Supporting Information

Catalytic Formation of Silyl Enol Ethers and Its Applications for Aldol-Type Condensation and Aminomethylation Reactions

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General Information. All operations were carried out in an inert-atmosphere glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Toluene, hexanes and Et_2O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All organic substrates were received from commercial sources and used without further purification. The ^{1}H, ^{2}H, ^{13}C and ^{31}P NMR spectra were recorded on a 300 or 400 MHz Varian FT-NMR spectrometer. GC and GC-MS spectra were recorded from a Hewlett-Packard HP 6890 and Agilent 6850 spectrometers, respectively. Elemental analysis was performed at the Midwest Microlab, Indianapolis, IN.

Representative Procedure of the Catalytic Reaction: Silyl Enol Ether Formation. In a glove box, a ketone (2.0 mmol), CH_2=$CHSiMe_3$ (4.0 mmol) and complex **1** (7 mg, 0.5 mol %) were dissolved in toluene (3 mL) in a 25 mL Schlenk tube equipped with a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath set at 120 °C for 8-15 h. The tube was cooled to room temperature, and the crude product mixture was analyzed by GC-MS. For the detection of ethylene, the oven temperature of GC-MS was set at 25 °C (retention time = 1-2 min).

Aldol Condensation Reaction. The experiment was performed by following a reported procedure.[1] After evaporation of the solvent from the silyl enol ether solution, the crude product residue of **2** was dissolved in CH_2Cl_2 (2-3 mL). In a separate 100 mL Schlenk flask, $TiCl_4$ (3.0 mmol) was added to a cooled CH_2Cl_2 solution (5 mL) of 4-nitrobenzaldehyde (3.0 mmol) at 0 °C. After stirring for 15 min, the solution was cooled to -78 °C, and the CH_2Cl_2 solution of **2** was added dropwise via a syringe to the reaction flask. After stirring at -40 °C for 1 h, water (3 mmol) was added to the reaction flask, and the resulting mixture was stirred at 0 °C for 8 h. The reaction mixture was quenched by adding saturated Na_2CO_3 solution (10 mL), and the organic layer was extracted with Et_2O (3 × 20 mL). The ether solution was dried with anhydrous $MgSO_4$, and the Aldol product **3** was isolated by a column chromatograph on silica gel (*n*-hexanes/CH_2Cl_2).

Acylation Reaction. The experiment was performed by following a reported procedure.[2] The crude product residue of **2** (2.0 mmol) was dissolved in CH_2Cl_2 (2-3 mL). In a separate 100 mL Schlenk flask, $TiCl_4$ (3.0 mmol) was added to a cooled CH_2Cl_2 (5 mL) solution of acyl chloride (2.5 mmol) at 0 °C. After stirring for about 15 min, the crude product solution of **2** was added dropwise at -78 °C, and the mixture was further stirred for 1 h at -40 °C. The reaction mixture was quenched by adding aqueous NH_4Cl solution (10 mL), and the organic layer was extracted with Et_2O (3 × 20 mL). The combined ether solution was dried by anhydrous $MgSO_4$, and the product **4** was isolated by a column chromatograph on silica gel (EtOAc/*n*-hexanes).

Fluorination Reaction. The experiment was performed by following a reported procedure.[3] In a 50 mL Schlenk flask, the crude product residue of **2** (2.0 mmol) was dissolved in CH_3CN (2 mL), and the solution was cooled to 0 °C in an ice bath. Selectfluor® (2.0 mmol) was added in several portions to the solution under N_2 purge. The reaction mixture was stirred while it was allowed to gradually warm to room temperature over 8 h. The solvent was evaporated, water (10 mL) was added to the residue, and the organic layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine solution, and dried over anhydrous Na_2SO_4. The analytically pure product **5** was isolated by a column chromatography on silica gel (EtOAc/*n*-hexanes).

Aminomethylation Reaction. The experiment was performed by following a reported procedure.[4] In a 100 mL Schlenk flask, *t*-BuOOH (0.10 mL, 5-6 *M* in decane) was added dropwise to a mixture of *N,N*-dimethylaniline (1.5 mmol), CuBr (0.025 μmol) and the crude product **2** (0.50 mmol) dissolved in CH_3CN (5 mL) at room temperature. The resulting mixture was stirred at 50 °C for 12 h. The mixture was filtered through a pad of celite, and the solvent was removed under a reduced pressure. The residue was purified by a column chromatography on silica gel to afford the desired product **6**.

Deuterium Labeling Study. In a glove box, $C_6D_5COCD_3$ (26 mg) with CH_2=$CHSiMe_3$ (40 mg, 2.0 equiv) and **1** (0.5 mol %) were dissolved in toluene-d_8 (0.5 mL) in a J-Young NMR tube with a Teflon screw cap. The tube was brought out of the glove box, and was stirred in an

oil bath set at 120 °C for 12 h. The tube was cooled to room temperature, and the crude product mixture was analyzed by ^{1}H and ^{2}H NMR (Figure S1).

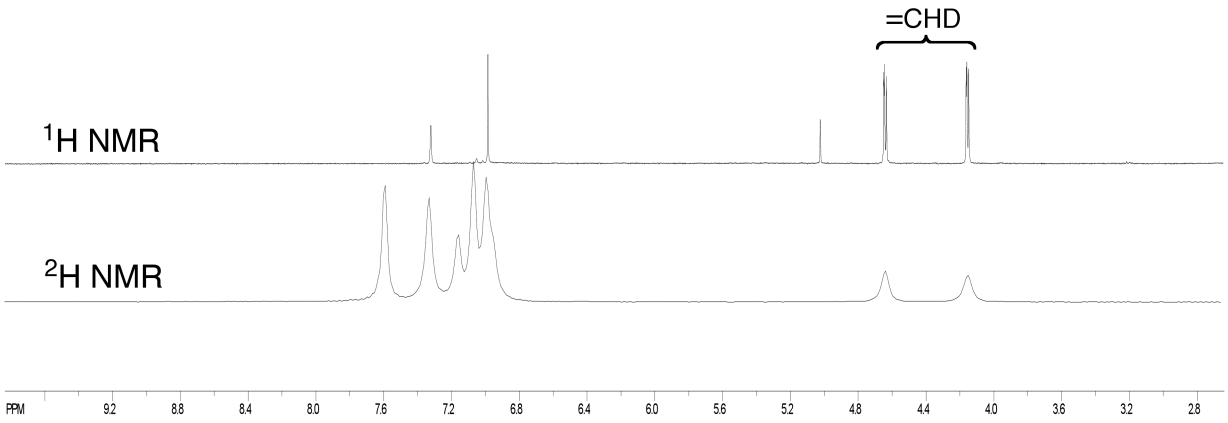

Figure S1. The ^{1}H and ^{2}H NMR Spectra of **3a**-*d*.

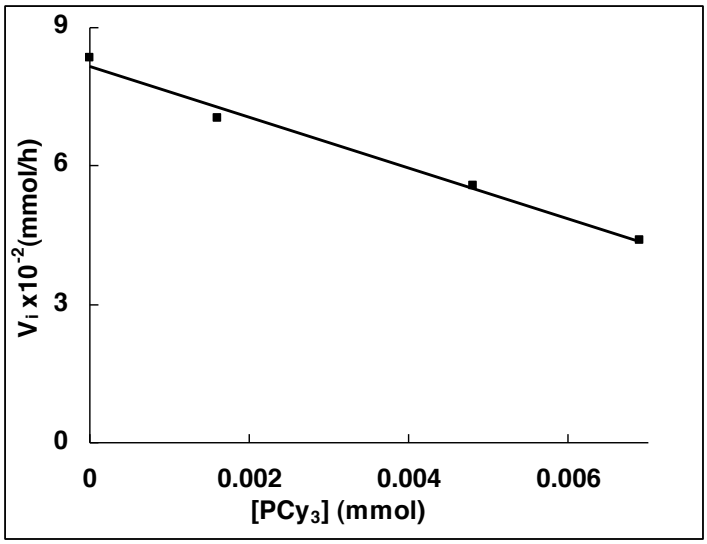

Figure S2. Plot of the Initial Rate (v_i) vs [PCy_3] for the Coupling Reaction of Acetophenone and CH_2=$CHSiMe_3$.

Phosphine Inhibition Study. In a glove box, acetophenone (0.20 mmol), CH_2=$CHSiMe_3$ (0.40 mmol), **1** (1 mg, 0.5 mol %) and C_6Me_6 (2 mg, internal standard) were dissolved in

toluene-d_8 (0.5 mL) solution in a J-Young NMR tube with a Teflon screw cap. A predissolved PCy_3 in toluene-d_8 solution (5 μL, 1.0 *M*) was added to the tube via syringe. The tube was brought out of the glove box and was heated in an oil bath set at 120 °C. The reaction was monitored by ^{1}H NMR in 30 min intervals. The rate was measured by the ^{1}H integration of the product peak, and was normalized against the internal standard peak. The k_{obs} was estimated from the first order plot of *ln*[product] vs reaction time.

Hammett Study. In the glove box, **1** (0.5 mol %), *para*-X-C_6H_4COMe (0.20 mmol), CH_2=$CHSiMe_3$ (0.40 mmol) and C_6Me_6 (26 mg, internal standard) were dissolved in toluene-d_8 (0.5 mL) in a J-Young NMR tube with a Teflon screw cap. The tube was brought out of the box and was immersed in an oil bath set at 120 °C. The reaction progress was monitored by ^{1}H NMR in 30 min intervals by measuring the ^{1}H integration of the product peaks, which were normalized against the internal standard peak. The k_{obs} was estimated from a first–order plot of *ln*[product] vs reaction time (Figure S3).

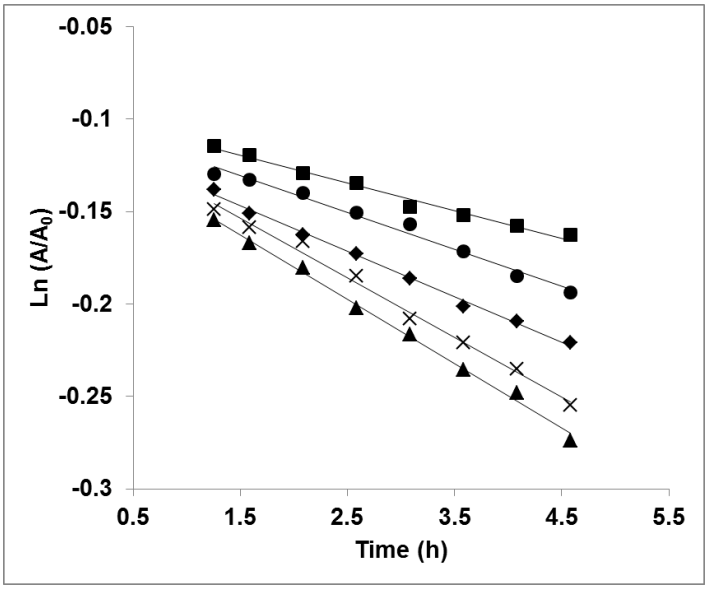

Figure S3. First–Order Plots of *ln*[product] vs Reaction Time for the Coupling Reaction of *para*-Substituted *p*-X-$C_6H_4COCH_3$ (X = OMe(■), CH_3(●), H(◆), Cl(✕), Br(▲)) with CH_2=$CHSiMe_3$.

Characterization Data of Organic Products

For **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H), 7.5-7.4 (m, 3H), 5.44 (s, 1H), 3.99 (s, 1H), 3.35 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.6, 150.5, 147.4, 136.3, 134.2, 129.0, 126.7, 123.9, 69.3, 47.2 ppm. GC-MS *m/z* = 271 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[5]

For **3b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.44 (m, 1H), 4.04 (s, 1H), 3.33 (m, 2H), 2.39 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 199.1, 150.5, 147.2, 145.0, 133.7, 129.5, 128.3, 126.6, 123.7, 69.3, 46.8, 21.7 ppm. GC-MS *m/z* = 285 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[6]

For **3c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.44 (m, *J* = 4.0 Hz, 1H), 4.10 (s, 1H), 3.85 (s, 3H), 3.31 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 198.2, 164.4,150.7, 147.4, 130.8, 129.5, 126.8, 124.0, 114.2, 69.6, 55.8, 46.8 ppm. GC-MS *m/z* = 301 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[6]

For **3d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.44 (m, 1H), 4.10 (s, 1H), 3.65 (m, 1H), 3.31 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 198.2, 164.4, 150.7, 147.4, 130.8, 129.5, 126.8, 124.0, 114.2, 69.6, 47.3 ppm. GC-MS *m/z* = 350 (M^+). Anal. Calcd for $C_{15}H_{12}NO_4Br$: C, 51.45; H, 3.45. Found C, 51.26; H, 3.54.

For **3e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 5.45 (m, 1H), 3.77 (s, 1H), 3.33 (m, 2H) ppm.

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 198.4, 150.3, 147.6, 140.8, 134.7, 129.8, 129.4, 126.8, 124.1, 69.3, 47.3 ppm. GC-MS *m/z* = 305 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[6]

For **3f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.93 (m, 4H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.61 (m, 3H), 5.51 (m, 1H), 3.97 (s, 1H), 3.51 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.6, 150.5, 147.5, 136.2, 133.7, 132.6, 130.5, 129.9, 129.3, 128.1, 127.3, 126.8, 124.1, 123.6, 69.7, 47.3 ppm. GC-MS *m/z* = 321 (M^+). Anal. Calcd for $C_{19}H_{15}NO_4$: C, 71.02; H, 4.71. Found C, 70.91; H, 4.63.

For **3g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.26 (m, 3H), 6.95 (m, 1H), 5.43 (m, 1H), 3.95 (s, 1H), 3.35 (m, 2H), 3.00 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 200.7, 150.9, 150.6, 147.5, 137.1, 129.7, 126.8, 124.0, 118.0, 116.6, 111.0, 69.6, 47.2, 40.7 ppm. GC-MS *m/z* = 314 (M^+). Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77. Found C, 65.14; H, 5.47.

For **3h** (*syn*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.62-7.44 (m, 5H), 5.34 (d, *J* = 2.3 Hz, 1H), 4.08 (s, 1H), 3.79 (m, 1H), 1.15 (d, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 205.3, 149.3, 147.1, 135.1, 134.0, 129.1, 128.7, 127.1, 123.7, 72.5, 46.8, 11.2 ppm. GC-MS m/z = 285 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[7]

For **3h** (*anti*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.62-7.44 (m, 5H), 5.08 (d, *J* = 7.2 Hz, 1H), 4.08 (s, 1H), 3.82 (m, 1H), 1.15 (d, *J* = 7.2 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 204.4, 149.8, 147.6, 136.1, 133.8, 129.0, 128.6, 127.8, 123.8, 75.9, 47.8, 15.9 ppm. GC-MS *m/z* = 285 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[7]

For **3i** (*syn*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.3-6.8 (m, 14H), 5.70 (d, *J* = 3.4 Hz 1H), 4.78 (d, *J* = 3.4 Hz, 1H), 3.90 (s, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 202.1, 148.8, 147.6, 146.0, 138.1, 129.4, 133.4, 132.1, 130.4, 128.7, 128.3, 127.2, 124.1, 74.5, 60.0 ppm. GC-MS *m/z* = 347 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[8]

For **3i** (*anti*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-6.85 (m, 14H), 5.55 (d, *J* = 8.9 Hz, 1H), 4.68 (d, *J* = 3.4 Hz, 1H), 3.50 (s, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 198.1, 148.0, 147.0, 145.3, 137.9, 129.3, 133.5, 132.1, 130.4, 128.7, 128.4, 127.5, 124.3, 76.5, 62.3 ppm. GC-MS *m/z* = 347 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[8]

For **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2-7.4 (m, 8H), 5.06 (s, 1H), 4.98 (d, *J* = 8.9 Hz, 1H), 3.00 (m, 1H), 2.73 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 209.0, 153.6, 148.7, 148.0, 136.2, 136.1, 128.2, 128.0, 126.8, 124.5, 124.0, 75.0, 53.1, 29.7 ppm. GC-MS *m/z* = 283 (M^+). Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63. Found C, 67.97; H, 4.51.

For **3k**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.54-7.23 (m, 3H), 5.11 (d, *J* = 8.0 Hz, 1H), 5.02 (s, 1H), 2.89 (m, 2H), 2.75 (m, 1H), 1.68 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 201.6, 148.7, 147.8, 144.4, 134.6, 132.2, 129.0, 128.3, 127.8, 127.2, 123.8, 74.8, 53.9, 28.9, 26.2 ppm. GC-MS *m/z* = 297 (M^+). Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09. Found C, 68.97; H, 4.93.

For **3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6-7.4 (m, 12H), 3.09 (s, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 196.5, 137.5, 135.9, 134.0, 130.9, 128.9, 129.6, 26.7 ppm. GC-MS *m/z* = 260 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[9]

For **3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.52-7.32 (m, 10H), 2.93 (t, *J* = 6.1 Hz, 2H), 1.78 (t, *J* = 6.1 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 190.3, 137.0, 136.2, 136.0,

130.4, 128.4, 128.6, 28.5, 23.0 ppm. GC-MS *m/z* = 274 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[9]

For **3n**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.52-7.32 (m, 10H), 3.15 (d, *J* = 15.6 Hz, 2H), 2.45 (t, *J* = 13.8 Hz, 2H), 1.48 (m, 1H), 0.96 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 190.9, 137.0, 136.4, 136.2, 130.6, 128.8, 128.7, 44.6, 32.8, 29.8, 27.5 ppm. GC-MS *m/z* = 330 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[10]

For **3o**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H), 5.26 (s, 1H), 3.73 (s, 1H), 2.44 (m, *J* = 13.8 Hz, 1H), 2.60-1.20 (m, 10H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 217.7, 149.8, 147.2, 126.9, 123.6, 72.6, 57.4, 44.0, 29.3, 29.2, 24.0, 23.7 ppm. GC-MS *m/z* = 263 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[11]

For **3p** (*syn*): ^1H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 5.26 (s, 1H), 4.00 (s, 1H), 3.26-1.68 (m, 8H), 1.37 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 214.4, 148.1, 146.8, 130.1, 123.9, 77.7, 47.9, 42.9, 35.7, 34.7, 25.3, 22.5 ppm. GC-MS *m/z* = 263 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[12]

For **3p** (*anti*): ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 2H), 7.47 (d, *J* = 8.9 Hz, 2H), 5.03 (s, 1H), 4.25 (s, 1H), 3.26-1.68 (m, 8H), 1.14 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 219.0, 147.6, 146.8, 129.3, 123.0, 76.9, 52.7, 39.2, 37.1, 27.5, 20.7, 16.1 ppm. GC-MS *m/z* = 263 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[12]

For **3q** (*syn*): ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 2H), 5.17 (s, 1H), 3.97 (s, 1H), 2.81 (m, 1H), 2.02 (s, 3H), 1.44 (m, 2H), 1.09 (m, 4H), 0.69 (t, *J*

= 6.6 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 211.1, 150.6, 147.2, 126.5, 123.6, 69.0, 50.6, 43.6, 31.2, 23.1, 22.4, 13.9 ppm. GC-MS *m/z* = 265 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[13]

For **3q** (*anti*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 2H), 4.94 (s, 1H), 3.74 (s, 1H), 2.81 (m, 1H), 2.02 (s, 3H), 1.44 (m, 2H), 1.09 (m, 4H), 0.69 (t, *J* = 6.6 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 213.1, 149.8, 147.1, 127.1, 123.4, 72.9, 58.8, 31.5, 27.3, 23.4, 13.8 ppm. GC-MS *m/z* = 265 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[13]

For **4a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9-7.4 (m, 5H), 6.18 (s, 1H), 4.05 (s, 1H), 2.18 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 193.8, 183.3, 134.8, 132.3, 128.6, 127.0, 96.7, 25.9 ppm. GC-MS *m/z* = 162 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[2]

For **5a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8-7.2 (m, 5H), 5.55 (d, J_{HF} = 46.9 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 193.1 (d, J_{CF} = 15.0 Hz), 145.4, 132.4, 130.4 and 127.6, 84.0 (d, J_{CF} = 188.9 Hz) ppm. GC-MS m/z = 138 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[3]

For **5j:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.30 (m, 4H), 5.14 (m, J_{HF} = 51.0 Hz, 1H), 3.35 (m, 1H), 3.08 (m, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 199.9 (d, J_{CF} = 14.9 Hz), 149.7, 136.4, 133.7, 128.3, 126.9, 124.4, 91.7 (d, J_{CF} = 189.9 Hz), 33.2 (d, J_{CF} = 21.4 Hz) ppm. GC-MS *m/z* = 150 (M^+). The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[3]

For **5k:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0-7.25 (m, 4H), 5.14 (ddd, J_{HF} = 46.9 Hz, J_{HH} = 12.8, 5.2 Hz, 1H), 3.12 (m, 2H), 2.56 (m, 1H), 2.34 (m, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 193.6 (d, J_{CF} = 14.8 Hz), 143.2, 134.4, 131.4, 128.9, 128.0, 127.4, 91.2 (d, J_{CF} = 188.4

Hz), 30.4 (d, J_{CF} = 19.4 Hz), 27.1 (d, J_{CF} = 11.6 Hz) ppm. GC-MS *m/z* = 164 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[3]

For **6a:** ^1H NMR (300 MHz, $CDCl_3$) δ 7.95-6.72 (m, 10H), 3.85 (t, *J* = 7.0 Hz, 2H), 3.24 (t, *J* = 7.0 Hz, 2H), 2.98 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 199.7, 148.8, 137.1, 133.4, 129.5, 128.8, 128.2, 116.7, 112.6, 48.1, 38.7, 35.3 ppm. GC-MS *m/z* = 239 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[4]

For **6j:** ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-6.75 (m, 5H), 3.89 (dd, *J* = 15.1, 4.5 Hz, 1H), 3.28 (dd, *J* = 15.1, 8.0 Hz, 1H), 2.96 (s, 3H), 2.53-2.45 (m, 1H), 2.37-1.63 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 220.2, 148.8, 129.3, 116.5, 112.3, 52.5, 48.4, 39.2, 38.1, 29.2, 20.8 ppm. GC-MS *m/z* = 203 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[4]

For **6k:** ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-6.70 (m, 5H), 3.89 (dd, *J* = 15.1, 5.6 Hz, 1H), 3.26 (dd, *J* = 15.3, 7.2 Hz, 1H), 3.02 (s, 3H), 2.78 (m, 1H), 2.50-1.42 (m, 8H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 212.5, 149.0, 129.2, 115.9, 111.7, 52.2, 49.2, 42.3, 39.6, 32.5, 27.9, 25.0 ppm. GC-MS *m/z* = 217 (M^+). The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[4]

References:

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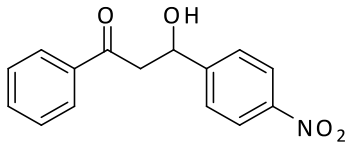
The ^{1}H and ^{13}C NMR Spectra of Selected Organic Products



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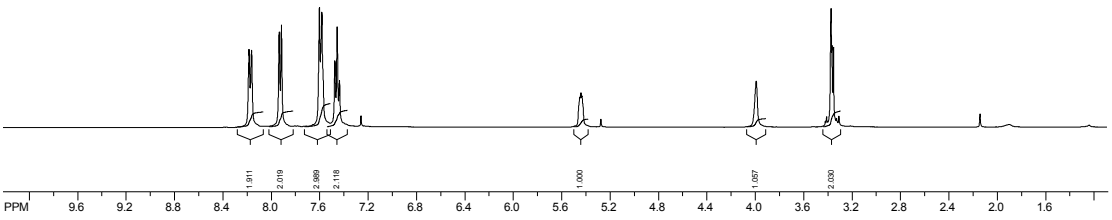

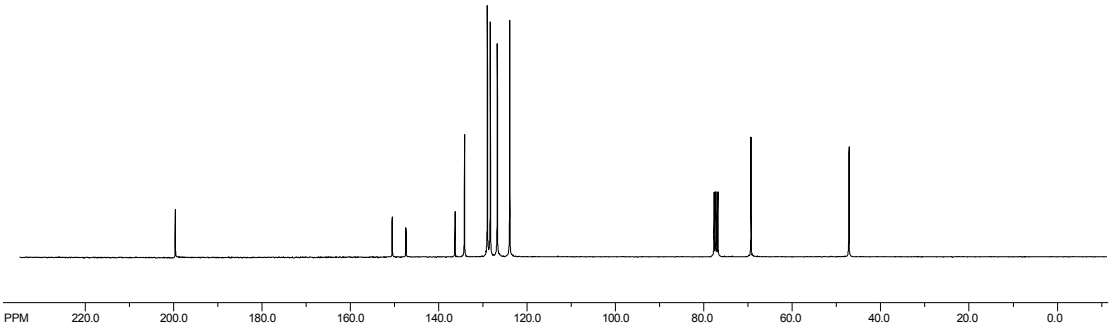

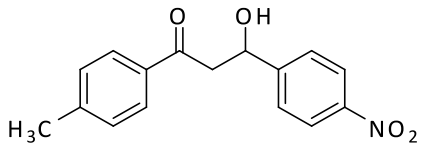
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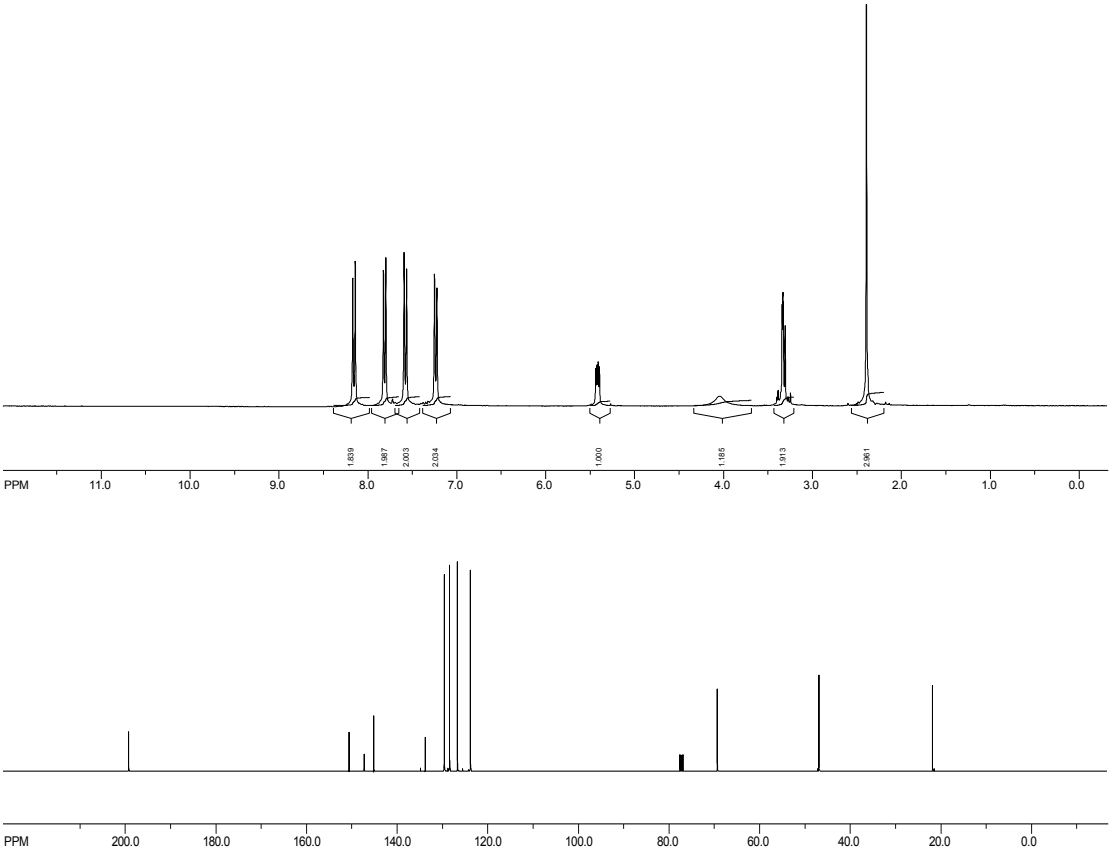
OH
H3C
NO2

3b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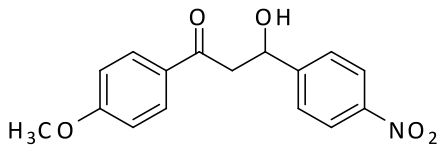
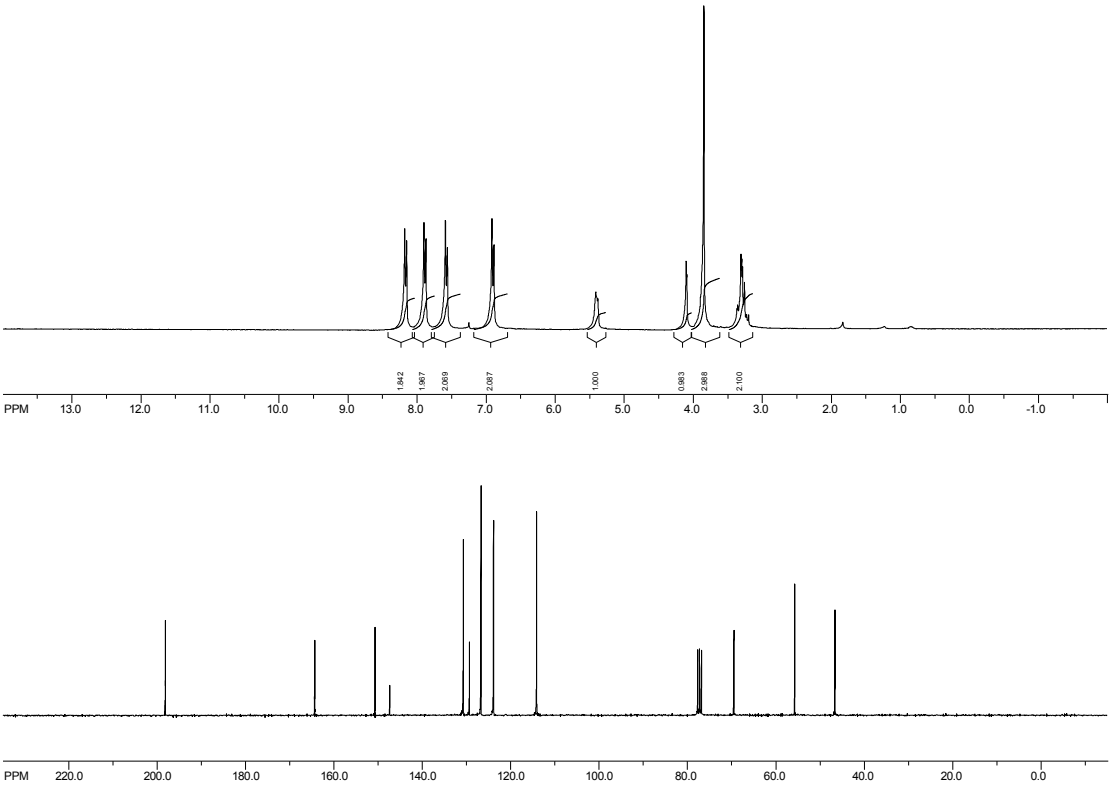
1.987
2.003
2.034
1.000
1.185
1.913
2.961
PPM
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


O
OH
H3CO
NO2

3c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1.987
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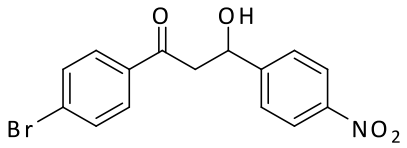
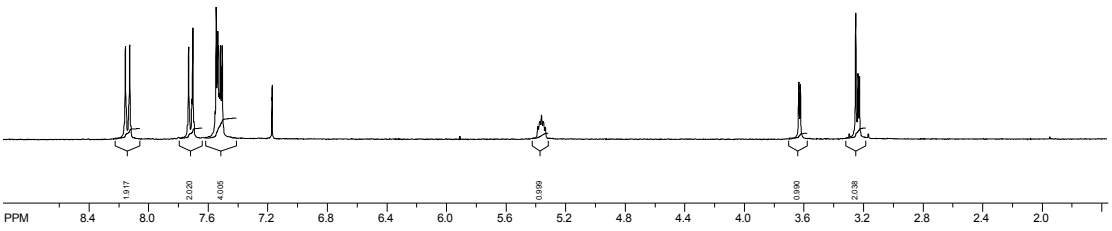
2.087
1.000
0.983
2.988
2.100
PPM 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
PPM 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0


O
OH
Br
NO2

3d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0.999
0.990
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PPM
8.4
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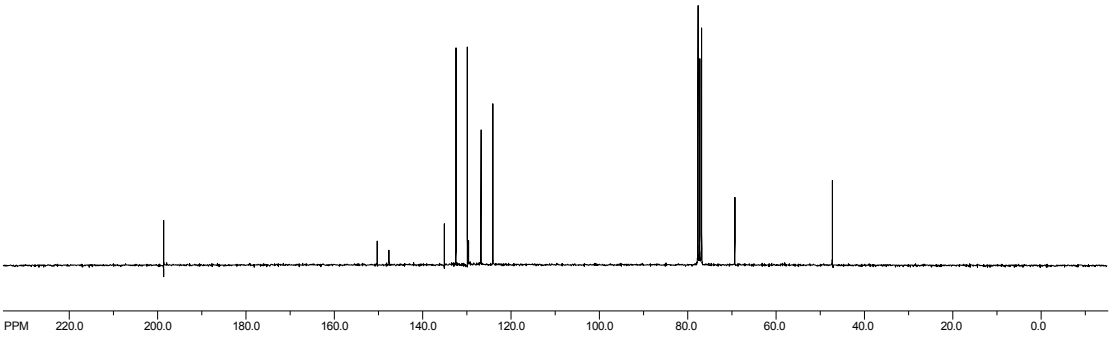
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0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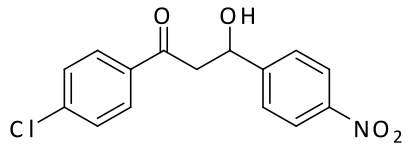
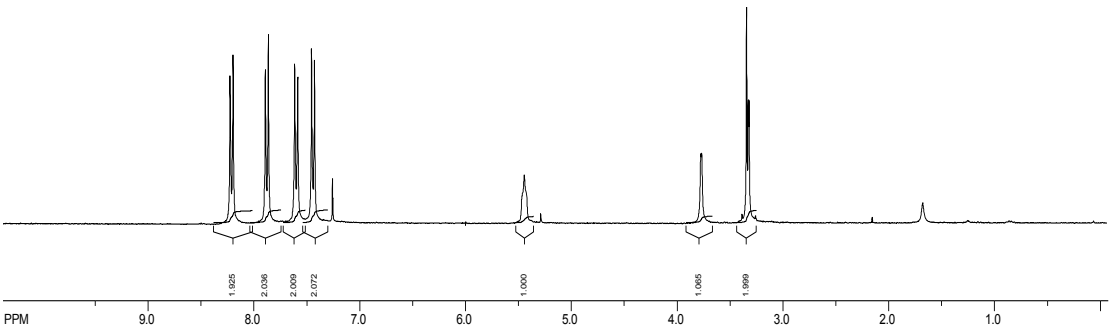
100.0
80.0
60.0
40.0
20.0
0.0


O
OH
Cl
NO2

3e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2.009
2.072
1.000
1.065
1.999
PPM
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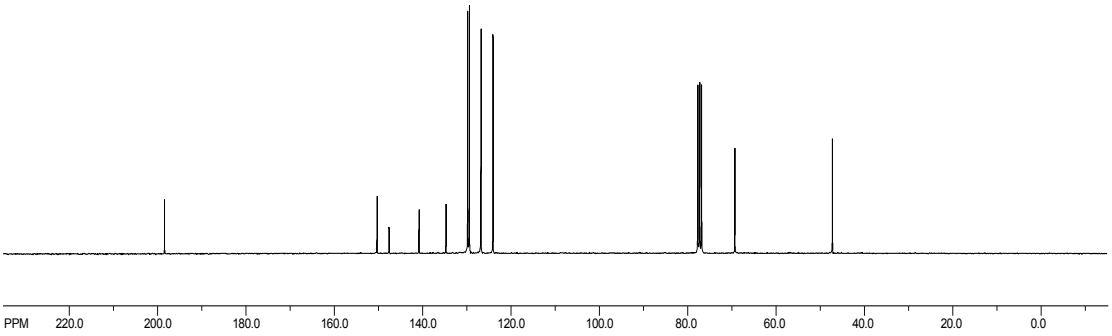
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


PPM
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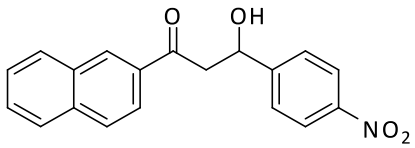
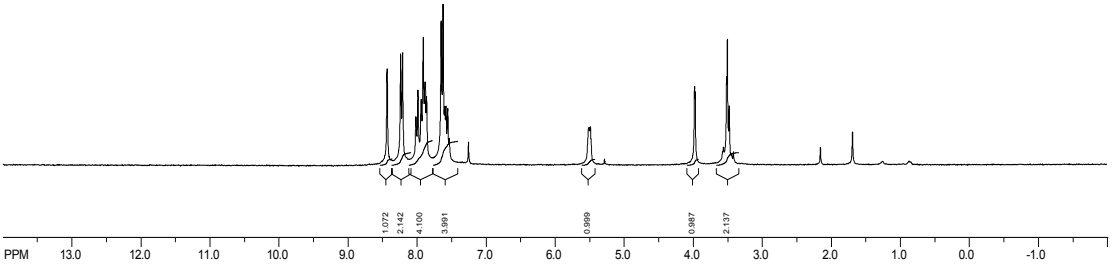
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


O
OH
NO2

3f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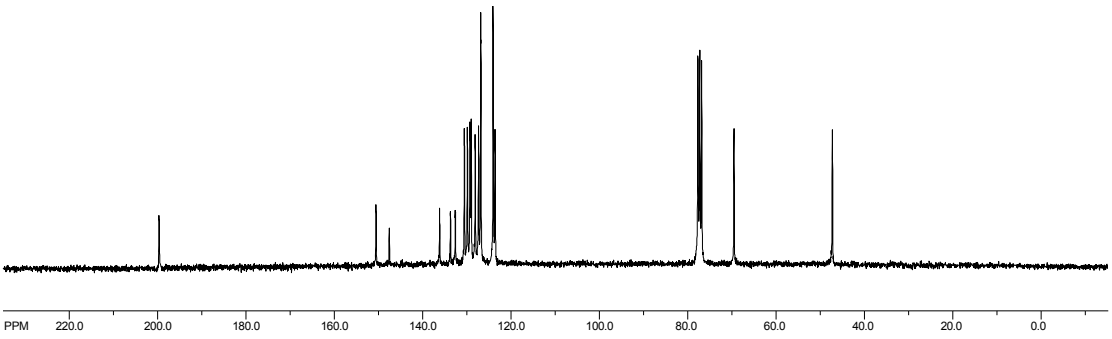
2.142
4.100
3.991
0.999
0.987
2.137
PPM 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0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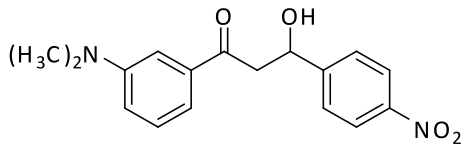
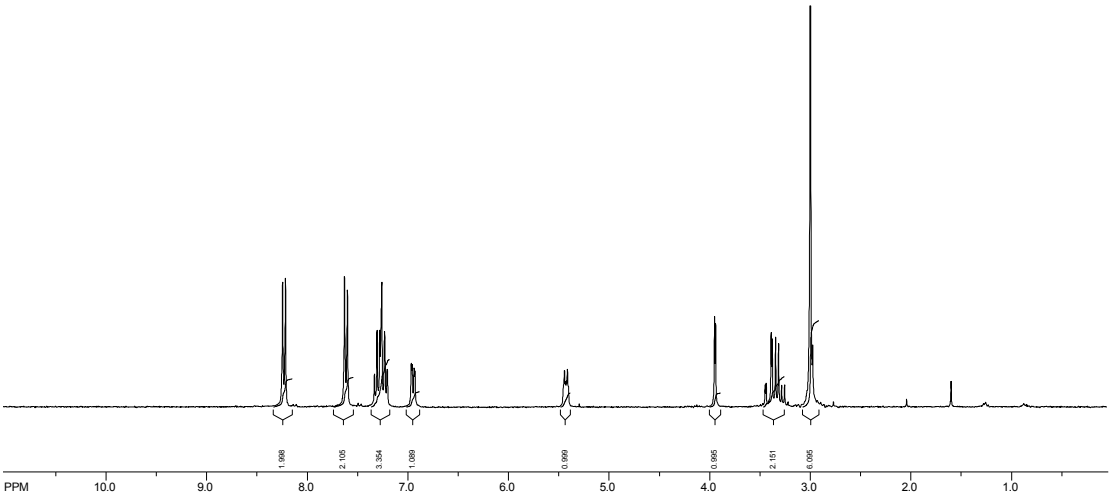

O
OH
(H3C)2N
NO2

3g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2.105
3.354
1.089
0.999
0.995
2.151
6.095
PPM
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9.0
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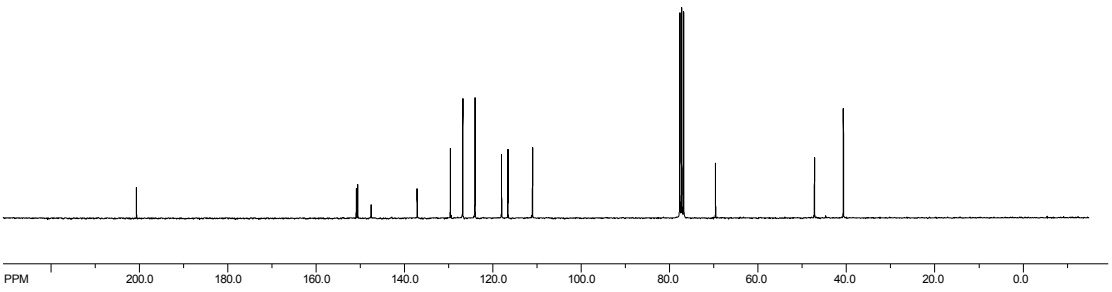
6.0
5.0
4.0
3.0
2.0
1.0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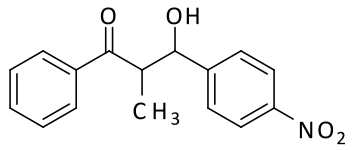
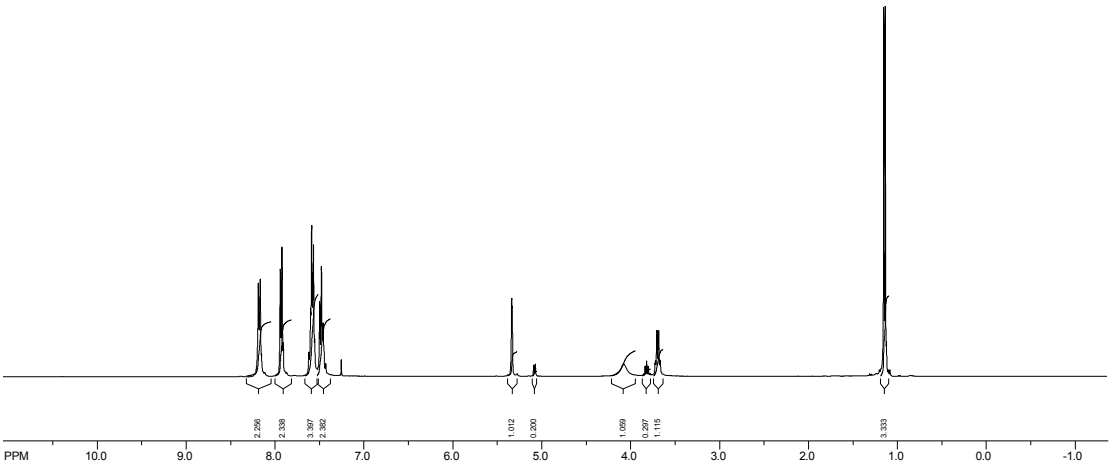
120.0
100.0
80.0
60.0
40.0
20.0
0.0


O
OH
CH3
NO2

3h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2.382
1.012
0.200
1.069
0.297
1.115
3.333
PPM
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9.0
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7.0
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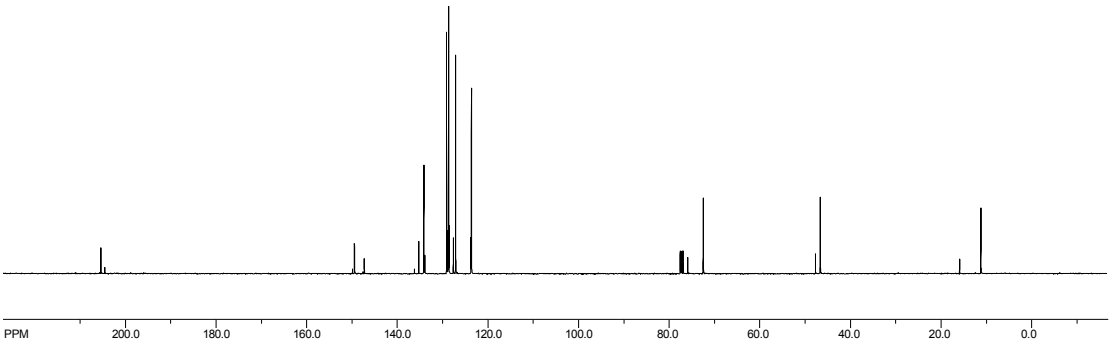
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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80.0
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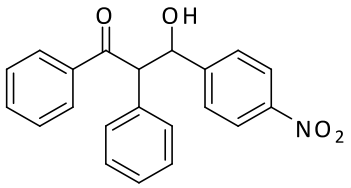
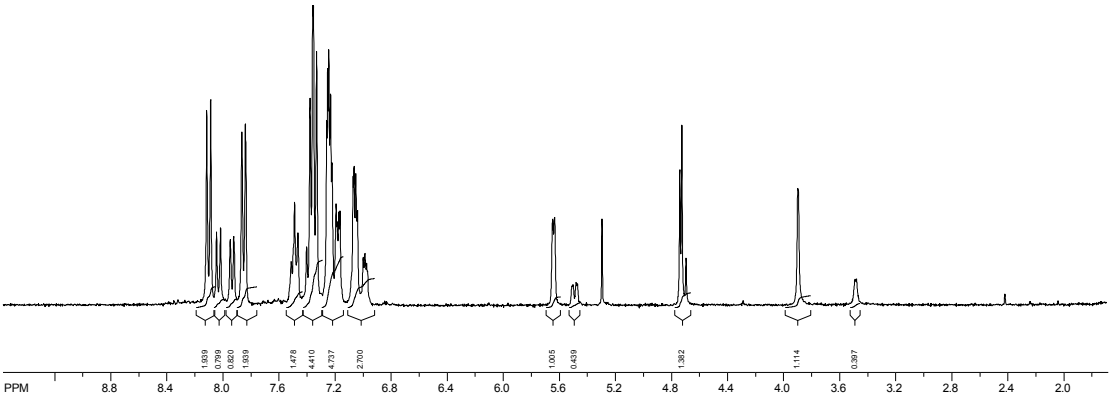
40.0
20.0
0.0


O
OH
NO2

3i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0.799
0.800
1.809
1.478
4.410
4.737
2.700
1.005
0.439
1.382
1.114
0.397
PPM
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
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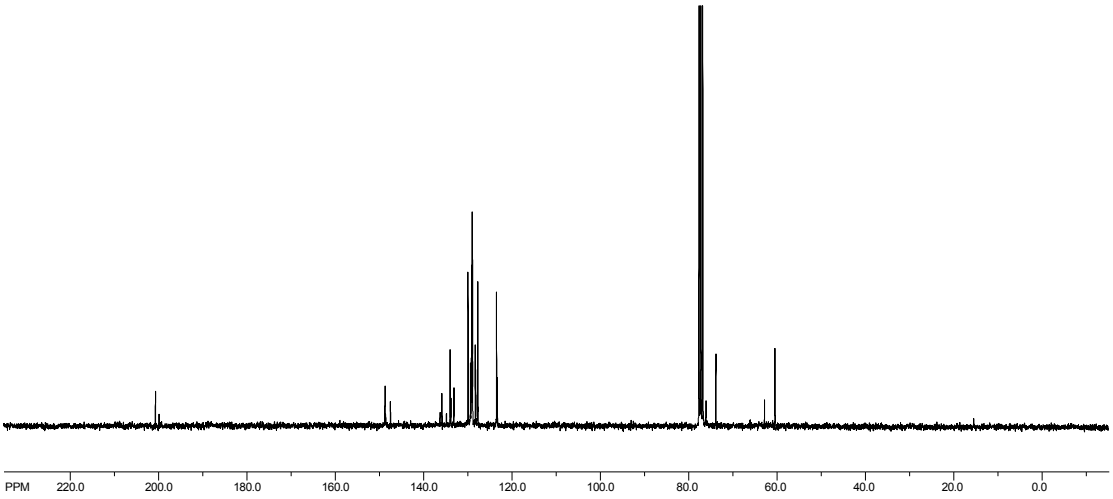
4.4
4.0
3.6
3.2
2.8
2.4
2.0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60.0
40.0
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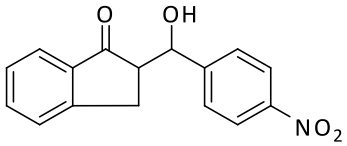
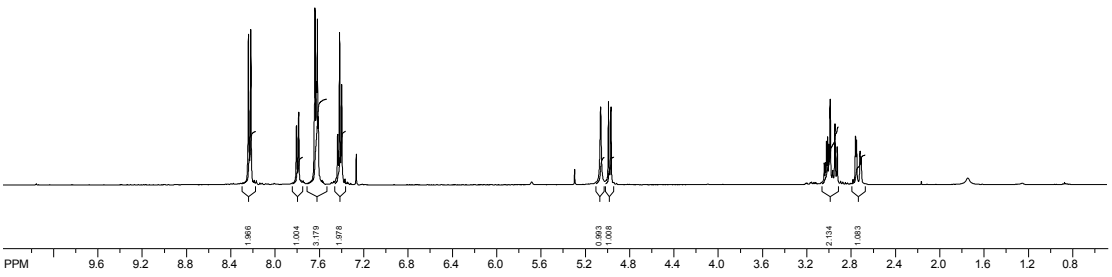
0.0


O
OH
NO2

3j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0.993
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2.134
1.083
PPM
9.6
9.2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
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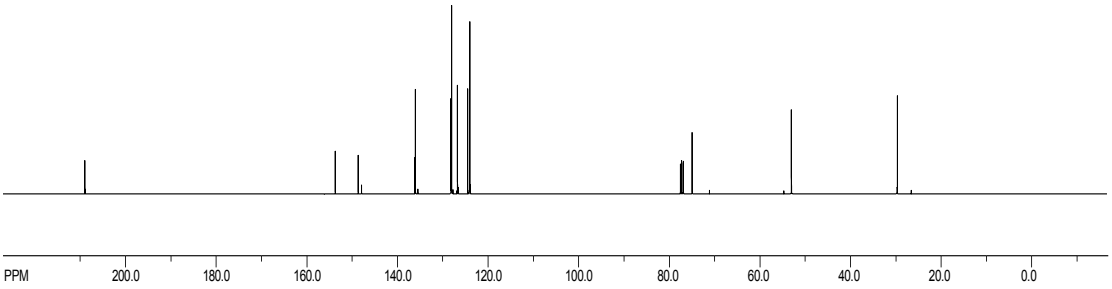
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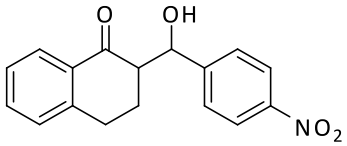
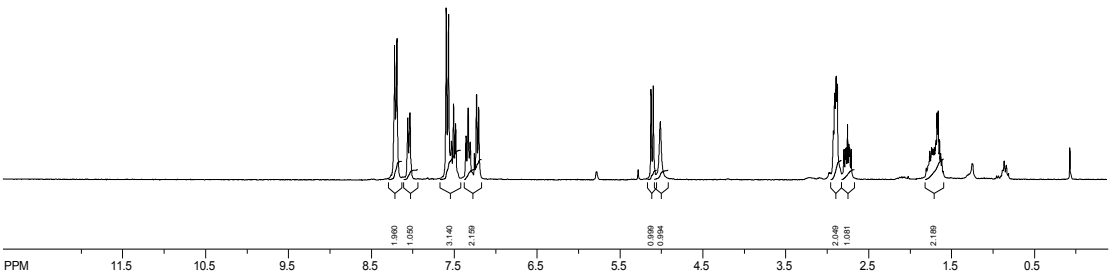
0.0


O
OH
NO2

3k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0.994
2.049
1.081
2.189
PPM
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8.5
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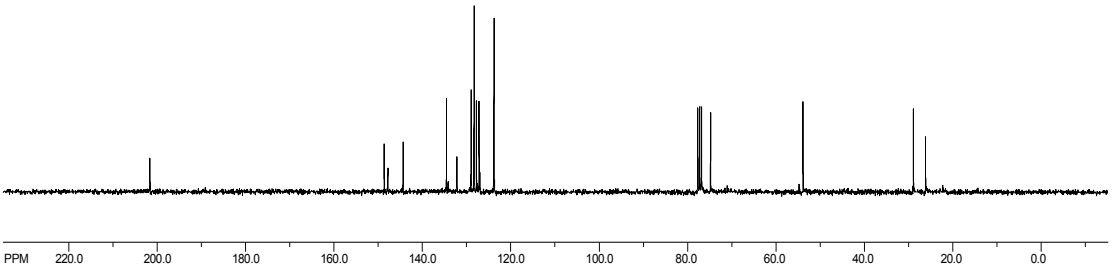
6.5
5.5
4.5
3.5
2.5
1.5
0.5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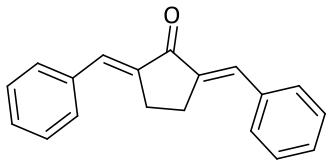
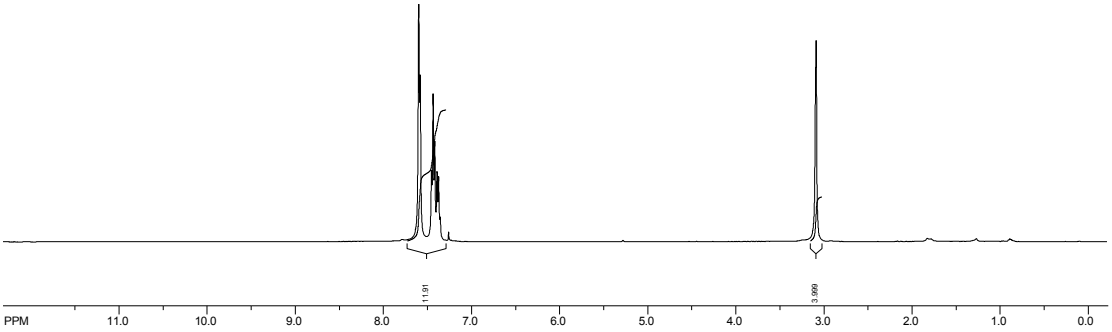
0.0



3l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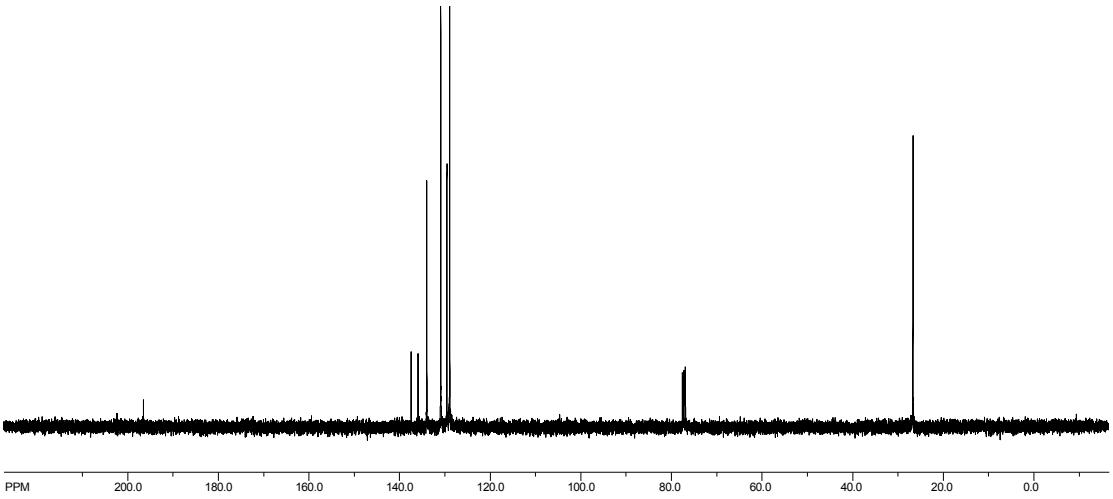
0.0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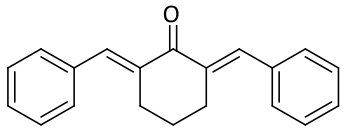
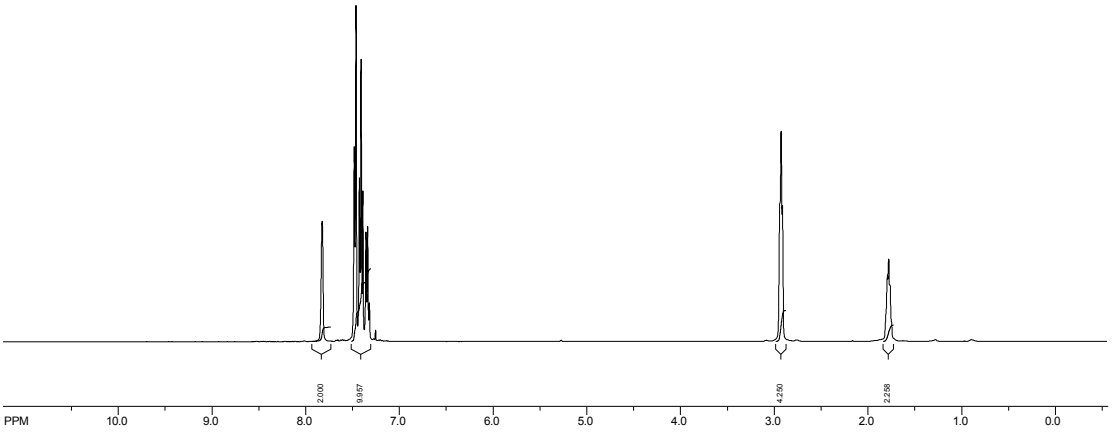


3m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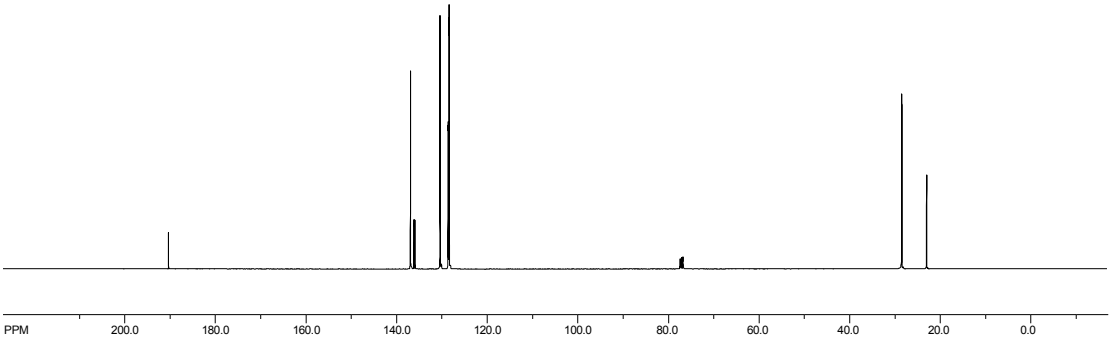
3.0
2.0
1.0
0.0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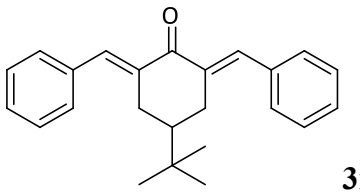
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0



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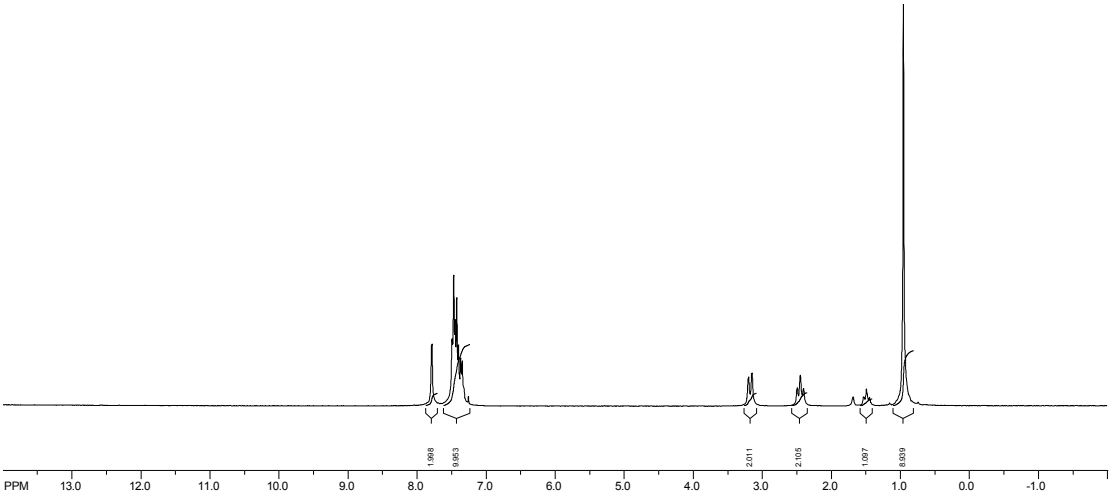
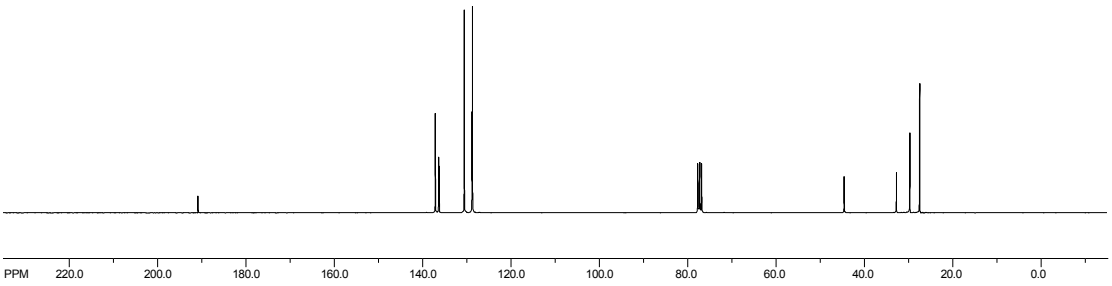
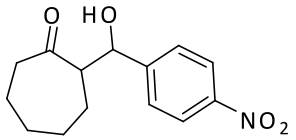
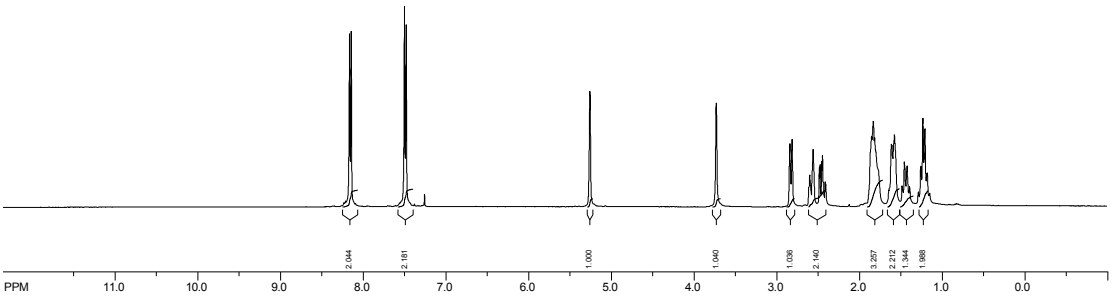

1.998
9.963
2.011
2.105
1.097
8.939
PPM 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


PPM 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0


O
HO
NO2

3o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2.161
1.000
1.040
1.035
2.140
3.357
2.212
1.344
1.888
PPM
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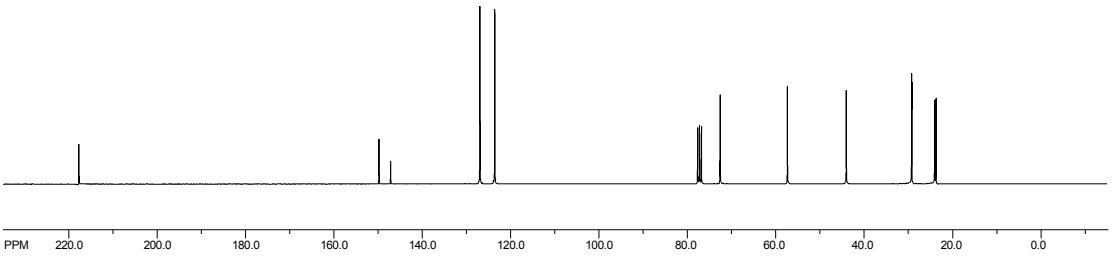
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


PPM
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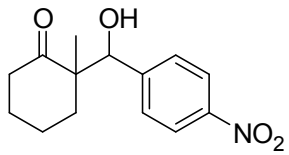
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0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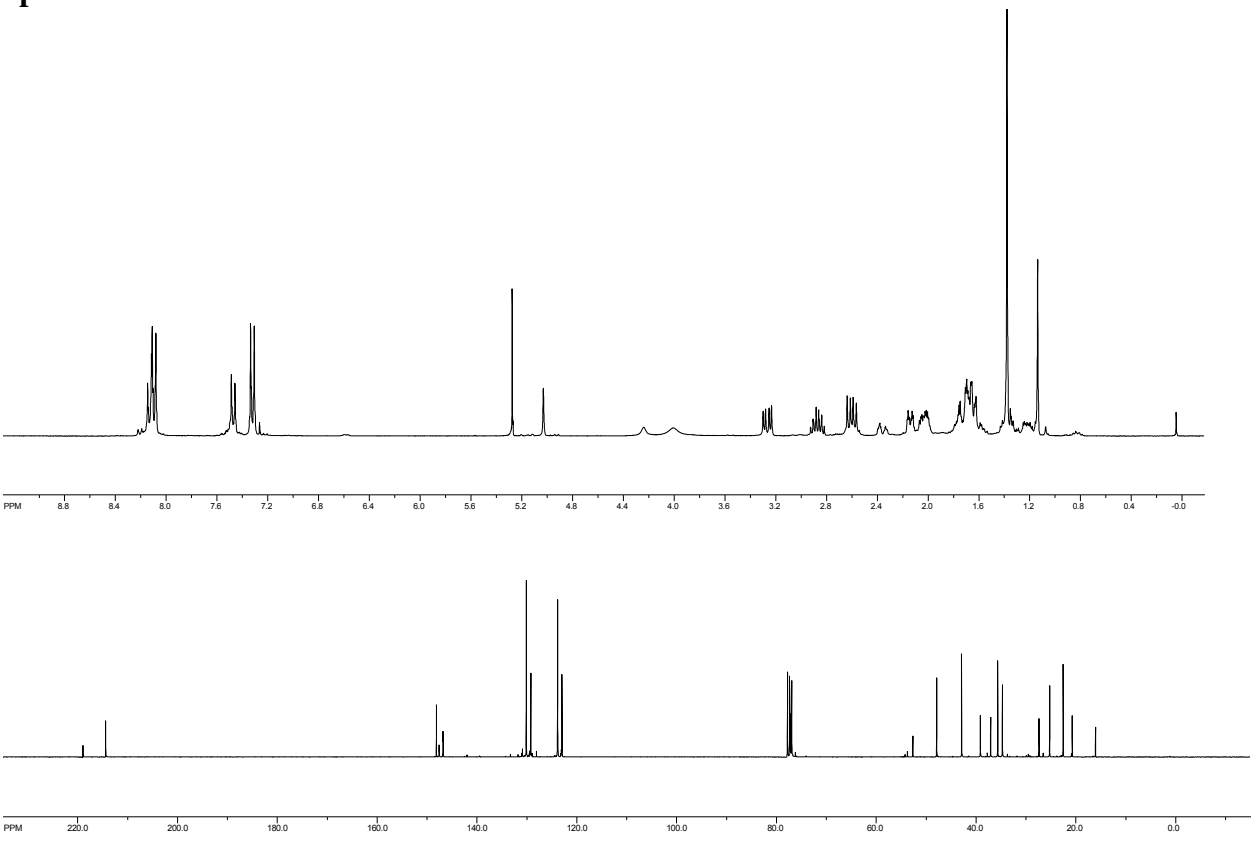
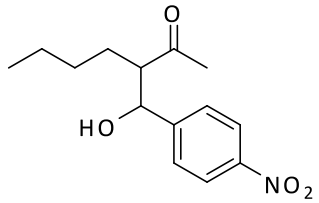
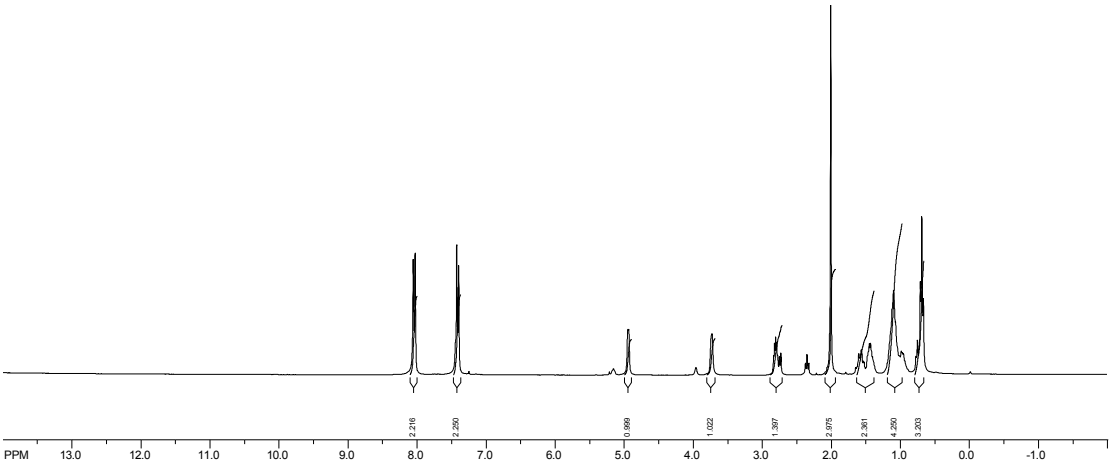
OH
NO2

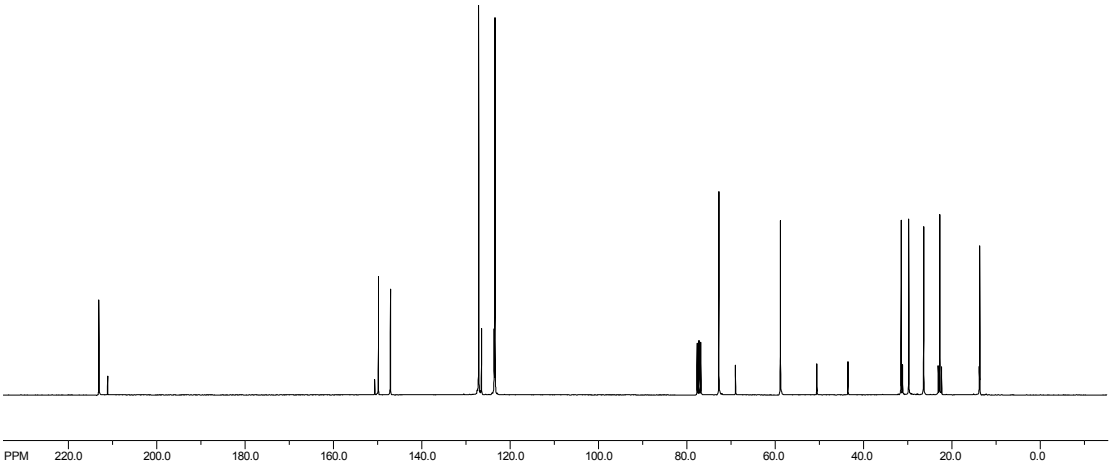
3p

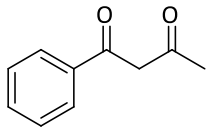

PPM
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
-0.0
PPM
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


O
HO
NO2

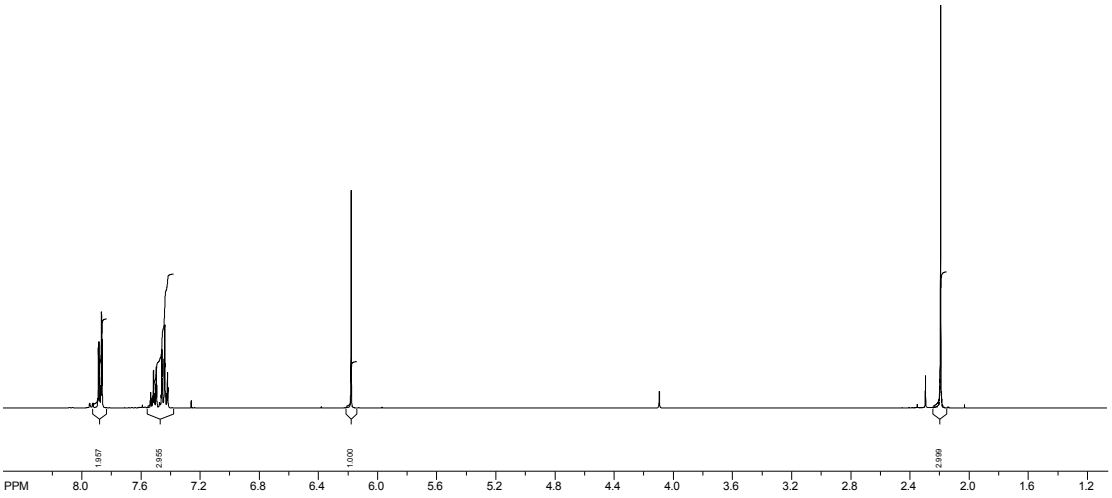
3q

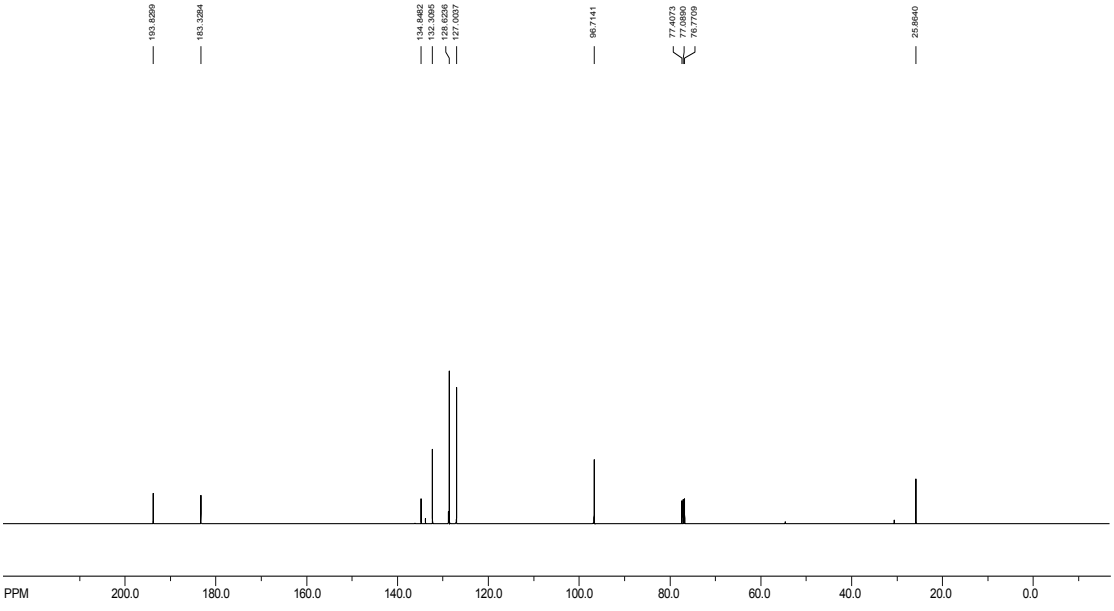

2.216
2.290
0.999
1.022
1.397
2.975
2.361
4.250
3.203
PPM 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

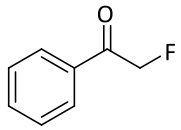

PPM 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0



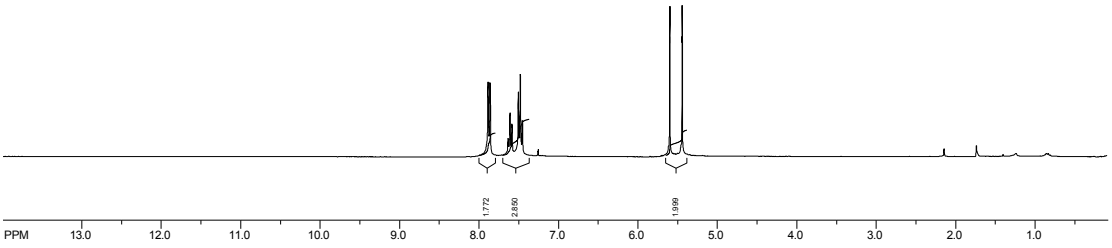
4a


1.957
2.955
1.000
2.999
PPM
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2


193.8299
183.3284
134.8482
132.3095
128.6236
127.0037
96.7141
77.4073
77.0890
76.7709
25.8640
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


O
F

5a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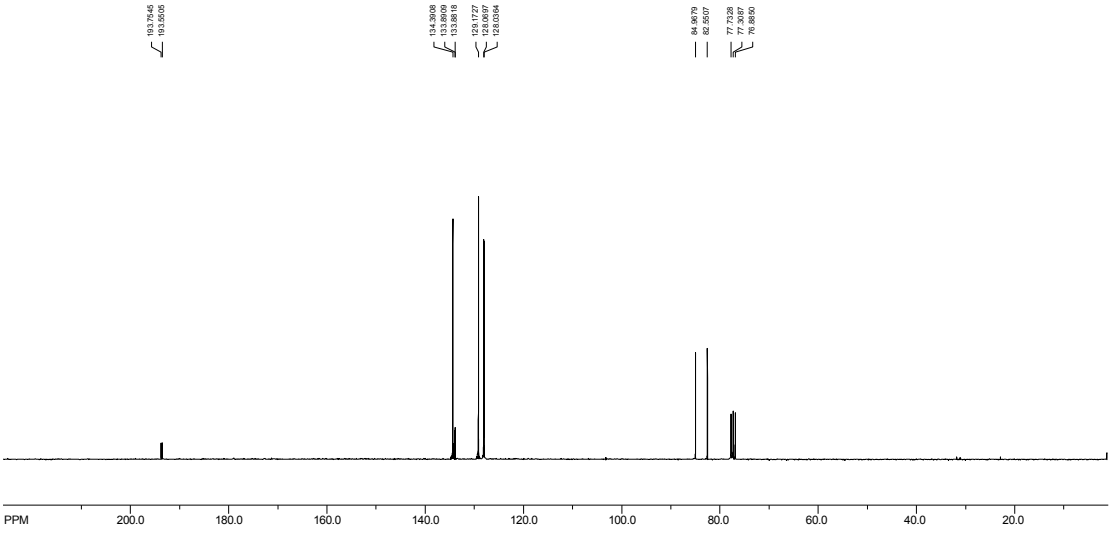
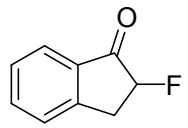
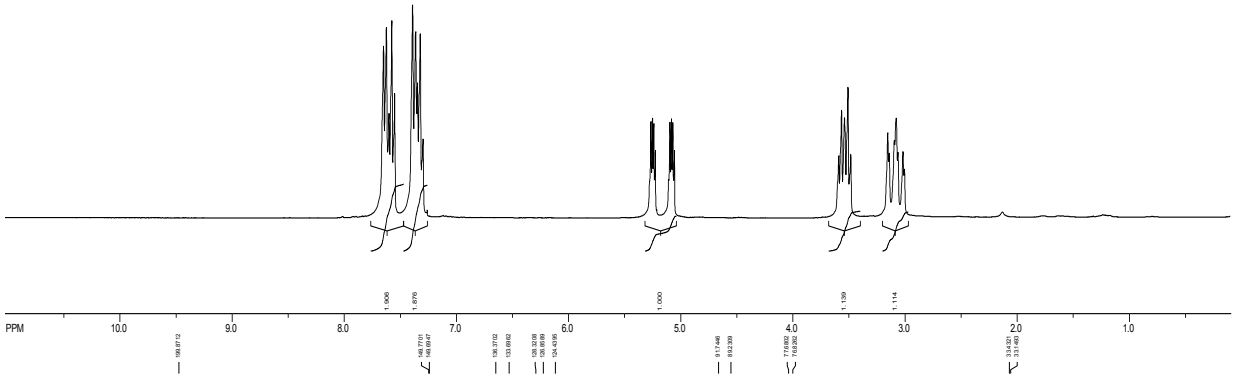
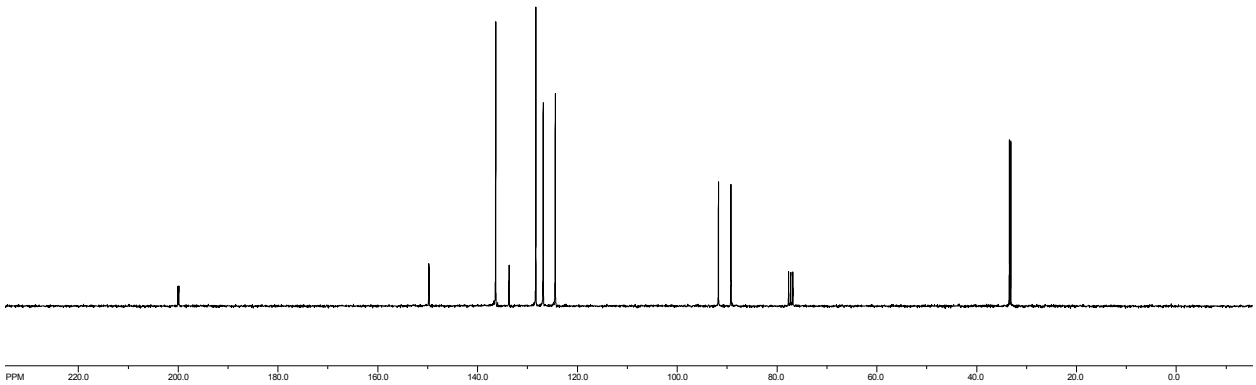
2.850
1.999
PPM
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

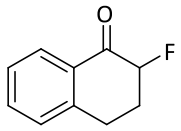

193.7545
193.3505
134.3908
133.8909
133.5816
129.1727
128.0997
128.0094
84.9679
82.5507
77.7328
77.3087
76.8850
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0


O
F

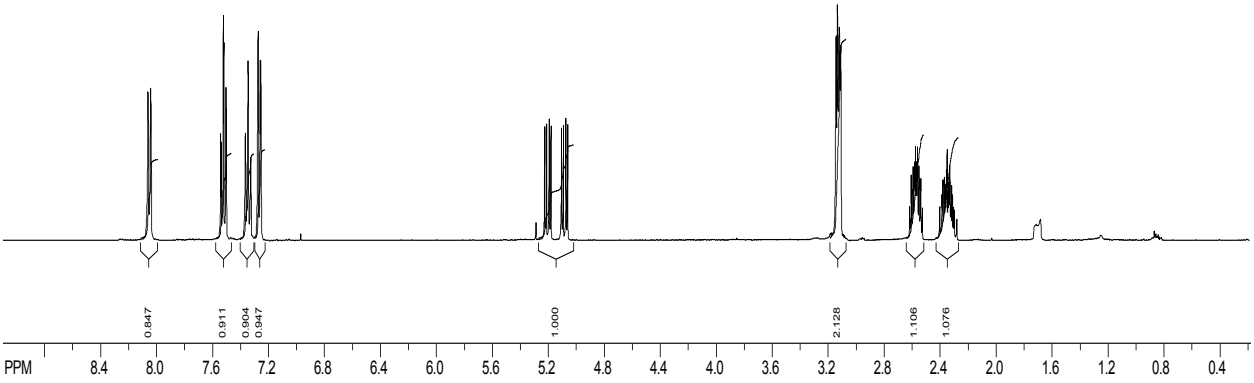
5j


1.906
1.876
1.000
1.139
1.114
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


PPM
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


O
F

5k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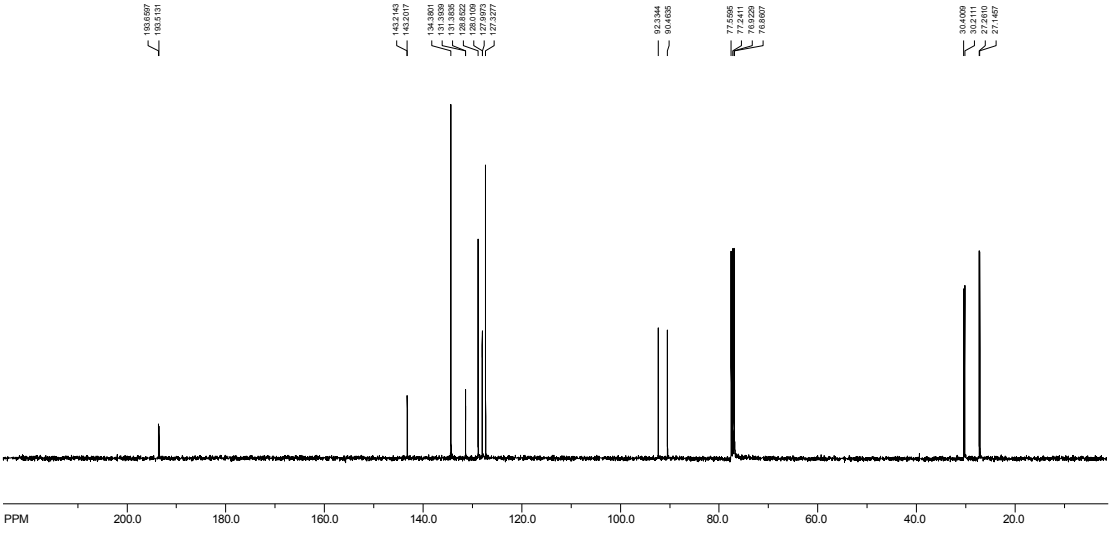
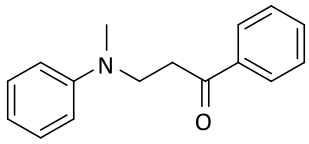
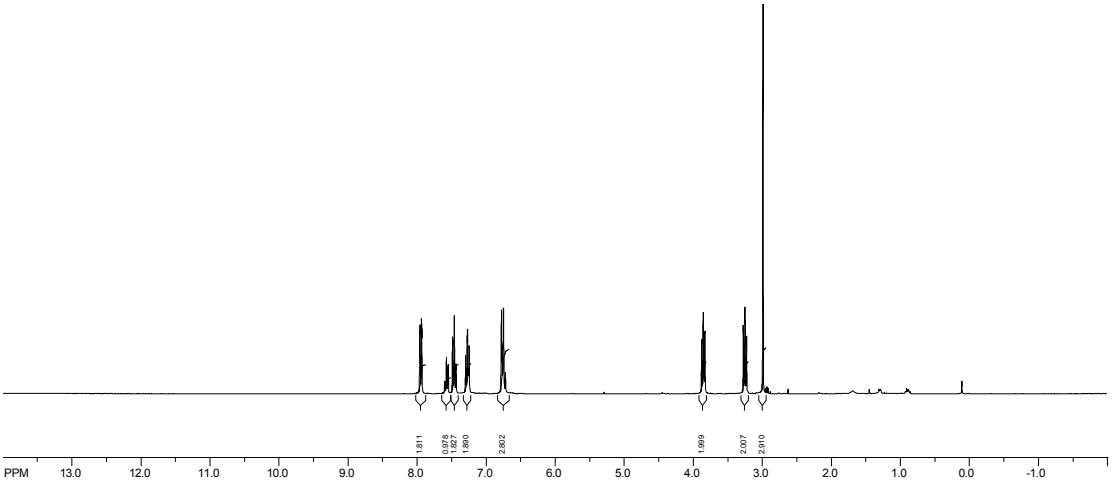
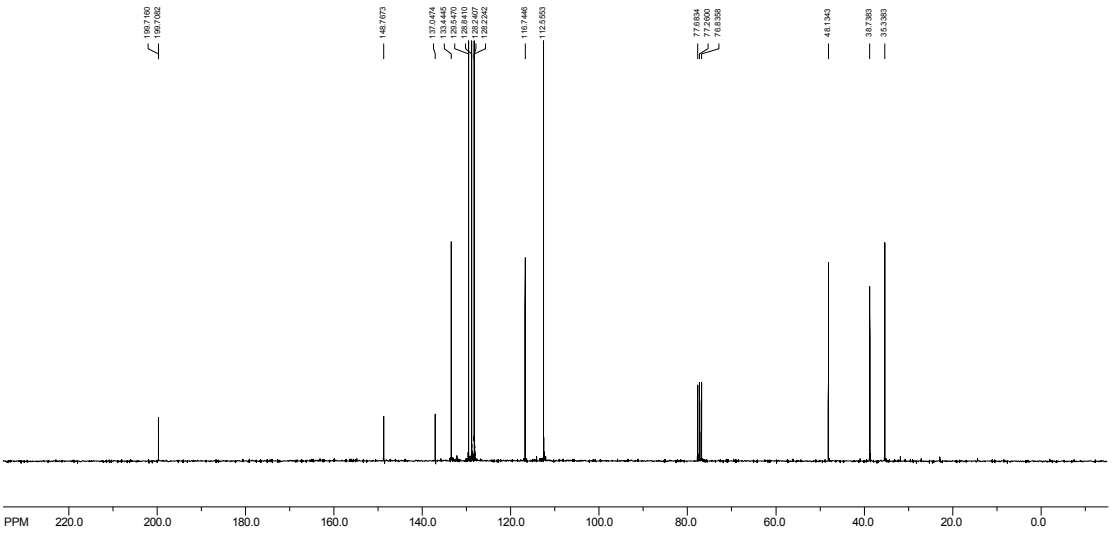
0.911
0.904
0.947
1.000
2.128
1.106
1.076
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

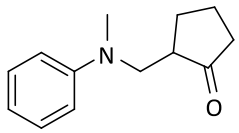

193.6697
193.5131
143.2143
143.2017
134.3891
131.7099
131.3835
128.8522
128.0109
127.9979
127.3277
92.3344
90.4635
77.5595
77.2411
76.9229
76.6897
30.4009
30.1711
27.2610
27.1467
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0



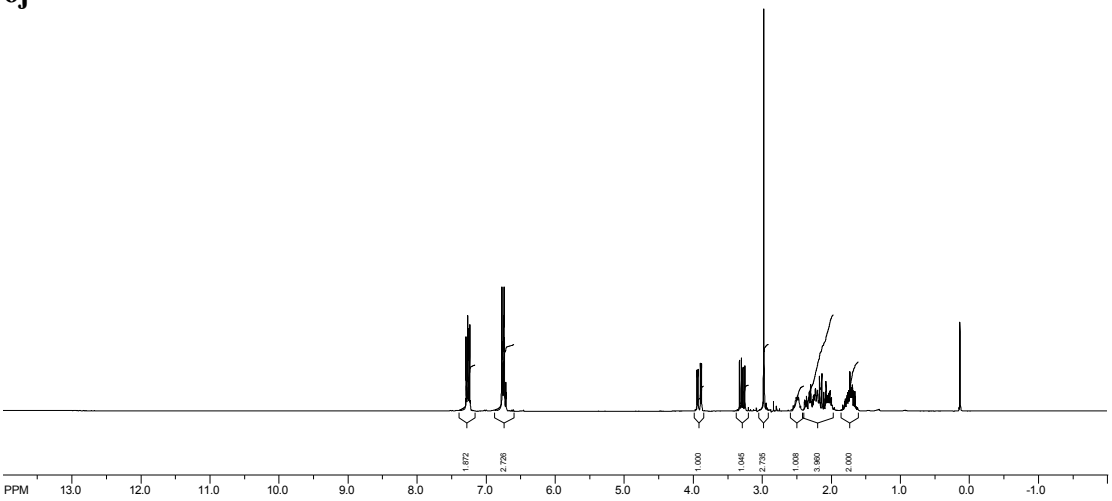
6a


1.811
0.978
1.957
1.890
2.802
1.999
2.007
2.910
PPM 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


197.760
199.708
148.767
137.047
133.444
129.440
128.841
128.240
128.226
116.746
112.555
77.683
77.266
76.839
48.134
38.738
35.338
PPM 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0


N
O

6j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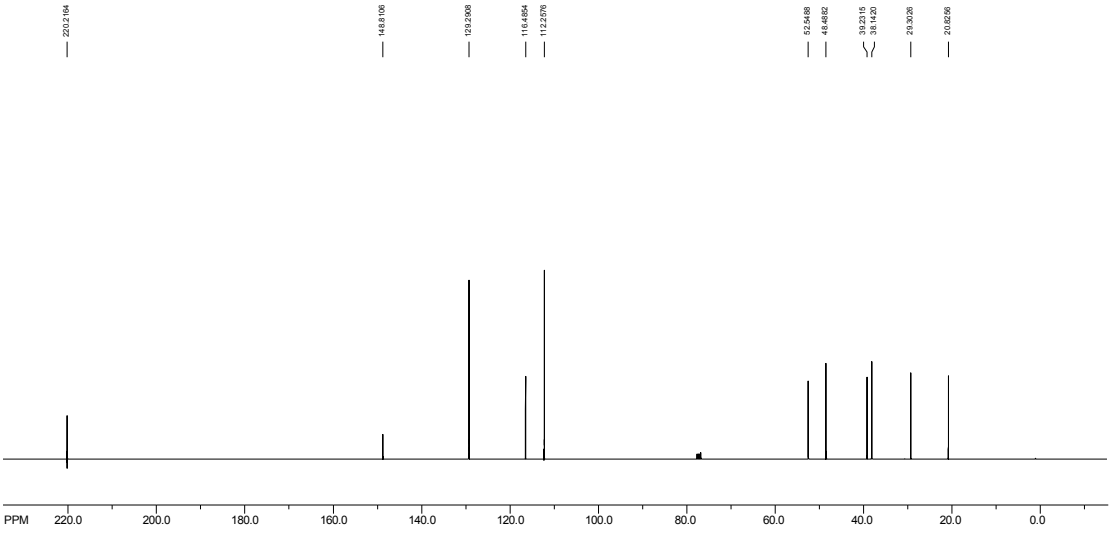
1.000
1.045
2.735
1.008
3.960
2.000
PPM
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0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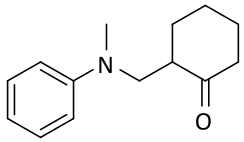
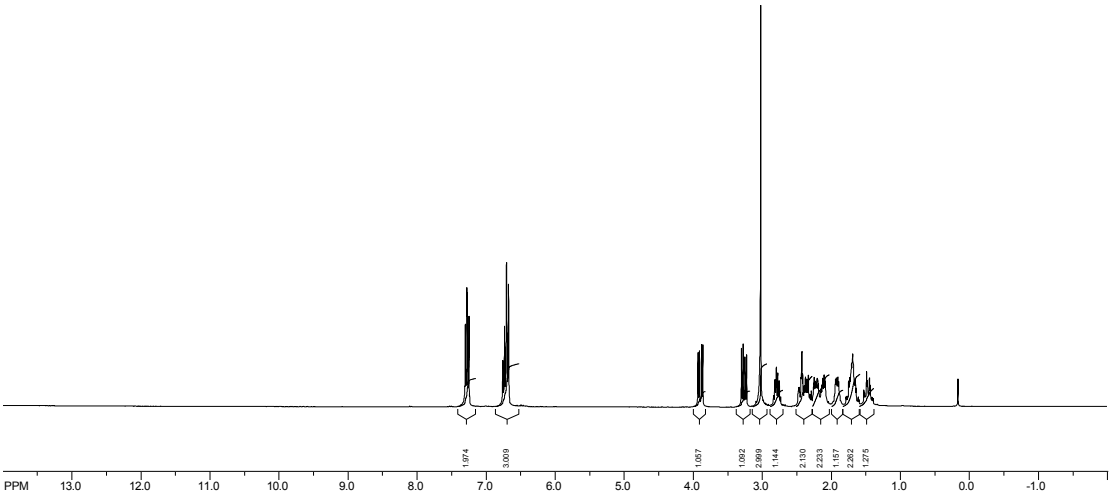
129.2908
116.4864
112.2576
52.5488
48.4862
39.0215
38.1420
29.3026
20.6826
PPM
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0


N
O

6k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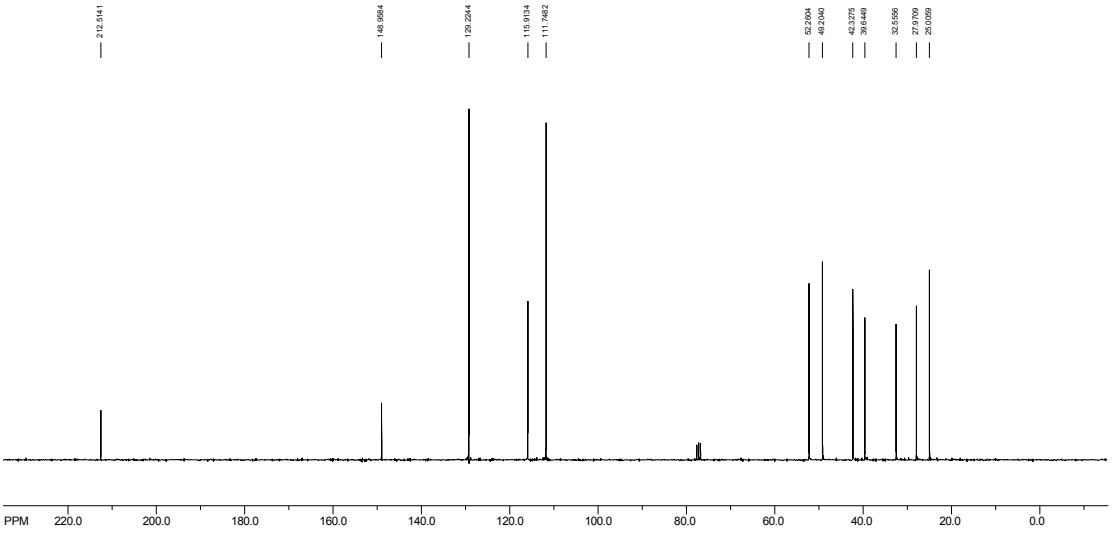
3.009
1.057
1.092
2.999
1.144
2.130
2.233
1.157
2.262
1.275
PPM 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0


212.5141
148.9984
129.2244
115.9134
111.7482
52.2604
49.2340
42.3275
39.6449
32.5556
27.9709
25.0099
PPM 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0.0