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Supplementary information

Synthesis and Property of a Novel Cu(II)−pyridineoxazoline Containing Polymeric Catalyst for Asymmetric Diels−Alder Reaction

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Experimental Methods

Materials

2-acetylpyridine (98%, J&K Scientific Ltd.), hydrogen peroxide (H_2O_2, 30%, AR, Beijing Chemical Co.), 4-nitrobenzaldehyde (98%, J&K Scientific Ltd.), 4-methoylbenzadehyde (98%, J&K Scientific Ltd.), and 2-naphthaldehyde (98%, J&K Scientific Ltd.) were used as purchased. Benzaldehyde (98%, J&K Scientific Ltd.) was distilled before used.

Substrate synthesis.

2-acetylpyridine N-oxide. 2-acetylpyridine (10.9 g, 90 mmol) and H_2O_2 (30%, 10.9 g, 96 mmol) were dissolved in acetic acid (45 mL). The mixture was heated to 70 ºC for 24 hours. After cooling to room temperature and removal of solvent under vacuum, the residue was obtained as colorless crystals by column chromatography with ethyl acetate as eluent. Yield: 75%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 2.82 (s, 3H, -COC*H*$_3$), 7.29-7.41 (m, 2H, 3, 4-*H* of pyridine), 7.69-7.73 (dd, 1H, 5-*H* of pyridine), 8.19-8.23 (dd, 1H, 2-*H* of pyridine).

(E)-2-cinnamoylpyridine N-oxide (4a). 2-acetylpyridine *N*-oxide (1.08g, 7.9 mmol) and benzaldehyde (1.68 g, 15.8 mmol) were dissolved in methanol (40 mL), and the mixture was cooled to 0 ºC. Then, 1M potassium hydroxide (1.6 mL, 1.6 mmol) was added into the mixture dropwise. The reaction mixture was stirred at this temperature until completion (TLC). It was then neutralized with 2M HCl (0.78 mL, 1.6 mmol), diluted with water (80 mL) and extracted with 3×60 mL portions of CH_2Cl_2. The organic phase was dried with Na_2SO_4, filtered and concentrated under reduced pressure. The product was isolated as yellow solids by column chromatography with ethyl acetate as eluent. Yield: 45%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.32-7.42 (m, 5H, 3, 4-*H* of pyridinyl group, 3, 4, 5-*H* of benzyl group), 7.61-7.72 (m, 3H, 5-*H* of pyridinyl group, 2, 6-*H* of benzyl group), 7.73-7.84 (m, 2H, *H* of vinyl group), 8.22-8.26 (d, 1H, 2-*H* of pyridinyl group). ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 124.3, 125.6, 127.3, 127.7, 128.8, 128.9, 130.8, 134.6, 140.5, 144.3, 147.3, 186.3.

(E)-2-(3-(4-nitrophenyl)acryloyl)pyridine N-oxide (4b). 4b was prepared as yellow solids with a similar method. Yield: 80%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.38-7.48 (m, 2H, 3, 4-*H* of pyridinyl group), 7.76-7.81 (m, 3H, 5-*H* of pyridinyl group, m-*H* to–NO_2 in benzyl group), 7.82-7.91 (m, 2H, *H* of vinyl group), 8.14-8.21 (m, 3H, 2-*H* of pyridinyl group. ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 124.1, 125.9, 127.7, 128.0, 128.3, 129.3, 140.1, 140.5, 140.8, 146.7, 148.8, 185.8.

(E)-2-(3-(4-methoxyphenyl)acryloyl)pyridine N-oxide (4c). 4c was prepared as yellow solids with a similar method. Yield: 42%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 6.88-6.92 (d, 2H, o-*H* to–OCH_3 in benzyl group), 7.33-7.41 (m, 2H, 3, 4- *H* of pyridinyl group), 7.57-7.63 (m, 3H, *H* of vinyl group, m-*H*to–OCH_3 in benzyl group), 7.65-7.69 (m, 1H, 5-*H* of pyridinyl group), 7.74-7.80 (d, 1H, *H* of vinyl group), 8.22-8.26 (dd, 1H, 2-*H* of pyridinyl group). ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 55.4, 114.4, 122.1, 125.6, 127.2, 127.4, 127.5, 130.7, 140.5, 144.5, 147.5, 162.0, 186.2.

(E)-2-(3-(naphtha-2-yl)acryloyl)pyridine N-oxide (4d). 4d was prepared as yellow solids with a similar method. Yield: 85%. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.35-7.45 (m, 2H, 3, 4-*H* of pyridinyl group), 7.48-7.55 (m, 2H, *H* of naphthyl group), 7.70-7.75 (dd, 1H, 5-*H* of pyridinyl group), 7.77-7.90 (m, 5H, *H* of naphthyl group), 7.95-8.07 (m, 2H, *H* of vinyl gourp), 8.27-8.32 (dd, 1H, 2-*H* of pyridinyl group). ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 124.1, 124.4, 126.2, 126.7, 127.4, 127.5, 127.7, 127.8, 128.7, 128.7, 131.0, 132.2, 133.3, 134.6, 140.5, 144.6, 147.3, 186.1.

D−A Reaction Products

Products reacted from 4a (endo-5a and exo-5a). Mixture analysis: Chiral HPLC analysis (Daicel CHIRALPAK AD-H, isopropanol/hexane = 15/85, 1.0 mL/min, 25 ºC, UV detector 254 nm). t_R(exo) = 9.7 min, t_R(exo) = 10.7 min, t_R(endo minor) = 11.5 min, t_R(endo major) = 12.4 min.

5a (42.3% ee, 97/3 endo/exo): ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.53-1.69 (m, 1H), 1.85-2.01 (d, 1H), 3.09 (s, 1H), 3.33-3.36 (d, 1H), 3.40 (s, 1H), 4.52-4.58 (dd, 1H), 5.84-5.90 (dd, 1H), 6.43-6.49 (dd, 1H), 7.10-7.17 (m, 1H), 7.18-7.42 (m, 6H), 7.38-7.43 (dd, 1H), 8.13-8.16 (dd, 1H).

Products reacted from 4b (endo-5b and exo-5b). Mixture analysis: Chiral HPLC analysis (Daicel CHIRALPAK AD-H, isopropanol/hexane = 20/80, 1.0 mL/min, 25 ºC, UV detector 254 nm). t_R(exo) = 17.5 min, t_R(endo minor)

= 20.8 min, t_R(endo major) = 30.9 min.

5b (52.3% ee, 96/4 endo/exo): ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.60-1.66 (m, 1H), 1.96-2.05 (d, 1H), 3.13 (s, 1H), 3.36 (s, 1H), 3.40-3.46 (s, 1H), 4.45-4.48 (dd, 1H), 5.85-5.89 (dd, 1H), 6.47-6.51 (dd, 1H), 7.32-7.43 (m, 3H), 7.42-7.50 (m, 2H), 8.10-8.14 (dd, 2H), 8.14-8.16 (t, 1H).

Products reacted from 4c (endo-5c and exo 5c). Mixture analysis: Chiral HPLC analysis (Daicel CHIRALPAK AD-H, isopropanol/hexane = 10/90, 1.0 mL/min, 25 ºC, UV detector 254 nm). t_R(exo) = 22.0 min, t_R(exo) = 26.5 min, t_R(endo minor) = 29.7 min, t_R(endo major) = 31.5 min.

5c (45.2% ee, 98/2 endo/exo):^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.52-1.60 (m, 1H), 1.86-1.95 (d, 1H), 3.04 (s, 1H), 3.24-3.30 (d, 1H), 3.36 (s, 1H), 3.79 (s, 3H), 4.42-4.48 (dd, 1H), 5.84-5.88 (dd, 1H), 6.42-6.47 (dd, 1H), 6.75-6.90 (d, 2H), 7.25-7.36 (m, 4H), 7.38-7.43 (dd, 1H), 8.16-8.19 (d, 1H).

Products reacted from 4d (endo-5d and exo 5d). Mixture analysis: Chiral HPLC analysis (Daicel CHIRALPAK AD-H, isopropanol/hexane = 3/97, 1.0 mL/min, 25 ºC, UV detector 254 nm). t_R(exo) = 26.7 min, t_R(exo) = 29.9 min, t_R(endo minor) = 34.0 min, t_R(endo major) = 36.4 min.

5d (44.8% ee, 97/3 endo/exo): ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.58-1.64 (dd, 1H), 1.94-2.02 (d, 1H), 3.20 (s, 1H), 3.40 (s, 1H), 3.48-3.54 (d, 1H), 4.55-4.62 (dd, 1H), 5.88-5.94 (dd, 1H), 6.48-6.54 (dd, 1H), 7.29-7.52 (m, 6H), 7.74-7.82 (m, 4H), 8.16-8.26 (d, 1H).

Table S1. Summary of preparing polymer−Cu(II) complex under various conditions[a]

Entry	CuX_2	Solvent	$([PyOx]:[Cu])_0$[b]	$([PyOx]:[Cu])_t$[c]	Solubility(in THF)
1	$Cu(OTf)_2$	THF	1: 2	1:1.00	+
2	$Cu(OTf)_2$	THF	1: 1.5	1:1.01	+
3	$Cu(OTf)_2$	THF	1: 0.75	1:0.76	+−
4	$Cu(OTf)_2$	THF	1: 0.5	1:0.48	+−
5	$Cu(OTf)_2$	THF	1: 0.25	1:0.22	−

[a] All experiments were carried out under nitrogen at room temperature; +: soluble, +−: partially soluble, −: insoluble; [b] The molar ratio of added $Cu(OTf)_2$ and PyOx groups of **P1**; [c] The molar ratio of $Cu(OTf)_2$ and PyOx groups determined by gravimetric analysis.

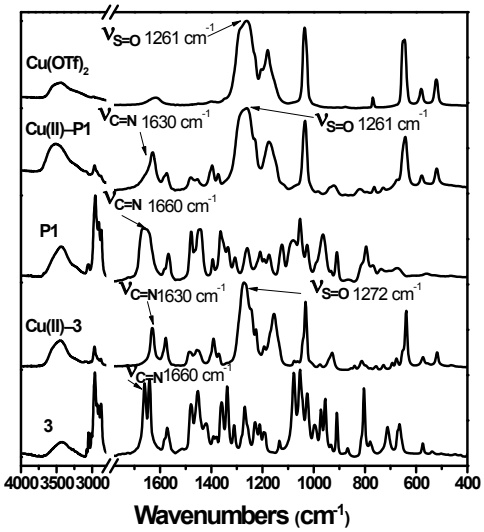

Figure S1. FT-IR spectra of **3, Cu(II)−3, P1, Cu(II)−P1** and **$Cu(OTf)_2$**. All samples were characterized in solid state as KBr plates.

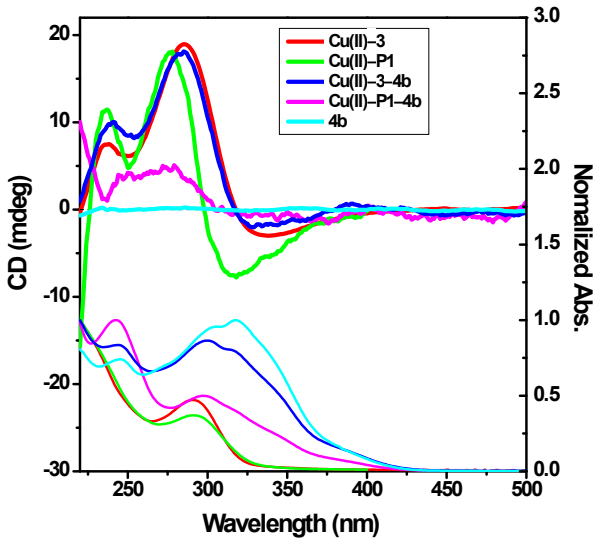

Figure S2. UV-Vis absorption and CD spectra of **Cu(II)−3**, **Cu(II)−P1**, **Cu(II)−3−4b** and **Cu(II)−P1−4b** in THF solution at 25 °C. 2 molar equivalent **4b** was added to **Cu(II)−3** and **Cu(II)−P1** with a concentration of 9×10^{-5} mol·L^{-1}. The UV-Vis spectra were normalized at the highest peaks.

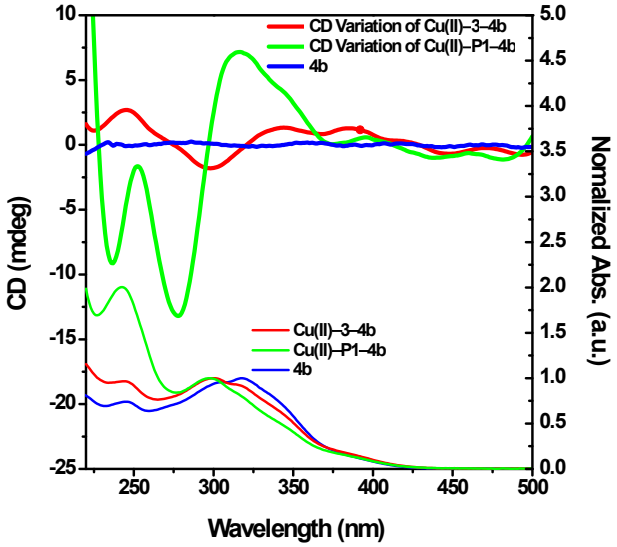

Figure S3 UV-Vis absorption spectra of **Cu(II)−3−4b**, **Cu(II)−P1−4b**, and **4b** in THF solution at 25 °C (lower). CD spectra of **Cu(II)−3−4b** and **Cu(II)−P1−4b** obtained after the subtraction of those of the corresponding complexes (upper). UV-Vis absorption spectra were normalized at 300 nm.

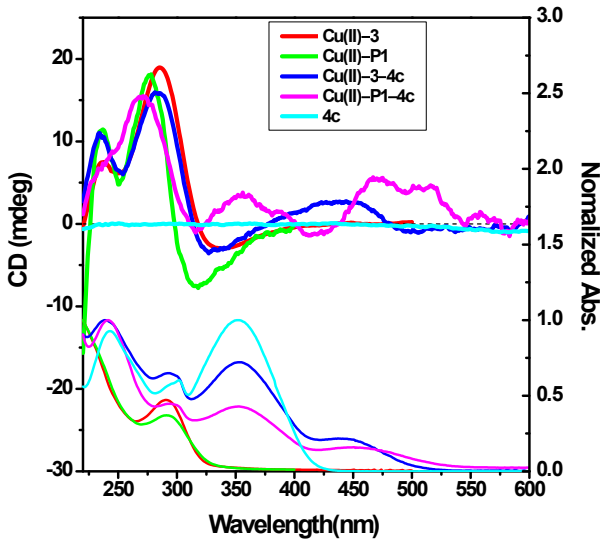

Figure S4. UV-Vis absorption and CD spectra of **Cu(II)−3**, **Cu(II)−P1**, **Cu(II)−3−4c** and **Cu(II)−P1−4c** in THF solution at 25 °C. 2 molar equivalent **4c** was added to **Cu(II)−3** and **Cu(II)−P1** with a concentration of 9×10^{-5} mol·L^{-1}. The UV-Vis spectra were normalized at the highest peaks.

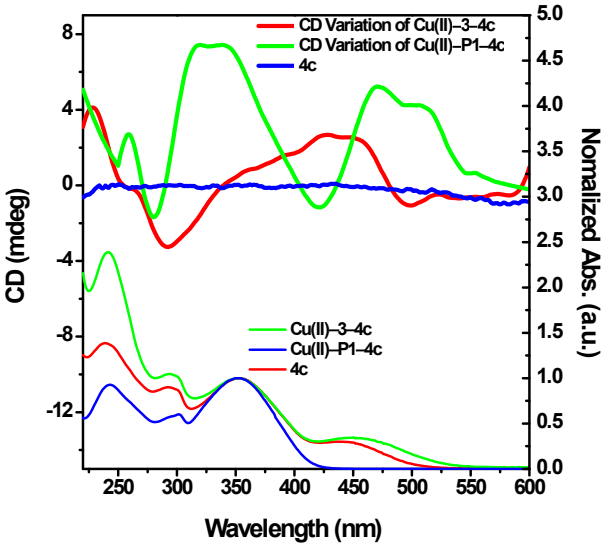

Figure S5 UV-Vis absorption spectra of **Cu(II)−3−4c**, **Cu(II)−P1−4c**, and **4c** in THF solution at 25 °C (lower). CD spectra of **Cu(II)−3−4c** and **Cu(II)−P1−4c** obtained after the subtraction of those of the corresponding complexes (upper). UV-Vis absorption spectra were normalized at 350 nm.

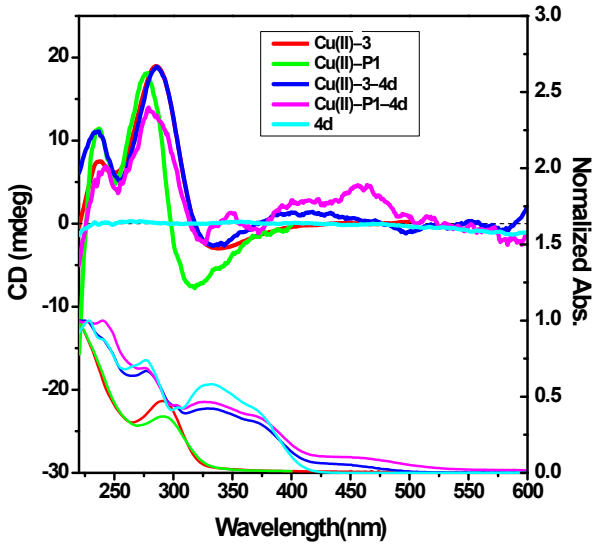

Figure S6. UV-Vis absorption and CD spectra of **Cu(II)−3**, **Cu(II)−P1**, **Cu(II)−3−4d** and **Cu(II)−P1−4d** in THF solution at 25 °C. 2 molar equivalent **4d** was added to **Cu(II)−3** and **Cu(II)−P1** with a concentration of 9×10^{-5} mol·L^{-1}. The UV-Vis spectra were normalized at the highest peaks.

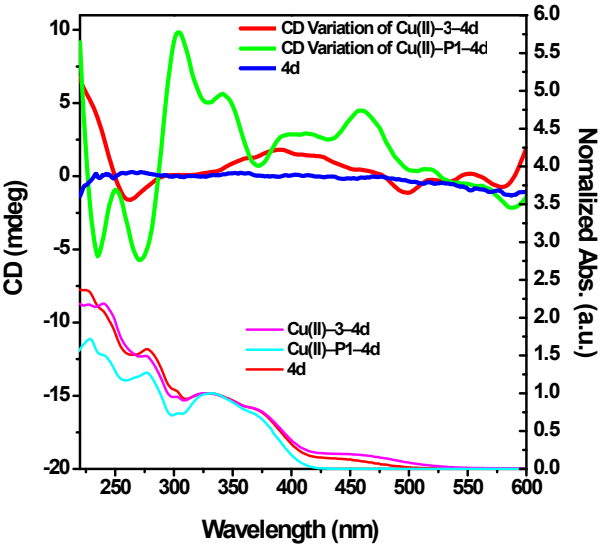

Figure S7 UV-Vis absorption spectra of **Cu(II)−3−4d**, **Cu(II)−P1−4d**, and **4d** in THF solution at 25 °C (lower). CD spectra of **Cu(II)−3−4d** and **Cu(II)−P1−4d** obtained after the subtraction of those of the corresponding complexes (upper). UV-Vis absorption spectra were normalized at 300 nm.