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

¹H and ¹³C 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.



Figure S4. AFM image of GO.



Figure S5. Raman image of GO.



Figure S6. XRD 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 CH₃CN (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(1*H*-indol-3-yl)butan-1-ol (3a)



¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (101 MHz, CDCl₃): δ 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-1*H*-indol-3-yl)butan-1-ol (3b)



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (101 MHz, CDCl₃): δ 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 [C₂₀H₁₈F₂N₂O + Na]⁺ 363.1285, found 363.1290.

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



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (101 MHz, CDCl₃): δ 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 $[C_{20}H_{18}Cl_2N_2O + Na]^+$ 395.0694, found 395.0690.

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



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (101 MHz, CDCl₃): δ 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-1*H*-indol-3-yl)butan-1-ol (3e)



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (101 MHz, CDCl₃): δ 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 [C₂₀H₁₈I₂N₂O + Na]⁺ 578.9406, found 578.9404.

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



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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, CH₃), 2.27 (dt, J = 7.6, 15.4 Hz, 2H), 1.74-1.66 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 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-1*H*-indol-3-yl)butan-1-ol (**3**g)



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), 6.78 (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(1*H*-indole-5-carboxylic acid) (3h)



Brown amorphous solid. ¹H NMR (400 MHz, DMSO- d_6): 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- d_6): 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 [C₂₀H₁₈F₂N₂O + H]⁺ 341.1465, found 341.1483. 4,4-Bis(6-methyl-1*H*-indol-3-yl)butan-1-ol (**3**j)



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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, 2CH₃), 2.29-2.23 (m, 2H), 1.7-1.63 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 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) calcd for [C₂₂H₂₄N₂O + H]⁺ 333.1967, found 333.1950.

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



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (101 MHz, CDCl₃): δ 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) calcd for [C₂₀H₁₈N₄O₅ + Na]⁺ 417.1175, found 417.1235.

3,3'-(4-Hydroxybutane-1,1-diyl)bis(1H-indole-4-carbonitrile) (3I)



Brown amorphous solid. ¹H NMR (400 MHz, DMSO-*d*₆): δ 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). ¹³C NMR (101 MHz, DMSO-*d*₆): δ 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 calcd for C₂₂H₁₈N₄O: C, 74.56; H, 5.12; N, 15.81. Found C, 74.19; H, 5.37; N, 15.53.

4,4-Bis(1-methyl-1*H*-indol-3-yl)butan-1-ol (**3m**)



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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, CH₃), 3.69 (t, J = 6.6 Hz, 2H), 2.31 (dt, J = 7.6, 10.0 Hz, 2H), 1.75-1.68 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 132.6, 122.8, 121.6, 116.6, 114.9, 114.1, 113.8, 104.4, 58.4, 29.0, 27.9, 27.7, 26.9. MS (ESI): 333 (M+H⁺, 100). These assignments matched with those previously published.¹

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



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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, NCH₃), 2.60-2.53 (m, 2H), 2.37 (s, 6H, CH₃), 1.75-1.63 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 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(1*H*-indol-3-yl)methyl)phenyl)methanol (30)



Brown amorphous solid. ¹H NMR (400 MHz, DMSO- d_6): δ 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, CH₂). ¹³C NMR (101 MHz, DMSO- d_6): δ 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(1*H*-indol-3-yl)methyl)phenyl)ethan-1-ol (**3p**)



Brown amorphous solid. ¹H NMR (400 MHz, DMSO-*d*₆): δ 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, 2H, 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 (t, *J* = 5.2 Hz, 1H), 3.64 (dt, *J* = 7.2, 12.6 Hz, 2H), 2.86 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆): δ 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 [C₂₅H₂₂N₂O + K]⁺ 405.1369, found 405.1390.

3,3'-(Phenylmethylene)bis(1*H*-indole) (**3q**)



Brown amorphous solid. ¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (101 MHz, CDCl₃): δ 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. ¹H NMR (400 MHz, CDCl₃): δ 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, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 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 ¹H and ¹³C Spectra

¹H and ¹³C NMR Spectra for **3a**













¹H and ¹³C NMR Spectra for **3f**







¹H and ¹³C NMR Spectra for **3g**

¹H and ¹³C NMR Spectra for **3h**



¹H and ¹³C NMR Spectra for **3i**





-23000 -22000 -21000 -20000 -19000 -18000

-17000

-15000 -14000 -13000 -12000 -11000 10000 -9000 -8000 -7000 -6000 -5000 -4000 -3000 -2000 -1000 -0

-- 1000

--2000





$^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR Spectra for **31**



f1 (ppm)









¹H and ¹³C NMR Spectra for **30**











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6. References

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