Electronic Supporting Information for:

Combining the Catalytic Enantioselective Reaction of Visible-Light-Generated Radicals with a By-Product Utilization System

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1. General Information

All catalytic reactions were carried out under an atmosphere of nitrogen with magnetic stirring in a Schlenk tube (10 mL). The catalysts Δ -IrS¹ and Δ -RhS² were synthesized according to our published procedures. Δ/Λ -RhO were synthesized with some modifications (see Section 2).³ nitrogen from calcium hydride (CH₃CN, Solvents were distilled under CH₂Cl₂), sodium/benzophenone (THF, Et₂O). HPLC grade of acetone, methanol, and ethanol was used without further purification. Dry 1,4-dioxane was bought from Alfa-Aesar. Reagents that were purchased from commercial suppliers were used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irregular shaped, 230-400 mesh, pH 6.8, pore volume: 0.81 mL \times g⁻¹, mean pore size: 66 Å, specific surface: 492 m² \times g⁻¹, particle size distribution: 0.5% < 25 µm and 1.7% > 71 µm, water content: 1.6%). ¹H NMR, ¹⁹F NMR and proton decoupled ¹³C NMR spectra were recorded on Bruker Avance 300 (300 MHz), or Bruker AM (500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ¹H NMR spectroscopy: $\delta = 7.26$ ppm (CDCl₃). ¹⁹F NMR spectroscopy: $\delta = 0$ ppm (CFCl₃). ¹³C NMR spectroscopy: $\delta = 77.0$ ppm (CDCl₃). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI technique. HPLC chromatography on chiral stationary phase was performed with an Agilent 1200 or Agilent 1260 HPLC system. Optical rotations were measured on a Krüss P8000-T polarimeter with $\left[\alpha\right]_{D^{22}}$ values reported in degrees with concentrations reported in g/100 mL. The EPR spectrometer is from Bruker (model esp300), with a modified Varian rectangular X-band cavity and the modulation frequency was set to 100 kHz, the modulation amplitude was 0.1 mT. The Stern-Volmer quenching experiments were recorded on a Spectra Max M5 microplate reader in a 10.0 mm quartz cuvette.

Light sources and emission spectra of the lamps

A 21 W compact fluorescent lamp (CFL, OSRAM DULUX[®] SUPERSTAR Micro Twist) or 24 W Blue LEDs (Hongchangzhaoming from Chinese Taobao, https://hongchang-led.taobao.com) served as light sources. Figures S1 and S2 display their emission spectra.



Figure S1. Emission spectrum of the 21 W CFL lamp.



Figure S2. Emission spectrum of the 24 W blue LEDs.

2. Modifications for the Synthesis of Λ/Δ -RhO

Racemic **RhO** complex was synthesized according to our previous procedures,³ in which the enantiopure **RhO** was obtained through a proline-mediated route resulting in a loss of at least 50% of rhodium complex. Herein, we modified the resolution process using a chiral auxiliary (*R*)-Aux, namely (*R*)-3-fluoro-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol, instead of proline. The corresponding complexes Λ/Δ -(*R*)-**RhO** are stable and could be separated by flash chromatography, thus improving the atom economy of the catalyst synthesis.



To the mixture of *rac*-**RhO** (249 mg, 0.3 mmol) and K₂CO₃ (82.8 mg, 0.6 mmol) in absolute ethanol (6.0 mL) was added (*R*)-3-fluoro-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol ((*R*)-Aux, 91 mg, 0.33 mmol) in one portion, After stirring at 70 °C overnight, the reaction mixture was cooled to room temperature and concentrated to dryness. The residue was directly subjected to a flash chromatography on silica gel (EtOAc/n-hexane = 1/100 to 1:10) giving Δ -(*R*)-**RhO** (117 mg, 45% yield) as a yellow solid and Λ -(*R*)-**RhO** (112 mg, 43% yield) as a yellow solid, respectively. The bis-acetonitrile catalysts could be obtained after removing of auxiliary following our previously reported procedures.²

Δ -(*R*)-RhO

¹H NMR (500 MHz, CD₂Cl₂) δ 8.02-7.98 (m, 1H), 7.72-7.68 (m, 1H), 7.62-7.58 (m, 1H), 7.55-7.51 (m, 2H), 7.46 (dd, J = 8.8, 2.0 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.31-7.27 (m, 1H), 7.02-6.94 (m, 3H), 6.92-6.84 (m, 3H), 6.67 (d, J = 7.6 Hz, 1H), 6.64-6.48 (m, 3H), 6.37-6.33 (m, 1H), 6.21 (d, J = 7.6 Hz, 2H), 5.96 (ddd, J = 12.8, 7.8, 0.8 Hz, 1H), 4.92 (dd, J = 9.7, 4.6 Hz, 1H), 4.83 (dd, J = 9.7, 9.0 Hz, 1H), 4.11 (dd, J = 9.0, 4.6 Hz, 1H), 1.44 (s, 9H), 1.32 (s, 9H).

¹³C NMR (125 MHz, CD₂Cl₂) δ 175.23, 175.21, 172.0, 171.9, 170.54, 170.50, 169.3, 169.1, 167.1,

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166.9, 165.44, 165.41, 164.1 (d, *J* = 257.5 Hz), 150.1, 150.0, 148.60, 148.56, 141.3, 139.1, 138.6, 134.5, 133.4, 133.3, 133.2, 131.9, 131.4, 131.11, 131.10, 130.8, 130.7, 127.9, 127.5 (2C), 125.7, 125.6, 123.7, 123.3, 123.1, 122.4, 120.60, 120.56, 115.3, 113.0, 111.3, 110.5, 100.2 (d, *J* = 6.4 Hz), 98.7 (d, *J* = 24.1 Hz), 75.0, 69.9, 35.5, 35.4, 31.81, 31.80.

IR (film): *v* (cm⁻¹) 2958, 2904, 2869, 1622, 1589, 1528, 1478, 1445, 1374, 1273, 1224, 1092, 1031, 930, 813, 782, 732, 698, 529, 455,

HRMS (ESI, *m*/*z*) calcd for C₄₉H₄₄FN₃O₄Rh [M+H]⁺: 860.2365, found: 860.2357.

Λ-(*R***)-RhO**

¹H NMR (500 MHz, CD₂Cl₂) δ 8.15-8.11 (m, 1H), 7.74-7.44 (m, 7H), 7.00-6.94 (m, 9H), 6.46-6.28 (m, 3H), 6.04-5.90 (m, 2H), 4.37 (dd, J = 9.3, 7.8 Hz, 1H), 4.24 (dd, J = 16.8, 8.2 Hz, 1H), 4.21 (dd, J = 16.8, 8.2 Hz, 1H), 1.43 (s, 9H), 1.30 (s, 9H).

¹³C NMR (125 MHz, CD₂Cl₂) δ 175.03, 175.00, 172.0, 171.9, 171.81, 171.79, 168.5, 168.2, 168.0, 167.7, 165.51, 165.50, 163.2 (d, J = 253.9 Hz), 150.6, 149.6, 149.0, 148.2, 141.3, 139.1, 138,6, 135.6, 133.3, 132.6, 132.5, 131.3, 131.2, 130.5, 130.2, 128.5, 127.4, 127.2, 125.53, 125.50, 123.9, 123.5, 123.0, 122.3, 119.62, 119.60, 115.2, 114.2, 110.9, 110.8, 102.6 (d, J = 8.3 Hz), 98.5 (d, J = 18.5 Hz), 75.6, 69.3, 35.44, 35.37, 31.8, 31.6.

IR (film): *v* (cm⁻¹) 2958, 2901, 2870, 1623, 1589, 1528, 1478, 1444, 1373, 1273, 1224, 1092, 1030, 979, 931, 814, 783, 733, 698, 529, 456.

HRMS (ESI, *m*/*z*) calcd for C₄₉H₄₄FN₃O₄Rh [M+H]⁺: 860.2365, found: 860.2357.

3. Synthesis of Substrates

3.1 General procedure A



To a mixture of diethyl (cyanomethyl)phosphonate (20 mmol) and a 37% aqueous solution of formaldehyde (80 mmol), a saturated aqueous solution of potassium carbonate (37.5 mmol) was added at room temperature dropwise over 30 min. After stirring for an additional 2 h, the reaction was quenched with saturated aqueous ammonium chloride (20 mL). Afterwards, the reaction mixture was extracted with diethyl ether (3×12.5 mL). The organic layers were combined and dried over sodium sulfate. The solvent was evaporated using a rotary evaporator, and the remaining colorless oil was purified by flash chromatography using pentane/CH₂Cl₂ (2/1) giving the pure product **S1** as a colorless oil (70% yeild).

To a solution of **S1** (14 mmol) in dry ether (20 mL) was added phosphorus(III) bromide (5 mmol) at -10 °C. The temperature was allowed to rise to 20 °C and stirring was continued for 3 h. Water (10 mL) was then added and the mixture was extracted with diethyl ether (3 × 30 mL). The organic phase was washed with brine (20 mL), dried with sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/ CH₂Cl₂, 1/1) to give **S2** as a colorless oil (89% yield).

To a solution of **S2** (2.0 mmol) in methanol (5 mL) was added corresponding sodium aryl sulfinate (3.0 mmol). After 2.5 h of reflux, the mixture was concentrated under reduced pressure, the thereby obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na₂SO₄, filtered and the filtrate was evaporated and purified by chromatography (EtOAc/n-hexane, 1/1) to give corresponding products **2a-h**. The characteristic data of **2a** are in accord with literature.⁴

3.2 General procedure B



To a solution of corresponding alcohol (ROH, 10 mmol) and triethylamine (15 mmol) in acetone (15 mL) was added acryloyl chloride (13 mmol) dropwise at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was warmed to room temperature and stirred for additional 5 h. The resulting mixture was concentrated, then taken up in EtOAc (50 mL) and washed with brine (3×10 mL). The organic extracts were dried over anhydrous Na₂SO₄, concentrated by rotary evaporation. Purification by column chromatography (n-hexane/EtOAc, 9/1) affored corresponding ester **S3**.

To a solution of a 37% aqueous solution of formaldehyde (7.0 mmol) and ester **S3** (5 mmol) in 5 mL 1,4-dioxane-water (1:1, v/v) was added DABCO (7.0 mmol) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was partitioned with EtOAc (50 mL) and water (20 mL). The organic layer was separated and washed with brine (5 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/n-hexane, 1/1) to afford corresponding alcohol ester **S4**.

To a solution of **S4** (5 mmol) in dry ether (10 mL) was added phosphorus(III) bromide (1.7 mmol) dropwise at -10 °C. The temperature was allowed to rise to 20 °C and stirring was continued for 3 h. Water (20 mL) was then added and the mixture was extracted with diethyl ether (3 × 10 mL). The organic phase was washed with saturated sodium chloride solution (5 mL), dried with sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (pentane/CH₂Cl₂, 1/1) to give corresponding brominated compound s7

To a solution of **S5** (2.0 mmol) in methanol (5 mL) was added corresponding sodium aryl sulfinate (3.0 mmol). After 2.5 h of reflux, the mixture was concentrated under reduced pressure, the thereby obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na₂SO₄, filtered and the filtrate was evaporated and purified by chromatography (EtOAc/n-hexane, 1/1) to give corresponding products **2j-m**.

3.3 General procedure C



To a solution of methyl phenyl sulfone (1.25 g, 8.0 mmol) in THF (40 mL) cooled at -78 °C, n-BuLi (1.6 M in n-hexane, 5.5 mL, 8.8 mmol) was added dropwise under argon atmosphere. The resulting solution was stirred at 0 °C for 30 min, and then cooled back to -78 °C. A solution of 2,3,4,5,6-pentafluorobenzaldehyde (1.72g, 8.8 mmol) in THF (2.0 mL) was added dropwise and the temperature was allowed to slowly raise to room temperature, and the solution was stirred until methylphenylsulfone disappeared by TLC. A saturated aqueous solution of NH₄Cl (20 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried with Na₂SO₄ and evaporated under reduced pressure.

Without further purification, the resulting alcohol was dissolved in dry CH_2Cl_2 (25 mL) under argon atmosphere, cooled to 0 °C, then Et₃N (11.2 mL, 80 mmol) and methanesulfonyl chloride (0.93 mL, 12 mmol) were added continuously. After stirring at room temperature for 90 min, a saturated aqueous solution of NH₄Cl (30 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried (Na₂SO₄) and the solvent was evaporated. The residue was purified by flash chromatography (n-hexane/EtOAc, 5/1) to afford compound **5** (1.73g, 65%) as a white solid.

S5.

3.4 Analytical data of unreported starting materials

2-(Tosylmethyl)acrylonitrile (2b)

According to the general procedure A, compound 2b was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.83-7.76 (m, 2H), 7.43-7.36 (m, 2H), 6.20 (s, 1H), 5.98 (s, 1H), 3.91 (d, *J* = 0.8 Hz, 2H), 2.46 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 145.9, 139.3, 134.4, 130.1, 128.7, 116.5, 111.6, 59.8, 21.7.

IR (film): v (cm⁻¹) 2985, 2226, 1315, 1288, 1144, 1084, 975, 813, 772, 676, 608, 580, 524.

HRMS (ESI, *m/z*) calcd for C₁₁H₁₁NO₂SNa [M+Na]⁺: 244.0403, found: 244.0398.

2-(((4-Bromophenyl)sulfonyl)methyl)acrylonitrile (2c)



According to the general procedure A, compound 2c was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 8.13-7.85 (m, 4H), 6.26 (s, 1H), 6.05 (s, 1H), 3.98 (d, J = 0.8 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 139.8, 139.7, 136.3, 132.9, 130.2, 116.4, 111.2, 59.8.

IR (film): v (cm⁻¹) 2929, 2222, 1569, 1385, 1314, 1281, 1241, 1151, 1130, 1073, 1006, 968, 902, 819, 790, 709, 617, 579.

HRMS (ESI, *m*/*z*) calcd for C₁₀H₈NO₂SNa [M+Na]⁺: 307.9351, found: 307.9347.

2-(((4-(Trifluoromethyl)phenyl)sulfonyl)methyl)acrylonitrile (2d)

According to the general procedure A, compound 2d was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 6.26 (s, 1H), 6.05 (t, J = 0.8 Hz, 1H), 3.98 (d, J = 0.8 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 140.9, 140.0, 136.4 (q, *J* = 33.2 Hz), 129.4, 126.7 (q, *J* = 3.6 Hz), 122.9 (q, *J* = 273.2 Hz), 116.2, 111.0, 59.8.

¹⁹F NMR (282 MHz, CDCl₃) δ –63.30 (s, 3F).

IR (film): *v* (cm⁻¹) 2986, 2926, 2232, 1406, 1320, 1247, 1161, 1141, 1086, 1060, 1015, 972, 905, 844, 799, 698, 582.

HRMS (ESI, *m/z*) calcd for C₁₁H₈F₃NO₂SNa [M+Na]⁺: 298.0120, found: 298.0114.

2-((o-Tolylsulfonyl)methyl)acrylonitrile (2e)

According to the general procedure A, compound 2e was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, J = 8.0 Hz, 1H), 7.62-7.53 (m, 1H), 7.44-7.36 (m, 2H), 6.18 (s, 1H), 6.00 (s, 1H), 3.96 (s, 2H), 2.73 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 139.3, 138.4, 135.5, 134.6, 133.0, 131.1, 126.8, 116.4, 111.3, 58.9, 20.4.

IR (film): *v* (cm⁻¹) 2991, 2936, 2229, 1594, 1454, 1404, 1314, 1285, 1243, 1199, 1153, 1122, 1058, 960, 897, 806, 761, 698, 579.

HRMS (ESI, *m*/*z*) calcd for C₁₁H₁₁NO₂SNa [M+Na]⁺: 244.0403, found: 244.0398.

2-((Mesitylsulfonyl)methyl)acrylonitrile (2f)

According to the general procedure A, compound 2f was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.00 (s, 2H), 6.20 (s, 1H), 6.00 (d, *J* = 0.8 Hz, 1H), 3.92 (d, *J* = 0.8 Hz, 2H), 2.66 (s, 6H), 2.33 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 144.5, 140.5, 139.0, 132.5, 131.5, 116.6, 111.4, 59.5, 23.0, 21.1.

IR (film): v (cm⁻¹) 2985, 2220, 1593, 1454, 1308, 3183, 1272, 1143, 971, 670, 605, 572.

HRMS (ESI, *m/z*) calcd for C₁₃H₁₅NO₂SNa [M+Na]⁺: 272.0716, found: 272.0710.

2-((Naphthalen-2-ylsulfonyl)methyl)acrylonitrile (2g)

According to the general procedure A, compound 2g was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 8.75 (d, *J* = 8.4 Hz, 1H), 8.34-8.26 (m, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.82-7.56 (m, 3H), 6.11 (s, 1H), 5.84 (s, 1H), 4.12 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 139.1, 136.2, 134.2, 132.1, 132.0, 129.5, 129.2, 128.8, 127.2, 124.3, 123.4, 116.2, 111.3, 59.2.

IR (film): *v* (cm⁻¹) 2929, 2234, 2186, 1505, 1311, 1256, 1164, 1114, 977, 905, 800, 770, 737, 640, 573, 538, 474.

HRMS (ESI, *m*/*z*) calcd for C₁₄H₁₁NO₂SNa [M+Na]⁺: 280.0403, found: 280.0396.

2-((Naphthalen-1-ylsulfonyl)methyl)acrylonitrile (2h)

According to the general procedure A, compound 2h was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 8.51 (s, 1H), 8.10-7.84 (m, 4H), 7.77-7.59 (m, 2H), 6.20 (s, 1H), 5.97 (s, 1H), 4.01 (s, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 139.4, 135.7, 134.2, 132.0, 131.0, 129.9, 129.8, 129.6, 128.1, 128.0, 122.7, 116.5, 111.5, 59.8.

IR (film): *v* (cm⁻¹) 2992, 2937, 2229, 1592, 1454, 1403, 1314, 1286, 1242, 1200, 1153, 1123, 1063, 959, 897, 761, 679, 578.

HRMS (ESI, *m*/*z*) calcd for C₁₄H₁₁NO₂SNa [M+Na]⁺: 280.0403, found: 280.0398.

Ethyl 2-(((4-methoxyphenyl)sulfonyl)methyl)acrylate (2j)

According to the general procedure **B**, compound **2j** was obtained as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 7.78-7.72 (m, 2H), 7.00-6.94 (m, 2H), 6.47 (s, 1H), 5.88 (s, 1H), 4.12 (s, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 164.8, 163.8, 133.0, 130.9, 130.0, 129.4, 114.2, 61.4, 57.7, 55.6, 14.0.

IR (film): v (cm⁻¹) 2984, 1716, 1591, 1496, 1463, 1413, 1308, 1252, 1187, 1139, 1086, 1020, 962,

899, 837, 778, 670, 526.

HRMS (ESI, *m*/*z*) calcd for C₁₃H₁₆O₅SNa [M+Na]⁺: 307.0611, found: 307.0604.

Pent-4-yn-1-yl 2-((phenylsulfonyl)methyl)acrylate (2k)

According to the general procedure **B**, compound **2k** was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.90-7.84 (m, 2H), 7.68-7.62 (m, 1H), 7.59-7.51 (m, 2H), 6.51 (s, 1H), 5.92 (s, 1H), 4.16 (s, 2H), 4.09 (t, *J* = 6.3 Hz, 2H), 2.24 (td, *J* = 7.0, 2.6 Hz, 2H), 1.98 (t, 2.6 Hz, *J* = 1H), 1.84-1.74 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) *δ* 164.7, 138.4, 133.9, 133.5, 129.1, 129.0, 128.7, 82.8, 69.1, 64.0, 57.5, 27.4, 15.2.

IR (film): v (cm⁻¹) 3262, 1705, 1626, 1292, 1245, 1142, 1080,749, 684, 523, 480.

HRMS (ESI, *m*/*z*) calcd for C₁₅H₁₆O₄SNa [M+Na]⁺: 315.0662, found: 315.0655.

(E)-3,7-Dimethylocta-2,6-dien-1-yl 2-((phenylsulfonyl)methyl)acrylate (2l)

According to the general procedure **B**, compound **2l** was obtained as a colorless oil (*contains about* 5% of *Z*-isomer derived from geraniol).

¹H NMR (300 MHz, CDCl₃) δ 7.90-7.84 (m, 2H), 7.67-7.59 (m, 1H), 7.57-7.49 (m, 2H), 6.51 (s, 1H), 5.94 (s, 1H), 5.25-5.17 (m, 1H), 5.12-5.04 (m, 1H), 4.46 (d, J = 7.1 Hz, 2H), 4.16 (s, 2H), 2.13-1.95 (m, 4H), 1.69 (s, 3H), 1.66 (s, 3H), 1.61 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 164.8, 142.6, 138.5, 133.8, 133.3, 131.9, 129.2, 129.0, 128.8, 123.6, 117.8, 62.4, 57.5, 39.5, 26.3, 25.7, 17.7, 16.5.

IR (film): *v* (cm⁻¹) 2926, 1718, 1446, 1385, 1313, 1245, 1182, 1145, 1084, 965, 892, 809, 754, 660, 523.

HRMS (ESI, *m*/*z*) calcd for C₂₀H₂₆O₄SNa [M+Na]⁺: 385.1444, found: 385.1427.

3-(1,3-Dioxoisoindolin-2-yl)propyl 2-((phenylsulfonyl)methyl)acrylate (2m)



According to the general procedure **B**, compound **2m** was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.90-7.82 (m, 4H), 7.77-7.69 (m, 2H), 7.66-7.49 (m, 3H), 6.49 (s, 1H), 5.89 (s, 1H), 4.14 (s, 2H), 4.02 (t, *J* = 6.2 Hz, 2H), 3.76 (t, *J* = 6.9 Hz, 2H), 2.02-1.92 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 168.2, 164.6, 138.5, 134.1, 133.8, 133.7, 132.0, 129.1, 128.8, 123.3, 62.7, 57.5, 34.8, 27.5.

IR (film): *v* (cm⁻¹) 2959, 1707, 1445, 1403, 1375, 1307, 1199, 1161, 1083, 1054, 969, 921, 791, 755, 681, 607, 558.

HRMS (ESI, *m*/*z*) calcd for C₂₁H₁₉NO₆SNa [M+Na]⁺: 436.0825, found: 436.0828.

(E)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)hepta-2,6-dien-1-one (1d)



According to the reported precedures,⁵ compound **1d** was obtained as a colorless liquid.

¹H NMR (300 MHz, CDCl₃) δ 7.40-7.16 (m, 2H), 6.00 (s, 1H), 5,95-5.75 (m, 1H), 5.14-5.00 (m, 2H), 2.60 (s, 3H), 2.51-2.41 (m, 2H), 2.36-2.24 (m, 2H), 2.28 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 165.1, 151.8, 150.4, 144.4, 137.1, 121.5, 115.5, 111.2, 32.2, 32.0, 14.6, 13.8.

IR (film): *v* (cm⁻¹) 2927, 1705, 1639, 1581, 1476, 1411, 1376, 1344, 1294, 1243, 1139, 960, 914, 805, 753, 700, 626, 586, 407.

HRMS (ESI, *m/z*) calcd for C₁₂H₁₆N₂ONa [M+Na]⁺: 227.1155, found: 227.1155.

(E)-1,2,3,4,5-Pentafluoro-6-(2-(phenylsulfonyl)vinyl)benzene (5)

According to the general procedure C, compound 5 was obtained as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.98-7.92 (m, 2H), 7.73-7.65 (m, 2H), 7.63-7.55 (m, 2H), 7.22 (d, J

= 16.8 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 147.6-147.2 (m), 144.2-143.8 (m), 140.8-140.2 (m), 139.5, 136.4-135.8 (m), 135.5-135.1 (m), 134.0, 129.6, 128.0, 125.9-125.7 (m), 108.4-107.8 (m).

¹⁹F NMR (282 MHz, CDCl₃) δ –138.10 - –138.32 (m, 2F), –148.58 - –148.82 (m, 1F), –160.56 - –160.84 (m, 2F).

IR (film): *v* (cm⁻¹) 1650, 1495, 1419, 1301, 1146, 1082, 1001, 963, 845, 816, 749, 685, 550. HRMS (ESI, *m/z*) calcd for C₁₄H₇F₅O₂SNa [M+Na]⁺: 356.9979, found: 356.9970.

4. General Procedure



A dried 10 mL Schlenk tube was charged with **2a** (20.7 mg, 0.10 mmol), **\Delta-RhO** (6.6 mg, 8.0 mol%) and **HE-1** (42.2 mg, 0.15 mmol, synthesized following a reported procedure⁶). The tube was purged with nitrogen for three times. Then, 1,4-dioxane (1.0 mL, 0.10 M, bubbling with nitrogen gas for five minutes before addition) was added via syringe followed by addition of **1a** (32.8 mg, 0.2 mmol) under nitrogen atmosphere. The tube was sealed and positioned approximately 5 cm away from a 21 W compact fluorescent lamp. The reaction was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was diluted with CH₂Cl₂. The combined organic layers were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc) to afford the products **3a** and **4a**. Racemic samples were obtained by carrying out the reactions with *rac*-**RhO**. The enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.

5. Screening of Reaction Conditions



Table S1. Effect of Lewis acid catalysts^a

^{*a*} Reaction conditions: **1a** (0.20 mmol), **2a** (0.10 mmol), Lewis acid (8.0 mol%) and **HE-1** (0.15 mmol) in 1,4-dioxane (0.1 M) were stirred at room temperature for 24 h with a 21 W CFL. ^{*b*} Δ -**RhPP** was synthesized according to our previous report.⁷ ^{*c*} (20 mol%) of Sc(OTf)₃ was employed. ^{*d*} (200 mol%) of LiBF₄ was employed.





^{*a*} Reaction conditions: **1a** (0.20 mmol), **2a** (0.10 mmol), Δ -**RhO** (8.0 mol%) and indicated Hantzsch ester (0.15 mmol) in 1,4-dioxane (0.1 M) were stirred at room temperature for 24 h with a 21 W CFL.

Table S3. Effect of different solvents^a



^{*a*} Reaction conditions: **1a** (0.10 mmol), **2a** (0.05 mmol), Δ -**RhO** (8.0 mol%) and **HE-1** (0.075 mmol) in indicated solvent (0.1 M) were stirred at room temperature for 24 h or 35 °C for 15 h with a 21 W CFL. ^{*b*} The reduced product, 1-(3,5-dimethyl-1*H*-pyrazol-1-yl)butan-1-one⁸, was detected in less than 5% yield.

Table S4. Effect of light source^a



^{*a*} Reaction conditions: **1a** (0.20 mmol), **2a** (0.10 mmol), Δ -RhO (8.0 mol%) and HE-1 (0.15 mmol) in 1,4-dioxane (1.0 mL, 0.1 M) were stirred at room temperature for 24 h with the indicated light source. ^{*b*} See Figure S1 for emission spectrum. ^{*c*} See Figure S2 for emission spectrum.

6. Mechanistic Studies

6.1 Identification of RhO-1a Intermediate



To a solution of *rac*-**RhO** (83.1 mg, 0.1 mmol) in CH₂Cl₂ (2 mL) was added α , β -unsaturated *N*-acylpyrazole **1a** (16.4 mg, 0.1 mmol). The mixture was stirred at room temperature for 1 minute and then the solvent was removed in vacuum. The procedure was repeated for another 3 times until the ligand exchange finished completely (detected by ¹H NMR). The resulting solid was recrystallized from CH₂Cl₂/Et₂O giving pure **RhO-1a**, which was characterized by single crystal X-ray diffraction (see Section 11).

6.2 Control Experiments

6.2.1 Using BHT as a radical trap



As shown above, when BHT (3.0 equiv) was added to the reaction $1a+2a \rightarrow 3a+4a$ under standard conditions, the reaction was significantly inhibited delivering 3a and 4a in decreased yields.

6.2.2 Using TEMPO as a radical trap



When TEMPO (3.0 equiv) was added to the reaction $1a+2a \rightarrow 3a+4a$ under standard conditions, the reaction was completely inhibited.

6.2.3 Using 1,1-diphenyl ethylene a radical trap



When the 1,1-diphenylethylene (3.0 equiv) was added to the reaction $1a+2a\rightarrow 3a+4a$ under standard conditions, the reaction was partly inhibited and the yields of the products were decreased to 20% for 3a and 22% for 4a.

All these control experiments indicate that radical processes might be involved in the present transformation.

6.3 Stern-Volmer Quenching Experiments

6.3.1 UV-Vis absorption spectra and luminescence emission spectra

As shown in Figure S3, both **HE-1** and **RhO-1a** absorb visible light with wavelength < 425 nm. In order to simulate the reaction conditions, the luminescence quenching experiments were performed with the photoredox mediator Hantzsch ester alone (see section 6.3.2) and with the mixture of Hantzsch ester and **RhO** in a molar ratio of 2 : 1 (see section 6.3.3), respectively.



Figure S3. UV-Vis absorption spectra and luminescence emission spectra. Concentration for absorption spectra in 1,4-dioxane: **HE-1** = 0.05 mM, **RhO** = 0.05 mM, **RhO-1a** = 0.05 mM. Concentration for emission spectra of **HE-1** in 1,4-dioxane = 0.5 mM.

6.3.2 Quenching experiments with the Hantzsch ester alone

The solutions of **HE-1** (0.5 mM in 1,4-dioxane) were excited at $\lambda = 360$ nm and the emission was measured at 455 nm (emission maximum). For each quenching experiment, after degassed with a nitrogen stream for 5 minutes, the emission intensity of the solution (1 mL) of **HE-1** with different concentration of quencher (0, 0.05, 0.10, 0.15, 0.20, 0.25 mM) in a screw-top 10.0 mm quartz cuvette was collected.



Figure S4. Stern-Volmer plots. I_0 and I are respective luminescence intensities in the absence and presence of the indicated concentrations of the corresponding quencher. [HE-1] = 0.5 mM, Ex = 360 nm, Em = 455 nm.

6.3.3 Quenching experiments with Hantzsch ester and RhO.

The solutions of **HE-1** (0.5 mM) and **RhO** (0.25 mM) in 1,4-dioxane were excited at $\lambda = 360$ nm and the emission was measured at 455 nm (emission maximum). For each quenching experiment, after degassed with a nitrogen stream for 5 minutes, the emission intensity of the solution (1 mL) of **HE-1** and **RhO** with different concentration of quencher (0, 0.05, 0.10, 0.15, 0.20, 0.25 mM) in a screw-top 10.0 mm quartz cuvette was collected. A very rapid coordination of **1a** with **RhO** is expected based on our previous work.⁹



Figure S5. Stern-Volmer plots. I_0 and I are respective luminescence intensities of the solution of **HE-1** (black one) or the mixture of **HE-1** and **RhO** (red one) in the absence and presence of the indicated concentrations of the quencher **1a**. Ex = 360 nm, Em = 455 nm.

Results: **RhO-1a** and **RhO** can quench the luminescence while substrate **1a** and substrate **2a** are not capable of quenching (Figure S4). **RhO** might quench the luminescence of **HE-1** via competitive absorption (inner filter effect).¹⁰ Considering the similar absorption of **RhO-1a** and **RhO** (Figure S3), the in situ generated **RhO-1a** can quench the luminescence of the mixture of **HE-1** and **RhO** slightly (Figure S5), indicating **RhO-1a** might undergoes a photoinduced electron transfer with **HE-1**. Furthermore, **RhO-1a** as the major existing species of rhodium complexes, is most likely responsible for oxidative quenching of photoexcited **HE-1**, which is further supported by cyclic voltammetry studies (see Section 6.4).

6.4 Cyclic Voltammetry

All cyclic voltammetry experiments were carried out using analytical grade CH₂Cl₂ as the solvent containing 0.1 M Bu₄NPF₆ as the electrolyte and 1 mM of the analyte. Cyclic voltammetry experiments were conducted with a computer controlled Eco Chemie Autolab PGSTAT302N potentiostat in a Metrohm electrochemical cell containing a 1 mm diameter planar glassy carbon (GC) disk electrode (eDAQ), a platinum wire auxiliary electrode (Metrohm) and a silver wire miniature reference electrode (eDAQ) that was connected to the test solution via a salt bridge containing 0.5 M *n*Bu₄NPF₆ in CH₃CN. Accurate potentials were referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple, which was used as an internal standard. All solutions used for the voltammetric experiments were deoxygenated by purging with high purity argon gas and measurements were performed in a Faraday cage at room temperature (22 ± 2 °C).

Substrate **1a** showed one chemically irreversible reduction process with a cathodic peak potential (E_p^{red}) at -2.59 V vs. Fc/Fc⁺ (Figure S6, red curve). **RhO-1a** could be reduced with an E_p^{red} at approximately -1.62 V vs. Fc/Fc⁺ and oxidised with an E_p^{ox} at approximately +1.32 V vs. Fc/Fc⁺, both in chemically irreversible processes (Figure S6, blue curve). It is noteworthy that coordination of the cyclometalated rhodium catalyst could significantly decrease reductive potential of **1a**.

Besides, **HE-1** could be oxidised in a chemically irreversible process with an anodic peak potential (E_p^{ox}) at approximately 0.50 V *vs*. Fc/Fc⁺ (Figure S7). According to luminescence emission spectra (Figure S3, maximum wavelength = 455 nm, corresponding to 2.73 eV), the redox potential of photoexcited **HE-1** is estimated as –2.23 V *vs*. Fc/Fc⁺, which is feasible to selectively reduce **RhO-1a** instead of free **1a**.



Figure S6. CV of compound 1a and RhO-1a.



Figure S7. CV of compound HE-1.

6.5 Evidence for the Formation of Sulfonyl Radical

6.5.1 Trapping experiments with but-3-en-2-one



To trap the sulfonyl radical, but-3-en-2-one which is not able to bind the Rh catalyst was added to act as a sulphonyl trap. As shown, the expected radical trapping product **4a'** could be obtained in S23 28% yield, along with the formation of **3a** and **4a**, indicating the involvement of sulfonyl radical. **4-(Phenylsulfonyl)butan-2-one (4a')**¹¹ ¹H NMR (300 MHz, CDCl₃) δ 7.95-7.87 (m, 2H), 7.71-7.53 (m, 3H), 3.41-3.33 (m, 2H), 2.96-2.88 (m, 2H), 2.17 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.0, 133.9, 129.4, 127.9, 50.5, 35.8, 29.8. All characteristic data are consistent with the literature report.¹¹

6.5.2 EPR experiments

EPR spectra were recorded at room temperature using DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) as free radical spin trapping agent. According to general procedure, the reaction of **1a** and **2a** under standard conditions with the addition of 10 μ L DMPO solution (1M in H₂O) was stirred with 21 W CFL for 30 min. Then, a portion of the reaction mixture was taken out to an EPR tube and measured by EPR (9.18142 GHz; Mod. Frequency = 100 kHz; Mod. Ampl. = 0.08 mT).

As shown in Figure S8, two sets of signals were observed, one of which is simulated as signals 1 with 6 lines (g = 2.006; $\alpha_N = 9.5$ G, $\alpha_H^\beta = 12.9$ G) and further signed as EPR signals of sulforyl radical adducts.¹² These results suggest more than one radical species including sulforyl radicals are involved in this transformation.



Figure S8. EPR experiments with the addition of DMPO (X band, r.t.). **A**: experimental signals; **B**: simulated signal 1 (g = 2.006, $\alpha_N = 9.5$ G, $\alpha_H^{\beta} = 12.9$ G); **C**: residual of signals (A-B); **D**: simulated signals 2 (g = 2.006, $\alpha_N = 1.200$ mT, $\alpha_H^{\beta} = 1.280$ mT); **E**: residual of signals (C-D).

6.6 Determination of the Quantum Yield

The quantum yield of the title reaction $1a+2a \rightarrow 3a+4a$ was determined by a method and setups developed by Prof. Dr. Eberhard Riedle's Group.¹³ As light source 420 nm LEDs were employed. A powermeter was used as detector. The measurement was accomplished in a dark room with a 1.1 W red LEDs.

Step 1: The radiant power of light transmitted by the cuvette with a blank solution was measured as $P_{\text{blank}} = 46.25 \text{ mW}$.

Step 2: The reaction mixture of **1a** (65.6 mg, 0.40 mmol), **2a** (41.6 mg, 0.20 mmol), *rac*-**RhO** (13.2 mg, 8.0 mol%), **HE-1** (84.4 mg, 1.5 equiv) in 1,4-dioxane (2.0 mL, 0.1 M) was filled into a fluorescence cuvette with a stirring bar and septum and degassed by bubbling with nitrogen (10 min). Then, the cuvette was put into the setups and illuminated with the 420 nm LEDs. The transmitted radiant power $\underline{P_{sample}} = 3.6 \text{ mW}$ was noted. The transmitted radiant power was monitored during the irradiation and remained constant.

Step 3: After illumination for <u>2 hours (t = 2 × 3600 s)</u>, the amount of the formed **3a** was determined as $9.257 \times 10^{-5} \mod (n_{\text{product}})$ by ¹H NMR.

Step 4: The overall quantum yield can be calculated as following:

$$\begin{aligned} \text{Quantum Yield} &= \frac{N_{product}}{N_{photon}} = \frac{N_A \times n_{product}}{\frac{P_{absorbed} \times \text{t}}{\lambda}} = \frac{h \times \text{c} \times N_A \times n_{product}}{(P_{blank} - P_{sample}) \times \text{t} \times \lambda} \\ &= \frac{6.626 \times 10^{-34} \text{Js} \times 2.998 \times 10^8 \text{ms}^{-1} \times 6.022 \times 10^{23} \text{mol}^{-1} \times 9.257 \times 10^{-5} \text{mol}}{(46.25 - 3.6) \times 10^{-3} \text{Js}^{-1} \times 2 \times 3600 \text{s} \times 420 \times 10^{-9} \text{m}} = 0.09. \end{aligned}$$

where $N_{product}$ is the number of product **3a** formed; N_{photon} is the number of photons absorbed; N_A is Avogadro's constant; $n_{product}$ is the molar amount of product **3a** formed; $P_{absorbed}$ is the radiant power absorbed; t is the irradiation time; h is the Planck's constant; c is the speed of light; λ is the wavelength of light source, P_{blank} is the radiant power transmitted by the cuvette with a blank solution; P_{sample} is the radiant power transmitted by the cuvette.

7. Experimental and Analytical Data of Products

(01) Table 2, entry 1

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), 2-((phenylsulfonyl)methyl)acrylonitrile **2a** (20.8 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at room temperature, afforded 19.6 mg (85%) of **3a** as a colorless oil and **4a** (28.2mg, 92%) as a yellow oil.



(S)-6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-4-methyl-2-methylene-6-oxon-hexanenitrile (3a)

Enantiomeric excess of **3a** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 96% (HPLC: 254 nm, n-hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 40 °C, t_r (major) = 6.8 min, t_r (minor) = 6.4 min).

 $[\alpha]_{D}^{22} = +21.1^{\circ} (c \ 1.0, CH_2Cl_2).$

¹H NMR (300 MHz, CDCl₃) δ 5.95 (s, 1H), 5.91 (s, 1H), 5.78-5.75 (m, 1H), 3.13 (dd, J = 16.5, 5.8 Hz, 1H), 2.99 (dd, J = 16.5, 7.3 Hz, 1H), 2.54 (s, 3H), 2.52-2.38 (m, 2H), 2.23 (s, 3H), 2.23-2.09 (m, 1H), 1.07 (d, J = 6.6 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) *δ* 172.4, 152.0, 144.0, 132.0, 121.7, 118.6, 111.2, 41.5, 41.2, 28.5, 19.3, 14.5, 13.8.

IR (film): *v* (cm⁻¹) 2965, 2929, 2221, 1722, 1583, 1437, 1379, 1333, 1240, 1171, 1137, 996, 960, 904, 805, 745, 642, 559.

HRMS (ESI, *m*/*z*) calcd for C₁₃H₁₇N₃ONa [M+Na]⁺: 254.1264, found: 254.1259.

(*R*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-(phenylsulfonyl)butan-1-one (4a)

Enantiomeric excess of **4a** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 85% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r _{S26} $(major) = 12.0 min, t_r (minor) = 10.8 min).$

 $[\alpha]_D^{22} = +47.6^\circ (c \ 1.0, CH_2Cl_2).$

¹H NMR (500 MHz, CDCl₃) δ 7.95-7.91 (m, 2H), 7.68-7.63 (m, 1H), 7.59-7.53 (m, 2H), 5.94 (s, 1H), 3.89-3.82 (m, 1H), 3.76 (dd, J = 17.4, 4.4 Hz, 1H), 3.27 (dd, J = 17.4, 8.8 Hz, 1H), 2.45 (s, 3H), 2.21 (s, 3H), 1.38 (d, J = 6.8 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) *δ* 170.0, 152.6, 144.1, 136.9, 133.8, 129.14, 129.12, 111.5, 56.1, 35.8, 14.3, 14.0, 13.8.

IR (film): *v* (cm⁻¹) 2929, 1721, 1585, 1446, 1382, 1304, 1141, 1081, 1030, 986, 961, 911, 814, 757, 728, 688, 582, 547.

HRMS (ESI, *m*/*z*) calcd for C₁₅H₁₉N₂O₃S [M+H]⁺: 307.1111, found: 307.1107.

(02) Table 2, entry 2

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), 2-(tosylmethyl)acrylonitrile **2b** (22.1 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at room temperature, afforded 16.1 mg (68%) of **3a** as a colorless oil and **4b** (21.4mg, 70%) as a yellow oil. Enantiomeric excess of **3a** was determined as 96% ee.



(*R*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-tosylbutan-1-one (4b)

Enantiomeric excess of **4b** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 79% (HPLC: 254 nm, n-hexane/ isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 14.8 min, t_r (minor) = 11.0 min). $[\alpha]_D^{22} = +10.8^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.82-7.78 (m, 2H), 7.37-7.33 (m, 2H), 5.94 (s, 1H), 3.86-3.78 (m, 1H), 3.74 (dd, J = 17.4, 4.4 Hz, 1H), 3.24 (dd, J = 17.4, 8.8 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 2.21 (s, 3H), 1.37 (d, J = 6.8 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 170.1, 152.5, 144.8, 144.1, 133.9, 129.8, 129.1, 111.5, 56.1, 35.9, 21.6, 14.3, 14.0, 13.8.

IR (film): *v* (cm⁻¹) 2929, 1721, 1589, 1396, 1330, 1293,1261, 1139, 1082, 1026, 987, 962, 908, 870, 758, 721, 640, 555.

HRMS (ESI, *m*/*z*) calcd for C₁₆H₂₀N₂O₃SNa [M+Na]⁺: 343.1087, found: 343.1080.

(03) Table 2, entry 3

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), 2-(((4-bromophenyl)sulfonyl)methyl)acrylonitrile **2c** (28.5 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at room temperature, afforded 18.9 mg (81%) of **3a** as a colorless oil, and afforded **4c** (33.8 mg, 88%) as a white solid. Enantiomeric excess of **3a** was determined as 97% ee.



(*R*)-3-((4-bromophenyl)sulfonyl)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)butan-1-one (4c)

Enantiomeric excess of **4c** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 80% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 12.9 min, t_r (minor) = 11.2 min). $[\alpha]_D^{22} = +13.1^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.80-7.76 (m, 2H), 7.71-7.67 (m, 2H), 5.96 (s, 1H), 3.89-3.81 (m, 1H), 3.76 (dd, J = 17.4, 4.8 Hz, 1H), 3.24 (dd, J = 17.4, 8.4 Hz, 1H), 2.45 (s, 3H), 2.21 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 169.7, 152.7, 144.1, 135.9, 132.5, 130.7, 129.3, 111.6, 56.2, 35.8, 14.3, 13.9, 13.8.

IR (film): *v* (cm⁻¹) 2981, 1727, 1575, 1446, 1384, 112, 1279, 1134, 1075, 988, 961, 914, 824, 761, 684, 576.

HRMS (ESI, *m*/*z*) calcd for C₁₅H₁₇BrN₂O₃SNa [M+Na]⁺: 407.0035, found: 407.0024.

(04) Table 2, entry 4

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1H-pyrazol-1-yl)but-2-

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en-1-one **1a** (32.8 mg, 0.20 mmol), 2-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl) acrylonitrile **2d** (22.1 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at room temperature, afforded 18.4 mg (78%) of **3a** as a colorless oil, and afforded 29.2 mg (78%) of **4d** as a white solid. Enantiomeric excess of **3a** was determined as 95% ee.



(*R*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-((4-(trifluoromethyl)phenyl)sulfonyl)butan-1-one (4d) Enantiomeric excess of 4d was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 76% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 10.3 min, t_r (minor) = 9.2 min). A white solid. $[\alpha]_D^{22} = +19.9^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 5.95 (s, 1H), 3.94-3.86 (m, 1H), 3.78 (dd, J = 17.4, 4.9 Hz, 1H), 3.24 (dd, J = 17.4, 8.3 Hz, 1H), 2.43 (s, 3H), 2.20 (s, 3H), 1.42 (d, J = 6.9 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 169.6, 152.7, 144.2, 140.6, 135.5 (q, J = 33.2 Hz), 129.8, 126.2 (q, J = 3.6 Hz), 124.2, 123.0 (q, J = 273.2 Hz), 111.7, 56.2, 35.8, 14.2, 13.9, 13.8.

¹⁹F NMR (282 MHz, CDCl₃) δ –63.3 (s, 3F).

IR (film): *v* (cm⁻¹) 2965, 1725, 1584, 1451, 1378, 1317, 1166, 1060, 1036, 984, 960, 890, 844, 743, 677, 545.

HRMS (ESI, *m/z*) calcd for C₁₆H₁₇F₃N₂O₃SNa [M+Na]⁺: 397.0804, found: 397.0794.

(05) Table 2, entry 5

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), 2-((*o*-tolylsulfonyl)methyl)acrylonitrile **2e** (22.1 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at room temperature, afforded 16.8 mg (71%) of **3a** as a colorless oil, and afforded 23.0 mg (72%) of **4e** as a yellow oil. Enantiomeric excess of **3a** was determined as 95% ee.



(*R*)-1-(3,5-Mimethyl-1*H*-pyrazol-1-yl)-3-(*o*-tolylsulfonyl)butan-1-one (4e)

Enantiomeric excess of **4e** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 86% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 12.2 min, t_r (minor) = 10.8 min). $[\alpha]_D^{22} = +15.4^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, J = 7.9 Hz, 1H), 7.51-7.47 (m, 1H), 7.35-7.29 (m, 2H), 5.93 (s, 1H), 3.99-3.91 (m, 1H), 3.75 (dd, J = 17.4, 4.4 Hz, 1H), 3.27 (dd, J = 17.4, 8.6 Hz, 1H), 2.73 (s, 3H), 2.43 (s, 3H), 2.20 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) *δ* 170.1, 152.5, 144.0, 138.9, 135.2, 133.7, 132.8, 131.3, 126.3, 111.5, 54.8, 35.7, 20.5, 14.3, 13.7, 13.4.

IR (film): *v* (cm⁻¹) 2981, 1722, 1586, 1452, 1382, 1308, 1144, 1031, 986, 961, 807, 758, 662, 554. HRMS (ESI, *m/z*) calcd for C₁₆H₂₀N₂O₃SNa [M+Na]⁺: 343.1087, found: 343.1080.

(06) Table 2, entry 6

According to the general procedure, the reaction of (*E*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), 2-((mesitylsulfonyl)methyl)acrylonitrile **2f** (24.9 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at 35 °C, afforded 13.5 mg (57%) of **3a** as a colorless oil, and afforded 20.9 mg (60%) of **4f** as a yellow oil. Enantiomeric excess of **3a** was determined as 94% ee.



(*R*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-(mesitylsulfonyl)butan-1-one (4f)

Enantiomeric excess of **4f** was established by HPLC analysis using a Daicel Chiralpak IA column, ee = 89% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 9.6 min, t_r (minor) = 10.9 min). $[\alpha]_D^{22} = -28.4^\circ$ (*c* 0.10, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 6.93 (s, 2H), 5.93 (s, 1H), 3.97-3.89 (m, 1H), 3.78 (dd, J = 17.0, 4.6 s₃₀

Hz, 1H), 3.27 (dd, *J* = 17.0, 8.6 Hz, 1H), 2.68 (s, 6H), 2.43 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H), 1.41 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 170.3, 152.4, 144.0, 143.3, 140.8, 132.3, 131.1, 111.4, 55.4, 35.4, 23.0, 21.0, 14.3, 13.7, 13.2.

IR (film): *v* (cm⁻¹) 2959, 1718, 1591, 1449, 1416, 1378, 1306, 1262, 1134, 1101, 1023, 962, 799, 749, 728, 681, 642, 569.

HRMS (ESI, *m*/*z*) calcd for C₁₈H₂₅N₂O₃S [M+H]⁺: 349.1580, found: 349.1573.

(07) Table 2, entry 7

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), ethyl 2-((naphthalen-2-ylsulfonyl)methyl)acrylonitrile **2g** (25.7 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at 35 °C, afforded 19.4 mg (82%) of **3a** as a colorless oil, and afforded 31.3 mg (88%) of **4g** as a yellow oil. Enantiomeric excess of **3a** was determined as 94% ee.



(R)-1-(3,5-Dimethyl-1H-pyrazol-1-yl)-3-(naphthalen-2-ylsulfonyl)butan-1-one (4g)

Enantiomeric excess of **4g** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 83% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 13.5 min, t_r (minor) = 14.3 min). $[\alpha]_D^{22} = +39.2^\circ$ (*c* 1.0, CH₂Cl₂)

¹H NMR (300 MHz, CDCl₃) δ 8.80 (d, *J* = 8.6 Hz, 1H), 8.31 (d, *J* = 7.3 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.75-7.53 (m, 3H), 5.89 (s, 1H), 4.22-4.08 (m, 1H), 3.82 (dd, *J* = 17.2, 4.4 Hz, 1H), 3.34 (dd, *J* = 17.2, 8.8 Hz, 1H), 2.39 (s, 3H), 2.14 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 170.0, 152.4, 144.0, 135.3, 134.3, 132.2, 131.8, 129.3, 129.1, 128.7,

127.0, 124.5, 124.2, 111.4, 55.6, 35.8, 14.2, 13.8, 13.6.

IR (film): *v* (cm⁻¹) 2937, 1722, 1586, 1385, 1313, 1269, 1188, 1151, 1122, 964, 886, 805, 771, 742, 707, 663, 592.

HRMS (ESI, *m*/*z*) calcd for C₁₉H₂₀N₂O₃SNa [M+Na]⁺: 379.1087, found: 379.1078.

(08) Table 2, entry 8

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), ethyl 1-((naphthalen-2-ylsulfonyl)methyl)acrylonitrile **2h** (25.7 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at 35 °C, afforded 18.4 mg (78%) of **3a** as a colorless oil, and afforded 29.9 mg (84%) of **4h** as a yellow oil. Enantiomeric excess of **3a** was determined as 91% ee.



(*R*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-(naphthalen-1-ylsulfonyl)butan-1-one (4h)

Enantiomeric excess of **4h** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 80% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 18.7 min, t_r (minor) = 16.5 min. $[\alpha]_D^{22} = +15.6^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 8.50 (s, 1H), 8.03-7.87 (m, 4H), 7.71-7.57 (m, 2H), 5.88 (s, 1H), 4.02-3.88 (m, 1H), 3.84 (dd, J = 17.4, 4.6 Hz, 1H), 3.27 (dd, J = 17.4, 8.4 Hz, 1H), 2.36 (s, 3H), 2.19 (s, 3H), 1.43 (d, J = 6.8 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 170.0, 152.5, 144.0, 135.4, 134.0, 132.1, 131.1, 129.4, 129.34, 129.30, 127.9, 127.6, 123.6, 111.5, 56.2, 36.0, 14.1, 14.0, 13.7.

IR (film): *v* (cm⁻¹) 2924, 1721, 1586, 1451, 1382, 1305, 1122, 1073, 1029, 985, 961, 910, 862, 815, 752, 703, 644, 553, 474.

HRMS (ESI, *m/z*) calcd for C₁₉H₂₁N₂O₃S [M+H]⁺: 357.1267, found: 357.1259.

(09) Table 2, entry 9

According to the general procedure, the reaction of (*E*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), ethyl ethyl 2-((phenylsulfonyl)methyl)acrylate **2i**¹⁴ (25.4 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with

visible light for 24 hours at room temperature, afforded 18.3 mg (65%) of **3b** as a colorless oil, and afforded 20.8 mg (68%) of **4a** as a yellow oil. Enantiomeric excess of **4a** was determined as 84% ee.



Ethyl (S)-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-methyl-2-methylene-6-oxohexanoate (3b)

Enantiomeric excess of **3b** was established by HPLC analysis using a Daicel Chiralcel OJ-H column, ee = 94% (HPLC: 254 nm, n-hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (major) = 6.9 min, t_r (minor) = 7.6 min). $[\alpha]_D^{22} = +14.2^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 6.19 (d, J = 1.6 Hz, 1H), 5.93 (s, 1H), 5.57-5.53 (m, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.11 (dd, J = 16.4, 5.2 Hz, 1H), 2.93 (dd, J = 16.4, 7.4 Hz, 1H), 2.53 (s, 3H), 2.47-2.29 (m, 3H), 2.22 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H),1.00 (d, J = 6.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) *δ* 173.2, 167.2, 151.6, 144.0, 139.2, 126.2, 110.9, 60.6, 41.7, 39.1, 28.8, 19.8, 14.6, 14.2, 13.8.

IR (film): *v* (cm⁻¹) 2967, 1718, 1630, 1583, 1440, 1409, 1377, 1329, 1242, 1185, 1148, 1025, 994, 959, 807, 746, 684, 553.

HRMS (ESI, *m*/*z*) calcd for C₁₅H₂₂N₂O₃Na [M+Na]⁺: 301.1523, found: 301.1527.

(10) Table 2, entry 10

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), ethyl 2-(((4-methoxyphenyl)sulfonyl)methyl)acrylate **2j** (28.4 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at 35 °C, afforded 18.3 mg (65%) of **3b** as a colorless oil, and afforded 21.2 mg (63%) of **4i** as a yellow oil. Enantiomeric excess of **3b** was determined as 92% ee.



(*R*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-((4-methoxyphenyl)sulfonyl)butan-1-one (4i)

Enantiomeric excess of **4i** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 81% (HPLC: 254 nm, n-hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 40 °C, t_r (major) = 14.4 min, t_r (minor) = 11.9 min). $[\alpha]_D^{22} = +10.0^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.87-7.81 (m, 2H), 7.03-7.67 (m, 2H), 5.94 (s, 1H), 3.88 (s, 3H), 3.85-3.71 (m, 2H), 3.27 (dd, J = 17.4, 8.8 Hz, 1H), 2.46 (s, 3H), 2.21 (s, 3H), 1.37 (d, J = 6.8 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 170.1, 163.8, 152.5, 144.1, 131.3, 128.3, 114.3, 111.5, 56.3, 55.7, 36.0, 14.3, 14.1, 13.8.

IR (film): *v* (cm⁻¹) 2922, 1716, 1587, 1457, 1372, 1310, 1264, 1130, 1080, 1020, 960, 842, 411, 758, 562.

HRMS (ESI, *m/z*) calcd for C₁₆H₂₀N₂O₄SNa [M+Na]⁺: 359.1036, found: 359.1027.

(11) Table 2, entry 11

According to the general procedure, the reaction of (*E*)-1-(3,5-dimethyl-1H-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), ethyl hex-4-yn-1-yl 2-((phenylsulfonyl)methyl)acrylate **2k** (30.6 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at 35 °C, afforded 19.0 mg (60%) of **3c** as a colorless oil, and afforded 21.1 mg (69%) of **4a** as a yellow oil. Enantiomeric excess of **4a** was determined as 82% ee.



(S)-Pent-4-yn-1-yl-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-methyl-2-methylene-6-oxohexanoate (3c)

Enantiomeric excess of **3c** was established by HPLC analysis using a Daicel Chiralcel OJ-H column, ee = 92% (HPLC: 254 nm, n-hexane/isopropanol = 98:2, flow rate 1.0 mL/min, 25 °C, t_r (major) = 10.0 min, t_r (minor) = 11.8 min). $[\alpha]_D^{22} = +10.4^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 6.20 (d, J = 1.4 Hz, 1H), 5.94 (s, 1H), 5.59-5.56 (m, 1H), 4.24 (t, J = 6.3 Hz, 2H), 3.11 (dd, J = 16.4, 5.4 Hz, 1H), 2.94 (dd, J = 16.4, 7.4 Hz, 1H), 2.53 (s, 3H), 2.47-2.36 (m, 2H), 2.31 (td, J = 6.8, 2.6 Hz, 3H), 2.23 (s, 3H), 1.97 (t, J = 2.6 Hz, 1H), 1.96-1.87 (m, 2H), 1.00 (d, J = 6.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 173.1, 167.0, 151.7, 144.0, 138.9, 126.6, 111.0, 83.1, 69.0, 63.2,
41.6, 39.1, 28.7, 27.5, 19.8, 15.3, 14.6, 13.8.

IR (film): *v* (cm⁻¹) 3296, 2960, 2928, 1718, 1629, 1583, 1438, 1409, 1379, 1330, 1244, 1182, 1149, 1077, 996, 959, 809, 726, 637, 523.

HRMS (ESI, *m*/*z*) calcd for C₁₈H₂₄N₂O₃Na [M+Na]⁺: 339.1679, found: 339.1673.

(12) Table 2, entry 12

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), (E)-3,7-dimethylocta-2,6-dien-1-yl 2-((phenylsulfonyl)methyl) acrylate **2l** (*contains about 5% of Z-isomer derived from geraniol*, 36.2 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4- dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at 35 °C, afforded 23.9 mg (62%) of **3d** as a colorless oil, and afforded 22.0 mg (72%) of **4a** as a yellow oil. Enantiomeric excess of **4a** was determined as 83% ee.



(*E*)-3,7-Dimethylocta-2,6-dien-1-yl (*S*)-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-methyl-2-methylene -6-oxohexanoate (3d)

Enantiomeric excess of **3d** was established by HPLC analysis using a Daicel Chiralpak IG column, ee = 92% (HPLC: 254 nm, n-hexane/isopropanol = 99.1:0.9, flow rate 1.0 mL/min, 25 °C, t_r (major) = 12.4 min, t_r (minor) = 13.3 min). $[\alpha]_{D}^{22} = +15.7^{\circ}$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 6.20 (d, J = 1.4 Hz, 1H), 5.94 (s, 1H), 5.58-5.55 (m, 1H), 5.40-5.34 (m, 1H), 5.11-5.05 (m, 1H), 4.66 (d, 7.0 Hz, 2H), 3.11 (dd, J = 16.4, 5.4 Hz, 1H), 2.94 (dd, J = 16.4, 7.8 Hz, 1H), 2.53 (s, 3H), 2.47-2.29 (m, 3H), 2.22 (s, 3H), 2.13-2.01 (m, 4H), 1.71 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 1.00 (d, J = 6.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) *δ* 173.2, 167.2, 151.6, 144.0, 142.0, 139.1, 131.8, 126.3, 123.8, 118.4, 111.0, 61.7, 41.6, 39.5, 39.1, 28.7, 26.3, 25.7, 19.9, 17.7, 16.5, 14.6, 13.8.

IR (film): *v* (cm⁻¹) 3298, 3172, 2963, 2925, 2873, 1633, 1598, 1519, 1462, 1381, 1316, 1244, 1158, 1079, 1005, 956, 870, 770, 661, 544.

HRMS (ESI, *m/z*) calcd for C₂₃H₃₄N₂O₃Na [M+Na]⁺: 409.2462, found: 409.2454.

(13) Table 2, entry 13

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), 3-(1,3-dioxoisoindolin-2-yl)propyl 2-((phenylsulfonyl) methyl)acrylate **2m** (41.3 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 24 hours at 35 °C, afforded 31.9 mg (73%) of **3e** as a colorless oil, and afforded 23.9 mg (78%) of **4a** as a yellow oil. Enantiomeric excess of **4a** was determined as 82% ee



(*S*)-3-(1,3-Dioxoisoindolin-2-yl)propyl 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-methyl-2-methylene -6-oxohexanoate (3e)

Enantiomeric excess of **3e** was established by HPLC analysis using a Daicel Chiralcel OJ-H column, ee = 92% (HPLC: 254 nm, n-hexane/isopropanol = 80:20, flow rate 1.0 mL/min, 25 °C, t_r (major) = 17.4 min, t_r (minor) = 20.5 min). $[\alpha]_D^{22} = +13.7^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.84-7.80 (m, 2H), 7.72-7.68 (m, 2H), 6.17 (s, 1H), 5.92 (s, 1H), 5.55 (s, 1H), 4.17 (t, *J* = 6.2 Hz, 2H), 3.82 (t, *J* = 6.9 Hz, 2H), 3.10 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.92 (dd, *J* = 16.4, 7.7 Hz, 1H), 2.51 (s, 3H), 2.45-2.33 (m, 2H), 2.32-2.26 (m, 1H), 2.21 (s, 3H), 2.11-2.04 (m, 2H), 0.99 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 173.1, 168.2, 166.9, 151.6, 143.9, 138.7, 133.9, 132.0, 126.7, 123.2, 110.9, 62.0, 41.6, 39.0, 35.1, 28.7, 27.6, 19.8, 14.6, 13.8.

IR (film): *v* (cm⁻¹) 2959, 2928, 1772, 1709, 1583, 1439, 1377, 1330, 1244, 1182, 1148, 1080, 1046, 959, 805, 747, 528.

HRMS (ESI, *m*/*z*) calcd for C₂₄H₂₇N₃O₅Na [M+Na]⁺: 460.1843, found: 460.1832.

(14) Eq 1, reaction of 1b

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) pent-2-en-1-one **1b** (35.6 mg, 0.20 mmol), 2-((phenylsulfonyl)methyl)acrylonitrile **2a** (20.8 mg,
0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 48 hours at room temperature, afforded 20.1 mg (82%) of **3f** as a colorless oil, and afforded 27.2 mg (85%) of **4j** as a yellow oil.

(S)-6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-4-ethyl-2-methylene-6-oxohexanenitrile (3f)

Enantiomeric excess of **3f** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 87% (HPLC: 254 nm, n-hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 40 °C, t_r (major) = 6.8 min, t_r (minor) = 8.5 min). $[\alpha]_D^{22} = +4.0^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 5.96 (s, 1H), 5.90 (s, 1H), 5.77-5.75 (m, 1H), 3.14-3.04 (m, 2H), 2.53 (s, 3H), 2.38-2.31 (m, 3H), 2.23 (s, 3H), 1.55-1.43 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 172.7, 151.9, 144.0, 132.1, 121.7, 118.7, 111.2, 38.7, 38.1, 34.6, 25.9, 14.6, 13.8, 10.8.

IR (film): *v* (cm⁻¹) 2925, 2221, 1721, 1643, 1583, 1380, 1341, 1271, 1017, 959, 806, 745, 686, 578. HRMS (ESI, *m/z*) calcd for C₁₄H₁₉N₃ONa [M+Na]⁺: 268.1420, found: 268.1417.

(*R*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-(phenylsulfonyl)pentan-1-one (4j)

Enantiomeric excess of **4j** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 87% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 12.6 min, t_r (minor) = 11.8 min). $[\alpha]_D^{22} = -4.2^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.94-7.90 (m, 2H), 7.65-7.61 (m, 1H), 7.56-7.50 (m, 2H), 5.94 (s, 1H), 3.85-3.79 (m, 1H), 3.77 (dd, J = 17.6, 6.3 Hz, 1H), 3.28 (dd, J = 17.6, 5.8 Hz, 1H), 2.43 (s, 3H), 2.22 (s, 3H), 2.11-2.01 (m, 1H), 1.72-1.62 (m, 1H), 1.02 (t, J = 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 170.2, 152.4, 144.2, 137.6, 133.7, 129.1, 129.0, 111.5, 61.6, 33.7, 21.8, 14.3, 13.8, 11.2.

IR (film): *v* (cm⁻¹) 2969, 2931, 1720, 1586, 1447, 1409, 1379, 1298, 1262, 1141, 1081, 959, 629, 693, 595, 563.

HRMS (ESI, *m/z*) calcd for C₁₆H₂₀N₂O₃SNa [M+Na]⁺: 343.1087, found: 343.1079.

(15) Eq 1, reaction of 1c

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) hex-2-en-1-one **1c** (38.5 mg, 0.20 mmol), 2-((phenylsulfonyl)methyl)acrylonitrile **2a** (20.8 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 40 hours at 35 °C, afforded 20.3 mg (78%) of **3g** as a colorless oil, and afforded 26.7 mg (80%) of **4k** as a yellow oil.



(S)-6-(3,5-Dimethyl-1H-pyrazol-1-yl)-2-oxoethyl)-2-methyleneheptanenitrile (3g)

Enantiomeric excess of **3g** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 77% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 40 °C, t_r (major) = 6.2 min, t_r (minor) = 5.5 min). $[\alpha]_D^{22} = +11.8^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 5.95 (s, 1H), 5.89 (s, 1H), 5.74 (s, 1H), 3.16-3.00 (m, 2H), 2.53 (s, 3H), 2.46-2.30 (m, 3H), 2.23 (s, 3H), 1.49-1.35 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) *δ* 172.7, 151.9, 144.0, 132.0, 121.8, 118.7, 111.2, 39.1, 38.6, 35.6, 33.0, 19.7, 14.5, 14.1, 13.8.

IR (film): *v* (cm⁻¹) 2961, 2930, 2222, 1721, 1620, 1585, 1548, 1440, 1409, 1380, 1337, 1239, 1173, 1108, 958, 867, 805, 742, 648, 578, 412.

HRMS (ESI, *m/z*) calcd for C₁₅H₂₁N₃ONa [M+Na]⁺: 282.1577, found: 282.1579.



(*R*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-(phenylsulfonyl)hexan-1-one (4k)

Enantiomeric excess of **4k** was established by HPLC analysis using a Daicel Chiralpak AD-H column, ee = 78% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 13.0 min, t_r (minor) = 16.3 min). $[\alpha]_D^{22} = -7.0^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 7.96-7.88 (m, 2H), 7.68-7.44 (m, 3H), 5.94 (s, 1H), 3.96-3.84 (m, 1H), 3.76 (dd, J = 17.6, 6.4 Hz, 1H), 3.24 (dd, J = 17.6, 5.8 Hz, 1H), 2.41 (s, 3H), 2.21 (s, 3H), 2.08-1.90 (m, 1H), 1.67-1.29 (m, 3H), 0.89 (t, J = 7.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 170.2, 152.4, 144.1, 137.6, 133.6, 129.1, 129.0, 111.4, 60.2, 34.4, 30.5, 19.9, 14.2, 13.8. 13.7.

IR (film): *v* (cm⁻¹) 2963, 2931, 2874, 1723, 1586, 1445, 1381, 1303, 1176, 1141, 1082, 1030, 999, 961, 933, 808, 730, 691, 591, 563, 410.

HRMS (ESI, *m*/*z*) calcd for C₁₇H₂₂N₂O₃SNa [M+Na]⁺: 357.1243, found: 357.1247.

(16) Eq 1, reaction of 1d

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) hepta-2,6-dien-1-one **1d** (40.9 mg, 0.20 mmol), 2-((phenylsulfonyl)methyl)acrylonitrile **2a** (20.8 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 40 hours at 35 °C, afforded 16.5 mg (61%) of **3h** as a colorless oil, and afforded 21.5 mg (62%) of **4l** as a yellow oil.



(S)-4-(2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2-oxoethyl)-2-methyleneoct-7-enenitrile (3h)

Enantiomeric excess of **3h** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 79% (HPLC: 254 nm, n-hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 40 °C, t_r (major) = 6.9 min, t_r (minor) = 5.7 min). $[\alpha]_D^{22} = +6.0^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 5.95 (s, 1H), 5.90 (s, 1H), 5.87-5.71 (m, 2H), 5.07-4.93 (m, 2H), 3.08-3.02 (m, 2H), 2.53 (s, 3H), 2.48-2.32 (m, 3H), 2.23 (s, 3H), 2.18-2.08 (m, 2H), 1.58-1.48 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 172.5, 152.0, 144.0, 137.9, 132.1, 121.6, 118.6, 115.1, 111.2, 39.0, 38.4, 32.8, 32.6, 30.7, 14.5, 13.8.

IR (film): *v* (cm⁻¹) 2925, 2223, 1722, 1640, 1584, 1409, 1380, 1338, 1245, 1171, 1032, 959, 915, 806, 745, 644, 562, 410.

HRMS (ESI, *m*/*z*) calcd for C₁₆H₂₁N₃ONa [M+Na]⁺: 294.1577, found: 294.1580.



(R)-1-(3,5-Dimethyl-1H-pyrazol-1-yl)-3-(phenylsulfonyl)hept-6-en-1-one (4l)

S39

Enantiomeric excess of **41** was established by HPLC analysis using a Daicel Chiralpak AD-H column, ee = 83% (HPLC: 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 40 °C, t_r (major) = 14.1 min, t_r (minor) = 17.2 min). $[\alpha]_D^{22} = -1.2^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 7.95-7.89 (m, 2H), 7.66-7.48 (m, 3H), 5.94 (s, 1H), 5.78-5.62 (m, 1H), 5.03-4.93 (m, 2H), 3.98-3.86 (m, 1H), 3.78 (dd, *J* = 17.6, 6.4 Hz, 1H), 3.28 (dd, *J* = 17.6, 5.8 Hz, 1H), 2.41 (s, 3H), 2.22 (s, 3H), 2.26-2.04 (m, 3H), 1.76-1.64 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) *δ* 170.0, 152.4, 144.1, 137.6, 136.5, 133.7, 129.1, 129.0, 116.1, 111.4, 59.7, 34.4, 30.5, 27.7, 14.2, 13.7.

IR (film): *v* (cm⁻¹) 2928, 1722, 1585, 1479, 1444, 1381, 1311, 1177, 1142, 1083, 1029, 916, 808, 732, 691, 588, 562, 410.

HRMS (ESI, *m/z*) calcd for C₁₈H₂₂N₂O₃SNa [M+Na]⁺: 369.1243, found: 369.1244.

(17) Eq 2

According to the general procedure, the reaction of (E)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl) but-2-en-1-one **1a** (32.8 mg, 0.20 mmol), (E)-1,2,3,4,5-pentafluoro-6-(2-(phenylsulfonyl)vinyl) benzene **5** (25.7 mg, 0.10 mmol), Δ -**RhO** (6.6 mg, 8.0 mol%), diethyl 2,6-diethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.2 mg, 1.5 equiv) in 1,4-dioxane (1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 48 hours at room temperature, afforded 21.1 mg (54%) of **6** as a colorless oil, and afforded 21.1 mg (59%) of **4a** as a yellow oil. Enantiomeric excess of **4a** was determined as 81% ee.



(*R*,*E*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-methyl-5-(perfluorophenyl)pent-4-en-1-one (6)

Enantiomeric excess of **6** was established by HPLC analysis using a Daicel Chiralpak IG column, ee = 93% (HPLC: 254 nm, n-hexane/isopropanol = 99:1, flow rate 1.0 mL/min, 25 °C, t_r (major) = 11.4 min, t_r (minor) = 10.4 min). $[\alpha]_D^{22} = -12.0^\circ$ (*c* 0.5, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 6.56 (dd, J = 16.4, 7.6 Hz, 1H), 6.33 (dd, J = 16.4, 1.0 Hz, 1H), 5.96 (s, 1H), 3.28 (dd, J = 16.4, 7.6 Hz, 1H), 3.17 (dd, J = 16.4, 6.8 Hz, 1H), 3.12-3.04 (m, 1H), 2.53 (s, 1H), 3.28 (dd, J = 16.4, 7.6 Hz, 1H), 3.17 (dd, J = 16.4, 6.8 Hz, 1H), 3.12-3.04 (m, 1H), 2.53 (s, 1H), 3.28 (dd, J = 16.4, 7.6 Hz, 1H), 3.17 (dd, J = 16.4, 6.8 Hz, 1H), 3.12-3.04 (m, 1H), 2.53 (s, 1H), 3.17 (dd, J = 16.4, 6.8 Hz, 1H), 3.12-3.04 (m, 1H), 2.53 (s, 1H), 3.12 (dd, J = 16.4, 6.8 Hz, 1H), 3.12 (s, 1H), 3.12 (dd, J = 16.4, 6.8 Hz, 1H), 3.12 (dd, J

3H), 2.24 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 172.2, 152.0, 144.3 (br), 144.1, 113.4, 111.2, 41.6, 34.6, 20.0, 14.6, 13.8.

¹⁹F NMR (282 MHz, CDCl₃) δ –143.40 - –143.60 (m, 2F), –157.51 - –157.71 (m, 1F), –163.40 - –163.64 (m, 2F).

IR (film): v (cm⁻¹) 2923, 1728, 1583, 1520, 1494, 1459, 1412, 1378, 1353, 1317, 1248, 1136, 997, 967, 802, 746.

HRMS (ESI, *m/z*) calcd for C₁₇H₁₅F₅N₂ONa [M+Na]⁺: 381.0997, found: 381.0987.

8. Transformations of the Products

8.1 Reduction of (S)-4a



To a solution of (*S*)-1-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-(phenylsulfonyl)butan-1-one (*S*)-4a (*obtained by the reactions catalyzed by* Λ -*RhO*, 85% ee, 30.6 mg, 0.10 mmol) in THF/H₂O (4/1, 1.0 mL, 0.1 M) at 0 °C was added NaBH₄ (38.0 mg, 1.0 mmol). The reaction mixture was stirred at room temperature for 6 hours. The reaction was quenched with aqueous 2 N HCl (1.0 mL) at room temperature and extracted with CH₂Cl₂ (4×10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/n-hexane = 1:1) to afford **7** (20.9 mg, 0.098 mmol, yield: 98%) as a white solid.

(S)-3-(Phenylsulfonyl)butan-1-ol (7)

Enantiomeric excess of **7** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 85% (HPLC: 254 nm, n-hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 40 °C, t_r (major) = 19.1 min, t_r (minor) = 18.1 min). $[\alpha]_D^{22} = -15.8^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 7.93-7.85 (m, 2H), 7.70-7.54 (m, 3H), 3.86 (dt, *J* = 11.0, 5.6 Hz, 1H), 3.69 (ddd, *J* = 11.0, 8.4, 5.0 Hz, 1H), 3.41-3.28 (m, 1H), 2.31-2.17 (m, 2H), 1.69 (ddt, *J* = 14.1, 8.8, 5.2 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) *δ* 137.2, 133.7, 129.1, 129.0, 59.3, 57.1, 32.2, 13.7.

IR (film): *v* (cm⁻¹) 3341, 3208, 3143, 2928, 2876, 1581, 1447, 1380, 1294, 1140, 1060, 1005, 796, 766, 731, 691, 663, 589, 547.

HRMS (ESI, *m*/*z*) calcd for C₁₀H₁₄O₃SNa [M+Na]⁺: 237.0564, found: 237.0556.

8.2 Transamidation to 8 for Single Crystal X-ray Diffraction



To a solution of (R)-6-(3,5-dimethyl-1H-pyrazol-1-yl)-4-methyl-2-methylene-6-oxohexanenitrile

(*R*)-3a (*obtained by the reactions catalyzed by* Λ -*RhO*, 96% ee, 23.1 mg, 0.10 mmol) in THF (0.1 mL, 1 M) was added 6-ethoxybenzo[*d*]thiazol-2-amine (97.0 mg, 0.50 mmol). The reaction mixture was stirred at 80 °C for 40 hours. After the start material was converted completely, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/n-hexane = 1:1) to afford **8** (29.6 mg, 90% yield) as a white solid.

(R)-5-Cyano-N-(6-ethoxybenzo[d]thiazol-2-yl)-3-methylhex-5-enamide (8)

Enantiomeric excess of **8** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 96% (HPLC: 254 nm, n-hexane/isopropanol = 85:15, flow rate 1.0 mL/min, 40 °C, t_r (major) = 30.6 min, t_r (minor) = 22.9 min). $[\alpha]_D^{22} = -8.0^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 11.24 (brs, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.31 (d, J = 2.5 Hz, 1H), 7.06 (dd, J =8.8, 2.5 Hz, 1H), 5.85 (s, 1H), 5.66 (s, 1H), 4.10 (q, J = 7.0, 2H), 2.55-2.27 (m, 4H), 2.12 (dd, J = 13.6, 7.0, 1H), 1.45 (t, J = 7.0, 3H), 0.98 (d, J = 6.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) *δ* 169.9, 157.3, 156.3, 141.8, 133.2, 132.4, 121.1, 121.0, 118.4, 115.9, 105.3, 64.2, 41.2, 41.0, 29.2, 19.0, 14.8.

IR (film): *v* (cm⁻¹) 3182, 2975, 2921, 2218, 2047, 1688, 1605, 1551, 1460, 1259, 1223, 1114, 1060, 942, 822, 747, 666.

HRMS (ESI, *m/z*) calcd for C₁₇H₁₉N₃O₂SNa [M+Na]⁺: 330.1271, found: 330.1264.

8.3 Transamidation of (R)-3a with 4-Methoxyaniline



To a solution of (*R*)-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-4-methyl-2-methylene-6-oxohexanenitrile (*R*)-3a (*obtained by the reactions catalyzed by* Λ -*RhO*, 96% ee, 23.1 mg, 0.10 mmol) in THF (0.1 mL, 1 M) was added 4-methoxyaniline (62.0 mg, 0.50 mmol). The reaction mixture was stirred at 80 °C for 24 hours. After the starting material was consumed completely, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/n-hexane = 1:2) to afford 9 (24.3 mg, 94% yield) as a white solid.

(*R*)-5-Cyano-*N*-(4-methoxyphenyl)-3-methylhex-5-enamide (9)

Enantiomeric excess of **9** was established by HPLC analysis using a Daicel Chiralpak OD-H column, ee = 96% (HPLC: 254 nm, n-hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 40 °C, t_r (major) = 40.1 min, t_r (minor) = 36.2 min). $[\alpha]_D^{22} = -2.4^\circ$ (*c* 1.0, CH₂Cl₂).

¹H NMR (300 MHz, CDCl₃) δ 7.44-7.36 (m, 2H), 7.24 (brs, 1H), 6.89-6.83 (m, 2H), 5.94 (s, 1H), 5.77 (s, 1H), 3.78 (s, 3H), 2.47-2.33 (m, 3H), 2.28-2.16 (m, 2H), 1.07 (d, *J* = 6.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 169.4, 156.5, 132.5, 130.8, 121.9, 121.2, 119.0, 114.2, 55.5, 43,4, 41.0, 29.8, 19.1.

IR (film): *v* (cm⁻¹) 3299, 2960, 2837, 2226, 2180, 1655, 1605, 1536, 1509, 1460, 1236, 1171, 1032, 939, 829, 638, 524.

HRMS (ESI, *m*/*z*) calcd for C₁₅H₁₈N₂O₂Na [M+Na]⁺: 281.1260, found: 281.1254.

9. HPLC Traces of the Products

Enantiomeric purities of the reaction products were determined with a Daicel Chiralpak OD-H, IA, IG or Chiralcel OJ-H column (250×4.6 mm) on an Agilent 1200 or 1260 Series HPLC System using n-hexane/isopropanol as a mobile phase. The column temperature was 25 °C or 40 °C and UV-absorption was measured at 254 nm.



Figure S9. HPLC traces of rac-3a.



Figure S10. HPLC traces of (S)-3a (Table 2, Entry 1).



Figure S11. HPLC traces of (*S*)-3a (Table 2, Entry 2).



Figure S12. HPLC traces of (*S*)-3a (Table 2, Entry 3).



Figure S13. HPLC traces of (*S*)-3a (Table 2, Entry 4).



Figure S14. HPLC traces of (S)-3a (Table 2, Entry 5).



Figure S15. HPLC traces of (S)-3a (Table 2, Entry 6).



Figure S16. HPLC traces of (*S*)-3a (Table 2, Entry 7).



Figure S17. HPLC traces of (S)-3a (Table 2, Entry 8).



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.675	BB	0.1717	739.68506	65.26010	49.6411
2	7.465	BB	0.1964	750.38104	56.89471	50.3589

Figure S.	18. HPLC	traces	of	rac-3b.
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Figure S19. HPLC traces of (S)-3b (Table 2, Entry 9).



Figure S20. HPLC traces of (S)-3b (Table 2, Entry 10).



Figure S21. HPLC traces of *rac-3c*.



Figure S22. HPLC traces of (*S*)-3c (Table 2, Entry 11).



Figure S23. HPLC traces of rac-3d.



Figure S24. HPLC traces of (*S*)-3d (Table 2, Entry 12).



Figure S25. HPLC traces of rac-3e.



Figure S26. HPLC traces of (*S*)-3e (Table 2, Entry 13).



Figure S27. HPLC traces of rac-3f.



Figure S28. HPLC traces of (*S*)-3f (Eq 1).



Peak	RetTime	Туре	Width	Area	Height	Area	
#	[min]		[min]	[mAU*s]	[mAU]	%	
							I
1	5.699	BB	0.0842	103.63793	18.82326	50.1234	
2	6.868	BV R	0.1682	103.12770	7.32530	49.8766	

Figure S29	. HPLC traces	of <i>rac</i> -3g.
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Figure S30. HPLC traces of (*S*)-3g (Eq 1).



Figure	<i>S31</i> .	HPLC	traces	of	rac-3	βh.
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Figure S32. HPLC traces of (*S*)-3h (Eq 1)



Figure S33. HPLC traces of rac-4a.



Figure S34. HPLC traces of (*R*)-4a (Table 2, Entry 1).







Figure S36. HPLC traces of (R)-4a (Table 2, Entry 11).



Figure S37. HPLC traces of (*R*)-4a (Table 2, Entry 12).



Figure S38. HPLC traces of (R)-4a (Table 2, Entry 13).



Peak	RetTime	Туре	Width	Aı	rea	Hei	ght	Area
#	[min]		[min]	mAU	*s	[mAU]	8
1	11.665	BB	0.2457	117.	34642	7.	30317	9.6634
2	13.455	BB	0.4386	1096.	.99194	38.	51152	90.3366

Figure S39. HPLC traces of (*R*)-4a (Eq 2).



Figure S40. HPLC traces of rac-4b.



Figure S41. HPLC traces of (*R*)-4b (Table 2, Entry 2).



Figure S42. HPLC traces of rac-4c.



Figure S43. HPLC traces of (*R*)-4c (Table 2, Entry 3).



Figure S44. HPLC traces of rac-4d.



Figure S45. HPLC traces of (*R*)-4d (Table 2, Entry 4).



Figure S46. HPLC traces of rac-4e.



Figure S47. HPLC traces of (*R*)-4e (Table 2, Entry 5).



Figure S48. HPLC traces of rac-4f.



Figure S49. HPLC traces of (*R*)-4f (Table 2, Entry 6).







Figure S51. HPLC traces of (*R*)-4g (Table 2, Entry 7).



Figure S52. HPLC traces of rac-4h.



Figure S53. HPLC traces of (*R*)-4h (Table 2, Entry 8).



Peak	RetTime	Туре	Width	Ar	rea	Hei	.ght	Area
#	[min]		[min]	mAU	*s	[mAU]	ક
1	13.228	BB	0.2937	2962.	84375	156.	46800	49.9486
2	15.284	BB	0.5000	2968.	93872	89.	30674	50.0514
Total	ls :			5931.	78247	245.	77474	





Figure S55. HPLC traces of (R)-4i (Table 2, Entry 10).



Figure S56. HPLC traces of rac-4j.



Figure S57. HPLC traces of (*R*)-4j (Eq 1).



Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.853	BB	0.4152	786.22095	27.53284	50.1074
2	16.056	BB	0.5255	782.84998	21.56517	49.8926





Figure S59. HPLC traces of (*R*)-4k (Eq 1).



con	neer zine	.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	1120 011	74 64	inc agine	74 64	
#	[min]		[min]	[mAU*s]	[mAU]	%	
							l
1	13.907	BB	0.4614	268.51575	8.45767	50.1923	
2	17.040	BB	0.5746	266.45828	6.74868	49.8077	

Figure 3	<i>S60</i> .	HPLC	traces	of	rac- 41 .
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Figure S61. HPLC traces of (*R*)-4l (Eq 1).






Figure S63. HPLC traces of (*R*)-6 (Eq 2).



#	[1111]		[1111]	IIIAO		LIUMO	1	0
1	17.960	BB	0.5034	258.	47421	7.8	38221	49.9812
2	19.316	BB	0.5286	258.	66904	7.4	45366	50.0188
Total	s:			517.	14325	15.3	33587	

Figure S64. HPLC traces of rac-7.



Figure S65. HPLC traces of (S)-7.







Figure S67. HPLC traces of (*R*)-**8**.



Figure S68. HPLC traces of *rac-9*.



Figure S69. HPLC traces of (*R*)-9.

10. HPLC Traces of the Robustness Screen

Table S5. Reaction compatibility in the present of additives a

DM 1a	P Me + A	N Add SO ₂ Ph $A-F$.0 equiv $A-F$ 1.0 equiv 1	litive (1.0 ed RhO (8.0 md E-1 (1.5 eq ,4-dioxane,	quiv) bl%) uiv) r.t. (R)	Me -3a	+ DMP Me (S)-4a
		Additive	(<i>R</i>)- 3 a	()	5)-4a
Entry	Additive	Recovered ^b	Yield ^b	ee ^c	Yield ^b	ee ^c
1	$M_{10} N_3$	88%	86%	96% ee	85%	86% ee
2	Br	94%	86%	96% ee	85%	83% ee
3		99%	86%	96% ee	92%	83% ee
4	K S S S S S S S S S S S S S S S S S S S	88%	82%	96% ee	88%	83% ee
5		95%	86%	95% ee	92%	85% ee
6	MeO N Bn	99%	86%	96% ee	85%	83% ee
7		96%	82%	96% ee	92%	85% ee
8		99%	82%	95% ee	92%	83% ee
9		99%	86%	96% ee	92%	85% ee
10	У	94%	86%	96% ee	92%	85% ee
11	ОН	92%	86%	96% ee	89%	83% ee



^{*a*} Reaction conditions: **1a** (0.20 mmol), **2a** (0.10 mmol), Δ -**RhO** (8.0 mol%), **HE-1** (0.15 mmol) and additives (0.1 mmol) in 1,4-dioxane (1.0 mL, 0.1 M) were stirred at room temperature for 24 h irradiated with 21 W CFL. ^{*b*} Isolated yield. ^{*c*} Determined by HPLC on a chiral stationary phase.



Figure S70. HPLC traces of (R)-3a (Table S5, Entry 1).



Figure S71. HPLC traces of (*S*)-3a (Table S5, Entry 1).



Figure S72. HPLC traces of (R)-3a (Table S5, Entry 2).



Figure S73. HPLC traces of (*S*)-4a (Table S5, Entry 2).



Figure S74. HPLC traces of (R)-3a (Table S5, Entry 3).



Figure S75. HPLC traces of (*S*)-4a (Table S5, Entry 3).



Figure S76. HPLC traces of (*R*)-3a (Table S5, Entry 4).



Totals : 1.69076e4 936.81437

Figure S77. HPLC traces of (*S*)-4a (Table S5, Entry 4).



Figure S78. HPLC traces of (*R*)-3a (Table S5, Entry 5).



Figure S79. HPLC traces of (*S*)-4a (Table S5, Entry 5).



Figure S80. HPLC traces of (*R*)-3a (Table S5, Entry 6).



Figure S81. HPLC traces of (*S*)-4a (Table S5, Entry 6).



Figure S82. HPLC traces of (*R*)-3a (Table S5, Entry 7).



Figure S83. HPLC traces of (*S*)-4a (Table S5, Entry 7).



Figure S84. HPLC traces of (*R*)-3a (Table S5, Entry 8).



Figure S85. HPLC traces of (*S*)-4a (Table S5, Entry 8).



Figure S86. HPLC traces of (*R*)-3a (Table S5, Entry 9).



Figure S87. HPLC traces of (*S*)-4a (Table S5, Entry 9).



Figure S88. HPLC traces of (R)-3a (Table S5, Entry 10).



Figure S89. HPLC traces of (S)-4a (Table S5, Entry 10).



Figure S90. HPLC traces of (*R*)-3a (Table S5, Entry 11).



Figure S91. HPLC traces of (S)-4a (Table S5, Entry 11).



Figure S92. HPLC traces of (R)-3a (Table S5, Entry 12).

2671.82182 356.36902

Totals :



Figure S93. HPLC traces of (S)-4a (Table S5, Entry 12).



Figure S94. HPLC traces of (*R*)-3a (Table S5, Entry 13).



Figure S95. HPLC traces of (S)-4a (Table S5, Entry 13).



Figure S96. HPLC traces of (R)-3a (Table S5, Entry 14).



Figure S97. HPLC traces of (S)-4a (Table S5, Entry 14).



Figure S98. HPLC traces of (*R*)-3a (Table S5, Entry 15).



Figure S99. HPLC traces of (S)-4a (Table S5, Entry 15).



Figure S100. HPLC traces of (*R*)-3a (Table S5, Entry 16).



Figure S101. HPLC traces of (*S*)-4a (Table S5, Entry 16).

11. Single-Crystal X-Ray Diffraction Studies

X-ray data were collected with a Bruker 3 circuit D8 Quest diffractometer with MoKα radiation (microfocus tube with multilayer optics) and Photon 100 CMOS detector at 100 K. Scaling and absorption correction was performed by using the SADABS software package of Bruker. Structures were solved using direct methods in SHELXT and refined using the full matrix least squares procedure in SHELXL-2014. The hydrogen atoms were placed in calculated positions and refined as riding on their respective C atom, and Uiso(H) was set at 1.2 Ueq(Csp²) and 1.5 Ueq(Csp³). Disorder was refined using restraints for both the geometry and the anisotropic displacement factors. The absolute configuration of **4d** and **9** have been determined.

11.1 Crystal structure of RhO-1a

Single crystals of **RhO-1a** suitable for X-ray diffraction were obtained by slow diffusion from a solution of raacemic **RhO-1a** (20 mg) in CH_2Cl_2 (2.0 mL) layered with ethyl ether (1.0 mL) at room temperature for several days in a NMR tube.

Crystal structure, data and details of the structure determination for **RhO-1a** are presented in the Figure S102 and Table S6.



Figure S102. Crystal structure of RhO-1a.

Table S6. Crystal data and structure refinement for **RhO-1a**.

Crystal data

Identification code Habitus, colour Crystal size Crystal system Space group Unit cell dimensions

Volume 3Cell determination Empirical formula Moiety formula Formula weight Density (calculated) Absorption coefficient F(000)

Data collection:

Diffractometer type Wavelength Temperature Theta range for data collection Index ranges Data collection software Cell refinement software Data reduction software

Solution and refinement:

Reflections collected Independent reflections Completeness to theta = 25.242° Observed reflections Reflections used for refinement Absorption correction Max. and min. transmission Largest diff. peak and hole Solution Refinement Treatment of hydrogen atoms Programs used

Data / restraints / parameters Goodness-of-fit on F² R index (all data) R index conventional [I>2sigma(I)] hxqE104_0m nugget, pale yellow 0.34 x 0.25 x 0.23 mm³ Triclinic P-1 Z = 2a = 11.9931(5) Å $\alpha = 89.480(1)^{\circ}$. b = 13.7713(6) Å $\beta = 67.088(1)^{\circ}$. c = 14.7325(6) Å $\gamma = 79.592(1)^{\circ}$. 2199.33(16) Å³ 9783 peaks with Theta 2.6 to 27.5° . C44 H46 Cl2 F6 N4 O3 P Rh C₄₃ H₄₄ N₄ O₃ Rh, F₆ P, C H₂ Cl₂ 997.63 1.506 Mg/m^3 0.616 mm⁻¹ 1020

Bruker D8 QUEST area detector 0.71073 Å 100(2) K 2.248 to 27.564°. -15<=h<=15, -17<=k<=17, -19<=l<=18 APEX3 (Bruker AXS Inc., 2015)¹⁵ SAINT V8.35A (Bruker AXS Inc., 2015)¹⁶ SAINT V8.35A (Bruker AXS Inc., 2015)

82467 10124 [R(int) = 0.0338] 99.9 % 9422[I > 2(I)]10124 Semi-empirical from equivalents¹⁷ 0.87 and 0.820.438 and -0.606 e.Å⁻³ Direct methods Full-matrix least-squares on F² Calculated positions, constr. ref. XT V2014/1 (Bruker AXS Inc., 2014)¹⁸ SHELXL-2014/7 (Sheldrick, 2014)¹⁹ DIAMOND (Crystal Impact)²⁰ ShelXle (Hübschle, Sheldrick, Dittrich, 2011)²¹ 10124 / 144 / 590 1.038 wR2 = 0.0560R1 = 0.0223

11.2 Crystal structure of 4d

Single crystals of **4d** suitable for X-ray diffraction were obtained by slow diffusion from a solution of **4d** (20 mg) in ethyl ether (0.5 mL) layered with n-hexane (0.5 mL) at 4 $^{\circ}$ C for several days in a NMR tube.

Crystal structure, data and details of the structure determination for **4d** are presented in the Figure S103 and Table S7.



Figure S103. Crystal structure of 4d.

Table S7. Crystal data and structure refinement for 4d.

Crystal data

Identification code hxq119b_0m block, colourless Habitus, colour 0.31 x 0.13 x 0.08 mm³ Crystal size Crystal system Tetragonal Space group P43212 Z = 8 $\alpha = 90^{\circ}$. Unit cell dimensions a = 7.1300(2) Å b = 7.1300(2) Å $\beta = 90^{\circ}$. c = 66.238(2) Å3367.3(2) \AA^3 $\gamma = 90^{\circ}$. Volume 9348 peaks with Theta 2.5 to 25.2°. Cell determination **Empirical** formula C16 H17 F3 N2 O3 S Moiety formula $C_{16} H_{17} F_3 N_2 O_3 S$ 374.37 Formula weight 1.477 Mg/m^3 Density (calculated) Absorption coefficient 0.242 mm⁻¹ 1552 F(000) Data collection: Bruker D8 QUEST area detector Diffractometer type Wavelength 0.71073 Å Temperature 110(2) K 2.460 to 25.262°. Theta range for data collection Index ranges -8<=h<=8, -8<=k<=8, -79<=l<=79 APEX3 (Bruker AXS Inc., 2015)¹⁵ Data collection software Cell refinement software SAINT V8.37A (Bruker AXS Inc., 2015)¹⁶ Data reduction software SAINT V8.37A (Bruker AXS Inc., 2015) Solution and refinement: Reflections collected 35175 3048 [R(int) = 0.0499]Independent reflections Completeness to theta = 25.242° 99.9 % Observed reflections $2921[I > 2\sigma(I)]$ Reflections used for refinement 3048 Semi-empirical from equivalents¹⁷ Absorption correction 0.98 and 0.84 Max. and min. transmission $0.00(3)^{22}$ Flack parameter (absolute struct.) 0.308 and -0.260 e.Å⁻³ Largest diff. peak and hole "Dual space" Solution Full-matrix least-squares on F^2 Refinement Treatment of hydrogen atoms Calculated positions, constr. ref. XT V2014/1 (Bruker AXS Inc., 2014)¹⁸ Programs used SHELXL-2014/7 (Sheldrick, 2014)¹⁹ DIAMOND (Crystal Impact)²⁰ ShelXle (Hübschle, Sheldrick, Dittrich, 2011)²¹ Data / restraints / parameters 3048 / 0 / 229 Goodness-of-fit on F^2 1.224 R index (all data) wR2 = 0.1020R index conventional [I>2sigma(I)] R1 = 0.0479

11.3 Crystal structure of 9

Single crystals of compound **9**, which was obtained via transamidation of (*R*)-**3a** (*obtained from the reactions catalyzed by* Λ -*RhO*, suitable for X-ray diffraction were obtained by slow diffusion from a solution of **9** (30 mg) see Section 8.3), in CH₂Cl₂ (0.5 mL) layered with n-hexane (0.5 mL) at room temperature for several days in a NMR tube.

Crystal structure, data and details of the structure determination for **9** are presented in the Figure S104 and Table S8.



Figure S104. Crystal structure of 9.

Table S8. Crystal data and structure refinement for 9.

Crystal data

Identification code Habitus, colour Crystal size Crystal system Space group Unit cell dimensions Volume Cell determination **Empirical** formula Moiety formula Formula weight Density (calculated) Absorption coefficient F(000) Data collection: Diffractometer type Wavelength Temperature Theta range for data collection Index ranges Data collection software Cell refinement software Data reduction software Solution and refinement: Reflections collected Independent reflections Completeness to theta = 25.242° Observed reflections Reflections used for refinement Absorption correction Max. and min. transmission Flack parameter (absolute struct.) Largest diff. peak and hole Solution Refinement Treatment of hydrogen atoms ref. Programs used

Data / restraints / parameters Goodness-of-fit on F² R index (all data) R index conventional [I>2sigma(I)] lsp182_0m plate, colourless 0.45 x 0.40 x 0.04 mm³ Monoclinic Z = 8P21 $\alpha = 90^{\circ}$. a = 15.7976(9) Å b = 12.9960(8) Å $\beta = 112.625(2)^{\circ}$. c = 17.9469(11) Å $\gamma = 90^{\circ}$. 3401.0(4) Å³ 9782 peaks with Theta 2.7 to 26.4° . C17 H19 N3 O2 S C17 H19 N3 O2 S 329.41 1.287 Mg/m^3 0.203 mm⁻¹ 1392

Bruker D8 QUEST area detector 0.71073 Å 100(2) K 2.144 to 26.420°. -19<=h<=19, -16<=k<=16, -22<=l<=19 APEX3 (Bruker AXS Inc., 2015)¹⁵ SAINT V8.37A (Bruker AXS Inc., 2015)¹⁶ SAINT V8.37A (Bruker AXS Inc., 2015)

40409 13945 [R(int) = 0.0372] 99.9 % $12300[I > 2\sigma(I)]$ 13945 Semi-empirical from equivalents¹⁷ 0.99 and 0.91 $0.01(2)^{22}$ 0.241 and -0.264 e.Å⁻³ Direct methods Full-matrix least-squares on F² CH calculated positions, constr. ref., NH located, isotr. XT V2014/1 (Bruker AXS Inc., 2014)¹⁸ SHELXL-2014/7 (Sheldrick, 2014)¹⁹ DIAMOND (Crystal Impact²⁰ ShelXle (Hübschle, Sheldrick, Dittrich, 2011)²¹ 13945 / 1 / 853 1.037

wR2 = 0.0759R1 = 0.0353

12. NMR Spectra of New Compounds







1H



S104












hxq-5-118 F

---63.30 f19 CDC13 /opt/topspin3.2 prk 3 F₃C 2d ¹⁹F NMR (282 MHz, CDCl₃)























































1H

C NMK (125 M	IHZ, CDCI ₃)	1							
$ \begin{array}{c} $	6°691 		 A 129.	— 111.	22:27 27:00	~ 76.7	 		







1H





1H




f19 CDC13 /opt/topspin3.2 prk 4



---63.26





1H



13C



































1H



13C








































13. References

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