Supporting Information

Rhodium(II)-Catalyzed Intramolecular Annulation of 1-Sulfonyl-1,2,3-Triazoles with Indoles: Facile Synthesis of Functionalized Tetrahydro-*β*-Carbolines

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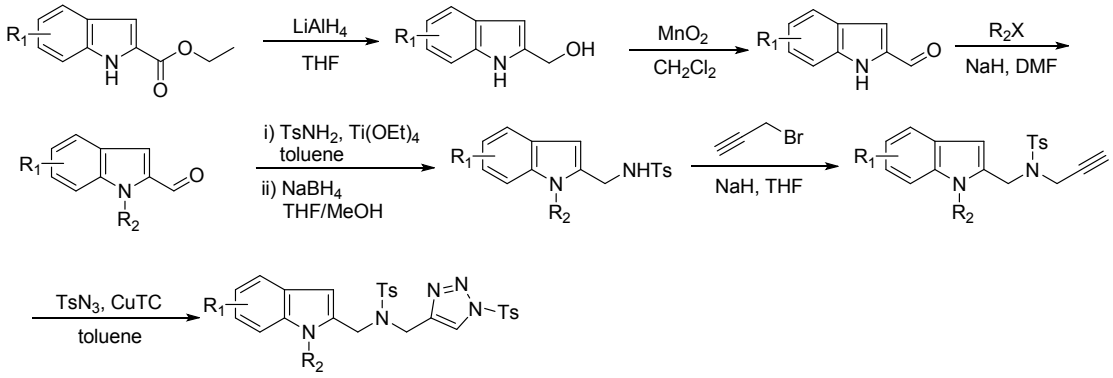
1. General Information

NMR spectra were recorded on Bruker AV III 600 NMR spectrometer and Bruker AV 400 instrument. Solvent signal was used as reference for ^{1}H NMR ($CDCl_3$, 7.26 ppm) and ^{13}C NMR ($CDCl_3$, 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, td = triple doublet, m = multiplet. Infrared (IR) spectra were recorded on a FTIR-8400S spectrometer. High-resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2 HDMS.
Reactions were monitored by Thin Layer Chromatography on plates (GF_{254}) supplied by Yantai Chemicals (China). If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China). Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980).

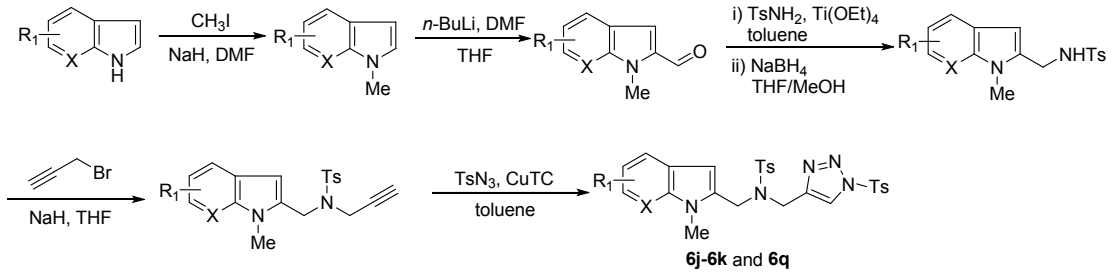
2. Procedure for the Preparation of Triazole Substrates

Procedure A: Triazoles **6a-6i**, **6l-6m** and **6s-6w** were prepared referring to the literature procedures[1-4] as described below.



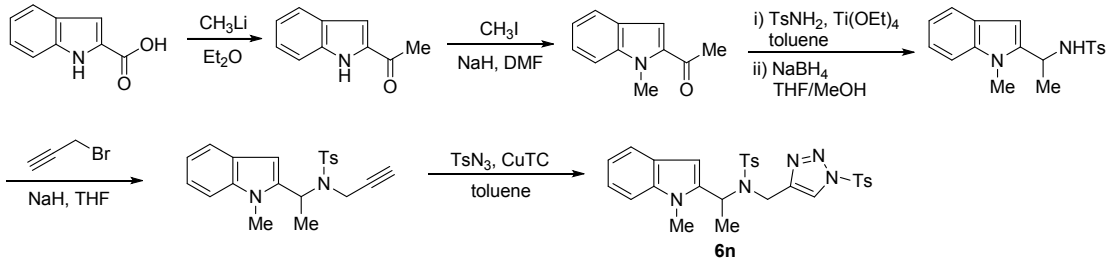
6a-6i, 6l-6m and **6s-6w**

Procedure B: Triazoles **6j-6k** and **6q** were prepared referring to the literature procedures[2-5] as described below.



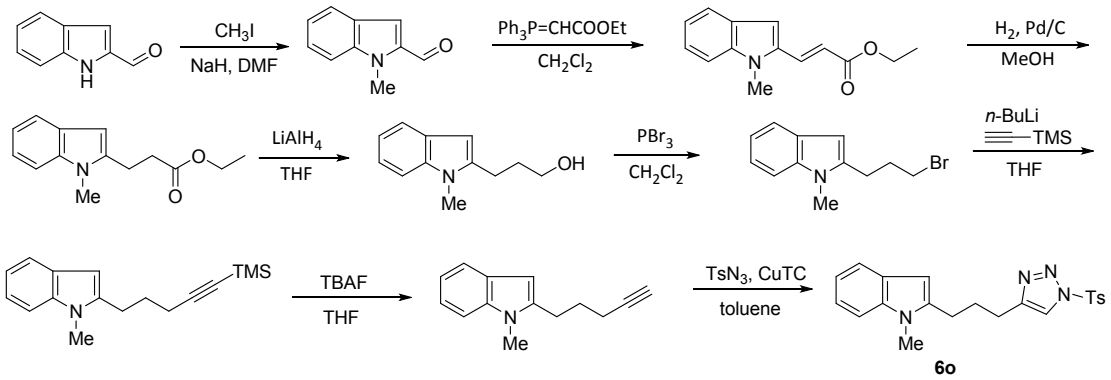
6j-6k and **6q**

Procedure C: Triazole **6n** was prepared referring to the literature procedures[3-4, 6] as described below.

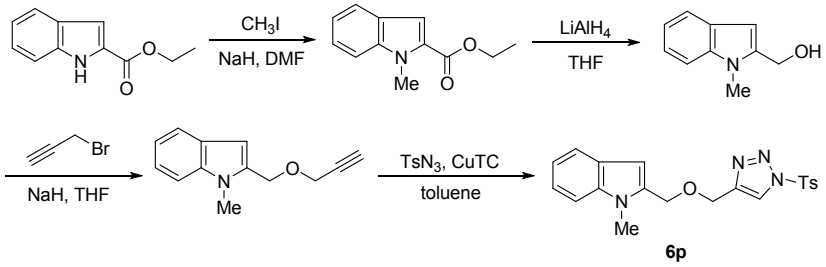


6n

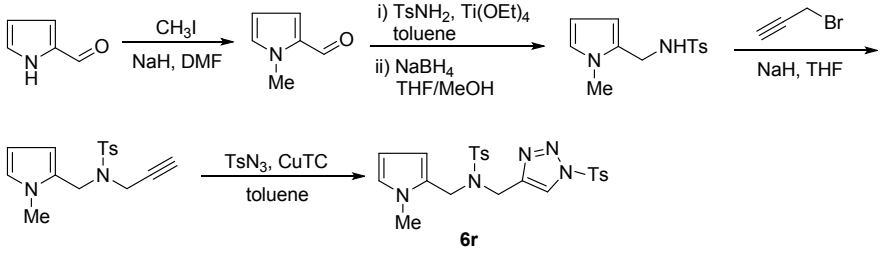
Procedure D: Triazole **6o** was prepared referring to the literature procedures[2, 4, 7-8] as described below.



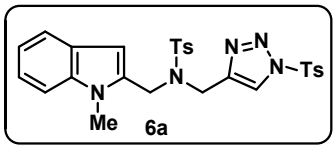
Procedure E: Triazole **6p** was prepared referring to the literature procedures[1, 4, 9] as described below.



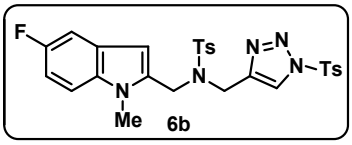
Procedure F: Triazole **6r** was prepared referring to the literature procedures[2-4] as described below.



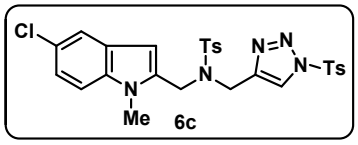
3. Analysis Data of Triazole Substrates



4-methyl-*N*-((1-methyl-1*H*-indol-2-yl)methyl)-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6a): Yield: 90%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.52-7.50 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.26-7.22 (m, 3H), 7.10 (td, *J* = 7.7 Hz, 0.6 Hz, 1H), 6.48 (s, 1H), 4.67 (s, 2H), 4.35 (s, 2H), 3.79 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.5, 144.3, 142.8, 138.4, 136.0, 133.0, 132.3, 130.6, 130.0, 128.8, 127.3, 127.1, 122.4, 120.8, 119.9, 109.5, 104.9, 44.7, 40.7, 30.0, 22.0, 21.7; IR ν_{max} (KBr): 3420, 3152, 2927, 2365, 1594, 1395, 1336, 1194, 1161, 1091, 814, 749 cm^{-1}; HRMS m/z calcd for $C_{27}H_{27}N_5NaO_4S_2$ $[M+Na]^+$: 572.1402; found: 572.1404.

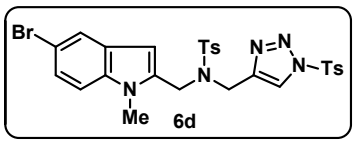


***N*-((5-fluoro-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6b):** Yield: 84%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.51 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 8.9 Hz, 4.3 Hz, 1H), 7.12 (dd, *J* = 9.4 Hz, 2.4 Hz, 1H), 6.97 (td, *J* = 9.1 Hz, 2.4 Hz, 1H), 6.41 (s, 1H), 4.64 (s, 2H), 4.35 (s, 2H), 3.76 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0 (d, *J* = 234.3 Hz), 147.5, 144.4, 142.8, 135.9, 135.0, 134.0, 132.9, 130.5, 130.0, 128.8, 127.3, 127.2 (d, *J* = 10.1 Hz), 122.3, 110.7 (d, *J* = 26.5 Hz), 110.1 (d, *J* = 9.8 Hz), 105.5 (d, *J* = 23.6 Hz), 104.6 (d, *J* = 4.5 Hz), 44.7, 41.0, 30.2, 21.9, 21.6; IR ν_{max} (KBr): 3152, 3066, 2926, 2359, 2332, 1593, 1487, 1394, 1329, 1193, 1154, 1091, 904, 675 cm^{-1}; HRMS m/z calcd for $C_{27}H_{26}FN_5NaO_4S_2$ $[M+Na]^+$: 590.1308; found: 590.1311.

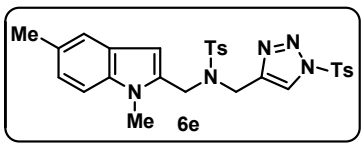


***N*-((5-chloro-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6c):** Yield: 89%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.51 (s, 1H), 7.44 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.19-7.16 (m, 2H), 6.39 (s, 1H), 4.65 (s, 2H), 4.34 (s, 2H), 3.77 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 144.5, 142.7, 136.7, 135.7, 133.7, 132.8, 130.6,

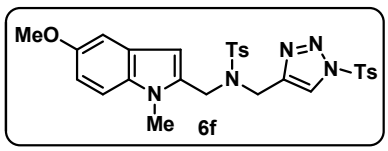
130.0, 128.8, 128.0, 127.3, 125.5, 122.7, 122.3, 120.1, 110.5, 104.3, 44.7, 41.0, 30.2, 22.0, 21.7; IR ν_{max} (KBr): 3149, 2922, 2359, 2241, 1595, 1473, 1393, 1336, 1193, 1179, 1163, 1092, 975 cm^{-1}; HRMS m/z calcd for $C_{27}H_{26}ClN_5NaO_4S_2$ $[M+Na]^+$: 606.1012; found: 606.1016.



***N*-((5-bromo-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6d):** Yield: 79%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.62-7.59 (m, 3H), 7.52 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.30 (dd, *J* = 8.7 Hz, 1.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.39 (s, 1H), 4.65 (s, 2H), 4.34 (s, 2H), 3.77 (s, 3H), 2.46 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 144.5, 142.7, 137.0, 135.9, 133.7, 132.9, 130.6, 130.0, 128.8, 128.7, 127.4, 125.2, 123.3, 122.3, 113.2, 110.9, 104.3, 44.7, 41.0, 30.2, 22.0, 21.7; IR ν_{max} (KBr): 3436, 3147, 2361, 2242, 1595, 1471, 1392, 1336, 1193, 1179, 1162, 1092 cm^{-1}; HRMS m/z calcd for $C_{27}H_{26}BrN_5NaO_4S_2$ $[M+Na]^+$: 650.0507; found: 650.0502.

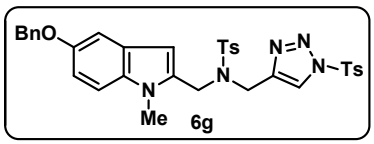


***N*-((1,5-dimethyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6e):** Yield: 83%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.51 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.29 (s, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.07 (dd, *J* = 8.4 Hz, 1.1 Hz, 1H), 6.38 (s, 1H), 4.65 (s, 2H), 4.34 (s, 2H), 3.75 (s, 3H), 2.45 (s, 3H), 2.44 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.9, 144.7, 143.3, 137.3, 136.4, 133.5, 132.6, 131.0, 130.4, 129.5, 129.2, 127.8, 124.5, 122.8, 120.8, 109.6, 104.8, 45.2, 41.2, 30.5, 22.4, 22.1, 21.9; IR ν_{max} (KBr): 3434, 3135, 2921, 2357, 1594, 1405, 1329, 1194, 1178, 1159, 1089, 674, 575 cm^{-1}; HRMS m/z calcd for $C_{28}H_{29}N_5NaO_4S_2$ $[M+Na]^+$: 586.1559; found: 586.1556.

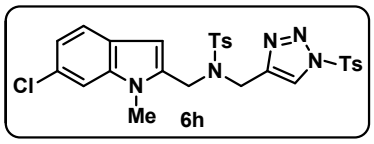


***N*-((5-methoxy-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6f):** Yield: 77%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.50 (s, 1H), 7.35 (d, *J* =

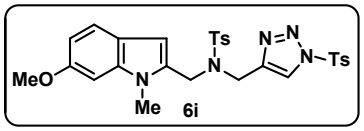
8.4 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.9 Hz, 2.4 Hz, 1H), 6.38 (s, 1H), 4.62 (s, 2H), 4.35 (s, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.4, 147.4, 144.3, 143.0, 135.9, 133.8, 133.0, 132.7, 130.6, 130.0, 128.8, 127.4, 127.4, 122.3, 112.8, 110.2, 104.4, 102.5, 56.0, 44.9, 41.0, 30.1, 22.0, 21.7; IR ν_{max} (KBr): 3366, 3158, 2920, 2849, 2363, 1489, 1398, 1336, 1195, 1162, 668, 587 cm^{-1}; HRMS m/z calcd for $C_{28}H_{29}N_5NaO_5S_2$ $[M+Na]^+$: 602.1508; found: 602.1509.



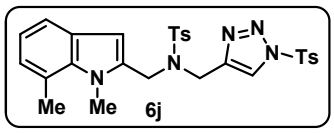
***N*-((5-(benzyloxy)-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6g):** Yield: 93%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.52 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.06 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.40 (s, 1H), 5.09 (s, 2H), 4.63 (s, 2H), 4.36 (s, 2H), 3.75 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.4, 147.4, 144.2, 142.8, 137.7, 135.7, 133.8, 132.8, 132.7, 130.5, 129.9, 128.7, 128.6, 127.8, 127.5, 127.3, 127.2, 122.3, 113.3, 110.1, 104.4, 104.0, 70.8, 44.7, 40.8, 30.0, 21.9, 21.6; IR ν_{max} (KBr): 3155, 3031, 2923, 1594, 1487, 1394, 1330, 1193, 1153, 1092, 901, 754 cm^{-1}; HRMS m/z calcd for $C_{34}H_{33}N_5NaO_5S_2$ $[M+Na]^+$: 678.1821; found: 678.1821.



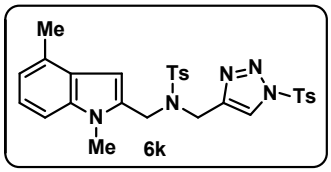
***N*-((6-chloro-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6h):** Yield: 83%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.56 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.25-7.22 (m, 3H), 7.04 (dd, *J* = 8.4 Hz, 1.7 Hz, 1H), 6.45 (s, 1H), 4.63 (s, 2H), 4.34 (s, 2H), 3.70 (s, 3H), 2.46 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 144.4, 142.7, 138.7, 135.9, 133.1, 132.9, 130.6, 130.0, 128.8, 128.4, 127.3, 125.6, 122.4, 121.7, 120.6, 109.5, 105.0, 44.7, 40.8, 30.1, 22.0, 21.7; IR ν_{max} (film): 3436, 2921, 2850, 1595, 1395, 1338, 1194, 1160, 1090, 812, 666 cm^{-1}; HRMS m/z calcd for $C_{27}H_{26}ClN_5NaO_4S_2$ $[M+Na]^+$: 606.1012; found: 606.1016.



***N*-((6-methoxy-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6i):** Yield: 93%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.77 (dd, *J* = 8.5 Hz, 2.2 Hz, 1H), 6.74 (d, *J* = 1.7 Hz, 1H), 6.39 (s, 1H), 4.62 (s, 2H), 4.33 (s, 2H), 3.89 (s, 3H), 3.73 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9, 147.4, 144.2, 142.9, 139.1, 135.9, 133.0, 130.9, 130.5, 129.9, 128.8, 127.3, 122.3, 121.4, 121.3, 110.1, 104.9, 93.0, 55.8, 45.0, 40.8, 30.0, 21.9, 21.7; IR ν_{max} (KBr): 3142, 2942, 2838, 1617, 1402, 1329, 1193, 1176, 1160, 1089, 673, 576 cm^{-1}; HRMS m/z calcd for $C_{28}H_{29}N_5NaO_5S_2$ $[M+Na]^+$: 602.1508; found: 602.1507.

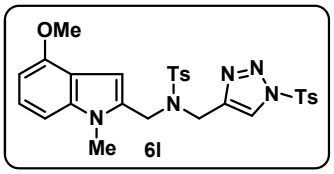


***N*-((1,7-dimethyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6j):** Yield: 95%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.49 (s, 1H), 7.35-7.31 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.98-6.93 (m, 2H), 6.45 (s, 1H), 4.64 (s, 2H), 4.35 (s, 2H), 4.05 (s, 3H), 2.78 (s, 3H), 2.44 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 144.2, 142.9, 137.2, 135.6, 132.8, 132.4, 130.5, 129.9, 128.7, 127.8, 127.3, 125.4, 122.3, 121.5, 119.9, 118.9, 105.6, 45.2, 40.8, 33.1, 21.9, 21.6, 20.3; IR ν_{max} (KBr): 3155, 3049, 2926, 1592, 1392, 1331, 1155, 1091, 965, 750 cm^{-1}; HRMS m/z calcd for $C_{28}H_{29}N_5NaO_4S_2$ $[M+Na]^+$: 586.1559; found: 586.1559.

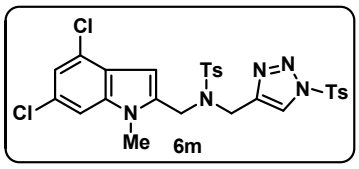


***N*-((1,4-dimethyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6k):** Yield: 96%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.54 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.19-7.14 (m, 2H), 6.92 (d, *J* = 6.2 Hz, 1H), 6.47 (s, 1H), 4.70 (s, 2H), 4.38 (s, 2H), 3.80 (s, 3H), 2.47 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 144.2, 142.8, 138.0, 135.8, 132.8, 131.6, 130.5, 130.2, 129.8, 128.7, 127.2, 126.9, 122.4, 120.0, 107.0, 103.3, 44.7, 40.6, 30.1, 21.9, 21.6, 18.6; IR ν_{max} (KBr): 3417, 3134, 2923, 2357, 1592, 1392, 1347, 1195, 1165, 1089, 971, 675, 585 cm^{-1}; HRMS m/z calcd for $C_{28}H_{29}N_5NaO_4S_2$ $[M+Na]^+$:

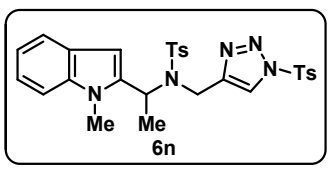
586.1559; found: 586.1560.



***N*-((4-methoxy-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6l):** Yield: 88%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.58 (s, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 4.66 (s, 2H), 4.34 (s, 2H), 3.90 (s, 3H), 3.75 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.2, 147.4, 144.1, 142.7, 139.7, 135.7, 132.9, 130.6, 130.5, 129.8, 128.7, 127.2, 123.2, 122.3, 117.6, 102.9, 102.1, 99.6, 55.3, 44.7, 40.4, 30.2, 21.9, 21.6; IR ν_{max} (KBr): 3135, 2930, 2836, 1582, 1501, 1391, 1352, 1258, 1195, 1165, 1089, 676 cm^{-1}; HRMS m/z calcd for $C_{28}H_{29}N_5NaO_5S_2$ $[M+Na]^+$: 602.1508; found: 602.1508.

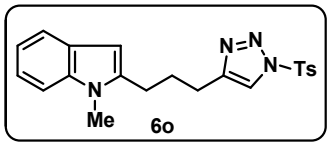


***N*-((4,6-dichloro-1-methyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6m):** Yield: 90%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.61 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.13 (s, 1H), 7.06 (s, 1H), 6.48 (s, 1H), 4.65 (s, 2H), 4.34 (s, 2H), 3.69 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 144.5, 142.4, 138.8, 135.7, 134.0, 132.8, 130.6, 130.0, 128.8, 128.1, 127.2, 126.3, 124.6, 122.5, 120.1, 108.3, 103.3, 44.5, 40.7, 30.5, 22.0, 21.7; IR ν_{max} (KBr): 3380, 3154, 2920, 2359, 1387, 1337, 1195, 1163, 1089, 963, 667, 587 cm^{-1}; HRMS m/z calcd for $C_{27}H_{25}Cl_2N_5NaO_4S_2$ $[M+Na]^+$: 640.0623; found: 640.0629.



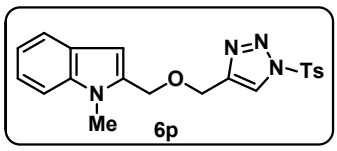
4-methyl-*N*-(1-(1-methyl-1*H*-indol-2-yl)ethyl)-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6n): Yield: 56%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.30-7.26 (m, 4H), 7.25-7.23 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.12 (td, *J* = 7.8 Hz, 0.8 Hz, 1H), 6.47 (s, 1H), 5.58 (q, *J* = 6.9 Hz, 1H), 4.41 (d, *J* = 16.7 Hz, 1H), 4.26 (d, *J* = 16.7 Hz, 1H), 3.71 (s, 3H), 2.44 (s, 3H), 2.43

(s, 3H), 1.43 (d, J = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.1, 145.1, 144.2, 137.8, 137.2, 137.1, 133.0, 130.4, 130.0, 128.7, 127.6, 126.8, 122.7, 122.1, 120.8, 119.9, 109.4, 102.4, 49.9, 38.2, 29.9, 21.9, 21.7, 16.3; IR ν_{max} (KBr): 3153, 2982, 2926, 2359, 1592, 1467, 1389, 1331, 1196, 1090, 1009, 688, 583 cm^{-1}; HRMS m/z calcd for $C_{28}H_{29}N_5NaO_4S_2$ $[M+Na]^+$: 586.1559; found: 586.1559.



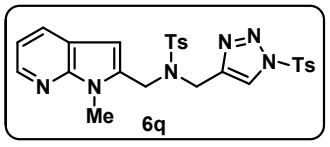
6o

1-methyl-2-(3-(1-tosyl-1*H*-1,2,3-triazol-4-yl)propyl)-1*H*-indole (6o): Yield: 71%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.1 Hz, 2H), 7.90 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.2 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.28 (s, 1H), 3.63 (s, 3H), 2.86 (t, J = 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 2.44 (s, 3H), 2.15-2.09 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 147.2, 140.0, 137.4, 133.2, 130.5, 128.6, 127.8, 120.7, 120.6, 119.8, 119.3, 108.9, 99.1, 29.5, 27.7, 26.1, 24.8, 21.8; IR ν_{max} (film): 3437, 2918, 2849, 1594, 1467, 1389, 1193, 1179, 1091, 1009, 671 cm^{-1}; HRMS m/z calcd for $C_{21}H_{23}N_4O_2S$ $[M+H]^+$: 395.1542; found: 395.1544.



6p

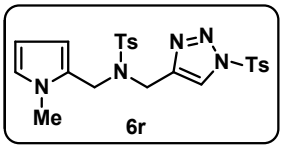
1-methyl-2-(((1-tosyl-1*H*-1,2,3-triazol-4-yl)methoxy)methyl)-1*H*-indole (6p): Yield: 91%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 1H), 7.25 (dd, J = 7.8 Hz, 7.2 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 6.52 (s, 1H), 4.75 (s, 2H), 4.63 (s, 2H), 3.74 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.5, 144.9, 138.2, 134.8, 132.9, 130.5, 128.8, 127.1, 122.4, 122.2, 120.9, 119.6, 109.3, 103.6, 64.8, 62.2, 29.9, 21.9; IR ν_{max} (KBr): 3141, 2926, 1928, 1590, 1471, 1385, 1193, 1172, 1085, 673, 584 cm^{-1}; HRMS m/z calcd for $C_{20}H_{20}N_4NaO_3S$ $[M+Na]^+$: 419.1154; found: 419.1151.



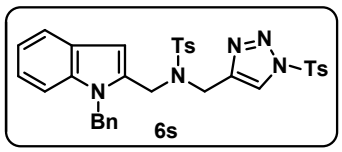
6q

4-methyl-*N*-((1-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-2-yl)methyl)-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6q): Yield: 79%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, J = 4.6 Hz, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 7.9 Hz, 2H), 7.58 (s, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.02 (dd, J = 7.5 Hz, 4.8 Hz, 1H), 6.45 (s, 1H),

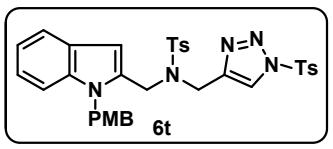
4.68 (s, 2H), 4.36 (s, 2H), 3.84 (s, 3H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.0, 147.6, 144.4, 143.4, 142.4, 135.9, 133.1, 132.8, 130.6, 129.9, 128.8, 128.6, 127.3, 122.6, 119.7, 116.1, 102.6, 44.6, 40.7, 28.5, 21.9, 21.6; IR ν_{max} (KBr): 3140, 3028, 2359, 1596, 1458, 1391, 1355, 1311, 1196, 1166, 1088, 811, 688, 585 cm^{-1}; HRMS m/z calcd for $C_{26}H_{27}N_6O_4S_2$ $[M+H]^+$: 551.1535; found: 551.1539.



4-methyl-*N*-((1-methyl-1*H*-pyrrol-2-yl)methyl)-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6r): Yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.36 (s, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.45 (s, 1H), 6.01 (s, 1H), 5.90 (s, 1H), 4.38 (s, 2H), 4.28 (s, 2H), 3.51 (s, 3H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 144.0, 143.4, 135.7, 133.0, 130.4, 129.9, 128.7, 127.2, 124.7, 123.9, 122.1, 111.7, 107.1, 44.7, 41.2, 33.8, 21.9, 21.6; IR ν_{max} (film): 3146, 2924, 2854, 1595, 1395, 1335, 1195, 1161, 1091, 1009, 814, 670 cm^{-1}; HRMS m/z calcd for $C_{23}H_{25}N_5NaO_4S_2$ $[M+Na]^+$: 522.1246; found: 522.1244.

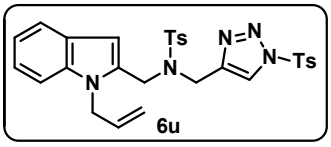


***N*-((1-benzyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6s):** Yield: 95%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.59-7.56 (m, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.26-7.19 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.97 (dd, *J* = 7.8 Hz, 1.5 Hz, 2H), 6.62 (s, 1H), 5.50 (s, 2H), 4.60 (s, 2H), 4.35 (s, 2H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 144.1, 142.7, 138.2, 137.8, 135.8, 132.9, 132.2, 130.5, 129.8, 128.7, 127.3, 127.2, 126.1, 122.6, 122.5, 120.9, 120.0, 110.1, 105.7, 46.4, 44.5, 40.7, 21.9, 21.5; IR ν_{max} (KBr): 3137, 3029, 2930, 1595, 1390, 1330, 1197, 1163, 1091, 897, 676, 583 cm^{-1}; HRMS m/z calcd for $C_{33}H_{31}N_5NaO_4S_2$ $[M+Na]^+$: 648.1715; found: 648.1719.

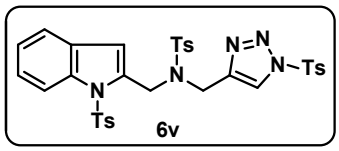


***N*-((1-(4-methoxybenzyl)-1*H*-indol-2-yl)methyl)-4-methyl-*N*-**

((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6t): Yield: 92%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.57 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.21 (td, *J* = 7.2 Hz, 0.9 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.58 (s, 1H), 5.42 (s, 2H), 4.58 (s, 2H), 4.35 (s, 2H), 3.75 (s, 3H); 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.9, 147.4, 144.1, 142.7, 138.2, 135.8, 132.9, 132.2, 130.5, 129.9, 129.8, 128.7, 127.4, 127.3, 127.3, 122.6, 122.5, 120.8, 120.0, 114.1, 110.1, 105.7, 55.3, 45.9, 44.6, 40.8, 21.9, 21.6; IR ν_{max} (KBr): 3418, 3164, 2932, 2359, 1595, 1513, 1395, 1337, 1155, 1089, 674, 582 cm^{-1}; HRMS m/z calcd for $C_{34}H_{33}N_5NaO_5S_2$ $[M+Na]^+$: 678.1821; found: 678.1819.

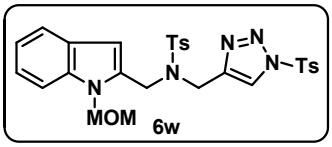


***N*-((1-allyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6u):** Yield: 78%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.56 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.24-7.21 (m, 3H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.53 (s, 1H), 5.97-5.90 (m, 1H), 5.10 (dd, *J* = 10.3 Hz, 1.1 Hz, 1H), 4.89-4.86 (m, 2H), 4.85 (dd, *J* = 17.1 Hz, 1.0 Hz, 1H), 4.64 (s, 2H), 4.38 (s, 2H), 2.44 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 144.2, 142.6, 137.8, 135.8, 133.5, 132.9, 131.9, 130.5, 129.8, 128.7, 127.3, 122.5, 122.4, 120.8, 119.9, 116.3, 109.9, 105.3, 45.4, 44.5, 40.7, 21.9, 21.6; IR ν_{max} (KBr): 3393, 3137, 2922, 2359, 2330, 1595, 1461, 1394, 1201, 1162, 673, 584 cm^{-1}; HRMS m/z calcd for $C_{29}H_{29}N_5NaO_4S_2$ $[M+Na]^+$: 598.1559; found: 598.1559.



4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)-*N*-((1-tosyl-1*H*-indol-2-yl)methyl)benzenesulfonamide (6v): Yield: 86%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.26-7.22 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.55 (s, 1H), 4.91 (s, 2H), 4.61 (s, 2H), 2.42 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.5, 145.2, 144.3, 142.8, 137.4, 136.8, 136.1, 135.2, 132.9, 130.6, 130.1, 129.9, 129.4, 128.7, 127.4, 126.5, 124.7, 123.9, 123.0, 120.9, 114.6, 111.4, 46.6, 42.8, 21.9, 21.6; IR ν_{max} (KBr): 3420, 3148, 3066, 2922, 2361, 2332, 1595, 1451, 1373, 1341, 1147, 1090 cm^{-}

[1]; HRMS m/z calcd for $C_{33}H_{32}N_5O_6S_3$ $[M+H]^+$: 690.1515; found: 690.1516.

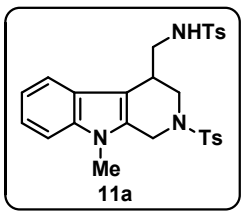


***N*-((1-(methoxymethyl)-1*H*-indol-2-yl)methyl)-4-methyl-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)benzenesulfonamide (6w):** Yield: 87%; [1]H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.63 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.25-7.19 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 5.56 (s, 2H), 4.69 (s, 2H), 4.37 (s, 2H), 3.29 (s, 3H), 2.42 (s, 3H), 2.41 (s, 3H); [13]C NMR (100 MHz, $CDCl_3$) δ 147.4, 144.3, 142.7, 138.4, 135.8, 132.8, 132.3, 130.5, 129.9, 128.7, 127.4, 127.3, 123.0, 122.6, 120.9, 120.6, 110.0, 106.7, 74.0, 55.9, 44.5, 41.0, 21.9, 21.6; IR ν_{max} (film): 3056, 2928, 2357, 1595, 1460, 1395, 1342, 1195, 1160, 1091, 1010, 740 cm^{-1}; HRMS m/z calcd for $C_{28}H_{29}N_5NaO_5S_2$ $[M+Na]^+$: 602.1508; found: 602.1506.

4. General Procedures for Rhodium(II)-Catalyzed Intramolecular Annulation of 1-Sulfonyl-1,2,3-Triazoles with Indoles

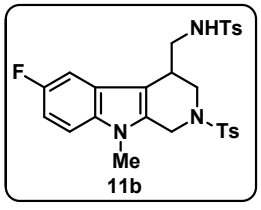
A 10 mL pressure tube, fitted with a rubber septum, was charged with triazole (0.20 mmol, 1.0 equiv.), $Rh_2(OOct)_4$ (1.6 mg, 0.002 mmol, 0.01 equiv.). The reaction vessel was added freshly distilled 1,2-dichloroethane (1.0 mL) and then was sealed with a teflon screwcap and placed in an oil bath preheated to 140 °C. The resulting solution was heated at this temperature for 5 min, then $NaBH_3CN$ (25.1 mg, 0.4 mmol, 2.0 equiv.) was added, and the reaction mixture was stirred at 80 °C for 3 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (eluent: petroleum ether/EtOAc) to give the product **11a-11w**.

5. Analysis Data of Annulation Products



11a

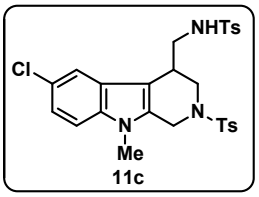
4-methyl-*N*-((9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)benzenesulfonamide (11a): Yield: 86%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.20 (td, *J* = 8.0 Hz, 0.9 Hz, 1H), 7.11 (td, *J* = 8.0 Hz, 0.8 Hz, 1H), 5.10 (t, *J* = 6.5 Hz, 1H), 4.68 (d, *J* = 14.4 Hz, 1H), 4.00 (dd, *J* = 12.3 Hz, 2.2 Hz, 1H), 3.91 (d, *J* = 14.3 Hz, 1H), 3.56 (s, 3H), 3.40-3.32 (m, 2H), 3.13 (ddd, *J* = 13.8 Hz, 9.2 Hz, 5.8 Hz, 1H), 2.84 (dd, *J* = 12.3 Hz, 3.4 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 143.4, 137.3, 137.2, 133.9, 130.9, 130.1, 129.8, 127.5, 127.1, 125.7, 121.9, 119.9, 118.4, 109.1, 108.0, 46.0, 44.9, 43.0, 34.1, 29.6, 21.7, 21.6; IR ν_{max} (KBr): 3273, 2922, 2851, 2359, 2330, 1718, 1348, 1325. 1163, 1154, 1088, 753, 683, 547 cm^{-1}; HRMS m/z calcd for $C_{27}H_{29}N_3NaO_4S_2$ $[M+Na]^+$: 546.1497; found: 546.1498.



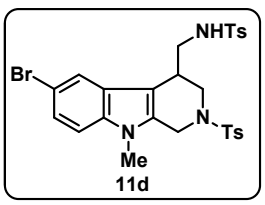
11b

***N*-((6-fluoro-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11b):** Yield: 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.15 (dd, *J* =

8.9 Hz, 4.2 Hz, 1H), 7.10 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 6.93 (td, *J* = 9.0 Hz, 2.4 Hz, 1H), 4.94 (t, *J* = 6.3 Hz, 1H), 4.64 (d, *J* = 14.5 Hz, 1H), 3.97 (dd, *J* = 12.4 Hz, 2.6 Hz, 1H), 3.92 (d, *J* = 14.5 Hz, 1H), 3.56 (s, 3H), 3.35-3.31 (m, 1H), 3.28 (ddd, *J* = 13.8 Hz, 7.2 Hz, 4.2 Hz, 1H), 3.10 (ddd, *J* = 14.1 Hz, 9.3 Hz, 5.7 Hz, 1H), 2.87 (dd, *J* = 12.4 Hz, 3.4 Hz, 1H), 2.45 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1 (d, *J* = 236.3 Hz), 144.3, 143.7, 137.0, 133.9, 133.9, 132.7, 130.2, 129.9, 127.5, 127.2, 125.9 (d, *J* = 9.7 Hz), 110.2 (d, *J* = 26.3 Hz), 109.8 (d, *J* = 9.7 Hz), 108.0 (d, *J* = 4.5 Hz), 103.5 (d, *J* = 23.6 Hz), 46.0, 44.6, 43.1, 34.1, 29.9, 21.7, 21.6; IR ν_{max} (KBr): 3420, 3282, 2361, 1487, 1339, 1160, 1089, 731, 552 cm^{-1}; HRMS m/z calcd for $C_{27}H_{28}FN_3NaO_4S_2$ $[M+Na]^+$: 564.1403; found: 564.1401.

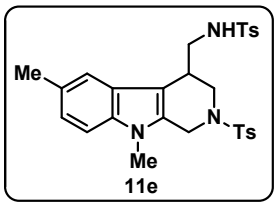


***N*-((6-chloro-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11c):** Yield: 77%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.74 (m, 4H), 7.41-7.36 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.16-7.12 (m, 2H), 4.93 (t, *J* = 6.2 Hz, 1H), 4.64 (d, *J* = 14.6 Hz, 1H), 3.98 (dd, *J* = 12.5 Hz, 1.9 Hz, 1H), 3.92 (d, *J* = 14.6 Hz, 1H), 3.56 (s, 3H), 3.36-3.32 (m, 1H), 3.29-3.24 (m, 1H), 3.10 (ddd, *J* = 13.9 Hz, 9.4 Hz, 5.8 Hz, 1H), 2.86 (dd, *J* = 12.4 Hz, 3.2 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.3, 143.7, 136.8, 135.7, 133.8, 132.5, 130.2, 130.0, 127.5, 127.2, 126.6, 125.8, 122.2, 117.8, 110.2, 107.7, 45.9, 44.6, 43.0, 33.8, 29.8, 21.7, 21.7; IR ν_{max} (KBr): 3420, 3292, 2924, 2363, 1597, 1475, 1339, 1158, 1089, 814, 713, 553 cm^{-1}; HRMS m/z calcd for $C_{27}H_{28}ClN_3NaO_4S_2$ $[M+Na]^+$: 580.1107; found: 580.1111.



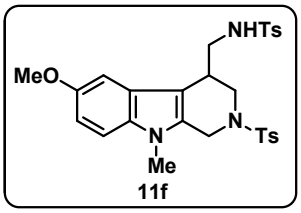
***N*-((6-bromo-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11d):** Yield: 83%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.74 (m, 4H), 7.57 (d, *J* = 1.7 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.26 (dd, *J* = 8.7 Hz, 1.7 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 4.94 (t, *J* = 6.4 Hz, 1H), 4.65 (d, *J* = 14.5 Hz, 1H), 3.99 (dd, *J* = 12.5 Hz, 2.6 Hz, 1H), 3.91 (d, *J* = 14.3 Hz, 1H), 3.55 (s, 3H), 3.36-3.32 (m, 1H), 3.26 (ddd, *J* = 13.9 Hz, 7.0 Hz, 4.1 Hz, 1H), 3.09 (ddd, *J* = 14.4 Hz, 9.6 Hz, 5.9 Hz, 1H), 2.85 (dd, *J* = 12.5 Hz, 3.4 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.3, 143.7,

136.8, 136.0, 133.9, 132.4, 130.2, 130.0, 127.5, 127.3, 127.3, 124.8, 120.9, 113.3, 110.6, 107.7, 45.9, 44.7, 43.0, 33.8, 29.8, 21.7, 21.7; IR ν_{max} (KBr): 3389, 3292, 2924, 2361, 2332, 1473, 1340, 1158, 1089 cm^{-1}; HRMS m/z calcd for $C_{27}H_{28}BrN_3NaO_4S_2$ $[M+Na]^+$: 624.0602; found: 624.0604.



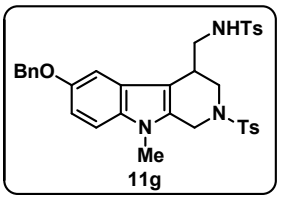
11e

***N*-((6,9-dimethyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (6e):** Yield: 88%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.78-7.75 (m, 4H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.30-7.27 (m, 3H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.02 (dd, *J* = 8.3 Hz, 1.0 Hz, 1H), 5.06 (dd, *J* = 6.9 Hz, 5.8 Hz, 1H), 4.65 (d, *J* = 14.3 Hz, 1H), 3.98 (dd, *J* = 12.5 Hz, 2.1 Hz, 1H), 3.91 (d, *J* = 14.3 Hz, 1H), 3.54 (s, 3H), 3.38-3.31 (m, 2H), 3.12 (ddd, *J* = 15.1 Hz, 10.6 Hz, 7,7 Hz, 1H), 2.85 (dd, *J* = 12.4 Hz, 3.2 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 143.4, 137.1, 135.7, 133.9, 131.0, 130.1, 129.8, 129.2, 127.5, 127.2, 125.8, 123.5, 118.1, 108.9, 107.4, 46.0, 44.9, 43.1, 34.0, 29.6, 21.7, 21.6, 21.5; IR ν_{max} (KBr): 3293, 2921, 2359, 2325, 1597, 1332, 1159, 1089, 814, 668, 549 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_4S_2$ $[M+Na]^+$: 560.1654; found: 560.1659.

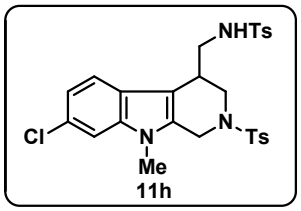


11f

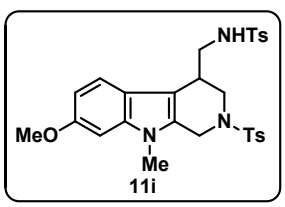
***N*-((6-methoxy-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11f):** Yield: 80%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.84 (dd, *J* = 8.8 Hz, 2.3 Hz, 1H), 5.05 (t, *J* = 6.5 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H), 4.00 (dd, *J* = 12.4 Hz, 2.1 Hz, 1H), 3.87-3.84 (m, 4H), 3.54 (s, 3H), 3.39-3.35 (m, 1H), 3.33-3.28 (m, 1H), 3.14 (ddd, *J* = 14.1 Hz, 9.1 Hz, 6.2 Hz, 1H), 2.82 (dd, *J* = 12.3 Hz, 3.4 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.5, 144.2, 143.5, 137.2, 133.9, 132.5, 131.3, 130.1, 129.9, 127.5, 127.1, 126.1, 112.0, 109.9, 107.7, 100.4, 56.0, 46.1, 45.1, 43.1, 34.2, 29.7, 21.7, 21.6; IR ν_{max} (KBr): 3428, 3303, 2926, 1596, 1487, 1330, 1160, 1089, 816, 730, 552 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_5S_2$ $[M+Na]^+$: 576.1603; found: 576.1605.



***N*-((6-(benzyloxy)-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11g):** Yield: 76%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.71 (m, 4H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.41-7.35 (m, 4H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.15-7.11 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 5.10 (s, 2H), 4.98 (t, *J* = 5.9 Hz, 1H), 4.66 (d, *J* = 14.4 Hz, 1H), 3.98 (d, *J* = 12.3 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 3.53 (s, 3H), 3.37-3.28 (m, 2H), 3.17-3.10 (m, 1H), 2.82 (d, *J* = 12.2 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 144.2, 143.5, 137.6, 137.1, 133.8, 132.6, 131.4, 130.1, 129.9, 128.7, 127.9, 127.8, 127.5, 127.1, 126.0, 112.6, 109.9, 107.6, 101.9, 70.9, 46.1, 45.0, 43.1, 34.1, 29.7, 21.7, 21.6; IR ν_{max} (KBr): 3299, 2925, 2862, 1597, 1484, 1340, 1161, 1088, 923, 676, 551 cm^{-1}; HRMS m/z calcd for $C_{34}H_{35}N_3NaO_5S_2$ $[M+Na]^+$: 652.1916; found: 652.1918.

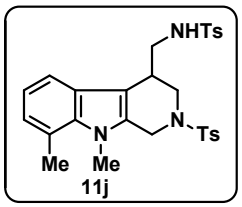


***N*-((7-chloro-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11h):** Yield: 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 1.6 Hz, 1H), 7.07 (dd, *J* = 8.4 Hz, 1.7 Hz, 1H), 4.96 (t, *J* = 6.4 Hz, 1H), 4.67 (d, *J* = 14.5 Hz, 1H), 4.00 (dd, *J* = 12.4 Hz, 2.1 Hz, 1H), 3.88 (d, *J* = 14.5 Hz, 1H), 3.54 (s, 3H), 3.38-3.34 (m, 1H), 3.29 (ddd, *J* = 13.8 Hz, 7.0 Hz, 4.6 Hz, 1H), 3.11 (ddd, *J* = 14.2 Hz, 9.4 Hz, 6.1 Hz, 1H), 2.82 (dd, *J* = 12.4 Hz, 3.4 Hz, 1H), 2.45 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.3, 143.6, 137.8, 137.2, 134.0, 131.7, 130.2, 129.9, 128.1, 127.5, 127.1, 124.3, 120.7, 119.3, 109.3, 108.4, 45.9, 44.9, 43.0, 34.1, 29.8, 21.7, 21.6; IR ν_{max} (KBr): 3334, 2919, 2848, 1647, 1479, 1326, 1158, 1088, 943, 813, 669, 572 cm^{-1}; HRMS m/z calcd for $C_{27}H_{28}ClN_3NaO_4S_2$ $[M+Na]^+$: 580.1107; found: 580.1109.

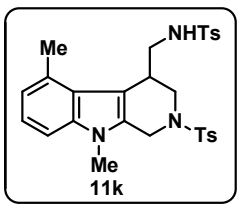


***N*-((7-methoxy-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11i):** Yield: 78%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.39-7.36 (m, 3H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.76 (dd, *J* = 8.7 Hz, 2.3 Hz, 1H), 6.71 (d, *J* = 2.3 Hz, 1H), 4.95 (dd, *J* = 6.9 Hz, 5.8 Hz, 1H), 4.62 (d, *J* =

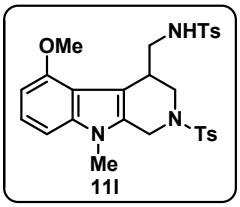
14.2 Hz, 1H), 3.94 (dd, *J* = 12.4 Hz, 2.1 Hz, 1H), 3.90 (d, *J* = 14.2 Hz, 1H), 3.86 (s, 3H), 3.51 (s, 3H), 3.36-3.29 (m, 2H), 3.16-3.10 (m, 1H), 2.85 (dd, *J* = 12.2 Hz, 3.2 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.6, 144.2, 143.5, 138.1, 137.2, 134.0, 130.1, 129.9, 129.7, 127.5, 127.1, 120.1, 119.0, 109.3, 107.8, 93.4, 55.9, 46.0, 45.0, 43.0, 34.1, 29.7, 21.7, 21.6; IR ν_{max} (KBr): 3285, 2922, 1623, 1597, 1330, 1164, 1088, 950, 669, 553 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_5S_2$ $[M+Na]^+$: 576.1603; found: 576.1603.



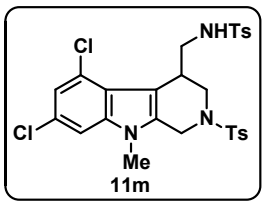
***N*-((8,9-dimethyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11j):** Yield: 79%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.39-7.36 (m, 3H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.1 Hz, 1H), 5.00 (dd, *J* = 6.8 Hz, 5.7 Hz, 1H), 4.68 (d, *J* = 14.3 Hz, 1H), 4.02 (d, *J* = 12.3 Hz, 1H), 3.85 (d, *J* = 14.3 Hz, 1H), 3.81 (s, 3H), 3.37-3.30 (m, 2H), 3.12-3.06 (m, 1H), 2.78 (dd, *J* = 12.3 Hz, 2.7 Hz, 1H), 2.72 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 143.5, 137.2, 136.1, 134.0, 131.2, 130.2, 129.9, 127.5, 127.1, 126.5, 125.0, 121.3, 120.2, 116.4, 108.2, 45.8, 44.7, 43.2, 34.1, 32.8, 21.7, 21.6, 20.2; IR ν_{max} (KBr): 3392, 3291, 2924, 2363, 1597, 1460, 1408, 1332, 1158, 1093, 819, 681, 552 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_4S_2$ $[M+Na]^+$: 560.1654; found: 560.1652.



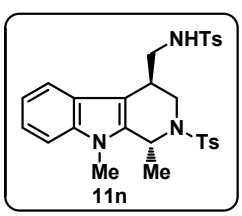
***N*-((5,9-dimethyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11k):** Yield: 64%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.09-7.06 (m, 2H), 6.88-6.85 (m, 1H), 5.29 (dd, *J* = 7.1 Hz, 6.4 Hz, 1H), 4.84 (d, *J* = 14.4 Hz, 1H), 4.21 (d, *J* = 12.1 Hz, 1H), 3.85 (d, *J* = 14.4 Hz, 1H), 3.56-3.52 (m, 4H), 3.41 (ddd, *J* = 14.2 Hz, 7.9 Hz, 3.9 Hz, 1H), 3.03 (ddd, *J* = 14.4 Hz, 11.0 Hz, 5.8 Hz, 1H), 2.73-2.67 (m, 4H), 2.46 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 143.4, 137.4, 137.3, 134.1, 130.3, 130.2, 130.1, 129.8, 127.4, 127.1, 124.6, 121.9, 121.4, 108.7, 106.8, 45.8, 45.5, 43.1, 35.2, 29.6, 21.7, 21.6, 19.8; IR ν_{max} (KBr): 3280, 2924, 2259, 1597, 1458, 1333, 1160, 1090, 814, 669, 548 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_4S_2$ $[M+Na]^+$: 560.1654; found: 560.1658.



***N*-((5-methoxy-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11l):** Yield: 65%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 5.40 (t, *J* = 6.1 Hz, 1H), 4.68 (d, *J* = 14.3 Hz, 1H), 4.02 (d, *J* = 12.4 Hz, 1H), 3.98 (s, 3H), 3.80 (d, *J* = 14.3 Hz, 1H), 3.58-3.52 (m, 1H), 3.50 (s, 3H), 3.48-3.44 (m, 1H), 3.06 (ddd, *J* = 13.0 Hz, 8.9 Hz, 5.1 Hz, 1H), 2.69 (dd, *J* = 12.4 Hz, 2.6 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5, 144.1, 142.8, 138.6, 137.5, 134.0, 130.1, 129.5, 129.0, 127.5, 127.0, 122.7, 116.0, 108.0, 102.5, 99.9, 55.2, 46.1, 45.9, 43.0, 34.5, 29.8, 21.7, 21.6; IR ν_{max} (KBr): 3431, 3294, 2931, 1597, 1500, 1336, 1325, 1154, 1089, 817, 670 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_5S_2$ $[M+Na]^+$: 576.1603; found: 576.1602.



***N*-((5,7-dichloro-9-methyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11m):** Yield: 53%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79-7.75 (m, 4H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.27-7.26 (m, 2H), 7.11 (s, 1H), 7.06 (s, 1H), 5.14 (t, *J* = 6.6 Hz, 1H), 4.79 (d, *J* = 14.6 Hz, 1H), 4.20 (d, *J* = 12.5 Hz, 1H), 3.81 (d, *J* = 14.6 Hz, 1H), 3.64 (d, *J* = 10.0 Hz, 1H), 3.60-3.54 (m, 1H), 3.52 (s, 3H), 3.02-2.96 (m, 1H), 2.67 (d, *J* = 12.2 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.4, 143.4, 138.3, 137.3, 134.0, 132.5, 130.2, 129.8, 127.7, 127.5, 127.3, 126.1, 122.1, 120.9, 108.8, 108.0, 45.5, 43.0, 34.2, 30.0, 21.7, 21.7; IR ν_{max} (KBr): 3256, 2921, 2363, 1333, 1162, 947, 811, 668, 551 cm^{-1}; HRMS m/z calcd for $C_{27}H_{27}Cl_2N_3NaO_4S_2$ $[M+Na]^+$: 614.0718; found: 614.0718.



***N*-((1,9-dimethyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11n):** Yield: 70%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.27-7.25 (m, 3H), 7.22 (dd, *J* = 7.9 Hz, 7.1 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 5.25 (q, *J* = 6.6 Hz, 1H), 5.20 (dd, *J* = 7.2

Hz, 5.5 Hz, 1H), 4.14 (d, J = 13.6 Hz, 1H), 3.60 (s, 3H), 3.37-3.30 (m, 2H), 3.27 (dd, J = 13.6 Hz, 2.4 Hz, 1H), 2.89-2.83 (m, 1H), 2.46 (s, 3H), 2.38 (s, 3H), 1.22 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.8, 143.4, 138.4, 137.5, 137.3, 136.0, 130.1, 129.8, 127.0, 126.9, 125.7, 122.1, 120.0, 118.5, 109.3, 107.8, 48.1, 44.5, 40.2, 34.4, 30.1, 21.7, 21.6, 18.3; IR ν_{max} (film): 3297, 3056, 2980, 2926, 1733, 1597, 1471, 1330, 1159, 1090, 814, 745 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_4S_2$ $[M+Na]^+$: 560.1654; found: 560.1656.

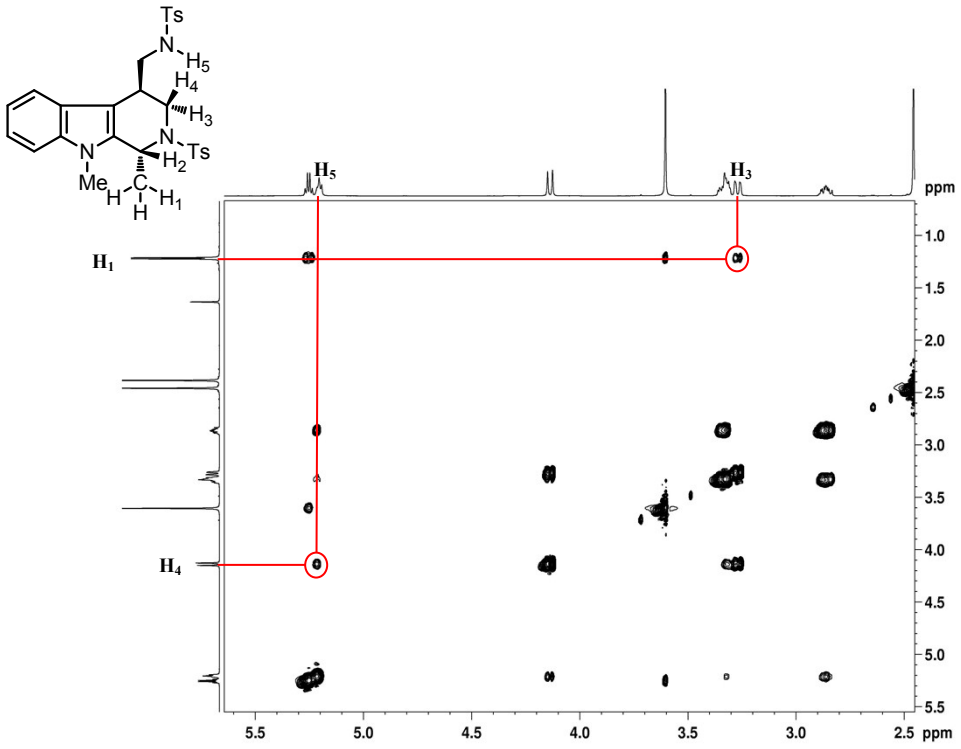
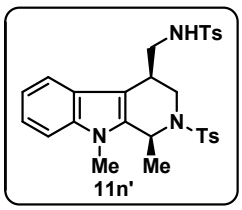


Figure S5-1 The NOESY spectrum for **11n** ($CDCl_3$, 600 MHz)



***N*-((-1,9-dimethyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11n′):** Yield: 12%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60-7.57 (m, 4H), 7.29 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.2 Hz, 1H), 7.18 (ddd, J = 8.2 Hz, 7.0 Hz, 1.1 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 7.8 Hz, 1H), 6.90 (ddd, J = 7.8 Hz, 7.0 Hz, 0.8 Hz, 1H), 5.23 (q, J = 6.8 Hz, 1H), 4.13 (dd, J = 9.2 Hz, 3.5 Hz, 1H), 3.98 (dd, J = 14.2 Hz, 6.4 Hz, 1H), 3.65 (s, 3H), 3.40 (dd, J = 14.2 Hz, 10.7 Hz, 1H), 3.36-3.28 (m, 2H), 3.21-3.16 (m, 1H), 2.45 (s, 3H), 2.26 (s, 3H), 1.50 (d, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.8, 143.6, 138.4, 137.5, 137.2, 136.0,

129.9, 129.6, 127.3, 126.9, 125.0, 122.0, 119.9, 118.3, 109.5, 104.5, 47.5, 43.6, 41.5, 32.4, 29.8, 21.7, 21.5, 20.4; IR ν_{max} (film): 3272, 2920, 1470, 1326, 1157, 1088, 1018, 812, 664 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_4S_2$ $[M+Na]^+$: 560.1654; found: 560.1654.

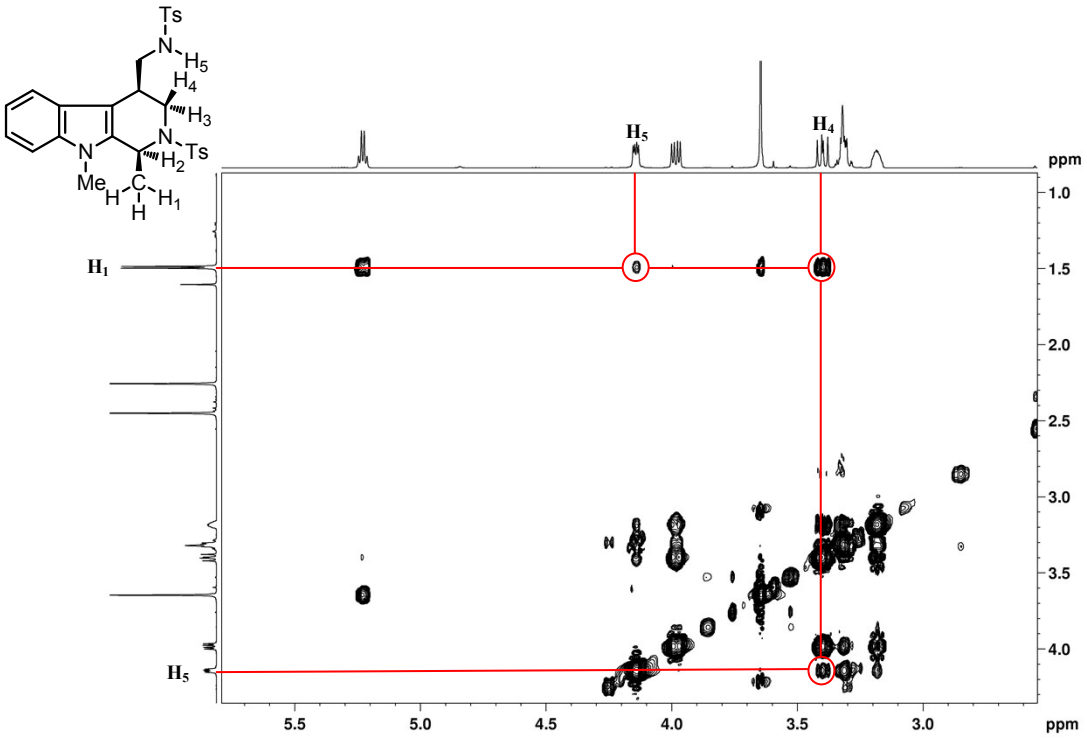
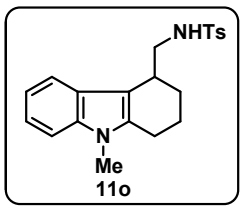
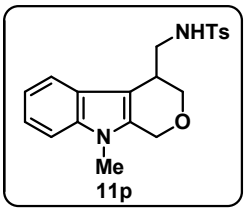


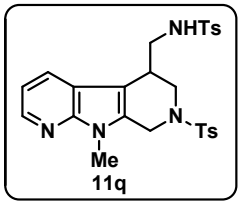
Figure S5-2 The NOESY spectrum for **11n′** ($CDCl_3$, 600 MHz)



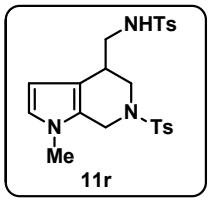
4-methyl-*N*-((9-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)methyl)benzenesulfonamide (11o): Yield: 53%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 7.25-7.24 (m, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 4.29 (t, J = 5.4 Hz, 1H), 3.61 (s, 3H), 3.36-3.31 (m, 1H), 3.28-3.23 (m, 1H), 3.23-3.19 (m, 1H), 2.72-2.63 (m, 2H), 2.43 (s, 3H), 2.02-1.96 (m, 1H), 1.95-1.80 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 137.9, 137.0, 136.7, 129.8, 127.3, 126.1, 120.9, 119.3, 117.9, 109.0, 107.8, 46.6, 32.9, 29.2, 26.7, 22.1, 21.7, 20.3; IR ν_{max} (KBr): 3295, 2933, 2859, 1923, 1598, 1470, 1321, 1159, 1093, 1053, 814, 737, 554 cm^{-1}; HRMS m/z calcd for $C_{21}H_{24}N_2NaO_2S$ $[M+Na]^+$: 391.1456; found: 391.1457.



4-methyl-*N*-((9-methyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indol-4-yl)methyl)benzenesulfonamide (11p): Yield: 54%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 4.93 (t, *J* = 5.8 Hz, 1H), 4.84 (d, *J* = 14.6 Hz, 1H), 4.74 (d, *J* = 14.6 Hz, 1H), 4.10 (dd, *J* = 11.6 Hz, 2.0 Hz, 1H), 3.79 (dd, *J* = 11.6 Hz, 3.7 Hz, 1H), 3.56 (s, 3H), 3.36-3.30 (m, 2H), 3.17-3.13 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.2, 137.1, 136.8, 134.1, 129.6, 127.1, 126.0, 121.6, 119.7, 118.2, 109.1, 106.1, 68.1, 63.2, 45.7, 33.3, 29.6, 21.6; IR ν_{max} (KBr): 3246, 2933, 2367, 1598, 1470, 1325, 1150, 1094, 1072, 740, 551 cm^{-1}; HRMS m/z calcd for $C_{20}H_{22}N_2NaO_3S$ $[M+Na]^+$: 393.1249; found: 393.1253.

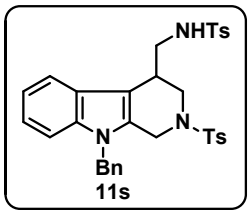


4-methyl-*N*-((9-methyl-7-tosyl-6,7,8,9-tetrahydro-5*H*-pyrrolo[2,3-*b*:5,4-*c*']dipyridin-5-yl)methyl)benzenesulfonamide (11q): Yield: 62%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 4.2 Hz, 1H), 7.88 (d, *J* = 3.8 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.07 (dd, *J* = 4.2 Hz, 3.8 Hz, 1H), 5.02 (t, *J* = 5.5 Hz, 1H), 4.72 (d, *J* = 14.8 Hz, 1H), 4.01 (d, *J* = 12.4 Hz, 1H), 3.91 (d, *J* = 14.8 Hz, 1H), 3.71 (s, 3H), 3.41-3.36 (m, 1H), 3.33-3.27 (m, 1H), 3.19-3.13 (m, 1H), 2.85 (d, *J* = 12.4 Hz, 1H), 2.45 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.3, 144.4, 143.6, 142.8, 137.1, 133.6, 131.6, 130.2, 129.9, 127.5, 127.1, 126.5, 118.4, 116.0, 106.4, 46.0, 45.2, 42.9, 34.0, 28.1, 21.7, 21.6; IR ν_{max} (KBr): 3408, 3280, 2923, 1597, 1325, 1162, 1087 cm^{-1}; HRMS m/z calcd for $C_{26}H_{29}N_4O_4S_2$ $[M+H]^+$: 525.1630; found: 525.1631.

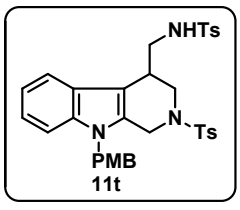


4-methyl-*N*-((1-methyl-6-tosyl-4,5,6,7-tetrahydro-1*H*-pyrrolo[2,3-*c*]pyridin-4-yl)methyl)benzenesulfonamide (11r): Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 6.45 (s, 1H), 5.85 (s, 1H), 4.86 (t, *J* = 6.0 Hz, 1H), 4.29 (d, *J* = 13.5 Hz, 1H), 3.87 (d, *J* = 13.5 Hz, 1H), 3.53 (d, *J* = 10.2 Hz, 1H), 3.42 (s, 3H), 3.18-3.09 (m, 1H), 3.05-2.94 (m, 3H), 2.43 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 144.0, 143.5, 137.0, 133.8, 130.0, 129.8, 127.5, 127.1, 123.4, 121.8, 115.9, 105.4, 46.2, 45.6, 42.9, 34.5, 33.3, 21.6, 21.6; IR ν_{max} (KBr): 3315, 2921, 1596, 1340, 1162, 1089, 818, 661, 549 cm^{-1}; HRMS m/z calcd for $C_{23}H_{27}N_3NaO_4S_2$ $[M+Na]^+$: 496.1341; found: 496.1344.

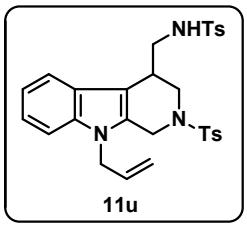


***N*-((9-benzyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11s):** Yield: 86%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.27-7.24 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.17 (ddd, *J* = 7.8 Hz, 7.0 Hz, 1.0 Hz, 1H), 7.13 (ddd, *J* = 7.8 Hz, 7.0 Hz, 0.8 Hz, 1H), 6.98-6.95 (m, 2H), 5.23 (d, *J* = 16.9 Hz, 1H), 5.12 (d, *J* = 16.9 Hz, 1H), 5.06 (dd, *J* = 6.8 Hz, 5.8 Hz, 1H), 4.62 (d, *J* = 14.6 Hz, 1H), 4.01 (dd, *J* = 12.4 Hz, 1.3 Hz, 1H), 3.75 (d, *J* = 14.6 Hz, 1H), 3.43-3.37 (m, 2H), 3.17-3.11 (m, 1H), 2.82 (dd, *J* = 12.4 Hz, 3.0 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.1, 143.5, 137.3, 137.2, 136.8, 134.0, 130.9, 130.1, 129.9, 129.1, 127.9, 127.5, 127.2, 126.3, 125,9, 122.3, 120.3, 118.6, 109.8, 108,8, 47.1, 45.8, 44.9, 43.1, 34.3, 21.7, 21.6; IR ν_{max} (KBr): 3302, 3059, 2292, 1597, 1453, 1332, 1162, 1090, 814, 743 cm^{-1}; HRMS m/z calcd for $C_{33}H_{33}N_3NaO_4S_2$ $[M+Na]^+$: 622.1810; found: 622.1812.



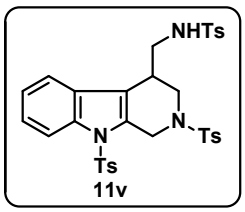
***N*-((9-(4-methoxybenzyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11t):** Yield: 74%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.17 (ddd, *J* = 7.8 Hz, 7.1 Hz, 0.9 Hz, 1H), 7.13 (ddd, *J* = 7.9 Hz, 7.0 Hz, 0.9 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.18 (d, *J* = 16.5 Hz, 1H), 5.07 (dd, *J* = 7.5 Hz, 6.8 Hz, 1H), 5.04 (d, *J* = 16.5 Hz, 1H), 4.60 (d, *J* = 14.6 Hz, 1H), 4.00 (dd, *J* = 12.4 Hz, 1.5 Hz, 1H), 3.76 (s, 3H), 3.72 (d, *J* = 14.6 Hz, 1H), 3.43-3.35 (m, 2H), 3.17-3.10 (m, 1H), 2.80 (dd, *J* = 12.4 Hz, 3.1 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 144.1, 143.5, 137.3, 137.1, 133.9, 130.9, 130.1, 129.9, 128.8, 127.7, 127.5, 127.2, 125.9, 122.2, 120.2, 118.5, 114.5, 109.8, 108.7, 55.4, 46.6, 45.8, 44.9, 43.2, 34.3, 21.7, 21.6; IR ν_{max} (KBr): 3392, 3293, 2923, 2359, 2332, 1612, 1597, 1513, 1458, 1336, 1162, 1090, 814, 663,

548 cm^{-1}; HRMS m/z calcd for $C_{34}H_{35}N_3NaO_5S_2$ $[M+Na]^+$: 652.1916; found: 652.1917.



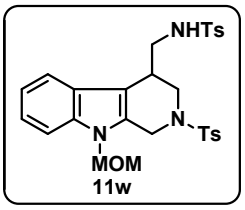
11u

***N*-((9-allyl-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11u):** Yield: 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.19 (dd, *J* = 8.2 Hz, 7.0 Hz, 1H), 7.12 (dd, *J* = 7.8 Hz, 7.0 Hz, 1H), 5.90-5.82 (m, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 5.07 (dd, *J* = 6.6 Hz, 6.2 Hz, 1H), 4.85 (d, *J* = 17.0 Hz, 1H), 4.66 (d, *J* = 14.4 Hz, 1H), 4.61-4.52 (m, 2H), 4.02 (dd, *J* = 12.5 Hz, 1.8 Hz, 1H), 3.88 (d, *J* = 14.4 Hz, 1H), 3.42-3.34 (m, 2H), 3.12 (ddd, *J* = 13.6 Hz, 9.1 Hz, 5.6 Hz, 1H), 2.84 (dd, *J* = 12.4 Hz, 3.1 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 143.5, 137.3, 136.8, 134.1, 132.7, 130.7, 130.1, 129.9, 127.5, 127.1, 125.8, 122.1, 120.1, 118.5, 117.1, 109.6, 108.5, 45.9, 45.7, 44.9, 42.9, 34.2, 21.7, 21.6; IR ν_{max} (KBr): 3293, 2920, 1597, 1457, 1335, 1161, 1089, 662 cm^{-1}; HRMS m/z calcd for $C_{29}H_{31}N_3NaO_4S_2$ $[M+Na]^+$: 572.1654; found: 572.1656.



11v

***N*-((2,9-ditosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11v):** Yield: 63%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.31 (td, *J* = 7.3 Hz, 1.0 Hz, 1H), 7.29-7.28 (m, 1H), 7.27-7.26 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.23 (t, *J* = 6.5 Hz, 1H), 5.15 (d, *J* = 16.5 Hz, 1H), 4.12 (d, *J* = 12.7 Hz, 1H), 4.08 (dd, *J* = 16.5 Hz, 1.0 Hz, 1H), 3.32-3.26 (m, 2H), 3.05 (ddd, *J* = 15.2 Hz, 11.0 Hz, 6.1 Hz, 1H), 2.73 (dd, *J* = 12.7 Hz, 2.6 Hz, 1H), 2.47 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.5, 144.3, 143.6, 137.4, 136.1, 135.3, 134.5, 130.7, 130.3, 130.2, 129.9, 128.4, 127.4, 127.1, 126.6, 125.1, 124.1, 118.9, 117.6, 114.4, 45.1, 44.7, 44.0, 34.5, 21.7, 21.6; IR ν_{max} (film): 3292, 3063, 2923, 2856, 2359, 1596, 1452, 1336, 1161, 1089, 813, 737 cm^{-1}; HRMS m/z calcd for $C_{33}H_{34}N_3O_6S_3$ $[M+H]^+$: 664.1610; found: 664.1614.



***N*-((9-(methoxymethyl)-2-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indol-4-yl)methyl)-4-methylbenzenesulfonamide (11w):** Yield: 77%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.75 (m, 4H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.41-7.35 (m, 3H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 5.30 (s, 2H), 5.11 (t, *J* = 6.5 Hz, 1H), 4.78 (d, *J* = 14.7 Hz, 1H), 4.07 (d, *J* = 12.4 Hz, 1H), 3.94 (d, *J* = 14.7 Hz, 1H), 3.41-3.34 (m, 2H), 3.20 (s, 3H), 3.16-3.10 (m, 1H), 2.84 (d, *J* = 12.4 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.2, 143.5, 137.5, 137.2, 134.0, 130.9, 130.1, 129.9, 127.5, 127.1, 126.1, 122.6, 120.8, 118.6, 110.2, 109.5, 74.2, 56.1, 45.7, 44.7, 42.9, 34.2, 21.7, 21.6; IR ν_{max} (KBr): 3297, 2921, 1597, 1458, 1334, 1161, 1087, 815 cm^{-1}; HRMS m/z calcd for $C_{28}H_{31}N_3NaO_5S_2$ $[M+Na]^+$: 576.1603; found: 576.1605.

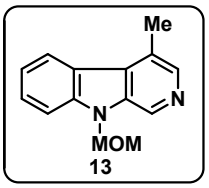
6. The Procedure for the One-pot Three-steps Reaction

A dried flask was charged with copper(I) thiophene-2-carboxylate (CuTC, 3.8 mg, 0.02 mmol, 0.1 equiv.), toluene (2.0 mL), and the alkyne (0.20 mmol, 1.0 equiv.). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (0.22 mmol, 1.1 equiv.) was added slowly, and the reaction mixture was allowed to warm to room temperature and keep stirring until the completion of the reaction. The solvent was evaporated *in vacuo* and the residue was redissolved in freshly distilled 1,2-dichloroethane (1.0 mL) in a 10 mL pressure tube. The mixture was placed in an oil bath preheated to 140 °C for 5 min, then $NaBH_3CN$ (25.1 mg, 0.4 mmol, 2.0 equiv.) was added, and the reaction mixture was stirred at 80 °C for 3 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (eluent: petroleum ether/EtOAc) to give the product **11a-11c**, **11e-11f** and **11s**.

7. Preparation of 9-(methoxymethyl)-4-methyl-9*H*-pyrido[3,4-*b*] indole

An aqueous solution of sodium hydroxide (30% w/w, 133 mg, 1.00 mmol) was added to a solution of **11w** (111 mg, 0.20 mmol) in DMSO (1.0 mL). The mixture was heated to around 125 °C, and

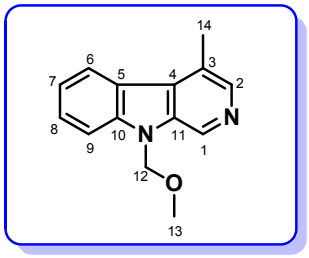
then stirred at this temperature for 1 h. The reaction was monitored by TLC. After the reaction was complete, the mixture was allowed to cool to room temperature and diluted with water (10 mL). The aqueous solution was then extracted with ethyl acetate (3×15 mL). The extracts were combined and dried with anhydrous Na_2SO_4. Evaporation of the solvent gave a crude oil which was purified by flash chromatography (eluent: Et_2O/MeOH 20:1) to give the product **13**.



9-(methoxymethyl)-4-methyl-9*H*-pyrido[3,4-*b*]indole (13): Yield: 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.30 (s, 1H), 8.21 (d, J = 7.9 Hz, 1H), 7.64-7.58 (m, 2H), 7.35 (ddd, J = 7.9 Hz, 6.3 Hz, 1.8 Hz, 1H), 5.74 (s, 2H), 3.30 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 141.0, 136.5, 130.4, 128.1, 127.9, 127.3, 123.9, 122.5, 120.8, 110.0, 74.5, 56.4, 17.5; IR ν_{max} (film): 2940, 1617, 1456, 1427, 1327, 1263, 1160, 1102, 1064, 730 cm^{-1}; HRMS m/z calcd for $C_{14}H_{15}N_2O$ $[M+H]^+$: 227.1184; found: 227.1186.

Note: only ^{1}H MNR data of **13** was provided in reference 14 (in our paper). However, it seemed that the documented data was incorrect. The structure of **13** obtained in our hands was unambigously confirmed by extensive spectroscopic study as well as its transformation into **14**, a well-known compound[10].

Table S7-1. NMR Data for **13**



No.	^{1}H[a]	^{13}C[a]	DEPT[a]	HMBC[b]
1	8.88 (s)	130.4	CH	2
2	8.30 (s)	141.0	CH	1, 14
3		127.3	C	2, 14
4		127.9	C	1, 2, 6, 14
5		122.5	C	2, 6, 7, 9
6	8.21 (d, J = 7.9)	123.9	CH	8
7	7.35 (ddd, J = 7.9, 6.3, 1.8)	120.8	CH	9
8	7.60 (m)	128.1	CH	6
9	7.61 (m)	110.0	CH	6, 7
10		141.2	C	6, 12
11		136.9	C	1, 12
12	5.74 (s)	74.5	CH_2	13
13α	3.30 (s)	56.4	CH_3	12
14	2.84 (s)	17.5	CH_3	2

[a]Recorded in $CDCl_3$ at 400 MHz, [b]Carbons that correlate with the proton resonance.

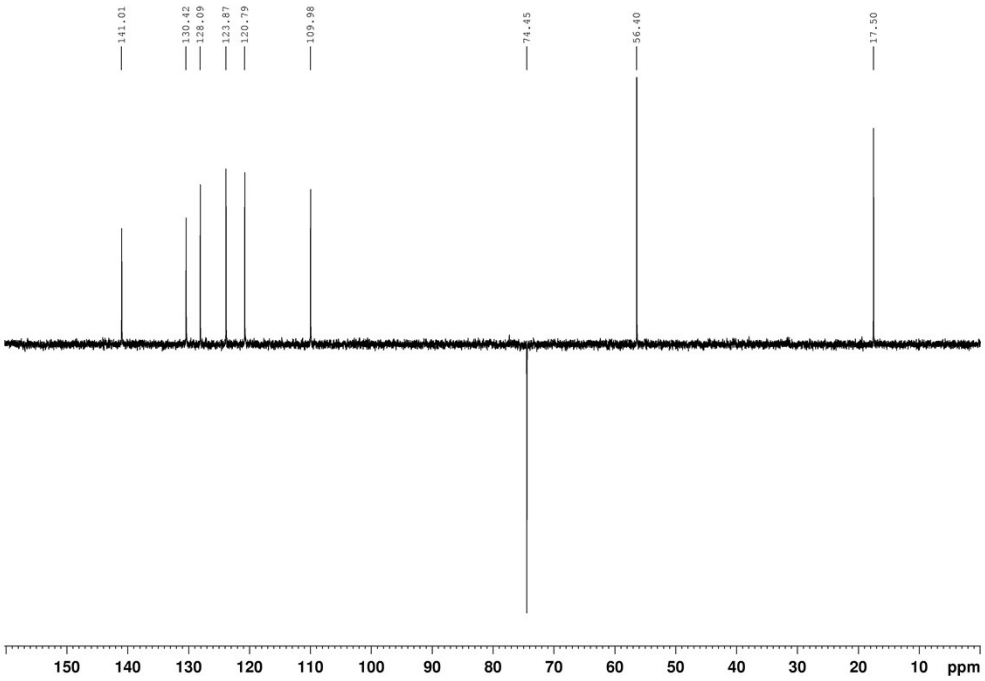


Figure S7-1 The DEPT spectrum for **13**

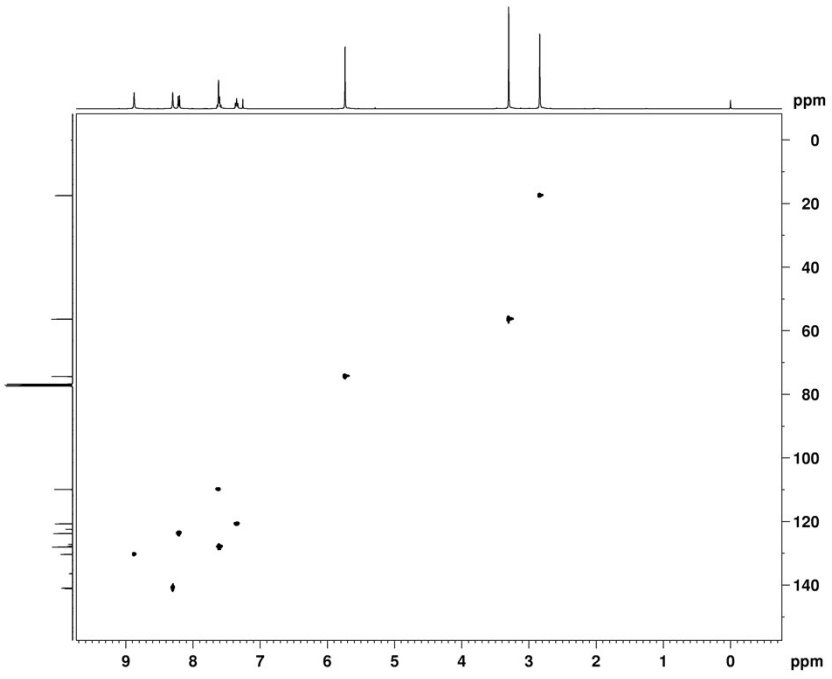


Figure S7-2 The HSQC spectrum for **13**

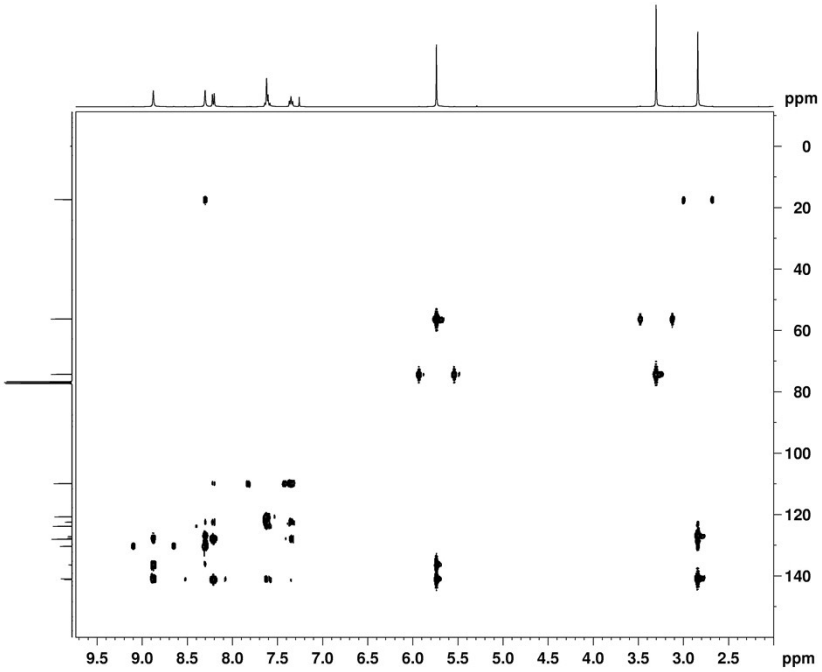


Figure S7-3 The HMBC spectrum for **13**

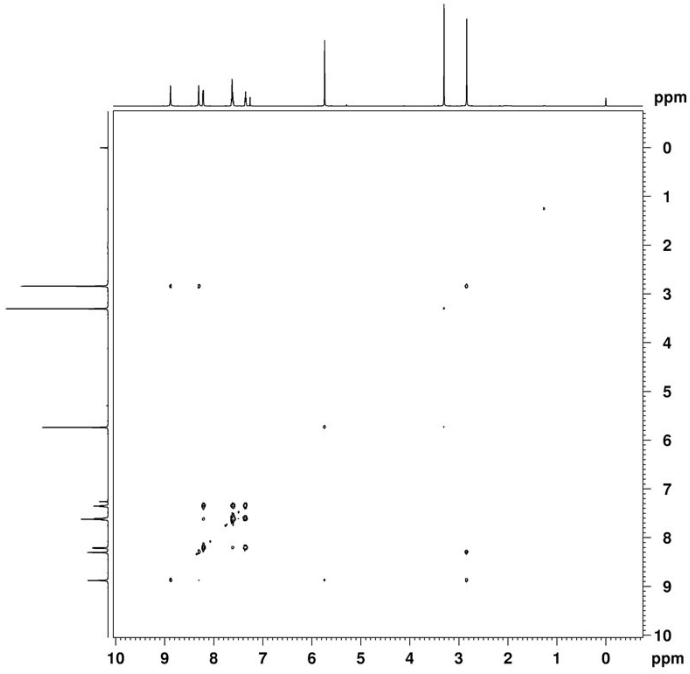


Figure S7-4 The ^{1}H-^{1}H COSY spectrum for **13**

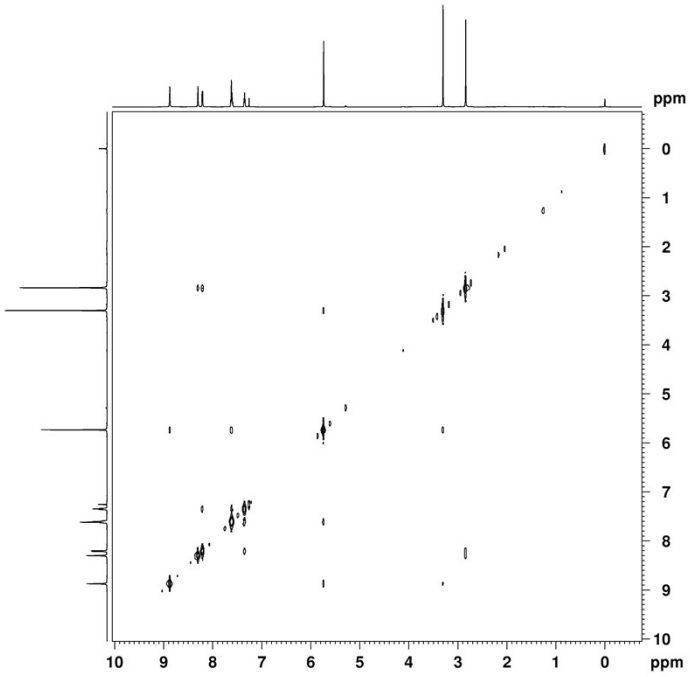
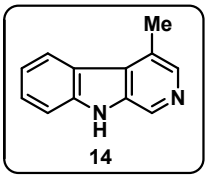


Figure S7-5 The NOESY spectrum for **13**

Preparation of 4-methyl-9*H*-pyrido[3,4-*b*]indole (14)

Trifluoromethanesulfonic acid (35 μL, 0.39 mmol, 3.0 equiv.) was added to an ice-cooled mixture of **13** (30.0 mg, 0.13 mmol), MeOH (53 μL, 1.30 mmol, 10.0 equiv.), and trimethyl orthoformate (143 μl, 1.30 mmol, 10.0 equiv.) in nitromethane (2.0 mL). The resulting mixture was heated at 100 °C for 1 h. After the reaction was complete, the mixture was allowed to cool to room temperature and diluted with water (10 mL). The resulting solution was extracted with ethyl acetate (3×15 mL) and the combined extracts were dried with Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by a silica gel flash column chromatography (eluent: EtOAc/MeOH) to give the *N*-deprotected *β*-carboline **14**.



14

4-methyl-9*H*-pyrido[3,4-*b*]indole (14): Yield: 70%; ^{1}H NMR (600 MHz, DMSO) δ 11.62 (s, 1H), 8.75 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.14 (s, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 2.78 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 140.9, 139.1, 136.0, 132.3, 128.0, 126.8, 126.6, 123.8, 121.6, 119.8, 112.3, 17.5; IR ν_{max} (film): 3464, 3048, 2851, 1624, 1570,

1461, 1423, 1328, 1133, 1070, 718 cm^{-1}; HRMS m/z calcd for $C_{12}H_{11}N_2$ $[M+H]^+$: 183.0922; found: 183.0924.

References

[1]. C. F. Li, H. Liu, J. Liao, Y. J. Cao, X. P. Liu, and W. J. Xiao, *Org. Lett.* 2007, **9**, 1847-1850.

[2]. C. W. Zheng, Y. P. Lu, J. K. Zhang, X. K. Chen, Z. Chai, W. Y. Ma, and G. Zhao, *Chem. Eur. J.* 2010, **16**, 5853-5857.

[3]. M. Bandini, A. Gualandi, M. Monari, A. Romaniello, D. Savoia, M Tragni, *J. Organomet. Chem.* 2011, **696**, 337-347.

[4]. J. Raushel, and V. V. Fokin, *Org. Lett.* 2010, **12**, 4952-495.

[5]. N. Gigant, E. Claveau, P. Bouyssou, and I. Gillaizeau, *Org. Lett.* 2012, **14**, 844-847.

[6]. M. Sechi, M. Derudas, R. Dallocchio, A. Dessì, A. Bacchi, L. Sannia, F. Carta, M. Palomba, O. Ragab, C. Chan, R. Shoemaker, S. Sei, R. Dayam, and N. Neamati. *J. Med. Chem.* 2004, **47**, 5298-5310.

[7]. A. Tsotinis, P. A. Afroudakis, K. Davidson, A. Prashar, and D. Sugde, *J. Med. Chem.* 2007, **50**, 6436-6440.

[8]. Y. Abe, H. Takikawa, and K. Mori, *Biosci. Biotechnol. Biochem.* 2001, **65**, 732-735.

[9]. Y. Q. Zhang, D. Y. Zhu, Z. W. Jiao, B. S. Li, F. M. Zhang, Y. Q. Tu, and Z. G. Bi, *Org. Lett.* 2011, **13**, 3458-3461.

[10]. M. E. Rhepperle, J . F. Liu, F. Soucy, Y. Ye, R. S. Murray, R. Prakash, J. D. Little, A. Castro, H. Mazdiyasni, P. E. Fleming, and D. Reynolds. U.S. Patent 2004/0235839, 2004.

8. X-ray Crystallographic Studies for 11a

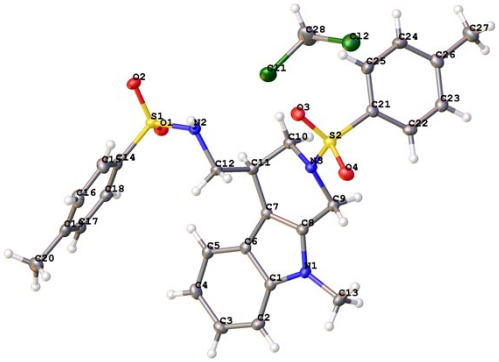


Figure S8-1. ORTEP drawing of **11a** with 30% thermal ellipsoids.

Table S8-1 Crystal data and structure refinement for **11a**

Identification code	**11a**
Empirical formula	$C_{28}H_{31}Cl_2N_3O_4S_2$
Formula weight	608.58
Temperature / K	106.6
Crystal system	triclinic
Space group	P-1
a / Å, b / Å, c / Å	9.7402(4), 11.9977(7), 13.1123(5)
α/°, β/°, γ/°	71.536(4), 83.542(4), 81.195(4)
Volume / Å^3	1432.95(12)
Z	2
ρ_{calc} / mg mm^{-3}	1.410
μ / mm^{-1}	0.412
F(000)	636
Crystal size / mm^3	0.55 × 0.45 × 0.45
2Θ range for data collection	6.34 to 52°
Index ranges	$-12 \le h \le 12$, $-10 \le k \le 14$, $-16 \le l \le 16$
Reflections collected	9944
Independent reflections	5606[R(int) = 0.0244 (inf-0.9Å)]
Data/restraints/parameters	5606/0/355
Goodness-of-fit on F^2	1.036
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0383, wR_2 = 0.0843
Final R indexes [all data]	R_1 = 0.0485, wR_2 = 0.0899
Largest diff. peak/hole / e Å^{-3}	0.395/-0.392

Flack Parameters	N
Completeness	0.998

Table S8-2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **11a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	1036.3(5)	850.1(4)	2567.7(4)	15.13(12)
S2	1264.4(5)	6292.7(5)	522.4(4)	16.66(12)
Cl2	6012.1(6)	4579.9(6)	2473.9(5)	36.70(16)
Cl1	4557.1(6)	2518.1(6)	3559.1(6)	38.66(17)
O1	1486.9(13)	661.6(13)	3621.7(11)	19.7(3)
O3	1582.1(14)	5436.9(13)	-46.1(11)	22.3(3)
O2	1829.9(14)	251.1(13)	1862.0(11)	21.4(3)
N1	-1667.3(16)	5748.7(15)	4043.5(13)	16.2(4)
N3	842.1(16)	5589.4(15)	1772.2(13)	15.8(4)
N2	959.1(16)	2258.4(14)	1929.6(13)	15.2(3)
O4	159.6(13)	7252.3(13)	191.4(11)	20.9(3)
C14	-692.1(19)	491.0(17)	2747.3(16)	15.5(4)
C5	-1405(2)	2606.0(18)	5257.8(16)	17.4(4)
C21	2805.8(19)	6916.9(18)	485.7(15)	15.8(4)
C2	-3194(2)	4591.2(19)	5560.5(16)	18.8(4)
C18	-1361(2)	151.1(18)	3772.5(16)	17.2(4)
C9	147(2)	6280.6(18)	2479.2(16)	17.2(4)
C11	820.4(19)	3607.5(18)	3077.1(15)	14.9(4)
C8	-554.2(19)	5423.0(18)	3402.8(15)	15.3(4)
C7	-229.2(19)	4225.0(17)	3709.5(15)	14.2(4)
C22	2790(2)	7852.7(19)	902.2(16)	18.3(4)
C23	4030(2)	8264.8(19)	934.3(16)	19.5(4)
C25	4041(2)	6428.6(19)	72.4(17)	21.4(5)
C17	-2724(2)	-103.2(18)	3894.2(17)	19.4(4)
C15	-1396(2)	602.6(19)	1847.4(17)	21.0(4)
C10	1739.7(19)	4503.9(18)	2324.5(16)	16.7(4)
C19	-3446(2)	2.8(18)	3006.5(17)	20.7(5)
C1	-2086.0(19)	4731.8(18)	4776.8(16)	16.0(4)
C3	-3388(2)	3451.7(19)	6183.4(16)	20.5(5)
C20	-4914(2)	-299(2)	3135(2)	29.2(5)
C27	6651(2)	8179(2)	627.8(19)	29.3(5)
C12	36.9(19)	3068.0(18)	2434.5(16)	16.2(4)
C24	5277(2)	6855(2)	108.9(18)	23.8(5)
C26	5295(2)	7763.2(19)	554.3(16)	20.5(5)
C16	-2766(2)	370.7(19)	1982.8(17)	23.2(5)
C13	-2262(2)	6952.0(18)	3986.5(18)	23.5(5)
C4	-2499(2)	2466.5(19)	6044.7(16)	20.3(4)
C6	-1190.6(19)	3746.9(17)	4603.1(15)	14.8(4)

C28	6169(2)	3086(2)	3251(2)	41.4(7)

Table S8-3 Anisotropic Displacement Parameters ($Å^2×10^3$) for **11a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	14.9(2)	15.2(3)	14.8(2)	-4.5(2)	-0.81(18)	-0.71(18)
S2	15.7(2)	20.4(3)	14.1(2)	-5.0(2)	-0.82(18)	-4.0(2)
Cl2	42.5(4)	34.2(4)	30.0(3)	-7.5(3)	5.6(3)	-5.3(3)
Cl1	22.3(3)	30.2(3)	61.9(4)	-15.4(3)	2.3(3)	0.4(2)
O1	18.4(7)	22.9(8)	16.7(7)	-4.2(6)	-3.2(5)	-1.4(6)
O3	23.8(8)	27.7(9)	19.5(8)	-12.1(7)	0.5(6)	-6.8(6)
O2	20.6(7)	19.0(8)	24.1(8)	-8.8(7)	2.0(6)	1.4(6)
N1	19.1(9)	13.7(9)	15.6(8)	-5.1(7)	0.8(6)	-2.0(7)
N3	17.1(8)	15.2(9)	14.6(9)	-4.6(7)	1.0(6)	-2.2(7)
N2	17.2(8)	15.3(9)	12.9(8)	-4.6(7)	0.2(6)	-1.5(7)
O4	17.8(7)	25.5(8)	16.7(7)	-2.3(7)	-3.7(5)	-1.4(6)
C14	16.9(10)	11.3(10)	18.1(10)	-4.2(8)	-1.3(7)	-1.5(8)
C5	19.1(10)	15.3(10)	17.7(10)	-4.5(9)	-3.8(8)	-1.2(8)
C21	17.5(10)	16.7(10)	11.7(10)	-1.3(8)	-0.9(7)	-3.9(8)
C2	18.9(10)	20.0(11)	17.9(10)	-7.9(9)	0.0(8)	-0.1(8)
C18	18.8(10)	16.2(10)	17.4(10)	-6.6(9)	-3.6(8)	0.0(8)
C9	19(1)	15.7(10)	16.9(10)	-5.3(9)	-0.4(8)	-2.5(8)
C11	14.3(9)	15.6(10)	14.8(10)	-4.6(8)	-2.6(7)	-0.6(8)
C8	15.3(10)	17.3(10)	14.1(10)	-5.8(9)	-0.5(7)	-2.4(8)
C7	14.6(10)	15.3(10)	12.7(10)	-3.4(8)	-2.3(7)	-2.3(7)
C22	17.6(10)	21.4(11)	14.3(10)	-4.5(9)	1.3(8)	-0.9(8)
C23	24.3(11)	19.1(11)	15.1(10)	-4.7(9)	-0.8(8)	-4.2(8)
C25	22.6(11)	18.7(11)	24.3(11)	-9.0(9)	0.9(8)	-3.3(8)
C17	20(1)	16.3(11)	20.9(11)	-6.1(9)	3.1(8)	-1.3(8)
C15	25.6(11)	21.3(11)	16.4(10)	-4.0(9)	-1.3(8)	-7.6(9)
C10	13.6(10)	18.6(11)	19.1(10)	-7.4(9)	-1.0(7)	-1.9(8)
C19	19(1)	15.0(11)	29.3(12)	-8.6(9)	-2.1(8)	-1.2(8)
C1	18(1)	16.6(10)	14.3(10)	-5.1(9)	-3.0(7)	-2.8(8)
C3	19.1(10)	24.7(12)	16.1(10)	-3.8(9)	1.5(8)	-5.3(8)
C20	20.3(11)	31.1(13)	40.6(14)	-15.4(12)	-1.4(9)	-7.2(9)
C27	22.5(12)	35.8(14)	31.7(13)	-11.6(11)	0.3(9)	-9(1)
C12	13.3(10)	15.8(10)	20.8(11)	-8.3(9)	0.5(7)	-1.0(8)
C24	18.0(11)	24.7(12)	28.2(12)	-10(1)	4.3(8)	-0.7(9)
C26	20.4(11)	23.9(12)	16.4(10)	-3.4(9)	-1.0(8)	-6.1(9)
C16	27.6(12)	21.9(12)	22.3(11)	-5.9(10)	-9.7(9)	-6.0(9)
C13	29.8(12)	15.4(11)	23.2(12)	-6.0(9)	1.9(9)	1.0(9)

C4	23.0(11)	17.5(11)	17.3(10)	1.3(9)	-3.6(8)	-6.4(8)
C6	15.5(10)	16(1)	14.5(10)	-5.7(8)	-3.6(7)	-2.7(8)
C28	24.2(13)	37.2(15)	57.8(18)	-5.2(14)	-12.3(11)	-1.7(11)

Table S8-4 Bond Lengths for **11a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.4359(14)	C21	C25	1.387(3)
S1	O2	1.4355(14)	C2	C1	1.395(3)
S1	N2	1.6249(17)	C2	C3	1.382(3)
S1	C14	1.7731(19)	C18	C17	1.388(3)
S2	O3	1.4288(15)	C9	C8	1.494(3)
S2	N3	1.6265(16)	C11	C7	1.499(3)
S2	O4	1.4426(14)	C11	C10	1.535(3)
S2	C21	1.767(2)	C11	C12	1.534(3)
Cl2	C28	1.752(3)	C8	C7	1.361(3)
Cl1	C28	1.761(2)	C7	C6	1.439(3)
N1	C8	1.381(2)	C22	C23	1.384(3)
N1	C1	1.379(3)	C23	C26	1.397(3)
N1	C13	1.453(3)	C25	C24	1.389(3)
N3	C9	1.476(2)	C17	C19	1.389(3)
N3	C10	1.477(2)	C15	C16	1.385(3)
N2	C12	1.482(2)	C19	C20	1.507(3)
C14	C18	1.391(3)	C19	C16	1.396(3)
C14	C15	1.391(3)	C1	C6	1.421(3)
C5	C4	1.388(3)	C3	C4	1.403(3)
C5	C6	1.399(3)	C27	C26	1.505(3)
C21	C22	1.393(3)	C24	C26	1.392(3)

Table S8-5 Bond Angles for **11a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	N2	107.68(9)	C12	C11	C10	111.09(16)
O1	S1	C14	106.95(9)	N1	C8	C9	123.87(17)
O2	S1	O1	119.85(8)	C7	C8	N1	110.61(17)
O2	S1	N2	106.43(8)	C7	C8	C9	125.49(17)
O2	S1	C14	108.49(9)	C8	C7	C11	122.44(17)
N2	S1	C14	106.79(9)	C8	C7	C6	106.94(17)
O3	S2	N3	107.53(9)	C6	C7	C11	130.10(18)
O3	S2	O4	119.77(9)	C23	C22	C21	119.20(18)
O3	S2	C21	107.46(9)	C22	C23	C26	121.3(2)
N3	S2	C21	108.02(9)	C21	C25	C24	119.4(2)
O4	S2	N3	105.79(8)	C18	C17	C19	121.12(19)

O4	S2	C21	107.80(9)	C16	C15	C14	119.36(19)
C8	N1	C13	126.19(17)	N3	C10	C11	108.98(15)
C1	N1	C8	108.05(16)	C17	C19	C20	121.38(19)
C1	N1	C13	125.73(16)	C17	C19	C16	118.33(19)
C9	N3	S2	118.57(13)	C16	C19	C20	120.27(19)
C9	N3	C10	114.69(15)	N1	C1	C2	129.91(18)
C10	N3	S2	118.70(12)	N1	C1	C6	108.17(16)
C12	N2	S1	116.85(13)	C2	C1	C6	121.90(19)
C18	C14	S1	120.50(15)	C2	C3	C4	121.50(18)
C15	C14	S1	119.26(15)	N2	C12	C11	113.12(15)
C15	C14	C18	120.19(18)	C25	C24	C26	121.10(19)
C4	C5	C6	119.17(18)	C23	C26	C27	121.3(2)
C22	C21	S2	120.57(15)	C24	C26	C23	118.36(19)
C25	C21	S2	118.78(16)	C24	C26	C27	120.31(19)
C25	C21	C22	120.61(18)	C15	C16	C19	121.35(19)
C3	C2	C1	117.69(19)	C5	C4	C3	120.79(19)
C17	C18	C14	119.62(18)	C5	C6	C7	134.84(18)
N3	C9	C8	105.91(16)	C5	C6	C1	118.93(17)
C7	C11	C10	109.17(16)	C1	C6	C7	106.22(17)
C7	C11	C12	108.38(15)	Cl2	C28	Cl1	112.59(13)

Table S8-6 Torsion Angles for **11a**.

A	**B**	**C**	**D**	**Angle/°**
S1	N2	C12	C11	97.86(17)
S1	C14	C18	C17	178.70(15)
S1	C14	C15	C16	-177.30(16)
S2	N3	C9	C8	160.03(13)
S2	N3	C10	C11	-143.00(14)
S2	C21	C22	C23	175.26(15)
S2	C21	C25	C24	-175.45(16)
O1	S1	N2	C12	-57.94(15)
O1	S1	C14	C18	2.35(19)
O1	S1	C14	C15	179.55(16)
O3	S2	N3	C9	-165.57(14)
O3	S2	N3	C10	47.27(16)
O3	S2	C21	C22	174.78(16)
O3	S2	C21	C25	-7.66(19)
O2	S1	N2	C12	172.37(13)
O2	S1	C14	C18	132.94(16)
O2	S1	C14	C15	-49.86(19)

N1	C8	C7	C11	172.41(17)
N1	C8	C7	C6	0.0(2)
N1	C1	C6	C5	179.74(17)
N1	C1	C6	C7	-1.2(2)
N3	S2	C21	C22	-69.47(18)
N3	S2	C21	C25	108.09(17)
N3	C9	C8	N1	-157.66(17)
N3	C9	C8	C7	20.0(3)
N2	S1	C14	C18	-112.71(17)
N2	S1	C14	C15	64.49(18)
O4	S2	N3	C9	-36.50(16)
O4	S2	N3	C10	176.34(14)
O4	S2	C21	C22	44.42(18)
O4	S2	C21	C25	-138.02(16)
C14	S1	N2	C12	56.63(16)
C14	C18	C17	C19	-1.6(3)
C14	C15	C16	C19	-1.4(3)
C21	S2	N3	C9	78.73(15)
C21	S2	N3	C10	-68.43(16)
C21	C22	C23	C26	0.2(3)
C21	C25	C24	C26	0.1(3)
C2	C1	C6	C5	-1.8(3)
C2	C1	C6	C7	177.22(18)
C2	C3	C4	C5	-1.3(3)
C18	C14	C15	C16	-0.1(3)
C18	C17	C19	C20	178.58(19)
C18	C17	C19	C16	0.1(3)
C9	N3	C10	C11	68.6(2)
C9	C8	C7	C11	-5.5(3)
C9	C8	C7	C6	-177.93(18)
C11	C7	C6	C5	7.9(4)
C11	C7	C6	C1	-170.86(19)
C8	N1	C1	C2	-177.0(2)
C8	N1	C1	C6	1.3(2)
C8	C7	C6	C5	179.6(2)
C8	C7	C6	C1	0.8(2)
C7	C11	C10	N3	-46.3(2)
C7	C11	C12	N2	-169.85(16)
C22	C21	C25	C24	2.1(3)
C22	C23	C26	C27	-177.6(2)

C22	C23	C26	C24	1.9(3)
C25	C21	C22	C23	-2.2(3)
C25	C24	C26	C23	-2.1(3)
C25	C24	C26	C27	177.5(2)
C17	C19	C16	C15	1.3(3)
C15	C14	C18	C17	1.5(3)
C10	N3	C9	C8	-51.5(2)
C10	C11	C7	C8	18.3(3)
C10	C11	C7	C6	-171.16(19)
C10	C11	C12	N2	70.2(2)
C1	N1	C8	C9	177.18(18)
C1	N1	C8	C7	-0.8(2)
C1	C2	C3	C4	0.6(3)
C3	C2	C1	N1	179.02(19)
C3	C2	C1	C6	0.9(3)
C20	C19	C16	C15	-177.1(2)
C12	C11	C7	C8	-102.8(2)
C12	C11	C7	C6	67.7(3)
C12	C11	C10	N3	73.13(19)
C13	N1	C8	C9	-5.0(3)
C13	N1	C8	C7	177.01(19)
C13	N1	C1	C2	5.1(3)
C13	N1	C1	C6	-176.55(18)
C4	C5	C6	C7	-177.6(2)
C4	C5	C6	C1	1.1(3)
C6	C5	C4	C3	0.4(3)

Table S8-7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **11a**.

Atom	***x***	***y***	***z***	**U(eq)**
H2	830	2397	1230	18
H5	-822	1949	5167	21
H2A	-3781	5242	5660	23
H18	-898	95	4373	21
H9A	-531	6910	2095	21
H9B	823	6629	2733	21
H11	1403	2975	3574	18
H22	1955	8196	1156	22
H23	4023	8888	1214	23
H25	4042	5821	-226	26
H17	-3161	-349	4582	23

H15	-951	831	1161	25
H10A	2388	4692	2738	20
H10B	2272	4168	1797	20
H3	-4126	3335	6706	25
H20A	-4911	-1035	2991	44
H20B	-5475	317	2637	44
H20C	-5292	-369	3858	44
H27A	6825	8834	1	44
H27B	7394	7544	669	44
H27C	6600	8426	1261	44
H12A	-669	2636	2912	19
H12B	-433	3702	1876	19
H24	6106	6529	-169	29
H16	-3242	462	1380	28
H13A	-1893	7185	4526	35
H13B	-3256	6989	4109	35
H13C	-2031	7477	3286	35
H4	-2644	1711	6485	24
H28A	6579	3000	3917	50
H28B	6793	2625	2862	50

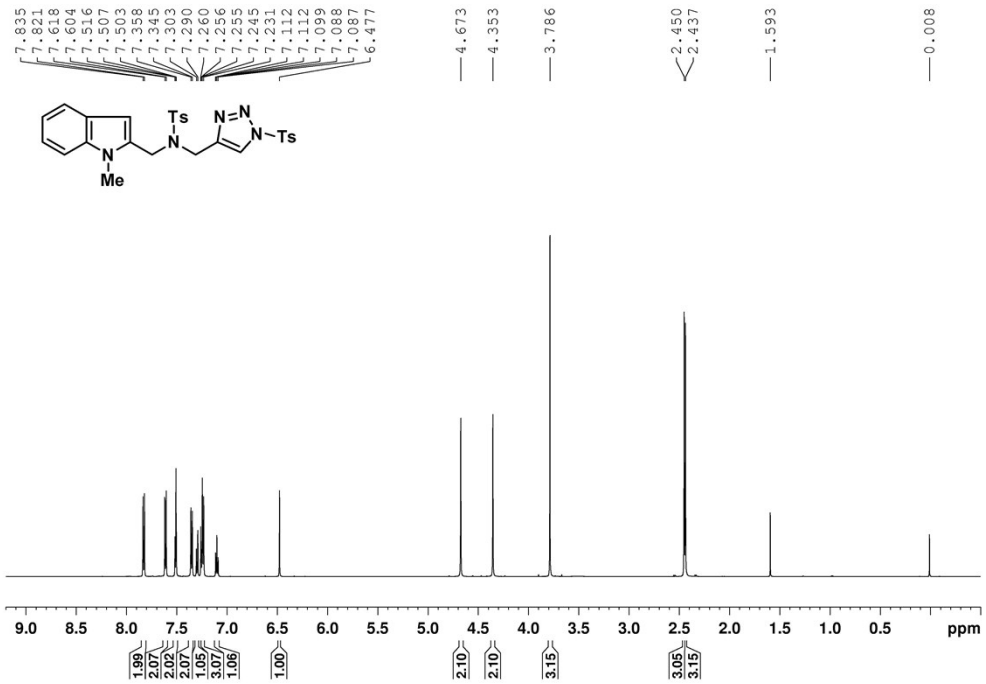
Experimental

Single crystals of $C_{28}H_{31}Cl_2N_3O_4S_2$ **[11a]** were recrystallised from CH_2Cl_2 mounted in inert oil and transferred to the cold gas stream of the diffractometer.

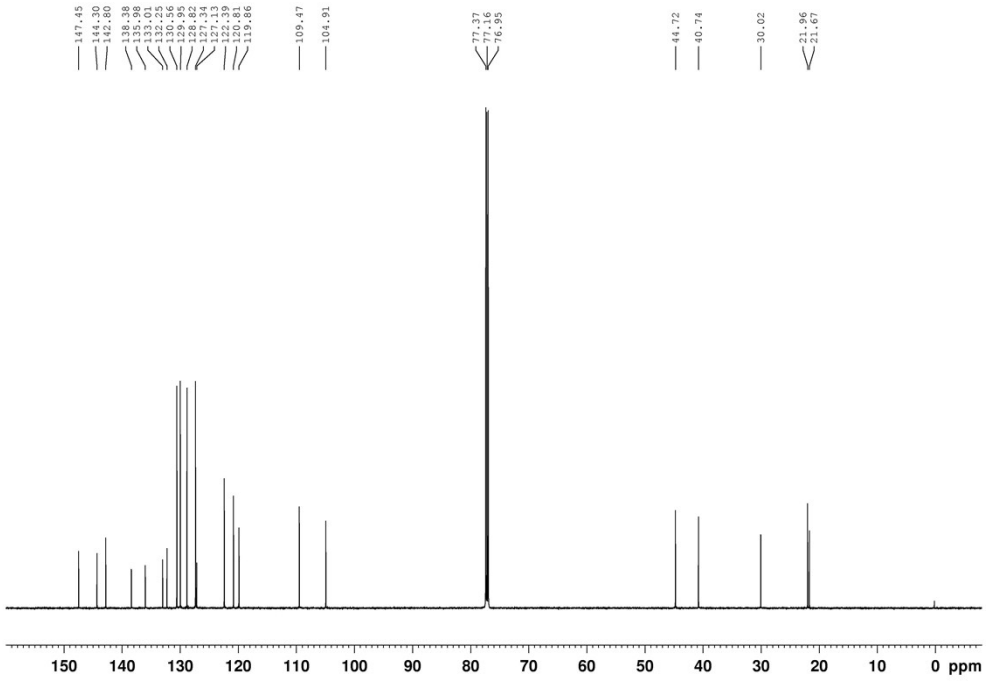
Crystal structure determination of 11a

Crystal Data. $C_{28}H_{31}Cl_2N_3O_4S_2$, M =608.58, triclinic, a = 9.7402(4) Å, b = 11.9977(7) Å, c = 13.1123(5) Å, α = 71.536(4) , β = 83.542(4) , γ = 81.195(4) , U = 1432.95(12) Å^3, T = 106.6, space group P-1 (no. 2), Z = 2, μ(Mo Kα) = 0.412, 9944 reflections measured, 5606 unique (R_{int} = 0.0244) which were used in all calculations. The final $wR(F_2)$ was 0.0899 (all data).

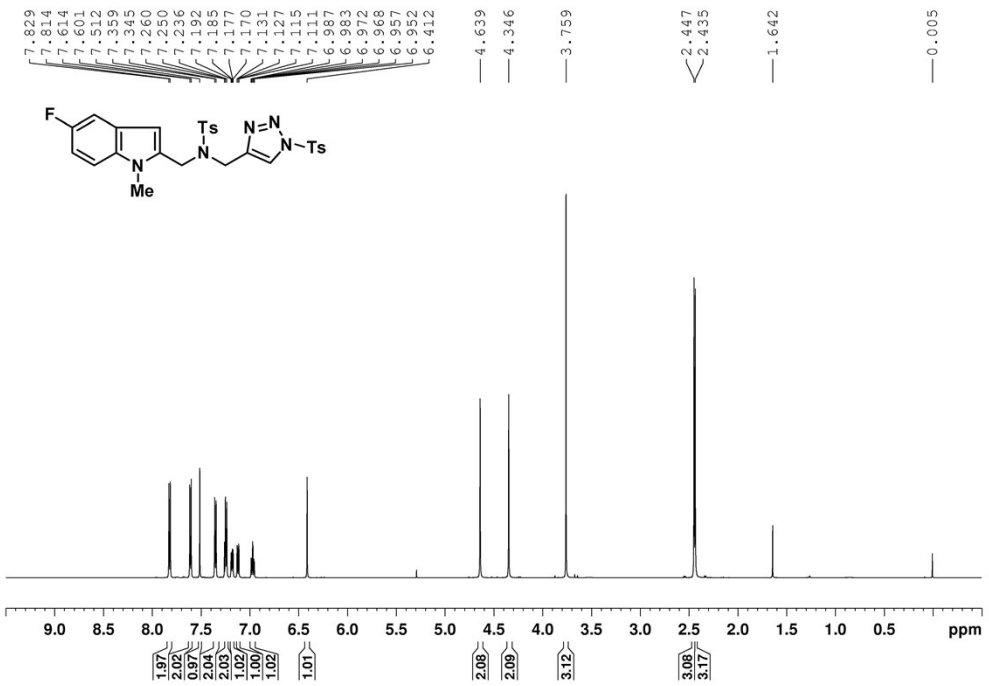
9. NMR Spectrum



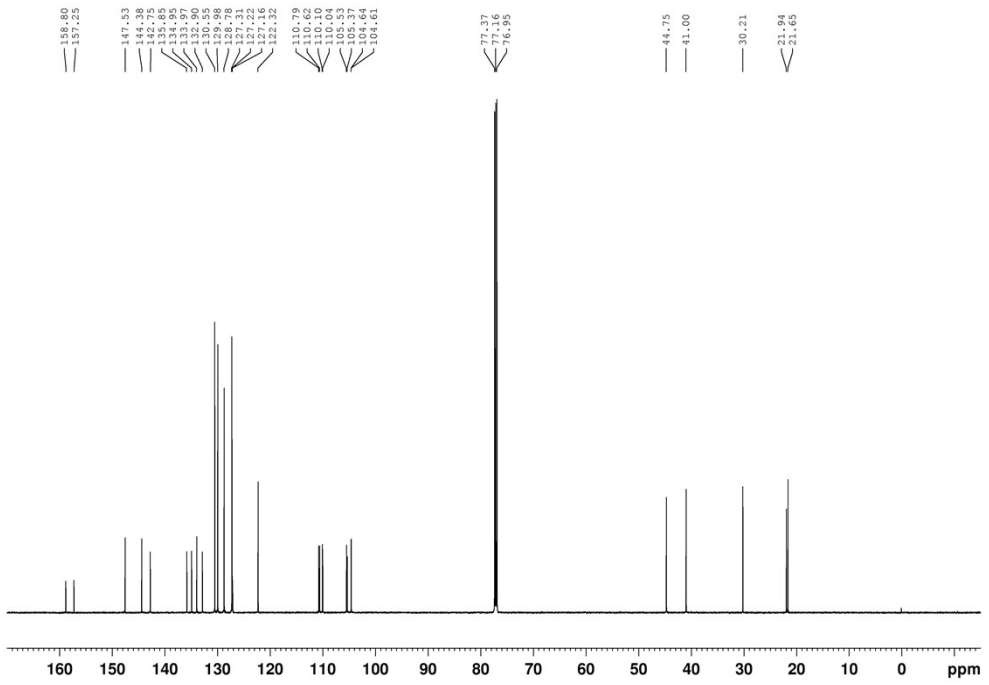
^{1}H NMR Spectrum for **6a** ($CDCl_3$, 600 MHz)



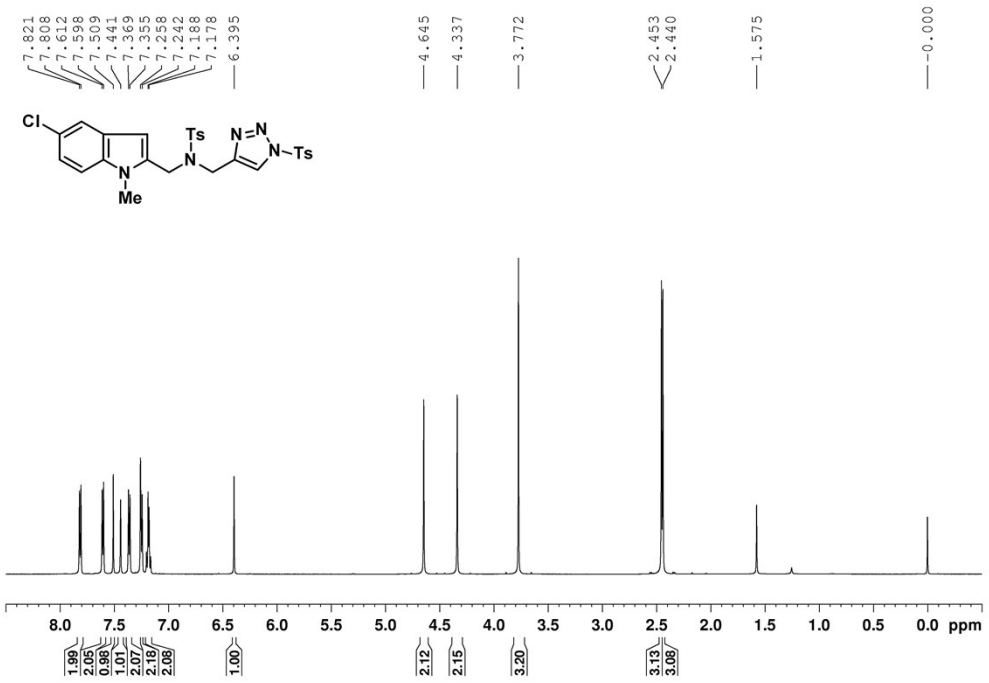
^{13}C NMR Spectrum for **6a** ($CDCl_3$, 150 MHz)



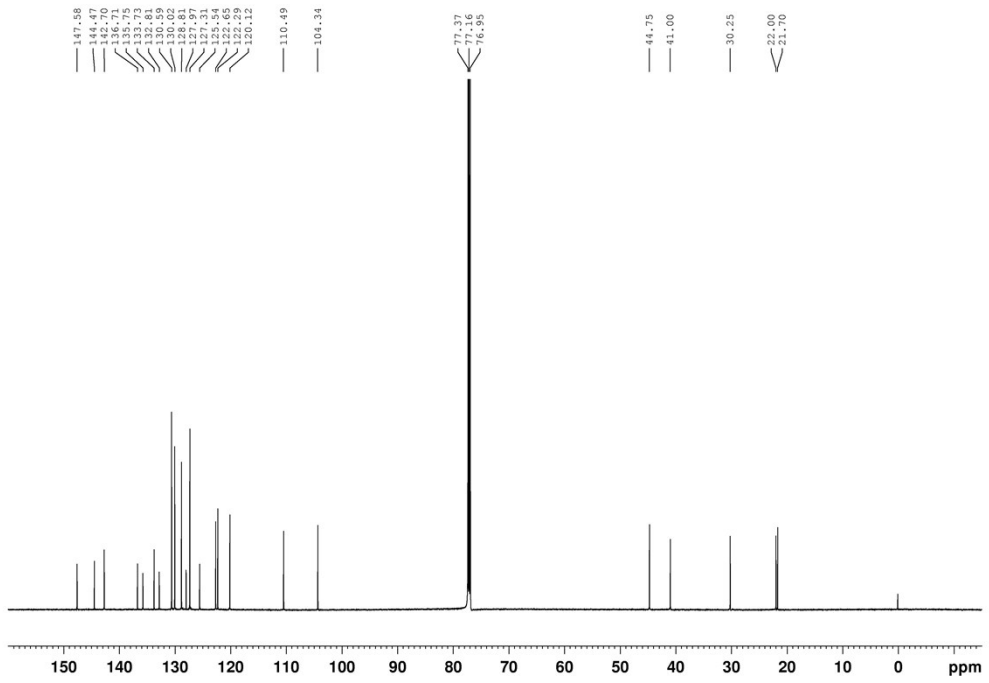
^{1}H NMR Spectrum for **6b** ($CDCl_3$, 600 MHz)



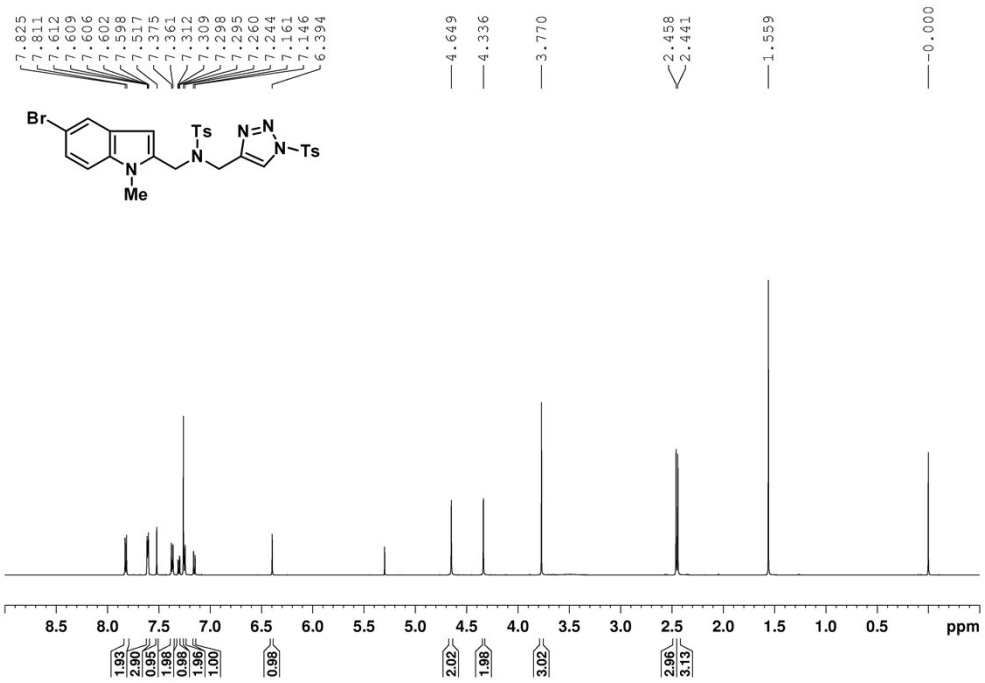
^{13}C NMR Spectrum for **6b** ($CDCl_3$, 150 MHz)



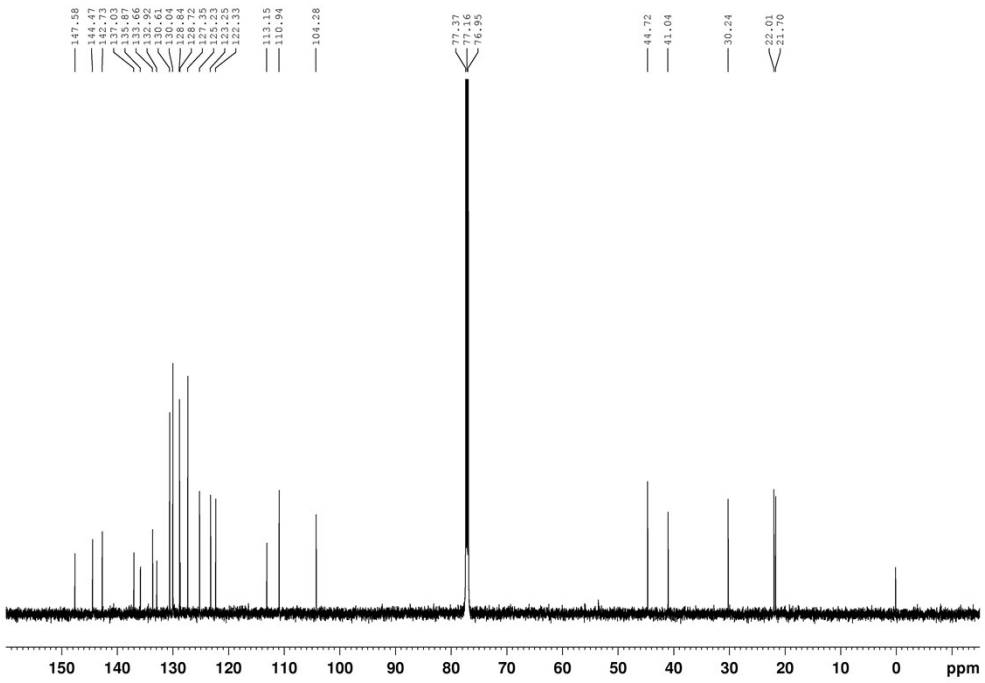
^{1}H NMR Spectrum for **6c** ($CDCl_3$, 600 MHz)



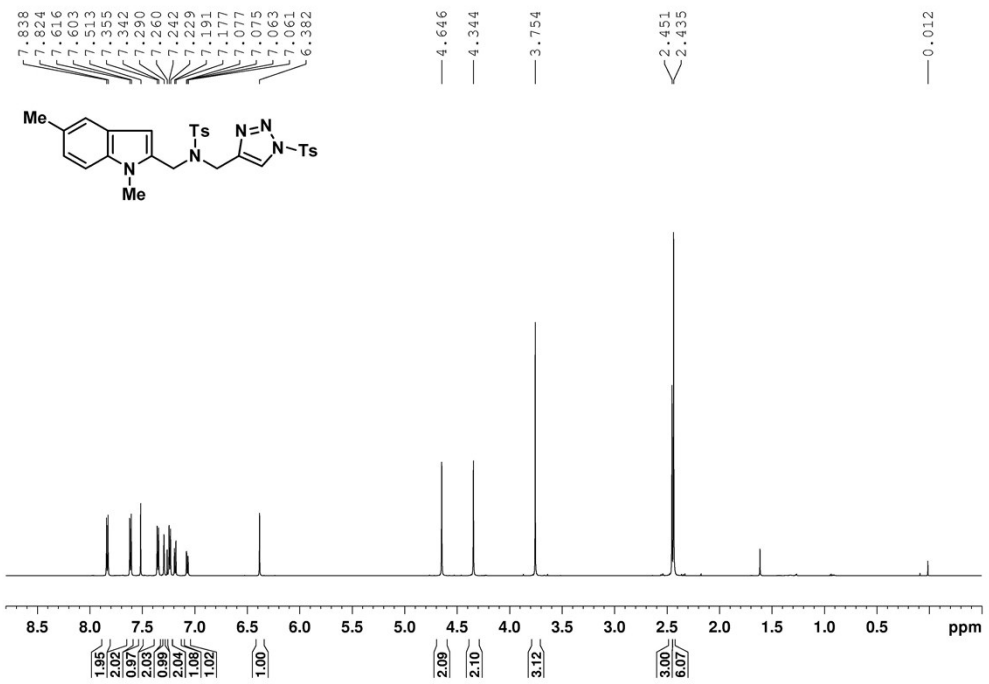
^{13}C NMR Spectrum for **6c** ($CDCl_3$, 150 MHz)



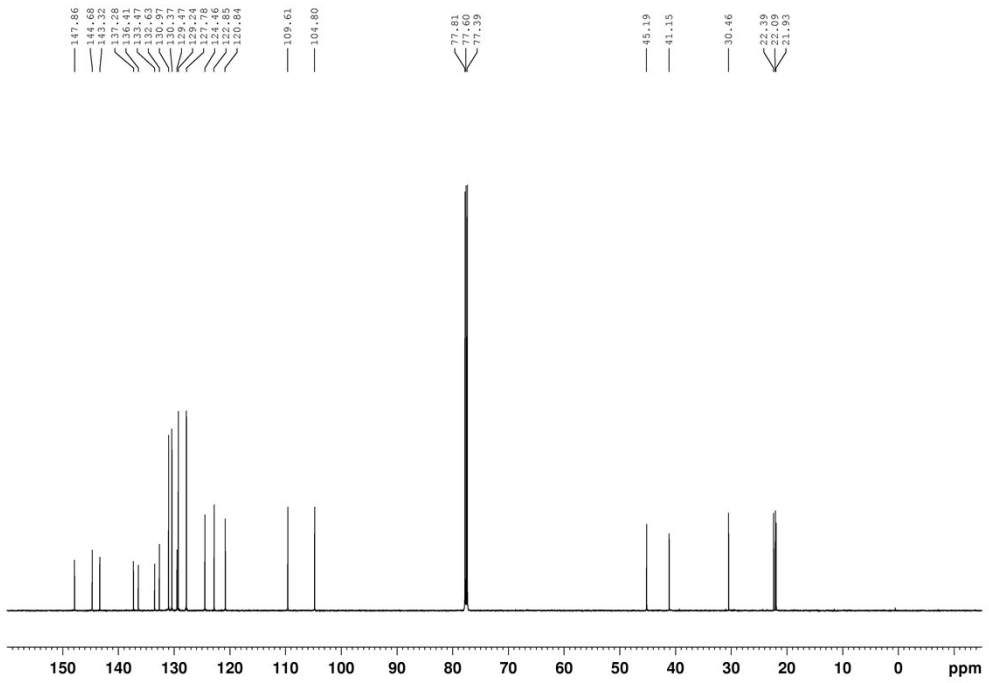
^{1}H NMR Spectrum for **6d** ($CDCl_3$, 600 MHz)



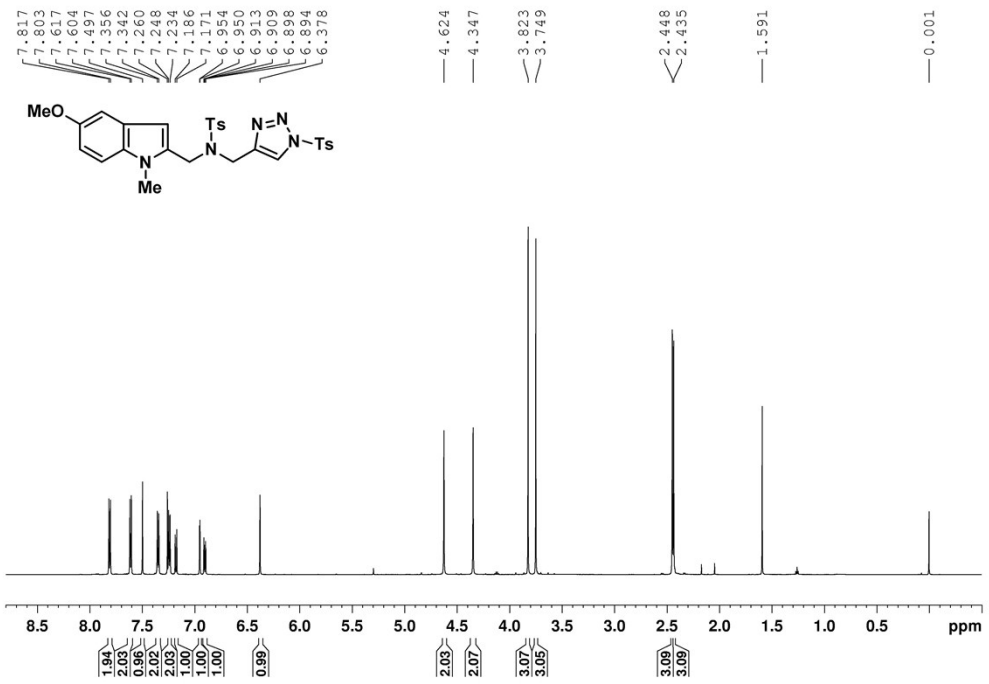
^{13}C NMR Spectrum for **6d** ($CDCl_3$, 150 MHz)



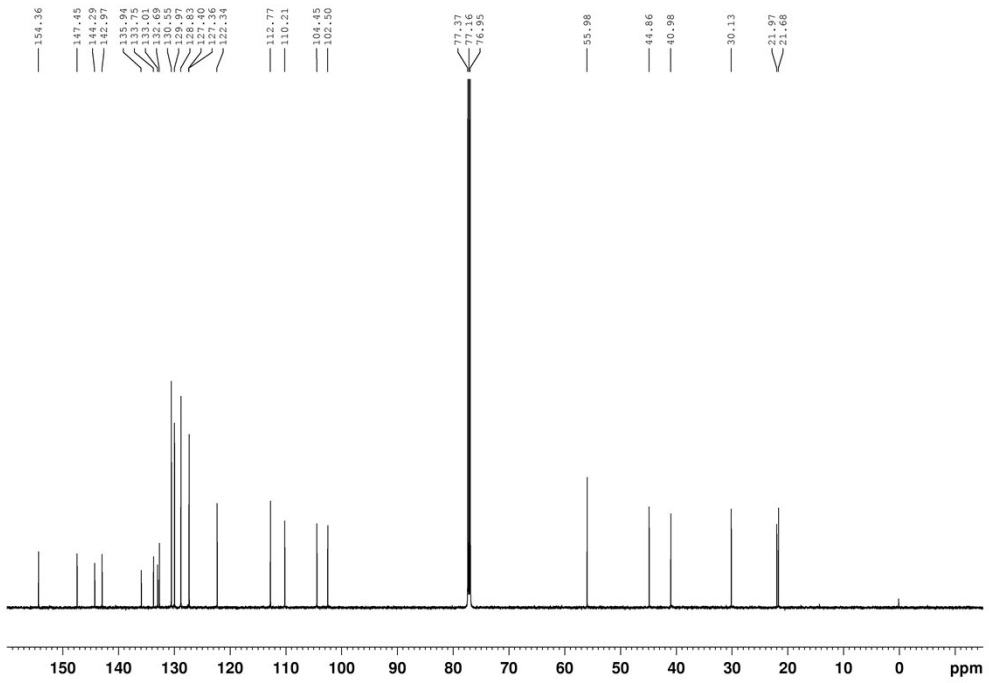
^{1}H NMR Spectrum for **6e** ($CDCl_3$, 600 MHz)



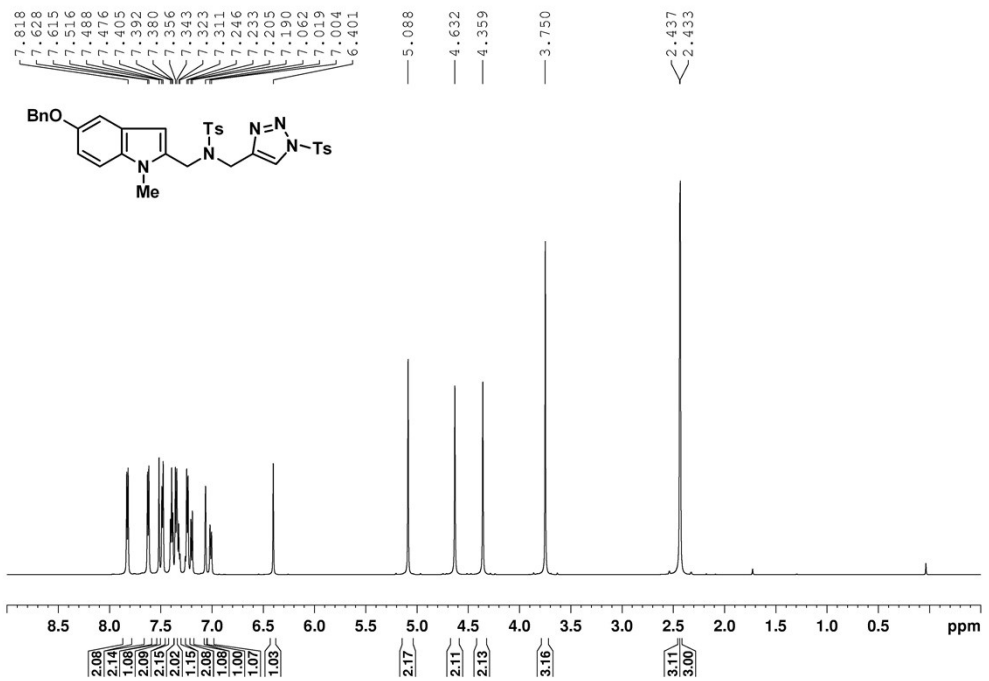
^{13}C NMR Spectrum for **6e** ($CDCl_3$, 150 MHz)



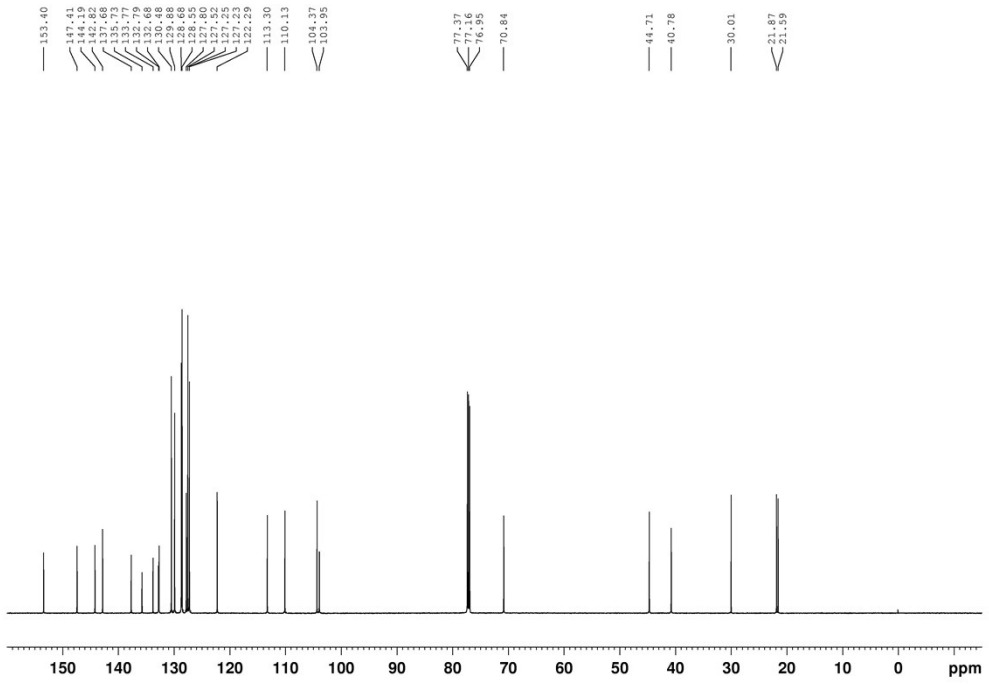
^{1}H NMR Spectrum for **6f** ($CDCl_3$, 600 MHz)



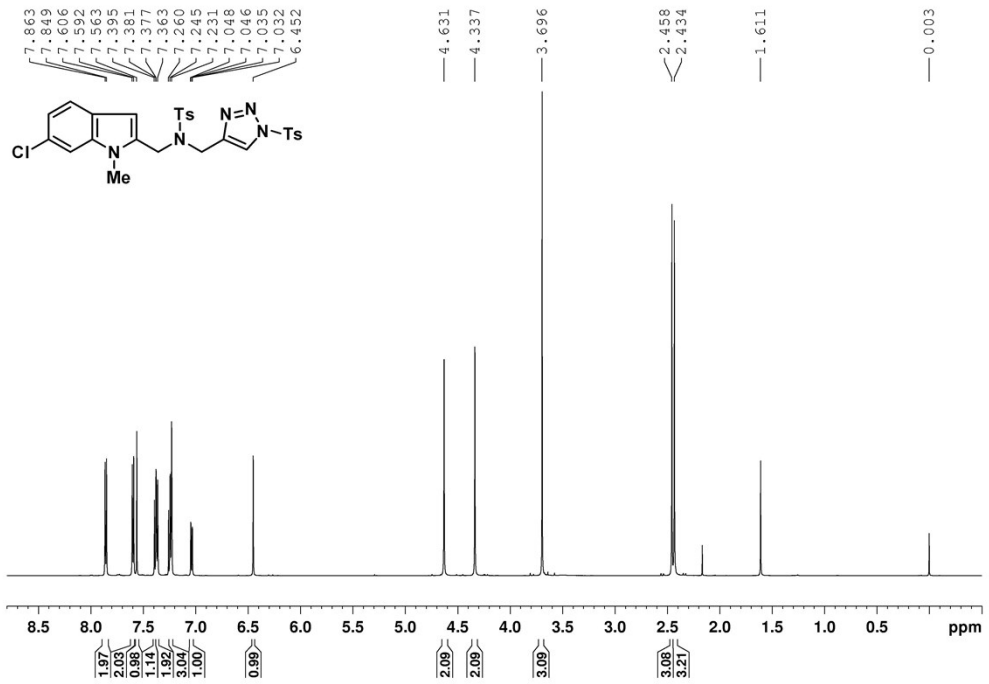
^{13}C NMR Spectrum for **6f** ($CDCl_3$, 150 MHz)



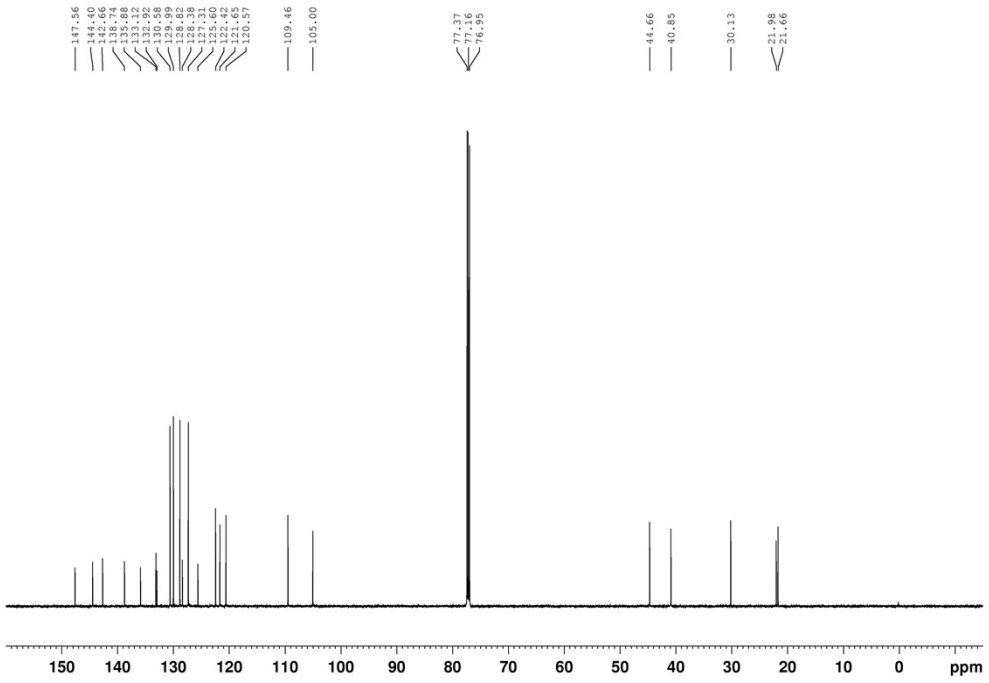
^{1}H NMR Spectrum for **6g** ($CDCl_3$, 600 MHz)



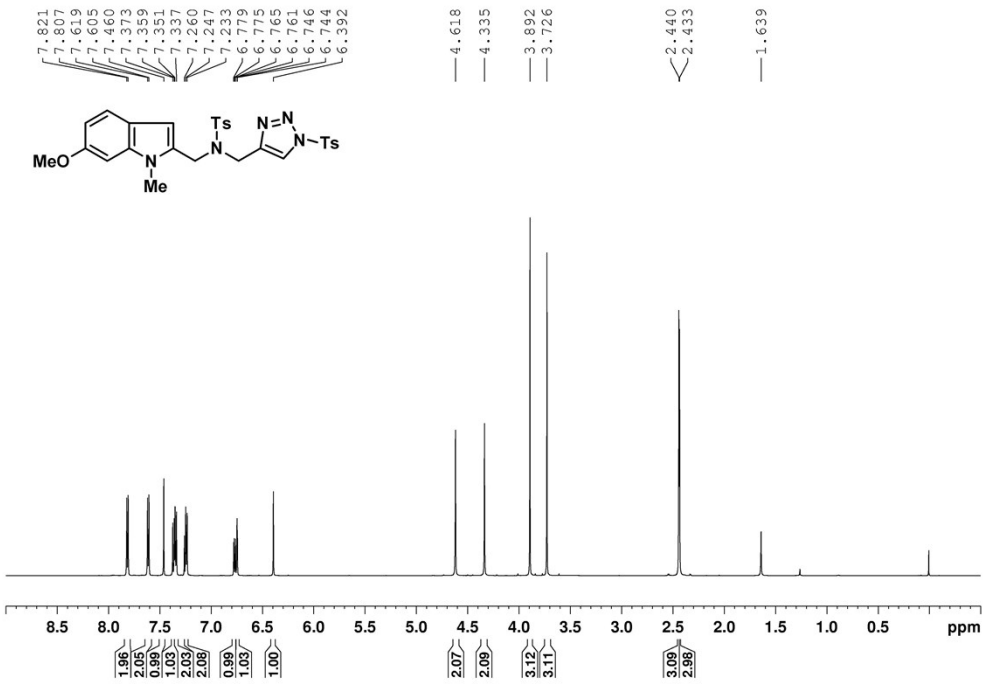
^{13}C NMR Spectrum for **6g** ($CDCl_3$, 150 MHz)



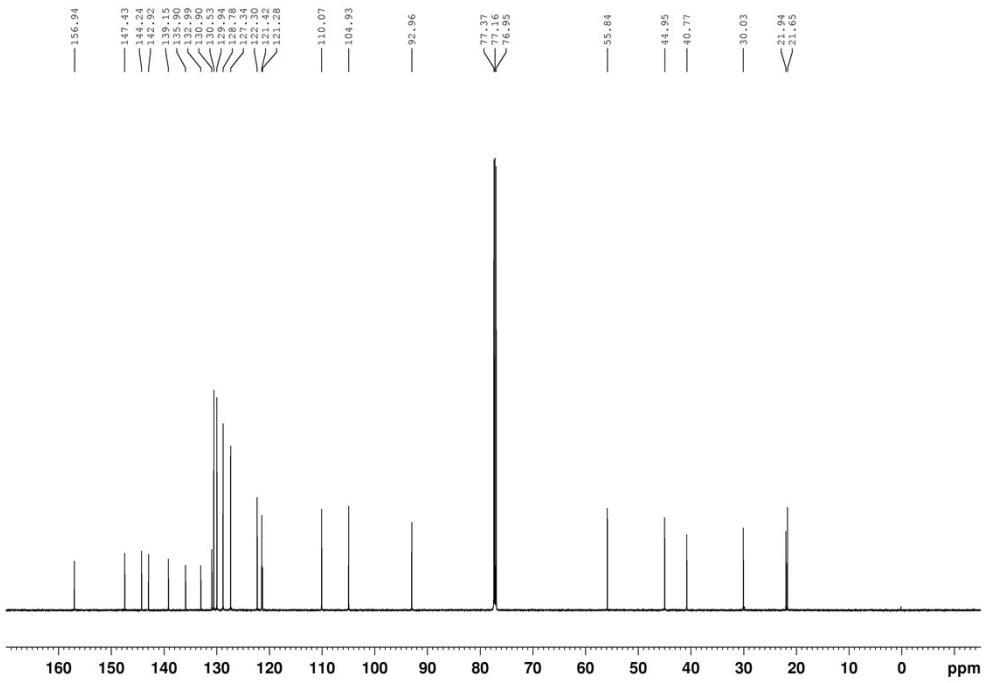
^{1}H NMR Spectrum for **6h** ($CDCl_3$, 600 MHz)



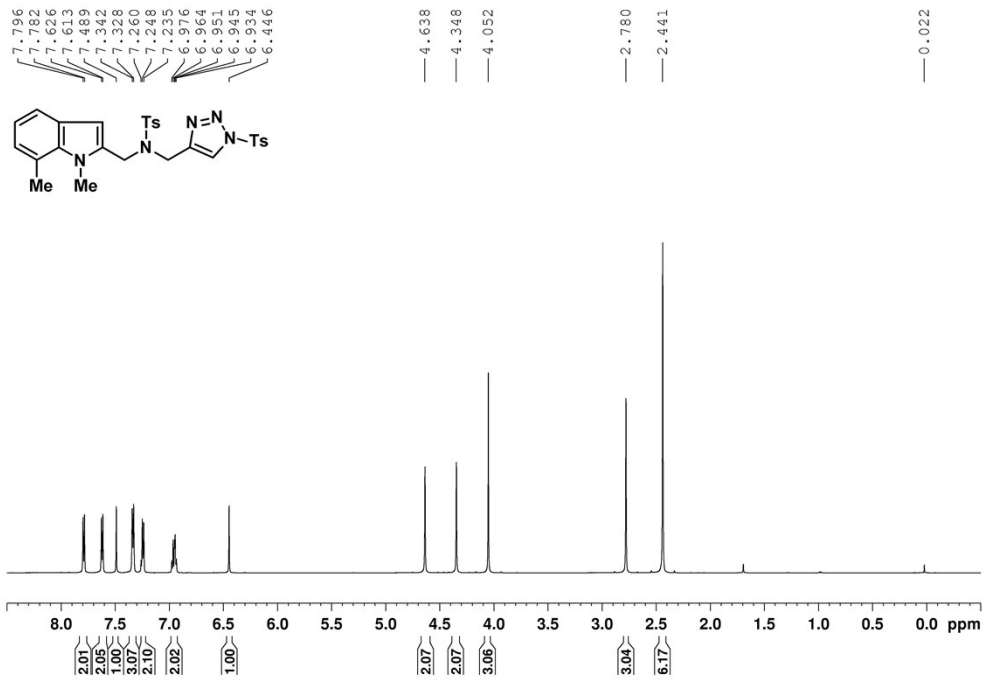
^{13}C NMR Spectrum for **6h** ($CDCl_3$, 150 MHz)



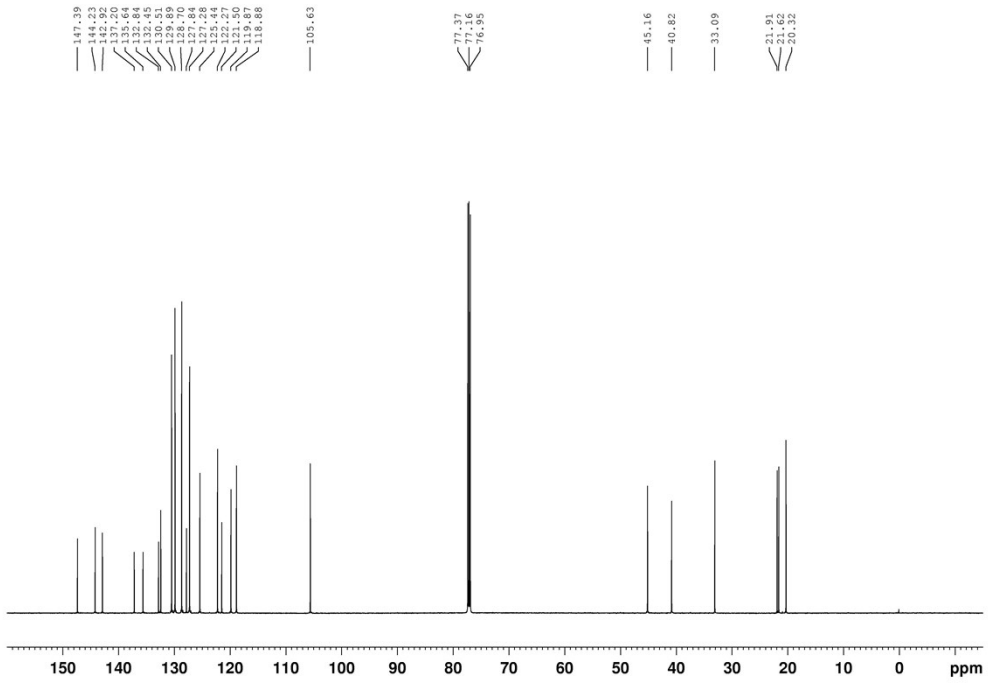
^{1}H NMR Spectrum for **6i** ($CDCl_3$, 600 MHz)



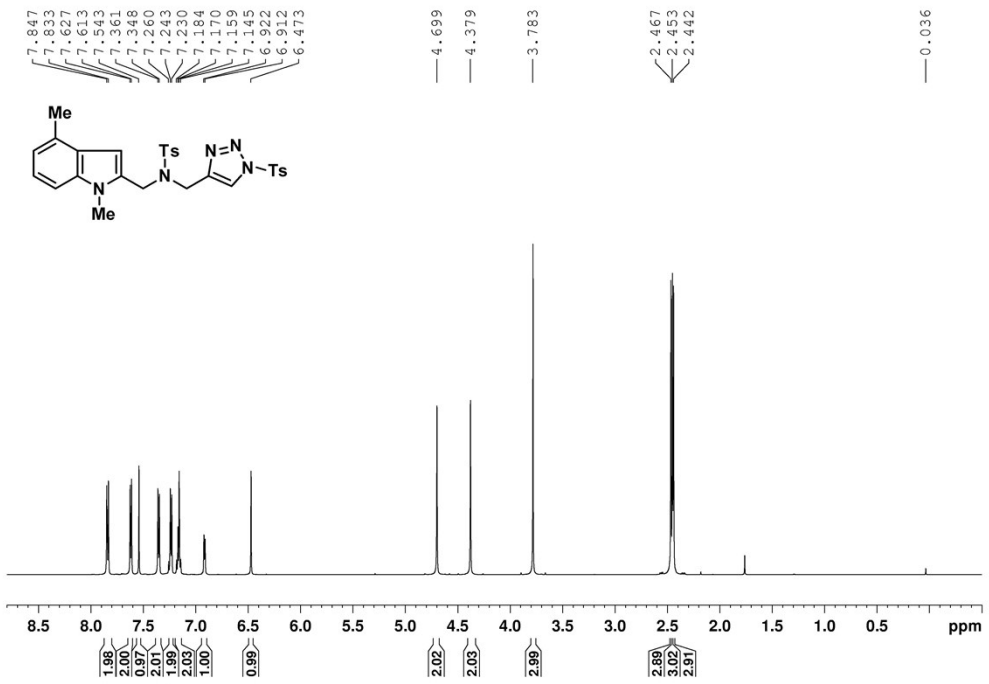
^{13}C NMR Spectrum for **6i** ($CDCl_3$, 150 MHz)



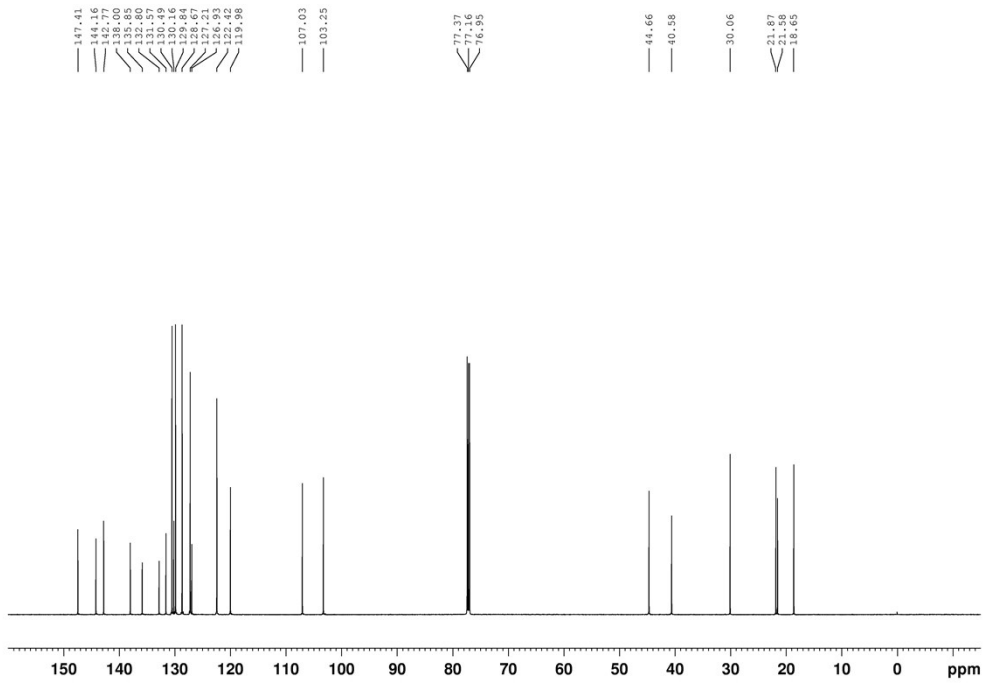
^{1}H NMR Spectrum for **6j** ($CDCl_3$, 600 MHz)



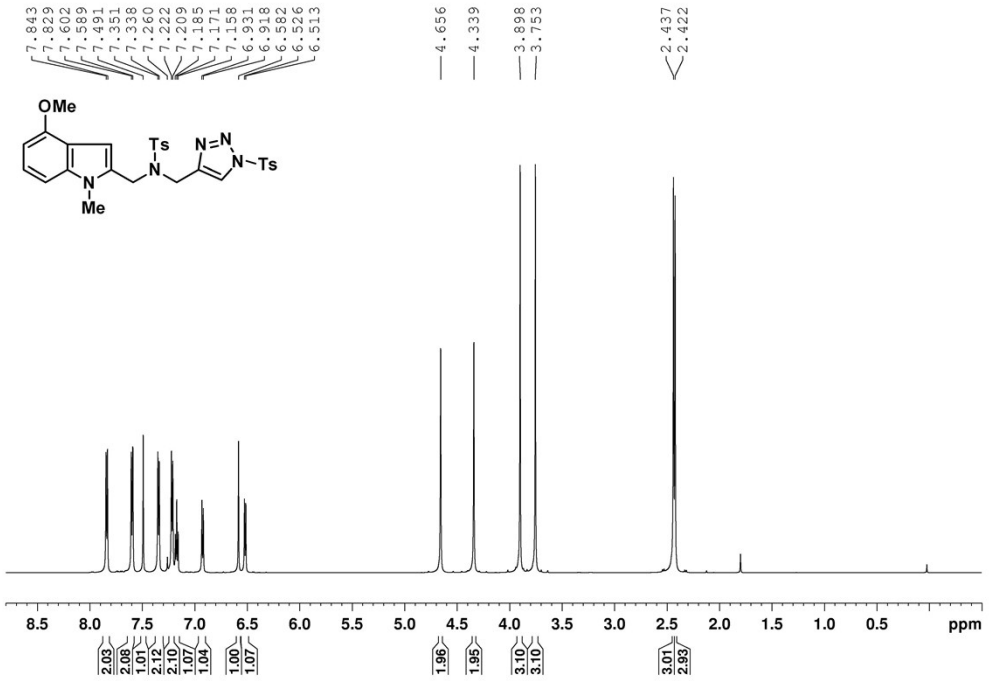
^{13}C NMR Spectrum for **6j** ($CDCl_3$, 150 MHz)



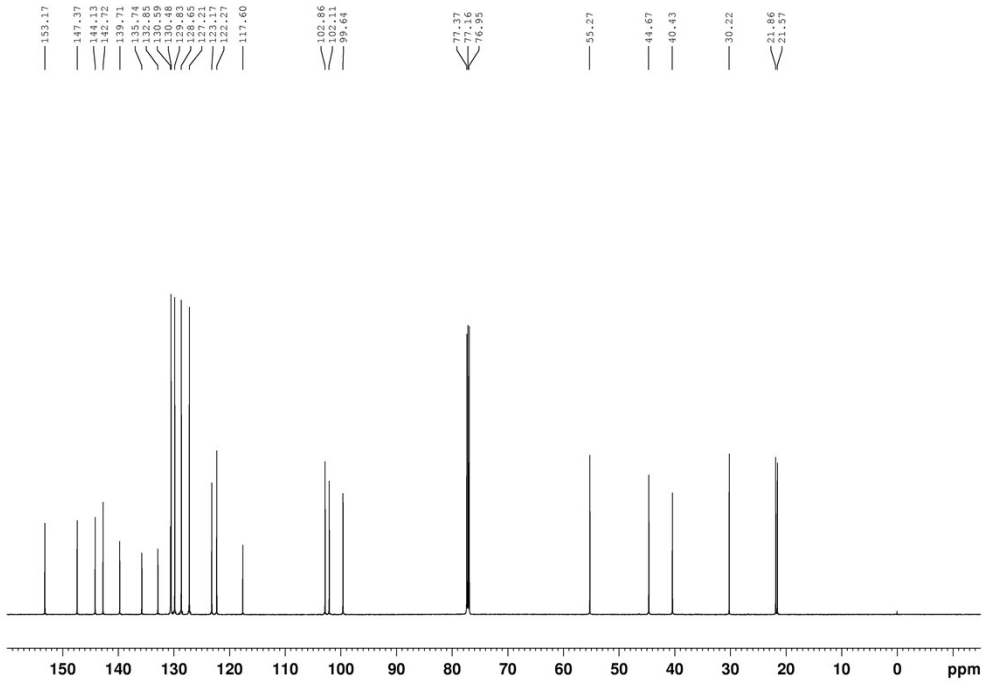
^{1}H NMR Spectrum for **6k** ($CDCl_3$, 600 MHz)



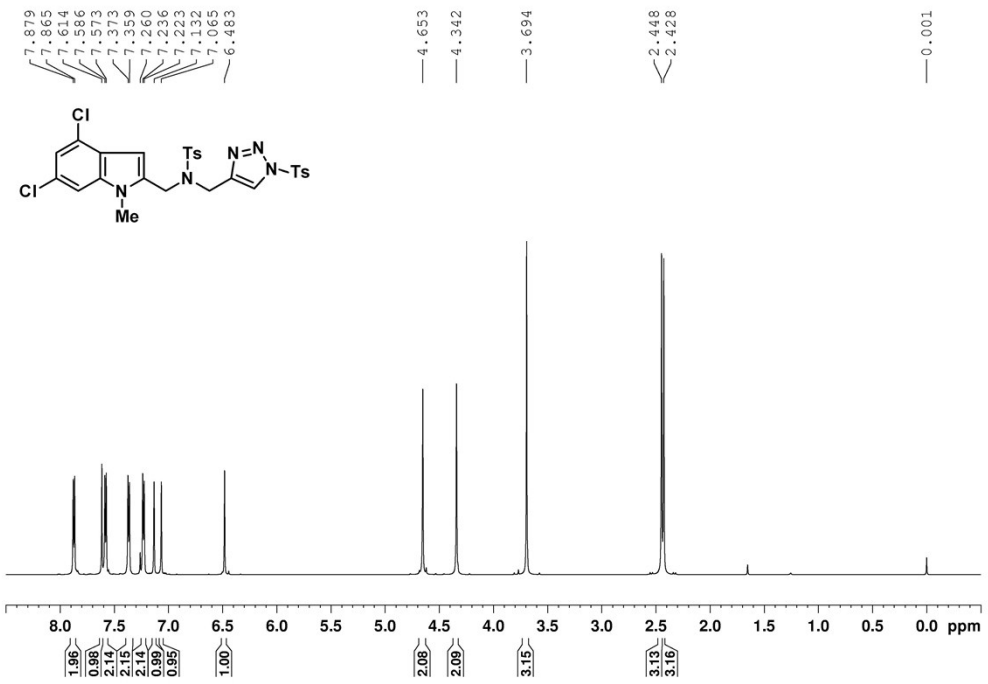
^{13}C NMR Spectrum for **6k** ($CDCl_3$, 150 MHz)



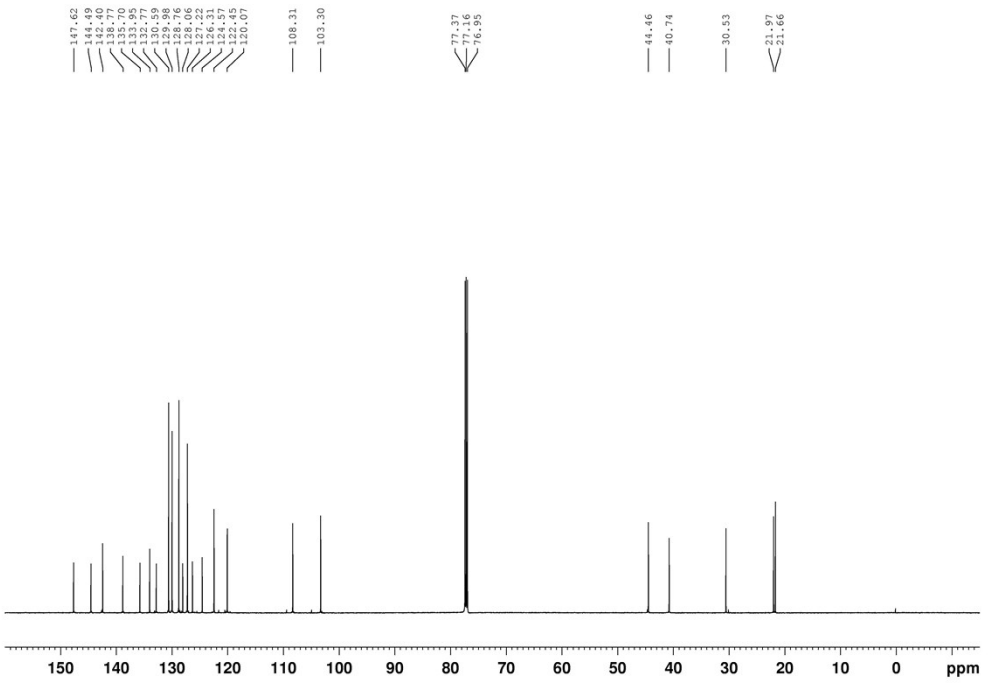
^{1}H NMR Spectrum for **6l** ($CDCl_3$, 600 MHz)



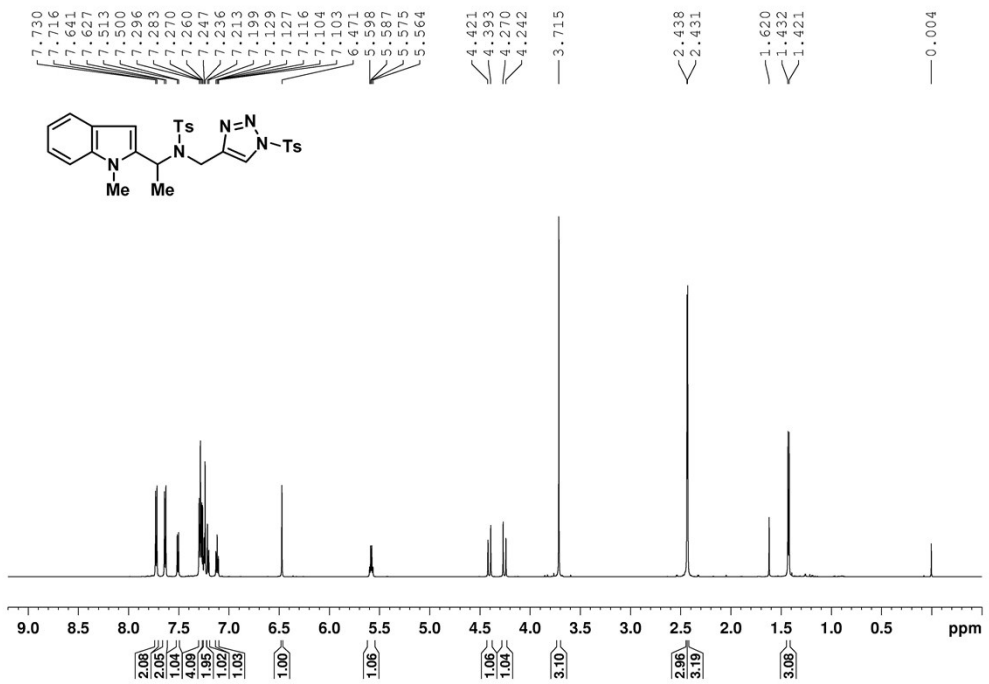
^{13}C NMR Spectrum for **6l** ($CDCl_3$, 150 MHz)



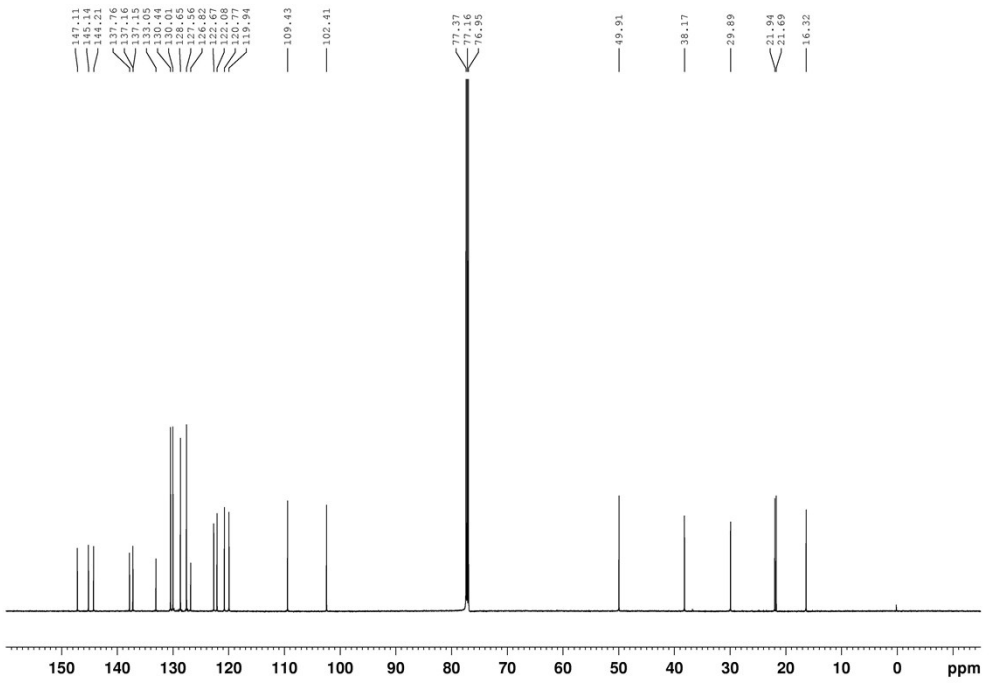
^{1}H NMR Spectrum for **6m** ($CDCl_3$, 600 MHz)



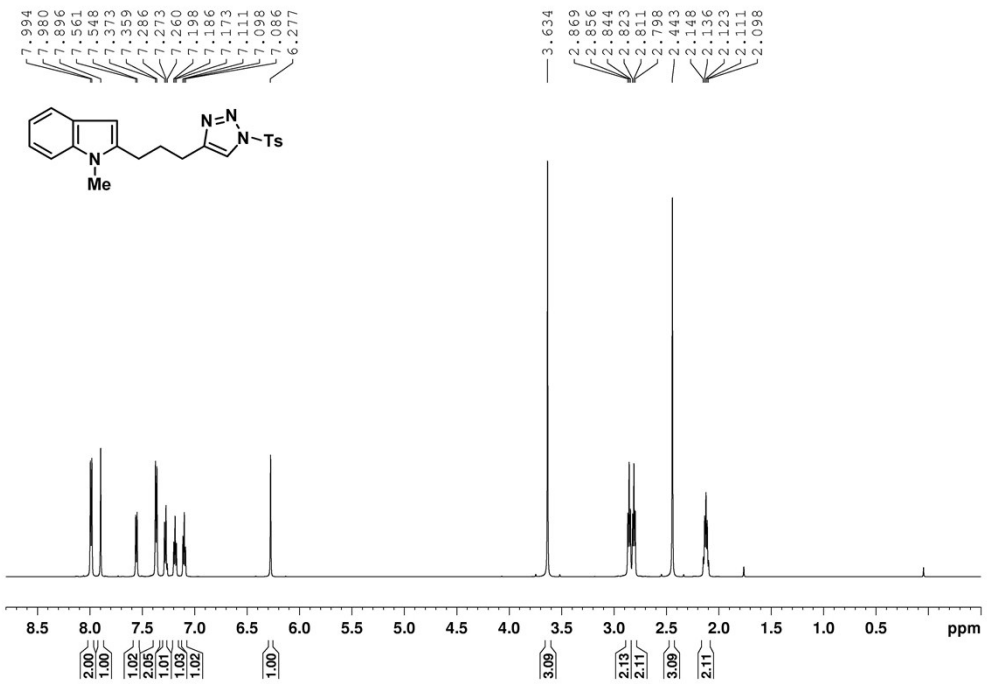
^{13}C NMR Spectrum for **6m** ($CDCl_3$, 150 MHz)



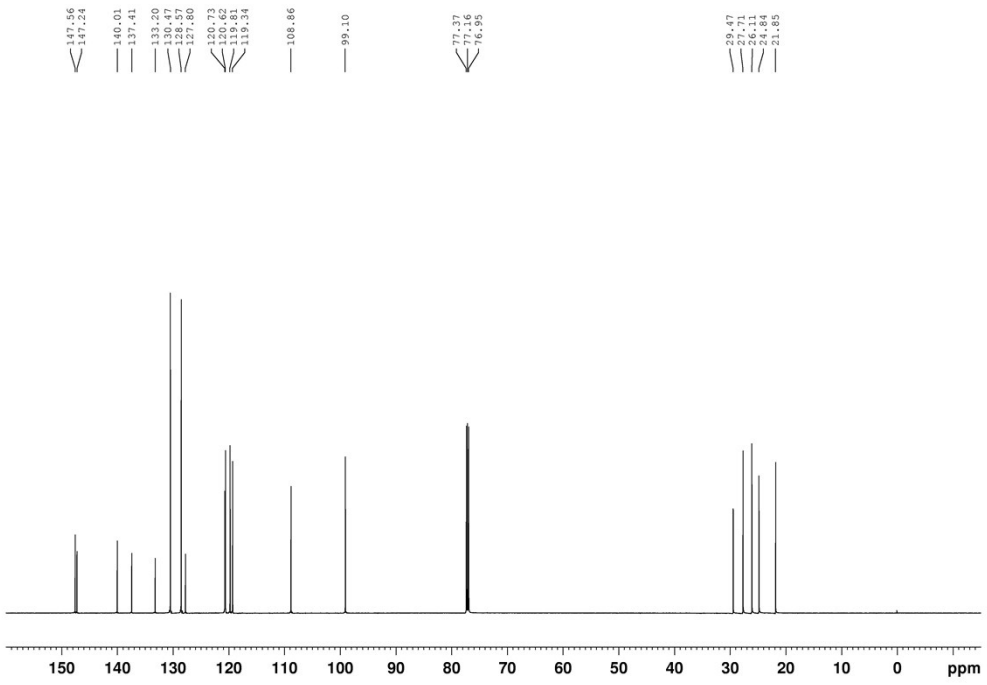
^{1}H NMR Spectrum for **6n** ($CDCl_3$, 600 MHz)



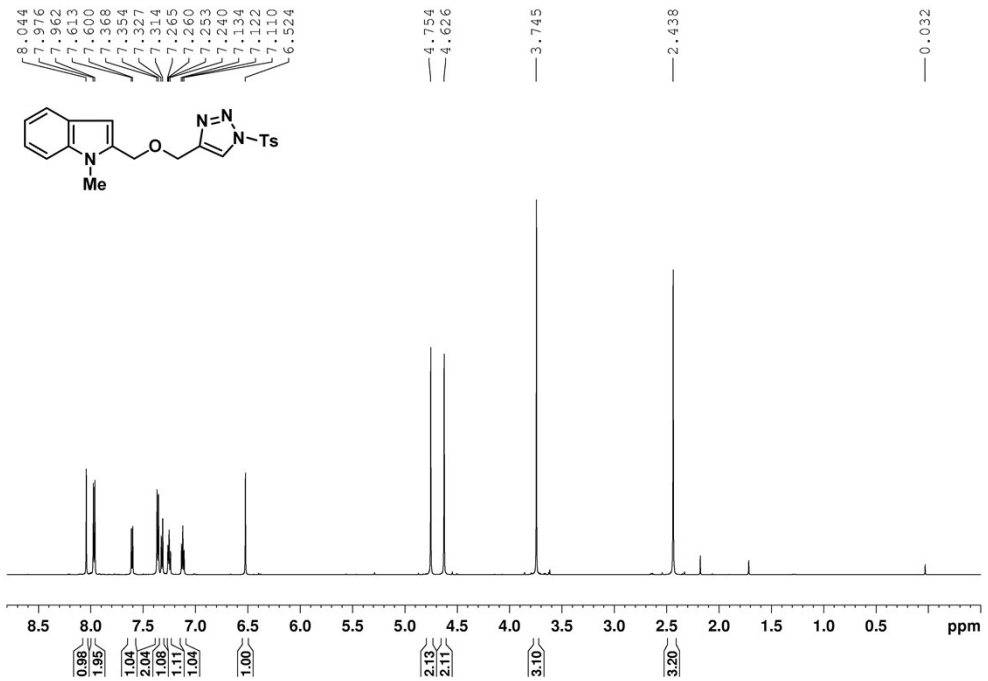
^{13}C NMR Spectrum for **6n** ($CDCl_3$, 150 MHz)



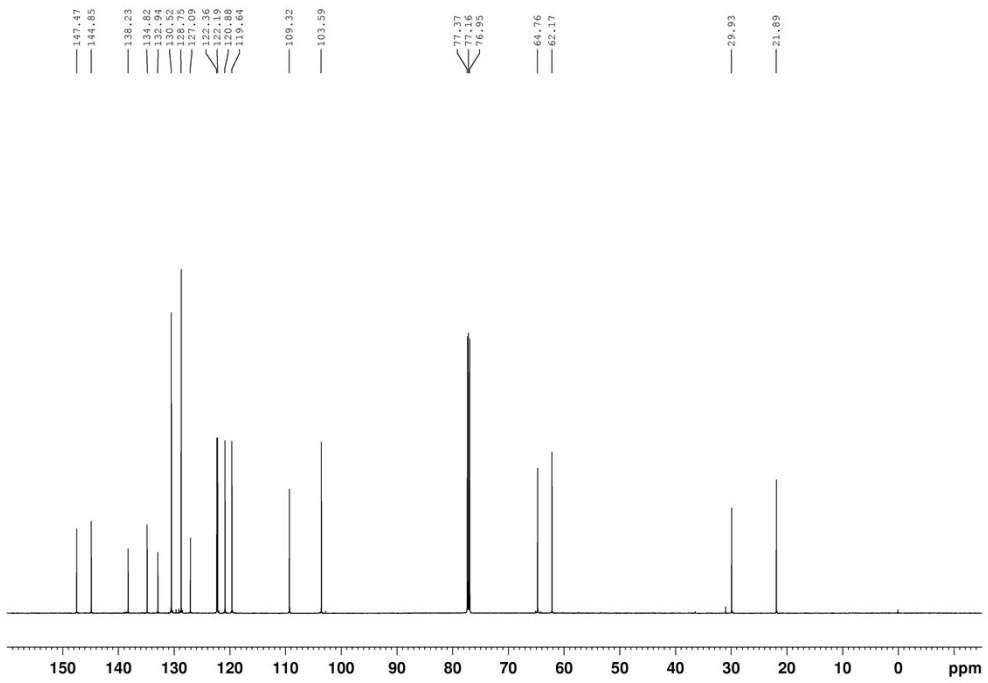
^{1}H NMR Spectrum for **6o** ($CDCl_3$, 600 MHz)



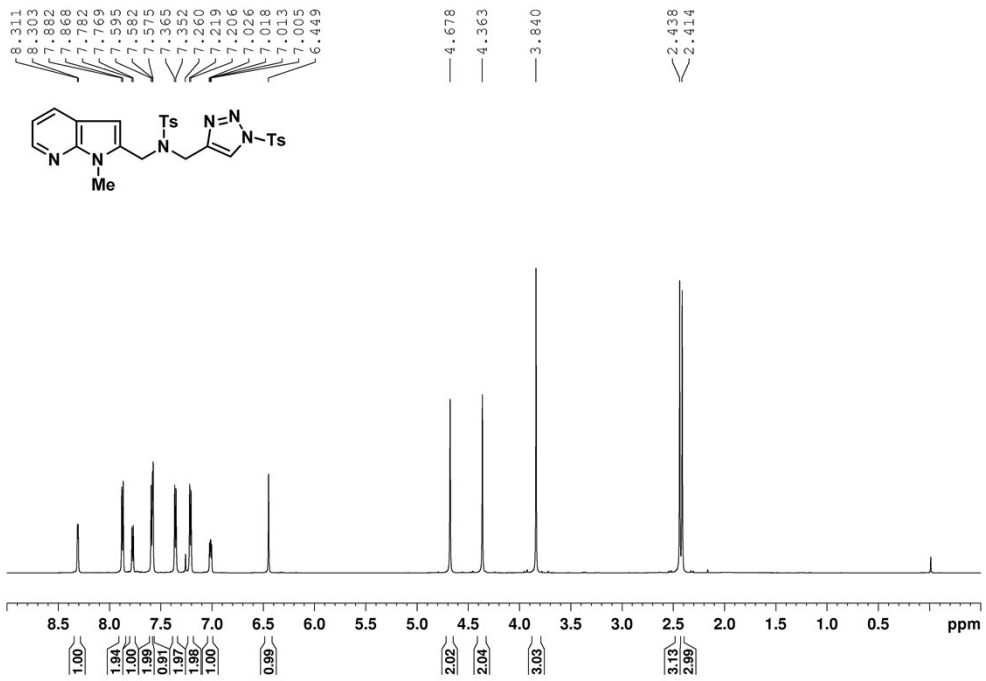
^{13}C NMR Spectrum for **6o** ($CDCl_3$, 150 MHz)



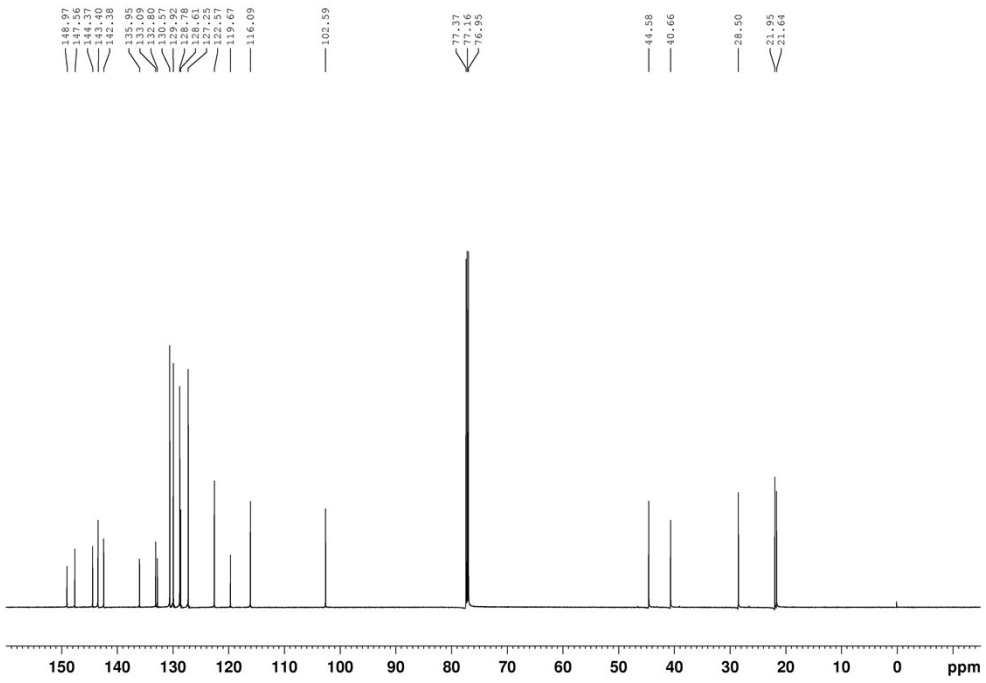
^{1}H NMR Spectrum for **6p** ($CDCl_3$, 600 MHz)



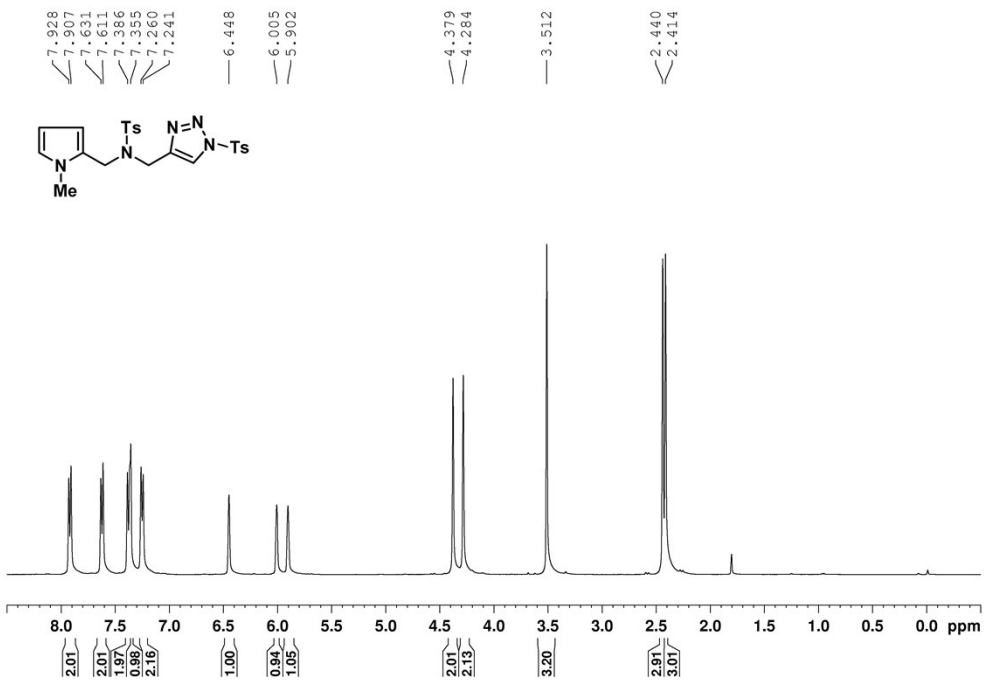
^{13}C NMR Spectrum for **6p** ($CDCl_3$, 150 MHz)



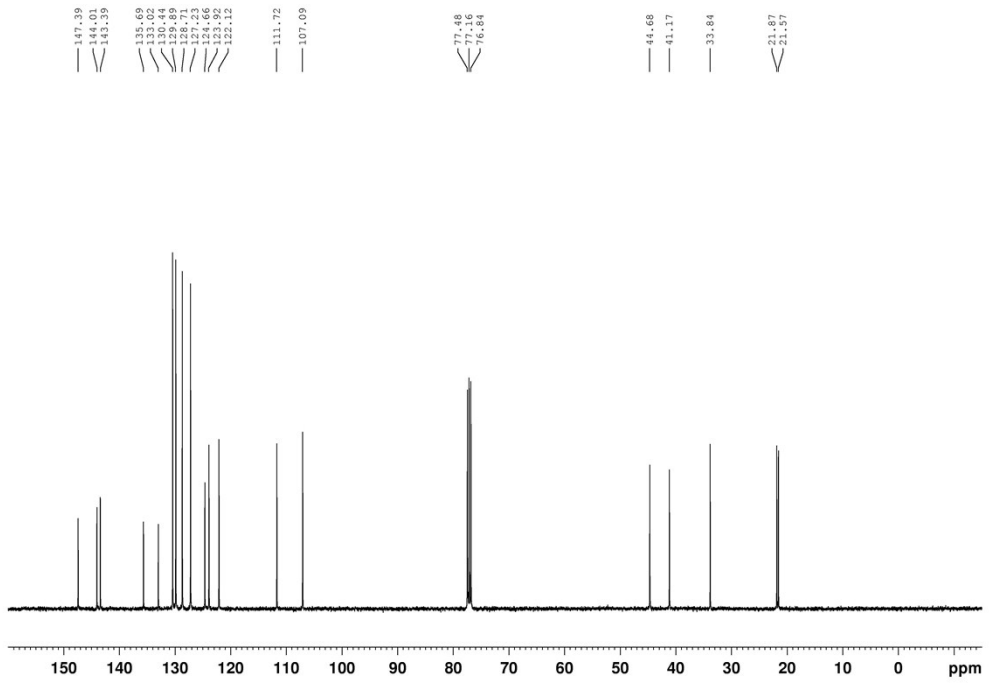
^{1}H NMR Spectrum for **6q** ($CDCl_3$, 600 MHz)



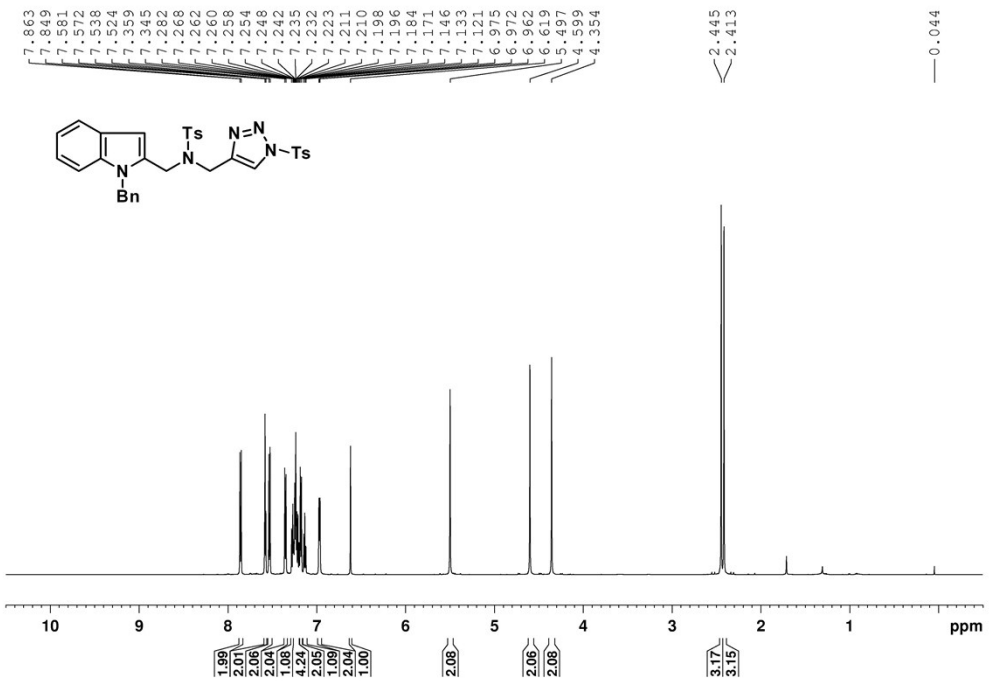
^{13}C NMR Spectrum for **6q** ($CDCl_3$, 150 MHz)



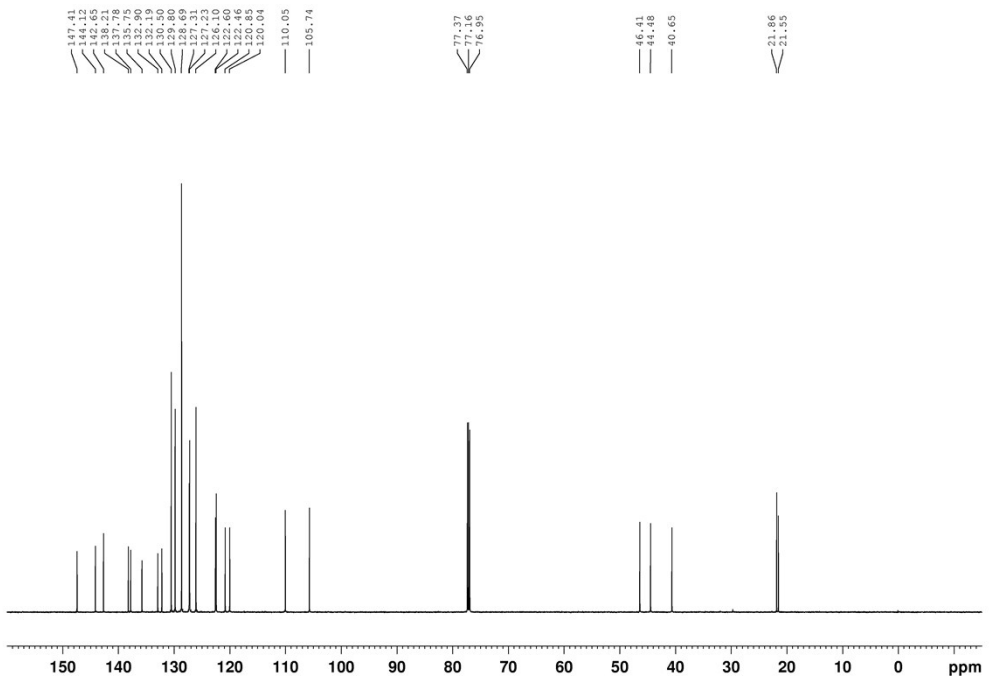
^{1}H NMR Spectrum for **6r** ($CDCl_3$, 400 MHz)



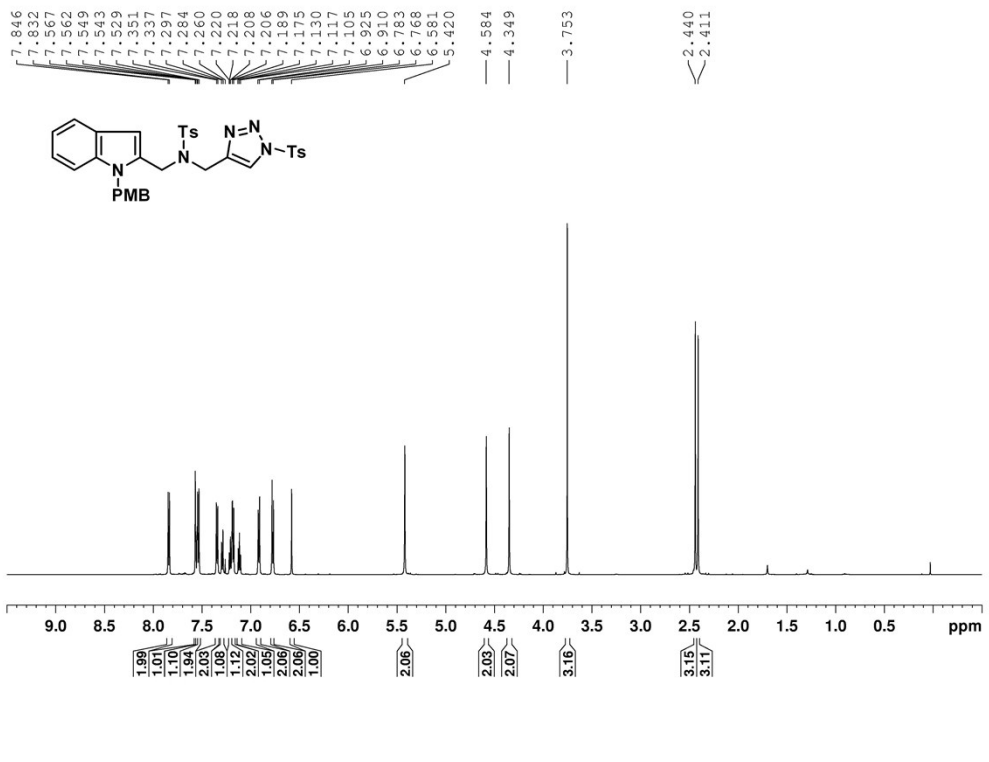
^{13}C NMR Spectrum for **6r** ($CDCl_3$, 100 MHz)



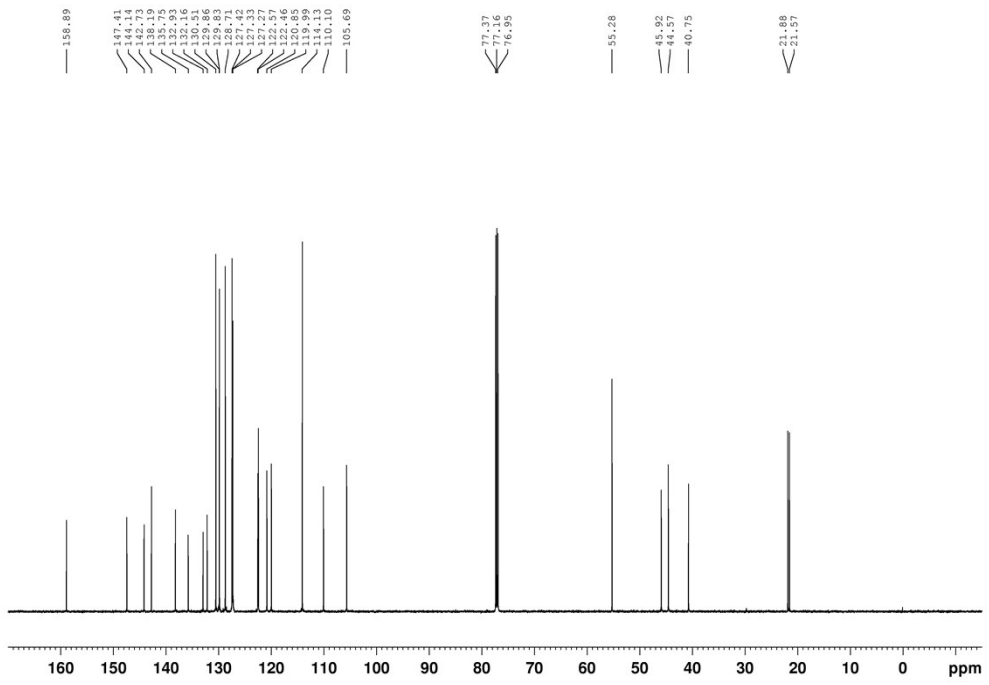
^{1}H NMR Spectrum for **6s** ($CDCl_3$, 600 MHz)



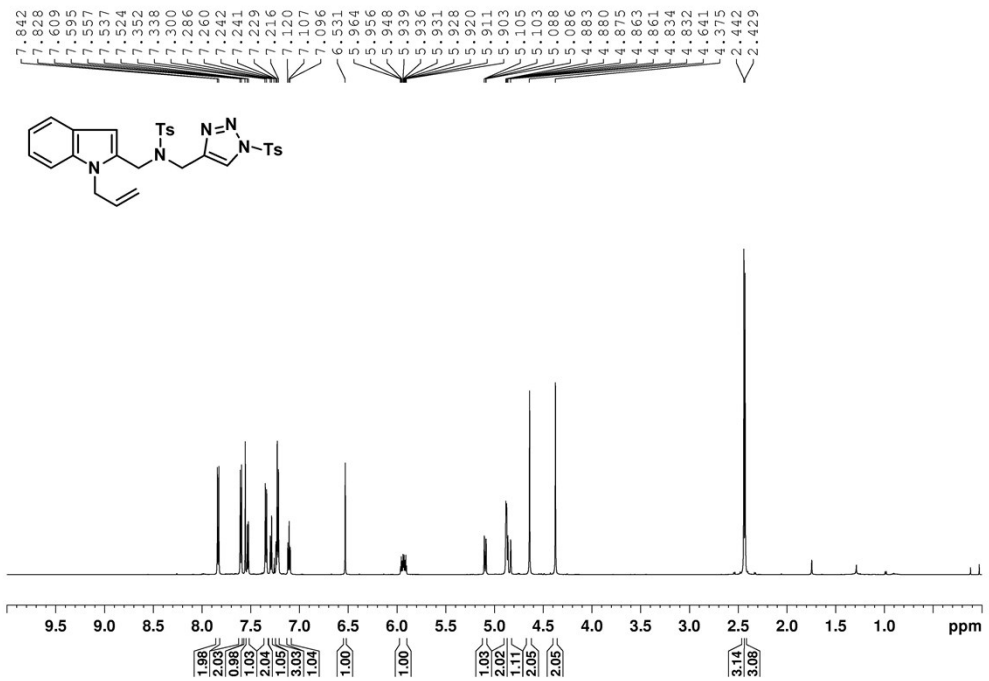
^{13}C NMR Spectrum for **6s** ($CDCl_3$, 150 MHz)



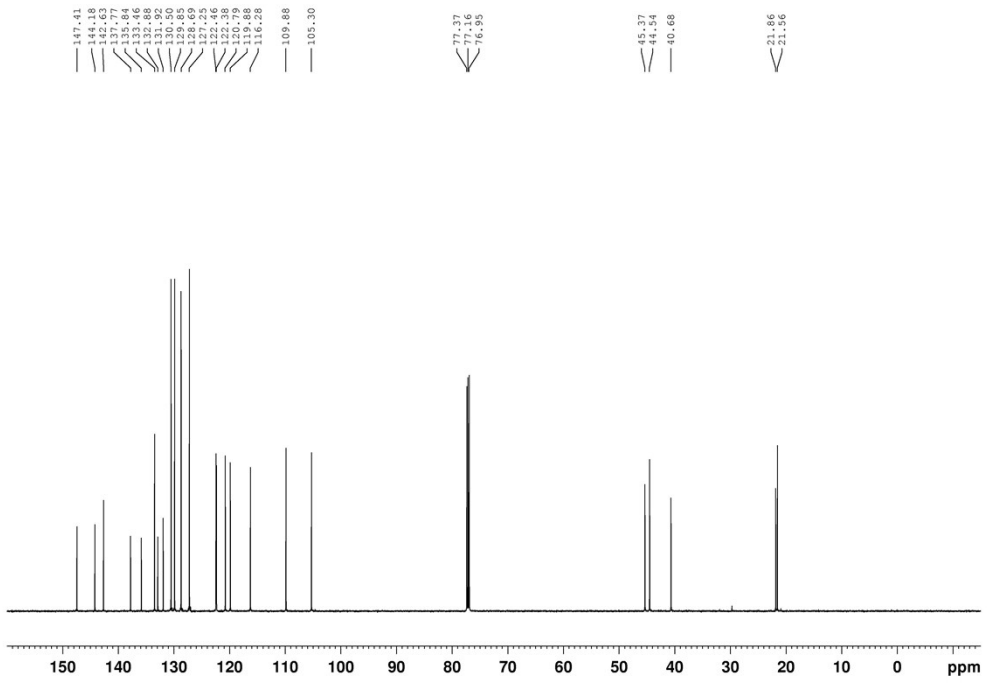
^{1}H NMR Spectrum for **6t** ($CDCl_3$, 600 MHz)



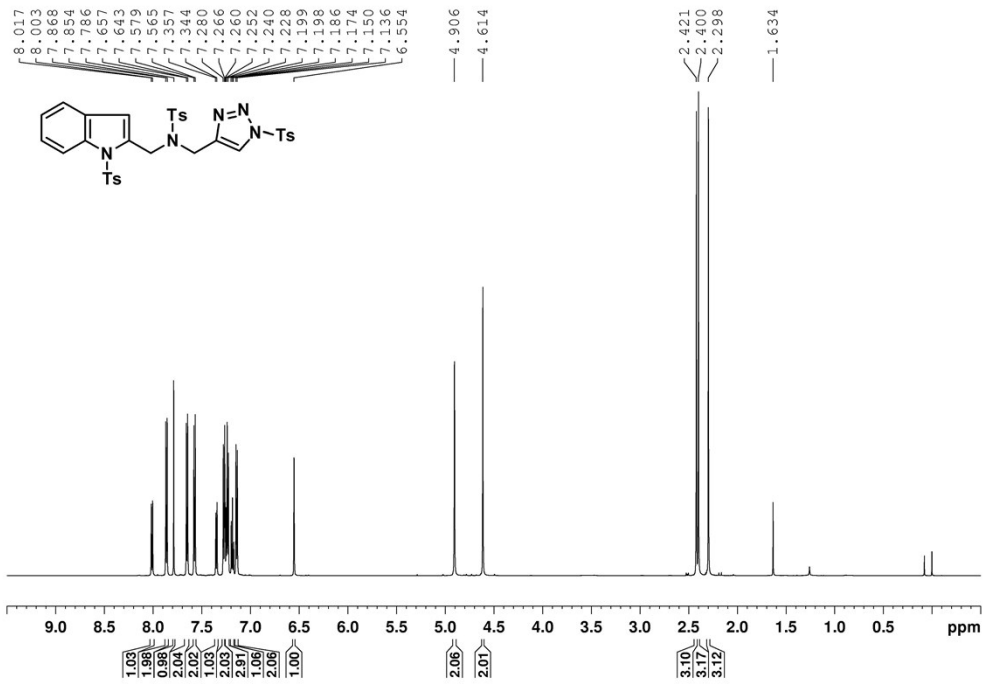
^{13}C NMR Spectrum for **6t** ($CDCl_3$, 150 MHz)



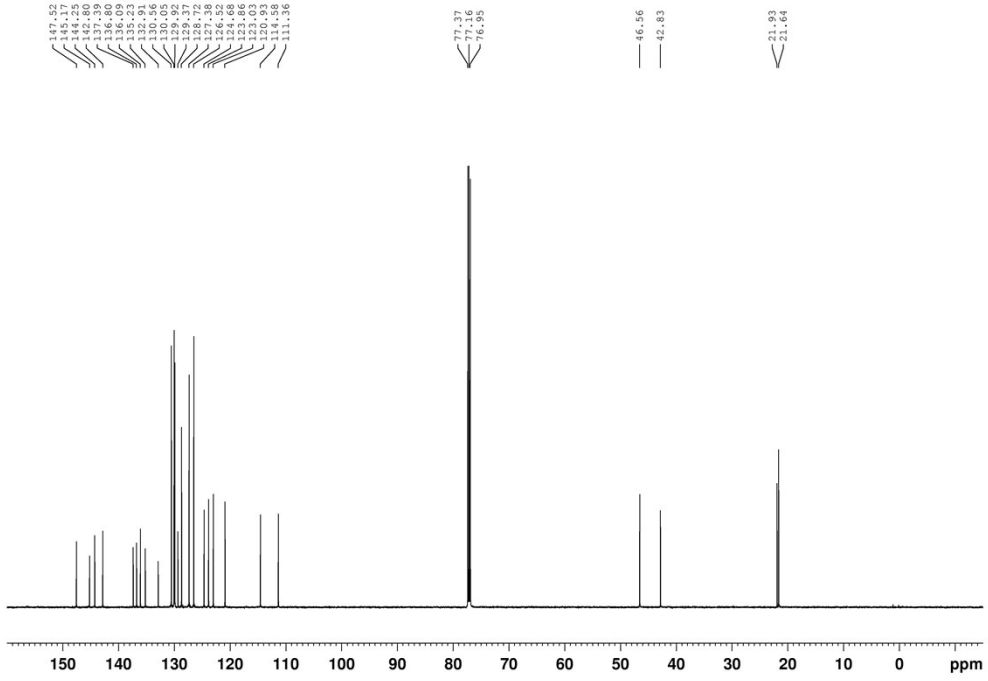
^{1}H NMR Spectrum for **6u** ($CDCl_3$, 600 MHz)



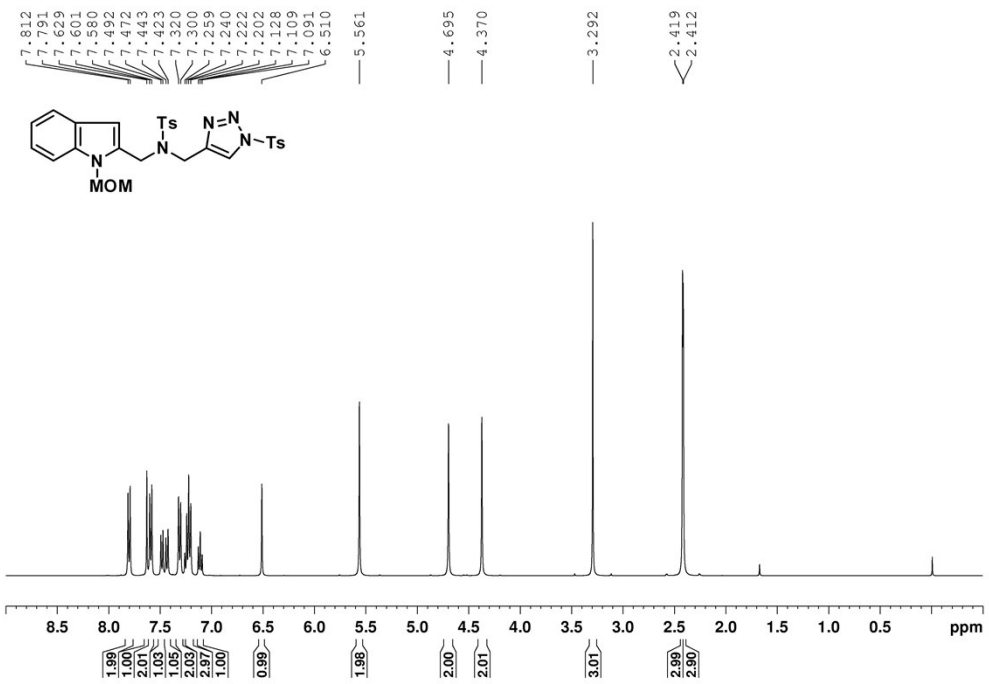
^{13}C NMR Spectrum for **6u** ($CDCl_3$, 150 MHz)



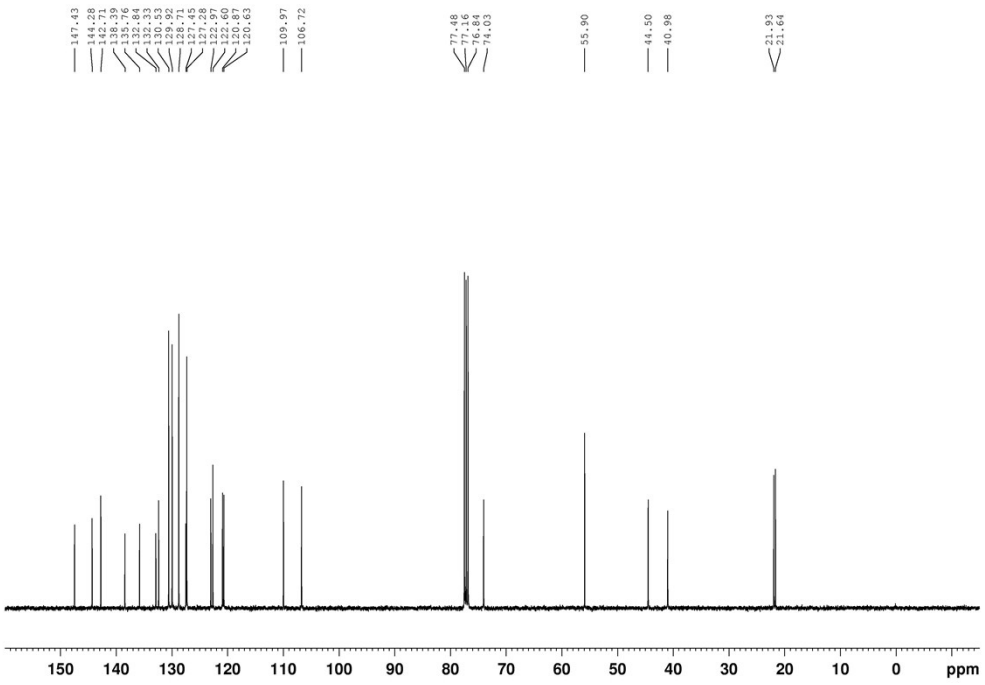
^{1}H NMR Spectrum for **6v** ($CDCl_3$, 600 MHz)



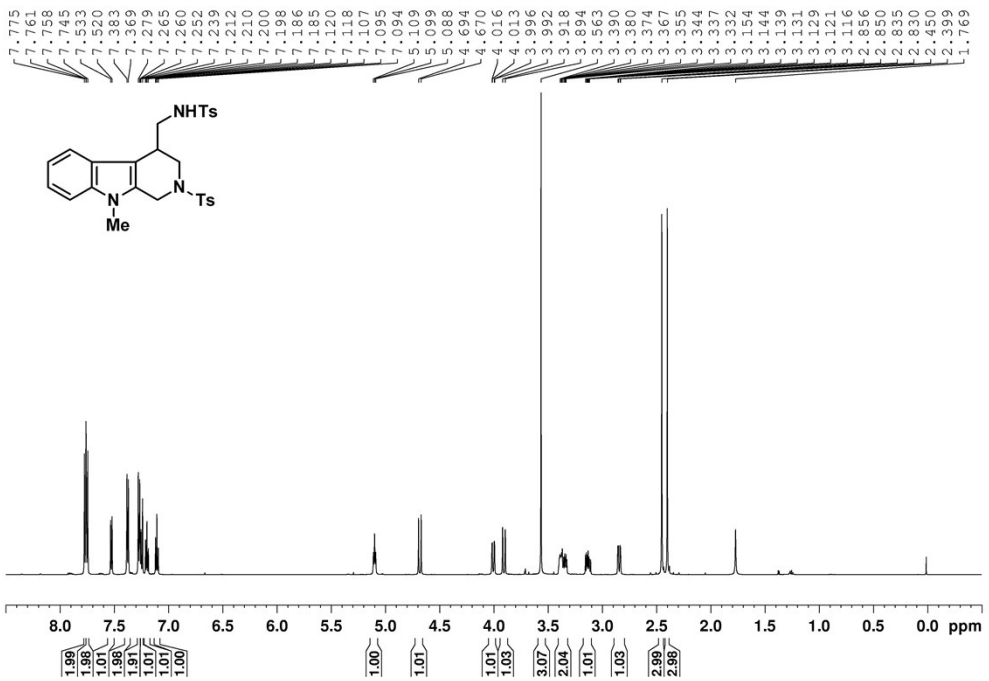
^{13}C NMR Spectrum for **6v** ($CDCl_3$, 150 MHz)



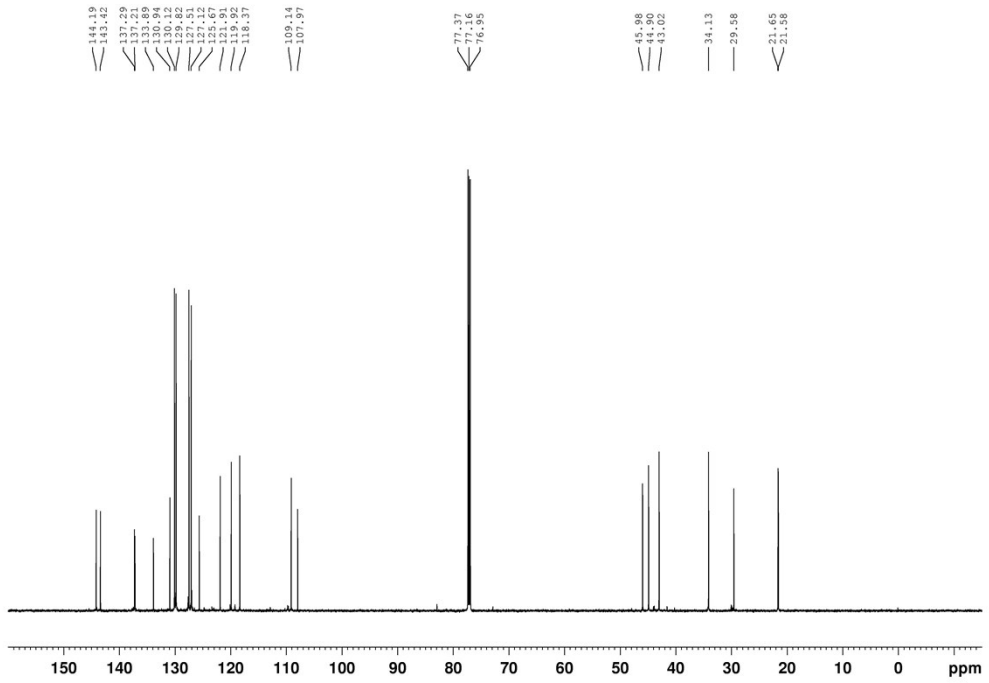
^{1}H NMR Spectrum for **6w** ($CDCl_3$, 600 MHz)



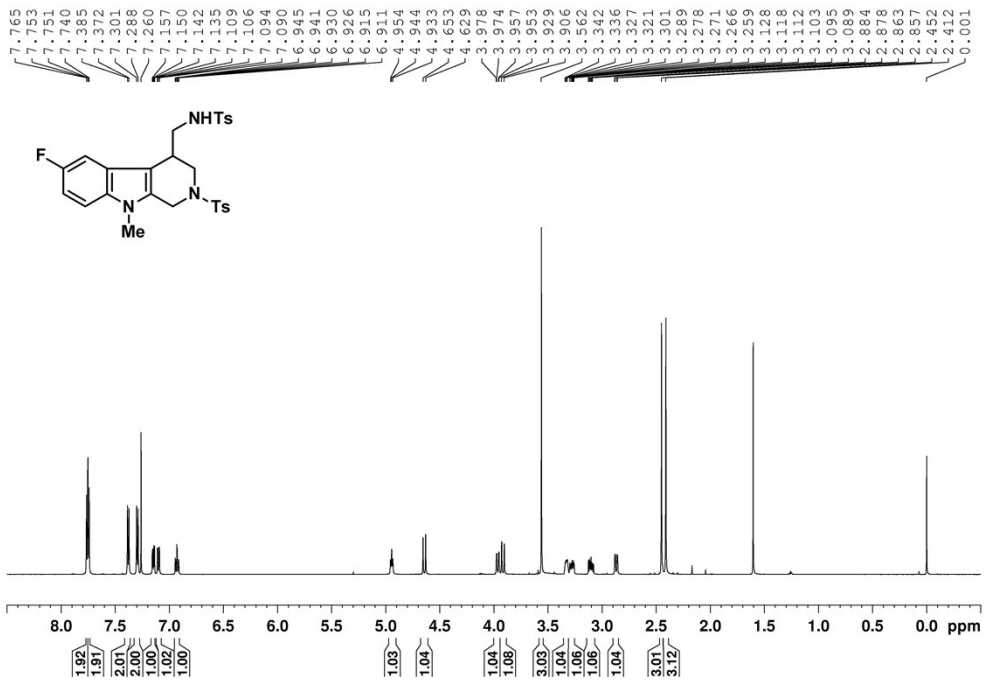
^{13}C NMR Spectrum for **6w** ($CDCl_3$, 150 MHz)



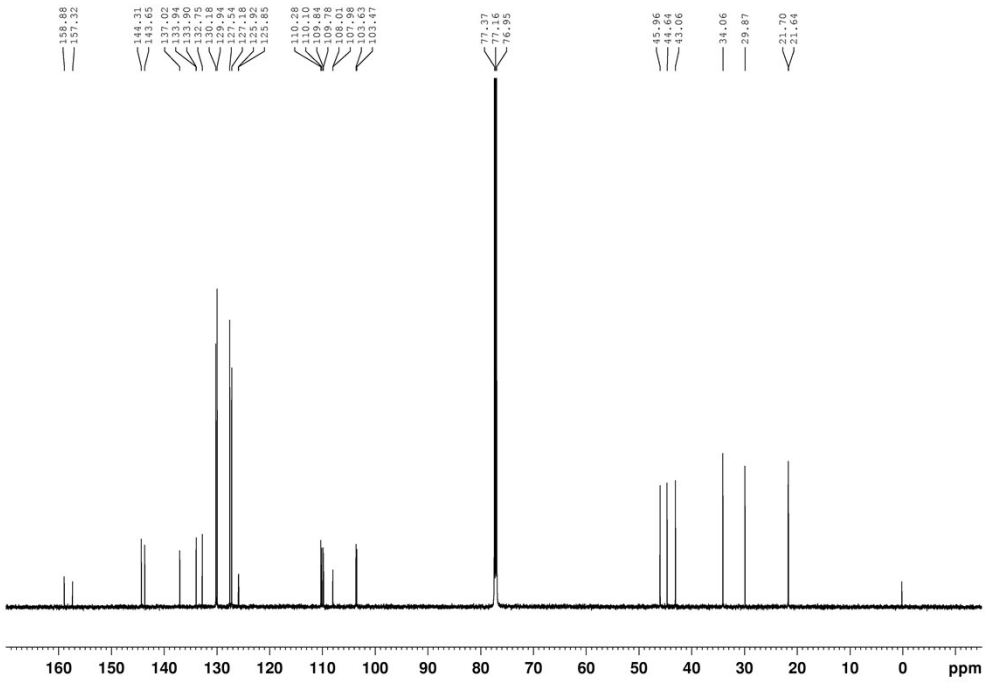
^{1}H NMR Spectrum for **11a** ($CDCl_3$, 600 MHz)



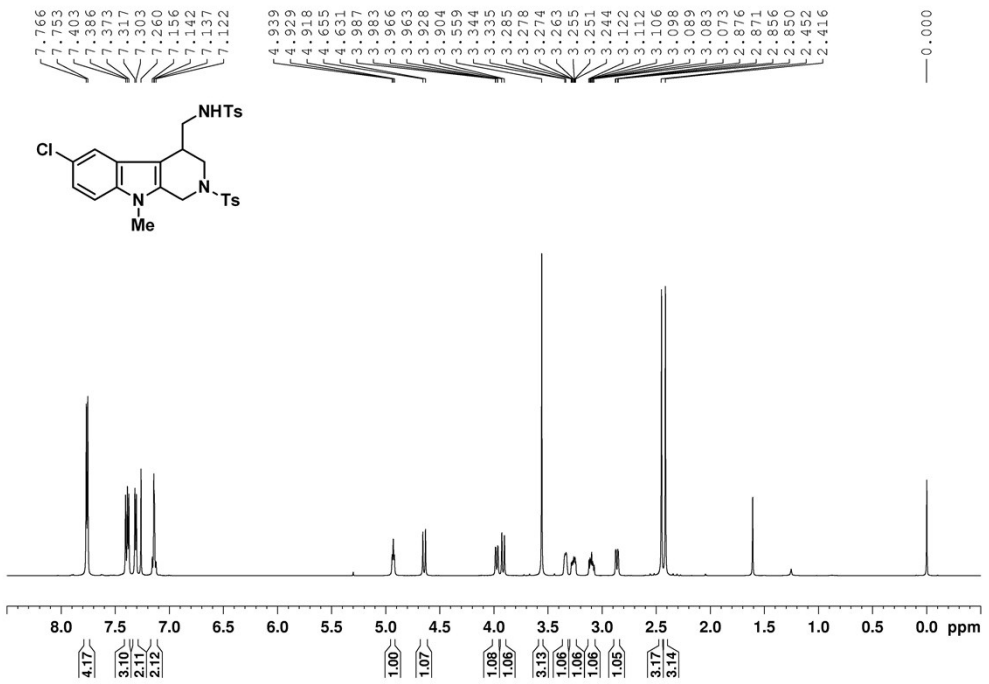
^{13}C NMR Spectrum for **11a** ($CDCl_3$, 150 MHz)



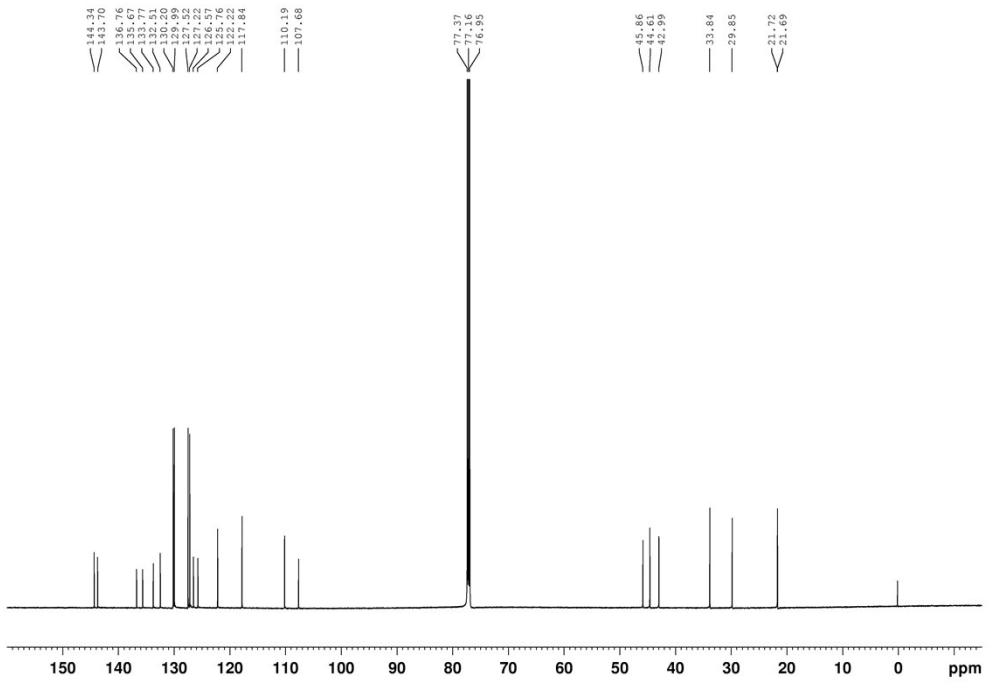
^{1}H NMR Spectrum for **11b** ($CDCl_3$, 600 MHz)



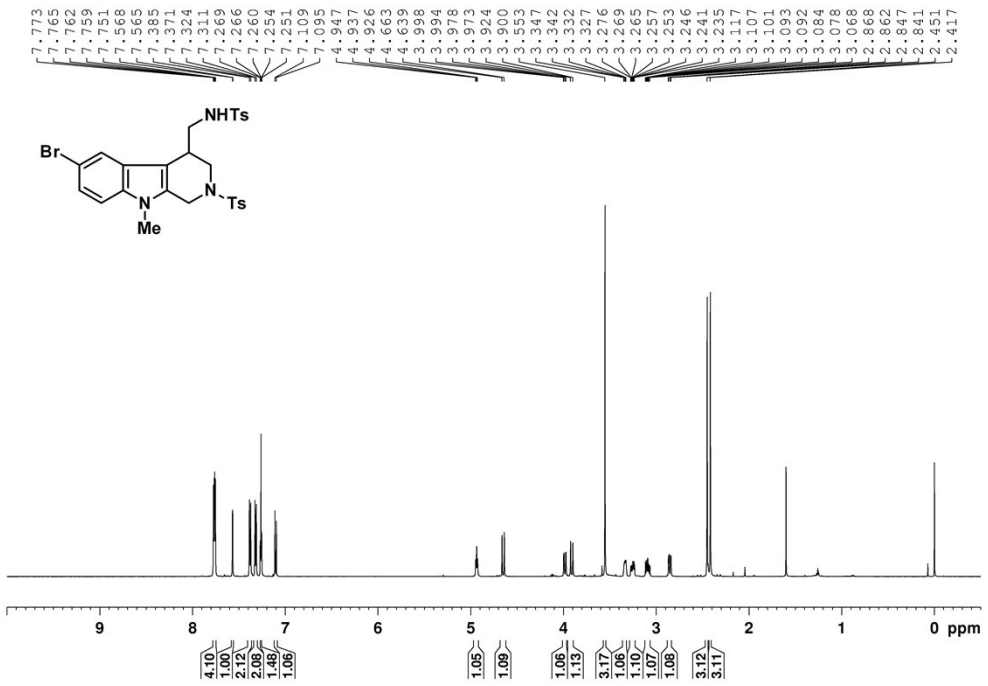
^{13}C NMR Spectrum for **11b** ($CDCl_3$, 150 MHz)



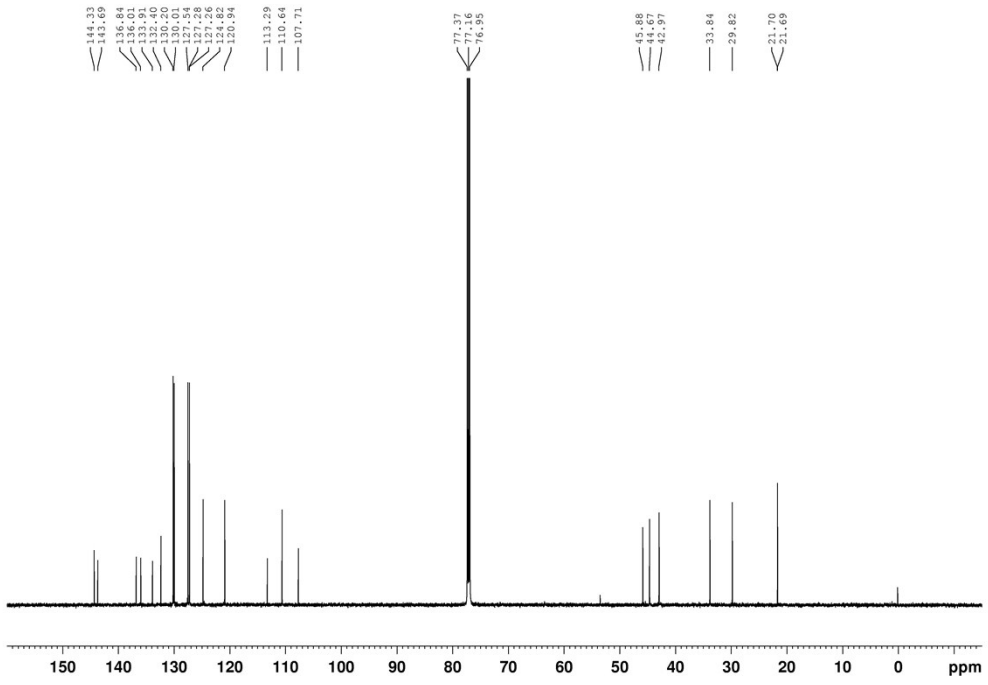
^{1}H NMR Spectrum for **11c** ($CDCl_3$, 600 MHz)



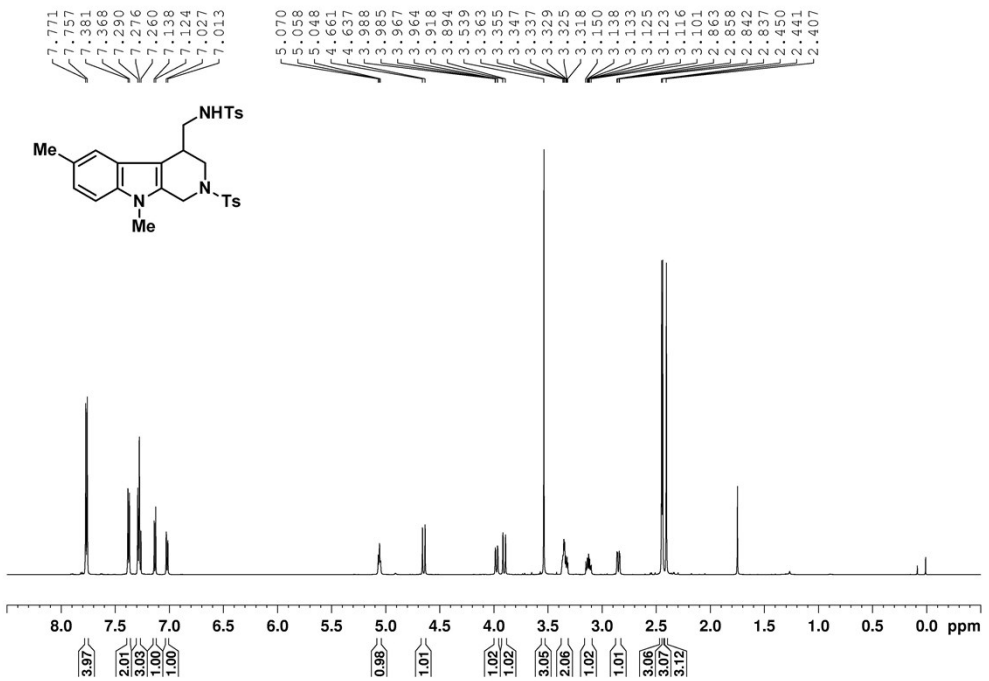
^{13}C NMR Spectrum for **11c** ($CDCl_3$, 150 MHz)



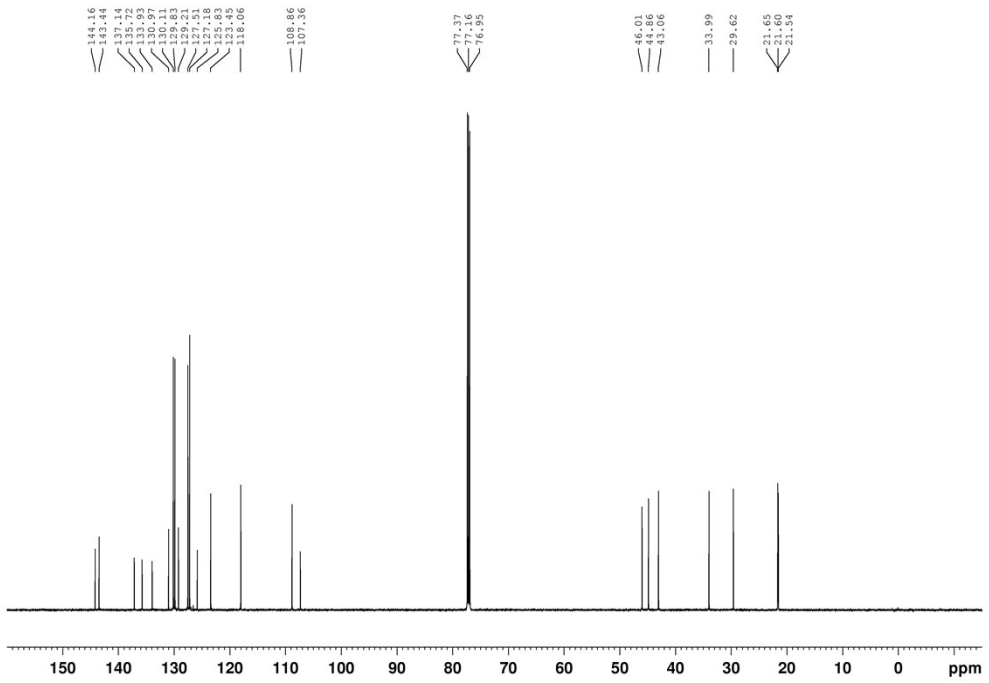
^{1}H NMR Spectrum for **11d** ($CDCl_3$, 600 MHz)



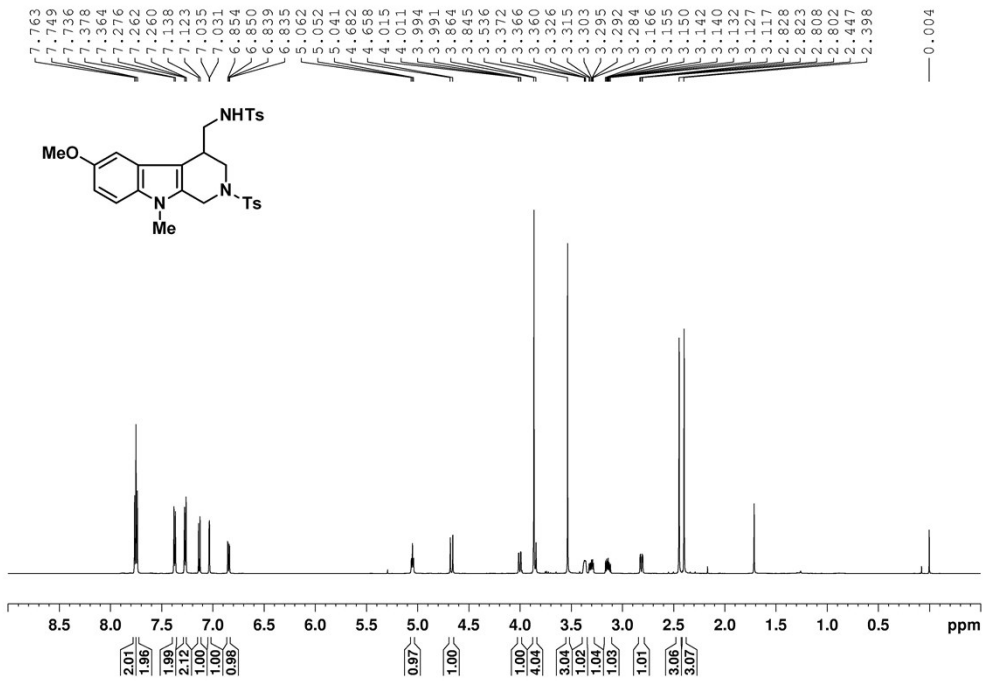
^{13}C NMR Spectrum for **11d** ($CDCl_3$, 150 MHz)



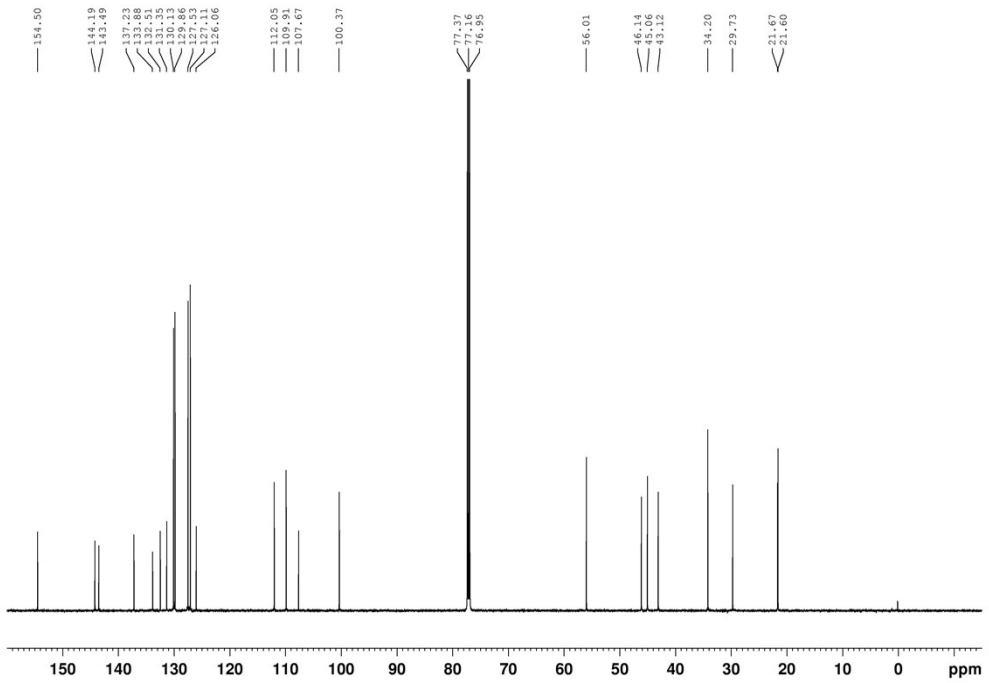
^{1}H NMR Spectrum for **11e** ($CDCl_3$, 600 MHz)



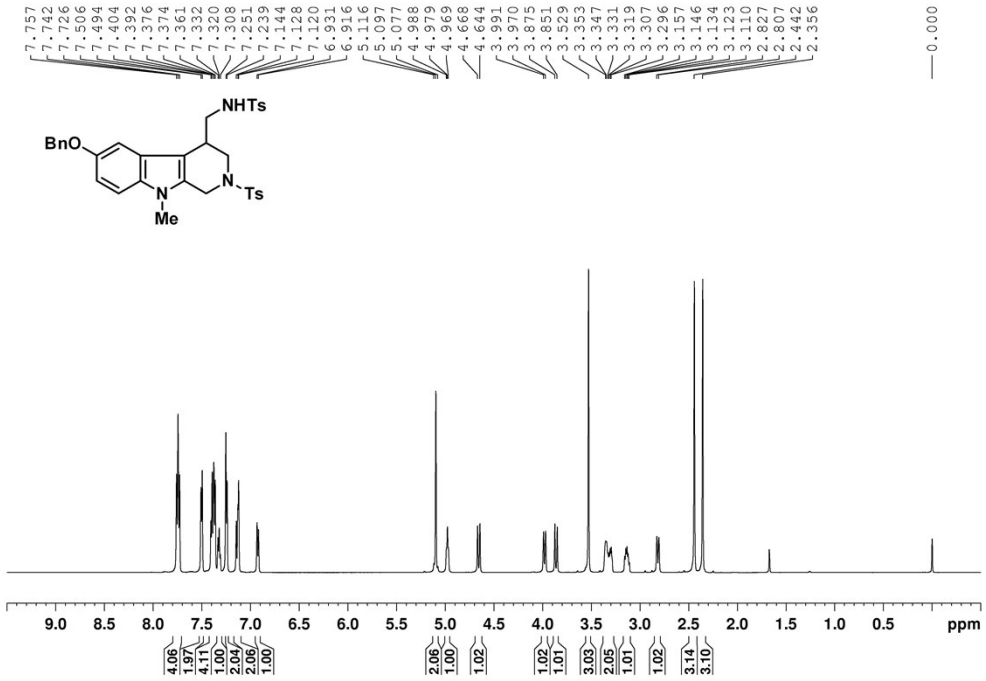
^{13}C NMR Spectrum for **11e** ($CDCl_3$, 150 MHz)



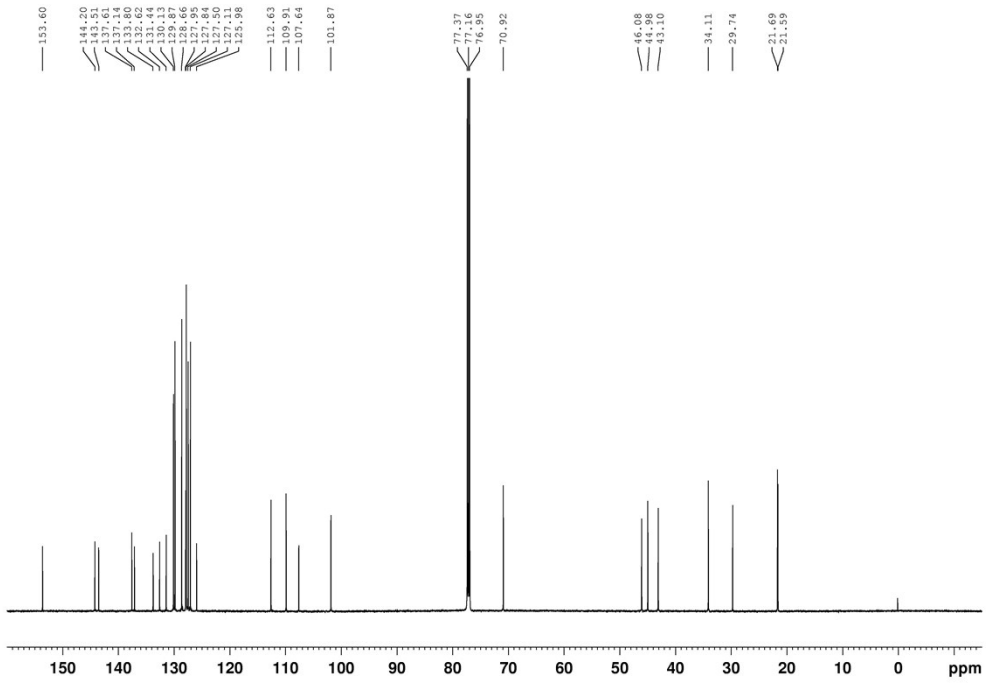
^{1}H NMR Spectrum for **11f** ($CDCl_3$, 600 MHz)



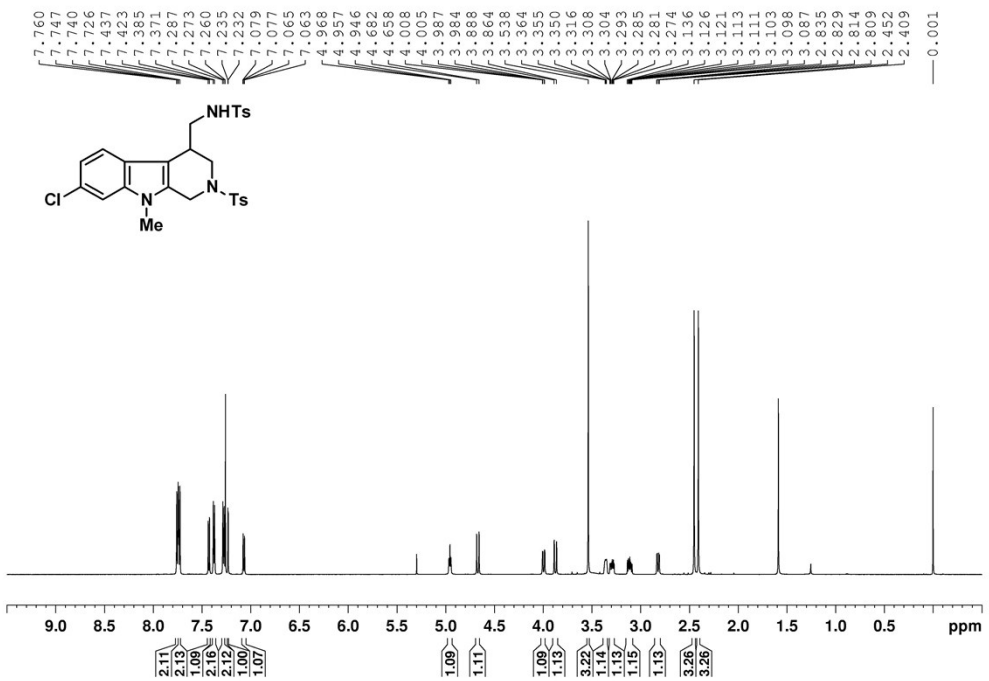
^{13}C NMR Spectrum for **11f** ($CDCl_3$, 150 MHz)



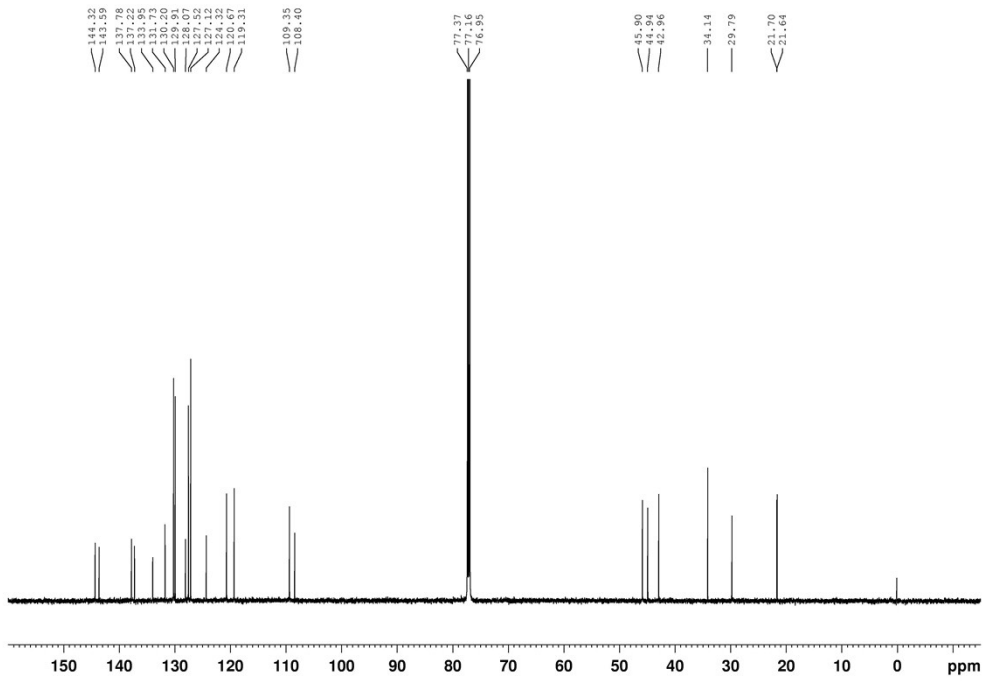
^{1}H NMR Spectrum for **11g** ($CDCl_3$, 600 MHz)



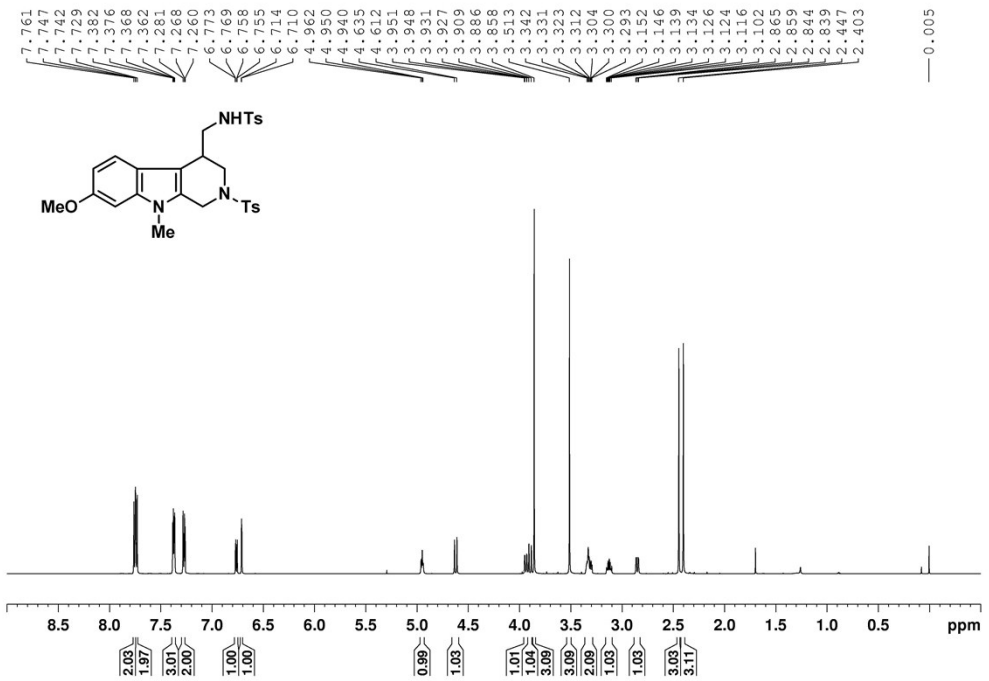
^{13}C NMR Spectrum for **11g** ($CDCl_3$, 150 MHz)



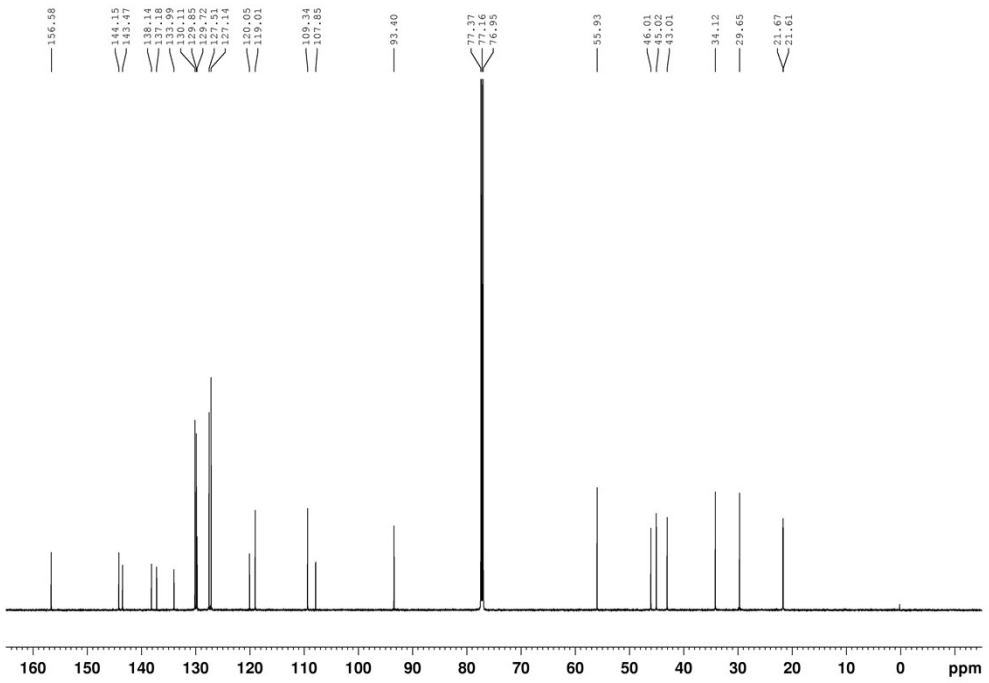
^{1}H NMR Spectrum for **11h** ($CDCl_3$, 600 MHz)



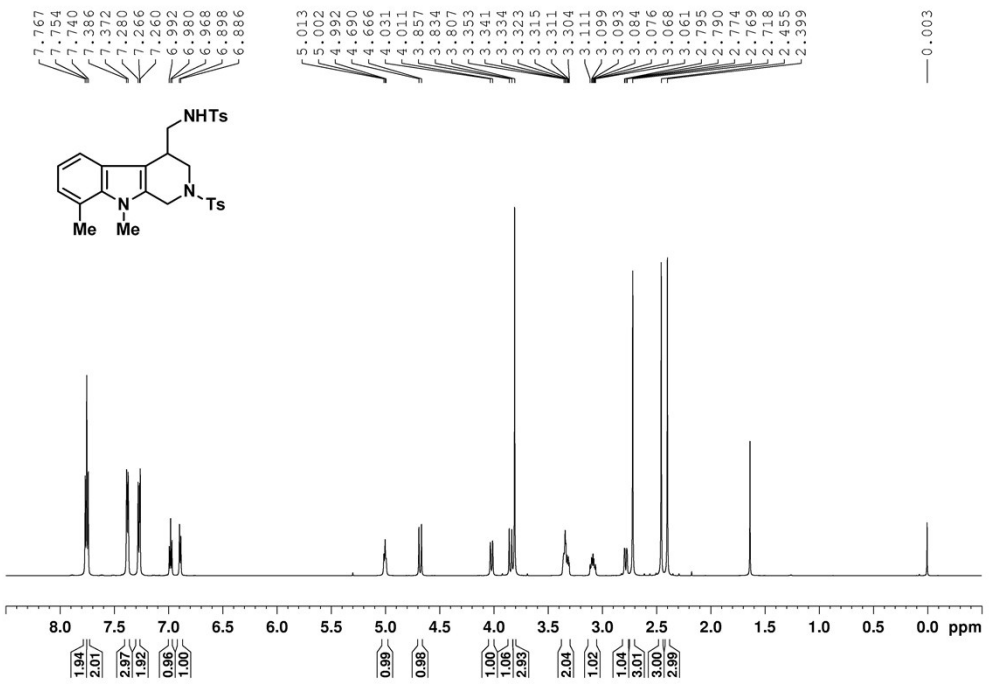
^{13}C NMR Spectrum for **11h** ($CDCl_3$, 150 MHz)



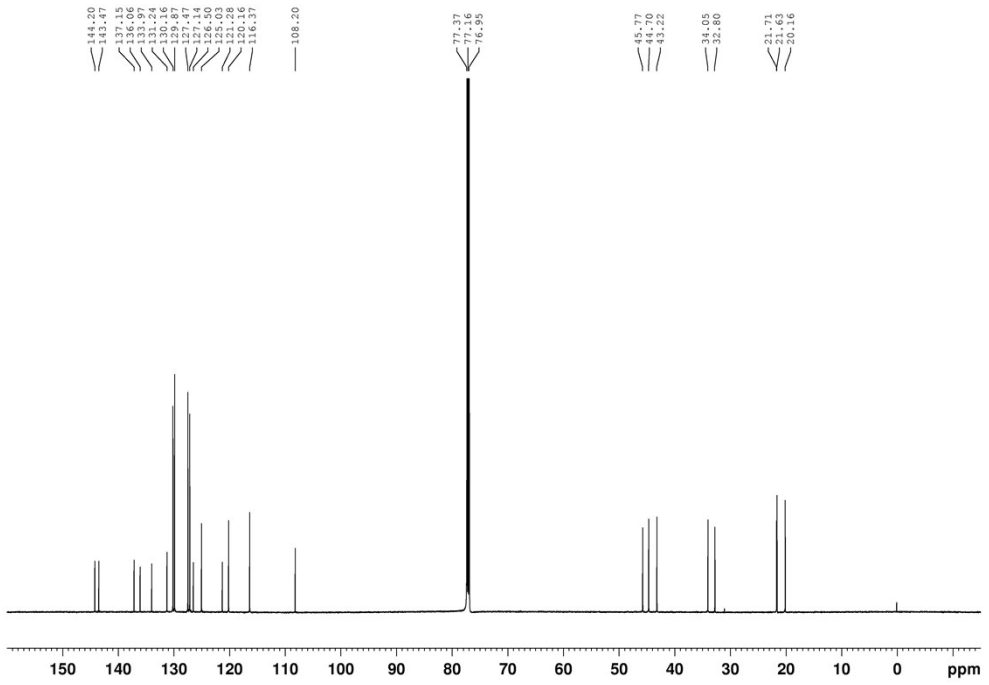
^{1}H NMR Spectrum for **11i** ($CDCl_3$, 600 MHz)



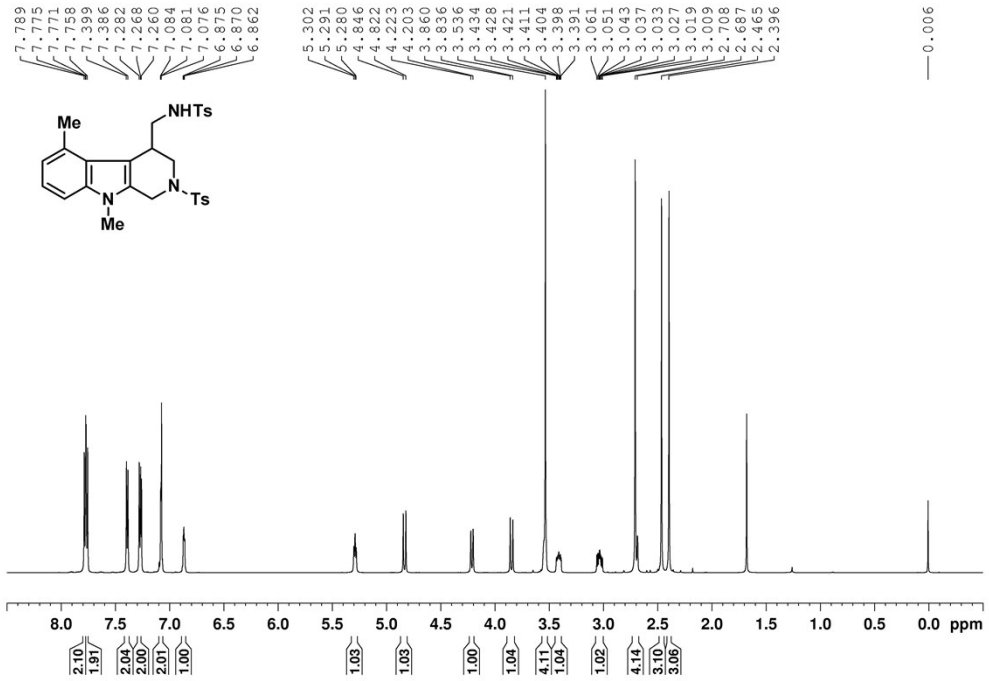
^{13}C NMR Spectrum for **11i** ($CDCl_3$, 150 MHz)



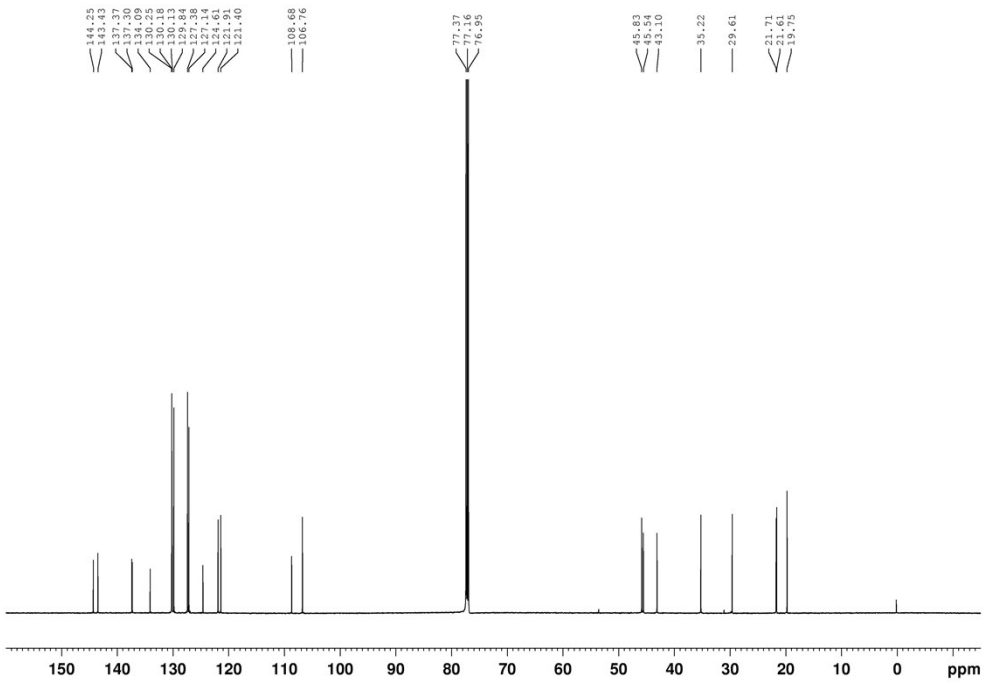
^{1}H NMR Spectrum for **11j** ($CDCl_3$, 600 MHz)



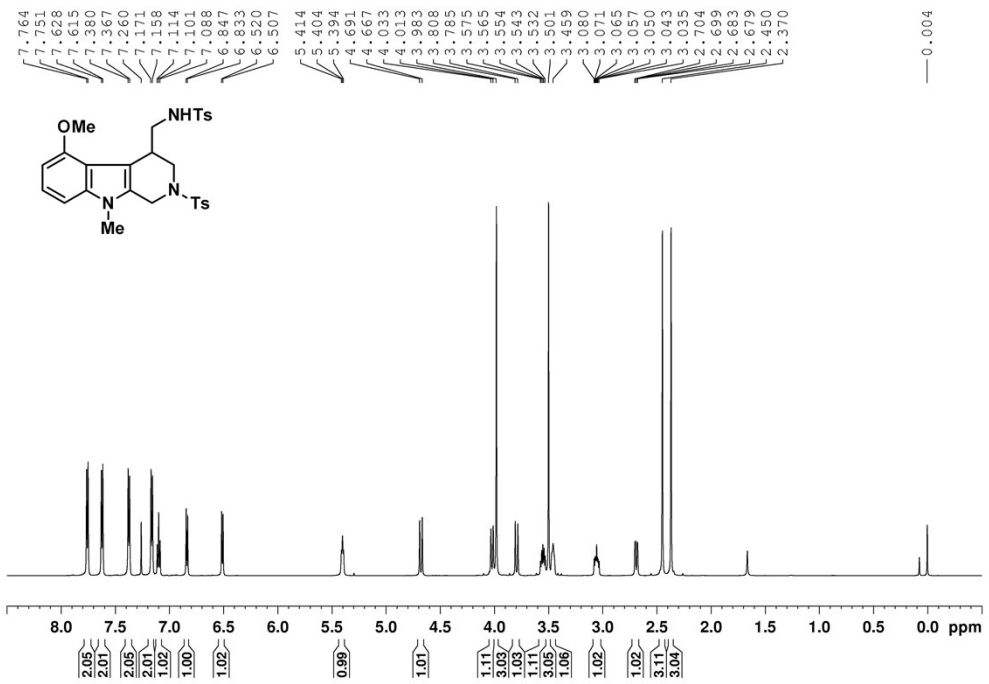
^{13}C NMR Spectrum for **11j** ($CDCl_3$, 150 MHz)



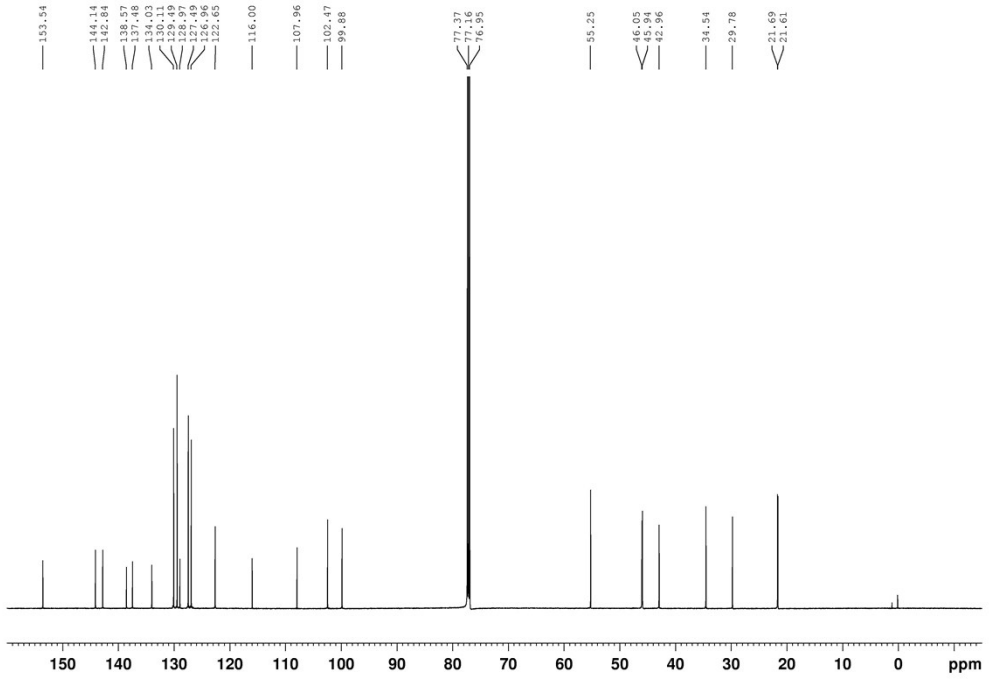
^{1}H NMR Spectrum for **11k** ($CDCl_3$, 600 MHz)



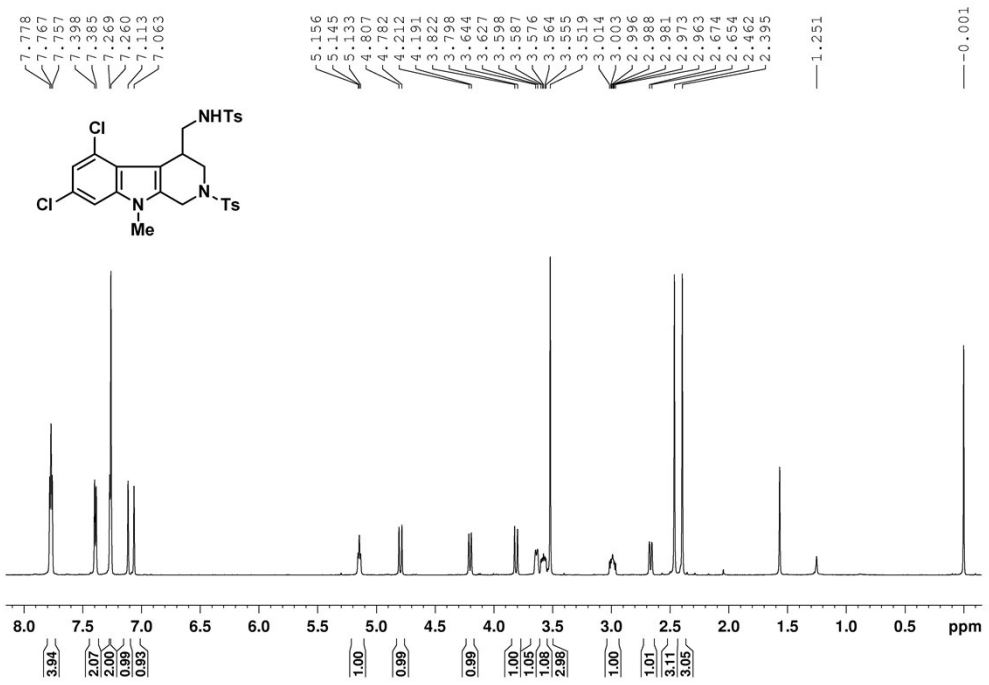
^{13}C NMR Spectrum for **11k** ($CDCl_3$, 150 MHz)



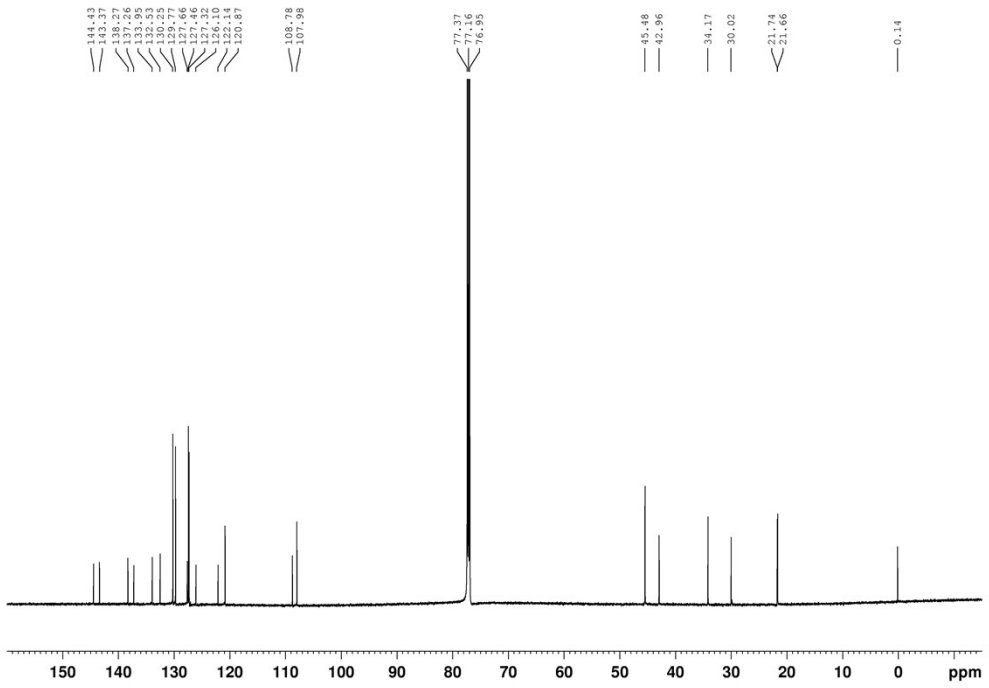
^{1}H NMR Spectrum for **11l** ($CDCl_3$, 600 MHz)



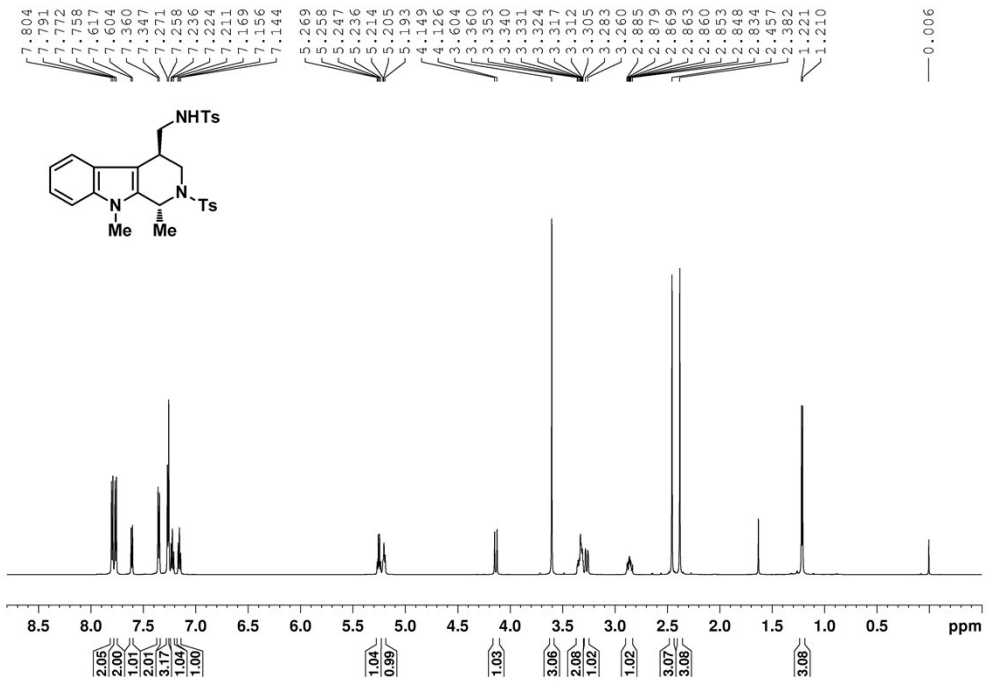
^{13}C NMR Spectrum for **11l** ($CDCl_3$, 150 MHz)



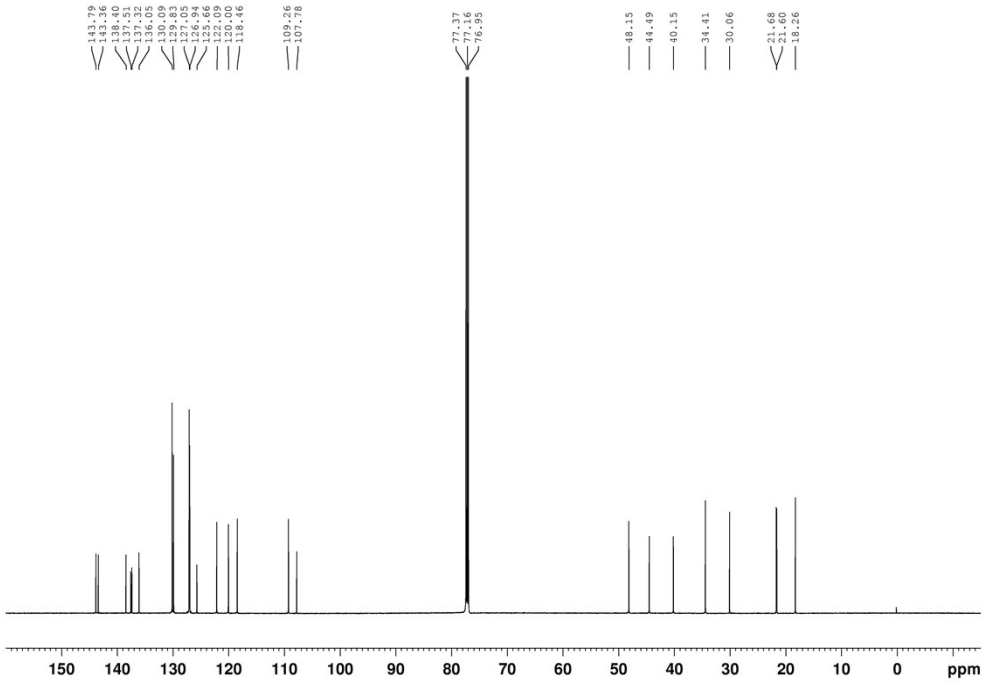
^{1}H NMR Spectrum for **11m** ($CDCl_3$, 600 MHz)



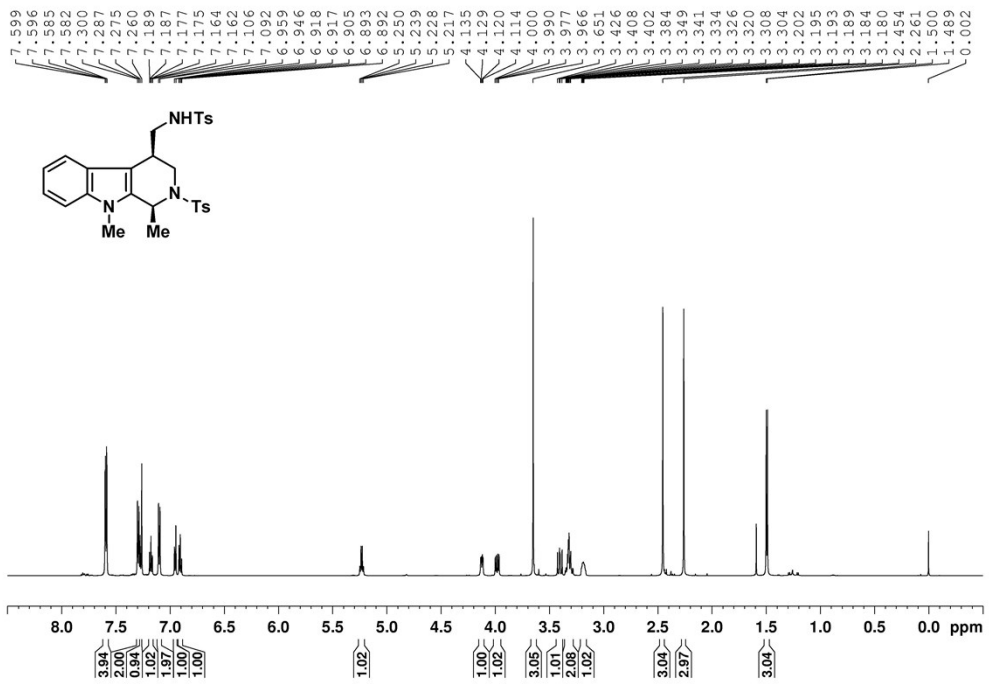
^{13}C NMR Spectrum for **11m** ($CDCl_3$, 150 MHz)



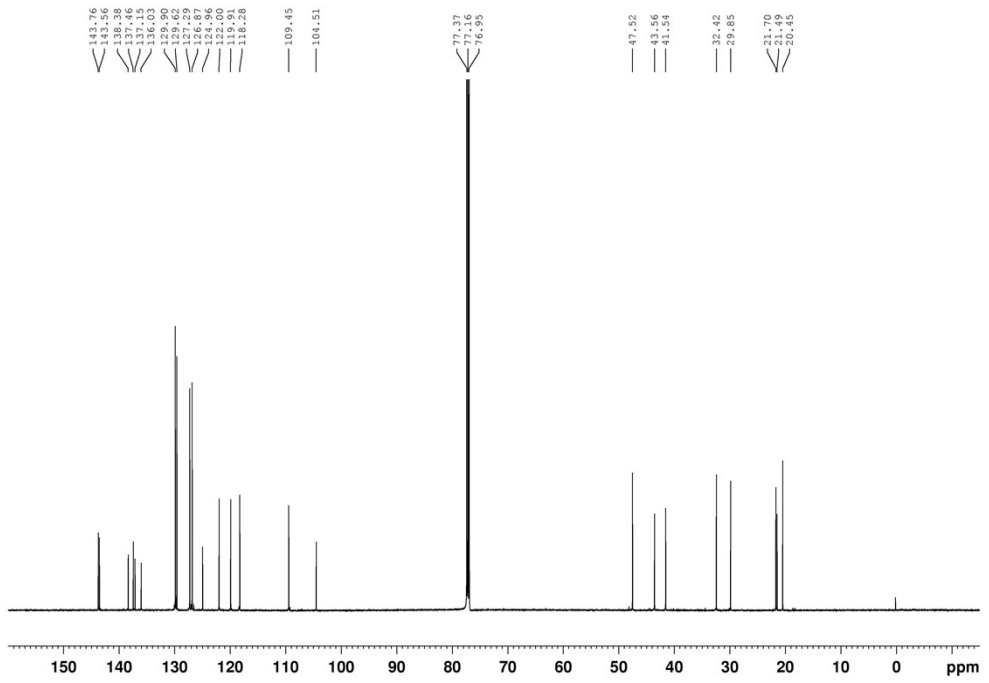
^{1}H NMR Spectrum for **11n** ($CDCl_3$, 600 MHz)



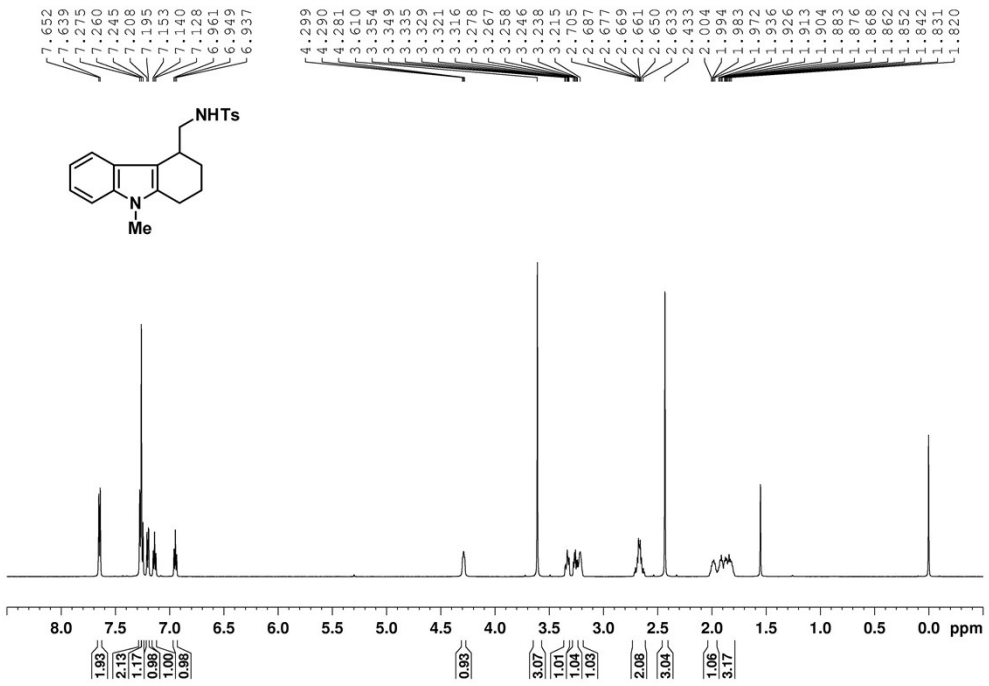
^{13}C NMR Spectrum for **11n** ($CDCl_3$, 150 MHz)



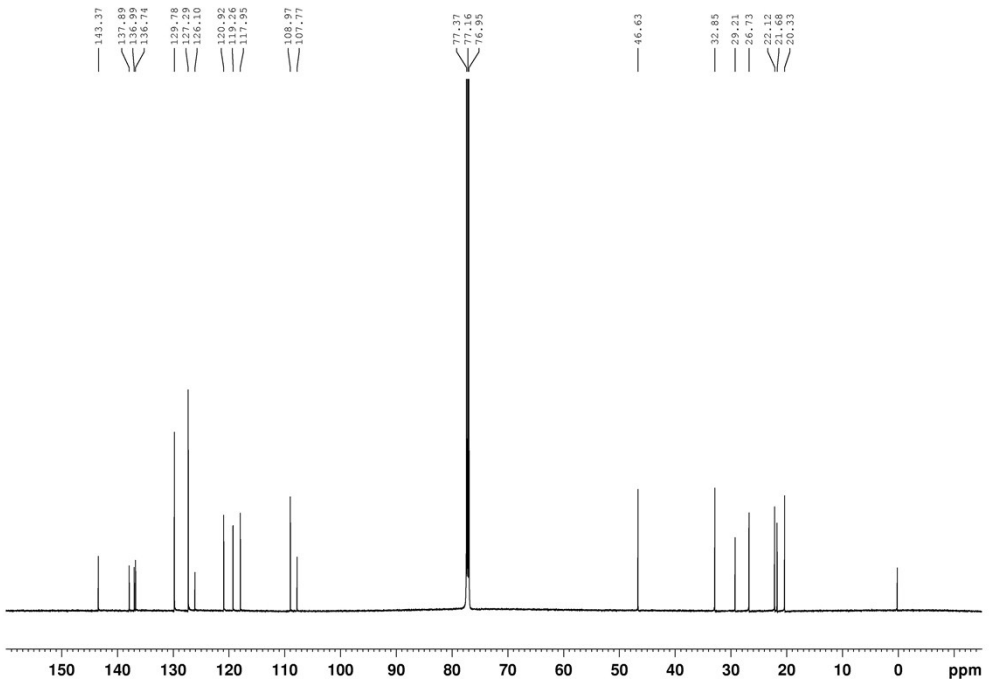
^{1}H NMR Spectrum for **11n′** ($CDCl_3$, 600 MHz)



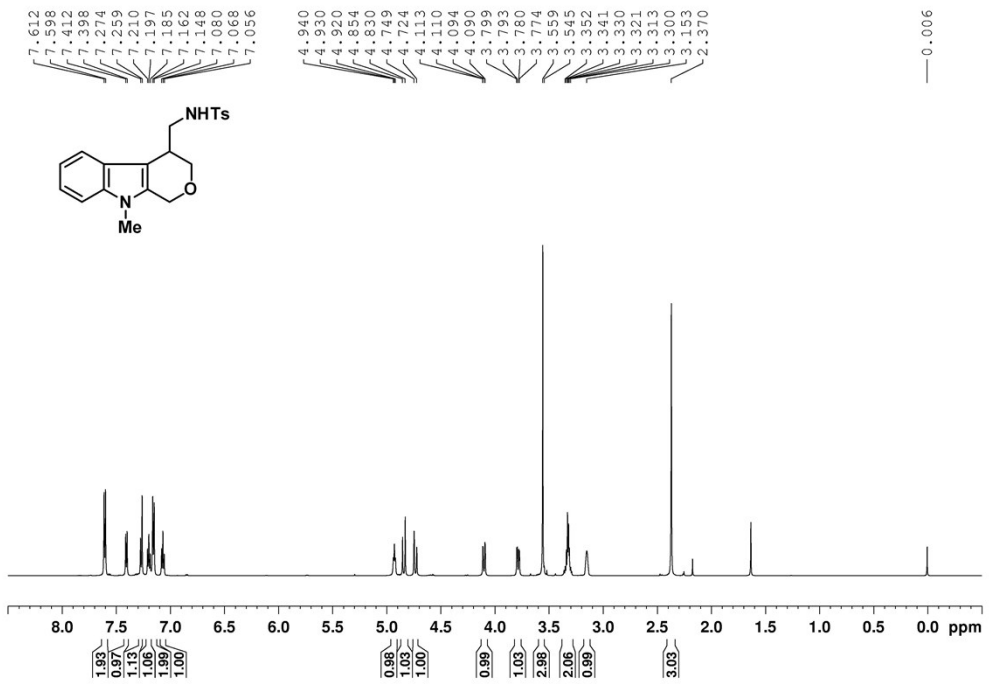
^{13}C NMR Spectrum for **11n′** ($CDCl_3$, 150 MHz)



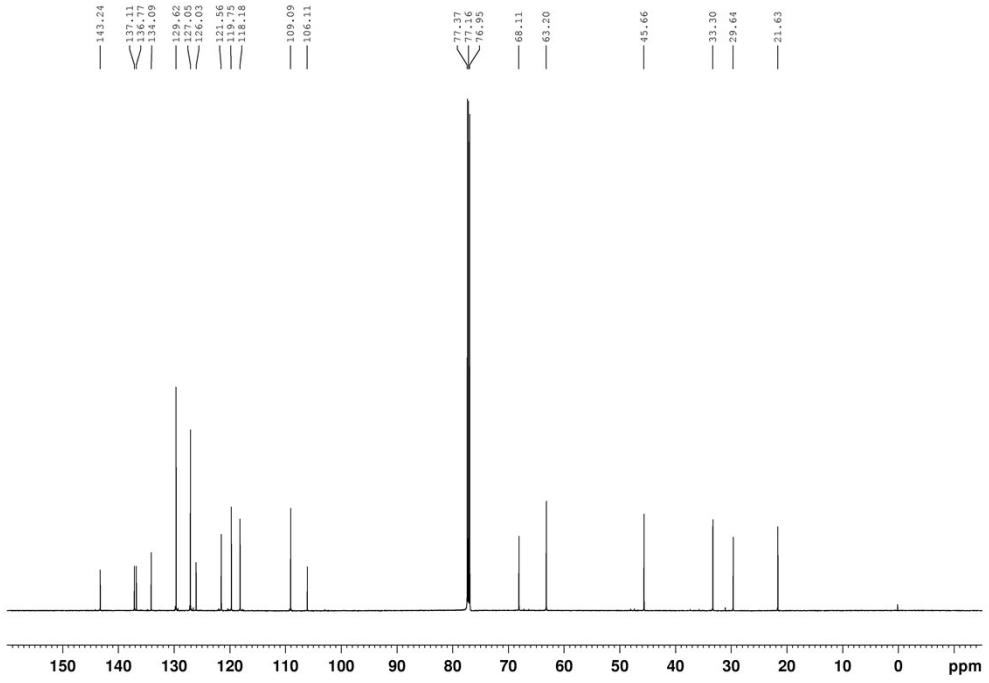
^{1}H NMR Spectrum for **11o** ($CDCl_3$, 600 MHz)



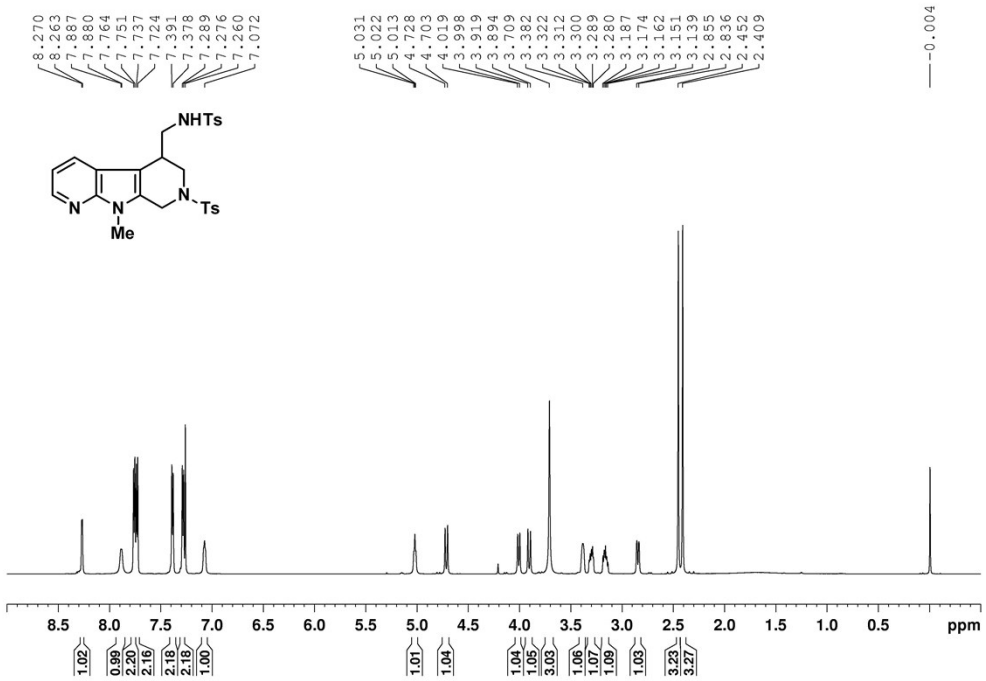
^{13}C NMR Spectrum for **11o** ($CDCl_3$, 150 MHz)



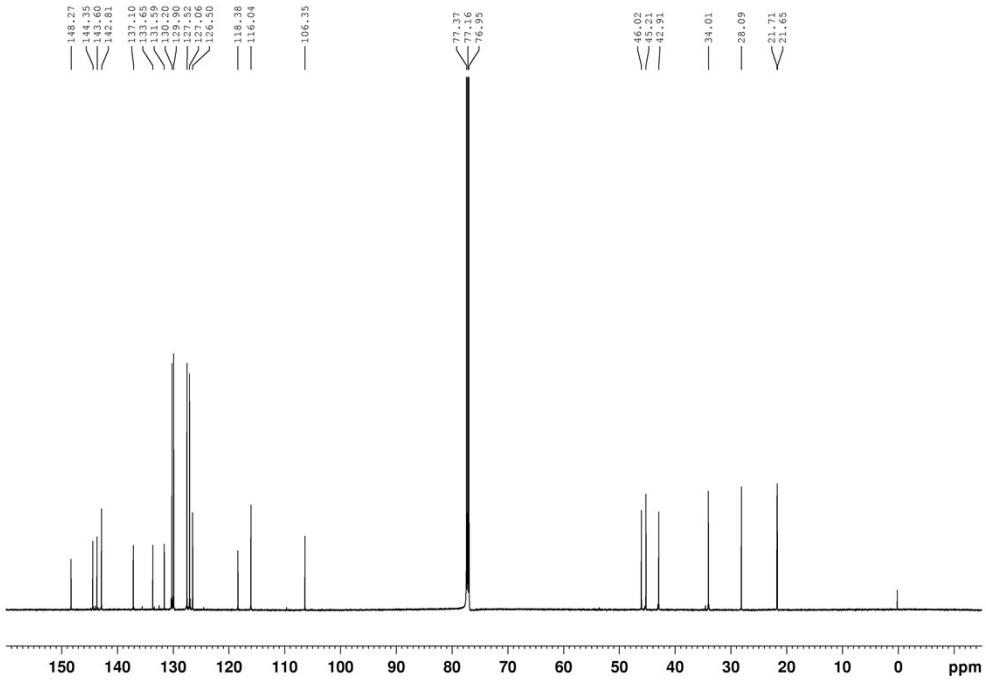
^{1}H NMR Spectrum for **11p** ($CDCl_3$, 600 MHz)



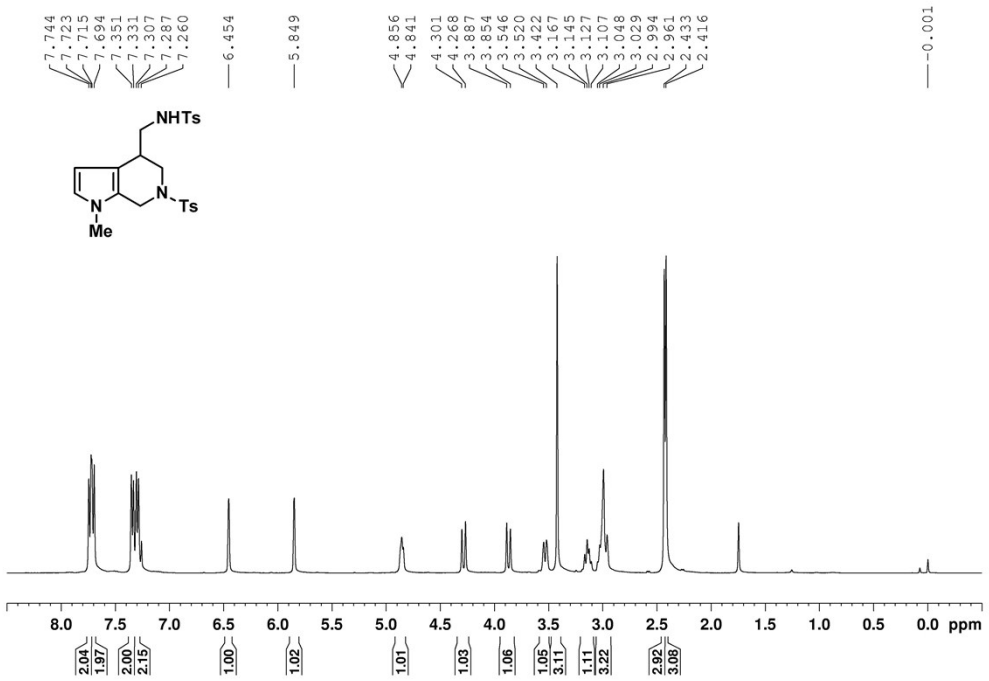
^{13}C NMR Spectrum for **11p** ($CDCl_3$, 150 MHz)



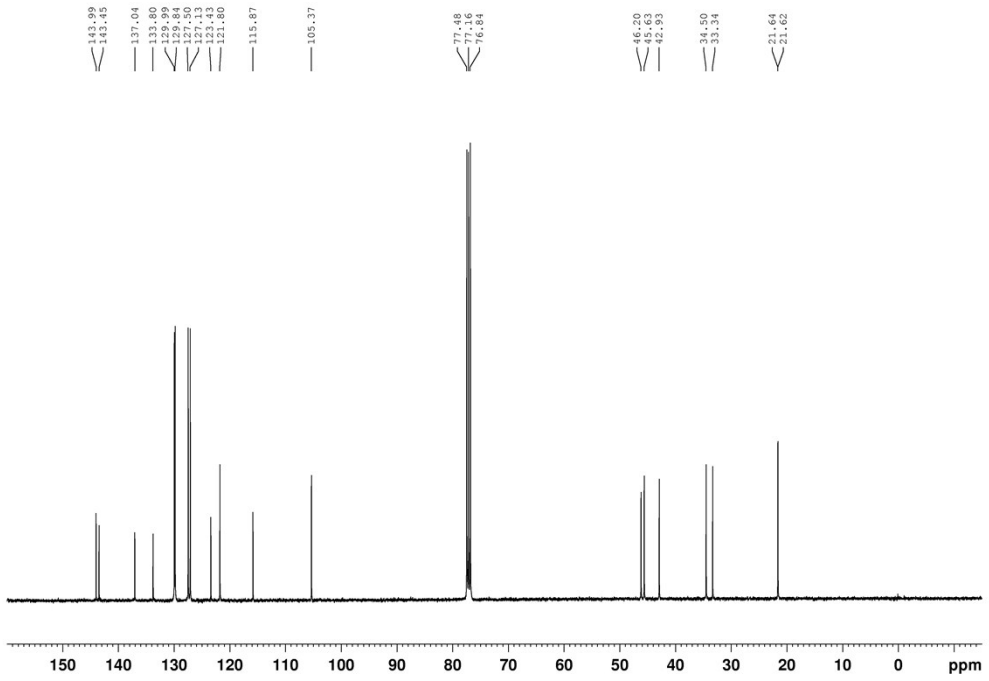
^{1}H NMR Spectrum for **11q** ($CDCl_3$, 600 MHz)



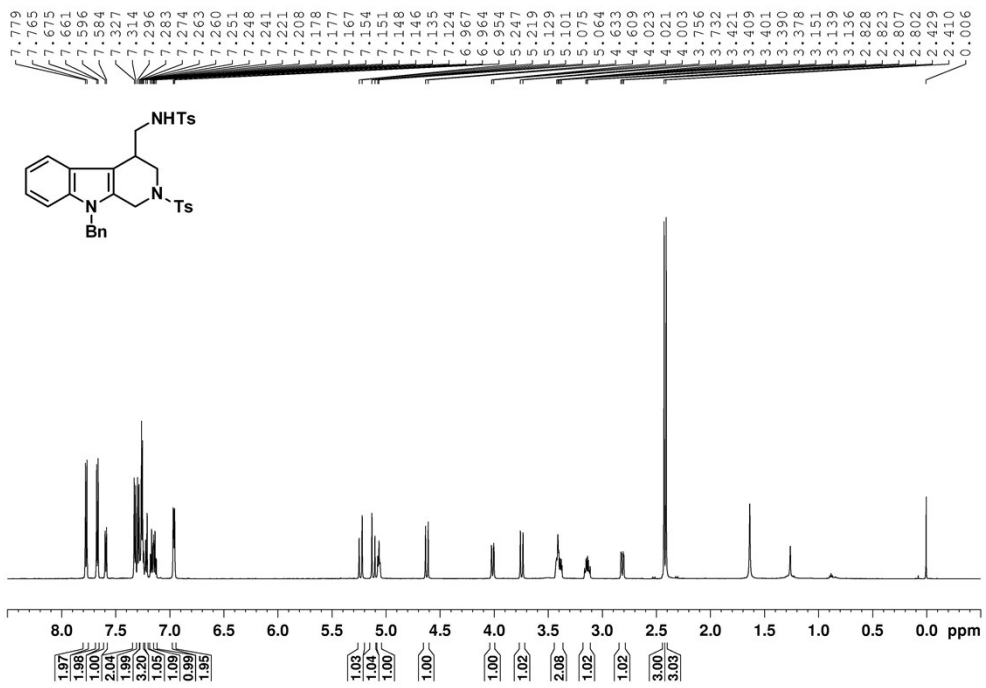
^{13}C NMR Spectrum for **11q** ($CDCl_3$, 150 MHz)



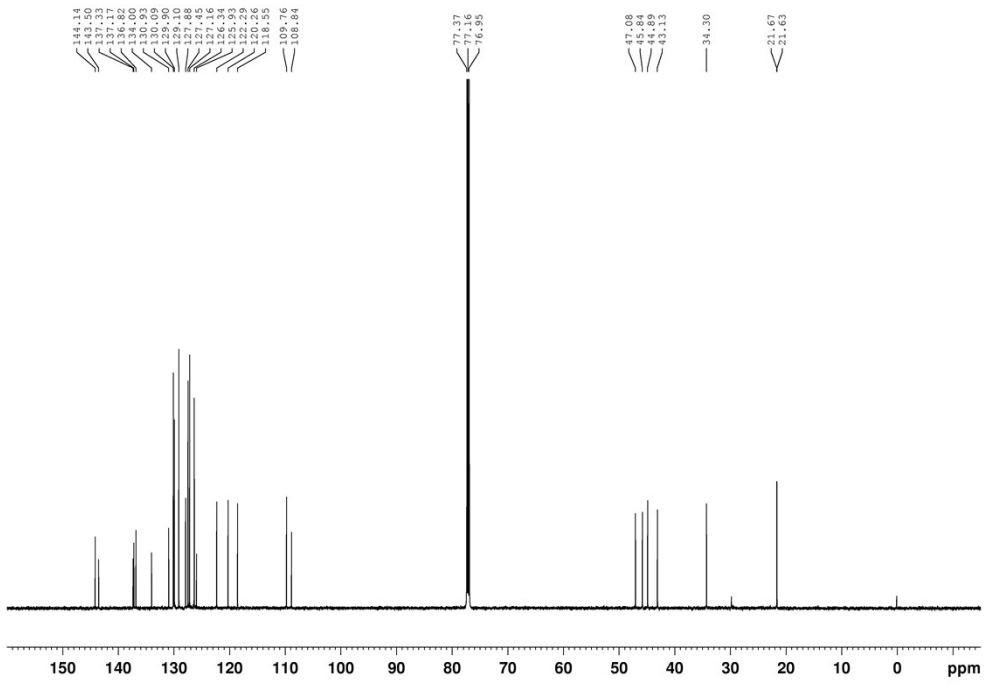
^{1}H NMR Spectrum for **11r** ($CDCl_3$, 400 MHz)



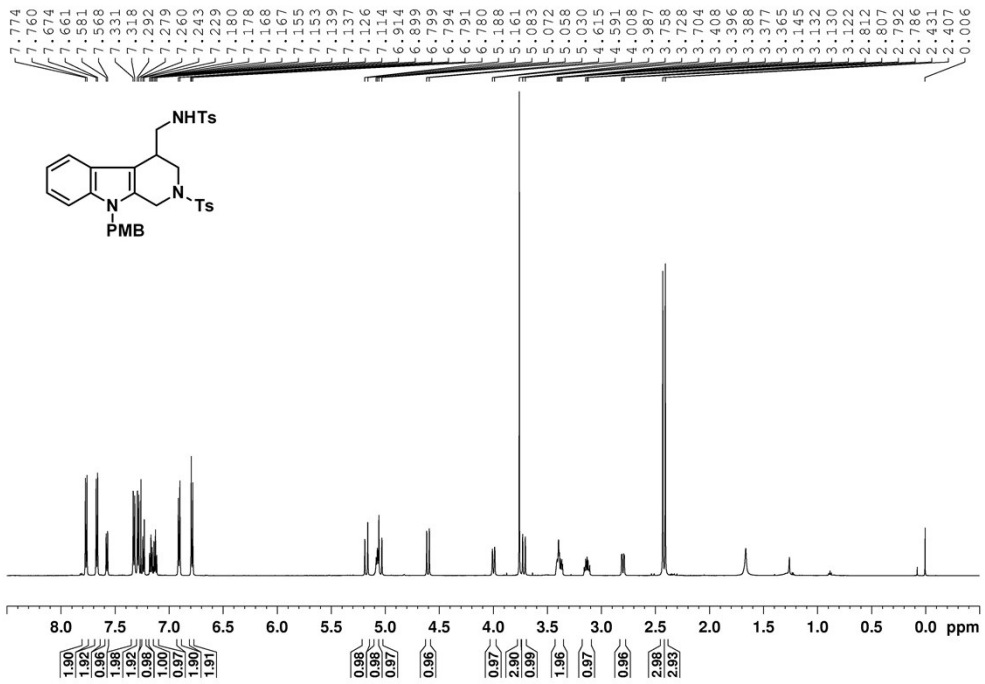
^{13}C NMR Spectrum for **11r** ($CDCl_3$, 100 MHz)



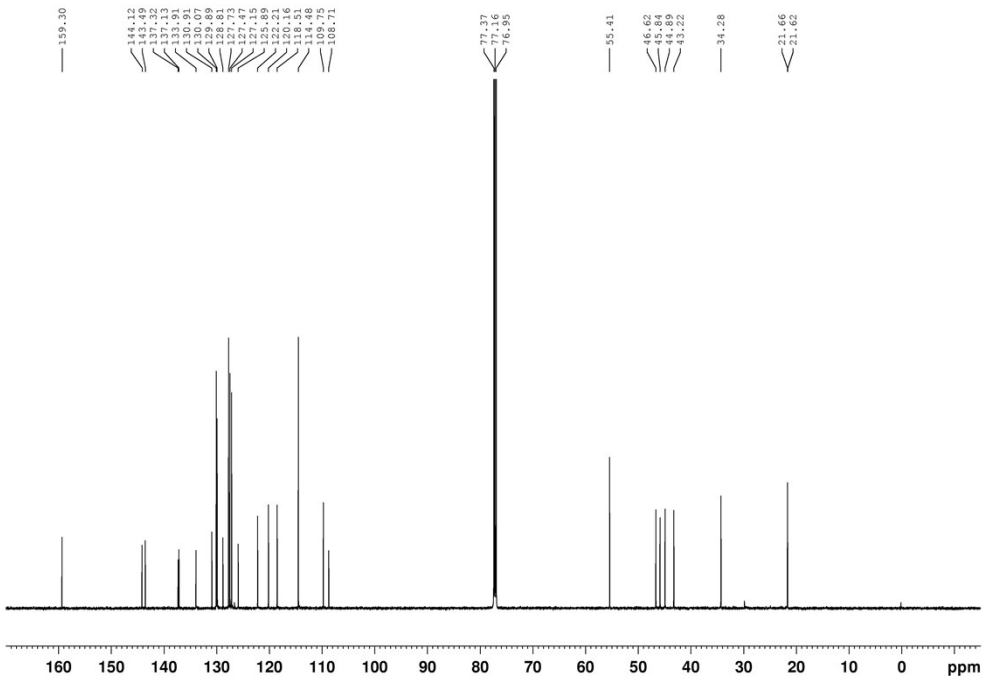
^{1}H NMR Spectrum for **11s** ($CDCl_3$, 600 MHz)



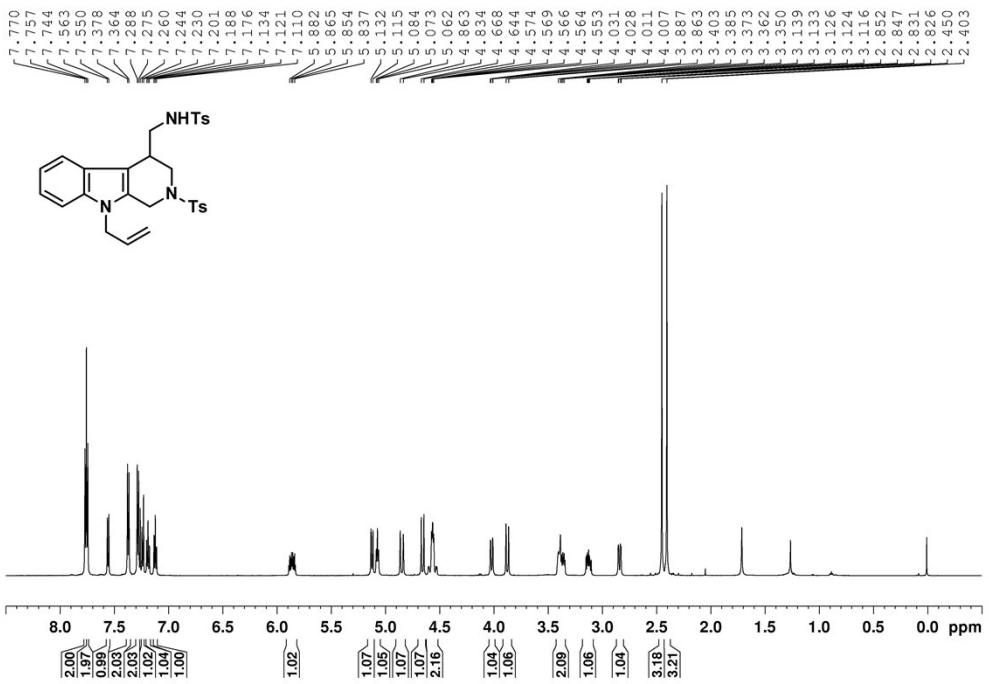
^{13}C NMR Spectrum for **11s** ($CDCl_3$, 150 MHz)



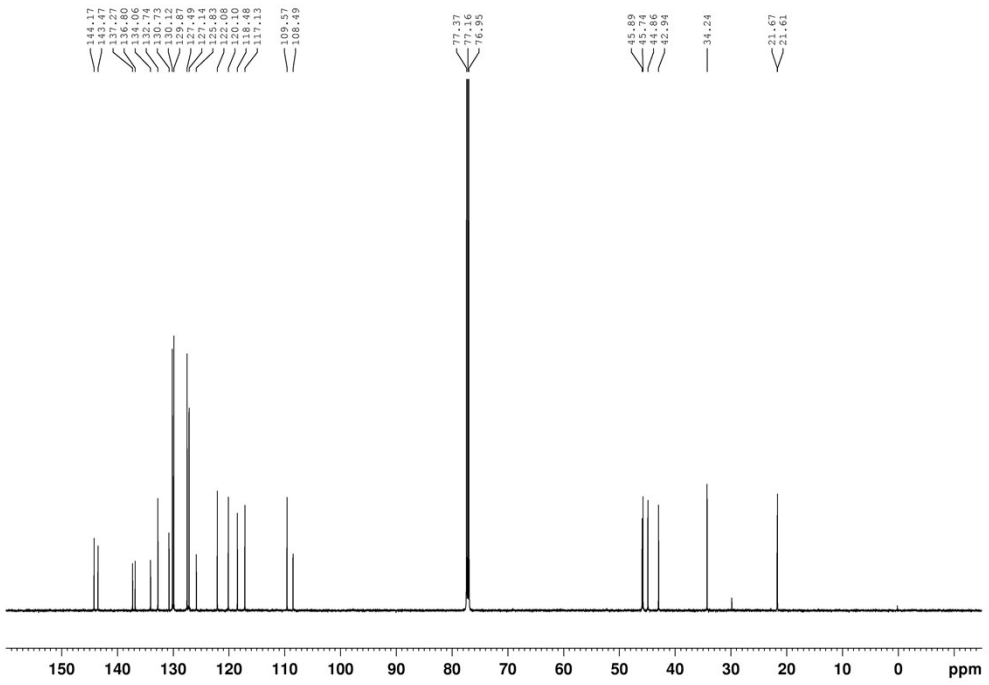
^{1}H NMR Spectrum for **11t** ($CDCl_3$, 600 MHz)



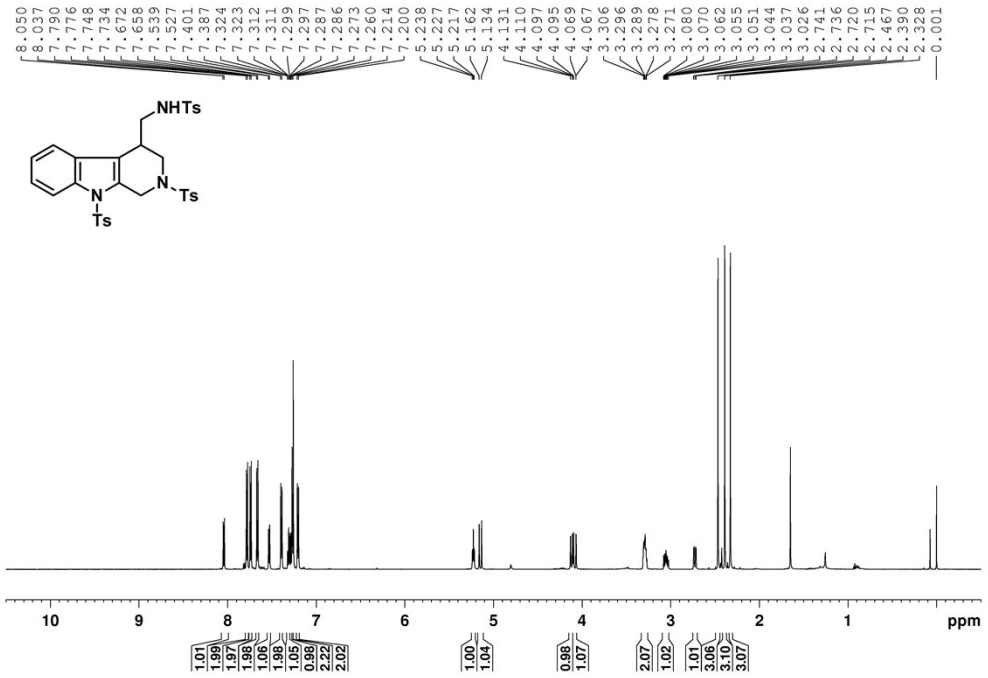
^{13}C NMR Spectrum for **11t** ($CDCl_3$, 150 MHz)



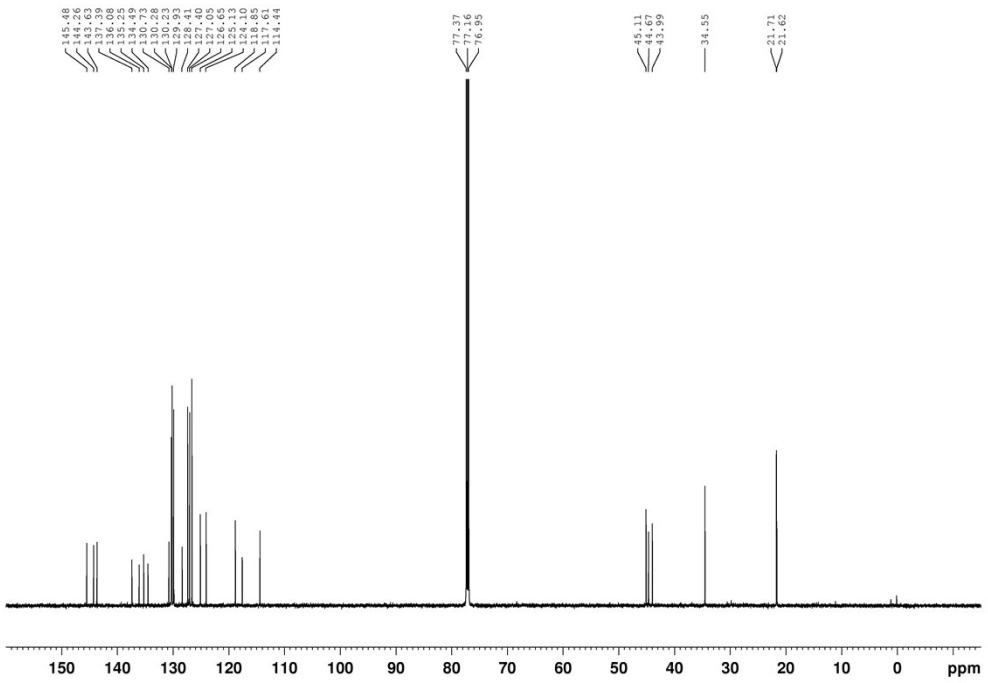
^{1}H NMR Spectrum for **11u** ($CDCl_3$, 600 MHz)



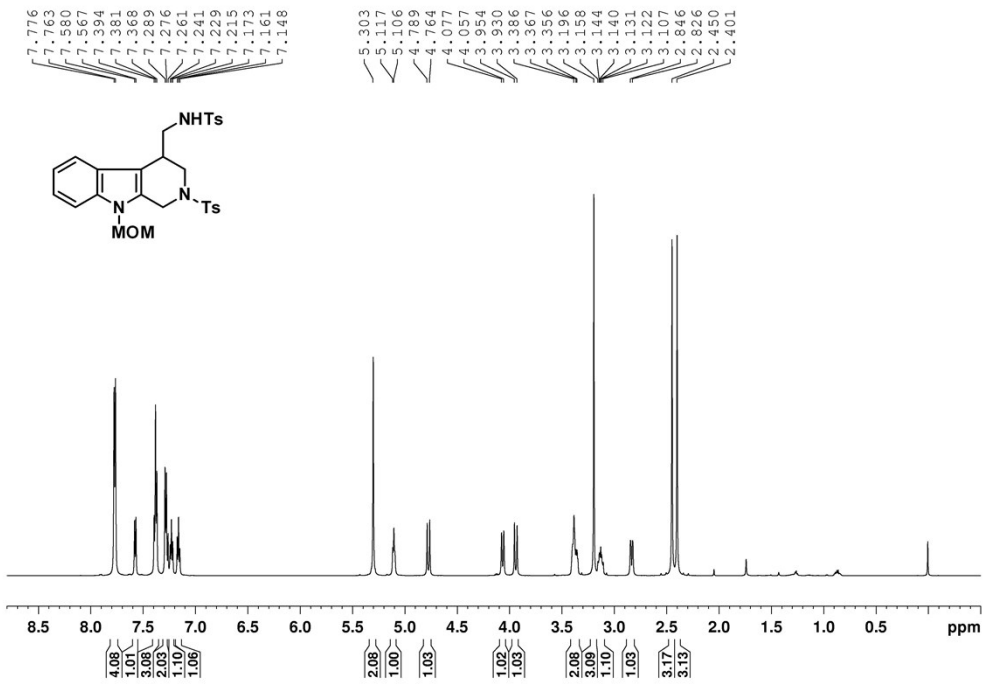
^{13}C NMR Spectrum for **11u** ($CDCl_3$, 150 MHz)



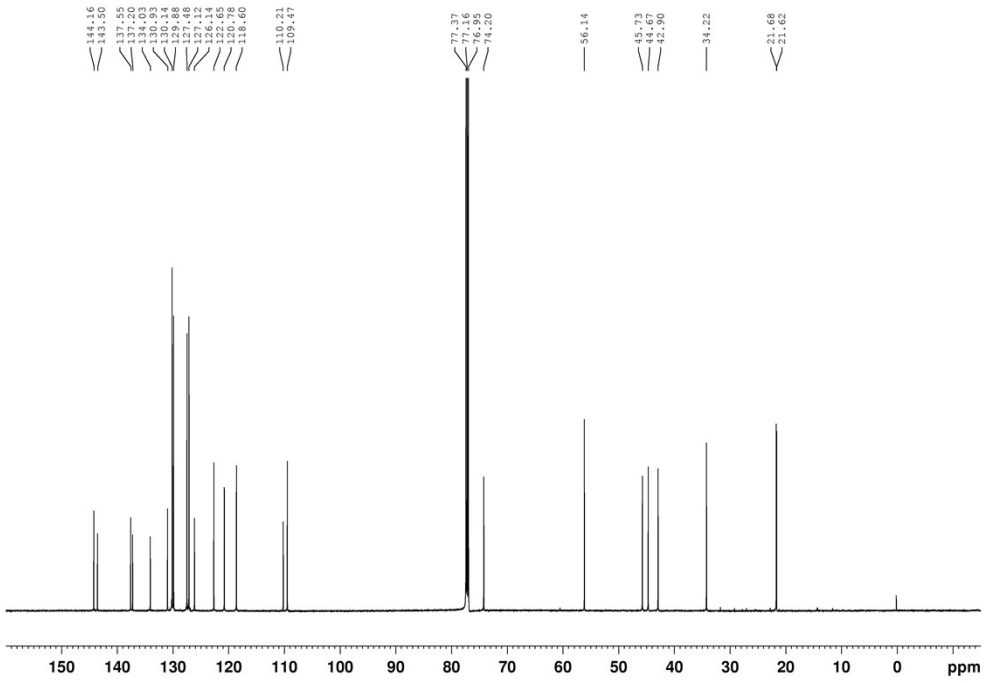
^{1}H NMR Spectrum for **11v** ($CDCl_3$, 600 MHz)



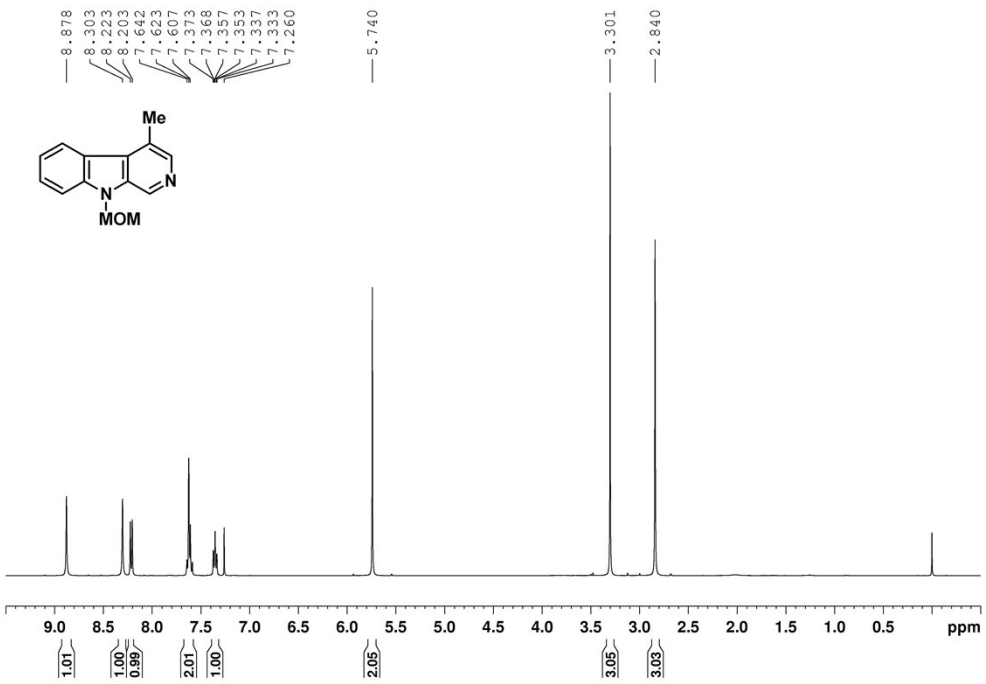
^{13}C NMR Spectrum for **11v** ($CDCl_3$, 150 MHz)



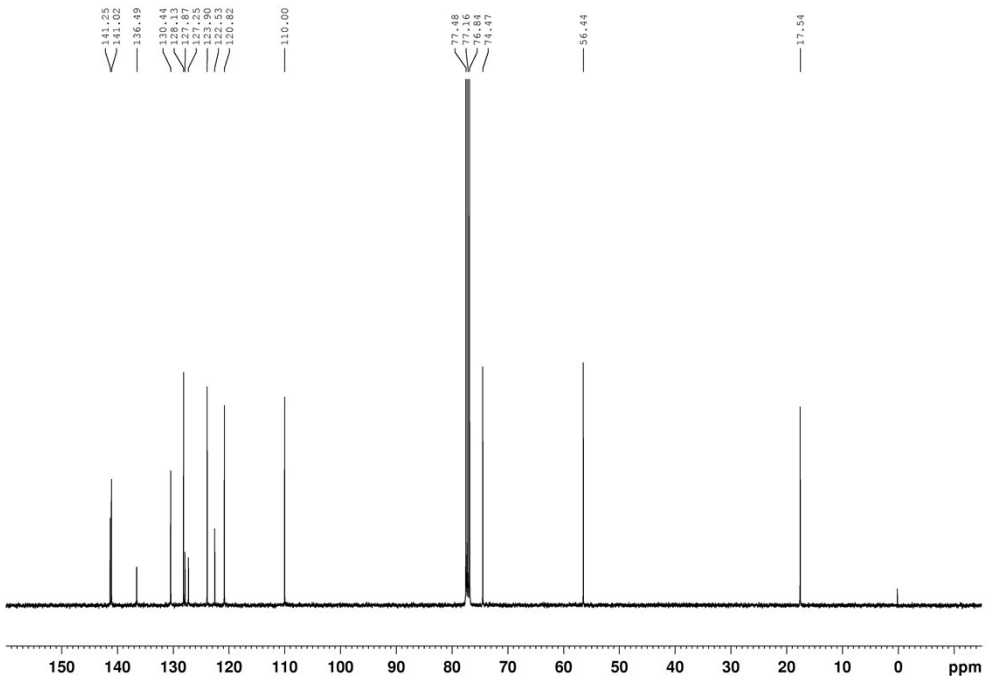
^{1}H NMR Spectrum for **11w** ($CDCl_3$, 600 MHz)



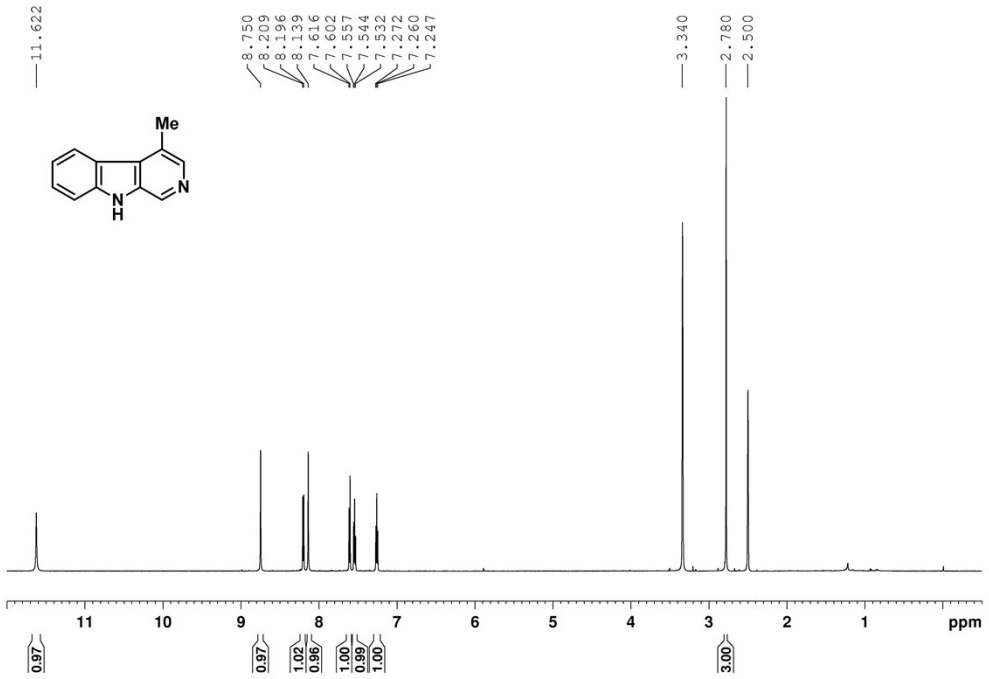
^{13}C NMR Spectrum for **11w** ($CDCl_3$, 150 MHz)



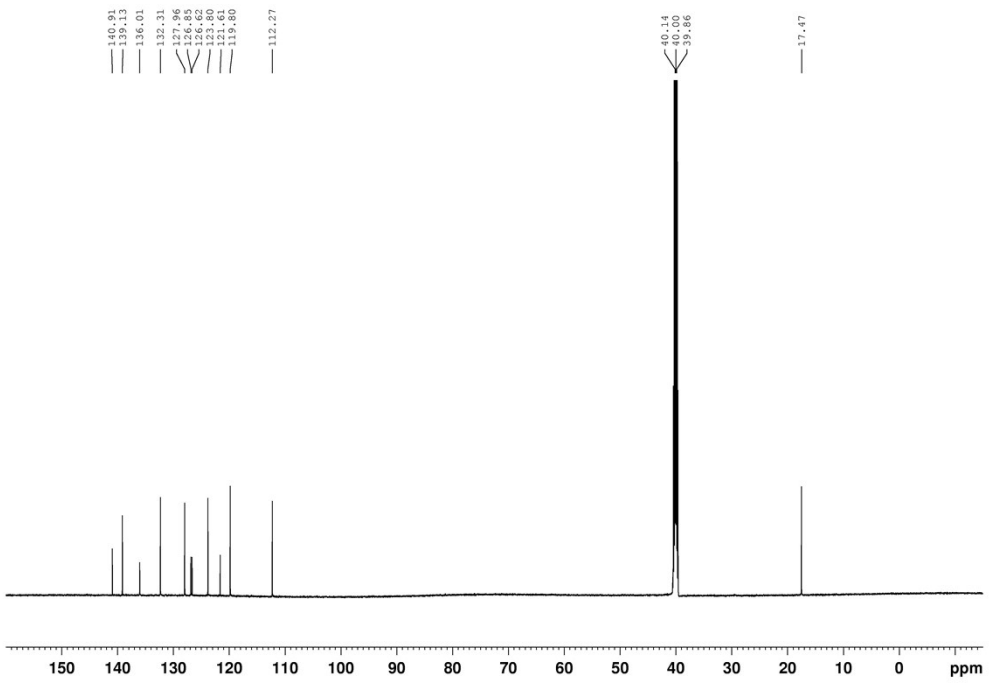
^{1}H NMR Spectrum for **13** ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum for **13** ($CDCl_3$, 150 MHz)



^{1}H NMR Spectrum for **14** (DMSO, 600 MHz)



^{13}C NMR Spectrum for **14** (DMSO, 150 MHz)