Electronic Supporting Information

Asymmetric Alkylation of Remote C(sp³)–H Bonds by Merging Proton-Coupled Electron Transfer with Chiral Lewis Acid Catalysis

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1. General Information

All reactions were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Light-induced catalytic reactions were performed in 10 mL Schlenk tubes at 27 °C under an atmosphere of argon and under irradiation with two 24 W blue LED lamps ($\lambda_{\text{max}} = 450$ nm; company: Hongchangshaoming, website: http://hongchang-led.taobao.com) as light sources. Solvents were distilled under argon from calcium hydride (CH$_3$CN, CH$_2$Cl$_2$) or sodium/benzophenone (THF, toluene). The chiral Lewis acid catalyst $\Lambda$-RhO$_{1,2}$ benzamides 1a–p,$^{3,4,5}$ $\alpha,\beta$-unsaturated imidazoles 2a–m,$^{6}$ $\alpha,\beta$-unsaturated pyrazole 2n,$^{6}$ photocatalysts PC1–3,$^{4}$ and phosphate base B1–3$^{4}$ were synthesized according to the published procedures. All others reagents were purchased from commercial suppliers (TCI, Aldrich, Alfa and J&K) and used without further purification. Flash column chromatography was performed with silica gel (300-400 mesh, pH = 6.7–7.0). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM (400 MHz) or Bruker AM (500 MHz) spectrometer at ambient temperature. NMR standards were used as follows: CDCl$_3$ = 7.26 ppm ($^1$H NMR), 77.0 ppm ($^{13}$C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 T FT-MS instrument using ESI technique. Optical rotations were measured on Anton Paar MCP 500 polarimeter at concentrations of 1.0 g/100 mL. UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 in a 10.0 mm quartz cuvette. Enantiomeric excess of the products were determined by HPLC analysis on chiral stationary phases.

2. Synthesis of the Substrates and Racemic Products

2.1 Synthesis of the Benzamide Substrates

Benzamide substrates 1a, 1b, 1d, 1f, 1g, 1h, and 1n were synthesized according to published procedures.$^{4,5}$ Other benzamides 1c, 1e, 1i–m, and 1o–p were synthesized according to the reported procedures with some modifications.$^{3–5}$

The experimental data of compounds 1c, 1e, 1i–m, and 1o–p are shown below.

![Image of synthesis reaction]

2-Methoxy-N-(4-methylpentyl)benzamide (1c)

A solution of 4-methylpentan-1-amine$^4$ (1.01 g, 10.0 mmol), 2-methoxybenzoyl chloride (1.87 g, 11.0 mmol), and triethyl amine (2.91 mL, 21.0 mmol) in CH$_2$Cl$_2$ (25 mL) was stirred at room temperature for 4 h. The reaction mixture was diluted with CH$_2$Cl$_2$ (30 mL), washed with 1 M HCl (2 x 30 mL) and water (2 x 30 mL), then dried over Na$_2$SO$_4$ and concentrated. The crude
product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1e (1.88 g, 8.0 mmol, yield: 80%) as a white solid.

1H NMR (400 MHz, CDCl3): δ (ppm) 8.21 (dd, J = 7.8, 1.8 Hz, 1H), 7.85 (m, 1H), 7.43 (ddd, J = 8.3, 7.3, 1.9 Hz, 1H), 7.08 (td, J = 7.8, 1.0 Hz, 1H), 7.03–6.93 (d, J = 8.4 Hz, 1H), 3.96 (s, 3H), 3.44 (td, J = 7.1, 5.7 Hz, 2H), 1.69–1.52 (m, 3H), 1.28 (dt, J = 11.2, 6.9 Hz, 2H), 0.91 (d, J = 6.6 Hz, 6H).

13C NMR (101 MHz, CDCl3): δ (ppm) 165.0, 157.3, 132.4, 132.1, 121.7, 121.1, 111.2, 55.8, 39.8, 35.2, 27.6, 27.3, 22.4.

IR (film): ν (cm⁻¹) 2953, 2868, 1652, 1599, 1533, 1483, 1466, 1366, 1297, 1238, 1182, 1161, 1104, 1022, 756.

HRMS (ESI, m/z) calcd for C₁₄H₂₂NO₂ (M+H)⁺: 236.1645, found: 236.1644

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**N-(3-Cyclobutylpropyl)-4-methoxybenzamide (1e)**

To a solution of acetonitrile (0.41 g, 10.0 mmol) in tetrahydrofuran (THF, 25 mL) at -78 °C was added lithium diisopropylamide (LDA, 2.0 M in n-hexane, 5.0 mL, 10.0 mmol) dropwise over 10 min. The reaction mixture was stirred at -78 °C for 40 min. 1-(Bromomethyl)cyclobutane (1.63 g, 11.0 mol) in THF (5 mL) was added dropwise. The resulting solution was stirred at room temperature for 12 h. An aqueous solution of NH₄Cl (sat., 20 mL) was added. The resulting mixture was extracted with CH₂Cl₂ (2x30 mL). The organic layers were combined, dried over Na₂SO₄ and filtered. The solvent was evaporated under reduced pressure to afford 3-cyclobutylpropanenitrile (0.92 g, 8.4 mmol, yield: 84%), which was used without further purification.

Subsequently, a dry round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with LiAlH₄ (0.67 g, 17.6 mmol) and diethyl ether (42 mL). The suspension was stirred at 0 °C, into which 3-cyclobutylpropanenitrile (0.92 g, 8.4 mmol) in diethyl ether (10 mL) was added dropwise. The mixture was heated at reflux for 3 h, cooled down to 0 °C, quenched with NaOH (10% in water, 5 mL), then dried over excess MgSO₄. After filtration and evaporation of the solvent, 3-cyclobutylprop-1-amine was obtained. To a solution of the produced 3-cyclobutylprop-1-amine in CH₂Cl₂ (21 mL), 4-methoxybenzoyl chloride (1.57 g, 9.2 mmol) and triethyl amine (2.44 mL, 17.6 mmol) were added. The mixture was stirred at room temperature for 4 h, then diluted with CH₂Cl₂ (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1e (1.36 g, 5.5
mmol, yield: 65% over two steps) as a white solid.

\[^1\text{H}\text{ NMR (500 MHz, CDCl}_3\text{): }\delta\text{ (ppm) 7.81–7.63 (m, 2H), 7.01–6.80 (m, 2H), 6.17 (s, 1H), 3.84 (s, 3H), 3.39 (dd, }J = 12.8, 6.9\text{ Hz, 2H), 2.37–2.18 (m, 1H), 2.10–1.97 (m, 2H), 1.89–1.73 (m, 2H), 1.64–1.55 (m, 2H), 1.54–1.39 (m, 4H).}\]

\[^{13}\text{C NMR (125 MHz, CDCl}_3\text{): }\delta\text{ (ppm) 166.9, 161.9, 128.6, 127.1, 113.6, 55.3, 39.9, 35.7, 34.2, 28.3, 27.4, 18.3.}\]

IR (film): \(\nu\text{ (cm}^{-1}\text{) 2931, 2859, 1632, 1607, 1546, 1504, 1462, 1441, 1299, 1255, 1178, 1032, 844, 768, 608.}\)

HRMS (ESI, \(m/z\) calcd for C\(_{15}\)H\(_{22}\)NO\(_2\) (M+H): 248.1645, found: 248.1645.

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\text{4-Methoxy-N-(2,2,4-trimethylpentyl)benzamide (1i)}
\]

A solution of 2,2,4-trimethylpentan-1-amine\(^{5c}\) (1.55 g, 12.0 mmol), 4-methoxybenzoyl chloride (1.70 g, 13.2 mmol), triethyl amine (3.49 mL, 25.2 mmol) in CH\(_2\)Cl\(_2\) (30 mL) was stirred at room temperature for 4 h. The resulting mixture was diluted with CH\(_2\)Cl\(_2\) (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), then dried over Na\(_2\)SO\(_4\) and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1i (2.00 g, 7.6 mmol, yield: 63%) as a white solid.

\[^1\text{H NMR (500 MHz, CDCl}_3\text{): }\delta\text{ (ppm) 7.72 (d, }J = 8.8\text{ Hz, 2H), 6.92 (d, }J = 8.8\text{ Hz, 2H), 6.08 (s, 1H), 3.84 (s, 3H), 3.28 (d, }J = 6.2\text{ Hz, 2H), 1.85–1.64 (m, 1H), 1.22 (d, }J = 5.4\text{ Hz, 2H), 0.96 (s, 6H), 0.94 (d, }J = 6.7\text{ Hz, 6H).}\]

\[^{13}\text{C NMR (125 MHz, CDCl}_3\text{): }\delta\text{ (ppm) 167.1, 162.0, 128.5, 127.3, 113.7, 55.3, 50.0, 48.9, 35.2, 25.5, 25.4, 24.0.}\]

IR (film): \(\nu\text{ (cm}^{-1}\text{) 2956, 2869, 1637, 1607, 1546, 1505, 1466, 1366, 1310, 1254, 1176, 1032, 843, 767.}\)

HRMS (ESI, \(m/z\) calcd for C\(_{16}\)H\(_{26}\)NO\(_2\) (M+H): 264.1958, found: 264.1957.

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\text{A solution of 2,2,4-trimethylpentan-1-amine, ethyl chloroacetate, and triethyl amine in CH}_2\text{Cl}_2\text{ was stirred at room temperature for 4 h. The resulting mixture was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1j (2.00 g, 7.6 mmol, yield: 63%) as a white solid.}\]
N-(1-Isobutylcyclohexyl)methyl)-4-methoxybenzamide (1j)

To a solution of cyclohexanecarbonitrile (2.73 g, 25.0 mmol) in THF (62 mL) at -78 °C was added LDA (2.0 M in n-hexane, 12.5 mL, 25.0 mmol) dropwise over 10 min. The mixture was stirred at -78 °C for 40 min. 1-Bromo-2-methylpropane (3.74 g, 27.5 mmol) in THF (8 mL) was added dropwise. The resulting solution was stirred at room temperature for 12 h. An aqueous solution of NH₄Cl (sat., 40 mL) was added. The resulting mixture was extracted with CH₂Cl₂ (2 x 40 mL). The combined organic layers were washed with water (2 x 40 mL), then dried over Na₂SO₄ and filtered. The solvent was evaporated under reduced pressure to afford 1-isobutylcyclohexanecarbonitrile (3.30 g, 20.0 mmol, yield: 80%), which was used without further purification.

Subsequently, a dry round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with LiAlH₄ (0.96 g, 25.2 mmol) and diethyl ether (60 mL). The suspension was stirred at 0 °C, into which 1-isobutylcyclohexanecarbonitrile (1.98 g, 12.0 mmol) in diethyl ether (10 mL) was added dropwise. The mixture was heated at reflux for 3 h, cooled down to 0 °C, quenched with NaOH (10% in water, 4 mL) at 0 °C, then dried over excess MgSO₄. After filtration and evaporation of the solvent, (1-isobutylcyclohexyl)methanamine was obtained.

To a solution of the produced (1-isobutylcyclohexyl)methanamine in CH₂Cl₂ (30 mL), 4-methoxybenzoyl chloride (2.24 g, 13.2 mmol) and triethyl amine (3.49 mL, 25.2 mmol) was added. The mixture was stirred at room temperature for 4 h, then diluted with CH₂Cl₂ (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), then dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1j (1.61 g, 5.3 mmol, yield: 44% over two steps) as a white solid.

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.72 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.98 (s, 1H), 3.84 (s, 3H), 3.42 (d, J = 6.6 Hz, 6H), 1.83–1.68 (m, 1H), 1.59–1.44 (m, 4H), 1.44–1.31 (m, 6H), 1.27 (d, J = 5.3 Hz, 2H), 0.96 (d, J = 6.6 Hz, 6H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 167.0, 162.0, 128.5, 127.4, 113.7, 55.4, 45.7, 45.4, 37.1, 34.2, 26.2, 25.7, 23.2, 21.6.

IR (film): ν (cm⁻¹) 2927, 2863, 1636, 1606, 1544, 1504, 1462, 1309, 1253, 1176, 1033, 842, 766.

HRMS (ESI, m/z) calcd for C₁₉H₂₉NO₂ (M+H)⁺: 304.2271, found: 304.2270

4-Methoxy-N-(5-methylhexan-2-yl)benzamide (1k)

A solution of 4-methylpentan-1-amine³ (1.50 g, 13.0 mmol), 4-methoxybenzoyl chloride (2.43 g, 14.3 mmol) and triethyl amine (3.78 mL, 27.3 mmol) in CH₂Cl₂ (32 mL) was stirred at room temperature for 4 h. The reaction mixture was diluted with CH₂Cl₂ (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), then dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1k (1.79 g, 7.2 mmol, yield: 55%) as a white solid.
1H NMR (500 MHz, CDCl₃): δ (ppm) 7.72 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 5.83 (s, 1H), 4.26–4.04 (m, 1H), 3.84 (s, 3H), 1.60–1.43 (m, 3H), 1.29–1.23 (m, 2H), 1.22 (d, J = 6.6 Hz, 3H), 0.88 (d, J = 6.6 Hz, 6H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 166.2, 162.0, 128.5, 127.4, 113.6, 55.4, 45.8, 35.1, 34.9, 28.0, 22.5, 21.1.

IR (film): ν (cm⁻¹) 2959, 2869, 1628, 1609, 1576, 1537, 1506, 1304, 1303, 1256, 1178, 1030, 844, 770.

HRMS (ESI, m/z) calcd for C₁₅H₂₄NO₂ (M+H)^+: 250.1801, found: 250.1800

N-(2,5-Dimethylhexan-2-yl)-4-methoxybenzamide (1l)

A solution of 2,5-dimethylhexan-2-amine (0.77 g, 6.0 mmol), 4-methoxybenzoyl chloride (1.12 g, 6.6 mmol), triethylamine (1.75 mL, 12.6 mmol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 4 h. The reaction mixture was diluted with CH₂Cl₂ (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), then dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1l (1.00 g, 3.8 mmol, yield: 63%) as a white solid.

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.68 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.77 (s, 1H), 3.84 (s, 3H), 1.87–1.68 (m, 2H), 1.53 (dp, J = 13.2, 6.6 Hz, 1H), 1.42 (s, 6H), 1.23–1.13 (m, 2H), 0.89 (d, J = 6.6 Hz, 6H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 166.3, 161.8, 128.4 (2C), 113.6, 55.4, 53.9, 38.3, 33.2, 28.3, 27.0, 22.7.

IR (film): ν (cm⁻¹) 2955, 2868, 1638, 1606, 1538, 1503, 1466, 1385, 1365, 1294, 1255, 1177, 1033, 843, 768, 612.

HRMS (ESI, m/z) calcd for C₁₆H₂₅NO₂Na (M+Na)^+: 286.1777, found: 286.1774.

4-Methoxy-N-(4-phenylbutyl)benzamide (1m)

A dry round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged
with LiAlH₄ (0.80 g, 21.0 mmol) and diethyl ether (50 mL). The suspension was stirred at 0 °C, into which 4-phenylbutanenitrile (1.45 g, 10.0 mmol) in diethyl ether (10 mL) was added dropwise. The mixture was heated at reflux for 3 h, cooled down to 0 °C, quenched with NaOH (10% in water, 4 mL) at 0 °C, then dried over MgSO₄. After filtration and evaporation of the solvent, 4-phenylbutan-1-amine was obtained. To a solution of the produced 4-phenylbutan-1-amine in CH₂Cl₂ (20 mL), 4-methoxybenzoyl chloride (1.18 g, 11.0 mmol) and triethylamine (2.12 mL, 21.0 mmol) was added. The mixture was stirred at room temperature for 4 h, then diluted with CH₂Cl₂ (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), then dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1m (1.58 g, 5.6 mmol, yield: 56% over two steps) as a white solid.

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.71 (d, J = 8.9 Hz, 2H), 7.36 – 7.22 (m, 2H), 7.22 – 7.12 (m, 3H), 6.90 (d, J = 8.9 Hz, 2H), 6.09 (s, 1H), 3.83 (s, 3H), 3.44 (dd, J = 12.8, 6.9 Hz, 2H), 2.65 (t, J = 7.4 Hz, 2H), 1.79 – 1.56 (m, 4H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 167.0, 162.0, 142.1, 128.6, 128.4, 128.3, 127.0, 125.8, 113.6, 55.3, 39.8, 35.5, 29.3, 28.7.

IR (film): ν (cm⁻¹) 2938, 1632, 1607, 1577, 1533, 1502, 1458, 1253, 1183, 1108, 1032, 845, 767, 741, 695, 609.

HRMS (ESI, m/z) calcd for C₁₈H₂₁NO₂Na (M+Na)⁺: 306.1464, found: 306.1462.

4-Methoxy-N-(4-methyloctyl)benzamide (1o)

To a solution of 4-methyloctanoic acid (2.37 g, 15.0 mmol) in CH₂Cl₂ (50 mL) was added oxaly chloride (1.40 mL, 16.5 mmol) dropwise, then 3 drops of DMF was added. The mixture was stirred at room temperature until no more gas bubbles were observed (within 4 h). The solvent was removed under reduced pressure to afford the crude acid chloride, which was redissolved in THF (30 mL) at 0 °C. Subsequently, aqueous NH₃ (30% in water, 30 mL) was added dropwise over 10 min. The mixture was warmed to room temperature, then stirred overnight. The resulting solution was diluted with 20 mL EtOAc and extracted with EtOAc (2 x 20 mL). The combined organic layer was washed with brine (2 x 30 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure to afford 4-methyloctanamide (2.12 g, 13.5 mmol, yield: 90%), which was used without further purification.

A dry round-bottomed flask equipped with a magnetic stir bar was charged with LiAlH₄ (1.08 g, 28.3 mmol) and THF (45 mL). The suspension was stirred at 0 °C, into which 4-methyloctanamide (2.12 g, 13.5 mmol) in THF (5 mL) was added dropwise. The mixture was
warmed to room temperature and stirred overnight. The resulting suspension was cooled again to 0 °C, then quenched with ice water (3 mL) and NaOH (4 mL, 10% in water), dried over excess MgSO₄. After filtration and evaporation of the solvent, 4-methyloctan-1-amine was obtained. To a solution of the produced 4-methyloctan-1-amine in CH₂Cl₂ (32 mL), 4-methoxybenzoyl chloride (2.52 g, 14.8 mmol) and triethyl amine (3.93 mL, 28.4 mmol) was added. The mixture was stirred at room temperature for 4 h, then diluted with CH₂Cl₂ (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1o (1.75 g, 6.3 mmol, yield: 47% over two steps) as a white solid.

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.75 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.40 (s, 1H), 3.82 (s, 3H), 3.56–3.25 (m, 2H), 1.74–1.45 (m, 2H), 1.46–1.31 (m, 2H), 1.31–1.04 (m, 7H), 0.93–0.78 (m, 6H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 167.0, 161.9, 128.6, 127.1, 113.5, 55.3, 40.3, 36.5, 34.2, 32.5, 29.2, 27.2, 22.9, 19.5, 14.0.

IR (film): ν (cm⁻¹) 2955, 2927, 2857, 1632, 1546, 1504, 1462, 1299, 1254, 1178, 1033, 844, 768.

HRMS (ESI, m/z) calcd for C₁₇H₂₇NO₂Na (M+Na)⁺: 300.1934, found: 300.1935.

5-((tert-Butyldiphenylsilyl)oxy)-4-methylpentan-1-ol (S1)

To a solution of tert-butyldipheny((2-methylpent-4-en-1-yl)oxy)silane⁵ᵃ,b (4.06 g, 12.0 mmol) in anhydrous THF (30 mL) was added dropwise BH₃ (1.0 M in THF, 12.0 mL, 12.0 mmol) at 0 °C. The solution was stirred at 0 °C for 1.5 h, into which a premixed solution of NaOH (2.0 M in water, 30 mL) and H₂O₂ (30% in water, 14 mL) was added dropwise at 0 °C. The resulting mixture was stirred for 3 h, then diluted with H₂O (30 mL) and extracted with Et₂O (3 x 30 mL). The combined organic layer was washed with H₂O (20 mL), dried (MgSO₄), filtered and concentrated. The crude product was purified by flash column chromatography (EtOAc/n-hexane = 1:20 to 1:10) to afford S1 (2.56 g, 7.2 mmol, yield: 60%) as a colorless oil.

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.66 (dd, J = 7.9, 1.5 Hz, 4H), 7.44–7.33 (m, 6H),
3.61–3.55 (m, 2H), 3.54–3.49 (m, 1H), 3.49–3.44 (m, 1H), 1.72–1.62 (m, 1H), 1.61–1.52 (m, 1H), 1.52–1.46 (m, 2H), 1.45–1.42 (m, 1H), 1.21–1.11 (m, 1H), 1.05 (d, J = 2.8 Hz, 9H), 0.92 (dd, J = 11.1, 6.3 Hz, 3H).

13C NMR (125 MHz, CDCl3): δ (ppm) 135.6, 134.0, 129.5, 127.5, 68.7, 63.2, 35.5, 30.2, 29.1, 26.9, 19.3, 16.8.

IR (film): ν (cm⁻¹) 2965, 2930, 2857, 1471, 1421, 1389, 1111, 1007, 823, 739, 701, 614, 504.

HRMS (ESI, m/z) calcd for C22H32O2SiNa (M+Na)⁺: 379.2063, found: 379.2062.

2-(5-(tert-Butyldiphenylsilyl)oxy)-4-methylpentylisoindole-1,3-dione (S2)

To a solution of compound S1 (2.56 g, 7.2 mmol), phthalimide (1.27 g, 8.6 mmol) and Ph3P (2.25 g, 8.6 mmol) in anhydrous THF (30 mL) was added diethyl azodicarboxylate (DEAD, 1.50 g, 8.6 mmol) dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (EtOAc/n-hexane = 1:20) to afford S2 (3.25 g, 6.7 mmol, yield: 93%) as a colorless oil.

1H NMR (500 MHz, CDCl3): δ (ppm) 7.83 (dd, J = 5.4, 3.0 Hz, 2H), 7.69 (dd, J = 5.5, 3.0 Hz, 2H), 7.64 (dd, J = 7.6, 1.4 Hz, 4H), 7.41–7.33 (m, 6H), 3.70–3.64 (m, 2H), 3.46 (p, J = 3.9 Hz, 2H), 1.77–1.57 (m, 3H), 1.57–1.47 (m, 1H), 1.22–1.11 (m, 1H), 1.00 (s, 9H), 0.91 (d, J = 6.7 Hz, 3H).

13C NMR (125 MHz, CDCl3): δ (ppm) 168.4, 135.6, 133.6, 133.9, 133.9, 133.8, 132.2, 129.5, 127.5, 123.1, 68.6, 38.2, 35.4, 30.2, 26.9, 26.8, 26.1, 19.2, 16.6.

IR (film): ν (cm⁻¹) 2930, 2856, 1774, 1715, 1467, 1427, 1395, 1361, 1111, 823, 741, 719, 702, 614, 504.

HRMS (ESI, m/z) calcd for C30H35NO3SiNa (M+Na)⁺: 508.2278, found: 508.2285.

N-(5-(tert-Butyldiphenylsilyl)oxy)-4-methylpentyl-4-methoxybenzamide (1p)

To a solution of S2 (3.25 g, 6.7 mmol) in anhydrous EtOH (30 mL) was added anhydrous hydrazine (0.74 g, 14.7 mmol). The mixture was heated at 60 °C for 4 h, then cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure. The crude product was suspended in Et2O (30 mL) and filtered. The filtrate was concentrated under reduced pressure to afford 5-(tert-butyldiphenylsilyl)oxy)-4-methylpentan-1-amine. The amine was redissolved in CH2Cl2 (30 mL), then 4-methoxybenzoyl chloride (1.26 g, 7.4 mmol) and triethyl amine (1.95 mL, 14.1 mmol) were added. The resulting solution was stirred at room temperature for 4 h, then
diluted with CH$_2$Cl$_2$ (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), dried over Na$_2$SO$_4$ and concentrated. The crude product was purified by silica gel column chromatography (EtOAc/n-hexane = 1:4) to afford benzamide 1p (2.59 g, 5.3 mmol, 79% yield for two steps) as a colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.71 (d, $J = 8.9$ Hz, 2H), 7.65 (dd, $J = 7.8$, 1.7 Hz, 4H), 7.44–7.31 (m, 6H), 6.88 (d, $J = 8.9$ Hz, 2H), 6.20 (s, 1H), 3.81 (s, 3H), 3.56–3.46 (m, 2H), 3.43–3.31 (m, 2H), 1.75–1.62 (m, 1H), 1.62–1.43 (m, 3H), 1.22–1.13 (m, 1H), 1.05 (s, 9H), 0.92 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 167.0, 161.9, 135.5, 133.9, 129.4, 128.5, 127.5, 127.0, 113.5, 68.6, 55.2, 40.1, 35.4, 30.3, 27.0, 26.8, 19.2, 16.6.

IR (film): $\nu$ (cm$^{-1}$) 2957, 2930, 2857, 1632, 1606, 1545, 1504, 1462, 1303, 1254, 1178, 1111, 1032, 844, 823, 768, 740, 613, 504.

HRMS (ESI, $m/z$) calcd for C$_{30}$H$_{39}$NO$_3$SiNa (M+Na)$^+$: 512.2591, found: 512.2587.

### 2.2 Synthesis of Racemic Products as HPLC References

A dried Schlenk tube (10 mL) was charged with photoredox mediator [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCF$_3$bpy)](PF$_6$) (4 or 6 mol%), racemic rhodium catalyst rac-RhO (8 mol%), tetrabutylammonium dibutyl phosphate (5 or 8 mol%), 4 Å MS (100 mg), benzamides 1a–p (0.15 mmol) and $\alpha,\beta$-unsaturated 2-acyl imidazoles 2a–m (0.10 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH$_2$Cl$_2$ (0.50 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the indicated time (monitored by TLC), the reaction mixture was concentrated and purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford the corresponding racemic products 3a–j, 3n, 3q–za as HPLC reference for the determination of enantiomeric excess.
3. Rhodium-Catalyzed Asymmetric Photoredox Reactions

**General procedure.** A dried 10 mL Schlenk tube was charged with photoredox mediator [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (4 or 6 mol%), chiral rhodium catalyst Λ-RhO (8 mol%), tetrabutylammonium dibutyl phosphate (5 or 8 mol%), 4 Å MS (200 mg), benzamides 1a–p (0.30 mmol), and α,β-unsaturated 2-acyl imidazoles 2a–m (0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the indicated time (monitored by TLC), the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford the corresponding nonracemic product 3a–j, 3n or 3q–za. The enantiomeric excess was determined by HPLC analysis on chiral stationary phase.

**Exemplary reaction setup and 24 W Blue LED lamp:**
A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)2(5,5'-dCF₂bpy)](PF₆) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.016 mmol), 4 Å MS (200 mg), benzamide 1a (70.5 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 38 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/hexane = 1:5 to 1:4) to afford product 3a as a white solid (55.5 mg, 0.124 mmol, yield: 62%). Enantiomeric excess was established as 97% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, tᵣ (minor) = 8.7 min, tᵣ (major) = 17.1 min). [α]D²⁵ = -7.2° (c = 1.0, CH₂Cl₂).

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.70 (d, J = 8.6 Hz, 2H), 7.36–7.29 (m, 1H), 7.29–7.23 (m, 2H), 7.22–7.11 (m, 6H), 7.06 (s, 1H), 6.89 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 7.7 Hz, 2H), 6.28 (s, 1H), 3.83 (s, 3H), 3.75 (dd, J = 16.1, 12.0 Hz, 1H), 3.46–3.21 (m, 4H), 1.66 (dt, J = 15.2, 7.5 Hz, 2H), 1.49–1.34 (m, 1H), 1.34–1.26 (m, 1H), 0.95 (s, 3H), 0.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 191.0, 167.0, 162.0, 143.4, 141.2, 138.0, 130.1, 129.2, 128.8, 128.6, 128.3, 127.6, 127.1, 126.5, 126.2, 125.3, 113.6, 55.3, 49.7, 40.6, 39.7, 37.8, 36.1, 25.1, 24.8, 24.1.

IR (film): ν (cm⁻¹) 2962, 1683, 1633, 1605, 1543, 1444, 1405, 1306, 1257, 1178, 1089, 1028, 844, 800, 765, 703, 692.

HRMS (ESI, m/z) calcd for C₃₂H₅₆N₆O₃Na (M+Na)+: 532.2570, found: 532.2557.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)2(5,5'-dCF₂bpy)](PF₆) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.016 mmol), 4 Å MS (200 mg), benzamide 1a (70.5 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2b (42.4 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 41 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/hexane = 1:5 to 1:4) to afford product 3b as a white solid (55.5 mg, 0.124 mmol, yield: 62%). Enantiomeric excess was established as 97% ee by HPLC analysis using a Chiralpak OD-H column. (HPLC conditions: OD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, tᵣ (minor) = 8.7 min, tᵣ (major) = 17.1 min). [α]D²⁵ = -7.2° (c = 1.0, CH₂Cl₂).
conditions: OD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 15.5 min, t_r (major) = 17.6 min. [α]_D^{25} = 36.8° (c = 1.0, CH₂Cl₂).

1H NMR (400 MHz, CDCl₃): δ (ppm) 7.71 (d, J = 8.4 Hz, 2H), 7.25–7.15 (m, 4H), 7.15–7.05 (m, 2H), 6.92 (s, 1H), 6.89 (d, J = 8.4 Hz, 2H), 6.30 (s, 1H), 3.87–3.71 (m, 7H), 3.49–3.23 (m, 4H), 1.77–1.56 (m, 2H), 1.47–1.34 (m, 1H), 1.34–1.27 (m, 1H), 0.95 (s, 3H), 0.85 (s, 3H).

13C NMR (101 MHz, CDCl₃): δ (ppm) 192.0, 167.1, 162.0, 143.2, 141.5, 129.8, 129.1, 128.7, 128.6, 127.5, 127.1, 126.7, 126.1, 113.6, 55.3, 49.0, 40.6, 39.5, 37.8, 36.0, 35.9, 25.2, 25.0, 24.1.

IR (film): ν (cm⁻¹) 2960, 1674, 1633, 1606, 1544, 1504, 1467, 1407, 1291, 1254, 1178, 1030, 915, 845, 767, 703, 608.

HRMS (ESI, m/z) calcd for C₂₇H₃₃N₃O₃Na (M+Na)^+: 470.2414, found: 470.2406.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃ bpy)](PF₆) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1a (70.5 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2c (48.0 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 46 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3c as a white solid (47.5 mg, 0.100 mmol, yield: 50%). Enantiomeric excess was established as 95% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 18.5 min, t_r (major) = 21.2 min). [α]_D^{25} = 19.5° (c = 1.0, CH₂Cl₂).

1H NMR (400 MHz, CDCl₃): δ (ppm) 7.70 (d, J = 8.6 Hz, 2H), 7.24–7.05 (m, 5H), 7.11 (s, 2H), 6.89 (d, J = 8.6 Hz, 2H), 6.29 (s, 1H), 5.30–5.14 (m, 1H), 3.84 (s, 3H), 3.76 (dd, J = 15.8, 11.2 Hz, 1H), 3.47–3.35 (m, 3H), 3.31 (dd, J = 11.2, 3.5 Hz, 1H), 1.75–1.59 (m, 2H), 1.42 (m, 1H), 1.36–1.28 (m, 1H), 1.25 (d, J = 6.6 Hz, 3H), 1.19 (d, J = 6.7 Hz, 3H), 0.96 (s, 3H), 0.85 (s, 3H).

13C NMR (101 MHz, CDCl₃): δ (ppm) 192.5, 167.1, 162.0, 142.6, 141.5, 129.8, 129.1, 128.7, 127.5, 127.1, 126.7, 126.1, 120.7, 113.6, 55.4, 49.6, 48.9, 40.6, 40.1, 37.8, 36.1, 25.2, 25.0, 24.1, 23.4, 23.2.

IR (film): ν (cm⁻¹) 2963, 1674, 1634, 1606, 1545, 1504, 1462, 1453, 1395, 1294, 1255, 1178, 1088, 1030, 916, 845, 801, 768, 703, 608.

HRMS (ESI, m/z) calcd for C₂₉H₃₇N₃O₃Na (M+Na)^+: 498.2727, found: 498.2721.
A dried 10 mL Schlenk tube was charged with \([\text{Ir(dF(CF}_3)ppy)}_2(5,5'-\text{dCF}_3\text{bpy})](\text{PF}_6)\) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst \(\Lambda-\text{RhO}\) (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (4.51 mg, 0.0100 mmol), 4 Å MS (200 mg), benzamide \(\text{1a}\) (70.5 mg, 0.30 mmol), and \(\alpha,\beta\)-unsaturated 2-acyl imidazole \(\text{2d}\) (58.4 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous \(\text{CH}_2\text{Cl}_2\) (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/\(n\)-hexane = 1:5 to 1:4) to afford product \(\text{3d}\) as a white solid (65.4 mg, 0.124 mmol, yield: 62%). Enantiomeric excess was established as 93% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: \(n\)-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, \(t_r\) (minor) = 16.2 min, \(t_r\) (major) = 32.1 min). \([\alpha]D_{25} = -16.2^\circ\) (c = 1.0, \(\text{CH}_2\text{Cl}_2\)).

\(^1\text{H NMR (500 MHz, CDCl}_3\)): \(\delta\) (ppm) 7.70 (d, \(J = 8.8\) Hz, 2H), 7.38–7.32 (m, 1H), 7.32–7.27 (m, 2H), 7.22 (s, 1H), 7.18–7.10 (m, 2H), 7.08 (s, 1H), 6.93–6.85 (m, 4H), 6.82 (d, \(J = 7.7\) Hz, 2H), 6.33 (s, 1H), 3.83 (s, 3H), 3.73 (dd, \(J = 16.3, 12.0\) Hz, 1H), 3.45–3.34 (m, 2H), 3.34–3.23 (m, 2H), 1.70–1.58 (m, 2H), 1.42–1.32 (m, 1H), 1.31–1.21 (m, 1H), 0.92 (s, 3H), 0.82 (s, 3H).

\(^{13}\text{C NMR (125 MHz, CDCl}_3\)): \(\delta\) (ppm) 190.7, 167.0, 162.0, 143.3, 138.0, 136.9 (d, \(J = 3.3\) Hz, 2C), 131.3 (d, \(J = 7.7\) Hz, 2C), 129.3, 128.8, 128.6, 128.5, 127.1, 126.7, 125.3, 114.4, 114.2, 113.6, 55.3, 49.0, 40.6, 39.7, 37.7, 36.0, 25.0, 24.7, 24.1.

IR (film): \(\nu\) (cm\(^{-1}\)) 2962, 1684, 1633, 1605, 1544, 1505, 1443, 1405, 1306, 1254, 1224, 1178, 1030, 964, 843, 764, 735, 692.

HRMS (ESI, \(m/z\)) calcd for \(\text{C}_{32}\text{H}_{34}\text{FN}_3\text{O}_3\text{Na} (\text{M+Na})^+\): 550.2476, found: 550.2472.
added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3e as a white solid (59.7 mg, 0.110 mmol, yield: 55%). Enantiomeric excess was established as 94% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t<sub>r</sub> (minor) = 17.4 min, t<sub>r</sub> (major) = 30.8 min). [α]<sup>D</sup><sup>25</sup> = -29.2° (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

1H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.70 (d, J = 8.8 Hz, 2H), 7.37–7.33 (m, 1H), 7.33–7.28 (m, 2H), 7.22 (d, J = 1.0 Hz, 1H), 7.16 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 1.0 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 6.85–6.79 (m, 2H), 6.22 (s, 1H), 3.84 (s, 3H), 3.72 (dd, J = 16.8, 12.4 Hz, 1H), 3.44–3.34 (m, 2H), 3.34–3.25 (m, 2H), 1.70–1.59 (m, 2H), 1.41–1.33 (m, 1H), 1.28 (d, J = 9.3 Hz, 1H), 0.93 (s, 3H), 0.83 (s, 3H).

13C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 190.5, 167.0, 162.0, 143.3, 139.9, 138.0, 132.0, 131.3, 129.3, 128.8, 128.6, 128.5, 127.7, 127.1, 126.8, 125.4, 113.7, 55.3, 49.1, 40.5, 39.6, 37.7, 36.0, 25.0, 24.8, 24.2.

IR (film): ν (cm<sup>-1</sup>) 2961, 1683, 1632, 1605, 1443, 1405, 1306, 1178, 1092, 1030, 964, 844, 763, 735, 692.

HRMS (ESI, m/z) calcd for C<sub>32</sub>H<sub>34</sub>ClN<sub>3</sub>O<sub>3</sub>Na (M+Na)<sup>+</sup>: 566.2181, found: 566.2175.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(5,5'-dCF<sub>3</sub>bpym)](PF<sub>6</sub>) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (4.51 mg, 0.0100 mmol), 4 Å MS (200 mg), benzamide 1a (70.5 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2f (70.4 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 41 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3f as a white solid (79.8 mg, 0.136 mmol, yield: 68%). Enantiomeric excess was established as 93% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t<sub>r</sub> (minor) = 17.2 min, t<sub>r</sub> (major) = 29.1 min). [α]<sup>D</sup><sup>25</sup> = -28.3° (c = 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

1H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.70 (d, J = 8.4 Hz, 2H), 7.40–7.24 (m, 5H), 7.21 (s, 1H), 7.12–6.98 (m, 3H), 6.90 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 7.3 Hz, 2H), 6.26 (s, 1H), 3.83 (s, 3H), 3.71 (dd, J = 14.7, 10.8 Hz, 1H), 3.45–3.35 (m, 2H), 3.35–3.20 (m, 2H), 1.72–1.54 (m, 2H),
1.41–1.26 (m, 2H), 0.93 (s, 3H), 0.83 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 190.5, 167.0, 162.0, 143.3, 140.4, 138.0, 131.7, 130.7, 129.3, 128.8, 128.6, 128.5, 127.1, 126.8, 125.4, 120.1, 113.7, 55.3, 49.2, 40.5, 39.6, 37.7, 36.0, 25.0, 24.7, 24.2.

IR (film): $\nu$ (cm$^{-1}$) 2961, 2928, 1686, 1632, 1606, 1545, 1503, 1443, 1406, 1306, 1255, 1178, 1030, 763, 692.

HRMS (ESI, $m/z$) calcd for C$_{32}$H$_{34}$BrN$_3$O$_3$Na (M+Na)$^+$: 610.1675, found: 610.1675.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCF$_3$bpy)](PF$_6$) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst $\Lambda$-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (4.51 mg, 0.0100 mmol), 4 Å MS (200 mg), benzamide 1a (70.5 mg, 0.30 mmol), and $\alpha,\beta$-unsaturated 2-acyl imidazole 2g (68.4 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH$_2$Cl$_2$ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 45 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3g as a white solid (75.0 mg, 0.130 mmol, yield: 65%). Enantiomeric excess was established as 92% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, $t_r$ (minor) = 11.8 min, $t_r$ (major) = 19.6 min). $[\alpha]_{D}^{25}$ = -7.2° (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.71 (d, $J$ = 8.8 Hz, 2H), 7.43 (d, $J$ = 8.1 Hz, 2H), 7.37–7.31 (m, 1H), 7.31–7.24 (m, 4H), 7.22 (d, $J$ = 1.0 Hz, 1H), 7.08 (d, $J$ = 0.9 Hz, 1H), 6.88 (d, $J$ = 8.8 Hz, 2H), 6.82–6.75 (m, 2H), 6.35 (s, 1H), 3.83 (s, 3H), 3.77 (td, $J$ = 13.2, 4.6 Hz, 1H), 3.45–3.31 (m, 4H), 1.71–1.58 (m, 2H), 1.41–1.33 (m, 1H), 1.33–1.26 (m, 1H), 0.95 (s, 3H), 0.84 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 190.2, 167.0, 162.0, 145.6, 143.1, 137.9, 130.3, 129.4, 128.9, 128.6, 128.5, 126.9 (d, $J$ = 2.2 Hz, 2C), 126.8, 125.3, 124.4 (dd, $J$ = 7.3 Hz, 3.7 Hz, 4C), 124.4, 123.1, 113.6, 55.3, 49.5, 40.5, 39.5, 37.7, 36.0, 25.0, 24.7, 24.2.

IR (film): $\nu$ (cm$^{-1}$) 2962, 1683, 1632, 1606, 1545, 1503, 1444, 1405, 1326, 1255, 1164, 1115, 1068, 1017, 964, 844, 764, 692.

HRMS (ESI, $m/z$) calcd for C$_{33}$H$_{33}$F$_3$N$_3$O$_3$ (M+H)$^+$: 578.2625, found: 578.2627.
A dried 10 mL Schlenk tube was charged with [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCF$_3$bpy)](PF$_6$) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1a (70.5 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2i (57.6 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH$_2$Cl$_2$ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3h as a white solid (42.9 mg, 0.082 mmol, yield: 41%). Enantiomeric excess was established as 95% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t$_r$ (minor) = 15.4 min, t$_r$ (major) = 33.4 min). [α]$_D^{25}$ = -17.2° (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.71 (d, J = 8.7 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.28–7.23 (m, 3H), 7.21 (s, 1H), 7.06 (d, J = 8.8 Hz, 3H), 7.01 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 7.4 Hz, 2H), 6.19 (s, 1H), 3.84 (s, 3H), 3.69 (dd, J = 15.0, 10.9 Hz, 1H), 3.45–3.25 (m, 4H), 2.29 (s, 3H), 1.72–1.62 (m, 2H), 1.42–1.34 (m, 1H), 1.34–1.28 (m, 1H), 0.95 (s, 3H), 0.84 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ (ppm) 191.2, 167.0, 162.0, 143.4, 138.1, 138.0, 135.7, 129.9, 129.2, 128.7, 128.6, 128.3, 128.3, 127.1, 126.4, 125.3, 113.6, 55.3, 49.3, 40.6, 39.8, 37.8, 36.1, 25.1, 24.8, 24.1, 20.9.

IR (film): ν (cm$^{-1}$) 2961, 2870, 1684, 1633, 1606, 1544, 1503, 1443, 1405, 1307, 1254, 1178, 1030, 964, 844, 763, 733, 692.

HRMS (ESI, m/z) calcd for C$_{33}$H$_{38}$N$_3$O$_3$ (M+H)$^+$: 524.2907, found: 524.2911.
added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5) to afford product 3i as a white solid (53.4 mg, 0.102 mmol, yield: 51%). Enantiomeric excess was established as 95% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 7:30, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 7.2 min, t_r (major) = 13.5 min). [α]_D^25 = -12.0° (c = 1.0, CH_2Cl_2).

\[ \text{IR (film): } \nu (\text{cm}^{-1}) = 2960, 2869, 1685, 1633, 1606, 1544, 1503, 1443, 1405, 1307, 1254, 1178, 1030, 963, 845, 763, 692. \]

HRMS (ESI, m/z) calcd for C_{33}H_{38}N_{3}O_{3} (M+H)^+: 524.2907, found: 524.2912.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)](PF_6) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1a (70.5 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2j (57.6 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH_2Cl_2 (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5) to afford product 3j as a white solid (41.9 mg, 0.080 mmol, yield: 40%). Enantiomeric excess was established as 90% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 7.8 min, t_r (major) = 13.5 min). [α]_D^25 = -5.4° (c = 1.0, CH_2Cl_2).

\[ \text{IR (film): } \nu (\text{cm}^{-1}) = 2960, 2869, 1685, 1633, 1606, 1544, 1503, 1443, 1405, 1307, 1254, 1178, 1030, 963, 845, 763, 692. \]

HRMS (ESI, m/z) calcd for C_{33}H_{38}N_{3}O_{3} (M+H)^+: 524.2907, found: 524.2912.
$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 191.3, 167.1, 162.0, 140.0, 137.9, 137.8, 130.2, 129.2, 128.9, 128.7, 128.6, 128.2, 127.1, 126.3, 125.9, 125.4, 125.3, 125.1, 113.6, 55.3, 43.7, 40.9, 40.7, 37.8, 37.3, 24.6, 24.3, 24.2, 20.7.

IR (film): $\nu$ (cm$^{-1}$) 2962, 2871, 1684, 1633, 1606, 1544, 1503, 1444, 1406, 1306, 1255, 1178, 1029, 966, 844, 802, 761, 736, 692.

HRMS (ESI, $m/z$) calcd for C$_{33}$H$_{38}$N$_3$O$_3$ (M+H)$^+$: 524.2907, found: 524.2910.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCF$_3$bpy)](PF$_6$) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst $\Lambda$-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1b (70.5 mg, 0.30 mmol), and $\alpha$,$\beta$-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH$_2$Cl$_2$ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3n as a white solid (40.7 mg, 0.080 mmol, yield: 40%). Enantiomeric excess was established as 77% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, $t_r$ (minor) = 12.7 min, $t_r$ (major) = 17.9 min). [$\alpha$]$_D^{25}$ = -6.4° (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.34 (dd, $J$ = 2.4, 1.6 Hz, 1H), 7.33–7.28 (m, 2H), 7.26–7.22 (m, 3H), 7.21 (d, $J$ = 1.0 Hz, 1H), 7.20–7.15 (m, 5H), 7.05 (d, $J$ = 1.0 Hz, 1H), 7.01 (ddd, $J$ = 8.1, 2.6, 1.0 Hz, 1H), 6.73 (d, $J$ = 7.9 Hz, 2H), 6.36 (s, 1H), 3.82 (s, 3H), 3.75 (dd, $J$ = 16.2, 11.9 Hz, 1H), 3.39 (dt, $J$ = 11.1, 6.9 Hz, 2H), 3.36–3.28 (m, 2H), 1.71–1.62 (m, 2H), 1.44–1.35 (m, 1H), 1.32–1.26 (m, 1H), 0.95 (s, 3H), 0.85 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 191.0, 167.3, 159.8, 143.4, 141.2, 138.0, 136.3, 130.1, 129.4, 129.2, 128.8, 128.3, 127.6, 126.5, 126.2, 125.3, 118.6, 117.6, 112.2, 55.4, 49.8, 40.7, 39.7, 37.8, 36.1, 25.1, 24.8, 24.1.

IR (film): $\nu$ (cm$^{-1}$) 2961, 2871, 1684, 1640, 1583, 1537, 1492, 1446, 1405, 1305, 1242, 1043, 964, 914, 757, 692.

HRMS (ESI, $m/z$) calcd for C$_{32}$H$_{36}$N$_3$O$_3$ (M+H)$^+$: 510.2751, found: 510.2752.
A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₂bpy)][PF₆] (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1e (74.1 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 46 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3q as a white solid (53.2 mg, 0.102 mmol, yield: 51%). Enantiomeric excess was established as 95% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, tᵣ (minor) = 8.8 min, tᵣ (major) = 15.2 min). [α]D₂⁵ = -34.8° (c = 1.0, CH₂Cl₂).

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.67 (d, J = 8.8 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.22 (s, 1H), 7.21–7.12 (m, 5H), 7.08 (s, 1H), 6.90 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 7.5 Hz, 2H), 6.04 (s, 1H), 3.84 (s, 3H), 3.83–3.77 (m, 1H), 3.44–3.35 (m, 3H), 3.32 (dd, J = 16.0, 3.8 Hz, 1H), 2.27–2.06 (m, 2H), 1.86–1.77 (m, 1H), 1.75–1.61 (m, 6H), 1.48–1.39 (m, 1H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 190.7, 167.0, 162.0, 143.4, 141.7, 138.2, 129.4, 129.2, 128.8, 128.6, 128.4, 127.9, 127.2, 126.6, 126.3, 125.5, 113.7, 55.4, 47.0, 44.76, 40.6, 40.1, 34.6, 28.9, 28.4, 24.9.

IR (film): ν (cm⁻¹) 2931, 2855, 1684, 1633, 1606, 1544, 1504, 1444, 1405, 1307, 1254, 1178, 1030, 964, 845, 765, 735, 702.

HRMS (ESI, m/z) calcd for C₃₃H₃₀N₅O₃(M+H)+: 522.2751, found: 522.2757.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₂bpy)][PF₆] (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1f (78.4 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 38 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3r as a white solid (68.5 mg, 0.128 mmol, yield: 64%). Enantiomeric excess was established as 97% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, tᵣ (minor) = 9.0 min, tᵣ (major) = 20.0 min). [α]D²⁵ = -20.0° (c = 1.0, CH₂Cl₂).

1H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.8 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.29–7.24 (m, 2H), 7.23–7.12 (m, 6H), 7.05 (d, J = 0.9 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 7.1 Hz, 2H), 6.35
(s, 1H), 3.82 (s, 3H), 3.80–3.73 (m, 1H), 3.49 (dd, J = 11.2, 3.5 Hz, 1H), 3.41–3.24 (m, 3H), 1.72–1.57 (m, 4H), 1.58–1.47 (m, 3H), 1.47–1.35 (m, 4H), 1.35–1.27 (m, 1H).

13C NMR (101 MHz, CDCl3): δ (ppm) 190.8, 167.0, 161.9, 143.2, 141.9, 137.9, 129.8, 129.2, 128.7, 128.6, 128.3, 127.7, 127.0, 126.5, 126.2, 125.3, 113.5, 55.3, 48.4, 47.1, 40.8, 40.5, 34.8, 34.4, 34.4, 24.9, 24.8, 24.2.

IR (film): ν (cm⁻¹) 2951, 2869, 1684, 1633, 1606, 1543, 1504, 1445, 1405, 1307, 1254, 1178, 1030, 963, 845, 764, 703.

HRMS (ESI, m/z) calcd for C34H38N3O3 (M+H)⁺: 536.2907, found: 536.2908.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF3)ppy)2(5,5'-dCF3bpy)](PF6) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1g (82.5 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH2Cl2 (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 42 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3s as a white solid (65.9 mg, 0.120 mmol, yield: 60%). Enantiomeric excess was established as 95% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, tᵣ (minor) = 9.3 min, tᵣ (major) = 20.5 min). [α]D²⁵ = -11.5° (c = 1.0, CH2Cl2).

1H NMR (500 MHz, CDCl3): δ (ppm) 7.73 (d, J = 8.8 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 7.6 Hz, 2H), 7.21–7.14 (m, 6H), 7.06 (s, 1H), 6.88 (d, J = 8.7 Hz, 2H), 6.69 (d, J = 7.7 Hz, 2H), 6.40 (s, 1H), 3.83 (s, 3H), 3.68 (dd, J = 15.0, 11.6 Hz, 1H), 3.52–3.37 (m, 3H), 3.34 (dd, J = 15.0, 3.6 Hz, 1H), 1.92–1.58 (m, 3H), 1.58–1.44 (m, 6H), 1.42–1.31 (m, 3H), 1.19–1.10 (m, 1H), 1.10–0.99 (m, 1H).

13C NMR (125 MHz, CDCl3): δ (ppm) 191.3, 167.1, 162.0, 143.4, 140.8, 138.0, 130.5, 129.2, 128.8, 128.7, 128.3, 127.6, 127.2, 126.4, 126.2, 125.2, 113.6, 55.3, 47.8, 40.7, 39.2, 38.4, 31.8, 31.7, 29.3, 26.9, 25.9, 23.0, 21.5.

IR (film): ν (cm⁻¹) 2929, 2860, 1684, 1634, 1606, 1544, 1503, 1444, 1406, 1306, 1254, 1178, 1030, 966, 914, 845, 763, 703.

HRMS (ESI, m/z) calcd for C35H40N3O3 (M+H)⁺: 550.3064, found: 550.3071.
A dried 10 mL Schlenk tube was charged with [Ir(dF(CF\(_3\))ppy)\(_2\)(5,5'-dCF\(_3\)bpy)](PF\(_6\)) (13.75 mg, 0.0120 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), non-racemic benzamide 1h (92.2 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH\(_2\)Cl\(_2\) (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 42 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3t as a white solid (59.3 mg, 0.102 mmol, yield: 51%). Enantiomeric excess was established as (2:8:1 d.r.) by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, t\(_r\) (minor) = 11.0 min, t\(_r\) (major) = 23.4 min). [α]\(_D\)\(25\) = -5.5° (c = 1.0, CH\(_2\)Cl\(_2\)).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.72 (d, \(J\) = 8.8 Hz, 2H), 7.33 (t, \(J\) = 7.4 Hz, 1H), 7.27 (t, \(J\) = 7.5 Hz, 2H), 7.24–7.14 (m, 6H), 7.06 (d, \(J\) = 0.9 Hz, 1H), 6.91 (d, \(J\) = 8.8 Hz, 2H), 6.75 (d, \(J\) = 7.8 Hz, 2H), 6.57 (s, 1H), 3.89–3.77 (m, 4H), 3.56 (s, 3H), 3.44 (dt, \(J\) = 13.4, 4.9 Hz, 1H), 3.38–3.22 (m, 3H), 2.46–2.28 (m, 3H), 1.33 (d, \(J\) = 4.0 Hz, 2H), 1.02 (s, 3H), 0.92 (s, 3H).

\(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm) 190.7, 174.1, 166.8, 162.1, 143.5, 141.1, 138.1, 130.2, 129.3, 128.8, 128.7, 128.3, 127.6, 126.8, 126.5, 126.3, 125.3, 113.7, 55.4, 51.6, 51.3, 45.9, 42.3, 39.8, 39.7, 37.1, 31.1, 26.9, 24.8.

IR (film): ν (cm\(^{-1}\)) 2962, 1732, 1684, 1640, 1606, 1542, 1503, 1443, 1406, 1307, 1256, 1177, 1088, 1030, 845, 801, 765, 703.

HRMS (ESI, \(m/z\)) calcd for C\(_{35}\)H\(_{39}\)N\(_3\)O\(_5\)Na (M+Na\(^+\)): 604.2781, found: 604.2776.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF\(_3\))ppy)\(_2\)(5,5'-dCF\(_3\)bpy)](PF\(_6\)) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1i (78.9 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH\(_2\)Cl\(_2\) (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3u as a white solid (70.9 mg, 0.132 mmol, yield: 66%). Enantiomeric excess was established as 96% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC
conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 11.8 min, t_r (major) = 17.6 min. [α]_D^{25} = -16.1° (c = 1.0, CH₂Cl₂).

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.65 (d, J = 8.8 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.30–7.24 (m, 2H), 7.24–7.12 (m, 6H), 7.06 (s, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 7.3 Hz, 2H), 6.03 (s, 1H), 3.89–3.80 (m, 4H), 3.39 (dd, J = 15.9, 4.1 Hz, 1H), 3.31–3.23 (m, 3H), 1.53–1.40 (m, 2H), 1.07 (d, J = 3.1 Hz, 6H), 1.05 (d, J = 3.8 Hz, 6H).

13C NMR (101 MHz, CDCl₃): δ (ppm) 190.8, 167.1, 162.0, 143.4, 141.4, 138.0, 130.3, 129.2, 128.8, 128.6, 128.3, 127.5, 127.2, 126.5, 126.2, 125.3, 113.6, 55.3, 53.6, 51.4, 47.2, 39.7, 37.8, 36.4, 27.2, 27.1, 26.9, 26.7.

IR (film): ν (cm⁻¹) 2962, 2927, 2860, 1684, 1643, 1605, 1542, 1444, 1406, 1305, 1254, 1176, 1030, 844, 802, 764, 703, 692.

HRMS (ESI, m/z) calcd for C₃₄H₄₀N₃O₃ (M+H)⁺: 538.3064, found: 538.3068.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 0.0080 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3v as a white solid (58.9 mg, 0.102 mmol, yield: 51%). Enantiomeric excess was established as 94% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 17.6 min, t_r (major) = 23.3 min). [α]_D^{25} = -14.4° (c = 1.0, CH₂Cl₂).

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.57 (d, J = 8.8 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.31–7.25 (m, 2H), 7.24–7.16 (m, 6H), 7.06 (d, J = 0.9 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 7.8 Hz, 2H), 5.88 (s, 1H), 3.89–3.78 (m, 4H), 3.57–3.49 (m, 2H), 3.46 (dd, J = 15.9, 4.4 Hz, 1H), 3.23 (dd, J = 10.6, 4.4 Hz, 1H), 1.63–1.37 (m, 12H), 1.14 (s, 3H), 1.11 (s, 3H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 190.8, 167.0, 161.9, 143.4, 141.5, 138.0, 130.4, 129.3, 128.8, 128.6, 128.4, 127.6, 127.2, 126.6, 126.2, 125.3, 113.7, 55.3, 54.6, 45.1, 44.0, 39.6, 38.4, 38.0, 36.0, 35.8, 27.1, 26.8, 26.1, 21.6 (2C).

IR (film): ν (cm⁻¹) 2927, 2860, 1683, 1650, 1531, 1502, 1452, 1405, 1306, 1253, 1176, 1030, 843, 734, 703.

HRMS (ESI, m/z) calcd for C₃₇H₄₄N₄O₃ (M+H)⁺: 578.3377, found: 578.3378.
A dried 10 mL Schlenk tube was charged with \([\text{Ir}(\text{dF(CF}_3\text{)ppy})_2(5,5'-\text{dCF}_3\text{bpy})](\text{PF}_6)\) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst \(\Lambda-\text{RhO}\) (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), racemic benzamide \(1\text{k}\) (74.7 mg, 0.30 mmol), and \(\alpha,\beta\)-unsaturated 2-acyl imidazole \(2\text{a}\) (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH\(_2\)Cl\(_2\) (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 46 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product \(3\text{w}\) as a white solid (85.8 mg, 0.164 mmol, yield: 82%, d.r. = 1:1). Enantiomeric excess was established as 97% ee/89% ee by HPLC analysis using a Chiralpak IB column. (HPLC conditions: IB, wavelength = 254 nm, eluents: n-hexane/isopropanol = 75:25, flow rate = 0.5 mL/min, temperature = 30 °C, \(t_r\) (syn, major) = 59.5 min, \(t_r\) (syn, minor) = 71.3 min, \(t_r\) (anti, major) = 78.1 min, \(t_r\) (anti, minor) = 131.9 min). The d.r. value was determined by \(^1\text{H} \text{NMR}\) of \(3\text{w}\) (after purified by flash chromatography).

\(^1\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.76 (d, \(J = 8.8 \text{ Hz}\), 2H), 7.34–7.31 (m, 1H), 7.26 (s, 2H), 7.24–7.20 (m, 6H), 7.09 (d, \(J = 0.8 \text{ Hz}\), 1H), 6.88 (d, \(J = 8.8 \text{ Hz}\), 2H), 6.69 (d, \(J = 7.6 \text{ Hz}\), 2H), 5.87 (d, \(J = 8.3 \text{ Hz}\), 1H), 4.10–4.05 (m, 1H), 3.89–3.80 (m, 4H), 3.46 (d, \(J = 7.3 \text{ Hz}\), 2H), 1.77–1.66 (m, 1H), 1.56–1.50 (m, 1H), 1.38–1.31 (m, 2H), 1.18 (d, \(J = 6.5 \text{ Hz}\), 3H), 0.92 (s, 3H), 0.79 (s, 3H).

\(^13\text{C} \text{NMR}\) (101 MHz, CDCl\(_3\)): \(\delta\) (ppm) 190.9, 166.2, 161.8, 143.3, 141.4, 138.0, 130.0, 129.2, 128.7, 128.6, 128.5, 127.5, 127.2, 126.5, 126.3, 125.3, 113.5, 55.3, 49.4, 46.2, 39.8, 37.1, 36.1, 31.2, 26.8, 24.9, 21.8.

IR (film): \(\nu\) (cm\(^{-1}\)) 2963, 2932, 1685, 1631, 1605, 1537, 1503, 1452, 1406, 1306, 1253, 1177, 1030, 964, 914, 844, 761, 702.

HRMS (ESI, \(m/z\)) calcd for \(\text{C}_{33}\text{H}_{38}\text{N}_3\text{O}_3\) (M+H): 524.2907, found: 524.2909.

A dried 10 mL Schlenk tube was charged with \([\text{Ir}(\text{dF(CF}_3\text{)ppy})_2(5,5'-\text{dCF}_3\text{bpy})](\text{PF}_6)\) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst \(\Lambda-\text{RhO}\) (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide \(1\text{l}\) (78.9 mg, 0.30 mmol), and \(\alpha,\beta\)-unsaturated 2-acyl imidazole \(2\text{a}\) (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH\(_2\)Cl\(_2\) (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 44 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to...
1:4) to afford product 3x as a white solid (55.9 mg, 0.104 mmol, yield: 52%). Enantiomeric excess was established as 91% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 10.0 min, t_r (major) = 17.2 min). [α]_D^{25} = -15.3° (c = 1.0, CH2Cl2).

1H NMR (500 MHz, CDCl3): δ (ppm) 7.60 (d, J = 8.6 Hz, 2H), 7.36–7.29 (m, 1H), 7.26 (t, J = 7.5 Hz, 2H), 7.22–7.13 (m, 6H), 7.05 (s, 1H), 6.86 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 7.5 Hz, 2H), 5.80 (s, 1H), 3.87–3.73 (m, 4H), 3.39–3.24 (m, 2H), 1.91–1.77 (m, 2H), 1.40 (s, 6H), 1.37–1.27 (m, 2H), 0.96 (s, 3H), 0.84 (s, 3H).

13C NMR (125 MHz, CDCl3): δ (ppm) 191.0, 166.4, 161.8, 143.5 (2C), 141.4, 138.1, 130.1, 129.2, 128.8, 128.4, 128.3, 127.5, 126.5, 126.1, 125.3, 113.6, 55.4, 53.9, 49.8, 39.6, 35.9, 34.7, 34.6, 27.1, 27.0, 25.1, 24.8.

IR (film): ν (cm⁻¹) 2965, 914, 844, 765, 702.

HRMS (ESI, m/z) calcd for C_{34}H_{40}N_{3}O_{3} (M+H)^+: 538.3064, found: 538.3072.

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF3)ppy)2(5,5'-dCF3bpy)](PF6) (13.75 mg, 0.0120 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1m (84.9 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH2Cl2 (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 47 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3ya as a white solid (44.6 mg, 0.080 mmol, yield: 40%, d.r. = 1:1). Enantiomeric excess was established as 90% ee / 84% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 65:35, flow rate = 0.5 mL/min, temperature = 30 °C, t_r (syn, major) = 19.5, t_r (syn, minor) = 40.5 min, t_r (anti, minor) = 23.1 min), t_r (anti, major) = 35.5 min). The d.r. value was determined by 1H NMR of 3ya (after purified by flash chromatography).

1H NMR (500 MHz, CDCl3): δ (ppm) 7.63 (d, J = 8.8 Hz, 2H), 7.36–7.33 (m, 1H), 7.25 (d, J = 1.1 Hz, 2H), 7.25–7.20 (m, 6H), 7.13–7.09 (m, 3H), 6.97 (d, J = 0.7 Hz, 1H), 6.93–6.88 (m, 4H), 6.80 (d, J = 7.6 Hz, 2H), 6.01 (s, 1H), 3.81 (s, 3H), 3.66–3.60 (m, 2H), 3.39–3.22 (m, 2H), 2.92–2.86 (m, 1H), 1.79–1.66 (m, 1H), 1.47–1.40 (m, 2H), 1.24–1.16 (m, 2H).

13C NMR (125 MHz, CDCl3): δ (ppm) 190.2, 166.8, 161.9, 143.2, 141.9, 138.1, 129.4, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.8, 127.1, 126.6, 126.5, 126.2, 125.5, 113.6, 55.3, 51.3, 47.4, 44.3, 39.7, 31.1, 27.8.

IR (film): ν (cm⁻¹) 2929, 1682, 1633, 1605, 1543, 1503, 1451, 1405, 1307, 1253, 1178, 1029, 845, s25
A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1p (146.8 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 43 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3z as a white solid (68.4 mg, 0.124 mmol, yield: 62%, d.r. = 1.2:1). Enantiomeric excess was established as 95% ee / 93% ee by HPLC analysis using a Chiralpak OD-H column. (HPLC conditions: OD-H, wavelength = 254 nm, eluents: n-hexane/isopropanol = 60:40, flow rate = 1 mL/min, temperature = 30 °C, tₛ (syn, minor) = 5.4 min, tᵣ (syn, major) = 14.8 min, tₛ (anti, minor) = 9.2 min, tᵣ (anti, major) = 38.4 min). The d.r. value was determined by ¹H NMR of 3z (after purified by flash chromatography).

¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.67 (d, J = 8.8 Hz, 2H), 7.30–7.28 (m, 1H), 7.26–7.23 (m, 2H), 7.21 (d, J = 0.9 Hz, 1H), 7.18–7.16 (m, 5H), 7.05 (d, J = 0.9 Hz, 1H), 6.87 (d, J = 1.3 Hz, 2H), 6.70 (d, J = 3.2 Hz, 2H), 6.19 (s, 1H), 3.83 (s, 3H), 3.87–3.80 (m, 1H), 3.45–3.38 (m, 3H), 3.21 (dd, J = 15.4, 3.8 Hz, 1H), 1.76–1.65 (m, 1H), 1.65–1.55 (m, 2H), 1.54–1.45 (m, 2H), 1.23–1.14 (m, 5H), 0.90–0.85 (m, 6H).

¹³C NMR (125 MHz, CDCl₃): δ (ppm) 191.1, 166.9, 162.0, 143.5, 141.1, 138.0, 130.3, 129.2, 129.1, 128.7, 128.6, 128.3, 127.7, 127.5, 126.2, 125.2, 113.6, 55.3, 48.4, 40.6, 39.3, 38.3, 36.9, 34.3, 25.7, 23.8, 23.6, 22.0, 14.1.

IR (film): ν (cm⁻¹) 2956, 2930, 1684, 1633, 1606, 1544, 1503, 1444, 1406, 1306, 1254, 1178, 1031, 965, 914, 844, 760, 703.

HRMS (ESI, m/z) calcd for C₃₅H₄₂N₃O₃ (M+H)⁺: 552.3220, found: 552.3225.
degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 46 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3za as a colorless oil (76.3 mg, 0.100 mmol, yield: 50%, d.r. = 2.2:1). Enantiomeric excess was established as 90% ee (major diastereoisomer) by HPLC analysis using a Chiralpak IC column. (HPLC conditions: IC, wavelength = 254 nm, eluents: n-hexane/isopropanol = 60:40, flow rate = 1 mL/min, temperature = 30 °C, t_r (minor) = 11.2 min, t_r (major) = 14.5 min). The d.r. value was determined by 1H NMR of 3za (after purified by flash chromatography).

\[ \text{[}\alpha\text{]}_D^{25} = -3.0^\circ (c = 1.0, \text{CHCl}_3) \]

(\text{major diastereoisomer})

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.68–7.63 (m, 6H), 7.41–7.28 (m, 8H), 7.24 (t, \(J = 7.7\) Hz, 2H), 7.21–7.17 (m, 3H), 7.16–7.14 (m, 2H), 7.04 (d, \(J = 0.9\) Hz, 1H), 6.89 (d, \(J = 8.8\) Hz, 2H), 6.67 (d, \(J = 8.0\) Hz, 2H), 5.91 (s, 1H), 3.97–3.76 (m, 2H), 3.84 (s, 3H), 3.63 (dd, \(J = 11.8, 4.0\) Hz, 1H), 3.56 (d, \(J = 10.4\) Hz, 1H), 3.38 (d, \(J = 10.4\) Hz, 1H), 3.31 (dd, \(J = 15.5, 3.9\) Hz, 2H), 3.24–3.13 (m, 1H), 1.39–1.35 (m, 2H), 1.31–1.28 (m, 1H), 1.10 (s, 9H), 0.80 (s, 3H).

(Major diastereoisomer)

13C NMR (125 MHz, CDCl₃): δ (ppm) 190.9, 166.9, 162.0, 143.5, 140.9, 138.1, 135.9, 135.9, 133.6, 130.3, 129.6, 129.6, 129.2, 128.8, 128.6, 128.3, 127.6, 126.4, 126.2, 125.3, 113.6, 67.8, 55.4, 46.6, 40.9, 40.6, 39.7, 32.8, 27.1, 23.6, 19.4, 19.2. (Major diastereoisomer)

IR (film): ν (cm⁻¹) 2960, 2928, 2855, 1686, 1639, 1606, 1545, 1503, 1444, 1406, 1306, 1256, 1178, 1105, 1087, 1029, 804, 757, 702, 611, 503. (Major diastereoisomer)

HRMS (ESI, \(m/z\)) calcd for C₄₈H₅₉N₅O₄SiNa (M+Na)⁺: 786.3697, found: 786.3688.

4. Synthetic Transformation and Absolute Configuration Assignment of the Products

4.1 Transformation of Product 3a to its Ester Derivative

To a solution of asymmetric photoredox product 3a (94% ee, 160.0 mg, 0.314 mmol) in anhydrous CH₃CN (3.0 mL) was added 4 Å MS (314 mg) under argon atmosphere. The suspension was stirred vigorously at 25 °C under argon atmosphere for 0.5 h, then methyl trifluoromethansulfonate (53.0 μL, 0.472 mmol) was added. After being stirred at 25 °C for additional 2 h, (4-bromophenyl)methanol (117.4 mg, 0.628 mmol) and DBU (56.0 μL, 0.378 mmol) were added at 0 °C. The resulting suspension was stirred at 0 °C for 3 h, then concentrated into dryness. The residue was purified by flash chromatography on silica gel (acetone/n-hexane = 1:5) to afford S3 (121.8 mg, 0.221 mmol, 70% yield) as a white solid. Enantiomeric excess was established as 94% ee by HPLC analysis using a Chiralpak OJ column. (HPLC conditions: OJ, wavelength = 254 nm, eluents: n-hexane/isopropanol = 50:50, flow rate = 0.8 mL/min,
temperature = 25 °C, \( t_r \) (minor) = 12.0 min, \( t_r \) (major) = 43.7 min). \([\alpha]_D^{25} = 40.5^\circ \) (c = 1.0, CH\(_2\)Cl\(_2\)).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) 7.70 (d, \( J = 8.8 \) Hz, 2H), 7.34 (d, \( J = 8.4 \) Hz, 2H), 7.23–7.16 (m, 3H), 7.15–7.09 (m, 2H), 6.90 (d, \( J = 8.8 \) Hz, 2H), 6.85 (d, \( J = 8.4 \) Hz, 2H), 6.18 (s, 1H), 4.87–4.75 (m, 2H), 3.83 (s, 3H), 3.35 (td, \( J = 7.6, 2.3 \) Hz, 2H), 3.05 (dd, \( J = 10.6, 5.2 \) Hz, 1H), 2.82–2.72 (m, 2H), 1.72–1.49 (m, 2H), 1.30–1.19 (m, 2H), 0.89 (s, 3H), 0.81 (s, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) (ppm) 172.6, 166.9, 162.0, 140.6, 134.8, 131.4, 129.5, 129.4, 128.6, 127.7, 127.0, 126.5, 121.8, 113.6, 65.1, 55.3, 50.5, 40.5, 37.6, 35.4, 24.8, 24.7, 24.3.

IR (film): \( \nu \) (cm\(^{-1}\)) 2961, 2871, 1734, 1632, 1606, 1544, 1504, 1453, 1369, 1294, 1255, 1178, 1146, 1070, 1031, 1012, 844, 804, 766, 737, 704.

HRMS (ESI, \( m/z \)) calcd for C\(_{30}\)H\(_{34}\)BrNO\(_4\)Na (M+Na): 574.1563, found: 574.1564.

4.2 Absolute Configuration Assignment of the Products

The absolute configuration of product 3a (94% ee, synthesized through the asymmetric photoredox reaction catalyzed by \( \Lambda\)-RhO) was assigned as S by single crystal X-ray diffraction of its ester derivative S3 (See Section 7 for crystallographic data of S3). The configurations of all other products were assigned in analogy.

5. Mechanistic Studies

5.1 Control experiments

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\(^a\) Taken from entry 4 of Table 1. \(^b\) isolated yield. \(^c\) ee determined by chiral HPLC. \(^d\) not determined.

**Entry 2:** A dried 10 mL Schlenk tube was charged with [Ir(dF(CF\(_3\))ppy)\(_2\)](5,5'-dCF\(_3\)bpy)](PF\(_6\)) (4.58 mg, 0.0040 mmol), chiral rhodium catalyst \( \Lambda\)-RhO (6.64 mg, 0.0080 mmol), tetrabutylammonium dibutyl phosphate (3.61 mg, 0.0080 mmol), 4 Å MS (100 mg), benzamide 1a (35.1 mg, 0.15 mmol), and \( \alpha,\beta \)-unsaturated 2-acyl imidazole 2a (27.4 mg, 0.10 mmol). Anhydrous CH\(_2\)Cl\(_2\) was added (0.5
The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C under air for the 38 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3a (10.7 mg, 0.021 mmol, yield: 21%) with 36% ee.

**Entry 3:** A dried 10 mL Schlenk tube was charged with [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(5,5'-dCF<sub>3</sub> bpy)](PF<sub>6</sub>) (9.16 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), TEMPO (62.5 mg, 0.40 mmol) benzamide 1a (70.2 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added (1.0 mL). The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C under argon for the 40 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford product 3a (5.1 mg, 0.010 mmol, yield: 5%).

**Entry 4:** A dried 10 mL Schlenk tube was charged with [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(5,5'-dCF<sub>3</sub> bpy)](PF<sub>6</sub>) (9.16 mg, 0.0080 mmol), chiral rhodium catalyst Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), BHT (132.2 mg, 0.60 mmol) benzamide 1a (70.2 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added (1.0 mL). The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After stirred at 27 °C under argon for the 38 h, no new product was observed. As a result, 85% of 1a (59.7 mg, 0.255 mmol) and 80% of 2a (43.8 mg, 0.160 mmol) were recovered.

**Remarks:** The catalytic reaction in the presence of air or radical inhibitor BHT (3.0 equiv.) results in a significantly reduced yield and enantioselectivity. Addition of TEMPO (2.0 equiv.) at the standard conditions leads to no observation of product 3a. These results fully support a radical pathway during the catalysis.

### 5.2 Radical Trapping Experiments

![Radical Trapping Experiment](image)

- in the presence of Λ-RhO: 3a (24% yield, 90% ee); S5 (37% yield);
- in the absence of Λ-RhO: 3a (trace); S5 (46% yield).

**In the presence of Λ-RhO:** A dried 10 mL Schlenk tube was charged with [Ir(dF(CF<sub>3</sub>)ppy)<sub>2</sub>(5,5'-dCF<sub>3</sub> bpy)](PF<sub>6</sub>) (9.16 mg, 0.0080 mmol), Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1a (70.2 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction
mixture was degassed and backfilled with argon for three cycles. Degassed CH₂Cl₂ (1.0 mL) and 3-buten-2-one (S₄, 16.6 µL, 0.20 mmol) were added. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for 38 h, the reaction was concentrated then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford products 3a (24.4 mg, 0.048 mmol, yield: 24%) with 90% ee and S₅ (22.6 mg, 0.074 mmol, yield: 37%).

\[ \text{1H NMR (500 MHz, CDCl}_3) \delta (ppm) 7.74 (d, } J = 8.7 \text{ Hz, 2H), 6.92 (d, } J = 8.7 \text{ Hz, 2H), 6.20 (s, 1H), 3.84 (s, 3H), 3.40 (q, } J = 6.9 \text{ Hz, 2H), 2.43–2.30 (m, 2H), 2.14 (s, 3H), 1.61–1.51 (m, 2H), 1.51–1.44 (m, 2H), 1.27–1.20 (m, 2H), 0.86 (s, 6H).} \]

HRMS (ESI, m/z) calcd for C₁₈H₂₇NO₃Na (M+Na)+: 328.1883, found: 328.1883.

All spectroscopic data were in agreement with the literature.⁴

In the absence of Λ-RhO: A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5’-dCF₃bpy)](PF₆) (9.16 mg, 0.0080 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide 1a (70.2 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed CH₂Cl₂ (1.0 mL) and 3-buten-2-one (S₄, 16.6 µL, 0.20 mmol) were added. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for 38 h, the reaction was concentrated then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4) to afford S₅ (28.0 mg, 0.092 mmol, yield: 46%). Only trace amount of 3a was observed in the reaction.

5.3 Isolation of a Side Product

Performed in analogy to entry 3 of Table 1. A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5’-dCF₃bpy)](PF₆) (9.16 mg, 0.0080 mmol), Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (9.03 mg, 0.0200 mmol), 4 Å MS (200 mg), benzamide 1a (70.2 mg, 0.30 mmol), and α,β-unsaturated 2-acyl imidazole 2a (54.8 mg, 0.20 mmol). The reaction
mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (1.0 mL) was added. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for 38 h, the reaction was concentrated then purified by flash chromatography on silica gel (acetone/n-hexane = 1:5 to 1:4). Main product 3a as isolated as a white solid (75.3 mg, 0.148 mmol, yield: 74%) with 94% ee. Meanwhile, a side product S6 (11.0 mg, 0.020 mmol, yield: 10%) was also isolated.

![Image of S6](image)

1H NMR (500 MHz, CDCl₃): δ (ppm) 7.56–7.44 (m, 5H), 7.31 (d, J = 7.1 Hz, 2H), 7.23 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 0.9 Hz, 1H), 6.92 (d, J = 0.9 Hz, 1H), 4.69–4.61 (m, 1H), 4.21–4.12 (m, 1H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 188.8, 143.0, 141.9, 138.4, 129.3, 129.0, 128.6, 128.3, 127.2, 126.7, 126.5, 125.8, 50.5, 43.2.

IR (film): ν (cm⁻¹) 2922, 1679, 1597, 1492, 1446, 1418, 1310, 1148, 1032, 975, 893, 759, 696.

HRMS (ESI, m/z) calcd for C₃₆H₂₈N₄O₂Na (M+Na)+: 571.2104, found: 571.2110.

5.4 Synthesis of a Potential Intermediate Complex rac-S7

A solution of substrate 2a (20.0 mg, 0.073 mmol) and racemic rhodium catalyst rac-RhO (60.0 mg, 0.072 mmol) in CH₂Cl₂ (1.5 mL) was stirred at room temperature overnight, then n-hexane (5.0 mL) was slowly added. The mixture was stirred for additional 10 minutes. The pale yellow precipitate was collected, washed with n-hexane (1 x 5.0 mL) and dried in high vacuum to afford rac-S7 (70.0 mg, yield: 95%).

1H NMR (500 MHz, CDCl₃): δ (ppm) 8.20 (d, J = 15.4 Hz, 1H), 8.02 (s, 1H), 7.88 (d, J = 6.7 Hz, 1H), 7.84 (d, J = 6.7 Hz, 1H), 7.74 (t, J = 6.8 Hz, 2H), 7.67 (dd, J = 8.8, 1.8 Hz, 4H), 7.52 (td, J = 8.7, 1.8 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.39–7.27 (m, 4H), 7.27–7.23 (m, 1H), 7.22–7.13 (m, 2H), 7.12–7.01 (m, 4H), 6.62 (dd, J = 7.6, 4.3 Hz, 2H), 6.41 (d, J = 15.4 Hz, 1H), 6.28 (d, J = 1.5 Hz, 1H), 1.21 (s, 9H), 1.09 (s, 9H).

13C NMR (125 MHz, CDCl₃): δ (ppm) 182.4, 172.2, 170.0, 163.1, 162.8, 158.5, 158.2, 152.0, 150.8,
150.3, 148.4, 148.3, 145.3, 137.4, 137.0, 135.4, 134.5, 133.5, 133.4, 133.0, 132.2, 132.0, 131.8, 131.6, 130.9, 129.6, 129.4, 129.3, 126.6, 126.3, 126.0, 124.3, 124.2, 124.1, 118.7, 112.2, 111.7, 111.6, 111.1, 35.2, 35.1, 31.6, 31.5.

IR (film): \( \nu \) (cm\(^{-1}\)) 2961, 1619, 1591, 1537, 1492, 1448, 1404, 1386, 1117, 1081, 1035, 842, 770, 735, 557.

HRMS (ESI, \( m/z \)) calcd for C\(_{52}H_{60}N_4O_3Rh\) (M-PF\(_6\))^+: 877.2619, found: 877.2690.

### 5.5 Other Lewis Acid Catalysts

1. **Replacing \( \Lambda\)-RhO with chiral Ni\(^{II}\)-BOX as the Lewis acid catalyst**

   ![Diagram](image1)

   A dried 10 mL Schlenk tube was charged with chiral BOX ligand (0.010 mmol, 3.34 mg) and Ni(ClO\(_4\))\(_2\)\(6\)H\(_2\)O (0.010 mmol, 3.65 mg), anhydrous CH\(_2\)Cl\(_2\) (0.5 mL) was added. The mixture was stirred at room temperature for 30 min, then [Ir(dF(CF\(_3\))ppy)\(_2\)(5,5'-dCF\(_3\)bpy)](PF\(_6\)) (4.58 mg, 0.0040 mmol), tetrabutylammonium dibutyl phosphate (3.61 mg, 0.0080 mmol), 4 Å MS (50 mg), benzamide 1a (35.1 mg, 0.15 mmol), and \( \alpha,\beta \)-unsaturated 2-acyl imidazole 2a (27.4 mg, 0.10 mmol) were added. The reaction mixture was degassed and backfilled with argon for three cycles. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. The mixture was stirred at 27 °C for 33 h. As a result, product 3a was not observed and 15% yield of side product S6 (8.2 mg, 0.015 mmol) was isolated. Meanwhile, 86% of 1a (30.2 mg, 0.129 mmol) and 60% of 2a (16.4 mg, 0.060 mmol) were recovered.

2. **Replacing \( \Lambda\)-RhO with chiral Cu\(^{II}\)-BOX as the Lewis acid catalyst**

   ![Diagram](image2)

   A dried 10 mL Schlenk tube was charged with chiral BOX ligand (0.010 mmol, 3.34 mg) and Cu(ClO\(_4\))\(_2\)\(6\)H\(_2\)O (0.010 mmol, 3.65 mg), anhydrous CH\(_2\)Cl\(_2\) (0.5 mL) was added. The mixture was stirred at room temperature for 30 min, then [Ir(dF(CF\(_3\))ppy)\(_2\)(5,5'-dCF\(_3\)bpy)](PF\(_6\)) (4.58 mg, 0.0040 mmol), tetrabutylammonium dibutyl phosphate (3.61 mg, 0.0080 mmol), 4 Å MS (50 mg), benzamide 1a (35.1 mg, 0.15 mmol), and \( \alpha,\beta \)-unsaturated 2-acyl imidazole 2a (27.4 mg, 0.10 mmol) were added. The reaction mixture was degassed and backfilled with argon for three cycles. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. The mixture was stirred at 27 °C for 33 h. As a result, product 3a was not observed and 12% yield of 15% yield of side product S6 (8.2 mg, 0.015 mmol) was isolated. Meanwhile, 86% of 1a (30.2 mg, 0.129 mmol) and 60% of 2a (16.4 mg, 0.060 mmol) were recovered.
A dried 10 mL Schlenk tube was charged with chiral Box ligand (0.010 mmol, 3.34 mg) and Cu(OTf)$_2$ (0.010 mmol, 3.61 mg), anhydrous CH$_2$Cl$_2$ (0.5 mL) was added. The mixture was stirred at room temperature for 30 min, then [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCF$_3$bpyp)](PF$_6$) (4.58 mg, 0.0040 mmol), tetrabutylammonium dibutyl phosphate (3.61 mg, 0.0080 mmol), 4 Å MS (50 mg), benzamide 1a (35.1 mg, 0.15 mmol), and α,β-unsaturated 2-acyl imidazole 2a (27.4 mg, 0.10 mmol) were added. The reaction mixture was degassed and backfilled with argon for three cycles. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. The mixture was stirred at 27 °C for 33 h. As a result, product 3a was not observed and 12% yield of side product S6 (6.6 mg, 0.012 mmol) was isolated. Meanwhile, 88% of 1a (30.9 mg, 0.132 mmol) and 60% of 2a (16.4 mg, 0.060 mmol) were recovered.

5.6 Other α,β-Unsaturated Carbonyl Compounds as Radical Acceptors

(1) α,β-Unsaturated 2-acylpyrazole as radical acceptor

A dried 10 mL Schlenk tube was charged with [Ir(dF(CF$_3$)ppy)$_2$(5,5'-dCF$_3$bpyp)](PF$_6$) (9.17 mg, 0.0080 mmol), rhodium catalyst Δ/Λ-RhO (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (100 mg), benzamide 1a (70.2 mg, 0.30 mmol), and α,β-unsaturated 2-acylpyrazole 2n (32.8 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH$_2$Cl$_2$ (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (ethyl acetate/n-hexane = 1:5 to 1:4) to afford product S8 as a colorless oil (8.0 mg, 0.02 mmol, yield: 10%).

$^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.72 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 6.15 (s, 1H), 5.95 (s, 1H), 3.84 (s, 3H), 3.50–3.37 (m, 2H), 3.15 (dd, $J = 15.7$, 2.7 Hz, 1H), 2.83 (dd, $J = 15.7$, 10.6 Hz, 1H), 2.53 (s, 3H), 2.22 (s, 3H), 2.14–2.07 (m, 1H), 1.72–1.58 (m, 4H), 0.92–0.88 (m, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 174.5, 167.0, 162.1, 151.7, 144.0, 128.6, 127.2, 113.7, 111.0, 55.4, 40.8, 37.8, 37.6, 36.9, 35.2, 29.7, 24.6, 24.3, 24.1, 14.7, 13.8.

IR (film): ν (cm$^{-1}$) 2962, 2927, 1724, 1632, 1606, 1545, 1504, 1462, 1377, 1326, 1258, 1177, 1106, 1030, 963, 843, 801.

HRMS (ESI, $m/z$) calcd for C$_{23}$H$_{33}$N$_3$O$_3$Na (M+Na)$^+$: 422.2414, found: 422.2425.
(2) Chalcone as radical acceptor

\[ \text{PMP} - \text{N} - \text{H} + \text{Ph} - \text{O} - \text{Ph} \xrightarrow{\Delta/\Lambda-\text{RhO}} \text{PMP} - \text{N} - \text{Ph} - \text{O} - \text{Ph} \]

A dried 10 mL Schlenk tube was charged with \([\text{Ir(dF(CF}_3)ppy)_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)\) (9.17 mg, 0.0080 mmol), rhodium catalyst \(\Delta/\Lambda-\text{RhO}\) (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (100 mg), benzamide 1a (70.2 mg, 0.30 mmol), and \((E)\)-chalcone 2o (41.6 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Anhydrous \(\text{CH}_2\text{Cl}_2\) (1.0 mL) was added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. The reaction mixture was stirred at 27 °C for the 48 h, only trace of product S9 was observed. The starting material 87% of 1a (61.1 mg, 0.261 mmol) and 80% of 2o (33.3 mg, 0.160 mmol) were recovered.

5.7 UV/Vis-Absorption Spectra

All the samples were freshly prepared as a 0.10 mM solution in dichloromethane. Their UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 in a 10.0 mm quartz cuvette. Not only the sensitizers \([\text{Ir(dF(CF}_3)ppy}_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)\) but also the Lewis acid catalyst \(\text{rac-RhO}\) and intermediate \(\text{rac-S7}\) absorb in the visible region.

![UV/Vis-Absorption Spectra](image)

**Figure S1.** UV/Vis-absorption spectra of the different components in \(\text{CH}_2\text{Cl}_2\) (0.1 mM). a.u. = absorbance units. **Red:** rhodium catalyst \(\text{rac-RhO}\); **blue:** intermediate complex \(\text{rac-S7}\); **green:** a mixture of photocatalyst PC1 and phosphate base B1; **pink:** a mixture of intermediate complex \(\text{rac-S7}\), photocatalyst PC1 and phosphate base B1.
5.8 Alternative Radical Addition Mechanism

A radical addition mechanism cannot be excluded in the catalytic reaction or might compete with the suggested radical-radical recombination mechanism. As illustrated in Figure S2, visible-light-induced PCET converts the amide N-H into an amidyl radical which then undergoes an intramolecular 1,5-HAT, thereby converting the δ-C-H group into a carbon-centered radical B. The subsequently conjugate radical addition to the rhodium-coordinated α,β-unsaturated 2-acyl imidazole forms a new C-C bond in an asymmetric fashion. The intermediate G is reduced with PC− and protonated to obtain H. Upon release of the product and coordination of new substrate a new catalytic cycle can be initiated (H→C).

Figure S2. Alternative conjugate radical addition mechanism.
6. Chiral HPLC Chromatography

6.1 Determination of Enantioselectivities of the Asymmetric Photoredox Reactions

Enantiomeric excess of the compounds 3a-j, 3n, 3q-za were determined with a Daicel Chiralpak OD-H (250 x 4.6 mm), Daicel Chiralpak IB (250 x 4.6 mm), Daicel Chiralpak IC (250 x 4.6 mm), or Daicel Chiralpak AD-H (250 x 4.6 mm) HPLC column on an Agilent 1260 Series HPLC System using n-hexane/isopropanol as the mobile phase. The column temperature was 30 °C, and UV-absorption was measured at 254 nm.

Figure S3. HPLC trace for the racemic reference rac-3a and non-racemic product (S)-3a.
Figure S4. HPLC trace for the racemic reference \textit{rac-3b} and non-racemic product (\textit{S})-3b.

HPLC: Agilent 1260 Series HPLC System
Column: Daicel chiralpak OD-H (250 x 4.6 nm)
Mobile phase: \textit{n}-hexane/isopropanol = 80:20
Flow rate = 1.0 mL/min
Column temperature = 30 °C
Detection wavelength = 254 nm

\textit{rac-3b} (reference)
Figure S5. HPLC trace for the racemic reference rac-3c and non-racemic product (S)-3c.
Figure S6. HPLC trace for the racemic reference rac-3d and non-racemic product (S)-3d.
**Figure S7.** HPLC trace for the racemic reference *rac*-3e and non-racemic product (S)-3e.
Figure S8. HPLC trace for the racemic reference *rac*-3f and non-racemic product (S)-3f.
Figure S9. HPLC trace for the racemic reference rac-3g and non-racemic product (S)-3g.
Figure S10. HPLC trace for the racemic reference *rac-3h* and non-racemic product *(S)-3h*. 

HPLC: Agilent 1260 Series HPLC System
Column: Daicel chiralpak AD-H (250 x 4.6 nm)
Mobile phase: *n*-hexane/isopropanol = 80:20
Flow rate = 1.0 mL/min
Column temperature = 30 °C
Detection wavelength = 254 nm

*rac-3h* (reference)
Figure S11. HPLC trace for the racemic reference rac-3i and non-racemic product (S)-3i.
Figure S12. HPLC trace for the racemic reference \( \textit{rac-3j} \) and non-racemic product \((S)-3j\).
**Figure S13.** HPLC trace for the racemic reference $\textit{rac}$-3n and non-racemic product (S)-3n.
Figure S14. HPLC trace for the racemic reference \textit{rac-3q} and non-racemic product (\textit{S}-3q).
HPLC: Agilent 1260 Series HPLC System
Column: Daicel chiralpak AD-H (250 x 4.6 nm)
Mobile phase: n-hexane/isopropanol = 70:30
flow rate = 1.0 mL/min
Column temperature = 30 °C
Detection wavelength = 254 nm

*rac-3r* (reference)

**Figure S15.** HPLC trace for the racemic reference *rac-3r* and non-racemic product (S)-3r.
Figure S16. HPLC trace for the racemic reference *rac-3s* and non-racemic product (S)-3s.
Figure S17. HPLC trace for the racemic reference *rac*-3t and non-racemic product 3t (28:1 d.r.).
Figure S18. HPLC trace for the racemic reference rac-3u and non-racemic product (S)-3u.

HPLC: Agilent 1260 Series HPLC System
Column: Daicel chiralpak AD-H (250 x 4.6 nm)
Mobile phase: n-hexane/isopropanol = 70:30
flow rate = 1.0 mL/min
Column temperature = 30 °C
Detection wavelength = 254 nm

rac-3u (reference)
Figure S19. HPLC trace for the racemic reference rac-3v and non-racemic product (S)-3v.
Figure S20. HPLC trace for the racemic reference rac-3w and non-racemic product (S)-3w.
Figure S21. HPLC trace for the racemic reference rac-3x and non-racemic product (S)-3x.
Figure S22. HPLC trace for the racemic reference $rac$-3ya and non-racemic product ($S$)-3ya.
Figure S23. HPLC trace for the racemic reference rac-3z and non-racemic product (S)-3z.
Figure S24. HPLC trace for the racemic reference rac-3za (major diastereoisomer) and non-racemic product (S)-3za (major diastereoisomer).
6.2 Determination of Enantiopurity of the Transformation Product S3

Optical purities of compound S3 (before and after crystallization) were determined with a Daicel Chiralpak OJ column on an Agilent 1260 Series HPLC System. The column temperature was 25 °C and UV-absorption was measured at 254 nm.

HPLC: Agilent 1260 Series HPLC System
Column: Daicel chiralpak OJ (250 x 4.6 nm)
Mobile phase: n-hexane/isopropanol = 50:50
flow rate = 0.8 mL/min
Column temperature = 25 °C
Detection wavelength = 254 nm
rae-S3 (reference)
Figure S25. HPLC trace of rac-S3 (reference compound synthesized from rac-3a), (S)-S3 (synthesized from product 3a with 94% ee) and crystalline product (S)-S3.
7. Single Crystal X-Ray Diffraction

Single crystals of S3 suitable for X-ray diffraction were obtained from a solution of the compound in dichloromethane layered with diethyl ether and n-hexane at room temperature. Diffraction data were collected on a Agilent SuperNova system. X-ray single crystal diffractometer with Cu-Kα radiation (λ = 1.54184 Å) at 173k. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on F2 data of one twin domain using SHELXL-97. Data collection and refinement statistics are given in Table S2. Crystallographic data (excluding structure factors) for S3 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1554166.

Figure S26. Crystal structure of (S)-S3. ORTEP drawing with 50% probability thermal ellipsoids.
Table S2. Crystal data and structure refinement for (S)-3S.

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8. References


9. NMR Spectra

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 101 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 101 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 101 MHz)
$^{1}H$ NMR (CDCl$_3$, 500 MHz)

$^{13}C$ NMR (CDCl$_3$, 125 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 101 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^{1}H$ NMR (CDCl$_3$, 400 MHz)

$^{13}C$ NMR (CDCl$_3$, 101 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^{1}H$ NMR (CDCl$_3$, 500 MHz)

$^{13}C$ NMR (CDCl$_3$, 125 MHz)

3ya (dr = 1:1)
$3z$ (dr = 1.2:1)

$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
major diastereoisomer

3za

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^{1}H$ NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)
S6

$^1$H NMR (CDCl$_3$, 500 MHz)

S6

$^{13}$C NMR (CDCl$_3$, 125 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 101 MHz)