SUPPORTING INFORMATION

$FeCl_3/SiO_2$ catalyzed bis-indolylation of acetal and ketal: A highly atom economic approach to selective deprotection of protected carbohydrate

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Experimental section

All reagents were purchased either from Sigma Aldrich chemical Co., USA, Acros chemical company or SRL India and were used as received unless otherwise specified. Commercially supplied petroleum ether (60−80 °C) and ethyl acetate was distilled before use. Indole and triethyl orthoformate were purchased from SRL, India; N-Methyl Indole, 2-Methyl Indole, 2-Phenyl Indole, 5-Bromo Indole, 5-Methoxy Indole, 5-Nitro Indole, Benzaldehyde dimethyl acetal and 4-Anisaldehyde dimethyl acetal were purchased from Spectrocem Pvt. Ltd. India; 2,2- Dimethoxypropane, carbohydrate derivatives **2a-b** and **2g** were purchased from Acros Organics and used as received. Diethyl acetals (**1c** and **1d**),[1] dimethyl acetal and other protected compounds (**1f**, **1h**, **1i**)[2] and protected carbohydrates (**2c-f** and **2h**)[2, 3] were prepared according to the literature report. Column chromatography was performed on silica gel (60−120 mesh, 0.12−0.25 mm) and silica gel 230-400 nesh was used for the preparation of supported reagent. Analytical thin-layer chromatography (TLC) was performed on 0.25 mm extra-hard silica gel plates with a UV_{254} fluorescent indicator. The identity of known synthesized products was confirmed by comparison with their melting points and spectral data with those reported earlier. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 MHz spectrometers (400 MHz for ^{1}H and 100 MHz for ^{13}C). FTIR spectra were recorded on Bruker Alpha II FTIR spectrometer on Neat or KBr pellets. Mass spectra (HRMS) were obtained from XEVO G2-XS QTOF (Waters) using 70 ev in positive ion mode. Field-emission scanning electron microscope (FESEM) (model: Sigma 300, Carl ZEISS Pvt., Ltd.) with 5 kV acceleration voltage was used to explore the surface morphology and elemental analysis of silica supported ferric chloride.

Preparation of silica supported Ferric Chloride

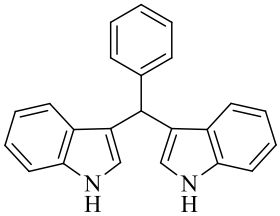
Typically, to the slurry of silica gel (240-300 mesh, 40g) in acetone (80 mL), anhydrous ferric chloride (5.0 g, 30.83 mmol) was added with vigorous stirring for 1hr. The excess acetone was removed under reduced pressure and then the mixture was dried under vacuum for 24 hrs to obtain a free flowing solid. The catalyst was stored in a brown colour bottle at 4^{o}C for longer shelf life.

General procedure for the synthesis of BIMs/deprotection of protected carbohydrates.

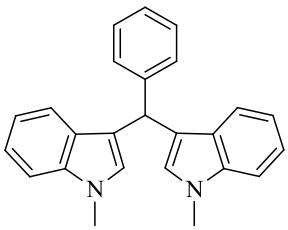
In a glass vial, catalyst ($FeCl_3/SiO_2$) (20 mg, 2 mol% of $FeCl_3$), acetal (1.0 mmol) and indole (2.0 mmol) were added successively (for carbohydrate substrate, 0.2 to 0.3 mL alcohol was needed). The reaction mixture was stirred for stipulated time mentioned in the Table 2 and 3. After completion of reaction, the reaction mixture was diluted with EtOAc (5 mL) and

filtered. The filtrate was evaporated under vacuum. The desired product was isolated either by crystallization or by column chromatography using ethyl acetate-hexane (1:3 to 3:1).

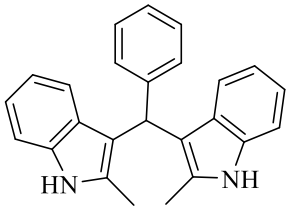
Physical and Spectral data of Bis-indole products 4a-r and 4u-x:



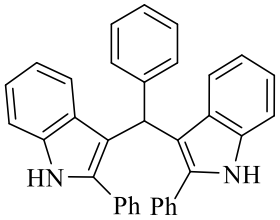
3,3'-(phenyl methylene)bis(1H-indole) (**4a**):[4] Yield: 90%, light yellow solid, m. p. 150-152^{o}C, lit. m. p. 152 ^{o}C; IR (KBr) ν_{max} 3394, 1596, 1452, 1417, 1355 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.33-7.18 (m, 5H), 7.06-7.02 (m, 2H), 6.66 (d, *J* = 1.6 Hz, 2H), 5.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 136.7, 128.7, 128.2, 127.1, 126.2, 123.6, 121.9, 120.0, 119.7, 119.2, 111.1, 40.2.



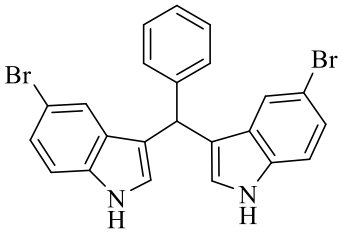
3,3'-(phenyl methylene)bis(1-methyl-1H-indole) (**4b**):[4] Yield: 92%, light pink solid, m. p. 200-202 ^{o}C, lit. m. p. 200-201 ^{o}C; IR (KBr) ν_{max} 1470, 1422, 1324, 1228, 1198, 1151, 1053 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.23 (m, 11H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.58 (s, 2H), 5.93 (s,1H), 3.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 137.4, 128.7, 128.3, 128.2, 127.5, 126.1, 121.4, 120.1, 118.7, 118.3, 109.1, 40.1, 32.7.



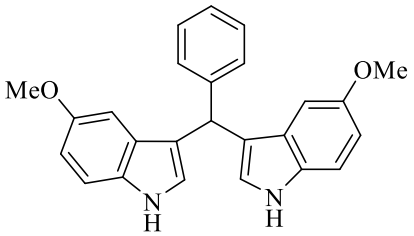
3,3'-(phenyl methylene)bis(2-methyl-1H-indole) (**4c**):[4] Yield: 91%, light pink solid, m. p. 252-254 ^{o}C, lit. m. p. 257-258 ^{o}C; IR (KBr) ν_{max} 3390, 1454, 1421, 1337, 1292, 1129, 1072 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 2H), 7.27-7.20 (m, 7H), 6.89 (t, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 7.2 Hz, 2H), 5.93 (s, 1H), 2.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 135.5, 132.5, 129.2, 128.7, 128.4, 126.2, 120.0, 118.9, 118.4, 112.6, 110.8, 39.0, 12.4.



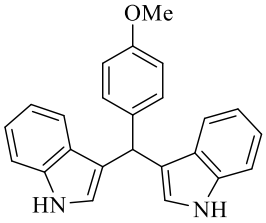
3,3'-(phenyl methylene)bis(2-phenyl-1H-indole) (**4d**):[5] Yield: 70%, white solid, m. p. 252-254 ^{o}C, lit. m. p. 260 ^{o}C; IR (KBr) ν_{max} 3416, 1445, 1309, 1236, 1020, 740 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.37 (s, 2H), 7.39-7.15 (m, 17H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 2H), 5.99(s, 1H); ^{13}C NMR (100MHz, DMSO-d$_6$) δ145.0, 136.8, 135.8, 133.2, 129.2, 128.8, 128.7, 128.5, 127.7, 126.5, 121.4, 121.3, 119.00, 114.7, 111.8, 55.4, 40. 3.



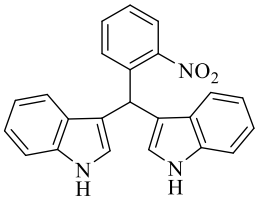
3,3'-(phenyl methylene)bis(5-bromo-1H-indole) (**4e**):[4] Yield: 85 %, light pink solid, m. p. 250-252 ^{o}C, lit. m. p. 253-255 ^{o}C; IR (KBr) ν_{max} 3410, 1593, 1554, 1445, 1325, 1213, 1173, 1029 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.10 (s, 2H), 7.44 (s, 2H), 7.36-7.28 (m, 6H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.18-7.15 (m, 2H), 6.90 (d, *J* = 2.0 Hz, 2H), 5.87 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 144.8, 135.7, 128.8, 128.7, 126.5, 125.7, 123.9, 121.7, 118.1, 114.1, 111.4, 39.3.



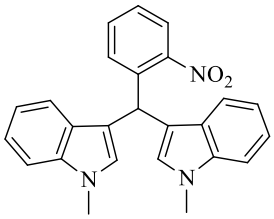
3,3'-(phenyl methylene)bis(5-methoxy-1H-indole) (**4f**):[6] Yield: 90%, light pink solid, m. p. 214-216 ^{o}C, lit. m. p. 215-216 ^{o}C; IR (KBr) ν_{max} 3389, 1483, 1445, 1206, 1169, 1029, 719 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.67 (s, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), -7.25 (d, *J* = 8.8 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 2H), 6.74-6.69 (m, 4H), 5.76 (s, 1H), 3.56 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 153.1, 145.5,132.2, 128.8, 128.4, 127.5, 126.2, 124.7, 118.1, 112.5, 111.0, 101.9, 55.7, 40.2.



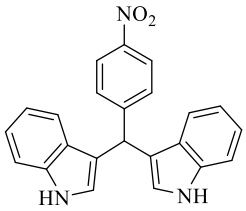
3,3'-((4-methoxy phenyl) methylene)bis(1H-indole) (**4g**):[4] Yield: 85%, white solid, m. p. 192-194 ^{o}C, lit. m. p. 190-192 ^{o}C; IR (KBr) ν_{max} 3391, 1506, 1451, 1246, 1016, 741 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.80 (s, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.27(d, *J* = 4.8Hz, 2H), 7.25 (d, *J* = 5.6 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.87-6.79 (m, 6H), 5.77 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 157.8, 137.4, 137.0, 129.6, 127.1, 123.9, 121.3, 119.6, 118.9, 118.6, 113.8, 111.9, 55.4, 39.3.



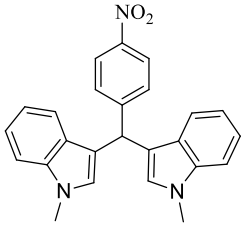
3,3'-((2-nitrophenyl)methylene)bis(1H-indole) (**4h**):[7] Yield: 93%, light yellow solid, m. p. 138-140 ^{o}C, lit. m. p.; IR (KBr) ν_{max} 3391, 1757, 1512, 1343, 1218, 1088, 740 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.44-7.37 (m, 4H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 149.8, 138.0, 136.7, 132.3, 131.1, 127.2, 126.8, 124.4, 123.8, 122.2, 119.8, 119.6, 117.7, 111.1, 76.7, 34.8.



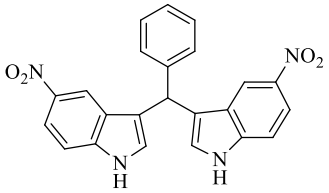
3,3'-((2-nitrophenyl)methylene)bis(1-methyl-1H-indole) (**4i**): Yield: 91%, light yellow solid, m. p. 160-162 ^{o}C; IR (KBr) ν_{max} 3052, 1514, 1467, 1339, 1120, 781 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.8 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 8 Hz, 3H), 7.23 (d, *J* =7.6 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 2H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.80 (s, 2H), 6.40 (s, 1H), 3.71 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 149.8, 138.1, 137.4, 133.1, 131.0, 128.9, 128.1, 127.0, 124.5, 121.8, 119.2, 119.1, 115.7, 110.3, 34.2, 32.8; HRMS calcd for ($C_{25}H_{21}N_3O_2 + H^+$) 396.1712, found : 396.1692 (M + H$^+$).



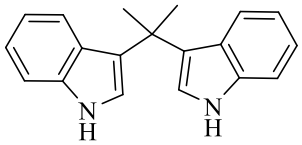
3,3'-((4-nitrophenyl)methylene)bis(1H-indole) (**4j**):[4] Yield: 87%, light yellow solid, m. p. 220-222 ^{o}C, lit. m. p. 219-220 ^{o}C; IR (KBr) ν_{max} 3453, 1504, 1453, 1337, 1097, 741 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.94 (s, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 4H), 6.03 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 153.6, 146.2, 137.1, 129.9, 126.8, 124.3, 123.9, 121.6, 119.4, 118.9, 117.1, 112.1, 39.4.



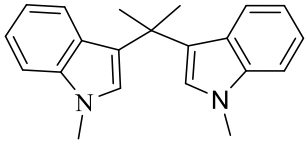
3,3'-((4-nitrophenyl)methylene)bis(1-methyl-1H-indole) (**4k**):[8a,b] Yield: 82%, light yellow solid, m. p.236-238 ^{o}C, lit. m. p. 240-242 ^{o}C; IR (KBr) ν_{max} 3733, 1506, 1469, 1331, 1007, 732 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.95-6.90 (m, 4H), 6.05 (s, 1H), 3.71 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 153.4, 146.3, 137.4, 129.9, 128.6, 127.1, 124.0, 121.7, 119.5, 119.1, 116.4, 110.2, 39.4, 32.8.



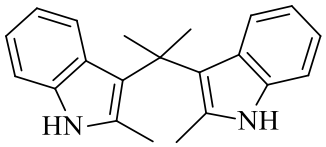
3,3'-(phenyl methylene)bis(5-nitro-1H-indole) (**4l**):[4] Yield: 82 %, light yellow solid, m. p. 250-252 ^{o}C, lit. m. p. 253-255 ^{o}C; IR (KBr) ν_{max} 3288, 1508, 1464, 1378, 1313, 1087 cm^{-1}; ^{1}H NMR (400 MHz, DMDO-d$_6$) δ 11.98 (s, 2H), 8.32 (s, 2H), 7.99-7.96 (dd, *J* = 9.2, 2.0 Hz, 2H), 7.55 (d, *J* = 9.2 Hz, 2H), 7.40 (d, *J* = 7.6Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.14 (bs, 2H), 6.21 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 144.2, 140.7, 140.2, 128.9, 128.7, 128.1, 126.9, 126.9, 126.5, 126.2, 121.0, 117.1, 112.6, 38.9.



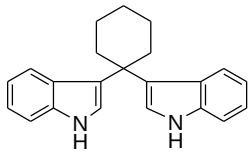
3,3'-(propane-2,2-diyl)bis(1H-indole) (**4m**):[1] Yield: 95%, white solid, m. p.156-158 ^{o}C, lit. m. p. 160 ^{o}C; IR (KBr) ν_{max} 3394, 2309, 1453, 1333, 1094, 1008, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.15-7.11 (m, 2H), 7.07 (d, *J* = 2.4 Hz, 2H), 6.96-6.92 (m, 2H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 126.3, 125.5, 121.4, 121.3, 120.5, 118.7, 111.1, 34.9, 30.0.



3,3'-(propane-2,2-diyl)bis(1-methyl-1H-indole) (**4n**): Yield: 86%, white solid, m. p. 130 ^{o}C; IR (KBr) ν_{max} 3744, 1463, 1322, 1225, 1049, 734 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.4 Hz, 1H), 6.96 - 6.93 (m, 2H), 3.78 (s, 3H), 1.96 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 126.7, 125.5, 124.1, 121.5, 120.9, 118.1,109.1, 35.0, 32.7, 31.0, 30.3 HRMS calcd for ($C_{21}H_{22}N_2$ + H^+) 303.1861, found : 303.1849(M + H^+).

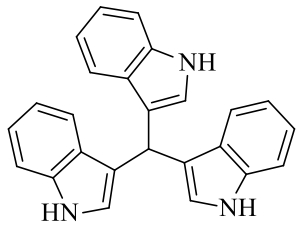


3,3'-(propane-2,2-diyl)bis(2-methyl-1H-indole) (**4o**): Yield: 83%, white solid, m. p. 130 ^{o}C; IR (KBr) ν_{max} 3378, 2310, 1546, 1453, 1340, 1014, 740 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.53 (s, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.6 Hz, 2H), 6.67 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 6H), 1.92 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.4, 130.1, 128.2, 120.2, 119.6, 119.4, 118.0, 110.6, 37.7, 32.2, 14.5; HRMS calcd for $C_{21}H_{22}N_2$ 302.1783, found : 302.1747 (M^+).

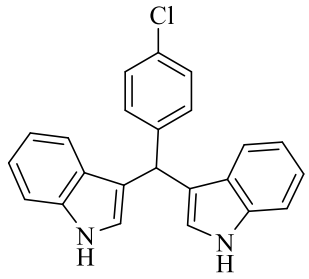


3-(1-(1H-indol-3-yl)cyclohexyl)-1H-indole (**4p**): [4,9] Yield: 85 %; white solid, m. p. 117-119 ^{o}C; lit. 118-120 ^{o}C; FT-IR (KBr) νmax 3166, 2977, 2309, 1699, 1533, 1411, 1057, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H),

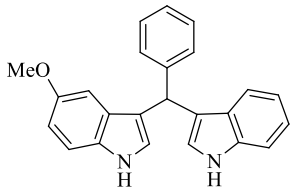
7.09 (t, *J* = 8.8 Hz, 4H), 6.92 (t, *J* = 7.6 Hz, 2H), 2.57 (d, *J* = 6 Hz, 4H), 1.69-1.62 (m, 6H); ^{13}C NMR (100 MHz, CDCl3) δ 137.0, 126.3, 123.7, 122.0, 121.5, 121.2, 118.5, 111.1, 39.5, 36.8, 26.8, 23.0.



Tri(1H-indol-3-yl)methane (**4q**):[4] Yield: 91%, off-white solid, m.p. 248-250 ^{o}C, lit. m. p. 244-245 ^{o}C; IR (KBr) ν_{max} 3386, 1454, 1336, 1216, 1086, 743 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.71 (s, 3H), 7.39 (d, *J* = 7.6 Hz, 3H), 7.33 (d, *J* = 8.0 Hz, 3H), 7.01 (t, *J* = 7.6 Hz, 3H), 6.93 (s, 3H), 6.85 (t, *J* = 7.2 Hz, 3H), 6.04 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.0, 127.2, 123.6, 121.1, 119.7, 118.7, 118.4, 111.8, 31.4

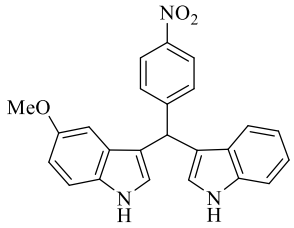


3,3'-((4-chlorophenyl)methylene)bis(1H-indole) (**4r**):[4] Yield: 86%, light orange solid, m. p. 74-76 ^{o}C, lit. m. p. 75-76 ^{o}C ; IR (KBr) ν_{max} 3733, 2309, 1693, 1516, 1219, 1089, 772 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.39 (d, *J* = 8.8 Hz, 4H), 7.31-7.25 (m, 5H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.67 (d, *J* = 1,6 Hz, 2H), 5.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 136.7, 131.8, 130.1, 128.4, 126.9, 123.6, 122.1, 119.8, 119.4, 119.2, 111.1, 39.6

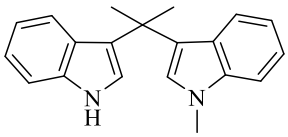


3-((1H-indol-3-yl)(phenyl)methyl)-5-methoxy-1H-indole (**4u**): Yield: 61%, off-white solid, m. p. 156-158 ^{o}C; IR (KBr) ν_{max} 3404, 1484, 1206, 1018 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.83 (s, 1H), 7.42-7.20 (m, 10H), 7.03 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 12.0 Hz, 2H), 5.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 144.0, 136.8, 131.8,

128.7, 128.2, 127.5, 127.1, 126.2, 124.4, 123.7, 121.9, 120.0, 119.6, 119.4, 119.2, 112.0, 111.7, 111.1, 101.9, 55.9, 40.3; HRMS calcd for ($C_{24}H_{20}N_2O$–H^+) 351.1497, found: 351.1516 (M – H^+).

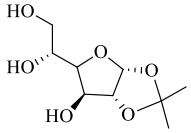


3-((1H-indol-3-yl)(4-nitrophenyl)methyl)-5-methoxy-1H-indole (**4v**): Yield: 70%, light yellow solid, m. p. 180-182 ^oC; IR (KBr) ν_{max} 3448, 1501, 1341, 1201, 1062, 920, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 2H), 8.06 (s, 1H), 7.95 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.42- 7.28 (m, 3H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.89 (dd, *J* = 6.4, 2.4 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.71 (s, 1H), 6.67 (s, 1H), 5.96 (s, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 151.8, 146.6, 136.8, 131.8, 129.5, 127.1, 126.7, 124.4, 123.7, 123.6, 122.3, 119.6, 118.0, 117.8, 112.3, 112.0, 111.3, 101.6, 76.7, 55.9, 40.2; HRMS calcd for ($C_{24}H_{19}N_3O_3$+H^+) 398.1505, found: 398.1513 (M + H^+)

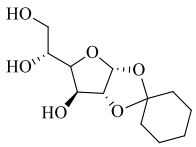


3-(2-(1H-indol-3-yl)propan-2-yl)-1-methyl-1H-indole (**4x**): Yield: 51%, off-white solid, m. p. 102-104 ^oC; IR (KBr) ν_{max} 3420, 1482, 1326, 1215, 1012 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.47 (q, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.18-7.11 (m, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.96-6.90 (m, 3H), 3.78 (s, 3H), 1.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.1, 128.8, 126.7, 126.4, 125.6, 125.4, 124.0, 121.4, 121.3, 120.9, 120.6, 118.7, 118.1, 111.0, 109.2, 109.1, 100.9, 76.7, 34.9, 32.7, 30.2, 30.0; HRMS calcd for ($C_{20}H_{20}N_2$ + H^+) 289.1705, found: 289.1718 (M + H^+)

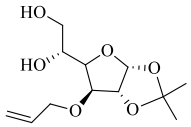
Physical and Spectral data of deprotected carbohydrate products 5a-h:



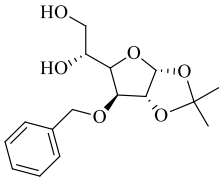
1-((3aR,6S,6aR)-6-hydroxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol (**5a**):[10] Yield: 87%, white solid, m. p. 159-160 ^{o}C; IR (KBr) ν_{max} 3427, 3306, 2985, 2933, 1385, 1224, 1076, 1003, 857cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 5.79 (s, 1H), 5.13 (s, 1H), 4.64 (d, *J* = 5.2 Hz, 1H), 4.45 (s, 1H), 4.37 (s, 1H), 4.03 (s, 1H), 3.83 (d, *J* = 8.0 Hz, 1H), 3.69 (s, 1H), 3.54 (s, 1H), 3.34 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 110.8, 104.9, 85.2, 80.5, 73.7, 68.9, 64.1, 27.1, 26.6.



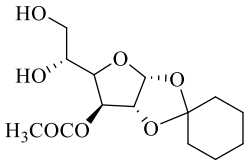
1-((3a'R,6'S,6a'R)-6'-hydroxytetrahydrospiro[cyclohexane-1,2'-furo[2,3-d][1,3]dioxol]-5'-yl)ethane-1,2-diol (**5b**):[11] Yield: 80%, white solid, m. p. 165 ^{o}C: IR (KBr) ν_{max} 3389, 3292, 2931, 1428, 1232, 1037, 957 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 5.79 (d, *J* = 3.6 Hz, 1H), 5.12 (d, *J* = 4.4 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 4.45 (t, *J* = 5.6 Hz, 1H), 4.36 (d, *J* = 3.6 Hz, 1H), 4.04 (s, 1H), 3.83 (dd, *J* = 6.4, 2.4 Hz, 1H), 3.68 (s, 1H), 3.54 (d, *J* = 11.2 Hz, 1H), 3.36 (d, *J* = 5.6 Hz, 1H), 1.56-1.33 (m, 10H); ^{13}C NMR (100 MHz, DMSO-d6) δ 111.3, 104.5, 84.7, 80.5, 73.8, 68.9, 64.1, 36.5, 35.7, 24.9, 24.1, 23.7.



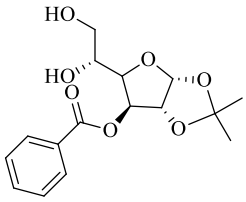
1-((3aR,6S,6aR)-6-(allyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol (**5c**):[2] Yield: 85%, light yellow liquid; IR (KBr) ν_{max} 2984, 2933, 1378, 1215, 1072, 1010, 855 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.94-5.84 (m, 2H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.55 (d *J* = 3.6 Hz, 1H), 4.15 (dd, *J* = 7.6, 5.2 Hz, 1H), 4.10-4.04 (m, 2H), 4.01 (d, *J* = 3.2 Hz, 1H), 3.97 (d, *J* = 2.8 Hz, 1H), 3.79 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.68 (dd, *J* = 6.0, 5.6 Hz, 1H), 1.47 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 133.9, 117.9, 111.7, 105.0, 82.1, 81.7, 79.8, 71.2, 69.0, 64.3, 26.6, 26.1.



1-((3aR,6S,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)ethane-1,2-diol (**5d**):[2] Yield: 85%, light yellow liquid; IR (KBr) ν_{max} 2984, 2936, 1455, 1377, 1214, 1072, 1012, 857, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 5.95 (d, *J* = 4.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 4.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.15-4.11 (m, 1H), 4.05-4.01 (s, 1H), 3.81 (dd, *J* = 8.0 Hz, 3.6 Hz, 1H), 3.71 (dd, *J* = 6.0, 6.5 Hz, 1H), 1.50 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 128.7, 128.3, 127.9, 111.8, 105.1, 82.1, 82.0, 79.9, 72.2, 69.2, 64.3, 26.7, 26.2

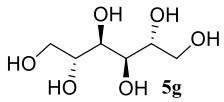


(3a'R,6'S,6a'R)-5'-(1,2-dihydroxyethyl)tetrahydrospiro [cyclohexane-1,2'-furo[2,3-d][1,3] dioxol]-6'-yl acetate (**5e**):[2] Yield: 80%, light yellow liquid; IR (KBr) ν_{max} 2936, 2860, 1736, 1371, 1232, 1016, 928 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.93 (d, *J* = 3.6 Hz, 1H), 5.30 (d, *J* = 2.4 Hz, 1H), 4.58 (d, *J* = 3.6 Hz, 1H), 4.19 (dd, *J* = 6.8, 2.4 Hz, 1H), 3.86 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.75 (dd, *J* = 6.0, 5.6 Hz, 1H), 3.69-3.64 (m 1H), 2.17 (d, *J* = 5.2 Hz, 4H), 1.74 (d, *J* = 6.0 Hz, 2H) 1.69-1.64 (m, 2H), 1.56 (d, *J* = 4.4 Hz, 5H), 1.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 113.2, 104.4, 82.6, 79.4, 76.9, 68.1, 64.1, 36.2, 35.7, 24.8, 23.8, 23.5, 20.8



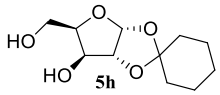
(3aR,6S,6aR)-5-(1,2-dihydroxyethyl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl benzoate (**5f**):[12] Yield: 87%, colourless liquid; IR (KBr) ν_{max} 2988, 2937, 1718, 1452, 1265, 1067, 1015, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (t, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 6.03 (d, *J* = 3.6 Hz, 1H), 5.54 (d, *J* = 2.4 Hz, 1H), 4.74 (d, *J* = 4.0 Hz, 1H), 4.34-4.31(m, 1H), 3.91-3.87 (m, 1H), 3.80-3.75 (m, 2H), 1.58 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 166.6, 134.0, 130.0, 128.7, 128.6, 112.5, 105.0, 83.1, 79.7, 76.7, 68.3, 64.2, 26.7, 26.2

Spectral data of D-mannitol (5g)



D-Mannitol (**5g**):Yield: 92%, dirty white solid, m. p. 164-165 ^{o}C; IR ν_{max} 3398, 2950, 1080, 1020 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 3.85 (m, *2*H), 3.79-3.74 (m, 4H), 3.67 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 70.7, 69.1, 63.2. (Spectra was matched with the commercially available compound)

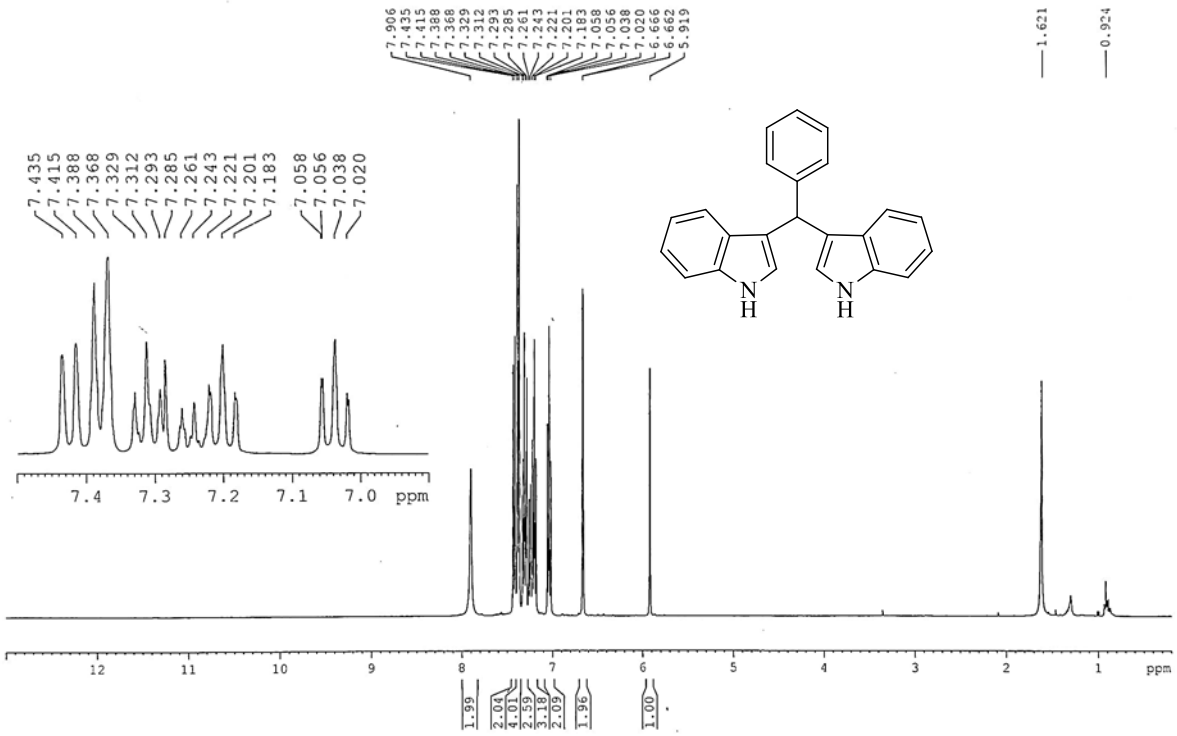
Spectral data of 5h



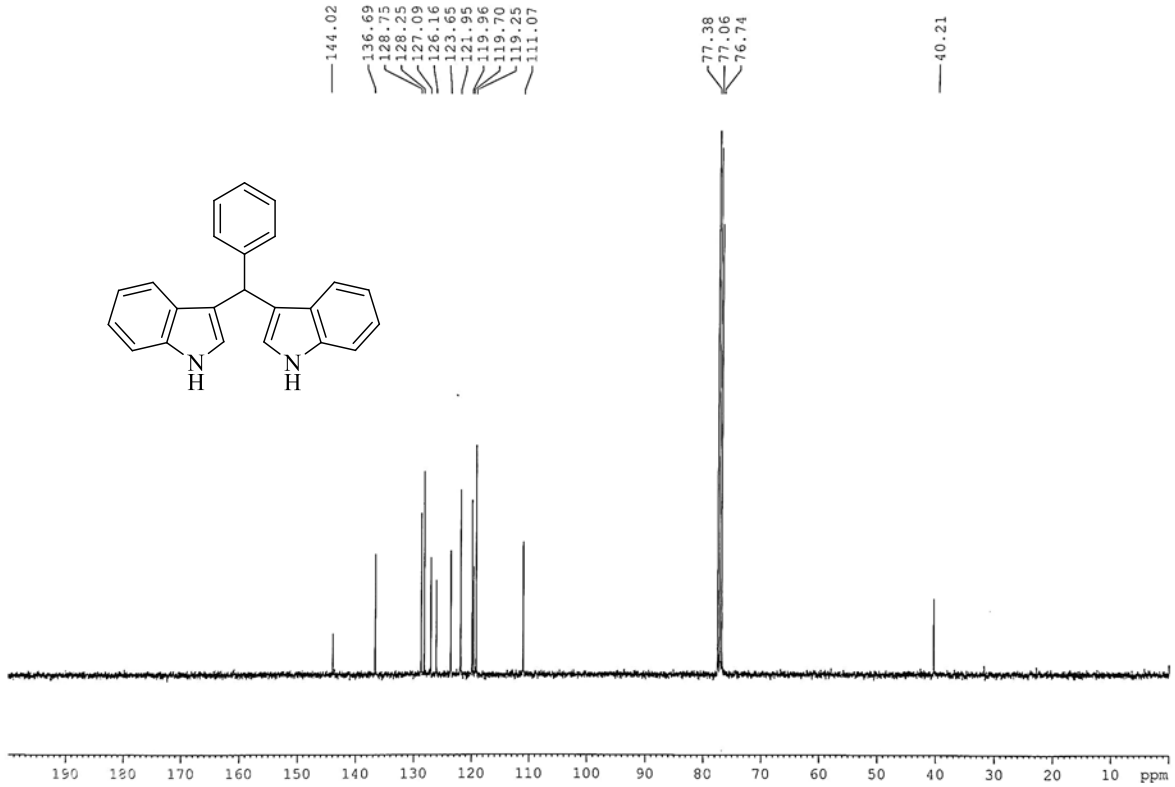
(3a'R, 5'R, 6'S, 6a'R)-5'-(hydroxymethyl)tetrahydrospiro[cyclohexane-1,2'-furo[2,3-d][1,3]dioxol]-6'ol (**5h**): [2] Yield: white solid, m. p. 180-182 ^{o}C, IR(neat)) ν_{max} 3240, 2932, 1441, 1110, 1065, 1018, 940 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (d, *J* = 3.6 Hz, 1H), 4.51 (d, *J* = 3.6 Hz, 1H), 4.33 (bs, 1H), 4.18-4.01 (m, 3H), 3.19 (bs, 1H), 2.18 (bs, 1H), 1.72-1.54 (m, 8H), 1.40 (m, 2H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 112.5,104.5, 85.2, 78.8, 76.9, 61.1, 36.4, 35.7, 24.9, 23.9, 23.6.

^{1}H and ^{13}C NMR spectra of bisindoles (4a-r and 4u-x)

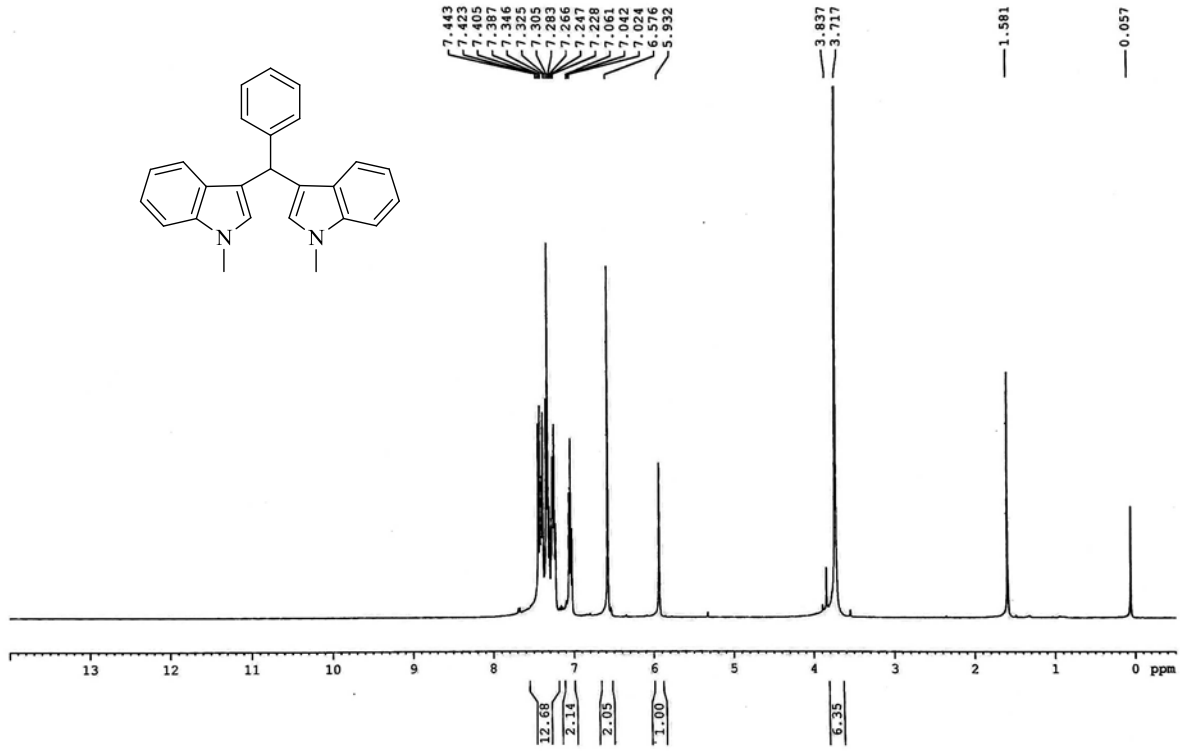
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



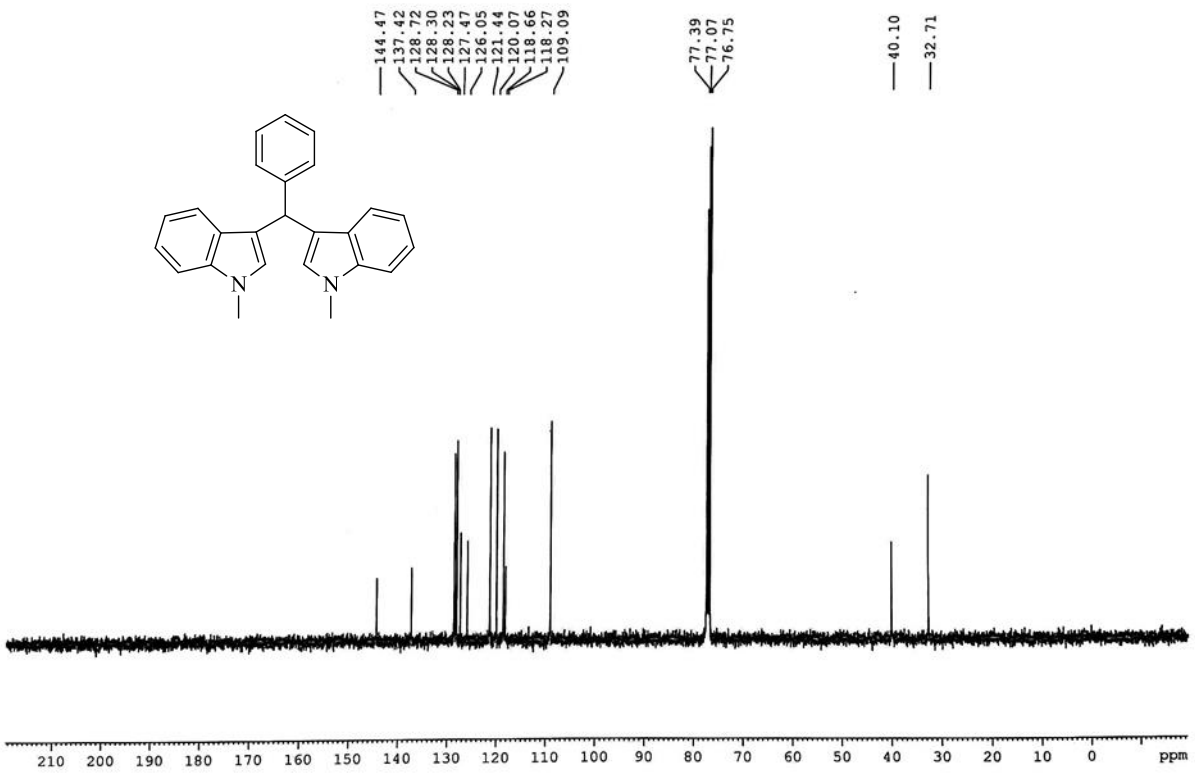
^{13}C NMR (100 MHz, $CDCl_3$) of **4a**



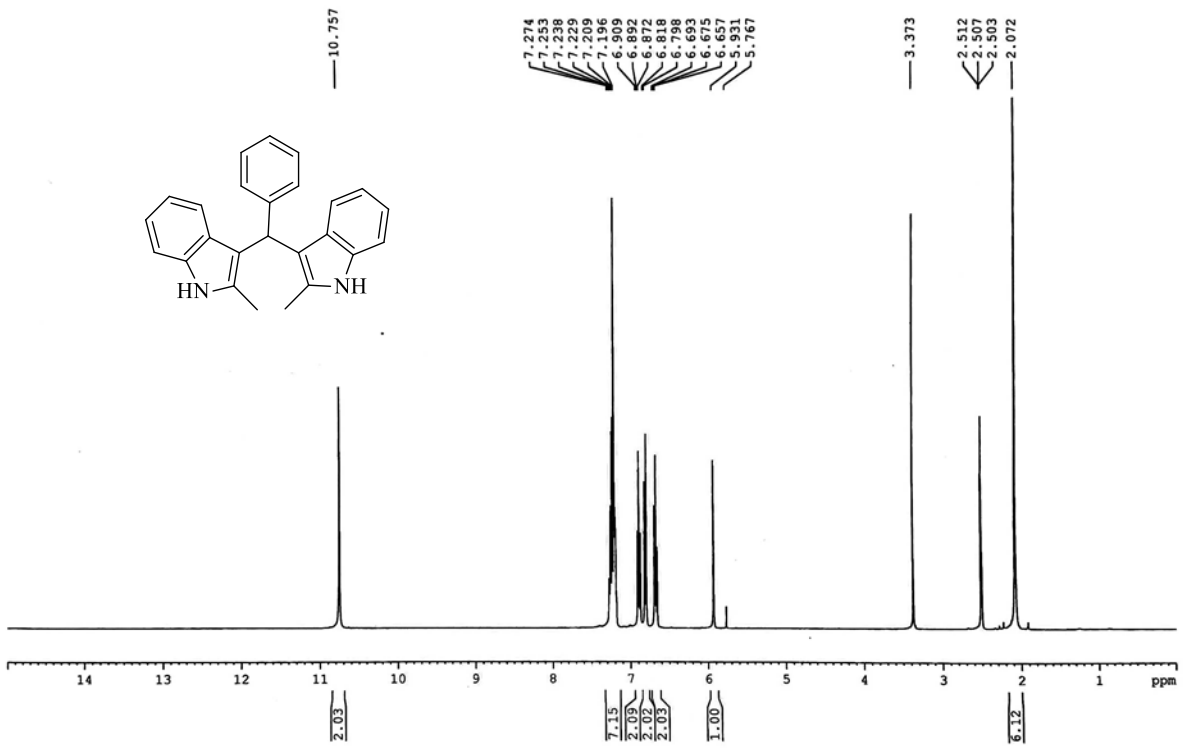
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



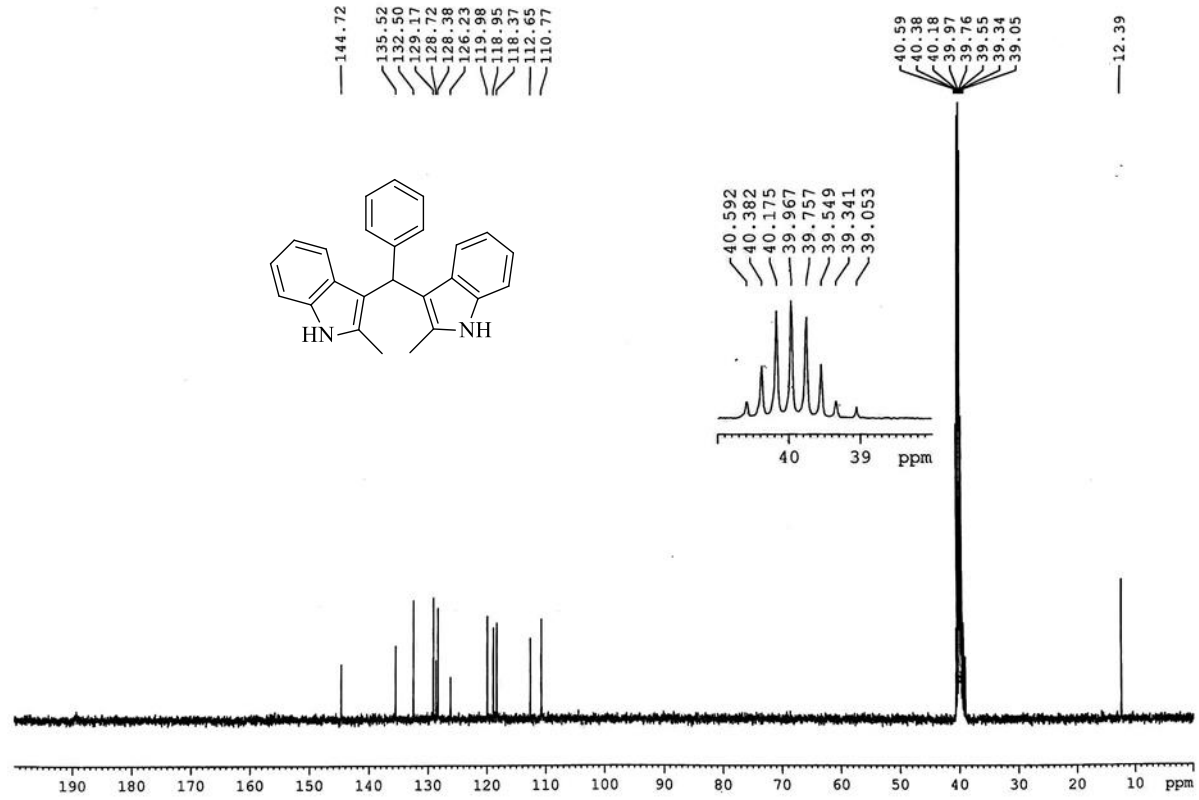
^{13}C NMR (100 MHz, $CDCl_3$) of **4b**



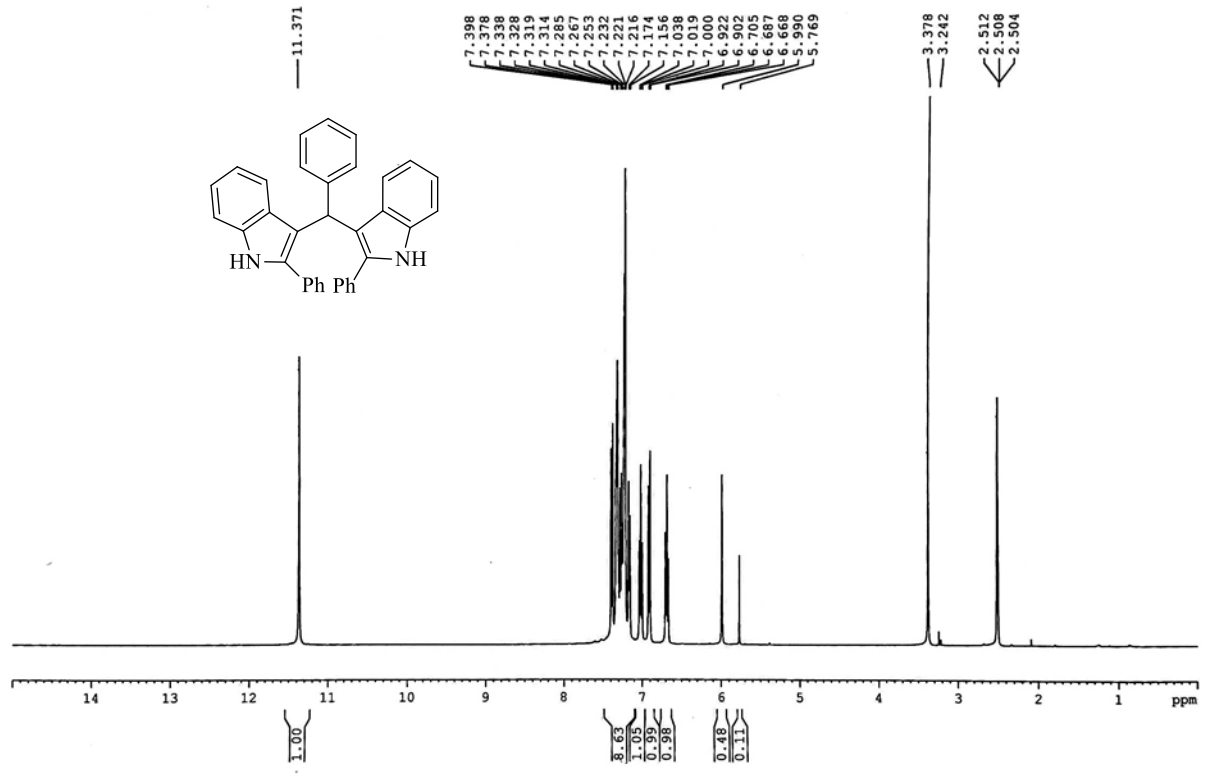
^{1}H NMR (400 MHz, DMSO-d_6) of **4c**



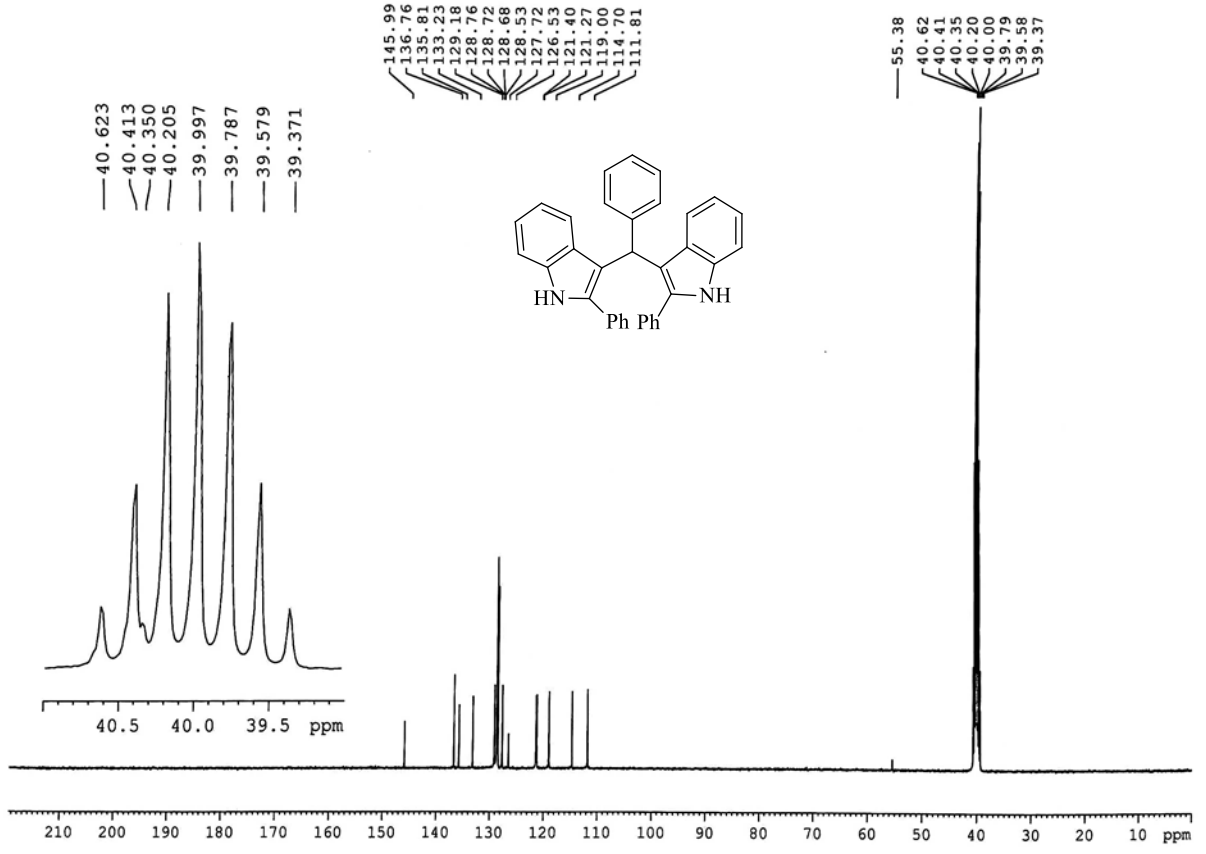
^{13}C NMR (100 MHz, DMSO-d_6) of **4c**



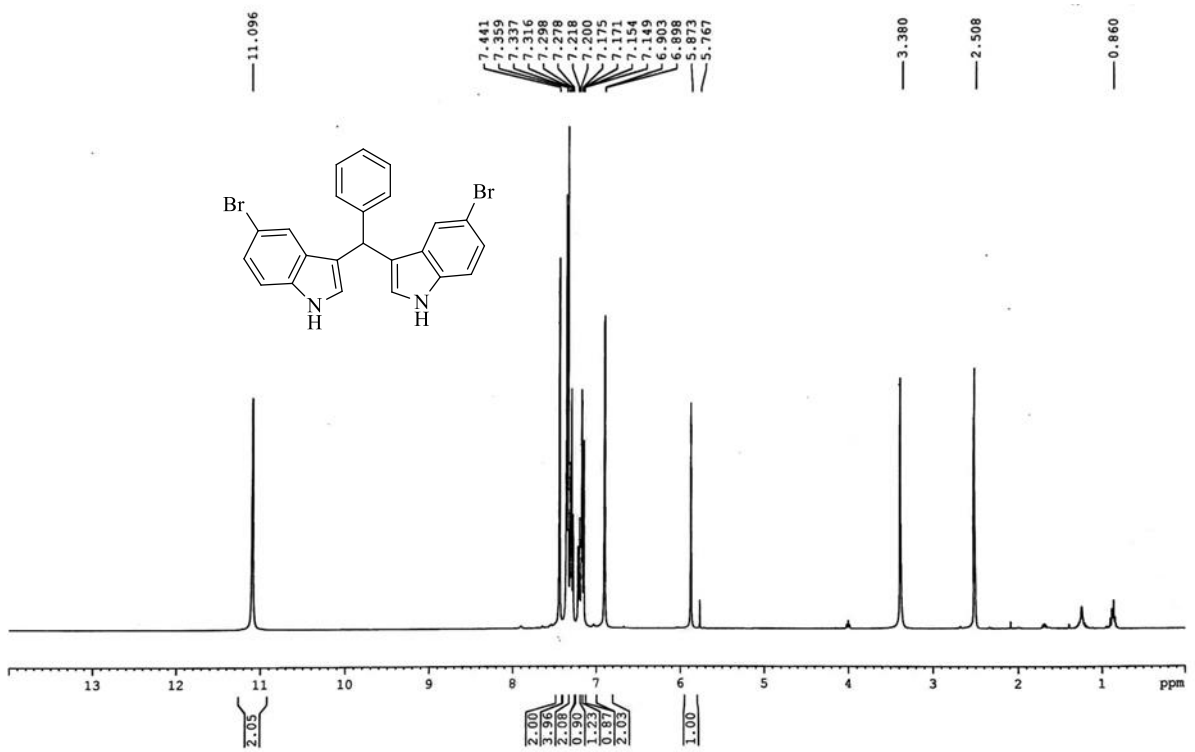
^{1}H NMR (400 MHz, DMSO-d_6) of **4d**



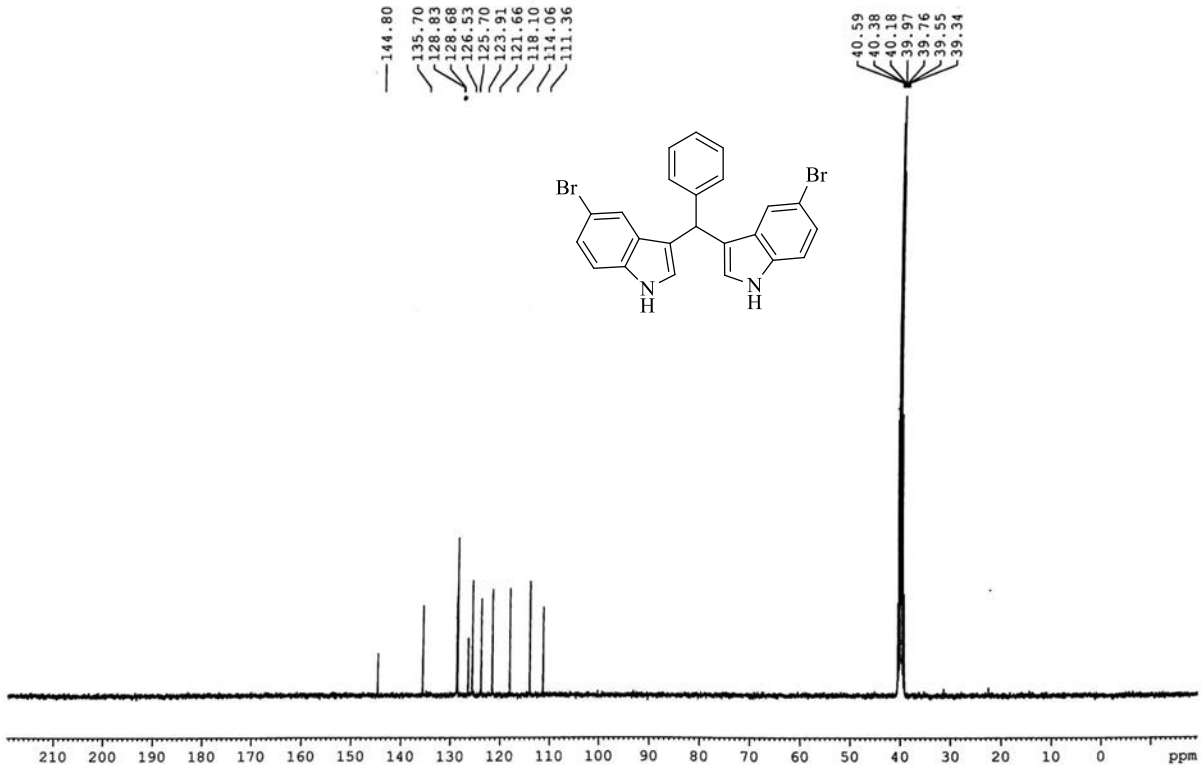
^{13}C NMR (100 MHz, DMSO-d_6) of **4d**



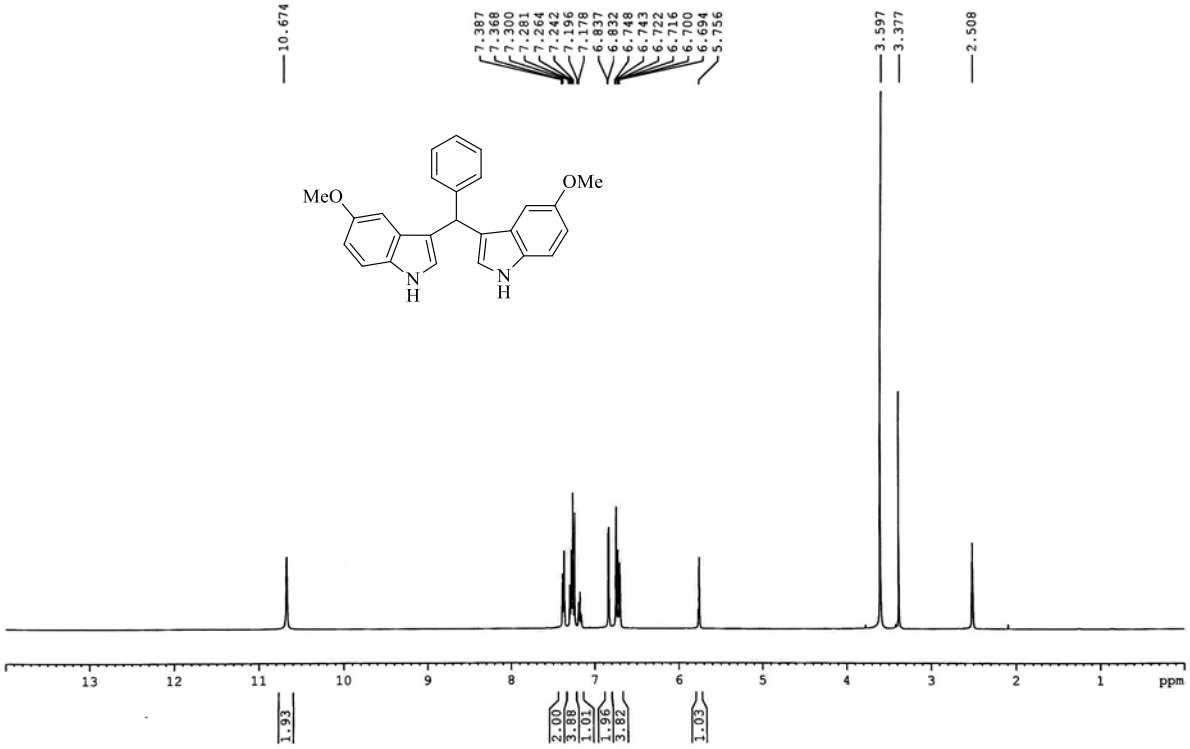
^{1}H NMR (400 MHz, DMSO-d_6) of **4e**



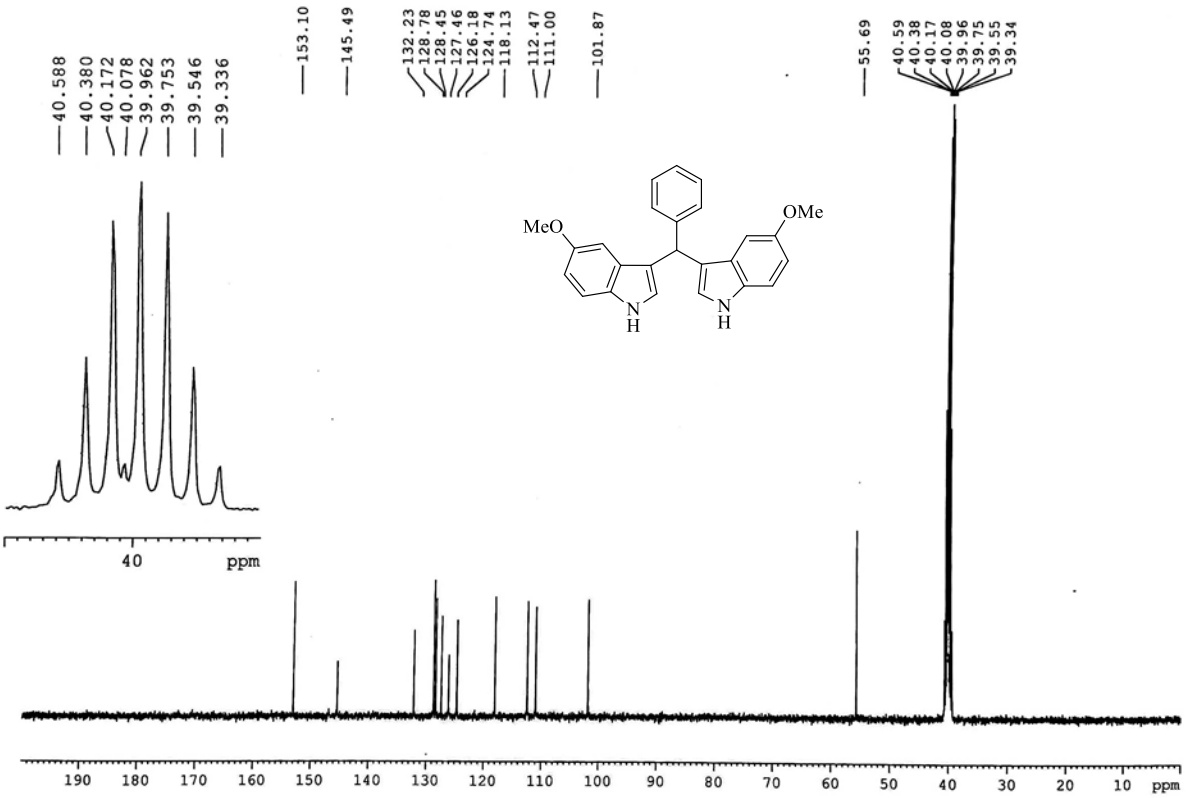
^{13}C NMR (100 MHz, DMSO-d_6) of **4e**



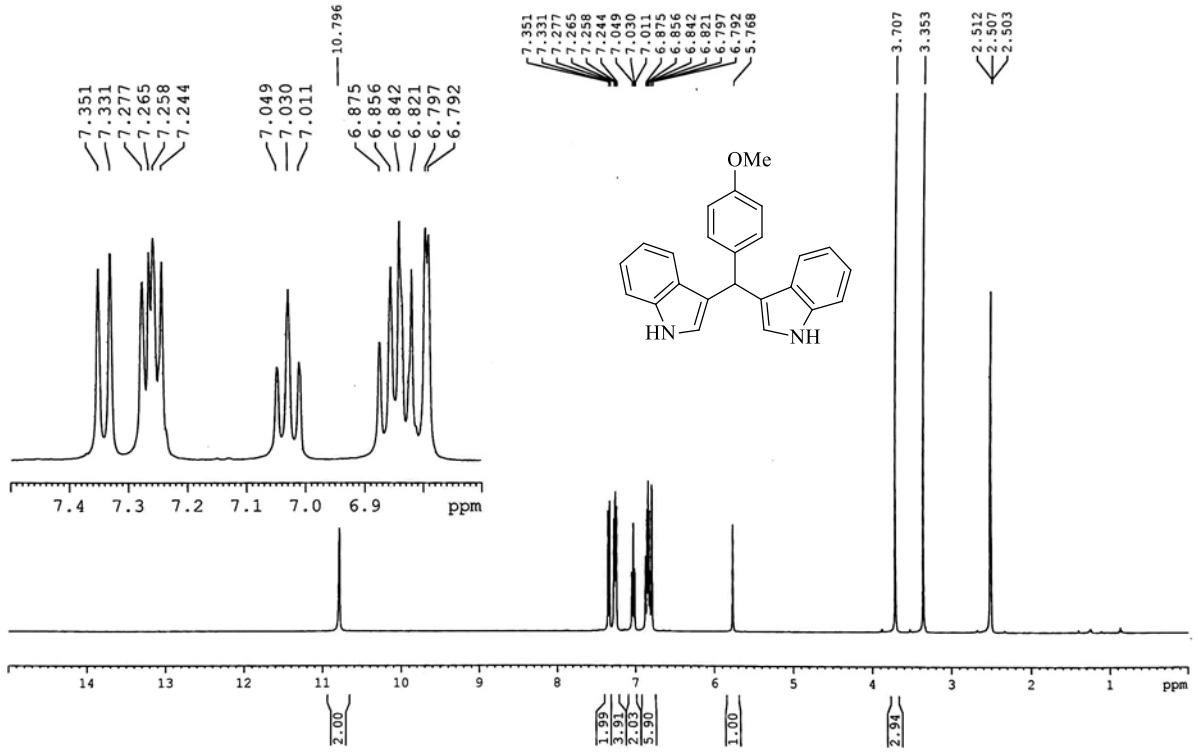
^{1}H NMR (400 MHz, DMSO-d_6) of **4f**



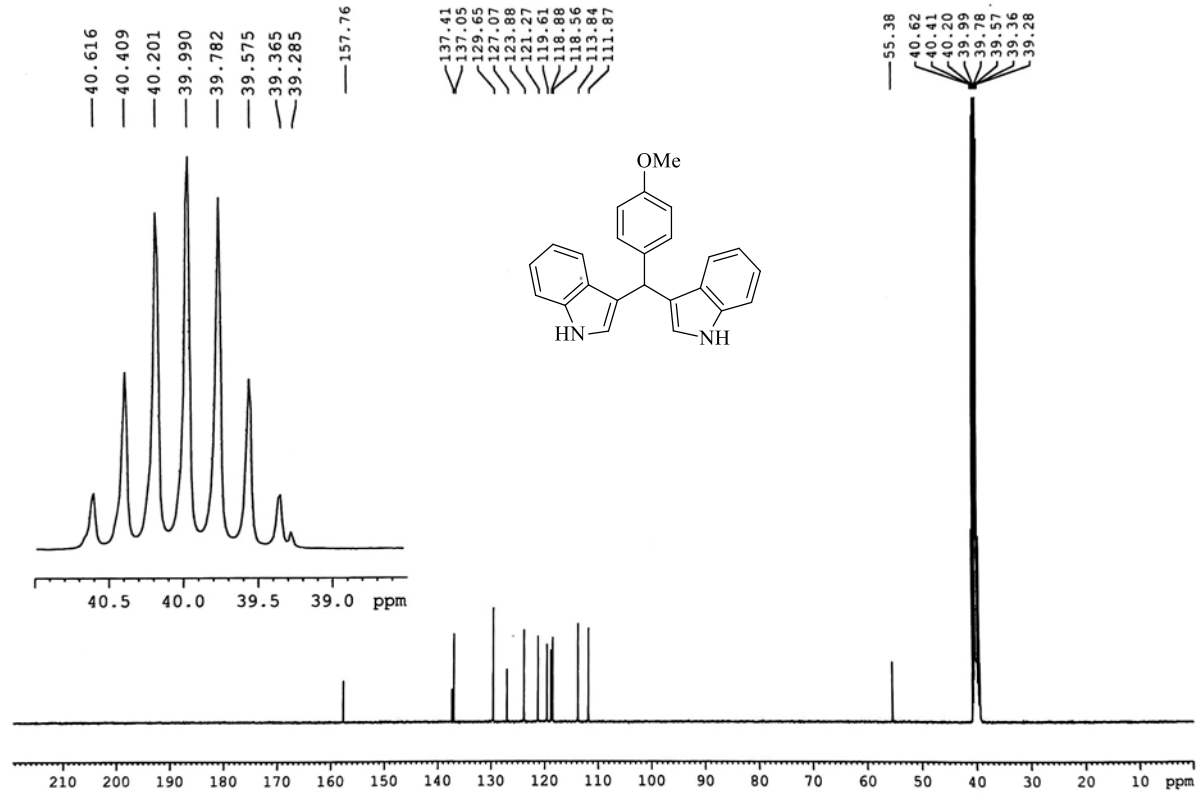
^{13}C NMR (100 MHz, DMSO-d_6) of **4f**



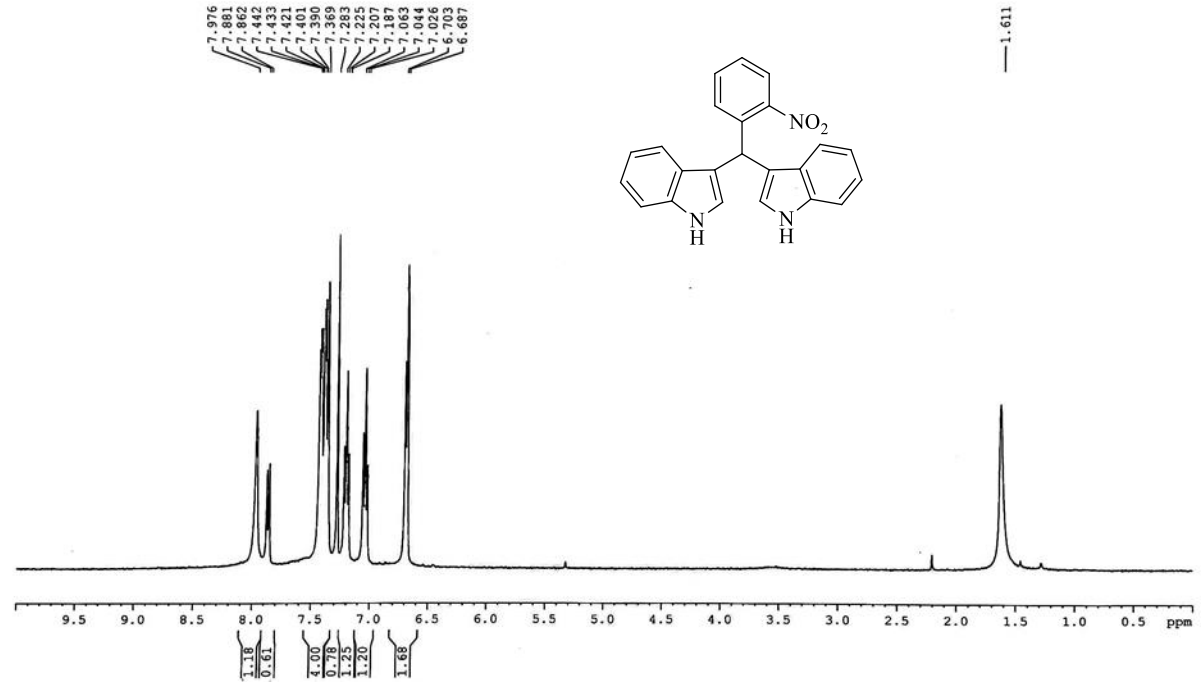
^{1}H NMR (400 MHz, DMSO-d_6) of **4g**



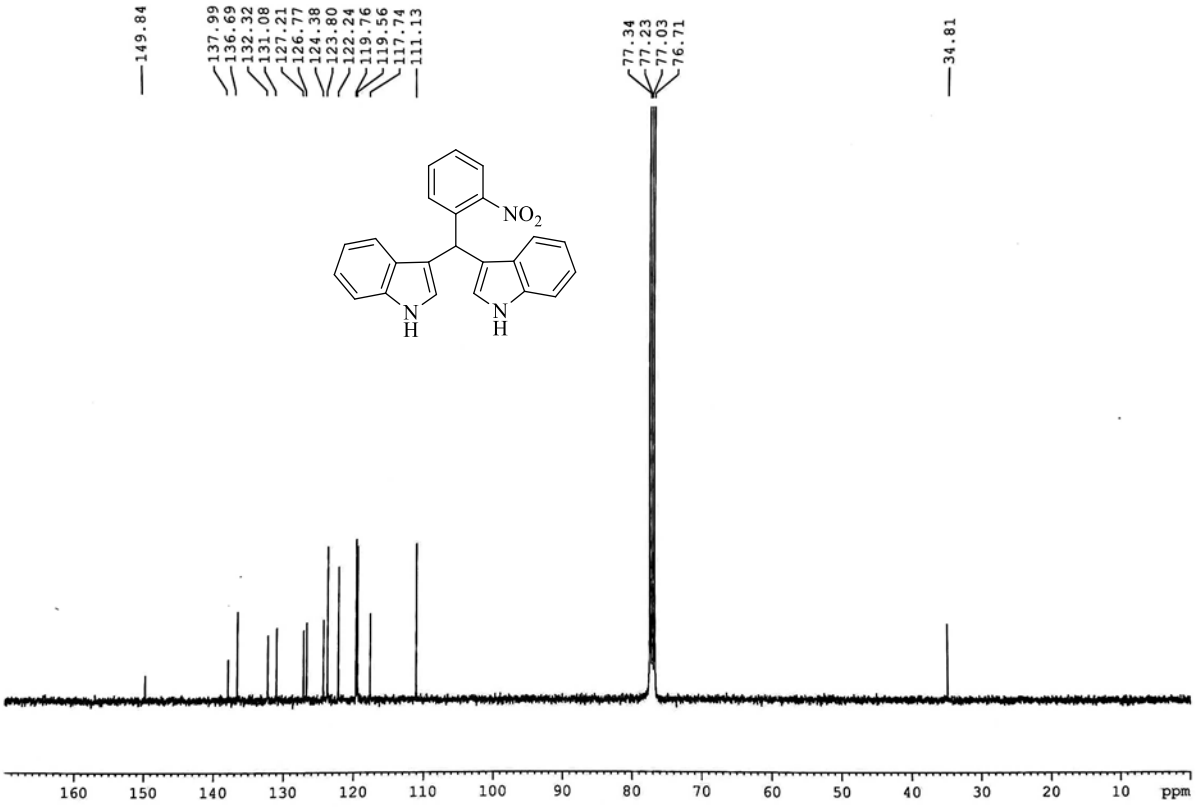
^{13}C NMR (100 MHz, DMSO-d_6) of **4g**



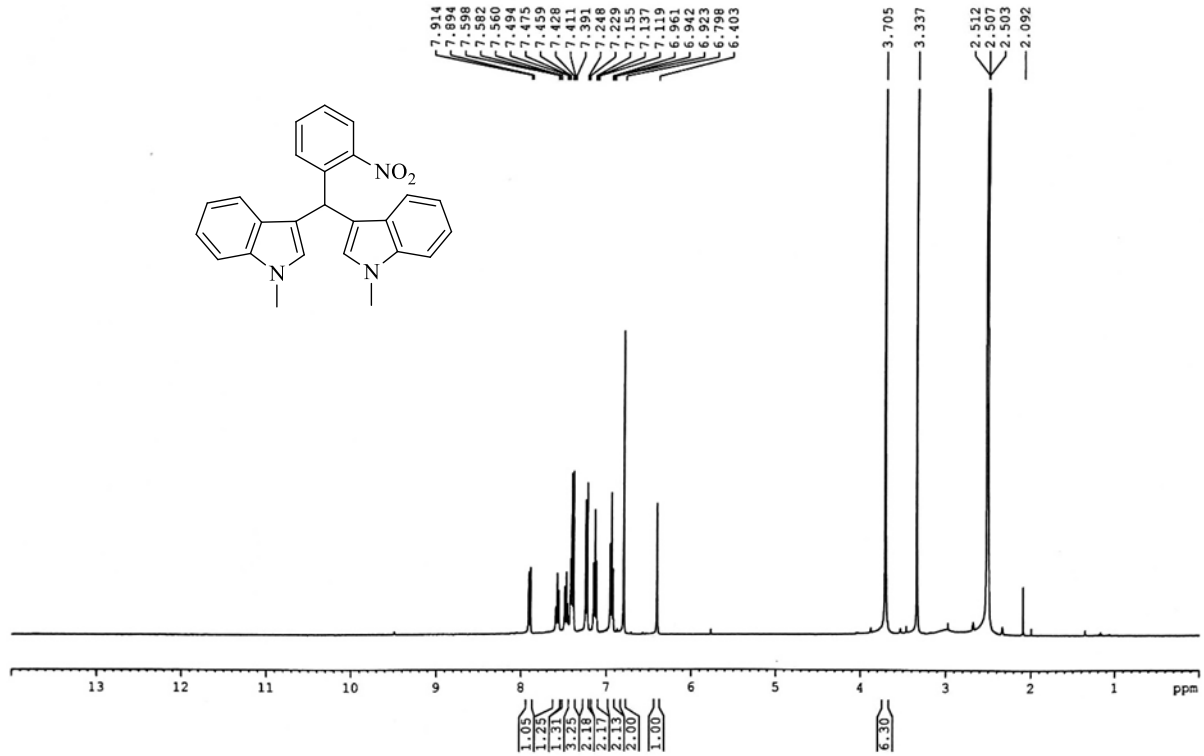
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



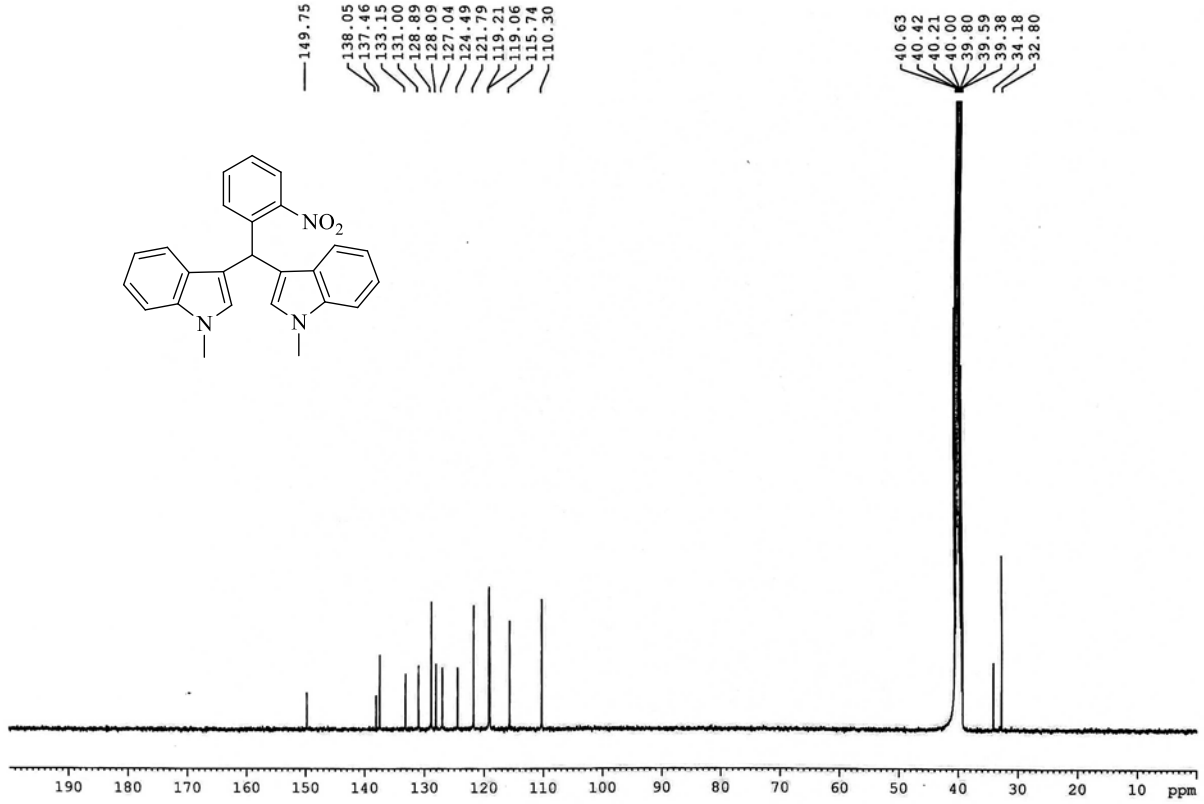
^{13}C NMR (100 MHz, $CDCl_3$) of **4h**



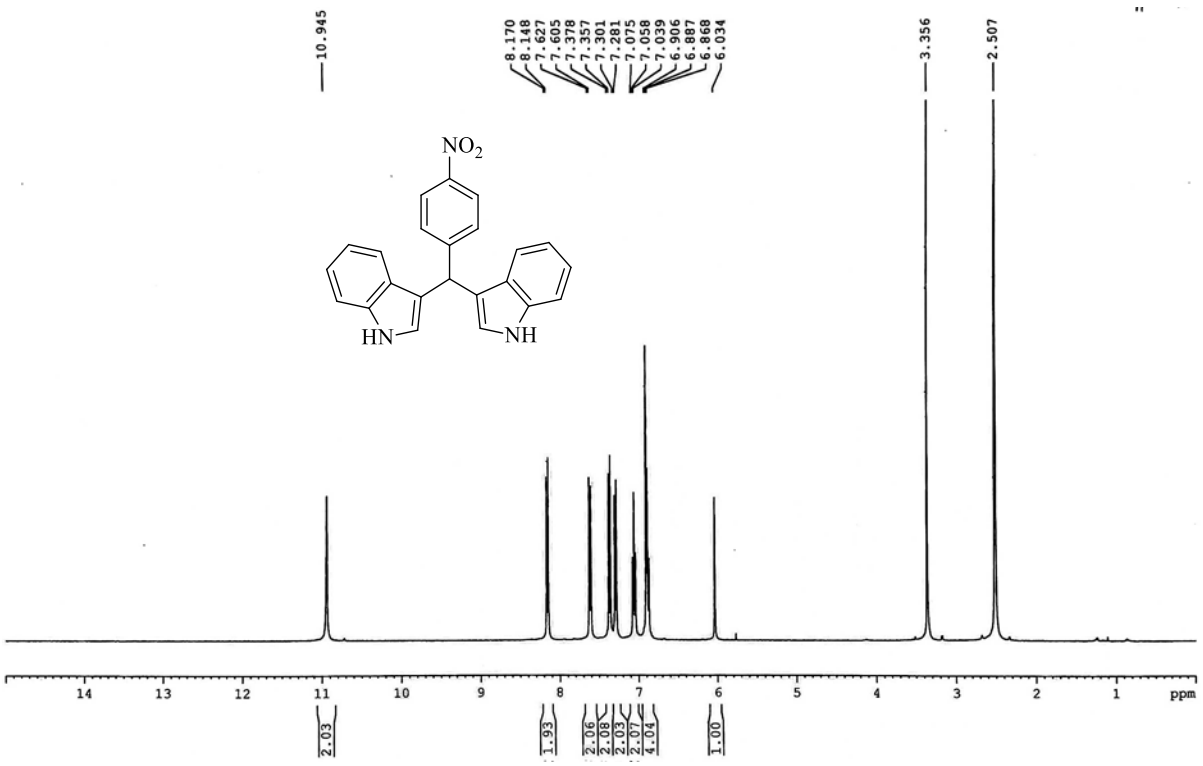
^{1}H NMR (400 MHz, DMSO-d_6) of **4i**



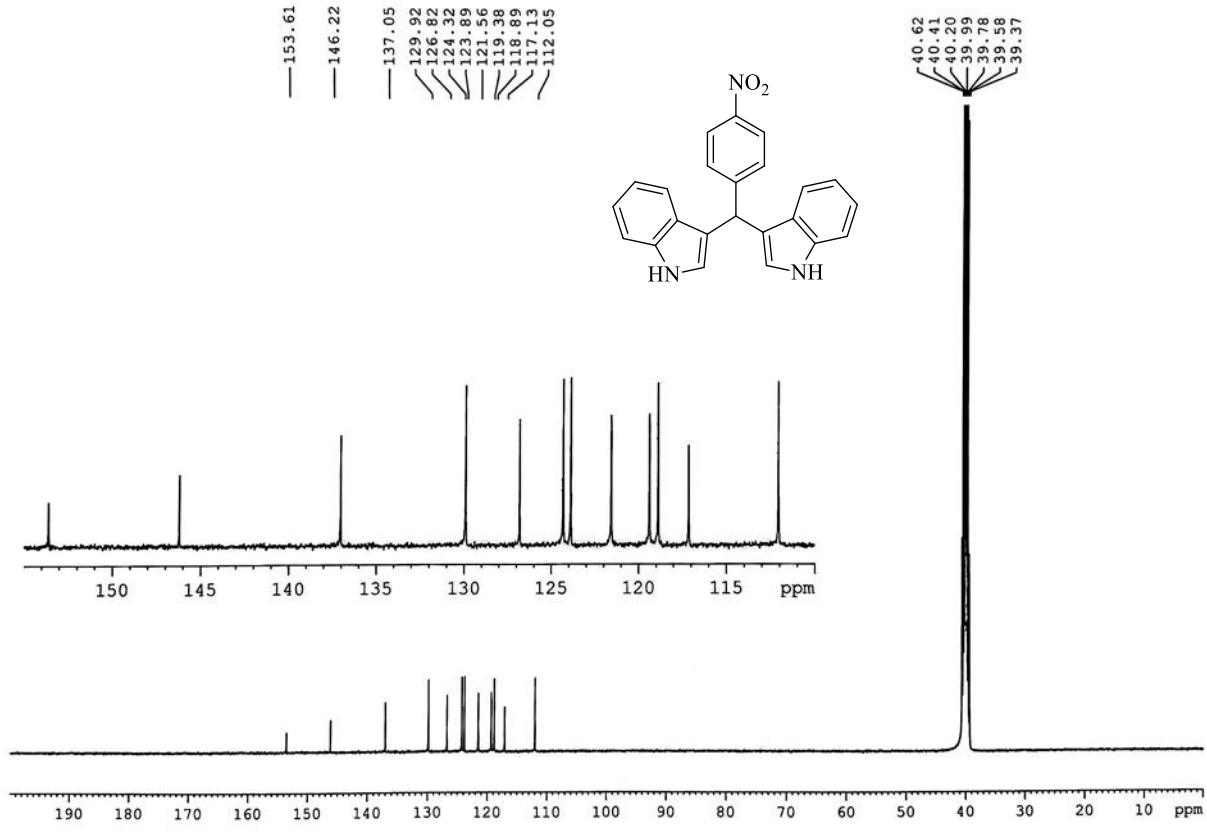
^{13}C NMR (100 MHz, DMSO-d_6) of **4i**



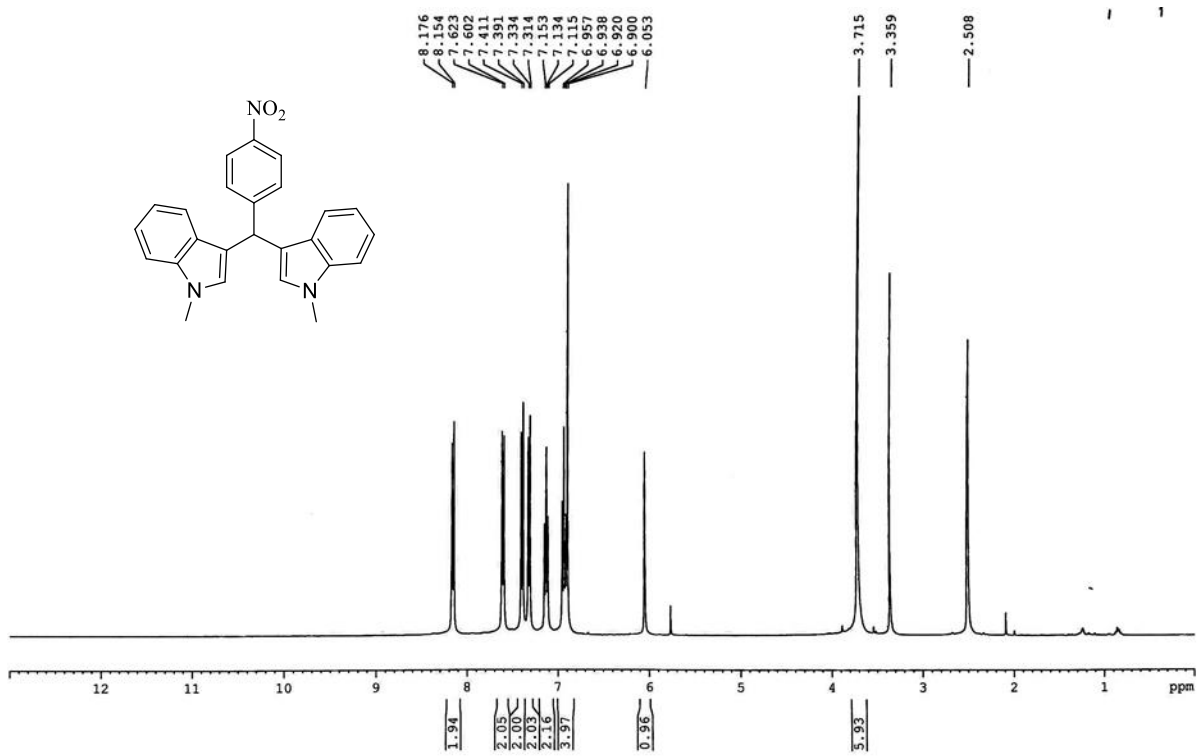
^{1}H NMR (400 MHz, DMSO-d_6) of **4j**



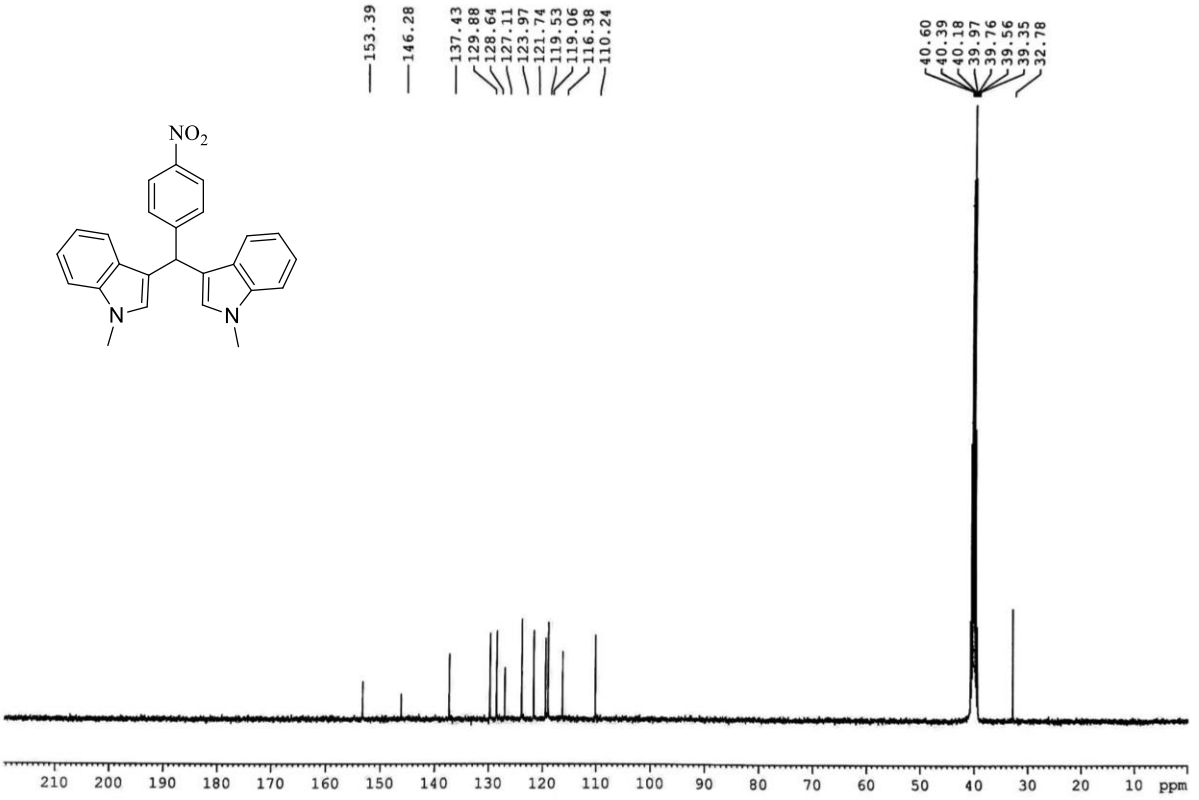
^{13}C NMR (100 MHz, DMSO-d_6) of **4j**



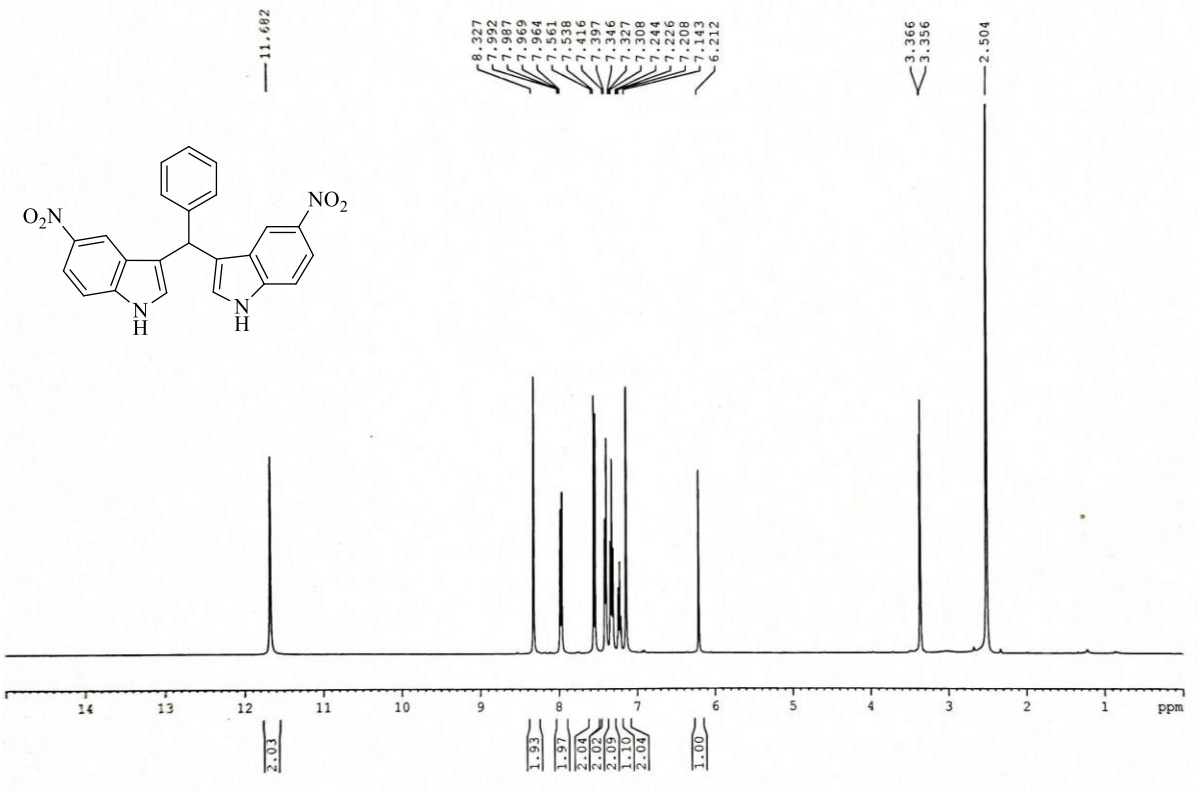
^{1}H NMR (400 MHz, DMSO-d_6) of **4k**



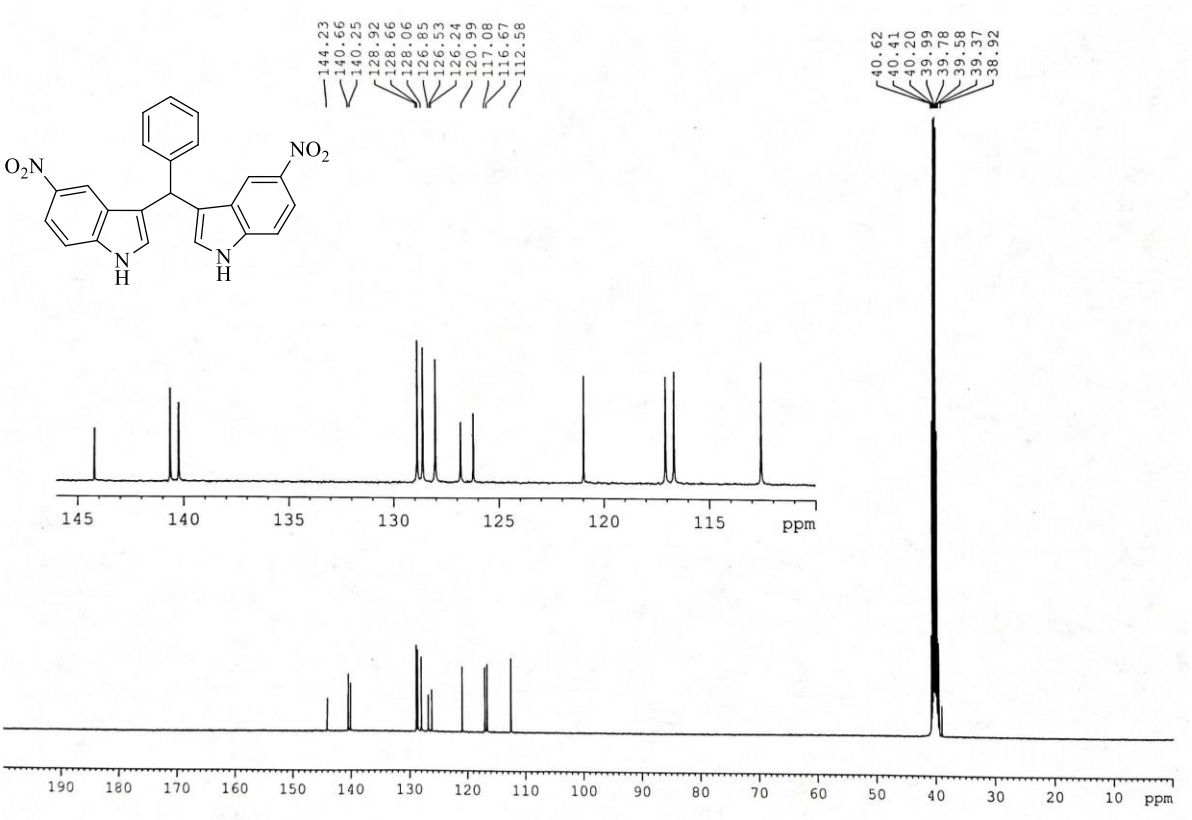
^{13}C NMR (100 MHz, DMSO-d_6) of **4k**



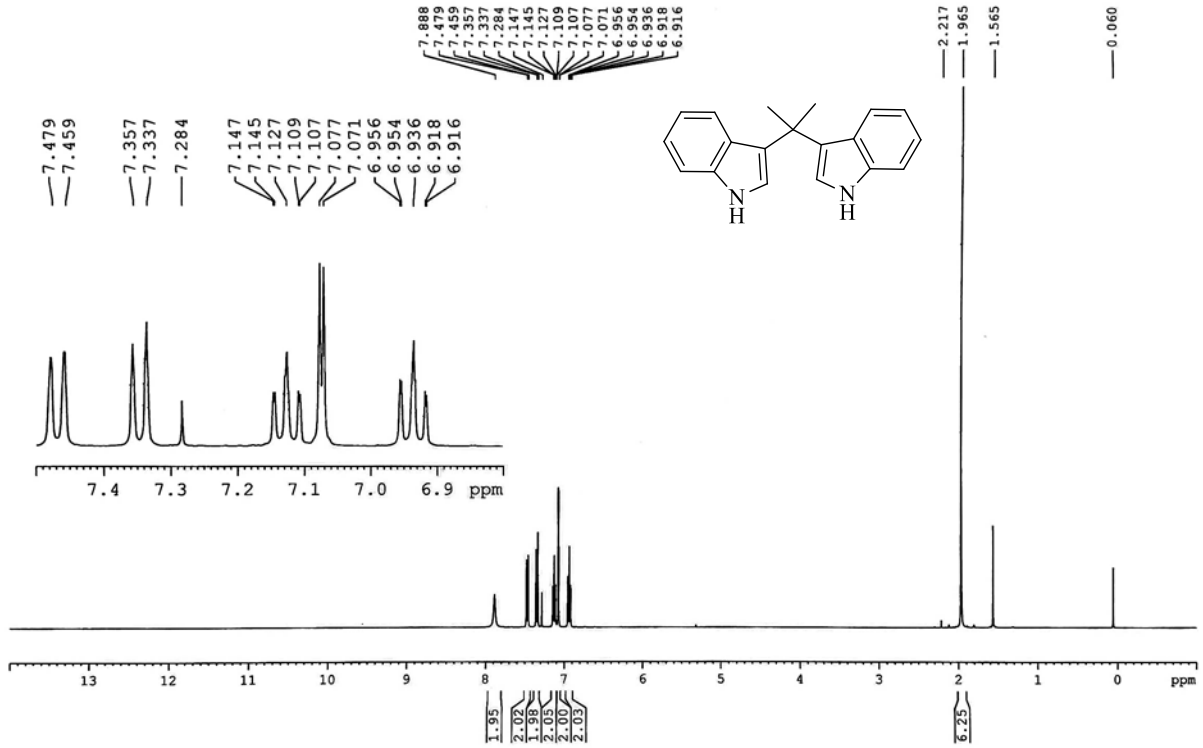
^{1}H NMR (400 MHz, DMSO-d$_6$) of **4l**



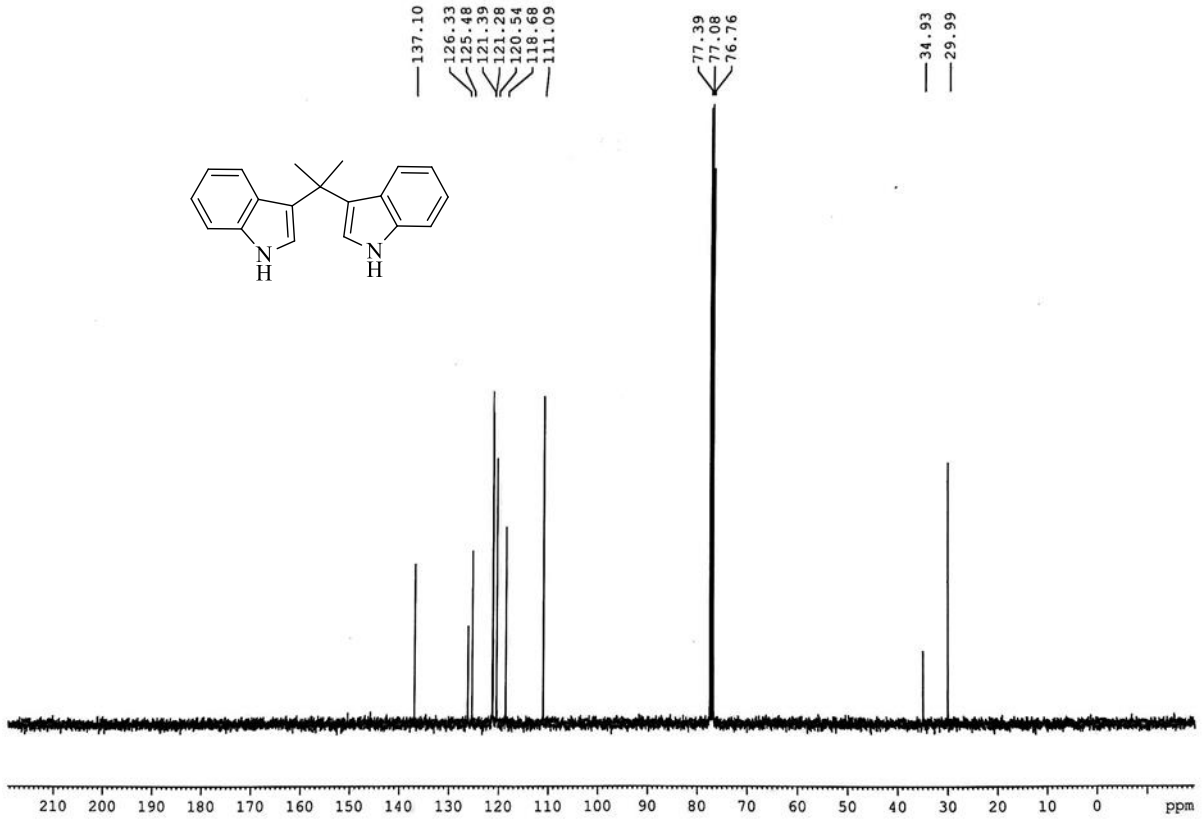
^{13}C NMR (100 MHz, DMSO-d$_6$) of **4l**



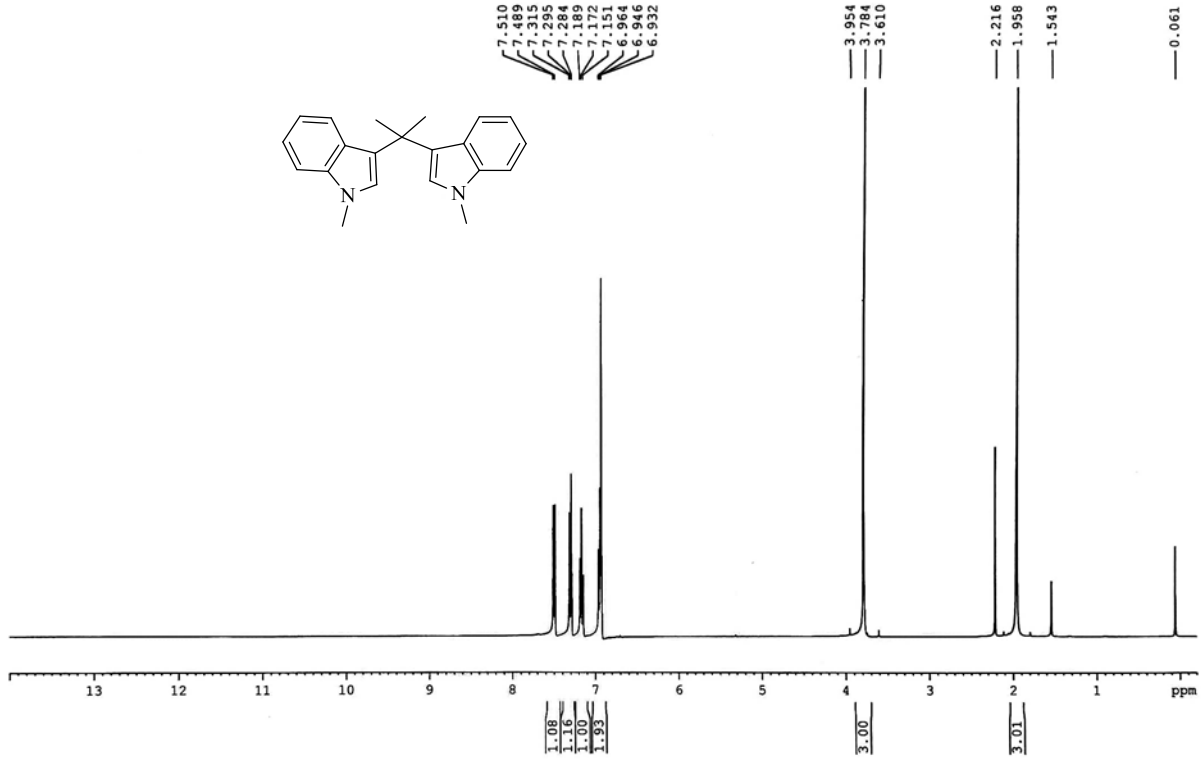
^{1}H NMR (400 MHz, $CDCl_3$) of **4m**



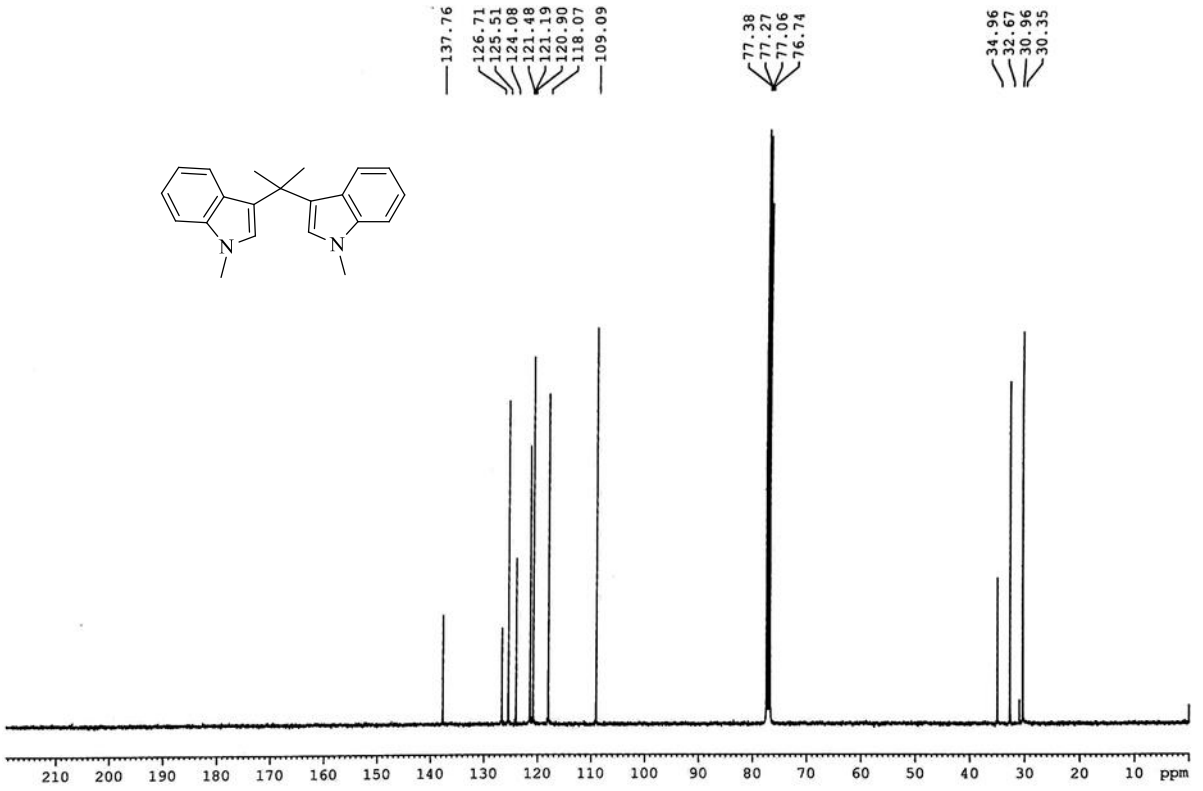
^{13}C NMR (100 MHz, $CDCl_3$) of **4m**



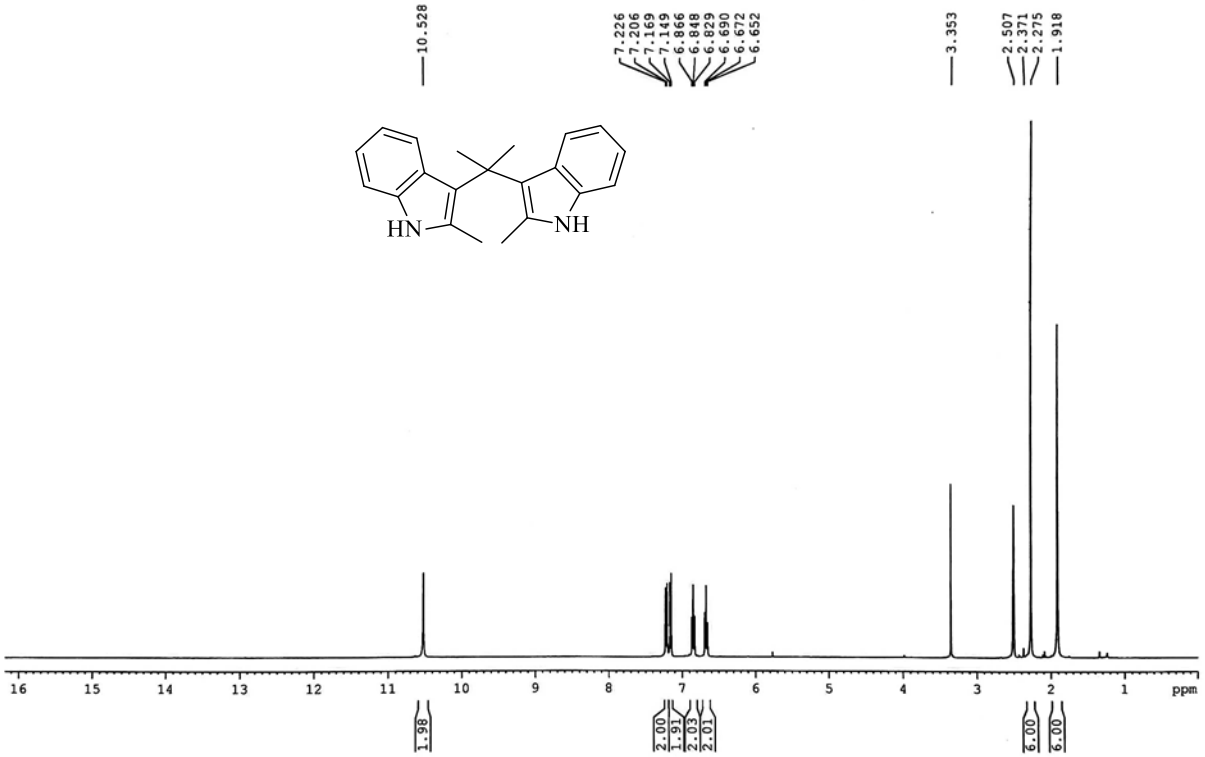
^{1}H NMR (400 MHz, $CDCl_3$) of **4n**



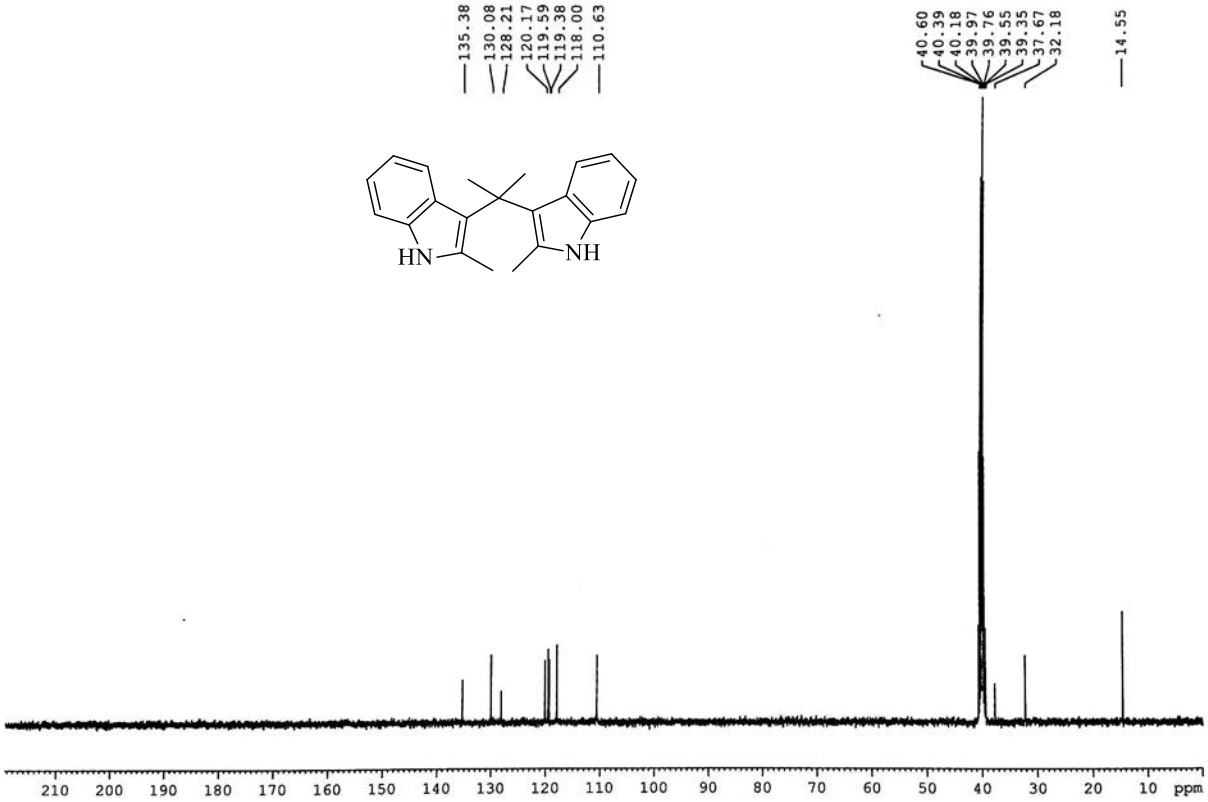
^{13}C NMR (100 MHz, $CDCl_3$) of **4n**



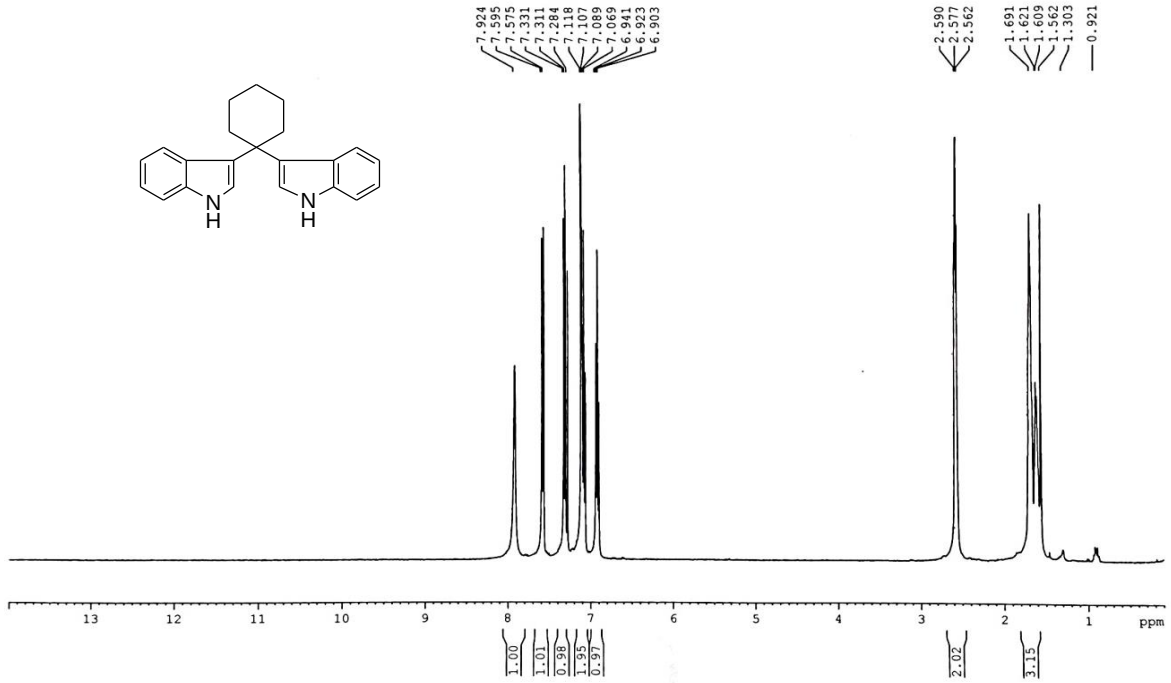
^{1}H NMR (400 MHz, DMSO-d_6) of **4o**



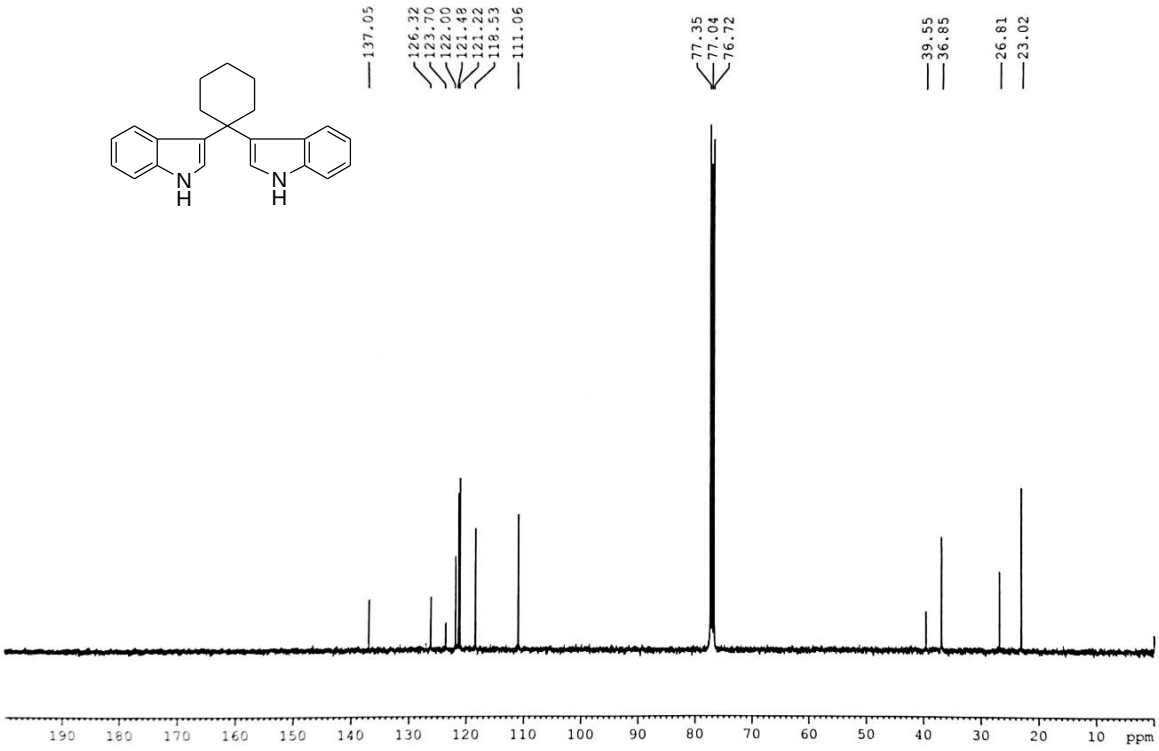
^{13}C NMR (100 MHz, DMSO-d_6) of **4o**



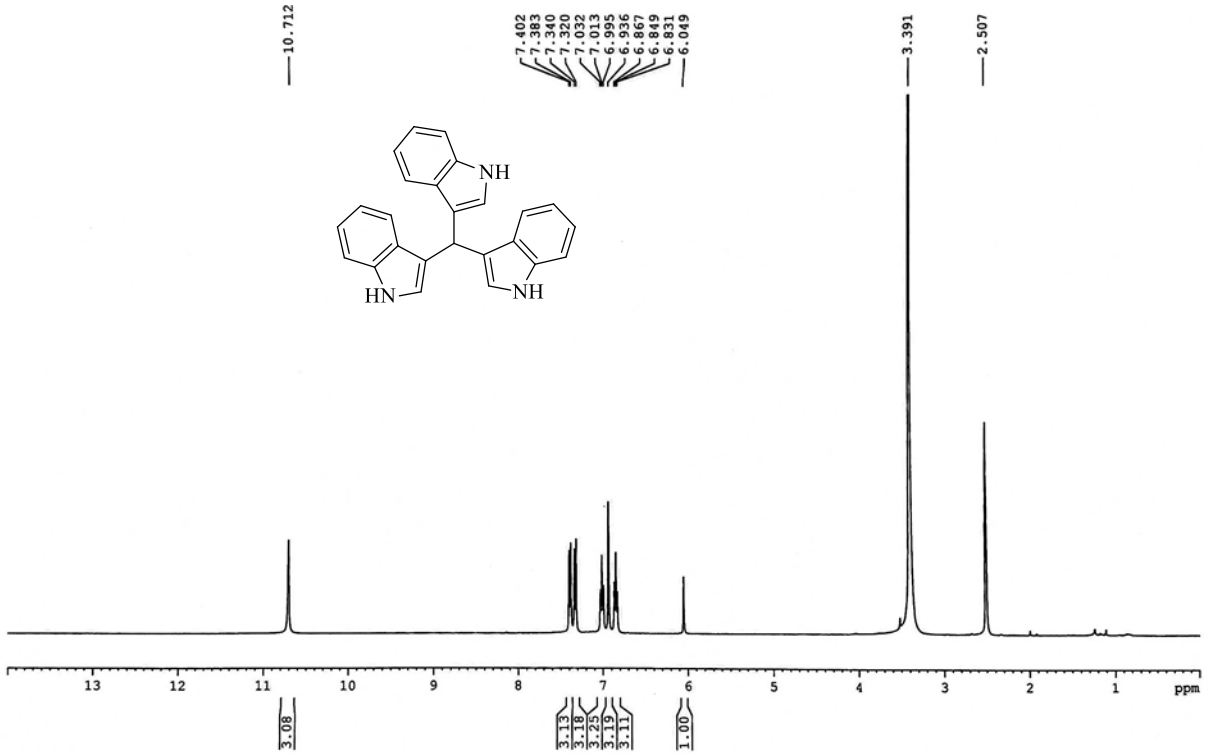
^{1}H NMR (400 MHz, $CDCl_3$) of **4p**



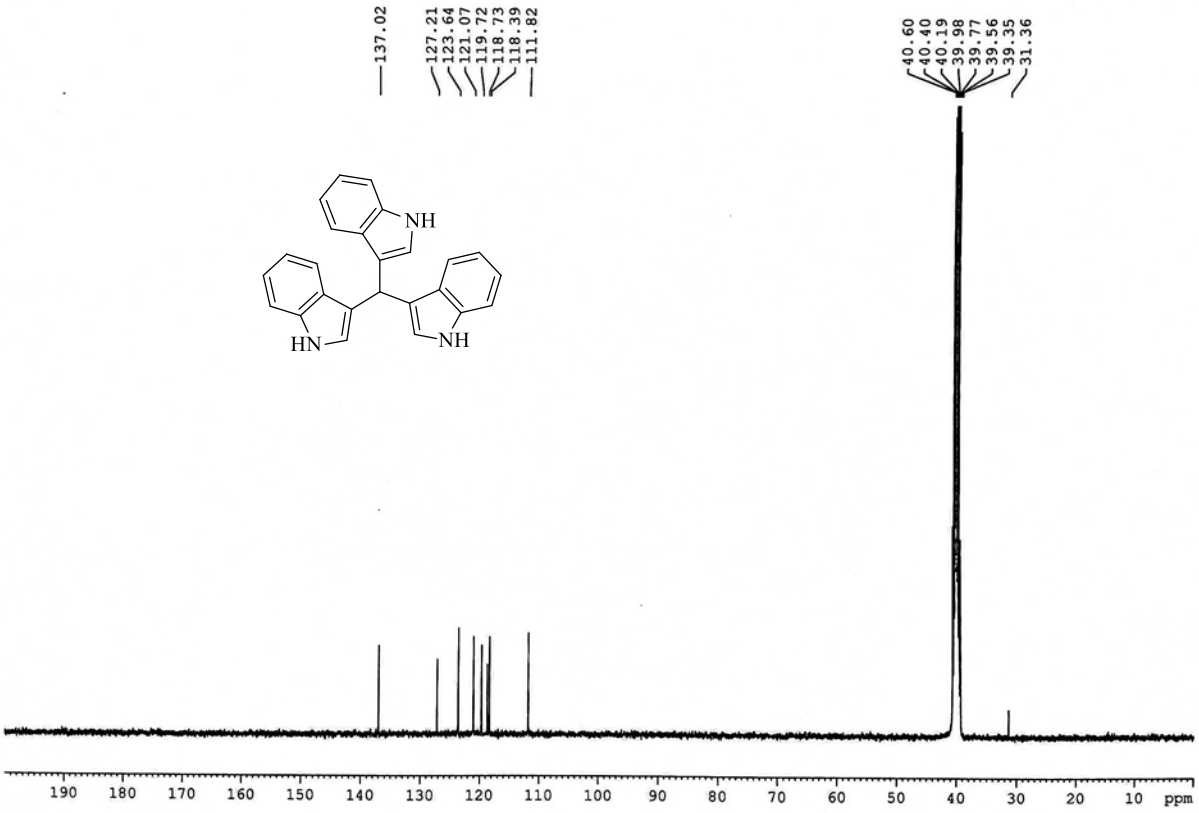
^{13}C NMR (100 MHz, $CDCl_3$) of **4p**



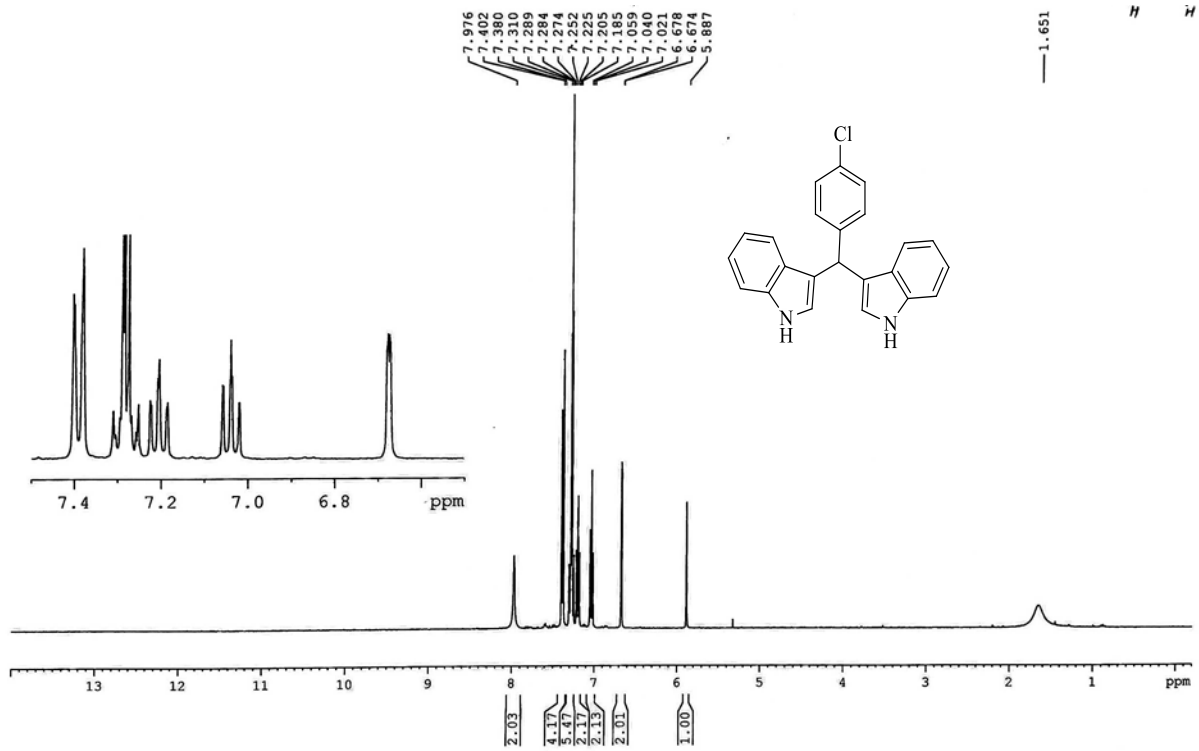
^{1}H NMR (400 MHz, DMSO-d_6) of **4q**



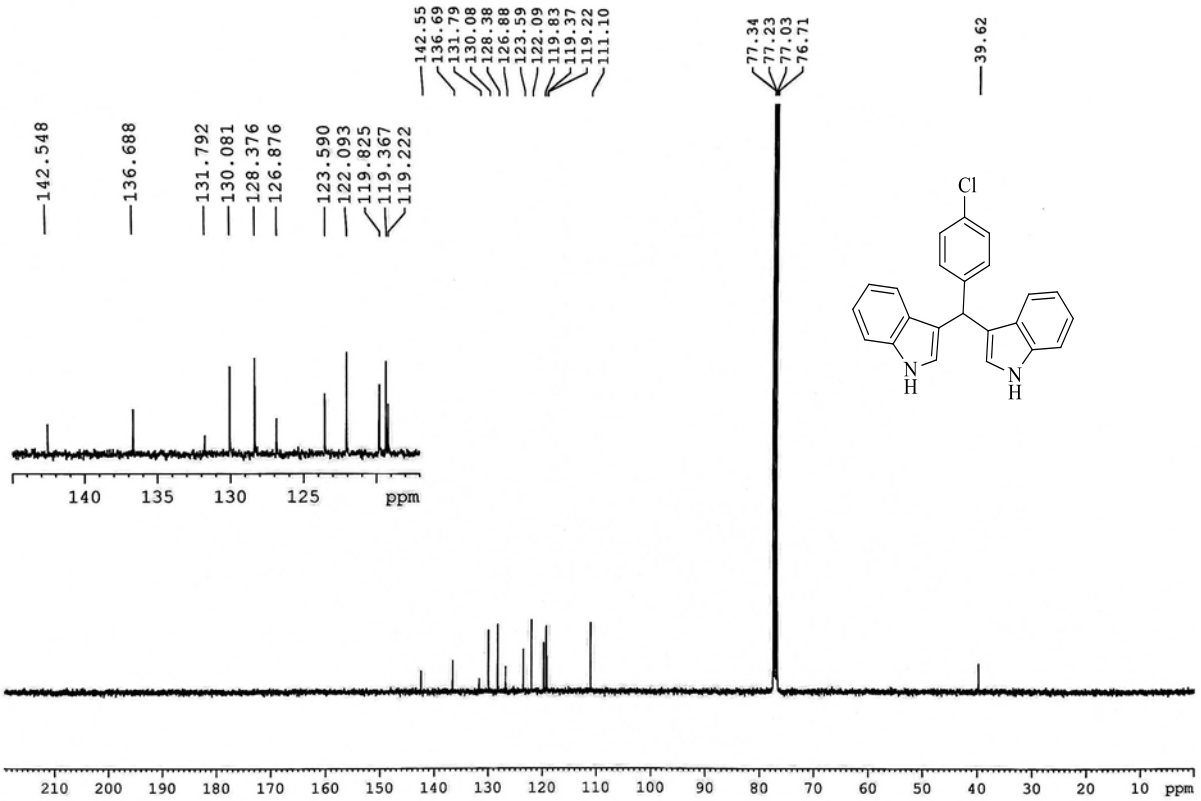
^{13}C NMR (100 MHz, DMSO-d_6) of **4q**



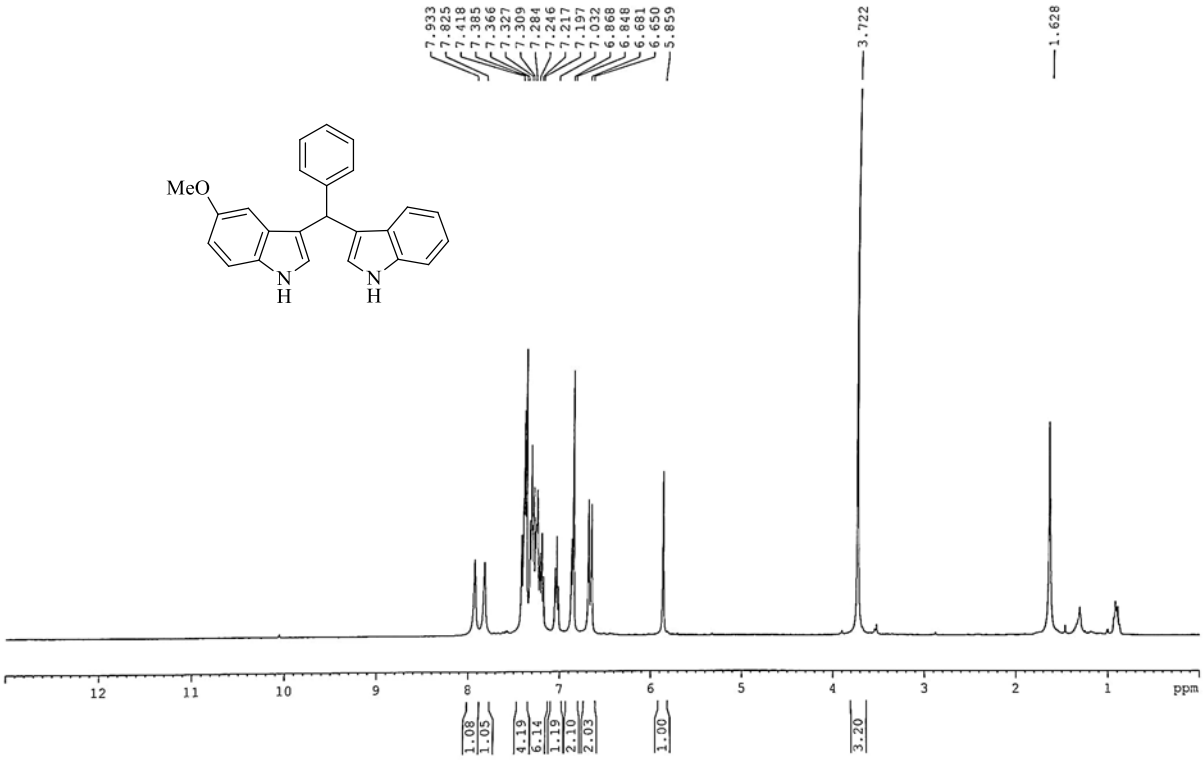
^{1}H NMR (400 MHz, $CDCl_3$) of **4r**



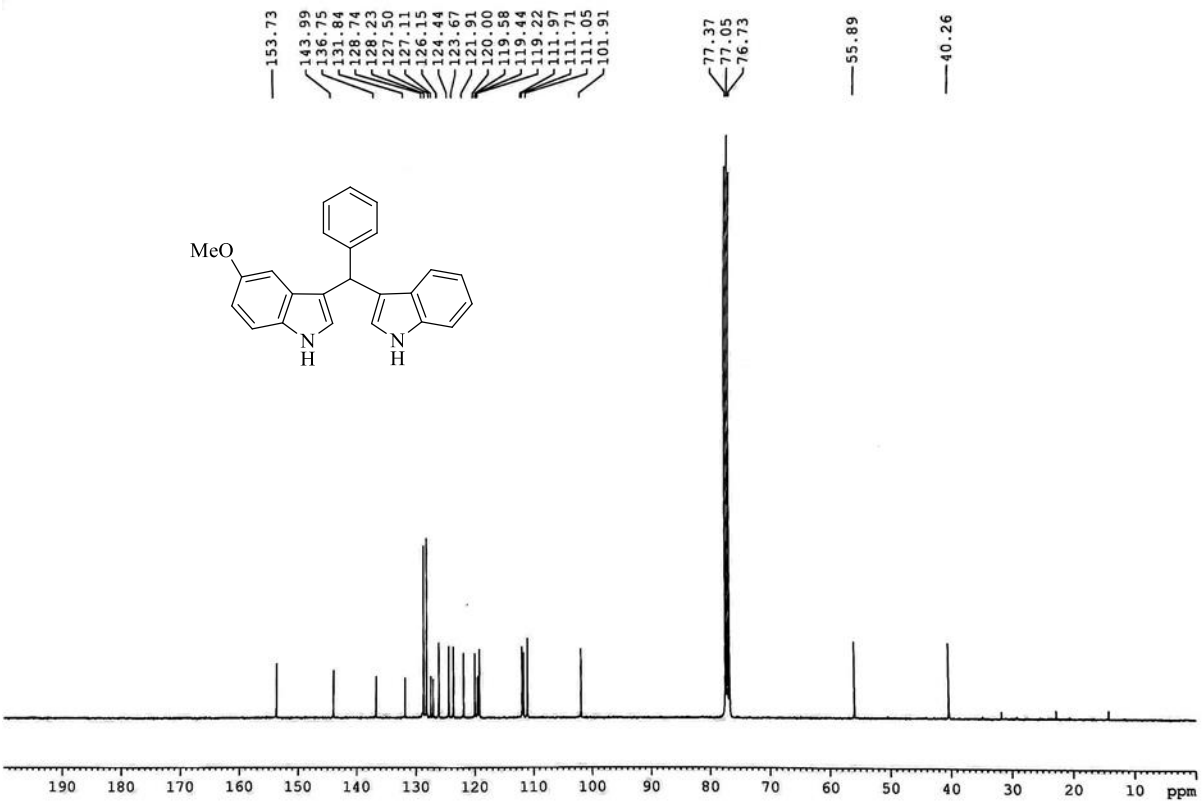
^{13}C NMR (100 MHz, $CDCl_3$) of **4r**



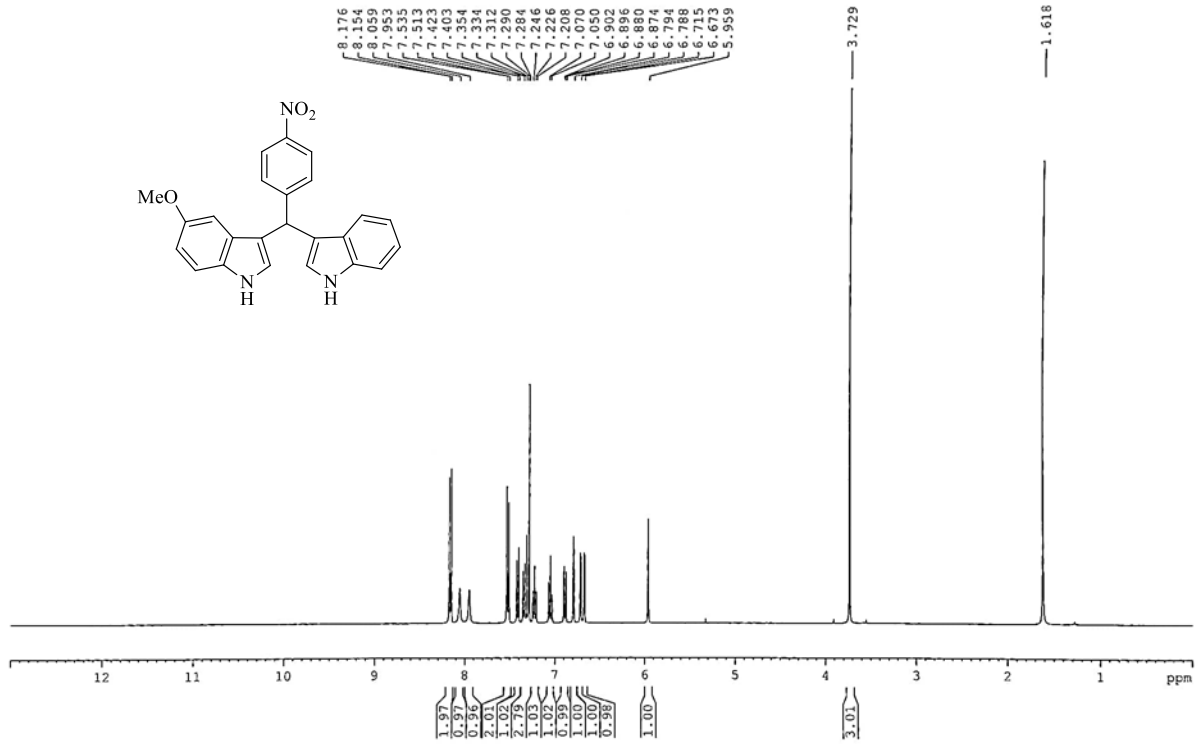
^{1}H NMR (400 MHz, $CDCl_3$) of **4u**



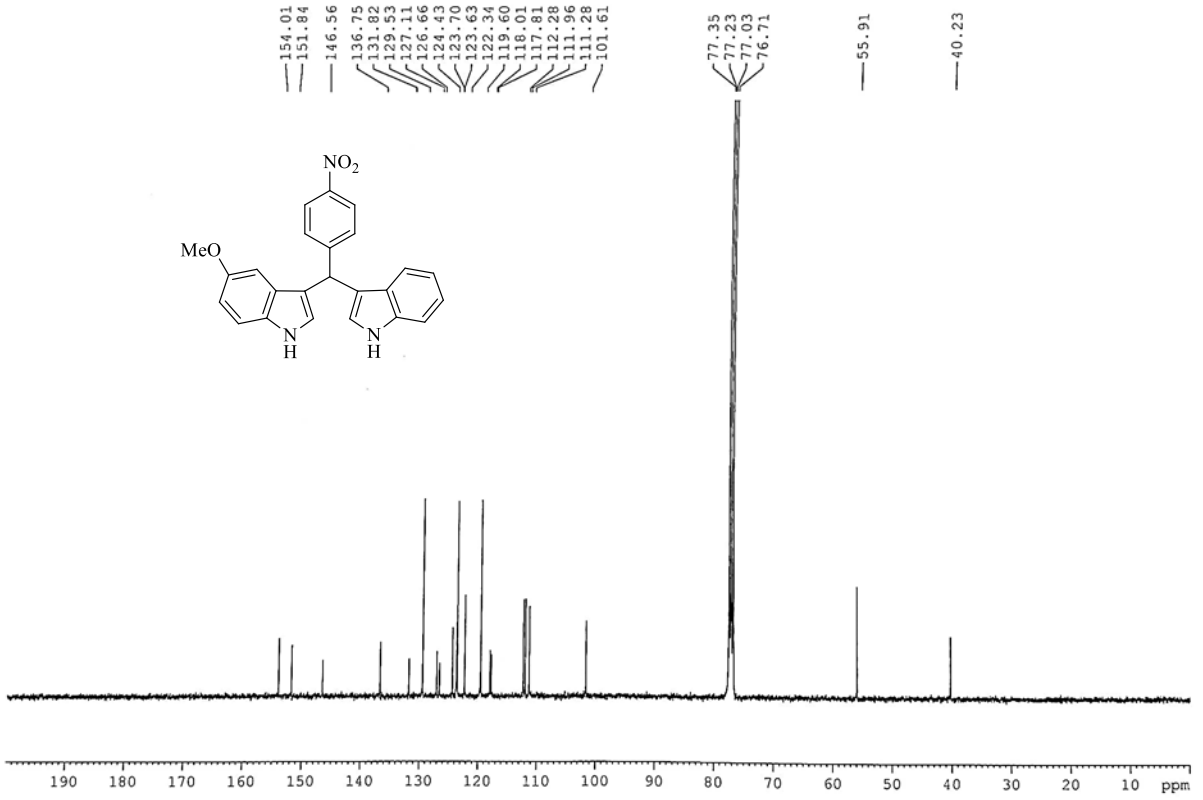
^{13}C NMR (100 MHz, $CDCl_3$) of **4u**



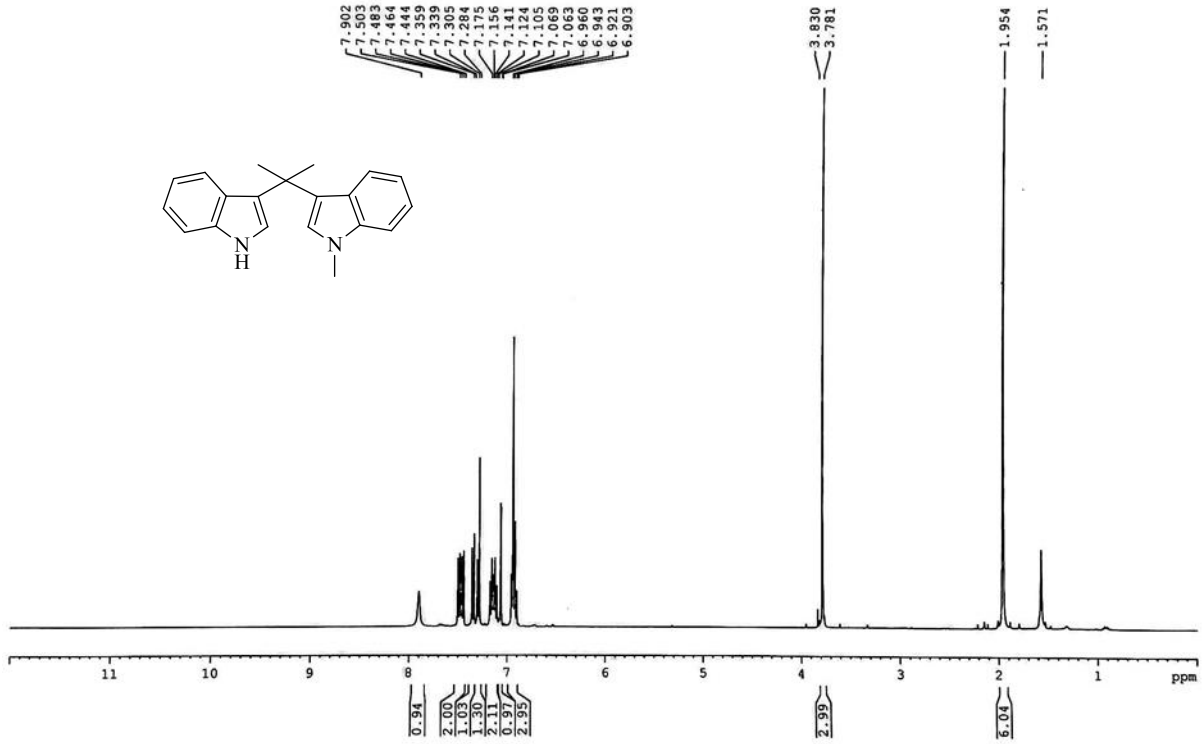
^{1}H NMR (400 MHz, $CDCl_3$) of **4v**



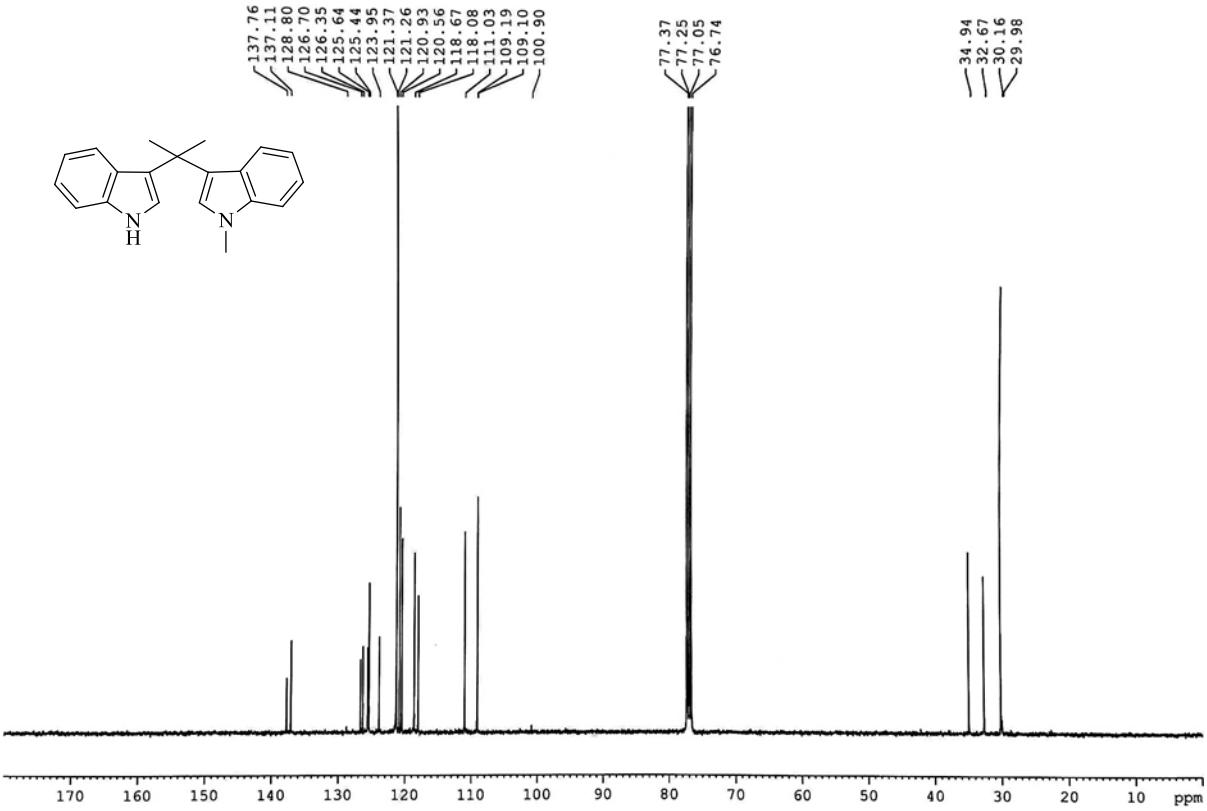
^{13}C NMR (100 MHz, $CDCl_3$) of **4v**



^{1}H NMR (400 MHz, $CDCl_3$) of **4x**

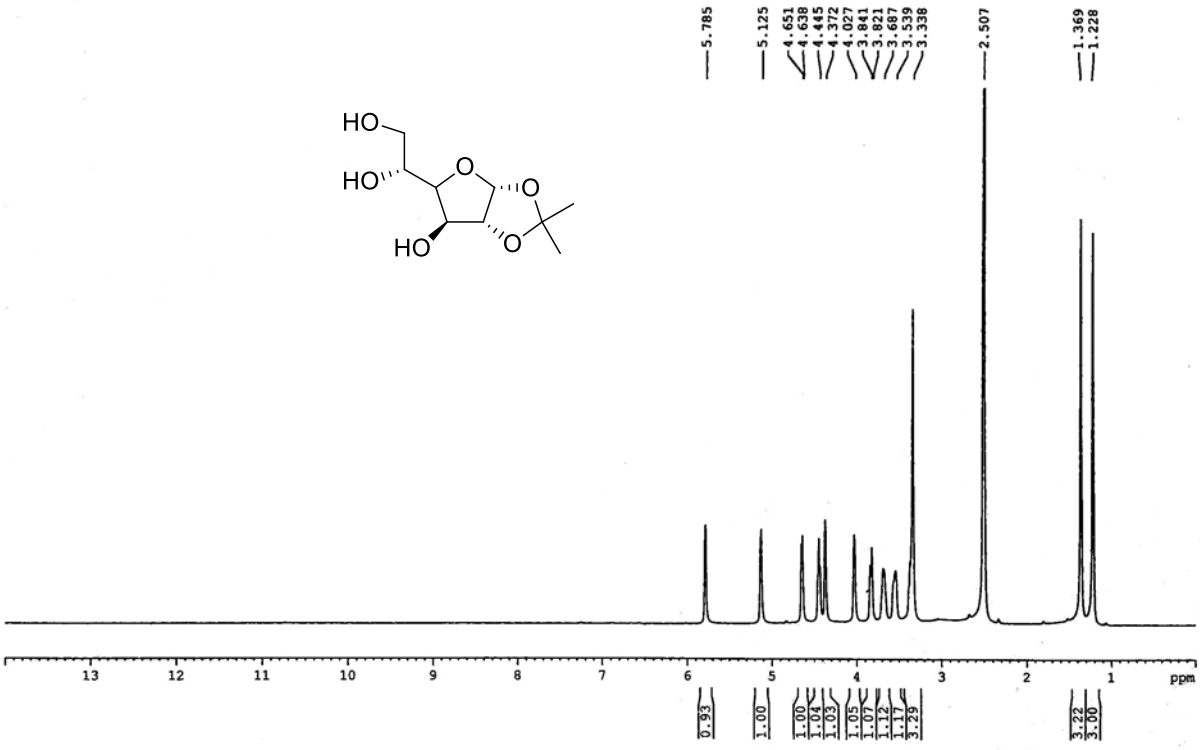


^{13}C NMR (100 MHz, $CDCl_3$) of **4x**

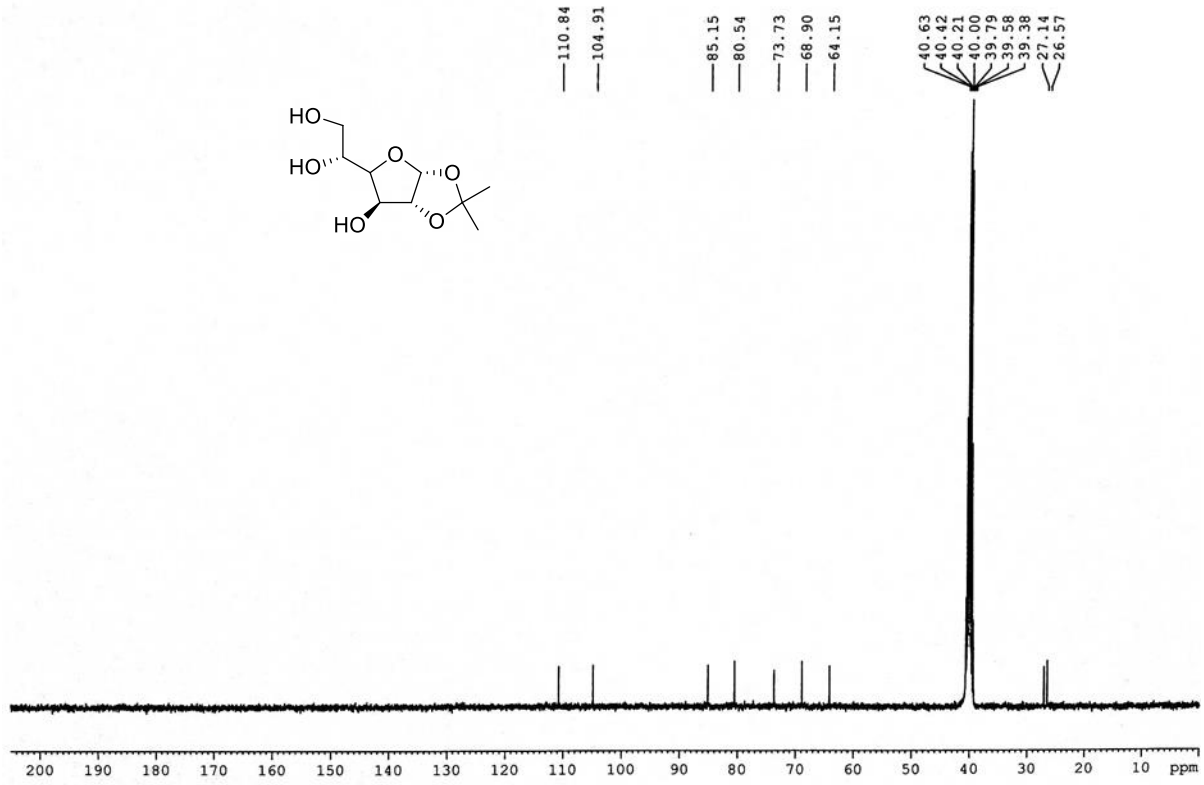


^{1}H and ^{13} NMR spectra of 5

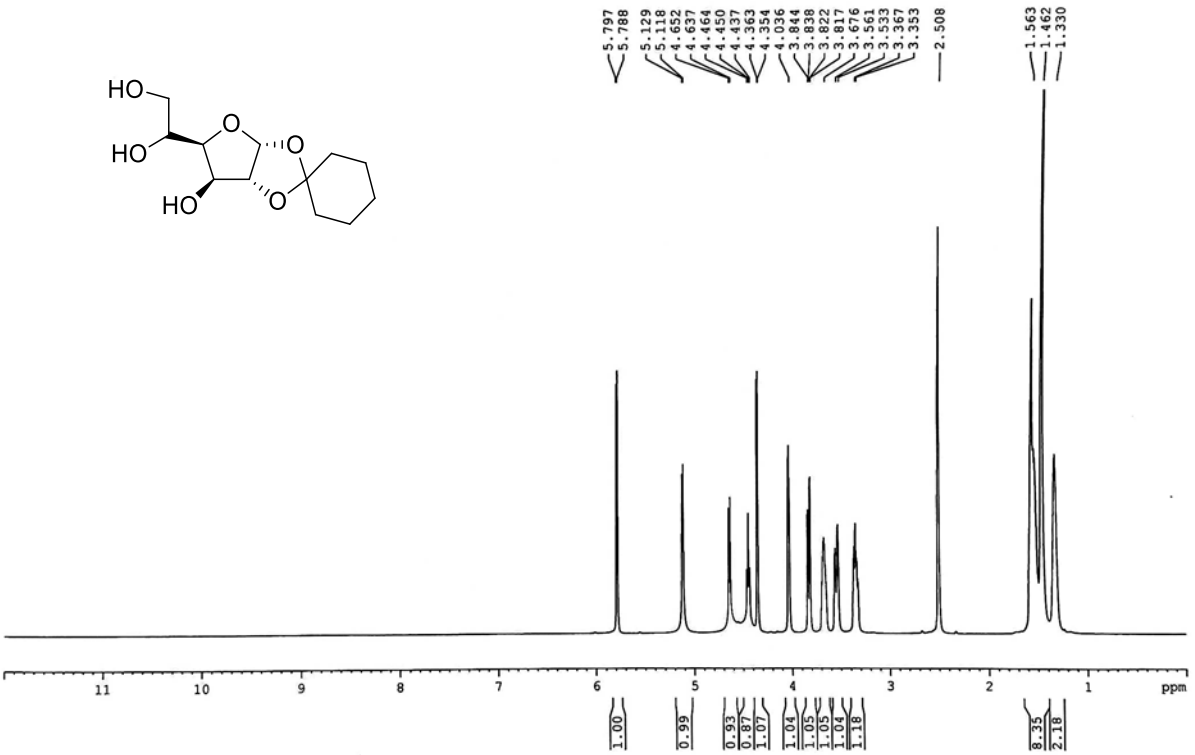
^{1}H NMR (400 MHz, DMSO-d_6) of **5a**



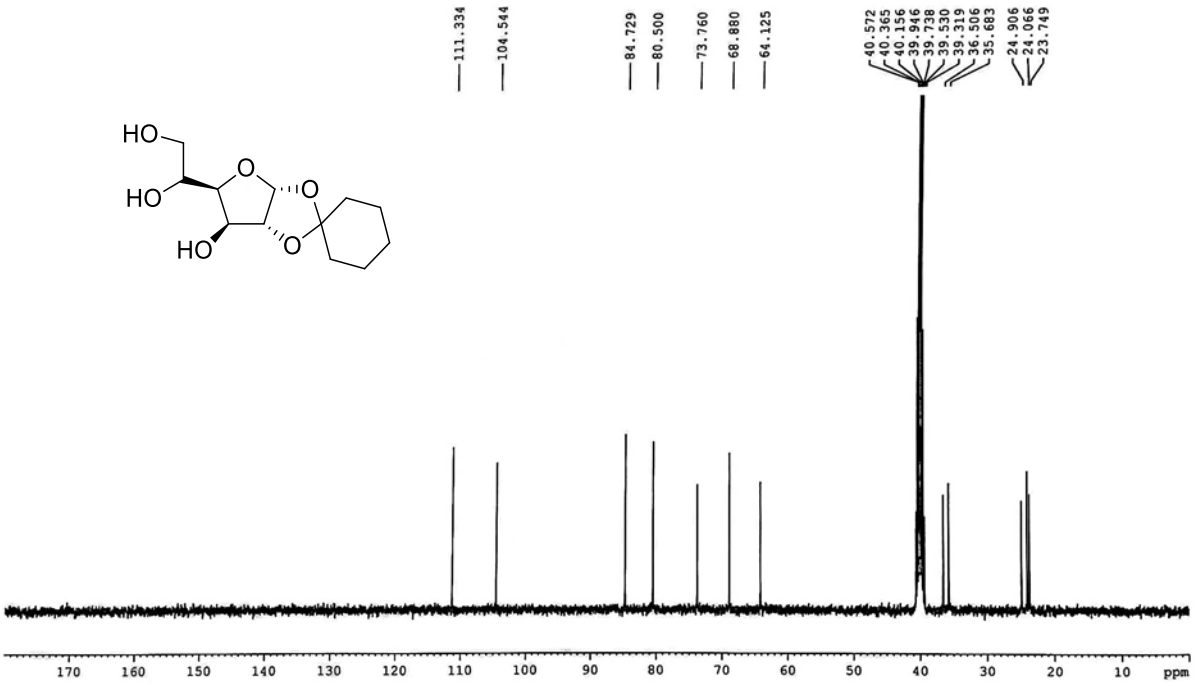
^{13}C NMR (100 MHz, DMSO-d_6) of **5a**



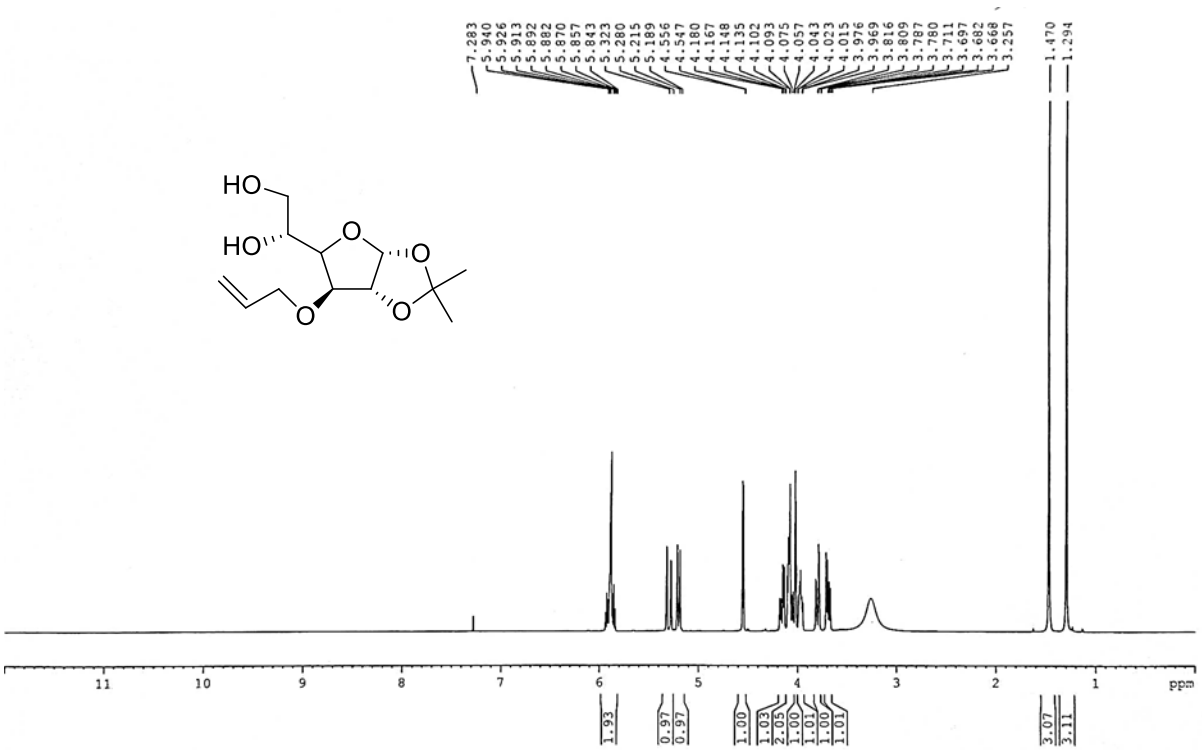
^{1}H NMR (400 MHz, DMSO-d_6) of **5b**



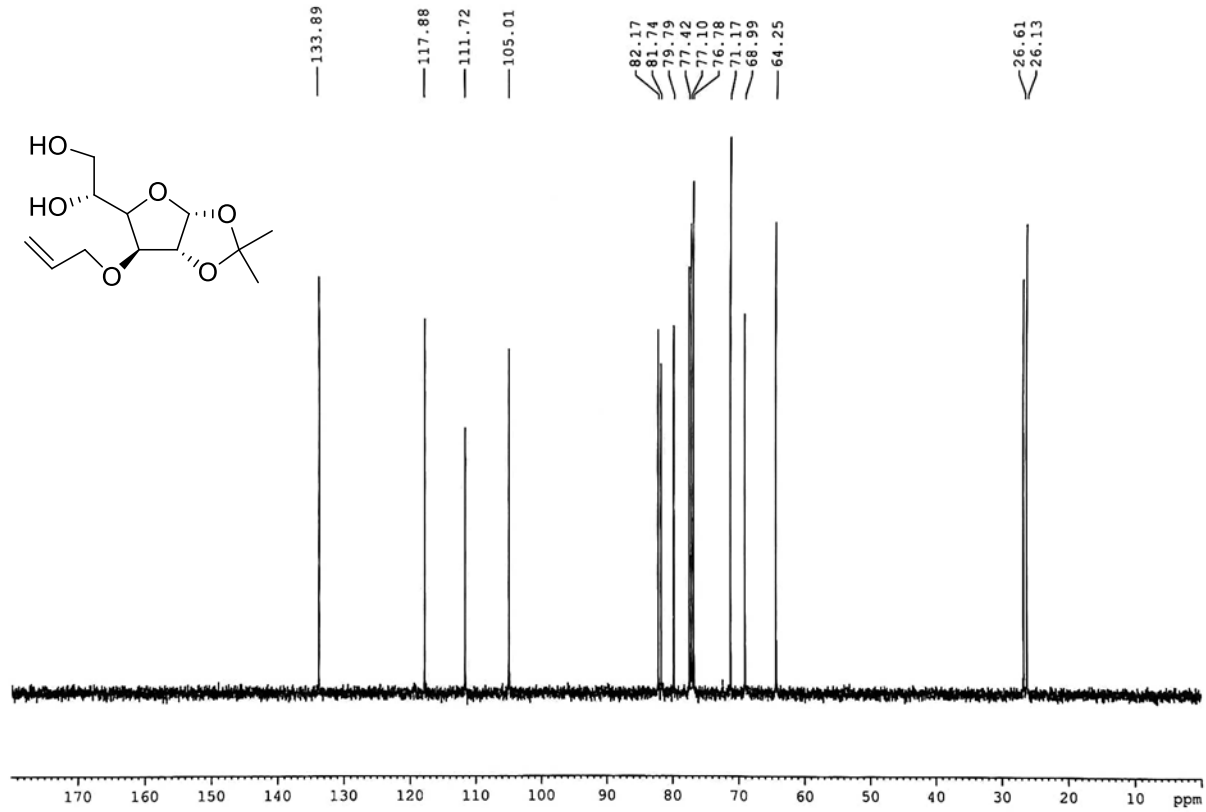
^{13}C NMR (100 MHz, DMSO-d_6) of **5b**



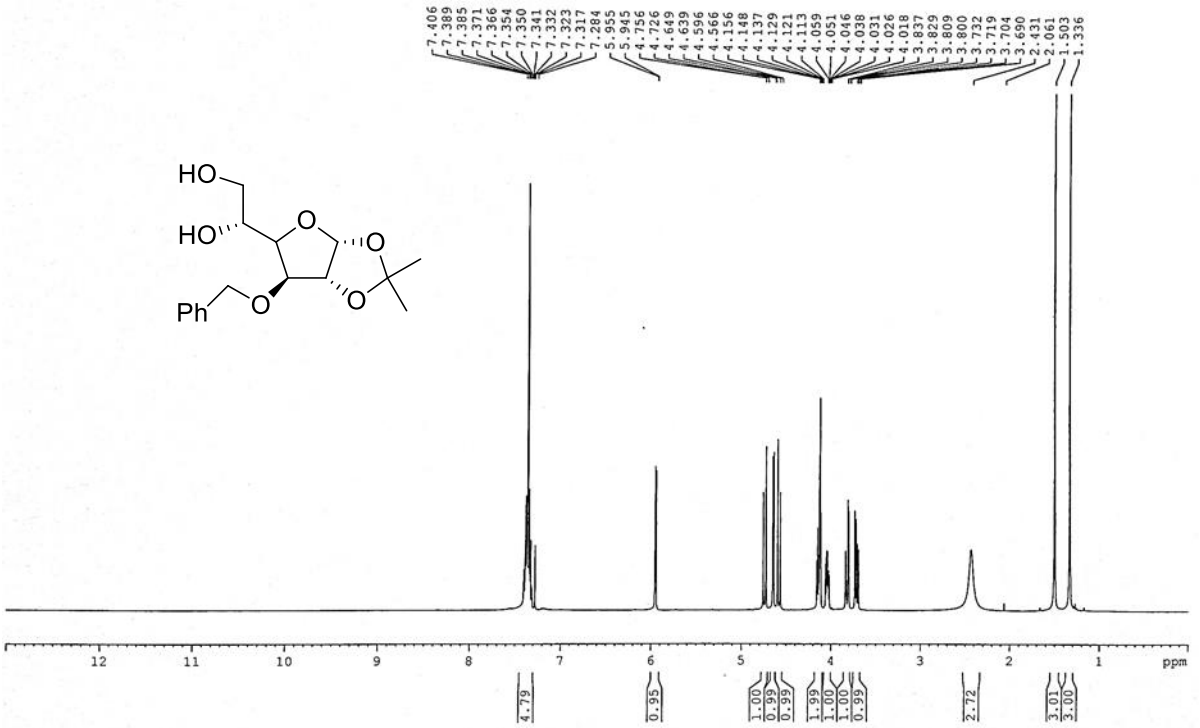
^{1}H NMR (400 MHz, $CDCl_3$) of **5c**



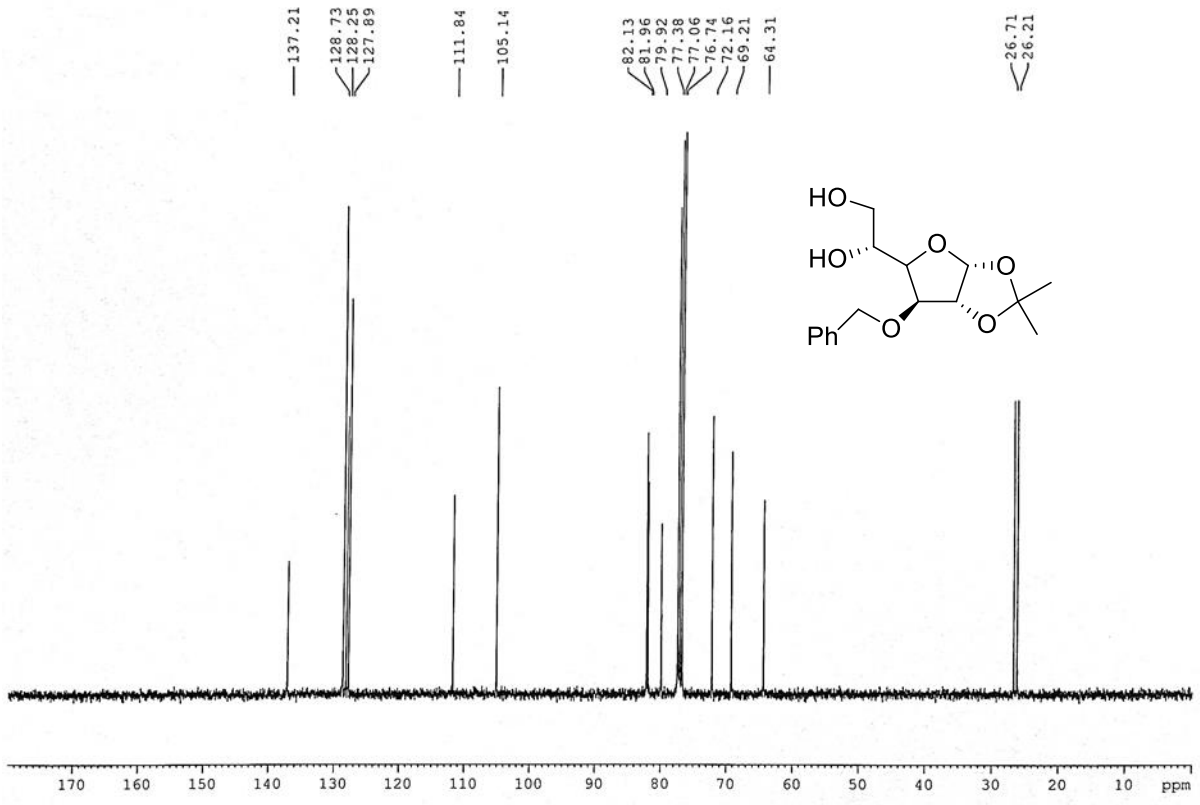
^{13}C NMR (100 MHz, $CDCl_3$) of **5c**



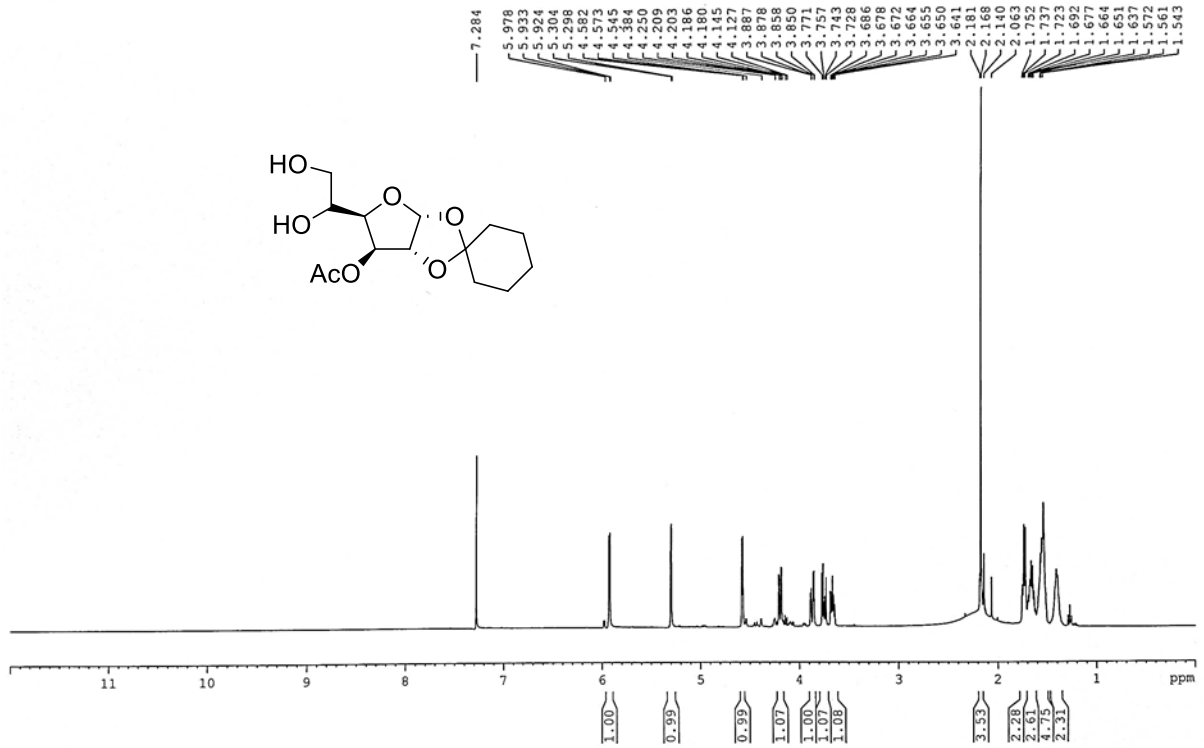
^{1}H NMR (400 MHz, $CDCl_3$) of **5d**



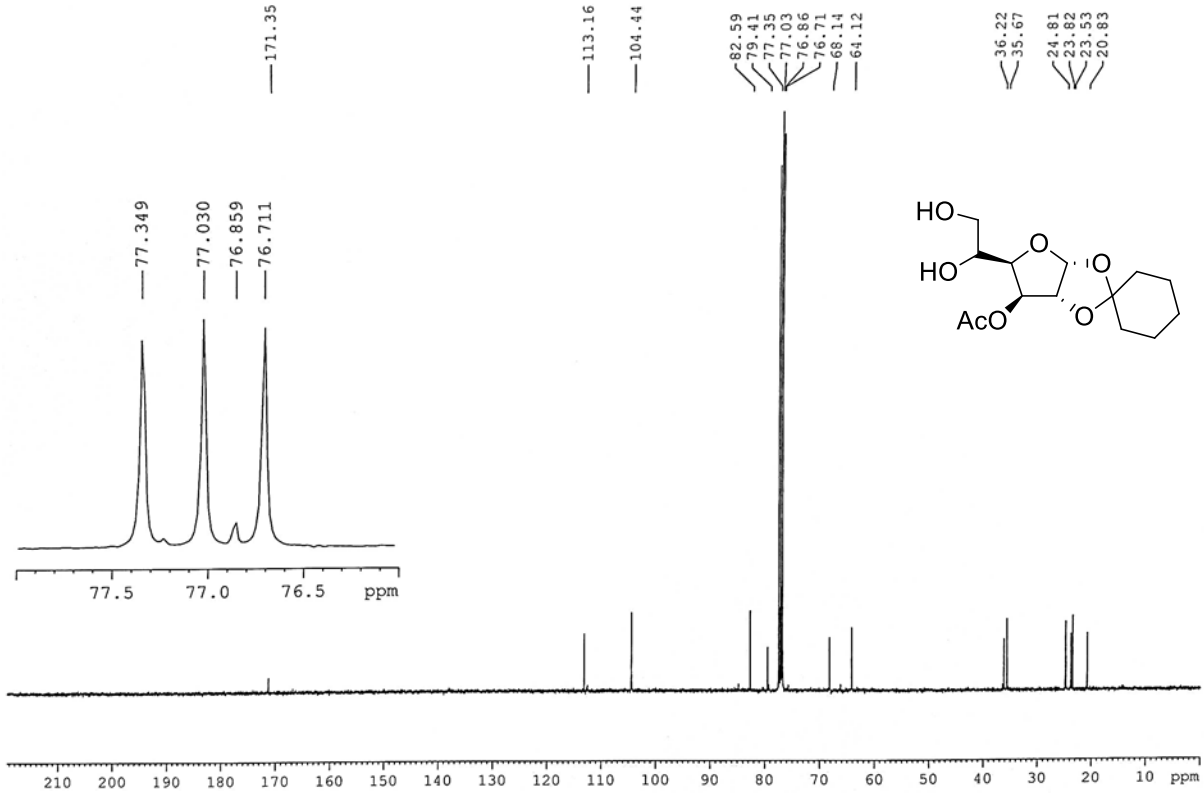
^{13}C NMR (100 MHz, $CDCl_3$) of **5d**



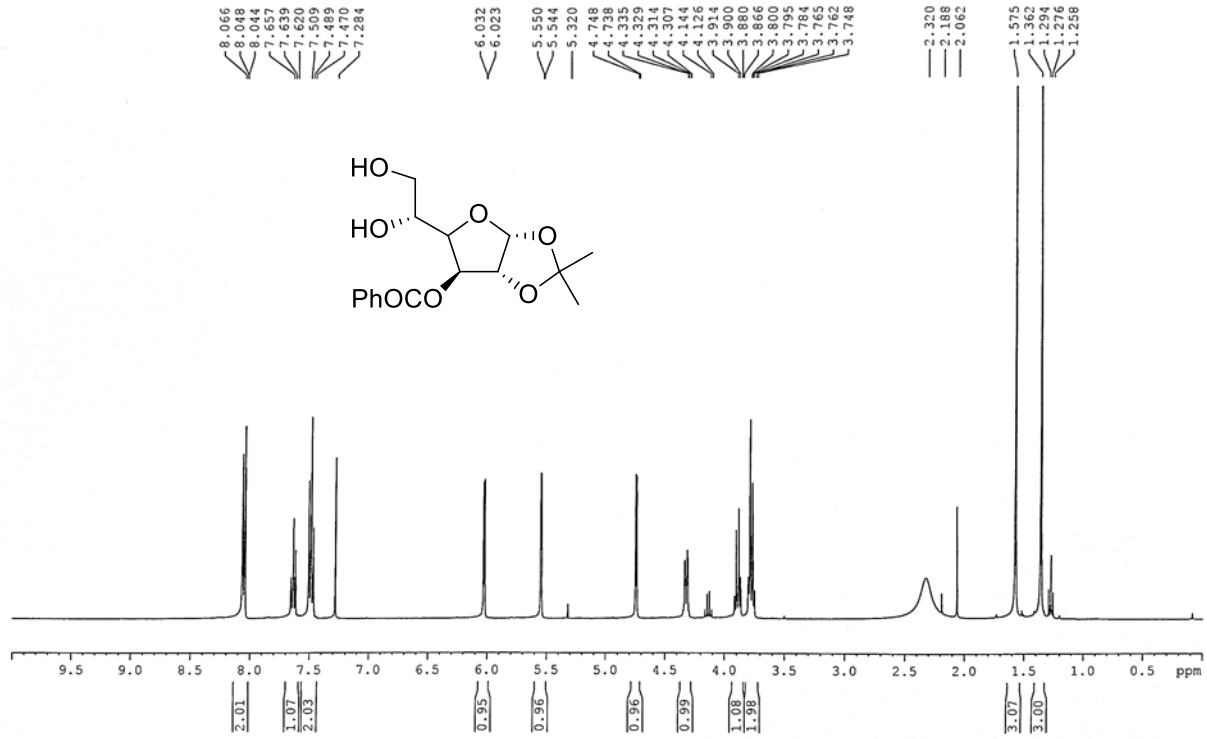
^{1}H NMR (400 MHz, $CDCl_3$) of **5e**



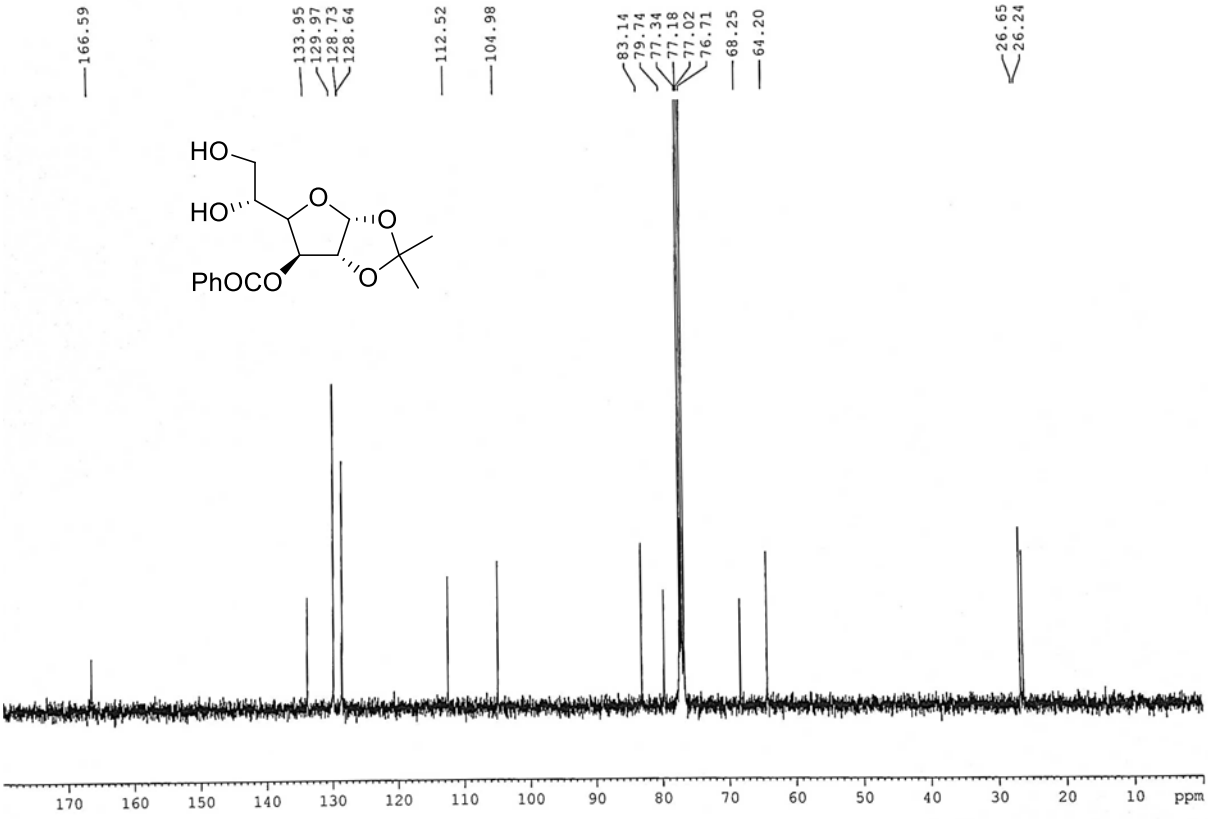
^{13}C NMR (100 MHz, $CDCl_3$) of **5e**



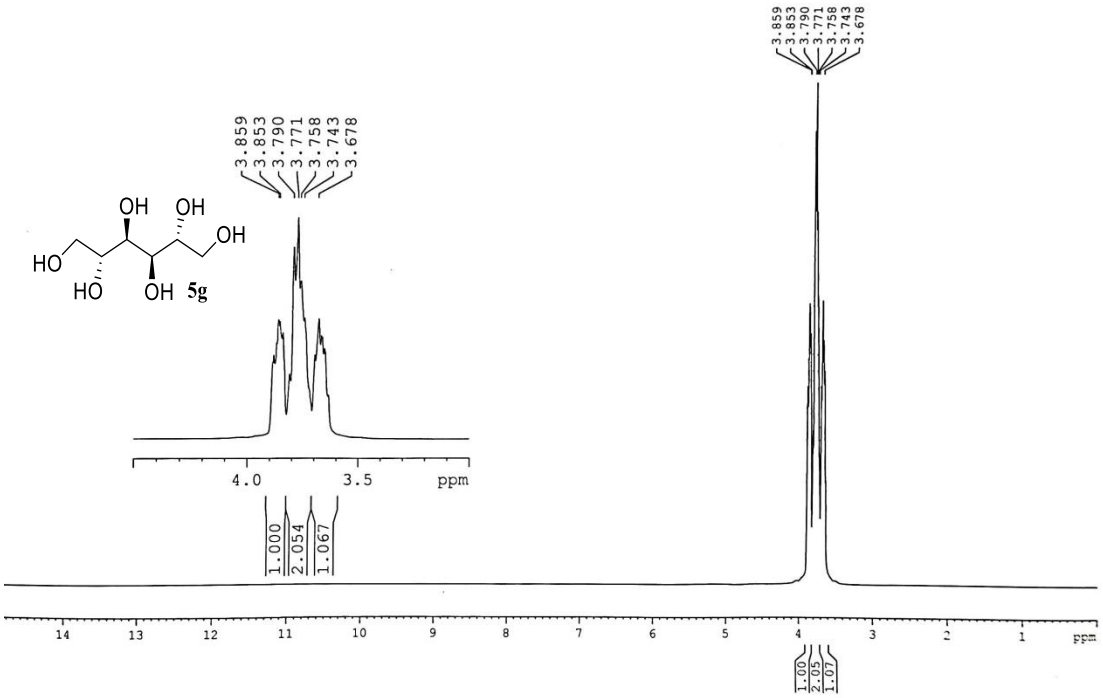
^{1}H NMR (400 MHz, $CDCl_3$) of **5f**



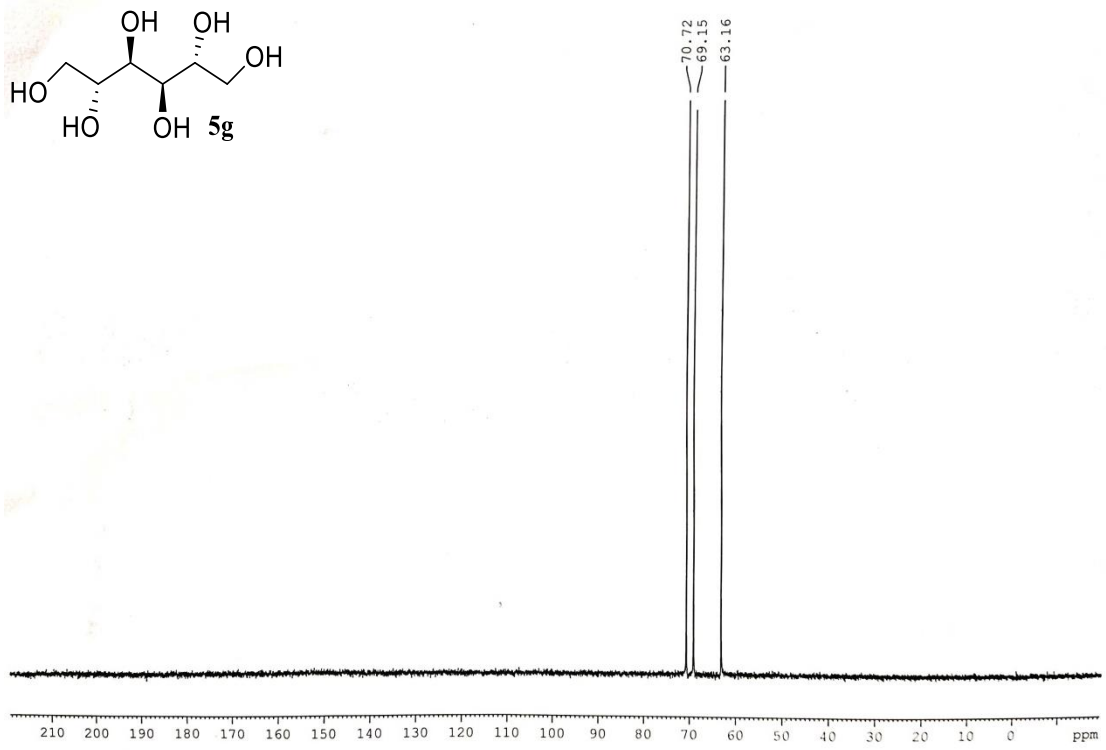
^{13}C NMR (100 MHz, $CDCl_3$) of **5f**



^{1}H NMR (400 MHz, D_2O) of **5g**

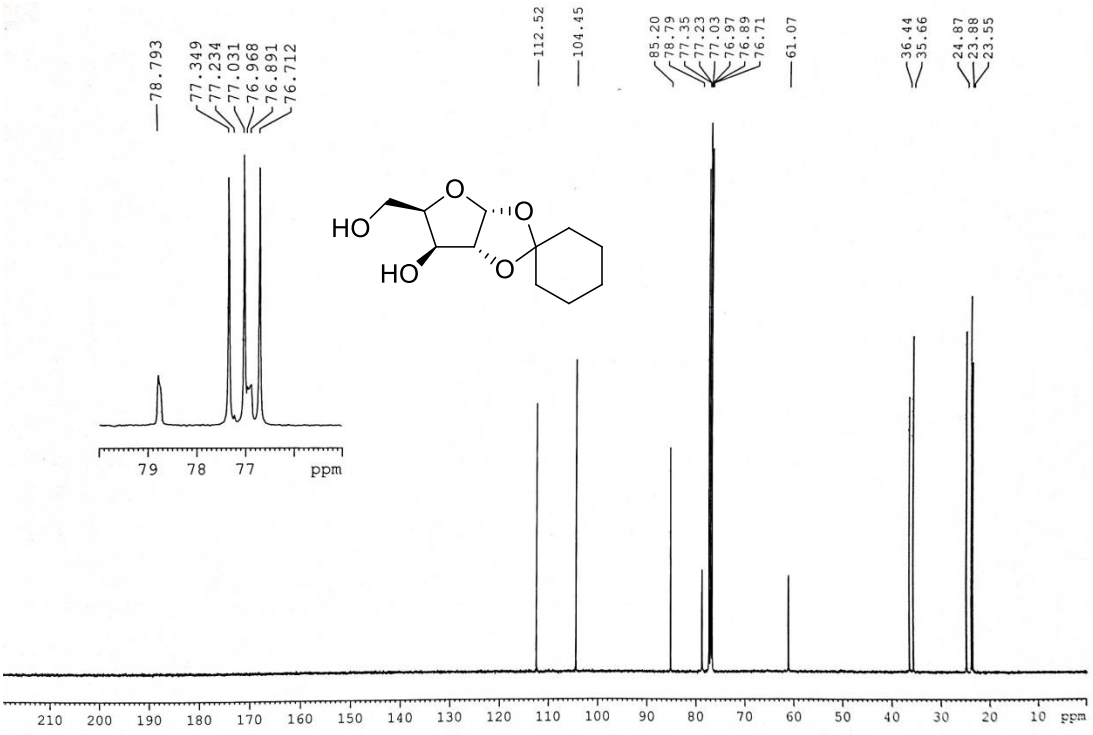


^{13}C NMR (100 MHz, D_2O) of **5g**

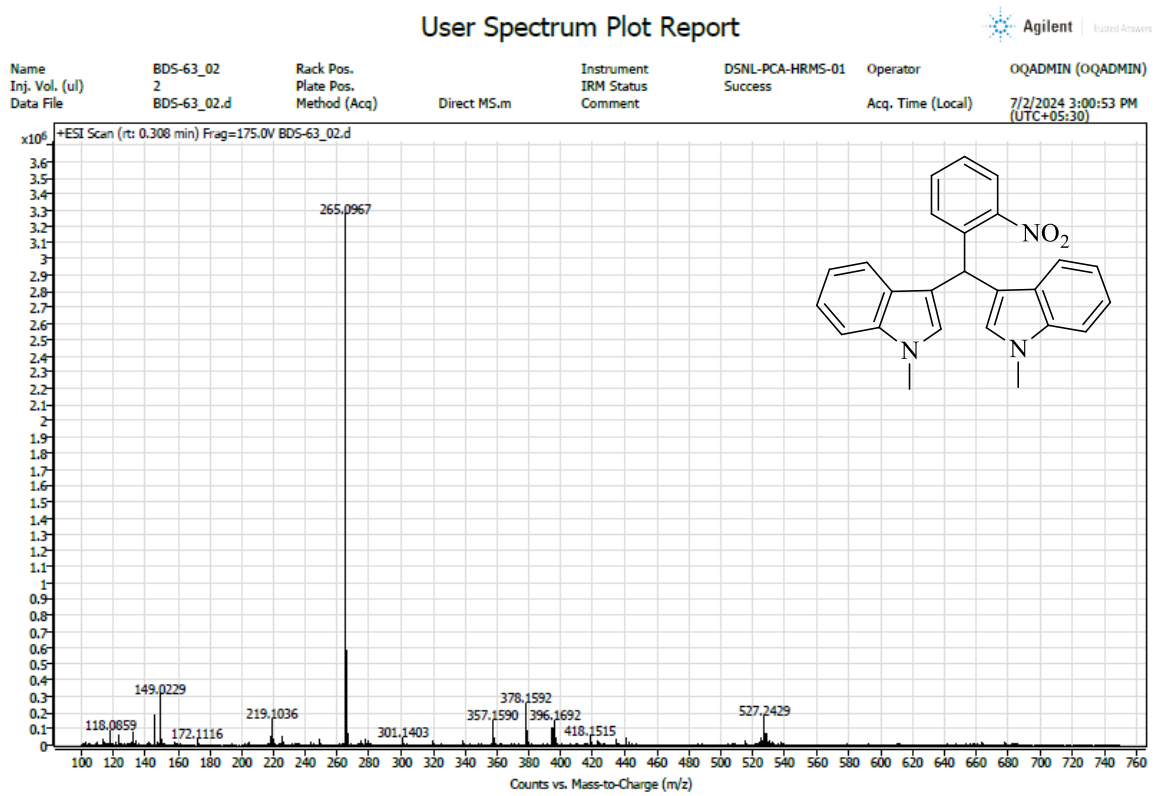


^{1}H NMR (400 MHz, $CDCl_3$) of **5h**

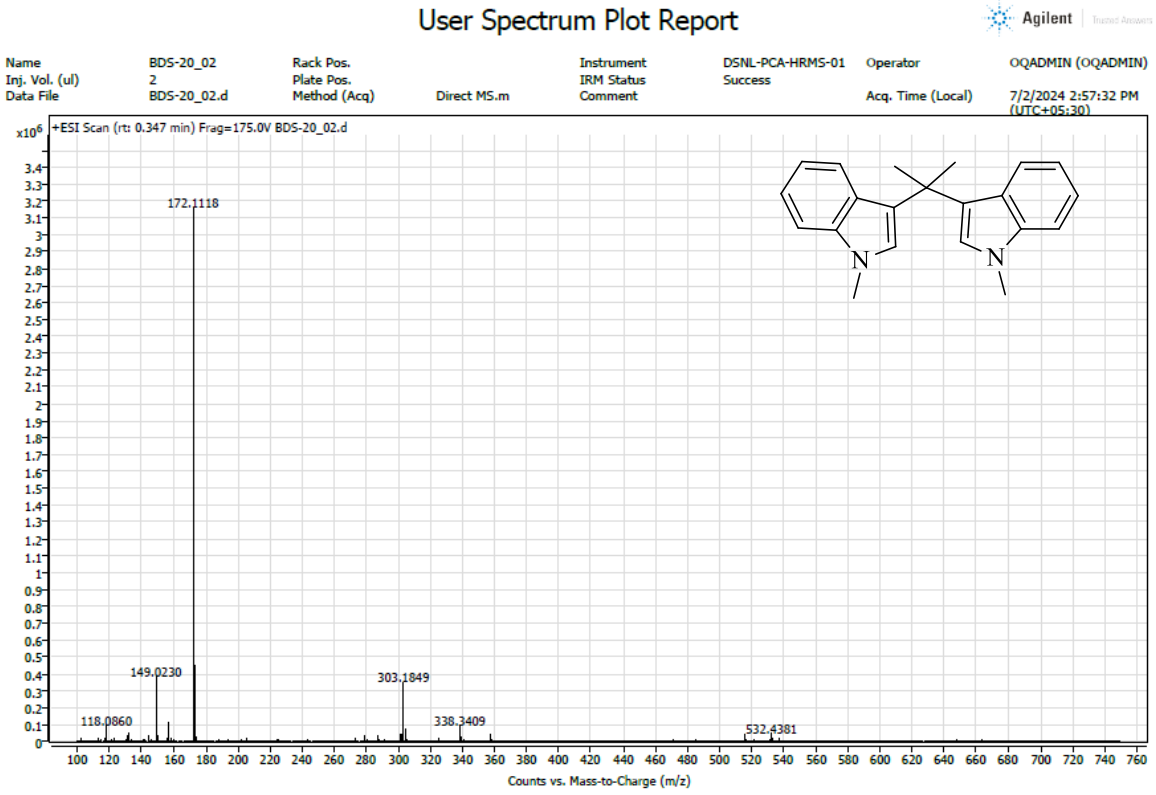
^{13}C NMR (100 MHz, $CDCl_3$) of **5h**



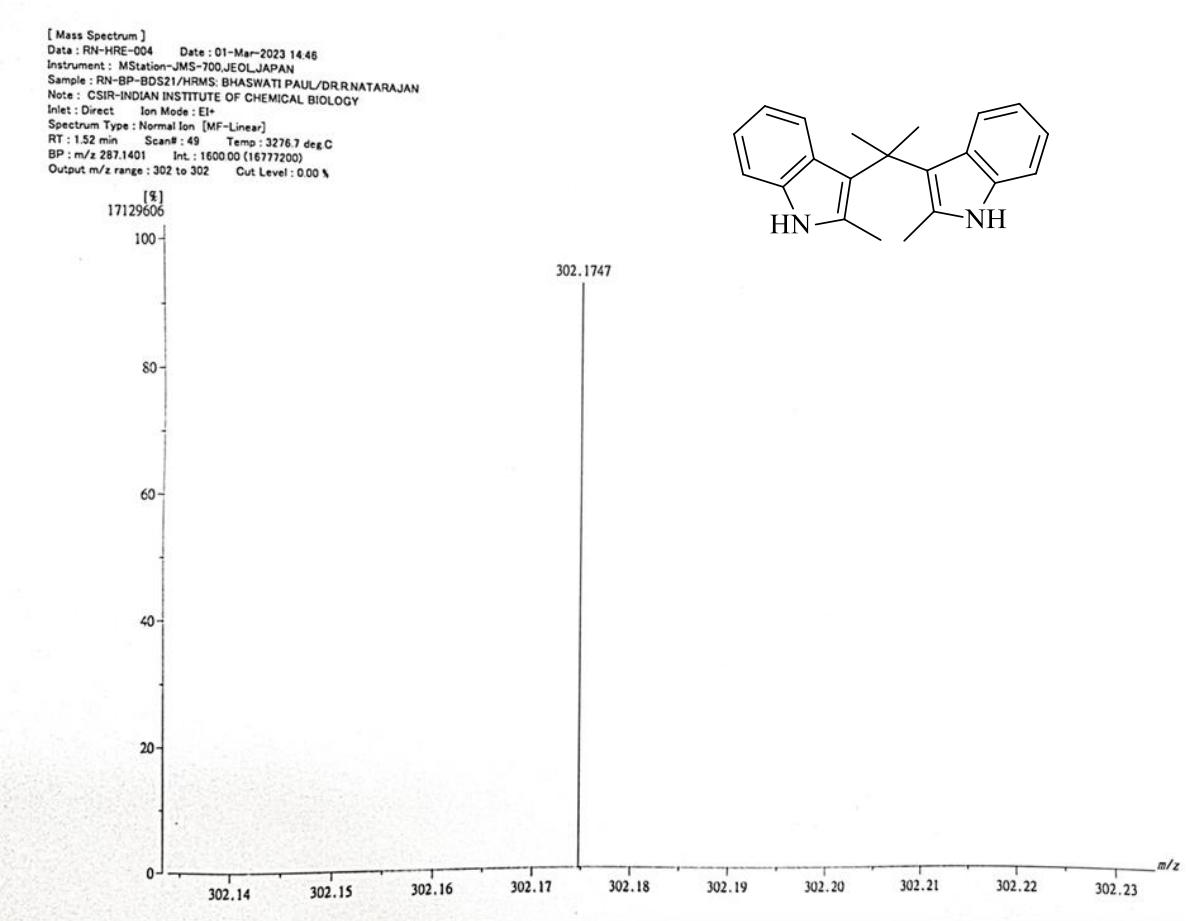
HRMS spectra of 4i



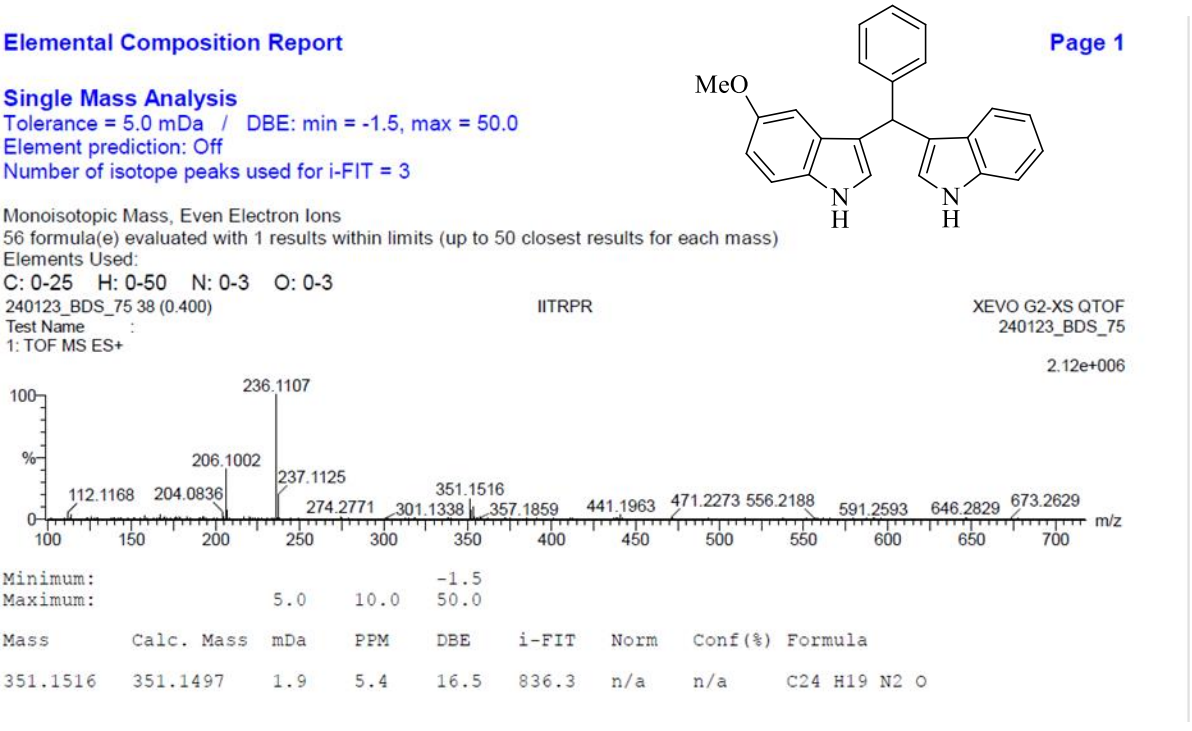
HRMS spectra of **4n**



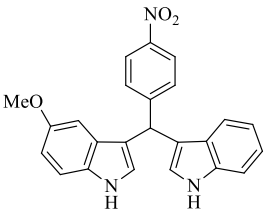
HRMS spectra of 4o



HRMS spectra of **4u**



HRMS spectra of **4v**

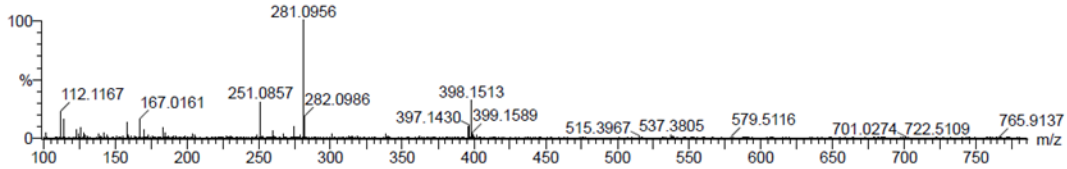


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
22 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-25 H: 0-50 N: 0-3 O: 0-3

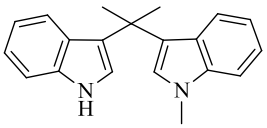
240123_BDS_73 41 (0.437) IITRPR XEVO G2-XS QTOF
Test Name : 240123_BDS_73
1: TOF MS ES+
5.20e+005



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
398.1513	398.1505	0.8	2.0	16.5	676.4	n/a	n/a	C24 H20 N3 O3

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
398.1513	398.1505	0.8	2.0	16.5	676.4	n/a	n/a	C24 H20 N3 O3

HRMS spectra of **4x**

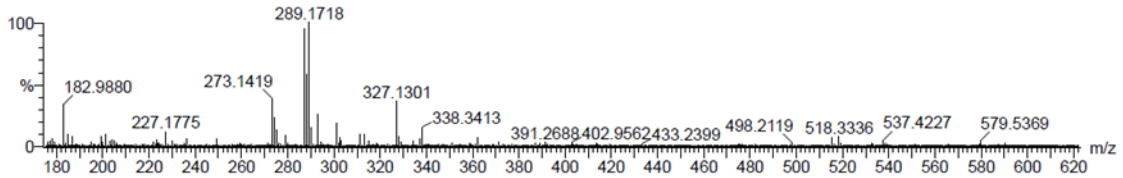


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
64 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-25 H: 0-50 N: 0-3 O: 0-3

240123_BDS_76 79 (0.809) IITRPR XEVO G2-XS QTOF
Test Name : 240123_BDS_76
1: TOF MS ES+
1.04e+005



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
289.1718	289.1705	1.3	4.5	11.5	738.9	n/a	n/a	C20 H21 N2

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