Supporting Information

for

Dearomatization of Tryptophols via a Vanadium-Catalyzed Asymmetric Epoxidation and Ring-Opening Cascade

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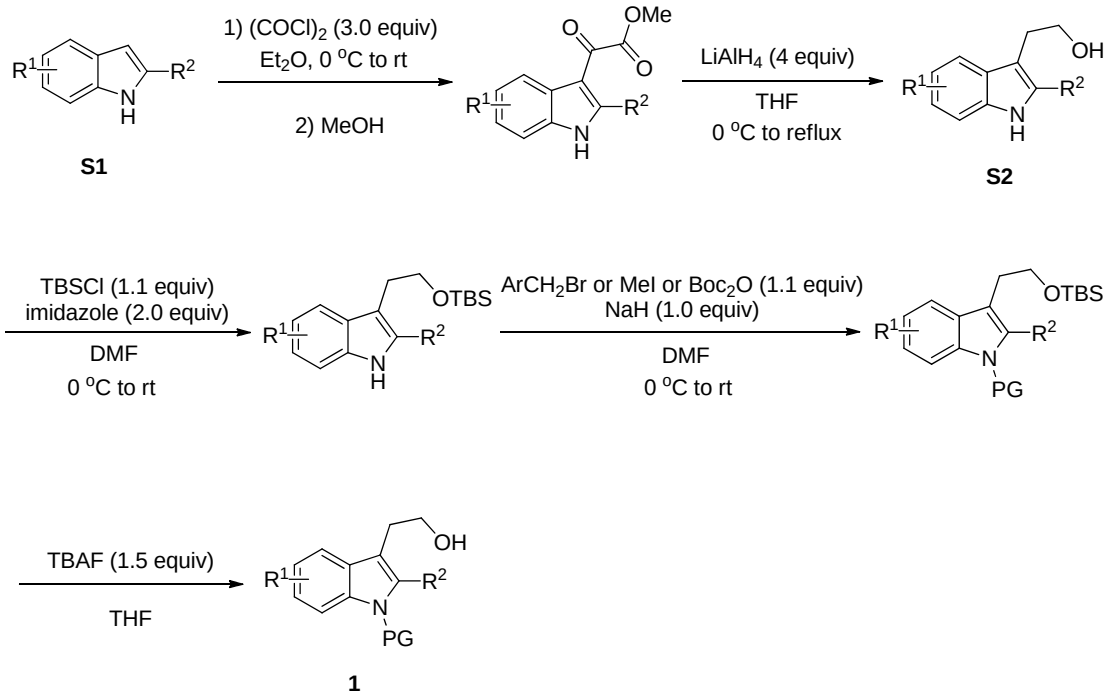
1. General methods.

Unless stated otherwise, all reactions were carried out in flame-dried glassware. All solvents were purified and dried according to standard methods prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

2. Experimental sections

2.1 General method for the preparation of 1a-1q

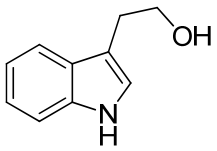


To a solution of indole **S1** (10.0 mmol, 1.0 equiv) in dry Et_2O (50 mL) was added dropwise oxalyl chloride (2.7 mL, 30.0 mmol, 3.0 equiv) at 0 °C. Then the ice bath was removed and the resultant yellow slurry was stirred for 6 h at room temperature and then cooled to 0 °C, followed by quenching with MeOH (2.0 mL, 50.0 mmol, 5.0 equiv). The crude reaction mixture was filtered and washed with cold Et_2O. Then the solid was dried and used directly for the next step without further

purification. A solution of the above solid in THF (20 mL) was added dropwise to a suspension of $LiAlH_4$ (1.52 g, 40 mmol, 4.0 equiv) in THF (40 mL) at 0 °C. The solution was stirred for 4 h at room temperature and quenched by H_2O (1.5 mL), 10% aqueous NaOH (3.0 mL), H_2O (4.5 mL) slowly at 0 °C. The solution was then filtered and washed with EtOAc. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure to give the corresponding crude product **S2**.

tert-Butyldimethylsilylchloride (1.66 g, 11 mmol, 1.1 equiv) was added to a solution of tryptophol (10.0 mmol, 1.0 equiv) and imidazole (1.36 g, 20.0 mmol, 2.0 equiv) in DMF (50 mL) at 0 °C. The ice bath was then removed and the reaction mixture was stirred at room temperature for 3 h. The mixture was quenched with water (40 mL) and extracted with EtOAc (3 × 30 mL), then the combined organic layers were washed with water, brine, separated, and dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was used directly for the next step without further purification. To a solution of the above TBS-tryptophol in THF (50 mL) was added NaH (400.0 mg, 10.0 mmol, 1.0 equiv, 60% dispersion in mineral oil) at 0 °C. After stirring at 0 °C for 15 min and then at rt for 1 h, the reaction mixture was cooled to 0 °C, treated with MeI (700 µl, 11 mmol, 1.1 equiv) or BnBr (1.88 g, 11 mmol, 1.1 equiv) or 1-(bromomethyl)naphthalene (2.43 g, 11 mmol, 1.1 equiv) or 9-(bromomethyl)anthracene (2.98 g, 11 mmol, 1.1 equiv) or Boc_2O (2.4 g, 11 mmol, 1.1 equiv), and then allowed to stir at rt for 6-12 h. After the reaction was complete (monitored by TLC), aqueous saturated $NaHCO_3$ (30 mL) was added slowly. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (30 mL), separated, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was further treated with *tetra-n*-butylammonium fluoride (15 mmol, 1.5 equiv), after 24 h, the mixture was worked up and purified by column chromatography on silica gel (2:1, PE-EtOAc) to afford the desired product **1**.

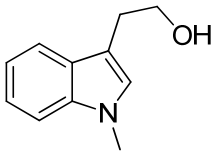
Note: All the yields provided for the substrates **1** (**1a** to **1q**) were calculated from the starting indoles **S1**.



2-(1H-indol-3-yl)ethanol (1a)

Pale yellow solid, 1.5 g, 93% yield. Analytical data for **1a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (brs, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 6.9 Hz, 1H), 7.07 (s, 1H), 3.94-3.88 (m, 2H), 3.04 (t, *J* = 6.3 Hz, 2H), 1.55 (s, 1H).

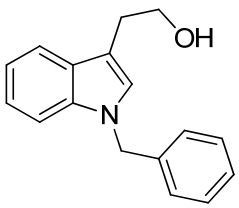
（S. Gore, S. Baskaran and B. König, *Org. Lett.*, 2012, **14**, 4568.）



2-(1-methyl-1H-indol-3-yl)ethanol (1b)

Pale yellow oil, 1.3 g, 74% yield. Analytical data for **1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 3.6 Hz, 2H), 7.06-7.02 (m, 1H), 6.69 (s, 1H), 3.73 (t, *J* = 6.8 Hz, 2H), 3.48 (s, 2H), 2.88 (t, *J* = 6.8 Hz, 2H), 2.78 (brs, 1H).

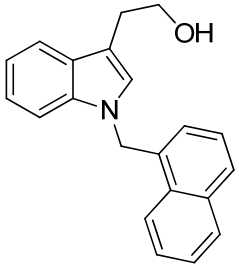
(O. Lozano, G. Blessley, T. Martinez del Campo, A. L. Thompson, G. T. Giuffredi, M. Bettati, M. Walker, R. Borman and V. Gouverneur, *Angew. Chem., Int. Ed.*, 2011, **50**, 8105.)



2-(1-benzyl-1H-indol-3-yl)ethanol (1c)

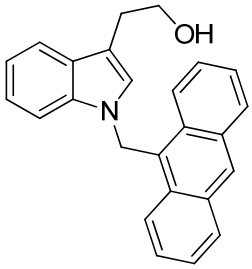
Pale yellow oil, 1.9 g, 76% yield. Analytical data for **1c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.30-7.13 (m, 7H), 7.01 (s, 1H), 5.29 (s, 2H), 3.93-3.88 (m, 2H), 3.04 (t, *J* = 6.3 Hz, 2H), 1.48 (brs, 1H).

(S. J. Garden, R. B. da Silva and A. C. Pinto, *Tetrahedron*, 2002, **58**, 8399.)



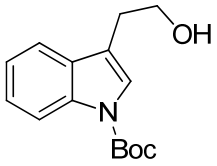
2-(1-(naphthalen-1-ylmethyl)-1H-indol-3-yl)ethanol (1d)

Yellow solid, 2.3 g, 76% yield. Analytical data for **1d**: Mp = 84-87 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.89 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.54-7.50 (m, 2H), 7.36-7.32 (m, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 5.73 (s, 2H), 3.87 (m, 2H), 3.01 (t, *J* = 6.4 Hz, 2H), 1.46 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ137.0, 133.7, 132.4, 130.9, 128.9, 128.4, 128.1, 126.6, 126.5, 126.0, 125.5, 125.2, 122.6, 122.0, 119.3, 119.1, 111.5, 109.7, 62.7, 47.7, 28.8; IR (film): ν_{max} (cm^{-1}) = 3673, 2987, 2901, 1597, 1468, 1376, 1327, 1260, 1177, 1041, 1011, 796, 772, 742; MS (ESI): 302 $[M+1]^+$; HRMS (ESI) calcd for $C_{21}H_{20}NO$ $[M+1]^+$: 302.1539. Found: 302.1543.



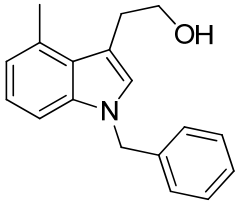
2-(1-(anthracen-9-ylmethyl)-1H-indol-3-yl)ethanol (1e)

Yellow solid, 2.6 g, 74% yield. Analytical data for **1e**: Mp = 155-157 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.15-8.07 (m, 4H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.52-7.46 (m, 4H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.34 (s, 1H), 6.11 (s, 2H), 3.69-3.65 (m, 2H), 2.77 (t, *J* = 6.3 Hz, 2H), 1.23 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 131.5, 131.3, 129.3, 129.0, 128.3, 127.1, 125.7, 125.3, 125.0, 123.5, 122.0, 119.4, 119.2, 110.8, 109.3, 62.5, 41.9, 28.6; IR (film): ν_{max} (cm^{-1}) = 3276, 3055, 2922, 1623, 1458, 1340, 1237, 1098, 891, 731; MS (ESI): 352 $[M+1]^+$; HRMS (ESI) calcd for $C_{25}H_{22}NO$ $[M+1]^+$: 352.1696. Found: 352.1695.



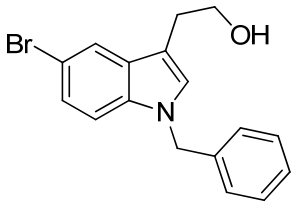
***tert*-butyl 3-(2-hydroxyethyl)-1H-indole-1-carboxylate (1f)**

Pale yellow oil, 1.7 g, 65% yield. Analytical data for **1f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.47 (s, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.24 (m, 1H), 3.92 (m, 2H), 2.96 (t, *J* = 6.6 Hz, 2H), 1.66 (s, 9H), 1.61 (brs, 1H). (H.-C. Hsu and D.-R. Hou, *Tetrahedron Lett.*, 2009, **50**, 7169.)



2-(1-benzyl-4-methyl-1H-indol-3-yl)ethanol (1g)

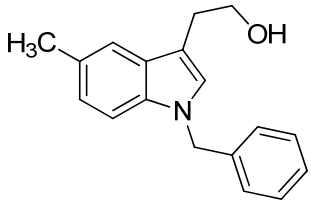
Brown yellow solid, 750 mg, 28% yield. Analytical data for **1g**: Mp = 58-62 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.13 (m, 3H), 7.04-6.97 (m, 4H), 6.83 (s, 1H), 6.79 (d, *J* = 6.4 Hz, 1H), 5.08 (s, 2H), 3.78 (t, *J* = 6.8 Hz, 2H), 3.10 (t, *J* = 6.8 Hz, 2H), 2.65 (s, 3H), 2.19 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ137.8, 137.3, 131.1, 128.9, 127.7, 127.0, 126.9, 126.7, 122.1, 121.2, 112.2, 107.9, 63.7, 50.0, 30.6, 20.6; IR (film): v_{max} (cm^{-1}) = 3321, 2918, 2857, 1605, 1548, 1494, 1430, 1358, 1327, 1242, 1158, 1044, 730, 695, 611; MS (ESI): 266 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO$ $[M+1]^+$: 266.1539. Found: 266.1541.



2-(1-benzyl-5-bromo-1H-indol-3-yl)ethanol (1h)

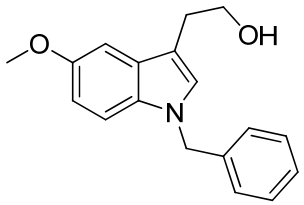
Brown yellow oil, 2.4 g, 73% yield. Analytical data for **1h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.6 Hz, 1H), 7.28-7.21 (m, 4H), 7.11-7.05 (m, 3H), 6.99 (s, 1H),

5.21 (s, 2H), 3.85 (t, J = 6.4 Hz, 2H), 2.94 (t, J = 6.4 Hz, 2H), 1.63 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ137.0, 135.3, 129.8, 128.8, 127.7, 126.6, 124.6, 121.6, 112.5, 111.2, 111.2, 62.5, 50.0, 28.4; IR (film): v_{max} (cm^{-1}) = 3350, 2925, 1605, 1468, 1354, 1296, 1169, 1051, 864, 788, 733, 698, 646; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{17}H_{17}BrNO$ $[M+1]^+$: 330.0488. Found: 330.0487.



2-(1-benzyl-5-methyl-1H-indol-3-yl)ethanol (1i)

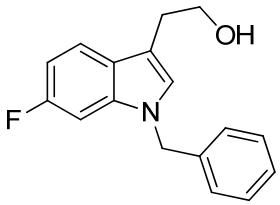
Brown yellow solid, 1.3 g, 49% yield. Analytical data for **1i**: Mp = 61-64 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.30-7.24 (m, 3H), 7.15 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 7.2 Hz, 2H), 7.01 (d, J = 8.4 Hz, 1H), 6.96 (s, 1H), 5.24 (s, 2H), 3.88 (t, J = 6.4 Hz, 2H), 3.00 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 1.55 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ137.6, 135.2, 128.7, 128.5, 128.4, 127.5, 126.7, 123.5, 118.7, 110.7, 109.5, 62.6, 49.9, 28.7, 21.4; IR (film): v_{max} (cm^{-1}) = 3263, 2921, 2852, 1603, 1553, 1487, 1450, 1380, 1355, 1311, 1173, 1039, 788, 735, 703, 639; MS (ESI): 266 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO$ $[M+1]^+$: 266.1539. Found: 266.1543.



2-(1-benzyl-5-methoxy-1H-indol-3-yl)ethanol (1j)

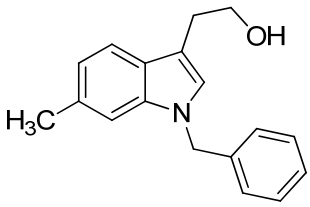
Brown yellow solid, 2.0 g, 71% yield. Analytical data for **1j**: Mp = 44-47 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 3H), 7.14 (d, J = 9.2 Hz, 1H), 7.09 (d, J = 7.2 Hz, 2H), 7.06 (d, J = 2.4 Hz, 1H), 6.98 (s, 1H), 6.84 (dd, J = 8.9, 2.4 Hz, 1H), 5.23 (s, 2H), 3.89 (t, J = 6.4 Hz, 2H), 3.85 (s, 3H), 3.00 (t, J = 6.4 Hz, 2H), 1.66 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ153.8, 137.7, 132.0, 128.7, 128.5, 127.5, 127.2, 126.7, 122.0, 111.0, 110.6, 100.9, 62.6, 55.9, 50.0, 28.7; IR (film): v_{max} (cm^{-1}) = 3525,

3420, 2919, 1617, 1577, 1486, 1451, 1394, 1351, 1221, 1180, 1100, 1041, 897, 832, 796, 697, 635; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1492.



2-(1-benzyl-6-fluoro-1H-indol-3-yl)ethanol (1k)

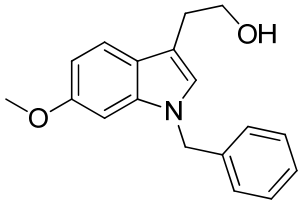
Pale yellow solid, 1.1 g, 41% yield. Analytical data for **1k**: Mp = 62-64 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 1H), 7.32-7.24 (m, 3H), 7.10 (d, *J* = 6.8 Hz, 2H), 6.98 (s, 1H), 6.94-6.84 (m, 2H), 5.19 (s, 2H), 3.87 (t, *J* = 6.4 Hz, 2H), 2.99 (t, *J* = 6.4 Hz, 2H), 1.64 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, *J* = 236.8 Hz), 136.9, 128.7, 127.7, 126.8, 126.7, 126.7, 124.6, 119.7 (d, *J* = 10.1 Hz), 111.7, 107.8 (d, *J* = 24.4 Hz), 96.1 (d, *J* = 26.1 Hz), 62.6, 50.0, 28.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.52; IR (film): v_{max} (cm^{-1}) = 3446, 2899, 1618, 1555, 1483, 1449, 1333, 1241, 1162, 1063, 900, 816, 791, 769, 707, 621; MS (ESI): 270 $[M+1]^+$; HRMS (ESI) calcd for $C_{17}H_{17}FNO$ $[M+1]^+$: 270.1289. Found: 270.1289.



2-(1-benzyl-6-methyl-1H-indol-3-yl)ethanol (1l)

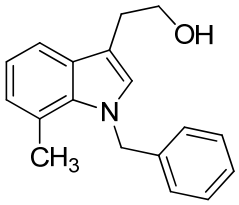
Brown yellow oil, 1.3 g, 49% yield. Analytical data for **1l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.27-7.21 (m, 3H), 7.07-7.04 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 1H), 5.16 (s, 2H), 3.82 (t, *J* = 6.5 Hz, 2H), 2.95 (t, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 1.93 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ137.7, 137.2, 131.7, 128.7, 127.5, 126.7, 126.0, 120.9, 118.7, 111.3, 109.6, 62.6, 49.6, 28.7, 21.9; IR (film): v_{max} (cm^{-1}) = 3356, 3028, 2917, 1620, 1554, 1468, 1452, 1377, 1355, 1326,

1170, 1039, 797, 733, 704; MS (ESI): 266 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO$ $[M+1]^+$: 266.1539. Found: 266.1539.



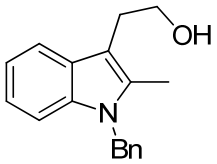
2-(1-benzyl-6-methoxy-1H-indol-3-yl)ethanol (1m)

Brown yellow solid, 500 mg, 18% yield. Analytical data for **1m**: Mp = 77-80 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 1H), 7.29-7.20 (m, 3H), 7.08 (d, *J* = 6.4 Hz, 2H), 6.85 (s, 1H), 6.77 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.71 (d, *J* = 2.0 Hz, 1H), 5.16 (s, 2H), 3.83 (t, *J* = 6.4 Hz, 2H), 3.76 (s, 3H), 2.95 (t, *J* = 6.4 Hz, 2H), 1.84 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 137.5, 137.4, 128.7, 127.5, 126.7, 125.4, 122.5, 119.6, 111.4, 108.8, 93.4, 62.6, 55.6, 49.7, 28.7; IR (film): v_{max} (cm^{-1}) = 3263, 2925, 2854, 1621, 1557, 1491, 1451, 1376, 1357, 1261, 1168, 1043, 794, 740, 708, 630; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1490.



2-(1-benzyl-7-methyl-1H-indol-3-yl)ethanol (1n)

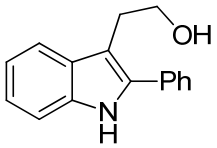
Pale yellow solid, 1.2 g, 45% yield. Analytical data for **1n**: Mp = 60-62 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.28-7.20 (m, 3H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.93-6.89 (m, 4H), 5.53 (s, 2H), 3.91-3.86 (m, 2H), 3.02 (t, *J* = 6.4 Hz, 2H), 2.51 (s, 3H), 1.57 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.5, 129.0, 128.7, 128.5, 127.2, 125.3, 124.8, 121.2, 119.4, 116.9, 111.3, 62.5, 51.9, 28.6, 19.4; IR (film): v_{max} (cm^{-1}) = 3253, 2931, 2861, 1603, 1494, 1450, 1414, 1354, 1330, 1168, 1049, 781, 745, 703, 637; MS (ESI): 266 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO$ $[M+1]^+$: 266.1539. Found: 266.1539.



tert-butyl 3-(2-hydroxyethyl)-1H-indole-1-carboxylate (1o)

Pale yellow oil, 870 mg, 33% yield. Analytical data for **1o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 1H), 7.16-7.12 (m, 4H), 7.09-7.07 (m, 2H), 6.89 (d, *J* = 6.4 Hz, 2H), 5.12 (s, 2H), 3.75 (t, *J* = 6.8 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 2.41 (brs, 1H), 2.22 (s, 3H).

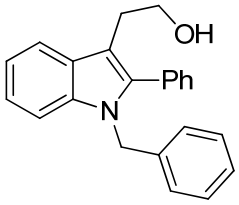
(V. Khedkar, A. Tillack, K. Michali and M. Beller, *Tetrahedron*, 2005, **61**, 7622.)



2-(2-phenyl-1H-indol-3-yl)ethanol (1p)

Pale yellow solid, 1.2 g, 51% yield. Analytical data for **1p**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (brs, 1H), 7.61-7.53 (m, 3H), 7.42-7.28 (m, 4H), 7.20-7.09 (m, 2H), 3.89 (t, *J* = 6.6 Hz, 2H), 3.11 (t, *J* = 6.6 Hz, 2H), 1.73 (brs, 1H).

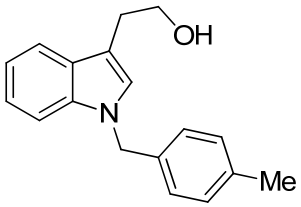
(C. Liu, W. Zhang, L.-X. Dai and S.-L. You, *Org. Lett.*, 2012, **14,** 4525.)



2-(1-benzyl-2-phenyl-1H-indol-3-yl)ethanol (1q)

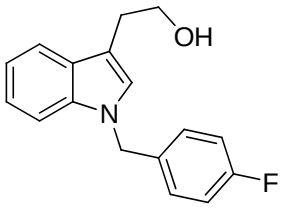
White solid, 200 mg, 6.1% yield. Analytical data for **1q**: Mp = 113-115 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 1H), 7.38-7.33 (m, 5H), 7.25-7.16 (m, 6H), 6.92 (d, *J* = 6.8 Hz, 2H), 5.20 (s, 2H), 3.84 (t, *J* = 6.8 Hz, 2H), 3.01 (t, *J* = 6.8 Hz, 2H), 1.45 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.1, 136.7, 131.5, 130.6, 128.5, 128.4, 128.3, 128.0, 127.0, 126.0, 122.0, 119.7, 119.0, 110.4, 109.4, 63.2, 47.5, 28.2; IR (film): ν_{max} (cm^{-1}) = 2921, 2318, 1603, 1464, 1340, 1043, 1011, 736, 698;

MS (ESI): 328 $[M+1]^+$; HRMS (ESI) calcd for $C_{23}H_{22}NO$ $[M+1]^+$: 328.1696. Found: 328.1695.



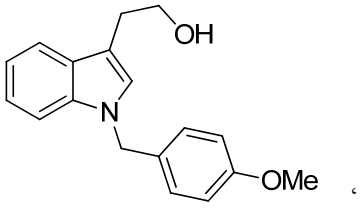
2-(1-(4-methylbenzyl)-1H-indol-3-yl)ethanol (1r)

Pale yellow solid, 2.3 g, 88% yield. Analytical data for **1r**: Mp = 42-44 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.12 – 7.07 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.97 (s, 1H), 5.20 (s, 2H), 3.86 (t, *J* = 6.4 Hz, 2H), 3.00 (t, *J* = 6.4 Hz, 2H), 2.29 (s, 3H), 1.61 (brs, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.8, 134.4, 129.4, 128.1, 126.9, 126.5, 121.9, 119.1,119.0, 111.2, 109.8, 62.7, 49.7, 28.7, 21.1; IR (film): v_{max} (cm^{-1}) = 3331, 2920, 1613, 1514, 1466, 1436, 1333, 1179, 1021, 797, 736; MS (ESI): 266 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO$ $[M+1]^+$: 266.1539. Found: 266.1543.



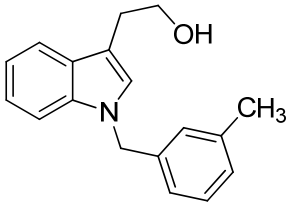
2-(1-(4-fluorobenzyl)-1H-indol-3-yl)ethanol (1s)

Yellow solid, 1.6 g, 60% yield. Analytical data for **1s**: Mp = 38-40 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.19 (td, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.15 – 7.07 (m, 3H), 7.00 - 6.96 (m, 3H), 5.24 (s, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 3.03 (t, *J* = 6.4 Hz, 2H), 1.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 161.0, 136.7, 133.2 (d, *J* = 3.2 Hz), 128.5 (d, *J* = 8.1 Hz), 128.1, 126.4, 122.1, 199.2 (d, *J* = 16.7 Hz), 115.7 (d, *J* = 21.5 Hz), 111.6, 109.7, 62.7, 49.3, 28.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.79; IR (film): v_{max} (cm^{-1}) = 3253, 2929, 1603, 1508, 1466, 1331, 1218, 1154, 1053, 816, 737; MS (ESI): 270 $[M+1]^+$; HRMS (ESI) calcd for $C_{17}H_{17}FNO$ $[M+1]^+$: 270.1289. Found: 270.1290.



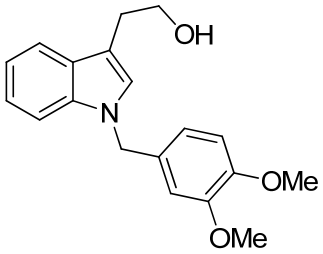
2-(1-(4-methoxybenzyl)-1H-indol-3-yl)ethanol (1t)

Yellow oil, 2.3 g, 83% yield. Analytical data for **1t**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.20 (m, 1H), 7.14 – 7.06 (m, 1H), 6.99 (s, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.21 (s, 2H), 3.88 (s, 2H), 3.77 (s, 3H), 3.02 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ159.1, 136.8, 129.6, 128.3, 128.2, 126.5, 121.9, 119.2, 119.1, 114.2, 111.4, 109.9, 62.7, 55.3, 49.4, 28.8; IR (film): ν_{max} (cm^{-1}) = 3356, 2930, 1612, 1511, 1465, 1244, 1174, 1031, 818, 735; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1491.



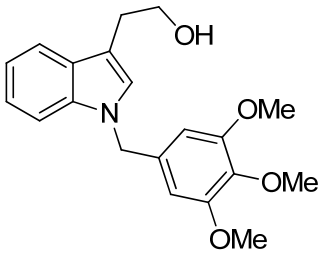
2-(1-(3-methylbenzyl)-1H-indol-3-yl)ethanol (1u)

Yellow oil, 1.9 g, 72% yield. Analytical data for **1u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 5.24 (s, 2H), 3.90 (t, *J* = 6.0 Hz, 2H), 3.04 (t, *J* = 6.0 Hz, 2H), 2.30 (s, 3H), 1.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.5, 136.8, 128.4, 127.6, 124.0, 121.9, 119.0, 111.3, 109.8, 62.7, 49.9, 28.7, 21.4; IR (film): ν_{max} (cm^{-1}) = 3336, 2920, 1610, 1465, 1332, 1260, 1174, 1039, 737; MS (ESI): 266 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO$ $[M+1]^+$: 266.1539. Found: 266.1540.



2-(1-(3,4-dimethoxybenzyl)-1H-indol-3-yl)ethanol (1v)

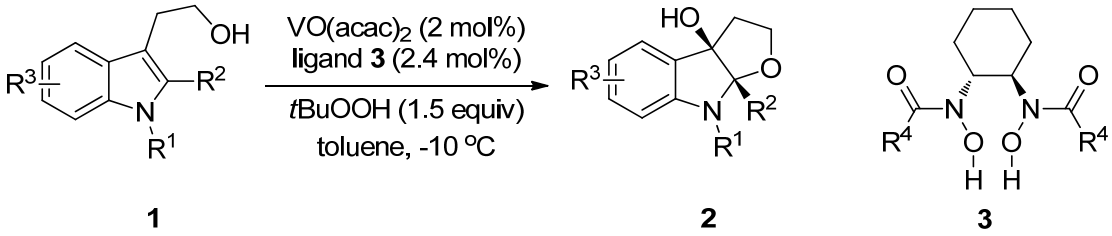
Pale yellow solid, 2.3 g, 74% yield. Analytical data for **1v**: Mp = 48-50 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 6.9 Hz, 1H), 6.98 (s, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 2H), 5.21 (s, 2H), 3.94 – 3.81 (m, 5H), 3.79 (s, 3H), 3.03 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 148.5, 136.9, 129.8, 126.4, 121.9, 119.4, 119.2, 119.0, 111.3, 111.2, 110.2, 109.7, 62.7, 55.9, 55.9, 49.7, 28.7; IR (film): v_{max} (cm^{-1}) = 3262, 2916, 1588, 1517, 1463, 1333, 1264, 1240, 1158, 1137, 1017, 871, 734, 669; MS (ESI): 312 $[M+1]^+$; HRMS (ESI) calcd for $C_{19}H_{22}NO_3$ $[M+1]^+$: 312.1594. Found: 312.1594.



2-(1-(3,4,5-trimethoxybenzyl)-1H-indol-3-yl)ethanol (1w)

Pale yellow solid, 2.56 g, 75% yield. Analytical data for **1w**: Mp = 95-97 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.22 (m, 1H), 7.14 (m, 1H), 7.00 (s, 1H), 6.36 (s, 2H), 5.20 (s, 2H), 3.89 (t, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 3.75 (s, 6H), 3.04 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 137.3, 136.9, 133.1, 128.1, 126.5, 121.9, 119.2, 119.0, 111.5, 109.7, 103.9, 62.7, 60.8, 56.0, 50.1, 28.7; IR (film): v_{max} (cm^{-1}) = 3286, 2933, 1592, 1507, 1464, 1418, 1328, 1235, 1120, 1000, 819, 736; MS (ESI): 342 $[M+1]^+$; HRMS (ESI) calcd for $C_{20}H_{24}NO_4$ $[M+1]^+$: 342.1700. Found: 342.1705.

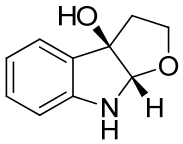
2.2 General procedure for the cascade asymmetric epoxidation/ring opening reaction



1 **2** **3**

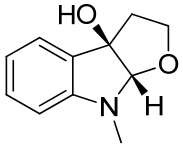
To a solution of $VO(acac)_2$ (0.01 mmol, 2.6 mg) in toluene (1 mL) was added ligand **3** (0.012 mmol), and the mixture was stirred for 1 h at room temperature. The above mixture was cooled to -10 ℃, *t*-Butylhydroperoxide (0.75 mmol, 104 ul, 70% aqueous solution) and substrate **1** (0.5 mmol) were then added and the stirring was continued at the same temperature. The process of epoxidation was monitored by TLC. After the reaction was complete, aqueous saturated Na_2SO_3 (2 mL) was added slowly. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 2 mL). The combined organic layers were washed with brine (10 mL), separated, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (4:1, PE-EtOAc) to afford the desired product **2**.

Note: The synthesis of ligand **3** was followed the procedures reported by: a) W. Zhang, A. Basak, Y. Kosugi, Y. Hoshino and H. Yamamoto, *Angew. Chem., Int. Ed.*, 2005, **44**, 4389; b) W. Zhang and H. Yamamoto, *J. Am. Chem. Soc.*, 2007, **129**, 286.



(3a*R*,8a*S*)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2a)

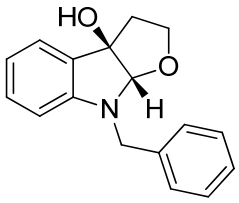
Brown oil, 56 mg, 63% yield, 61% ee. Analytical data for **2a**: $[\alpha]_D^{26}$ = -86.7 (c = 0.5, $CHCl_3$, 61% ee); ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 5.29 (s, 1H), 4.58 (brs, 1H), 3.98-3.94 (m, 1H), 3.64-3.55 (m, 1H), 3.11 (brs, 1H), 2.43-2.33 (m, 1H), 2.30-2.23 (m, 1H). The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL \cdot min^{-1}$, λ = 254 nm, t (major) = 22.6 min, t (minor) = 15.3 min. The absolute configuration was assigned as (3a*R*,8a*S*) by comparing the optical rotation with the same compound reported in the literature. [$[\alpha]_D^{25}$ = -114 (c = 0.84, $CHCl_3$, 99% ee) T. Hirose, T. Sunazuka, D. Yamamoto, N. Kojima, T. Shirahata, Y. Harigaya, I. Kuwajima, S. Ōmura *Tetrahedron*, 2005, **61**, 6015.]



(3a*R*,8a*S*)-8-methyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2b)

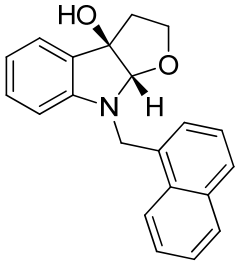
Brown oil, 63 mg, 66% yield, 43% ee. Analytical data for **2b**: $[\alpha]_D^{26}$ = -53.5 (c = 0.5, $CHCl_3$, 43% ee); ^1H NMR (300 MHz, $CDCl_3$) δ 7.24-7.15 (m, 1H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 5.06 (s, 1H), 3.97 (t, *J* = 7.5 Hz, 1H), 3.56-3.48 (m, 1H), 2.93 (s, 1H), 2.85 (s, 3H), 2.39-2.21 (m, 2H). The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL \cdot min^{-1}$, λ = 254 nm, t (major) = 8.4 min, t (minor) = 9.9 min.

(T. Hirose, T. Sunazuka, D. Yamamoto, N. Kojima, T. Shirahata, Y. Harigaya, I. Kuwajima and S. Ōmura *Tetrahedron*, 2005, **61**, 6015.)



(3a*R*,8a*S*)-8-benzyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2c)

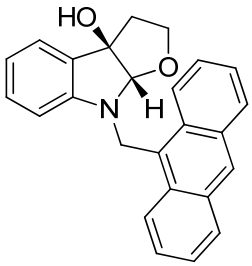
Brown oil, 94 mg, 70% yield, 87% ee. Analytical data for **2c**: $[\alpha]_D^{21}$ = -119.8 (c = 0.2, $CHCl_3$, 84% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 5H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 1H), 4.46 (AB, J_{AB} = 16.0 Hz, 1H), 4.38 (BA, J_{BA} = 16.0 Hz, 1H), 3.99 (t, *J* = 7.5 Hz, 1H), 3.64-3.57 (m, 1H), 2.77 (brs, 1H), 2.40-2.33 (m, 1H), 2.30-2.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 138.2, 130.3, 130.2, 128.6, 127.4, 127.2, 123.9, 118.0, 106.3, 103.6, 87.9, 67.2, 49.1, 41.4; IR (film): ν_{max} (cm^{-1}) = 3359, 2872, 1608, 1488, 1355, 1316, 1259, 1160, 1076, 1011, 942, 796, 742, 696; MS (ESI): 268 $[M+1]^+$; HRMS (ESI) calcd for $C_{21}H_{20}NO_2$ $[M+1]^+$: 268.1332. Found: 268.1333. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL{\cdot}min^{-1}$, λ = 254 nm, t (major) = 10.2 min, t (minor) = 11.3 min.



(3a*R*,8a*S*)-8-(naphthalen-1-ylmethyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2d)

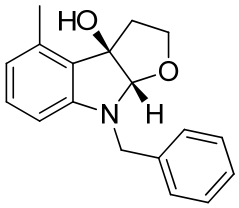
Brown oil, 125 mg, 79% yield, 80% ee. Analytical data for **2d**: $[\alpha]_D^{25}$ = -90.9 (c = 0.5, $CHCl_3$, 80% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 1H), 7.84-7.82 (m, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.46-7.41 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 1H), 4.89-4.80 (m, 2H), 3.96 (t, *J* = 8.0 Hz, 1H), 3.66-3.60 (m, 1H), 2.81 (brs, 1H), 2.38-2.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 133.8, 132.8, 131.4, 130.5, 130.3, 128.9, 127.9, 126.2, 125.8, 125.6, 125.1, 124.0, 123.0, 118.2, 106.5,

103.1, 87.9, 67.5, 46.7, 41.3; IR (film): ν_{max} (cm^{-1}) = 3347, 2961, 1607, 1486, 1366, 1162, 1112, 1009, 943, 896, 869, 775, 739, 626; MS (ESI):328 $[M+1]^+$; HRMS (ESI) calcd for $C_{21}H_{20}NO_2$ $[M+1]^+$: 318.1489. Found: 318.1486. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL \cdot min^{-1}$, λ = 254 nm, t (major) = 15.6 min, t (minor) = 13.6 min.



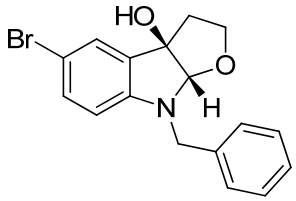
(3a*R*,8a*S*)-8-(anthracen-9-ylmethyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2e)

Brown oil, 104 mg, 56% yield, 10% ee. Analytical data for **2e**: $[\alpha]_D^{22}$ = -154.4 (c = 0.1, $CHCl_3$, 10% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.35 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.50-7.43 (m, 4H), 7.31-7.24 (m, 2H), 6.81-6.77 (m, 2H), 5.37 (AB, J_{AB} = 13.6 Hz, 1H), 5.28 (BA, J_{BA} = 13.6 Hz, 1H), 4.72 (s, 1H), 3.95-3.91 (m, 1H), 3.61-3.55 (m, 1H), 2.34-2.27 (m, 2H), 1.93 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 131.4, 130.6, 129.1, 128.2, 126.2, 125.0, 124.4, 118.2, 106.1, 100.1, 87.2, 67.5, 40.5, 40.5; IR (film): ν_{max} (cm^{-1}) = 3531, 2924, 1605, 1487, 1459, 1299, 1241, 1160, 1117, 1023, 943, 882, 781, 727, 618; MS (ESI): 368 $[M+1]^+$; HRMS (ESI) calcd for $C_{25}H_{22}NO_2$ $[M+1]^+$: 368.1645. Found: 368.1643. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL \cdot min^{-1}$, λ = 254 nm, t (major) = 22.6 min, t (minor) = 13.4 min.



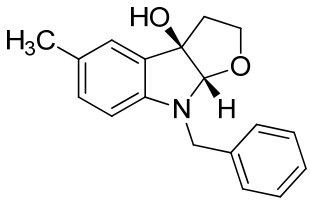
(3a*R*,8a*S*)-8-benzyl-4-methyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2g)

Brown oil, 73 mg, 52% yield, 86% ee. Analytical data for **2g**: $[\alpha]_D^{26}$ = -116.0 (c = 0.5, $CHCl_3$, 86% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 4H), 7.23-7.21 (m, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 5.23 (s, 1H), 4.48 (AB, J_{AB} = 16.0 Hz, 1H), 4.39 (BA, J_{BA} = 16.0 Hz, 1H), 4.05-4.01 (m, 1H), 3.71-3.65 (m, 1H), 2.45-2.32 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 138.6, 135.7, 130.5, 128.9, 127.6, 127.4, 120.4, 104.8, 104.2, 88.6, 67.3, 49.6, 40.4, 17.9; IR (film): ν_{max} (cm^{-1}) = 3375, 2977, 2928, 1720, 1608, 1511, 1468, 1465, 1368, 1254, 1165, 1032; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1489. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 8.6 min, t (minor) = 11.4 min.



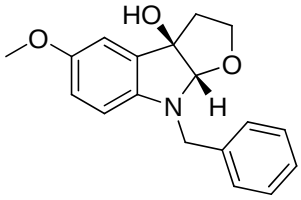
(3a*R*,8a*S*)-8-benzyl-5-bromo-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2h)

Brown solid, 75 mg, 43% yield, 90% ee. Analytical data for **2h**: $[\alpha]_D^{25}$ = -103.3 (c = 0.5, $CHCl_3$, 90% ee); Mp = 106-109 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.0 Hz, 1H), 7.32-7.22 (m, 5H), 7.18-7.15 (m, 1H), 6.21 (d, *J* = 8.4 Hz, 1H), 5.25 (s, 1H), 4.46 (AB, J_{AB} = 16.0 Hz, 1H), 4.37 (BA, J_{BA} = 16.0 Hz, 1H), 4.05-4.00 (m, 1H), 3.66-3.59 (m, 1H), 2.67 (brs, 1H), 2.42-2.34 (m, 1H), 2.30-2.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 137.5, 132.9, 132.2, 128.7, 127.3, 127.3, 126.9, 109.3, 107.8, 103.6, 87.6, 67.2, 49.0, 41.4; IR (film): ν_{max} (cm^{-1}) = 3317, 2883, 1601, 1483, 1351, 1129, 1065, 1013, 926, 882, 819, 753, 697, 639; MS (ESI): 346 $[M+1]^+$; HRMS (ESI) calcd for $C_{17}H_{17}BrNO_2$ $[M+1]^+$: 346.0437. Found: 346.0439. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.0 min, t (minor) = 13.4 min.



(3a*R*,8a*S*)-8-benzyl-5-methyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2i)

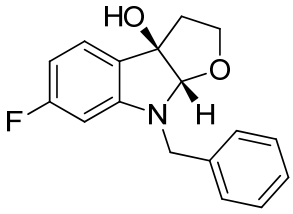
Brown oil, 74 mg, 53% yield, 85% ee. Analytical data for **2i**: $[\alpha]_D^{25}$ = -105.6 (c = 0.5, $CHCl_3$, 85% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 4H), 7.23-7.20 (m, 1H), 7.09 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.23 (d, *J* = 8.0 Hz, 1H), 5.23 (s, 1H), 4.46 (AB, J_{AB} = 16.0 Hz, 1H), 4.37 (BA, J_{BA} = 16.0 Hz, 1H), 4.04-4.00 (m, 1H), 3.67-3.60 (m, 1H), 2.54 (brs, 1H), 2.42-2.35 (m, 1H), 2.32-2.27 (m, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 138.4, 130.7, 130.3, 128.5, 127.3, 127.3, 127.1, 124.4, 106.3, 103.9, 88.0, 67.2, 49.4, 41.3, 20.7; IR (film): ν_{max} (cm^{-1}) = 3400, 3029, 2867, 1614, 1496, 1355, 1315, 1119, 1070, 1017, 945, 799, 736, 696; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1488. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 9.5 min, t (minor) = 10.3 min.



(3a*R*,8a*S*)-8-benzyl-5-methoxy-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2j)

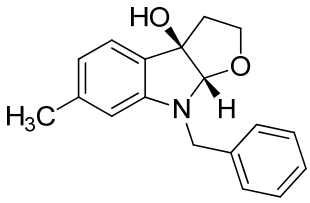
Brown solid, 79 mg, 53% yield, 88% ee. Analytical data for **2j**: $[\alpha]_D^{24}$ = -96.3 (c = 0.5, $CHCl_3$, 88% ee); Mp = 96-98 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 4H), 7.24-7.20 (m, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.66 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.24 (d, *J* = 8.4 Hz, 1H), 5.24 (s, 1H), 4.43 (AB, J_{AB} = 16.0 Hz, 1H), 4.35 (BA, J_{BA} = 16.0 Hz, 1H), 4.06-4.01 (m, 1H), 3.70 (s, 3H), 3.68-3.63 (m, 1H), 2.71 (brs, 1H), 2.43-2.35 (m, 1H), 2.30 (ddd, *J* = 12.1, 5.4, 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 144.6, 138.4, 131.2, 128.5, 127.4, 127.1, 115.5, 110.4, 107.1, 104.4, 87.9, 67.2, 56.1, 50.0, 41.3; IR (film): ν_{max} (cm^{-1}) = 3335, 2956, 1594, 1492, 1281, 1215, 1118, 1038,

1006, 949, 870, 804, 757, 698, 637; MS (ESI): 298 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_3$ $[M+1]^+$: 298.1438. Found: 298.1436. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 16.7 min, t (minor) = 19.3 min.



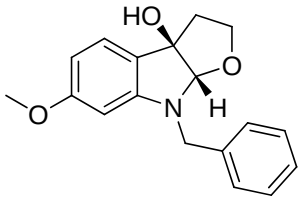
(3a*R*,8a*S*)-8-benzyl-6-fluoro-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2k)

Brown solid, 83 mg, 58% yield, 83% ee. Analytical data for **2k**: $[\alpha]_D^{25}$ = -89.8 (c = 0.5, $CHCl_3$, 83% ee); Mp = 118-120 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 5H), 7.16 (dd, *J* = 8.4, 5.6 Hz, 1H), 6.38-6.33 (m, 1H), 6.04 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.26 (s, 1H), 4.44 (AB, J_{AB} = 16.0 Hz, 1H), 4.38 (BA, J_{BA} = 16.0 Hz, 1H), 4.06-4.01 (m, 1H), 3.66-3.60 (m, 1H), 2.55 (brs, 1H), 2.43-2.35 (m, 1H), 2.30-2.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, *J* = 243.1 Hz), 152.0 (d, *J* = 12.2 Hz), 137.4, 128.7, 127.4, 127.3, 125.7, 124.7 (d, *J* = 11.0 Hz), 104.1 (d, *J* = 23.1 Hz), 103.8, 94.2 (d, *J* = 27.1 Hz), 87.4, 67.4, 48.9, 41.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.08; IR (film): ν_{max} (cm^{-1}) = 3363, 2964, 1599, 1492, 1324, 1245, 1225, 1098, 1008, 949, 899, 823, 758, 698, 622; MS (ESI): 286 $[M+1]^+$; HRMS (ESI) calcd for $C_{17}H_{17}FNO_2$ $[M+1]^+$: 286.1238. Found: 286.1239. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.1 min, t (minor) = 11.8 min.



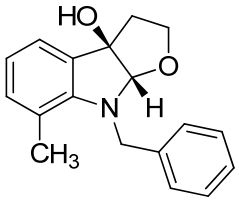
(3a*R*,8a*S*)-8-benzyl-6-methyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2l)

Brown solid, 84 mg, 60% yield, 85% ee. Analytical data for **2l**: $[\alpha]_D^{25}$ = -94.7 (c = 0.5, $CHCl_3$, 85% ee); Mp = 88-91 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 4H), 7.23-7.20 (m, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.17 (s, 1H), 5.19 (s, 1H), 4.45 (AB, J_{AB} = 16.0 Hz, 1H), 4.37 (BA, J_{BA} = 16.0 Hz, 1H), 4.00-3.95 (m, 1H), 3.63-3.57 (m, 1H), 2.72 (brs, 1H), 2.39-2.31 (m, 1H), 2.27-2.23 (m, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 140.6, 138.3, 128.6, 127.4, 127.3, 127.1, 123.6, 118.8, 107.0, 103.8, 87.7, 67.3, 49.0, 41.4, 21.9; IR (film): ν_{max} (cm^{-1}) = 3323, 2880, 1619, 1495, 1346, 1290, 1151, 1060, 1015, 955, 823, 760, 700, 635; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1490. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 9.7 min, t (minor) = 11.3 min.



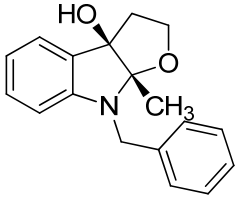
(3a*R*,8a*S*)-8-benzyl-6-methoxy-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2m)

Brown oil, 64 mg, 43% yield, 83% ee. Analytical data for **2m**: $[\alpha]_D^{26}$ = -92.4 (c = 0.5, $CHCl_3$, 83% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 4H), 7.25-7.21 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 6.24 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.92 (d, *J* = 2.0 Hz, 1H), 5.26 (s, 1H), 4.48 (AB, J_{AB} = 16.0 Hz, 1H), 4.40 (BA, J_{BA} = 16.0 Hz, 1H), 4.07-4.02 (m, 1H), 3.69 (s, 3H), 3.67-3.61 (m, 1H), 2.45-2.38 (m, 1H), 2.33 (brs, 1H), 2.32-2.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 152.2, 138.3, 128.9, 127.7, 127.5, 124.7, 123.0, 104.2, 102.7, 93.5, 87.8, 67.7, 55.6, 49.2, 41.6; IR (film): ν_{max} (cm^{-1}) = 3397, 2939, 1619, 1497, 1268, 1208, 1115, 1016, 946, 815, 697, 637; MS (ESI): 298 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_3$ $[M+1]^+$: 298.1438. Found: 298.1436. The enantiomeric excess was determined by Daicel Chiralpak OD-H, n-hexane/2-propanol = 80/20, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 7.4 min, t (minor) = 8.9 min.



(3a*R*,8a*S*)-8-benzyl-7-methyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2n)

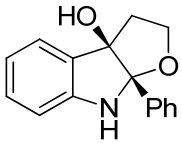
Yellow solid, 100 mg, 71% yield, 89% ee. Analytical data for **2n**: $[\alpha]_D^{26}$ = -107.4 (c = 0.5, $CHCl_3$, 89% ee); Mp = 75-77 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.21 (m, 5H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 5.14 (s, 1H), 4.75 (AB, J_{AB} = 16.8 Hz, 1H), 4.61 (BA, J_{BA} = 16.8 Hz, 1H), 3.98-3.95 (m, 1H), 3.65-3.59 (m, 1H), 2.43-2.35 (m, 2H), 2.28-2.30 (m, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 139.7, 133.5, 131.6, 128.6, 127.0, 126.8, 121.9, 119.7, 119.4, 104.9, 87.2, 67.0, 52.0, 41.2, 19.1; IR (film): ν_{max} (cm^{-1}) = 3359, 2870, 1603, 1464, 1308, 1220, 1001, 951, 781, 747, 725, 694; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1488. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL{\cdot}min^{-1}$, λ = 254 nm, t (major) = 9.0 min, t (minor) = 12.8 min.



(3a*R*,8a*S*)-8-benzyl-8a-methyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2o)

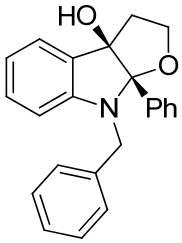
Yellow solid, 100 mg, 71% yield, 48% ee. Analytical data for **2o**: $[\alpha]_D^{25}$ = -41.0 (c = 0.5, $CHCl_3$, 48% ee); Mp = 73-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 5H), 7.25-7.19 (m, 1H), 7.03 (td, *J* = 8.0, 1.2 Hz, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.18 (d, *J* = 7.6 Hz, 1H), 4.51 (AB, J_{AB} = 16.8 Hz, 1H), 4.32 (BA, J_{BA} = 16.8 Hz, 1H), 3.90-3.86 (m, 1H), 3.49-3.42 (m, 1H), 2.45-2.32 (m, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 139.3, 130.3, 129.6, 128.5, 126.8, 126.7, 123.7, 117.7, 106.2, 104.2, 87.8, 65.0, 46.4, 41.4, 19.9; IR (film): ν_{max} (cm^{-1}) = 3418, 1607, 1483, 1349,

1294, 1133, 1096, 1040, 1019, 922, 732; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1487. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 5.8 min, t (minor) = 9.6 min.



(3a*R*,8a*S*)-8a-phenyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2p)

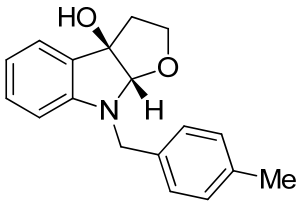
Yellow oil, 113 mg, 89% yield, 85% ee. Analytical data for **2p**: $[\alpha]_D^{21}$ = -119.8 (c = 0.2, $CHCl_3$, 85% ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.39-7.32 (m, 3H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.66 (brs, 1H), 4.21-4.15 (m, 1H), 3.79-3.65 (m, 1H), 2.43-2.38 (m, 2H), 1.64 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 139.0, 130.1, 129.2, 128.5, 128.2, 126.8, 124.6, 119.2, 108.5, 104.7, 89.8, 65.9, 40.8; IR (film): ν_{max} (cm^{-1}) = 3359, 3030, 2872, 1608, 1488, 1355, 1316, 1259, 1160, 1076, 1011, 942, 796, 742, 696; MS (ESI): 254 $[M+1]^+$; HRMS (ESI) calcd for $C_{16}H_{16}NO_2$ $[M+1]^+$: 254.1176. Found: 254.1175. The enantiomeric excess was determined by Phenomenex Lux Cellulose-4, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 12.2 min, t (minor) = 9.3 min.



(3a*R*,8a*S*)-8-benzyl-8a-phenyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2q)

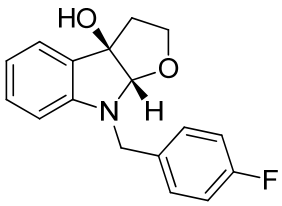
Pale yellow solid, 128 mg, 75% yield, 75% ee. Analytical data for **2q**: $[\alpha]_D^{21}$ = -46.1 (c = 0.5, $CHCl_3$, 75% ee); Mp = 108-110 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.48 (m, 2H), 7.40-7.19 (m, 9H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H),

6.31 (d, J = 8.0 Hz, 1H), 4.31-4.17 (m, 3H), 3.86-3.79 (m, 1H), 2.47-2.43 (m, 2H), 1.58 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 138.7, 137.3, 128.6, 128.6, 128.3, 127.2, 126.7, 118.2, 109.1, 106.7, 89.2, 65.9, 48.8, 41.4; IR (film): ν_{max} (cm^{-1}) = 3499, 2969, 2330, 1609, 1489, 1447, 1357, 1125, 1026, 967, 886, 805, 734, 700, 649; MS (ESI): 344 $[M+1]^+$; HRMS (ESI) calcd for $C_{23}H_{22}NO_2$ $[M+1]^+$: 344.1465. Found: 344.1467. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 14.1 min, t (minor) = 13.0 min.



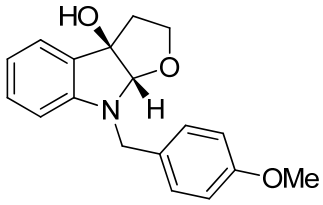
(3aR,8aS)-8-(4-methylbenzyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2r)

Brown oil, 100 mg, 70% yield, 84% ee. Analytical data for **2r**: $[\alpha]_D^{19}$ = -106.5 (c = 0.5, $CHCl_3$, 84% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 7.2 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.08 – 7.05 (m, 3H), 6.67 (t, J = 7.2 Hz, 1H), 6.33 (d, J = 8.0 Hz, 1H), 5.18 (s, 1H), 4.40 (AB, J_{AB} = 15.9 Hz, 1H), 4.32 (BA, J_{BA} = 16.0 Hz, 1H), 3.95 (t, J = 8.8 Hz, 1H), 3.61 – 3.54 (m, 1H), 2.86 (s, 1H), 2.37 – 2.22 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 136.7, 135.0, 130.3, 130.2, 129.2, 127.4, 123.8, 117.9, 106.3, 103.5, 87.8, 67.2, 48.8, 41.4, 21.1; IR (film): ν_{max} (cm^{-1}) = 3381, 2867, 1609, 1488, 1316, 1159, 1115, 1011, 944, 805, 740, 627; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1490. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.2 min, t (minor) = 13.5 min.



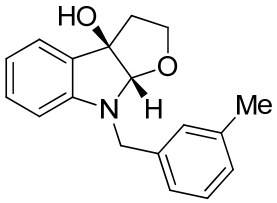
(3aR,8aS)-8-(4-fluorobenzyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2s)

Brown oil, 62 mg, 43% yield, 87% ee. Analytical data for **2s**: $[\alpha]_D^{19}$ = -96.6 (c = 0.5, $CHCl_3$, 87% ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 3H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.34 (d, *J* = 8.1 Hz, 1H), 5.25 (s, 1H), 4.47 (AB, J_{AB} = 15.9 Hz, 1H), 4.38 (BA, J_{BA} = 16.2 Hz, 1H), 4.08 – 4.02 (m, 1H), 3.68 – 3.59 (m, 1H), 2.49 – 2.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, *J* = 243.7 Hz), 150.1, 133.7 (d, *J* = 3.1 Hz), 130.2 (d, *J* = 26.5 Hz), 128.8 (d, *J* = 7.9 Hz), 123.7, 118.1, 115.4, 115.2, 106.2, 103.5, 87.8, 67.2, 48.5, 41.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.74; IR (film): ν_{max} (cm^{-1}) = 3382, 2871, 1608, 1488, 1352, 1219, 1156, 1073, 1011, 944, 822, 742, 624; MS (ESI): 286 $[M+1]^+$; HRMS (ESI) calcd for $C_{17}H_{17}FNO_2$ $[M+1]^+$: 286.1238. Found: 286.1239. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL \cdot min^{-1}$, λ = 254 nm, t (major) = 12.1 min, t (minor) = 9.4 min.



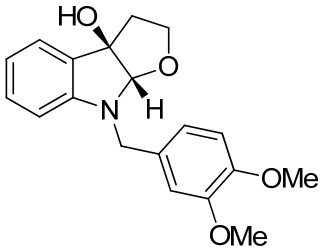
(3aR,8aS)-8-(4-methoxybenzyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2t)

Brown oil, 96 mg, 64% yield, 84% ee. Analytical data for **2t**: $[\alpha]_D^{16}$ = -116.3 (c = 0.5, $CHCl_3$, 84% ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 3H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 8.1 Hz, 1H), 5.24 (s, 1H), 4.44 (AB, J_{AB} = 15.6 Hz, 1H), 4.33 (BA, J_{BA} = 15.6 Hz, 1H), 4.04 (t, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 3.67 – 3.59 (m, 1H), 2.47 – 2.37 (m, 2H), 2.34 – 2.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 150.3, 130.3, 130.1, 130.0, 128.6, 123.8, 117.9, 113.9, 106.3, 103.4, 87.8, 67.2, 55.2, 48.4, 41.3; IR (film): ν_{max} (cm^{-1}) = 3372, 2933, 1609, 1488, 1354, 1243, 1173, 1011, 943, 817, 742, 625; MS (ESI): 298 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_3$ $[M+1]^+$: 298.1438. Found: 298.1445. The enantiomeric excess was determined by Daicel Chiralcel OD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL \cdot min^{-1}$, λ = 254 nm, t (major) = 17.5 min, t (minor) = 23.1 min.



(3aR,8aS)-8-(3-methylbenzyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2u)

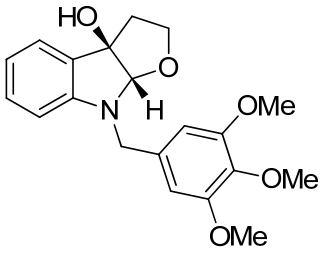
Brown oil, 99 mg, 70% yield, 76% ee. Analytical data for **2u**: $[\alpha]_D^{18}$= -94.6 (c = 0.5, $CHCl_3$, 76% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.11 – 7.06 (m, 3H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 1H), 4.43 (AB, J_{AB} = 16.0 Hz, 1H), 4.34 (BA, J_{BA} = 16.0 Hz, 1H), 4.02 – 3.97 (m, 1H), 3.64 – 3.58 (m, 1H), 2.67 (s, 1H), 2.41 – 2.33 (m, 1H), 2.30 – 2.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 138.1, 138.1, 130.3, 130.1, 128.5, 128.1, 127.9, 124.4, 123.8, 117.9, 106.3, 103.5, 87.9, 67.2, 49.0, 41.4, 21.5; IR (film): ν_{max} (cm^{-1}) = 3383, 2868, 1608, 1488, 1346, 1315, 1162, 1074, 1012, 942, 739, 694; MS (ESI): 282 $[M+1]^+$; HRMS (ESI) calcd for $C_{18}H_{20}NO_2$ $[M+1]^+$: 282.1489. Found: 282.1491. The enantiomeric excess was determined by Daicel Chiralcel OD-H, n-hexane/2-propanol = 90/10, ν = 1.0 mL·min^{-1}, λ = 254 nm, t (major) = 10.4 min, t (minor) = 14.5 min.



(3aR,8aS)-8-(3,4-dimethoxybenzyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2v)

Brown oil, 91 mg, 55% yield, 66% ee. Analytical data for **2v**: $[\alpha]_D^{19}$ = -74.7 (c = 0.5, $CHCl_3$, 66% ee); ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 10.8 Hz, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 4.43 (AB, J_{AB} = 15.6 Hz, 1H), 4.31 (BA, J_{BA} = 15.9 Hz, 1H), 4.03 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.67 – 3.58 (m,

1H), 2.76 (s, 1H), 2.45 – 2.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 149.1, 148.1, 130.6, 130.4, 130.1, 123.7, 119.5, 118.0, 111.0, 110.7, 106.4, 103.6, 88.0, 67.3, 55.9, 55.8, 49.2, 41.4; IR (film): ν_{max} (cm^{-1}) = 3357, 2932, 1609, 1514, 1417, 1251, 1129, 1023, 944, 862, 809, 745, 653; MS (ESI): 328 $[M+1]^+$; HRMS (ESI) calcd for $C_{19}H_{22}NO_4$ $[M+1]^+$: 328.1543. Found: 328.1549. The enantiomeric excess was determined by Daicel Chiralpak AD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL{\cdot}min^{-1}$, λ = 254 nm, t (major) = 27.3 min, t (minor) = 29.5 min.

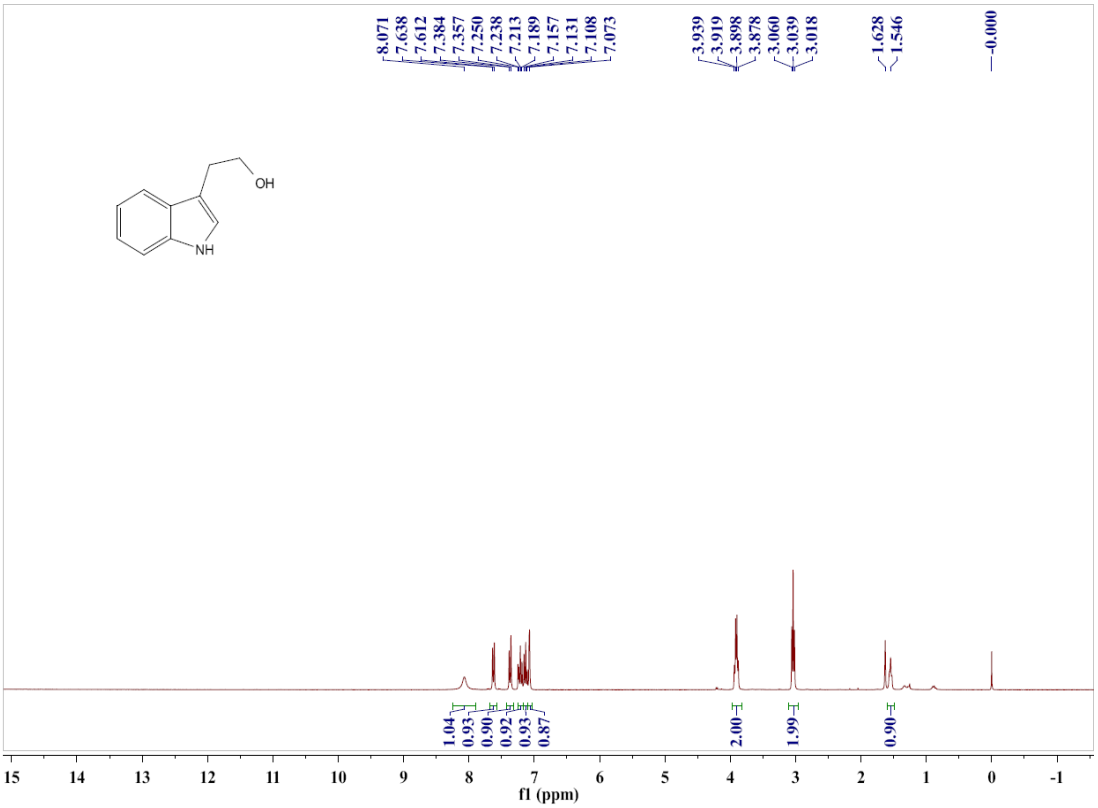


(3aR,8aS)-8-(3,4,5-trimethoxybenzyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-3a-ol (2w)

Brown oil, 100 mg, 56% yield, 39% ee. Analytical data for **2w**: $[\alpha]_D^{18}$ = -40.5 (c = 0.5, $CHCl_3$, 39% ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 7.2 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.72 (t, J = 7.2 Hz, 1H), 6.58 (s, 2H), 6.37 (d, J = 7.8 Hz, 1H), 5.26 (s, 1H), 4.43 (AB, J_{AB} = 15.9 Hz, 1H), 4.30 (BA, J_{BA} = 15.9 Hz, 1H), 4.05 (t, J = 7.5 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 6H), 3.69 – 3.60 (m, 1H), 2.86 (s, 1H), 2.47 – 2.30 (m, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 150.2, 136.7, 134.0, 130.2, 130.1, 123.7, 118.0, 106.3, 104.0, 103.9, 87.7, 67.1, 60.7, 55.9, 49.9, 41.4; IR (film): ν_{max} (cm^{-1}) = 3403, 2938, 1592, 1490, 1327, 1232, 1120, 1006, 910, 730, 622; MS (ESI): 358 $[M+1]^+$; HRMS (ESI) calcd for $C_{20}H_{24}NO_5$ $[M+1]^+$: 358.1649. Found: 358.1653. The enantiomeric excess was determined by Daicel Chiralcel OD-H, n-hexane/2-propanol = 90/10, ν = 1.0 $mL{\cdot}min^{-1}$, λ = 254 nm, t (major) = 30.7 min, t (minor) = 24.9 min.

3. Copies of ^{1}H NMR and ^{13}C NMR spectra of the compounds

1a



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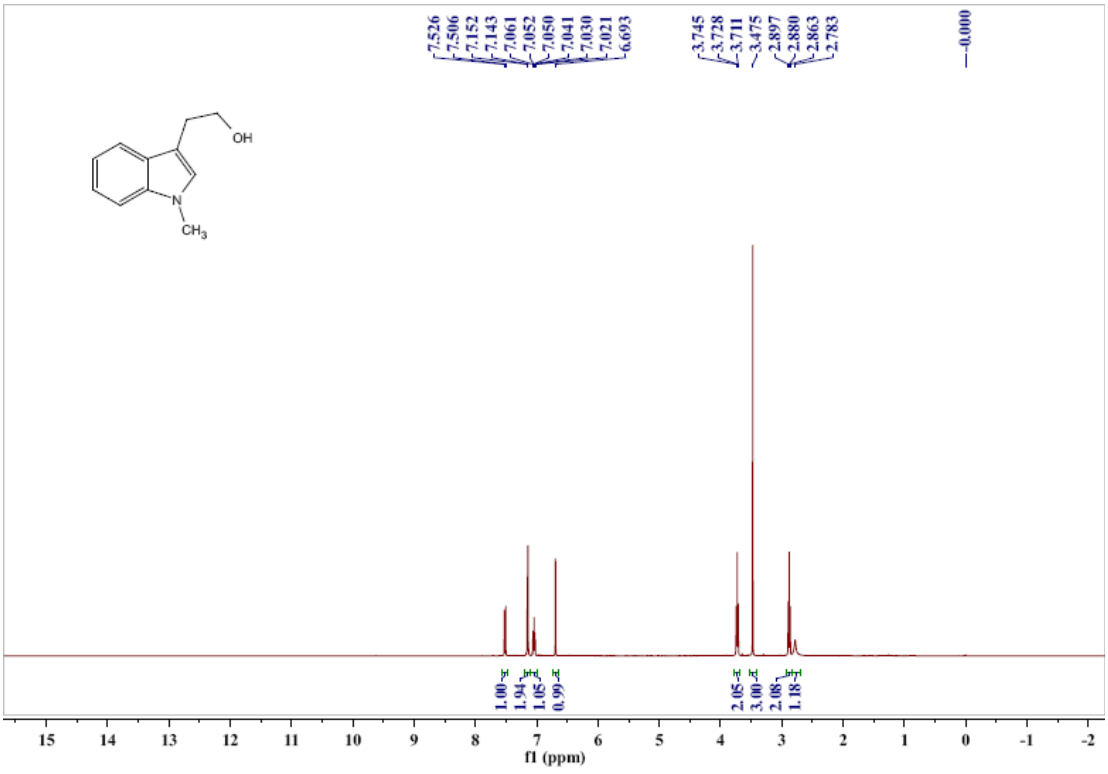

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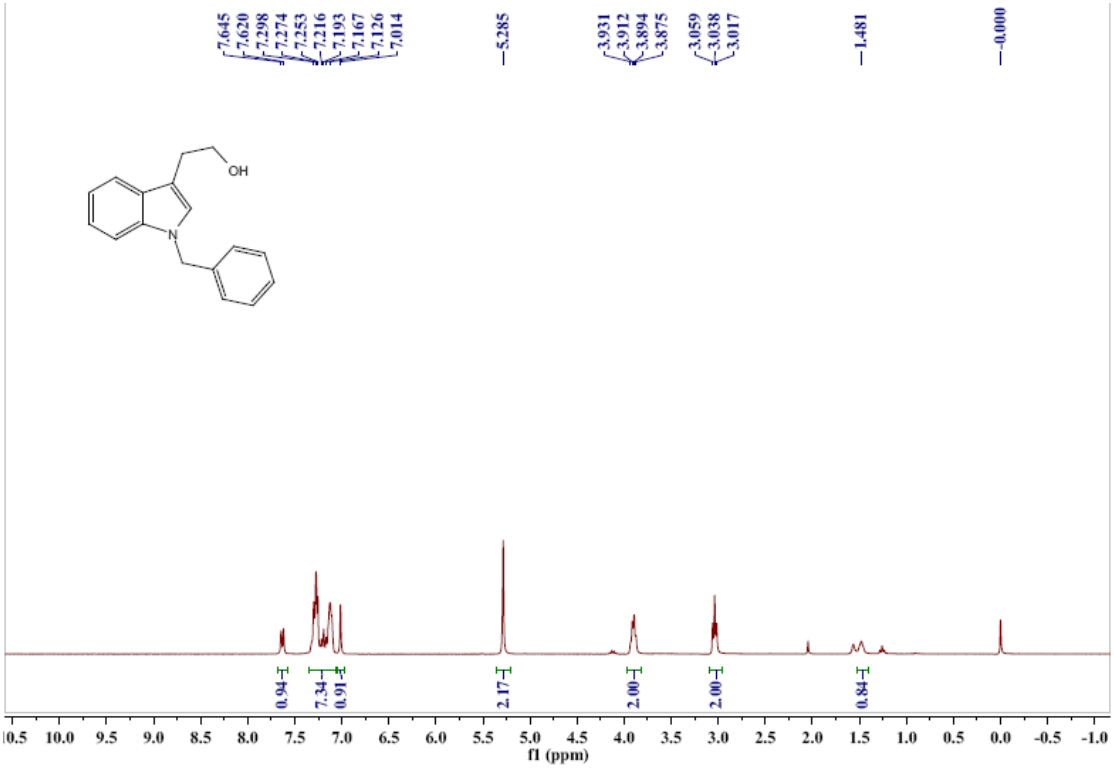
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7.167
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7.014
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3.912
3.894
3.875
3.059
3.038
3.017
1.481
0.000
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N
0.94
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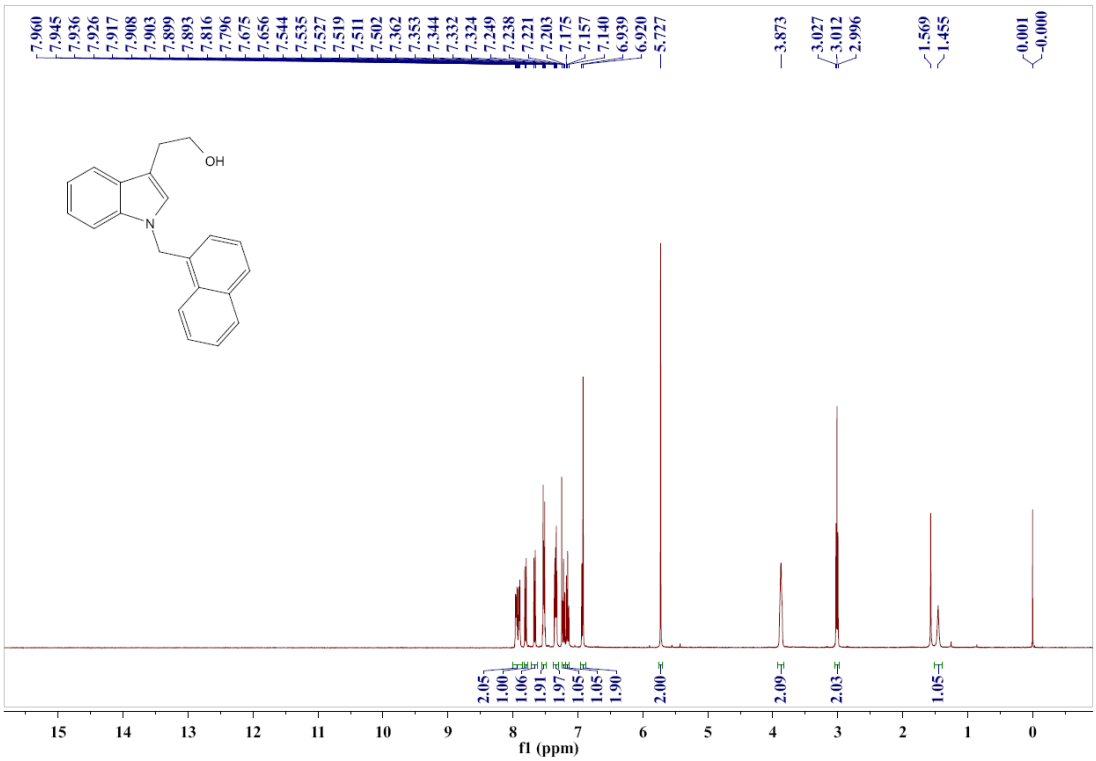
0.91
2.17
2.00
2.00
0.84
f1 (ppm)

1d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7.945
7.936
7.926
7.917
7.908
7.903
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7.893
7.816
7.796
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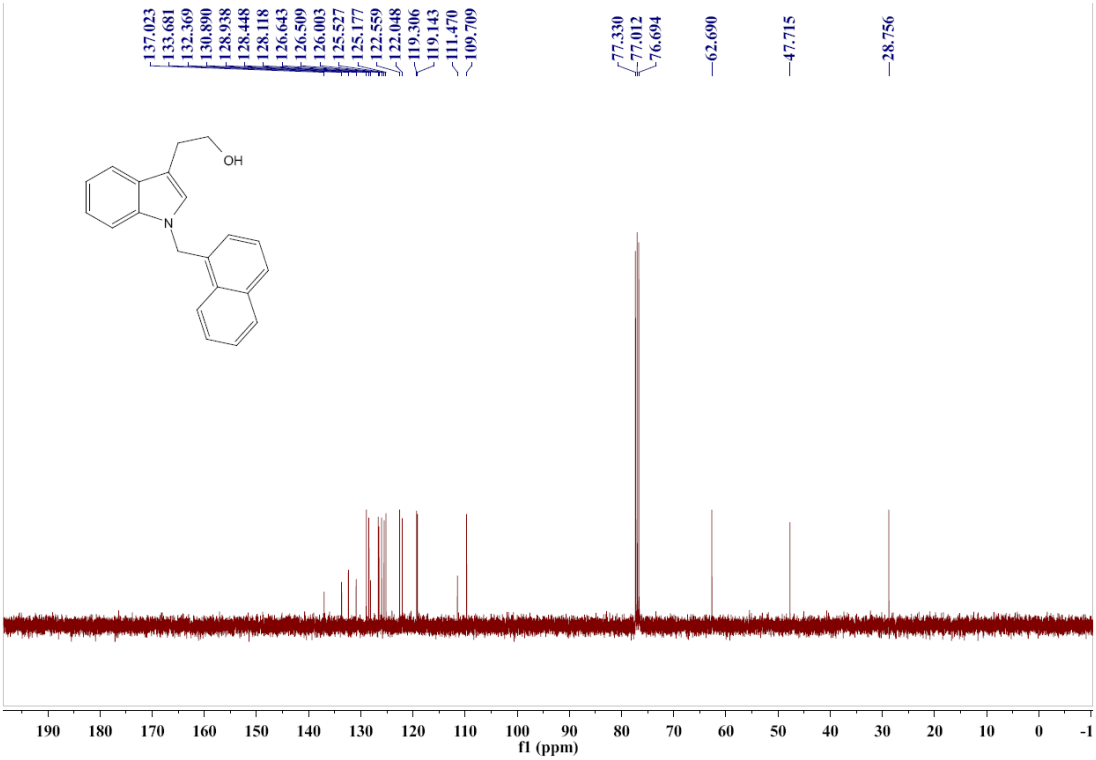
7.656
7.544
7.535
7.527
7.519
7.511
7.502
7.362
7.353
7.344
7.332
7.324
7.249
7.238
7.221
7.203
7.175
7.157
7.140
6.939
6.920
5.727
3.873
3.027
3.012
2.996
1.569
1.455
0.001
-0.000
OH
N
2.05
1.00
1.06
1.91
1.97
1.05
1.05
1.90
2.00
2.09
2.03
1.05
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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122.559
122.048
119.306
119.143
111.470
109.709
77.330
77.012
76.694
62.690
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28.756
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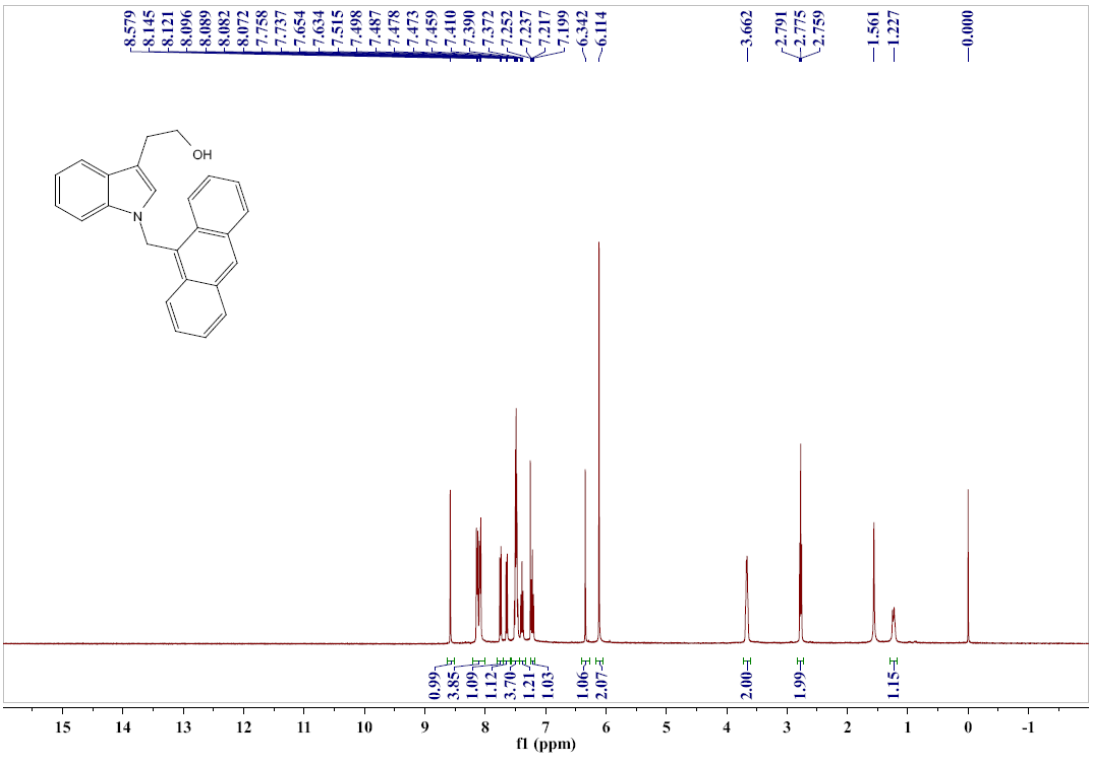
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

1e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8.082
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7.654
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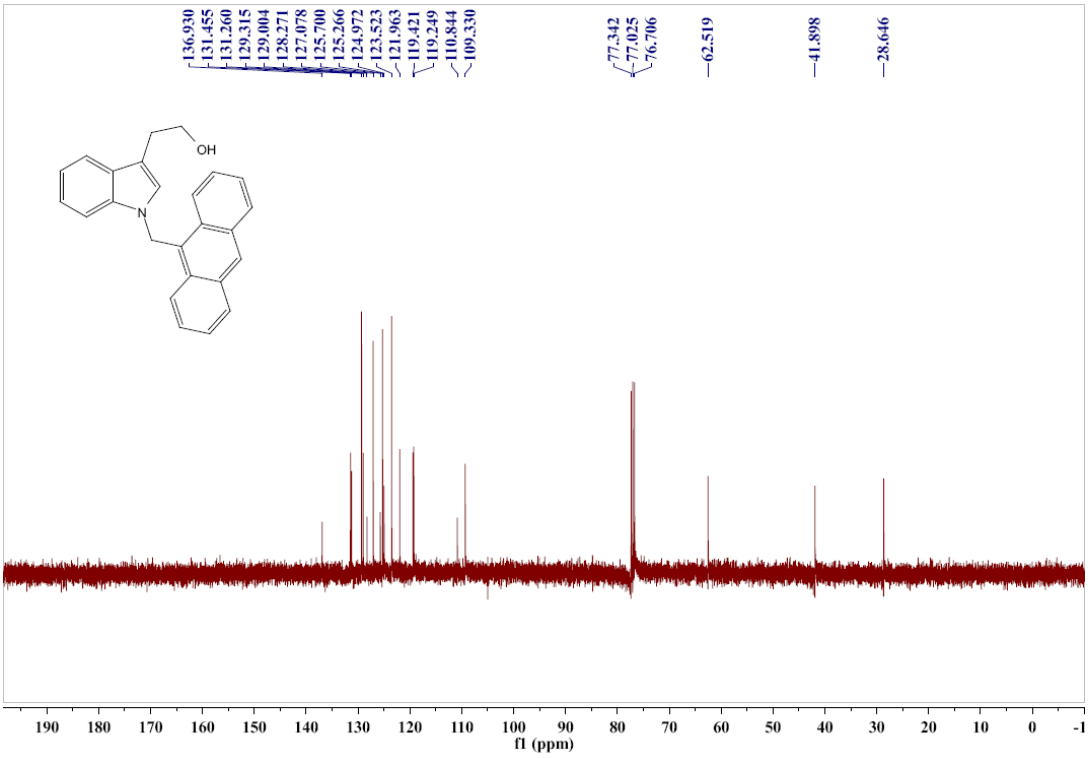
7.487
7.478
7.473
7.459
7.410
7.390
7.372
7.252
7.237
7.217
7.199
6.342
6.114
3.662
2.791
2.775
2.759
1.561
1.227
0.000
OH
N
0.99
3.85
1.09
1.12
3.70
1.21
1.03
1.06
2.07
2.00
1.99
1.15
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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125.700
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119.421
119.249
110.844
109.330
77.342
77.025
76.706
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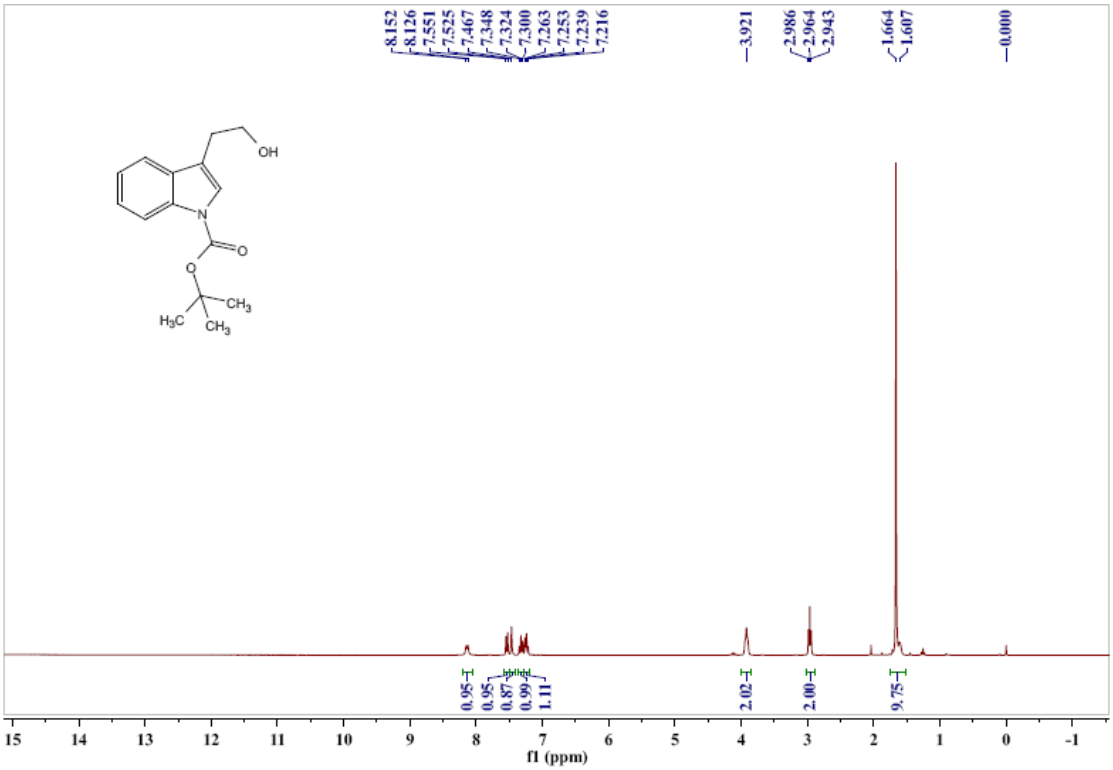
28.646
OH
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

1f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7.253
7.239
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2.986
2.964
2.943
1.664
1.607
0.000
OH
N
O
O
CH3
H3C
CH3
0.95
0.95
0.87
0.99
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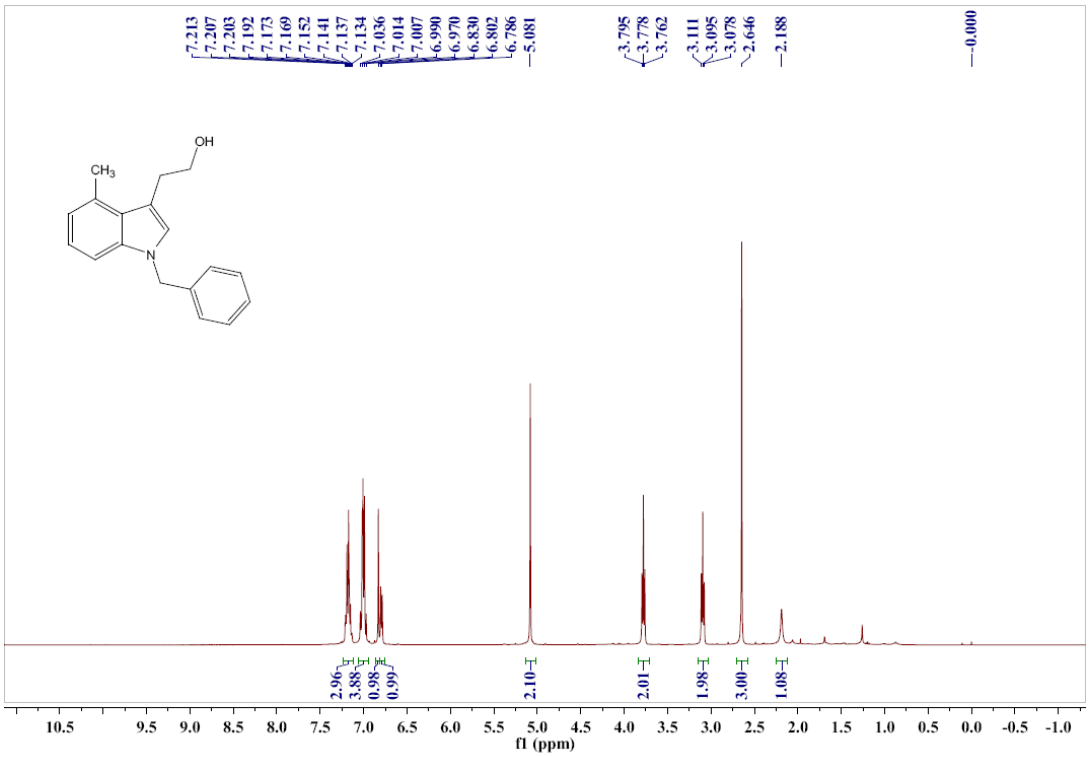
2.02
2.00
9.75
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

1g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7.152
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7.134
7.036
7.014
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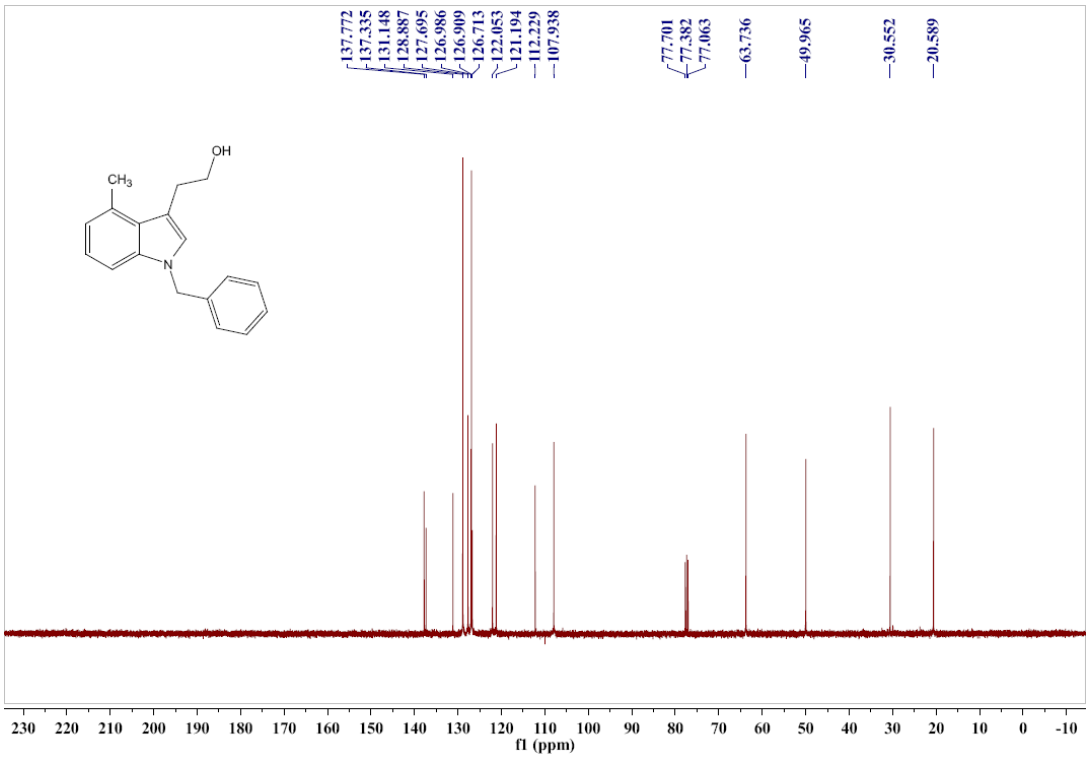
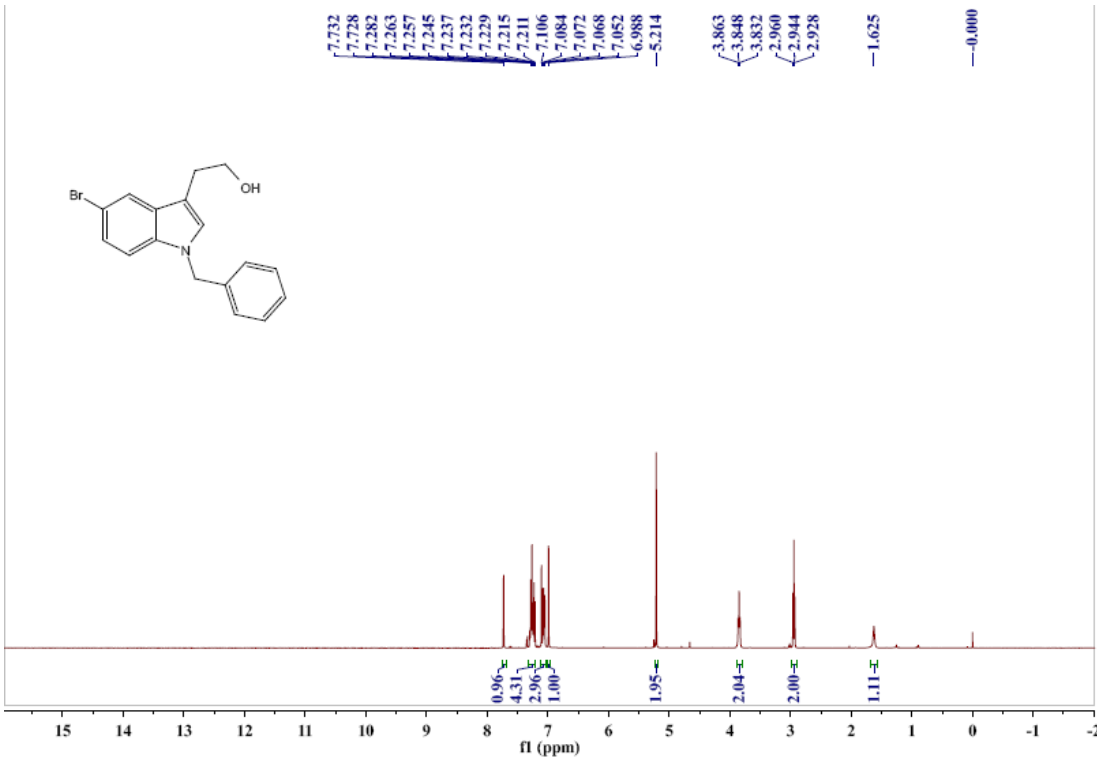
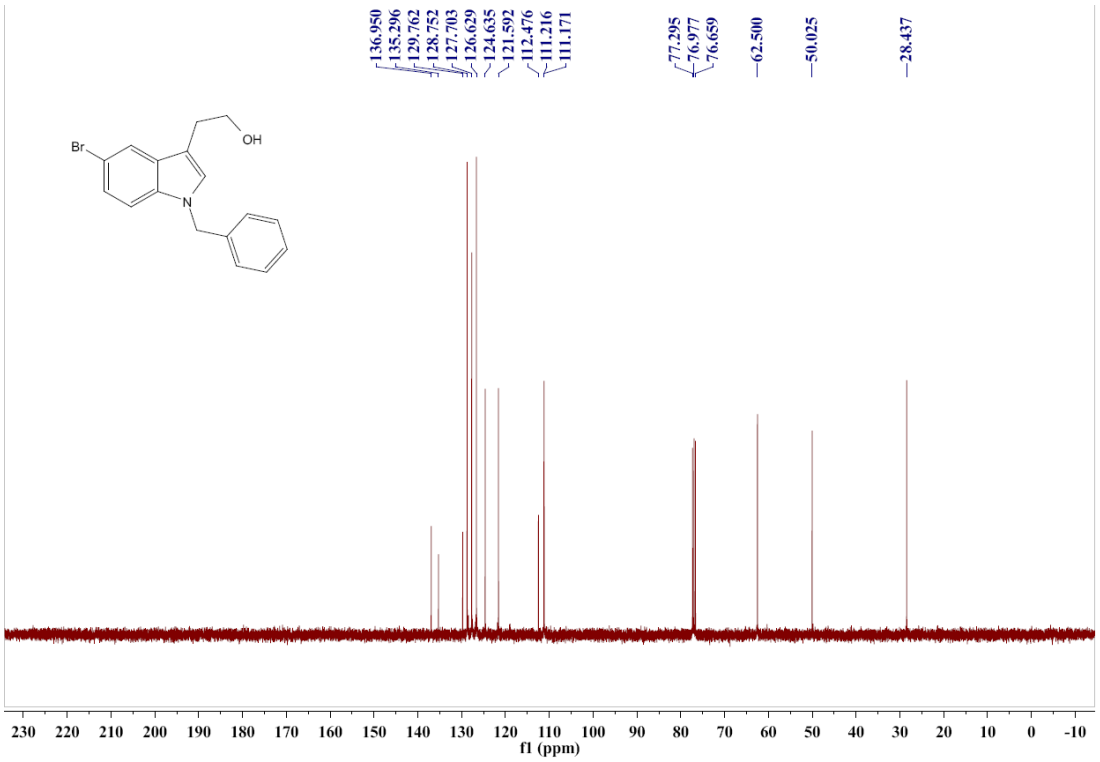
6.990
6.970
6.830
6.802
6.786
5.081
3.795
3.778
3.762
3.111
3.095
3.078
2.646
2.188
0.000
OH
CH3
N
2.96
3.88
0.98
0.99
2.10
2.01
1.98
3.00
1.08
f1 (ppm)

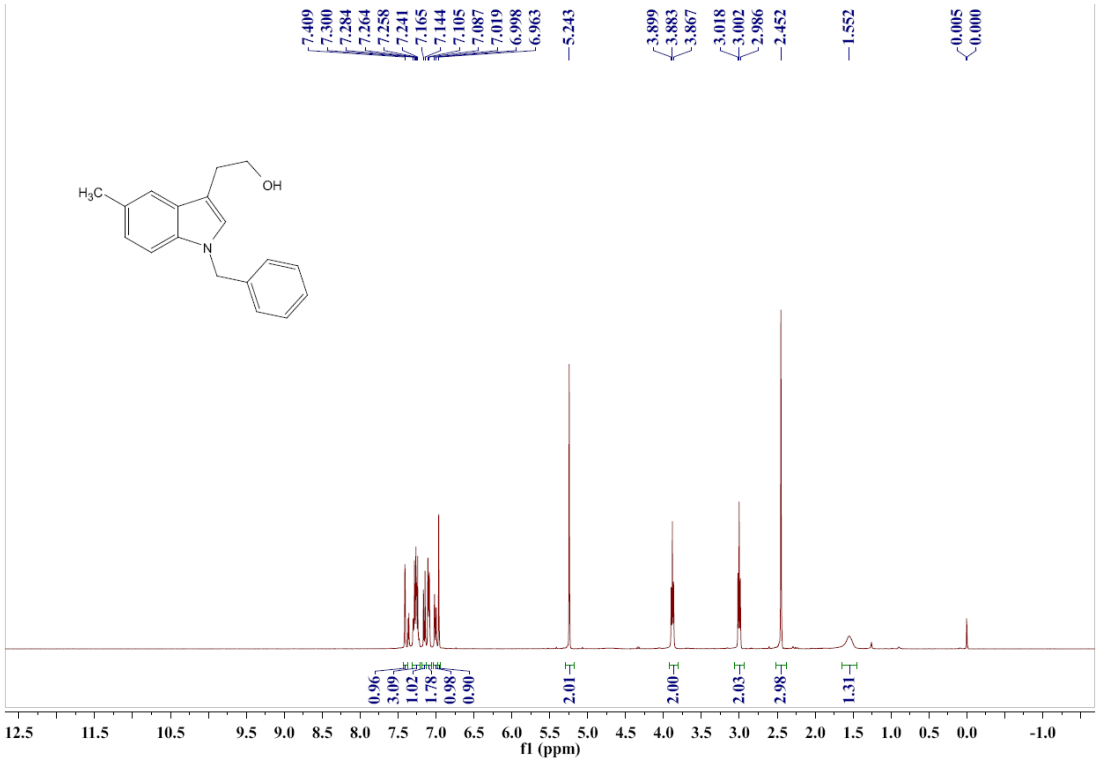

137.772
137.335
131.148
128.887
127.695
126.986
126.909
126.713
122.053
121.194
112.229
107.938
77.701
77.382
77.063
63.736
49.965
30.552
20.589
OH
CH3
N
f1 (ppm)

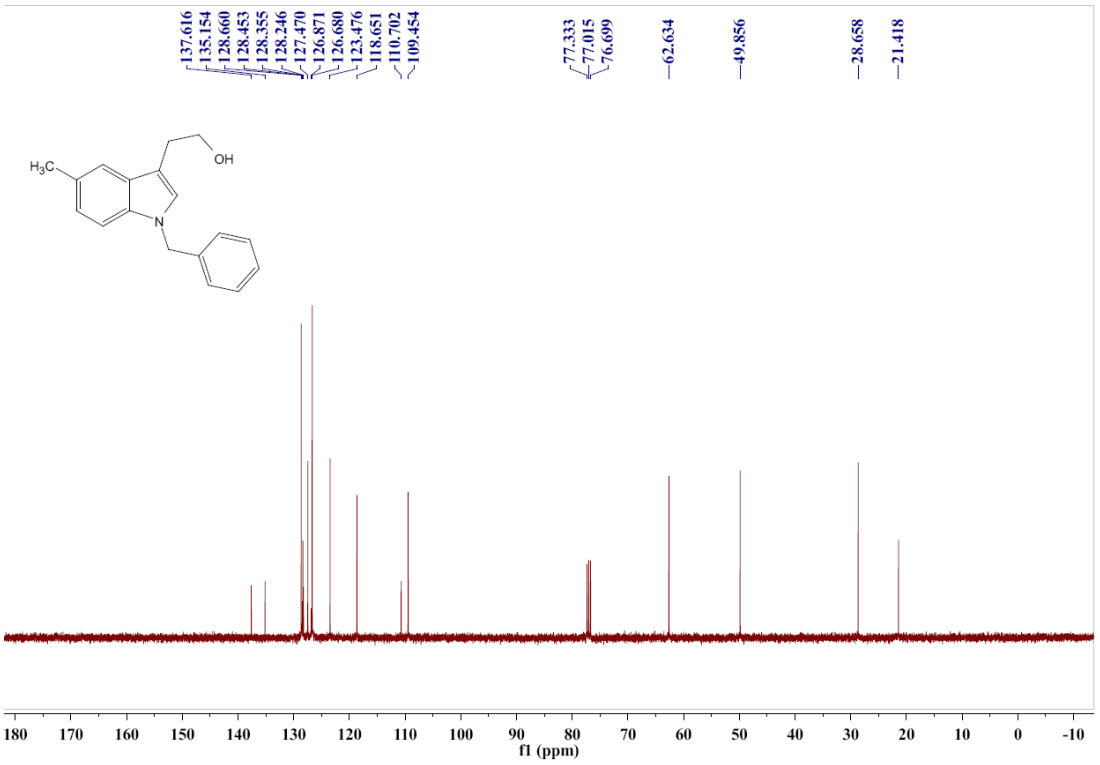
1h


7.732
7.728
7.282
7.263
7.257
7.245
7.237
7.232
7.229
7.215
7.211
7.106
7.084
7.072
7.068
7.052
6.988
5.214
3.863
3.848
3.832
2.960
2.944
2.928
1.625
0.000
Br
OH
N
0.96
4.31
2.96
1.00
1.95
2.04
2.00
1.11
f1 (ppm)

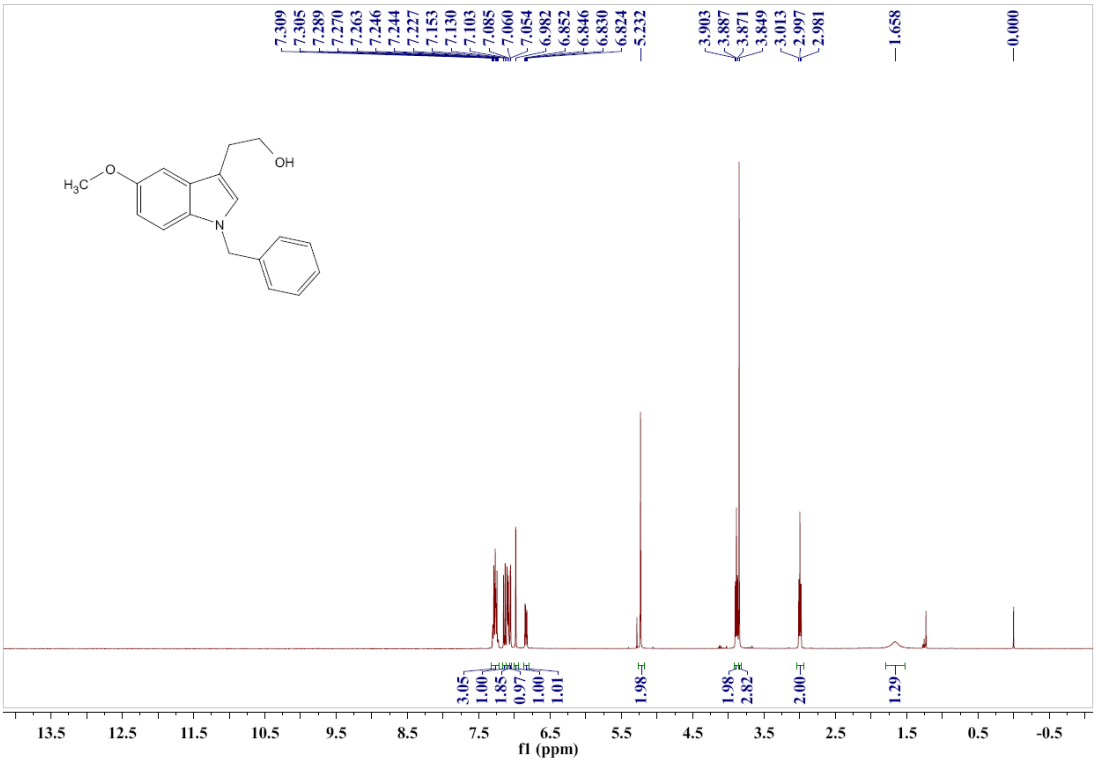

136.950
135.296
129.762
128.752
127.703
126.629
124.635
121.592
112.476
111.216
111.171
77.295
76.977
76.659
62.500
50.025
28.437
Br
OH
N
f1 (ppm)

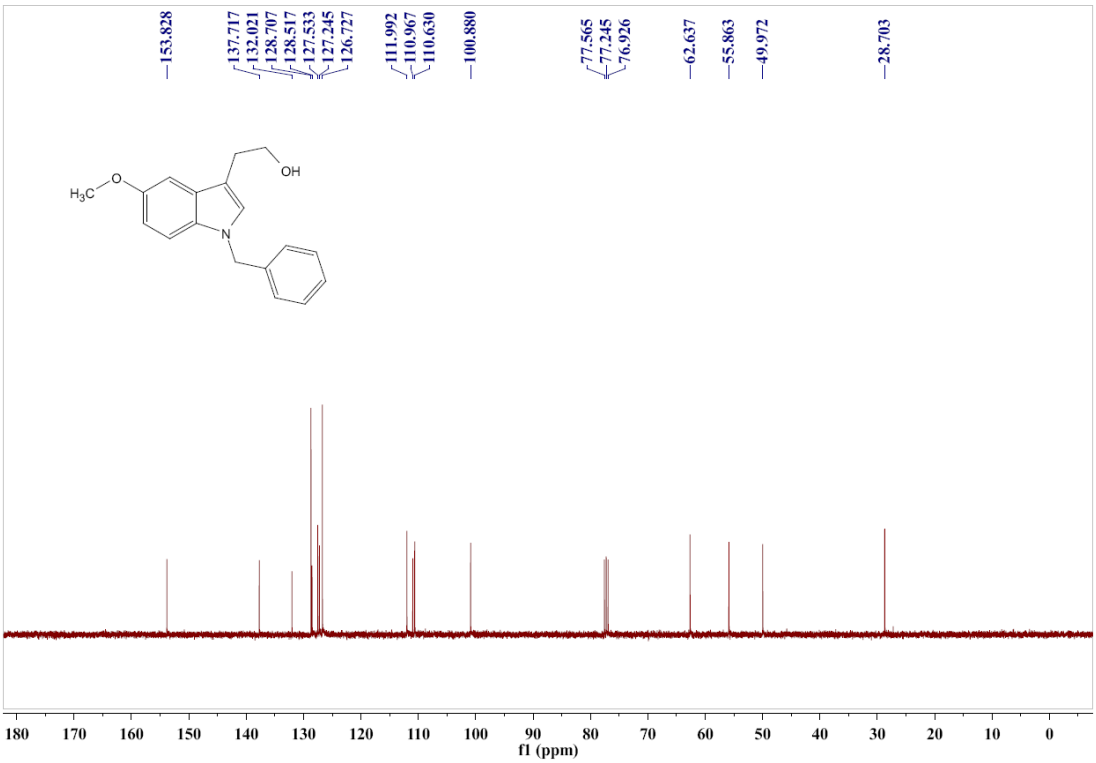
1i


7.409
7.300
7.284
7.264
7.258
7.241
7.165
7.144
7.105
7.087
7.019
6.998
6.963
5.243
3.899
3.883
3.867
3.018
3.002
2.986
2.452
1.552
0.005
0.000
H3C
OH
N
0.96
3.09
1.02
1.78
0.98
0.90
2.01
2.00
2.03
2.98
1.31
f1 (ppm)

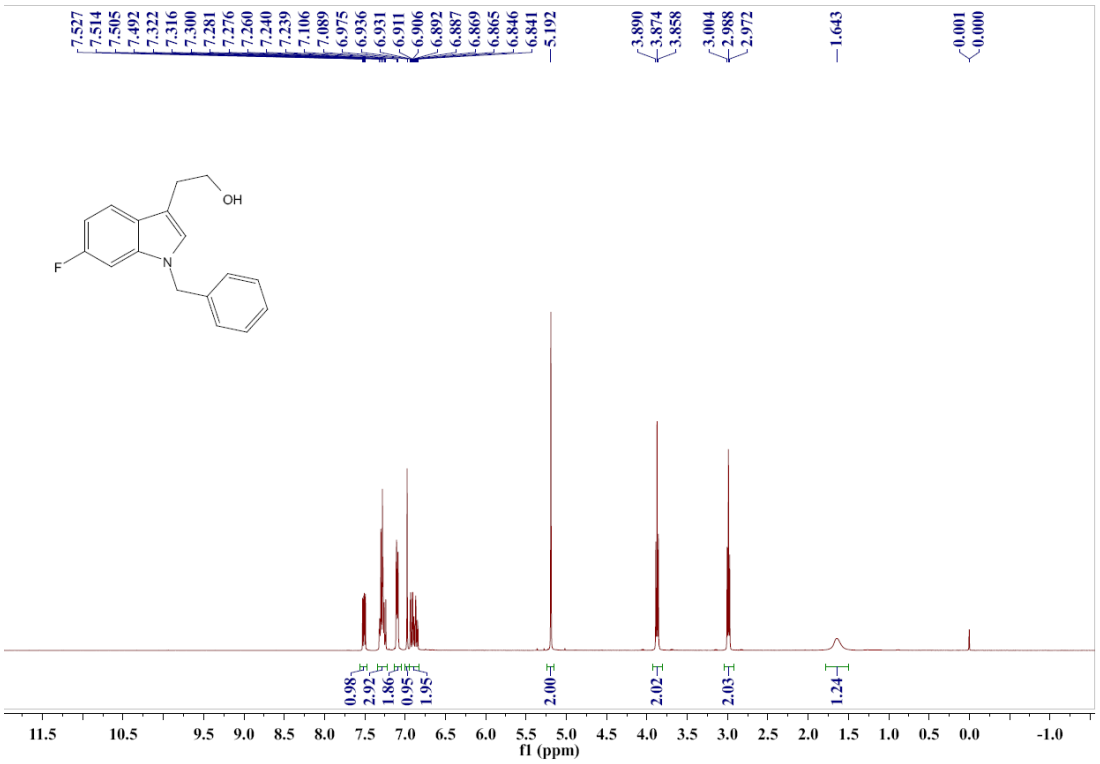

137.616
135.154
128.660
128.453
128.355
128.246
127.470
126.871
126.680
123.476
118.651
110.702
109.454
77.333
77.015
76.699
62.634
49.856
28.658
21.418
H3C
OH
N
f1 (ppm)

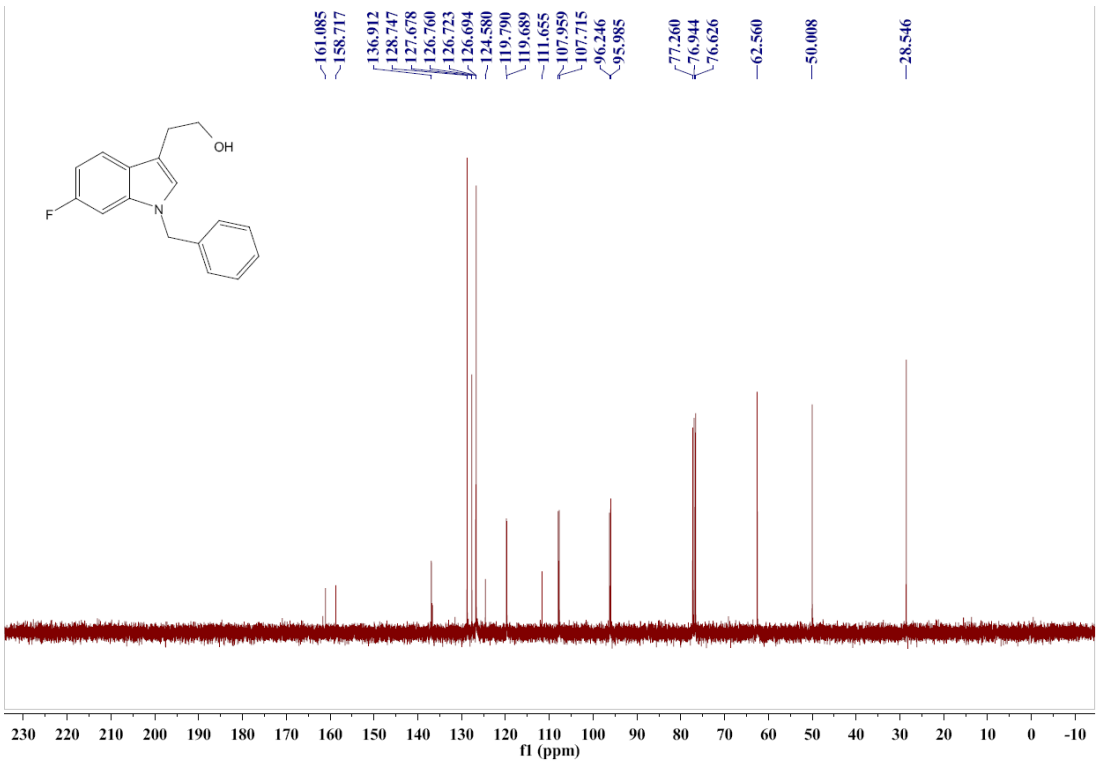
1j

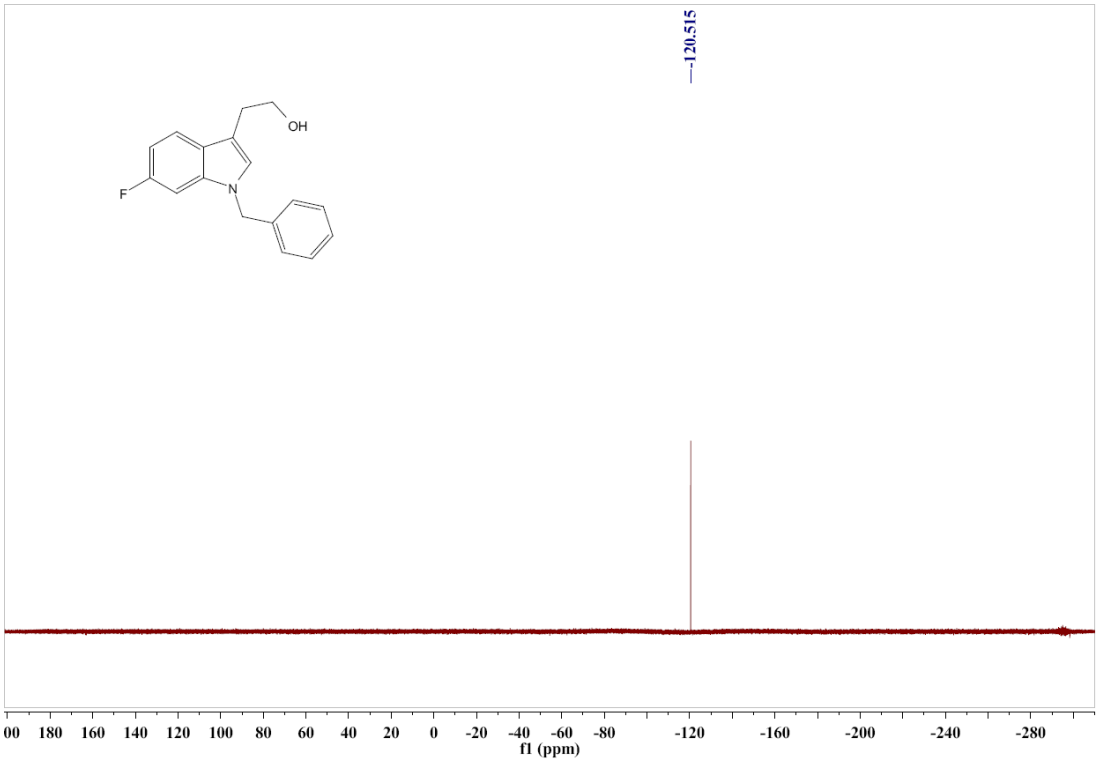

7.309
7.305
7.289
7.270
7.263
7.246
7.244
7.227
7.153
7.130
7.103
7.085
7.060
7.054
6.982
6.852
6.846
6.830
6.824
5.232
3.903
3.887
3.871
3.849
3.013
2.997
2.981
1.658
0.000
OH
O
H3C
N
3.05
1.00
1.85
0.97
1.00
1.01
1.98
1.98
2.82
2.00
1.29
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


153.828
137.717
132.021
128.707
128.517
127.533
127.245
126.727
111.992
110.967
110.630
100.880
77.565
77.245
76.926
62.637
55.863
49.972
28.703
OH
O
H3C
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

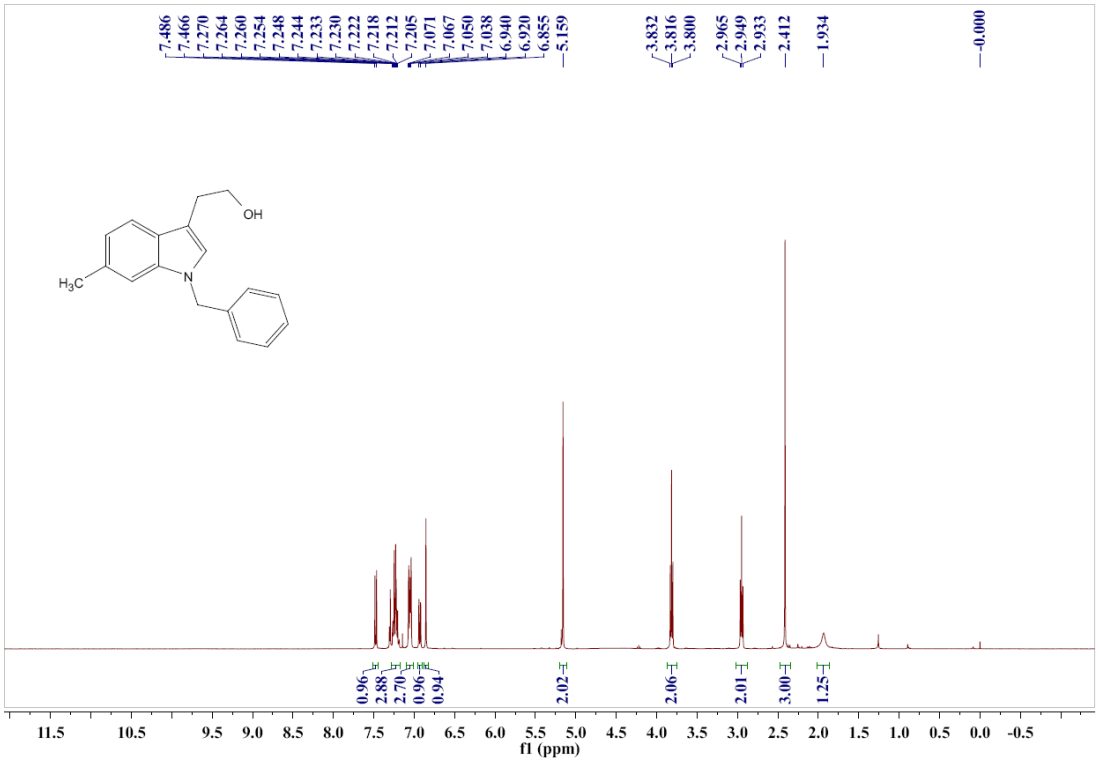
1k

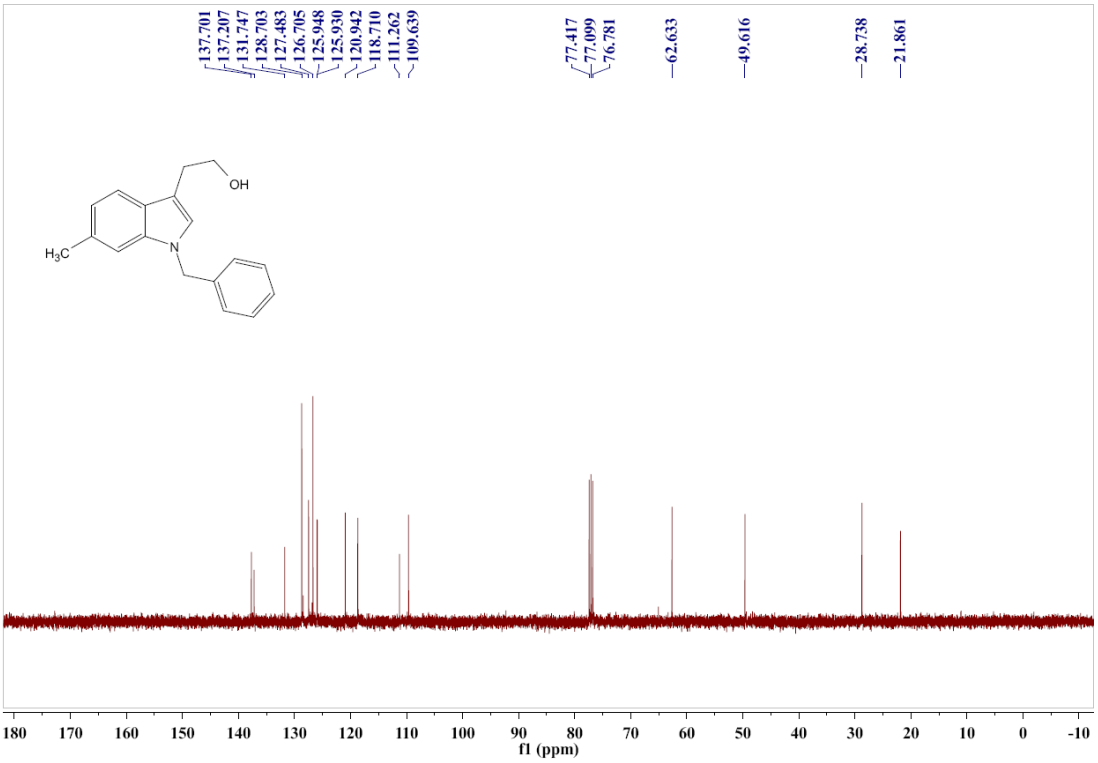

7.527
7.514
7.505
7.492
7.322
7.316
7.300
7.281
7.276
7.260
7.240
7.239
7.106
7.089
6.975
6.936
6.931
6.911
6.906
6.892
6.887
6.869
6.865
6.846
6.841
5.192
3.890
3.874
3.858
3.004
2.988
2.972
1.643
0.001
0.000
OH
F
N
0.98
2.92
1.86
0.95
1.95
2.00
2.02
2.03
1.24
f1 (ppm)


161.085
158.717
136.912
128.747
127.678
126.760
126.723
126.694
124.580
119.790
119.689
111.655
107.959
107.715
96.246
95.985
77.260
76.944
76.626
62.560
50.008
28.546
OH
F
N
f1 (ppm)

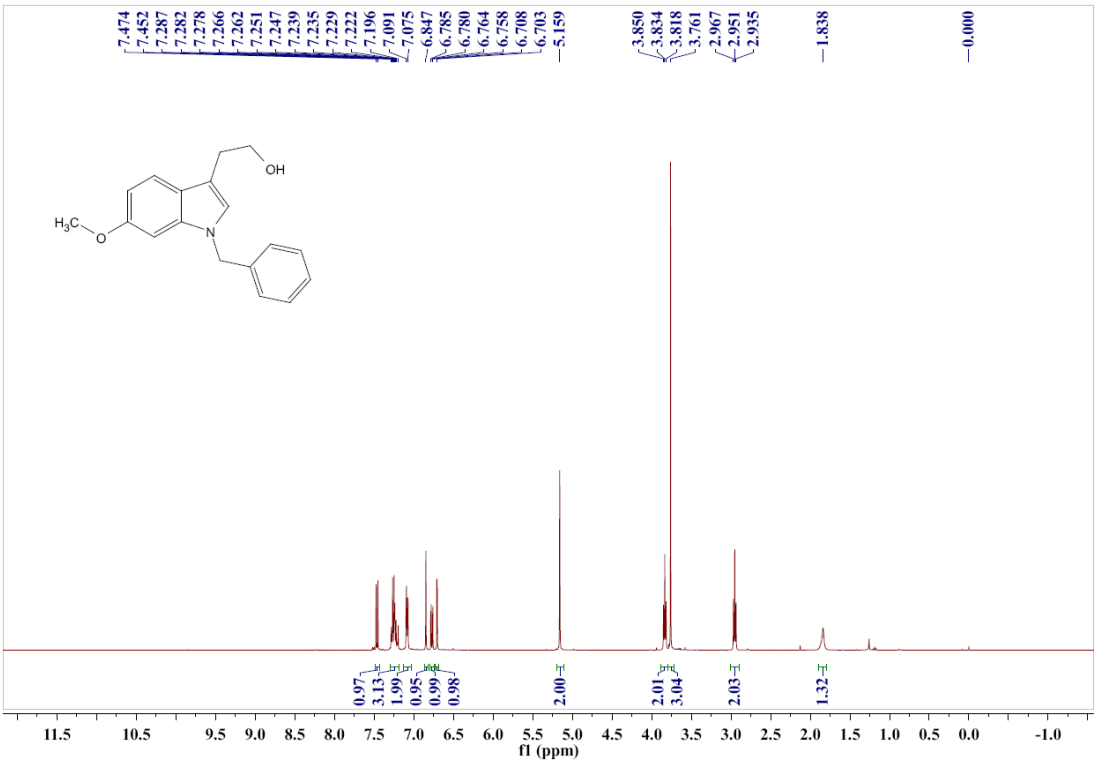

-120.515
OH
F
N
00 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -120 -160 -200 -240 -280
f1 (ppm)

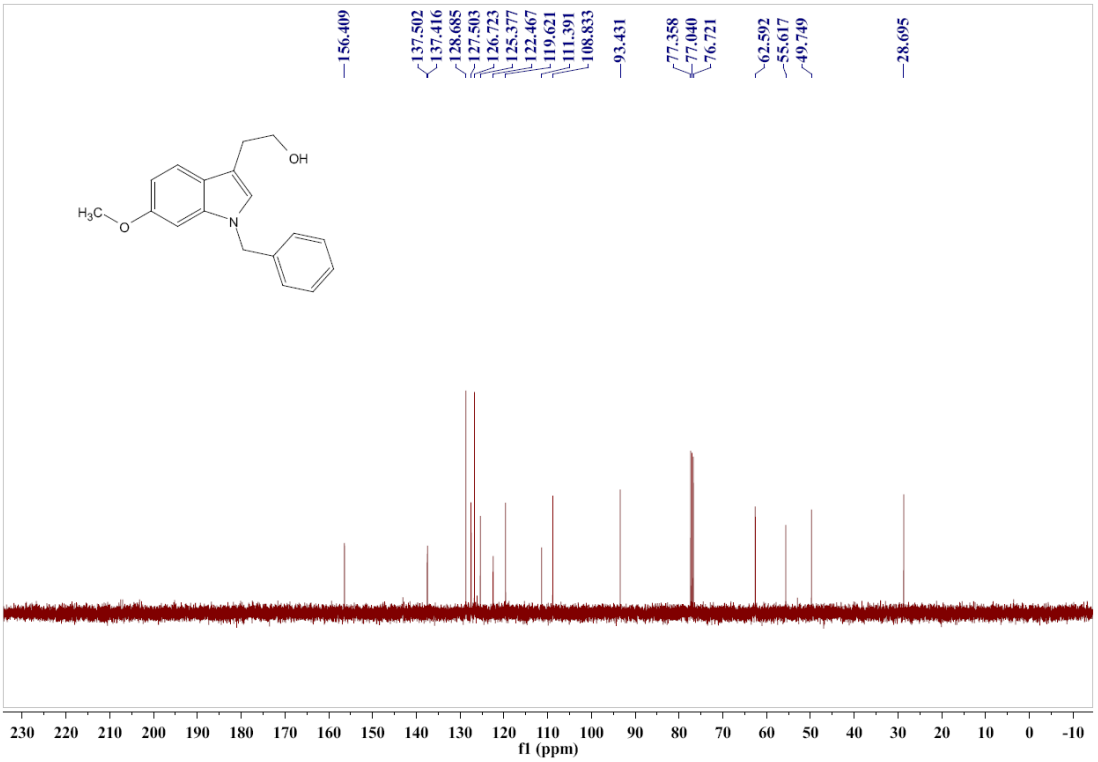
1l


7.486
7.466
7.270
7.264
7.260
7.254
7.248
7.244
7.233
7.230
7.222
7.218
7.212
7.205
7.071
7.067
7.050
7.038
6.940
6.920
6.855
5.159
3.832
3.816
3.800
2.965
2.949
2.933
2.412
1.934
-0.000
OH
H3C
N
0.96
2.88
2.70
0.96
0.94
2.02
2.06
2.01
3.00
1.25
f1 (ppm)

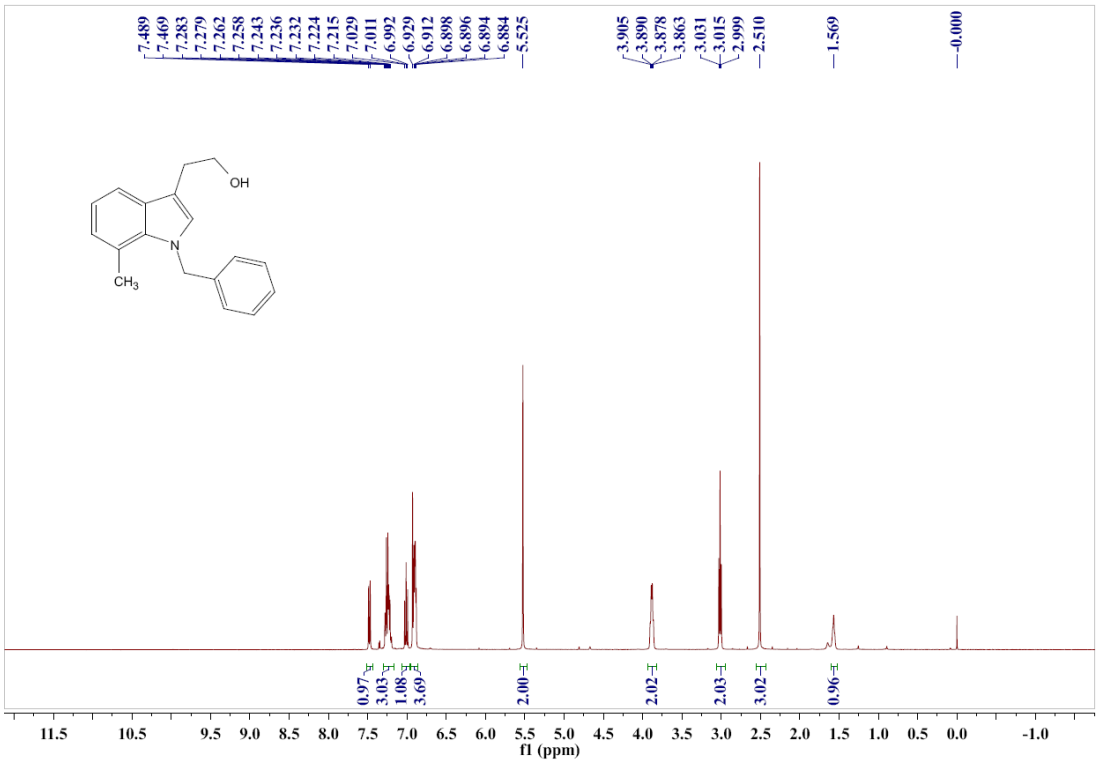

137.701
137.207
131.747
128.703
127.483
126.705
125.948
125.930
120.942
118.710
111.262
109.639
77.417
77.099
76.781
62.633
49.616
28.738
21.861
OH
H3C
N
f1 (ppm)

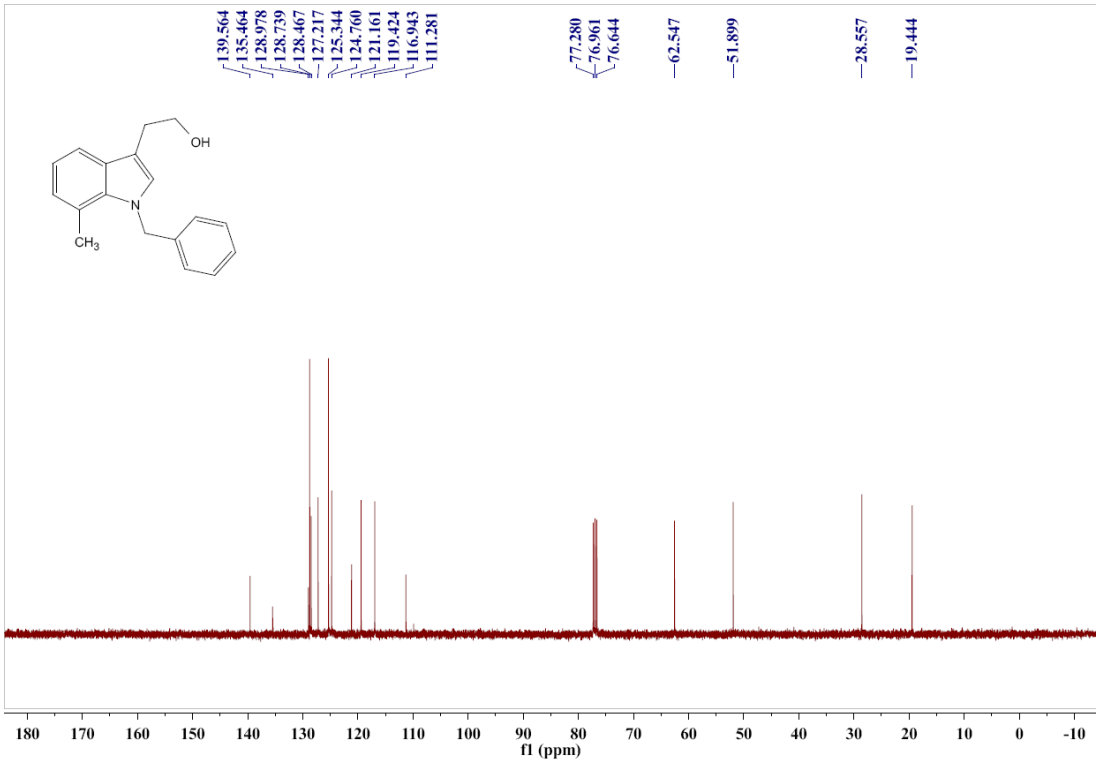
1m


7.474
7.452
7.287
7.282
7.278
7.266
7.262
7.251
7.247
7.239
7.235
7.229
7.222
7.196
7.091
7.075
6.847
6.785
6.780
6.764
6.758
6.708
6.703
5.159
3.850
3.834
3.818
3.761
2.967
2.951
2.935
1.838
0.000
OH
H3C
O
N
0.97
3.13
1.99
0.95
0.99
0.98
2.00
2.01
3.04
2.03
1.32
f1 (ppm)

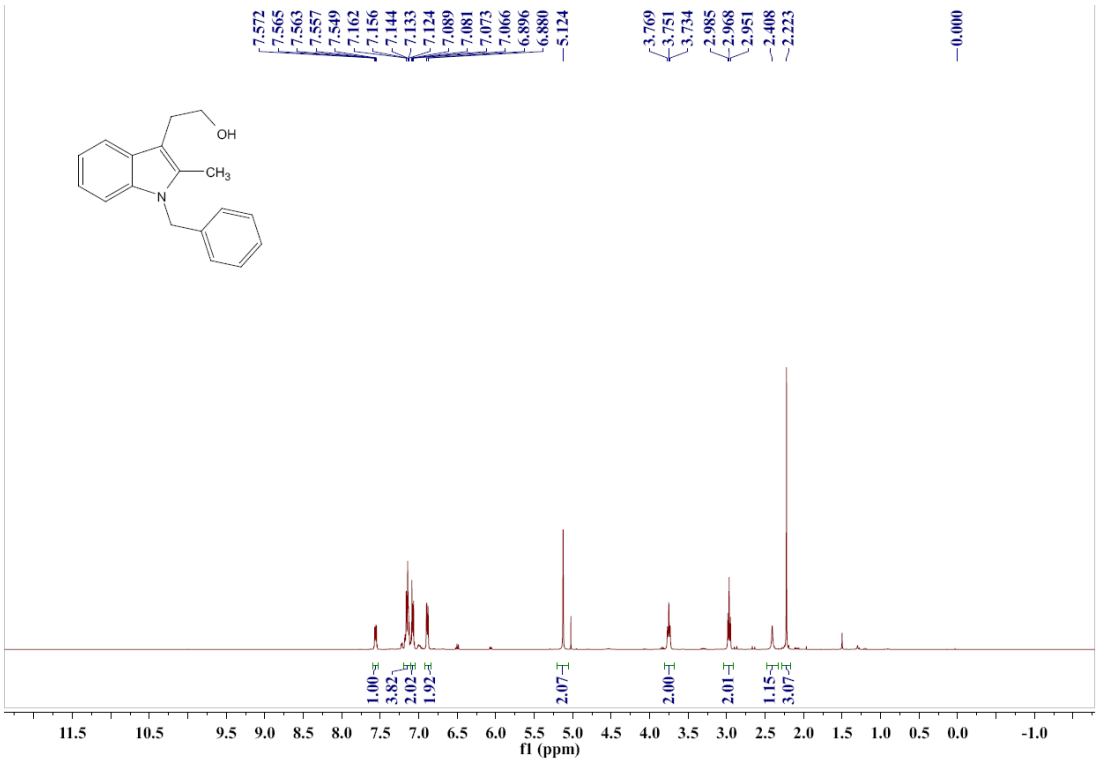

156.409
137.502
137.416
128.685
127.503
126.723
125.377
122.467
119.621
111.391
108.833
93.431
77.358
77.040
76.721
62.592
55.617
49.749
28.695
OH
H3C
O
N
f1 (ppm)

1n

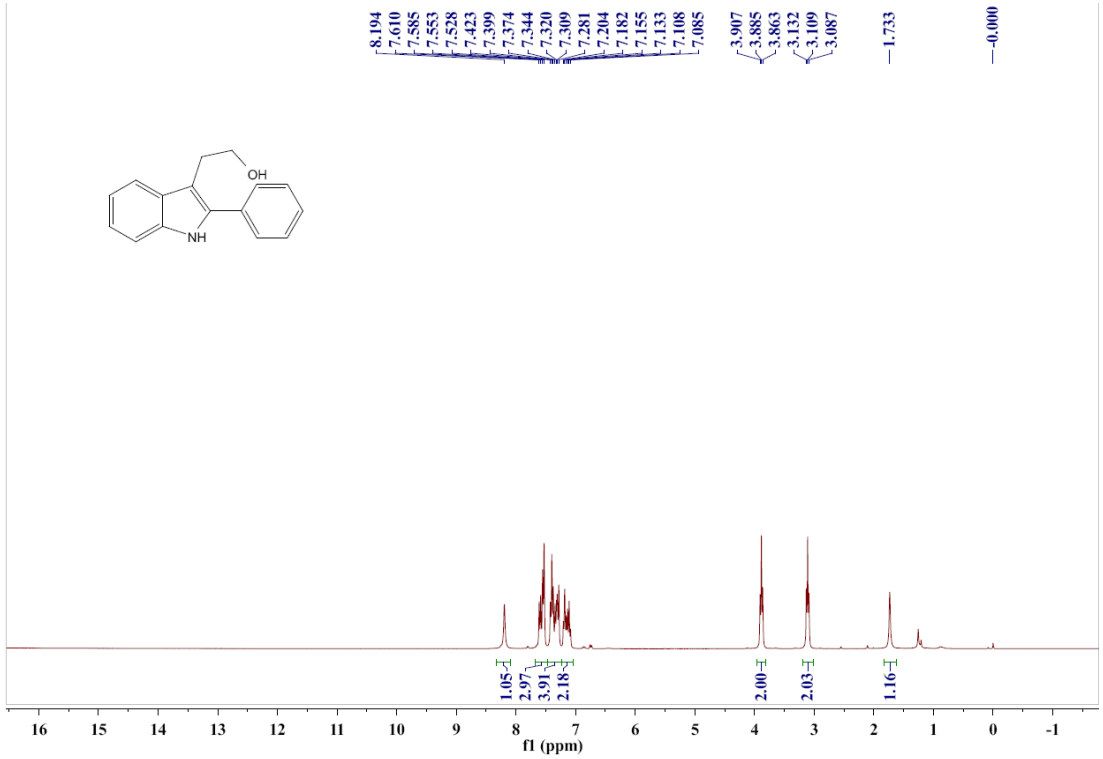

7.489
7.469
7.283
7.279
7.262
7.258
7.243
7.236
7.232
7.224
7.215
7.029
7.011
6.992
6.929
6.912
6.898
6.896
6.894
6.884
5.525
3.905
3.890
3.878
3.863
3.031
3.015
2.999
2.510
1.569
0.000
OH
N
CH3
0.97
3.03
1.08
3.69
2.00
2.02
2.03
3.02
0.96
f1 (ppm)


139.564
135.464
128.978
128.739
128.467
127.217
125.344
124.760
121.161
119.424
116.943
111.281
77.280
76.961
76.644
62.547
51.899
28.557
19.444
OH
N
CH3
f1 (ppm)

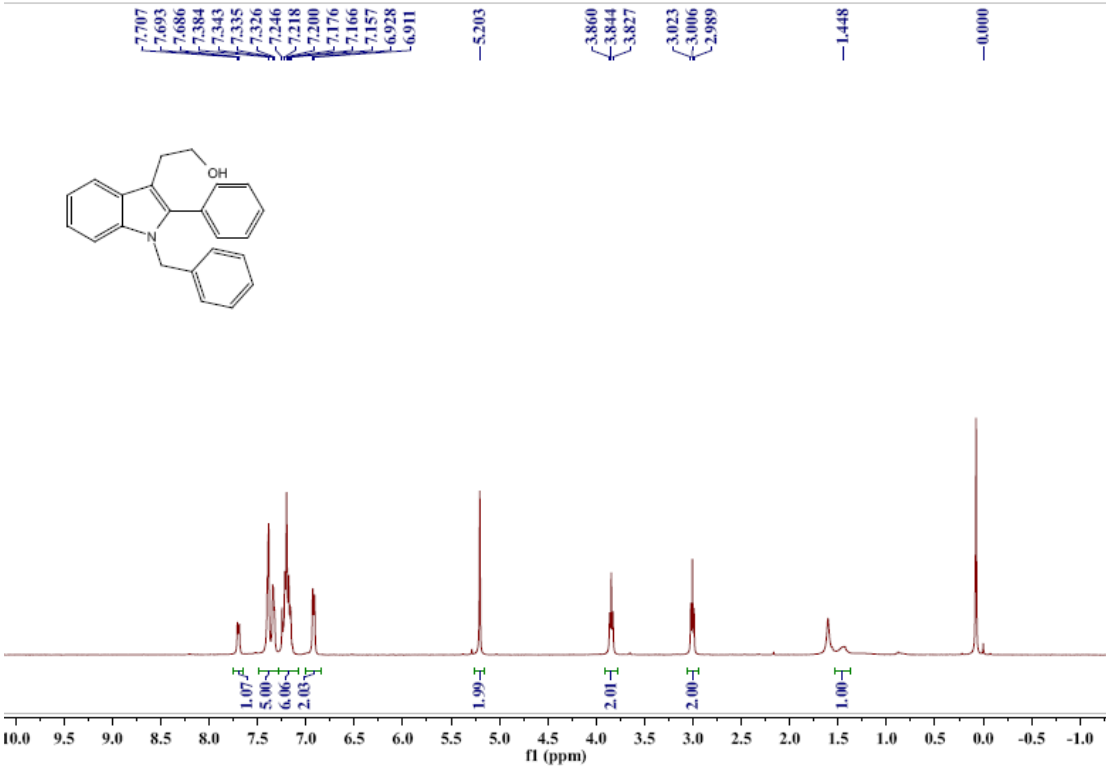
1o

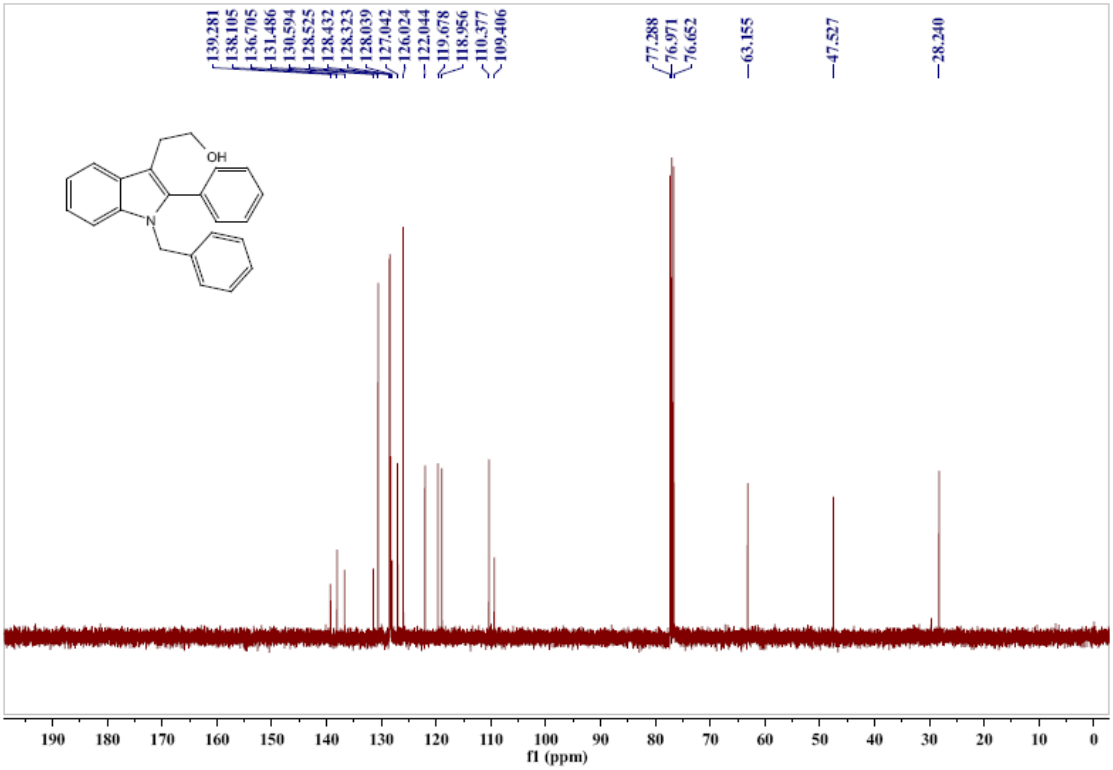

7.572
7.565
7.563
7.557
7.549
7.162
7.156
7.144
7.133
7.124
7.089
7.081
7.073
7.066
6.896
6.880
5.124
3.769
3.751
3.734
2.985
2.968
2.951
2.408
2.223
0.000
OH
CH3
N
1.00
3.82
2.02
1.92
2.07
2.00
2.01
1.15
3.07
f1 (ppm)

1p

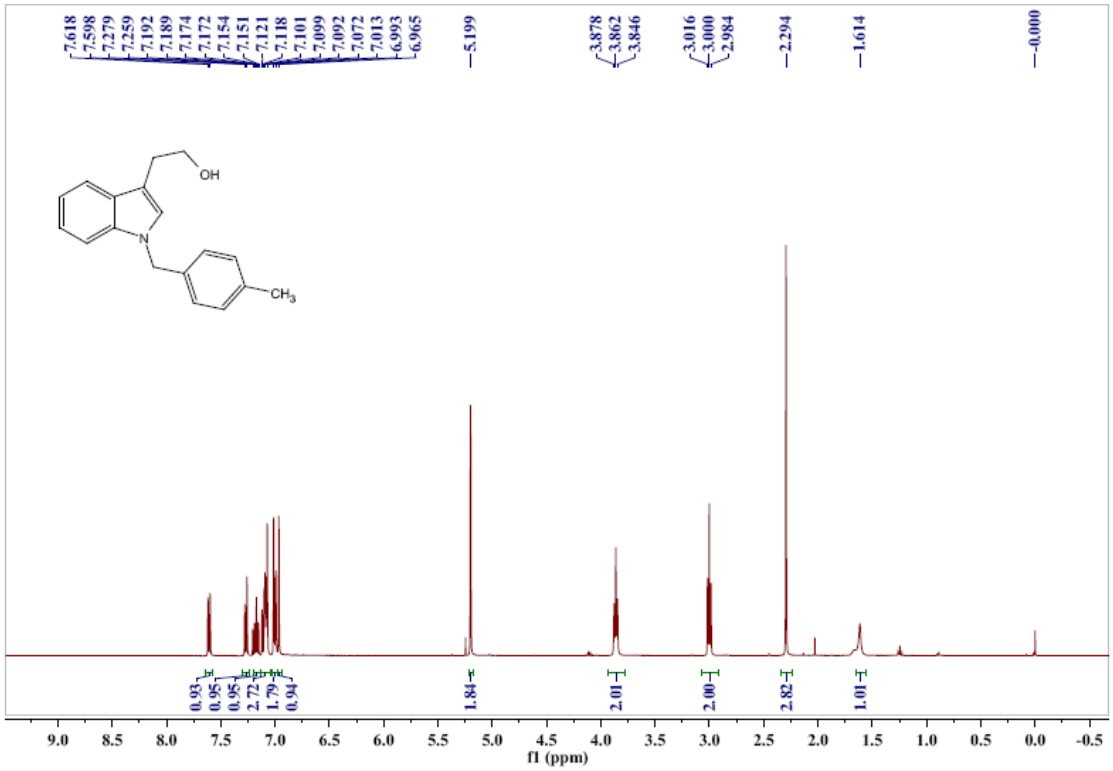

8.194
7.610
7.585
7.553
7.528
7.423
7.399
7.374
7.344
7.320
7.309
7.281
7.204
7.182
7.155
7.133
7.108
7.085
3.907
3.885
3.863
3.132
3.109
3.087
1.733
-0.000
OH
NH
1.05
2.97
3.91
2.18
2.00
2.03
1.16
f1 (ppm)

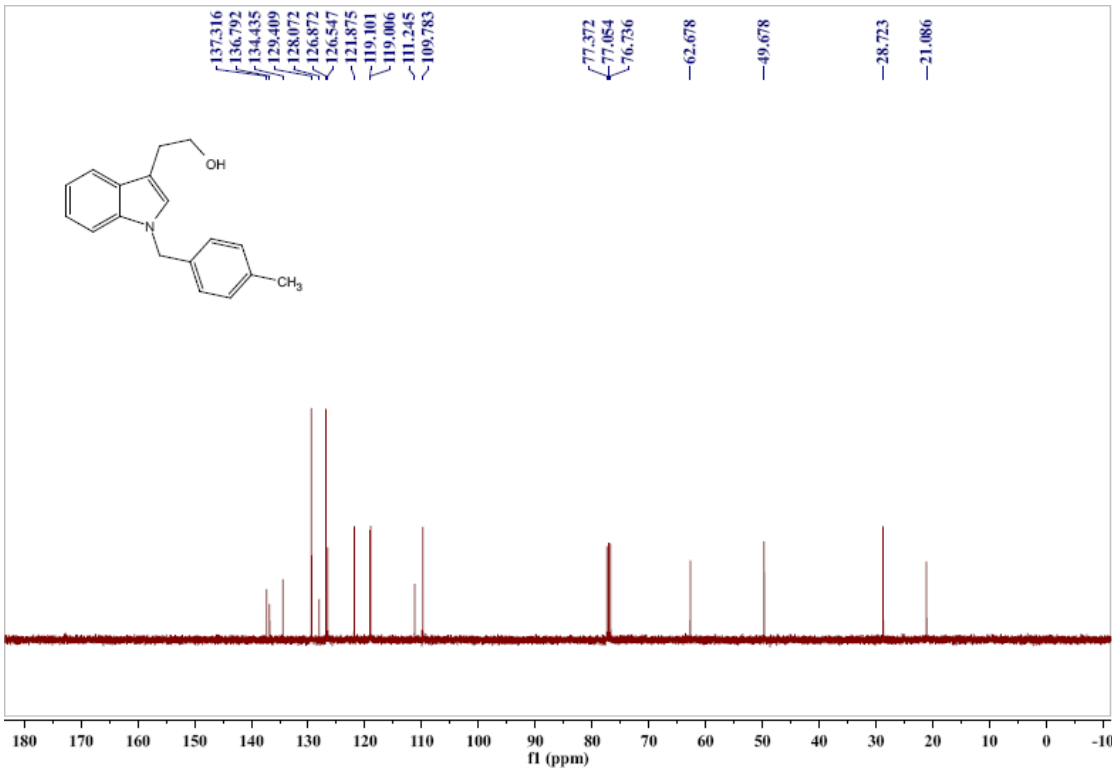
1q


7.707
7.693
7.686
7.384
7.343
7.335
7.326
7.246
7.218
7.200
7.176
7.166
7.157
6.928
6.911
5.203
3.860
3.844
3.827
3.023
3.006
2.989
1.448
0.000
OH
N
1.07
5.00
6.06
2.03
1.99
2.01
2.00
1.00
fl (ppm)


139.281
138.105
136.705
131.486
130.594
128.525
128.432
128.323
128.039
127.042
126.024
122.044
119.678
118.956
110.377
109.406
77.288
76.971
76.652
63.155
47.527
28.240
OH
N
fl (ppm)

1r


7.618
7.598
7.279
7.259
7.192
7.189
7.174
7.172
7.154
7.151
7.121
7.118
7.101
7.099
7.092
7.072
7.013
6.993
6.965
5.199
3.878
3.862
3.846
3.016
3.000
2.984
2.294
1.614
0.000
OH
N
CH3
0.93
0.95
0.95
2.72
1.79
0.94
1.84
2.01
2.00
2.82
1.01
f1 (ppm)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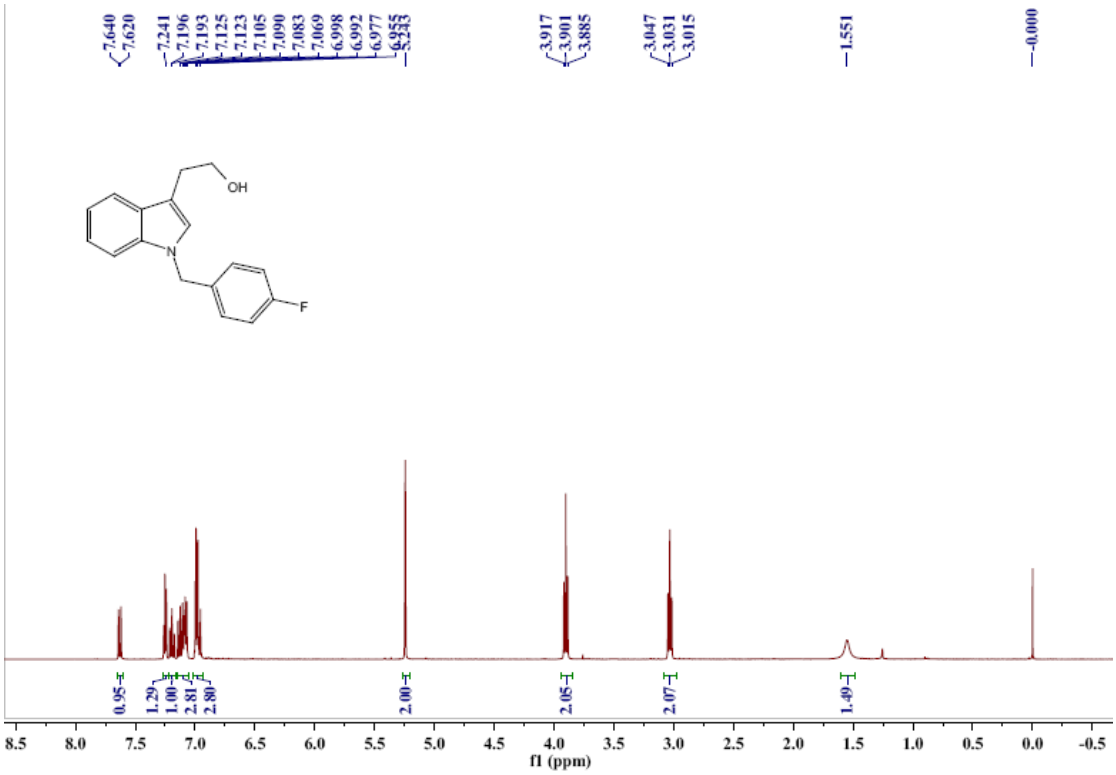
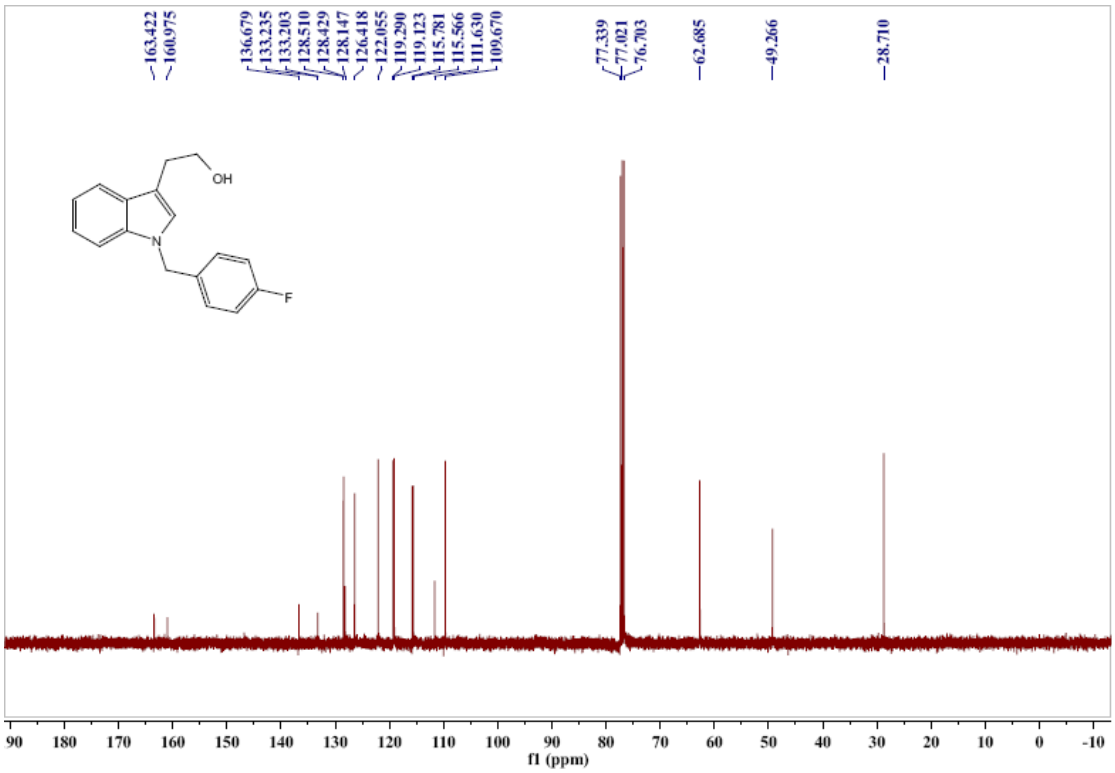
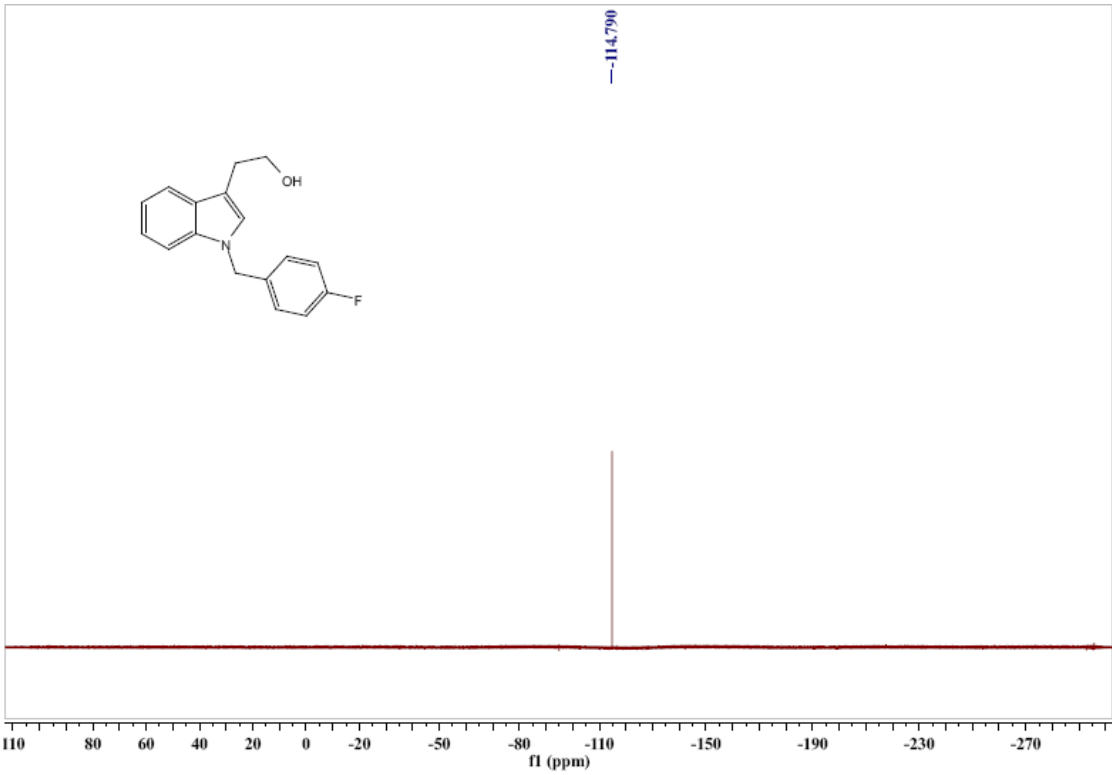
134.435
129.409
128.072
126.872
126.547
121.875
119.101
119.006
111.245
109.783
77.372
77.054
76.736
62.678
49.678
28.723
21.086
OH
N
CH3
f1 (ppm)

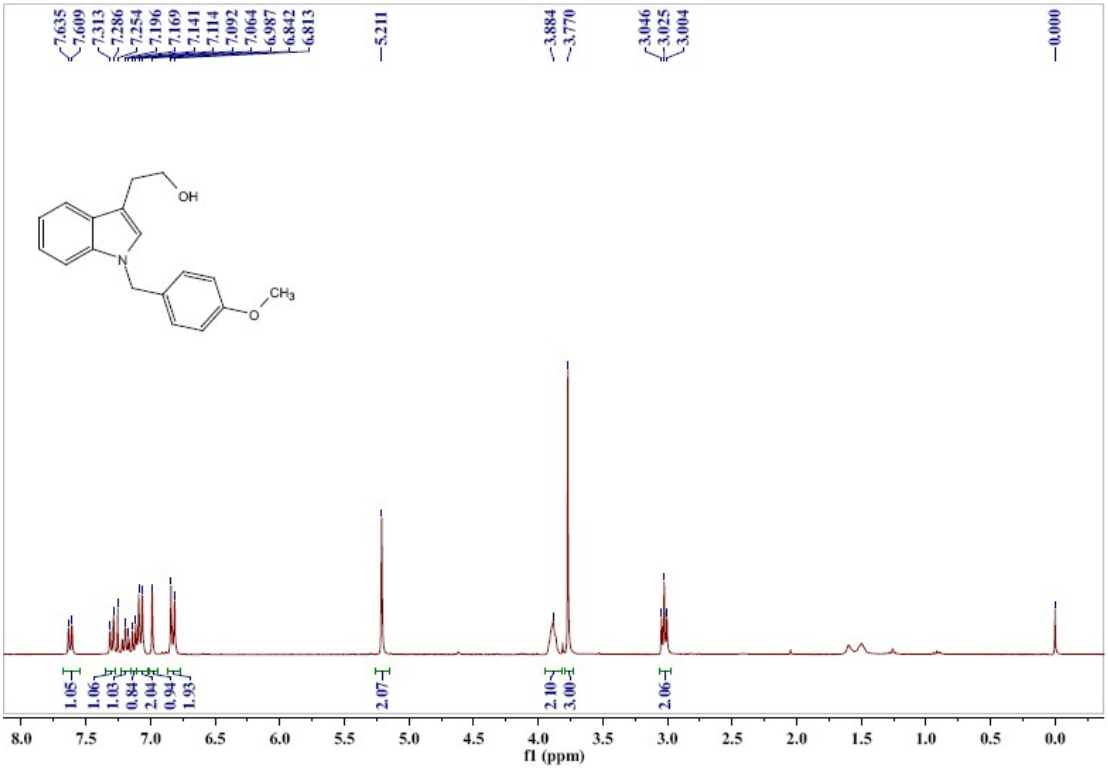
1s


7.640
7.620
7.241
7.196
7.193
7.125
7.123
7.105
7.090
7.083
7.069
6.998
6.992
6.977
6.955
6.933
3.917
3.901
3.885
3.047
3.031
3.015
1.551
0.000
OH
N
F
0.95
1.29
1.00
2.81
2.80
2.00
2.05
2.07
1.49
f1 (ppm)


163.422
160.975
136.679
133.235
133.203
128.510
128.429
128.147
126.418
122.055
119.290
119.123
115.781
115.566
111.630
109.670
77.339
77.021
76.703
62.685
49.266
28.710
OH
N
F
f1 (ppm)


-114.790
OH
N
F
110
80
60
40
20
0
-20
-50
-80
-110
-150
-190
-230
-270
f1 (ppm)

1t


7.635
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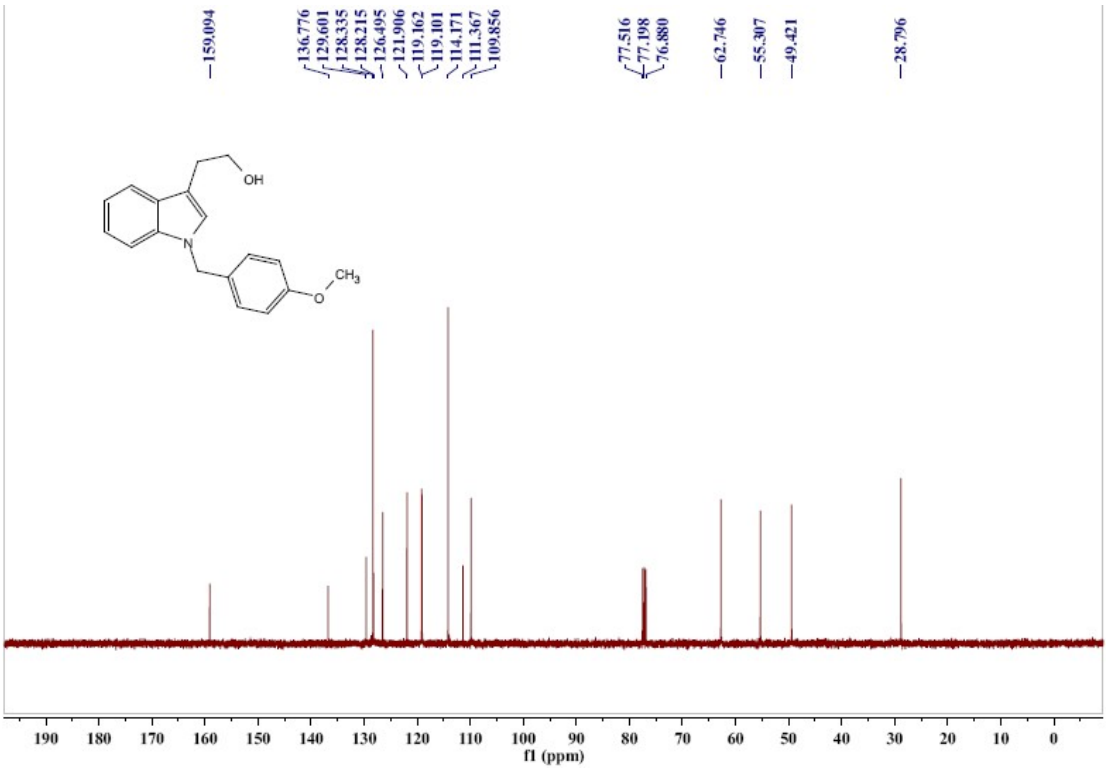
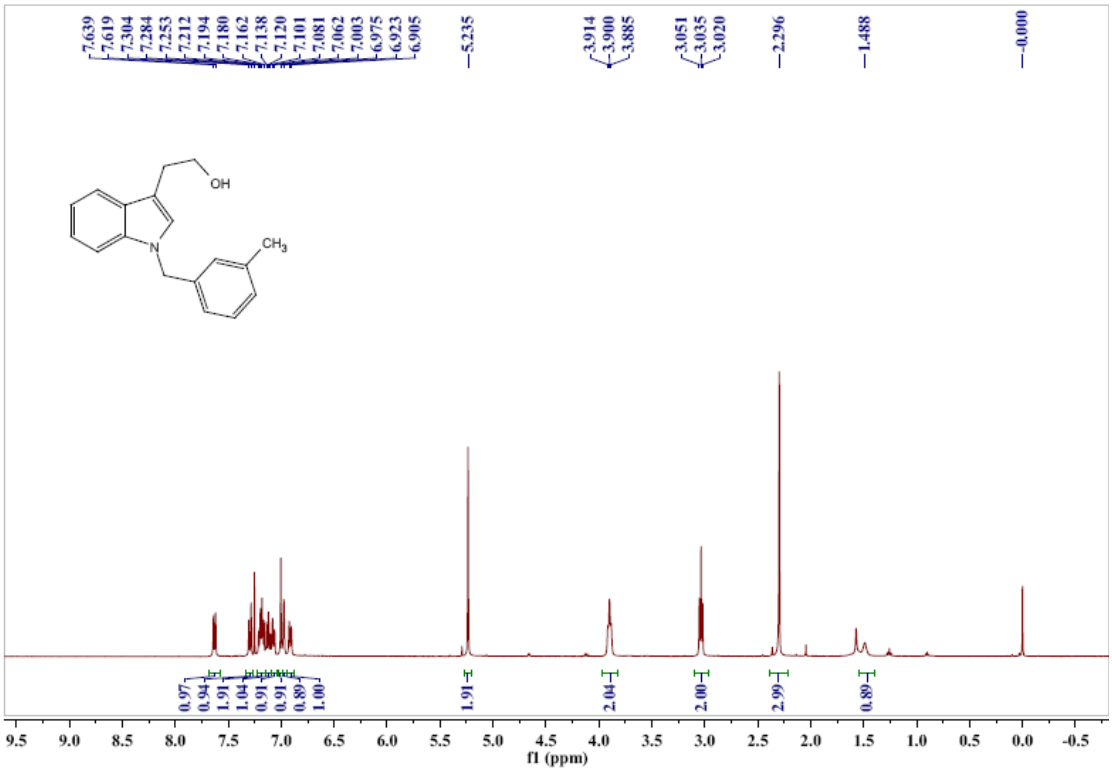
7.313
7.286
7.254
7.196
7.169
7.141
7.114
7.092
7.064
6.987
6.842
6.813
5.211
3.884
3.770
3.046
3.025
3.004
0.000
OH
N
O
CH3
1.05
1.06
1.03
0.84
2.04
0.94
1.93
2.07
2.10
3.00
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.094
136.776
129.601
128.335
128.215
126.495
121.906
119.162
119.101
114.171
111.367
109.856
77.516
77.198
76.880
62.746
55.307
49.421
28.796
OH
N
O
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1u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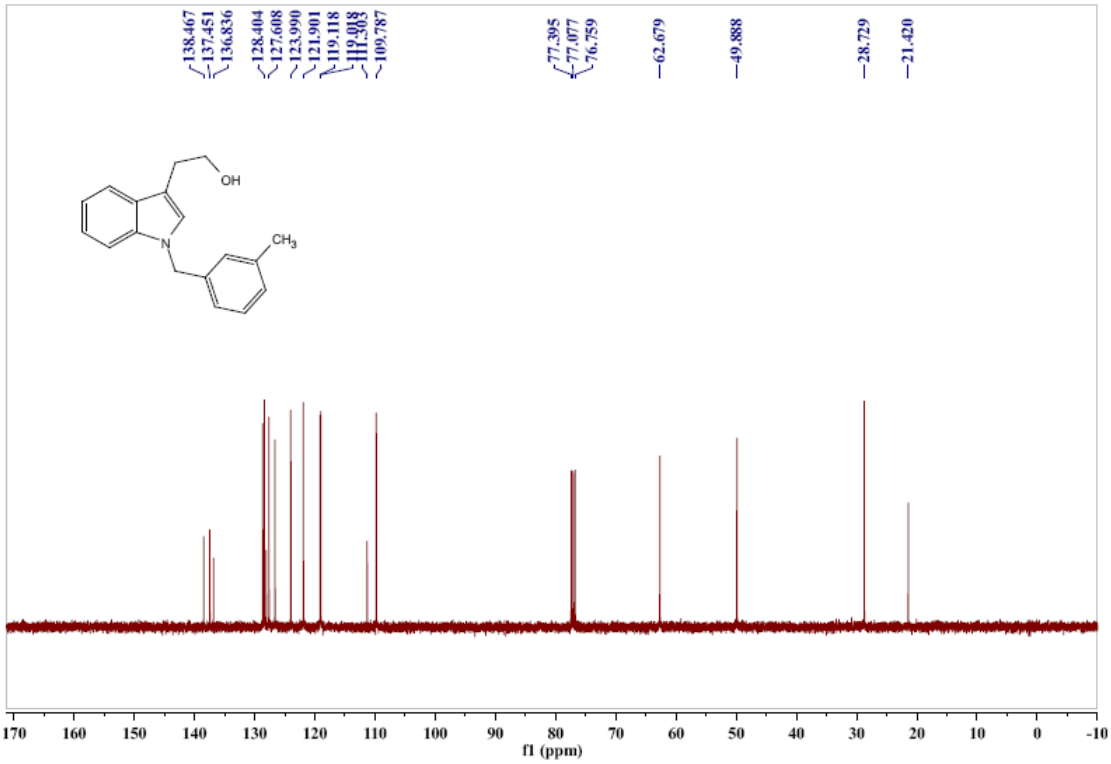
7.253
7.212
7.194
7.180
7.162
7.138
7.120
7.101
7.081
7.062
7.003
6.975
6.923
6.905
5.235
3.914
3.900
3.885
3.051
3.035
3.020
2.296
1.488
0.000
OH
N
CH3
0.97
0.94
1.91
1.04
0.91
0.91
0.89
1.00
1.91
2.04
2.00
2.99
0.89
f1 (ppm)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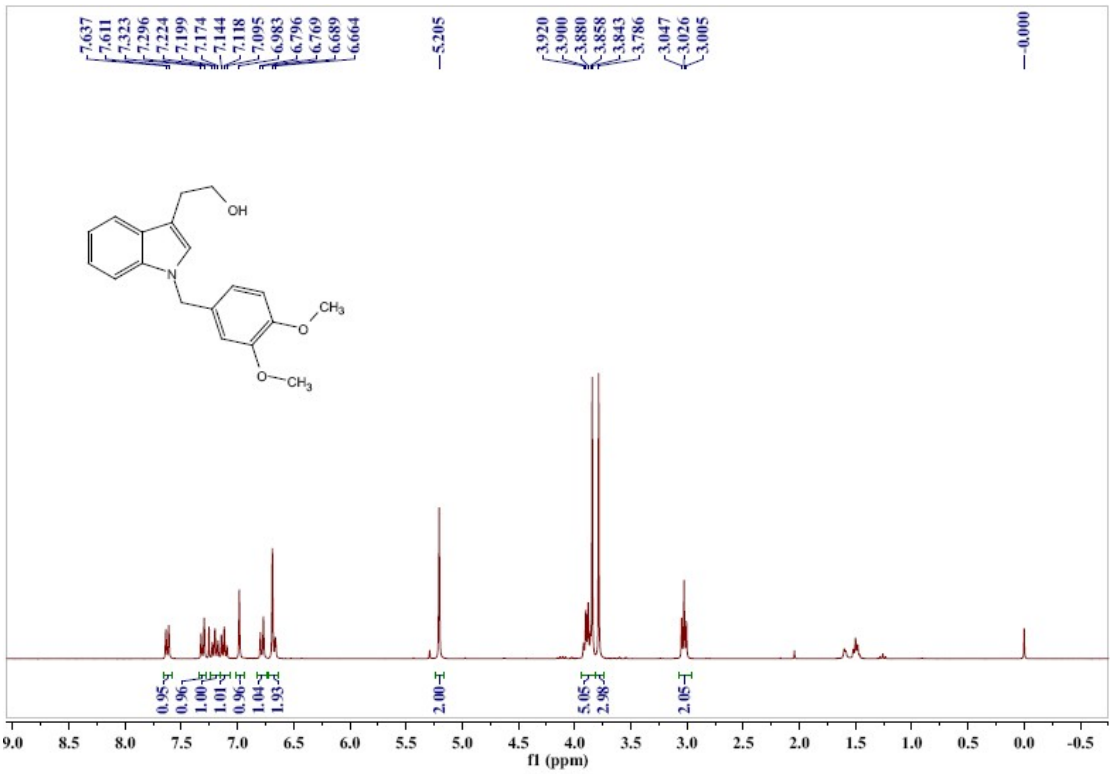
137.451
136.836
128.404
127.608
123.990
121.901
119.118
109.787
77.395
77.077
76.759
62.679
49.888
28.729
21.420
OH
N
CH3
f1 (ppm)

1v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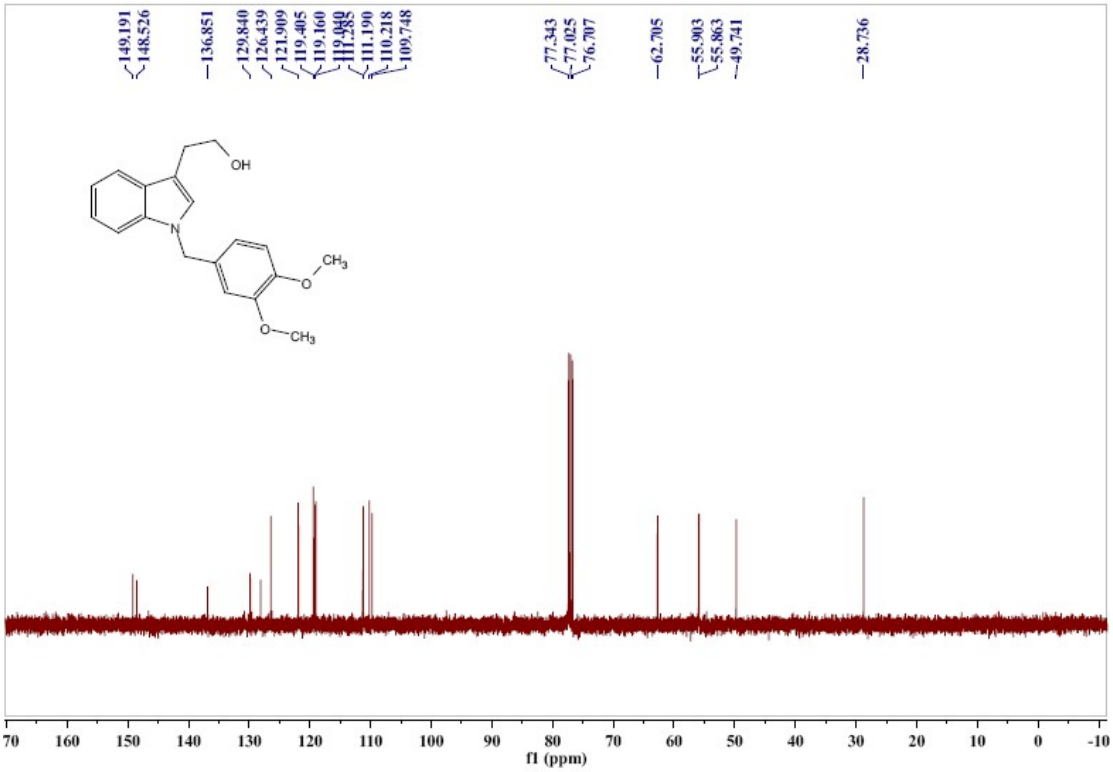
7.611
7.323
7.296
7.224
7.199
7.174
7.144
7.118
7.095
6.983
6.796
6.769
6.689
6.664
5.205
3.920
3.900
3.880
3.858
3.843
3.786
3.047
3.026
3.005
0.000
OH
N
O
CH3
O
CH3
0.95
0.96
1.00
1.01
0.96
1.04
1.93
2.00
5.05
2.98
2.05
f1 (ppm)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148.526
136.851
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121.909
119.405
119.160
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110.218
109.748
77.343
77.025
76.707
62.705
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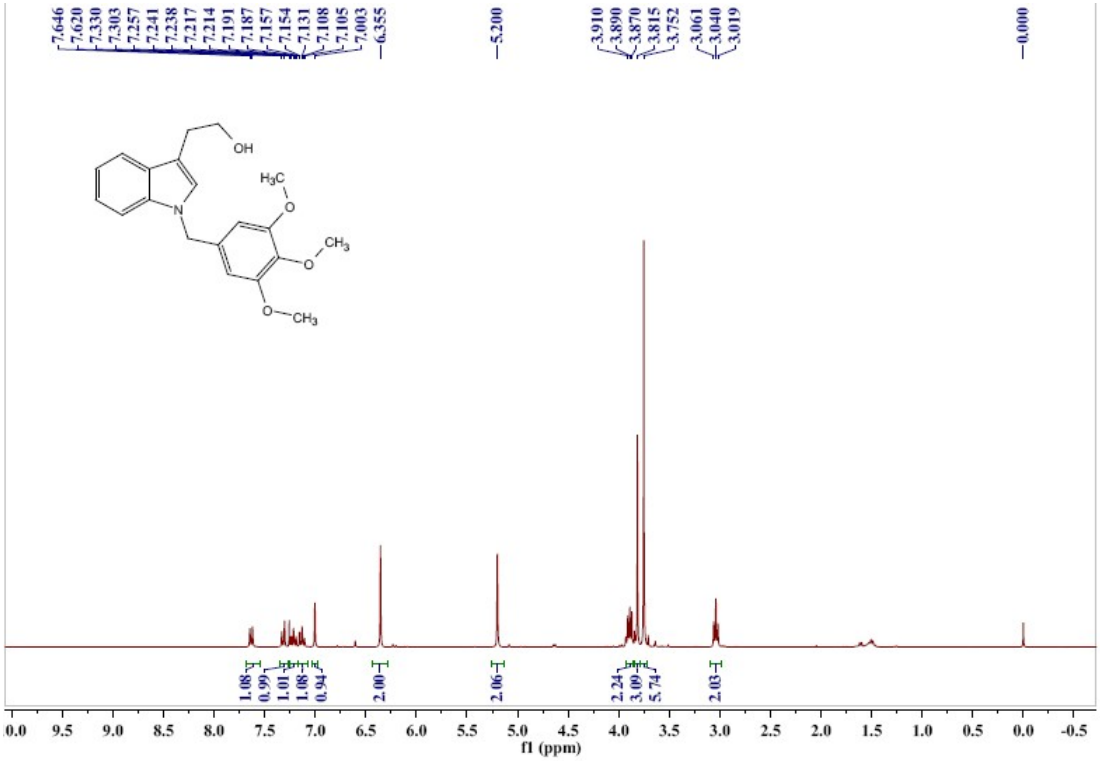
55.863
49.741
28.736
OH
N
O
CH3
O
CH3
f1 (ppm)

1w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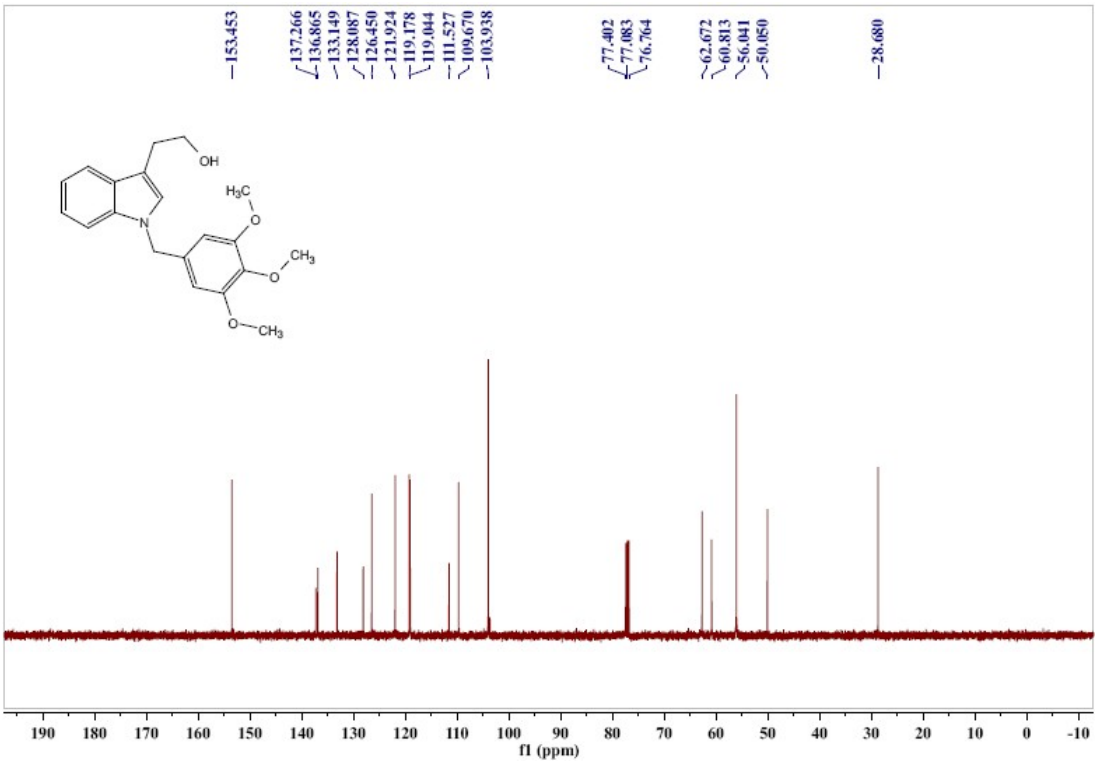
7.620
7.330
7.303
7.257
7.241
7.238
7.217
7.214
7.191
7.187
7.157
7.154
7.131
7.108
7.105
7.003
6.355
5.200
3.910
3.890
3.870
3.815
3.752
3.061
3.040
3.019
0.000
OH
H3C
O
N
O
CH3
O
CH3
1.08
0.99
1.01
1.08
0.94
2.00
2.06
2.24
3.09
5.74
2.03
fl (ppm)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133.149
128.087
126.450
121.924
119.178
119.044
111.527
109.670
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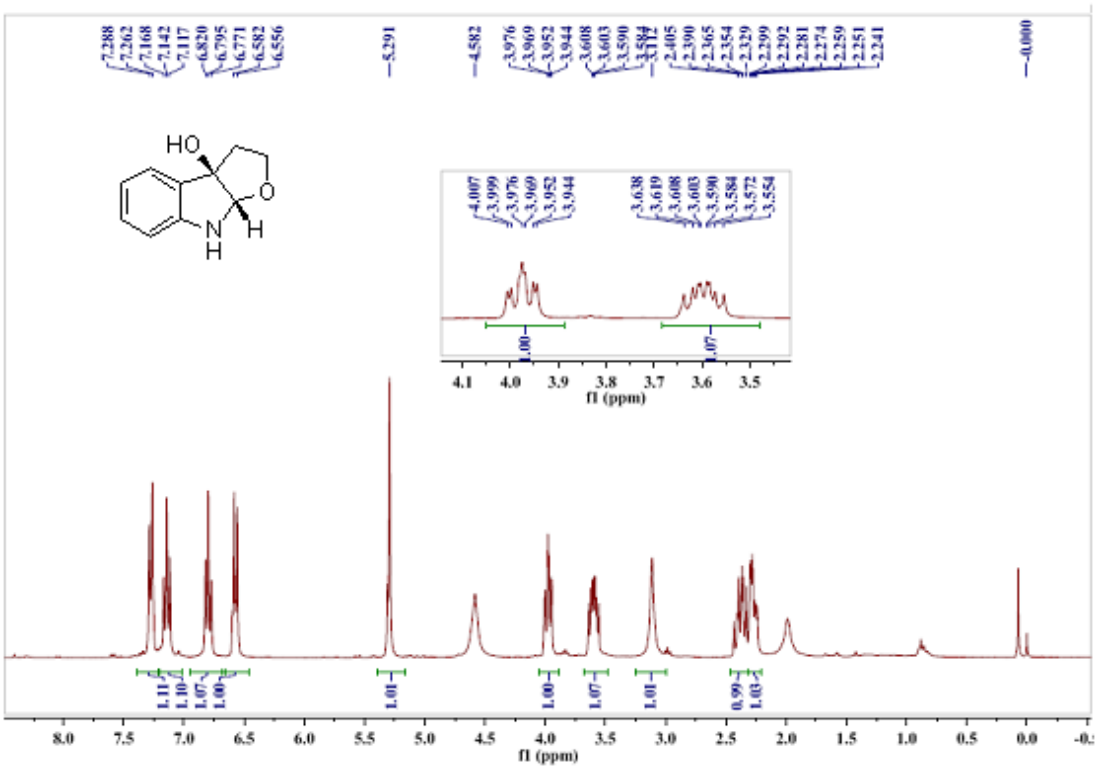
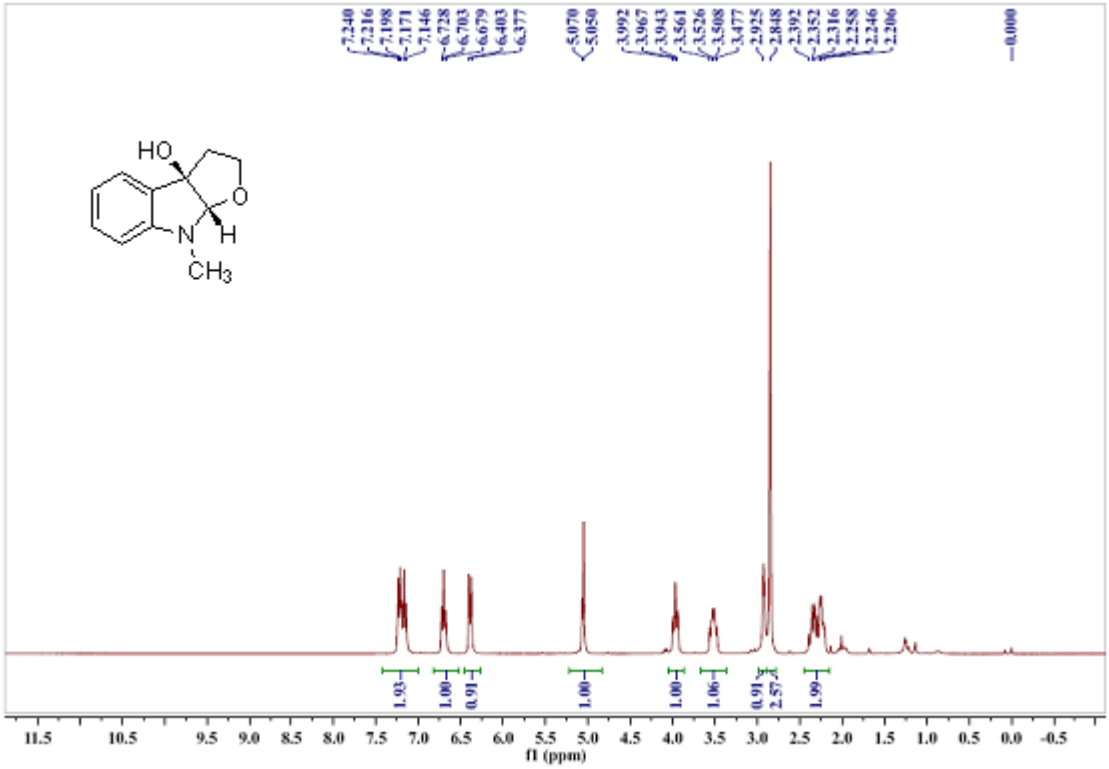
77.402
77.083
76.764
62.672
60.813
56.041
50.050
28.680
OH
H3C
O
N
O
CH3
O
CH3
fl (ppm)

2a



2b



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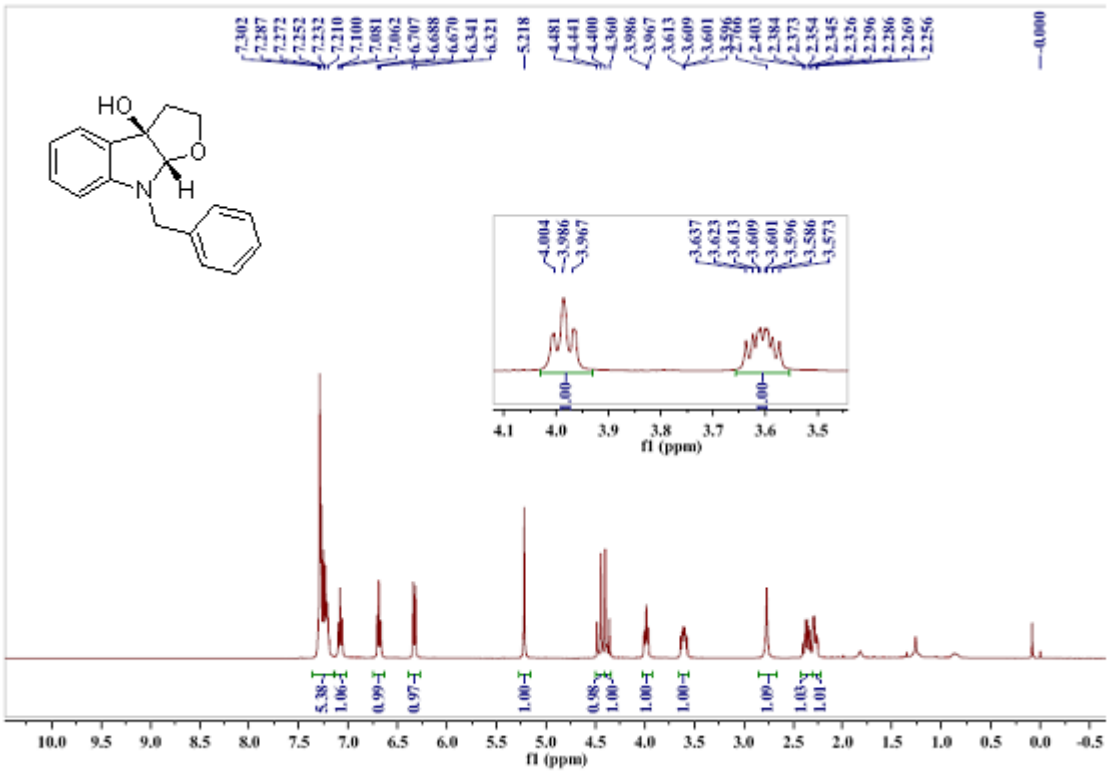

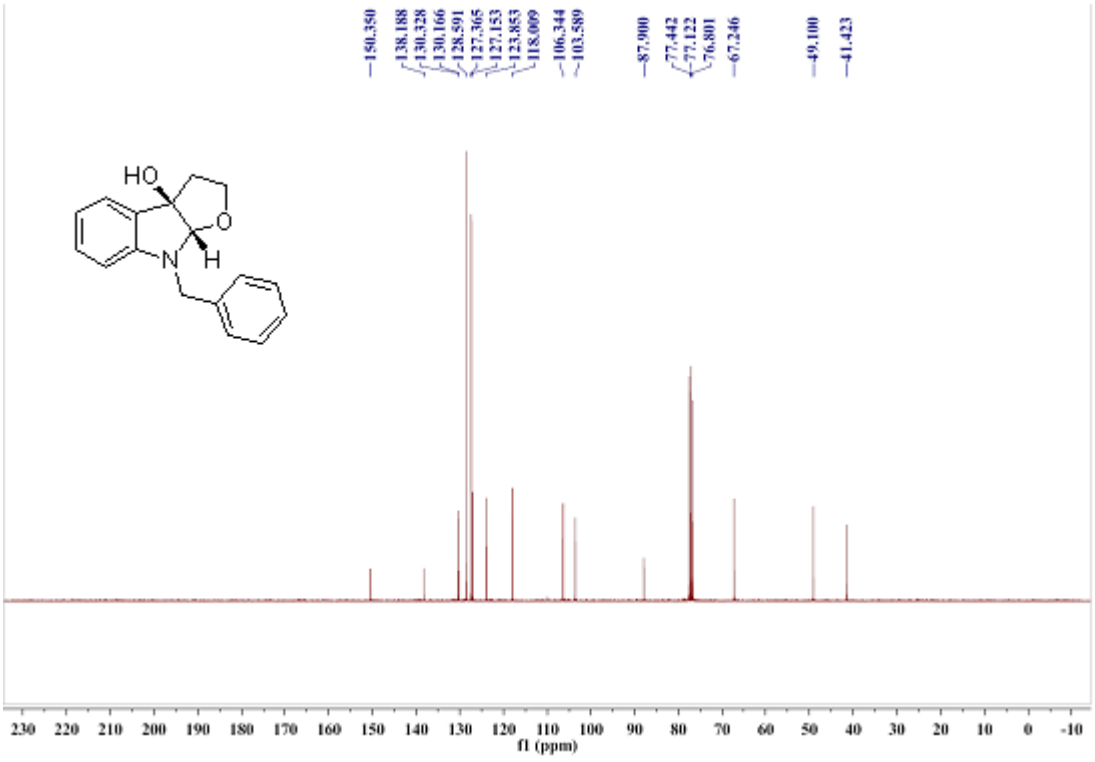

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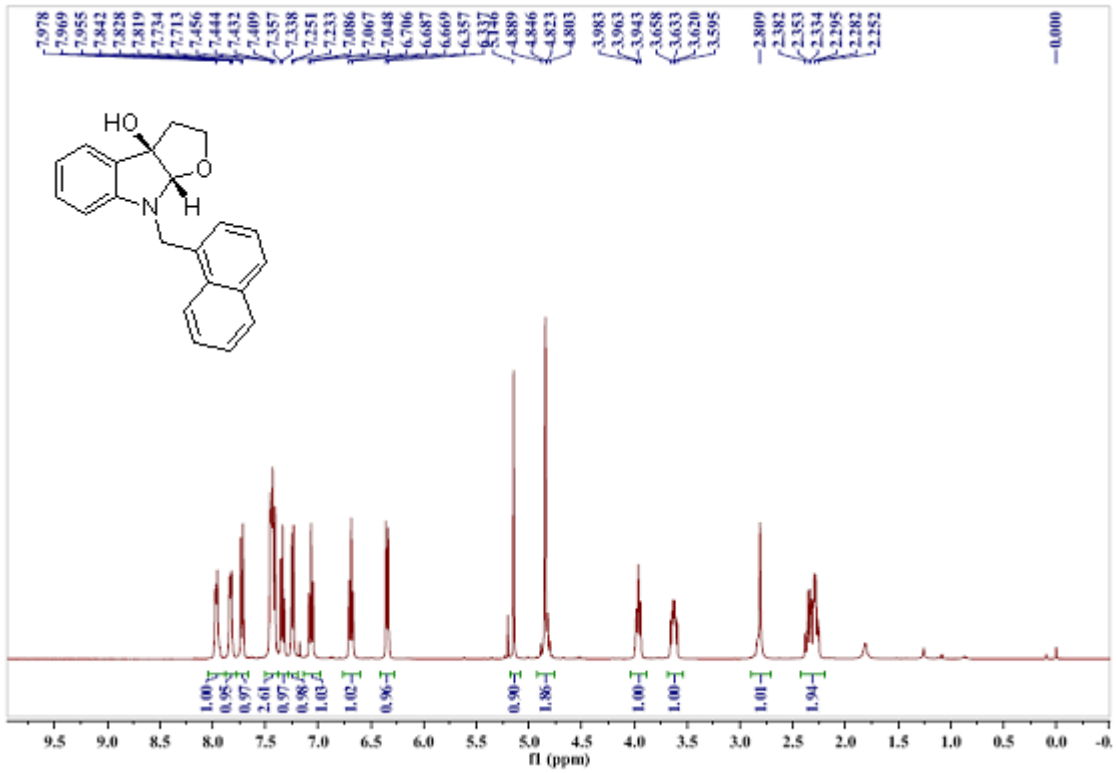
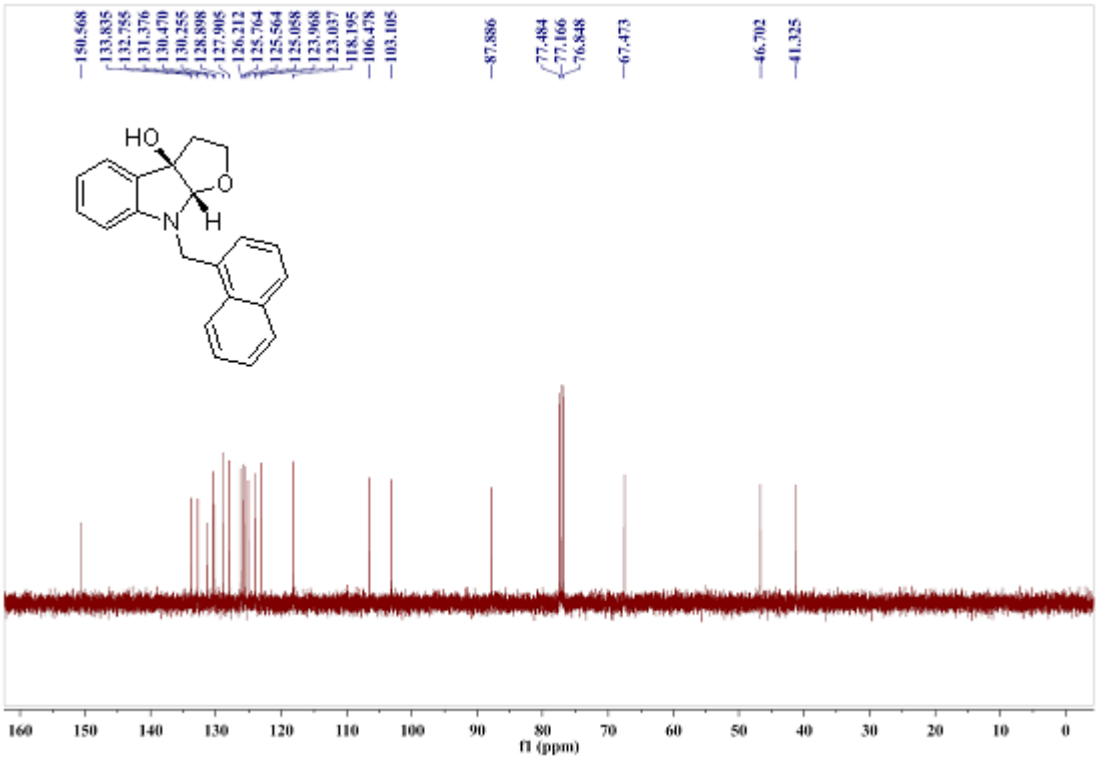
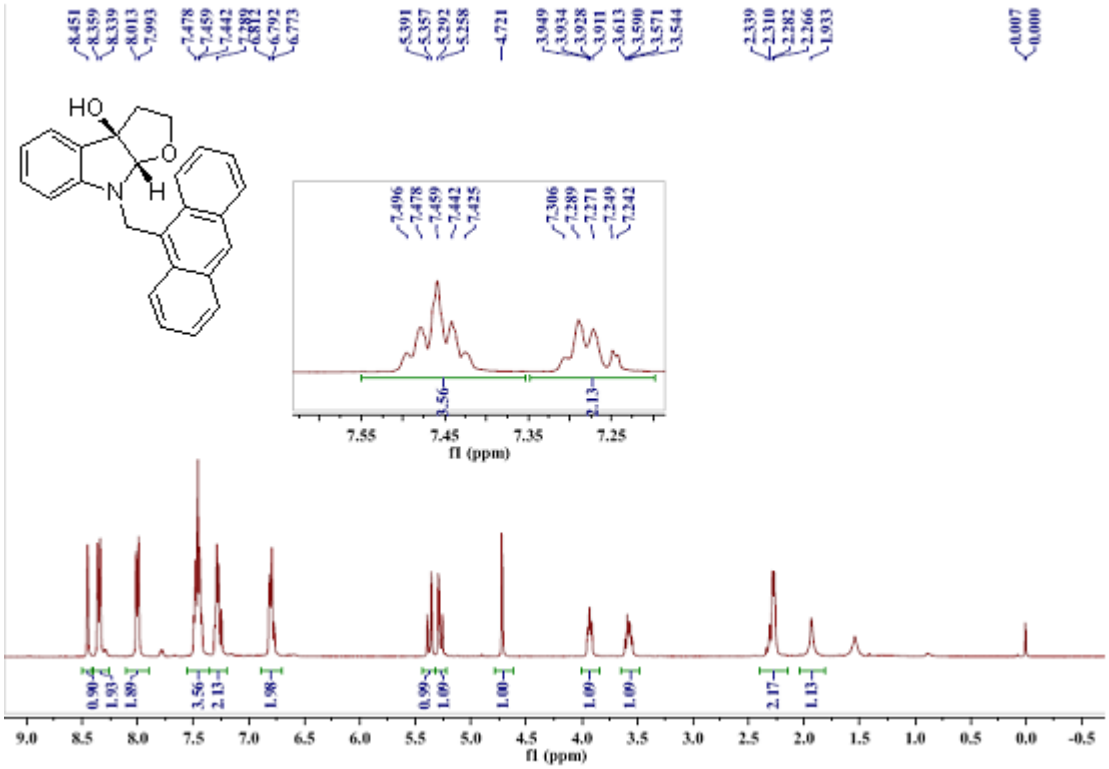
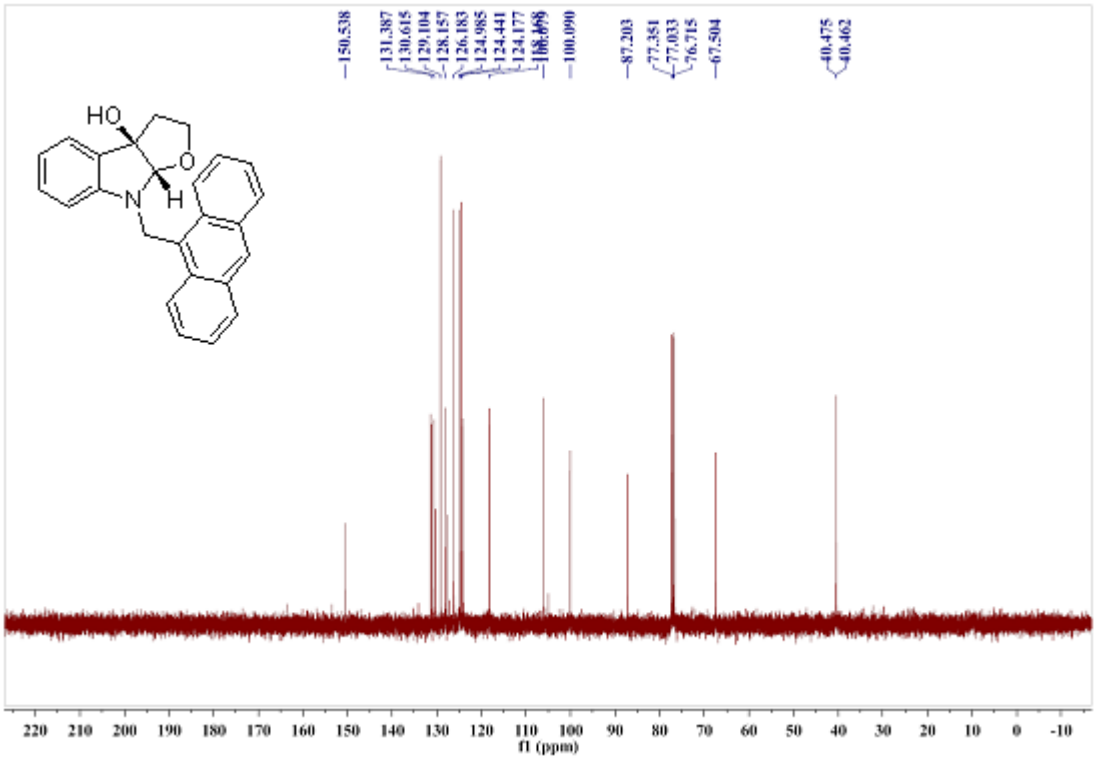


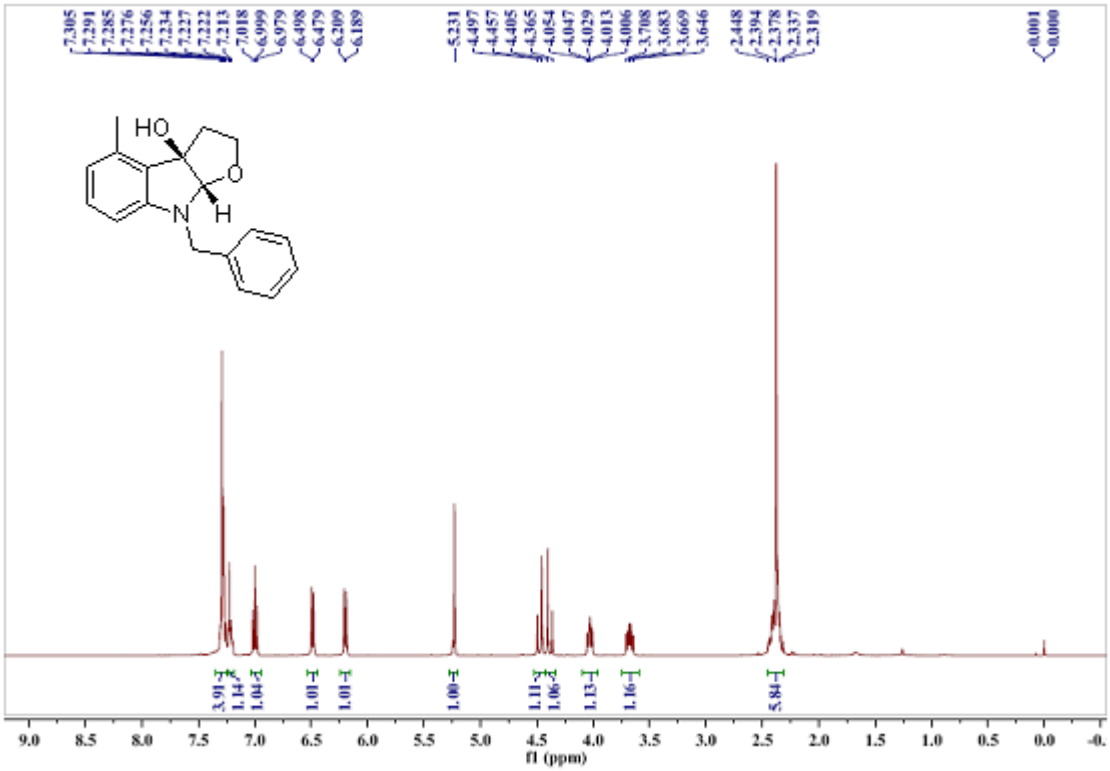


2e





2g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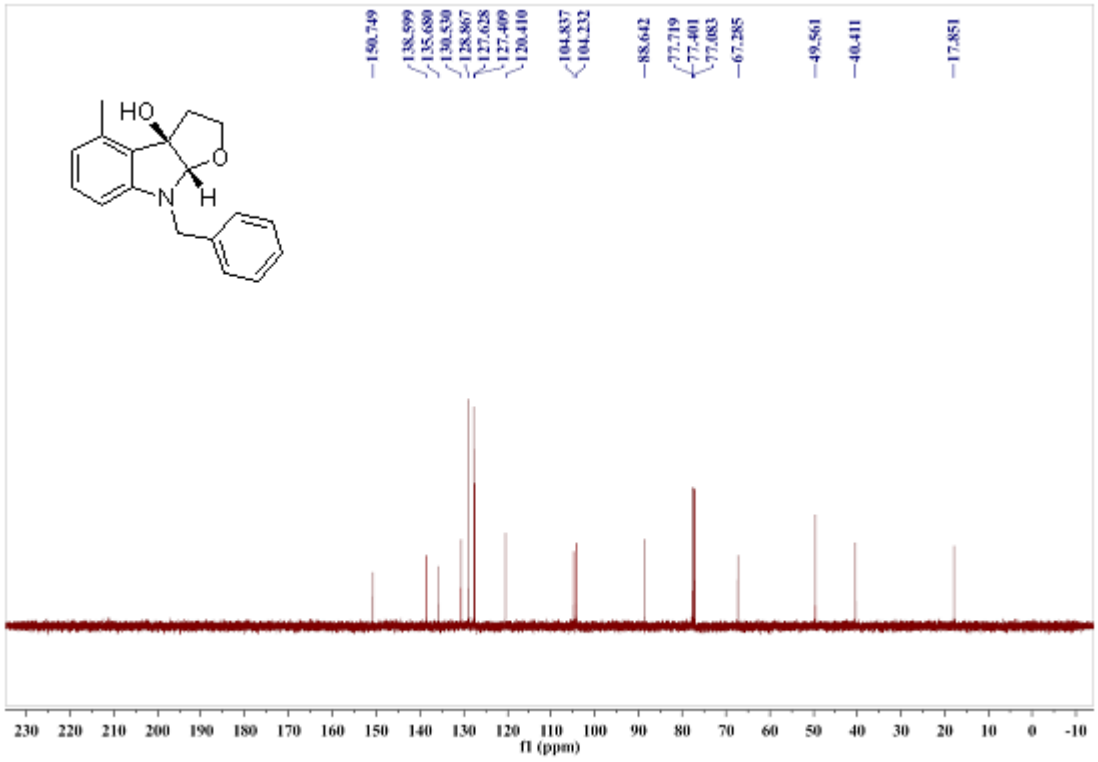
7.256
7.234
7.227
7.222
7.213
7.018
6.999
6.979
6.498
6.479
6.209
6.189
5.231
4.497
4.457
4.405
4.365
4.054
4.047
4.029
4.013
4.006
3.708
3.683
3.669
3.646
2.448
2.394
2.378
2.337
2.319
0.001
0.000
HO
O
N
H
3.91
1.14
1.04
1.01
1.01
1.00
1.11
1.06
1.13
1.16
5.84
f1 (ppm)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120.410
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104.232
88.642
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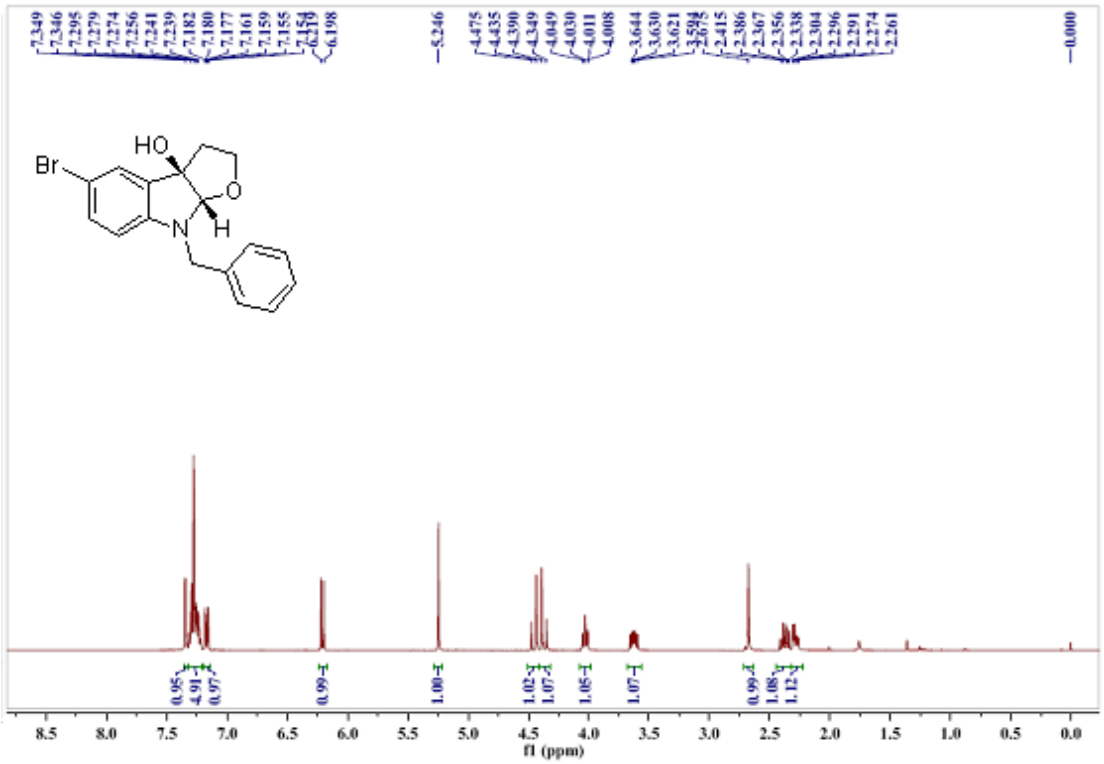
77.083
67.285
49.561
40.411
17.851
HO
O
N
H
f1 (ppm)

2h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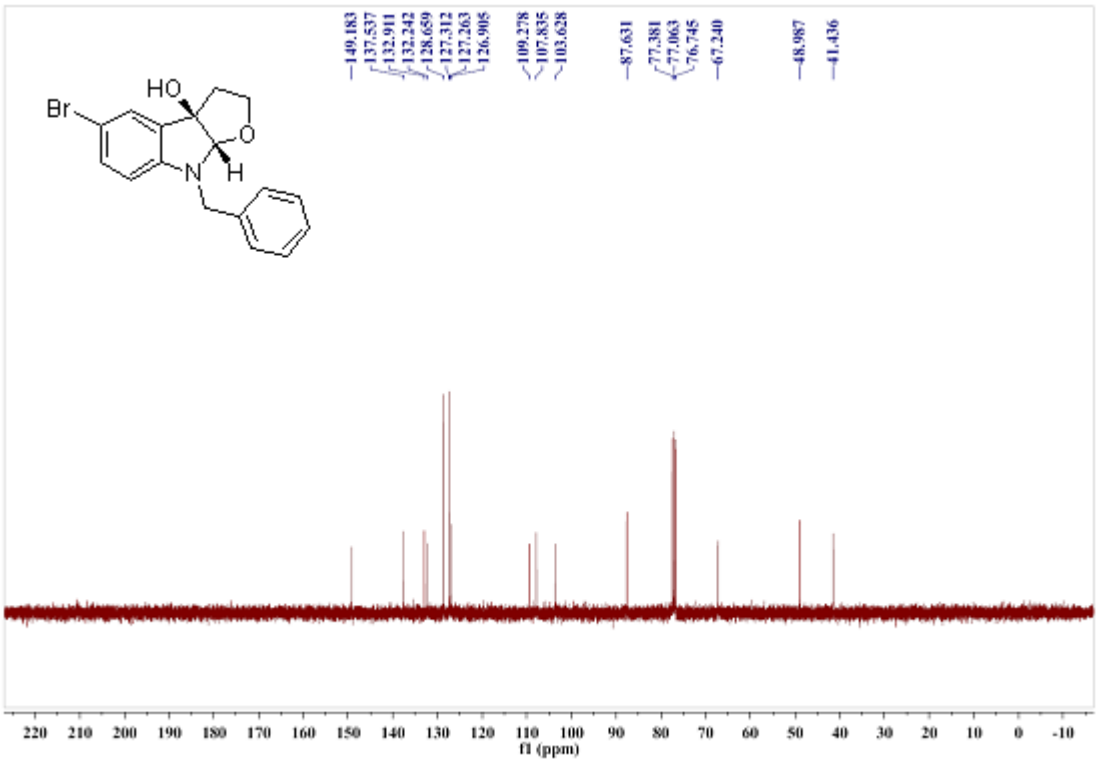
7.346
7.295
7.279
7.274
7.256
7.241
7.239
7.182
7.180
7.177
7.161
7.159
7.155
7.154
7.150
6.198
5.246
4.475
4.435
4.390
4.349
4.049
4.030
4.011
4.008
3.644
3.630
3.621
3.594
3.575
2.415
2.386
2.367
2.356
2.338
2.304
2.296
2.291
2.274
2.261
0.000
HO
Br
O
N
H
0.95
4.91
0.97
0.99
1.00
1.02
1.07
1.05
1.07
0.99
1.08
1.12
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
f1 (ppm)


149.183
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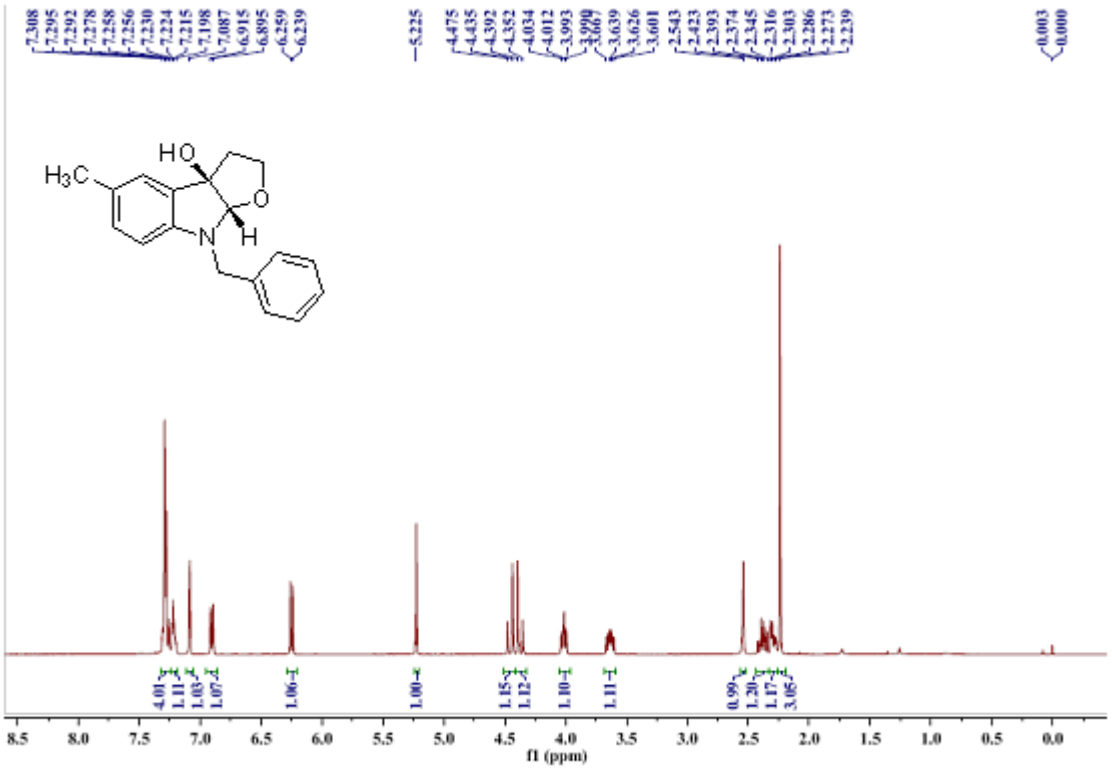
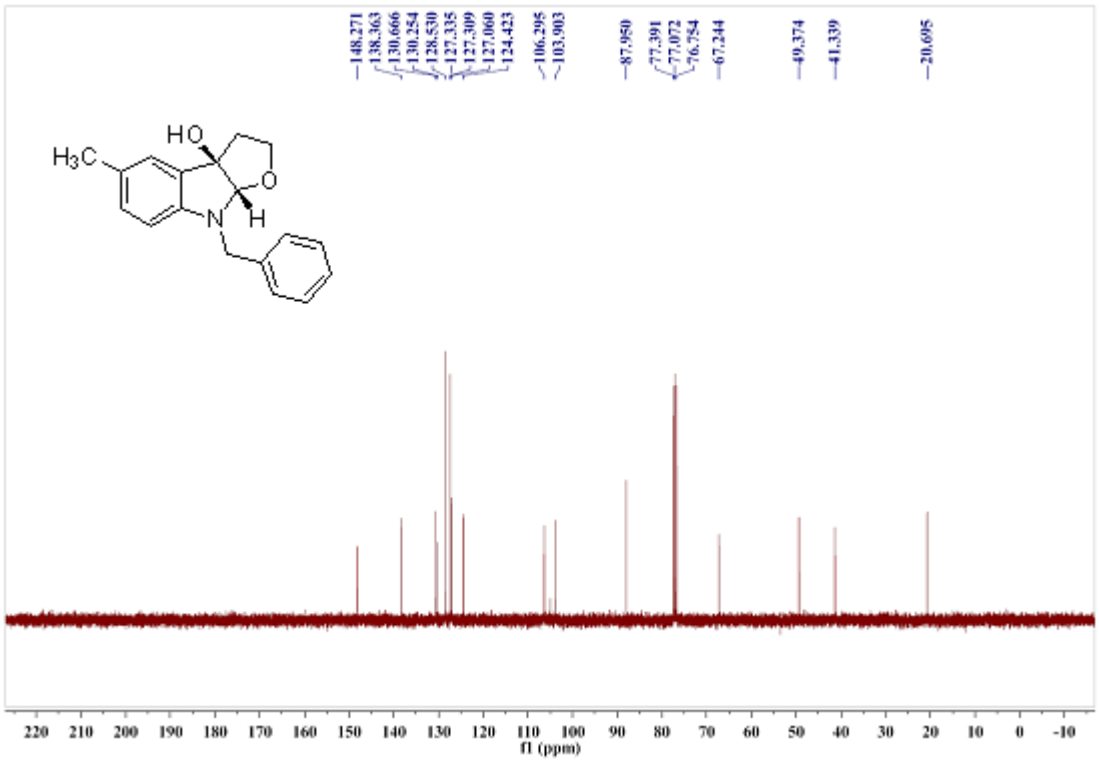
132.911
132.242
128.659
127.312
127.263
126.905
109.278
107.835
103.628
87.631
77.381
77.063
76.745
67.240
48.987
41.436
HO
Br
O
N
H
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2i





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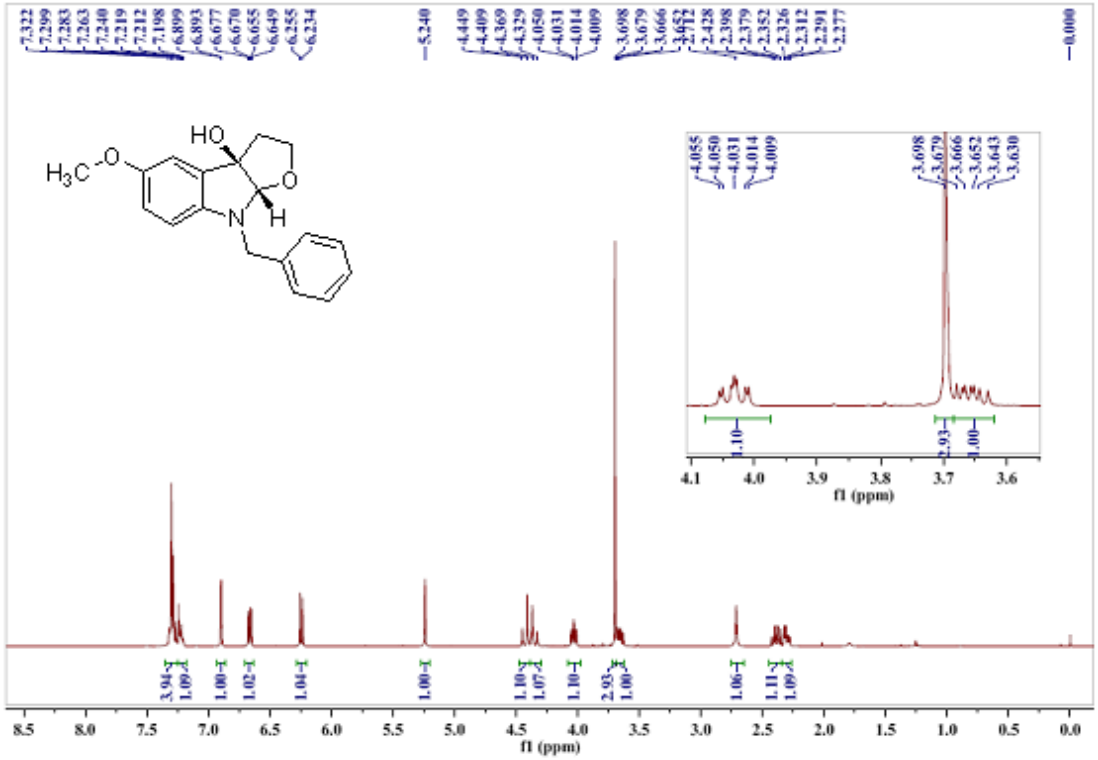
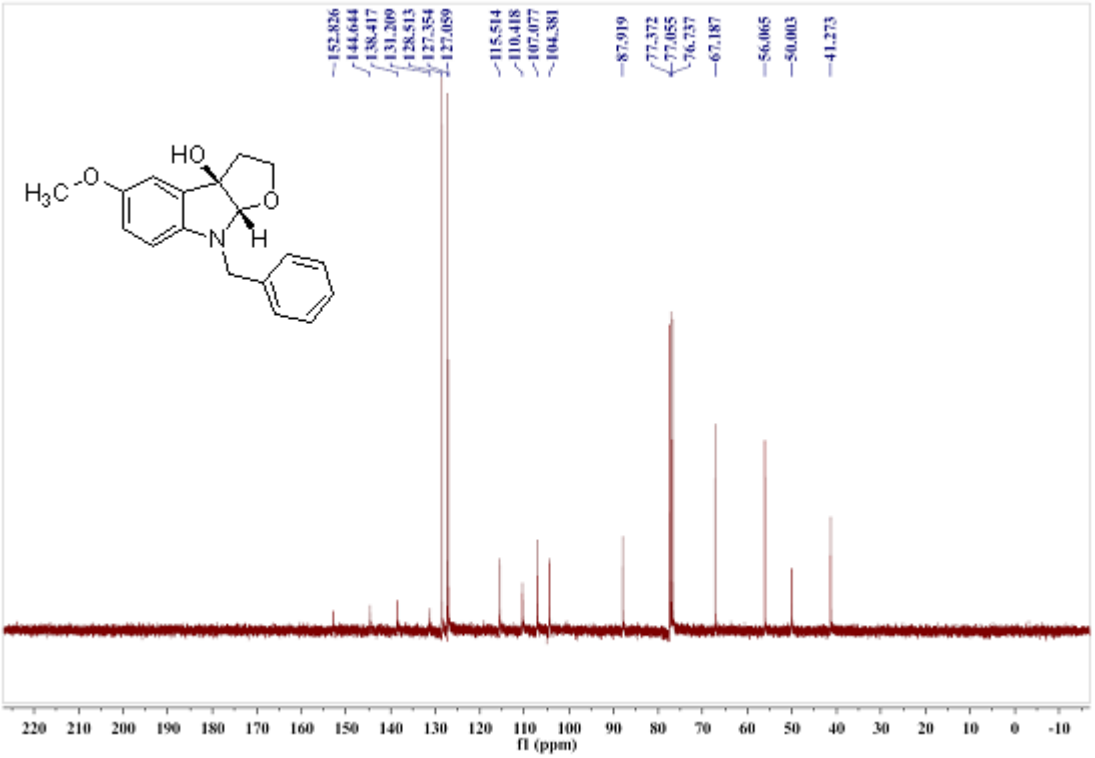
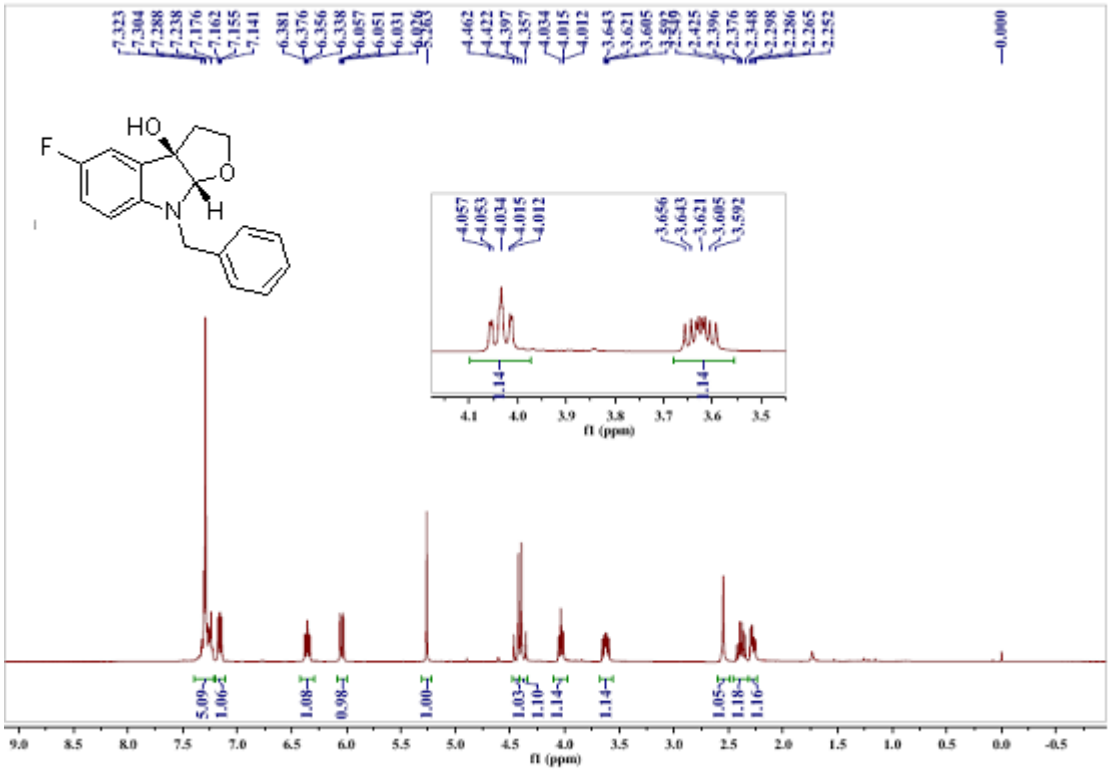
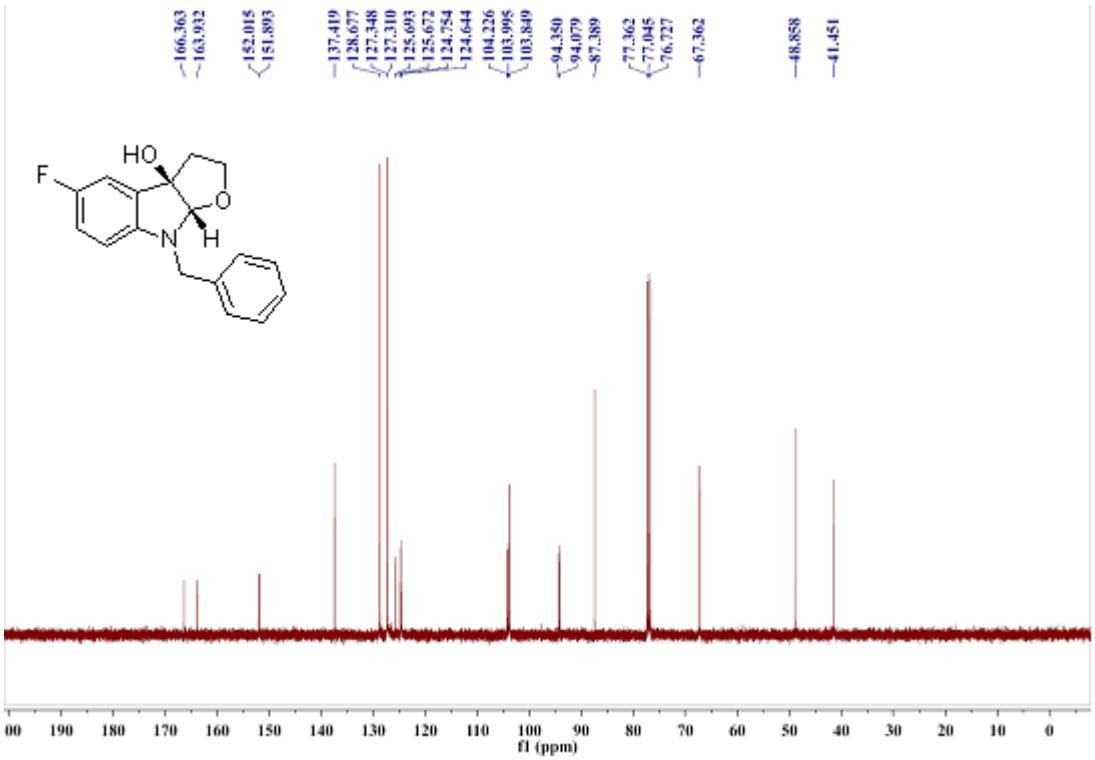
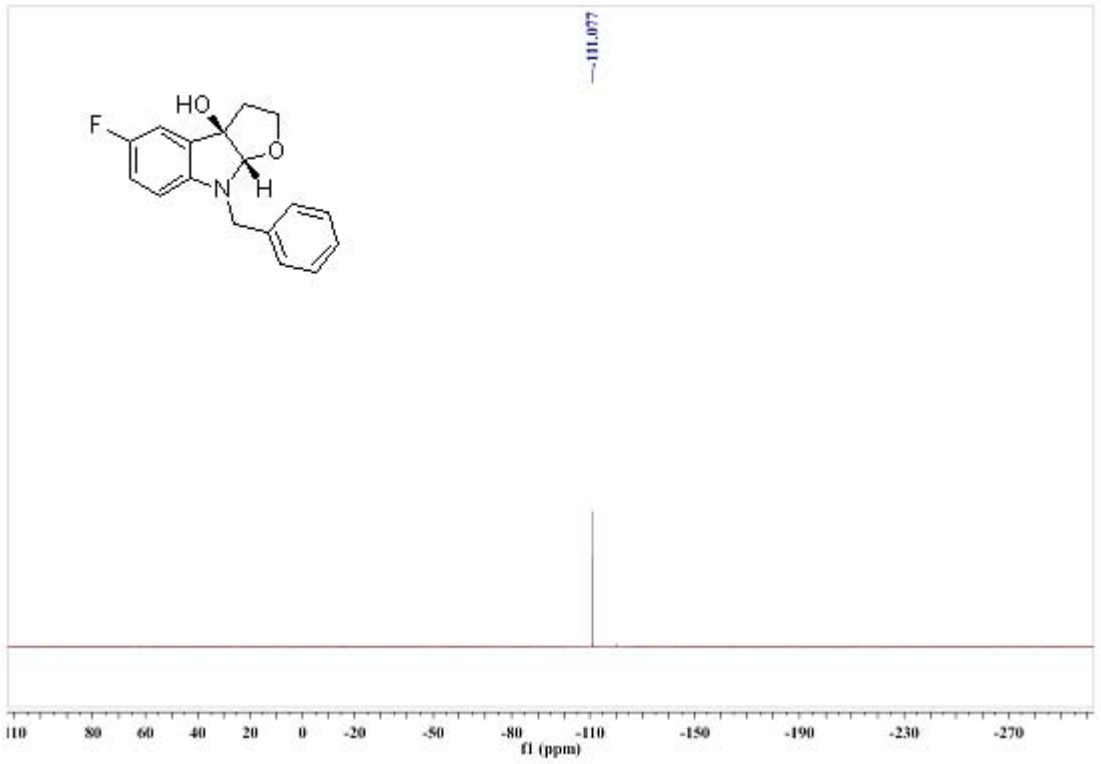




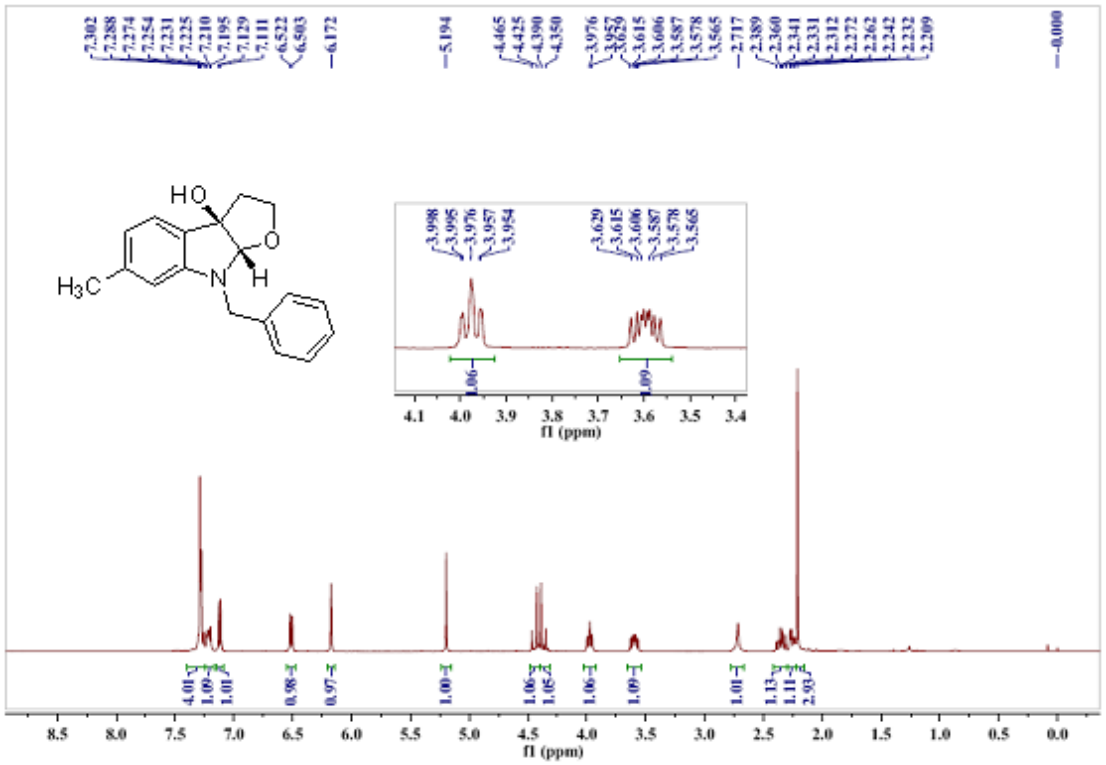
2k

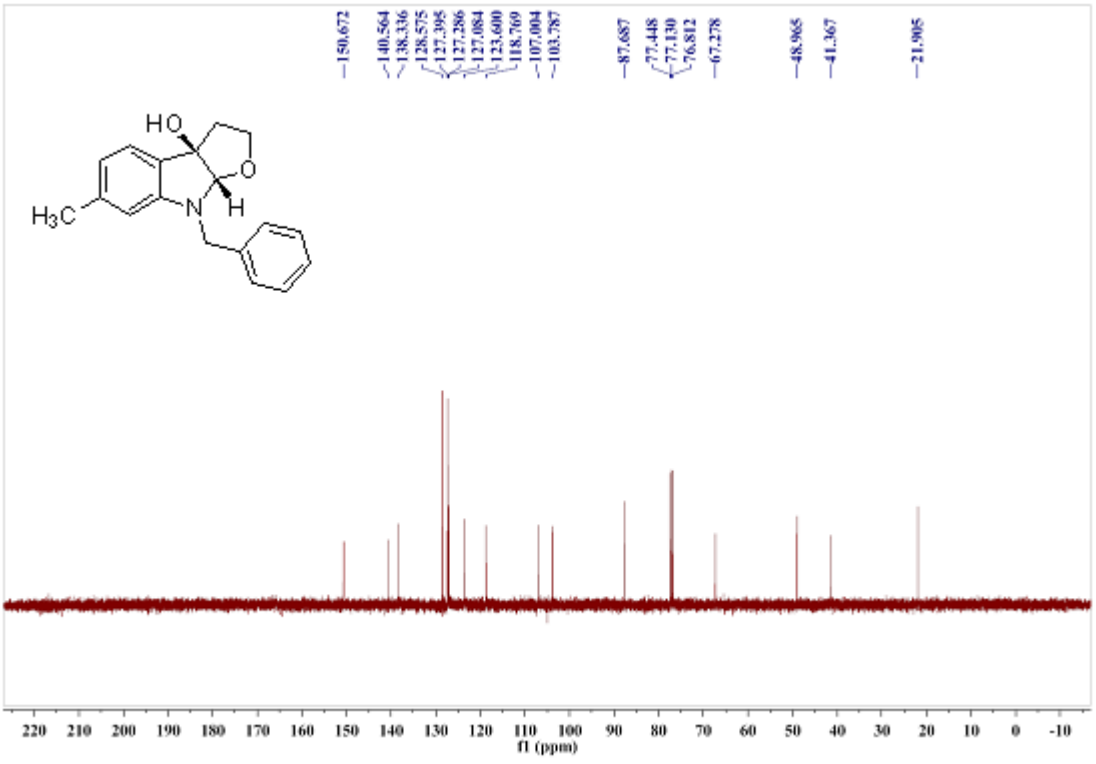






2l





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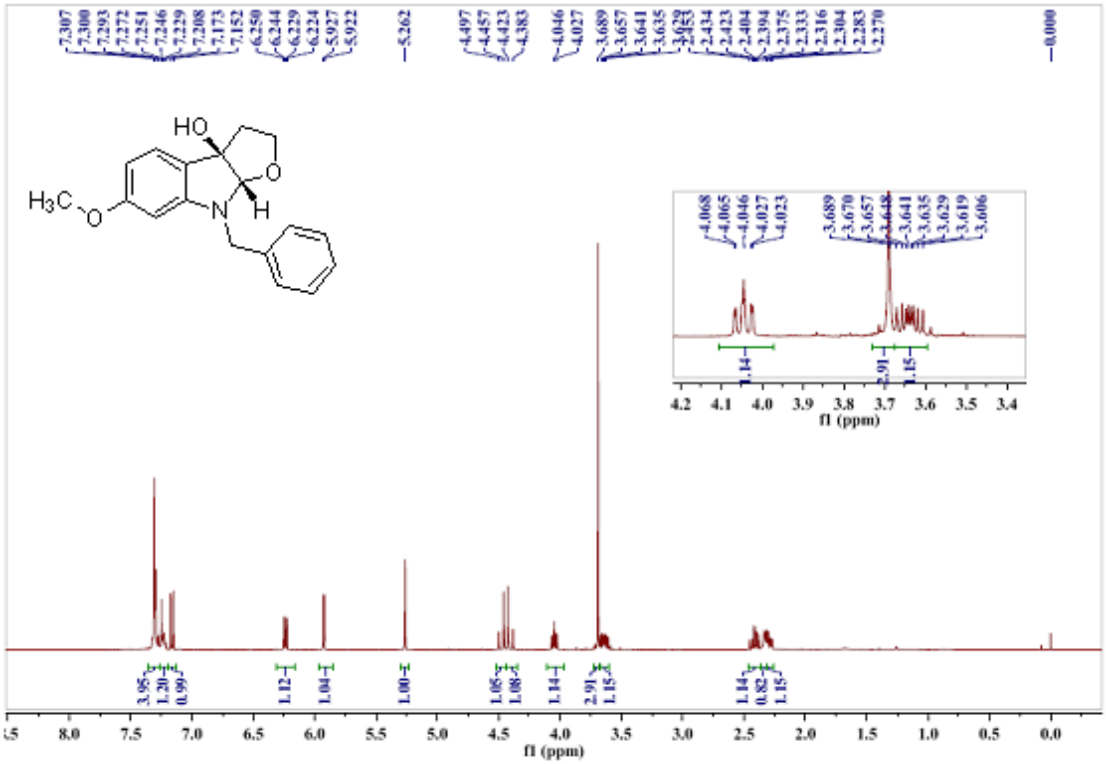

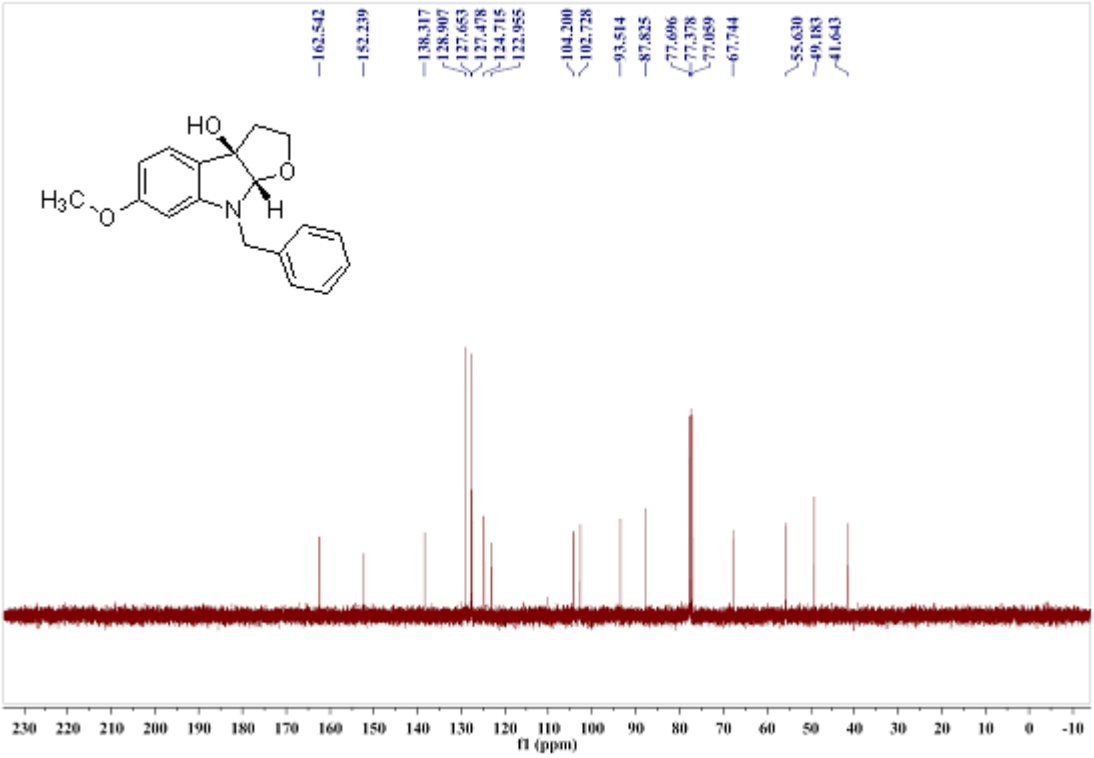

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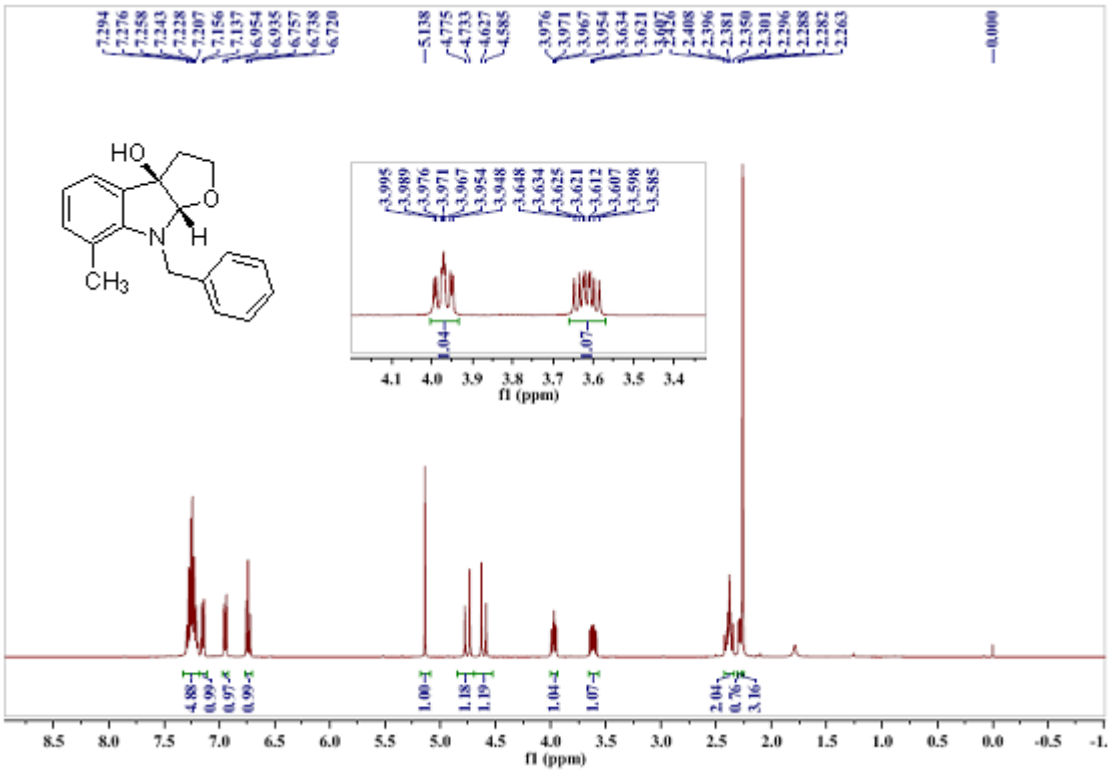

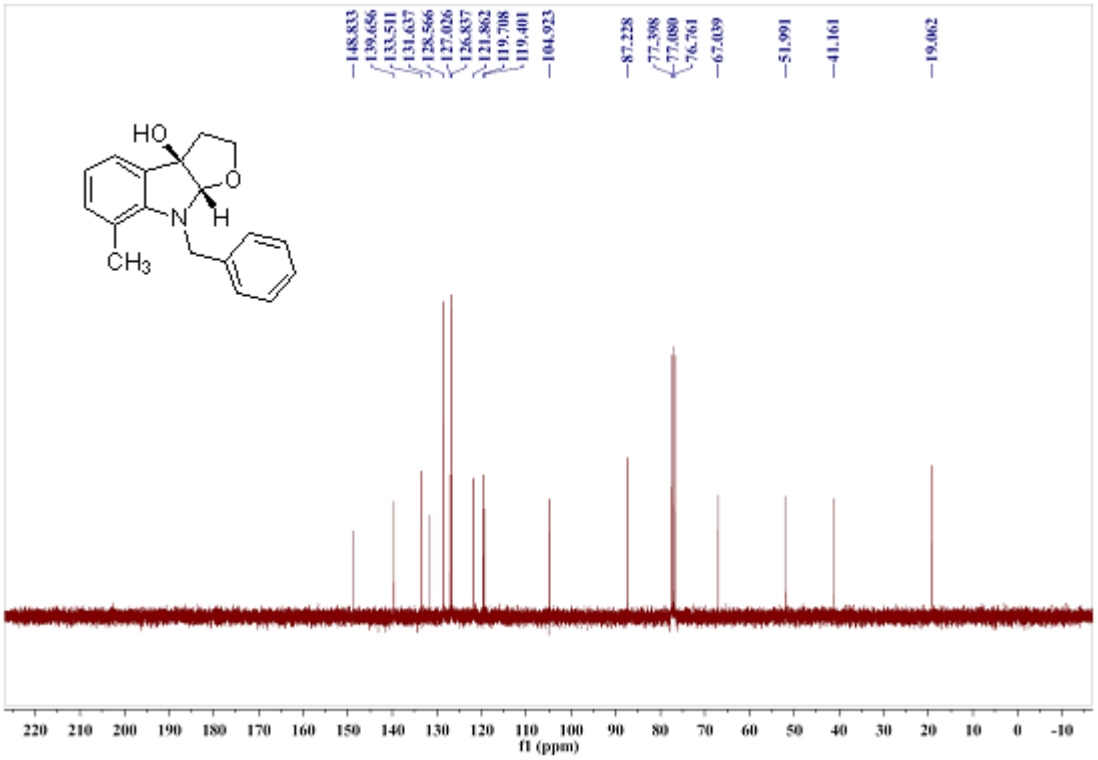

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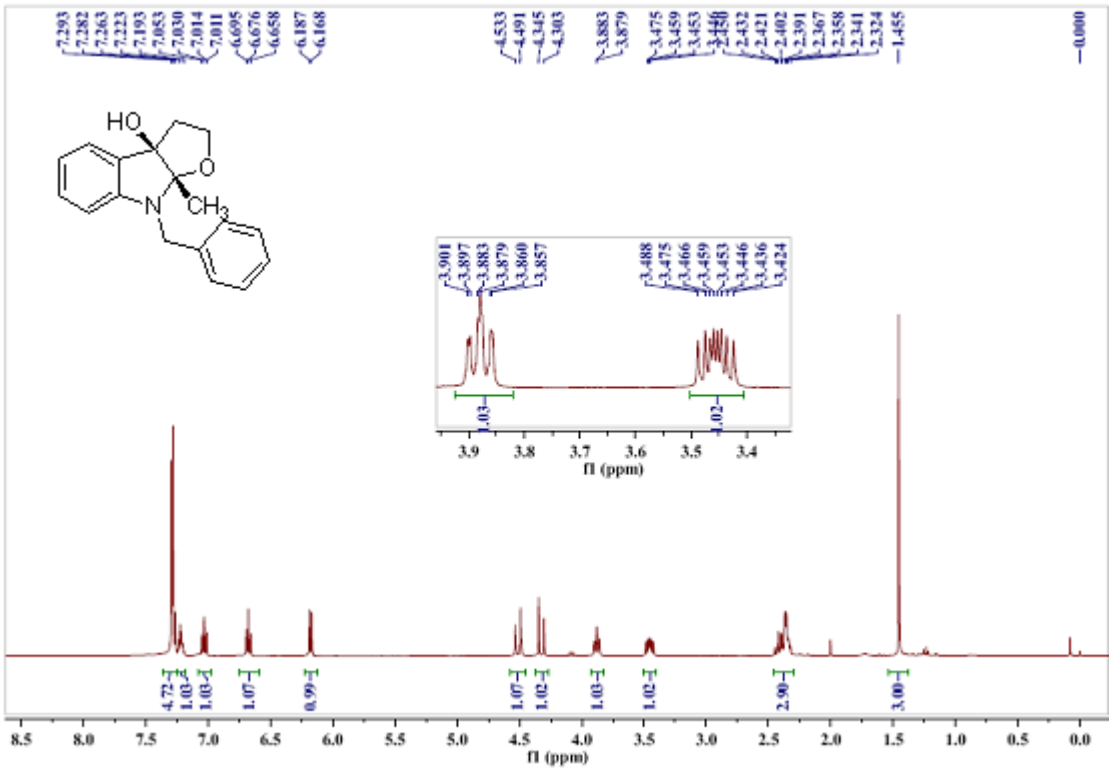

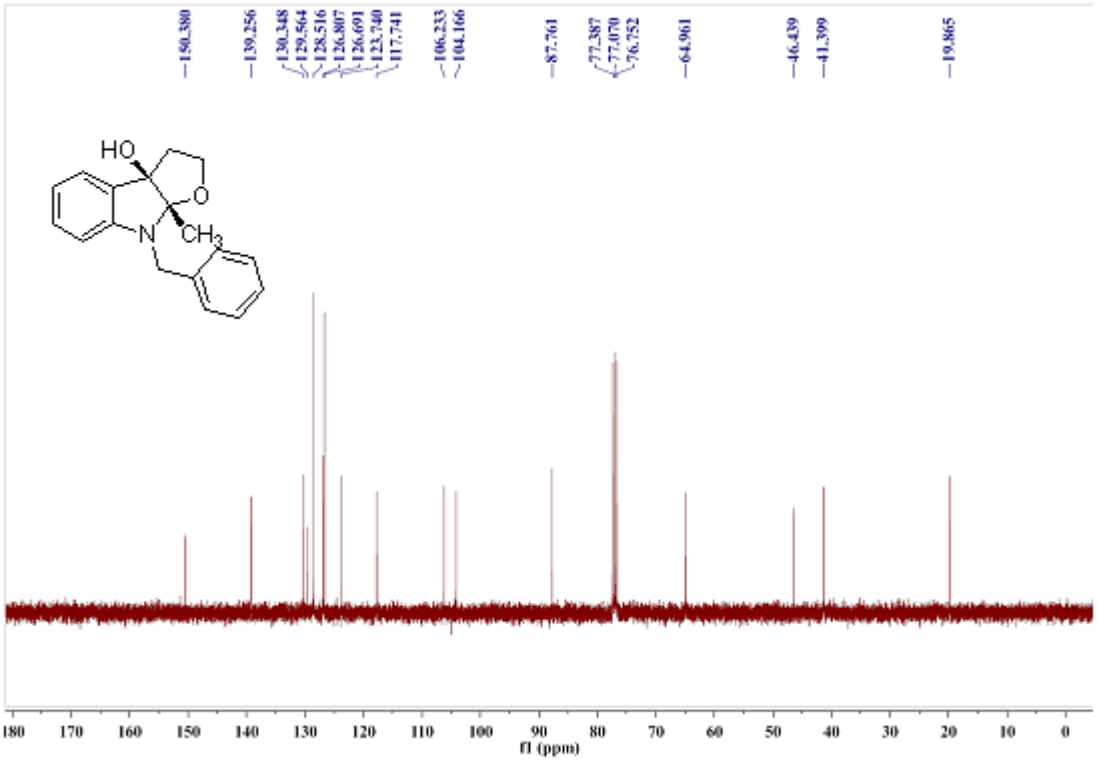

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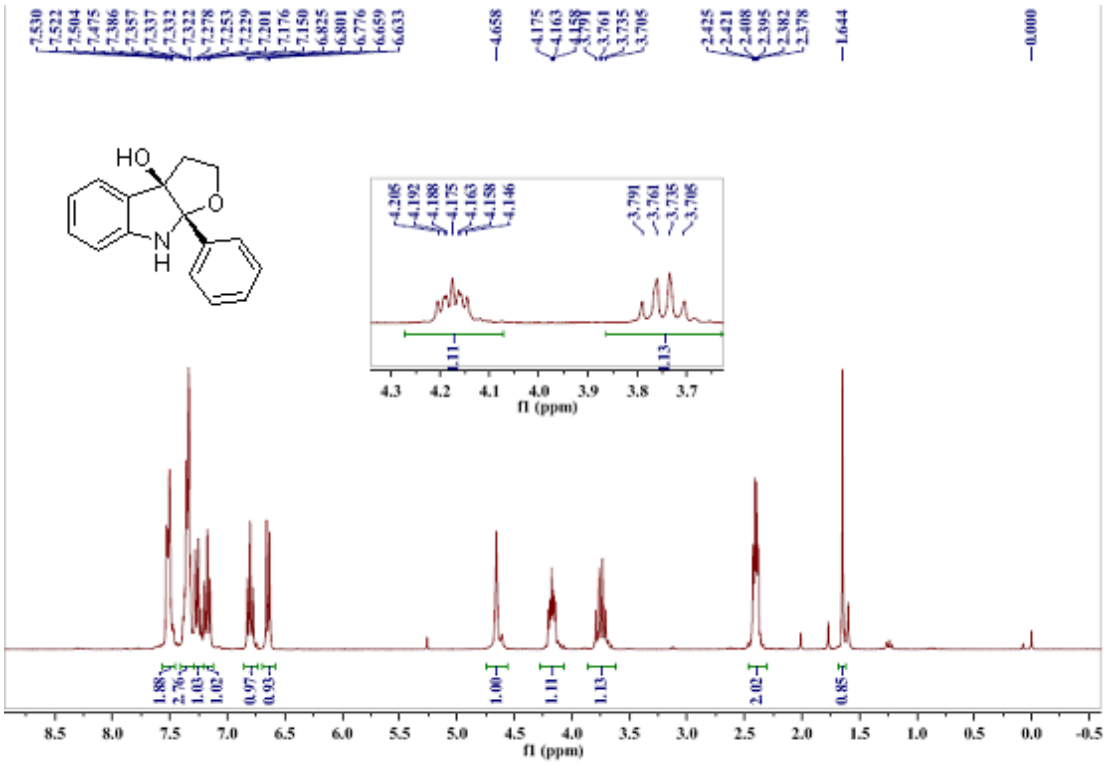

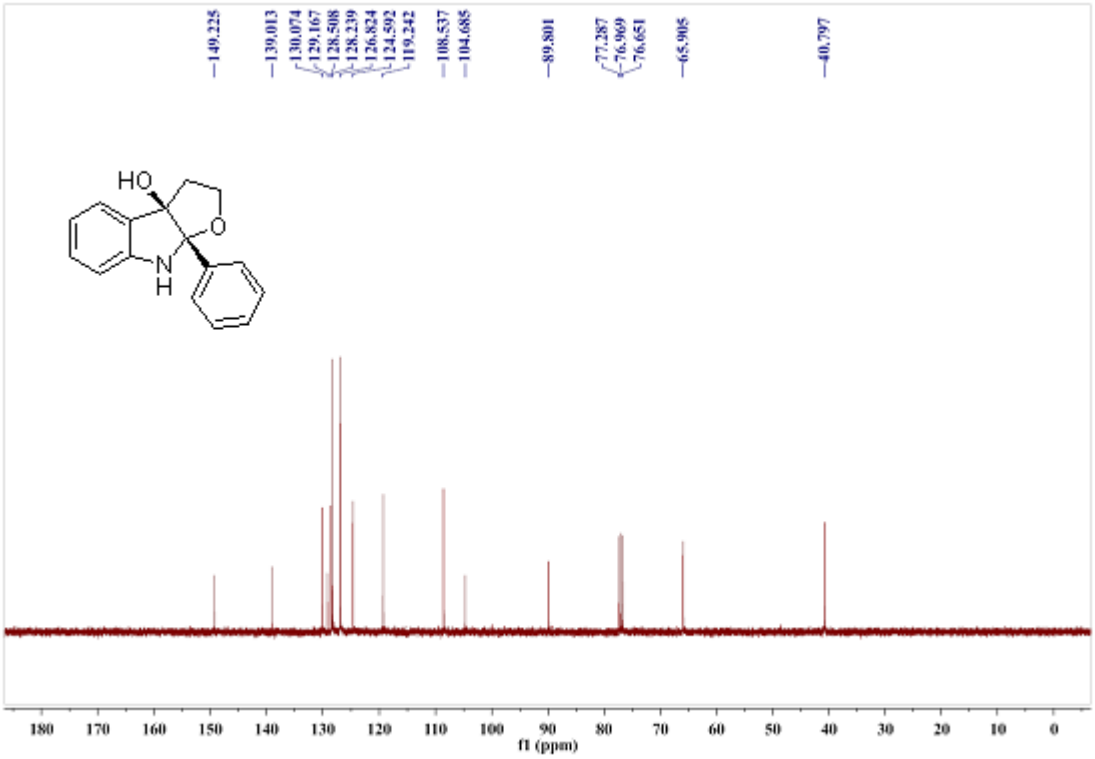

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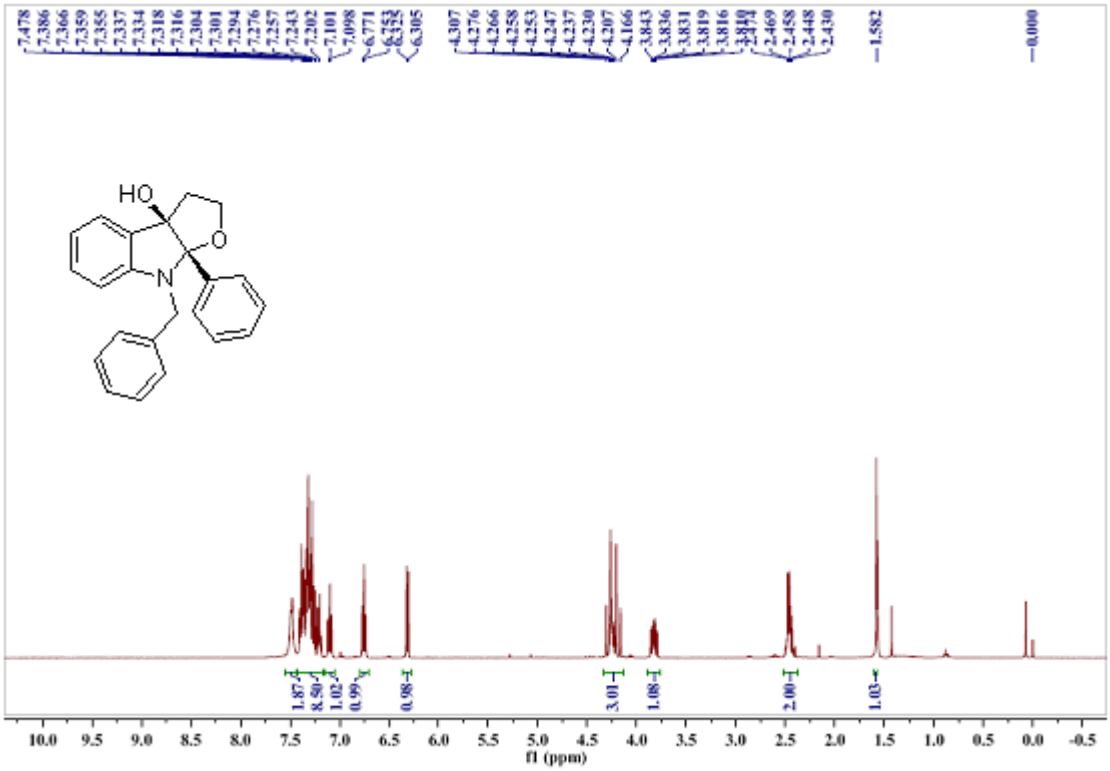
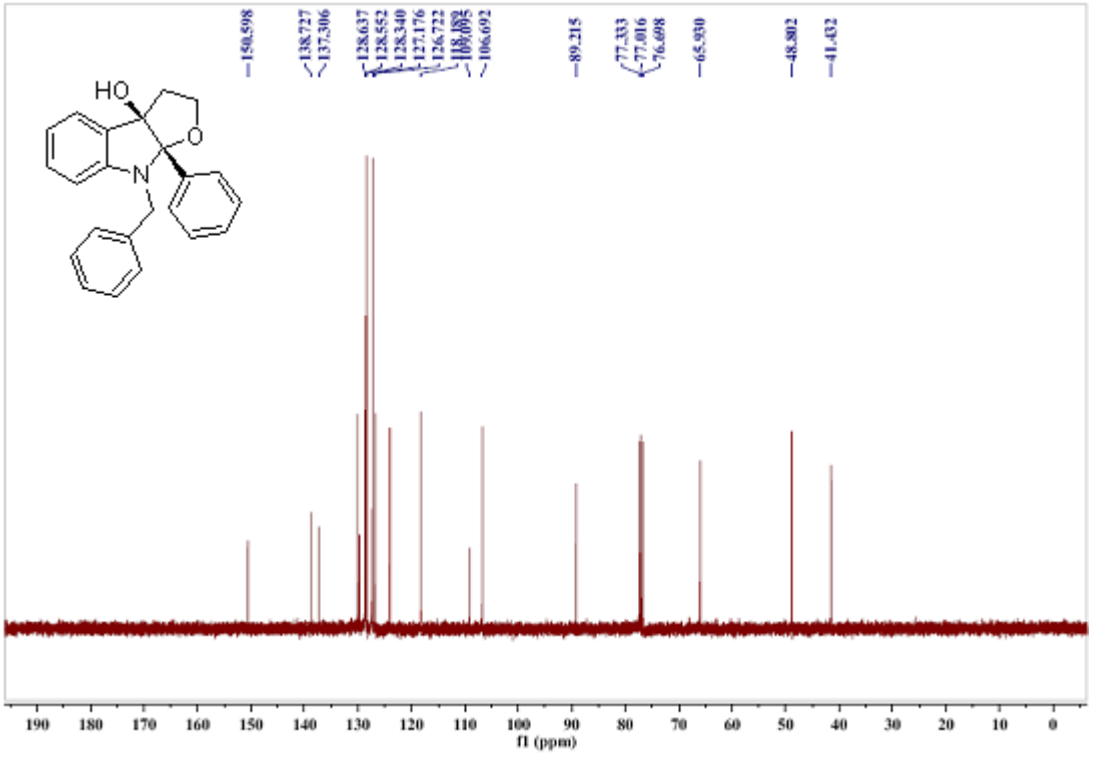
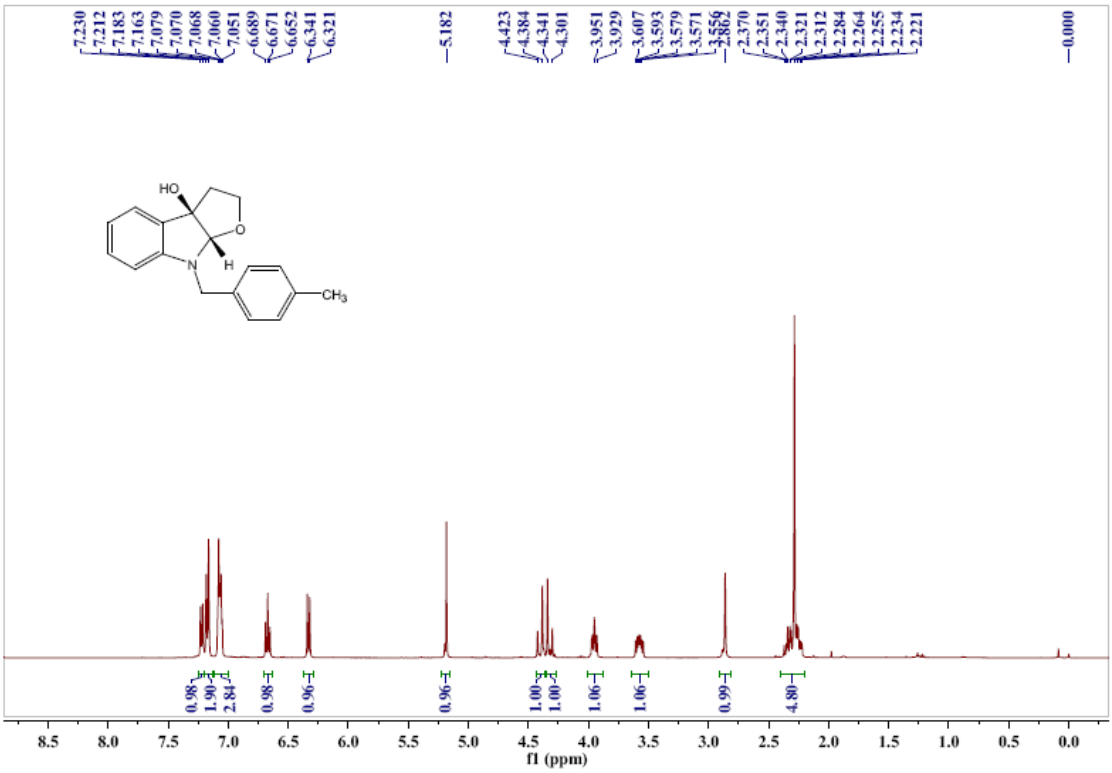




2r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6.321
5.182
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2.321
2.312
2.284
2.264
2.255
2.234
2.221
0.000
HO
O
N
H
CH3
0.98
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0.96
0.96
1.00
1.00
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1.06
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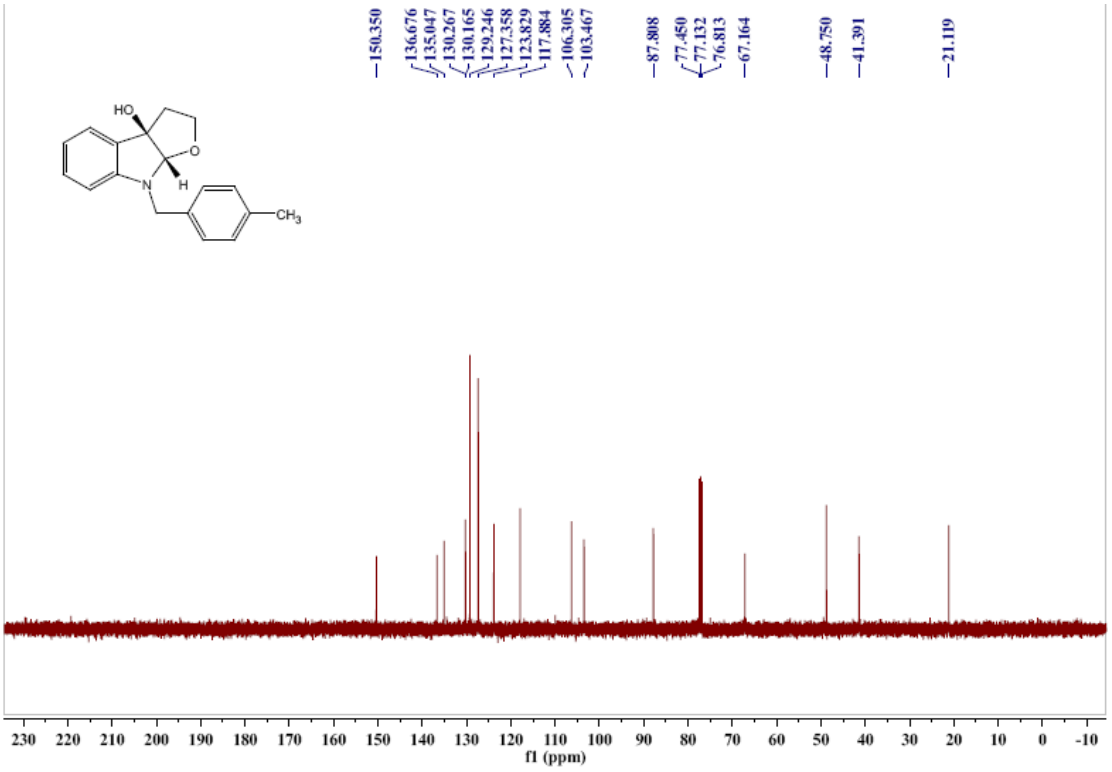
4.80
f1 (ppm)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123.829
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106.305
103.467
87.808
77.450
77.132
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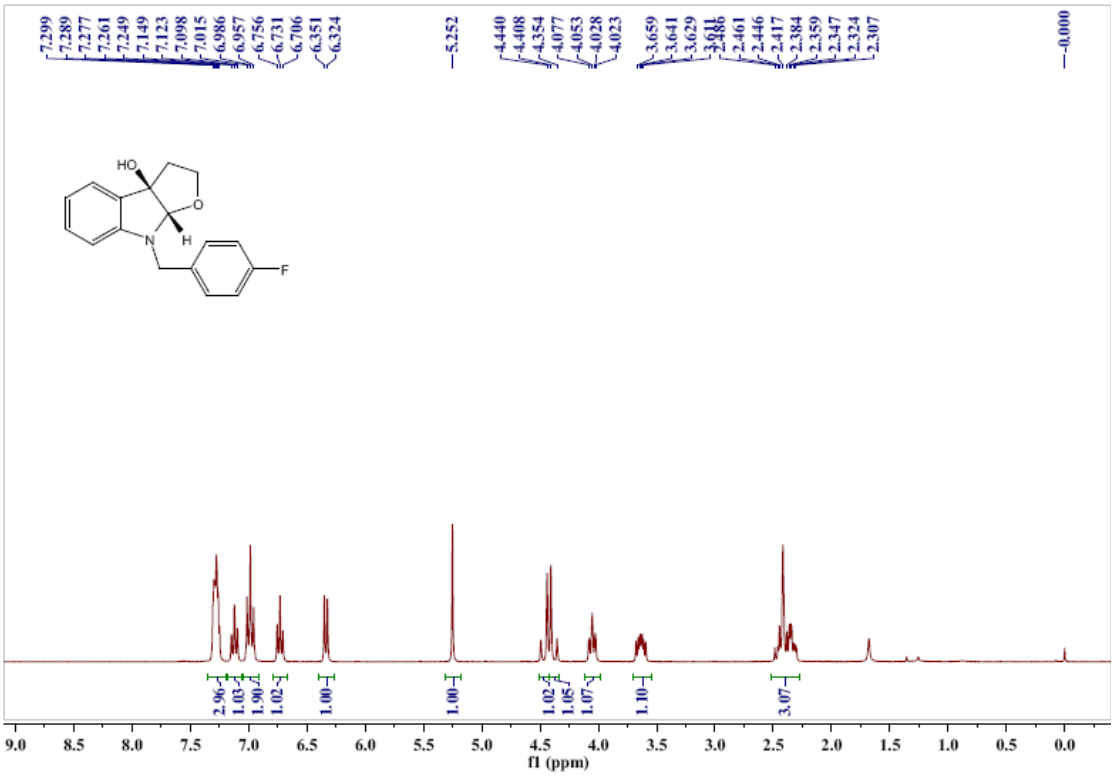
67.164
48.750
41.391
21.119
HO
O
N
H
CH3
f1 (ppm)

2s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4.077
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4.028
4.023
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3.641
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2.324
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0.000
HO
O
N
H
F
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1.00
1.02
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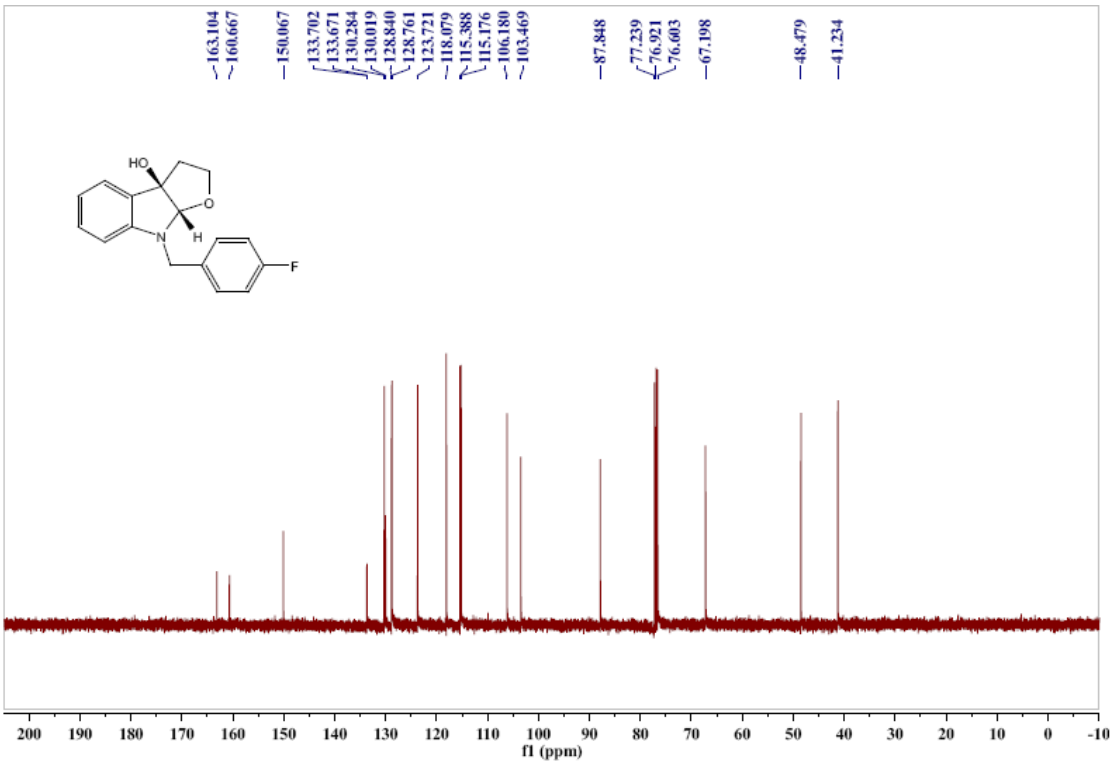
1.07
1.10
3.07
fl (ppm)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130.284
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128.840
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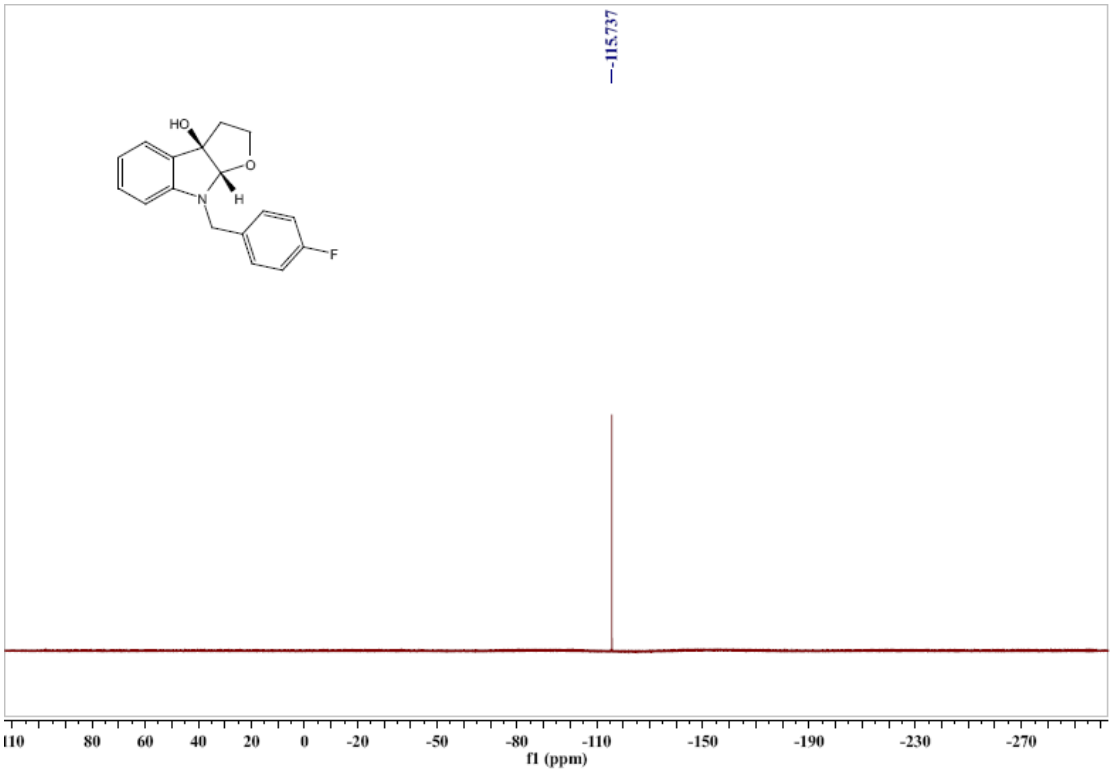
123.721
118.079
115.388
115.176
106.180
103.469
87.848
77.239
76.921
76.603
67.198
48.479
41.234
HO
O
N
H
F
fl (ppm)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O
N
H
F
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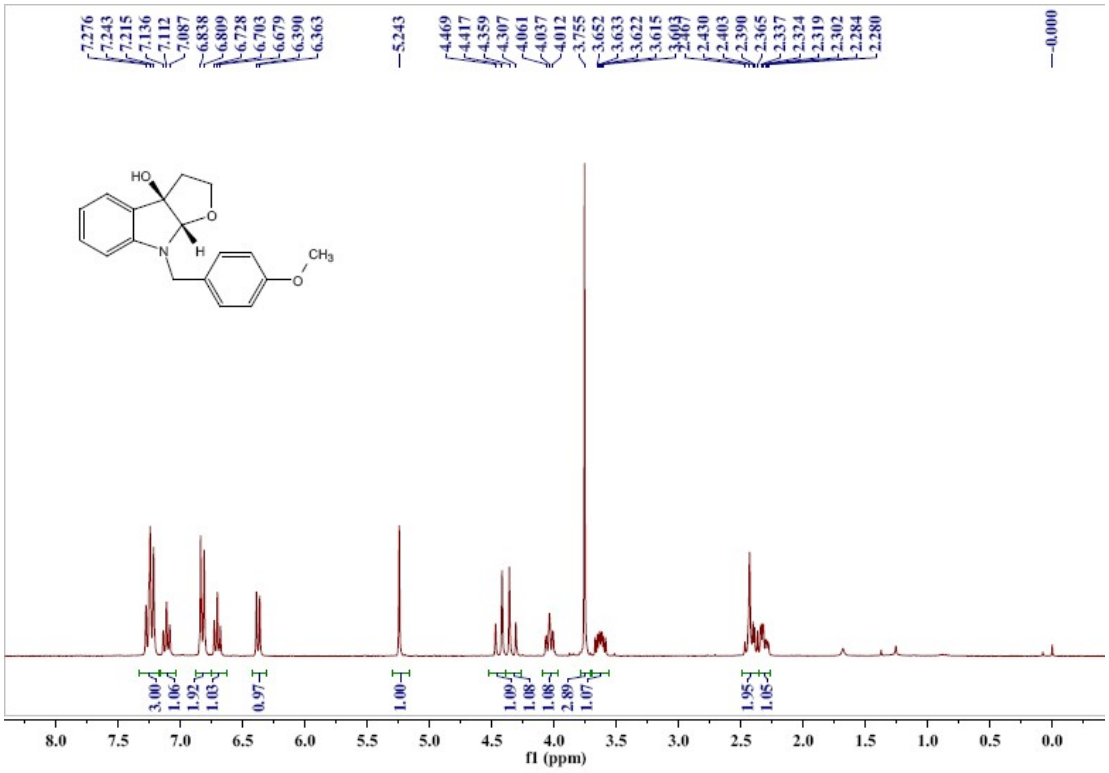
-110
-150
-190
-230
-270
f1 (ppm)

2t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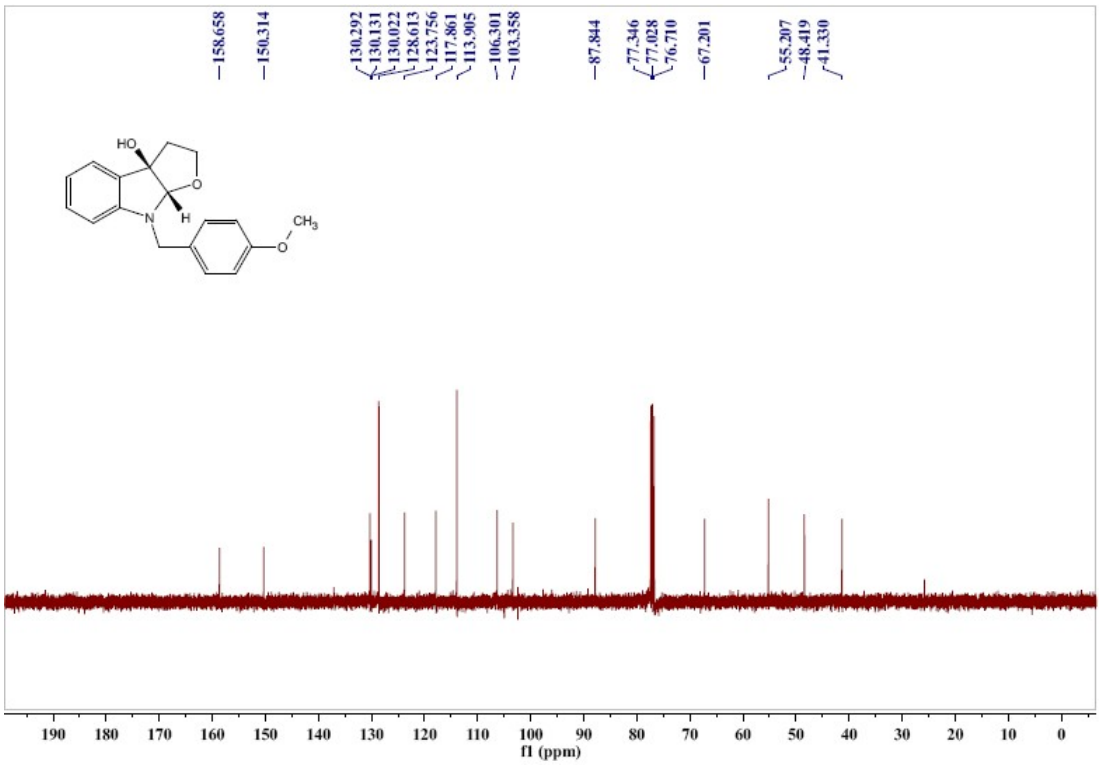
6.679
6.390
6.363
5.243
4.469
4.417
4.359
4.307
4.061
4.037
4.012
3.755
3.652
3.633
3.622
3.615
2.430
2.403
2.390
2.365
2.337
2.324
2.319
2.302
2.284
2.280
0.000
HO
O
N
H
CH3
O
3.00
1.06
1.92
1.03
0.97
1.00
1.09
1.08
1.08
2.89
1.07
1.95
1.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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103.358
87.844
77.346
77.028
76.710
67.201
55.207
48.419
41.330
HO
O
N
H
CH3
O
190
180
170
160
150
140
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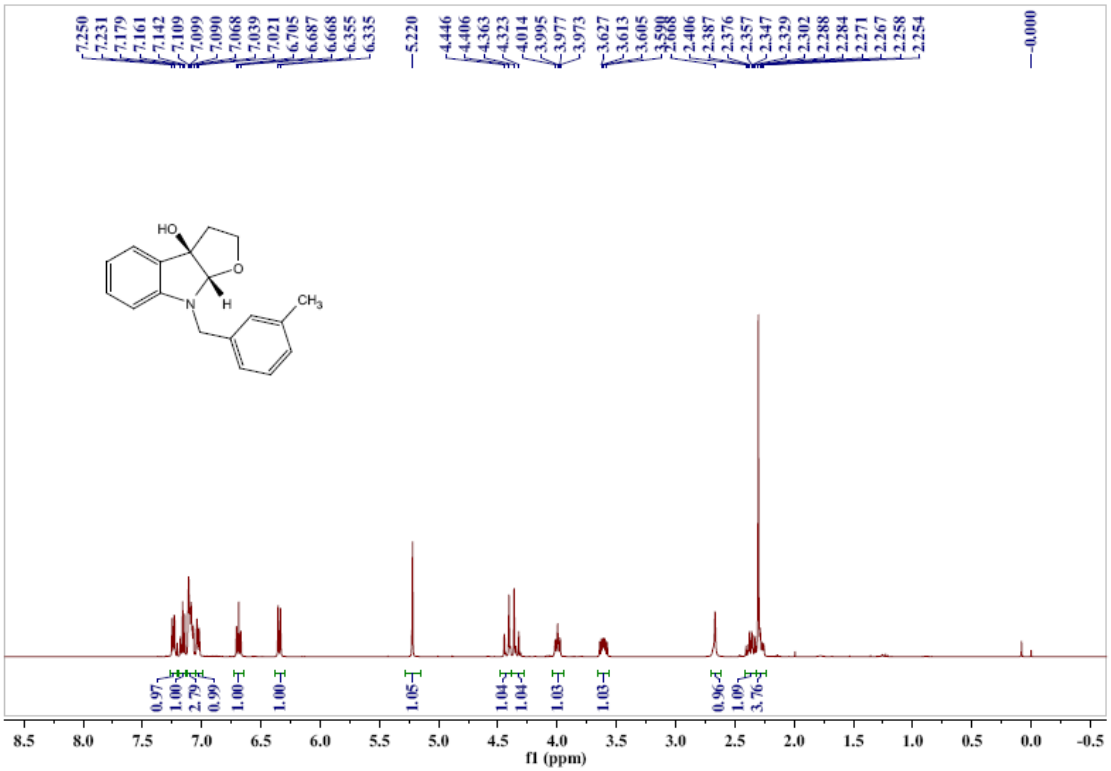
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2u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7.039
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6.668
6.355
6.335
5.220
4.446
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3.973
3.627
3.613
3.605
3.588
3.568
2.406
2.387
2.376
2.357
2.347
2.329
2.302
2.288
2.284
2.271
2.267
2.258
2.254
-0.000
HO
O
N
H
CH3
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1.00
2.79
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1.00
1.00
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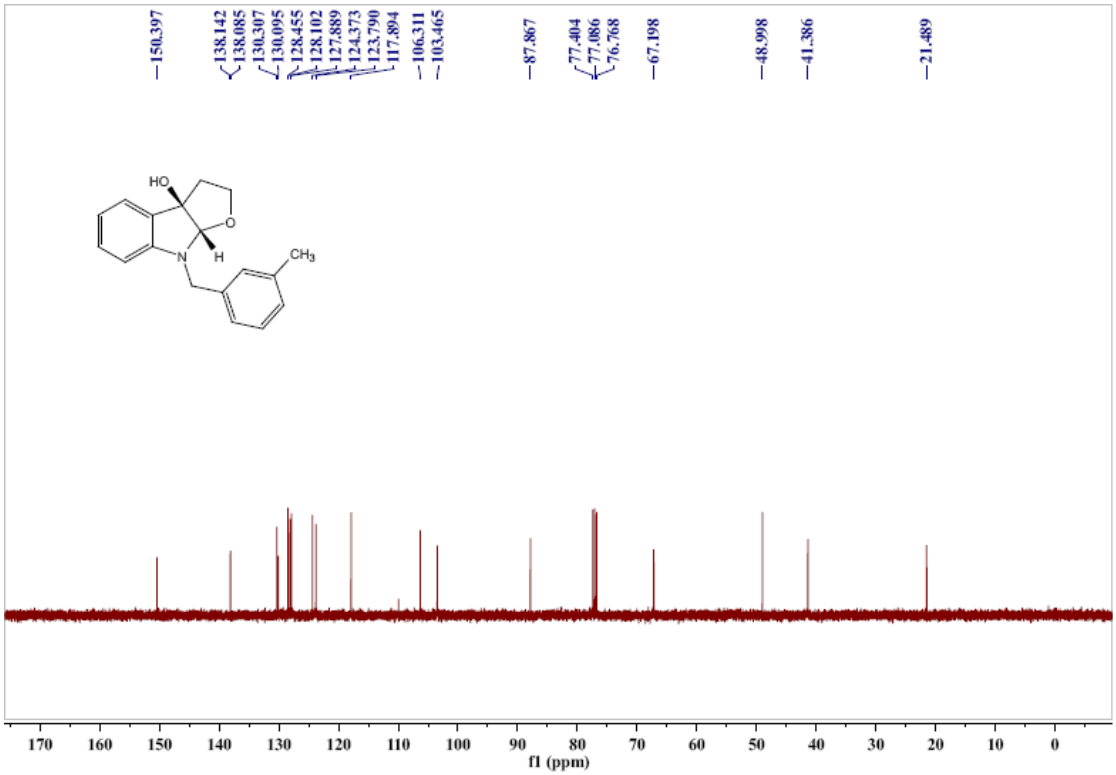
1.04
1.04
1.03
1.03
0.96
1.09
3.76
f1 (ppm)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87.867
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67.198
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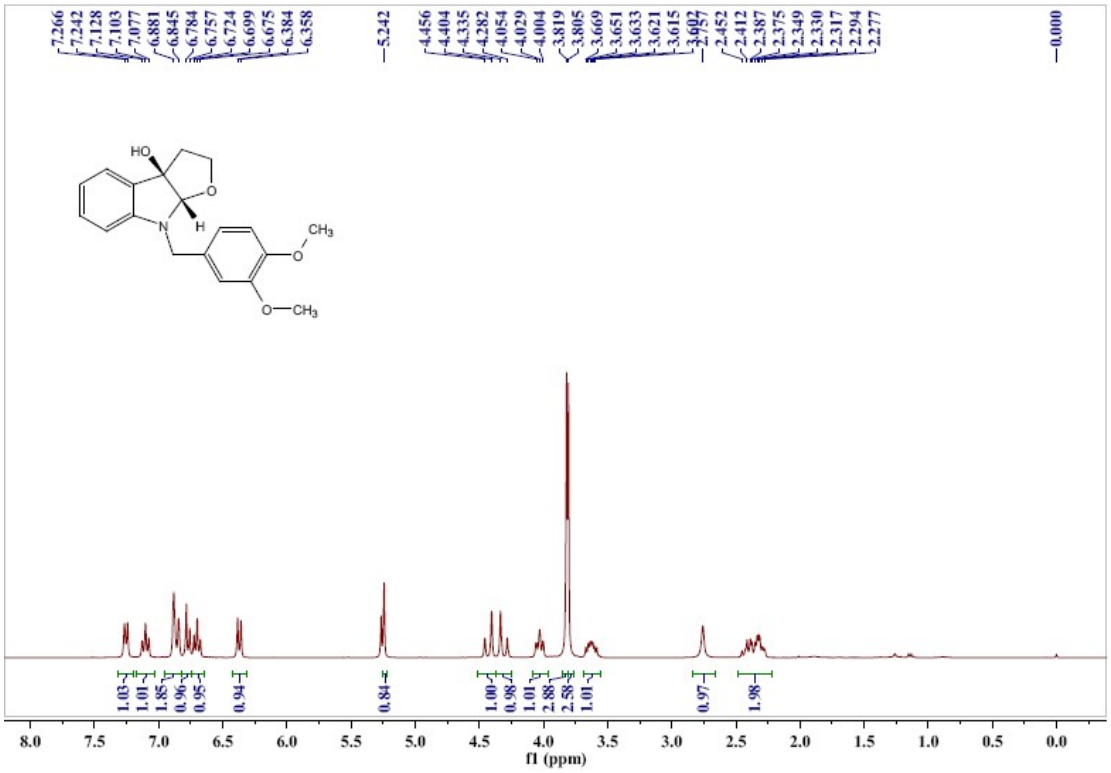
HO
O
N
H
CH3
f1 (ppm)

2v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3.651
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3.615
3.602
2.757
2.452
2.412
2.387
2.375
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2.317
2.294
2.277
0.000
HO
O
N
H
CH3
O
O—CH3
1.03
1.01
1.85
0.96
0.95
0.94
0.84
1.00
0.98
1.01
2.88
2.58
1.01
0.97
1.98
8.0
7.5
7.0
6.5
6.0
5.5
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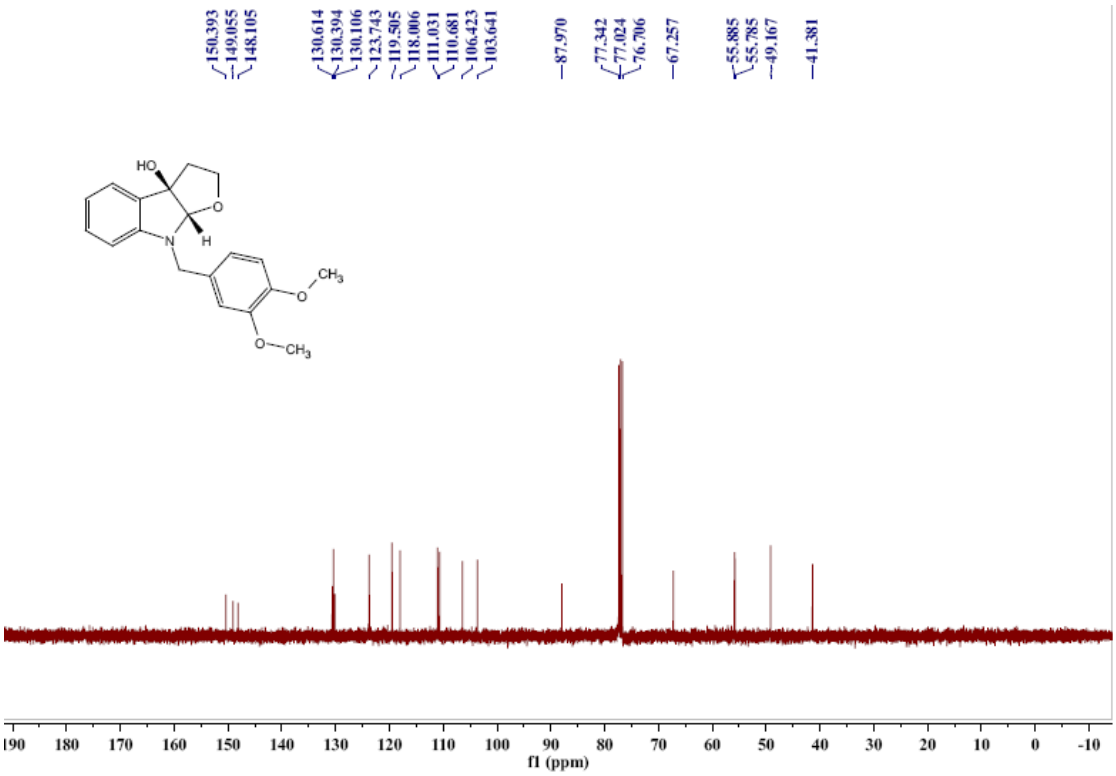
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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106.423
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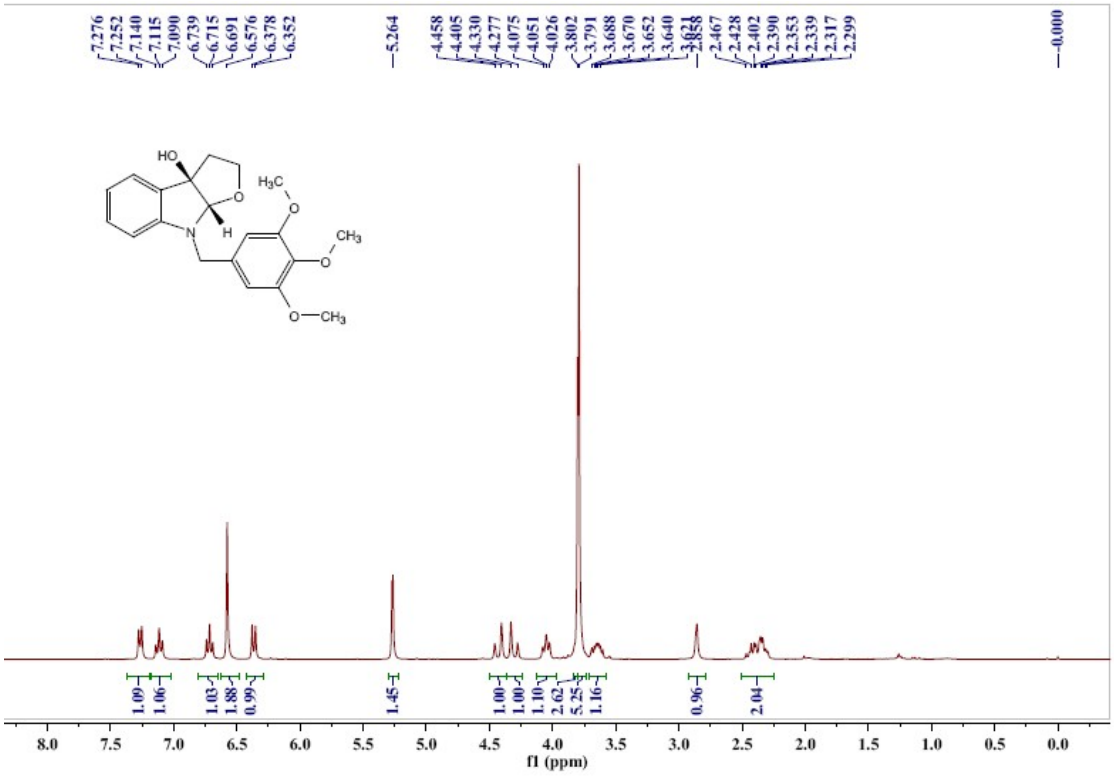
87.970
77.342
77.024
76.706
67.257
55.885
55.785
49.167
41.381
HO
O
N
H
CH3
O
O—CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2w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6.352
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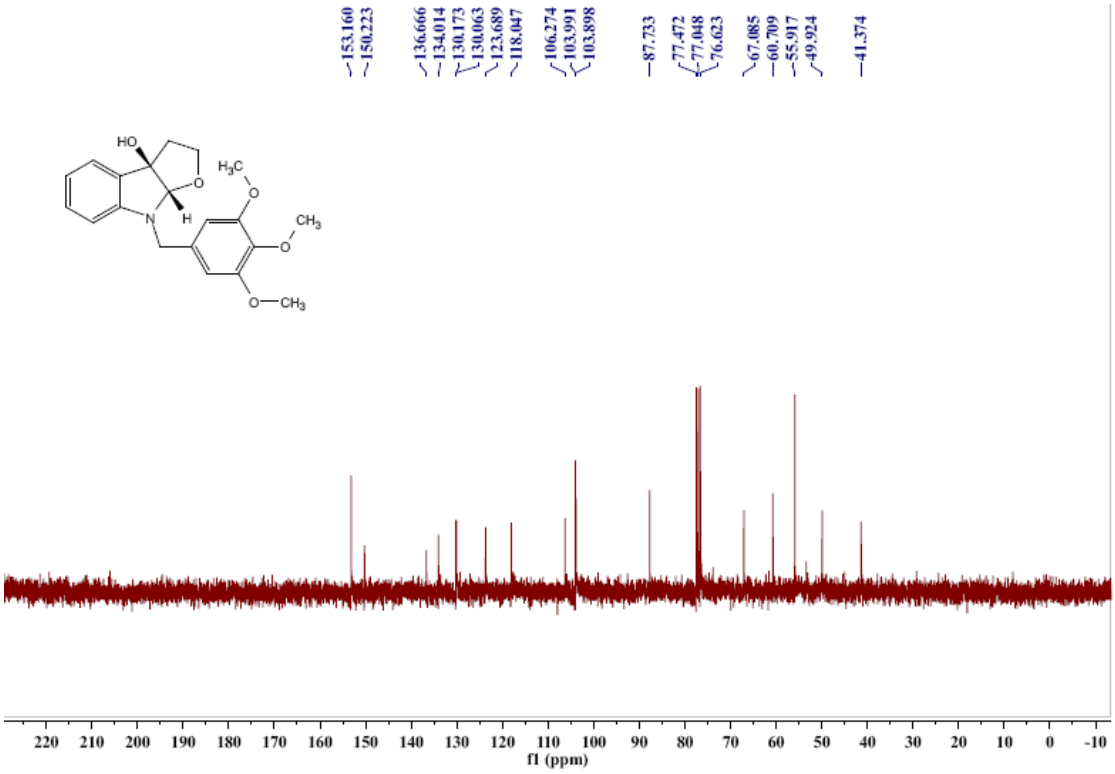
4.405
4.330
4.277
4.075
4.051
4.026
3.802
3.791
3.688
3.670
3.652
3.640
3.621
2.467
2.428
2.402
2.390
2.353
2.339
2.317
2.299
0.000
HO
H3C
O
CH3
N
H
1.09
1.06
1.03
1.88
0.99
1.45
1.00
1.00
1.10
2.62
5.25
1.16
0.96
2.04
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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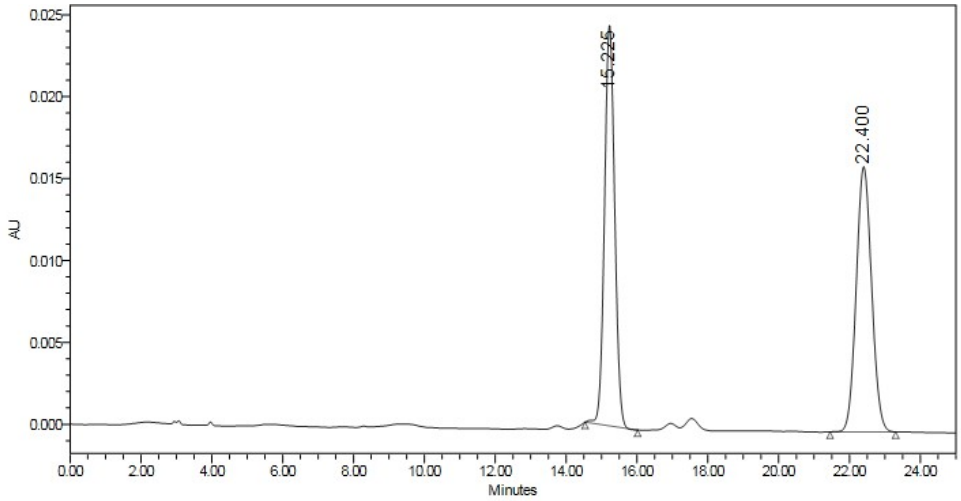
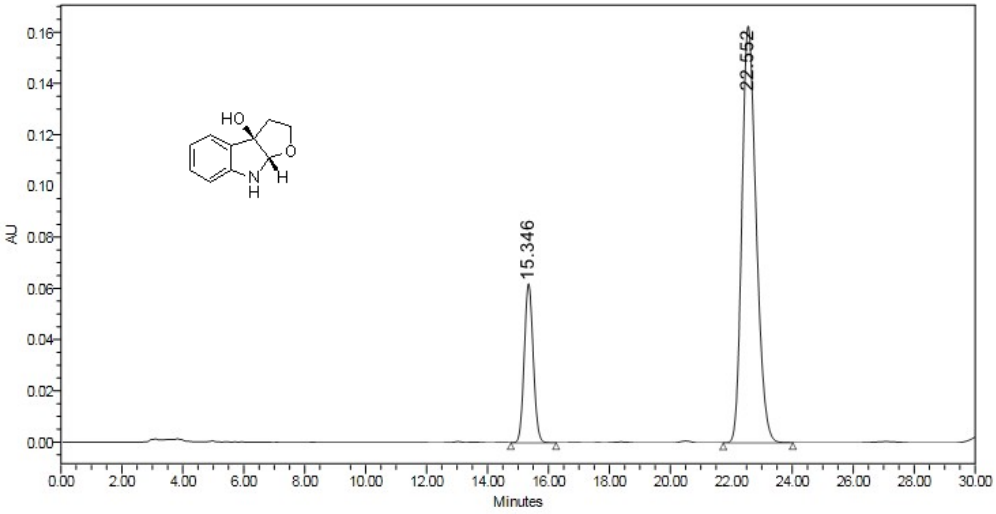
103.991
103.898
87.733
77.472
77.048
76.623
67.085
60.709
55.917
49.924
41.374
HO
H3C
O
CH3
N
H
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4. Copies of HPLC analysis

2a

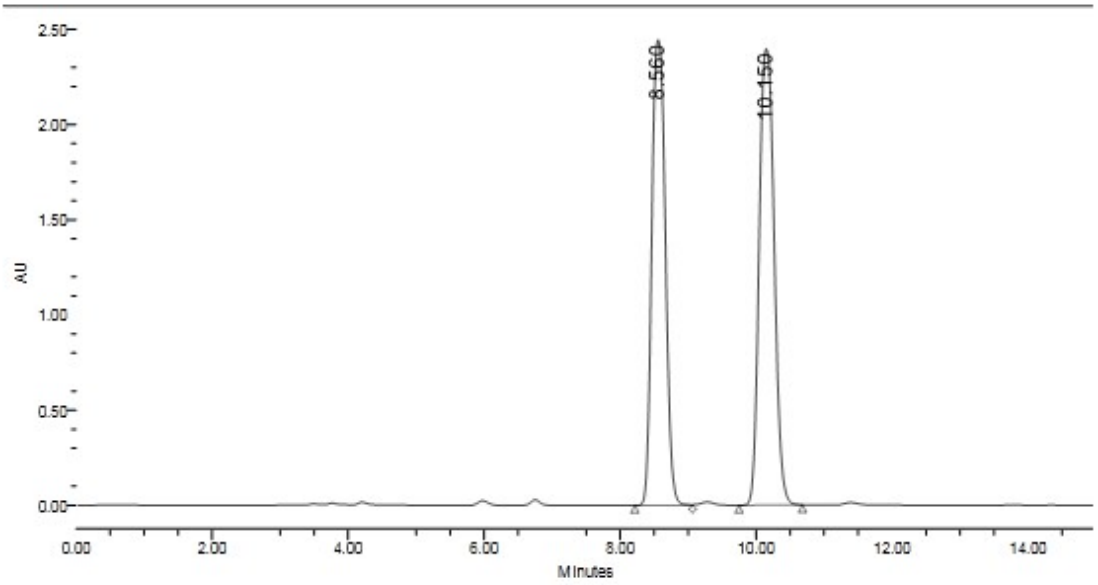


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.225	487616	49.96	24463	60.20
2	22.400	488301	50.04	16173	39.80

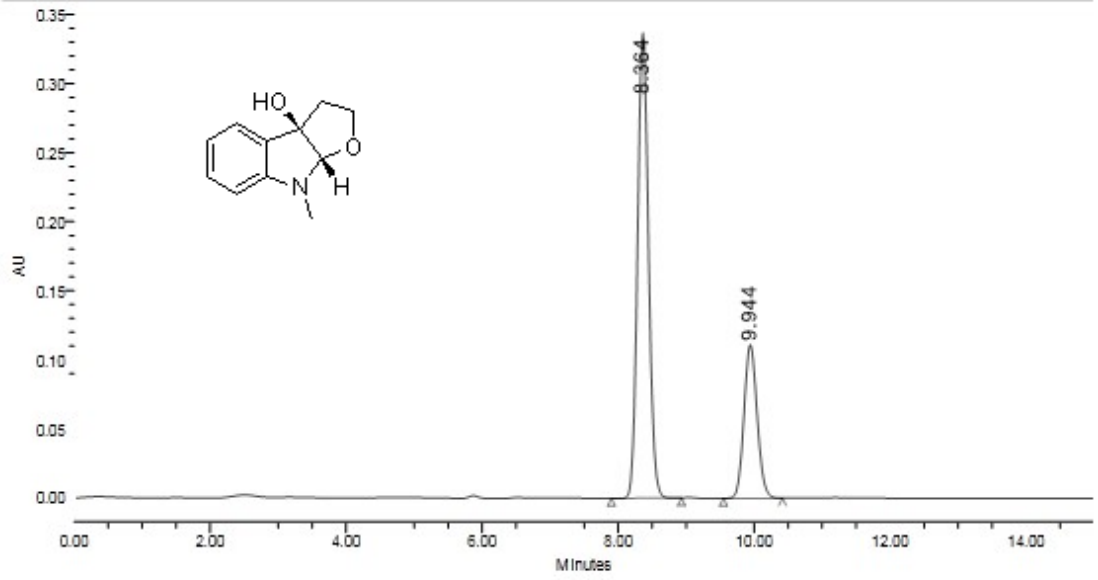


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.346	1269924	19.38	62122	27.62
2	22.552	5283147	80.62	162761	72.38

2b

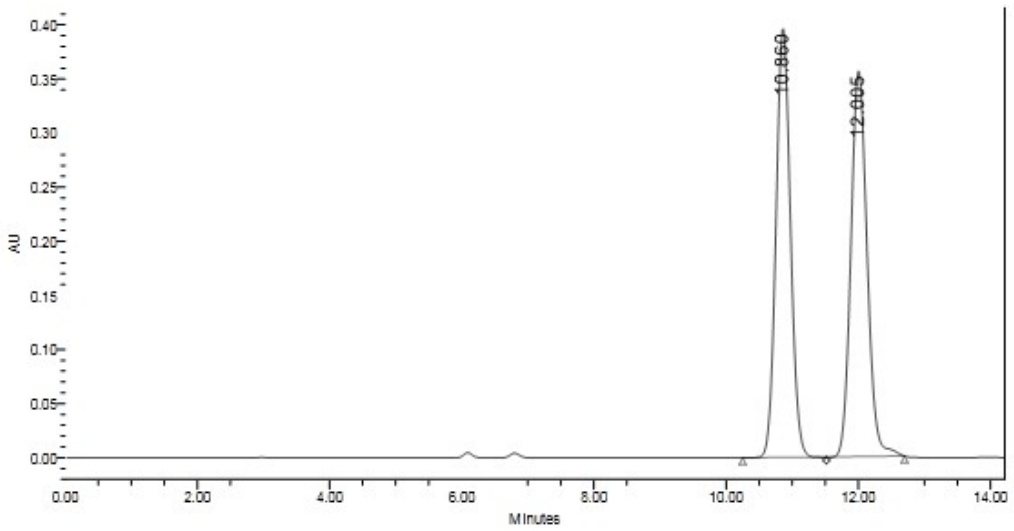


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.560	33726230	47.89	2448866	50.51
2	10.150	36703185	52.11	2399186	49.49

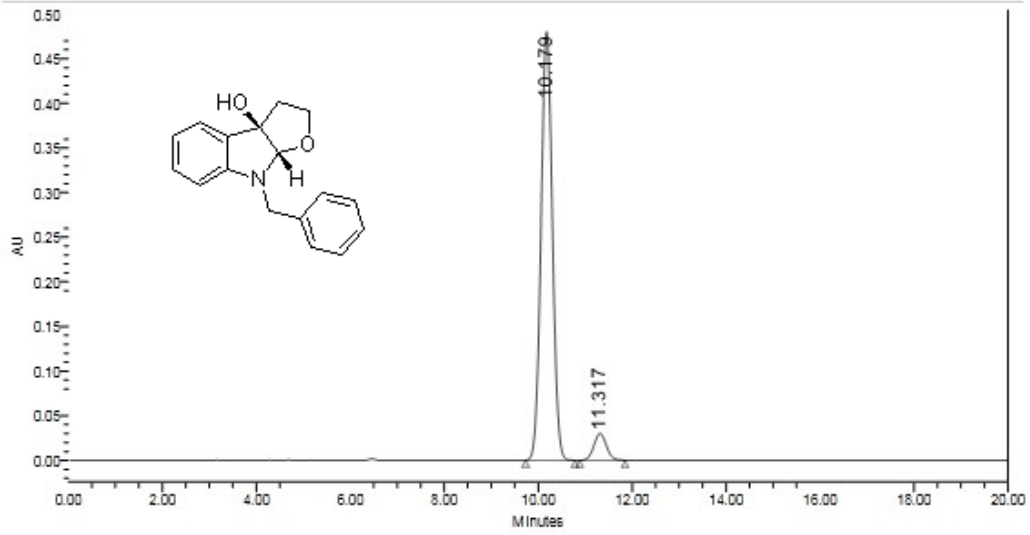


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.364	3763324	71.63	337056	75.15
2	9.944	1490485	28.37	111444	24.85

2c

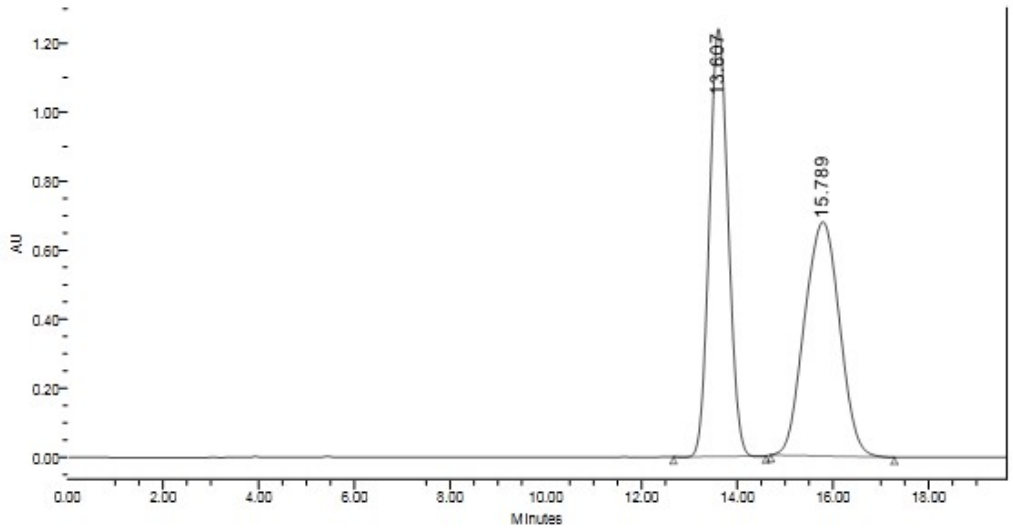


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.860	6018530	49.82	396643	52.67
2	12.005	6062109	50.18	356472	47.33

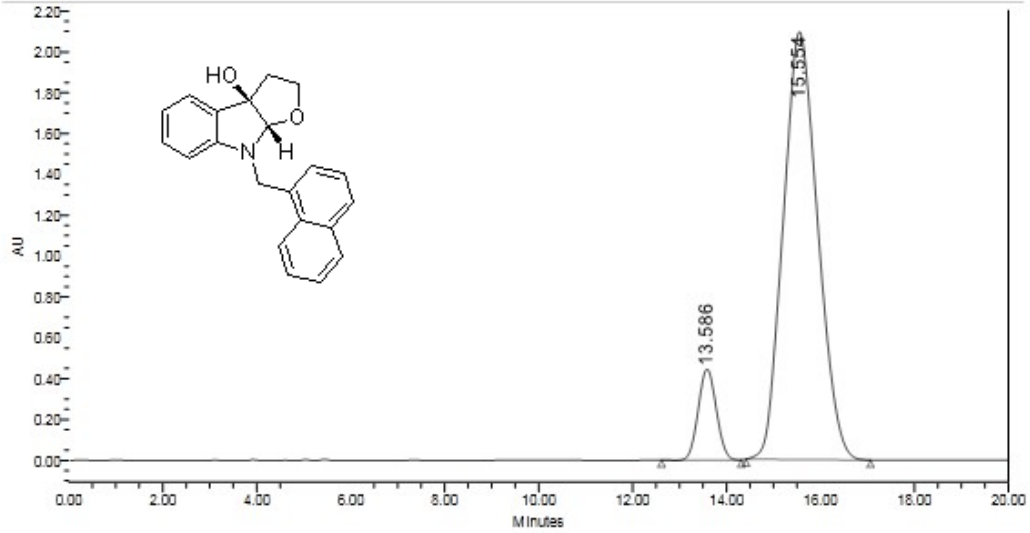


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.179	8045499	93.56	480468	94.11
2	11.317	554021	6.44	30067	5.89

2d

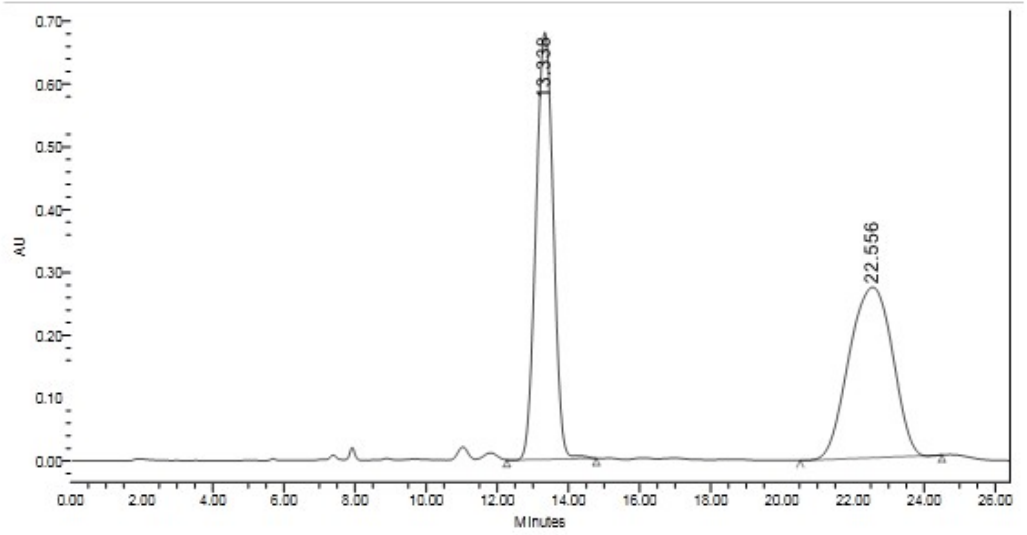


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.607	33949734	49.53	1239097	64.62
2	15.789	34590867	50.47	678456	35.38

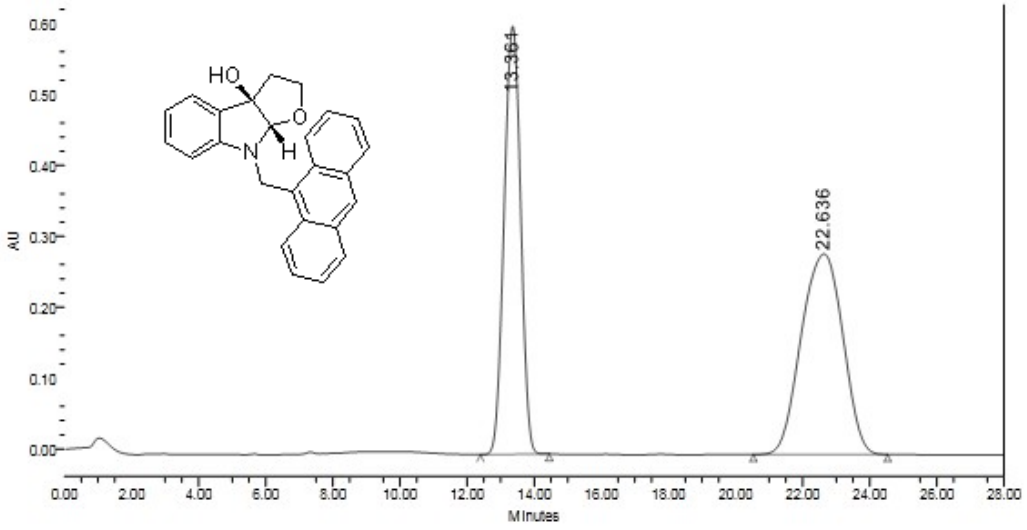


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.586	11898755	10.03	444333	17.50
2	15.554	106717195	89.97	2094441	82.50

2e

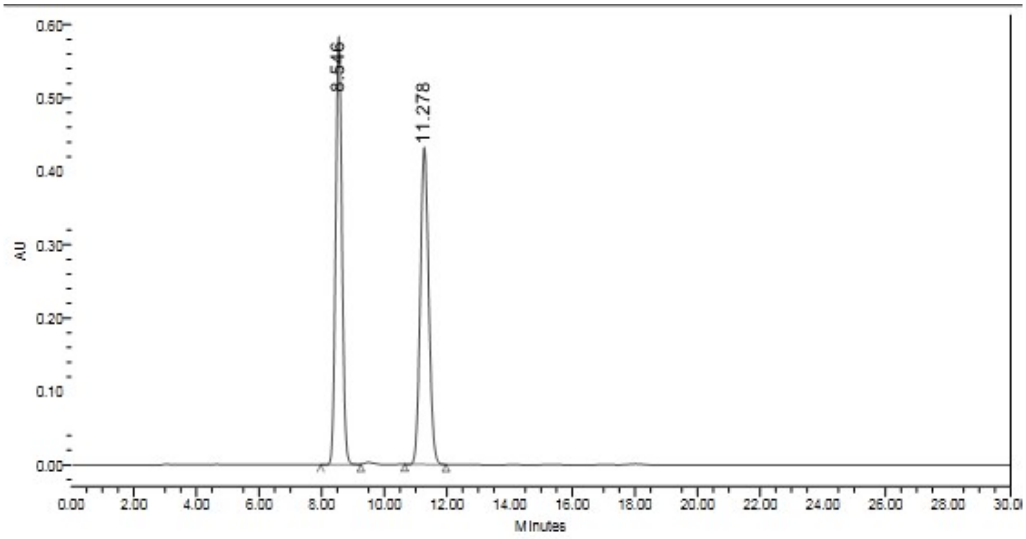


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.338	23098132	49.94	680330	71.48
2	22.556	23156095	50.06	271491	28.52

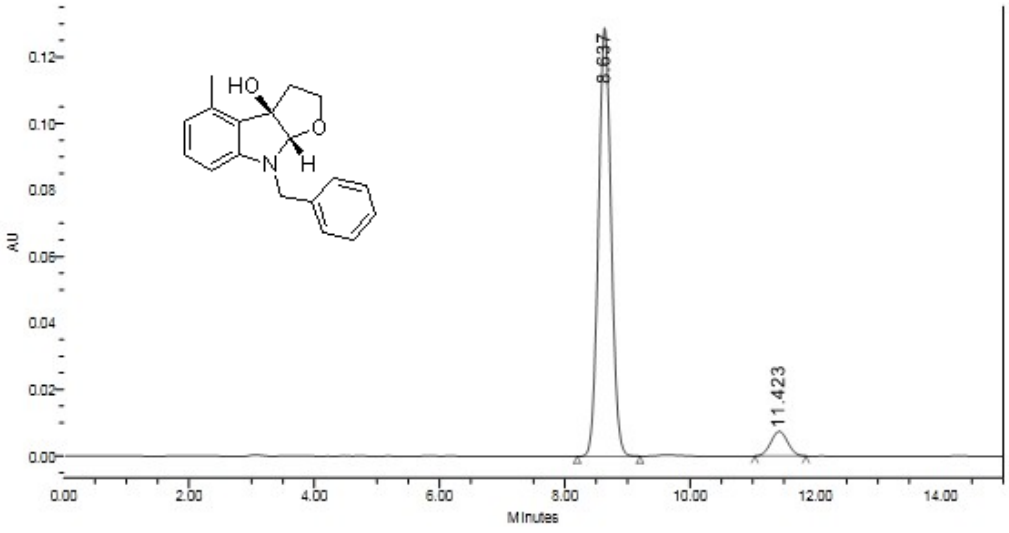


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.361	20637026	45.84	603422	68.09
2	22.636	24378581	54.16	282814	31.91

2g

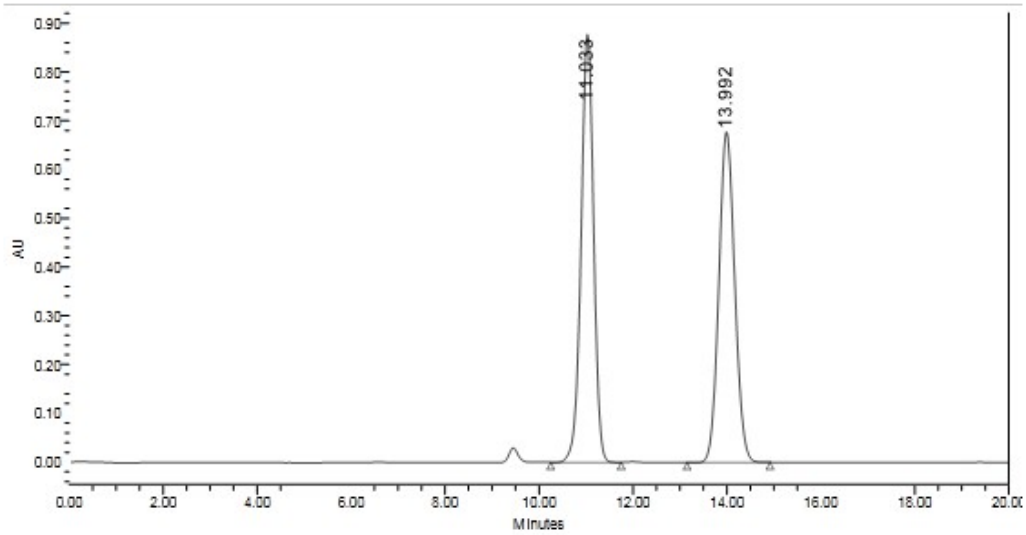


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.546	8168284	50.04	583910	57.44
2	11.278	8153992	49.96	432628	42.56

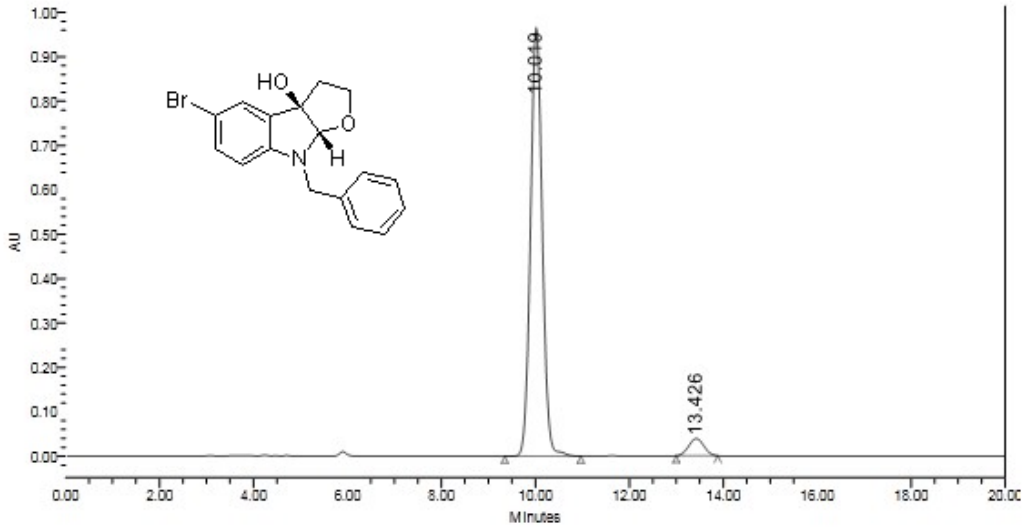


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.637	1817465	92.83	128955	94.54
2	11.423	140421	7.17	7448	5.46

2h

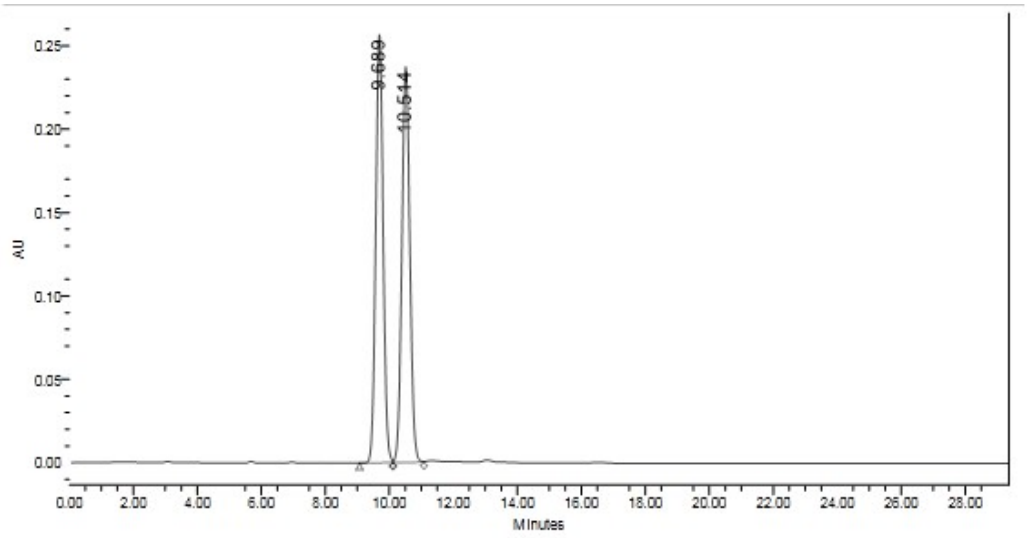


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.033	16266792	50.54	877634	56.41
2	13.992	15917941	49.46	678273	43.59

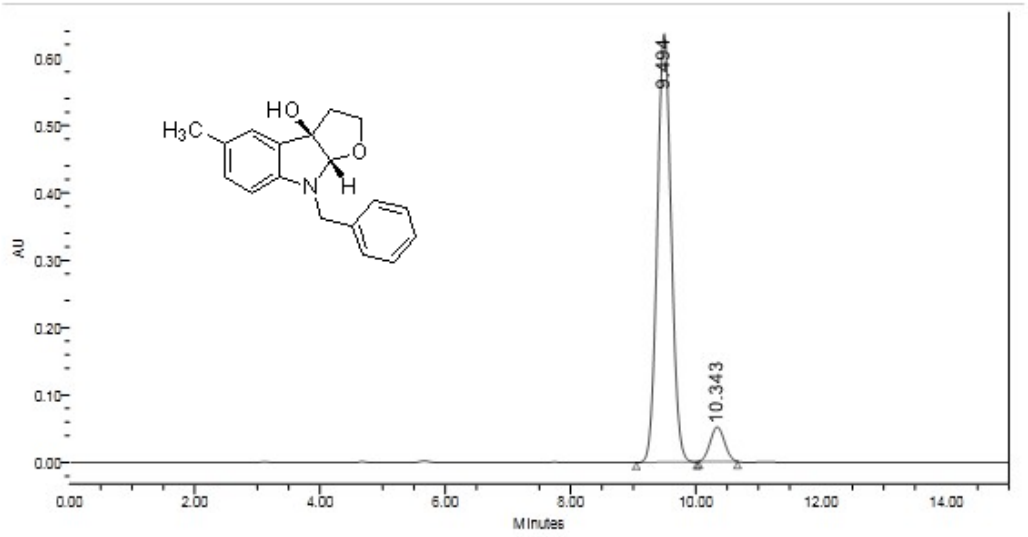


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.019	16762312	95.05	965974	96.15
2	13.426	873140	4.95	38638	3.85

2i

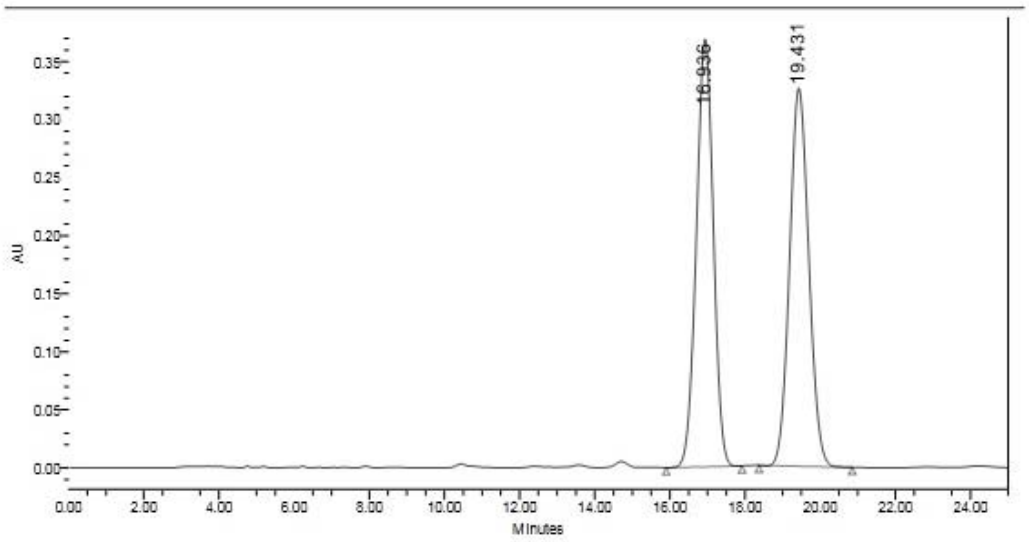


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.689	4115531	50.06	257006	52.00
2	10.514	4105899	49.94	237283	48.00

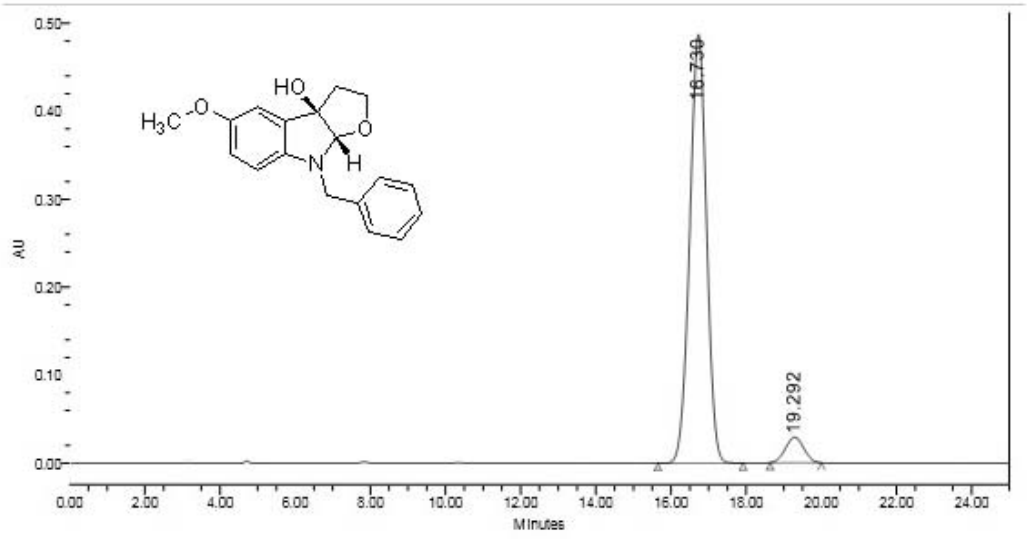


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.494	9821140	92.34	636543	92.56
2	10.343	814358	7.66	51162	7.44

2j

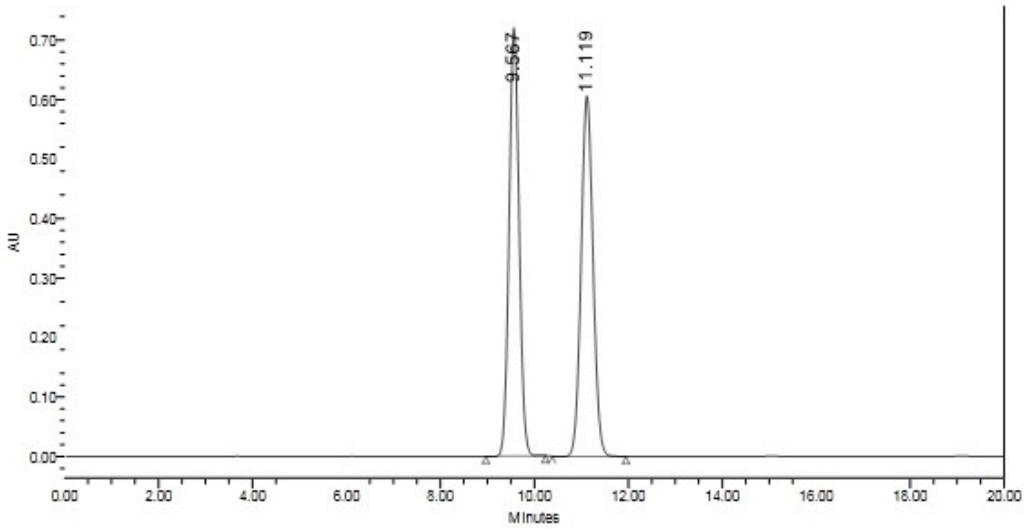


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	16.936	11560079	50.03	368472	53.08
2	19.431	11544966	49.97	325752	46.92

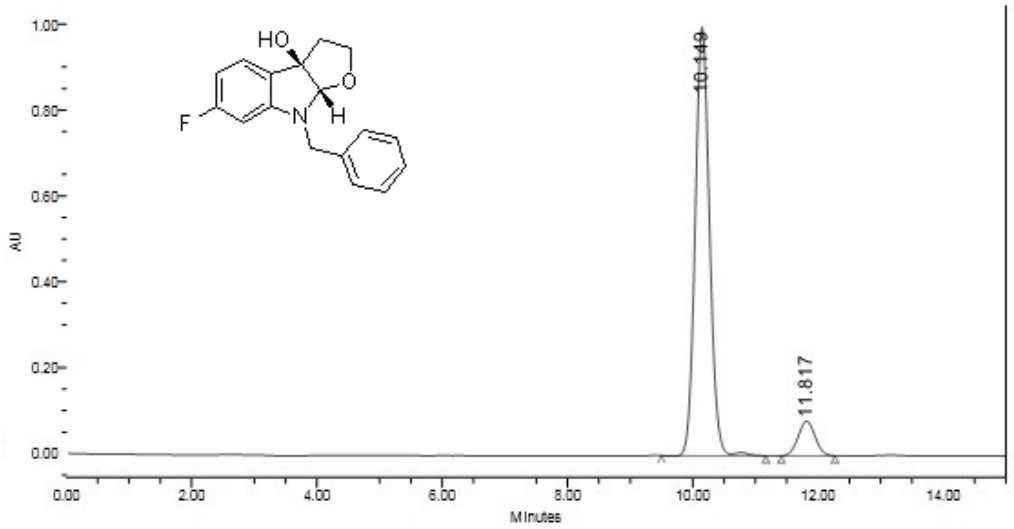


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	16.730	15130959	93.87	487489	94.40
2	19.292	988745	6.13	28918	5.60

2k

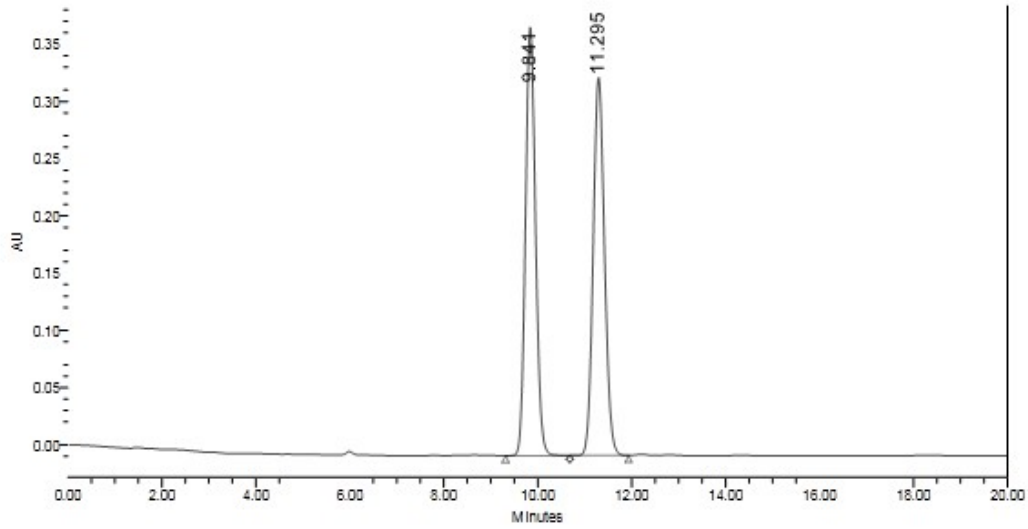


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.567	10664057	49.92	720264	54.29
2	11.119	10696394	50.08	606420	45.71

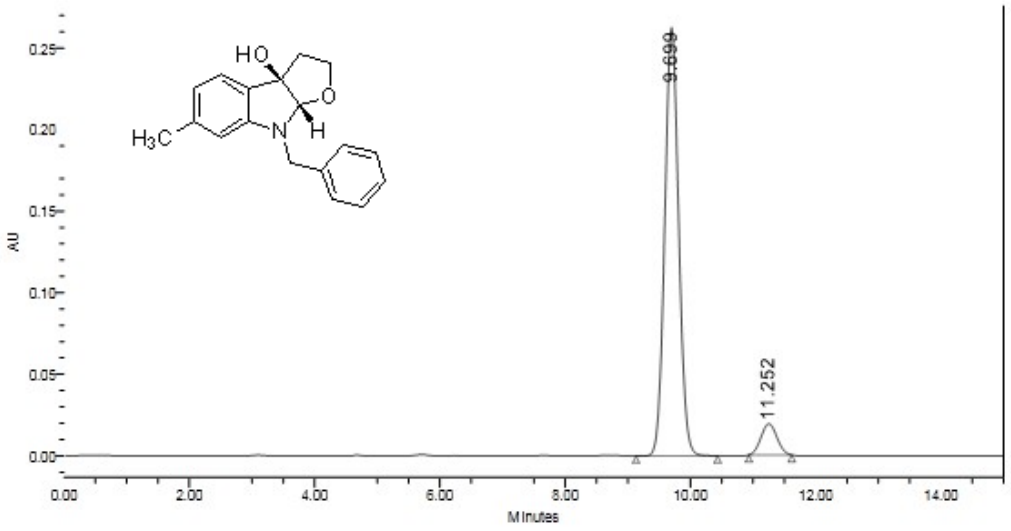


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.149	15859655	91.31	998267	92.53
2	11.817	1510290	8.69	80604	7.47

2l

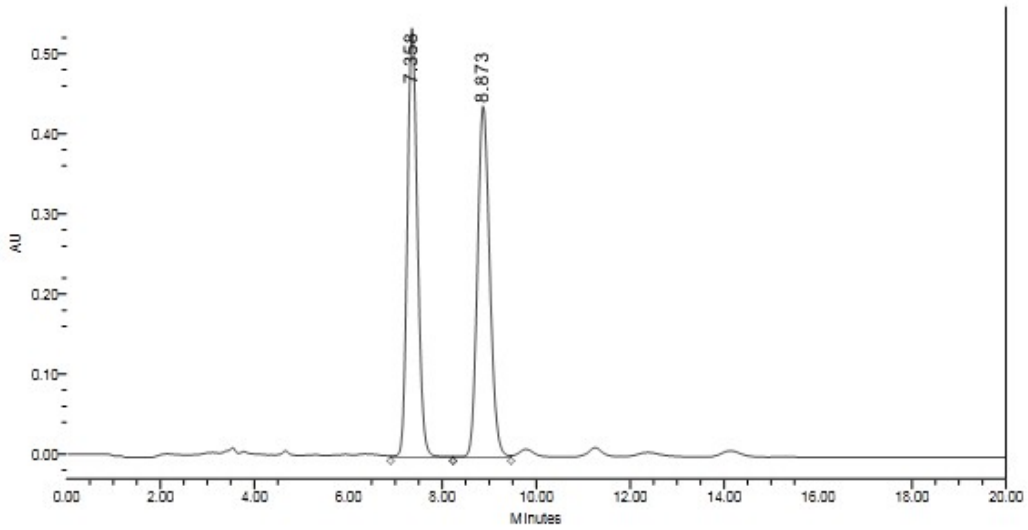


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.841	5550888	50.07	375207	53.16
2	11.295	5535274	49.93	330549	46.84

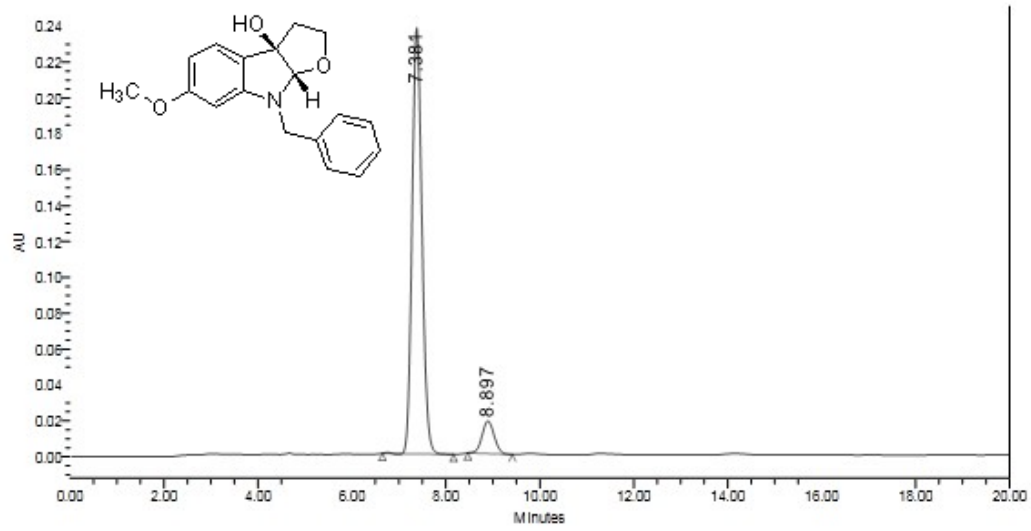


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.699	4053387	92.26	262765	93.19
2	11.252	339903	7.74	19200	6.81

2m

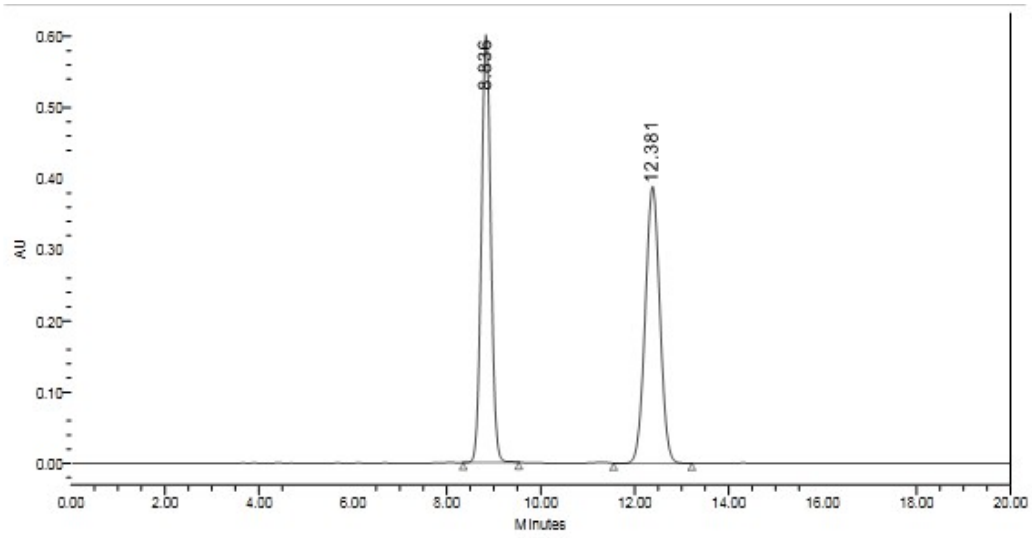


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.358	8041079	50.18	537161	55.03
2	8.873	7984177	49.82	438970	44.97

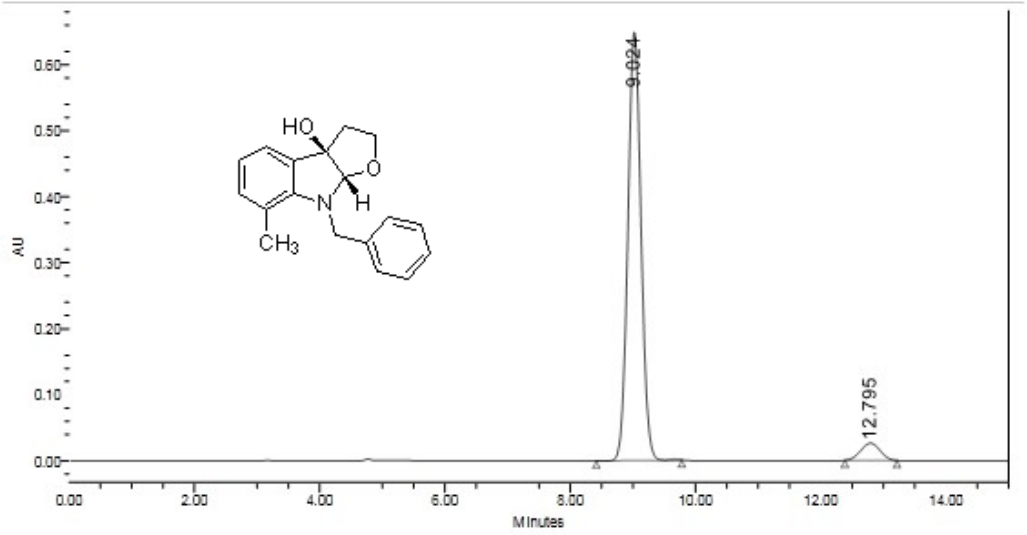


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	7.381	3460406	91.35	237693	92.88
2	8.897	327565	8.65	18226	7.12

2n

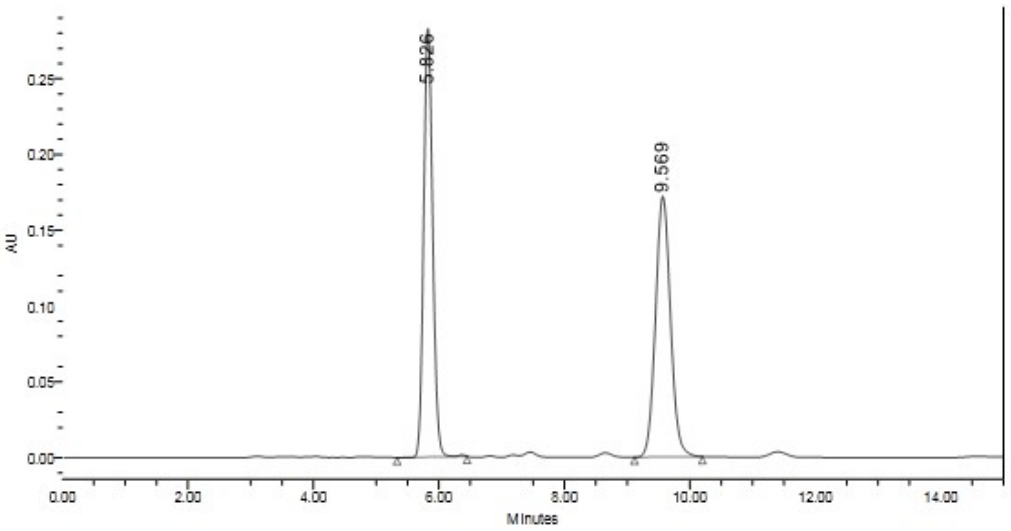


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	8.836	8423061	50.10	601357	60.72
2	12.381	8388018	49.90	389012	39.28

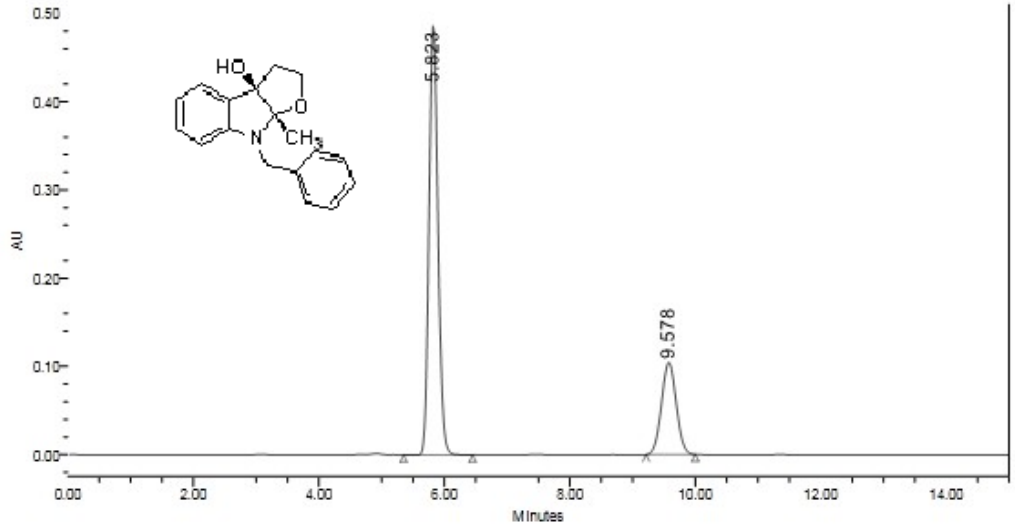


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.024	9434176	94.34	650122	96.14
2	12.795	565940	5.66	26083	3.86

2o

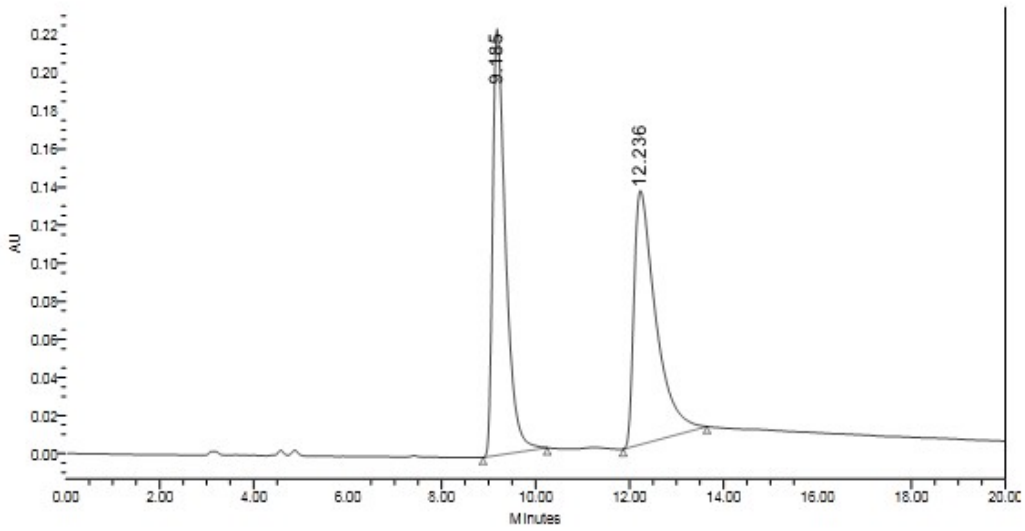


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.826	2822808	49.73	283695	62.24
2	9.569	2853921	50.27	172130	37.76

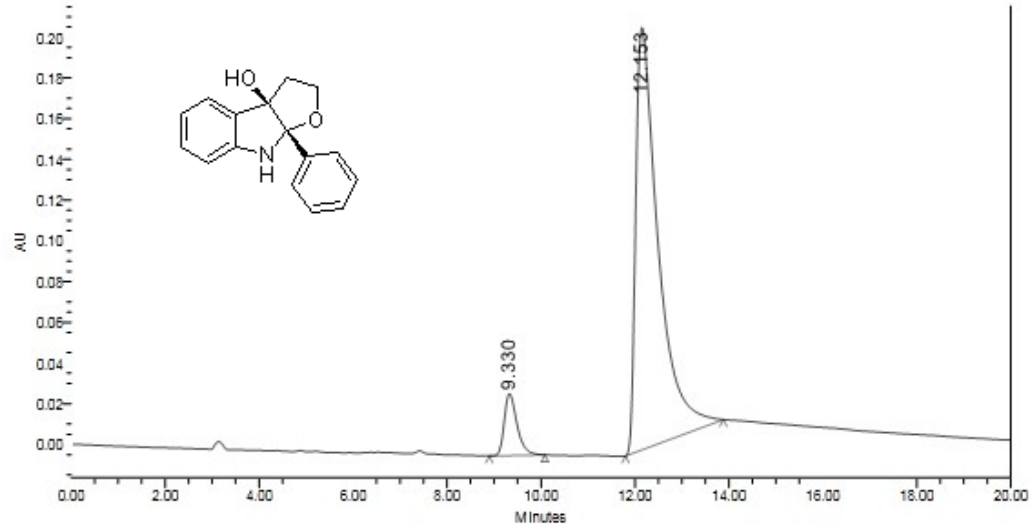


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	5.823	4828704	73.91	488154	82.36
2	9.578	1704608	26.09	104575	17.64

2p

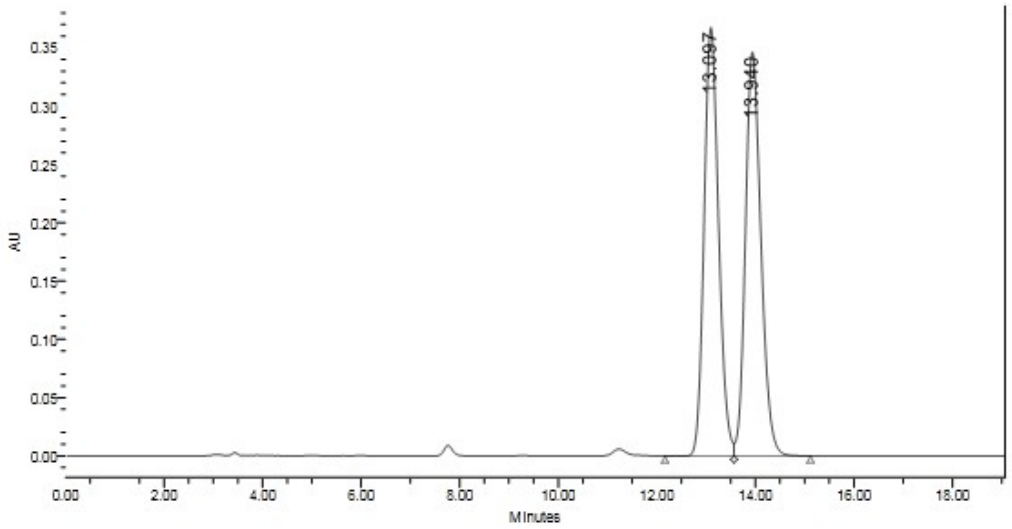


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.185	4285893	49.86	224115	62.68
2	12.236	4309115	50.14	133439	37.32

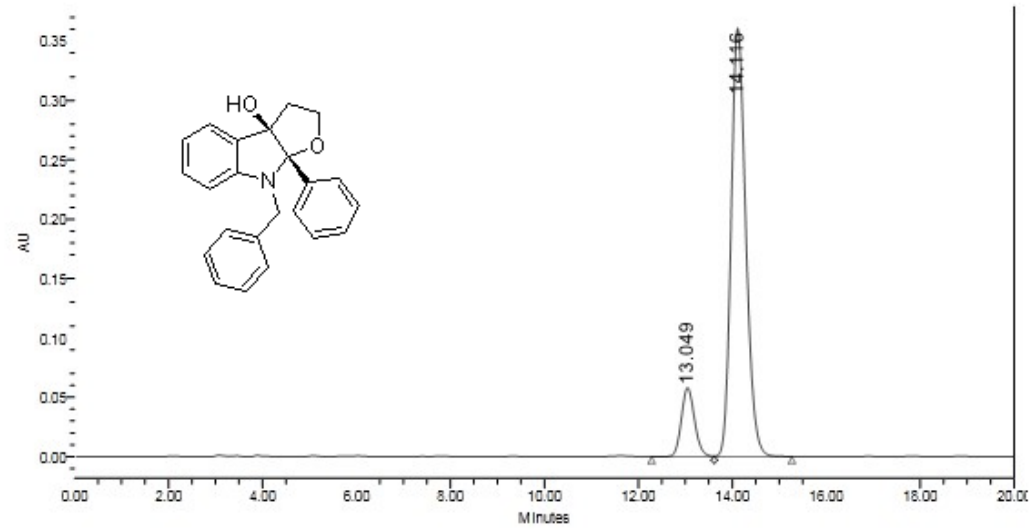


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.330	573966	7.65	30413	12.79
2	12.153	6927982	92.35	207446	87.21

2q

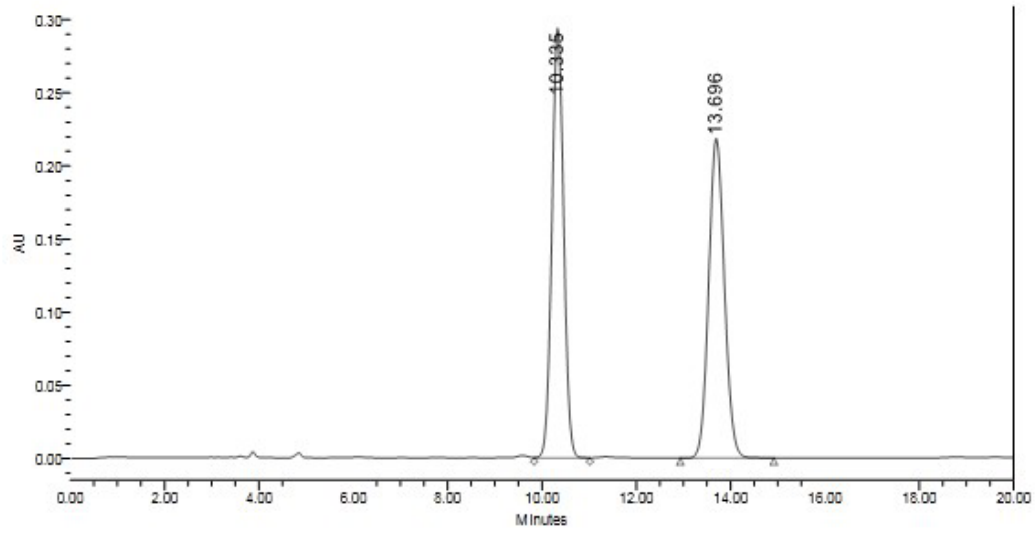


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.097	7533678	49.86	367863	51.47
2	13.940	7574838	50.14	346809	48.53

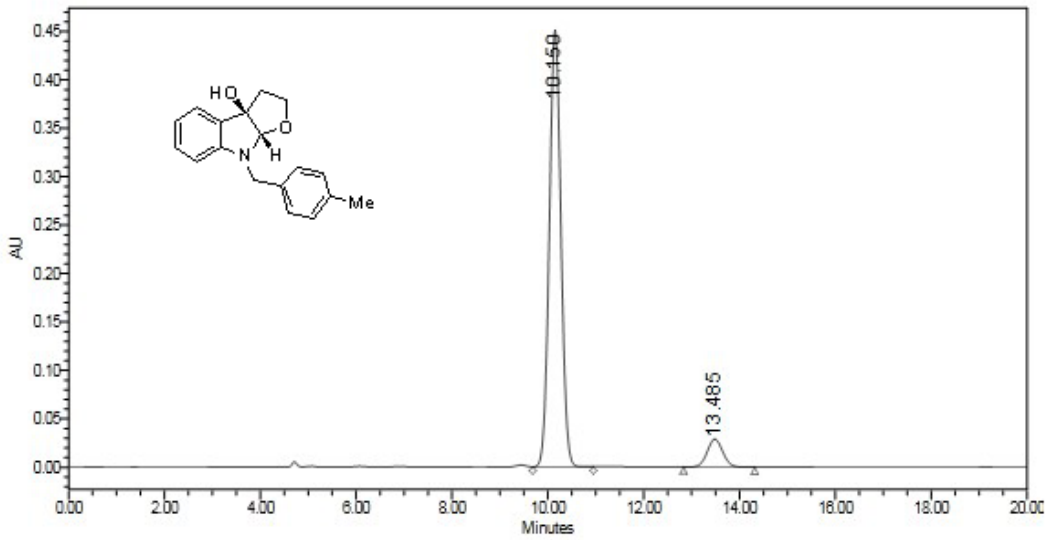


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	13.049	1130060	12.60	58088	13.86
2	14.116	7835950	87.40	360986	86.14

2r

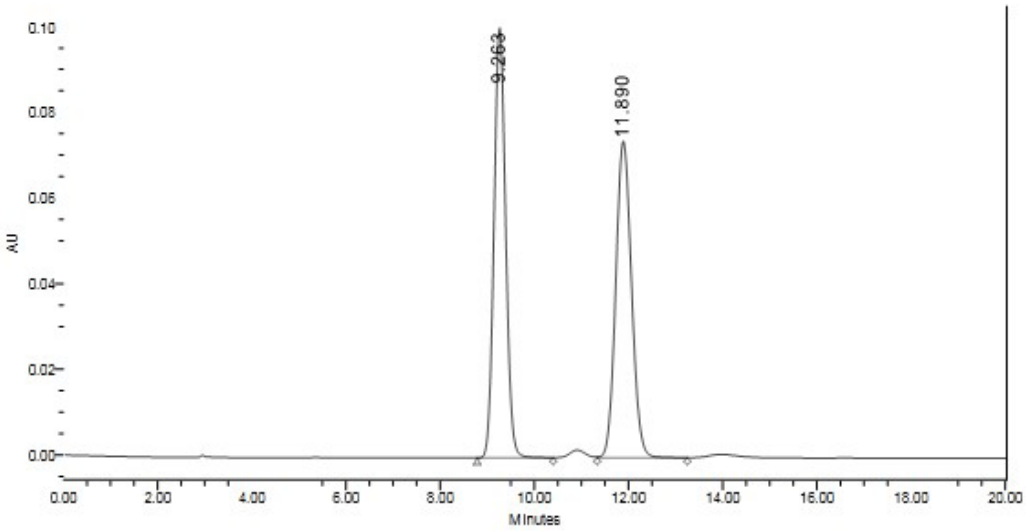


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.335	5082867	50.12	293980	57.35
2	13.696	5057628	49.88	218586	42.65

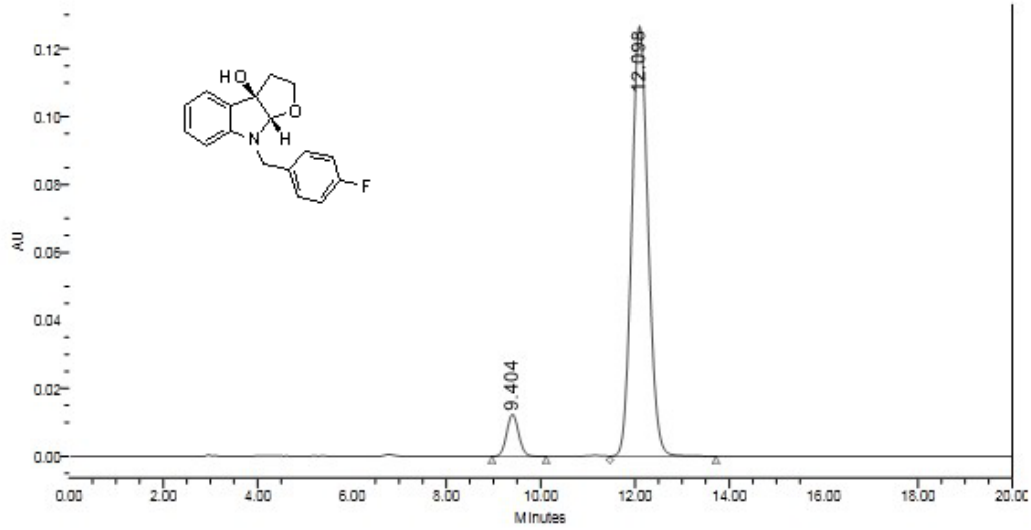


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.150	7590609	92.10	451453	93.98
2	13.485	651019	7.90	28912	6.02

2s

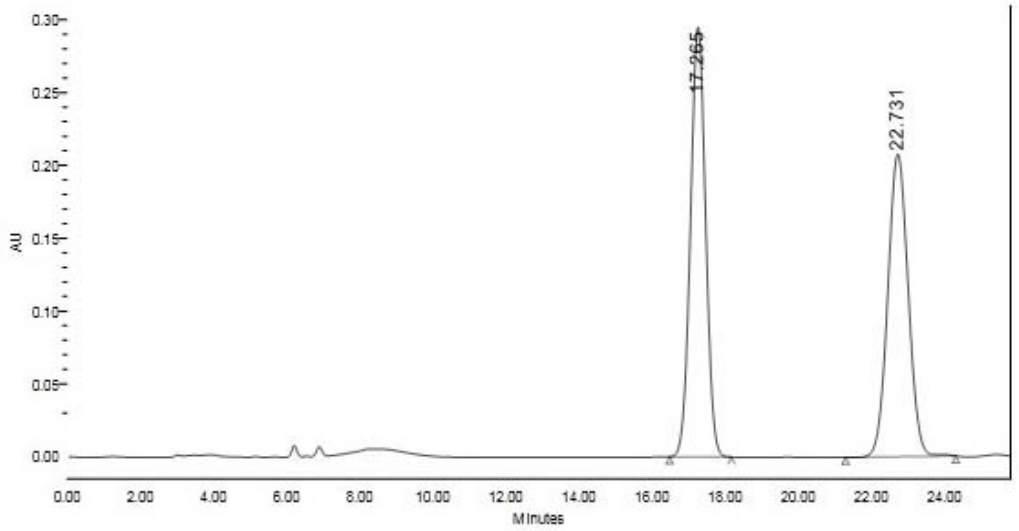


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.263	1717039	49.96	100426	57.59
2	11.890	1719965	50.04	73959	42.41

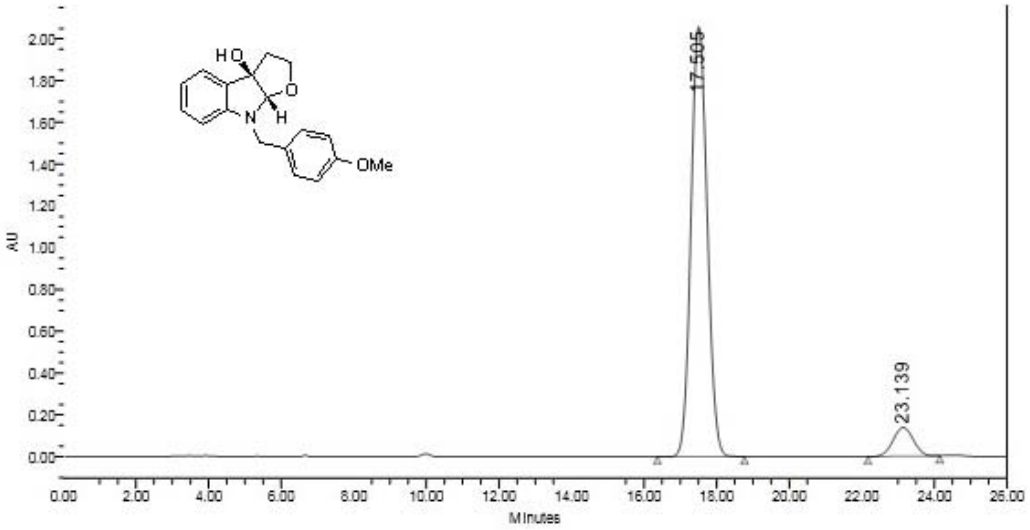


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.404	218339	6.70	12353	8.88
2	12.098	3040808	93.30	126709	91.12

2t

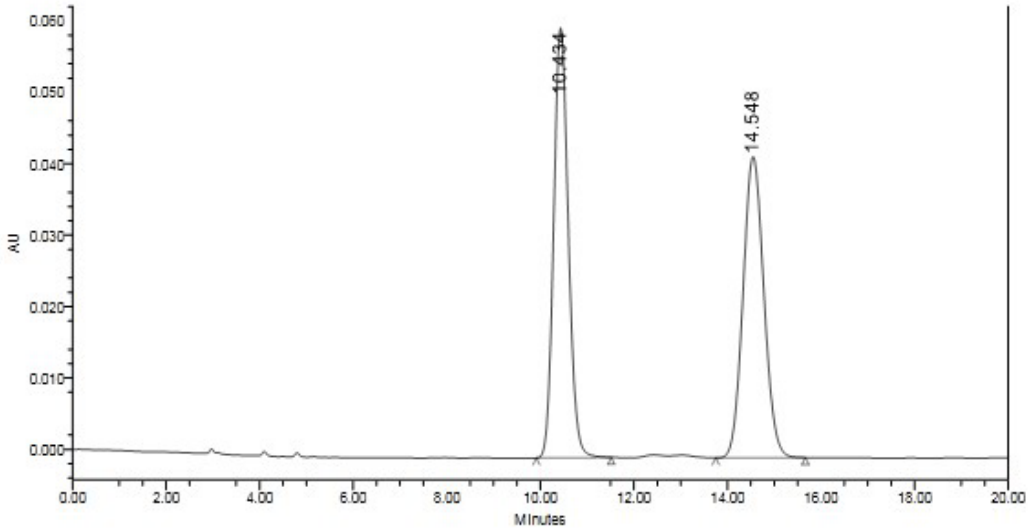


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	17.265	8494359	51.41	295040	58.69
2	22.731	8026928	48.59	207699	41.31

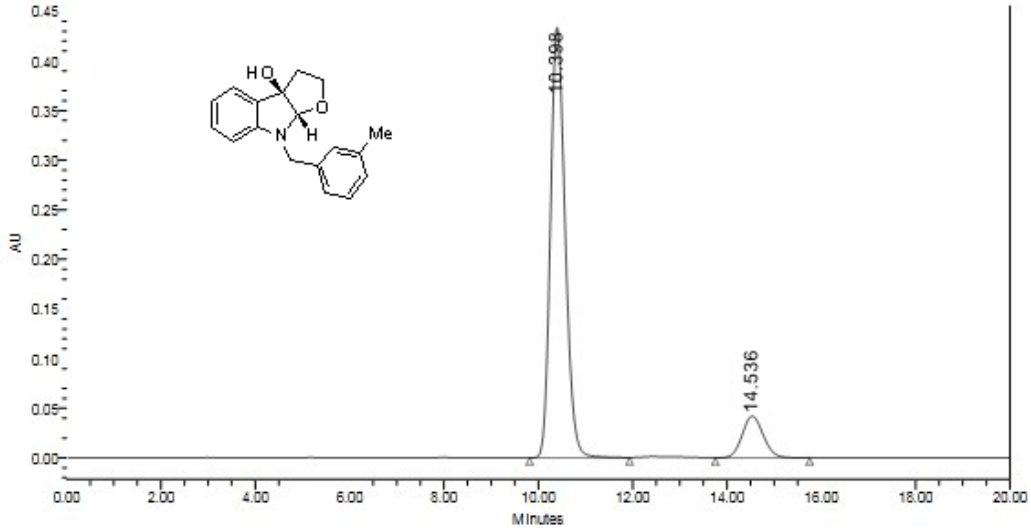


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	17.505	63800622	92.25	2059288	93.73
2	23.139	5359680	7.75	137837	6.27

2u

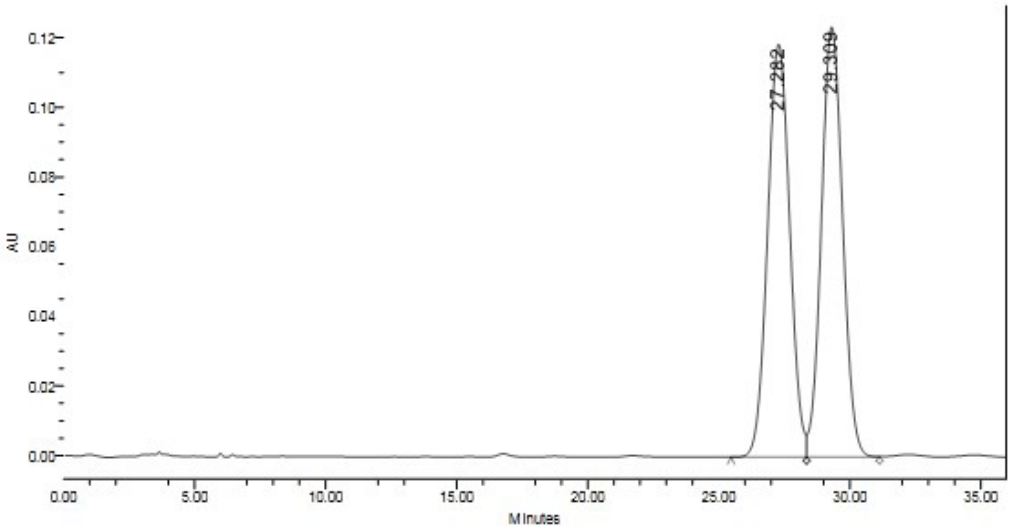


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.434	1305188	50.03	60218	58.81
2	14.548	1303640	49.97	42170	41.19

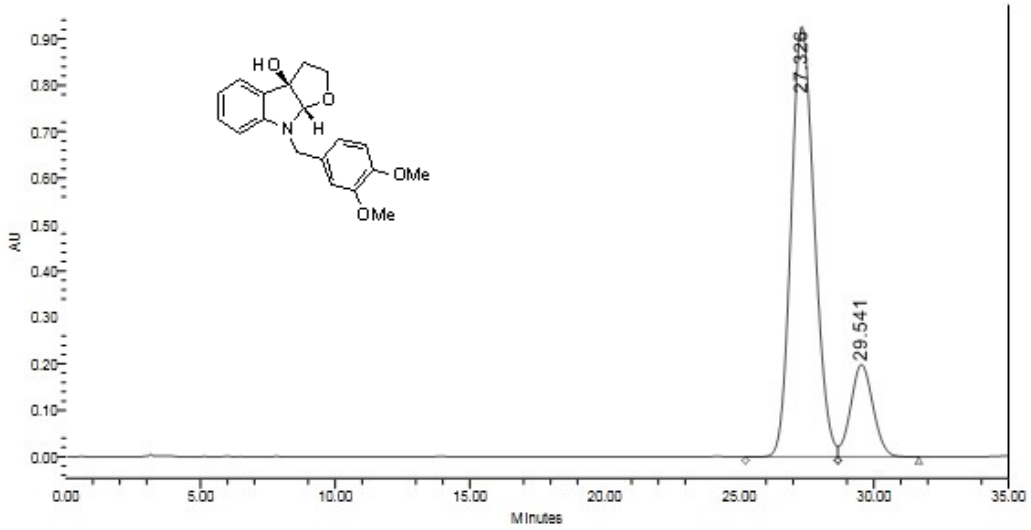


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	10.398	9371631	87.83	433710	91.19
2	14.536	1298693	12.17	41906	8.81

2v

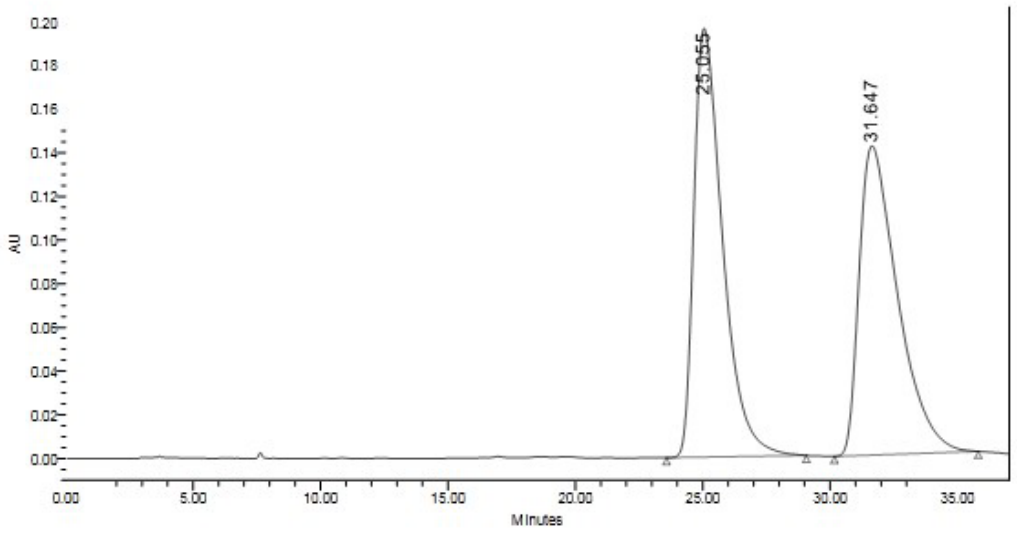


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	27.282	6954287	49.98	118550	48.99
2	29.309	6959932	50.02	123460	51.01

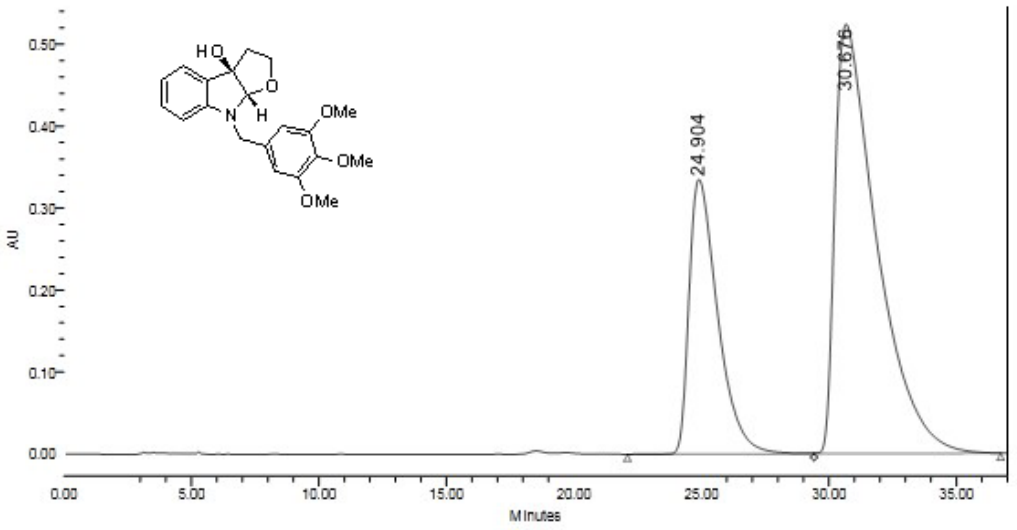


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	27.326	55414630	82.89	926550	82.34
2	29.541	11439700	17.11	198679	17.66

2w

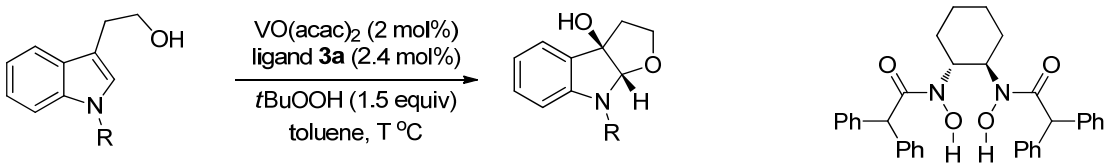


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	25.055	15376395	50.88	196277	58.10
2	31.647	14846914	49.12	141538	41.90



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	24.904	26204713	30.53	335197	39.00
2	30.676	59628935	69.47	524235	61.00

5. Table S1. Optimization of the reaction conditions – more protecting groups

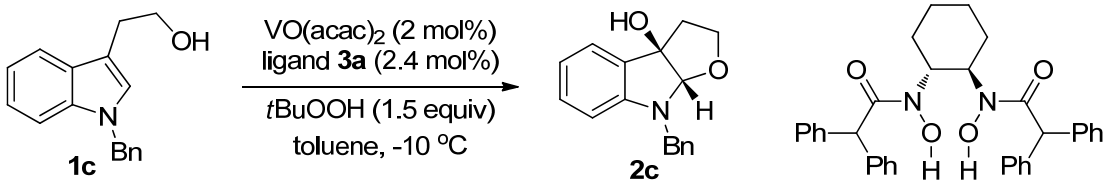


1 **2** **3a**

entry	**1**, R	T	time (h)	yield of **2** (%)[b]	ee (%)[c]
1	**1c**, Bn	0	12	**2c** 62	82
	1c, Bn	-10	24	**2c** 70	87
2	**1d**, 1-naphthyl	0	18	**2d** 79	80
	1d, 1-naphthyl	-10	24	**2d** 62	79
3	**1r**, 4-methylbenzyl	0	24	**2r** 70	84
	1r, 4-methylbenzyl	-10	24	**2r** 69	86
4	**1s**, 4-fluorobenzyl	0	24	**2s** 43	87
	1s, 4-fluorobenzyl	-10	24	**2s** 62	86
5	**1t**, 4-methoxybenzyl	0	24	**2t** 64	84
6	**1u**, 3-methylbenzyl	0	24	**2u** 70	76
7	**1v**, 3,4-dimethoxybenzyl	0	24	**2v** 56	66
8	**1w**, 3,4,5-trimethoxybenzyl	0	24	**2w** 56	39

[a] Reaction conditions: 0.5 mmol **1**, 2.0 mol% $VO(acac)_2$, 2.4 mol% ligand **3a** and 0.75 mmol *t*BuOOH (70% wt aqueous solution) in toluene (1.0 mL) at 0 ℃ or -10 ℃ . [b] Isolated yield. [c] Determined by HPLC analysis (Chiralpak AD-H or Chiralcel OD-H).

6. The gram-scale reaction



1c 1.26 g, 5 mmol

2c 66% yield, 87% ee

3a