Supplementary Materials

CuBr Catalyzed Oxidation/Coupling: An Efficient and Applicable Strategy for the Synthesis of 2-Aryl Benzimidazoles from 1-Fluoro-2-nitrobenzene and Benzylamines

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General procedure for the synthesis of 3a-h

A **so**lution of 1-fluoro-2-nitrobenzene (5mmol) and arylamine (5 mmol) in 10 mL DMF containing K_2CO_3 (5.5 mmol) was stirred at 80 °C for 5-6 h. After cooling to room temperature the mixture reaction was filtered through Celite. Then the filtrate was concentrated and added to a saturated aq. solution of NaCl and then extracted with ethyl acetate. The organic phases was dried over sodium sulfate and then evaporated under vacuum. The products were purified by column chromatography over silica gel.

General procedure for the synthesis of 4a-h

To a stirred solution of the o-nitroarene (1 mmol) in methanol and saturated ammonium chloride solution (4 mL, 1:1), zinc dust (10 mmol) was added portion-wise over 15 min at 0 °C. After completion of the reaction (TLC), the reaction mixture was filtered through a layer of Celite, then the methanol was removed under vacuum and the aqueous residue was extracted with EtO_2 (3×15 mL). The organic phases were dried over Na_2SO_4 and then concentrated. The crude product was purified by column chromatography over silica gel.

General procedure for synthesis of benzimidazole derivatives 5a-h

A solution of the as-synthesized 2-aminoaniline 4a-h (0.2 mmol), K2CO3 (0.6 mmol, 83 mg) and CuBr (0.02 mmol, 2.8 mg) in DMSO (2 mL) was provided. The mixture was allowed to stir under air (1atm) at 120 °C for 14 h. After completion of the reaction, the resulting solution was cooled to room temperature and filtered. Afterward, the filtrate was evaporated using a rotary evaporator. Then the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 to 2:1) as eluent to provide **5a-h**. All the products were

identified and characterized by comparison of mp, IR, and ^{1}HNMR and ^{13}CNMR spectroscopy with those reported in literatures.

2-Phenyl-1*H*-benzimidazole (5a)

Colorless solid; mp 282-284 °C; IR (KBr); υ(cm^{-1}): 1620 (C=N); ^{1}H NMR (DMSO-d$_6$, 250 MHz): δ = 7.14–7.25 (m, 2 H), 7.44–7.61 (m, 5 H), 8.20 (d, J = 7.2 Hz, 2 H), 12.94 (s, 1 H, NH) ppm; ^{13}C NMR (DMSO-d$_6$): δ = 122.1, 126.4, 128.4, 128.9, 129.2, 129.8, 130.1, 151.2.

2-(4-Chlorophenyl)-1*H*-benzimidazole (5b)

Colorless solid; mp 292–293 °C; IR (KBr); υ(cm^{-1}): 1626 (C=N); ^{1}H NMR (DMSO-d$_6$, 250 MHz): δ = 7.18–7.21 (m, 2 H), 7.60 (m, 4 H), 8.17 (d, J = 8.6 Hz, 2 H), 12.99 (s, 1 H, NH) ppm; ^{13}C NMR (DMSO-d$_6$): δ = 111.4, 118.9, 121.9, 122.7, 128.1, 129, 134.5 150.1.

2-(4-Methylphenyl)-1*H*-benzimidazole (5c)

Colorless solid; mp 270–272 °C; IR (KBr); υ(cm-1): 1620 (C=N); 1H NMR (DMSO-d$_6$, 250 MHz): δ = 2.35 (s, 3 H), 7.15–7.20 (m, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.46–7.56 (m, 2 H), 8.07 (d, J = 8.1 Hz, 2 H), 12.84 (s, 1H) ppm; ^{13}C NMR (DMSO-d$_6$): δ = 20.9, 121.9, 126.3, 127.4, 128.9, 129.4, 139.5, 151.3.

2-(4-Nitrophenyl)-1*H*-benzimidazole (5d)

Yellow solid; mp312–314 °C; IR (KBr); υ(cm^{-1}): 1620 (C=N); ^{1}H NMR (DMSO-d$_6$, 250 MHz): δ = 7.22–7.26 (m, 2 H), 7.62 (m, 2 H), 8.38 (m, 4 H), 13.27 (s, 1 H, NH) ppm; ^{13}C NMR (DMSO-d$_6$): δ = 111.7, 119.3, 122.3, 123.4, 124.1, 127.2, 135.9, 147.6, 148.9.

2-(4-Methoxyphenyl)-1*H*-benzimidazole (5e)

Colorless solid; mp 216-218 °C; IR (KBr); υ(cm^{-1}): 1612 (C=N); ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 3.78 (s, 3 H), 7.10 (d, *J* = 8.8 Hz, 2 H), 7.16 (q, *J* = 3.01 Hz, 2 H), 7.50 (m, 2 H), 8.12 (d, *J* = 8.8 Hz, 2 H), 12.76 (s, 1 H) ppm; ^{13}C NMR (DMSO-d_6): δ = 55.2, 111.0, 114.3, 118.4, 121.5, 122.0, 122.6, 128.0, 151.3, 160.5.

2-(2-Chlorophenyl)-1*H*-benzimidazole (5f)

White crystals, mp 253-255 °C, IR (KBr, cm^{-1}): 1623 (C=N), 3433 (NH) cm^{-1}. ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 2.73 (s, 1H), 7.92 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.67 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.57-7.52 (m, 3H), 7.25 (s, 2H). ^{13}C NMR (DMSO-d_6): δ = 149.57, 132.56, 132.11, 131.67, 130.82, 130.45, 127.91.

4-(1*H*-benzimidazol-2-yl)phenol (5g)

Pale-yellow solid; M.p. 254–255 °C; IR (KBr); υ(cm^{-1}): 1620 (C=N); ^{1}HNMR (DMSO-d_6, 250 MHz): δ = 6.93 (dd, J_1 = 8.5, J_2 = 1.2 Hz, 2 H), 7.10–7.22 (m, 2 H), 7.52–7.53 (m, 2 H), 8.02 (d, *J* = 8.6 Hz, 2 H), 10.07 (s, 1 H), 12.65 (s, 1 H) ppm; ^{13}C NMR (DMSO-d_6, 250 MHz): δ = 115.7, 121.0, 121.6, 128.1, 151.8, 159.1 ppm.

4-(1*H*-benzimidazol-2-yl)benzonitrile (5h)

Colorless solid; mp 262-265 °C; IR (KBr); υ(cm^{-1}): 1612 (C=N); ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 7.22–7.24 (m, 2 H), 7.50–7.70 (m, 2 H) 7.97 (d, *J* = 8.3 Hz, 2 H), 8.31 (d, *J* = 8.3 Hz,

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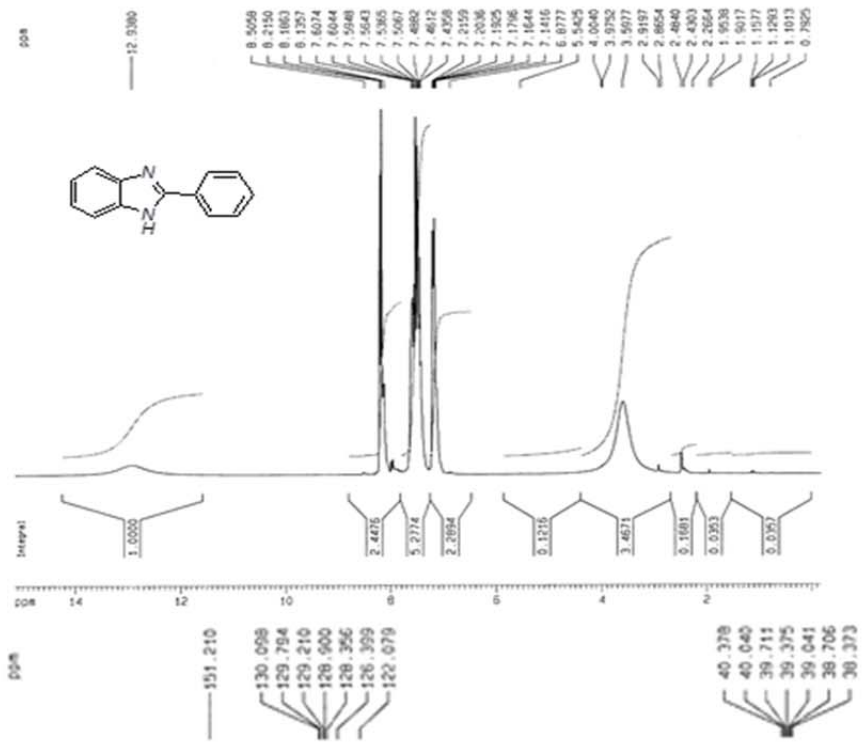
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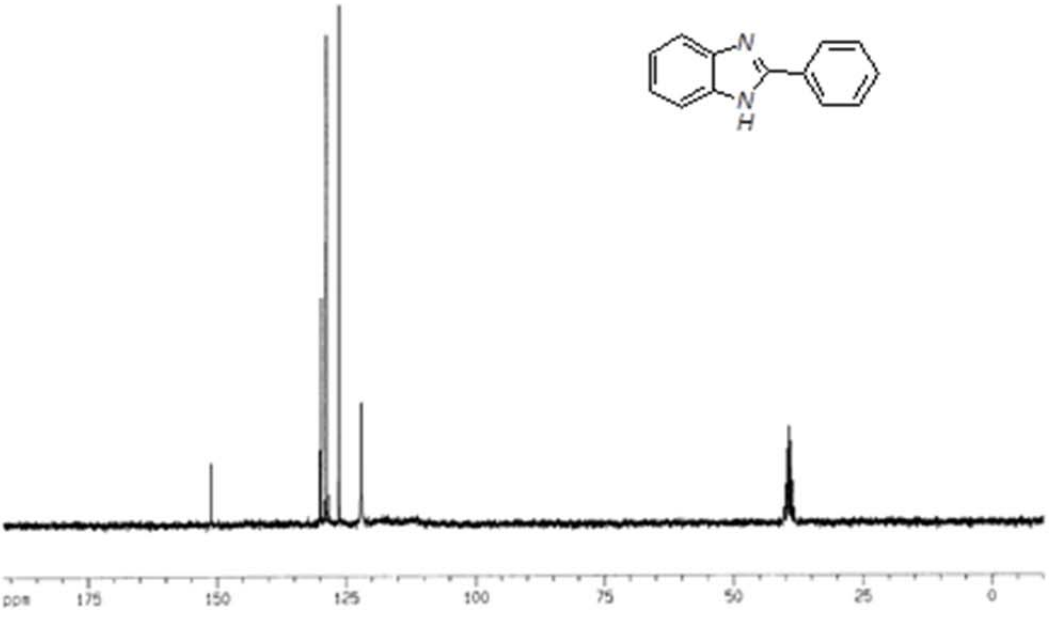
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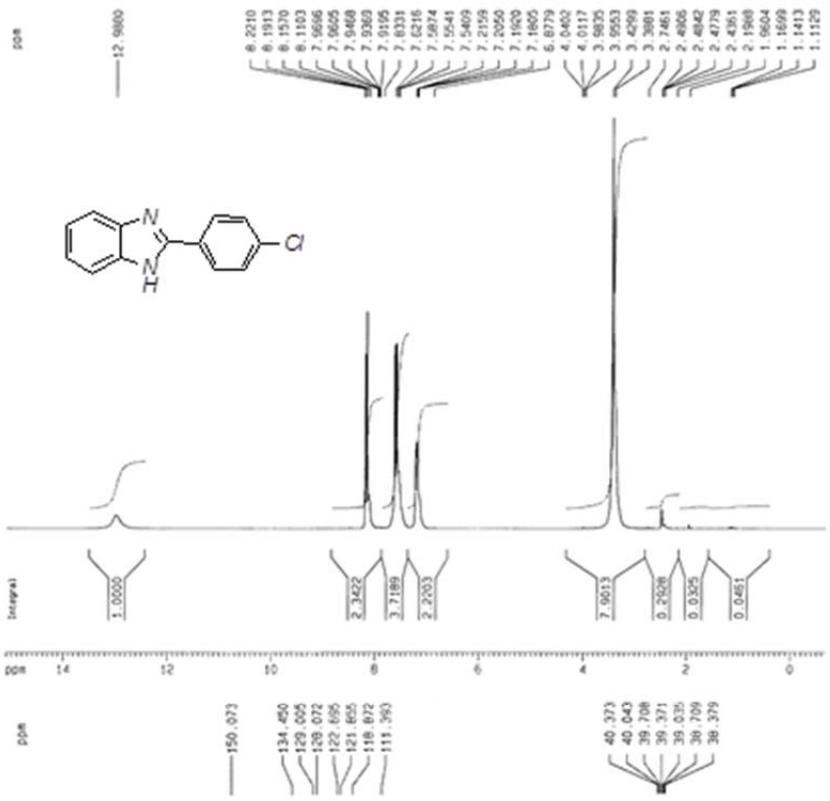
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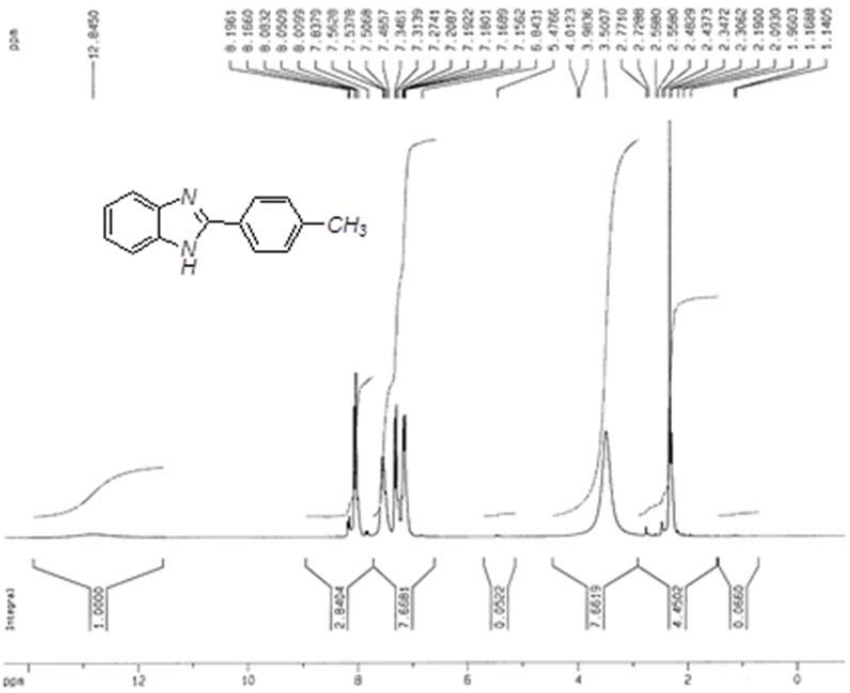
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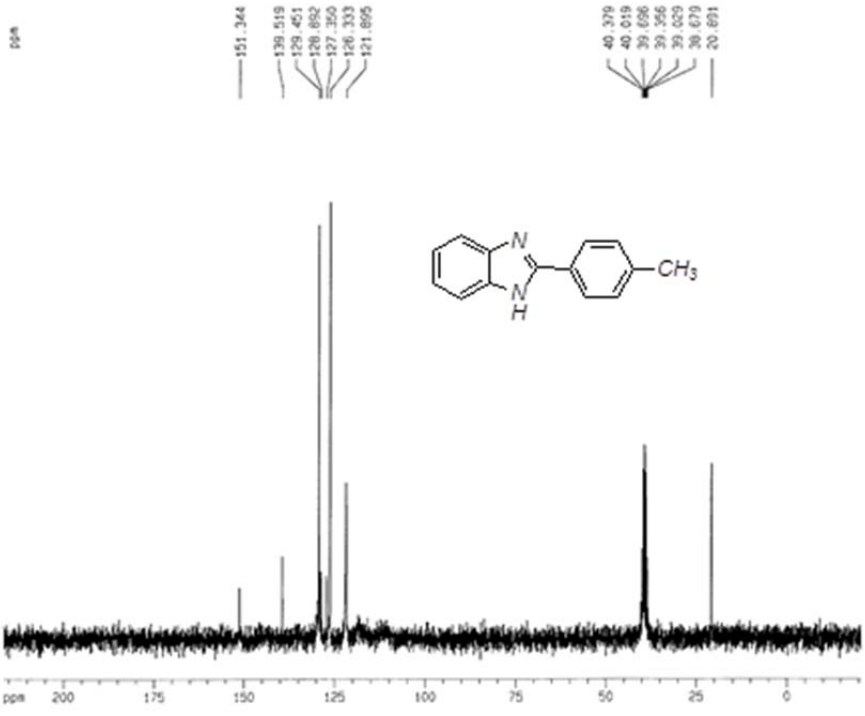
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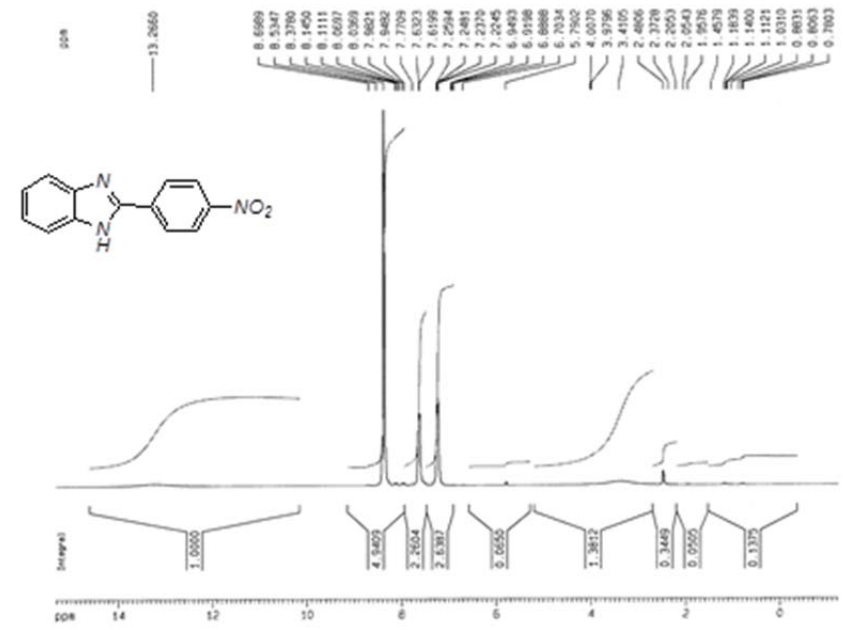
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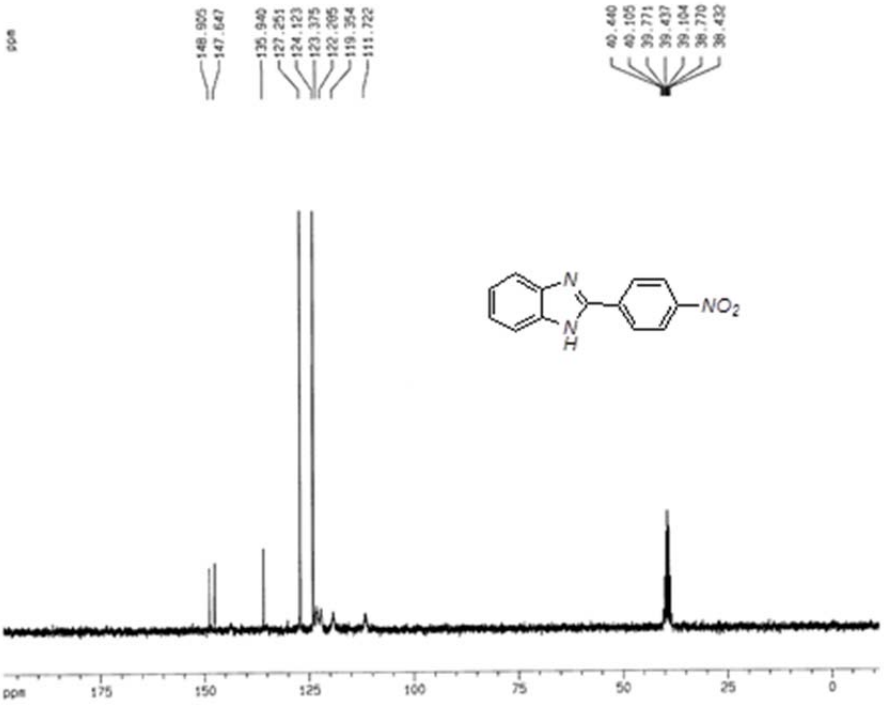
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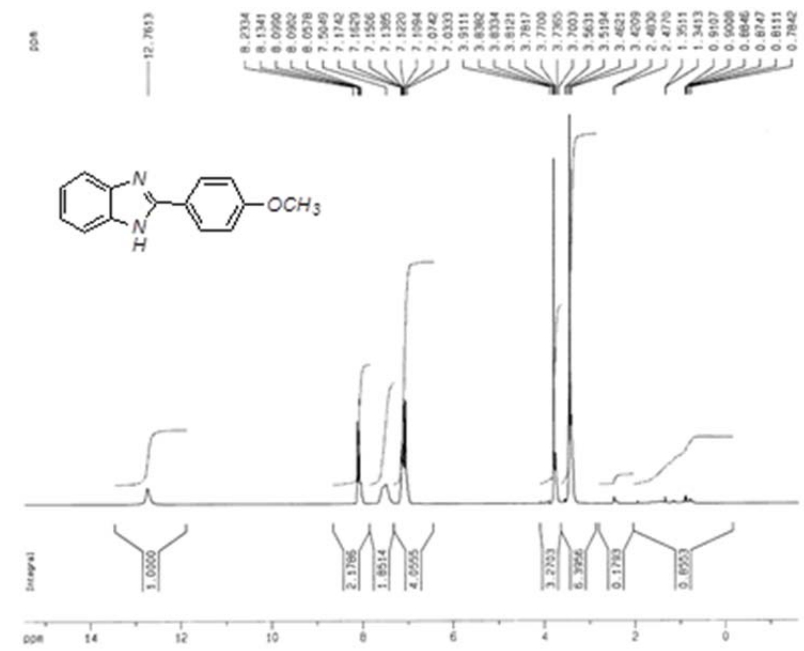
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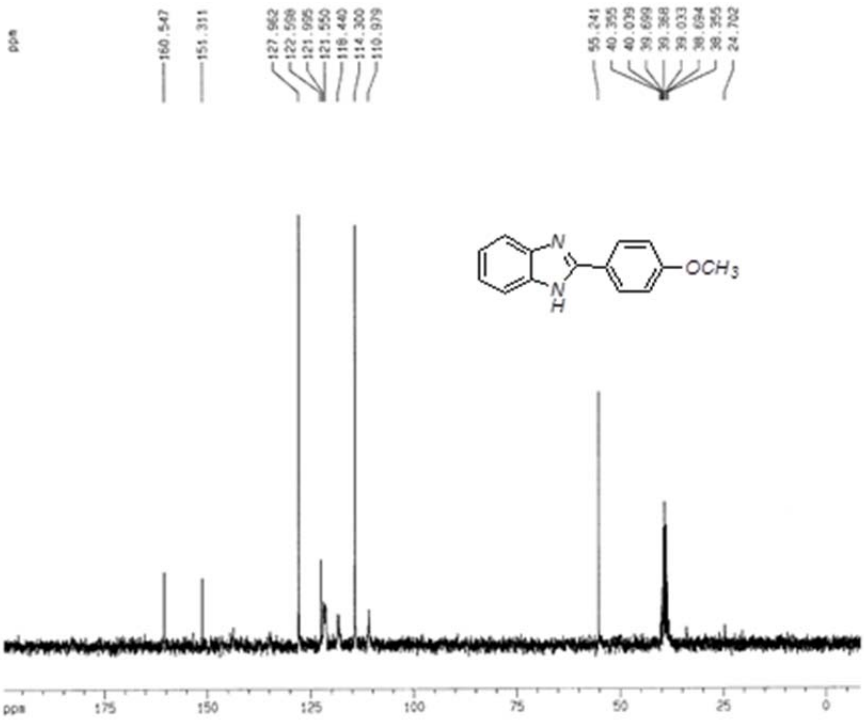
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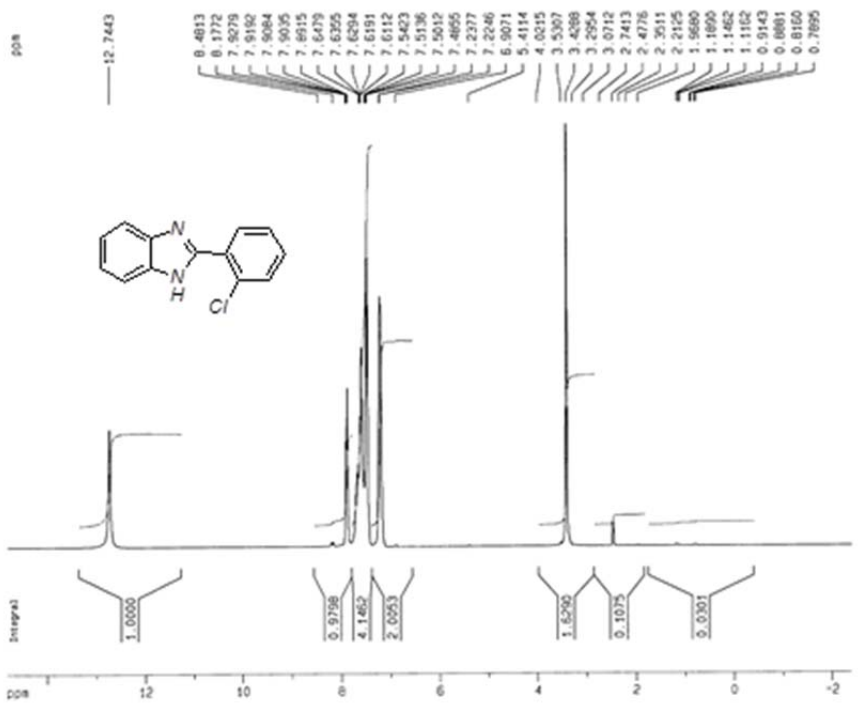
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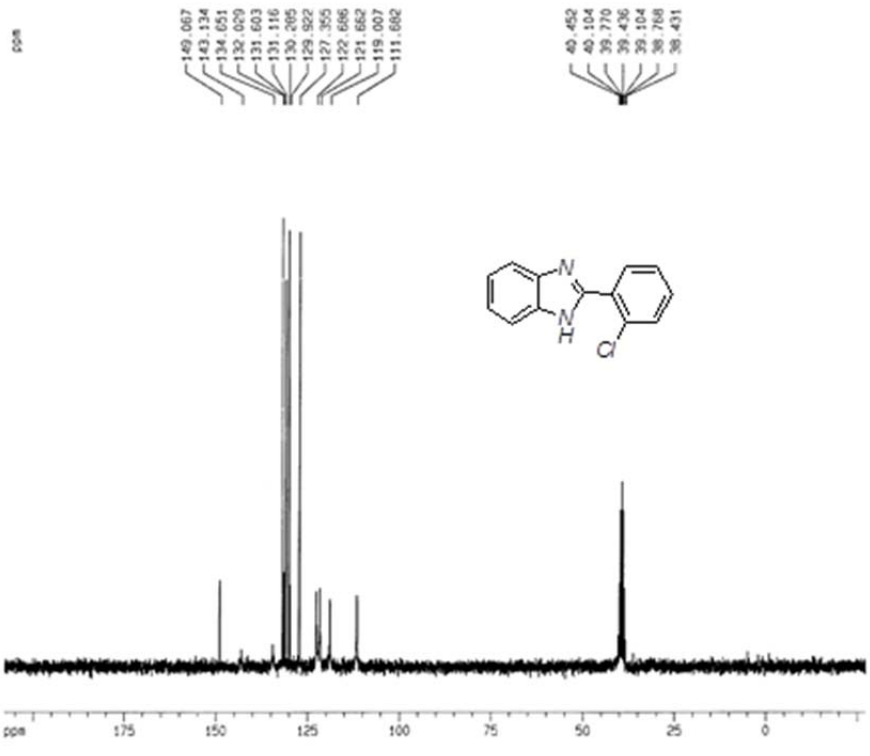
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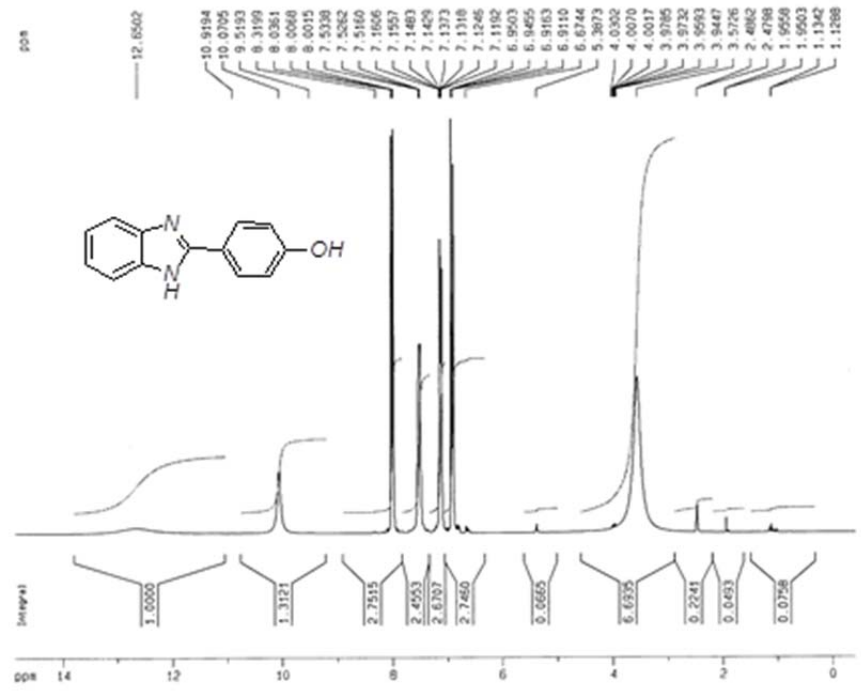
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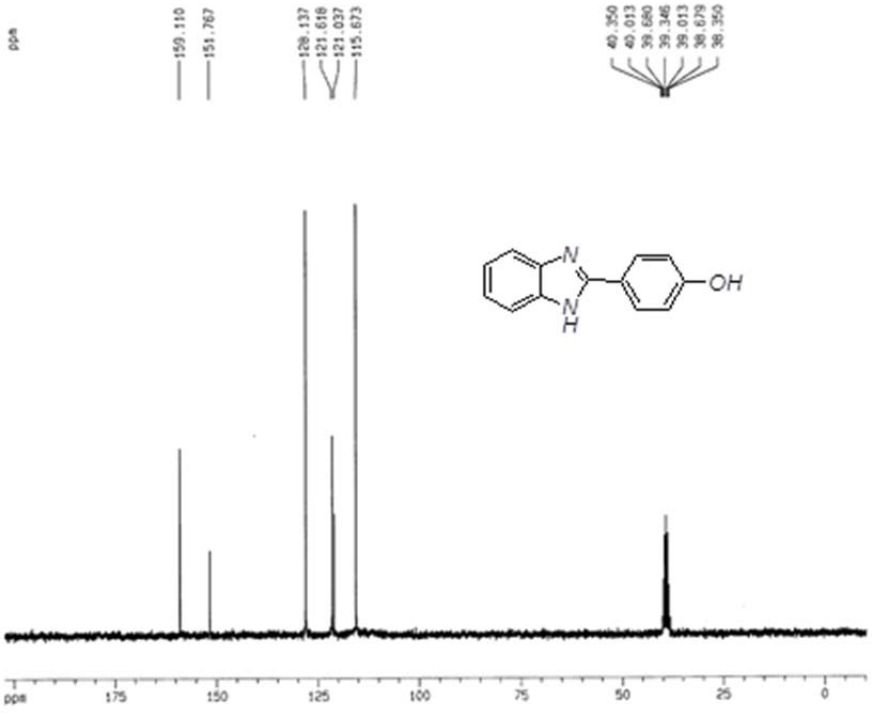
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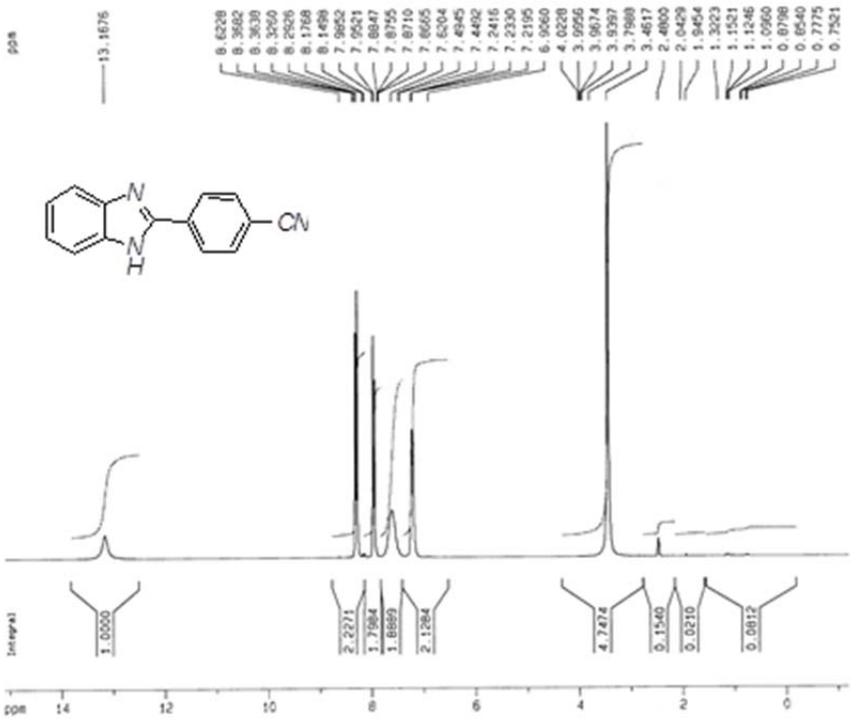
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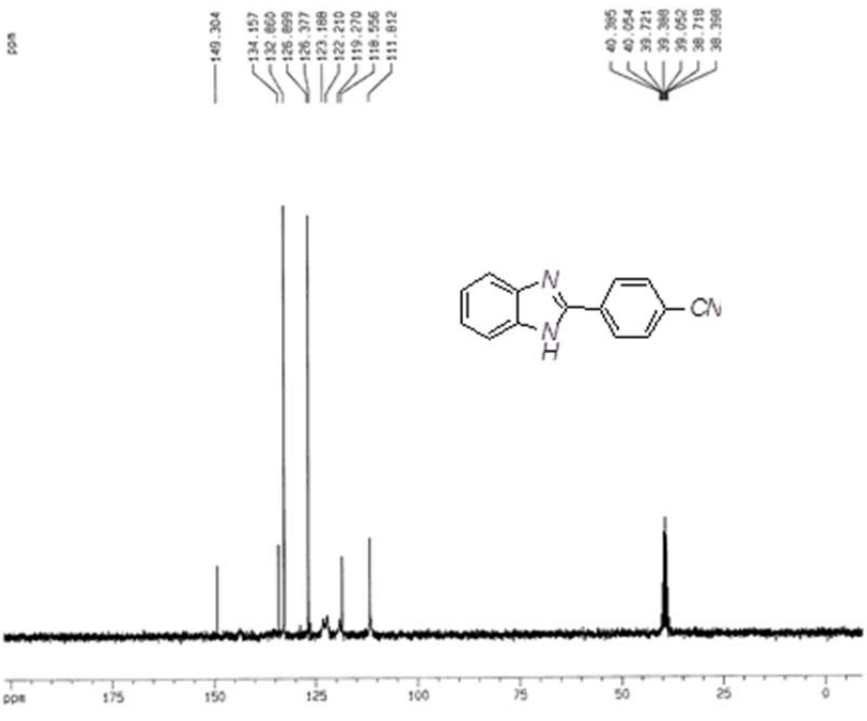
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