

# Graphene Oxide Catalyzed Ketone $\alpha$ -Alkylation with Alkenes: Enhancement of Graphene Oxide Activity by Hydrogen Bonding

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## **Materials**

All materials used in the manuscript have been purchased from commercial suppliers and used without further purification. All starting materials reported in the manuscript have been previously described in literature and are commercially available. Synthetic graphite powder (Sigma Aldrich,  $\leq 20$   $\mu\text{m}$  lateral size), sulfuric acid (PharmcoAper, ACS grade 95-98%), nitric acid (BDH, ACS grade 69-70%), potassium permanganate (Sigma Aldrich, ACS grade), hydrogen peroxide (BDH, 35 w/w %), Whatman filter paper (grade 5, 47 mm), hydrochloric acid (BDH, ACS grade 36.5-38.0%).

### **Preparation of Graphene Oxide (GO)**

Graphene oxide (GO) was synthesized by Hummer's method with subtle modification in the chemical recipe.<sup>1,2</sup> In brief, the graphite powder (2 g, Sigma Aldrich, < 20  $\mu\text{m}$ ) was mixed with 55 mL of sulfuric acid (PharmcoAAPER, ACS grade 95-98%) in a 250 mL flask. The mixture was stirred in an ice bath for 15 min. After that, 12 mL of nitric acid (BDH, ACS grade 69-70%) was added to the mixture and stirring was continued for another 15 minutes using an ice bath to cool the reaction mixture. Then, a total of 10 g of  $\text{KMnO}_4$  (Sigma Aldrich, ACS grade) was added in a small portion-wise fashion (total of 6 portions), while stirring the reaction mixture in an ice bath. After 2 hours of stirring in an ice bath, the mixture was stirred in water bath at 45  $^{\circ}\text{C}$  for 6 hours to complete the oxidation of graphite. Then, the reaction was quenched by pouring the mixture into 500 mL of ice containing 10 mL of  $\text{H}_2\text{O}_2$  (BDH, 35 w/w%). The resulting mixture was filtered through a filter paper (Whatman, grade 5 with a diameter of 47 mm). The resulting brown solid filter cake was re-suspended in ~4% HCl aqueous solution and washed with HCl solution with the same concentration 5 times by centrifugation at 8000 rpm for 30 minutes and the supernatant was carefully decanted. The washing procedure was performed 10 times with acetone by centrifugation at 10000 rpm for 45 minutes. Finally, the precipitate was dried in vacuum oven for 3 days before further use.

### **Preparation of Reduced Graphene Oxide (rGO)**

It has been reported the microwave irradiation is a very efficient and quick heating approach to fabricate rGO.<sup>3</sup> In this work, synthesis of the rGO material was performed according to the following procedure: 500 mg of GO powder obtained as described above was placed in a round bottomed flask (100 mL) and heated in a microwave reactor (CEM Discover SP, 300 Watts) for 30 seconds. This procedure was performed in a fume hood using a condenser (attached to the neck of the round bottom flask) to release any gaseous species that was generated during the microwave heating of GO. After microwave heating, the brown colored GO powder was reduced to give black and fluffy rGO powder.

### **Preparation of Holey Graphene Oxide (h-GO)**

The h-GO material was fabricated following the published protocol.<sup>4</sup> In brief, an ice cooled mixture of graphite powder (20 mg), 98% sulfuric acid (8 mL), 70% nitric acid (2 mL) and KMnO<sub>4</sub> (100 mg, ACS grade) was heated in a microwave reactor (CEM DiscoverSP, 300Watts) for 40 seconds. After microwave heating, the reaction mixture was transferred to a beaker containing 200 mL of ice and 5 mL of 35% H<sub>2</sub>O<sub>2</sub>. The quenched reaction mixture was filtered using polycarbonate filter paper (0.2  $\mu$ m pore size), and the product was washed with dilute hydrochloric acid (4%), deionized water, and ethanol (95%). After cleaning, the product was dried under vacuum at room temperature for 3 days before any catalytic testing.

### **Purification of GO**

We extensively clean our GO catalysts with H<sub>2</sub>O<sub>2</sub>, HCl and then acetone to remove any possible acid/metal impurities.<sup>1,2,4</sup> XPS and AAS analysis confirms that our GO catalysts do not contain any acid and metal impurities to the detection level (see below). We have specifically avoided using base wash in our cleaning procedures to avoid any changes of the functional groups on the GO during base wash. Literature reports indicate that base wash could result in epoxy group ring opening, even eliminating some functional groups, and reduction of GO. We routinely performed XPS (X-ray photoelectron spectroscopy) and AAS (atomic absorption spectroscopy) measurements to determine if trace quantities of transition metals were involved in the ketone alkylation reactions. XPS analysis indicated less than 50 ppm of trace metal contaminants (detection limit). AAS analysis indicated less than 1 ppm of trace metal contaminants for the following metals: Mn <0.20 ppm, Fe <0.60 ppm, Cu <0.30 ppm, Cd <0.20 ppm, Zn <0.10 ppm, Ni <1.0ppm, Pb <1.0 ppm, Au < 1.0 ppm) as determined by comparison with standard metal ion solutions (detection limit). These results support metal-free carbocatalyzed process and indicate that our extensive purification process excludes the presence of metallic impurities.

### Elemental Analysis of GO

The elemental composition change of the GO catalyst was studied before and after the alkylation reactions (GO recovered after the alkylation reactions is referred to as ‘recovered GO’) by energy dispersive X-ray spectroscopy (EDXS) and X-ray photoelectron microscopy (XPS). For elemental analysis, GO was recovered by filtration from the reaction mixture and cleaned by subsequent washes with ethanol and water. The EDXS and XPS samples were prepared by drop casting GO and recovered GO on conductive copper tape and gold-coated silicon substrate for EDAX and XPS, respectively. Both XPS and EDXS data support the conclusion that oxygen containing functional groups are largely maintained in the recovered GO. The results are shown in Table SI-1, Table SI-2, Table SI-3, Table-SI-4, Figure SI-1, Figure SI-2, Figure SI-3. Note that sulfur (S) was present as sulfate functional group in GO and recovered GO catalyst. S species in all samples were found with S2p<sub>3/2</sub> between 168-169 eV, attributed to sulfate groups, with various amounts ranging from 1-6%. Due to the low signal to noise ratio, peak positions and percentages of S may suffer from errors.

**Table SI-1.** Summary of Elemental Analysis of GO and Recovered GO Catalyst.

Catalyst	EDXS measurement				XPS measurement			
	Atomic %	Atomic %	Atomic %	C/O	Atomic %	Atomic %	Atomic %	C/O
	C	O	S		C	O	S	
GO	64.6	34.0	1.3	1.9	67.9	31.4	0.7	2.2
Recovered								
GO	66.9	32.0	1.0	2.1	70.2	29.3	0.5	2.4

**Table SI-2.** Summary of Elemental Analysis of GO and Recovered GO Catalyst before and after the Reactions in Presence and Absence of Olefin and Ketone Substrates.

XPS measurement				
Catalyst	Atomic % C	Atomic % O	Atomic % S	C/O
GO	67.9	31.4	0.7	2.2
GO + Olefin Substrate	71.8	22.2	6.1	3.2
GO + Ketone Substrate	64.9	32.0	5.1	2.0
GO Without Any Substrate	60.5	34.5	3.0	1.8

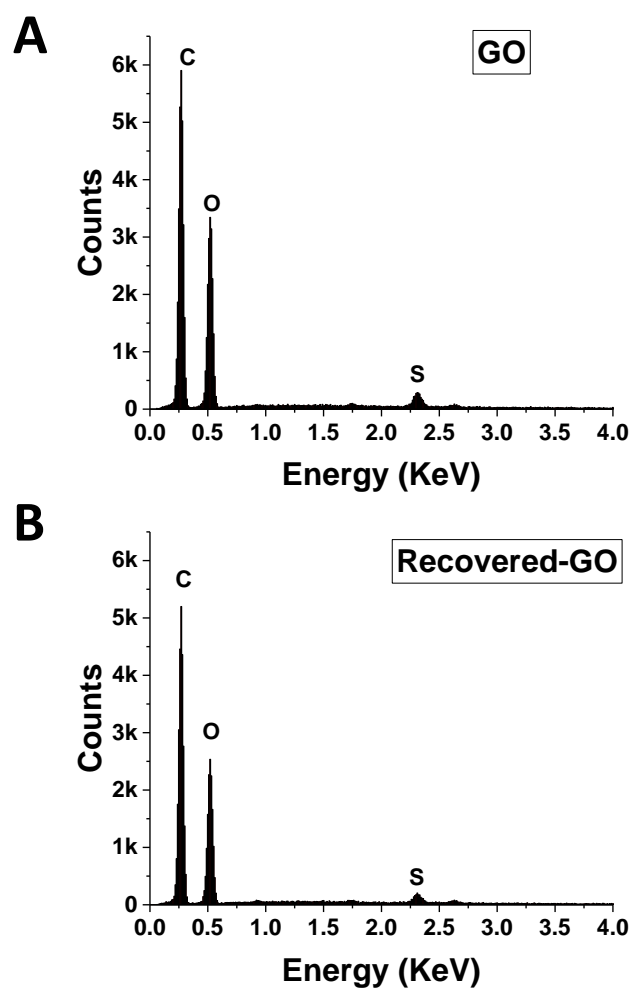


**Table SI-3.** The Calculated Relative % of Different Types of Carbon from the Deconvolution of XPS High Resolution C1s Peak in GO and Recovered GO Catalyst and GO Catalyst after the Reactions in Presence and Absence of Olefin and Ketone Substrates.

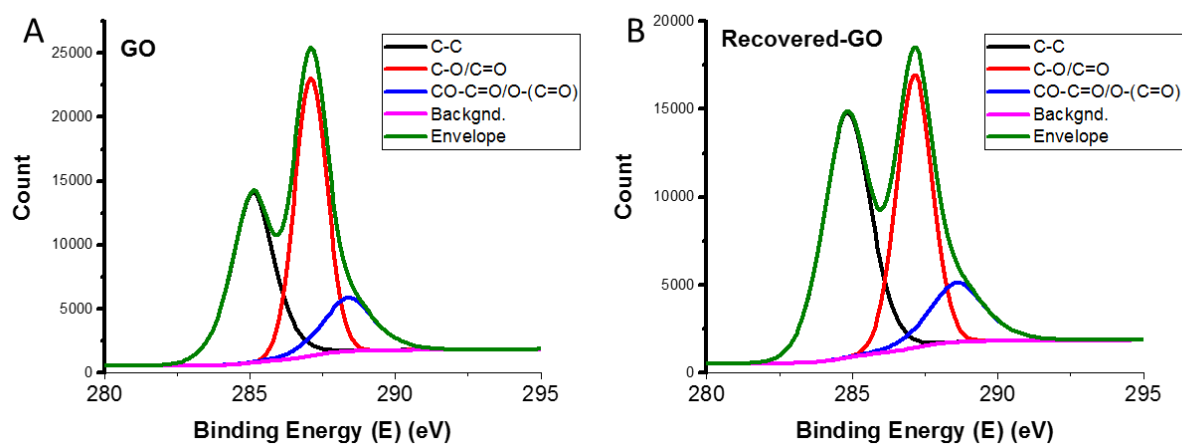
Sample	% C-C (284.28 eV)	% C-O/C=O (286.56 eV)	% CO-C=O/O-(C=O)-O (288.65 eV)
GO	26.8	30.3	10.7
Recovered GO	32.5	27.0	9.7
GO + Olefin Substrate	52.9	15.5	3.3
GO + Ketone Substrate	31.7	23.5	9.8
GO Without Any Substrate	29.3	21.1	10.1

**Table SI-4.** . Summary of Elemental Analysis of GO and Recovered GO After Up to 6 Runs.

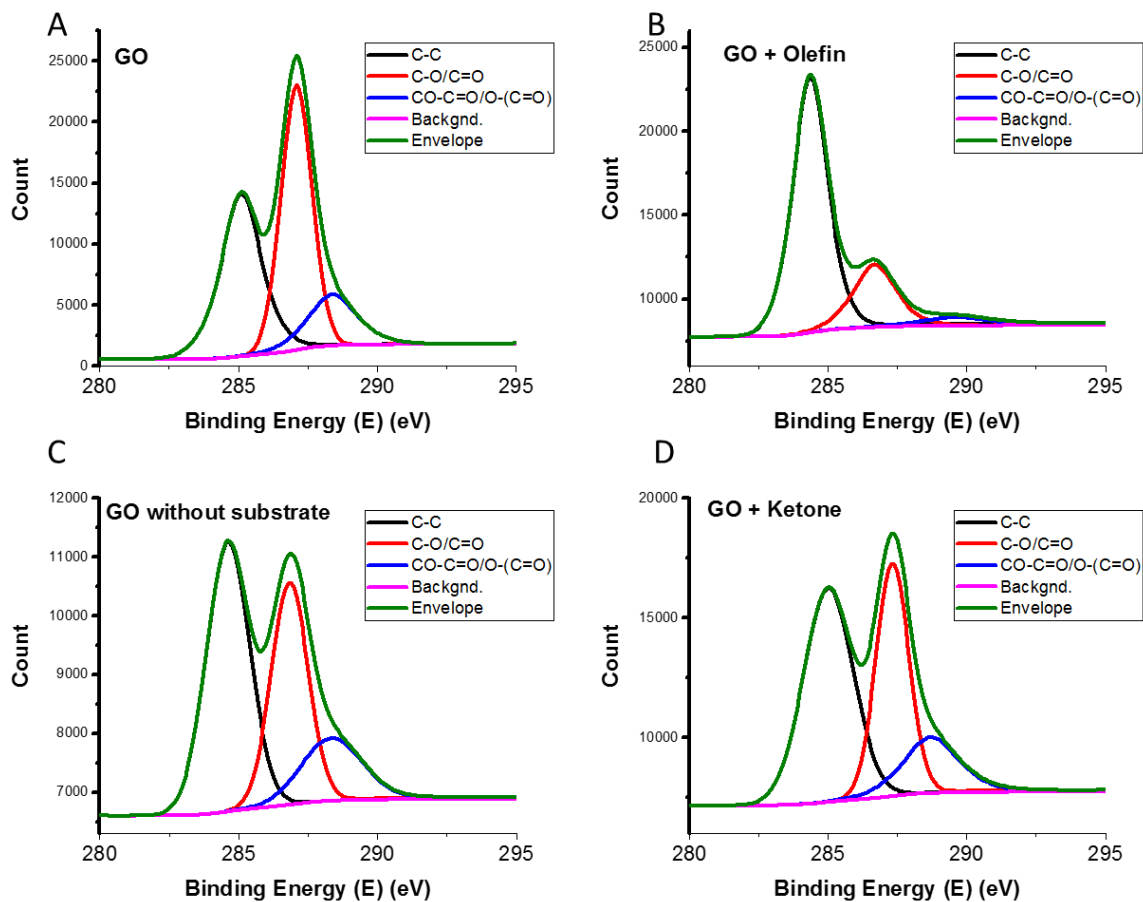
Sample	% C-C (284.28 eV)	% C- O/C=O (286.56 eV)	% CO- C=O/O- (C=O)-O (288.65 eV)	Atomic % C	Atomic % O	Atomic % S	C/O
GO	26.19	30.84	10.04	67.87	31.39	0.73	2.16
Recovered GO-1	32.51	27.02	9.69	70.16	29.32	0.52	2.39
Recovered GO-6	50.23	21.08	5.53	76.84	21.41	1.75	3.59



**Figure SI-1.** EDXS Spectra of GO and Recovered GO Catalyst.



**Figure SI-2.** XPS Survey Spectra of GO and Recovered GO Catalyst.



**Figure SI-3.** XPS Survey Spectra of GO before and after the Reactions in Presence and Absence of Olefin and Ketone Substrates.

### Surface Area Measurement

The surface area of the GO and the recovered GO catalyst was measured by methylene blue (MB) dye adsorption method. The detailed description can be found in the previous publication.<sup>4</sup> In brief, known mass of GO/recovered GO catalysts was mixed with MB (2 mg/mL) in water and then stirred for 24 hours to reach maximum adsorption of MB dye on the GO surface. Here, for each mg of GO sample, 0.750 mL of MB (2 mg/mL) was added so that the total mass of MB dye remained 1.5 times higher than the GO samples. After 24 hours of stirring, the mixture was centrifuged at 5000 rpm for 5 minutes and the MB concentration in the supernatant was determined by measuring its absorbance at wavelength of 664 nm. Finally, the surface area of GO samples was measured by calculating the total amount of MB dye adsorbed on known mass of GO samples. Each mg of adsorbed methylene blue represents 2.54 m<sup>2</sup> of the surface area.<sup>4</sup>

**Table SI-5.** The Calculated Surface Area of GO and Recovered GO Catalyst.

Sample	Surface area (m <sup>2</sup> /g)
GO catalyst	1008.6
Recovered GO catalyst	873.6

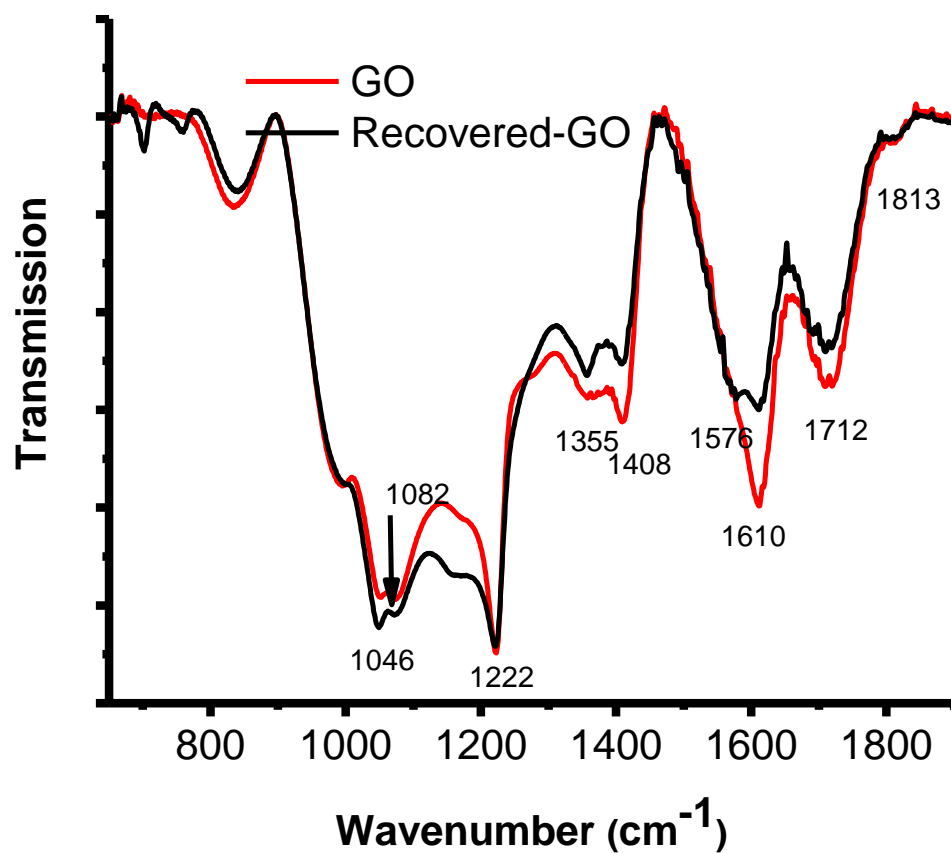
### Conductivity Measurements

Conductivity Measurements were performed using a previously described method.<sup>1</sup> In brief, for conductivity measurements, GO and recovered GO films were prepared via vacuum filtration on Anodisc membranes. After the films were dried in a vacuum over at room temperature for 3 days, the sheet resistance of GO and recovered GO films was measured using a manual four point resistivity probe (Lucas Laboratories, model 302). The conductivity of the films was calculated from the sheet resistance and thickness using the formula given below.

$$\text{Conductivity} = \frac{1}{\text{Sheet resistance} \times \text{thickness}}$$

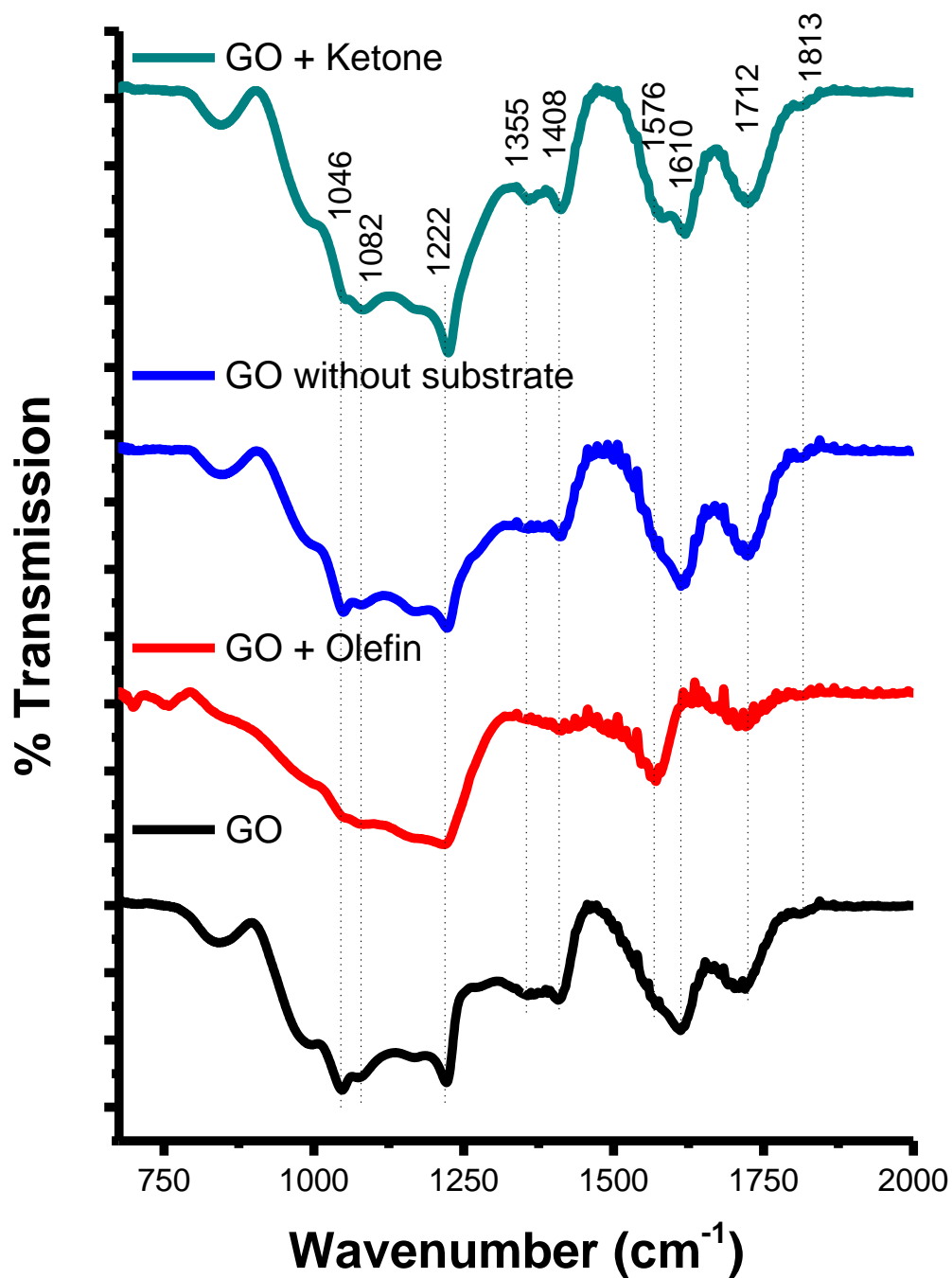
### FT-IR Measurements

FT-IR spectra of the GO and the recovered GO catalysts (deposited on CaF<sub>2</sub> window) were acquired with a Perkin Elmer Spotlight 300 system using transmission mode.



**Figure SI-4.** The FT-IR Spectra of GO and Recovered GO Catalysts, Transmission Mode.





**Figure SI-5.** The FT-IR Spectra of GO before and after the Reactions in Presence and Absence of Olefin and Ketone Substrates.

### **Atomic Absorption Spectroscopy (AAS) Measurements**

Atomic Absorption Spectroscopy (AAS) measurements to determine if trace quantities of transition metals were present in the GO catalyst were carried out with GO samples dispersed in water (1 mg/mL) using the Thermo Scientific iCE 3000 atomic absorption spectrometer.

### Additional Discussion – Characterization Studies

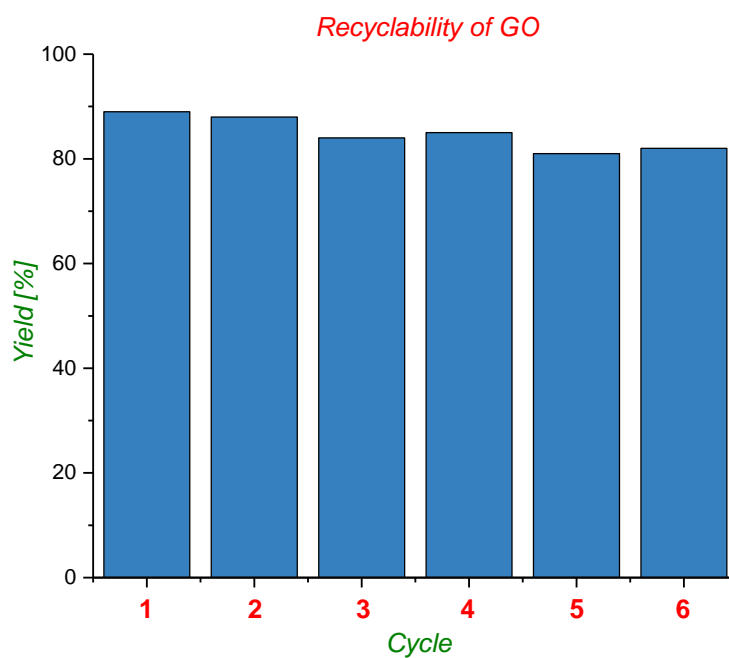
Several results in the characterization studies to elucidate the key role of graphene-materials before and after the reactions, referred to as ‘GO’ and ‘recovered GO’ should be highlighted.

(1) Surface area (SA) of the recovered GO ( $\Delta$  of 86.6%) is very different from the reduction of GO to rGO ( $\Delta$  of 26.8%) observed during the related isomerization process not involving carbonyl substrates,<sup>1</sup> and suggests only a minor increase in  $\pi$ -stacking interactions on the material surface.

(2) EDXS analysis of the GO material indicates that the majority of the oxygen functionalities have been maintained on the GO surface during the reaction. Note that this finding (10.0% increase) is in sharp contrast to the isomerization process not involving carbonyl substrates, wherein the vast majority of oxygen functionalities have been removed from the surface (77.4% increase).

(3) FTIR measurements indicate no change in the intensity of signals at 1222, 1712, 1408, 1813  $\text{cm}^{-1}$ , attributed to C–O (C–OH/C–O–C, hydroxyl/ epoxide), C=O (carbonyl groups), carboxylic acid RCOO–H bending vibrations and anhydride C=O stretching vibrations. In contrast, in the related isomerization process not involving carbonyl substrates all of these signals have either decreased or disappeared, indicative of pronounced reduction of GO to rGO.

(4) Calculation of the carboxylic acid content in the GO catalyst used for the alkylation indicated that GO contains 0.68 mol of C/0.32 mol of O, with 10.7% C (8.0 mmol C per g of GO) in the form of carboxylic acid functional groups based on the XPS data. The GO material recovered after the alkylation reactions contains 0.70 mol of C and 0.29 mol of O, with 9.7% C (7.3 mmol C per g of recovered GO) in the form of carboxylic acid functional groups. This represents a 0.15 mmol  $\text{g}^{-1}$  loss of carboxylic acid functional groups during the catalysis, consistent with a proton isomerization mechanism on the graphene surface.

**Recyclability Studies Referred to from the Main Manuscript**

**Figure SI-6.** Recyclability of GO in ketone-alkylation reaction. Conditions: styrene (1.0 equiv), 1,3-diphenylpropane-1,3-dione (3.0 equiv), GO (200 wt%),  $\text{CHCl}_3$  (0.20 M), 80 °C. See pages SI-48 to SI-50 for details.

### Additional Mechanistic Studies Referred to from the Main Manuscript

Additional studies to gain insight into the mechanism of carbocatalyzed ketone  $\alpha$ -alkylation were conducted, see pages SI-39 to SI-47 for details:

- (1) Hammett study using differently substituted 4-arylalkenes showed an excellent correlation (a  $\rho^+$  value of -0.64,  $R^2 = 0.99$ ;  $\rho$  value of -1.00,  $R^2 = 0.83$ ). This indicates build-up of a partial positive charge at the benzylic carbon in the transition state, and can be compared with a  $\rho$  value of -2.2 for solvolysis of aryl tosylates
- (2) Intermolecular competition experiments with differently substituted ketones revealed that steric hindrance plays an important role in these reactions, consistent with coordination to the GO surface.
- (3) Intermolecular competition experiments between styrenes and benzylic alcohols revealed that alcohols are intrinsically more reactive substrates. Furthermore, 1° alcohols are more reactive than 2° alcohols. This trend of reactivity is opposite to the conventional alkylation selectivity.
- (4) Intermolecular competition experiments between ketones and arenes as nucleophiles revealed that electron-rich arenes are intrinsically more reactive substrates, consistent with substrate activation by  $\pi$ -stacking interactions.
- (5) Careful monitoring of the alkylation reaction of 1,3-diphenylpropane-1,3-dione with styrene as electrophile revealed no detectable intermediates formed during the course of the reaction. Initial rate measurements revealed that the overall reaction rate does not change significantly over the course of the reaction, and that electron-rich arenes are coupled preferentially to carbonyls (**1a**,  $v_{\text{initial}} = 3.39 \times 10^{-2} \text{ mM s}^{-1}$ ; 1,3-dimethoxybenzene,  $v_{\text{initial}} = 1.40 \times 10^{-1} \text{ mM s}^{-1}$ ).
- (6) Examination of different leaving groups indicated high selectivity for the alkylation using alcohol in the presence of acetate, as well as bromide and chloride. This selectivity is opposite from that expected of alkylations under standard and transition-metal-catalyzed conditions. Such unconventional alkylation selectivity may be of particular interest for chemoselective manipulation of functional groups using graphene-based materials.

### List of Known Compounds/General Methods

All compounds reported in the manuscript have been previously described in literature or are commercially available. Unless indicated otherwise, all experiments involving graphene oxide were set up under ambient conditions. Graphene oxide (GO) was prepared by a modified Hummers method.<sup>1,2</sup> Holey-GO (h-GO) was prepared according to the published procedure.<sup>4</sup> Graphite powder was purchased from Sigma Aldrich (282863) and used as received. Reduced graphene oxide (rGO) was prepared according to the published procedure.<sup>3</sup> All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were used as received unless otherwise noted. All other chemicals were purchased at the highest commercial grade and used as received. All products were identified using  $^1\text{H}$  NMR and GC-MS analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on Bruker spectrometers at 500 ( $^1\text{H}$  NMR) and 125 MHz ( $^{13}\text{C}$  NMR). All shifts are reported in parts per million (ppm) relative to residual  $\text{CHCl}_3$  peak (7.27 and 77.2 ppm,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, respectively). All coupling constants ( $J$ ) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 39.00 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument. All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS and HRMS data are given for all compounds in the Supporting Information for characterization purposes.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS and HRMS data are reported for all new compounds.

## Experimental Procedures and Characterization Data

**General procedure for the GO-catalyzed ketone  $\alpha$ -alkylation.** A 2-dram vial equipped with a stir bar was charged with an olefin substrate (1.0 equiv), ketone substrate (typically, 3.0 equiv), and GO (typically, 200 wt%). Chloroform (typically, 0.50 mL) was added at room temperature, the reaction mixture was placed in an oil bath, and stirred for the indicated time at a given temperature. After the indicated time, the reaction mixture was cooled down to room temperature. The sample was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples. Unless stated otherwise, the crude product was purified by chromatography on silica gel. Routinely, GC-MS analysis was used as a method of analysis to confirm the product distribution and alkylation selectivity. In all examples reported in the manuscript, selectivity and product distribution have been determined by analysis of crude reaction mixtures. In all examples reported in the manuscript, the observed alkylation selectivity (branched/linear) is >99:1. In all examples reported in the manuscript, the observed mono-/bis-alkylation selectivity is >99:1. In all examples reported in the manuscript, the observed selectivity with respect to ketone is >99:1.

**Representative procedure for the GO-catalyzed ketone  $\alpha$ -alkylation.** A 2-dram vial equipped with a stir bar was charged with styrene (**2a**, 15 mg, 0.144 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), GO (30 mg, 200 wt%), and chloroform (0.50 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 15 h. The reaction mixture was cooled down to room temperature. Analysis of the reaction mixture by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS indicated >98% conversion. Purification by chromatography on silica gel afforded the title product **3a** (27.6 mg). Yield 94%. Characterization data are included in the section below.

## Extended Optimization Studies Referred to From the Main Manuscript

Table SI-6. GO-Catalyzed Alkylation of Pentane-2,4-dione with Styrene.<sup>a</sup>

entry	catalyst	loading (wt%)	solvent	T (°C)	conversion <sup>b</sup> (%)	yield <sup>b</sup> (%)	TON <sup>c</sup> (x 10 <sup>-3</sup> )
1 <sup>d</sup>	r-GO	200	CHCl <sub>3</sub>	80	<2	<2	-
2 <sup>e</sup>	h-GO	200	CHCl <sub>3</sub>	80	<2	<2	-
3 <sup>f</sup>	graphite	200	CHCl <sub>3</sub>	80	<2	<2	-
4 <sup>g</sup>	GO	200	DMSO	80	20	<2	-
5	GO	200	DMF	80	12	<2	-
6	GO	200	CH <sub>3</sub> CN	80	26	<2	-
7	GO	200	H <sub>2</sub> O	80	>98	<2	-
8	GO	200	CH <sub>2</sub> Cl <sub>2</sub>	80	>98	71	3.41
9	GO	200	Toluene	80	>98	65	3.13
10	GO	200	CH <sub>3</sub> NO <sub>2</sub>	80	>98	61	2.93
11	GO	200	THF	80	37	<2	-
12	GO	200	CHCl <sub>3</sub>	80	>98	96	4.62
13	GO	200	DCE	80	>98	85	4.09
14	GO	200	NMP	80	>98	<2	-
15	GO	200	Dioxane	80	45	5	0.24
16 <sup>h</sup>	GO	200	-	80	>98	90	4.33
17	GO	200	CHCl <sub>3</sub>	120	>98	87	4.18
18	GO	200	CHCl <sub>3</sub>	RT	<2	<2	-
19	GO	100	CHCl <sub>3</sub>	80	>98	86	8.27
20	GO	50	CHCl <sub>3</sub>	100	69	64	12.31
21	GO	20	CHCl <sub>3</sub>	100	75	64	30.77
22	GO	20	CHCl <sub>3</sub>	120	77	58	27.88
23 <sup>i</sup>	GO	20	CHCl <sub>3</sub>	80	73	60	28.85
24 <sup>j</sup>	GO	20	CHCl <sub>3</sub>	80	76	57	27.40
25	GO	5	CHCl <sub>3</sub>	80	13	11	21.15
26 <sup>i</sup>	GO	200	CHCl <sub>3</sub>	80	>98	91	4.38
27 <sup>j</sup>	GO	200	CHCl <sub>3</sub>	80	>98	90	4.33
28 <sup>k</sup>	GO	200	CHCl <sub>3</sub>	80	>98	78	3.75
29 <sup>l</sup>	GO	200	CHCl <sub>3</sub>	80	>98	67	3.22
30 <sup>m</sup>	GO	200	CHCl <sub>3</sub>	80	>98	93	4.47

<sup>a</sup>Conditions: unless indicated otherwise, on bench, to a solution of olefin and ketone substrates (typically, 3.0 equiv, 0.20 M), GO was added, the reaction vial was capped, and the reaction was stirred vigorously at a given temperature for 15 h. <sup>b</sup>Relative reactivity values determined from product distribution by <sup>1</sup>H NMR and GC/MS of crude reaction mixtures and comparison with authentic samples. Yield refers to the conversion of ketone to the alkylated product. Conversion = (100-SM). <sup>c</sup>TON (turnover number) = mol of products/mass of GO (Dreyer, D. R.; Jia, H. P.; Bielawski, C. W. *Angew. Chem. Int. Ed.* **2010**, *49*, 6813). <sup>d</sup>Reduced graphene oxide prepared according to ref. 3. <sup>e</sup>Holey graphene oxide prepared according to ref. 4. <sup>f</sup>Graphite (Sigma Aldrich 282863). <sup>g</sup>Entries 4-30: graphene oxide prepared by a modified Hummers method (ref. 1-2). <sup>h</sup>Neat. <sup>i</sup>1.0 M in CHCl<sub>3</sub>. <sup>j</sup>0.05 M in CHCl<sub>3</sub>. <sup>k</sup>Ketone (2.0 equiv). <sup>l</sup>Ketone (1.2 equiv). <sup>m</sup>Carried out using strict Schlenk techniques with deoxygenated solvents under argon.

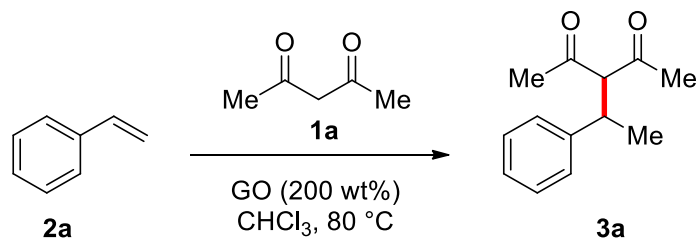


### Additional Discussion – Optimization Studies

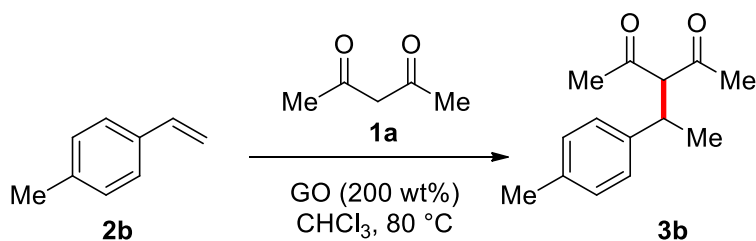
After extensive optimization, we found that the desired  $\alpha$ -alkylation product was obtained in 96% yield using GO (modified Hummers method,<sup>1-2</sup> 200 wt%) in  $\text{CHCl}_3$  at 80 °C. Importantly, the product was obtained with exquisite mono-alkylation selectivity via a formal activation of the  $\text{C}(\text{sp}^3)$  hybridized C–H bond. Interestingly, the application of other graphene-based materials, including reduced GO (r-GO)<sup>3</sup> (entry 1), microwave-enabled holey-GO (h-GO)<sup>4</sup> (entry 2) and natural flake graphite (entry 3) did not promote the desired C–C bond forming reaction. Among a set of representative solvents, most efficient reaction was observed in  $\text{CHCl}_3$  (entries 4-15); however, high reactivity was also observed under neat conditions (entry 16), showing another advantage of the current protocol. In contrast, graphene-catalyzed reactions are often highly sensitive to solvent concentration. Importantly, the utilization of lower catalyst loading led to efficient conversion (entries 19-25) (*vide infra*), giving a very favorable comparison with the GO-catalyzed oxidation of alcohols. Furthermore, high reactivity was observed with close to equimolar ratio of the coupling products (entry 28-29). This finding together with the low sensitivity to solvent concentration (entry 26-27) suggests that olefin isomerization does not compete under the reaction conditions. As anticipated, control experiments revealed that the alkylation product is not formed in the absence of GO, in line with the critical role of carbocatalyst in the reaction. Finally, while all optimization experiments were performed under standard bench-top set-up to enhance operational-utility of the protocol (entries 1-29), a control reaction with rigorous exclusion of oxygen (entry 30) afforded the product in excellent yield, indicating that the process is not inhibited in the absence of oxygen.

GO-Catalyzed Ketone  $\alpha$ -Alkylation Using Olefins

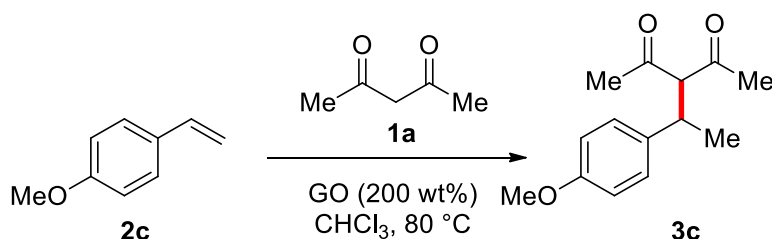
## 3-(1-Phenylethyl)pentane-2,4-dione (Table 1, Entry 1)



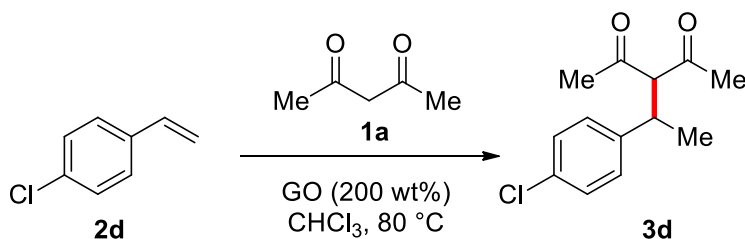
According to the general procedure, the reaction of styrene (**2a**, 15 mg, 0.144 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 94% yield (27.6 mg). Colorless oil. Branched/linear >99:1. **3a**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (t,  $J$  = 7.5 Hz, 2 H), 7.23-7.17 (m, 3 H), 4.04 (d,  $J$  = 11.3 Hz, 1 H), 3.64-3.55 (m, 1 H), 2.27 (s, 3 H), 1.84 (s, 3 H), 1.22 (d,  $J$  = 6.9 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.7, 203.6, 143.2, 129.0, 127.4, 127.2, 76.9, 40.6, 30.0, 29.9, 21.0. HRMS calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 227.1048 found 227.1050.

3-(1-(*p*-Tolyl)ethyl)pentane-2,4-dione (Table 1, Entry 2)

According to the general procedure, the reaction of 1-methyl-4-vinylbenzene (**2b**, 15 mg, 0.127 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 94% yield. Colorless oil. Branched/linear >99:1. **3b**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.09 (q,  $J$  = 8.2 Hz, 4 H), 4.02 (d,  $J$  = 11.3 Hz, 1 H), 3.56 (dq,  $J$  = 13.7, 6.9 Hz, 1 H), 2.30 (s, 3 H), 2.27 (s, 3 H), 1.85 (s, 3 H), 1.20 (d,  $J$  = 6.9 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.80, 203.79, 140.1, 136.7, 129.6, 127.3, 77.0, 40.2, 29.92, 29.88, 21.2. HRMS calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 241.1204 found 241.1206.

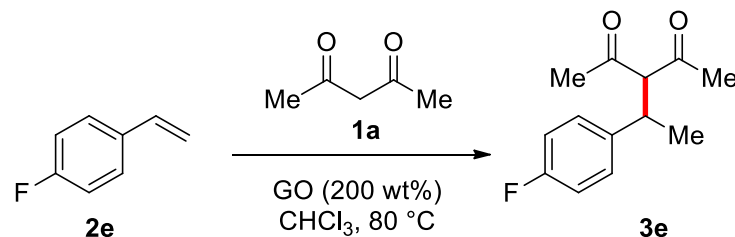
**3-(1-(4-Methoxyphenyl)ethyl)pentane-2,4-dione** (Table 1, Entry 3)

According to the general procedure, the reaction of 1-methoxy-4-vinylbenzene (**2c**, 15 mg, 0.112 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 53% yield. Colorless oil. Branched/linear >99:1. **3c**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11 (d,  $J$  = 8.5 Hz, 2 H), 6.83 (d,  $J$  = 8.5 Hz, 2 H), 3.99 (d,  $J$  = 11.3 Hz, 1 H), 3.78 (s, 3 H), 3.55 (dq,  $J$  = 13.7, 6.8 Hz, 1 H), 1.85 (s, 3 H), 1.19 (d,  $J$  = 6.9 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.9, 203.8, 158.6, 135.2, 128.4, 114.3, 77.2, 55.4, 39.9, 30.0, 29.9, 21.2. HRMS calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 257.1154 found 257.1155.

**3-(1-(4-Chlorophenyl)ethyl)pentane-2,4-dione** (Table 1, Entry 4)

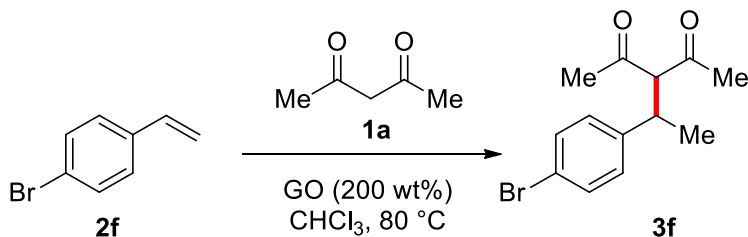
According to the general procedure, the reaction of 1-chloro-4-vinylbenzene (**2d**, 15 mg, 0.108 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 75% yield. Colorless oil. Branched/linear >99:1. **3d**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (d,  $J$  = 8.3 Hz, 2 H), 7.13 (d,  $J$  = 8.3 Hz, 2 H), 3.99 (d,  $J$  = 11.3 Hz, 1 H), 3.59 (dq,  $J$  = 13.6, 6.8 Hz, 1 H), 2.26 (s, 3 H), 1.87 (s, 3 H), 1.19 (d,  $J$  = 6.9 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.3, 203.2, 141.8, 132.9, 129.2, 128.8, 76.8, 39.9, 30.0, 29.8, 20.9. HRMS calcd for  $\text{C}_{13}\text{H}_{15}\text{ClO}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 261.0658 found 261.0659.

**3-(1-(4-Fluorophenyl)ethyl)pentane-2,4-dione** (Table 1, Entry 5)



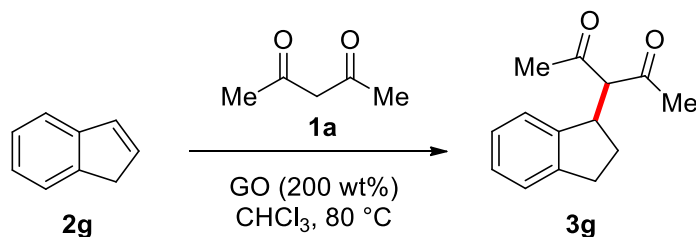
According to the general procedure, the reaction of 1-fluoro-4-vinylbenzene (**2e**, 15 mg, 0.123 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 83% yield. Colorless oil. Branched/linear >99:1. **3e**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (dd,  $J$  = 8.4, 5.4 Hz, 2 H), 6.99 (t,  $J$  = 8.6 Hz, 2 H), 3.99 (d,  $J$  = 11.3 Hz, 1 H), 3.60 (dq,  $J$  = 13.7, 6.8 Hz, 1 H), 2.26 (s, 3 H), 1.85 (s, 3 H), 1.20 (d,  $J$  = 6.9 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.4, 203.3, 162.8, 160.9, 138.9, 138.9, 129.0, 128.9, 115.9, 115.8, 77.0, 39.80, 30.0, 29.8, 21.1.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.6. HRMS calcd for  $\text{C}_{13}\text{H}_{15}\text{FO}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 245.0954 found 245.0956.

### 3-(1-(4-Bromophenyl)ethyl)pentane-2,4-dione (Table 1, Entry 6)



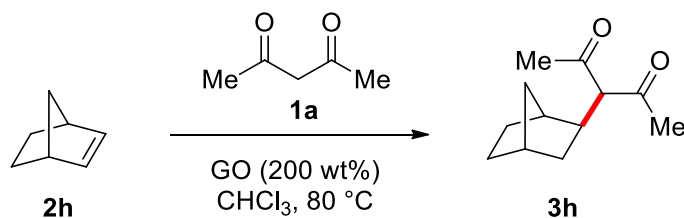
According to the general procedure, the reaction of 1-bromo-4-vinylbenzene (**2f**, 15 mg, 0.082 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 84% yield. Colorless oil. Branched/linear >99:1. **3f**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J$  = 8.4 Hz, 2 H), 7.07 (d,  $J$  = 8.3 Hz, 2 H), 3.99 (d,  $J$  = 11.3 Hz, 1 H), 3.58 (dq,  $J$  = 13.7, 6.9 Hz, 1 H), 2.26 (s, 3 H), 1.87 (s, 3 H), 1.19 (d,  $J$  = 6.9 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.23, 203.15, 142.3, 132.1, 129.2, 120.9, 76.7, 39.9, 30.0, 29.8, 20.9. HRMS calcd for  $\text{C}_{13}\text{H}_{15}\text{BrO}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 305.0153 found 305.0154.

### 3-(2,3-Dihydro-1H-inden-1-yl)pentane-2,4-dione (Table 1, Entry 7)

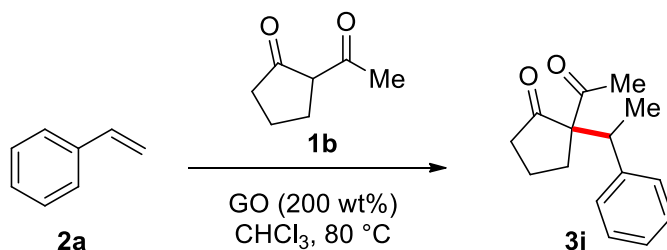


According to the general procedure, the reaction of 1*H*-indene (**1g**, 15 mg, 0.129 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in CHCl<sub>3</sub> for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 67% yield. Colorless oil. Branched/linear >99:1. **3g**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (d,  $J$  = 7.3 Hz, 1 H), 7.18 (t,  $J$  = 7.3 Hz, 1 H), 7.12 (t,  $J$  = 7.3 Hz, 1 H), 7.03 (d,  $J$  = 7.5 Hz, 1 H), 4.02 (dd,  $J$  = 13.9, 8.8 Hz, 1 H), 3.88 (d,  $J$  = 10.1 Hz, 1 H), 2.98-2.90 (m, 1 H), 2.90-2.83 (m, 1 H), 2.31-2.25 (m, 1 H), 2.20 (s, 3 H), 2.17 (s, 3 H), 1.79-1.67 (m, 1 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  204.2, 203.7, 144.0, 143.6, 127.5, 126.6, 125.1, 124.3, 74.0, 44.7, 31.3, 31.0, 30.2, 29.4. HRMS calcd for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>Na (M<sup>+</sup> + Na) 239.1048 found 239.1050.

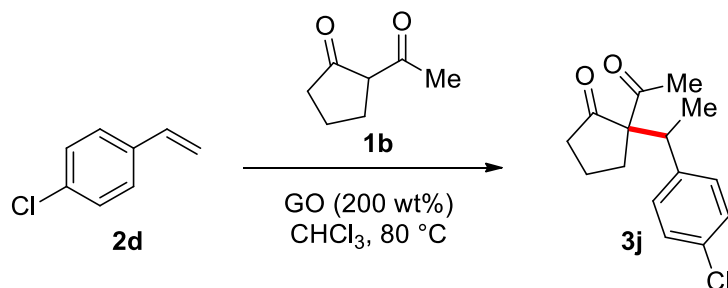
### 3-Bicyclo[2.2.1]heptan-2-yl)pentane-2,4-dione (Table 1, Entry 8)



According to the general procedure, the reaction of norbornene (**2h**, 15 mg, 0.159 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in CHCl<sub>3</sub> for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 80% yield. Colorless oil. Exo-/endo >99:1. **3h**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.47 (d,  $J$  = 11.8 Hz, 1 H), 2.38-2.28 (m, 1 H), 2.24 (s, 1 H), 2.18 (s, 3 H), 2.13 (s, 3 H), 1.83 (d,  $J$  = 2.3 Hz, 1 H), 1.54-1.46 (m, 3 H), 1.32-1.28 (m, 2H), 1.21-1.13 (m, 2 H), 0.99-0.88 (m, 1 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  204.5, 204.2, 76.5, 41.9, 39.3, 36.9, 36.3, 35.7, 30.2, 29.8, 29.4, 28.6. HRMS calcd for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>Na (M<sup>+</sup> + Na) 217.1204 found 217.1206.

**2-Acetyl-2-(1-phenylethyl)cyclopentanone** (Table 1, Entry 9)

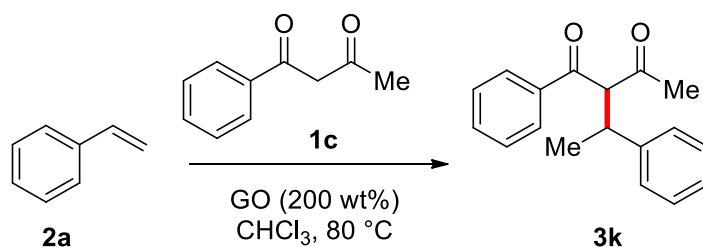
According to the general procedure, the reaction of styrene (**2a**, 15 mg, 0.144 mmol, 1.0 equiv), 2-acetylcyclopentanone (**1b**, 54.5 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in CHCl<sub>3</sub> for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 50% yield. Colorless oil. Branched/linear >99:1. Two diastereoisomers (1:1), ratio determined by <sup>1</sup>H NMR. Further purification by chromatography afforded an analytical sample of the pure less polar isomer. **3i**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 (d,  $J$  = 7.9 Hz, 2 H), 7.21 (d,  $J$  = 6.5 Hz, 1 H), 7.14 (d,  $J$  = 7.5 Hz, 2 H), 3.80 (q,  $J$  = 6.9 Hz, 1 H), 2.75 (dd,  $J$  = 11.8, 7.5 Hz, 1 H), 2.40-2.33 (m, 1 H), 2.20-2.13 (m, 2 H), 2.09 (s, 3 H), 1.92-1.82 (m, 1 H), 1.79-1.66 (m, 1 H), 1.22 (d,  $J$  = 7.0 Hz, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  216.2, 203.2, 142.4, 128.8, 128.0, 127.2, 77.45, 74.7, 44.3, 39.6, 27.4, 26.3, 19.7, 19.0. HRMS calcd for C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>Na (M<sup>+</sup> + Na) 253.1204 found 253.1206.

**2-Acetyl-2-(1-(4-chlorophenyl)ethyl)cyclopentanone** (Table 1, Entry 10)

According to the general procedure, the reaction of 1-chloro-4-vinylbenzene (**2d**, 15 mg, 0.108 mmol, 1.0 equiv), 2-acetylcyclopentanone (**1b**, 40.9 mg, 3.0 equiv, 0.324 mmol), and GO (30 mg, 200 wt%) in CHCl<sub>3</sub> for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 60% yield. Colorless oil. Branched/linear >99:1. Two diastereoisomers (1:1), ratio determined by <sup>1</sup>H NMR. Further purification by chromatography afforded an analytical sample of the pure less polar isomer. **3j**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 (d,  $J$  = 7.0 Hz, 2 H), 7.07 (d,

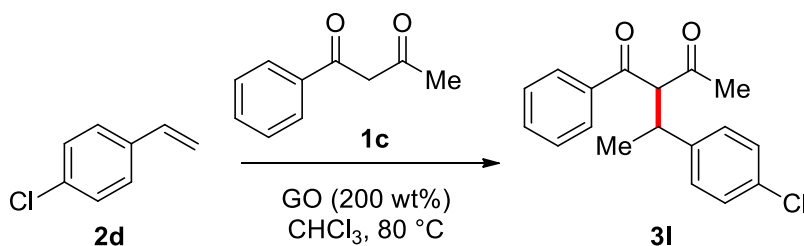
$J = 7.2$  Hz, 2 H), 3.77 (d,  $J = 6.2$  Hz, 1 H), 2.74-2.67 (m, 1 H), 2.38-2.33 (m, 1 H), 2.19-2.10 (m, 2 H), 2.08 (s, 3 H), 2.93-2.85 (m, 2 H), 2.77-2.69 (m, 2 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  215.9, 202.8, 140.9, 133.0, 129.3, 129.0, 74.5, 43.7, 39.5, 27.2, 26.3, 19.6, 18.8. HRMS calcd for  $\text{C}_{15}\text{H}_{17}\text{ClO}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 287.0815 found 287.0816.

### 1-Phenyl-2-(1-phenylethyl)butane-1,3-dione (Table 1, Entry 11)



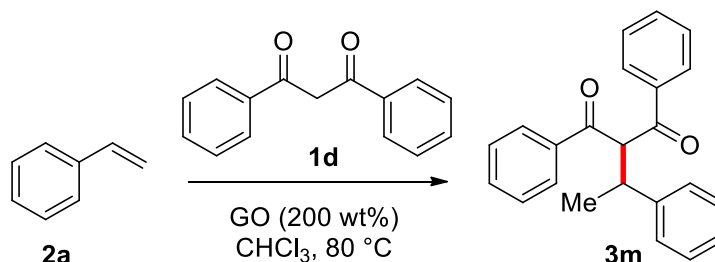
According to the general procedure, the reaction of styrene (**2a**, 15 mg, 0.144 mmol, 1.0 equiv), 1-phenylbutane-1,3-dione (**1c**, 70.1 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 82% yield. Colorless oil. Branched/linear >99:1. Two diastereoisomers (1:1), ratio determined by  $^1\text{H}$  NMR. **3k**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 7.6$  Hz, 2 H), 7.80 (d,  $J = 7.6$  Hz, 2 H), 7.62 (t,  $J = 7.2$  Hz, 1 H), 7.55-7.47 (m, 3 H), 7.39-7.34 (m, 2 H), 7.34-7.28 (m, 4 H), 7.24 (d,  $J = 6.8$  Hz, 1 H), 7.25-7.14 (m, 4 H), 7.08 (t,  $J = 6.6$  Hz, 1 H), 4.92 (d,  $J = 10.9$  Hz, 1 H), 4.83 (d,  $J = 11.0$  Hz, 1 H), 3.98-3.79 (m, 2 H), 2.26 (s, 3 H), 1.92 (s, 3 H), 1.32 (d,  $J = 6.9$  Hz, 3 H), 1.23 (d,  $J = 6.7$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.9, 203.4, 195.42, 195.38, 143.6, 143.3, 137.4, 137.2, 134.0, 133.6, 129.1, 129.0, 128.8, 128.6, 127.7, 127.5, 127.2, 126.8, 71.7, 71.0, 41.1, 40.5, 28.1, 27.7, 21.8, 20.5. HRMS calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 289.1204 found 289.1206.

### 2-(1-(4-Chlorophenyl)ethyl)-1-phenylbutane-1,3-dione (Table 1, Entry 12)



According to the general procedure, the reaction of 1-chloro-4-vinylbenzene (**2d**, 15 mg, 0.108 mmol, 1.0 equiv), 1-phenylbutane-1,3-dione (**1c**, 52.6 mg, 3.0 equiv, 0.324 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 81% yield. Colorless oil. Branched/linear >99:1. Two diastereoisomers (1:1), ratio determined by  $^1\text{H}$  NMR. **3l**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J$  = 7.1 Hz, 2 H), 7.81 (d,  $J$  = 7.1 Hz, 2 H), 7.63 (t,  $J$  = 6.8 Hz, 1 H), 7.42-7.37 (m, 3 H), 7.38 (t,  $J$  = 6.9 Hz, 3 H), 7.30 (d,  $J$  = 7.3 Hz, 2 H), 7.23 (d,  $J$  = 7.6 Hz, 2 H), 7.14 (s, 4 H), 4.86 (d,  $J$  = 10.7 Hz, 1 H), 4.77 (d,  $J$  = 10.9 Hz, 1 H), 7.39-7.38 (m, 2 H), 2.24 (s, 3 H), 1.92 (s, 3 H), 1.29 (d,  $J$  = 6.4 Hz, 3 H), 1.20 (d,  $J$  = 6.2 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.4, 203.0, 195.11, 195.06, 142.2, 141.9, 137.2, 137.0, 134.2, 133.8, 132.9, 132.5, 129.2, 129.11, 129.06, 128.94, 128.90, 128.8, 128.7, 71.6, 70.9, 40.4, 39.8, 28.1, 27.7, 21.7, 20.4. HRMS calcd for  $\text{C}_{18}\text{H}_{17}\text{ClO}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 323.0815 found 323.0816.

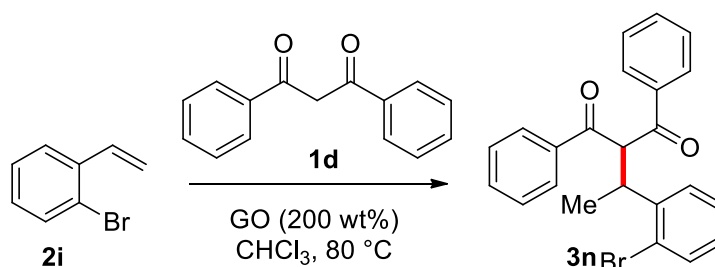
### 1,3-Diphenyl-2-(1-phenylethyl)propane-1,3-dione (Table 1, Entry 13)



According to the general procedure, the reaction of styrene (**1a**, 15 mg, 0.144 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 96.9 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 85% yield. Colorless oil. Branched/linear >99:1. **3m**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J$  = 7.6 Hz, 2 H), 7.76 (d,  $J$  = 7.6 Hz, 2 H), 7.57 (t,  $J$  = 7.3 Hz, 1 H), 7.51-7.37 (m, 3 H), 7.29 (dd,  $J$  = 9.7, 5.8 Hz, 3 H), 7.19 (t,  $J$  = 7.6 Hz, 2 H), 7.09 (t,  $J$  = 7.3 Hz, 1 H), 5.62 (d,  $J$  = 10.1 Hz, 1 H), 4.16-4.03 (m, 1 H), 1.36 (d,  $J$  = 7.0 Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  195.1, 194.8, 144.0, 137.3, 137.1, 133.7, 133.2, 129.02, 128.99, 128.7, 128.62, 128.57, 127.9, 126.8, 65.1, 41.3, 20.4. HRMS calcd for  $\text{C}_{23}\text{H}_{20}\text{O}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 351.1361 found 351.1362.

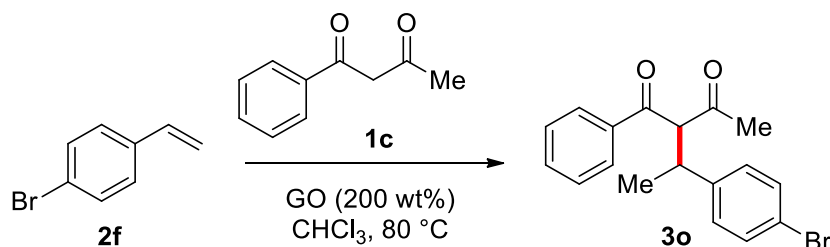
### 2-(1-(2-Bromophenyl)ethyl)-1,3-diphenylpropane-1,3-dione (Table 1, Entry 14)





According to the general procedure, the reaction of 1-bromo-2-vinylbenzene (**2i**, 15 mg, 0.082 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 55.2 mg, 3.0 equiv, 0.246 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 55% yield. Colorless oil. Branched/linear >99:1. **3n**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.7$  Hz, 2 H), 7.87 (d,  $J = 7.8$  Hz, 2 H), 7.55 (t,  $J = 7.3$  Hz, 1 H), 7.51 (d,  $J = 7.9$  Hz, 1 H), 7.47 (t,  $J = 7.3$  Hz, 1 H), 7.42 (t,  $J = 7.5$  Hz, 2 H), 7.34 (t,  $J = 7.5$  Hz, 2 H), 7.19 (d,  $J = 7.7$  Hz, 1 H), 7.11 (t,  $J = 7.5$  Hz, 1 H), 6.99 (t,  $J = 7.6$  Hz, 1 H), 5.81 (s, 1 H), 4.55–4.41 (m, 1 H), 1.35 (d,  $J = 6.9$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 194.8, 143.0, 137.2, 136.8, 133.7, 133.5, 133.3, 129.04, 128.97, 128.8, 128.7, 128.2, 127.6, 62.4, 39.4, 18.6. HRMS calcd for  $\text{C}_{23}\text{H}_{19}\text{BrO}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 429.0466 found 429.0468.

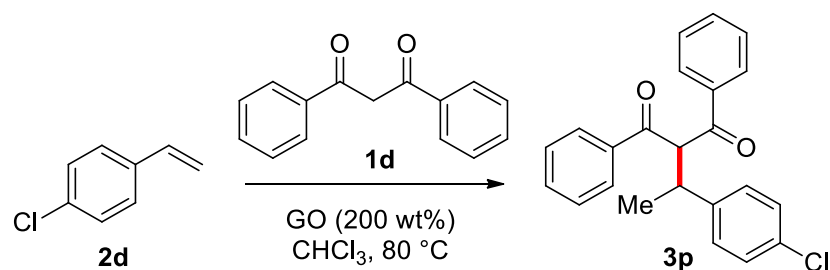
## 2-(1-(4-Bromophenyl)ethyl)-1-phenylbutane-1,3-dione (Table 1, Entry 15)



According to the general procedure, the reaction of 1-bromo-4-vinylbenzene (**2f**, 15 mg, 0.082 mmol, 1.0 equiv), 1-phenylbutane-1,3-dione (**1c**, 55.2 mg, 3.0 equiv, 0.246 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 74% yield. Colorless oil. Branched/linear >99:1. Two diastereoisomers (1:1), ratio determined by  $^1\text{H}$  NMR. **3o**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 7.6$  Hz, 2 H), 7.81 (d,  $J = 7.6$  Hz, 2 H), 7.63 (t,  $J = 7.2$  Hz, 1 H), 7.54–7.49 (m, 3 H), 7.45 (d,  $J = 7.8$  Hz, 2 H), 7.39 (t,  $J = 7.4$  Hz, 2 H), 7.30 (d,  $J = 7.8$  Hz, 2 H), 7.17 (d,  $J = 7.8$  Hz, 2 H), 7.08 (d,  $J = 7.9$  Hz, 2 H), 4.86 (d,  $J = 10.8$  Hz, 1 H), 4.77 (d,  $J = 10.9$  Hz, 1 H), 3.92–3.77 (m, 2 H), 2.23 (s, 3 H), 1.92 (s, 3 H),

1.29 (d,  $J = 6.8$  Hz, 3 H), 1.20 (d,  $J = 6.6$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  203.4, 202.9, 195.06, 195.03, 142.7, 142.5, 137.2, 137.0, 134.1, 133.8, 132.1, 131.7, 129.4, 129.3, 129.11, 129.05, 128.9, 128.7, 121.0, 120.6, 71.5, 70.8, 40.5, 39.8, 28.2, 27.7, 21.6, 20.3. HRMS calcd for  $\text{C}_{18}\text{H}_{17}\text{BrO}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 367.0310 found 367.0312.

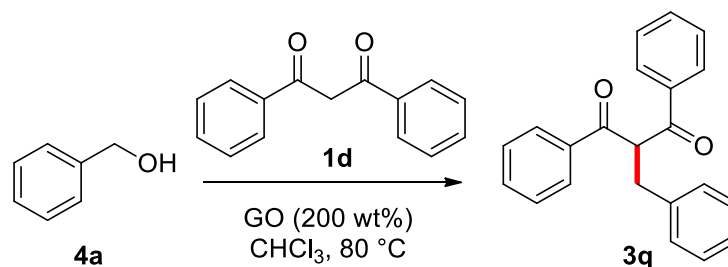
**2-(1-(4-Chlorophenyl)ethyl)-1,3-diphenylpropane-1,3-dione** (Table 1, Entry 16)



According to the general procedure, the reaction of 1-chloro-4-vinylbenzene (**2d**, 15 mg, 0.108 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 72.7 mg, 3.0 equiv, 0.324 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 81% yield. Colorless oil. Branched/linear >99:1.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 7.2$  Hz, 2 H), 7.76 (d,  $J = 7.3$  Hz, 2 H), 7.62-7.55 (m, 1 H), 7.51-7.40 (m, 3 H), 7.31 (t,  $J = 7.0$  Hz, 2 H), 7.21 (d,  $J = 7.6$  Hz, 2 H), 7.16 (d,  $J = 7.5$  Hz, 2 H), 5.56 (d,  $J = 10.0$  Hz, 1 H), 4.16-3.99 (m, 1 H), 1.33 (d,  $J = 6.5$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  194.9, 194.5, 142.6, 137.2, 136.9, 133.9, 133.4, 132.4, 129.3, 129.1, 129.0, 128.74, 128.68, 65.0, 40.7, 20.4. HRMS calcd for  $\text{C}_{23}\text{H}_{19}\text{ClO}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 358.0971 found 358.0972.

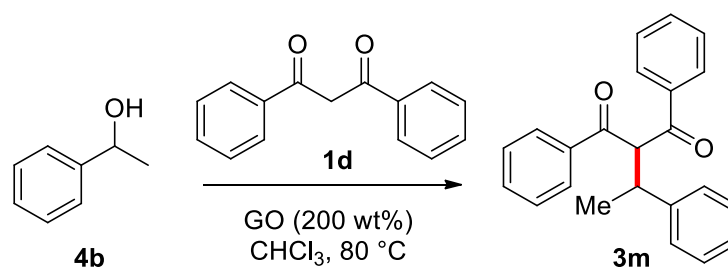
GO-Catalyzed Ketone  $\alpha$ -Alkylation Using Alcohols

## 2-Benzyl-1,3-diphenylpropane-1,3-dione (Scheme 1, Entry 1)



According to the general procedure, the reaction of phenylmethanol (**4a**, 15 mg, 0.139 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 93.5 mg, 3.0 equiv, 0.417 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 61% yield. Colorless oil. Mono-/bis-alkylation selectivity >99:1. **3q**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 7.9$  Hz, 4 H), 7.55 (t,  $J = 7.2$  Hz, 2 H), 7.42 (t,  $J = 7.5$  Hz, 4 H), 7.26-7.21 (m, 4 H), 7.20-7.15 (m, 1 H), 5.53 (t,  $J = 6.6$  Hz, 1 H), 3.47 (d,  $J = 6.6$  Hz, 2 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 139.3, 136.2, 133.7, 129.2, 129.0, 128.8, 126.8, 59.2, 35.4. HRMS calcd for  $\text{C}_{22}\text{H}_{18}\text{O}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 337.1204 found 337.1206.

## 1,3-Diphenyl-2-(1-phenylethyl)propane-1,3-dione (Scheme 1, Entry 2)

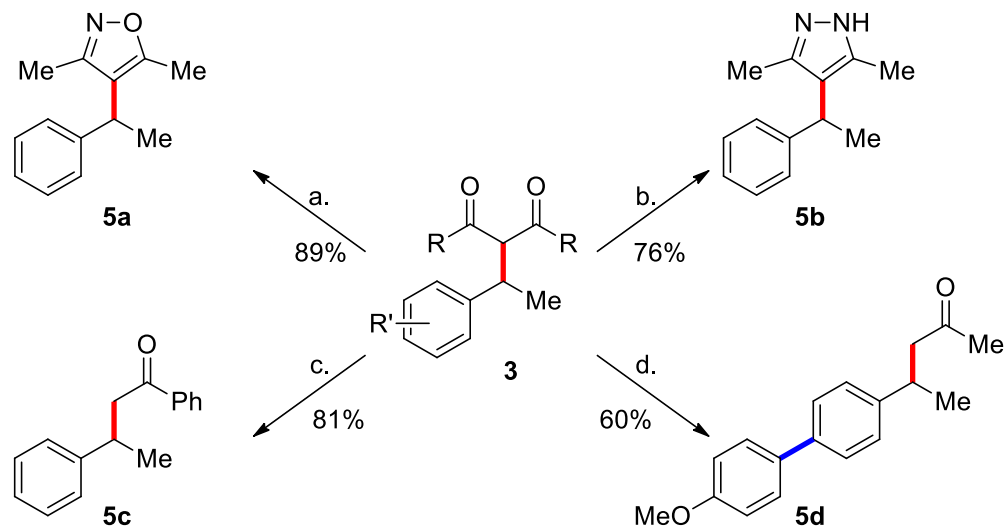


According to the general procedure, the reaction of 1-phenylethanol (**4b**, 15 mg, 0.123 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 82.8 mg, 3.0 equiv, 0.369 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  for 15 h at  $80^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 67% yield. Colorless oil. Branched/linear >99:1. **3m**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 7.6$  Hz, 2 H), 7.76 (d,  $J = 7.6$  Hz, 2 H), 7.57 (t,  $J = 7.3$  Hz, 1 H), 7.51-7.37 (m, 3H), 7.29 (dd,  $J = 9.7, 5.8$  Hz, 3 H), 7.19 (t,  $J = 7.6$  Hz, 2 H), 7.09 (t,  $J = 7.3$  Hz, 1 H), 5.62 (d,  $J = 10.1$  Hz, 1 H), 4.16-4.03 (m, 1 H), 1.36 (d,  $J = 7.0$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$

195.1, 194.8, 144.0, 137.3, 137.1, 133.7, 133.2, 129.02, 128.99, 128.7, 128.62, 128.57, 127.9, 126.8, 65.1, 41.3, 20.4. HRMS calcd for  $C_{23}H_{20}O_2Na$  ( $M^+ + Na$ ) 351.1361 found 351.1362.

## Product Transformations: Synthetic Utility of $\alpha$ -Alkylation Products

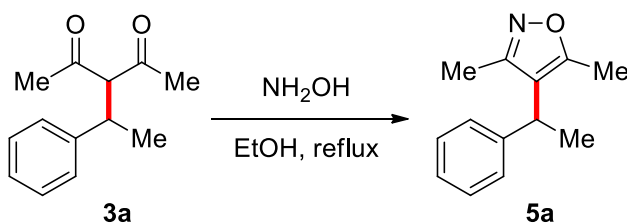
**Scheme SI-1.** Transformations of Ketone  $\alpha$ -Alkylation Products.<sup>a</sup>



<sup>a</sup>Conditions: **a.**  $\text{NH}_2\text{OH}$ ; **b.**  $\text{NH}_2\text{NH}_2$  **c.**  $\text{K}_2\text{CO}_3$ ; **d.**  $\text{Pd}(\text{OAc})_2$ , 4-MeO- $\text{C}_6\text{H}_4\text{-B}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ .

Note: all reactions were performed directly after  $\alpha$ -ketone alkylation in a one-pot fashion. The yields correspond to 2-3 chemical steps.

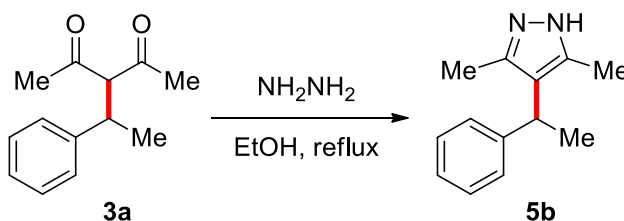
### 3,5-Dimethyl-4-(1-phenylethyl)isoxazole (Scheme 2, **5a**)



One-pot alkylation/cyclization. According to the general alkylation procedure, a 2-dram vial equipped with a stir bar was charged with styrene (**2a**, 30 mg, 0.288 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 86.4 mg, 3.0 equiv, 0.864 mmol), GO (60 mg, 200 wt%), and chloroform (1.0 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature, filtered and concentrated under vacuum. Hydroxylamine HCl (60.0 mg, 3.0 equiv, 0.864 mmol) and EtOH (2 mL) were added, and the reaction mixture was stirred at reflux 3 hours. After the indicated time, the reaction mixture was cooled down to room temperature, and

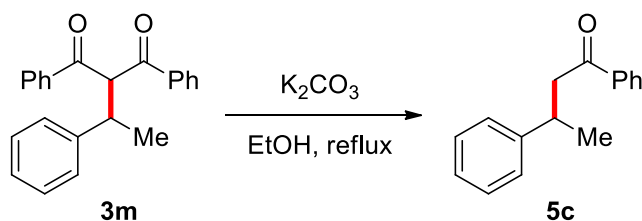
concentrated under vacuum. Purification by chromatography on silica gel afforded the title product (51.6 mg). Yield 89% (2 steps). **5a**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t,  $J = 7.2$  Hz, 2 H), 7.23 (d,  $J = 7.1$  Hz, 1 H), 7.20 (d,  $J = 7.7$  Hz, 2 H), 4.01 (q,  $J = 7.2$  Hz, 1 H), 2.29 (s, 3 H), 2.05 (s, 3 H), 1.61 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 159.7, 143.7, 128.6, 127.2, 126.5, 117.6, 33.5, 20.0, 11.8, 11.0. HRMS calcd for  $\text{C}_{13}\text{H}_{15}\text{NONa}$  ( $\text{M}^+ + \text{Na}$ ) 224.1051 found 224.1052.

### 3,5-Dimethyl-4-(1-phenylethyl)-1H-pyrazole (Scheme 2, **5b**)



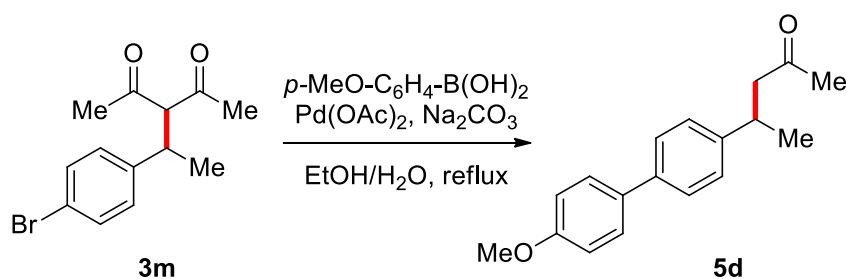
One-pot alkylation/cyclization. According to the general alkylation procedure, a 2-dram vial equipped with a stir bar was charged with styrene (**2a**, 30 mg, 0.288 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 86.4 mg, 3.0 equiv, 0.864 mmol), GO (60 mg, 200 wt%), and chloroform (1.0 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature, filtered and concentrated under vacuum. Hydrazine (aq., 3.0 equiv, 0.864 mmol) and EtOH (2 mL) were added, and the reaction mixture was stirred at reflux 3 hours. After the indicated time, the reaction mixture was cooled down to room temperature, and concentrated under vacuum. Purification by chromatography on silica gel afforded the title product (43.8 mg). Yield 76% (2 steps). **5b**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.77 (s, 1 H), 7.28 (t,  $J = 7.2$  Hz, 2 H), 7.23 (d,  $J = 7.3$  Hz, 2 H), 7.18 (t,  $J = 6.9$  Hz, 1 H), 4.11 (q,  $J = 7.0$  Hz, 1 H), 2.14 (s, 6 H), 1.62 (d,  $J = 7.2$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  145.7, 142.0, 128.3, 127.4, 125.8, 119.4, 34.2, 20.4, 11.8. HRMS calcd for  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{Na}$  ( $\text{M}^+ + \text{Na}$ ) 223.1211 found 223.1212.

### 1,3-Diphenylbutan-1-one (Scheme 2, **5c**)



**One-pot alkylation/retro-Claisen.** According to the general alkylation procedure, a 2-dram vial equipped with a stir bar was charged with styrene (**2a**, 30 mg, 0.288 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 193.8 mg, 3.0 equiv, 0.864 mmol), GO (60 mg, 200 wt%), and chloroform (1.0 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature, filtered and concentrated under vacuum.  $\text{K}_2\text{CO}_3$  (3.0 equiv, 0.864 mmol and EtOH (2 mL) were added, and the reaction mixture was stirred at reflux 10 hours. After the indicated time, the reaction mixture was cooled down to room temperature, and concentrated under vacuum. Purification by chromatography on silica gel afforded the title product (52.3 mg). Yield 81% (2 steps). **5c**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.5$  Hz, 2 H), 7.56 (t,  $J = 7.0$  Hz, 1 H), 7.46 (t,  $J = 7.3$  Hz, 2 H), 7.37-7.27 (m, 4 H), 7.25-7.19 (m, 1 H), 3.53 (dd,  $J = 13.3, 6.7$  Hz, 1 H), 3.36-3.30 (m, 1 H), 3.26-3.17 (m, 1 H), 1.36 (d,  $J = 6.7$  Hz, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 146.7, 137.4, 133.1, 128.73, 128.70, 128.2, 127.0, 126.4, 47.2, 35.7, 22.0. HRMS calcd for  $\text{C}_{16}\text{H}_{16}\text{ONa}$  ( $\text{M}^+ + \text{Na}$ ) 247.1099 found 247.1100.

#### 4-(4'-Methoxy-[1,1'-biphenyl]-4-yl)pentan-2-one (Scheme 2, **5d**)



**One-pot alkylation/Suzuki cross-coupling/retro-Claisen.** According to the general alkylation procedure, a 2-dram vial equipped with a stir bar was charged with 1-bromo-4-vinylbenzene (**2f**, 30 mg, 0.164 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 86.4 mg, 3.0 equiv, 0.864 mmol), GO (60

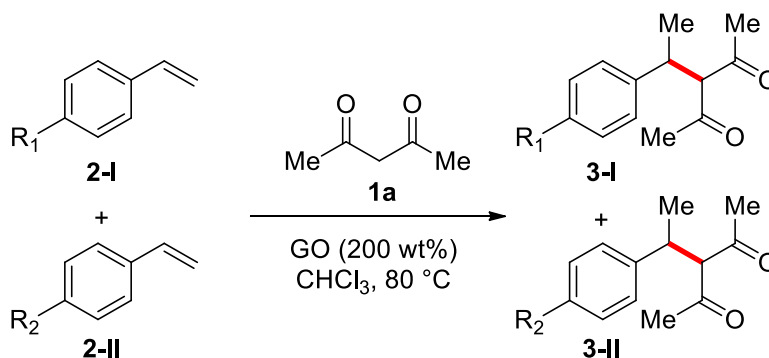
mg, 200 wt%), and chloroform (1.0 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature, filtered and concentrated under vacuum. 4-Methoxyphenylboronic acid (1.5 equiv, 30.4 mg, 0.20 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 5 mol%), Na<sub>2</sub>CO<sub>3</sub> (3.0 equiv, 0.864 mmol) and EtOH/water (1 mL/1 mL) were added, and the reaction mixture was stirred at reflux 12 hours. After the indicated time, the reaction mixture was cooled down to room temperature, and concentrated under vacuum. Purification by chromatography on silica gel afforded the title product (26.4 mg). Yield 60% (3 steps). **5d**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.57-7.45 (m, 4 H), 7.28 (d,  $J$  = 5.9 Hz, 2 H), 6.98 (d,  $J$  = 7.5 Hz, 2 H), 3.86 (s, 3 H), 3.36 (dd,  $J$  = 13.4, 6.6 Hz, 1 H), 2.84-2.77 (m, 1 H), 2.73-2.68 (m, 1 H), 2.11 (s, 3 H), 1.31 (d,  $J$  = 6.5 Hz, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  208.0, 159.2, 144.8, 139.1, 133.7, 128.2, 127.3, 127.0, 114.4, 55.5, 52.2, 35.2, 30.8, 22.2. HRMS calcd for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>Na (M<sup>+</sup> + Na) 291.1361 found 291.1362.



## Selectivity Studies – Alkenes: Electronics

**General Procedure.** According to the general procedure, a 2-dram vial equipped with a stir bar was charged with two olefin substrates (olefin I, 15.0 mg, 1.0 equiv; olefin II, 1.0 equiv), pentane-2,4-dione (**1a**, 0.5 equiv), GO (60 mg, 200 wt%), and  $\text{CHCl}_3$  (0.75 mL) at room temperature. The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for the indicated time. The reaction mixture was cooled down to room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples. The Hammett plot<sup>5</sup> was obtained by plotting  $\log(k_X/k_H)$  vs.  $\sigma$  and  $\sigma^+$  values ( $Y = -0.636X + 0.210$ ,  $R^2 = 0.994$ ;  $Y = -1.001X + 0.339$ ,  $R^2 = 0.833$  for  $\sigma^+$  and  $\sigma$ , respectively). This can be compared with ( $\log(k_X/k_H)$  vs.  $\sigma$  and  $\sigma^+$  of ( $Y = -0.681X - 0.079$ ,  $R^2 = 0.994$ ;  $Y = -1.118X + 0.058$ ,  $R^2 = 0.903$  for  $\sigma^+$  and  $\sigma$ ) in the GO-catalyzed alkylation of arenes with olefins.<sup>1</sup>

**Table SI-7.** Selectivity Study in the GO-Catalyzed  $\alpha$ -Alkylation of Pentane-2,4-dione.<sup>a</sup>



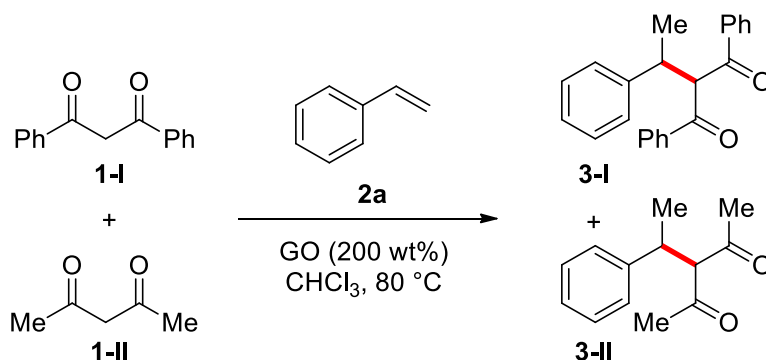
Entry	<b>2-I</b> (R <sub>1</sub> )	<b>2-II</b> (R <sub>2</sub> )	Olefin (equiv)	<b>3-I:3-II</b> (R <sub>1</sub> :R <sub>2</sub> ) <sup>b</sup>
1	H-	Cl-	2.0	58.5:41.5
2	H-	F-	2.0	64.7:35.3
3	H-	Me-	2.0	70.6:29.4
4	H-	MeO-	2.0	83.9:16.1

<sup>a</sup>Conditions: olefin (1.0 equiv), ketone (0.50 equiv), GO (200 wt%),  $\text{CHCl}_3$  (0.20 M), 80 °C. All reactions carried out using 2-dram vials, reagents weighted out on bench, GO was prepared by a modified Hummers method. <sup>b</sup>Determined by  $^1\text{H}$  NMR and/or GC-MS.

## Selectivity Studies – Ketones

**General Procedure.** According to the general procedure, a 2-dram vial equipped with a stir bar was charged with two ketone substrates (ketone-I, 1.0 equiv; ketone-II, 1.0 equiv.), styrene (**2a**, 15 mg, 0.144 mmol, 1.0 equiv), GO (30 mg, 200 wt%), and  $\text{CHCl}_3$  (0.75 mL) at room temperature. The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for the indicated time. The reaction mixture was cooled down to room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples.

**Table SI-8.** Selectivity Study in the GO-Catalyzed  $\alpha$ -Alkylation of Ketones.<sup>a</sup>



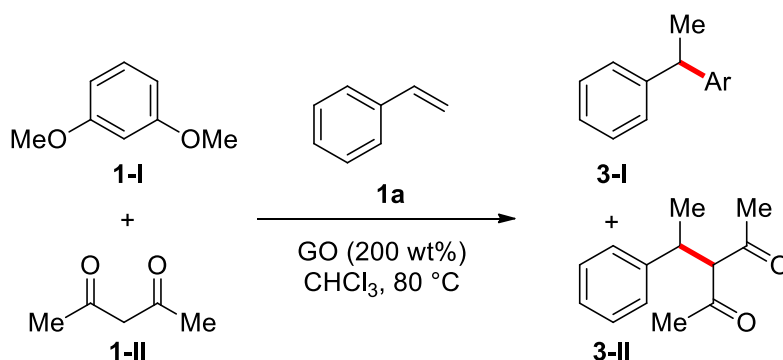
Entry	<b>1-I</b> (R <sub>1</sub> )	<b>1-II</b> (R <sub>2</sub> )	Ketone (equiv)	<b>3-I:3-II</b> (R <sub>1</sub> :R <sub>2</sub> ) <sup>b</sup>
1	Ph	Me	2.0	66:34

<sup>a</sup>Conditions: olefin (0.50 equiv), ketone-I (1.0 equiv), ketone-II (1.0 equiv), GO (200 wt%),  $\text{CHCl}_3$  (0.20 M), 80 °C. All reactions carried out using 2-dram vials, reagents weighted out on bench, GO was prepared by a modified Hummers method. <sup>b</sup>Determined by  $^1\text{H}$  NMR and/or GC-MS.

## Selectivity Studies – Nucleophile: Arene vs. Ketone

**General Procedure.** According to the general procedure, a 2-dram vial equipped with a stir bar was charged with 1,3-dimethoxybenzene (0.288 mmol, 1.0 equiv), pentane-2,4-dione (0.288 mmol, 1.0 equiv), styrene (**1a**, 15 mg, 0.144 mmol, 0.5 equiv), GO (30 mg, 200 wt%), and  $\text{CHCl}_3$  (0.75 mL) at room temperature. The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for the indicated time. The reaction mixture was cooled down to room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples.

**Table SI-9.** Selectivity Study in the GO-Catalyzed  $\alpha$ -Alkylation of Ketones.<sup>a</sup>



Entry	<b>1-I</b> (R <sub>1</sub> )	<b>1-II</b> (R <sub>2</sub> )	Olefin (equiv)	<b>3-I:3-II</b> (R <sub>1</sub> :R <sub>2</sub> ) <sup>b</sup>
1	Arene	Ketone	0.5	19.8:1

<sup>a</sup>Conditions: olefin (0.5 equiv), arene (1.0 equiv), ketone (1.0 equiv), GO (200 wt%),  $\text{CHCl}_3$  (0.20 M), 80 °C. All reactions carried out using 2-dram vials, reagents weighted out on bench, GO was prepared by a modified Hummers method. <sup>b</sup>Determined by  $^1\text{H}$  NMR and/or GC.

## Selectivity Studies – Alkylating Reagent: Alcohol vs. Olefin

**General Procedure.** According to the general procedure, a 2-dram vial equipped with a stir bar was charged with 1-phenylethanol (15.0 mg, 1.0 equiv, 0.123 mmol), 1-methyl-4-vinylbenzene (14.5 mg, 1.0 equiv, 0.123 mmol), pentane-2,4-dione (**1a**, 6.3 mg, 0.5 equiv, 0.063 mmol), GO (60 mg, 200 wt%), and  $\text{CHCl}_3$  (0.75 mL) at room temperature. The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for the indicated time. The reaction mixture was cooled down to room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples.

**Table SI-10.** Selectivity Study in the GO-Catalyzed  $\alpha$ -Alkylation of Pentane-2,4-dione.<sup>a</sup>

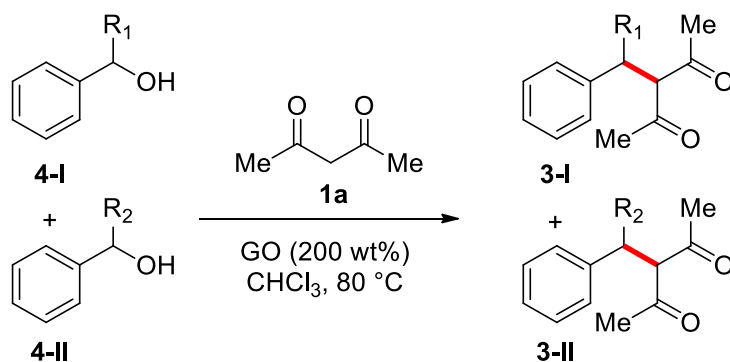
Entry	<b>2-I</b>	<b>2-II</b>	Alcohol/Olefin (equiv)	<b>3-I:3-II</b> ( $R_1:R_2$ ) <sup>b</sup>
1	Alcohol	Olefin	2.0	87:13

<sup>a</sup>Conditions: Alcohol (1.0 equiv.), olefin (1.0 equiv), ketone (0.50 equiv), GO (200 wt%),  $\text{CHCl}_3$  (0.20 M), 80 °C. All reactions carried out using 2-dram vials, reagents weighted out on bench, GO was prepared by a modified Hummers method. <sup>b</sup>Determined by  $^1\text{H}$  NMR and/or GC-MS.

## Selectivity Studies – Benzyl Alcohols

**General Procedure.** According to the general procedure, a 2-dram vial equipped with a stir bar was charged with two alcohol substrates (alcohol-I, 1.0 equiv; alcohol-II, 1.0 equiv), pentane-2,4-dione (0.5 equiv), GO (60 mg, 200 wt%), and  $\text{CHCl}_3$  (0.75 mL) at room temperature. The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for the indicated time. The reaction mixture was cooled down to room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples.

**Table SI-11.** Selectivity Study in the GO-Catalyzed  $\alpha$ -Alkylation of Ketones.<sup>a</sup>



Entry	1-I (R <sub>1</sub> )	1-II (R <sub>2</sub> )	Alcohol (equiv)	3-I:3-II (R <sub>1</sub> :R <sub>2</sub> ) <sup>b</sup>
1	H	Me	2.0	58:42

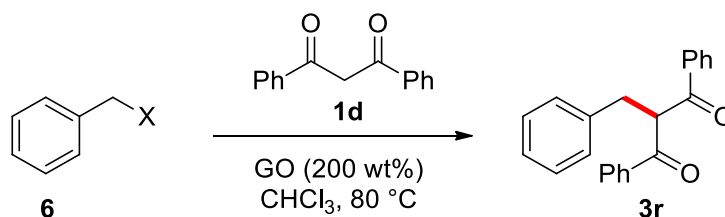
<sup>a</sup>Conditions: alcohol-I (1.0 equiv), alcohol-II (1.0 equiv), ketone (0.50 equiv), GO (200 wt%),  $\text{CHCl}_3$  (0.20 M), 80 °C. All reactions carried out using 2-dram vials, reagents weighted out on bench, GO was prepared by a modified Hummers method.

<sup>b</sup>Determined by  $^1\text{H}$  NMR and/or GC-MS.

### Effect of the Alkylating Reagent

**General Procedure.** A 2-dram vial equipped with a stir bar was charged with alkylating reagent (**5**, 15 mg, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**2d**, 3.0 equiv), GO (30 mg, 200 wt%), and chloroform (0.50 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for the indicated time. The reaction mixture was cooled down to room temperature. After The sample was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples.

**Table SI-12.** Alkylation of 1,3-Diphenylpropane-1,3-dione with Different Alkylating Reagents.<sup>a</sup>



Entry	X	Conversion of <b>6</b> (%) <sup>b</sup>	Recovery of <b>6</b> (%) <sup>b</sup>	Yield of <b>3r</b> (%) <sup>b</sup>
1	Cl	<5	>95	<5
2	Br	20	71	5
3	HO	>98	<2	65
4	AcO	10	90	8
5	H <sub>2</sub> N	>98	<2 <sup>c</sup>	<2

<sup>a</sup>Conditions: alkylating reagent (1.0 equiv), ketone (3.0 equiv), GO (200 wt%),  $\text{CHCl}_3$  (0.20 M), 80 °C. All reactions carried out using 2-dram vials, reagents weighted out on bench. GO was prepared by a modified Hummers method. <sup>b</sup>Determined by  $^1\text{H}$  NMR and/or GC-MS. <sup>c</sup>Unidentified decomposition products.

### Determination of $\alpha$ -Alkylation Reaction Profile

**General Procedure.** According to the general procedure, a 2-dram vial equipped with a stir bar was charged with styrene (**1a**, 15 mg, 0.144 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 96.8 mg, 3.0 equiv, 0.432 mmol), and GO (30 mg, 200 wt%) in  $\text{CHCl}_3$  (0.50 mL). The reaction vial was capped, the reaction mixture was placed in a preheated oil bath, and stirred at 80 °C for the indicated time. After the indicated time, the reaction mixture was cooled down to room temperature using ice-bath. The reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples.

The relative reactivity of ketone  $\alpha$ -alkylation with olefins was studied by determining initial rates at low conversion.<sup>6</sup> In all cases, linear correlations were found by plotting concentration vs. time.

### Determination of the Relative Rate of Ketone $\alpha$ -Alkylation using Olefins

**Conditions:**

[styrene] = 0.30 M

[ketone] = 0.90 M

[GO] = 60 mg/mL

$Y = 0.0000339X - 0.001725$ ,  $R^2 = 0.998$

$v_{\text{initial-ketone}} = 3.39 \times 10^{-2} \text{ mM s}^{-1}$

*This can be compared with the relative rate for GO-catalyzed alkylation of arenes:<sup>1</sup>*

[styrene] = 0.20 M

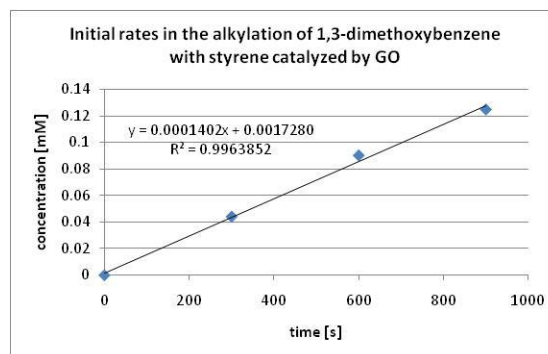
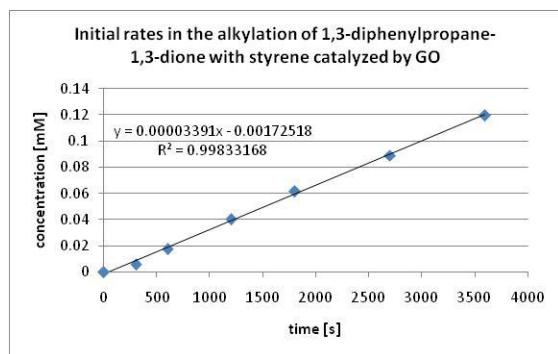
[arene] = 0.60 M

[GO] = 40 mg/mL

$Y = 0.000140X + 0.00173$ ,  $R^2 = 0.996$

$v_{\text{initial-arene}} = 1.40 \times 10^{-1} \text{ mM s}^{-1}$

$v_{\text{initial-ketone}}/v_{\text{initial-arene}} = 0.24$



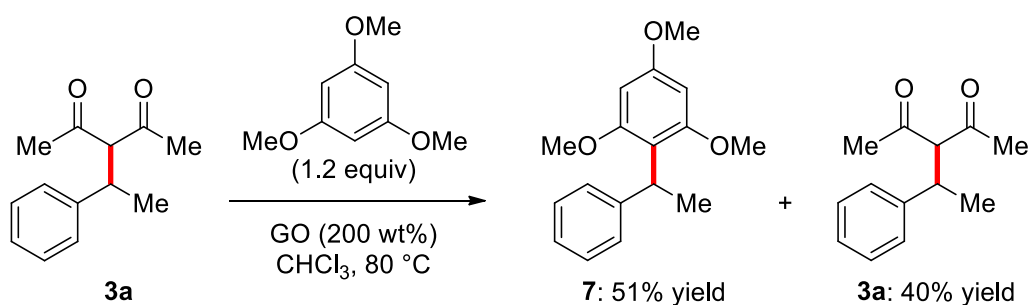
Careful monitoring of the  $\alpha$ -alkylation reaction of 1,3-diphenylpropane-1,3-dione with styrene as electrophile revealed no detectable intermediates formed during the course of the reaction. The observed Hammett selectivity in the  $\alpha$ -alkylation of pentane-2,4-dione with styrene ( $\rho^+ = -0.63$ ;  $\rho = -1.00$ ) and alkylation of 1,3-dimethoxybenzene using styrene ( $\rho^+ = -0.68$ ;  $\rho = -1.12$ ) indicate the presence of an electronically similar intermediate in the transition state of the reaction. Furthermore, olefins and alcohols as electrophiles react at comparable rates in the  $\alpha$ -alkylation of pentane-2,4-dione and 1,3-dimethoxybenzene. Taken together, these findings are consistent with the presence of a carbinol intermediate in the  $\alpha$ -alkylation of arenes using olefins, with the hydration as a kinetically relevant step in the reaction. Further studies on the mechanism of alkylation reactions with sustainable electrophiles catalyzed by graphene-based materials are underway in our laboratory.



## Reversibility of Ketone $\alpha$ -Alkylation

**General Procedure.** A 2-dram vial equipped with a stir bar was charged with 3-(1-phenylethyl)pentane-2,4-dione (**3a**, 40.8 mg, 0.20 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (40.4 mg, 1.2 equiv, 0.24 mmol), GO (81.6 mg, 200 wt%), and  $\text{CHCl}_3$  (1.0 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 15 h. The reaction mixture was cooled down to room temperature. The sample was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard and comparison with authentic samples. Conversion (**3a**) = 60%. Yield (**7**) = 51%.

**Scheme SI-2.** Determination of Reversibility of Ketone  $\alpha$ -Alkylation.<sup>a</sup>



<sup>a</sup>Conditions: 3-(1-phenylethyl)pentane-2,4-dione (1.0 equiv), 1,3,5-trimethoxybenzene (1.2 equiv), GO (200 wt%),  $\text{CHCl}_3$  (0.20 M), 80 °C, 15 h.

## Control Experiments in Ketone $\alpha$ -Alkylation

### Control Experiments without GO

*General Procedure.* A 2-dram vial equipped with a stir bar was charged with styrene (**2a**, 15 mg, 0.144 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), and chloroform (0.50 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 15 h. The reaction mixture was cooled down to room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard. Conversion <2%. Yield <2%.

### Control Experiments with Benzoic Acid

*General Procedure.* A 2-dram vial equipped with a stir bar was charged with styrene (**2a**, 15 mg, 0.144 mmol, 1.0 equiv), pentane-2,4-dione (**1a**, 43.2 mg, 3.0 equiv, 0.432 mmol), benzoic acid (30 mg, 0.288 mmol, 200 wt%), and chloroform (0.50 mL). The reaction vial was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 15 h. The reaction mixture was cooled down to room temperature. The reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain selectivity, conversion and yield using internal standard. Conversion <2%. Yield <2%.

### Recycling of GO in Large-scale Reactions

*General Procedure.* A 25 mL round-bottom flask vial equipped with a stir bar was charged with styrene (**2a**, 0.15 g, 1.44 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 0.97 g, 3.0 equiv, 4.32 mmol), GO (0.30 g, 200 wt%), and chloroform (5.0 mL). The flask was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 3 h. GO was filtered, the reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain conversion and yield using internal standard. Run 1. Conversion 100%. Yield 89%. The recovered GO was washed with  $\text{CH}_2\text{Cl}_2$  (5 x 5 mL), and dried under high vacuum. A small sample of the recovered GO (10 mg) was used for analysis, and the rest of the recovered GO for the recycling reaction.

**First recycling:** A 25 mL round-bottom flask vial equipped with a stir bar was charged with styrene (**2a**, 0.12 g, 1.15 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 0.78 g, 3.0

equiv, 3.46 mmol), GO (0.24 g, 200 wt%), and chloroform (5.0 mL). The flask was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 3 h. GO was filtered, the reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain conversion and yield using internal standard. Run 2. Conversion 100%. Yield 88%. The recovered GO was washed with  $\text{CH}_2\text{Cl}_2$  (5 x 5 mL), and dried under high vacuum. A small sample of the recovered GO (10 mg) was used for analysis, and the rest of the recovered GO for the recycling reaction.

**Second recycling:** A 25 mL round-bottom flask vial equipped with a stir bar was charged with styrene (**2a**, 0.10 g, 0.96 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 0.65 g, 3.0 equiv, 2.88 mmol), GO (0.20 g, 200 wt%), and chloroform (4.0 mL). The flask was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 3 h. GO was filtered, the reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain conversion and yield using internal standard. Run 3. Conversion 100%. Yield 84%. The recovered GO was washed with  $\text{CH}_2\text{Cl}_2$  (5 x 5 mL), and dried under high vacuum. A small sample of the recovered GO (10 mg) was used for analysis, and the rest of the recovered GO for the recycling reaction.

**Third recycling:** A 25 mL round-bottom flask vial equipped with a stir bar was charged with styrene (**2a**, 80 mg, 0.77 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 0.52 g, 3.0 equiv, 2.31 mmol), GO (0.16 g, 200 wt%), and chloroform (3.0 mL). The flask was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 3 h. GO was filtered, the reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain conversion and yield using internal standard. Run 4. Conversion 100%. Yield 85%. The recovered GO was washed with  $\text{CH}_2\text{Cl}_2$  (5 x 5 mL), and dried under high vacuum. A small sample of the recovered GO (10 mg) was used for analysis, and the rest of the recovered GO for the recycling reaction.

**Fourth recycling:** A 25 mL round-bottom flask vial equipped with a stir bar was charged with styrene (**2a**, 60 mg, 0.58 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 0.39 g, 3.0 equiv, 1.73 mmol), GO (0.12 g, 200 wt%), and chloroform (3.0 mL). The flask was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 3 h. GO was filtered, the reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain conversion and yield using internal standard. Run 5. Conversion 100%. Yield 81%. The recovered GO was washed with  $\text{CH}_2\text{Cl}_2$  (5 x 5 mL), and dried on vacuum. A small sample of the recovered GO (10 mg) was used for analysis, and the rest of the recovered GO for the recycling reaction.

**Fifth recycling:** A 25 mL round-bottom flask vial equipped with a stir bar was charged with styrene (**2a**, 40 mg, 0.38 mmol, 1.0 equiv), 1,3-diphenylpropane-1,3-dione (**1d**, 0.26 g, 3.0 equiv, 1.15 mmol), GO (80 mg, 200 wt%), and chloroform (3.0 mL). The flask was capped, the reaction mixture was placed in an oil bath, and stirred at 80 °C for 3 h. GO was filtered, the reaction mixture was analyzed by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) and GC-MS to obtain conversion and yield using internal standard. Run 6: Conversion 100%. Yield 82%. The recovered GO was washed with  $\text{CH}_2\text{Cl}_2$  (5 x 5 mL), dried under vacuum, and used for analysis.

## References

1. Hu, F.; Patel, M.; Luo, F.; Flach, C.; Mendelsohn, R.; Garfunkel, E.; He, H.; Szostak, M. *J. Am. Chem. Soc.* **2015**, *135*, 14473.
2. Patel, M.; Luo, F.; Khoshi, M. R.; Rabie, E.; Zhang, Q.; Flach, C. R.; Mendelsohn, R.; Garfunkel, E.; Szostak, M.; He, H. *ACS Nano* **2016**, *9*, 2305.
3. Y. Zhu, S. Murali, M. D. Stoller, A. Velamakanni, R. D. Piner and R. S. Rouff, *Carbon*, **2010**, *48*, 2118.
4. M. Patel, W. Feng, K. Savaram, M. R. Khoshi, R. Huang, J. Sun, E. Rabie, C. Flach, R. Mendelsohn, E. Garfunkel, H. He, *Small*, **2015**, *11*, 3358.
5. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* **1991**, *91*, 165.
6. J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill, **2002**.



