Supporting Information for

Graphene Oxide as a Green Carbon Material for Cross-Coupling of Indoles with Ethers via Oxidation and Friedal-Craft Reaction

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1. General Methods

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis were carried out on a Perkin-Elmer 240B instrument. HRFABMS spectra were recorded on a FTMS apparatus. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

Raman spectra were collected with a Horiba Jobin Y von-Labram HR UV-Visible-NIR Raman Microscope Spectrometer, using a 632 nm laser. The spectra were the average of 10 scans at a resolution of 2 cm$^{-1}$ between 1000-2000 cm$^{-1}$ Raman Shift.

2. Characterization of GO

GO was prepared by graphite oxidation using the Hummers and Offeman method and subsequent exfoliation. Further details and GO characterization have been previously reported.

Figure S1. (A) SEM image of graphite. (B) SEM image of GO.

Figure S2. TEM image of graphite.

Figure S3. TEM image of GO.
3. ESI-MS Investigation

ESI-MS of crude mixtures after 60 min of the onset of reaction for identifying the possible intermediates
4. General Procedure and Spectroscopic Data of the Products 3

To a solution of indole (0.3 mmol) and THF (108 mg) in CH$_3$CN (1 mL) was added GO (35 mg) under an air atmosphere and the mixture was stirred at 25°C for 6 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:1) to yield the corresponding product 3.

4,4-Di(1H-indol-3-yl)butan-1-ol (3a)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91 (s, 2H, NH), 7.60 (d, $J$ = 7.9 Hz, 2H, Ar-H), 7.25 (d, $J$ = 7.9 Hz, 2H, Ar-H), 7.16 (t, $J$ = 7.3 Hz, 2H, Ar-H), 7.05 (t, $J$ = 7.3 Hz, 2H, Ar-H), 6.82 (s, 2H, Ar-H), 4.46 (t, $J$ = 7.2 Hz, 1H), 3.59 (t, $J$ = 6.3 Hz, 2H), 2.25 (dd, $J$ = 15.0, 7.4 Hz, 2H), 2.05 (s, 1H, OH), 1.66-1.59 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 136.6, 127.1, 121.7, 121.6, 120.0, 119.5, 119.0, 111.2, 63.0, 33.8, 32.0, 31.4. MS (ESI): 305 (M+H$^+$, 100). These assignments matched with those previously published.¹

4,4-Bis(5-fluoro-1H-indol-3-yl)butan-1-ol (3b)

Brown amorphous solid. $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.09 (s, 2H, NH), 7.18 (t, $J$ = 9.2 Hz, 2H, Ar-H), 7.17 (t, $J$ = 9.2 Hz, 2H, Ar-H), 7.00 (d, $J$ = 1.1 Hz, 2H, Ar-H), 6.86 (dt, $J$ = 1.1, 9.2 Hz, 2H, Ar-H), 4.30 (t, $J$ = 7.5 Hz, 1H), 3.65 (t, $J$ = 6.4 Hz, 2H), 2.23 (dd, $J$ = 15.4, 7.5 Hz, 2H), 1.86 (s, 1H, OH), 1.68-1.50 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 157.8 (d, $J$ = 233.7 Hz), 133.1, 127.1 (d, $J$ = 9.6 Hz), 123.3, 119.6 (d, $J$ = 4.7 Hz), 111.8 (d, $J$ = 9.7 Hz), 110.2 (d, $J$ = 26.4 Hz), 104.3 (d, $J$ = 23.4 Hz), 62.9, 33.9, 31.3. HRMS (ESI) calcd for [C$_{20}$H$_{18}$F$_2$N$_2$O + Na]$^+$ 363.1285, found 363.1290.

4,4-Bis(5-chloro-1H-indol-3-yl)butan-1-ol (3c)

Brown amorphous solid. $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.14 (s, 2H, NH), 7.49 (d, $J$ = 2.0 Hz, 2H, Ar-H), 7.17 (d, $J$ = 8.6 Hz, 2H, Ar-H), 7.08 (dd, $J$ = 8.6, 2.0 Hz, 2H, Ar-H), 6.93 (d, $J$ = 2.0 Hz, 2H, Ar-H), 4.30 (t, $J$ = 7.5 Hz, 1H), 3.63 (t, $J$ = 6.5 Hz, 2H), 2.20 (dt, $J$ = 7.7, 10.8 Hz, 2H), 1.63-
1.56 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 135.0, 127.9, 124.7, 123.0, 122.1, 119.1, 118.9, 112.3, 62.9, 33.8, 31.4, 31.2. HRMS (ESI) calcd for [C$_{20}$H$_{16}$Cl$_2$N$_2$O + Na]$^+$ 395.0694, found 395.0690.

4,4-Bis(5-bromo-1H-indol-3-yl)butan-1-ol (3d)

Brown amorphous solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12 (s, 2H, NH), 7.64 (d, $J = 1.7$ Hz, 2H, Ar-H), 7.22 (dd, $J = 8.6$, 1.7 Hz, 2H, Ar-H), 7.17 (d, $J = 8.6$ Hz, 2H, Ar-H), 6.98 (d, $J = 2.3$ Hz, 2H, Ar-H), 4.32 (t, $J = 7.3$ Hz, 1H), 3.66 (t, $J = 6.5$ Hz, 2H), 2.22 (dt, $J = 7.6$, 13.1 Hz, 2H), 1.66-1.59 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 135.3, 128.6, 124.7, 122.8, 122.0, 119.2, 112.7, 112.4, 62.9, 33.8, 31.5, 31.3. MS (ESI): 461 (M+H$^+$, 50), 463 (M+H$^+$, 100). These assignments matched with those previously published.$^1$

4,4-Bis(5-iodo-1H-indol-3-yl)butan-1-ol (3e)

Brown amorphous solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.09 (s, 2H, NH), 7.87 (d, $J = 1.2$ Hz, 2H, Ar-H), 7.39 (dd, $J = 8.5$, 1.6 Hz, 2H, Ar-H), 7.09 (d, $J = 8.5$ Hz, 2H, Ar-H), 6.91 (d, $J = 2.2$ Hz, 2H, Ar-H), 4.2 (t, $J = 7.8$ Hz, 1H), 3.67 (t, $J = 6.5$ Hz, 2H), 2.21 (dt, $J = 7.7$, 10.7 Hz, 2H), 1.66-1.57 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 135.7, 130.2, 129.4, 128.3, 122.4, 118.8, 113.3, 82.8, 62.9, 33.7, 31.5, 31.3. HRMS (ESI) calcd for [C$_{20}$H$_{18}$I$_2$N$_2$O + Na]$^+$ 578.9406, found 578.9404.

4,4-Bis(5-methyl-1H-indol-3-yl)butan-1-ol (3f)

Brown amorphous solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (s, 2H, NH), 7.41 (s, 2H, Ar-H), 7.22 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.00 (d, $J = 8.3$ Hz, 2H, Ar-H), 6.91 (s, 2H, Ar-H), 4.45 (t, $J = 7.4$ Hz, 1H), 3.67 (t, $J = 6.6$ Hz, 2H), 2.43 (s, 6H, CH$_3$), 2.27 (dt, $J = 7.6$, 15.4 Hz, 2H), 1.74-1.66 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 135.0, 128.2, 127.3, 123.4, 121.8, 119.6, 119.2, 110.8, 63.2,
33.8, 32.0, 31.6, 21.6. MS (ESI): 333 (M+H^+, 100). These assignments matched with those previously published.¹

4,4-Bis(5-methoxy-1H-indol-3-yl)butan-1-ol (3g)

Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 7.85 (s, 2H, NH), 7.44 (d, J = 8.7 Hz, 2H, Ar-H), 6.83 (s, 2H, Ar-H), 6.71 (dd, J = 8.7, 2.3 Hz, 2H, Ar-H), 4.38 (t, J = 7.4 Hz, 1H), 3.81 (s, 6H, OCH₃) 3.63 (t, J = 6.5 Hz, 2H), 2.27-2.18 (m, 2H), 1.70-1.60 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 156.3, 137.3, 121.6, 120.3, 120.1, 120.0, 109.0, 94.8, 63.1, 55.7, 34.0, 31.9, 31.5. MS (ESI): 365 (M+H^+, 100). These assignments matched with those previously published.²

3,3’-(4-Hydroxybutane-1,1-diyl)bis(1H-indole-5-carboxylic acid) (3h)

Brown amorphous solid. ¹H NMR (400 MHz, DMSO-d₆): δ 11.16 (s, 2H, NH), 8.15 (s, 2H, Ar-H), 7.64 (d, J = 8.3 Hz, 2H, Ar-H), 7.35 (d, J = 8.3 Hz, 2H, Ar-H), 7.34 (s, 2H, Ar-H), 4.46 (t, J = 7.0 Hz, 1H), 2.30-2.15 (m, 2H), 1.95-1.85 (m, 2H), 1.52-1.40 (m, 2H). ¹³C NMR (101 MHz, DMSO-d₆): δ 169.0, 139.5, 126.6, 124.1, 122.6, 122.2, 121.3, 120.4, 111.5, 61.2, 33.7, 32.1, 31.8. HRMS (ESI) calcd for [C₂₂H₂₀N₂O₅]+ K⁺ 431.1009, found 431.1002.

4,4-Bis(6-fluoro-1H-indol-3-yl)butan-1-ol (3i)

Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 8.07 (s, 2H, NH), 7.43 (d, J = 8.7 Hz, 1H, Ar-H), 7.42 (d, J = 8.7 Hz, 1H, Ar-H), 6.99 (d, J = 9.6 Hz, 2H, Ar-H), 6.97 (d, J = 2.3 Hz, 2H, Ar-H), 6.78 (dt, J = 2.3, 9.6 Hz, 2H, Ar-H), 4.43 (t, J = 7.5 Hz, 1H, Ar-H), 3.67 (t, J = 6.5 Hz, 2H, Ar-H), 2.25 (dd, J = 8.7 Hz, 2H, Ar-H), 1.70-1.63 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 159.9 (d, J = 237.3 Hz), 126.51 (d, J = 12.3 Hz), 123.6, 121.6 (d, J = 3.5 Hz), 120.1 (d, J = 10.1 Hz), 119.9, 107.8 (d, J = 24.4 Hz), 97.4 (d, J = 25.9 Hz), 63.0, 33.8, 31.7, 31.3. HRMS (ESI) calcd for [C₂₀H₁₃F₂N₂O + H]^+ 341.1465, found 341.1483.

4,4-Bis(6-methyl-1H-indol-3-yl)butan-1-ol (3j)
Brown amorphous solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (s, 2H, NH), 7.46 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.09 (s, 2H, Ar-H), 6.87 (dd, $J = 8.1$, 1.0 Hz, 2H, Ar-H), 6.86 (s, 2H, Ar-H), 4.43 (t, $J = 7.5$ Hz, 1H), 4.34 (t, $J = 7.1$ Hz, 1H), 3.64 (t, $J = 6.6$ Hz, 2H), 2.44 (s, 6H, 2CH$_3$), 2.29-2.23 (m, 2H), 1.7-1.63 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 137.1, 131.5, 125.0, 120.9, 120.8, 120.0, 119.2, 111.1, 63.1, 33.9, 31.9, 31.5, 21.6. HRMS (ESI) caleld for [C$_{22}$H$_{24}$N$_2$O + H]$^+$ 333.1967, found 333.1950.

4,4-Bis(7-nitro-1H-indol-3-yl)butan-1-ol (3k)

Brown amorphous solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.86 (s, 2H, NH), 8.12 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.84 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.29 (s, 2H, Ar-H), 7.10 (t, $J = 7.8$ Hz, 2H, Ar-H), 4.57 (t, $J = 7.2$ Hz, 1H), 3.75 (t, $J = 5.5$ Hz, 2H), 2.45-2.30 (m, 2H), 1.65-1.55 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 133.0, 130.7, 130.0, 127.4, 123.8, 120.9, 119.4, 118.8, 62.7, 33.5, 31.8, 31.1. HRMS (ESI) caleld for [C$_{20}$H$_{18}$N$_4$O$_5$ + Na]$^+$ 417.1175, found 417.1235.

3,3’-(4-Hydroxybutane-1,1-diyl)bis(1H-indole-4-carbonitrile) (3l)

Brown amorphous solid. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 11.41 (d, $J = 2.2$ Hz, 2H, NH), 7.69 (dd, $J = 8.2$, 0.8 Hz, 2H, Ar-H), 7.41 (dd, $J = 7.3$, 0.8 Hz, 2H, Ar-H), 7.18 (t, $J = 7.3$ Hz, 2H, Ar-H), 7.12 (d, $J = 2.2$ Hz, 2H, Ar-H), 5.23 (t, $J = 7.2$ Hz, 1H), 4.35 (t, $J = 5.2$ Hz, 1H, OH), 3.45 (dt, $J = 6.7$, 12.2 Hz, 2H), 2.08 (dt, $J = 7.2$, 12.2 Hz, 2H), 1.73-1.64 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ 137.4, 126.4, 125.8, 125.7, 121.1, 119.6, 119.2, 117.3, 101.4, 61.6, 34.4, 32.2, 31.5. MS (ESI): 355 (M+H$^+$, 100). Anal caleld for C$_{22}$H$_{18}$N$_4$O: C, 74.56; H, 5.12; N, 15.81. Found C, 74.19; H, 5.37; N, 15.53.

4,4-Bis(1-methyl-1H-indol-3-yl)butan-1-ol (3m)
Brown amorphous solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.65 (d, $J$ = 7.9 Hz, 2H, Ar-H), 7.30 (d, $J$ = 8.2 Hz, 2H, Ar-H), 7.23 (t, $J$ = 7.9 Hz, 2H, Ar-H), 7.08 (t, $J$ = 7.9 Hz, 2H, Ar-H), 6.90 (s, 2H, Ar-H), 4.53 (t, $J$ = 7.5 Hz, 1H), 3.74 (s, 6H, CH$_3$), 3.69 (t, $J$ = 6.6 Hz, 2H), 2.31 (dt, $J$ = 7.6, 10.0 Hz, 2H), 1.75-1.68 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 132.6, 122.8, 121.6, 116.6, 114.9, 114.1, 113.8, 104.4, 58.4, 29.0, 27.9, 26.9. MS (ESI): 333 (M+H$^+$, 100). These assignments matched with those previously published.$^1$

4,4-Bis(1,2-dimethyl-1H-indol-3-yl)butan-1-ol (3n)

Brown amorphous solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J$ = 8.0 Hz, 2H, Ar-H), 7.25 (d, $J$ = 8.0 Hz, 2H, Ar-H), 7.14 (t, $J$ = 7.5 Hz, 2H, Ar-H), 7.04 (t, $J$ = 7.5 Hz, 2H, Ar-H), 4.52 (t, $J$ = 7.9 Hz, 1H), 3.70 (t, $J$ = 6.7 Hz, 2H), 3.63 (s, 6H, NCH$_3$), 2.60-2.53 (m, 2H), 2.37 (s, 6H, CH$_3$), 1.75-1.63 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 136.6, 132.8, 127.3, 120.0, 119.5, 118.6, 114.4, 108.5, 63.2, 35.6, 32.3, 31.5, 29.4, 10.9. MS (ESI): 361 (M+H$^+$, 100). These assignments matched with those previously published.$^3$

(2-(Di(1H-indol-3-yl)methyl)phenyl)methanol (3o)

Brown amorphous solid. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 10.79 (d, $J$ = 1.5 Hz, 2H, NH), 7.44 (d, $J$ = 7.5 Hz, 1H, Ar-H), 7.35 (d, $J$ = 8.1 Hz, 2H, Ar-H), 7.30 (d, $J$ = 7.9 Hz, 2H, Ar-H), 7.21-7.15 (m, 1H, Ar-H), 7.09 (d, $J$ = 3.9 Hz, 2H, Ar-H), 7.04 (t, $J$ = 7.2 Hz, 2H, Ar-H), 6.86 (t, $J$ = 7.2 Hz, 2H, Ar-H), 6.65 (d, $J$ = 2.1 Hz, 2H, Ar-H), 6.10 (s, 1H), 5.19 (t, $J$ = 5.3 Hz, 1H, OH), 4.61 (d, $J$ = 5.3 Hz, 2H, CH$_2$). $^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta$ 142.4, 139.9, 137.1, 128.2, 127.4, 127.2, 126.8, 126.1, 124.4, 121.3, 119.5, 118.6, 118.1, 111.9, 61.1, 35.0. MS (ESI): 353 (M+H$^+$, 100). These assignments matched with those previously published.$^4$

2-(2-(Di(1H-indol-3-yl)methyl)phenyl)ethan-1-ol (3p)
Brown amorphous solid. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 10.81 (s, 2H, NH), 7.35 (d, \(J = 8.1\) Hz, 2H, Ar-H), 7.24 (d, \(J = 8.1\) Hz, 2H, Ar-H), 7.22 (d, \(J = 8.1\) Hz, 1H, Ar-H), 7.12 (t, \(J = 8.1\) Hz, 1H, Ar-H), 7.07 (t, \(J = 8.1\) Hz, 2H, Ar-H), 7.04 (t, \(J = 8.1\) Hz, 2H, Ar-H), 6.86 (t, \(J = 7.4\) Hz, 2H, Ar-H), 6.60 (s, 2H, Ar-H), 6.07 (s, 1H, OH), 4.77 (dt, \(J = 5.2\) Hz, 1H), 3.64 (dt, \(J = 7.2, 12.6\) Hz, 2H), 2.86 (t, \(J = 7.2\) Hz, 2H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)): \(\delta\) 143.2, 137.4, 137.1, 130.3, 128.6, 127.1, 126.3, 126.2, 124.5, 121.3, 119.5, 118.6, 118.4, 111.9, 62.6, 36.5, 35.8. HRMS (ESI) calcd for \([\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}+\text{K}]^+\) 405.1369, found 405.1390.

3,3’-(Phenylmethylene)bis(1\(H\)-indole) (3q)

Brown amorphous solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.78 (s, 2H, NH), 7.45 (d, \(J = 8.1\) Hz, 2H, Ar-H), 7.39 (d, \(J = 7.1\) Hz, 2H, Ar-H), 7.36 (d, \(J = 8.1\) Hz, 2H, Ar-H), 7.33 (t, \(J = 7.9\) Hz, 2H, Ar-H), 7.27 (d, \(J = 7.1\) Hz, 1H, Ar-H), 7.22 (dt, \(J = 0.8, 7.9\) Hz, 2H, Ar-H), 7.06 (dt, \(J = 0.8, 7.9\) Hz, 2H, Ar-H), 6.62 (t, \(J = 7.9\) Hz, 2H, Ar-H), 5.93 (s, 1H, Ar-H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 144.1, 136.7, 128.8, 128.3, 127.1, 126.2, 123.7, 122.0, 120.0, 119.7, 119.3, 111.1, 40.2. MS (ESI): 323 (M+H\(^+\), 100). These assignments matched with those previously published.\(^5\)

3,3’-(Ethane-1,1-diyl)bis(1\(H\)-indole) (3r)

Brown amorphous solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.84 (s, 2H, NH), 7.61 (d, \(J = 7.9\) Hz, 2H, Ar-H), 7.36 (d, \(J = 8.1\) Hz, 2H, Ar-H), 7.20 (dt, \(J = 1.0, 7.1\) Hz, 2H, Ar-H), 7.08 (dt, \(J = 1.0, 8.1\) Hz, 2H, Ar-H), 6.90 (d, \(J = 2.1\) Hz, 2H, Ar-H), 4.71 (dq, \(J = 6.5, 7.1\) Hz, 1H), 1.84 (d, \(J = 7.1\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 136.7, 126.9, 121.8, 121.7, 121.2, 119.8, 119.0, 111.1, 28.2, 21.8. MS (ESI): 261 (M+H\(^+\), 100). These assignments matched with those previously published.\(^6\)
5. Copies of $^1$H and $^{13}$C Spectra

$^1$H and $^{13}$C NMR Spectra for 3a
$^1$H and $^{13}$C NMR Spectra for 3b
$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra for 3c
$^1$H and $^{13}$C NMR Spectra for 3d
$^1$H and $^{13}$C NMR Spectra for 3e
$^1$H and $^{13}$C NMR Spectra for 3f
$^1$H and $^{13}$C NMR Spectra for 3g
$^1$H and $^{13}$C NMR Spectra for 3h
$^1$H and $^{13}$C NMR Spectra for 3i
$^1$H and $^{13}$C NMR Spectra for 3j
$^1$H and $^{13}$C NMR Spectra for 3k
$^1$H and $^{13}$C NMR Spectra for $3l$
$^1$H and $^{13}$C NMR Spectra for 3m
$^1$H and $^{13}$C NMR Spectra for 3n
$^1$H and $^{13}$C NMR Spectra for 3o
$^1$H and $^{13}$C NMR Spectra for 3p
$^1$H and $^{13}$C NMR Spectra for 3q
$^1$H and $^{13}$C NMR Spectra for 3r
6. References