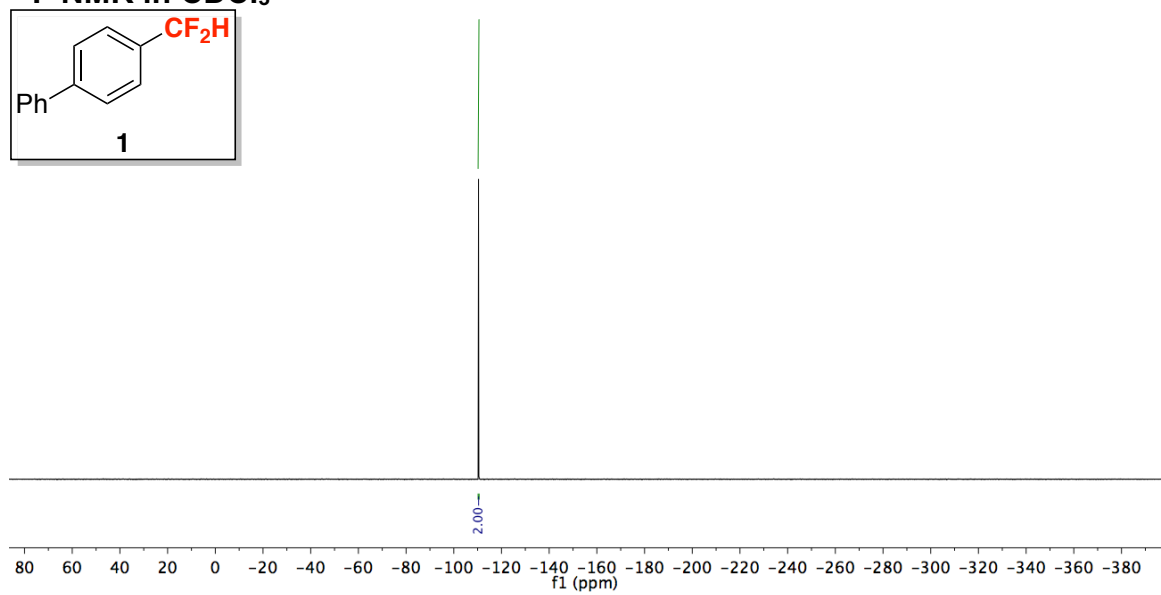
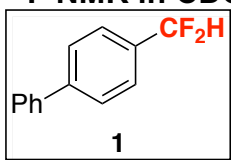
## 6. NMR Spectra

### i. 1 Synthesized Using PBSF

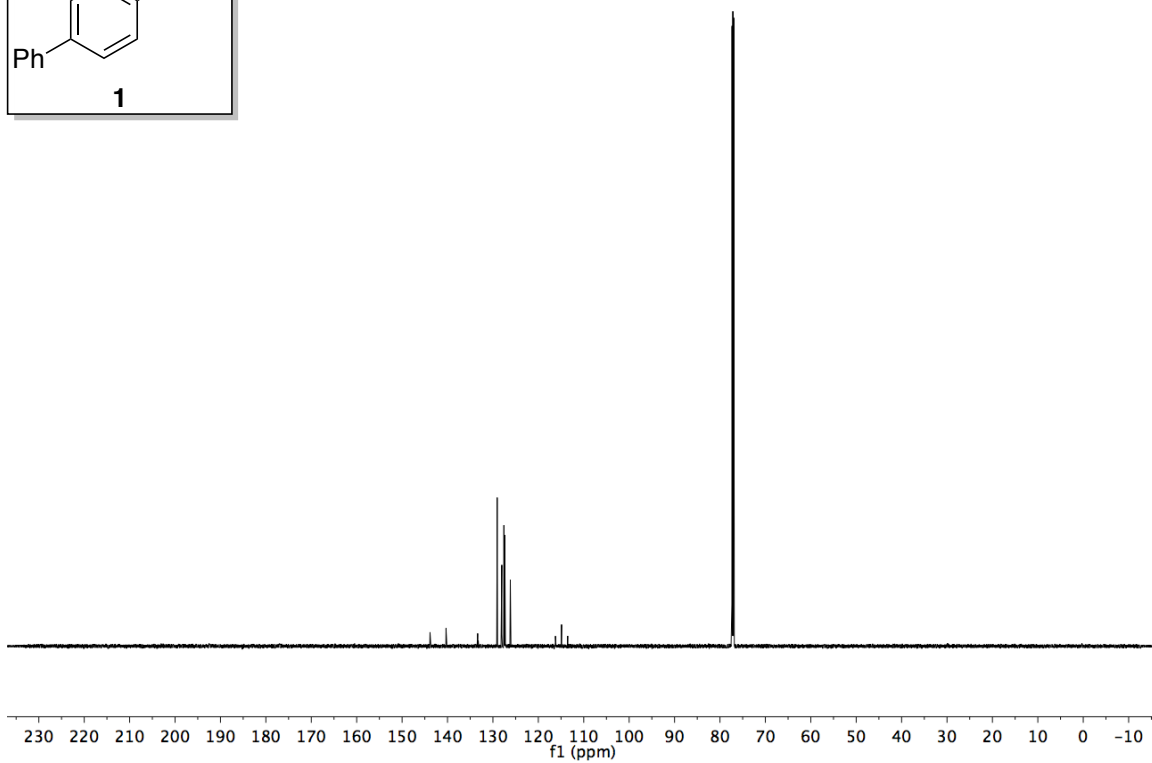
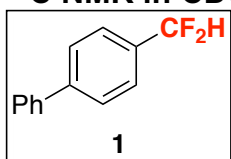
$^1\text{H}$  NMR in  $\text{CDCl}_3$



$^{19}\text{F}$  NMR in  $\text{CDCl}_3$

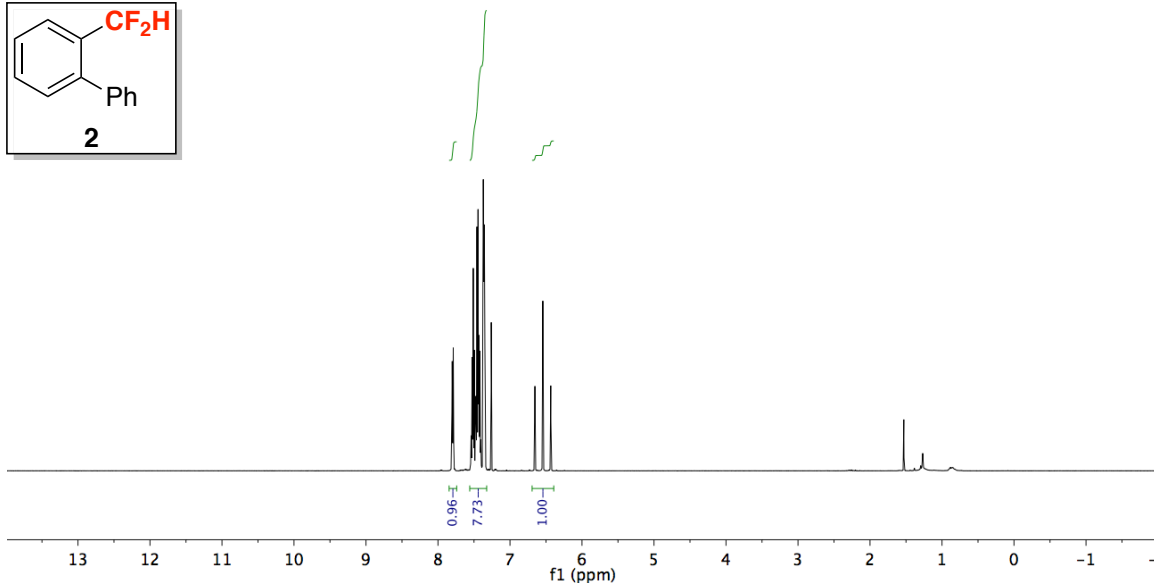
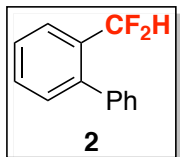


<sup>13</sup>C NMR in CDCl<sub>3</sub>

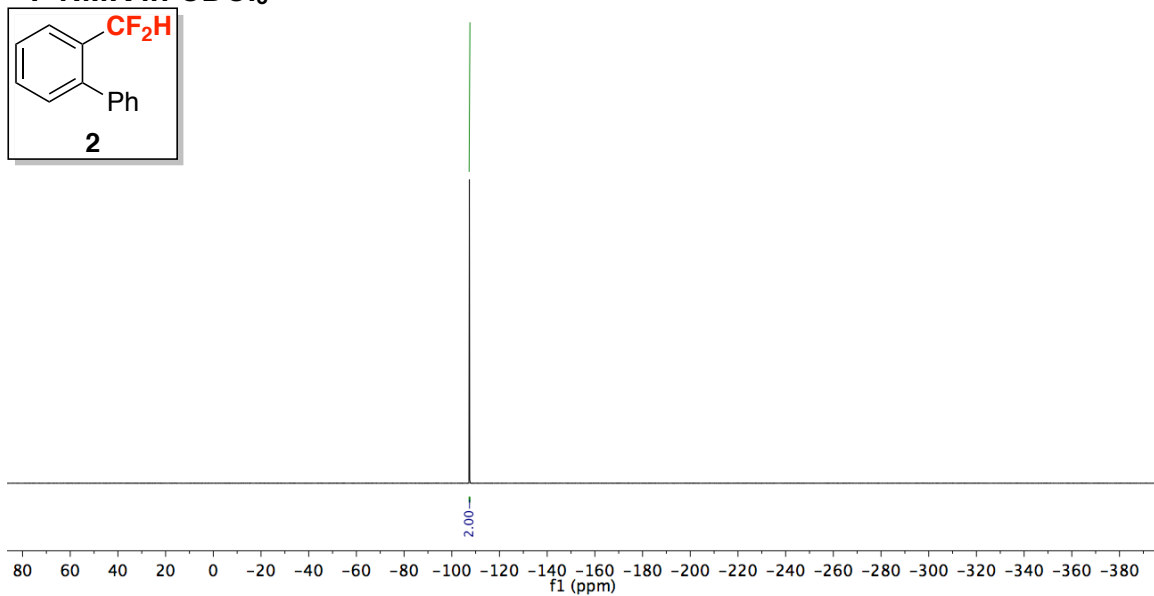
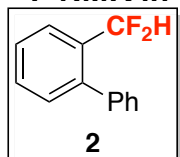


ii. 2 Synthesized Using PBSF

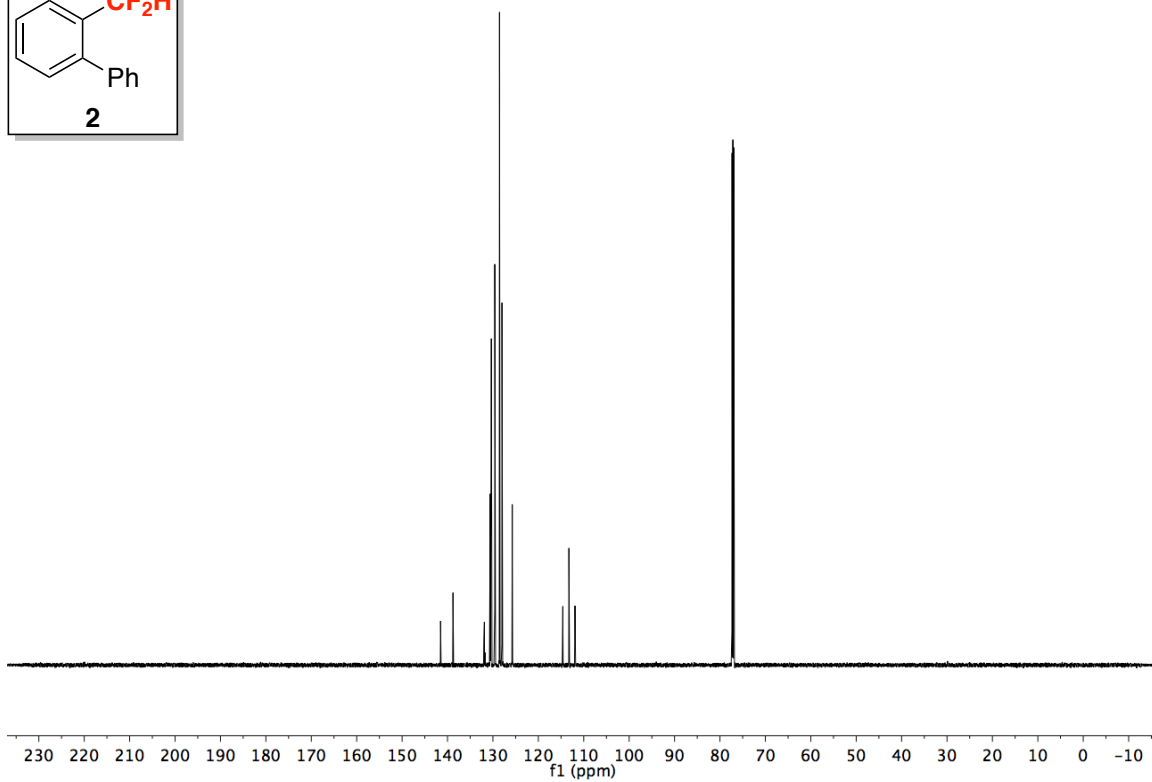
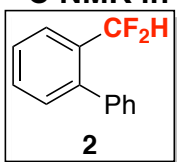
$^1\text{H}$  NMR in  $\text{CDCl}_3$



$^{19}\text{F}$  NMR in  $\text{CDCl}_3$



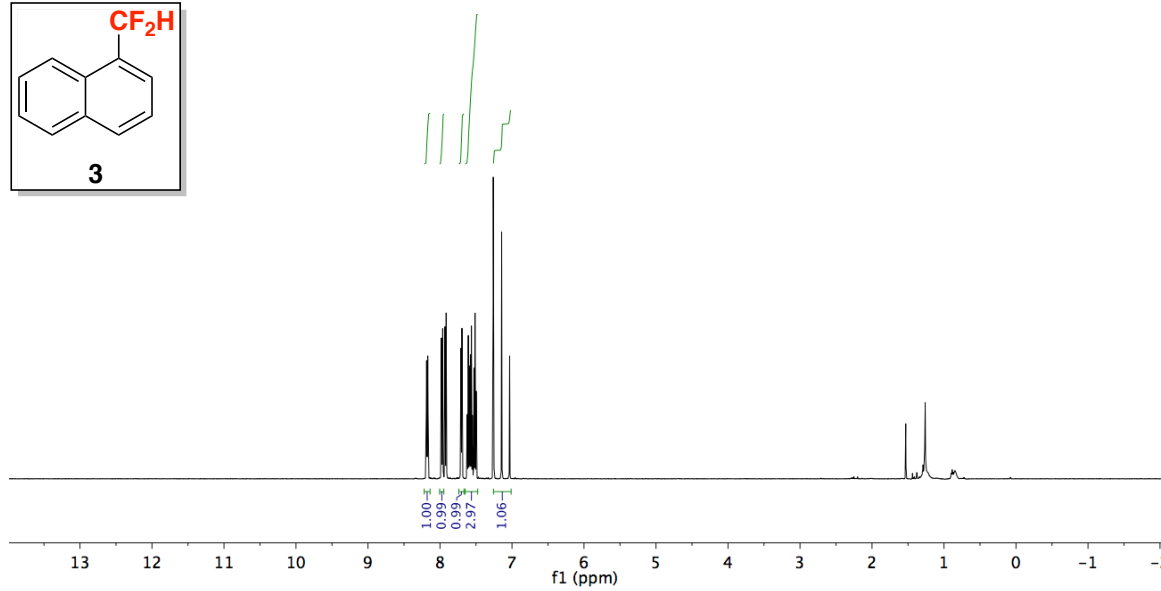
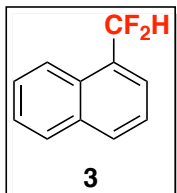
<sup>13</sup>C NMR in CDCl<sub>3</sub>



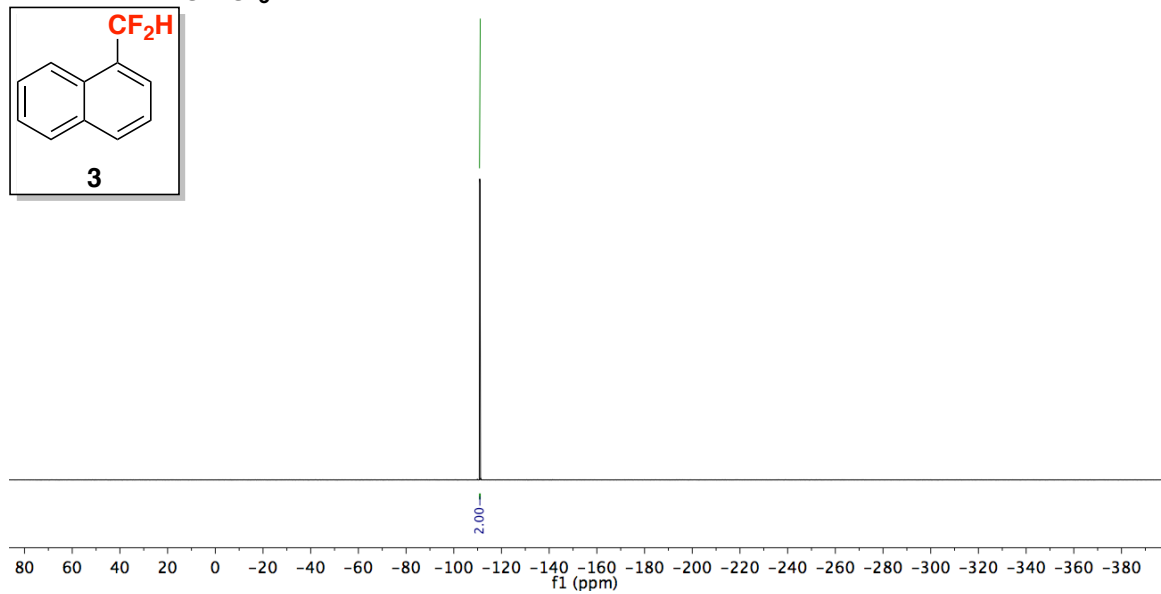
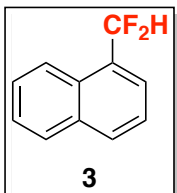


iii. **3 Synthesized Using PBSF**

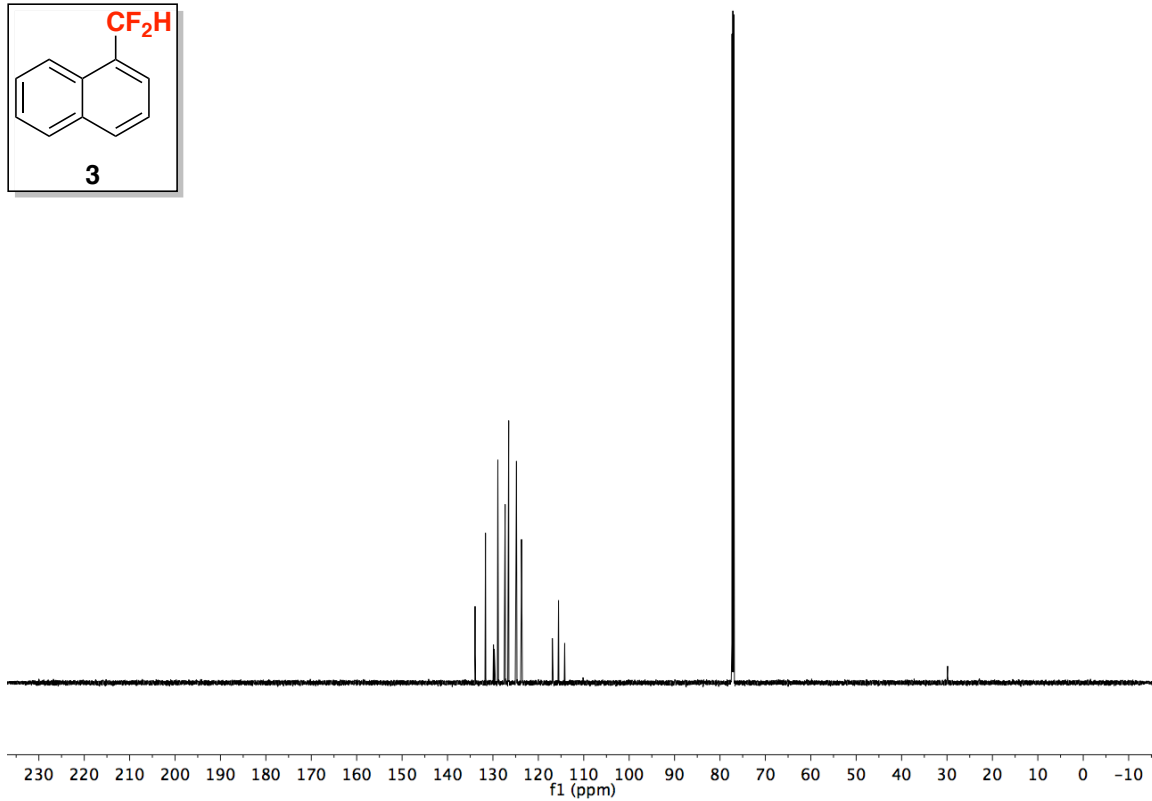
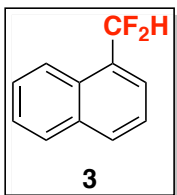
**<sup>1</sup>H NMR in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR in CDCl<sub>3</sub>**

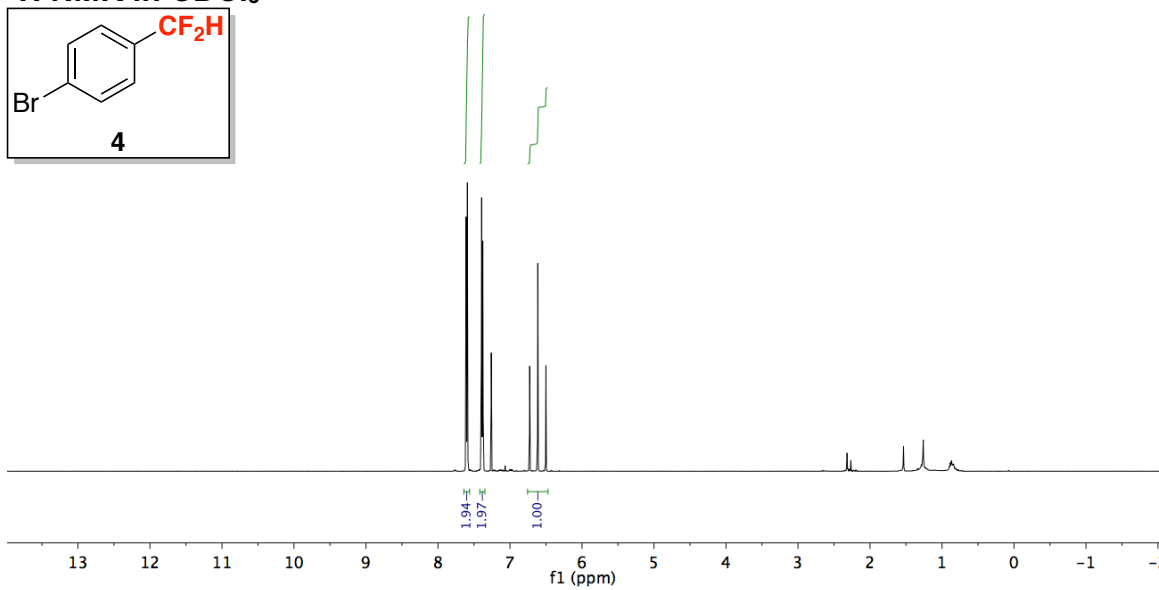
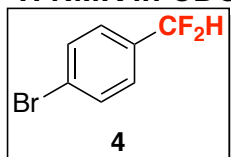


<sup>13</sup>C NMR in CDCl<sub>3</sub>

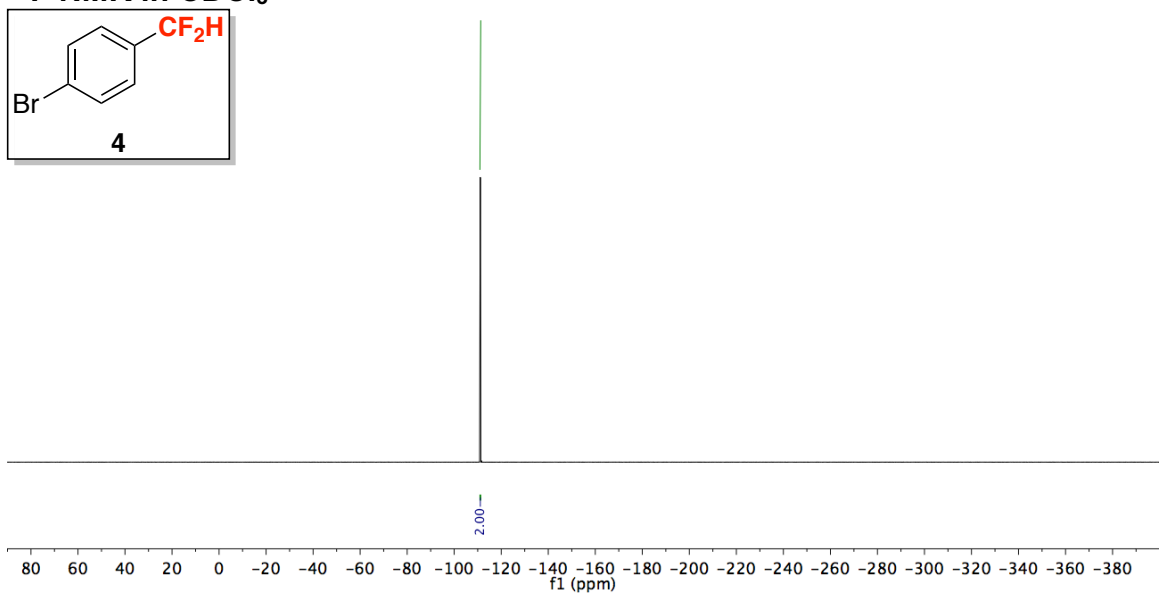
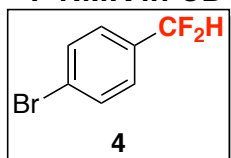


iv. **4 Synthesized Using PBSF**

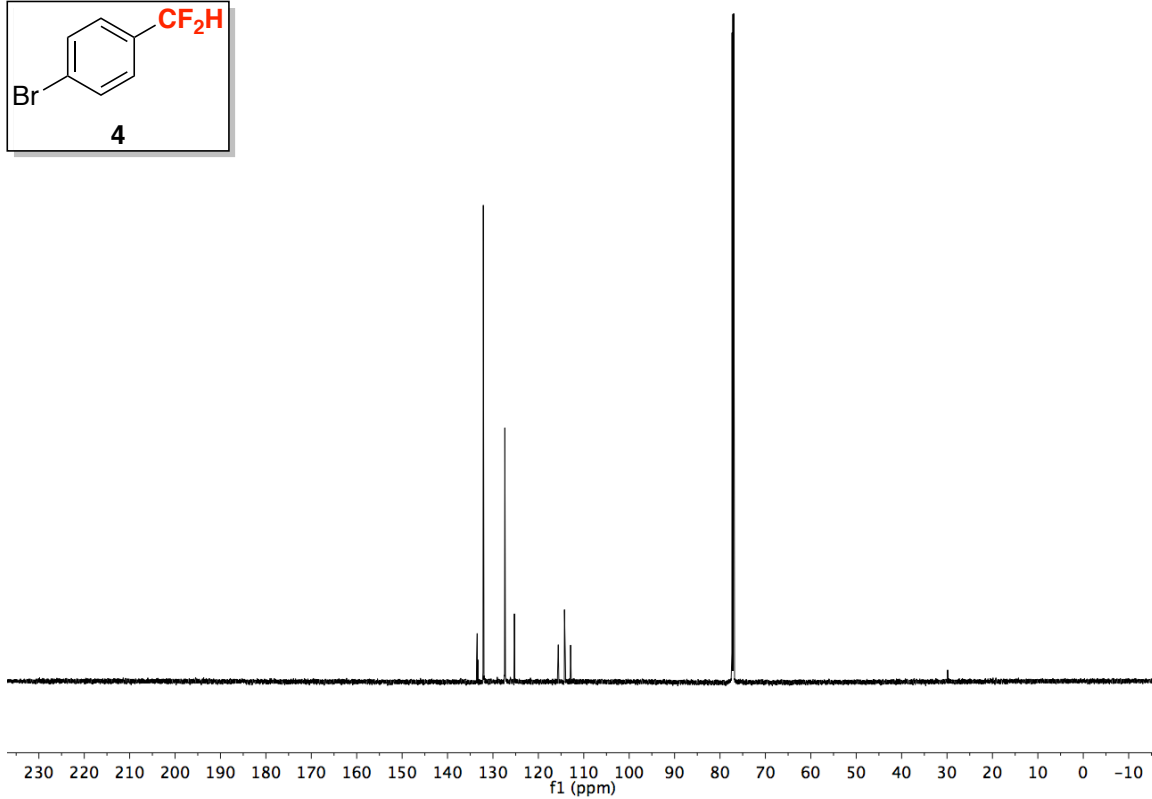
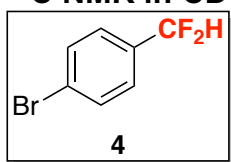
**$^1\text{H}$  NMR in  $\text{CDCl}_3$**



**$^{19}\text{F}$  NMR in  $\text{CDCl}_3$**

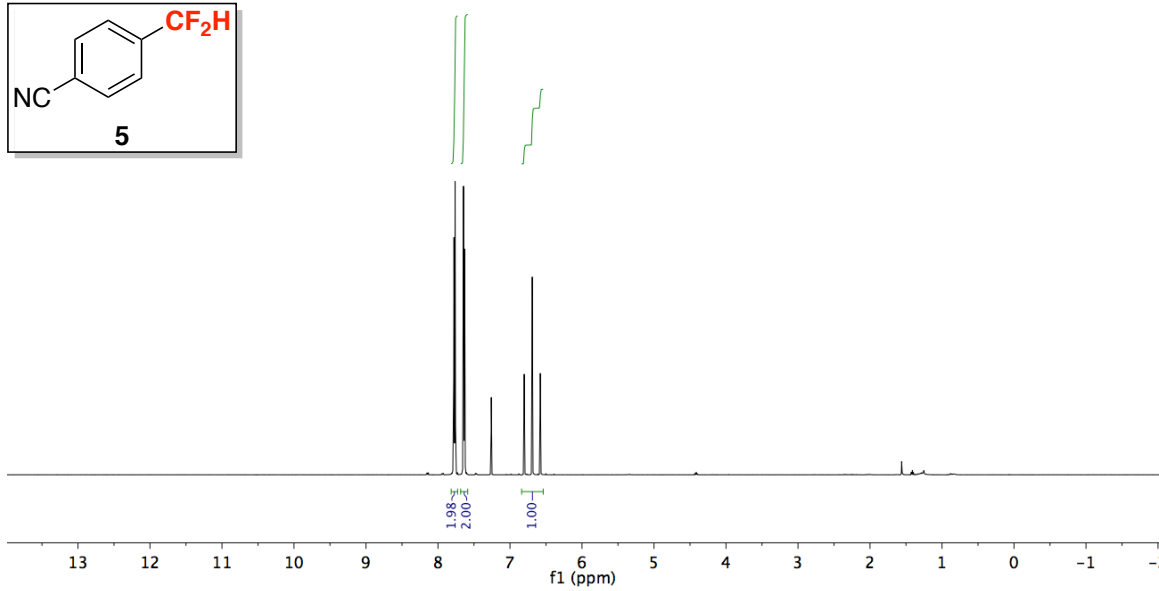
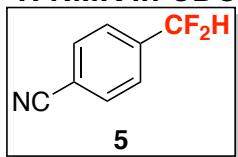


<sup>13</sup>C NMR in CDCl<sub>3</sub>

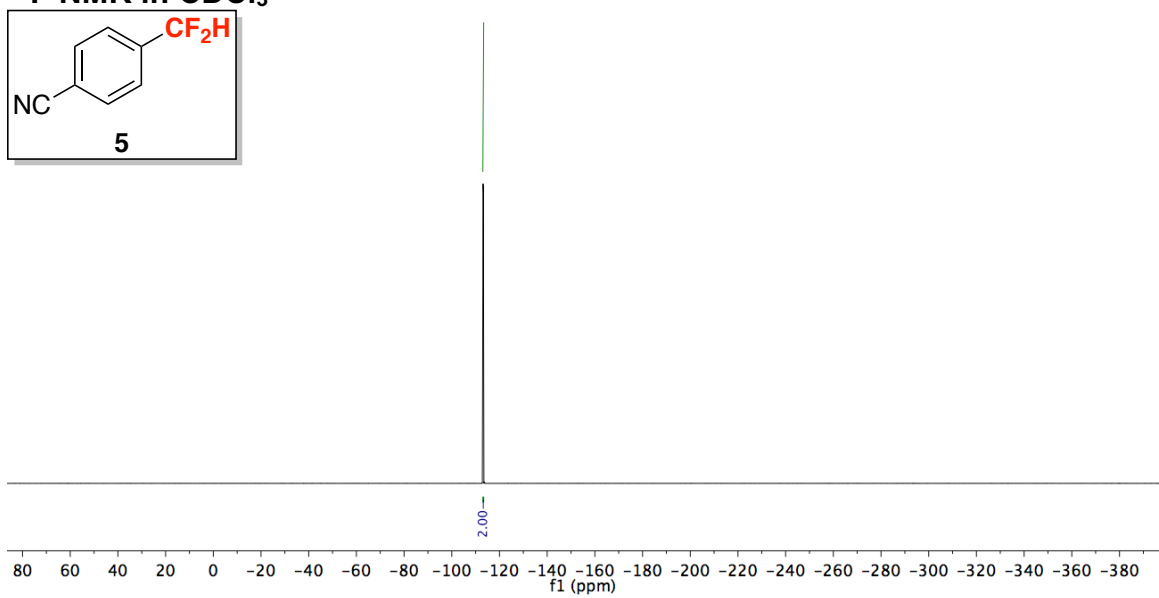
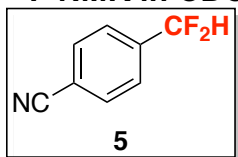


v. **5 Synthesized Using PBSF**

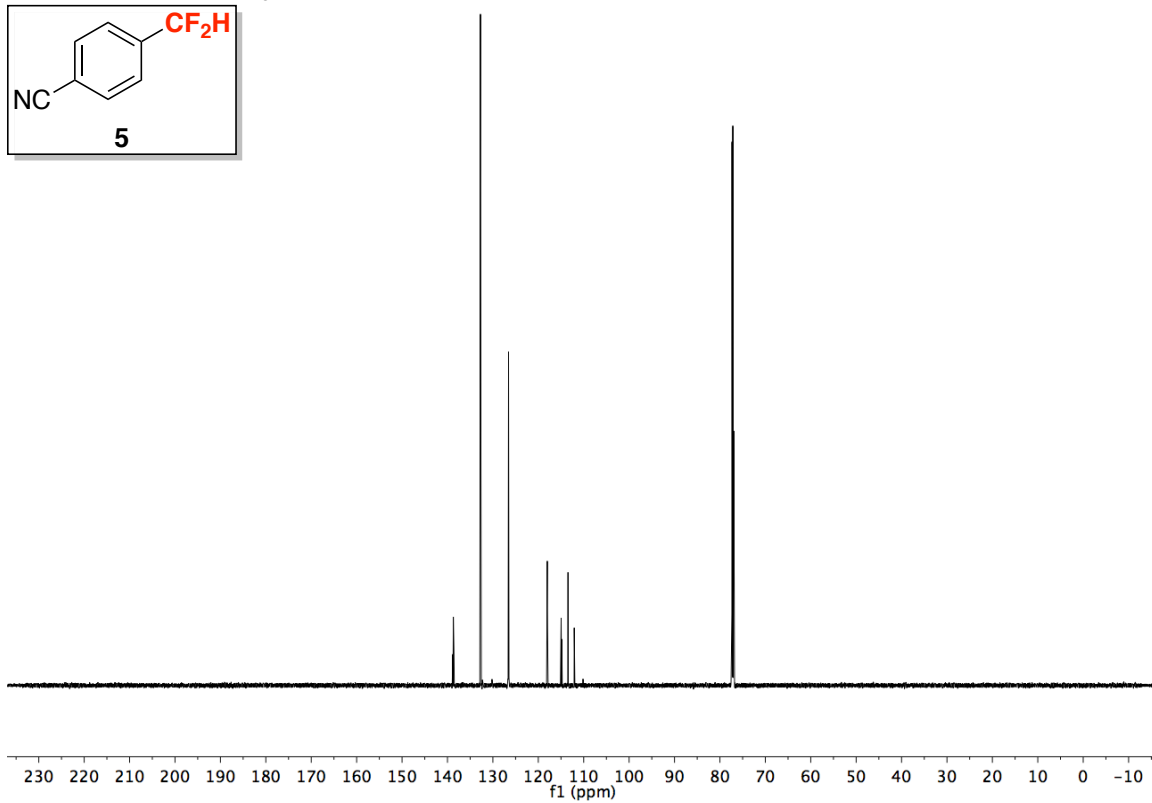
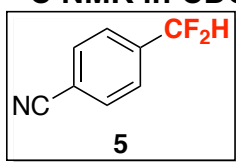
**<sup>1</sup>H NMR in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR in CDCl<sub>3</sub>**

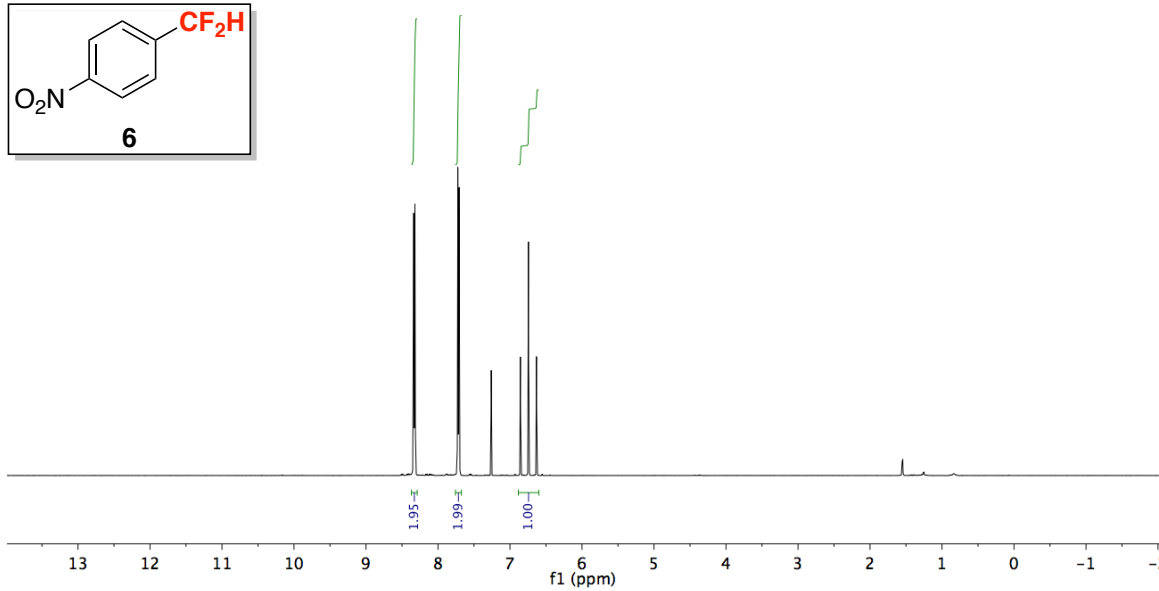
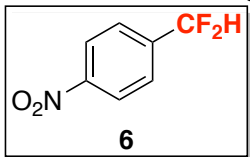


<sup>13</sup>C NMR in CDCl<sub>3</sub>

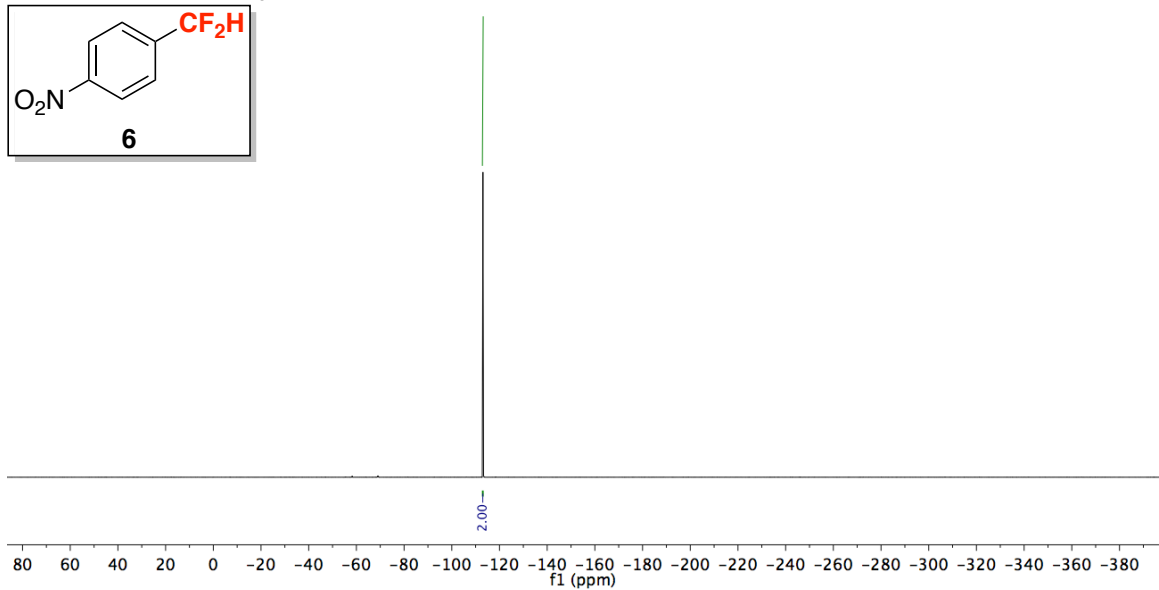
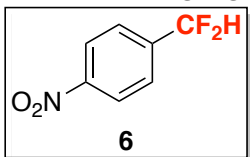


vi. **6 Synthesized Using PBSF**

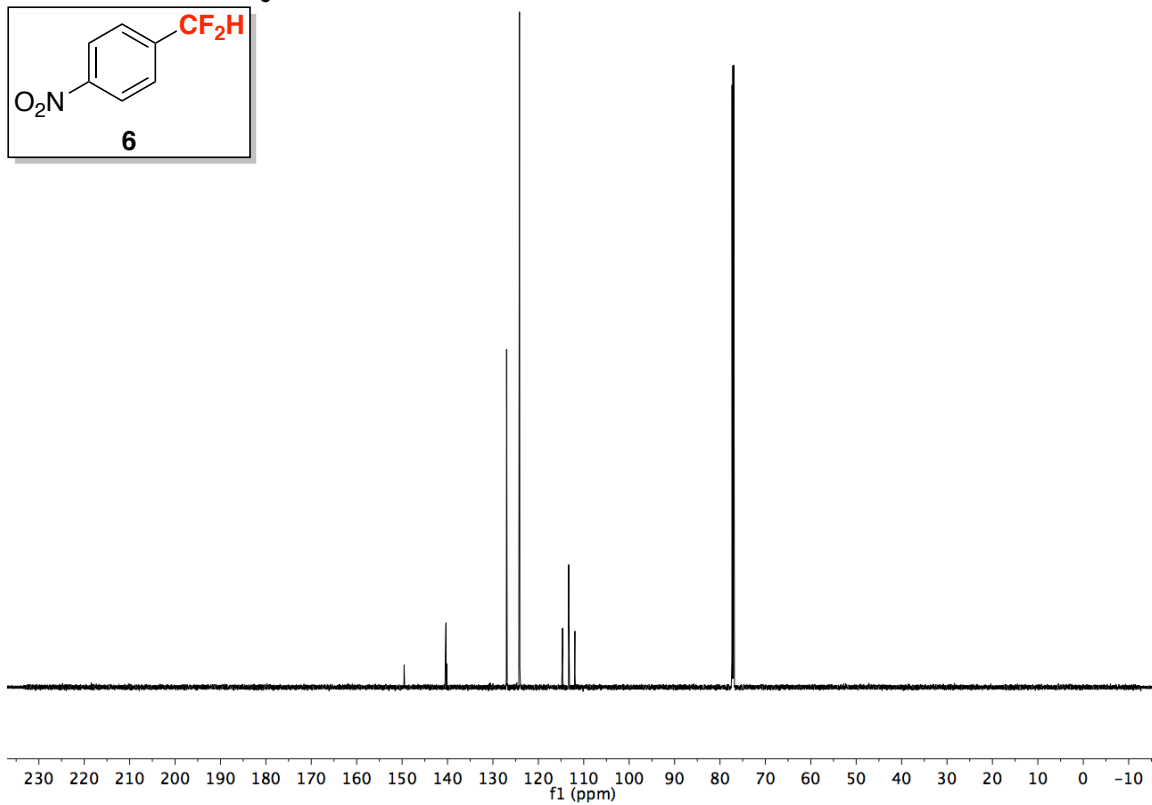
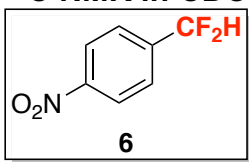
**<sup>1</sup>H NMR in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR in CDCl<sub>3</sub>**



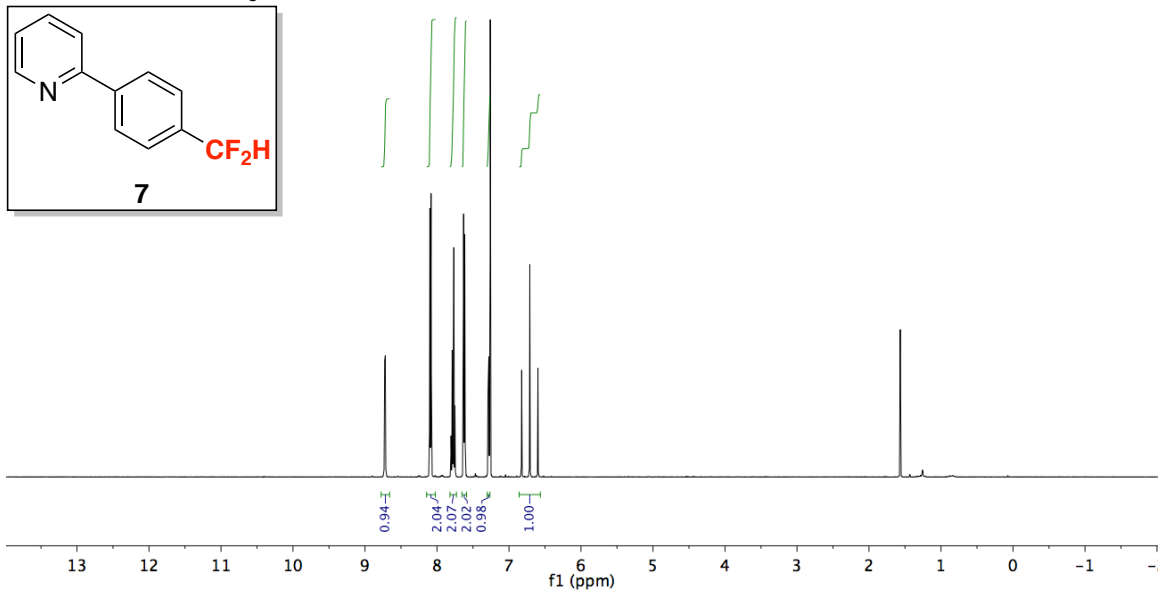
<sup>13</sup>C NMR in CDCl<sub>3</sub>



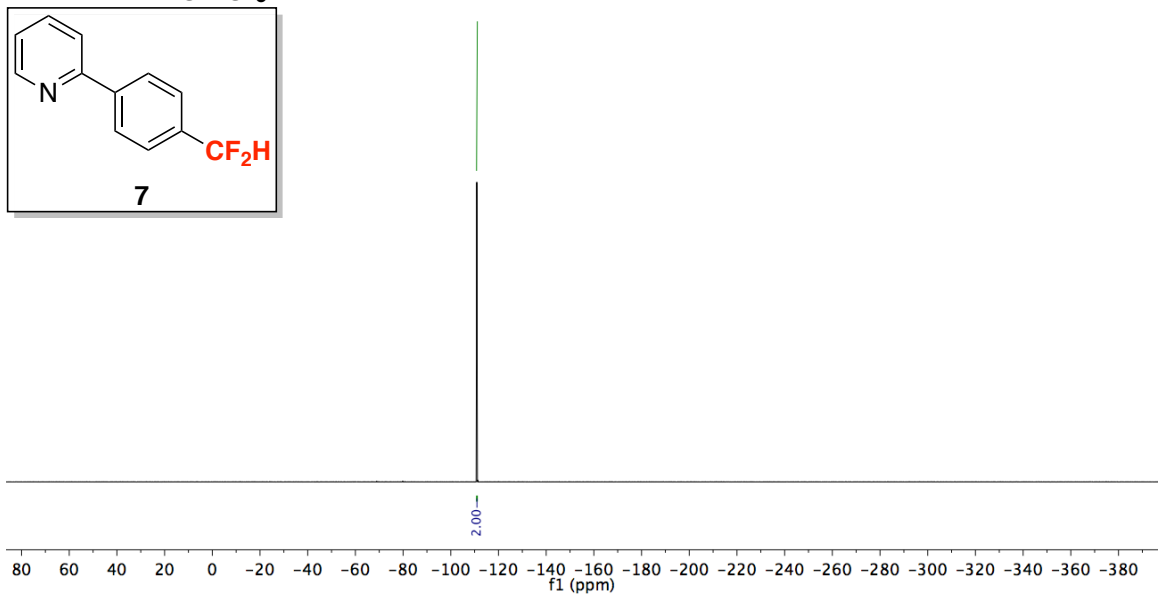


vii. **7 Synthesized Using PBSF**

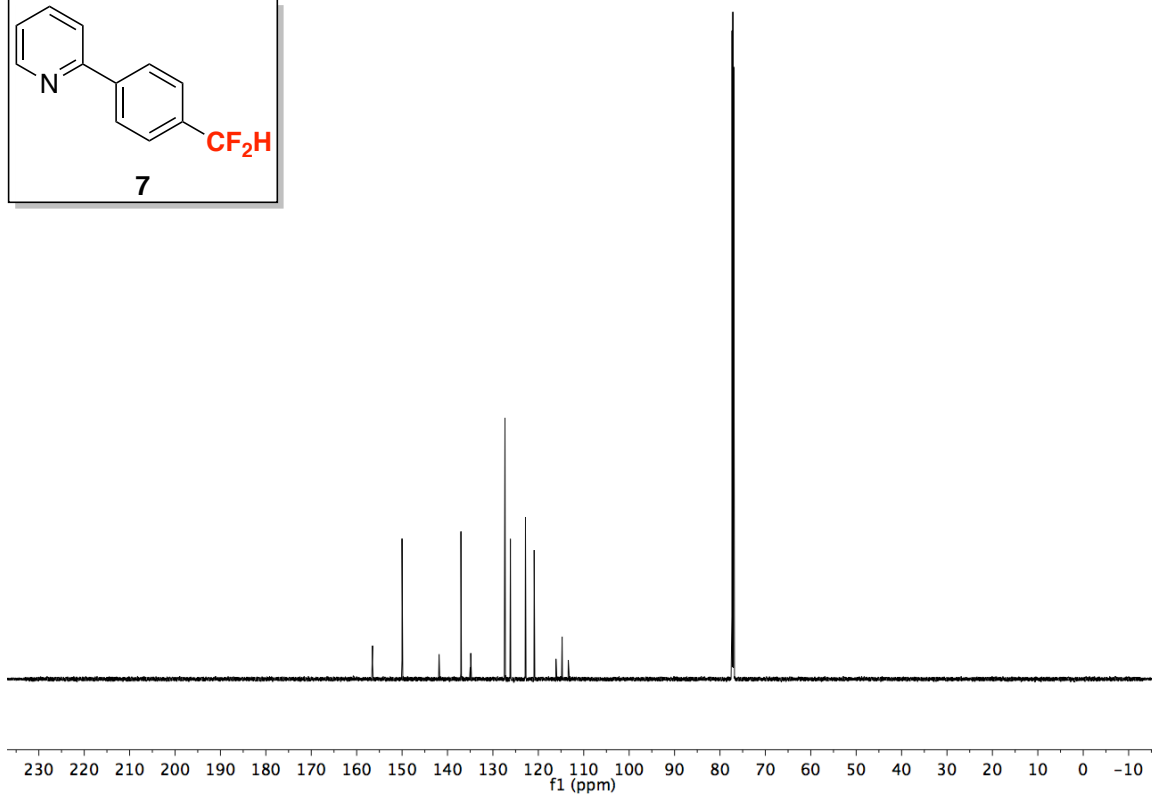
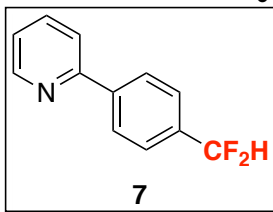
**$^1\text{H}$  NMR in  $\text{CDCl}_3$**



**$^{19}\text{F}$  NMR in  $\text{CDCl}_3$**

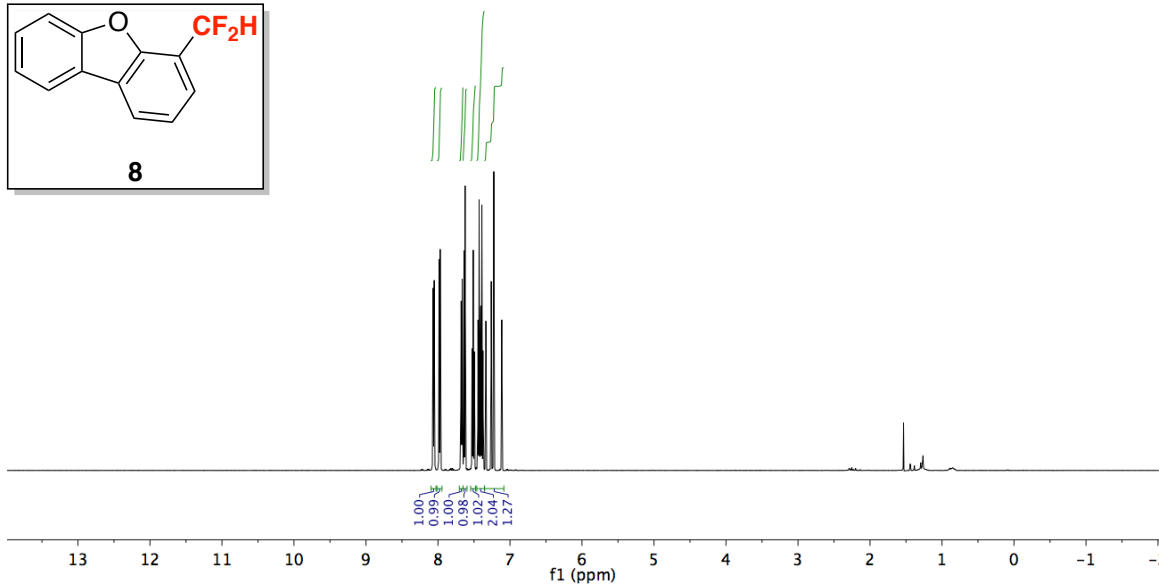
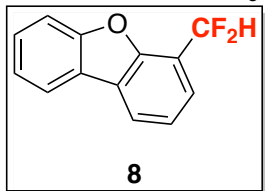


<sup>13</sup>C NMR in CDCl<sub>3</sub>

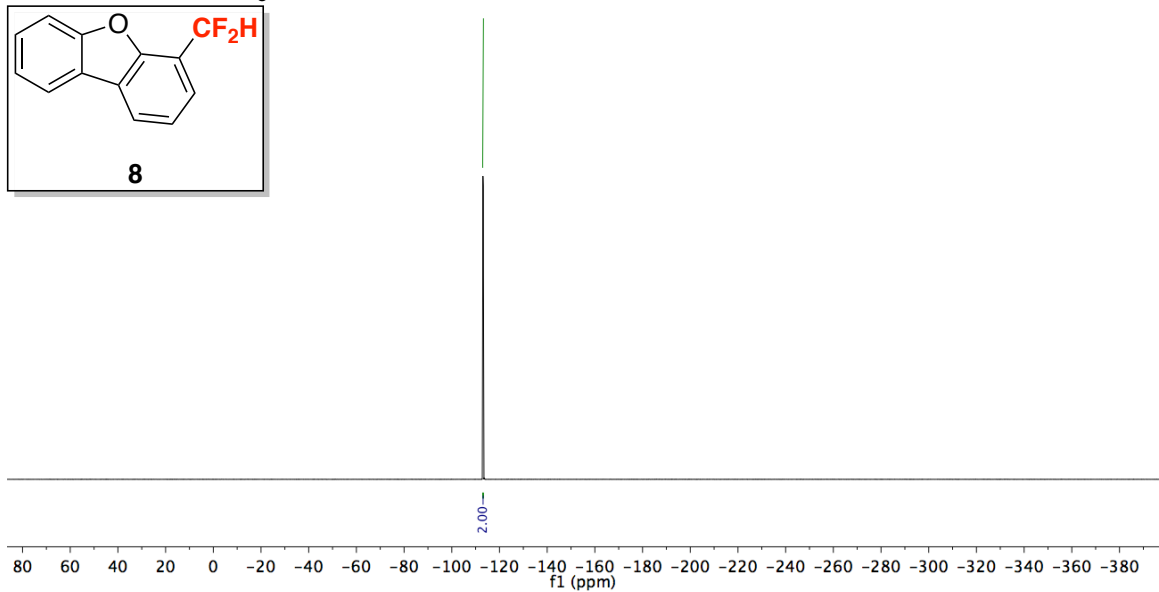
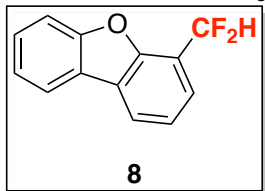


viii. **8** Synthesized Using PBSF

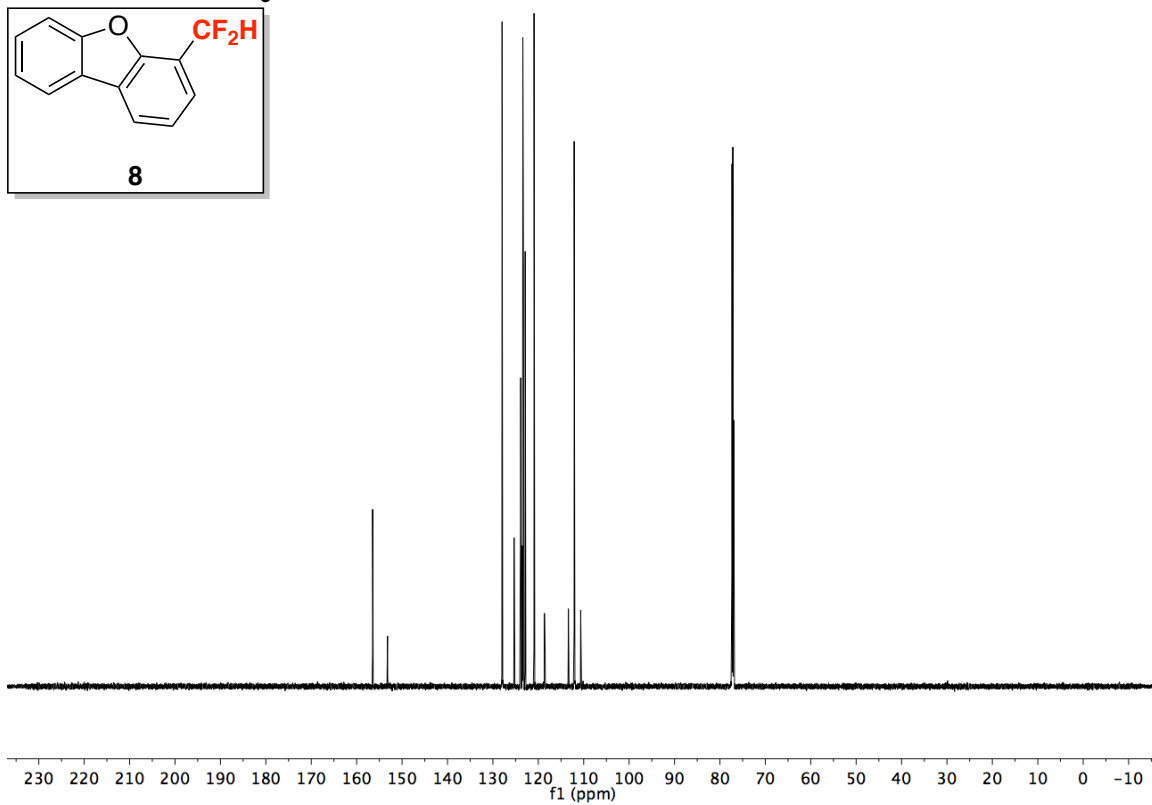
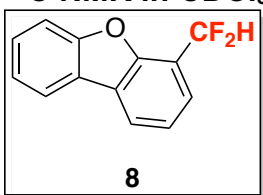
**<sup>1</sup>H NMR in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR in CDCl<sub>3</sub>**

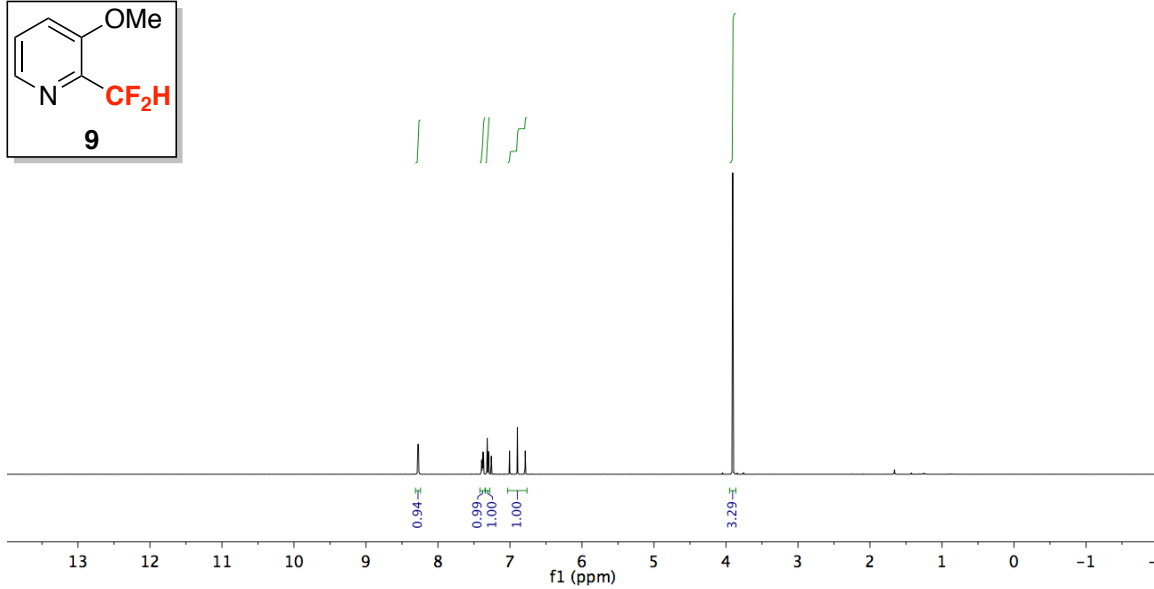
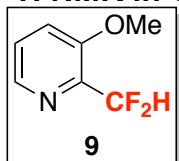


<sup>13</sup>C NMR in CDCl<sub>3</sub>

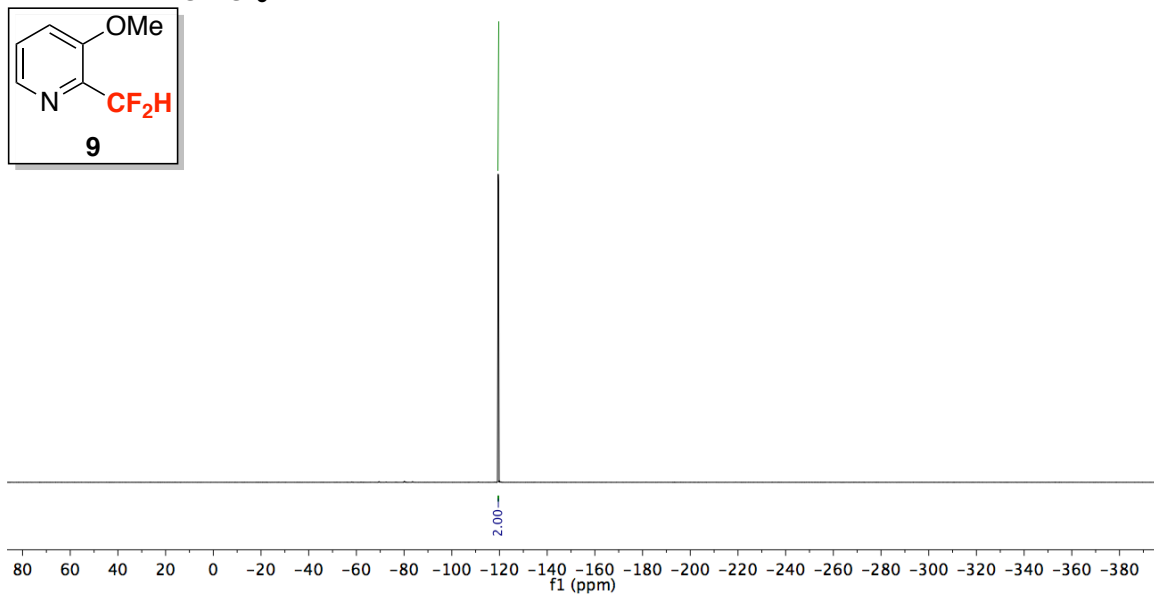
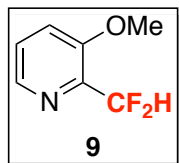


ix. **9** Synthesized Using PBSF

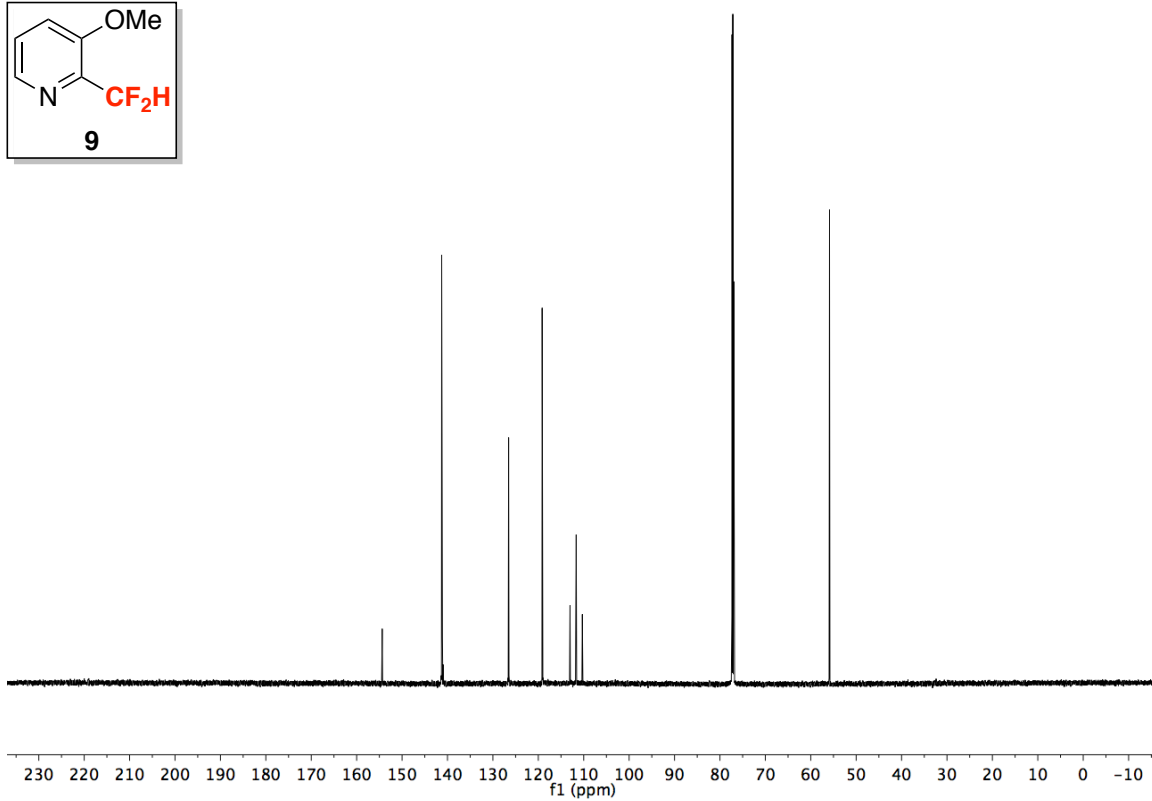
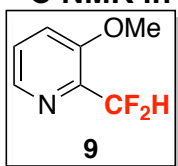
**<sup>1</sup>H NMR in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR in CDCl<sub>3</sub>**

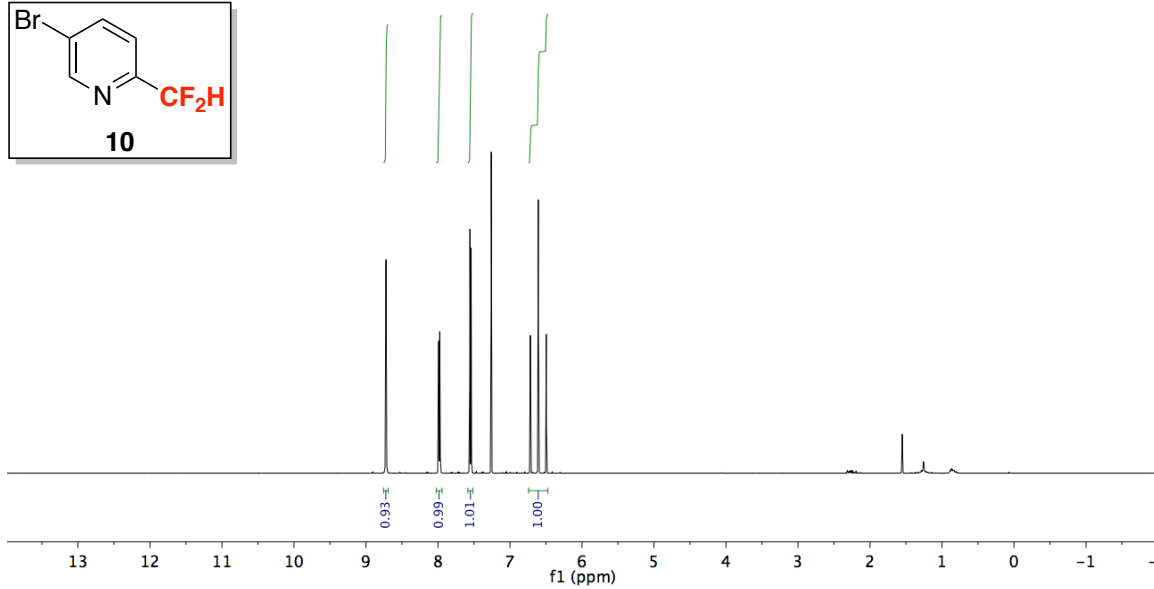
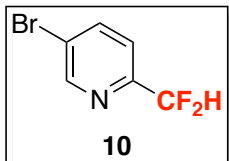


<sup>13</sup>C NMR in CDCl<sub>3</sub>

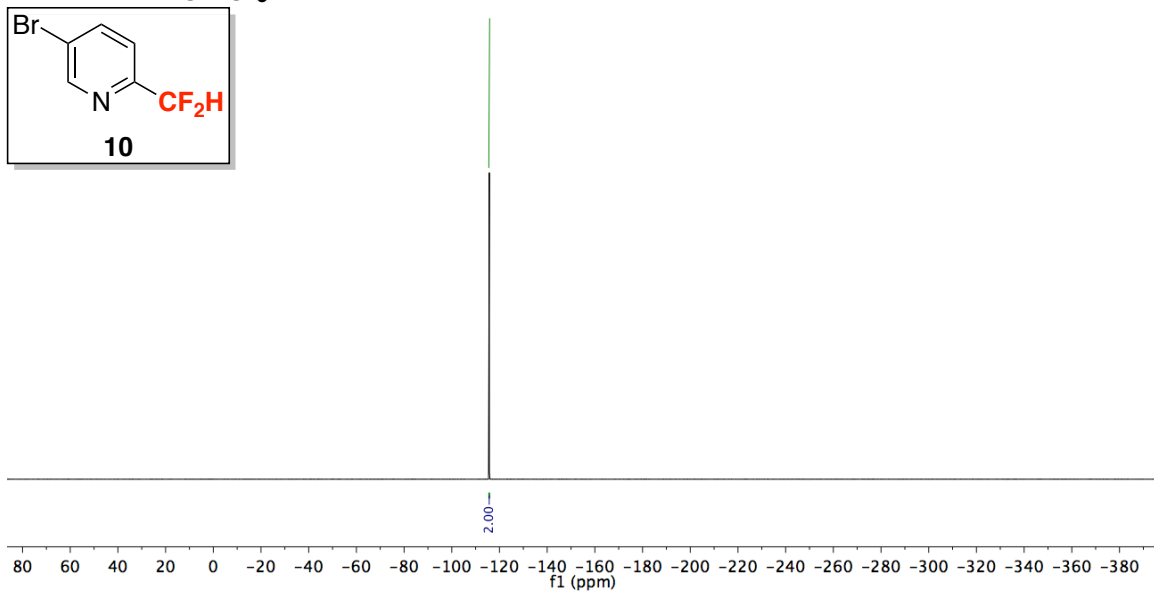
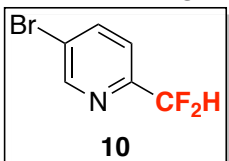


x. **10 Synthesized Using PBSF**

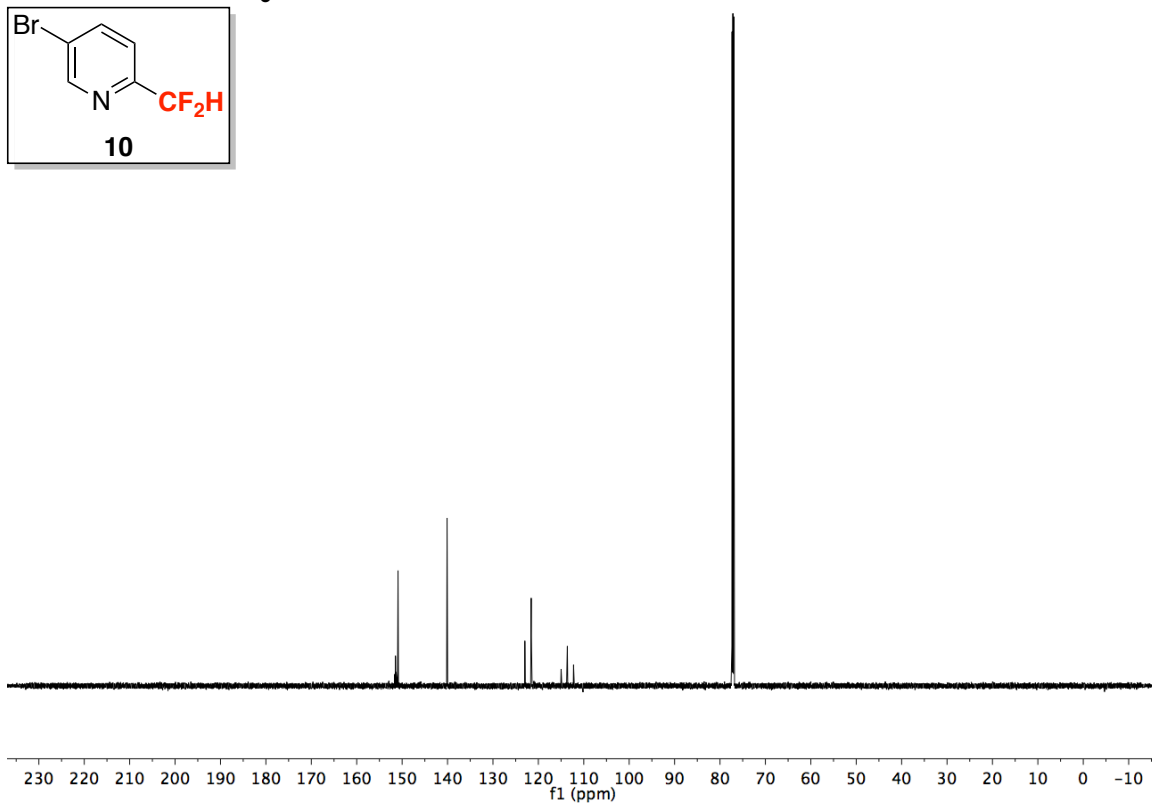
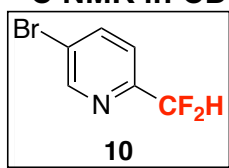
**$^1\text{H}$  NMR in  $\text{CDCl}_3$**



**$^{19}\text{F}$  NMR in  $\text{CDCl}_3$**



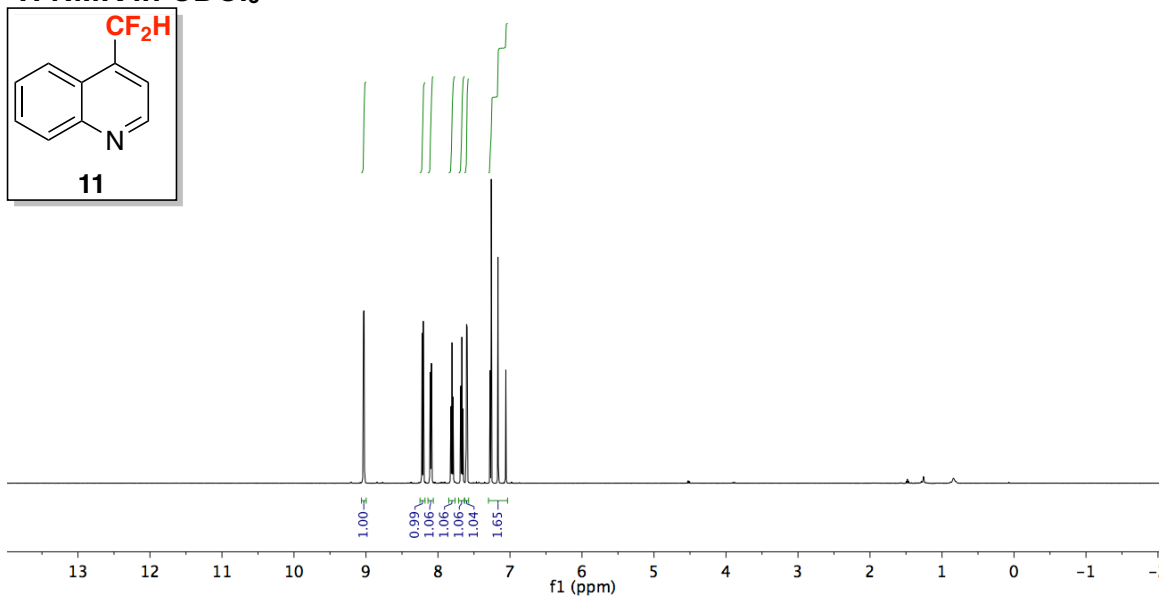
<sup>13</sup>C NMR in CDCl<sub>3</sub>



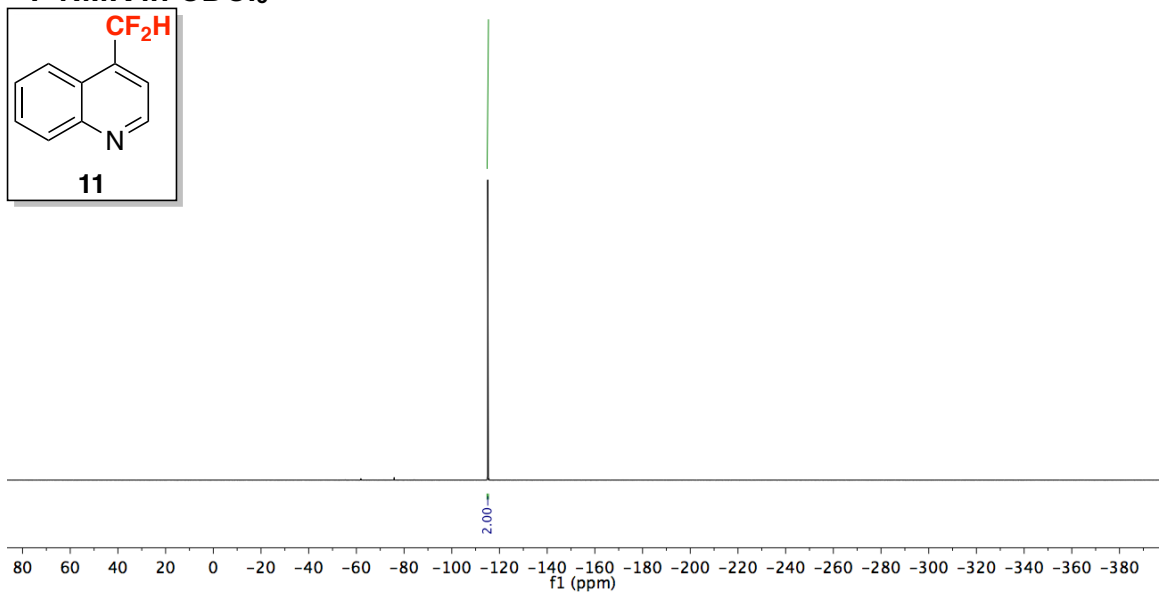


xi. **11 Synthesized Using PBSF**

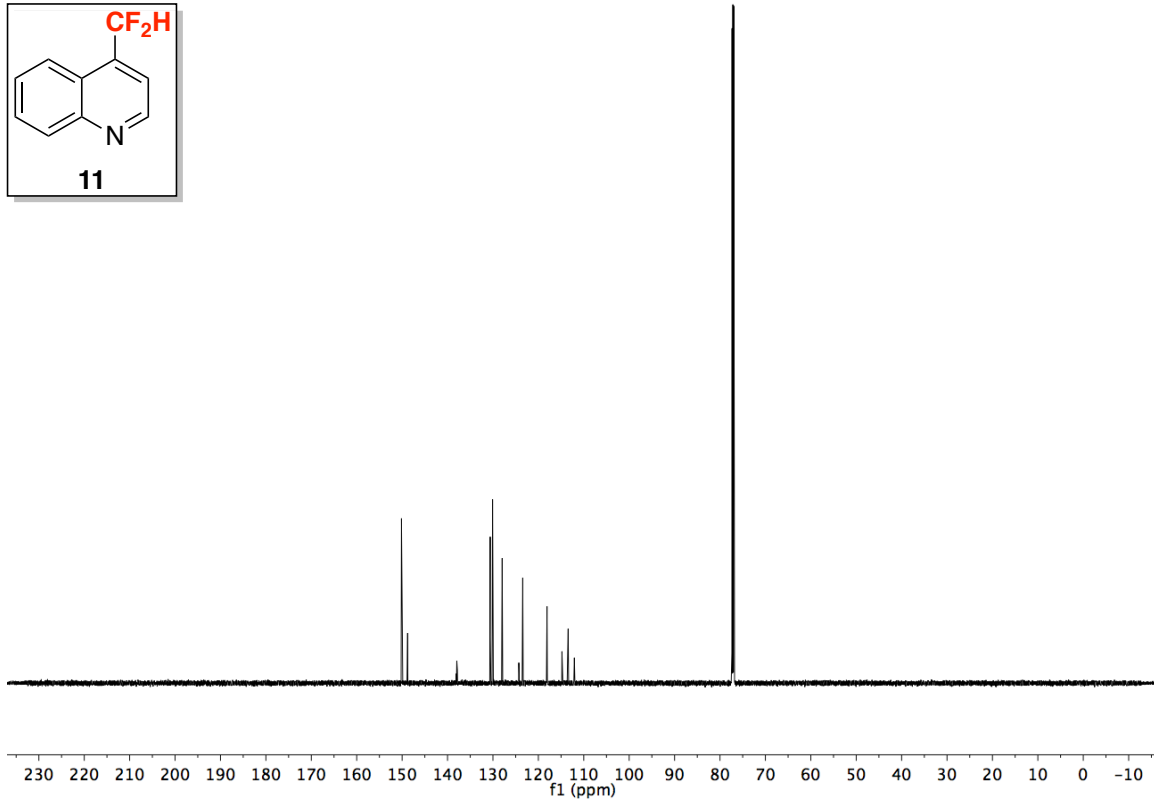
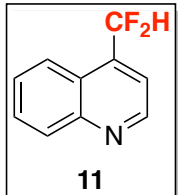
**<sup>1</sup>H NMR in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR in CDCl<sub>3</sub>**

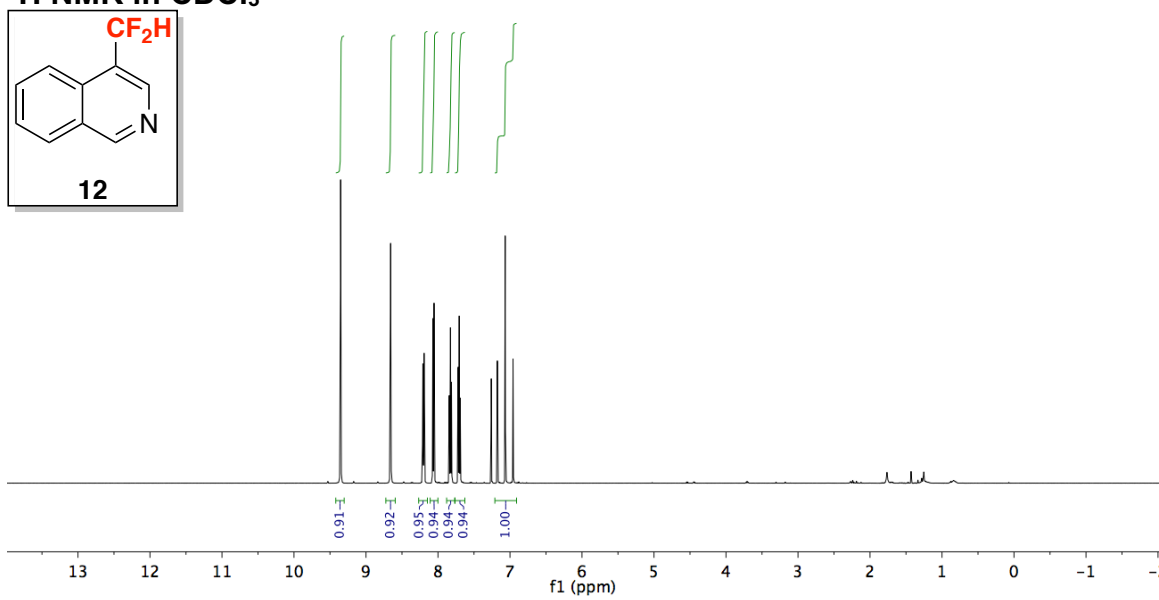


<sup>13</sup>C NMR in CDCl<sub>3</sub>

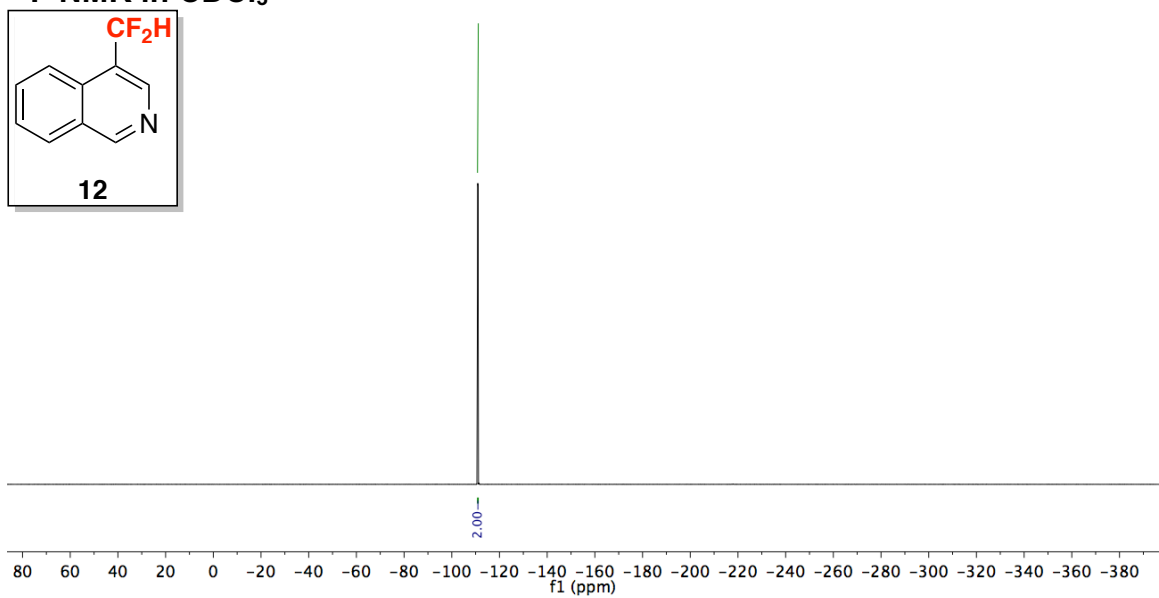


xii. **12 Synthesized Using PBSF**

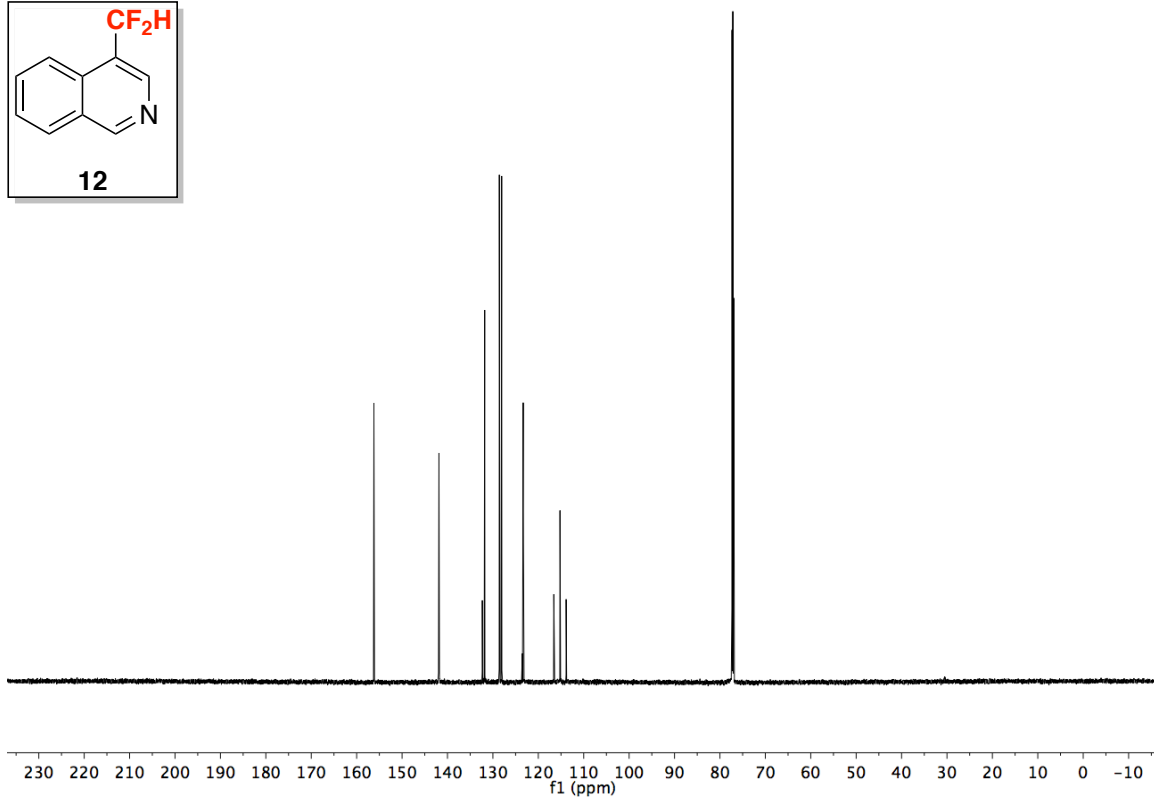
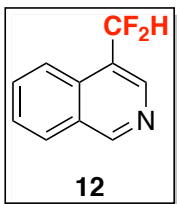
**<sup>1</sup>H NMR in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR in CDCl<sub>3</sub>**

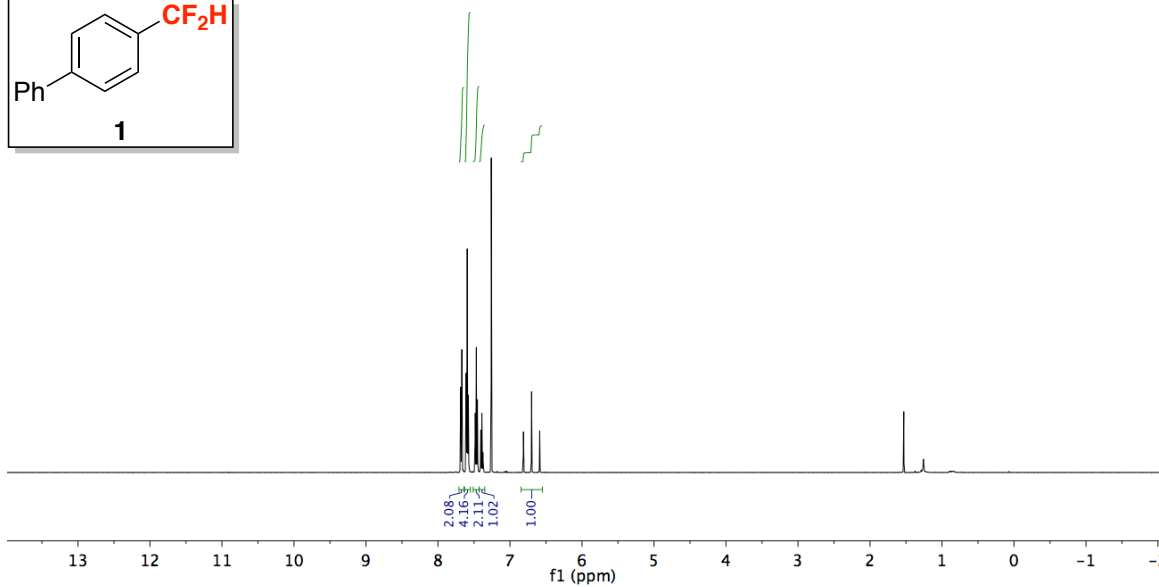
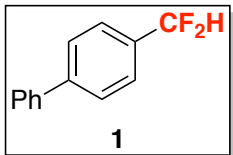


<sup>13</sup>C NMR in CDCl<sub>3</sub>

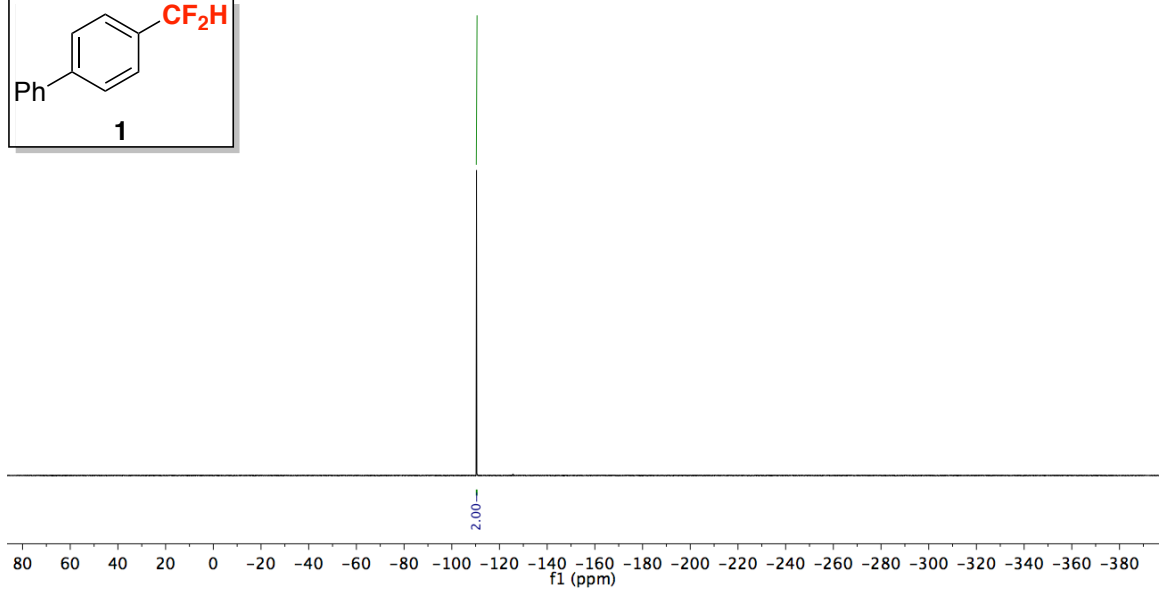
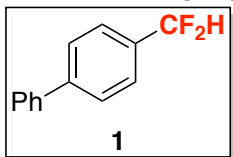


xiii. **1** Synthesized Using  $Tf_2O$

$^1H$  NMR in  $CDCl_3$

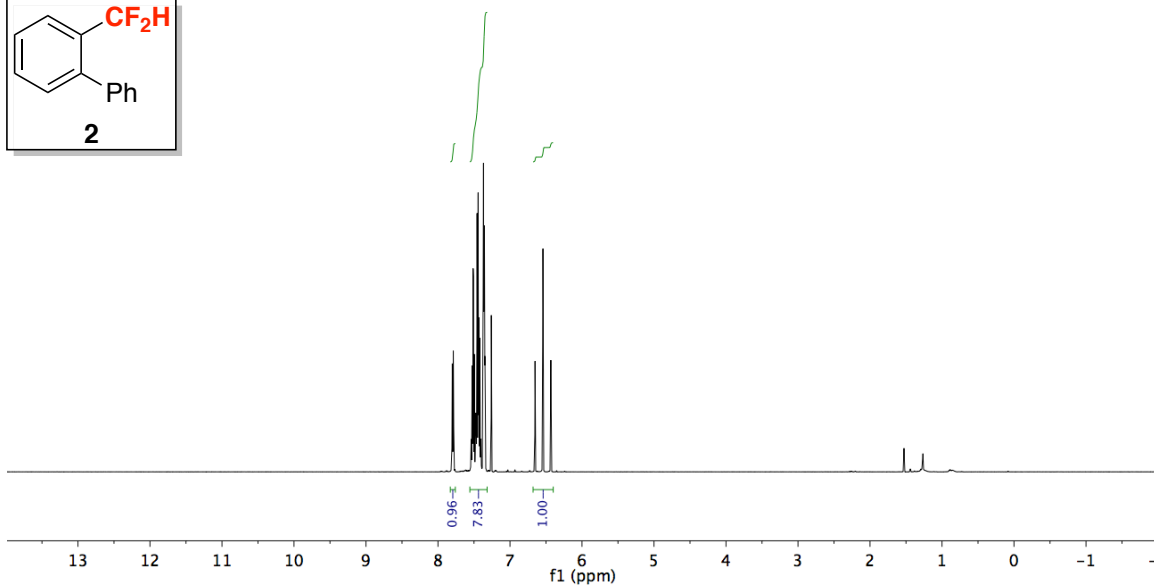
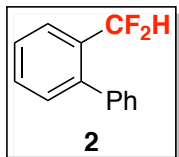


$^{19}F$  NMR in  $CDCl_3$

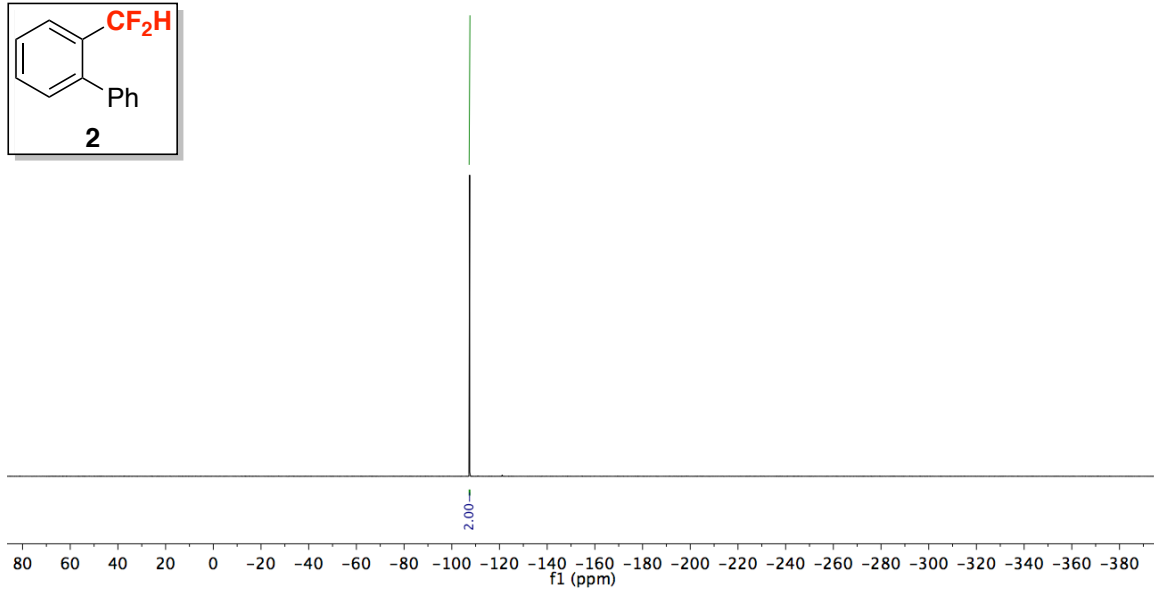
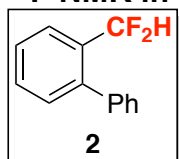


xiv. **2** Synthesized Using  $Tf_2O$

$^1H$  NMR in  $CDCl_3$

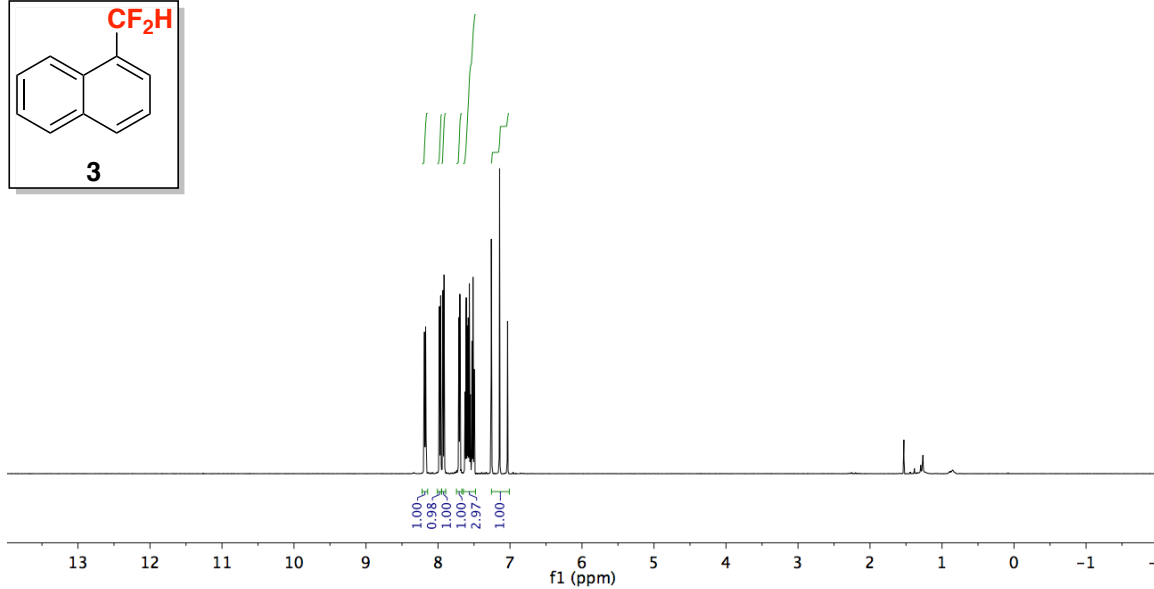
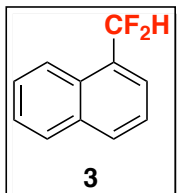


$^{19}F$  NMR in  $CDCl_3$

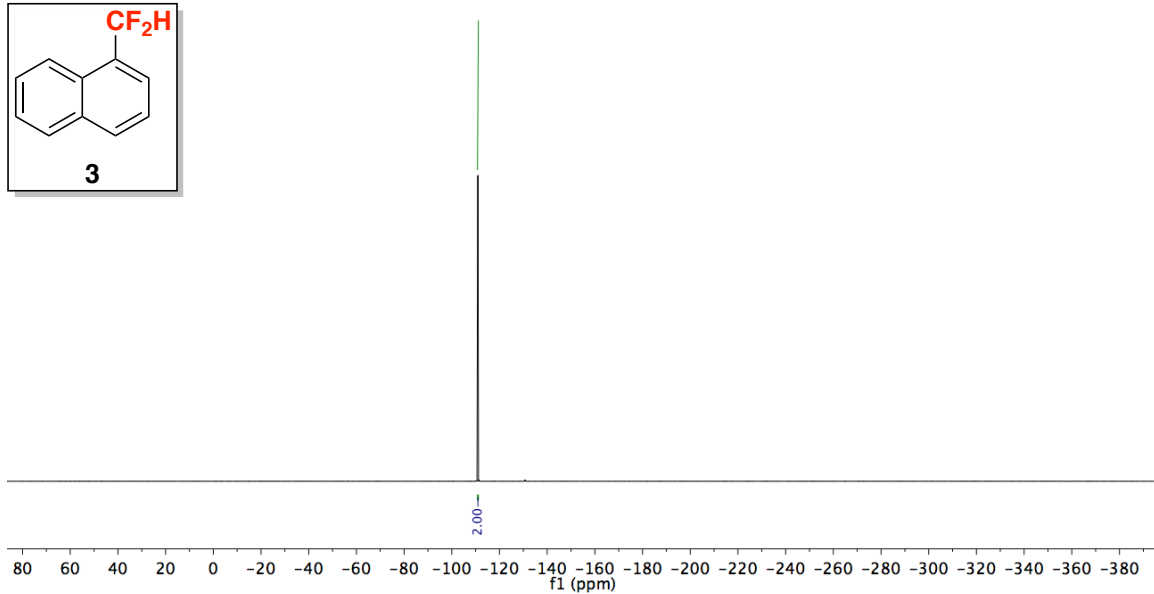
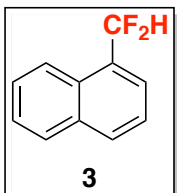


xv. **3** Synthesized Using  $Tf_2O$

$^1H$  NMR in  $CDCl_3$

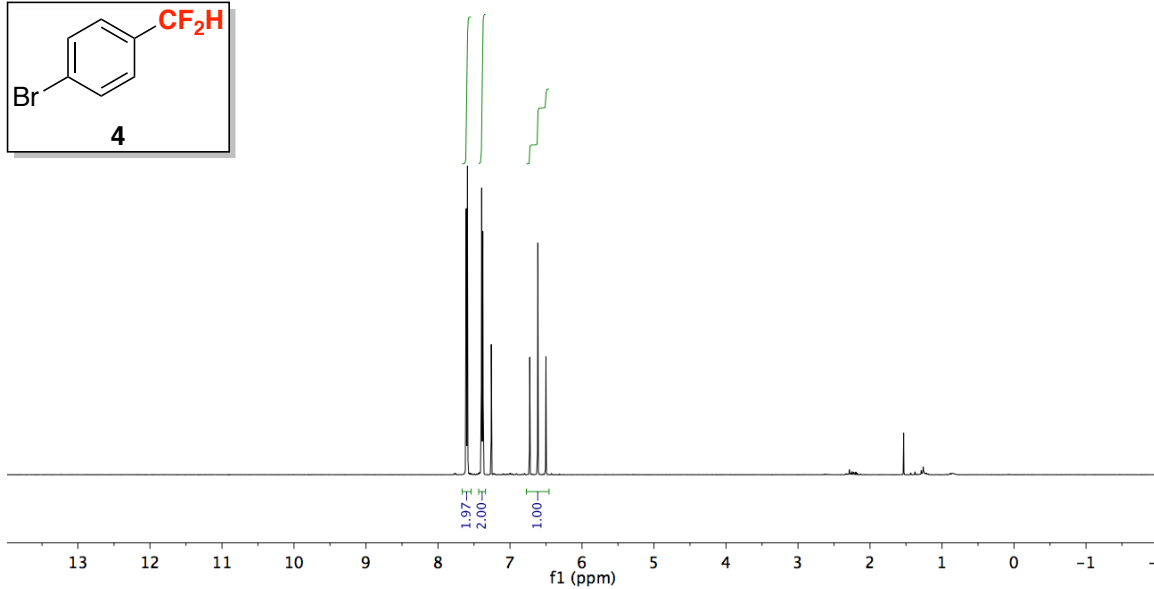
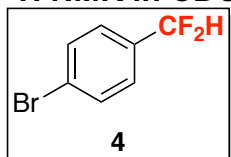


$^{19}F$  NMR in  $CDCl_3$

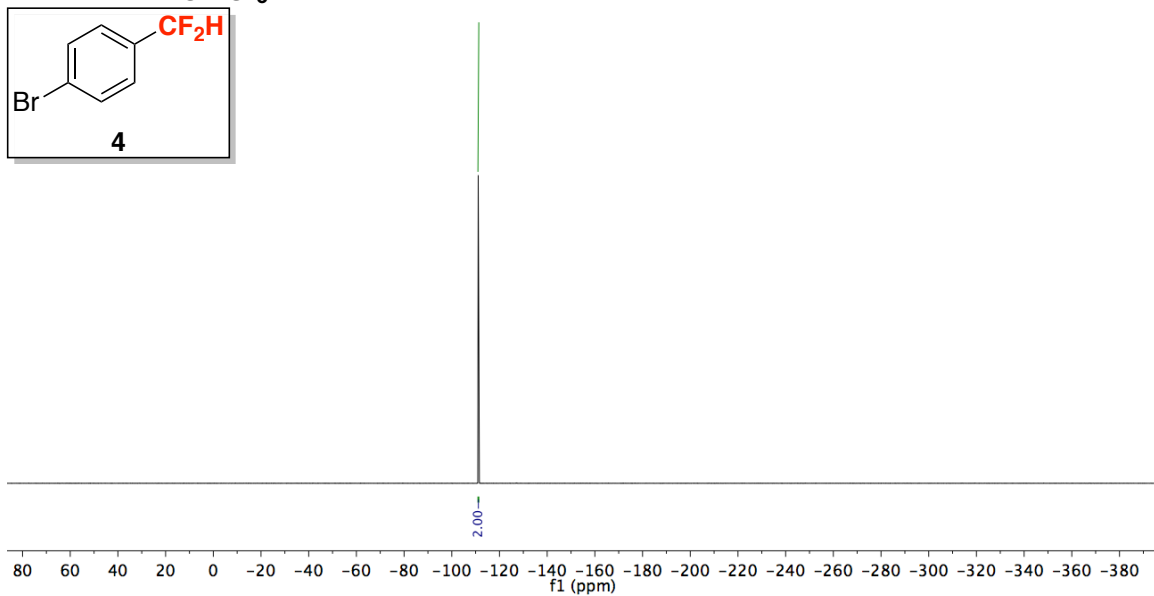
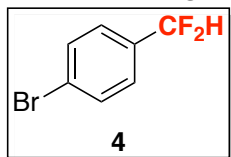


xvi. **4** Synthesized Using  $Tf_2O$

$^1H$  NMR in  $CDCl_3$



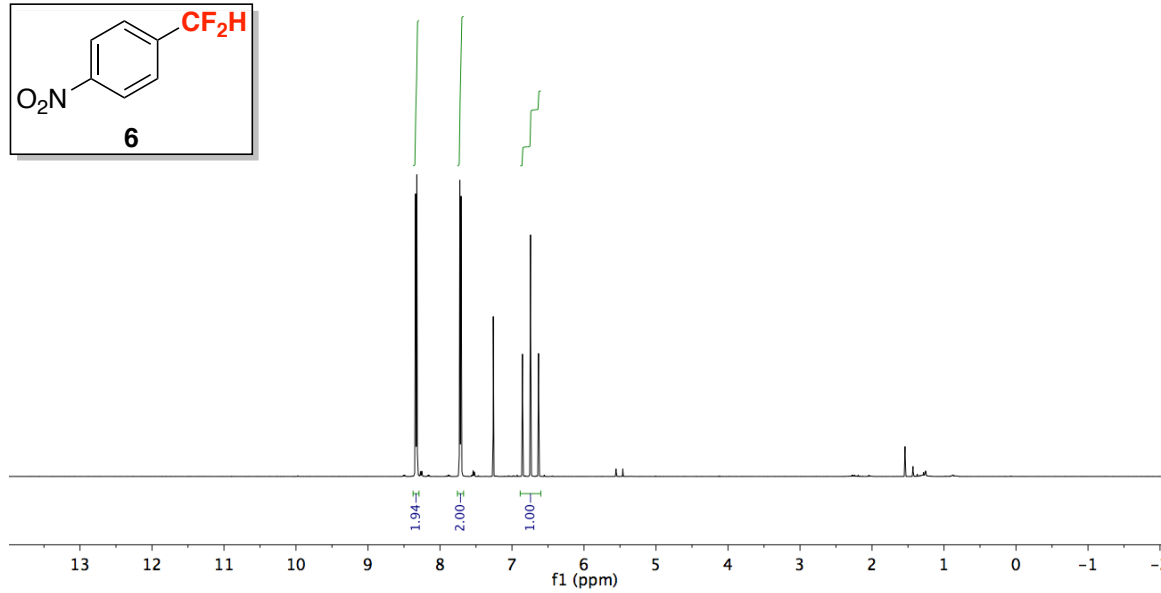
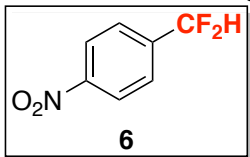
$^{19}F$  NMR in  $CDCl_3$



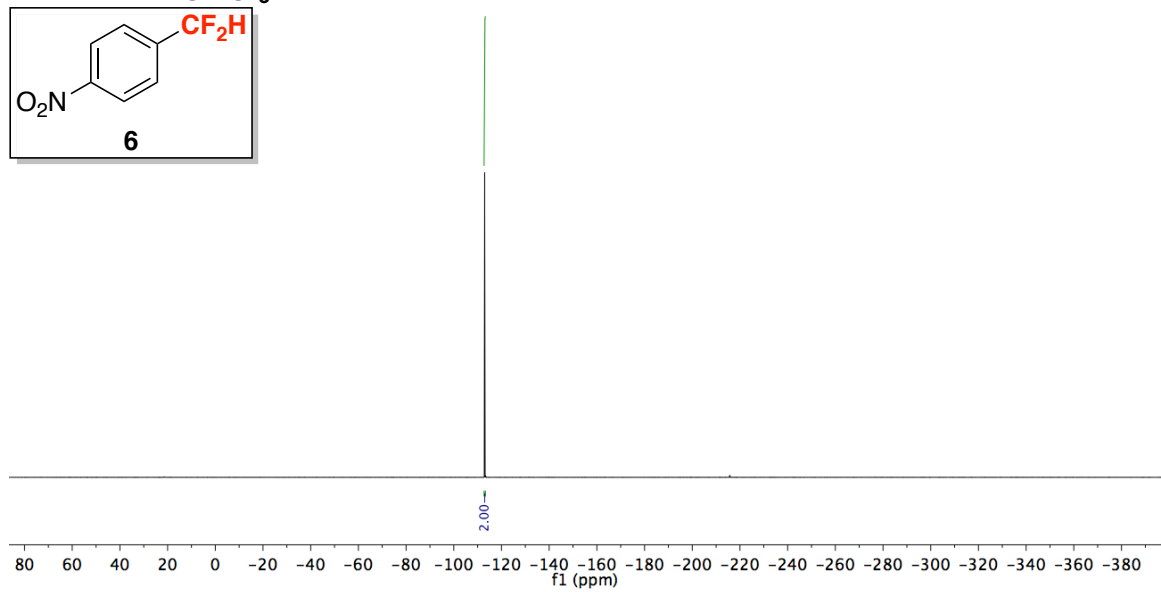
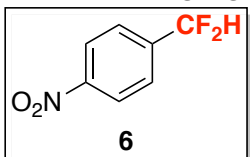


xvii. **6** Synthesized Using  $Tf_2O$

$^1H$  NMR in  $CDCl_3$

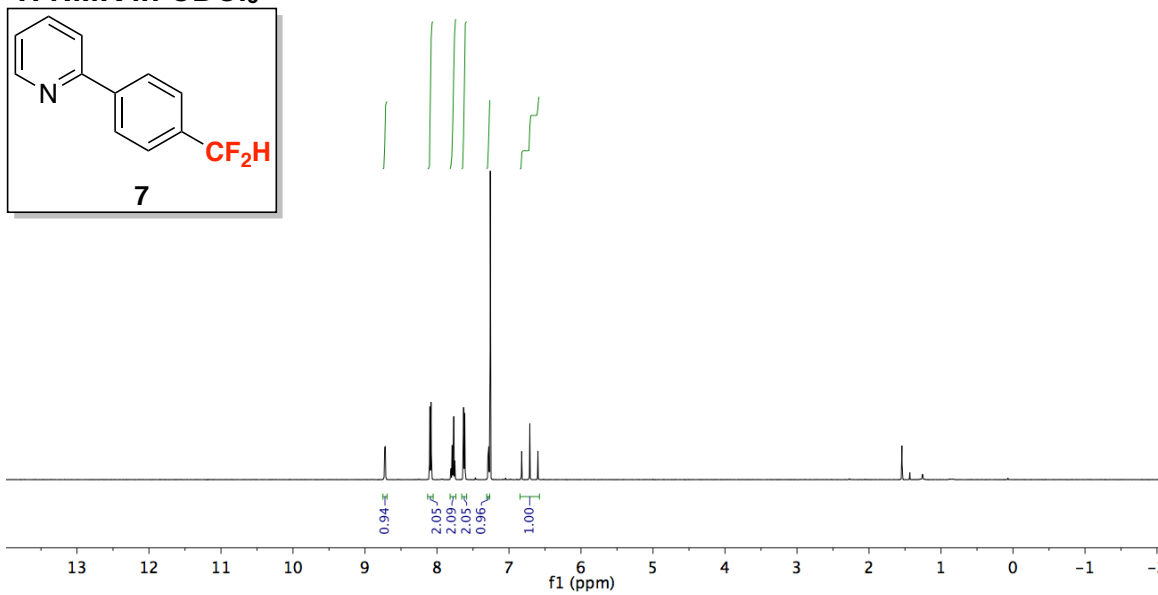


$^{19}F$  NMR in  $CDCl_3$

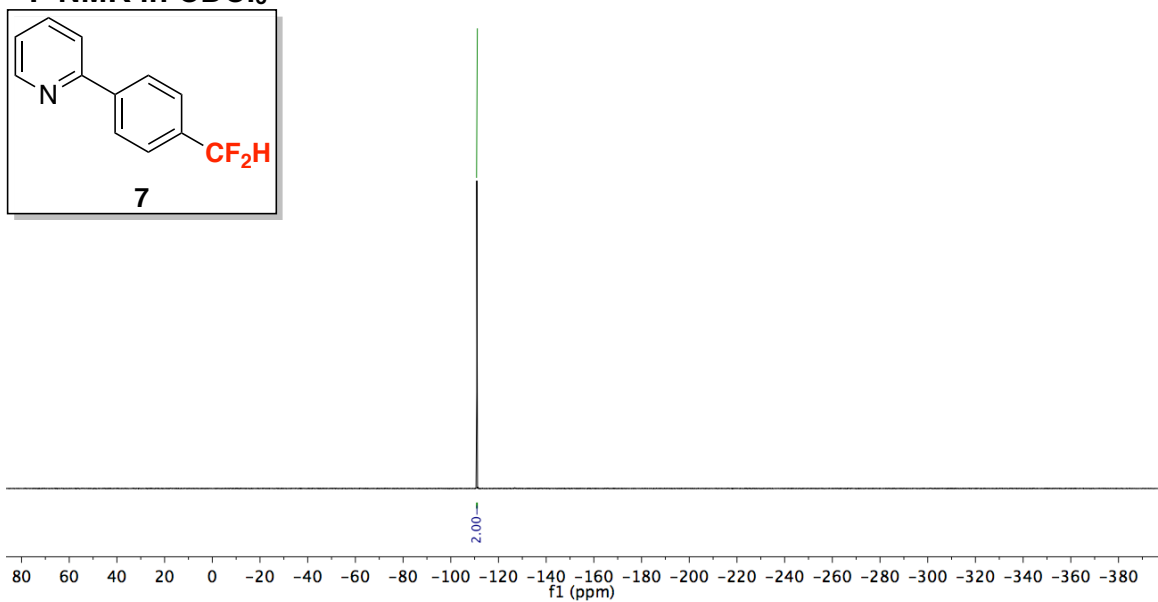


xviii. **7** Synthesized Using  $Tf_2O$

$^1H$  NMR in  $CDCl_3$

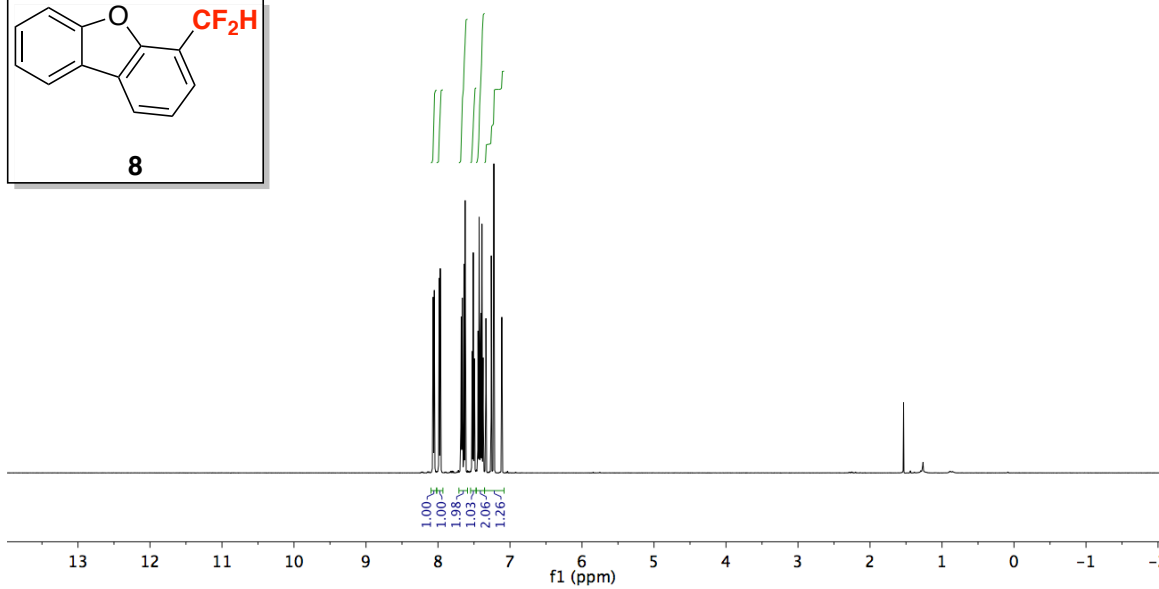
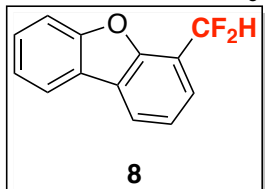


$^{19}F$  NMR in  $CDCl_3$

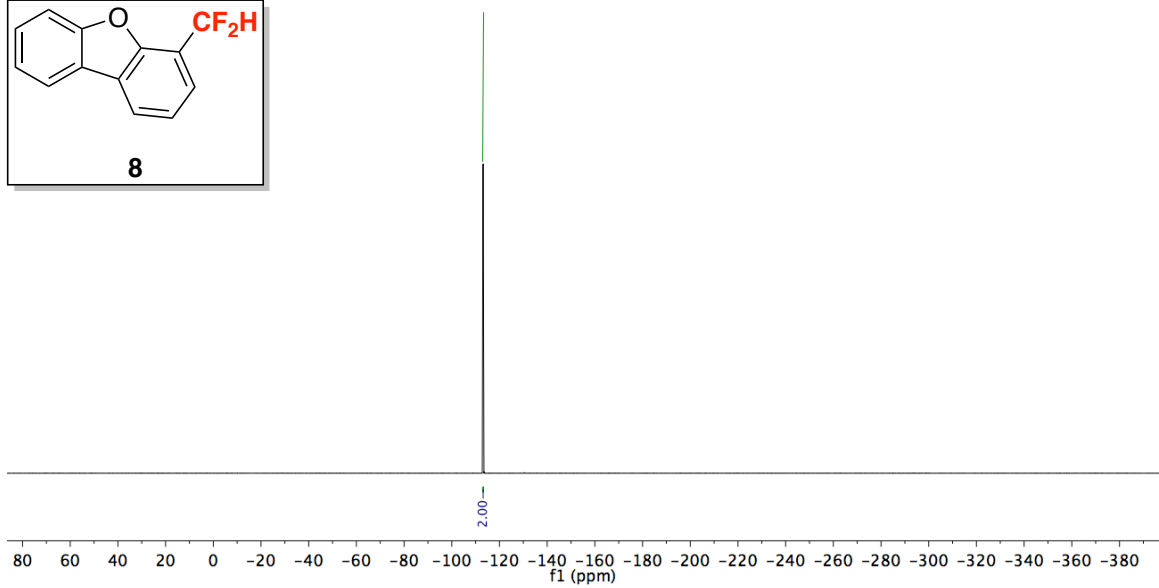
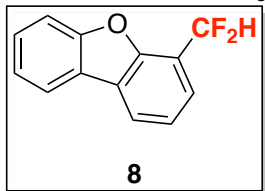


xix. **8** Synthesized Using  $Tf_2O$

$^1H$  NMR in  $CDCl_3$

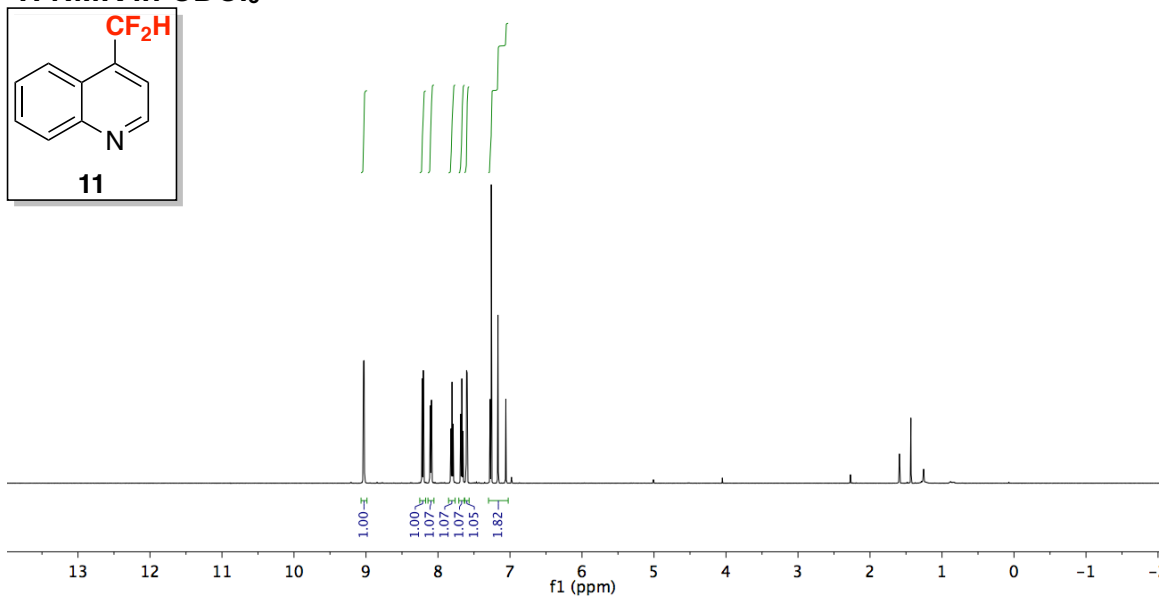


$^{19}F$  NMR in  $CDCl_3$

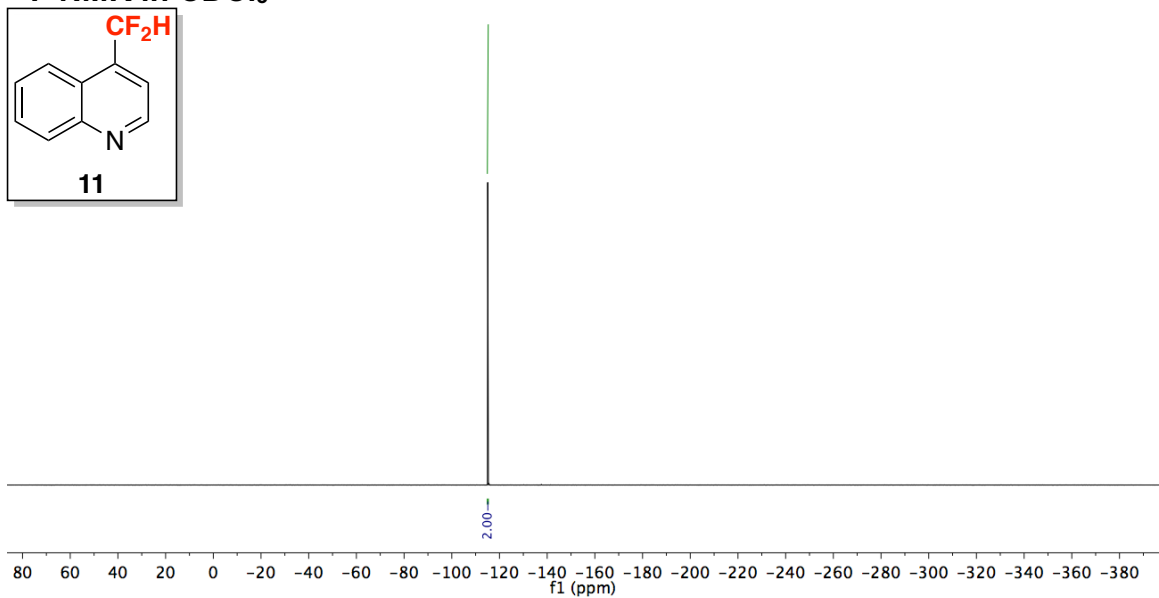


xx. **11 Synthesized Using Tf<sub>2</sub>O**

**<sup>1</sup>H NMR in CDCl<sub>3</sub>**

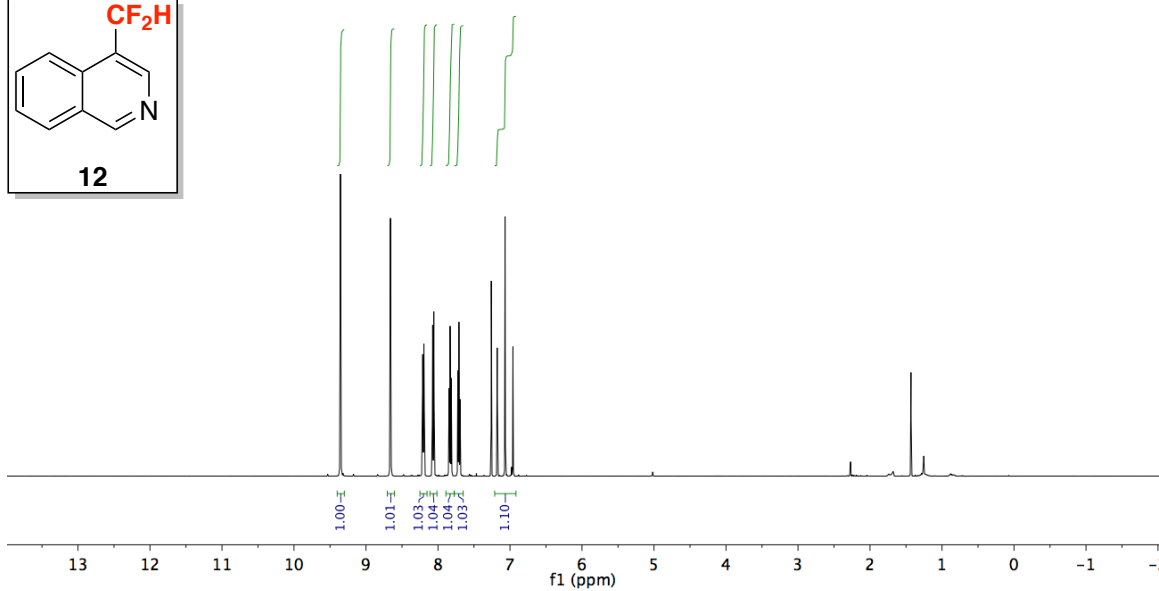
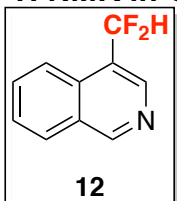


**<sup>19</sup>F NMR in CDCl<sub>3</sub>**



xxi. **12 Synthesized Using Tf<sub>2</sub>O**

**<sup>1</sup>H NMR in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR in CDCl<sub>3</sub>**

