Electronic Supplementary Information For

A diiodo-BODIPY postmodified metal-organic framework for efficient heterogeneous organo-photocatalysis

Ying Quan,[a] Qiu-Yan Li,*[a] Quan Zhang,[b] Wen-Qiang Zhang,[a] Han Lu,[a] Jun-Hao Yu,[a] Jian Chen,[a] Xinsheng Zhao*[c] and Xiao-Jun Wang*[a]

[a]Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou 221116, P. R. China.

E-mail: xjwang@jsnu.edu.cn (X.-J. Wang); qyli@jsnu.edu.cn (Q.-Y. Li)

[b]Key Laboratory of Carbohydrate Chemistry and Biotechnology, Ministry of Education, School of Biotechnology, Jiangnan University, Wuxi 214122 , P. R. China

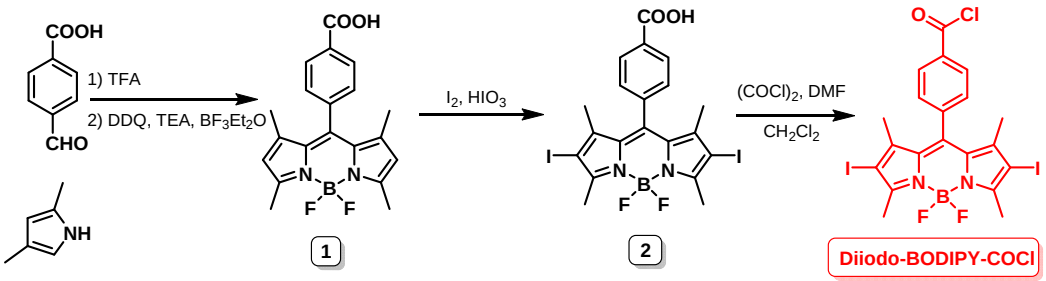
[c]School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, P. R. China.

E-mail: xinshengzhao@jsnu.edu.cn (X. Zhao)

General method and materials

Unless specifically mentioned, all chemicals are commercially available and were used as received. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled over sodium/benzophenone ketyl and CaH_2 under a nitrogen atmosphere prior to use, respectively. NMR spectra were taken on a Bruker AV400 at room temperature. The powder X-ray diffraction (PXRD) measurements were taken on a Bruker D8 diffractometer using Cu-K_α radiation (λ = 1.5418 Å) at room temperature. Field-emission scanning electron microscopy (FE-SEM) images were obtained on a HITACHI S-4800 instrument operating at 10 kV with Au coated. X-ray fluorescence (XRF) analysis was performed on Rigaku ZSX Primus II. ESR spectra were recorded at room temperature using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation.

Synthesis and Characterizations



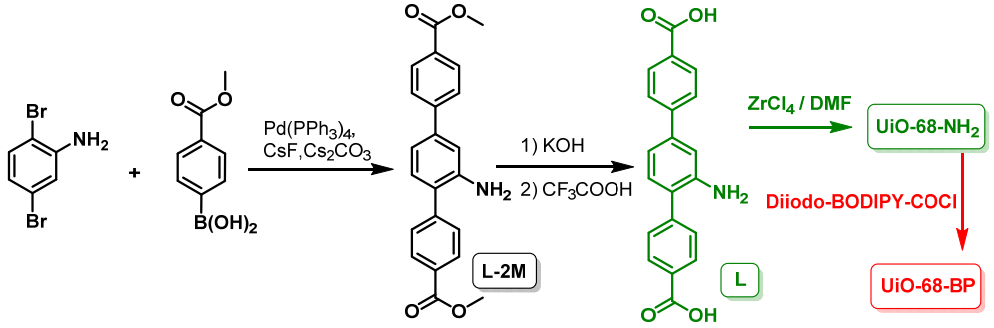
Scheme S1. The synthetic route of Diiodo-BODIPY-COCl.

Compound 1[S1]: 4-formylbenzoic acid (3.0 g, 20 mmol) and 2,4-dimethylpyrrole (3.8g, 40 mmol) were dissolved into 100 mL dichloromethane, which was degased by nitrogen for 2 h. Then, trifluoroacetic acid (TFA, 0.1 mL) was added and stirred under nitrogen overnight at room temperature. Subsequently, a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 9.1 g, 40 mmol) in dichloromethane (150 mL) was added into the reaction mixture with continuous stirring for 4 h. Then, triethylamine (TEA, 30 mL) was added and stirred for 30 min. $BF_3{\cdot}OEt_2$ (30 mL) was added and stirred for another 3 h. The mixture was treated with water (200 mL) and extracted with dichloromethane (100 mL x 5). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography (CH_2Cl_2 : MeOH = 50:1, v/v) to provide compound **1** as a brown red solid (0.81 g, 2.2 mmol; yield: 11%). ^1H NMR (400 MHz, $CDCl_3$): 8.13 (d, 2H, J = 8.1 Hz), 7.55 (d, 2H, J = 8.0 Hz), 6.21 (s, 2H), 2.45 (s, 6H), 1.33 (s, 6H) ppm.

Compound 2[S2]: Compound **1** (3.4 g, 9.2 mmol) and iodine (4.6 g, 18 mmol) were dissolved into 50 mL EtOH and to this solution was added iodic acid (4.0 g, 23 mmol) dissolved in 5 mL water. The reaction mixture was stirred at 60 °C for 1 h. Then, the reaction mixture was cooled to room temperature and extracted by EtOAc (50 mL x 3). The combined organic layer was washed by saturated $Na_2S_2O_3$ solution, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography (CH_2Cl_2 : MeOH = 50:1, v/v) to provide compound **2** as a deep red solid (5.3 g, 8.5 mmol; yield: 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 2.66 (s, 6H), 1.39 (s, 6H) ppm.

Diiodo-BODIPY-COCl: To a dichloromethane (10 mL) solution of compound **2** (28 mg, 0.045 mmol) was added oxalyl chloride (57 mg, 0.45 mmol) and one drop of DMF as catalyst. The reaction mixture was stirred at room temperature, and monitored by TLC. After around one hour, carboxylic acid was changed into acyl chloride. Then, the mixture was evaporated under vacuo, and used as such without purification.

Preparation of nanoscale metal-organic framework UiO-68-NH_2 and UiO-68-BP



Scheme S2. Preparations for MOF **UiO-68-NH_2** and **UiO-68-BP**.

Compound L-2M[S3]: CsF (0.3 g, 2.0 mmol) and Cs_2CO_3 (3.9 g, 12.0 mmol) were dissolved into 2 mL water. Then, 80 mL newly distilled THF was added into the solution. The reaction mixture were degassed by nitrogen for 2 h. To the solution were added 2,5-dibromoaniline (1.0 g, 4.0 mmol) and 4-(methoxycarbonyl)-phenylboronic acid (1.8 g, 10.0 mmol) under nitrogen protection. Subsequently, $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol) and $Pd(dppf)Cl_2$ (0.29 g, 0.40 mmol) as catalysts were added into the reaction mixture, which was heated at 70 °C for 24 h. Then, the reaction solution was cooled to room temperature. 100 mL water was added into the mixture, which was extracted by dichloromethane (50 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography (CH_2Cl_2 : EtOAc = 100:10, v/v) to

provide compound **L-2M** as a light yellow solid (1.05 g, 2.9 mmol; yield: 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.09 (m, 4H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.06 (d, *J* = 1.3 Hz, 1H), 3.95 (s, 6H) ppm.

Compound L[S4]: The methyl ester **L-2M** (0.87 g, 2.41 mmol) was dissolved into 80 mL THF and heated to 60 ^{o}C. Then, KOH (1.75 g, 31.3 mmol) in 50 mL CH_3OH was added into the above solution, which was stirred at 60 ^{o}C. After 6 h, the reaction mixture was cooled to room temperature. The suspension was collected by filtration, and simply washed by THF. After that, the solid was suspended into 50 mL THF. Then, 5 mL TFA was added into the mixture and stirred for 2 h at room temperature. The solid was collected by filtration and dried in air to give the ligand **L** as yellow solid (0.56 g, 1.68 mmol; yield: 70%). ^{1}H NMR (400 MHz, DMSO) δ 8.03 (d, *J* = 8.1 Hz, 4H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.17-7.15 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 1H) 5.11 (br, 2H) ppm.

MOF UiO-68-NH_2: The nanoscale metal-organic framework UiO-68-NH_2 was prepared according to the reported method and modified.[S6] Ligand **L** (180 mg, 0.54 mmol) and $ZrCl_4$ (126 mg, 0.54 mmol) were dissolved into 300 mL DMF. Then, 22.5 mL HAc and 3 mL H_2O were added into the above solution, respectively. The reaction mixture was stirred at 1000 rpm and 100 ^{o}C for 2 days. The suspension was collected by centrifugation at 10000 rpm and washed with DMF and ethanol, respectively. The solid was dried in vacuum at 50 ^{o}C for 24 h, giving a light yellow solid (160 mg, yield: 52%). The powder XRD pattern of product was similar to the simulated pattern generated from single crystal data (Fig. 2d), confirming its UiO-68 topological framework and the phase purity. Furthermore, SEM images of the product give its particle size around 100 nm.

UiO-68-BP: The as-synthesized UiO-68-NH_2 (100 mg) was suspended in 10 mL 10% TEA/EtOH, and stirred for 12 h at room temperature. Then, the suspension was collected by centrifugation at 10000 rpm, and then immersed in newly distilled 5 mL THF with stirring for 1 h. After that, suspension was collected by centrifugation and re-suspended newly distilled 5 mL THF with stirring for another 1 h. This process repeated 3 times to remove EtOH and TEA. Next, the solid was suspended into 3 mL THF, which was sonicated for 1 h. After that, the newly prepared diiodo-BODIPY-COCl (28 mg compound 2) was added into the mixture, which was stirred under dark. After 1 day, the solid was collected by centrifugation and washed THF, DMF and EtOH, respectively. The as-synthesized product was dried in vacuum at 40 ^{o}C for 2 days, giving a red solid.

The loading amount of diiodo-BODIPY was calculated from the ratio of the heavy elements Zr:I by X-ray fluorescence (XRF) analysis, indicating ~11% of organic ligand in UiO-68-NH_2 was functionalized with diiodo-BODIPY. Besides, through lowering the feeding amount of diiodo-BODIPY-COCl, other loading amount of diiodo-BODIPY samples (UiO-68-BP' and UiO-68-BP" refer to ~2% and ~7% of organic linkers in MOF was functionalized by diiodo-BODIPY, respectively.) were prepared by the similar procedure.

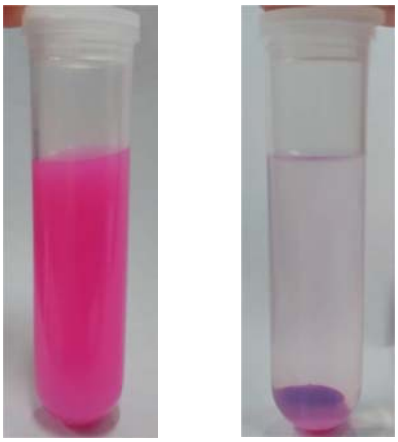


Figure S1. Suspension of **UiO-68-BP** in CH_3CN (left) and the mixture of the suspension after centrifugation (right).

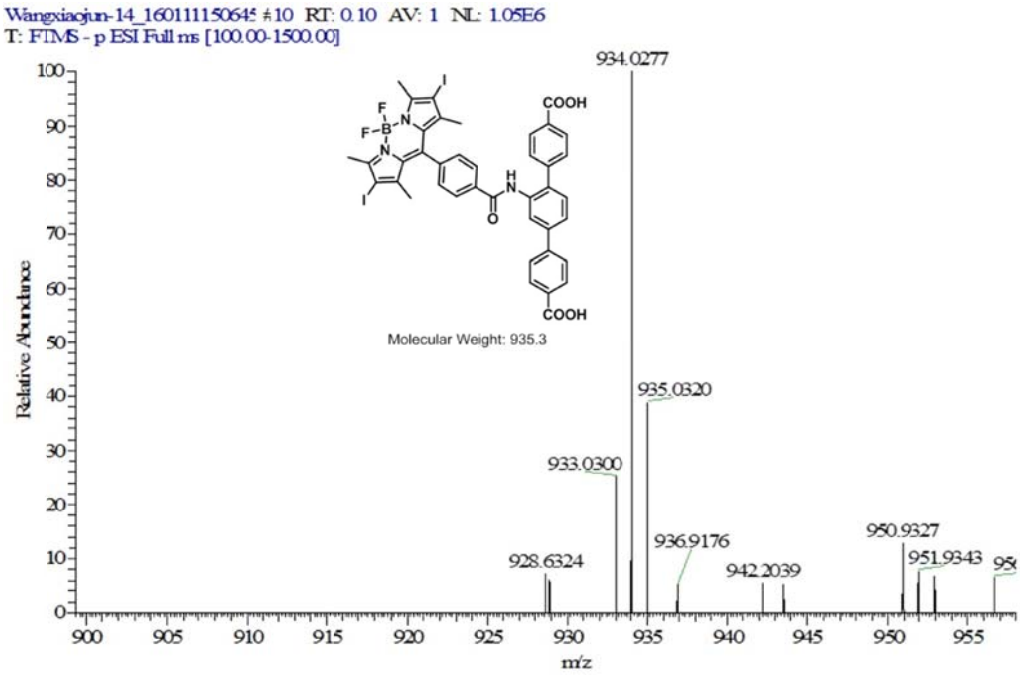


Figure S2. ESI-MS (negative mode) of 934.03 corresponding to $[M-H]^-$ of the ligand after digestion of UiO-68-BP, indicating the covalent conjugation.

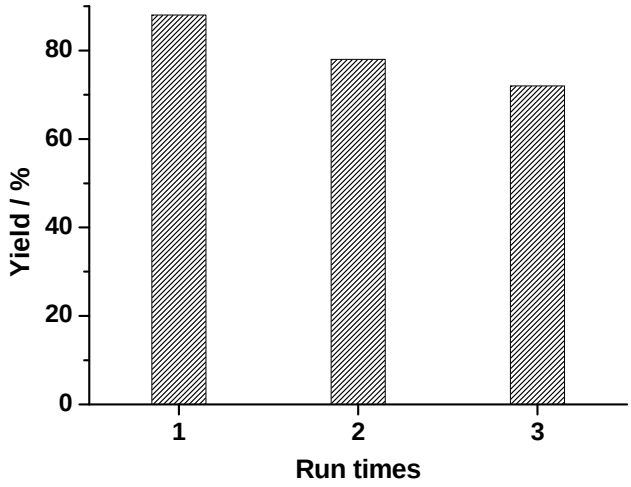
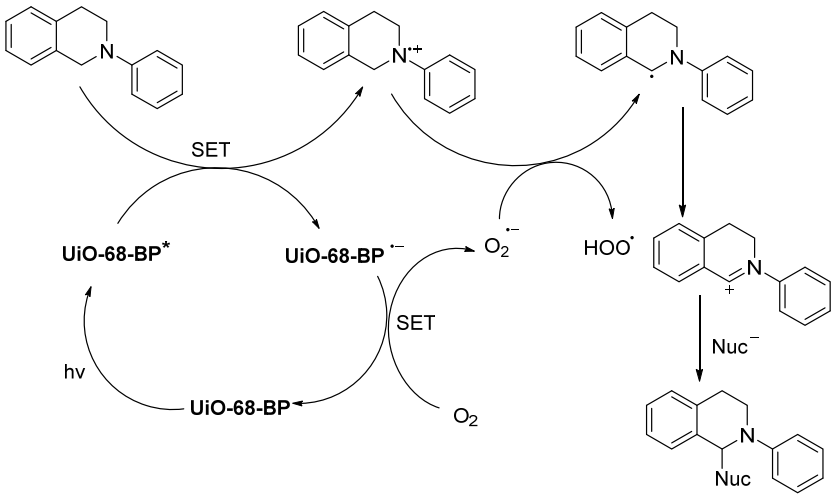


Fig. S3 Recycling experiments of **UiO-68-BP** for the reaction of *N*-phenyltetrahydroisoquinoline and CH_3NO_2.



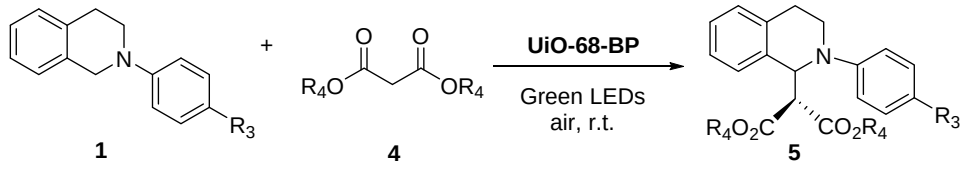
Scheme S3. Proposed mechanism for the photocatalytic aerobic CDC reaction of *N*-phenyltetrahydroisoquinoline and CH_3NO_2 with **UiO-68-BP**.

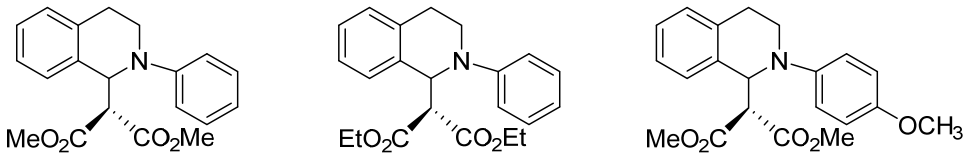
General procedure for Aerobic CDC reactions of tetrahydroisoquinolines 1 with nitroalkanes 3 or malonates 4 catalyzed by UiO-68-BP

The weighed catalyst 2 mg **UiO-68-BP** and 0.1 mmol **1** were added into 1 mL CH_3NO_2 (or 1 mL malonates). The reaction mixture with stirring was irradiated by green LEDs for 3 hours under air at room temperature. ^{1}H NMR spectroscopy with methyl 3,5-dinitrobenzoate as an internal standard was employed to determine the yield. The catalyst for cyclic reaction was recycled by centrifugation

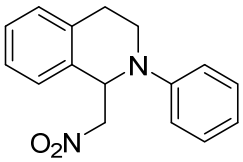
at 10 000 rpm and washed by fresh CH_3NO_2 two times.

Table S1 Aerobic CDC reactions of tetrahydroisoquinolines **1** with malonates **4** catalyzed by **UiO-68-BP**

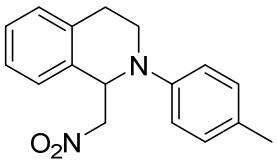




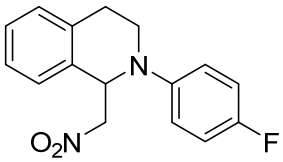
5a: 89% **5b:** 84% **5c:** 87%



3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 5H), 7.13 (d, J = 7.3 Hz, 1 H), 6.98 (d, J = 8.5 Hz, 2H), 6.86 (t, J = 7.3 Hz, 1H), 5.55 (t, J = 7.8 Hz, 1 H), 4.87 (dd, J = 11.5, 7.8 Hz, 1H), 4.57 (dd, J = 12.0, 6.8 Hz, 1H), 3.69-3.60 (m, 2H), 3.11-3.03 (m, 1H), 2.79 (dt, J = 16.3, 5.0 Hz, 1H) ppm.

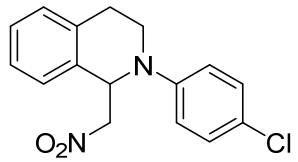


3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.10 (m, 4H), 7.06 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 5.47 (t, J = 7.9 Hz, 1H), 4.82 (dd, J = 12.0, 8.1 Hz, 1H), 4.54 (dd, J = 12.0, 7.0 Hz, 1H), 3.62-3.51 (m, 2H), 3.06-3.01 (m, 1H), 2.72 (dt, J = 16.0, 4.1 Hz, 1H), 2.25 (s, 3H) ppm.

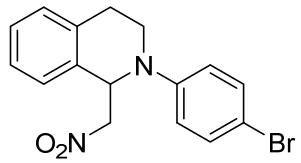


3c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.11 (m, 4H), 6.91-6.87 (m, 4H), 5.43 (dd, J = 8.5, 5.9 Hz, 1H), 4.84 (dd, J = 12.1 Hz, 8.7 Hz, 1H), 4.57 (dd, J = 12.0 Hz, 5.9 Hz, 1H), 3.67-3.52 (m, 2H),

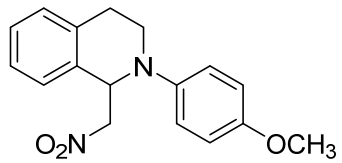
3.03-2.96 (m, 1H), 2.71 (dt, *J* = 16.3 Hz, 4.2 Hz, 1H) ppm.



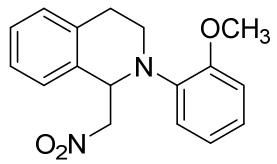
3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.11 (m, 6H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.48 (t, *J* = 7.5 Hz, 1H), 4.83 (dd, *J* = 11.9, 8.2 Hz, 1H), 4.56 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.68-3.51 (m, 2H), 3.04 (ddd, *J* = 15.4, 8.5, 6.2 Hz, 1H), 2.77 (dt, *J* = 16.1, 4.6 Hz, 1H) ppm.



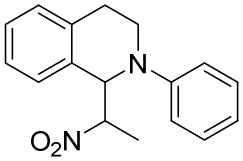
3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.30-7.11 (m, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.48 (t, *J* = 8.0 Hz, 1 H), 4.85 (dd, *J* = 12.0, 8.0 Hz, 1H), 4.57 (dd, *J* = 12.0, 6.8 Hz, 1H), 3.68-3.54 (m, 2H), 3.14-3.01 (m, 1H), 2.79 (dt, *J* = 16.1, 4.8, 1H) ppm.



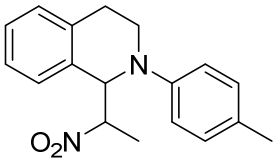
3f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.13 (m, 4H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 5.39 (dd, *J* = 8.6, 5.8 Hz, 1H), 4.82 (dd, *J* = 11.9, 8.6 Hz, 1H), 4.56 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.75 (s, 3H), 3.62-3.52 (m, 2H), 3.06-2.98 (m, 1H), 2.70 (dt, J = 16.5, 4.1 Hz, 1H) ppm.



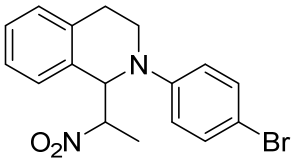
3g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.12 (m, 4H), 7.05-7.01 (m, 1H), 6.90-6.81 (m, 3H), 5.52 (dd, *J* = 8.0, 5.0 Hz, 1H), 4.81 (dd, *J* = 12.0, 8.6 Hz, 1 H), 4.52 (dd, *J* = 12.0, 5.2, 1H), 3.82 (s, 3H), 3.44-3.61 (m, 2 H), 3.01-2.94 (m, 1H), 2.79-2.74 (m, 1H) ppm.



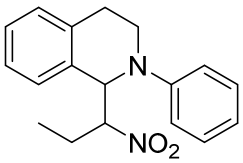
3h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.09 (m, 6H), 7.02-6.97 (m, 2H), 6.83-6.79 (m, 1H), 5.26-5.22 (m, 1H), [5.10-5.01 (m), 4.94-4.84 (m), 1H], [3.89-3.80 (m), 3.62-3.53 (m), 2H], [3.11-3.01 (m), 2.96-2.83 (m), 1H)], [1.69 (d, J= 6.9 Hz), 1.53 (d, J= 6.9 Hz), 3H] ppm.



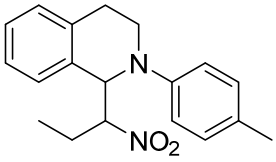
3i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.99 (m, 6 H), 6.92-6.87 (m, 2H), 5.20-5.12 (m, 1 H), 5.04-4.85 (m, 1H), [3.83-3.76 (m), 3.59-3.48 (m), 2H], [3.07-2.96 (m), 2.91-2.77 (m), 2H], [2.25 (s), 2.23 (s), 3H], [1.67 (d, J = 6.9 Hz), 1.51 (d, J = 6.9), 3H] ppm.



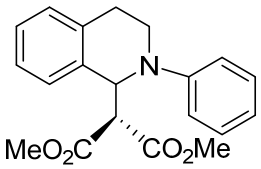
3j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.01 (m, 6 H), 6.85-6.83 (m, 2H), 5.20-5.13 (m, 1 H), [5.03-4.99 (m), 4.90-4.84 (m), 1H], [3.83-3.78 (m), 3.60-3.46 (m), 2H], [3.07-3.01 (m), 2.95-2.85 (m), 2H], [1.67 (d, J = 6.8 Hz), 1.55 (d, J = 6.8), 3H] ppm.



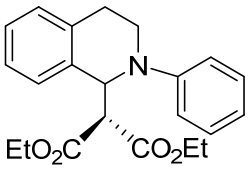
3k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.12 (m, 6H), 6.99-6.92 (m, 2H), 6.83-6.77 (m, 1H), [5.24 (d, J = 9.1 Hz), 5.12 (d, J = 9.2 Hz), 1H], [4.89-4.84 (m), 4.70-4.65 (m), 1H], [3.88-3.81 (m), 3.69-3.49 (m), 2H], [3.10-3.03 (m), 2.93-2.83 (m), 2H], [2.16-2.05 (m), 1.89-1.78 (m), 2H], 0.95-0.92 (m, 3H) ppm.



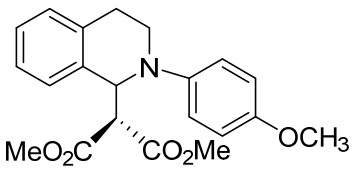
3l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.95 (m, 3H), 6.89-6.80 (m, 2H), [5.15 (d, J = 12.0 Hz), 5.04 (d, J = 9.5 Hz), 1H], [4.87-4.80 (m), 4.69-4.62 (m), 1H], [3.65-3.79 (m), 3.64-3.45 (m), 2H], [3.05-2.98 (m), 2.88-2.75 (m), 2H], 2.30 (s, 3H), [2.17-2.01 (m), 1.88-1.76 (m), 2H], 0.90-0.95 (m, 3H) ppm.



5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.08 (m, 6H), 6.98 (d, J = 8.0 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H), 5.71 (d, 1H, J = 9.3 Hz), 3.95 (d, J = 9.4 Hz, 1H), 3.77-3.58 (m, 5H), 3.55 (s, 3H), 3.09 (ddd, J = 15.6, 9.0, 6.3 Hz, 1H), 2.86 (dt, 1H, J =16.4, 5.0 Hz) ppm.

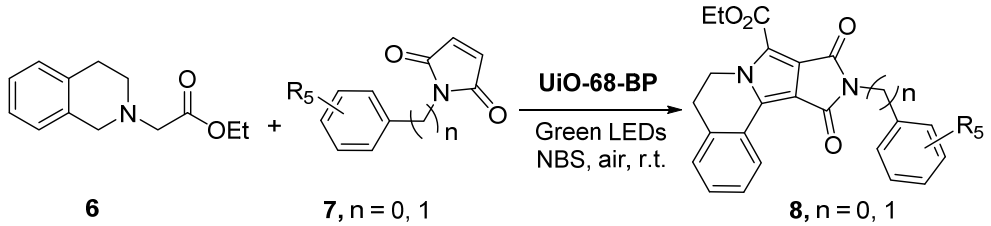


5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.08 (m, 6 H), 6.98 (d, J = 8.0 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 5.73 (d, J = 9.2 Hz, 1H), 4.23-3.95 (m, 4 H), 3.92 (d, J = 9.2 Hz, 1H), 3.75-3.60 (m, 2 H), 3.10-3.02 (m, 1 H), 2.87(dt, J = 16.4, 5.2 Hz, 1H), 1.17 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H) ppm.



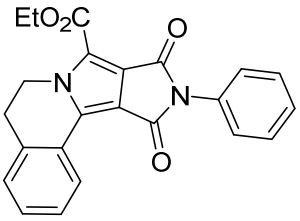
5c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.15 (m, 2H), 7.10-7.08 (m, 2H), 6.95 (d, J = 9.1 Hz, 2H), 6.78 (d, J = 9.1 Hz, 2H), 5.48 (d, J = 9.4 Hz, 1H), 3.97(d, J = 9.4 Hz, 1H), 3.72 (s, 3H), 3.69-3.63 (m, 4H), 3.61 (s, 3H), 3.58-3.53(m, 1H), 3.01(ddd, J = 16.6, 10.2, 6.3 Hz, 1H), 2.74(dt, J = 16.7, 4.4 Hz, 1H) ppm.

General procedure for oxidation-[3+2] cycloaddition-aromatization tandem reaction of 6 with 7 catalyzed by UiO-68-BP

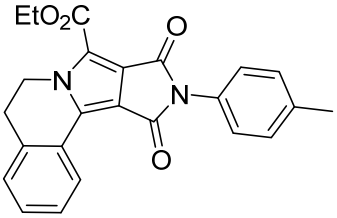


6 **7,** n = 0, 1 **8,** n = 0, 1

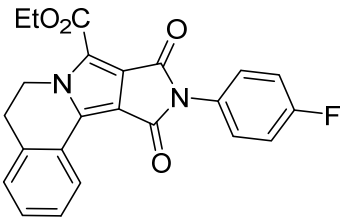
Compound **6** (0.12 mmol), **7** (0.10 mmol) and **UiO-68-BP** (2 mg) was dissolved into 1 mL CH_3CN. The reaction mixture with stirring was irradiated by green LEDs for 2 hours under air at room temperature. Subsequently, NBS (0.12 mmol) was added into the reaction mixture, which was stirred for further 10 min. ^{1}H NMR spectroscopy with methyl 3,5-dinitrobenzoate as an internal standard was employed to determine the yield.



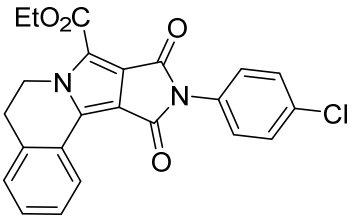
8a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 2H), 7.43-7.32 (m, 5H), 7.29 (d, *J* = 7.5 Hz, 1H), 4.77 (q, *J* = 8.0 Hz, 2H), 4.44 (q, *J* = 7.0 Hz, 2H), 3.18 (t, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 8.0 Hz, 3H) ppm.



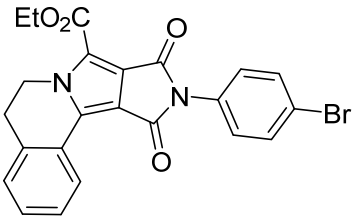
8b: ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.2 Hz, 1H), 7.42-7.38 (m, 2H), 7.30 (s, 1H), 7.28 (s, 4H), 4.85-4.71 (m, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H), 2.40 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H) ppm.



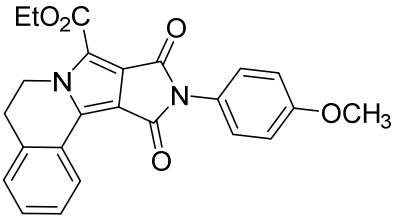
8c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59-8.55 (m, 1H), 7.44-7.35 (m, 6H), 7.30 (d, *J* = 6.7 Hz, 1H), 4.78 (t, *J* = 6.8 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H) ppm.



8d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60-8.53 (m, 1H), 7.49-7.35 (m, 6H), 7.30 (d, *J* = 6.8 Hz, 1H), 4.78 (t, *J* = 6.3 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H) ppm.

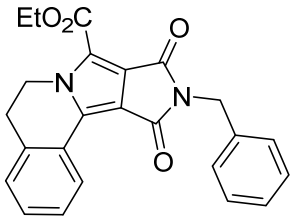


8e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (t, *J* = 6.2 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.41-7.38 (m, 4H), 7.31 (t, *J* = 4.8 Hz, 1H), 4.78 (t, *J* = 5.8 Hz, 2H), 4.47-4.41 (m, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H) ppm.

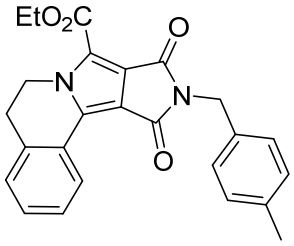


8f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.1 Hz, 1H), 7.43-7.30 (m, 5H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.76 (t, *J* = 6.7 Hz, 2H), 4.45-4.40 (m, 2H), 3.84 (s, 3H), 3.18 (t, *J* = 6.7 Hz, 2H), 1.48 (t, *J* =

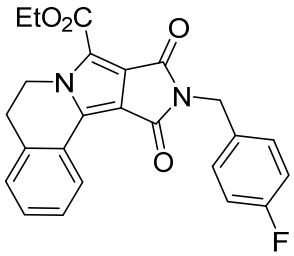
7.0 Hz, 3H) ppm.



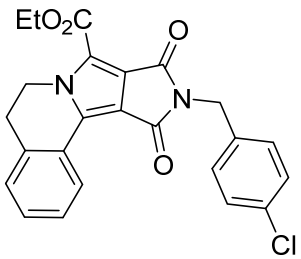
8g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 7.0 Hz, 1H), 7.45-7.30 (m, 8H), 4.80 (s, 2H), 4.72 (d, *J* = 6.9 Hz, 2H), 4.45-4.40 (m, 2H), 3.14 (d, *J* = 6.8 Hz, 2H), 1.48 (t, *J* = 7.0 Hz, 3H) ppm.



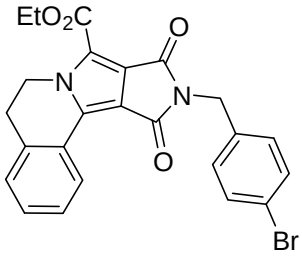
8h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 6.7 Hz, 1H), 7.43-7.30 (m, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.76-4.70 (m, 4H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.14 (t, *J* = 6.9 Hz, 2H), 2.30 (s, 4H), 1.47 (t, *J* = 7.1 Hz, 4H) ppm.



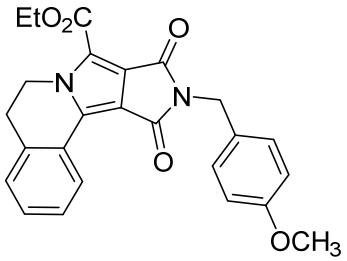
8i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.1 Hz, 1H), 7.44-7.25 (m, 5H), 6.98 (t, *J* = 7.8 Hz, 2H), 4.76-4.69 (m, 4H), 4.45-4.40 (m, 2H), 3.13 (t, *J* = 6.6 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H) ppm.



8j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53-8.48 (m, 1H), 7.45-7.32 (m, 4H), 7.28 (s, 2H), 4.76-4.71 (m, 4H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 4H) ppm.



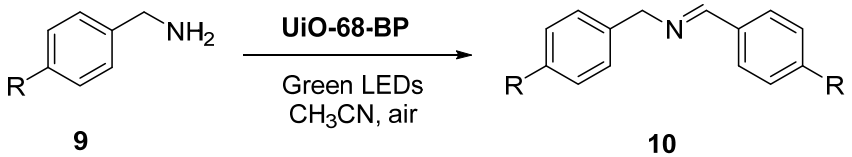
8k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.47-7.27 (m, 6H), 4.77-4.69 (m, 4H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H) ppm.



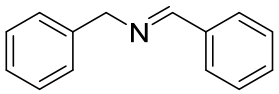
8l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 6.6 Hz, 1H), 7.44-7.33 (m, 5H), 6.83 (t, *J* = 8.2 Hz, 2H), 4.76-4.69 (m, 4H), 4.45-4.40 (m, 2H), 3.14 (t, *J* = 6.7 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H) ppm.

Other examples of photocatalytic organic reactions by UiO-68-BP:

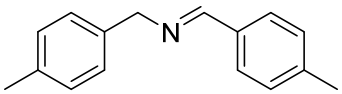
(1) Aerobic Oxidative Amine Coupling



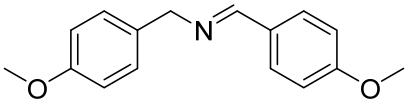
9 **10**



10a: 93%

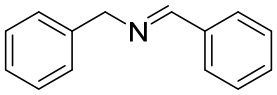


10b: 92%

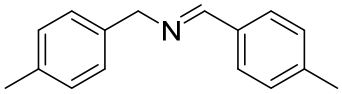


10c: 89%

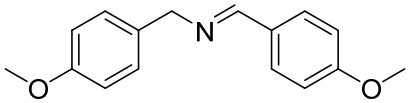
Compound **9** (0.2 mmol) and **UiO-68-BP** (2 mg) was dissolved into 2 mL CH_3CN. The reaction mixture with stirring was irradiated by green LEDs for 2 hours under air at room temperature. ^1H NMR spectroscopy with methyl 3,5-dinitrobenzoate as an internal standard was employed to determine the yield.



10a: ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.83-7.77 (m, 2H), 7.43 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.35 (d, *J* = 4.5 Hz, 4H), 7.31-7.26 (m, 1H), 4.84 (s, 2H) ppm.

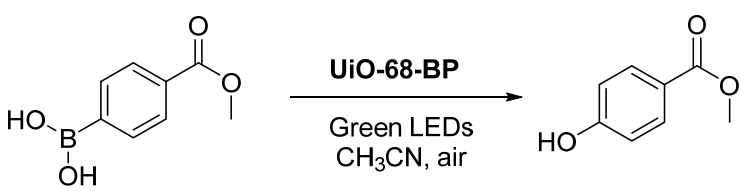


10b: ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 8.0, 2.2 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.77 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H) ppm.



10c: ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.90 (dd, *J* = 16.9, 8.8 Hz, 4H), 4.73 (s, 2H), 3.84 (s, 3H), 3.80 (s, 3H) ppm.

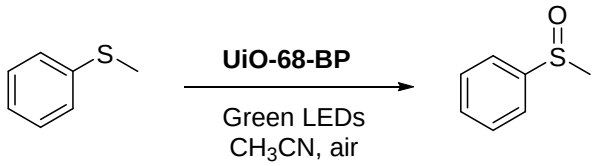
(2) Oxidative Hydroxylation of Arylboronic Acids



Methyl 4-boronobenzoate (0.1 mmol), DIPEA (0.2 mmol) and **UiO-68-BP** (2 mg) was dissolved into

2 mL CH_3CN. The reaction mixture with stirring was irradiated by green LEDs for 4 hours under air at room temperature. ^1H NMR spectroscopy with methyl 3,5-dinitrobenzoate as an internal standard was employed to determine the yield (90%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H) ppm.

(3) Photo Oxidation of Thioanisole



Thioanisole (0.2 mmol) and **UiO-68-BP** (2 mg) was dissolved into 2 mL CH_3CN. The reaction mixture with stirring was irradiated by green LEDs for 5 hours under air at room temperature. ^1H NMR spectroscopy with methyl 3,5-dinitrobenzoate as an internal standard was employed to determine the yield (93%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.0, 1.6 Hz, 2H), 7.57-7.49 (m, 3H), 2.73 (s, 3H) ppm.

References:

S1. A. Singh, W.-T. Yip and R. L. Halterman, *Org. Lett.*, 2012, **14**, 4046-4049.

S2. S. Kolemen, O. A. Bozdemir, Y. Cakmak, G. Barin, S. Erten-Ela, M. Marszalek, J.-H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Gratzel and E. U. Akkaya, *Chem. Sci.*, 2011, **2**, 949-954.

S3. A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. Eur. J.*, 2011, **17**, 6643-6651.

S4. C. He, K. Lu, D. Liu and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 5181-5184.