

Artificial Photosynthesis Directed toward Organic Synthesis

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1. General procedure

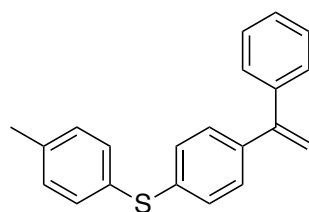
All experiments were performed under an inert gas unless otherwise noted. Photocatalytic reactions were performed in PhotoRedOx Box with LEDs ($\lambda = 365$ nm, P205-18-1 365 nm) purchased from HepatoChem Inc. unless otherwise noted. Two LED lamps purchased from Kessil ($\lambda = 370$ nm, PR160L-370) were used in 1 mmol scale reactions. A Xe lamp (300 W) on an ASAHI SPECTRA HAL-320 was a solar simulator. ^1H , ^{13}C and ^{19}F NMR spectra were measured on a JEOL ECA 600 (600 MHz for ^1H , 151 MHz for ^{13}C , 564 MHz for ^{19}F) at ambient temperature. Chemical shifts are reported as δ in ppm and internally referenced to tetramethylsilane (0.00 ppm for ^1H), CDCl_3 (77.2 ppm for ^{13}C), dimethyl sulfoxide- d_6 (DMSO- d_6 , 2.50 ppm for ^1H , 39.5 ppm for ^{13}C) or benzotrifluoride (-62.6 ppm for ^{19}F). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, and m = multiplet). GC-MS analyses were performed on Agilent 6850 series network GC system and Agilent 5975C series Mass Selective Detector (EI) [column: HP-5MS capillary column ($l = 30$ m, $d = 0.25$ mm, film thickness = 0.25 μm)]. High-resolution mass spectra (HRMS) were obtained from JMS-700 (FAB, JEOL). IR spectra were obtained from JASCO FT/IR6100. μGC -TCD analyses were conducted in a dual channel micro gas chromatography (μGC) system coupled to a thermal conductivity detector (TCD, Agilent 490). For thin-layer chromatography (TLC) analysis through this work, Merck percolated TLC plates (silica gel 60 GF254 0.25 mm) were used. The products were purified by flash chromatography using glass columns with silica gel 60 N (spherical, neutral, diameter: $40\text{--}100$ μm) purchased from Kanto Chemical or pre-packed Biotage SNAP columns with Biotage Isolera Automated Flash Chromatography System. DFT calculations were carried out using the Gaussian 09 program package. Geometries were optimized at the B3LYP/6-31G(d,p) level of theory. Free energies (ΔG°) were computed at 298.15 K at the same level. The calculations did not take into account the effects of solvent.

2. Materials

All materials were used directly without further purification. Tetrahydrofuran dehydrated stabilizer free (**2e**), *N,N*-dimethylacetamide (**2f**), tetramethylurea (**2h**), toluene (**2j**), acetonitrile dehydrated (water content = 24 ppm), dichloromethane, dichloromethane dehydrated, methanol dehydrated, ethyl acetate (EtOAc), *n*-hexane, dimethyl sulfoxide-*d*₆, cesium hydroxide monohydrate, lithium carbonate, lithium chloride, and perchloric acid were purchased from Kanto Chemical. TiO₂ (Aeroxide P25), α -methylstyrene (**1a**), *N*-methylacetamide (**2g**), lithium hydroxide, tetrabutylammonium hydroxide aqueous solution (1 M), lithium tetraphenylborate tris(1,2-dimethoxyethane), water-¹⁸O (97 atom % ¹⁸O) and benzotrifluoride were purchased from Sigma-Aldrich. 4-Fluoro- α -methylstyrene (**1d**), 4-chloro- α -methylstyrene (**1e**), 4-*tert*-butylstyrene (**1g**), tetrahydropyran (**2d'**), terfenadine (**10**), α -(4-piperidyl)benzhydrol (**12**), lithium acetate, sodium borohydride, 1,1,2,2-tetrachloroethane, and oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium(IV) (TiO(tpyp)) were purchased from Tokyo Chemical Industry. Acetonitrile (**2a**, water content = 2609 ppm), acetone dehydrated (**2b**), acetaldehyde (**2c**), 1,4-dioxane (**2d**), acetic acid (**2i**), methanol, potassium hydroxide, sodium hydroxide, lithium sulfate monohydrate, trilithium phosphate, diisobutylaluminium hydride (DIBAL-H) in hexane (1.0 M), hydrogen peroxide, and hydrochloric acid were purchased from FUJIFILM Wako Pure Chemical Corporation. Lithium bromide and toluene (for column chromatography) were purchased from Kishida Chemical. Propionitrile (**2a'**), lithium tetrafluoroborate was purchased from Acros Organics. Chloroform-*d* was purchased from CIL.

Ag/TiO₂ and Pt (5 wt%)/TiO₂ were prepared by the reported impregnation method.¹ Cu/TiO₂ was prepared by the reported impregnation method.² SrTiO₃:Al, RhCr/SrTiO₃:Al (Rh, Cr: 0.1 wt%), and RhCrCo/SrTiO₃:Al (Rh, Cr, Co: 0.1 wt%) was prepared by the reported impregnation method.³

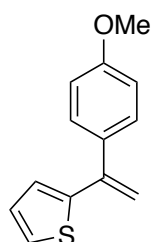
1q⁴ and **1s**⁵ were synthesized by reported procedures. According to a reported procedure,⁶ **1n**, **1p**, and known compounds (**1b**,⁷ **1c**,⁷ **1f**,⁸ **1h**,⁹ **1i**,⁴ **1j**,¹⁰ **1k**,⁹ **1l**,¹¹ **1m**,¹¹ **1o**¹² and **1r**¹³) were prepared.



1n

(4-(1-Phenylvinyl)phenyl)(p-tolyl)sulfane (1n): white solid; ¹H NMR (600 MHz, CDCl₃): δ 7.34–7.30 (m, 7H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.44 (d, *J* = 1.2 Hz, 1H), 5.42 (d, *J* = 1.2 Hz, 1H), 2.35 (s, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 149.6, 141.5, 139.7, 138.0, 137.0, 132.8, 131.1, 130.3, 129.3, 129.0, 128.5, 128.4, 128.0,

114.4, 21.3; HRMS (FAB): m/z calcd. for $C_{21}H_{18}S$ (M) 302.1129, found 302.1138; FT-IR (KBr, cm^{-1}): 1491.



1p

2-(1-(4-Methoxyphenyl)vinyl)thiophene (1p): colorless oil, 1H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 5.4$ Hz, 1H), 6.99–6.97 (m, 1H), 6.94–6.93 (m, 1H), 6.89 (d, $J = 7.8$ Hz, 2H), 5.50 (s, 1H), 5.20 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.8, 145.3, 143.0, 133.7, 129.7, 127.4, 126.5, 125.1, 113.7, 112.8, 55.5; HRMS (FAB): m/z calcd. for $C_{13}H_{13}OS$ (M+H) 217.0687, found 217.0689; FT-IR (KBr, cm^{-1}): 1250, 1032.

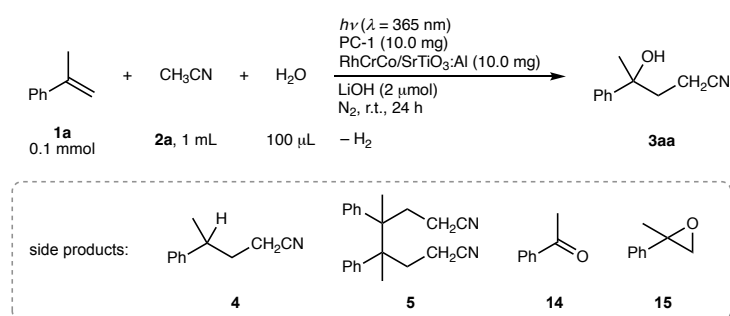
3aa,¹⁴ **3ha**,¹⁵ **3hb**,¹⁶ **3hc**,¹⁷ **4**,¹⁸ **5**,¹⁹ **6**,¹⁶ **7**,²⁰ **8**,²¹ **9**,²² **10**,²³ **11**,²⁴ **13**,⁵ **14**,²⁵ and **15**²⁵ are known compounds.

3. Optimization

Representative procedure

An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar, Ag (0.5 wt%)/TiO₂ (10.0 mg) and RhCrCo/SrTiO₃:Al (10.0 mg). The vessel was sealed with a rubber septum and placed under nitrogen before **1a** (0.10 mmol), **2a** (1 mL) and an aqueous solution of LiOH (0.02 M, 100 μ L) were added. The mixture was sonicated and then stirred under LED-light irradiation (λ = 365 nm). After 24 h, the gas phase was analyzed by μ GC-TCD. The reaction mixture diluted with EtOAc was analyzed by GC-MS using an internal standard (*n*-tridecane). The mixture was dried over Na₂SO₄. After filtration through a 0.45 μ m membrane filter and concentration under reduced pressure (80 mmHg, 40 $^{\circ}$ C), an aliquot with an internal standard (1,1,2,2-tetrachloroethane) was monitored by ¹H NMR analysis.

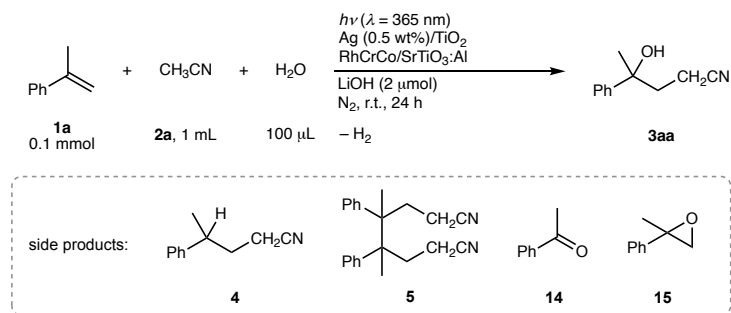
Supplementary Table S1. Evaluation of TiO₂-based photocatalyst



Entry	PC-1	Yield (%) ^a					H ₂ (μ mol) ^b
		3aa	4	5	14	15	
1	Pristine TiO ₂ (P25)	31	<1	8	7	<1	150
2	Ag (0.3 wt%)/TiO ₂	62	<1	7	2	<1	160
3	Ag (0.5 wt%)/TiO ₂	72	<1	9	4	1	160
4	Ag (1 wt%)/TiO ₂	62	<1	6	3	<1	180
5	Ag (5 wt%)/TiO ₂	35	<1	1	2	2	130
6	Cu (0.5 wt%)/TiO ₂	44	<1	7	6	2	150
7	Cu (5 wt%)/TiO ₂	44	<1	3	3	<1	130

^aDetermined by ¹H NMR. ^bDetermined by μ GC-TCD.

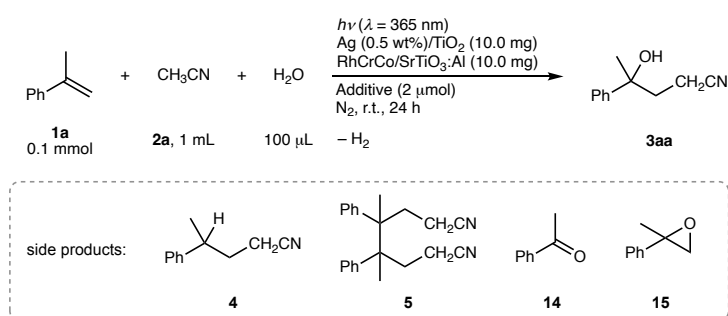
Supplementary Table S2. Evaluation of photocatalyst equivalent



Entry	Ag (0.5 wt%)/TiO ₂ (mg)	RhCrCo/SrTiO ₃ :Al (mg)	Yield (%) ^a					H ₂ (μ mol) ^b
			3aa	4	5	14	15	
1	10.0	10.0	72	<1	9	4	1	160
2	10.0	5.0	35	<1	5	2	<1	120
3	10.0	20.0	55	<1	1	6	3	190
4	5.0	10.0	32	<1	<1	5	5	130
5	20.0	10.0	41	<1	7	2	<1	140
6	20.0	20.0	63	<1	9	4	<1	170

^aDetermined by ¹H NMR. ^bDetermined by μ GC-TCD.

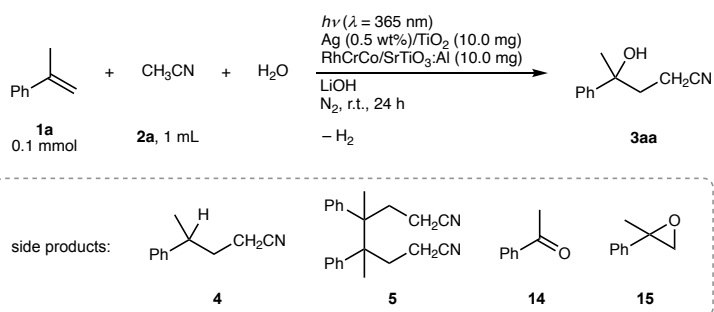
Supplementary Table S3. Evaluation of additive



Entry	Additive	Yield (%) ^a					H ₂ (μ mol) ^b
		3aa	4	5	14	15	
1	—	41	<1	2	5	7	170
2	LiOH	72	<1	9	4	1	160
3	NaOH	54	<1	4	4	1	180
4	KOH	50	<1	5	4	3	170
5	CsOH	37	<1	2	3	2	140
6	<i>n</i> Bu ₄ NOH	27	<1	<1	4	3	180
7	Li ₃ PO ₄	60	<1	6	5	3	180
8	Li ₂ CO ₃	51	<1	7	3	<1	150
9	LiCl	47	<1	4	3	2	150
10	LiBr	52	<1	5	3	1	150

^aDetermined by ¹H NMR. ^bDetermined by μ GC-TCD.

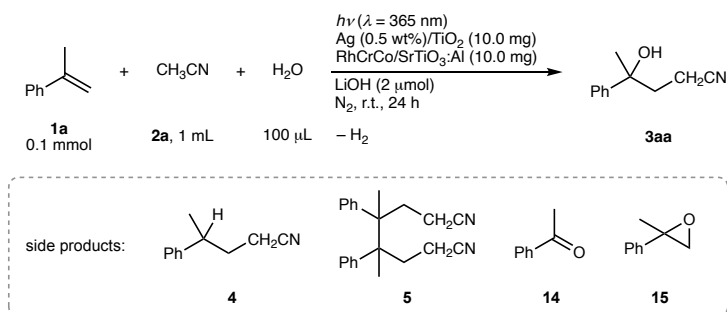
Supplementary Table S4. Evaluation of solvent mixture



Entry	H ₂ O (μL)	LiOH (μmol)	Yield (%) ^a					H ₂ (μmol) ^b
			3aa	4	5	14	15	
1	50	1	34	<1	3	2	2	150
2	100	2	72	<1	9	4	1	160
3	500	10	52	<1	4	3	<1	190
4	1000	20	32	<1	5	<2	<1	210
5	100	0	41	<1	2	5	7	170
6	100	5	54	<1	5	3	<1	160
7	100	10	41	<1	6	2	<1	150

^aDetermined by ¹H NMR. ^bDetermined by μGC-TCD.

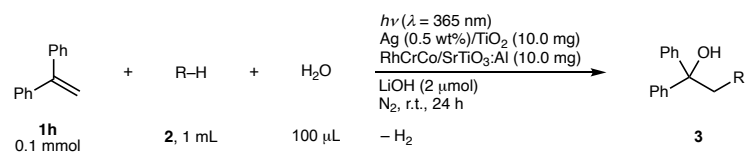
Supplementary Table S5. Control experiments



Entry	Changes from standard conditions	Yield (%) ^a					H ₂ (μ mol) ^b
		3aa	4	5	14	15	
1	—	72	<1	9	4	1	160
2	Without Ag/TiO ₂	<1	<1	<1	14	12	220
3	Using TiO ₂ instead of Ag/TiO ₂	31	<1	8	7	<1	150
4	Without RhCrCo/SrTiO ₃ :Al	<1	14	1	<1	<1	<10
5	Without H ₂ O ^c	<1	<1	<1	1	<1	20
6	Without LiOH	41	<1	2	5	7	170
7	Under air	<1	<1	<1	16	5	20
8	In the dark	<1	<1	<1	<1	<1	0

^aDetermined by ¹H NMR. ^bDetermined by μ GC-TCD. ^cDehydrated acetonitrile was used.

Supplementary Table S6. Successful/unsuccessful C–H partners



Entry	Structure of 2	Conv. of 1h (%) ^a	Structure of 3	Yield of 3 (%) ^a
1		100		91
2		<1		<1
3		60 (100) ^b		51 (81) ^b
4		16		<1
5		<1		<1

^aDetermined by ¹H NMR. ^bReaction time: 48 h.

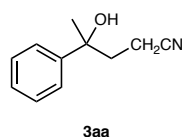
4. Isolated yields and characterization of products

General procedure A

An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar, Ag (0.5 wt%)/TiO₂ (10.0 mg) and RhCrCo/SrTiO₃:Al (10.0 mg). The vessel was sealed with a rubber septum and placed under nitrogen before **1** (0.10 mmol), **2** (1 mL) and an aqueous solution of LiOH (0.02 M, 100 μ L) were added (**1** that was not volatile was added with photocatalysts). The mixture was sonicated and then stirred under LED-light irradiation ($\lambda = 365$ nm). After 24 h, the gas phase was analyzed by μ GC-TCD. The reaction mixture was diluted with EtOAc and dried over Na₂SO₄. After filtration through a 0.45 μ m membrane filter and concentration under reduced pressure (80 mmHg, 40 $^{\circ}$ C), an aliquot with an internal standard (1,1,2,2-tetrachloroethane) was monitored by ¹H NMR analysis. The crude product was purified by flash column chromatography on silica gel.

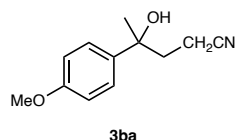
General procedure B

An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar, **1h** (0.10 mmol), Ag (0.5 wt%)/TiO₂ (10.0 mg) and RhCrCo/SrTiO₃:Al (10.0 mg). The vessel was sealed with a rubber septum and placed under nitrogen before **2** (1 mL) and an aqueous solution of LiOH (0.02 M, 100 μ L) were added. The mixture was sonicated and then stirred under LED-light irradiation ($\lambda = 365$ nm). After 24 h, the gas phase was analyzed by μ GC-TCD. The reaction mixture was diluted with water. EtOAc or a mixture of EtOAc and hexane was added. After being shaken, the mixture was centrifuged (3,500 rpm, 3 min). The organic layer was separated. The aqueous phase was subjected to additional three organic solvent addition–centrifugation–extraction cycles. The combined organic extracts were dried over Na₂SO₄, filtrated, and the filtrate was concentrated under reduced pressure (80 mmHg, 40 $^{\circ}$ C). An aliquot with an internal standard (1,1,2,2-tetrachloroethane) was monitored by ¹H NMR analysis. The crude product was purified by flash column chromatography on silica gel.



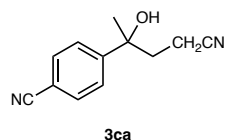
4-Hydroxy-4-phenylpentanenitrile (**3aa**)¹⁴

According to the general procedure A, **1a** (11.9 mg, 0.101 mmol) and **2a** (1 mL) were used. H₂ was detected (0.16 mmol). The product (**3aa**, 9.5 mg, 0.054 mmol, 53%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/4) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.41–7.36 (m, 4H), 7.30–7.27 (m, 1H), 2.43–2.38 (m, 1H), 2.17–2.15 (m, 2H), 2.11–2.06 (m, 1H), 1.74 (s, 1H), 1.63 (s, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 145.6, 128.8, 127.5, 124.7, 120.3, 73.8, 39.8, 30.9, 12.3; HRMS (FAB): m/z calcd. for C₁₁H₁₃NNaO (M+Na) 198.0895, found 198.0901; FT-IR (neat, NaCl, cm⁻¹): 3468, 2249.



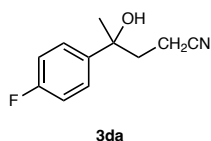
4-Hydroxy-4-(4-methoxyphenyl)pentanenitrile (**3ba**)

According to the general procedure A, **1b** (14.8 mg, 0.100 mmol) and **2a** (1 mL) were used. H_2 was detected (0.18 mmol). The product (**3ba**, 10.4 mg, 0.051 mmol, 51%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 1/9, and then EtOAc/hexane = 1/3) as a white solid: ^1H NMR (600 MHz, CDCl_3): δ 7.31 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 3.81 (s, 3H), 2.41–2.36 (m, 1H), 2.14–2.07 (m, 3H), 1.73 (s, 1H), 1.60 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 158.9, 137.7, 126.0, 120.4, 114.1, 73.5, 55.5, 39.8, 30.8, 12.4; HRMS (FAB): m/z calcd. for $\text{C}_{12}\text{H}_{15}\text{NNaO}_2$ ($\text{M}+\text{Na}$) 228.1000, found 228.0995; FT-IR (KBr, cm^{-1}): 3429, 2259, 1251, 1029.



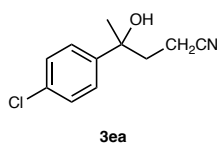
4-(4-cyano-2-hydroxybutan-2-yl)benzonitrile (**3ca**)

According to the general procedure A, **1c** (14.5 mg, 0.101 mmol) and **2a** (1 mL) were used. H_2 was detected (0.14 mmol). The product (**3ca**, 4.0 mg, 0.020 mmol, 20%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 2/3) as a colorless oil: ^1H NMR (600 MHz, CDCl_3): δ 7.68 (d, J = 7.8 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 2.45–2.40 (m, 1H), 2.18–2.16 (m, 2H), 2.11–2.06 (m, 1H), 1.86 (s, 1H), 1.65 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 151.0, 132.6, 125.8, 119.8, 118.7, 111.6, 73.7, 39.5, 30.7, 12.2; HRMS (FAB): m/z calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{NaO}$ ($\text{M}+\text{Na}$) 223.0847, found 223.0853; FT-IR (neat, NaCl, cm^{-1}): 3471, 2248, 2229.



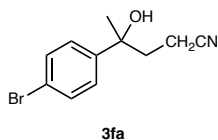
4-(4-Fluorophenyl)-4-hydroxypentanenitrile (**3da**)

According to the general procedure A, **1d** (14.0 mg, 0.103 mmol) and **2a** (1 mL) were used. H_2 was detected (0.15 mmol). The product (**3da**, 6.8 mg, 0.035 mmol, 34%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 1/9, and then EtOAc/hexane = 1/4) as a colorless oil: ^1H NMR (600 MHz, CDCl_3): δ 7.39–7.36 (m, 2H), 7.07–7.04 (m, 2H), 2.43–2.38 (m, 1H), 2.15–2.07 (m, 3H), 1.78 (s, 1H), 1.62 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 163.0, 161.3, 141.4, 141.4, 126.6, 126.6, 120.2, 115.6, 115.5, 73.5, 39.8, 30.9, 12.3; ^{19}F NMR (564 MHz, CDCl_3): δ -115.4; HRMS (FAB): m/z calcd. for $\text{C}_{11}\text{H}_{12}\text{FNNaO}$ ($\text{M}+\text{Na}$) 216.0801, found 216.0793; FT-IR (neat, NaCl, cm^{-1}): 3466, 2250.



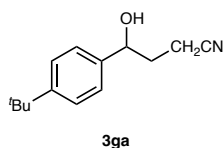
4-(4-Chlorophenyl)-4-hydroxypentanenitrile (**3ea**)

According to the general procedure A, **1e** (15.8 mg, 0.104 mmol) and **2a** (1 mL) were used. H₂ was detected (0.18 mmol). The product (**3ea**, 8.3 mg, 0.040 mmol, 38%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 1/7, and then EtOAc/hexane = 1/4) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.34 (s, 4H), 2.43–2.38 (m, 1H), 2.17–2.06 (m, 3H), 1.77 (s, 1H), 1.61 (s, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 144.2, 133.4, 128.9, 126.3, 120.1, 73.5, 39.7, 30.9, 12.3; HRMS (FAB): *m/z* calcd. for C₁₁H₁₂ClNNaO (M+Na) 232.0505, found 232.0500; FT-IR (neat, NaCl, cm⁻¹): 3459, 2250.



4-(4-Bromophenyl)-4-hydroxypentanenitrile (**3fa**)

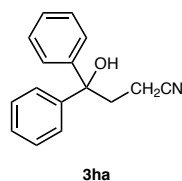
According to the general procedure A, **1f** (19.7 mg, 0.100 mmol) and **2a** (1 mL) were used. H₂ was detected (0.16 mmol). The product (**3fa**, 9.3 mg, 0.037 mmol, 37%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 1/8, and then EtOAc/hexane = 1/4) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.49 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 2.43–2.38 (m, 1H), 2.15–2.05 (m, 3H), 1.81 (s, 1H), 1.61 (s, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 144.7, 131.8, 126.7, 121.5, 120.1, 73.5, 39.6, 30.8, 12.2; HRMS (FAB): *m/z* calcd. for C₁₁H₁₂BrNNaO (M+Na) 276.0000, found 275.9988; FT-IR (neat, NaCl, cm⁻¹): 3465, 2250.



4-(4-*tert*-Butylphenyl)-4-hydroxybutanenitrile (**3ga**)

According to the general procedure A, **1g** (16.0 mg, 0.100 mmol), **2a** (2 mL) and LiOH (0.02 M, 200 μL) were used. H₂ was detected (0.17 mmol). The product (**3ga**, 7.6 mg, 0.035 mmol, 35%) was isolated by flash column chromatography on silica gel (two times: EtOAc/hexane = 1/9, and then EtOAc/hexane = 1/4) as a yellow oil: ¹H NMR (600 MHz, CDCl₃): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.81 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.55 (ddd, *J* = 16.8, 7.8, 7.8 Hz, 1H), 2.42 (ddd, *J* = 16.8, 7.2, 5.4 Hz, 1H), 2.12–1.99 (m, 2H), 1.96 (s, 1H), 1.32 (s, 9H); ¹³C NMR (151 MHz, CDCl₃): δ 151.6, 140.1, 125.9, 125.6, 119.8, 72.4, 34.8, 34.3, 31.5,

14.0; HRMS (FAB): m/z calcd. for $C_{14}H_{19}NNaO$ ($M+Na$) 240.1364, found 240.1362; FT-IR (neat, NaCl, cm^{-1}): 3446, 2250.

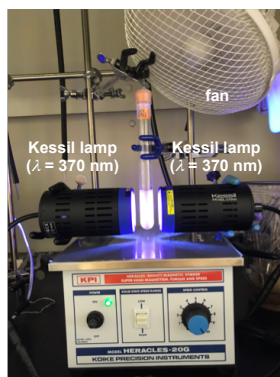
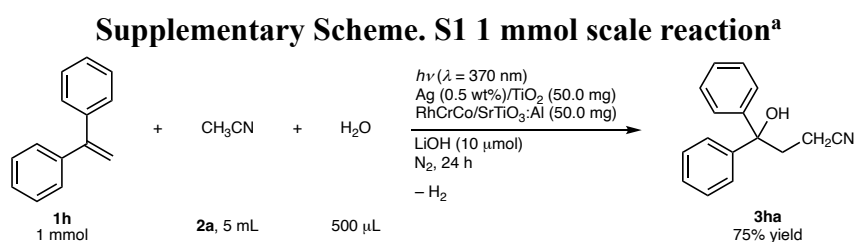


4-Hydroxy-4,4-diphenylbutanenitrile (**3ha**)¹⁵

According to the general procedure A, **1h** (18.0 mg, 0.100 mmol) and **2a** (1 mL) were used. H_2 was detected (0.18 mmol). The product (**3ha**, 16.9 mg, 0.071 mmol, 71%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 1/25, and then EtOAc/hexane = 1/9) as a white solid: 1H NMR (600 MHz, $CDCl_3$): δ 7.37–7.32 (m, 8H), 7.28–7.25 (m, 2H), 2.66 (t, J = 7.8 Hz, 2H), 2.30 (t, J = 7.8 Hz, 2H), 2.18 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 145.3, 128.7, 127.8, 126.0, 120.4, 77.3, 37.9, 12.4; HRMS (FAB): m/z calcd. for $C_{16}H_{15}NNaO$ ($M+Na$) 260.1051, found 260.1041; FT-IR (KBr, cm^{-1}): 3418, 2258.

1 mmol scale reaction

According to the general procedure A, **1h** (180.3 mg, 1.00 mmol), **2a** (5 mL), Ag (0.5 wt%)/ TiO_2 (50.0 mg), RhCrCo/Sr TiO_3 :Al (50.0 mg), LiOH (0.02 M, 500 μ L), two kessil lamps (λ = 370 nm) and a fan were used. The product (**3ha**, 178.6 mg, 0.75 mmol, 75%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/9) as a white solid.

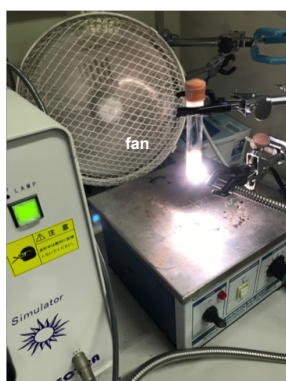
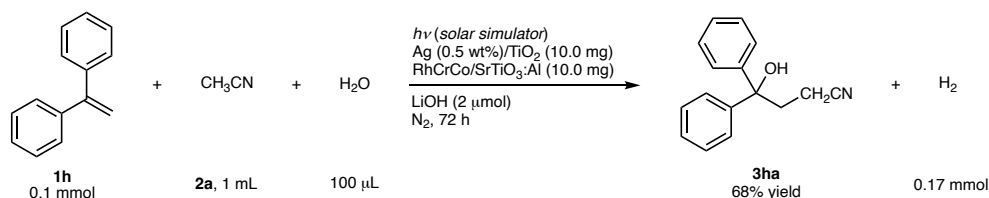


^aIsolated yield.

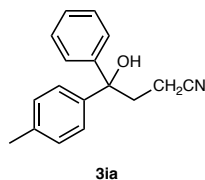
Solar simulator

According to the general procedure A, **1h** (18.2 mg, 0.101 mmol), **2a** (1 mL), a solar simulator and a fan were used. H₂ was detected (0.17 mmol). After 72 h, the product (**3ha**, 16.3 mg, 0.069 mmol, 68%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/9) as a white solid

Supplementary Scheme. S2 Sunlight-induced reaction^a

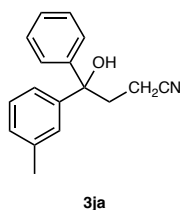


^aIsolated yield. H₂ was quantified by μ GC-TCD.



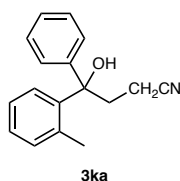
4-Hydroxy-4-phenyl-4-(p-tolyl)butanenitrile (**3ia**)

According to the general procedure A, **1i** (19.5 mg, 0.100 mmol) and **2a** (1 mL) were used. H₂ was detected (0.19 mmol). The product (**3ia**, 17.4 mg, 0.069 mmol, 69%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/9) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.36–7.31 (m, 4H), 7.27–7.23 (m, 3H), 7.14 (d, J = 8.4 Hz, 2H), 2.64 (t, J = 7.8 Hz, 2H), 2.35–2.25 (m, 5H), 2.12 (s, 1H); ¹³C NMR (151 MHz, CDCl₃): δ 145.4, 142.4, 137.6, 129.4, 128.7, 127.7, 126.0, 126.0, 120.5, 77.2, 37.9, 21.2, 12.4; HRMS (FAB): m/z calcd. for C₁₇H₁₇NNaO (M+Na) 274.1208, found 274.1195; FT-IR (neat, NaCl, cm⁻¹): 3462, 2250.



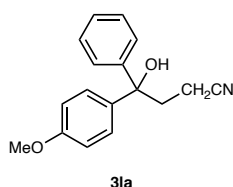
4-Hydroxy-4-phenyl-4-(*m*-tolyl)butanenitrile (**3ja**)

According to the general procedure A, **1j** (19.4 mg, 0.100 mmol) and **2a** (1 mL) were used. After 48 h, H₂ was detected (0.20 mmol). The product (**3ja**, 16.9 mg, 0.067 mmol, 67%) was isolated by flash column chromatography on silica gel (two times: EtOAc/hexane = 1/9, and then EtOAc/hexane = 1/9) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.37–7.32 (m, 4H), 7.28–7.25 (m, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.17 (s, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 2.66–2.63 (m, 2H), 2.33 (s, 3H), 2.31–2.28 (m, 2H), 2.14 (s, 1H); ¹³C NMR (151 MHz, CDCl₃): δ 145.4, 145.2, 138.5, 128.7, 128.6, 128.6, 127.8, 126.7, 126.0, 123.1, 120.5, 77.3, 38.0, 21.8, 12.4; HRMS (FAB): *m/z* calcd. for C₁₇H₁₇NNaO (M+Na) 274.1208, found 274.1218; FT-IR (neat, NaCl, cm⁻¹): 3457, 2250.



4-Hydroxy-4-phenyl-4-(*o*-tolyl)butanenitrile (**3ka**)

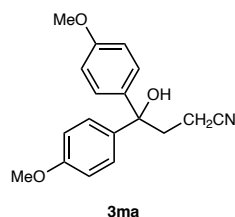
According to the general procedure A, **1k** (19.4 mg, 0.100 mmol) and **2a** (1 mL) were used. After 48 h, H₂ was detected (0.20 mmol). The product (**3ka**, 11.6 mg, 0.046 mmol, 46%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/9) as a white solid: ¹H NMR (600 MHz, CDCl₃): δ 7.67 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.32–7.23 (m, 7H), 7.10 (d, *J* = 6.6 Hz, 1H), 2.69 (ddd, *J* = 13.2, 10.8, 5.4 Hz, 1H), 2.63 (ddd, *J* = 13.2, 10.2, 5.4 Hz, 1H), 2.35 (ddd, *J* = 16.8, 10.2, 5.4 Hz, 1H), 2.21 (ddd, *J* = 16.8, 10.8, 5.4 Hz, 1H), 2.02 (s, 1H), 1.94 (s, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 144.6, 142.6, 137.0, 133.1, 128.6, 128.4, 127.6, 126.1, 126.0, 125.8, 120.5, 37.9, 21.4, 12.4; ¹³C NMR (151 MHz, DMSO-*d*₆): δ 145.3, 143.9, 136.8, 132.1, 127.7, 127.2, 126.4, 125.9, 125.8, 125.2, 120.7, 75.8, 37.2, 21.0, 11.5; HRMS (FAB): *m/z* calcd. for C₁₇H₁₇NNaO (M+Na) 274.1208, found 274.1207; FT-IR (KBr, cm⁻¹): 3566, 2244.



4-Hydroxy-4-(4-methoxyphenyl)-4-phenylbutanenitrile (**3la**)

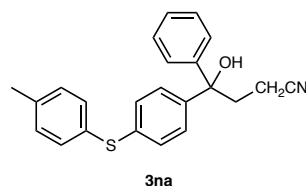
According to the general procedure A, **1l** (21.0 mg, 0.100 mmol) and **2a** (1 mL) were used. H₂

was detected (0.17 mmol). The product (**3la**, 17.2 mg, 0.064 mmol, 64%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/4) as a colorless oil: ^1H NMR (600 MHz, CDCl_3): δ 7.36–7.32 (m, 4H), 7.28–7.25 (m, 3H), 6.85 (d, J = 9.0 Hz, 2H), 3.79 (s, 3H), 2.64–2.61 (m, 2H), 2.36–2.31 (m, 1H), 2.28–2.22 (m, 1H), 2.11 (s, 1H); ^{13}C NMR (151 MHz, CDCl_3): δ 159.1, 145.4, 137.6, 128.7, 127.7, 127.3, 126.0, 120.5, 114.0, 77.1, 55.4, 38.0, 12.4; HRMS (FAB): m/z calcd. for $\text{C}_{17}\text{H}_{17}\text{NNaO}_2$ ($\text{M}+\text{Na}$) 290.1157, found 290.1151; FT-IR (neat, NaCl, cm^{-1}): 3466, 2250, 1253, 1032.



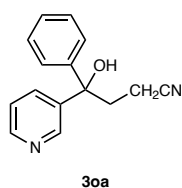
4-Hydroxy-4,4-bis(4-methoxyphenyl)butanenitrile (**3ma**)

According to the general procedure A, **1m** (23.9 mg, 0.099 mmol) and **2a** (1 mL) were used. After 48 h, H_2 was detected (0.16 mmol). The product (**3ma**, 15.6 mg, 0.052 mmol, 53%) was isolated by flash column chromatography on silica gel (two times: EtOAc/hexane = 1/4, and then EtOAc/hexane = 1/4) as a pale yellow oil: ^1H NMR (600 MHz, CDCl_3): δ 7.25 (d, J = 8.4 Hz, 4H), 6.85 (d, J = 9.0 Hz, 4H), 3.79 (s, 6H), 2.59 (t, J = 8.4 Hz, 2H), 2.28 (t, J = 8.4 Hz, 2H), 2.09 (s, 1H); ^{13}C NMR (151 MHz, CDCl_3): δ 159.0, 137.7, 127.3, 120.5, 114.0, 76.8, 55.5, 38.1, 12.4; HRMS (FAB): m/z calcd. for $\text{C}_{18}\text{H}_{19}\text{NNaO}_3$ ($\text{M}+\text{Na}$) 320.1263, found 320.1274; FT-IR (neat, NaCl, cm^{-1}): 3474, 2249, 1251, 1032.



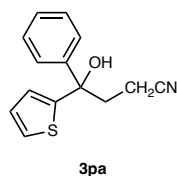
4-Hydroxy-4-phenyl-4-(4-(p-tolylthio)phenyl)butanenitrile (**3na**)

According to the general procedure A, **1n** (30.0 mg, 0.099 mmol) and **2a** (1 mL) were used. After 48 h, H_2 was detected (0.13 mmol). The product (**3na**, 15.9 mg, 0.044 mmol, 44%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 1/30, and then EtOAc/hexane = 1/6) as a colorless oil: ^1H NMR (600 MHz, CDCl_3): δ 7.35–7.31 (m, 6H), 7.28–7.25 (m, 1H), 7.23 (d, J = 9.0 Hz, 2H), 7.17–7.14 (m, 4H), 2.63–2.60 (m, 2H), 2.35 (s, 3H), 2.30–2.28 (m, 2H), 2.08 (s, 1H); ^{13}C NMR (151 MHz, CDCl_3): δ 145.0, 143.2, 138.4, 137.6, 133.3, 130.4, 130.2, 129.0, 128.8, 127.9, 126.7, 126.0, 120.3, 77.2, 37.9, 21.4, 12.4; HRMS (FAB): m/z calcd. for $\text{C}_{23}\text{H}_{21}\text{NOS}$ (M) 359.1344, found 359.1351; FT-IR (neat, NaCl, cm^{-1}): 3457, 2250, 1491.



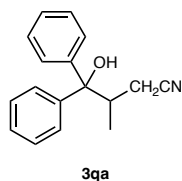
4-Hydroxy-4-phenyl-4-(pyridine-3-yl)butanenitrile (**30a**)

According to the general procedure A, **1o** (18.1 mg, 0.100 mmol) and **2a** (1 mL) were used. After 48 h, H₂ was detected (0.15 mmol). The product (**30a**, 12.8 mg, 0.054 mmol, 54%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 1/2, and then EtOAc/hexane = 3/2) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 8.59 (s, 1H), 8.47 (d, *J* = 4.2 Hz, 1H), 7.70 (ddd, *J* = 8.4, 2.4, 1.8 Hz, 1H), 7.38–7.36 (m, 4H), 7.32–7.30 (m, 1H), 7.27–7.25 (m, 1H), 2.81 (s, 1H), 2.72–2.64 (m, 2H), 2.38–2.28 (m, 2H); ¹³C NMR (151 MHz, CDCl₃): δ 148.5, 147.5, 144.4, 141.4, 134.3, 129.0, 128.2, 126.0, 123.6, 120.1, 75.9, 37.7, 12.2; HRMS (FAB): *m/z* calcd. for C₁₅H₁₅N₂O (M+H) 239.1184, found 239.1182; FT-IR (neat, NaCl, cm⁻¹): 3432, 3148, 2249.



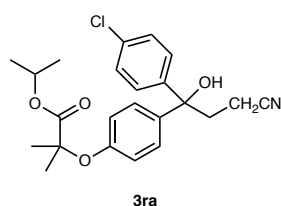
4-Hydroxy-4-(4-methoxyphenyl)-4-(thiophen-2-yl)butanenitrile (**3pa**)

According to the general procedure A, **1p** (21.8 mg, 0.101 mmol) and **2a** (1 mL) were used. H₂ was detected (0.14 mmol). The product (**3pa**, 5.2 mg, 0.019 mmol, 19%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/4) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.35 (d, *J* = 9.0 Hz, 2H), 7.27–7.26 (m, 1H), 6.96 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.91 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 2.67 (ddd, *J* = 13.8, 10.2, 6.0 Hz, 1H), 2.63 (ddd, *J* = 13.8, 10.2, 6.0 Hz, 1H), 2.45 (ddd, *J* = 16.8, 10.2, 6.0 Hz, 1H), 2.30 (s, 1H), 2.24 (ddd, *J* = 16.8, 10.2, 6.0 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃): δ 159.4, 151.4, 136.0, 127.1, 127.1, 125.7, 124.7, 120.1, 114.0, 75.8, 55.5, 39.5, 12.5; HRMS (FAB): *m/z* calcd. for C₁₅H₁₅NNaO₂S (M+Na) 296.0721, found 296.0712; FT-IR (neat, NaCl, cm⁻¹): 3456, 2249, 1251, 1030.



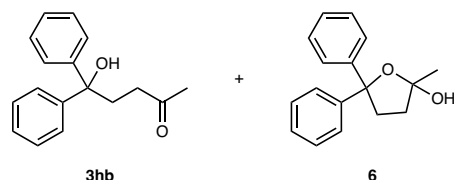
4-Hydroxy-3-methyl-4,4-diphenylbutanenitrile (**3qa**)

According to the general procedure A, **1q** (19.4 mg, 0.100 mmol), **2a** (2 mL), Ag (0.5 wt %)/TiO₂ (20.0 mg), RhCrCo/SrTiO₃:Al (20.0 mg) and LiOH (0.02 M, 200 μ L) were used. H₂ was detected (0.19 mmol). The product (**3qa**, 10.2 mg, 0.041 mmol, 41%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.46–7.42 (m, 4H), 7.35–7.30 (m, 4H), 7.25–7.21 (m, 2H), 3.09 (dq, J = 10.2, 7.2, 3.6 Hz, 1H), 2.34 (dd, J = 16.8, 3.6 Hz, 1H), 2.24 (dd, J = 16.8, 10.2 Hz, 1H), 2.23 (s, 1H), 1.17 (d, J = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 145.1, 144.8, 128.9, 128.8, 127.5, 127.4, 125.8, 125.4, 120.0, 79.9, 38.6, 20.3, 14.8; HRMS (FAB): m/z calcd. for C₁₇H₁₈NO (M+H) 252.1388, found 252.1389; FT-IR (neat, NaCl, cm⁻¹): 3473, 2248.



Isopropyl 2-(4-(1-(4-chlorophenyl)-3-cyano-1-hydroxyprop-1-yl)phenoxy)-2-methylpropanoate (**3ra**)

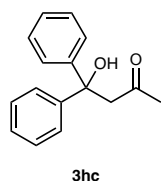
According to the general procedure A, **1r** (35.9 mg, 0.100 mmol) and **2a** (1 mL) were used. H₂ was detected (0.14 mmol). The product (**3ra**, 21.5 mg, 0.052 mmol, 52%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/5) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.31–7.26 (m, 4H), 7.19 (d, J = 9.0 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 5.06 (sep, J = 6.6 Hz, 1H), 2.61 (ddd, J = 13.8, 10.2, 6.0 Hz, 1H), 2.57 (ddd, J = 13.8, 10.2, 6.0 Hz, 1H), 2.33 (ddd, J = 17.4, 10.2, 6.0 Hz, 1H), 2.20 (ddd, J = 17.4, 10.2, 6.0 Hz, 1H), 2.13 (s, 1H), 1.58 (s, 6H), 1.20 (d, J = 6.6 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃): δ 173.6, 155.4, 143.7, 138.3, 133.6, 128.8, 127.6, 126.9, 120.2, 118.8, 79.4, 76.8, 69.2, 37.9, 25.6, 21.7, 12.3; HRMS (FAB): m/z calcd. for C₂₃H₂₆ClNNaO₄ (M+Na) 438.1448, found 438.1452; FT-IR (neat, NaCl, cm⁻¹): 3478, 2250, 1729.



5-hydroxy-5,5-diphenylpentan-2-one (**3hb**) and 2-methyl-5,5-diphenyltetrahydrofuran-2-ol (**6**)¹⁶

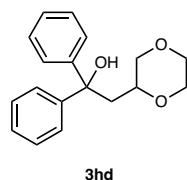
According to the general procedure A, **1h** (18.1 mg, 0.100 mmol) and **2b** (1 mL) were used. H₂ was detected (0.18 mmol). The 1:1 equilibrium mixture (**3hb**+**6**, 19.2 mg, 0.075 mmol, 75%) was isolated by flash column chromatography on silica gel (three times: EtOAc/toluene = 3/97, EtOAc/toluene = 1/19, and then EtOAc/hexane = 1/7) as a white solid: ¹H NMR (600

MHz, CDCl₃): **3hb**: δ 7.45–7.40 (m, 4H), 7.32–7.26 (m, 4H), 7.23–7.18 (m, 2H), 2.73 (s, 1H), 2.60 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.09 (s, 3H); **6**: 7.45–7.40 (m, 4H), 7.32–7.26 (m, 4H), 7.23–7.18 (m, 2H), 2.88 (ddd, J = 12.6, 10.8, 7.2 Hz, 1H), 2.67 (ddd, J = 12.6, 7.2, 3.0 Hz, 1H), 2.34 (s, 1H), 2.19 (ddd, J = 12.6, 7.2, 3.0 Hz, 1H), 1.93–1.87 (m, 1H), 1.65 (s, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 210.1, 147.4, 146.9, 146.6, 128.4, 128.3, 128.2, 127.1, 127.0, 126.9, 126.3, 126.2, 125.9, 106.0, 89.4, 77.7, 38.8, 38.6, 38.3, 35.2, 30.3, 27.9; HRMS (FAB): m/z calcd. for C₁₇H₁₈NaO₂ (M+Na) 277.1204, found 277.1209.



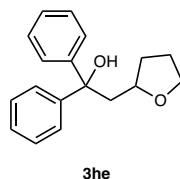
4-hydroxy-4,4-diphenylbutan-2-one (**3hc**)¹⁷

According to the general procedure A, **1h** (18.0 mg, 0.100 mmol) and **2c** (1 mL) were used. H₂ was detected (0.17 mmol). The product (**3hc**, 12.4 mg, 0.052 mmol, 52%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 3/97, and then EtOAc/hexane = 1/9) as a white solid: ¹H NMR (600 MHz, CDCl₃): δ 7.38 (d, J = 8.4 Hz, 4H), 7.30 (t, J = 8.4 Hz, 4H), 7.21 (t, J = 7.8 Hz, 2H), 5.12 (s, 1H), 3.42 (s, 2H), 2.17 (s, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 210.5, 146.4, 128.5, 127.2, 125.8, 53.1, 32.0; ¹³C NMR (151 MHz, DMSO-*d*₆): δ ; 207.9, 147.5, 127.8, 126.3, 125.5, 75.8, 54.0, 31.6 HRMS (FAB): m/z calcd. for C₁₆H₁₆NaO₂ (M+Na) 263.1048, found 263.1047; FT-IR (KBr, cm⁻¹): 3482, 3429, 3397, 1696.



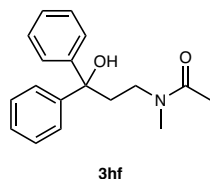
2-(2-Hydroxy-2,2-diphenyleth-1-yl)-1,4-dioxane (**3hd**)

According to the general procedure A, **1h** (18.0 mg, 0.100 mmol) and **2d** (1 mL) were used. After 48 h, H₂ was detected (0.27 mmol). The product (**3hd**, 20.5 mg, 0.072 mmol, 72%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/7) as a white solid: ¹H NMR (600 MHz, CDCl₃): δ 7.46–7.44 (m, 2H), 7.40–7.38 (m, 2H), 7.34 (t, J = 7.8 Hz, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 4.78 (s, 1H), 3.74 (dd, J = 10.2, 2.4 Hz, 1H), 3.69–3.58 (m, 4H), 3.53 (ddd, J = 10.8, 10.8, 3.6 Hz, 1H), 3.37 (dd, J = 10.8, 9.6 Hz, 1H), 2.35 (dd, J = 14.4, 2.4 Hz, 1H), 2.28 (dd, J = 15.0, 10.2 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃): δ 147.6, 146.4, 128.4, 128.3, 127.0, 126.9, 126.3, 125.8, 78.2, 74.5, 71.0, 66.7, 66.5, 41.8; HRMS (FAB): m/z calcd. for C₁₈H₂₀NaO₃ (M+Na) 307.1310, found 307.1320; FT-IR (KBr, cm⁻¹): 3451, 1118.



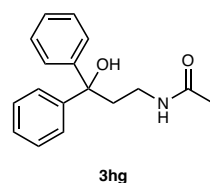
2-(2-Hydroxy-2,2-diphenyleth-1-yl)tetrahydrofuran (3he)

According to the general procedure A, **1h** (18.0 mg, 0.100 mmol) and **2e** (1 mL) were used. After 36 h, H₂ was detected (0.32 mmol). The product (**3he**, 19.7 mg, 0.073 mmol, 73%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a white solid: ¹H NMR (600 MHz, CDCl₃): δ 7.51–7.49 (m, 2H), 7.44–7.42 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 5.48 (s, 1H), 3.93–3.85 (m, 2H), 3.72 (ddd, *J* = 8.4, 8.4, 6.0 Hz, 1H), 2.63 (dd, *J* = 14.4, 1.8 Hz, 1H), 2.26 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.03–1.98 (m, 1H), 1.93–1.86 (m, 1H), 1.80–1.73 (m, 1H), 1.59–1.54 (m, 1H); ¹³C NMR (151 MHz, CDCl₃): δ 148.1, 146.8, 128.2, 126.8, 126.6, 126.4, 125.8, 78.3, 68.3, 46.0, 32.6, 25.3; ¹³C NMR (151 MHz, DMSO-*d*₆): δ 148.2, 127.8, 127.7, 126.1, 126.0, 125.7, 125.5, 76.3, 76.1, 66.4, 46.0, 32.1, 25.1 HRMS (FAB): *m/z* calcd. for C₁₈H₂₀NaO₂ (M+Na) 291.1361, found 291.1354; FT-IR (KBr, cm⁻¹): 3564, 1066.



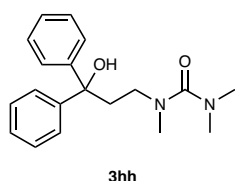
N-(3-Hydroxy-3,3-diphenylprop-1-yl)-N-methylacetamide (3hf)

According to the general procedure B, **1h** (18.0 mg, 0.100 mmol), **2f** (1 mL) and RhCrCo/SrTiO₃:Al (20.0 mg) were used. After 36 h, H₂ was detected (0.19 mmol). EtOAc was used for extraction. The product (**3hf**, 13.9 mg, 0.049 mmol, 49%) was isolated by flash column chromatography on silica gel (two times: EtOAc/hexane = 1/1, and then EtOAc/hexane = 1/1) as a white solid: ¹H NMR (600 MHz, DMSO-*d*₆) major rotamer: δ 7.51 (d, *J* = 7.2 Hz, 4H), 7.30–7.14 (m, 6H), 5.77 (s, 1H), 3.13 (t, *J* = 7.8 Hz, 2H), 2.73 (s, 3H), 2.54 (t, *J* = 7.8 Hz, 2H), 1.84 (s, 3H); minor rotamer: δ 7.45 (d, *J* = 7.8 Hz, 4H), 7.30–7.14 (m, 6H), 5.74 (s, 1H), 3.23 (t, *J* = 7.8 Hz, 2H), 2.84 (s, 3H), 2.41 (t, *J* = 7.8 Hz, 2H), 1.83 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆): rotameric mixture: δ 169.6, 169.0, 148.0, 147.8, 127.9, 127.8, 126.3, 126.1, 125.5, 75.4, 75.3, 46.1, 43.2, 39.0, 37.9, 35.7, 32.5, 21.6, 20.8; HRMS (FAB): *m/z* calcd. for C₁₈H₂₁NNaO₂ (M+Na) 306.1470, found 306.1478; FT-IR (KBr, cm⁻¹): 3340, 1621.



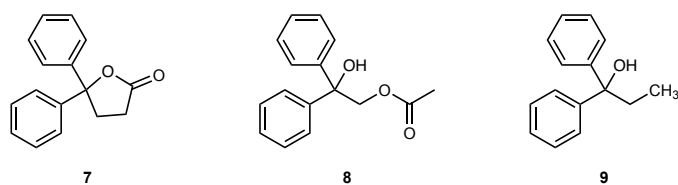
***N*-(3-Hydroxy-3,3-diphenylprop-1-yl)- acetamide (3hg)**

According to the general procedure B, **1h** (18.1 mg, 0.100 mmol), **2g** (1 mL) were used. After 72 h, H₂ was detected (0.19 mmol). A mixed organic solvent (EtOAc/hexane = 1/1) was used for extraction. The product (**3hg**, 11.3 mg, 0.042 mmol, 42%) was isolated by flash column chromatography on silica gel (three times: EtOAc/hexane = 2/1, acetone/hexane = 2/1, and then acetone/hexane = 1/2) as a white solid: ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.73 (t, *J* = 5.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 4H), 7.27 (t, *J* = 7.8 Hz, 4H), 7.16 (t, *J* = 7.8 Hz, 2H), 5.70 (s, 1H), 2.99–2.95 (m, 2H), 2.39–2.36 (m, 2H), 1.72 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆): 169.0, 147.9, 127.8, 126.1, 125.6, 75.7, 40.5, 35.0, 22.5; HRMS (FAB): *m/z* calcd. for C₁₇H₁₉NNaO₂ (M+Na) 292.1313, found 292.1307; FT-IR (KBr, cm⁻¹): 3357, 3319, 1619.



1-(3-Hydroxy-3,3-diphenylprop-1-yl)-1,3,3-trimethylurea (3hh)

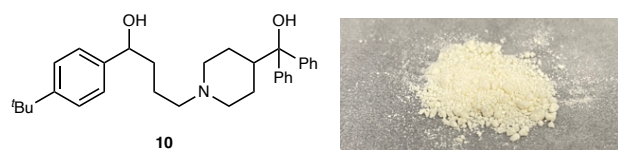
According to the general procedure B, **1h** (18.0 mg, 0.100 mmol), **2h** (1 mL) were used. After 96 h, H₂ was detected (0.20 mmol). A mixed organic solvent (EtOAc/hexane = 1/4) was used for extraction. The product (**3hh**, 11.1 mg, 0.036 mmol, 36%) was isolated by flash column chromatography on silica gel (two times: EtOAc/toluene = 1/2, and then EtOAc/hexane = 1/1) as a colorless oil: ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.45 (d, *J* = 7.2 Hz, 4H), 7.27 (t, *J* = 7.2 Hz, 4H), 7.16 (t, *J* = 7.2 Hz, 2H), 5.74 (s, 1H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.64 (s, 3H), 2.60 (s, 6H), 2.47 (t, *J* = 7.8 Hz, 2H); ¹³C NMR (151 MHz, DMSO-*d*₆): 164.4, 148.0, 127.7, 126.1, 125.6, 75.6, 46.1, 38.3, 38.2, 36.0; HRMS (FAB): *m/z* calcd. for C₁₉H₂₄N₂NaO₂ (M+Na) 335.1735, found 335.1735; FT-IR (NaCl, cm⁻¹): 3358, 1618.



5,5-diphenyldihydrofuran-2(3*H*)-one(7),²⁰ 2-Hydroxy-2,2-diphenylethyl acetate (8),²¹ and 1,1-Diphenylpropan-1-ol (9)²²

According to the general procedure A, **1h** (17.8 mg, 0.099 mmol) and **2i** (1 mL) were used. H₂ (0.10 mmol) and CO₂ (not quantified) were detected. After flash column chromatography on silica gel (EtOAc/hexane = 1/19 to 1/9), a part of **8** (1.5 mg, 0.006 mmol, 6%) was isolated as a white solid, but **7** and **9** were not completely separated from impurities. Combined fractions containing each compound were subjected to additional flash column chromatography on silica gel (EtOAc/hexane = 1/19, or 1/9) and the pure products (**9**, 3.6 mg, 0.017 mmol, 17%, a white

solid, or **7**, 0.6 mg, 0.003 mmol, 3%, a colorless oil, respectively) were partially isolated: **7**: ^1H NMR (600 MHz, CDCl_3): δ 7.42 (d, J = 7.8 Hz, 4H), 7.35 (t, J = 7.8 Hz, 4H), 7.28 (t, J = 7.8 Hz, 2H), 2.91 (t, J = 7.2 Hz, 2H), 2.58 (t, J = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3): δ 176.2, 143.2, 128.8, 128.1, 125.6, 89.9, 35.9, 29.2; HRMS (FAB): m/z calcd. for $\text{C}_{16}\text{H}_{14}\text{NaO}_2$ ($\text{M}+\text{Na}$) 261.0891, found 261.0891; **8**: δ 7.41 (d, J = 7.8 Hz, 4H), 7.31 (t, J = 7.8 Hz, 4H), 7.22 (t, J = 7.8 Hz, 2H), 2.33 (q, J = 7.2 Hz, 2H), 2.07 (s, 1H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 147.1, 128.3, 126.9, 126.3, 78.7, 34.6, 8.3; HRMS (FAB): m/z calcd. for $\text{C}_{15}\text{H}_{16}\text{NaO}$ ($\text{M}+\text{Na}$) 235.1099, found 235.1094.



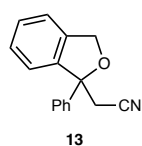
Terfenadine (**10**)²³

An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar, Ag (0.5 wt%)/ TiO_2 (50 mg), and $\text{RhCrCo/SrTiO}_3\text{:Al}$ (50 mg). The vessel was sealed with a rubber septum and placed under nitrogen before a stock solution of 4-*tert*-butylstyrene (**1g**, 160.8 mg, 1.00 mmol) in **2a** (20 mL) and an aqueous solution of LiOH (0.02 M, 2 mL) were added. The mixture was sonicated and then stirred under LED-light irradiation (two Kessil lamps, λ = 370 nm, see Supplementary Scheme S1). After 24 h, the reaction mixture was filtrated through a 0.45 μm membrane filter with EtOAc. The filtrate was dried over Na_2SO_4 , filtrated, and concentrated under reduced pressure (80 mmHg, 40 $^\circ\text{C}$). An aliquot with an internal standard (1,1,2,2-tetrachloroethane) was monitored by ^1H NMR analysis (**3ga**: 32%, **11**: 15%). After flash column chromatography on silica gel (EtOAc/hexane = 1/9), a mixture of **3ga** and **11** was obtained as a yellow oil with some impurities (133.0 mg).

A solution of DIBAL-H in hexane (1 M, 1.8 mL, 1.8 mmol) was added over 10 min to a solution of the mixture containing **3ga** and **11** (133.0 mg) in CH_2Cl_2 (7.0 mL) at -84 $^\circ\text{C}$ under nitrogen and the mixture was allowed to stir at that temperature for 3 h. The reaction was quenched at -84 $^\circ\text{C}$ by addition of EtOAc (0.6 mL) followed by an aqueous solution of HCl (1 M, 2.4 mL). The mixture was then allowed to warm to room temperature. The aqueous layer was extracted with EtOAc (3×5 mL) and the combined organic layers were washed with brine (5 mL), and then dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. After flash column chromatography on silica gel (EtOAc/hexane = 1/4), an equilibrium mixture of an aldehyde and a hemiacetal was isolated as a pale yellow oil (83.9 mg, 0.38 mmol).

To a solution of the equilibrium mixture (83.9 mg, 0.38 mmol) in methanol (6 mL), α -(4-piperidyl)benzhydrol (**12**, 104.0 mg, 0.39 mmol) was added under nitrogen. The reaction mixture was heated to 50 $^\circ\text{C}$ for 1 h. The reaction solution was then cooled with an ice-water bath to 0 $^\circ\text{C}$, and sodium borohydride (28.8 mg, 0.76 mmol) was added slowly. The reaction

mixture was stirred at room temperature for 30 min. The reaction was quenched by addition of water (2 mL) and then concentrated under reduced pressure. The residue was dissolved in water (3 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried with Na₂SO₄, filtered and concentrated. After flash column chromatography on silica gel (methanol/CH₂Cl₂ = 1/9), terfenadine (**10**, 177.1 mg, 0.38 mmol) was isolated as a white solid: ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.50 (d, *J* = 8.4 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 2H), 5.22 (s, 1H), 4.45 (t, *J* = 6.6 Hz, 1H), 2.81 (t, *J* = 13.8 Hz, 2H), 2.45 (t, *J* = 12.0 Hz, 1H), 2.21 (t, *J* = 6.6 Hz, 2H), 1.84 (m, 2H), 1.58–1.15 (m, 18H); ¹³C NMR (151 MHz, DMSO-*d*₆): 148.7, 147.3, 143.4, 127.7, 125.7, 125.7, 125.4, 124.5, 78.4, 72.0, 58.0, 53.6, 53.5, 43.5, 40.0, 37.4, 34.0, 31.2, 25.9, 23.0; HRMS (FAB): *m/z* calcd. for C₃₂H₄₂NO₂ (M+H) 472.3216, found 472.3200. ¹H and ¹³C NMR spectra of the synthesized **10** are consistent with those of the authentic sample purchased from Tokyo Chemical Industry.



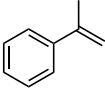
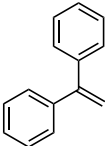
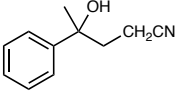
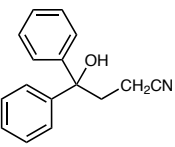
1-(2-cyanoethyl)-1-phenyl-1,3-dihydroisobenzofuran (**13**)⁵

According to the general procedure A, **1s** (21.0 mg, 0.100 mmol) and **2a** (1 mL) were used. After 48 h, H₂ was detected (0.15 mmol). The product (**9**, 9.6 mg, 0.039 mmol, 39%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/9) as a colorless oil: ¹H NMR (600 MHz, CDCl₃): δ 7.49–7.47 (m, 2H), 7.36–7.28 (m, 5H), 7.27–7.21 (m, 2H), 5.19 (d, *J* = 12.6 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 2.59 (ddd, *J* = 13.8, 10.8, 6.0 Hz, 1H), 2.48 (ddd, *J* = 13.8, 9.6, 5.4 Hz, 1H), 2.31 (ddd, *J* = 17.4, 9.6, 6.0 Hz, 1H), 2.24 (ddd, *J* = 17.4, 10.8, 5.4 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃): δ 143.6, 142.4, 139.2, 128.8, 128.5, 128.0, 127.7, 125.0, 121.9, 121.6, 120.0, 90.0, 72.3, 37.3, 12.7; HRMS (FAB): *m/z* calcd. for C₁₇H₁₅NNaO (M+Na) 272.1051, found 272.1057.

5. DFT calculation

DFT calculations were carried out using the Gaussian 09 program package. Geometries were optimized at the B3LYP/6-31G(d,p) level of theory. Free energies (ΔG°) were computed at 298.15 K at the same level. The calculations did not take into account the effects of solvent.

Supplementary Table S7. Computed energies

name	structure	Gibbs free energy (kJ mol ⁻¹)
1a		-915907.8581
1h		-1419200.585
2a	CH ₃ CN	-348503.1491
H₂O	H ₂ O	-200632.1313
3aa		-1461885.274
3ha		-1965160.951
H₂	H ₂	-3097.706222

Cartesian Coordinates

1a

Element	X	Y	Z
C	-4.05857200	-2.01695000	0.35102000
C	-2.66423500	-2.00141500	0.31964600
C	-1.95605800	-0.82414000	0.02205900
C	-2.70352300	0.33108100	-0.27236000
C	-4.09542000	0.31691600	-0.24290000
C	-4.78188700	-0.85772100	0.07261600
H	-4.57919200	-2.93916300	0.59318400
H	-2.12339500	-2.91473300	0.54446500

H	-2.18479600	1.24224700	-0.55267600
H	-4.64655500	1.22263000	-0.47987300
H	-5.86766600	-0.87043900	0.09094400
C	-0.46742100	-0.80330900	0.00725900
C	0.25102300	-2.09353000	-0.31909000
H	0.10593400	-2.84578000	0.46568400
H	-0.11886600	-2.53255800	-1.25251900
H	1.32634000	-1.92644200	-0.41653900
C	0.22735700	0.31072800	0.28407100
H	1.31242000	0.31894800	0.24913400
H	-0.25508800	1.23864700	0.57249100

1h

Element	X	Y	Z
C	-4.40962400	-0.70490500	0.88796600
C	-3.10319500	-0.90803900	1.32988400
C	-2.04722800	-1.06318200	0.41610800
C	-2.34658900	-1.02716300	-0.95679100
C	-3.65219200	-0.82077500	-1.39883700
C	-4.68938800	-0.65777200	-0.47864300
H	-5.21153700	-0.59424100	1.61239200
H	-2.89476700	-0.96893000	2.39364800
H	-1.54578900	-1.15010500	-1.67910600
H	-3.85939600	-0.78582700	-2.46461800
H	-5.70760000	-0.50351400	-0.82364400
C	-0.64371300	-1.23169000	0.89036500
C	-0.18704400	-0.53236700	1.94539100
H	0.81353900	-0.68430900	2.33610400
H	-0.80301700	0.20868300	2.44372100
C	0.24325600	-2.19131300	0.17227200
C	-0.24564500	-3.43159800	-0.27331100
C	1.59768600	-1.89255600	-0.05210400
C	0.59598700	-4.34857200	-0.90049800
H	-1.29028800	-3.67962900	-0.11416900
C	2.43893900	-2.80830400	-0.68220800

H	1.98323700	-0.92475000	0.25354400
C	1.94220300	-4.04162700	-1.10682700
H	0.19947300	-5.30562900	-1.22738600
H	3.48131500	-2.55335600	-0.85121400
H	2.59622900	-4.75388600	-1.60131000

2a

Element	X	Y	Z
C	-3.45920000	0.15056300	0.02879800
H	-3.10191000	-0.88290700	0.01576900
H	-3.10190200	0.65598200	-0.87273800
H	-4.55266700	0.14297000	0.01563400
C	-2.97241500	0.83900700	1.22123500
N	-2.58558300	1.38597800	2.16865600

H₂O

Element	X	Y	Z
O	-1.63441800	0.66916100	0.00000000
H	-0.67041100	0.71761600	0.00000000
H	-1.91053700	1.59405200	0.00000000

3aa

Element	X	Y	Z
C	-1.21673200	-3.42932700	-0.04743800
C	0.01501800	-3.52819200	0.60110200
C	0.87444100	-2.43057500	0.64853500
C	0.51968400	-1.21350800	0.04870300
C	-0.72391800	-1.12326900	-0.59022100
C	-1.58312400	-2.22184600	-0.64127600
H	-1.88466800	-4.28468700	-0.08628300
H	0.31030900	-4.46191100	1.07102000
H	1.82587000	-2.53083000	1.16173200
H	-1.01450700	-0.18155000	-1.04278900
H	-2.54166800	-2.13064400	-1.14420200
C	1.43528100	0.01871400	0.12209600

C	1.19664500	0.72341000	1.47701100
H	1.47024200	0.04125100	2.28766400
H	0.12397800	0.91686400	1.56960900
C	1.95915600	2.05753700	1.62561100
H	3.04294200	1.89904700	1.60955300
H	1.71577700	2.71057600	0.78193300
C	1.62300700	2.74511900	2.87393300
N	1.35052900	3.27833300	3.86864000
O	1.05603300	0.99002300	-0.86429100
H	1.19167700	0.59303000	-1.73596400
C	2.91350200	-0.35385800	-0.09328200
H	3.31205800	-0.96812000	0.71862400
H	3.03072800	-0.91908600	-1.02400700
H	3.52227500	0.55064000	-0.16838800

3ha

Element	X	Y	Z
C	-1.33543900	-3.41413800	-0.05081300
C	0.01206400	-3.66804400	0.19588400
C	0.93022800	-2.61703500	0.26629800
C	0.51404900	-1.29131200	0.09691800
C	-0.84631000	-1.04954400	-0.16403800
C	-1.76164300	-2.09701400	-0.23440300
H	-2.04686800	-4.23277700	-0.10564600
H	0.35884500	-4.68875300	0.32883100
H	1.97507100	-2.84040600	0.44494900
H	-1.18243700	-0.03059900	-0.32768600
H	-2.80760200	-1.88429500	-0.43561100
C	1.46352300	-0.07517700	0.14961700
C	1.11973100	0.80053700	1.38187600
H	1.31087900	0.23716400	2.29873900
H	0.04897700	1.01780600	1.35943200
C	1.90559600	2.12781900	1.40407200
H	2.98314600	1.93648400	1.44779900
H	1.71403900	2.68178300	0.48013300

C	1.53452600	2.96413500	2.54691300
N	1.23142100	3.61511100	3.45936700
O	1.17190600	0.77147600	-0.97646400
H	1.04419900	0.20014300	-1.74591700
C	2.95374400	-0.45993300	0.16126800
C	3.54301700	-1.05886300	1.28711000
C	3.76601300	-0.19897400	-0.94798600
C	4.89583100	-1.39805700	1.29455400
H	2.94412500	-1.27028400	2.16804500
C	5.12012100	-0.53996700	-0.94382500
H	3.33951500	0.29794200	-1.81153800
C	5.69083000	-1.14254900	0.17599800
H	5.32800200	-1.85980100	2.17755400
H	5.72910100	-0.32535000	-1.81730000
H	6.74450600	-1.40489300	0.18166800

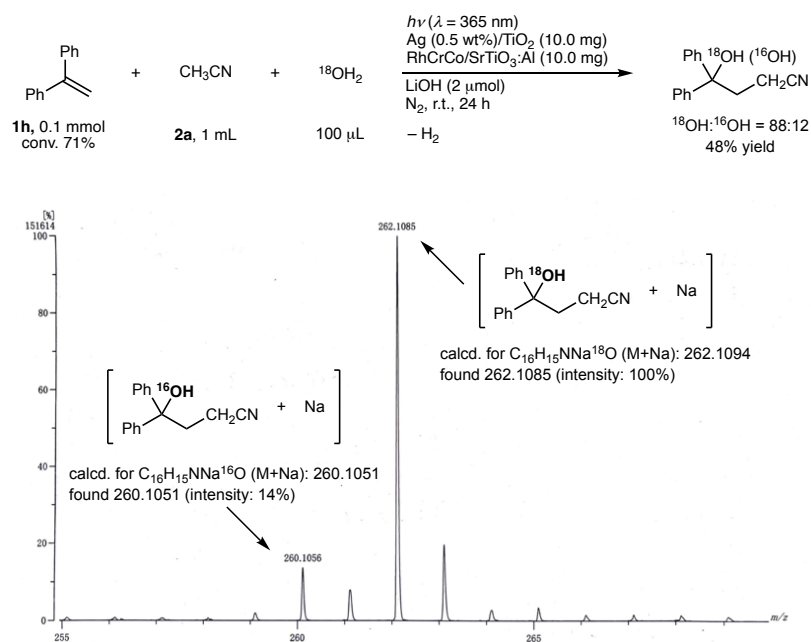
H₂

Element	X	Y	Z
H	-0.92458600	1.20535700	0.00000000
H	-1.66737900	1.20535700	0.00000000

6. Mechanistic study

Labelling experiment

According to the general procedure A, **1h** (17.8 mg, 0.099 mmol), **2a** (1 mL), and $^{18}\text{OH}_2$ (97 atom % ^{18}O) were used. The crude mixture was analyzed by FAB-MS. ^{18}OH was incorporated into the coupling product dominantly. ^{16}OH was observed to some extent, that might be derived from LiOH and H_2O adsorbed on the hydrophilic surfaces of the photocatalysts.

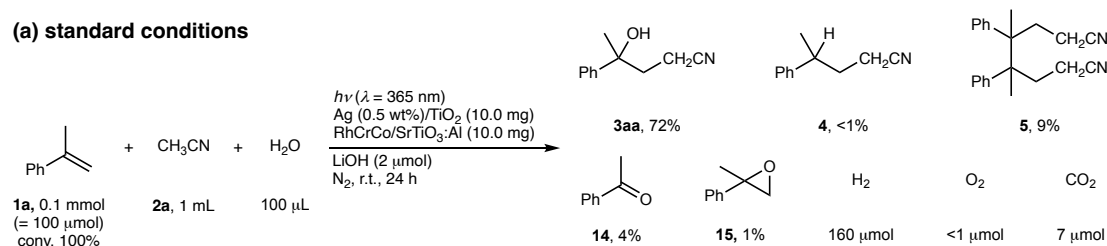


Supplementary Fig. S1 ^{18}O -labelling experiment.

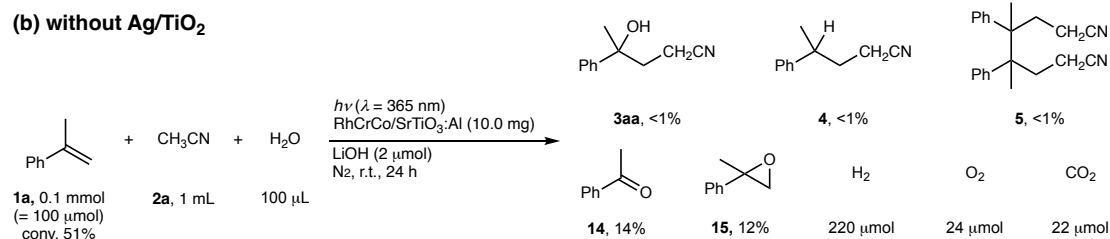
Gas-phase/liquid phase analysis

Results of gas-phase analysis were summarized in Supplementary Fig. S2. The μ GC-TCD spectra were shown in Supplementary Figs. S3 and S4. For comparison, μ GC-TCD spectra of prepared samples containing H_2 , O_2 , or CO_2 were shown in Supplementary Fig. S5. The channels 1, and 2 were for detection of smaller molecules (H_2 , O_2), and larger molecules (CO_2), respectively. Calibration lines for quantifying amounts of H_2 , O_2 and CO_2 were shown in Supplementary Fig. S6.

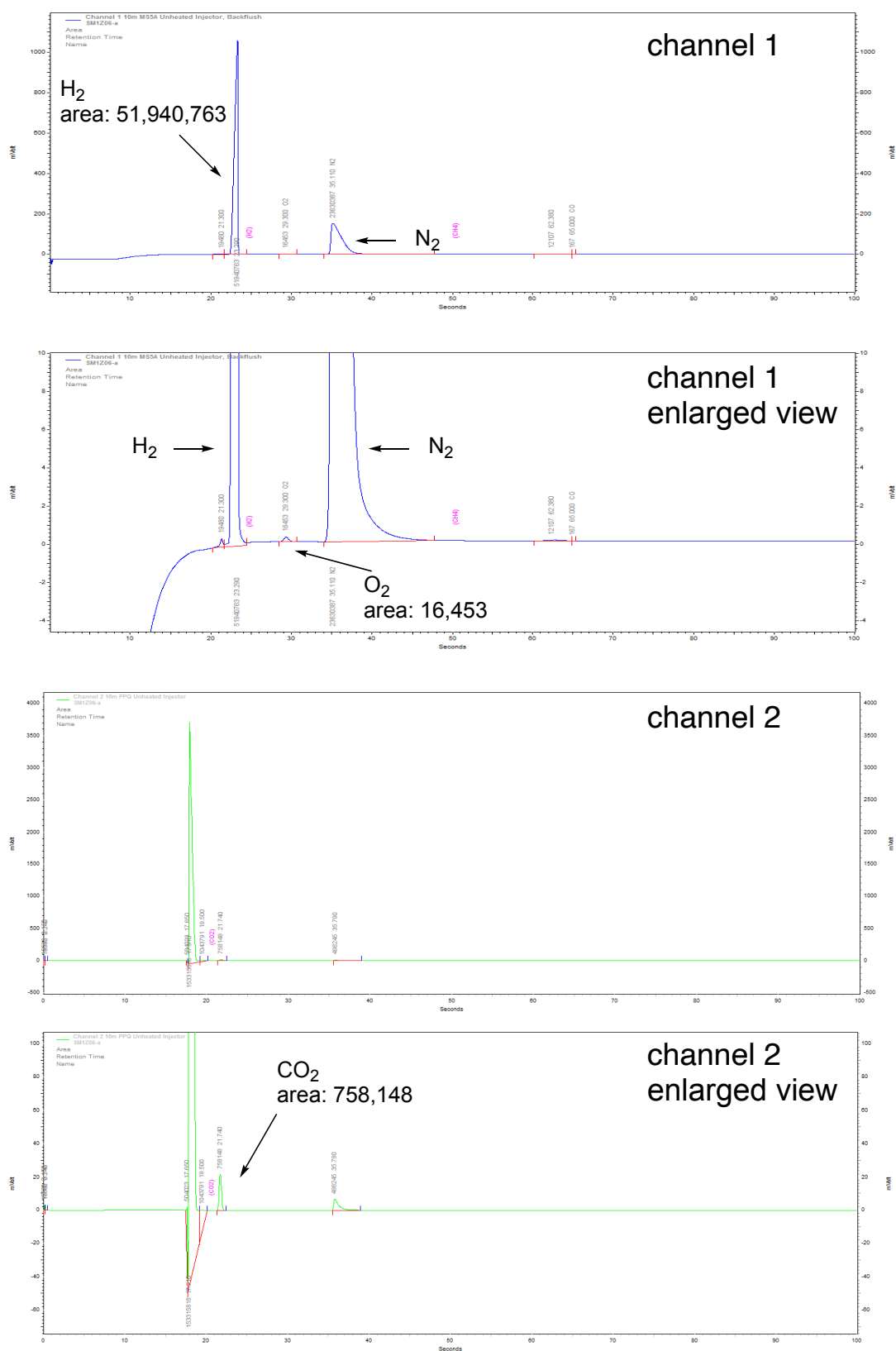
(a) standard conditions



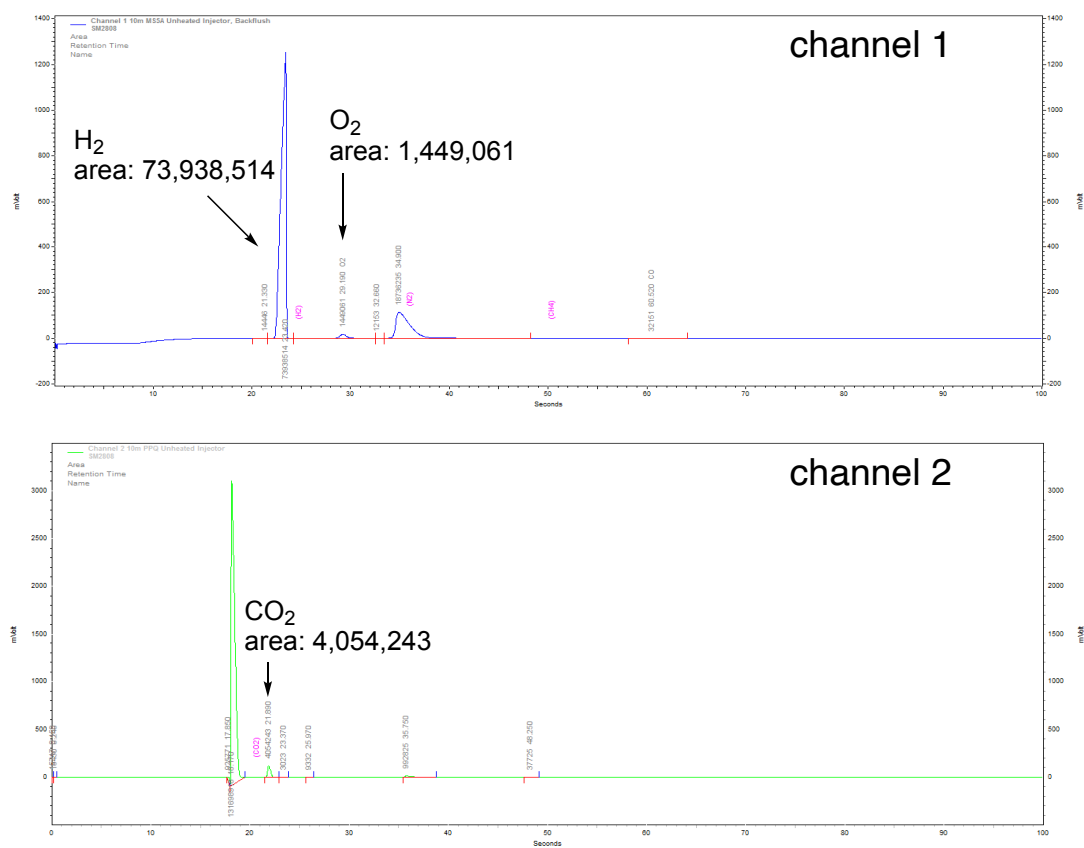
(b) without Ag/TiO₂



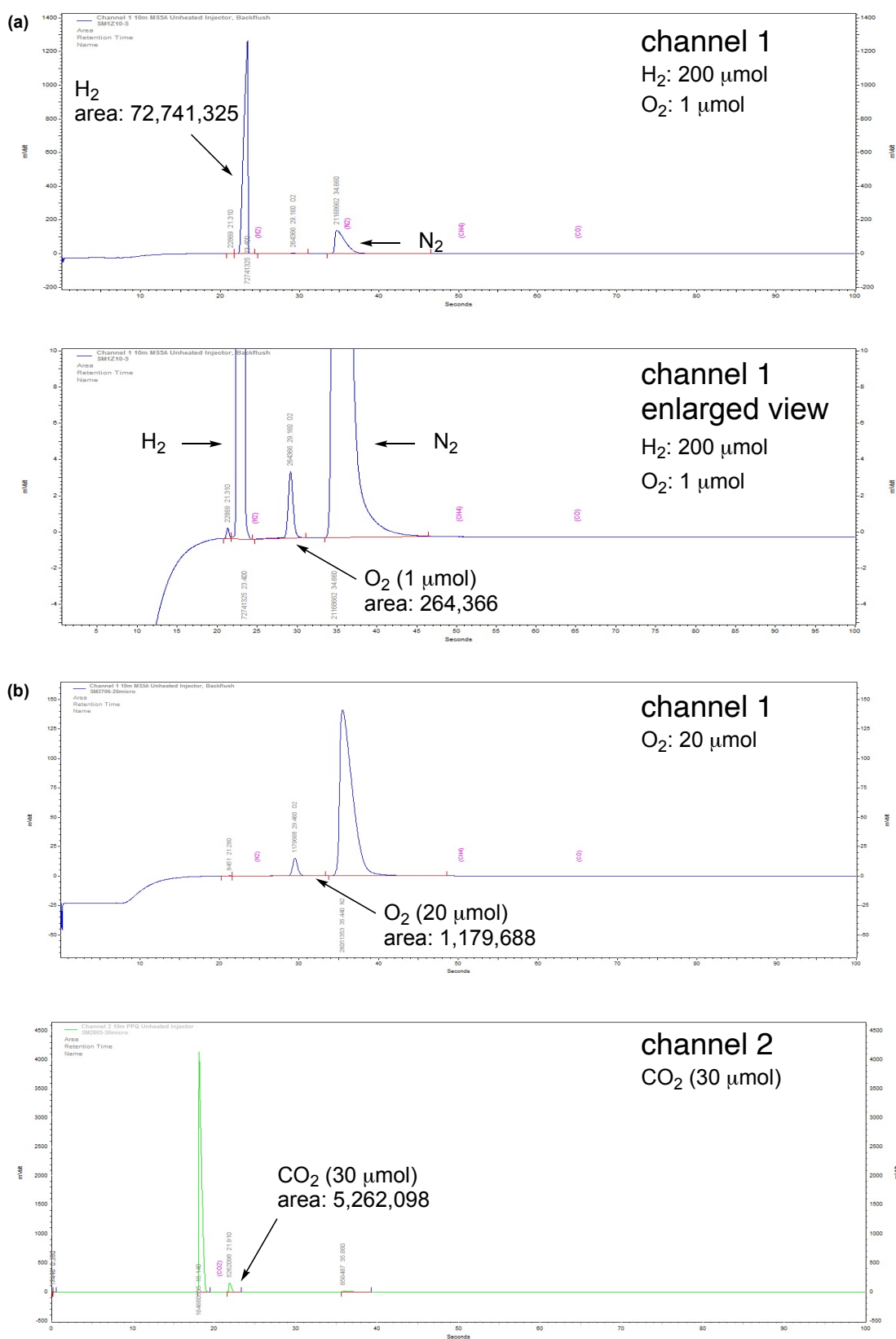
Supplementary Fig S2. Gas-phase/liquid-phase analysis. (a) Reactions under standard conditions, or (b) without Ag/TiO₂.



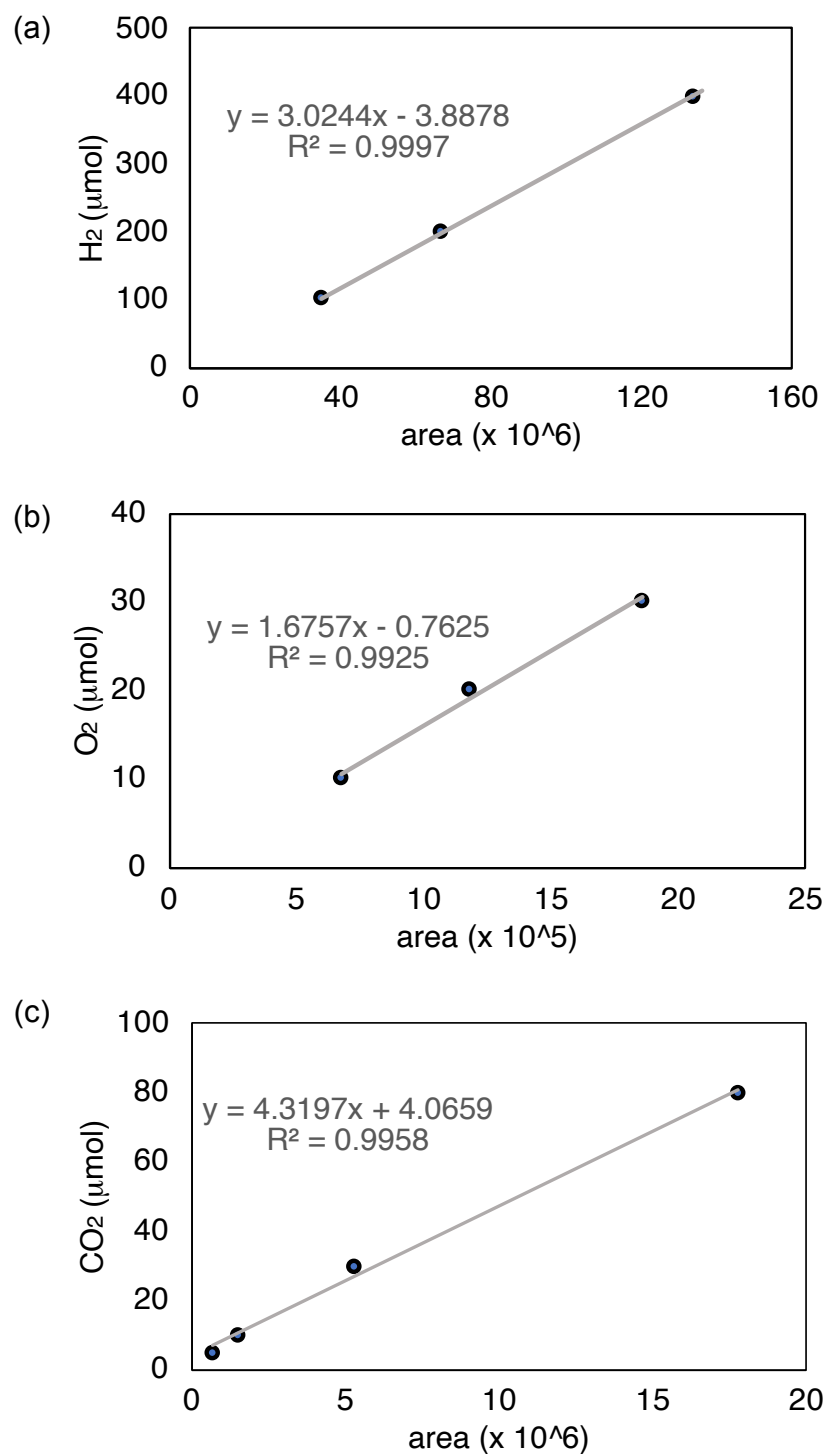
Supplementary Fig. S3 μ GC-TCD spectra of the gas-phase of the reaction under standard conditions.



Supplementary Fig. S4 μ GC-TCD spectra of the gas-phase of the reaction under the standard conditions without Ag/TiO₂.



Supplementary Fig. S5 μ GC-TCD spectra of the authentic gas samples containing (a) H₂ and O₂, or (b) O₂ and CO₂.



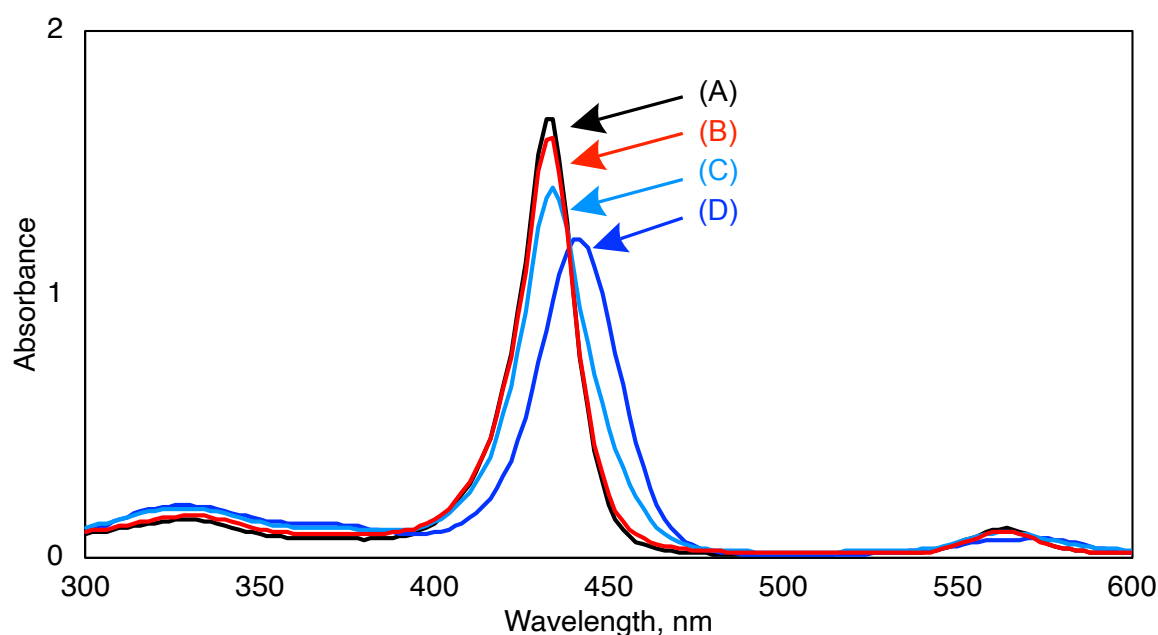
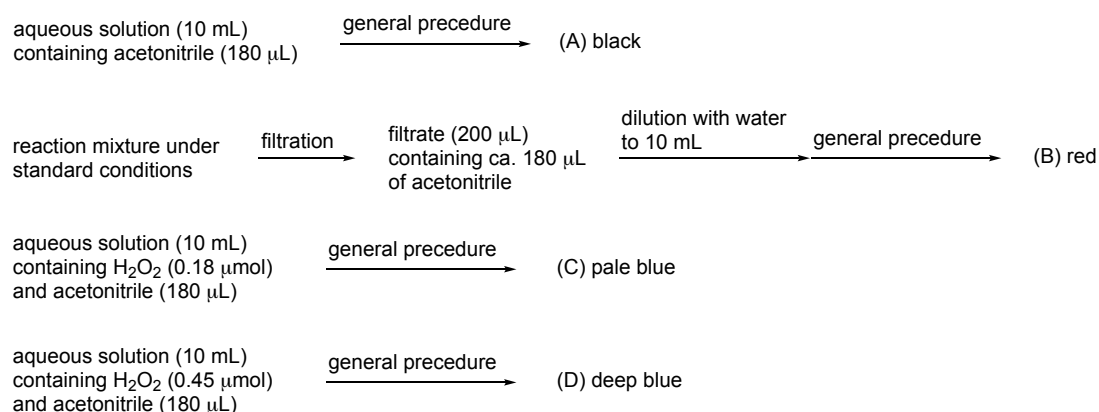
Supplementary Fig. S6 Calibration lines. (a) H_2 (range: 100–400 μmol). (b) O_2 (range: 10–30 μmol). (c) CO_2 (range: 5–80 μmol)

Analysis for H₂O₂ detection

General procedure

[TiO(tpypH₄)]⁴⁺ was used for H₂O₂ detection according to a literature.²⁶ [TiO(tpyp)] (3.4 mg) was dissolved in 100 mL of aqueous hydrochloric acid solution (50 mM) to form [TiO(tpypH₄)]⁴⁺. 0.25 mL of an aliquot was mixed with 0.25 mL of aqueous perchloric acid solution (4.8 M) and 0.25 mL of the [TiO(tpypH₄)]⁴⁺ solution. After 5 min at room temperature, the mixture was diluted with water to 2.5 mL and used for the UV-Vis absorption spectroscopy (Supplementary Fig. S7). As a result, the aliquot prepared from 200 μL of the reaction mixture (for reaction conditions, see Supplementary Fig. S2a) contained less than 0.18 μmol of H₂O₂. The total volume of the reaction mixture was 1100 μL. Therefore, the amount of H₂O₂ generated during the reaction was less than 1 μmol.

<sample preparation>

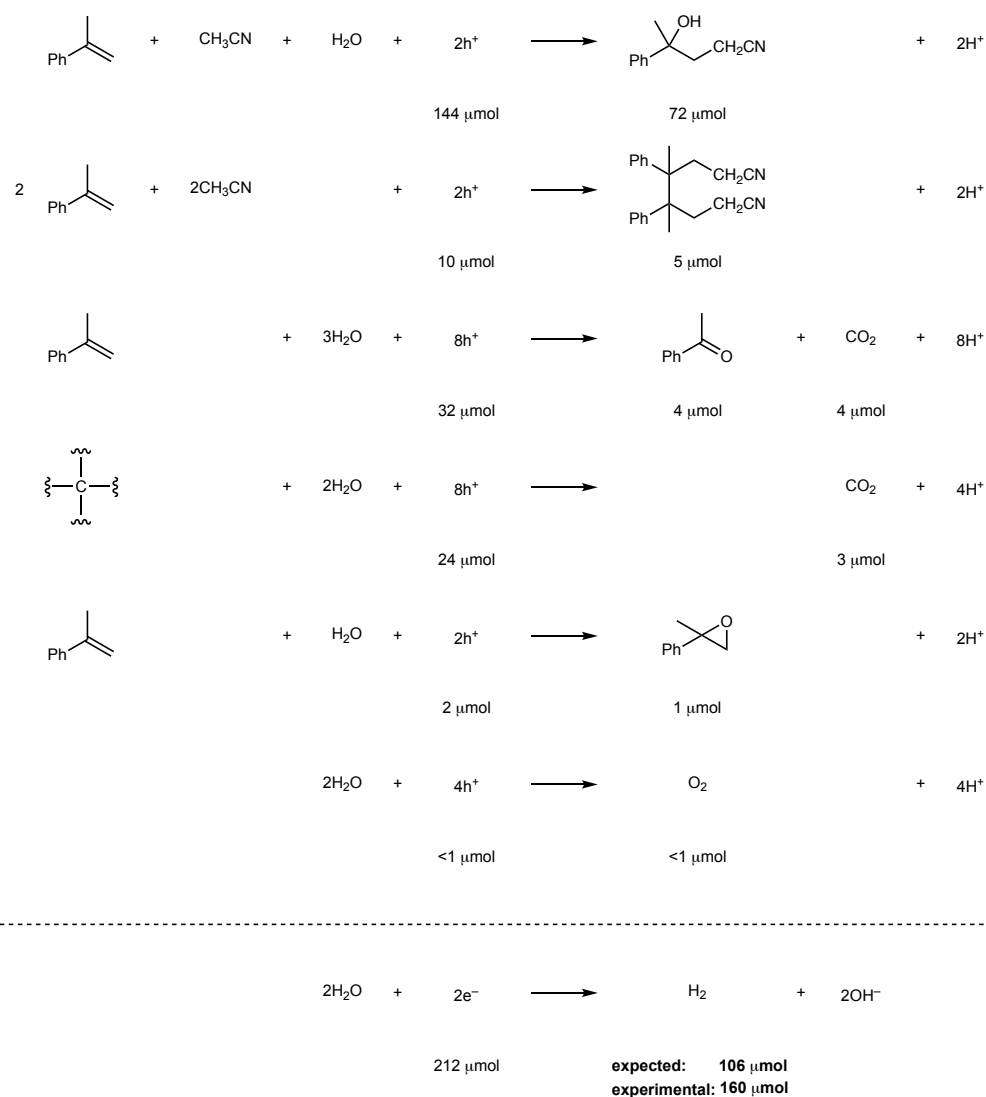


Supplementary Fig. S7 Analysis for H₂O₂ detection using [TiO(tpypH₄)]⁴⁺.

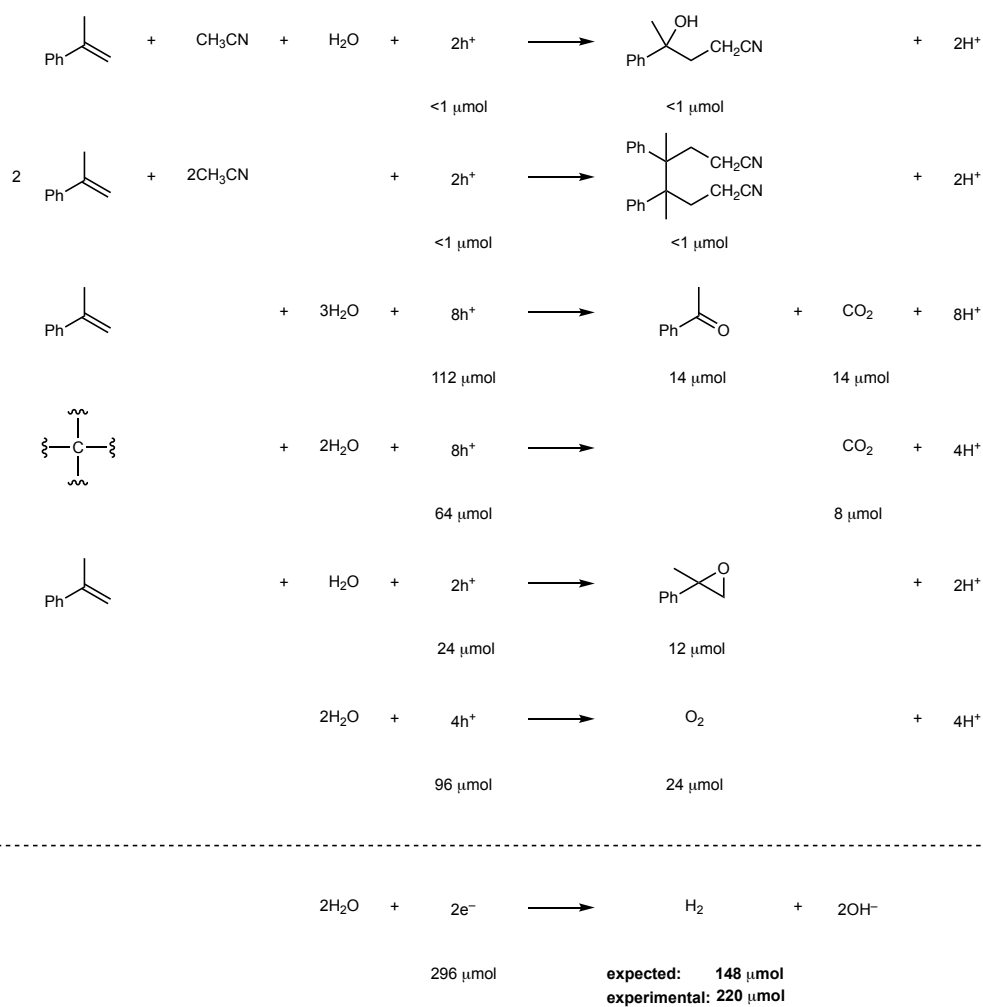
Elucidation of the mass balance

Based on the amounts of the identified products (Fig. S2), expected amounts of H_2 were calculated as shown in Supplementary Figs. S8. In the both reactions under the standard conditions or without AgTiO_2 , little larger amounts of H_2 were observed than expected. The gap would be attributed to oxidation of organic compounds, which has not been identified yet.

(a) standard conditions



(b) without Ag/TiO₂



Supplementary Fig. S8 Elucidation of the mass balance. (a) Reactions under standard conditions (Fig. S2), or (b) without Ag/TiO₂ (Fig. S2).

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8. Spectral data

