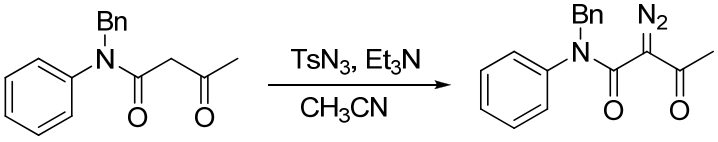
1. General Information

All reactions involving air- and moisture-sensitive reagents were carried out under a nitrogen atmosphere. Toluene, DMF, 1, 2-dichloroethane, DMSO, 1, 4- dioxane and CH_3CN were distilled from appropriate drying agents prior to use. All chemicals were purchased from Aldrich and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230~400 mesh) was used for column chromatography. IR spectra were recorded with an FT-IR spectrometer as KBr plates or as thin films and peaks are reported in cm^{-1}. Only representative absorptions are given. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker INOVA-400 and a Bruker AC-250. NMR spectras were recorded on a 400 instrument (400 MHz for ^1H and 100 MHz for ^{13}C). Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^1H, or to chloroform δ = 77.0 for ^{13}C as internal standard. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer.

2. Preparation of Substrates

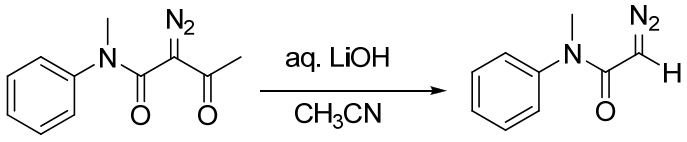
2.1 Preparation of *N*-benzyl-2-diazo-3-oxo-*N*-phenylbutanamide[1]



1 **1a**

To a solution of the keto anilides **1** (2-7 mmol) and 2 equiv of triethylamine dissolved in 10 mL of acetonitrile was added 1.1 equiv of tosyl azide. The solution was stirred for 6-24 h. When the starting keto anilides had disappeared (TLC) the solvent was evaporated (bath temperature < 35℃). The residue was dissolved in ether and washed successively with 10% NaOH solution and then H_2O. The organic fractions were then dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give **1b** as a Yellow solid.

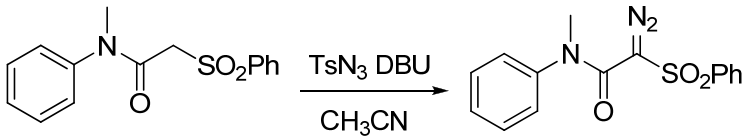
2.2 Preparation of 2-diazo-*N*-methyl-*N*-phenylacetamide[1]



1a **1pa**

The 2-diazo-N-methyl-3-oxo-N-phenylbutanamide (1.085 g, 5.0 mmol) was dissolved in CH_3CN (50 ml) in a 100 ml round bottomed flask. Aqueous lithium hydroxide (5 %, 50 ml) was added to the solution and the reaction vessel was flushed with nitrogen. The reaction was stirred at room temperature and the progress of the hydrolysis was monitored by TLC. After 7 hr, the reaction mixture was concentrated in vacuo and saturated NH_4Cl (3 x 5 ml) was added to the residue. It was then extracted with CH_2Cl_2 (3 x 5 ml). The combined organic layers were washed with water and dried over Na_2SO_4. The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography to give **1p** (0.857 g, 98 %) as a brown oil.

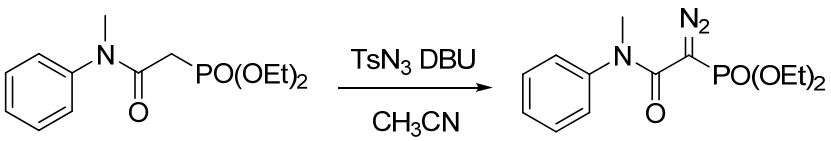
2.3 Preparation of 2-diazo-*N*-methyl-*N*-phenyl-2-(phenylsulfonyl)acetamide[2]



1u

The bromo amide and phenylsulfinic acid sodium salt (37.3 mmol) were added to N,N-dimethyl formamide (50 ml), then stirred for 3 h. After water (100 ml) was added, extraction with ethyl acetate was followed. The crude material was purified by column chromatography to give phenylsulfonyl amide. Into a solution of compound (13.91 mmol) in acetonitrile (50 ml) were added successively p-acetamido benzenesulfonyl azide (17.0mmol, 1.2 eq)and diaza(1,3)bicyclo[5.4.0]undecane (28.9 mmol., 2.1 eq) and stirred under N_2 atmosphere for 1.5 h at 0℃. At the end of the reaction, the solvent was removed under reduced pressure and the residue was dissolved in water (100 ml), extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was subjected to flash column chromatography to yield analytically pure phenylsulfonyl diazoacetamide **1u** as yellow soild.

2.4 Preparation of diethyl (1-diazo-2-methyl (phenyl) amino)-2-oxoethyl) phosphonate[2]

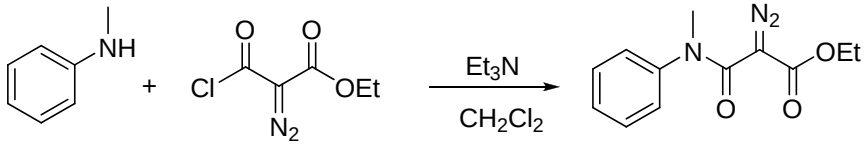


1v

Triethyl phosphate (1g, 6.0 mmol) was added under N_2 atmosphere to a stirring DCE solution (2 ml) of the bromoacetamide (1.14 g, 5.0 mmol). The mixture was refluxed until all bromoacetamide compounds had been consumed. The volatile compounds were then evaporated. The residue was purified by distillation under reduced pressure or by flash chromatography using to give 1.68 g (94.5 %) of product of phosphonate. Into a solution of phosphonate (1.34 g, 4.7 mmol) in acetonitrile (25 ml) were added successively p-acetamidobenzenesulfonyl azide (1.3g, 5.5 mmol) and diaza-(1,3)-bicyclo-[5.4.0]-undecane (1.7 ml, 11.0 mmol, 2.1 eq) and stirred under N_2 atmosphere for 1.5 hr at 0℃. At the end of the reaction, the solvent was removed under reduced pressure and the residue was dissolved in 50 ml water, extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The

residue was subjected to flash column chromatography to yield analytically pure diethyl 1-diazo-2-(methyl (phenyl) amino)-2-oxoethylphosphonate **1v** (0.295 g, 95 %) as a yellow solid.

2.5 Preparation of ethyl 2-diazo-3-(methyl(phenyl)amino)-3-oxopropanonate[4]



1pb

A solution of N-(methyl)aniline (550 mg, 2.26 mmol, 1 equiv) in CH_2Cl_2 (6.30 mL) was cooled to 0℃ under argon. Distilled Et_3N (1.49 mL, 10.60 mmol, 4.7 equiv) and ethyl 2-diazomalonyl chloride (400 mg, 2.26 mmol, 1 equiv) were successively added dropwise. After 6 hr of stirring at room temperature, a solution of HCl 1 M (2.60 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 10 ml). The combined CH_2Cl_2 phases were then dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give **1pb** (806 mg, 93%) as a yellow solid.

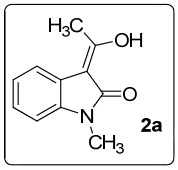
References:

1. a) Etkin, N.; Babu, S.; fooks. C.; Durst, T. *J. Org. Chem*. **1990**, *55*, 1093; b) Gauthier. D.; Dodd R.; Dauban P. *Tetrahedron*. **2009**, *65*, 8542.
2. Villalgordo, J.; Enderli, A.; Heimgartner, L. *Helvetica Chemica Acta.* **1995**, *78*, 1983-1998.
3. a) Park, C.; Nagle, A.; Yoon,C. H.; Chen, C. l.; Jung, K. W. *J. Org. Chem*. **2009**, *74*, 6231; b) Miah, S.; Alexandra M. Z.; Moody, C. *Tetrahedron*. **1996**, *52*, 2489-2514.
4. Miah, S.; Slawin, A.; Moody, C. J. *Tetrahedron*, **1996**, *52*, 2489-2514.

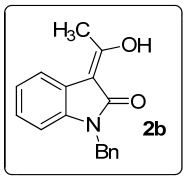
3. General procedures for Silver-Catalyzed Intramolecular Cyclization of Diazocompounds

Under a nitrogen atmosphere, Ag (OTf) (3.9 mg, 0.03 mmol, 5 mol %) was added to flame-dried round-bottomed flask. The flask was then sealed, the flask was evacuated and backfilled with argon three times. A solution of 2-diazo-N-methyl-3-oxo-N-phenylbutanamide (65.1 mg, 0.30 mmol, 1 equiv) in 3 mL 1, 4- dioxide was added using a syringe. The mixture was stirred at 100℃ until substrate disappeared as judged by TLC. After cooling to room temperature, the solution was removed in vacuo to yield a residue, which was purified by silica gel using a proper eluent to afford pure **2a** as a Purple solid (56.7 mg, 90%). The purified material was dried under oil-pump vacuum.

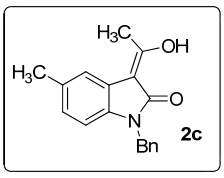
4. Characterization of the Products



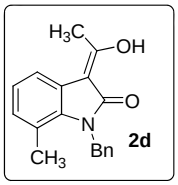
3-(1-hydroxyethylidene)-1-methylindolin-2-one (2a): Gray solid, mp 88-90 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3 H), 3.35 (s, 3 H), 6.95 (d, *J*= 7.6 Hz, 1 H), 7.08-7.13 (m, 1 H), 7.20-7.26 (m, 1 H), 7.37 (d, *J*=7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.26, 25.64, 101.76, 108.35, 119.66, 122.07, 122.21, 125.19, 138.88, 171.03, 172.85. IR (neat): 541.62, 593.32, 743.39, 893.61, 1087.88, 1162.54, 1367.44, 1462.92, 1605.34, 1655.26, 1715.33, 2125.26, 2923.90, 3282.91 cm^{-1}; MS (EI): m/z (%): 189 (100) $[M]^{+}$, 174 (74).



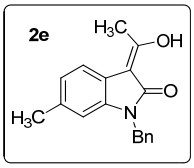
1-benzyl-3-(1-hydroxyethylidene) indolin-2-one (2b): Purple solid, mp 120-122 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.46 (s, 3 H), 5.03 (s, 2 H), 6.84 (d, *J*= 6.8 Hz, 1 H), 6.85-7.12 (m, 2 H), 7.37 (d, *J*= 6.8 Hz, 1H), 7.22-7.35 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.32, 43.22, 101.61, 109.31, 119.73, 122.10, 122.32, 125.15, 127.17, 127.55, 128.72, 136.01, 137.98, 171.04, 173.21. IR (neat): 640.39, 693.91, 732.09, 895.41, 1189.88, 1296.46, 1430.21, 1598.82, 1626.86, 1659.03, 1736.84, 2852.38, 2919.04, 3398.90 cm^{-1}; MS (EI): m/z (%): 265 (100) $[M]^{+}$, 91 (100).



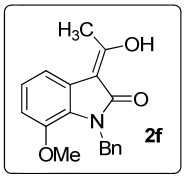
1-benzyl-3-(1-hydroxyethylidene)-5-methylindolin-2-one (2c): Purple solid, mp 106-108 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.36 (s, 3 H), 2.47 (s, 3 H), 5.01 (s, 2 H), 6.72 (d, *J*= 8.0 Hz, 1 H), 6.91 (d, *J*= 8.0 Hz, 1H), 7.18 (s, 1 H), 7.23-7.31 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.36, 21.38, 43.23, 101.66, 109.03, 120.54, 122.41, 125.67, 127.14, 127.50, 128.70, 131.52, 135.89, 136.11, 171.07, 172.93. IR (neat): 725.84, 802.31, 893.58, 1163.66, 1196.03, 1292.01, 1354.42, 1429.58, 1480.48, 1634.59, 1656.68, 2854.84, 2921.18, 3411.76 cm^{-1}; MS (EI): m/z (%): 279 (15) $[M]^{+}$, 91 (100).



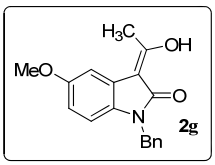
1-benzyl-3-(1-hydroxyethylidene)-7-methylindolin-2-one (2d): Purple solid, mp 152-154 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.32 (s, 3 H), 2.48 (s, 3 H), 5.32 (s, 2 H), 6.87 (d, *J*= 7.2 Hz, 1 H), 6.99 (t, *J*= 7.6 Hz, 1 H), 7.09 (d, *J*= 7.6 Hz, 2 H), 7.20-7.30 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.97, 20.51, 44.53, 101.31, 117.83, 120.25, 122.13, 123.01, 125.55, 127.13, 128.80, 129.02, 136.14, 137.87, 171.78, 173.52. IR (neat): 604.19, 730.32, 899.62, 1024.66, 1190.80, 1380.83, 1443.79, 1631.76, 1726.12, 2853.05, 2923.22, 3399.87 cm^{-1}; MS (EI): m/z (%): 279 (15) $[M]^+$, 91 (100), 43 (43).



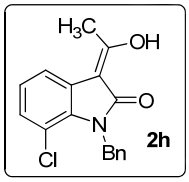
1-benzyl-3-(1-hydroxyethylidene)-6-methylindolin-2-one (2e): Purple solid, mp120-122^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.23 (s, 3 H), 2.36 (s, 3 H), 4.94 (s, 2 H), 6.59 (s, 1 H), 6.80 (d, *J*= 7.6 Hz, 1 H), 7.16-7.24 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.20, 21.70, 43.13, 101.65, 109.99, 119.52, 119.63, 122.85, 127.08, 127.49, 128.72, 135.30, 136.14, 138.29, 171.30, 172.03. IR (neat): 698.90, 806.69, 860.78, 1159.18, 1200.44, 1301.95, 1452.74, 1625.92, 1660.08, 1729.09, 2853.34, 2923.01, 3411.74 cm^{-1}; MS (EI): m/z (%): 279 (45) $[M]^+$, 91 (100).



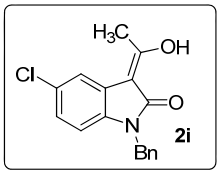
1-benzyl-3-(1-hydroxyethylidene)-7-methoxyindolin-2-one (2f): Gray solid, mp 126-128 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.48 (s, 3 H), 3.74 (s, 3 H), 5.36 (s, 2 H), 6.76 (t, *J*= 3.6 Hz, 1 H), 7.04 (d, *J*= 4.4 Hz, 2H), 7.22-7.25 (m, 1 H), 7.27-7.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.45, 45.33, 55.63, 101.86, 109.00, 112.87, 122.62, 124.02, 126.01, 126.92, 127.11, 128.29, 138.55, 145.70, 171.02, 174.08. IR (neat): 687.05, 721.21, 882.71, 1008.91, 1173.61, 1257.84, 1347.38, 1444.96, 1580.99, 1631.23, 1729.11, 2849.92, 2921.30, 3407.76 cm^{-1}; MS (EI): m/z (%): 295 (38) $[M]^+$, 91 (100).



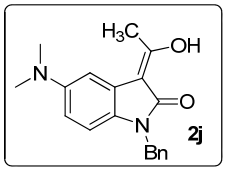
1-benzyl-3-(1-hydroxyethylidene)-5-methoxyindolin-2-one (2g): Purple solid, mp 142-144^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3 H), 3.78 (s, 3 H), 5.01 (s, 2 H), 6.63-6.66 (m, 1 H), 6.72 (d, *J*= 8.4 Hz, 1H), 6.97(d, *J*= 2.0 Hz, 1 H), 7.22-7.31 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.30, 43.29, 55.84, 101.82, 107.30, 109.47, 109.59, 123.47, 127.15, 127.53, 128.72, 132.14, 136.07, 155.65, 170.99, 173.44. IR (neat): 701.60, 771.05, 900.59, 1023.47, 1188.55, 1461.32, 1588.37, 1649.12, 1732.40, 2853.97, 2924.44, 3383.69 cm^{-1}; MS (EI): m/z (%): 295 (44) $[M]^+$, 91 (100).



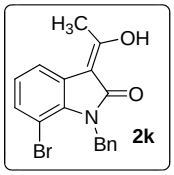
1-benzyl-7-chloro-3-(1-hydroxyethylidene) indolin-2-one (2h): Purple solid, mp 118-120 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.49 (s, 3 H), 5.50 (s, 2 H), 7.00 (t, *J*= 7.6 Hz, 1 H), 7.08 (d, *J*=8 Hz, 1H), 7.18-7.30 (m, 6 H),.^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.70, 44.46, 100.93, 116.10, 118.17, 122.88, 125.29, 126.39, 127.12, 127.36, 128.53, 133.59, 137.73, 171.63, 175.01. IR (neat): 722.53, 781.03, 870.09, 1023.91, 1178.15, 1444.71, 1599.87, 1663.73, 1732.80, 2853.42, 2922.77, 3387.71 cm^{-1}; MS (EI): m/z (%): 299 (16) $[M]^+$, 301 (5.7), 91 (100).



1-benzyl-5-chloro-3-(1-hydroxyethylidene) indolin-2-one (2i): Purple solid, mp 119-121 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3 H), 5.00 (s, 2 H), 6.72 (d, *J*= 8.4 Hz, 1 H), 7.03-7.06 (m, 1H), 7.22-7.30 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.49, 43.31, 101.01, 110.08, 119.76, 123.79, 124.77, 127.11, 127.61, 127.70, 128.69, 128.79, 135.59, 170.79, 174.61. IR (neat): 698.82, 801.99, 1028.75, 1078.89, 1184.35, 1273.65, 1312.07, 1468.82, 1601.06, 1653.25, 1721.57, 2855.19, 2924.91, 3393.10 cm^{-1}; MS (EI): m/z (%): 299 (54) $[M]^+$, 301 (18), 91 (100).

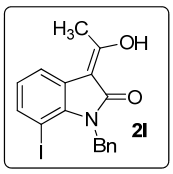


1-benzyl-5-(dimethylamino)-3-(1-hydroxyethylidene) indolin-2-one (2j): Yellow solid, mp120-122^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.46 (s, 3 H), 2.90 (s, 6 H), 5.00 (s, 2 H), 6.64-6.57(m, 1 H), 6.71 (d, *J*= 8.8 Hz, 1 H), 7.85 (d, *J*= 2.4 Hz, 1 H), 7.21-7.31 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.34, 41.89, 43.21, 61.61, 102.13, 106.46, 109.62, 110.73, 116.92，123.20, 127.15, 127.42, 130.16, 136.28, 147.38, 170.82, 172.60. IR (neat): 697.22, 729.74, 914.91, 939.97, 1198.03, 1311.77, 1646.61, 1717.48, 2852.98, 2920.71, 3405.58 cm^{-1}; MS (EI): m/z (%): 308 (16) $[M]^+$, 135(100).

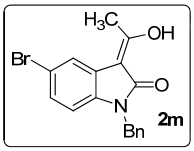


1-benzyl-7-bromo-3-(1-hydroxyethylidene) indolin-2-one (2k): Purple solid, mp 154-156 ^{o}C.

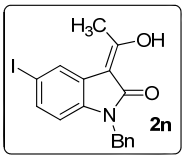
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.49 (s, 3 H), 5.55 (s, 2 H), 6.94 (t, *J*= 8.4 Hz, 1 H), 7.16 (d, *J*=7.2 Hz, 2H), 7.20-7.30 (m, 4 H), 7.34 (d, *J*=7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.75, 44.10, 100.78, 103.18, 118.70, 123.25, 125.58, 126.24, 127.05, 128.51, 130.73, 134.91, 137.65, 171.79, 175.02. IR (neat): 696.04, 725.28, 760.39, 869.77, 1016.16, 1178.77, 1226.50, 1303.55, 1441.28, 1651.97, 1723.48, 2853.16, 2923.20, 3399.59 cm^{-1}; MS (EI): m/z (%): 343 (13) $[M]^+$, 345 (13), 91 (100).



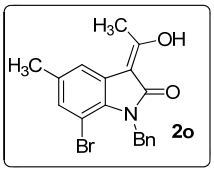
(1-benzyl-3-(1-hydroxyethylidene)-7-iodoindolin-2-one (2l): Purple solid, mp 150-152 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.49 (s, 3 H), 5.59 (s, 2 H), 6.80 (t, *J*= 8.0 Hz, 1 H), 7.11 (d, *J*=7.6 Hz, 2 H), 7.21-7.30 (m, 3 H), 7.38 (d, *J*=7.6 Hz, 1 H), 7.58 (d, *J*=8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.75, 43.34, 100.51, 119.46, 123.72, 125.37, 126.14, 126.98, 128.52, 137.41, 137.70, 137.87, 172.01, 174.75. IR (neat): 722.22, 867.52, 1017.76, 1166.28, 1431.70, 1660.23, 1736.57, 2853.57, 2921.86, 3389.69 cm^{-1}. MS (EI): m/z (%): 391 (7) $[M]^+$, 91 (100), 43(64).



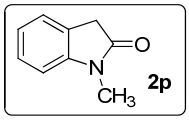
1-benzyl-5-bromo-3-(1-hydroxyethylidene) indolin-2-one (2m): Gray solid, mp 138-140 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.46 (s, 3 H), 5.01 (s, 2 H), 6.69 (d, *J*= 8.4 Hz, 1 H), 7.19-7.45 (m, 6H), 7.46 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.52, 43.31, 100.91, 110.61, 115.07, 122.55, 124.25, 127.77, 127.67, 127.73, 128.81, 135.55, 136.70, 170.72, 171.68. IR (neat): 694.74, 796.80, 1025.35, 1072.06, 1174.56, 1269.19, 1305.29, 1459.32, 1585.68, 1647.37, 1722.36, 2852.74, 2921.37, 3414.80 cm^{-1}; MS (EI): m/z (%): 343 (35) $[M]^+$, 345 (40), 91 (100).



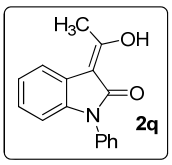
1-benzyl-3-(1-hydroxyethylidene)-5-iodoindolin-2-one (2n): Gray solid, mp 148-150 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.49 (s, 3 H), 4.93 (s, 2 H), 6.80 (d, *J*= 8.4 Hz, 2 H), 7.20-7.29 (m, 4 H), 7.66 (d, *J*= 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.62, 43.30, 85.21, 100.68, 111.25, 124.76, 127.15, 127.77, 128.27, 128.85, 133.69, 135.58, 137.37, 170.55, 174.65. IR (neat): 695.90, 874.58, 1022.43, 1073.02, 1185.07, 1268.42, 1312.41, 1462.95, 1596.48, 1630.03, 1652.54, 1731.84, 2852.64, 2922.63, 3404.06 cm^{-1}; MS (EI): m/z (%): 391 (14) $[M]^+$, 91 (100).



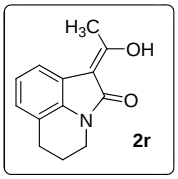
1-benzyl-7-bromo-3-(1-hydroxyethylidene)-5-methylindolin-2-one (2o): Gray solid, mp 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.33 (s, 3 H), 2.48 (s, 3 H), 5.50 (s, 2 H), 7.09(s, 1 H), 7.14 (d, *J*= 8.4 Hz, 3 H), 7.19-7.29 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.74, 20.80, 43.96, 100.77, 102.72, 119.59, 125.46, 126.19, 126.97, 128.47, 130.99, 132.71, 133.01, 137.67, 171.77, 174.63. IR (neat): 718.19, 838.45, 869.59, 1168.37, 1304.67, 1441.84, 1661.37, 1717.89, 2122.88, 2919.88, 3413.37 cm^{-1}. MS (EI): m/z (%): 357 (17) $[M]^+$, 359 (17), 91(100), 43(22).



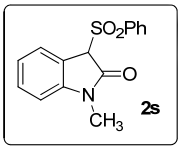
1-methylindolin-2-one (2p): Gray solid, mp 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.20 (s, 3 H), 3.50 (s, 2 H), 6.81 (d, *J*= 7.6 Hz, 1 H), 7.01-7.05 (m, 1 H), 7.22-7.30 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.06, 35.56, 107.97, 122.24, 124.21, 124.43, 127.80, 145.16, 174.97. IR (neat): 651.51, 752.09, 945.61, 1088.32, 1263.16, 1343.50, 1369.20, 1464.78, 1495.61, 1612.62, 1705.14, 2854.70, 2921.23, 3387.08 cm^{-1}; MS (EI): m/z (%): 147 (61) $[M]^+$, 118 (100).



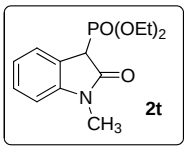
3-(1-hydroxyethylidene)-1-phenylindolin-2-one (2q): Purple solid, mp 86-88°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.52 (s, 3 H), 6.96-6.98 (m, 1 H), 7.15(t, *J*= 4.4 Hz, 2 H), 7.41-7.46 (m, 4 H), 7.54(t, *J*= 7.6 Hz, 2 H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.58, 101.58, 109.72, 119.83, 122.27, 122.60, 125.18, 126.68, 128.06, 129.56, 133.96, 138.66, 170.62, 174.10. IR (neat): 695.23, 741.23, 878.91, 1206.53, 1456.54, 1469.49, 1596.06, 1656.68, 2852.43, 2921.12, 3411.62 cm^{-1}; MS (EI): m/z (%): 251 (100) $[M]^+$, 236 (68), 180 (48).



1-(1-hydroxyethylidene)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one (2r): Gray solid, mp150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03-2.09 (m, 2 H), 2.42 (s, 3 H), 2.83 (t, *J*= 7.6 Hz, 2 H), 3.82-3.85 (m, 2 H), 6.95-7.01 (m, 2 H), 7.17 (d, *J*= 3.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.14, 21.33, 24.65, 38.44, 102.60, 117.47, 120.43, 120.67, 121.64, 123.85, 134.94, 169.88, 172.78. IR (neat): 744.64, 884.23, 1025.74, 1095.85, 1161.19, 1238.85, 1287.67, 1358.53, 1453.16, 1658.36, 1727.43, 2853.23, 2923.99, 3411.76 cm^{-1}; MS (EI): m/z (%): 215 (31) $[M]^+$, 200 (27), 43 (100).

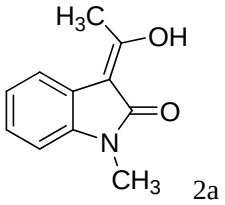


1-methyl-3-(phenylsulfonyl) indolin-2-one (2s): Gray solid, mp 173-175 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.98 (s, 3 H), 4.90 (s, 1 H), 6.67 (d, *J*= 7.6 Hz, 1 H), 7.14 (t, *J*= 7.6 Hz, 1 H), 7.34-7.44 (m, 3 H), 7.58-7.61 (m, 1 H), 7.68(d, *J*= 8.0 Hz, 3 H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.32, 68.21, 108.36, 118.00, 123.16, 127.05, 128.54, 129.37, 130.65, 134.25, 135.88, 144.63, 166.44. IR (neat): 535.30, 562.95, 607.46, 688.99, 750.90, 832.56, 1079.07, 1127.01, 1158.31, 1312.02, 1466.77, 1610.52, 1715.16, 2856.08, 2925.17, 3394.06 cm^{-1}; MS (EI): m/z (%): 287 (6) $[M]^+$, 146 (100), 77(76).

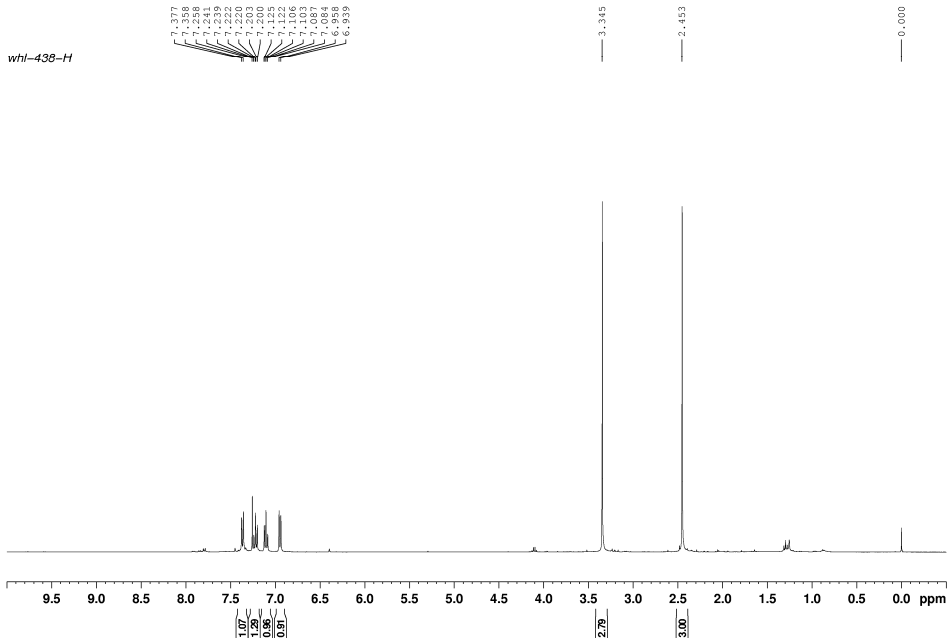


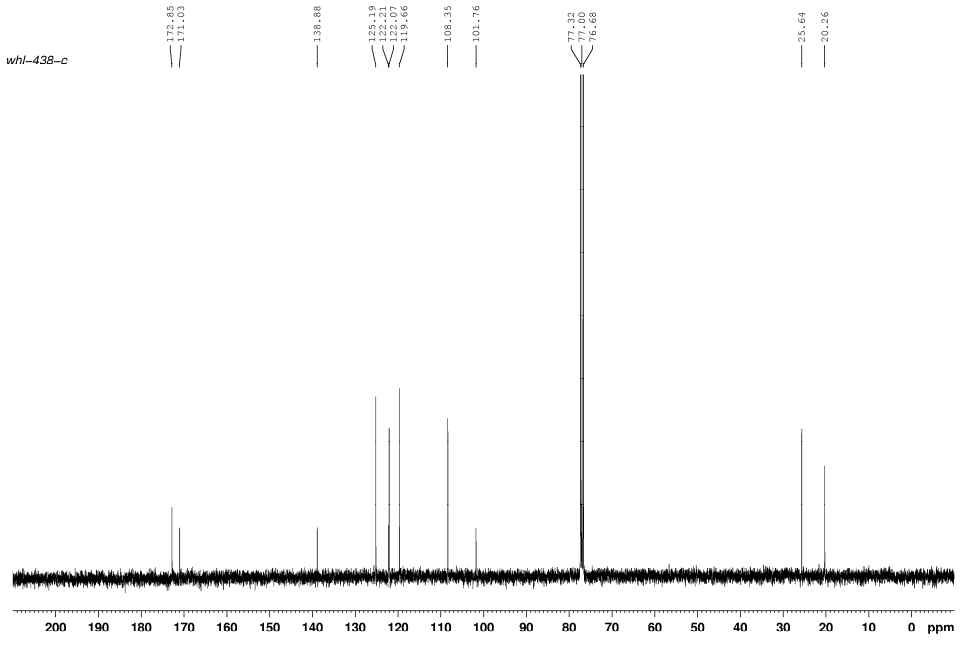
Diethyl (1-methyl-2-oxoindolin-3-yl)phosphonate (2t): Gray solid, mp 90-92 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (t, *J*= 6.8 Hz, 3 H), 1.41 (t, *J*= 6.8 Hz, 3 H), 4.01-4.09 (m, 2 H), 4.13 (s, 1 H), 4.22-4.30 (m, 2 H), 6.90 (d, *J*= 7.6 Hz, 1 H), 7.7.01-7.11 (m, 1 H), 7.33 (t, *J*= 7.6 Hz, 1 H), 7.52 (d, *J*= 6.8 Hz, 1 H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.26, 16.37, 26.56, 45.61, 63.02, 63.90, 108.22, 117.68, 120.77, 122.69, 129.25, 143.18, 170.18. IR (neat): 753.12, 965.17, 1024.30, 1258.35, 1375.03, 1471.21, 1611.73, 1716.42, 2926.38, 3412.64cm^{-1}; MS (EI): m/z (%): 283 (53) $[M]^+$, 147 (94), 146 (94), 91(100).

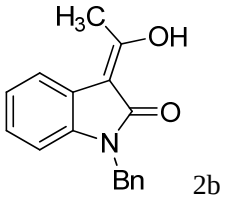
5. NMR Charts



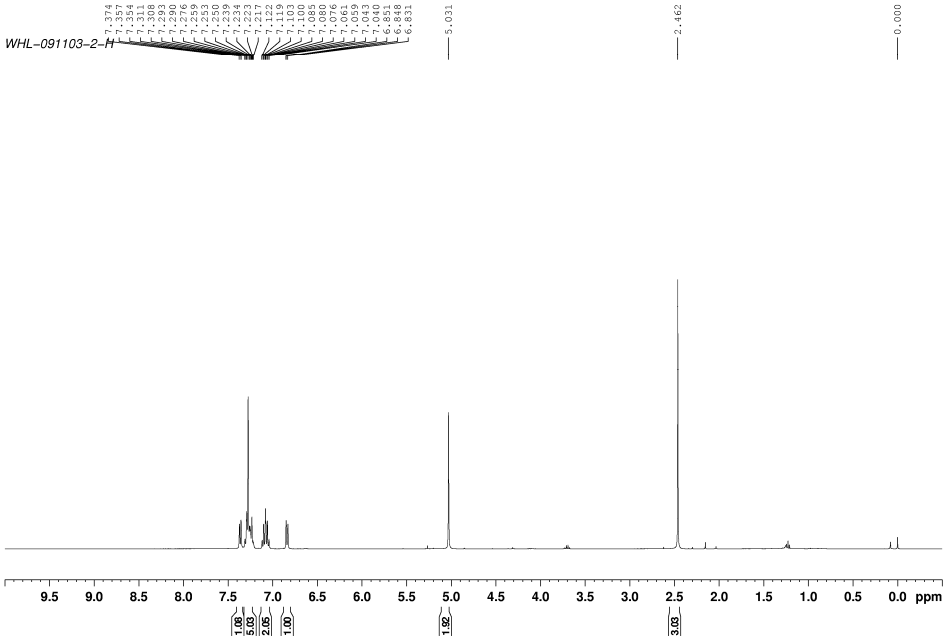
2a






H3C
OH
O
N
Bn

2b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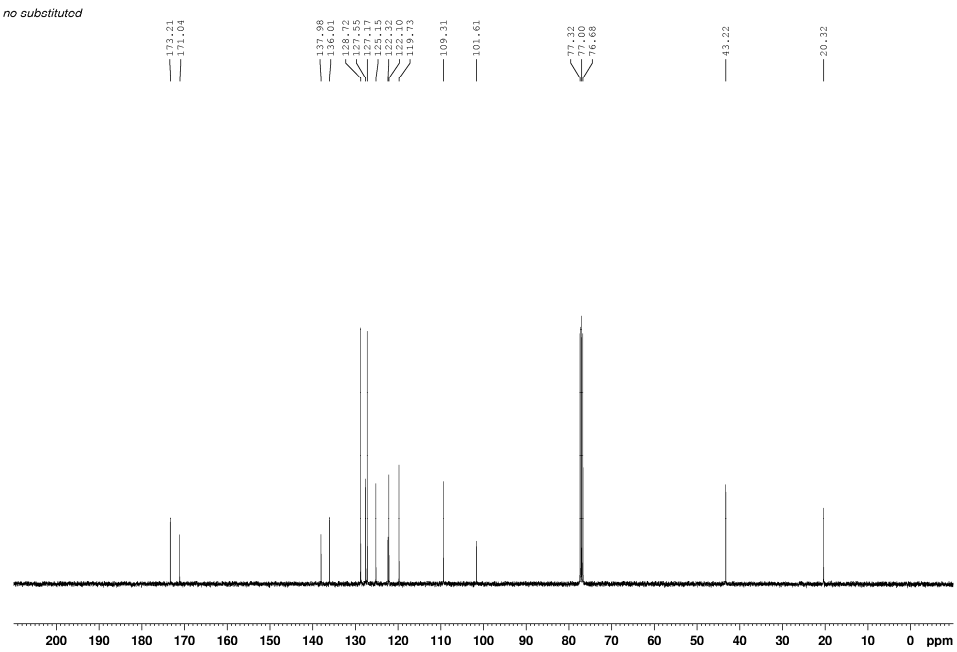
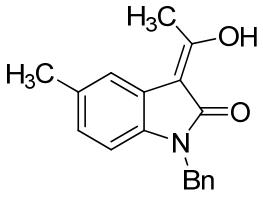
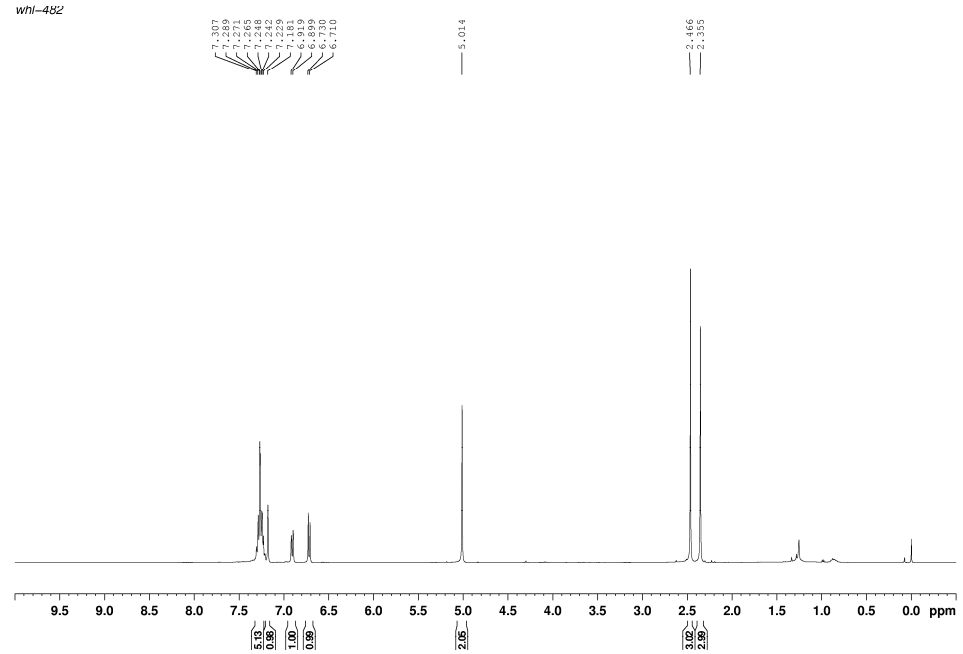
7.344
7.311
7.308
7.293
7.290
7.276
7.259
7.253
7.250
7.239
7.234
7.223
7.217
7.122
7.119
7.103
7.100
7.085
7.080
7.076
7.061
7.059
7.043
7.040
6.851
6.848
6.831
5.031
2.462
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.08
5.03
2.05
1.00
1.92
3.05


no substituted
173.21
171.04
137.98
136.01
128.72
127.55
127.17
123.15
122.32
122.10
119.73
109.31
101.61
77.32
77.00
76.68
43.22
20.32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
H3C
O
N
Bn

2c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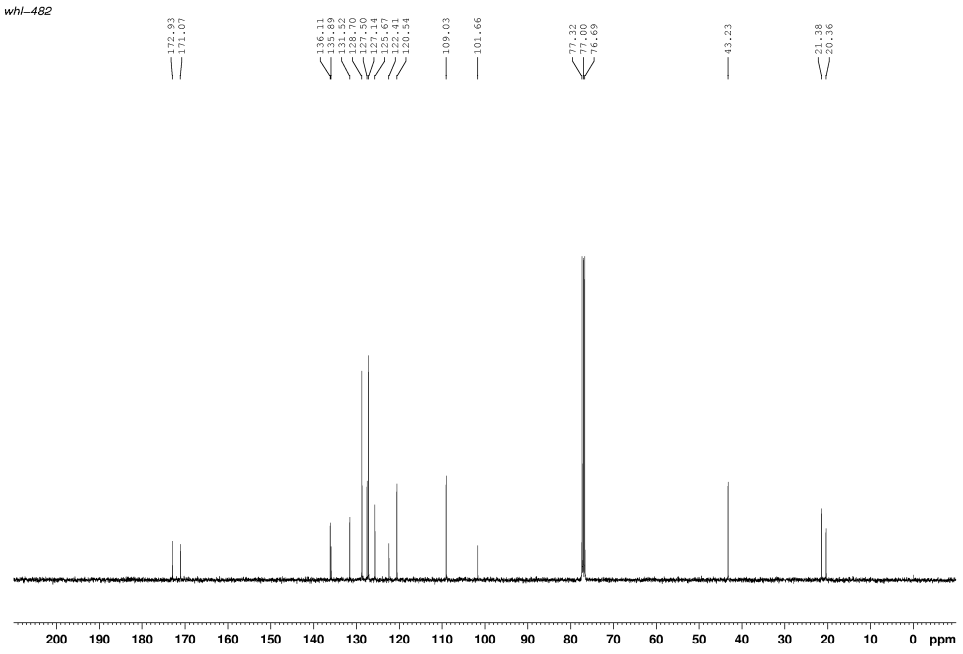
7.289
7.271
7.265
7.248
7.239
7.223
7.181
6.919
6.899
6.730
6.710
5.014
2.466
2.355
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.13
0.98
1.00
0.99
2.05
3.02
2.89


whl-482
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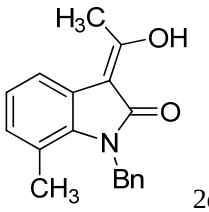
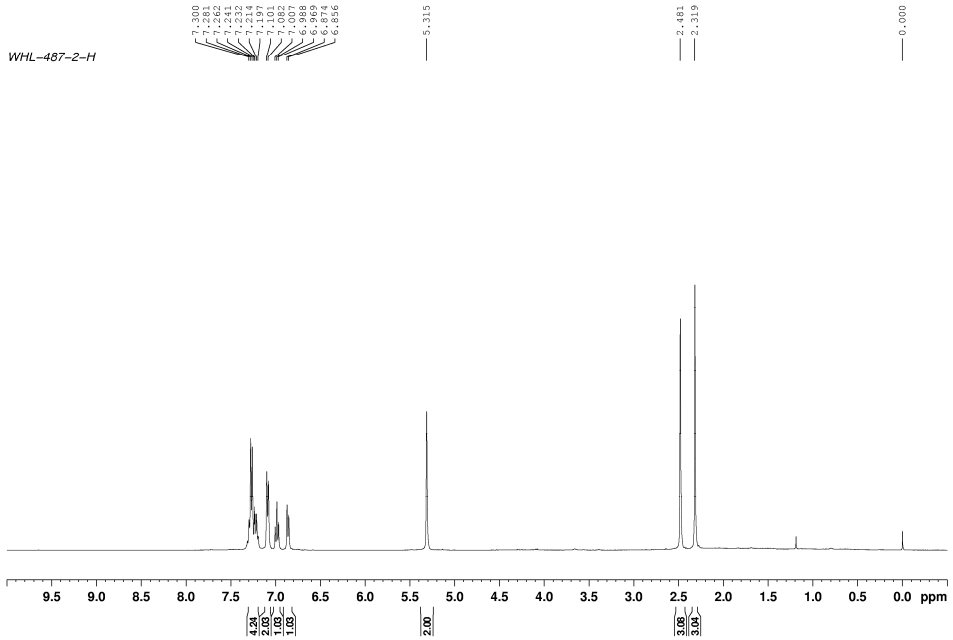
171.07
136.11
135.89
131.52
129.70
128.50
127.14
125.67
122.41
120.44
109.03
101.66
77.32
77.00
76.69
43.23
21.38
20.36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
O
N
Bn
CH3

2d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7.262
7.241
7.232
7.214
7.170
7.101
7.082
7.007
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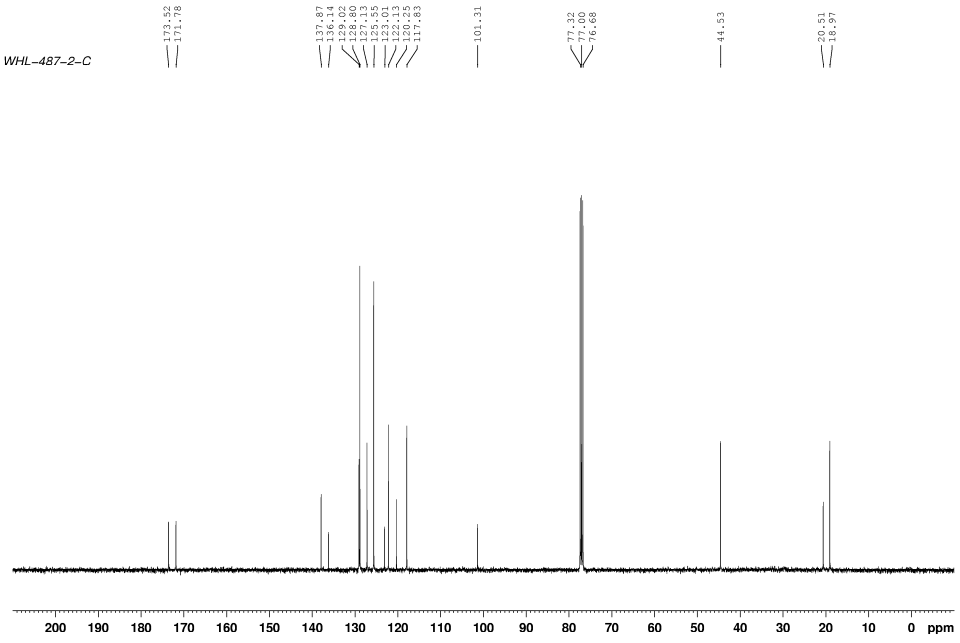
6.969
6.874
6.856
5.315
2.481
2.319
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.24
2.03
1.03
1.05
2.00
3.08
3.04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171.78
137.87
136.14
129.02
128.80
127.13
125.55
123.01
122.13
120.35
117.83
101.31
77.32
77.00
76.68
44.53
20.51
18.97
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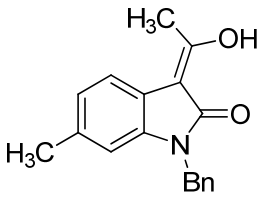
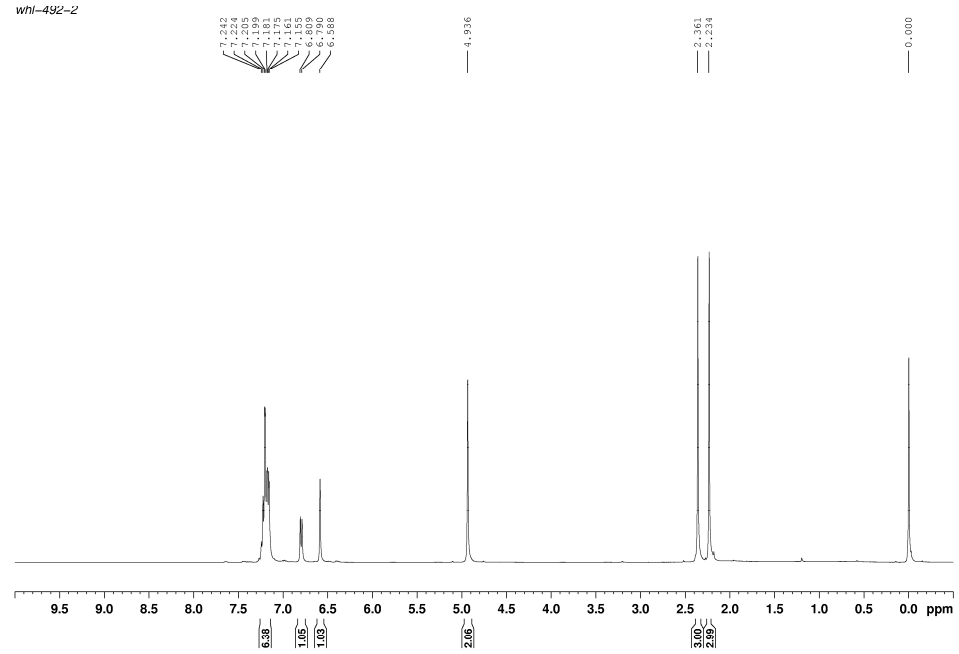

H3C
OH
O
N
H3C
Bn

2e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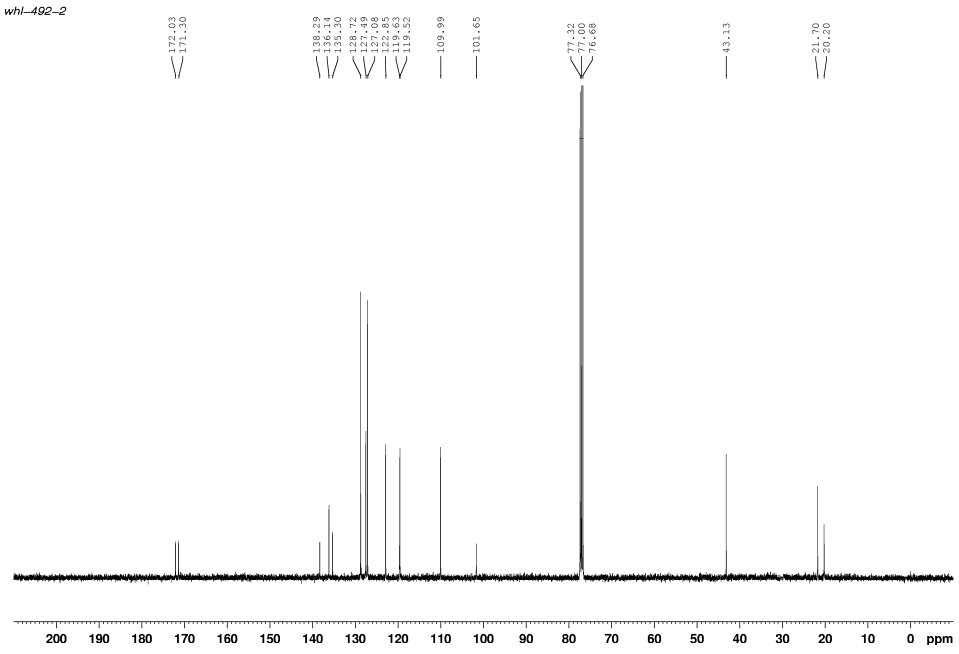
7.224
7.205
7.199
7.181
7.175
7.161
7.155
6.809
6.790
6.588
4.936
2.361
2.234
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.38
1.05
1.03
2.06
3.00
2.89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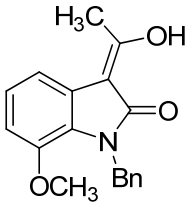
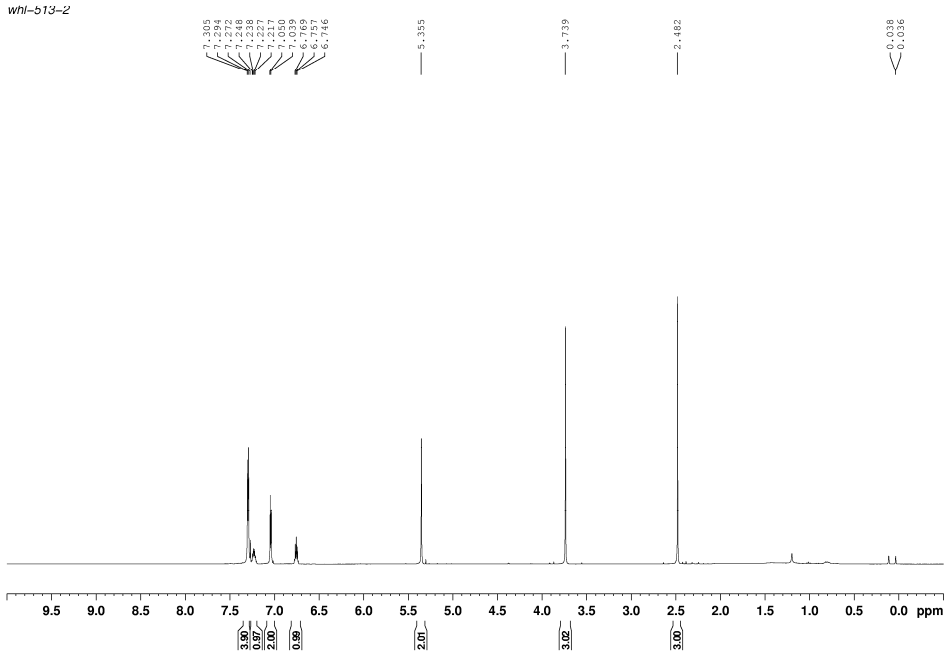
171.30
138.29
136.14
135.90
129.72
127.49
127.08
122.85
119.63
119.52
109.99
101.65
77.32
77.00
76.68
43.13
21.70
20.20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
O
N
Bn
OCH3

2f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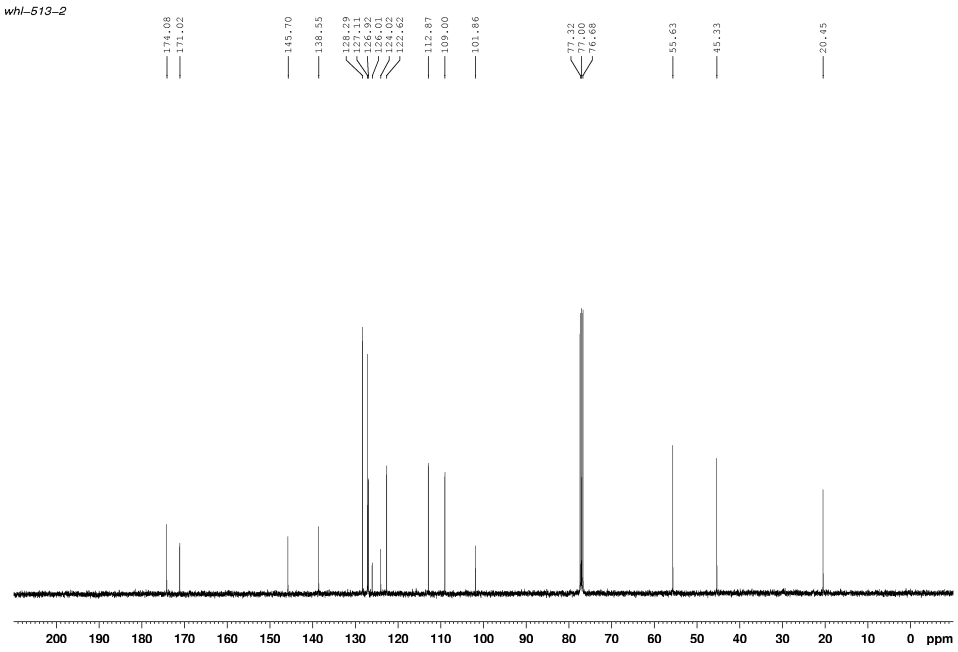
7.272
7.248
7.238
7.227
7.217
7.050
7.039
6.769
6.757
6.746
5.355
3.739
2.482
0.038
0.036
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.90
0.97
2.00
0.99
2.01
3.02
3.00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171.02
145.70
138.55
128.29
127.11
126.92
126.01
124.02
122.62
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109.00
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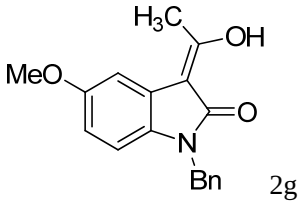
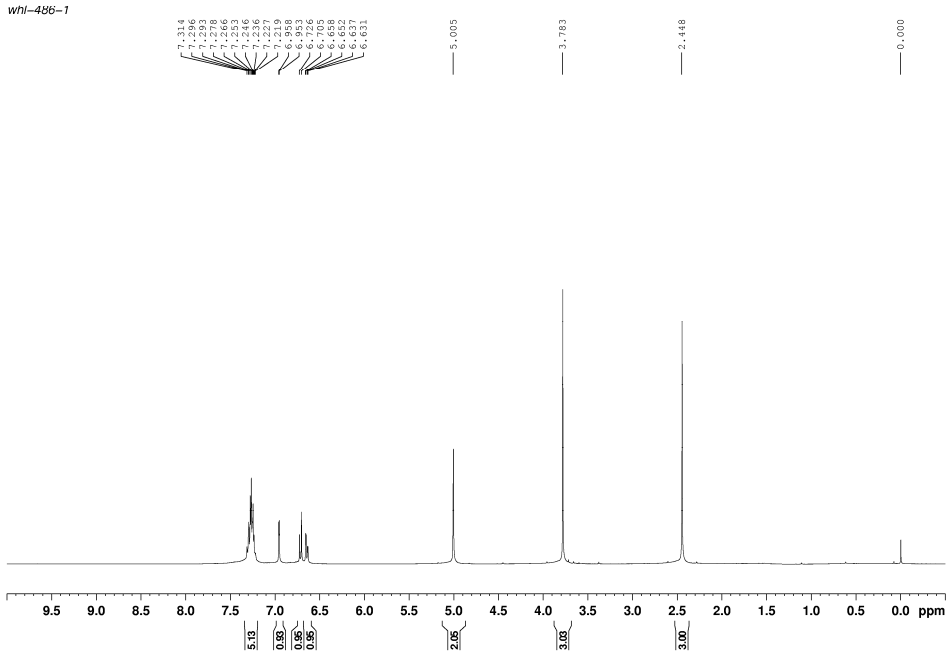
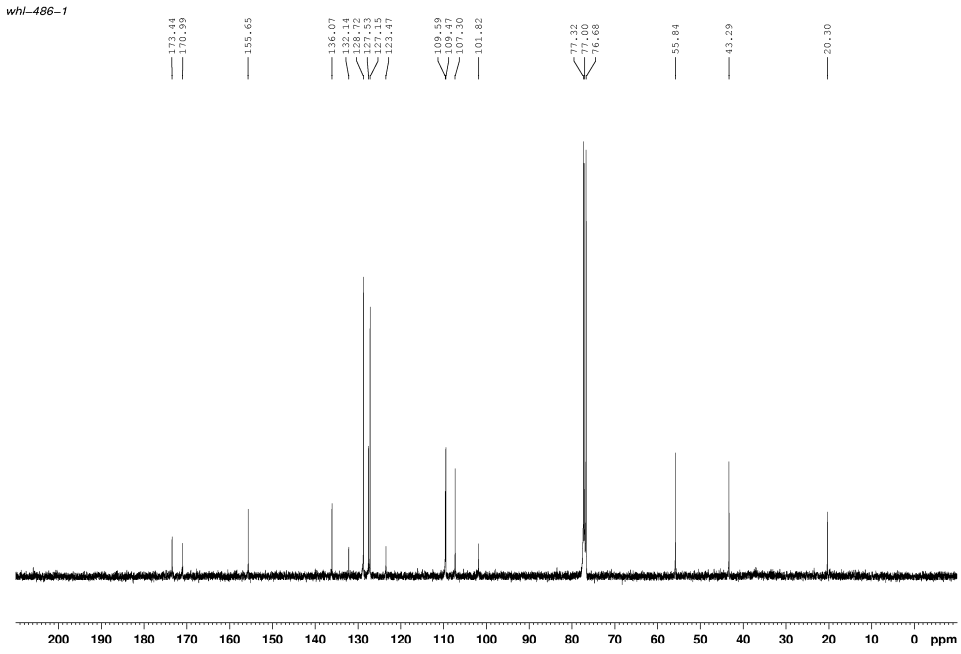
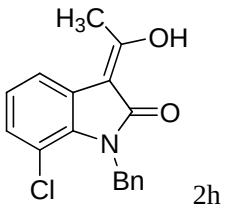
77.00
76.68
55.63
45.33
20.45
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
MeO
O
N
Bn

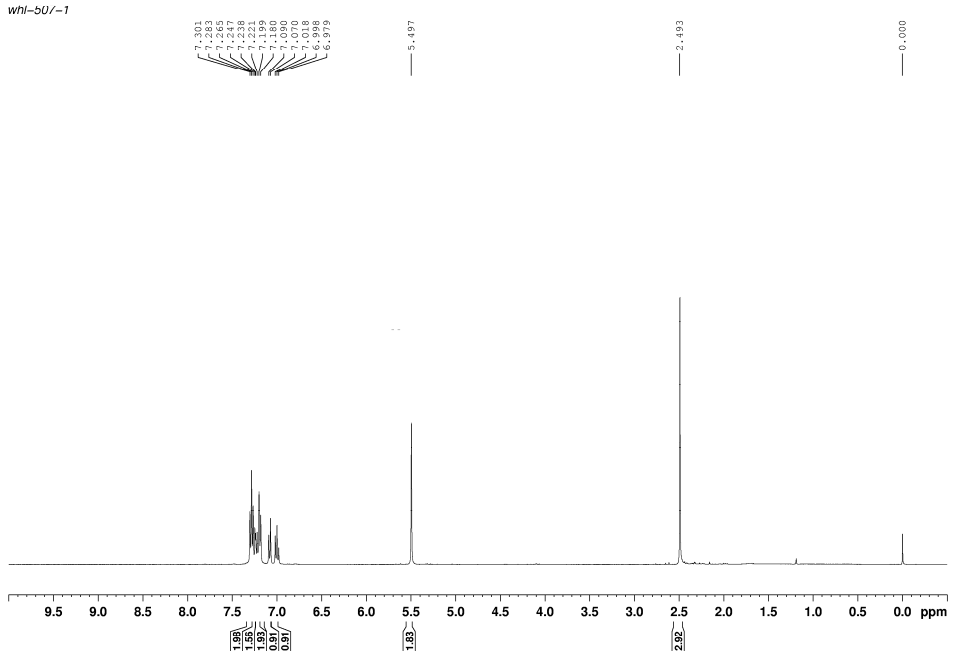
2g

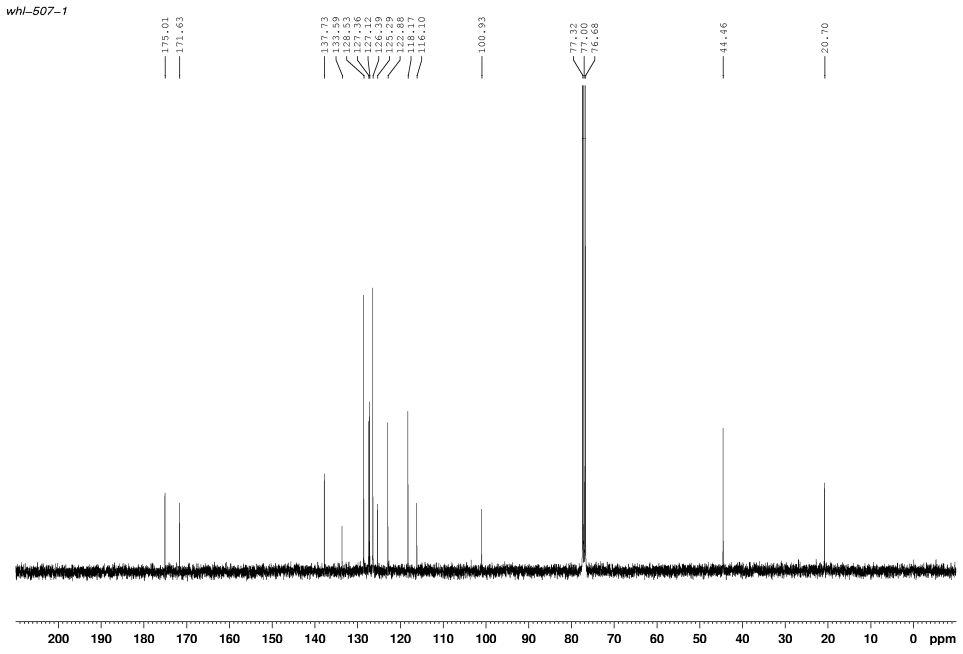

whl-486-1
7.314
7.296
7.283
7.278
7.266
7.253
7.246
7.236
7.227
7.219
6.988
6.953
6.726
6.705
6.658
6.642
6.637
6.631
5.005
3.783
2.448
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.13
0.89
0.95
0.95
2.05
3.03
3.00

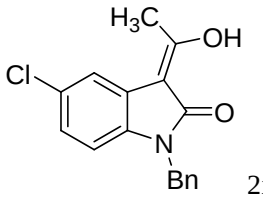

whl-486-1
173.44
170.99
155.65
136.07
132.14
128.72
127.53
127.15
123.47
109.59
109.47
107.30
101.82
77.32
77.00
76.68
55.84
43.29
20.30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
O
N
Bn
Cl

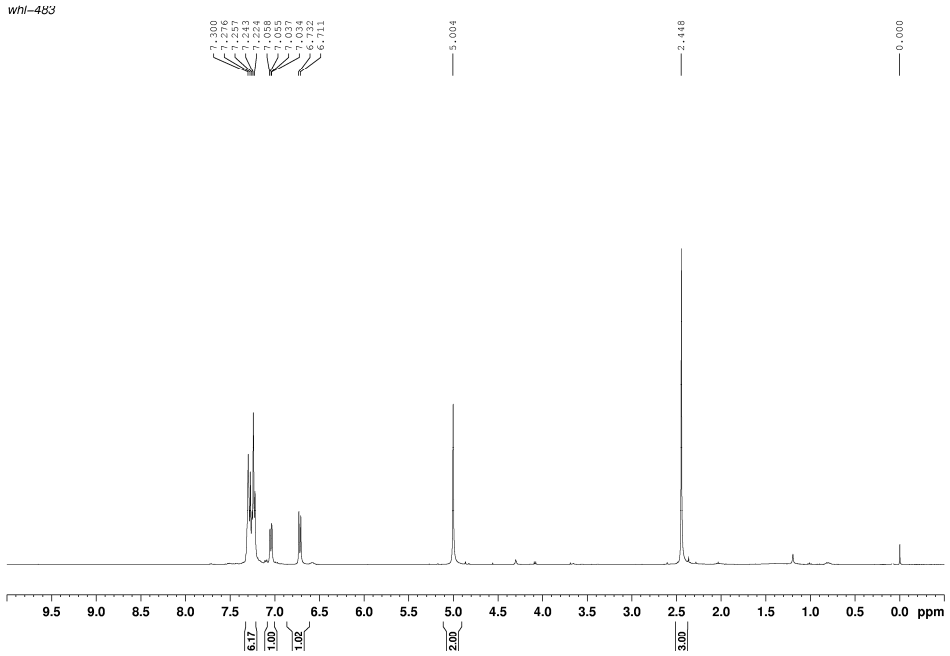
2h

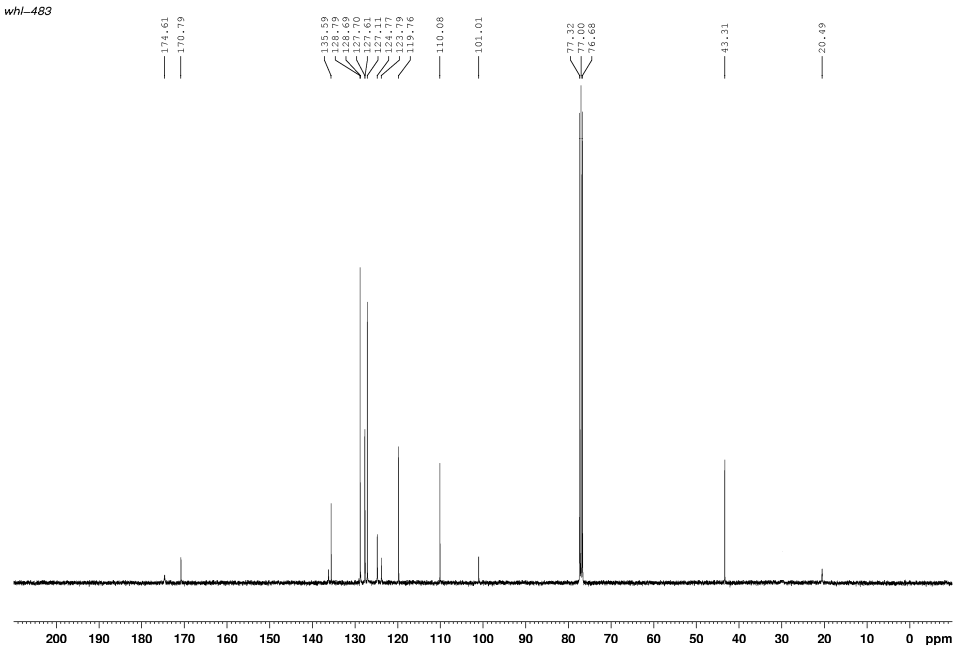

whl-507-1
7.301
7.283
7.265
7.247
7.238
7.221
7.199
7.180
7.090
7.070
7.018
6.998
6.979
5.497
2.493
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.98
1.55
1.99
0.96
0.91
1.83
2.82

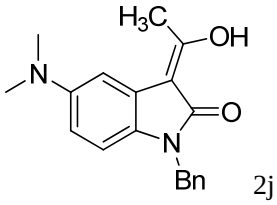

whl-507-1
175.01
171.63
137.73
133.59
128.53
127.36
127.12
126.39
125.29
122.88
118.17
116.10
100.93
77.32
77.00
76.68
44.46
20.70
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
Cl
O
N
Bn

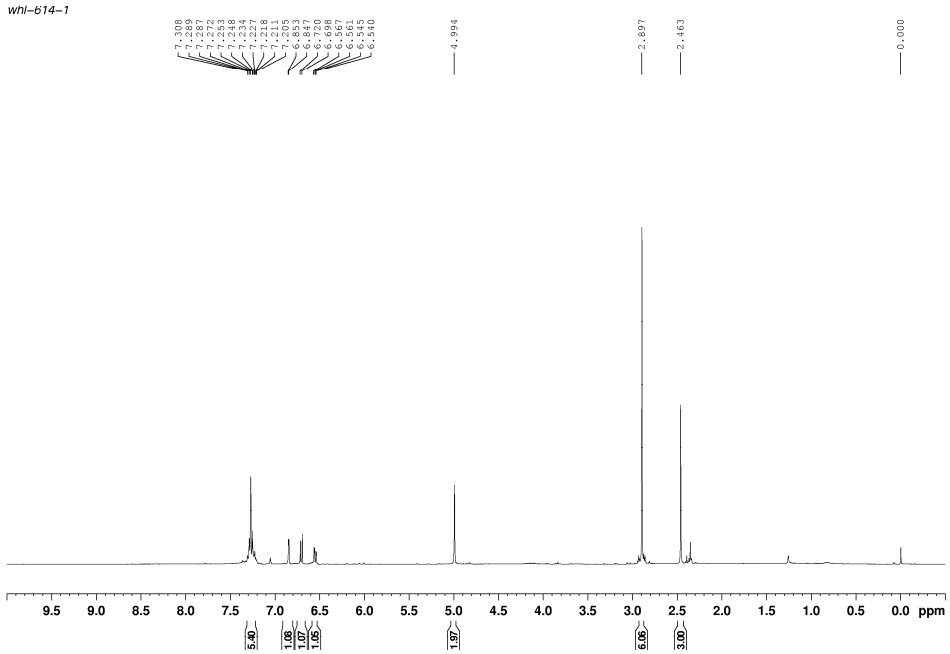
2i

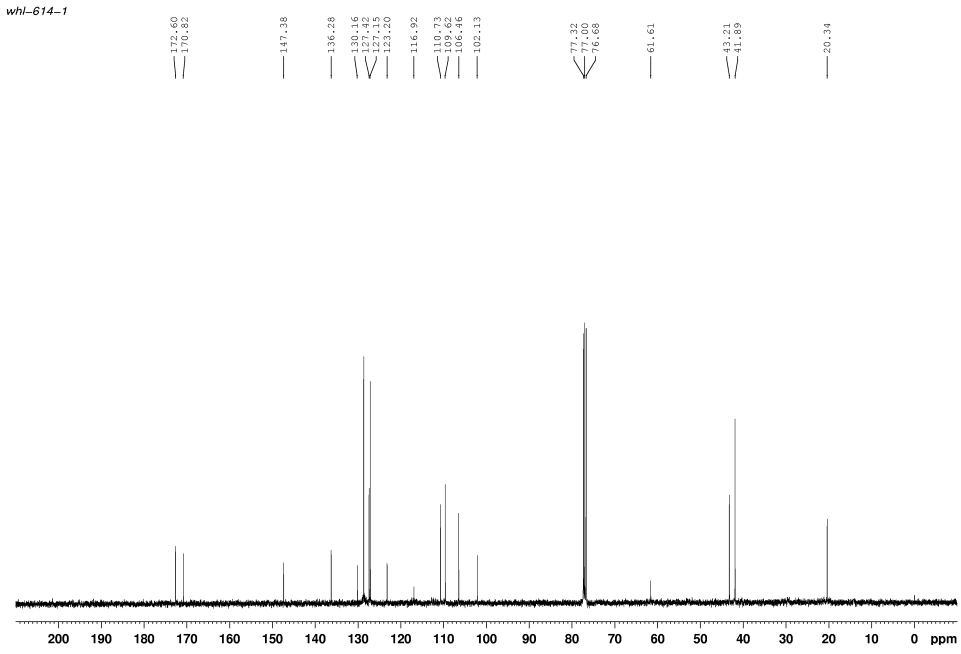

whl-483
7.300
7.276
7.257
7.243
7.224
7.058
7.055
7.037
7.034
6.732
6.711
5.004
2.448
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.17
1.00
1.02
2.00
3.00

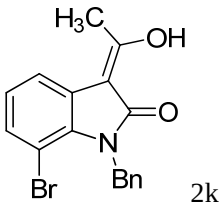

whl-483
174.61
170.79
135.59
128.79
128.69
127.70
127.61
127.11
124.77
123.79
119.76
110.08
101.01
77.32
77.00
76.68
43.31
20.49
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
N
O
N
Bn

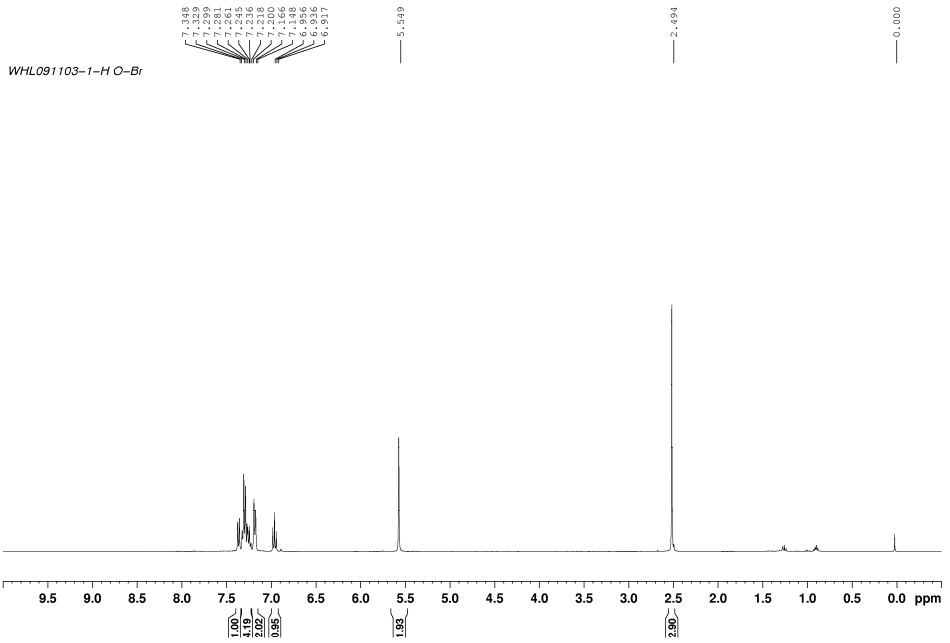
2j

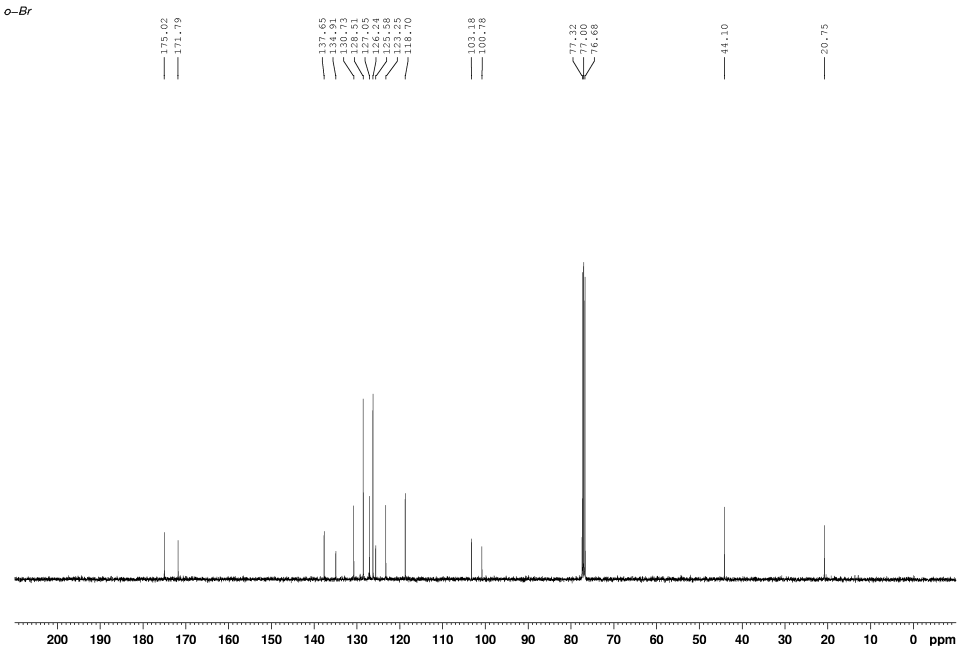

whl-614-1
7.308
7.289
7.287
7.272
7.253
7.238
7.234
7.227
7.218
7.211
7.205
6.853
6.847
6.780
6.768
6.567
6.561
6.545
6.540
4.994
2.897
2.463
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.40
1.08
1.07
1.05
1.00
1.97
6.06
3.00

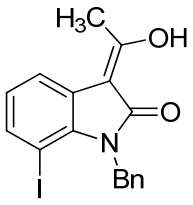

whl-614-1
172.60
170.82
147.38
136.28
130.16
127.42
127.15
123.20
116.92
110.73
109.62
106.46
102.13
77.32
77.00
76.68
61.61
43.21
41.89
20.34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
O
N
Bn
Br

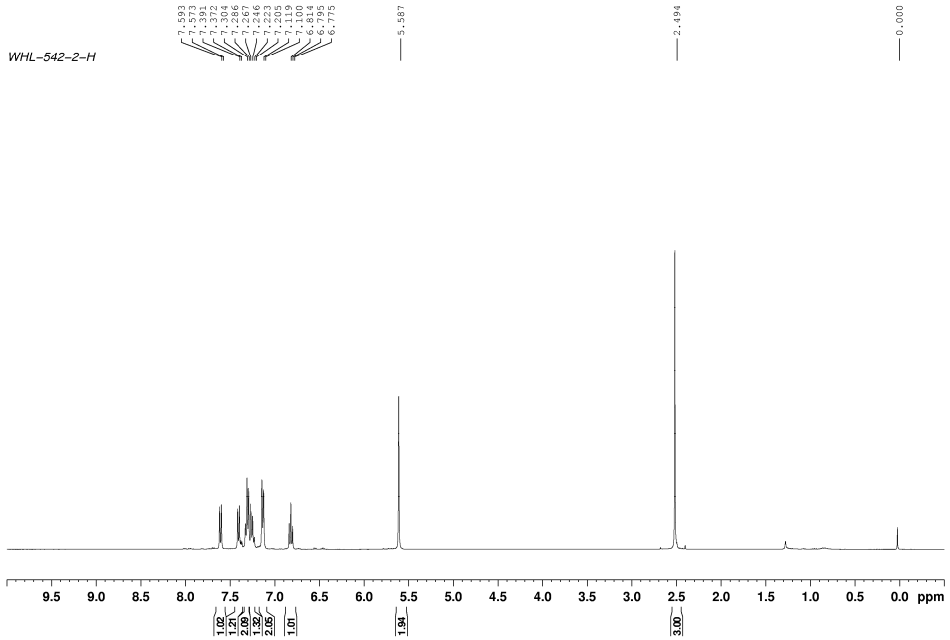
2k

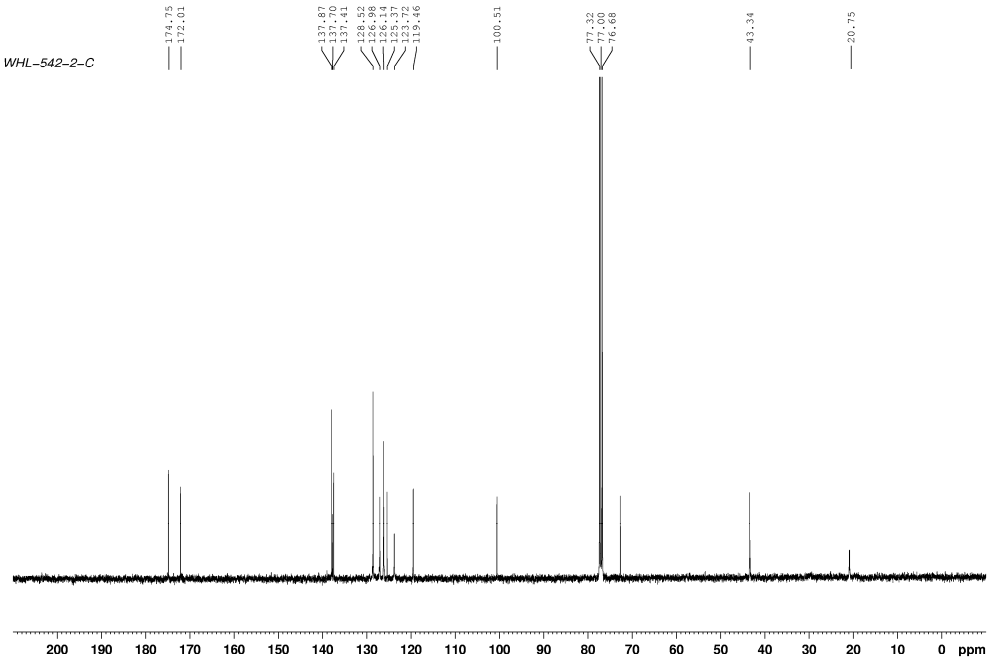

WHL091103-1-H O-Br
7.348
7.329
7.299
7.281
7.261
7.245
7.236
7.208
7.200
7.166
7.148
6.936
6.936
6.917
5.549
2.494
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.19
2.20
0.95
1.93
2.90

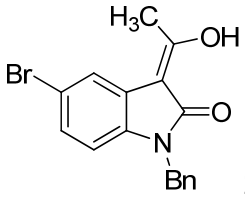

o-Br
175.02
171.79
137.65
134.91
130.73
128.31
127.35
126.24
125.58
123.25
118.70
103.18
100.78
77.32
77.00
76.68
44.10
20.75
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
O
N
Bn
I

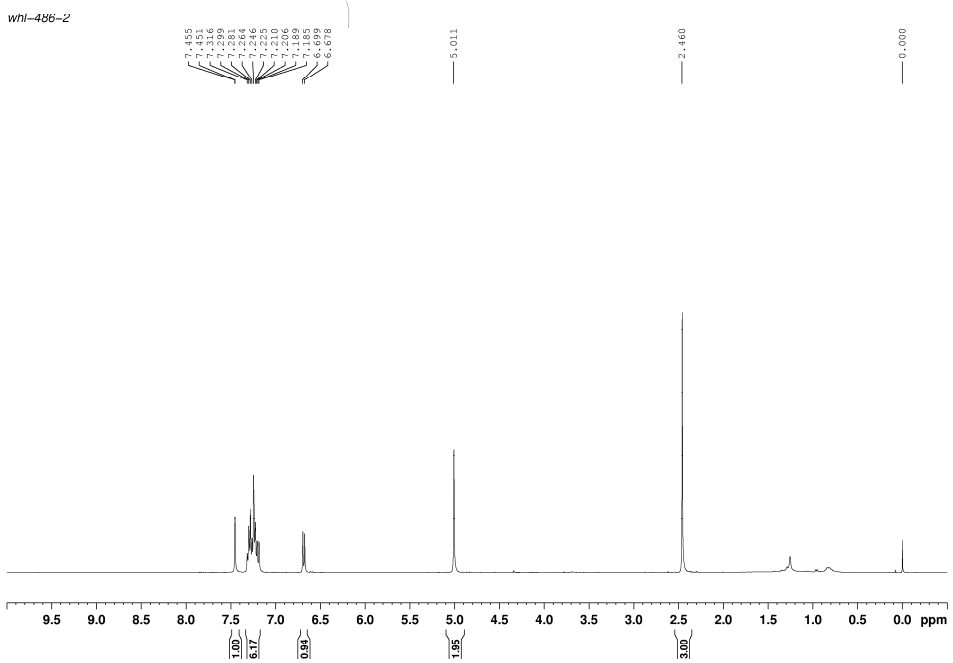
2l

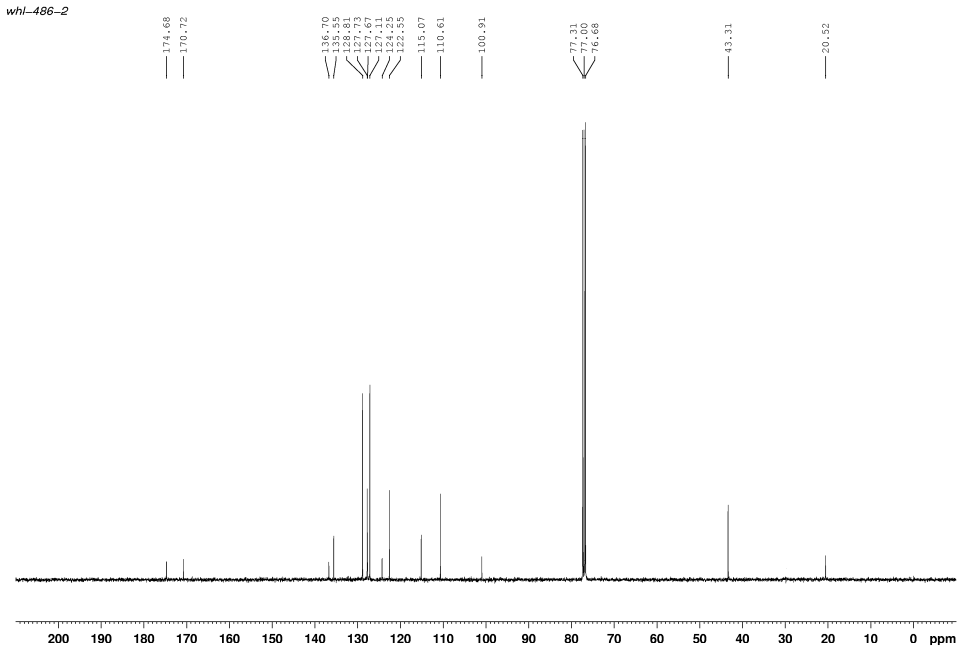

WHL-542-2-H
7.593
7.573
7.391
7.372
7.304
7.286
7.267
7.246
7.223
7.205
7.189
7.100
6.814
6.795
6.775
5.587
2.494
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.25
2.08
1.32
2.05
1.01
1.94
3.00

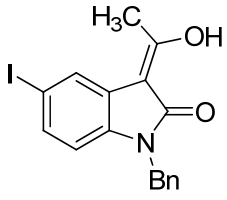

WHL-542-2-C
174.75
172.01
137.87
137.70
137.41
128.52
126.98
126.14
125.37
123.72
119.46
100.51
77.32
77.00
76.68
43.34
20.75
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
Br
O
N
Bn

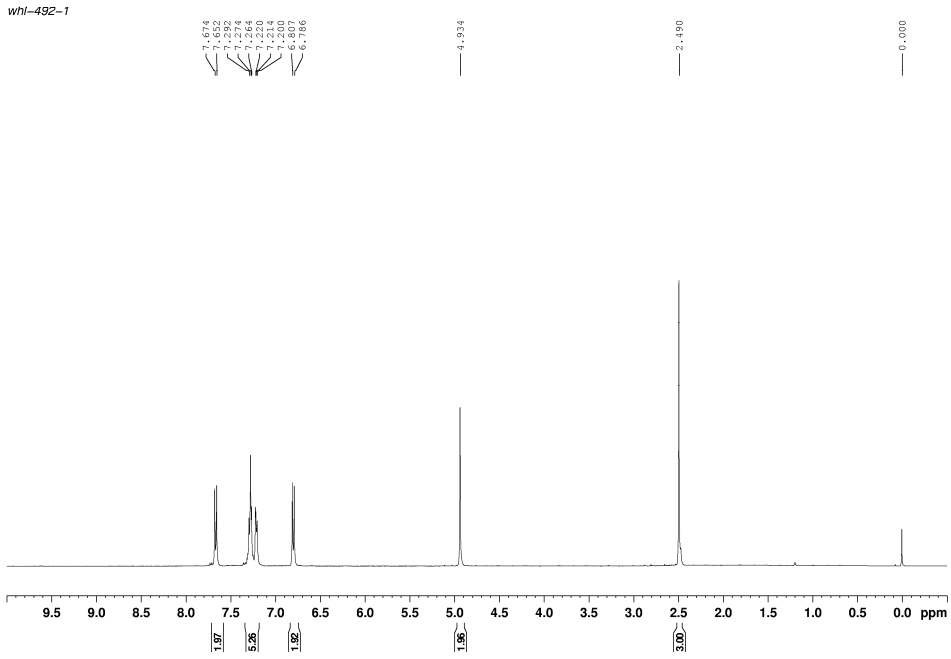
2m

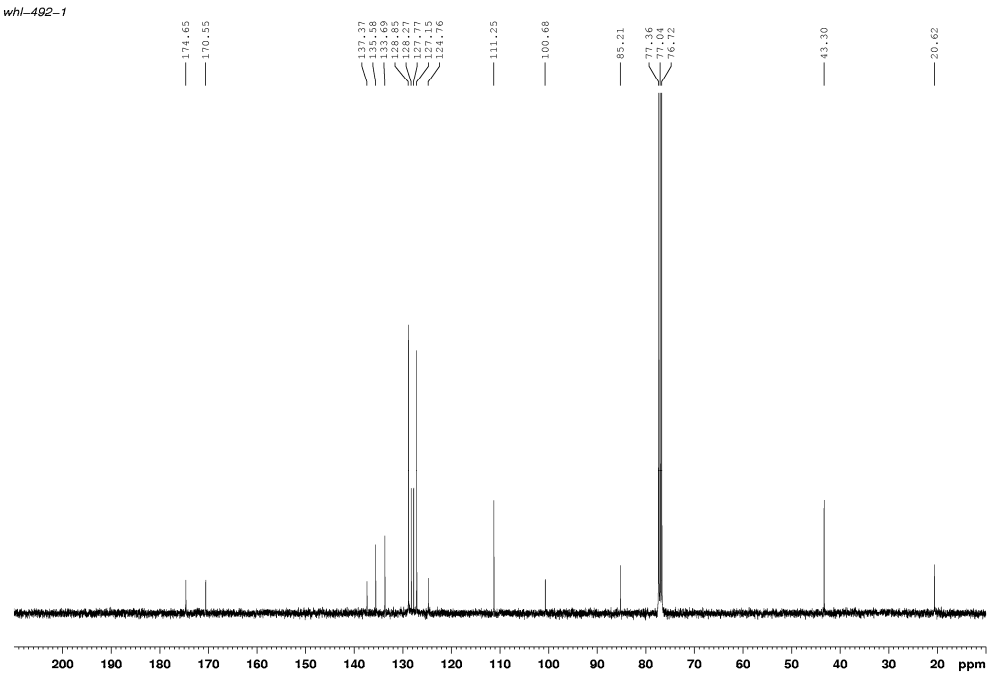

whl-486-2
7.455
7.451
7.316
7.299
7.281
7.264
7.246
7.225
7.210
7.206
7.189
7.185
6.679
6.678
5.011
2.460
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
6.17
0.94
1.95
3.00

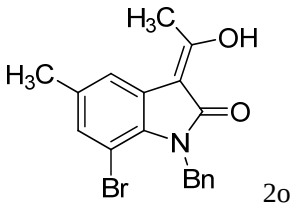

whl-486-2
174.68
170.72
136.70
135.55
128.81
127.73
127.67
127.11
124.25
122.55
115.07
110.61
100.91
77.31
77.00
76.68
43.31
20.52
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
I
O
N
Bn

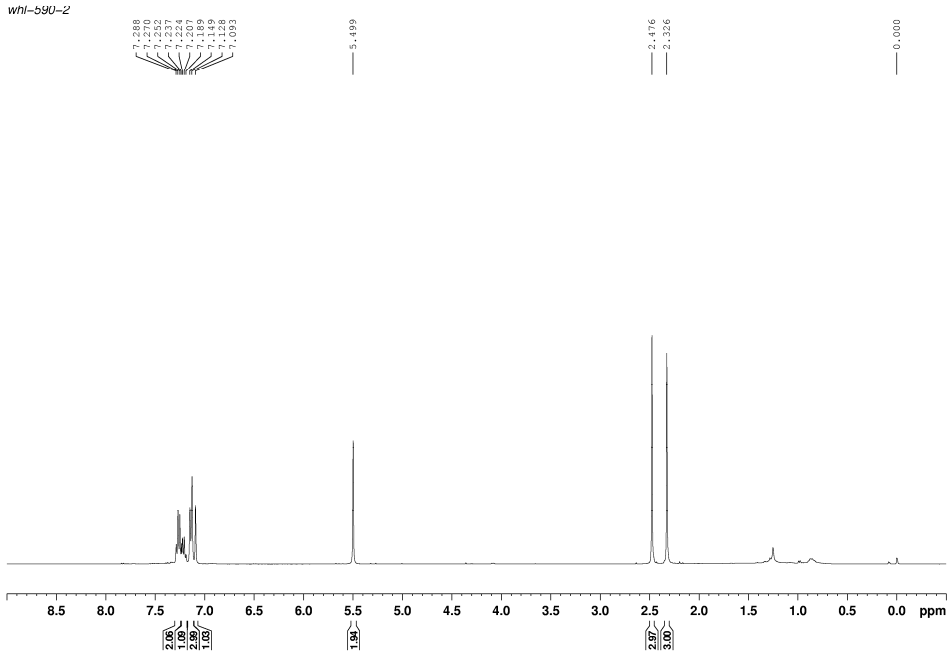
2n

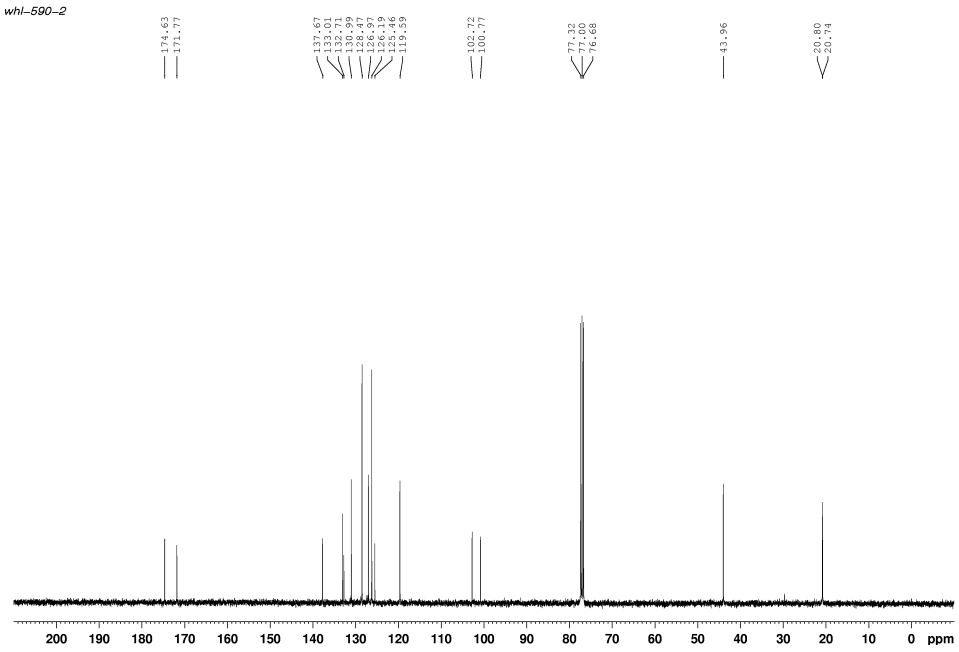

whl-492-1
7.674
7.672
7.292
7.274
7.264
7.220
7.214
7.200
6.807
6.786
4.934
2.490
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.97
5.25
1.92
1.98
3.00

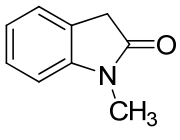

whl-492-1
174.65
170.55
137.37
135.58
133.69
128.85
128.27
127.77
127.15
124.76
111.25
100.68
85.21
77.36
77.04
76.72
43.30
20.62
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


H3C
OH
H3C
O
N
Bn
Br

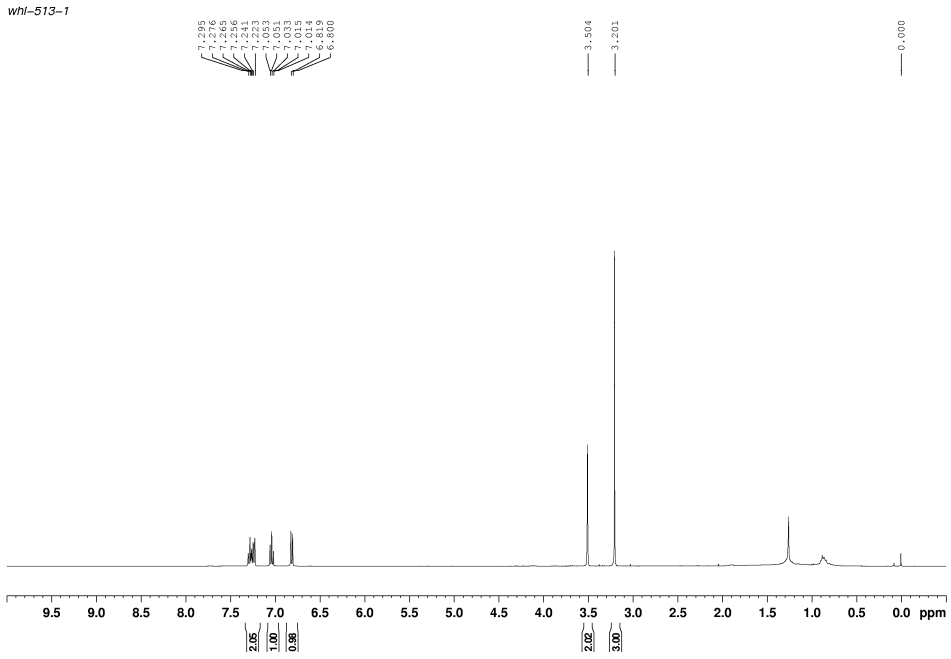
2o

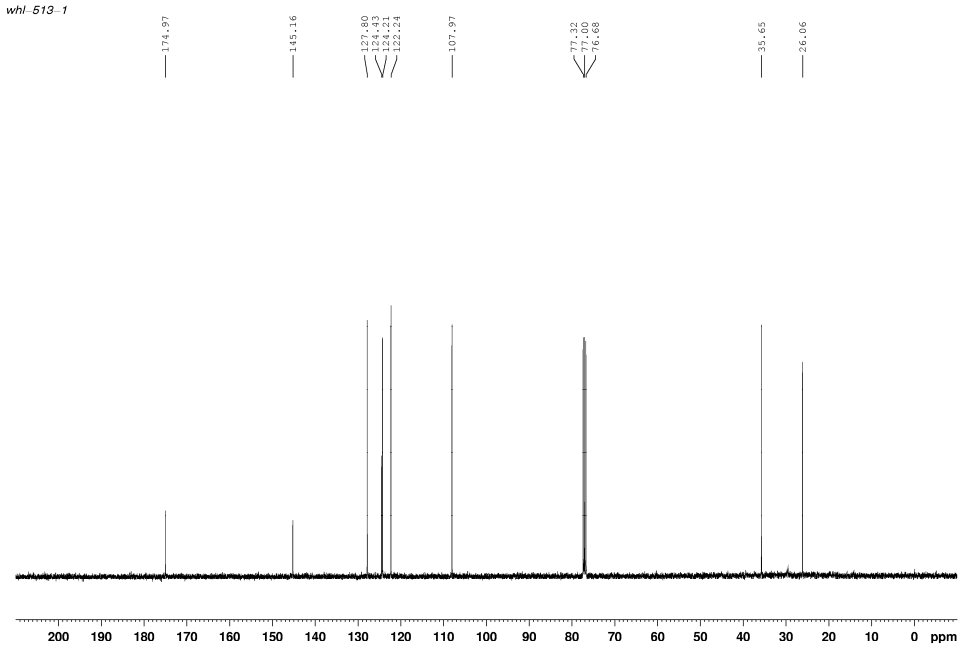

whl-590-2
7.288
7.270
7.252
7.237
7.224
7.207
7.189
7.149
7.128
7.093
5.499
2.476
2.326
0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05
1.09
2.89
1.09
1.94
2.97
3.00

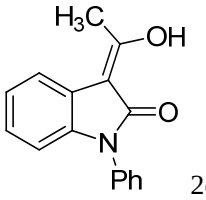

whl-590-2
174.63
171.77
137.67
133.01
132.71
130.99
128.47
126.97
126.19
122.46
119.59
102.72
100.77
77.32
77.00
76.68
43.96
20.80
20.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
N
CH3

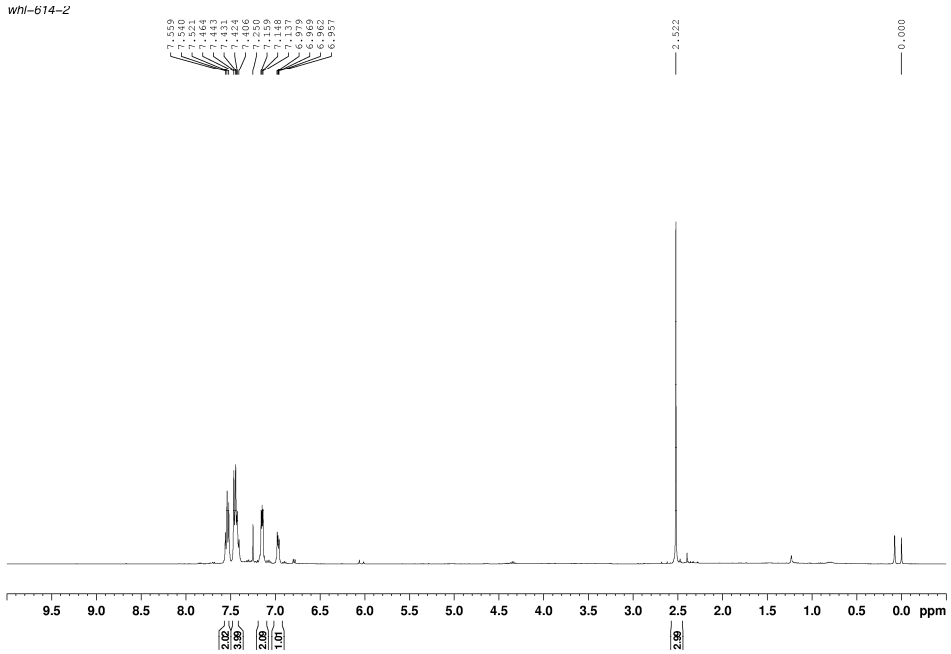
2p

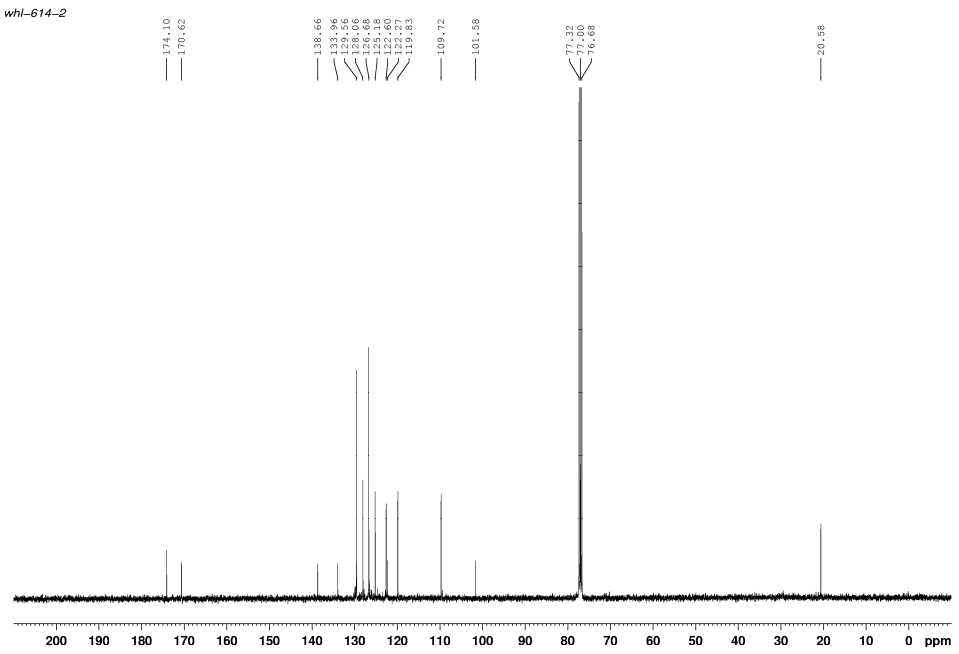

whl-513-1
7.295
7.276
7.265
7.256
7.241
7.223
7.053
7.051
7.033
7.015
7.014
6.819
6.800
3.504
3.201
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05
1.00
0.98
2.02
3.00

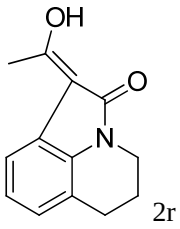

whl-513-1
174.97
145.16
127.80
124.43
124.21
122.24
107.97
77.32
77.00
76.68
35.65
26.06
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


H3C
OH
O
N
Ph

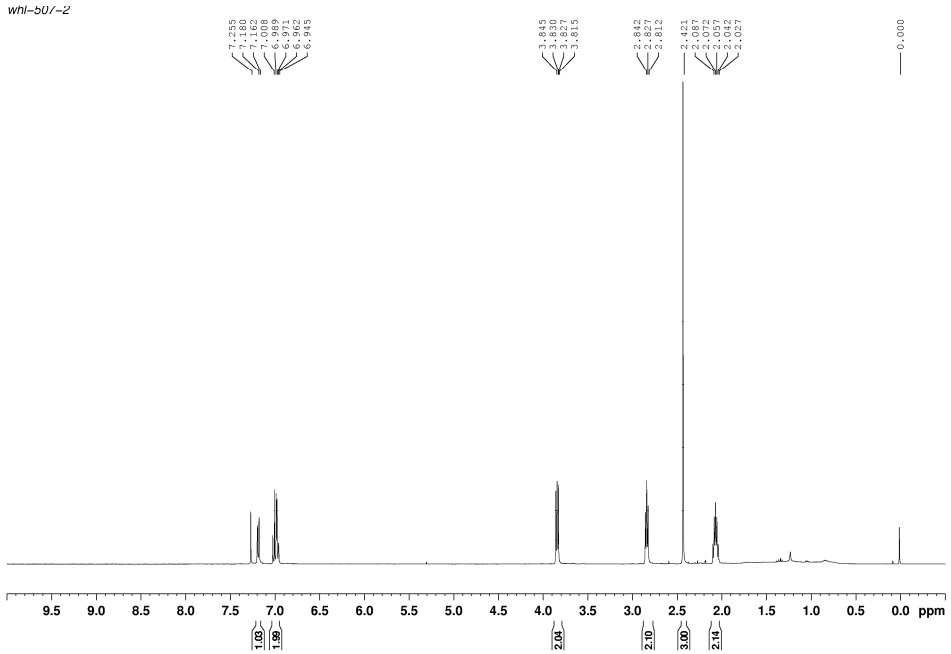
2q

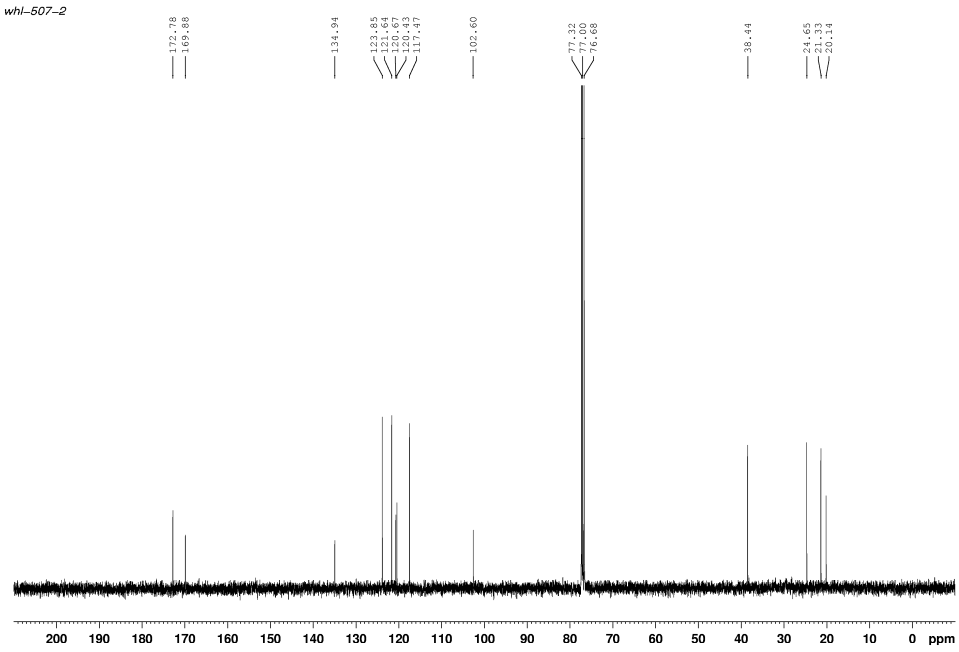

whl-614-2
7.559
7.540
7.521
7.446
7.443
7.431
7.424
7.406
7.250
7.159
7.148
7.137
6.979
6.969
6.962
6.957
2.522
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
3.89
2.00
1.01
2.99

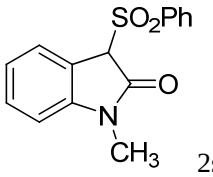

whl-614-2
174.10
170.62
138.66
133.96
129.56
128.06
126.68
126.18
122.60
122.27
119.83
109.72
101.58
77.32
77.00
76.68
20.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OH
O
N

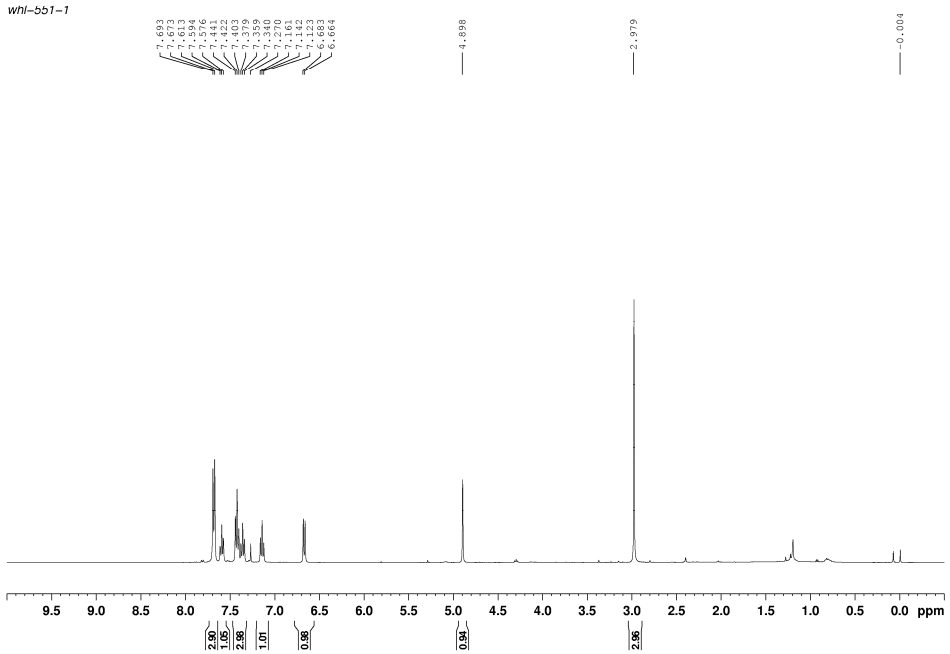
2r

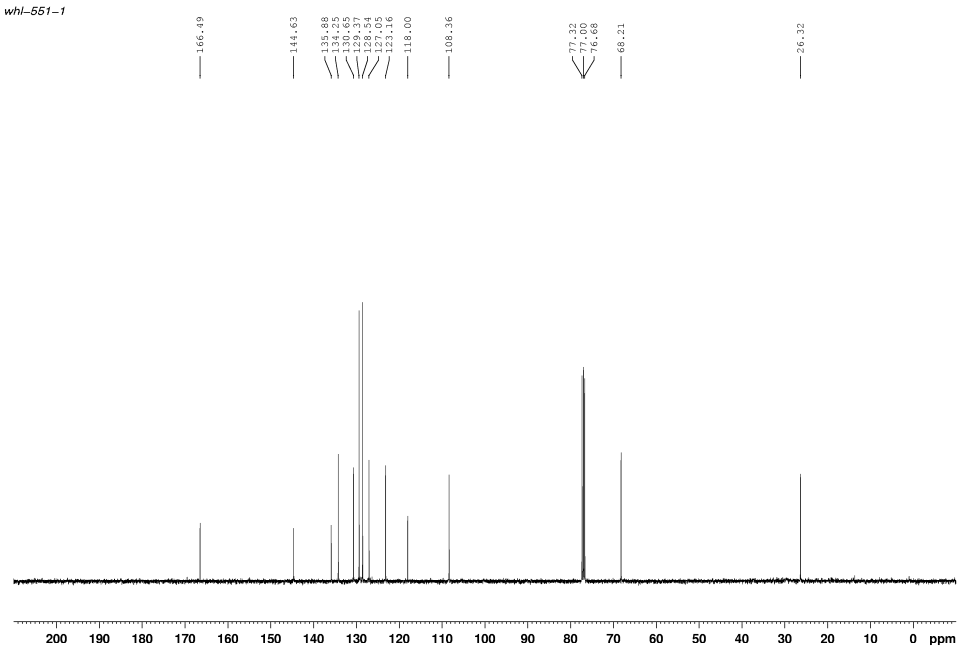

whl-507-2
7.255
7.180
7.162
7.008
6.959
6.941
6.962
6.945
3.845
3.830
3.827
3.815
2.842
2.827
2.812
2.421
2.057
2.052
2.042
2.027
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.05
1.99
2.04
2.10
3.00
2.14

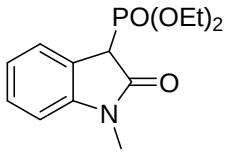

whl-507-2
172.78
169.88
134.94
123.85
121.64
120.67
120.43
117.47
102.60
77.32
77.00
76.68
38.44
24.65
21.33
20.14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


SO2Ph
O
N
CH3

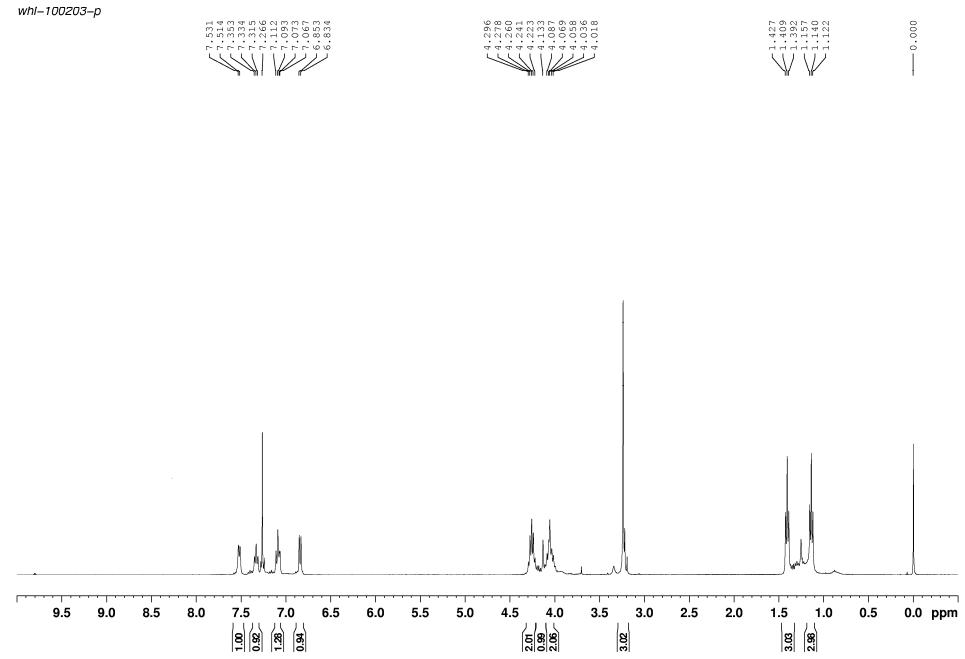
2s

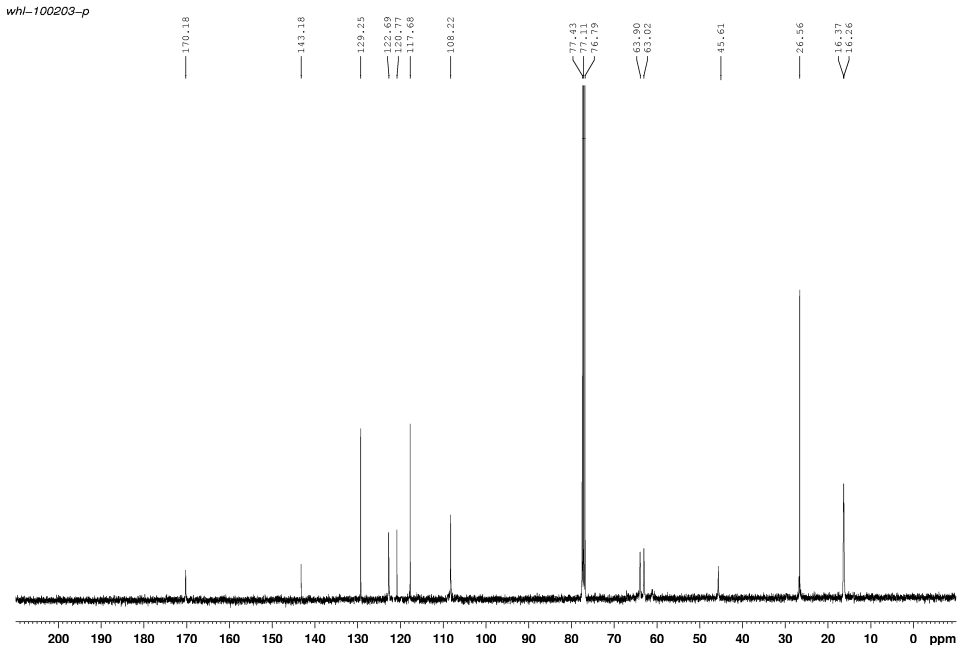

whl-551-1
7.693
7.673
7.613
7.594
7.576
7.441
7.422
7.403
7.379
7.359
7.340
7.270
7.161
7.142
7.123
6.683
6.664
4.898
2.979
-0.004
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.05
2.08
1.01
0.98
0.94
2.96


whl-551-1
166.49
144.63
135.88
134.25
130.65
129.37
128.54
127.35
123.16
118.00
108.36
77.32
77.00
76.68
68.21
26.32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

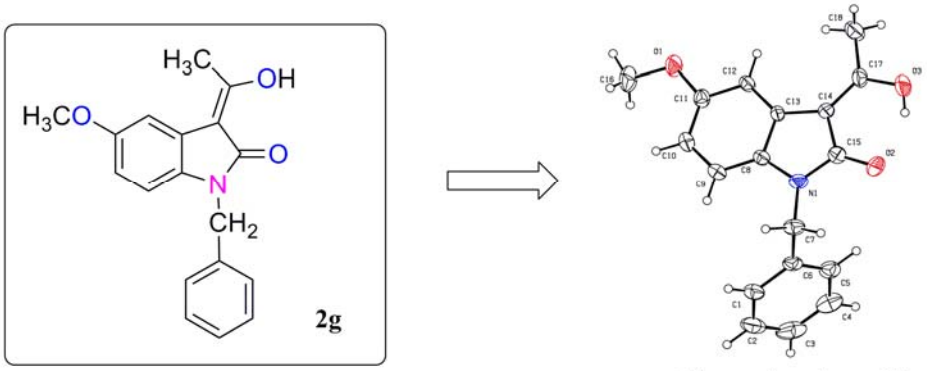

PO(OEt)2
O
N

2t


whl-100203-p
7.531
7.514
7.353
7.338
7.315
7.266
7.112
7.093
7.073
7.067
6.853
6.834
4.296
4.278
4.260
4.241
4.223
4.133
4.087
4.069
4.058
4.036
4.018
1.427
1.409
1.392
1.157
1.140
1.122
0.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.92
1.28
0.94
2.01
0.99
2.06
3.02
3.03
2.99


whl-100203-p
170.18
143.18
129.25
122.69
120.77
117.68
108.22
77.43
77.11
76.79
63.90
63.02
45.61
26.56
16.37
16.26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

6. The crystal structure of 2g



X-ray structure of 2g

Crystal Number: Summary of Data CCDC 777495

Formula: $C_{18}H_{17}N_1O_3$

Unit cell parameters: a 8.486(4) b 11.448(5) c 15.685(7) beta 97.745(9) space group P21/n

Datablock: p-1

Bond precision: C-C = 0.0055 A Wavelength=0.71073

Cell: a=8.486(4) b=11.448(5) c=15.685(7)
alpha=90 beta=97.745(9) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1509.9(12)	1510.0(12)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C18 H17 N O3	?
Sum formula	C18 H17 N O3	C18 H17 N O3
Mr	295.33	295.33
Dx,g cm-3	1.299	1.299
Z	4	4
Mu (mm-1)	0.089	0.089
F000	624.0	624.0
F000'	624.30	
h,k,lmax	10,13,18	10,13,18
Nref	2810	2795
Tmin,Tmax	0.969,0.979	0.970,0.979
Tmin'	0.969	

Correction method= NONE

Data completeness= 0.995 Theta(max)= 25.490

R(reflections)= 0.0703(1376) wR2(reflections)= 0.1973(2795)

S = 1.018 Npar= 203