Cu(OTf)$_2$ loaded protonated trititanate nanotubes catalyzed reaction: A facile method to furo[2,3-\textit{b}]quinoxalines synthesis

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1. General experimental details

Titanium dioxide (anatase 99%, TiO$_2$-LAB) was purchased from Merck, India. Analytical reagent (A.R) grade chemicals of sodium hydroxide pellets (97%), potassium iodide (98%), copper sulphate (98%), hydrochloric acid (37%), and ethanol (99.9) were supplied by Merck, India and used without any further purification. De-ionized water used for catalysts synthesis and washing process. All the solvents, α-phenylenediamines, ethyl glyoxalate and terminal alkynes were purchased from the Merck, Aldrich, Alfa-æsar chemical companies and used without further purification.

Powder X-ray diffraction (PXRD) data were recorded using a D8 ADVANCE X-ray diffractometer (Bruker), with $\lambda_{CuK\alpha}=1.54056$ Å. Transmission electron microscopy (TEM) measurements were carried out by using a FEI Tecnai F20ST electron microscope operated at 200 keV. For the TEM measurements, all samples were sonicated in ethanol and the resulting dispersions were transferred onto holey carbon coated copper grids (200 mesh). Specific surface area (SSA) and average pore diameter were calculated from N$_2$-adsorption desorption isotherms recorded at 77 K using a surface area analyzer, Micromeritics ASAP 2020. Prior to measurements, all samples were outgassed at 150 °C under vacuum ($10^{-3}$ mbar) for 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the SSA, while the pore size distributions were derived from the desorption branches of the isotherms based on the Barrett-Joyner-Halenda (BJH) model.

Melting points of the synthesized compounds were recorded on Guna apparatus and are uncorrected. Infrared spectra of the title compounds were recorded on Bruker Alpha-Eco ATR-FTIR (Attenuated total reflection-Fourier Transform Infrared) interferometer with single reflection sampling module equipped with ZnSe crystal. The $^1$H and $^{13}$C-NMR were recorded in CDCl$_3$ and DMSO using Bruker DRX (400 MHz for $^1$H and 100 MHz for $^{13}$C) and Bruker DRX (500 MHz for $^1$H and 125 MHz for $^{13}$C) spectrometers using TMS as internal standard. Chemical shifts (δ) are expressed as ppm. Multiplicities in the $^1$H-NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet; coupling constants are reported in Hz. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV.

2. Characterization data of furo[2,3-b]quinoxalines

2-Phenylfuro[2,3-b]quinoxaline (4)

Pale yellow solid; mp 160-164 °C; IR, vmax (ZnSe)/cm$^{-1}$: 3067 (Ar-C-H), 1609 (C=C), 1435 (C=N), 1209 (C-O-C); $^1$H NMR (400 MHz, CDCl$_3$, δ ppm): 8.19 - 8.16 (m, 1H, Ar-H), 8.13 - 8.10 (m, 1H, Ar-H), 8.04 – 8.02 (m, 2H, Ar-H), 7.76 - 7.72 (m, 2H, Ar-H), 7.56 - 7.51 (m, 3H, Ar-H), 7.29 (s, 1H, Ar-H); $^{13}$C NMR (100 MHz, CDCl$_3$, δ ppm): 164.59 (Ar-C), 162.86 (Ar-C), 160.88 (Ar-C), 154.16 (Ar-C), 145.24 (Ar-C), 142.97 (Ar-C), 135.68 (Ar-C), 131.51 (Ar-C), 130.41 (Ar-C), 129.23 (Ar-C), 128.34 (Ar-C), 126.27 (Ar-C), 119.03 (Ar-C), 112.44 (Ar-C), 100.61 (Ar-C); MS (ESI): 247.0835
7-Methyl-2-phenylfuro[2,3-b]quinoxaline (5)

Green-yellow solid; mp 182-185 °C; IR, νmax (ZnSe)/сm−1: 3059 (Ar-C-H), 2875 (ali-C-H), 1620 (C=C), 1407 (C=N), 1250 (C-O-C); 1H NMR (400 MHz, CDCl3, δ ppm): 8.07-7.99 (m, 3H, Ar-H), 7.94 (d, J = 24.4 Hz, A-H), 7.59 - 7.51 (m, 4H, Ar-H), 7.28 (d, J = 8.4 Hz, 1H, Ar-H), 2.62 (s, 3H, Ar-CH3); 13C NMR (100 MHz, CDCl3, δ ppm): 164.33 (Ar-C), 154.41 (Ar-C), 144.80 (Ar-C), 142.24 (Ar-C), 138.70 (Ar-C), 129.90 (Ar-C), 128.71 (Ar-C), 128.60 (Ar-C), 126.15 (Ar-C), 99.97 (Ar-C), 21.66 (Ar-CH3); HRMS: Anal. Calcd for C17H13N2O ([M+H]+): 261.1088; Found: 261.1022.

6,7-Dimethyl-2-phenylfuro[2,3-b]quinoxaline (6)

Greenish yellow solid; mp 201-204 °C; IR, νmax (ZnSe)/сm−1: 3010 (Ar-C-H), 2859 (ali-C-H), 1620 (C=C), 1427 (C=N), 135.03 (Ar-C), 132.75 (Ar-C), 132.08 (Ar-C), 129.84 (Ar-C), 128.94 (Ar-C), 117.77 (Ar-C), 113.33 (Ar-C), 111.02 (Ar-C), 108.71 (Ar-C), 22.99 (Ar-CH3), 20.73 (Ar-CH3); MS (ESI): 275.1148 ([M+H]+), Anal. Calcd for C18H15N2O: C, 78.52; H, 5.49; N, 10.17%; Found: C, 78.55; H, 5.55; N, 10.21%.

7-Methoxy-2-phenylfuro[2,3-b]quinoxaline (7)

Pale yellow solid; mp 193-196 °C; IR, νmax (ZnSe)/сm−1: 2998 (Ar-C-H), 2901 (ali-C-H), 1620 (C=C), 155.83 (Ar-C), 145.71 (Ar-C), 138.12 (Ar-C), 134.63 (Ar-C), 129.12 (Ar-C), 111.50 (Ar-C), 56.20 (Ar-OCH3), MS (ESI): 277.0955 ([M+H]+), Anal. Calcd for C17H13N2O2: C, 73.63; H, 4.73; N, 10.10 %; Found: C, 73.59; H, 4.67; N, 10.15%.

7-Chloro-2-phenylfuro[2,3-b]quinoxaline (8)

Greenish yellow solid; mp 191-194 °C; IR, νmax (ZnSe)/сm−1: 809 – 8.07 (m, 1H, Ar-H), 8.04 – 8.02 (m, 1H,
Ar-H), 7.84 (d, J = 6.4 Hz, 2H, Ar-H), 7.67 – 7.64 (m, 2H, Ar-H), 7.25 (d, J = 6.0 Hz, 2H, Ar-H) 7.13 (s, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 164.33 (Ar-C), 156.83 (Ar-C), 146.00 (Ar-C), 141.26 (Ar-C), 135.31 (Ar-C), 133.61 (Ar-C), 120.58 (Ar-C), 118.25 (Ar-C), 112.25 (Ar-C), 111.58 (Ar-C), 108.78 (Ar-C), 98.66 (Ar-C); MS (ESI): 281.0453 ([M+H]+), Anal. Calcd for C₁₆H₁₀N₂OCl: C, 68.21; H, 3.58; N, 9.94%; Found: C, 68.15; H, 3.50; N, 9.89%.

6,7-Dichloro-2-phenylfuro[2,3-b]quinoxaline (9)
Pale white solid; mp 240-241 °C; IR νmax (ZnSe)/cm⁻¹: 3005 (Ar-C-H), 1600 (C=C), 1420 (C=N), 1197 (C-O-C), 756 (C-Cl); ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.07 – 7.82 (m, 4H, Ar-H), 7.58 (d, J = 8.8 Hz, 1H, Ar-H), 7.42 (t, J = 7.2 Hz, 1H, Ar-H) 7.33 – 7.25 (m, 2H, Ar-H); MS (ESI): 315.0067 ([M+H]+), Anal. Calcd for C₁₆H₉N₂OCl₂: C, 60.78; H, 2.87; N, 8.86%; Found: C, 60.83; H, 2.91; N, 8.90%.

7-Fluoro-2-phenylfuro[2,3-b]quinoxaline (10)
Greenish yellow solid; mp 180-183 °C; IR, νmax (ZnSe)/cm⁻¹: 3055 (Ar-C-H), 1629 (C=C), 1423 (C=N), 1205 (C-O-C); ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.19-8.17 (m, 1H, Ar-H), 8.13 – 8.12 (m, 1H, Ar-H), 7.94 (d, J = 6.4 Hz, 2H, Ar-H), 7.77 - 7.74 (m, 2H, Ar-H), 7.35 (d, J = 6.4 Hz, 2H, Ar-H), 7.23 (s, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 161.11 (Ar-C), 151.19 (Ar-C), 139.02 (Ar-C), 135.48 (Ar-C), 126.68 (Ar-C), 125.49 (Ar-C), 125.38 (Ar-C), 125.02 (Ar-C), 122.93 (Ar-C), 122.53 (Ar-C), 96.75 (Ar-C); MS (ESI): 265.0737 ([M+H]+), Anal. Calcd for C₁₆H₁₀FN₂O: C, 72.45; H, 3.80; N, 10.56%; Found: C, 72.47; H, 3.77; N, 10.60%.

2-(m-Tolyl)furo[2,3-b]quinoxaline (13)
Greenish yellow solid; mp 185-187 °C; IR, vmax (ZnSe)/cm⁻¹: 3048 (Ar-C-H), 1423 (C=N), 1197 (C-C), 756 (C-Cl); ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.19 - 8.17 (m, 1H, Ar-H), 8.13 – 8.12 (m, 1H, Ar-H), 7.94 (d, J = 6.4 Hz, 2H, Ar-H), 7.77 - 7.74 (m, 2H, Ar-H), 7.35 (d, J = 6.4 Hz, 2H, Ar-H), 7.23 (s, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 162.66 (Ar-C), 158.27 (Ar-C), 154.19 (Ar-C), 145.27 (Ar-C), 143.00 (Ar-C), 135.70 (Ar-C), 131.53 (Ar-C), 130.44 (Ar-C), 129.25 (Ar-C), 128.36 (Ar-C), 126.30 (Ar-C), 119.05 (Ar-C), 112.46 (Ar-C), 100.63 (Ar-C), 21.66 (Ar-CH₃); HRMS: Anal. Calcd for C₁₇H₁₃N₂O ([M+H]+): 261.1088; Found: 261.1022.

2-(P-Tolyl)furo[2,3-b]quinoxaline (14)
Greenish yellow solid; mp 183-185 °C; IR, vmax (ZnSe)/cm⁻¹: 3010 (Ar-C-H), 1620 (C=C), 1409 (C=N), 1192 (C-O-C); ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.20 (s, 1H, Ar-H), 7.42 (d, J = 5.2 Hz, 2H, Ar-H), 7.32 – 7.28 (m, 3H, Ar-H), 7.17 (d, J = 6.8 Hz, 2H, Ar-H), 7.03 (d, J = 6.8 Hz, 2H, Ar-H), 2.22 (s, 3H, Ar-CH₃); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 161.98 (Ar-C), 160.25 (Ar-C), 158.26 (Ar-C), 151.55 (Ar-C), 143.80 (Ar-C), 141.24 (Ar-C), 137.69 (Ar-C), 129.71 (Ar-C), 127.59 (Ar-C), 127.24 (Ar-C), 125.15 (Ar-C), 124.75 (Ar-C), 98.96 (Ar-C), 20.66 (Ar-CH₃); HRMS: Anal. Calcd for C₁₇H₁₃N₂O ([M+H]⁺): 261.1088; Found: 261.1022.

2-(4-Methoxyphenyl)furo[2,3-b]quinoxaline (15)
Greenish yellow solid; mp 188-191 °C; IR, vmax (ZnSe)/cm⁻¹: 3062 (Ar-C-H), 2897 (ali-C-H), 1609 (C=C), 1435 (C=N), 1059 (-O-CH₃); ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.50 - 7.48 (m, 2H, Ar-H), 7.39 – 7.37 (m, 3H, Ar-H), 7.31 (d, J = 8.8 Hz, 2H, Ar-H), 3.87 (s, 3H, Ar-OCH₃); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 162.26 (Ar-C), 154.69 (Ar-C), 143.53 (Ar-C), 141.54 (Ar-C), 141.22 (Ar-C), 140.59 (Ar-C), 140.19 (Ar-C), 138.30 (Ar-C), 134.29 (Ar-C), 132.20 (Ar-C), 127.54 (Ar-C), 100.52 (Ar-C), 98.86 (Ar-C), 55.28 (Ar-OCH₃); MS (ESI): 277.0937 ([M+H]⁺), Anal. Calcd for C₁₇H₁₃N₂O₂: C, 73.63; H, 4.73; N, 10.10; Found: C, 73.57; H, 4.69; N, 9.99%.

7-Methyl-2-(m-tolyl)furo[2,3-b]quinoxaline (17)
Pale yellow solid; mp 183-186 °C; IR, vmax (ZnSe)/cm⁻¹: 3056 (Ar-C-H), 2865 (C=C), 1435 (C=N), 1256 (C-O-C); ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.06-7.98 (m, 1H, Ar-H), 7.92-7.81 (m, 3H, Ar-H), 7.57 – 7.55 (m, 1H, Ar-H), 7.43 (t, J = 7.6 Hz, 1H, Ar-H), 7.31 (d, J = 8.2 Hz, 1H, Ar-H), 7.23 (s, 1H, Ar-H), 2.61 (s, 3H, Ar-CH₃), 2.46 (s, 3H, Ar-CH₃); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 161.18 (Ar-C), 156.78 (Ar-C), 135.03 (Ar-C), 132.03 (Ar-C), 132.75 (Ar-C), 129.84 (Ar-C), 128.94 (Ar-C), 117.77 (Ar-C), 113.33 (Ar-C), 111.02 (Ar-C), 108.71, 22.29 (Ar-CH₃), 20.73 (Ar-CH₃); MS (ESI): 275.1179 ([M+H]⁺), Anal. Calcd for C₁₈H₁₅N₂O: C, 78.52; H, 5.49; N, 10.17; Found: C, 78.57; H, 5.39; N, 10.13%.

2-(4-Methoxyphenyl)-7-methylfuro[2,3-b]quinoxaline (18)
Greenish yellow solid; mp 189-191 °C; IR, vmax (ZnSe)/cm⁻¹: 3049 (Ar-C-H), 2865 (C=C), 1420 (C=N), 1199 (C-O-C), 1055 (-O-CH₃); ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.00 – 7.97 (m, 1H, Ar-H), 7.72 – 7.67 (m, 3H, Ar-H), 7.42 – 7.39 (m, 1H, Ar-H), 7.33 – 7.30 (m, 1H, Ar-H), 7.23 – 7.22 (m, 1H, Ar-H), 7.13 (s, 1H, Ar-H) 3.78 (s, 3H, Ar-OCH₃), 2.36 (s, 3H, Ar-CH₃); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 161.13 (Ar-C), 156.73 (Ar-C), 134.98 (Ar-C), 132.69 (Ar-C), 132.03 (Ar-C), 129.79 (Ar-C), 128.89 (Ar-C), 117.72 (Ar-C), 112.44 (Ar-C), 100.61
(Ar-C), 53.73 (Ar-OCH₃), 20.68 (Ar-CH₃); MS (ESI): 291.1107 ([M+H]+), Anal. Calcd for C₁₈H₁₅N₂O₂: C, 74.21; H, 5.19; N, 9.62; Found: C, 74.17; H, 5.25; N, 9.58%.

2-(4-Methoxyphenyl)-6,7-dimethylfuro[2,3-b]quinoxaline (19)
Greenish yellow solid; mp 205-208 °C; IR, ν max (ZnSe)/cm⁻¹: 3015 (Ar-C-H), 2890 (ali-C-H), 1623 (C=C), 1211 (C-O-C), 1093 (-O-CH₃); ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.50 – 7.49 (m, 1H, Ar-H), 7.40 – 7.38 (m, 2H, Ar-H), 7.31 – 7.26 (m, 2H, Ar-H), 6.87 (d, J = 9.2 Hz, 2H, Ar-H), 3.79 (s, 3H, Ar-OCH₃), 2.61 (s, 3H, Ar-CH₃), 2.46 (s, 3H, Ar-CH₃); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 162.12 (Ar-C), 160.59 (Ar-C), 158.55 (Ar-C), 145.00 (Ar-C), 142.72 (Ar-C), 142.05 (Ar-C), 139.82 (Ar-C), 138.92 (Ar-C), 127.74 (Ar-C), 123.30 (Ar-C), 121.00 (Ar-C), 118.68 (Ar-C), 110.17 (Ar-C), 98.34 (Ar-C), 53.23 (Ar-OCH₃), 22.51 (Ar-CH₃), 20.95 (Ar-CH₃); MS (ESI): 305.1275 ([M+H]+), Anal. Calcd for C₁₉H₁₇N₂O₂: C, 74.73; H, 5.61; N, 9.17%; Found: C, 74.78; H, 5.66; N, 9.24%.

7-Chloro-2-(m-tolyl)furo[2,3-b]quinoxaline (20)
Greenish yellow solid; mp 195-198 °C; IR, ν max (ZnSe)/cm⁻¹: 3015 (Ar-C-H), 2855 (ali-C-H), 1615 (C=C), 1420 (C=N), 1210 (C-O-C), 720 (C-Cl); ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.98 (t, J = 6.4 Hz, 1H, Ar-H), 7.71-7.66 (m, 3H, Ar-H), 7.41 (t, J = 12 Hz, 1H, Ar-H), 7.32 (t, J = 6.0 Hz, 1H, Ar-H), 7.22 (d, J = 5.6 Hz, 2H, Ar-H), 7.11 (s, 1H, Ar-H), 2.35 (s, 3H, Ar-CH₃); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 162.21 (Ar-C), 157.81 (Ar-C), 144.01 (Ar-C), 141.73 (Ar-C), 141.06 (Ar-C), 138.83 (Ar-C), 137.93 (Ar-C), 128.75 (Ar-C), 122.31 (Ar-C), 120.01 (Ar-C), 117.61 (Ar-C), 100.07 (Ar-C), 21.76 (Ar-CH₃); MS (ESI): 295.0622 ([M+H]+), Anal. Calcd for C₁₇H₁₂N₂OCl: C, 69.04; H, 4.09; N, 9.47%; Found: C, 68.99; H, 3.98; N, 9.50%.

7-Fluoro-2-(m-tolyl)furo[2,3-b]quinoxaline (21)
Greenish yellow solid; mp 191-194 °C; IR, ν max (ZnSe)/cm⁻¹: 3023 (Ar-C-H), 2801 (ali-C-H), 1634 (C=C), 1439 (C=N), 1227 (C-O-C); ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.00 (t, J = 6.4 Hz, 1H, Ar-H), 7.72-7.67 (m, 3H, Ar-H), 7.42 (t, J = 12 Hz, 1H, Ar-H), 7.34 (t, J = 6.0 Hz, 1H, Ar-H), 7.23 (d, J = 5.6 Hz, 1H, Ar-H), 7.13 (s, 1H, Ar-H), 2.37 (s, 3H, Ar-CH₃); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 162.11 (Ar-C), 160.16 (Ar-C), 154.87 (Ar-C), 154.24 (Ar-C), 145.71 (Ar-C), 138.12 (Ar-C), 135.76 (Ar-C), 134.63 (Ar-C), 129.12 (Ar-C), 127.17 (Ar-C), 121.25 (Ar-C), 102.23 (Ar-C), 98.50 (Ar-C), 21.30 (Ar-CH₃); MS (ESI): 279.0922 ([M+H]+), Anal. Calcd for C₁₇H₁₂FN₂O: C, 73.11; H, 4.33; N, 10.03%; Found: C, 73.15; H, 4.30; N, 9.97%.

3. NMR (¹H & ¹³C) and HRMS spectra of furo[2,3-b]quinoxalines