

## Supporting Information

### **Carbocatalytic Reductive Coupling Reactions via Electron Transfer from Graphene to Aryldiazonium Salt**

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#### **General information**

ESR spectra were measured by JEOL JES-X320. XPS spectra were measured by JEOL JPS-9030 with pass energy 50 and 20 eV, survey and narrow respectively. GC analyses were carried out by Shimadzu GC-2014 equipped with FID detector. Elemental analyses were performed by PERKINELMER 2400II. EDX analysis was performed by JEOL JSM-IT100. Freeze-drying of GO and rGO was performed by ADVANTEC DRZ350WC.

#### **Preparation of GO**

Graphite (12.0 g) was stirred in 95% wt.%  $\text{H}_2\text{SO}_4$  (300 mL).  $\text{KMnO}_4$  (36.0 g) was gradually added to the solution while keeping the temperature  $<10^\circ\text{C}$  using an ice bath. The mixture was then stirred at  $35^\circ\text{C}$  for 2 h. The resulting mixture was diluted with water (300 mL) under vigorous stirring and cooling so that the temperature did not exceed  $50^\circ\text{C}$ . The suspension was further treated with 30% wt.% aq.  $\text{H}_2\text{O}_2$  (30 mL). The resulting suspension was purified by repeated centrifugation with water.

#### **Preparation of rGO<sub>H</sub>**

GO (2.0 g) was dispersed in water (200 mL), then hydrazine monohydrate (2.0 mL) was added and stirred at  $90^\circ\text{C}$  for 2 h. After cooling, rGO<sub>H</sub> was purified by washing with water, and freeze-dried.

#### **Preparation of rGO<sub>B</sub>**

GO (1.0 g) was dispersed in water (170 mL). NaOH (6.7 g) was added into the GO dispersion. The mixture was refluxed for 2 h. Subsequently, the base-treated GO was filtrated and re-dispersed in water (170 mL). Then, 37% aq. HCl (16.7 mL) was added into the dispersion. The mixture was refluxed for another 2 h. rGO<sub>B</sub> was filtered, washed by water and acetone, and freeze-dried.

### **Preparation of rGO<sub>T</sub>**

Freeze-dried GO was put into an electric furnace and heated at 300 °C for overnight. During the heating, exfoliation of GO occurred. As obtained rGO<sub>T</sub> was used without purification.

### **Typical procedure for Table 1**

To the dispersion of DMSO (2.0 mL), furan (218.2 µL, 3.0 mmol) and carbon catalyst (10.0 mg), was added DMSO solution (1.0 mL) of 4-bromodiazonium tetrafluoroborate (81.2 mg, 0.3 mmol) dropwise at room temperature. The reaction mixture was stirred for 6 h at 40 °C under Ar atmosphere. After the reaction, the reaction mixture was analyzed by GC using *n*-dodecane as an internal standard.

### **Typical procedure for Table 2**

To the dispersion of DMSO (4.0 mL), furans, thiophene or *N*-Boc-pyrrole (6.0 mmol) and rGO<sub>B</sub> (20.0 mg), was added DMSO solution (2.0 mL) of arylziazonium tetrafluoroborate (0.6 mmol) dropwise at room temperature. The reaction mixture was stirred for 6 h at 40 °C under Ar atmosphere. The reaction mixture was poured into a mixture of Et<sub>2</sub>O and water. The Et<sub>2</sub>O layer was extracted and washed with water twice. Anhydrous MgSO<sub>4</sub> was added to the resulting solution, and filtrated. Then, the mixture was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography (10:1 hexane/ethyl acetate) to give the product.

### **Oxidative coupling of 3,4-dimethoxytoluene**

The dispersion of 1,2-dichloroethane (2.0 mL), GO (100 mg), 3,4-dimethoxytoluene (479 µL, 3.0 mmol) and boron trifluoride diethyl etherate (380 µL, 3.0 mmol) were reacted under Ar atmosphere at 60 °C for 8 h. After the reaction, the reaction mixture was filtrated and the recovered GO was washed with ethyl acetate and water. The resulting solution was analyzed by GC using *n*-dodecane as an internal standard (64% yield). Recovered GO was dried under reduced pressure at 50 °C and the weight of recovered GO was 70.2 mg.

### **Reductive coupling using the recovered GO from the oxidative coupling reaction**

To the dispersion of DMSO (14 mL), furan (1.5 mL, 21 mmol) and the recovered GO

(70.2 mg), was added DMSO solution (7.0 mL) of 4-bromodiazonium tetrafluoroborate (569 mg, 2.1 mmol) at room temperature. The reaction mixture was stirred for 6 h at 40 °C under Ar atmosphere. After the reaction, the reaction mixture was analyzed by GC using *n*-dodecane as an internal standard (58% yield).

#### **ESR measurements for carbon samples.**

ESR measurements were performed with an ESR at room temperature for samples sealed in a quartz sample tube. Mn<sup>2+</sup> marker, standard, was measured with sample to calculate accurate g-value and to correct magnetic field. Typical spectrometer parameters were shown as below.

Microwave power: 1 mW.

Microwave Freq.: 9.433 GHz.

Scan time: 2 min.

Magnetic Field:  $335.7 \pm 15$  mT.

Modulation Freq.: 100 kHz.

Modulation width: 0.1 mT.

Receiver gain: 10\*2.or 50

Time constant: 0.1 s.

#### **Typical procedure for spin trap experiment**

rGO<sub>B</sub> (3.0 mg) was added to the mixture solution of DMSO (200 μL), DMPO (20 μL) and phenyldiazonium tetrafluoroborate (19.1 mg, 0.3 mmol). Then, the reaction mixture was filtrated using PTFE membrane filter, and ESR spectra for the resulting solution was measured. Spectrometer parameters were shown as below.

Microwavepower: 1 mW.

Microwave Freq.: 9.431 GHz.

Scan time: 1 min.

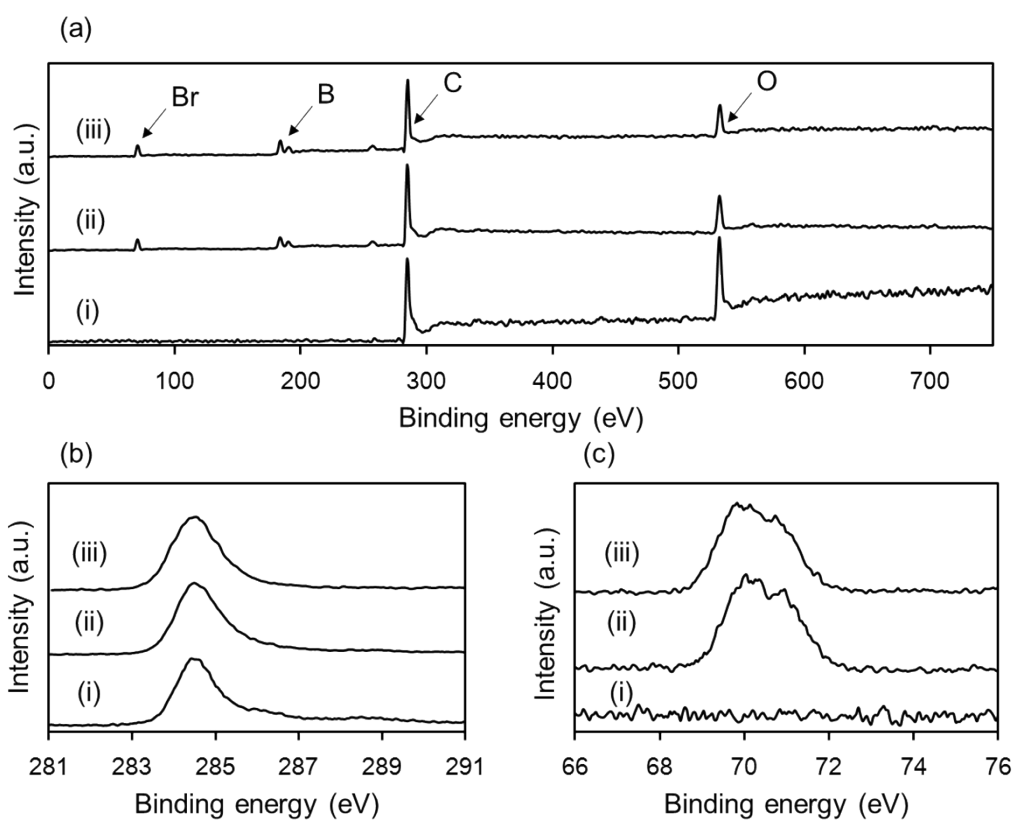
Modulationamplitude: 0.1 mT.

Modulation Freq.: 100 kHz.

Receiver gain: 10\*2.

Time constant: 0.03.

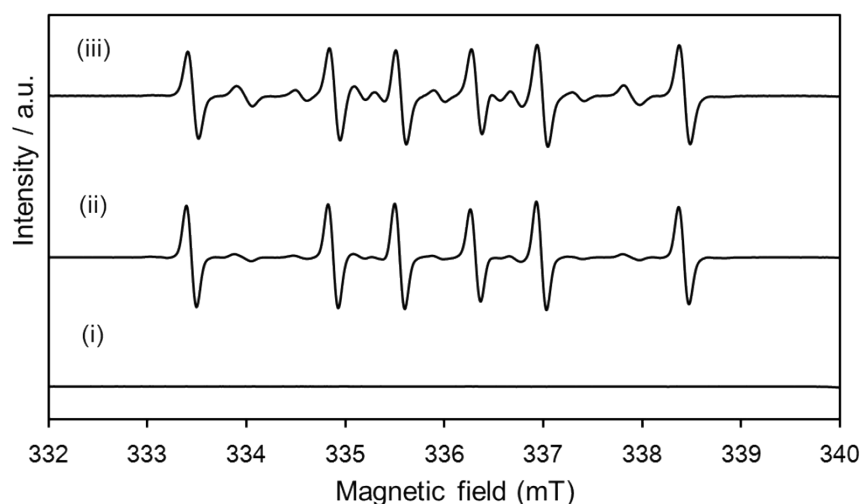
#### **Additional Figures and Tables.**



**Figure S1.** (a) XPS survey analysis, (b) C 1s analysis, and (c) Br 3p analysis of (i) rGO<sub>B</sub>, (ii) rGO<sub>B</sub> after 1st cycle, and (iii) rGO<sub>B</sub> after 5th cycle.

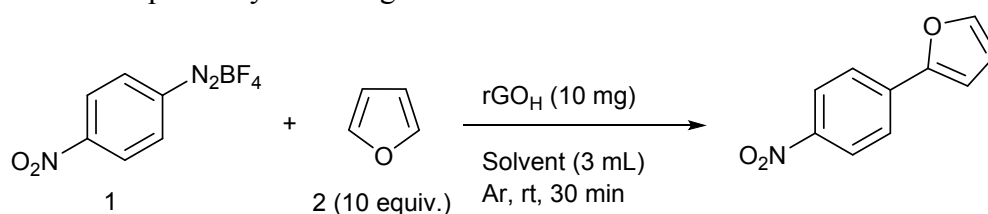
**Table S1.** Elemental analysis of rGO<sub>B</sub> before and after the reactions by EDX.

Sample	C at%	O at%	Br at%	S w%
rGO <sub>B</sub>	79.8	20.2	0	0
rGO <sub>B</sub> after 1 <sup>st</sup> cycle	85.5	9.5	4.3	0.7
rGO <sub>B</sub> after 5 <sup>th</sup> cycle	86.6	8.3	4.3	0.8

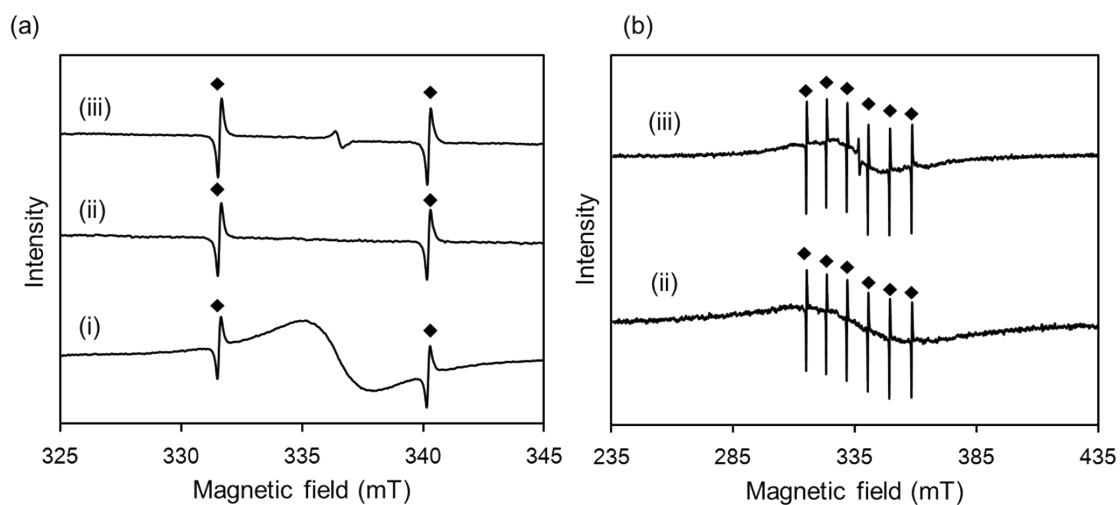


**Figure S2.** ESR spectra for the spin trap experiment using DMPO. (i) rGO<sub>B</sub> + DMSO, (ii) rGO<sub>B</sub> + phenyldiazonium tetrafluoroborate + DMSO, and (iii) rGO<sub>B</sub> + phenyldiazonium tetrafluoroborate + furan + DMSO. Stable DMPO adducts were observed when phenyldiazonium tetrafluoroborate was used, suggesting that the reaction pass through the radical intermediate.

**Table S2.** Exploratory screening of the reaction conditions.



Entry	Solvent (3 mL)	Yield (%)	Entry	DMSO (mL)	Yield (%)
1	EtOH/H <sub>2</sub> O	23	1	1	46
2	Acetone/H <sub>2</sub> O	33	2	1.5	49
3	DMF	32	3	2	54
4	DMA	37	4	3	58
5	DMSO	58	5	6	45



**Figure S3.** ESR spectra of (i) rGO<sub>B</sub>, (ii) rGO<sub>H</sub>, and (iii) GO. (a) Narrow range and (b) wide range. Signals marked by ◆ are derived from Mn<sup>2+</sup> marker. From narrow range analysis, rGO<sub>T</sub> seems to have no radical, however wide range analysis revealed that GO and rGO<sub>T</sub> have quite broad signals. The amount of spin was calculated using the areas of these broad signals.

**Table S3.** Number of spins calculated from the area of ESR spectra (Figure S2) and the amount of sample used for the ESR analysis.

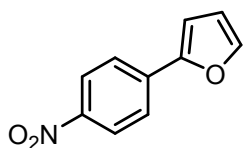
Sample	Number of spins / g
rGO <sub>B</sub>	$2 \times 10^{17}$
rGO <sub>B</sub> after 1 <sup>st</sup> cycle	$1.9 \times 10^{19}$
rGO <sub>B</sub> after 5 <sup>th</sup> cycle	$1.0 \times 10^{19}$
GO	$2.3 \times 10^{17}$

**Table S4.** Elemental analysis of GO and rGOs.

	C (w%)	H (w%)	N (w%)	S (w%)
GO	43.8	1.9	0	6.0
rGO <sub>B</sub>	67.0	2.2	0	0
rGO <sub>H</sub>	73.2	1.8	3.2	0
rGO <sub>T</sub>	68.0	1.9	0	0

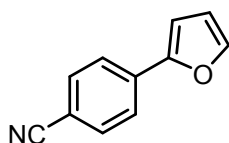
**Product data**

2-(4-Nitrophenyl)-furan<sup>1</sup>



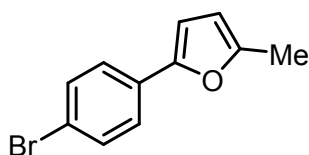
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 1.7 Hz, 1H), 6.88 (d, *J* = 3.4 Hz, 1H), 6.56 (dd, *J* = 3.4, 1.7 Hz, 1H)

2-(4-cyanophenyl)-furan<sup>1</sup>



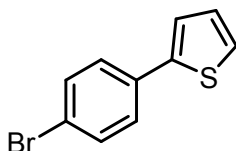
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 1.7 Hz, 1H), 6.81 (d, *J* = 3.4 Hz, 1H), 6.53 (dd, *J* = 3.4, 1.7 Hz, 1H)

2-(4-Bromophenyl)-5-methylfuran<sup>2</sup>



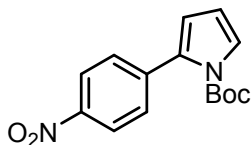
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.45 (m, 4H), 6.54 (d,  $J = 3.2$  Hz, 1H), 6.05 (dq,  $J = 3.2, 0.9$  Hz, 1H), 2.36-2.35 (d,  $J = 0.9$  Hz, 3H)

2-(4-Bromophenyl)-thiophene<sup>3</sup>



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.45 (m, 4H), 7.30 (d,  $J = 4.3$  Hz, 2H), 7.08 (dd,  $J = 4.3, 4.3$  Hz, 1H)

2-(4-Nitrophenyl)-1*H*-pyrrole-1-carboxylic acid 1,1-dimethylethyl ester<sup>1</sup>



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d,  $J = 8.9$  Hz, 2H), 7.51 (d,  $J = 8.9$  Hz, 2H), 7.41 (dd,  $J = 3.3, 1.7$  Hz, 1H), 6.32 (dd,  $J = 3.4, 1.7$  Hz, 1H), 6.27 (dd,  $J = 3.4, 3.3$  Hz, 1H), 1.43 (s, 9H)

Reference

1. M. D. Perretti, D. M. Monzón, F. P. Crisóstomo, V. S. Martína and R. Carrillo, *Chem. Commun.*, 2016, **52**, 9036.
2. T. J. Donohoe and J. F. Bower, *PNAS*, 2010, **107**, 3373.
3. L. Zhi, H. Zhang, Z. Yang, W. Liu and B. Wang, *Chem. Commun.*, 2016, **52**, 6431.