Supplementary Information (SI) for:

Graphene oxide as a recyclable phase transfer catalyst

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References
1. General
All chemicals used in this study were obtained from commercial sources and used without further purification. The organocatalysts examined in this study were prepared according to the literature procedure. The chromatographic purification of the products was conducted by flash chromatography using Merck silica gel 60 (230–400 mesh). Thin-layer chromatography was conducted on Merck silica gel 60F plates.

1.1 Materials
Natural graphite (Bay Carbon, SP-1 graphite), sulfuric acid (95-97%), hydrogen peroxide (30 wt.%), potassium permanganate, sodium nitrate, potassium hydroxide, sodium hydroxide, and cesium hydroxide were obtained from commercial sources and used as received.

2. General Procedure for GO preparation
GO was prepared from natural graphite powder by the modified Hummers and Offenman’s method using sulfuric acid, potassium permanganate, and sodium nitrate. ¹

2.1 Characterization
Raman spectroscopy measurements were taken using a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (514 nm). X-ray photoemission spectroscopy (XPS) measurements were made by a SIGMA PROBE (ThermoVG, U.K.) with a monochromatic Al-Kα X-ray source at 100 W.

![Raman spectra of GO](image)

**Figure S1.** Raman spectra of GO.
Figure S2. XPS of GO.

Figure S3. High-resolution C1s sectra of GO.

Figure S4. AFM image of GO.
Figure S5. GO Phase-transfer catalyst in the Michael addition reaction.

Table S1 Recycling of graphene oxide as a Michael addition catalyst

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*All cycles were carried out with 1a (25 mg, 0.1676 mmol), 2 (1.5 equiv.), KOH (1.1 equiv.), and 0.5 mg ml⁻¹ GO aqueous (0.5 ml) in MC (1 ml).

3. General procedure for the Michael Addition

Graphene oxide was dispersed in DI water to make concentration of 0.5 mg/ml and potassium hydroxide (10.3 mg, 1.1 equiv.) as a base was added to 0.5 ml of this solution. And then was added to mixture of MC solution which included reactants, trans-β-nitrostyrene (1a, 25 mg, 0.1676 mmol, 1 equiv.), and 2,4-pentanedione (2, 0.03ml, 1.5 equiv.) in a 5 ml vial. The reaction mixture was vigorously stirred by using one magnetic bar at a stirring speed of 900 rpm at room temperature. After completion of the reaction, which was monitored by TLC, an
aqueous HCl solution (1 N, 1 mL) was added to quench the reaction and then extracted with CH$_2$Cl$_2$ (3 x 5 mL). The combined organic phase was washed with water and dried over anhydrous Na$_2$SO$_4$, and the solvent was concentrated. The obtained crude product was purified by column chromatography on silica gel to afford the Michael addition product 3a. After the reaction was over the used GO was recovered by simple filtration and washing with MC using nylon membrane filter, 0.45µm pore size. The residual part was then dried by vacuum desiccator for several hours in order to recover GO.

4. Product Characterization

![3a](image)

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 3a as a white solid (83% yield). Analytical data was matched with previously reported values. $^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): δ 7.26-7.19 (m, 3H), 7.12-7.10 (m, 2H), 4.58-4.55 (m, 2H), 4.30 (d, 1H, $J = 10.5$ Hz), 4.21-4.17 (m, 1H), 2.23 (s, 3H), 1.87 (s, 3H); HPLC (AD-H, Hexane : iPrOH = 90 : 10, 1.0 mL/min, 220 nm): $t_{\text{major}} = 10.5$ min, $t_{\text{minor}} = 14.1$ min; ~7% ee.

**Configuration assignment:** The absolute stereochemistry was assigned as (R) by comparison of the retention time of HPLC with the literature data.$^2$

![3b](image)

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 3b as a white solid (80% yield). Analytical data was matched with previously reported values. $^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): δ 7.20-6.97 (m 4H), 4.54-4.52 (m, 2H), 4.28 (d, $J = 10.8$ Hz, 1H), 4.17-4.11 (m, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 1.86 (s, 3H)$^2$

![3c](image)

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 3c as a white solid (77% yield). Analytical data was matched with previously reported values. $^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): δ 7.03 (d, $J = 8.7$ Hz, 3H), 6.76 (d, $3J = 8.7$ Hz, 2H), 4.53-4.51 (m, 2H), 4.23 (d, $J = 11.1$ Hz, 1H), 4.16-4.08 (m, 1H), 3.69 (s, 3H), 2.19 (s, 3H), 1.86 (s, 3H)$^3$
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 3d as a white solid (69% yield). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.13 - 7.09 (m, 2H), 6.97 - 6.91 (m, 2H), 4.58 - 4.49 (m, 2H), 4.27 (d, $J = 10.8$, 1H), 4.21 - 4.13 (m, 1H), 2.20 (s, 3H), 1.89 (s, 3H)

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 3e as a white solid (79% yield). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.23 (d, $J = 8.4$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 4.55 (d, $J = 6.3$ Hz, 2H), 4.14 (d, $J = 10.5$ Hz, 1H), 4.20 - 4.12 (m, 1H), 2.20 (s, 3H), 1.90 (s, 3H)

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 3f as a white solid (75% yield). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.46 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 4.62 (d, $J = 6.3$ Hz, 2H), 4.25 (d, $J = 6.0$ Hz, 1H), 4.26 - 4.18 (m, 1H), 2.29 (s, 3H), 1.98 (s, 3H)

Purification by column chromatography (4:1 = Hexane : EtOAc) afforded 3g as a white solid (78% yield). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.28 - 7.23 (m, 1H), 6.93 - 6.89 (m, 2H), 4.68 - 4.66 (m, 2H), 4.58 - 4.51 (m, 1H), 4.40 (d, $J = 9.9$ Hz, 1H), 2.29 (s, 3H), 2.07 (s, 3H)
Purification by column chromatography (5 : 1 = Hexane : Acetone) afforded 5a as a white solid (80% yield). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.32-7.27 (m, 3H), 7.18-7.15 (m, 2H), 4.71-4.60 (m, 2H), 4.35-4.23 (m, 2H), 2.65-2.44 (m, 2H), 2.38-2.25 (m, 1H), 2.20-2.04 (m, 1H), 1.07 (t, $J$ = 7.2 Hz, 3H), 0.78 (t, $J$ = 7.2 Hz, 3H)$^2$

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 5b as a white solid (50% yield). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.33-7.21 (m, 5H), 4.96-4.83 (m, 2H), 4.24 (td, $J$ = 8.8, 5.7 Hz, 1H), 3.86 (d, $J$ = 9.2 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H)$^2$

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 5c as a white solid (79% yield, 1 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.33-7.25 (m, 3H), 7.21-7.18 (m, 2H), 4.83-4.81 (m, 1 H), 4.78-4.76 (m, 1 H), 4.29-4.17 (m, 1 H), 4.12 (d, $J$ = 9.6 Hz, 0.5 H), 4.03 (d, $J$ = 9.6 Hz, 0.5 H), 3.77-3.53 (s, 3H), 2.29-2.05 (s, 3H); dr = 1 : 1 (determined by integration of $^1$H NMR)$^2$

Purification by column chromatography (5 : 1 = Hexane : Acetone) afforded 5d as a white solid. Analytical data was matched with previously reported values (80% yield, 1.5:1 mixture of diastereomers).

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.32-7.27 (m, 3H), 7.22-7.19 (m, 2H), 4.89-4.76 (m, 2H), 4.26-4.18 (m, 2 H), 4.12 (d, $J$ = 9.9 Hz, 0.6H) 4.03 (d, 0.4 H, $J$ = 9.9 Hz), 3.96 (q, 1H, $J$ = 7.2 Hz), 2.30-2.05 (s, 3H), 1.28-1.00 (t, $J$ = 7.2 Hz, 4H); dr = 1.5 : 1 (determined by integration of $^1$H
Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 5e as a white solid (83% yield, 4.9 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.34-7.29 (m, 3H), 7.25-7.20 (m, 2H), 4.85-4.82 (m 0.4H), 4.77-4.65 (m, 2H), 4.23-4.10 (m, 1H), 4.03 (d, J = 10.2 Hz, 0.83H), 3.92 (d, J = 10.2 Hz, 0.17H), 2.30-2.06 (s, 3H), 1.47 - 1.11 (s, 9H)$^2$

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded 5f as a white solid (66% yield, 7.3 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.24-7.34 (m, 5H), 5.01 (dd, J = 11.1, 13.2 Hz, 0.12H), 4.86 (dd, J = 11.4 Hz and J = 13.5 Hz, 0.88H), 4.60-4.51 (dd, J = 3.9 Hz and 13.2 Hz, 1H), 4.39-4.28 (dd, J = 3.9 and J = 11.1 Hz, 1H), 2.61-2.54 (m, 1H), 2.33 (s, 3H), 2.26-2.14 (m, 1H), 2.03-1.93 (m, 1H), 1.80-1.65 (m, 3H); dr = 7.3 : 1 (determined by integration of $^1$H NMR)$^2$

Purification by column chromatography (4:1 = Hexane : EtOAc) afforded 5g as a colorless oil (82% yield, 99:1 mixture of diastereomers). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 7.31-7.23 (m, 5H), 5.17 (dd, J = 4.2 and 13.5 Hz, 1H), 5.01 (dd, J = 10.8 Hz and J = 13.5Hz, 1H), 4.08 (dd, J = 3.9 Hz and 10.8 Hz, 1H), 3.75 (s, 3H), 2.40-2.32 (m, 2H), 2.05-1.82 (m, 4H); dr >99 : 1 (determined by integration of $^1$H NMR)$^2$
Purification by column chromatography (4:1 = Hexane : EtOAc) afforded 5h as a colorless oil (81% yield, 99:1 mixture of diastereomers). Analytical data was matched with previously reported values.

$^1$H NMR (300 MHz, CDCl$_3$, Me$_4$Si): δ 7.34-7.27 (m, 5H), 5.18 (dd, J = 3.9 and 13.6 Hz, 1H), 5.01 (dd, J = 10.9 and 13.5Hz, 1H), 4.24-4.17 (m, 1H), 4.08 (dd, J = 3.9 and 10.9Hz, 1H), 2.40-2.32 (m, 2H), 2.07-1.74 (m, 4H), 1.27 (t, J = 7.1Hz, 1H); dr >99 : 1 (determined by integration of $^1$H NMR)$^2$

5. $^1$H NMR Spectra for Table 2

3a (Entry 1, Table 3)
(a) Product by GO PTC

![Graph](image1.png)

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(b) Product by CE and only base

![Graph](image2.png)

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(a) Enantiomeric selective property of 3a product with the GO PTC and it showed ~7% enantiomeric excess. (b) The CE PTC product and only base treated product were racemic in comparison to GO PTC product. The 2D template structure of GO helps to get an enantiomerically selective product even though the ee value is not high. Now our current work is focused on improving the yield and enantiomeric selectivity of GO PTC product.
3b (Entry 2, Table 3)

3c (Entry 3, Table 3)
3d (Entry 4, Table 3)

3e (Entry 5, Table 3)
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3f (Entry 6, Table 3)

3g (Entry 7, Table 3)
6. $^1$H NMR Spectra for Table 4

5a (Entry 1, Table 4)

5b (Entry 2, Table 4)
5c (Entry 3, Table 4)

5d (Entry 4, Table 4)
5e (Entry 5, Table 4)

5f (Entry 6, Table 4)
5g (Entry 7, Table 4)

5h (Entry 8, Table 4)
Reference
