

**Oxone mediated annulation of 2-aminobenzamides and 1,2-diaminobenzenes
with a *sec*-amine *via* imine-*N*-oxide: New syntheses of 2,3-dihydroquinazolin-
4(1*H*)-ones and 1*H*-benzimidazoles**

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Supporting Information

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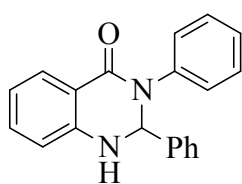
General Information: All the required chemicals such as isatoicanhydride, primary and secondary amines, oxone[®](2KHSO₅·KHSO₄·K₂SO₄) were purchased from Sigma-Aldrich India Ltd., NaCl and solvents used in this study were procured from SD Fine Chem. Ltd., India. Melting points of all the compounds were recorded on Veego programmable melting point apparatus and are uncorrected. IR spectra were recorded on a PerkinElmer FT-IR 240-C spectrophotometer using KBr optics. ¹H NMR spectra were recorded on Bruker AV 300 MHz in CDCl₃ and DMSO-d₆ using TMS as internal standard. ESI-MS spectra were recorded on QSTARXL hybrid MS/MS system (Applied Biosystems, USA). All the reactions were monitored by thin layer chromatography (TLC) on precoated silica gel 60 F254 (mesh); spots were visualized with UV light. Merck silica gel (60-120 mesh) was used for column chromatography.

Typical procedure for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones (3): 2-Amino-*N*-phenyl benzamide **1a** (0.5 g, 2.36 mmol), dibenzylamine **2a** (0.68 mL, 3.54 mmol), oxone (1.09 g, 3.54 mmol) and THF-H₂O (2:1, 10 mL) were taken into a round bottomed flask and stirred at room temperature for 5 hours. Progress of the reaction was monitored by TLC and after completion of the reaction; the reaction mixture was extracted with ethyl acetate (3x10 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by normal column chromatography (silica gel 60-120 mesh, gradient solvent system of a mixture of hexane-EtOAc) furnished 2,3-diphenyl-2,3-dihydroquinazolin-4(1*H*)-one **3a** (0.63 g, 89%) as a white solid (m.p. 205-208 °C).

Typical procedure for the synthesis of 1*H*-benzimidazoles (5): *o*-Phenylenediamine **4a** (0.5 g, 4.63 mmol), dibenzylamine **2a** (1.33 mL, 6.94 mmol), oxone (2.13 g, 6.94 mmol) and THF-H₂O (2:1, 10 mL) were taken into a round bottomed flask and stirred at room temperature for 6 hours. Progress of the reaction was monitored by TLC and after

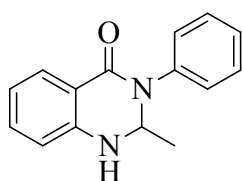
completion of the reaction; the reaction mixture was extracted with ethyl acetate (3x10 mL). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification of the crude product by normal column chromatography (silica gel 60-120 mesh, gradient solvent system of a mixture of hexane-EtOAc) furnished 2-phenyl-1*H*-benzo[*d*]imidazole **5a** (0.55 g, 62%) as a white solid (m.p. 295-297 °C).

Characterization data:



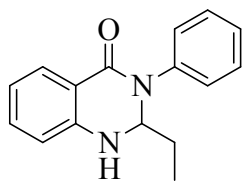
2,3-diphenyl-2,3-dihydroquinazolin-4(1*H*)-one¹ (3a): White solid; m.p.

205-208 °C (Lit. 205-206 °C); ¹H NMR (300 MHz, DMSO-*d*₆+CDCl₃): δ = 7.88 (d, *J* = 7.70 Hz, 1H), 7.40-7.37 (m, 2H), 7.31-7.14 (m, 9H), 6.83 (br s, 1H), 6.78-6.71 (m, 2H), 6.12 (d, *J* = 2.20 Hz, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆+CDCl₃): δ = 162.36, 145.57, 140.15, 139.76, 133.01, 127.99, 127.77, 127.69, 126.02, 125.86, 125.66, 117.44, 115.18, 114.16, 73.25; IR (KBr): ν 3307, 2995, 2921, 2834, 1634, 1586, 1504, 1408, 1245, 1169, 1072, 944, 758, 698 cm⁻¹; ESI-MS: *m/z* 301 (M+H); ESI-HRMS: *m/z* 301.13368 (calcd. 301.13409).



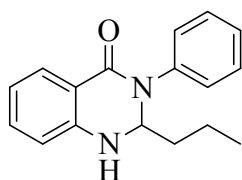
2-methyl-3-phenyl-2,3-dihydroquinazolin-4(1*H*)-one² (3b): White

solid; m.p. 163-165 °C (Lit. 164-166 °C); ¹H NMR (300 MHz, DMSO-*d*₆+CDCl₃): δ = 7.86 (d, *J* = 7.74 Hz, 1H), 7.44-7.27 (m, 6H), 6.81-6.74 (m, 2H), 6.09 (br s, 1H), 5.23-5.18 (q, *J* = 5.47, 5.85 Hz, 1H), 1.37 (d, *J* = 5.66 Hz, 3H); ¹³C NMR (75 MHz, DMSO-*d*₆+CDCl₃): δ = 162.15, 146.12, 139.56, 132.78, 129.39, 128.33, 127.73, 126.96, 126.25, 117.41, 114.34, 67.61, 19.76; IR (KBr): ν 3298, 2995, 2929, 1634, 1586, 1508, 1408, 1326, 1261, 1074, 763, 696 cm⁻¹; ESI-MS: *m/z* 239 (M+H); ESI-HRMS: *m/z* 239.11789 (calcd. 239.11844).



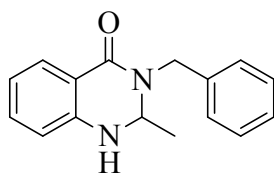
2-ethyl-3-phenyl-2,3-dihydroquinazolin-4(1H)-one (3c): White solid;

m.p. 149-151 °C; ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 7.87 (d, J = 7.98 Hz, 1H), 7.44-7.26 (m, 6H), 6.80-6.76 (m, 2H), 6.11 (br s, 1H), 4.94 (dd, J = 3.30, 5.50 Hz, 1H), 2.02-1.87 (m, 1H), 1.79-1.67 (m, 1H), 0.87 (t, J = 7.43 Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 161.67, 145.63, 140.22, 132.83, 128.32, 127.75, 126.62, 126.01, 117.31, 115.39, 114.34, 72.83, 25.66, 8.73; IR (KBr): ν 3288, 2986, 2912, 1627, 1501, 1455, 1400, 1326, 1259, 1068, 949, 763, 693 cm^{-1} ; ESI-MS: m/z 253 (M+H); ESI-HRMS: m/z 253.13354 (calcd. 253.13409).



3-phenyl-2-propyl-2,3-dihydroquinazolin-4(1H)-one (3d): Yellow

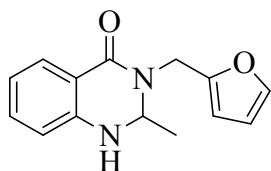
solid; m.p. 113-116 °C; ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 7.89 (d, J = 7.70 Hz, 1H), 7.44-7.36 (m, 4H), 7.32-7.25 (m, 2H), 6.83-6.74 (m, 2H), 5.85 (br s, 1H), 5.02-4.97 (dd, J = 3.30, 3.57 Hz, 1H), 2.01-1.88 (m, 1H), 1.70-1.59 (m, 1H), 1.43-1.18 (m, 2H), 0.81 (t, J = 7.42 Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 161.79, 145.63, 140.31, 132.96, 128.43, 127.91, 126.68, 126.12, 117.58, 115.64, 114.54, 71.66, 34.85, 17.67, 13.01; IR (KBr): ν 3312, 2924, 2861, 1654, 1600, 1540, 1497, 1441, 1326, 1260, 1056, 1014, 890, 756, 693 cm^{-1} ; ESI-MS: m/z 267 (M+H); ESI-HRMS: m/z 267.14922 (calcd. 267.14974).



3-benzyl-2-methyl-2,3-dihydroquinazolin-4(1H)-one² (3e): White

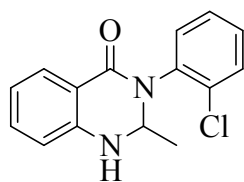
solid; m.p. 160-162 °C (Lit. 160-162 °C); ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 7.88 (d, J = 7.98 Hz, 1H), 7.34-7.24 (m, 6H), 6.78 (t, J = 7.43, 7.70 Hz, 1H), 6.68 (d, J = 8.25 Hz,

1H), 5.36 (d, $J = 15.40$ Hz, 1H), 4.80-4.75 (q, $J = 6.05$ Hz, 1H), 4.10 (d, $J = 15.68$ Hz, 1H), 1.36 (d, $J = 6.05$ Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6 + \text{CDCl}_3$): $\delta = 162.16, 145.67, 136.82, 132.59, 127.87, 127.59, 126.93, 126.59, 117.31, 114.65, 114.24, 64.09, 46.13, 19.00$; IR (KBr): ν 3268, 2973, 2925, 1625, 1508, 1477, 1311, 1250, 1165, 1025, 869, 760, 692 cm^{-1} ; ESI-MS: m/z 253 (M+H); ESI-HRMS: m/z 253.13354 (calcd. 253.13409).



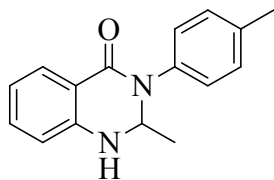
3-(furan-2-ylmethyl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one

(3f): Pale yellow solid; m.p. 91-93 °C; ^1H NMR (300 MHz, $\text{DMSO-d}_6 + \text{CDCl}_3$): $\delta = 7.80$ (d, $J = 7.98$ Hz, 1H), 7.38 (m, 1H), 7.24 (t, $J = 6.87$ Hz, 1H), 6.76-6.67 (m, 2H), 6.33 (s, 2H), 5.08 (d, $J = 15.68$ Hz, 1H), 4.91-4.85 (q, $J = 6.05, 5.77$ Hz, 1H), 4.30 (d, $J = 15.40$ Hz, 1H), 1.35 (d, $J = 5.77$ Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6 + \text{CDCl}_3$): $\delta = 161.42, 149.69, 145.52, 141.07, 132.22, 127.01, 116.57, 113.92, 113.80, 109.39, 107.37, 63.83, 38.70, 18.60$; IR (KBr): ν 3383, 2923, 2856, 1648, 1598, 1520, 1432, 1253, 1117, 964, 752, 691 cm^{-1} ; ESI-MS: m/z 243 (M+H); ESI-HRMS: m/z 243.11301 (calcd. 243.11335).

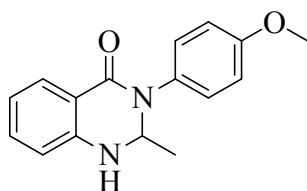


3-(2-chlorophenyl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one³ (3g):

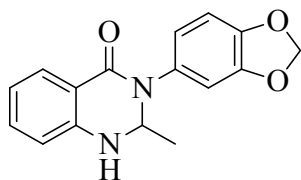
White solid; m.p. 163-164 °C (Lit. 162 °C); ^1H NMR (300 MHz, $\text{DMSO-d}_6 + \text{CDCl}_3$): $\delta = 7.84$ (d, $J = 7.70$ Hz, 1H), 7.51 (d, $J = 7.43$ Hz, 1H), 7.34-7.28 (m, 4H), 6.82-6.76 (m, 2H), 6.17 (br s, 1H), 5.30-5.21 (m, 1H), 1.31 (d, $J = 5.77$ Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6 + \text{CDCl}_3$): $\delta = 162.33, 146.77, 136.14, 132.78, 131.93, 131.46, 129.29, 128.37, 127.70, 127.16, 126.57, 117.34, 114.23, 65.73, 19.38$; IR (KBr): ν 3325, 2989, 2930, 1636, 1513, 1400, 1325, 1165, 1088, 863, 756, 714 cm^{-1} ; ESI-MS: m/z 273 (M+H); ESI-HRMS: m/z 273.07892 (calcd. 273.07947).



2-methyl-3-(p-tolyl)-2,3-dihydroquinazolin-4(1H)-one (3h): White solid; m.p. 155-157 °C; ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 7.85 (d, J = 6.98 Hz, 1H), 7.31-7.17 (m, 5H), 6.81-6.73 (m, 2H), 5.98 (br s, 1H), 5.20-5.14 (q, J = 6.04, 5.85 Hz, 1H), 2.36 (s, 3H), 1.36 (d, J = 6.04 Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 162.16, 136.84, 135.96, 132.61, 130.08, 128.89, 127.68, 126.73, 117.38, 115.07, 114.21, 67.57, 20.22, 19.71; IR (KBr): ν 3306, 2971, 2923, 1626, 1515, 1449, 1329, 1170, 1055, 851, 753 cm^{-1} ; ESI-MS: m/z 253 ($\text{M}+\text{H}$); ESI-HRMS: m/z 253.13354 (calcd. 253.13409).

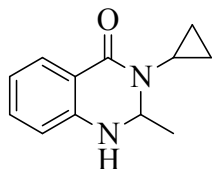


3-(4-methoxyphenyl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (3i): Pale yellow solid; m.p. 177-180 °C; ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 7.86 (d, J = 7.70 Hz, 1H), 7.32-7.21 (m, 3H), 6.93 (d, J = 9.08 Hz, 2H), 6.82-6.78 (m, 2H), 5.80 (br s, 1H), 5.20-5.14 (q, J = 6.05, 5.77 Hz, 1H), 3.82 (s, 3H), 1.37 (d, J = 6.05 Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 162.68, 157.86, 132.90, 132.43, 128.50, 128.08, 122.16, 117.82, 114.44, 113.87, 113.33, 67.98, 54.90, 20.08; IR (KBr): ν 3306, 2978, 2927, 1621, 1512, 1407, 1240, 1165, 1027, 827, 753, 681 cm^{-1} ; ESI-MS: m/z 269 ($\text{M}+\text{H}$); ESI-HRMS: m/z 269.12845 (calcd. 269.12900).



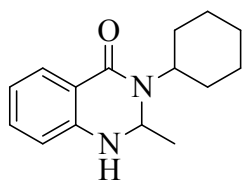
3-(benzo[d][1,3]dioxol-5-yl)-2-methyl-2,3-dihydroquinazolin-4(1H)-one (3j): Brown solid; m.p. 159-162 °C; ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 7.80 (d, J = 7.70 Hz, 1H), 7.28 (t, J = 7.97, 8.80 Hz, 1H), 6.85-6.73 (m, 5H), 6.01 (s, 2H), 5.18-5.12 (q, J = 6.05, 5.77 Hz, 1H), 1.36 (d, J = 6.05 Hz, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 162.68, 157.86, 132.90, 132.43, 128.50, 128.08, 122.16, 117.82, 114.44, 113.87, 113.33, 67.98, 54.90, 20.08; IR (KBr): ν 3306, 2978, 2927, 1621, 1512, 1407, 1240, 1165, 1027, 827, 753, 681 cm^{-1} ; ESI-MS: m/z 269 ($\text{M}+\text{H}$); ESI-HRMS: m/z 269.12845 (calcd. 269.12900).

d_6+CDCl_3): $\delta = 162.01, 146.66, 146.04, 145.29, 133.91, 132.80, 132.32, 127.16, 119.94, 116.71, 113.82, 108.11, 107.02, 100.35, 67.29, 19.20$; IR (KBr): ν 3337, 3232, 2929, 1662, 1600, 1511, 1466, 1369, 1240, 1166, 1019, 956, 889, 751, 692 cm^{-1} ; ESI-MS: m/z 283 (M+H); ESI-HRMS: m/z 283.10802 (calcd. 283.10827).



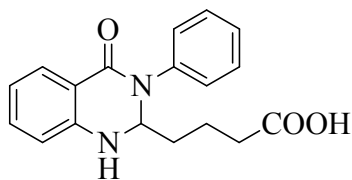
3-cyclopropyl-2-methyl-2,3-dihydroquinazolin-4(1H)-one (3k): Pale

yellow solid; m.p. 122-124 °C; 1H NMR (300 MHz, $DMSO-d_6+CDCl_3$): $\delta = 7.83$ (d, $J = 7.74$ Hz, 1H), 7.24 (t, $J = 8.68, 8.12$ Hz, 1H), 6.73 (t, $J = 7.36, 7.55$ Hz, 1H), 6.67 (d, $J = 8.12$ Hz, 1H), 5.68 (br s, 1H), 4.88-4.82 (q, $J = 6.04$ Hz, 1H), 2.66-2.59 (m, 1H), 1.41 (d, $J = 5.85$ Hz, 3H), 1.11-1.02 (m, 1H), 0.86-0.72 (m, 2H), 0.64-0.56 (m, 1H); ^{13}C NMR (75 MHz, $DMSO-d_6+CDCl_3$): $\delta = 164.03, 145.15, 132.66, 127.19, 116.98, 114.40, 114.20, 66.25, 26.48, 19.01, 8.96, 4.83$; IR (KBr): ν 3246, 2927, 2866, 1613, 1556, 1409, 1332, 1245, 1161, 1024, 956, 812, 765, 689 cm^{-1} ; ESI-MS: m/z 203 (M+H); ESI-HRMS: m/z 203.11804 (calcd. 203.11844).



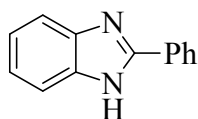
3-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1H)-one (3l): Pale

yellow solid; m.p. 165-167 °C; 1H NMR (300 MHz, $DMSO-d_6+CDCl_3$): $\delta = 7.82$ (d, $J = 7.98$ Hz, 1H), 7.24 (t, $J = 8.25$ Hz, 1H), 6.77 (t, $J = 7.42, 7.70$ Hz, 1H), 6.68 (d, $J = 7.98$ Hz, 1H), 4.92-4.86 (q, $J = 6.05, 5.77$ Hz, 1H), 4.45-4.36 (m, 1H), 1.86-1.52 (m, 6H), 1.45-1.25 (m, 7H); ^{13}C NMR (75 MHz, $DMSO-d_6+CDCl_3$): $\delta = 161.02, 145.04, 132.07, 127.44, 117.23, 116.08, 114.28, 60.39, 52.11, 30.82, 30.30, 25.27, 25.12, 24.69, 21.88$; IR (KBr): ν 3255, 2930, 2855, 1609, 1503, 1420, 1323, 1248, 1152, 1037, 955, 864, 750, 700 cm^{-1} ; ESI-MS: m/z 245 (M+H); ESI-HRMS: m/z 245.16484 (calcd. 245.16539).



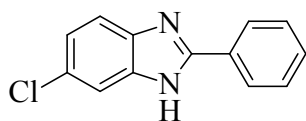
4-(4-oxo-3-phenyl-1,2,3,4-tetrahydroquinazolin-2-yl)butanoic

acid (3m): Pale yellow oil; ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 11.87 (br s, 1H), 7.74 (d, J = 7.43 Hz, 1H), 7.44-7.25 (m, 6H), 6.97 (br s, 1H), 6.89-6.69 (m, 2H), 5.07-5.04 (m, 1H), 2.16-1.86 (m, 3H), 1.71-1.41 (m, 3H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 172.70, 160.17, 144.88, 139.29, 131.84, 127.25, 126.49, 125.46, 124.80, 115.77, 113.87, 113.39, 70.07, 31.70, 31.03, 18.60; IR (neat): ν 3403, 2928, 1714, 1630, 1498, 1449, 1416, 1330, 1253, 1157, 1026, 860, 756, 696 cm^{-1} ; ESI-MS: m/z 311 (M+H); ESI-HRMS: m/z 311.13911 (calcd. 311.13957).



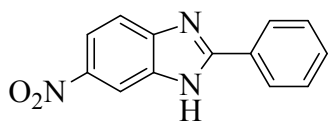
2-phenyl-1H-benzo[d]imidazole⁴ (5a): White solid; m.p. 295-297 °C

(Lit. 296-298 °C); ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 8.21-8.18 (m, 2H), 7.64-7.58 (m, 2H), 7.52-7.42 (m, 3H), 7.25-7.19 (m, 2H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 150.69, 138.33, 129.08, 128.76, 127.76, 125.69, 121.21, 114.68; IR (KBr): ν 3337, 3232, 2929, 1481, 1369, 1272, 1145, 1024, 956, 821, 751 cm^{-1} ; ESI-MS: m/z 195 (M+H); ESI-HRMS: m/z 195.09214 (calcd. 195.09222).



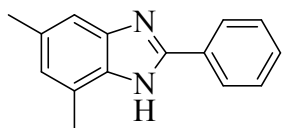
6-chloro-2-phenyl-1H-benzo[d]imidazole⁴ (5b): White solid;

m.p. 214-216 °C (Lit. 213-215 °C); ^1H NMR (300 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 8.18-8.15 (m, 2H), 7.60 (s, 1H), 7.56-7.42 (m, 4H), 7.19-7.15 (dd, J = 1.65 Hz, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-d}_6+\text{CDCl}_3$): δ = 152.64, 129.58, 129.46, 128.34, 127.08, 126.39, 122.20, 118.28, 115.57, 114.43; IR (KBr): ν 3358, 3228, 2956, 1493, 1361, 1298, 1156, 1019, 972, 836, 733 cm^{-1} ; ESI-MS: m/z 229 (M+H); ESI-HRMS: m/z 229.05320 (calcd. 229.05325).



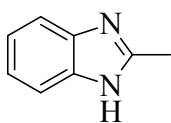
6-nitro-2-phenyl-1H-benzo[d]imidazole⁴ (5c): Yellow solid;

m.p. 203-206 °C (Lit. 204-206 °C); ¹H NMR (300 MHz, DMSO-d₆+CDCl₃): δ = 8.52 (d, *J* = 1.92 Hz, 1H), 8.22-8.12 (m, 3H), 7.68 (d, *J* = 8.80 Hz, 1H), 7.53-7.48 (m, 3H); ¹³C NMR (75 MHz, DMSO-d₆+CDCl₃): δ = 155.75, 142.69, 130.30, 128.72, 128.43, 126.69, 117.59, 114.15, 111.57; IR (KBr): ν 3402, 3211, 2912, 1491, 1369, 1257, 1139, 1036, 978, 812, 737 cm⁻¹; ESI-MS: *m/z* 240 (M+H); ESI-HRMS: *m/z* 240.07722 (calcd. 240.07730).



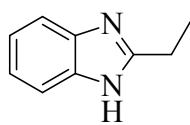
5,7-dimethyl-2-phenyl-1H-benzo[d]imidazole⁵ (5d): Yellow solid;

m.p. 189-191 °C (Lit. 190-191 °C); ¹H NMR (300 MHz, CDCl₃): δ = 7.98-7.97 (m, 2H), 7.34-7.29 (m, 3H), 7.14 (s, 1H), 6.79 (s, 1H), 2.50 (s, 3H), 2.36 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 150.21, 137.11, 135.21, 133.30, 130.12, 128.75, 128.18, 126.70, 125.68, 124.60, 111.75, 21.52, 16.94; IR (KBr): ν 3373, 3245, 2901, 1501, 1345, 1222, 1164, 1022, 958, 832, 748 cm⁻¹; ESI-MS: *m/z* 223 (M+H); ESI-HRMS: *m/z* 223.12341 (calcd. 223.12352).

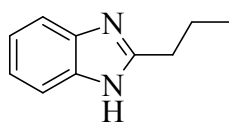


2-methyl-1H-benzo[d]imidazole⁶ (5e): Light yellow solid, m.p. 174-176 °C

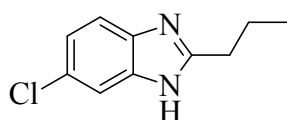
(Lit. 173-174 °C); ¹H NMR (300 MHz, CDCl₃): δ = 8.41 (br s, 1H), 7.52-7.49 (m, 2H), 7.17-7.14 (m, 2H), 2.60 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 151.75, 139.23, 121.65, 114.63, 15.09; IR (KBr): ν 3352, 2965, 1574, 1435, 1211, 1064, 987, 841, 739 cm⁻¹; ESI-MS: *m/z* 133 (M+H); ESI-HRMS: *m/z* 133.07648 (calcd. 133.07657).



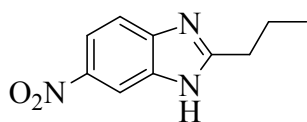
2-ethyl-1H-benzo[d]imidazole⁷ (5f): White solid, m.p. 170-172 °C (Lit. 171-173 °C); ¹H NMR (300 MHz, CDCl₃): δ = 7.54-7.52 (m, 2H), 7.21-7.19 (m, 2H), 2.98-2.94 (q, J = 7.63 Hz, 2H), 1.41 (t, J = 7.63 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 156.33, 138.09, 122.20, 114.49, 22.41, 12.30; IR (KBr): ν 3413, 3125, 2929, 1541, 1430, 1213, 1084, 954, 822 cm⁻¹; ESI-MS: m/z 147 (M+H); ESI-HRMS: m/z 147.09211 (calcd. 147.09222).



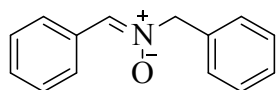
2-propyl-1H-benzo[d]imidazole⁶ (5g): White solid; m.p. 149-152 °C (Lit. 150-152 °C); ¹H NMR (300 MHz, CDCl₃): δ = 7.73-7.70 (m, 2H), 7.24-7.20 (m, 2H), 2.84 (t, J = 7.5 Hz, 2H), 1.97-1.88 (m, 2H), 1.06 (t, J = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 154.81, 138.19, 121.79, 113.67, 31.93, 21.17, 14.03; IR (KBr): ν 3403, 3195, 2902, 1551, 1386, 1277, 1023, 977, 812, 755 cm⁻¹; ESI-MS: m/z 161 (M+H); ESI-HRMS: m/z 161.10771 (calcd. 161.10787).



6-chloro-2-propyl-1H-benzo[d]imidazole⁸ (5h): Light yellow solid, m.p. 156-158 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.69-7.68 (m, 1H), 7.20-7.16 (m, 2H), 2.82 (t, J = 7.78 Hz, 2H), 1.78-1.72 (m, 2H), 1.06 (t, J = 7.47 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 156.15, 143.31, 133.54, 127.23, 122.17, 118.86, 109.90, 31.90, 21.08, 13.67; IR (KBr): ν 3375, 3125, 2926, 1544, 1385, 1210, 1075, 978, 801, 746 cm⁻¹; ESI-MS: m/z 195 (M+H); ESI-HRMS: m/z 195.06881 (calcd. 195.06890).



6-nitro-2-propyl-1H-benzo[d]imidazole⁹ (5i): Light yellow solid, m.p. 136-138 °C (Lit. 135-137 °C); ¹H NMR (300 MHz, CDCl₃): δ = 8.27 (s, 1H), 8.16 (d, *J* = 8.92 Hz, 1H), 7.74 (d, *J* = 8.92 Hz, 1H), 2.89 (t, *J* = 7.25 Hz, 2H), 2.02-1.93 (m, 2H), 1.00 (t, *J* = 7.33 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 160.16, 144.44, 142.95, 139.22, 118.93, 115.03, 112.34, 31.52, 20.87, 13.98; IR (KBr): ν 3325, 3101, 2978, 1521, 1345, 1238, 1075, 986, 856, 732 cm⁻¹; ESI-MS: *m/z* 206 (M+H); ESI-HRMS: *m/z* 206.09283 (calcd. 206.09295).

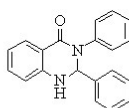
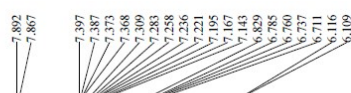


N-benzylidene-1-phenylmethanamine oxide¹⁰ (A): Pale yellow solid; m.p. 82-84 °C (Lit. 81-83 °C); ¹H NMR (300 MHz, CDCl₃): δ = 8.22-8.20 (m, 2H), 7.49-7.37 (m, 9H), 5.06 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ = 134.25, 133.16, 130.42, 130.34, 129.18, 128.92, 128.57, 128.40, 71.19; IR (KBr): ν 3070, 2987, 1560, 1510, 1478, 1356, 1225, 1159, 1035, 956, 852, 712 cm⁻¹; ESI-MS: *m/z* 212 (M+H); ESI-HRMS: *m/z* 212.10748 (calcd. 212.10754).

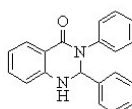
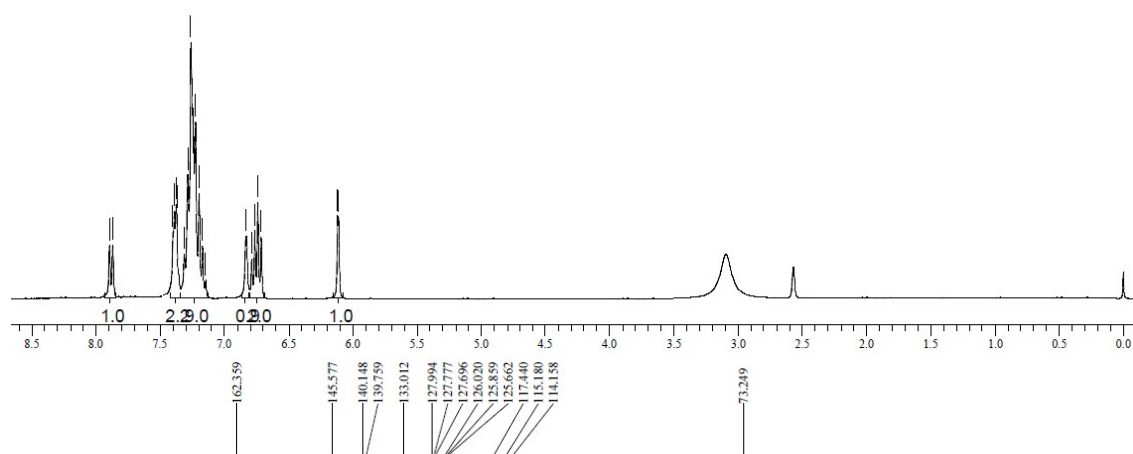
References:

1. N. Razavi and B. Akhlaghinia, *New J. Chem.*, 2016, **40**, 447-457.
2. M. Sharma, R. Mahar, S. K. Shukla, R. Kant and P. M. S. Chauhan, *Tetrahedron Lett.*, 2013, **54**, 6171-6177.
3. S. K. Ghosh and R. Nagarajan, *RSC Adv.*, 2016, **6**, 27378-27387.
4. D. Xue and Y. Long, *J. Org. Chem.*, 2014, **79**, 4727-4734.
5. Z. Lv, J. Liu, W. Wei, J. Wu, W. Yu and J. Chang, *Adv. Synth. Catal.*, 2016, **358**, 2759-2766.
6. S. Majumdar, A. Chakraborty, S. Bhattacharjee, S. Debnath and D. K. Maiti, *Tetrahedron Lett.*, 2016, **57**, 4595-4598.
7. M. S. Mayo, X. Yu, X. Zhou, X. Feng, Y. Yamamoto and M. Bao, *Org. Lett.*, 2014, **16**, 764-767.
8. K. Selvam and M. Swaminathan, *Tetrahedron Lett.*, 2011, **52**, 3386-3392.
9. D. Yang, H. Fu, L. Hu, Y. Jiang and Y. Zhao, *J. Org. Chem.*, 2008, **73**, 7841-7844.
10. S. Murahashi, H. Mitsui, T. Shiota, T. Tsuda and S. Watanabe, *J. Org. Chem.*, 1990, **55**, 1736-1744.

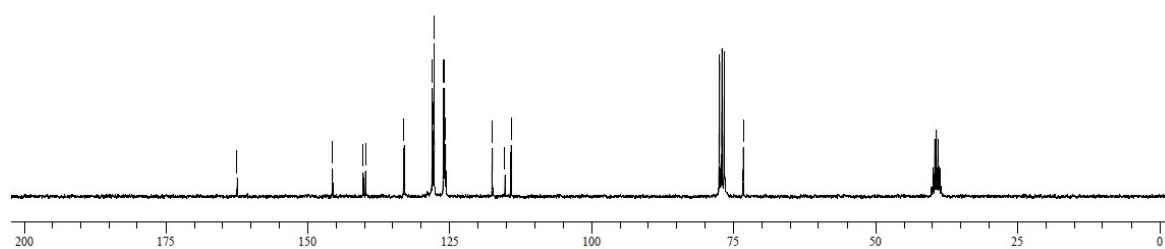
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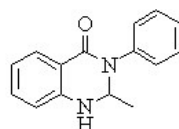


3a

DMSO- d_6 + $CDCl_3$ 1H NMR 300 MHz

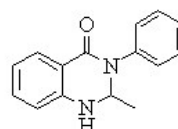
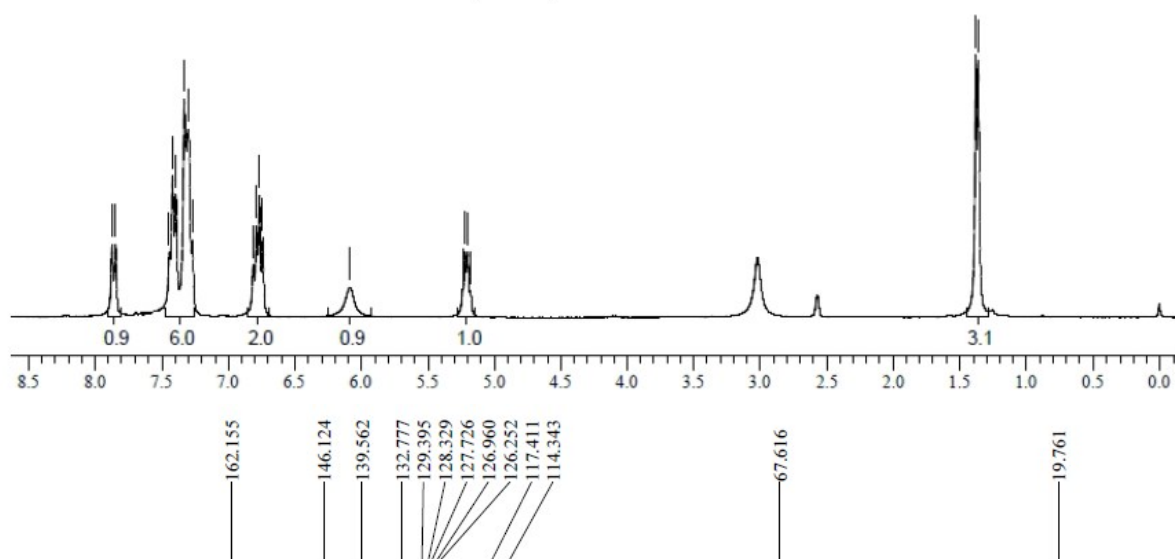
3a

DMSO- d_6 +CDCl $_3$ ^{13}C NMR 75 MHz



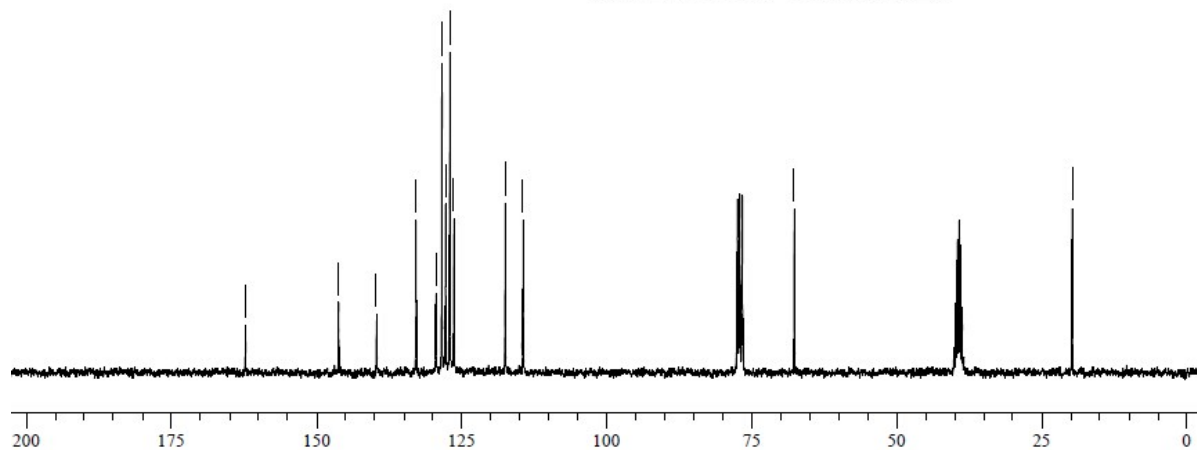
3b

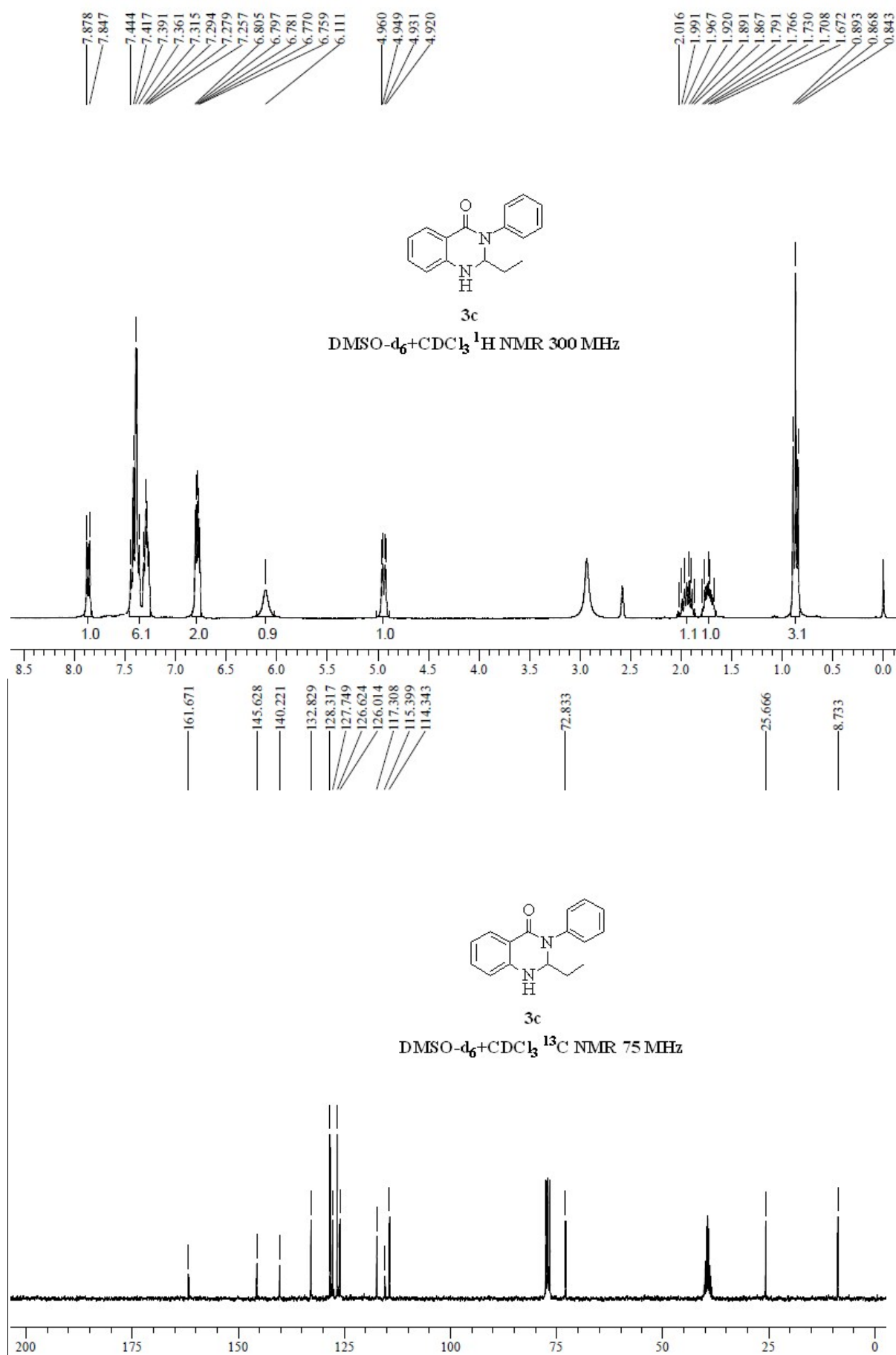
DMSO- d_6 + CDCl_3 ^1H NMR 300 MHz

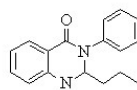


3b

DMSO- d_6 + CDCl_3 ^{13}C NMR 75 MHz

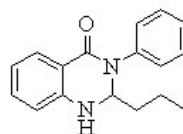
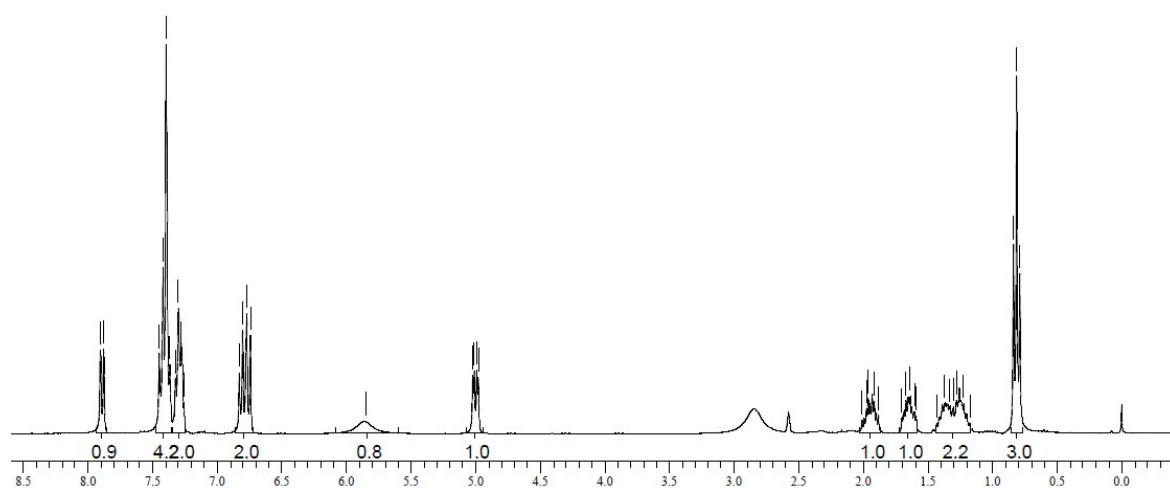






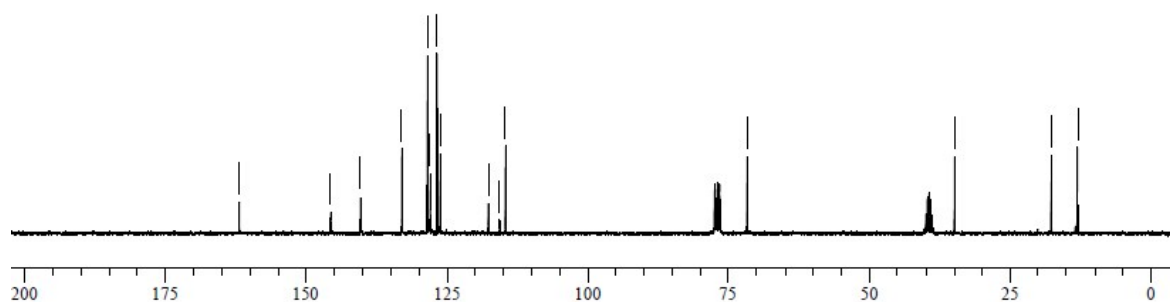
3d

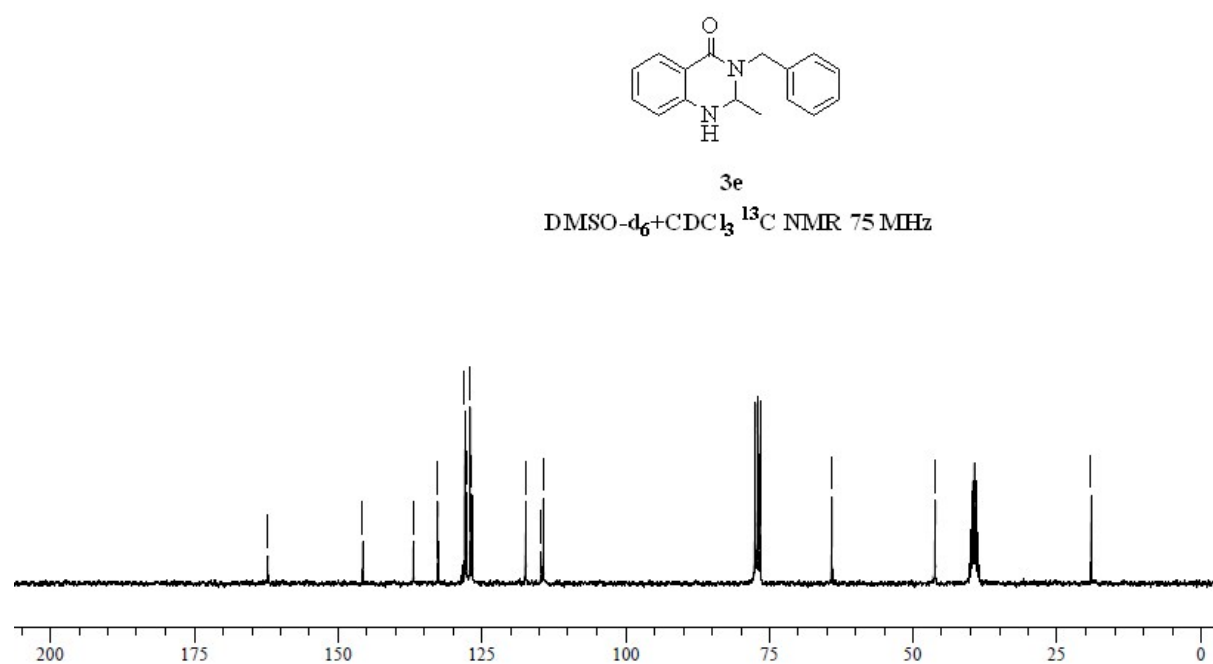
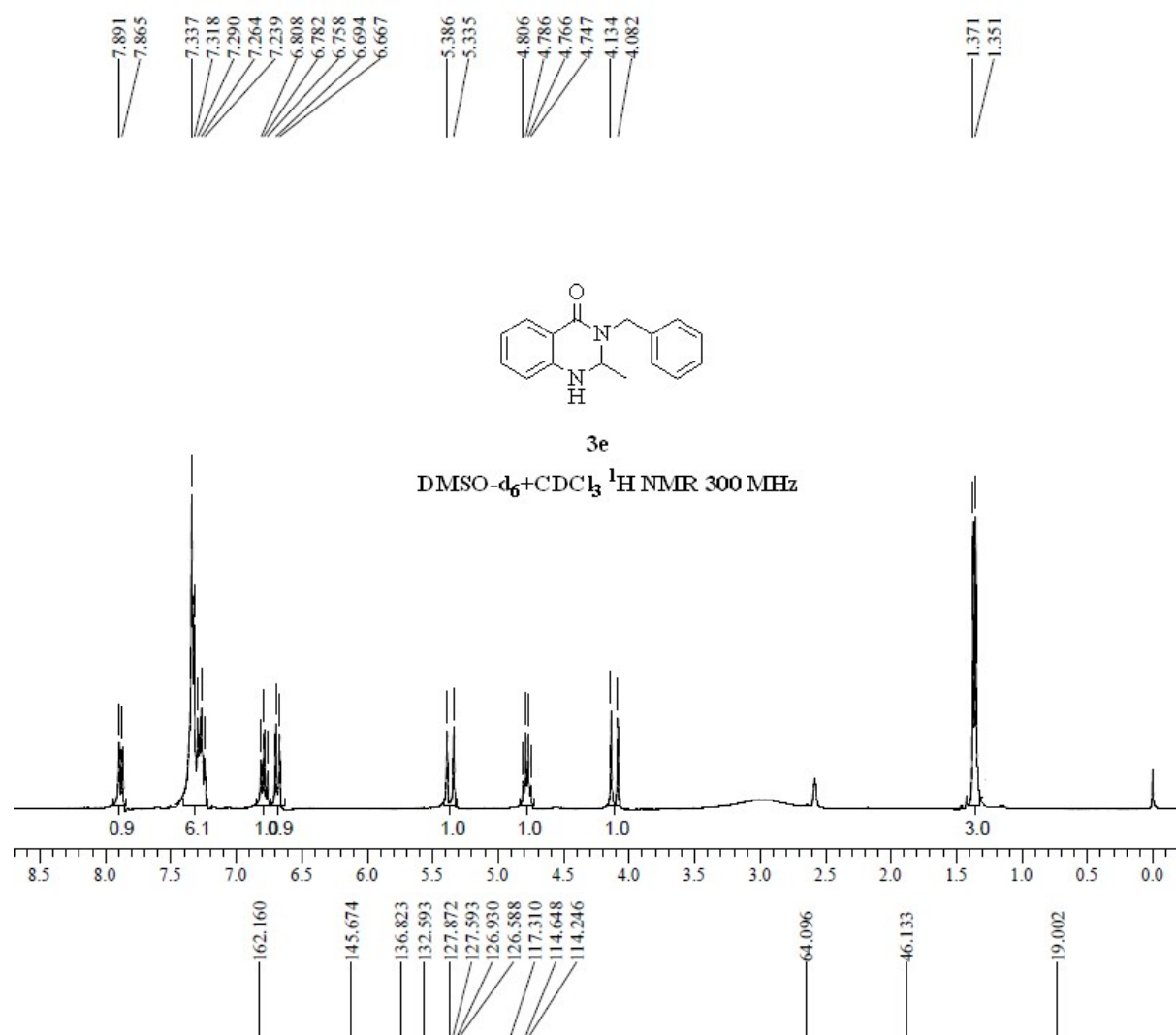
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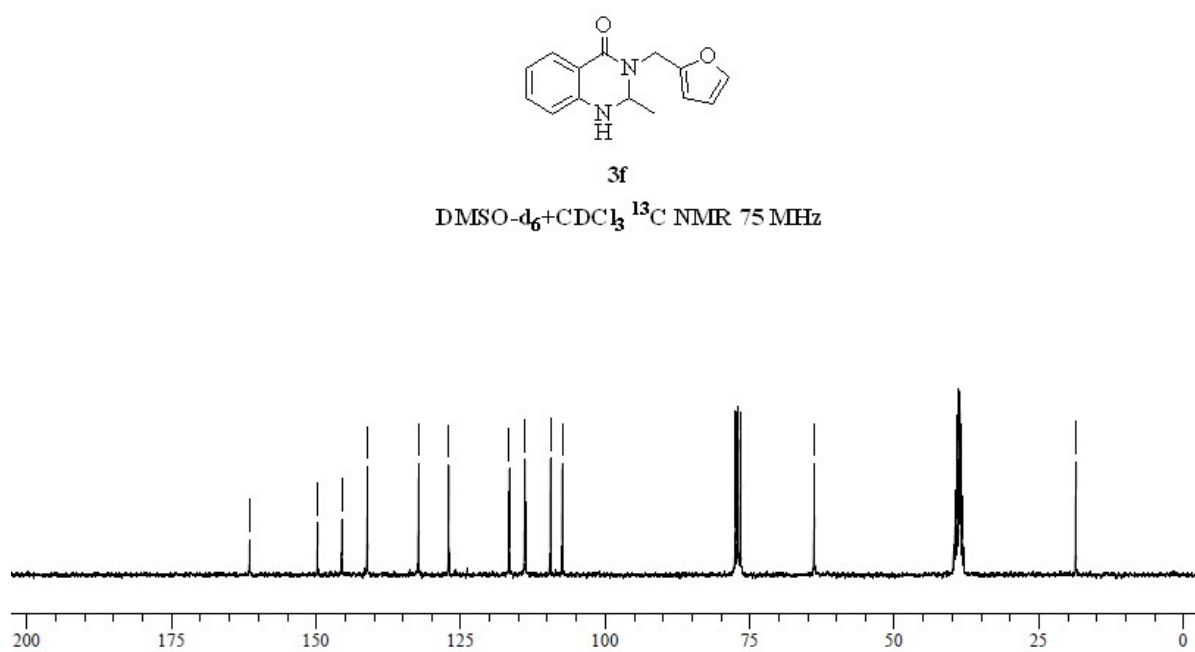
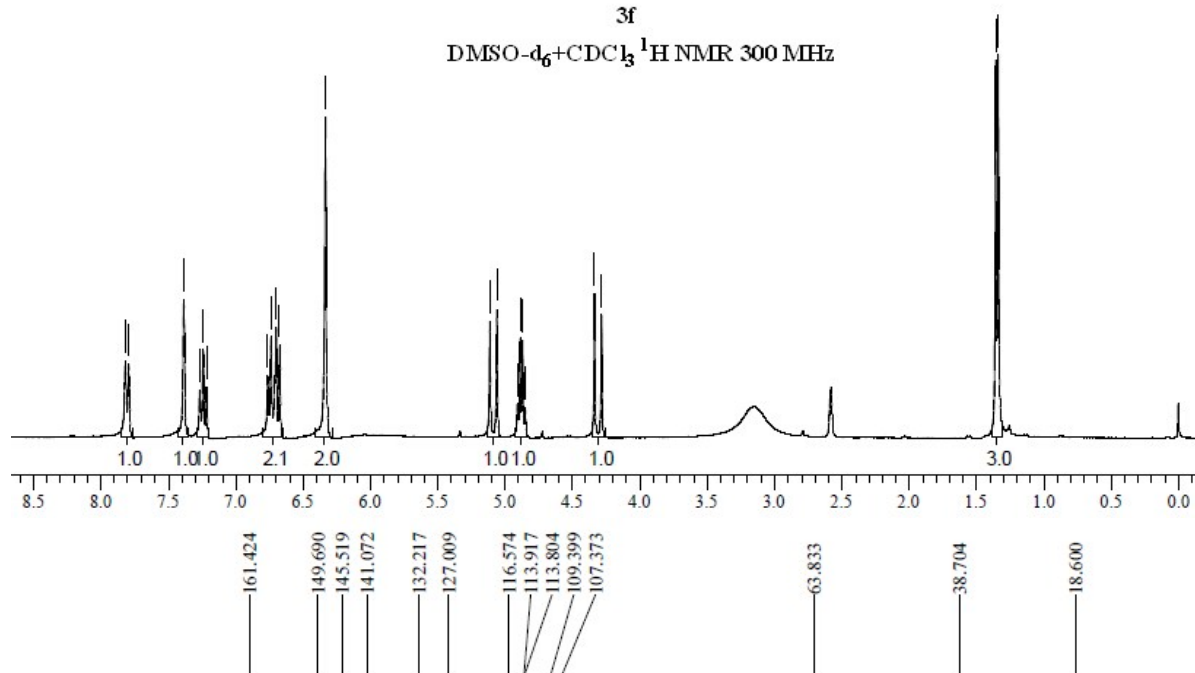


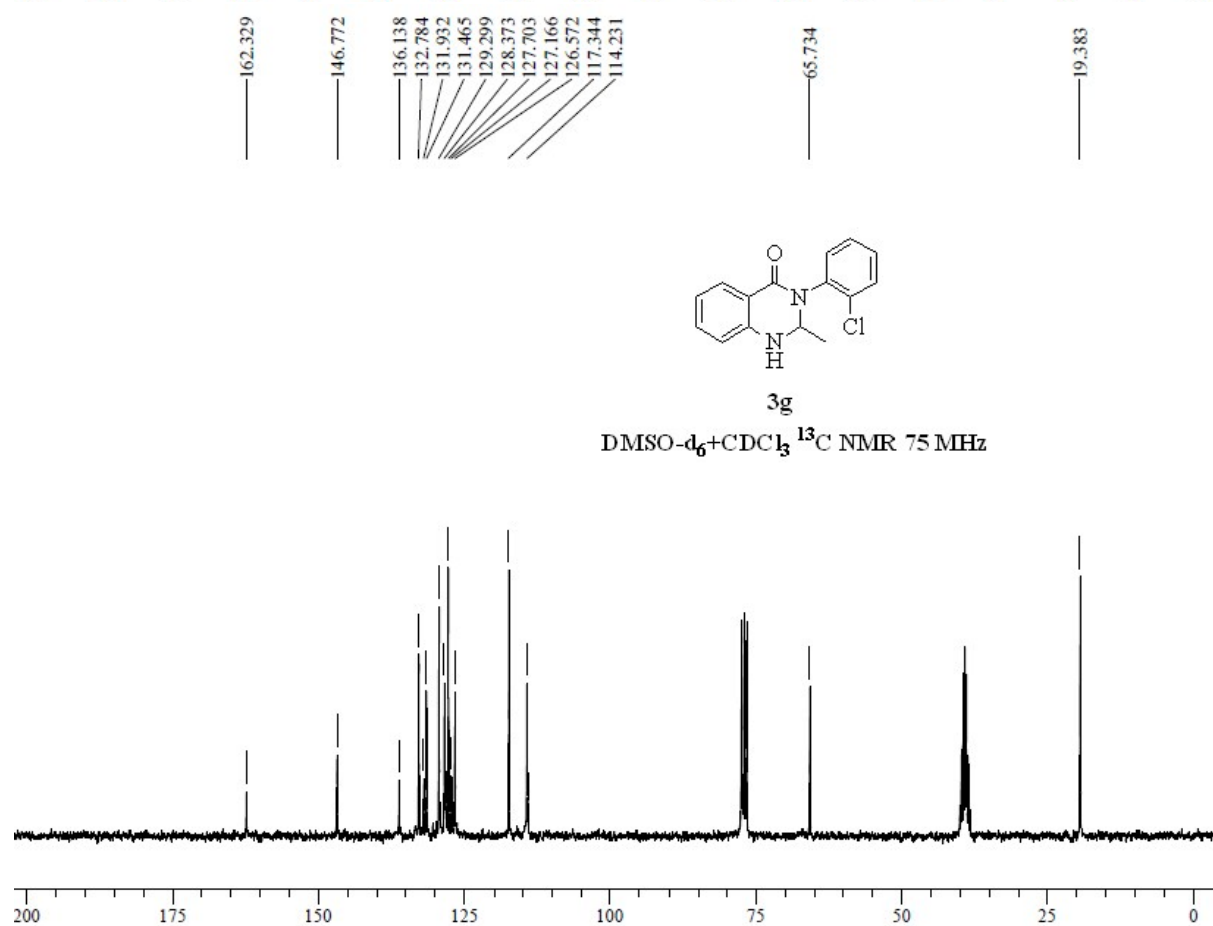
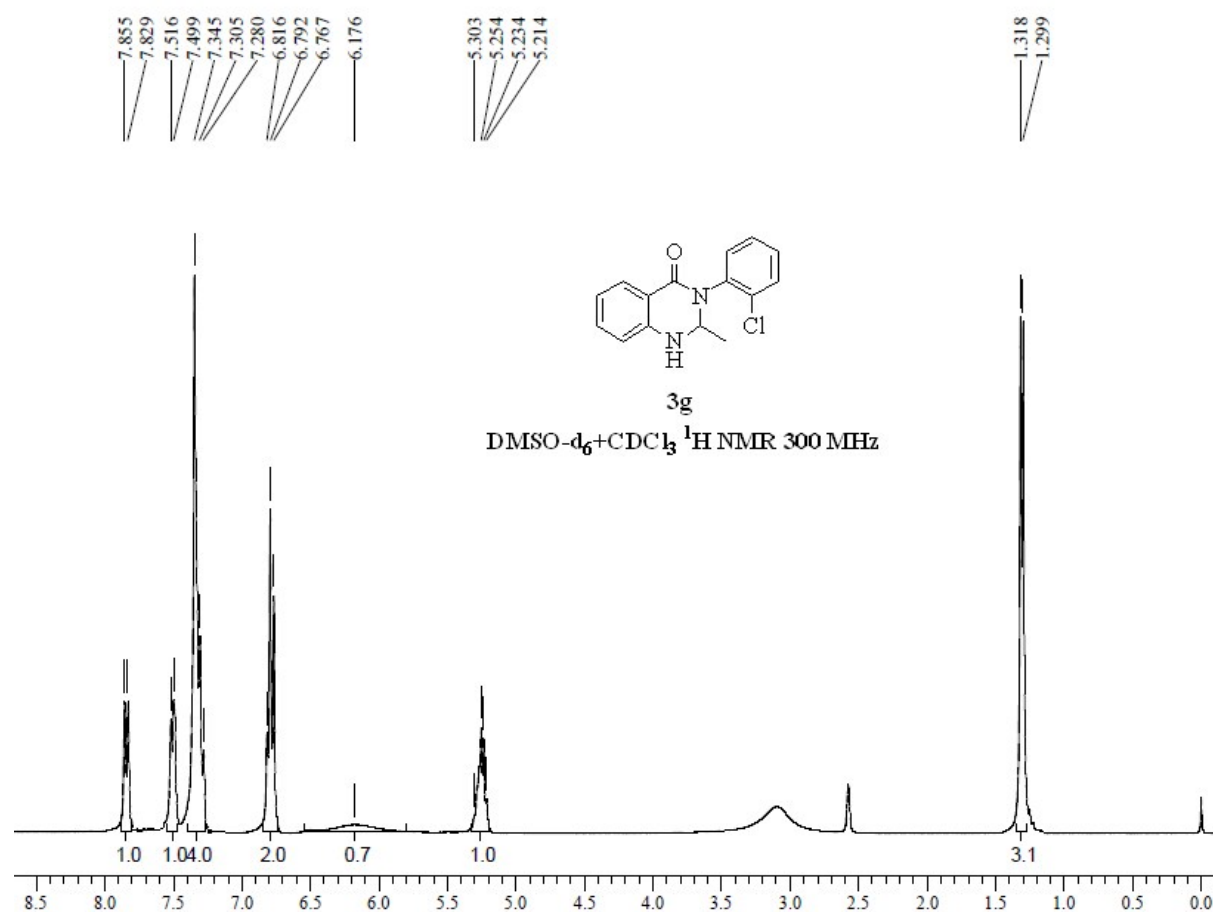
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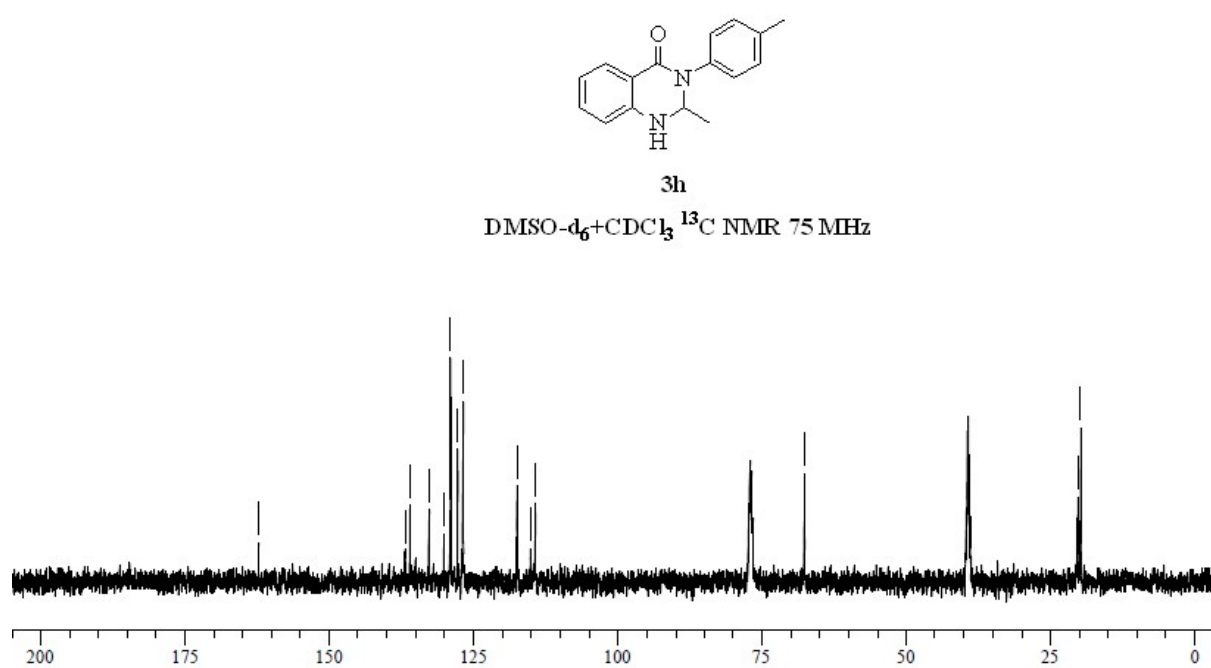
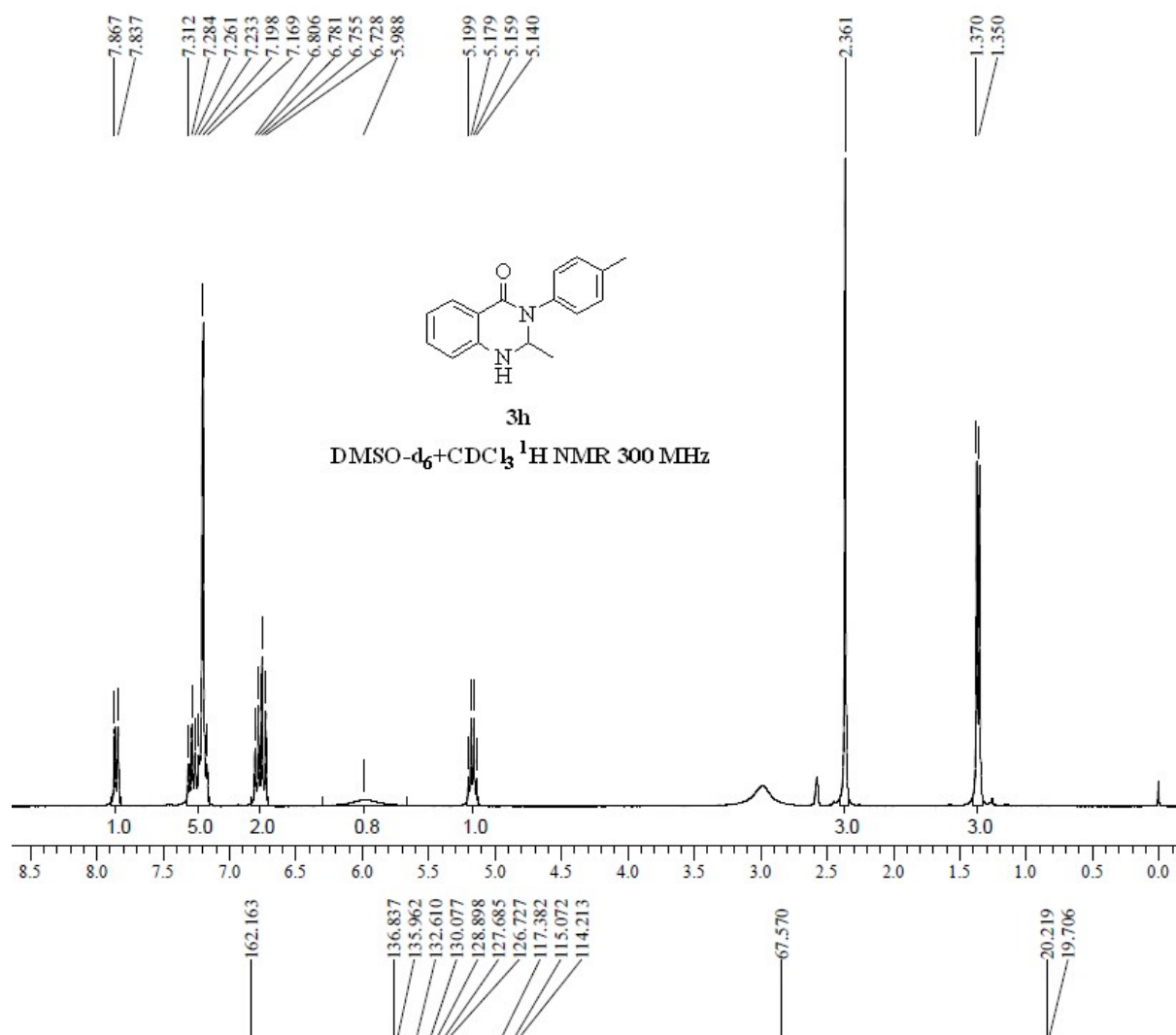
DMSO- d_6 +CDCl $_3$ ^{13}C NMR 75 MHz

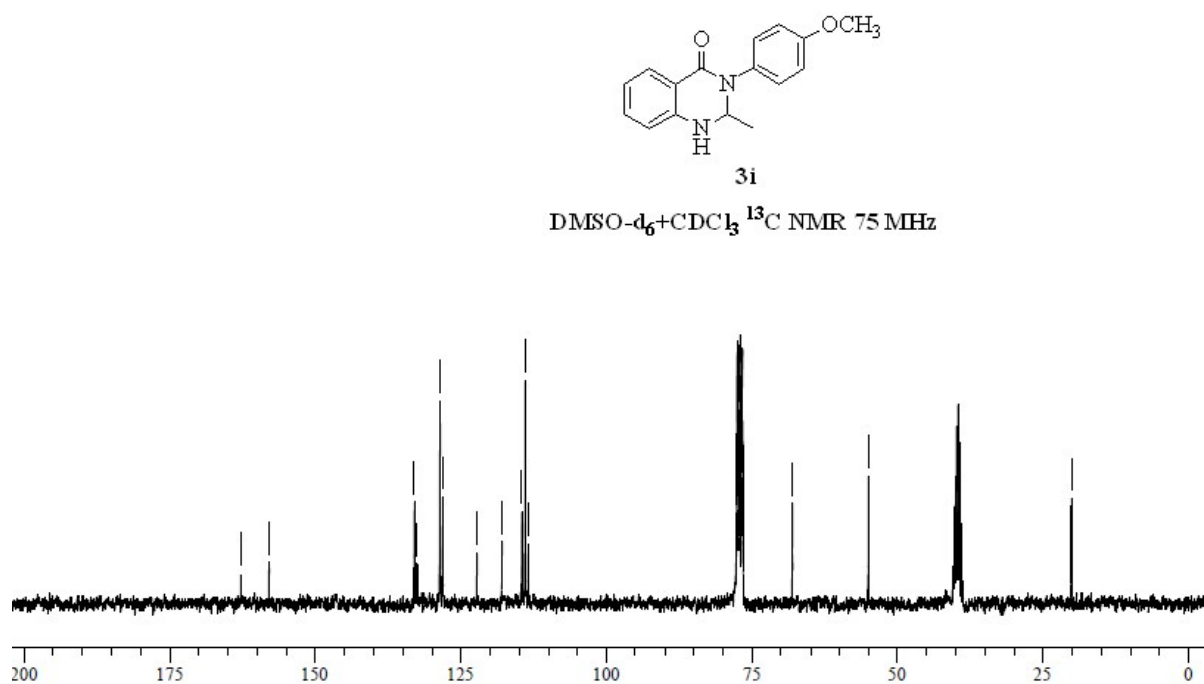
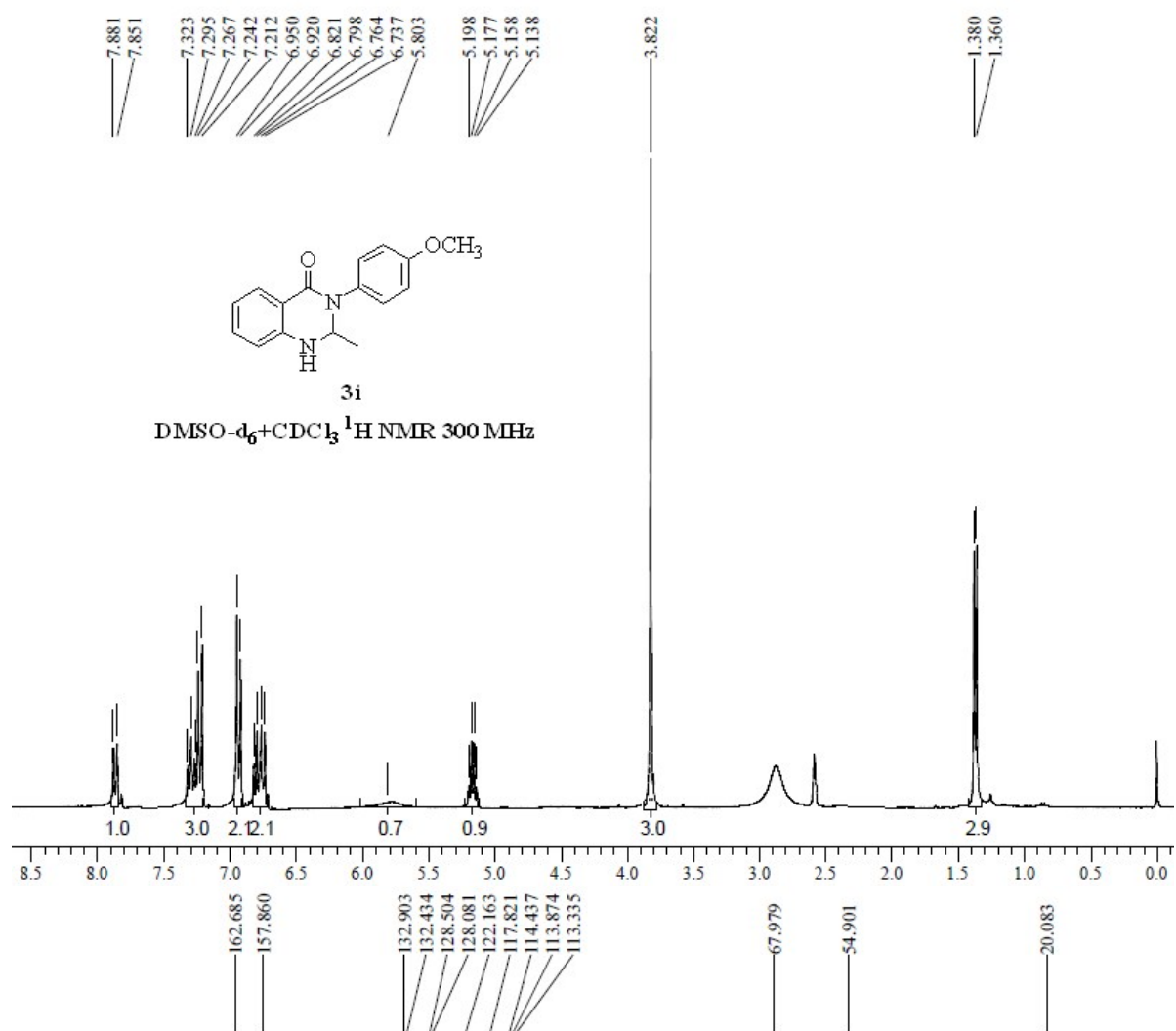


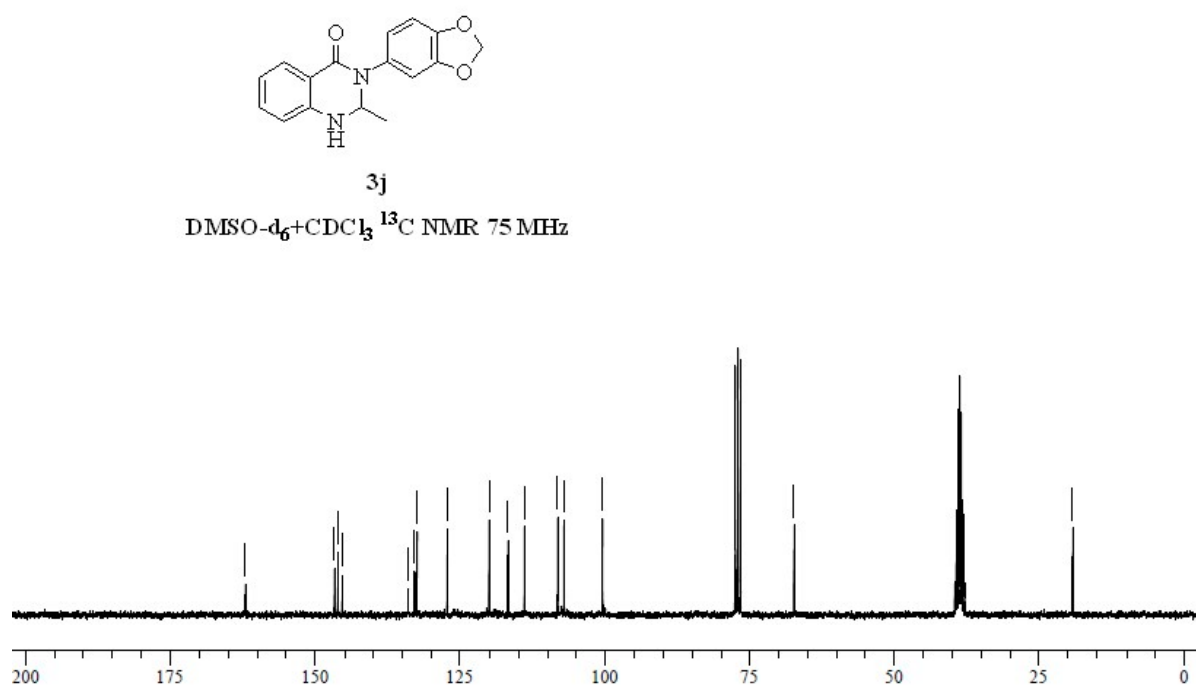
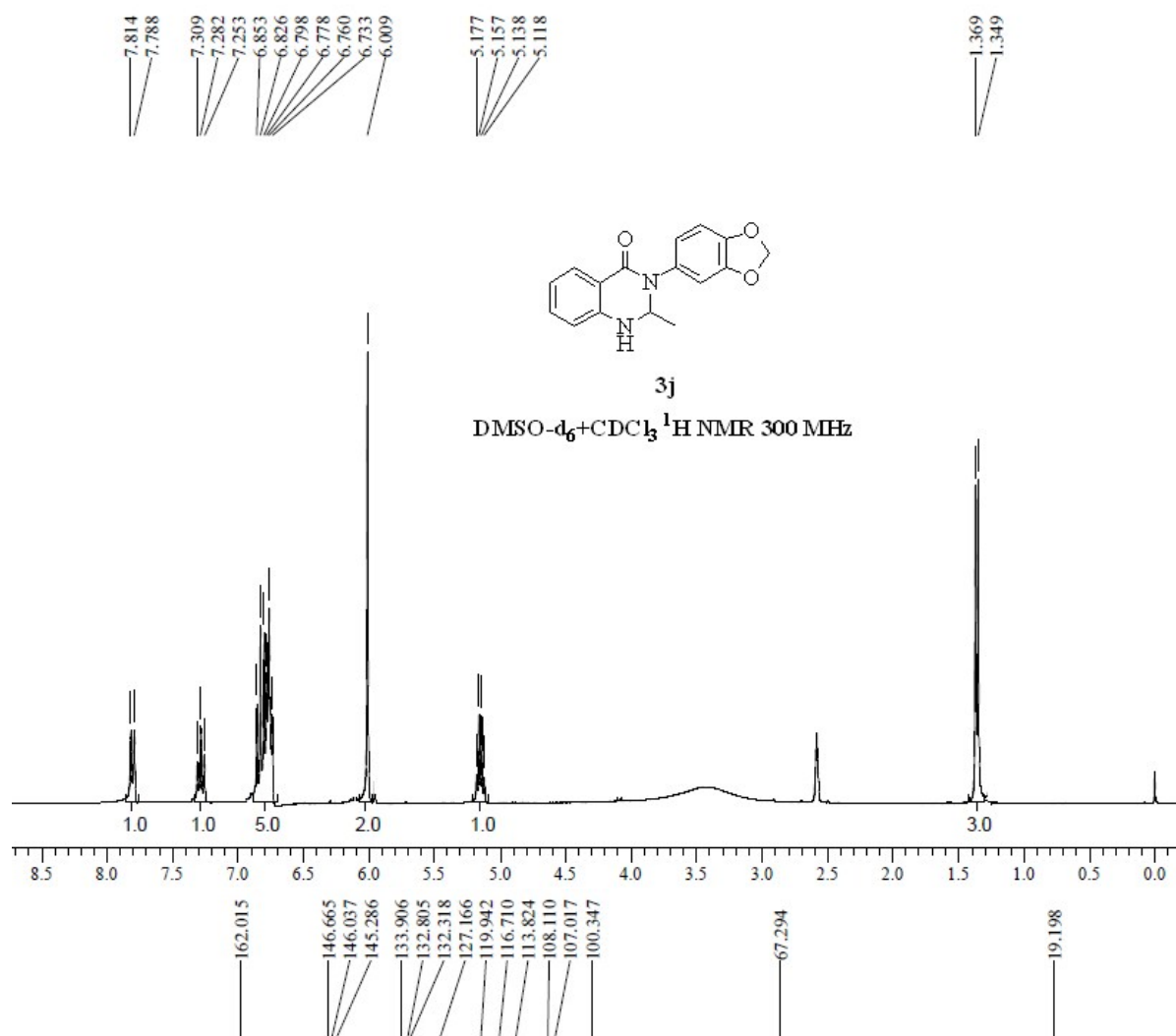


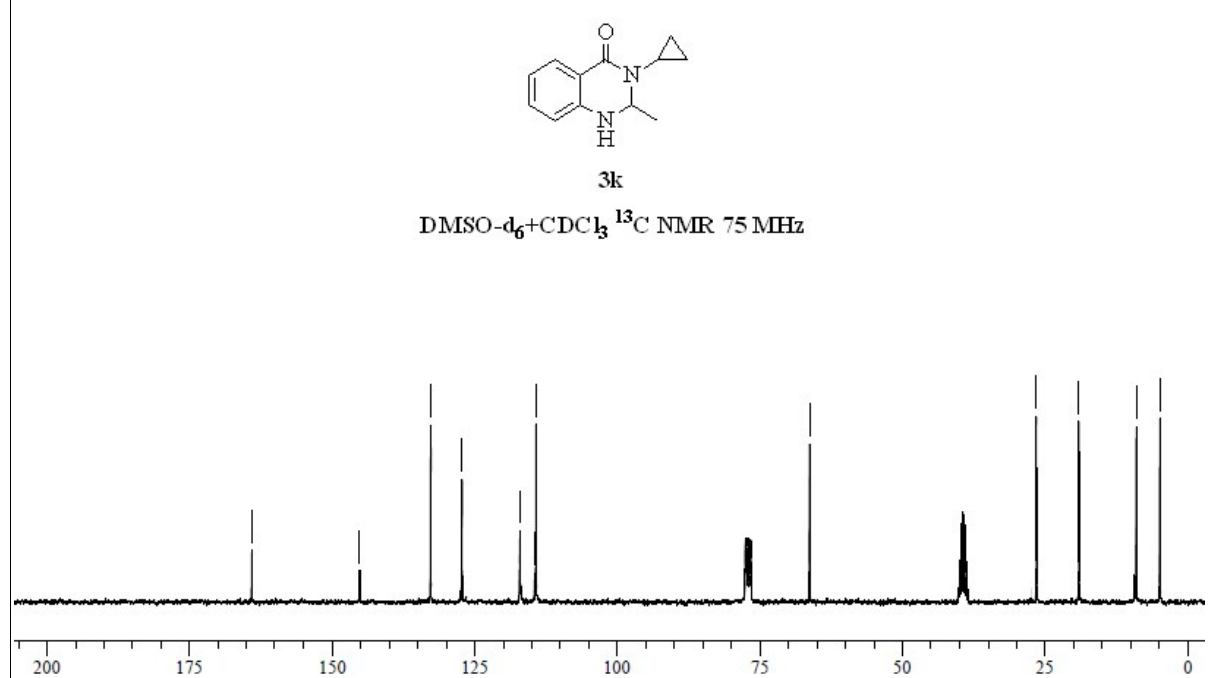
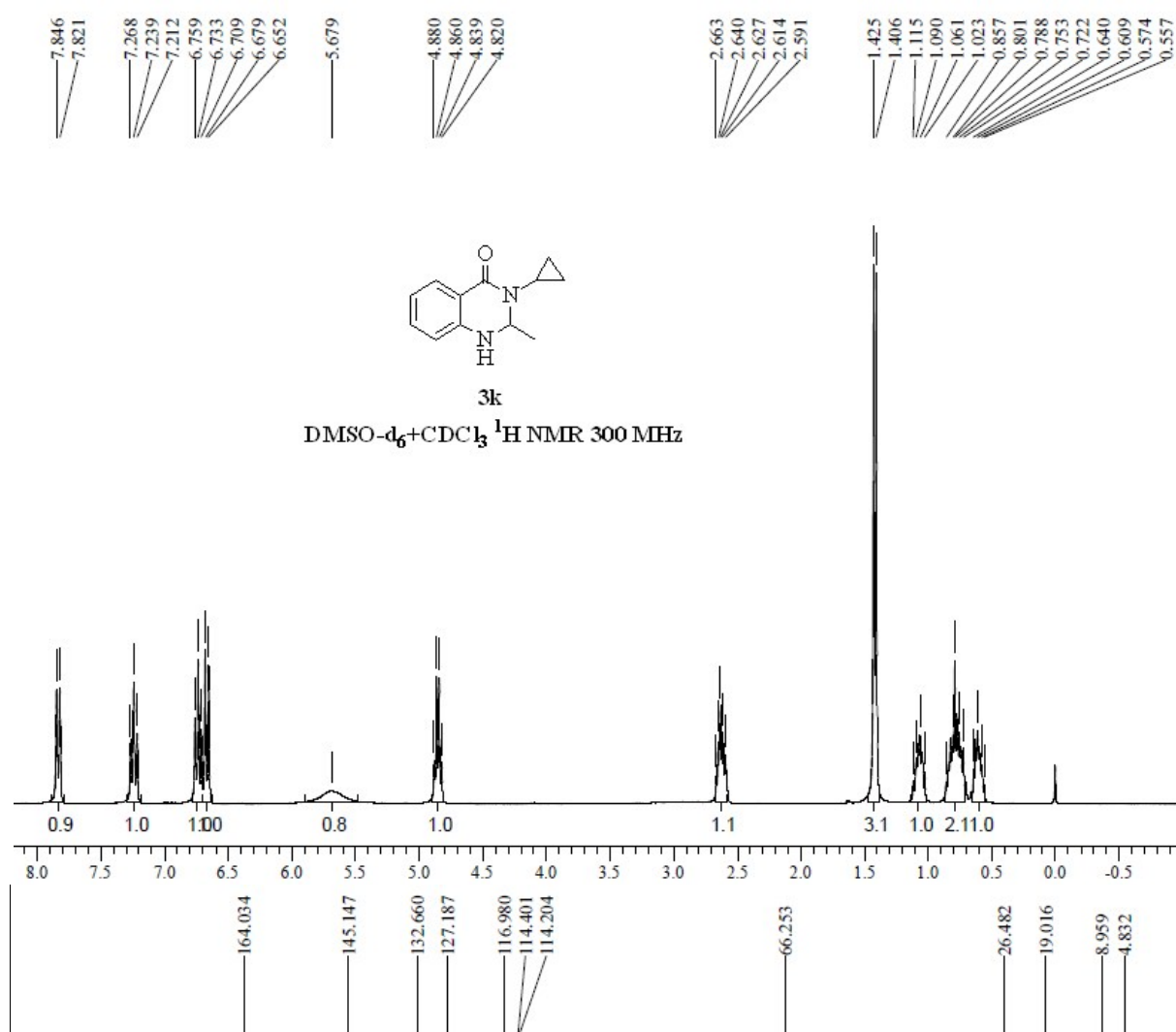


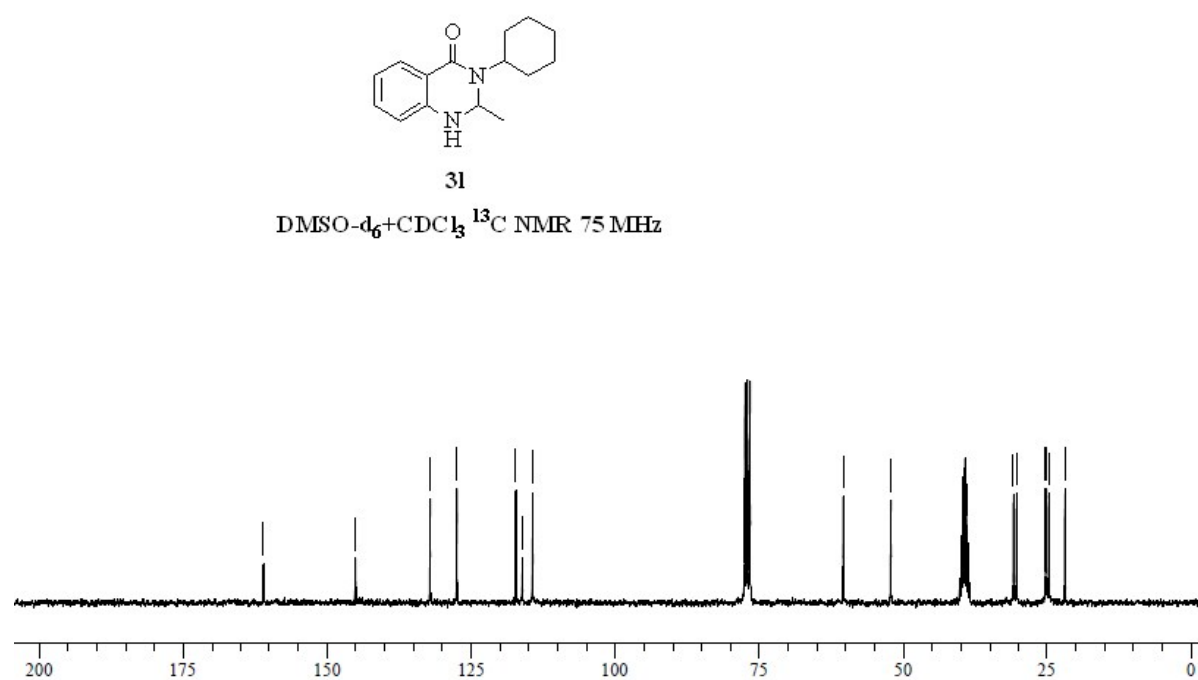
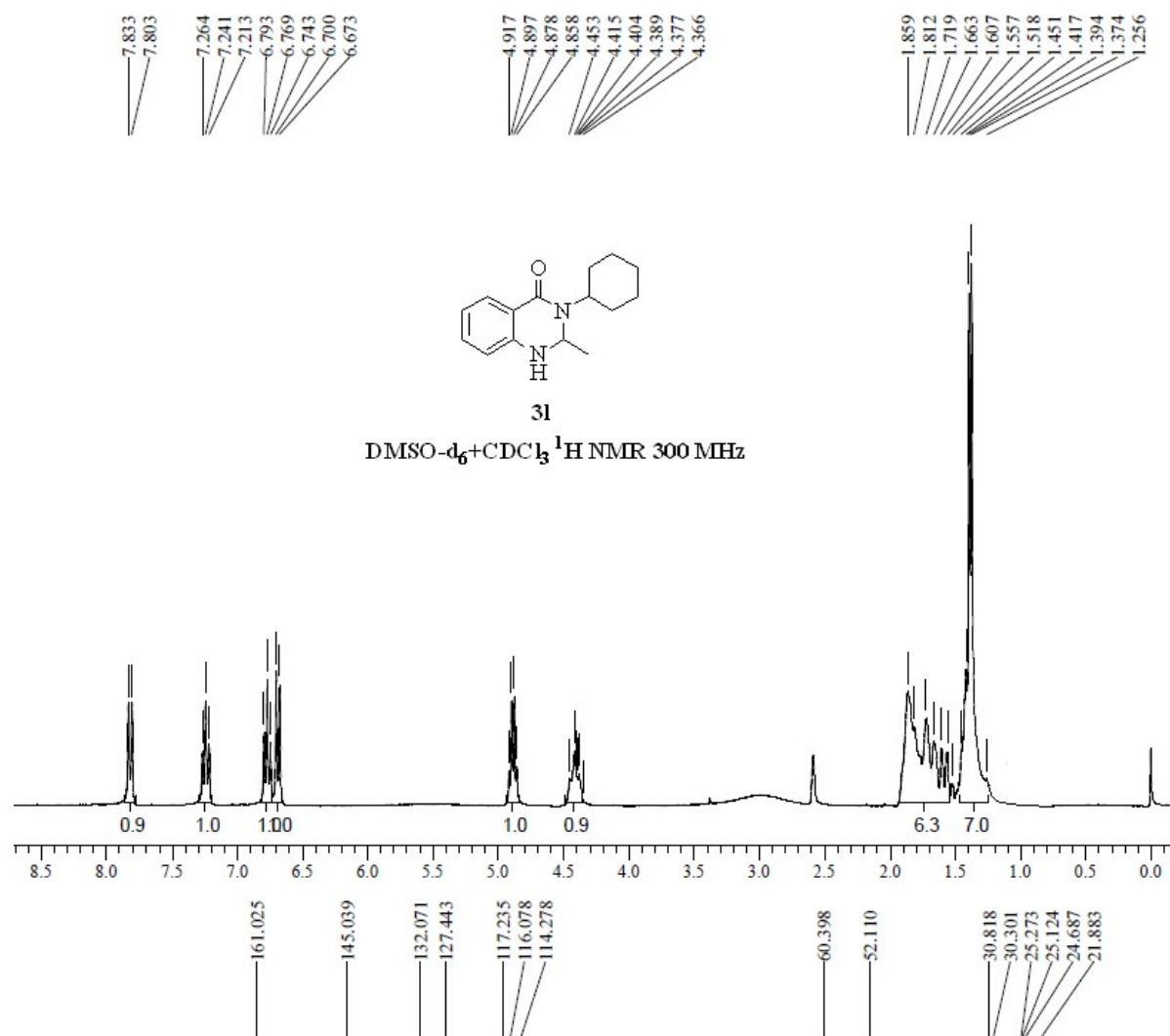


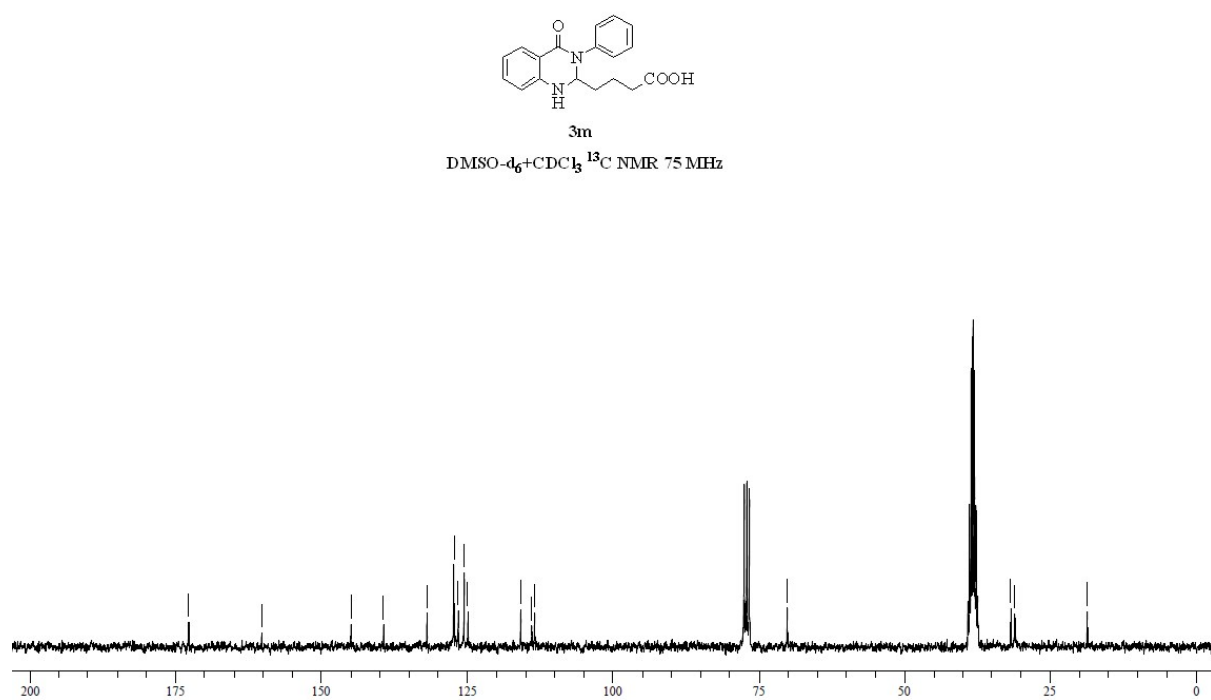
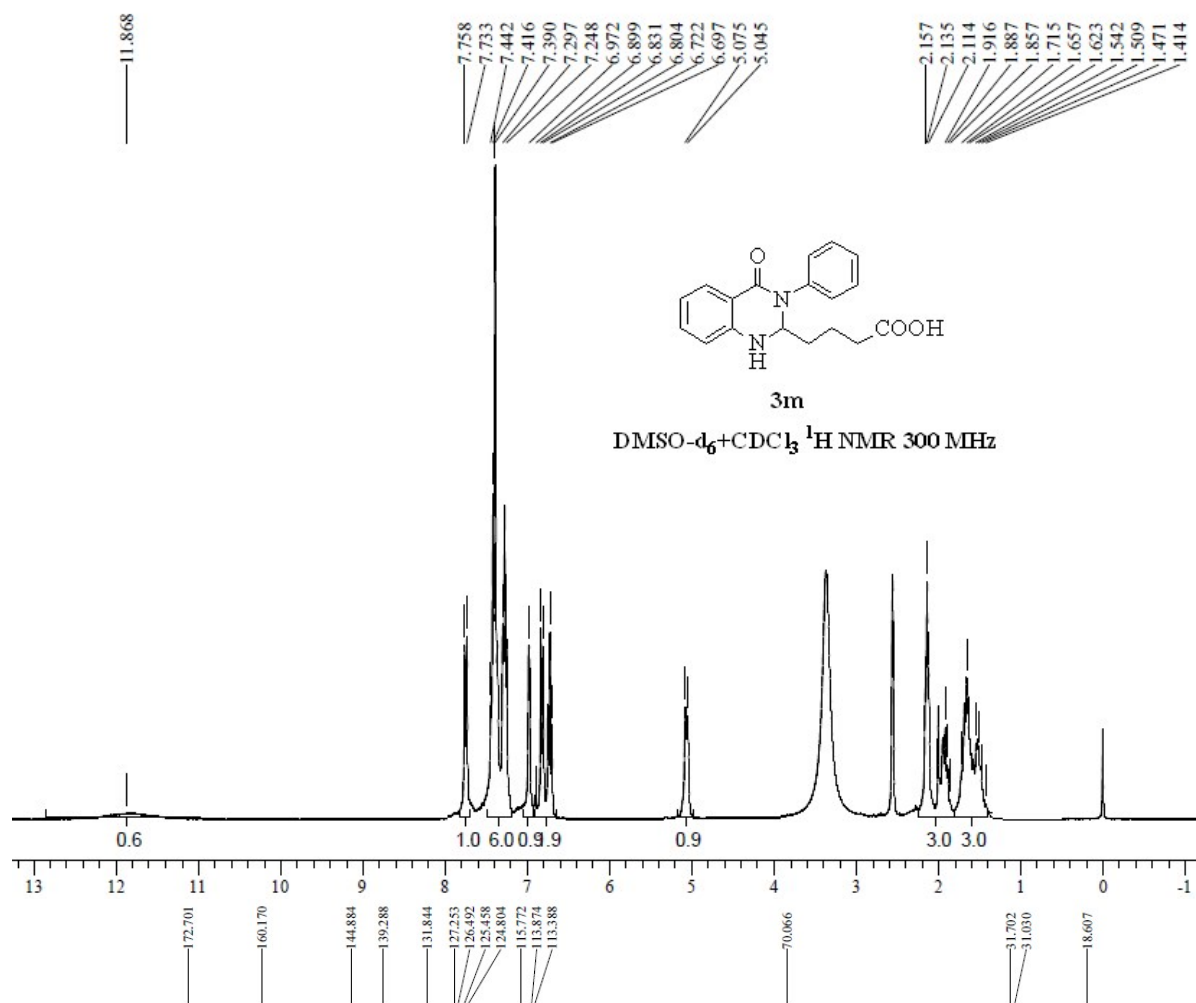


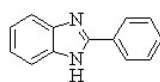






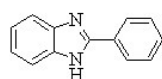
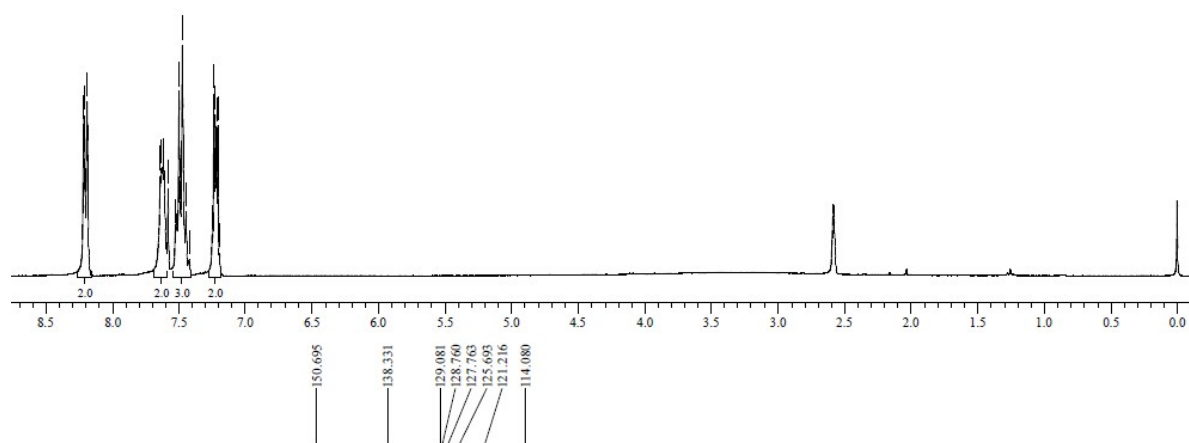






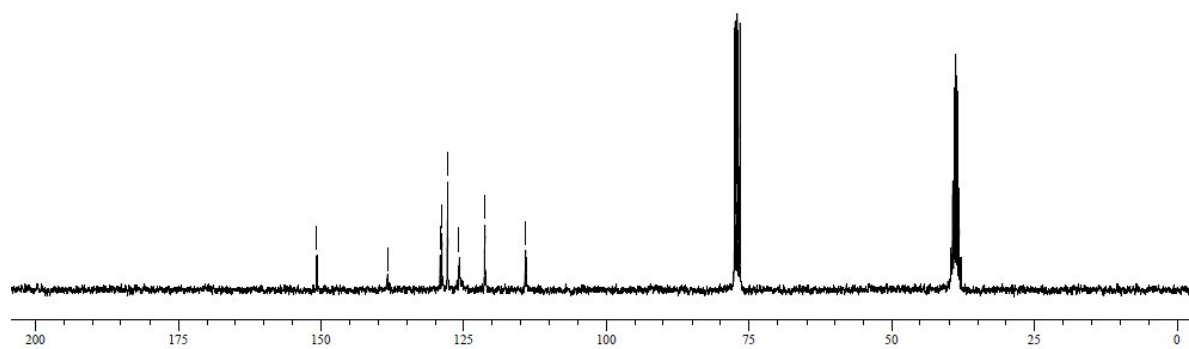
5a

DMSO- d_6 +CDCl $_3$ ^1H NMR 300 MHz

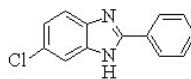


5a

DMSO- d_6 +CDCl $_3$ ^{13}C NMR 75 MHz

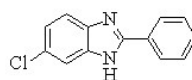
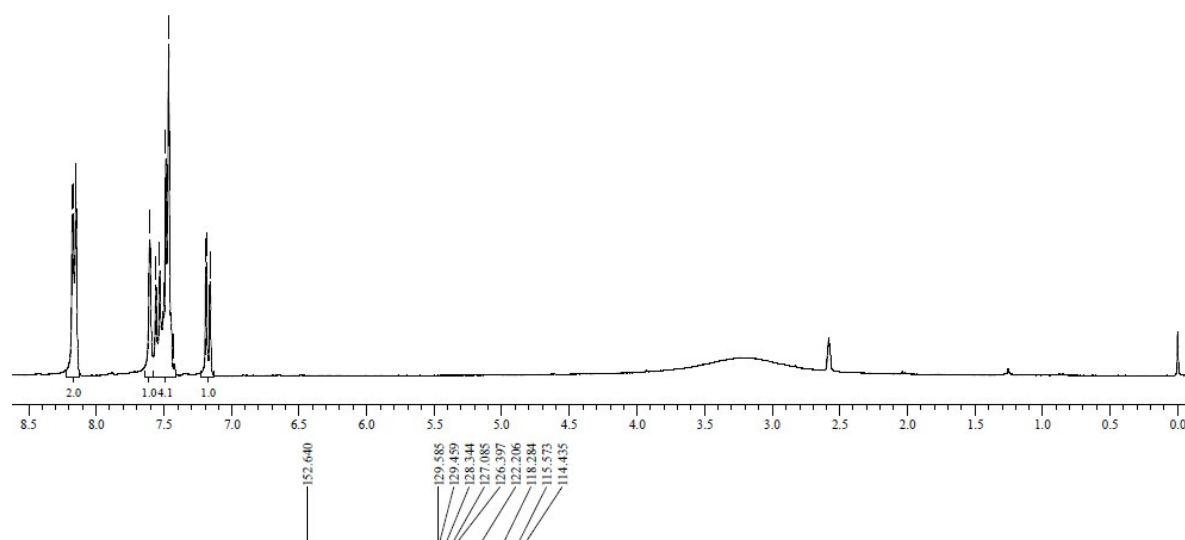


8.178
8.172
8.152
8.148
7.604
7.599
7.530
7.505
7.487
7.464
7.422
7.190
7.185
7.162
7.156



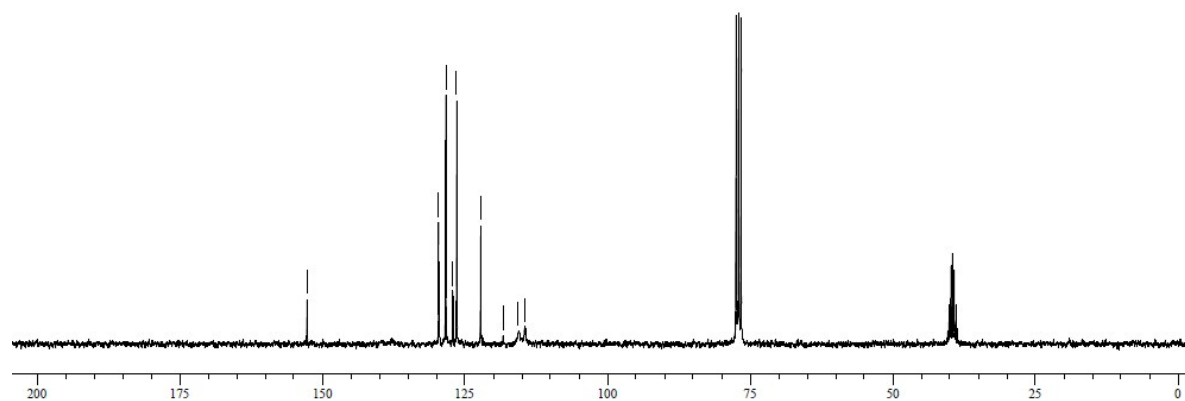
5b

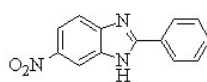
DMSO- d_6 +CDCl $_3$ ^1H NMR 300 MHz



5b

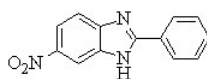
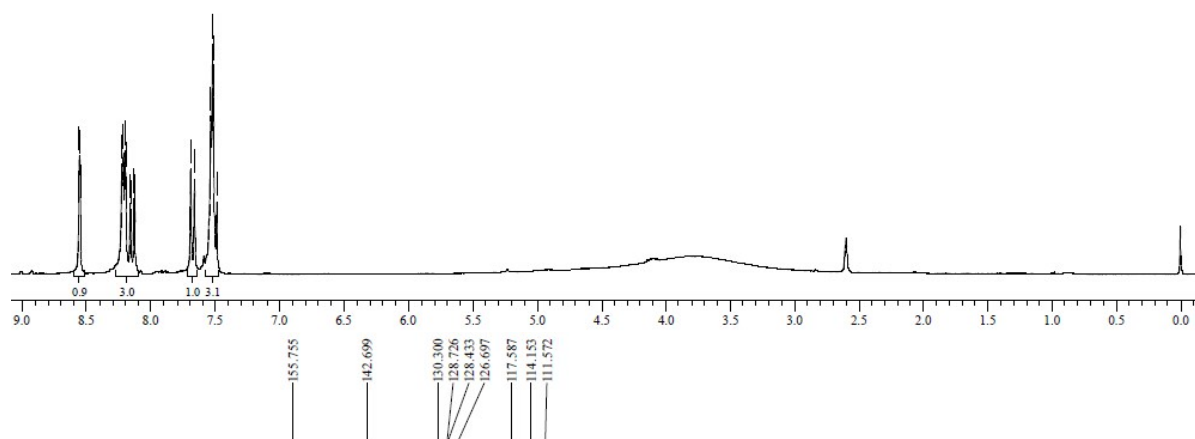
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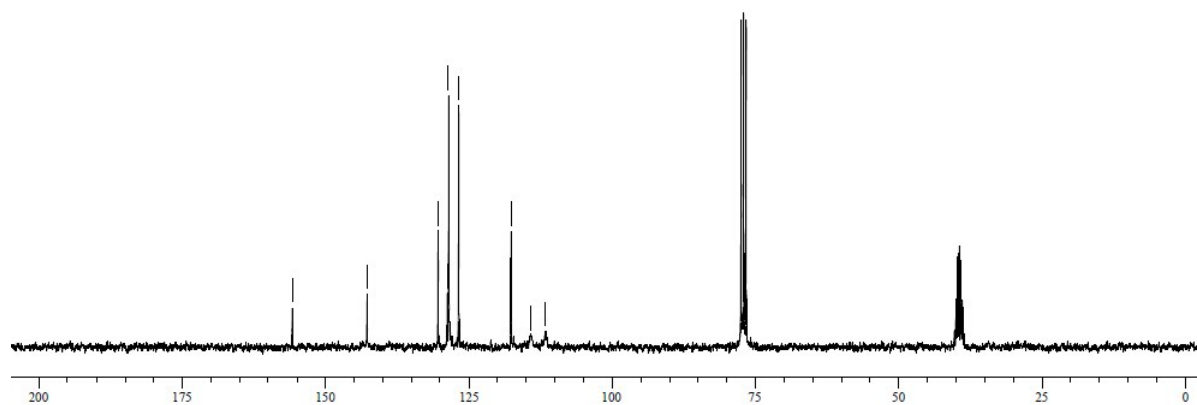
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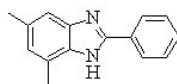
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5c

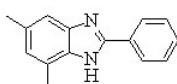
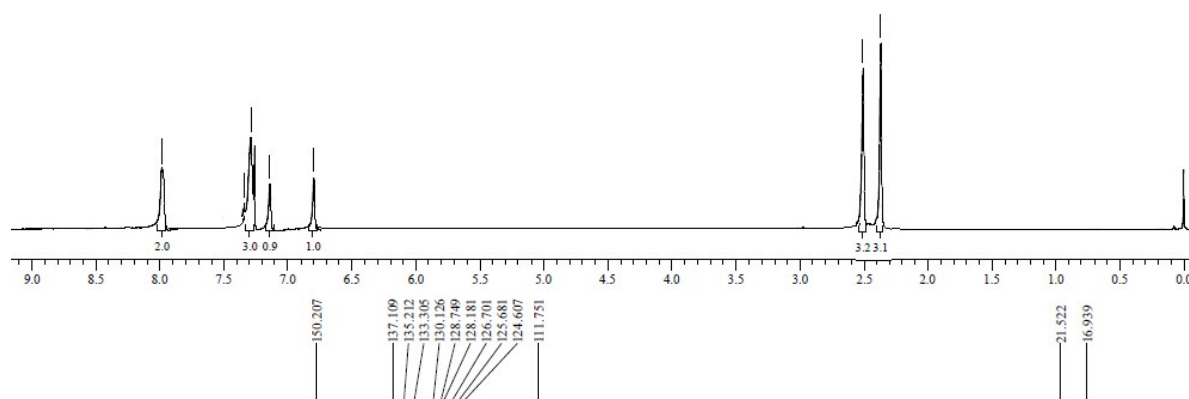
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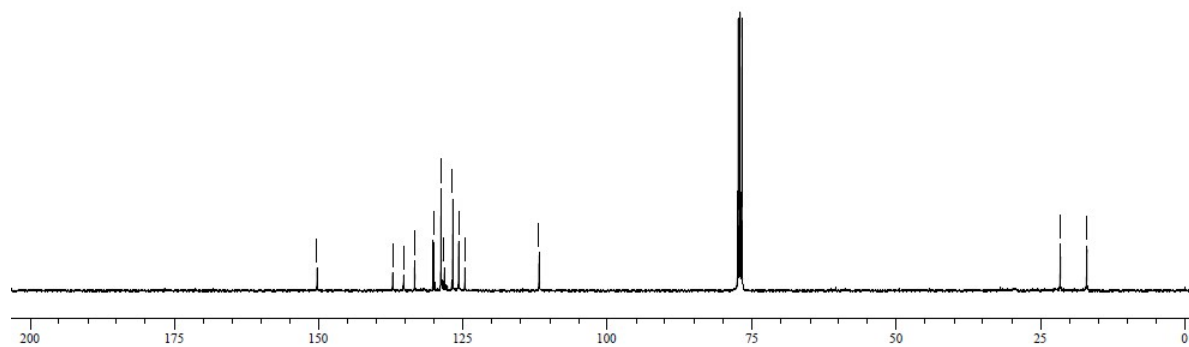
5d

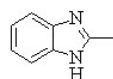
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5d

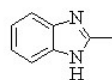
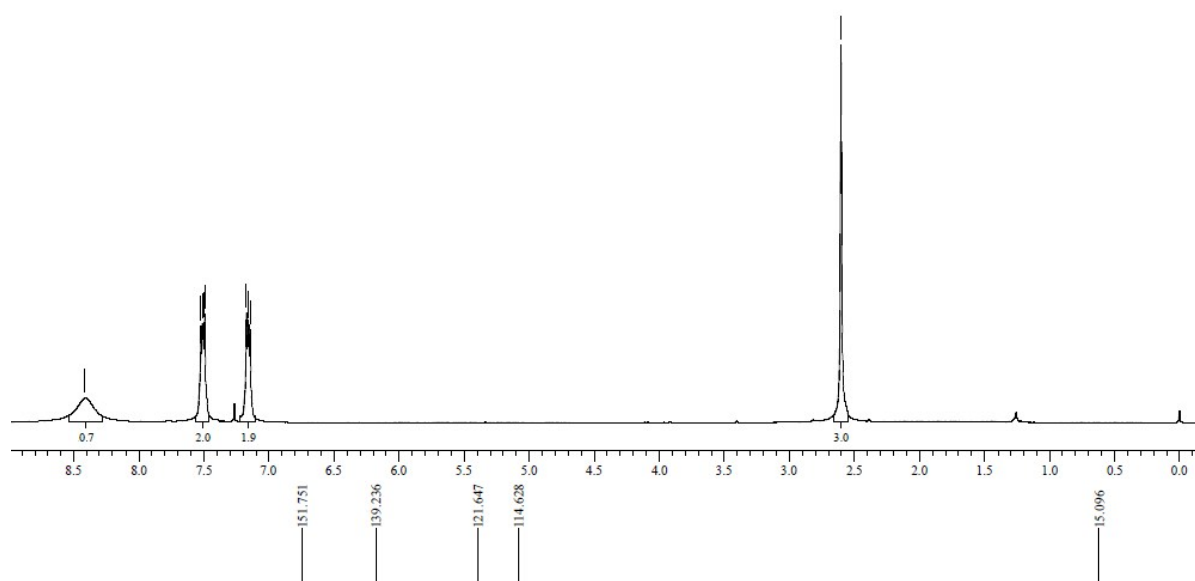
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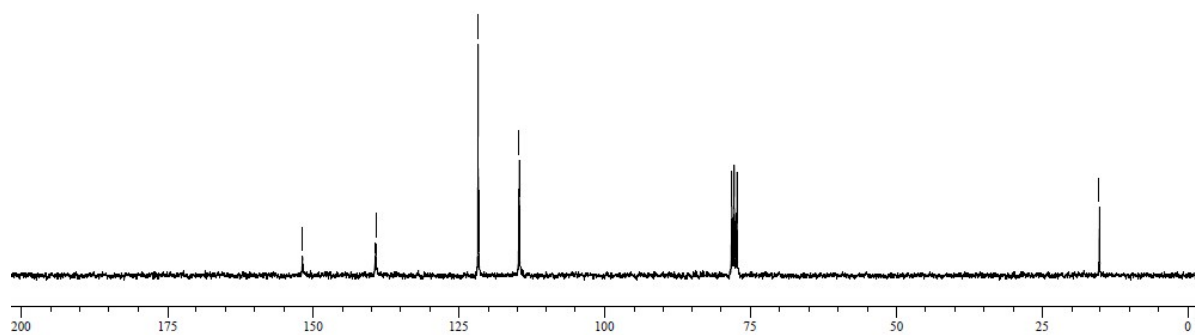
5e

CDCl_3 ^1H NMR 300 MHz



5e

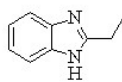
CDCl_3 ^{13}C NMR 75 MHz



7.545
7.539
7.534
7.527
7.207
7.198
7.188

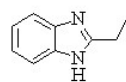
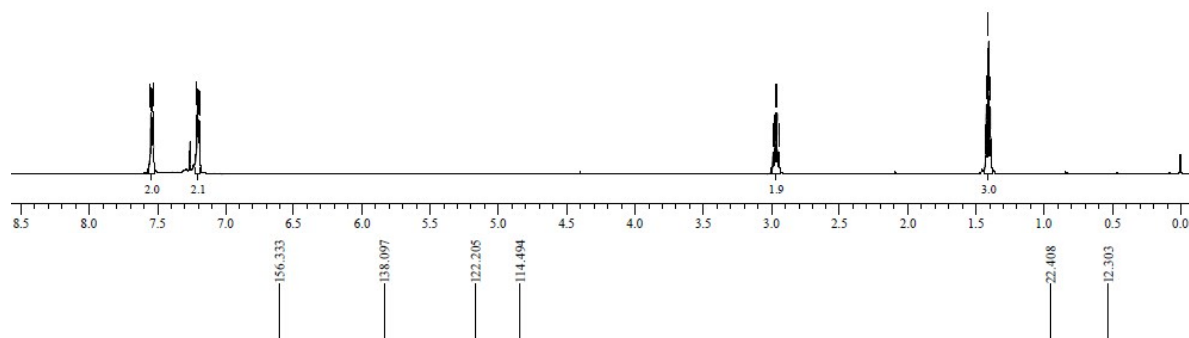
2.985
2.970
2.955
2.939

1.423
1.407
1.392



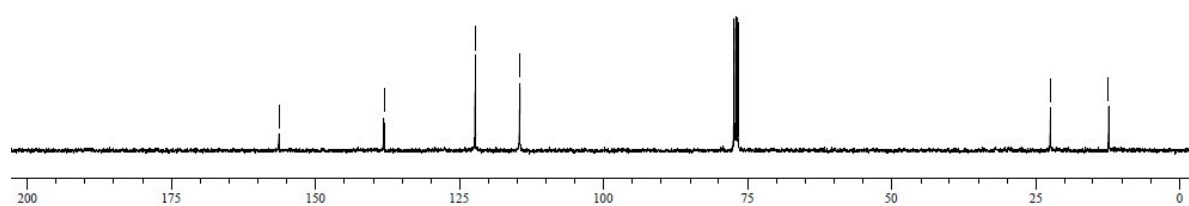
5f

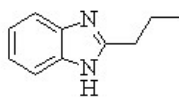
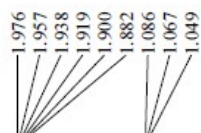
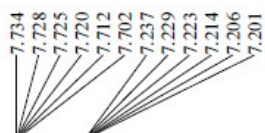
CDCl₃ ¹H NMR 300 MHz



5f

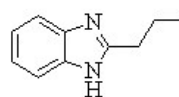
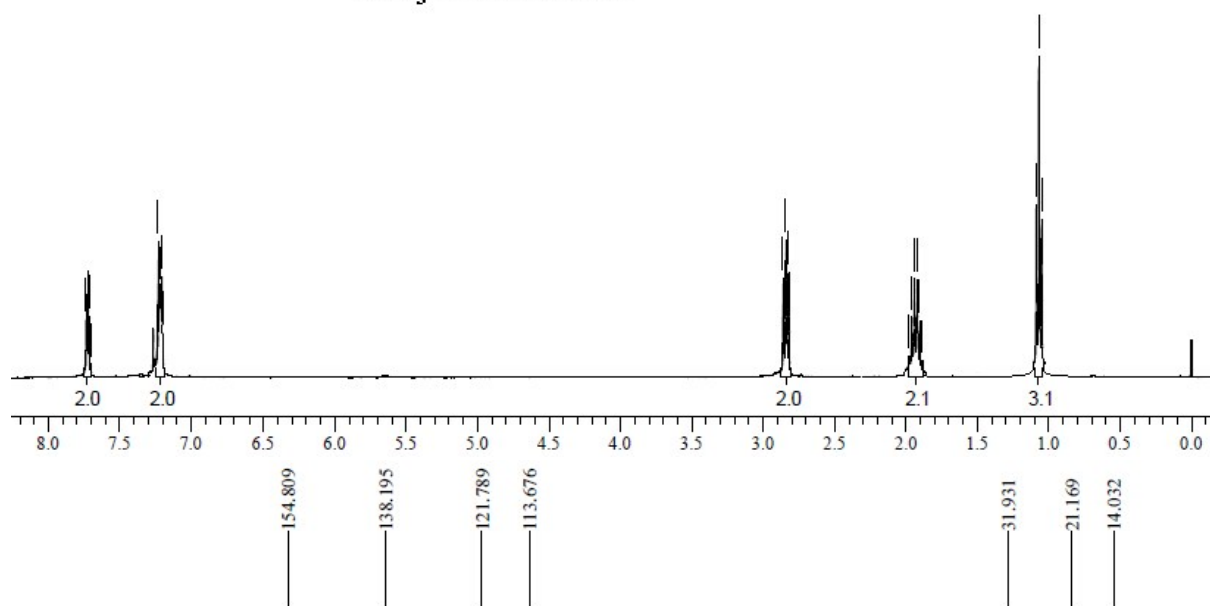
CDCl₃ ¹³C NMR 75 MHz





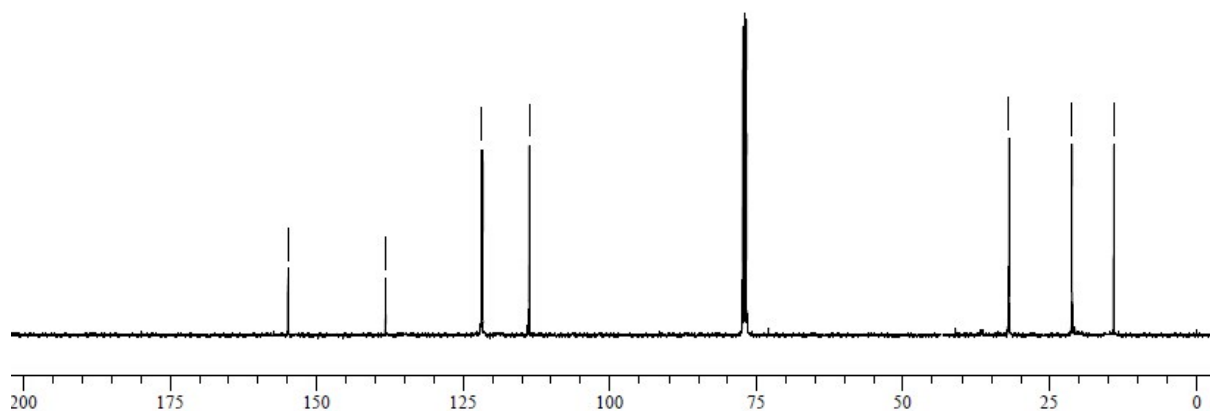
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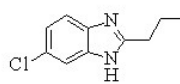
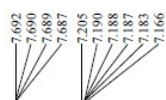
CDCl_3 ^1H NMR 300 MHz



5g

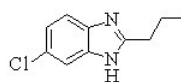
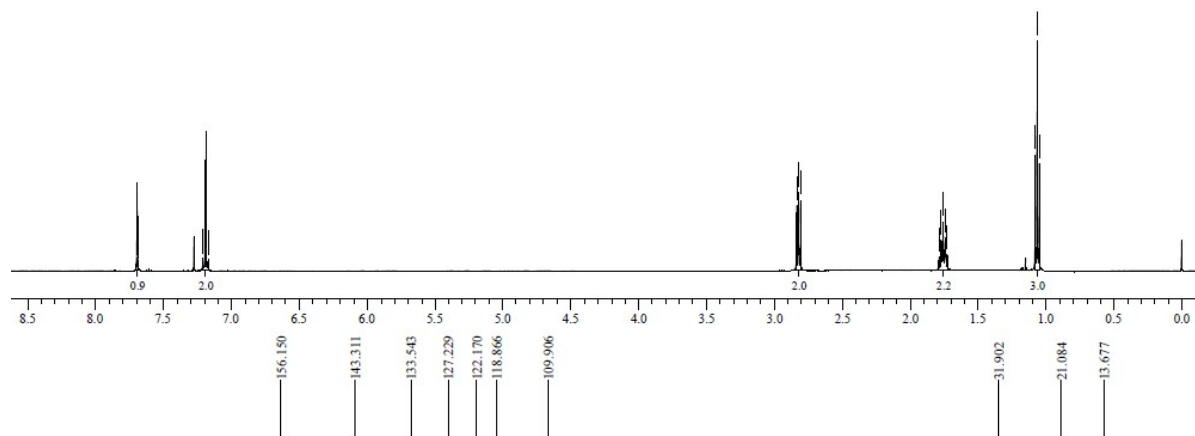
CDCl_3 ^{13}C NMR 75 MHz





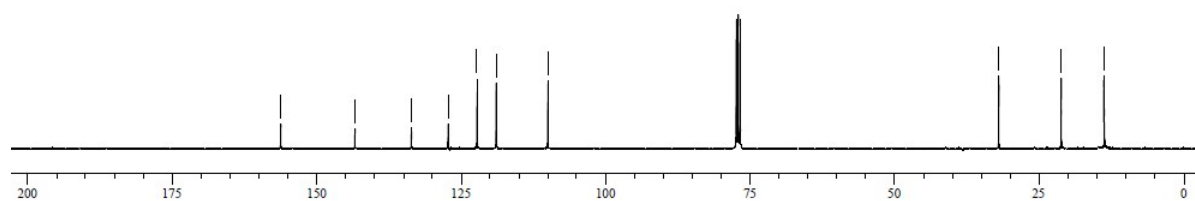
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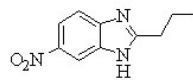
CDCl_3 ^1H NMR 300 MHz



5h

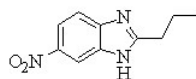
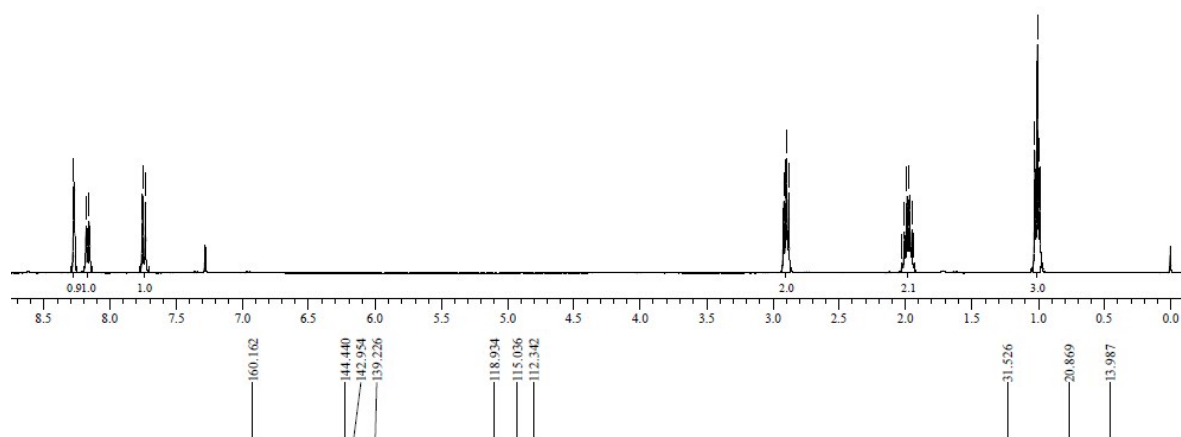
CDCl_3 ^{13}C NMR 75 MHz





5i

CDCl_3 ^1H NMR 300 MHz



5i

CDCl_3 ^{13}C NMR 75 MHz

