Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Copper-catalyzed reductive Amination of Aromatic and Aliphatic Ketones With Anilines Using Environmental-friendly Molecular Hydrogen

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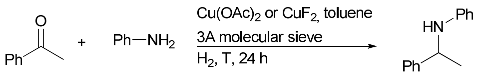
1. Experimental Section – General Information

Unless otherwise stated, all reactions were run under an argon atmosphere with exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. All isolated compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, high resolution mass spectrometry (HRMS) and HPLC. NMR spectra were recorded on Bruker AV 300 or AV 400. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are related to solvent peaks [chloroform: 7.26 (^{1}H), 77.00 (^{13}C)], respectively. All measurements were carried out at room temperature unless otherwise stated. Mass spectra were in general recorded on a Finnigan MAT 95-XP (Thermo Electron) or on a 6210 Time-of-Flight LC/MS (Agilent). Gas chromatography was performed on a HP 6890 with a HP5 column.

Reagents: Unless otherwise stated, commercial reagents were used without purification. The molecular sieve was used without activation.

2. Advanced Experimental Details for the Optimization with CuF_2 and $Cu(OAc)_2$

Table I Optimization with $Cu(OAc)_2$ and CuF_2[a]



Entry	catalyst loading [mol%]	T [°C]	p [bar]	yield with $Cu(OAc)_2$ [%][b]	yield with CuF_2 [%][b]
1	/	120	80	/	/
2	2	80	50	8	7
3	5	80	50	21	14
4	10	80	50	42	70
5	5	80	80	22	23
6	10	80	80	33	72
7	5	100	20	21	13
8	10	100	20	67	55
9	2	100	50	40	6
10	5	100	50	31	17
11	10	100	50	85	71
12	2	100	80	48	6
13	5	100	80	36	12
14	10	100	80	71	80
15	2	120	20	43	7
16	5	120	20	68	11
17	10	120	20	81	47
18	2	120	50	81	9
19	5	120	50	82	59
20	10	120	50	72	81
21	2	120	80	78	17
22	5	120	80	83	38
23	10	120	80	72	83

[a]Reaction conditions: 0.5 mmol **1a**, 0.5 mmol **2a**, $Cu(OAc)_2$ or CuF_2, 1.5 mL toluene, H_2, T, 24 h; [b]Determined by GC methods using hexadecane as an internal standard.

3. Reductive Amination of Ketones using molecular Hydrogen:

All catalytic hydrogenation experiments were carried out in a Parr Instruments 4560 series autoclave (300 mL) containing an alloy plate with wells for seven 4 mL glass vials.

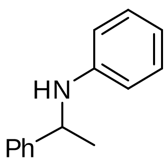
Under an argon atmosphere, a glass vial was charged with $Cu(OAc)_2$ (1.8 mg, 0.01 mmol), ketone **1** (0.5 mmol, 60.1mg), amine **2** (0.5 mmol), 3Å molecular sieve (300mg) und 1.5 mL toluene. A magnetic stirring bar was added. Afterwards, the vial was capped with a septum equipped with a syringe and set in the alloy plate, which was then placed into the autoclave. Once sealed, the autoclave was purged 3 times with hydrogen, then pressurized to 50 bar and heated at 120 °C for 24 hours to give the corresponding secondary amine **3**. After the reaction, the autoclave was cooled to 25°C, depressurized and the reaction mixture was purified by column chromatography on silica gel (eluent: heptane/ethyl acetate = 9:1). The isolated compounds were then analyzed by NMR, GCMS and HRMS.

4. Reductive Amination of Aldehydes using molecular Hydrogen:

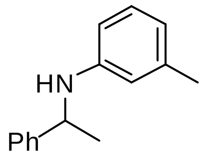
All catalytic hydrogenation experiments were carried out in a Parr Instruments 4560 series autoclave (300 mL) containing an alloy plate with wells for seven 4 mL glass vials.

Under an argon atmosphere, a glass vial was charged with Cu(OAc)2 (1.8 mg, 0.01 mmol), aldehyde **4** (0.5 mmol), aniline **2a** (0.5 mmol, 46.6 mg), 3Å molecular sieve (300 mg) and 1.5 mL toluene. A magnetic stirring bar was added. Afterwards, the vial was capped with a septum equipped with a syringe and set in the alloy plate, which was then placed into the autoclave. Once sealed, the autoclave was purged 3 times with hydrogen, then pressurized to 50 bar and heated at 120 °C for 24 hours to give the corresponding secondary amine **5**. After the reaction, the autoclave was cooled to 25 °C, depressurized and the reaction mixture was purified by column chromatography on silica gel (eluent: heptane/ethyl acetate = 9:1). The isolated compounds were then analyzed by NMR, GCMS and HRMS.

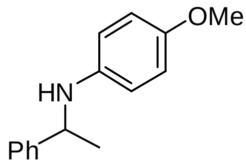
5. Analytical Data



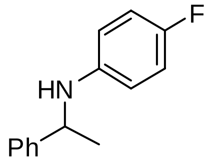
***N*-(1-Phenylethyl)aniline (3a).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.44 (d, *J* = 6.5 Hz, 3 H), 3.99 (br s, 1 H), 4.40 (q, *J* = 6.7 Hz, 1 H), 6.41-6.46 (m, 2 H), 6.56 (dd, *J* = 7.6, *J* = 7.6, 1 H), 6.97-7.05 (m, 2 H), 7.11-7.18 (m, 1 H), 7.20-7.32 (m, 4 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 25.0, 53.4, 113.3, 117.2, 125.8, 126.8, 128.6, 129.1, 145.1, 147.2; **GCMS-EI** (70eV): m/z (%) = 197 (M^+, 43), 183 (15), 182 (100), 105 (58), 104 (13), 93 (37), 79 (11), 77 (32), 51 (10). **HRMS** (ESI-TOF, m/z) calcd. for $C_{14}H_{16}N$ $(M+H)^+$, 198.1277; found 198.1281.



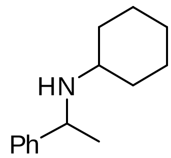
3-Methyl-*N*-(1-phenylethyl)aniline (3b). **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.42 (d, *J* = 6.8 Hz, 3 H), 2.13 (s, 3 H), 3.93 (br s, 1 H), 4.40 (q, *J* = 6.8 Hz, 1 H), 6.23 (d, *J* = 8.1 Hz, 1 H), 6.29 (s, 1 H), 6.40 (d, *J* = 7.4, 1 H), 6.90 (dd, *J* = 7.7, *J* = 7.7, 1 H), 7.11-7.17 (m, 1 H), 7.20-7.31 (m, 4 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 21.6, 24.9, 53.4, 110.3, 114.1, 118.2, 125.8, 126.8, 128.6, 129.0, 138.8, 145.3, 147,2. **GCMS-EI** (70eV): m/z (%) = 211 (M^+, 47), 197 (16), 196 (100), 107 (33), 106 (14), 105 (42), 91 (14), 79 (11), 77 (17). **HRMS** (ESI-TOF, m/z) calcd. for $C_{15}H_{18}N$ $(M)^+$, 212.1434; found 212.1438.



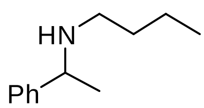
4-Methoxy-*N*-(1-phenylethyl)aniline (3c). **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 6.7 Hz, 3 H), 3.61 (s, 3H), 4.33 (q, *J* = 6.7 Hz, 1 H), 6.36-6.43 (m, 2 H), 6.58-6.64 (m, 2 H), 7.11-7.17 (m, 1 H), 7.20-7.31 (m, 4 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 25.1, 54.2, 55.7, 114.5, 114.7, 125.8, 126.8, 128.6, 141.5, 145.4, 151.8; **GCMS-EI** (70eV): m/z (%) = 228 (16), 227 (M^+, 92), 213 (16), 212 (100), 123 (43), 122 (17), 108 (42), 105 (65), 103 (10), 79 (14), 77 (20). **HRMS** (ESI-TOF, m/z) calcd. for $C_{15}H_{18}NO$ $(M+H)^+$, 228.1383; found 228.1382.



4-Fluoro-*N*-(1-phenylethyl)aniline (3d). **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.52 (d, *J* = 6.7 Hz, 3 H), 4.00 (br s, 1 H), 4.43 (q, *J* = 6.7 Hz, 1 H), 6.41-6.48 (m, 2 H), 6.76-6.84 (m, 2 H), 7.21-7.27 (m, 1 H), 7.30-7.39 (m, 4 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 25.1, 54.1, 114.1 (d, *J* = 7.2 Hz), 115.5 (d, *J* = 22.1 Hz), 125.8, 126.9, 128.7, 143.5 (d, *J* = 1.4 Hz), 144.9, 155.6 (d, *J* = 234.5 Hz). **GCMS-EI** (70eV): m/z (%) = 215 (M^+, 53), 201(13), 200 (84), 122 (13), 111 (47), 105 (100), 103 (12), 95 (17), 79 (14), 77 (21). **HRMS** (ESI-TOF, m/z) calcd. for $C_{14}H_{15}NF$ $(M+H)^+$, 216.1183; found 215.1187.

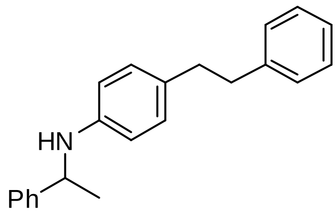


***N*-(1-Phenylethyl)cyclohexanamine (3e).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.00-1.09 (m, 5 H), 1.33 (d, *J* = 6.6 Hz, 3 H), 1.51-1.60 (m, 1 H), 1.62-1.75 (m, 3 H), 1.94-2.02 (m, 1 H), 2.23-2.32 (m, 1 H), 3.96 (d, *J* = 6.6 Hz, 1 H) 7.20-7.25 (m, 1 H), 7.27-.7.35 (m, 4 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 25.0, 25.1, 25.3, 26.2, 33.3, 34.6, 53.7, 54.5, 126.5, 126.7, 128.4, 146.4. **GCMS-EI** (70eV): m/z (%) = 203 (M^+, 7), 189 (15), 188 (100), 160 (30), 106 (34), 105 (95), 104 (10), 103 (12), 79 (18), 77 (19), 56 (34), 41 (10). **HRMS** (ESI-TOF, m/z) calcd. for $C_{14}H_{22}N$ $(M+H)^+$, 204.1747, found 204.1749.

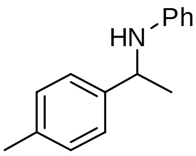


***N*-(1-Phenylethyl)butan-1-amine (3f).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 0.84-0.90 (m, 3 H), 1.25-1.32 (m, 2 H), 1.36 (d, *J* = 6.7 Hz, 3 H), 1.42-1.52 (m, 2 H), 2.37-2.55 (m, 2 H), 3.76 (q, *J* = 6.6 Hz, 1 H), 7.20-7.26 (m, 1 H);

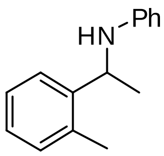
7.29-7.34 (m, 4H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 14.5, 20.1, 24.4, 32.4, 47.6, 58.5, 126.6, 126.9, 128.4, 145.9. **GCMS-EI** (70eV): m/z (%) = 177 (M^+, 2), 163 (13), 162 (94), 134 (14), 105 (100), 79 (14), 77 (15). **HRMS** (ESI-TOF, m/z) calcd. for $C_{12}H_{20}N$ $(M+H)^+$, 178.1590, found 178.1594.



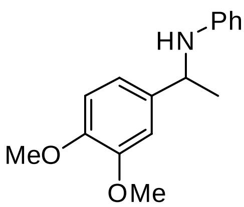
4-Phenethyl-*N*-(1-phenylethyl)aniline (3g). **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.43 d, *J* = 6.7 Hz, 3H), 2.63-2.79 (m, 4 H) 3.92 (br s, 1 H), 4.40 (q, *J* = 6.8 Hz, 1 H), 6.35-6.41 (m, 2 H), 6.82-6.87 (m, 2 H), 7.05-7.32 (10 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 25.0, 37.0, 38.3, 53.7, 113.4, 125.7, 125.8, 126.8, 128.2, 128.4, 128.6, 129.0, 130.6, 142.2, 145.3, 145.4. **GCMS-EI** (70eV): m/z (%) = 301 (M^+, 33), 286 (10), 211(20), 210 (100), 106 (82), 105 (63), 91 (18), 79 (11), 77 (13). **HRMS** (ESI-TOF, m/z) calcd. for $C_{22}H_{24}N$ $(M+H)^+$, 302.1903, found 302.1898.



***N*-(1-p-Tolylethyl)aniline (3h).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.52 (d, *J* = 6.8 Hz, 3 H), 2.34 (s, 3 H), 4.09 (br s, 1 H), 4.48 (q, *J* = 6.7 Hz, 1 H), 6.51-6.57 (m, 2 H), 6.66 (dd, *J* = 7.3, *J* = 7.3 Hz, 1 H), 7.08-7.18 (m, 4 H), 7.25-7.31 (m, 2 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 21.1, 25.1, 53.2, 113.4, 117.3, 125.8, 129.1, 129.4, 136.5, 142.2, 147.3. **GCMS-EI** (70eV): m/z (%) = 211 (M^+, 34), 196 (53), 120 (14), 119 (100), 117 (15), 104 (12), 77 (24), 93 (33), 91 (25), 65 (11). **HRMS** (ESI-TOF, m/z) calcd. for $C_{15}H_{18}N$ $(M+H)^+$, 212.1433, found 212.1433.

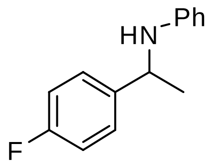


***N*-(1-o-Tolylethyl)aniline (3i).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 6.6 Hz, 3 H), 2.44 (s, 3 H), 4.11 (br s, 1 H), 4.68 (q, *J* = 6.7 Hz, 1 H), 6.42-6.50 (m, 2 H), 6.61-6.68 (dd, *J* = 7.3, *J* = 7.3 Hz, 1 H), 7.05-7.21 (m, 5 H), 7.40-7.47 (m, 1 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 19.0, 23.0, 49.9, 113.1, 117.3, 124.7, 126.6, 126.7, 129.2, 130.6, 134.6, 142.7, 147.2. **GCMS-EI** (70eV): m/z (%) = 212 (11), 211 (M^+, 65), 197 (14), 196 (88), 120 (19), 119 (100), 118 (26), 117 (24), 115 (10), 104 (18), 93 (45), 91 (32), 77 (29), 65 (13). **HRMS** (ESI-TOF, m/z) calcd. for $C_{15}H_{18}N$ $(M+H)^+$, 212.1434, found 212.1436.

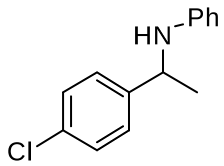


***N-(*1-(3,4-Dimethoxyphenyl)ethyl)aniline (3j).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.51 (d, *J* = 6.6 Hz, 3 H), 3.86 (d, *J* = 1.2 Hz, 6 H), 4.43 (q, *J* = 6.7 Hz, 1 H), 6.51-6.57 (m, 2 H), 6.66 (dd, *J* = 7.4 Hz, *J* = 7.4 Hz, 1 H), 6.80-6.84 (m, 1 H), 6.90-6.95 (m, 2 H), 7.07-7.14 (m, 2 H). **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 25.0, 53.4, 55.8, 55.9, 109.0, 118.2, 113.4, 117.3, 117.7, 129.1, 137.8, 147.3, 147.8, 149.1. **GCMS-EI** (70eV): m/z (%) = 257 (M^+, 17), 242 (7), 166 (13), 165 (100), 150 (9), 121 (5), 104 (5), 77 (10), **HRMS** (ESI-TOF, m/z) calcd. for $C_{16}H_{19}NO_2Na$ $(M+Na)^+$, 280.1308, found 280.1302.

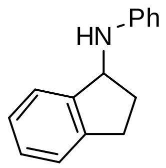
Electronic Supplementary Material (ESI) for Green Chemistry



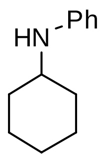
***N*-(1-(4-Fluorophenyl)ethyl)aniline (3k).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.51 (d, *J* = 6.8 Hz, 3 H), 4.09 (br s, 1 H), 4.47 (q, *J* = 6.7 Hz, 1 H), 6.48-6.53 (m, 2 H), 6.64-6.71 (m, 1 H), 6.97-7.05 (m, 2 H), 7.07-7.15 (m, 2 H); 7.30-7.38 (m, 2 H); **^{13}C NMR** (75.5 MHz, ,$CDCl_3$): δ = 25.2, 53.0, 113.4, 115.5 (d, *J* = 21.1 Hz), 117.5, 127.4 (d, *J* = 8.1 Hz), 129.2, 140.9 (d, *J* = 2.7 Hz), 147.0, 161.8 (d, *J* = 244.5). **GCMS-EI** (70eV): m/z (%) = 215 (M^+, 58), 201 (14), 200 (98), 123 (100), 104 (13), 103 (43), 93 (63), 77 (39), 51 (13). **HRMS** (ESI-TOF, m/z) calcd. for $C_{14}H_{15}NF$ $(M+H)^+$, 216.1183, found 216.1187.



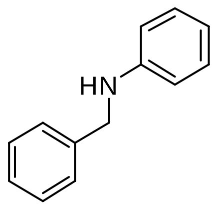
***N*-(1-(4-Chlorophenyl)ethyl)aniline (3l).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.50 (d, *J* = 6.7 Hz, 3 H), 4.08 (br s, 1 H), 4.46 (q, *J* = 6.7 Hz, 1 H), 6.46-6.52 (m, 2 H), 6.64-6.71 (m, 1 H), 7.06-7.14 (m, 2 H), 7.26-7.34 (m, 4 H); **^{13}C NMR** (75.5 MHz, ,$CDCl_3$): δ = 25.1, 53.1, 113.4, 117.6, 127.3, 128.8, 129.2, 132.5, 143.8, 146.9. **GCMS-EI** (70eV): m/z (%) = 233 (17), 231 (M^+, 51), 218 (32), 217 (14), 216 (100), 141 (31), 140 (10), 139 (95), 104 (20), 103 (57), 93 (71), 90 (16), 77 (56), 65 (11), 51 (17). **HRMS** (ESI-TOF, m/z) calcd. for $C_{14}H_{15}NCl$ $(M+H)^+$, 232.0888, found 232.0885.



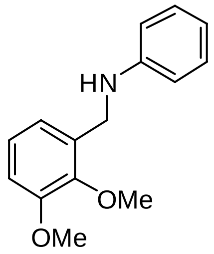
***N*-Phenyl-2,3-dihydro-1H-inden-1-amine (3m).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.87-2.01 (m, 1 H), 2.55-2.68 (m, 1 H), 2.86-3.11 (m, 2 H), 3.97 (br s, 1 H), 5.04 (t, *J* = 6.7 Hz, 1 H), 6.71-6.79 (m, 3 H), 7.18-7.32 (m, 5 H), 7.37-7.43 (m, 1 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 30.3, 33.9, 58.7, 113.2, 117.5, 124.3, 124.9, 126.7, 128.0, 129.4, 143.7, 144.6, 147.7. **GCMS-EI** (70eV): m/z (%) = 209 (M^+, 39), 118 (11), 117 (100), 116 (20), 115 (45), 93 (69), 91 (15), 77 (11). **HRMS** (ESI-TOF, m/z) calcd. for $C_{15}H_{16}N$ $(M+H)^+$, 210.1277, found 210.1272.



***N*-Cyclohexylaniline (3n).** **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ = 1.08-1.48 (m, 5 H), 1.60-1.72 (m, 1 H), 1.72-1.85 (m, 2 H), 2.00-2.14 (m, 2 H), 3.21-3.32 (m, 1 H), 3.56 (br s, 1 H), 6.57-6.63 (m, 2 H), 6.67 (dd, *J* = 7.3 Hz, *J* = 7.3 Hz, 1 H), 7.12-7.21 (m, 2 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 25.1, 26.0, 33.5, 51.8, 113.2, 116.9, 129.3, 147.4. **GCMS-EI** (70eV): m/z (%) = 175 (M^+, 37), 133 (12), 132 (100), 119 (12), 118 (19), 93 (12), 77 (11), **HRMS** (ESI-TOF, m/z) calcd. for $C_{12}H_{18}N$ $(M+H)^+$, 176.1434, found 176.1433.



***N*-Benzylaniline (5a)**; **^{1}H NMR** (300.1 MHz, $CDCl_3$): 4.10 (br s, 1 H), 4.35 (s, 2 H), 6.63-6.69 (m, 2 H), 6.74 (dd, *J* = 7.4 Hz, *J* = 7.4 Hz, 1 H), 7.16-7.23 (m, 2 H); 7.26-7.42 (m, 4 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 48.3, 112.8, 117.6, 127.2, 127.5, 128.6, 129.2, 139.4, 148.1; **GCMS-EI** (70eV): m/z (%) = 184 (11), 183 (M^+, 80), 182 (31), 106 (19), 92 (10), 91 (100), 77 (20), 65 (19), 51 (11). **HRMS** (ESI-TOF, m/z) calcd. for $C_{13}H_{14}N$ $(M+H)^+$, 184.1121; found 184.1121.



***N*-(2,3-Dimethoxybenzyl)aniline (5b)**; **^{1}H NMR** (300.1 MHz, $CDCl_3$): 3.88 (s, 6 H), 4.37 (s, 2 H), 6.64-6.74 (m, 3 H), 6.84-6.88 (m, 1 H), 6.93-6.98 (m, 1 H), 6.99-7.06 (m, 1 H), 7.14-7.22 (m, 2 H); **^{13}C NMR** (75.5 MHz, $CDCl_3$): δ = 43.3, 55.8, 60.9, 111.6, 113.1, 117.6, 121.0, 124.2, 129.3, 133.1, 147.1, 148.2, 152.8. **GCMS-EI** (70eV): m/z (%) = 244 (16), 243 (M^+, 97), 151 (62), 136 (100), 106 (24), 93 (10), 91 (40), 77 (23), 65 (19). **HRMS** (ESI-TOF, m/z) calcd. for $C_{15}H_{18}NO_2$ $(M+H)^+$, 244.1332; found 244.1337.

6. Copies of ^{1}H NMR and ^{13}C NMR spectra

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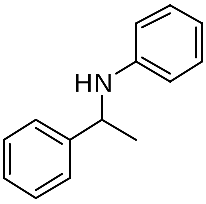

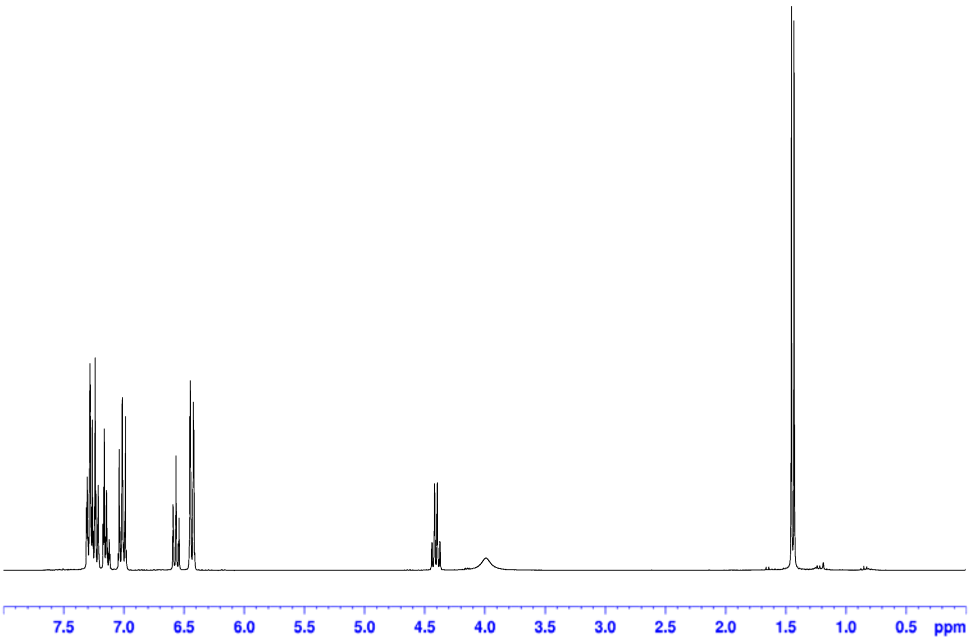

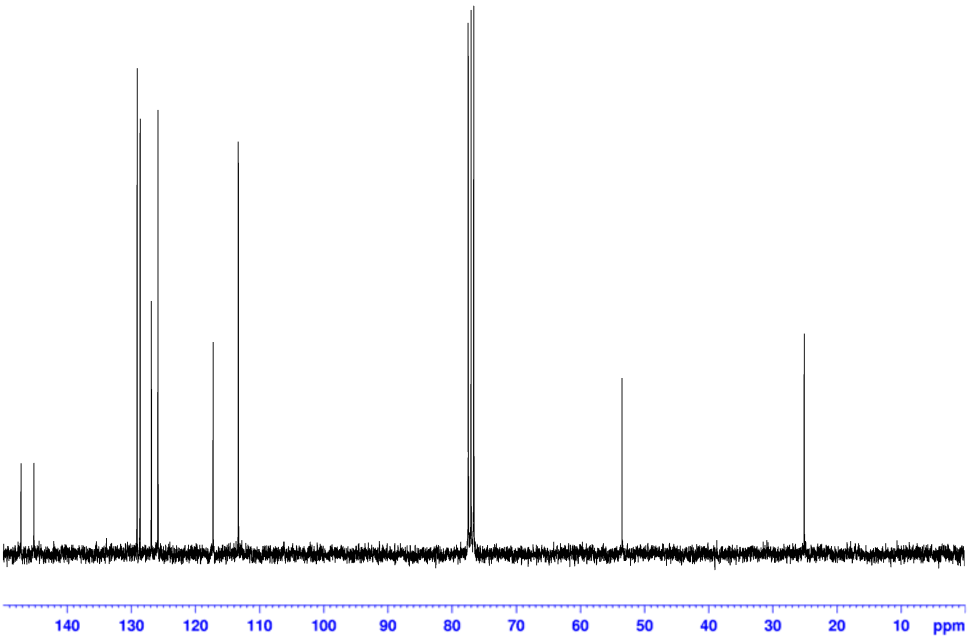

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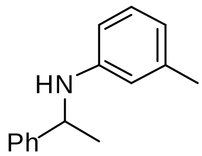
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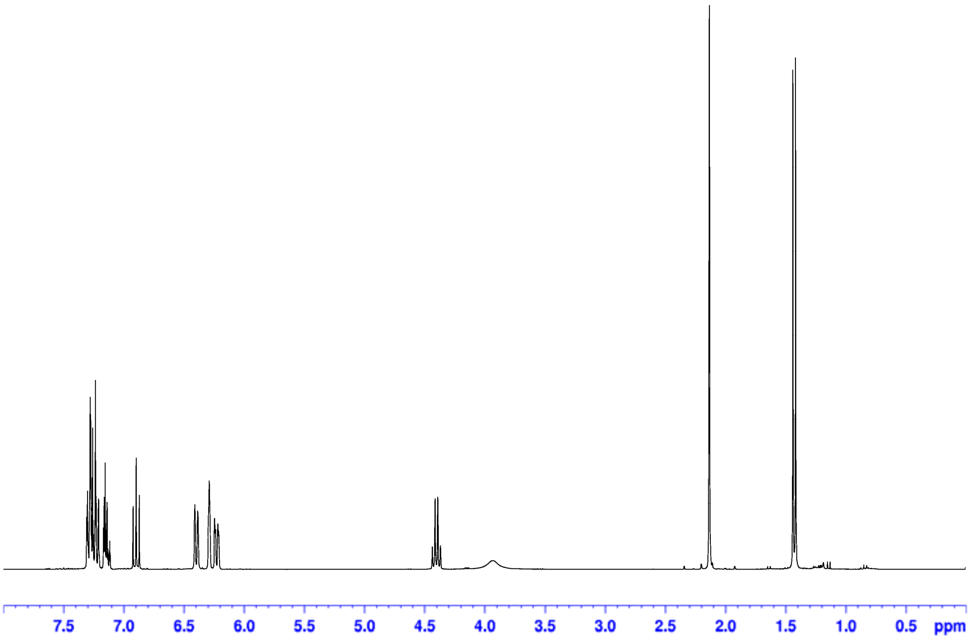
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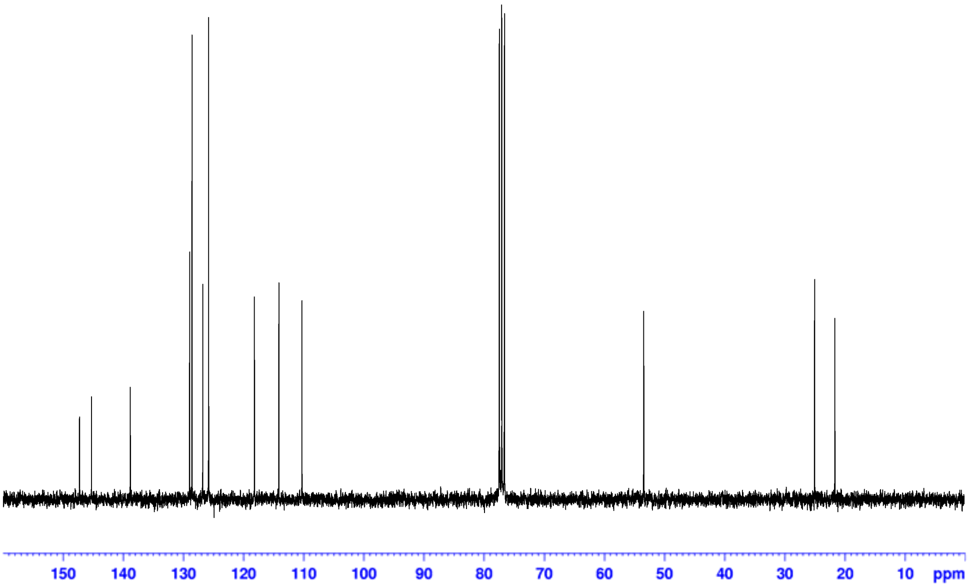
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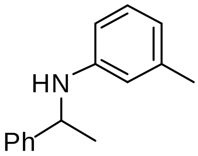
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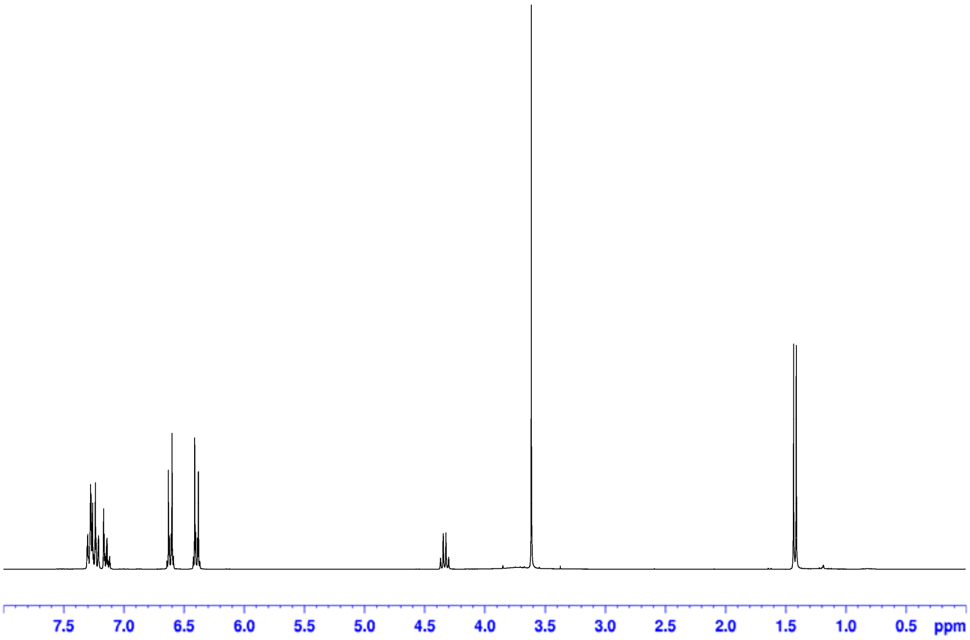
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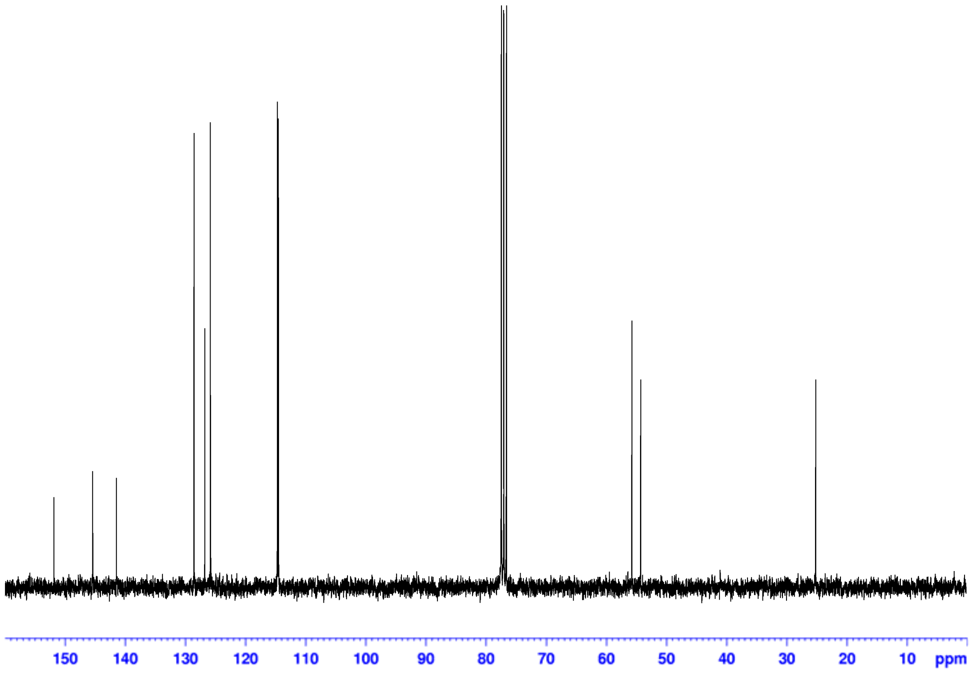
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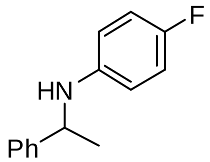
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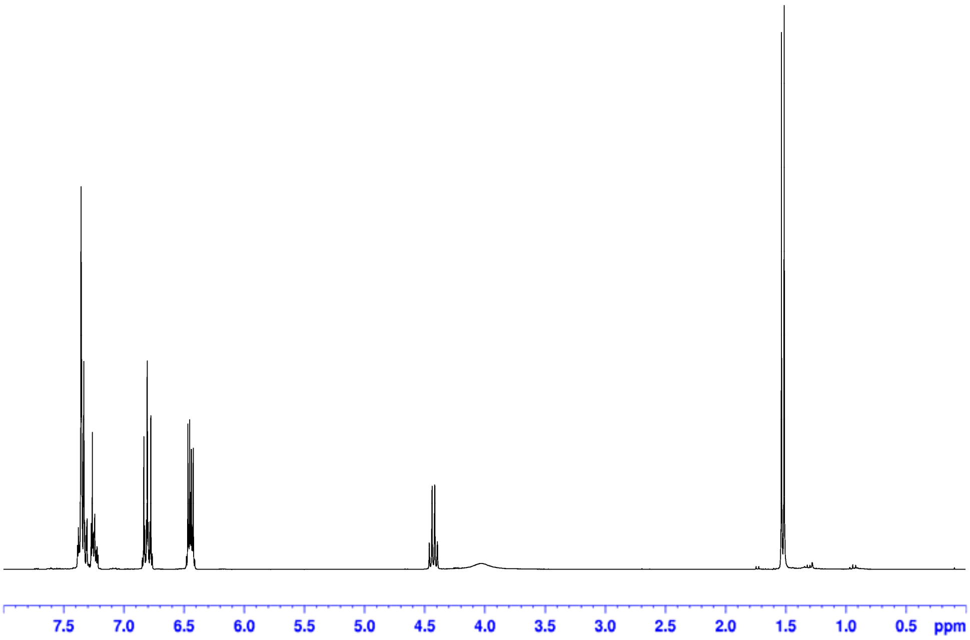
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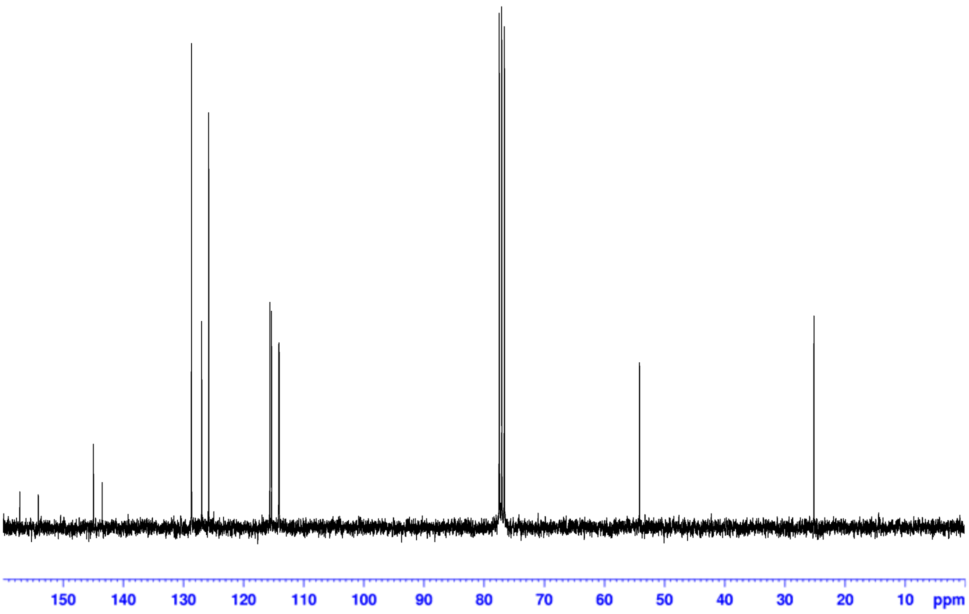
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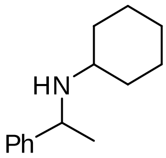
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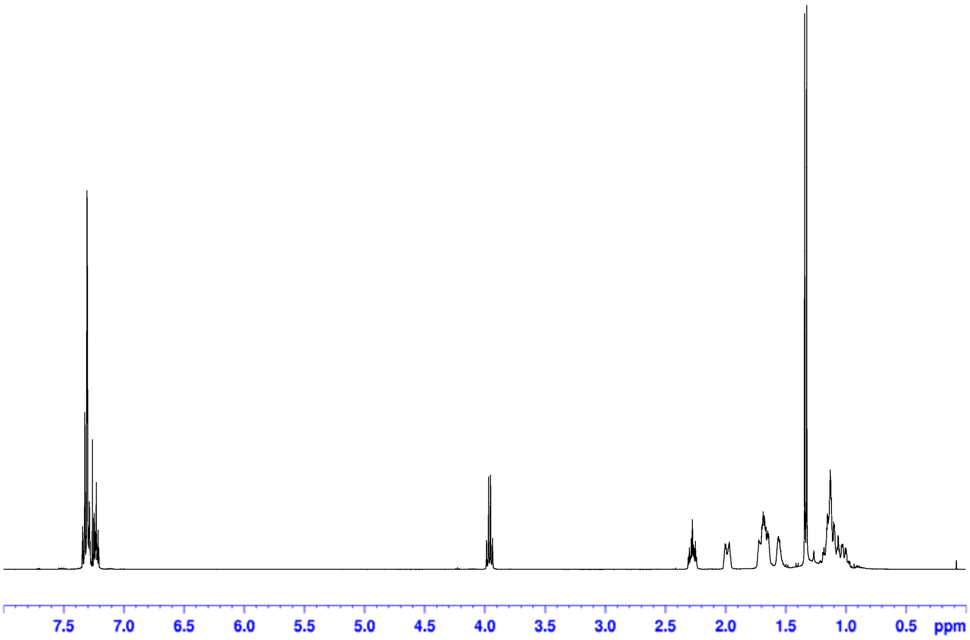
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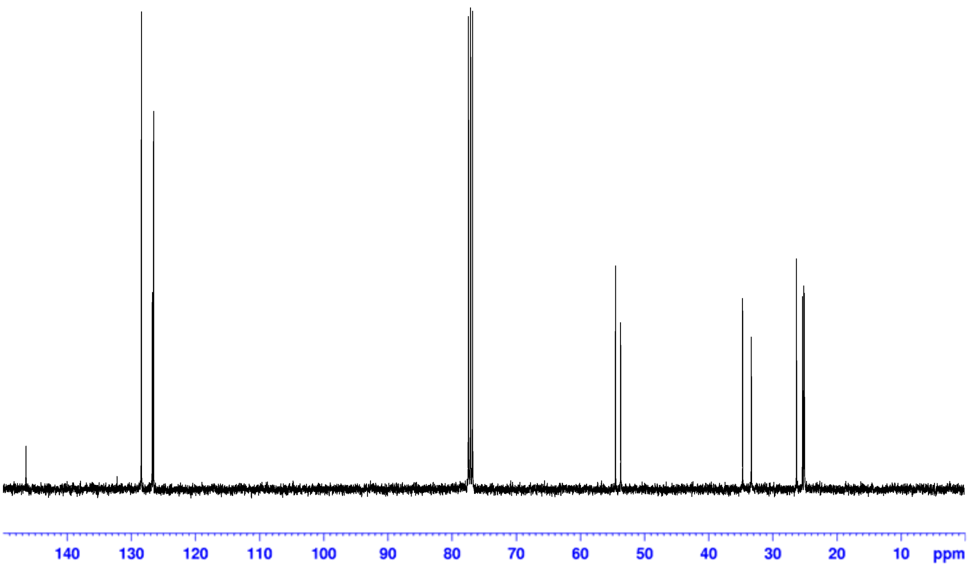
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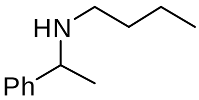
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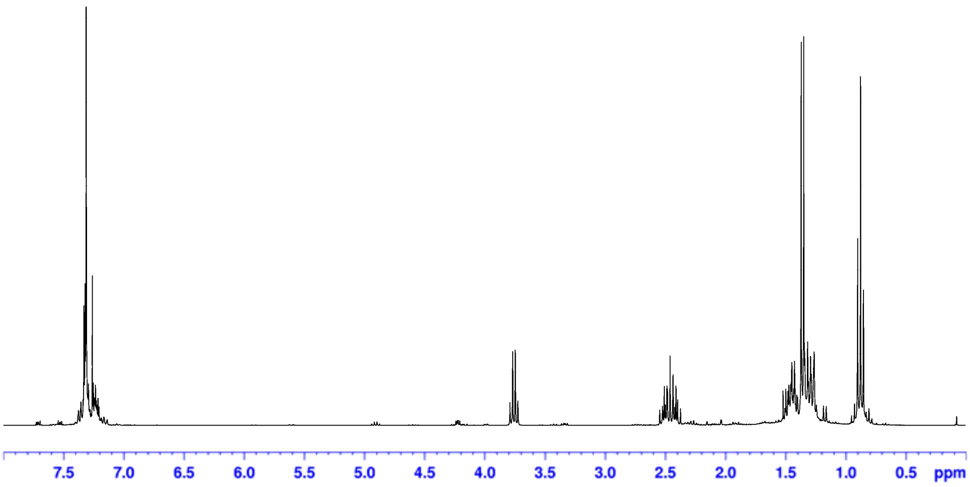
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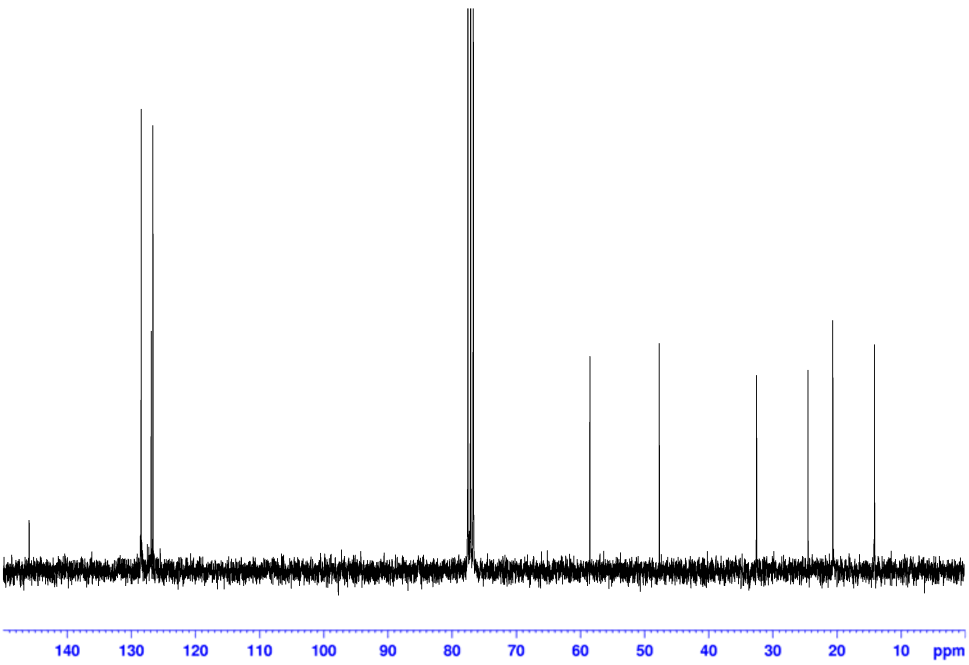
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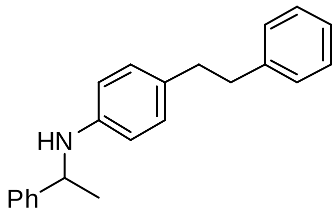
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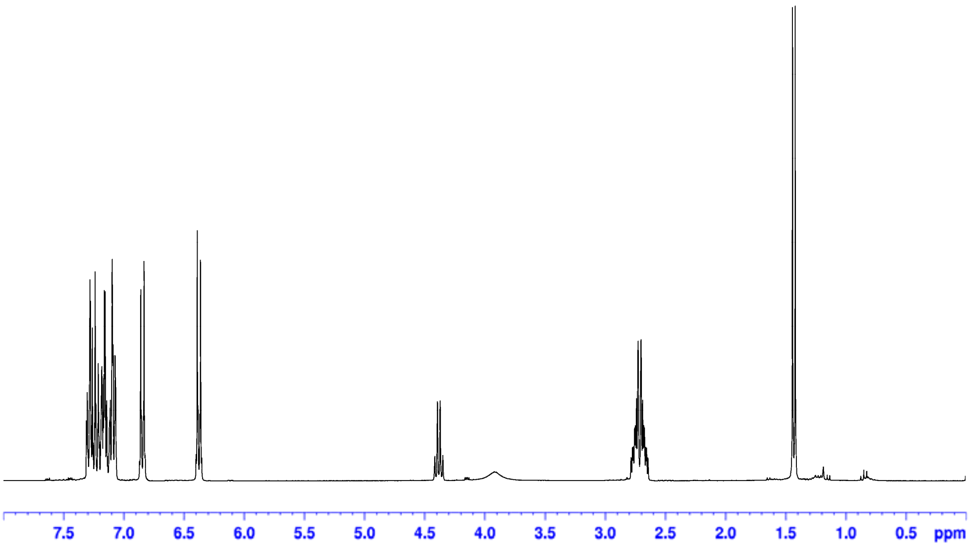
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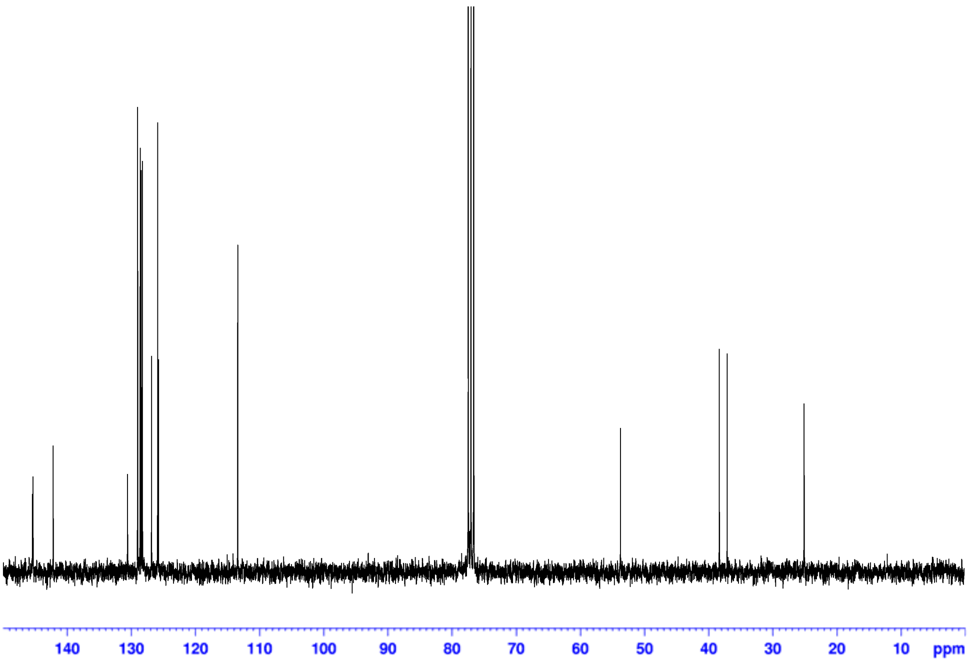
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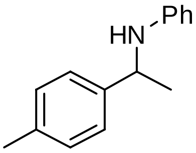
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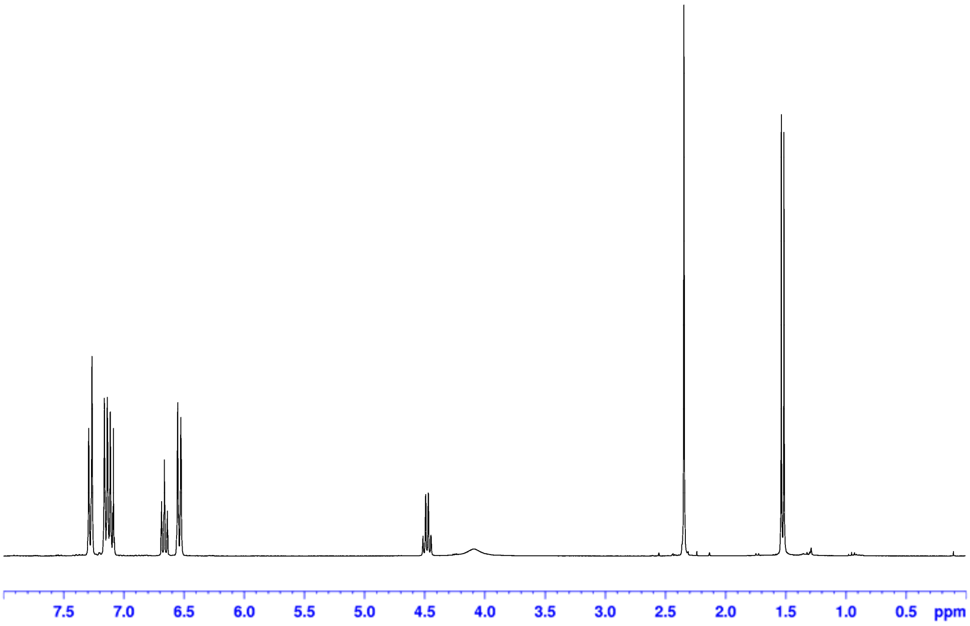
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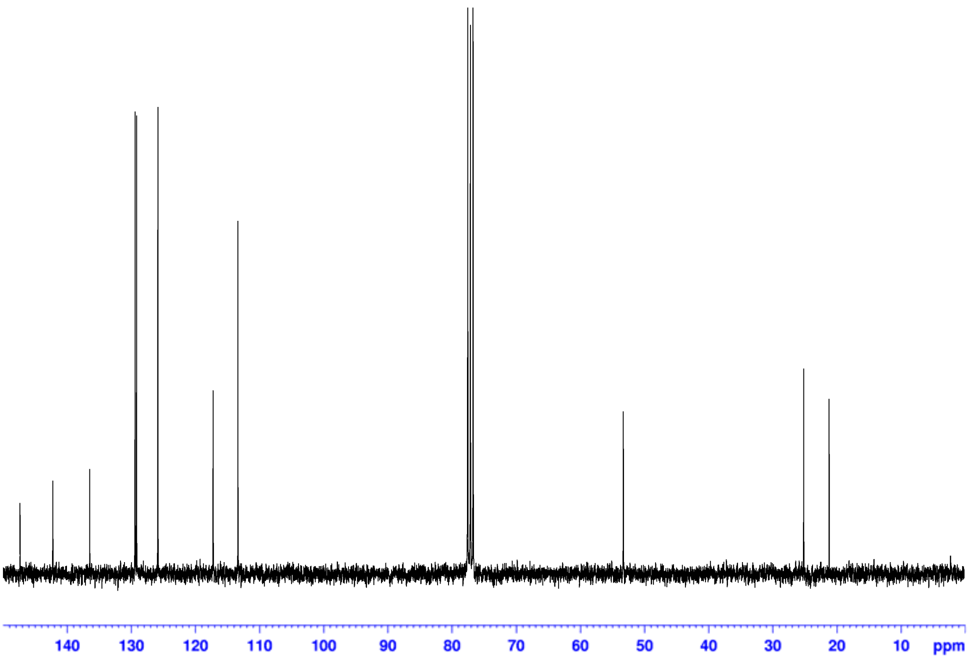
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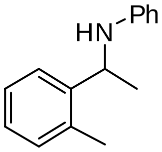
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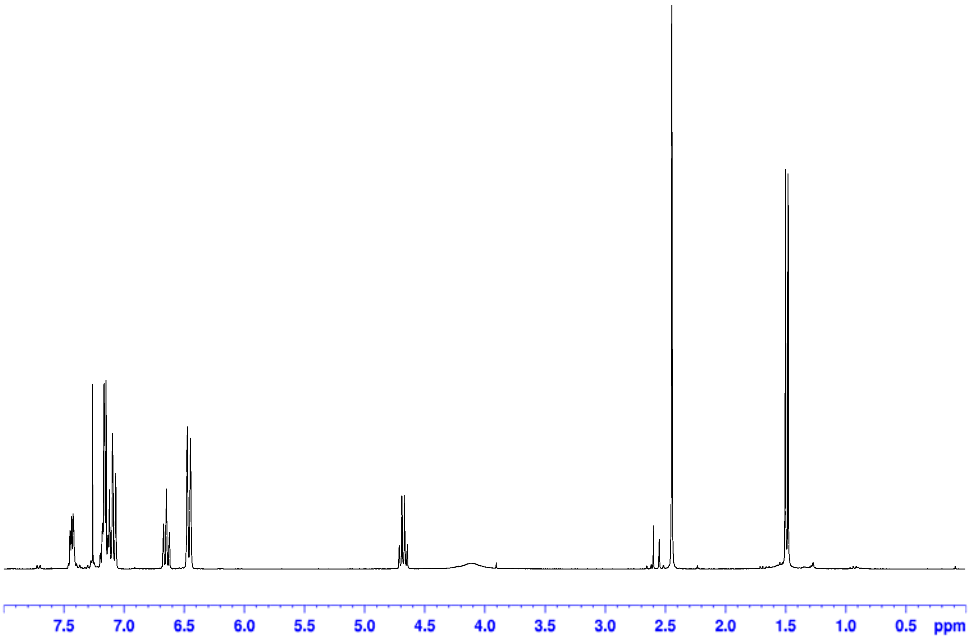
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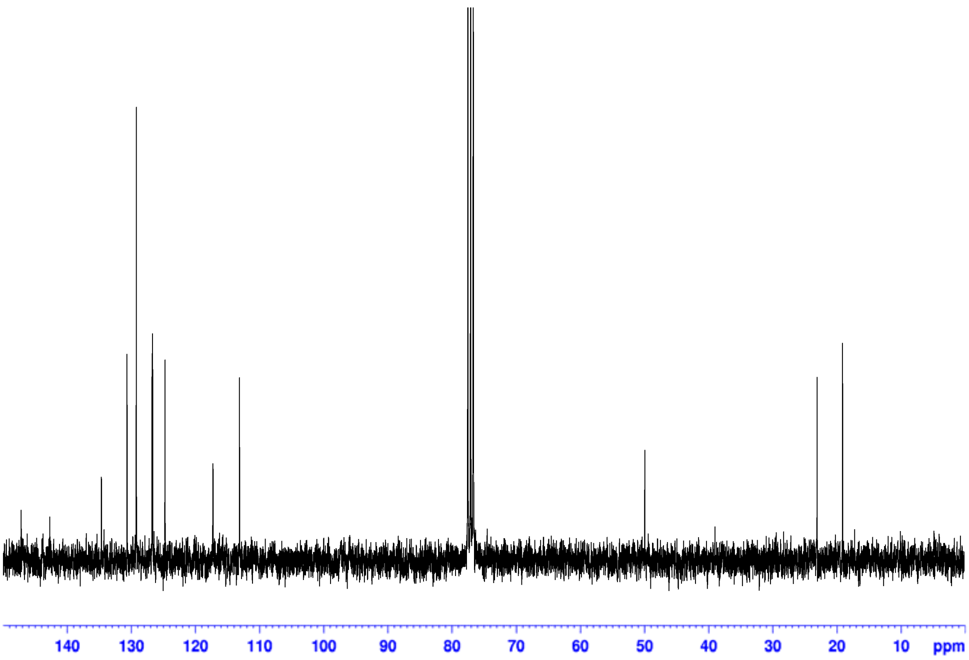
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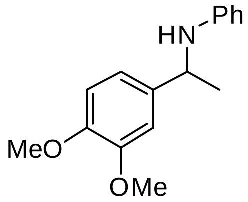
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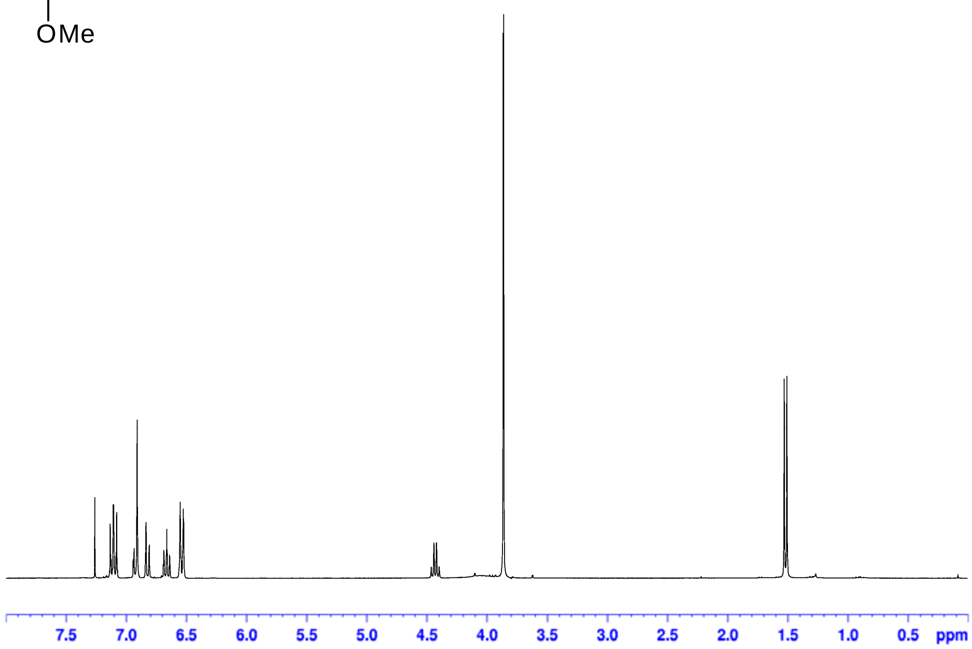
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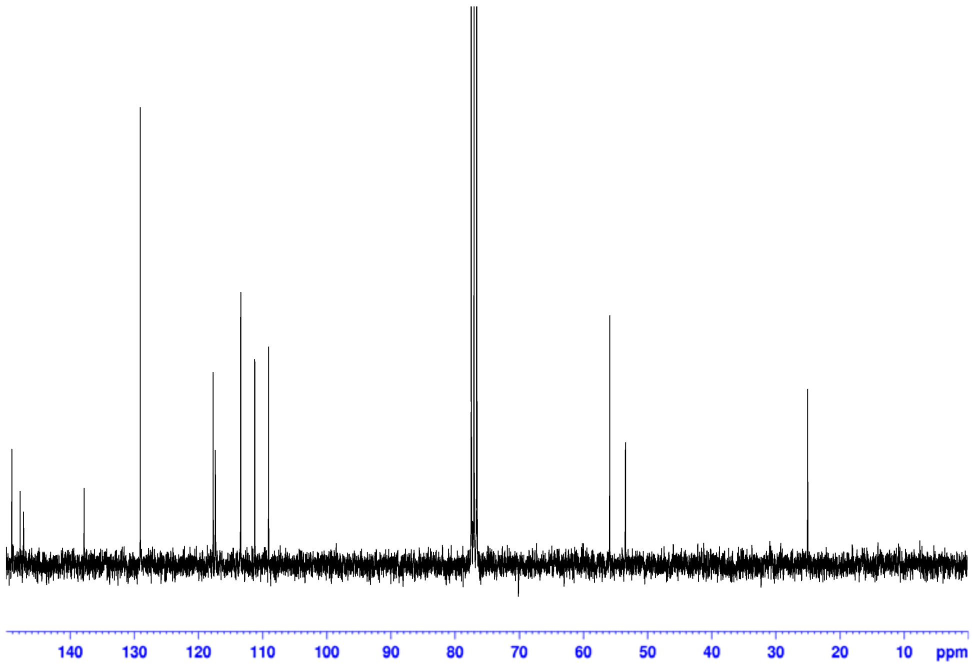
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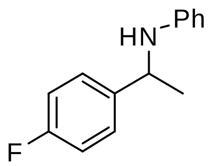
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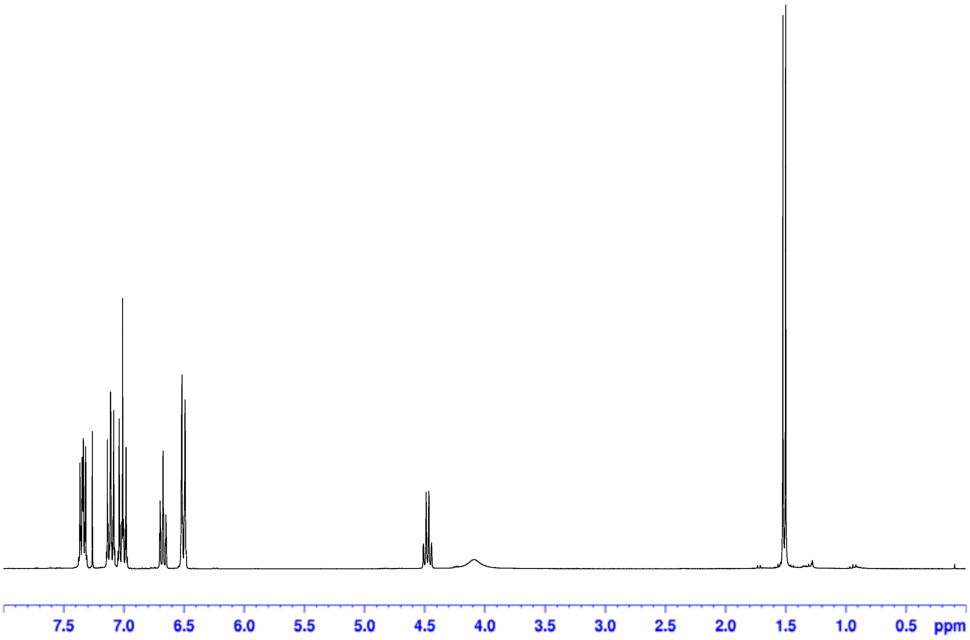
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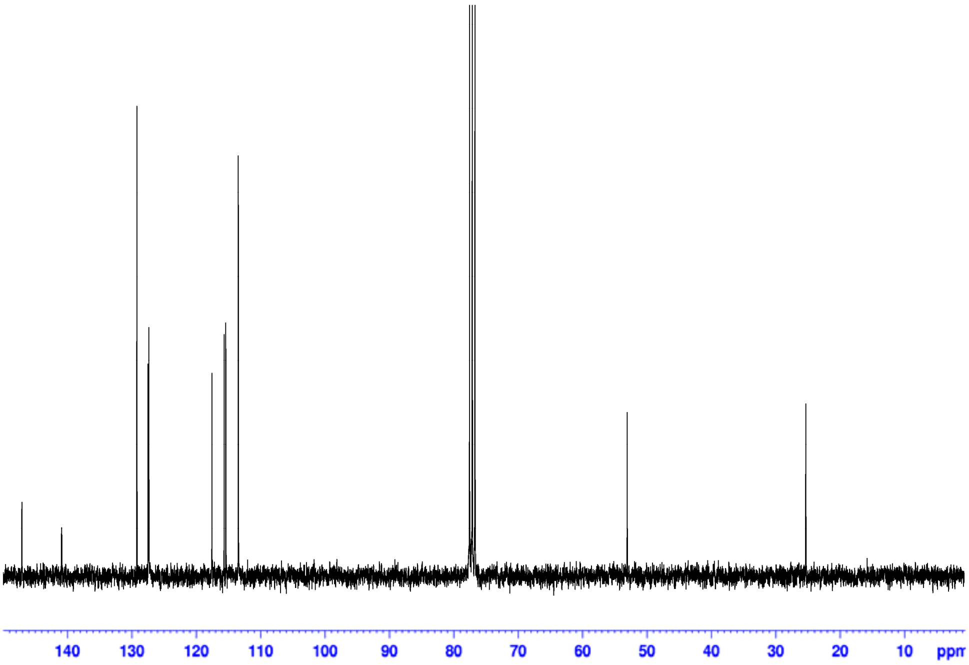
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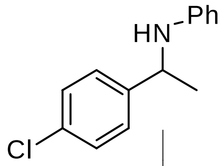
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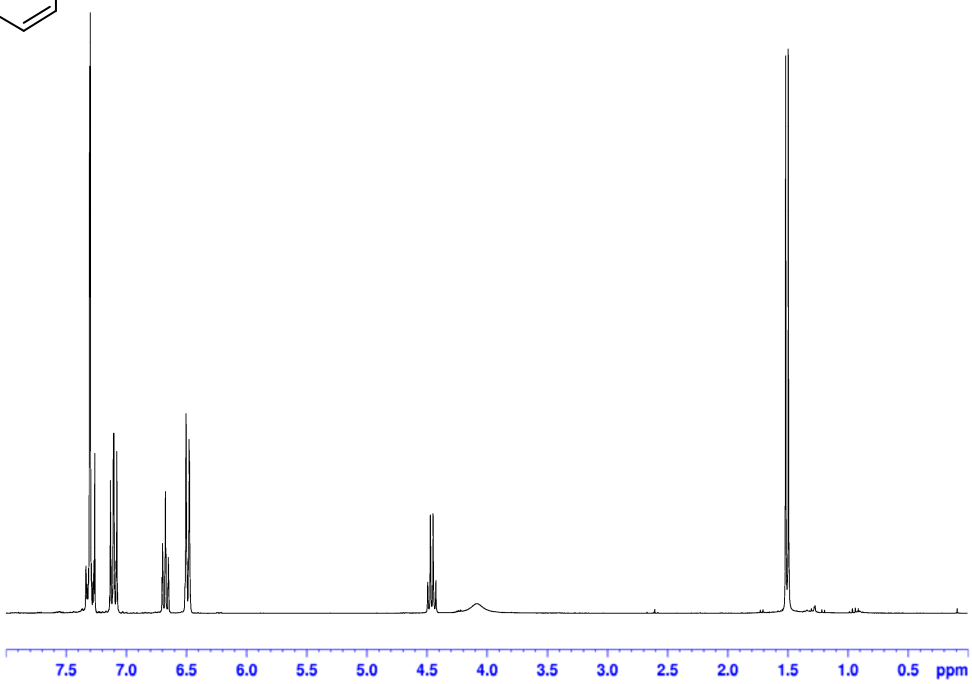
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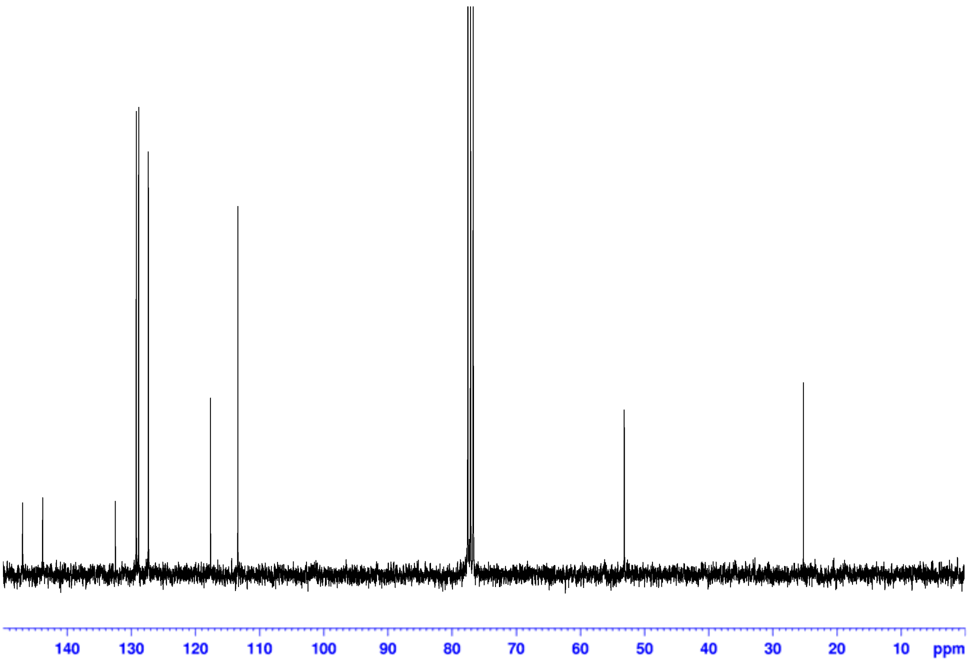
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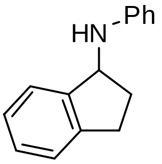
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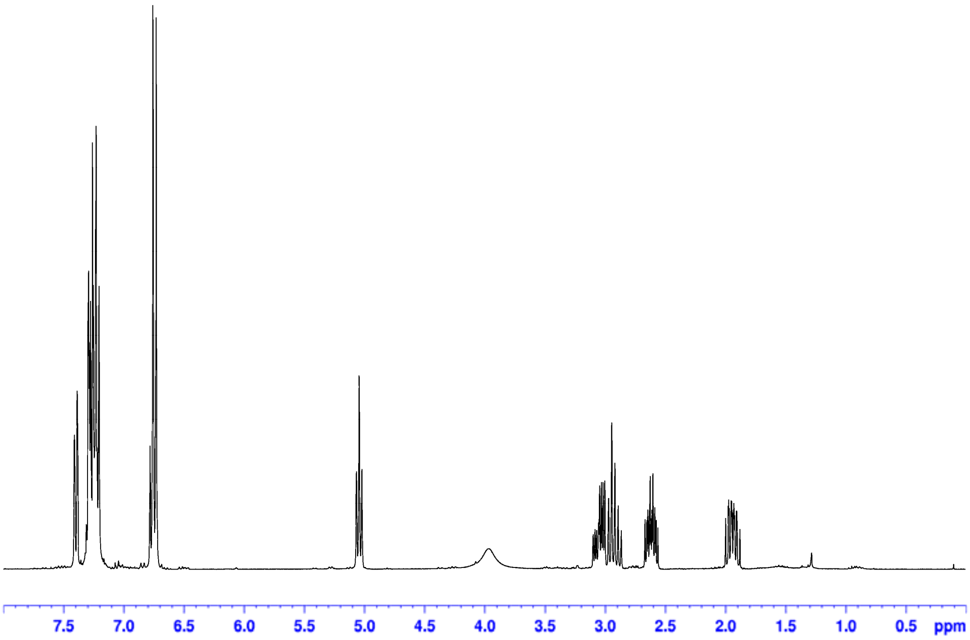
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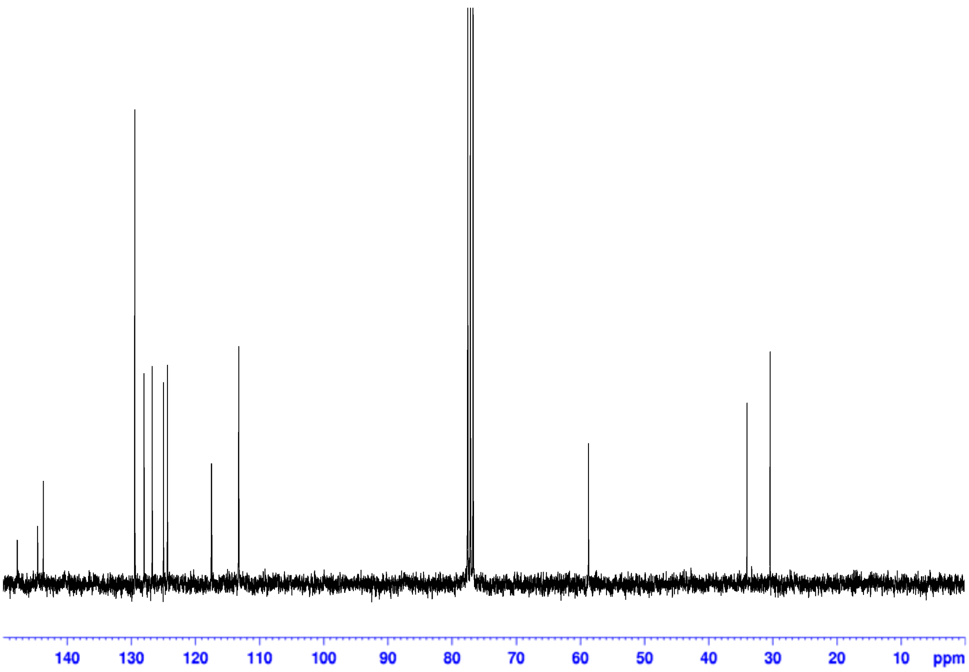
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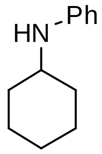
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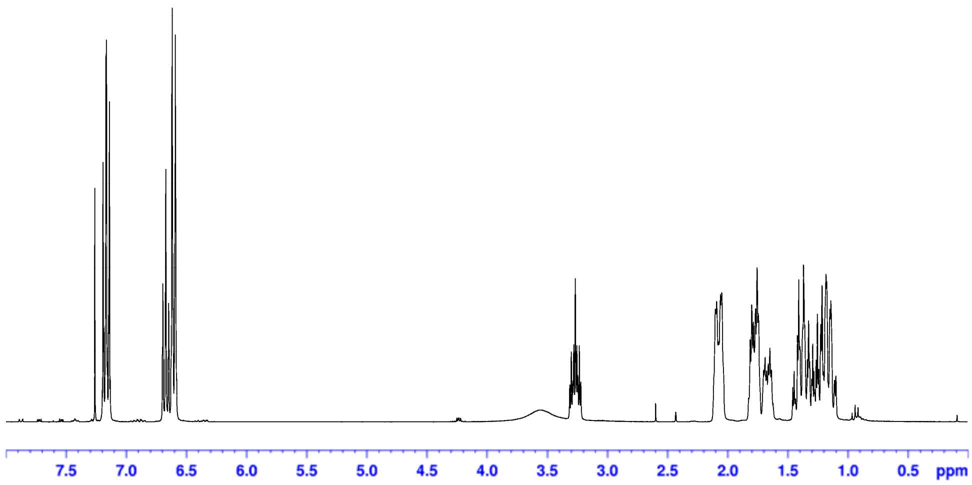
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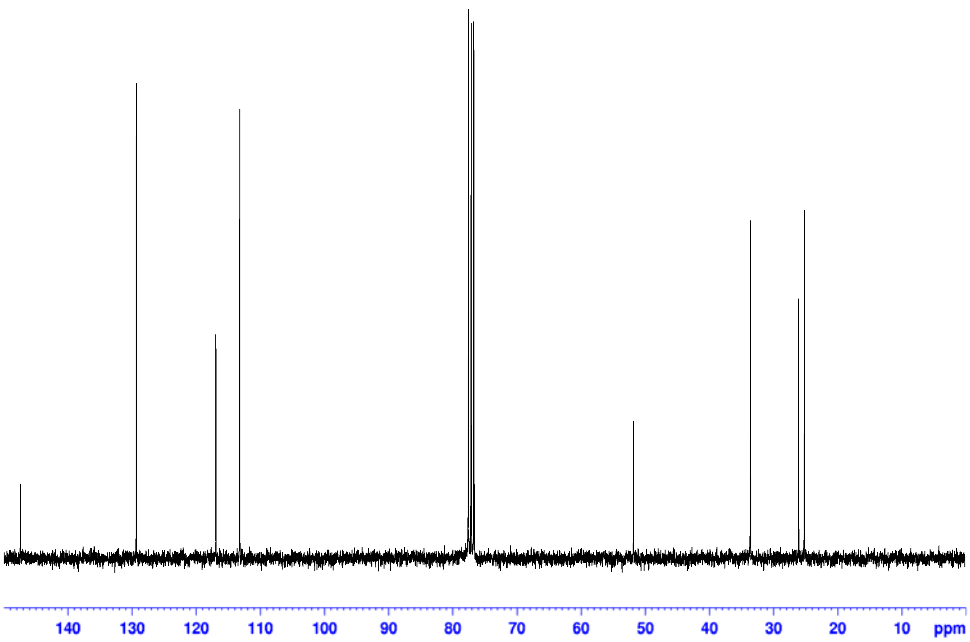
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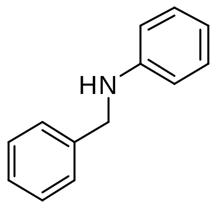
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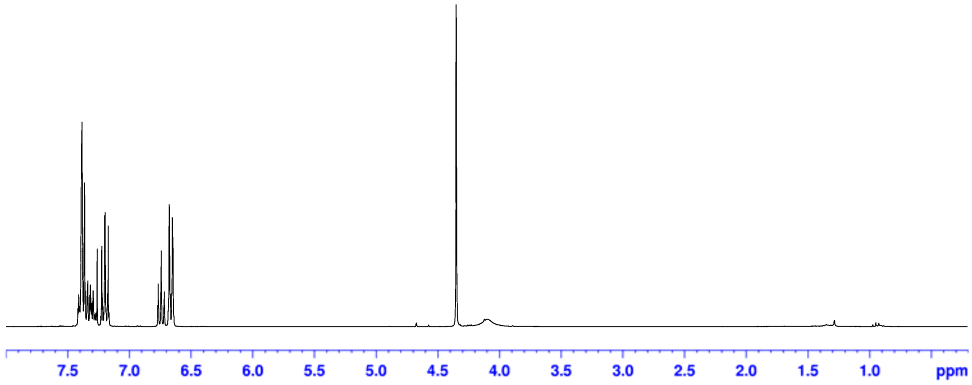
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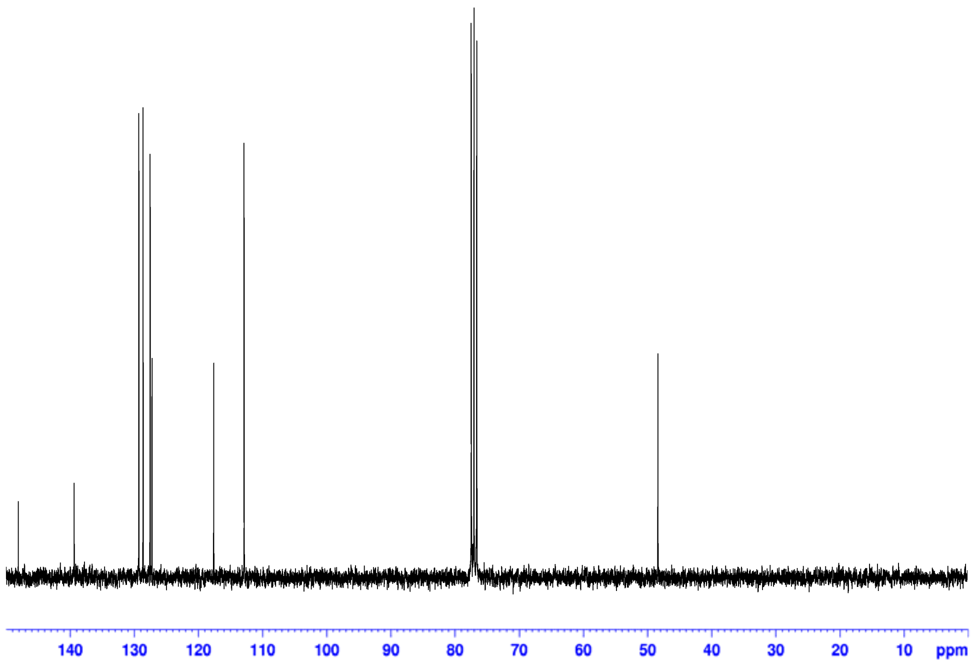
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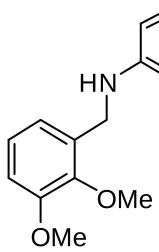
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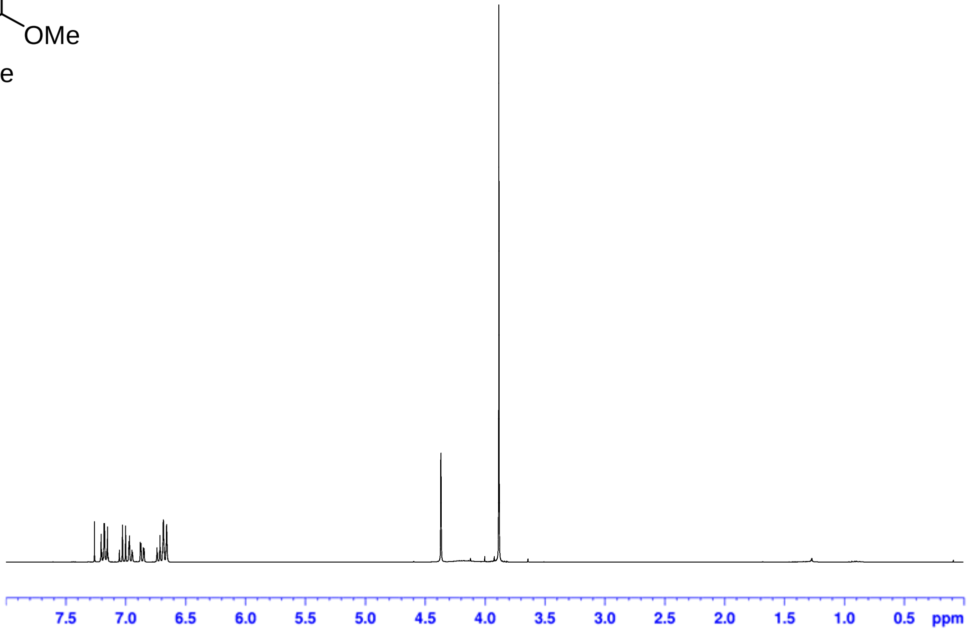
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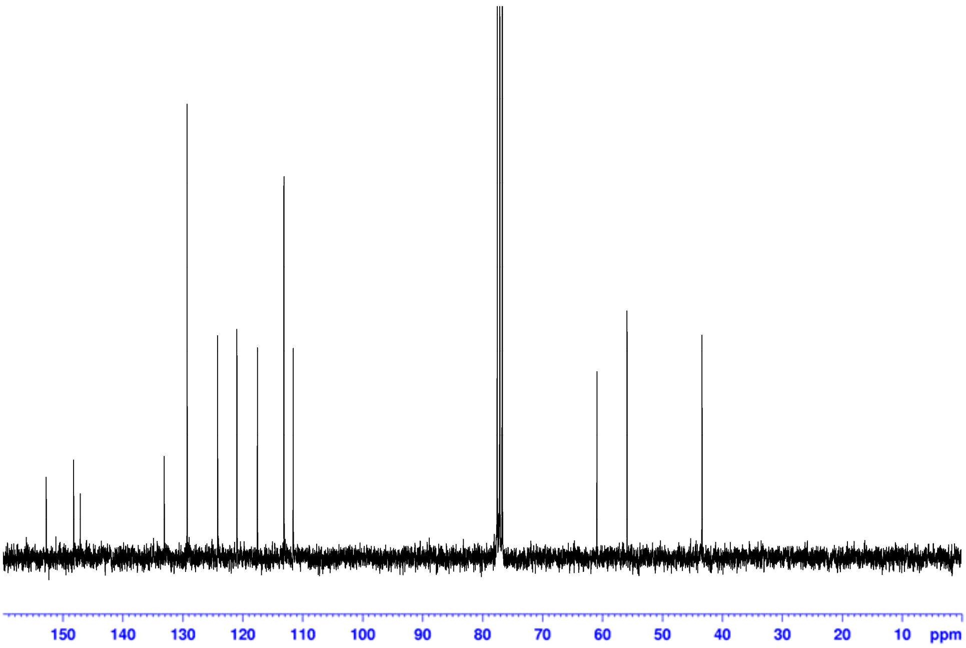
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