Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Catalytic Reduction of Amides to Amines by Electrophilic Phosphonium Cations via FLP Hydrosilylation

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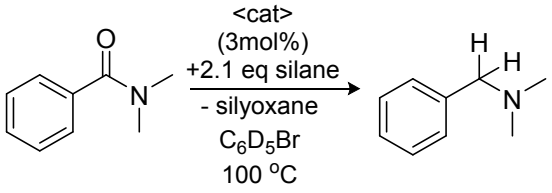
1 Materials and Methods

General Remarks

All preparations and manipulations were carried out under an anhydrous N_2 atmosphere using standard Schlenk and glovebox techniques. All glassware was oven-dried and cooled under vacuum before use. Commercial available reagents such as Et_3SiH, $PhSiH_3$, Ph_2SiH_2, Ph_3SiH, $HSiMe(OEt)_2$, amides, $B(C_6F_5)_3$, and C_6D_5Br were purchased from Sigma Aldrich or Apollo Scientific and used without further purification unless indicated otherwise. $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (**2**),[1] $[Et_3Si][B(C_6F_5)_4]*2(C_7H_8)$,[1] 1,3-dimesityl-4,5-dihydroimidazol-3-ium-2-ylidene,[2] $[(SIMes)PPh_2][B(C_6F_5)_4]$,[3] and $[(SIMes)PFPh_2][B(C_6F_5)_4]_2$ (**3**),[3] were prepared following procedures described in literature. All amides that were not commercial available could be synthesised on a multigram scale using literature procedures.[4,5] CH_2Cl_2, Et_2O, *n*-pentane, and toluene were dried using an Innovative Technologies solvent purification system. C_6D_5Br (Aldrich) was deoxygenated and stored over 4 Å molecular sieves before use. Reactions were monitored using NMR spectroscopy. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, Varian Agilent DD2 500 MHz spectrometer, and Varian Agilent DD2 600 MHz spectrometer. Data for ^1H NMR spectroscopy is reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, dt = doublet of triplets, br = broad), coupling constant (Hz), integration. Data for ^{13}C NMR is reported in terms of chemical shift (δ / ppm). High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART). Mass spectroscopy experiments were run for isolated products and reaction mixtures, however in some cases the high fragmentation of compounds or volatility did not allow for mass peak identification.

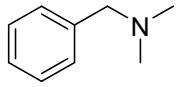
2 General Procedure of Hydrodeoxygenation of Amides



3mol% of catalyst (6.0 mg, 0.0011 mol) was added to a small vial and dissolved in C_6D_5Br (1 mL). $PhSiH_3$ (27.4 µL, 0.33 mmol, 2.1 eq) was micro syringed into the vial, along with amide (20.0 mg, 0.11 mmol, 1 eq). The mixture was stirred in an oil bath for 24h at 100°C. The crude product was quenched with water and NaOH (1 mL), and stirred for 3h at ambient temperature. The mixture was extracted with diethyl ether and dried over $MgSO_4$ to give pure product. The resulting amines were characterized using ^1H NMR, ^{13}C NMR and DART MS.

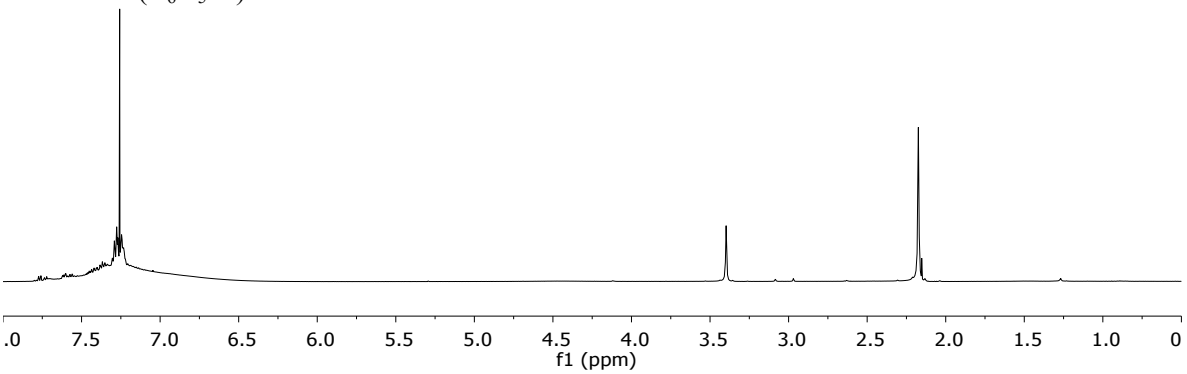
3 Characterization Data from the Reduction of Amides

3.1 N,N-dimethylbenzamine[6]

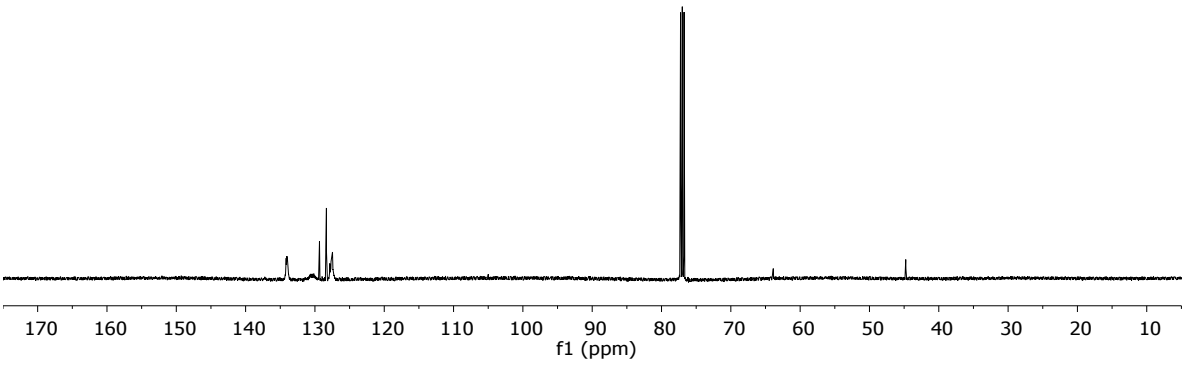


^{1}H NMR (500 MHz, C_6D_5Br) δ = 2.18 (s, 3H), 3.41 (s, 2H), 7.10-7.37 (m, 5H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 44.7, 63.9, 127.6, 128.3, 129.3, 134.1 ppm. **DART MS m/z:** 136.1121 for calculated $M+H^+$ 136.11262

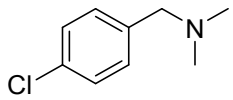
^{1}H NMR: (C_6D_5Br)



^{13}C NMR: ($CDCl_3$)

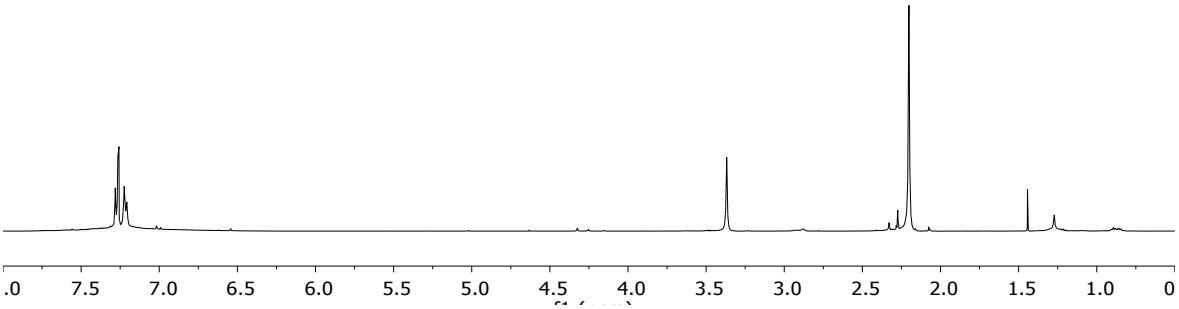


3.2 4-chlorobenzamine[6]

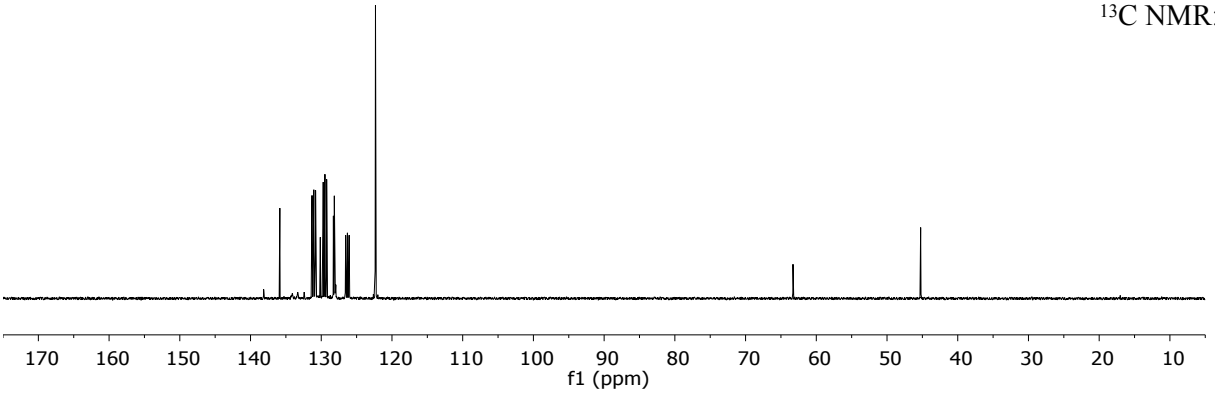


^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.20 (s, 6H), 3,37 (s, 2H), 7.20-7.30 (m, 4H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 45.4, 63.5, 128.2, 129.8, 130.1, 135.9 ppm. **DART MS m/z:** 170.07365 for calculated $M+H^+$ 170.07365

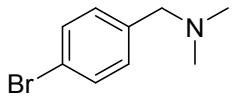
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: (C_6D_5Br)

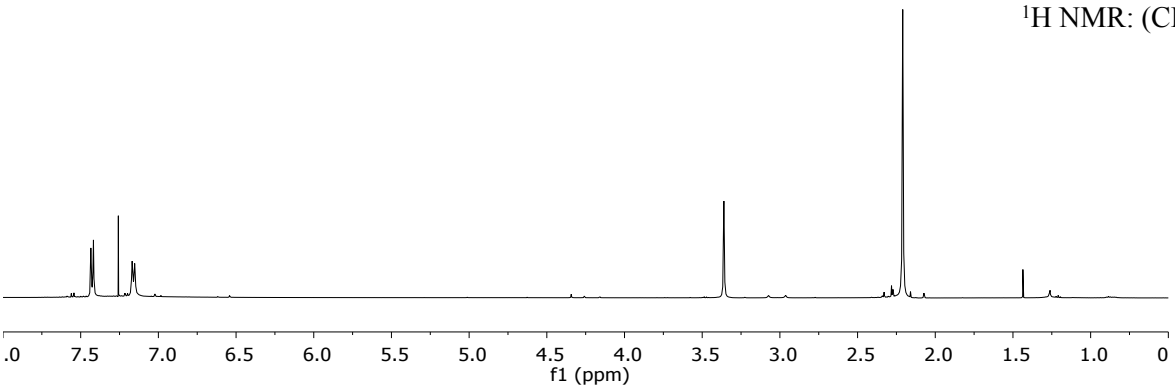


3.3 4-bromobenzamine[6]

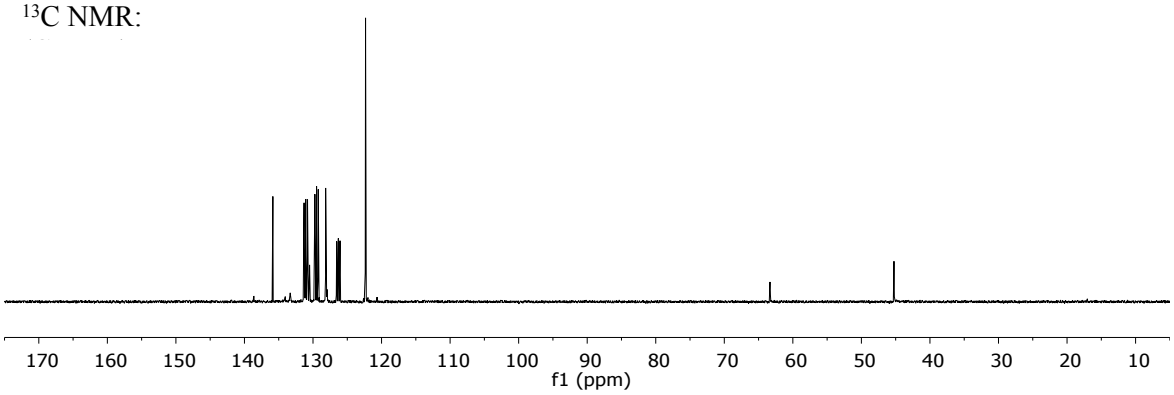


^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.82 (s, 6H), 2.93 (s, 2H), 7.16 (d, 2H), 7.43 (d, 2H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 45.3, 63.2, 128.1, 129.8, 130.5, 135.9 ppm. **DART MS m/z:** 214.02314 for calculated $M+H^+$ 214.02314

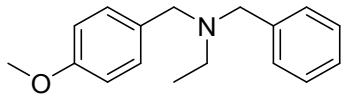
^{1}H NMR: ($CDCl_3$)



^{13}C NMR:

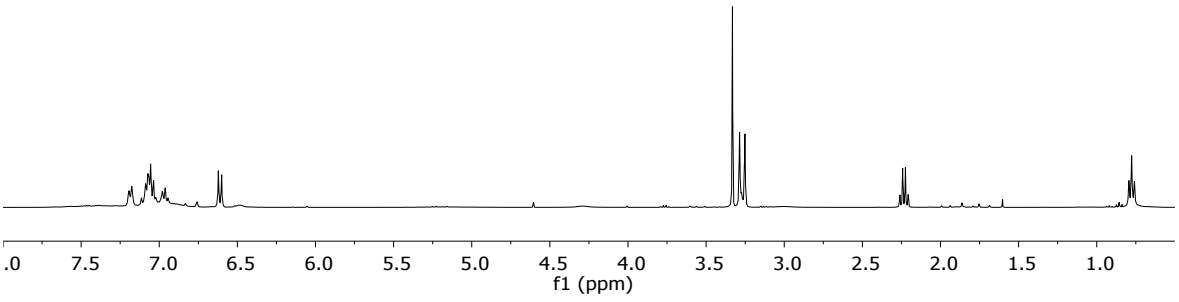


3.4 N-benzyl-N-ethyl-4-methoxybenzamide

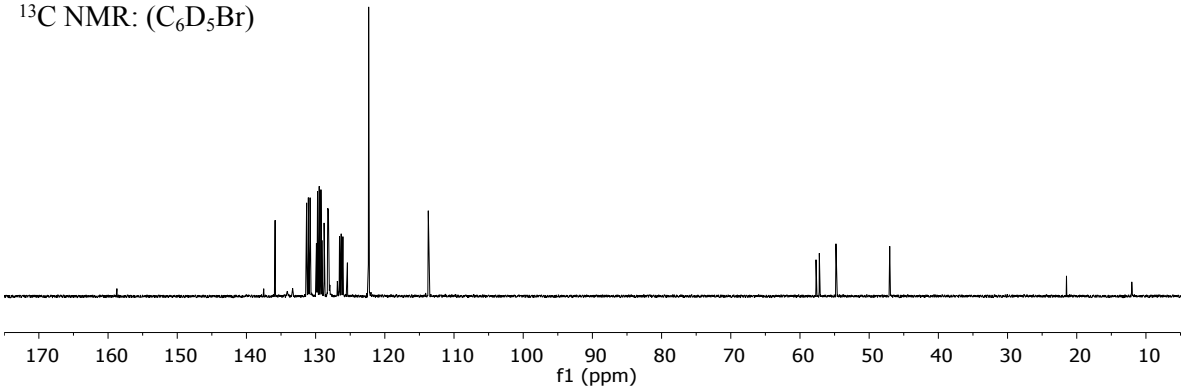


^{1}H NMR (500 MHz, C_6D_5Br) δ = 0.78 (t, 3H), 2.23 (q, 2H), 3.27 (d, 4H), 3.33 (s, 3H), 6.62 (d, 2H), 6.95-7.10 (m, 7H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 12.1, 47.0, 54.8, 57.5, 113.7, 126.8, 128.2, 128.8, 129.8, 129.93, 135.9, 158.7 ppm. **DART MS m/z:** 256.1714 for calculated M+H$^+$ 256.1714

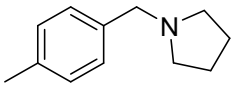
^{1}H NMR: (C_6D_5Br)



^{13}C NMR: (C_6D_5Br)

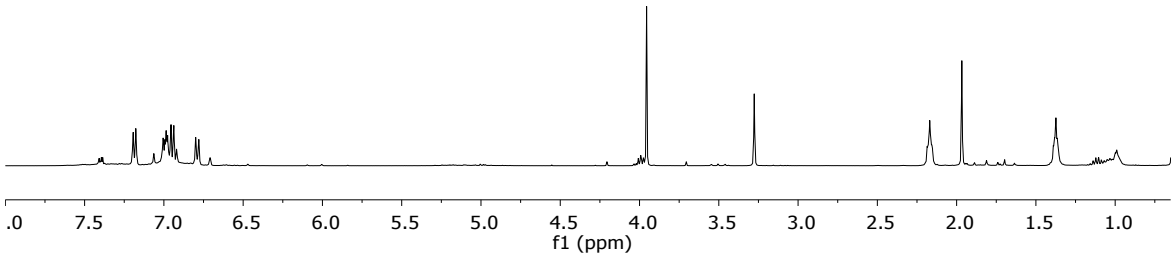


3.5 N-4-tolyoyl pyrolidine



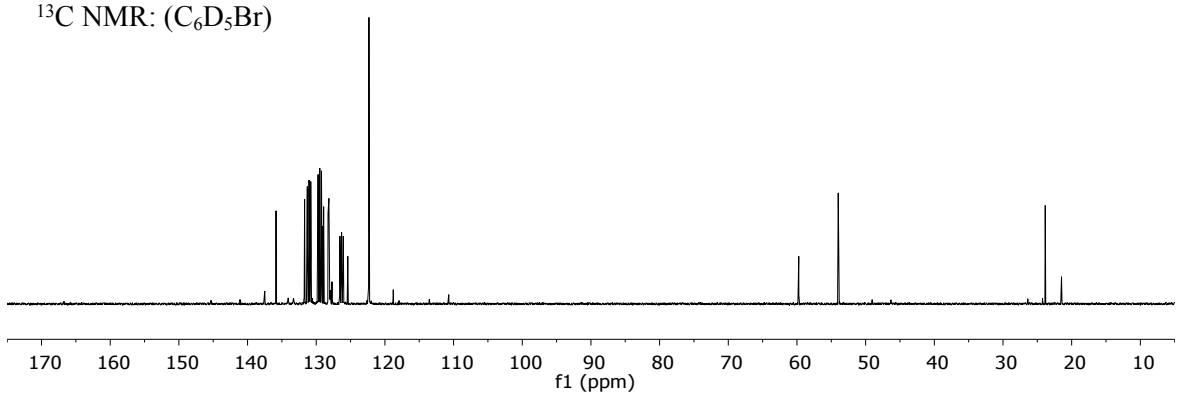
^{1}H NMR (500 MHz, C_6D_5Br) δ = 1.38 (s, 2H), 1.97 (s, 3H), 2.17 (t, 2H), 3.28 (s, 2H), 6.78 (d, 2H), 7.18 (d, 2H) ppm. **^{13}CNMR (125 MHz, C_6D_5Br)** δ = 23.76, 30.38, 38.75, 53.91, 60.15, 68.19, 122.27, 126.38, 129.33, 135.43, 136.68, 167.74 ppm. **DART MS m/z:** 176.143 92 for calculated M+ H^+ 176.143 92

Reaction Mixture ^{1}H NMR: (C_6D_5Br)

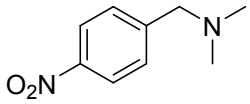


Phenylsilane

^{13}C NMR: (C_6D_5Br)

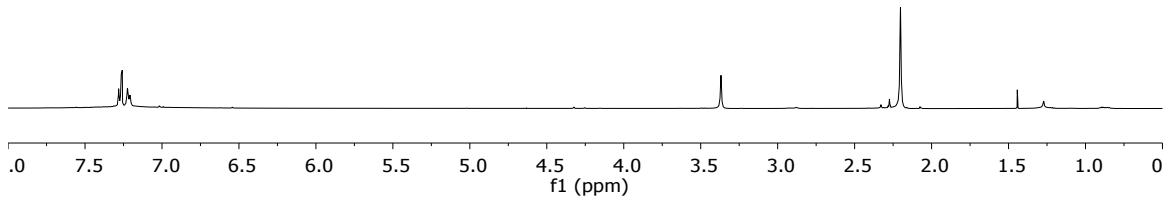


3.6 N,N-dimethyl-4-nitrobenzamine[6]

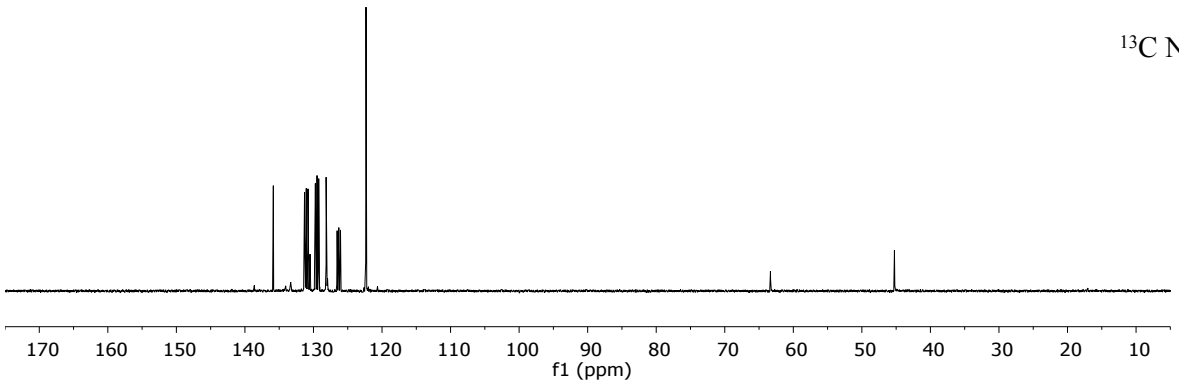


^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.20 (s, 6H), 3.37 (s, 2H), 7.22 (d, 2H), 7.27 (d, 2H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 45.3, 64.5, 128.2, 129.8, 130.8, 135.9 ppm. **DART MS m/z:** 181.09770 for calculated $M+H^+$ 181.09770

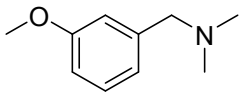
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: (C_6D_5Br)

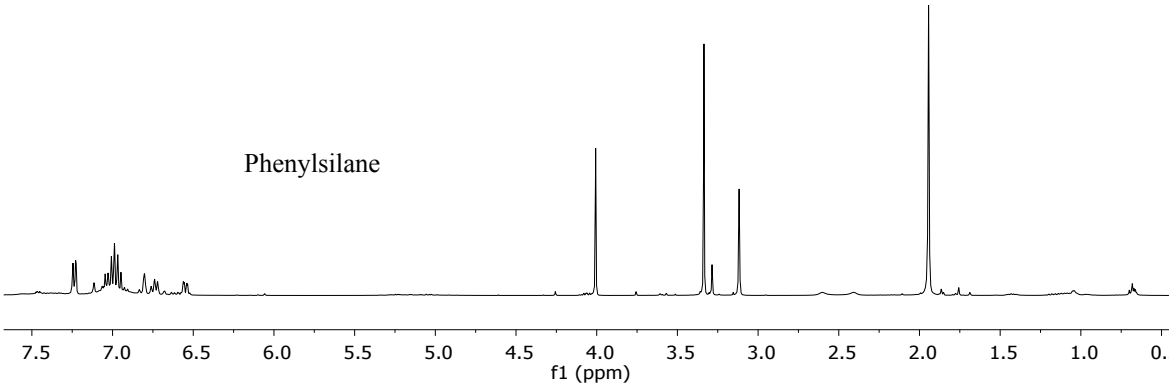


3.7 N,N-dimethyl-3-methoxybenzamine[7]

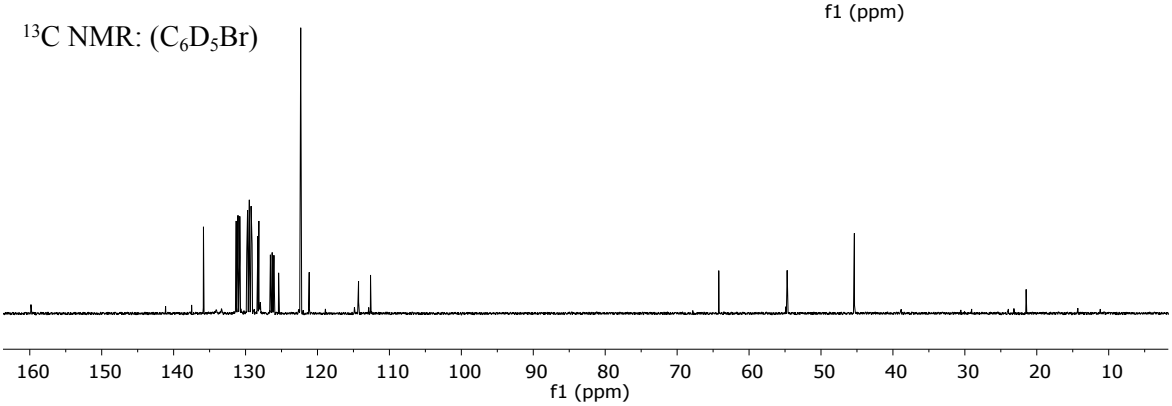


^{1}H NMR (500 MHz, C_6D_5Br) δ = 1.94 (s, 6H), 3.12 (s, 2H), 3.34 (s, 3H), 6.70 (d, 2H), 7.25 (d, 2H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 43.36, 54.71, 64.21, 112.63, 114.29, 121.98, 126.55, 129.83, 130.80, 135.85, 159.85 ppm. **DART MS m/z:** 166.12319 for calculated $M+H^+$ 166.12319

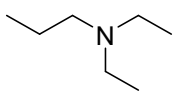
Reaction Mixture ^{1}H NMR: (C_6D_5Br)



^{13}C NMR: (C_6D_5Br)

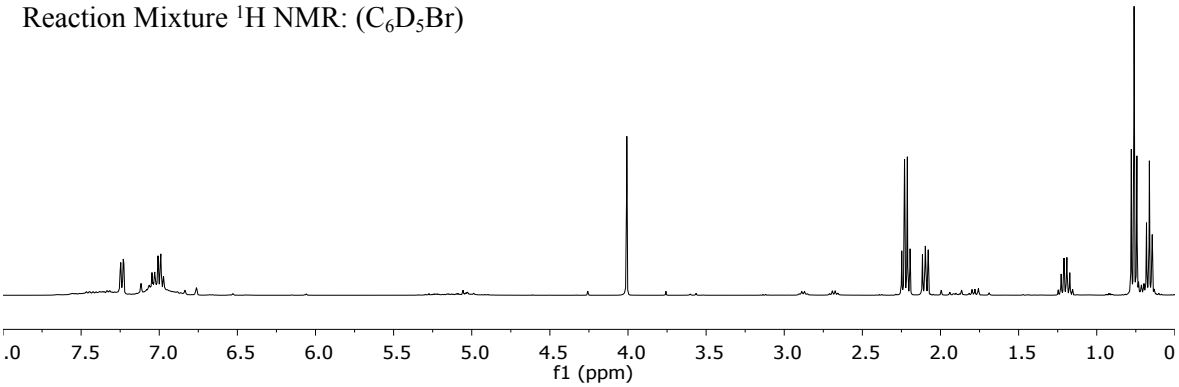


3.8 N,N-diethylpropionamine[8]

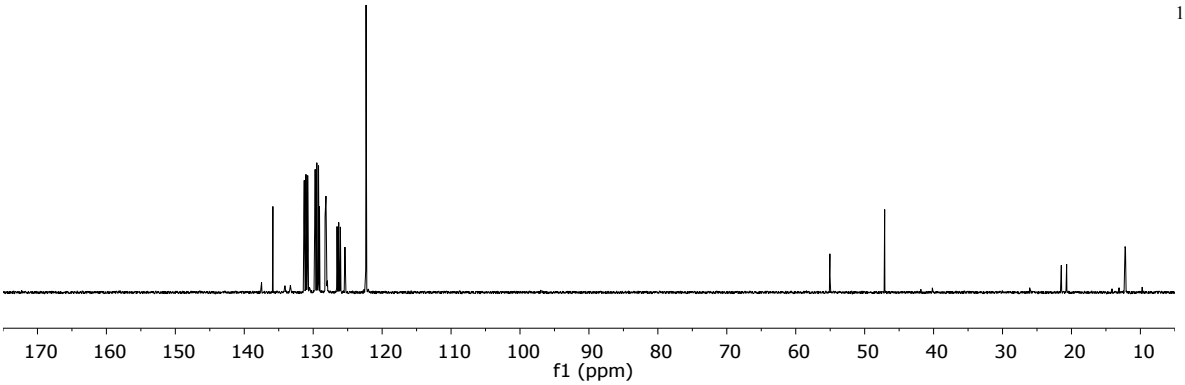


^{1}H NMR (500 MHz, C_6D_5Br) δ = 0.66 (t, 3H), 0.76 (t, 6H), 1.20 (sept, 2H), 2.10 (t, 2H), 2.22 (q, 4H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 12.1, 20.7, 47.1, 55.1 ppm. **DART MS m/z:** 116.14392 for calculated $M+H^+$ 116.14392

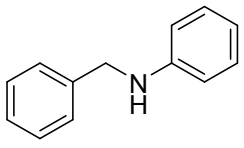
Reaction Mixture ^{1}H NMR: (C_6D_5Br)



^{13}C NMR: (C_6D_5Br)



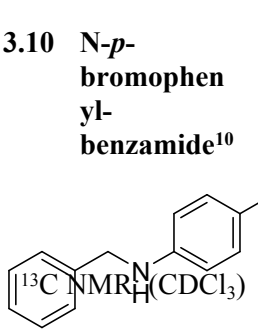
3.9 N-phenyl-benzamide[9]



^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.00 (br, 1H), 4.24 (s, 1H), 6.57 (d, $^3J_{HH}$ = 7.6 Hz, 2H), 6.64 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.07 (dd, $^3J_{HH}$ = 8.6 Hz, 7.2 Hz, 2H), 7.32-7.14 (m, 5H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 48.5, 113.1, 117.8, 127.3, 127.6, 128.7, 129.3, 139.3, 147.9 ppm. **DART MS m/z:** 184.11211 for calculated $M+H^+$ 184.11262

^{1}H NMR: ($CDCl_3$)

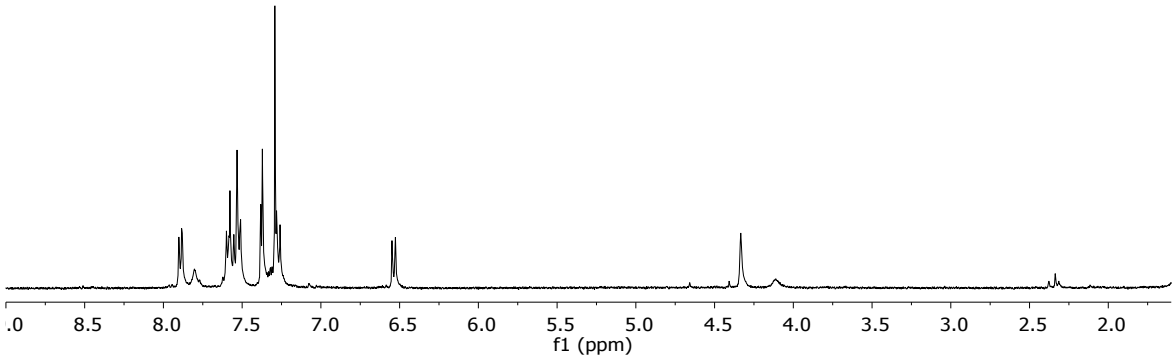
3.10 N-*p*-bromophenyl-benzamide[10]



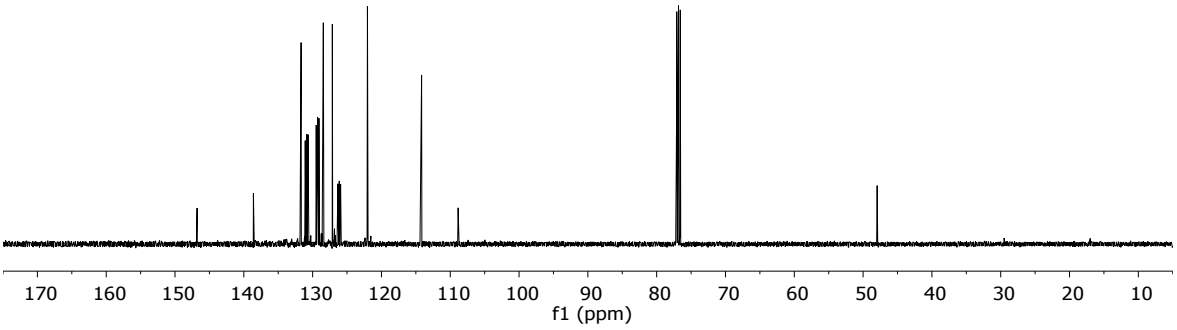
^{13}C NMR ($CDCl_3$)

^{1}H NMR (500 MHz, C_6D_5Br) δ = 3.99 (br, 1H), 4.22 (s, 2H), 6.43 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.14-7.33 (m, 5H), 7.40-7.52 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 47.9, 108.9, 114.1, 122.0, 127.1, 128.9, 131.7, 138.6, 147.8 ppm. **DART MS m/z:** 262.02258 for calculated $M+H^+$ 262.02314

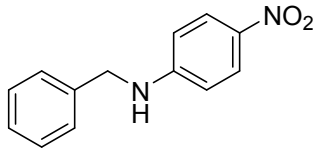
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

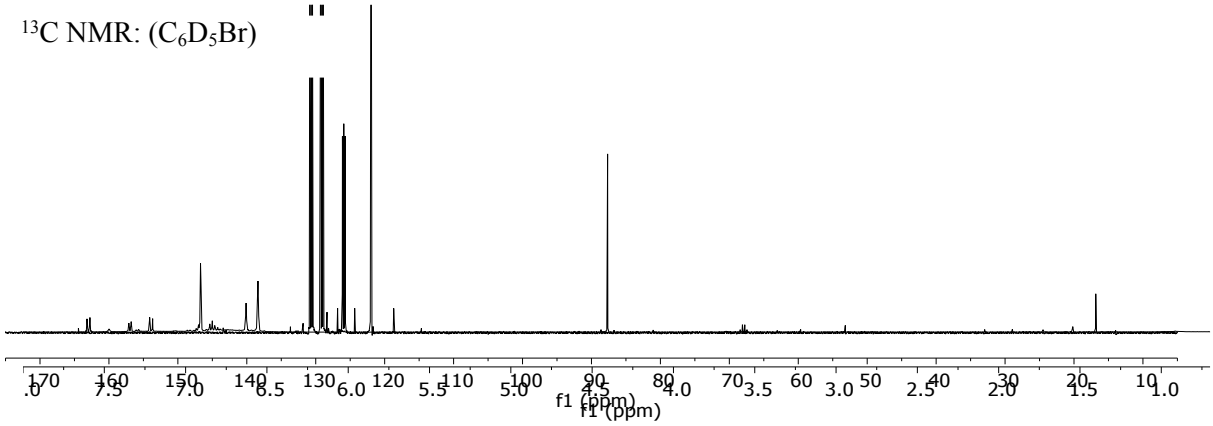


3.11 N-*p*-nitrophenyl-benzamide[11]



^{1}H NMR (500 MHz, C_6D_5Br) δ = 4.71 (s, 2H), 7.07-7.21 (m, 5H), 7.52 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 7.78 (s, 1H), 7.90 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 53.2, 114.6, 188.8, 124.5, 127.9, 128.4, 131.8, 133.7, 143.5 ppm. **DART MS m/z:** 229.09770 for calculated

^{13}C NMR: (C_6D_5Br)

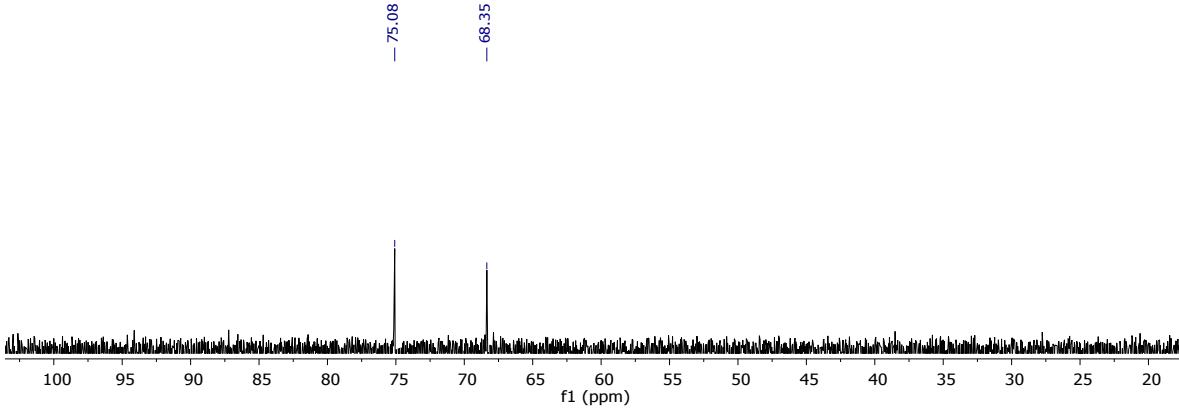


$M+H^+$ 229.09770

4 Stoichiometric Reactions with Catalyst 2

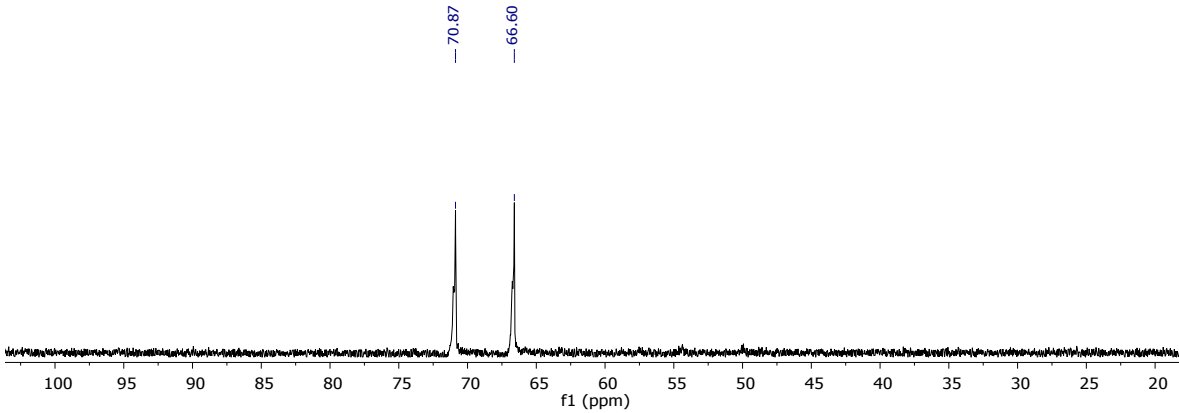
4.1 Stoichiometric Reaction of Catalyst 2 with Dibenzylamine

^{31}P $\{^{1}H\}$ NMR: (CH_2Cl_2)



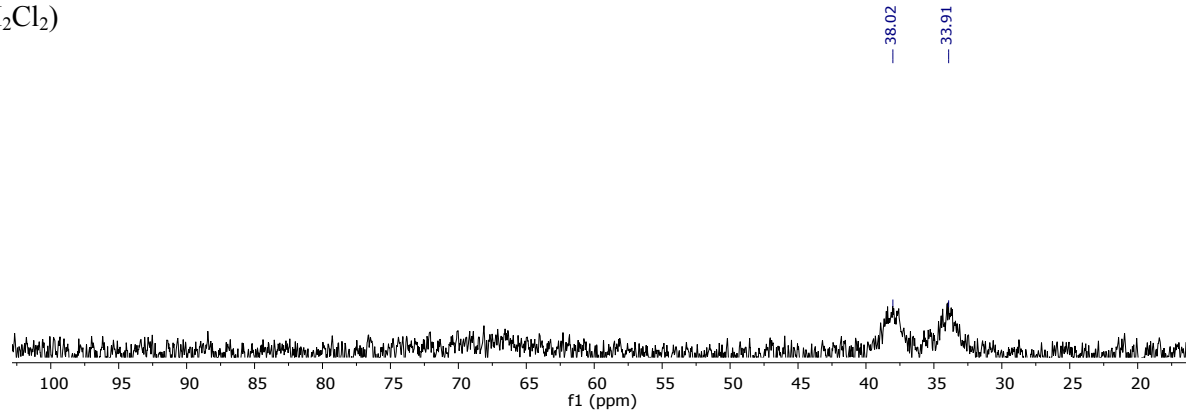
4.2 Stoichiometric Reaction of Catalyst 2 with N-phenylbenzamide

^{31}P $\{^{1}H\}$ NMR: (CH_2Cl_2)

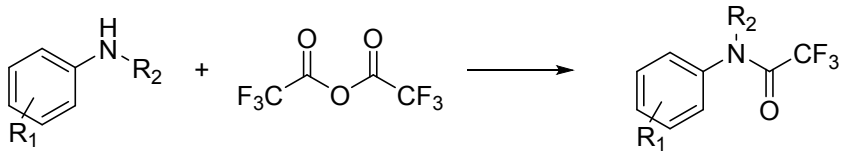


4.3 Stoichiometric Reaction of Catalyst 2 with N-benzylbenzamide

^{31}P {^{1}H} NMR: (CH_2Cl_2)



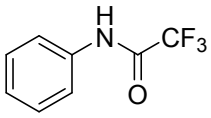
5 General Procedure for Preparing CF3-substitutes Amides



A solution of amine (2.7 mmol) and 10 mL dichloromethane was added to a 20 mL vial followed by stirring. Trifluoroacetic anhydride (2 eq, 5.4 mmol) was added to the mixture and stirred overnight at room temperature. The organic phase was extracted with saturated sodium carbonate and dried over $MgSO_4$, resulting in quantitative yield.

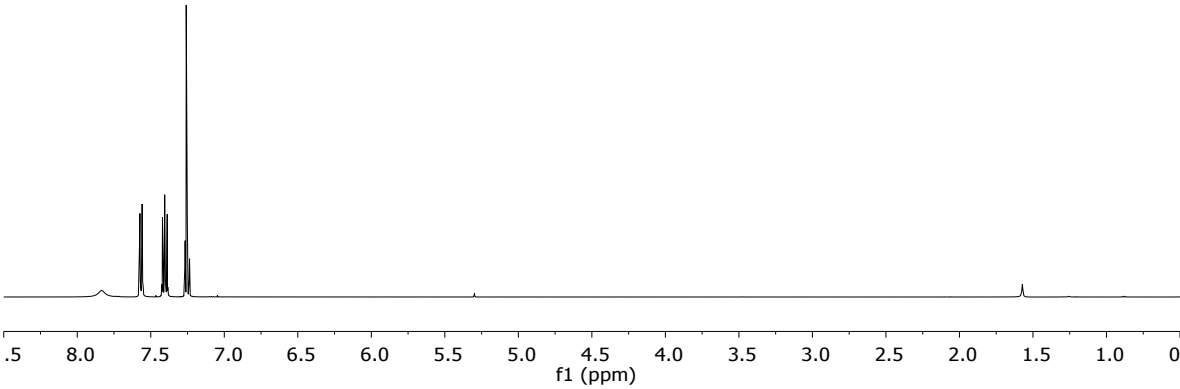
6 Characterization Data from the Reduction of Amides

6.1 2,2,2-trifluoro-N-phenylacetamide[12]

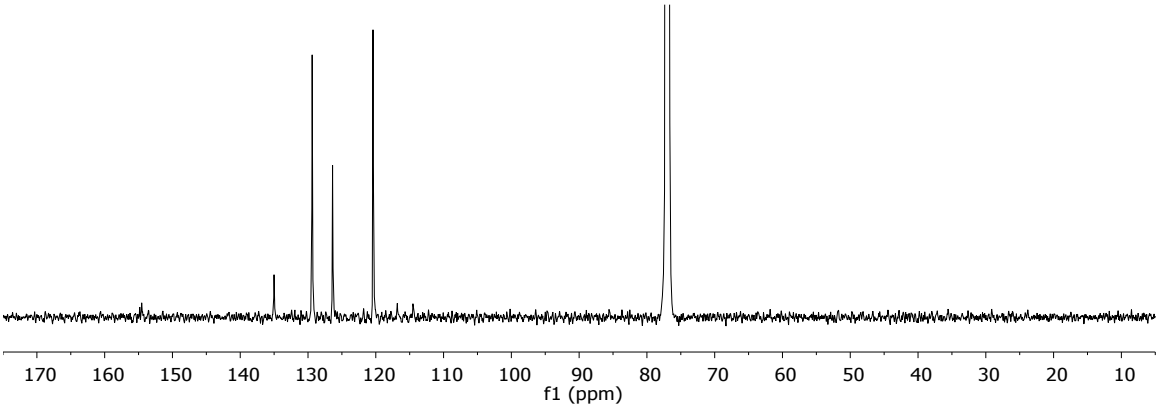


^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.09 (br, 1 H), 7.52 (d, 2H), 7.33 (t, 2H), 7.18 (t, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 115.7 (q, $^{1}J_{CF}$ = 288.5 Hz), 120.5, 126.5, 129.3, 134.9, 155.0 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.7 ppm. **DART MS m/z:** 190.04754 for calculated $M+H^+$ 190.04797

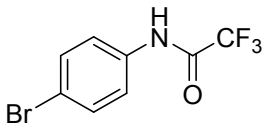
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

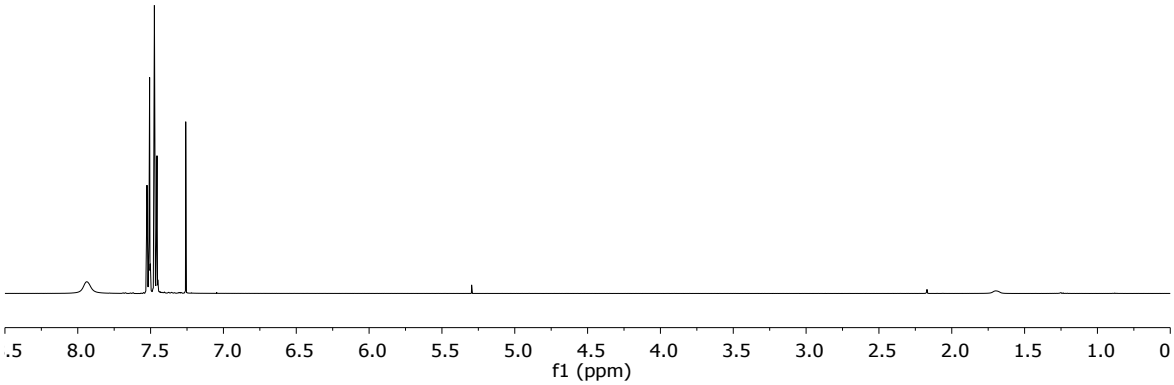


6.2 N-(4-bromophenyl)-2,2,2-trifluoroacetamide[13]

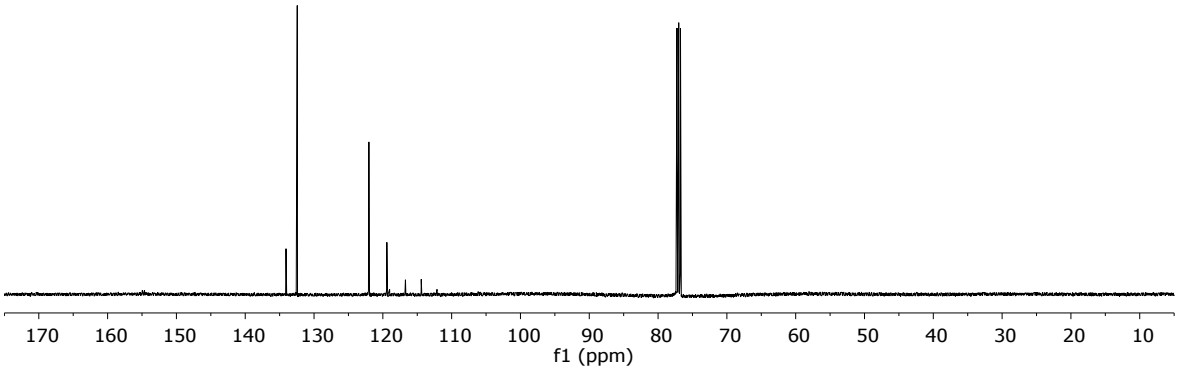


^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 (br, 1 H), 7.50 (m, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 115.6 (q, $^{1}J_{CF}$ = 288.7 Hz), 119.3, 122.0, 132.4, 134.2, 154.7 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.7 ppm. **DART MS m/z:** 267.95849 for calculated $M+H^+$ 267.95849

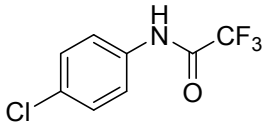
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

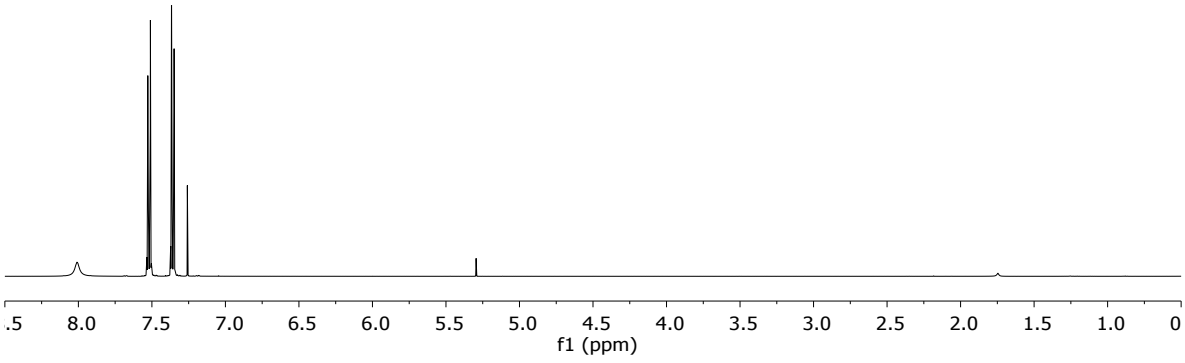


6.3 N-(4-chlorophenyl)-2,2,2-trifluoroacetamide

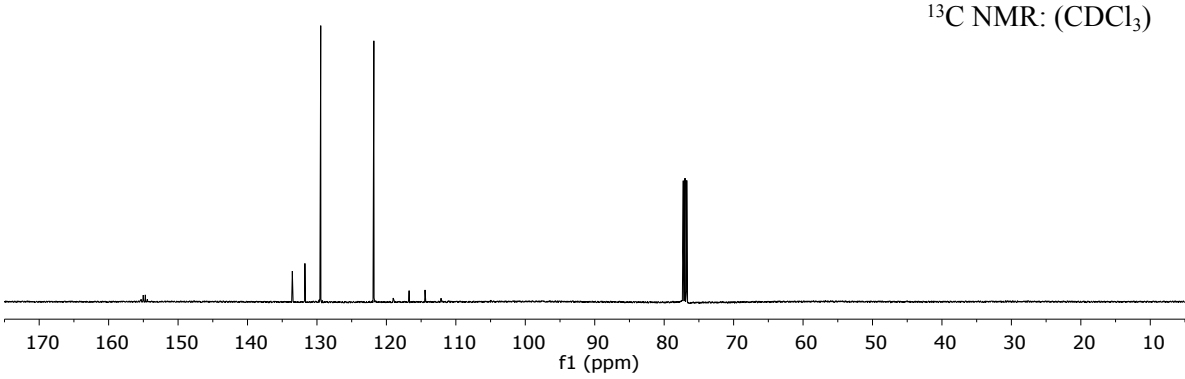


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 (br, 1 H), 7.52 (m, 2H), 7.37 (m, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 115.6 (q, $^{1}J_{CF}$ = 288.6 Hz), 121.8, 129.5, 131.7. 133.6, 154.6 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.7 ppm. **DART MS m/z:** 224.00900 for calculated $M+H^+$ 224.00900

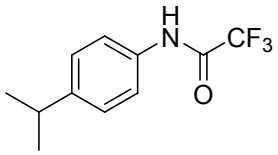
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

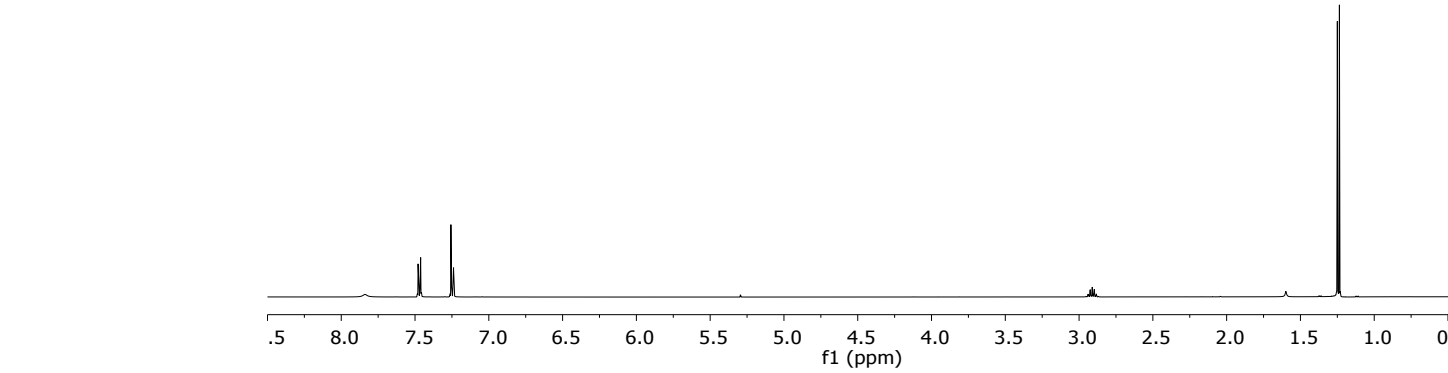


6.4 2,2,2- trifluoro-N-(4-isopropylphenyl)-acetamide

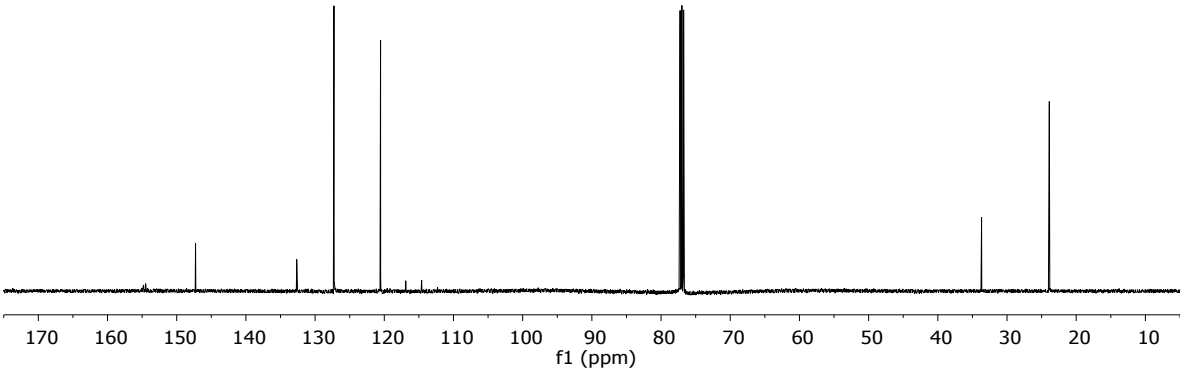


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84 (br, 1 H), 7.47 (m, 2H), 7.25 (m, 2H), 2.91 (sept, 2H), 1.24 (s, 6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 23.9, 33.7, 115.7 (q, $^{1}J_{CF}$ = 288.7 Hz), 120.5, 127.3, 132.6, 147.3, 154.6 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.7 ppm. **DART MS m/z:** 232.09468 for calculated M+H^{+} 232.09492

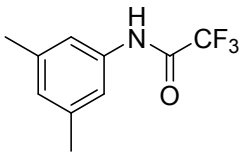
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

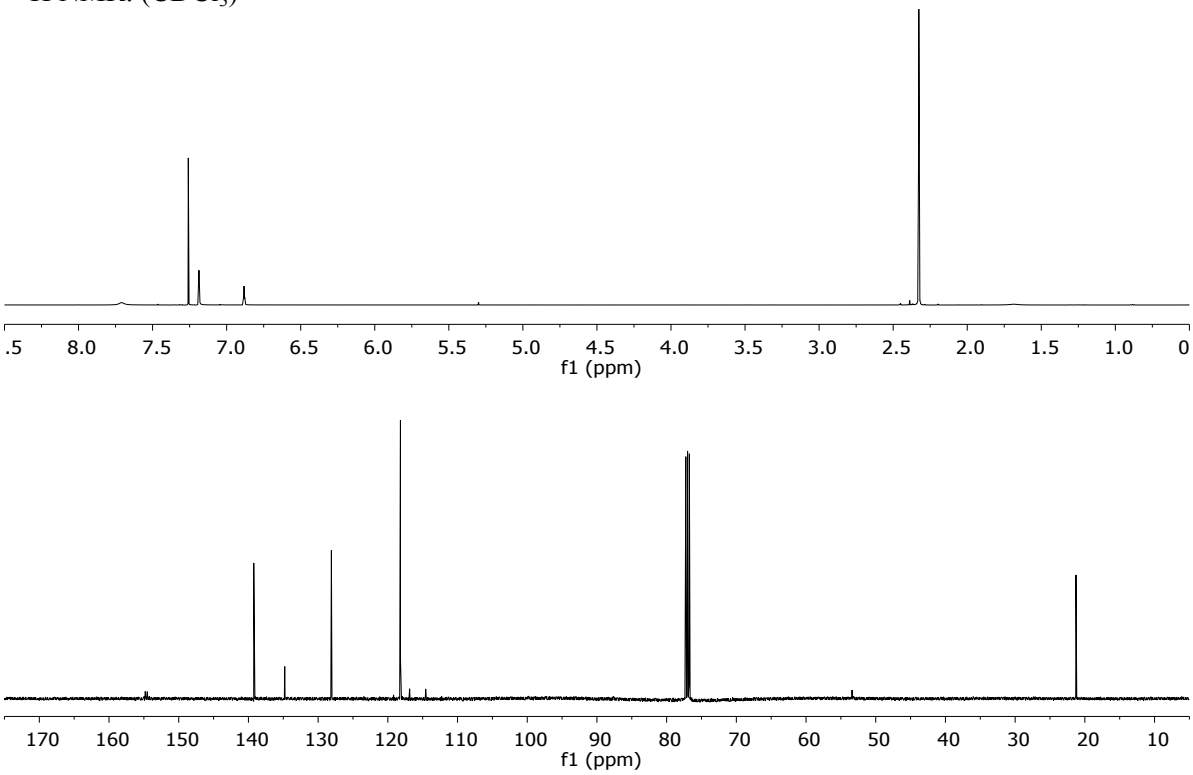


6.5 2,2,2-trifluoro-N-(3,5-methylphenyl)-acetamide

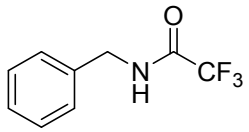


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.79 (br, 1H), 7.18 (m, 2 H), 6.88 (m, 1H), 2.32 (s, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 21.3, 115.7 (q, $^{2}J_{CF}$ = 288.8 Hz), 118.2, 128.1, 134.8, 139.2, 154.6 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.8 ppm. **DART MS m/z:** 218.07884 for calculated M+H^{+} 218.07927

^{1}H NMR: ($CDCl_3$)

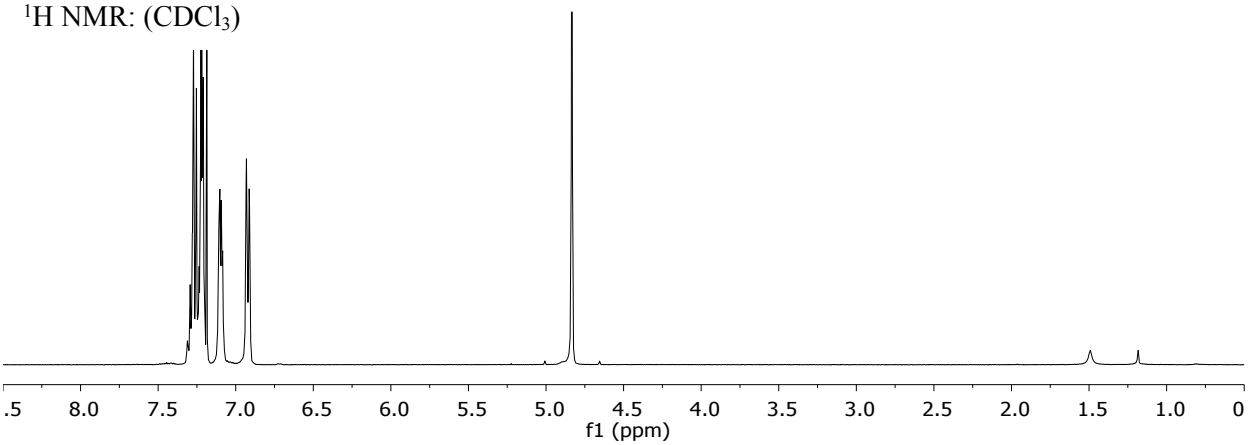


6.6 2,2,2- trifluoro-N-benzylacetamide[14]

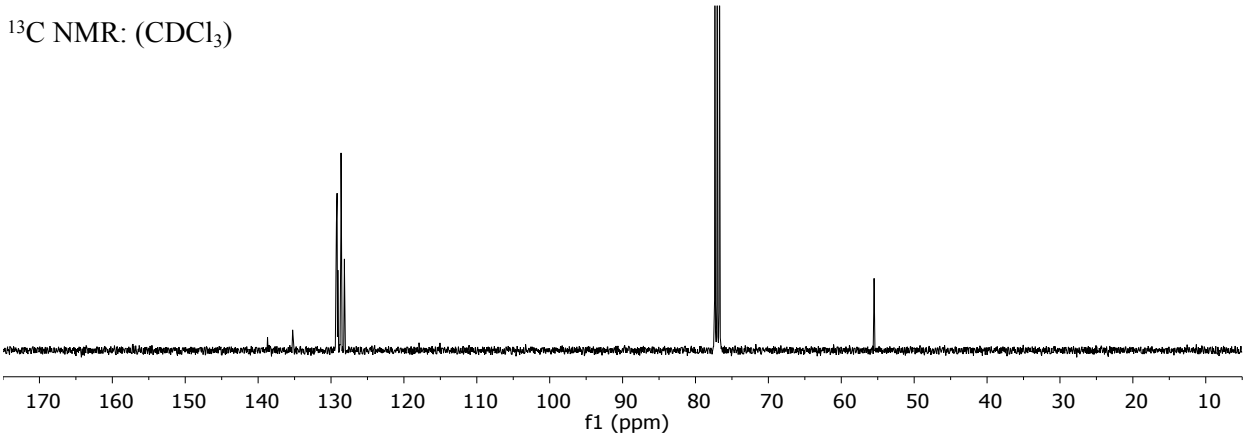


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44 (br, 1H), 7.32-7.20 (m, 2H), 7.14-7.07 (m, 1H), 6.92 (d, $^3J_{HH}$ = 7.0 Hz, 2H), 4.83 (s, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 55.5, 115.1, 128.2, 128.6, 129.2, 135.3, 157.3 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.6 ppm. **DART MS m/z:** 204.05728 for calculated $M+H^+$ 204.05915

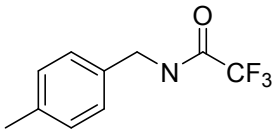
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)



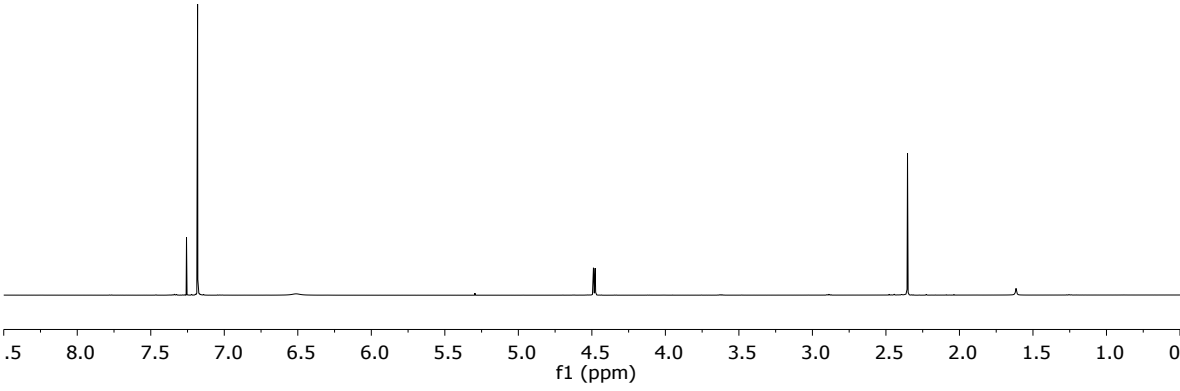
6.7 2,2,2- trifluoro-N-(4-methybenzyl)-acetamide

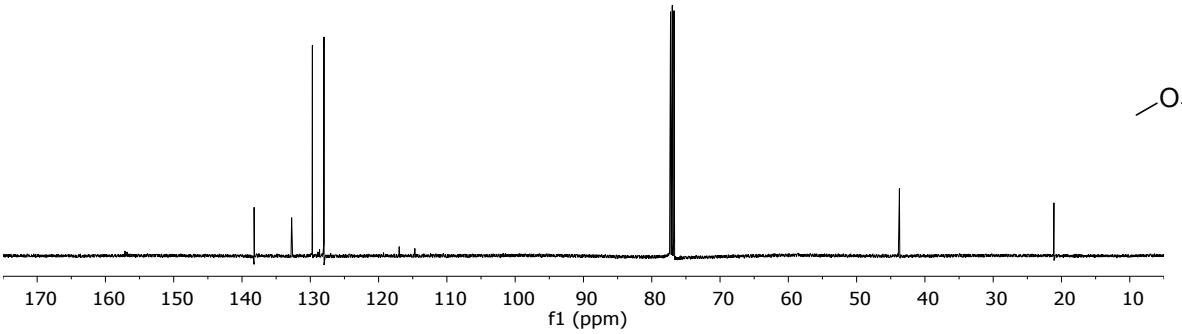


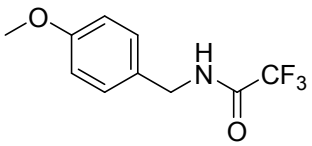
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.18 (s, 4H), 6.51 (br, 1 H), 4.48 (dt, 2H), 2.35 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 21.1, 43.7, 115.8 (q, $^{1}J_{CF}$ = 287.9 Hz), 128.0, 129.7, 132.7, 138.2, 156.0 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.9 ppm. **DART MS m/z:** 218.07998 for calculated $M+H^+$ 218.07927

^{1}H NMR: ($CDCl_3$)

6.8 2,2,2-trifluoro-N-(4-methoxyphenyl)-acetamide

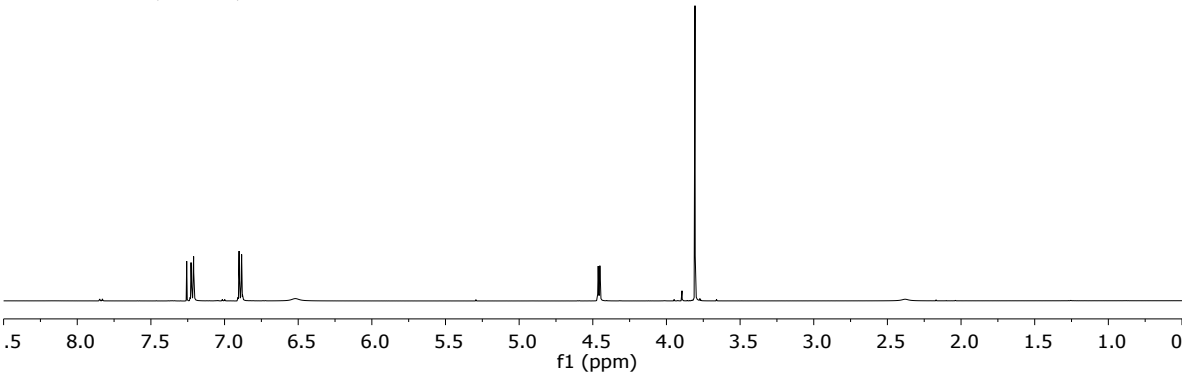






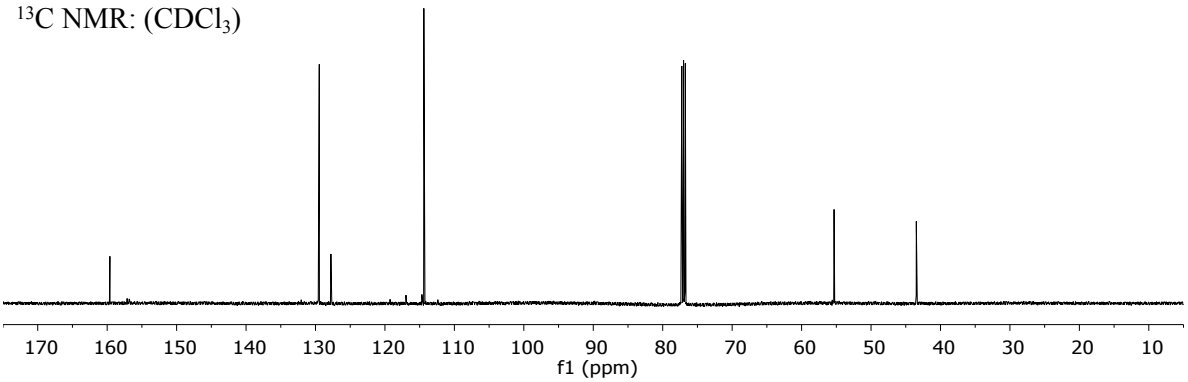
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.24-7.19 (m, 2H), 6.90 (m, 2 H), 6.53 (s, 1H), 4.46 (s, 2H), 3.81 (s, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 43.5, 55.3, 114.4, 116.9, 127.8, 129.4, 156.8, 159.6 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.9 ppm. **DART MS m/z:** 234.18542 for

^{1}H NMR: ($CDCl_3$)

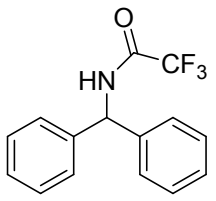


calculated $M+H^+$ 266.07927

^{13}C NMR: ($CDCl_3$)

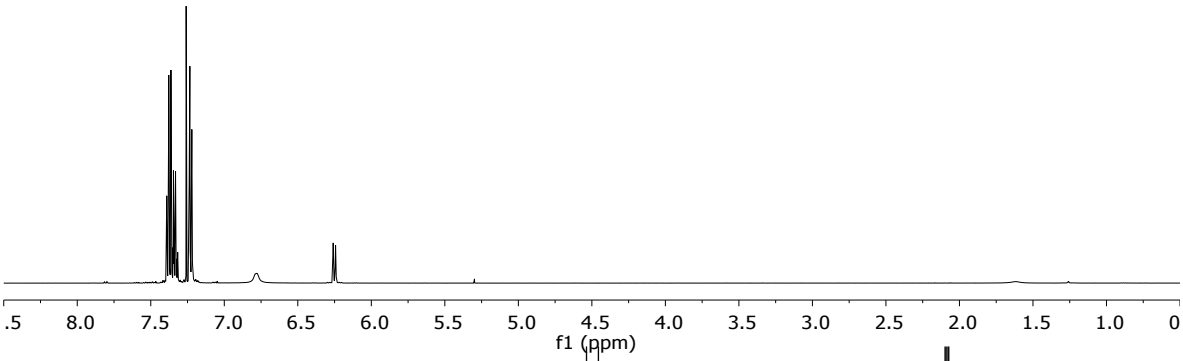


6.9 2,2,2-trifluoro-N-(diphenylmethyl)- acetamide

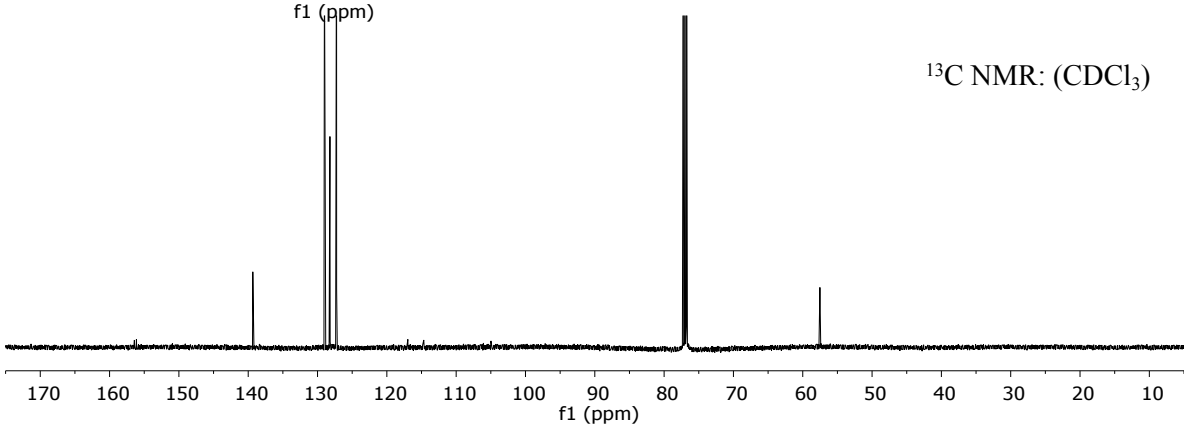


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.40-7.31 (m, 6H), 7.23 (m, 4 H), 6.78 (s, 1H), 6.25 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 57.5, 115.8 (q, $^{1}J_{CF}$ = 288.2 Hz), 127.2, 128.2, 129.0, 139.3, 156.3 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -75.6 ppm. **DART MS m/z:** 280.09483 for calculated $M+H^+$ 280.09492

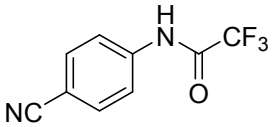
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

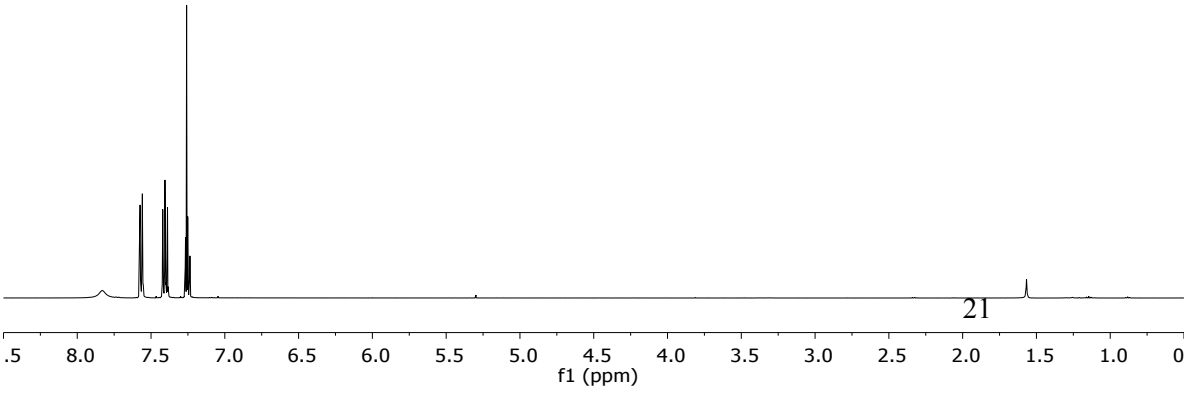


6.10 2,2,2-trifluoro-N-(4-methoxyphenyl)- acetamide[13]

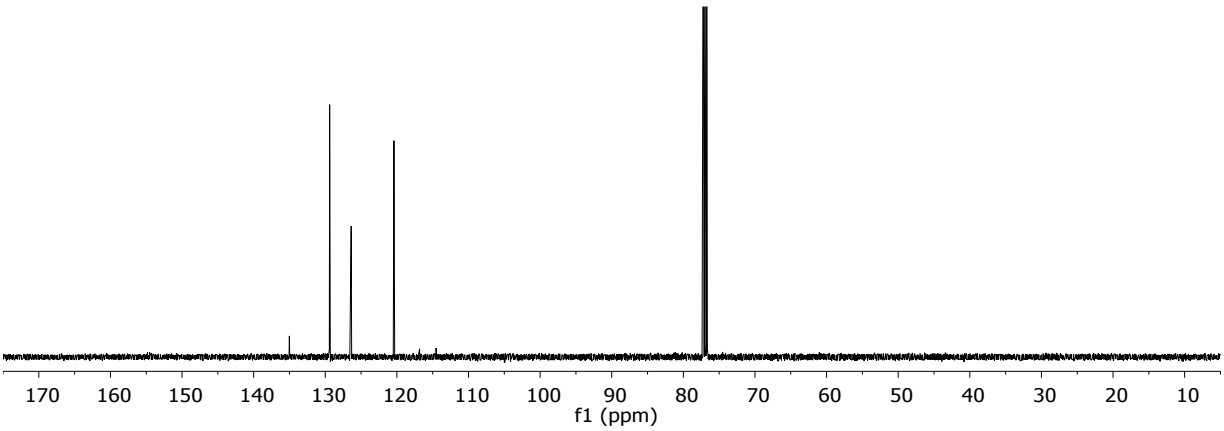


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83 (s, 1H), 7.60 – 7.53 (m, 2H), 7.44 – 7.35 (m, 2H), 7.29 – 7.21 (m, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 105.1, 115.2 (q, $^{1}J_{CF}$ = 288.6 Hz), 120.6, 126.4, 129.4, 135.1, 154.8 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -77.6 ppm. **DART MS m/z:** 215.04401 for calculated $M+H^+$ 215.04322

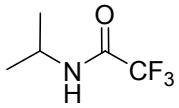
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

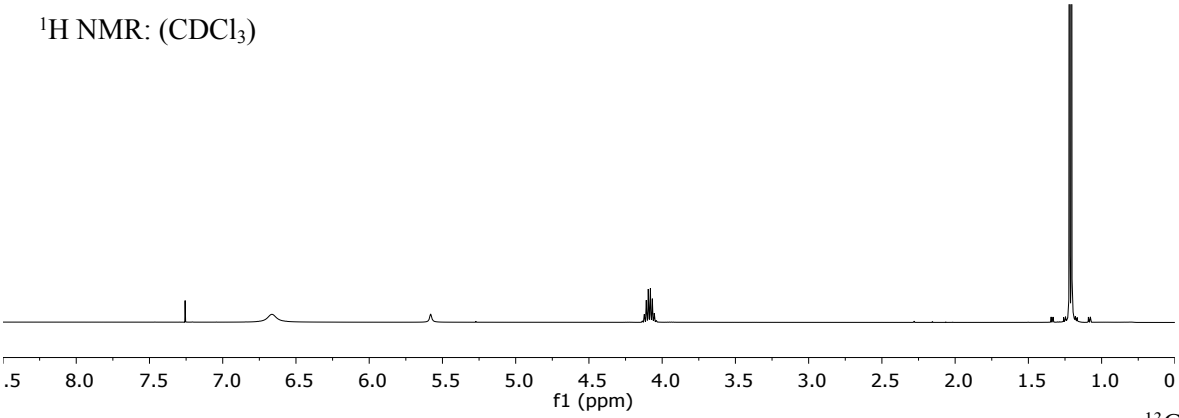


6.11 2,2,2-trifluoro-N-(1-methylethyl)- acetamide

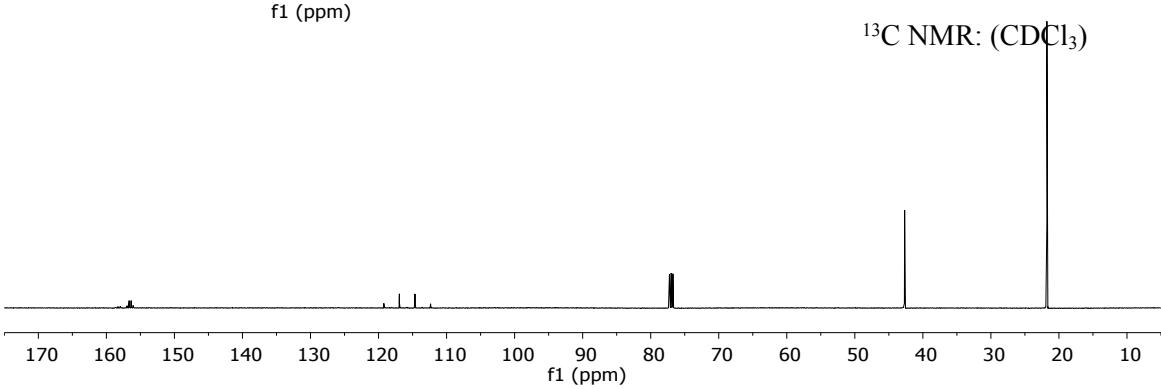


^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.66 (br, 1H), 4.09 (m, 1 H), 1.21 (d, J=6.6 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 21.7, 42.8, 115.8 (q, $^{1}J_{CF}$ = 287.7 Hz), 156.4 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -76.3 ppm. **DART MS m/z:** 156.06339 for calculated $M+H^+$ 156.06362

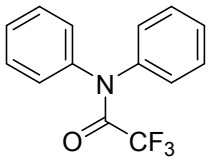
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

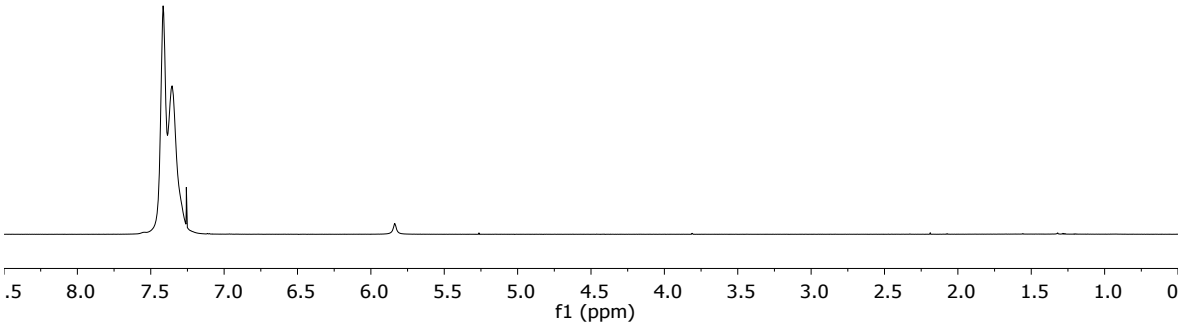


6.12 2,2,2-trifluoro-N,N-diphenyl- acetamide

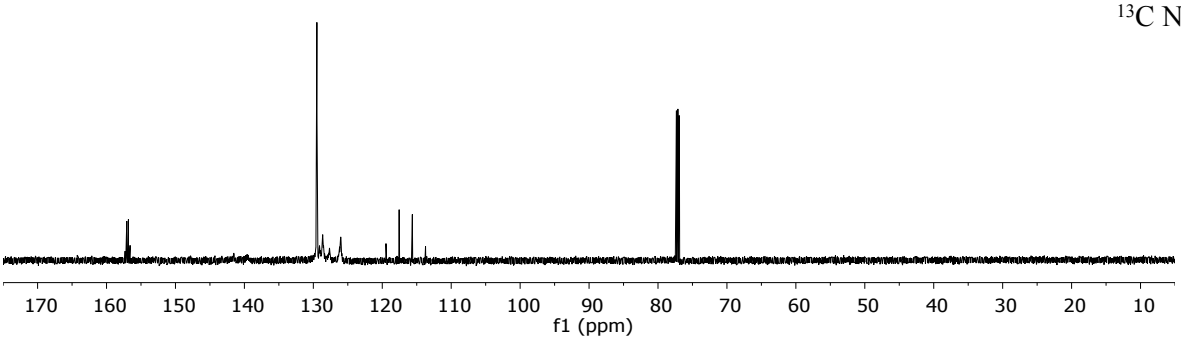


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42 (s, 1H), 7.35 (s, 1H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 116.6 (q, $^{1}J_{CF}$ = 288.6 Hz), 126.1, 128.6, 129.5, 141.6, 157.1 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -66.8 ppm. **DART MS m/z:** 266.07825 for calculated $M+H^+$ 234.06972

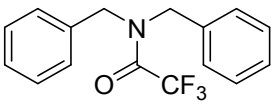
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

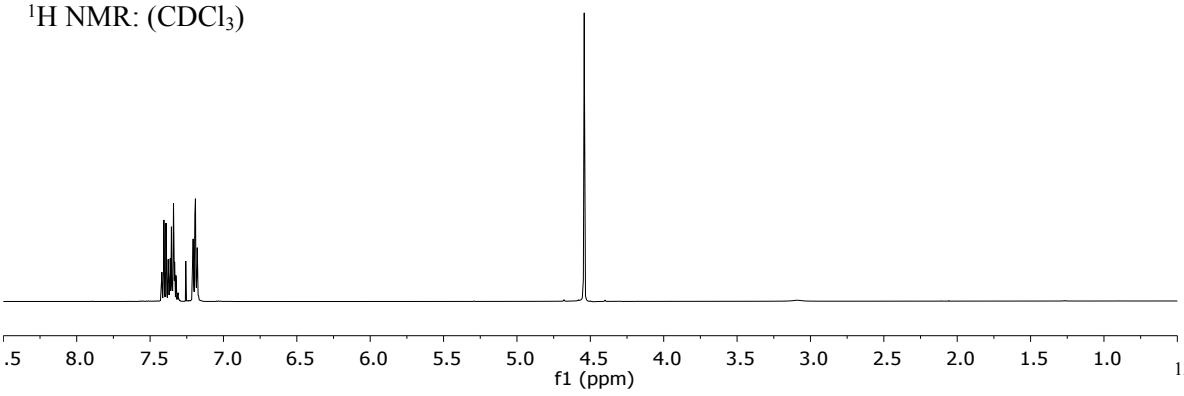


6.13 2,2,2-trifluoro-N,N-bis(phenylmethyl)- acetamide[15]

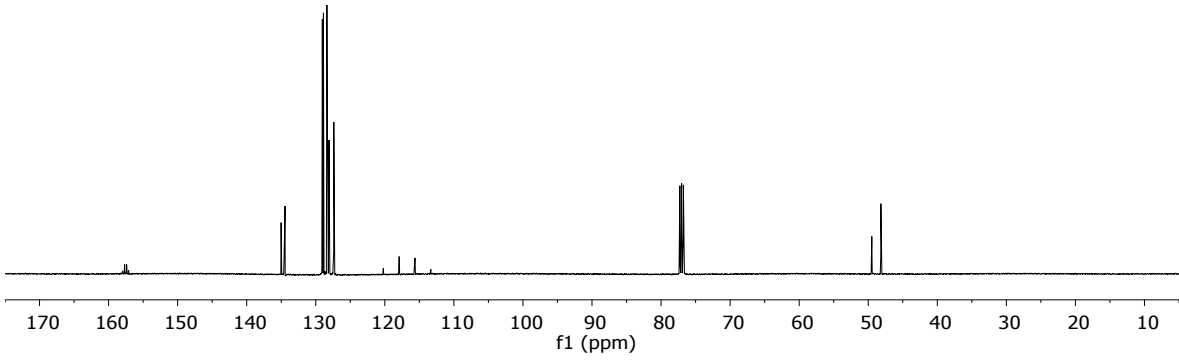


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.49 – 7.34 (m, 6H), 7.24 (m, 4H), 4.59 (s, 4H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 48.2, 49.5, 116.8 (q, $^{1}J_{CF}$ = 288.0 Hz), 127.4, 128.1, 128.3, 128.4, 128.9, 129.0, 134.5, 157.4 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -67.8 ppm. **DART MS m/z:** 294.10955 for calculated $M+H^+$ 294.11057

^{1}H NMR: ($CDCl_3$)

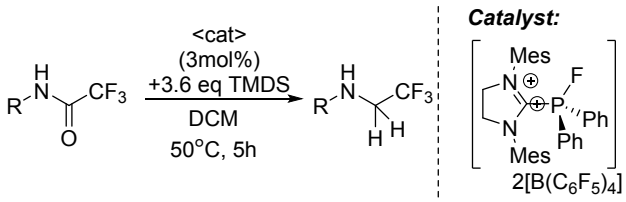


^{13}C NMR: ($CDCl_3$)



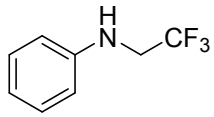
7 General Procedure of Hydrodeoxygenation of Amides

A solution of amide (1.6 mmol) and tetramethyldisiloxane (3.2 mmol, 3 eq) were added in 10 mL of dichloromethane. 3mol% of $[(SiMes)PFPh_2][B(C_6F_5)_4]_2$ was added to the mixture and stirred at 50°C for 5 hours. The resulting product was isolated through silica column chromatography (50:50 diethyl ether/pentane). Isolated product was characterized using ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and DART MS.



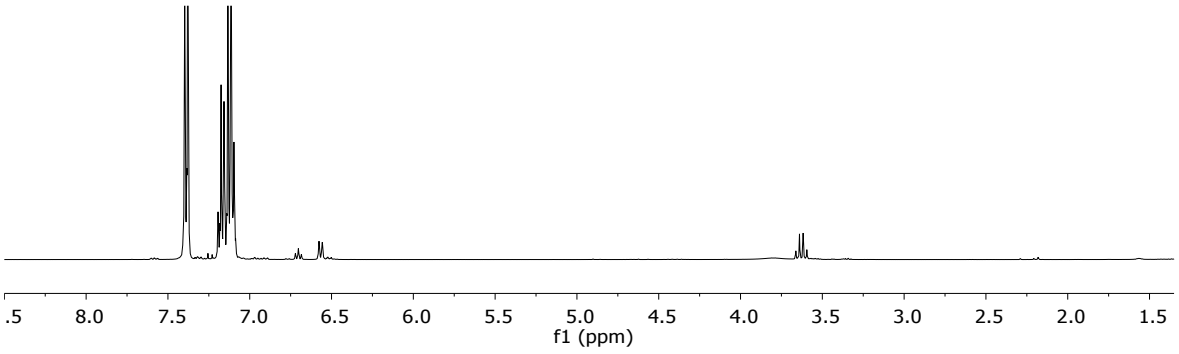
8 Characterization Data from the Reduction of CF3-subsituted Amides

8.1 N-(2,2,2-trifluoroethyl)- benzenamine[16]

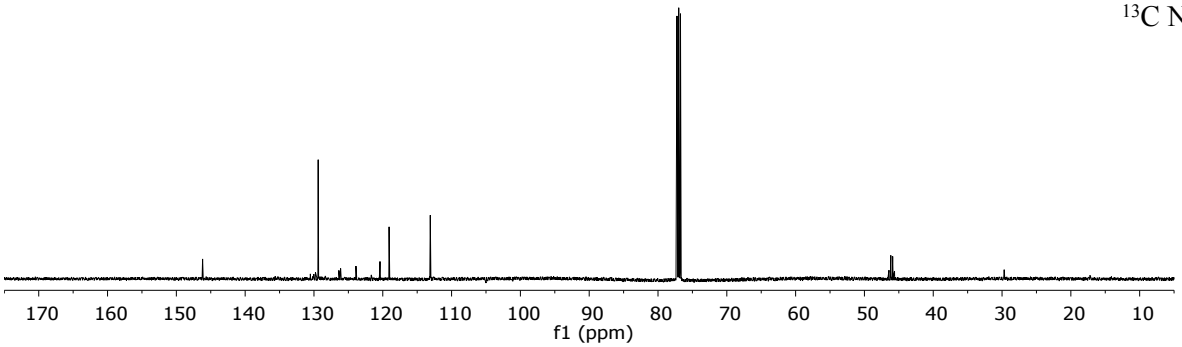


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.47 (d, $^{3}J_{HH}$ = 7.1 Hz, 2H), 7.31-7.13 (m, 3H), 3.80 (br, 1H), 3.71 (q, $^{3}J_{HF}$ = 8.9 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 46.3 (q, $^{2}J_{CF}$ = 33.6 Hz), 113.1, 119.1, 125.1 (q, $^{1}J_{CF}$ = 279.9 Hz), 129.4, 146.2 **ppm. ^{19}F NMR (375 MHz, $CDCl_3$)** δ = -72.4 ppm. **DART MS m/z:** 176.06847 for calculated $M+H^+$ 176.06871

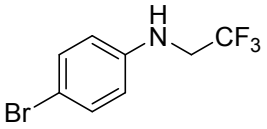
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

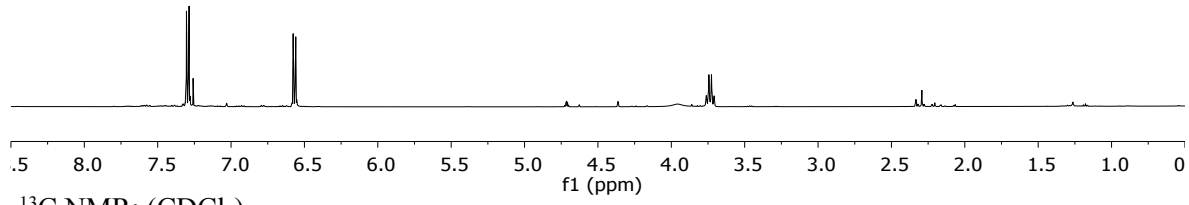


8.2 4-bromo-N-(2,2,2-trifluoroethyl)- benzenamine

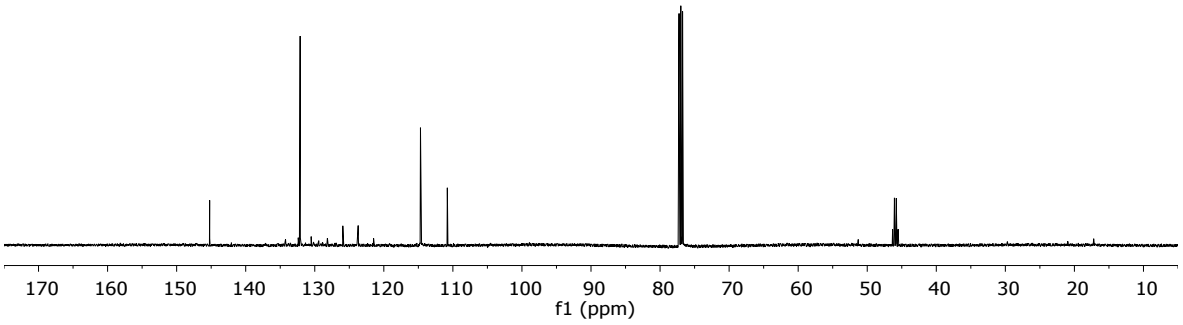


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35 – 7.26 (m, 2H), 6.60 – 6.53 (m, 2H), 3.95 (br, 1H), 3.74 (qd, $^{3}J_{PH}$ = 8.8, $^{3}J_{HH}$ = 6.7 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 46.1 (q, $^{2}J_{CF}$ = 33.7 Hz), 110.8, 114.7, 124.8 (q, $^{1}J_{CF}$ = 280.0 Hz), 132.1, 145.2 **ppm. ^{19}F NMR (375 MHz, $CDCl_3$)** δ = -72.3 ppm. **DART MS m/z:** 253.97899 for calculated $M+H^+$ 253.97922

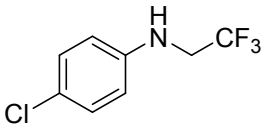
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

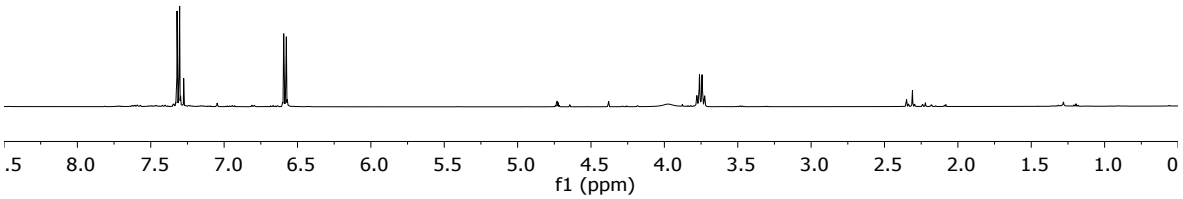


8.3 4-chloro-N-(2,2,2-trifluoroethyl)- benzenamine[16]



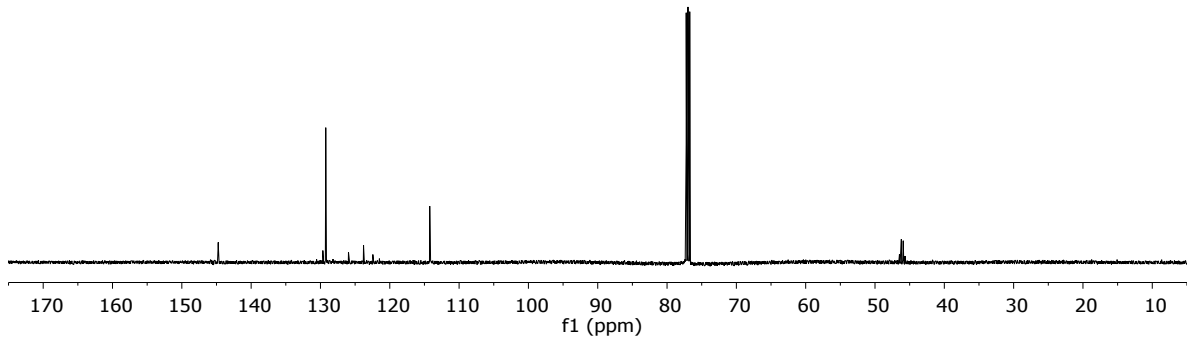
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 – 7.29 (m, 2H), 6.63 – 6.56 (m, 2H), 3.98 (br, 1H), 3.77 (qd, $^{3}J_{PH}$ = 8.8, $^{3}J_{HH}$ = 6.7 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 46.2 (q, $^{2}J_{CF}$ = 33.6 Hz), 114.2, 124.4, 129.2, 130.5, 144.7 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -72.3 ppm. **DART MS m/z:** 210.02930 for

^{1}H NMR: ($CDCl_3$)

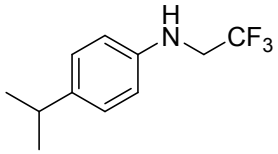


calculated $M+H^+$ 210.02974

^{13}C NMR: ($CDCl_3$)

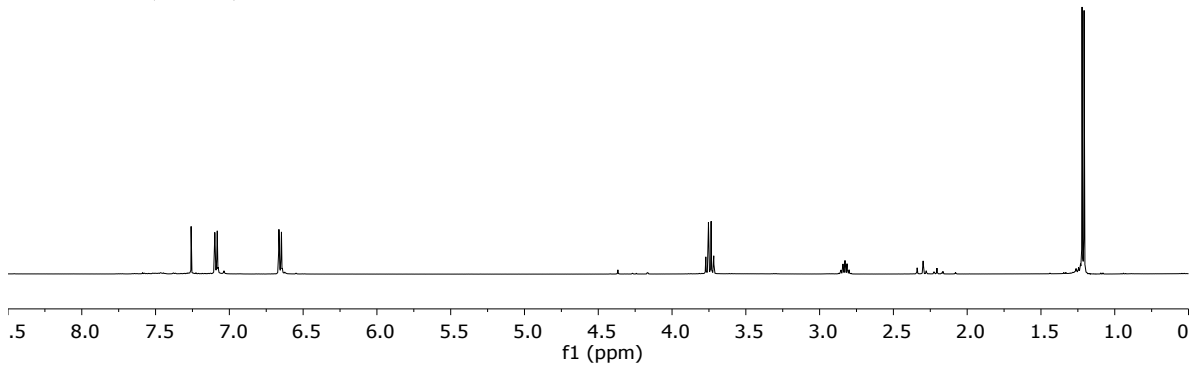


8.4 4-(1-methylethyl-N-(2,2,2-trifluoroethyl)- benzenamine

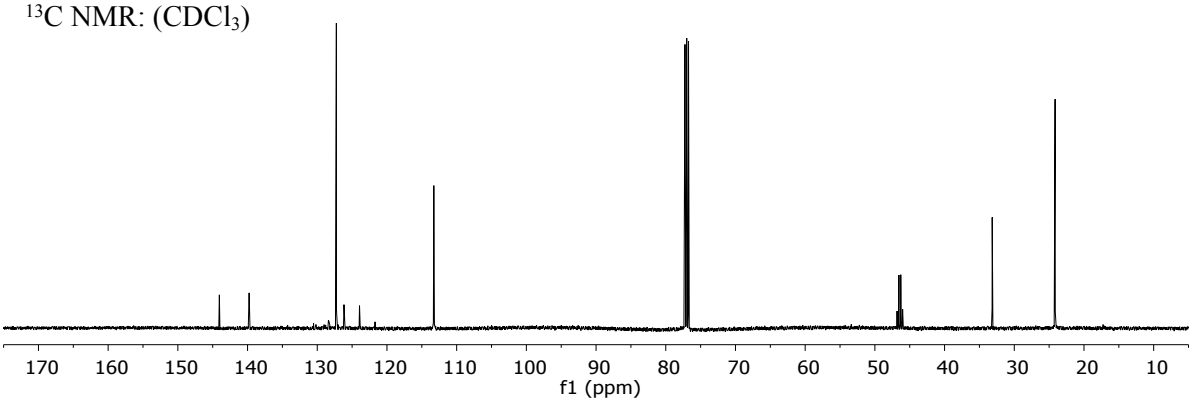


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.12 – 7.05 (m, 2H), 6.68 – 6.61 (m, 2H), 3.75 (q, $^3J_{HF}$ = 9.0 Hz, 2H), 2.83 (hept, $^3J_{HH}$ = 6.9 Hz, 1H), 1.22 (d, $^3J_{HH}$ 6.9 Hz, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 24.1, 33.2, 46.7 (q, $^2J_{CF}$ = 33.4 Hz), 113.3, 125.1 (q, $^1J_{CF}$ = 279.8 Hz), 127.7, 139.8, 144.1 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -72.4 ppm. **DART MS m/z:** 218.11542 for calculated $M+H^+$ 218.11566

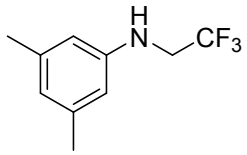
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

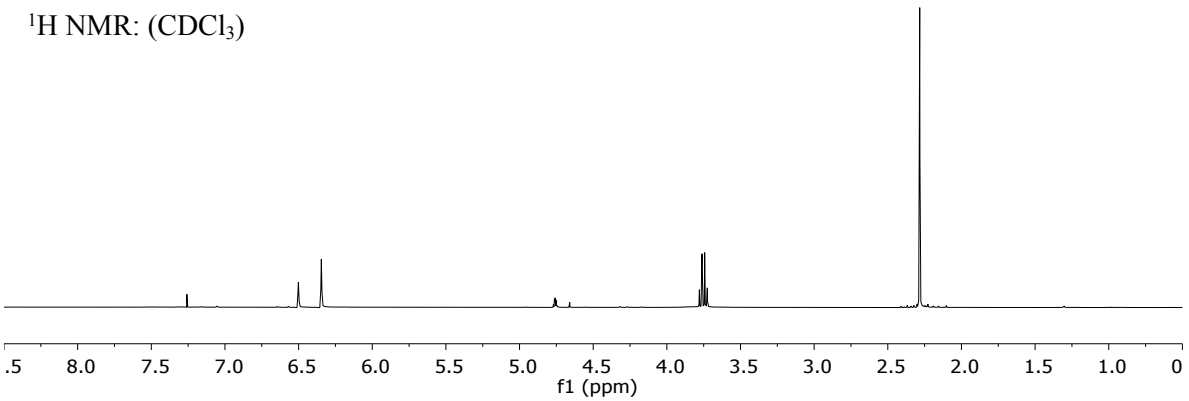


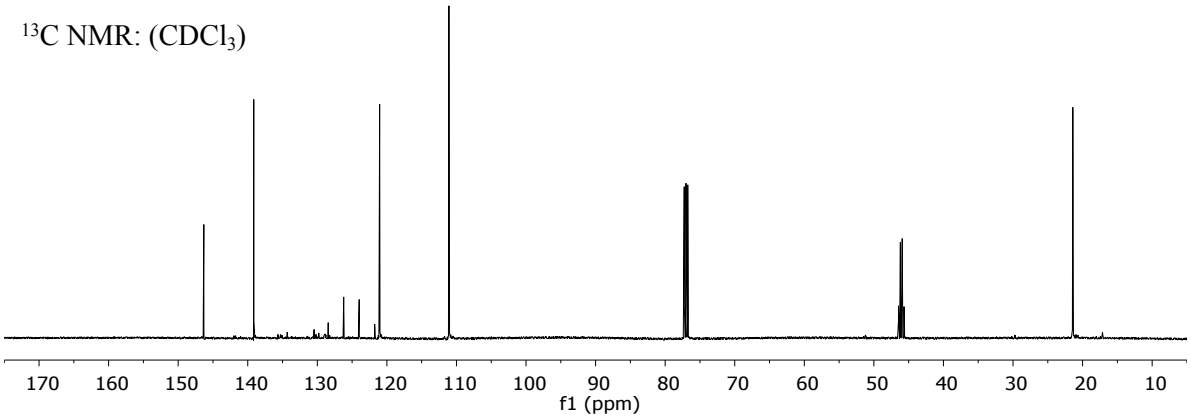
8.5 3,5-methyl -N-(2,2,2-trifluoroethyl)- benzenamine



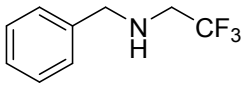
^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.50 (tt, $^3J_{HH}$ = 1.4, $^4J_{HH}$= 0.7 Hz, 1H), 6.35 (dt, $^3J_{HH}$ = 1.5, $^4J_{HH}$ = 0.7 Hz, 2H), 3.75 (q, $^3J_{HF}$ = 9.0 Hz, 2H), 2.34 – 2.21 (m, 6H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 21.4, 46.4 (q, $^2J_{CF}$ = 33.5 Hz), 111.1, 121.0, 127.3 (q, $^1J_{CF}$ = 280.0 Hz), 139.1, 146.3 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -72.7 ppm. **DART MS m/z:** 204.10091 for calculated $M+H^+$ 204.10001

^{1}H NMR: ($CDCl_3$)



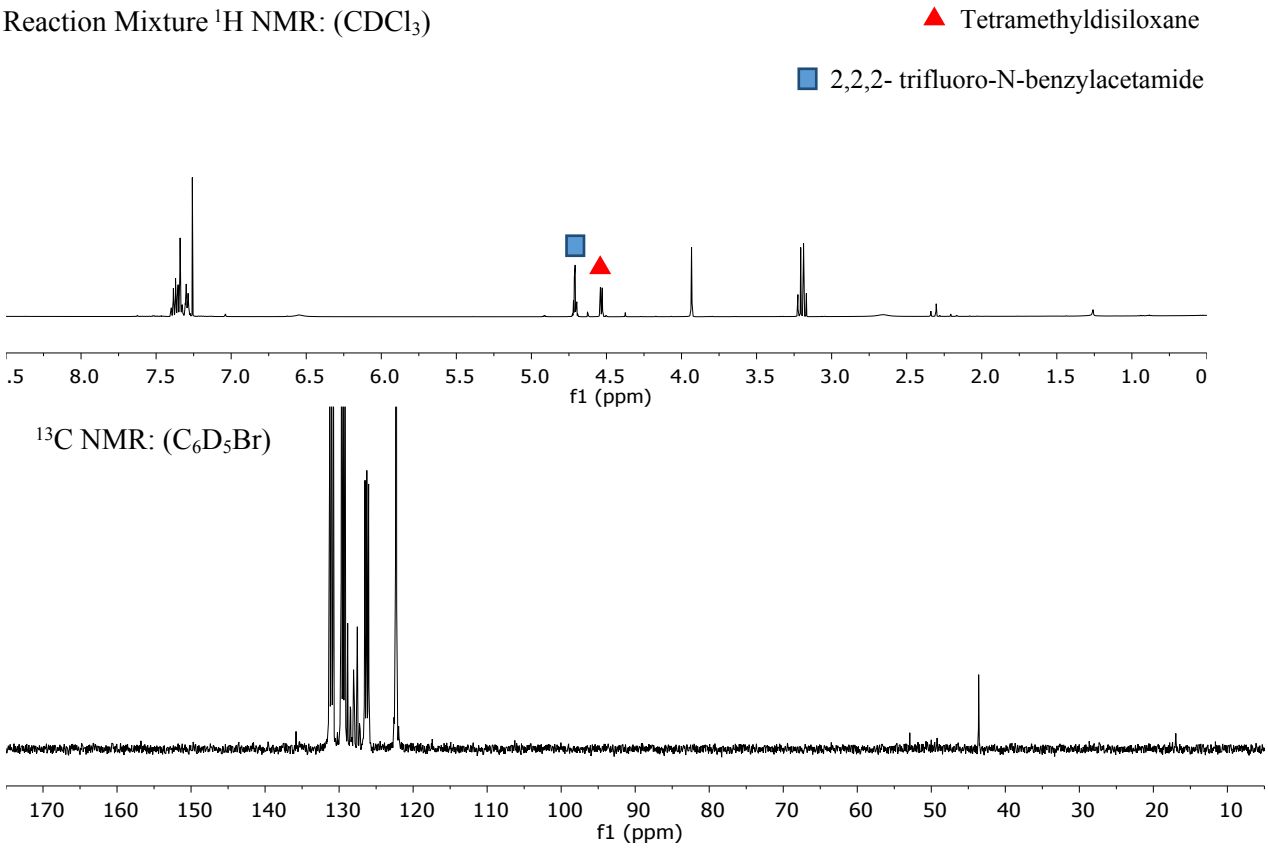


8.6 N-(2,2,2-trifluoroethyl)- benzenemethanamine

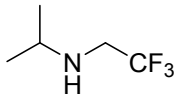


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42-7.25 (m, 5H), 6.55 (br, 1H), 4.93 (s, 2H), 3.20 (q, $^{3}J_{HF}$ = 9.3 Hz, 2H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 43.6, 52.9, 127.5, 128.1, 128.5, 128.9, 135.8 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -69.6 ppm. **DART MS m/z:** 190.08436 for calculated $M+H^+$ 190.08436

Reaction Mixture ^{1}H NMR: ($CDCl_3$)

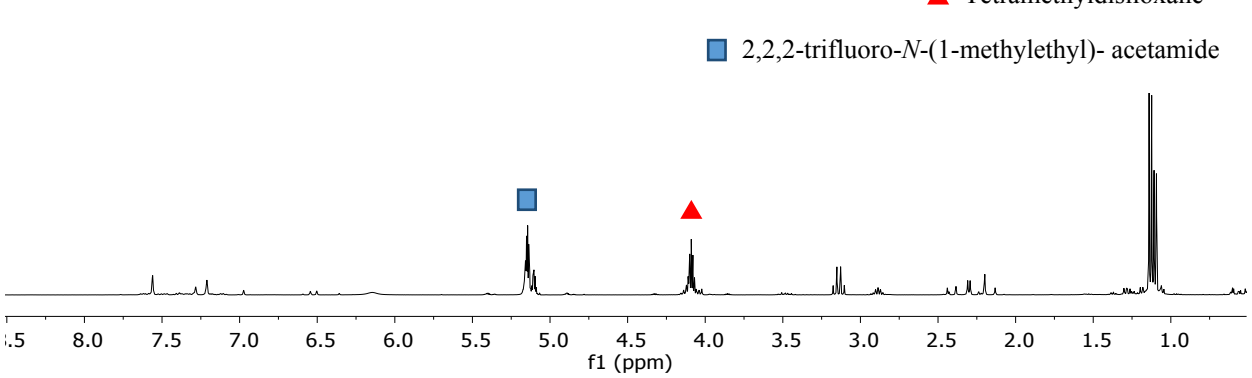


8.7 N-(2,2,2-trifluoroethyl)-2-propanamine

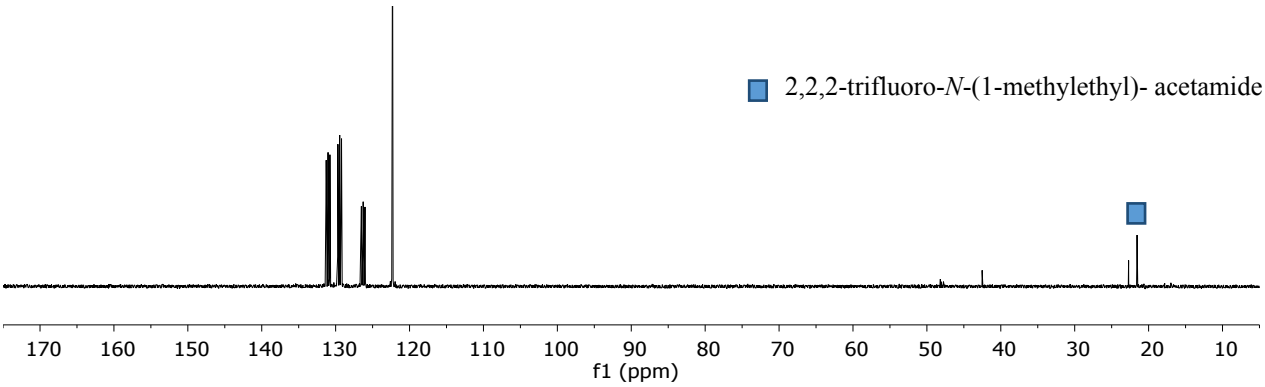


^{1}H NMR (500 MHz, C_6D_5Br) δ = 4.70 (hept, 1H), 4.63 (s, 1H), 2.32 (q, 2H), 2,21 (d, 6H) ppm. **^{13}C NMR (125 MHz, C_6D_5Br)** δ = 22.7, 42.6, 48.0, 129.9 ppm. **^{19}F NMR (375 MHz, C_6D_5Br)** δ = -71.65 ppm.

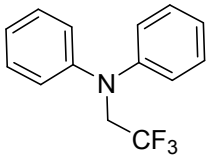
Reaction Mixture ^{1}H NMR: (C_6D_5Br)



Reaction Mixture ^{13}C NMR: (C_6D_5Br)

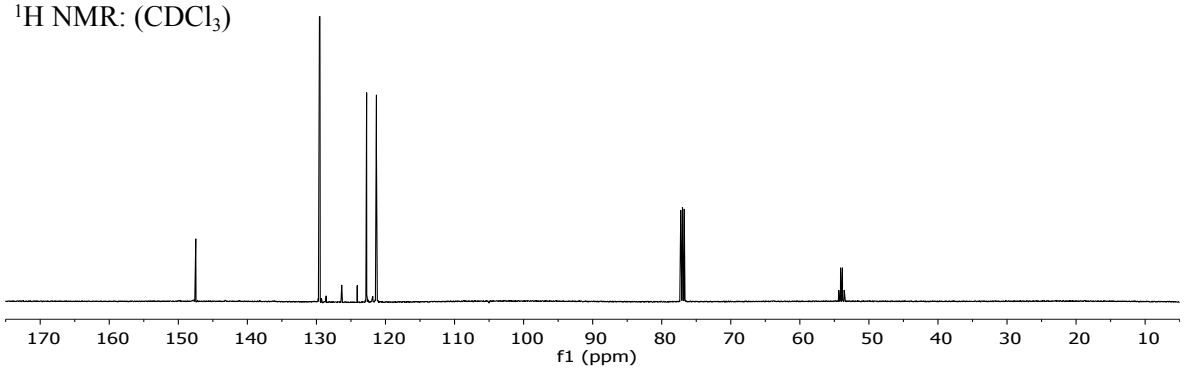


8.8 N-(phenyl)-N-(2,2,2-trifluoroethyl)- benzenamine

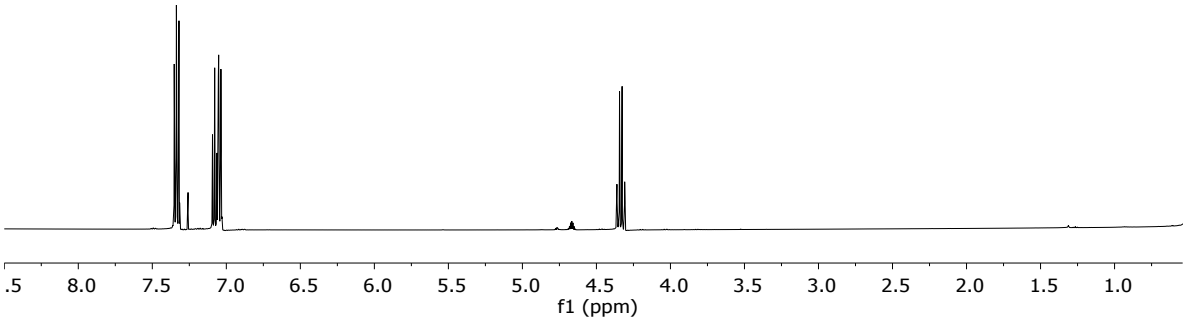


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 (m, 4H), 7.05 (m 6H), 4.33 (q, $^{3}J_{HF}$ = 8.7 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 54.2 (q, $^{2}J_{CF}$ = 33.2 Hz), 121.3, 122.7, 126.3 (q, $^{1}J_{CF}$ = 282.8 Hz), 129.5, 147.5 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -69.6 ppm. **DART MS m/z:** 252.10062 for calculated $M+H^+$ 252.10001

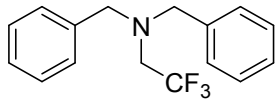
^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)

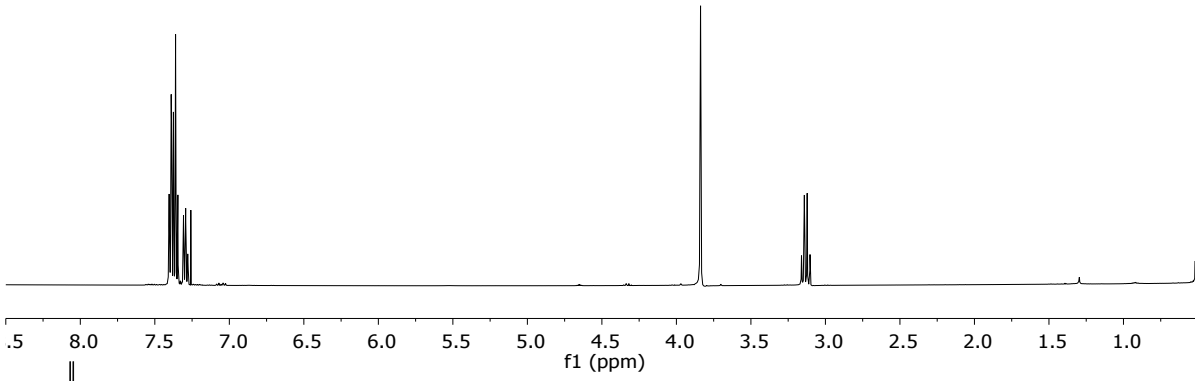


8.9 N-(phenylmethyl)-N-(2,2,2-trifluoroethyl)- benzenemethanamine

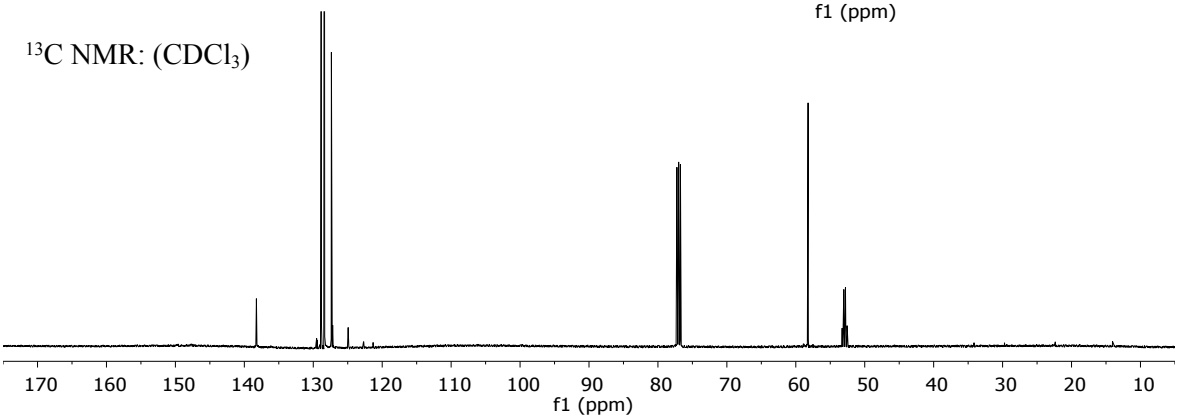


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36 (m, 10H), 3.84 (s, 4H), 3.13 (q, $^{3}J_{HF}$ = 9.7 Hz, 2H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 52.8, 58.2 (q, $^{2}J_{CF}$ = 30.0 Hz), 124.9, 127.4 (q, $^{1}J_{CF}$ = 282.6 Hz), 128.4, 128.8, 138.3 ppm. **^{19}F NMR (375 MHz, $CDCl_3$)** δ = -67.9 ppm. **DART MS m/z:** 280.13144 for calculated $M+H^+$ 280.13131

^{1}H NMR: ($CDCl_3$)



^{13}C NMR: ($CDCl_3$)



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