Versatile, mild, and selective reduction of various carbonyl groups using an electron-deficient boron catalyst

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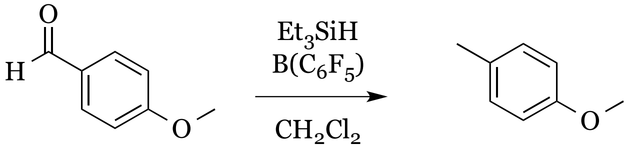
1. General Methods

Reagent chemicals were obtained from commercial sources and used without further purification. Flash chromatography was performed with columns of 40–63 Å silica gel, 230–400 mesh (Silicycle, Québec City, Canada). Thin-layer chromatography (TLC) was performed on plates of EMD 250-μm silica 60-F_{254}. The phrase "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator while maintaining the water-bath temperature below 40 °C. Residual solvent was removed from samples at high vacuum (<0.1 torr). The term "high vacuum" refers to vacuum achieved by mechanical a belt-drive oil pump. All NMR spectra were acquired at ambient temperature with a Bruker Ultra Shield Plus 400, and were referenced to TMS or a residual protic solvent.

Electrospray ionization (ESI) mass spectrometry for small-molecule characterization was performed with a Micromass LCT at the Mass Spectrometry Facility in the Department of Chemistry at the University of Wisconsin–Madison. {NIH 1S10OD020022-1}

2. Experimental Procedures and Characterization Data

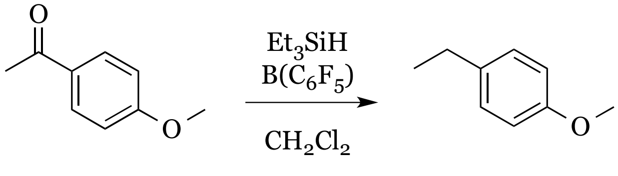
4-Methoxytoluene



p-Anisaldehyde (0.055 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.19 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 4-Methoxytoluene (0.039 g, 79%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.01 (d, *J* = 8.3 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 1H), 3.78 (s, 3H), 2.27 (s, 3H).
*Checked against Sigma-Aldrich: http://www.sigmaaldrich.com/spectra/fnmr/FNMR001412.PDF

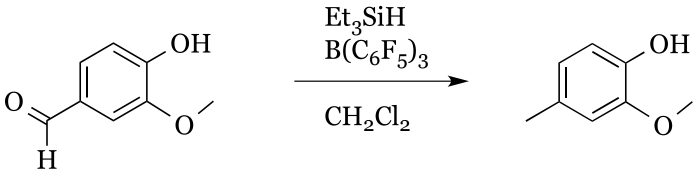
4-Ethylanisole



p-Methoxyacetophenone (0.061 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.19 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 4-Ethylanisole (0.042 g, 75%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). *Checked against: Wang, B., Sun, H., Sun, Z., *Eur. J. Org. Chem.* **2009**, *22*, 3688-3692.

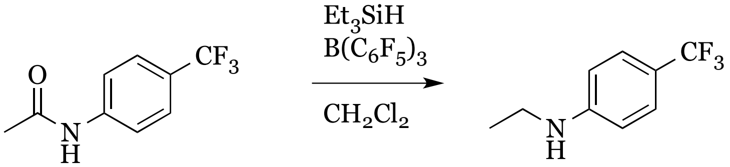
2-Methoxy-4-methylphenol



Vanillin (0.062 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.13 mL, 0.818 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 2-Methoxy-4-methylphenol (0.044 g, 78%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.81 (d, *J* = 7.8 Hz, 1H), 6.70 – 6.61 (m, 3H), 5.42 (s, 1H), 3.87 (s, 3H), 2.29 (s, 3H). *Checked against Sigma-Aldrich: http://www.sigmaaldrich.com/spectra/fnmr/FNMR006218.PDF

4-Trifluoromethyl-N-ethylaniline



4-Trifluromethylacetanilide (0.083 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.2 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 4-Trifluoromethyl-N-ethylaniline (0.070 g, 91%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 6.58 (d, *J* = 8.1 Hz, 2H), 3.89 (bs, 1H), 3.25 – 3.12 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 150.7, 126.6 (q, *J* = 3.9 Hz), 125.0 (q, *J* = 270.4 Hz), 118.5 (q, *J* = 32.6 Hz), 111.7, 38.0, 14.6. *Corrected ^{13}C-NMR spectral data from incorrect data in: Sajiki, H. *Org. Lett.* **2004**, *6*, 4977-4980. Authors might not have realized that F is a spin active nucleus

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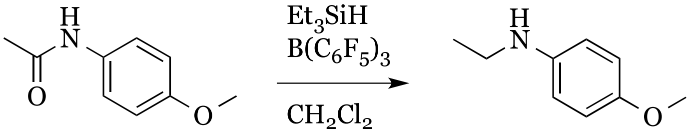
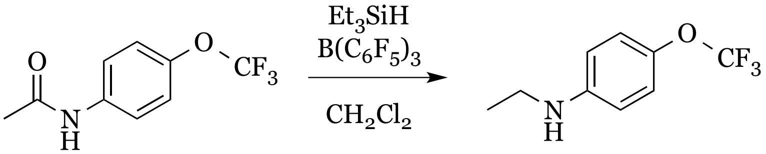
4-Methoxy-N-ethylaniline



4-Methoxy-N-Acetylaniline (0.067 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.20 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (1.050 g, 0.204 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 4-Methoxy-N-ethylaniline (0.051 g, 82%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.79 (d, *J* = 8.9 Hz), 6.63 (d, *J* = 8.9 Hz), 3.76 , 3.12 (q, *J* = 7.1 Hz), 1.23 (t, *J* = 7.1 Hz).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 153.0, 140.9, 115.2, 115.0, 55.9, 40.38, 14.6. *Checked against: Nacario, R., Kotakonda, S., Fouchard, D. M. D., Tillekeratne, L. M. V., Hudson, R. A. *Org. Lett.* **2005**, *7*, 471-474.

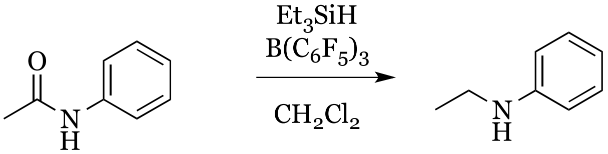
4-Trifluoromethoxy-N-ethylaniline



4-(Trifluoromethoxy)-N-Acetylaniline (0.086 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.20 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 4-Trifluoromethoxy-N-ethylaniline (0.054 g, 87%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.03 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 9.0 Hz, 2H), 3.61 (bs, 1H), 3.17 – 3.09 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 147.2, 140.2, 122.4, 120.7 (q, *J* = 255.6 Hz), 112.8, 38.6, 14.8.

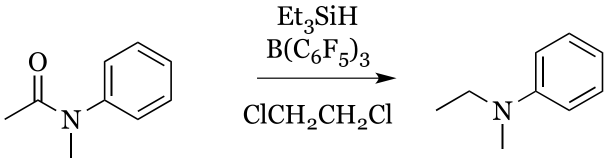
N-Ethylaniline



Acetanilide (0.055 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.20 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield N-Ethylaniline (0.046 g, 94%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (t, *J* = 7.5 Hz, 2H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.5 Hz, 2H), 3.61 (bs, 1H), 3.55 (bs, 1H), 3.16 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 129.2, 117.2, 112.7, 38.5, 14.9. **HRMS** (ESI) *m/z* 122.0963 [calc'd for $C_8H_{11}N$ (M+H$^+$) 122.0964.

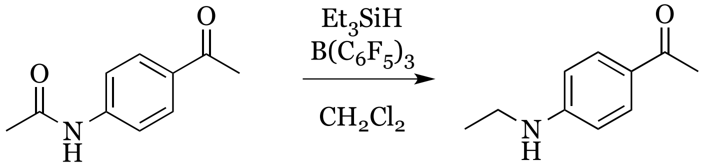
N-Methyl-N-ethylaniline



N-Methylacetanilide (0.061 g, 0.409 mmol) was dissolved in dichloroethane (4.1 mL) in a scintillation vial. Triethylsilane (0.33 mL, 2.045 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir at 60˚C for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield N-Methyl-N-ethylaniline (0.041 g, 74%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23 (dd, *J* = 9.1, 7.6 Hz, 2H), 6.79 – 6.59 (m, 3H), 3.40 (q, *J* = 7.1 Hz, 2H), 2.90 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 149.1, 129.2, 116.0, 112.4, 46.8, 37.5, 11.2. **HRMS** (ESI) *m/z* 136.1120 [calc'd for $C_9H_{13}N$ (M+H$^+$) 136.1121.

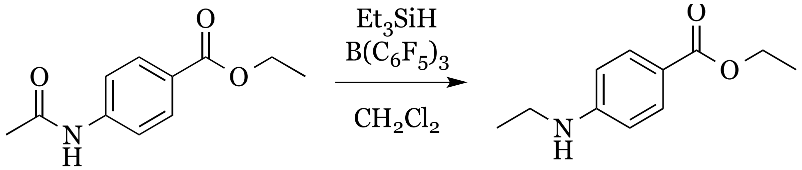
4-Ethylaminoacetophenone



4-(Acetamido)acetophenone (0.072 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.20 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 4-(Ethylamino)acetophenone (0.058 g, 88%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.16 (s, 3H), 1.21 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 168.1, 140.4, 135.5, 128.3, 120.1, 28.3, 24.5, 15.6 **HRMS** (ESI) *m/z* 164.1070 [calc'd for $C_{10}H_{13}NO$ (M+H$^+$) 164.1070.

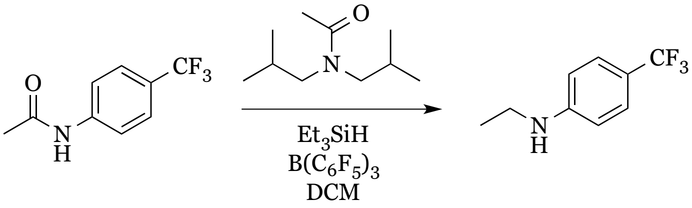
Ethyl-4-ethylaminobenzoate



Ethyl-4-(acetamido)benzoate (0.085 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.20 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield Ethyl-4-(ethylamino)benzoate (0.069 g, 87%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.22 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 166.9, 151.9, 131.4, 118.5, 111.3, 60.2, 37.9, 14.6, 14.5. **HRMS** (ESI) *m/z* 194.1176 [calc'd for $C_{11}H_{15}NO_2$ (M+H$^+$) 194.1176].

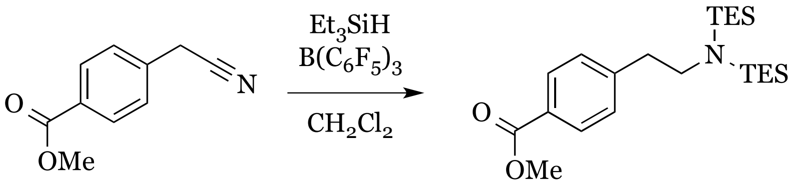
Inhibitory Study:



4-Trifluromethylacetanilide (0.083 g, 0.409 mmol) and N-acetyldiisobutylamine (0.070 g, 0.409 mmol) were dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.67 mL, 4.09 mmol) was then added followed by tris(pentafluorophenyl)borane (0.315 g, 0.614 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 4-Trifluoromethyl-N-ethylaniline (0.037 g, 48%). Without the molar excess of borane, no product formation was observed.

Characterization Data: See Above

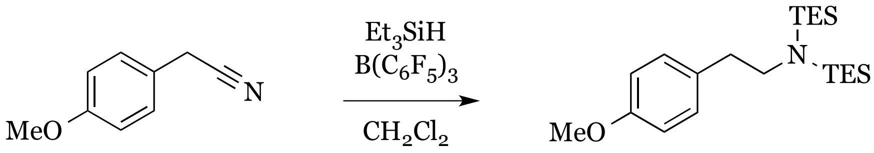
2-(4'-Methylcarboxylate)-N,N-bis(triethylsilyl)phenethylamine



Methyl 4-(cyanomethyl) benzoate (0.071 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.19 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 2-(4'-Methoxy)-N,N-bis(triethylsilyl)phenethylamine (0.139 g, 84%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.05 – 2.85 (m, 2H), 2.78 – 2.64 (m, 2H), 0.98 (t, *J* = 7.9 Hz, 18H), 0.68 (q, *J* = 7.9 Hz, 12H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.1, 145.7, 129.8, 128.5, 128.0, 52.0, 47.6, 42.5, 7.6, 5.7. **HRMS** (ESI) *m/z* 408.2745 [calc'd for $C_{22}H_{41}NO_2Si_2$ (M+H$^+$) 408.2749]

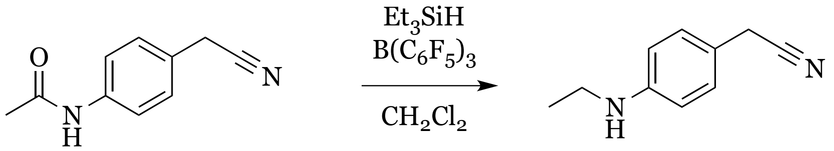
2-(4'-Methoxy)-N,N-bis(triethylsilyl)phenethylamine



4-Methyoxyphenylacetonitrile (0.060 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.19 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 2-(4'-Methoxy)-N,N-bis(triethylsilyl)phenethylamine (0.128 g, 83%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.97 – 2.82 (m, 2H), 2.65 – 2.54 (m, 2H), 0.97 (t, *J* = 7.9 Hz, 18H), 0.67 (q, *J* = 7.9 Hz, 12H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 157.9, 132.4, 129.4, 113.8, 55.2, 48.2, 41.4, 7.6, 5.7. **HRMS** (ESI) *m/z* 380.2793 [calc'd for $C_{21}H_{41}NOSi_2$ (M+H$^+$) 380.2799]

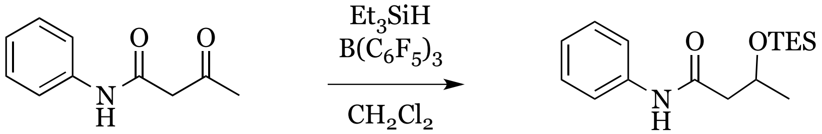
4-Ethylaminophenylacetonitrile



4-Acetamidylphenylacetonitrile (0.071 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.19 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield 4-Ethylaminophenylacetonitrile (0.060 g, 92%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 8.6 Hz, 2H), 3.63 (s, 3H), 3.15 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 148.13, 128.89, 118.69, 117.76, 113.02, 38.43, 22.81, 14.79. **HRMS** (ESI) *m/z* 161.1072 [calc'd for $C_{10}H_{12}N_2$ (M+H$^+$) 161.1073.

Acetoacetanilide Triethylsilylether (Mixture of E/Z Amide Conformations)

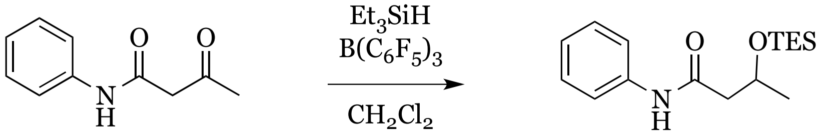


Acetoacetanilide (0.072 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.20 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield acetoacetanilide triethylsilylether (0.118 g, 89%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.71 (s, 0.4H), 8.38 (s, 0.6H), 7.53 – 7.45 (m, 2H), 7.35 – 7.24 (m, 2H), 7.16 – 7.03 (m, 1H), 4.34 – 4.16 (m, 1H), 2.69 – 2.31 (m, 2H), 1.29 (d, *J* = 6.3 Hz, 1.2H), 1.24 (d, *J* = 6.3 Hz, 1.8H), 0.98 (t, *J* =

7.9 Hz, 3.6H), 0.93 (t, *J* = 7.9 Hz, 2.4H), 0.66 (q, *J* = 7.9 Hz, 2.4H), 0.52 (q, *J* = 7.9 Hz, 1.6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.9, 170.0, 137.9, 137.6, 129.0, 128.96, 124.5, 124.2, 120.2, 119.8, 66.0, 65.0, 46.6, 44.9, 23.0, 23.0, 6.8, 6.4, 4.8, 4.8. **HRMS** (ESI) *m/z* 294.1880 [calc'd for $C_{16}H_{27}NO_2Si$ (M+H$^+$) 294.1884]

Acetoacetanilide Triethylsilylether (Mixture of E/Z Amide Conformations)



Acetoacetanilide (0.072 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.20 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield acetoacetanilide triethylsilylether (0.118 g, 89%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.71 (s, 0.4H), 8.38 (s, 0.6H), 7.53 – 7.45 (m, 2H), 7.35 – 7.24 (m, 2H), 7.16 – 7.03 (m, 1H), 4.34 – 4.16 (m, 1H), 2.69 – 2.31 (m, 2H), 1.29 (d, *J* = 6.3 Hz, 1.2H), 1.24 (d, *J* = 6.3 Hz, 1.8H), 0.98 (t, *J* = 7.9 Hz, 3.6H), 0.93 (t, *J* = 7.9 Hz, 2.4H), 0.66 (q, *J* = 7.9 Hz, 2.4H), 0.52 (q, *J* = 7.9 Hz, 1.6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.9, 170.0, 137.9, 137.6, 129.0, 128.96, 124.5, 124.2, 120.2, 119.8, 66.0, 65.0, 46.6, 44.9, 23.0, 23.0, 6.8, 6.4, 4.8, 4.8. **HRMS** (ESI) *m/z* 294.1880 [calc'd for $C_{16}H_{27}NO_2Si$ (M+H$^+$) 294.1884]

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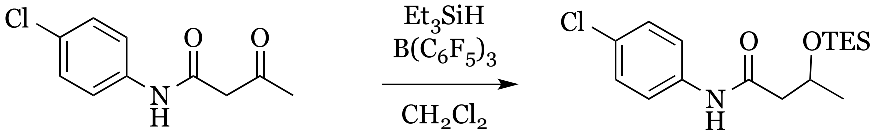
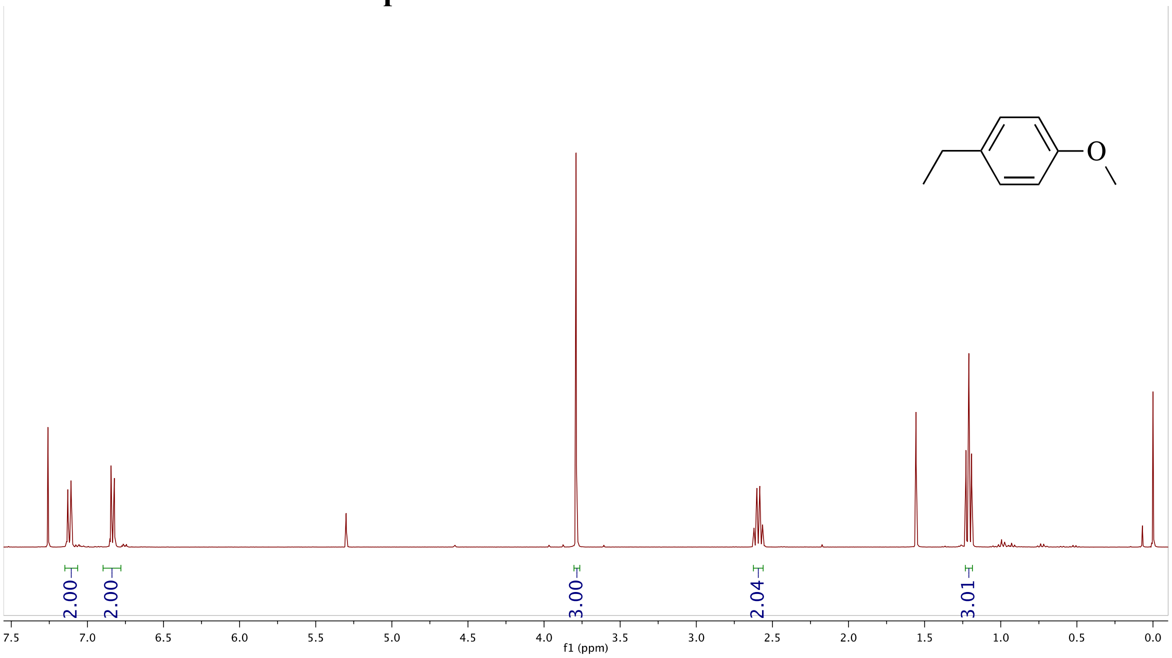
p-Chloro-Acetoacetanilide Triethylsilylether

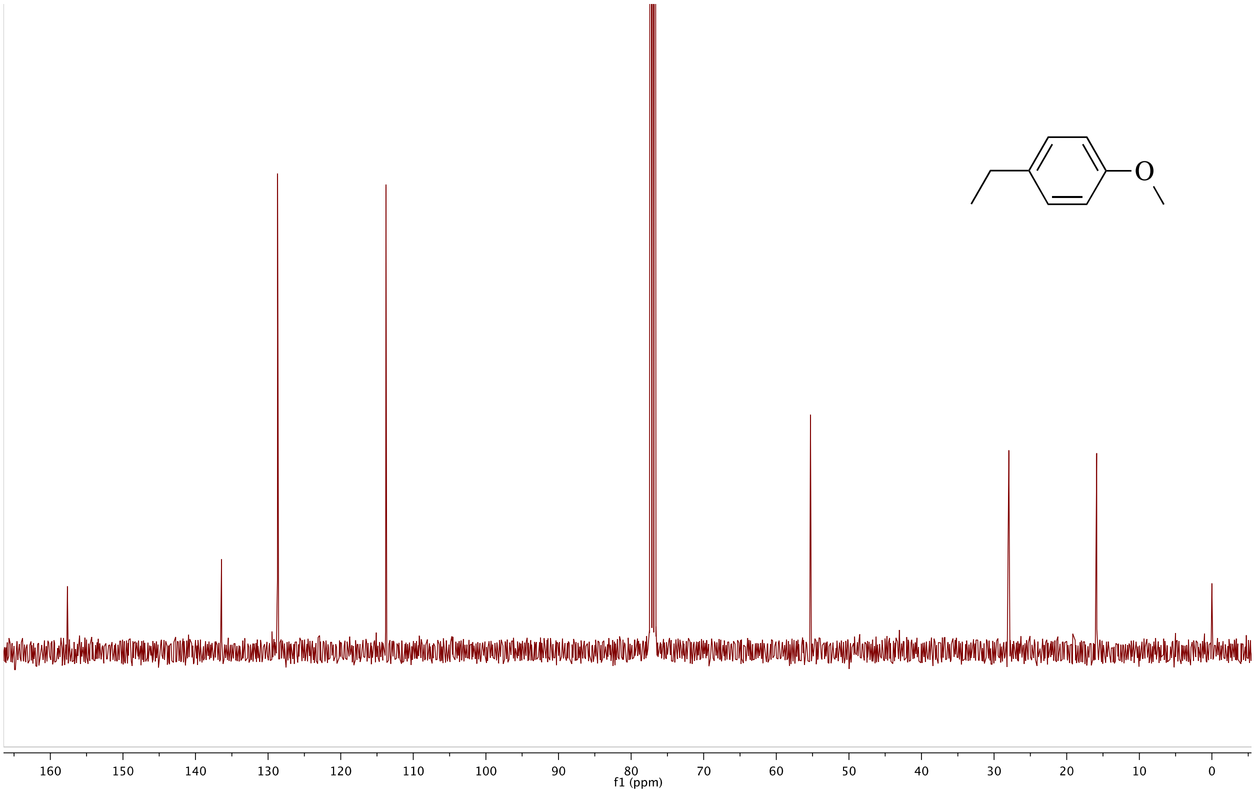


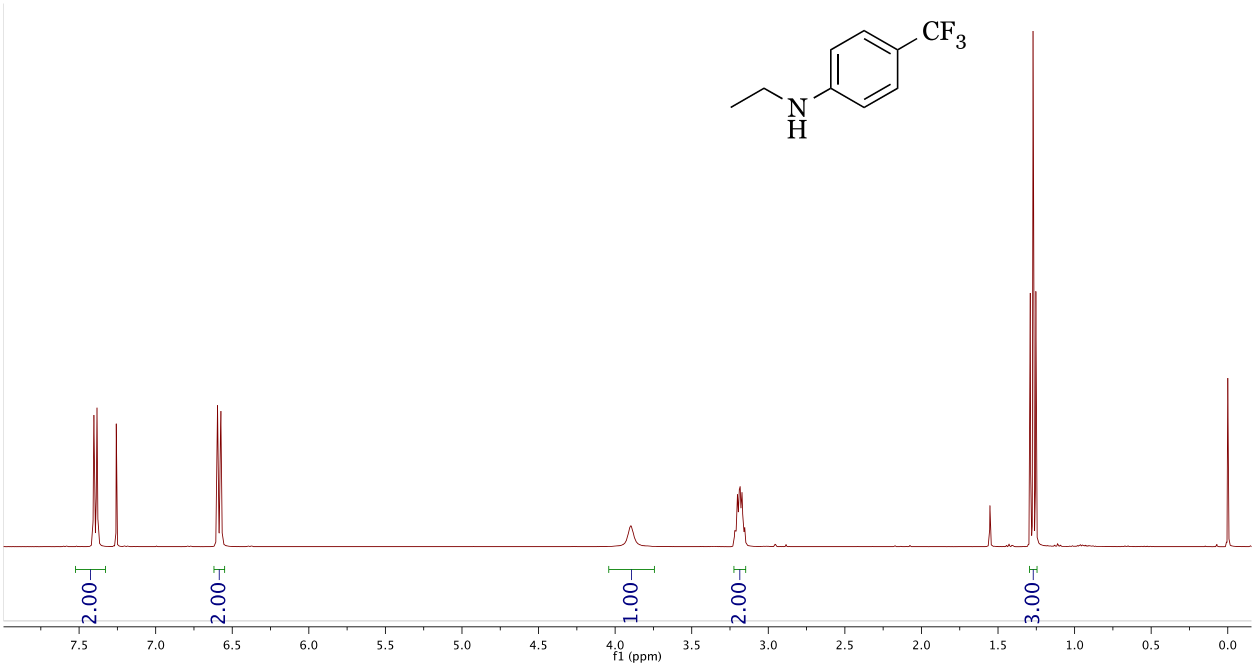
p-Chloroacetoacetanilide (0.086 g, 0.409 mmol) was dissolved in dichloromethane (4.1 mL) in a scintillation vial. Triethylsilane (0.20 mL, 1.227 mmol) was then added followed by tris(pentafluorophenyl)borane (0.021 g, 0.0409 mmol). The reaction was allowed to stir for 8 hours before being concentrated under reduced pressure and purified by flash chromatography to yield *p*-chloroacetanilide triethylsilylether (0.120 g, 90%).

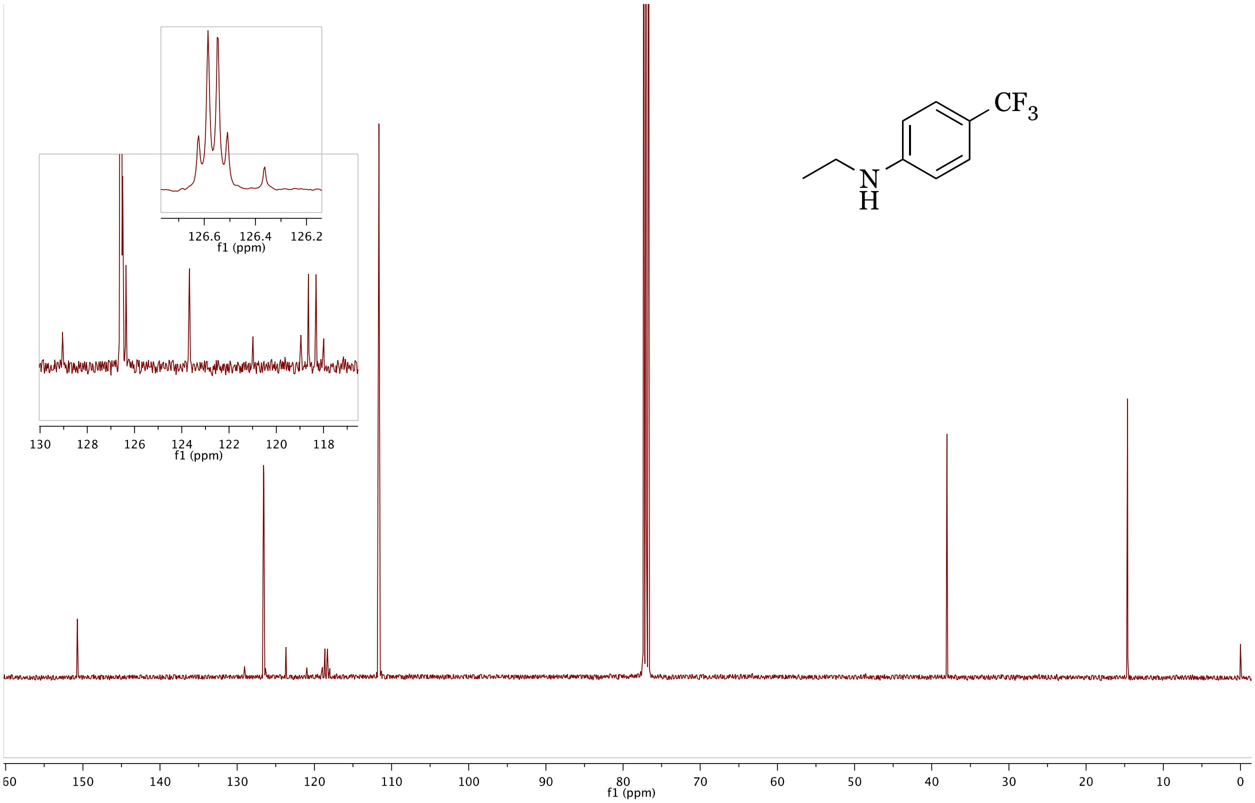
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.61 (bs, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 4.35 – 4.23 (m, 1H), 2.65 (dd, *J* = 14.9, 3.8 Hz, 1H), 2.40 (dd, *J* = 14.9, 5.6 Hz, 1H), 1.30 (d, *J* = 6.3 Hz, 3H), 0.98 (t, *J* = 7.9 Hz, 8H), 0.66 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.6, 136.7, 129.0, 128.8, 120.8, 66.0, 46.7, 23.0, 6.8, 4.8 **HRMS** (ESI) *m/z* 328.1490 [calc'd for $C_{16}H_{26}NO_2ClSi$ (M+H$^+$) 328.1494]

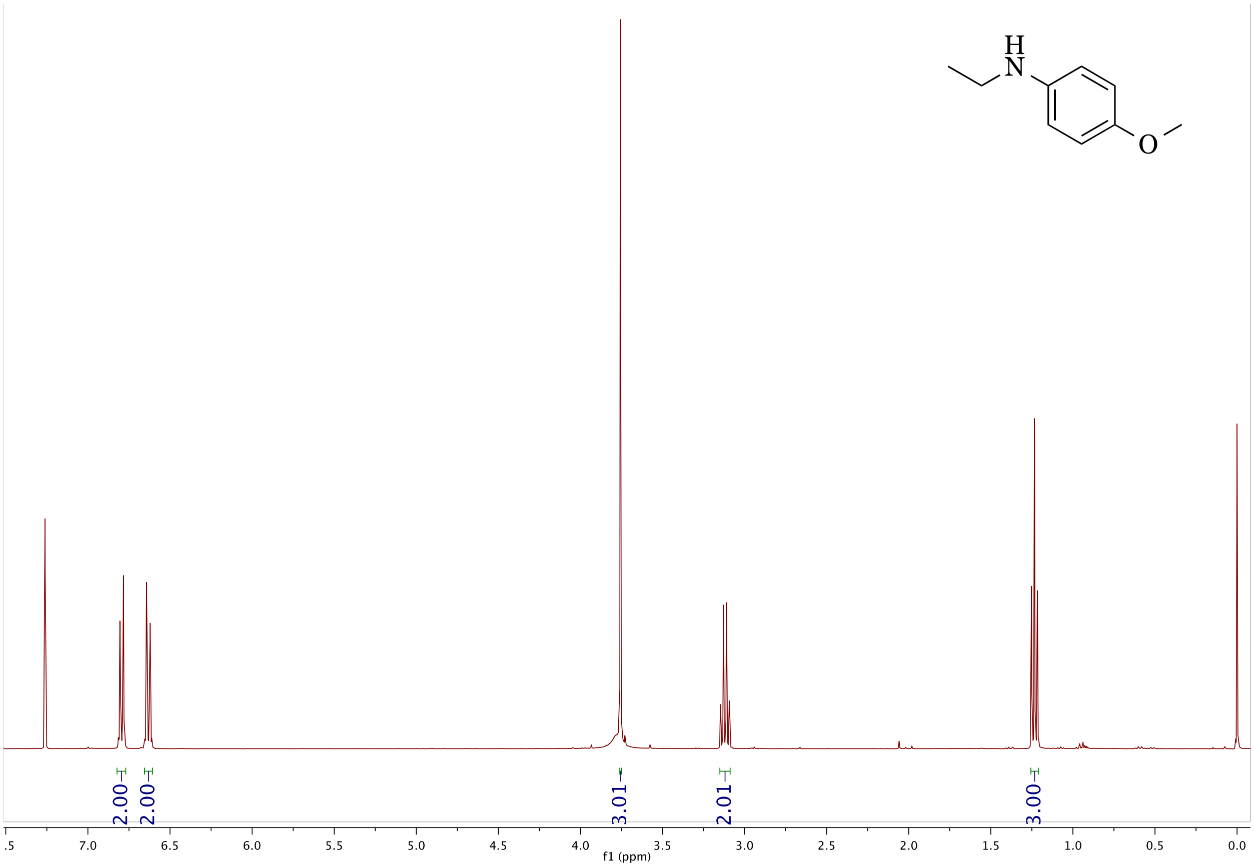
3. ^{1}H-NMR and ^{13}C-NMR Spectra

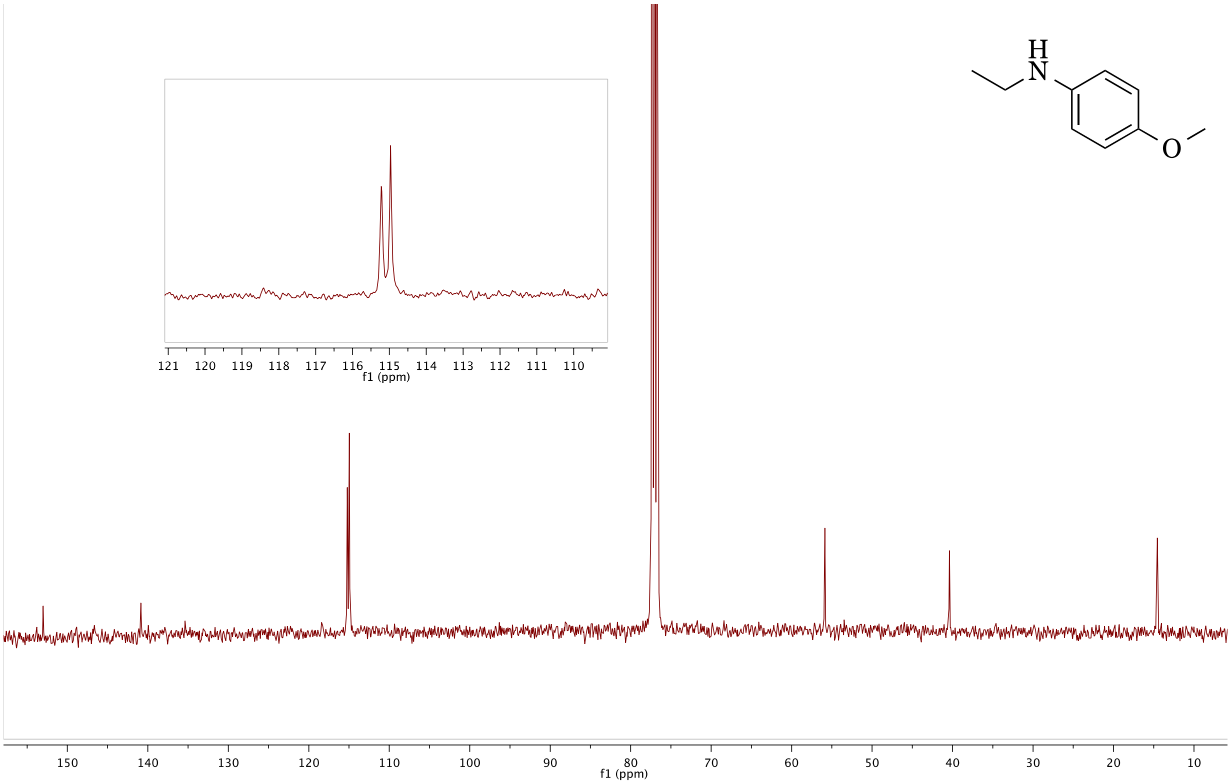


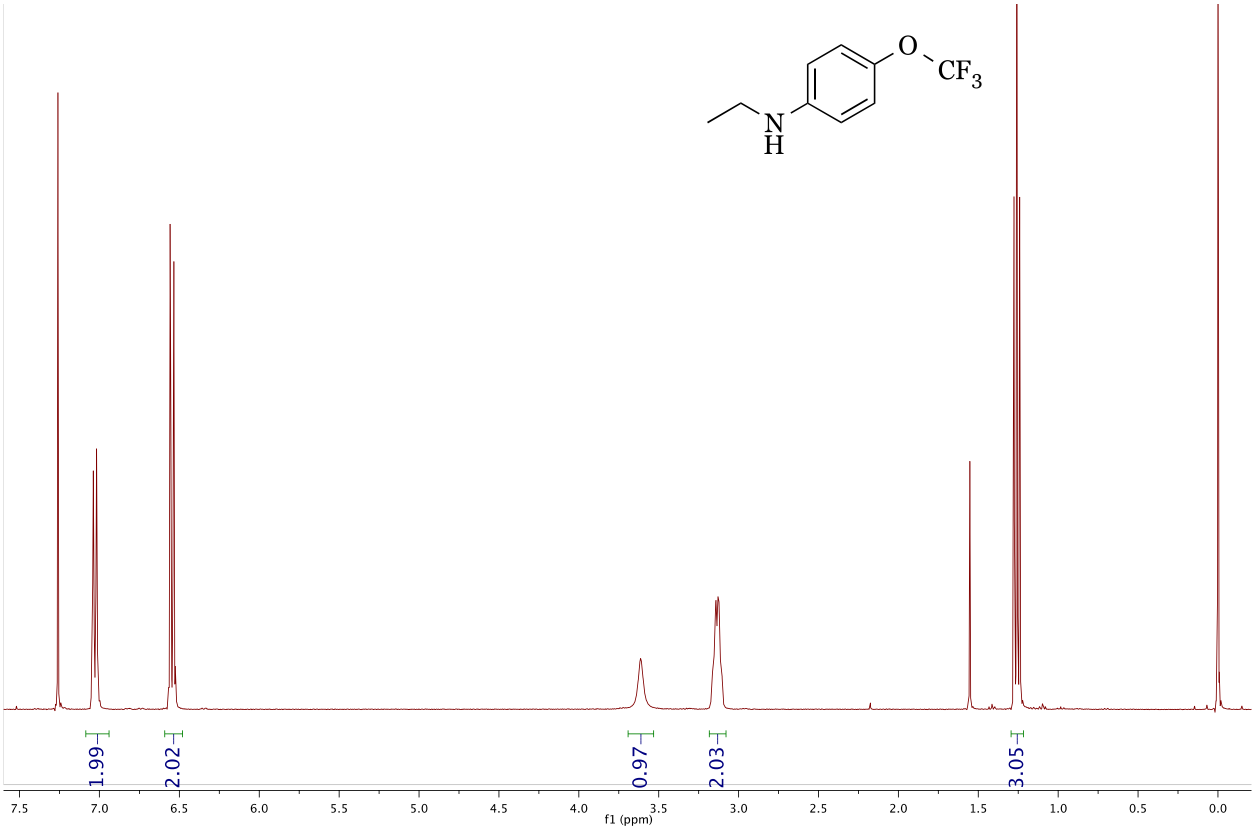


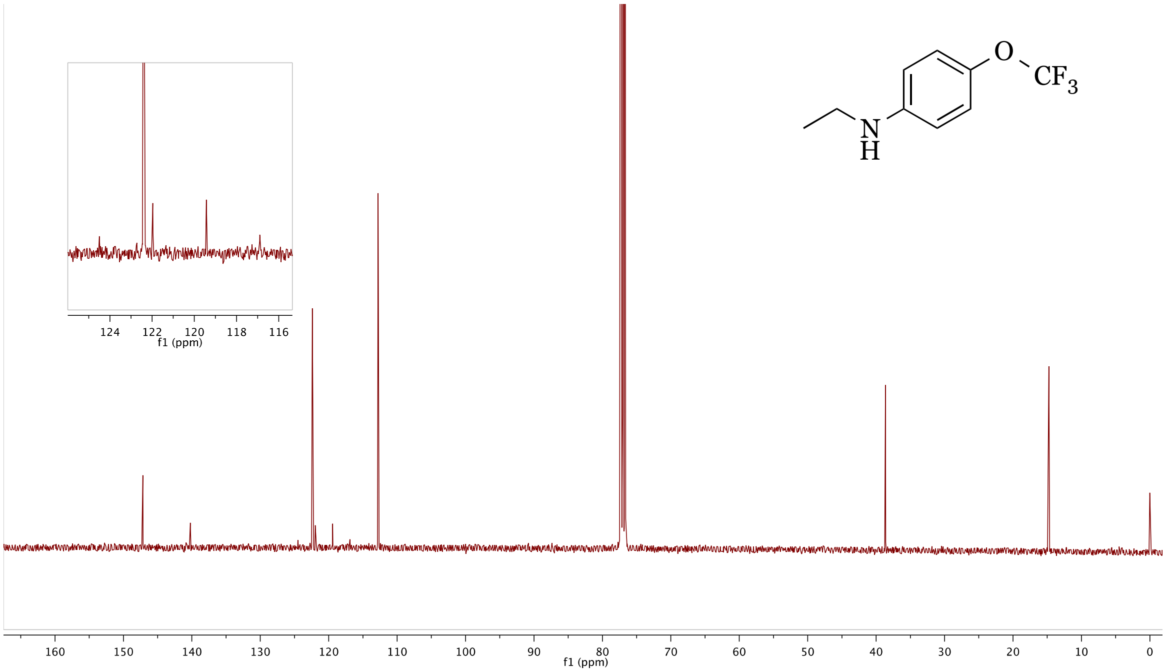

CF$_3$
N
H
2.00
2.00
1.00
2.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

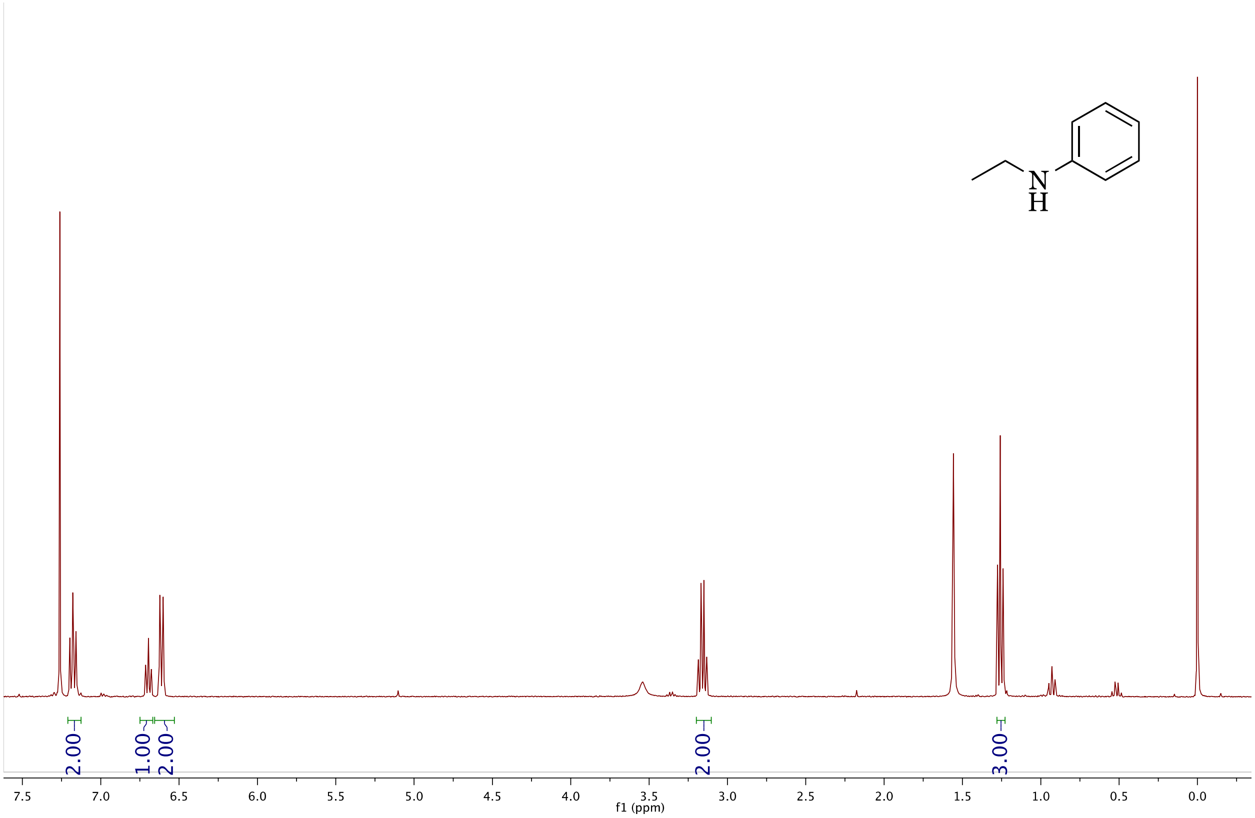

CF$_3$
N
H
126.6
126.4
126.2
f1 (ppm)
130
128
126
124
122
120
118
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

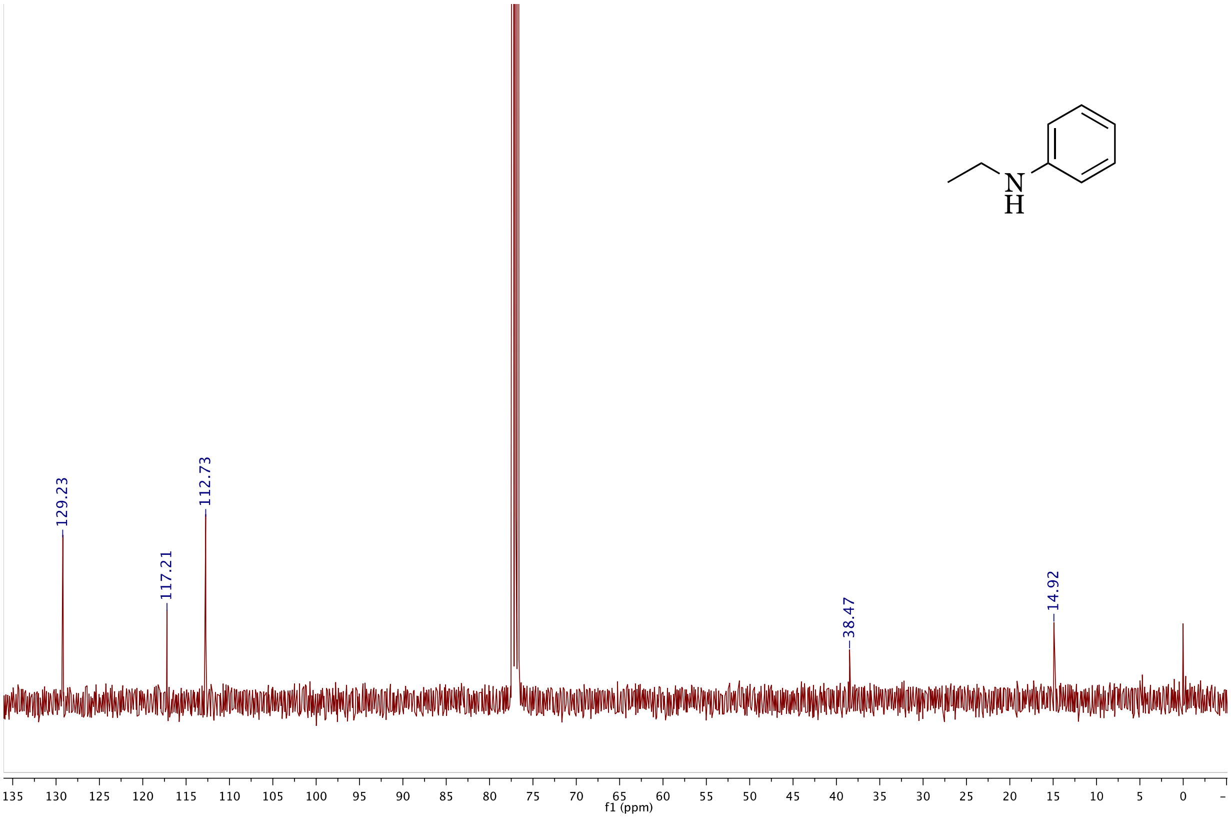

H
N
O
2.00
2.00
3.01
2.01
3.00
.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

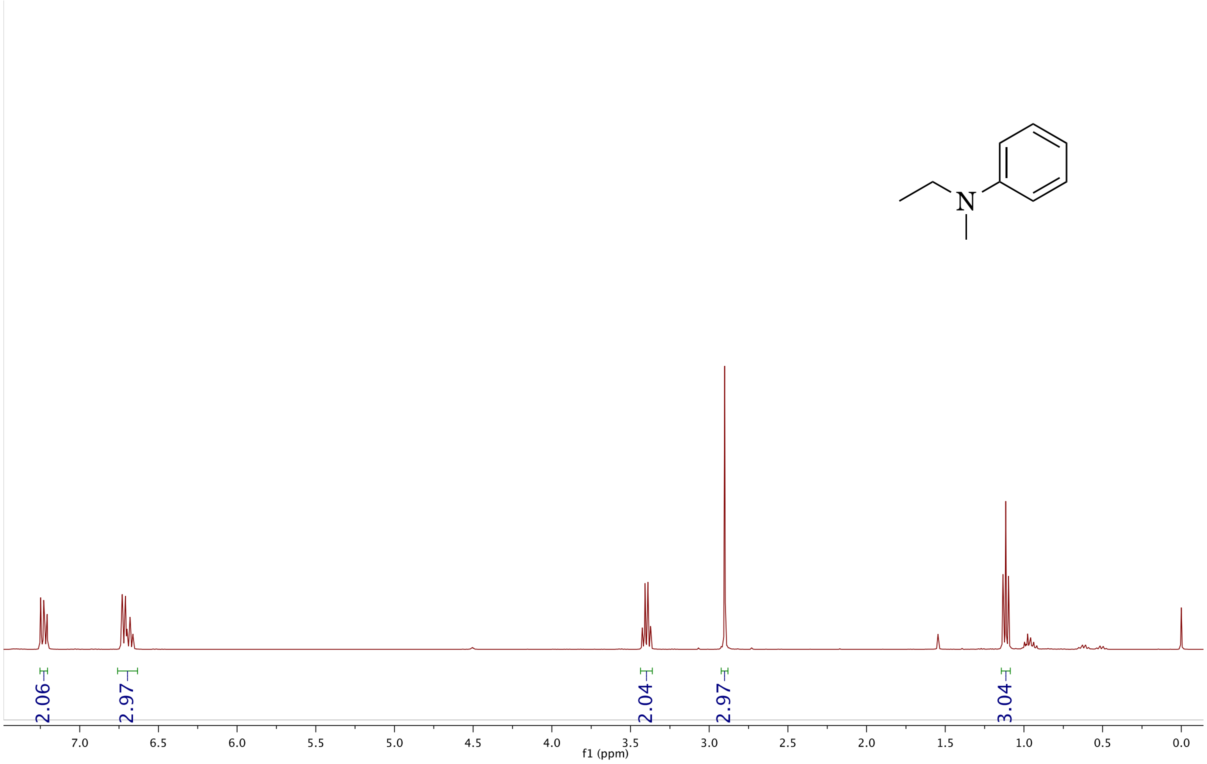

H
N
O
121
120
119
118
117
116
115
114
113
112
111
110
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

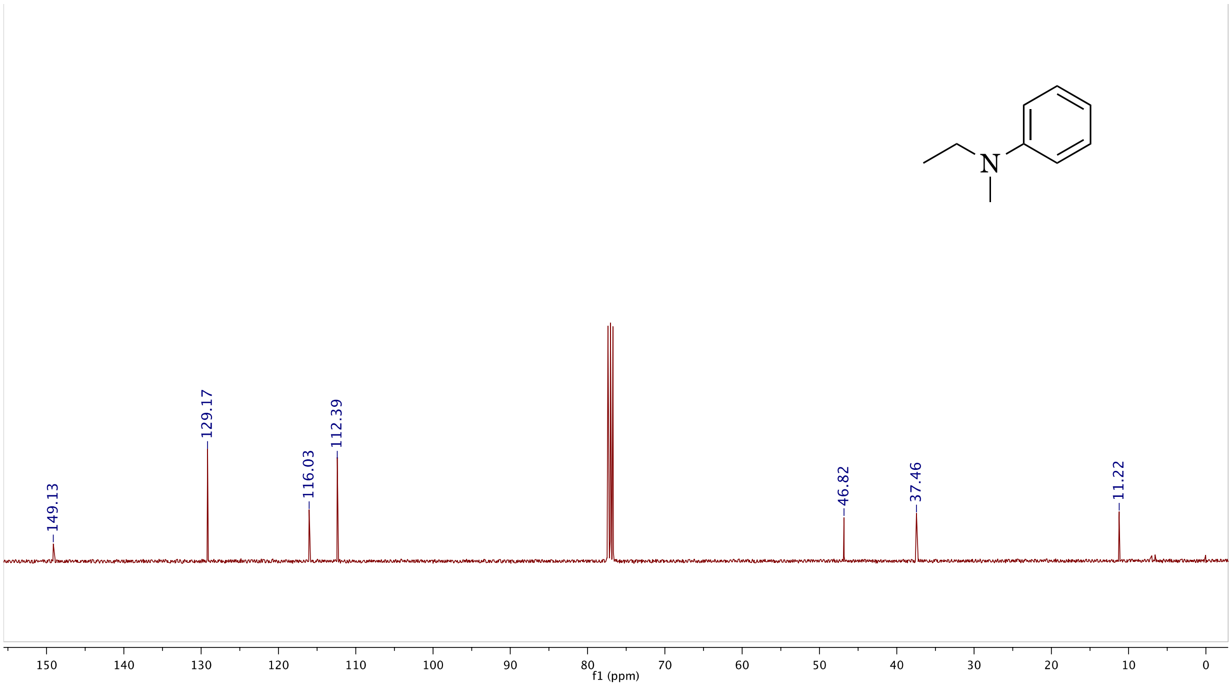

O
CF3
N
H
1.99
2.02
0.97
2.03
3.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

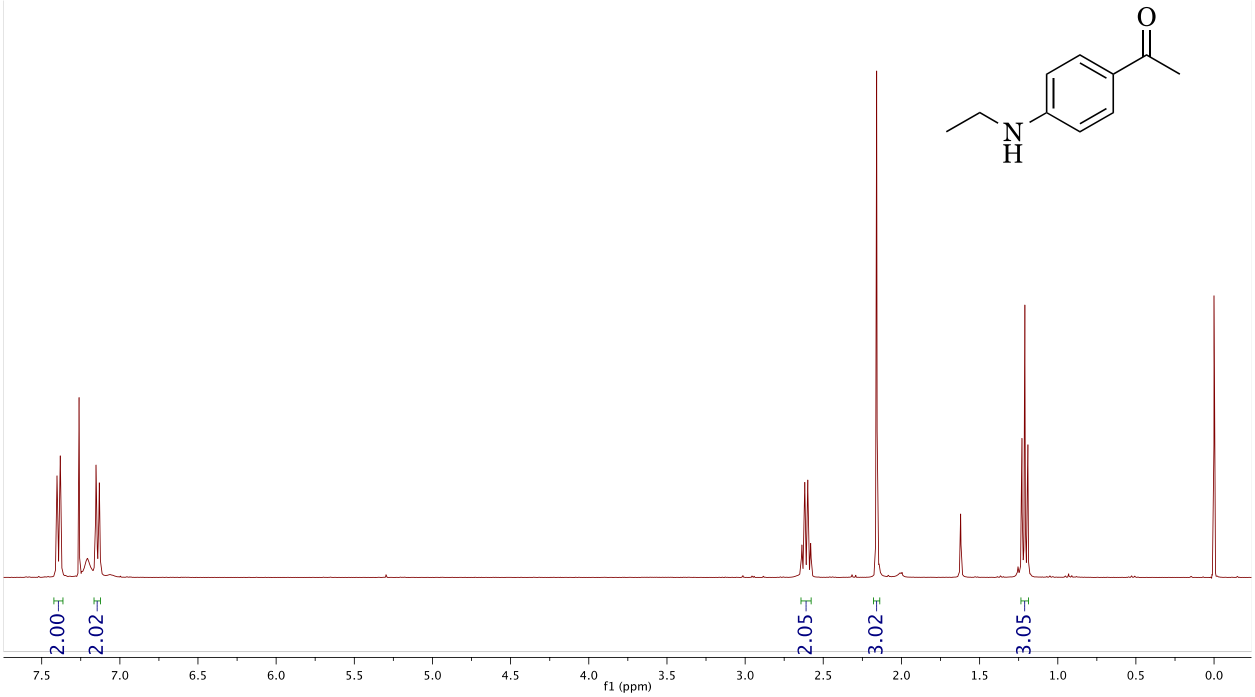

O
CF3
N
H
124
122
120
118
116
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

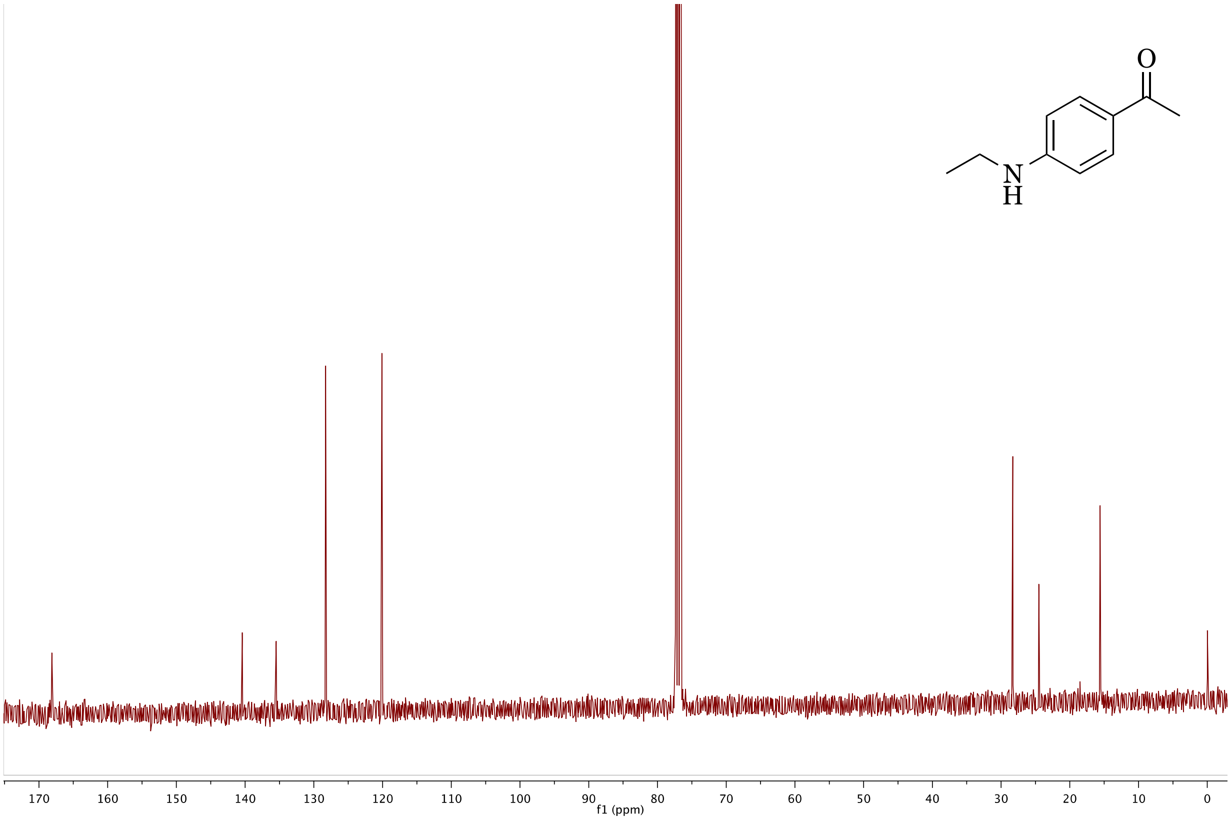

N
H
2.00
1.00
2.00
2.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

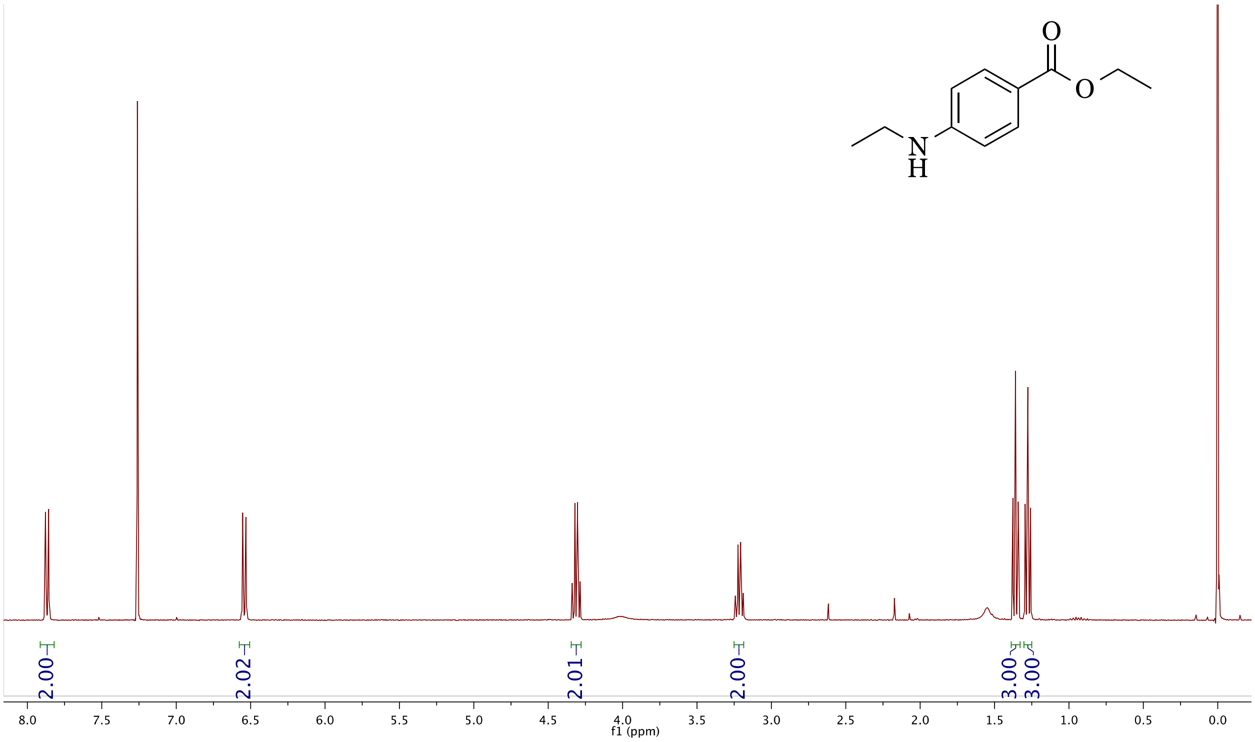

N
H
129.23
117.21
112.73
38.47
14.92
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

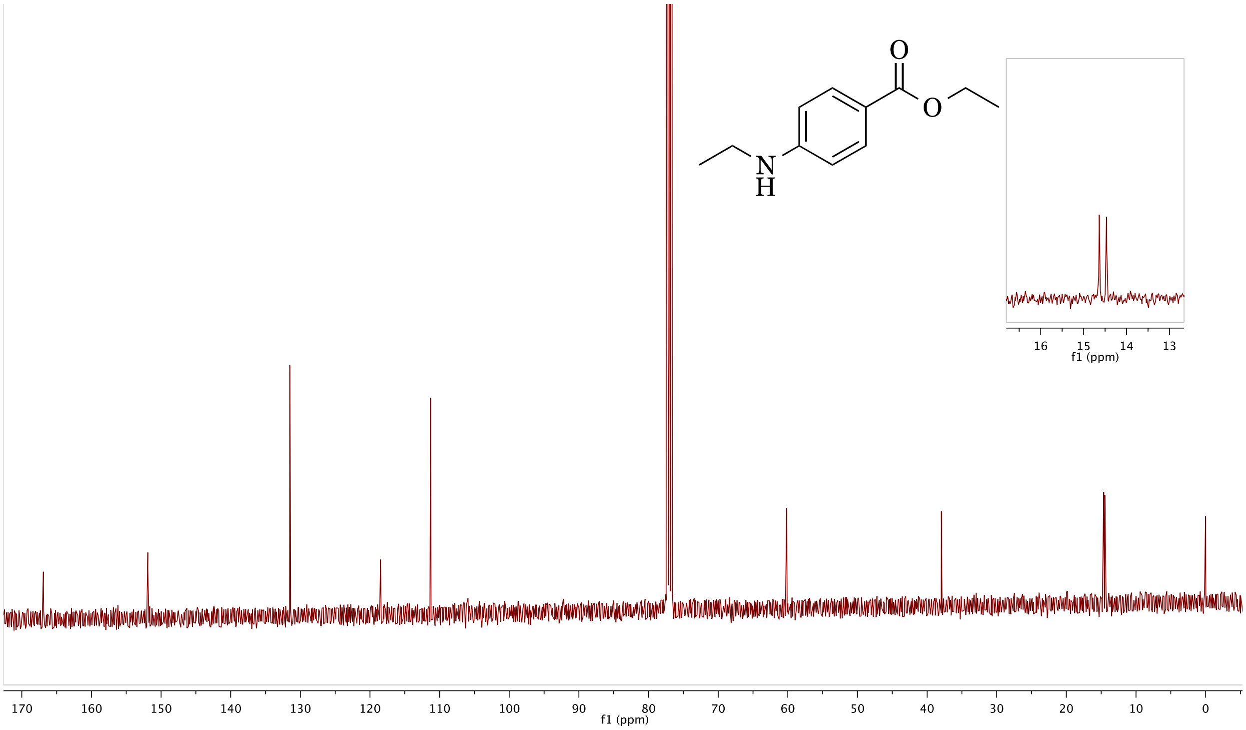

N
2.06
2.97
2.04
2.97
3.04
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

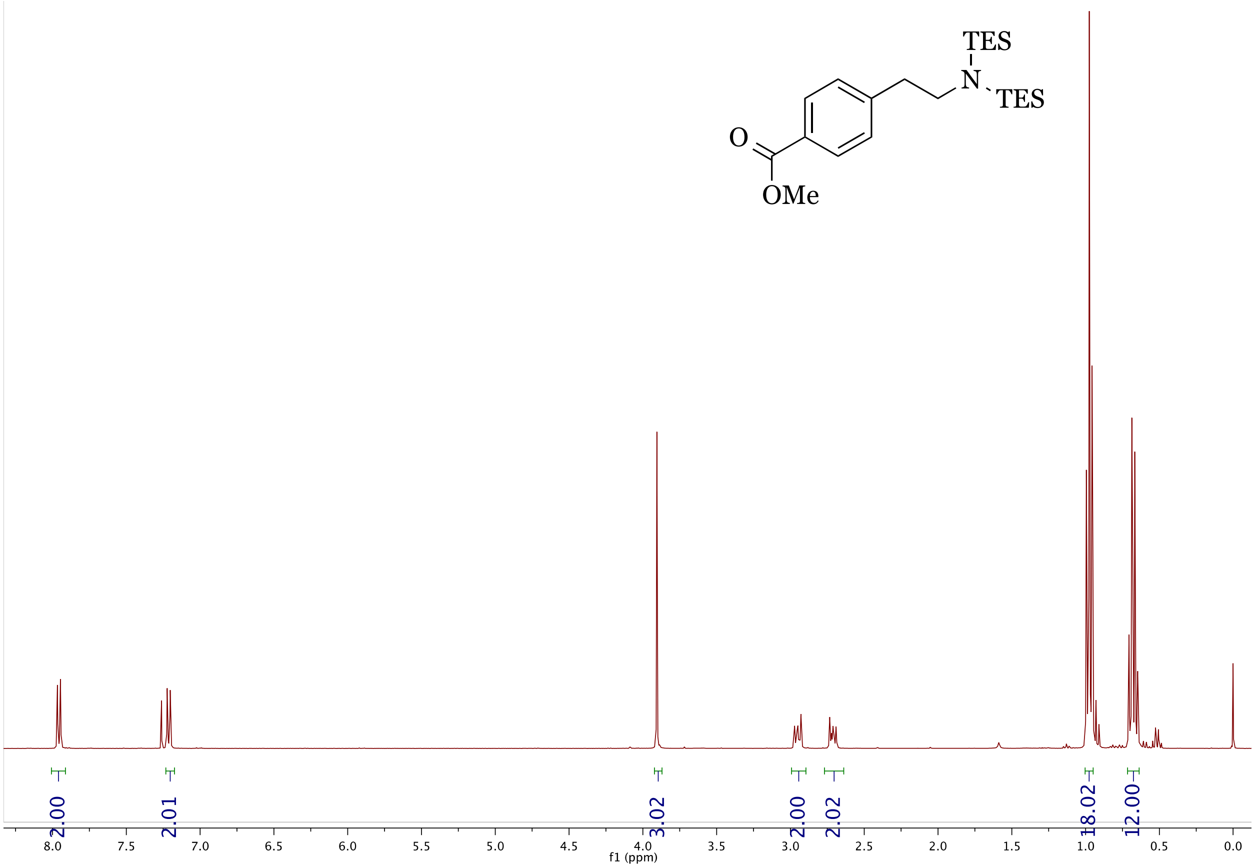

N
149.13
129.17
116.03
112.39
46.82
37.46
11.22
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

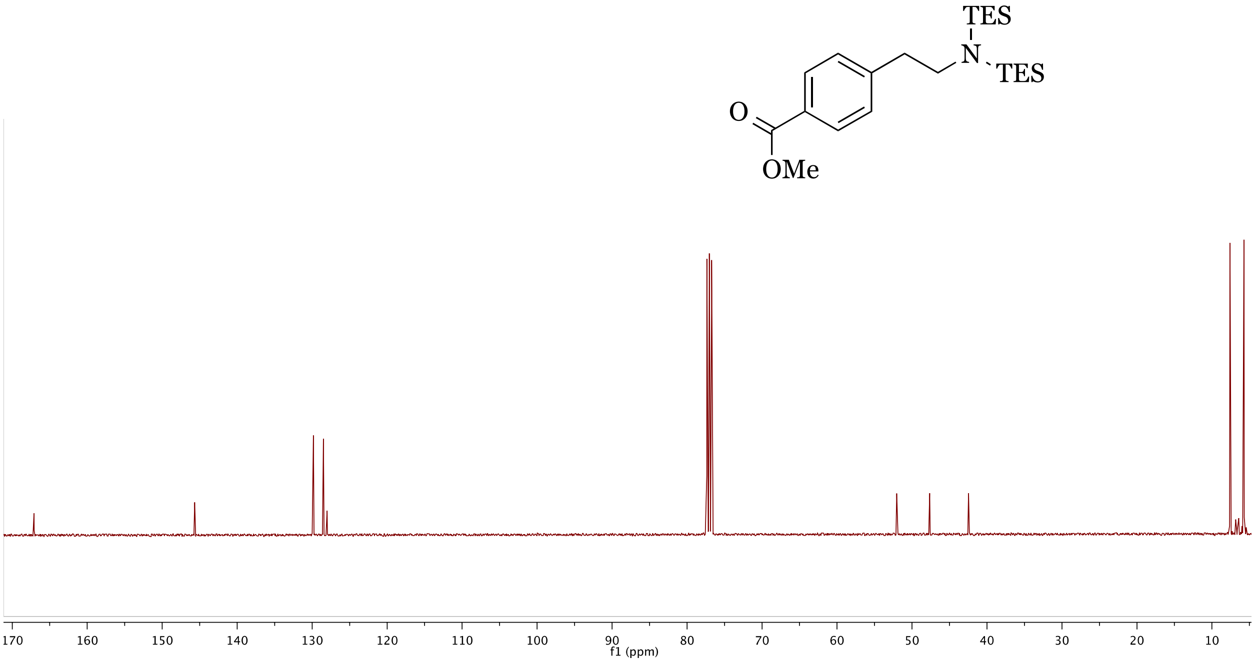

O
N
H
2.00
2.02
2.05
3.02
3.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

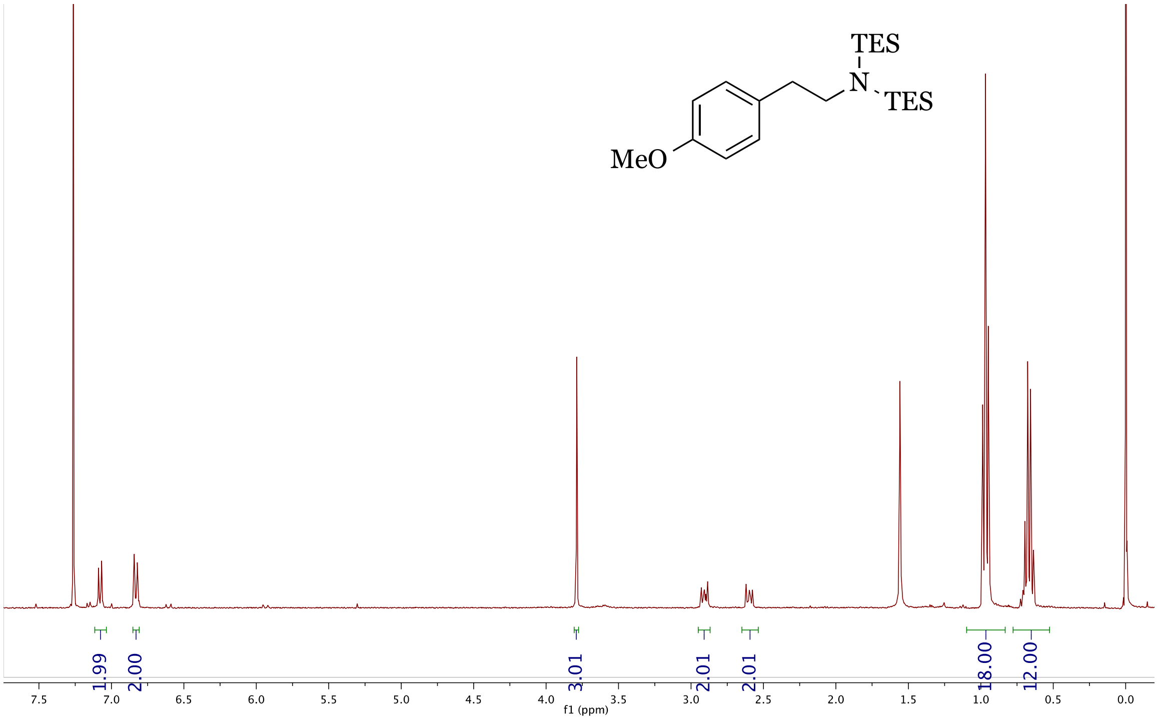

O
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
N
H
2.00
2.02
2.01
2.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

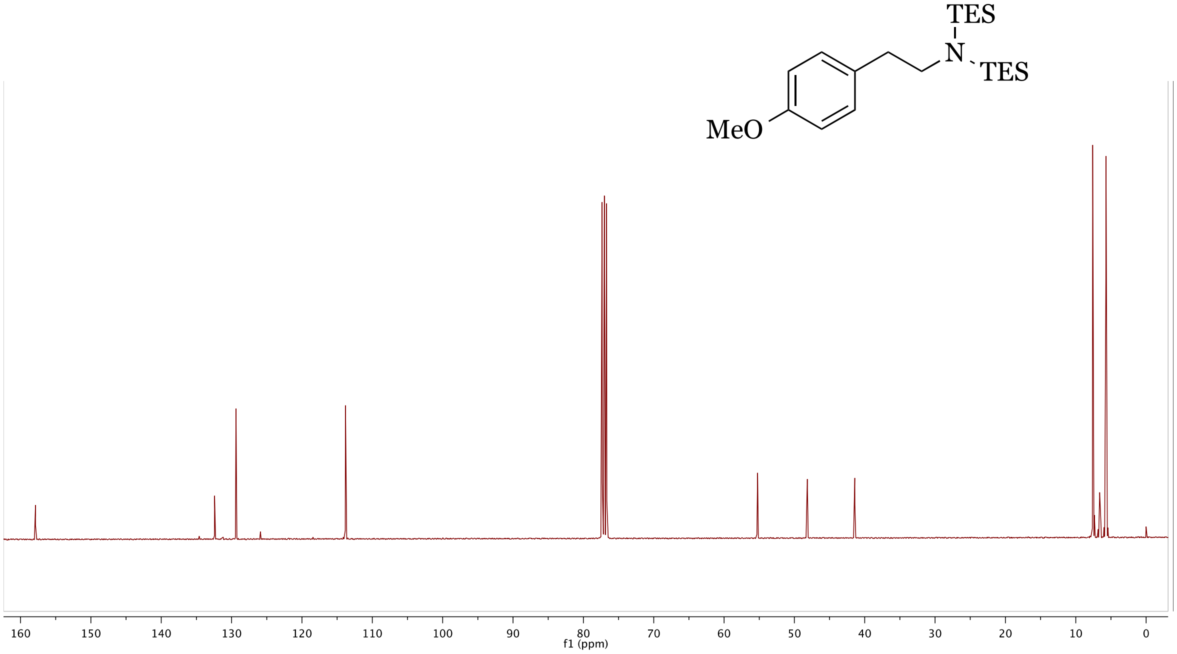

O
O
N
H
16
15
14
13
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TES
N
TES
O
OMe
2.00
2.01
3.02
2.00
2.02
18.02
12.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

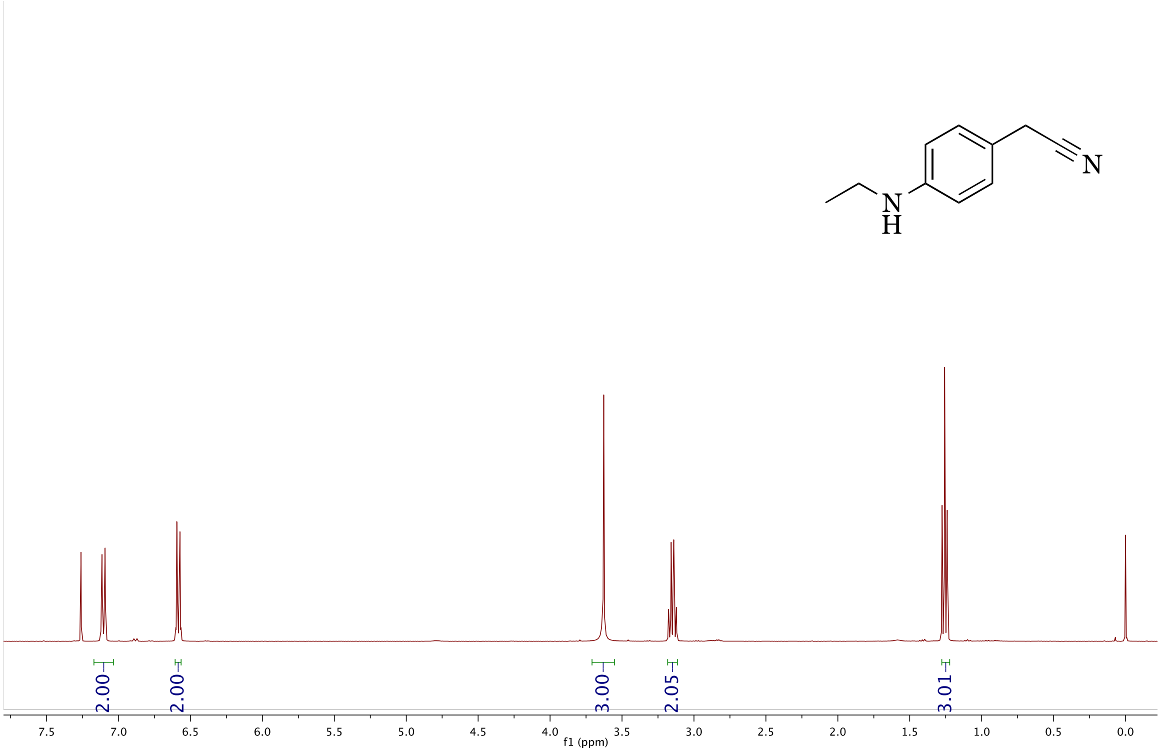

TES
N
TES
O
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

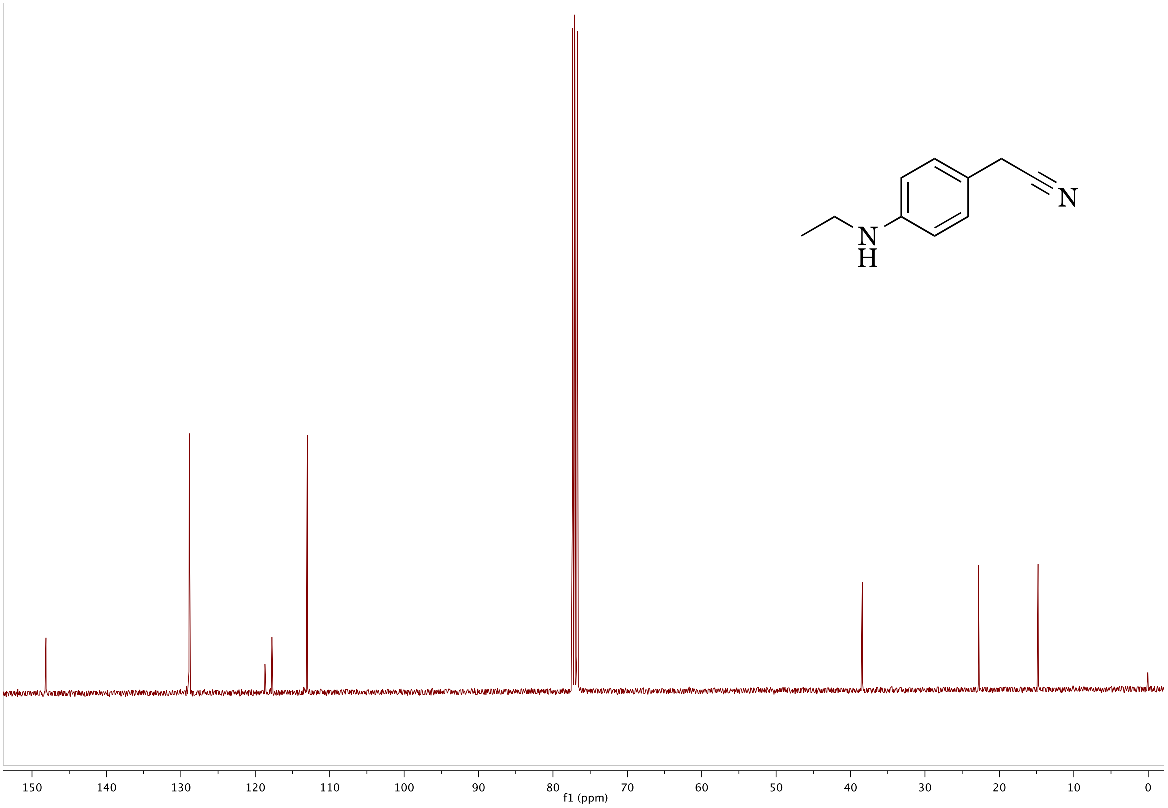


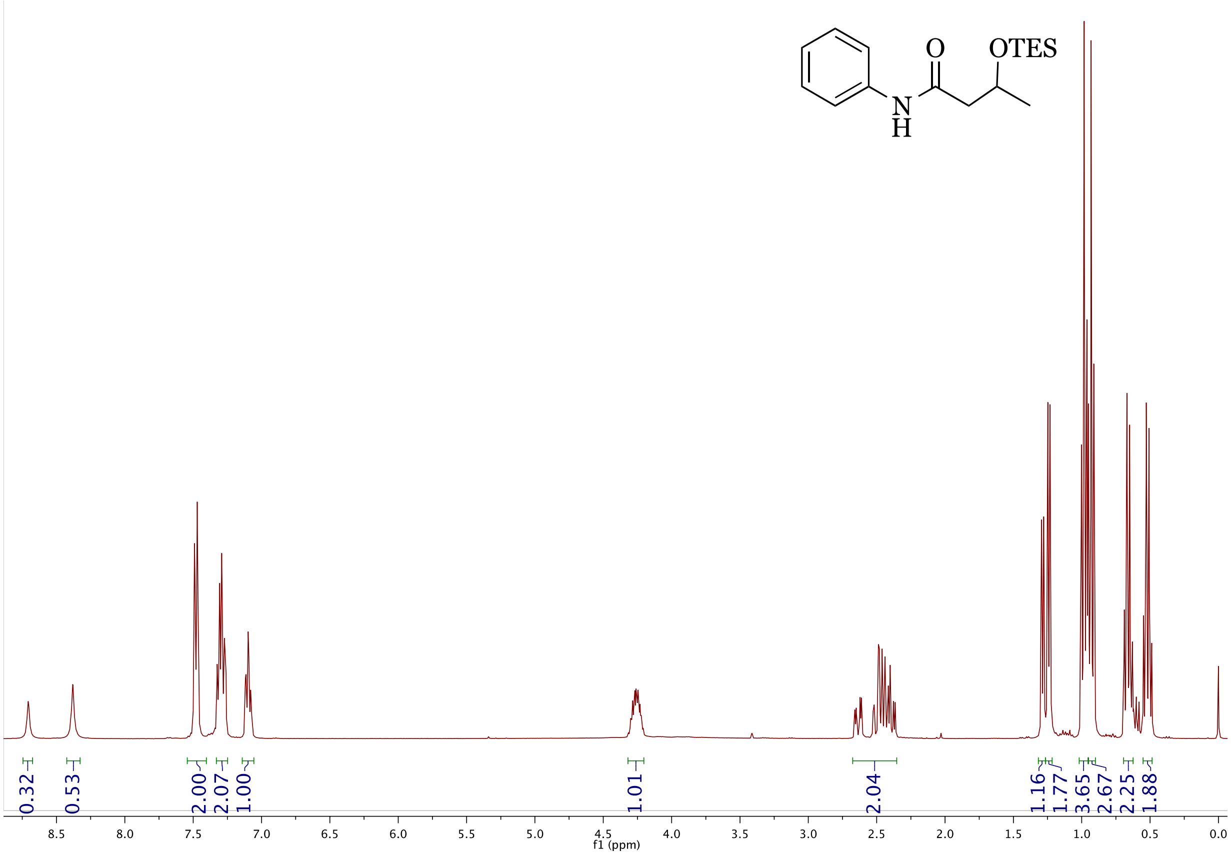
TES
N
TES
MeO
1.99
2.00
3.01
2.01
2.01
18.00
12.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

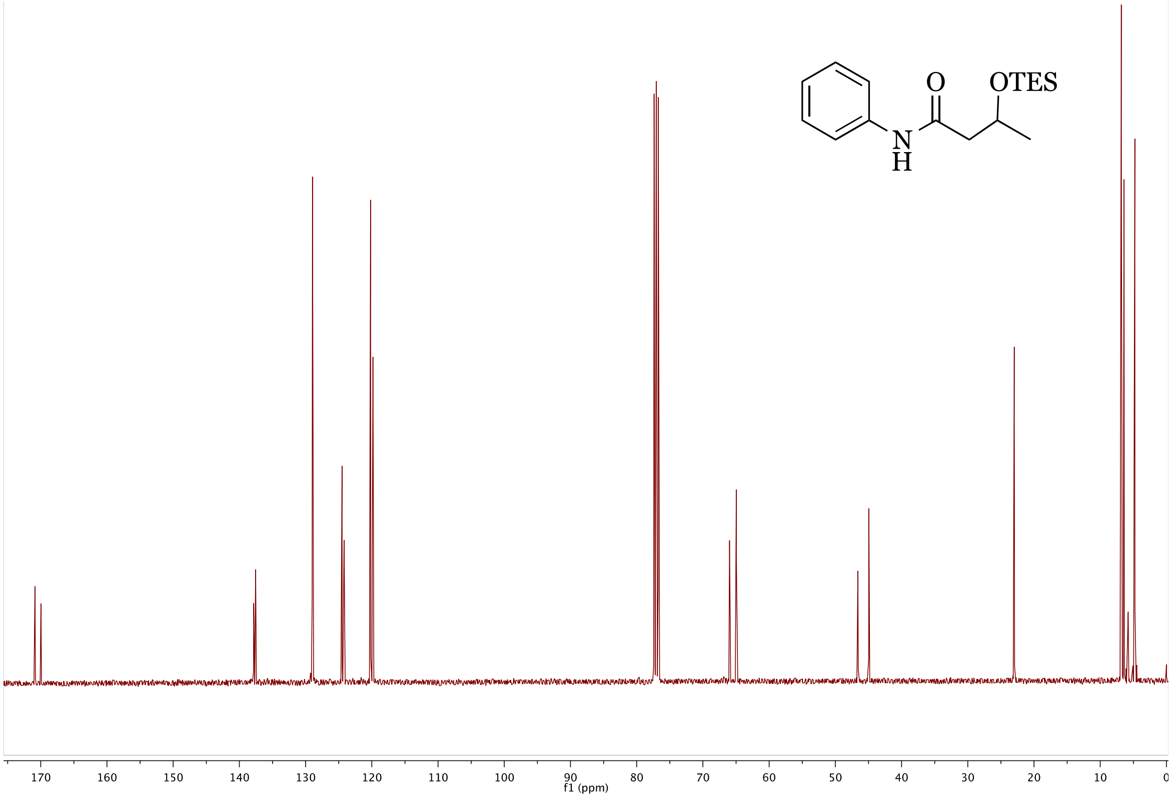


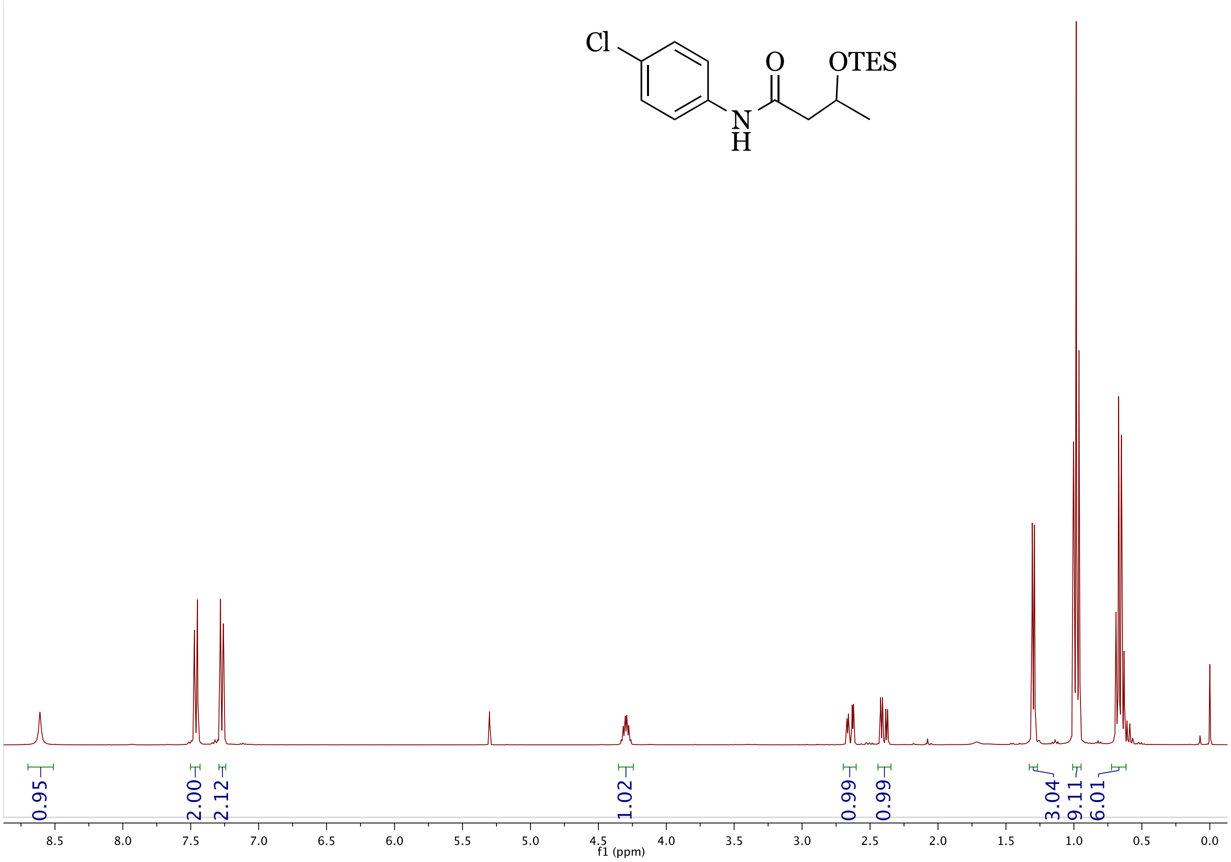
TES
N
TES
MeO
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

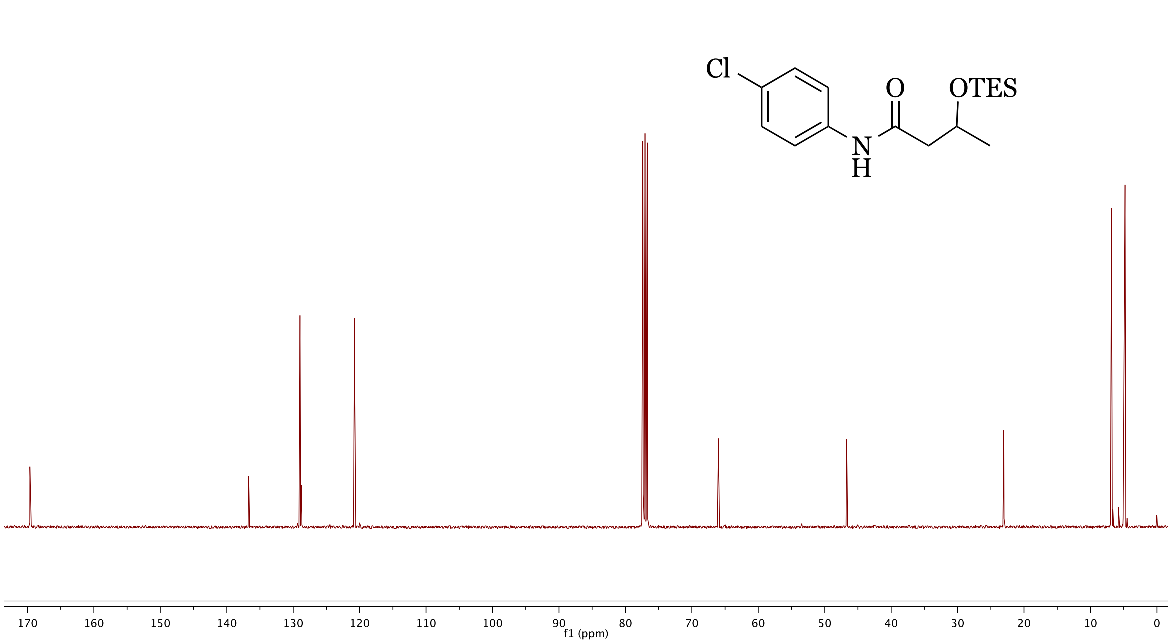

N
H
N
2.00
2.00
3.00
2.05
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
H
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OTES
N
H
0.32
0.53
2.00
2.07
1.00
1.01
2.04
1.16
1.77
3.65
2.67
2.25
1.88
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
OTES
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Cl
O
OTES
N
H
0.95
2.00
2.12
1.02
0.99
0.99
3.04
9.11
6.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Cl
O
OTES
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)