

**Water mediated chemoselective synthesis of 1,2-disubstituted benzimidazoles using
o-phenylenediamine and the extended synthesis of quinoxalines**

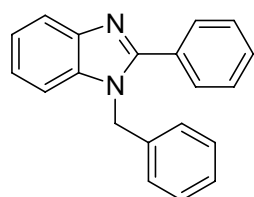
Jie-Ping Wan, Shi-Feng Gan, Jian-Mei Wu, Yuanjiang Pan*

*Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China
panyuanjiang@zju.edu.cn*

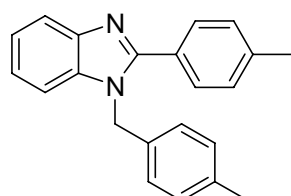
Contents

S1	General information
S2-S8	Analytical data
S9	References
S10-S41	¹ H and ¹³ C NMR spectra copies

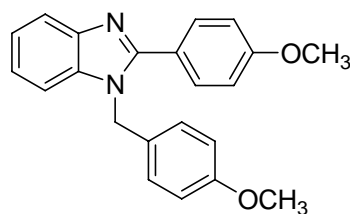
General: All reagents used in the experiments were obtained from commercial sources and used without further purification. Water used as reaction medium is deionized mineral water. All reactions were carried out at open atmosphere. NMR spectra were recorded on Bruker AVANCE DMX-500 spectrometry at 500MHz and 125MHz for ¹H and ¹³C NMR in DMSO-*d*₆, respectively. The NMR chemical shift was reported in ppm relative to 2.50 and 40.70 ppm of DMSO solvent as the standards of ¹H and ¹³C NMR, respectively. Melting points were tested by XT-4 apparatus without correcting temperature or cited from literature when applicable. Mass spectra were performed on a Bruker Esquire 3000plus mass spectrometer equipped with ESI interface and ion trap analyzer. The HRMS of new products were tested on Bruker 7-tesla FT-ICR MS equipped with an electrospray source.



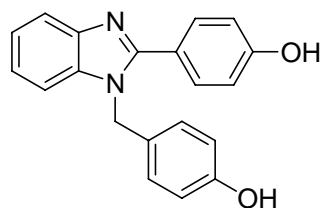
1-benzyl-2-phenyl-1H-benzo[d]imidazole (3a). White solid; mp: 133-134 °C;^[11] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 7.75-7.23 (m, 3 H), 7.53-7.45 (m, 4 H), 7.29-7.21 (m, 5 H), 7.00 (d, 2 H, *J* = 7.5 Hz), 5.58 (s, 2 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 154.42, 143.89, 138.10, 137.08, 131.33, 130.99, 130.21, 129.95, 128.64, 127.25, 123.86, 123.39, 120.46, 112.27, 48.63; ESI-MS [*M*+*H*⁺]: *m/z* = 285.



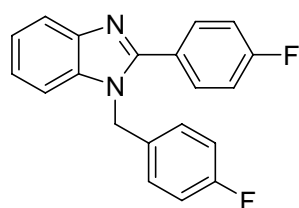
1-(4-methylbenzyl)-2-p-tolyl-1H-benzo[d]imidazole (3b). White solid; mp: 128-129 °C;^[11] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 7.70 (d, 1 H, *J* = 7.4 Hz), 7.62 (d, 2 H, *J* = 7.5 Hz), 7.42 (d, 1 H, *J* = 7.5 Hz), 7.33 (d, 2 H, *J* = 7.6 Hz), 7.25-7.20 (m, 2 H), 7.09 (d, 2 H, *J* = 7.5 Hz), 6.88 (d, 2 H, *J* = 7.5 Hz), 5.51 (s, 2 H), 2.37 (s, 3H), 2.22 (s, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 154.52, 143.88, 140.71, 137.84, 137.06, 135.13, 130.53, 130.11, 128.49, 127.19, 123.69, 123.29, 120.32, 112.23, 48.41, 22.11, 21.77; ESI-MS [*M*+*H*⁺]: *m/z* = 313.



1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3c). mp: 127-129 °C;^[11] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 7.68 (d, 3 H, *J* = 8.5 Hz), 7.43 (d, 1 H, *J* = 8.1 Hz), 7.23-7.20 (m, 2 H), 7.09 (d, 2 H, *J* = 8.7 Hz), 6.94 (d, 2 H, *J* = 8.5 Hz), 6.84 (d, 2 H, *J* = 8.6 Hz), 5.49 (s, 2 H), 3.82 (s, 3 H), 3.68 (s, 3 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 161.66, 159.80, 154.46, 143.91, 137.06, 131.79, 130.04, 128.67, 123.65, 123.59, 123.34, 120.23, 115.53, 115.44, 112.26, 56.59, 56.30, 48.20; ESI-MS [*M*+*H*⁺]: *m/z* = 345.

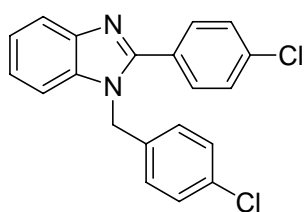


4-(1-(4-hydroxybenzyl)-1H-benzo[d]imidazol-2-yl)phenol (3d). Pale yellow solid; mp: 254-256 °C;^[21] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 10.82 (s, 1 H), 9.66 (brs, 1 H), 7.86 (d, 1 H, *J* = 8.0 Hz), 7.80 (d, 1 H, *J* = 8.0 Hz), 7.77 (d, 2 H, *J* = 8.5 Hz), 7.60-7.53 (m, 2 H), 7.10 (d, 2 H, *J* = 8.4 Hz), 6.98 (d, 2 H, *J* = 8.3 Hz), 6.71 (d, 2 H, *J* = 8.4 Hz), 5.63 (s, 2 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 162.94, 158.54, 151.91, 133.73, 133.08, 132.28, 129.35, 127.36, 126.88, 125.81, 117.56, 116.66, 115.57, 114.66, 113.92, 49.45; ESI-MS [*M*+*H*⁺]: *m/z* = 317.



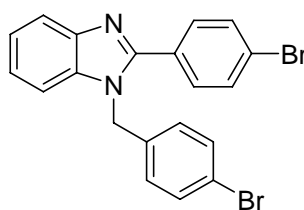
1-(4-fluorobenzyl)-2-(4-fluorophenyl)-1H-benzo[d]imidazole (3e). White solid; mp: 110-112 °C;^[31] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 7.79-7.74 (m, 3 H), 7.49 (d, 1 H, *J* = 9.0 Hz), 7.36 (t, 2 H, *J* = 8.8 Hz), 7.26-7.24 (m, 2 H), 7.10 (t, 2 H, *J* = 8.8 Hz), 7.05-7.01 (m, 2 H), 5.56 (s, 2 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 165.11, 163.56, 163.14, 161.62, 153.50, 143.81, 136.99, 134.19, 132.60, 129.40, 127.83, 123.99, 123.50, 120.50,

116.98 (m), 112.25, 47.96; ESI-MS $[M+H^+]$: $m/z = 321$.



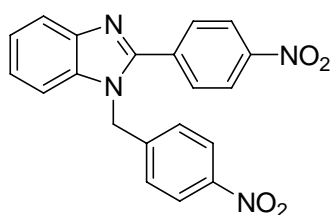
1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole (3f). White solid; mp: 137-139 °C;^[3] ^1H NMR (DMSO- d_6 , 500 MHz) δ 7.74 (d, 3 H, $J = 8.4$ Hz), 7.61 (d, 2 H, $J = 8.5$ Hz), 7.50 (d, 1 H, $J = 9.0$ Hz), 7.35 (d, 2 H, $J = 2$ H), 7.28-7.26 (m, 2 H), 7.00 (d, 2 H, $J = 8.4$ Hz), 5.59 (s, 2 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 153.66, 143.88,

136.44, 134.91, 133.70, 132.34, 130.53, 130.32, 130.13, 129.54, 124.72, 124.18, 120.85, 112.64, 48.36; ESI-MS $[M+H^+]$: $m/z = 353$.



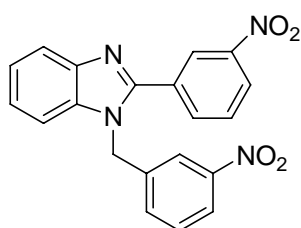
1-(4-bromobenzyl)-2-(4-bromophenyl)-1H-benzo[d]imidazole (3g). Pale yellow solid; mp: 160-162 °C;^[3] ^1H NMR (DMSO- d_6 , 500 MHz) δ 7.74 (d, 3 H, $J = 8.3$ Hz), 7.66 (d, 2 H, $J = 8.4$ Hz), 7.49 (d, 3 H, $J = 8.2$ Hz), 7.27-7.25 (m, 2 H), 6.94 (d, 2 H, $J = 8.3$ Hz), 5.57 (2 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 153.84, 143.87, 137.64, 137.21, 133.56, 133.34,

132.65, 130.48, 129.95, 125.37, 124.90, 124.37, 122.31, 120.92, 112.75, 48.52; ESI-MS $[M+H^+]$: $m/z = 443$.



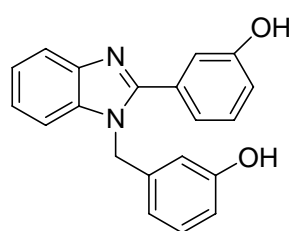
1-(4-nitrobenzyl)-2-(4-nitrophenyl)-1H-benzo[d]imidazole (3h). White solid; mp: 189-191 °C;^[1] ^1H NMR (DMSO- d_6 , 500 MHz) δ 8.33 (d, 2 H, $J = 8.6$ Hz), 8.15 (d, 2 H, $J = 8.4$ Hz), 8.00 (d, 2 H, $J = 8.5$ Hz), 7.80 (d, 1 H, $J = 9.0$ Hz), 7.54 (d, 1 H, $J = 8.1$ Hz), 7.34-7.31 (m, 2 H), 7.26 (d, 2 H, $J = 8.4$ Hz), 5.82 (s, 2 H); ^{13}C NMR

(DMSO- d_6 , 125 MHz) δ 152.26, 149.22, 148.10, 145.52, 143.84, 137.26, 137.14, 131.56, 128.63, 125.13, 125.15, 124.92, 124.15, 121.02, 112.45, 48.39; ESI-MS $[M+H^+]$: $m/z = 375$.

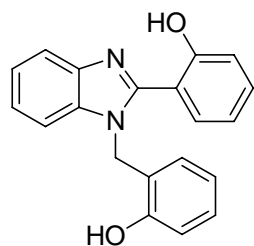


1-(3-nitrobenzyl)-2-(3-nitrophenyl)-1H-benzo[d]imidazole (3i). Pale yellow solid; mp: 167-168 °C;^[4] ^1H NMR (DMSO- d_6 , 500 MHz) δ 8.45 (s, 1 H), 8.37 (d, 1 H, $J = 8.2$ Hz), 8.18 (d, 1 H, $J = 7.7$ Hz), 8.13 (d, 1 H, $J = 8.0$ Hz), 7.96 (s, 1 H), 7.83-7.79 (m, 2 H), 7.64-7.57 (m, 2 H), 7.40 (d, 1 H, $J = 7.7$ Hz), 7.34-7.32 (m, 2 H), 5.82 (s, 2 H); ^{13}C NMR

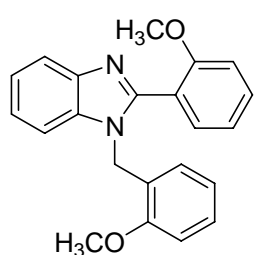
(DMSO- d_6 , 125 MHz) δ 152.31, 152.31, 149.28, 149.22, 143.78, 140.37, 137.31, 136.65, 134.10, 132.54, 132.01, 131.91, 125.90, 125.03, 124.29, 123.96, 122.58, 121.05, 112.53, 48.25; ESI-MS $[M+H^+]$: $m/z = 375$.



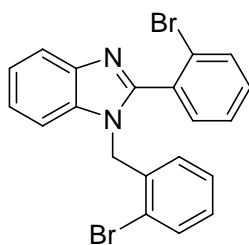
1-(3-hydroxybenzyl)-2-(3-hydroxyphenyl)-1H-benzo[d]imidazole (3j). Pink solid; mp: 243-245 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 10.48 (brs, 1 H), 9.71 (brs, 1 H), 7.92 (d, 1 H, $J = 8.0$ Hz), 7.79 (d, 1 H, $J = 8.0$ Hz), 7.63-7.55 (m, 2 H), 7.48 (t, 1 H, $J = 8.0$ Hz), 7.32 (s, 1 H), 7.28 (d, 1 H, $J = 7.5$ Hz), 7.21 (d, 1 H, $J = 8.0$ Hz), 7.11 (t, 1 H, $J = 8.0$ Hz), 6.74 (d, 1 H, $J = 8.0$ Hz), 6.58 (s, 2 H), 5.67 (s, 2 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 159.29, 159.12, 151.64, 137.07, 133.83, 132.61, 131.87, 131.20, 127.59, 127.21, 124.92, 121.40, 121.19, 118.06, 117.76, 116.38, 116.04, 114.74, 114.46, 49.73; ESI-MS [$\text{M}+\text{H}^+$]: $m/z = 317$.



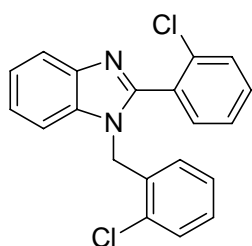
1-(2-hydroxybenzyl)-2-(2-hydroxyphenyl)-1H-benzo[d]imidazole (3k). Yellow solid; mp: 207-208 °C; ^{121}H NMR (DMSO- d_6 , 500 MHz) δ 11.14 (s, 1 H), 9.85 (s, 1 H), 7.72 (d, 1 H, $J = 7.5$ Hz), 7.43-7.33 (m, 3 H), 7.26-7.21 (m, 2 H), 7.04 (d, 2 H, $J = 8.0$ Hz), 6.91-6.87 (m, 1 H), 6.83 (d, 1 H, $J = 8.0$ Hz), 6.58 (t, 1 H, $J = 7.5$ Hz), 6.39 (d, 1 H, $J = 7.5$ Hz), 5.41 (s, 2 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 157.56, 155.60, 153.26, 143.00, 136.41, 132.56, 131.43, 129.55, 127.88, 123.82, 123.72, 123.21, 120.24, 120.19, 119.90, 117.61, 117.37, 116.22, 112.00, 44.44; ESI-MS [$\text{M}+\text{H}^+$]: $m/z = 317$.



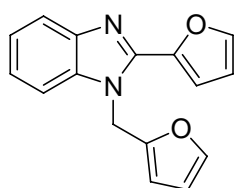
1-(2-methoxybenzyl)-2-(2-methoxyphenyl)-1H-benzo[d]imidazole (3l). White solid; mp: 151-153 °C; ^{111}H NMR (DMSO- d_6 , 500 MHz) δ 7.67 (d, 1 H, $J = 8.5$ Hz), 7.52 (t, 1 H, $J = 8.0$ Hz), 7.42 (d, 1 H, $J = 7.5$ Hz), 7.38 (d, 1 H, $J = 7.5$ Hz), 7.21-7.16 (m, 4 H), 7.07 (t, 1 H, $J = 7.5$ Hz), 6.92 (d, 1 H, $J = 8.0$ Hz), 6.75 (t, 1 H, $J = 7.5$ Hz), 6.58 (d, 1 H, $J = 7.5$ Hz), 5.21 (s, 2 H), 3.67 (s, 6 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 158.64, 158.08, 153.41, 143.63, 136.52, 133.56, 133.46, 130.65, 129.34, 125.46, 124.25, 123.67, 122.31, 121.76, 120.42, 113.17, 112.69, 112.40, 56.97, 56.88, 44.64; ESI-MS [$\text{M}+\text{H}^+$]: $m/z = 345$.



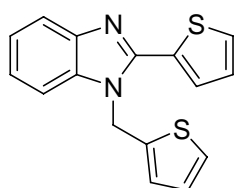
1-(2-bromobenzyl)-2-(2-bromophenyl)-1H-benzo[d]imidazole (3m). Pale yellow solid; mp: 175-178 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 7.79-7.75 (m, 2 H), 7.57-7.44 (m, 5 H), 7.30 (t, 2 H, $J = 8.1$ Hz), 7.19-7.16 (m, 2 H), 6.58 (d, 1 H, $J = 7.6$ Hz), 5.38 (s, 2 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 153.47, 143.63, 136.28, 136.21, 134.30, 134.22, 133.69, 133.61, 132.74, 131.22, 129.59, 129.51, 129.33, 124.84, 124.54, 124.05, 123.17, 121.10, 112.45, 49.01; ESI-MS [$\text{M}+\text{H}^+$]: $m/z = 443$.



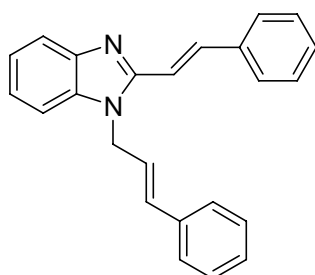
1-(2-chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazole (3n). Pale yellow crystal; mp: 158-159 °C;^[1] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 7.76 (d, 1 H, *J* = 8.5 Hz), 7.62 (d, 1 H, *J* = 7.5 Hz), 7.55 (t, 1 H, *J* = 8.0 Hz), 7.50 (d, 2 H, *J* = 8.0 Hz), 7.42 (t, 1 H, *J* = 7.5 Hz), 7.38 (d, 1 H, *J* = 8.0 Hz), 7.29 (t, 2 H, *J* = 4.5 Hz), 7.25 (d, 1 H, *J* = 7.5 Hz), 7.16 (t, 1 H, *J* = 7.5 Hz), 6.65 (d, 1 H, *J* = 8.0 Hz), 5.43 (s, 2 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 151.93, 143.67, 136.09, 134.58, 134.30, 133.36, 133.02, 132.77, 130.85, 130.63, 130.58, 130.54, 129.37, 128.59, 128.50, 124.24, 123.44, 120.78, 112.14, 46.25; ESI-MS [M+H⁺]: *m/z* = 353.



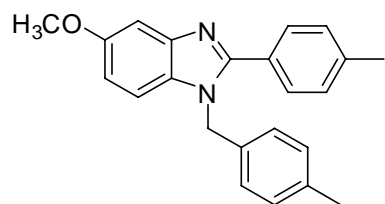
2-(furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzo[d]imidazole (3o). Brown solid; mp: 88-89 °C;^[3] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 8.17 (s, 1 H), 7.91 (d, 1 H, *J* = 7.8 Hz), 7.72 (d, 1 H, *J* = 7.8 Hz), 7.58 (d, 2 H, *J* = 8.0 Hz), 7.44-7.37 (m, 2 H), 6.88 (s, 1 H), 6.60 (s, 1 H), 6.41 (s, 1 H), 5.87 (s, 2 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 150.10, 148.08, 144.90, 143.29, 139.22, 135.47, 125.66, 125.62, 118.54, 117.12, 115.48, 114.20, 113.16, 112.08, 110.89, 42.83; ESI-MS [M+H⁺]: *m/z* = 265.



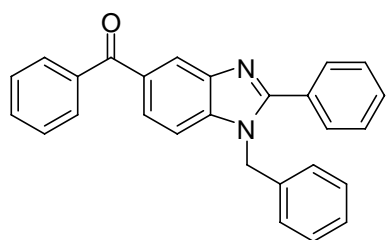
2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole (3p). Deep yellow solid; mp: 150-152 °C;^[3] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 8.06 (d, 1 H, *J* = 5.0 Hz), 8.03 (d, 1 H, *J* = 4.0 Hz), 7.93-7.90 (m, 1 H), 7.80-7.77 (m, 1 H), 7.47-7.44 (m, 3 H), 7.37 (t, 1 H, *J* = 4.5 Hz), 7.10 (d, 1 H, *J* = 4.0 Hz), 6.97-6.95 (m, 1 H), 6.05 (s, 2 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 146.58, 138.91, 137.69, 135.26, 133.83, 132.93, 129.98, 128.35, 128.18, 127.81, 125.97, 125.85, 117.82, 113.26, 44.96; ESI-MS [M+H⁺]: *m/z* = 297.



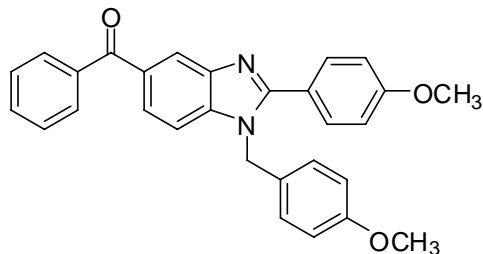
1-cinnamyl-2-(*E*)-styryl-1H-benzo[d]imidazole (3q). Pallow yellow oil; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 7.91 (d, 1 H, *J* = 16.0 Hz), 7.80 (d, 2 H, *J* = 7.5 Hz), 7.67-7.59 (m, 2 H), 7.57 (d, 1 H, *J* = 16.0 Hz), 7.42 (t, 2 H, *J* = 7.5 Hz), 7.36 (t, 3 H, *J* = 7.0 Hz), 7.28-7.21 (m, 5 H), 6.57 (d, 1 H, *J* = 16.0 Hz), 6.49-6.43 (m, 1 H), 5.28 (d, 2 H, *J* = 5.5 Hz); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 151.82, 144.12, 137.36, 137.14, 137.04, 136.53, 132.70, 130.14, 130.00, 129.82, 129.03, 128.72, 127.57, 126.38, 123.45, 123.39, 1219.84, 115.48, 111.70, 45.72; ESI-MS [M+H⁺]: *m/z* = 337. ESI-HRMS: Calcd for C₂₄H₂₁N₂ ([M+H]⁺), 337.1699; Found: 337.1694.



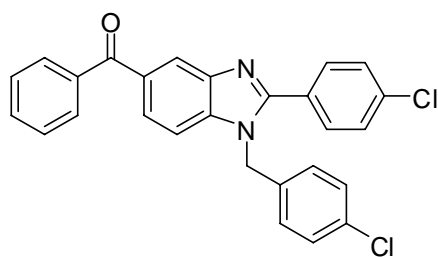
5-methoxy-1-(4-methylbenzyl)-2-p-tolyl-1H-benzo[d]imidazole (3r). Pale brown solid; mp: 128-130 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 7.76 (d, 2 H, J = 8.2 Hz), 7.67 (d, 1 H, J = 8.8 Hz), 7.51 (d, 2 H, J = 8.1 Hz), 7.29 (s, 1 H), 7.17-7.15 (m, 1 H), 7.13 (d, 2 H, J = 8.2 Hz), 7.03 (d, 2 H, J = 8.5 Hz), 5.65 (s, 2 H), 3.88 (s, 3 H), 2.43 (s, 3 H), 2.24 (s, 3 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 159.79, 152.42, 144.68, 139.46, 133.45, 133.88, 131.79, 131.35, 131.16, 129.11, 128.11, 122.81, 117.10, 115.58, 99.48, 57.72, 49.92, 22.84, 22.31; ESI-MS $[\text{M}+\text{H}^+]$: m/z = 343. ESI-HRMS: Calcd for $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$), 343.1805; Found: 343.1801.



5-benzoyl-1-benzyl-2-phenyl-1H-benzo[d]imidazole (3s). Pale brown solid; mp: 195-197 °C; $^{[3]}$ ^1H NMR (DMSO- d_6 , 500 MHz) δ 8.07 (s, 1 H), 7.77-7.71 (m, 5 H), 7.67 (d, 2 H, J = 8.3 Hz), 7.59-7.55 (m, 5 H), 7.34-7.25 (m, 3 H), 7.02 (d, 2 H, J = 7.3 Hz), 5.66 (s, 2 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.80, 156.63, 143.16, 140.24, 139.10, 137.71, 133.41, 132.72, 131.44, 130.76, 130.71, 130.30, 130.07, 129.65, 128.83, 127.34, 125.74, 125.53, 123.18, 112.53, 48.91; ESI-MS $[\text{M}+\text{H}^+]$: m/z = 389.

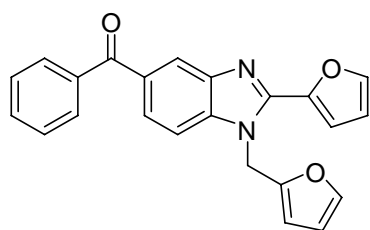


5-benzoyl-1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3t). Pale white solid; mp: 158-160 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 7.84 (s, 1 H), 7.82 (d, 1 H, J = 8.4 Hz), 7.75 (d, 2 H, J = 8.6 Hz), 7.65 (t, 4 H, J = 7.0 Hz), 7.51 (t, 2 H, J = 7.6 Hz), 7.13 (d, 2 H, J = 8.7 Hz), 6.96 (d, 2 H, J = 8.5 Hz), 6.88 (d, 2 H, J = 8.6 Hz), 5.57 (s, 2 H), 3.85 (s, 3 H), 3.71 (s, 3 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 197.24, 162.52, 160.29, 158.09, 147.35, 139.18, 136.73, 134.05, 132.29, 132.42, 131.18, 130.08, 129.71, 129.15, 126.07, 122.92, 120.40, 116.09, 115.90, 115.57, 57.02, 56.71, 48.96; ESI-MS $[\text{M}+\text{H}^+]$: m/z = 449 and $[\text{M}+\text{Na}^+]$: m/z = 471; ESI-HRMS: Calcd for $\text{C}_{29}\text{H}_{25}\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$), 449.1860; Found, 449.1850.



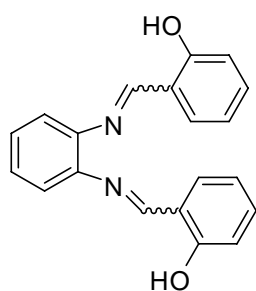
5-benzoyl-1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole (3u). Pale brown solid; mp: 164-166 °C; ^1H NMR (DMSO- d_6 , 500 MHz) δ 7.88 (d, 2 H, J = 8.0 Hz), 7.80 (d, 2 H, J = 8.4 Hz), 7.70-7.63 (m, 6 H), 7.52 (t, 2 H, J = 7.7 Hz), 7.38 (d, 2 H, J = 8.4 Hz), 7.04 (d, 2 H, J = 8.4 Hz), 5.67 (s, 2 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ

196.49, 156.42, 146.97, 138.80, 136.64, 136.53, 133.55, 133.42, 132.70, 132.18, 130.78, 130.26, 130.06, 129.58, 129.45, 129.35, 125.66, 120.47, 115.19, 48.32; ESI-MS $[M+H]^+$: $m/z = 457$; ESI-HRMS: Calcd for $C_{27}H_{19}Cl_2N_2O$ ($[M+H]^+$), 457.0869; Found, 457.0855.

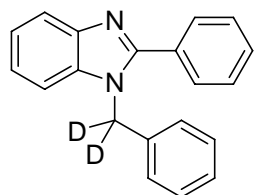


5-benzoyl-2-(furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzo[d]imidazole (3v). Brown solid; mp: 124-126 °C; 1H NMR (DMSO- d_6 , 500 MHz) δ 8.18 (s, 1 H), 8.08 (s, 1 H), 7.77 (t, 3 H, $J = 8.5$ Hz), 7.71-7.66 (m, 2 H), 7.59 (t, 3 H, $J = 8.0$ Hz), 7.40 (d, 1 H, $J = 3.5$ Hz), 6.82-6.80 (m, 1 H), 6.48 (d, 1 H, $J = 3.2$ Hz), 6.42-6.41 (m, 1 H),

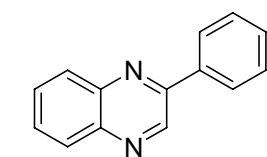
5.87 (s, 2 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 196.48, 150.65, 147.36, 147.03, 145.45, 144.59, 138.94, 136.10, 133.51, 132.56, 130.85, 129.64, 125.84, 119.95, 115.51, 114.94, 113.60, 111.80, 110.15, 42.33; ESI-MS $[M+H]^+$: $m/z = 369$; ESI-HRMS: Calcd for $C_{23}H_{17}N_2O_3$ ($[M+H]^+$), 369.1234; Found: 369.1233.



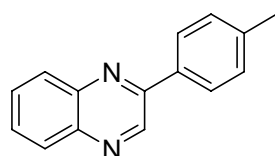
2,2'-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (5). Yellow solid; mp: 160-162 °C; 1H NMR (DMSO- d_6 , 500 MHz) δ 12.94 (s, 2 H), 8.94 (s, 2H), 7.68-7.65 (m, 2 H), 7.48-7.39 (m, 6 H), 7.00-6.95 (m, 4 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 1165.25, 161.57, 143.46, 134.64, 133.65, 129.01, 120.95, 120.68, 120.28, 117.86; ESI-MS $[M+H]^+$: $m/z = 317$.



1-benzyl- d_2 -2-phenyl-1H-benzo[d]imidazole (3a- d_2). White solid; 1H NMR (DMSO- d_6 , 500 MHz) δ 7.74-7.72 (m, 3 H), 7.53-7.46 (m, 4 H), 7.29-7.21 (m, 5 H), 7.00 (d, 2 H, $J = 7.2$ Hz); ESI-MS $[M+H]^+$: $m/z = 287$; $[M+Na]^+$: $m/z = 309$.



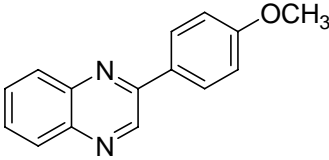
2-phenylquinoxaline (7a) Pale orange solid; mp: 75-76 °C;^[5] 1H NMR (DMSO- d_6 , 500 MHz) δ 9.59 (s, 1 H), 8.35 (d, 2 H, $J = 8.0$ Hz), 8.13 (t, 2 H, $J = 8.5$ Hz), 7.89-7.84 (m, 2 H), 7.61-7.57 (m, 3H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 152.17, 144.96, 142.60, 142.28, 137.23, 131.83, 131.63, 131.11, 130.41, 130.32, 130.05, 128.66; ESI-MS $[M+H]^+$: $m/z = 207$.

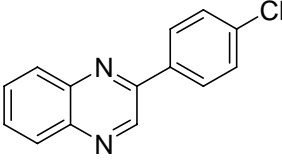


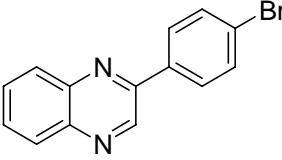
2-p-tolylquinoxaline (7b) Red solid; mp: 90-91 °C;^[5] 1H NMR (DMSO- d_6 , 500 MHz) δ 9.56 (s, 1 H), 8.25 (d, 2 H, $J = 8.0$ Hz), 8.12 (t, 2 H, $J = 8.1$ Hz), 7.88-7.80 (m, 2 H), 7.40 (d, 2 H, $J = 7.8$ Hz), 2.40 (s, 3 H); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ 152.10, 144.79, 142.60, 142.14, 141.51, 134.45, 131.73, 130.92, 130.83,

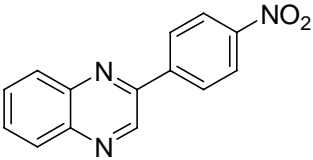
Supplementary Material (ESI) for Green Chemistry
This journal is © The Royal Society of Chemistry 2009

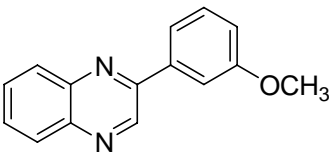
130.30, 130.02, 128.53, 22.15; ESI-MS [M+H⁺]: m/z = 221.

 **2-(4-methoxyphenyl)quinoxaline (7c)** White solid; mp: 99-101 °C; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 9.54 (s, 1 H), 8.32 (d, 2 H, *J* = 8.7 Hz), 8.10-8.07 (m, 2 H), 7.87-7.78 (m, 2 H), 7.14 (d, 2 H, *J* = 8.8 Hz), 3.86 (s, 3 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 162.46, 151.87, 144.66, 142.64, 141.88, 131.70, 130.54, 130.21, 130.17, 130.01, 129.61, 115.78, 56.60; ESI-MS [M+H⁺]: *m/z* = 237.

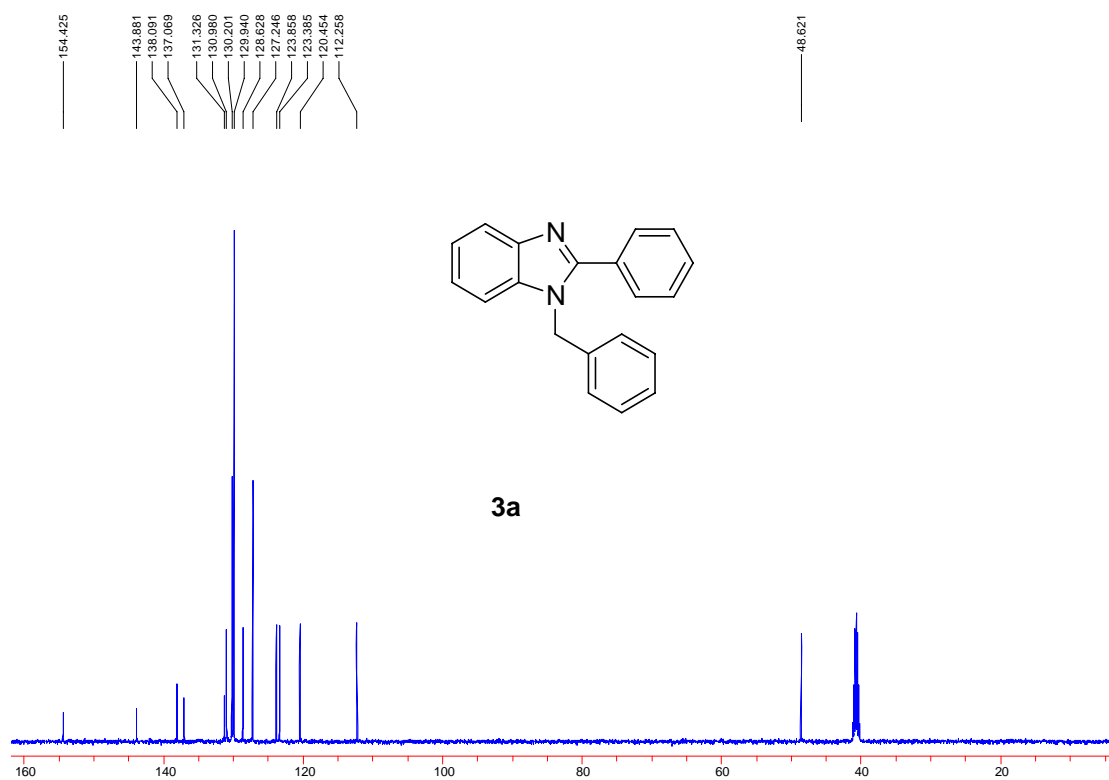
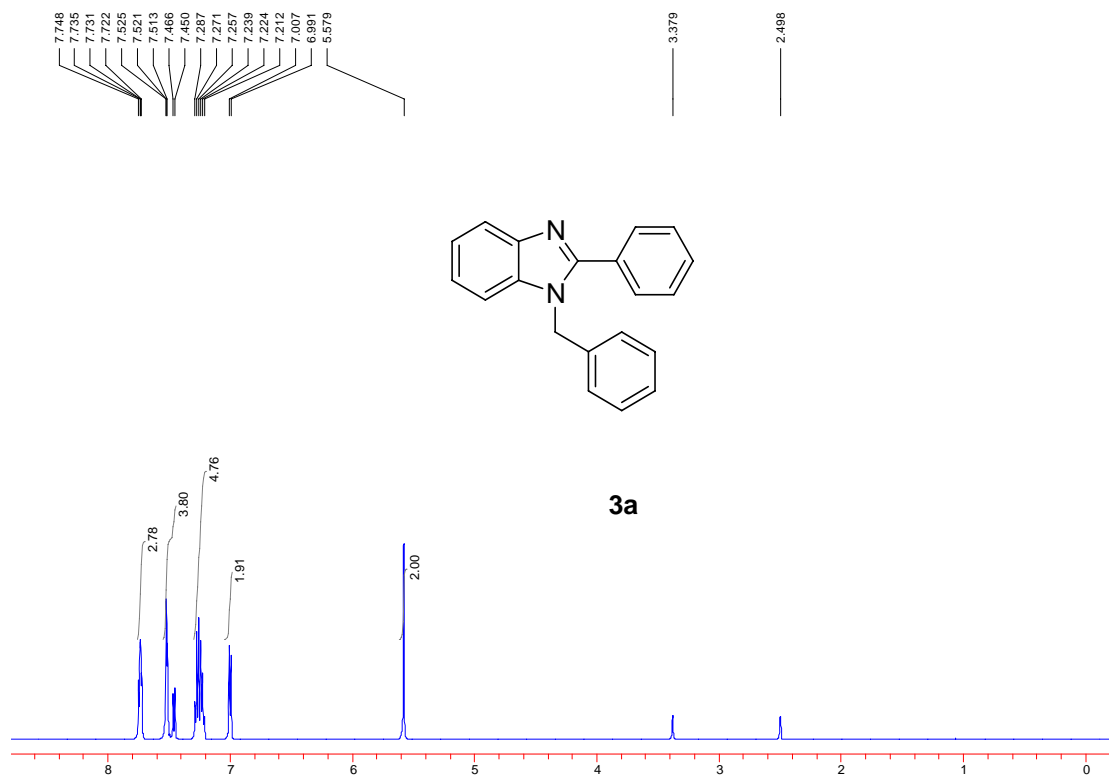
 **2-(4-chlorophenyl)quinoxaline (7d)** Pale yellow crystal; mp: 136-137 °C;^[6] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 9.56 (s, 1 H), 8.34 (d, 2 H, *J* = 8.5 Hz), 8.12-8.09 (m, 2 H), 7.88-7.82 (m, 2 H), 7.63 (d, 2 H, *J* = 9.0 Hz); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 150.96, 144.72, 142.47, 142.32, 136.60, 136.01, 131.90, 131.28, 130.37, 130.33, 130.04; ESI-MS [M+H⁺]: *m/z* = 241.

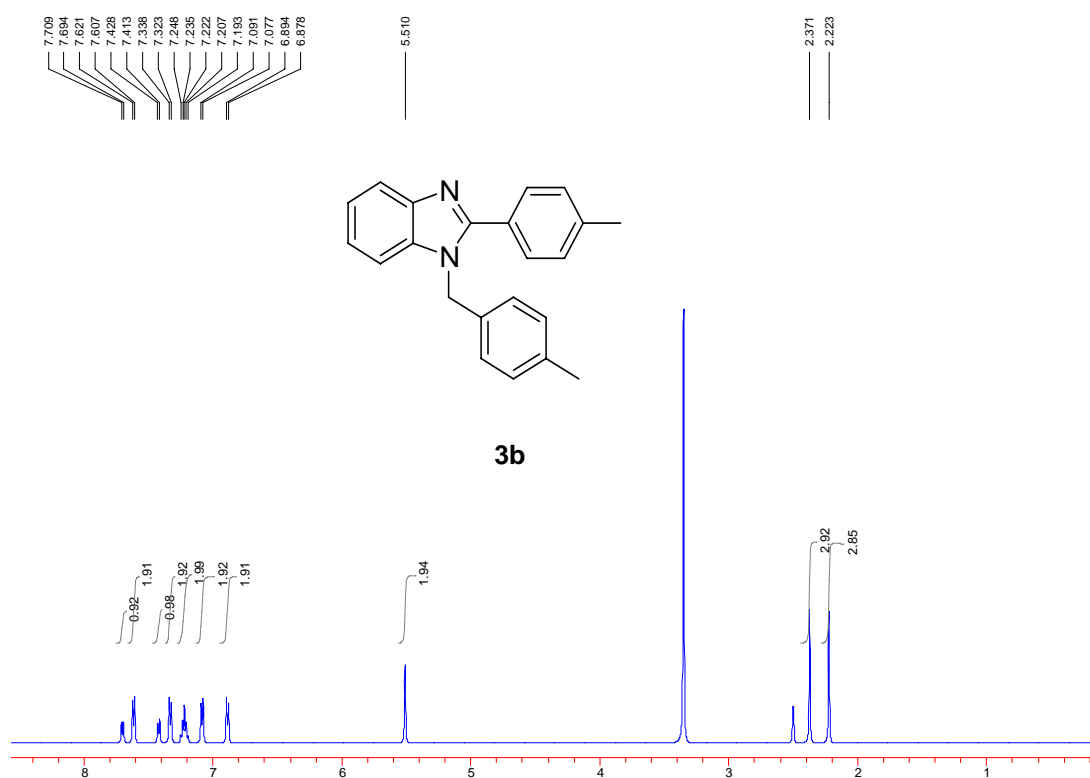
 **2-(4-bromophenyl)quinoxaline (7e)** Pale yellow solid; mp: 128-130 °C; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 9.59 (s, 1 H), 8.29 (d, 2 H, *J* = 7.4 Hz), 8.14-8.11 (m, 2 H), 7.89-7.80 (m, 2 H), 7.79 (d, 2 H, *J* = 7.5 Hz); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 151.09, 144.71, 142.48, 142.35, 136.38, 133.28, 131.94, 131.33, 130.62, 130.39, 130.06, 125.50; ESI-MS [M+H⁺]: *m/z* = 285.

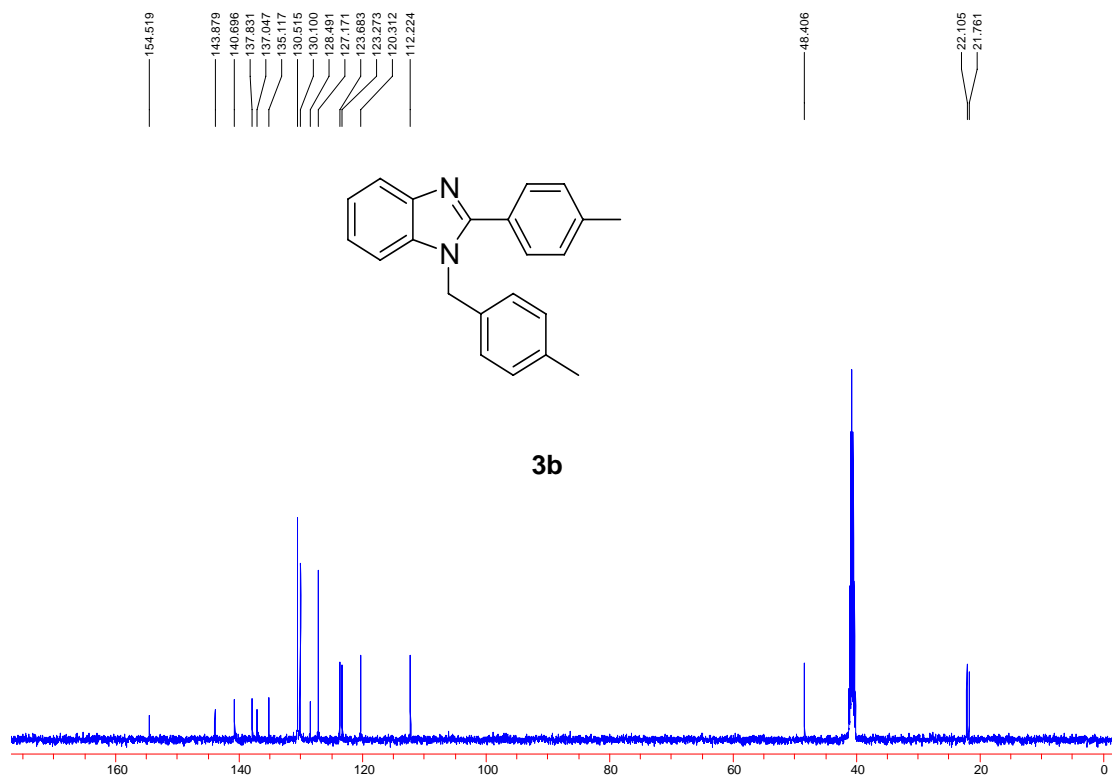
 **2-(4-nitrophenyl)quinoxaline (7f)** Yellow solid; mp: 190 °C;^[7] ¹H NMR (DMSO-*d*₆, 500 MHz) δ 9.65 (s, 1 H), 8.57 (d, 2 H, *J* = 8.5 Hz), 8.39 (d, 2 H, *J* = 8.5 Hz), 8.17-8.13 (m, 2 H), 7.93-7.90 (m, 2 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 150.10, 149.64, 145.13, 143.16, 142.71, 142.50, 132.28, 132.14, 130.79, 130.14, 129.92, 125.36; ESI-MS [M+H⁺]: *m/z* = 252.

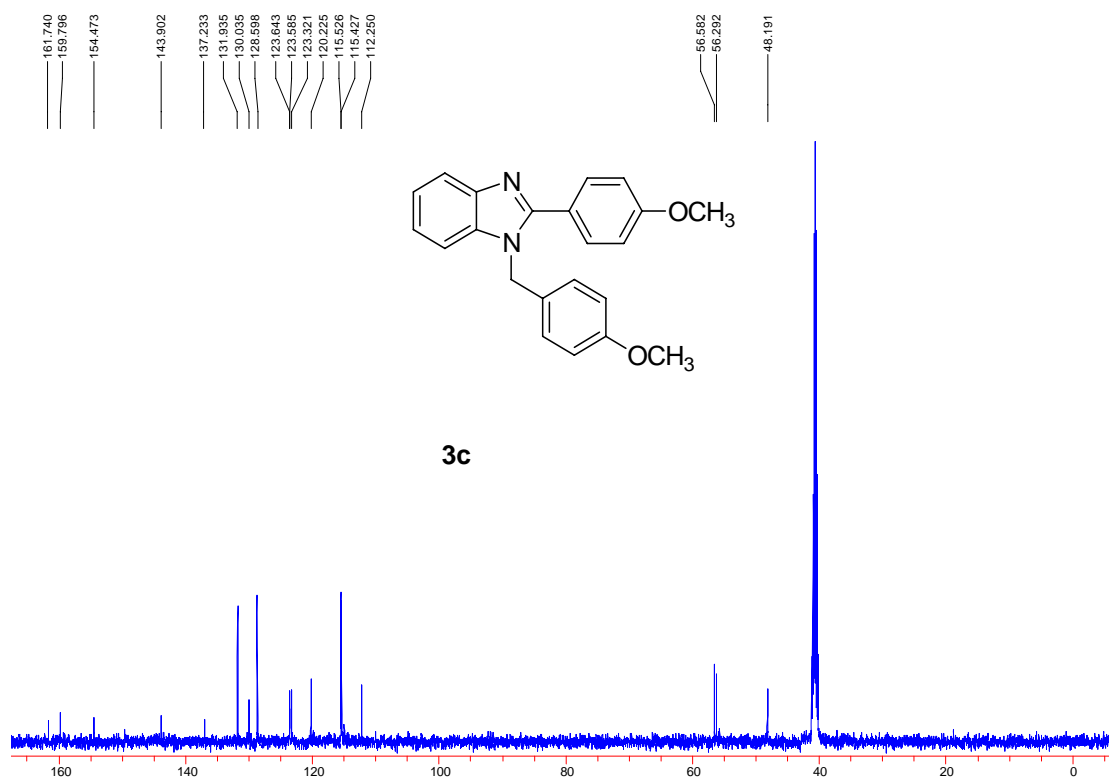
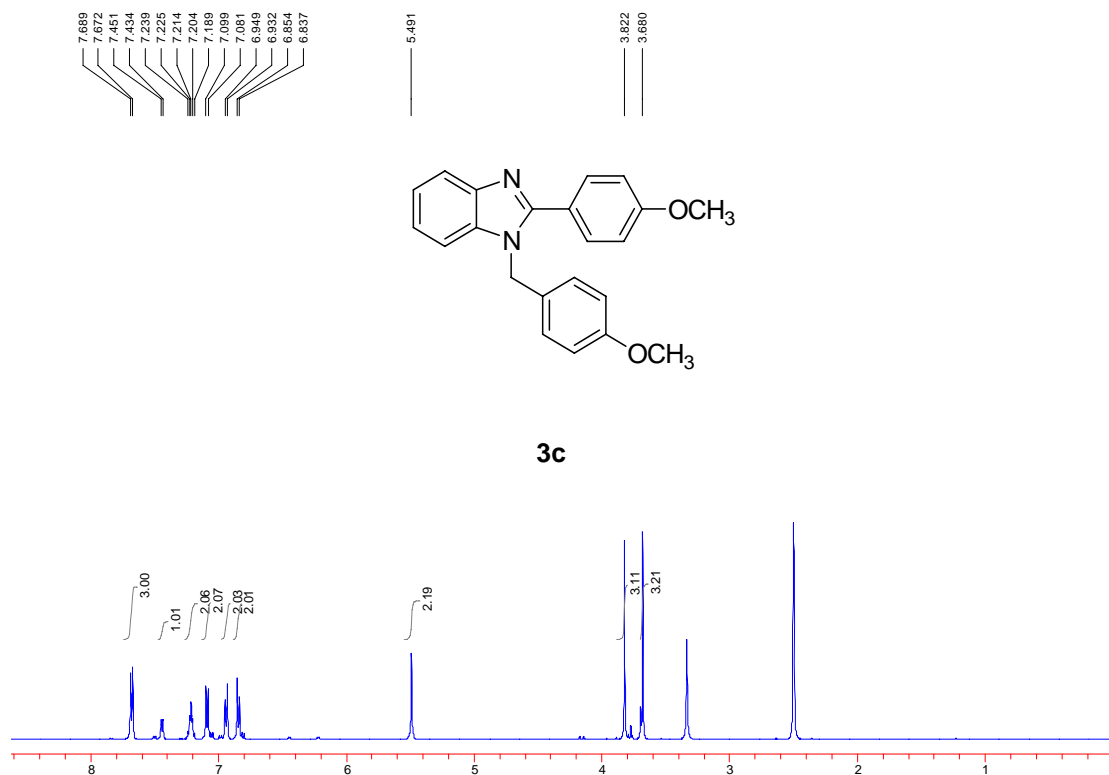
 **2-(3-methoxyphenyl)quinoxaline (7g)** Red solid; mp: 87-88 °C; ¹H NMR (DMSO-*d*₆, 500 MHz) δ 9.58 (s, 1 H), 8.16-8.11 (m, 2 H), 7.93-7.83 (m, 4 H), 7.51 (t, 1 H, *J* = 7.8 Hz), 7.15 (d, 1 H, *J* = 8.2 Hz), 3.89 (s, 3 H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ 161.07, 151.94, 145.06, 142.53, 142.34, 138.64, 131.81, 131.45, 131.13, 130.42, 130.03, 121.01, 117.45, 113.69, 56.52; ESI-MS [M+H⁺]: *m/z* = 237.

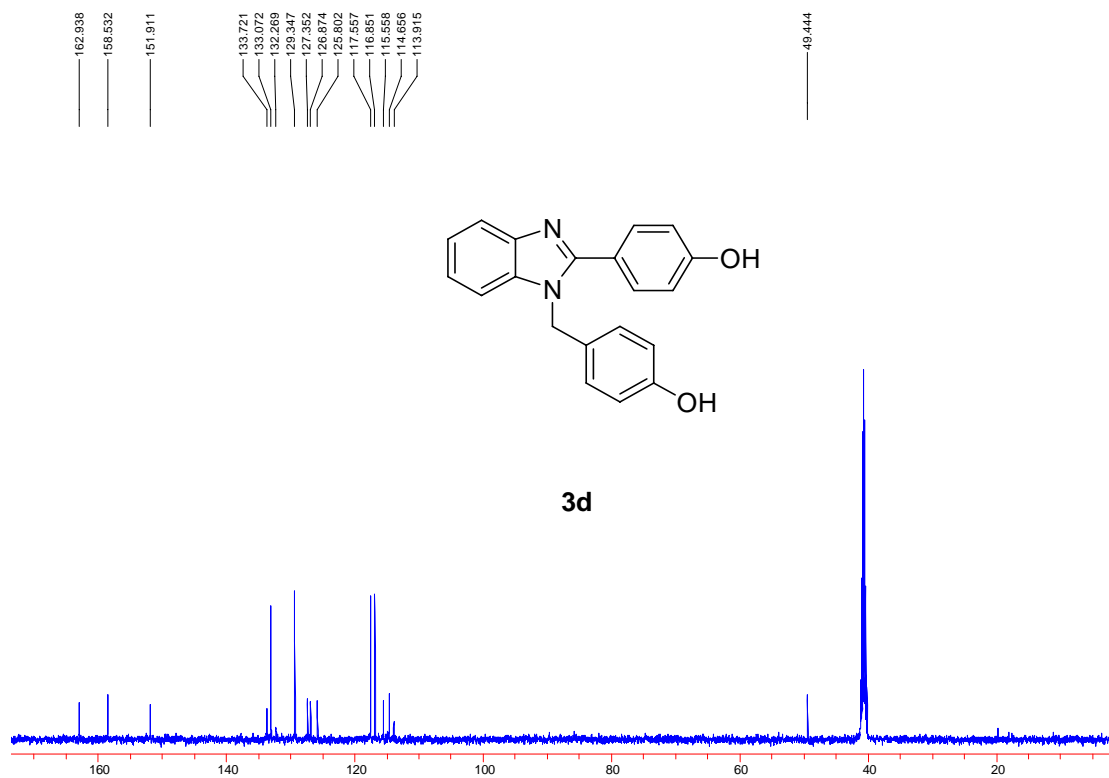
- [1] N. D. Kokare, J. N. Sangshetti, D. B. Shinde, *Synthesis* 2007, 2829.
- [2] V. Ravi, E. Ramu, K. Vljay, A. S. Rao, *Chem. Pharm. Bull.* 2007, **55**, 1254.
- [3] J. S. Yadav, B. V. S. Reddy, K. Premalatha, K. S. Shankar, *Can. J. Chem.* 2008, **86**, 124.
- [4] M. Chakrabarty, R. Mukherjee, S. Karmakar, Y. Harigaya, *Monatsh. Chem.* 2007, **138**, 1279.
- [5] C. Neochoritis, J. Stephanidou-Stephanatou, C. A. Tsoleridis, *Synlett* 2009, 302.
- [6] Y. Vara, E. Aldaba, A. Arrieta, J. L. Pizarro, M. I. Arriortua, F. P. Cossío, *Org. Biomol. Chem.* 2008, **6**, 1763.
- [7] C. S. Cho, S. G. Oh, *J. Mol. Catal. A* 2007, **276**, 205.

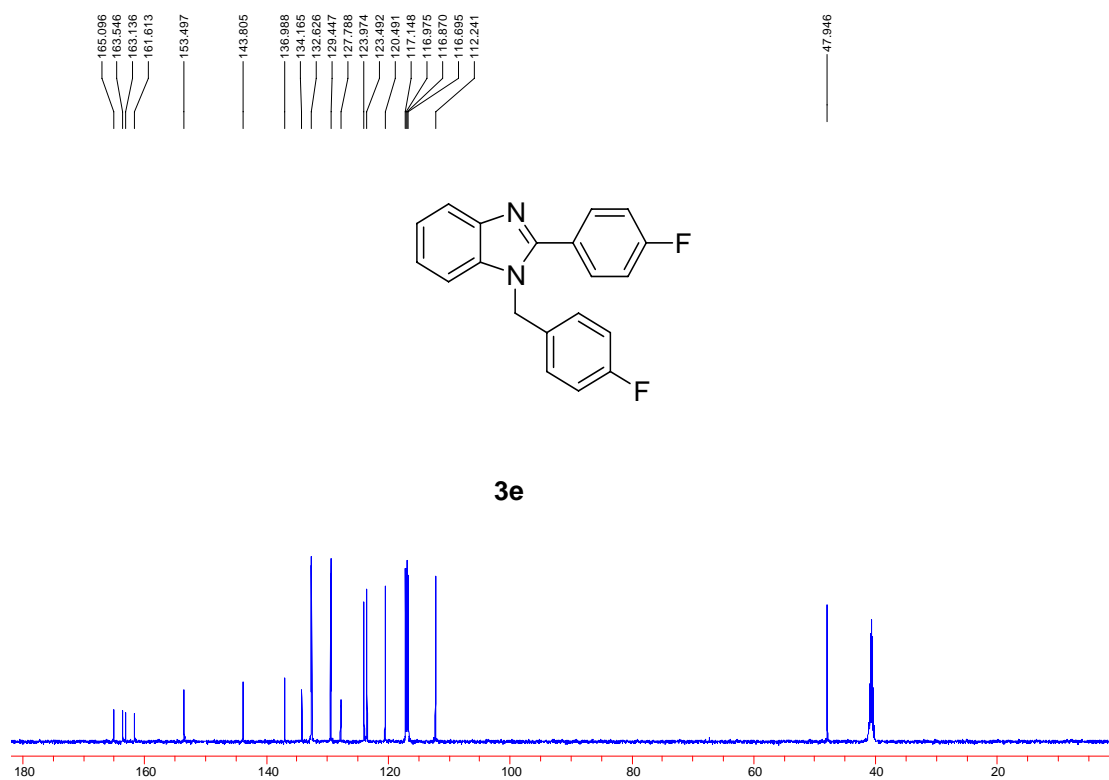
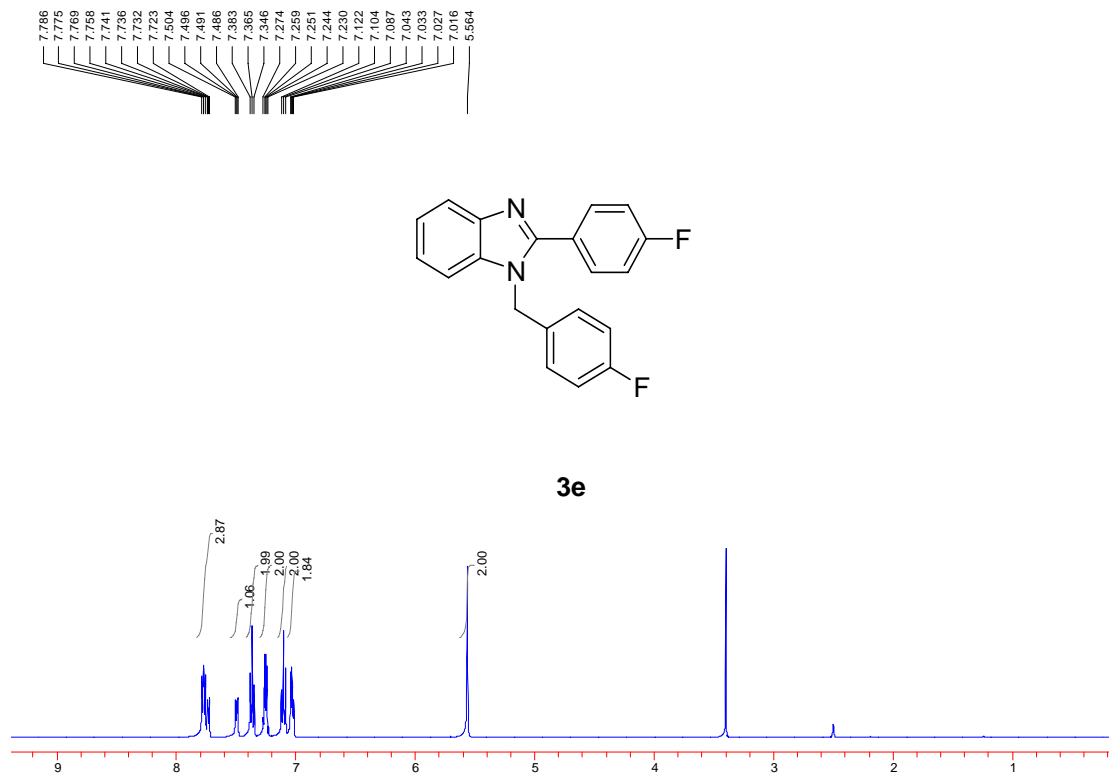


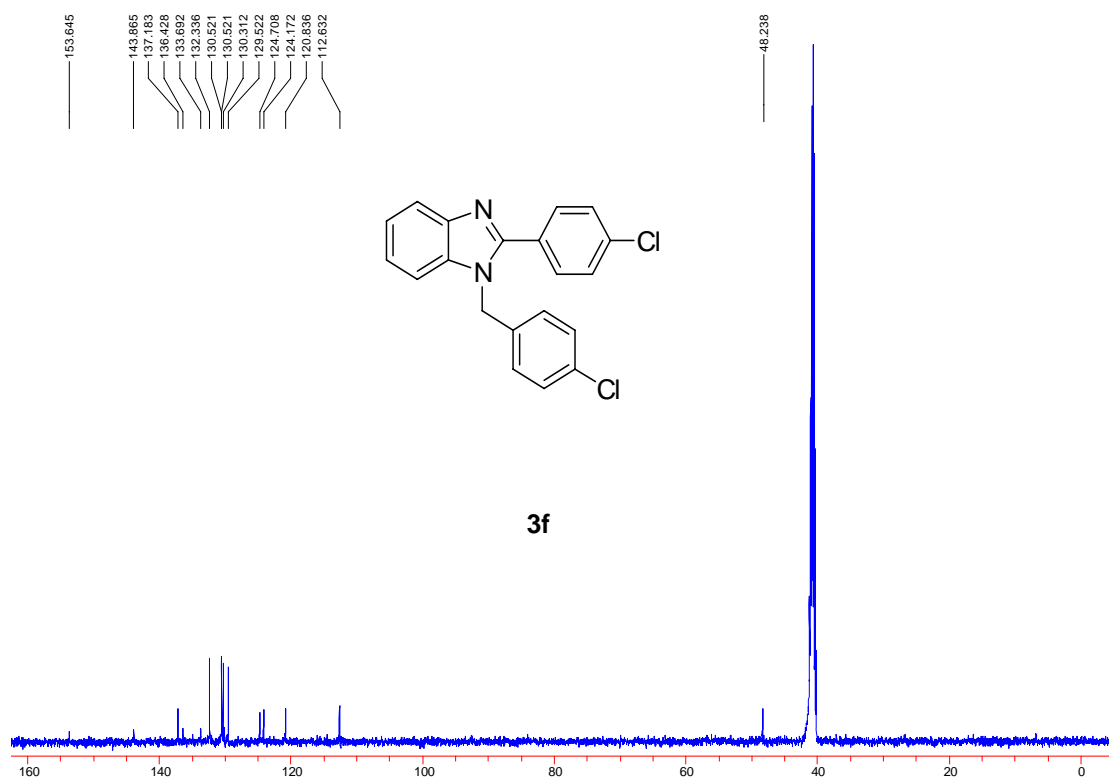
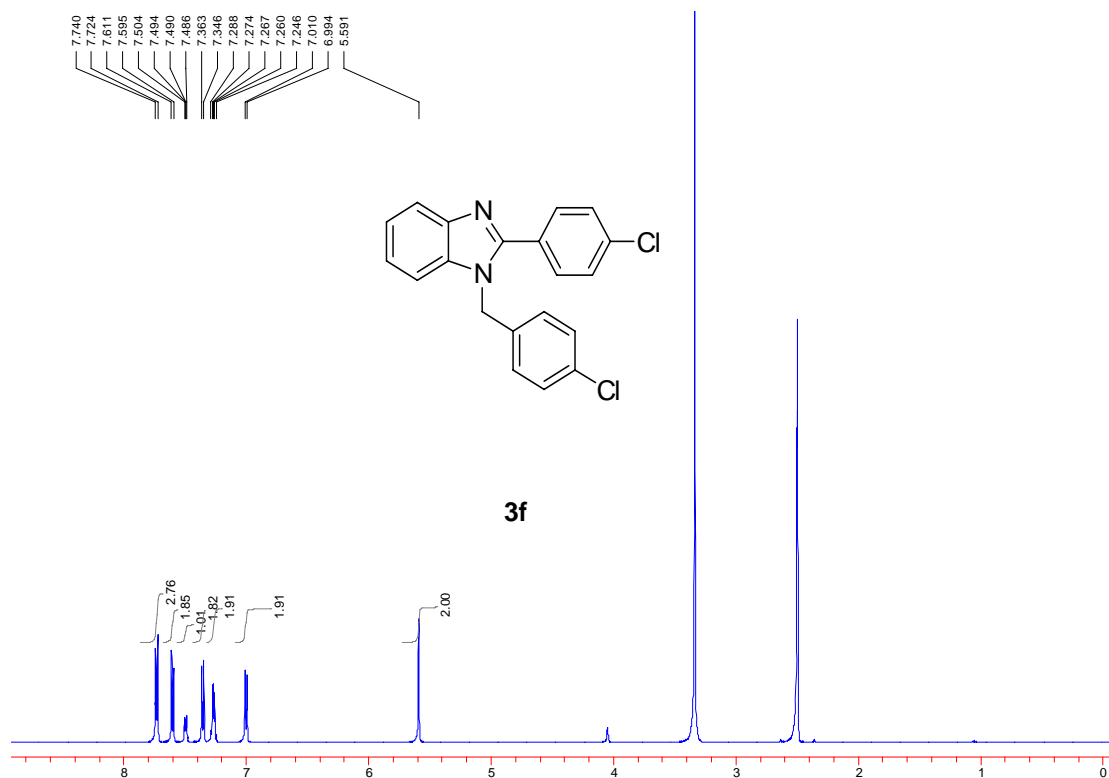


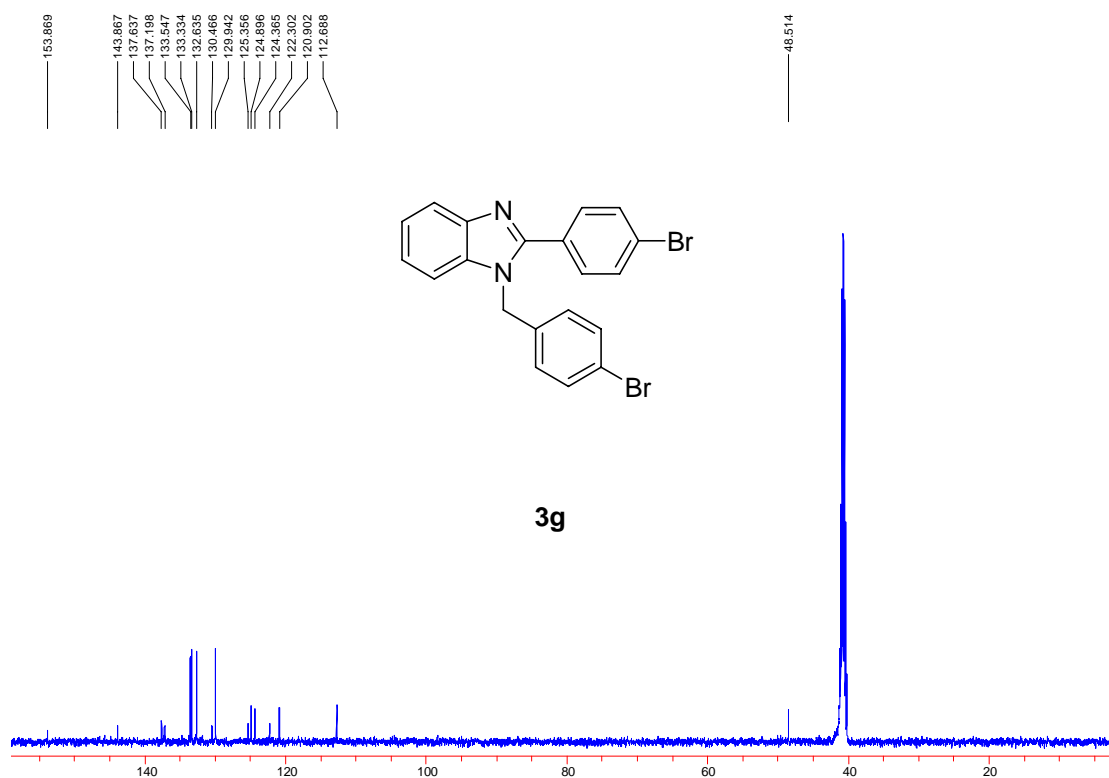
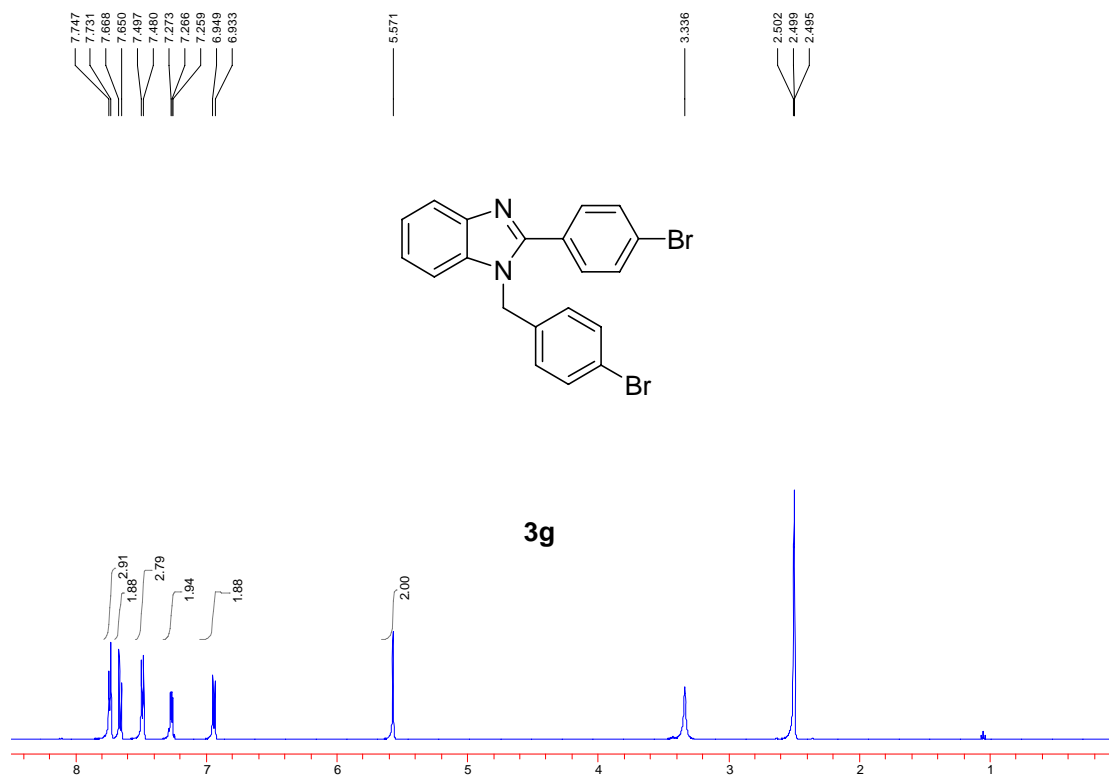


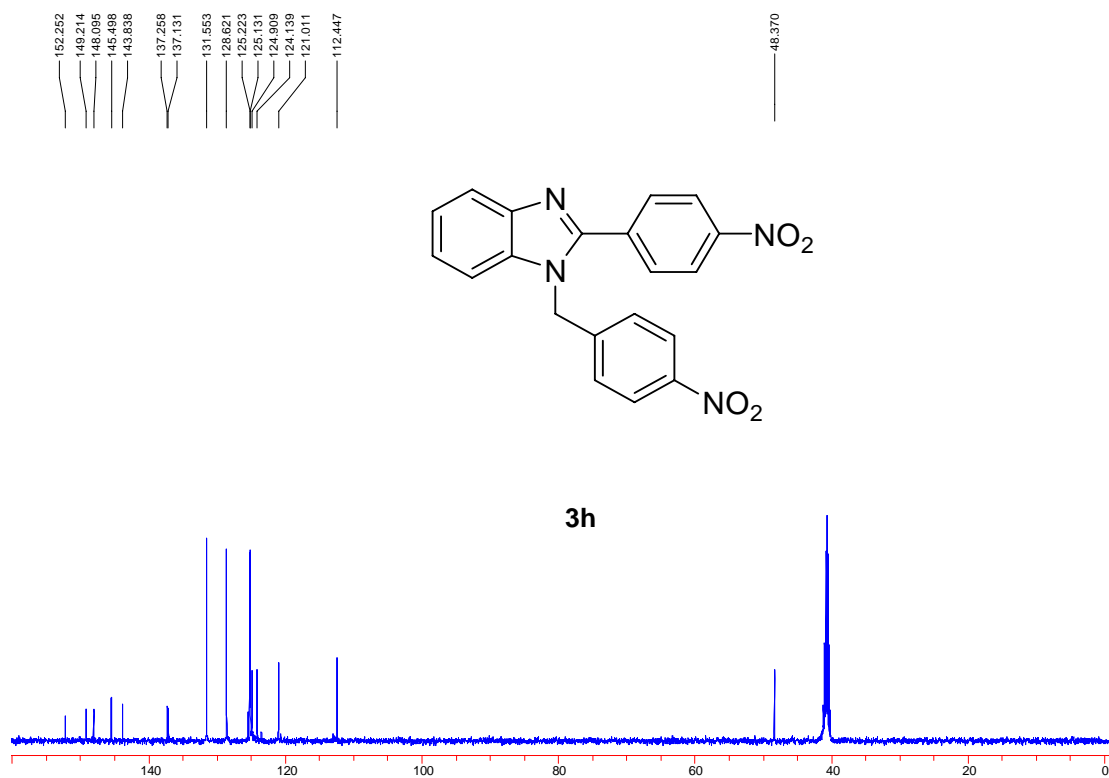
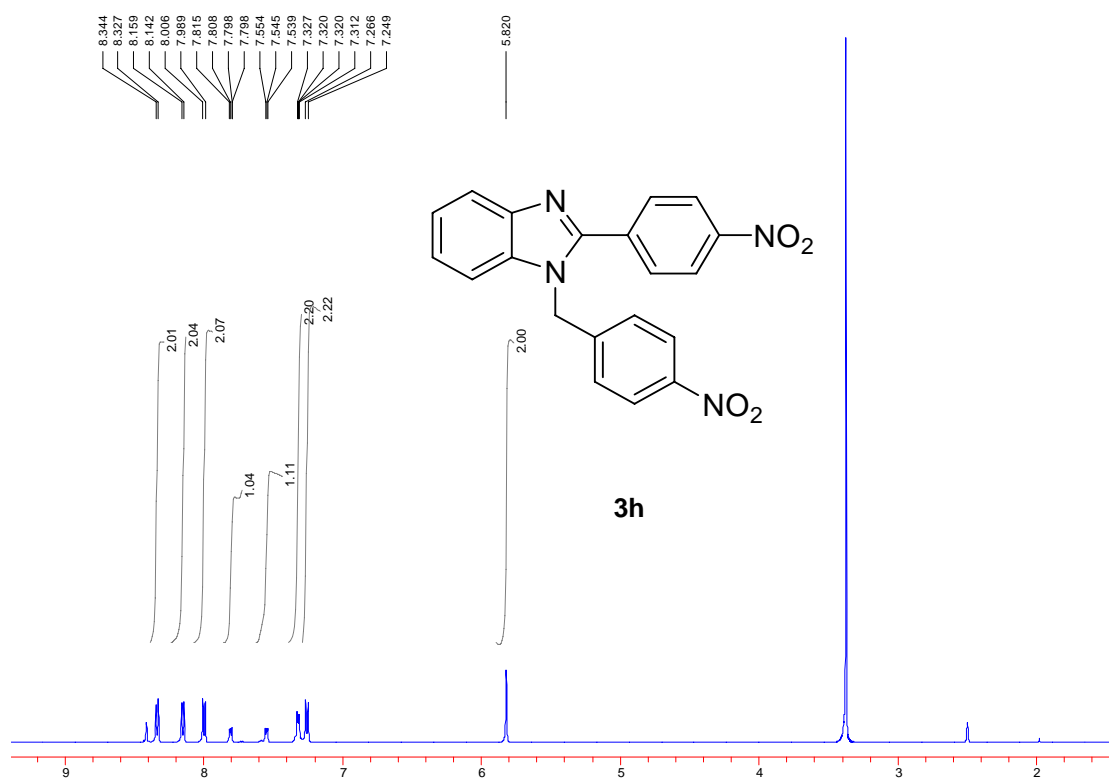


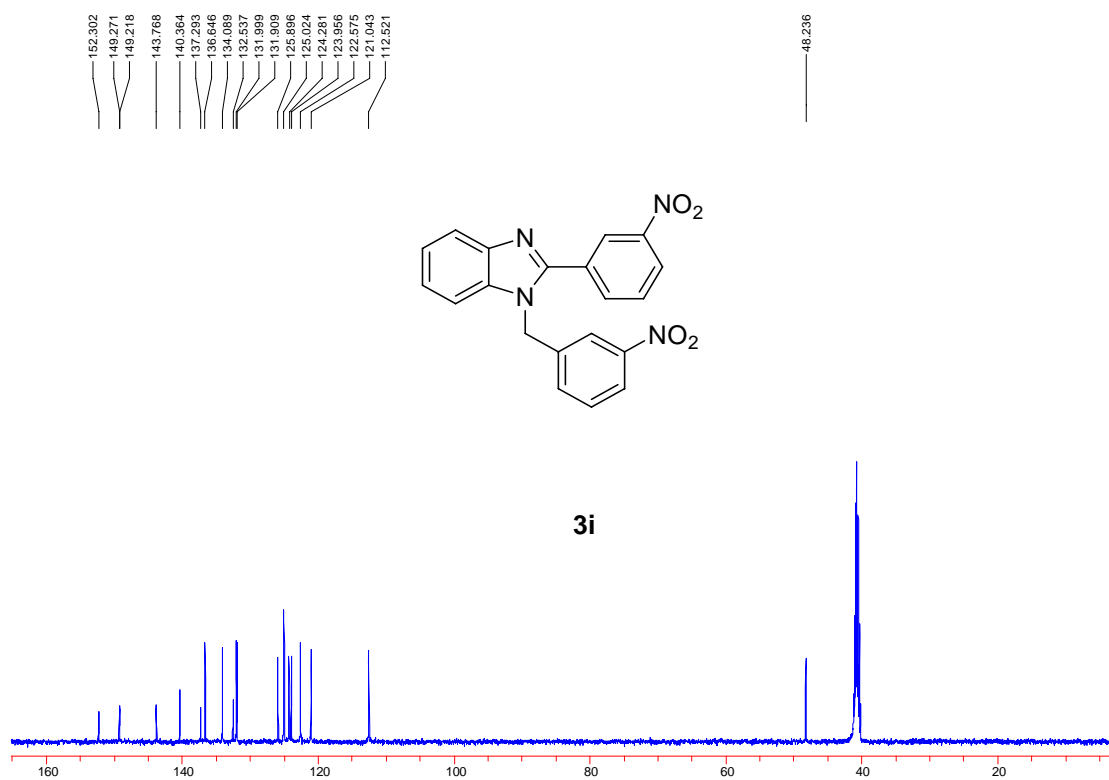
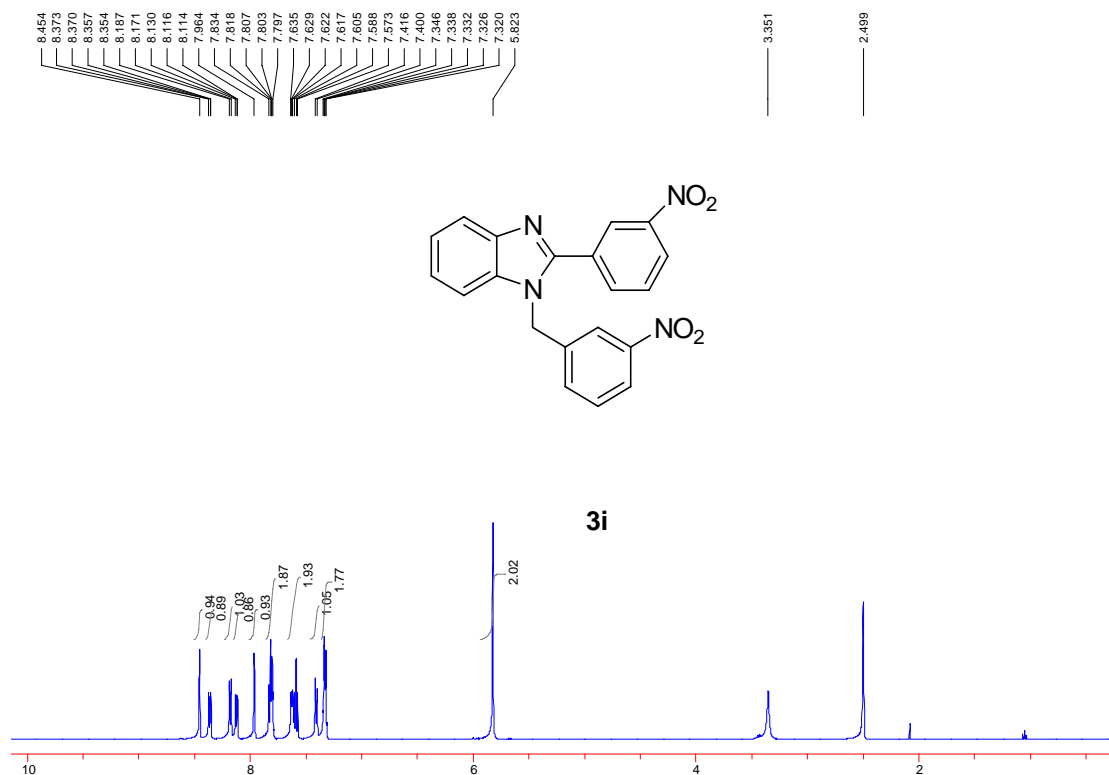


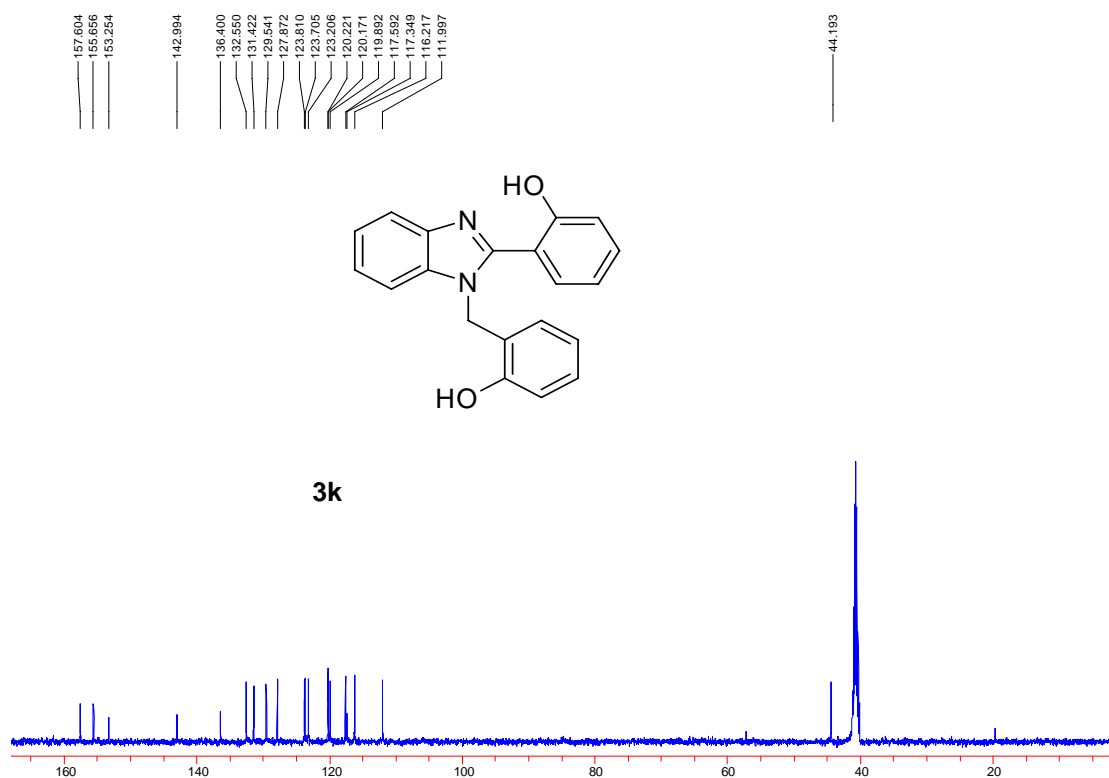
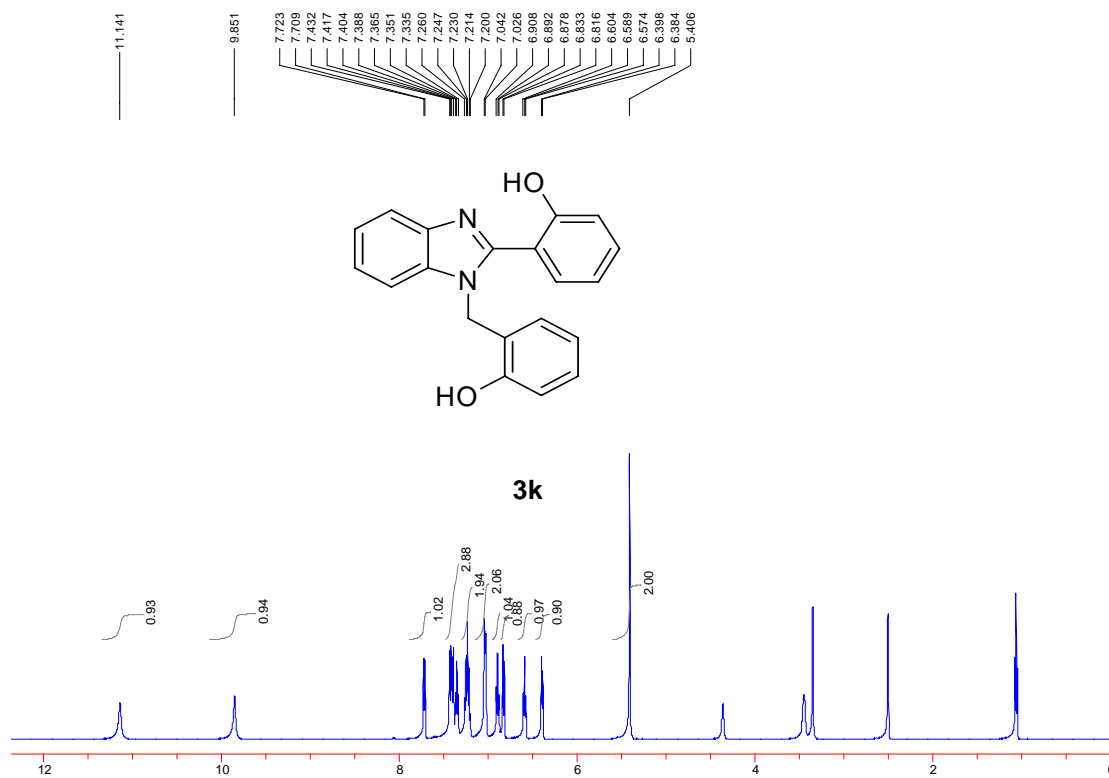


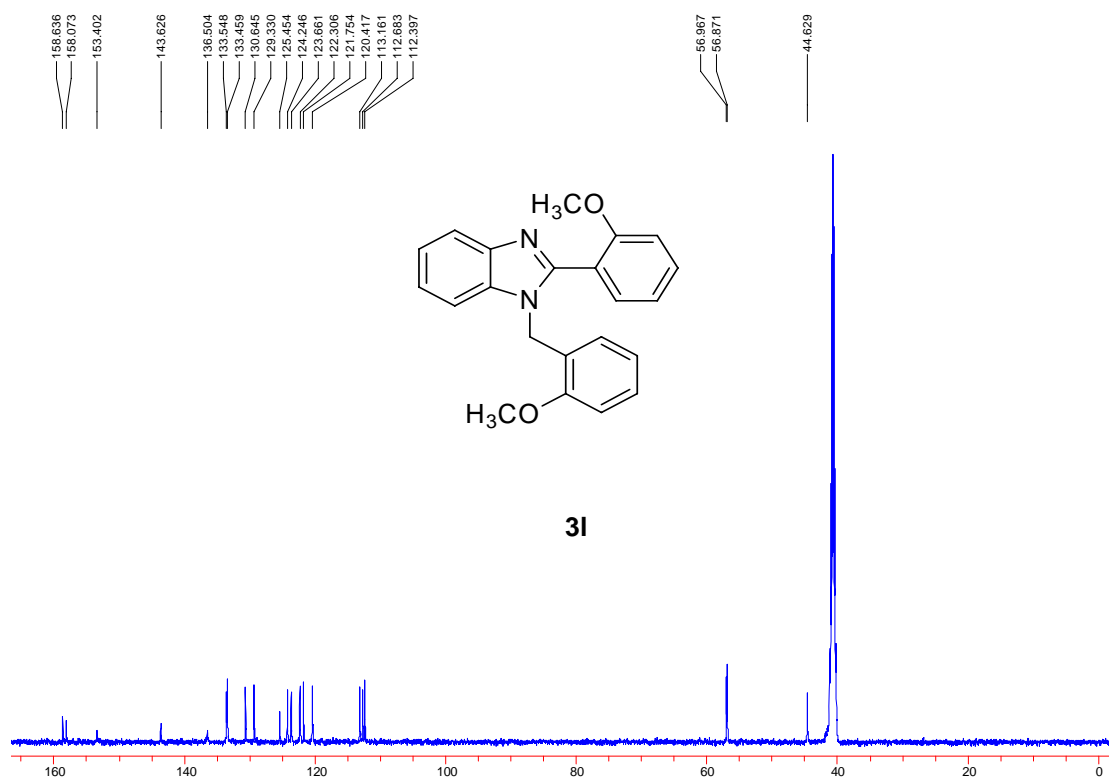
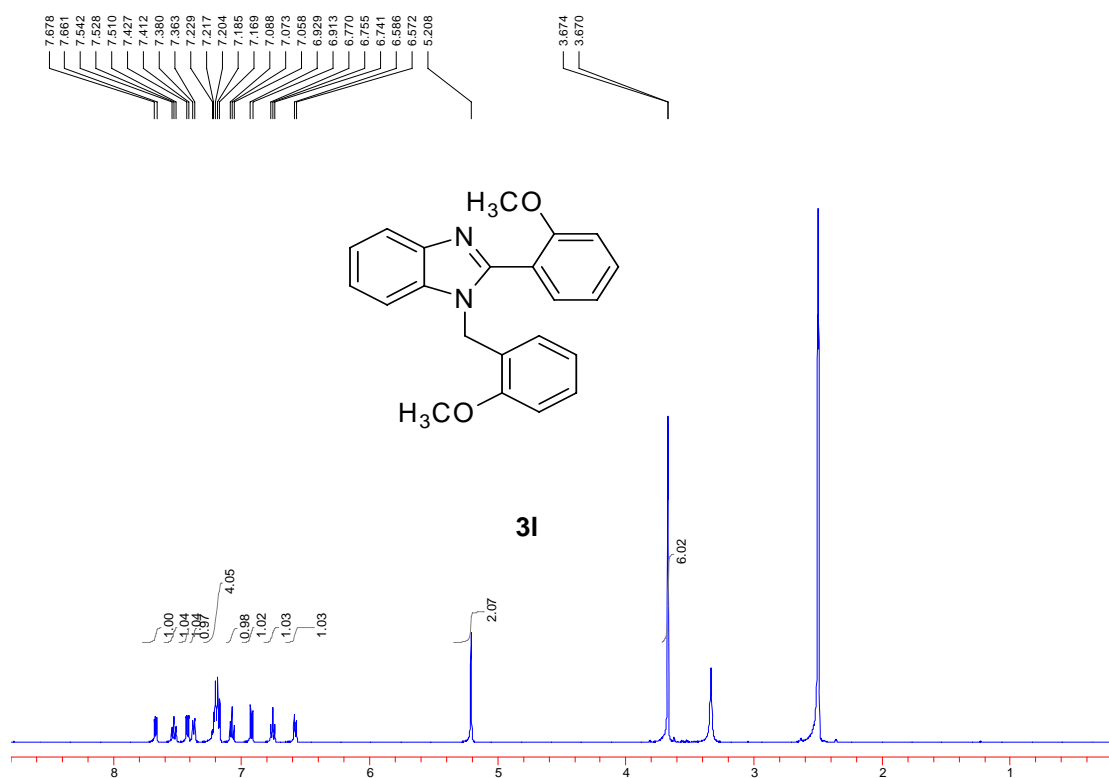


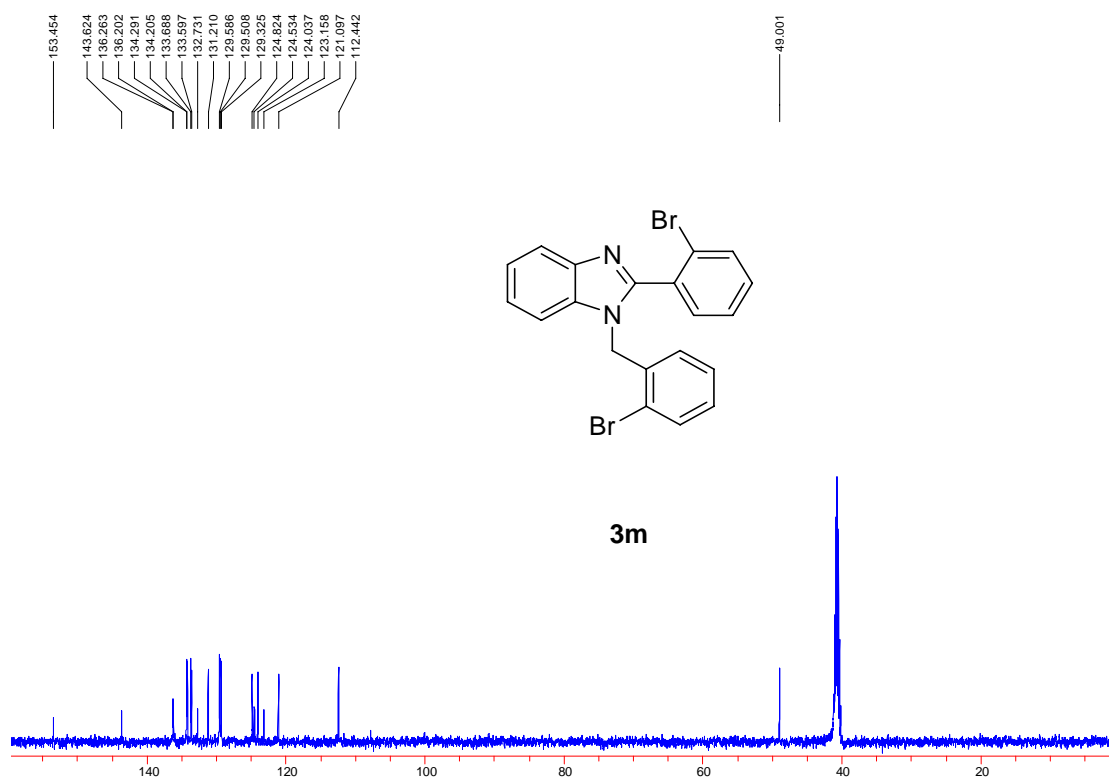
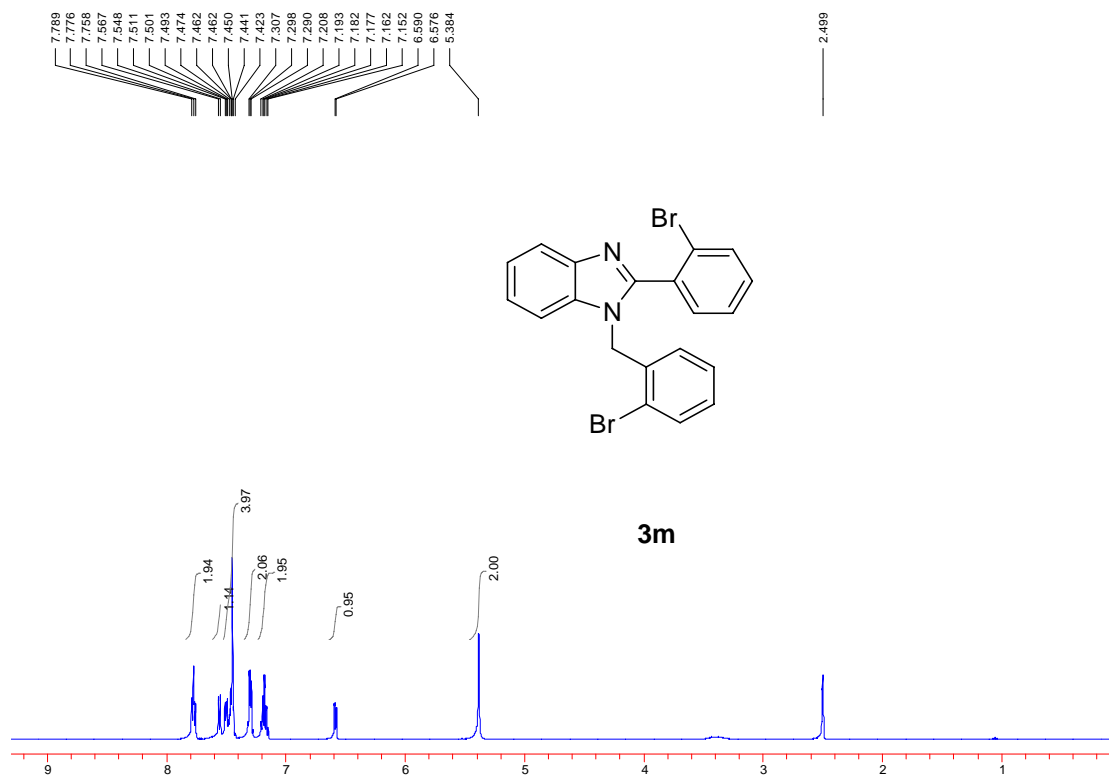


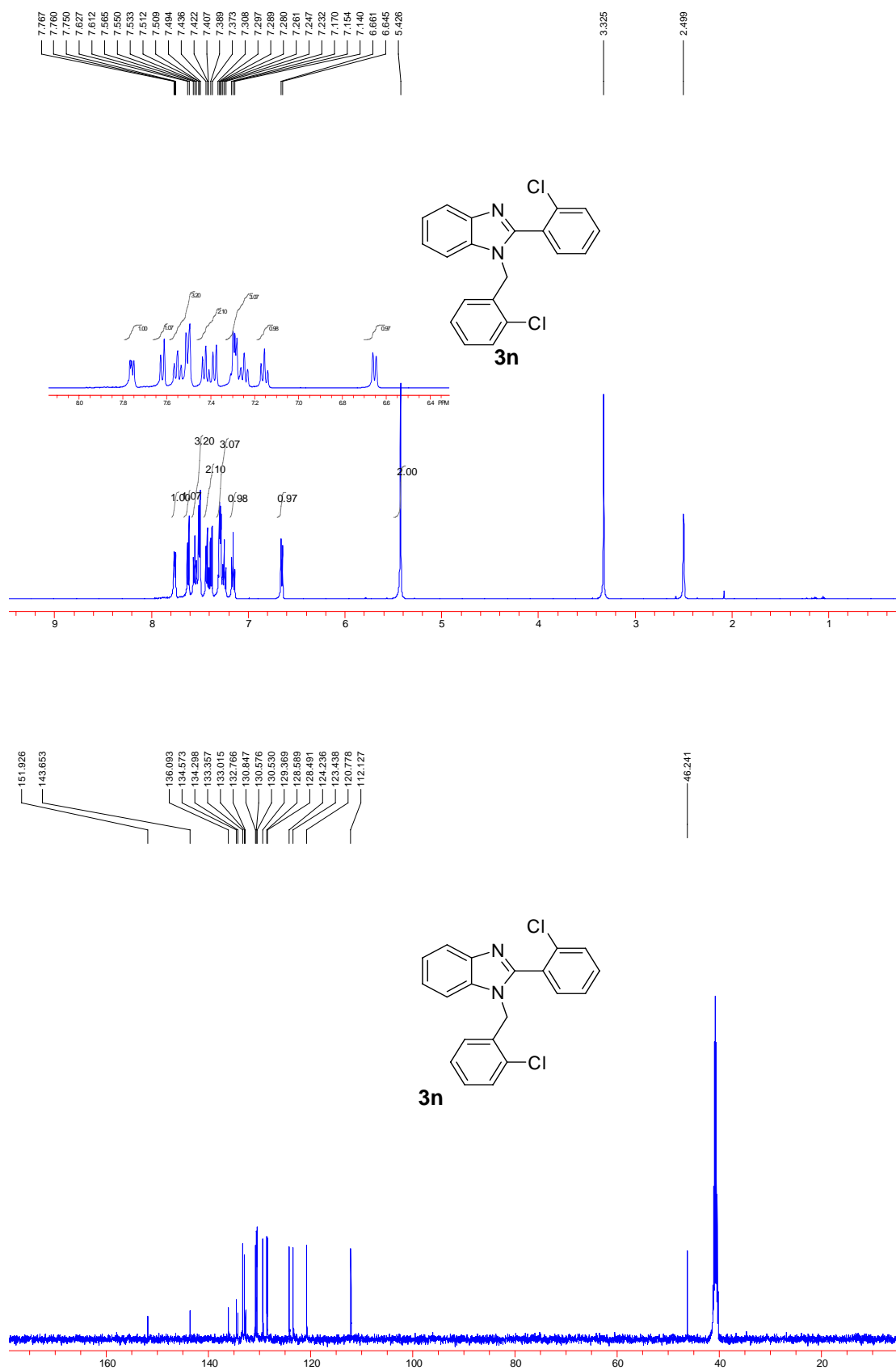


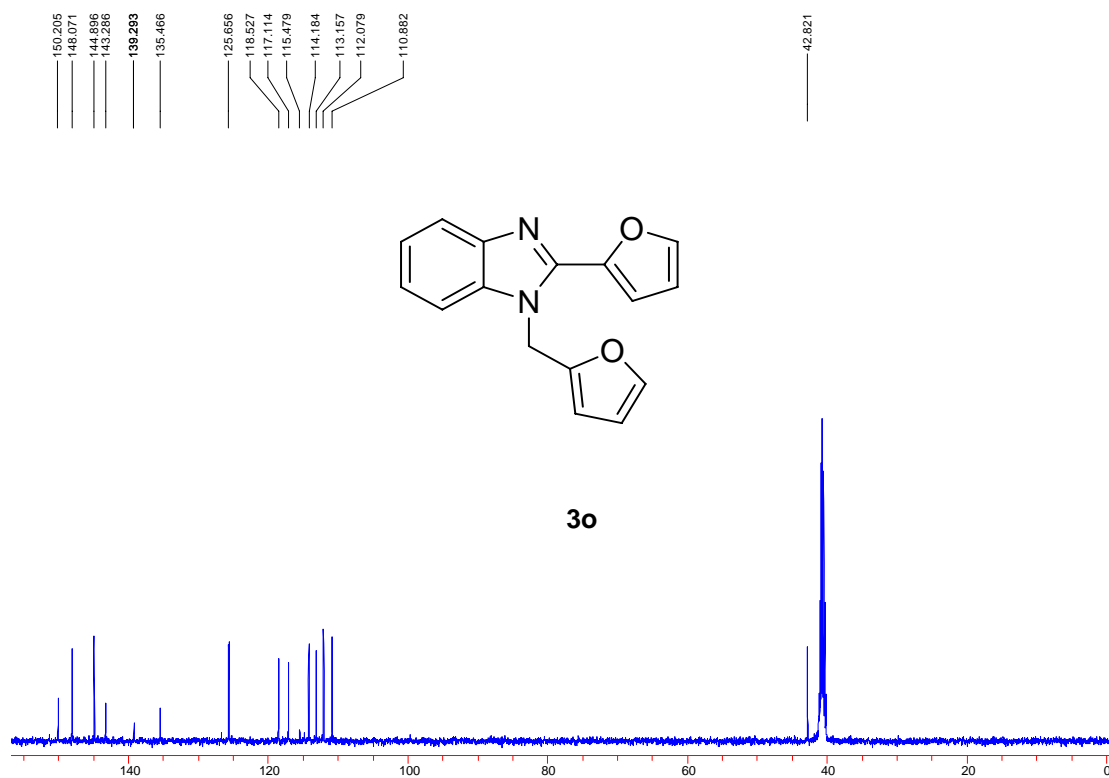
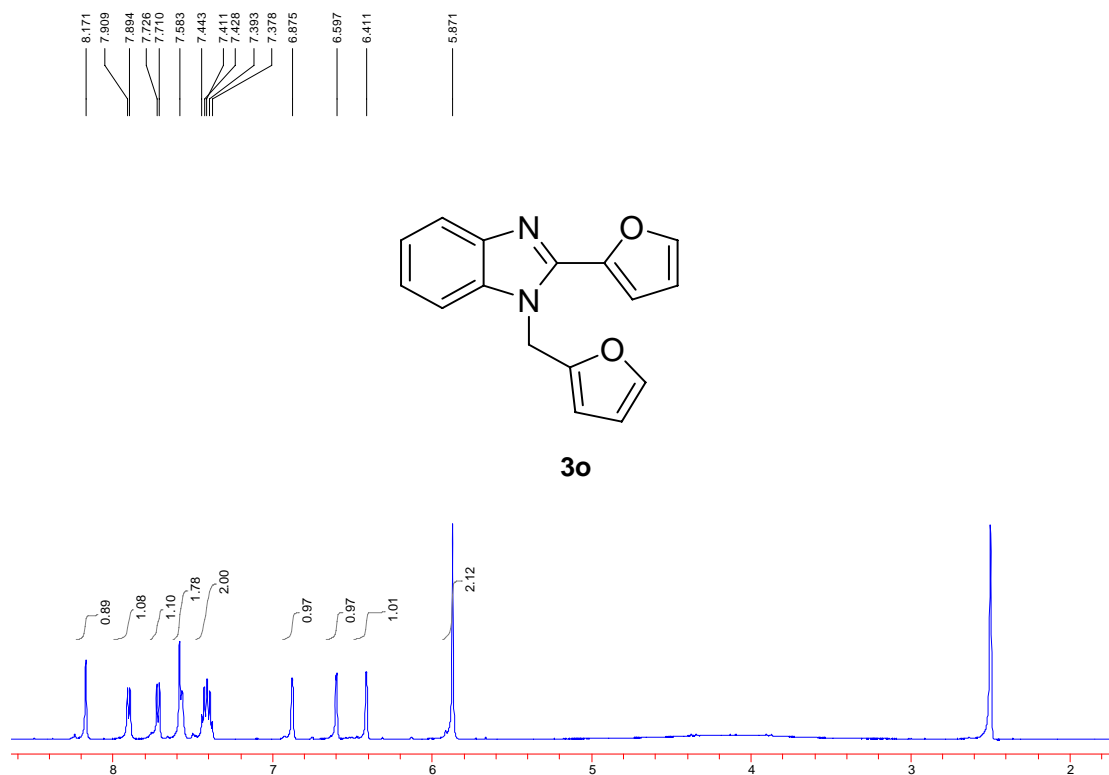


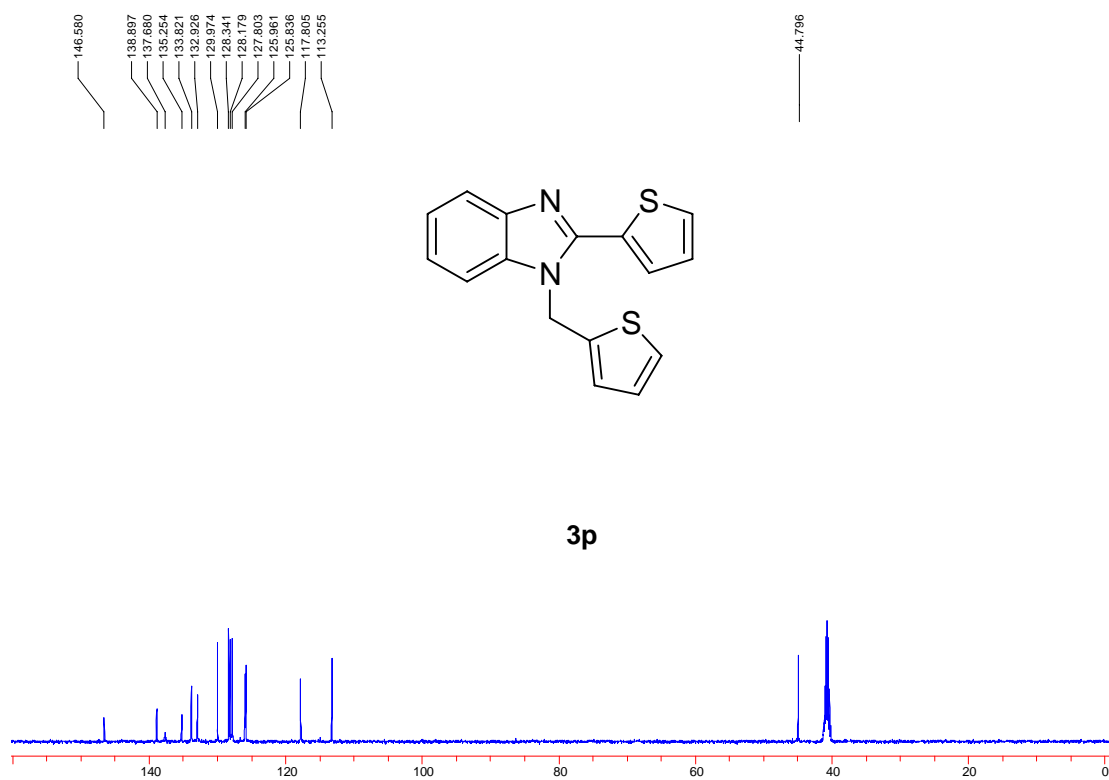
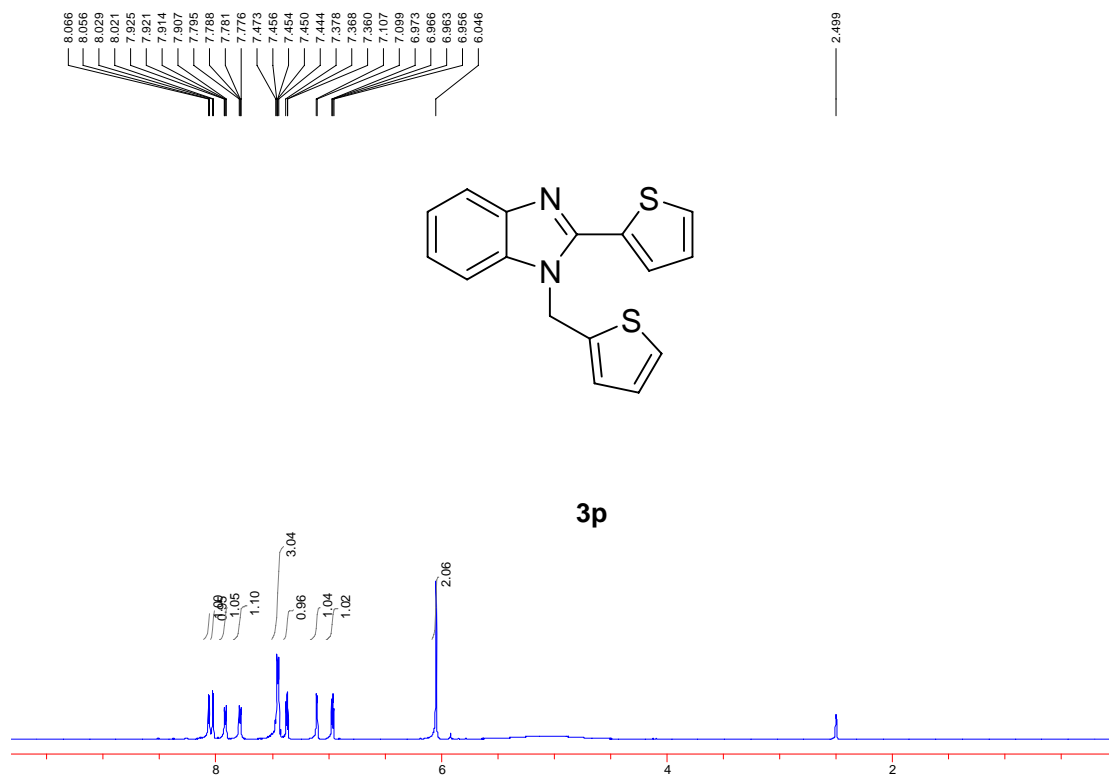


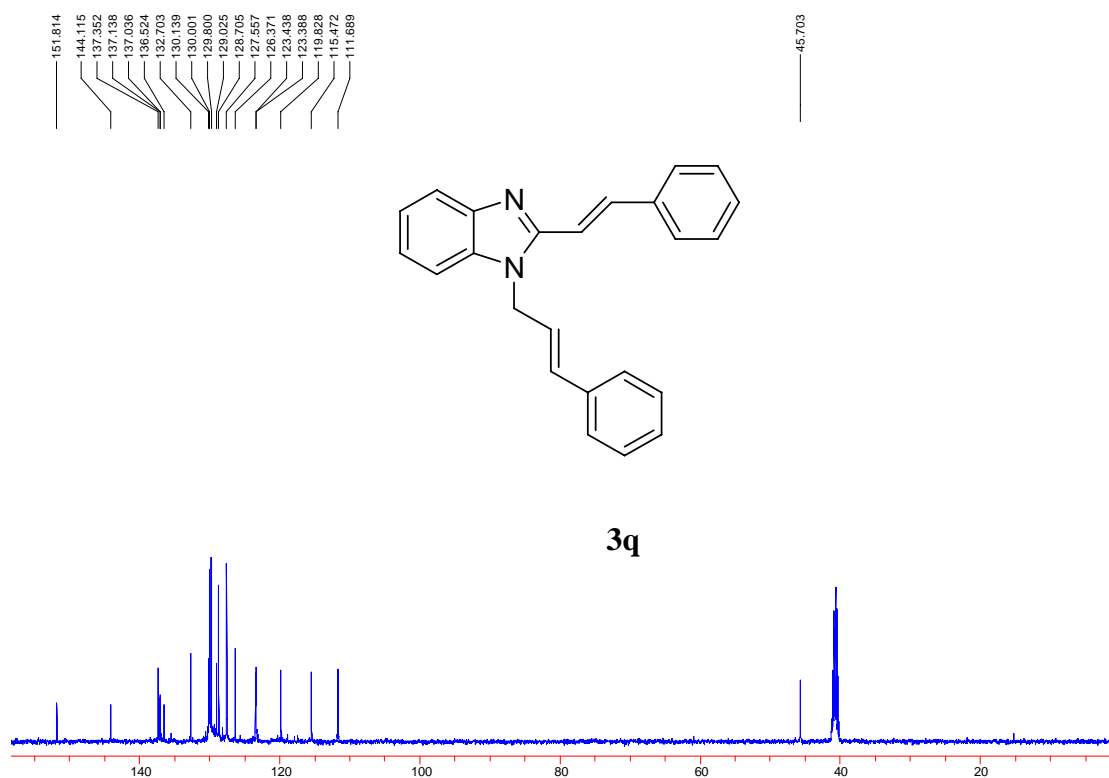
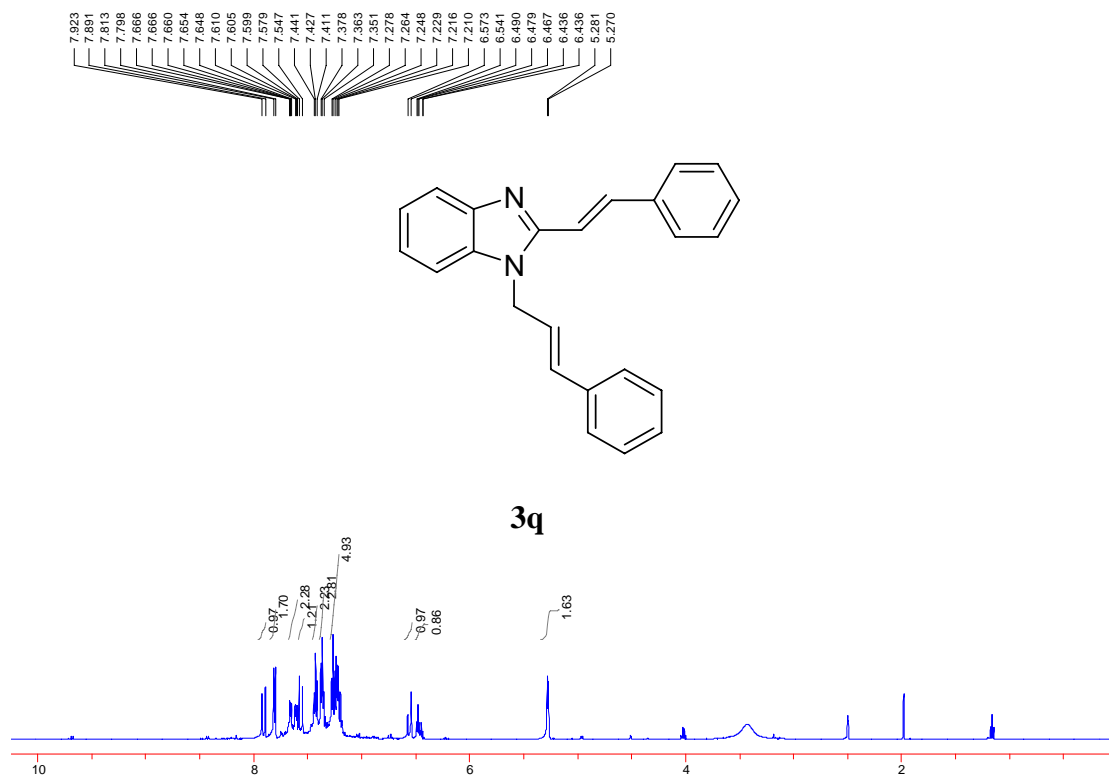


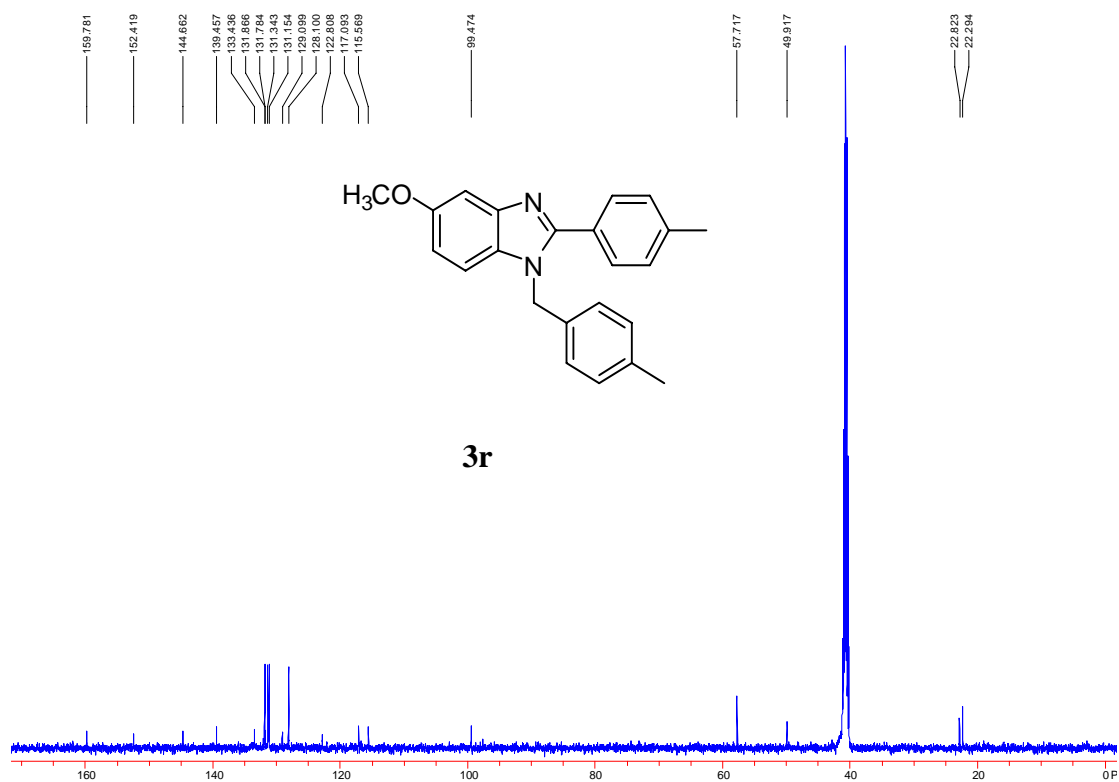
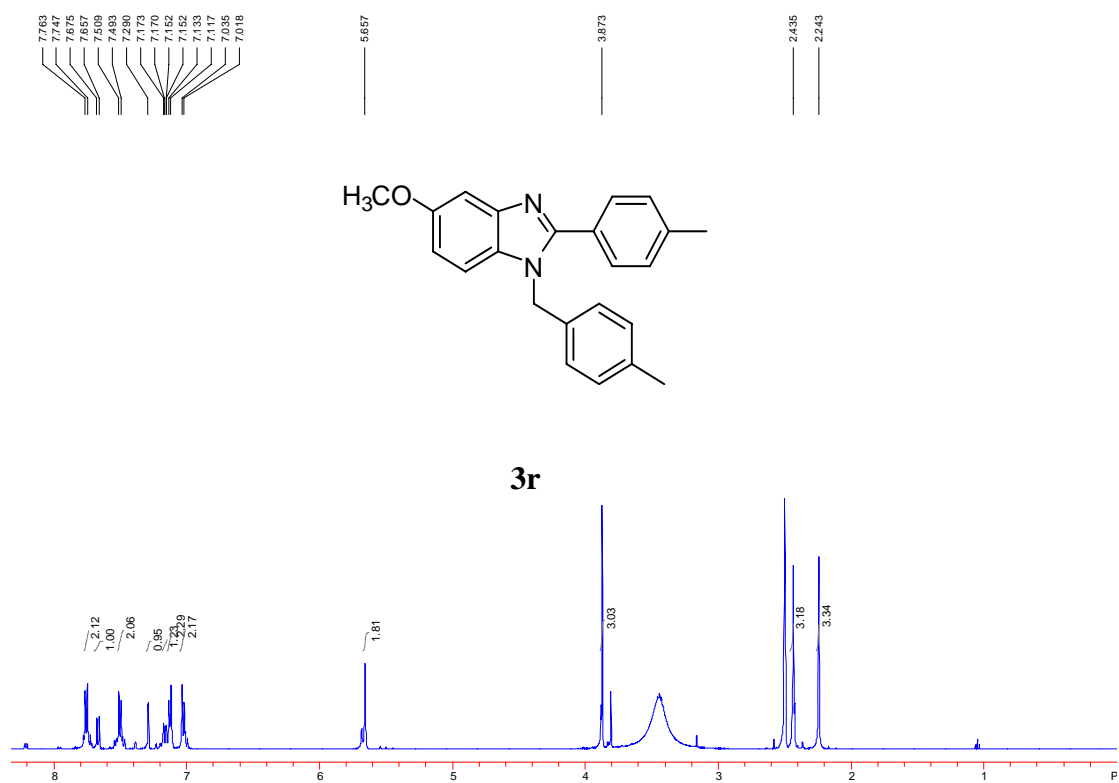


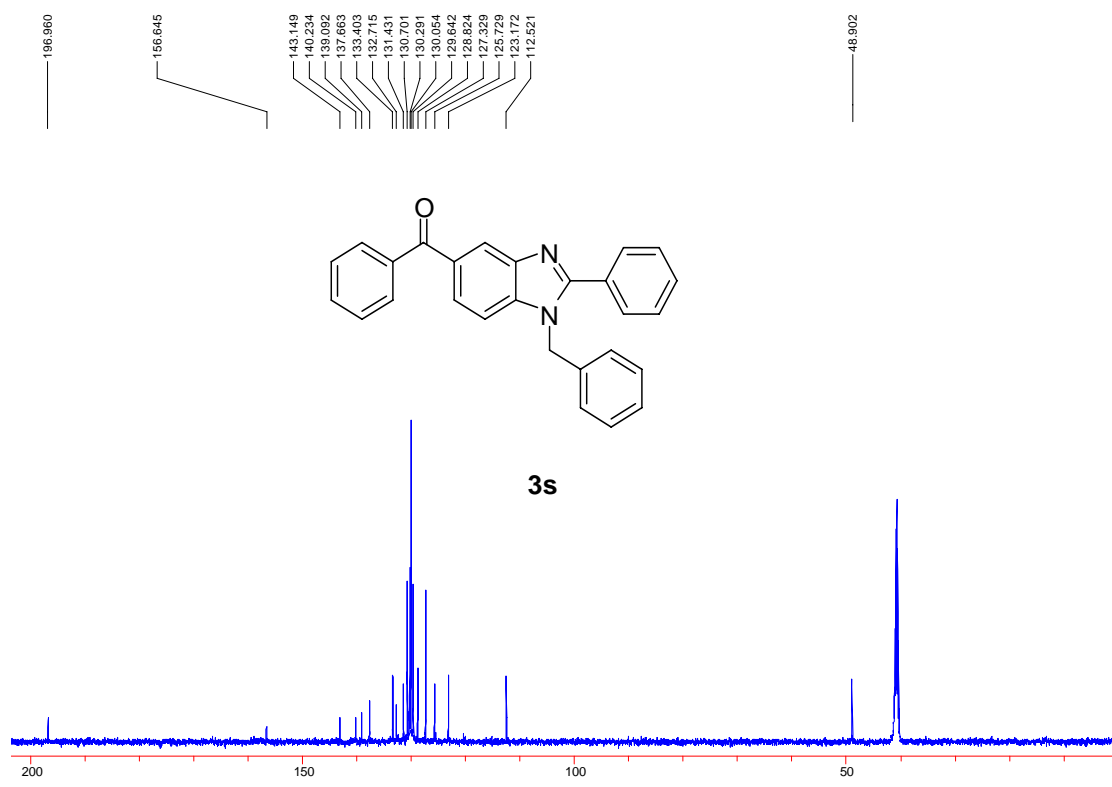
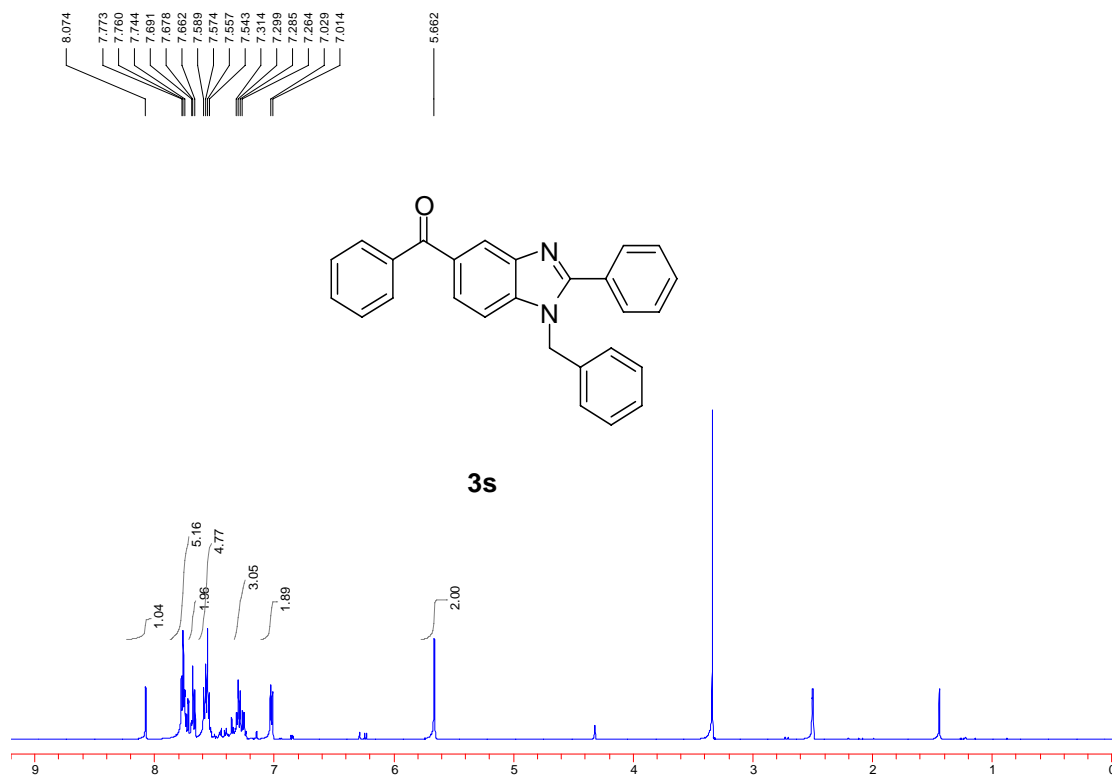


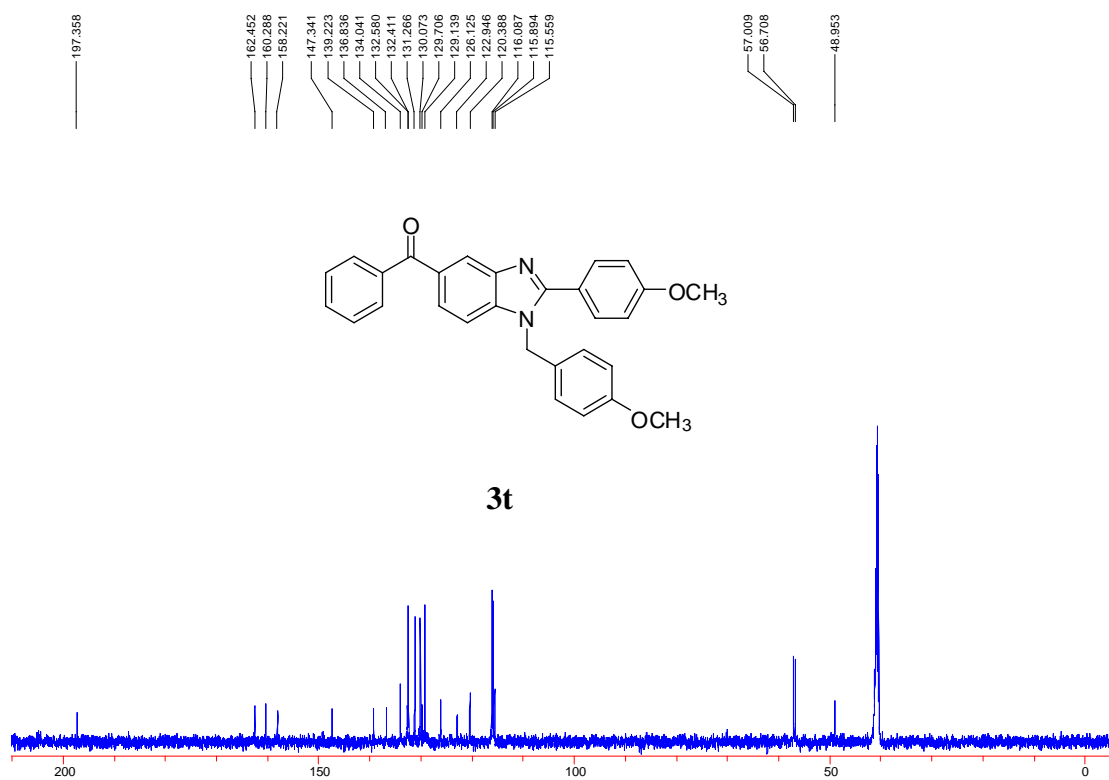
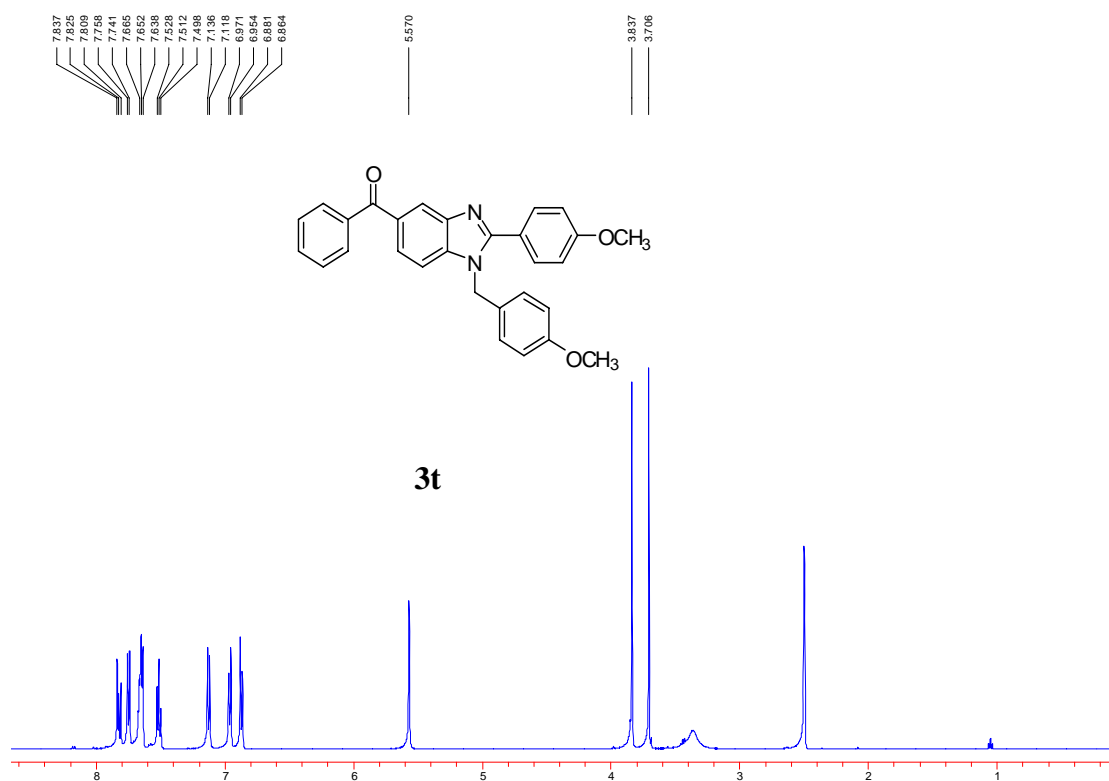


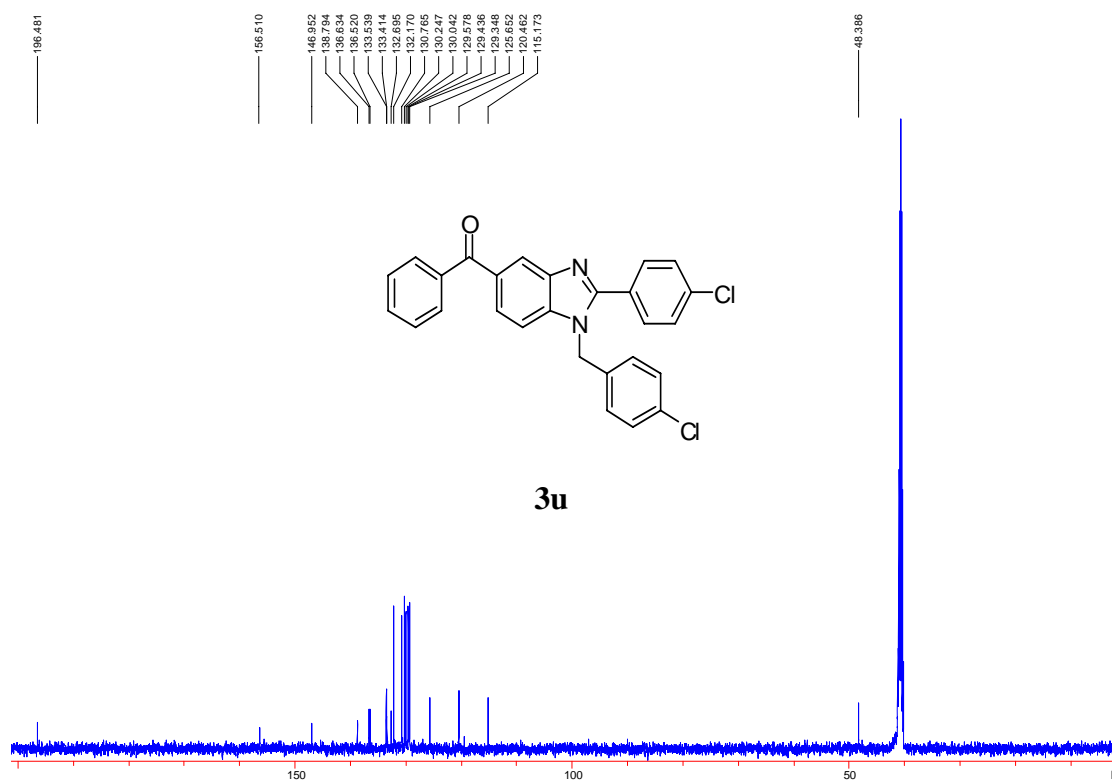
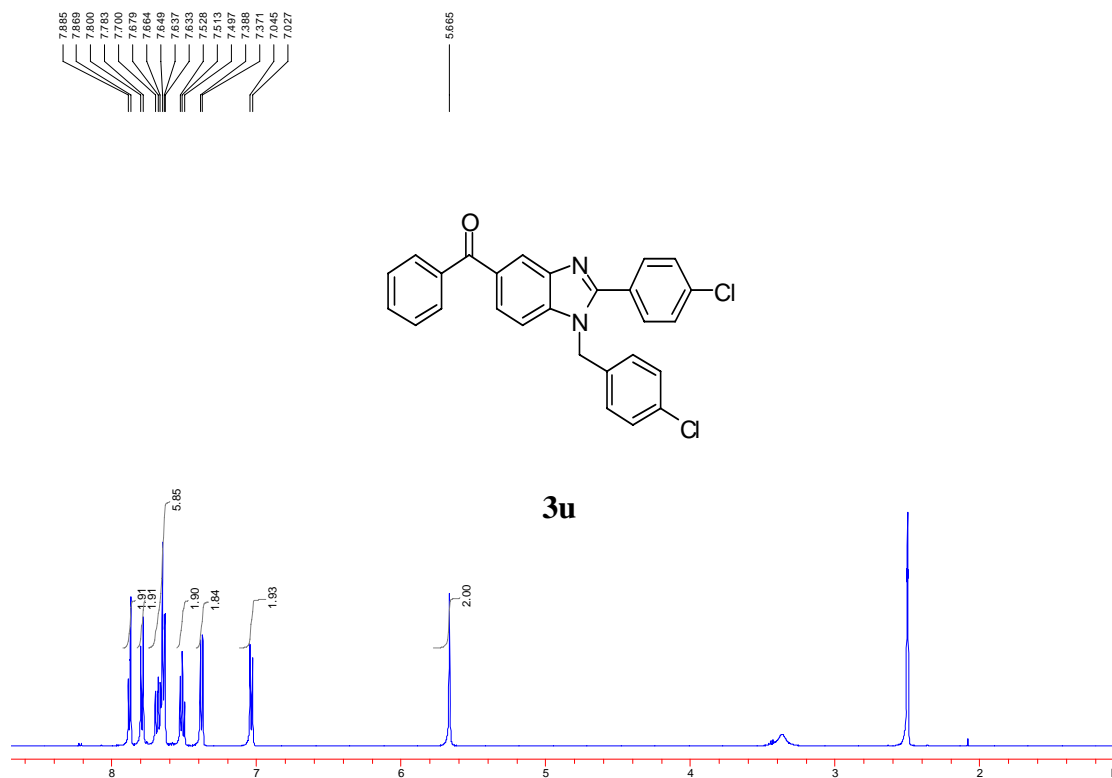


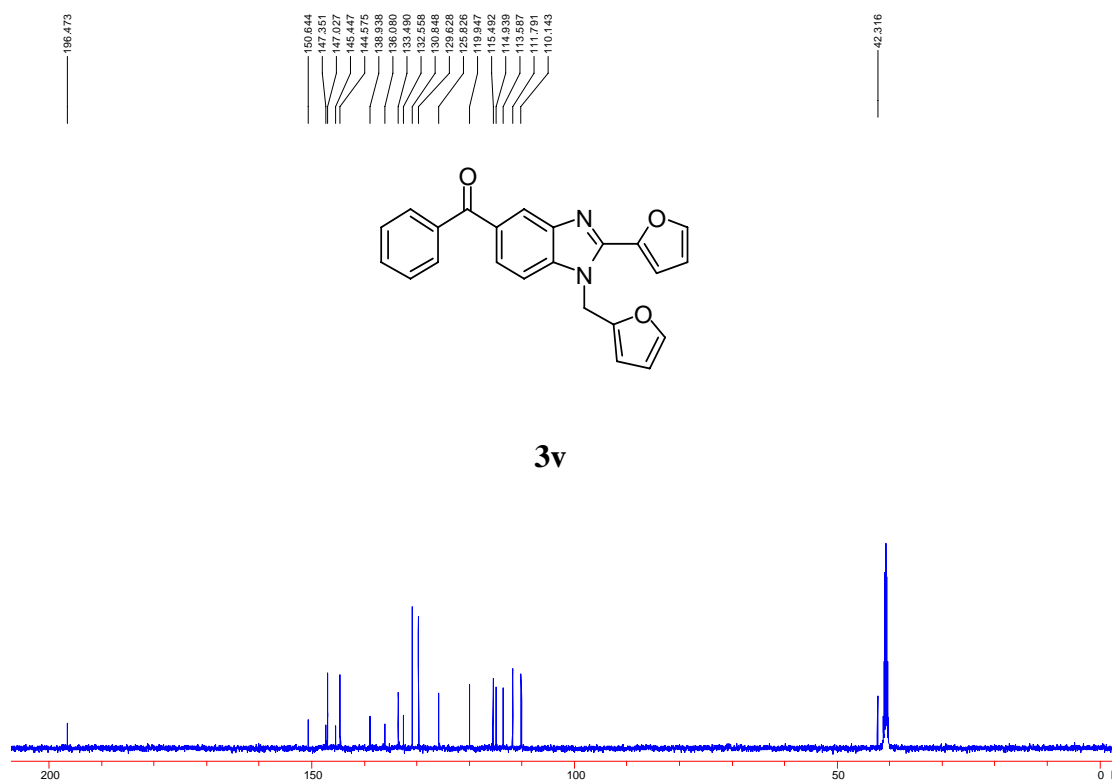
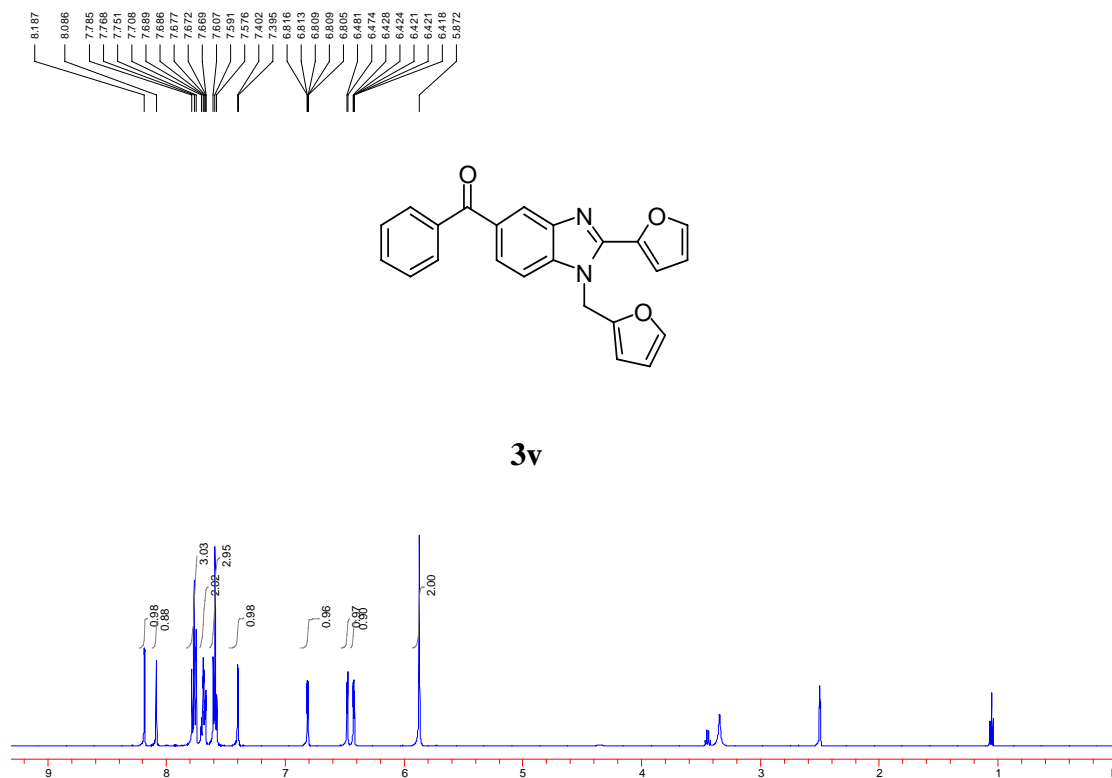


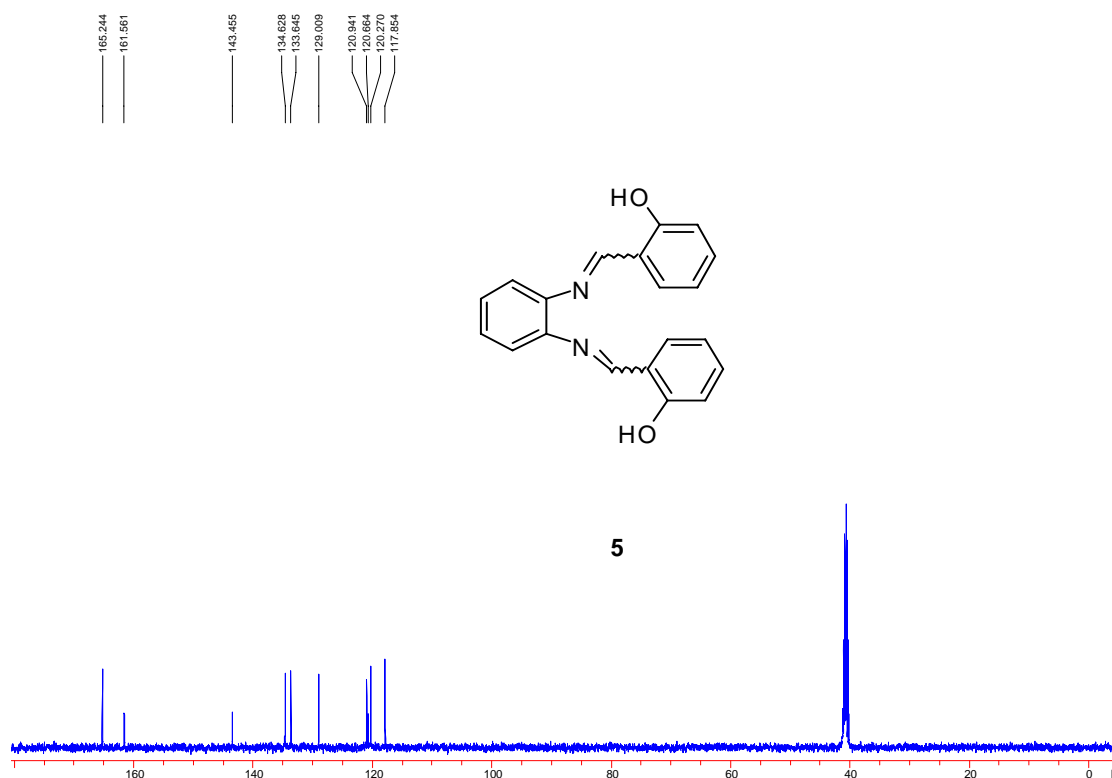
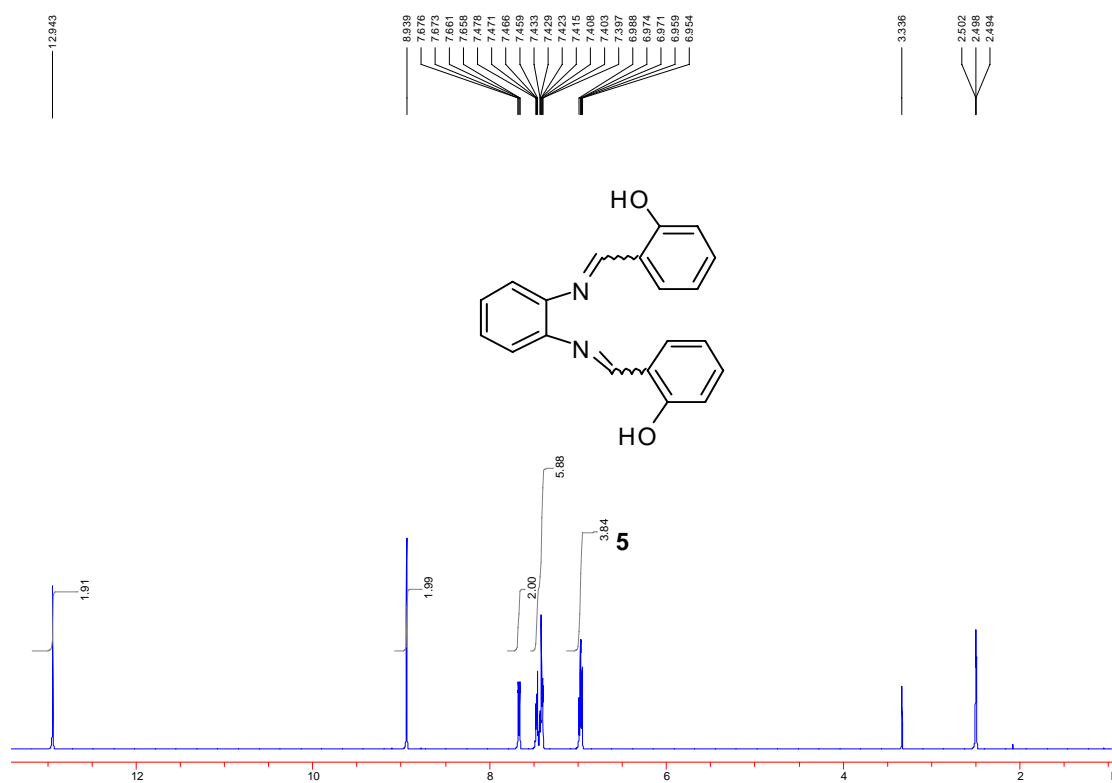


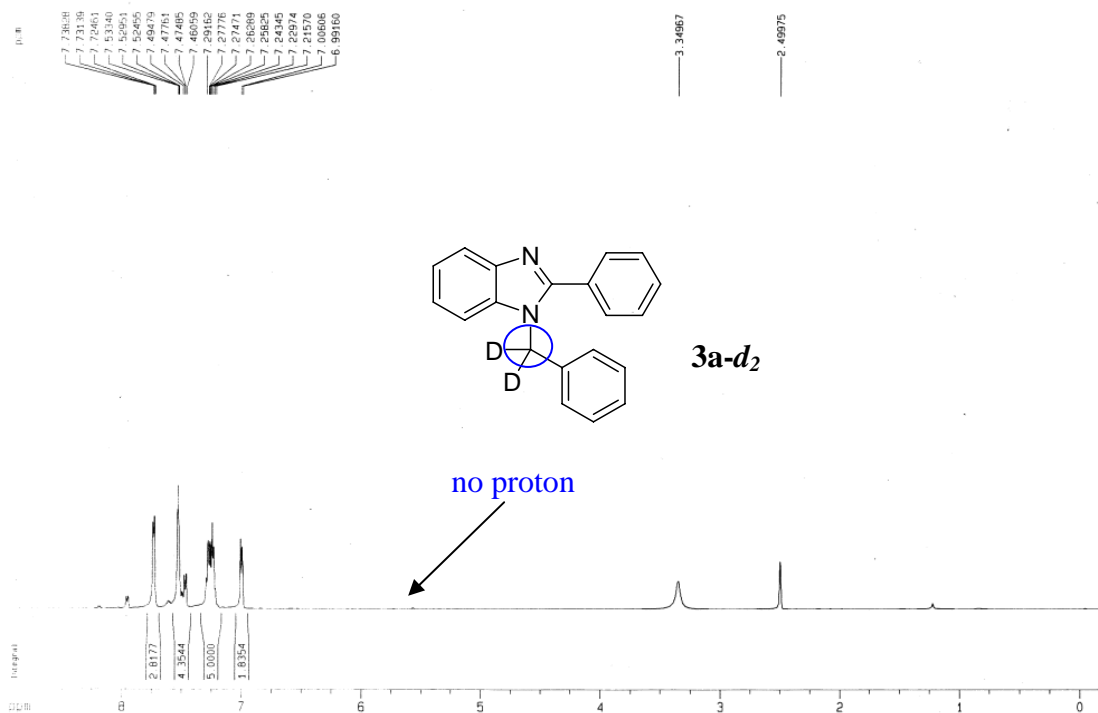












Spectrum 1A Plot - 2009-5-18 16:19

