Electronic Supplementary Information (ESI) for

Bis(terpyridine) Ru(III) complexes functionalized porous polycarbazole for visible-light driven chemical reactions

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Materials and general characterizations

All the chemicals and solvents were purchased with high-purity level. Unless otherwise stated, all reagents were used without further purification. 2-Acetylpyridine (98%), 3,5-dibromobenzaldehyde (98%), carbazole (98%), copper iodide (CuI, 98%), and iron(III) chloride ($FeCl_3$, 98%) were purchased from Energy Chemical Ltd. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 98%), anhydrous chloroform ($CHCl_3$, ≥99%), and methanol (CH_3OH, 98%) were purchased from Sigma-Aldrich. Ruthenium trichloride hexahydrate was purchased from bidepharm PLC.

Instrumentations and characterization

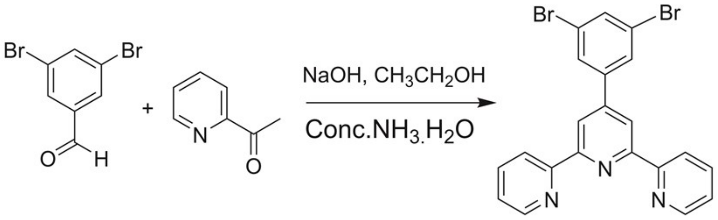
^1H and ^{13}C NMR spectra were recorded on a Bruker DMX400 NMR spectrometer. Solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR data were obtained from Bruker Advance III 400 spectrometer (Bruker, Germany). Mass spectrum was measured with a Microex LRF MALDI-TOF mass spectrometer. The thermal stability of the polymers was investigated in nitrogen atmosphere from room temperature to 800 °C with increase of 10 °C min^{-1} (Diamond TG/DTA, Perkin Elmer). The UV-vis absorption spectra were collected by Agilent Cary 5000 UV-vis-NIR spectrometer. Fluorescence emission spectra were measured with FS5 spectrofluorometer (Edinburgh Instruments, United Kingdom). The infrared (IR) spectra were obtained using a Perkin Elmer Spectrum One Fourier transform infrared (FT-IR) spectrometer (Perkin Elmer, USA). Gas sorption isotherms were obtained with Micromeritics TriStar II 3020 surface area and porosity analyzer (Micromeritics

Instrument Corporation, U.S.A.). The samples were degassed overnight at 120 °C. The obtained adsorption–desorption isotherms were evaluated to give the pore parameters, including Brunauer–Emmett–Teller (BET) specific surface area, pore size, and pore volume. The pore size distribution (PSD) was calculated from the adsorption branch with the nonlocal density function theory (NLDFT) approach. X-ray photoelectron spectroscopy (XPS) data were obtained from an ESCA-Lab220i-XL electron spectrometer (VG Scientific Ltd., U.K.). The metal contents were measured by inductively couple plasma-optical emission spectroscopy (ICP-OES 715 ES, Varian, USA) after digesting the polymers completely in mixture of nitric acid and sulfuric acid (V:V = 2:1).

Cyclic voltammetry (CV) was performed at 25 °C using a EG&G Princeton Applied Research VMP3 electrochemical work station (Biologic VMP3, France) at a scan rate of 100 mV s^{-1}. The solid samples of CPOPs (10 mg) were mixed with 10 wt% polytetrafluoroethylene (PTFE) and 4 mL ethanol under ultrasonication to obtain a well-dispersed suspension. To prepare the working electrode, the suspension was drop-casted on a Pt plate electrode and the resulting electrode was dried at 50 °C for 30 min prior to measurements. Pt wire, Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN) serve as counter electrode and reference electrode, respectively, and ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M in CH_3CN) was used as the supporting electrolyte.

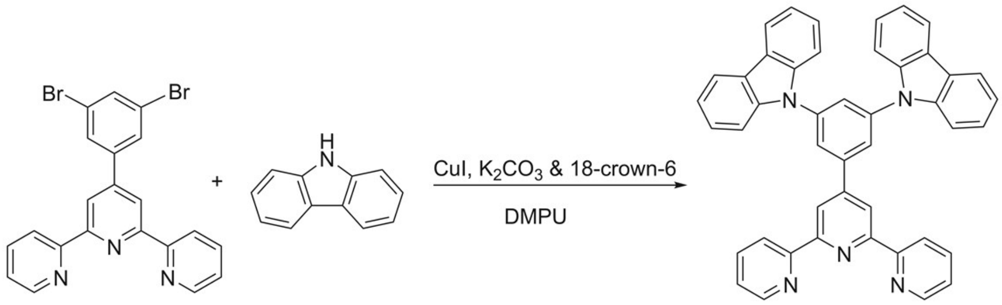
Electron paramagnetic resonance (EPR) spectra were collected with an ELEXSYS-II E500 CW-EPR spectrometer (Bruker, Germany). The mixtures of polymer, capturing agent 2,2,6,6-tetramethylpiperidine (TEMPO), and *N*,*N*-diisopropylethylamine (*i*Pr_2EtN) in air-saturated DMF were irradiated by 23 W white LED lamp for 3 min prior to EPR measurements.

Synthesis of 4'-(3,5-dibromophenyl)-2,2':6',2''-terpyridine



Into a 500 mL round bottom flask, 2-acetylpyridine (4.84 g, 40 mmol) and a solution of 3,5-dibromobenzaldehyde (5.27 g, 20 mmol) in ethanol (10.0 mL) were added. Then, KOH pellets (3.08 g, 85%, 40 mmol) and aqueous solution of NH_3 (60 mL, 29.3%) were added to the solution. The reaction mixture was stirred at 34 °C for 24 h, and then it was allowed to cool to 20 °C, and the off-white solid was collected by filtration and washed with ice-cold ethanol (10 mL). Recrystallization from ethanol afforded a white crystalline solid of 7.9 g with 85% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.76 (d, $J = 4.3$ Hz, 2H), 8.70–8.65 (m, 4H), 7.97 (s, 2H), 7.91 (t, $J = 7.7$ Hz, 2H), 7.77 (s, 1 H), 7.41–7.37 (m, 2H).

Synthesis of 9,9'-(5-([2,2':6',2''-terpyridin]-4'-yl)-1,3-phenylene)bis(9*H*-carbazole)



A 100 mL flask was charged with 9*H*-carbazole (2.43 g, 14.55 mmol), 4'-(3,5-dibromophenyl)-2,2':6',2''-terpyridine (2.10 g,4.50 mmol), CuI (0.19 g, 0.97 mmol), 18-crown-6 (0.09 g, 0.32 mmol), K_2CO_3 (4.02 g, 40.50 mmol), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 0.32 mL). The reaction mixture was stirred magnetically at 200 °C under N_2 protection for 2 days. After cooling to room temperature, the reaction system was quenched by 2 N hydrochloric acid, and the mixture was washed with aqueous ammonia (NH_3 (aq)) and water. Then, the mixture was extracted with CH_2Cl_2 and the solvent was evaporated. After TLC analysis, the crude product was purified with flash column chromatography using petroleum ether and dichloromethane (v/v = 4/1) as eluent. The desired fraction was collected and rotavaped, and finally it was dried in vacuum oven at 60 °C for 12 h to give the off-white powder of 0.856 g with 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.87 (s, 1H), 8.72 (d, $J = 7.0$ Hz, 4H), 8.25 (s, 2H), 8.21 (d, $J = 7.7$ Hz, 4H), 7.93 (d, $J = 9.7$ Hz, 3H), 7.63 (d, $J = 8.2$ Hz, 4H), 7.50 (t, $J = 7.7$ Hz, 4H), 7.43–7.32 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 156.17, 155.47, 148.95, 148.65, 142.49, 140.65, 140.18, 137.33, 126.34, 125.89, 124.87, 124.18, 123.71, 121.55, 120.50, 120.50, 119.21, 109.74. MS (MALDI-TOF) *m/z*: calculated for $C_{45}H_{29}N_5$: 639.76, found: 640.2.

Synthesis of [$(TPYCz)_2Ru](PF_6^-)_2$

$RuCl_3\cdot3H_2O$ (130 mg, 0.5 mmol) and 9,9'-(5-([2,2':6',2''-terpyridin]-4'-yl)-1,3-phenylene)bis(9*H*-carbazole) (366 mg, 0.99 mmol) were added to a mixture of ethanol/water (v/v = 1/1, 10 mL) in a round-bottom flask. The solution was refluxed overnight under an argon pressure, and then KOH (190 mg) was added in and the obtained mixture was kept refluxing for 2 h. After cooling to room temperature, the solvent was evaporated. To the crude product, NH_4PF_6 solution was added. The organic phase was extracted by DCM and the aqueous phase was discarded, the process repeated, finally washed with water alone. The solvent was evaporated and the residue was taken up in a minimal amount of acetonitrile, then poured into H_2O (350 mL) to give a heavy precipitate, which was filtered and dried in vacuum to give black solid (yield = 43.0%). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 9.02 (s, 4H), 8.56 (s, 4H), 8.51 (d, J = 8.2 Hz, 4H), 8.20 (t, J = 6.5 Hz, 8H), 8.08 (s, 2H), 7.80 (t, J = 7.9 Hz, 4H), 7.68 (d, J = 8.2 Hz, 8H), 7.50 (t, J = 7.7 Hz, 8H), 7.34–7.30 (m, 8H), 7.23 (s, 4H), 7.11–7.07 (m, 4H). ^{13}C NMR (101 MHz, CD_3CN) δ (ppm) 158.57, 158.52, 156.20, 141.47, 141.10, 141.05, 138.71, 128.15, 126.99, 126.19, 124.11, 121.28, 121.19, 121.10, 121.02, 120.92, 120.85, and 110.60.

Synthesis of CPOP-32

The synthesis of **CPOP-32** was according to the literature with slight modification, a 100 mL round bottom flask was charged with the ferric chloride (477 mg, 2.94 mmol) and degassed for 10 minutes, and then added 20 mL of anhydrous chloroform under nitrogen protection. In a 100 mL flask, 9,9'-(5-([2,2':6',2''-terpyridin]-4'-yl)-1,3-phenylene)bis(9*H*-carbazole) (TPYCz) (223 mg, 0.37 mmol) was dissolved in 30 mL anhydrous chloroform, and then transferred dropwise via dropping funnel to the ferric chloride suspension. The resulted mixture was stirred at room temperature for 24 hours under nitrogen protection. Methanol (50 mL) was added to the reaction mixture, and then the system was kept vigorously stirring for 2 hours. The solid was filtered and washed with tetrahydrofuran and chloroform. The obtained polymer was further purified by Soxhlet extraction with methanol for 24 hours. The purified solid was transferred to methanolic HCl solution (6 M, 50 mL) and heated for 2 days under stirring (the methanolic HCl solution was replaced by fresh one every 24 h). The precipitate was filtered, and subsequently washed with aqueous ammonia solution (10 wt%), and methanol, respectively. The resulting solid was finally purified through Soxhlet extraction by methanol, and dried in vacuum oven at 80 °C for 12 h to give **CPOP-32** with 94% yield.

Synthesis of CPOP-32-Ru

Synthesis of **CPOP-32-Ru** was conducted according to modified procedure. In 50 mL round bottom flask, **CPOP-32** (134 mg, 0.21 mmol) was added to the suspension of $RuCl_3 \cdot 3H_2O$ (55 mg, 0.21 mmol) in methanol (10 mL) under nitrogen atmosphere. The reaction mixture was kept refluxing at 90 °C for 1 day, and then the product was filtered and further purified by Soxhlet extractor using chloroform for 24 hours. Finally, the product was dried in vacuum oven at 80 °C for 12 h, and then a dark orange powder **CPOP-32-Ru** (90%) was obtained.

Synthesis of CPOP-32-Ru'

The **CPOP-32-Ru'** was synthesized according to a modified procedure. [(9,9'-(5-([2,2':6',2''-Terpyridin]-4'-yl)-1,3-phenylene)bis(9*H*-carbazole))$_2$Ru]$(PF_6^-)_2$ (Ru(TPYCz)$_2$$(PF_6^-)_2$, 360 mg, 0.26 mmol) was dissolved in 45 mL of anhydrous chloroform and then the resulted solution was transferred dropwise to a suspension of ferric chloride (750 mg, 4.62 mmol) in 30 mL of anhydrous chloroform. The mixture was stirred at room temperature for 1 day under nitrogen protection. Methanol (50 mL) was added to the reaction mixture, and then the system was kept vigorously stirring for 2 hours. Then the solid was filtered and washed with tetrahydrofuran and chloroform. The solid was further purified by Soxhlet extraction with methanol for 24 hours. The purified product was transferred to methanolic HCl solution (6 M, 50 mL) and heated for 2 days under stirring (the methanolic HCl solution was replaced by fresh one every 24 h). Then the precipitate was filtered, and subsequently washed with aqueous ammonia solution (10 wt%) and methanol, respectively. The resulting solid was finally purified through Soxhlet extraction by methanol, and dried in vacuum oven at 80 °C for 12 h to give **CPOP-32'** with 96% yield.

The product was used to synthesize **CPOP-32-Ru'**. **CPOP-32'** (134 mg, 0.21 mmol), $RuCl_3 \cdot 3H_2O$ (55 mg, 0.21 mmol), and methanol (10 mL) were used to give **CPOP-32-Ru'** of 89 % yield as dark orange powder.

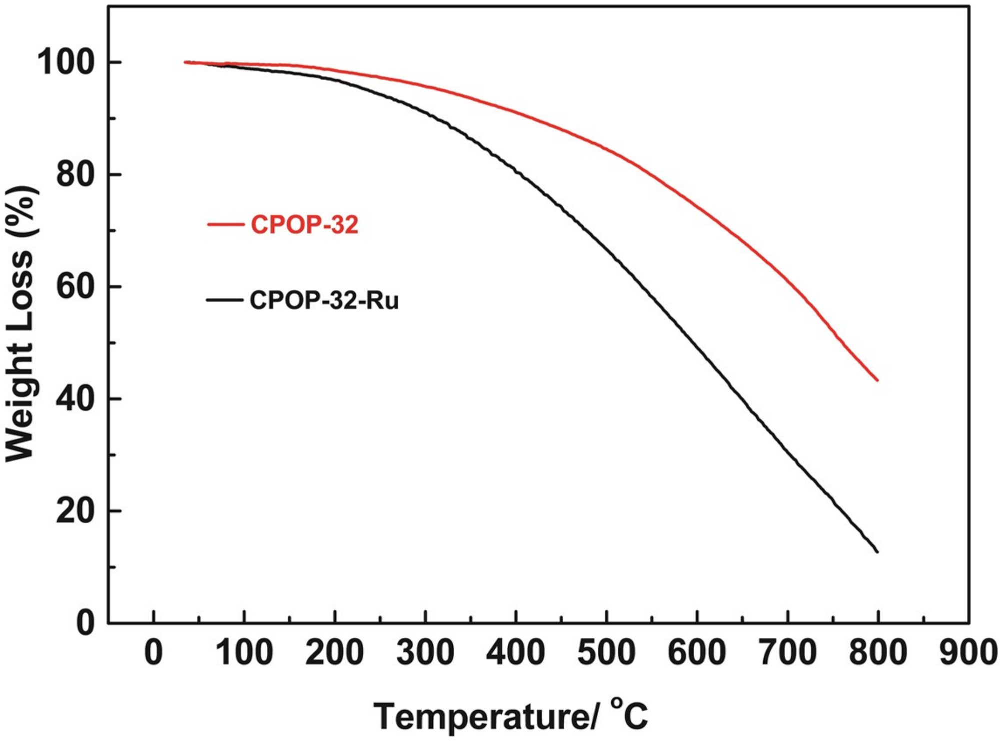


Fig. S1. TGA curves of **CPOP-32** and **CPOP-32-Ru**.

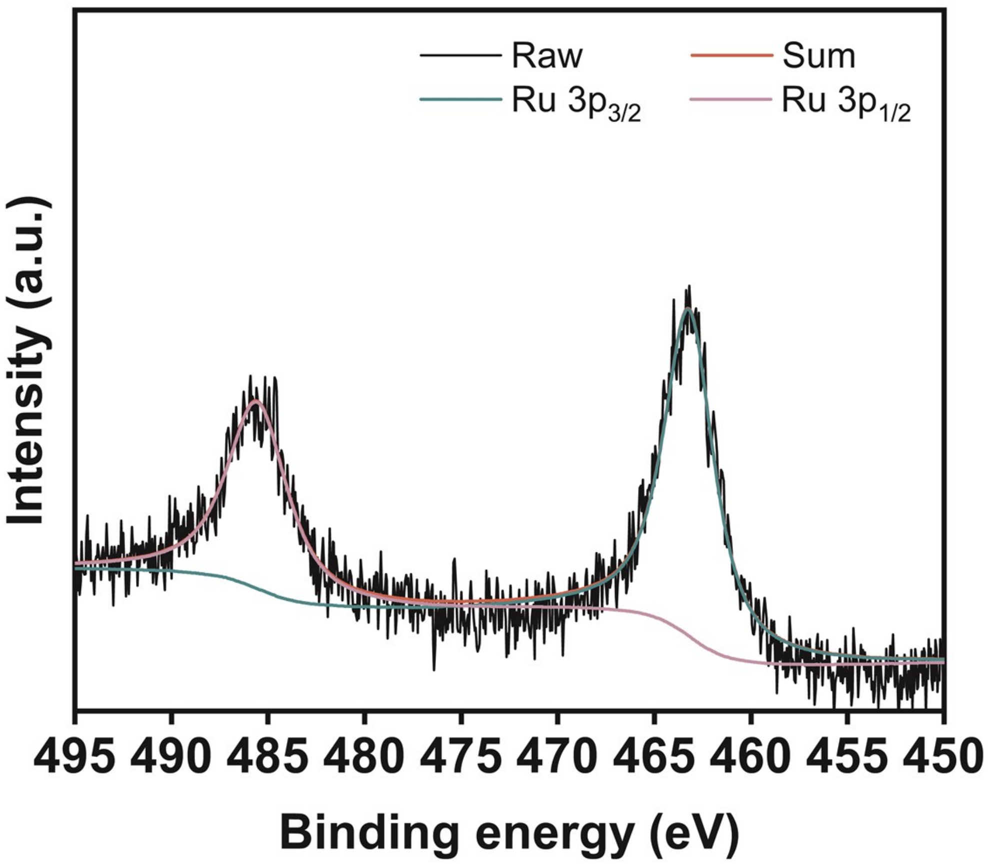


Fig. S2. XPS spectrum of Ru $3p_{3/2}$ of the Ru catalysts supported on **CPOP-32-Ru**.

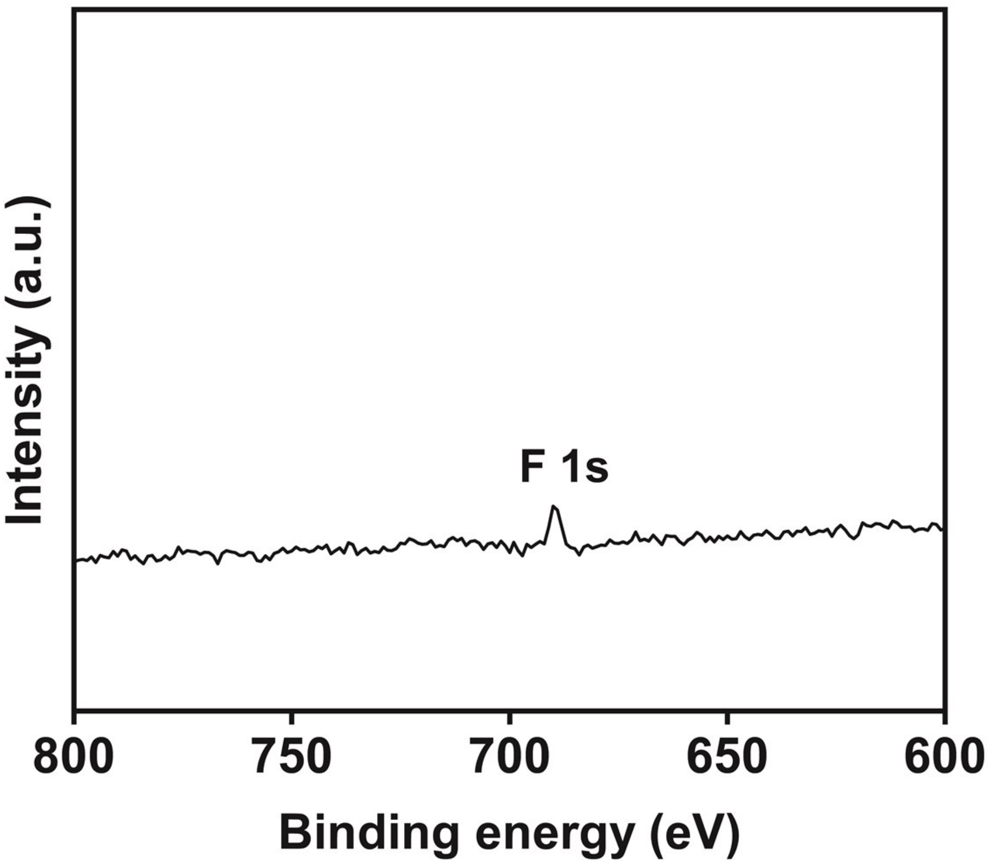


Fig. S3. XPS spectrum for Fe 3p of the chelated Fe on the **CPOP-32-Ru**.

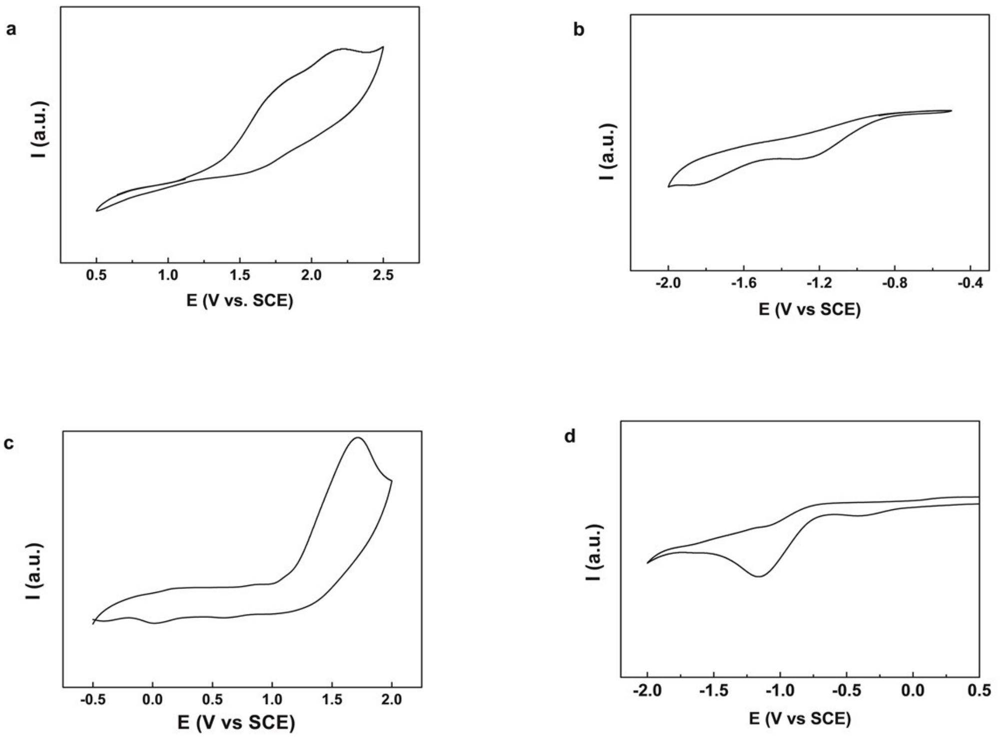


Fig. S4. Cyclic voltammograms of **CPOP-32-Ru** (a and b), and **CPOP-32-Ru'** (c and d) in deaerated CH_3CN with 0.1 M Bu_4PF_6 as supporting electrolyte with scan rate of 100 mV s^{-1}.

Table S1. Redox potentials (V) of **CPOP-32-Ru** and **CPOP-32-Ru'**.

Photosensitizer	E^{0-0}	$E_{1/2}(M/M^-)$	$E_{1/2}(M^+/M)$	$E_{1/2}(M^+/{}^*M)$	$E_{1/2}({}^*M/M^-)$
CPOP-32-Ru	2.55 [a]	–1.20 [b]	1.40 [b]	–1.15 [c]	1.35 [d]
CPOP-32-Ru'	2.43 [a]	–1.23 [b]	1.38 [b]	–1.05 [c]	1.20 [d]

[a] E^{0-0} is estimated from the intersection of UV-vis absorption and emission spectra. [b] All potentials are given in volts versus the saturated calomel electrode (SCE). [c] $E_{1/2}(M^+/{}^*M) = E_{1/2}(M^+/M) - E^{0-0}$. [d] $E_{1/2}({}^*M/M^-) = E_{1/2}(M/M^-) + E^{0-0}$.

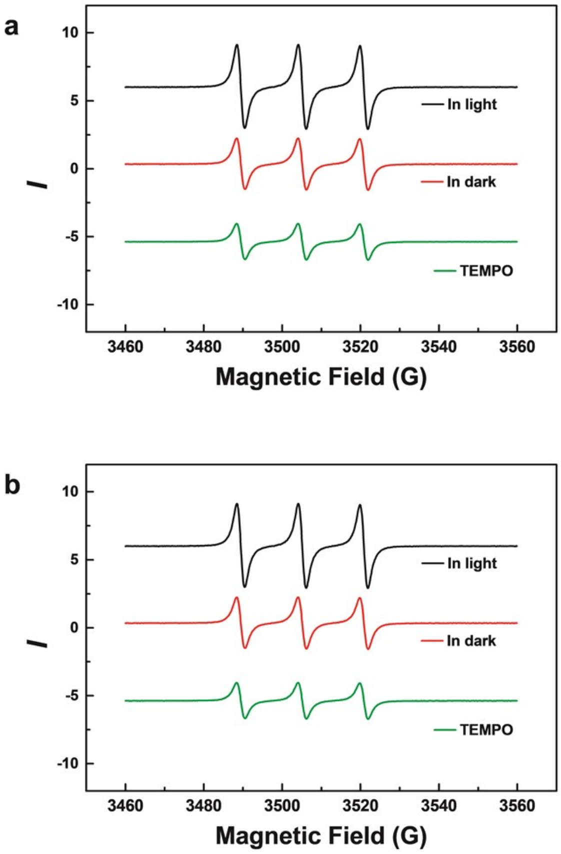
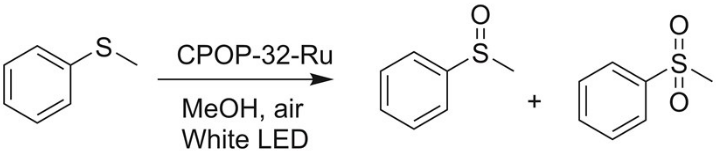


Fig. S5. EPR spectra for samples of **CPOP-32-Ru** (4.0 mg L^{-1}) (a), and **CPOP-32-Ru'** (4.0 mg L^{-1}) (b) in aerated DMF (100 μL) containing TEMPO (6.4×10^{-2} mM) and *i*Pr_2EtN (5.74×10^{-2} mM) at dark and after 5 minutes irradiation with 23 W white LED lamp at ordinary condition.



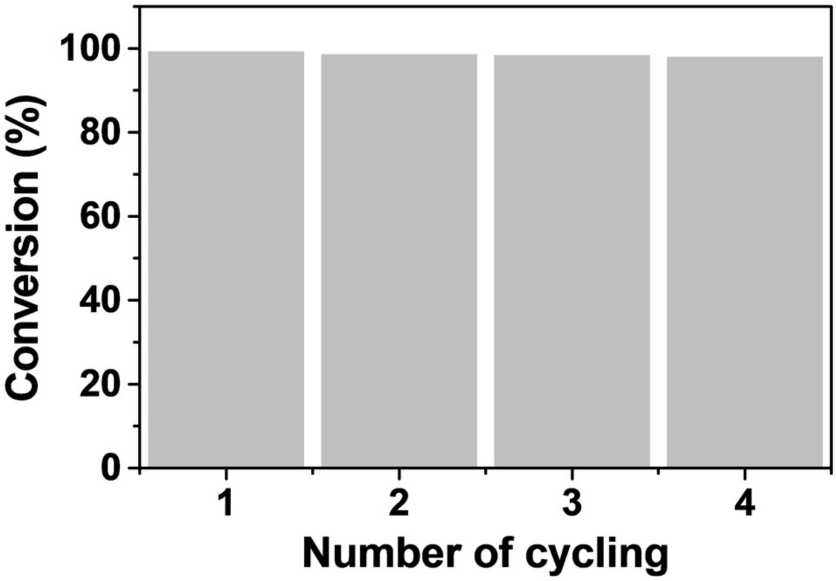


Fig. S6. Recyclability of **CPOP-32-Ru** photocatalyst in the sulfide oxidation of methyl(phenyl)sulfane to (methylsulfinyl)benzene. The catalyst was recycled from the reaction mixture by centrifugation, washed with methanol and dichloromethane, dried, and reused in a fresh reaction solution.

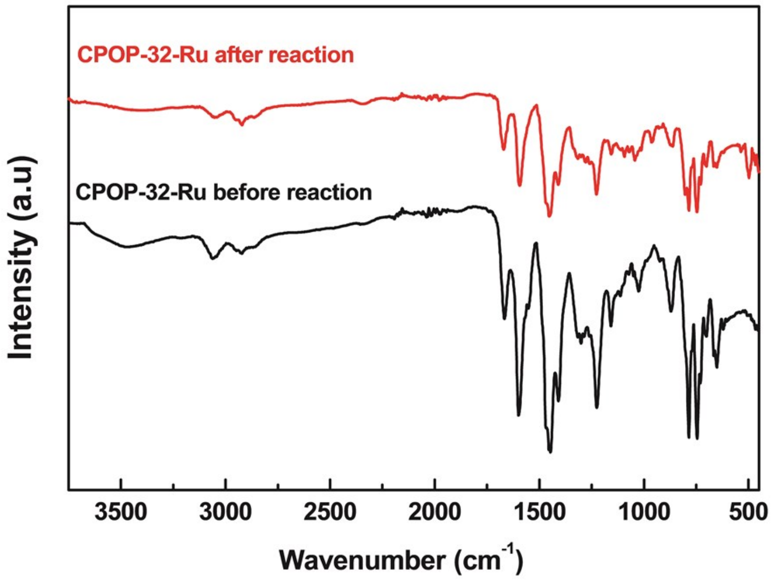


Fig. S7. The FT-IR spectra of **CPOP-32-Ru** before and after photocatalytic reactions.

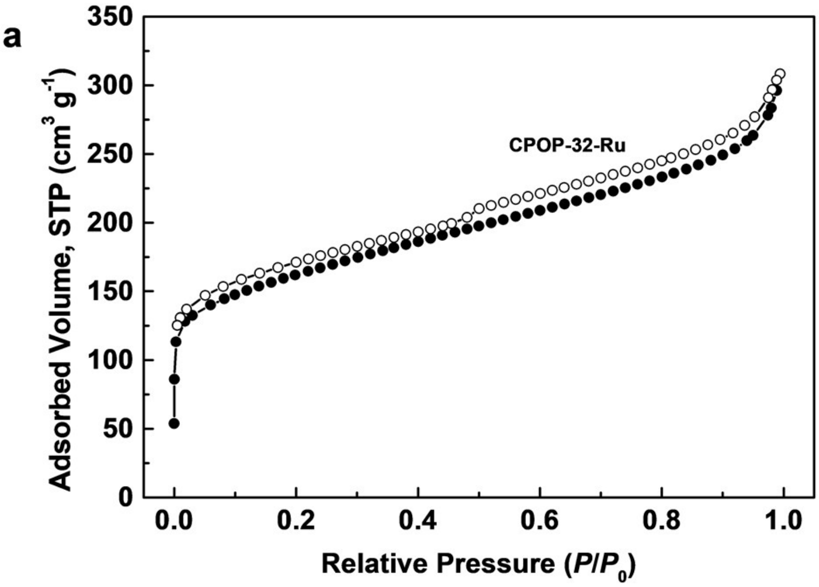
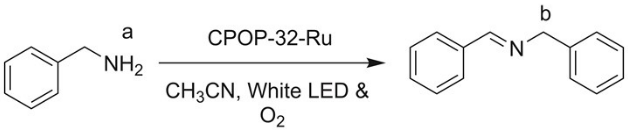


Fig. S8. Nitrogen sorption isotherm curve of **CPOP-32-Ru** at 77 K after photocatalytic reaction.

Table S2. Oxidative amine coupling using **CPOP-32-Ru** and **CPOP-32-Ru'** photocatalyst.

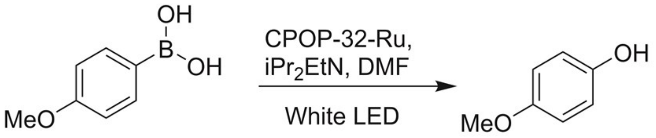


Entry	1	2	3	4	5	6	7
CPOP-32-Ru	+	–	+	–	+	+	+
CPOP-32-Ru'	–	+	–	–	–	–	–
Visible-light	+	+	–	+	+	+	+
O_2	+	+	+	+	–	+	+
KI	–	–	–	–	–	+	–
p-Benzoquinone	–	–	–	–	–	–	+
Yield [%]	99	91	NSD	NSD	8.2	6.0	14.1

Note: NSD means no significant detection.

Standard Reaction Condition: CPOP-32-Ru (or **CPOP-32-Ru'**) (1.0 μmol), phenylmethanamine (0.7 mmol), dry acetonitrile (MeCN, 1 mL), air, 23 W white LED lamp and room temperature. Conversions were determined by ^{1}H NMR.

Table S3. Controlled experiment to determine the specific condition by hydroxylation of (4-methoxyphenyl)boronic acid by **CPOP-32-Ru** and **CPOP-32-Ru'** photocatalyst.

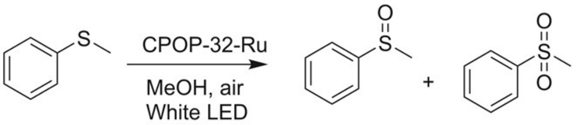


Entry	1	2	3	4	5	6	7	8
CPOP-32-Ru	+	–	–	–	+	–	+	+
CPOP-32-Ru'	–	+	–	–	–	–	–	–
Visible-light	+	+	–	+	–	+	+	+
Air	+	+	+	+	+	+	–	+
iPr_2	+	+	+	–	+	+	+	–
Yield [%]	97	96	NSD	NSD	NSD	trace	28	NSD

Note: NSD means no significant detection.

Standard Reaction Condition: 4-methoxyphenylboronic acid (0.5 mmol), **CPOP-32-Ru** (or **CPOP-32-Ru'**) (2.5 µmol), *i*Pr_2EtN (1.0 mmol), DMF (5 mL), air, 23 W white LED lamp and room temperature. Conversions were determined by ^1H NMR.

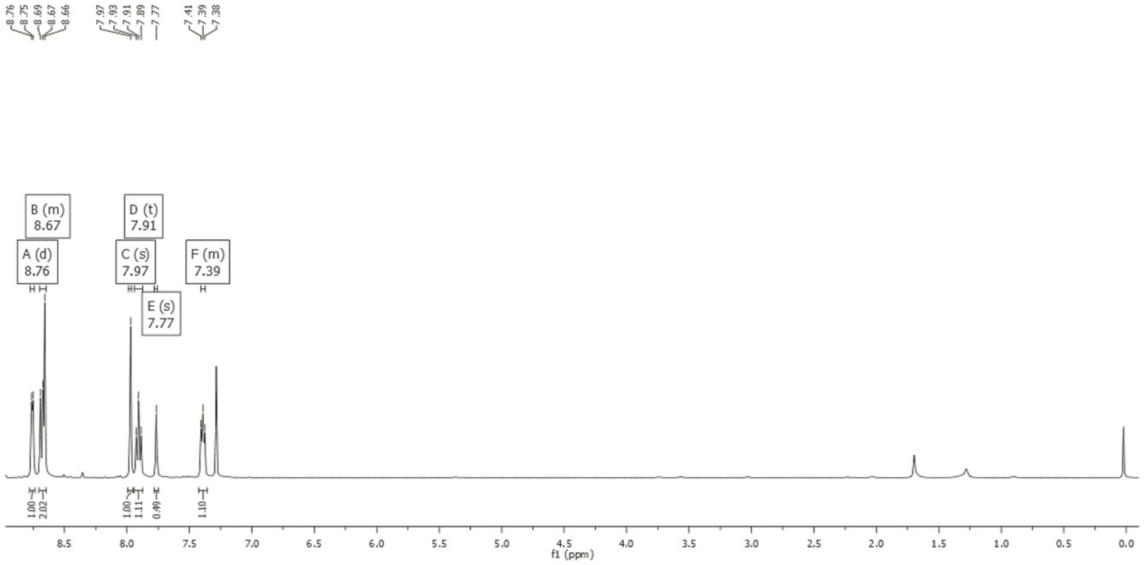
Table S4. Selective photocatalytic oxidation of sulfides.



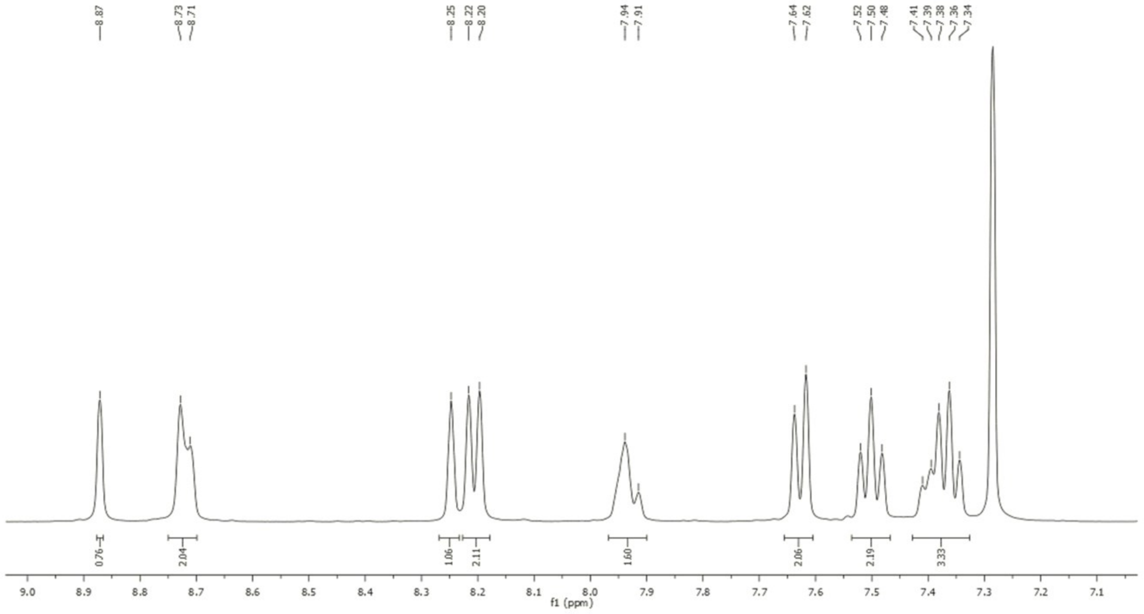
Entry	1[a]	2[b]	3	4	5	6
CPOP-32-Ru	+	+	–	–	+	+
CPOP-32-Ru'	–	–	+	–	–	–
Visible-light	+	+	+	+	–	+
Air	+	+	+	+	+	–
Conv. [%]	97	96	95	NSD	Trace	35

Note: NSD means no significant detection.

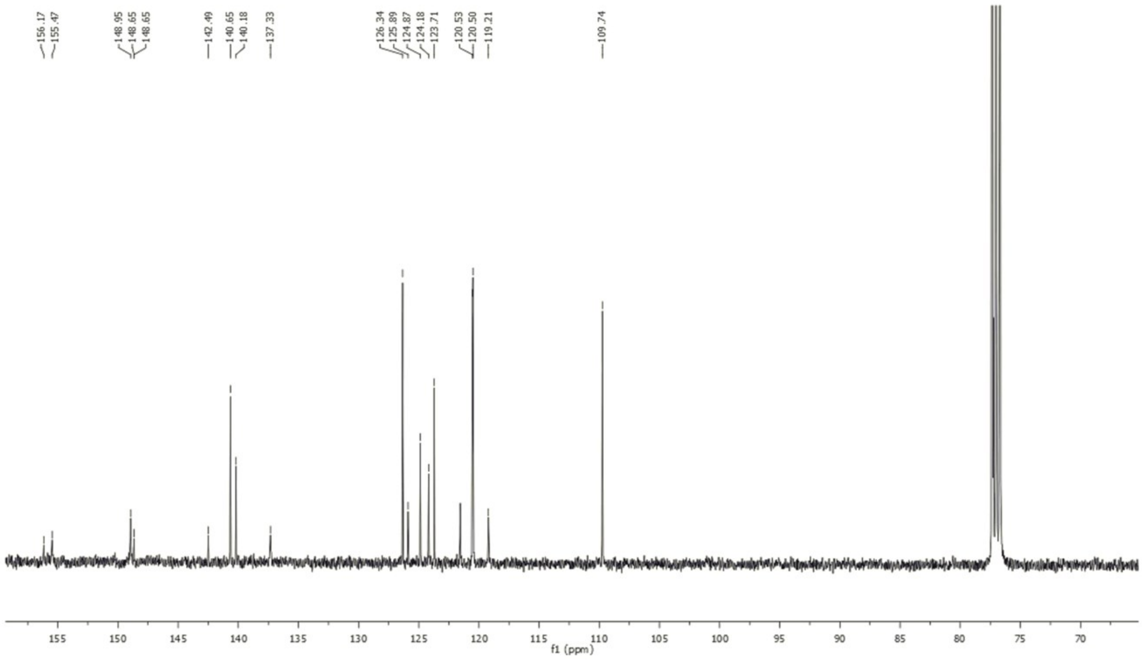
Standard Reaction Condition: CPOP-32-Ru (or **CPOP-32-Ru'**) (1.25 μmol), methyl(phenyl)sulfane (0.5 mmol), dried MeOH (0.5 mL), air, 23 W white LED lamp and room temperature. Conversions were determined by ^{1}H NMR. [a] Originally prepared photocatalyst. [b] After 4th Cycle.



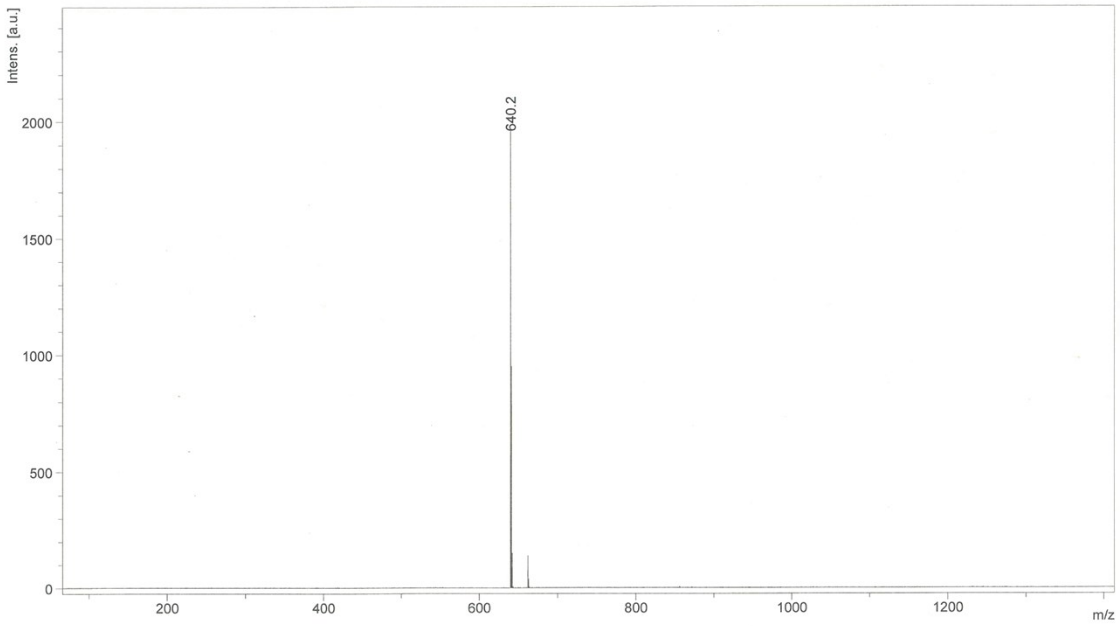
^{1}H NMR of 4'-(3,5-dibromophenyl)-2,2':6',2''-terpyridine.



^{1}H NMR of 9,9'-(5-([2,2':6',2''-terpyridin]-4'-yl)-1,3-phenylene)bis(9*H*-carbazole).



^{13}C NMR of 9,9'-(5-([2,2':6',2''-terpyridin]-4'-yl)-1,3-phenylene)bis(9*H*-carbazole).



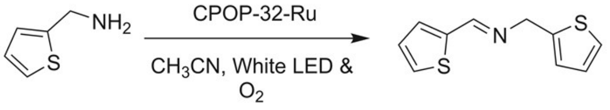
MALDI-TOF- MS of 9,9'-(5-([2,2':6',2''-terpyridin]-4'-yl)-1,3-phenylene)bis(9*H*-carbazole).

General procedure

Photocatalytic oxidative amine coupling of benzylamine

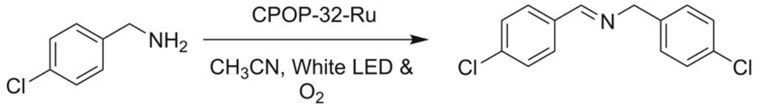
To a dry 5 mL flask containing **CPOP-32-Ru** (1.0 μmol), the respective substrate (0.27 mmol, 33.9 μL) in MeCN (1 mL) was added. The balloon filled with O_2 was attached to the condenser and the reaction mixture was stirred by irradiating with a white LED lamp (23 W) at a distance of about 10 cm until the reaction completed. The reaction progress was monitored by TLC and upon disappearance of the starting material, the polymer material was separated by centrifugation. After rotary evaporating, the ^{1}H NMR measurement for the crude reaction mixture in CD_3CN was used to determine reaction conversions and selectivities. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.34 (s, 1H), 7.73–7.52 (m, 2H), 7.46–7.24 (m, 8H), 4.66 (s, 2H).

Oxidative amine coupling of thiophen-2-ylmethanamine



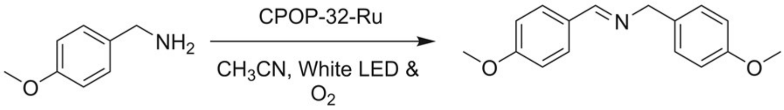
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are **CPOP-32-Ru** (1.0 μmol) and the substrate (0.27 mmol, 26.9 μL) in MeCN (1 mL). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.53 (s, 1H), 7.52 (dd, J = 17.2, 4.9 Hz, 1H), 7.44 (d, J = 3.5 Hz, 1H), 7.27 (d, J = 4.9 Hz, 2H), 6.98 (d, J = 3.5 Hz, 1H), 6.96 (d, J = 2.5 Hz, 2H), 4.91 (s, 2H).

Oxidative amine coupling of (4-chlorophenyl)methanamine



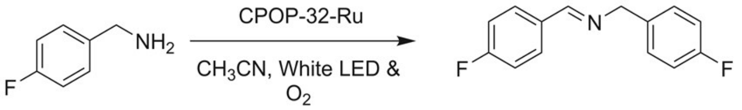
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are **CPOP-32-Ru** (1.0 μmol) and the substrate (0.27 mmol, 32.8 μL) in MeCN (1 mL). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.44 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.39–7.29 (m, 4H), 4.77 (s, 2H).

Oxidative amine coupling of (4-methoxyphenyl)methanamine



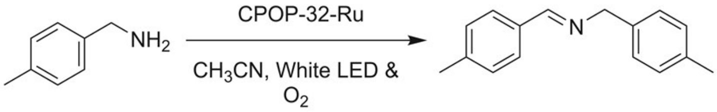
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are **CPOP-32-Ru** (1.0 μmol) and the substrate (0.27 mmol, 35.0 μL) in MeCN (1 mL). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.38 (s, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.27 (dd, J = 8.3, 4.2 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 4.68 (s, 2H), 3.85 (s, 3H), 3.79 (s, 3H).

Oxidative amine coupling of (4-fluorophenyl)methanamine



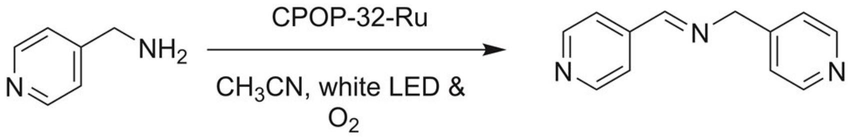
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are **CPOP-32-Ru** (1.0 μmol) and the substrate (0.27 mmol, 31.0 μL) in MeCN (1 mL). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.44 (s, 1H), 7.83 (d, J = 2.9 Hz, 2H), 7.38 (d, J = 3.3 Hz, 2H), 7.20 (t, J = 8.8 Hz, 2H), 7.11 (dd, J = 9.5, 6.1 Hz, 2H), 4.76 (s, 2H).

Oxidative amine coupling of *p*-tolylmethanamine



The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are **CPOP-32-Ru** (1.0 μmol) and the substrate (0.27 mmol, 33.9 μL) in MeCN (1 mL). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.42 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 4.73 (s, 2H).

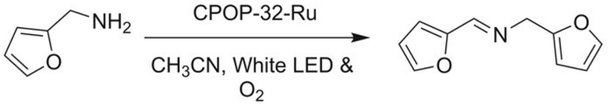
Oxidative amine coupling of pyridin-4-ylmethanamine



The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are **CPOP-**

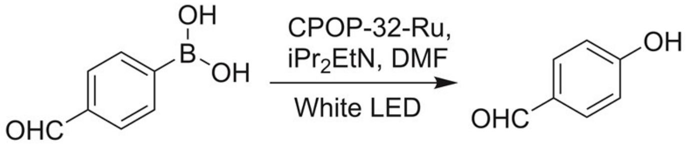
32-Ru (1.0 μmol) and the substrate (0.27 mmol, 27.4 μL) in MeCN (1 mL). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.46 (s, 1H), 7.77–7.65 (m, 2H), 7.59–7.51 (m, 2H), 7.43–7.36 (m, 2H), 7.32 (t, J = 8.7 Hz, 2H), 4.85 (s, 1H).

Oxidative amine coupling of furan-2-ylmethanamine



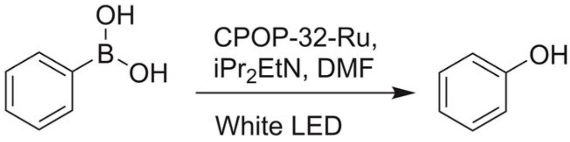
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are **CPOP-32-Ru** (1.0 μmol) and the substrate (0.27 mmol, 24.4 μL) in MeCN (1 mL). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 8.15 (s, 1H), 7.64 (s, 1H), 7.46 (d, J = 11.7 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 3.4 Hz, 1H), 6.57 (d, J = 1.8 Hz, 1H), 6.31 (d, J = 3.1 Hz, 1H), 4.70 (s, 2H).

General procedure for hydroxylation of 4-formylphenylboronic acid



The mixture of 4-formylphenylboronic acid (75 mg, 0.5 mmol), **CPOP-32-Ru** (2.5 μmol, based on monomer), *i*Pr_2EtN (140 μL, 1.0 mmol), and DMF (5.0 mL) was stirred under irradiating about 10 cm apart from a white LED lamp (23 W) for 10 hours with monitoring the reaction progress using thin layer chromatography, and the reaction was stopped following disappearance of the starting material. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 10.06 (s, 1H), 7.80 (d, J = 7.7 Hz, 2H), 6.99 (d, J = 7.8 Hz, 2H), 6.29 (s, 1H).

Hydroxylation of phenylboronic acid

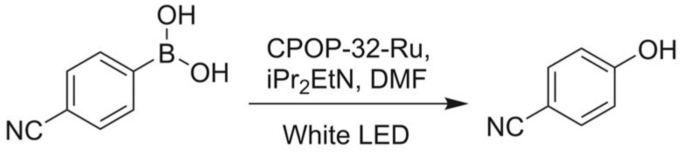


The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The mixture of phenylboronic acid (61 mg, 0.5 mmol), **CPOP-32-Ru** (2.5 μmol, based on monomer), iPr$_2$EtN (140 μL, 1.0 mmol), and DMF (5.0 mL) was stirred under irradiating about 10 cm apart from a white LED lamp (23 W) for 12 hours. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 7.80 (d, J = 7.2 Hz, 1H), 7.50–7.37 (m, 4H), 6.33 (s, 1H).

Hydroxylation of (4-methoxyphenyl)boronic acid

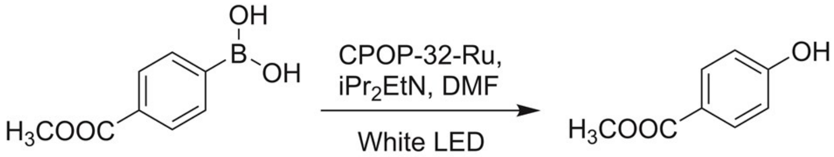
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The mixture of (4-methoxyphenyl)boronic acid (76 mg, 0.5 mmol), **CPOP-32-Ru** (2.5 μmol, based on monomer), iPr$_2$EtN (140 μL, 1.0 mmol), and DMF (5.0 mL) was stirred under irradiating about 10 cm apart from a white LED lamp (23 W) for 8 hours. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 7.74 (d, J = 7.6 Hz, 2H), 6.94 (d, J = 7.5 Hz, 2H), 6.08 (s, 1H), 3.83 (s, 3H).

Hydroxylation of (4-(4-cyanophenyl)boronic acid



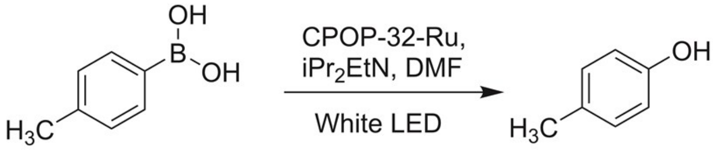
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The mixture of (4-(4-cyanophenyl)boronic acid (73.5 mg, 0.5 mmol), **CPOP-32-Ru** (2.5 μmol, based on monomer), *i*Pr$_2$EtN (140 μL, 1.0 mmol), and DMF (5.0 mL) was stirred under irradiating about 10 cm apart from a white LED lamp (23 W) for 12 hours. ^{1}H NMR (400 MHz, CD$_3$CN) δ (ppm) 7.92 (d, J = 7.5 Hz, 2H), 7.73 (d, J = 7.4 Hz, 2H), 6.41 (s, 1H).

Hydroxylation of (4-(methoxycarbonyl)phenyl)boronic acid



The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The mixture of (4-(methoxycarbonyl)phenyl)boronic acid (90 mg, 0.5 mmol), **CPOP-32-Ru** (2.5 μmol, based on monomer), *i*Pr$_2$EtN (140 μL, 1.0 mmol), and DMF (5.0 mL) was stirred under irradiating about 10 cm apart from a white LED lamp (23 W) for 10 hours. ^{1}H NMR (400 MHz, CD$_3$CN) δ (ppm) 8.00 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 7.5 Hz, 2H), 6.36 (s, 1H), 3.90 (s, 3H).

Hydroxylation of *p*-tolylboronic acid

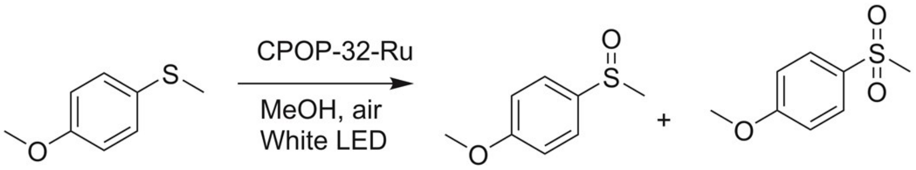


The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The mixture of *p*-tolylboronic acid (68 mg, 0.5 mmol), **CPOP-32-Ru** (2.5 μmol, based on monomer), *i*Pr_2EtN (140 μL, 1.0 mmol) and DMF (5.0 mL) was stirred under irradiating about 10 cm apart from a white LED lamp (23 W) for 8 hours. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 7.69 (d, J = 7.4 Hz, 2H), 7.22 (d, J = 7.4 Hz, 2H), 6.19 (s, 1H), 2.92 (s, 3H).

General procedure for selective photocatalytic oxidation of sulfides

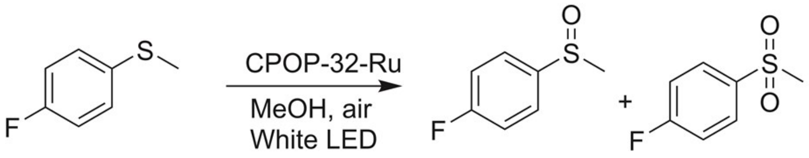
Oven dried 5 mL round bottom flask was charged with 0.5 mL dried MeOH, 0.5 mmol sulfides and **CPOP-32-Ru** (1.25 μmol, based on monomer), and the flask was fitted with condenser. Under open air, the mixture was magnetically stirred with irradiation of 23 W white LED lamp at a distance of around 10 cm. The reaction progress was monitored using TLC. Once the reaction was completed, the photocatalyst was collected by centrifugation and followed by evacuation of the solvent under vacuum. The conversions and selectivities were determined by ^{1}H NMR on the basis of the ratio between integrated peaks of product in $CDCl_3$ as solvent. The crude product of oxidation of thioanisole was taken as an example to illustrate the calculation procedure. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54–7.37 (m, 5H) and 2.64 (s, 3H).

Selective sulfide oxidation of (4-methoxyphenyl)(methyl)sulfane



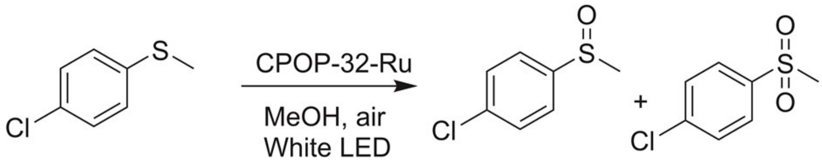
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are substrate (0.5 mmol, 70.0 μL), and **CPOP-32-Ru** (1.25 μmol, based on monomer) in 0.5 mL dried MeOH. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 2.47 (s, 3H).

Selective sulfide oxidation of (4-fluorophenyl)(methyl)sulfane



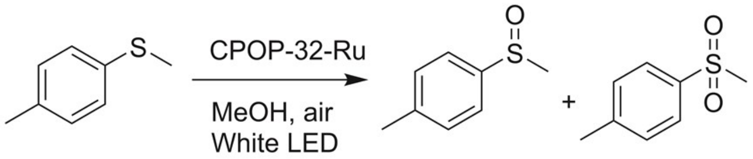
The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are substrate (0.5 mmol, 63.0 μL), and **CPOP-32-Ru** (1.25 μmol, based on monomer) in 0.5 mL dried MeOH. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28 (dd, J = 8.1, 5.1 Hz, 4H), 2.49 (s, 3H).

Selective sulfide oxidation of (4-chlorophenyl)(methyl)sulfane



The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are substrate (0.5 mmol, 66.0 μL), and **CPOP-32-Ru** (1.25 μmol, based on monomer) in 0.5 mL dried MeOH. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.23 (d, J = 1.9 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 2.43 (s, 3H).

Selective sulfide oxidation of methyl(*p*-tolyl)sulfane



The catalysis with **CPOP-32-Ru** was performed as abovementioned. The product is characterized according the general procedure. The reaction mixtures used are substrate (0.5 mmol, 67.9 μL), and **CPOP-32-Ru** (1.25 μmol, based on monomer) in 0.5 mL dried MeOH. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.21–7.13 (m, 2H), 7.08 (d, J = 7.7 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H).