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Accessory material

Experimental

General. All reagents were commercially available and used as received. **^{1}H NMR** and **13C NMR** spectra were recorded on a Varian UNITY/NOVA 300 MHz spectrometer using $CDCl_3$ or DMSO as solvent at room temperature, unless otherwise noted. Flash column chromatography was performed using 200-300 mesh silica gel. Chemical shifts were provided in δ relative to TMS, and expressed in ppm. Coupling constants J were given in Hz. Infrared spectra were recorded on a Vector 22 FT-IR analyzer using KBr pellets in the region 400-4000 cm^{-1}. The MS spectra were recorded with a Shimadzu LCMS-2010A spectrometer. All Mannich adducts and bisindolylalkanes are known and accord with those that have been previously reported in the literature.

General procedure for the synthesis of *N-D*-glycose-*p*-tolylsulfonyhydrazine [6]

To a solution of *p*-tolylsulfonyhydrazine (5 mmol) in ethanol (20 mL) was added glycose (5 mmol). The resulting mixture was heated to 90 ºC for 3h. The reaction mixture was allowed to cool to room temperature, filtered, the crude product purification by silica gel chromatography using 100-200 mesh ZCX II eluted by $CHCl_3$–CH_3OH afforded the target product.

***N-D*-glucosyl-*p*-tolylsulfonyhydrazine (catalyst 1):** [6] white solid (80% yield); mp 172-173 ºC. $[\alpha]_D^{20}$ +21.5 (c 0.5 in DMSO). IR (KBr) υ 3488, 3221, 1601, 1510, 910cm^{-1} ; ^{1}H NMR (DMSO, 300MHz) δ 8.79 (1H, d, J = 1.5, SO_2NH), 7.71 (2H, d, J = 8.1, ArH), 7.34 (2H, d, J = 8.1, ArH), 5.36 (1H, d, J = 7.8, sugar ring C^1-H), 4.88-2.91 (11H, m), 2.38 (3H, s, CH_3); ^{13}C NMR (DMSO, 300MHz) δ 143.41, 137.34, 130.00, 128.10, 90.69, 78.73, 77.72, 71.47, 71.25, 62.61, 21.87. ESI-MS m/z 371 $[M+Na]^+$.

***N-D*-galacosyl-*p*-tolylsulfonyhydrazine (catalyst 2):** [6] white solid (75% yield); mp 150-151 ºC. $[\alpha]_D^{20}$ +26.4 (c 0.5 in DMSO). IR (KBr) υ 3486, 3219, 1612, 1509,

908cm^{-1} ; ^{1}H NMR (DMSO, 300MHz) δ 8.84 (1H, d, J = 1.5, SO_2NH), 7.70 (2H, d, J = 8.4, ArH), 7.35 (2H, d, J = 8.4, ArH), 5.25(1H, d, J = 6.6, sugar ring C^1-H), 4.71-3.01 (11H, m), 2.37 (3H, s, CH_3); ^{13}C NMR(DMSO, 300MHz) δ 142.31, 131.25, 129.80, 128.12, 91.67, 79.63, 78.22, 70.36, 69.23, 61.60, 22.75; ESI-MS m/z 371 $[M+Na]^+$.

***N-D*-xylosyl-*p*-tolylsulfonyhydrazine (catalyst 3):** [6] white solid (78% yield); mp 160-161 ºC. $[\alpha]_D^{20}$ +32.5 (c 0.5 in DMSO) IR (KBr) υ 3475, 3215, 1598, 1502, 917cm^{-1} ;^{1}H NMR (DMSO, 300MHz) δ 8.87 (1H, d, J = 2.7, SO_2NH), 7.68 (2H, d, J = 8.4, ArH), 7.35 (2H, d, J = 8.4, ArH), 5.28 (1H, d, J = 5.7, sugar ring C^1-H), 4.95-2.88 (9H, m), 2.38 (3H, s, CH_3); ^{13}C NMR(DMSO, 300MHz) δ 148.26, 139.25, 132.12, 127.36, 87.52, 79.62, 75.81, 70.45, 70.32, 23.56; ESI-MS m/z 341 $[M+Na]^+$.

General procedure for direct three-component Mannich reaction

To a solution of catalyst 1 (10-30 mmol%) in H_2O (1 mL) was added aldehyde (1 mmol) and amine (1.1 mmol) , stired 15min, and added ketone (2 mmol). The mixture was stirred at room temperature and monitored by TLC until the starting material was consumed. Saturated brine (5 mL) was added, and the mixture was extracted with ethyl acetate, dried over anhydrous $MgSO_4$ and concentrated. Purification by silica gel chromatography (eluted with hexane–ethyl acetate) gave the desired product.

1,4-diphenyl-3-(*N*-phenylamino)propanone (Table 2 entry 1) [9j] oil, ν_{max} (KBr)/cm^{-1} 3200, 1702, 1601, 1510, 750. δ_H ($CDCl_3$, 300MHz) 7.88 (2H, d *J* = 4.2, ArH), 7.04~7.54 (10H, m, ArH), 6.67 (1H, s, ArH), 6.55 (2H, s, ArH), 4.97-5.01 (1H, m, CH), 3.44-3.48 (2H, m, CH_2); ^{13}C NMR($CDCl_3$, 300MHz) δ 198.31, 146.95, 142.99, 136.86, 133.59, 129.29, 129.01, 128.88, 128.39, 127.57, 126.60, 118.16, 114.19, 55.29, 46.58; ESI-MS m/z 302 $[M+H]^+$.

1,4-diphenyl-3-(*N*-*p*-CH_3O-phenylamino)propanone (Table 2 entry 2) [9j] brownish solid, mp 141-142 ºC. ν_{max} (KBr)/cm^{-1} 3202, 1701, 1605, 1511, 748; δ_H ($CDCl_3$, 300MHz) 7.92 -7.20 (10H, m, ArH), 6.68 (2H, s, ArH), 6.54 (2H, s, ArH), 4.95 -4.90 (1H, m, CH), 3.69 (3H, s, CH_3O), 3.46-3.42 (2H, m, CH_2); ^{13}C NMR($CDCl_3$, 300MHz) δ 198.45, 152.51, 143.38, 141.34, 136.92, 133.56, 128.98, 128.87, 128.38,

127.49, 126.64, 115.61, 114.92, 56.04, 56.01, 46.78; ESI-MS m/z 332 $[M+H]^+$.

2-[1'-(*N*-phenylamino)-1'-phenyl]methylcyclohexanone (Table 2 entry 3) [9j] colorless needles, mp 126-127 ºC. ν_{max} (KBr)/cm^{-1} 3370, 1701, 1600, 1511; δ_H ($CDCl_3$, 300MHz, *anti*/*syn* = 78/22) 7.36-7.16 (5H, m, ArH), 7.06-7.01 (2H, m, ArH), 6.62-6.50 (3H, m, ArH)), 4.78 (*syn*, 0.22H, d, *J* = 3.5, CH), 4.60 (*anti*, 0.78H, d, *J* = 7.0, CH), 2.75 -2.73 (1H, m, CH, 2.41-2.32 (2H, m, CH_2), 1.89-1.61 (6H, m, $3CH_2$); ^{13}C NMR($CDCl_3$, 300MHz) δ 212.45, 211.24, 147.43, 147.29, 140.66, 140.44, 132.89, 132.80, 129.49, 129.38, 129.31, 129.00, 128.82, 128.73, 118.13, 117.97, 114.31, 113.89, 57.73, 57.61, 57.16, 56.76, 42.81, 42.39, 31.87, 29.26, 28.30, 27.47, 25.27, 24.39; ESI-MS m/z 280 $[M+H]^+$.

2-[1'-(*N*-phenylamino)-1'-(*p*-Cl-phenyl)]methylcyclohexanone (Table 2 entry 4) [9j] colorless needles, mp 142-143 ºC. ν_{max} (KBr)/cm^{-1} 3370, 1701, 1600, 1511; δ_H ($CDCl_3$, 300MHz, anti/syn = 69/31) 7.31-7.22 (4H, m, ArH), 7.08-7.02 (2H, m, ArH), 6.66-6.60 (1H, m, ArH), 6.50-6.47 (2H, m, ArH), 4.71 (syn, 0.31H, d, *J* = 4.5, CH), 4.57 (anti, 0.69H, d, *J* = 6.6, CH), 2.79-2.76 (1H, m, CH), 2.41-2.35 (2H, m, CH_2) , 2.07-1.58 (6H, m, $3CH_2$); ^{13}C NMR($CDCl_3$, 300MHz) δ 212.50, 211.27, 147.45, 147.31, 140.68, 140.46, 132.91, 132.82, 129.40, 129.34, 129.02, 128.84, 118.65, 118.16, 117.99, 115.36, 114.33, 113.91, 57.76, 57.63, 57.19, 56.78, 42.83, 42.41, 31.89, 29.29, 28.31, 27.49, 25.29, 24.40; ESI-MS m/z 314 $[M+H]^+$.

2-[1'-(*N*-phenylamino)-1'(-*p*-Br-phenyl)]methylcyclohexanone (Table 2 entry 5) [9j] colorless needles, mp 158-159 ºC. ν_{max} (KBr)/cm^{-1} 3370, 1701, 1600, 1511; δ_H ($CDCl_3$, 300MHz, anti/syn = 58/42) 7.41-7.21 (4H, m, ArH), 7.09-7.03 (2H, m, ArH), 6.69-6.65 (1H, m, ArH), 6.55-6.49 (2H, m, ArH), 4.71 (syn, 0.42H, d, *J* = 4.0, CH), , 4.55 (anti, 0.58H, d, *J* = 6.5, CH) 2.71-2.70 (1H, m, CH), 2.40-2.34 (2H, m, CH_2), 2.06-1.53 (6H, m, $3CH_2$); ^{13}C NMR($CDCl_3$, 300MHz) δ 212.45, 211.23, 147.47, 147.33, 141.26, 141.07, 131.78, 131.70, 129.74, 129.54, 129.45, 129.38, 118.63, 118.18, 118.02, 115.38, 114.35, 113.93, 57.80, 57.57, 57.22, 56.74, 42.85, 42.44, 31.93, 29.27, 28.36, 27.53, 25.32, 24.45; ESI-MS m/z 359 $[M+H]^+$.

2-[1'-(*N*-phenylamino)-1'(-*p*-NO_2-phenyl)]methylcyclohexanone (Table 2 entry 6) [9j] yellow solid, mp 165-167 ºC. ν_{max} (KBr)/cm^{-1} 3359, 1708, 1592, 1505; δ_H ($CDCl_3$,

300MHz, anti/syn = 71/29) 8.15 (2H, d, *J* = 9.0, ArH), 7.58 (2H, d, *J* = 9.0, ArH), 7.12-7.05 (2H, m, ArH), 6.72-6.66 (1H, m, ArH), 6.55-6.49 (2H, m, ArH), 4.85 (syn, 0.42H, d, *J* = 3.8, CH), 4.70 (anti, 0.71H, d, *J* = 6.0, CH), 2.94-2.89 (1H, m, CH), 2.41-2.36 (2H, m, CH_2), 2.08-1.54 (6H, m, $3CH_2$); ^{13}C NMR($CDCl_3$, 300MHz) δ 211.84, 211.72, 149.99, 149.93, 149.85, 149.76, 147.18, 146.81, 129.46, 129.36, 128.81, 128.47, 123.86, 123.82, 118.58, 118.35, 114.26, 113.75, 58.13, 57.52, 57.34, 56.54, 42.77, 42.67, 32.40, 29.45, 28.17, 27.44, 25.33, 24.88; ESI-MS m/z 325 $[M+H]^+$.

2-[1'-(*N*-*p*-Cl-phenylamino)-1'-phenyl]methylcyclohexanone (Table 2 entry 7) [9j] colorless solid, mp 106-107 ºC. ν_{max} (KBr)/cm^{-1} 3402, 1696,1593, 1498; δ_H ($CDCl_3$, 300MHz, anti/syn = 50/50) 7.36-7.16 (5H, m, ArH), 7.02-6.98 (2H, m, ArH), 6.48-6.45 (2H, m, ArH), 4.74 (syn, 0.50H, d, *J* = 3.2, CH), 4.54 (anti, 0.50H, d, *J* = 6.9, CH), 2.79-2.76 (1H, m, CH), 2.42-2.30 (2H, m, CH_2), 2.01-1.61 (6H, m, $3CH_2$); ^{13}C NMR($CDCl_3$, 300MHz) δ 212.84, 211.39, 146.32, 146.11, 141.45, 141.24, 129.28, 129.08, 128.77, 127.67, 127.55, 127.45, 122.49, 122.39, 122.24, 116.45, 115.44, 115.03, 58.61, 57.69, 57.54, 56.77, 42.75, 42.33, 31.94, 28.86, 28.37, 27.43, 25.23, 24.24; ESI-MS m/z 313 $[M]^+$.

2-[1'-(*N*-*p*-Cl-phenylamino)-1'-(*p*-Cl-phenyl)]methylcyclohexanone (Table 2 entry 8) [9j] colorless solid, mp 97-98 ºC. ν_{max} (KBr)/cm^{-1} 3401, 1698, 1591, 1499; δ_H ($CDCl_3$, 300MHz, anti/syn = 52/48) 7.31-7.26 (4H, m, ArH), 7.01 (2H, d, *J* = 8.7, ArH), 6.43 (2H, d, *J* = 8.7, ArH), 4.67 (syn, 0.48H, d, *J* = 3.2, CH), 4.51 (anti,0.52H, d, *J* = 6.3, CH), 2.80-2.75 (1H, m, CH), 2.46-2.26 (2H, m, CH_2), 2.04-1.60 (6H, m, $3CH_2$); ^{13}C NMR($CDCl_3$, 300MHz) δ 212.48, 211.26, 145.99, 145.89, 140.11, 139.79, 133.07, 132.99, 129.19, 129.14, 129.09, 128.88, 128.81, 122.63, 122.44, 116.46, 115.42, 115.01, 58.04, 57.50, 57.34, 56.56, 42.76, 42.52, 32.07, 29.06, 28.31, 27.34, 25.24, 24.50; ESI-MS m/z 347 $[M]^+$.

2-[1'-(*N*-*p*-Cl-phenylamino)-1'-(*p*-NO_2-phenyl)]methylcyclohexanone (Table 2 entry 9) [9j] yellow solid, mp 119-120 ºC. ν_{max} (KBr)/cm^{-1} 3398, 1700,1602, 1500; δ_H ($CDCl_3$, 300MHz, anti/syn = 36/64) 8.14 (2H, d, *J* = 8.8, ArH), 7.52 (2H, d, *J* = 8.8, ArH), 7.01 (2H, d, *J* = 8.7, ArH), 6.41 (2H, d, *J* = 8.7, ArH), 4.78 (syn, 0.64H, d, *J* =

4.2, CH), 4.61 (anti,0.36H, d, *J* = 6.7, CH), 2.89-2.81 (1H, m, CH), 2.47-2.32 (2H, m, CH_2), 2.09-1.59 (6H, m, $3CH_2$); ^{13}C NMR($CDCl_3$, 300MHz) δ 211.84, 210.67, 149.59, 149.34, 147.24, 147.19, 145.52, 129.25, 129.16, 128.77, 128.70, 128.47, 128.40, 123.87, 123.04, 122.77, 115.36, 114.87, 58.31, 57.56, 57.19, 56.38, 42.85, 42.76, 32.53, 29.23, 28.24, 27.38, 25.28, 24.95; ESI-MS m/z 358 $[M]^+$.

2-[3'-Methyl-1'-*N*-phenylamino]butylcyclohexanone (Table 2 entry 10) [9j] colorless solid, mp 87-88 ºC. ν_{max} (KBr)/cm^{-1} 3385, 2936, 1675, 1598, 1497; δ_H ($CDCl_3$, 300MHz, major/ minor = 70/30) 7.15-6.54 (5H, m, ArH), 3.95 (1H, br, NH), 3.81-3.76 (major, 0.70H, m, CH), 3.61-3.58 (minor,0.30H, m, CH), 2.62-1.25 (12H, m, $5CH_2$+2CH), 0.92-0.85 (6H, m, $(CH_3)_2CH$); ^{13}C NMR($CDCl_3$, 300MHz) δ 212.97, 212.78, 148.23, 148.12, 129.59, 129.52, 116.90, 116.69, 113.03, 112.75, 54.31, 53.74, 52.18, 51.41, 43.15, 43.04, 42.93, 42.36, 30.93, 30.22, 27.72, 27.46, 25.68, 25.59, 25.42, 25.34 , 24.09 , 23.74, 22.58, 22.13; ESI-MS m/z 260 $[M+H]^+$.

2-[3'-Methyl-1'-(*N*-*p*-Cl-phenylamino)]butylcyclohexanone (Table 2 entry 11) [9j] colorless solid, mp 95-96 ºC. ν_{max} (KBr)/cm^{-1} 3382, 2935, 1695, 1599, 1491; δ_H ($CDCl_3$, 300MHz, major/ minor = 69/31) 7.05 (2H, d, *J* = 8.7, ArH), 6.47 (2H, d, *J* = 8.7, ArH), 4.05 (1H, br, NH), 3.70-3.65 (major, 0.70H, m, CH), 3.60-3.45 (minor,0.30H, m, CH), 2.62-1.48 (12H, m, $5CH_2$+2CH), 0.91-0.83 (6H, m, $(CH_3)_2CH$); ^{13}C NMR($CDCl_3$, 300MHz) δ 212.95, 212.70, 148.21, 148.10, 129.55, 129.46, 116.73, 116.42, 113.08, 112.64, 54.38, 53.68, 52.16, 51.36, 43.12, 43.01, 42.90, 42.32, 30.98, 30.12, 27.62, 27.42, 25.69, 25.55, 25.41, 25.30 , 24.19 , 23.72, 22.68, 22.15; ESI-MS m/z 294 $[M+H]^+$.

2-[1'-(2-furyl)-1'-(*N*-phenylamino)]methylcyclohexanone (Table 2 entry 12) [9j] brownish needles, mp 102-103ºC. ν_{max} (KBr)/cm^{-1} 3376, 2940, 1676, 1592, 1499; δ_H ($CDCl_3$, 300MHz, anti/syn = 57/43) 7.27- 7.08 (3H, m, ArH), 6.62-6.56 (3H, m, ArH), 6.27- 6.16 (2H, m, ArH), 4.89 (syn, 0.43H, d, *J* = 3.8, CH), 4.82 (anti,0.57H, d, *J* = 6.4, CH), 2.99-2.90(1H, m, CH), 2.41-2.35 (2H, m, CH_2), 2.05-1.60 (6H, m, $3CH_2$); ^{13}C NMR($CDCl_3$, 300MHz) δ 211.97, 211.13, 155.05, 154.08, 147.54, 147.38, 141.50, 141.37, 129.76, 129.40, 118.40, 118.25, 114.26, 113.96, 110.74, 110.59, 107.43, 107.16, 54.82, 54.42, 52.53, 52.26, 42.60, 42.46, 31.21, 30.07, 28.04, 27.30, 25.10,

24.68; ESI-MS m/z 270 $[M+H]^+$.

General procedure for the preparation of bisindolylalkanes

A solution of aldehyde (1 mmol) and catalyst **3** (0.2 mmol) in water (1 mL) was treated with indole (2 mmol). The resulting solution was stirred at room temperature and monitored by TLC until the starting material was consumed. Then saturated brine (5 mL) was added, extracted with ethyl acetate, and dried with anhydrate Na_2SO_4. The solvent was removed in vacuo and the resulting mixture was purified by silica gel chromatography (eluted with hexane–ethyl acetate) to give the desired product.

1,1-bis-3-indolyl propane (Table 4, entry 1) [5a] white solid, mp 72-73ºC. IR (KBr) υ 3499, 3101, 3030, 2951, 1709, 1590, 1253, 1060, 772 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$) δ 7.89 (bs, 2H, NH), δ 7.58 (d, 2H, *J* = 7.9Hz, , ArH), δ 7.33 (d, 2H, *J* = 7.9Hz, ArH) δ7.17-7.02 (m, 6H, ArH) δ 4.39 (t, 1H, *J* = 6.4Hz, CH), δ 2.27 (pent, 2H, *J* = 6.4Hz, CH_2), δ 1.03 (t, 3H, *J* = 6.4 Hz, CH_3); ^{13}C NMR($CDCl_3$, 300MHz) δ 136.78, 127.44, 121.92, 121.70, 120.51, 119.93, 119.19, 111.31, 36.27, 29.11, 13.51; ESI-MS m/z 274 $[M]^+$.

1,1-bis-3-indolyl butane (Table 4, entry 2) [14c] white solid, mp 155-156ºC. IR (KBr) υ 3500, 3100, 3027, 2953, 1709, 1589, 1251, 1058, 770 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.87 (bs, 2H, NH), δ 7.59 (d, 2H, *J* = 7.8 Hz, ArH), δ 7.32 (d, 2H, *J* = 7.8Hz, ArH) δ7.14-6.95 (m, 6H, ArH) δ 4.49 (t, 1H, *J* = 6.3Hz, CH), δ 1.44-1.79 (m, 4H, $2CH_2$), δ 0.99 (t, 3H, *J* = 6.3Hz, CH_3); ^{13}C NMR($CDCl_3$, 300MHz) δ 136.79, 127.42, 121.93, 121.85, 120.55, 119.89, 119.21, 111.35, 40.31, 3184, 26.22, 19.32; ESI-MS m/z 288 $[M]^+$.

3-methyl-1,1-bis-3-indolyl- butane (Table 4, entry 3)[14c] white solid, mp 162-163ºC. IR (KBr) υ 3510, 3103, 3036, 2958, 1699, 1590, 1250, 1065, 758 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.86 (bs, 2H, NH), δ 7.60 (d, 2H, *J* = 7.8Hz, ArH), δ 7.31 (d, 2H, *J* = 7.8Hz, ArH) δ7.15- 6.96 (m, 6H, ArH) δ 4.59 (t, 1H, *J* = 7.5Hz, CH),δ 2.09 (t, 2H, *J* = 7.2Hz, CH_2), δ 1.62-1.69 (m, 1H, $(CH_3)_2CH$) δ 0.98 (d, 6H, *J* = 6.6Hz ,$2CH_3$); ^{13}C NMR($CDCl_3$, 300MHz) δ 136.80, 127.35, 121.95, 121.68, 120.75, 119.85, 119.25, 111.38, 45.61, 32.08, 26.38, 23.30; ESI-MS m/z 302 $[M]^+$.

3,3′- bis(indoly)-Phenylmethane (Table 4, entry 4) [14c] colorless solid; mp 151-152

ºC. IR (KBr) υ 3412, 3053, 1610, 1598, 1456, 1092, 742 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.87 (bs, 2H, NH), δ 7.37-7.29 (m, 6H, ArH), δ 7.28-7.21 (m, 2H, ArH) δ7.21-7.11 (m, 3H, ArH) δ 6.98 (t, 2H, *J* = 6.7Hz, ArH), δ 6.63 (s, 2H, ArH), δ 5.87 (s, 1H, Ar-CH); ^{13}C NMR($CDCl_3$, 300MHz) δ 144.19, 136.88, 128.91, 128.40, 127.30, 126.32, 123.81, 122.12, 120.14, 119.93, 119.43, 111.26, 40.57; ESI-MS m/z 322 $[M]^+$.

3,3′- bis(indoly)-(4-chloro-Phenyl)methane (Table 4, entry 5) [14c] pink solid; mp 77-78 ºC. IR (KBr) υ 3411, 3056, 1600, 1499, 1452, 1088 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.90 (bs, 2H, NH), δ 7.34 (d, 4H *J* = 8.0 Hz, ArH), δ 7.27-7.13 (m, 6H, ArH) δ 6.99 (t, 2H, *J* = 8.0Hz, ArH) δ 6.62 (s, 2H, ArH), δ 5.84 (s, 1H, Ar-CH); ^{13}C NMR($CDCl_3$, 300MHz) δ 142.75, 136.89, 131.97, 130.26, 128.54, 127.09, 123.81, 122.27, 120.01, 119.56, 119.39, 111.36, 39.99; ESI-MS m/z 356 $[M]^+$

3,3′-bis(indoly)-(4-Bromo -Phenyl)methane (Table 4, entry 6)[14c] brown solid; mp 120-121 ºC. IR (KBr) υ 3410, 3058, 1599, 1501, 1450, 1086 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.90 (bs, 2H, NH), δ 7.35 (m, 6H, ArH), δ 7.21-7.12 (m, 4H, ArH) δ 6.99 (m, 2H, ArH) δ 6.62 (s, 2H, ArH), δ 5.82 (s, 1H, Ar-CH); ^{13}C NMR($CDCl_3$, 300MHz) δ 143.27, 136.88, 131.76, 131.49, 130.68, 127.08, 123.80, 122.28, 120.00, 119.57, 119.32, 111.33, 40.05; ESI-MS m/z 400 $[M]^+$.

3,3′- bis(indoly)-(4-Nitro -Phenyl)methane (Table 4, entry 7) [14c] yellow needles; mp 219-220 ºC. IR (KBr) υ 3421, 3056, 1594, 1508, 1457, 1341 cm^{-1}, ^{1}H NMR (300MHz, $CDCl_3$) δ 8.12 (d, 2H, J Hz), δ 7.99 (bs, 2H, NH), δ 7.48 (m, 2H, ArH) δ 7.34 (m, 4H, ArH) δ 7.18 (d, 2H, *J* = 8.8 Hz, ArH), δ 7.01(d, 2H, *J* = 8.8 Hz, ArH), δ 6.66 (s, 2H, ArH), δ 5.98 (s, 1H, Ar-CH); ^{13}C NMR($CDCl_3$+DMSO, 300MHz) δ 148.75, 139.89, 131.98, 130.27, 128.52, 127.05, 123.78, 122.17, 120.03, 119.76, 119.34, 111.24, 40.14; ESI-MS m/z 367 $[M]^+$.

3,3′-bis(indoly)-(3-Nitro-Phenyl)methane (Table 4, entry 8) [14c] yellow solid; mp 178-179 ºC. IR (KBr) υ 3420, 3059, 1592, 1505, 1450, 1340 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$) δ 8.05 (s, 2H), δ 7.90 (bs, 2H, NH), δ 7.73-7.50 (m, 3H, ArH), δ 7.35-7.31 (m, 4H, ArH) δ 7.20-7.17 (m, 2H, ArH), δ 7.01-6.98 (m, 2H, Hz, ArH), δ 6.68 (s, 2H, ArH), δ 5.98 (s, 1H, Ar-CH); ^{13}C NMR($CDCl_3$+DMSO, 300MHz) δ 148.73, 139.92, 138.89, 136.95, 131.24, 128.56, 127.16, 123.77, 122.18, 120.10, 119.74, 119.32,

111.14, 40.09; ESI-MS m/z 367 $[M]^+$.

3,3′-bis(indoly)-(4-methoxy-Phenyl)methane (Table 4, entry 9) [14c] brown needles; mp 185-186 ºC. IR (KBr) υ 3416, 3010, 1602, 1508, 1456, 1244, 1210 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.89 (bs, 2H, NH), δ 7.34-7.39 (m, 4H, ArH), δ 7.19 (s, 2H, ArH) δ 7.16 (t, 2H, *J* = 7.3 Hz, ArH) δ 6.98 (t, 2H, *J* = 7.3 Hz, ArH), δ 6.81 (d, 2H, *J* = 8.3 Hz, ArH), δ 6.64 (s, 2H, ArH), δ 5.83 (s, 1H, Ar-CH), δ 3.77 (s, 3H, CH_3O); ^{13}C NMR($CDCl_3$+DMSO, 300MHz) δ 136.89, 136.44, 129.79, 127.26, 123.73, 122.08, 120.24, 120.18, 119.38, 114.56, 113.80, 111.24, 55.54, 39.69;ESI-MS m/z 352 $[M]^+$.

3,3′-bis(indoly)-[4-(*N*,*N*′-di-methylamino)-Phenyl]methane (Table 4, entry 10) [14c] brown needles; mp 154-155 ºC. IR (KBr) υ 3409, 2928, 1599, 1501, 1456, 1245,1220 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.86 (bs, 2H, NH), δ 7.39 (d, 2H, *J* = 7.8Hz, ArH), δ 7.32 (d, 2H, *J* = 7.8Hz, ArH) δ 7.20-7.11 (m, 4H, ArH) δ 6.99-6.94 (m, 2H, ArH), δ 6.71-6.64 (m, 4H, ArH), δ 5.79 (s, 1H, Ar-CH), δ 2.90 [s, 6H, $(CH_3)_2N$]; ^{13}C NMR($CDCl_3$+DMSO, 300MHz) δ 148.56, 136.68, 132.72, 128.85, 126.79, 123.47, 120.74, 119.32, 119.05, 118.05, 112.27, 111.17, 36.34, 15.86; ESI-MS m/z 365 $[M]^+$.

3,3′-bis(indoly)-(4-hydroxy-Phenyl)methane (Table 4, entry 11) [14c] white needles; mp 161-162 ºC. IR (KBr) υ 3560, 3418, 3056, 1596, 1509, 1459, 1329 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.91 (bs, 2H, NH), δ 7.37 (m, 4H, , ArH), δ 7.22-7.13 (m, 4H, ArH) δ 7.03-6.96 (m, 2H, ArH) δ 6.76-6.71 (m, 2H, ArH), δ 6.65 (s, 2H, ArH), δ 5.83 (s, 1H, Ar-CH); ^{13}C NMR($CDCl_3$, 300MHz) δ 136.85, 136.42, 129.72, 127.18, 123.53, 122.25, 120.16, 120.08, 119.28, 114.76, 113.82, 111.20, 45.54; ESI-MS m/z 338 $[M]^+$.

3,3′-bis(indolyl)-(4-methyl-phenyl)methane (Table 4, entry 12) [14c] pink needles; mp 95-96 ºC. IR (KBr) υ 3411, 3040, 2928, 1598, 1507, 1216, 1048, 742 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.89 (bs, 2H, NH), δ 7.41-7.33 (m, 4H, ArH), δ 7.25-7.20 (m, 2H, ArH) δ 7.16 (t, 2H, *J* = 7.2Hz, ArH) δ 7.08 (d, 2H, *J* = 7.2 Hz, ArH), δ 6.66 (s, 2H, ArH), δ 5.86 (s, 1H, Ar-CH), δ 2.33 (s, 3H, CH_3); ^{13}C NMR($CDCl_3$, 300MHz) δ 141.16, 137.53, 136.88, 135.64, 129.09, 128.75, 127.32, 123.73, 122.06, 120.16, 119.39, 111.20, 40.13, 21.44; ESI-MS m/z 336 $[M]^+$.

3,3′-bis(indolyl)-(4-formyl-phenyl)methane (Table 4, entry 13) [14c] red needles; mp 125-126 ºC. IR (KBr) υ 3420, 3030, 2902, 1701, 1600, 1502, 1216 cm^{-1}; ^1H NMR

(300MHz, $CDCl_3$) δ 9.95 (s, 1H, HC = O) δ 7.95 (bs, 2H, NH), δ 7.78 (d, 2H, *J* = 8.0Hz, ArH), δ 7.49 (d, 2H, *J* = 8.0Hz, ArH), δ 7.37-7.31 (m, 4H, ArH), δ 7.16 (t, 2H, *J* = 7.1Hz, ArH), δ 6.99 (t, 2H, *J* = 7.1Hz, ArH), δ 6.65 (s, 2H, ArH), δ 5.95 (s, 1H, Ar-CH); ^{13}C NMR($CDCl_3$, 300MHz) δ 192.15, 151.56, 136.87, 135.01, 130.08, 129.58, 127.02, 123.81, 122.40, 119.88, 119.69, 118.79, 111.38, 40.83; ESI-MS m/z 350 $[M]^+$.

3,3′-bis(indolyl)-(2-furyl)methane (Table 4, entry 14) [14c] brown solids; mp 322-324 ºC. IR (KBr) υ 3412, 3100, 2927, 1590, 1507, 1215, 1049 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.93 (bs, 2H, NH), δ 7.46 (m, 2H, ArH), δ 7.35-7.31 (m, 3H, ArH) δ 7.15 (t, 2H, *J* = 8.1 Hz, ArH), δ 7.01 (t, 2H, *J* = 8.1Hz, ArH), δ 6.86 (s, 2H, ArH), δ 6.29-6.27 (m, 1H, ArH), δ 6.03-6.05 (m, 1H, ArH), δ 5.93 (s, 1H, Ar-CH); ^{13}C NMR($CDCl_3$, 300MHz) δ 157.23, 141.37, 136.72, 126.98, 123.24, 122.15, 119.88, 119.56, 117.41, 111.34, 110.36, 106.83, 34.49; ESI-MS m/z 312 $[M]^+$.

vibrindole[19] **A** brown needles; mp 78-79 ºC. IR (KBr) υ 3408, 2365, 1624, 1590, 1498, 1437, 1289, 1206, 1170, 1095 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$) δ 7.83 (bs, 2H, NH), δ 7.55 (d, 2H, *J* = 7.8Hz, , ArH), δ 7.32 (d, 2H, *J* = 7.8Hz, ArH) δ 7.16-7.10 (m, 3H, ArH), δ 7.05-6.99 (m, 3H, ArH), δ 6.89 (s, 2H, ArH), δ 4.66 (d, 1H, *J* = 6.9Hz, CH), δ 1.80 (d, 3H, *J* = 6.9Hz, CH_3); ^{13}C NMR($CDCl_3$, 300MHz) δ 136.84, 127.12, 121.97, 121.88, 121.42, 119.94, 119.22, 111.30, 28.55, 22.12; ESI-MS m/z 260 $[M]^+$.

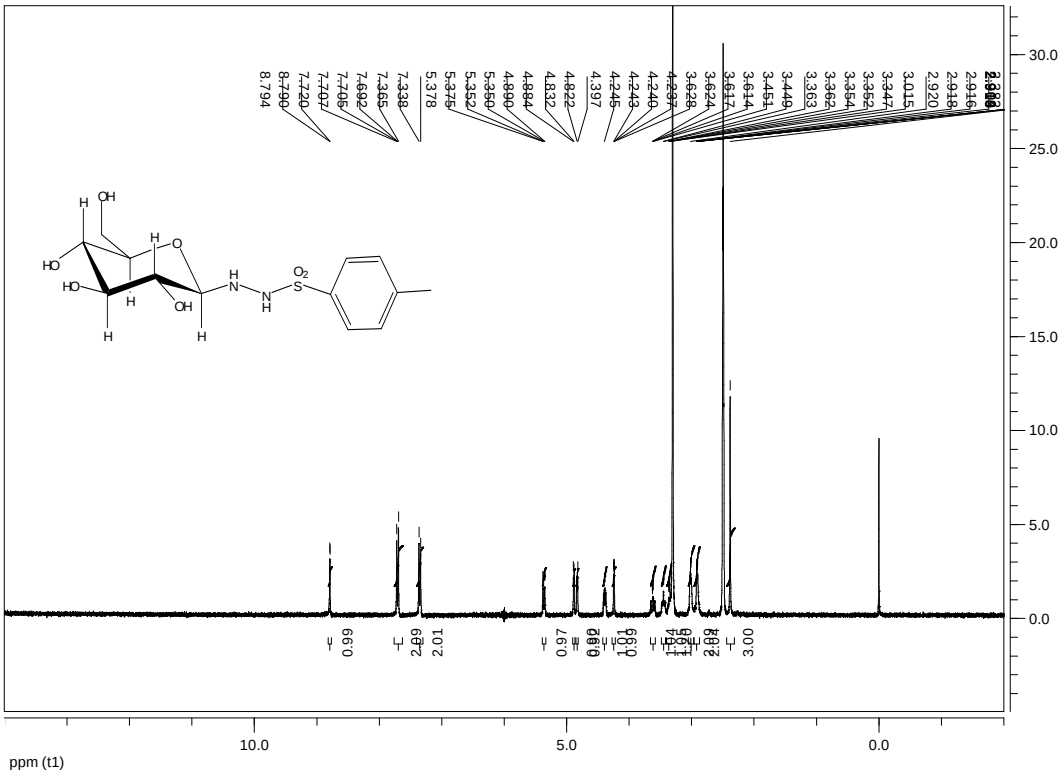
Trisindolylmethane [5a] white needles; mp 125-126 ºC. IR (KBr) υ 3429, 3401, 1618, 1480 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$) δ 9.87 (bs, 3H, NH), δ 7.36 (d, 3H, *J* = 7.9Hz, ArH), δ 7. 23 (d, 3H, *J* = 7.9 Hz, ArH), δ 6.99 (t, 3H, *J* = 7.9 Hz, ArH), δ 6.81 (t, 3H, *J* = 7.9 Hz, ArH), δ 6.70 (d, 3H, *J* = 2.4Hz, ArH), δ 6.38 (s, 1H, CH); ^{13}C NMR($CDCl_3$+DMSO, 300MHz) δ 136.75, 126.94, 123.38, 120.73, 119.46, 118.55, 118.04, 111.25, 31.36; ESI-MS m/z 361 $[M]^+$.

diindol-3-yl-methane [19] white solids; mp 168-169 ºC. IR (KBr) υ 3407, 1590, 1498, 1437, 1288, 1201, 1170, 1090 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 7.85 (bs, 2H, NH), δ 7.64 (d, 2H, *J* = 7.8Hz, ArH), δ 7.35 (d, 2H, *J* = 7.8Hz, ArH) δ 7.23-7.08 (m, 4H, ArH), δ 6.92 (s, 2H, ArH), δ 4.66 (s, 2H, CH_2); ^{13}C NMR($CDCl_3$, 300MHz) δ 136.65, 127.78, 122.39, 122.09, 119.43, 119.39, 115.93, 111.25, 21.60; ESI-MS m/z

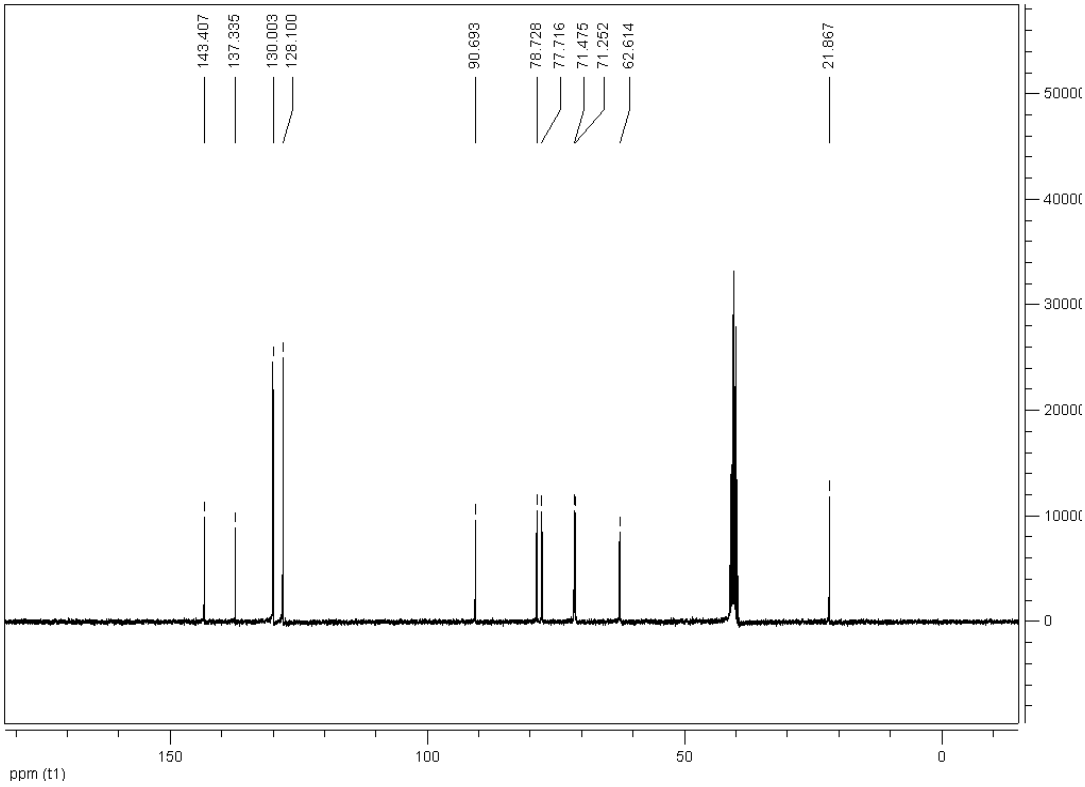
246 $[M]^+$.

^{1}H NMR and ^{13}C NMR spectra for some products:

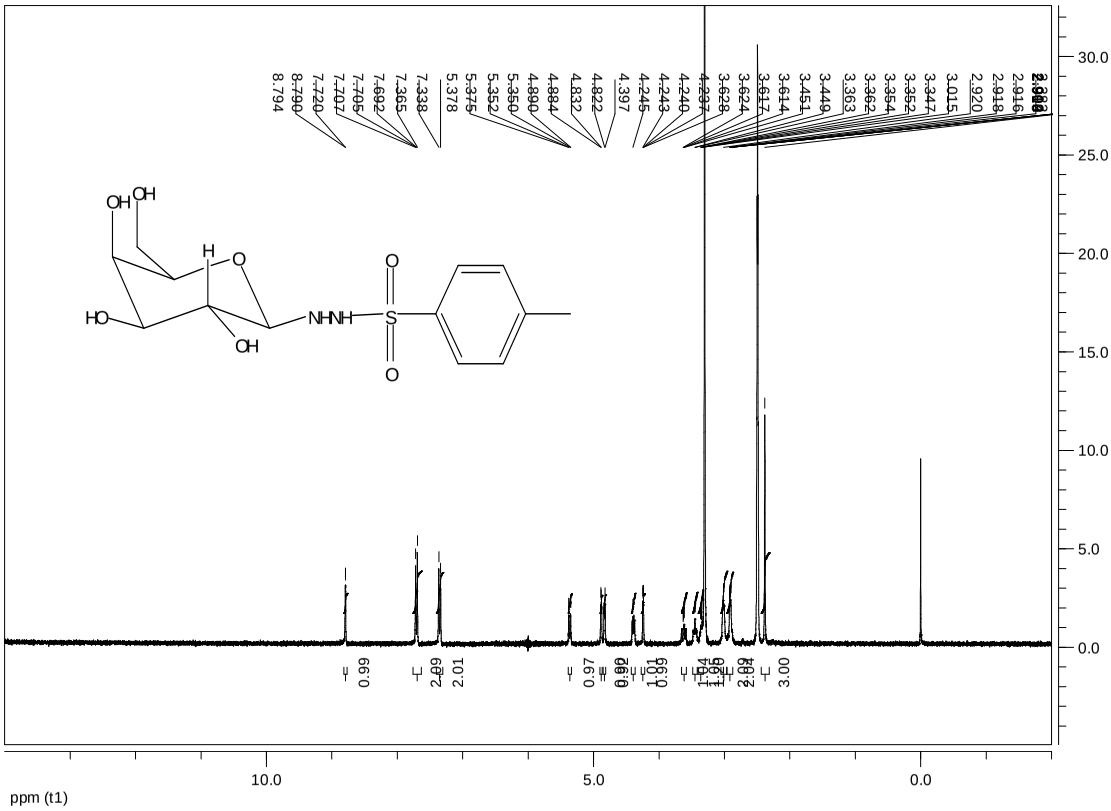
^{1}H NMR *N-D*-glucosyl-*p*-tolylsulfonyhydrazine (catalyst 1):



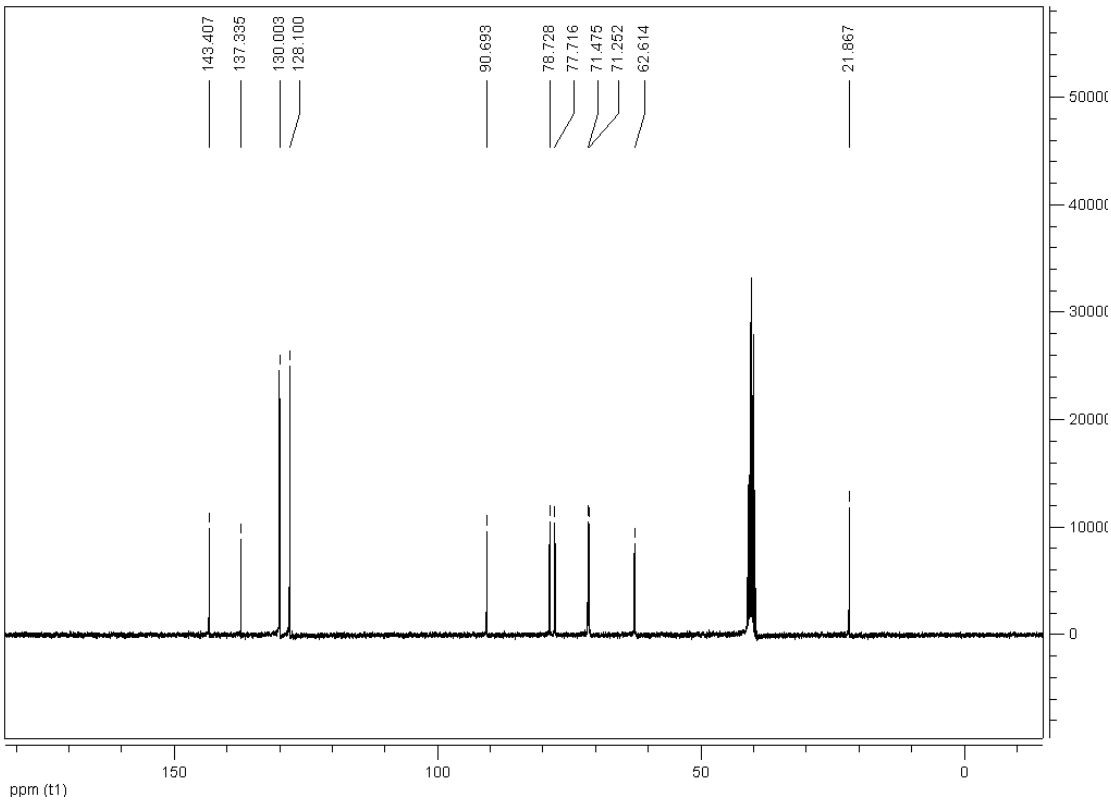
^{13}C NMR *N-D*-glucosyl-*p*-tolylsulfonyhydrazine (catalyst 1):



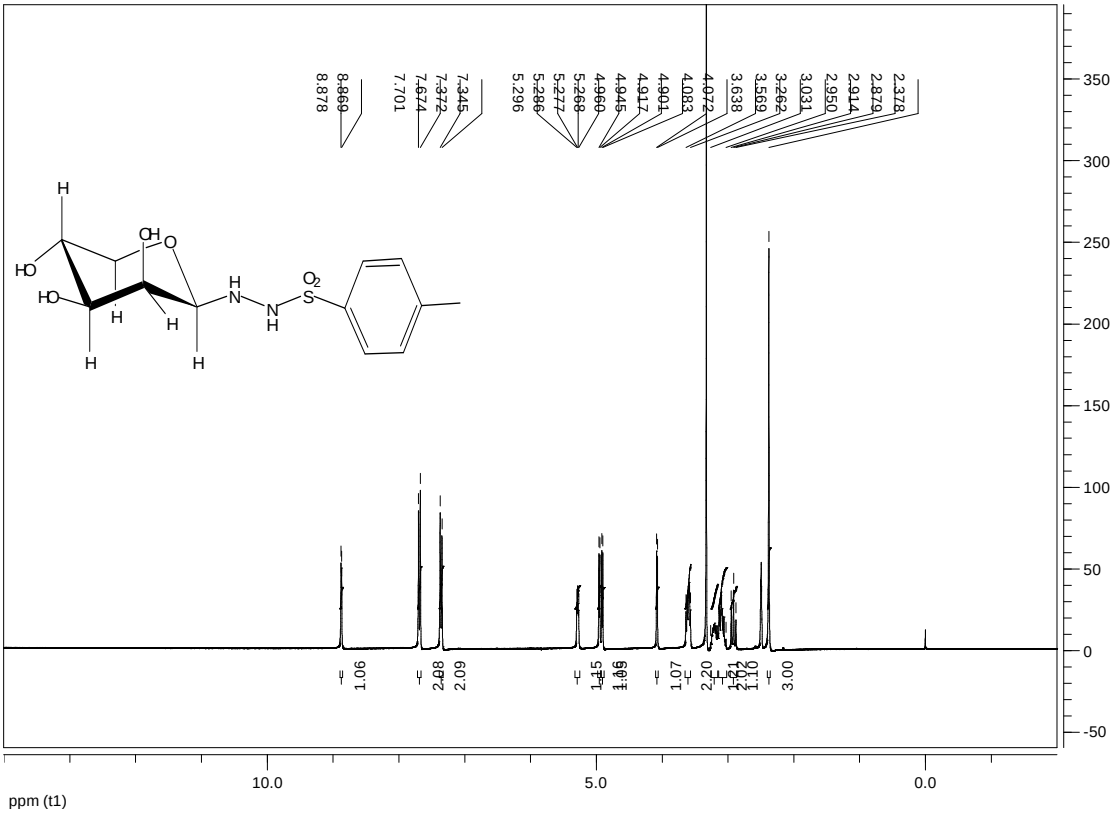
^{1}H NMR *N-D*-galacosyl-*p*-tolylsulfonyhydrazine (catalyst 2):



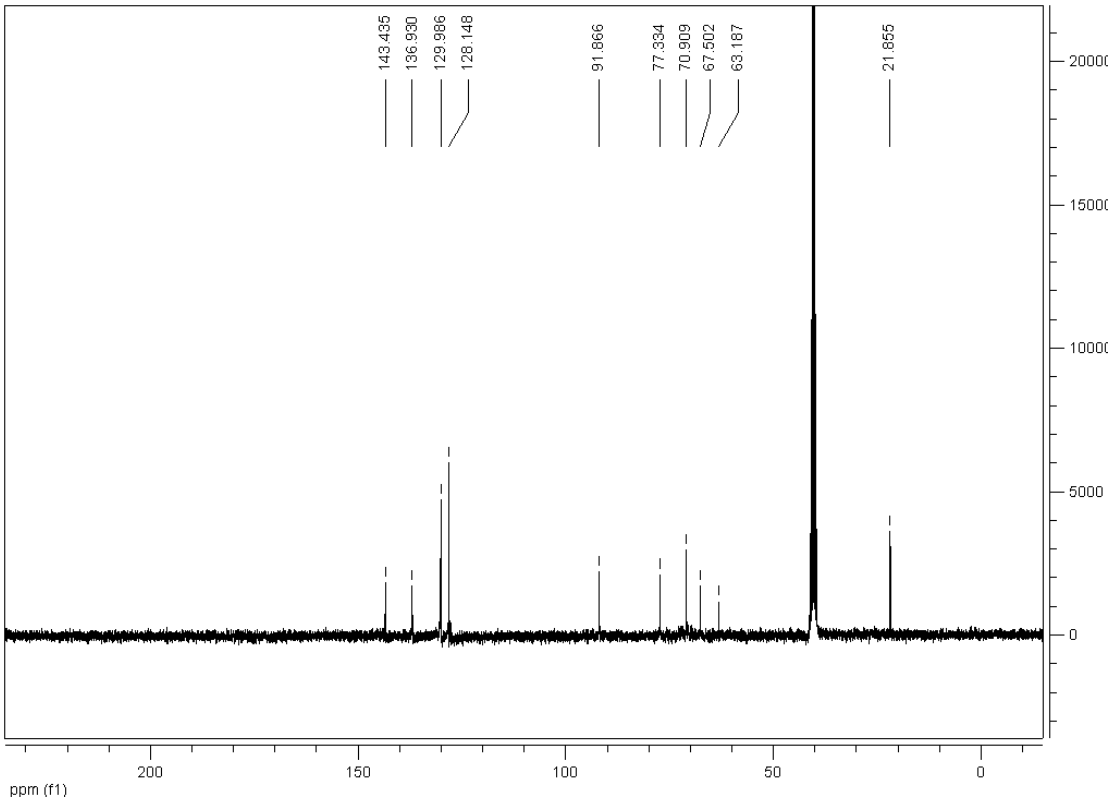
^{13}C NMR *N-D*-galacosyl-*p*-tolylsulfonyhydrazine (catalyst 2):



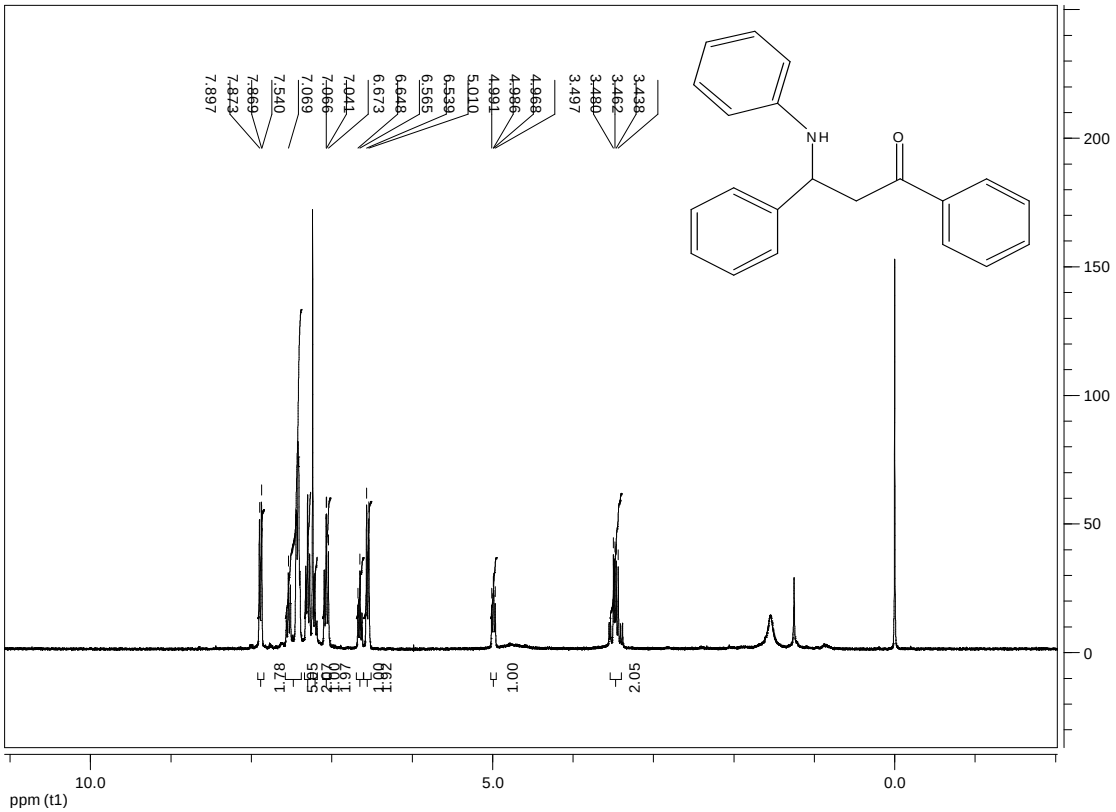
^{1}H NMR *N-D*-xylosyl-*p*-tolylsulfonyhydrazine (catalyst 3):



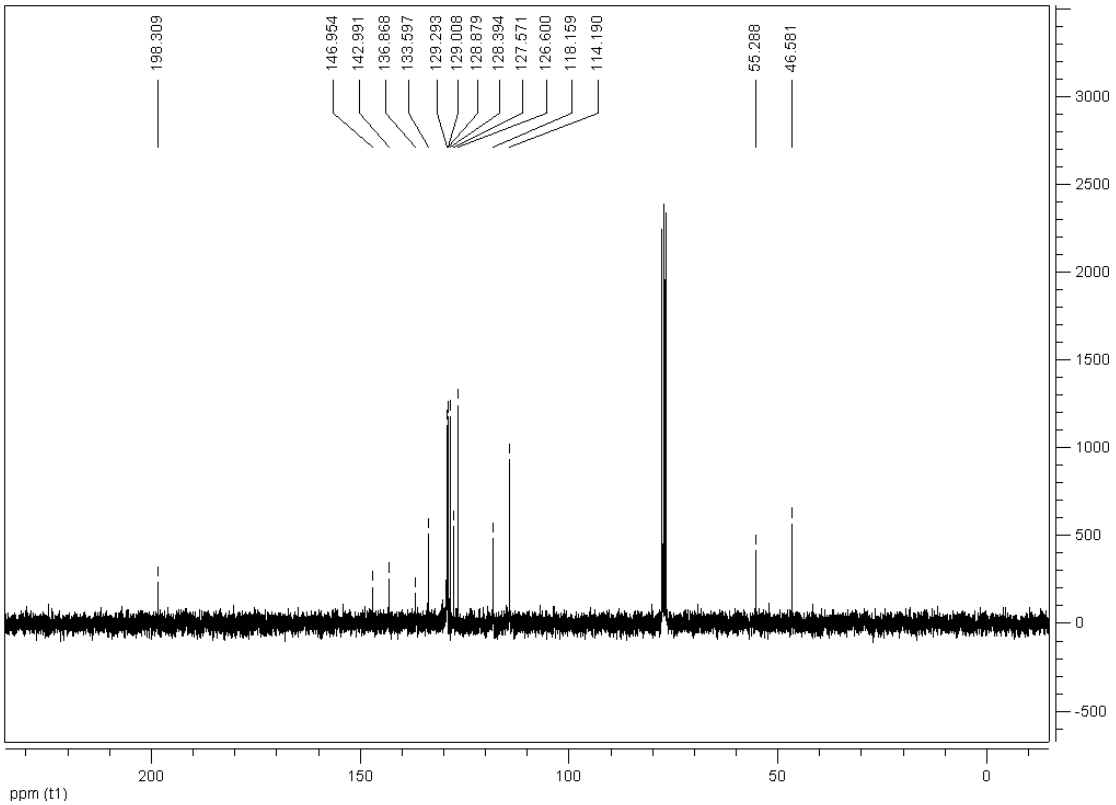
^{13}C NMR *N-D*-xylosyl-*p*-tolylsulfonyhydrazine (catalyst 3):



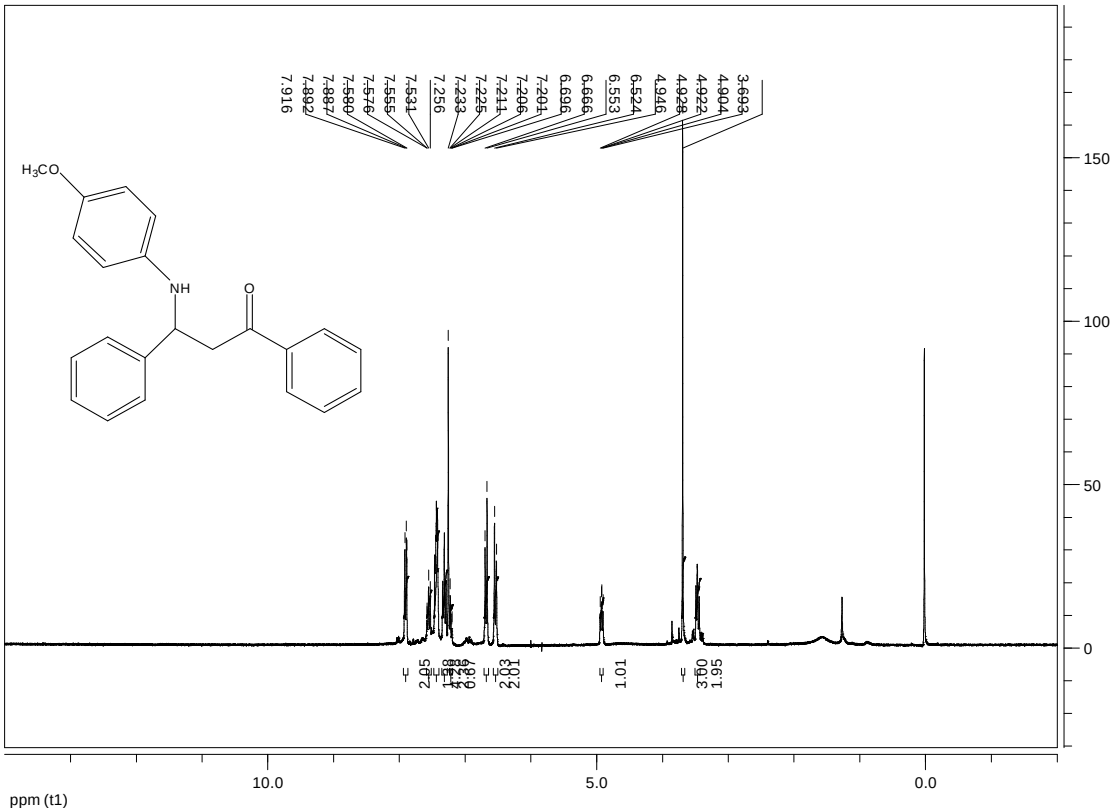
^{1}H NMR 1,4-diphenyl-3-(*N*-phenylamino)propanone (Table 2 entry 1):



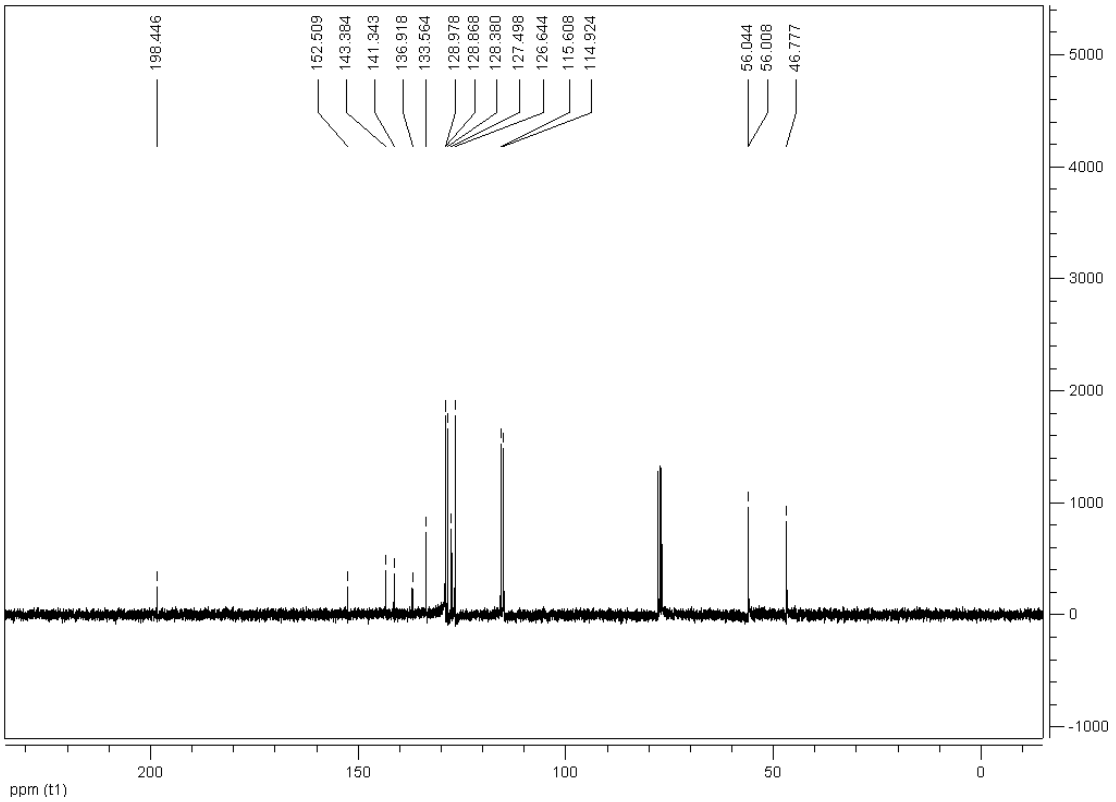
^{13}C NMR 1,4-diphenyl-3-(*N*-phenylamino)propanone (Table 2 entry 1):



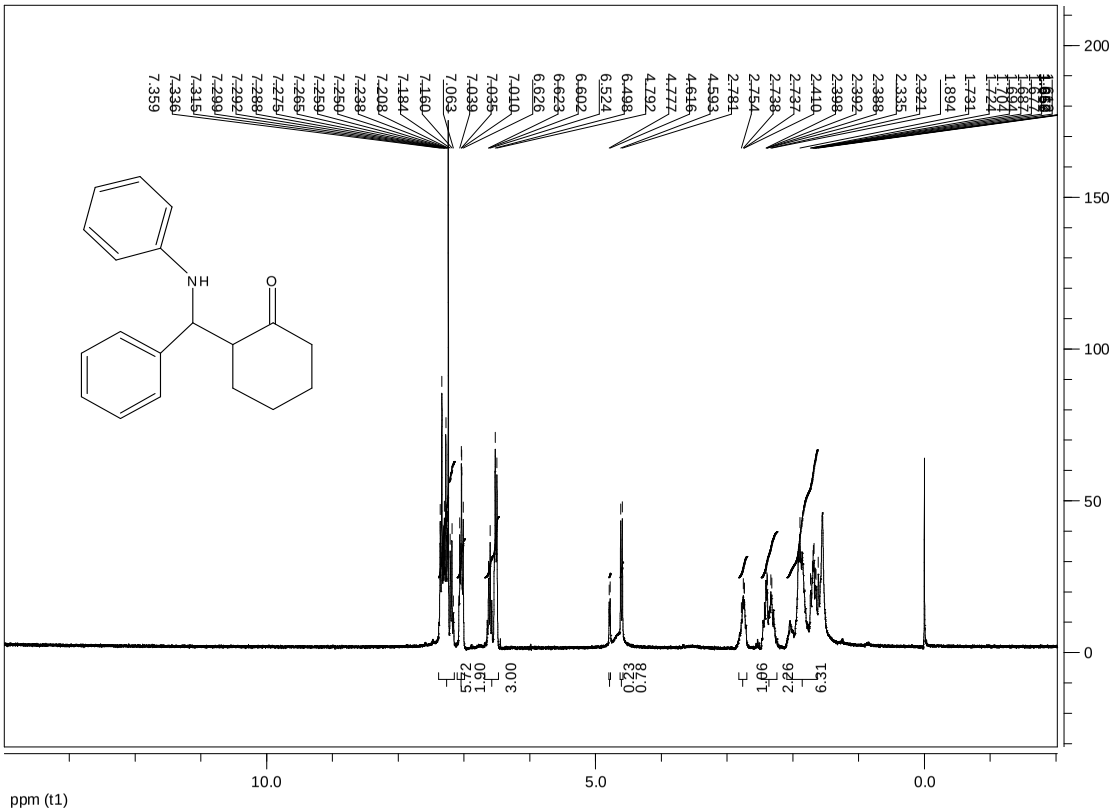
^{1}H NMR 1,4-diphenyl-3-(*N*-*p*-CH_3O-phenylamino)propanone (Table 2 entry 2):



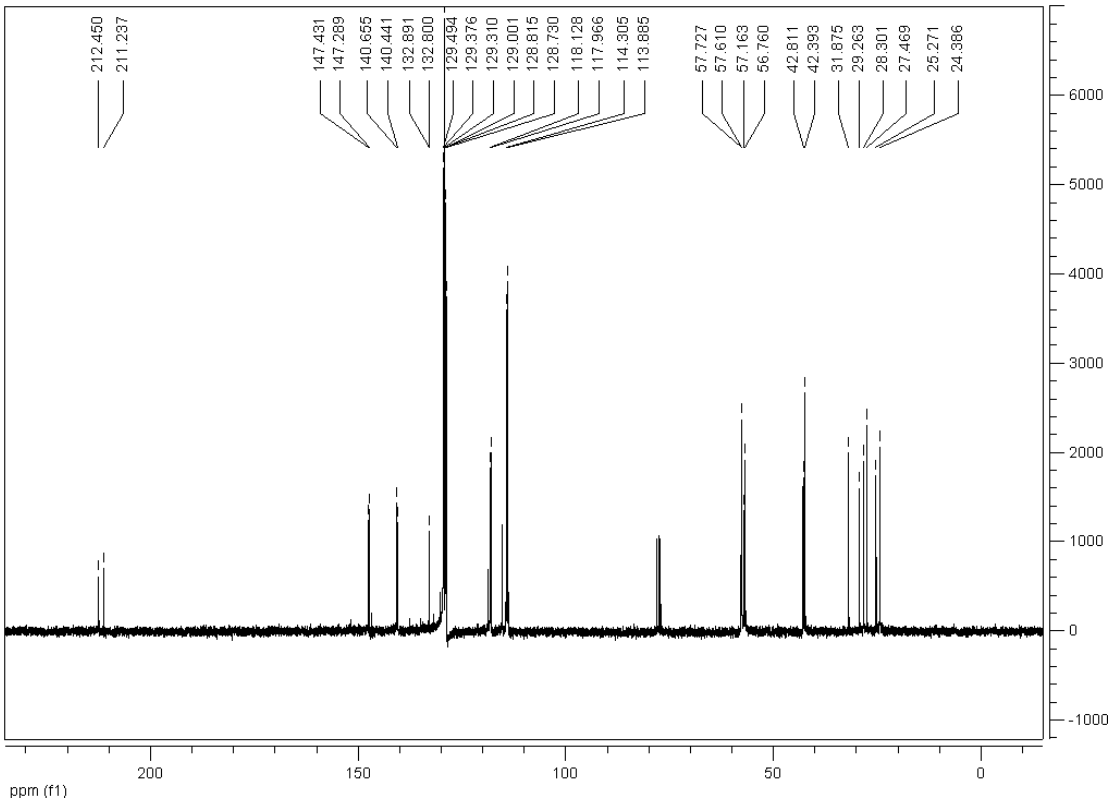
^{13}C NMR 1,4-diphenyl-3-(*N*-*p*-CH_3O-phenylamino)propanone (Table 2 entry 2):



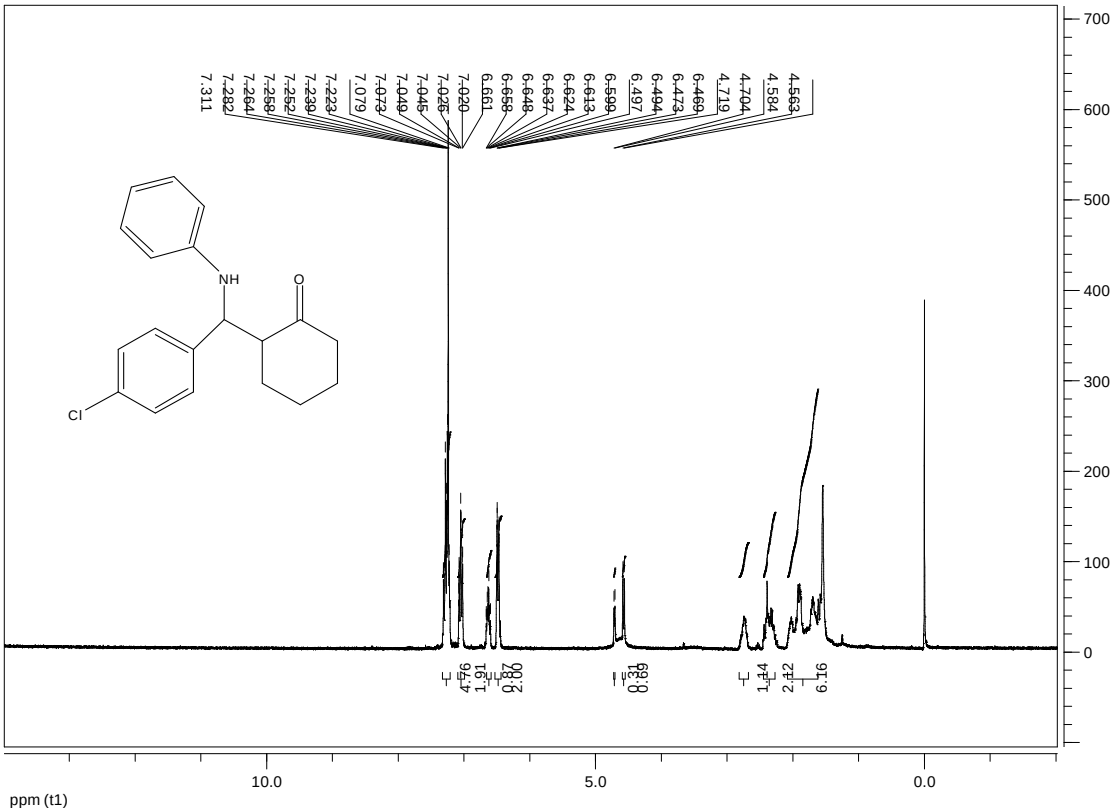
^{1}H NMR 2-[1’-(*N*-phenylamino)-1’-phenyl]methylcyclohexanone (Table 2 entry 3):



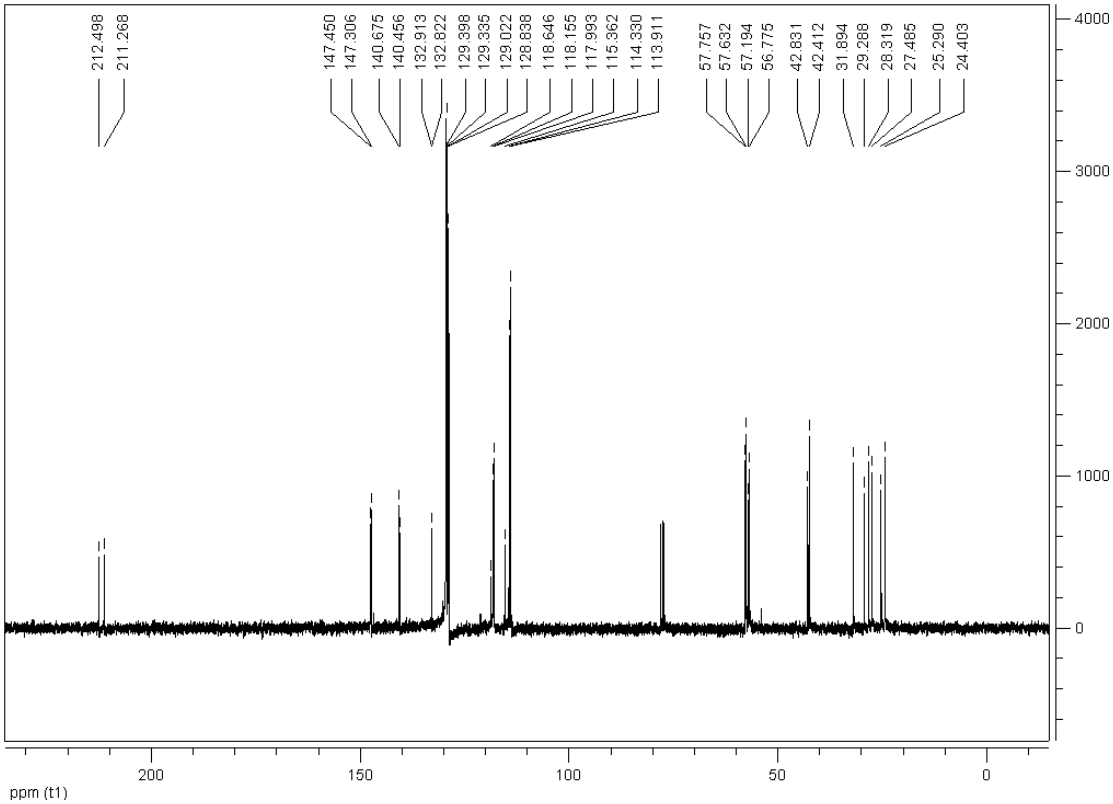
^{13}C NMR 2-[1’-(*N*-phenylamino)-1’-phenyl]methylcyclohexanone (Table 2 entry 3):



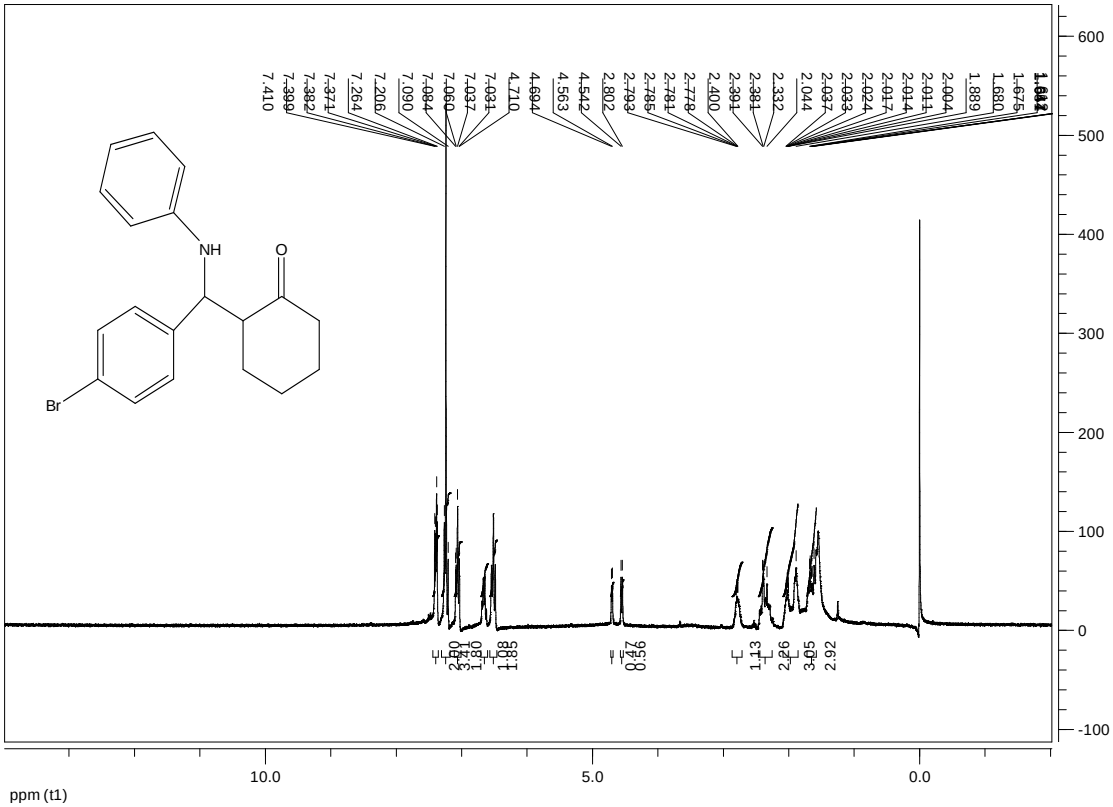
^{1}H NMR 2-[1'-(*N*-phenylamino)-1'-(*p*-Cl-phenyl)]methylcyclohexanone (Table 2 entry 4):



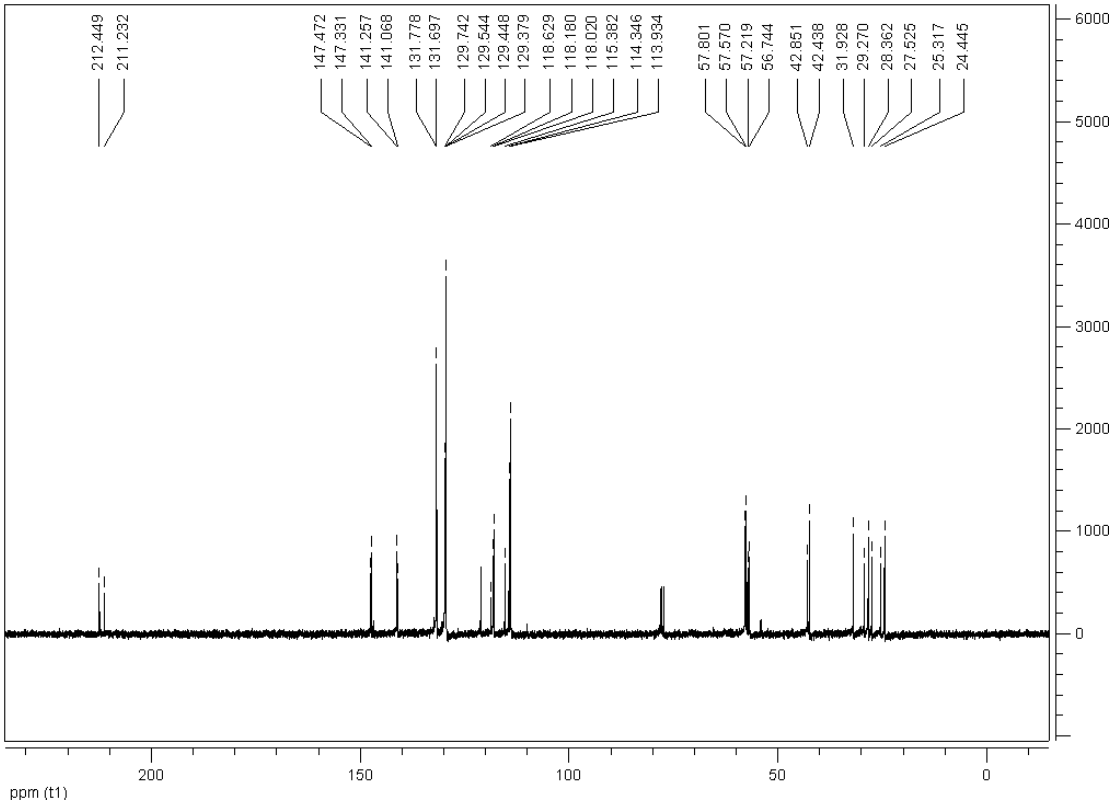
^{13}C NMR 2-[1'-(*N*-phenylamino)-1'-(*p*-Cl-phenyl)]methylcyclohexanone (Table 2 entry 4):



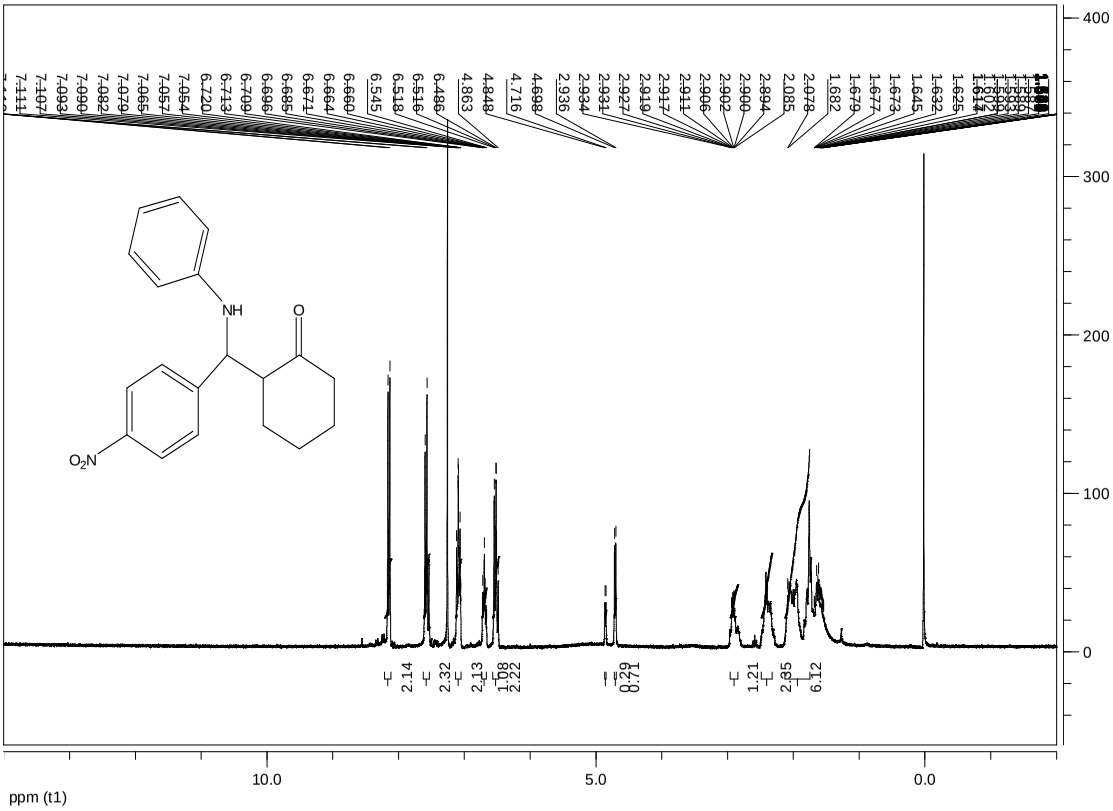
^{1}H NMR 2-[1'-(*N*-phenylamino)-1'(-*p*-Br-phenyl)]methylcyclohexanone (Table 2 entry 5):



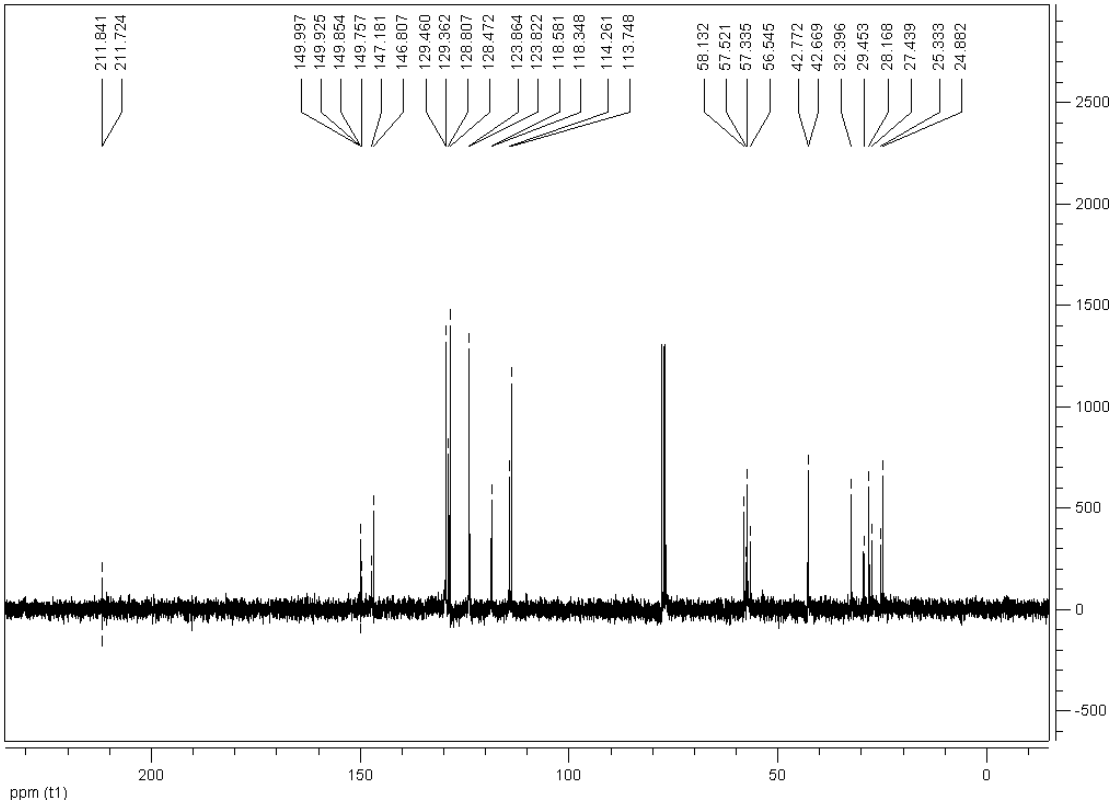
^{13}C NMR 2-[1'-(*N*-phenylamino)-1'(-*p*-Br-phenyl)]methylcyclohexanone (Table 2 entry 5):



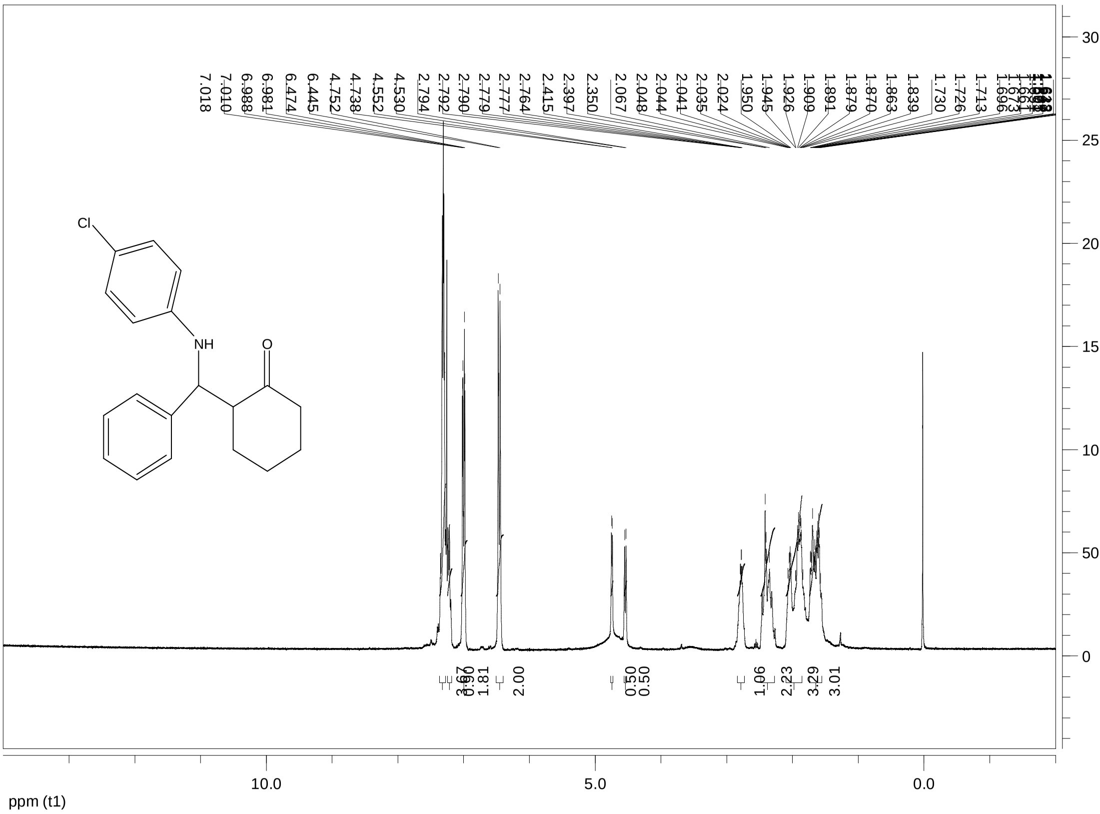
^{1}H NMR 2-[1'-(*N*-phenylamino)-1'(-*p*-NO_2-phenyl)]methylcyclohexanone(Table 2 entry 6):



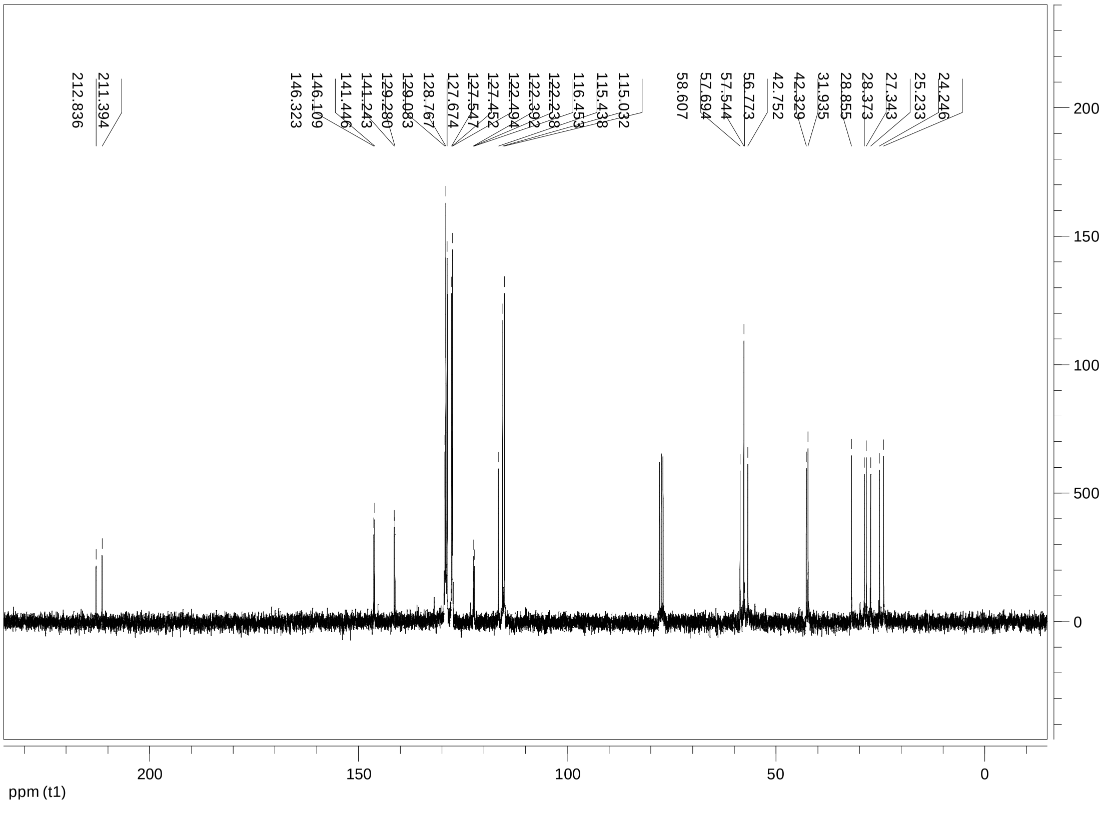
^{13}C NMR 2-[1'-(*N*-phenylamino)-1'(-*p*-NO_2-phenyl)]methylcyclohexanone(Table 2 entry 6):



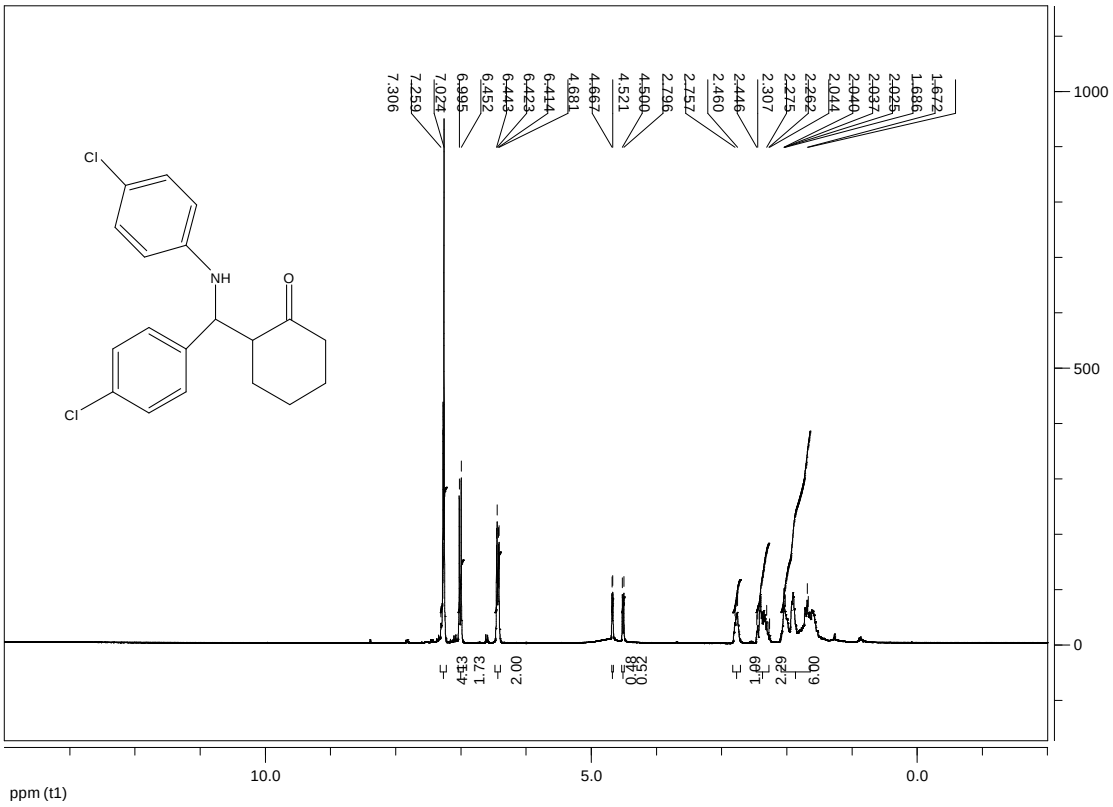
^{1}H NMR 2-[1’-(*N*-*p*-Cl-phenylamino)-1’-phenyl]methylcyclohexanone (Table 2 entry 7):



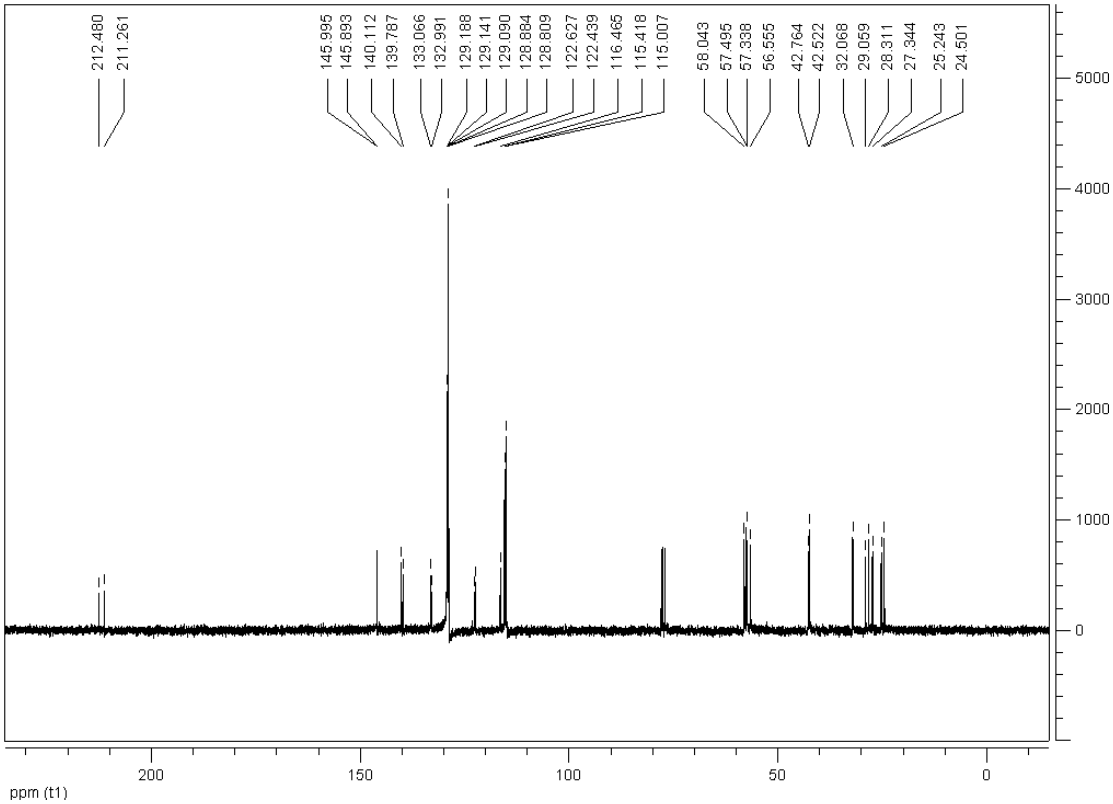
^{13}C NMR 2-[1’-(*N*-*p*-Cl-phenylamino)-1’-phenyl]methylcyclohexanone (Table 2 entry 7):



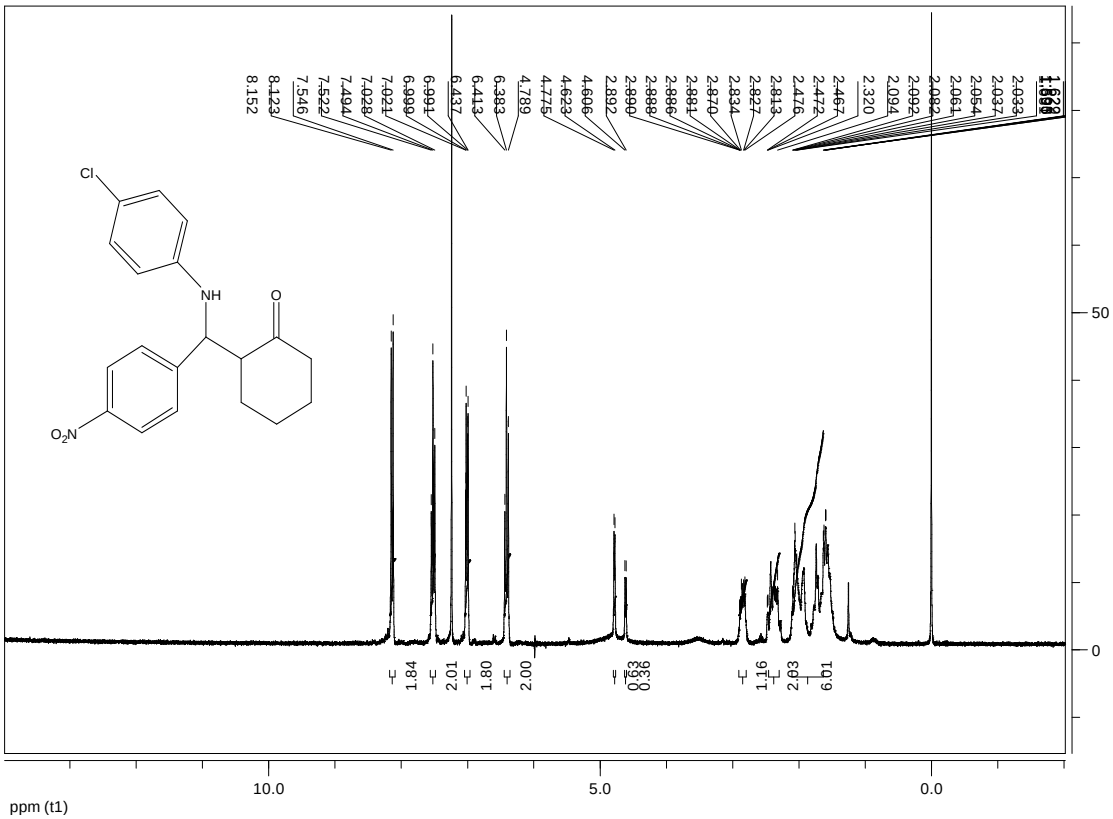
^{1}H NMR 2-[1'- (*N* - *p* -Cl-phenylamino) - 1'- (*p*-Cl-phenyl)] methylcyclohexanone (Table 2 entry 8):



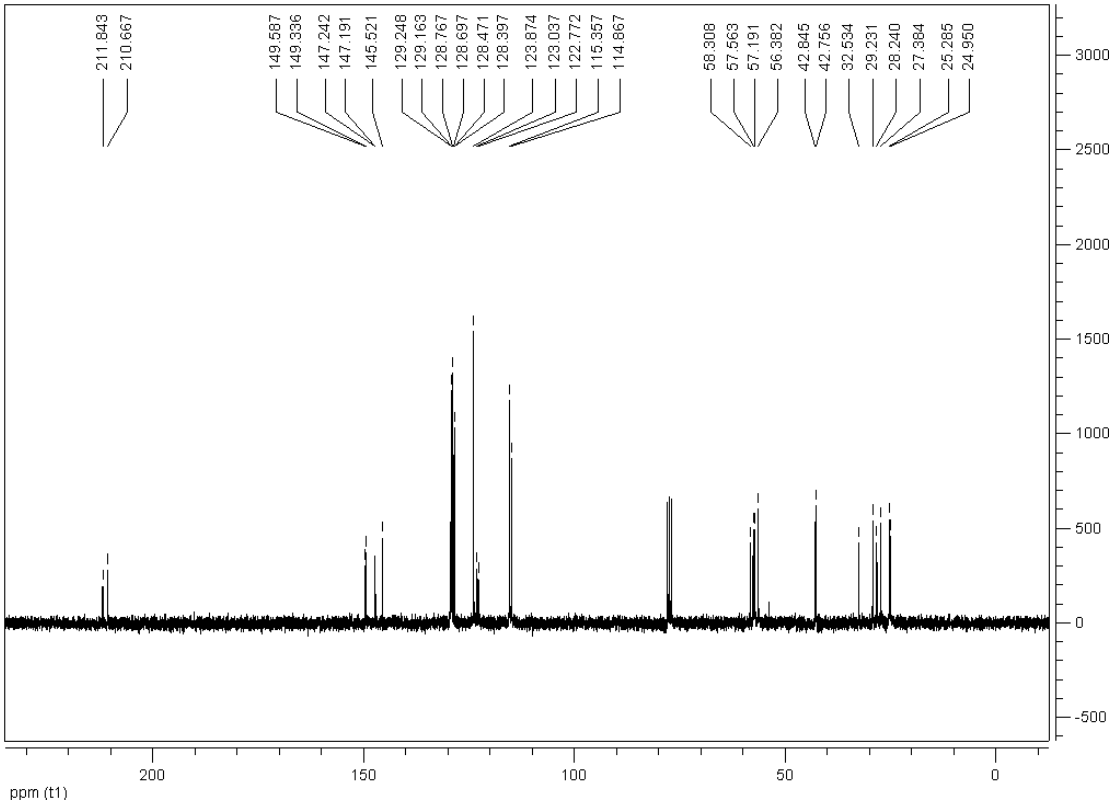
^{13}C NMR 2-[1'-(*N* - *p* -Cl-phenylamino) - 1'- (*p*-Cl-phenyl)] methylcyclohexanone (Table 2 entry 8):



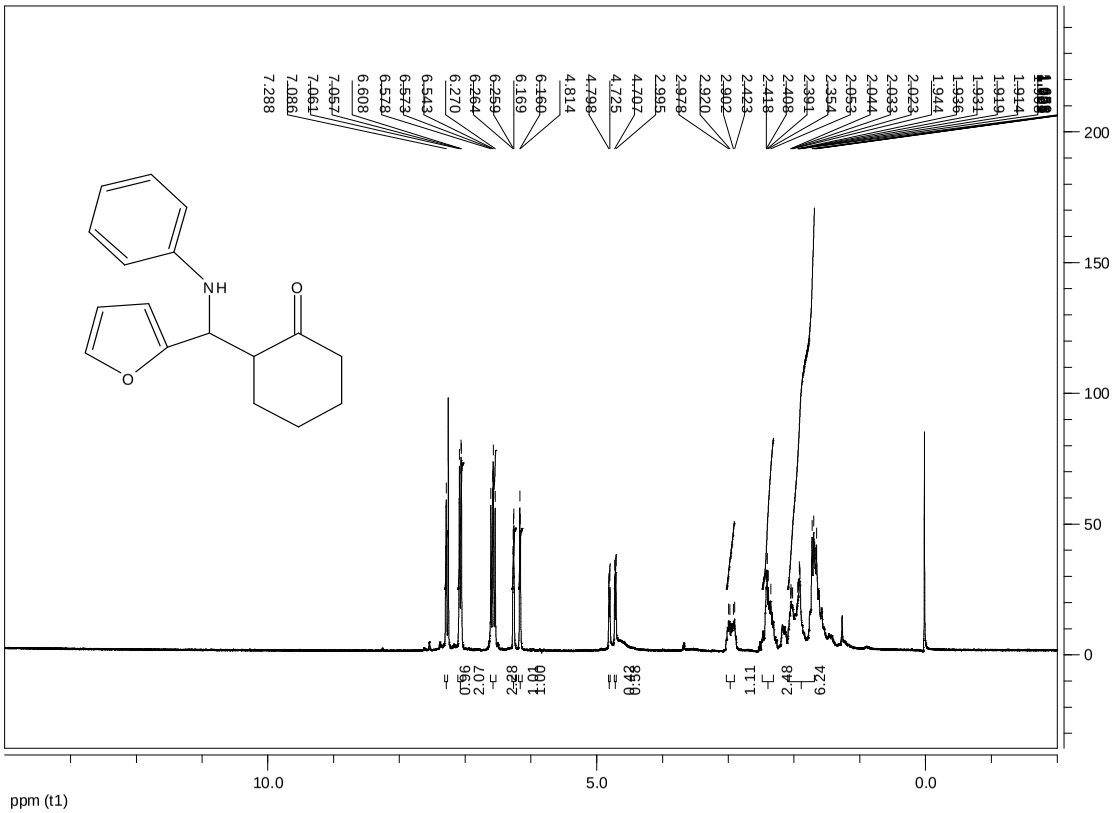
^{1}H NMR 2-[1'- (*N*-*p*-Cl-phenylamino) -1'-(*p*-NO_2-phenyl)] methylcyclohexanone (Table 2 entry 9):



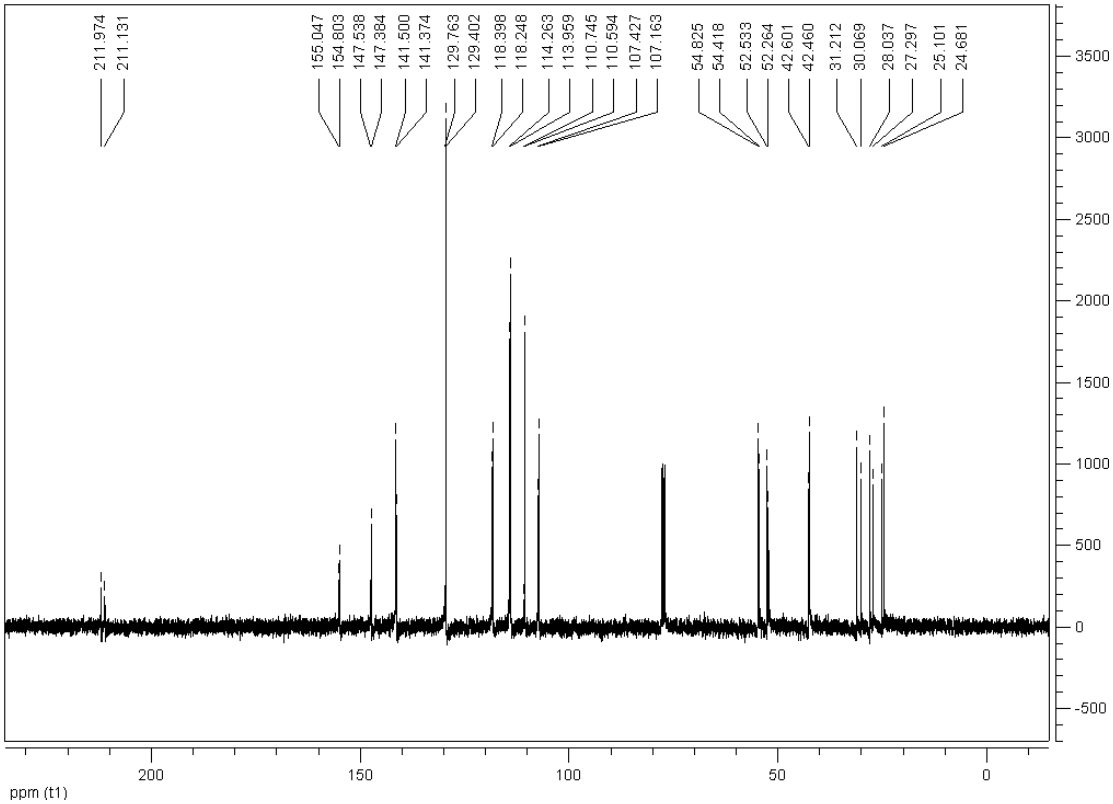
^{13}C NMR 2-[1'- (*N*-*p*-Cl-phenylamino) -1'-(*p*-NO_2-phenyl)] methylcyclohexanone (Table 2 entry 9):



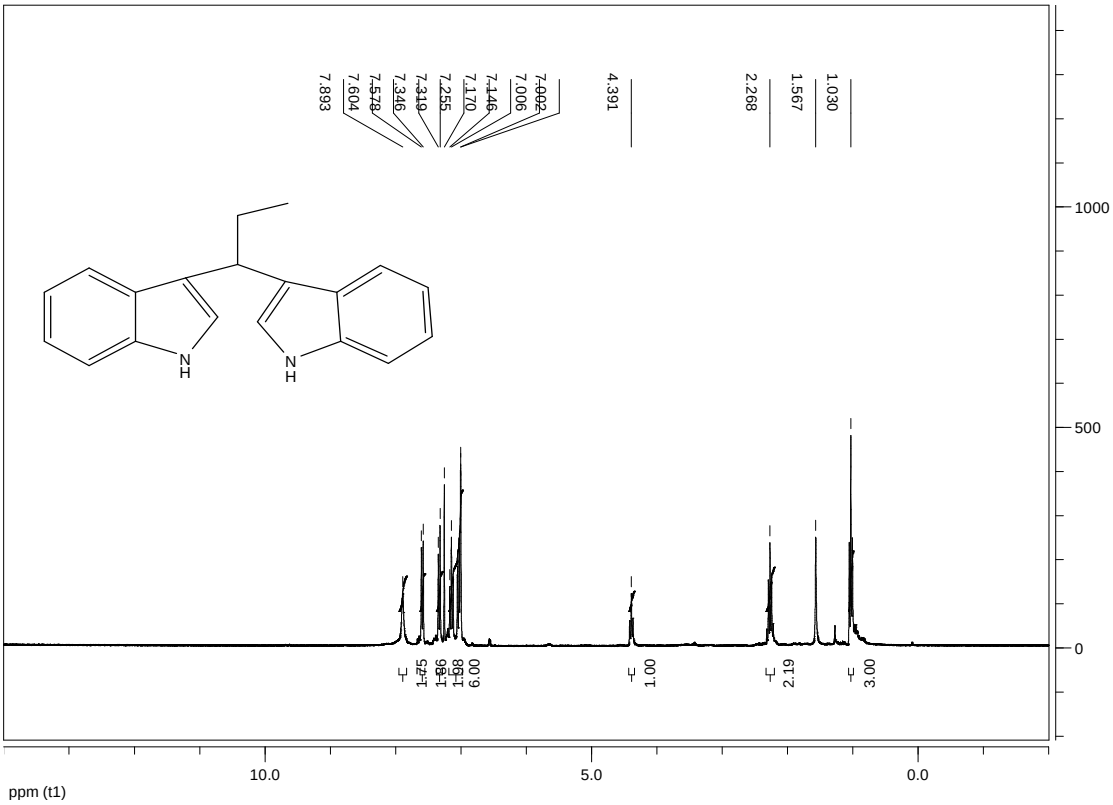
^{1}H NMR 2-[1'-(2-furyl)-1'-(*N*-phenylamino)]methylcyclohexanone (Table 2 entry 12):



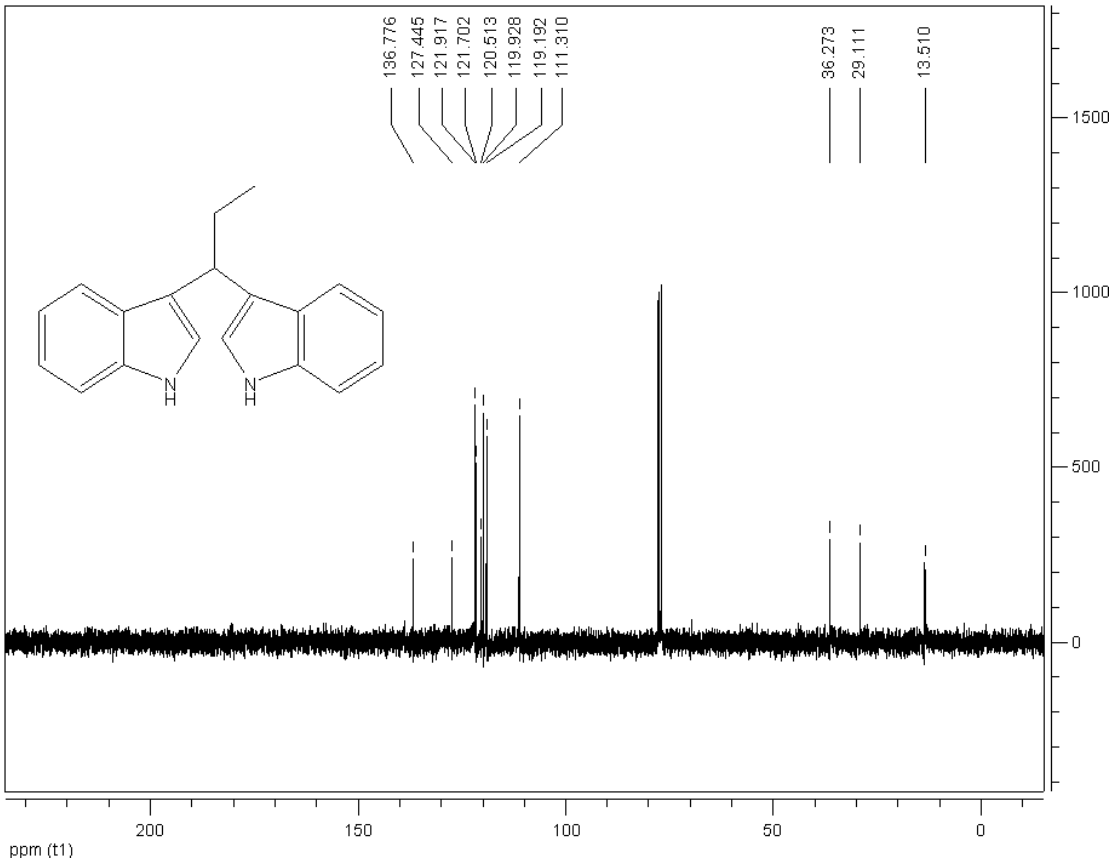
^{13}C NMR 2-[1'-(2-furyl)-1'-(*N*-phenylamino)]methylcyclohexanone (Table 2 entry 12):



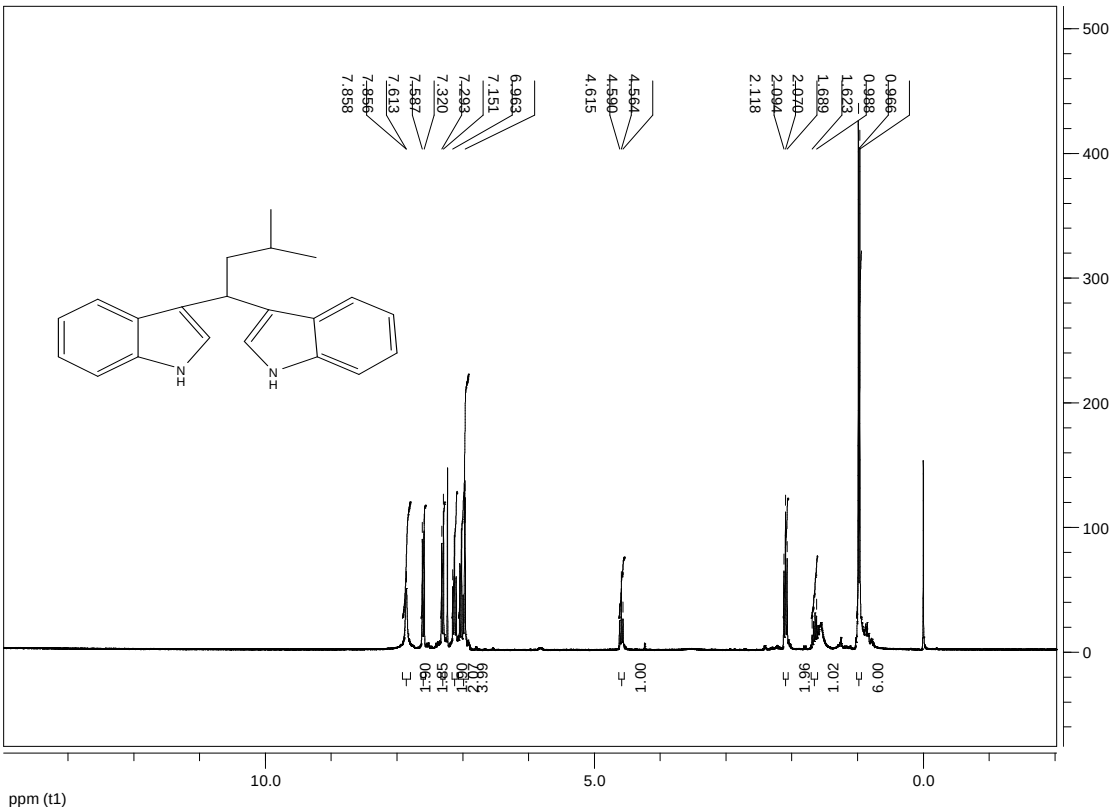
^{1}H NMR 1,1-bis-3-indolyl propane (Table 4, entry 1)



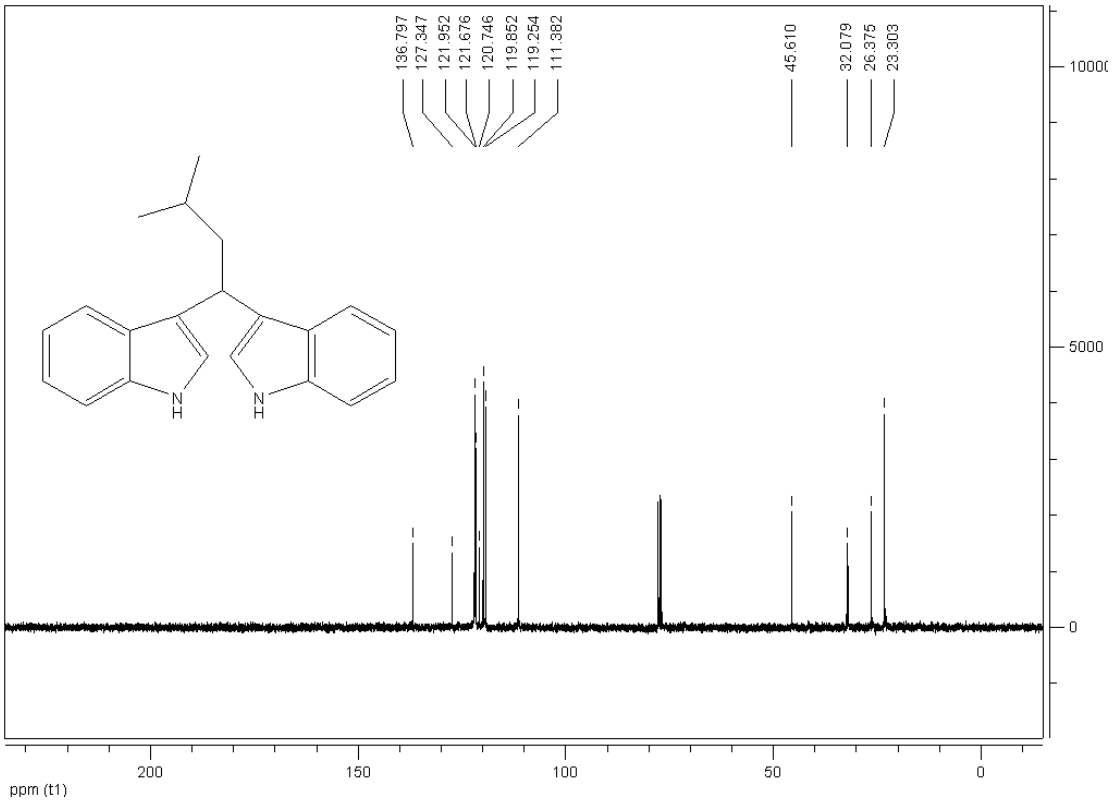
^{13}C NMR 1,1-bis-3-indolyl propane (Table 4, entry 1)



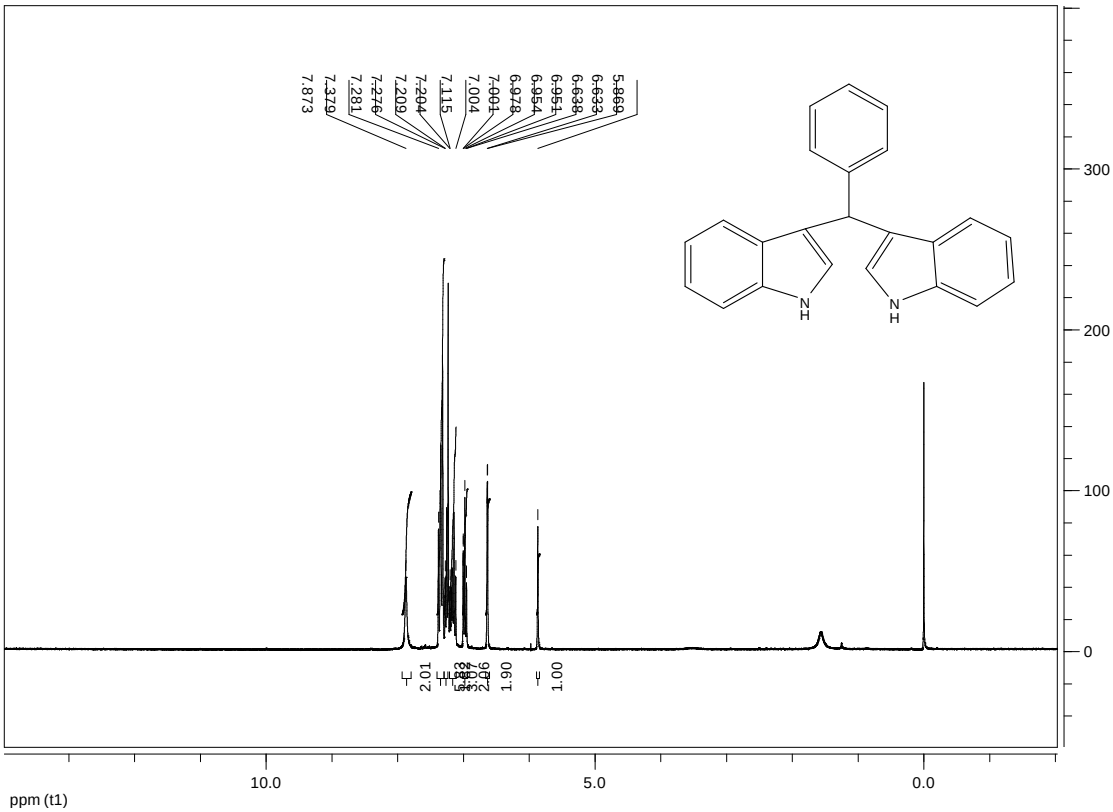
^{1}H NMR 3-methyl-1,1-bis-3-indolyl- butane (Table 4, entry 3)



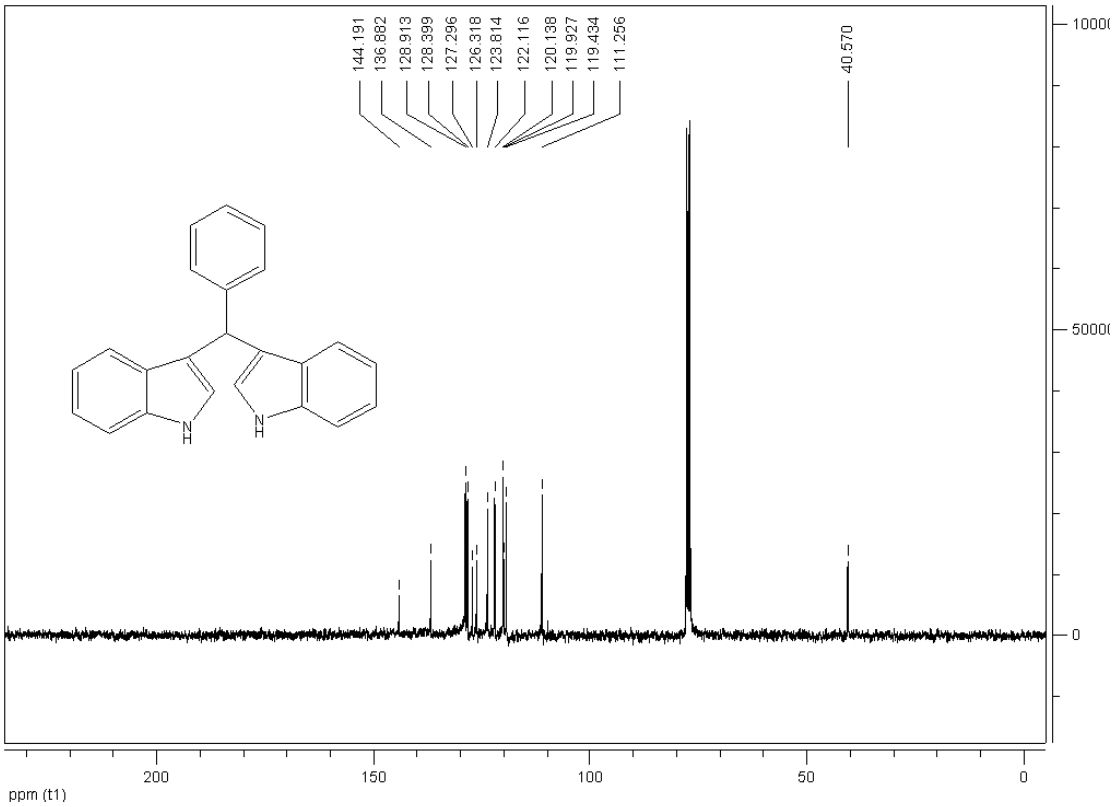
^{13}C NMR 3-methyl-1,1-bis-3-indolyl- butane (Table 4, entry 3)



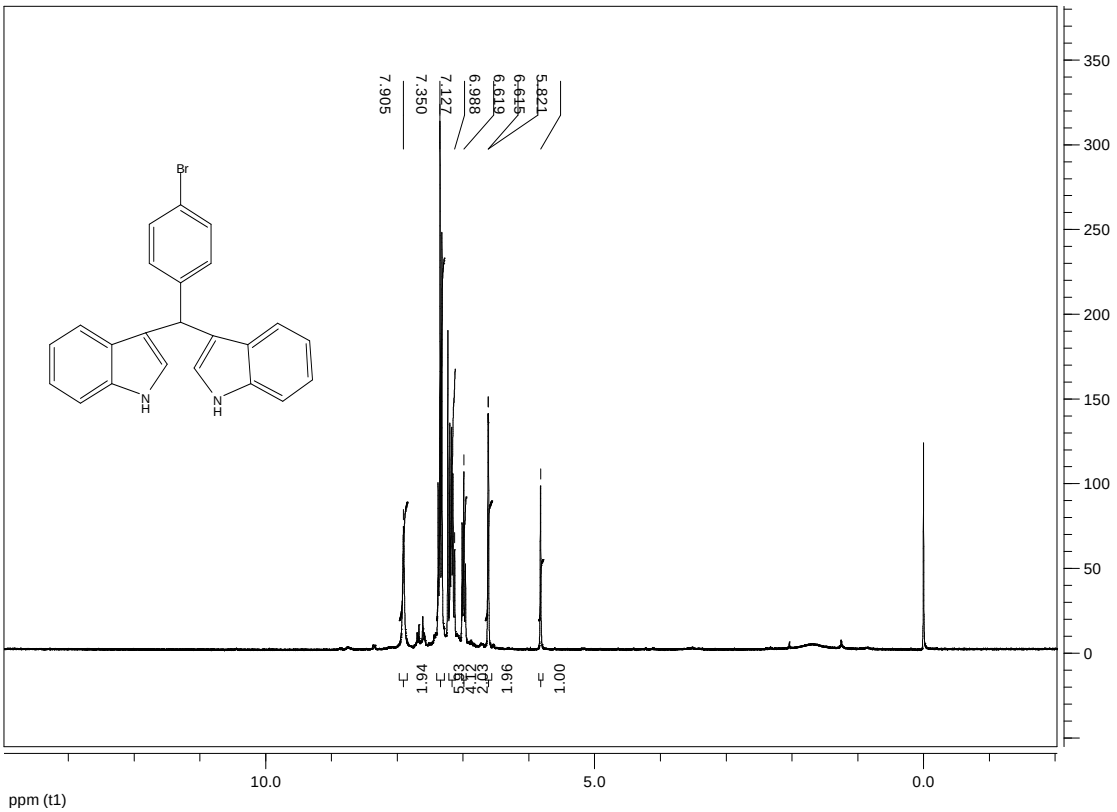
^{1}H NMR 3,3′- bis(indoly) - Phenylmethane (Table 4, entry 4)



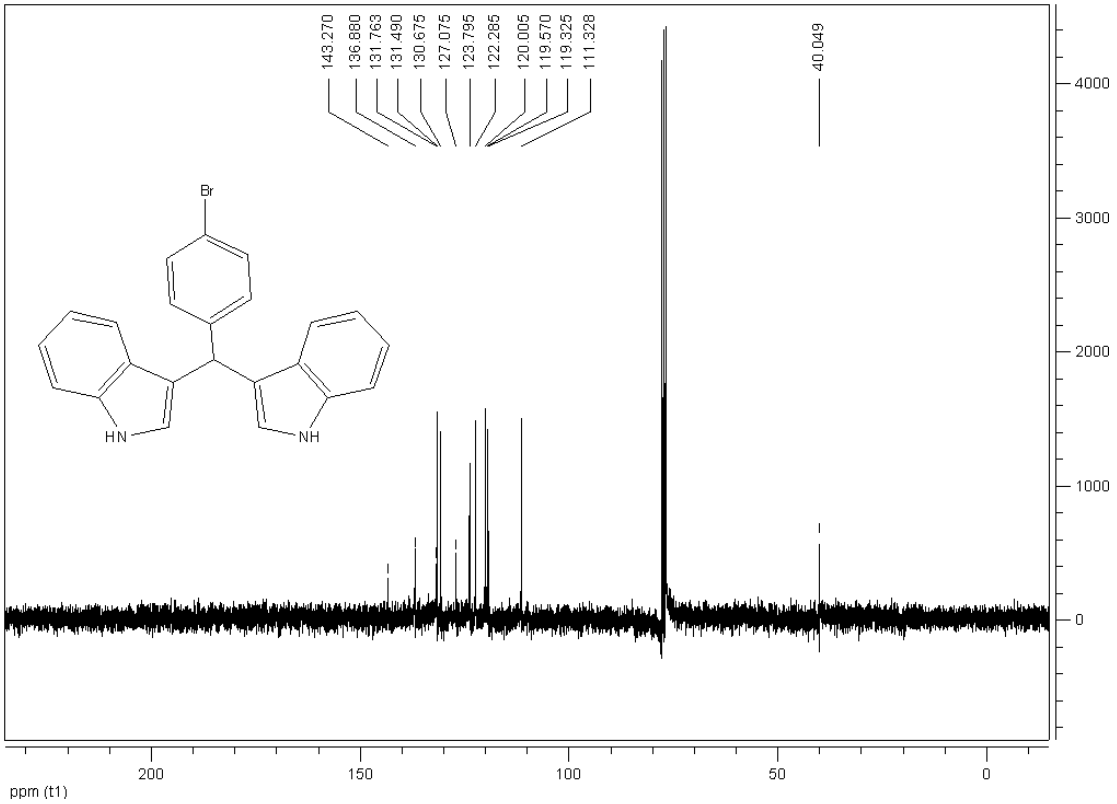
^{13}C NMR 3,3′- bis(indoly) - Phenylmethane (Table 4, entry 4)



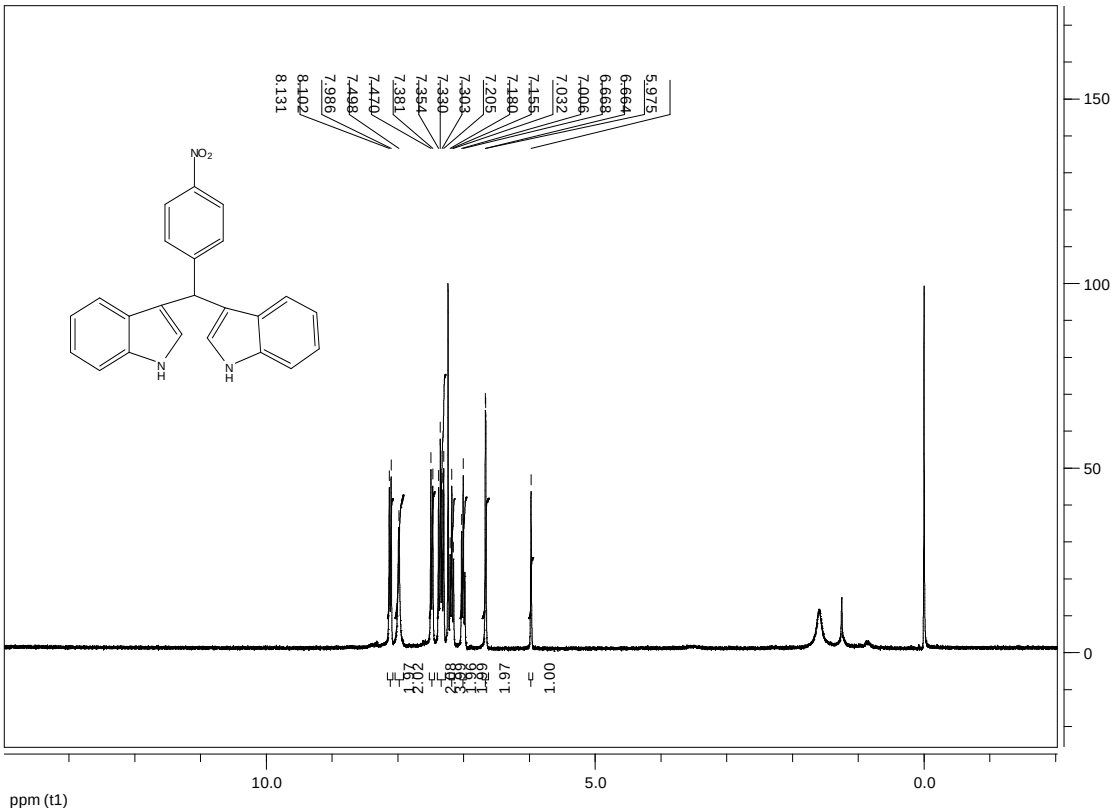
^{1}H NMR 3,3′-bis(indoly)-(4-Bromo -Phenyl)methane (Table 4, entry 6)



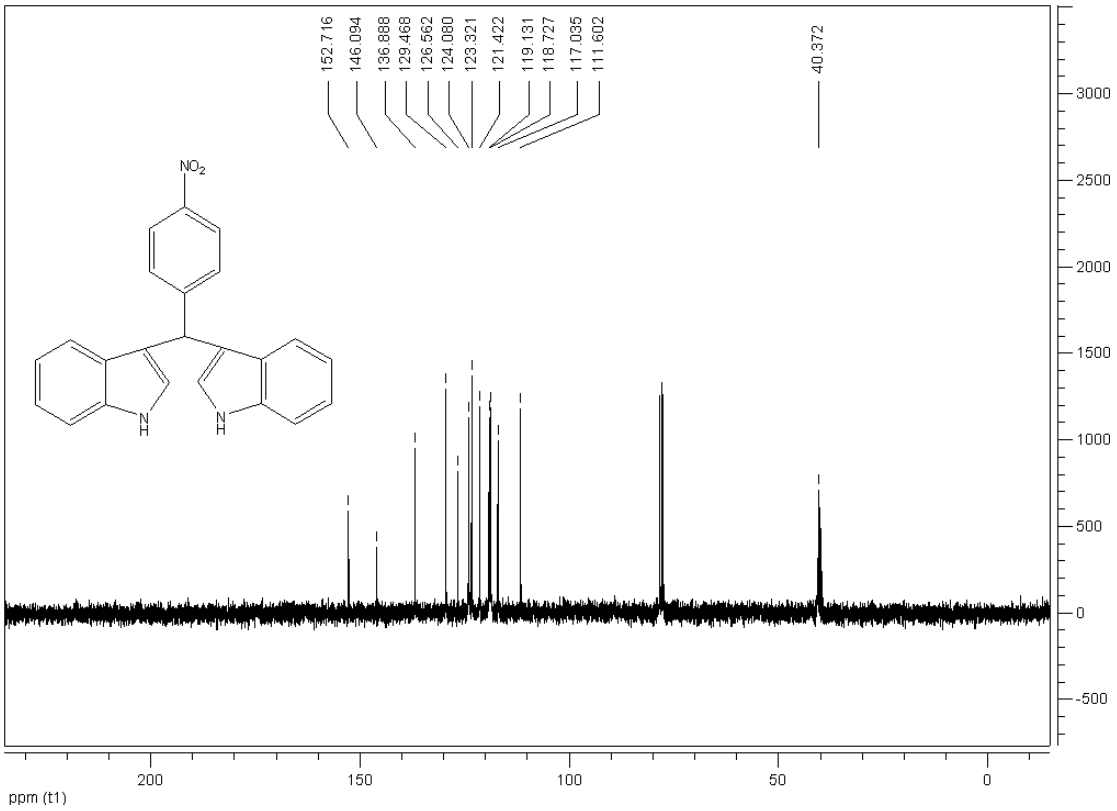
^{13}C NMR 3,3′-bis(indoly)-(4-Bromo -Phenyl)methane (Table 4, entry 6)



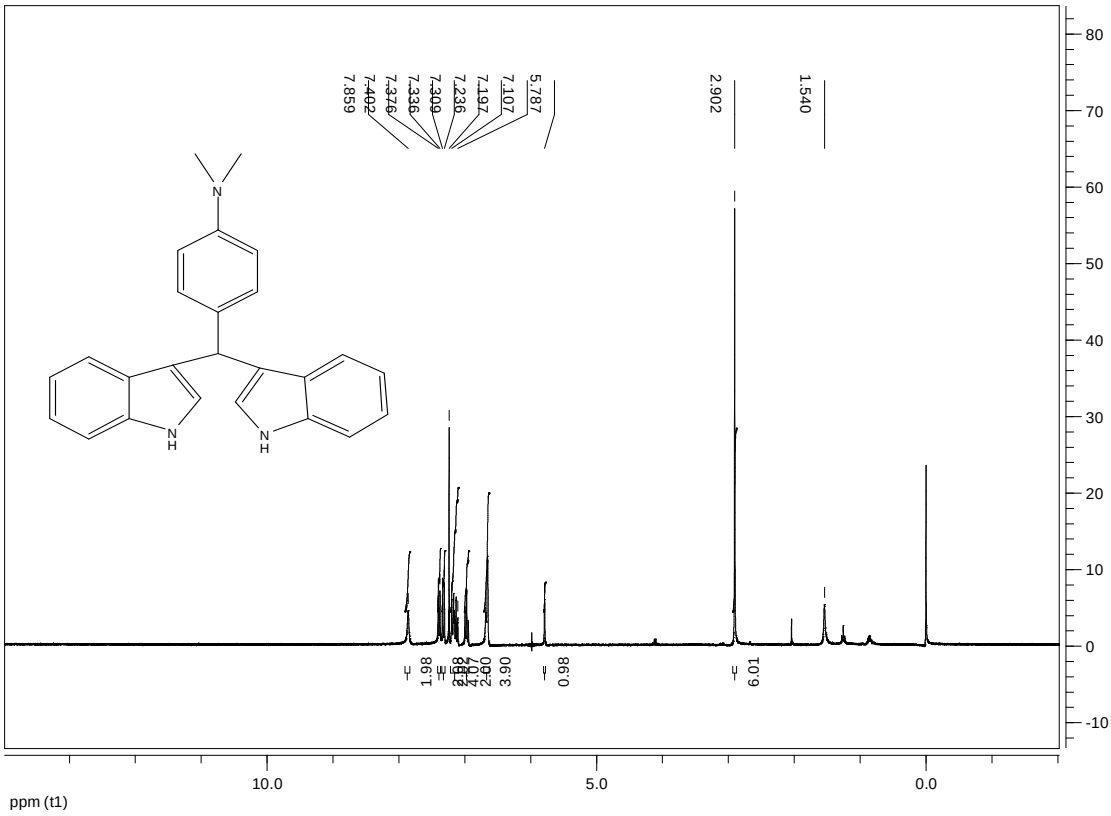
^{1}H NMR 3,3′- bis(indoly)-(4- Nitro -Phenyl)methane (Table 4, entry 7)



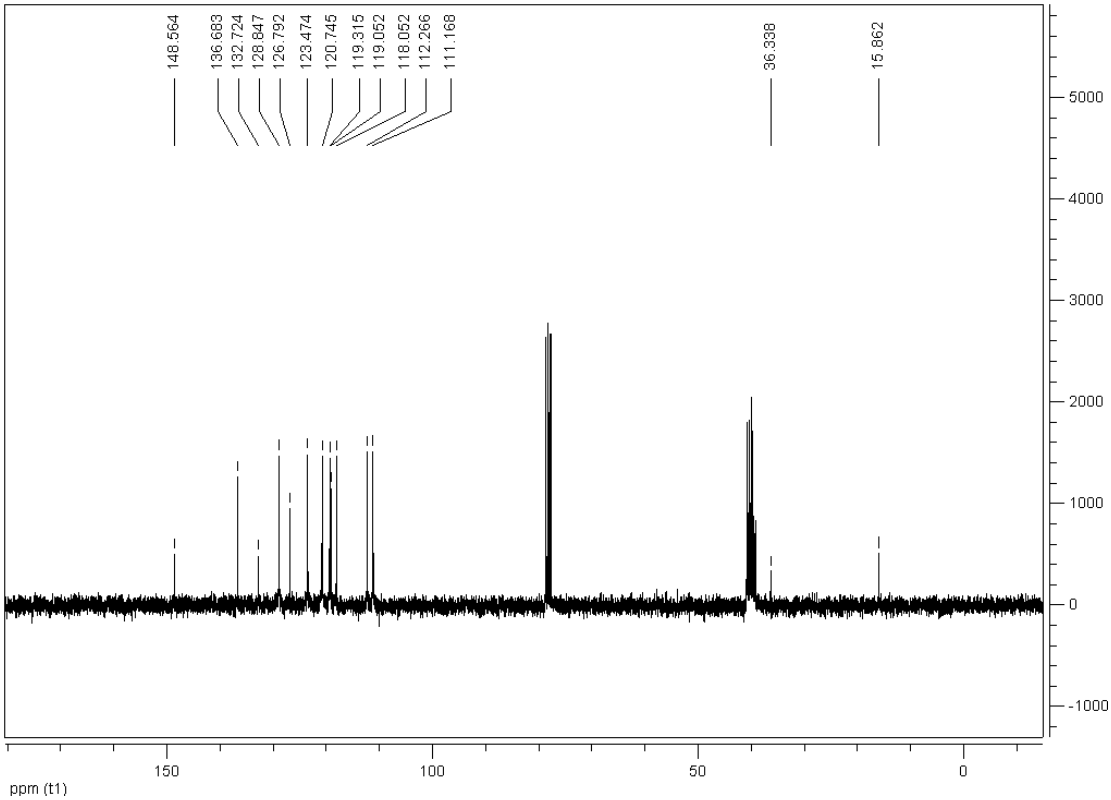
^{13}C NMR 3,3′- bis(indoly)-(4- Nitro -Phenyl)methane (Table 4, entry 7)



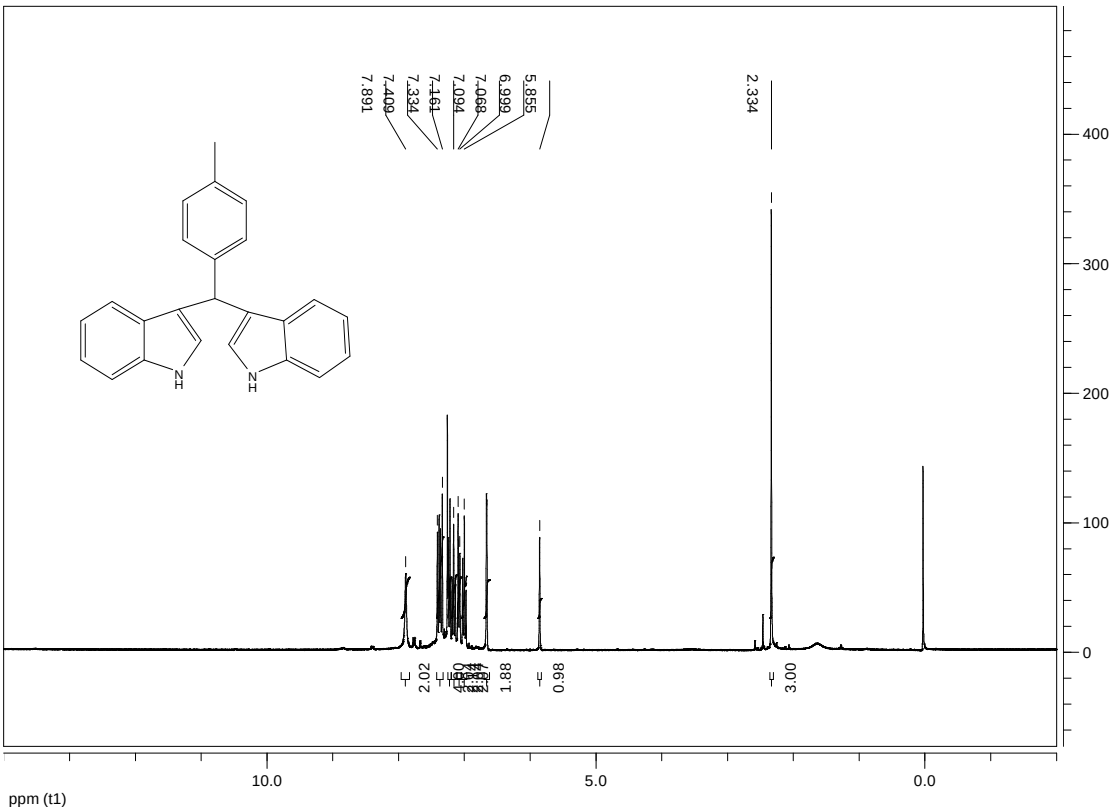
^{1}H NMR 3,3′- bis(indoly)-[4-(*N*,*N*′-di-methylamino)-Phenyl]methane (Table 4, entry 10)



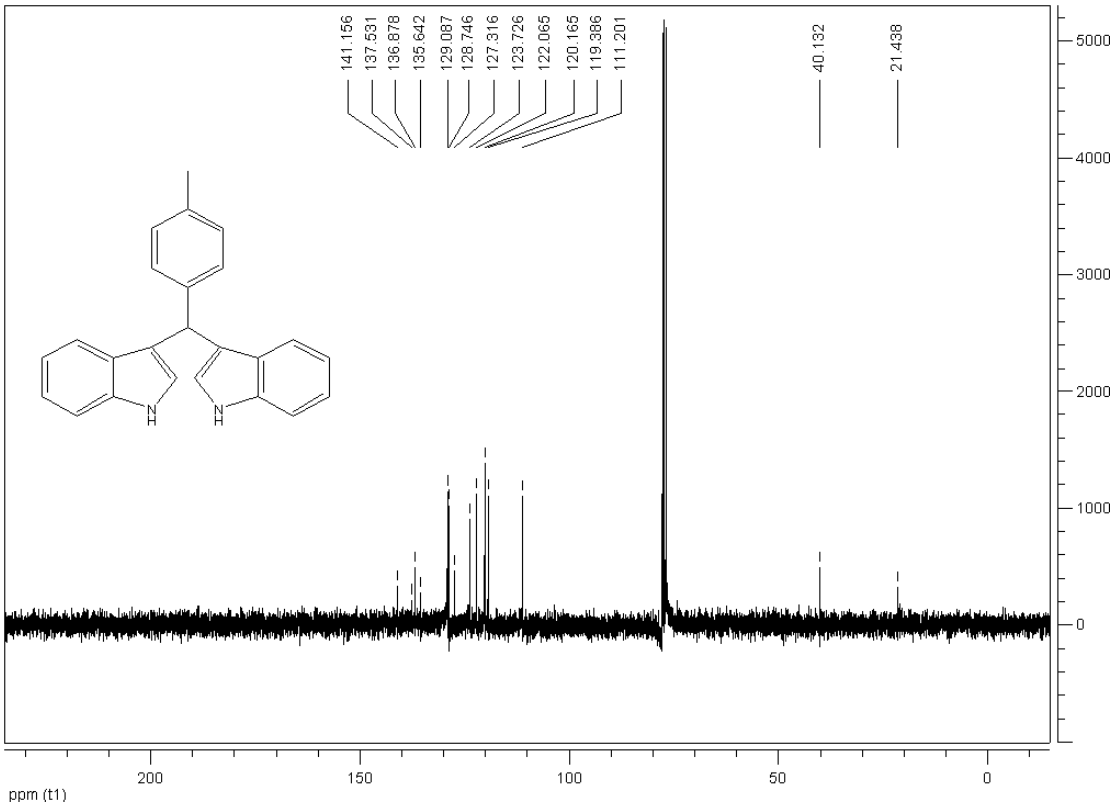
^{13}C NMR 3,3′- bis(indoly)-[4-(*N*,*N*′-di-methylamino)-Phenyl]methane (Table 4, entry 10)



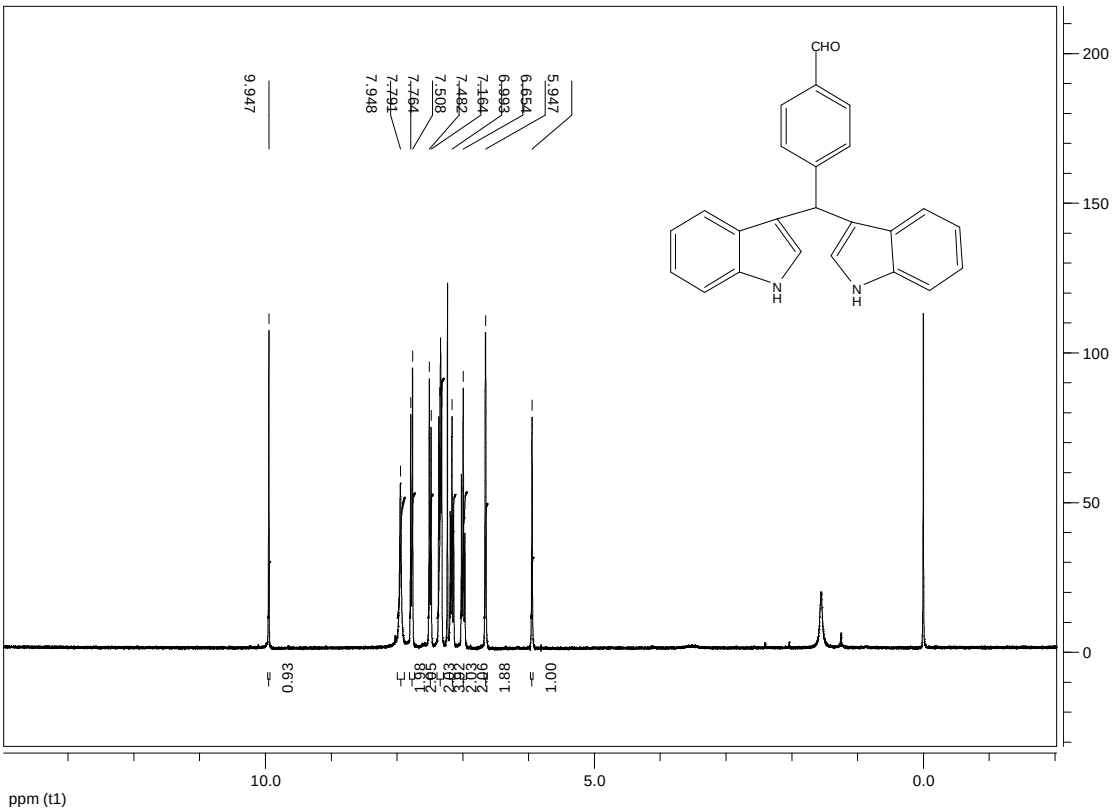
^{1}H NMR 3,3′-bis(indolyl)-(4-methyl-phenyl)methane (Table 4, entry 12)



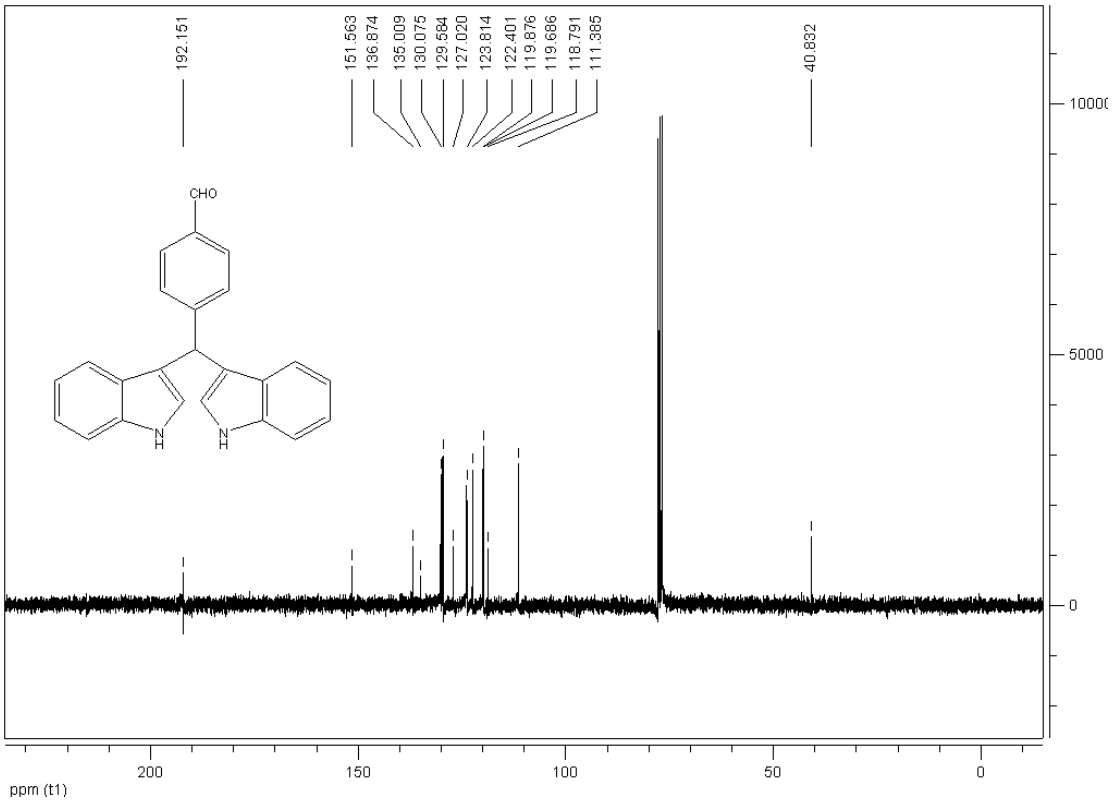
^{13}C NMR 3,3′-bis(indolyl)-(4-methyl-phenyl)methane (Table 4, entry 12)



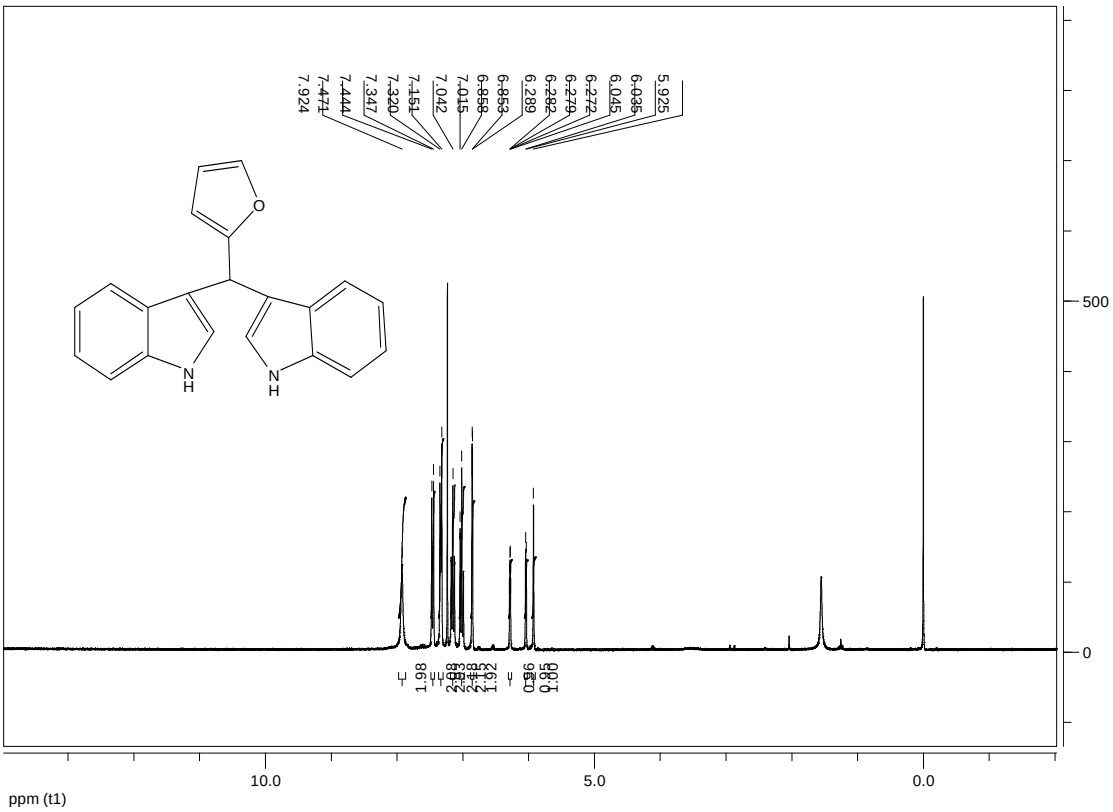
^{1}H NMR 3,3′-bis(indolyl)-(4-formyl-phenyl)methane (Table 4, entry 13)



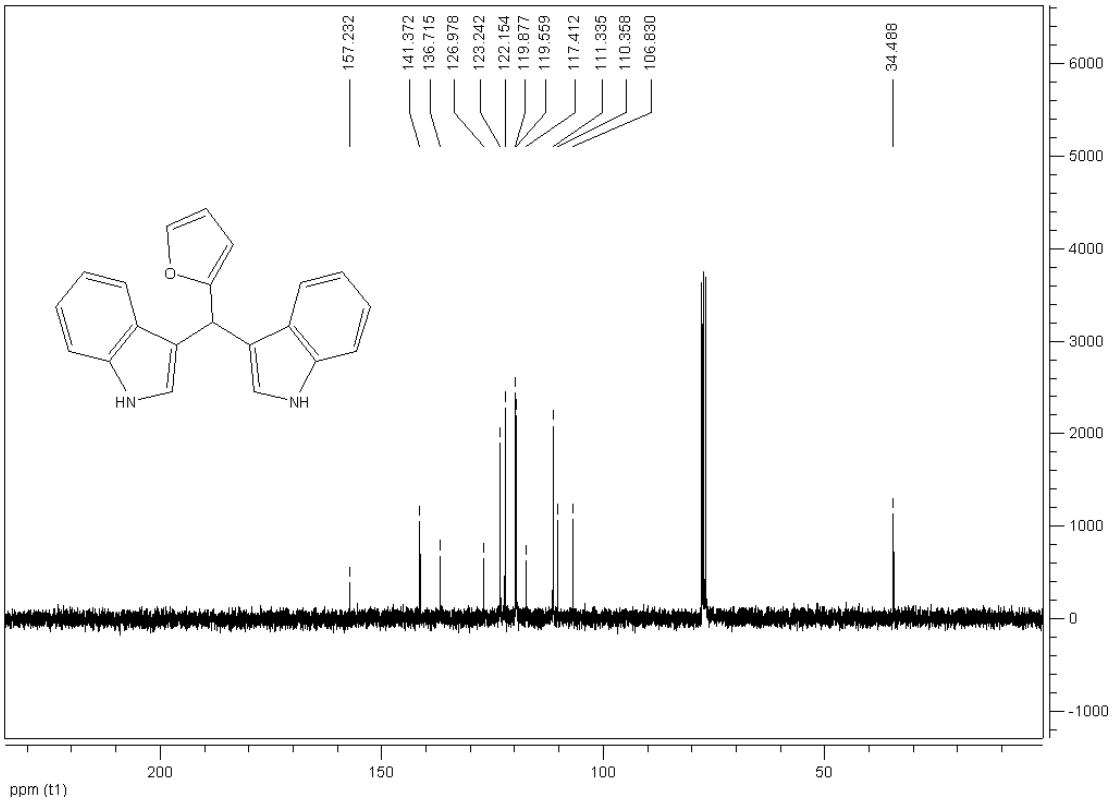
^{13}C NMR 3,3′-bis(indolyl)-(4-formyl-phenyl)methane (Table 4, entry 13)



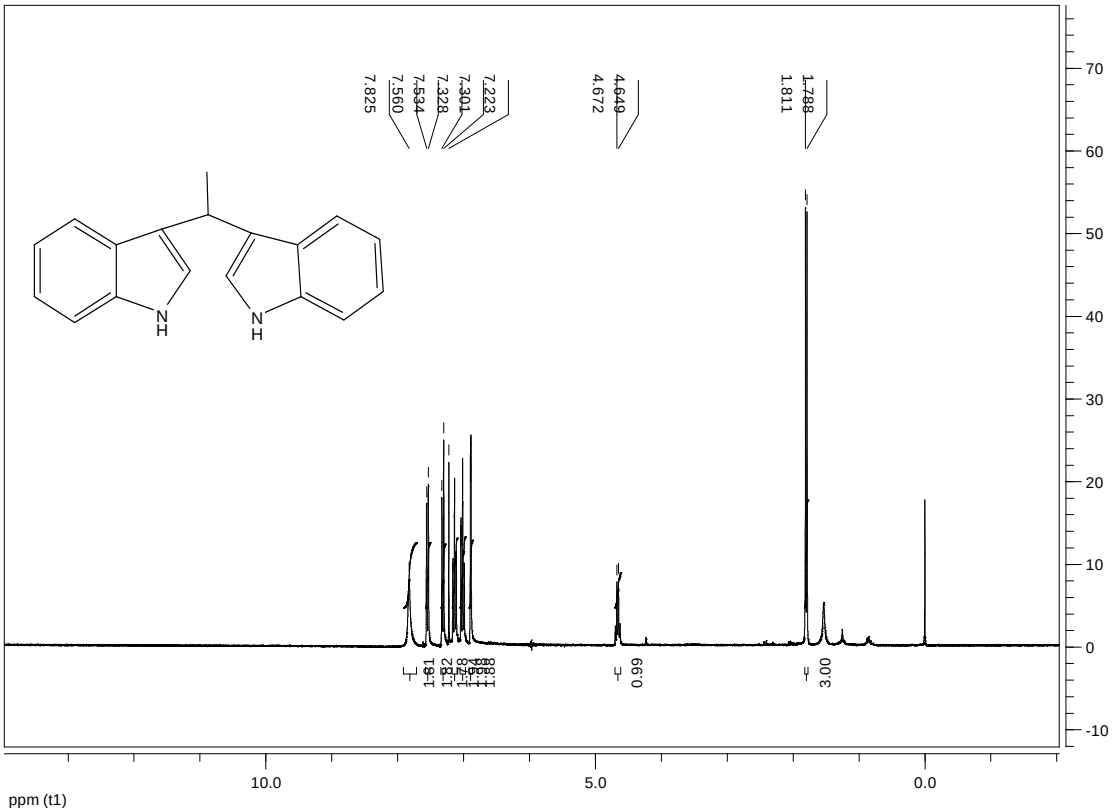
^{1}H NMR 3,3′-bis(indolyl)-(2-furanyl)methane (Table 4, entry 14)



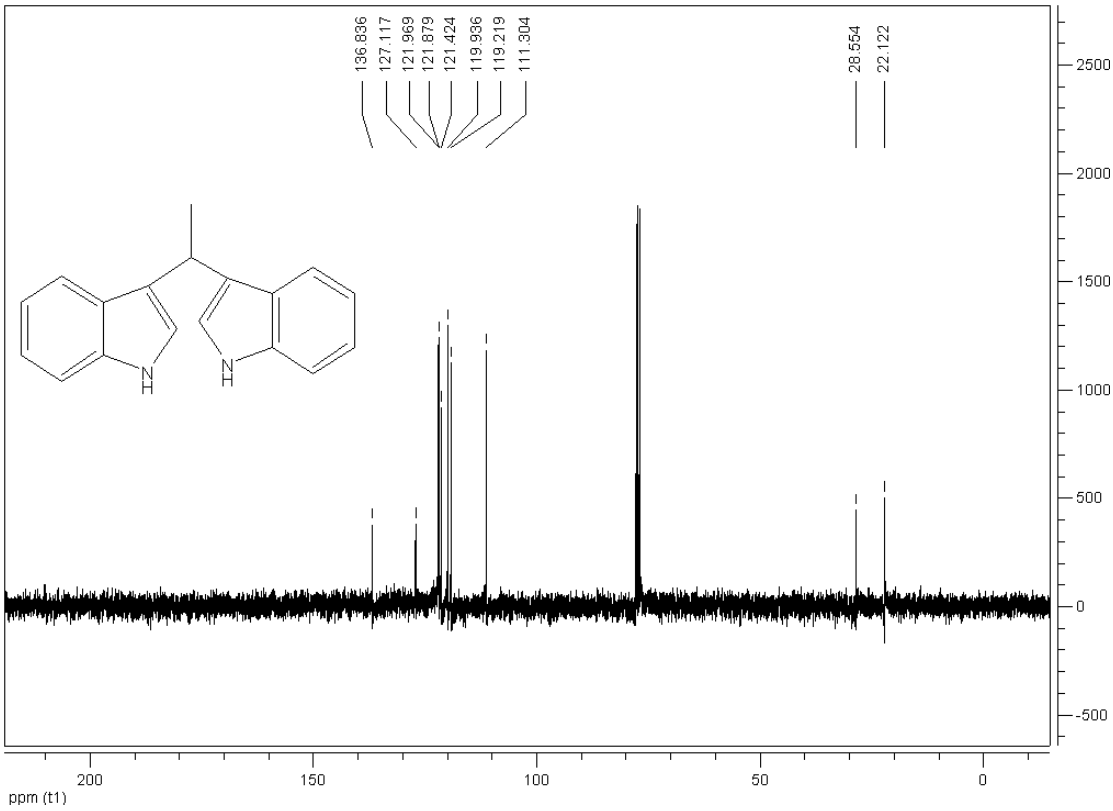
^{13}C NMR 3,3′-bis(indolyl)-(2-furanyl)methane (Table 4, entry 14)



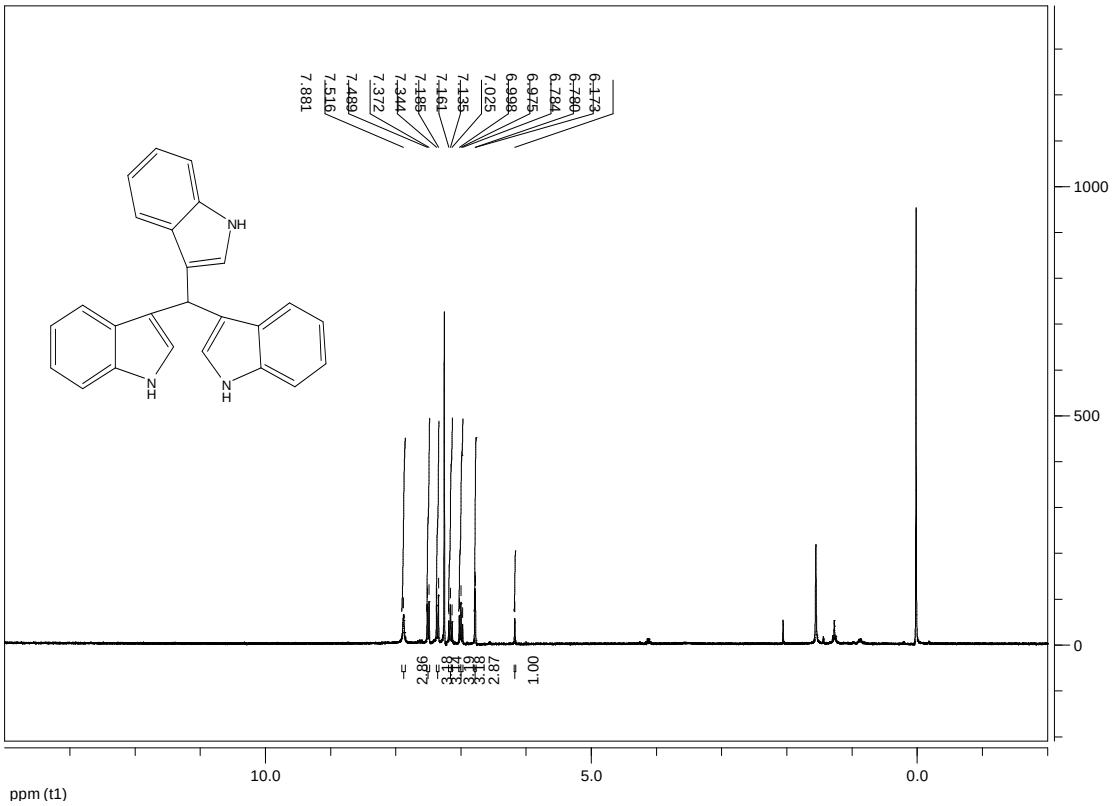
^{1}H NMR vibrindole A



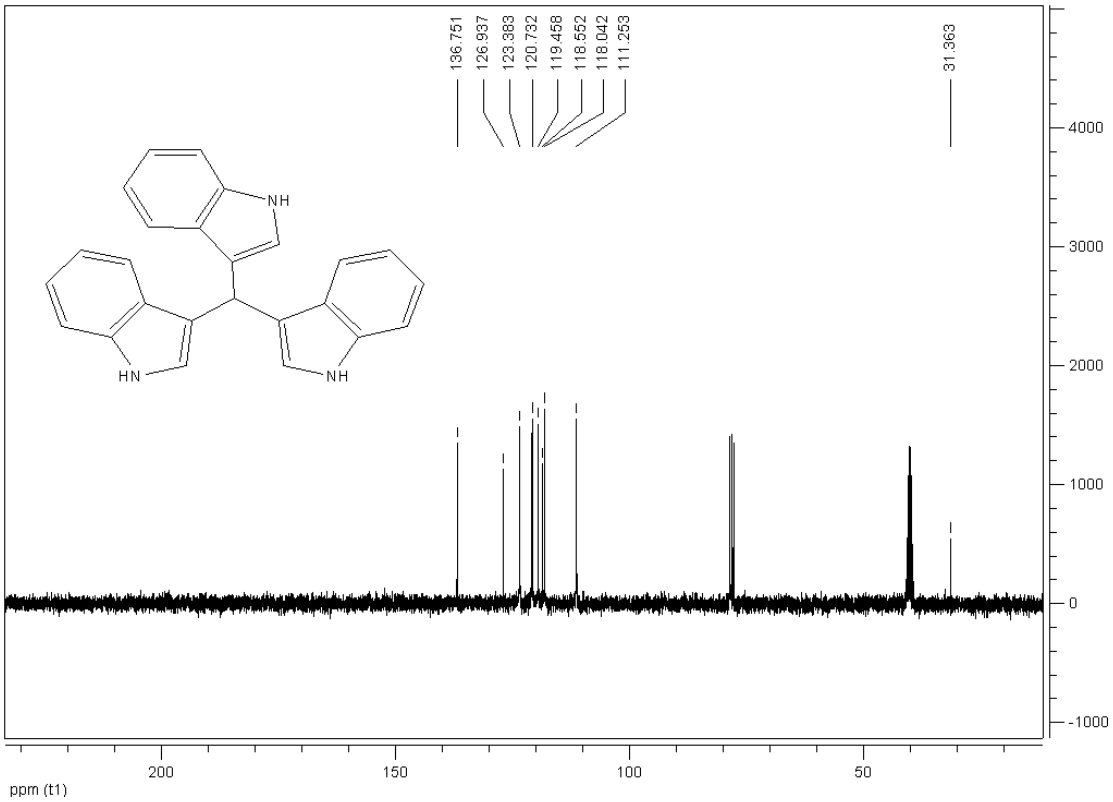
^{13}C NMR vibrindole A



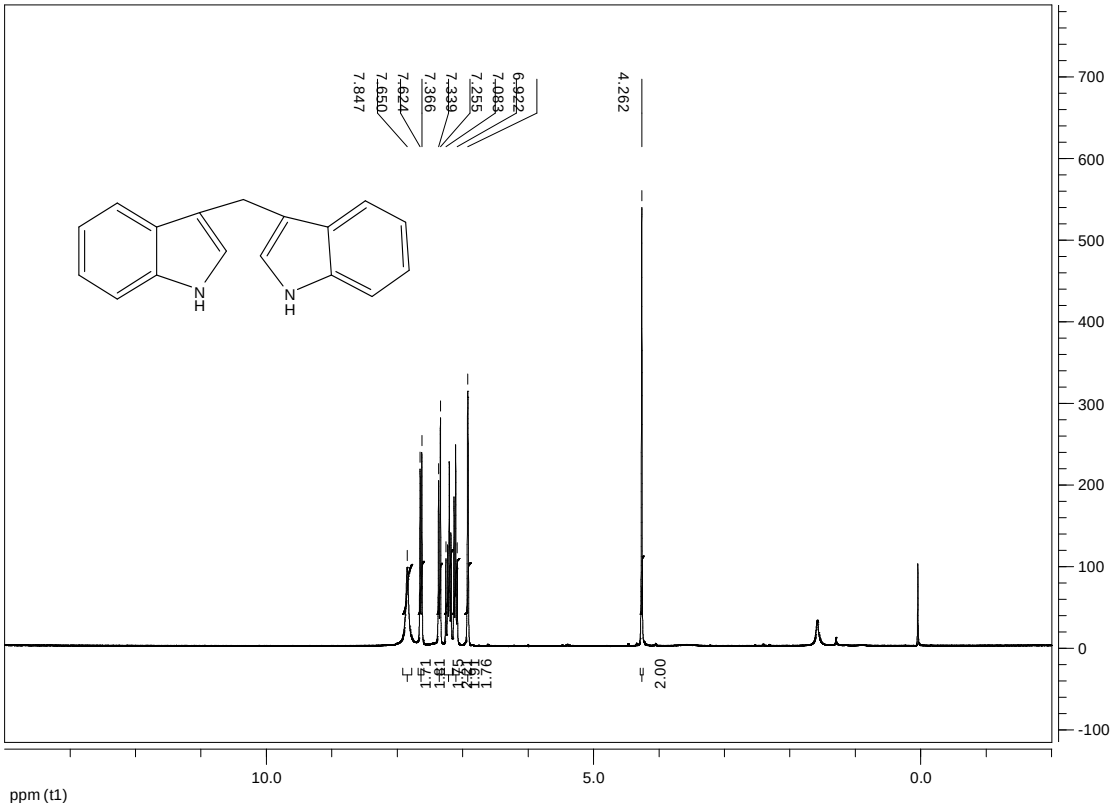
^{1}H NMR Trisindolylmethane



^{13}C NMR Trisindolylmethane



^{1}H NMR diindol-3-yl-methane



^{13}C NMR diindol-3-yl-methane