Direct Amination of Homoenolates Catalyzed by *N*-Heterocyclic Carbenes

Audrey Chan and Karl A. Scheidt*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

Supporting Information

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General Methods:

Dichloromethane was purified by passage through a bed of activated alumina. Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and p-anisaldehyde stain. Melting points (**mp**) were obtained on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. Infrared spectra (**IR**) were obtained on a Bio-Rad FTS-40 FTIR spectrophotometer. Infrared spectra were obtained as a thin film on a 25 x 4 mm NaCl disc. Proton nuclear magnetic resonances (**^{1}H NMR**) were recorded in deuterated solvents on a Varian Inova 500 (500 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm, δ) relative to the residual protio solvent ($CDCl_3$, δ 7.26; D_2O, δ 4.80; DMSO, δ 2.50, CD_3OD, δ 3.31) ^{1}H NMR spectroscopy splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), or septet (sep). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m) or broad (br). Coupling constants are reported in Hertz (Hz). Proton-decoupled (**^{13}C-NMR**) spectra were recorded on a Varian Inova 500 (125 MHz) spectrometer and are reported in ppm using the solvent as an internal standard ($CDCl_3$, δ 77.23; DMSO, δ 39.5, CD_3OD, δ 49.15). Electrospray mass spectra (**ESI-MS**) were obtained using a Micromass Quattro II Triple Quadrupole HPLC/MS/MS Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were purchased from Aldrich and used without further purification.

1-Acyl-2-aryldiazenes were prepared according to the general procedure by Bowman and coworkers,[1] Budil and coworkers,[2] and Buchwald and coworkers.[3] 4-Chloro cinnamaldehyde was prepared according to a procedure analogous to Moloney.[4] 3-methyl cinnamaldehyde, 3-(naphthalene-5-yl)acrylaldehyde, 3-(naphthalene-6-yl)acrylaldehyde, and 3-methoxy cinnamaldehyde was prepared according to the general procedure of Cacchi and coworkers.[5] 4-Methoxy cinnamaldehyde was purchased from Acros Chemical Company and the remaining aldehydes were commercially available from Sigma-Aldrich Chemical Company and distilled prior to use.

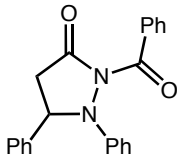
Typical Procedure for the amination of enals with benzoylaryldiazenes:

Into an oven-dried screw-capped glass tube equipped with a stir bar was charged with the *N*2-mesityl-*N*4-methyl-5-methyltriazolium tetrafluoroborate salt (14.4 mg, 0.0476 mmol) and 4 Å molecular sieves (150 mg) and capped in a nitrogen-filled drybox. The tube with the reagents was removed from the drybox and then purged with N_2. Into the tube was added a solution of 1-benzoyl-1-phenyldiazene (150 mg, 0.714 mmol) dissolved in CH_2Cl_2 (950 μL, 0.25 M). Next, distilled cinnamaldehyde (30 μL, 0.238 mmol) was added and the reaction mixture was cooled to 0 °C and DBU was added (10.7 μL, 0.0714 mmol). Upon DBU addition, the reaction turned brown then orange. After 24 h at 0 °C, the orange suspension was warmed to room temperature. The mixture was diluted with CH_2Cl_2 and filtered through a pad of silica gel and washed with

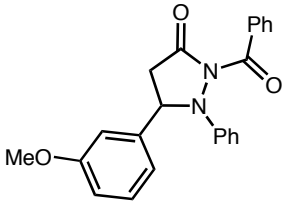
1. Bowman, W.R.; Forshaw, J.A.; Hall, K.P.; Kitchin, J.P.; Mott, A.W. *Tetrahedron.* **1996**, *52* (*11*), 3961-3972.
2. Srinivasan, V.; Jebaratnam, D.J.; Budil, D.E. *J. Org. Chem. Soc.* **1999**, *64*, 5644-5649.
3. Klapars, A.; Antilla, J.C.; Huang, X.; Buchwald, S.L. *J. Am. Chem. Soc.* **2001**, *123*, 7727-7729.
4. Baldwin, J.E.; Turner, S.C.M.; Moloney, M.G. *Tetrahedron*, **1994**, *50*, 9411-9424.
5. Battistuzzi, G.; Cacchi, S.; Fabrizi, G. *Org. Lett.* **2003**, *5(5)*, 777-780.

CH_2Cl_2 and Et_2O. The resulting residue was purified by flash column chromatography on silica gel.

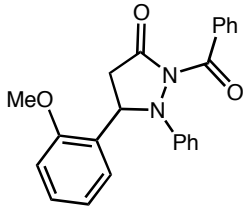
Characterization of pyrazolidin-3-ones:



2-Benzoyl-1,5-diphenylpyrazolidin-3-one (5): Purified with 10-15% ethyl acetate/hexanes, yielding 51 mg (63%) of **5** as a light tan foam. R_f = 0.40 (25% ethyl acetate/hexanes); Mp: 135-137 °C; IR (film) 3061, 2920, 1759, 1694, 1492, 1279, 1230, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63-7.59 (m, 4H); 7.53-7.50 (m, 1H); 7.47-7.44 (m, 2H); 7.40-7.33 (m, 5H); 7.12-7.09 (m, 3H); 5.11 (d, *J* = 8.3 Hz, 1H); 3.47 (dd, *J* = 17.1, 8.3 Hz, 1H); 2.82 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 166.3, 149.7, 139.7, 133.5, 132.5, 129.7, 129.3, 129.2, 128.5, 128.1, 126.3, 124.1, 117.2, 67.7, 38.6; LRMS (electrospray): Mass calculated for $C_{44}H_{36}N_4O_4Na$ $[2M + Na]^+$, 707. Found 707.

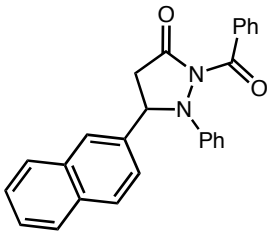


2-Benzoyl-5-(3-methoxyphenyl)-1-phenylpyrazolidin-3-one (6): Purified with 10-15% ethyl acetate/hexanes, yielding 69mg (60%) of **6** as a yellow foam. R_f = 0.39 (25% ethyl acetate/hexane); Mp: 45-47 °C; IR (film) 3061, 2922, 1759, 1695, 1598, 1491, 1275, 1230, 1194, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 2H); 7.53 (t, *J* = 7.3 Hz, 1H); 7.42-7.34 (m, 6H); 7.11 (d, *J* = 7.8 Hz, 4H); 6.92-6.90 (m, 1H); 5.11 (d, *J* = 8.3 Hz, 1H); 3.83 (s, 3H); 3.47 (dd, *J* = 17.1, 8.8 Hz, 1H); 2.80 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 166.3, 160.4, 149.6, 141.5, 133.5, 132.5, 130.3, 129.7, 129.3, 128.1, 123.9, 118.3, 116.9, 114.1, 111.6, 67.5, 55.5, 38.9; LRMS (electrospray): Mass calculated for $C_{46}H_{40}N_6O_6Na$ $[2M + Na]^+$, 767, Found 767.

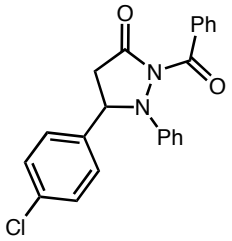


2-Benzoyl-5-(2-methoxyphenyl)-1-phenylpyrazolidin-3-one (7): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 53 mg (66%) of **7** as a yellow foam. R_f = 0.30 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 70-72 °C; IR (film) 3060, 2922, 1759, 1694, 1599, 1491, 1281, 1240, 1192, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.8

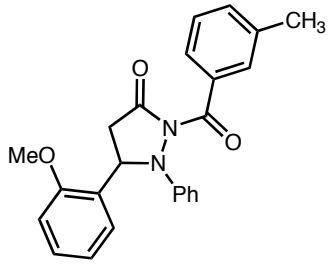
Hz, 1H); 7.66 (d, *J* = 6.8 Hz, 2H); 7.51 (t, *J* = 7.3 Hz, 1H); 7.41-7.32 (m, 5H); 7.11-7.03 (m, 4H); 6.95 (d, *J* = 7.8 Hz, 1H); 5.27 (d, *J* = 8.8 Hz, 1H); 3.86 (s, 3H); 3.44 (dd, *J* = 17.6, 8.8 Hz, 1H); 2.73 (d, *J* = 17.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 166.5, 156.5, 150.2, 133.8, 132.4, 129.7, 129.5, 129.3, 128.3, 128.1, 127.1, 123.6, 121.2, 116.8, 110.7, 64.5, 55.4, 38.0; LRMS (electrospray): Mass calculated for $C_{52}H_{40}N_4O_6Na$ $[2M + Na]^+$, 767. Found 767.



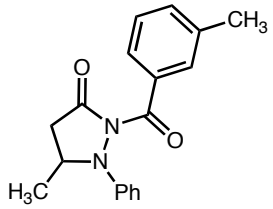
2-Benzoyl-5-(naphthalene-3-yl)-1-phenylpyrazolidin-3-one (8): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 55 mg (64%) of **8** as a light tan solid. R_f = 0.30 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 205-207 °C; IR (film) 3055, 2920, 1759, 1693, 1593, 1492, 1275, 1231, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H); 7.93 (d, *J* = 8.8 Hz, 1H); 7.88-7.87 (m, 2H); 7.63-7.57 (m, 3H); 7.54-7.49 (m, 3H); 7.38-7.35 (m, 4H); 7.16-7.11 (m, 3H); 5.25 (d, *J* = 8.3 Hz, 1H); 3.53 (dd, *J* = 17.1, 8.3 Hz, 1H); 2.93 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 166.4, 149.8, 136.9, 133.6, 133.5, 133.3, 132.5, 129.8, 129.3, 129.2, 128.5, 128.1, 127.9, 126.8, 126.7, 125.3, 124.2, 124.1, 117.3, 67.9, 38.5; LRMS (electrospray): Mass calculated for $C_{52}H_{40}N_4O_4Na$ $[2M + Na]^+$, 808. Found 808.



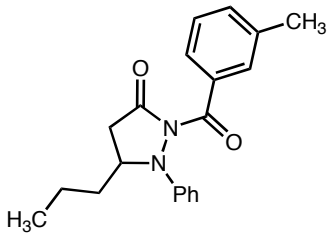
2-Benzoyl-5-(4-chlorophenyl)-1-phenylpyrazolidin-3-one (9): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 55 mg (61%) of **9** as a light yellow solid. R_f = 0.31 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 197-198 °C; IR (film) 3061, 2920, 1759, 1694, 1593, 1491, 1277, 1230, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H); 7.55-7.52 (m, 3H); 7.42-7.39 (m, 4H); 7.37-7.33 (m, 2H); 7.25-7.08 (m, 3H); 5.07 (d, *J* = 8.3 Hz, 1H); 3.48 (dd, *J* = 17.1, 8.8 Hz, 1H); 2.75 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 166.2, 149.5, 138.3, 134.4, 133.4, 132.7, 129.8, 129.4, 129.3, 128.2, 127.8, 124.3, 117.2, 67.1, 38.8; LRMS (electrospray): Mass calculated for $C_{44}H_{34}ClN_4O_4Na$ $[2M + Na]^+$, 777. Found 777.



2-(3-Methylbenzoyl)-5-(2-methoxypheny)-l-phenylpyrazolidin-3-one (10): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 53 mg (64%) of **10** as a light yellow foam. R_f = 0.28 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 61-64 °C; IR (film) 3060, 2921, 1760, 1693, 1597, 1491, 1285, 1236, 1200, 695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H); 7.46-7.44 (m, 2H); 7.38-7.27 (m, 5H); 7.11-7.03 (m, 4H); 6.95 (d, *J* = 8.3 Hz, 1H); 5.28 (d, *J* = 8.8 Hz, 1H); 3.86 (s, 3H); 3.43 (dd, *J* = 17.6, 9.3 Hz, 1H); 2.72 (d, *J* = 17.6 Hz, 1H); 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 166.6, 156.5, 150.2, 137.9, 133.8, 133.2, 129.8, 129.7, 129.5, 128.3, 127.9, 127.1, 126.4, 123.5, 121.2, 116.8, 110.7, 64.4, 55.4, 38.0, 21.5; LRMS (electrospray): Mass calculated for $C_{48}H_{44}N_4O_6Na$ $[2M + Na]^+$, 796. Found 796.

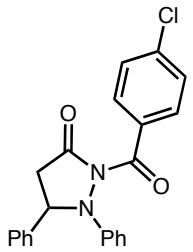


2-(3-Methylbenzoyl)-l-phenyl-5-methylpyrazolidin-3-one (11): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 73 mg (82%) of **11** as a light orange solid. R_f = 0.33 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 135-137 °C; IR (film) 3051, 2974, 1760, 1694, 1593, 1490, 1287, 1187, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H); 7.33-7.28 (m, 4H); 7.09-7.05 (m, 3H); 4.09-4.06 (m, 1H); 3.06 (dd, *J* = 17.1, 7.3 Hz, 1H); 2.38 (s, 3H); 2.26 (d, *J* = 17.1 Hz, 1H); 1.56 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 166.9, 149.9, 137.9, 133.6, 133.2, 129.8, 129.5, 127.9, 126.4, 124.1, 117.7, 61.4, 37.9, 21.5, 21.0; LRMS (electrospray): Mass calculated for $C_{36}H_{36}N_4O_4Na$ $[2M + Na]^+$, 611. Found 611.

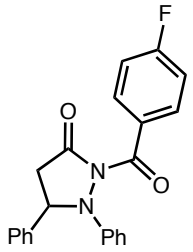


2-(3-Methylbenzoyl)-l-phenyl-5-propylpyrazolidin-3-one (12): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 70 mg (84%) of **12** as a yellow oil. R_f = 0.32 (5/35/60 ethyl acetate/dichloromethane/hexane); IR (film) 3047, 2958, 1760, 1694, 1593, 1490, 1284, 1232, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H); 7.33-7.28 (m, 4H); 7.05 (t, *J* =

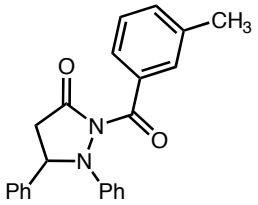
7.3 Hz, 1H); 7.02 (d, *J* = 7.8 Hz, 2H); 3.90-3.85 (m, 1H); 3.07 (dd, *J* = 17.1, 7.8 Hz, 1H); 2.37 (s, 3H); 2.28 (d, *J* = 17.6 Hz, 1H); 1.96-1.90 (m, 1H); 1.76-1.69 (m, 1H); 1.63-1.55 (m, 2H); 1.04 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 167.0, 150.4, 137.9, 133.7, 133.1, 129.7, 129.6, 127.9, 126.3, 123.9, 117.5, 65.9, 36.9, 36.7, 21.5, 19.7, 14.1; LRMS (electrospray): Mass calculated for $C_{40}H_{44}N_4O_4Na$ [2M + Na]$^+$, 667. Found 667.



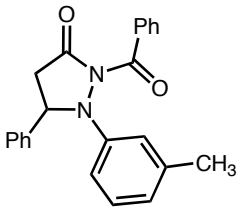
2-(4-Chlorobenzoyl)-1,5-diphenylpyrazolidin-3-one (13): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 61 mg (68%) of **13** as an yellow solid. R_f = 0.31 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 173-175 °C; IR (film) 3062, 2921, 1760, 1694, 1595, 1489, 1274, 1230, 738, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.53 (m, 4H); 7.46-7.39 (m, 2H); 7.38-7.30 (m, 5H); 7.12-7.07 (m, 3H); 5.09 (d, *J* = 8.3 Hz, 1H); 3.46 (dd, *J* = 17.1, 8.3 Hz, 1H); 2.83 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 165.3, 149.6, 139.5, 138.9, 131.8, 130.8, 129.8, 129.3, 128.6, 128.5, 126.4, 124.3, 117.3, 67.8, 38.4; LRMS (electrospray): Mass calculated for $C_{44}H_{34}ClN_4O_4Na$ [2M + Na]$^+$, 777. Found 777.



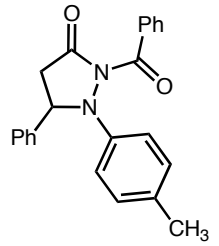
2-(4-Fluorobenzoyl)-1,5-diphenylpyrazolidin-3-one (14): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 52 mg (61%) of **14** as a light tan solid. R_f = 0.30 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 156-159 °C; IR (film) 3063, 2924, 1760, 1184, 1600, 1494, 1276, 1233, 847, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H); 7.58 (d, *J* = 7.8 Hz, 2H); 7.45 (t, *J* = 7.3 Hz, 2H); 7.39-7.32 (m, 3H); 7.11-7.03 (m, 5H); 5.09 (d, *J* = 8.3 Hz, 1H); 3.47 (dd, *J* = 17.1, 8.8 Hz, 1H); 2.83 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 165.2, 149.7, 139.6, 132.2, 132.1, 129.8, 129.3, 128.6, 126.4, 124.2, 117.2, 115.5, 115.3, 67.7, 38.5; LRMS (electrospray): Mass calculated for $C_{44}H_{34}FN_4O_4Na$ [2M + Na]$^+$, 744. Found 744.



2-(3-Methylbenzoyl)-1,5-diphenylpyrazolidin-3-one (15): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 62 mg (73%) of **15** as a light tan foam. R_f = 0.30 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 52-53 °C; IR (film) 3050, 2921, 1760, 1693, 1598, 1492, 1282, 1204, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.3 Hz, 2H); 7.45 (t, *J* = 7.8 Hz, 2H); 7.40-7.27 (m, 7H); 7.10 (d, *J* = 7.3 Hz, 3H); 5.11 (d, *J* = 8.3 Hz, 1H); 3.46 (dd, *J* = 17.1, 8.8 Hz, 1H); 2.81 (d, *J* = 17.1 Hz, 1H); 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 166.5, 149.8, 139.8, 137.9, 133.5, 133.3, 129.8, 129.7, 129.3, 128.5, 127.9, 126.4, 126.3, 124.0, 117.2, 67.7, 38.6, 21.5; LRMS (electrospray): Mass calculated for $C_{46}H_{40}N_4O_4Na$ $[2M + Na]^+$, 736. Found 736.



2-Benzoyl-1-(3-methylphenyl)-5-phenylpyrazolidin-3-one (16): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 59 mg (66%) of **16** as a light tan foam. R_f = 0.30 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 104-106 °C; IR (film) 3059, 2921, 1759, 1694, 1601, 1490, 1279, 1221, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (t, *J* = 6.8 Hz, 4H); 7.51 (t, *J* = 7.8 Hz, 1H); 7.45 (t, *J* = 7.3, 2H); 7.40-7.34 (m, 3H); 7.25-7.21 (m, 1H); 6.93-6.91 (m, 3H); 5.10 (d, *J* = 8.3 Hz, 1H); 3.47 (dd, *J* = 17.1, 8.8 Hz, 1H); 2.80 (d, *J* = 17.1 Hz, 1H); 2.34 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 166.3, 149.9, 139.8, 139.7, 133.6, 132.4, 129.5, 129.3, 129.2, 128.4, 128.1, 126.3, 125.0, 118.2, 114.1, 67.7, 38.6, 21.8; LRMS (electrospray): Mass calculated for $C_{46}H_{40}N_4O_4Na$ $[2M + Na]^+$, 736. Found 736.



2-Benzoyl-1-(4-methylphenyl)-5-phenylpyrazolidin-3-one (17): Purified with 5/25/70 ethyl acetate/dichloromethane/hexane, yielding 53 mg (63%) of **17** as a light yellow solid. R_f = 0.30 (5/35/60 ethyl acetate/dichloromethane/hexane); Mp: 151-152 °C; IR (film) 3047, 2921, 1757, 1691, 1599, 1493, 1276, 1231, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60-7.56 (m, 4H); 7.44 (t, *J* = 7.8 Hz, 2H); 7.39-7.32 (m, 3H); 7.19 (d, *J* = 7.8 Hz, 2H); 7.09 (d, *J* = 7.8 Hz, 3H); 5.10 (d,

J = 8.3 Hz, 1H); 3.47 (dd, *J* = 17.1, 8.8 Hz, 1H); 2.81 (d, *J* = 17.1 Hz, 1H); 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 166.2, 149.8, 143.4, 139.9, 130.6, 129.7, 129.6, 129.3, 128.9, 128.4, 126.3, 123.9, 117.1, 67.7, 38.9, 21.9; LRMS (electrospray): Mass calculated for $C_{46}H_{40}N_4O_4Na$ $[2M + Na]^+$, 736. Found 736.

Enantioselective aminations of enals with 1-acyl-2-aryldiazenes:
Into an oven-dried screw-capped glass tube equipped with a stir bar was charged with the triazolium salt **E** (15.3 mg, 0.0317 mmol) and 4 Å molecular sieves (150 mg) and capped in a nitrogen-filled drybox. The tube with the reagents was removed from the drybox and then purged with N_2. Into the tube was added a solution of 1-benzoyl-1-phenyldiazene (100 mg, 0.476 mmol) dissolved in CH_2Cl_2 (635 μL, 0.25 M). Next, distilled cinnamaldehyde (20 μL, 0.159 mmol) was added and the reaction mixture was cooled to 0 °C. Lastly, DBU (7.1 μL, 0.0476 mmol) was added to the reaction which turned the solution brown then orange. After 96 h at 0 °C, the orange suspension was allowed to warm to room temperature. The reaction was diluted with CH_2Cl_2 and filtered through a pad of silica gel and washed with CH_2Cl_2 and Et_2O. The resulting residue was purified by flash column chromatography on silica gel, 10-15% ethyl acetate/hexanes, yielding 33.1 mg (61%) of **18** as a light tan solid. R_f = 0.40 (25% ethyl acetate/hexanes).

Enantiomeric excess determined by HPLC on a Chiralcel AD-H column (20% IIPA/Hexanes, 1mL/min).

HPLC Trace of racemic **5**:

Data File C:\HPCHEM\2\DATA\ACHAN\AC7-0230.D Sample Name: AC7-023

AC7-037 racemic phenyl

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Acq. Operator   : mmb
                                                 Inj Volume : 5 µl
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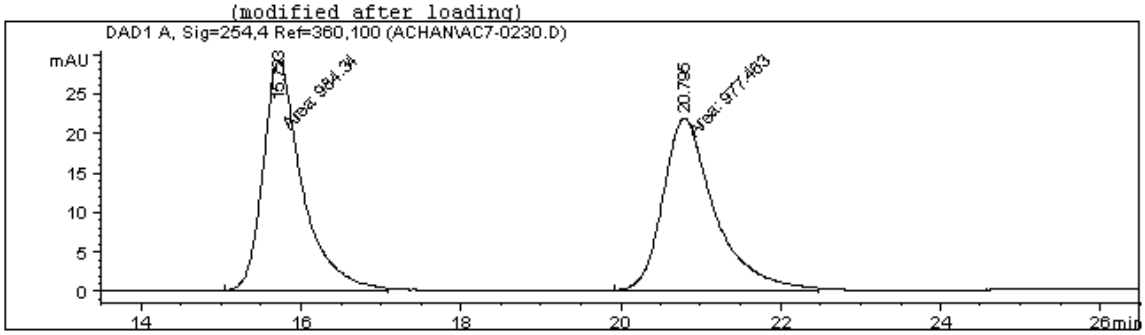


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Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals :                  1961.80359   50.75082

 Results obtained with enhanced integrator!
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HPLC Trace of enantioenriched **18**:

Data File C:\HPCHEM\2\DATA\ACHAN\AC7-2360.D Sample Name: AC7-236-1

AC7-236 chiral phenyl

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                                                Inj Volume : 5 µl
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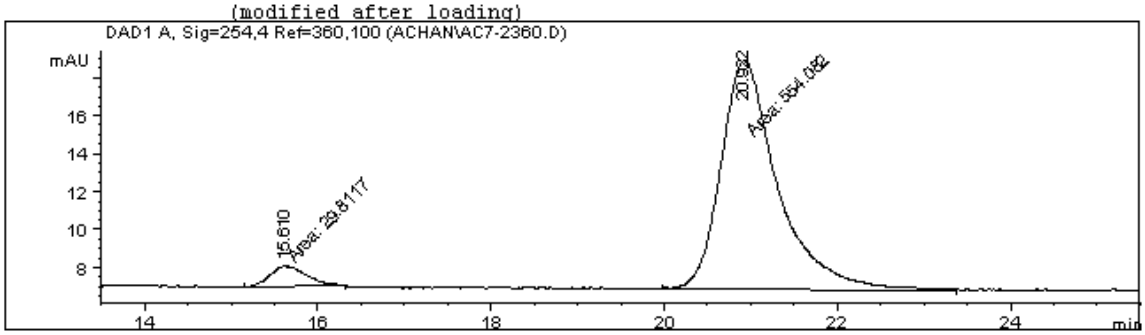


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals :                   583.89388   13.11430

 Results obtained with enhanced integrator!
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                          *** End of Report ***
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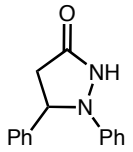
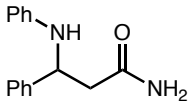
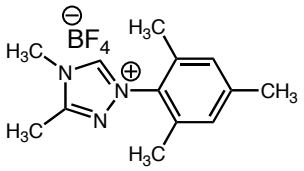
Procedure for synthesis of β-amino acid derivatives:



1,5-Diphenylpyrazolidin-3-one (19): Into a flame-dried 25 mL round-bottom flask equipped with a stir bar was added the 2-benzoyl-1,5-diphenylpyrazolidin-3-one (**5**) (100 mg, 0.292 mmol) and dissolved in THF/MeOH (3 mL, 1:2, 0.05 M). It was purged with N_2 and into it was added $Sm(OTf)_3$ (17.5 mg, 0.029 mmol). The reaction mixture was allowed to stir at room temperature under a positive pressure of N_2. After 1 h, the solvent was removed in vacuo and the residue was purified via flash chromatography, 25-40% ethyl acetate/hexanes, yielding 52 mg (75%) of **19** as a white solid. R_f = 0.23 (40% ethyl acetate/hexanes); Mp: 154-156 °C; IR (film) 3173, 3063, 2853, 1693, 1593, 1452, 1209, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H); 7.48 (d, *J* = 7.81 Hz, 2H); 7.42 (t, *J* = 7.3 Hz, 2H); 7.36-7.29 (m, 3H); 7.06 (d, *J* = 8.3 Hz, 3H); 4.94 (dd, *J* = 8.8, 2.9 Hz, 1H); 3.29 (dd, *J* = 16.6, 9.2 Hz, 1H); 2.53 (dd, *J* = 16.6, 2.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 151.4, 141.6, 129.5, 129.2, 128.2, 126.2, 123.2, 116.5, 70.1, 38.0; LRMS (electrospray): Mass calculated for $C_{15}H_{15}N_2O$ $[M+H]^+$, 239 Found 239.



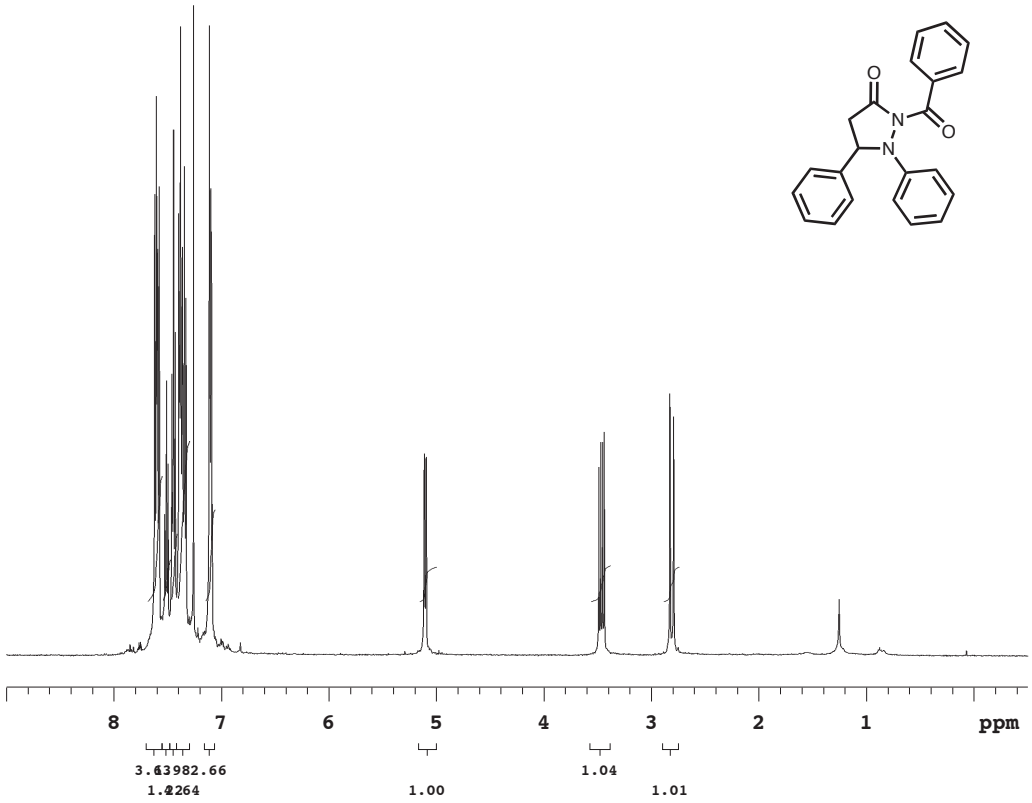
3-Phenyl-3-(phenylamino)propanamide (20): Into a flame-dried 25 mL round-bottom flask equipped with a stirbar was added 1,5-diphenylpyrazolidin-3-one (**19**) (43.5 mg, 0.183 mmol) and dissolved in EtOH (3.65 mL, 0.05 M). Into it was added a slurry of Raney 2800 nickel (approx. 325 mg, 5.5 mmol, previously washed 2 times with EtOH) and the reaction was allowed to stir at room temperature under an atmosphere of H_2 via a gas-filled double balloon. After 1 h, the reaction was deemed complete (as determined by thin layer chromatography) and it was filtered through a pad of Celite with EtOH. Solvent was removed and the residue was purified via flash chromatography, 50-90% ethyl acetate/hexane, yielding 42 mg (96 %) of **20** as a white solid. R_f = 0.21 (50% ethyl acetate/hexanes); Mp: 122-124 °C; IR (film) 3453, 3350, 3189, 3051, 2924, 1666, 1602, 1503, 1400, 748, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.3 Hz, 2H); 7.33-7.31 (m, 2H); 7.20 (d, *J* = 7.3 Hz, 1H); 7.10 (t, *J* = 7.3 Hz, 2H); 6.68 (t, *J* = 7.3 Hz, 1H); 6.53 (d, *J* = 7.8 Hz, 2H); 5.60 (s, b, 1H); 5.35 (s, br, 1H); 4.84 (s, br, 1H); 4.79 (t, *J* = 5.9 Hz, 1H); 2.75-2.66 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 146.9, 142.5, 129.3, 129.0, 127.6, 126.4, 118.1, 114.1, 55.5, 44.2; LRMS (electrospray): Mass calculated for $C_{15}H_{17}N_2O$ $[M + H]^+$, 241, Found 241.

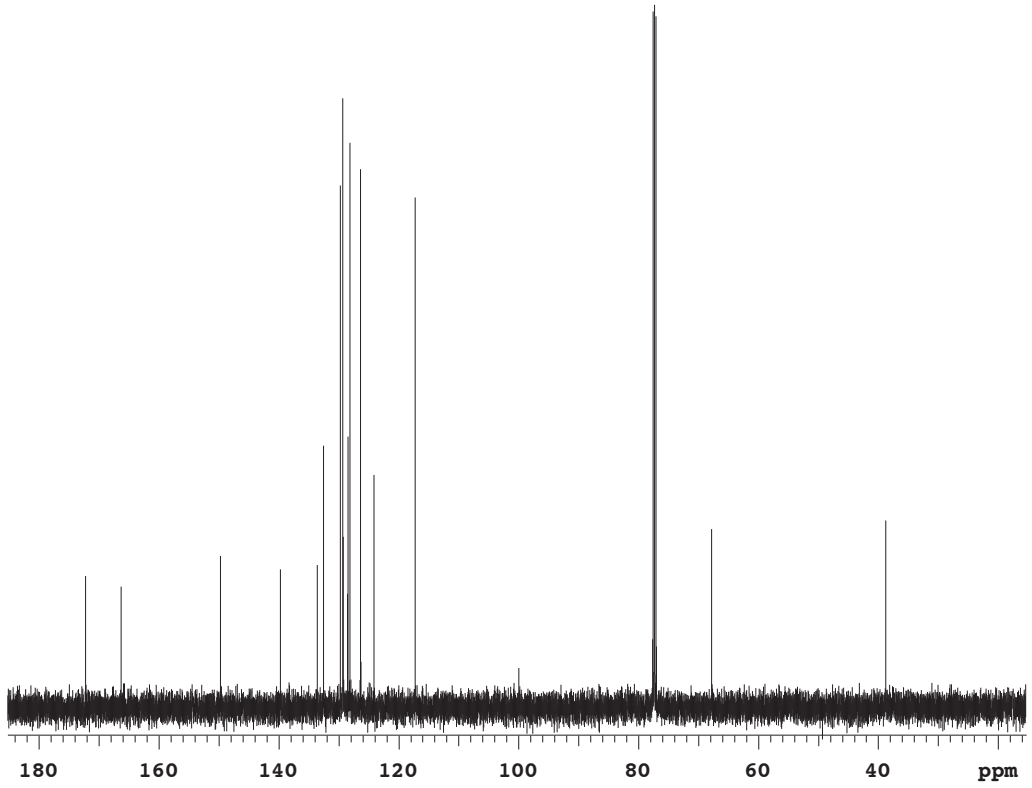


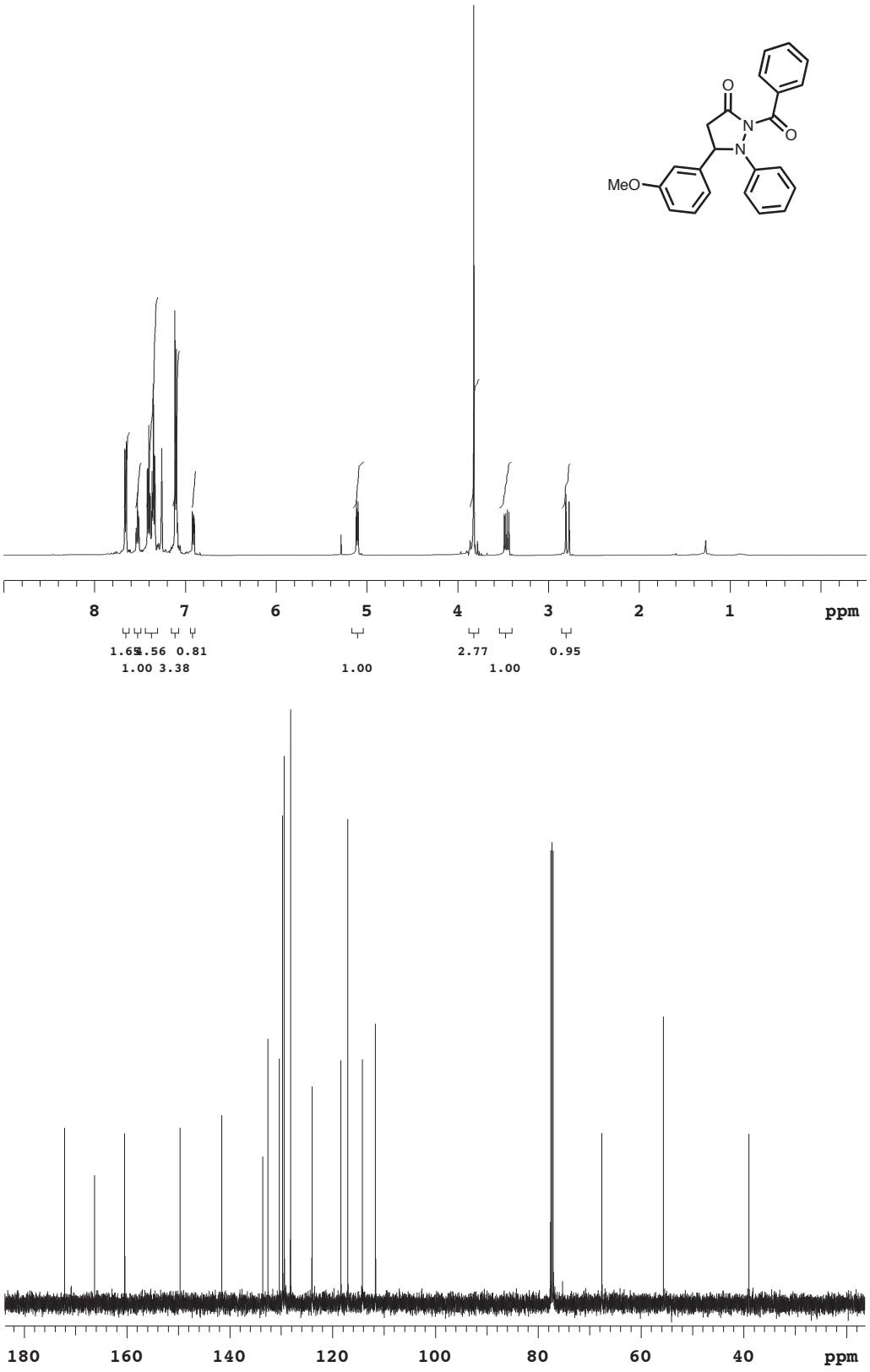
***N*2-Mesityl-*N*4-methyl-5-methyltriazolium tetrafluoroborate** (**D**): Procedure began with *N*-methyl acetamide and is analogous to the procedure reported by Rovis and coworkers.[6] Purified with 50-100% ethyl acetate/hexane, yielding 950 mg (46 %) of **D** as a light yellow solid. R_f = 0.25 (100% ethyl acetate); Mp: 130-132 °C; IR (film) 3107, 2972, 1597, 1456, 1062 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.51 (s, 1H); 6.97 (s, 2H); 4.03 (s, 3H); 2.67 (s, 3H); 2.64 (s, 3H); 2.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 144.9, 141.9, 135.3, 131.2, 129.8, 33.7, 21.4, 17.3, 10.3; LRMS (electrospray): Mass calculated for $C_{13}H_{18}BF_4N_3$ $[M - BF_4]^+$, 216. Found 216.

6. Kerr, M.S.; Alaniz, J.R.; Rovis, T. *J. Org. Chem.* **2005**, *70*. 5725-5728.

Select NMR Spectra:



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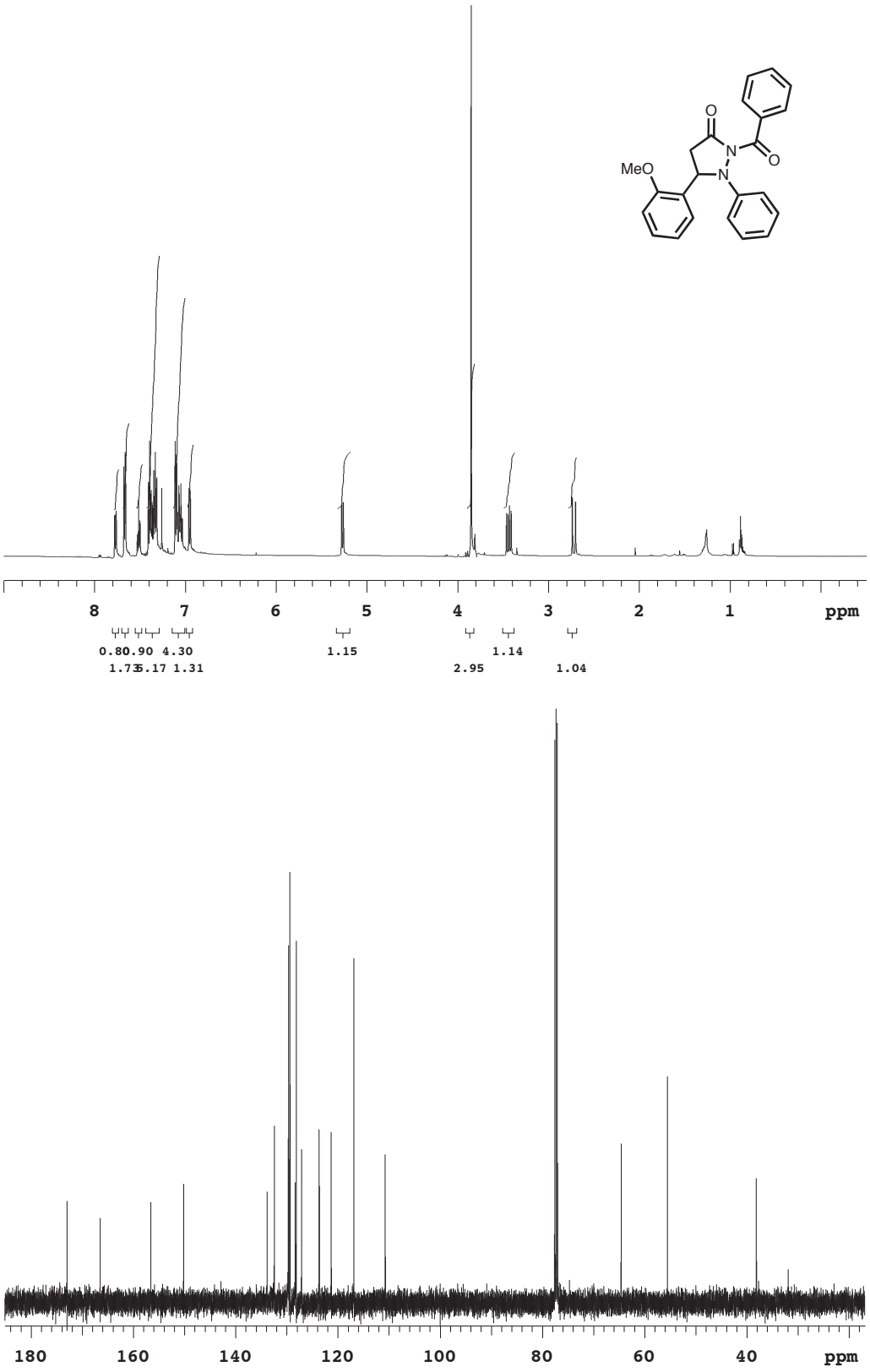
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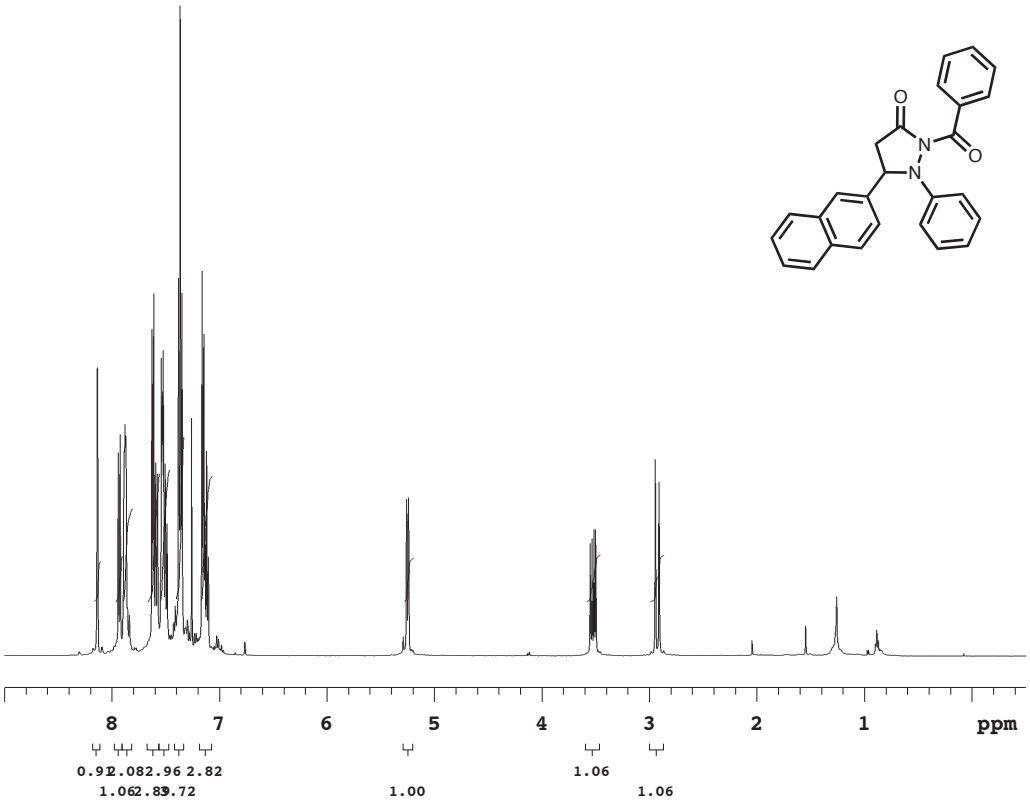
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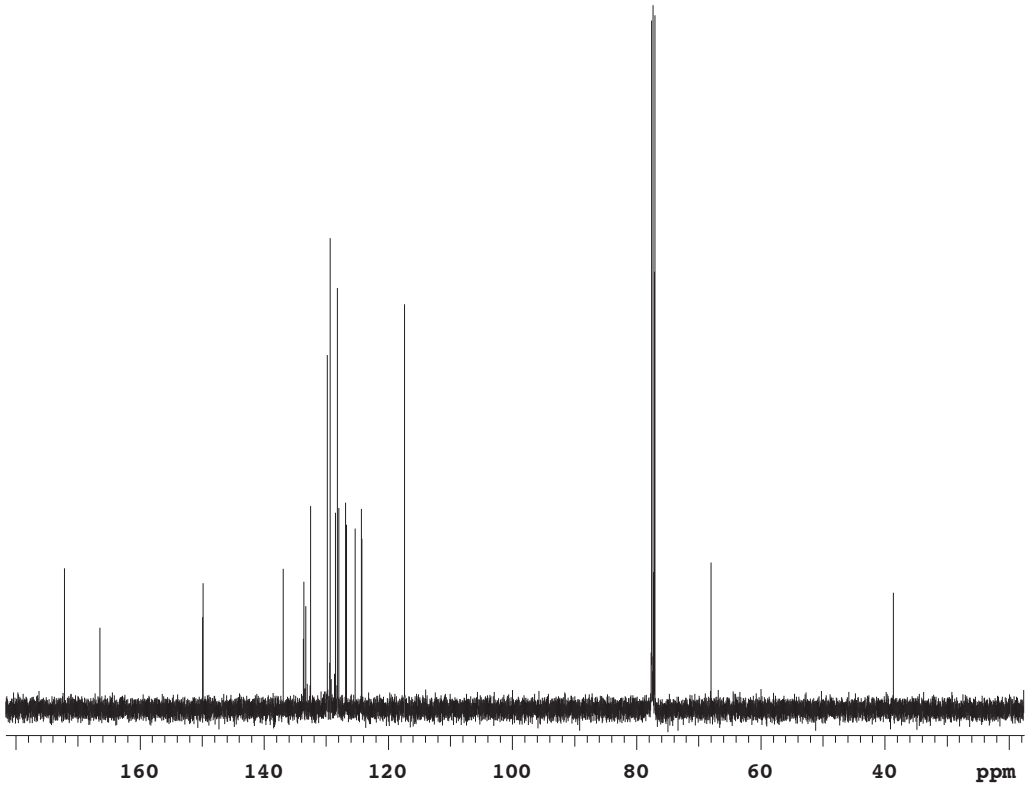
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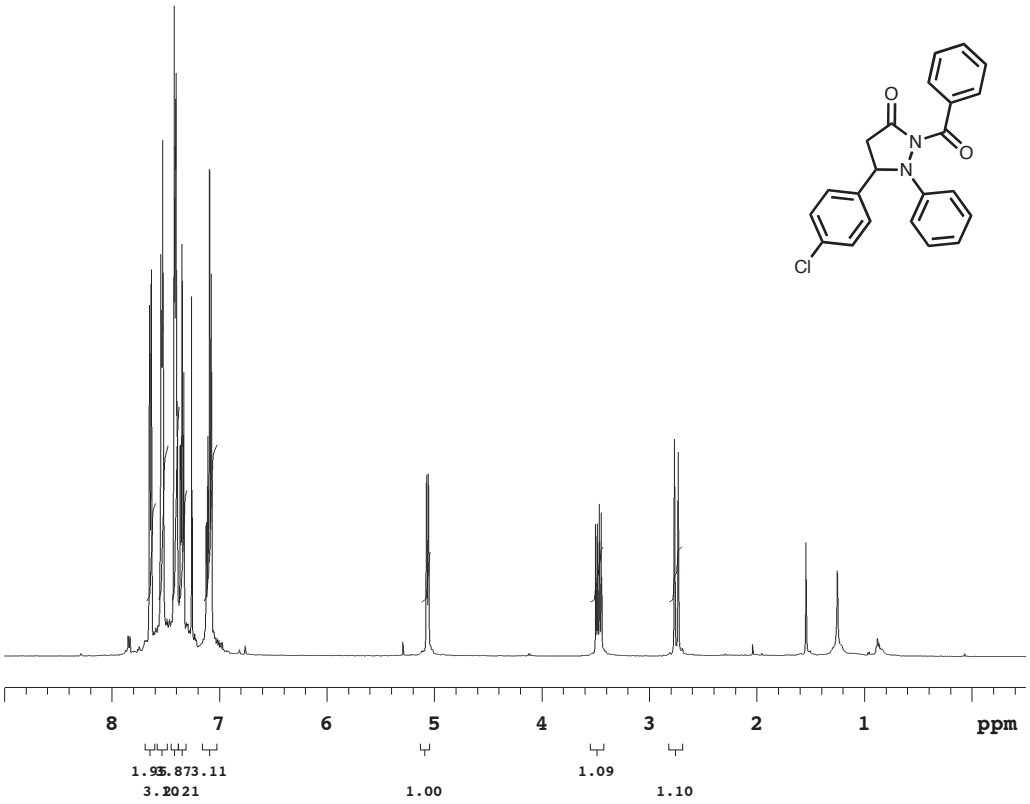
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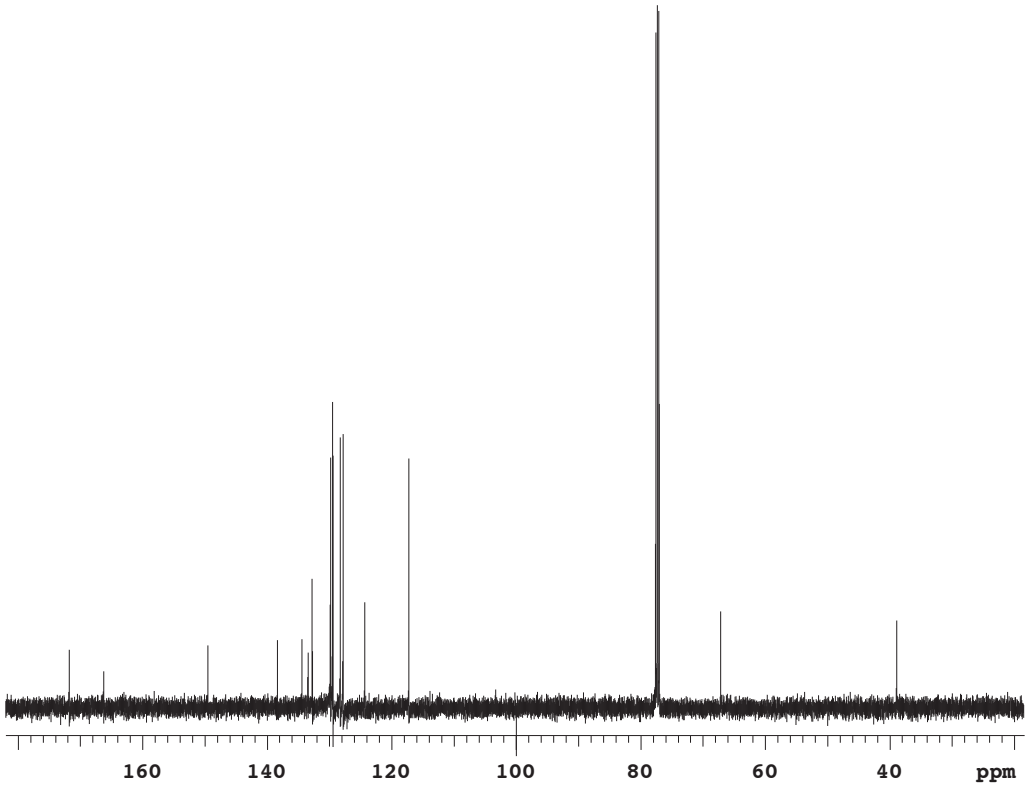
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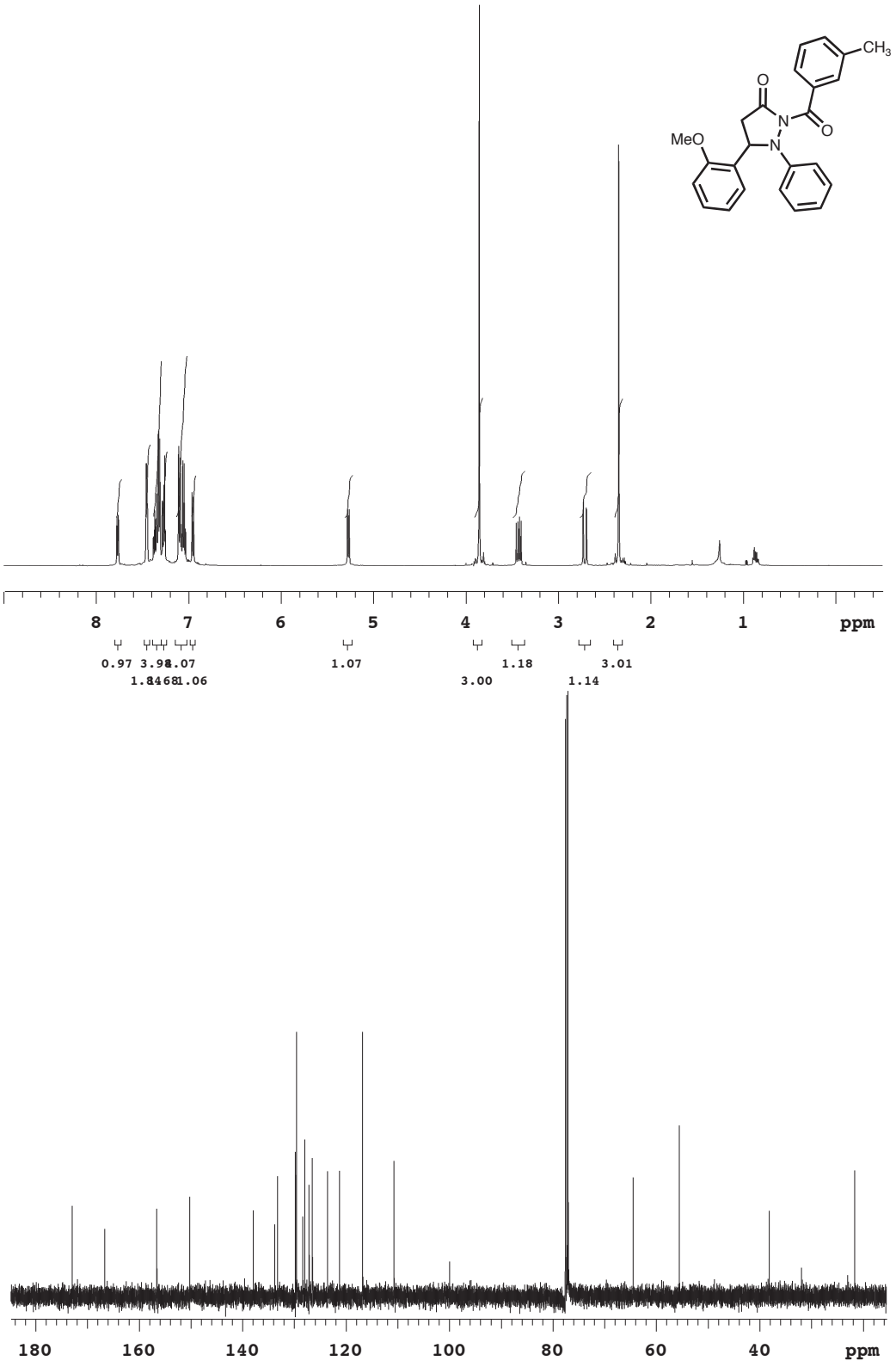
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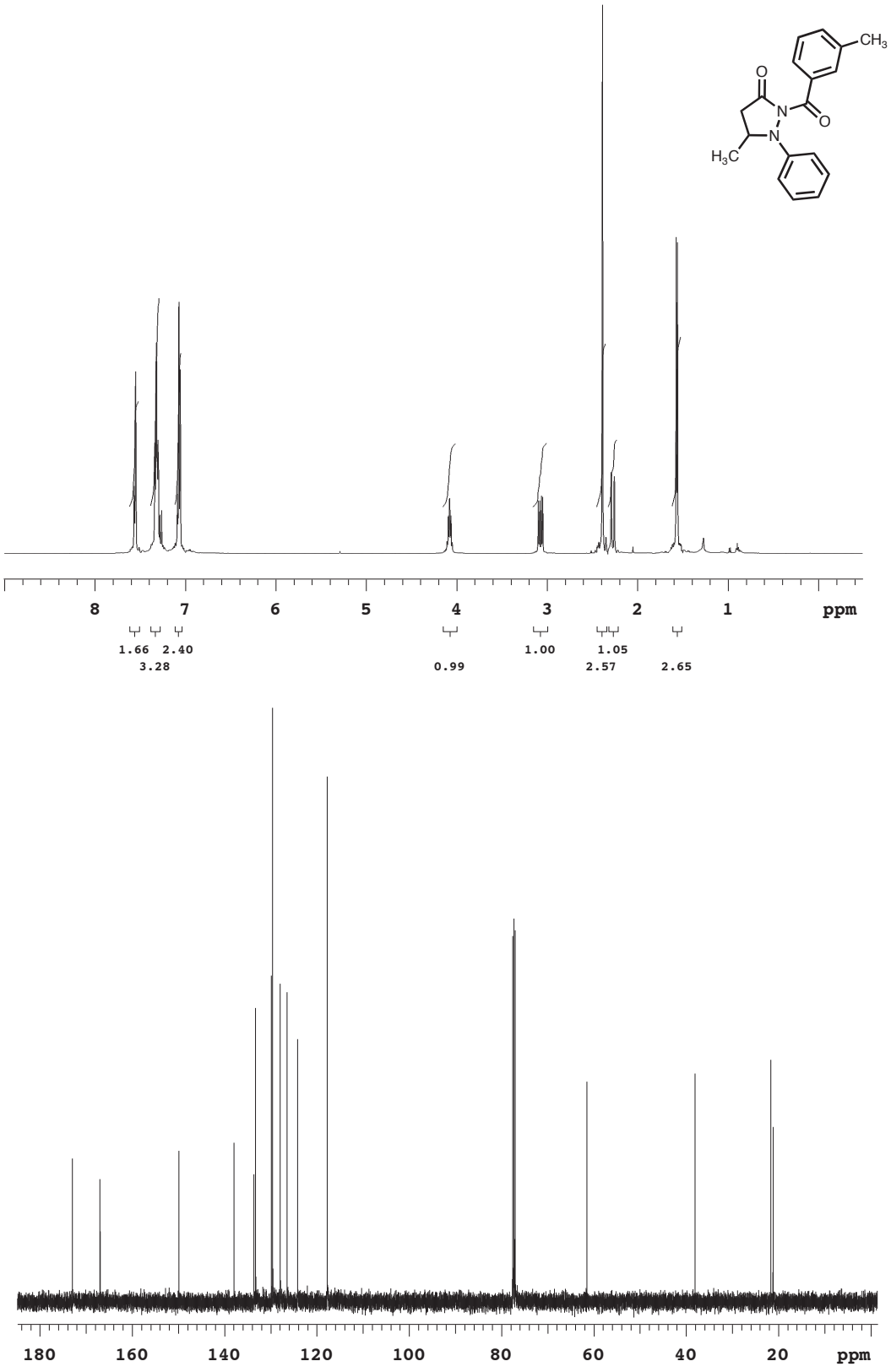
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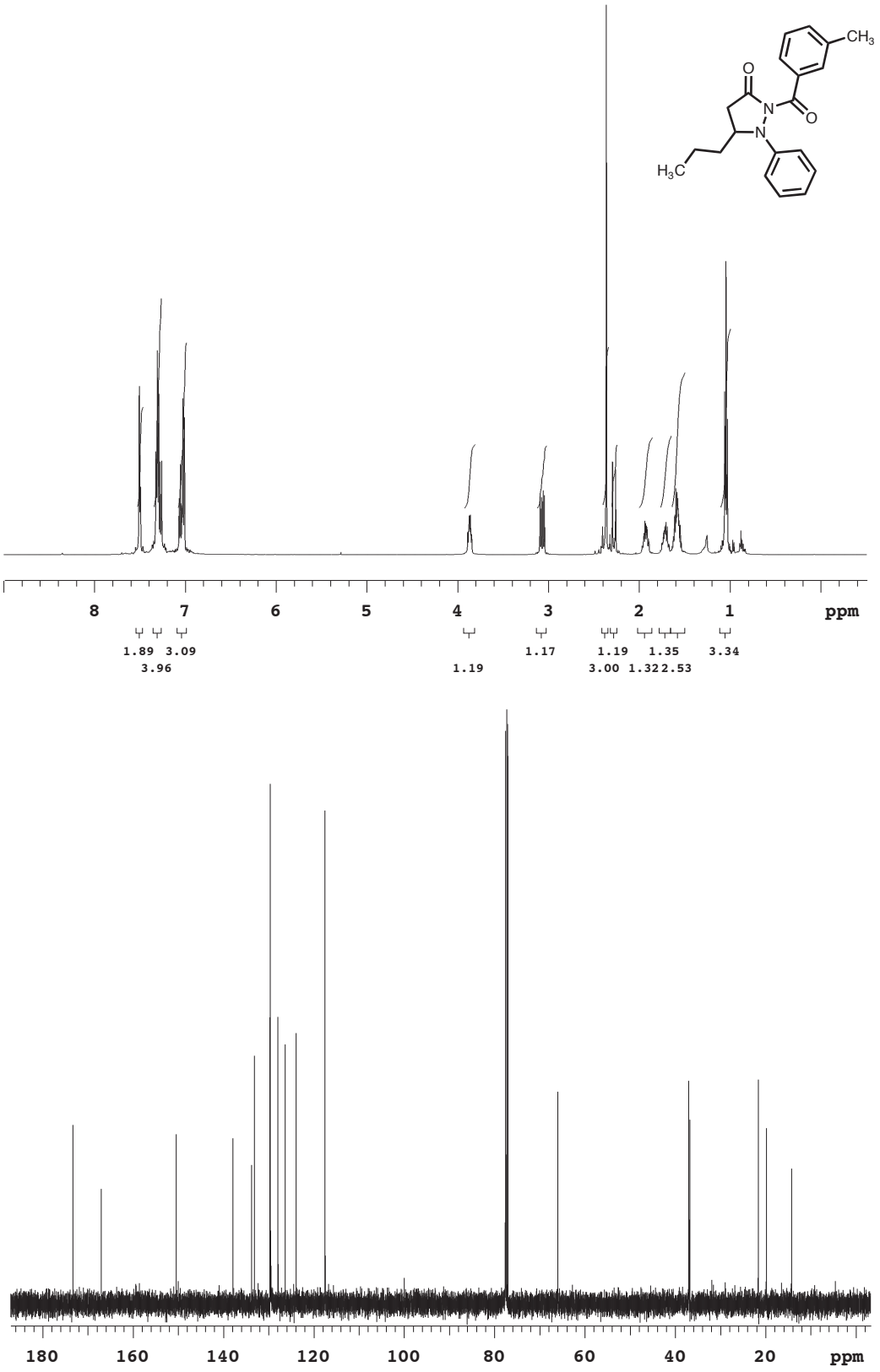
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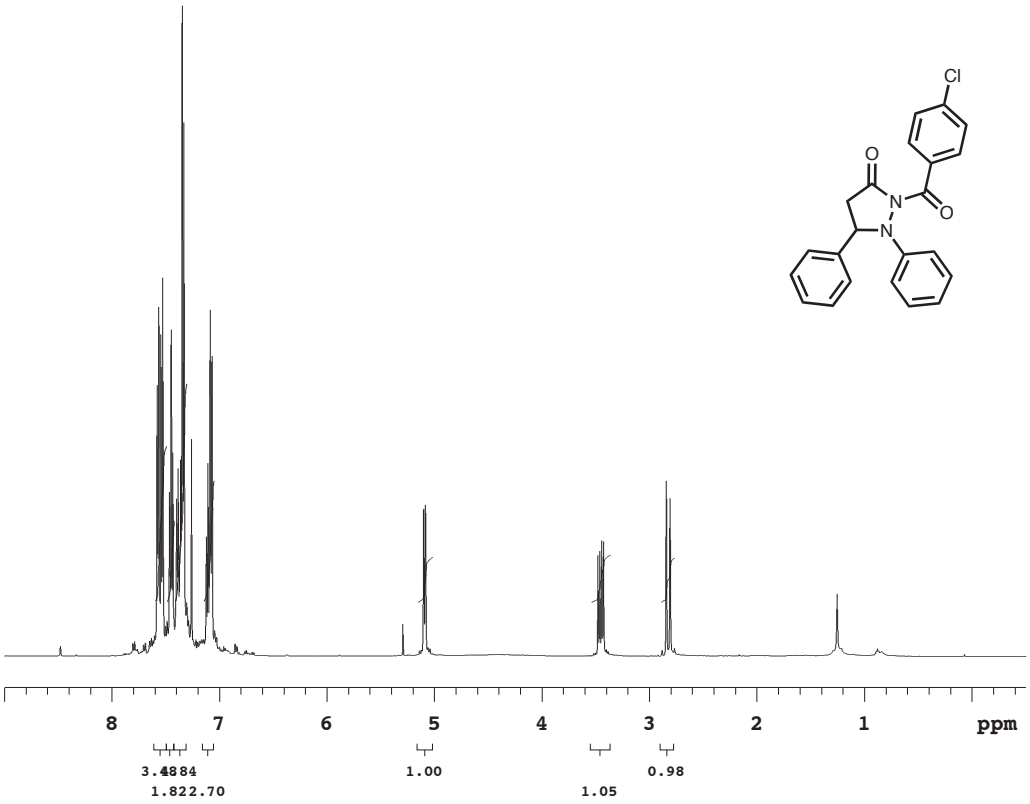
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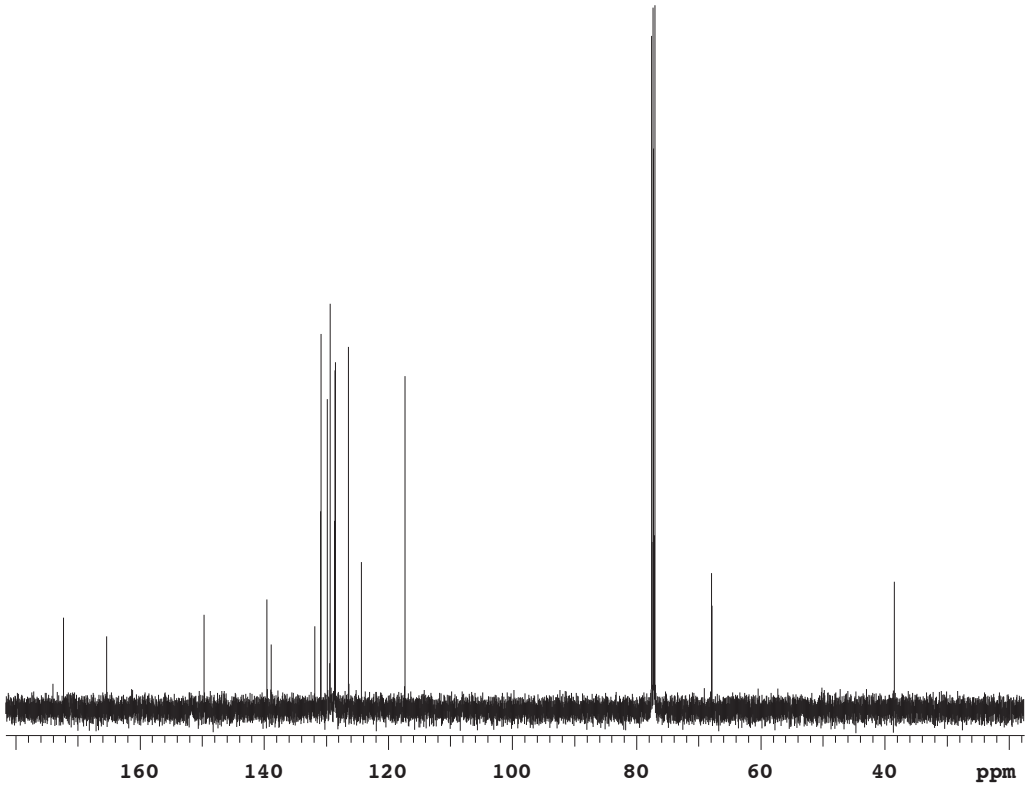
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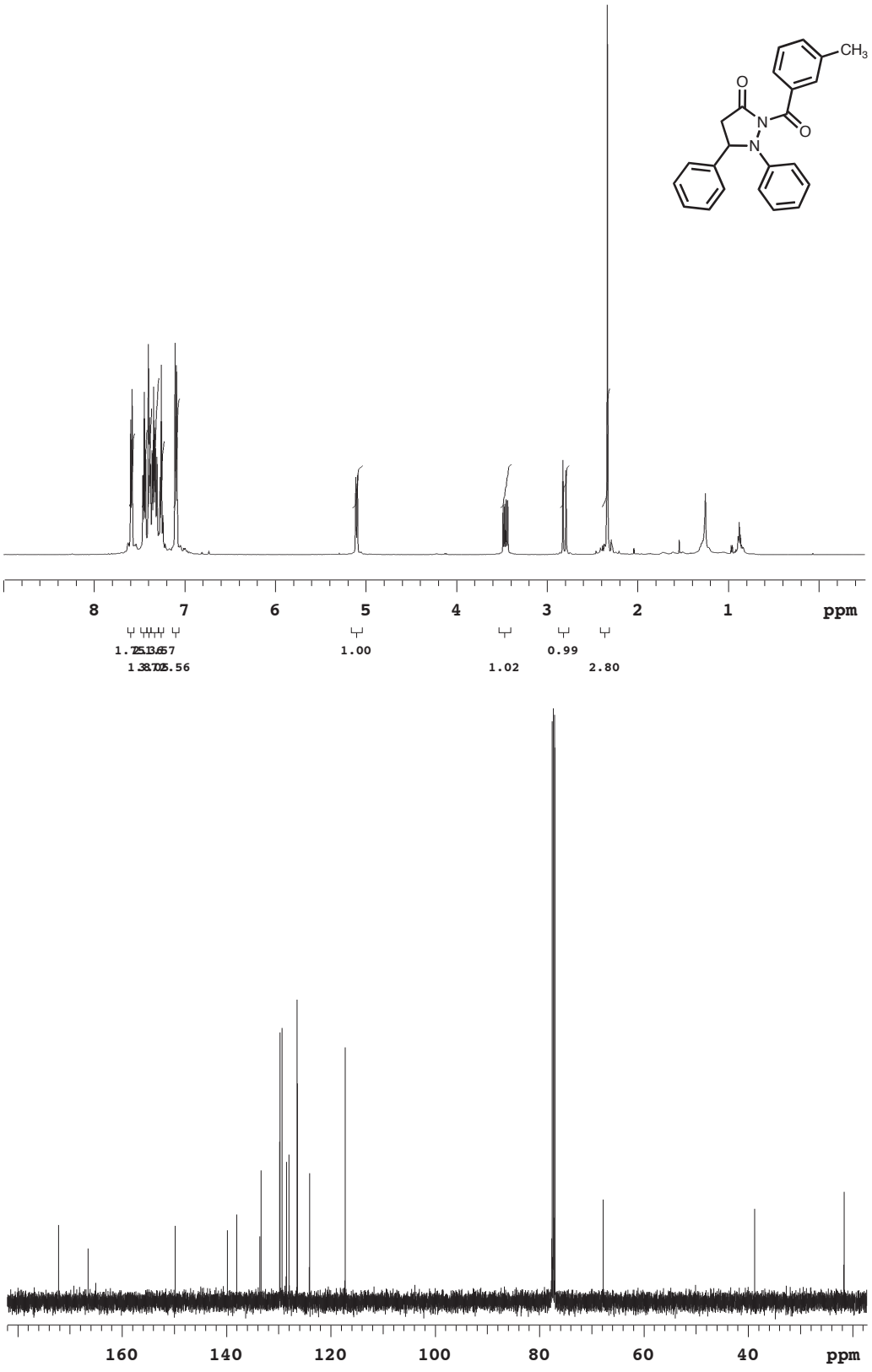
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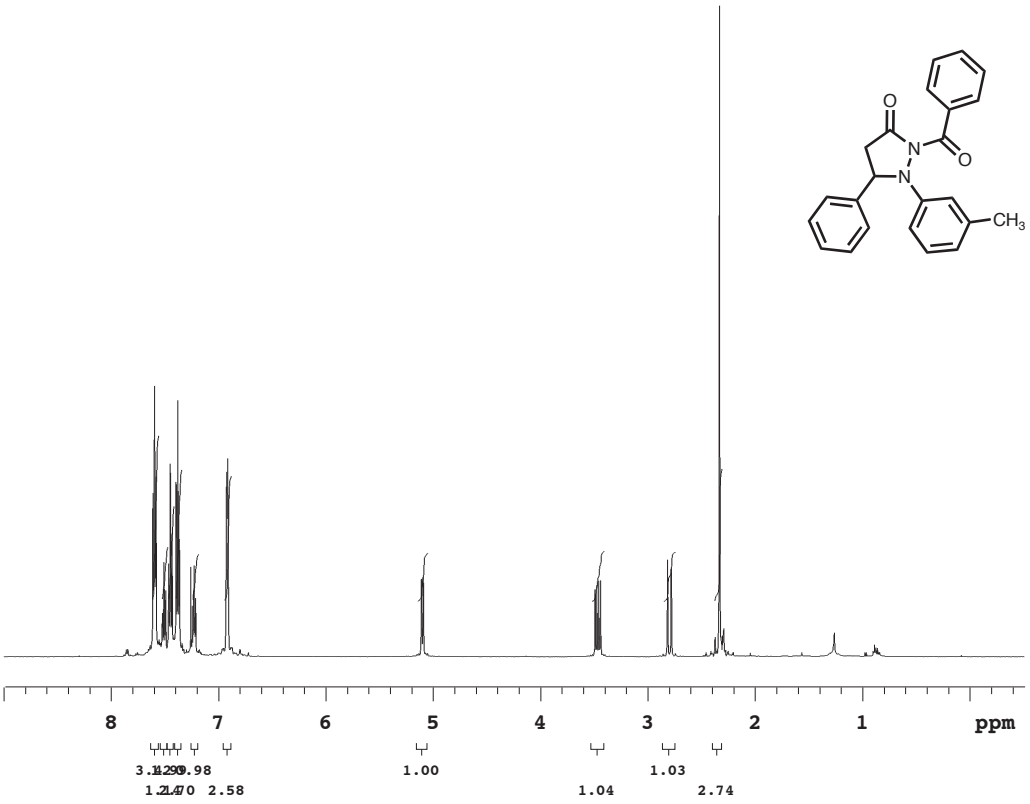
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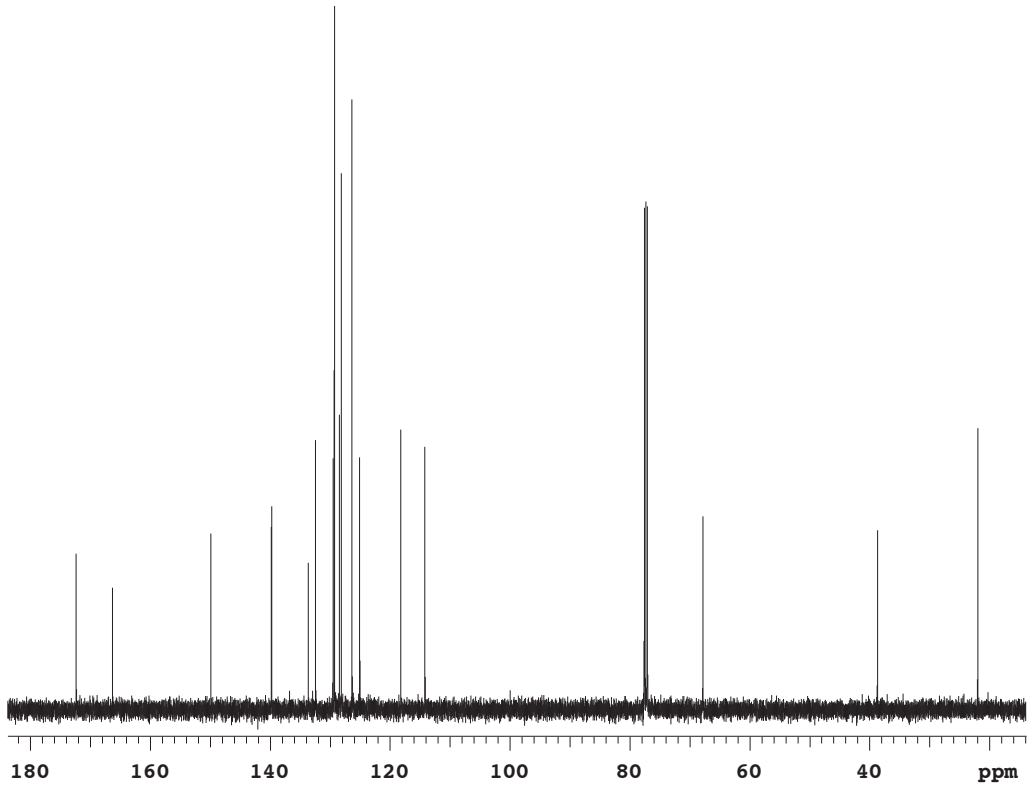
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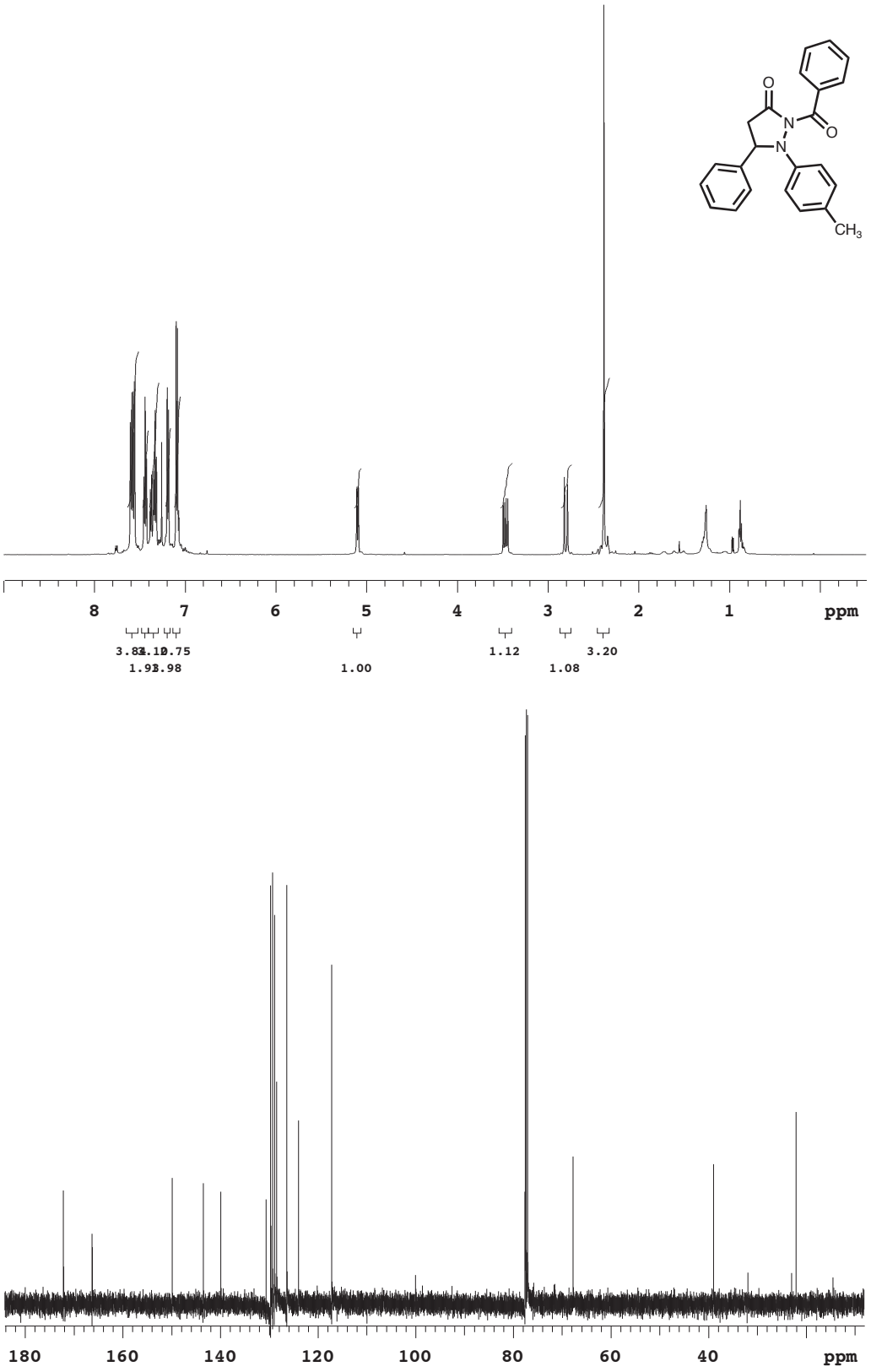
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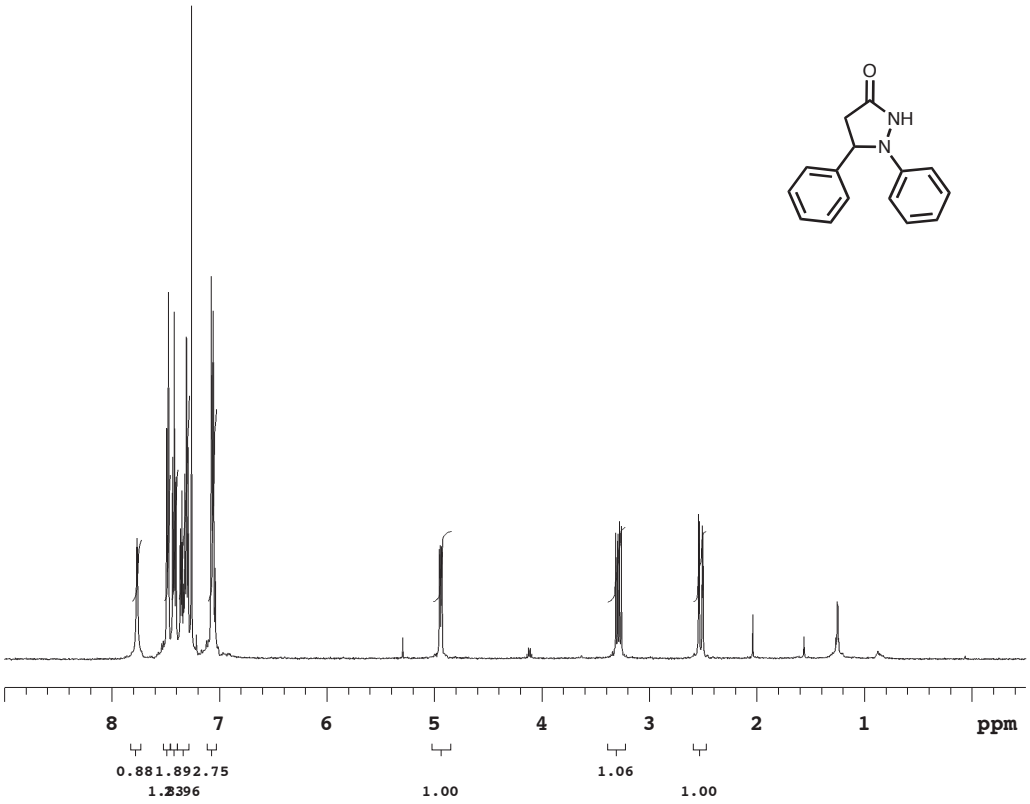
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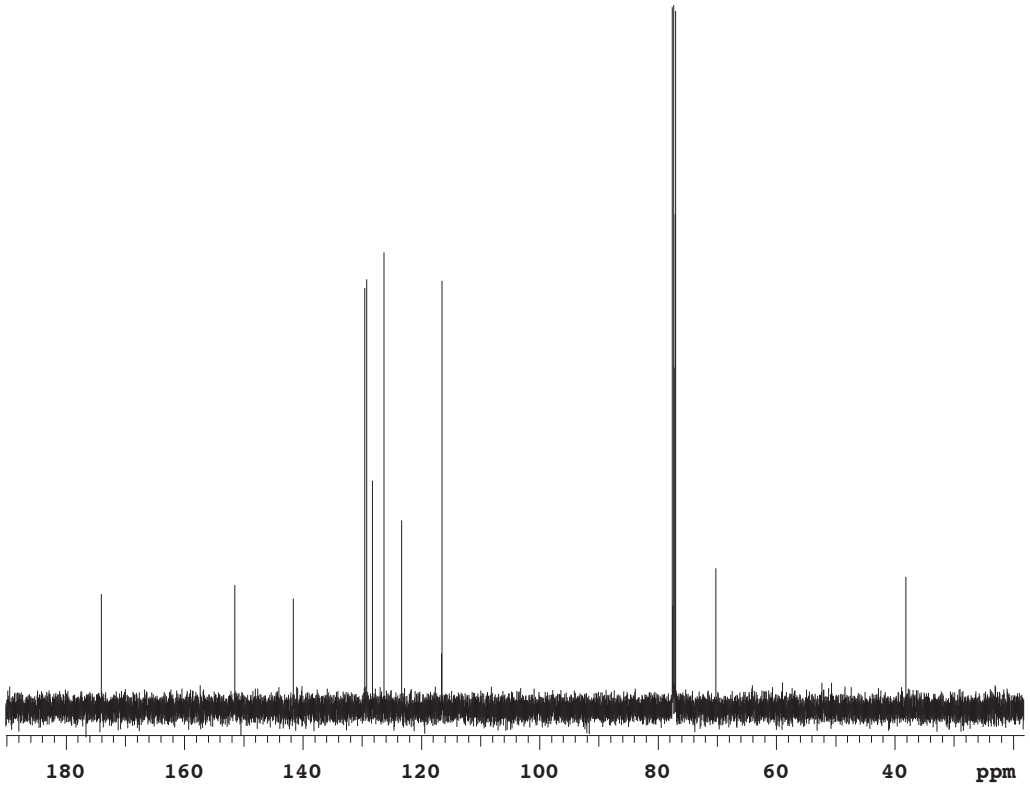
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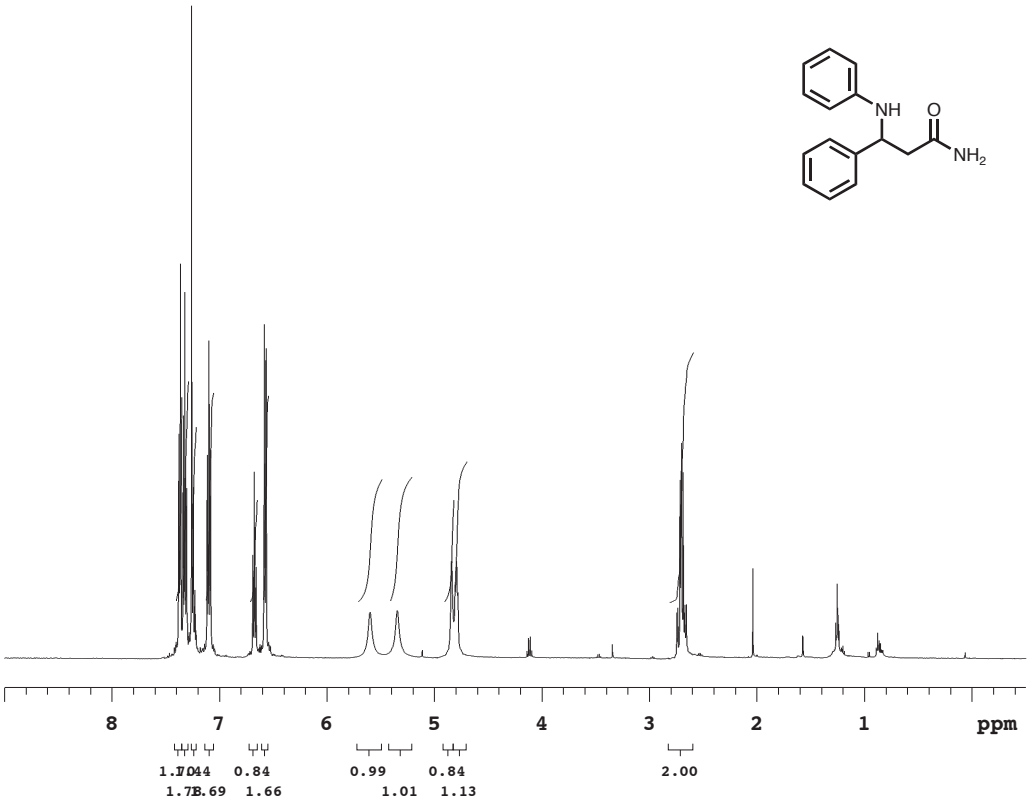
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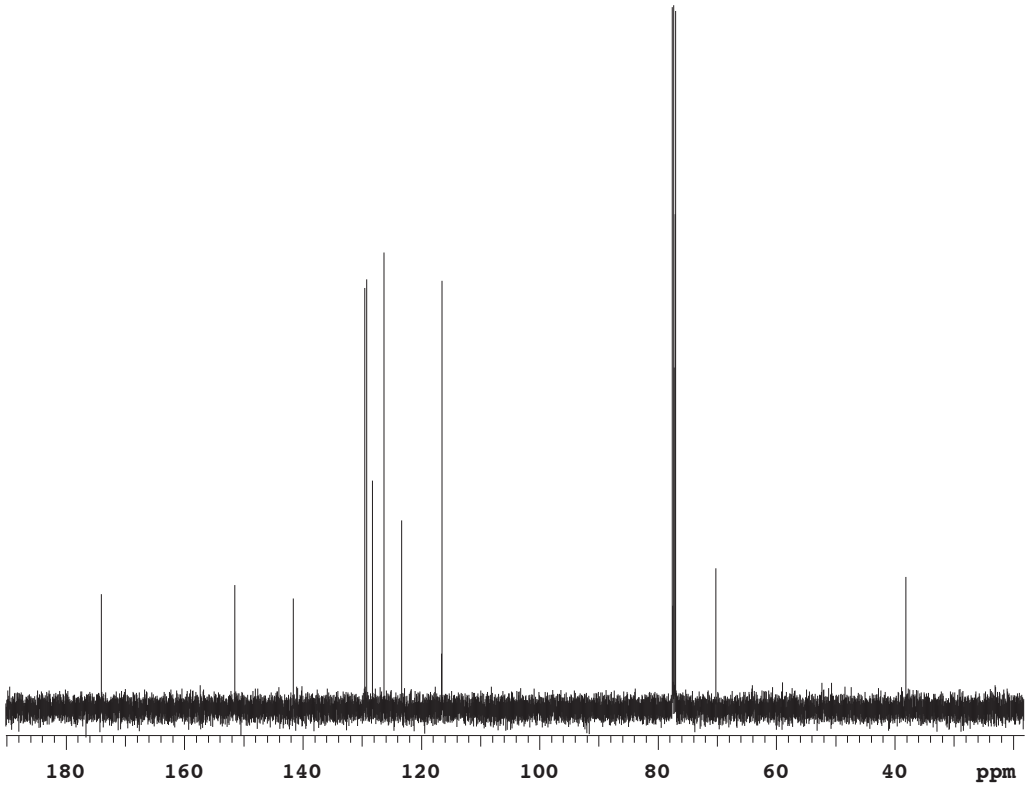
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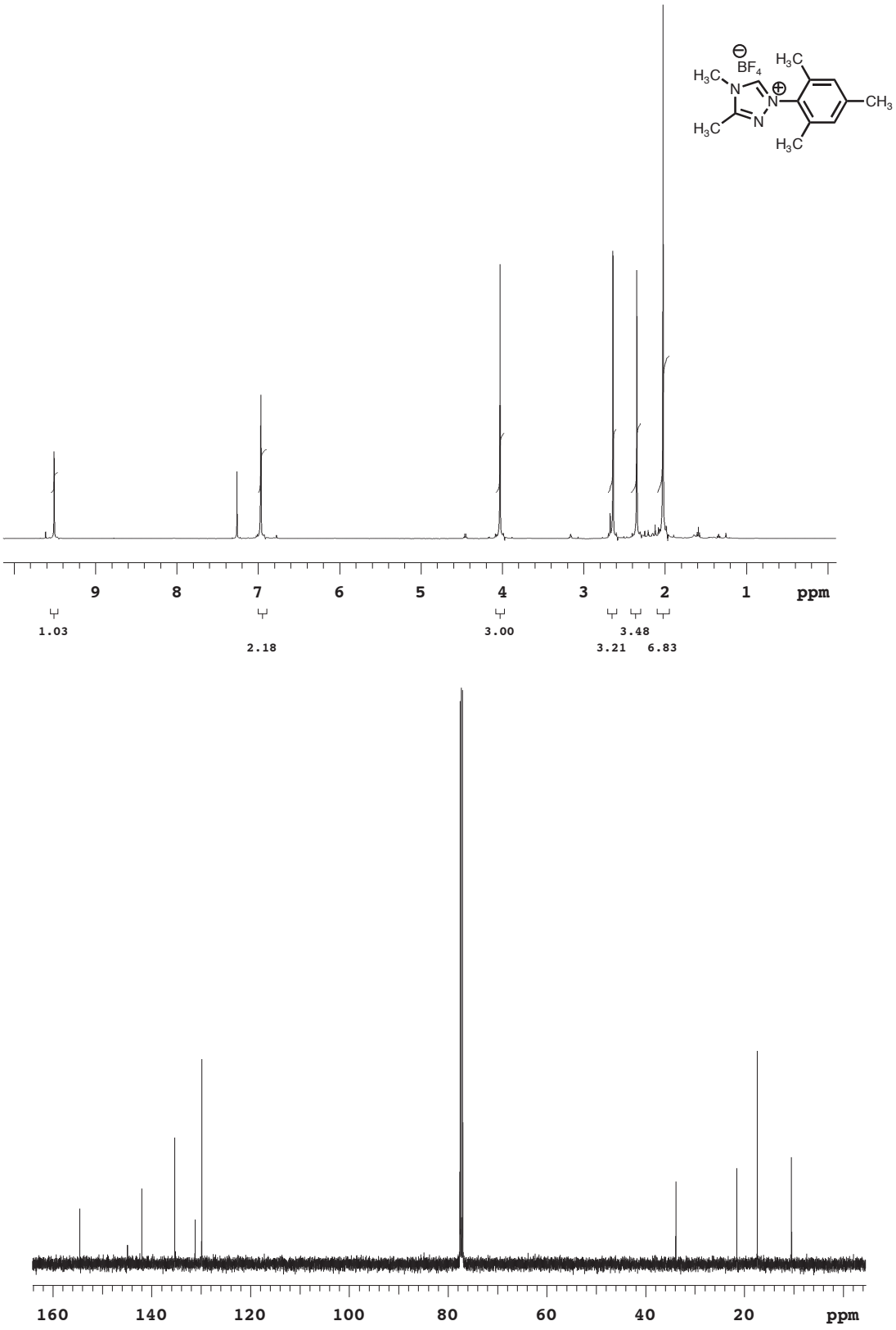
BF4
H3C
N
N
H3C
H3C
H3C
CH3
9
8
7
6
5
4
3
2
1
ppm
1.03
2.18
3.00
3.21
3.48
6.83
160
140
120
100
80
60
40
20
ppm