Supporting Information

An efficient copper-mediated aerobic oxidative Synthesis of Benzimidazo Fused quinazolines

Byanju Rai^a, Promod Kumar^a and Atul Kumar*^{a,b}

^aMedicinal and Process Chemistry Division, CSIR-Central Drug Research Institute(CDRI),Lucknow, 226031, India

^bAcademy of Scientific & Innovative Research (AcSIR), New Delhi, India.

E-mail: dratulsax@gmail.com; atul_kumar@cdri.res.in, Fax: +91-522-26 234051; Tel: +91-522-26 12411

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1. General Considerations

All the reagents and solvents were purchased from Sigma-Aldrich or Merck chemical Co. and were used directly without any further purification. Organic solvents were concentrated under reduced pressure on a Büchi rotary evaporator. The progress of reaction was checked by thinlayer chromatography. The plates were visualized first with UV illumination followed by iodine. ¹H NMR spectra were recorded at 300 or 400 MHz using Brucker DRX-300, or 400 spectrometer and are reported in parts per million (ppm) on the δ scale relative to TMS as an internal standard. Coupling constants (*J*) reported in Hz. ¹³C NMR spectra were recorded at 50, 75 or 100 MHz. Mass spectra were obtained using JEOL SX-102 (ESI) instrument. Elemental analysis was performed using a Perkin-Elmer autosystem XL analyzer.

2. General procedure for the synthesis of 2-(2-halophenyl)-1H-benzo[d]imidazole derivatives

2-Halobenzoic acid (10.0 mmol) and substituted 1,2-phenylenediamine (10.0 mmol) were added to a flask charged with polyphosphoric acid (PPA) (20.0 g) and the mixture was stirred at 160 °C for 10 h. The reaction solution was poured into crushed ice and neutralized with ice-cold NaHCO₃ aqueous solution till no gas was released. The reaction mass was then extracted with ethyl acetate (2 x 50 ml) and dried over anhydrous magnesium sulfate and concentrated. The crude compound was purified by recrystallisation from hot aq. ethanol to obtain pure desired solid product.

3. General Method for the Preparation of benzimidazo [1,2-c]quinazolines

A 50 flask equipped with a magnetic stirring bar charged with 2-(2-halophenyl)-1Hbenzoimidazole (1.0 mmol), benzaldehyde (1.2 mmol), NaN₃ (2.0 mmol), Cu-powder (10 mol%), L-proline (20 mol%), and Cs₂CO₃(1.0 mmol) were taken in 4.0 mL of DMSO. The reaction mixture was heated to 80 °C for 12 h under air atmosphere. After cooling, the mixture was poured into the EtOAc (50.0 mL), washed with brine (25.0 mL) and water (2 × 25.0 mL), dried over MgSO₄, and passed through a Celite. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography.

Table 1. Optimization of reaction conditions for the syn-thesis of Benzimidazo [1,2-c]quinazoline

| | Br NaN ₃ + | | | | | |
|-------|-----------------------|--------|---------------------------------|-----------------------|--------------------|--|
| | 1a | 2a | 3a | 4a | | |
| Entry | Catalyst | Ligand | Base | Solvent | Yield ^b | |
| 1 | CuI | А | Cs_2CO_3 | DMSO | 70 | |
| 2 | CuBr | А | Cs_2CO_3 | DMSO | 64 | |
| 3 | CuCl | А | Cs_2CO_3 | DMSO | 60 | |
| 4 | $Cu(OAc)_2$ | А | Cs_2CO_3 | DMSO | 40 | |
| 5 | - | А | Cs_2CO_3 | DMSO | 0 | |
| 6 | Cu powder | Α | Cs ₂ CO ₃ | DMSO | 89 | |
| 7 | Cu powder | В | Cs_2CO_3 | DMSO | 55 | |
| 8 | Cu powder | С | Cs_2CO_3 | DMSO | 50 | |
| 9 | Cu powder | D | Cs_2CO_3 | DMSO | 35 | |
| 10 | Cu powder | Е | Cs_2CO_3 | DMSO | 58 | |
| 11 | Cu powder | А | Cs_2CO_3 | DMF | 76 | |
| 12 | Cu powder | А | K_2CO_3 | DMSO | 40 | |
| 13 | Cu powder | А | K_3PO_4 | DMSO | 50 | |
| 14 | Cu powder | А | Cs_2CO_3 | CH ₃ CN | 44 | |
| 15 | Cu Powder | А | Cs_2CO_3 | DMSO: $CH_2Cl_2(1:3)$ | 16 | |
| 16. | Cu powder | А | Cs_2CO_3 | $DMSO:CH_2Cl_2(3:1)$ | 64 | |

^aReaction conditions:2-(2-bromophenyl)-1H-benzo[d]imidazole (1.0 mmol), Benzaldehyde (1.2 mmol), Sodium azide (2.0 mmol), Cu catalyst (10 mol%), Ligand (20 mol%), and Base (1.0 mmol) in solvents (4-5 mL), at 80 °C for 12hr. ^bIsolated yield



Ligands Screened

4. Characterization data for synthesized compounds

6-phenylbenzo[4,5]imidazo[1,2-c]quinazoline(4a)^{1,2}

Physical state: White solid; Yield 89%; mp 166-168 °C; ¹H NMR (400 MHz, CDCl₃) $\delta_{\rm H}$: 8.71 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.68 (t, J = 7.2 Hz, 1H), 7.64 (d, J = 1.6 Hz, 2H), 7.56-7.50 (m, 3H), 7.44 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.64 (d, J = 8.3 Hz, 1H); ¹³C NMR (75 MHz, CDCl3) $\delta_{\rm C}$: 148.5, 148.0, 144.4, 142.4, 134.3, 131.9, 131.0, 129.3, 129.2, 128.4, 128.3, 128.2, 125.6, 124.2, 122.6, 120.0, 118.4, 114.4; Molecular formula- C₂₀H₁₃N₃; ESI-MS (m/z): 296 (M+H)+; Analysis calculated for C₂₀H₁₃N₃: C 81.34, H 4.44, N 14.23, Found: C 81.30, H 4.45, N 14.25.

4-(benzo[4,5]imidazo[2,1-a]isoquinolin-6-yl)-N,N-dimethylaniline (4b)

Physical state: White solid; Yield 88%; mp 172-174 °C; ¹H NMR (400 MHz, DMSO-d₆) $\delta_{\rm H}$: 8.66-8.64 (m, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.71-7.67 (m, 1H), 7.60-7.56 (m, 3H), 7.41-7.37 (m, 1H), 7.11-7.06 (m, 1H), 6.98 (d, J = 8.4Hz, 1H), 6.80 (d, J = 8.8 Hz, 2H), 3.04 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm c}$: 152.4, 149.4, 148.6, 144.4, 142.8, 131.7, 129.7, 128.0, 127.6, 125.4, 124.1, 122.2, 121.28, 119.8, 118.1, 115.0, 111.8, 40.3; Molecular formula- C₂₂H₁₈N₄; ESI-MS (m/z): 339 (M+H)⁺; Analysis calculated for C₂₂H₁₈N₄: C 78.08, H 5.36, N 16.56, Found: C 78.05, H 5.42, N 16.58.

2,4-dichlorophenyl)benzo[4,5]imidazo[2,1-a]isoquinoline(4c)

Physical state: White solid; Yield 75%; mp > 250 °C; ¹H NMR (400 MHz, CDCl₃) $\delta_{\rm H}$: 8.71 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.78-7.74 (m, 1H), 7.70-7.63 (m, 2H), 7.57-7.51 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 8.3 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm c}$: 147.5, 144.9, 144.3, 142.1, 137.8, 134.5, 132.2, 132.0, 131.3, 130.3, 128.9, 128.8, 128.4, 128.4, 125.9, 124.3, 123.4, 120.2, 118.7, 112.8; Molecular formula-C₂₁H₁₁Cl₂N₂; ESI-MS (m/z): 364 (M+H)⁺; Analysis calculated for C₂₀H₁₁Cl₂N₃: C 65.95, H 3.04, N 11.54, Found: C 65.91, H 3.05, N 11.58.

6-(naphthalen-1-yl)benzo[4,5]imidazo[1,2-c]quinazoline (4d)

Physical state: White solid; Yield 94%; mp > 250 °C; ¹H NMR (400 MHz, CDCl₃ d₆) $\delta_{\rm H}$: 8.84 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 8.05 (t, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.87-7.72 (m, 4H), 7.55 (t, J = 7.2 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 6.3 Hz, 2H), 6.87 (t, J = 7.6 Hz, 1H), 5.93 (d, J = 8.4 Hz, 1H);¹³C NMR (75 MHz, CDCl₃) δ_c : 147.8, 147.6, 144.3, 142.5, 133.7, 131.9, 131.6, 131.1, 130.7, 129.0, 128.7, 128.5, 128.4, 127.8, 127.0, 126.9, 125.7, 125.6, 124.4, 124.3, 122.9, 119.8, 118.6, 113.9; Molecular formula- C₂₄H₁₅N₃; ESI-MS (m/z): 346 (M+H)⁺; Analysis calculated for C₂₄H₁₅N₃: C 83.46, H 4.38, N 12.17, Found: C 83.43, H 4.40, N 12.18.

4-nitrophenyl)benzo[4,5]imidazo[1,2-c]quinazoline (4e)

Physical state: Yellow solid; 65%; mp 240-242 °C; ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$: 8.80 (d, J = 7.6 Hz, 1H), 8.56 (d, J = 7.5 Hz, 2H), 8.03 (t, J = 7.2 Hz, 4H), 7.86 (t, J = 7.3 Hz, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 8.1Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H);¹³C NMR (75 MHz, CDCl₃ + DMSO-d₆) $\delta_{\rm c}$: 149.2, 144.2, 140.2, 132.4, 130.6, 129.0, 128.4, 125.9, 124.6, 124.2, 123.1, 120.0, 118.6, 114.2; Molecular formula- C₂₀H₁₂N₄O₂; ESI-MS (m/z): 341 (M+H)⁺; Analysis calculated for C₂₀H₁₂N₄O₂: C 70.58, H 3.55, N 16.46, Found: C 70.59, H 3.50, N 16.50.

6-(2,5-dimethoxyphenyl)benzo[4,5]imidazo[1,2-c]quinazoline (4f)

Physical state: White solid; Yield 82%; mp > 250 °C; ¹H NMR (300 MHz, DMSO-d₆) $\delta_{\rm H}$: 8.66 (d, *J* = 7.9 Hz, 1H), 8.00-7.89 (m, 3H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.3Hz, 1H), 7.31 (s, 3H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 8.3Hz, 1H), 3.80 (s, 3H), 3.55 (s, 3H); ¹³C NMR (75 MHz, DMSO-d₆) $\delta_{\rm c}$: 154.0, 151.4, 147.3, 146.5, 144.2, 142.5, 132.5, 129.4, 128.9, 128.4, 125.9, 124.2, 124.0, 123.3, 120.0, 118.5, 117.9, 115.7, 113.5, 56.5, 56.2; Molecular formula- C₂₂H₁₇N₃O₂; ESI-MS (m/z): 356 (M+H)⁺; Analysis calculated for C₂₂H₁₇N₃O₂: C 74.35, H 4.82, N 11.82, Found: C 74.38, H 4.83, N 11.85.

6-(3,5-dimethoxyphenyl)benzo[4,5]imidazo[1,2-c]quinazoline (4g)

Physical state: Light yellow solid; Yield 85%; mp > 250 °C; ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$: 8.76 (d, J = 7.9 Hz, 1H), 8.01 (t, J = 7.7 Hz, 2H), 7.81 (t, J = 7.3Hz, 1H), 7.72 (t, J = 7.7 Hz, 1H), 7.49 (t, J = 7.6Hz, 1H), 7.18 (t, J = 7.9 Hz, 1H), 6.85 (s, 2H), 6.76 (d, J = 7.8 Hz, 2H), 3.85 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm c}$: 161.6, 148.2, 147.9, 144.4, 142.3, 135.8, 131.9, 129.2, 128.3, 125.7, 124.2, 122.8, 119.9, 118.5, 114.6, 106.1, 103.4, 55.7; Molecular formula- $C_{22}H_{17}N_3O_2$; ESI-MS (m/z): 356 (M+H)⁺; Analysis calculated for $C_{22}H_{17}N_3O_2$: C 74.35, H 4.82, N 11.82, Found: C 74.30, H 4.84, N 11.85.

6-(2,4,5-trimethoxyphenyl)benzo[4,5]imidazo[1,2-c]quinazoline(4h)

Physical state: Yellow solid; Yield 80%; mp > 250 °C; ¹H NMR (300 MHz, DMSO-d₆) $\delta_{\rm H}$: 8.65 (d, *J* = 7.6 Hz, 1H), 7.99-7.87 (m, 3H),7.79 (t, *J* = 4.4Hz, 1H), 7.50 (t, *J* = 7.5Hz, 1H), 7.25 (t, *J* = 7.0Hz, 3H), 6.57 (d, *J* = 8.4Hz, 1H), 3.85 (s, 3H), 3.79(s, 6H); ¹³C NMR (75 MHz, DMSO-d₆) $\delta_{\rm c}$: 158.6, 153.3, 152.5, 149.1, 147.2, 144.4, 137.2, 134.6, 134.3, 133.5, 133.0, 130.6, 129.0, 127.8, 124.7, 123.3, 119.4, 111.2, 65.7, 61.5; Molecular formula-C₂₃H₁₉N₃O₃; ESI-MS (m/z): 386(M+H)⁺; Analysis calculated for C₂₃H₁₉N₃O₃: C 71.67, H 4.97, N 10.90, Found: C 71.69, H 5.00, N 10.85.

4-(benzo[4,5]imidazo[1,2-c]quinazolin-6-yl)phenol (4i)

Physical state: white solid; Yield 79%; mp 174-176 °C; ¹H NMR (400 MHz, DMSO-d₆) $\delta_{\rm H}$: 10.17 (s, 1H), 8.63-8.61 (m, 1H), 7.95-7.92 (m, 2H), 7.89-7.85 (m, 1H), 7.77-7.73 (m, 1H), 7.65-7.62 (m, 2H), 7.49-7.45 (m, 1H), 7.22-7.18 (m, 1H), 7.06-7.03 (m, 2H), 6.69 (d, J =8.4Hz, 1H); ¹³C NMR (75 MHz, DMSO-d₆) $\delta_{\rm c}$: 160.0, 149.2, 148.0, 144.4, 142.6, 132.3, 130.6, 129.7, 128.4, 128.2, 125.7, 125.3, 124.2, 122.7, 120.0, 118.4, 116.1, 114.7.; Molecular formula- C₂₀H₁₃N₃O; ESI-MS (m/z): 312(M+H)⁺; Analysis calculated for C₂₀H₁₃N₃O: C 77.16, H 4.21, N 13.50, Found: C 77.20, H 4.23, N 13.45.

6-(3,4,5-trimethoxyphenyl)benzo[4,5]imidazo[1,2-c]quinazoline (4j)

Physical state: White solid; Yield 81%; mp >250 °C; ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$: 8.78 (d, *J* = 7.0 Hz, 1H), 8.03 (d, *J* = 3.0 Hz, 2H),7.84 (t, *J* = 3.6 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.21(t, *J* = 4.9 Hz, 1H), 6.98 (s, 2H),6.81 (d, *J* = 8.3 Hz, 1H), 4.62 (s, 3H), 3.91 (s, 6H);¹³C NMR (100 MHz, DMSO-d₆) $\delta_{\rm c}$: 153.9, 148.6, 142.5, 132.4, 129.9, 129.6, 128.7, 128.3, 125.8, 124.2, 123.0, 120.0, 114.7, 106.5, 60.9, 56.7; Molecular formula-C₂₃H₁₉N₃O₃; ESI-MS (m/z): 386 (M+H)⁺; Analysis calculated for C₂₃H₁₉N₃O₃: C 71.67, H 4.97, N 10.90, Found: C 71.69, H 4.98, N 10.92.

9-nitro-6-(2,4,5-trimethoxyphenyl)benzo[4,5]imidazo[1,2-c]quinazoline(4k)

Physical state: White solid; Yield 65%; mp > 250 °C; ¹H NMR (400 MHz, DMSO-d₆) $\delta_{\rm H}$: 8.74(d, J = 2.3 Hz, 1H), 8.68-8.66 (m, 1H), 8.15-8.13 (m, 1H),8.01-7.93 (m, 2H), 7.85-7.81(m,1H), 7.23 (s, 2H), 6.75 (d, J = 9.7 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 6H);¹³C NMR (100 MHz, DMSO-d₆) $\delta_{\rm c}$: 154.0, 150.9, 148.3, 145.3, 143.9, 142.6, 140.0, 133.7, 133.4, 129.3, 129.2, 128.5, 124.6, 118.0, 115.4, 106.6, 60.9, 56.1.; Molecular formula- C₂₃H₁₈N₄O₅; ESI-MS (m/z): 431 (M+H)⁺;Analysis calculated for C₂₃H₁₈N₄O₅: C 64.18, H 4.22, N 13.02, Found: C 64.19, H 4.21, N 13.05.

4-(benzo[4,5]imidazo[1,2-c]quinazolin-6-yl)benzonitrile (4l)

Physical state: White solid; 60%, mp 230-232 °C; ¹H NMR (300 MHz, DMSO-d₆) $\delta_{\rm H}$: 8.39-8.32 (m, 3H), 7.88 (d, J = 7.7Hz, 1H), 7.67 (t, J = 7.4Hz, 2H), 7.56-7.36 (m, 6H); ¹³C NMR (75 MHz, DMSO-d₆) $\delta_{\rm c}$: 147.4, 146.3, 143.3, 136.9, 132.0, 131.4, 130.4, 128.4, 124.7, 124.2, 123.4, 123.1, 118.9, 115.6, 114.5, 111.5; Molecular formula-C₂₁H₁₂N₄; ESI-MS (m/z): 321 (M+H); Analysis calculated for C₂₁H₁₂N₄: C 78.73, H 3.78, N 17.49, Found: C 78.76, H 3.77, N 17.47.

9-nitro-6-(3,4,5-trimethoxyphenyl)benzo[4,5]imidazo[1,2-c]quinazoline(4m)

Physical state: White solid; Yield 61%; mp >250 °C; ¹H NMR (400 MHz, CDCl₃) $\delta_{\rm H}$: 8.32(d, J = 7.2 Hz, 1H), 8.31-8.07 (m, 1H), 7.76-7.71 (m, 1H), 7.46-7.32 (m, 4H), 6.54 (s, 2H), 3.75 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm c}$: 153.3, 152.7, 148.8, 143.7, 143.1, 137.3, 134.2, 133.2, 131.6, 128.1, 128.0, 126.4, 119.2, 118.5, 115.9, 111.7, 109.0, 105.0, 60.9, 56.1; Molecular formula- C₂₃H₁₈N₄O₅; ESI-MS (m/z): 431 (M+H)⁺;Analysis calculated for C₂₃H₁₈N₄O₅: C 64.18, H 4.22, N 13.02, Found: C 64.19, H 4.24, N 13.06.

6-(4-chlorophenyl)benzo[4,5]imidazo[1,2-c]quinazoline(4n)

Physical state: White solid; Yield 79%; mp 234-236°C; ¹H NMR (300 MHz, CDCl₃) δ_{H} : 8.68 (d, *J* = 8.2 Hz, 1H), 7.95-7.91 (m, 2H), 7.74 (t, *J* = 6.9 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 3H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 6.9 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ_{c} : 142.3, 137.3, 132.0, 130.0, 129.6, 129.0, 128.5, 128.2, 125.8, 124.3, 122.7, 120.2, 118.4, 114.2; Molecular formula-C₂₀H₁₂ClN₃;ESI-MS (m/z): 330 (M+H)⁺;Analysis calculated for C₂₀H₁₂ClN₃: C 72.84, H 3.67, N 12.74, Found: C 72.80, H 3.68, N 12.77.

9-nitro-6-phenylbenzo[4,5]imidazo[1,2-c]quinazoline (40)

Physical state: White solid; Yield 74%; mp 242-244 °C; ¹H NMR (400 MHz, CDCl₃) δ_{H} : 8.84 (d, J = 2.0 Hz, 1H), 8.77 (d, J = 7.8 Hz, 1H), 8.05-7.99 (m, 2H), 7.88 (t, J = 8.2 Hz, 1H), 7.79-7.68 (m, 6H), 6.68 (d, J = 9.2 Hz, 1H); ¹³C NMR (75 MHz, DMSO-d₆) δ_{c} : 153.3, 152.7, 148.8, 143.7, 143.1, 137.3, 134.2, 133.2, 131.6, 128.1, 128.0, 126.4, 119.2, 118.5, 115.9, 111.6, 109.0, 105.0, 60.9, 56.1; Molecular formula- C₂₀H₁₂N₄O₂; ESI-MS (m/z): 341 (M+H)⁺; Analysis calculated for C_{20s}H₁₂N₄O₂: C 70.58, H 3.55, N 16.46, Found: C 70.54, H 3.56, N 16.49.

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Figure 3: ¹H NMR of compound (4a)



Figure 4: ¹³ C NMR of compound (4a)



Figure 1: ¹H NMR of compound (4b)



Figure 2: ¹³C NMR of compound (4b)



Figure 5: ¹H NMR of compound (4c)



Figure 6: ¹³ C NMR of compound (4c)



Figure 7: ¹H NMR of compound (4d)



Figure 8: ¹³C NMR of compound (4d)



Figure 9: ¹H NMR of compound (4e)



Figure 10: ¹³ C NMR of compound (4e)



Figure 11: ¹H NMR of compound (4f)



Figure 12: ¹³ C NMR of compound (4f)



Figure 14: ¹³ C NMR of compound (4g)



Figure 15: ¹H NMR of compound (4h)



Figure 16: ¹³C NMR of compound (4h)



Figure 17: ¹H NMR of compound (4i)



Figure 18: ¹³C NMR of compound (4i)







Figure 20: ¹³ C NMR of compound (4j)



Figure 21: ¹H NMR of compound (4k)



Figure 22: ¹³ C NMR of compound (4k)



Figure 23: ¹H NMR of compound (4l)



Figure 24: ¹³C NMR of compound (4l)



Figure 25: ¹H NMR of compound (4m)



Figure 26: ¹³C NMR of compound (4m)







Figure 28: ¹³C NMR of compound (4n)



Figure 29 ¹H NMR of compound (40)



Figure 30: ¹³C NMR of compound (40)