Supporting Information for

Ru-Catalyzed Intermolecular Dearomatization Reaction of Indoles with Allylic Alcohols

Xiao Zhang, Ze-Peng Yang, Chuan Liu, and Shu-Li You*

State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
345 Lingling Lu, Shanghai 200032, China

E-mail: slyou@sioc.ac.cn

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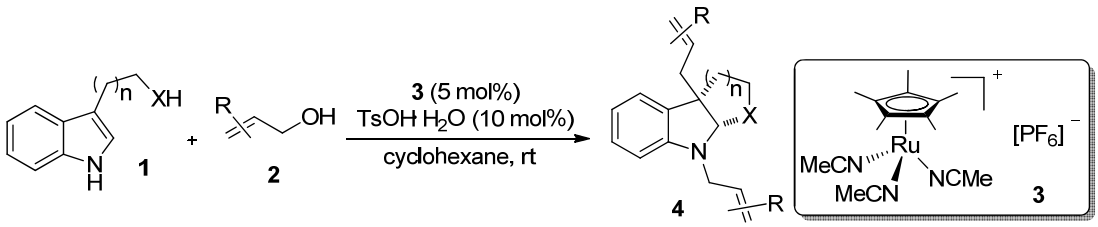
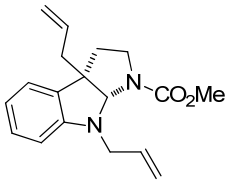
General methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were freshly distilled according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300, 400 MHz and 75, 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, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

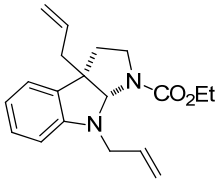
General procedure for ruthenium-catalyzed intermolecular dearomatization reaction of indoles with allylic alcohols:



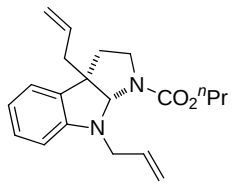
A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added **3** (5.04 mg, 0.010 mmol, 5 mol%), TsOH·H_2O (3.8 mg, 0.020 mmol, 10 mol%), indole derivatives **1** (0.20 mmol, 100 mol%), allylic alcohol (0.80 mmol, 400 mol%), cyclohexane (2 mL). The reaction mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), the mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to afford the desired product **4**. The characterization data of the products are summarized below.



4aa[1]. Colorless oil, 97% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 2.04-2.08 (m, 2H), 2.43-2.48 (m, 1H), 2.52-2.57 (m, 1H), 2.96-3.03 (m, 1H), 3.67 (s, 3H), 3.74-3.79 (m, 1H), 4.00-4.03 (m, 2H), 5.02-5.20 (m, 3H), 5.23-5.24 (m, 1H), 5.40 (s, 1H), 5.63-5.73 (m, 1H), 5.81-5.91 (m, 1H), 6.41 (d, J = 7.6 Hz, 1H), 6.62-6.65 (m, 1H), 7.01-7.07 (m, 2H).

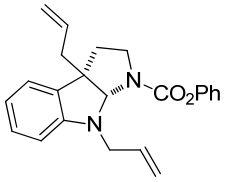


4ba. Colorless oil, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24-1.32 (m, 3H), 1.98-2.10 (m, 2H), 2.39-2.45 (m, 1H), 2.51-2.56 (m, 1H), 3.04-3.11 (m, 1H), 3.75-4.19 (m, 5H), 5.04-5.11 (m, 3H), 5.15-5.22 (m, 1H), 5.33 and 5.44 (br, 1H), 5.59-5.70 (m, 1H), 5.79-5.87 (m, 1H), 6.36 (d, J = 8.0 Hz, 1H), 6.64-6.67 (m, 1H), 7.01 (d, J = 7.2 Hz, 1H), 7.05-7.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 37.1, 37.5, 43.2, 43.4, 45.2, 48.6, 55.7, 56.9, 61.1, 61.2, 83.9, 84.3, 106.0, 115.7, 117.0, 117.3, 118.3, 122.7, 128.3, 132.1, 133.8, 134.2, 134.3, 150.0, 154.6, 155.5. IR (thin film): ν_{max} (cm^{-1}) = 3076, 3055, 2978, 2877, 1697, 1641, 1605, 1489, 1463, 1412, 1379, 1328, 1308, 1264, 1246, 1207, 1159, 1105, 1086, 1032, 993, 914, 768, 739, 668; HRMS (ESI) calcd for $C_{19}H_{25}N_2O_2$ $[M+H]^+$: 313.1916. Found: 313.1912.

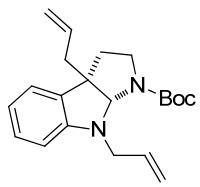


4ca. Colorless oil, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92-0.99 (m, 3H), 1.61-1.73 (m, 2H), 1.99-2.06 (m, 2H), 2.39-2.45 (m, 1H), 2.51-2.56 (m, 1H), 3.05-3.12 (m, 1H), 3.75-4.08 (m, 5H), 5.04-5.10 (m, 3H), 5.14-5.23 (m, 1H), 5.35 and 5.45 (br, 1H), 5.61-5.71 (m, 1H), 5.78-5.87 (m, 1H), 6.37 (d, J = 7.2 Hz, 1H),

6.63-6.67 (m, 1H), 7.01 (d, J = 7.2 Hz, 1H), 7.06 (dt, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.3, 10.4, 22.3, 37.2, 37.5, 43.2, 43.3, 45.1, 48.3, 48.6, 55.7, 56.8, 66.7, 67.0, 83.9, 84.3, 105.9, 106.0, 115.6, 117.0, 117.2, 118.3, 122.7, 128.2, 132.1, 133.8, 134.1, 134.3, 150.0, 154.7, 155.6. IR (thin film): ν_{max} (cm^{-1}) = 3076, 3055, 2965, 2879, 1697, 1641, 1605, 1490, 1461, 1413, 1365, 1329, 1308, 1262, 1207, 1159, 1086, 1031, 991, 943, 914, 885, 767, 739, 668, 617; HRMS (ESI) calcd for $C_{20}H_{27}N_2O_2$ $[M+H]^+$: 327.2073. Found: 327.2053.

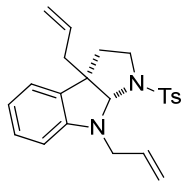


4da. Colorless oil, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10-2.18 (m, 2H), 2.44-2.62 (m, 2H), 3.13-3.31 (m, 1H), 3.93-4.12 (m, 3H), 5.06-5.24 (m, 4H), 5.49 and 5.54 (br, 1H), 5.63-5.73 (m, 1H), 5.79-5.89 (m, 1H), 6.41 (d, J = 7.6 Hz, 1H), 6.67-6.72 (m, 1H), 7.04 (d, J = 7.2 Hz, 1H), 7.08-7.22 (m, 4H), 7.33-7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.0, 37.4, 43.2, 43.4, 45.5, 45.7, 48.66, 48.73, 55.9, 57.0, 84.3, 84.5, 106.2, 115.7, 116.1, 117.3, 117.6, 118.6, 121.6, 121.7, 122.8, 125.26, 125.31, 128.4, 129.2, 129.3, 131.9, 133.6, 133.7, 133.9, 134.2, 149.9, 151.0, 151.1, 152.5, 153.7. IR (thin film): ν_{max} (cm^{-1}) = 3074, 2977, 2882, 1717, 1640, 1604, 1489, 1462, 1434, 1386, 1332, 1310, 1264, 1245, 1198, 1156, 1068, 1027, 993, 913, 873, 847, 787, 739, 687, 626; HRMS (ESI) calcd for $C_{23}H_{25}N_2O_2$ $[M+H]^+$: 361.1916. Found: 361.1904.

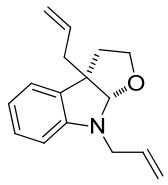


4ea. Colorless oil, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 and 1.50 (s, 9H), 1.97-2.07 (m, 2H), 2.40-2.45 (m, 1H), 2.51-2.56 (m, 1H), 3.02-3.04 (m, 1H), 3.68-4.07 (m, 3H), 5.06-5.10 (m, 3H), 5.18 (d, J = 17.2 Hz, 1H), 5.29 and 5.42 (br,

1H), 5.60-5.70 (m, 1H), 5.77-5.86 (m, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 6.64-6.65 (m, 1H), 6.99-7.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4, 37.2, 37.6, 43.3, 44.8, 45.4, 48.4, 48.6, 55.7, 56.8, 79.5, 80.1, 84.1, 84.4, 105.8, 115.4, 115.5, 116.8, 117.1, 118.2, 122.7, 128.2, 132.2, 134.0, 134.3, 134.5, 150.0, 150.1, 153.8, 154.6. IR (thin film): ν_{max} (cm^{-1}) = 2976, 2930, 2883, 1740, 1693, 1641, 1605, 1490, 1462, 1390, 1309, 1243, 1218, 1151, 1085, 1043, 1032, 992, 914, 888, 768, 739; HRMS (ESI) calcd for $C_{21}H_{29}N_2O_2$ $[M+H]^+$: 341.2229. Found: 341.2225.

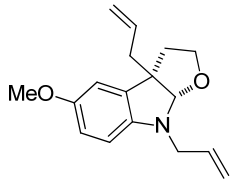


4fa. Colorless oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38-1.46 (m, 1H), 1.86-1.90 (m, 1H), 1.96-2.02 (m, 1H), 2.28-2.33 (m, 1H), 2.46 (s, 3H), 3.03-3.11 (m, 1H), 3.61-3.65 (m, 1H), 3.94-4.00 (m, 1H), 4.15-4.22 (m, 1H), 4.90-4.96 (m, 2H), 5.16 (d, *J* = 14.8 Hz, 1H), 5.23-5.28 (m, 2H), 5.34-5.45 (m, 1H), 5.82-5.91 (m, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 6.61-6.64 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 7.04-7.08 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 38.3, 43.0, 46.6, 47.9, 57.0, 86.6, 105.9, 116.2, 117.2, 118.3, 122.7, 127.2, 128.4, 129.8, 130.9, 133.7, 137.0, 143.6, 149.8. IR (thin film): ν_{max} (cm^{-1}) = 3073, 2916, 1639, 1606, 1489, 1465, 1445, 1415, 1398, 1337, 1302, 1252, 1176, 1154, 1124, 1103, 1078, 1055, 991, 952, 915, 876, 841, 807, 734, 708, 662; HRMS (ESI) calcd for $C_{23}H_{27}N_2O_2S$ $[M+H]^+$: 395.1793. Found: 395.1790.

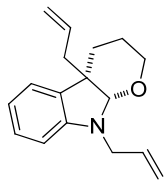


4ga. Colorless oil, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06-2.16 (m, 2H), 2.44-2.49 (m, 1H), 2.59-2.64 (m, 1H), 3.44-3.51 (m, 1H), 3.90-3.96 (m, 3H), 5.02-5.27 (m, 5H), 5.62-5.72 (m, 1H), 5.81-5.90 (m, 1H), 6.36 (d, *J* = 7.6 Hz, 1H),

6.64-6.68 (m, 1H), 7.04-7.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 42.6, 47.1, 55.9, 66.7, 101.2, 105.2, 116.4, 117.1, 118.0, 123.2, 128.0, 132.4, 134.1, 134.3, 150.2. IR (thin film): ν_{max} (cm^{-1}) = 3076, 2964, 2942, 2866, 2389, 1641, 1606, 1491, 1463, 1440, 1400, 1358, 1333, 1310, 1260, 1164, 1014, 949, 916, 871, 797, 740, 703, 664; HRMS (ESI) calcd for $C_{16}H_{20}NO$ $[M+H]^+$: 242.1545. Found: 242.1540.

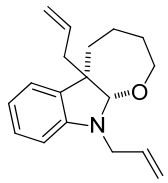


4ha. Colorless oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05-2.16 (m, 2H), 2.42-2.48 (m, 1H), 2.57-2.62 (m, 1H), 3.46-3.52 (m, 1H), 3.74 (s, 3H), 3.85-3.88 (m, 2H), 3.92-3.96 (m, 1H), 5.03-5.28 (m, 5H), 5.63-5.74 (m, 1H), 5.82-5.91 (m, 1H), 6.28 (d, *J* = 8.4 Hz, 1H), 6.64 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.8, 42.4, 48.0, 56.0, 56.1, 66.7, 101.9, 105.5, 111.1, 112.1, 116.4, 118.1, 134.0, 134.2, 134.5, 144.6, 152.4. IR (thin film): ν_{max} (cm^{-1}) = 3076, 2975, 2936, 2866, 1669, 1641, 1596, 1492, 1434, 1396, 1357, 1333, 1283, 1258, 1218, 1164, 1123, 1035, 1012, 951, 915, 883, 795, 747, 701, 653; HRMS (ESI) calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1651. Found: 272.1652.

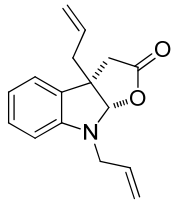


4ia. Red oil, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34-1.44 (m, 1H), 1.54-1.63 (m, 1H), 1.72-1.79 (m, 1H), 1.94-2.00 (m, 1H), 2.26-2.39 (m, 2H), 3.42-3.48 (m, 1H), 3.61-3.67 (m, 1H), 3.82-3.84 (m, 2H), 4.77 (s, 1H), 5.02 (dd, *J* = 16.8, 9.6 Hz, 2H), 5.17 (d, *J* = 11.6 Hz, 1H), 5.29 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.64-5.74 (m, 1H), 5.86-5.95 (m, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.69-6.72 (m, 1H), 6.98 (d, *J* = 6.8 Hz, 1H), 7.07-7.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 28.5, 43.3, 45.2, 47.0, 60.6, 95.9, 106.7, 116.4, 117.6, 117.8, 122.5, 127.7, 133.2, 134.1,

134.3, 149.5. IR (thin film): ν_{max} (cm^{-1}) = 3075, 2960, 2922, 2855, 1640, 1607, 1482, 1462, 1438, 1416, 1382, 1353, 1333, 1307, 1259, 1222, 1159, 1072, 1022, 956, 915, 863, 796, 739, 705; HRMS (ESI) calcd for $C_{17}H_{22}NO$ $[M+H]^+$: 256.1701. Found: 256.1698.

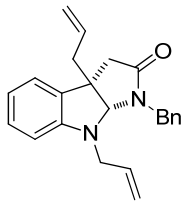


4ja. Red oil, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40-1.51 (m, 2H), 1.54-1.66 (m, 2H), 1.89 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.99-2.05 (m, 1H), 2.25 (d, *J* = 7.6 Hz, 2H), 3.42-3.48 (m, 2H), 3.86-3.88 (m, 2H), 4.77 (s, 1H), 4.96-5.01 (m, 2H), 5.14-5.17 (m, 1H), 5.24-5.29 (m, 1H), 5.52-5.62 (m, 1H), 5.82-5.92 (m, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 6.64-6.68 (m, 1H), 6.87-6.91 (m, 1H), 7.05-7.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 31.6, 33.5, 46.0, 52.8, 65.8, 100.3, 104.4, 116.5, 116.67, 116.72, 117.8, 123.3, 127.5, 132.9, 134.1, 134.2, 149.3. IR (thin film): ν_{max} (cm^{-1}) = 3075, 3054, 2977, 2928, 2857, 2361, 1640, 1605, 1490, 1463, 1438, 1416, 1389, 1359, 1302, 1260, 1242, 1167, 1090, 1060, 1027, 993, 915, 800, 738, 698, 665; HRMS (ESI) calcd for $C_{18}H_{24}NO$ $[M+H]^+$: 270.1858. Found: 270.1847.

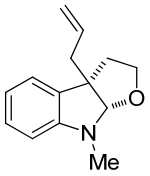


4ka. Colorless oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43-2.54 (m, 2H), 2.89 (s, 2H), 3.91-4.04 (m, 2H), 5.10-5.15 (m, 2H), 5.22-5.35 (m, 2H), 5.61-5.72 (m, 2H), 5.85-5.95 (m, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.14-7.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 41.2, 47.5, 51.8, 102.0, 107.6, 117.8, 119.3, 119.6, 123.4, 129.1, 132.0, 132.2, 132.9, 147.5, 174.8. IR (thin film): ν_{max} (cm^{-1}) = 3077, 2963, 2915, 2855, 1769, 1641, 1606, 1487, 1463, 1439, 1417, 1398, 1340, 1289, 1261, 1216, 1161, 1100, 1045, 1008, 898, 849, 797, 743, 670,

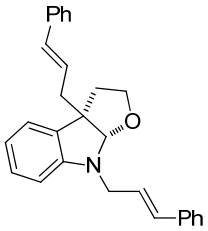
616; HRMS (ESI) calcd for $C_{16}H_{18}NO_2$ $[M+H]^+$: 256.1338. Found: 256.1342.



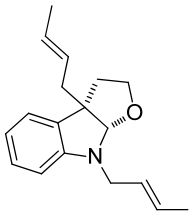
4la. Colorless oil, 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34-2.47 (m, 2H), 2.81 (s, 2H), 3.65 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.84 (dd, *J* = 16.5, 4.8 Hz, 1H), 4.12 (d, *J* = 15.3 Hz, 1H), 4.76 (s, 1H), 4.98-5.16 (m, 5H), 5.46-5.60 (m, 1H), 5.71-5.84 (m, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 6.9 Hz, 1H), 7.09-7.15 (m, 1H), 7.20-7.36 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.0, 43.6, 43.8, 49.3, 52.4, 85.3, 109.1, 117.3, 119.3, 119.5, 123.2, 127.5, 127.6, 128.6, 128.7, 132.7, 134.0, 134.7, 136.2, 149.3, 173.1. IR (thin film): ν_{max} (cm^{-1}) = 3072, 3029, 2977, 2918, 1689, 1641, 1605, 1487, 1461, 1416, 1356, 1332, 1291, 1261, 1201, 1154, 1094, 1063, 1028, 996, 921, 801, 744, 702; HRMS (ESI) calcd for $C_{23}H_{25}N_2O$ $[M]^+$: 345.1967. Found: 345.1954.



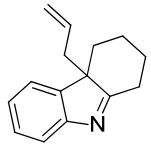
4ma. Colorless oil, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03-2.18 (m, 2H), 2.43-2.50 (m, 1H), 2.56-2.63 (m, 1H), 2.91 (s, 3H), 3.40-3.48 (m, 1H), 3.91-3.97 (m, 1H), 5.03-5.11 (m, 2H), 5.15 (s, 1H), 5.63-5.77 (m, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 6.66 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 7.08-7.13 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.8, 39.7, 42.3, 56.0, 67.0, 102.6, 104.8, 117.1, 117.9, 123.0, 128.2, 132.6, 134.3, 151.1. IR (thin film): ν_{max} (cm^{-1}) = 3052, 2967, 2926, 2869, 1640, 1607, 1493, 1444, 1429, 1388, 1357, 1331, 1301, 1258, 1228, 1155, 1120, 1015, 957, 915, 876, 798, 739, 698, 653; HRMS (ESI) calcd for $C_{14}H_{18}NO$ $[M+H]^+$: 216.1388. Found: 216.1383.



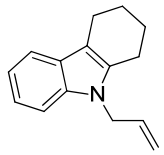
4gb. Colorless oil, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13-2.24 (m, 2H), 2.60-2.66 (m, 1H), 2.76-2.82 (m, 1H), 3.50-3.56 (m, 1H), 3.97-4.01 (m, 1H), 4.07-4.08 (m, 2H), 5.36 (s, 1H), 6.04-6.20 (m, 2H), 6.43-6.46 (m, 2H), 6.52-6.57 (m, 2H), 6.67-6.71 (m, 1H), 7.07-7.11 (m, 2H), 7.18-7.24 (m, 5H), 7.25-7.27 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.1, 41.8, 46.5, 56.4, 66.9, 101.2, 105.4, 117.4, 123.3, 125.8, 126.0, 126.1, 126.3, 127.2, 127.3, 128.3, 128.4, 128.5, 131.6, 132.4, 133.0, 136.8, 137.3, 150.2. IR (thin film): ν_{max} (cm^{-1}) = 3079, 3054, 3025, 2965, 2922, 2865, 1949, 1878, 1805, 1735, 1603, 1489, 1463, 1445, 1398, 1358, 1305, 1261, 1157, 1069, 1042, 1012, 963, 914, 872, 803, 736, 692; HRMS (ESI) calcd for $C_{28}H_{28}NO$ $[M+H]^+$: 394.2171. Found: 394.2161.



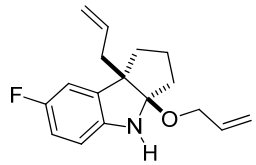
4gd. Colorless oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62-1.64 (m, 3H), 1.67-1.70 (m, 3H), 2.01-2.15 (m, 2H), 2.38 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.49-2.54 (m, 1H), 3.43-3.49 (m, 1H), 3.82-3.85 (m, 2H), 3.90-3.95 (m, 1H), 5.23 (s, 1H), 5.26-5.34 (m, 1H), 5.42-5.54 (m, 2H), 5.61-5.71 (m, 1H), 6.36 (d, *J* = 8.0 Hz, 1H), 6.63-6.67 (m, 1H), 7.01-7.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 18.0, 39.9, 41.3, 46.3, 56.1, 66.7, 101.0, 105.1, 116.9, 123.2, 126.7, 126.8, 127.5, 127.9, 128.5, 132.9, 150.3. IR (thin film): ν_{max} (cm^{-1}) = 3025, 2965, 2918, 2859, 1604, 1488, 1459, 1443, 1398, 1379, 1356, 1299, 1259, 1226, 1160, 1120, 1046, 1009, 961, 915, 878, 799, 737, 666, 628; HRMS (ESI) calcd for $C_{18}H_{24}NO$ $[M+H]^+$: 270.1858. Found: 270.1847.



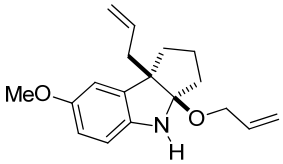
4naa[2]. Yellow solid, 42% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11-1.26 (m, 1H), 1.35-1.51 (m, 1H), 1.66-1.87 (m, 2H), 2.18-2.23 (m, 1H), 2.35-2.39 (m, 1H), 2.51-2.67 (m, 3H), 2.86-2.91 (m, 1H), 4.85-4.98 (m, 2H), 5.11-5.25 (m, 1H), 7.16-7.21 (m, 1H), 7.26-7.35 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 1H).



4nab[3]. Yellow oil, 49% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84-1.97 (m, 4H), 2.62-2.75 (m, 4H), 4.62 (dd, *J* = 3.0, 1.8 Hz, 2H), 4.88 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.09 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.85-5.97 (m, 1H), 7.03-7.15 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H).

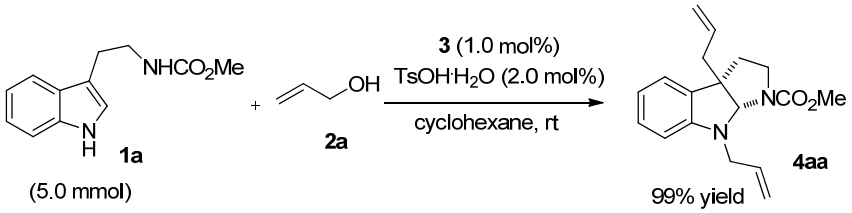


4oa. Yellow oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28-1.39 (m, 1H), 1.62-1.70 (m, 1H), 1.78-1.85 (m, 1H), 1.91-1.95 (m, 2H), 2.03-2.09 (m, 1H), 2.38 (s, 1H), 2.56 (d, *J* = 7.6 Hz, 2H), 3.73-3.87 (m, 2H), 5.07-5.14 (m, 2H), 5.18-5.23 (m, 2H), 5.82-5.91 (m, 1H), 6.15-6.18 (m, 1H), 6.69-6.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.5, 37.8, 40.5, 40.7, 45.5, 55.6, 104.9 (*J* = 7.8 Hz), 106.4, 110.8 (*J* = 23.3 Hz), 113.3 (*J* = 22.8 Hz), 115.5, 118.2, 134.9 (*J* = 7.2 Hz), 135.4, 135.9, 144.7, 156.1 (*J* = 232.8 Hz). R (thin film): ν_{max} (cm^{-1}) = 3416, 3076, 2956, 2870, 1707, 1640, 1609, 1491, 1442, 1417, 1389, 1355, 1287, 1258, 1181, 1147, 1079, 1025, 1002, 917, 865, 801, 746, 711, 680; HRMS (ESI) calcd for $C_{17}H_{21}FNO$ $[M+H]^+$: 274.1607. Found: 274.1608.



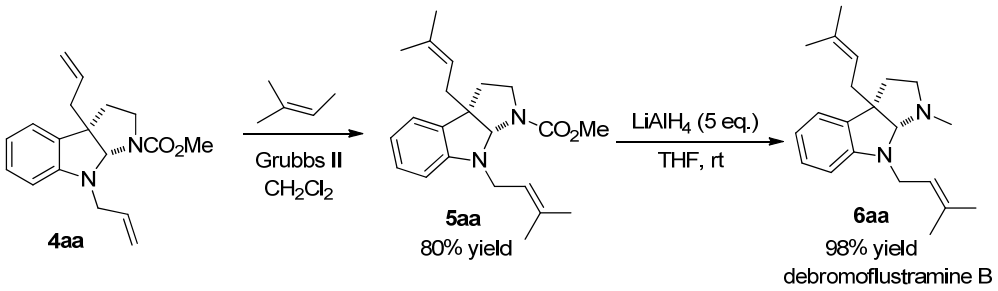
4pa. Yellow oil, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25-1.39 (m, 1H), 1.60-1.69 (m, 1H), 1.76-1.84 (m, 1H), 1.87-1.97 (m, 2H), 2.02-2.08 (m, 1H), 2.37 (s, 1H), 2.56 (d, *J* = 9.2 Hz, 2H), 3.70-3.87 (m, 2H), 3.74 (s, 3H), 5.04-5.13 (m, 2H), 5.16-5.25 (m, 2H), 5.67-5.78 (m, 1H), 5.84-5.93 (m, 1H), 6.21 (d, *J* = 8.4 Hz, 1H), 6.60 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.67 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 37.5, 40.5, 40.6, 45.7, 55.7, 56.0, 105.1, 106.3, 111.1, 111.7, 115.2, 117.8, 135.1, 135.8, 136.3, 143.0, 152.2. IR (thin film): ν_{max} (cm^{-1}) = 2963, 1411, 1260, 1090, 1019, 866, 798, 679; HRMS (ESI) calcd for $C_{18}H_{24}NO_2$ $[M+H]^+$: 286.1807. Found: 286.1810.

A gram-scale synthesis of 4aa.



A 50 mL flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added **3** (25.2 mg, 1.0 mol%), $TsOH{\cdot}H_2O$ (19.0 mg, 2.0 mol%), Indole derivatives **1a** (1.09 g, 5.0 mmol), allyl alcohol **2a** (1.16 g, 40 mmol), cyclohexane (10 mL). The reaction mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure, the residue was purified by column chromatography (PE/EA = 10/1) to afford the desired product **4aa** (1.48 g, 99% yield).

Concise synthesis of debromoflustramine B



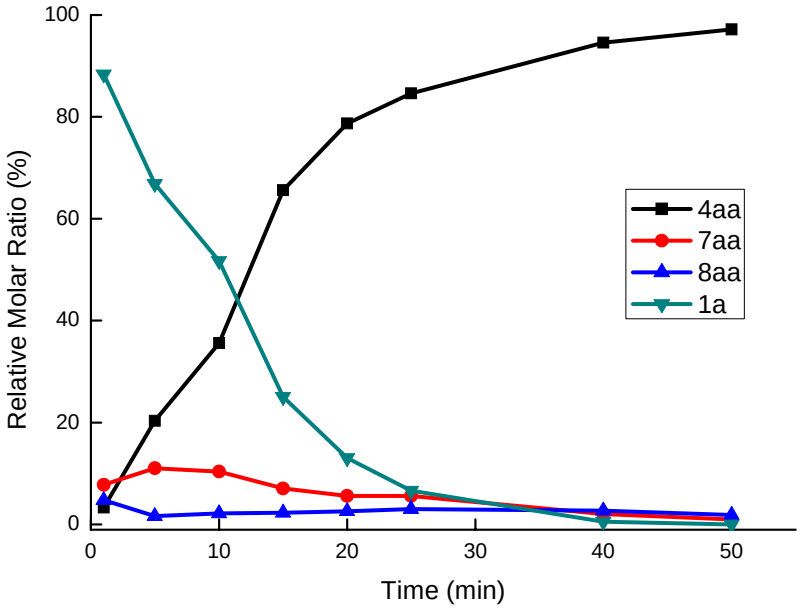
A 25 mL flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask was added **4aa** (89.4 mg, 0.30 mmol). The vessel was placed under vacuum and the atmosphere exchanged with argon three times before the addition of CH_2Cl_2 (5 mL) and 2-methyl-2-butene (210.0 mg, 3.00 mmol). Then the mixture was heated to 40 °C before Grubbs II (25.5 mg, 0.03 mmol) was added. Then, the reaction mixture was stirred at 40 °C. After the reaction was almost complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (PE/EA = 15/1) to afford the desired product **5aa**[1] as a colorless liquid (85.0 mg, 80% yield). Colorless oil, 80% yield. Analytical data for **5aa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.64-1.75 (m, 9H), 2.02 (br s, 2H), 2.38 (d, *J* = 7.2 Hz, 2H), 3.01-3.10 (m, 1H), 3.70-4.21 (m, 6H), 5.04 (s, 1H), 5.14 (s, 1H), 5.23-5.34 (m, 1H), 6.35-6.37 (m, 1H), 6.61-6.66 (m, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 7.03-7.08 (m, 1H).

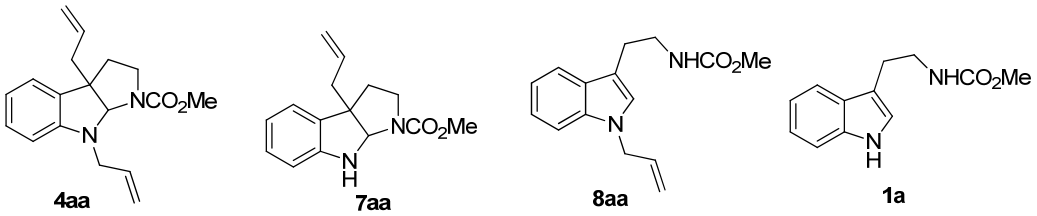
A flame-dried 25mL round bottom flask was cooled to room temperature and filled with argon. To this flask was added $LiAlH_4$[4] (22.8 mg, 0.6 mmol), the atmosphere exchanged with argon three times before the addition of THF (10 mL) and the slow addition of **5aa** (59.6 mg, 0.20 mmol). After the reaction was complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure, the residue was purified by column chromatography (PE/EA = 1/2) to afford the desired product **6aa**[1] as a

colorless liquid (60.8 mg, 98% yield). Analytical data for **6aa**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58 (s, 3H), 1.65 (s, 3H), 1.70 (s, 3H), 1.71 (s, 3H), 1.87-1.94 (m, 1H), 2.00-2.10 (m, 1H), 2.42 (d, *J* = 6.9 Hz, 2H), 2.48 (s, 3H), 2.52-2.60 (m, 1H), 2.63-2.70 (m, 1H), 3.76-3.84 (m, 1H), 3.89-3.96 (m, 1H), 4.26 (s, 1H), 4.94-4.99 (m, 1H), 5.14-5.19 (m, 1H), 6.39-6.44 (m, 1H), 6.64 (t, *J* = 6.9 Hz, 1H), 6.96 (d, *J* = 6.9 Hz, 1H), 7.00-7.06 (m, 1H).

Mechanistic investigation

The reaction of **1a** with **2a** was monitored by the HPLC analysis [Waters Spherisorb ® 5um Silica (0.46 cm x 25 cm), n-hexane/2-propanol = 90/10, v = 1.0 mL·min^{-1}, λ = 230 nm, t (**4aa**) = 3.81 min, t (**7aa**) = 4.93 min, t (**8aa**) = 6.13 min, t (**1a**) = 11.08 min]. At first, substrate **1a**, product **4aa** and the two intermediates **7aa** and **8aa** were synthesized respectively, and then mixed together in an equivalent amount. After obtaining the integration ratio of different compounds, we can use HPLC to obtain the relative molar ratio of four compounds. The results analyzed by HPLC were showed in the following figure:

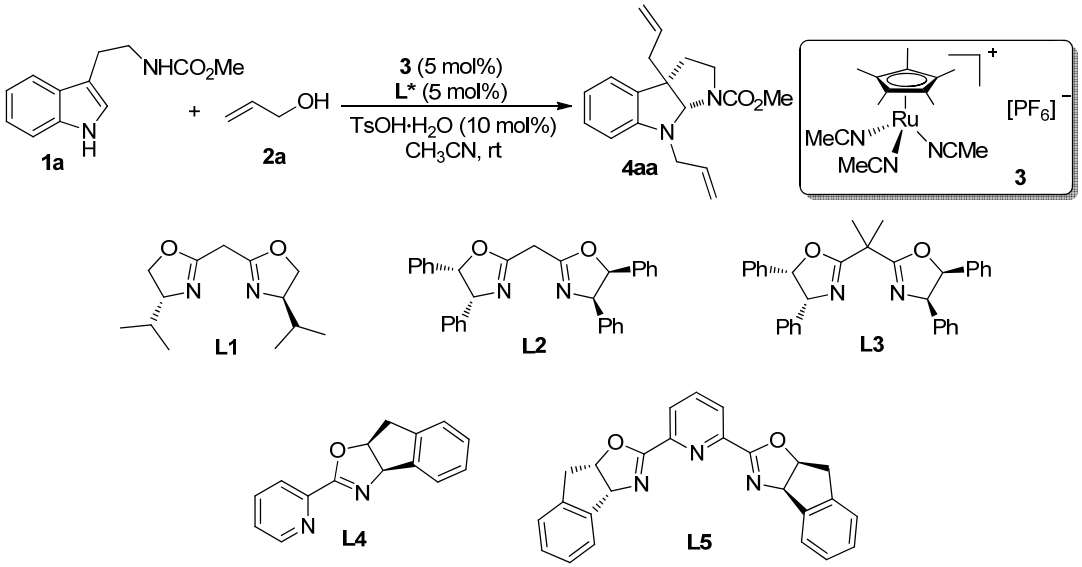




At the very beginning of the reaction, a large quantity of **7aa** and a small amount of **8aa** were generated. As the reaction proceeded, **7aa** was rapidly consumed by the allylic amination reaction, while it took eight hours for **8aa** to reach a full conversion.

General procedure for ruthenium-catalyzed intermolecular enantioselective dearomatization reaction of indoles with allylic alcohols [a]**:**

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added **3** (5.04 mg, 0.010 mmol, 5 mol%), **L*** (0.01 mmol, 5 mol%) and CH_3CN (1 mL), The reaction mixture was stirred at room temperature for one hour. After that, $TsOH{\cdot}H_2O$ (3.8 mg, 0.020 mmol, 10 mol%), indole derivatives **1a** (0.20 mmol, 100 mol%), allyl alcohol **2a** (0.80 mmol, 400 mol%), and another 1 mL CH_3CN were added to the flask. The reaction mixture was stirred at room temperature until the reaction was complete (monitored by TLC). Then, the mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtrated. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to afford the desired product **4aa**. The preliminary results for the enantioselective synthesis are summarized below.



entry	ligand	time (h)	**4aa** yield (%)[b]	ee (%)[c]
1	**L1**	12	91	0
2	**L2**	12	93	0
3	**L3**	12	69	5
4	**L4**	12	90	10
5	**L5**	12	27	3

[a] Reaction conditions: **1a** (0.2 mmol), allyl alcohol **2a** (0.8 mmol), **3** (5 mol%), **L*** (5 mol%), $TsOH{\cdot}H_2O$ (10 mol%) in CH_3CN at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis [column: Phenomenex Lu X 5u Amylose-2 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 50/1, $v = 0.51$ mL·min^{-1}, $\lambda = 254$ nm].

References

(1) A. W. Schammel, B. W. Boal, L. Zu, T. Mesganaw and N. K. Garg, *Tetrahedron*, 2010, **66**, 4687.

(2) N. Kagawa, J. P. Malerich and V. H. Rawal, *Org. Lett.*, 2008, **10**, 2381.

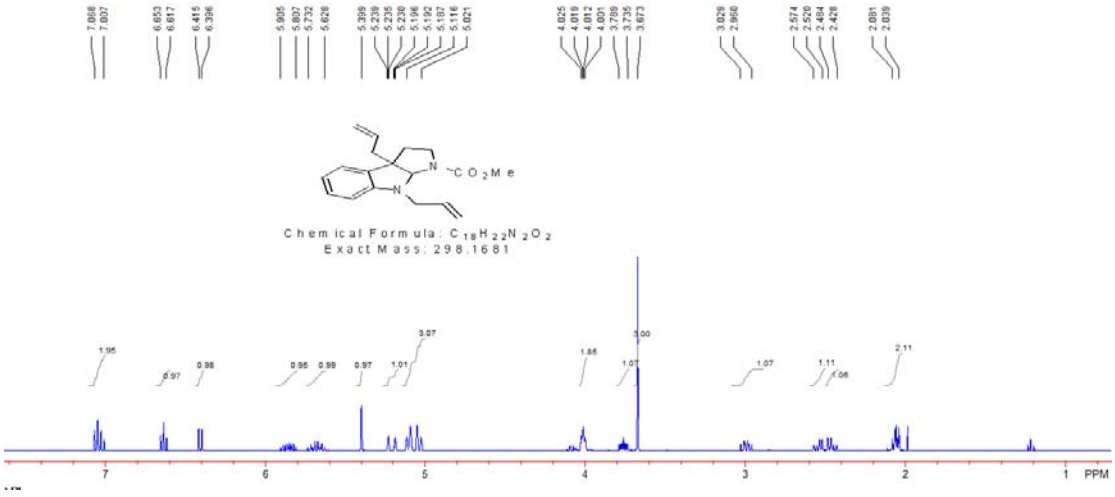
(3) A. A. El-Hamamy and J. Hill, J. Townend, *J. Chem. Soc., Perkin Trans. 1*, 1983, 573.

(4) J. F. Austin, S.-G. Kim, C. J. Sinz, W.-J. Xiao and D. W. C. MacMillan, *Proc. Natl. Acad. Sci. USA*, 2004, **101**, 5482.

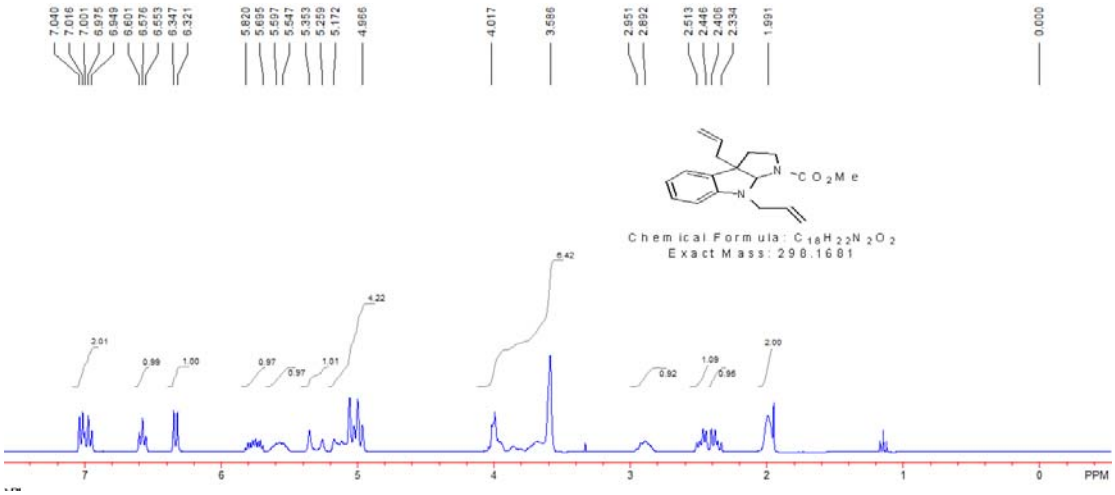
Copies of NMR Spectra

Compound **4aa**'s ^{1}H NMR Spectra

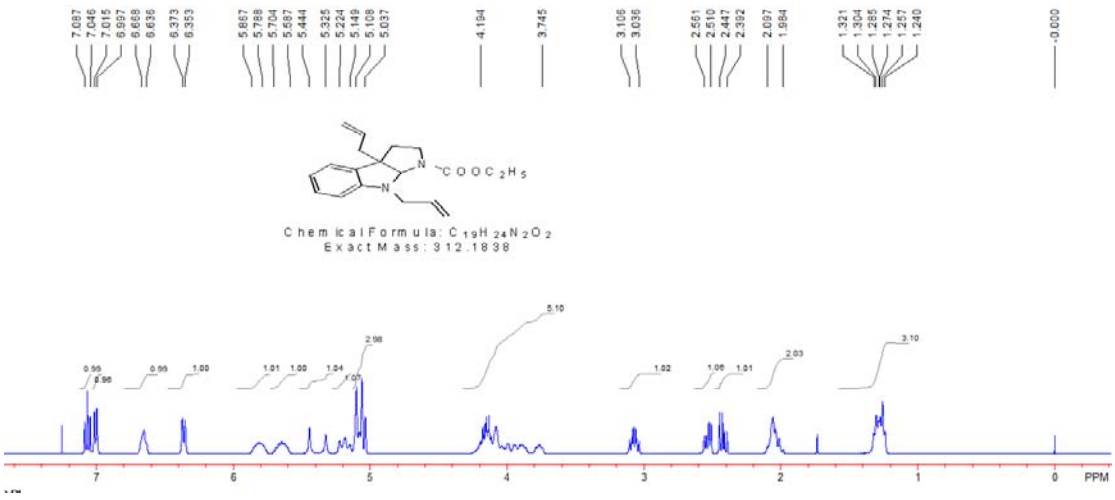
In d_6-DMSO (110°C)



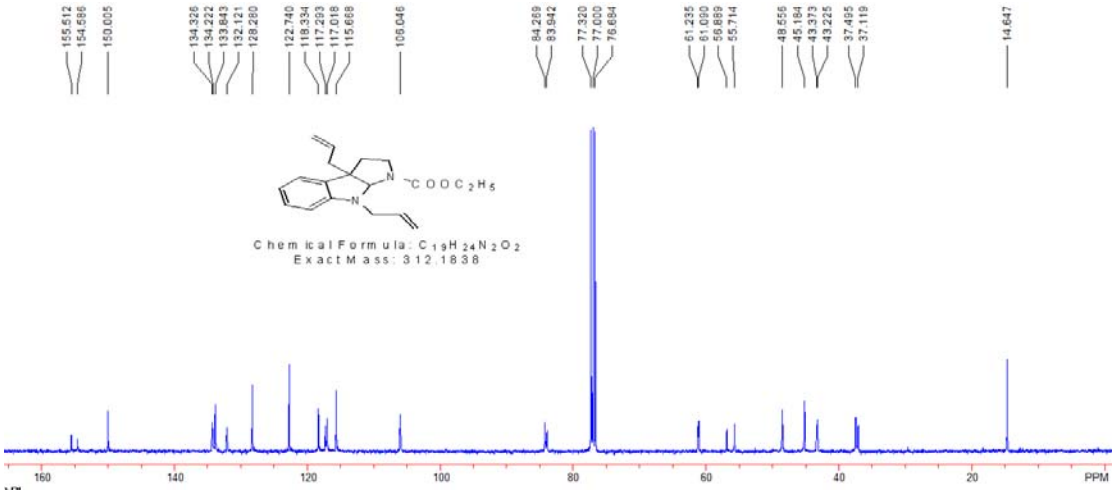
In $CDCl_3$ (rt)



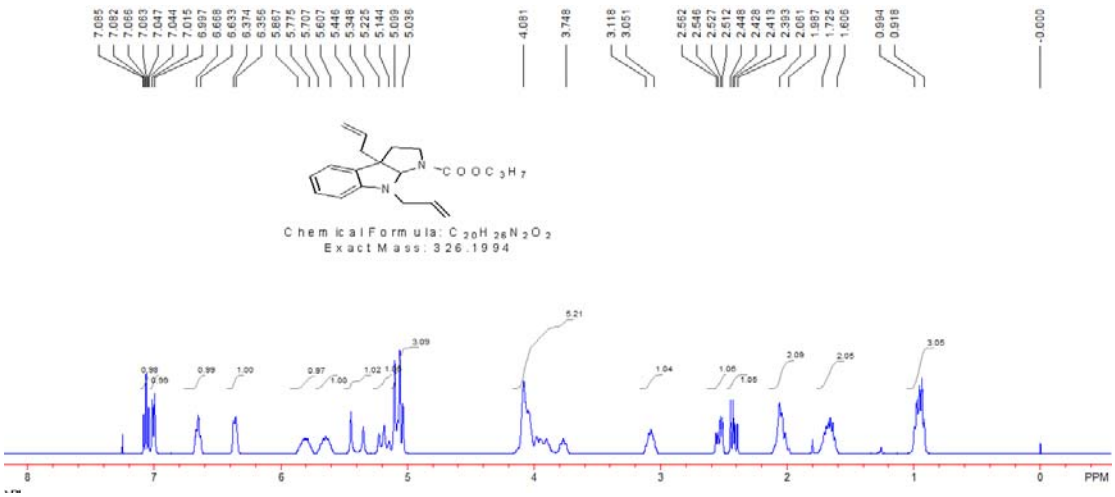
Compound **4ba**'s ^{1}H NMR Spectra



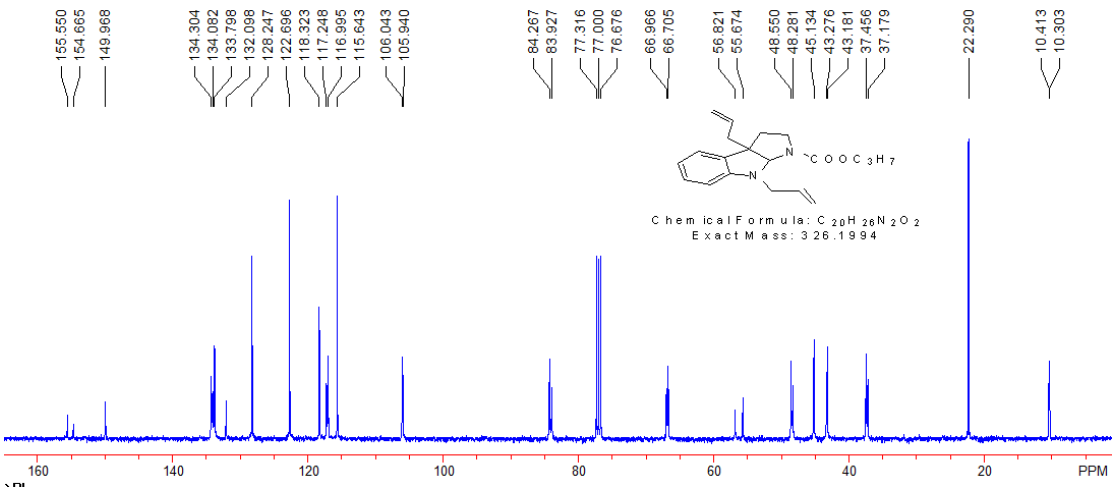
Compound **4ba**'s ^{13}C NMR Spectra



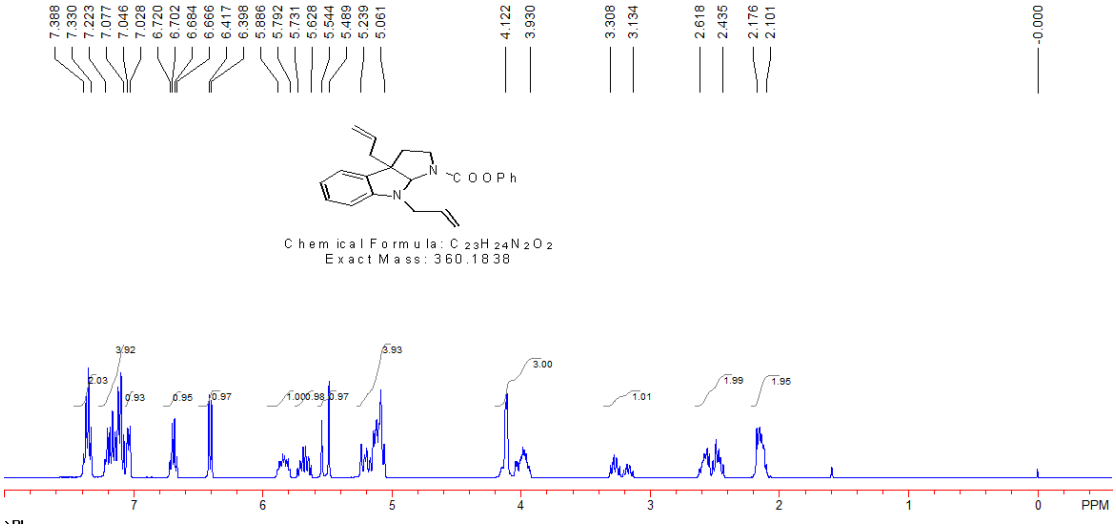
Compound **4ca**'s ^{1}H NMR Spectra



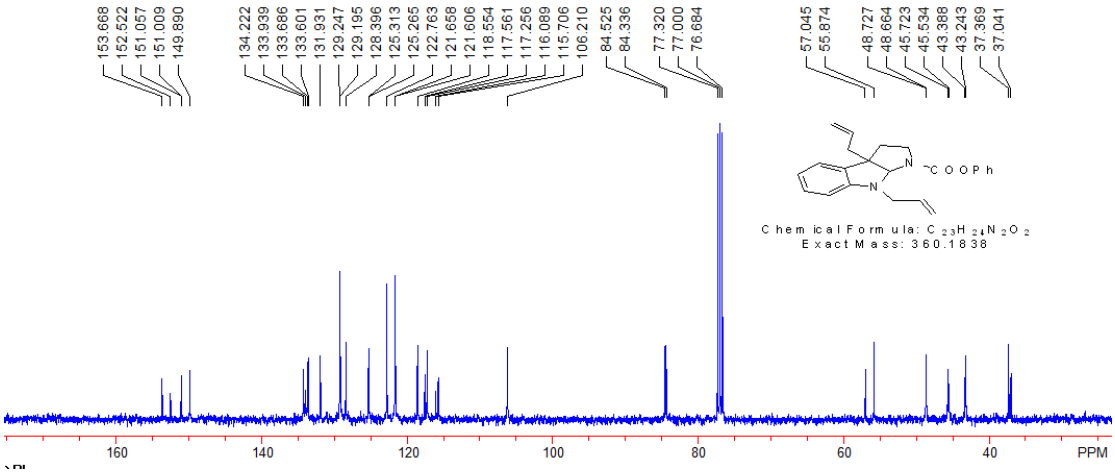
Compound **4ca**'s ^{13}C NMR Spectra



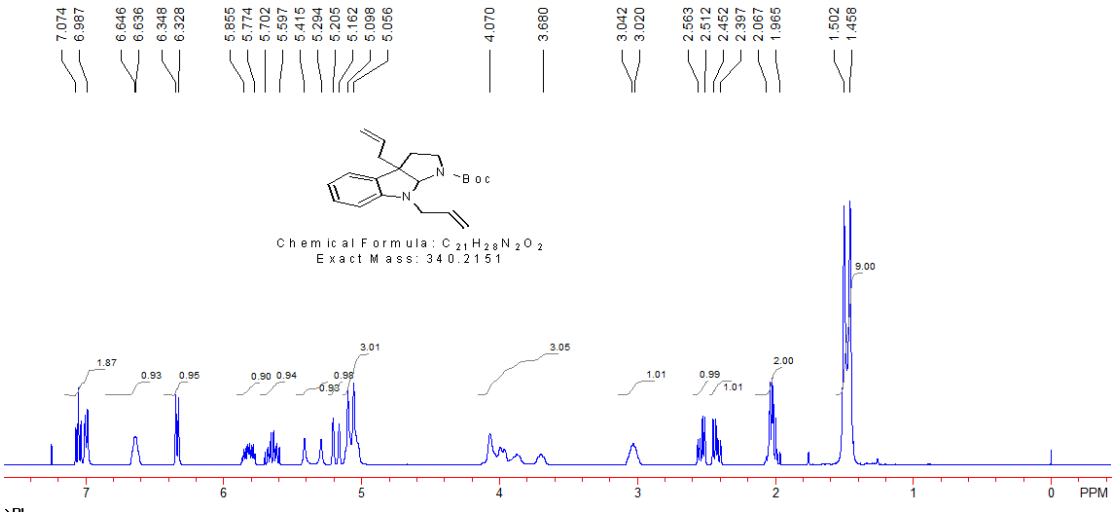
Compound **4da**'s ^{1}H NMR Spectra



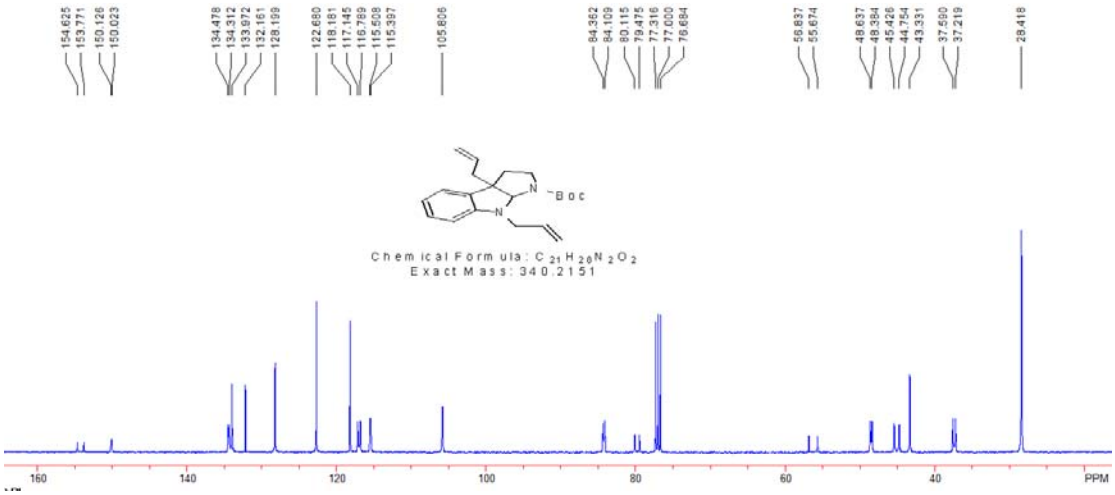
Compound **4da**'s ^{13}C NMR Spectra



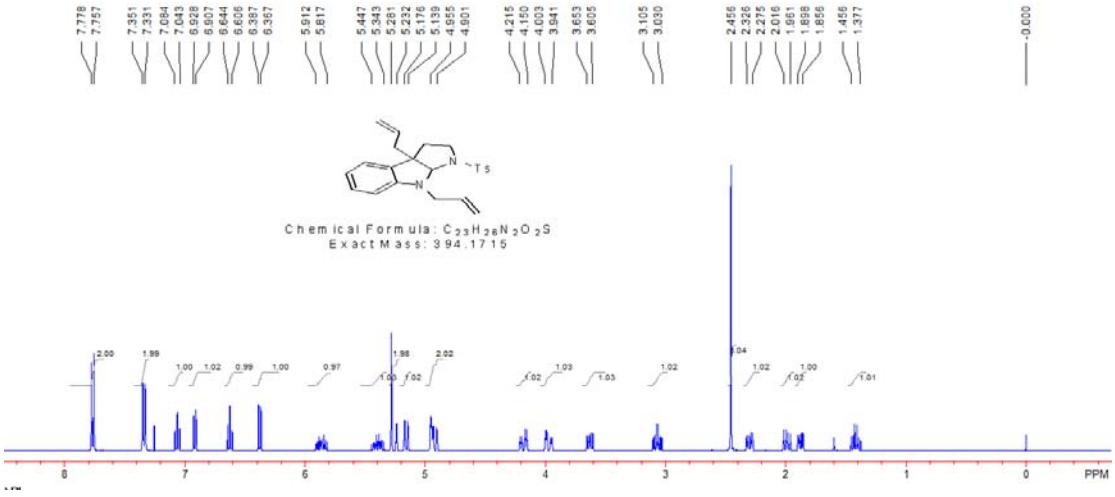
Compound **4ea**'s ^{1}H NMR Spectra



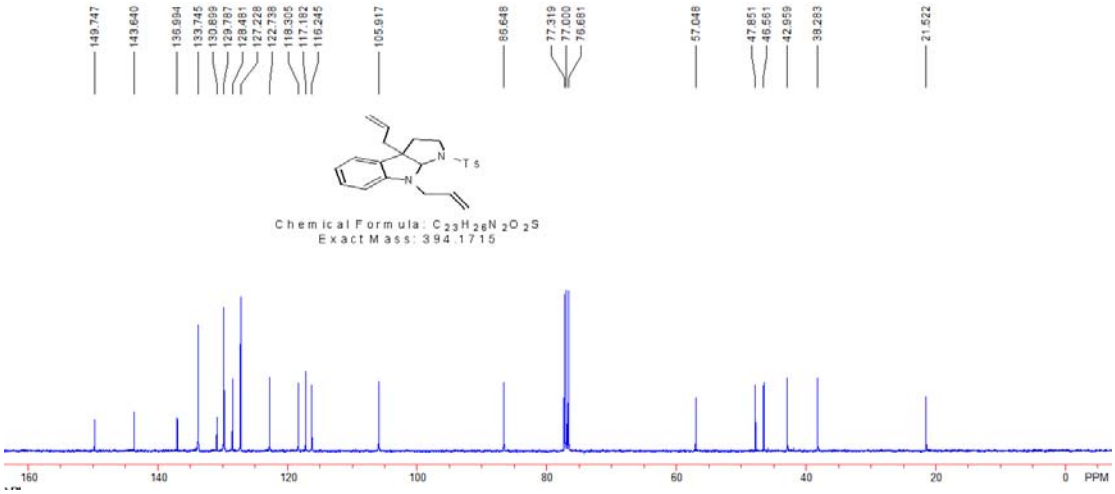
Compound **4ea**'s ^{13}C NMR Spectra



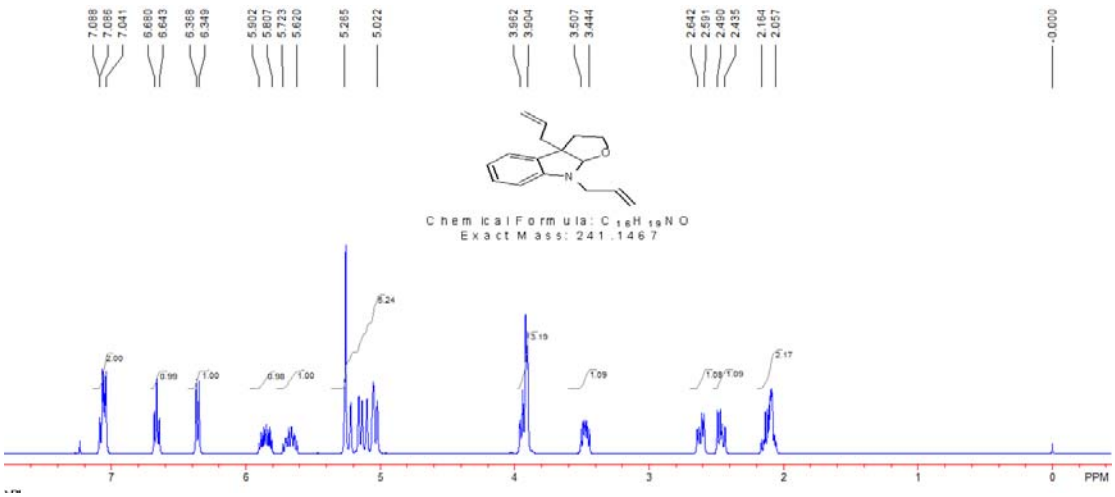
Compound **4fa**'s ^{1}H NMR Spectra



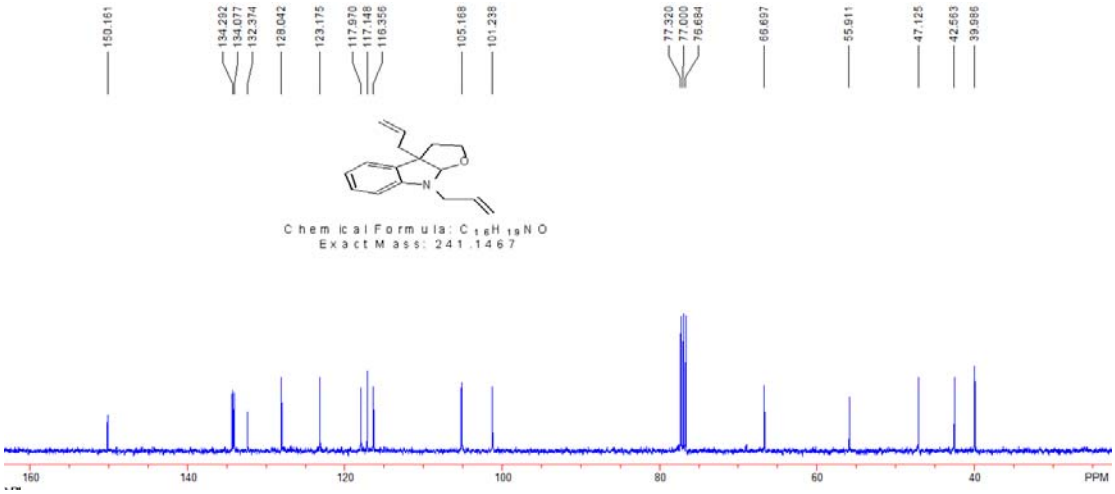
Compound **4fa**'s ^{13}C NMR Spectra



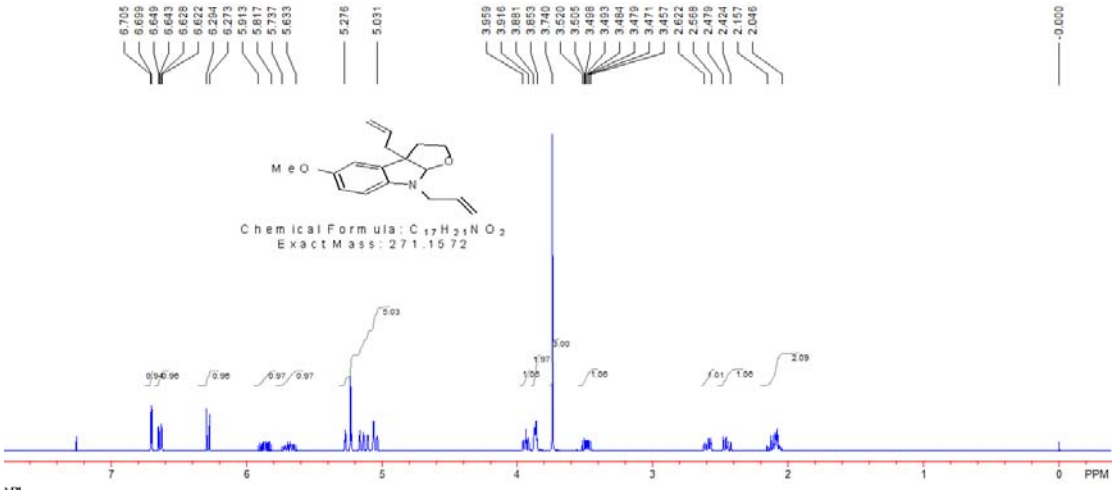
Compound **4ga**'s ^{1}H NMR Spectra



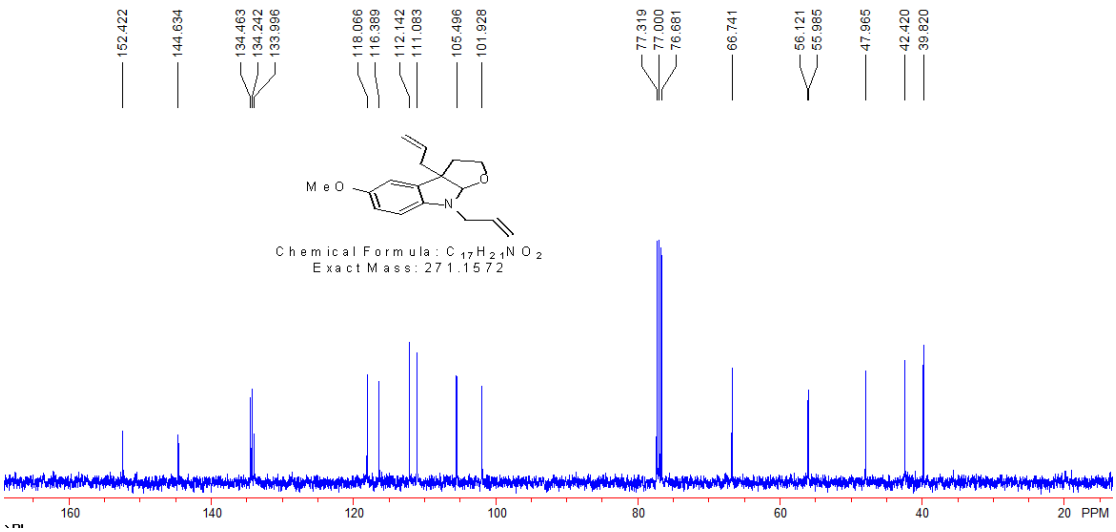
Compound **4ga**'s ^{13}C NMR Spectra



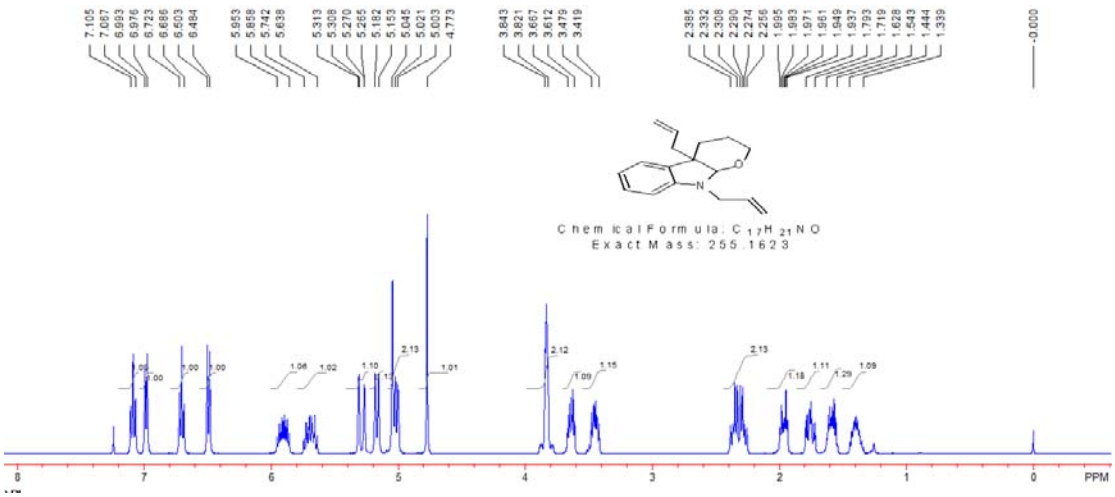
Compound **4ha**'s ^{1}H NMR Spectra



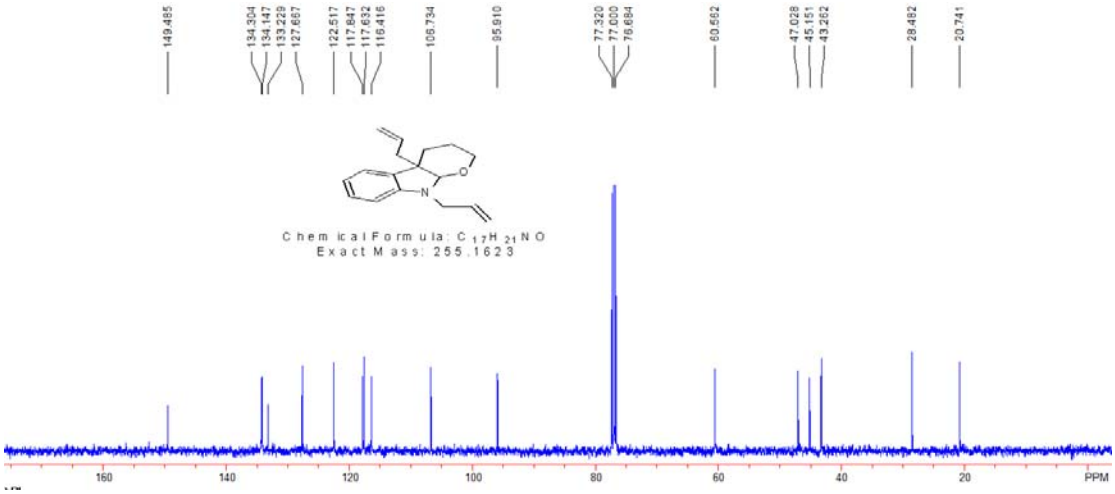
Compound **4ha**'s ^{13}C NMR Spectra



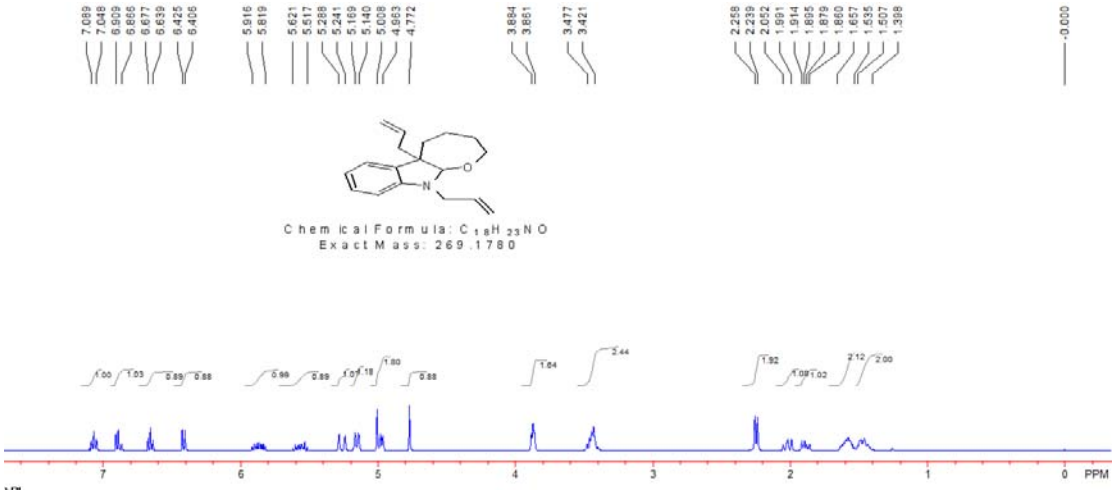
Compound **4ia**'s ^{1}H NMR Spectra



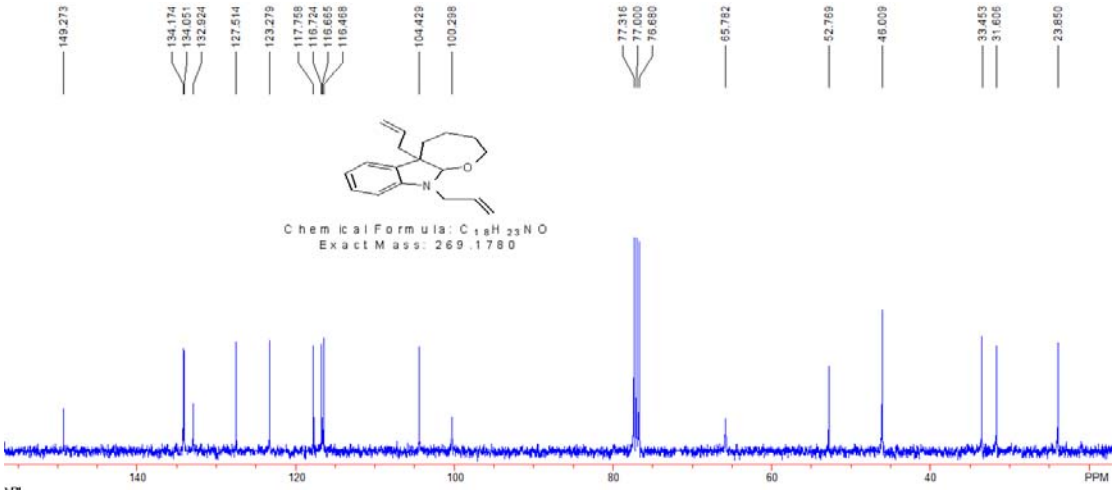
Compound **4ia**'s ^{13}C NMR Spectra



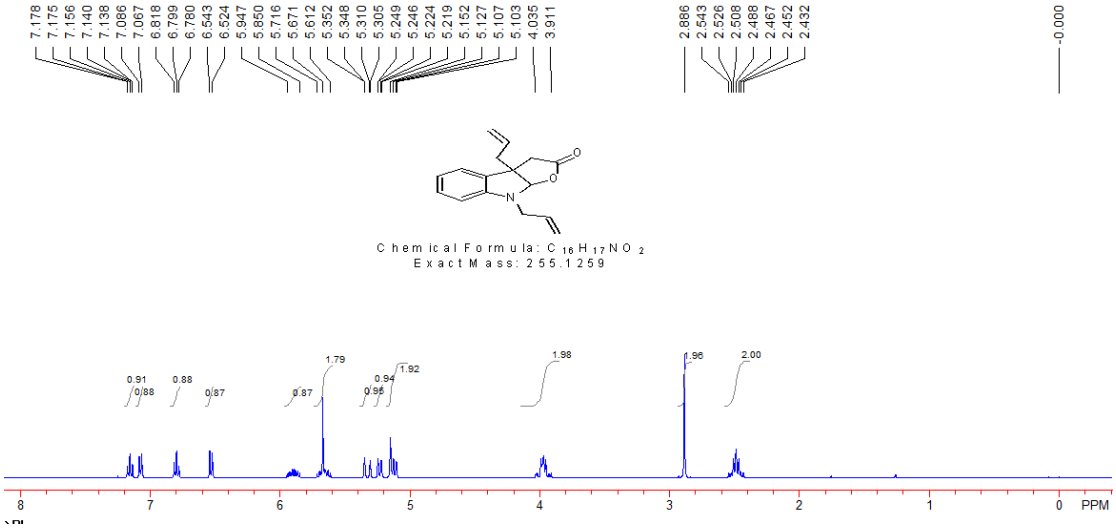
Compound **4ja**'s ^{1}H NMR Spectra



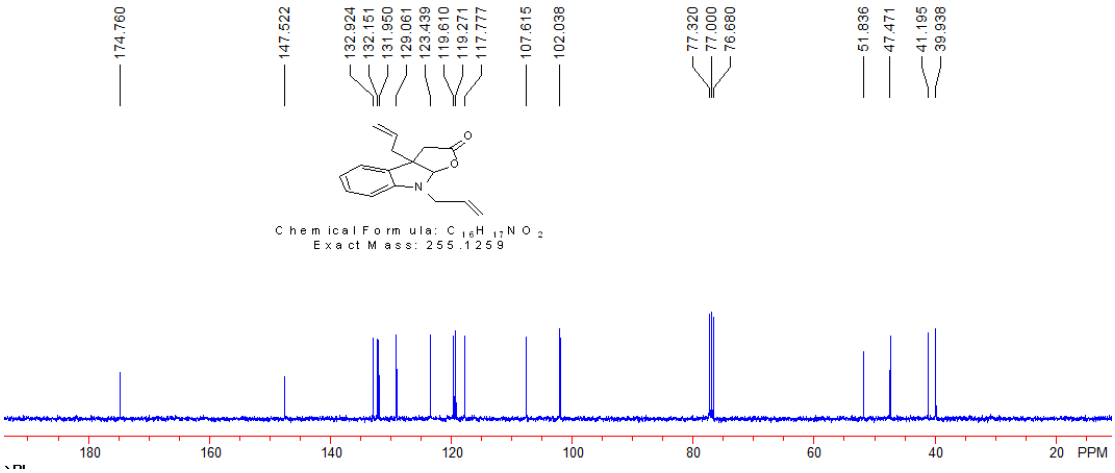
Compound **4ja**'s ^{13}C NMR Spectra



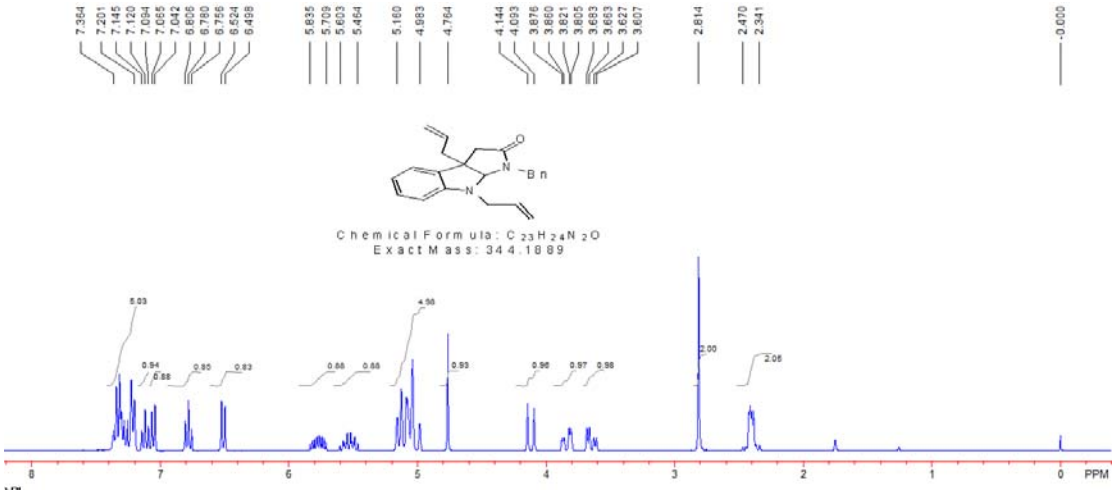
Compound **4ka**'s ^{1}H NMR Spectra



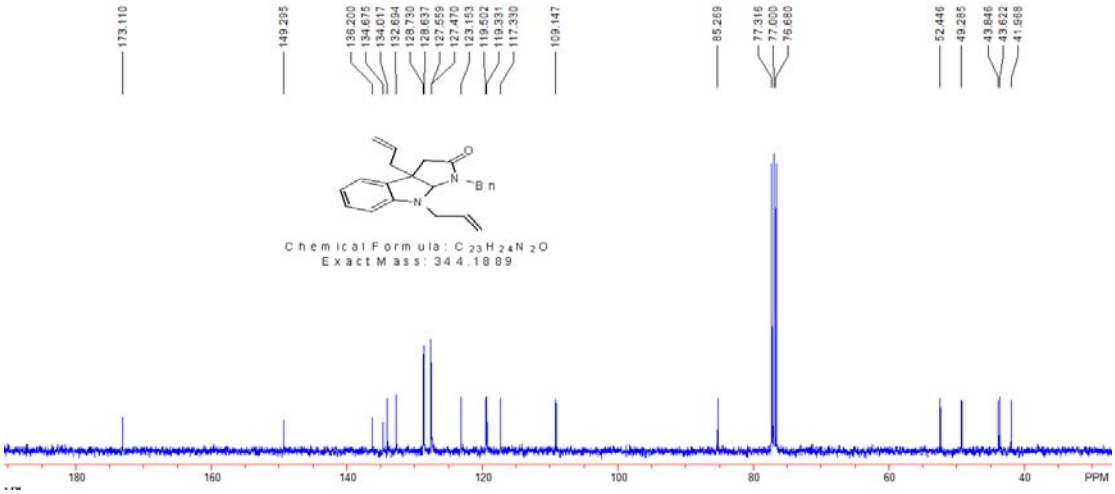
Compound **4ka**'s ^{13}C NMR Spectra



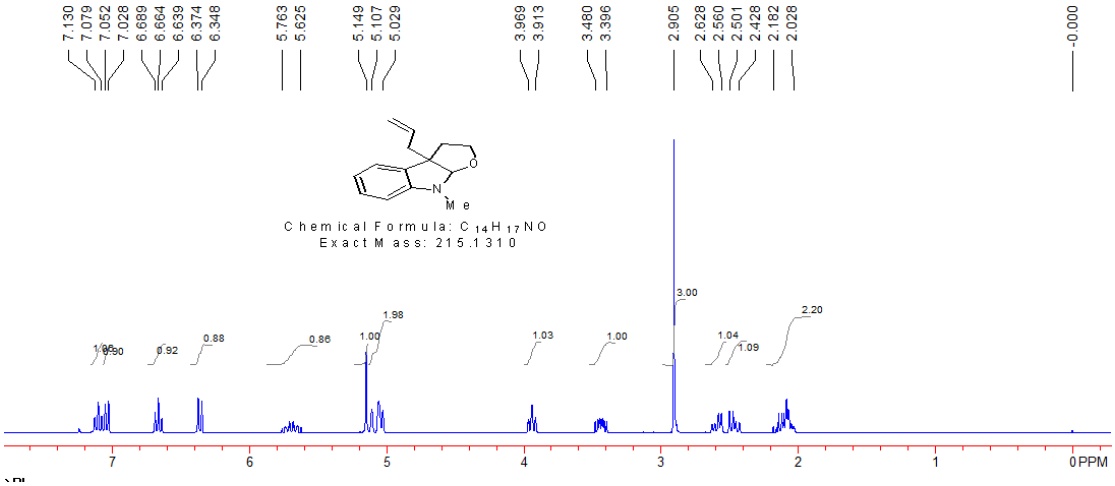
Compound **4la**'s ^{1}H NMR Spectra



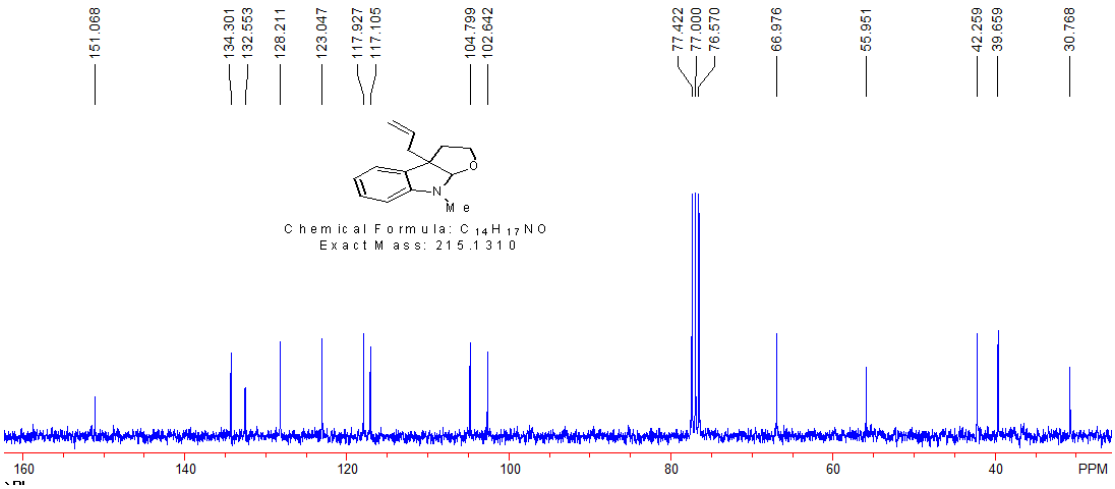
Compound **4la**'s ^{13}C NMR Spectra



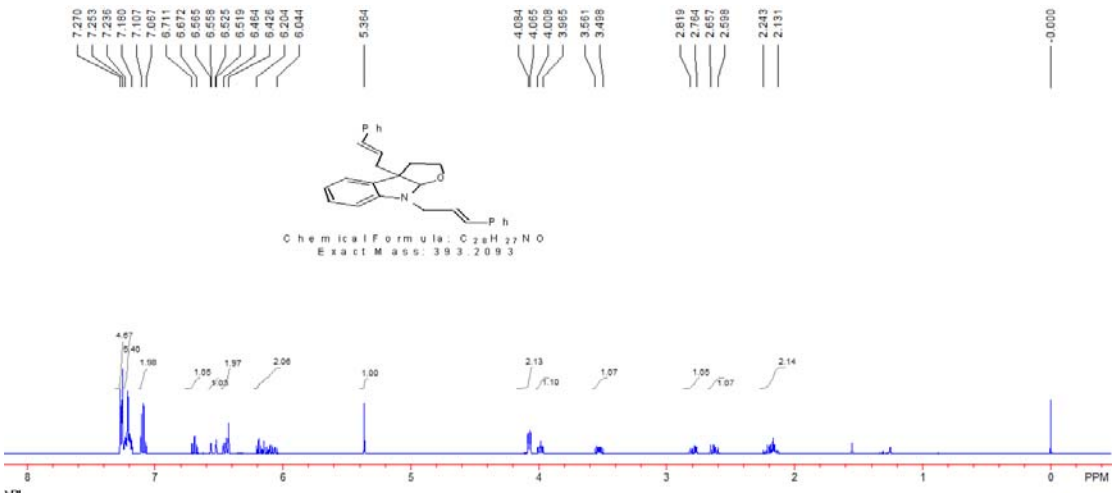
Compound **4ma**'s ^{1}H NMR Spectra



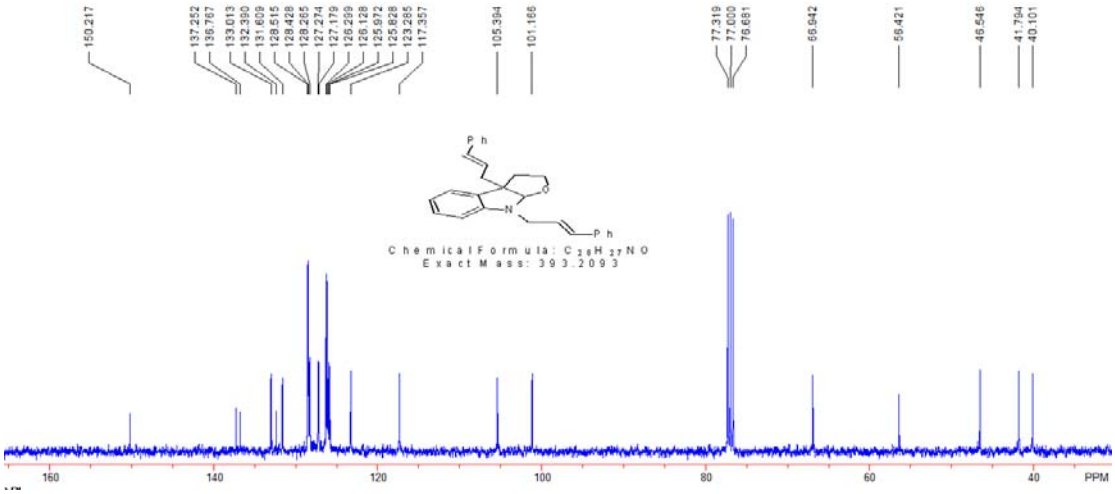
Compound **4ma**'s ^{13}C NMR Spectra



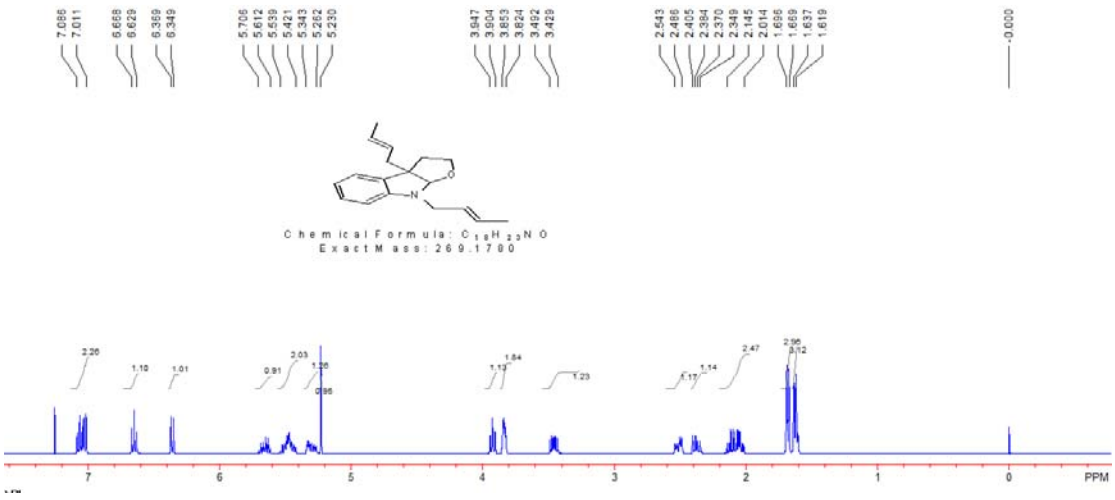
Compound **4gb**'s ^{1}H NMR Spectra



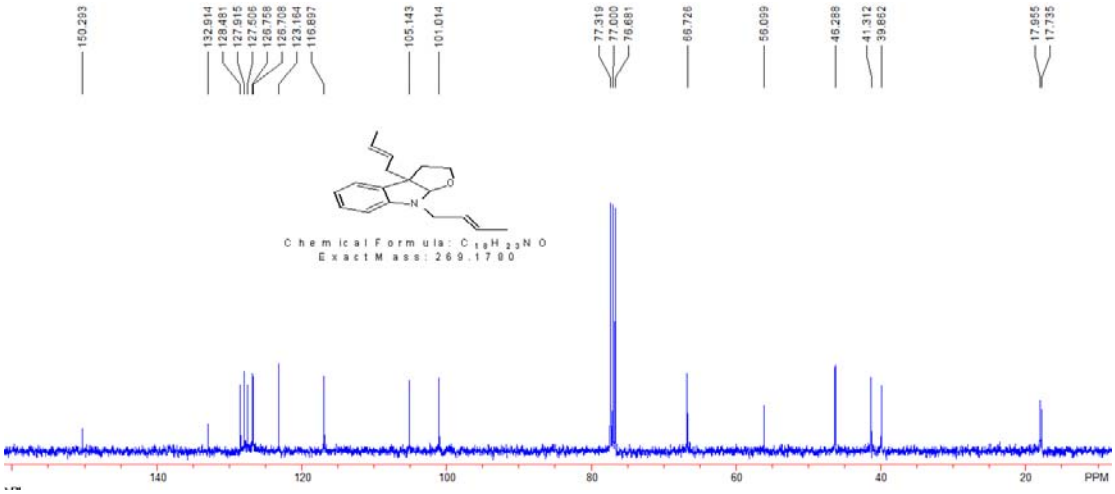
Compound **4gb**'s ^{13}C NMR Spectra



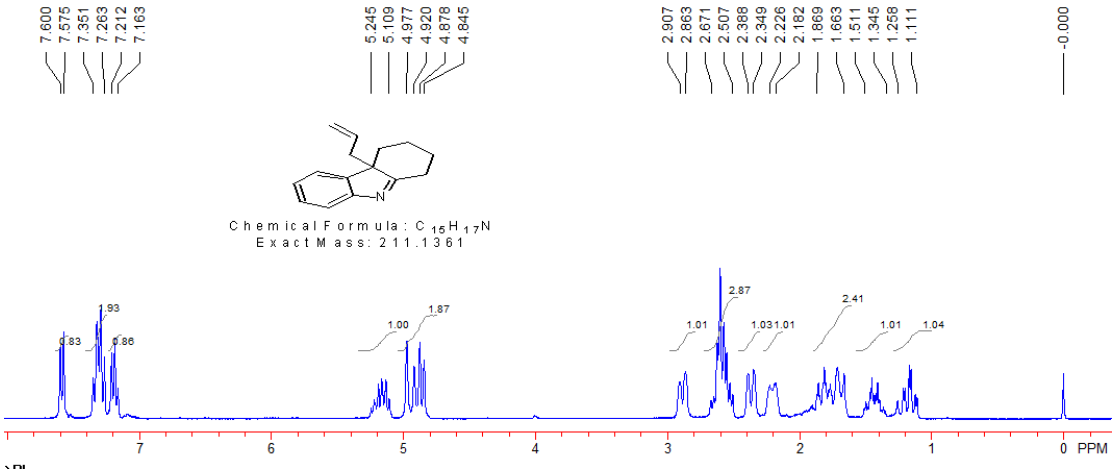
Compound **4gd**'s ^{1}H NMR Spectra



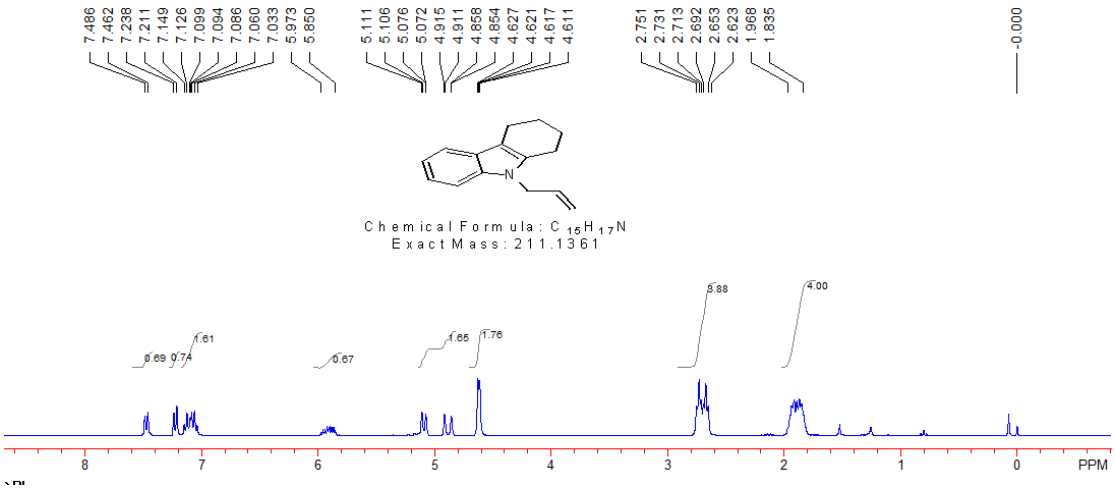
Compound **4gd**'s ^{13}C NMR Spectra



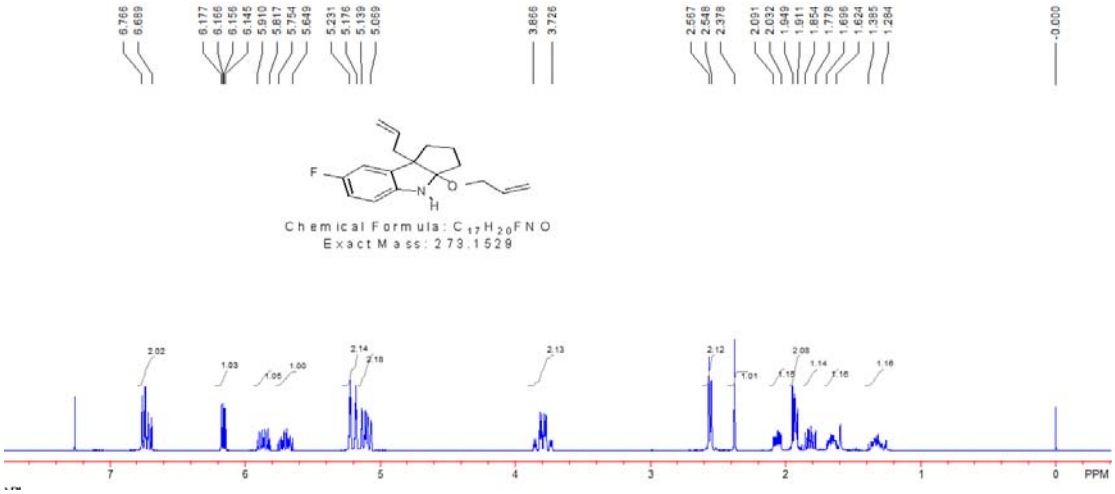
Compound **4naa**'s ^{1}H NMR Spectra



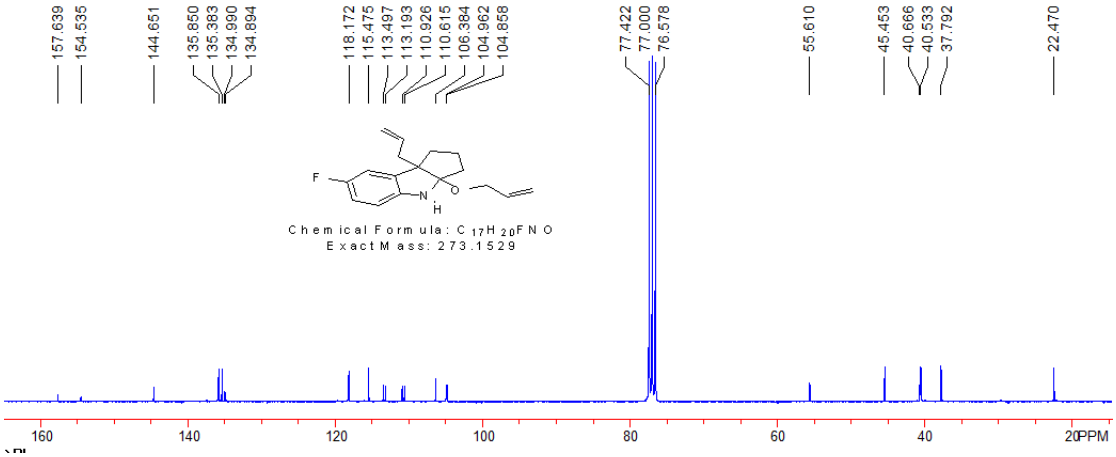
Compound **4nab**'s ^{1}H NMR Spectra



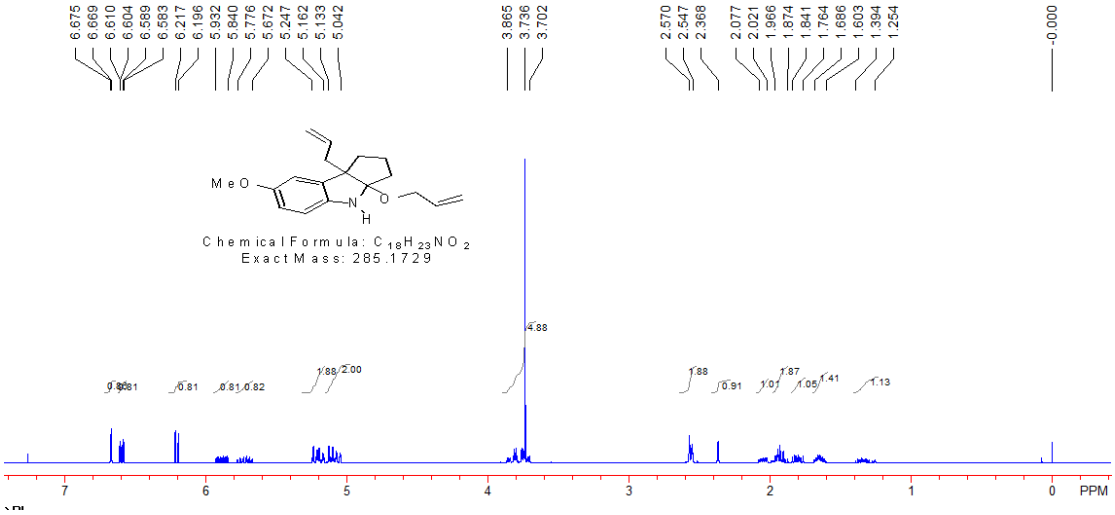
Compound **4oa**'s ^{1}H NMR Spectra



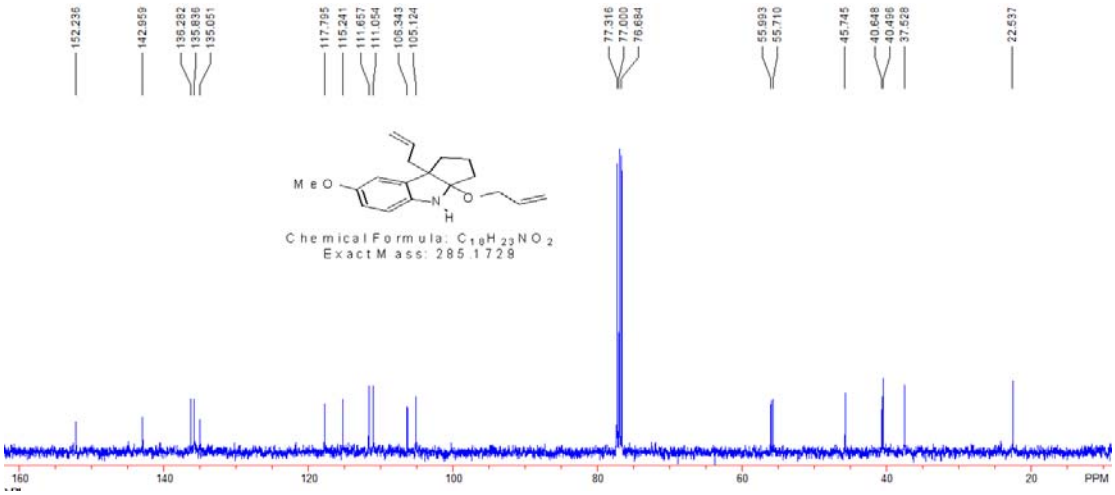
Compound **4oa**'s ^{13}C NMR Spectra



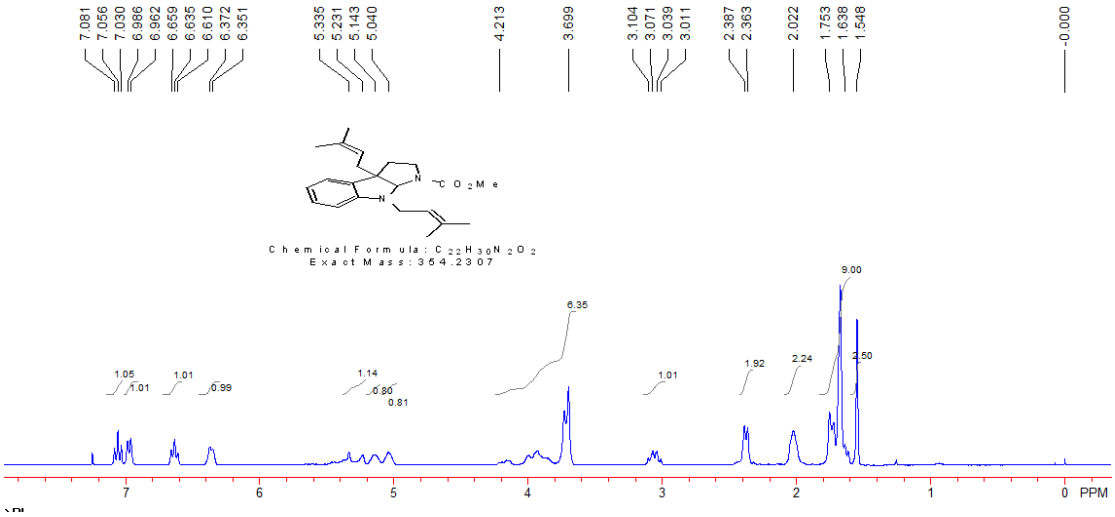
Compound **4pa**'s ^{1}H NMR Spectra



Compound **4pa**'s ^{13}C NMR Spectra



Compound **5aa**'s ^{1}H NMR Spectra



Compound **6aa**'s ^{1}H NMR Spectra