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Supplementary information

Bifunctional property of Pt nanoparticles deposited on TiO_2 for the photocatalytic sp^3C–sp^3C cross-coupling reactions between THF and alkanes†

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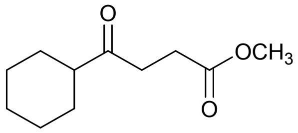
Contents

1. Synthesis of 2-cyclohexyltetrahydrofuran (**1a**)

2-cyclohexyltetrahydrofuran (**1a**) was prepared by following the procedure reported in the literature.[S1]

Synthesis of methyl-4-cyclohexyl-4-oxobutanoate:

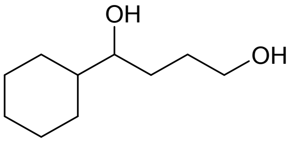
A solution of anhydrous LiBr (0.938 g, 10.8 mmol, 2.4 eq.) in THF (25 ml) was added to a stirred suspension of CuBr (0.775 g, 5.40 mmol, 1.2 eq.) in THF (14 ml) under an argon atmosphere and stirred at room temperature until homogeneity. Then, chloro(cyclohexyl)magnesium (2.0 M) in THF (2.70 ml, 5.40 mmol, 1.2 eq.) and methyl-4-chloro-4-oxobutanoate (0.682 g, 4.53 mmol, 0.1 eq.) were quickly and successively added to the stirred solution of salts and stirred for 1 hour and 15 minutes. After that, it was quenched with $NHCl_4$ (12 ml) and extracted 3 times with EtOAc. The product was purified by column chromatography and isolated as a colorless oil. The NMR data, δH (400 MHz, $CDCl_3$) 3.67 (3 H, s, $COOC\underline{H_3}$), 2.77 (2 H, t, $COC\underline{H_2}$), 2.59 (2 H, t, $C\underline{H_2}CO_2Me$), 2.40–2.35 (1 H, m, H'), and 1.88–1.24 (11 H, m, alkyl-CH), were consistent with those reported in the literature.[S1]



Methyl-4-cyclohexyl-4-oxobutanoate

Synthesis of 1-cyclohexylbutane-1,4-diol

A solution of methyl-4-cyclohexyl-4-oxobutanoate (0.4 g, 2.02 mmol, 0.4 eq.) in THF (4 ml) was added dropwise to a stirred solution of $LiAlH_4$ (2 M) in anhydrous THF (4 ml, 8 mmol, 2.96 eq.) at room temperature. The resulting mixture was stirred for 2 h and cooled to 273 K. The excess hydride was quenched by the addition of the following regents in the mentioned order: 2.4 ml water, 2.4 ml of 15% aqueous NaOH solution and 7.2 ml of water. Then the reaction mixture was warmed to room temperature under stirring, filtered through Celite and condensed in vacuum to obtain a colorless oil which underwent crystallization. The crude crystals so obtained were washed with hexane and dried under vacuum. The NMR data, δH (400 MHz, $CDCl_3$) 3.76-3.65 (2 H, m, $C\underline{H_2}OH$), 3.41–3.37 (1 H, m, $C\underline{H}OH$), 1.98 (1 H, br s, OH), and 1.86–0.98 (16 H, m, alkyl-CH+OH), were consistent with those reported in the literature.[S1]

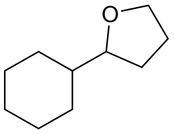


1-cyclohexylbutane-1,4-diol

Synthesis of 2-cyclohexyltetrahydrofuran (**1a**)

To a solution of 1-cyclohexylbutane-1,4-diol (0.276 g) in acetonitrile (8 ml), 5 mol% of $HAuCl_4$ was added. The solution was stirred under argon at 313 K for 20 h, followed by solvent evaporation in vacuum to give crude yellow oil. The NMR data, δ_H (400 MHz, $CDCl_3$) 3.84–3.78 (1 H, m, $OC\underline{H}H$), 3.73–3.61 (1 H, m, $OCH\underline{H}$), 3.50–3.45 (1 H, m, $\underline{H}COCH_2$), 1.93–0.94 (15 H, m, alkyl-CH); δ_C (400 MHz, $CDCl_3$)

84.18, 77.16 (t), 67.85, 43.21, 30.08, 29.33, 29.25, 26.71, 26.26, 26.10, and 25.99, were consistent with those reported in the literature.[S1]



2-cyclohexyltetrahydrofuran (**1a**)

2. Photochemical stability of **1a**

A photochemical reaction was performed to study the photochemical stability of **1a**. A solution of **1a** in a mixture of cyclohexane (3 ml) and THF (10 ul) was prepared and analyzed by GC-MS to confirm the initial concentration of **1a** (Table S1, entry 1). Then, the solution was transferred to a test tube which was sealed with a silicon septum, purged with argon and then photoirradiated with the xenon lamp for 24 h (21 mW cm^{-2} measured at 365 nm in wavelength). Then, the mixture was analyzed by GC-MS. The amount of **1a** did not change much during this reaction, indicating its high photochemical stability (Table S1, entry 2).

Table S1 Photochemical reaction of **1a**

Entry	Time (h)	Amount of **1a** (μmol)
1	0	3.7
2	24	3.4

3. Photocatalytic reaction between THF and cyclohexane for 24 h

Table S2 shows the results of the photocatalytic reaction tests performed for 1 h and 24 h with the Pt(0.1)/TiO_2 sample. The amount of the cross-coupling product **1a** did not increase much with an increase in the reaction time from 1 h to 24 h. On the other hand, the homo-coupling of cyclohexane to give **1e** increased significantly with time. The reaction for 24 h provided several new peaks in the GC-MS profile, probably arising from the successive reaction of cyclohexane. Further, the color of the catalyst changed from gray to pale yellow after the 24 h reaction. These results indicate that although the production rate of **1a** was high in the initial stage of reaction, it decreased later, presumably due to acceleration in the side reactions of other compounds and **1a** itself. The formation of **1a** and its consumption in the successive reactions would achieve similar rates to make the yield of **1a** become constant with time. So, to achieve high product selectivity in this photocatalytic reaction, it is suggested to prefer shorter contact time or short reaction time.

Table S2 Photocatalytic reaction tests between THF and cyclohexane with the Pt(0.1)/TiO_2 sample[a]

		Products (μmol)			Selectivity (%)	
Entry	Time (h)	**1a**	**1b+1c**	**1e**	S_{THF}	S_{CyH}
1	1	1.4	0.0	3.9	> 99	26
2	24	1.6	0.0	18.6	> 99	8

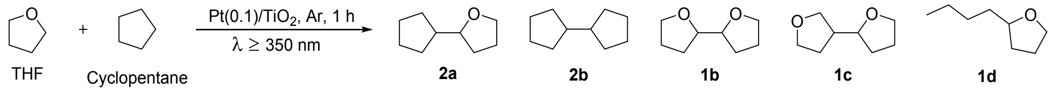
[a] Reaction conditions: 0.123 mmol of THF, 27.7 mmol of cyclohexane and, 50 mg of the Pt(0.1)/TiO_2 sample were used. Other conditions, product's abbreviation and selectivity calculation were the same as those in Table 2 in the main text.

4. Photocatalytic reaction of THF with cyclopentane and *n*-hexane

As mentioned in the main text, the Pt/TiO_2 photocatalyst promoted $sp^3C–sp^3C$ cross-coupling reaction proceeded with other alkanes such as cyclopentane and n-hexane, as well.

As another cyclic alkane, cyclopentane was tested for the coupling reaction with THF (Table S3). The reaction between THF and cyclopentane with the $Pt(0.1)/TiO_2$ photocatalyst gave 2-cyclopentyltetrahydrofuran (**2a**) as the only cross-coupling product along with the homo-coupling product from both cyclopentane (**2b**) and THF (**1b** and **1c**) and its deoxygenated product (**1d**) (Table S3, entry 1). On the other hand, the pristine TiO_2 sample showed low photocatalytic activity, which gave only a small amount of the cross-coupling product (**2a**) and the homo-coupling product of THF (**1b** and **1c**) (Table S3, entry 2).

Table S3 Photocatalytic $sp^3C–sp^3C$ cross-coupling between THF and cyclopentane[a]



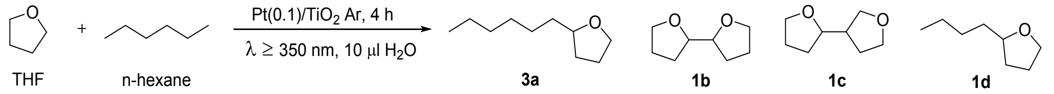
Entry	Reactants (mmol)		Photocatalyst	Products (µmol)[b]			
	THF	Cyclopentane		**2a**	**2b**	**1b+1c**	**1d**
1	1.2	32.1	$Pt(0.1)/TiO_2$	1.7	0.2	3.4	0.4
2	1.2	32.1	TiO_2	0.03	0.0	0.07	0.0

[a] Reaction conditions: 50 mg of the photocatalyst was used, the reaction time was 1 h, the wavelength of incident light was ≥350 nm, the light intensity was 21 mW cm^{-2}, and the reactor temperature was *ca*. 298 K. [b] Amount of **2a**, **2b**, and **1b**–**1d** was determined from the calibration curve of **1a** that was synthesized by following the procedure reported in the literature.[S1]

The photocatalytic cross-coupling of THF with *n*-hexane was also tested (Table S4). This reaction also gave a mixture of the homo-coupling and cross-coupling products. The reaction with the $Pt(0.1)/TiO_2$ photocatalyst gave 2-hexyltetrahydrofuran (**3a**) as the cross-coupling product along with the homo-coupling products from THF (**1b**–**1d**) (Table S4, entry 1). Under these conditions, the homo-coupling of *n*-hexane proceeded to a small extent to give 5-methylundecane and 5,6-dimethyldecane. On the other hand, reactions performed with the pristine TiO_2 sample did not give any kind of product (Table S4, entry 2).

These results also highlight the importance of Pt in these photocatalytic cross-coupling reactions.

Table S4 Photocatalytic $sp^3C–sp^3C$ cross-coupling between THF and *n*-hexane[a]



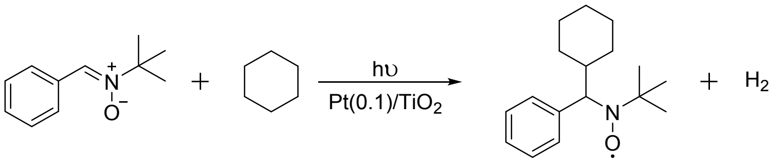
Entry	Reactants (mmol)		Photocatalyst	Products (µmol)[b]		
	THF	*n*-hexane		**3a**	**1b+1c**	**1d**
1	1.2	22.7	$Pt(0.1)/TiO_2$	0.2	4.8	1.7
2	1.2	22.7	TiO_2	0.0	0.0	0.0

[a] Reaction conditions: 10 µl of water, 50 mg of the photocatalyst was used, the reaction time was 4 h, the wavelength of incident light was ≥350 nm, the light intensity was 21 mW cm^{-2}, and the reactor temperature was *ca*. 298 K. [b] Amount of **3a** and **1b**–**1d** was determined from the calibration curve of **1a** that was synthesized by following the procedure

reported in the literature.[S1]

5. ESR measurements

ESR measurements were carried out to confirm the photooxidation of cyclohexane to radical species with the Pt(0.1)/TiO_2 photocatalyst under UV irradiation. PBN was used as a spin trapping agent. The wavelength of light was restricted to >400 nm so as to avoid the photodissociation of the reagents. This wavelength restriction decreased the activity of the Pt/TiO_2 photocatalyst which in turn affected the ESR measurement. Although the signals obtained under these experimental conditions were weak, we succeeded in trapping the cyclohexyl radical by PBN (eq. S1). The signals shown in the main text were assigned to the adduct of PBN and cyclohexyl radical, **a**.



a

(S1)

6. Temperature controlled reaction tests

As mentioned in the main text, the amount of **1a**, the cross-coupling product, steadily increased with increasing the reaction temperature under photoirradiation. The reaction temperature was precisely maintained by using a water bath. After the reaction for 1 hour, the photoirradiation was stopped and sampling was done at room temperature.

Table S5, entries 1–3 show the results of the temperature controlled reactions performed with the Pt(0.1)/TiO_2 photocatalyst. Under these conditions, the **1a** and the homo-coupling products of THF (**1b**–**1d**) were the main products. These values were plotted in the form of Arrhenius plot (the plot for **1a** was shown in Fig. S1a) and an apparent activation energies (E_a) were calculated. The value of $E_{a,cross}$ for **1a** was 65.5 kJ/mol, while that for homo-coupling of THF $E_{a,homo}$ was 37 kJ/mol.

Under the same reaction conditions, experiments were performed with bare TiO_2 sample. The results are shown in Table S5, entries 5 and 6, and the Arrhenius plot for **1a** is shown in Fig. S1b. The value of $E_{a,cross}$ for **1a** was 21 kJ/mol, while that for homo-coupling of THF $E_{a,homo}$ was 33 kJ/mol.

The similar $E_{a,homo}$ values for homo-coupling of THF and strikingly different $E_{a,cross}$ values for **1a** clearly indicate that thermally metal catalysis by the Pt nanoparticles should be involved in the cross-coupling reaction.

Table S5 Temperature controlled reactions between THF and cyclohexane with the Pt(0.1)/TiO_2 photocatalyst and the pristine TiO_2 photocatalyst [a]

Entry	Photocatalyst	Temperature (K)	Amount of products (µmol) [b]	
			1a	**1b**+**1c**+**1d**
1	Pt(0.1)/TiO_2	299	0.42	1.17
2		305	0.53	8.98
3		313	1.03	13.1
4[c]		313	0.00	0.00
5	TiO_2	308	0.05	0.32
6		313	0.06	0.39

[a] Reaction conditions: 1 ml of THF, 3 ml of cyclohexane and 50 mg of the photocatalyst sample were used, the reaction time was 1 h, the wavelength of light was ≥ 350 nm, and the light intensity was 20 mW cm^{-2} measured at 360 nm in wavelength. [b] See Table 2 in the main text. [c] The reaction was performed in dark.

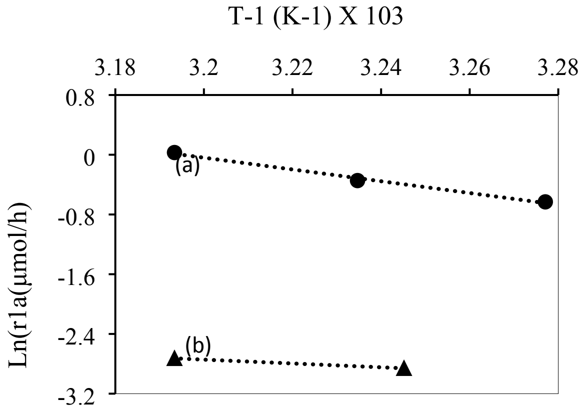


Fig. S1 Pseudo Arrhenius plot for temperature controlled photocatalytic reaction tests between THF and cyclohexane under light with (a) the Pt(0.1)/TiO_2 photocatalyst and (b) the pristine TiO_2 photocatalyst. $r_{\mathbf{1a}}$: formation rate of **1a** determined from the amount of **1a** yielded for the initial 1 h.

References

[S1] X. Jiang, E. K. London, D. J. Morris, G. J. Clarkson, M Wills, *Tetrahedron*, 2010, **66**, 9828–9834.