

*Electronic Supplementary Information for*

**A copper(I)/copper(II)-salen coordination polymer as a  
bimetallic catalyst for three-component strecker reactions and  
degradation of organic dyes**

Yun-Long Hou, Raymond Wai-Yin Sun, Xiao-Ping Zhou, Jun-Hao Wang and Dan Li\*

*Department of Chemistry and Research Institute for Biomedical and Advanced Materials, Shantou  
University, Guangdong 515063, P.R. China.*

*\*E-mail: dli@stu.edu.cn*

## A. Experimental Section

**General:** All starting materials were commercially purchased and used as received. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FT-IR spectrometer in the range of 400–4000  $\text{cm}^{-1}$ . Elemental analyses (C, H, N) were performed using a Vario EL III CHNS elemental analyzer. Thermogravimetric (TG) analysis was performed on a TA Instruments Q50 Thermogravimetric Analyzer under a nitrogen flow of (40 mL/min) at a typical heating rate of 10 K/min. Powder X-ray diffraction (PXRD) experiments were performed on a D8 Advance X-ray diffractometer with Cu- $K_{\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). UV-vis spectra were recorded with a Bio-Logic MOS-450/AF-CD Spectrometer. Catalytic yield values were determined by GC on a Supelco b-Dex 120 column. Diastereoselectivity values were determined by  $^1\text{H-NMR}$  using a 400 MHz Bruker NMR spectrometer.

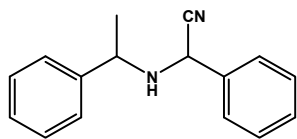
**Synthesis of  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$ .**<sup>1</sup> A solution of 1,2-cyclohexanediamine (0.924 g, 6 mmol) in MeOH (30 mL) was dropwisely added into a solution of 1H-imidazole-4-carbaldehyde (1.27 g, 13.2 mmol) in MeOH (50 mL), and the mixture was refluxed for 6 h to form a clear light-brown solution. To this solution was added a solution of  $\text{Cu}^{\text{II}}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (1.45 g, 6 mmol) in MeOH (20 mL), and the mixture was stirred for another 7 h at room temperature. The product was obtained as blue precipitates with an 80% yield which was collected by filtration, washed with MeOH, and air-dried. Elemental analysis (%): Calcd for  $[\text{Cu}^{\text{II}}(\text{SalHImCy})](\text{NO}_3)_2$  ( $\text{C}_{14}\text{H}_{18}\text{N}_8\text{O}_6\text{Cu}$ ): C, 36.72; H, 3.96; N, 24.47; Found: C, 36.67; H, 3.92; N, 24.00.

**Synthesis of coordination polymer (CP) 1:** A mixture of  $[\text{Cu}^{\text{II}}(\text{SalImCy})](\text{NO}_3)_2$  (0.0092 g, 0.02 mmol),  $\text{Cu}^{\text{I}}$  (0.0095 g, 0.05 mmol) in DMF (3 mL) and EtOH (1.5 mL), was heated in a 10-mL scintillation vial with a screw cap at 373 K for 12 h. CP 1 was isolated in a ~50% yield as reddish solid. Elemental analysis (%): Calcd for  $\{[\text{Cu}^{\text{II}}(\text{SalImCy})](\text{Cu}^{\text{I}})_2 \cdot \text{DMF}\}_n$  ( $\text{C}_{17}\text{H}_{23}\text{N}_7\text{O}_2\text{Cu}_3$ )<sub>n</sub>: C, 25.98; H, 2.95; N, 12.48; Found: C, 25.74; H, 3.15; N, 12.56. IR (KBr,  $\text{cm}^{-1}$ ): 2934.9w, 2853.2w, 1621.5vs, 1547.3m, 1472.9w, 1384.9m, 1276.4m, 1242.6w, 1114.6s, 1032.7m, 816.6m, 640.5m, 559.6w.

**General procedure for the three-component strecker condensation.** CP 1 was immersed in EtOH for 3 days and dried under vacuum at 343 K for 10 h. To the solution of aromatic aldehydes (1 mmol), (R)-(+)-1-phenylethylamine (1 mmol), trimethylsilyl cyanide (1.5 mmol) in  $\text{CD}_3\text{CN}$  (2 mL) was added 0.5 mol % of 1. The mixture was stirred at corresponding temperature and time. After completion of reaction (monitored by thin layer chromatography (TLC)), the reaction mixture was diluted with  $\text{CD}_3\text{CN}$  and analyzed by GC and  $^1\text{H-NMR}$  to obtain the corresponding yield and diastereoselectivity values. The relative stereochemistry of the products was determined by  $^1\text{H NMR}$  spectroscopy using the literature methods.<sup>2</sup> The catalyst was recovered by centrifugation and washed repeatedly with  $\text{CH}_3\text{CN}$ , dried and reused when required.

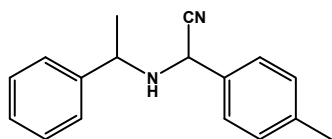
### Characterization of reaction products:

#### $\alpha$ -Phenyl1- $\alpha$ -[(1-phenylethyl)amino]-acetonitrile (Table 1, entry 1)



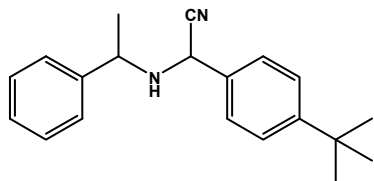
$^1\text{H-NMR}$  (400MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$ 7.28–7.40 (m, 20H, ArH), 4.68 (s, 1H, CHCN), 4.35 (s, 1H, CHCN), 4.07 (q,  $J = 6.5\text{Hz}$ , 1H, CHCH $_3$ ), 3.80 (q,  $J = 6.5\text{Hz}$ , 1H, CHCH $_3$ ), 1.30 (d,  $J = 6.5\text{Hz}$ , 3H, CHCH $_3$ ), 1.27 (d,  $J = 6.5\text{Hz}$ , 3H, CHCH $_3$ );  $m/z$  (EI): 224 (M-Me), 211 (M-HCN), 196 (M-HCN-Me), 105 ( $\text{C}_7\text{H}_7\text{N}$ ).

#### $\alpha$ -4-Methylphenyl1- $\alpha$ -[(1-phenylethyl)amino]-acetonitrile (Table 1, entry 2)



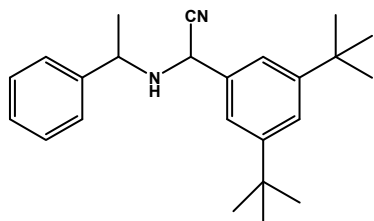
$^1\text{H-NMR}$  (400MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$ 7.14–7.40 (m, 18H, ArH), 4.61 (s, 1H, CHCN), 4.29 (s, 1H, CHCN), 4.05 (q,  $J = 6.5\text{Hz}$ , 1H, CHCH $_3$ ), 3.80 (q,  $J = 6.5\text{Hz}$ , 1H, CHCH $_3$ ), 2.28 (s, 3H, ArCH $_3$ ), 2.27 (s, 3H, ArCH $_3$ ), 1.29 (d,  $J = 6.5\text{Hz}$ , 3H, CHCH $_3$ ), 1.27 (d,  $J = 6.5\text{Hz}$ , 3H, CHCH $_3$ );  $m/z$  (EI): 235 (M-Me), 223 (M-HCN), 208 (M-HCN-Me), 105 ( $\text{C}_7\text{H}_7\text{N}$ ).

#### $\alpha$ -4-*tert*-Butylphenyl1- $\alpha$ -[(1-phenylethyl)amino]-acetonitrile (Table 1, entry 3)



$^1\text{H-NMR}$  (400MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$ 7.27–7.40 (m, 18H, ArH), 4.65 (s, 1H, CHCN), 4.31 (s, 1H, CHCN), 4.06 (q,  $J = 6.5\text{Hz}$ , 1H, CHCH $_3$ ), 3.80 (q,  $J = 6.5\text{Hz}$ , 1H, CHCH $_3$ ), 1.29 (d,  $J = 6.5\text{Hz}$ , 3H, CHCH $_3$ ), 1.27 (d,  $J = 3.8\text{Hz}$ , 3H, CHCH $_3$ ), 1.25 (s, 9H, ArC(CH $_3$ ) $_3$ ), 1.24 (s, 9H, ArC(CH $_3$ ) $_3$ );  $m/z$  (EI): 277 (M-Me), 265 (M-HCN), 250 (M-HCN-Me), 105 ( $\text{C}_7\text{H}_7\text{N}$ ).

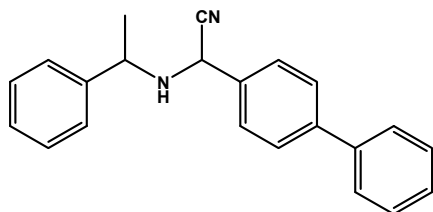
#### $\alpha$ -3,5-Di-*tert*-butylphenyl1- $\alpha$ -[(1-phenylethyl)amino]-acetonitrile (Table 1, entry 4)



$^1\text{H-NMR}$  (400MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$ 7.18-7.39 (m, 16H, ArH), 4.58 (s, 1H, CHCN), 4.29 (s, 1H, CHCN), 4.06 (q,  $J = 6.5\text{Hz}$ , 1H, CHCH $_3$ ), 3.72 (q,  $J = 6.5\text{Hz}$ , 1H, CHCH $_3$ ), 1.31 (d,  $J = 6.5\text{Hz}$ , 3H, CHCH $_3$ ), 1.26 (d,  $J = 6.5\text{Hz}$ , 3H, CHCH $_3$ ), 1.25 (bs, 36H, ArC(CH $_3$ ) $_3$ ).

Ar(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>; m/z (EI): 347 (M<sup>+</sup>), 321 (M-HCN), 306 (M-HCN-Me), 105 (C<sub>7</sub>H<sub>7</sub>N).

*α*-Biphenyl-1-*α*-[(1-phenylethyl)amino]-acetonitrile (Table 1, entry 5)



<sup>1</sup>H-NMR (400MHz, CD<sub>3</sub>CN) : δ7.20–7.62 (m, 28H, ArH), 4.74 (s, 1H, CHCN), 4.40 (s, 1H, CHCN), 4.10 (q, J = 6.5Hz, 1H, CHCH<sub>3</sub>), 3.84 (q, J = 6.5Hz, 1H, CHCH<sub>3</sub>), 1.32 (d, J = 6.5Hz, 3H, CHCH<sub>3</sub>), 1.29 (d, J = 6.5Hz, 3H, CHCH<sub>3</sub>); m/z (EI): 297 (M-Me), 285 (M-HCN), 270 (M-HCN-Me), 105 (C<sub>7</sub>H<sub>7</sub>N).

**Photocatalytic experiments.** The photocatalytic degradation of organic dyes by **1** was performed at ambient temperature (298 K). A 500 W xenon arc lamp surrounded with a water cooling system was fixed in the center of the reaction cell. The procedure is shown as follows: CP **1** (0.012 g) was dispersed into an aqueous solution (20 mL) containing either organic dye of MB, MO and RhB at (12 mg/L), followed by the addition of two drops of a hydrogen peroxide solution (30%). The mixture were illuminated under xenon arc lamp and stirred continuously by a magnetic stirrer. During the degradation process, the mixtures were withdrawn regularly from the reactor at different time intervals, and dispersed powders were removed by centrifugation. The separated samples were analyzed by UV/Vis spectrophotometry.

**X-ray crystallography.** Single crystal of **1** was mounted at the end of a glass fiber. Data collections were performed on a Bruker-AXS SMART CCD area detector diffractometer at 293(2) K using rotation scans with a scan width of 0.3° and Mo-Ka radiation (λ = 0.71073 Å). A summary of the crystallography data and structure refinement is given in Table S1. Empirical absorption corrections were carried out by utilizing the SADABS routine. The structures were solved by direct methods and refined by fullmatrix least squares refinements on the basis of F<sup>2</sup> (SHELXL-97). All non hydrogen atoms were anisotropically refined. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. The crystallographic calculations were conducted using the SHELXL-97 programs.<sup>3</sup>

## References

1. J.-M. Xiao and W. Zhang, *Inorg. Chem. Commun.*, 2009, **12**, 1175.
2. (a) Stout, D.; Black and L.; Matier, W. *J. Org. Chem.*, 1983, **48**, 5369; (b) Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.*, 1987, **109**, 908.
3. G. M. Sheldrick, SHELXL-97, Program for the refinement of the crystal structures, University of Göttingen, Göttingen, Germany, 1997.

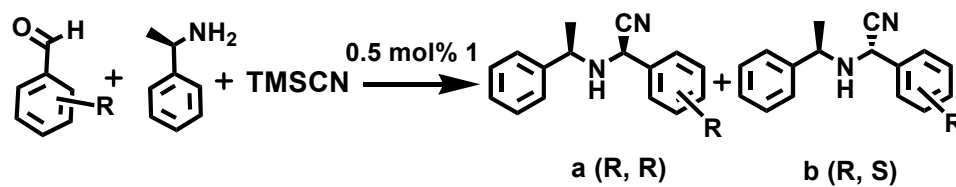
## B. Tables and Figures:

**Table S1.** Summary of the crystal data and structure refinement parameters of **1**.

Parameter	<b>1</b>
Chemical	C <sub>17</sub> H <sub>23</sub> N <sub>7</sub> OI <sub>2</sub> Cu <sub>3</sub>
Formula weight	785.84
Crystal system	triclinic
Space group	P-1
a (Å)	8.7985(8)
b (Å)	11.4531(11)
c (Å)	12.7944(12)
α (deg)	82.911(8)
β (deg)	70.969(8)
γ (deg)	88.819(8)
V (Å <sup>3</sup> )	1209.2(2)
Z	2
D <sub>Calcd</sub> (g cm <sup>-3</sup> )	2.158
μ(mm <sup>-1</sup> )	5.190
Reflections	4245
Unique	2114
R <sub>int</sub>	0.0852
Goodness-of-fit	1.029
R <sub>1</sub> <sup>a</sup> [I>2σ(I)]	0.0741
wR <sub>2</sub> <sup>b</sup> [I>2σ(I)]	0.1451
R <sub>1</sub> <sup>a</sup> [all refl.]	0.1715
wR <sub>2</sub> <sup>b</sup> [all refl.]	0.1861

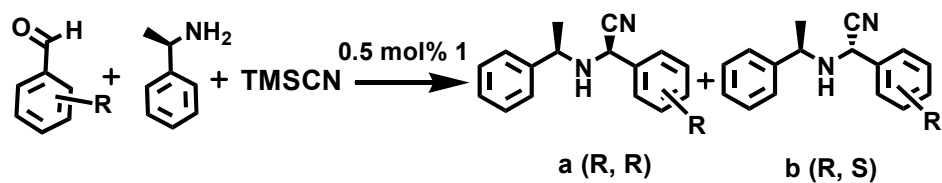
$$^a R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}; \quad ^b wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

**Table S2.** Asymmetric three component condensation catalyzed by **1** at 273 K.



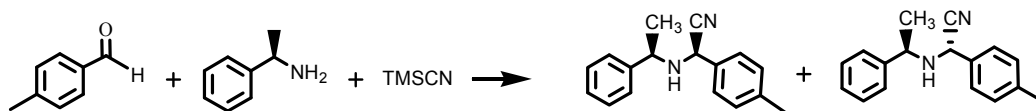
entry	substrate(R)	time (h)	yield (%)	a : b
1	H	4	99	67:33
2	4-methyl	4	95	67:33
3	4- <i>tert</i> -butyl	4	91	67:33
4	3,5-di- <i>tert</i> -butyl	4	93	68:32
5	4-phenyl	6	84	69:31

**Table S3.** Asymmetric three component condensation catalyzed by **1** at 298 K.



entry	substrate(R)	time (h)	yield (%)	a : b
1	H	1	99	67:33
2	4-methyl	1	96	68:32
3	4- <i>tert</i> -butyl	1	94	69:31
4	3,5-di- <i>tert</i> -butyl	2	93	69:31
5	4-phenyl	3	87	68:32

**Table S4.** Comparison of the effect of different catalysts on the formation of the  $\alpha$ -aminonitriles at 298 K<sup>a</sup>.



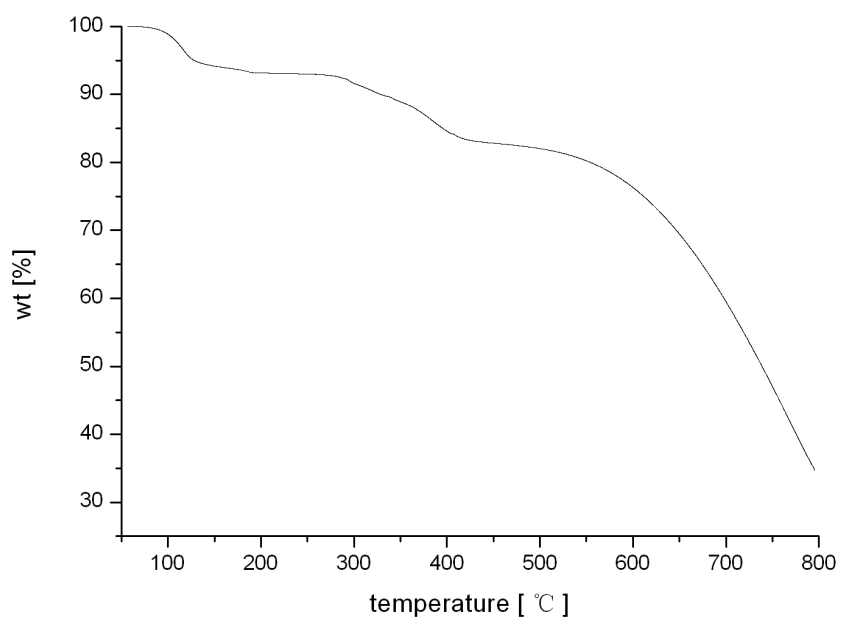
catalyst	catalyst load (mol %)	time (h)	yield (%) <sup>b</sup>
<b>1</b>	0.5	1	96
CuI	10	3	82
[Cu <sup>II</sup> (SalHImCy)](NO <sub>3</sub> ) <sub>2</sub>	0.5	3	87
[Cu <sup>II</sup> (SalHImCy)](NO <sub>3</sub> ) <sub>2</sub> / CuI	0.5/5	3	74
I <sub>2</sub>	10	3	64
Without Catalyst	—	3	12

<sup>a</sup>p-tolualdehyde (1 mmol), (R)-(+)-1-phenylethylamine (1 mmol), TMSCN (1.5 mmol) and 2 mL CD<sub>3</sub>CN, 0.5 mol % of **1**, sealed in a screw cap vial were stirred at 298 K.

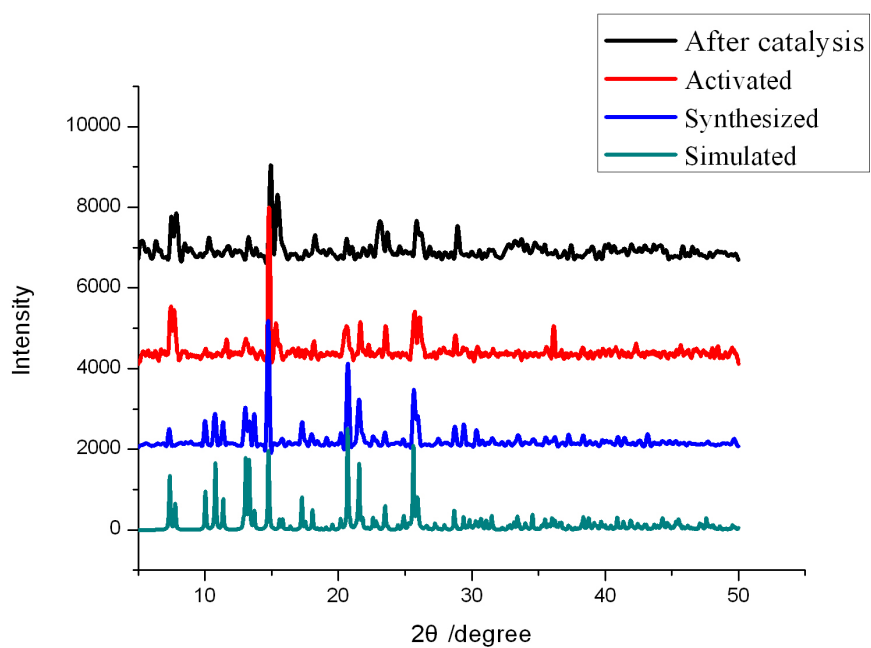
<sup>b</sup>% yields were determined by GC.



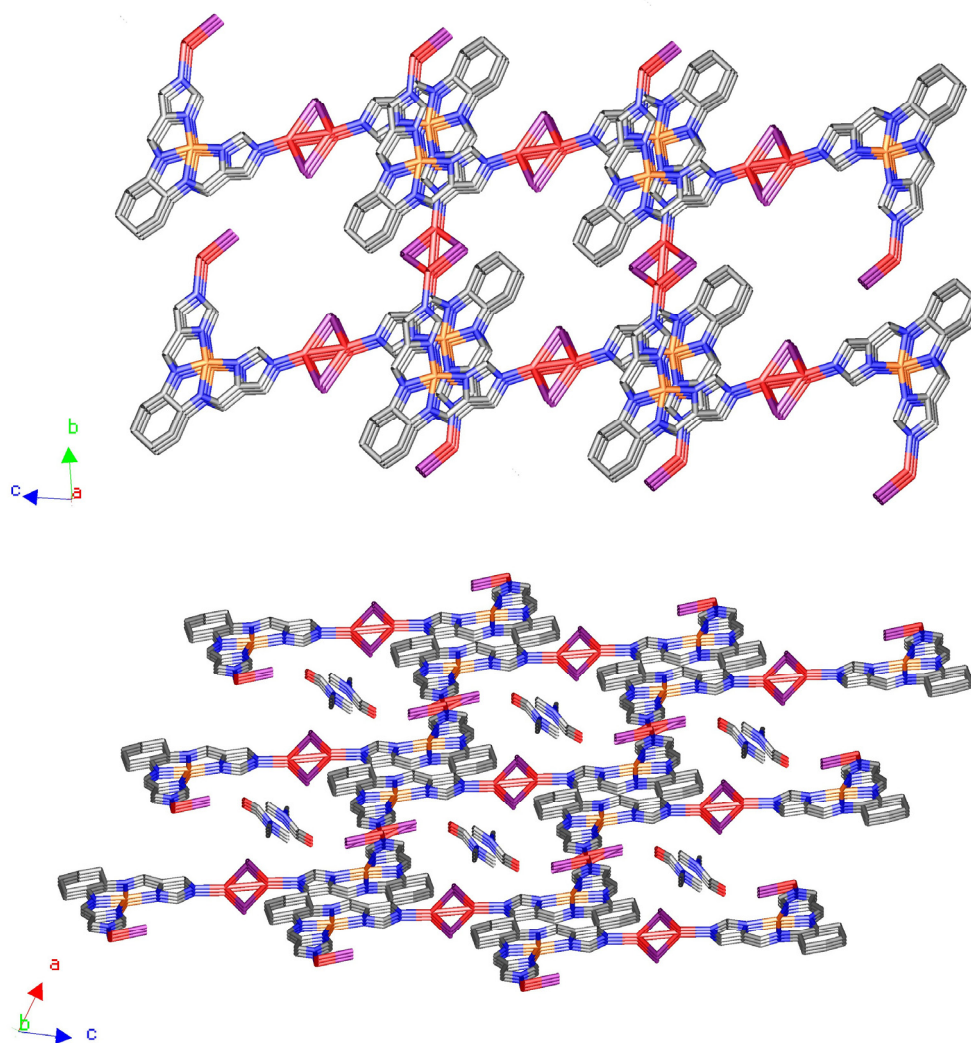
**Fig. S1** Thermogravimetric analysis of **1**.



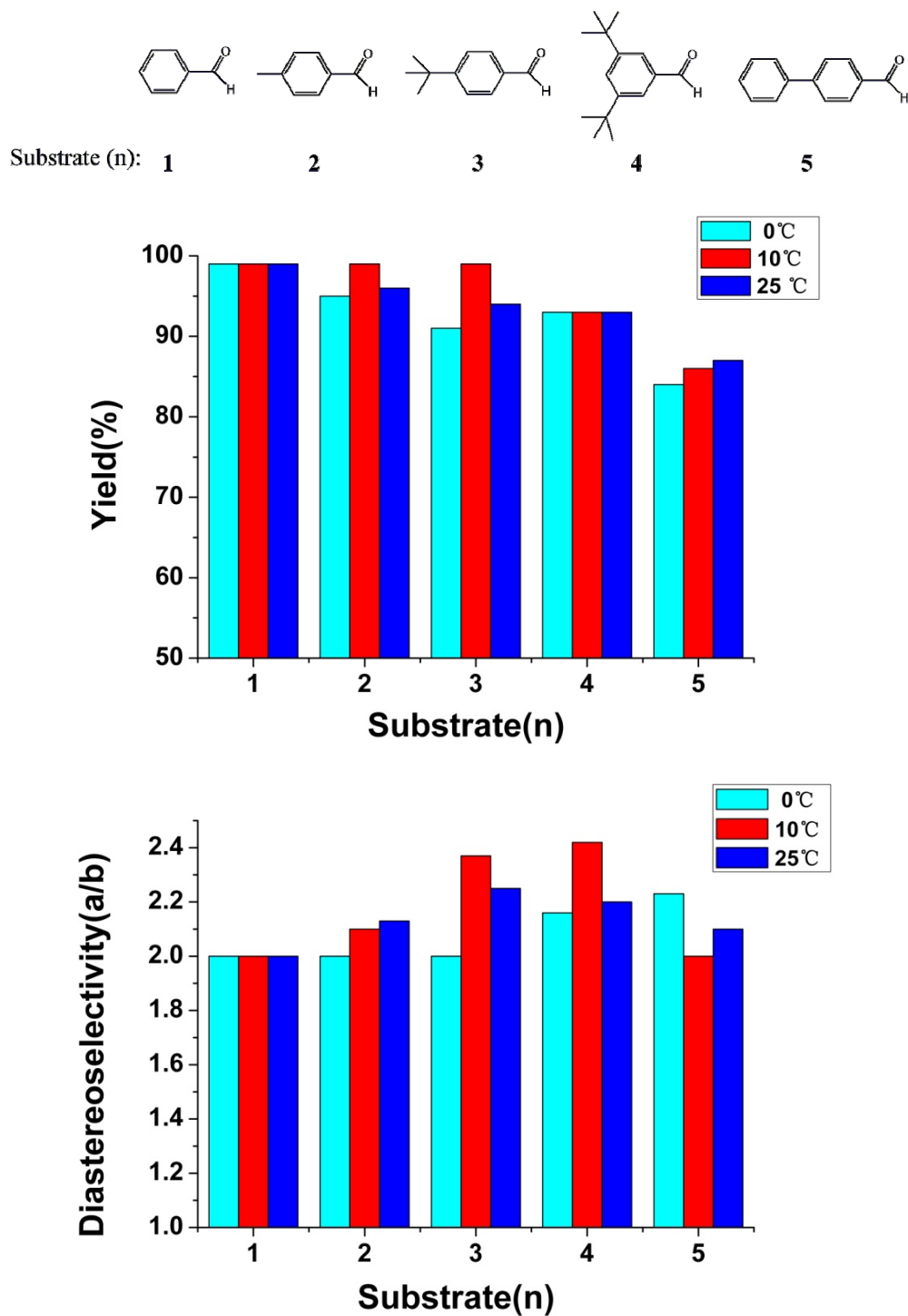
**Fig. S2** The PXRD patterns of **1** under different conditions.



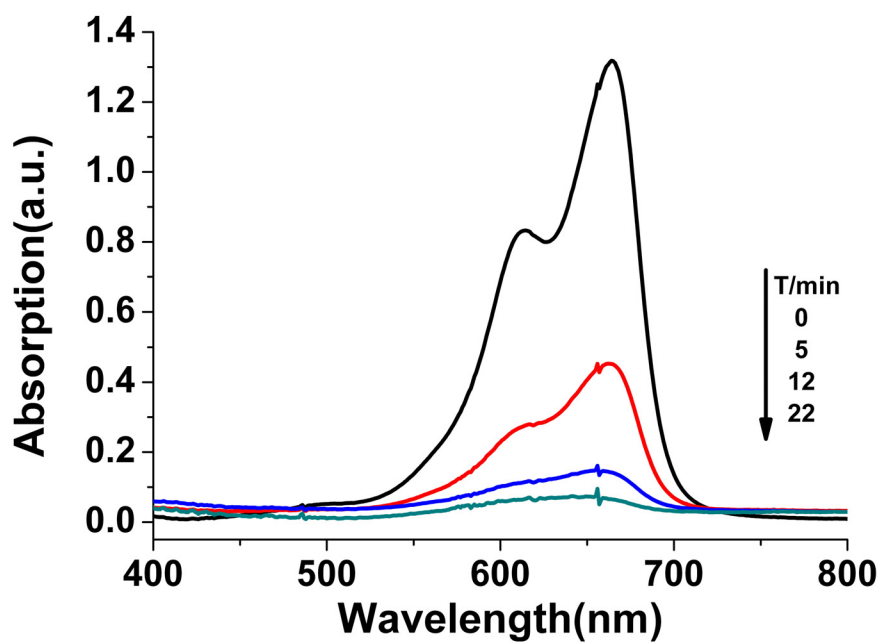
**Fig. S3** X-ray analysis of the stacking of 1D zigzag chains along *a*-axis and *b*-axis.



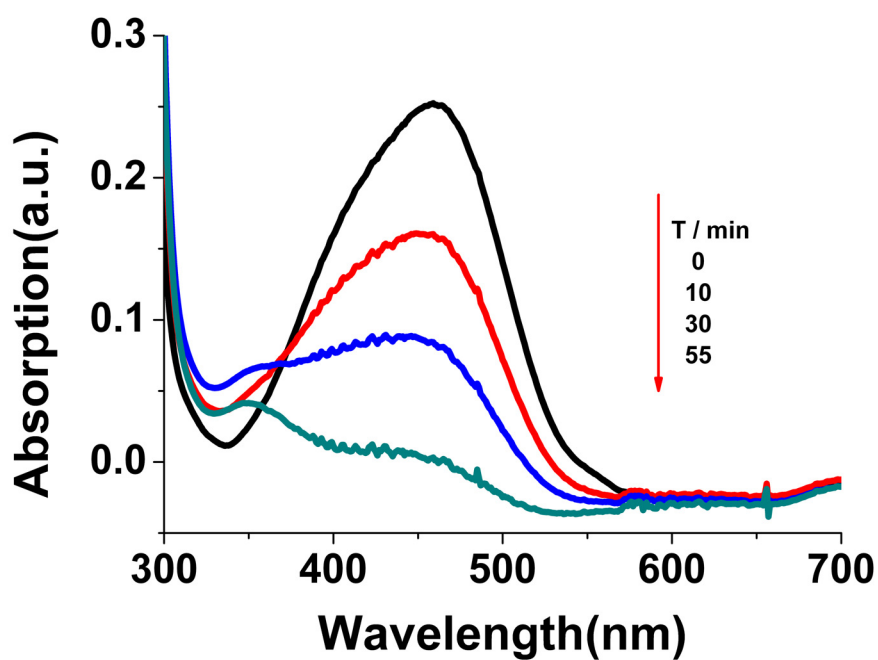
**Fig. S4.** % yield (upper) and diastereoselectivity (lower) of three-component strecker reaction catalyzed by **1** at different temperatures.



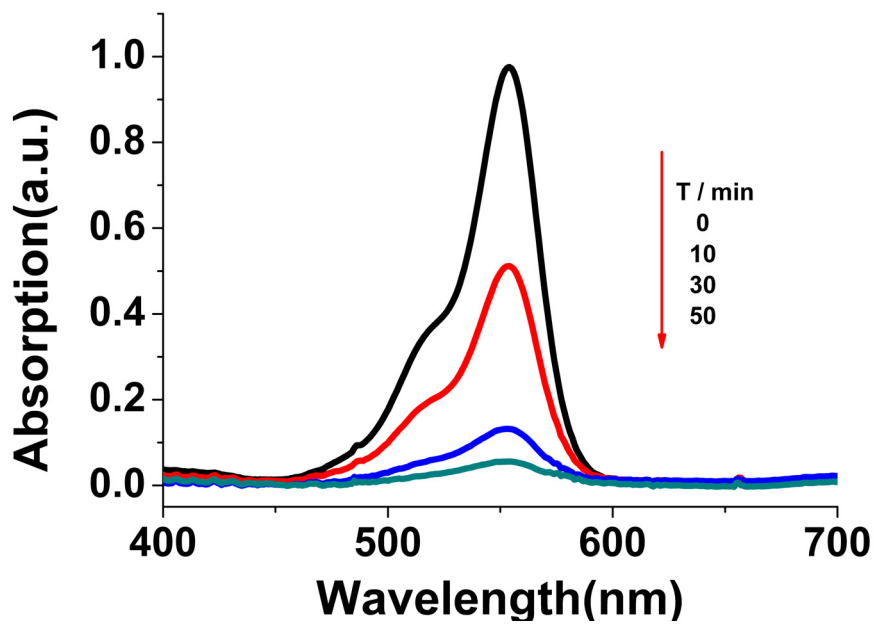
**Fig. S5.** Changes of the UV/Vis spectra of MB in the presence of **1** and light illumination from 0 to 22 mins.



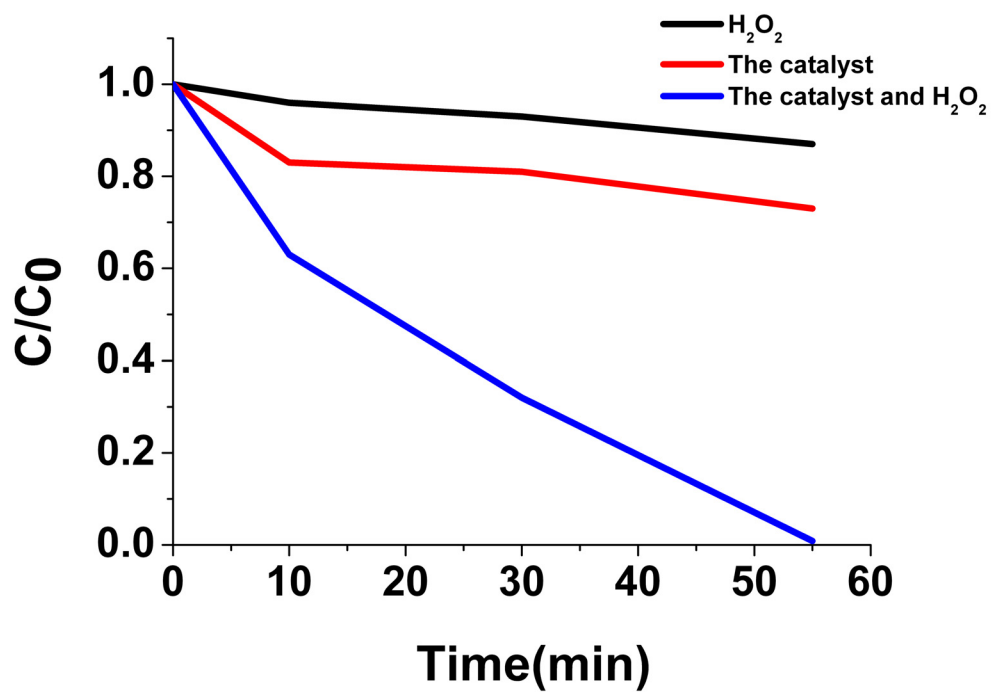
**Fig. S6.** Changes of the UV/Vis spectra of MO in the presence of **1** and light illumination from 0 to 55 mins.



**Fig. S7.** Changes of the UV/Vis spectra of RhB in the presence of **1** and light illumination from 0 to 50 mins.

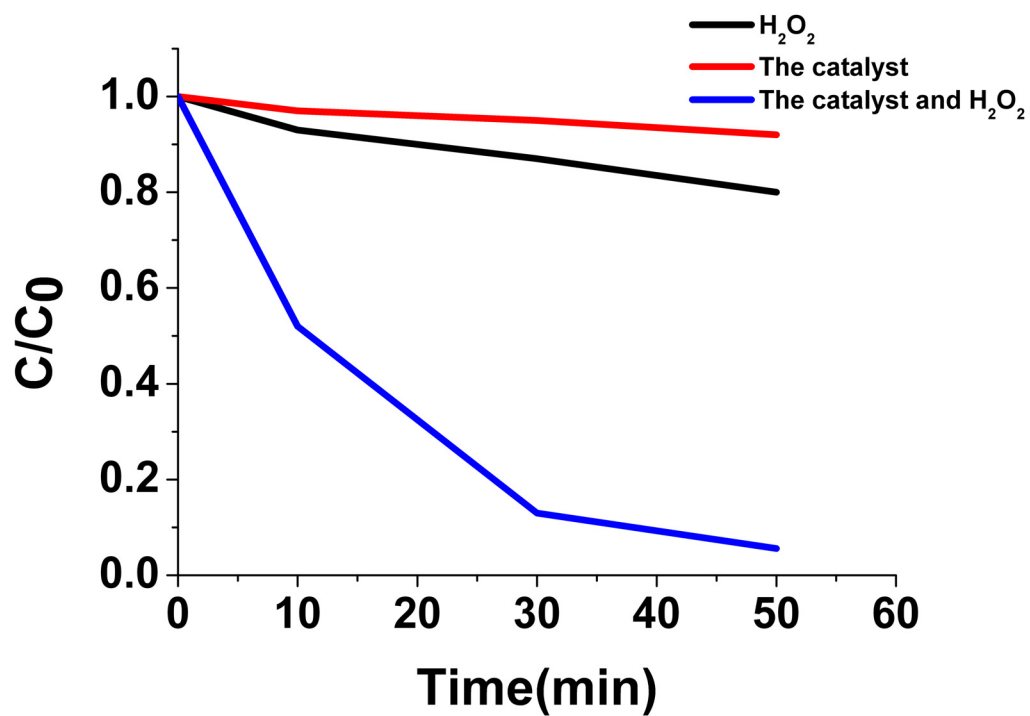


**Fig. S8.** Photodegradation of MO dye over different conditions.

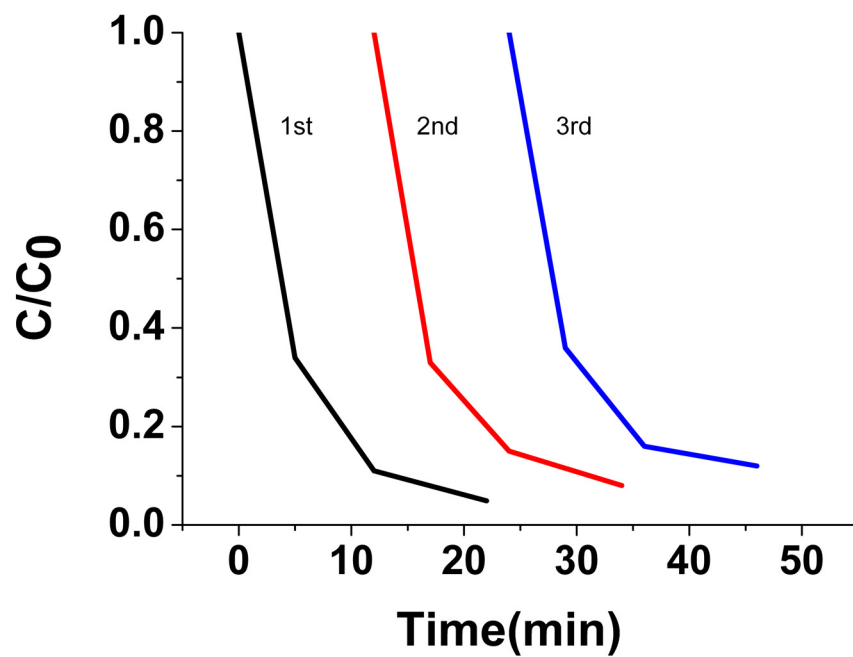




**Fig. S9.** Photodegradation of RB dye over different conditions.



**Fig. S10** Recycling test of **1** for MB photodegradation under visible light irradiation.



**Fig. S11** The PXRD patterns of **1** for photodegradation of MB after each cycle.

