Selective oxidations of benzylic alcohols by synergistic bisphosphonium and cobalt catalysis

Jia Ding †, Shuaishuai Luo†, Yuanli Xu, Qing An, Yi Yang*, Zhiwei Zuo*

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1. General information.

1.1 Materials and Methods

Reagents were purchased from Aldrich, TCI, Energy Chemical and J&K Reagents were purchased from Aldrich, TCI, Energy Chemical and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of argon unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. ¹H and ¹³C NMR spectra were recorded on an Agilent 400 (400 and 100 MHz) or Varian 400 (400 and 100 MHz), and are internally referenced to residual protio solvent signals (CDCl₃, δ 7.26 and 77.0 ppm). Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). ¹³C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. GC analyses were carried out on Agilent 7890B Infinity system. High Resolution Mass spectra were obtained from Thermo Fisher Q-Exactive High-resolution MS.

1.2 Electrochemical Measurements

Cyclic voltammetry experiments were carried out with a. CHI760E. electrochemical workstation (Shanghai Chenhua Instrument Plant, China) using a one compartment electrolysis cell consisting of a typical glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and a Ag/AgCl reference electrode. Before performing electrochemical cleaning, the electrode should be sonicated in ethanol and deionized water for 1~3 mins respectively to obtain a clean electrode. There is no graininess on the electrode surface when polishing on a Microcloth polishing

fleece coated with 1 μ M and 0.05 μ M alumina powder (both purchased from Shanghai Chenhua) and the polishing can be stopped. The electrode also consists of a porous plug on the one end which will allow contact between the field environment with the silver chloride electrolyte. Saturated potassium chloride is added inside the body of the electrode to stabilize the silver chloride concentration and in this condition the electrode's reference potential is known to be +0.197 V at 25 °C. The measurements were done in 0.001 M CH₃CN solution with 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆, TCI, Electrochemical grade) as supporting electrolyte at a scan rate of 200 mV/s. The redox potential was calibrated after each experiment against the ferrocenium/ferrocene couple (Fc⁺/Fc), which allowed conversion of all potentials to the aqueous saturated calomel electrode (SCE) scale by using E₀ (Fc⁺/Fc) = -0.20 V vs. SCE in CH₃CN. The working solution was frozen and thaw three times under argon before measurement and then kept under a positive argon pressure during the measurement.

2. Mechanistic experiments.

2.1 UV-Visible absorption and emission Spectra

UV-Vis spectra were collected on an Agilent Cary 5000 spectrophotometer. Emission spectra were collected on a Fluorolog-3 spectrofluorometer. Bisphosphonium catalyst **3** was degassed with a stream of Argon for 10 minutes, and then excited at 380 nm for the collection of the emission spectra.



Figure S1. UV-Vis spectra of Bisphosphonium catalyst 3.



Figure S2. Emission spectra of Bisphosphonium catalyst 3.

2.2 Luminescence Quenching Experiments (Stern-Volmer Studies).

Emission intensities were recorded using a Fluorolog-3 luminescence spectrometer. Bisphosphonium catalyst **3** was excited at 380 nm and the emission intensity was collected at **435** nm. In a typical experiment, to a $1*10^{-4}$ M solution of bisphosphonium catalyst **3** in TFE was added the appropriate amount of *p*-methoxy benzylic in a screwtop quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.



Figure S3. Stern-Volmer quenching experiments.

2.2 Kinetic isotope effect (KIE) experiment.

KIE determined from two parallel reaction:





Figure S4. Rares of the selective oxidation of PhCH₂OH and PhCD₂OH.

A 8-mL vial was charged with benzyl alcohol (0.2 mmol), bisphosphonium salt **3** (0.004 mmol, 2 mol%) and Co^{III}(dmgH)₂pyCl (0.004 mmol, 2 mol%) in TFE (1 mL) under N₂ atmosphere, and *n*-nonane (20 μ L, 0.2 mmol) was added to the reaction mixture as an internal standard. At each designated time interval, the solution was taken from the vial with a micro syringe (50 μ L). The quantification of the products was determined by gas chromatography. The rate of the reaction for PhCD₂OH (0.2 mmol) was performed under the same conditions.

KIE determined from Intermolecular competitive:



A 8-mL vial was charged with PhCH₂OH (0.1 mmol), PhCD₂OH (0.1 mmol), bisphosphonium salt **3** (0.004 mmol, 2 mol%) and Co^{III}(dmgH)₂pyCl (0.004 mmol, 2 mol%) in TFE (1 mL) under N₂ atmosphere. The solution then stirred at ambient temperature under the irradiation of 400 nm LED (photon flux, 2.5 W/cm²) for 5 min.

After then, the products were determined by TLC and GC-MS. Then the pure product was obtained by flash column chromatography on silica gel (1% diethyl ether in pentane) to afford corresponding stilbene derivatives **10/10-d** in 10% yield. ¹H NMR spectra for the isolated product indicated that the ratio of **10:10-d** is 2.0:1.

KIE determined from Intramolecular competitive:



A 8-mL vial was charged with PhCHDOH (0.2 mmol), bisphosphonium salt **3** (0.004 mmol, 2 mol%) and Co^{III}(dmgH)₂pyCl (0.004 mmol, 2 mol%) in TFE (1 mL) under N₂ atmosphere. The solution then stirred at ambient temperature under the irradiation of 400 nm LED (photon flux, 2.5 W/cm²) for 5 min. After then, the products were determined by TLC and GC-MS. Then the pure product was obtained by flash column chromatography on silica gel (1% diethyl ether in pentane) to afford corresponding stilbene derivatives **10/10-d** in 10% yield. ¹H NMR spectra for the isolated product indicated that the ratio of **10-d:10** is 2.0:1.

3. Reaction optimization.

F	2 mol% bisphosph 2 mol% cobaloxin slovent (0.2 M), LEDs (λmax	onium salt 3 ne catalyst := 400 nm, 2.5 W), r.t.	F H	
Entry	Slovent	yield ^b	conv. ^b	
1	TFE	98%	100%	
2	HFIP	56%	58%	
3	MeOH	35%	48%	
4	MeCN	85%	100%	
5	Acetone	54%	54%	
6	DCM	78%	100%	
7	DCE	58%	61%	
8	Toluene	14%	16%	
9	PhCF ₃	24%	26%	
10	EA	17%	18%	
11	DMSO	6%	18%	
12	DMF	2%	2%	

^aReaction conditions: A solution of 4-fluorobenzyl alcohol (0.2 mmol), bisphosphonium salt **3** (2 mol%) and cobaloxime catalyst (2 mol%) in solvent (1 mL) was irradiated with 2.5 W 400 nm LEDs for 6 hours at room temperature under argon atmosphere. ^bYield was determined by GC analysis of the crude mixture using PhOMe as an internal standard.

Table S1. Evaluation of the solvents	Table S1	. Evaluation	of the	solvents
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F	x mol% bisphosphon x mol% cobaloxime TFE (0.2 M), LEDs (λmax = 4	ium salt 3 catalyst 00 nm, 2.5 W), r.t.	F H
Entry	Equivalent of cat.	yield ^b	conv. ^b
1	x = 0.5	28%	28%
2	x = 1	60%	65%
3	x = 2	98%	100%
4	x = 3	94%	100%
5	x = 4	90%	100%

^aReaction conditions: A solution of 4-fluorobenzyl alcohol (0.2 mmol), bisphosphonium salt **3** and cobaloxime catalyst in solvent (1 mL) was irradiated with 2.5 W 400 nm LEDs for 6 hours at room temperature under argon atmosphere. ^bYield was determined by GC analysis of the crude mixture using PhOMe as an internal standard.

Table S2. Evaluation of the bisphosphonium salt 3 and cobaloxime catalysy loading.



Figure S5. Reaction time profiles of 4-Fluorobenzyl alcohol and 4-Fluorobenzaldehyde in photocatalytic selective oxidations.



^aBatch conditions: A solution of 4-fluorobenzyl alcohol (0.2 mmol), photocatalyst (2 mol%) and cobaloxime catalyst (2 mol%) in TFE (1 mL) was irradiated with 2.5 W 400 nm LEDs for 6 hours at room temperature under argon atmosphere. Flow conditions: A solution of 4-fluorobenzyl alcohol (3.0 mmol), photocatalyst (2 mol%) and cobaloxime catalyst (2 mol%) in TFE (15 mL) was fed into the reaction coil (ϕ 1/8 inch*4 m, t_r = 90 min) via a syringe pump with flow rate 50 µL/min and irradiated with 2.5 W 400 nm LEDs at room temperature. ^bYield was determined by GC analysis of the crude mixture using PhOMe as an internal standard.

Table S3. Comparation between batch and flow.

4. General Procedure.

4.1 General procedure for preparation of the bisphosphonium salts.

Bisphosphonium catalyst 3¹: A mixture of Cu(OTf)₂ (3.62 g, 10.0 mmol, 1.0 equiv.) and Binap (6.23 g, 10.0 mmol, 1.0 equiv.) in acetonitrile (300 mL) was stirred at room temperature for 30 min. The solvent was evaporated and the crude mixture was purified on silica gel chromatography (20% acetone in dichloromethane). The eluting yellow band was collected, and the resulting solution was concentrated under vacuum to a volume of 10 mL. Addition of diethyl ether (40 mL) caused the precipitation of compound 1 as a microcrystalline solid, which was washed with hexane $(2 \times 20 \text{ mL})$. Slow diffusion of diethyl ether into a concentrated solution of 1 in acetonitrile afforded yellow crystals (2.04 g, 22% yield). ¹H NMR (400 MHz, acetone-d₆): $\delta = 8.93-8.90$ (m, 2H), 8.80-8.74 (m, 4H), 8.36-8.29 (m, 4H), 8.00-7.94 (m, 12H), 7.82-7.77 (m, 8H). ¹³C NMR (100 MHz, acetone-d₆): $\delta = 140.5$ (d, J = 8 Hz), 139.7 (s), 137.8 (d, J = 9Hz), 136.9 (d, J = 2 Hz), 136.0 (d, J = 13 Hz), 135.5 (d, J = 13 Hz), 133.7 (dd, J = 12, 5 Hz), 131.7 (d, J = 14 Hz), 131.4-130.9 (m), 130.1 (dd, J = 11, 6 Hz), 120.3 (s), 119.7 (s), 117.6 (s), 117.1 (s), 113.6 (s), 113.0 (s). ¹⁹F NMR (376 MHz, acetone-d₆): $\delta =$ -78.91. ³¹**P NMR (acetone-d₆):** $\delta = 2.82$.

Bisphosphonium catalyst 6²: A mixture of Cu(OTf)₂ (434 mg, 1.2 mmol, 0.6 equiv.) and triphenylphosphine (877 mg, 2.0 mmol, 1.0 equiv.) in acetonitrile (20 mL) was stirred at room temperature for 3 h. The solvent was evaporated and the crude mixture was purified on silica gel chromatography (1% methanol in dichloromethane). A yellow powder was obtained (400 mg, 34% yield). (The triphenylphosphine were synthesized

according to literature procedures. ³) ¹H NMR (400 MHz, CDCl₃): $\delta = 8.77$ (s, 1H), 8.62-8.56 (m, 2H), 8.33-8.30 (m, 1H), 8.18-8.16 (m, 1H), 8.11-8.05 (m, 1H), 7.95-7.88 (m, 3H), 7.75-7.61 (m, 13H). ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 140.2$ (d, J = 5 Hz), 138.0 (d, J = 3 Hz), 137.9 (d, J = 8 Hz), 136.3 (s), 138.0 (d, J = 3 Hz), 137.9 (d, J = 8Hz), 136.3 (s), 135.1 (d, J = 2 Hz), 134.7 (d, J = 9 Hz), 134.5 (s), 134.3 (d, J = 10 Hz), 132.9 (s), 131.6 (d, J = 2 Hz), 131.1 (d, J = 13 Hz), 130.5 (d, J = 8 Hz), 129.8 (d, J =13 Hz), 129.7 (d, J = 53 Hz), 127.8 (s), 127.4 (d, J = 11 Hz), 126.0 (d, J = 6 Hz), 125.8 (d, J = 15 Hz), 115.1 (d, J = 89 Hz), 111.1 (d, J = 93 Hz), ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -78.03$. ³¹P NMR (162 MHz, CDCl₃): $\delta = 4.36$.

Bisphosphonium catalyst 7⁴: 1,4-bis(diphenylphosphino)naphtalene (160 mg, 0.32 mmol,1 equiv.), diphenylacetylene (140 mg, 0.78 mmol, 2.4 equiv.) and Cu(OTf)₂ (468 mg, 1.30 mmol, 4 equiv.) were dissolved in 32 mL of degazed acetonitrile. The mixture was heated at 100°C overnight. The solvent was evaporated and the crude mixture was purified on silica gel chromatography (20% acetone in dichloromethane). A yellow powder was obtained (100 mg, 54% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.42-8.37 (m, 2H), 7.89-7.83 (m, 8H), 7.77-7.74 (m, 4H), 7.69-7.65 (m, 8H), 7.63 (s, 2H), 7.32-7.31 (m, 4H), 7.25-7.19 (m, 6H), 7.05-7.02 (m, 2H), 6.95 (t, *J* = 7.6 Hz, 4H), 6.73-6.71 (m, 4H). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 160.2-160.1 (m), 136.8 (s), 136.7 (d, *J*C-P = 14 Hz), 136.4-136.1 (m), 135.2 (d, *J* = 11 Hz), 133.2 (d, *J* = 15 Hz), 132.5 (s), 131.3 (d, *J* = 4 Hz), 131.2 (d, *J* = 14 Hz), 130.5 (s), 129.9-129.8 (m), 129.4 (s), 129.4 (s), 129.0 (s), 122.3 (d, *J* = 79 Hz), 118.9 (d, *J* = 74 Hz), 118.4 (d, *J* = 92 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ = -78.24. ³¹P NMR (162 MHz, CDCl₃): δ = 1.13.

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Bisphosphonium catalyst 8⁵: 1,4-bis(diphenylphosphino)naphtalene (499 mg, 1.0 mmol, 1 equiv.), Bis-(4-fluorophenyl)acetylene (580 mg, 2.4 mmol, 2.4 equiv.) and Cu(OTf)₂ (1.45 g, 4.0 mmol, 4.0 equiv.) were dissolved in 100 mL of degazed acetonitrile. The mixture was heated at 100 °C overnight. The solvent was evaporated and the crude mixture was purified on silica gel chromatography (20% acetone in dichloromethane). A yellow powder was obtained (300 mg, 25 % yield). ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.37-8.33 (m, 2H), 7.90-7.80 (m, 12H), 7.71-7.66 (m, 10H), 7.38-7.34 (m, 4H), 7.00 (t, *J* = 8.8 Hz, 4H), 6.75-6.69 (m, 8H). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 164.2 (d, *J* = 14 Hz), 161.8 (d, *J* = 16 Hz), 159.9 (s), 136.6 (s), 136.2 (d, *J* = 1 Hz), 135.9 (d, *J* = 22 Hz), 135.1 (d, *J* = 11 Hz), 134.5 (d, *J* = 27 Hz), 133.3 (d, *J* = 7 Hz), 132.5 (d, *J* = 8 Hz), 130.9 (d, *J* = 14 Hz), 129.9 (d, *J* = 58 Hz), 128.9 (d, *J* = 99 Hz), 122.7 (d, *J* = 31 Hz), 121.7 (s), 119.7 (s), 118.2 (d, *J* = 92 Hz), 116.2 (d, *J* = 22 Hz). ¹⁹F NMR (376 MHz, CD₂Cl₂): δ = -78.50, -111.11, -111.82. ³¹P NMR (162 MHz, CD₂Cl₂): δ = 1.5.

Bisphosphonium salt 9: 1,4-bis(diphenylphosphino)naphtalene (499 mg, 1.0 mmol, 1 equiv.), Bis-(4-(trifluoromethyl)phenyl)acetylene (430 mg, 2.4 mmol, 2.4 equiv.) and Cu(OTf)₂ (1.45 g, 4.0 mmol, 4.0 equiv.) were dissolved in 100 mL of degazed acetonitrile. The mixture was heated at 100 °C overnight. The solvent was evaporated and the crude mixture was purified on silica gel chromatography (20% acetone in dichloromethane). A yellow powder was obtained (369 mg, 26 % yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.23-8.19 (m, 2H),7.95-7.90 (m, 8H), 7.81-7.75 (m, 4H), 7.72-7.67 (m, 8H), 7.57-7.54 (m, 5H), 7.51-7.49 (m, 5H), 7.28-7.26 (m, 4H), 6.96-6.94 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): $\delta = 158.8$ (t, J = 3 Hz), 139.5 (d, J = 13 Hz), 136.2 (s), 135.9 (s), 135.5 (d, J = 8 Hz), 135.3 (t, J = 11 Hz), 134.9 (d, J = 12 Hz), 134.2 (d, J =11 Hz), 132.4 (d, J = 15 Hz), 131.4 (d, J = 3 Hz), 131.2-130.7 (m), 130.8 (d, J = 14 Hz), 130.5 (s), 129.9 (t, J = 7 Hz), 129.1 (d, J = 13 Hz), 127.4 (d, J = 26 Hz), 125.5 (m), 124.7 (d, J = 26 Hz), 122.1 (d, J = 11 Hz), 121.9 (t, J = 4 Hz), 121.0 (d, J = 4 Hz), 119.0 (s), 117.7 (d, J = 77 Hz), 117.3 (d, J = 91 Hz). ¹⁹F NMR (376 MHz, CDCl₃): $\delta =$ -63.01, -63.13, -78.38. ³¹P NMR (162 MHz, CDCl₃): $\delta = 1.43$.

Characterization of Bisphosphonium salt 9:



Figure S6. ¹H NMR spectrum of bisphosphonium salt 9 (in CDCl₃).



Figure S7. ¹³C NMR spectrum of bisphosphonium salt 9 (in CDCl₃).



Figure S8. ¹⁹F NMR spectrum of bisphosphonium salt 9 (in CDCl₃).



Figure S9. ³¹P NMR spectrum of bisphosphonium salt 9 (in CDCl₃).



Figure S10. Cyclic voltammogram of bisphosphonium catalyst 9 recorded in acetonitrile with $Bu_4N^+PF_6^-(0.1 \text{ M})$ at a scan rate of 200 mVs⁻¹. Potentials vs Ag/AgCl.



Figure S11. UV-vis absorption spectrum of bisphosphonium catalyst 9.



Figure S12. Emission spectrum of bisphosphonium catalyst 9.

4.2 General procedure for bach reactions.

A customized photoredox reaction setup was used for parallel photoredox reactions to ensure the reaction efficiency and data reproducibility, in which up to 24 reactions can be performed simultaneously under identical conditions. The reaction vials which were placed in the water-cooled aluminum heat block were irradiated by the LED chips underneath. Through the effective cooling of the LED chips and reaction vails by the aluminum plate with continuous water flow, the heating effect of the high-power LEDs can be offset and the reaction temperature can be maintained at ambient temperature. Through this design, identical irradiation intensity and ambient temperature can be guaranteed for each reaction to ensure data consistency.



Figure S13. The batch reaction set-up.

General Procedure for photocatalytic reaction: A 8-mL vial was charged with alcohol (1.0 equiv.), bisphosphonium salt (0.02 equiv.) and Co^{III}(dmgH)₂pyCl (0.02 equiv.) in TFE (0.2 M). The vial was sealed with a polytertrafluoroethylene-lined cap, the reaction mixture was degassed by Argon sparging for 10 min, then irradiated with 400 nm LED (photon flux, 2.5 W/cm²). The reaction was stirred under irradiation at ambient temperature for 6-12 h. The reaction mixture was evaporated *in vacuo*, the residue was purified by flash chromatography.

4.3 General procedure for continuous flow photoreactions.



Figure S14. The continuous-flow reaction set-up.

Wrap the tubing evenly around the outside of the 400 nm LED lights (photon flux, 2.5 W/cm^2), and the total interal volume of the tubing is 8.0 mL. 400 nm LED lights were placed perpendicular to the LFR plates with 5 cm distance (photon flux, 2.5 W/cm^2). The photoreactor was placed in a thermostatic circulator to maintain an absolute room temperature of 24 °C, during the reaction. The liquid solution of the catalysts and reagents was loaded into micro syringe (25 mL) under Argon, then conveyed to the photoreactor with a syringe pump (FLOM, DUAL Pump, KP-22-13DC, $30-50 \mu$ L/min) through a section of 1/8" PFA tubing. The reactor effluent was collected, processed and analyzed.

5. Experimental procedures and spectral characterization of the products.



4-Fluorobenzaldehyde⁶ (**5**): According to the general procedure, 4-fluorobenzyl alcohol (25.2 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, colorless oil was obtained by flash chromatography (1% diethyl ether in pentane). Due to the low boiling point of the product, yield (96% yield) determined by GC-FID analysis with 20 µL PhOMe as internal standard. ¹H NMR (400 MHz, CDCl₃): $\delta = 9.96$ (s, 1H), 7.92-7.89 (m, 2H), 7.22-7.18 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 190.5$, 166.5 (d, *J*_{F-C} = 255 Hz), 132.9 (d, *J*_{F-C} = 30 Hz), 132.2 (d, *J*_{F-C} = 9 Hz), 116.3 (d, *J*_{F-C} = 22 Hz).



Benzaldehyde⁷ (10): According to the general procedure, benzyl alcohol (21.6 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, colorless oil was obtained by flash chromatography (1% diethyl ether in pentane). Due to the low boiling point of the product, yield (94% yield) determined by GC-FID analysis with 20 µL *n*-nonane as internal standard. ¹H **NMR (400 MHz, CDCl₃):** δ = 9.99 (s, 1H), 7.86-7.84 (m, 2H), 7.62-7.58 (m, 1H), 7.52-7.48 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 192.3, 136.2, 134.3, 129.6, 128.9.



2-Methylbenzaldehyde⁸ (**11**): According to the general procedure, 2-methylbenzyl alcohol (24.4 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 17.7 mg of colorless oil was obtained (74% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): $\delta = 10.18$ (s, 1H), 7.72 (d, J = 7.6, 1H), 7.41 (td, J = 7.2, 1.6 Hz, 1H), 7.28 (t, J = 6.8 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 2.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 192.2$, 140.0, 133.7, 133.2, 131.6, 131.3, 125.9, 19.1.



4-(tert-Butyl)benzaldehyde⁹ (12): According to the general procedure, 4-(tertbutyl)benzyl alcohol (32.8 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 30.8 mg of colorless oil was obtained (95% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 9.96 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 192.0, 158.3, 133.9, 129.6, 125.9, 35.2, 30.9.



4-Phenylbenzaldehyde⁶ (13): According to the general procedure, 4-phenylbenzyl

alcohol (36.8 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 36.1 mg of white powder was obtained (99% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): $\delta = 10.06$ (s, 1H), 7.97-7.94 (m, 2H), 7.76-7.74 (m, 2H), 7.65-7.62 (m, 2H), 7.51-7.46 (m, 2H), 7.45-7.40 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 191.8$ 147.1, 139.6, 135.1, 130.2, 128.9, 128.4, 127.6, 127.3.



4-methoxy benzaldehyde⁷ (14): According to the general procedure, 4-methoxybenzyl alcohol (27.6 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 21.5 mg of colorless oil was obtained (79% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): $\delta = 9.85$ (s, 1 H), 7.82-7.78 (m, 2H), 6.98-6.95 (m, 2H), 3.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 190.7$, 164.5, 131.9, 129.8., 114.2, 55.5.



4-(trifluoromethoxy)benzaldehyde⁶ (15): According to the general procedure, 4-(Trifluoromethoxy)benzyl alcohol (38.4 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 μ mol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 μ mol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 35.0 mg of light yellow oil was obtained (92% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): $\delta = 10.02$ (s, 1H), 7.97-7.94 (m, 2H), 7.37 (d, J = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 190.4$, 153.4 (d, $J_{F-C} = 2$ Hz), 134.5, 131.4, 120.6, 120.2 (d, $J_{F-C} = 257$ Hz).



4-(acetoxy)benzaldehyde¹⁰ (16): According to the general procedure, 4-(acetoxy)benzyl alcohol (33.2 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 27.9 mg of yellow oil was obtained (85% yield) by flash chromatography (1% diethyl ether in pentane). ¹H **NMR (400 MHz, CDCl₃):** δ = 9.98 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 2.33 (s, 3H); ¹³C **NMR (100 MHz, CDCl₃):** δ = 190.8, 168.6, 155.1, 133.8, 131.0, 122.2, 20.9.



4-Borylated benzaldehyde¹¹ (17): According to the general procedure, (4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol (46.8 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (7.3 mg, 8 µmol, 0.04 equiv.), Co(dmgH)₂pyCl (3.2 mg, 8 µmol, 0.04 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 36.2 mg of white powder was obtained (78% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): $\delta = 10.04$ (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 1.36 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 192.6, 138.0, 135.2, 128.7, 84.3, 24.8.$



2-Chlorobenzaldehyde¹² (18): According to the general procedure, 2-chlorobenzyl alcohol (28.5 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 21.4 mg of colorless oil was obtained (76% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): $\delta = 10.45$ (s, 1H), 7.88 (dd, $J = 7.6 \ 1.6 \ Hz$, 1H), 7.52-7.48 (m, 1H), 7.43-7.40 (m, 1H), 7.38-7.33 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 189.7$, 137.8, 135.0, 132.3, 130.5, 129.2, 127.2.



4-Chlorobenzaldehyde⁶ (19): According to the general procedure, 4-chlorobenzyl alcohol (28.5 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 μmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 μmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 24.6 mg of colorless oil was obtained (88% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 9.96 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 190.8, 140.9, 134.7, 130.8, 129.4.



3,4-dichlorobenzaldehyde¹³ **(20):** According to the general procedure, 3,4dichlorobenzyl alcohol (35.4 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 32.1 mg of white powder was obtained (92% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 9.92 (s, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.69 (dd, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 189.6, 139.0, 135.7, 133.9, 131.2, 131.1, 128.3.



1-Naphthaldehvde¹⁴ (21): According general to the procedure, 1naphthalenemethanol (31.6 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst 3 (7.3 mg, 8 µmol, 0.04 equiv.), Co(dmgH)₂pyCl (3.2 mg, 8 µmol, 0.04 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 12 h, 23.7 mg of yellow powder was obtained (76% yield) by flash chromatography (1% diethyl ether in pentane). ${}^{1}H$ **NMR (400 MHz, CDCl₃):** $\delta = 10.31$ (s, 1H), 9.24 (d, J = 8.8 Hz, 1H), 7.98 (d, J = 8.0Hz, 1H), 7.86-7.82 (m, 2H), 7.65-7.61 (m, 1H), 7.55-7.48 (m, 2H), ¹³C NMR (100 **MHz, CDCl₃**): $\delta = 193.2, 136.4, 134.9, 133.4, 131.0, 130.1, 128.7, 128.2, 126.6, 124.6,$ 124.5.



Furfural⁷ (22): According to the general procedure, furfuryl alcohol (19.6 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 μ mol, 0.02 equiv.),

Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 13.4 mg of yellow oil was obtained (70% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 9.49 (s, 1H), 7.56-7.56 (m, 1H), 7.13 (dd, *J* = 3.6 0.8 Hz, 1H), 6.46-6.45 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 177.5, 152.5, 147.8, 121.2, 112.3.



4-(2-hydroxyethyl)benzaldehyde⁷ **(23):** According to the general procedure, 2-(4-(hydroxymethyl)phenyl)ethanol (30.4 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 28.0 mg of colorless oil was obtained (93% yield) by flash chromatography (50% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 9.94 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.94 (t, *J* = 6.4 Hz, 2H), 2.41 (br, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 192.0, 146.2, 134.8, 130.0, 129.7, 63.0, 39.2.



1-(4-(tert-Butyl)phenyl)ethenone¹⁵ (24): According to the general procedure, 1-(4-tert-butylphenyl)ethan-1-ol (35.6 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 34.0 mg of colorless oil was obtained (96% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.90$ (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4

Hz, 2H), 2.58 (s, 3H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 197.8, 156.8, 134.6, 128.2, 125.5, 35.0, 31.0, 26.5.



1-(4-Fluorophenyl)ethan-1-one¹⁶ **(25):** According to the general procedure, 1-(4-Fluorophenyl)ethanol (28.0 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, colorless oil was obtained by flash chromatography (1% diethyl ether in pentane). Due to the low boiling point of the product, yield (95% yield) determined by GC-FID analysis with 20 µL PhOMe as internal standard. ¹H NMR (400 MHz, CDCl₃): δ = 7.78-7.74 (m, 2H), 6.91-6.89 (m, 2H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 195.8, 165.2 (d, *J*_{F-C} = 253 Hz), 133.1 (d, *J*_{F-C} = 3 Hz), 130.5 (d, *J*_{F-C} = 10 Hz), 115.0 (d, *J*_{F-C} = 22 Hz), 25.8.



Benzophenone¹⁶ (26): According to the general procedure, Benzhydrol (36.8 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 33.7 mg of white powder was obtained (93% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.82$ -7.79 (m, 4H), 7.60-7.56 (m, 2H), 7.49-7.45 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 196.6, 137.4, 132.3, 129.2, 128.2.$



1-Indanone¹⁵ (27): According to the general procedure, 1-Indanol (26.8 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 22.2 mg of yellow powder was obtained (84% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 3.12 (t, *J* = 6.0 Hz, 2H), 2.69-2.65 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 207.0, 155.1, 137.0, 134.5, 127.2, 126.6, 123.6, 36.1, 25.87.



1-(benzofuran-3-yl)propan-1-one (28): According to the general procedure, 1-(benzofuran-3-yl)propan-1-ol (35.2 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (7.3 mg, 8 µmol, 0.04 equiv.), Co(dmgH)₂pyCl (3.2 mg, 8 µmol, 0.04 equiv.), and MeCN (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 24.0 mg of white powder was obtained (69% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 8.26-8.23 (m, 2H), 7.54-7.49 (m, 1H), 7.39-7.34 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 2.90 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 196.3, 155.5, 150.5, 125.5, 124.4, 124.3, 122.8, 121.9, 111.4, 33.6, 8.2. HRMS (EI) *m/z* calcd for C₁₁H₁₀O₂ [M]⁺ 174.0675, found 174.0672. CI

3-Chloro-1-phenylpropan-1-one¹⁵ **(29):** According to the general procedure, 3-Chloro-1-phenyl-1-propanol (34.1 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 33.3 mg of yellow powder was obtained (99% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 3.92 (t, *J* = 6.8 Hz, 2H), 3.45 (t, *J* = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 196.6, 136.2, 133.5, 128.7, 128.0, 41.2, 38.6.



3-Hydroxy-1-phenylpropan-1-one¹⁵ (**30**): According to the general procedure, 1phenylpropane-1,3-diol (30.4 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (7.3 mg, 8 µmol, 0.04 equiv.), Co(dmgH)₂pyCl (3.2 mg, 8 µmol, 0.04 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 6 h, 26.2 mg of colorless oil was obtained (87% yield) by flash chromatography (50% diethyl ether in pentane). ¹H **NMR (400 MHz, CDCl₃):** δ = 7.97-7.94 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 4.02 (t, *J* = 5.6 Hz, 2H), 3.22 (t, *J* = 5.6 Hz, 2H), 2.73 (br, 1H); ¹³C **NMR (100 MHz, CDCl₃):** δ = 200.4, 136.5, 133.5, 128.6, 128.0, 58.0, 40.3.



1-(4-Chlorophenyl)-3-phenylpropan-1-one¹⁷ (31): According to the general

procedure, 1-(4-chlorophenyl)-3-phenylpropan-ol (49.3 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (3.7 mg, 4 µmol, 0.02 equiv.), Co(dmgH)₂pyCl (1.6 mg, 4 µmol, 0.02 equiv.), and TFE (1 mL) was used. Under the irradiation of 400 nm LED for 12 h, 31.2 mg of yellow powder was obtained (64% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 7.89 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.32-7.20 (m, 5H), 3.27 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 198.0, 141.0, 139.5, 135.1, 129.4, 128.9, 128.5, 128.4, 126.2, 40.4, 30.0.



(*E*)-4-Phenyl-3-buten-2-one¹⁸ (32): According to the general procedure, (*E*)-4-phenylbut-3-en-2-ol (29.6 mg, 0.2 mmol, 1.0 equiv.), bisphosphonium catalyst **3** (7.3 mg, 8 µmol, 0.04 equiv.), Co(dmgH)₂pyCl (3.2 mg, 8 µmol, 0.04 equiv.), and MeCN (1 mL) was used. Under the irradiation of 400 nm LED for 12 h, 15.6 mg of yellow oil was obtained (53% yield) by flash chromatography (1% diethyl ether in pentane). ¹H NMR (400 MHz, CDCl₃): δ = 7.52-7.47 (m, 3H), 7.39-7.36 (m, 3H), 6.69 (d, J = 16.4 Hz, 2H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 198.5, 143.4, 134.0, 130.3, 128.7, 128.0, 126.7, 27.1.

6. Spectra Data.

































¹³C NMR 100 MHz, CDCl₃



































¹³C NMR 100 MHz, CDCl₃













¹³C NMR 100 MHz, CDCl₃





¹³C NMR 100 MHz, CDCl₃





¹³C NMR 100 MHz, CDCl₃







Reference

- 1. S. Nieto, P. Metola, V. M. Lynch and E. V. Anslyn, *Organometallics*, 2008, 27, 3608-3610.
- 2. Z. Yang, J. Chen and S. Liao, ACS Macro Letters, 2022, 11, 1073-1078.
- A. Belyaev, Y.-T. Chen, Z.-Y. Liu, P. Hindenberg, C.-H. Wu, P.-T. Chou, C. Romero-Nieto and I. O. Koshevoy, *Chemistry – A European Journal*, 2019, 25, 6332-6341.
- 4. T. Delouche, A. Vacher, E. Caytan, T. Roisnel, B. Le Guennic, D. Jacquemin, M. Hissler and P.-A. Bouit, *Chemistry A European Journal*, 2020, **26**, 8226-8229.
- T. Delouche, A. Vacher, T. Roisnel, M. Cordier, J.-F. Audibert, B. Le Guennic, F. Miomandre, D. Jacquemin, M. Hissler and P.-A. Bouit, *Materials Advances*, 2020, 1, 3369-3377.
- 6. S. Ren, D. Cheng, X. Li and X. Xu, *Tetrahedron Letters*, 2021, **76**, 153234.
- 7. J. M. Hoover and S. S. Stahl, *Journal of the American Chemical Society*, 2011, **133**, 16901-16910.
- 8. S. Pradhan, V. Sharma and I. Chatterjee, *Organic Letters*, 2021, 23, 6148-6152.
- 9. Q. Feng and Q. Song, *The Journal of Organic Chemistry*, 2014, **79**, 1867-1871.
- 10. G.-Z. Wang, X.-L. Li, J.-J. Dai and H.-J. Xu, *The Journal of Organic Chemistry*, 2014, **79**, 7220-7225.
- 11. R. Bisht and B. Chattopadhyay, Journal of the American Chemical Society, 2016, 138, 84-87.
- H. Zhang, T. Guo, M. Wu, X. Huo, S. Tang, X. Wang and J. Liu, *Tetrahedron Letters*, 2021, 67, 152878.
- 13. I. B. Stone, J. Jermaks, S. N. MacMillan and T. H. Lambert, *Angewandte Chemie International Edition*, 2018, **57**, 12494-12498.
- M. Zhang, X.-A. Yuan, C. Zhu and J. Xie, *Angewandte Chemie International Edition*, 2019, 58, 312-316.
- B. Liu, F. Jin, T. Wang, X. Yuan and W. Han, *Angewandte Chemie International Edition*, 2017, 56, 12712-12717.
- 16. B. Hong, K. C. C. Aganda and A. Lee, Organic Letters, 2020, 22, 4395-4399.
- 17. M. Zhang, R. Ruzi, J. Xi, N. Li, Z. Wu, W. Li, S. Yu and C. Zhu, *Organic Letters*, 2017, **19**, 3430-3433.
- B. Xu, J.-P. Lumb and B. A. Arndtsen, *Angewandte Chemie International Edition*, 2015, 54, 4208-4211.