Supplementary Information

Tin (IV) chloride catalysed synthesis of di(indolyl)methanes during electrophilic substitution of indoles and 2-methyl indoles

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Spectroscopic data for 3a-3f & 4a-4h

3,3'-Bis(indolylmethyl)methane (**3a**): white solid (80%), Mp: 148 - 150 °C IR (KBr): 3404, 1456, 1339, 739 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.86 (2H, s), 7.45 (2H, d, *J* = 8.1 Hz), 7.34 (2H, d, *J* = 8.1 Hz), 7.10 (2H, t, *J* = 8.5 Hz), 7.04 (2H, d, *J* = 2.1 Hz), 6.89 (2H, t, *J* = 7.5 Hz), 1.94 (6H, s); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm): 137.1, 126.3, 125.5, 121.4, 121.3, 120.5, 118.7, 111.1, 34.9, 30.2. FAB: ($C_{19}H_{18}N_2$) = 274 [M^+]. Anal. Calcd. for $C_{19}H_{18}N_2$: C, 83.11; H, 6.51; N, 10.35%. Found: C, 83.21; H, 6.56; N, 10.21%.

4-Methyl-4-(1*H*-indol-3-yl)-pentan-2-one (**3b**): light yellow solid (85%), Mp: 78 -79 °C IR (KBr): 3306, 1690, 1432, 1349, 744 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.09 (1H, br.s), 7.83 (1H, d, *J* = 7.8 Hz), 7.38 (1H, d, *J* = 7.9 Hz), 7.26 – 7.11 (2H, m), 6.93 (1H, d, *J* = 2.4 Hz), 2.97 (2H, s), 1.74 (3H, s), 1.56 (6H, s); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm): 209.3, 137.2, 125.5, 123.6, 121.7, 120.8, 120.6, 119.2, 111.6, 55.1, 34.4, 31.7, 28.8. FAB:

($C_{14}H_{17}NO$) = 215 [M^+]. Anal. Calcd. for $C_{14}H_{17}NO$: C, 77.98; H, 8.12 N, 6.68%. Found: C, 78.14; H, 7.90; N, 6.51%.

3,3'-Bis(indolyl)cyclohexylmethane (**3c)**: light brown solid (82%), Mp: 72 - 73 °C IR (KBr): 3412, 1454, 1337, 742 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.91 (2H, br.s.), 7.57 (2H, d, *J* = 8.1 Hz), 7.30 (2H, d, *J* = 8.1 Hz), 7.26 (2H, s), 7.09 – 7.04 (2H, m), 6.93 – 6.88 (2H, m), 2.55 (4H, t, *J* = 5.6 Hz), 1.67 – 1.60 (6H, m); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm): 137.0, 126.3, 123.7, 122.0, 121.4, 121.2, 118.5, 111.0, 39.5, 36.8, 26.7, 23.0. FAB: ($C_{22}H_{22}N_2$) = 314 [M^+]. Anal. Calcd. for $C_{22}H_{22}N_2$: C, 84.21; H, 6.92; N, 8.83%. Found: C, 84.08; H, 7.01; N, 8.89%.

4,4-Bis-(1*H*-indol-3-yl)-pentane-2-one (**3d**): light yellow solid (78%), Mp: 196 - 198 °C IR (KBr): 3399, 1691, 1417, 1341, 750 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.78 (2H, br.s), 7.24 (2H, d, *J* = 7.9 Hz), 7.22 (2H, s), 7.09 (2H, d, *J* = 8.0 Hz), 6.87 (2H, t, *J* = 7.5 Hz), 6.63 (2H, t, *J* = 7.5 Hz), 3.38 (2H, s), 1.82 (3H, s), 1.46 (3H, s); ^{13}C-NMR (75.5 MHz, $CDCl_3$, ppm): 208.2, 137.1, 125.8, 121.8, 121.6, 120.5, 120.1, 117.9, 111.5, 53.0, 37.0, 31.7, 27.1. FAB: ($C_{21}H_{20}N_2O$) = 316 [M^+]. Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.63; H, 6.19; N, 8.72%. Found: C, 79.75; H, 6.33; N, 8.86%.

3-(indo-3-yl)cyclohex-2-en-l-one (**3e**): light yellow solid (80%), Mp: 194 – 196 °C IR (KBr): 3226, 1577, 1523, 1488, 1436, 1380, 737 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 10.90 (1H, s), 7.94 (1H, m), 7.96 – 7.89 (1H, m), 7.53 – 7.47 (1H, m), 7.25 – 7.18 (2H, m), 6.55 (1H, s), 2.38 (2H, t, *J* = 6.6 Hz), 2.15 – 2.05 (4H, m); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 198.2, 155.6, 138.5, 128.3, 125.6, 123.1, 121.6, 121.5, 121.2, 115.8, 112.8, 37.2, 28.2, 22.7. FAB: ($C_{14}H_{13}NO$) = 211 [M^+]. Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.79; H, 6.02; N, 6.49%. Found: C, 79.62; H, 6.16; N, 6.64%.

2,3,4,5,10,11-hexahydro-l 1-(indol-3-yl)- dibenz[b,f]azepine-l-one (**3f**): white solid (78%), Mp: 232 - 234 °C IR (KBr): 3357, 3293, 1577, 1522, 1487, 1436, 738 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 9.48 (1H, s), 8.0 (1H, s), 7.78 (1H, m), 7.17 (1H, m), 7.03 – 6.87 (4H,

m), 6.56 (2H, m), 6.38 (1H, m), 5.38 (1H, d, *J* = 5.3 Hz), 3.43 (1H, dd, *J* = 14.0, 6.1 Hz), 3.12 (1H, d, *J* = 13.8 Hz), 2.81 – 2.76 (2H, m), 2.29 (2H, t, *J* = 6.5 Hz), 2.09 – 1.98 (2H, m); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 194.1, 154.9, 141.3, 137.5, 131.8, 130.2, 127.6, 126.7, 123.1, 122.4, 121.4, 119.9, 119.7, 118.7, 118.1, 116.4, 111.7, 40.1, 37.4, 32.9, 32.1, 22.6. FAB: ($C_{22}H_{20}N_2O$) = 328 [M^+]. Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 80.37; H, 5.93; N, 8.31%. Found: C, 80.49; H, 6.10; N, 8.54%.

2-(2-Methyl-1*H*-indol-3-yl)-propan-2-ol (**4a**): white solid (72%), Mp: 177 - 178 °C IR (KBr): 3422, 3231, 2969, 1461, 1328, 734 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 9.95 (1H, br,s.), 7.50 (1H, t, *J* = 7.6 Hz), 7.22 (1H, d, *J* = 8.0 Hz), 6.95 (1H, t, *J* = 7.3 Hz), 6.83 (1H, d, *J* = 7.2 Hz), 2.85 (1H, s), 2.05 (3H, s), 1.84 (6H, s); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 136.2, 133.6, 128.6, 121.1, 120.8, 119.4, 112.9, 111.2, 67.6, 25.2, 14.4. HRMS: *m/z* = 189.135 [M^+]. Anal. calcd. for $C_{12}H_{15}NO$: C, 85.73; H, 5.93; N, 8.34%. Found: C, 85.79; H, 5.97; N, 8.39%.

4,4,9a-Trimethyl-2-(2-methyl-2,3-dihydro-1*H*-indol-3-yl)-4,4a,9,9a-tetrahydro-3*H*-carbazole (**4b**): white solid (21%), Mp: 169-170 °C IR (KBr): 3422, 3231, 2969, 1461, 1328, 734 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 7.83 (1H, s), 7.59 (1H, d, *J* = 6.6 Hz), 7.26 - 7.07(5H, m, 6'H, 8'H, 6H, 7H, 8H), 6.76 (1H, t, *J* = 6.9 Hz), 6.67 (1H, d, *J* = 7.2 Hz), 5.78 (1H, s), 2.78 (1H, s), 2.45 (3H, s), 2.45 (2H, s) & 2.23 (2H, d, *J* = 13.2) 1.35 (3H, s), 0.82 & 1.19 (6H, s); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 135.1, 130.9, 130.2, 130.1, 128.8, 127.8, 126.6, 121.2, 119.5, 119.2, 118.5, 110.2, 110.1, 62.7, 57.6, 44.3, 34.8, 30.8, 29.2, 20.7, 12.7. HRMS: *m/z* = 144.123 [M^+].

2-(2-Methyl-1*H*-indol-3-yl)-butane-2-ol (**4c**): light yellow solid (68%), Mp: 200 - 202 °C IR (KBr): 3422, 3226, 2970, 1462, 1328, 736 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 9.95 (1H, br,s.), 7.49 (1H, d, *J* = 7.4 Hz), 7.20 (1H, d, *J* = 8.1 Hz), 6.92 (1H, t, *J* = 7.8 Hz), 6.82 – 6.73 (1H, m), 2.89 (3H, s), 2.52 – 2.44 (5H, m), 2.70 (1H, s), 1.82 (3H, s); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 136.2, 133.6, 128.7, 121.1, 120.8, 119.4, 111.2, 110.3, 67.6, 31.2,

25.2, 15.2, 14.4. HRMS: *m/z* = 226.112 [M^+ + Na]. Anal. Calcd. for $C_{13}H_{17}NO$: C, 81.65; H, 5.35; N, 8.27%. Found: C, 81.73; H, 5.31; N, 8.31%.

4-Methyl-4-(2-methyl-1*H*-indol-3-yl)-pentan-2-one (**4d**): yellow solid (80%), Mp: 181 - 182 °C IR (KBr): 3422, 3226, 2969, 1668, 1613, 1461, 1327, 735 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 9.98 (1H, s), 7.52 (1H, d, *J* = 7.5 Hz), 7.23 (1H, d, *J* = 8.1 Hz), 6.98 – 6.93 (1H, m), 6.85 – 6.76 (1H, m), 2.89 (2H, s), 2.47 (3H, s), 2.04 (3H, s), 1.85 (6H, s); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 208.1, 137.0, 135.4, 132.7, 120.2, 119.9, 118.6, 112.0, 110.3, 66.7, 29.7, 24.4, 23.1, 13.5. HRMS: *m/z* = 229.135 [M^+].

4,4-Bis-(2-methyl-1*H*-indol-3-yl)-pentane-2-one (**4e**): light yellow solid (68%), Mp: 210 -211 °C IR (KBr): 3241, 2916, 1654, 1549, 1424, 1326, 736 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 10.41 (2H, s), 7.64 (2H, d, *J* = 8.4 Hz), 7.34 (2H, d, *J* = 8.4 Hz), 7.12 – 7.02 (4H, m), 2.99 (2H, s), 2.62 (6H, s), 2.54 (3H, s), 1.72 (3H, s); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 198.7, 136.7, 135.4, 128.0, 124.8, 122.0, 120.7, 120.0, 116.7, 111.7, 32.1, 28.7, 21.0, 13.6. HRMS: *m/z* = 344.113 [M^+]. Anal. Calcd. for $C_{23}H_{24}N_2O$: C, 82.67; H, 6.25; N, 8.37%. Found: C, 82.73; H, 6.19; N, 8.47%.

2,2'-Dimethyl 3,3'-bis(indolyl)cyclohexaylmethane (**4f**): light brown solid (82%), Mp: 81 - 82 °C IR (KBr): 3420, 3227, 2923, 1666, 1612, 1460, 1325, 734 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 10.0 (2H, s), 7.51 (2H, d, *J* = 7.4 Hz), 7.23 (2H, d, *J* = 7.8 Hz), 6.98 – 6.93 (2H, m), 6.84 – 6.75 (2H, m), 2.47 (6H, s), 2.06 – 2.03 (4H, m), 1.85 – 1.83 (6H, m); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 136.2, 133.6, 128.6, 121.1, 120.8, 118.9, 111.2, 110.2, 30.5, 30.3, 29.0, 25.2, 14.4. HRMS: *m/z* = 342.122 [M^+]. Anal. Calcd. for $C_{24}H_{26}N_2$: C, 83.45; H, 6.55; N, 8.47%. Found: C, 83.51; H, 6.47; N, 8.39%.

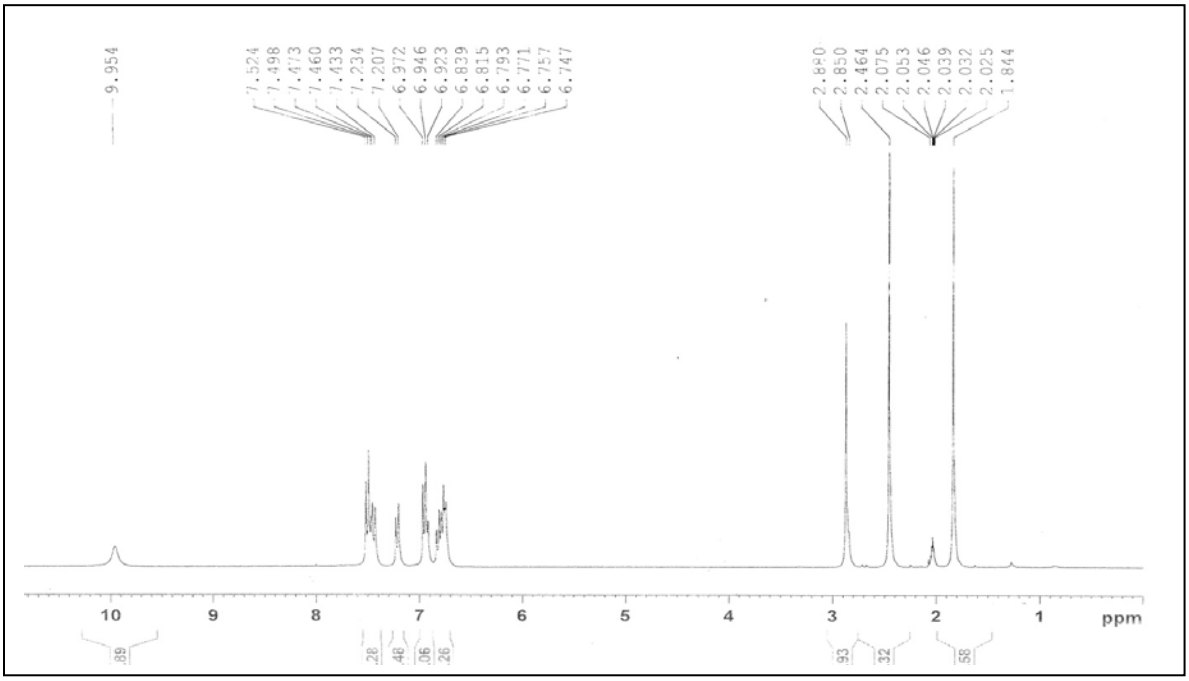
3-(indo-3-yl 2-methyl)cyclohex-2-en-l-one (**4g**): red solid (78%), Mp: 197-198 °C IR (KBr): 3171, 2934, 1620, 1554, 1454, 1243, 742 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 10.55 (1H, s), 7.67 (1H, d, *J* = 6.9 Hz), 7.35 (1H, d, *J* = 6.6 Hz), 7.13 – 7.04 (2H, m), 6.09 (1H, s),

2.94 – 2.89 (2H, m), 2.56 (3H, s), 2.41 (2H, t, *J* = 6.0), 2.18 – 2.10 (2H, m); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 197.3, 157.4, 135.9, 128.1, 126.9, 124.7, 121.3, 120.6, 119.4, 112.6, 110.9, 37.3, 30.5, 23.5, 13.2. HRMS: *m/z* = 225.113 [M^+].

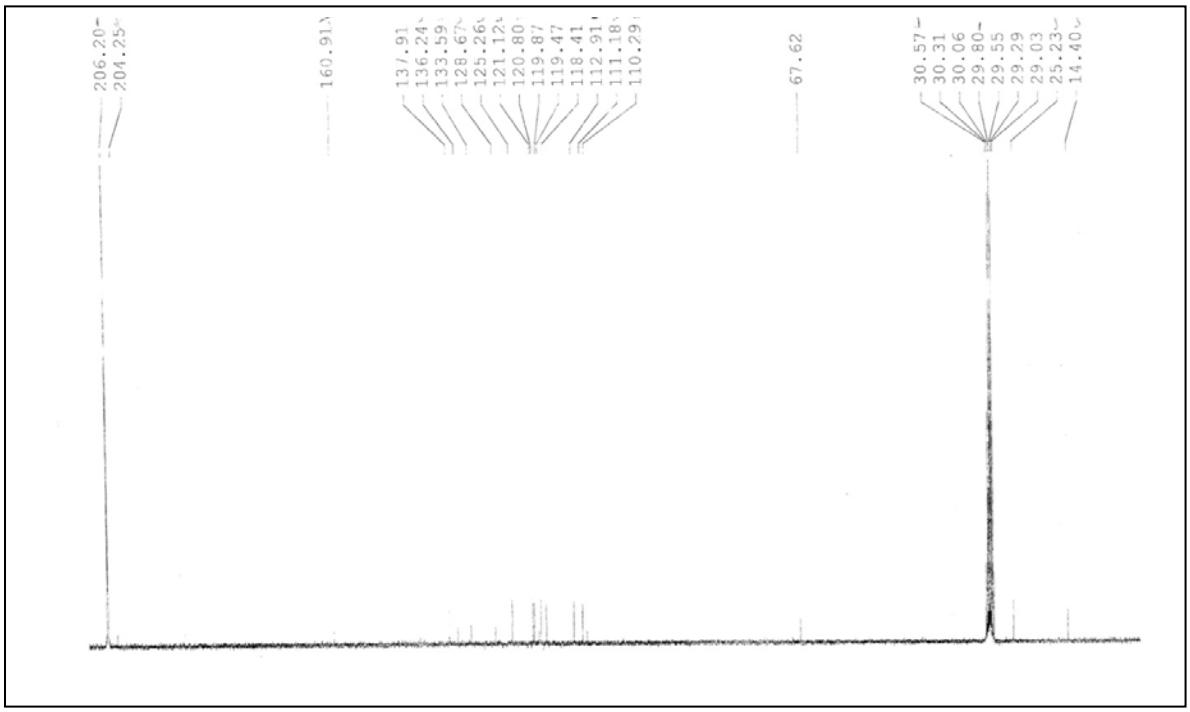
2,2'-Dimethyl 3,3'-bis(indolyl)cycloheptylmethane (**4h**): Yellow solid (70%), Mp: 213 - 215 °C IR (KBr): 3419, 3224, 2966, 1666, 1611, 1459, 1324, 733 cm^{-1}; ^{1}H-NMR (300 MHz, d_6-acetone): δ 10.22 (2H, br,s.), 7.73 (2H, d, *J* = 7.8 Hz), 7.45 (2H, d, *J* = 7.8 Hz), 7.16 (2H, t, *J* = 7.2 Hz), 7.02 (2H, m), 3.15-2.68 (12H, m), 2.06 (6H, s); ^{13}C-NMR (75.5 MHz, d_6-acetone, ppm): 136.4, 133.8, 128.8, 121.3, 119.7, 118.6, 113.1, 111.4, 30.8, 25.4, 14.6. HRMS: *m/z* = 356.253 [M^+]. Anal. calcd. for $C_{25}H_{28}N_2$: C, 85.75; H, 6.03; N, 8.71%. Found: C, 85.69; H, 5.97; N, 8.77%.

^{1}H NMR and ^{13}C NMR data of 4a, 4c, 4e, 4f & 4h

^{1}H NMR data of 2-(2-Methyl-1*H*-indol-3-yl)-propan-2-ol (4a)



^{13}C NMR data of 2-(2-Methyl-1*H*-indol-3-yl)-propan-2-ol (4a)



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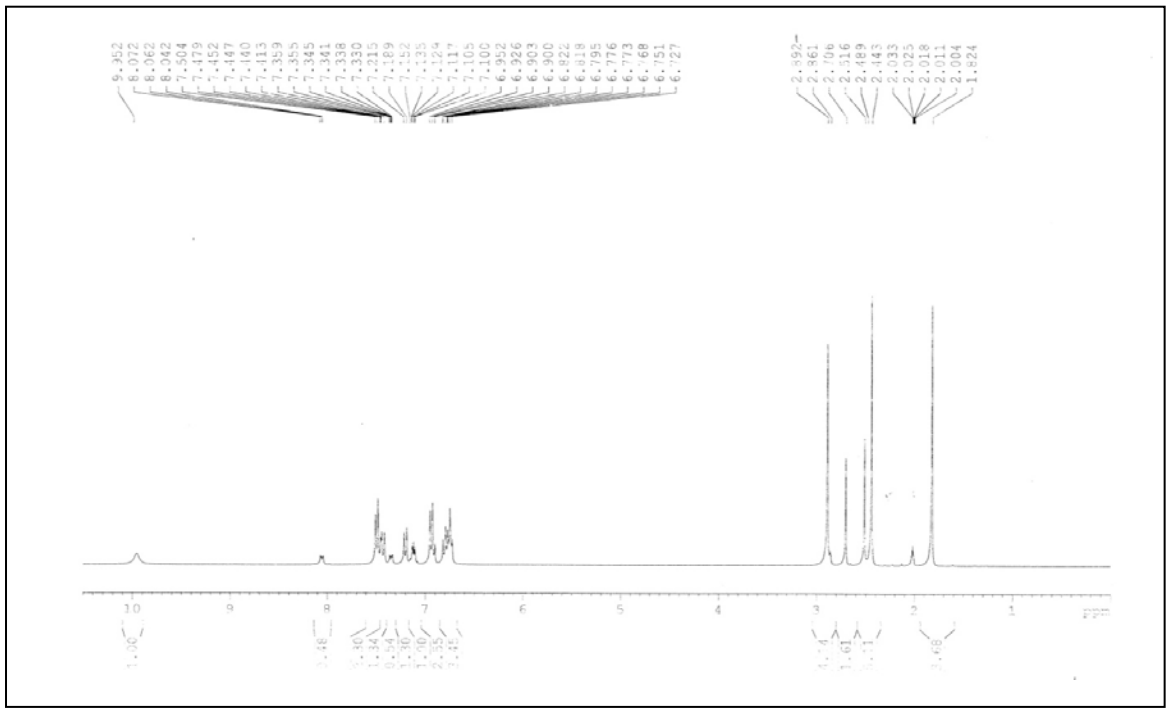

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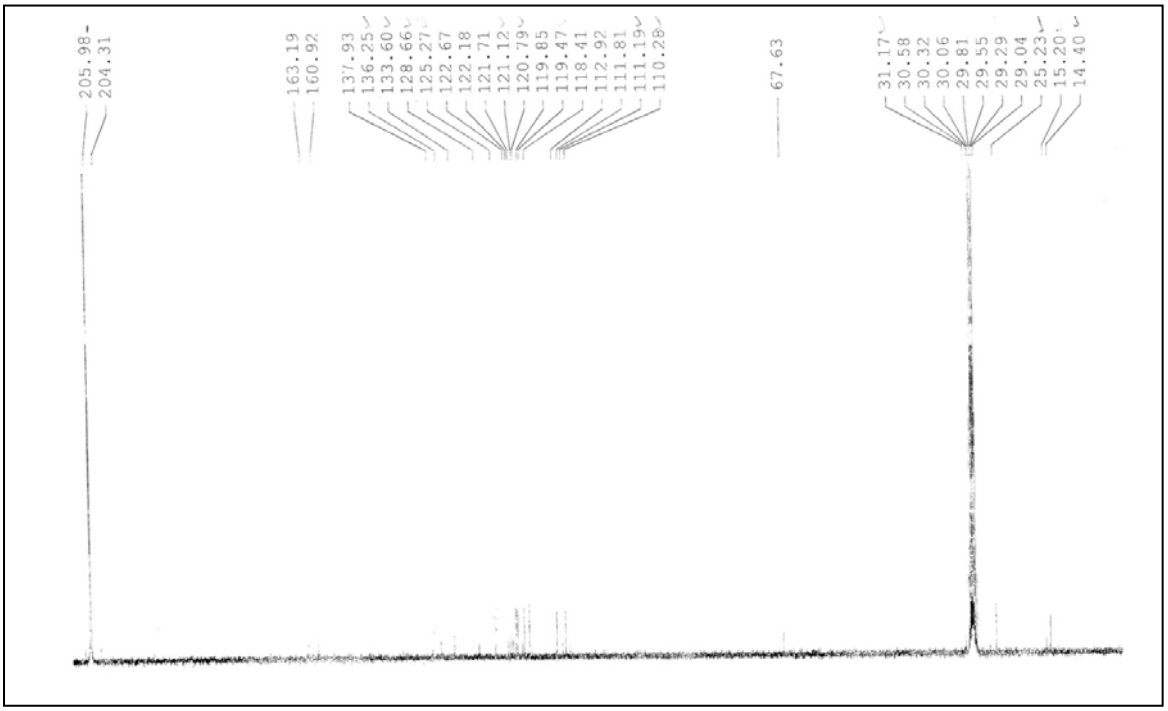

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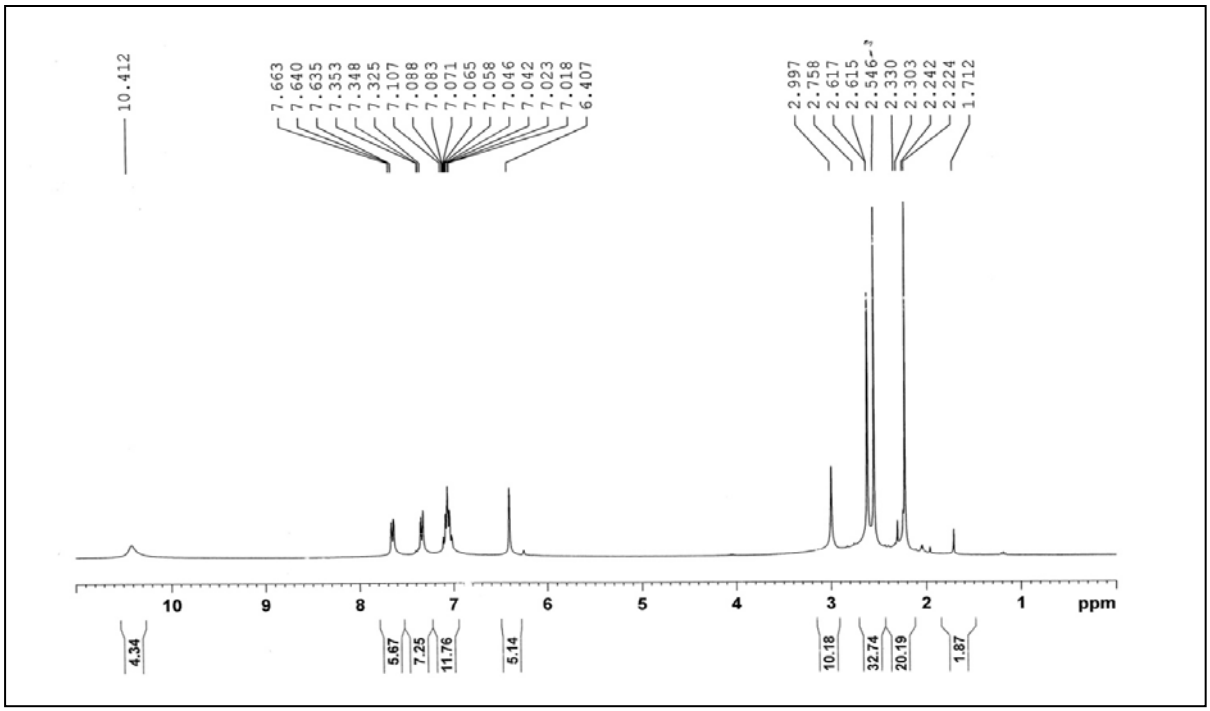

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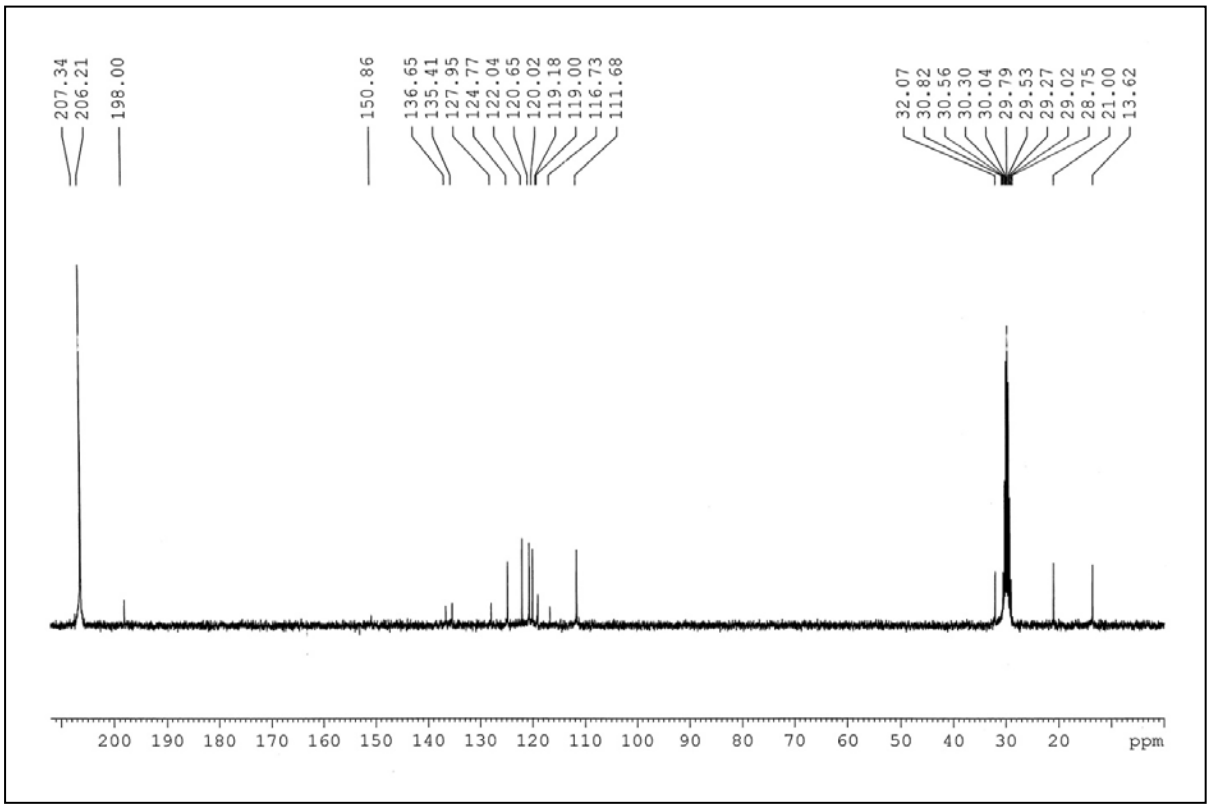
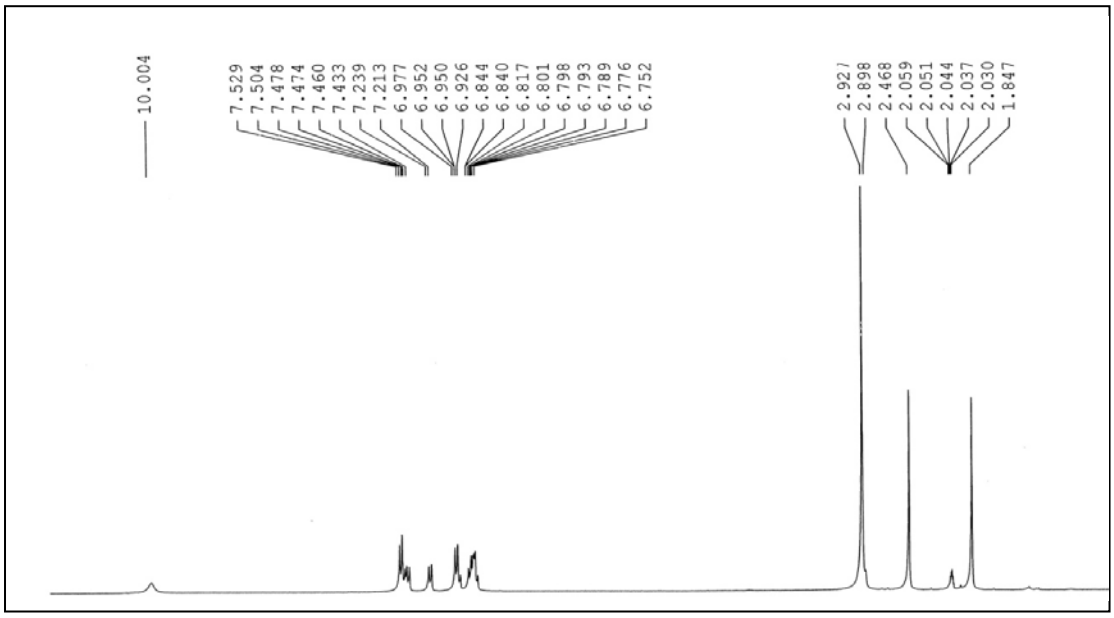
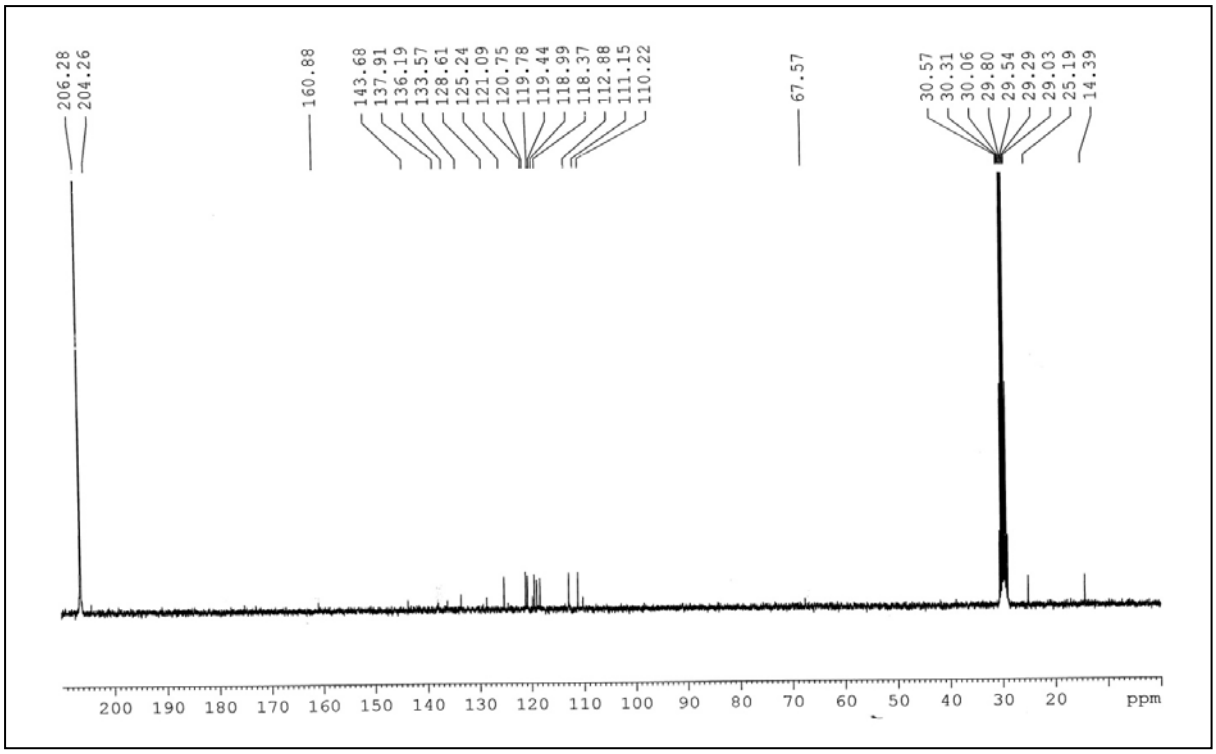


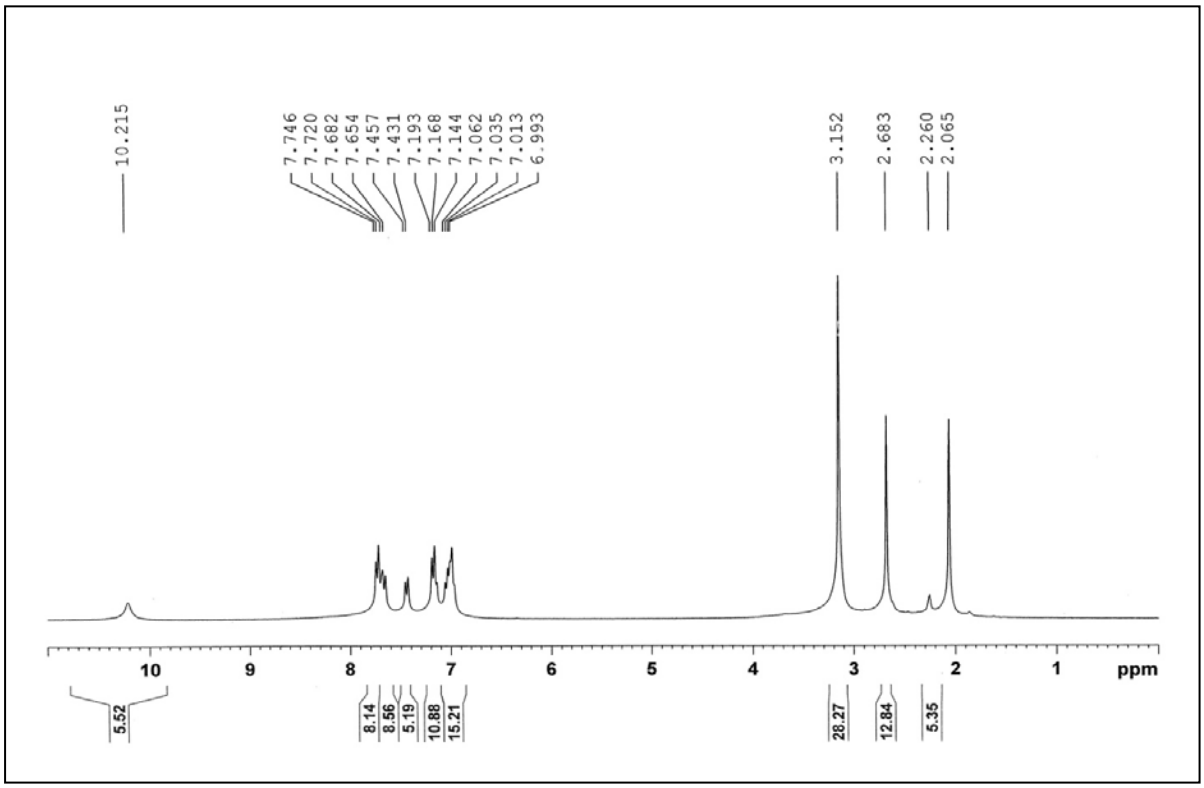
^{1}H NMR data of 2,2'-Dimethyl 3,3'-bis(indolyl)cyclohexaylmethane (4f)



^{13}C NMR data of 2,2'-Dimethyl 3,3'-bis(indolyl)cyclohexaylmethane (4f)



^{1}H NMR data of 2,2'-Dimethyl 3,3'-bis(indolyl)cycloheptylmethane (4h)



^{13}C NMR data of 2,2'-Dimethyl 3,3'-bis(indolyl)cycloheptylmethane (4h)