Supporting Information

Noble-metal free TiO_2 photocatalysis for selective C=C reduction of α,β-enones by CF_3SO_3H modification

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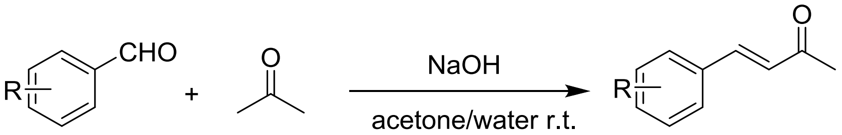
I. General Information

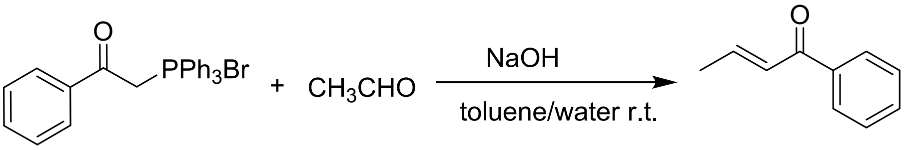
All reactions were performed under Ar atmosphere unless specifically indicated and with oven-dried glassware under magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Photochemical reactions were carried out using a 100 W 400 nm LED purchased from Au Light (Beijing) in standard Pyrex-glass bottles with sealable rubber-cap. We have high-power fan placed next to the setup to cool the bottle. And we measured the temperature of the reaction mixture to be 38 ^{o}C. This temperature is mild enough not to lead other non-photocatalytic reactions. We measured All photoreactions were stirred using a PTFE coated magnetic stir bar on a magnetic stir plate. Gas chromatography (GC) was performed on an Agilent 7890A instrument equipped with a split-mode capillary injection system and Agilent 5973 network mass spec detector (MSD). Yield refers to GC yield by referring to analytically pure material unless otherwise noted. Thin layer chromatography (TLC) was performed on SiliaPlate 250 μm thick silica gel plates provided by Qingdao chemicals. Column chromatography was performed using Qingdao Haiyang flash silica gel (200-300 mesh). Visualization was accomplished with short wave UV light (254 nm). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ solvent using 300 MHz, 400 MHz or 600 MHz Bruker Avance NMR instrument (referenced internally to Me_4Si). Chemical shifts (δ, ppm) are relative to tetramethylsilane (TMS) with the resonance of the non-deuterated solvent or TMS as the internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Accurate mass measurements were performed using a Thermo Fisher DFS mass spectrometer with EI ionization in FD-MS detection mode.

II. General procedure A for the preparation of α,β-enones via Claisen-Schmidt reaction



α,β-Enones were prepared using the reported procedure. Benzaldehyde (10 mmol) was added into a mixture solution of 4 ml acetone and 8 ml H_2O. Then 1.6 ml 5% NaOH aqueous solution was slowly added into the above mixture solution dropwise. Then the reaction mixture was stirred at room temperature for approximate 1-2 h with the monitoring of the disappearance of benzaldehyde and the formation of new spots in TLC plate. After the total consumption of benzaldehyde, the mixture was filtered off and water (5 mL) was added. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified through column chromatography (petroleum ether/EtOAc =100/1 to 30/1) to afford the corresponding α,β-enones. The product was analyzed by HR-EI-MS, ^1H NMR, and ^{13}C NMR.

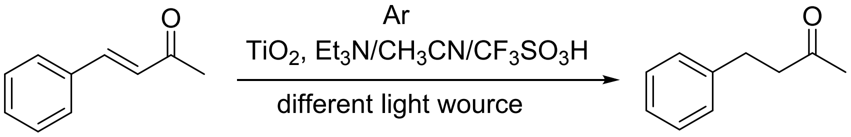
III. General procedure B for the preparation of α,β-enones via modified Wittig reaction



α,β-Enones were prepared using the reported procedure. Phenacyltriphenylphosphonium bromide (10 mmol) and NaOH (1mmol) was added into a mixture solution of 10 ml toluene and 5 ml H_2O. Then 2 ml acetaldehyde was slowly dropwise added into the above solution. Then the reaction mixture was stirred at room temperature for approximate 6 h with the monitoring of the disappear of Wittig reagent and the formation of new spots in TLC plate. After the total consumption of phenacyltriphenylphosphonium bromide, the mixture was filtered off and water (5 mL) was added. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified through column chromatography (petroleum ether/EtOAc =200/1 to 30/1) to afford the corresponding α,β-enones. The product was analyzed by HR-EI-MS, ^1H NMR, and ^{13}C NMR.

IV. Optimization of reaction conditions

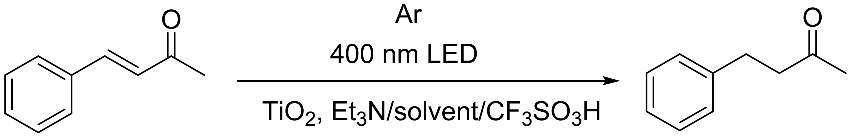
Table S1. TiO_2 Photocatalytic Reduction of C=C Bond of α,β-Enones using different light source[a]



Entry	Light source	Yield[b] (%)
1	300 W xenon lamp with 365 nm filter	98
2	300 W xenon lamp with 420 cut-off filter	18
3	100 W 400 nm LED	98
4	100 W 455 nm LED	trace

[a]Reaction conditions: (E)-4-phenylbut-3-en-2-one (0.1 mmol), photocatalyst P25 TiO_2 (20 mg), acetonitrile (0.9 ml) as solvent，triethylamine (0.1 ml) as hydrogen donor and hole sacrificial reagent under Ar atmosphere, CF_3SO_3H (0.006 mmol) with different illuminating source for 2 h at 5 cm distance. [b]Measured by GC by referring the integral area of the crude reaction mixture with commercially available standard compound by the FID detector.

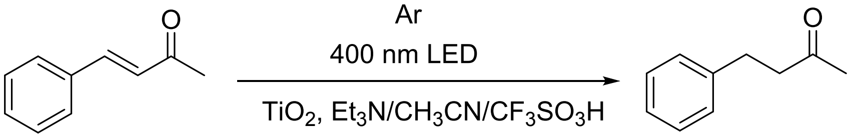
Table S2. TiO_2 Photocatalytic Reduction of C=C Bond of α,β-Enones using different solvent[a]



Entry	Solvent	Yield[b] (%)	Conversion(%)
1	CH_3CN	98	100
2	DMF	29	100
3	DMSO	0	20
4	n-hexane	12	18
5	toluene	28	55
6	H_2O	trace	28

[a]Reaction conditions: (E)-4-phenylbut-3-en-2-one (0.1 mmol), photocatalyst P25 TiO_2 (20 mg), solvent (0.9 ml)，triethylamine (0.1 ml) as hydrogen donor and hole sacrificial reagent under argon atmosphere, CF_3SO_3H 0.006 mmol with 400 nm LED illuminating for 2 h at 5 cm distance. Yields are measured by GC by referring the integral area of the crude reaction mixture with commercially available standard compound by the FID detector.

Table S3. TiO_2 Photocatalytic Reduction of C=C Bond of α,β-Enones with different hydrogen donor and hydrogen donor:solvent ratio.



Entry	Hydrogen donor	solvent	Yield(%)	Conversion(%)
1	Methanol	Methanol	22	100
2	Ethanol	Ethanol	51	100
3	Isopropanol	Isopropanol	8	23
4	triethylamine	CH_3CN	98	100
5	DIPEA	CH_3CN	19	33

6	Hantzsch's ester	CH_3CN	47	100
7[b]	triethylamine	CH_3CN	77	100
8[c]	triethylamine	CH_3CN	79	100
9[d]	triethylamine	CH_3CN	71	100
10[e]	triethylamine	CH_3CN	71	98

[a] Reaction conditions: (E)-4-phenylbut-3-en-2-one (0.1 mmol), photocatalyst P25 TiO_2 (20 mg), solvent (0.9 ml), hydrogen donor (0.1 ml) under Ar atmosphere, CF_3SO_3H 0.006 mmol with 400 nm LED illuminating for 2 h at 5 cm distance for entry1-5, while solvent (0.9 ml), hydrogen donor 100 mg for entry 6. Yields are measured by GC by referring the integral area of the crude reaction mixture with commercially available standard compounds by the FID detector. [b] CH_3CN: triethylamine= 0.95 ml:0.05 ml [c] CH_3CN: triethylamine= 0.8 ml:0.2 ml [d] CH_3CN: triethylamine= 0.7 ml:0.3ml [e] CH_3CN: triethylamine= 0.5 ml:0.5ml.

Table S4. TiO_2 Photocatalytic Reduction of C=C Bond of α,β-Enones with different basic and acidic co-catalyst.

Entry	Co-catalyst	Yield(%)	Conversion(%)
1	K_2CO_3	44	78
2	KOH	50	77
3	Cs_2CO_3	18	100
4	Benzoic acid	9	20
5	4-methoxy benzoic acid	16	100
6	Acetic acid	14	33
7	Formic acid	71	100
8	CF_3COOH	79	100
9	$MeSO_3H$	71	100
10	4-toluenesulfonic acid	36	65
11	CF_3SO_3H	98	100

[a] Reaction conditions: (E)-4-phenylbut-3-en-2-one (0.1 mmol), photocatalyst P25 TiO_2

(20 mg), CH_3CN (0.9 ml), Et_3N (0.1 ml) under argon atmosphere, co-catalyst (0.006 mmol) with 400 nm LED illuminating for 2 h at 5 cm distance. Yields are measured by GC by referring the integral area of the crude reaction mixture with commercially available standard compounds by the FID detector.

Table S5. Blank Control Experiments for TiO_2 Photocatalytic Reduction of C=C Bond of α,β-Enones

Entry	Deviation from the standard condition	Yield (%)	Conversion (%)
1	Without TiO_2	0	33
2	SiO_2 instead of TiO_2	0	44
3	Without illumination in dark	0	0
4	Without triethylamine	1	36
5	Heating to 80 °C in dark	0	0

V. General procedures for TiO_2 photocatalyzed reduction of C=C bond of α,β-enones with adding CF_3SO_3H

A 10 mL glass vial filled with 0.9 mL extra-dry acetonitrile, 0.1 ml triethylamine and 0.1 mmol as-prepared α,β-enones, and 20 mg P25-TiO_2 photocatalyst was capped with sealable rubber-cap and magnetically stirred in front of a 400 nm LED. A high power axial fan was placed beside the glass vial to keep the reaction under room temperature. Once the starting material was completely consumed (monitored by TLC, petroleum ether/EtOAc= 30/1), the mixture was concentrated in vacuo to dryness. The residue was purified through column chromatography (petroleum ether/EtOAc =200/1 to 50/1) to afford the corresponding C-C bond saturated product. The product was analyzed by GC-MS.

VI. Photocatalyst recycle perfomance for 5 cycles

For the photocatalyst stability test: after one standard reaction, the photocatalyst was separated by centrifugation, and washed by acetonitrile twice, and then transferred into the photo-reaction vessel, the following steps are the same to the procedure in the above mentioned standard photo-reaction protocols. The cycle stability test was repeated for consecutive five times.

Table S6. Photocatalyst recycle perfomance for 5 cycles of TiO_2 Photocatalytic Reduction of C=C Bond of α,β-Enones

Entry	1st run	2nd run	3rd run	4th run	5th run
Yield (%)	98	98	97	97	95
Conversion (%)	100	100	100	100	100

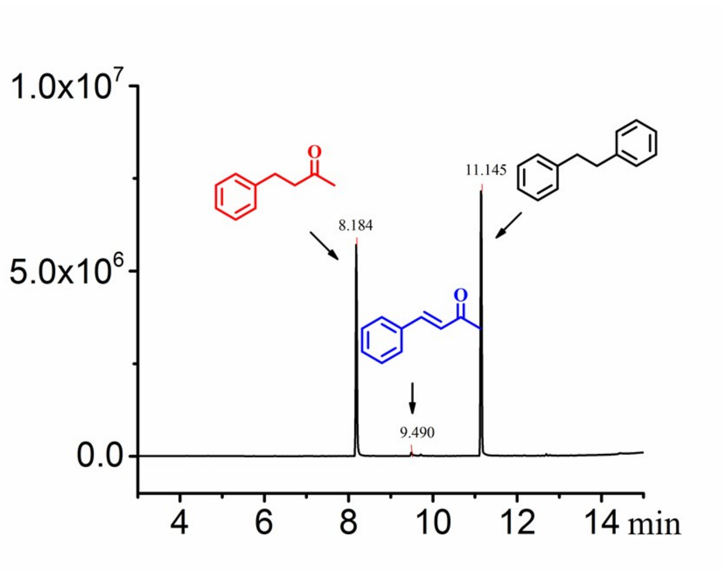
VII. TiO_2 photocatalyzed reduction of C=C bond of α,β-enones with adding CF_3SO_3H on gram scale

A 50 mL two-necked glass bottle was filled with 18 mL extra-dry acetonitrile and 2 ml triethylamine and 10 mmol as-prepared α,β-enones, and 100 mg P25-TiO_2 photocatalyst, 0.6 mmol CF_3SO_3H was added extremely slowly to the solution with ice-bath. After the completion of adding the reagent, the suspension was purged with Ar for 20 minutes and then magnetically stirred in front of a 400 nm LED illumination. A high power axial fan was placed beside the glass vial to keep the reaction under room temperature. Once the starting material was completely consumed (monitored by TLC, petroleum ether/EtOAc= 30/1), the mixture was filtered off and water (20 mL) was added. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL) for 3 times. The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified through column chromatography (petroleum ether/EtOAc =100/1 to 30/1) to afford the corresponding 1.4 g α,β-enones with an 95% isolated yield. The product was analyzed by HR-EI-MS, ^1H NMR, and ^{13}C NMR.

VIII. ATR-FTIR technique procedures and spectra of blank and control experiments

The ATR−FTIR spectroscopy experimental setup was similar to that described in Ref.22. The instrumental setup consisted of a self-modified ARK flow cell (Thermo Fisher) containing a ZnSe crystal on the bottom plate and a quartz window on the top plate. Twelve infrared bounces were allowed using a 45° internal reflection element (80 × 10 × 4 mm^3). The FTIR measurements were performed on a Nicolet 6700 FT-IR spectrometer with an MCT detector. IR spectra ranging from 4000 to 650 cm^{-1} were recorded by averaging 64 scans with a resolution of 4 cm^{-1}. A layer of CH_3CN/Et_3N solvent (9:1) was dripped onto the surface of the ZnSe crystal that was coated with a TiO_2 film. The crystal was then scanned to obtain the background spectrum.The substrate-containing solution was then dripped onto the surface, and adsorption equilibrium on the TiO_2 film was achieved after a balancing period of 3 h. TiO_2 film preparation: P25 was added in CH_3CN at a concentration of 0.25 g/mL. This suspension was placed in a 40 kHz ultrasonic bath for 20 min and then placed in an agate mortar for 10 min. The suspension (1.5 mL) was spread on the ZnSe crystal and dried for 1 h at 200 ^oC to remove CH_3CN.

IX. GC-MS spectra of the C-C saturated products of TiO_2 photocatalyzed reduction of C=C bond of α,β-enones with adding CF_3SO_3H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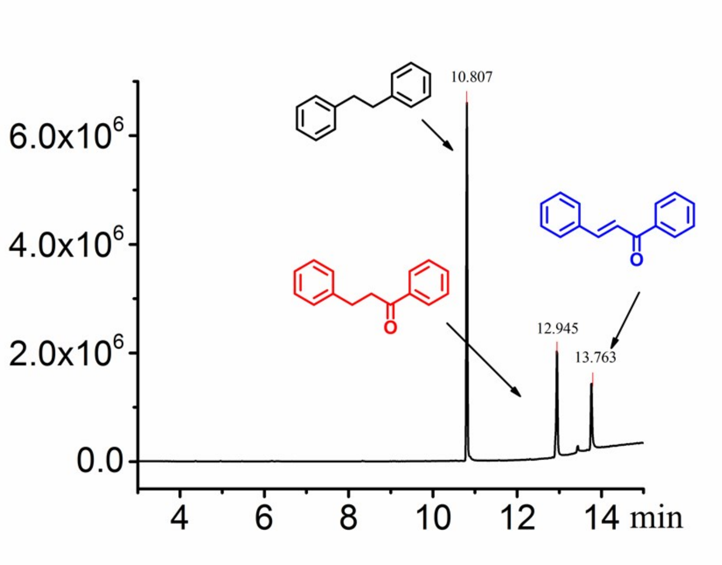
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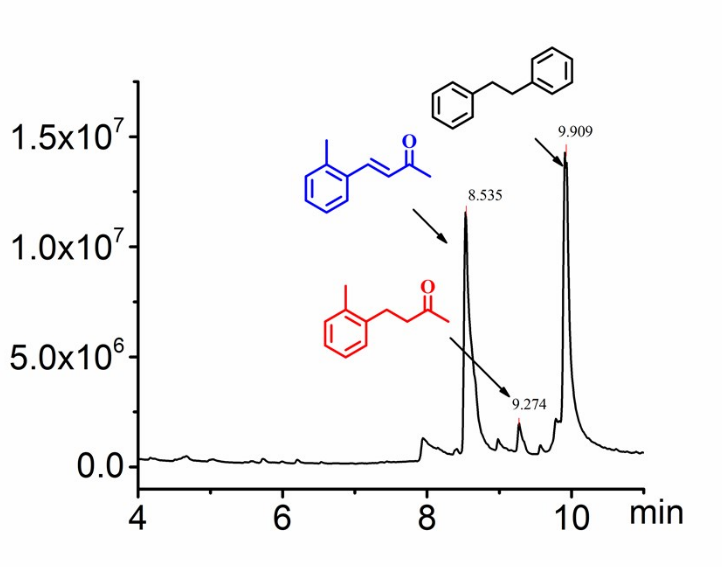
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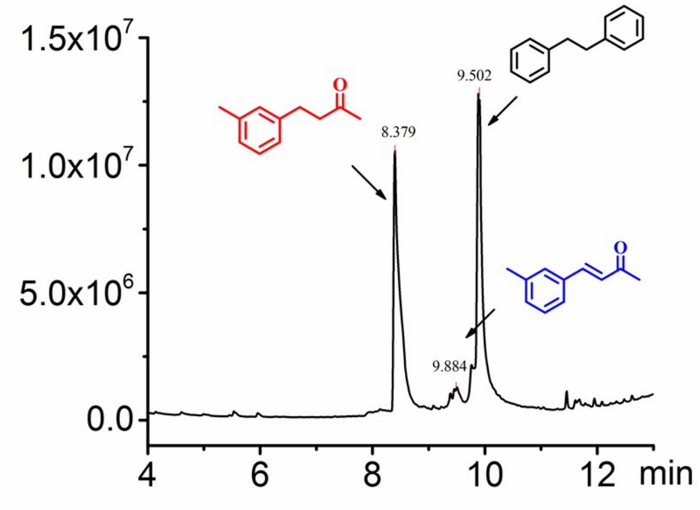
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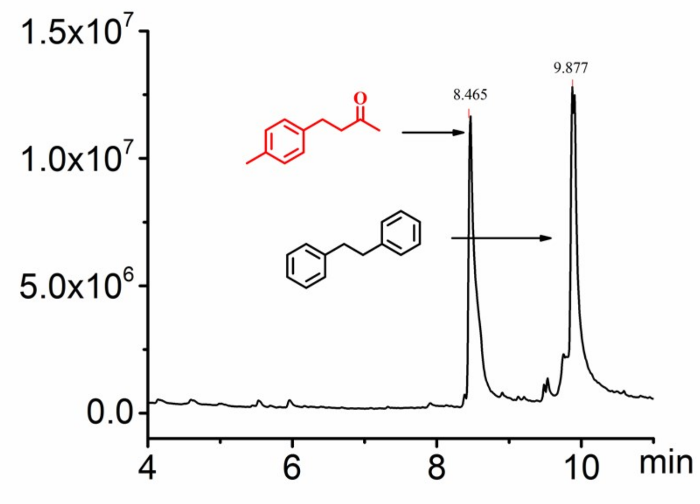
O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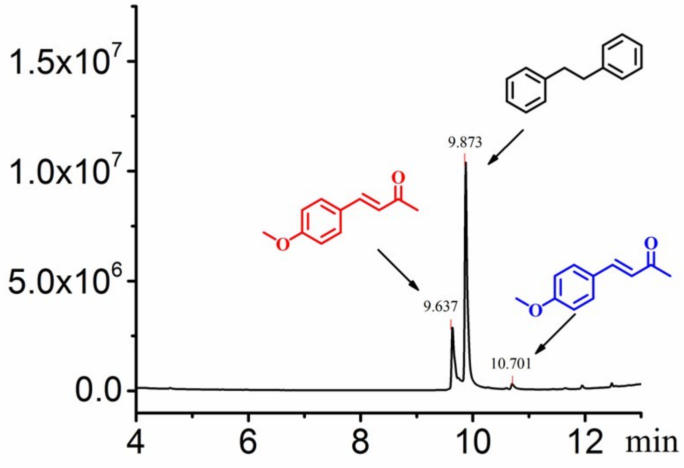
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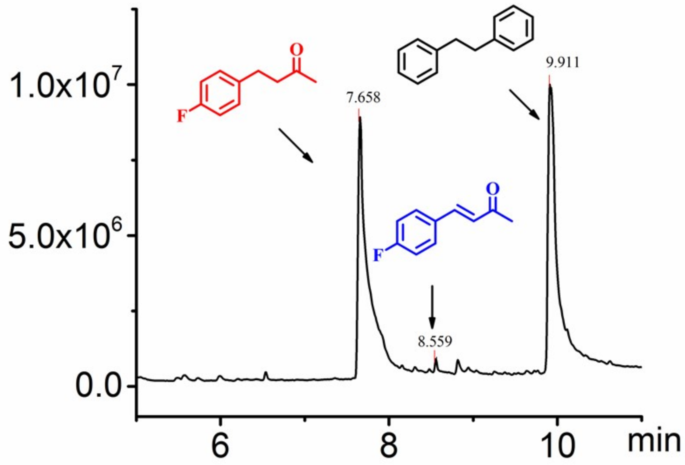
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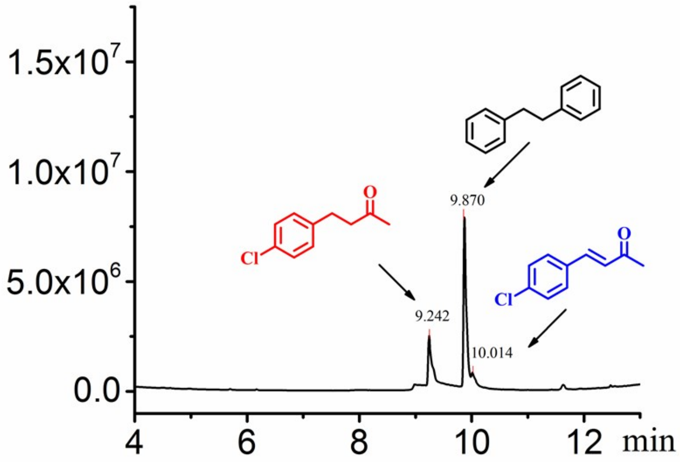
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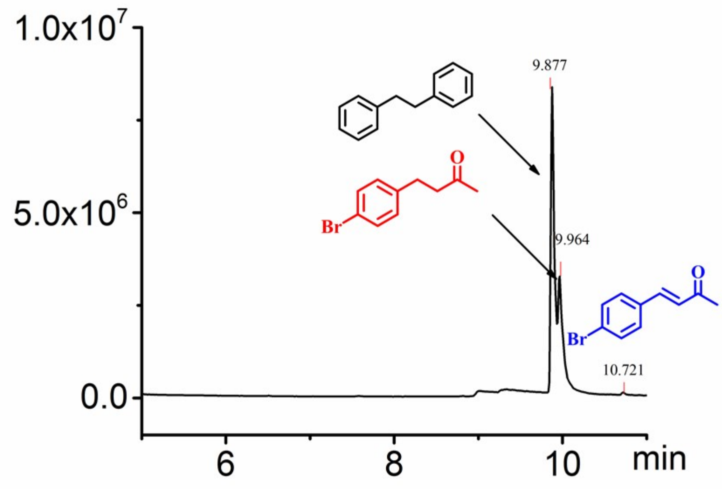
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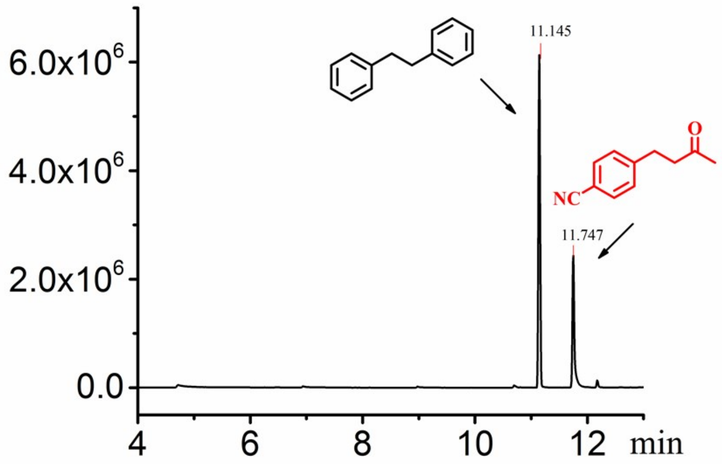
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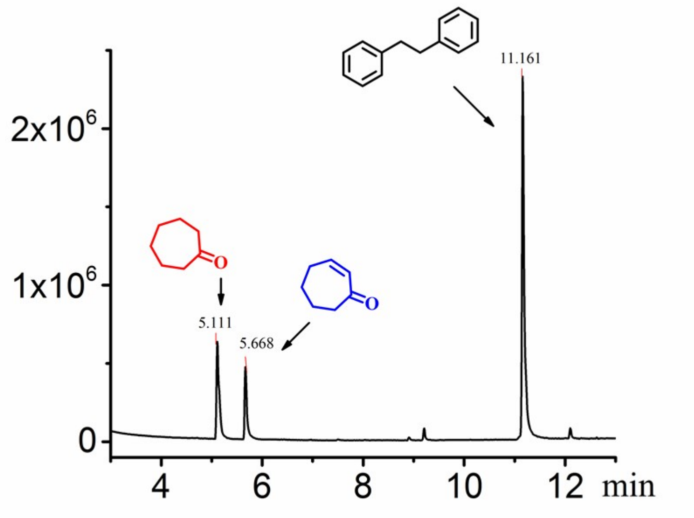
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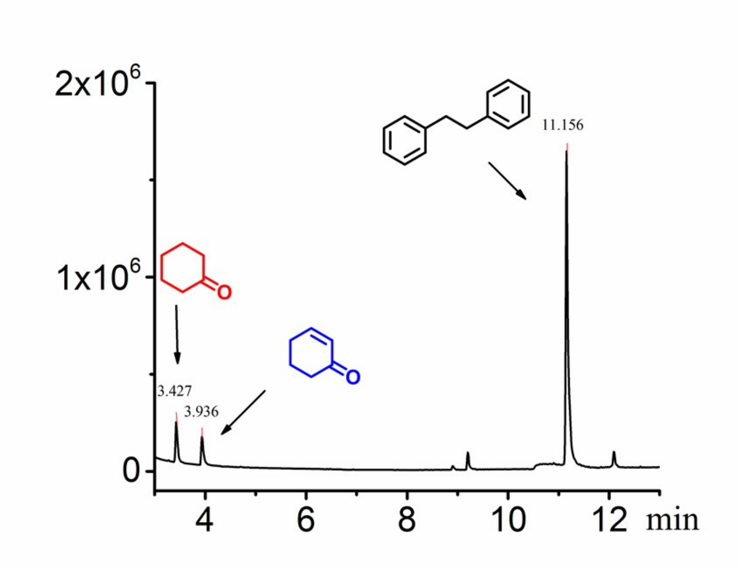
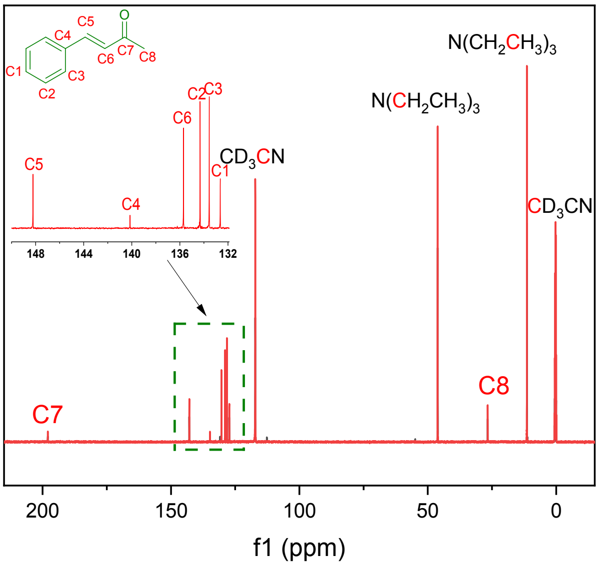


X. Surface Sensitive ^{13}C-NMR experiments using 4-methoxybenzoic acid on the influence of ^{13}C-NMR spectrum of 4-phenyl-3-buten-2-one adsorbed on P25 TiO_2 in CD_3CN in the presence of Et_3N and 4-methoxybenzoic acid



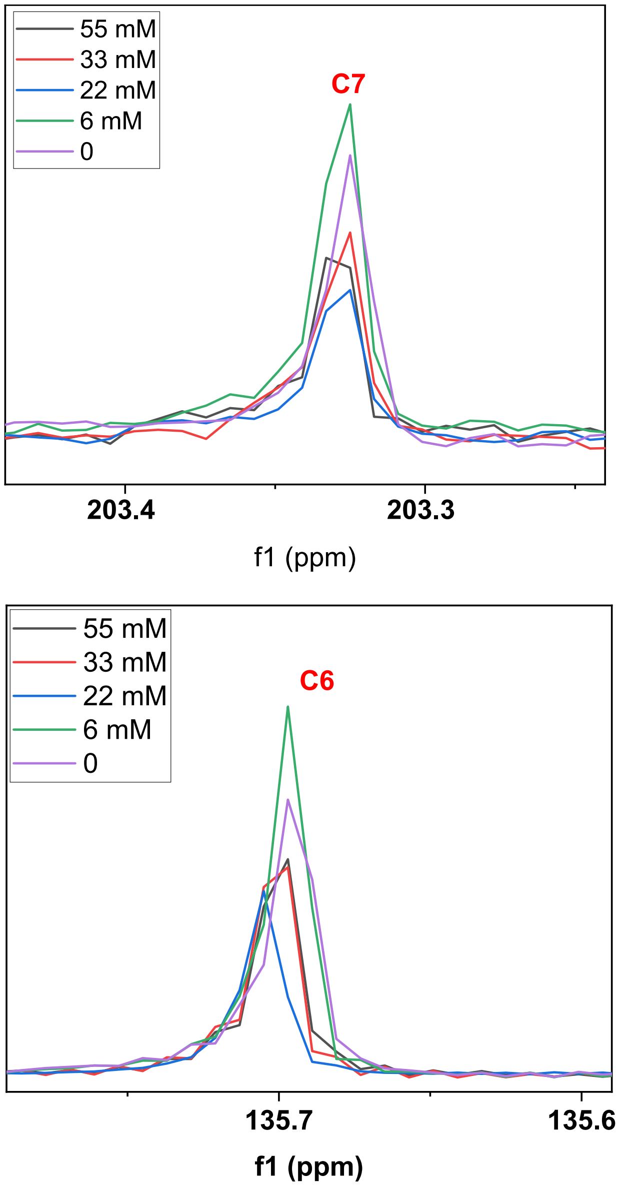


Figure S1. ^{13}C-NMR spectrum of 4-phenyl-3-buten-2-one adsorbed on P25 TiO_2 in CD_3CN in the presence of Et_3N and 6 mM 4-methoxybenzoic acid. (top) C7 (C=O) (middle) and C6 (olefinic C=C) (bottom) spectra with the addition of different amount of 4-methoxybenzoic acid (from 0 to 55 mM) were zoomed in for a closer look.

XI. AQE measurement of photocatalytic reaction

We have measured the power density of the irradiation source to be 164.0 mW/cm^{-2} and the irradiation area was 0.74 cm^{-2}, the 400 nm LED light irradiation time was

7200 s and the reacted 4-phenyl-3-buten-2-one was 0.1 mmol. The apparent quantum efficiency was calculated from the calculated the quantum efficiency of the reaction. AQE (%) =number of reacted 4-phenyl-3-buten-2-one /number of incident photons × 100= 1.13%