Supporting information

Green synthesis of stable Cu(0) nanoparticle onto reduced graphene oxide nanosheets: A reusable catalyst for the synthesis of symmetrical biaryls from arylboronic acids under base-free condition

List of the Contents

1. General Methods .................................................................S2
2. General experimental procedure and analytical data ................. S3
3. Some copies of$^1$H &$^{13}$C spectra ...........................................S8
4. References ..............................................................................S20
General Methods for synthesis of symmetrical biaryls

All reactions involving oxygen- or moisture-sensitive compounds were carried out under N₂ atmosphere using oven-dried or flame-dried glassware and standard syringe/septa techniques. Reaction temperatures refer to external bath temperatures. All dry solvents were distilled under N₂ immediately prior to use. Organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated using rotary evaporator at aspirator pressure (20-30 mm Hg). Reactions were monitored by thin-layer chromatography (TLC) using aluminium-backed MERCK 60 silica gel plates (0.2 mm thickness); the chromatograms were visualized first with ultraviolet light (254 nm) and then by immersion in solutions of p-anisaldehyde followed by heating. Flash column chromatography was performed with Merck silica gel 60 (230-400 mesh).

All Microwave (MW) reactions were carried out in a Synthos 3000 (Anton Paar) microwave reactor. The multitude microwave has a twin magnetron (2.45 GHz) with maximum output power of 1400 W. The output power can be controlled in unpulsed control mode over whole power range which is adjustable in 1 W increment. A Motorola 68xxx series microprocessor system control is used to measure temperature, pressure, time, and power during the reaction. The temperature and pressure were monitored throughout the reaction by an infrared detector. The temperature can be measured from 0 to 280 °C with uncertainty ±1%. The pressure can be measured from 0 to 86 bar with uncertainty ±0.2 bar. The microwave power is initially set at 550 W and reaction is run. However, during the course of the reaction, once the set pressure or temperature limit is reached, the reactor automatically adjusts the power by lowering it.

All NMR spectra were recorded on Bucker Advance DPX 300 MHz spectrometer. Chemical shifts are reported on the δ scale (ppm) downfield from tetramethylsilane (δ=0.0 ppm) using the residual solvent signal at δ=7.26 ppm (¹H) or δ=77 ppm (¹³C) as internal standard. Coupling constants are reported in Hz. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Acetone d-6 is used to compare superimposed NMR signals with CDCl₃. IR spectra were recorded as thin films on a silicon disc on a Perkin Elmer FT-IR spectrometer. ESI mass spectra were recorded on a Bucker Daltonic Data analysis 2.0
spectrometer. Yields refer to chromatographically purified compounds, unless otherwise stated.

**Experimental procedures:**

**Synthesis of Cu NPs on rGO nanosheets by *ex situ* process**

We have synthesized Cu(0) nanoparticles on rGO nanosheets by *ex-situ* method to examine whether the Cu(0) nanoparticles are trapped by multi layer graphene sheets or as well as in the surface of graphene sheets. First, 20 mL of GO-water suspension (0.0125 g/mL) was taken in a round bottom flask and then ascorbic acid (0.1M, 10 mL) was added drop wise on to the reaction mixture and heated at 80 °C for 1 h. After reduction of GO to rGO by ascorbic acid, Cu(OAc)$_2$.H$_2$O (0.8 g) was added to it and heated to 80 °C for another 1 h. The product was treated with H$_2$O$_2$ to remove excess amount of ascorbic acid and finally the solid product was separated by centrifuge and washed with ethanol followed by water and then dried in air oven at 60 °C.

**Synthesis of Cu NPs on rGO nanosheets using hydrazine hydrate**

Cu(OAc)$_2$.H$_2$O (0.8 g) was dissolved in water (10 mL) in a round bottom flask. GO-water suspension (20 mL of 0.0125 g/mL) was added to the above solution and stirred for 10 min. Finally, hydrazine hydrate (3 mL+ 10 mL water) was added drop wise on to the reaction mixture and heated at 80 °C for 40 min. When the color of the reaction mixture changed from brown to black due to reduction of both Cu(II) to Cu(0) and GO to rGO, the reaction mixture was cooled to room temperature and the product was separated by centrifuge. The product was washed with ethanol followed by water and then dried in air oven at 60 °C.
General procedure for the synthesis of symmetrical biaryls:
The Cu(0 nanoparticle-rGO composites (50 mg in 2 mL) was dispersed in DMF (2 mL) in a reaction tube. Phenylboronic acid (100 mg, 0.82 mmol) was added and the resulting mixture was microwave irradiated at 360 W for 12-15 min. After completion of the reaction the catalyst was recovered by simple filtration and the filtrate was poured into water. The organic product was extracted with ethyl acetate (3x10 mL). The combined organic fraction was dried over Na$_2$SO$_4$ and concentrated. The residue was purified by chromatography using silica gel (60-120 mesh) with hexane as eluent to afford the corresponding biaryls.

Analytical data:
XRD pattern of Cu(0) nanoparticle-rGO composite by *ex situ* method

![XRD Diagram](image)

Fig. S1. Powder XRD diffractogram of Cu(0) nanoparticle on rGO sheets by *ex situ* method
TEM images of the Cu(0) nanoparticles on rGO sheets synthesized using hydrazine hydrate

Fig. S2. HRTEM images of Cu(0) nanoparticles on rGO sheets synthesized using hydrazine hydrate as reducing agent. (a-e: HRTEM images and f: SAED image)

XRD pattern of Cu(0) nanoparticle on rGO sheets using hydrazine hydrate

Fig. S3. Powder XRD diffractogram of Cu(0) nanoparticle on rGO sheets using hydrazine hydrate
The XRD pattern shows a characteristic peak at $\theta$ value of 43.48, 50.58, 74.20, 90.00 and 95.16 corresponding to $d$-spacing of the Cu(0) nanoparticles as well as 2.08, 1.80, 1.27, 1.08 and 1.04 Å which evident for the formation of Cu (0) nanoparticles on the rGO nanosheets.

Spectroscopic data

1,1'-Biphenyl, 2a\(^1\): Colourless solid, mp 69-71 °C; yield 94%, $R_f = 0.6$ (100% hexanes).  \(^1\)H NMR (300 MHz, CDCl\(_3\)): $\delta$= 7.52-7.64 (m, 4H), 7.46 (t, $J$=7.4 Hz, 4H), 7.29-7.38 (m, 2H);  \(^1\)C NMR (75 MHz, CDCl\(_3\)): $\delta$ = 141.2, 128.7, 127.2, 127.1; IR (CHCl\(_3\)): 3032, 2956, 1597, 1483, 1465, 1009, 698.3, 729, 698 cm\(^{-1}\)

4,4'-Dimethyl-1,1'-biphenyl, 2b\(^1\): Colourless solid, mp 123-125 °C; yield 92%, $R_f = 0.53$ (100% hexanes).  \(^1\)H NMR (300 MHz, CDCl\(_3\)): $\delta$= 7.47 (d, $J$=8.1 Hz, 4H), 7.23 (d, $J$=7.8 Hz, 4H), 2.38 (s, 6H);  \(^1\)C NMR (75 MHz, CDCl\(_3\)): $\delta$ = 138.3, 136.7, 129.4, 126.8, 21.1; IR (CHCl\(_3\)): 2957, 1501, 1464, 1377, 1006.4, 803, 724.1 cm\(^{-1}\)

4,4'-Dimethoxy-1,1'-biphenyl, 2c\(^1\): Colourless solid, mp 171-175 °C; yield 94%, $R_f = 0.86$ (10% EtOAc in hexanes).  \(^1\)H NMR (300 MHz, CDCl\(_3\)): $\delta$= 7.47 (d, $J$=8.6 Hz, 4H), 6.95 (d, $J$=8.6 Hz, 4H), 3.84 (s, 6H);  \(^1\)C NMR (75 MHz, CDCl\(_3\)): $\delta$ = 158.1, 134.2, 127.7, 114.2, 55.3; IR (CHCl\(_3\)): 3154, 2958, 1730, 1608, 1500, 1465, 998, 730 cm\(^{-1}\)

4,4'-Dichloro-1,1'-biphenyl, 2d\(^1\): Colourless solid, mp 147-149 °C; yield 92%, $R_f = 0.6(100\%$ hexanes).  \(^1\)H NMR (300 MHz, CDCl\(_3\)): $\delta$= 7.36-7.52 (m, 8H);  \(^1\)C NMR (75 MHz, CDCl\(_3\)): $\delta$ = 138.4, 133.7, 129.0, 128.2; IR (CHCl\(_3\)): 2924, 1642, 1465, 1091, 1004, 851, 815, 723 cm\(^{-1}\)

4,4'-Dibromo-1,1'-biphenyl, 2e\(^1\): Colourless solid, mp 163-165 °C; yield 92%, $R_f = 0.63 (100\%$ hexanes).  \(^1\)H NMR (300 MHz, CDCl\(_3\)): $\delta$= 7.49 (d, $J$=8.2 Hz, 4H), 7.31 (d, $J$=8.2 Hz, 4H), 2.51 (s, 6H);  \(^1\)C NMR (75 MHz, CDCl\(_3\)): $\delta$ = 138.9, 132.0, 128.5, 121.9; IR (CHCl\(_3\)): 3015, 2924, 1903, 1467, 1382, 1067, 996, 720 cm\(^{-1}\)

[1,1'-Biphenyl]-4,4'-dicarbaldehyde, 2f\(^2\): Colourless solid, mp148-149 °C; yield 86%, $R_f = 0.63 (100\%$ hexanes).  \(^1\)H NMR (300 MHz, CDCl\(_3\)): $\delta$= 10.09 (s, 2H), 8.00 (d, $J$=8.2 Hz, 4H), 7.80 (d, $J$=8.2 Hz, 4H);  \(^1\)C NMR (75 MHz, CDCl\(_3\)): $\delta$ = 191.7, 145.6, 135.9, 130.4, 128.0; IR (CHCl\(_3\)): 2956.6, 2853.5, 1727.9,1604, 1093, 1023, 813.6 cm\(^{-1}\)
**3,3'-Dinitro-1,1'-biphenyl, 2g**^1^: Yellow solid, mp 200-203 °C; yield 94%, R_f = 0.25 (10% EtOAc in hexanes). ^1^H NMR (300 MHz, CDCl_3): δ = 8.50 (br s, 2H), 8.3 (d, J=8.1 Hz, 2H), 7.98 (d, J=7.7 Hz, 2H), 7.71 (t, J=7.9 Hz, 2H); ^13^C NMR (75 MHz, CDCl_3): δ = 148.9, 140.3, 133.1, 130.3, 123.3, 122.1; IR (CHCl_3): 3068, 2924, 1718, 1530, 1459, 1347, 1021, 743 cm⁻¹

**2,2'-Dinitro-1,1'-biphenyl, 2h**^3^: Yellow colour solid, mp 122-126 °C; yield 94%, R_f = 0.26 (10% EtOAc in hexanes). ^1^H NMR (300 MHz, CDCl_3): δ = 8.22 (d, J=8.1 Hz, 2H), 7.69 (t, J=7.3 Hz, 2H), 7.60 (t, J=7.3 Hz, 2H), 7.30 (d, J=7.4 Hz, 2H); ^13^C NMR (75 MHz, CDCl_3): δ = 147.2, 134.2, 133.4, 130.9, 129.1, 124.8; IR (CHCl_3): 3070.5, 2957.5, 1719.1, 1606.8, 1520.2, 1467, 1298, 743 cm⁻¹

**4,4'-Bis(methylthio)-1,1'-biphenyl, 2i**^4^: Very light yellow colour solid, mp 183-185 °C; yield 94%, R_f = 0.3 (100% hexanes). ^1^H NMR (300 MHz, CDCl_3): δ = 8.22 (d, J=8.1 Hz, 2H), 7.69 (t, J=7.3 Hz, 2H), 7.60 (t, J=7.3 Hz, 2H), 7.30 (d, J=7.4 Hz, 2H); ^13^C NMR (75 MHz, CDCl_3): δ = 137.5, 137.3, 127.1, 127.0, 15.9; IR (CHCl_3): 3079, 2916, 2855, 1596, 1478, 907, 733 cm⁻¹

**5,5'-Bibenzo[d][1,3]dioxole, 2j**^5^: Colourless solid, mp 144-146 °C; yield 94%, R_f = 0.63 (10% EtOAc in hexanes). ^1^H NMR (300 MHz, CDCl_3): δ = 6.73-6.94 (m, 6H), 5.91 (s, 4H); ^13^C NMR (75 MHz, CDCl_3): δ = 148.0, 146.8, 135.4, 120.3, 108.5, 107.5, 101.1; IR (CHCl_3): 2925, 1729, 1608, 1476, 1235, 1177, 1038, 932, 740 cm⁻¹

**4,4'-Bis(phenoxymethyl)-1,1'-biphenyl, 2k**^6^: Colourless solid, mp 151-153 °C; yield 90%, R_f = 0.54 (100% hexanes). ^1^H NMR (300 MHz, CDCl_3): δ = 6.81-7.42 (m, 18H), 4.96 (s, 4H); ^13^C NMR (75 MHz, CDCl_3): δ = 158.8, 137.2, 129.6, 128.6, 127.9, 127.5, 121.0, 114.9, 69.9; IR (CHCl_3): 3033, 2925, 1730, 1598, 1496, 1421, 1153, 1029, 752 cm⁻¹

**1,1'-Binaphthalene, 2l**^7^: Colourless solid, mp 157-158 °C; yield 94%, R_f = 0.58 (100% hexanes). ^1^H NMR (300 MHz, CDCl_3): δ = 6.90-8.13 (m, 14H); ^13^C NMR (75 MHz, CDCl_3): δ = 138.4, 133.5, 128.2, 127.9, 127.8, 126.6, 125.9, 125.8, 125.4; IR (CHCl_3): 3057.3, 2924.3, 1590.9, 1459.3, 1258.6, 1017.9, 911.7, 737 cm⁻¹
2b
References