

# Formal [4+1] Annulation of $\alpha,\alpha$ -Dialkyl $\beta$ -Oxo Amides and Dimethyl- sulfoxonium Methylide: a Synthetic Route to $\beta$ -Hydroxy- $\gamma$ -lactams

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## I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 25°C on a 300 or 400 and 100 MHz spectra, respectively, and TMS as internal standard. IR spectra (KBr) were recorded on FTIR-spectrophotometer in the range of 400–4000  $\text{cm}^{-1}$ . Elemental analyses were carried out on a Perkin-Elmer PE-2400 analyzer. All melting points were determined in open capillary tubes in a Thiele apparatus and were uncorrected.

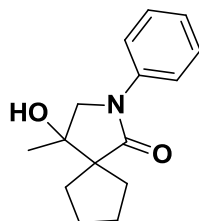
## II. Synthesis and Analytical data of compounds 3

### (I) Synthesis of compounds 3

#### Typical procedure for the preparation of substituted $\gamma$ -lactams (with 3a as an example):

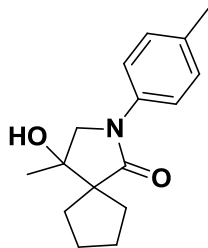
The Corey–Chaykovsky reagent was prepared by adding NaH (4.0 mmol) in one portion into a solution of trimethylsulfoxonium iodide **2** (1.2 mmol) in DMSO (5.0 mL) under stirring. The mixture was then stirred for 15 min at room temperature. To the above Corey–Chaykovsky reagent was added **1a** (1.0 mmol). The mixture was stirred at room temperature for 6.0 h. After the reaction was completed, the resulting mixture was poured into saturated aqueous  $\text{NH}_4\text{Cl}$  (100 mL), which was extracted with dichloromethane (3×30 mL). The combined organic phase was washed with water, dried over anhydrous  $\text{MgSO}_4$ , filtered, and evaporated *in vacuo*. The crude product was purified by flash silica gel chromatography (petroleum ether/ethyl acetate 4:1, v/v) to give **3a** as a white solid (82%).

### (II) Analytical data of compounds 3



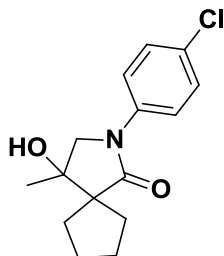
#### 4-Hydroxy-4-methyl-2-phenyl-2-azaspiro[4.4]nonan-1-one (**3a**)

White solid; mp: 93–95 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.39 (s, 3H), 1.61–1.63 (m, 1H), 1.72–1.76 (m, 4H), 1.83–1.91 (m, 3H), 1.98–2.02 (m, 1H), 3.71 (ABq,  $J_{\text{AB}} = 10.0$  Hz,  $\Delta\nu_{\text{AB}} = 15.0$  Hz, 2H), 7.12 (t,  $J = 7.5$  Hz, 1H), 7.36 (t,  $J = 7.5$  Hz, 2H), 7.62 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.1, 26.1, 26.2, 28.7, 33.0, 59.2, 60.4, 75.1, 119.5 (2C), 124.1, 128.7 (2C), 139.6, 178.7; IR (KBr, neat):  $\nu$  = 3404, 1670, 1599, 1501, 1406, 1326, 1231, 1142, 875, 754  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{15}\text{H}_{19}\text{NO}_2$ : C, 73.44; H, 7.81; N, 5.71; Found: C, 73.29; H, 7.86; N, 5.76. MS:  $m/z$   $[\text{M} + 1]^+$  calcd for  $\text{C}_{15}\text{H}_{19}\text{NO}_2^+$ : 246.1; found 246.1.



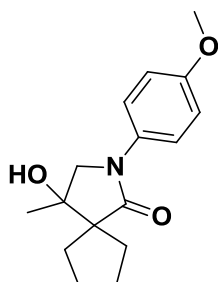
**4-Hydroxy-4-methyl-2-(*p*-tolyl)-2-azaspiro[4.4]nonan-1-one (3b)**

White solid; mp: 135–137 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.38 (s, 3H), 1.62 (br s, 1H), 1.73–1.77 (m, 4H), 1.86–1.88 (m, 3H), 1.98–2.02 (m, 1H), 2.32(s, 1H), 3.68 (ABq, *J*<sub>AB</sub> = 10.0 Hz, Δ*v*<sub>AB</sub> = 18.0 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 20.8, 21.2, 26.1, 26.2, 28.7, 33.1, 59.3, 60.4, 75.4, 119.6 (2C), 129.3 (2C), 133.8, 137.1, 178.3; IR (KBr, neat): ν = 3393, 2957, 1670, 1514, 1402, 1231, 814, 581, 515 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>21</sub>NO<sub>2</sub>: C, 74.10; H, 8.16; N, 5.40; Found: C, 74.31; H, 8.11; N, 5.16.



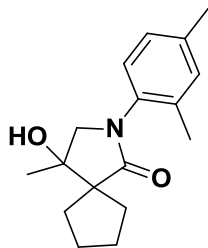
**2-(4-Chlorophenyl)-4-hydroxy-4-methyl-2-azaspiro[4.4]nonan-1-one (3c)**

White solid; mp: 143–144 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.39 (s, 3H), 1.61–1.74 (m, 5H), 1.84–1.86 (m, 3H), 1.98–2.02 (m, 1H), 3.67 (ABq, *J*<sub>AB</sub> = 10.0 Hz, Δ*v*<sub>AB</sub> = 19.0 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.2, 26.2, 26.3, 28.7, 33.4, 59.1, 60.5, 75.3, 120.5 (2C), 128.8 (2C), 129.2, 138.2, 178.5; IR (KBr, neat): ν = 3389, 2960, 1672, 1494, 1398, 1231, 1089, 829, 573 cm<sup>-1</sup>; Anal. Calcd for C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub>: C, 64.40; H, 6.49; N, 5.01; Found: C, 64.17; H, 6.53; N, 5.07.



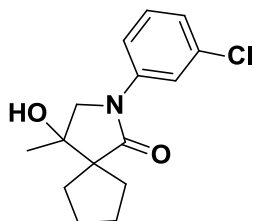
**4-Hydroxy-2-(4-methoxyphenyl)-4-methyl-2-azaspiro[4.4]nonan-1-one (3d)**

White solid; mp: 93–96 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.38 (s, 3H), 1.58–1.66 (m, 2H), 1.72–1.76 (m, 3H), 1.86–1.89 (m, 3H), 1.96–2.02 (m, 1H), 3.67 (ABq, *J*<sub>AB</sub> = 10.0 Hz, Δ*v*<sub>AB</sub> = 17.0 Hz, 2H), 3.79 (s, 3H), 6.89 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 21.2, 26.1, 26.2, 28.6, 33.1, 55.4, 59.6, 60.2, 75.4, 113.9 (2C), 121.2 (2C), 132.9, 156.3, 178.1; ν = 3419, 3128, 2953, 1670, 1516, 1398, 1288, 1252, 1032, 827 cm<sup>-1</sup>; Anal. Calcd for C<sub>16</sub>H<sub>21</sub>ClNO<sub>3</sub>: C, 69.79; H, 7.69; N, 5.09; Found: C, 69.98; H, 7.63; N, 5.15.



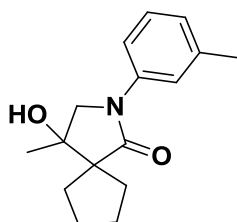
**2-(2,4-Dimethylphenyl)-4-hydroxy-4-methyl-2-azaspiro[4.4]nonan-1-one (3e)**

Yellow solid; mp: 88–91 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.38 (s, 3H), 1.73–1.76 (m, 2H), 1.84–1.99 (m, 5H), 2.11 (s, 3H), 2.23 (s, 3H), 3.28 (br s, 1H), 4.14 (d,  $J$  = 9.0 Hz, 1H), 4.57 (d,  $J$  = 9.0 Hz, 1H), 6.55 (d,  $J$  = 8.0 Hz, 1H), 6.90 (d,  $J$  = 8.5 Hz, 1H), 6.93 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 17.7 (2C), 20.3, 25.8, 25.9, 28.7, 31.5, 58.3, 61.9, 73.7, 115.1, 125.5, 127.0, 128.4, 131.7, 140.0, 181.4; IR (KBr, neat):  $\nu$  = 3442, 2955, 1771, 1616, 1512, 1387, 1308, 1263, 1138, 1032, 804  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{17}\text{H}_{21}\text{NO}_2$ : C, 74.69; H, 8.48; N, 5.12; Found: C, 74.42; H, 8.52; N, 5.17.



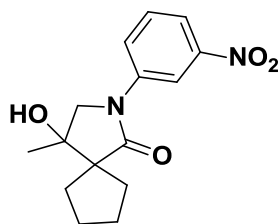
**2-(3-Chlorophenyl)-4-hydroxy-4-methyl-2-azaspiro[4.4]nonan-1-one (3f)**

Yellowish solid; mp: 105–108 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.31 (s, 3H), 1.52–1.56 (m, 1H), 1.63–1.71 (m, 3H), 1.75–1.96 (m, 5H), 3.60 (ABq,  $J_{\text{AB}}$  = 10.0 Hz,  $\Delta\nu_{\text{AB}}$  = 15.0 Hz, 2H), 7.01 (d,  $J$  = 8.0 Hz, 1H), 7.19 (t,  $J$  = 7.5 Hz, 1H), 7.44 (d,  $J$  = 8.5 Hz, 1H), 7.64 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.9, 26.0, 26.2, 28.5, 33.2, 59.0, 60.5, 74.9, 117.1, 119.4, 123.9, 129.6, 134.3, 140.6, 179.1; IR (KBr, neat):  $\nu$  = 3404, 2961, 1676, 1595, 1483, 1406, 1385, 1334, 1227, 876, 779, 681  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{ClNO}_2$ : C, 64.40; H, 6.49; N, 5.01; Found: C, 64.32; H, 6.42; N, 5.06;.



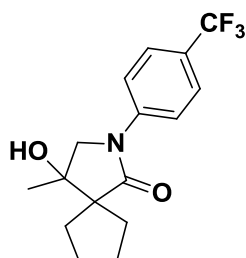
**4-Hydroxy-4-methyl-2-(m-tolyl)-2-azaspiro[4.4]nonan-1-one (3g)**

Yellow solid; mp: 98–100 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.38 (s, 3H), 1.59–1.63 (m, 1H), 1.72–1.76 (m, 3H), 1.83–2.01 (m, 4H), 2.35 (s, 3H), 3.69 (ABq,  $J_{\text{AB}}$  = 10.0 Hz,  $\Delta\nu_{\text{AB}}$  = 11.5 Hz, 2H), 6.94 (d,  $J$  = 7.5 Hz, 1H), 7.23 (t,  $J$  = 8.0 Hz, 1H), 7.36 (d,  $J$  = 8.0 Hz, 1H), 7.53 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.2, 21.5, 26.1, 26.2, 28.7, 32.9, 59.3, 60.4, 75.1, 116.5, 120.3, 124.9, 128.5, 138.5, 139.5, 178.7; IR (KBr, neat):  $\nu$  = 3369, 2959, 1666, 1495, 1391, 1333, 1231, 1188, 1142, 891, 773, 690  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}_2$ : C, 74.10; H, 8.16; N, 5.40; Found: C, 73.96; H, 8.12; N, 5.47.



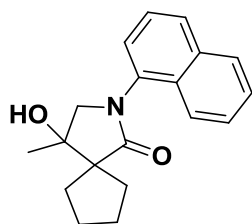
**4-Hydroxy-4-methyl-2-(3-nitrophenyl)-2-azaspiro[4.4]nonan-1-one (3h)**

White solid; mp: 140–142 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.42 (s, 3H), 1.63–1.78 (m, 4H), 1.82–1.91 (m, 4H), 2.00–2.05 (m, 1H), 3.76 (ABq,  $J_{\text{AB}} = 9.5$  Hz,  $\Delta\nu_{\text{AB}} = 14.0$  Hz, 2H), 7.50 (t,  $J = 8.0$  Hz, 1H), 7.94 (dd,  $J_1 = 1.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 8.15 (dd,  $J_1 = 1.0$  Hz,  $J_2 = 8.0$  Hz, 1H), 8.39 (t,  $J_1 = 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.9, 26.2, 26.3, 28.5, 33.6, 59.0, 60.7, 75.1, 113.6, 118.3, 124.8, 129.5, 140.6, 148.3, 179.5; IR (KBr, neat):  $\nu$  = 3358, 2962, 2869, 1663, 1421, 1406, 1329, 1221, 1132, 791, 759, 649  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4$ : C, 62.06; H, 6.25; N, 9.65; Found: C, 62.32; H, 6.17; N, 9.61.



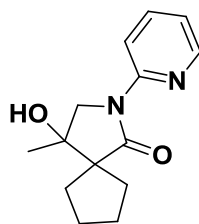
**4-Hydroxy-4-methyl-2-(4-(trifluoromethyl)phenyl)-2-azaspiro[4.4]nonan-1-one (3i)**

White solid; mp: 143–145 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.40 (s, 3H), 1.59–1.63 (m, 1H), 1.71–1.77 (m, 4H), 1.82–1.90 (m, 3H), 1.98–2.03 (m, 1H), 3.72 (ABq,  $J_{\text{AB}} = 10.0$  Hz,  $\Delta\nu_{\text{AB}} = 14.0$  Hz, 2H), 7.59 (d,  $J = 8.5$  Hz, 2H), 7.76 (d,  $J = 8.5$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.5, 25.7, 25.8, 28.1, 33.0, 58.5, 60.2, 74.6, 118.4 (q,  $^2J_{\text{C-F}} = 28$  Hz, 3C), 123.4 (q,  $^1J_{\text{C-F}} = 270$  Hz, 1C), 125.5 (2C), 142.1, 178.9; IR (KBr, neat):  $\nu$  = 3433, 2966, 1693, 1674, 1914, 1524, 1398, 1325, 1117, 1068, 841  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{F}_3\text{NO}_2$ : C, 61.33; H, 5.79; N, 4.47; Found: C, 61.14; H, 5.85; N, 4.42.



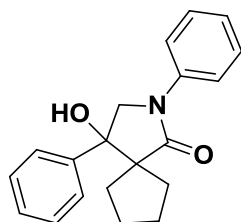
**4-Hydroxy-4-methyl-2-(naphthalen-1-yl)-2-azaspiro[4.4]nonan-1-one (3j)**

Yellowish solid; mp: 146–148 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.40 (s, 3H), 1.63–1.78 (m, 2H), 1.86–1.91 (m, 5H), 2.02–2.12 (m, 2H), 3.66 (ABq,  $J_{\text{AB}} = 10.0$  Hz,  $\Delta\nu_{\text{AB}} = 27.0$  Hz, 2H), 7.31 (d,  $J = 7.0$  Hz, 1H), 7.73–7.50 (m, 3H), 7.80 (d,  $J = 8.5$  Hz, 1H), 7.84–7.88 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.1, 26.1, 26.2, 28.3, 32.9, 59.3, 62.2, 76.3, 122.9, 124.6, 125.4, 126.1, 126.5, 127.9, 128.2, 130.0, 134.4, 135.4, 179.7; IR (KBr, neat):  $\nu$  = 3462, 2962, 1676, 1526, 1398, 1348, 1279, 1138, 741, 671  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{19}\text{H}_{21}\text{NO}_2$ : C, 77.26; H, 7.17; N, 4.74; Found: C, 77.52; H, 7.14; N, 4.66.



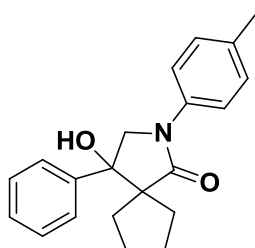
**4-Hydroxy-4-methyl-2-(pyridin-2-yl)-2-azaspiro[4.4]nonan-1-one (3k)**

White solid; mp: 100–102 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.39 (s, 3H), 1.60–2.06 (m, 8H), 3.88 (d, *J* = 11.5 Hz, 1H), 4.06 (d, *J* = 11.5 Hz, 1H), 7.01 (dd, *J*<sub>1</sub> = 5.5 Hz, *J*<sub>2</sub> = 7.0 Hz, 1H), 7.68 (dt, *J*<sub>1</sub> = 2.0 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 8.32 (d, *J* = 4.0 Hz, 2H), 8.40 (d, *J* = 8.5 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 20.7, 26.0, 26.1, 28.3, 33.4, 57.7, 61.1, 74.4, 114.7, 119.0, 137.4, 147.1, 151.7, 179.6; IR (KBr, neat): ν = 3447, 2959, 1672, 1585, 1468, 1437, 1396, 1319, 1221, 1147, 870, 787 cm<sup>-1</sup>; Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 68.27; H, 7.37; N, 11.37; Found: C, 68.46; H, 7.43; N, 11.30.



**4-Hydroxy-2,4-diphenyl-2-azaspiro[4.4]nonan-1-one (3n)**

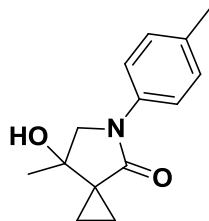
Yellowish solid; mp: 166–168 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.03–1.11 (m, 1H), 1.41–1.57 (m, 3H), 1.57–1.68 (m, 3H), 1.75–1.84 (m, 2H), 2.10–2.23 (m, 2H), 3.84 (d, *J* = 10.0 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 7.16 (t, *J* = 5.5 Hz, 1H), 7.35–7.44 (m, 5H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 24.7\*, 25.7, 26.0, 28.6, 29.7\*, 34.2, 39.9\*, 57.9, 61.7, 78.9, 119.7 (2C), 124.3, 126.1 (2C), 128.1, 128.4 (2C), 128.9 (2C), 139.5, 140.3, 178.1; IR (KBr, neat): ν = 3340, 1670, 1597, 1499, 1406, 1325, 1219, 750, 689 cm<sup>-1</sup>; Anal. Calcd for C<sub>20</sub>H<sub>21</sub>NO<sub>2</sub>: C, 78.15; H, 6.89; N, 4.56; Found: C, 77.96; H, 6.95; N, 4.59.



**4-Hydroxy-4-phenyl-2-(p-tolyl)-2-azaspiro[4.4]nonan-1-one (3o)**

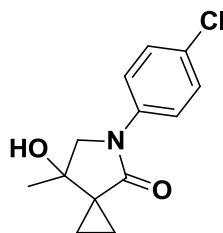
Yellowish solid; mp: 155–158 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.02–1.12 (m, 1H), 1.38–1.52 (m, 2H), 1.56–1.68 (m, 2H), 1.73–1.68 (m, 1H), 2.04–2.24 (m, 3H), 2.34 (s, 3H), 3.81 (d, *J* = 10.0 Hz, 1H), 4.46 (d, *J* = 10.0 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.33–7.43 (m, 3H), 7.57 (t, *J* = 8.0 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 20.8, 25.7, 26.0, 28.7, 34.2, 58.1, 61.7, 79.0, 119.7 (2C), 126.1 (2C), 128.1, 128.4 (2C), 129.4 (2C), 133.9, 137.1, 140.4, 177.8; IR (KBr, neat): ν = 3373, 2951, 1666, 1514,

1400, 1333, 1219, 812, 702  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}_2$ : C, 78.47; H, 7.21; N, 4.36; Found: C, 78.69; H, 7.25; N, 4.29.



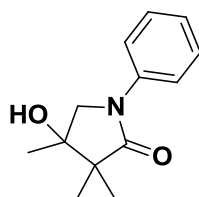
**7-Hydroxy-7-methyl-5-(p-tolyl)-5-azaspiro[2.4]heptan-4-one (3p)**

White solid; mp: 114–116 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.96–1.03 (m, 2H), 1.15–1.23 (m, 2H), 1.26 (s, 3H), 1.78 (br s, 1H), 2.32 (s, 3H), 3.89 (ABq,  $J_{\text{AB}}$  = 10.0 Hz,  $\Delta\nu_{\text{AB}}$  = 21.0 Hz, 2H), 7.16 (d,  $J$  = 8.5 Hz, 2H), 7.49 (d,  $J$  = 9.0 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.1, 13.2, 20.8, 23.8, 34.9, 61.0, 71.2, 119.6 (2C), 129.3 (2C), 133.9, 136.9, 173.9; IR (KBr, neat):  $\nu$  = 3362, 1728, 1670, 1516, 1419, 1309, 966, 822, 625, 513  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{14}\text{H}_{17}\text{NO}_2$ : C, 72.70; H, 7.41; N, 6.06; Found: C, 72.93; H, 7.36; N, 6.04.



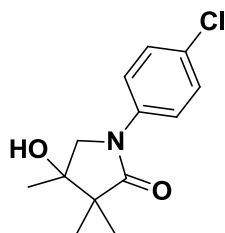
**5-(4-Chlorophenyl)-7-hydroxy-7-methyl-5-azaspiro[2.4]heptan-4-one (3q)**

Yellowish solid; mp: 133–136 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.96–1.06 (m, 2H), 1.14–1.18 (m, 2H), 1.25 (s, 3H), 2.13 (br s, 1H), 3.86 (ABq,  $J_{\text{AB}}$  = 10.0 Hz,  $\Delta\nu_{\text{AB}}$  = 19.0 Hz, 2H), 7.31 (d,  $J$  = 9.0 Hz, 2H), 7.55 (d,  $J$  = 9.0 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.3, 13.7, 23.7, 34.9, 60.8, 71.0, 120.6 (2C), 128.8 (2C), 129.3, 137.9, 174.3; IR (KBr, neat):  $\nu$  = 3344, 1678, 1501, 1394, 1306, 1223, 1144, 827, 739, 521  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{ClNO}_2$ : C, 62.03; H, 5.61; N, 5.56; Found: C, 62.22; H, 5.67; N, 5.52.



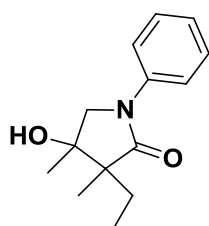
**4-Hydroxy-3,3,4-trimethyl-1-phenylpyrrolidin-2-one (3u)**

White solid; mp: 98–100 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.12 (s, 3H), 1.22 (s, 3H), 1.37 (s, 3H), 1.78 (s, 1H), 3.74 (ABq,  $J_{\text{AB}}$  = 10.0 Hz,  $\Delta\nu_{\text{AB}}$  = 34.0 Hz, 2H), 7.13 (t,  $J$  = 7.0 Hz, 1H), 7.36 (t,  $J$  = 7.5 Hz, 2H), 7.62 (d,  $J$  = 7.5 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 17.0, 21.1, 21.4, 49.4, 58.6, 75.2, 119.7 (2C), 124.3, 128.8 (2C), 139.4, 177.9; IR (KBr, neat):  $\nu$  = 3364, 1674, 1597, 1497, 1398, 1315, 1159, 1099, 763, 692, 633  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{13}\text{H}_{17}\text{NO}_2$ : C, 71.21; H, 7.81; N, 6.39; Found: C, 71.03; H, 7.88; N, 6.43.



**1-(4-Chlorophenyl)-4-hydroxy-3,3,4-trimethylpyrrolidin-2-one (3v)**

White solid; mp: 95–97 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.12 (s, 3H), 1.21 (s, 3H), 1.38 (s, 3H), 1.91 (br s, 1H), 3.66 (d,  $J$  = 11.0 Hz, 1H), 3.75 (d,  $J$  = 11.0 Hz, 1H), 7.31 (d,  $J$  = 9.0 Hz, 2H), 7.59 (d,  $J$  = 7.0 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 17.3, 21.2, 21.9, 49.8, 58.9, 75.4, 121.1 (2C), 129.0 (2C), 129.6, 138.3, 178.6; IR (KBr, neat):  $\nu$  = 3396, 2970, 1684, 1593, 1499, 1394, 1306, 1215, 1089, 829  $\text{cm}^{-1}$ ; Anal. Calcd for  $\text{C}_{13}\text{H}_{16}\text{ClNO}_2$ : C, 61.54; H, 6.36; N, 5.52; Found: C, 61.25; H, 6.40; N, 5.46.



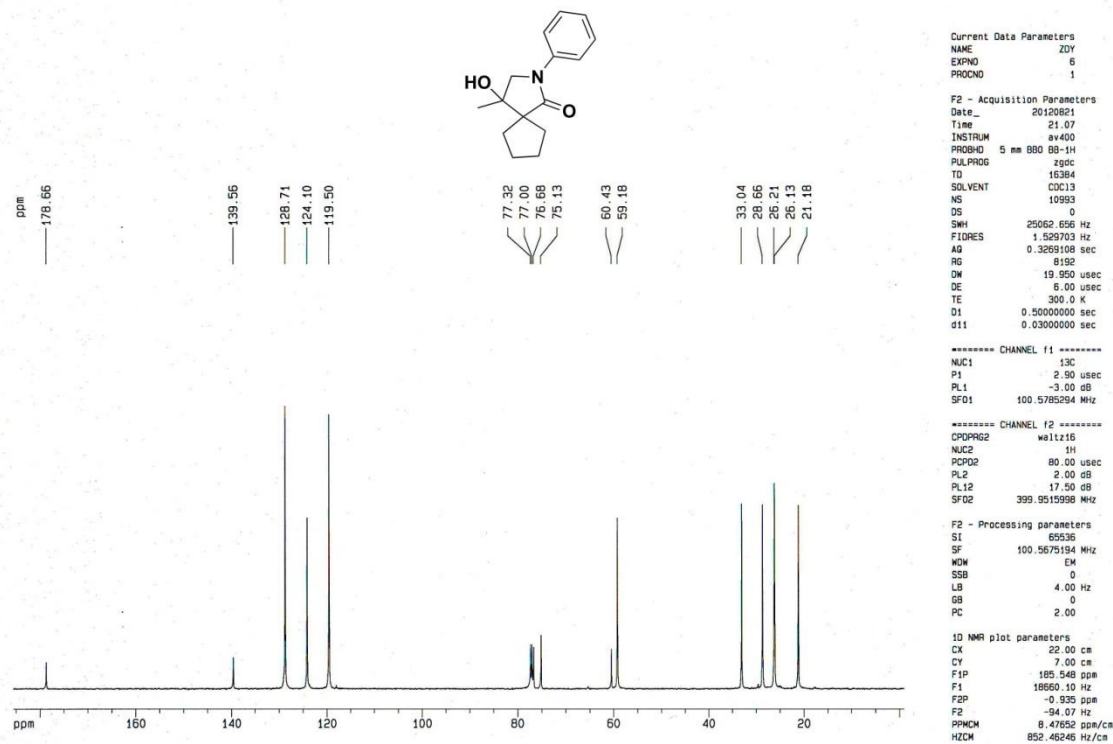
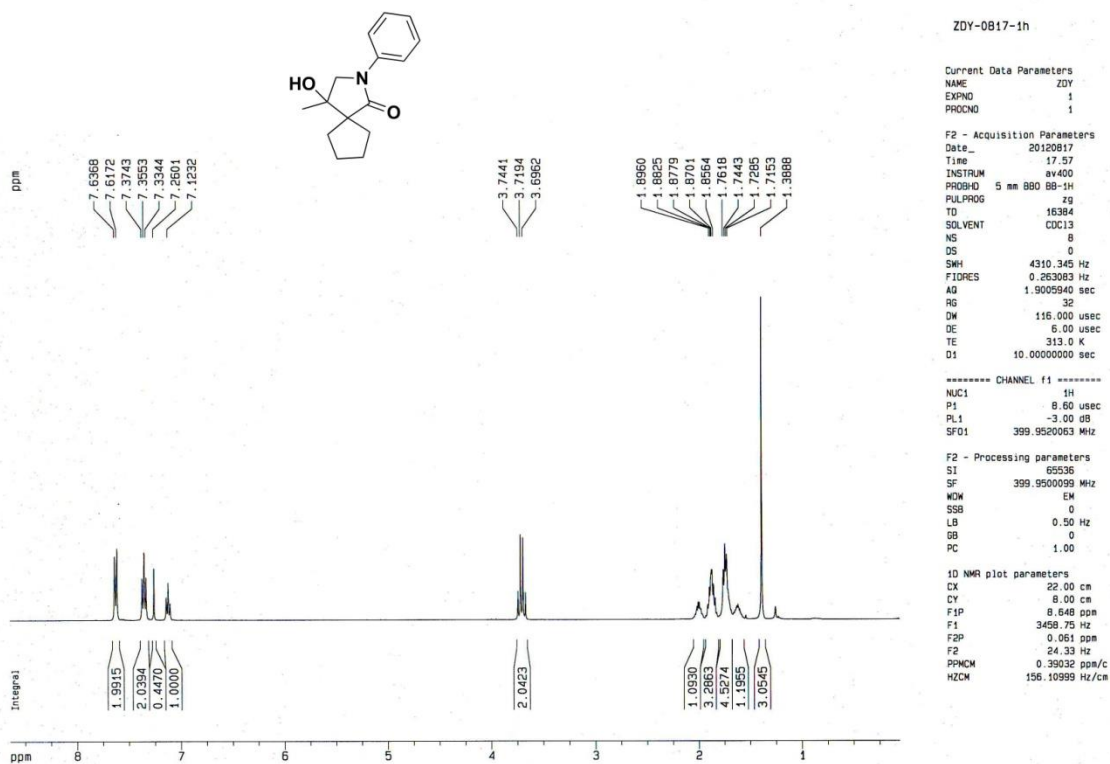
**3-Ethyl-4-hydroxy-3,4-dimethyl-1-phenylpyrrolidin-2-one (3w)**

White solid; mp: 71–74 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.06 (t,  $J$  = 7.5 Hz, 3H), 1.07 (s, 3H), 1.41 (s, 3H), 1.71–1.81 (m, 2H), 1.84 (br s, 1H), 3.70 (ABq,  $J_{\text{AB}}$  = 10.0 Hz,  $\Delta\nu_{\text{AB}}$  = 8.0 Hz, 2H), 7.13 (t,  $J$  = 7.5 Hz, 1H), 7.35 (t,  $J$  = 8.0 Hz, 2H), 7.61 (d,  $J$  = 8.0 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.7, 17.2, 22.9, 24.8, 51.4, 58.9, 75.7, 118.3\*, 119.7 (2C), 123.8\*, 124.3, 128.7, 8 (2C), 129.1\*, 139.3, 177.7; Anal. Calcd for  $\text{C}_{14}\text{H}_{19}\text{NO}_2$ : C, 72.07; H, 8.21; N, 6.00; Found: C, 71.84; H, 8.25; N, 6.07. (\* might belong to the minor diastereoisomer)

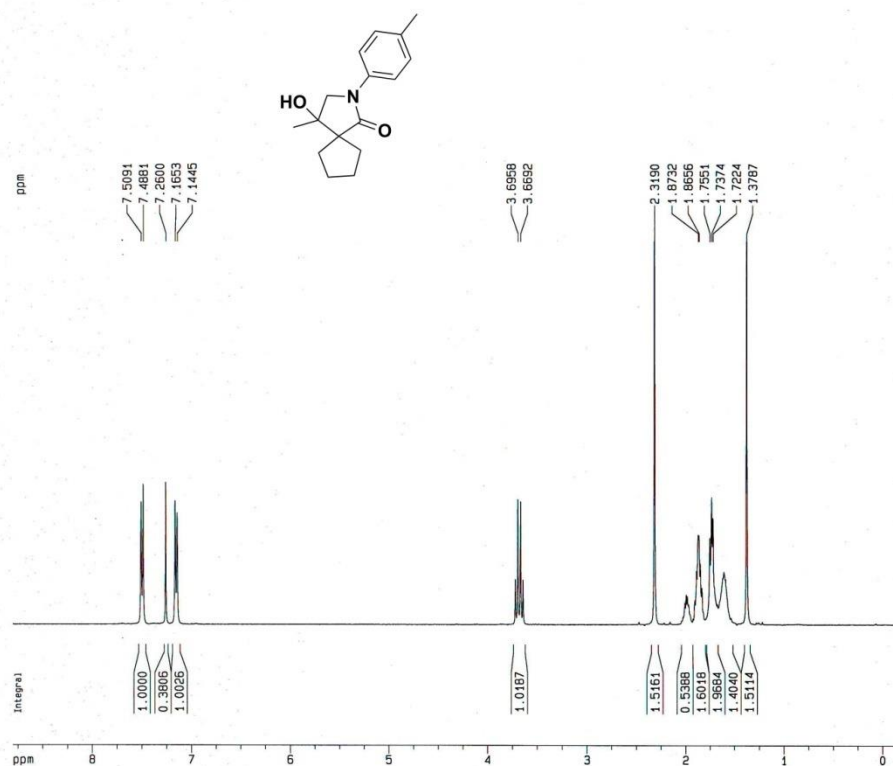


### III. Copies of NMR spectra for compounds 3

3a



3b



ZDY-0719-1

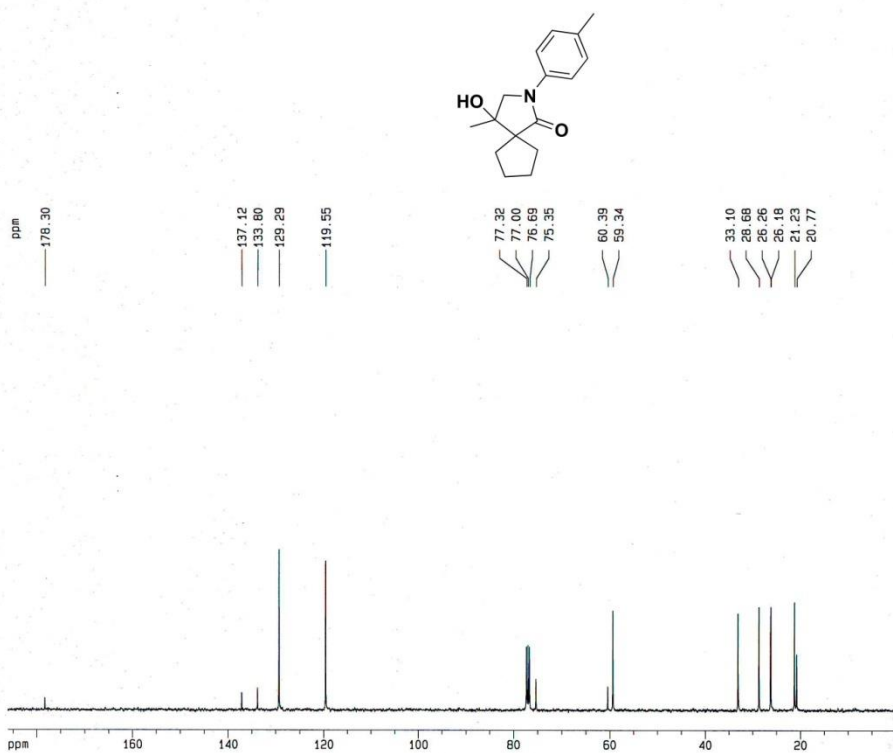
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 PROCNO 1

F2 - Acquisition Parameters  
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 PULPROG zg  
 TD 16384  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SMH 4432.624 Hz  
 FIDRES 0.270546 Hz  
 AQ 1.8481552 sec  
 RG 128  
 DM 112.800 usec  
 DE 6.00 usec  
 TE 313.0 K  
 D1 10.0000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
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 P1 6.50 usec  
 PL1 -3.00 dB  
 SFO1 399.9519288 MHz

F2 - Processing parameters  
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 SF 399.950160 MHz  
 WDM EM  
 SSB 0  
 LB 0.50 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
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 CY 12.00 cm  
 F1P 6.862 ppm  
 F1 3520.30 Hz  
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 F2 -79.46 Hz  
 PPMCM 0.40911 ppm/c  
 HZCM 163.62547 Hz/c



ZDY-0719-2

Current Data Parameters  
 NAME ZDY  
 EXPNO 3  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120720  
 Time 17.06  
 INSTRUM av400  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zgpg30  
 TD 16384  
 SOLVENT CDCl3  
 NS 1387  
 DS 0  
 SMH 2562.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 8192  
 DM 19.950 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.5000000 sec  
 d11 0.0300000 sec

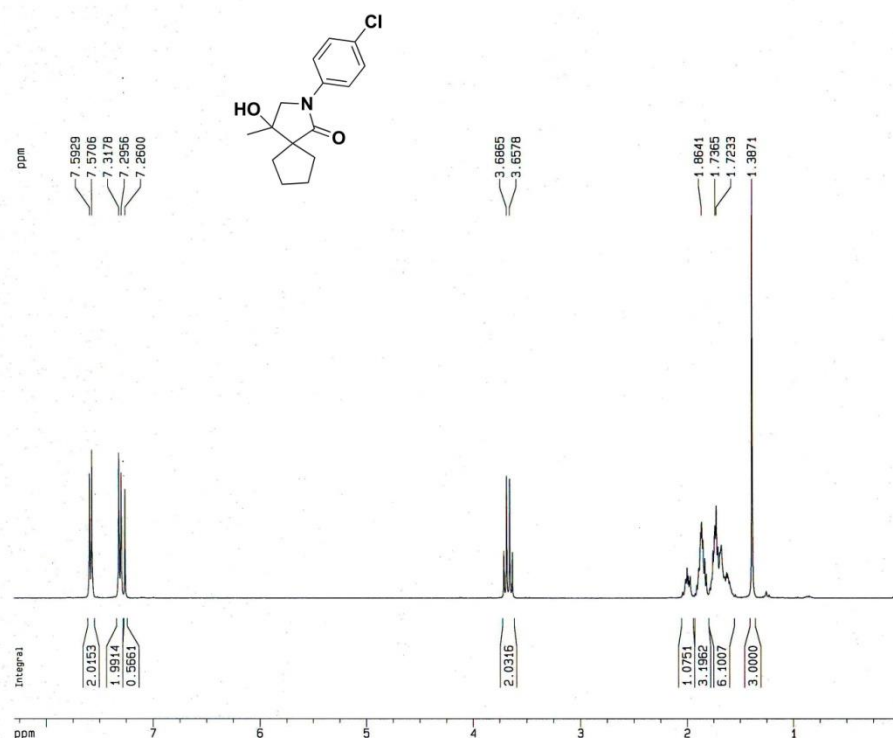
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 PL1 -3.00 dB  
 SFO1 100.5785294 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPROG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SFO2 399.9515998 MHz

F2 - Processing parameters  
 S1 65536  
 SF 100.5675133 MHz  
 WDM EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 4.00 cm  
 F1P 186.063 ppm  
 F1 18711.90 Hz  
 F2P -0.296 ppm  
 F2 -29.76 Hz  
 PPMCM 8.47087 ppm/c  
 HZCM 851.89471 Hz/c

3c



Zdy-0720-2h

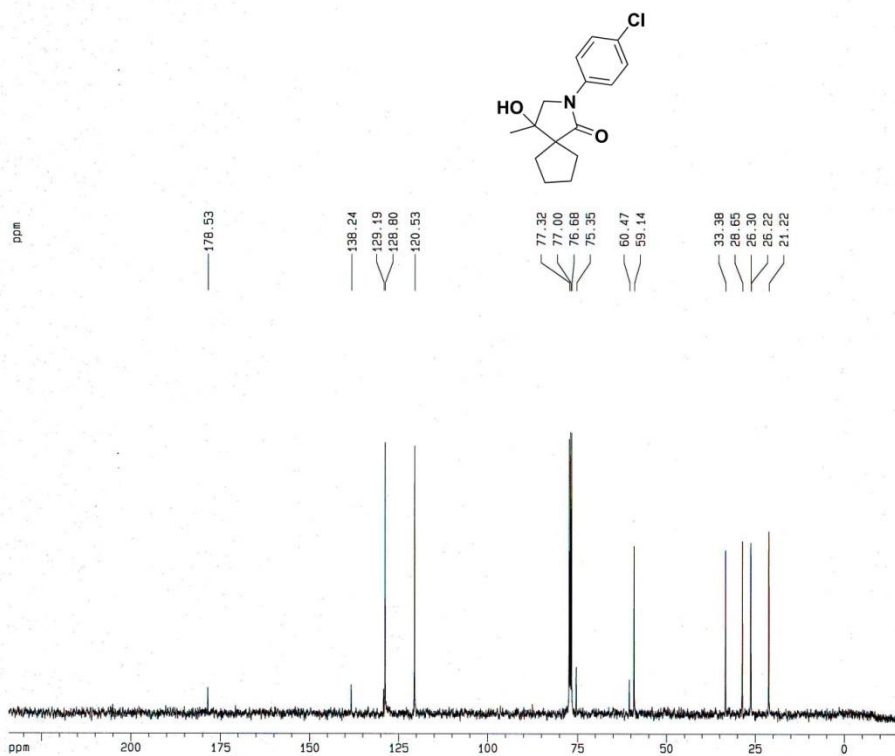
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 PROCNO 1

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 PULPROG zgpg30  
 TD 16384  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 4340.278 Hz  
 FIDRES 0.254910 Hz  
 AQ 1.8874868 sec  
 RG 32  
 DW 115.200 usec  
 DE 6.00 usec  
 TE 313.0 K  
 D1 10.0000000 sec

----- CHANNEL f1 -----  
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 P1 6.50 usec  
 PL1 -3.00 dB  
 SFO1 399.9519477 MHz

F2 - Processing parameters  
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 SF 399.9500104 MHz  
 WDW EM  
 SSB 0  
 LB 0.50 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 12.00 cm  
 F1P 8.299 ppm  
 F1 3319.31 Hz  
 F2P -0.035 ppm  
 F2 -13.90 Hz  
 PPMCM 0.37882 ppm/c  
 HZCM 151.50919 Hz/cm



ZDY-0817-3C

Current Data Parameters  
 NAME ZDY  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120817  
 Time 23.47  
 INSTRUM av400  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zgpg30  
 TD 16384  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 8192  
 DW 19.950 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.5000000 sec  
 d11 0.0300000 sec

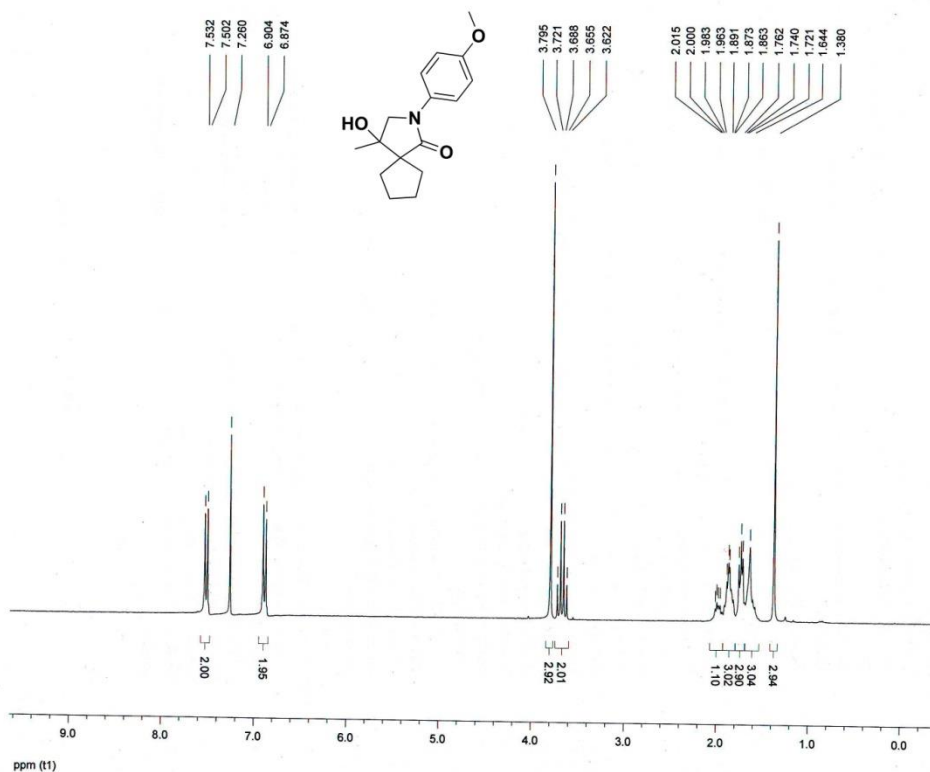
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 P1 2.90 usec  
 PL1 -3.00 dB  
 SFO1 100.5785294 MHz

----- CHANNEL f2 -----  
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 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 2.00 dB  
 PL12 17.50 dB  
 SFO2 399.9515998 MHz

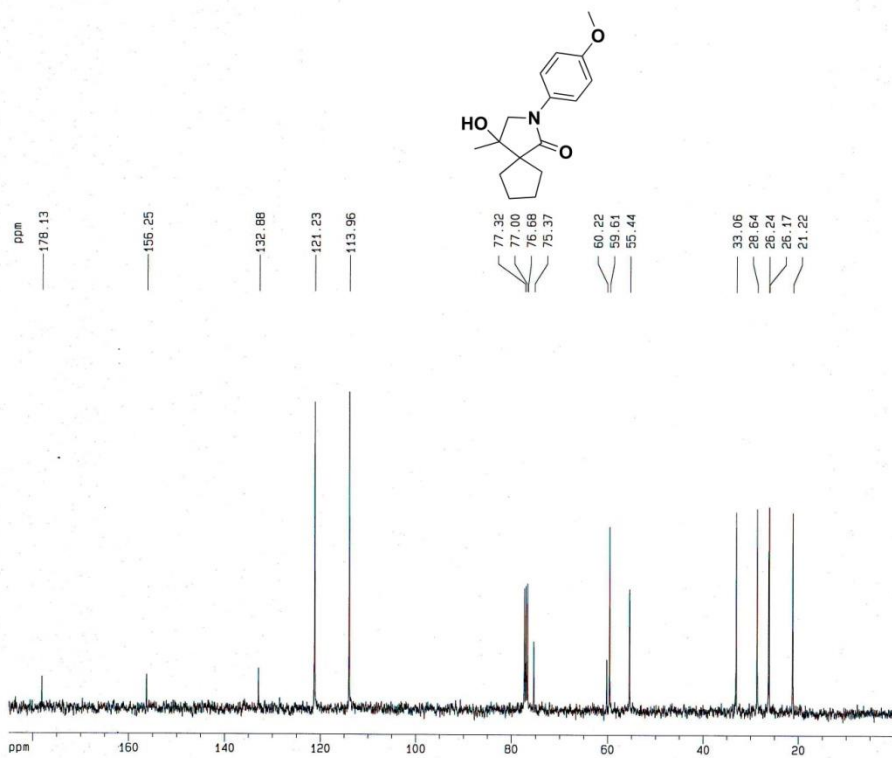
F2 - Processing parameters  
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 SF 100.5675106 MHz  
 WDW EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 2.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 7.00 cm  
 F1P 234.172 ppm  
 F1 23550.12 Hz  
 F2P -15.040 ppm  
 F2 -1512.53 Hz  
 PPMCM 11.32783 ppm/cm  
 HZCM 1139.21167 Hz/cm

3d



Date: 26 Jul 2012  
 Document's Title: 1  
 Spectrum Title: 1H  
 Frequency (MHz): (f1) 300.132  
 Original Points Count: (f1) 16384  
 Actual Points Count: (f1) 32768  
 Acquisition Time (sec): (f1) 2.6477  
 Spectral Width (ppm): (f1) 20.618  
 Pulse Program: ZG30  
 Temperature: 0  
 Number of Scans: 9  
 Acq. Date: Wed Jul 25 02:24:35 PM



ZDY-0906-4C

Current Data Parameters  
 NAME ZDY  
 EXPNO 4  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120906  
 Time 18.59  
 INSTRUM ex400  
 PROBHD 5 mm BBO 5H-1H  
 PULPROG zgpg30  
 TD 16384  
 SOLVENT CDCl3  
 NS 202  
 DS 0  
 SMH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 3152  
 DM 19.950 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.50000000 sec  
 d11 0.03000000 sec

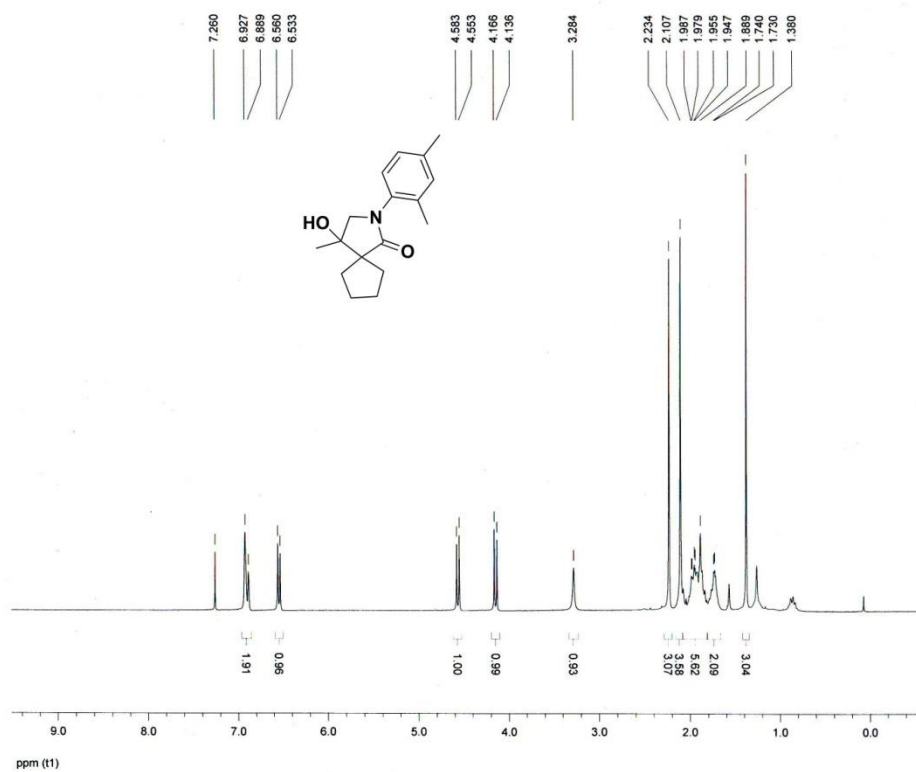
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 PL1 -3.00 dB  
 SFO1 100.5785294 MHz

----- CHANNEL f2 -----  
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 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.00 dB  
 SFO2 399.9515998 MHz

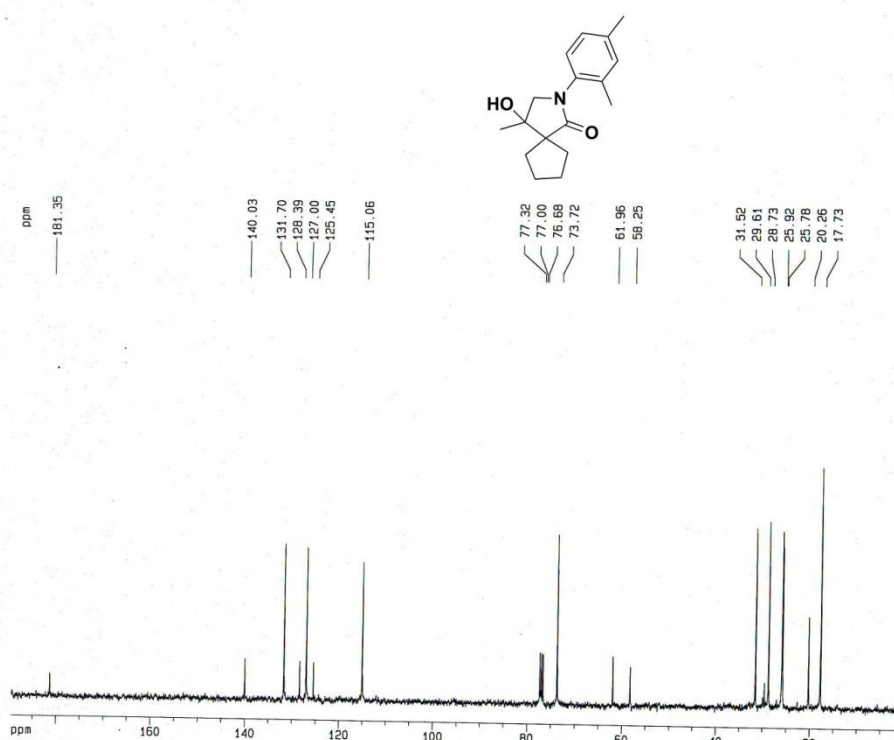
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 MDW EM  
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 LB 4.00 Hz  
 GB 0  
 PC 0.30

1D NMR plot parameters  
 CX 22.00 cm  
 CY 8.00 cm  
 F1P 184.956 ppm  
 F1 18500.60 Hz  
 F2P -0.790 ppm  
 F2 -79.43 Hz  
 PPMCM 8.44301 ppm/cm  
 HZCM 849.09241 Hz/cm

3e



Date: 17 Oct 2012  
 Document's Title: 1  
 Spectrum Title: 1H  
 Frequency (MHz): (f1) 300.132  
 Original Points Count: (f1) 16384  
 Actual Points Count: (f1) 32768  
 Acquisition Time (sec): (f1) 2.6477  
 Spectral Width (ppm): (f1) 20.618  
 Pulse Program: ZG30  
 Temperature: 0  
 Number of Scans: 7  
 Acq. Date: Wed Aug 29 02:22:09 PM



ZDY-0831-2C

Current Data Parameters  
 NAME ZDY  
 EXPNO 13  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 2012031  
 Time 18.30  
 INSTRUM av400  
 PROBNM 5 mm BBO BB-1H  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 209  
 DS 0  
 SFO1 25062.655 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3289108 sec  
 RG 8192  
 DM 19.950 usec  
 DE 8.00 usec  
 TE 300.0 K  
 D1 0.50000000 sec  
 d11 0.03000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 2.90 usec  
 PL1 -3.00 dB  
 SFO1 100.576294 MHz

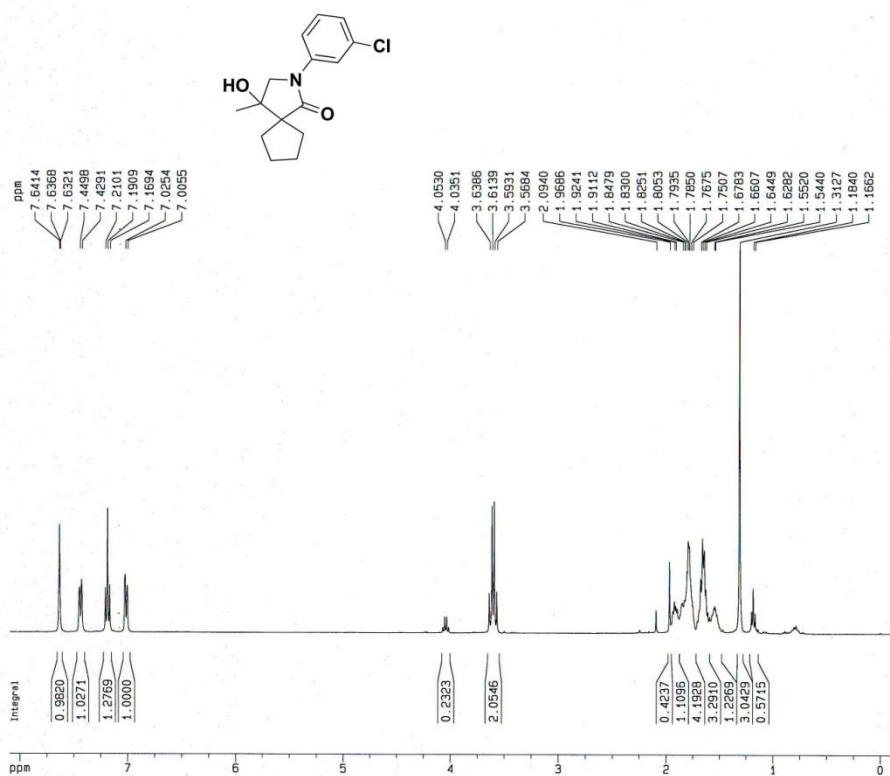
\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CH1PRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SFO2 399.9515988 MHz

F2 - Processing parameters  
 SI 69536  
 SF 100.5675266 MHz  
 KW 64  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 0.30

1D NMR plot parameters  
 CX 22.00 cm  
 CY 8.00 cm  
 F1P 189.456 ppm  
 F1 19053.11 Hz  
 F2P 0.712 ppm  
 F2 71.61 Hz  
 PRNOM 8.57825 ppm/cm  
 HZCM 862.79517 Hz/cm



3f



zhangdy0824-th

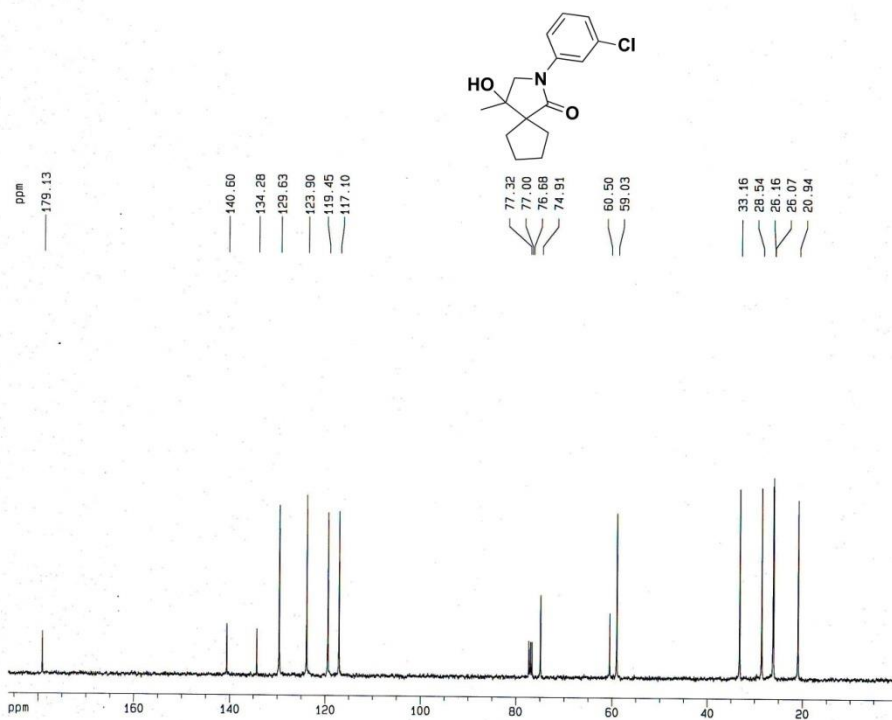
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 PROCNO 1

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 PULPROG zg  
 TD 16384  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SMH 5081.301 Hz  
 FIDRES 0.310138 Hz  
 AQ 1.6122355 sec  
 RG 128  
 DW 98.400 usec  
 DE 6.00 usec  
 TE 313.0 K  
 D1 10.00000000 sec

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 8.60 usec  
 PL1 -3.00 dB  
 SFO1 399.9521933 MHz

F2 - Processing parameters  
 SI 65536  
 SF 399.9500374 MHz  
 WDW EM  
 SSB 0  
 LB 0.50 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 12.00 cm  
 F1P 8.097 ppm  
 F1 3238.43 Hz  
 F2P -0.180 ppm  
 F2 -71.94 Hz  
 PPMCM 0.37623 ppm/c  
 HZCM 150.47133 Hz/cm



ZDY-0831-1C

Current Data Parameters  
 NAME ZDY  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120831  
 Time 18.06  
 INSTRUM av400  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zgpg30  
 TD 16384  
 SOLVENT CDCl3  
 NS 149  
 DS 0  
 SMH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 8192  
 DW 19.950 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.50000000 sec  
 d11 0.03000000 sec

===== CHANNEL f1 =====  
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 P1 2.90 usec  
 PL1 -3.00 dB  
 SFO1 100.5785294 MHz

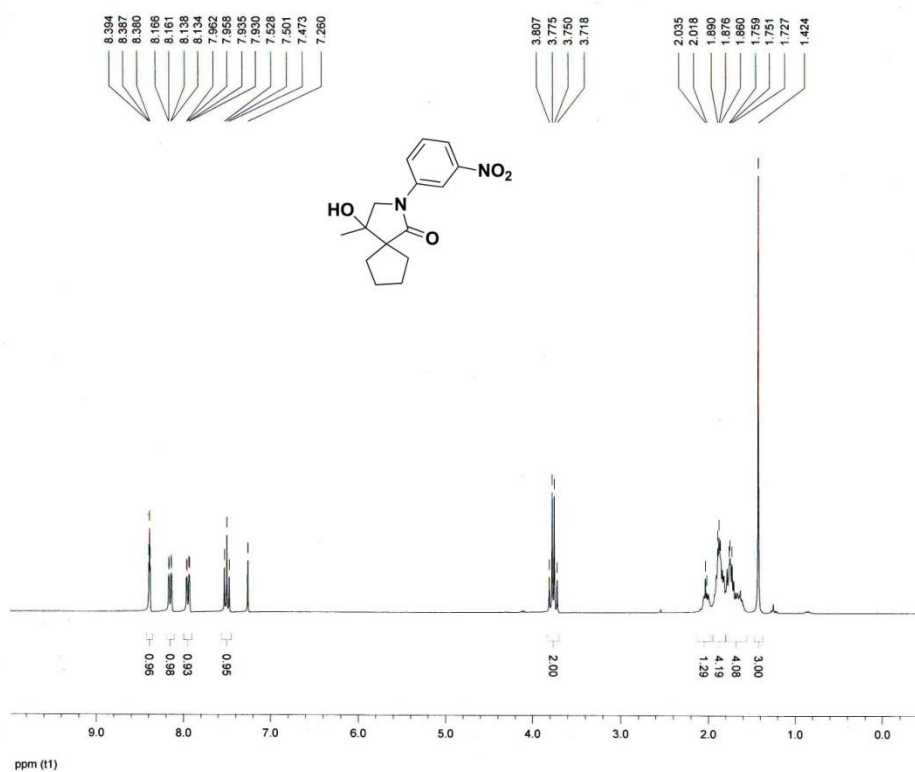
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 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SFO2 399.9515938 MHz

F2 - Processing parameters  
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 SF 100.5675240 MHz  
 WDW EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 0.30

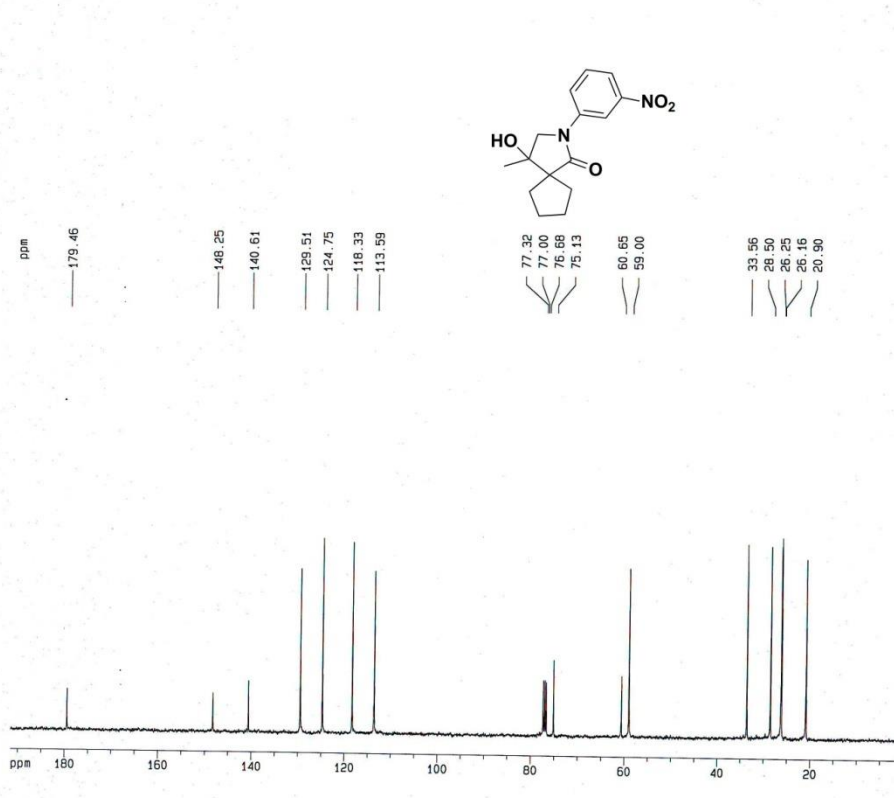
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 HZCM 850.71875 Hz/cm



3h



Date: 17 Oct 2012  
 Document's Title: 2  
 Spectrum Title: 1H  
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 Actual Points Count: (f1) 32768  
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 Spectral Width (ppm): (f1) 20.618  
 Pulse Program: ZG30  
 Temperature: 0  
 Number of Scans: 6  
 Acq. Date: Wed Aug 29 02:24:51 PM



0831-3C  
 ZDY-0831-3C

Current Data Parameters  
 NAME: ZDY  
 EXPNO: 12  
 PROCNO: 1

F2 - Acquisition Parameters  
 Date\_: 20120831  
 Time: 18:25  
 INSTRUM: av400  
 PROBHD: 5 mm BBO BB-1H  
 PULPROG: zgpg  
 TD: 16384  
 SOLVENT: CDCl3  
 NS: 792  
 DS: 0  
 SWH: 25062.656 Hz  
 FIDRES: 1.533703 Hz  
 AQ: 0.3269108 sec  
 RG: 8192  
 DW: 19.950 usec  
 DE: 6.00 usec  
 TE: 300.0 K  
 D1: 0.5000000 sec  
 d11: 0.0300000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1: 13C  
 P1: 2.90 usec  
 PL1: -3.00 dB  
 SFO1: 100.6261254 MHz

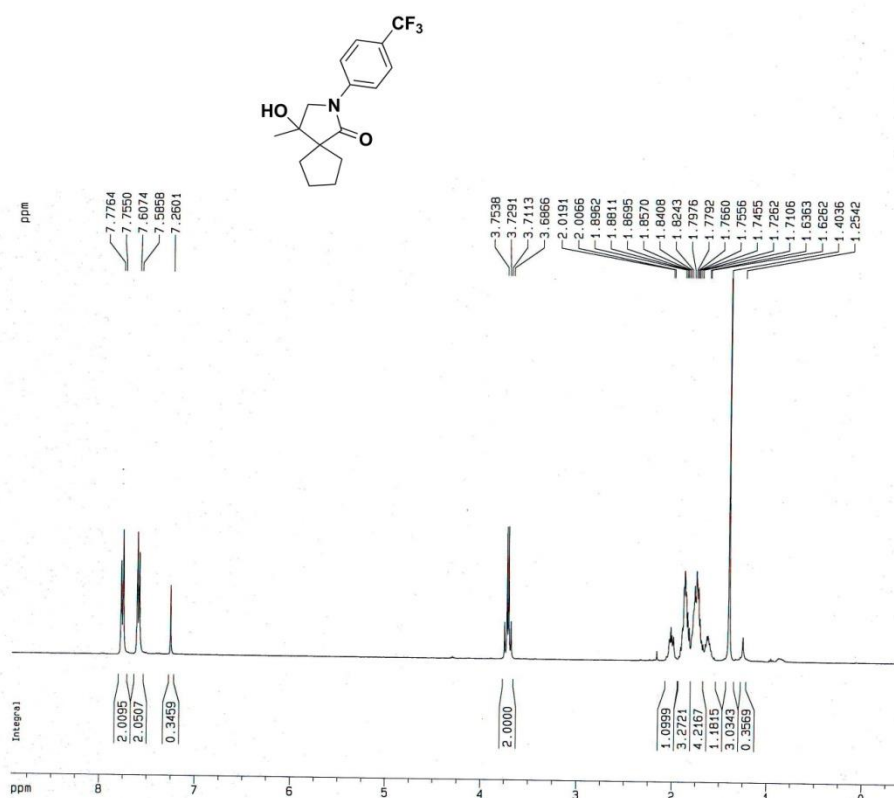
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 NUC2: 1H  
 PCPD2: 80.00 usec  
 PL2: -3.00 dB  
 PL12: 18.20 dB  
 SFO2: 399.9515998 MHz

F2 - Processing parameters  
 SI: 65536  
 SF: 100.6261254 MHz  
 NHX: EM  
 SSB: 0  
 LB: 4.00 Hz  
 GB: 0  
 PC: 0.30

ID NMR plot parameters  
 CX: 22.00 cm  
 CY: 5.00 cm  
 F1P: 151.537 ppm  
 F1: 15626.43 Hz  
 F2P: 0.739 ppm  
 F2: 74.29 Hz  
 PPMCM: 8.67266 ppm/cm  
 HZCM: 872.16605 Hz/cm



3i



ZDY-5-h

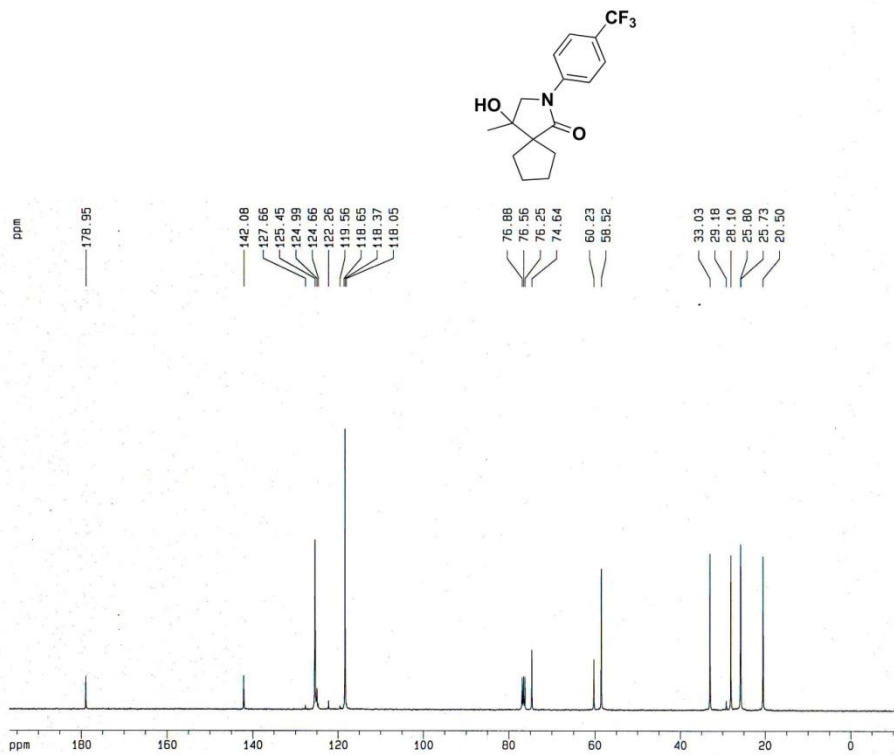
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 PROCNO 1

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 Time 0.15  
 INSTRUM av400  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zg  
 TD 16384  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 4562.044 Hz  
 FIDRES 0.278445 Hz  
 AQ 1.7957364 sec  
 RG 12  
 DM 109.600 usec  
 DE 6.00 usec  
 TE 313.0 K  
 D1 10.00000000 sec

----- CHANNEL f1 -----  
 NUC1 1H  
 P1 8.60 usec  
 PL1 -3.00 dB  
 SFO1 399.9519404 MHz

F2 - Processing parameters  
 SI 65536  
 SF 399.9500099 MHz  
 MDW EM  
 SSB 0  
 LB 0.50 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 12.00 cm  
 F1P 8.918 ppm  
 F1 3566.72 Hz  
 F2P -0.420 ppm  
 F2 -159.07 Hz  
 PPMCM 0.42446 ppm/c  
 HZCM 169.76332 Hz/cm



ZDY-0913-2C

Current Data Parameters  
 NAME ZDY  
 EXPNO 7  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120913  
 Time 20.15  
 INSTRUM av400  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zgpc  
 TD 16384  
 SOLVENT CDCl3  
 NS 4273  
 DS 0  
 SWH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 8192  
 DM 19.550 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.50000000 sec  
 d11 0.03000000 sec

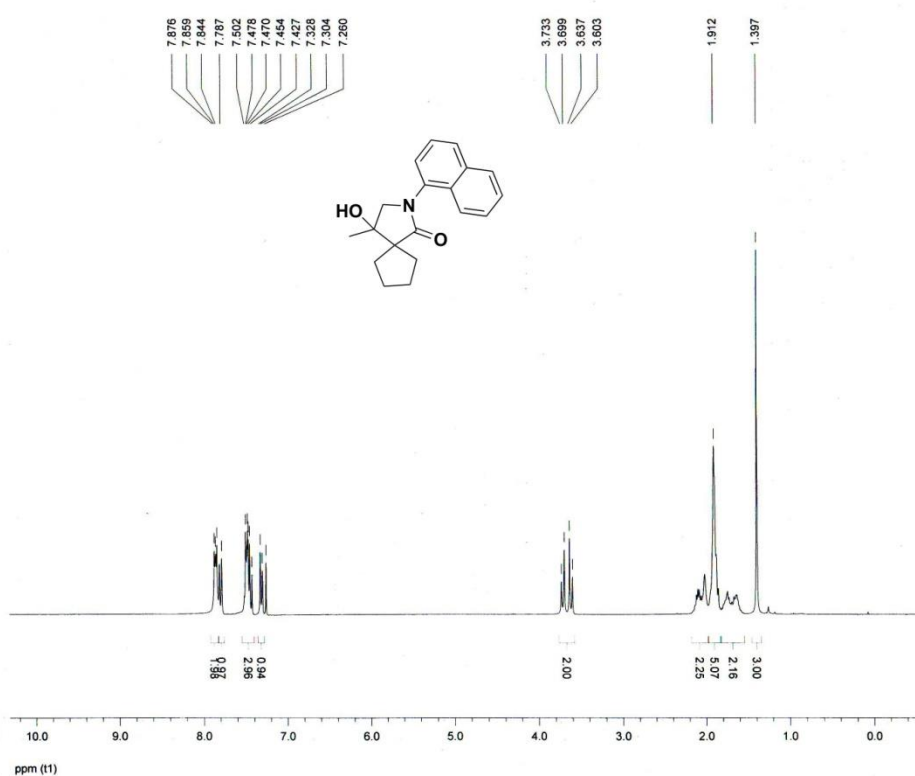
----- CHANNEL f1 -----  
 NUC1 13C  
 P1 2.90 usec  
 PL1 -3.00 dB  
 SFO1 100.5785294 MHz

----- CHANNEL f2 -----  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SFO2 399.9515999 MHz

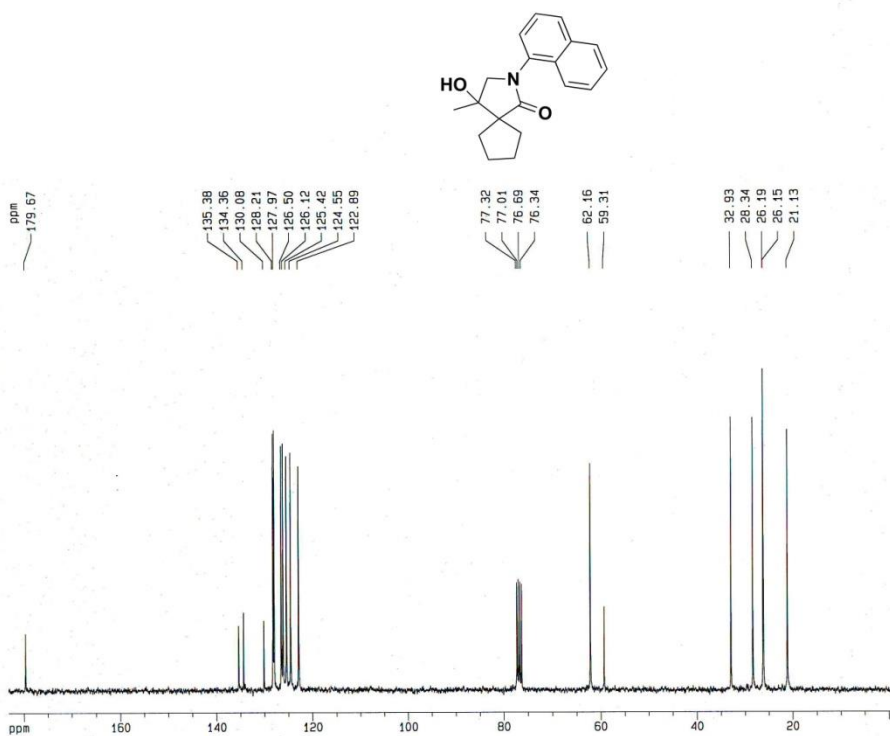
F2 - Processing parameters  
 SI 65536  
 SF 100.5675601 MHz  
 MDW EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 0.30

1D NMR plot parameters  
 CX 22.00 cm  
 CY 7.00 cm  
 F1P 196.796 ppm  
 F1 19791.33 Hz  
 F2P -11.545 ppm  
 F2 -1161.05 Hz  
 PPMCM 9.47006 ppm/cm  
 HZCM 952.38110 Hz/cm

3j



Date: 17 Oct 2012  
 Document's Title: 4  
 Spectrum Title: 1H  
 Frequency (MHz): (f1) 300.132  
 Original Points Count: (f1) 16384  
 Actual Points Count: (f1) 32768  
 Acquisition Time (sec): (f1) 2.6477  
 Spectral Width (ppm): (f1) 20.618  
 Pulse Program: ZG30  
 Temperature: 0  
 Number of Scans: 10  
 Acq. Date: Wed Sep 05 02:02:53 PM



ZDY-0906-3C

Current Data Parameters  
 NAME ZDY  
 EXPNO 2  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120906  
 Time 17.52  
 INSTRUM av400  
 PROBG 5 mm BBO BB-H  
 PULPROG zgpg  
 TD 16384  
 SOLVENT CDCl3  
 NS 505  
 DS 0  
 SMH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 512  
 DM 19.950 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.50000000 sec  
 d11 0.03000000 sec

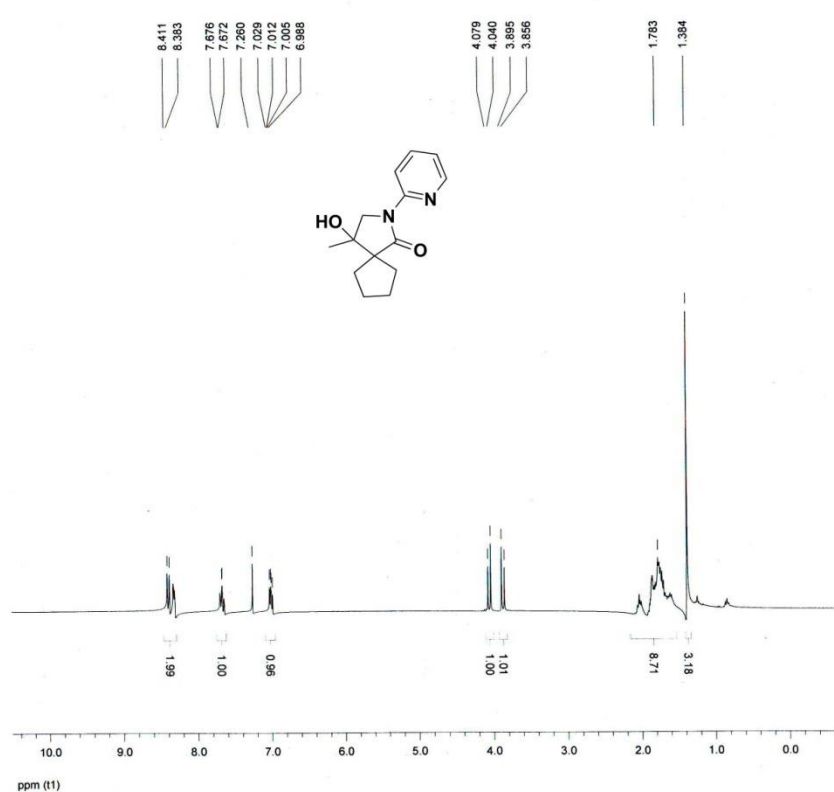
===== CHANNEL f1 =====  
 NUC1 13C  
 P1 2.90 usec  
 PL1 -3.00 dB  
 SFO1 100.5785294 MHz

===== CHANNEL f2 =====  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.00 dB  
 SFO2 399.9515998 MHz

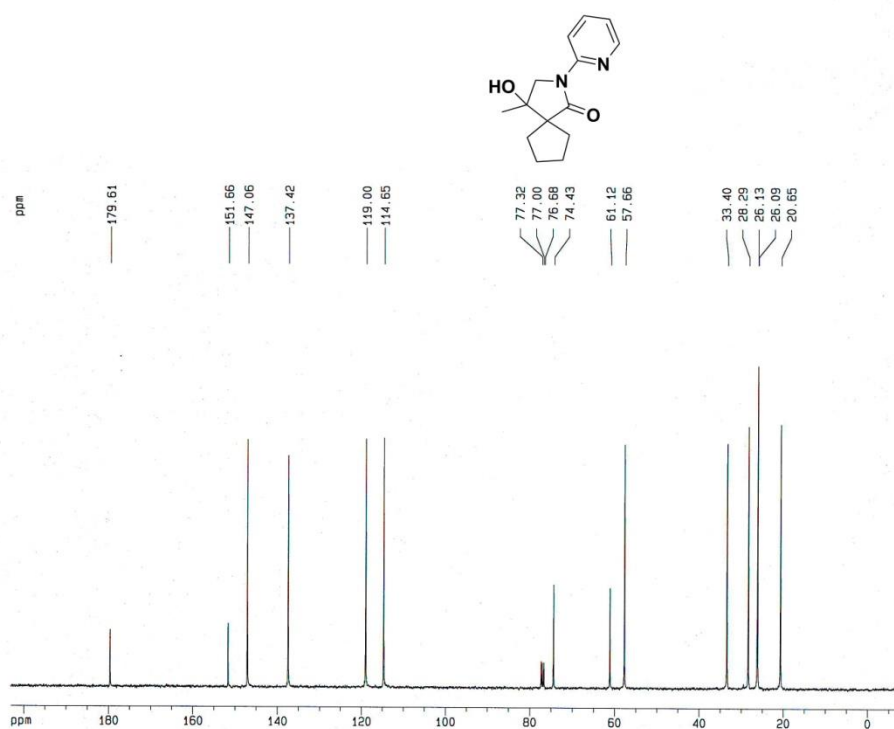
F2 - Processing parameters  
 SI 65536  
 SF 100.5675206 MHz  
 WDW EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 0.30

1D NMR plot parameters  
 CX 22.00 cm  
 CY 8.00 cm  
 F1P 183.234 ppm  
 F1 18427.40 Hz  
 F2P 0  
 F2 -185.80 Hz  
 RPKCM 8.41280 ppm/cm  
 HZCM 846.05450 Hz/cm

3k



Date: 17 Oct 2012  
 Document's Title: 1  
 Spectrum Title: 1H  
 Frequency (MHz): (f1) 300.132  
 Original Points Count: (f1) 16384  
 Actual Points Count: (f1) 32768  
 Acquisition Time (sec): (f1) 2.6477  
 Spectral Width (ppm): (f1) 20.618  
 Pulse Program: ZG30  
 Temperature: 0  
 Number of Scans: 7  
 Acq. Date: Wed Sep 19 02:27:53 PM



zdy-0921

Current Data Parameters  
 NAME zdy  
 EXPNO 4  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120924  
 Time 23.25  
 INSTRUM av400  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zgpg30  
 TD 16384  
 SOLVENT CDCl3  
 NS 244  
 DS 8  
 SWH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 8192  
 DM 19.250 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.5000000 sec  
 d11 0.0300000 sec

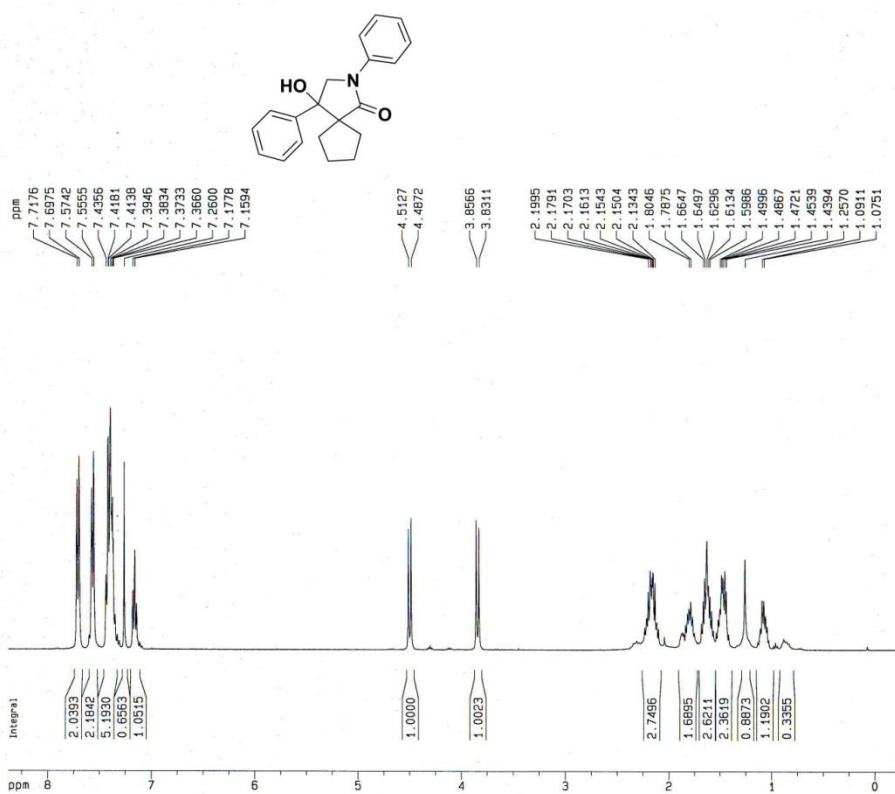
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 2.90 usec  
 PL1 -3.00 dB  
 SF01 100.5785294 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SF02 399.9515998 MHz

F2 - Processing parameters  
 S1 65936  
 SF 100.5675271 MHz  
 WDM EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 0.30

1D NMR plot parameters  
 CX 22.00 cm  
 CY 8.00 cm  
 F1P 203.106 ppm  
 F1 20425.91 Hz  
 F2P -7.561 ppm  
 F2 -760.39 Hz  
 PPMCM 9.57579 ppm/cm  
 HZCM 963.01361 Hz/cm

3n



ZDY-0B20-zh

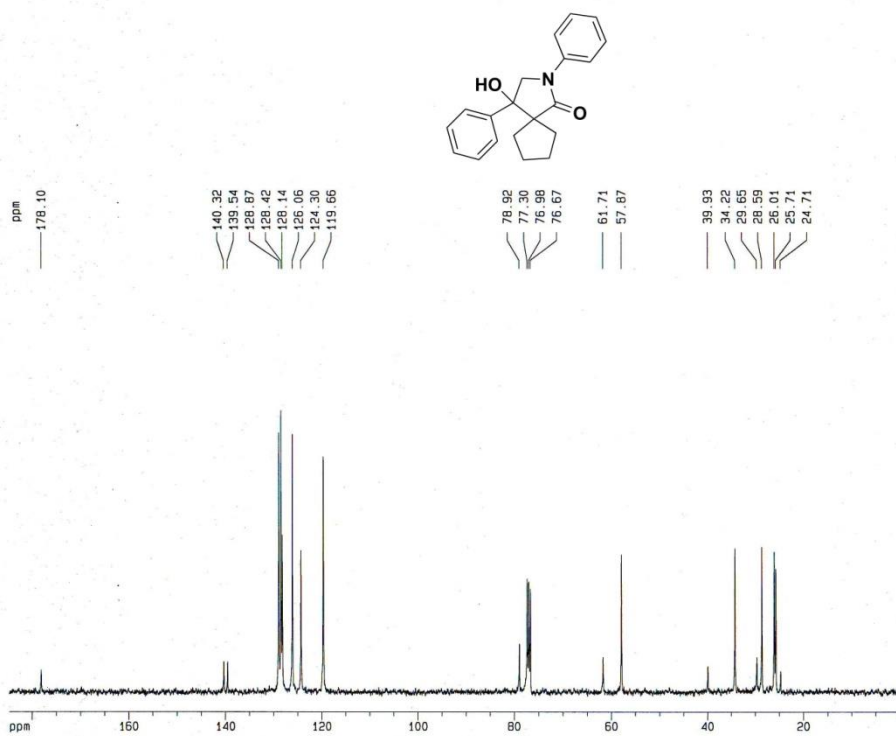
Current Data Parameters  
 NAME ZDY  
 EXPNO 5  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120821  
 Time 0.16  
 INSTRUM av400  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zg  
 TD 16384  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SMH 5144.033 Hz  
 FIDRES 0.319957 Hz  
 AQ 1.5925748 sec  
 RG 129  
 DM 97.200 usec  
 DE 6.00 usec  
 TE 313.0 K  
 D1 10.0000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 8.50 usec  
 PL1 -3.00 dB  
 SFO1 399.9519489 MHz

F2 - Processing parameters  
 SI 65536  
 SF 399.9500102 MHz  
 MDW  
 SSB 0  
 LB 0.50 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 6.00 cm  
 F1P 8.378 ppm  
 F1 3390.63 Hz  
 F2P -0.221 ppm  
 F2 -88.48 Hz  
 PPMCM 0.39085 ppm/cm  
 HZCM 156.32362 Hz/cm



ZDY-0B24-3C

Current Data Parameters  
 NAME ZDY  
 EXPNO 9  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120624  
 Time 23.40  
 INSTRUM av400  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zgdc  
 TD 16384  
 SOLVENT CDCl3  
 NS 2050  
 DS 0  
 SMH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 8192  
 DM 19.950 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.5000000 sec  
 d11 0.0300000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 2.70 usec  
 PL1 -3.00 dB  
 SFO1 100.5785294 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SFO2 399.9515998 MHz

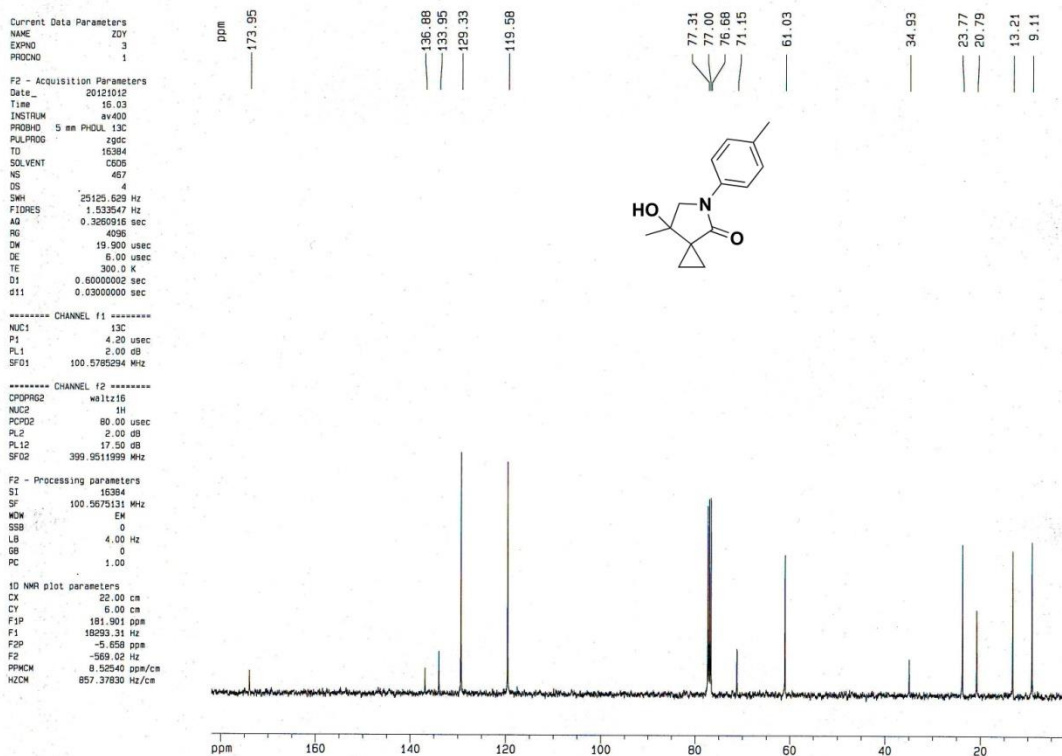
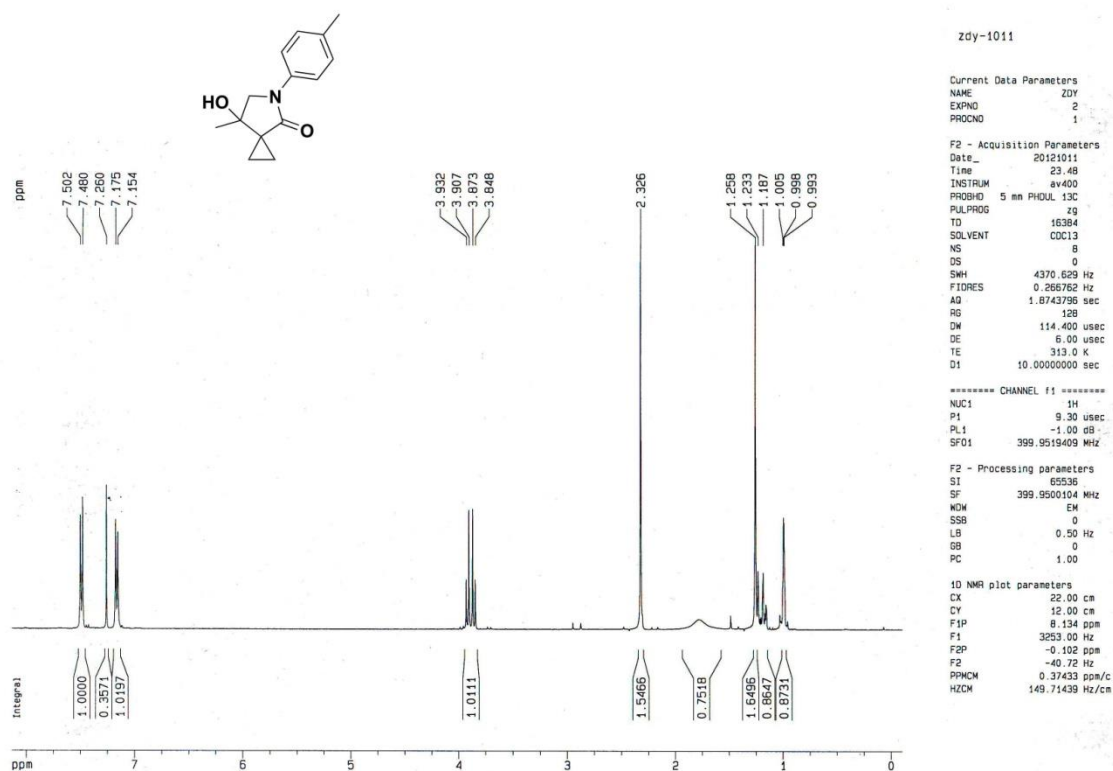
F2 - Processing parameters  
 SI 65536  
 SF 100.5675148 MHz  
 MDW EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 7.00 cm  
 F1P 184.742 ppm  
 F1 18579.06 Hz  
 F2P -0.038 ppm  
 F2 -3.85 Hz  
 PPMCM 8.39911 ppm/cm  
 HZCM 844.67737 Hz/cm

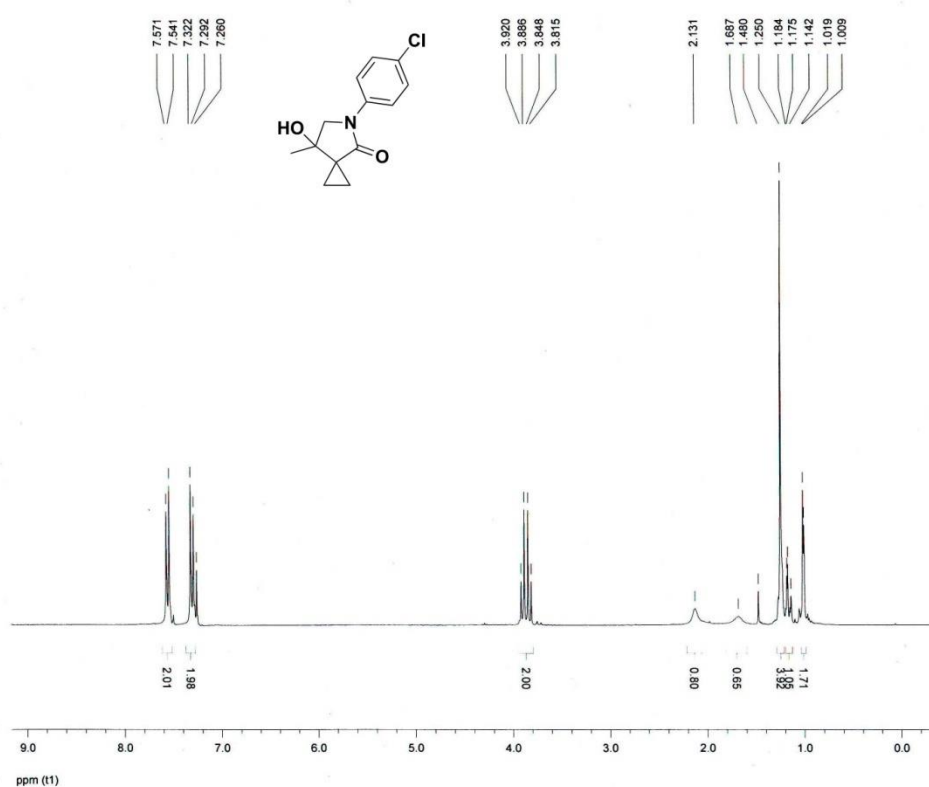




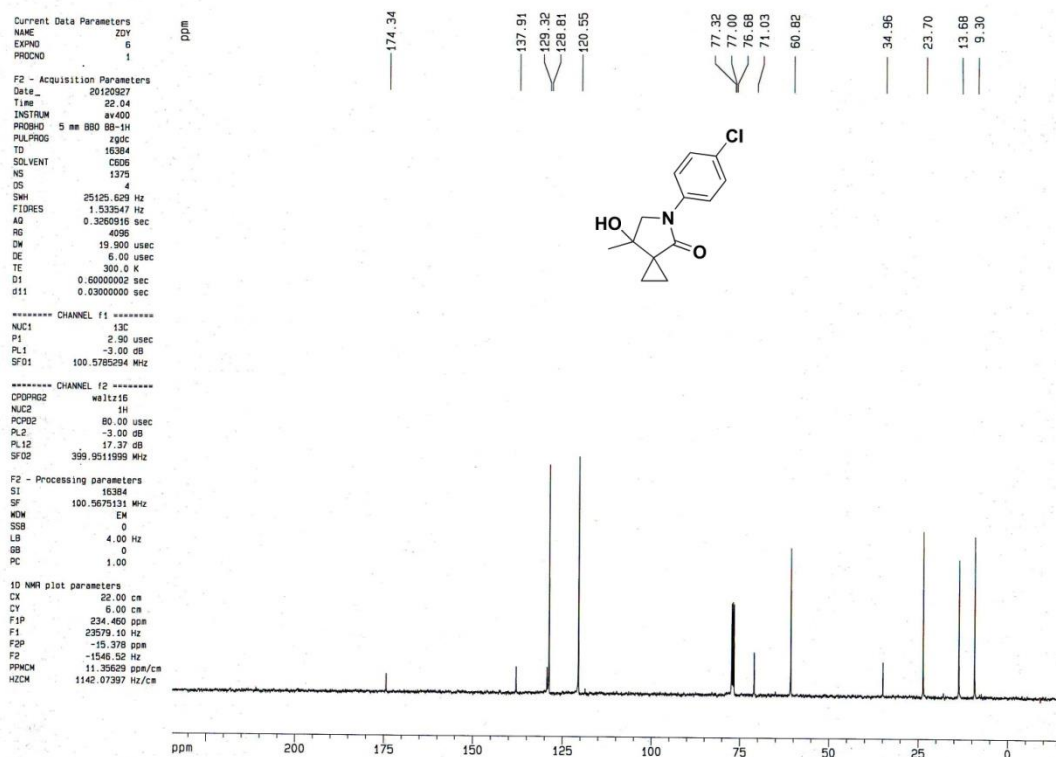
3p



3q



Date: 17 Oct 2012  
 Document's Title: 6  
 Spectrum Title: 1H  
 Frequency (MHz): (f1) 300.132  
 Original Points Count: (f1) 16384  
 Actual Points Count: (f1) 32768  
 Acquisition Time (sec): (f1) 2.6477  
 Spectral Width (ppm): (f1) 20.618  
 Pulse Program: ZG30  
 Temperature: 0  
 Number of Scans: 7  
 Acq. Date: Wed Sep 26 01:55:31 PM



Current Data Parameters  
 NAME: ZY  
 EXPNO: 6  
 PROCNO: 1

F2 - Acquisition Parameters  
 Date\_: 20120927  
 Time: 22.04  
 INSTRUM: av400  
 PROBHD: 5 mm BBO BB-HL  
 PULPROG: zgdc  
 TD: 16384  
 SOLVENT: CDCl3  
 NS: 1375  
 DS: 4  
 SWH: 25125.629 Hz  
 FIDRES: 1.533547 Hz  
 AQ: 0.3260916 sec  
 RG: 4096  
 DW: 19.900 usec  
 DE: 6.00 usec  
 TE: 300.0 K  
 D1: 0.6000000 sec  
 d11: 0.0300000 sec

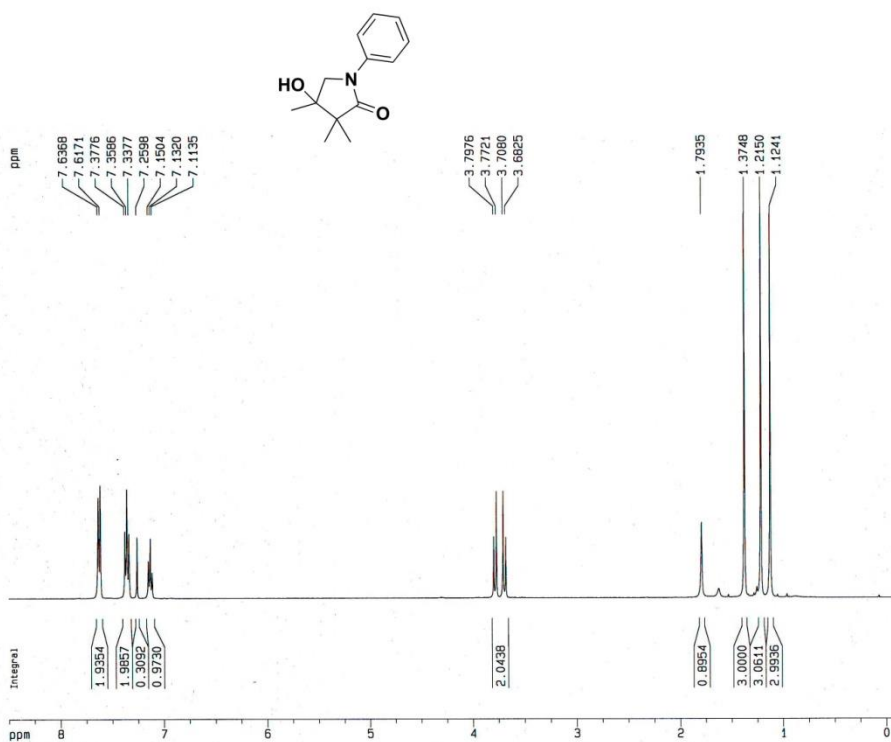
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1: 13C  
 P1: 2.90 usec  
 PL1: -3.00 dB  
 SFO1: 100.5785294 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2: waltz16  
 NUC2: 1H  
 PCPD2: 80.00 usec  
 PL2: -3.00 dB  
 PL12: 17.37 dB  
 SFO2: 399.9511999 MHz

F2 - Processing parameters  
 SI: 16384  
 SF: 100.5675131 MHz  
 WCN: EN  
 SSB: 0  
 LB: 4.00 Hz  
 GB: 0  
 PC: 1.00

1D NMR plot parameters  
 CX: 22.00 cm  
 CY: 6.00 cm  
 F1P: 234.460 ppm  
 F1: 23579.10 Hz  
 F2P: -15.378 ppm  
 F2: -1546.32 Hz  
 PPMCN: 11.35629 ppm/cm  
 HZCN: 1142.07397 Hz/cm

3u



zdy-2h-0921

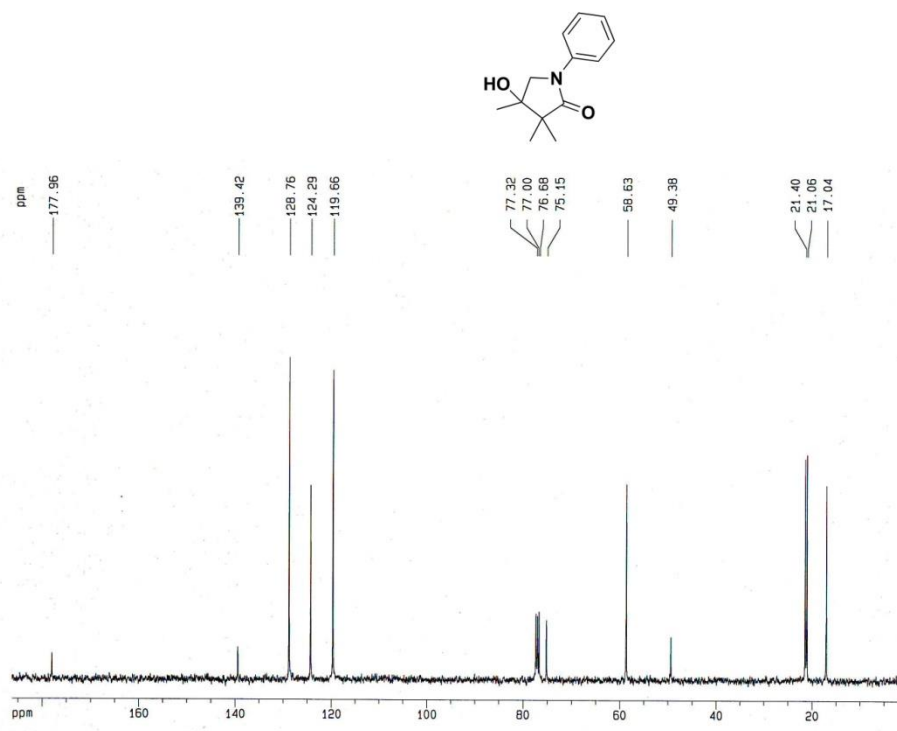
Current Data Parameters  
 NAME ZDY  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120921  
 Time 17.31  
 INSTRUM av400  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zg  
 TD 16384  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 5341.880 Hz  
 FIDRES 0.326243 Hz  
 AQ 1.5335923 sec  
 RG 32  
 DW 93.600 usec  
 DE 6.00 usec  
 TE 313.0 K  
 D1 10.0000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 8.50 usec  
 PL1 -3.00 dB  
 SFO1 399.9520214 MHz

F2 - Processing parameters  
 SI 65536  
 SF 399.9500102 MHz  
 WDW EM  
 SSB 0  
 LB 0.50 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 12.00 cm  
 F1P 8.501 ppm  
 F1 3400.07 Hz  
 F2P -0.118 ppm  
 F2 -47.23 Hz  
 PPMCM 0.39179 ppm/c  
 HZCM 156.69514 Hz/cm



zdy-0924-1C

Current Data Parameters  
 NAME ZDY  
 EXPNO 3  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120924  
 Time 23.21  
 INSTRUM av400  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zgdc  
 TD 16384  
 SOLVENT CDCl3  
 NS 198  
 DS 0  
 SWH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 8192  
 DW 19.950 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.5000000 sec  
 d11 0.0300000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 2.90 usec  
 PL1 -3.00 dB  
 SFO1 100.5782294 MHz

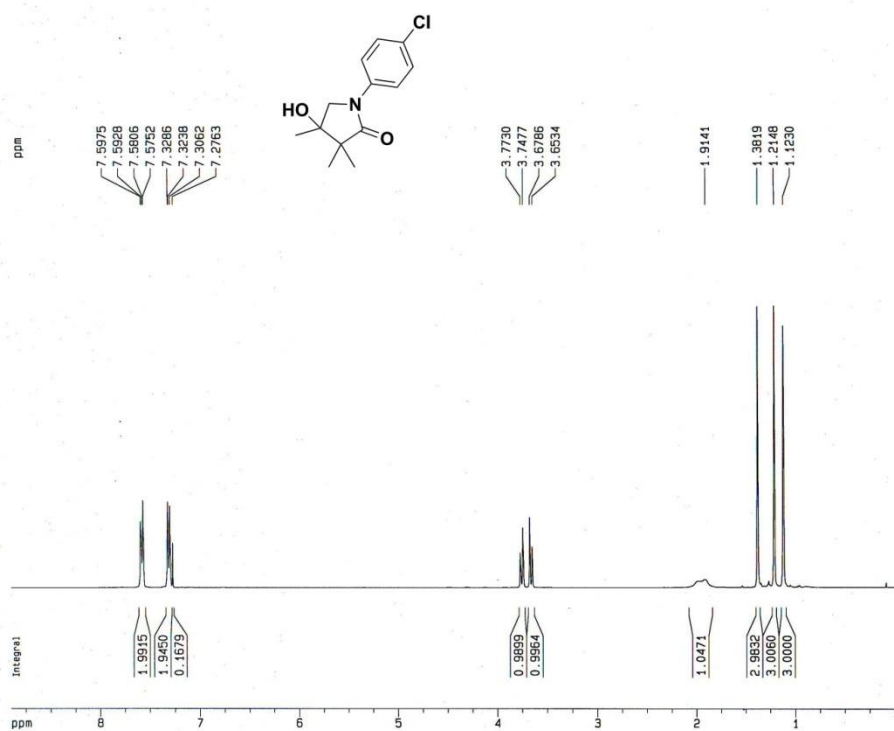
\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SFO2 399.9515998 MHz

F2 - Processing parameters  
 SI 65536  
 SF 100.5675171 MHz  
 WDW EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 0.30

1D NMR plot parameters  
 CX 22.00 cm  
 CY 8.00 cm  
 F1P 186.299 ppm  
 F1 18731.59 Hz  
 F2P 1.510 ppm  
 F2 151.81 Hz  
 PPMCM 8.39770 ppm/c  
 HZCM 844.53558 Hz/cm



3v



zdy-0629-1h

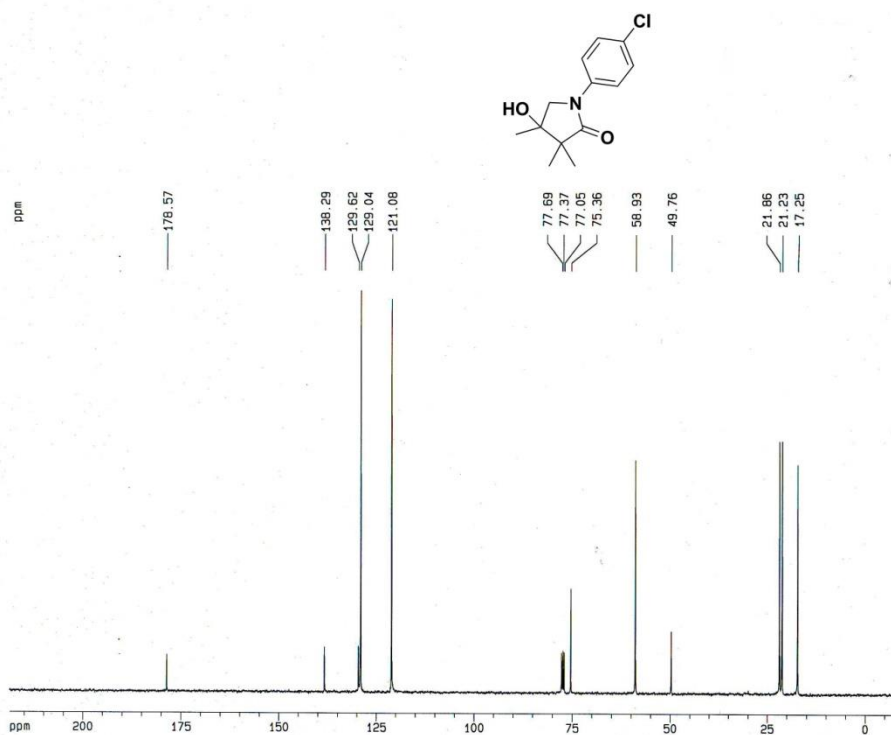
Current Data Parameters  
 NAME ZDY  
 EXPNO 9  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120629  
 Time 15.41  
 INSTRUM av400  
 PROBHD 5 mm PHDUL 13C  
 PULPROG zg  
 TD 16384  
 SOLVENT CDCl3  
 NS 8  
 DS 0  
 SWH 4844.961 Hz  
 FIDRES 0.295713 Hz  
 AQ 1.6908787 sec  
 RG 32  
 DW 103.200 usec  
 DE 6.00 usec  
 TE 313.0 K  
 D1 10.0000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 9.30 usec  
 PL1 -1.00 dB  
 SF01 399.9518187 MHz

F2 - Processing parameters  
 SI 65536  
 SF 399.9500034 MHz  
 WDW EM  
 SSB 0  
 LB 0.50 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 7.00 cm  
 F1P 8.900 ppm  
 F1 3259.57 Hz  
 F2P -0.067 ppm  
 F2 -26.80 Hz  
 PPMCM 0.40759 ppm/c  
 HZCM 163.01688 Hz/cm



zdy-0702

Current Data Parameters  
 NAME ZDY  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20120703  
 Time 0.18  
 INSTRUM av400  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zgpg  
 TD 16384  
 SOLVENT CDCl3  
 NS 654  
 DS 0  
 SWH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 6152  
 DW 19.950 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.5000000 sec  
 D11 0.0300000 sec

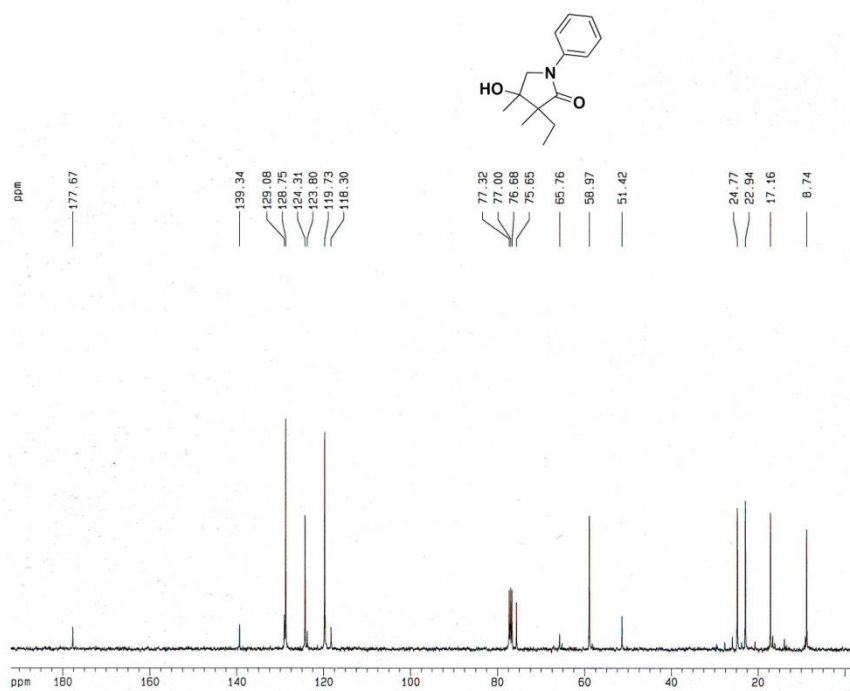
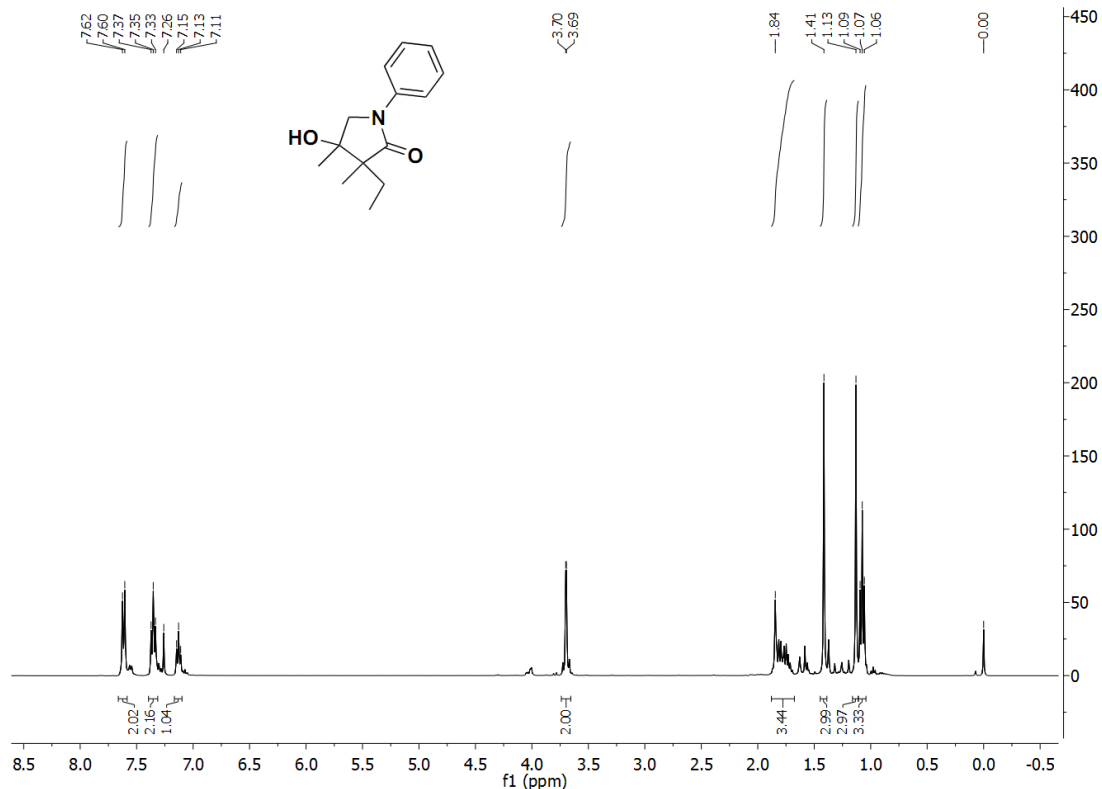
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 2.30 usec  
 PL1 -3.00 dB  
 SF01 100.5785294 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCDP2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SF02 399.9515998 MHz

F2 - Processing parameters  
 SI 65536  
 SF 100.5674828 MHz  
 WDW EM  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 10.00 cm  
 F1P 219.736 ppm  
 F1 21997.75 Hz  
 F2P -8.792 ppm  
 F2 -884.17 Hz  
 PPMCM 10.34216 ppm/c  
 HZCM 1040.08728 Hz/cm

3w



ZDY-1102-C13

Current Data Parameters  
 NAME ZDY  
 EXPNO 3  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20121106  
 Time 14.57  
 INSTRUM av400  
 PROBHD 5 mm QNP 1H/13  
 PULPROG zgpgc  
 TD 16384  
 SOLVENT CDCl3  
 NS 889  
 DS 0  
 SWH 25062.656 Hz  
 FIDRES 1.529703 Hz  
 AQ 0.3269108 sec  
 RG 8192  
 DW 19.550 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 0.50000000 sec  
 d11 0.03000000 sec

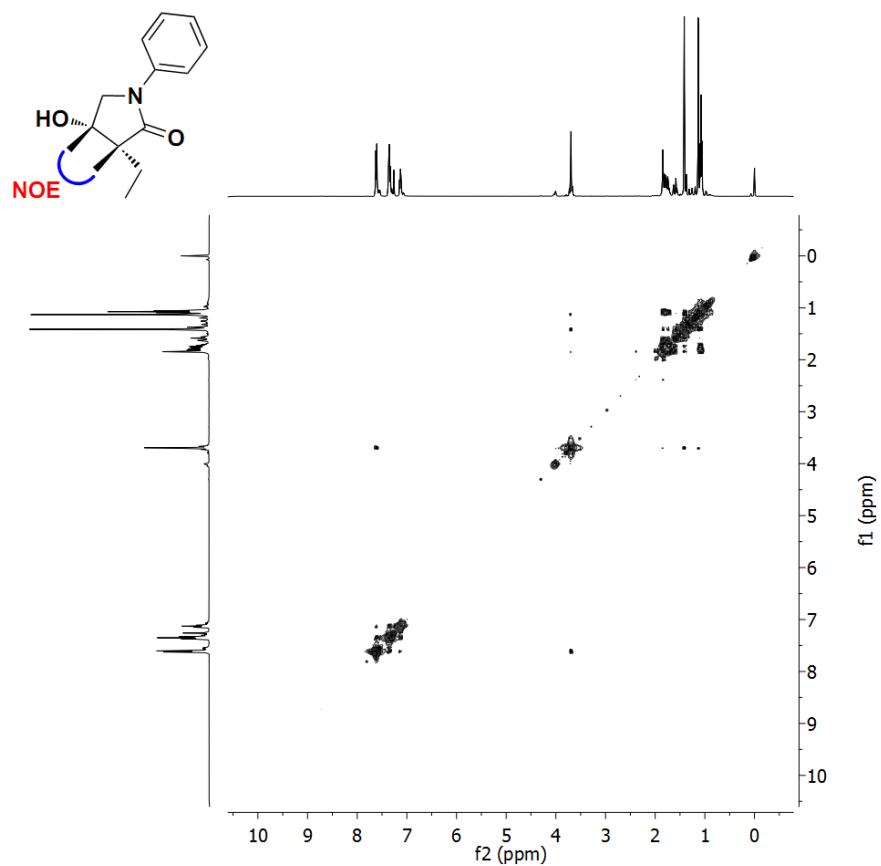
----- CHANNEL f1 -----  
 NUC1 13C  
 P1 2.70 usec  
 PL1 -3.00 dB  
 SF01 100.5785294 MHz

----- CHANNEL f2 -----  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -3.00 dB  
 PL12 18.20 dB  
 SF02 399.9515988 MHz

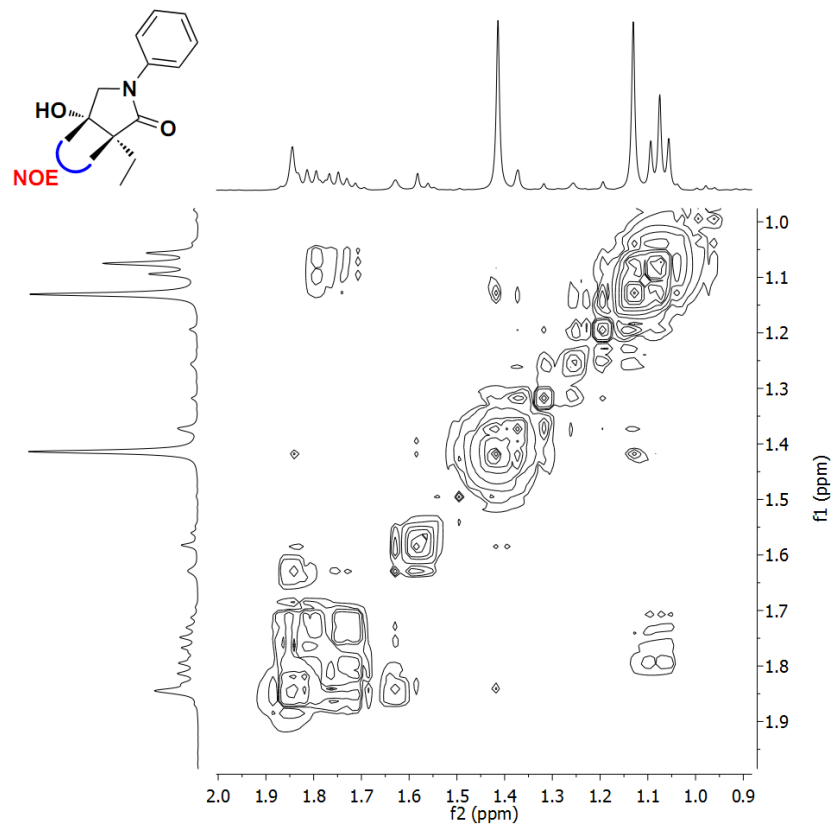
F2 - Processing parameters  
 SI 65536  
 SF 100.5675167 MHz  
 WDW EN  
 SSB 0  
 LB 4.00 Hz  
 GB 0  
 PC 1.30

1D NMR plot parameters  
 CX 22.00 cm  
 CY 6.00 cm  
 F1P 191.911 ppm  
 F1 19300.06 Hz  
 F2P -2.806 ppm  
 F2 -286.23 Hz  
 PPMCM 8.85081 ppm/cm  
 HZCM 890.10406 Hz/cm

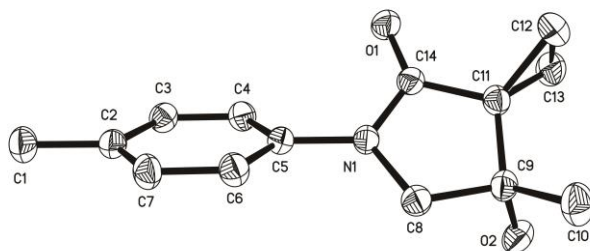
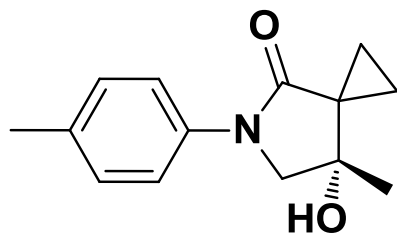
### 3w-NOESY



### 3w-NOESY-expanded



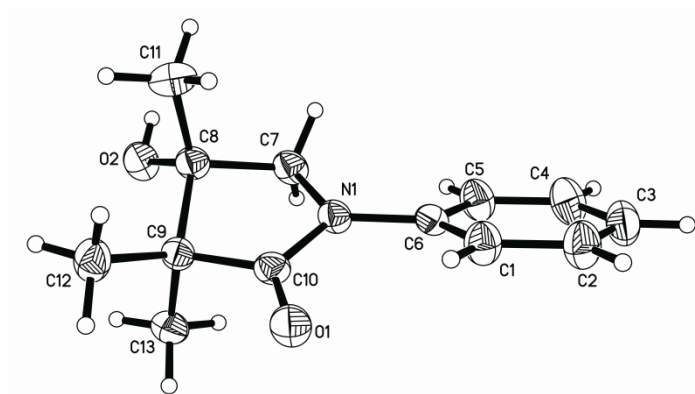
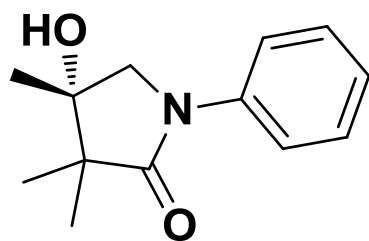
#### IV. ORTEP drawing of compound 3p



#### V. Crystal data for compound 3p

$C_{14}H_{17}NO_2$ , yellow,  $M = 231.29$ , monoclinic, space group  $P21/c$ ,  $a = 8.6775(18)$ ,  $b = 18.791(4)$ ,  $c = 7.5798(16)$  Å,  $V = 1233.2(4)$  Å<sup>3</sup>,  $\alpha = 90.00^\circ$ ,  $\beta = 93.79^\circ$ ,  $\gamma = 90.00^\circ$ ,  $Z = 4$ ,  $T = 273$  K,  $F_{000} = 496.0$ ,  $R_1 = 0.0543$ ,  $wR_2 = 0.1197$ . The hydrogen atoms were refined as rigid groups. CCDC deposition number: **906890** (3s). These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## VI. ORTEP drawing of compound 3u



## VII. Crystal data for compound 3u

$C_{13}H_{17}NO_2$ , white,  $M = 219.28$ , monoclinic, space group  $C2/C$ ,  $a = 22.590(5)$ ,  $b = 6.6126(16)$ ,  $c = 19.413(5)$  Å,  $V = 2448.5(10)$  Å<sup>3</sup>,  $\alpha = 90.00^\circ$ ,  $\beta = 122.398(3)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $Z = 8$ ,  $T = 273$  K,  $F_{000} = 944.0$ ,  $R_1 = 0.0323$ ,  $wR_2 = 0.1129$ . The hydrogen atoms were refined as rigid groups. CCDC deposition number: **908363** (3u). These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).