

Electronic Supporting Information

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

Wei Yuan,^a Zijun Zhou,^a Lei Gong^{*a} and Eric Meggers^{*a,b}

^aCollege of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China

^bFachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35043 Marburg, Germany

Contents

1. General Information.....	S2
2. Synthesis of the Substrates and Racemic Products.....	S2
2.1 Synthesis of the Benzamide Substrates.....	S2
2.2 Synthesis of the Racemic Products as HPLC References.....	S10
3. Rhodium-Catalyzed Asymmetric Photoredox Reactions.....	S11
4. Synthetic Transformation and Absolute Configuration Assignment of the Products ..	S27
4.1 Transformation of Product 3a to its Ester Derivative.....	S27
4.2 Absolute Configuration Assignment of the Products	S28
5. Mechanistic Studies.....	S28
5.1 Control experiments.....	S28
5.2 Radical Trapping Experiments.....	S29
5.3 Isolation of a Side Product.....	S30
5.4 Synthesis of a Potential Intermediate Complex <i>rac</i> - S7	S31
5.5 Other Lewis Acid Catalysts	S32
5.6 Other α,β -Unsaturated Carbonyl Compounds as Radical Acceptors.....	S33
5.7 UV/Vis-Absorption Spectra	S334
5.8 Alternative Radical Addition Mechanism	S35
6. Chiral HPLC Chromatography	S36
6.1 Determination of Enantioselectivities of Asymmetric Photoredox Reactions.....	S36
6.2 Determination of Enantiopurity of the Transformation Product S3	S58
7. Single Crystal X-Ray Diffraction.....	S60
8. References	S62
9. NMR Spectra	S63

1. General Information

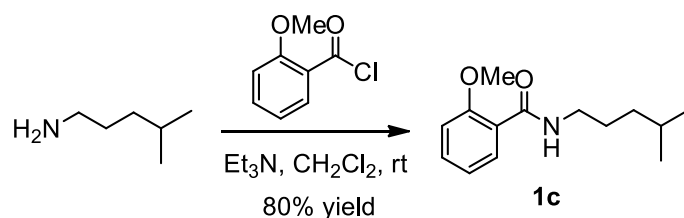
All reactions were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Light-induced catalytic reactions were performed in 10 mL Schlenk tubes at 27 °C under an atmosphere of argon and under irradiation with two 24 W blue LED lamps ($\lambda_{\max} = 450$ nm; company: Hongchangzhaoming, website: <http://hongchang-led.taobao.com>) as light sources. Solvents were distilled under argon from calcium hydride (CH_3CN , CH_2Cl_2) or sodium/benzophenone (THF, toluene). The chiral Lewis acid catalyst Λ -**RhO**,^{1,2} benzamides **1a–p**,^{3,4,5} α,β -unsaturated imidazoles **2a–m**,⁶ α,β -unsaturated pyrazole **2n**,⁶ photocatalysts **PC1–3**,⁴ and phosphate base **B1–3**⁴ were synthesized according to the published procedures. All other 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). ¹H NMR and ¹³C 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: $\text{CDCl}_3 = 7.26$ ppm (¹H NMR), 77.0 ppm (¹³C 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.



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

A solution of 4-methylpentan-1-amine⁴ (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_2Cl_2 (25 mL) was stirred at room temperature for 4 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with 1 M HCl (2 x 30 mL) and water (2 x 30 mL), then dried over Na_2SO_4 and concentrated. The crude

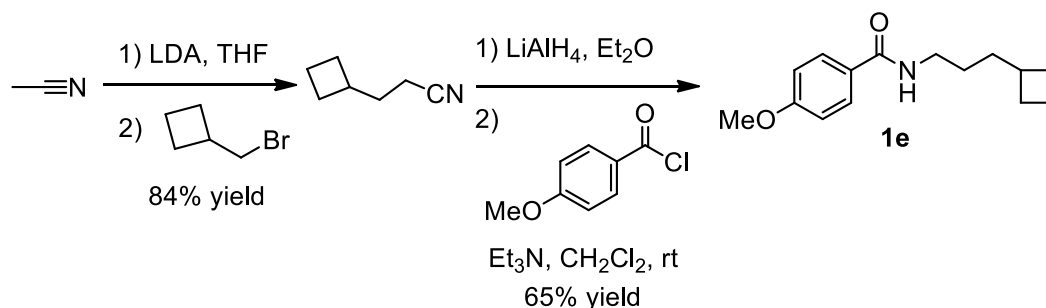
product was purified by silica gel column chromatography (EtOAc/*n*-hexane = 1:4) to afford benzamide **1c** (1.88 g, 8.0 mmol, yield: 80%) as a white solid.

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, 36.2, 27.6, 27.3, 22.4.

IR (film): ν (cm⁻¹) 2953, 2868, 1652, 1599, 1533, 1483, 1466, 1437, 1366, 1297, 1238, 1182, 1161, 1104, 1022, 756.

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



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 mmol) 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 (2 x 30 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-cyclobutylpropan-1-amine was obtained. To a solution of the produced 3-cyclobutylpropan-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

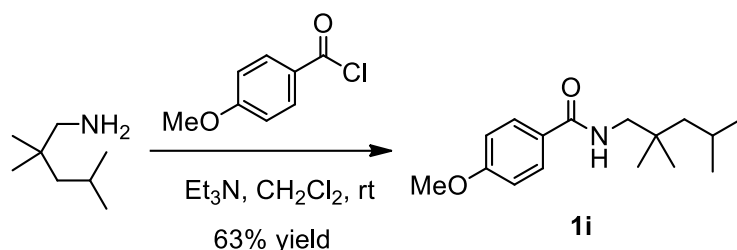
mmol, yield: 65% over two steps) as a white solid.

^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.81–7.63 (m, 2H), 7.01–6.80 (m, 2H), 6.17 (s, 1H), 3.84 (s, 3H), 3.39 (dd, $J = 12.8, 6.9$ 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}C NMR (125 MHz, CDCl_3): δ (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): ν (cm^{-1}) 2931, 2859, 1632, 1607, 1546, 1504, 1462, 1441, 1299, 1255, 1178, 1032, 844, 768, 608.

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



4-Methoxy-N-(2,2,4-trimethylpentyl)benzamide (**1i**)

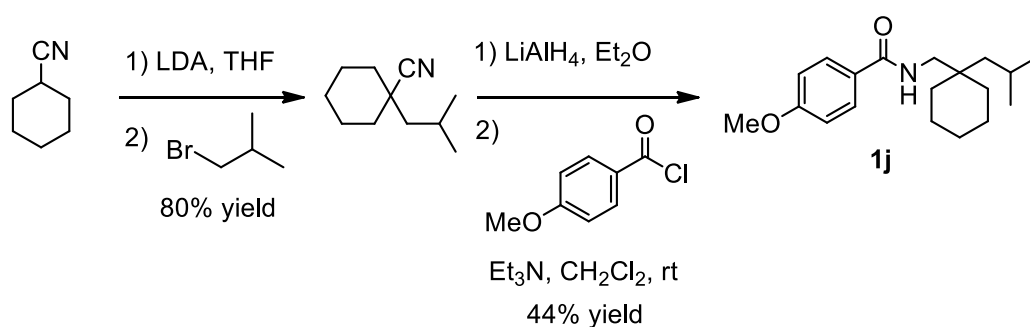
A solution of 2,2,4-trimethylpentan-1-amine^{5c} (1.55 g, 12.0 mmol), 4-methoxybenzoyl chloride (1.70 g, 13.2 mmol), triethyl amine (3.49 mL, 25.2 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 4 h. The resulting mixture was diluted with CH_2Cl_2 (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), then dried over Na_2SO_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.

^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.72 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.08 (s, 1H), 3.84 (s, 3H), 3.28 (d, $J = 6.2$ Hz, 2H), 1.85–1.64 (m, 1H), 1.22 (d, $J = 5.4$ Hz, 2H), 0.96 (s, 6H), 0.94 (d, $J = 6.7$ Hz, 6H).

^{13}C NMR (125 MHz, CDCl_3): δ (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): ν (cm^{-1}) 2956, 2869, 1637, 1607, 1546, 1505, 1466, 1366, 1310, 1254, 1176, 1032, 843, 767.

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



***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.

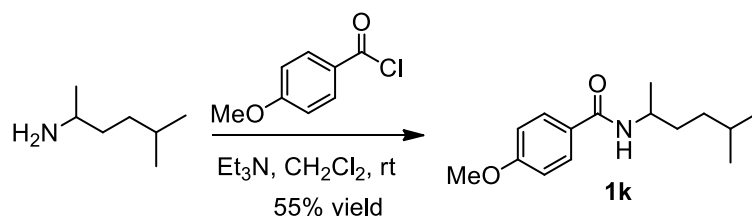
Subsequently, a dry round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with LiAlH₄ (0.96 g, 25.2 mmol) and diethyl ether (60 mL). The suspension was stirred at 0 °C, into which 1-isobutylcyclohexanecarbonitrile (1.98 g, 12.0 mmol) in diethyl ether (10 mL) was added 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* = 6.1 Hz, 2H), 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 C₁₉H₃₀NO₂ (M+H)⁺: 304.2271, found: 304.2270



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

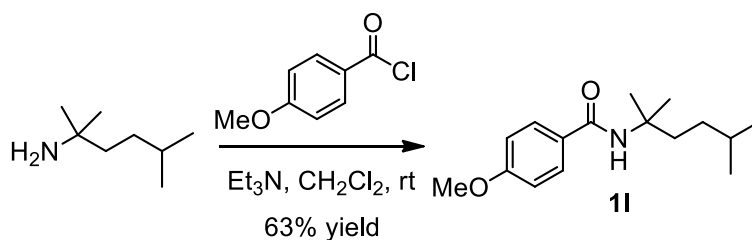
A solution of 4-methylpentan-1-amine³ (1.50 g, 13.0 mmol), 4-methoxybenzoyl chloride (2.43 g, 14.3 mmol) and triethyl amine (3.78 mL, 27.3 mmol) in CH₂Cl₂ (32 mL) was stirred at room temperature for 4 h. The reaction mixture was diluted with CH₂Cl₂ (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 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, CDCl_3): 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).

^{13}C NMR (125 MHz, CDCl_3): 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, 1454, 1303, 1256, 1178, 1030, 844, 770.

HRMS (ESI, m/z) calcd for $\text{C}_{15}\text{H}_{24}\text{NO}_2$ ($\text{M}+\text{H}$) $^+$: 250.1801, found: 250.1800



***N*-(2,5-Dimethylhexan-2-yl)-4-methoxybenzamide (**11**)**

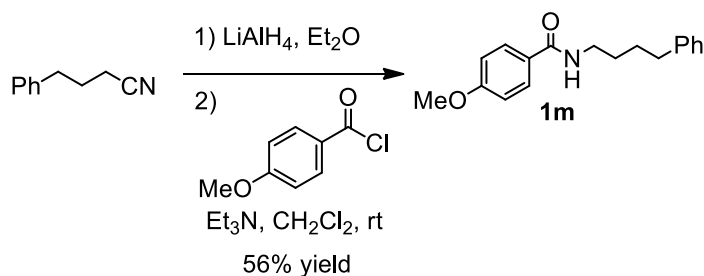
A solution of 2,5-dimethylhexan-2-amine³ (0.77 g, 6.0 mmol), 4-methoxybenzoyl chloride (1.12 g, 6.6 mmol), triethylamine (1.75 mL, 12.6 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 4 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with 1 M HCl (2 x 30 mL), water (2 x 30 mL), then dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography ($\text{EtOAc}/n\text{-hexane} = 1:4$) to afford benzamide **11** (1.00 g, 3.8 mmol, yield: 63%) as a white solid.

^1H NMR (500 MHz, CDCl_3): 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).

^{13}C NMR (125 MHz, CDCl_3): 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 $\text{C}_{16}\text{H}_{25}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 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

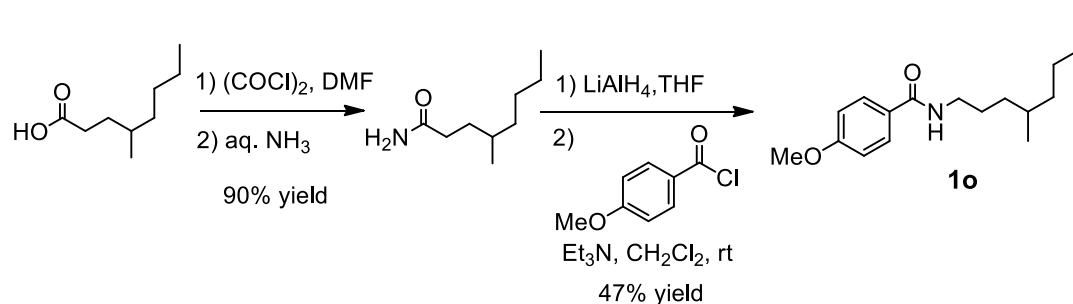
with LiAlH₄ (0.80 g, 21.0 mmol) and diethyl ether (50 mL). The suspension was stirred at 0 °C, into which 4-phenylbutanenitrile (1.45 g, 10.0 mmol) in diethyl ether (10 mL) was added dropwise. The mixture was heated at reflux for 3 h, cooled down to 0 °C, quenched with NaOH (10% in water, 4 mL) at 0 °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 (2.91 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 oxalyl 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

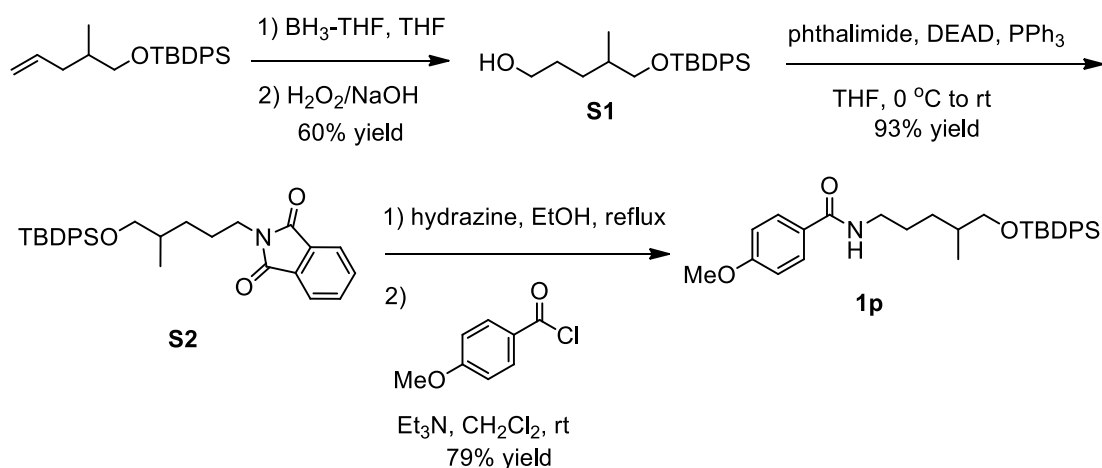
warmed to room temperature and stirred overnight. The resulting suspension was cooled again to 0 °C, then quenched with ice water (3 mL) and NaOH (4 mL, 10% in water), dried over excess MgSO₄. After filtration and evaporation of the solvent, 4-methyloctan-1-amine was obtained. To a solution of the produced 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).

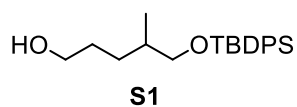
¹³C NMR (125 MHz, CDCl₃): δ (ppm) 167.0, 161.9, 128.6, 127.1, 113.5, 55.3, 40.3, 36.5, 34.2, 32.5, 29.2, 27.2, 22.9, 19.5, 14.0.

IR (film): ν (cm⁻¹) 2955, 2927, 2857, 1632, 1607, 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*-butyldiphenyl((2-methylpent-4-en-1-yl)oxy)silane^{5a,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),

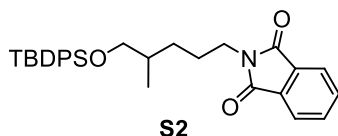
3.61-3.55 (m, 2H), 3.54-3.49 (m, 1H), 3.49-3.44 (m, 1H), 1.72-1.62 (m, 1H), 1.61-1.52 (m, 1H), 1.52-1.46 (m, 2H), 1.45-1.42 (m, 1H), 1.21-1.11 (m, 1H), 1.05 (d, $J = 2.8$ Hz, 9H), 0.92 (dd, $J = 11.1, 6.3$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): 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 $\text{C}_{22}\text{H}_{32}\text{O}_2\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 379.2063, found: 379.2062.

2-(5-((*tert*-Butyldiphenylsilyl)oxy)-4-methylpentyl)isoindoline-1,3-dione (**S2**)



To a solution of compound **S1** (2.56 g, 7.2 mmol), phthalimide (1.27 g, 8.6 mmol) and Ph_3P (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.

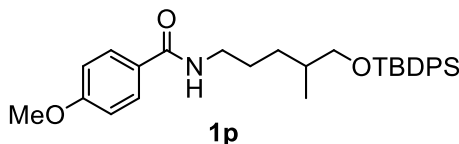
^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.83 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.69 (dd, $J = 5.5, 3.0$ Hz, 2H), 7.64 (dd, $J = 7.6, 1.4$ Hz, 4H), 7.41-7.33 (m, 6H), 3.70-3.64 (m, 2H), 3.46 (p, $J = 3.9$ Hz, 2H), 1.77-1.57 (m, 3H), 1.57-1.47 (m, 1H), 1.22-1.11 (m, 1H), 1.00 (s, 9H), 0.91 (d, $J = 6.7$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 168.4, 135.6, 135.6, 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 $\text{C}_{30}\text{H}_{35}\text{NO}_3\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 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 CH_2Cl_2 (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 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 **1p** (2.59 g, 5.3 mmol, 79% yield for two steps) as a colorless oil.

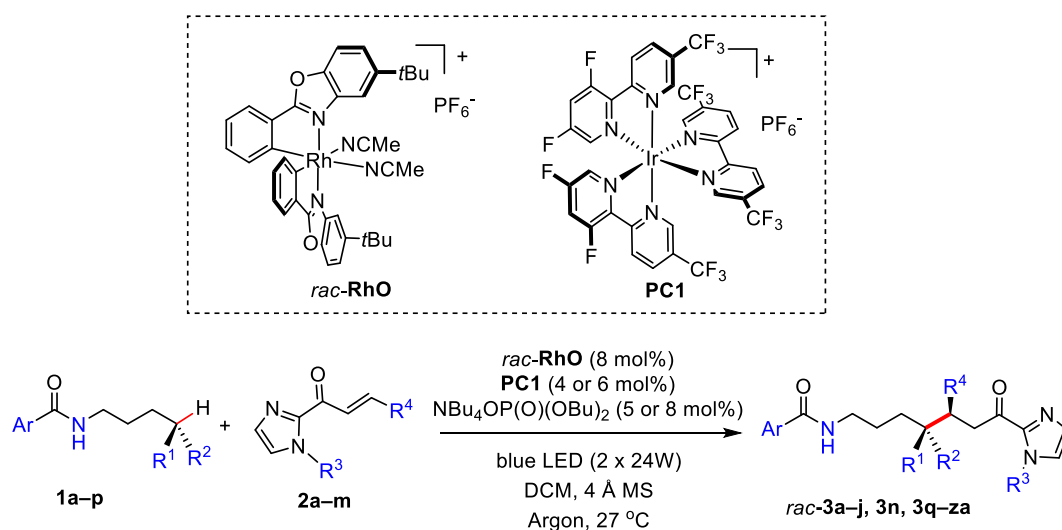
¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.71 (d, *J* = 8.9 Hz, 2H), 7.65 (dd, *J* = 7.8, 1.7 Hz, 4H), 7.44–7.31 (m, 6H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.20 (s, 1H), 3.81 (s, 3H), 3.56–3.46 (m, 2H), 3.43–3.31 (m, 2H), 1.75–1.62 (m, 1H), 1.62–1.43 (m, 3H), 1.22–1.13 (m, 1H), 1.05 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ (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): ν (cm⁻¹) 2957, 2930, 2857, 1632, 1606, 1545, 1504, 1462, 1427, 1303, 1254, 1178, 1111, 1032, 844, 823, 768, 740, 702, 613, 504.

HRMS (ESI, *m/z*) calcd for C₃₀H₃₉NO₃SiNa (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(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (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 α,β -unsaturated 2-acyl imidazoles **2a-m** (0.10 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous CH₂Cl₂ (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.

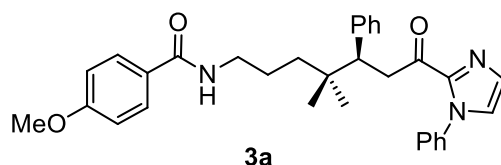
3. Rhodium-Catalyzed Asymmetric Photoredox Reactions



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:





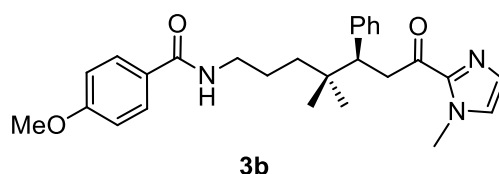
A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.016 mmol), 4 Å MS (200 mg), benzamide **1a** (70.5 mg, 0.30 mmol), and α,β -unsaturated 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/*n*-hexane = 1:5 to 1:4) to afford product **3a** as a white solid (81.5 mg, 0.160 mmol, yield: 80%). 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 = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, *t_r* (minor) = 8.7 min, *t_r* (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 C₃₂H₃₅N₃O₃Na (M+Na)⁺: 532.2570, found: 532.2557.



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 **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/*n*-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

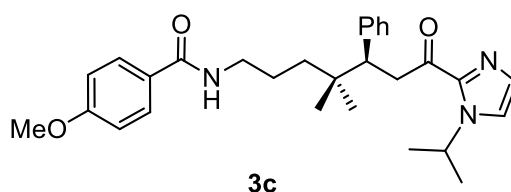
conditions: OD-H, wavelength = 254 nm, eluents: *n*-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 15.5 min, t_r (major) = 17.6 min). $[\alpha]_D^{25} = 36.8^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (400 MHz, CDCl_3): 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).

^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 192.0, 167.0, 162.0, 143.2, 141.6, 129.7, 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 $\text{C}_{27}\text{H}_{33}\text{N}_3\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 470.2414, found: 470.2406.



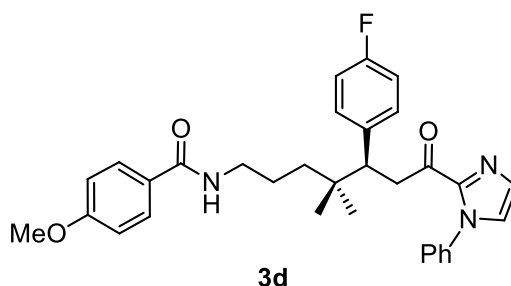
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **1a** (70.5 mg, 0.30 mmol), and α,β -unsaturated 2-acyl imidazole **2c** (48.0 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 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). $[\alpha]_D^{25} = 19.5^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.71 (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).

^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 192.5, 167.1, 162.0, 142.6, 141.5, 129.8, 129.1, 128.7, 127.5, 127.1, 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, 1673, 1633, 1606, 1545, 1504, 1462, 1453, 1395, 1294, 1255, 1178, 1088, 1030, 916, 845, 801, 768, 703, 608.

HRMS (ESI, m/z) calcd for $\text{C}_{29}\text{H}_{37}\text{N}_3\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 498.2727, found: 498.2721.



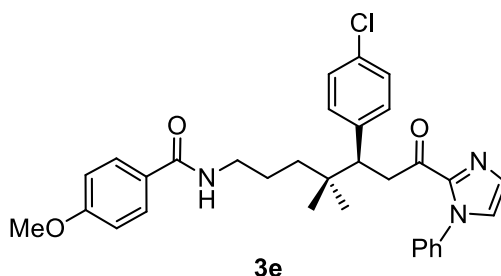
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (4.51 mg, 0.0100 mmol), 4 Å MS (200 mg), benzamide **1a** (70.5 mg, 0.30 mmol), and α,β -unsaturated 2-acyl imidazole **2d** (58.4 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 1:4) to afford product **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). $[\alpha]_D^{25} = -16.2^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): δ (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}C NMR (125 MHz, CDCl_3): δ (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): ν (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 $\text{C}_{32}\text{H}_{34}\text{FN}_3\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 550.2476, found: 550.2472.



A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (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 **2e** (61.6 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

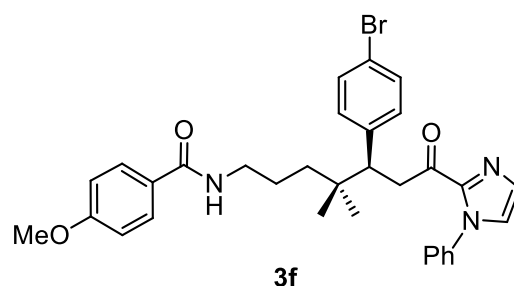
added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/*n*-hexane = 1:5 to 1:4) to afford product **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_r (minor) = 17.4 min, t_r (major) = 30.8 min). $[\alpha]_D^{25} = -29.2^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): 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).

^{13}C NMR (125 MHz, CDCl_3): 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^{-1}) 2961, 1683, 1632, 1606, 1544, 1503, 1443, 1405, 1306, 1254, 1178, 1092, 1030, 964, 844, 763, 735, 692.

HRMS (ESI, m/z) calcd for $\text{C}_{32}\text{H}_{34}\text{ClN}_3\text{O}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 566.2181, found: 566.2175.



A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (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_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 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_r (minor) = 17.2 min, t_r (major) = 29.1 min). $[\alpha]_D^{25} = -28.3^\circ$ ($c = 1.0$, CH_2Cl_2).

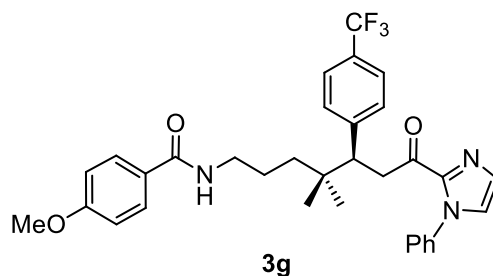
^1H NMR (500 MHz, CDCl_3) : δ (ppm) 7.70 (d, $J = 8.4$ Hz, 2H), 7.40–7.24 (m, 5H), 7.21 (s, 1H), 7.12–6.98 (m, 3H), 6.90 (d, $J = 8.5$ Hz, 2H), 6.81 (d, $J = 7.3$ Hz, 2H), 6.26 (s, 1H), 3.83 (s, 3H), 3.71 (dd, $J = 14.7, 10.8$ Hz, 1H), 3.45–3.35 (m, 2H), 3.35–3.20 (m, 2H), 1.72–1.54 (m, 2H),

1.41–1.26 (m, 2H), 0.93 (s, 3H), 0.83 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ (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): ν (cm^{-1}) 2961, 2928, 1686, 1632, 1606, 1545, 1503, 1443, 1406, 1306, 1255, 1178, 1030, 763, 692.

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



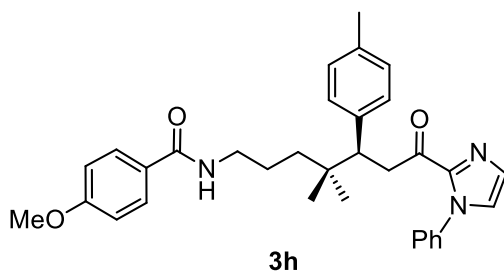
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (4.51 mg, 0.0100 mmol), 4 Å MS (200 mg), benzamide **1a** (70.5 mg, 0.30 mmol), and α,β -unsaturated 2-acyl imidazole **2g** (68.4 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 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). $[\alpha]_D^{25} = -7.2^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): δ (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): δ (ppm) 190.2, 167.0, 162.0, 145.6, 143.1, 137.9, 130.3, 129.4, 128.8, 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): ν (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 $\text{C}_{33}\text{H}_{35}\text{F}_3\text{N}_3\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 578.2625, found: 578.2627.



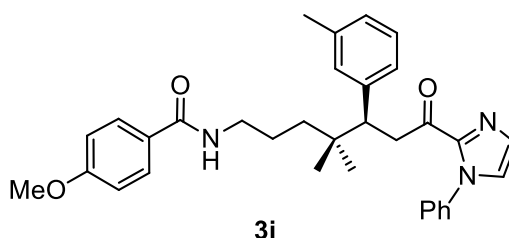
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **1a** (70.5 mg, 0.30 mmol), and α,β -unsaturated 2-acyl imidazole **2h** (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 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). $[\alpha]_D^{25} = -17.2^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H 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 $\text{C}_{33}\text{H}_{38}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 524.2907, found: 524.2911.



A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (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_2Cl_2 (1.0 mL) was

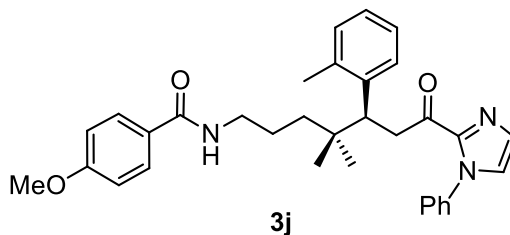
added under argon. The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C for the 48 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/*n*-hexane = 1:5) to afford product **3i** 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 = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 7.2 min, t_r (major) = 13.5 min). $[\alpha]_D^{25} = -12.0^\circ$ (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.70 (d, $J = 8.9$ Hz, 2H), 7.36–7.30 (m, 1H), 7.29–7.24 (m, 2H), 7.22 (d, $J = 1.0$ Hz, 1H), 7.11–7.04 (m, 2H), 6.98 (d, $J = 7.7$ Hz, 3H), 6.90 (d, $J = 8.9$ Hz, 2H), 6.77–6.72 (m, 2H), 6.15 (s, 1H), 3.84 (s, 3H), 3.74 (dd, $J = 14.6, 10.3$ Hz, 1H), 3.39 (dd, $J = 13.0, 6.1$ Hz, 2H), 3.34–3.25 (m, 2H), 2.26 (s, 3H), 1.74–1.61 (m, 2H), 1.47–1.36 (m, 1H), 1.35–1.27 (m, 1H), 0.95 (s, 3H), 0.85 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ (ppm) 191.1, 167.0, 162.0, 143.5, 141.1, 138.0, 137.0, 131.0, 129.2, 128.7, 128.6, 128.3, 127.4, 127.1, 126.9, 126.5, 126.4, 125.3, 113.6, 55.3, 49.7, 40.6, 39.7, 37.8, 36.1, 25.1, 24.8, 24.1, 21.4.

IR (film): ν (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 C₃₃H₃₈N₃O₃ (M+H)⁺: 524.2907, found: 524.2912.



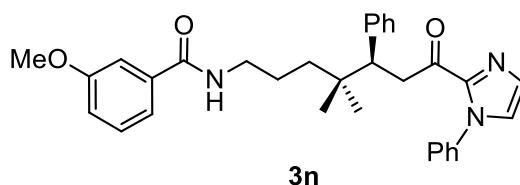
A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **1a** (70.5 mg, 0.30 mmol), and α,β -unsaturated 2-acyl imidazole **2j** (57.6 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. Degassed anhydrous 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 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) = 13.7 min). $[\alpha]_D^{25} = -5.4^\circ$ (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.76–7.68 (m, 2H), 7.33–7.27 (m, 2H), 7.24 (t, $J = 7.6$ Hz, 2H), 7.19 (d, $J = 0.9$ Hz, 1H), 7.11–7.03 (m, 4H), 6.91–6.84 (m, 2H), 6.63–6.56 (m, 2H), 6.37 (s, 1H), 3.83 (s, 3H), 3.74 (dd, $J = 11.5, 4.1$ Hz, 1H), 3.63 (dd, $J = 14.6, 11.6$ Hz, 1H), 3.42 (dd, $J = 12.6, 5.7$ Hz, 2H), 3.32 (dd, $J = 14.7, 4.1$ Hz, 1H), 2.18 (s, 3H), 1.74–1.63 (m, 2H), 1.57–1.49 (m, 1H), 1.44–1.34 (m, 1H), 0.99 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ (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): ν (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 $\text{C}_{33}\text{H}_{38}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 524.2907, found: 524.2910.



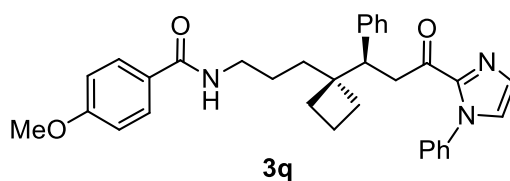
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **1b** (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 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 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). $[\alpha]_D^{25} = -6.4^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): δ (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): δ (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): ν (cm^{-1}) 2961, 2871, 1684, 1640, 1583, 1537, 1492, 1446, 1405, 1305, 1242, 1043, 964, 914, 757, 692.

HRMS (ESI, m/z) calcd for $\text{C}_{32}\text{H}_{36}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 510.2751, found: 510.2752.



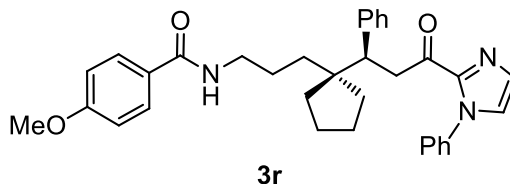
A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **1e** (74.1 mg, 0.30 mmol), and α,β -unsaturated 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, *t_r* (minor) = 8.8 min, *t_r* (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, 24.4, 14.9.

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 C₃₃H₃₆N₃O₃ (M+H)⁺: 522.2751, found: 522.2757.



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 **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, *t_r* (minor) = 9.0 min, *t_r* (major) = 20.0 min). [α]_D²⁵ = -20.0° (c = 1.0, CH₂Cl₂).

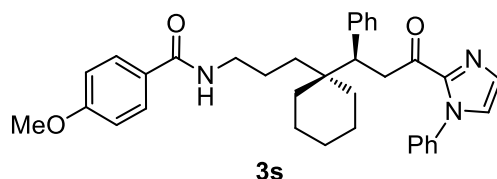
¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.29–7.24 (m, 2H), 7.23–7.12 (m, 6H), 7.05 (d, *J* = 0.9 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 7.1 Hz, 2H), 6.35

(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).

^{13}C NMR (101 MHz, CDCl_3): 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 $\text{C}_{34}\text{H}_{38}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}^+$): 536.2907, found: 536.2908.



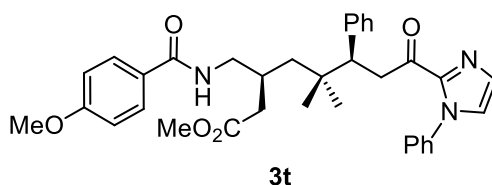
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **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 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 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, t_r (minor) = 9.3 min, t_r (major) = 20.5 min). $[\alpha]_{\text{D}}^{25} = -11.5^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): 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).

^{13}C NMR (125 MHz, CDCl_3): 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 $\text{C}_{35}\text{H}_{40}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}^+$): 550.3064, found: 550.3071.



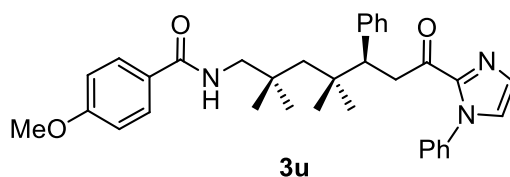
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (13.75 mg, 0.0120 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), non-racemic 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_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 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 (28:1 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). $[\alpha]_{\text{D}}^{25} = -5.5^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): δ (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): δ (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 $\text{C}_{35}\text{H}_{39}\text{N}_3\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 604.2781, found: 604.2776.



A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (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_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 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

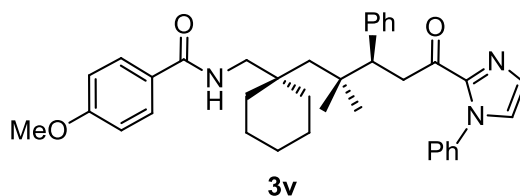
conditions: AD-H, wavelength = 254 nm, eluents: *n*-hexane/isopropanol = 70:30, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 11.8 min, t_r (major) = 17.6 min). $[\alpha]_D^{25} = -16.1^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): 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).

^{13}C NMR (101 MHz, CDCl_3): 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, 2926, 1684, 1643, 1606, 1542, 1503, 1444, 1406, 1305, 1254, 1176, 1030, 844, 802, 764, 703, 692.

HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{40}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}^+$): 538.3064, found: 538.3068.



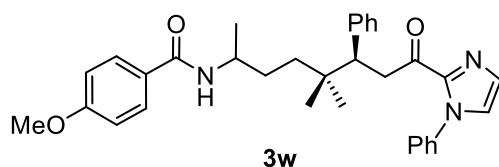
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **1j** (91.0 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_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 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). $[\alpha]_D^{25} = -14.4^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): 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).

^{13}C NMR (125 MHz, CDCl_3): 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, 1605, 1531, 1502, 1452, 1405, 1306, 1253, 1176, 1030, 843, 734, 703.

HRMS (ESI, m/z) calcd for $\text{C}_{37}\text{H}_{44}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}^+$): 578.3377, found: 578.3378.



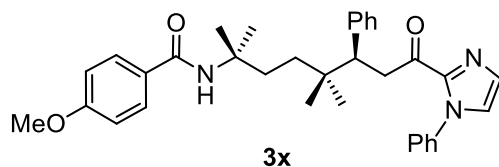
A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), racemic benzamide **1k** (74.7 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_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 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 **3w** 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, 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 ^1H NMR of **3w** (after purified by flash chromatography).

^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.76 (d, J = 8.8 Hz, 2H), 7.34–7.31 (m, 1H), 7.26 (s, 2H), 7.24–7.20 (m, 6H), 7.09 (d, J = 0.8 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 7.6 Hz, 2H), 5.87 (d, J = 8.3 Hz, 1H), 4.10–4.05 (m, 1H), 3.89–3.80 (m, 4H), 3.46 (d, J = 7.3 Hz, 2H), 3.30–3.22 (m, 1H), 1.77–1.66 (m, 1H), 1.56–1.50 (m, 1H), 1.38–1.31 (m, 2H), 1.18 (d, J = 6.5 Hz, 3H), 0.92 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ (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): ν (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 $\text{C}_{33}\text{H}_{38}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}^+$): 524.2907, found: 524.2909.



A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (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 **1l** (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_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 44 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/*n*-hexane = 1:5 to

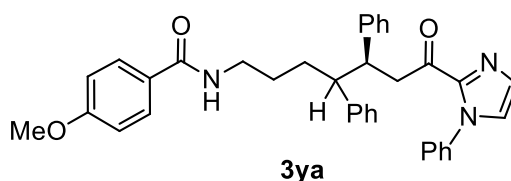
1:4) to afford product **3x** as a white solid (55.9 mg, 0.104 mmol, yield: 52%). Enantiomeric excess was established as 91% ee by HPLC analysis using a Chiralpak AD-H column. (HPLC conditions: AD-H, wavelength = 254 nm, eluents: *n*-hexane/isopropanol = 80:20, flow rate = 1.0 mL/min, temperature = 30 °C, t_r (minor) = 10.0 min, t_r (major) = 17.2 min). $[\alpha]_D^{25} = -15.3^\circ$ ($c = 1.0$, CH_2Cl_2).

^1H NMR (500 MHz, CDCl_3): 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).

^{13}C NMR (125 MHz, CDCl_3): 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}) 2963, 2929, 1684, 1650, 1605, 1533, 1495, 1445, 1045, 1305, 1252, 1176, 1030, 965, 914, 844, 765, 702.

HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{40}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 538.3064, found: 538.3072.



A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (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), 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 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 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).

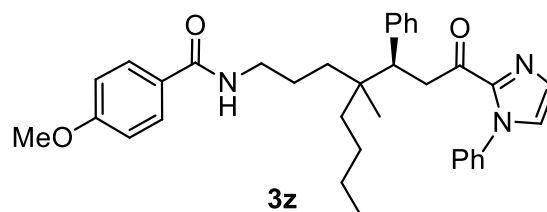
^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.63 (d, $J = 8.8$ Hz, 2H), 7.36–7.33 m, 1H), 7.25 (d, $J = 1.1$ Hz, 2H), 7.25–7.20 (m, 6H), 7.13–7.09 (m, 3H), 6.97 (d, $J = 0.7$ Hz, 1H), 6.93–6.88 (m, 4H), 6.80 (d, $J = 7.6$ Hz, 2H), 6.01 (s, 1H), 3.81 (s, 3H), 3.66–3.60 (m, 2H), 3.39–3.22 (m, 2H), 2.92–2.86 (m, 1H), 1.79–1.66 (m, 1H), 1.47–1.40 (m, 2H), 1.24–1.16 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 190.2, 166.8, 161.9, 143.2, 141.9, 138.1, 129.4, 128.9, 128.8, 128.7, 128.6, 128.5, 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,

763, 700.

HRMS (ESI, m/z) calcd for $C_{36}H_{36}N_3O_3$ ($M+H$)⁺: 558.2751, found: 558.2753.



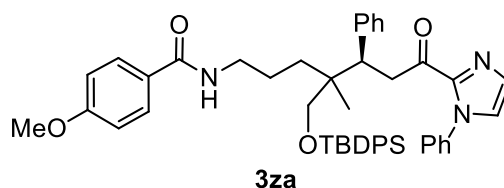
A dried 10 mL Schlenk tube was charged with $[Ir(dF(CF_3)ppy)_2(5,5'-dCF_3bpy)](PF_6)$ (9.17 mg, 0.0080 mmol), chiral rhodium catalyst Λ -**RhO** (13.28 mg, 0.0160 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **1o** (83.2 mg, 0.30 mmol), and α,β -unsaturated 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_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 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, t_r (syn, minor) = 5.4 min, t_r (syn, major) = 14.8 min, t_r (anti, minor) = 9.2 min, t_r (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, $CDCl_3$): 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, $CDCl_3$): 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 $C_{35}H_{42}N_3O_3$ ($M+H$)⁺: 552.3220, found: 552.3225.



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 **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 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). [α]_D²⁵ = -3.0° (c = 1.0, CHCl₃) (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)

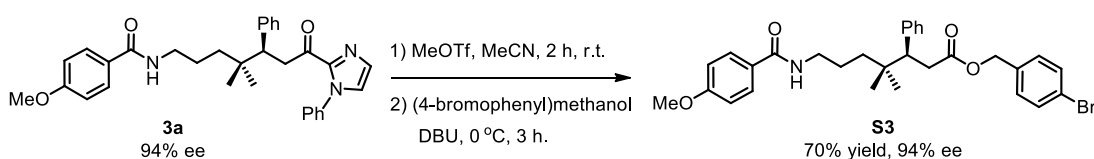
¹³C NMR (125 MHz, CDCl₃): δ (ppm) 190.9, 166.9, 162.0, 143.5, 140.9, 138.1, 135.9, 135.9, 133.6, 130.3, 129.6, 129.6, 129.2, 128.8, 128.6, 128.3, 127.6, 126.4, 126.2, 125.3, 113.6, 67.8, 55.4, 46.6, 40.9, 40.6, 39.7, 32.8, 27.1, 23.6, 19.4, 19.2. (Major diastereoisomer)

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 C₄₈H₅₃N₃O₄SiNa (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 trifluoromethanesulfonate (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_2Cl_2).

^1H NMR (500 MHz, CDCl_3): δ (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): δ (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, 35.8, 35.4, 24.8, 24.7, 24.3.

IR (film): ν (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 $\text{C}_{30}\text{H}_{34}\text{BrNO}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 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 Λ -**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

Table S1. Catalysis under air or in the presence of a radical inhibitor.

entry	atmosphere	additives	t (h)	yield (%) ^a	ee (%) ^b
1 ^c	argon	none	38	80	94
2	air	none	38	21	36
3	argon	BHT (3.0 eq)	40	5	– ^d
4	argon	TEMPO (2.0 eq)	38	0	– ^d

^aTaken from entry 4 of Table 1. ^bisolated yield. ^cee determined by chiral HPLC. ^dnot determined.

Entry 2: A dried 10 mL Schlenk tube was charged with $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(5,5'\text{-dCF}_3\text{bpy})](\text{PF}_6)$ (4.58 mg, 0.0040 mmol), chiral rhodium catalyst Λ -**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 α,β -unsaturated 2-acyl imidazole **2a** (27.4 mg, 0.10 mmol). Anhydrous CH_2Cl_2 was added (0.5

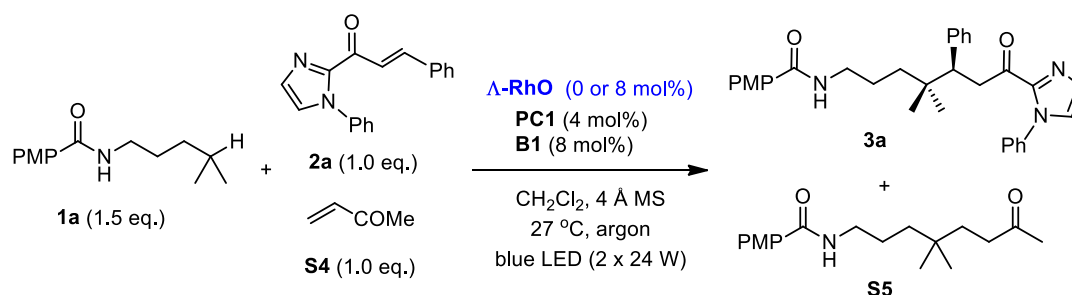
mL). The Schlenk tube was sealed and positioned approximately 3 cm away from two 24 W blue LED lamps. After being stirred at 27 °C under air for the 38 h, the reaction mixture was concentrated and then purified by flash chromatography on silica gel (acetone/*n*-hexane = 1:5 to 1:4) to afford product **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(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (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 CH₂Cl₂ 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(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (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 CH₂Cl₂ 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.

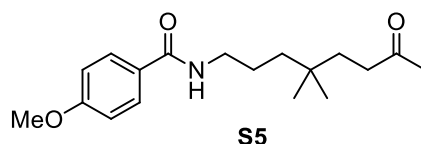
5.2 Radical Trapping Experiments



- 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(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (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%).



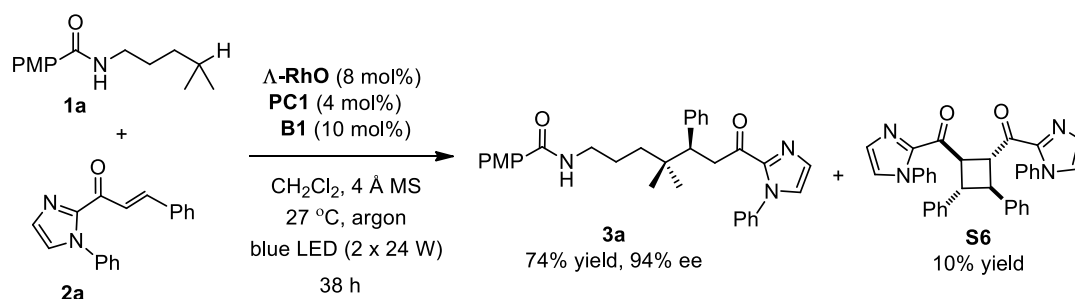
¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.74 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.20 (s, 1H), 3.84 (s, 3H), 3.40 (q, *J* = 6.9 Hz, 2H), 2.43–2.30 (m, 2H), 2.14 (s, 3H), 1.61–1.51 (m, 2H), 1.51–1.44 (m, 2H), 1.27–1.20 (m, 2H), 0.86 (s, 6H).

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

All spectroscopic data were in agreement with the literature.⁴

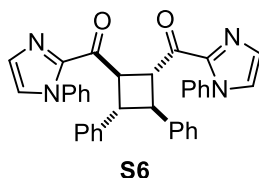
In the absence of Λ -RhO: A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (9.16 mg, 0.0080 mmol), tetrabutylammonium dibutyl phosphate (7.22 mg, 0.0160 mmol), 4 Å MS (200 mg), benzamide **1a** (70.2 mg, 0.30 mmol), and α,β -unsaturated 2-acyl imidazole **2a** (54.8 mg, 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.



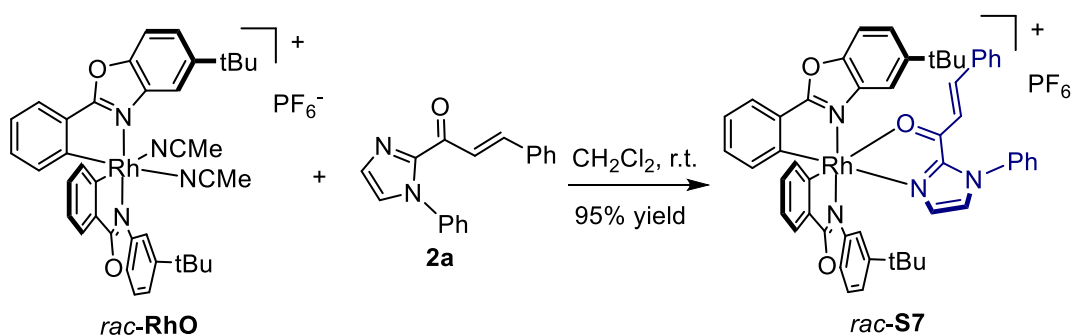
¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.56–7.44 (m, 5H), 7.31 (d, *J* = 7.1 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 0.9 Hz, 1H), 6.92 (d, *J* = 0.9 Hz, 1H), 4.69–4.61 (m, 1H), 4.21–4.12 (m, 1H).

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,

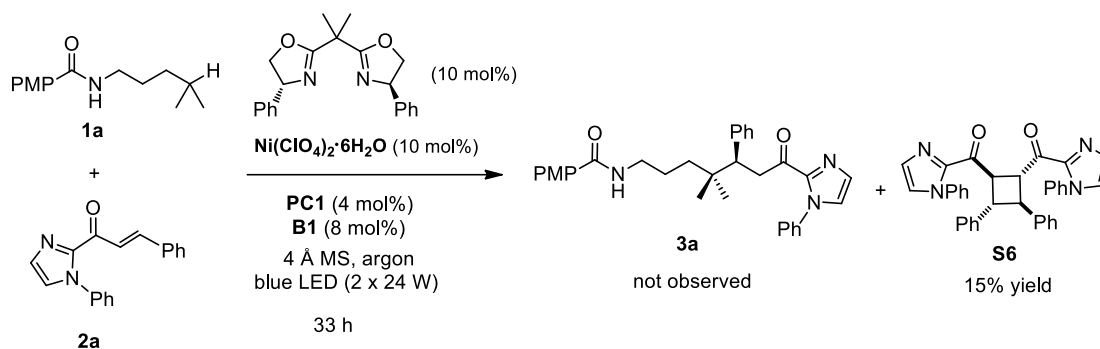
150.3, 148.4, 148.3, 145.3, 137.4, 137.0, 135.4, 134.5, 133.5, 133.4, 133.0, 132.2, 132.0, 131.8, 131.6, 130.9, 129.6, 129.4, 129.3, 126.6, 126.3, 126.0, 124.3, 124.2, 124.1, 118.7, 112.2, 111.7, 111.6, 111.1, 35.2, 35.1, 31.6, 31.5.

IR (film): ν (cm⁻¹) 2961, 1619, 1591, 1537, 1492, 1448, 1404, 1386, 1117, 1081, 1035, 842, 770, 735, 557.

HRMS (ESI, m/z) calcd for C₅₂H₄₆N₄O₃Rh (M-PF₆)⁺: 877.2619, found: 877.2690.

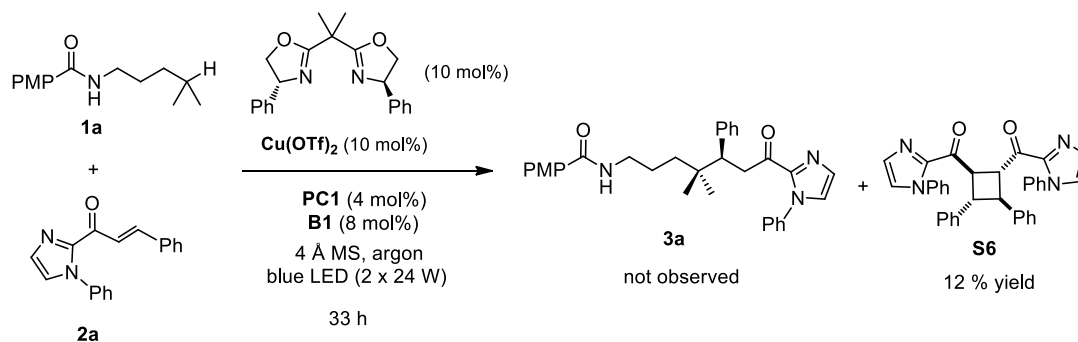
5.5 Other Lewis Acid Catalysts

(1) Replacing Λ -RhO with chiral Ni^{II}-BOX as the Lewis acid catalyst



A dried 10 mL Schlenk tube was charged with chiral BOX ligand (0.010 mmol, 3.34 mg) and Ni(ClO₄)₂·6H₂O (0.010 mmol, 3.65 mg), anhydrous CH₂Cl₂ (0.5 mL) was added. The mixture was stirred at room temperature for 30 min, then [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (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 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.

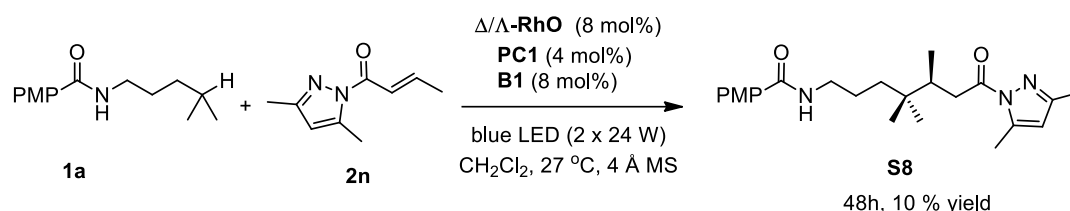
(2) Replacing Λ -RhO with chiral Cu^{II}-BOX as the Lewis acid catalyst



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 CH₂Cl₂ (0.5 mL) was added. The mixture was stirred at room temperature for 30 min, then [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (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(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (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 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 (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%).

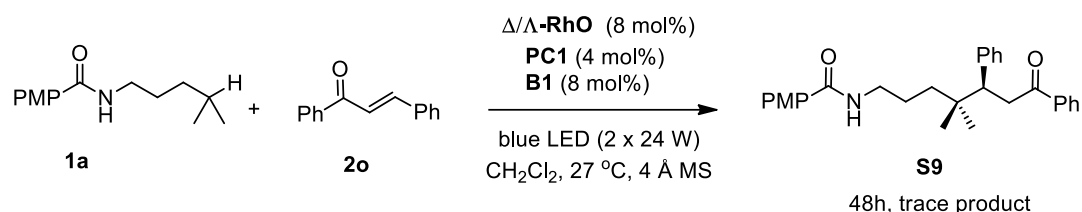
¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.72 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.15 (s, 1H), 5.95 (s, 1H), 3.84 (s, 3H), 3.50–3.37 (m, 2H), 3.15 (dd, *J* = 15.7, 2.7 Hz, 1H), 2.83 (dd, *J* = 15.7, 10.6 Hz, 1H), 2.53 (s, 3H), 2.22 (s, 3H), 2.14–2.07 (m, 1H), 1.72–1.58 (m, 4H), 0.92–0.88 (m, 9H).

¹³C NMR (101 MHz, CDCl₃) 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 C₂₃H₃₃N₃O₃Na (M+Na)⁺: 422.2414, found: 422.2425.

(2) Chalcone as radical acceptor



A dried 10 mL Schlenk tube was charged with [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) (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 (*E*)-chalcone **2o** (41.6 mg, 0.20 mmol). The reaction mixture was degassed and backfilled with argon for three cycles. 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. 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 [Ir(dF(CF₃)ppy)₂(5,5'-dCF₃bpy)](PF₆) but also the Lewis acid catalyst *rac*-RhO and intermediate *rac*-S7 absorb in the visible region.

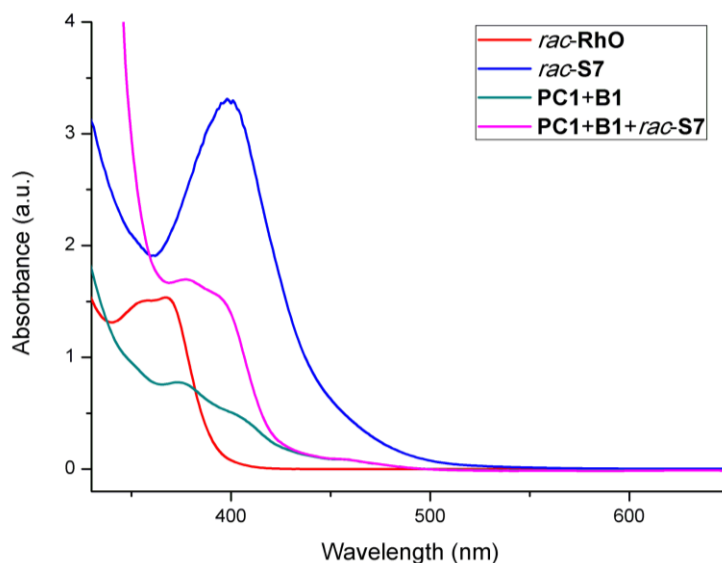


Figure S1. UV/Vis-absorption spectra of the different components in CH₂Cl₂ (0.1 mM). a.u. = absorbance units. Red: rhodium catalyst *rac*-RhO; blue: intermediate complex *rac*-S7; green: a mixture of photocatalyst PC1 and phosphate base B1; pink: a mixture of intermediate complex *rac*-S7, photocatalyst 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 $\text{PC}^{\cdot-}$ and protonated to obtain **H**. Upon release of the product and coordination of new substrate a new catalytic cycle can be initiated (**H** \rightarrow **C**).

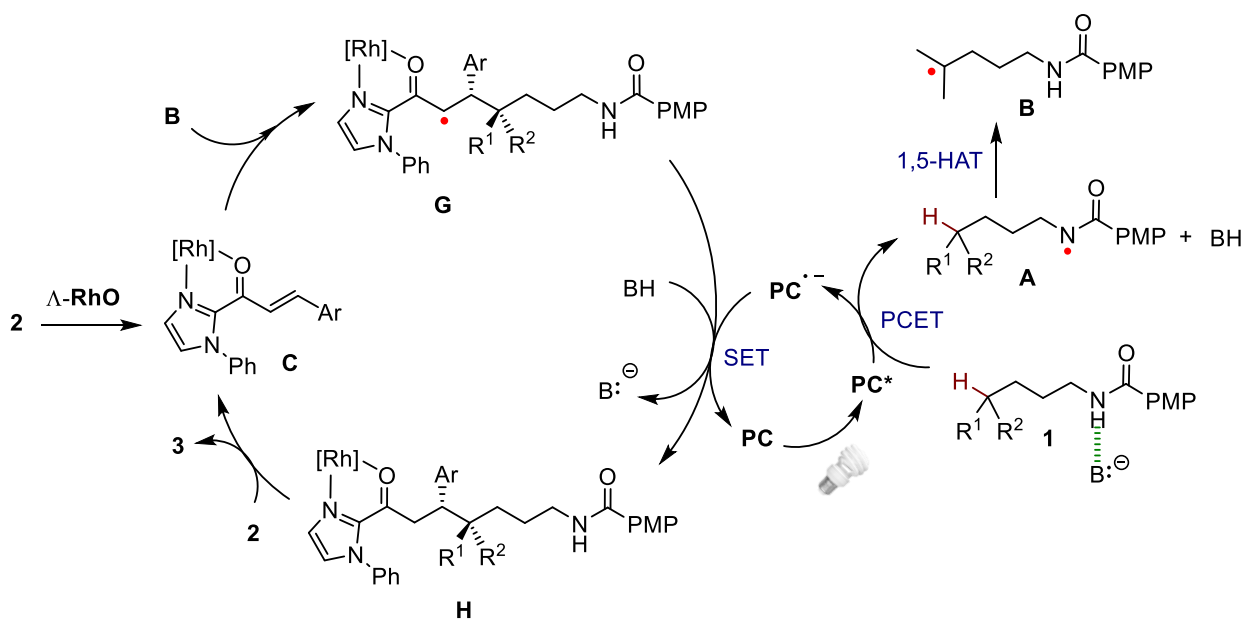
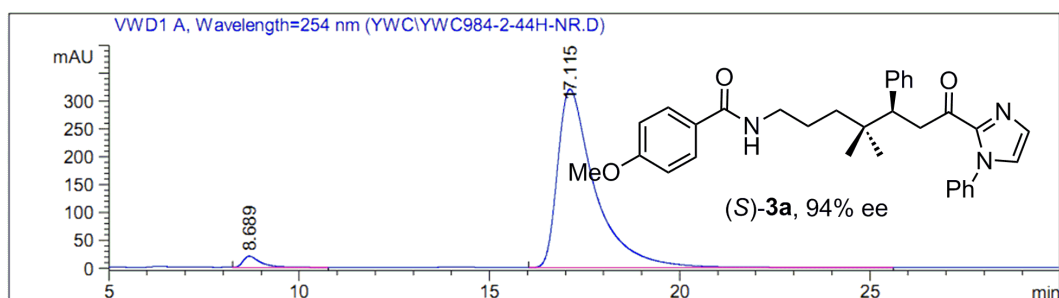
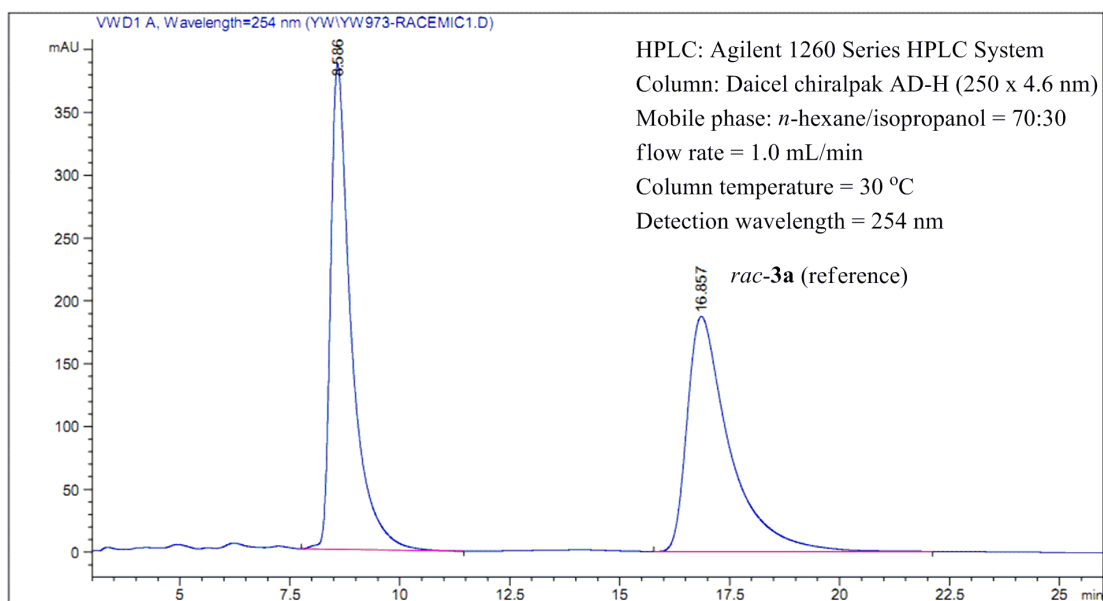


Figure S2. Alternative conjugate radical addition mechanism.

6. Chiral HPLC Chromatography

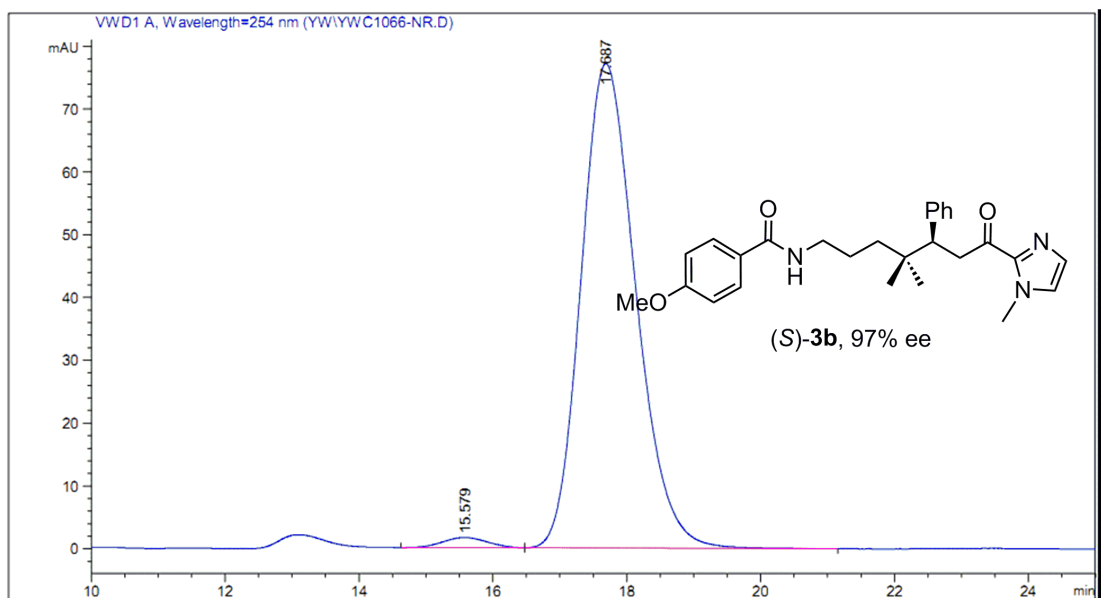
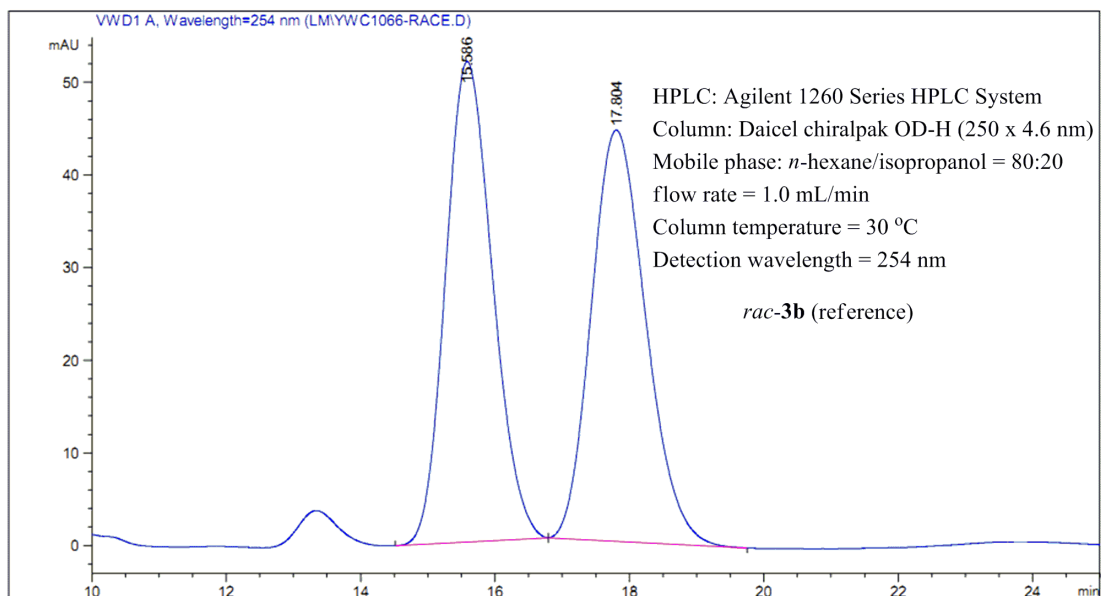
6.1 Determination of Enantioselectivities of the Asymmetric Photoredox Reactions

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.



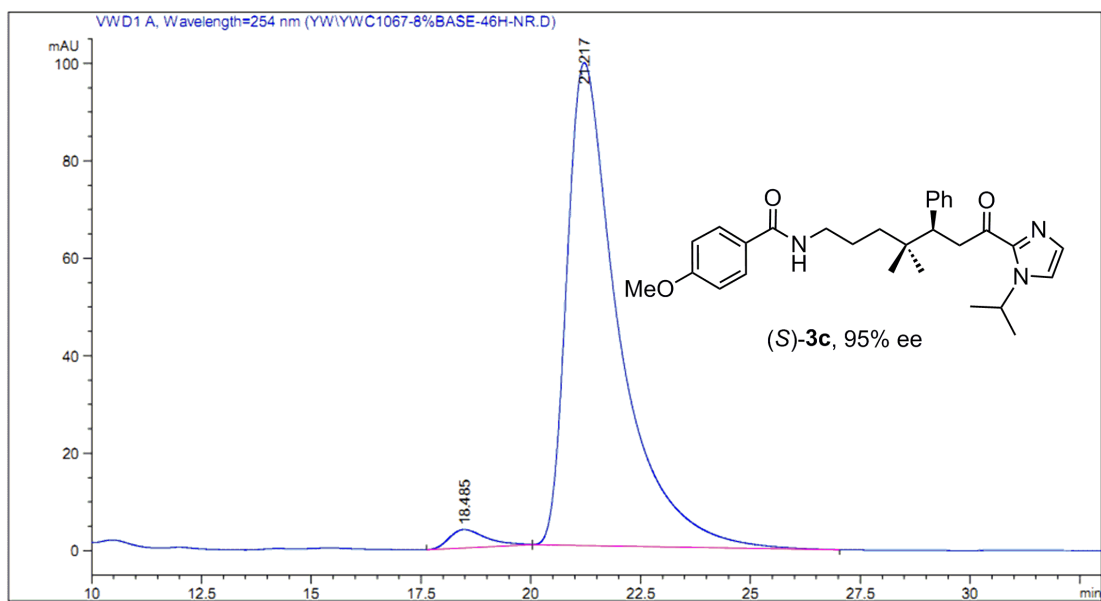
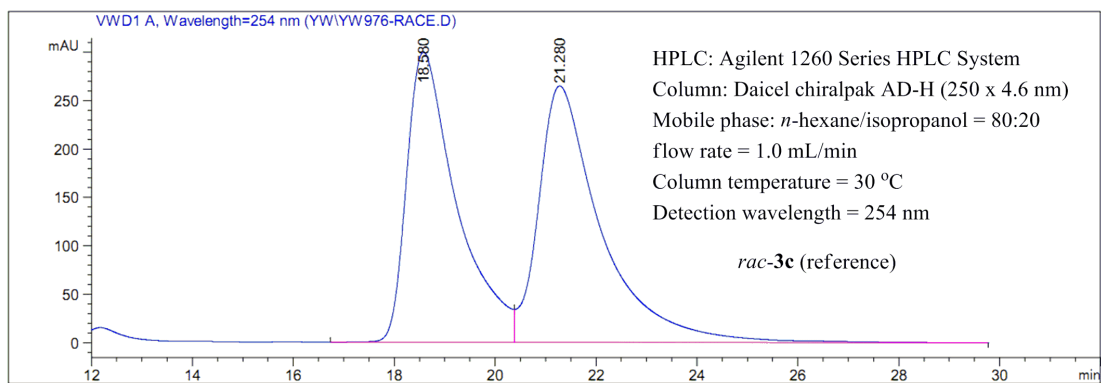
#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.689 VV	0.4863	670.84912	20.25961	2.9690
2	17.115 BB	0.9977	2.19243e4	320.64441	97.0310

Figure S3. HPLC trace for the racemic reference *rac*-**3a** and non-racemic product (*S*)-**3a**.



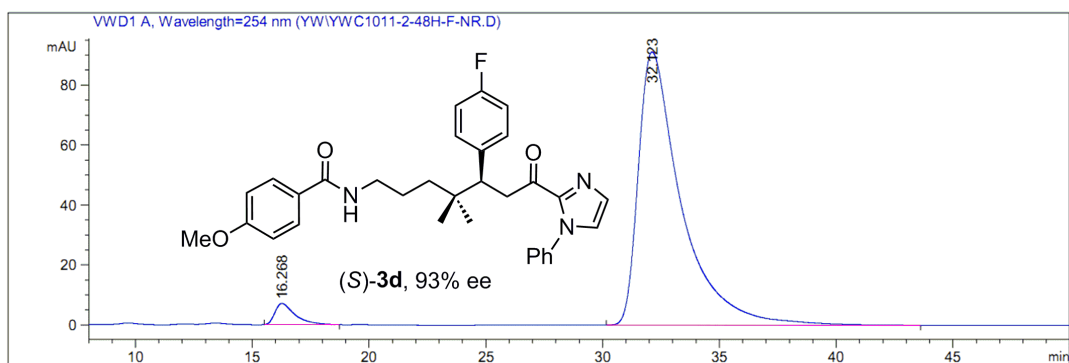
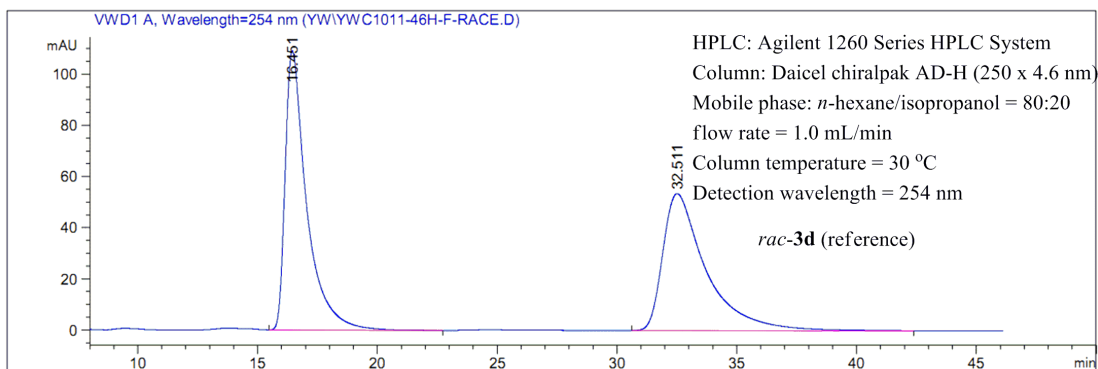
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.579	BV	0.6982	75.51305	1.62482	1.6919
2	17.687	VB	0.8834	4387.57422	77.15984	98.3081

Figure S4. HPLC trace for the racemic reference *rac*-**3b** and non-racemic product (*S*)-**3b**.



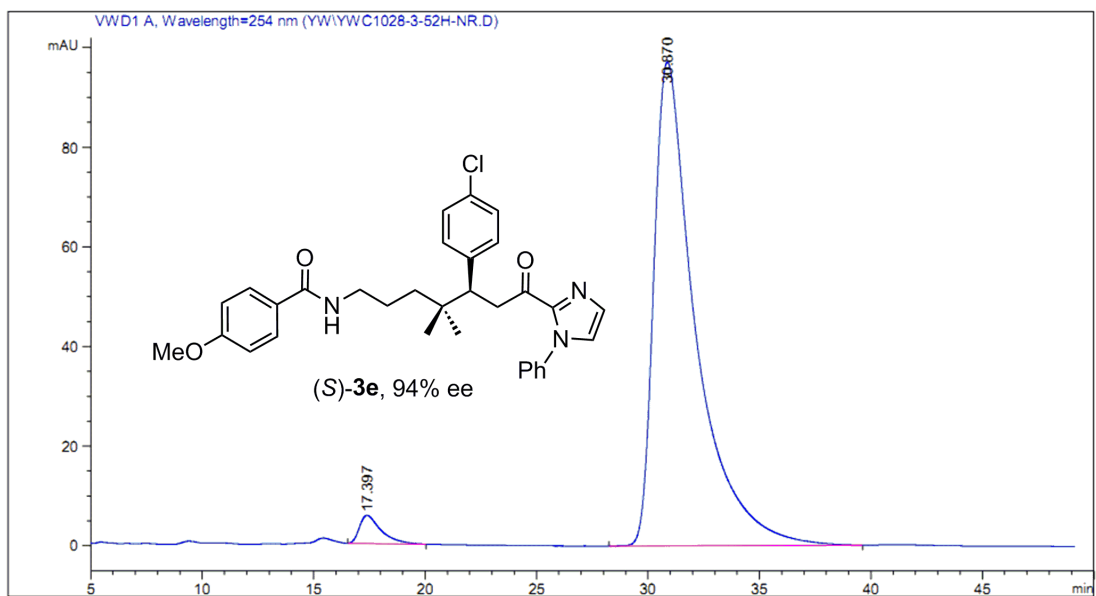
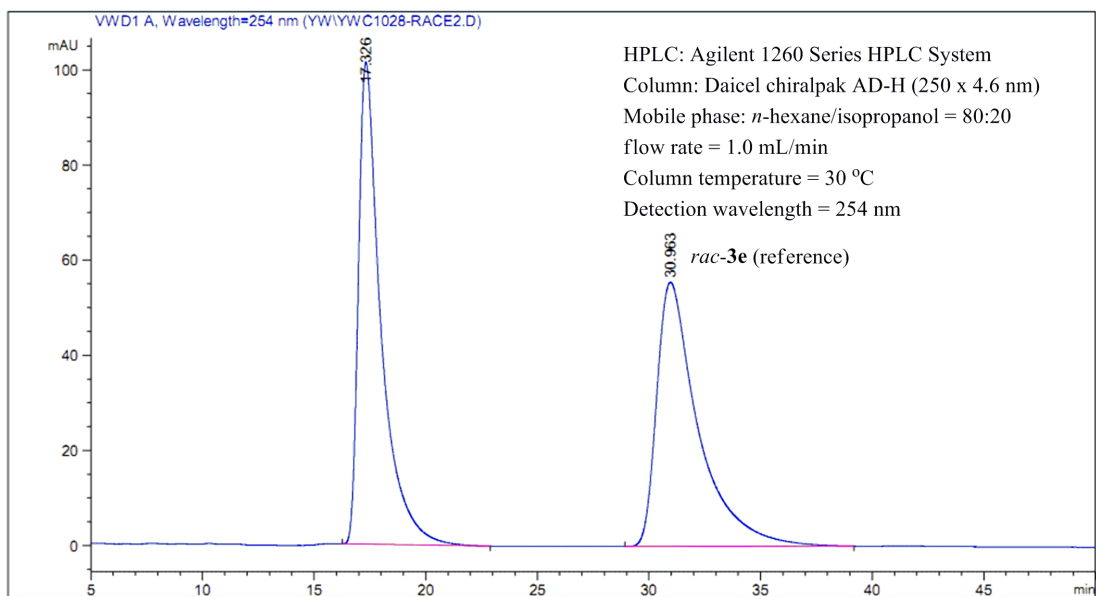
#	[min]	[min]	[mAU*s]	[mAU]	%
1	18.485 BB	0.7927	219.39349	3.77713	2.6311
2	21.217 BB	1.1941	8119.06934	99.07664	97.3689

Figure S5. HPLC trace for the racemic reference *rac*-**3c** and non-racemic product (*S*)-**3c**.



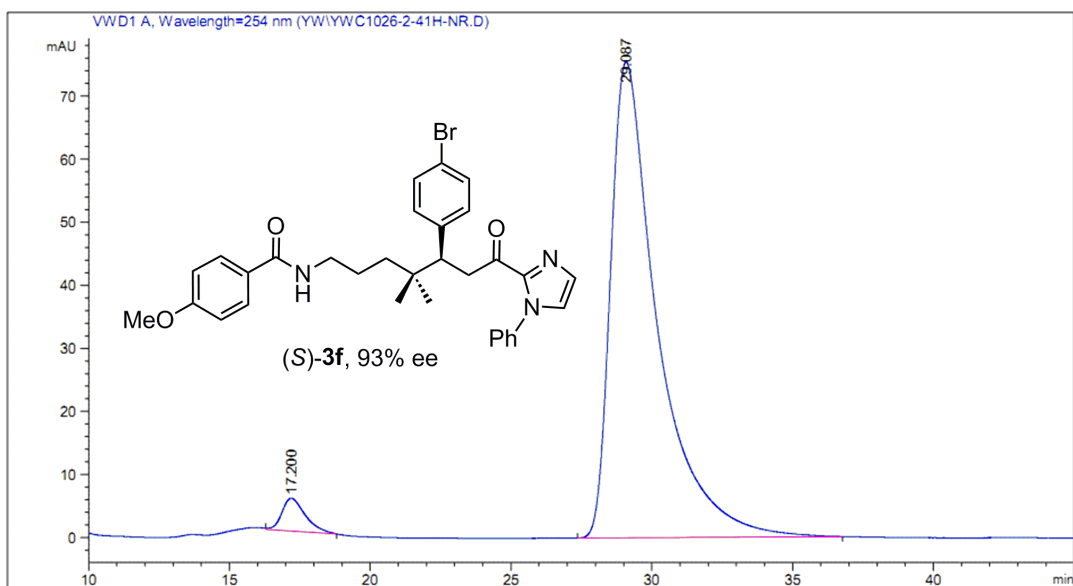
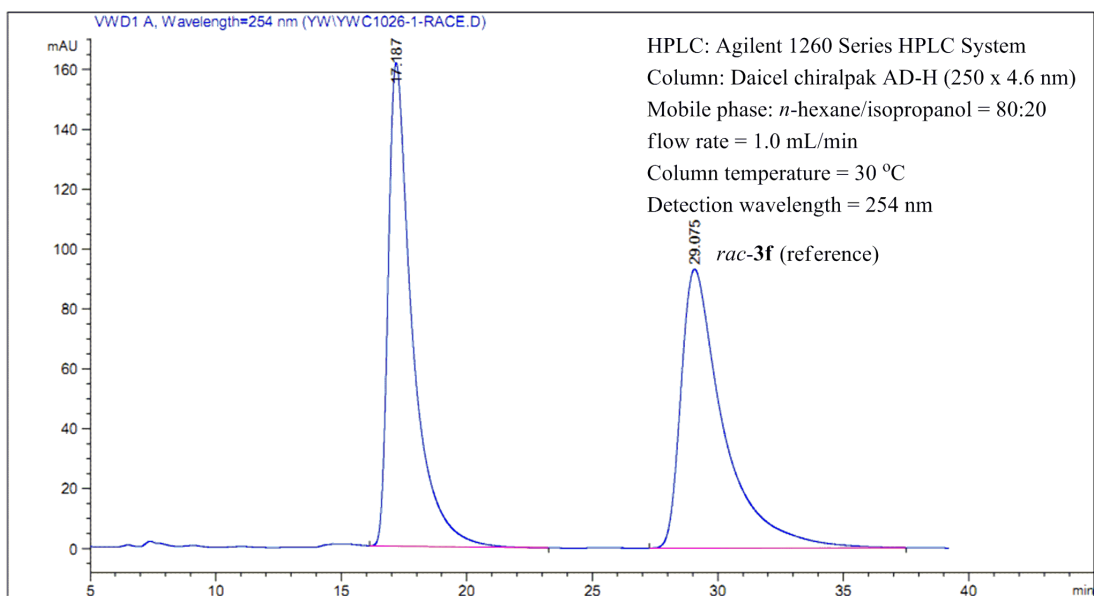
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	16.268	MM R	1.0033	428.05768	7.11085	3.5471
2	32.123	BB	1.8584	1.16398e4	91.11303	96.4529

Figure S6. HPLC trace for the racemic reference *rac*-**3d** and non-racemic product (*S*)-**3d**.



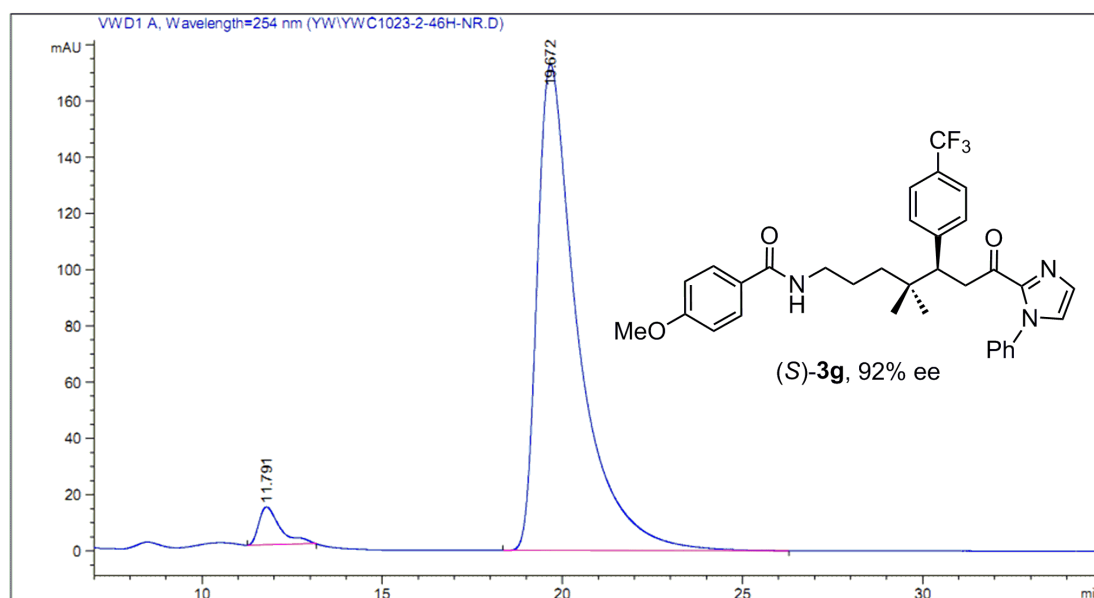
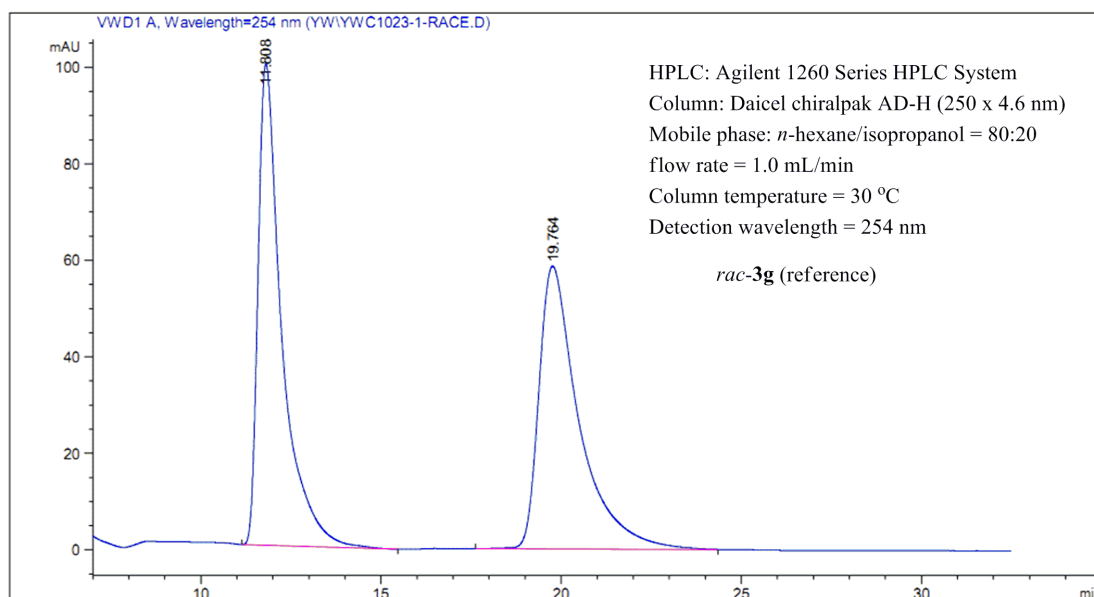
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	17.397	MM R	1.1266	383.56973	5.67450	2.9541
2	30.870	BB	1.8813	1.26008e4	97.14664	97.0459

Figure S7. HPLC trace for the racemic reference *rac*-**3e** and non-racemic product (*S*)-**3e**.



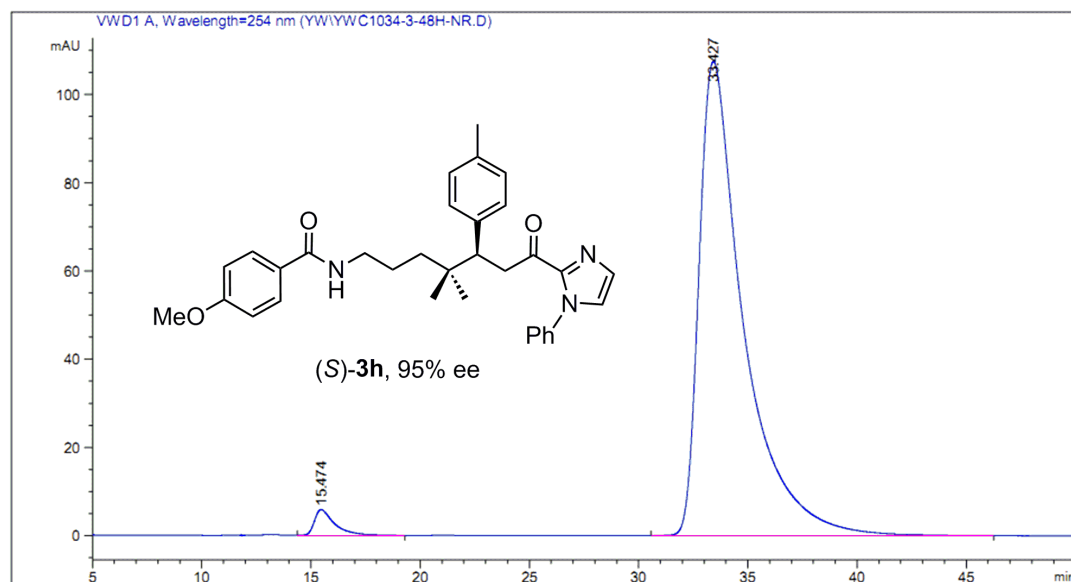
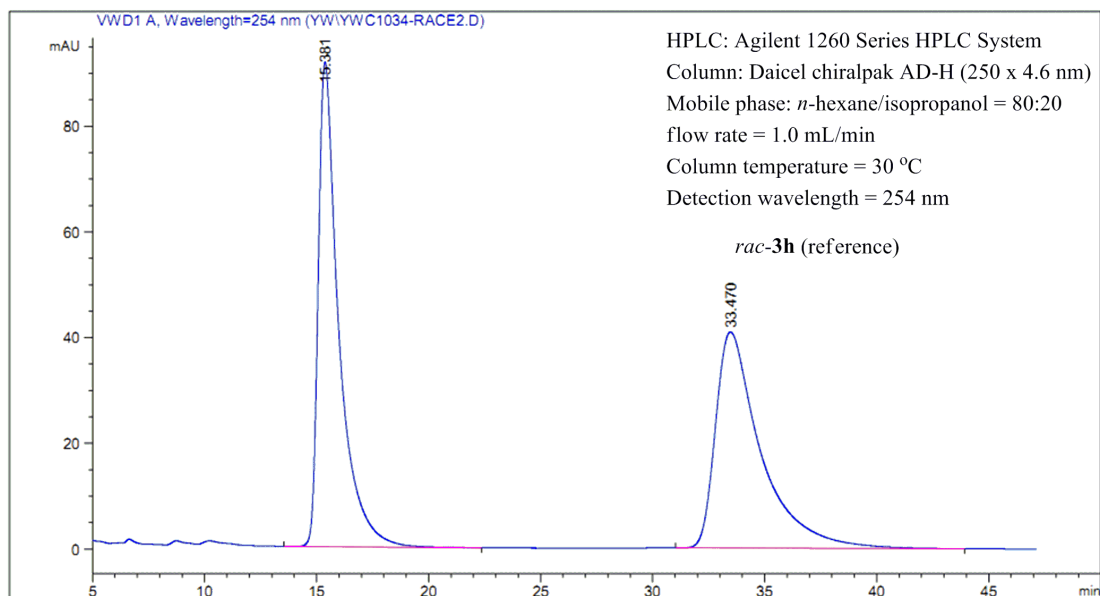
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.200	MM R	0.9621	301.16608	5.21706	3.3532
2	29.087	BB	1.6720	8680.26660	75.40808	96.6468

Figure S8. HPLC trace for the racemic reference *rac*-**3f** and non-racemic product (*S*)-**3f**.



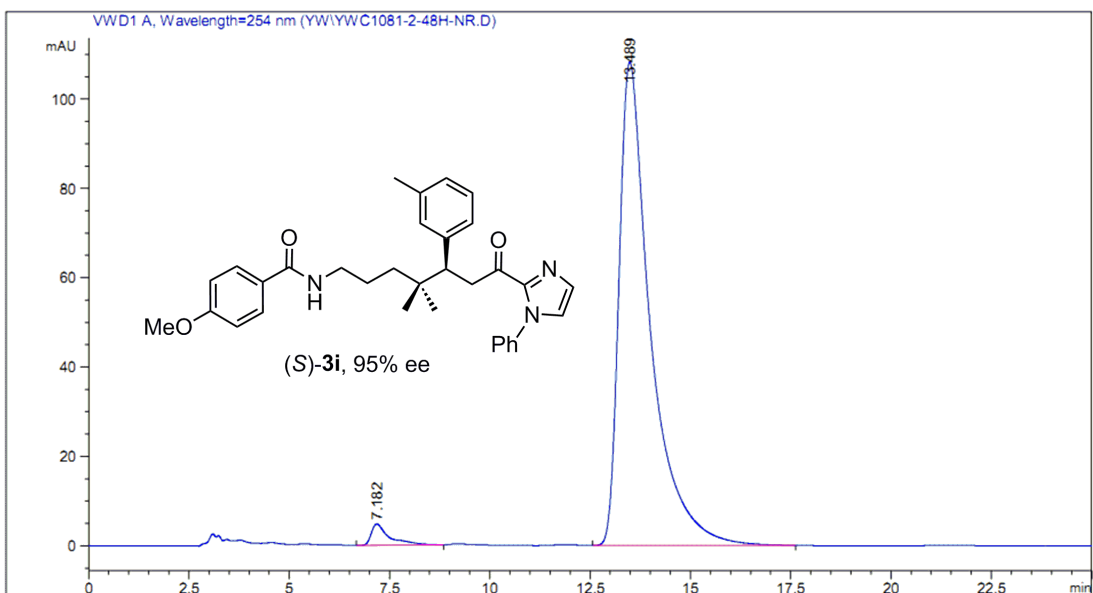
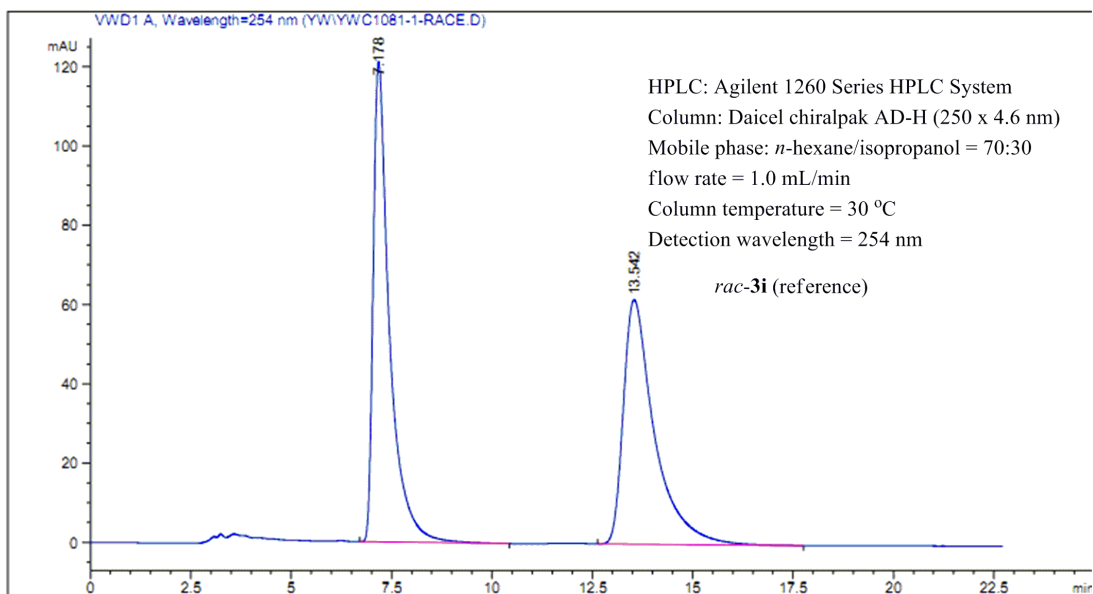
#	[min]	[min]	[mAU*s]	[mAU]	%
1	11.791	MM R	0.6883	556.81146	13.48351
2	19.672	BB	1.1402	1.36025e4	172.84161

Figure S9. HPLC trace for the racemic reference *rac*-**3g** and non-racemic product (*S*)-**3g**.



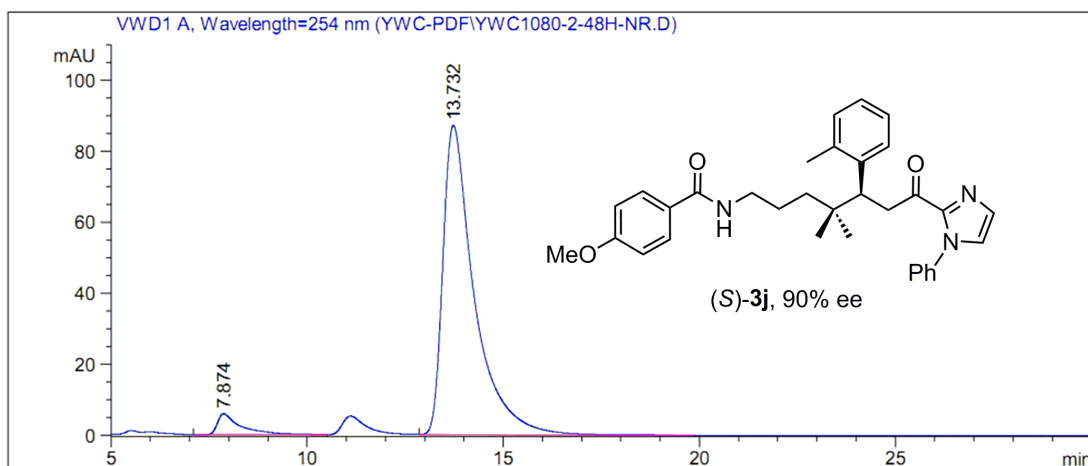
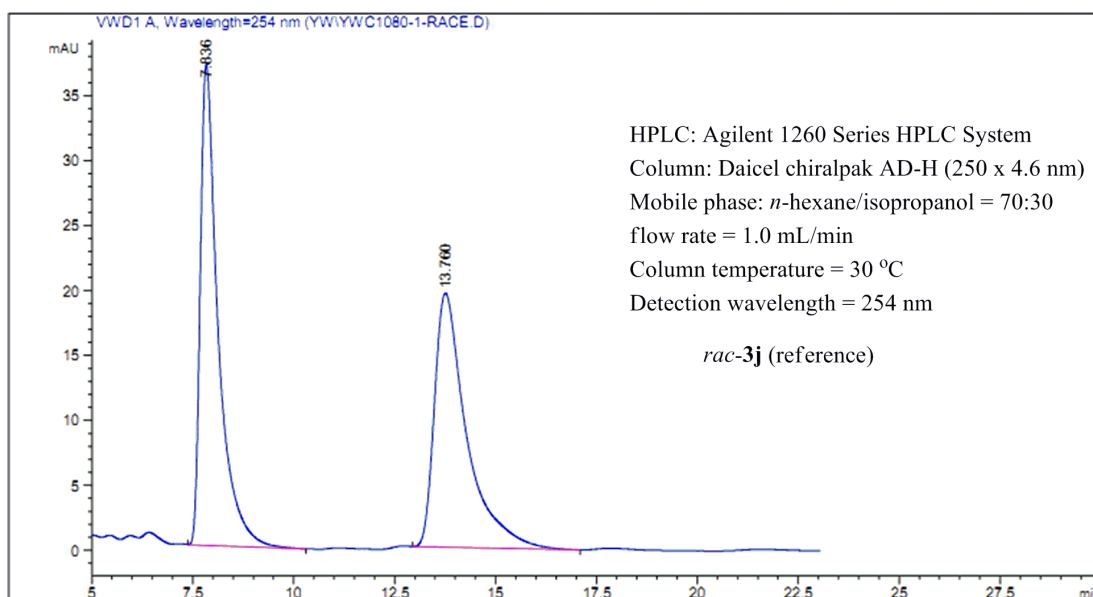
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.474	VB	0.9382	380.67908	5.85798	2.4462
2	33.427	BB	2.0350	1.51813e4	107.53974	97.5538

Figure S10. HPLC trace for the racemic reference *rac*-**3h** and non-racemic product (*S*)-**3h**.



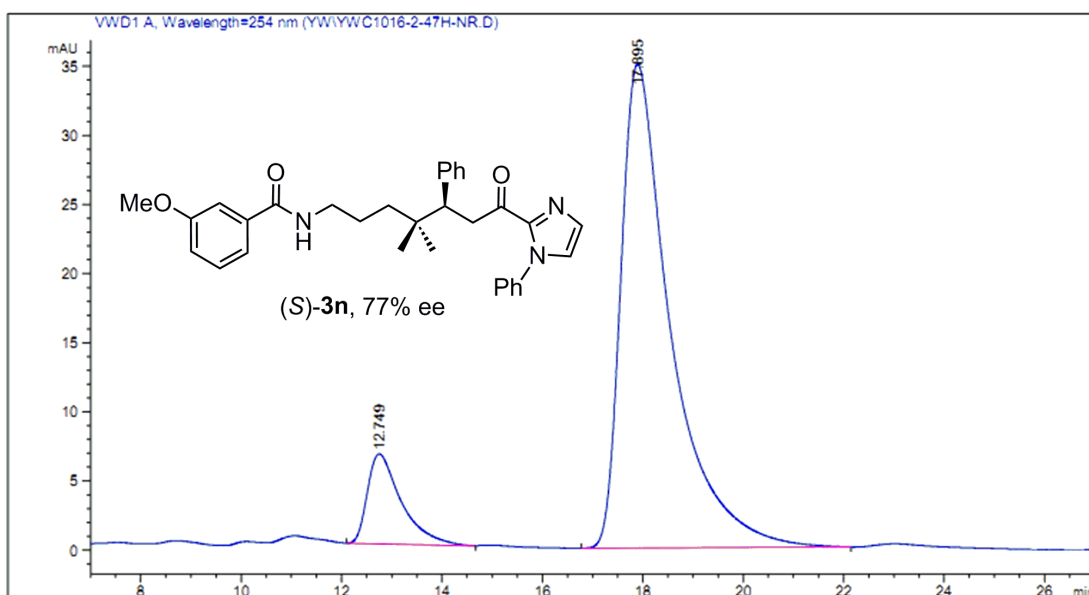
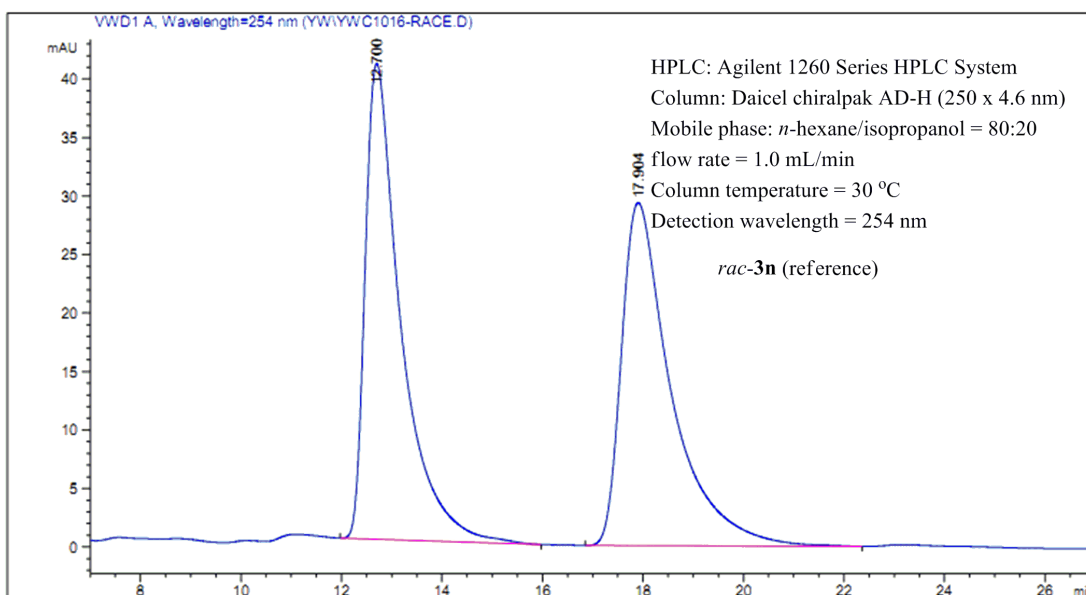
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.182	MM R	0.5283	150.90977	4.76061	2.5095
2	13.489	BB	0.7889	5862.70508	108.24775	97.4905

Figure S11. HPLC trace for the racemic reference *rac*-**3i** and non-racemic product (*S*)-**3i**.



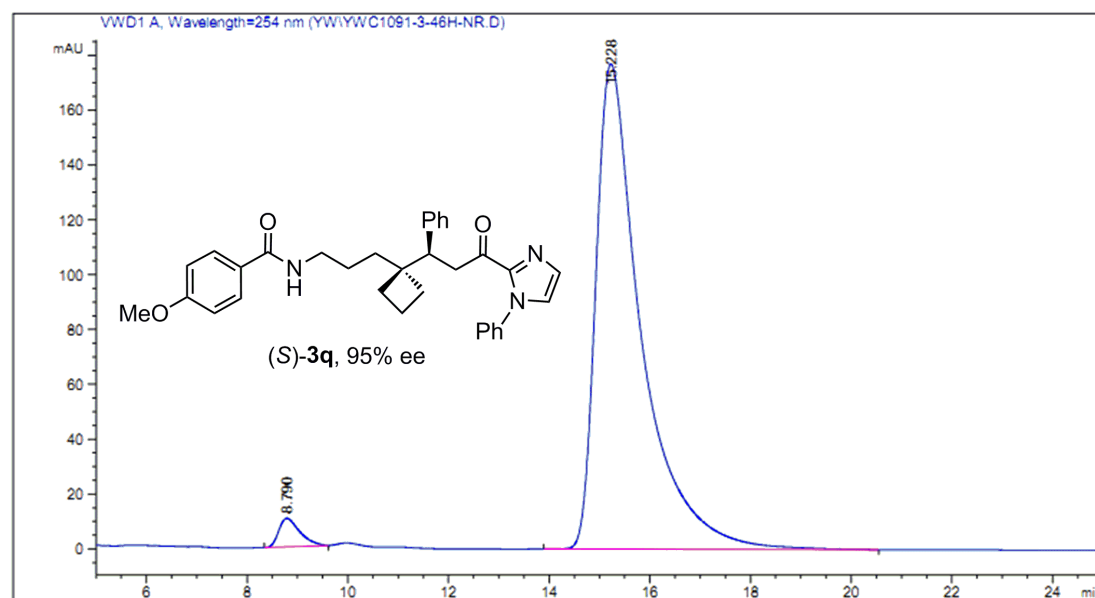
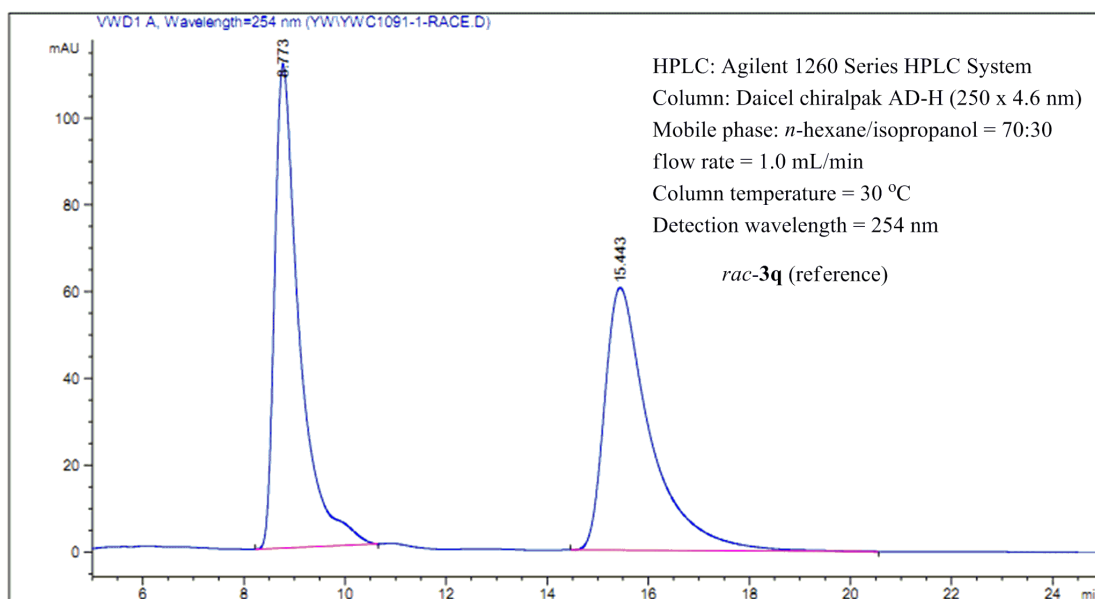
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.874	BB	0.5774	244.55865	5.87756	4.8001
2	13.732	VB	0.8133	4850.27734	87.15472	95.1999

Figure S12. HPLC trace for the racemic reference *rac*-**3j** and non-racemic product (*S*)-**3j**.



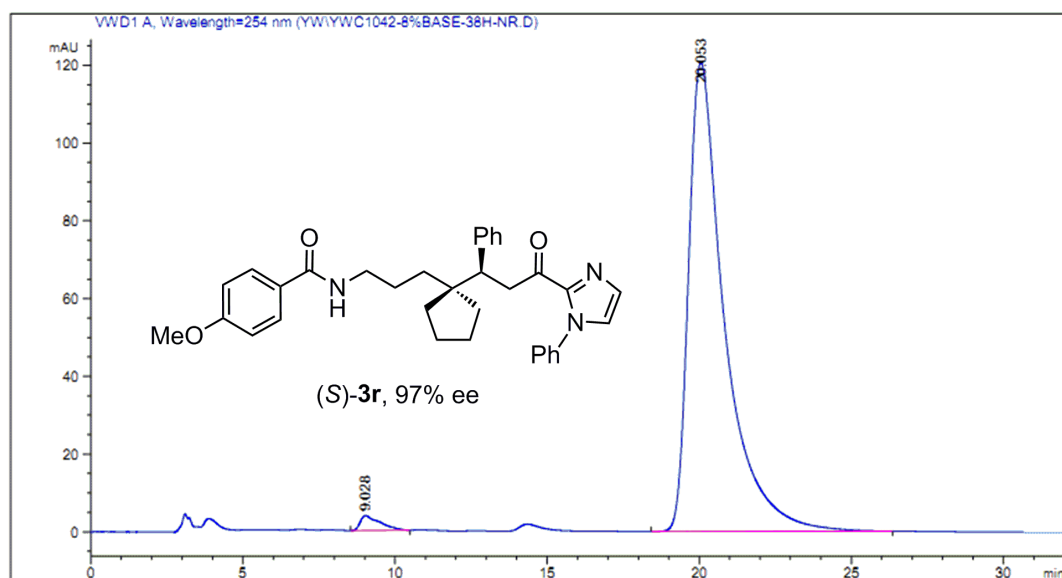
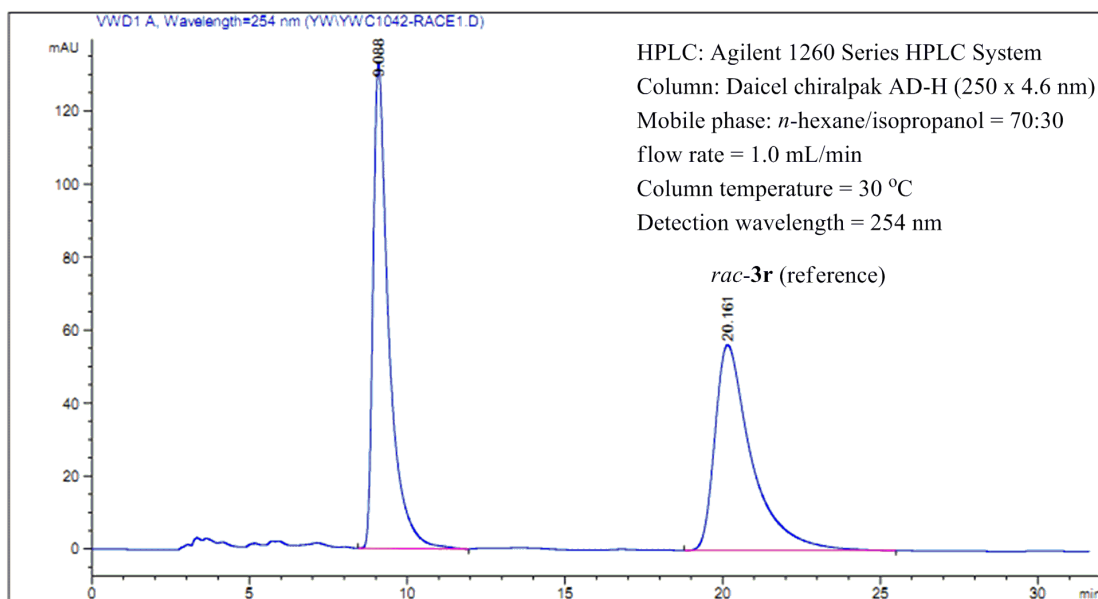
#	[min]	[min]	[mAU*s]	[mAU]	%	
1	12.749	BB	0.6752	304.22223	6.51022	11.2320
2	17.895	BB	0.9920	2404.32104	35.01975	88.7680

Figure S13. HPLC trace for the racemic reference *rac*-**3n** and non-racemic product (*S*)-**3n**.



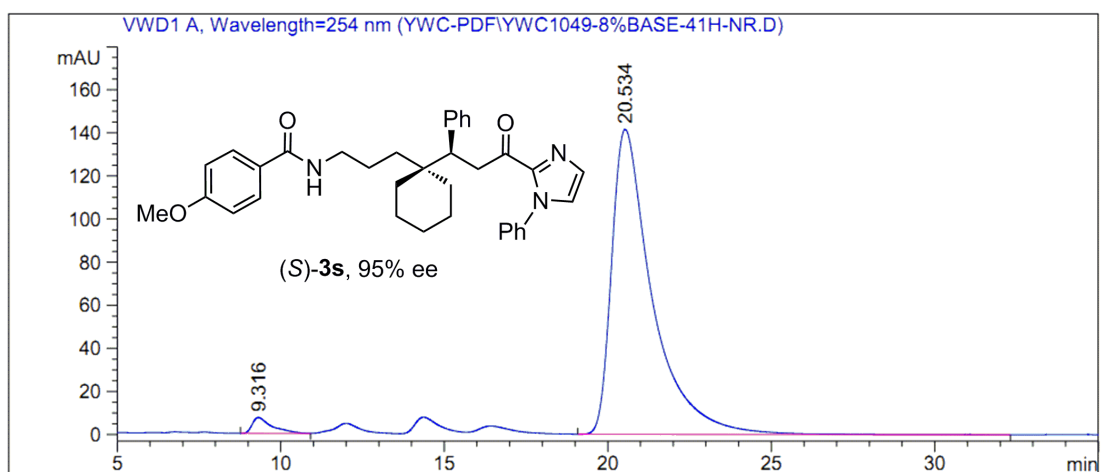
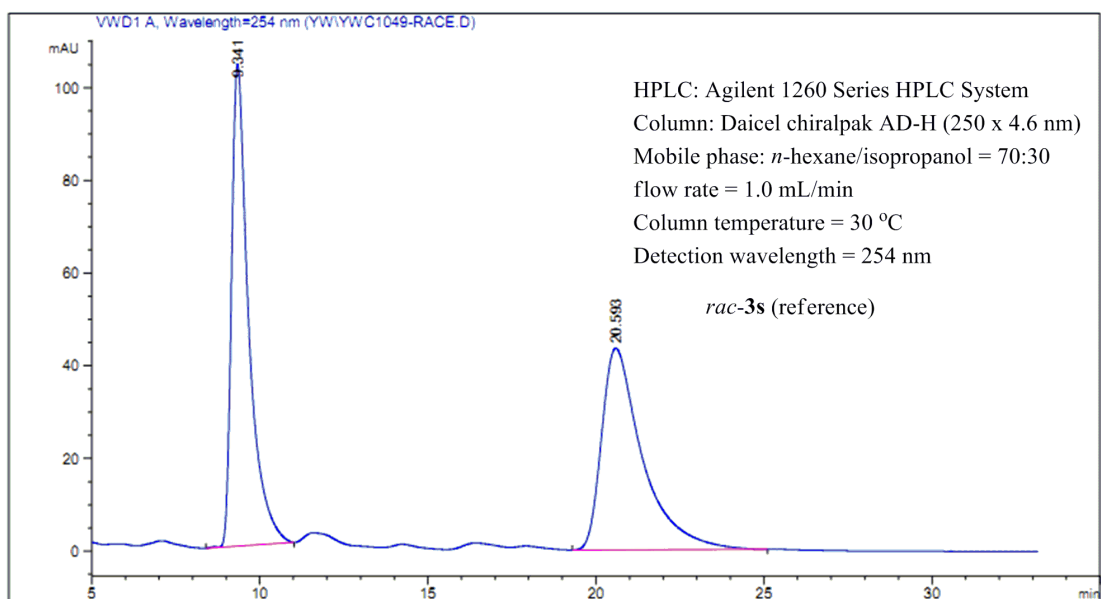
#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.790	BB	0.4349	300.78799	10.41629
2	15.228	BB	0.9103	1.10480e4	176.97964
					97.3496

Figure S14. HPLC trace for the racemic reference *rac*-**3q** and non-racemic product (*S*)-**3q**.



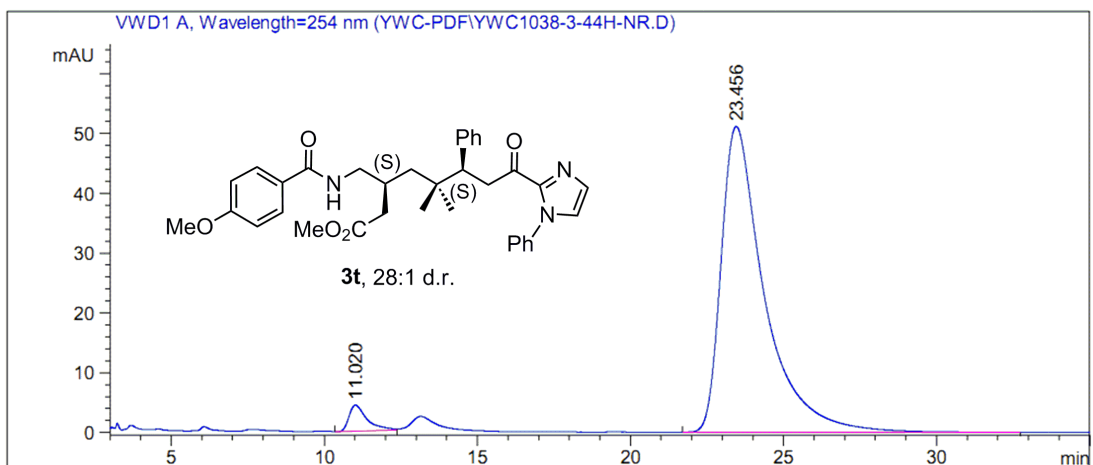
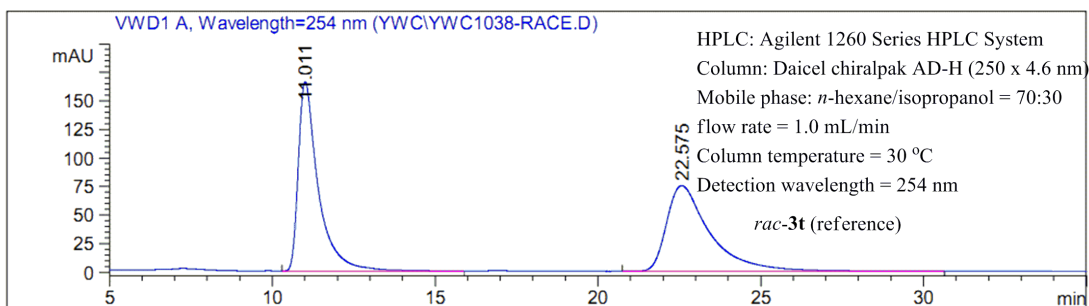
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.028	BB	0.6064	172.87802	3.87568	1.7196
2	20.053	BB	1.1952	9880.34277	120.67262	98.2804

Figure S15. HPLC trace for the racemic reference *rac*-**3r** and non-racemic product (*S*)-**3r**.



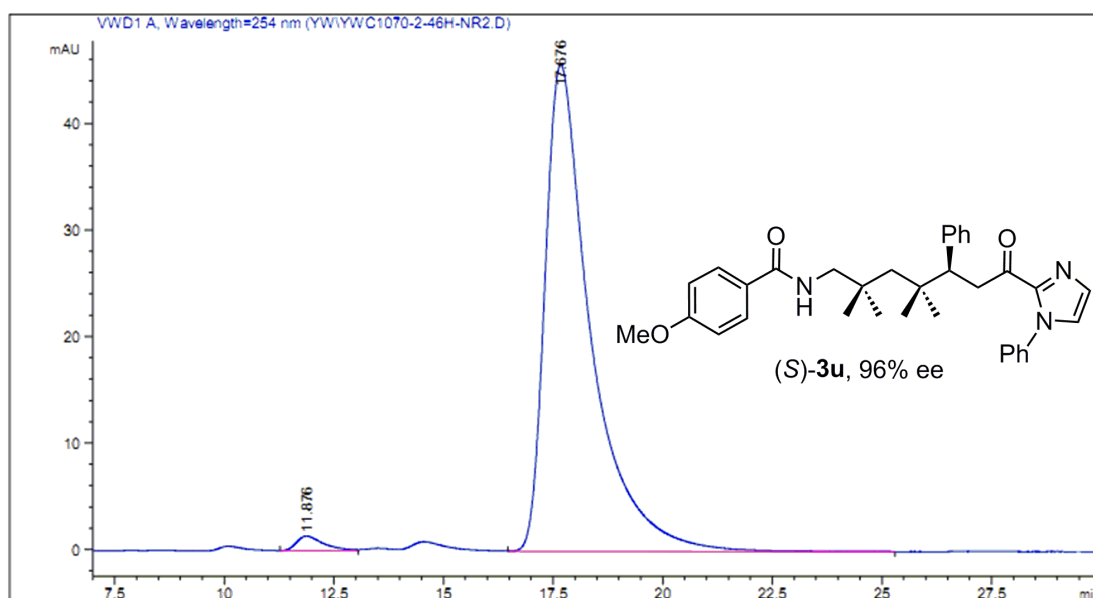
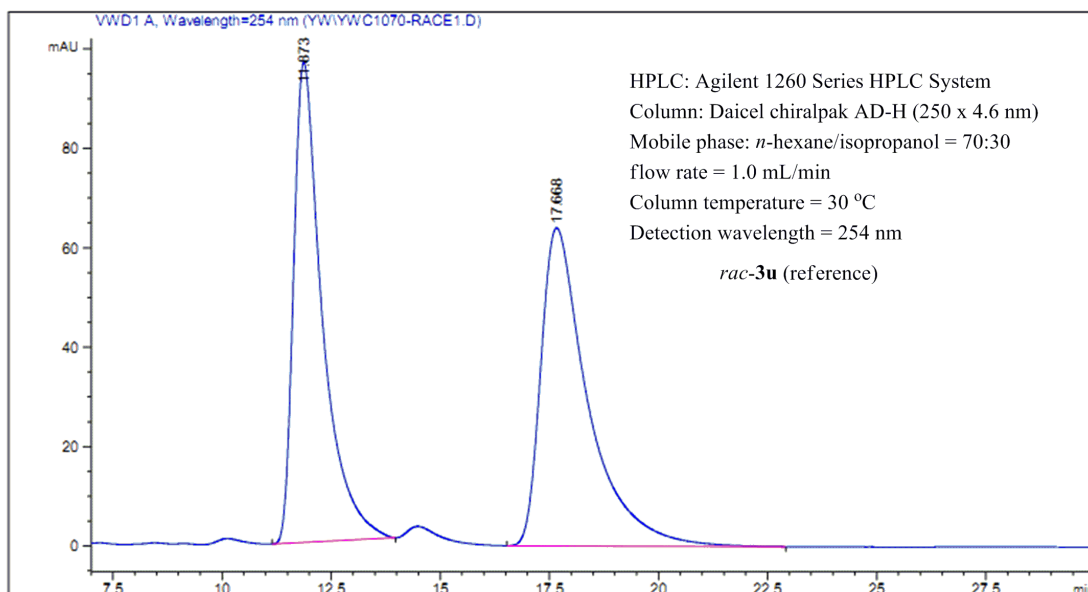
#	[min]	[min]	[mAU*s]	[mAU]	%
1	9.316 BV	0.6119	314.59412	7.40113	2.5113
2	20.534 BB	1.2628	1.22125e4	141.52296	97.4887

Figure S16. HPLC trace for the racemic reference *rac*-**3s** and non-racemic product (*S*)-**3s**.



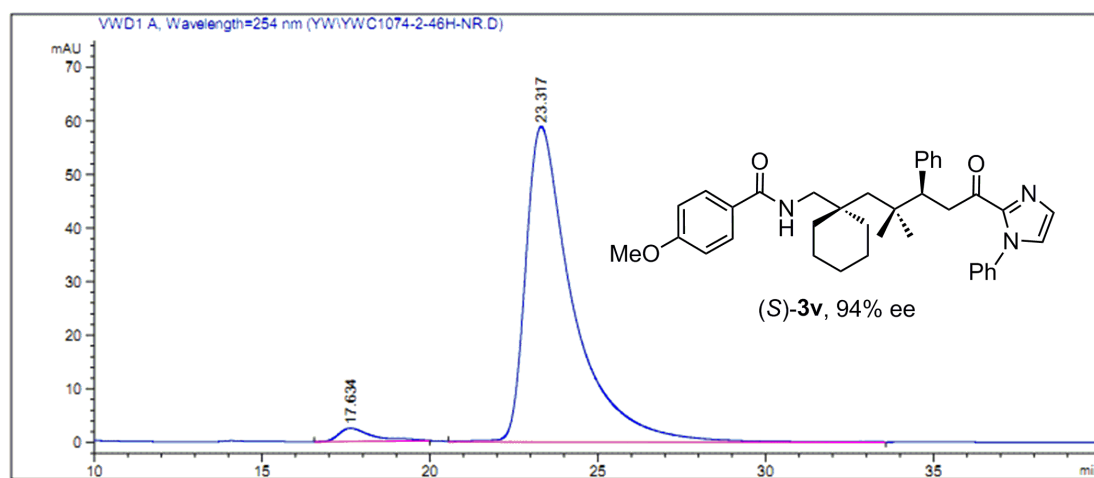
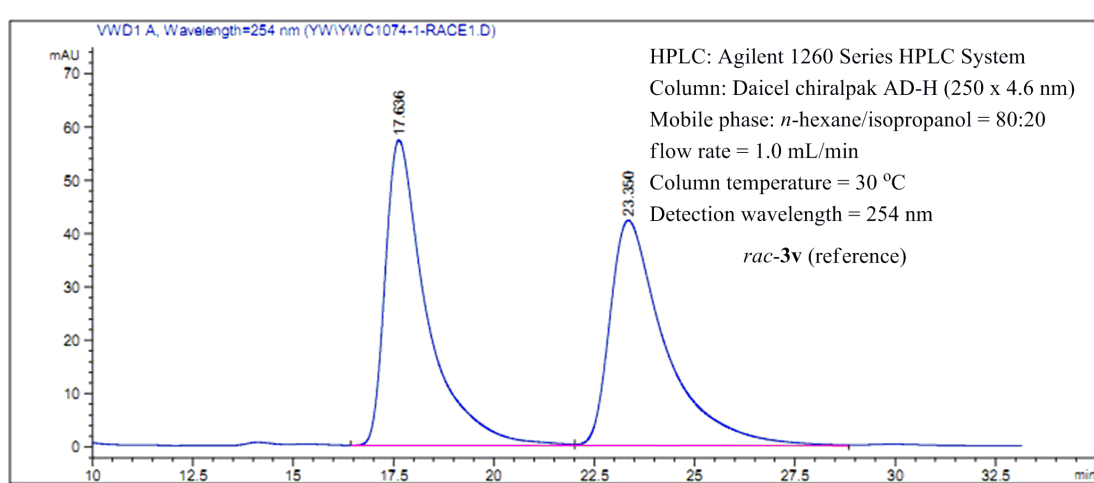
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.020	MM R	0.6870	180.85101	4.38758	3.4828
2	23.456	BB	1.4321	5011.89844	51.10966	96.5172

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



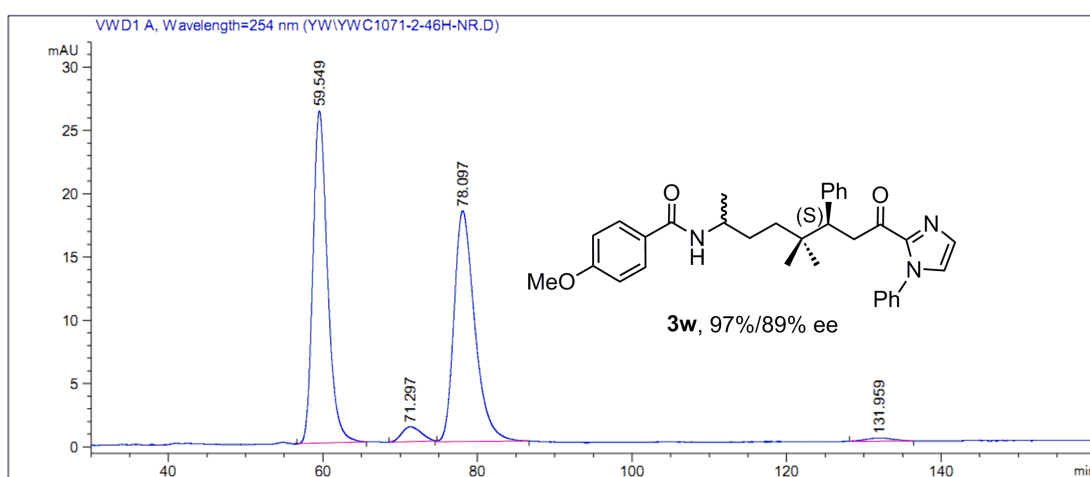
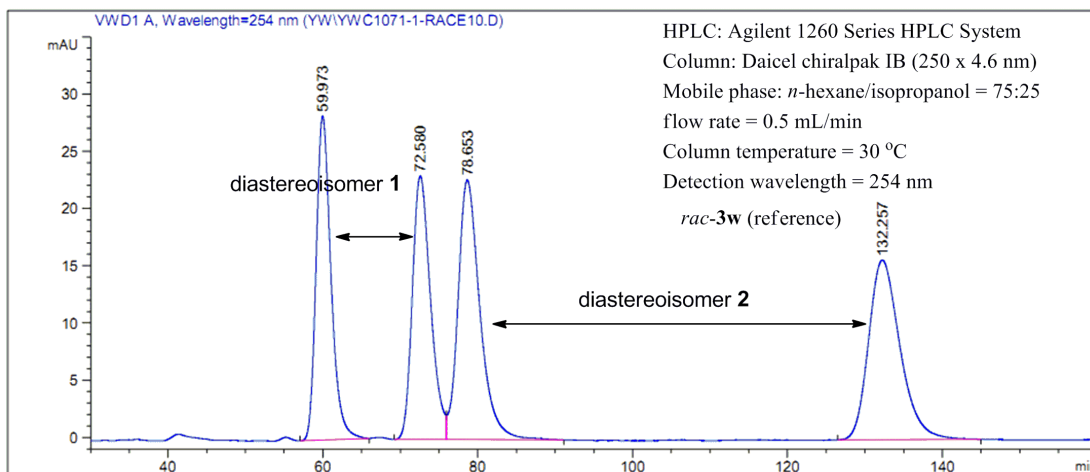
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.876	BV	0.6345	60.05131	1.37247	1.7808
2	17.676	BB	1.0584	3312.15430	45.65294	98.2192

Figure S18. HPLC trace for the racemic reference *rac*-**3u** and non-racemic product (*S*)-**3u**.



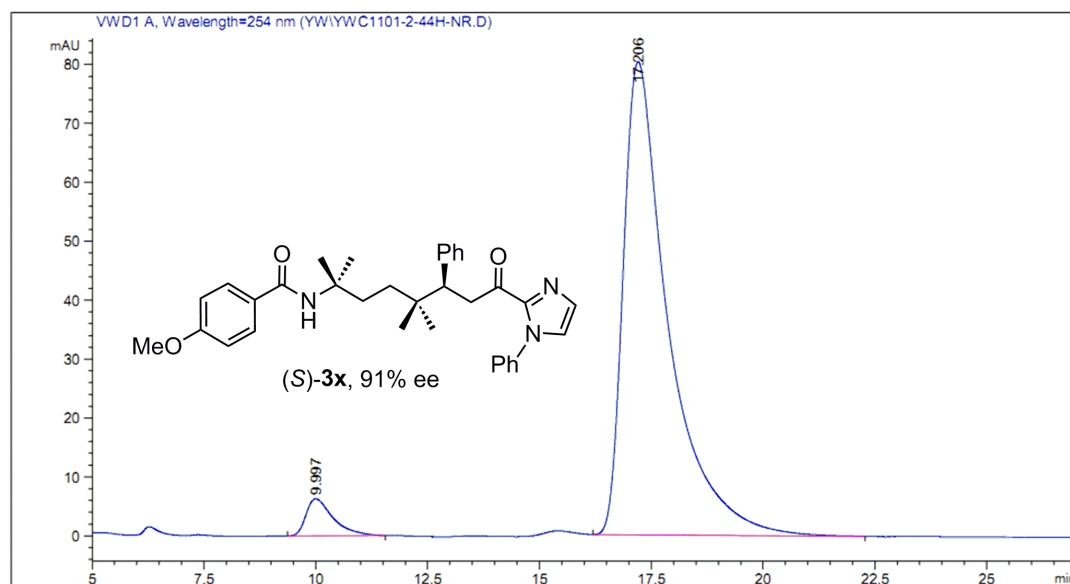
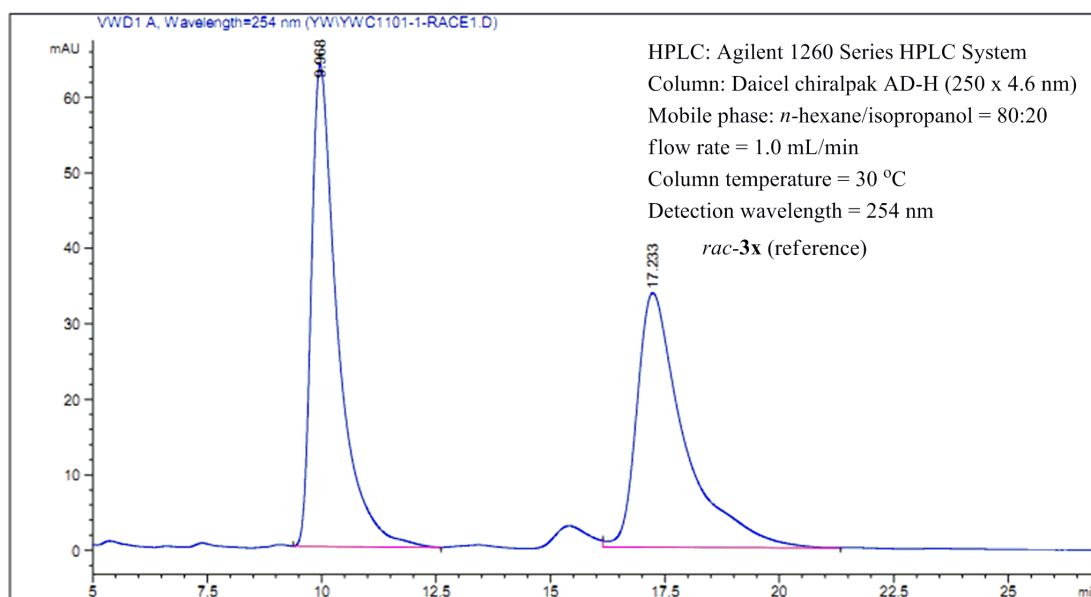
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.634	MM R	1.1755	174.99446	2.48121	2.9430
2	23.317	VB	1.4161	5771.17383	58.84816	97.0570

Figure S19. HPLC trace for the racemic reference *rac-3v* and non-racemic product (*S*)-**3v**.



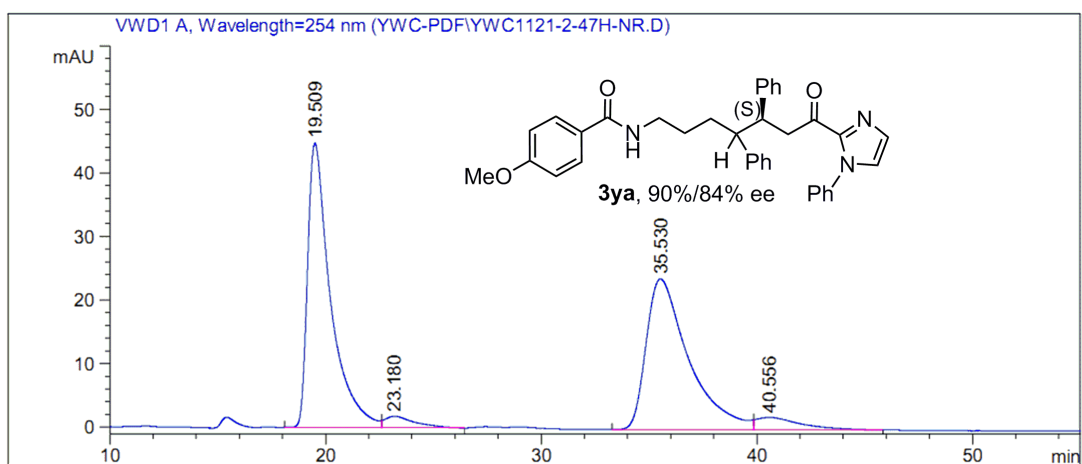
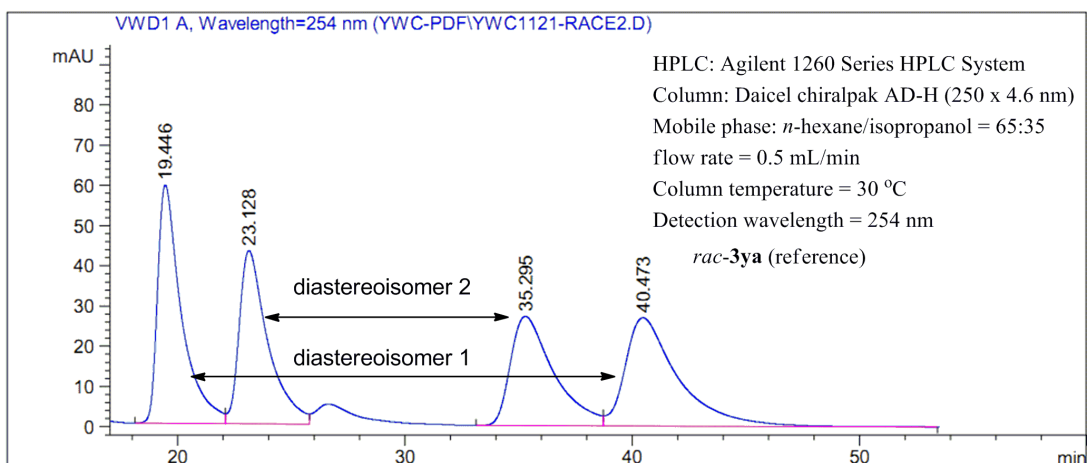
#	[min]		[min]	[mAU*s]	[mAU]	%
1	59.549	BB	1.9931	3442.56982	26.26591	48.4834
2	71.297	MM R	2.8644	201.97798	1.17520	2.8446
3	78.097	VB R	2.7367	3396.46216	18.23825	47.8340
4	131.959	BB	2.8695	59.50320	2.43285e-1	0.8380

Figure S20. HPLC trace for the racemic reference *rac*-**3w** and non-racemic product (*S*)-**3w**.



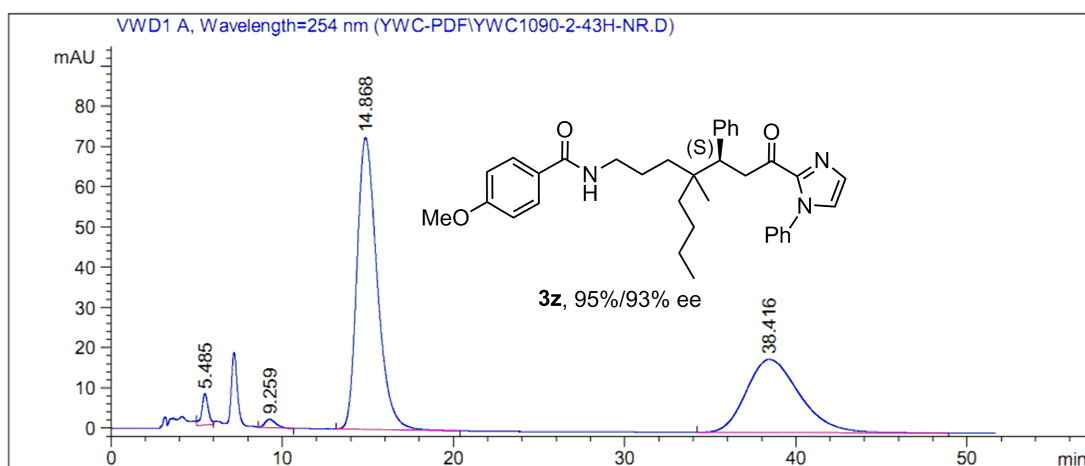
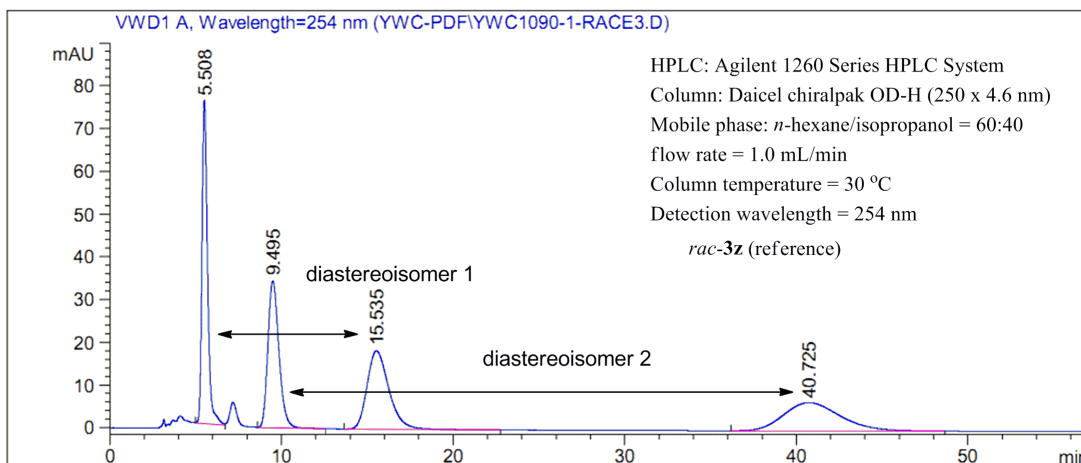
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.997	BB	0.6151	265.21799	6.29996	4.5219
2	17.206	BB	1.0086	5599.95947	80.30403	95.4781

Figure S21. HPLC trace for the racemic reference *rac*-**3x** and non-racemic product (*S*)-**3x**.



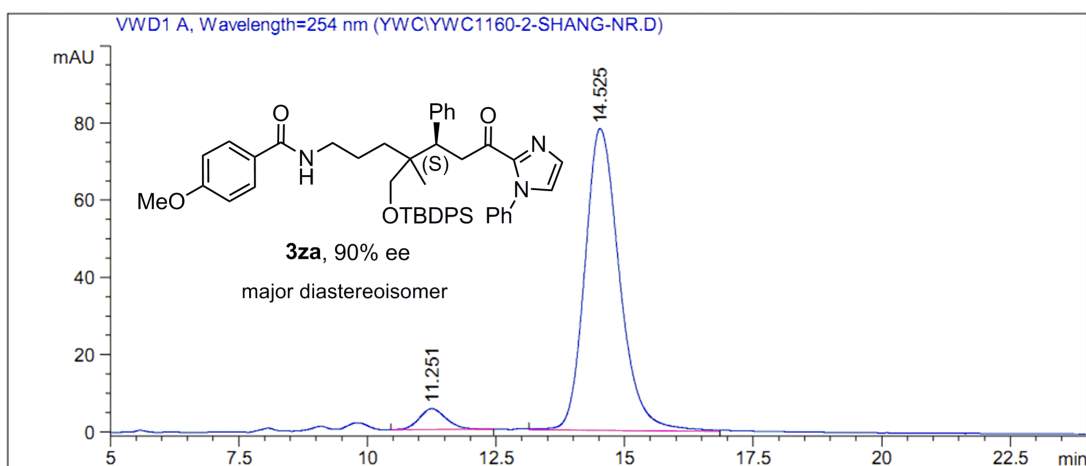
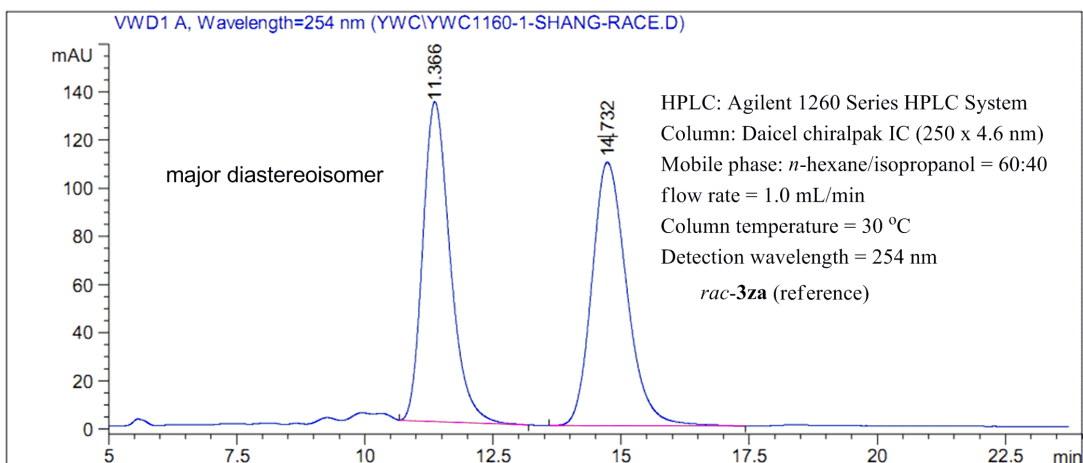
#	[min]		[min]	[mAU*s]	[mAU]	%	
1	19.509	MF	R	1.2320	3307.59717	44.74732	47.1093
2	23.180	FM	R	1.5888	173.83766	1.82354	2.4759
3	35.530	MF	R	2.2877	3258.50635	23.73907	46.4101
4	40.556	FM	R	2.3901	281.16705	1.96068	4.0046

Figure S22. HPLC trace for the racemic reference *rac*-**3ya** and non-racemic product (*S*)-**3ya**.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.485	VV	0.3909	203.90804	7.85421	2.0053
2	9.259	BB	0.6854	91.22704	2.07311	0.8972
3	14.868	BB	1.2512	5936.68506	72.51285	58.3830
4	38.416	BB	3.0337	3936.70508	18.18415	38.7146

Figure S23. HPLC trace for the racemic reference *rac*-**3z** and non-racemic product (*S*)-**3z**.

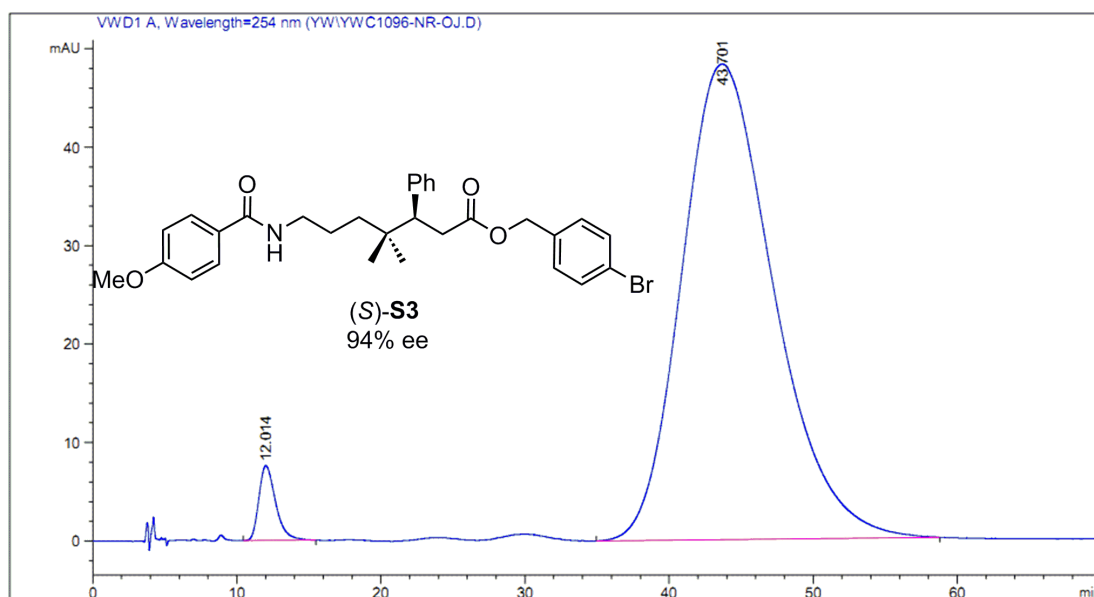
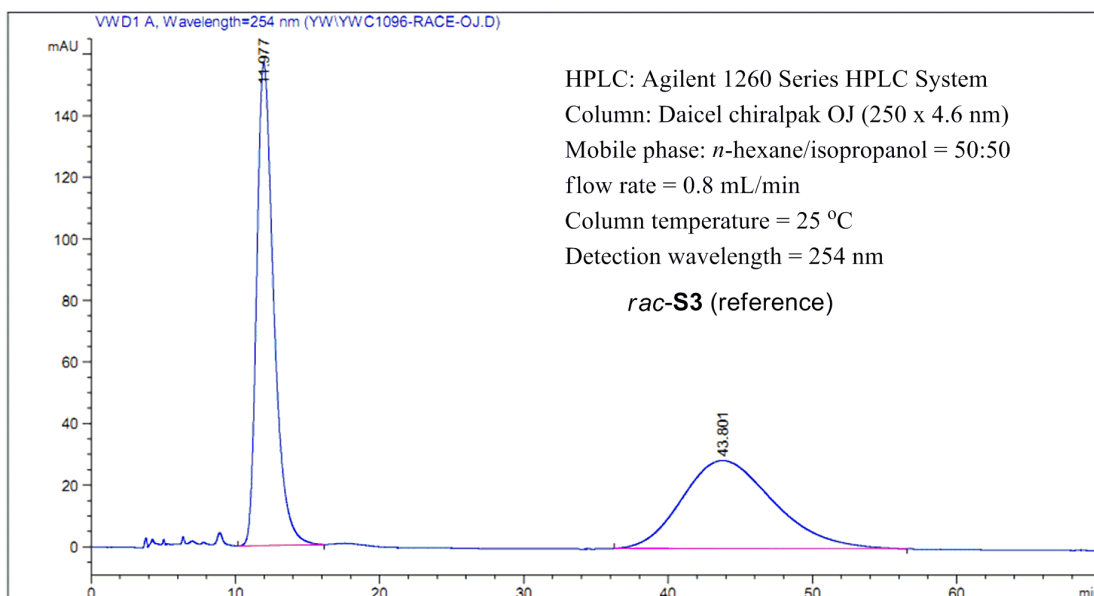


#	[min]	[min]	[mAU*s]	[mAU]	%
1	11.251	MM R	0.6102	197.84486	5.1234
2	14.525	VV	0.7193	3663.77026	94.8766

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.



#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.014	BB	1.2017	619.96820	7.61600	2.8147
2	43.701	BB	5.2416	2.14064e4	48.31013	97.1853

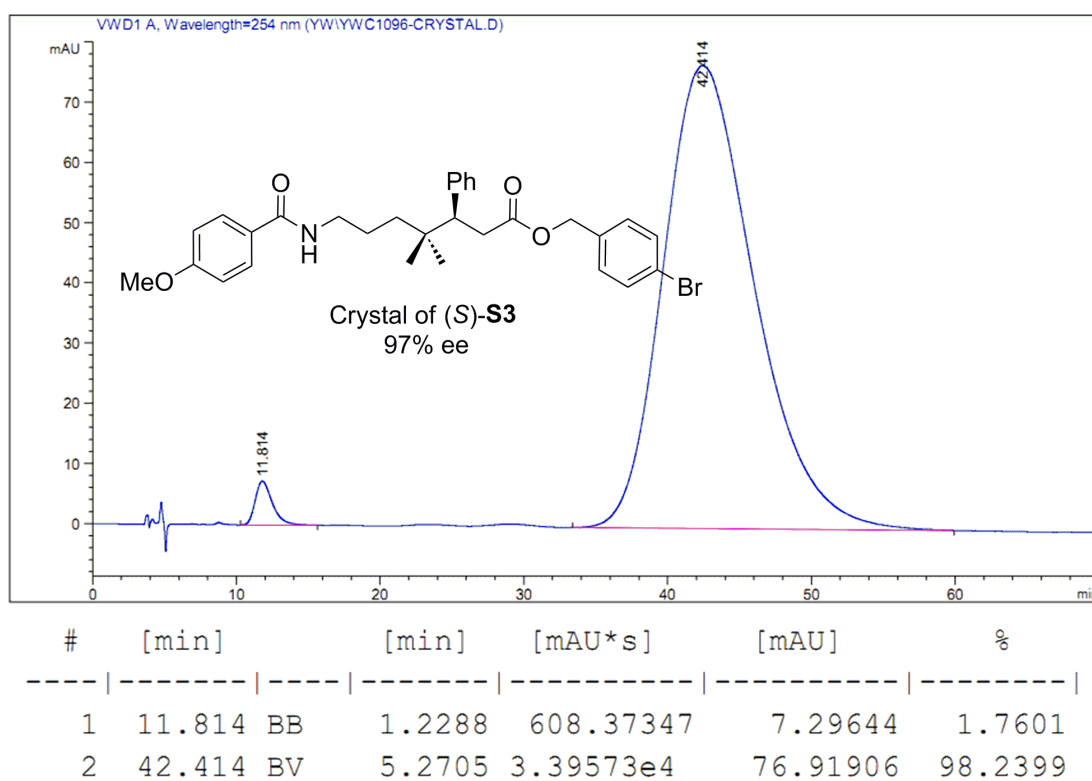


Figure S25. HPLC trace of *rac*-S3 (reference compound synthesized from *rac*-3a), (S)-S3 (synthesized from product 3a with 94% ee) and crystalline product (S)-S3.

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 SuperNowa system. X-ray single crystal diffractometer with Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) 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.

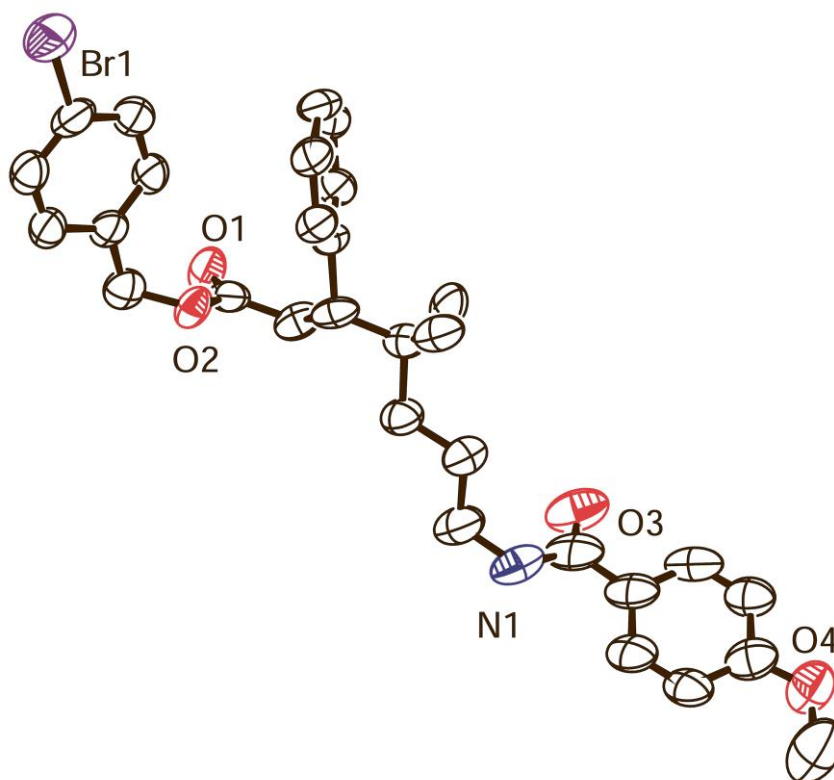


Figure S26. Crystal structure of (*S*)-**S3**. ORTEP drawing with 50% probability thermal ellipsoids.

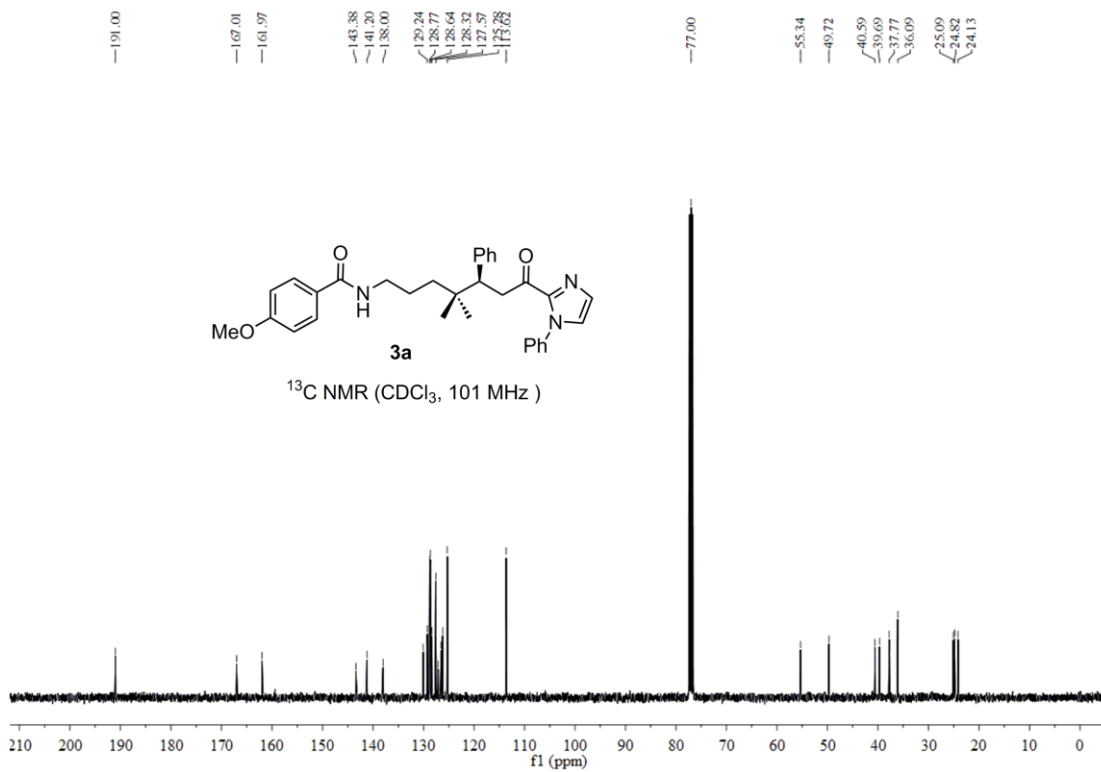
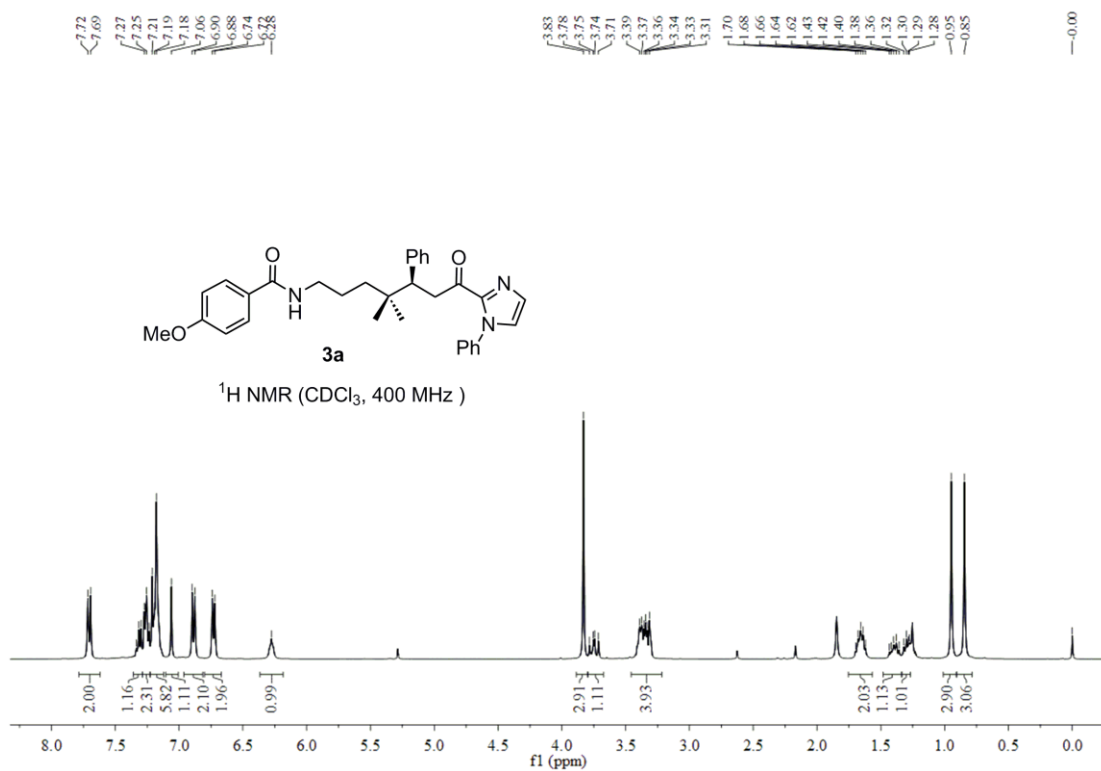
Table S2. Crystal data and structure refinement for (*S*)-**3S**.

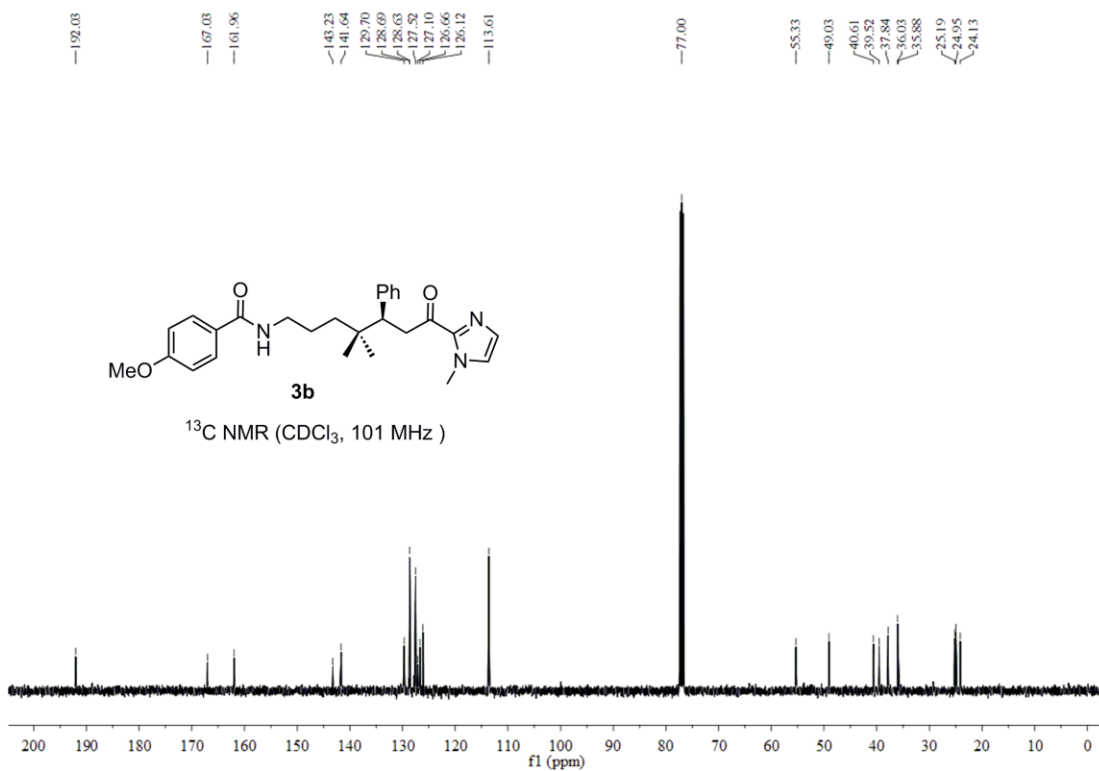
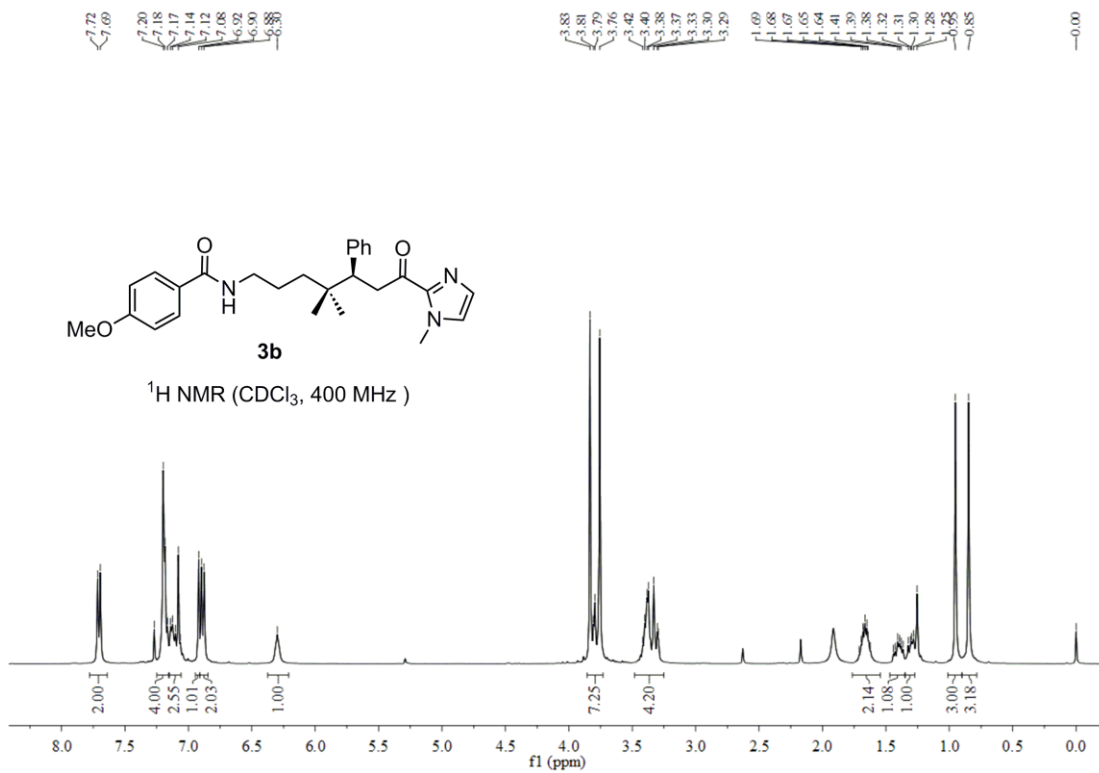
Identification code	<i>(S)</i> - 3S	
Empirical formula	C ₃₀ H ₃₃ BrNO ₄	
Formula weight	551.48	
Temperature	173(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 14.1916(9) Å	α = 90°.
	b = 5.8015(3) Å	β = 93.438(5)°.
	c = 16.4573(7) Å	γ = 90°.
Volume	1352.53(12) Å ³	
Z	2	
Density (calculated)	1.354 Mg/m ³	
Absorption coefficient	2.352 mm ⁻¹	
F(000)	574	
Crystal size	0.18 x 0.15 x 0.12 mm ³	
Theta range for data collection	4.00 to 61.16°.	
Index ranges	-16 ≤ h ≤ 15, -6 ≤ k ≤ 6, -18 ≤ l ≤ 17	
Reflections collected	8782	
Independent reflections	3917 [R(int) = 0.0576]	
Completeness to theta = 61.16°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7655 and 0.6768	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3917 / 1 / 326	
Goodness-of-fit on F ²	1.002	
Final R indices [I > 2σ(I)]	R1 = 0.0830, wR2 = 0.2551	
R indices (all data)	R1 = 0.1245, wR2 = 0.3480	
Absolute structure parameter	-0.04(7)	
Extinction coefficient	0.0025(13)	
Largest diff. peak and hole	0.589 and -1.119 e.Å ⁻³	

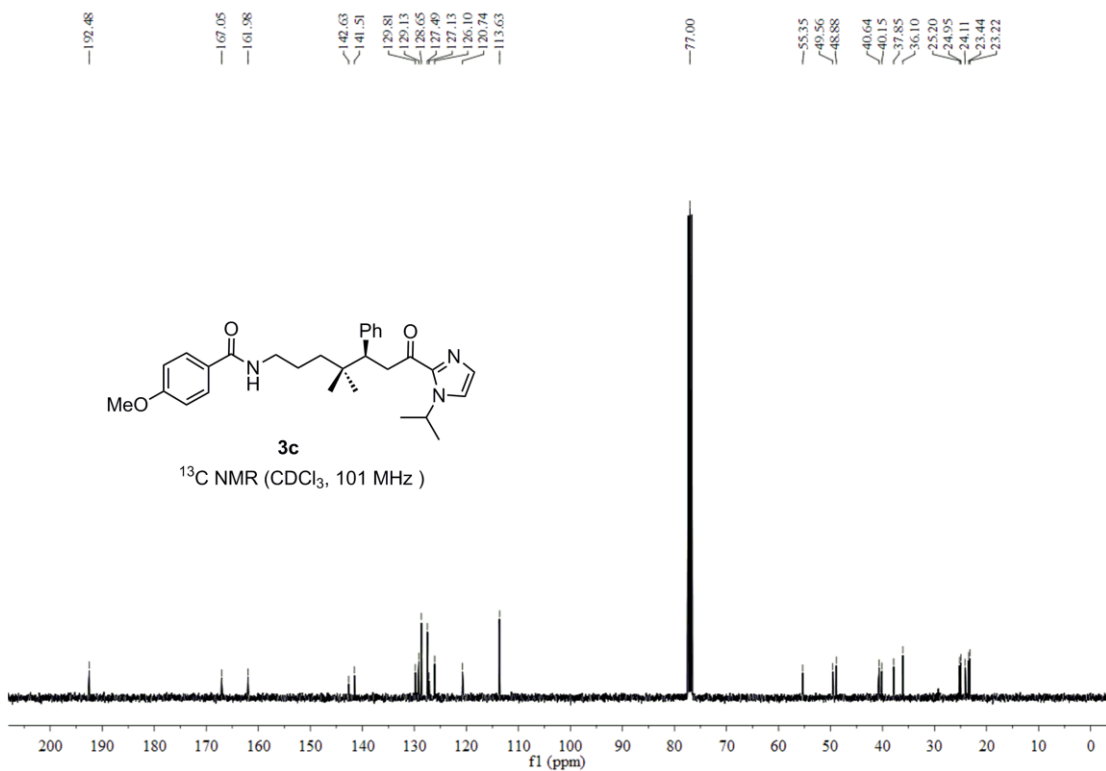
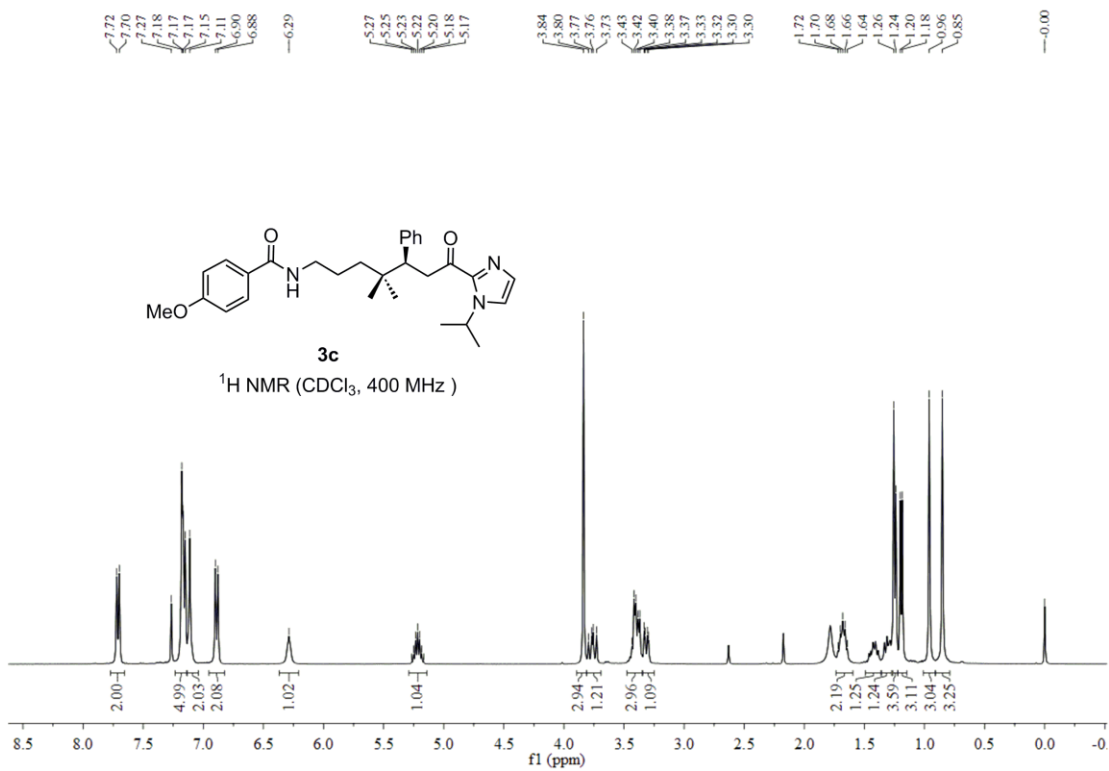
8. References

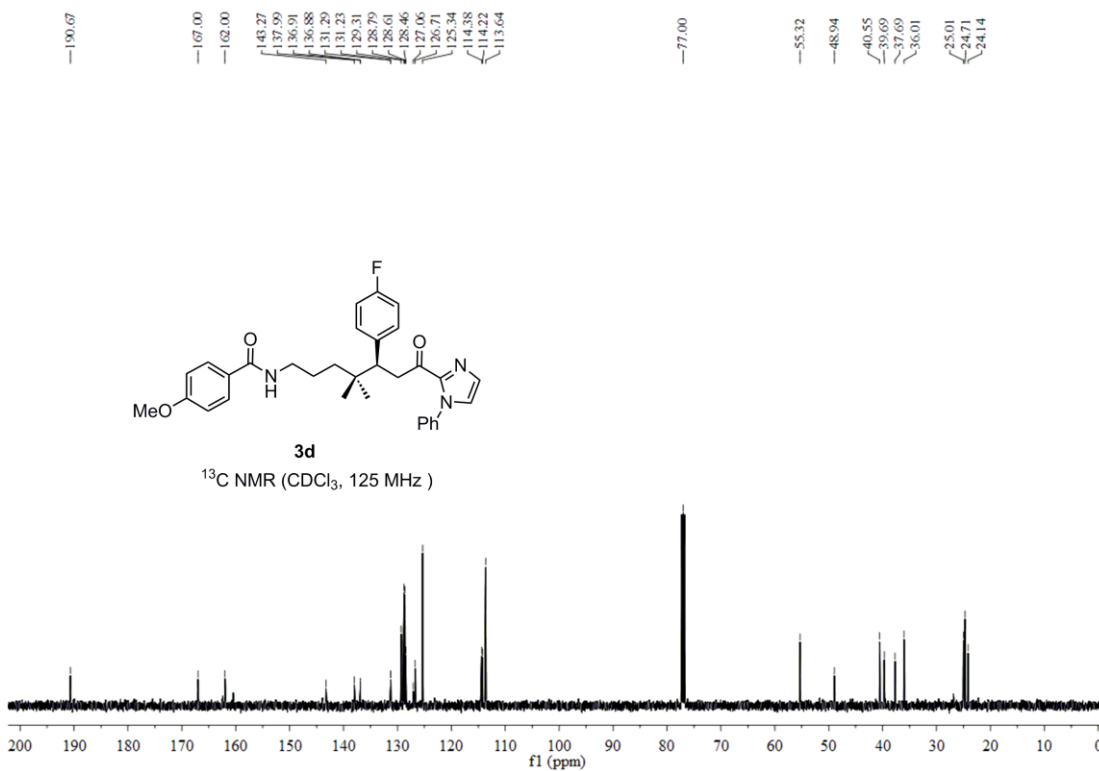
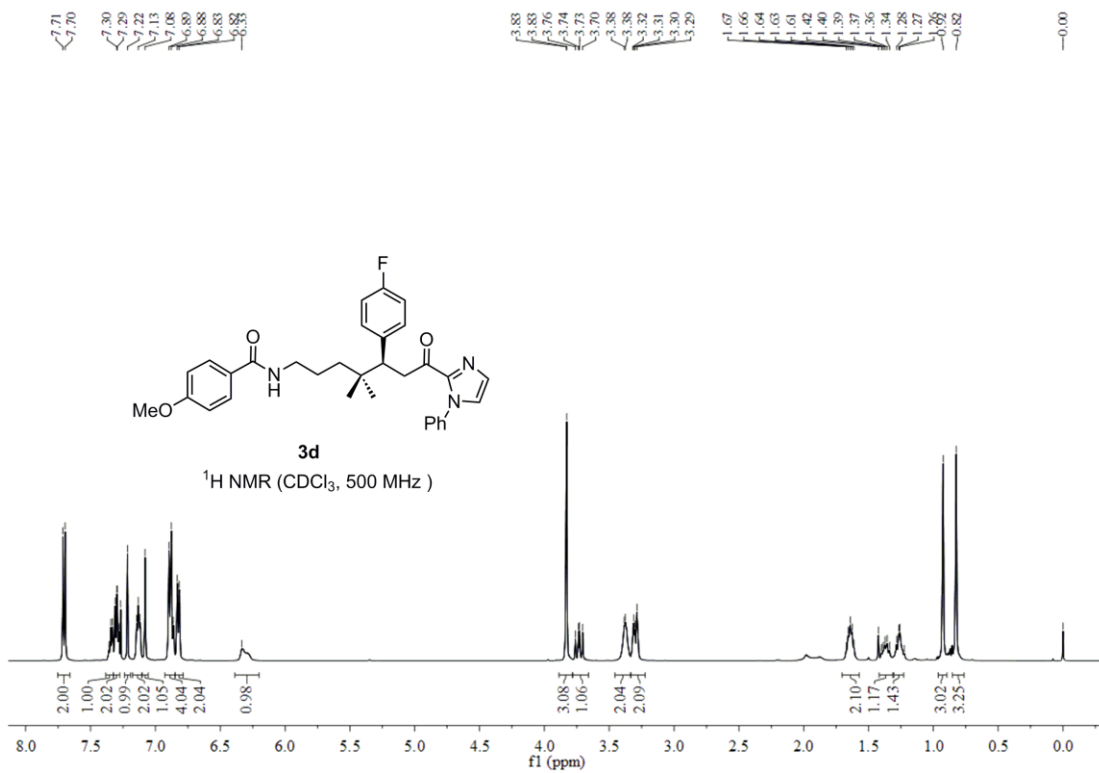
- 1 C. Wang, L.-A. Chen, H. Huo, X. Shen, K. Harms, L. Gong and E. Meggers, *Chem. Sci.*, 2015, **6**, 1094.
- 2 J. Ma, X. Shen, K. Harms and E. Meggers, *Dalton Trans.*, 2016, **45**, 8320.
- 3 J. C. K. Chu and T. Rovis, *Nature*, 2016, **539**, 272.
- 4 G. J. Choi, Q. Zhu, D. C. Miller, C. J. Gu and R. R. Knowles, *Nature*, 2016, **539**, 268.
- 5 (a) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix and P. L. Holland, *J. Am. Chem. Soc.*, 2015, **137**, 13244; (b) A. Gille and M. Hiersemann, *Org. Lett.*, 2010, **12**, 5258; (c) C. Martínez and K. Muñoz, *Angew. Chem., Int. Ed.*, 2015, **54**, 8287.
- 6 H. Huo, K. Harms and E. Meggers, *J. Am. Chem. Soc.*, 2016, **138**, 6936.

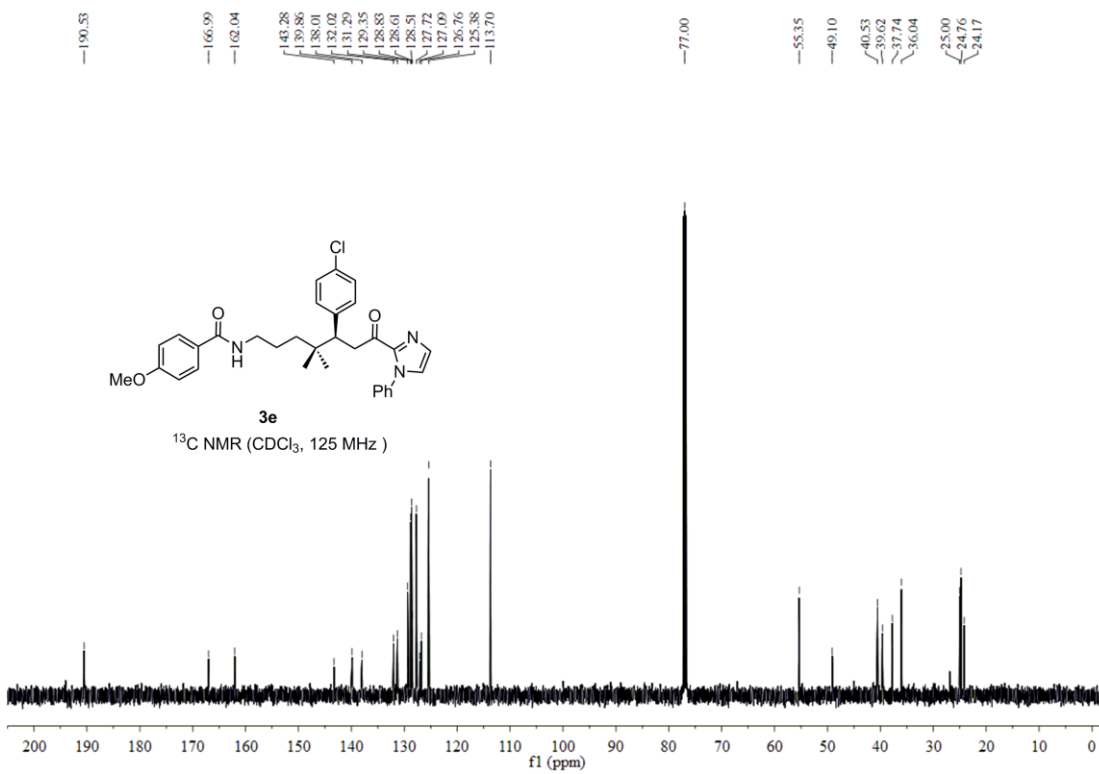
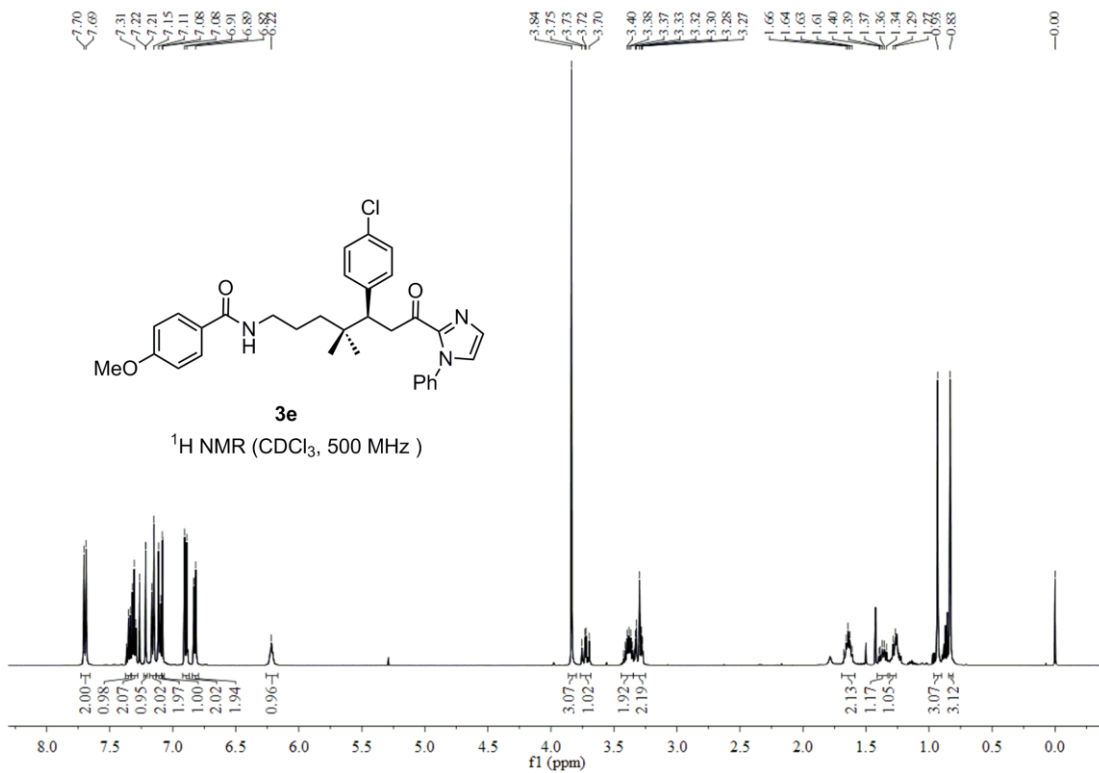
9. NMR Spectra

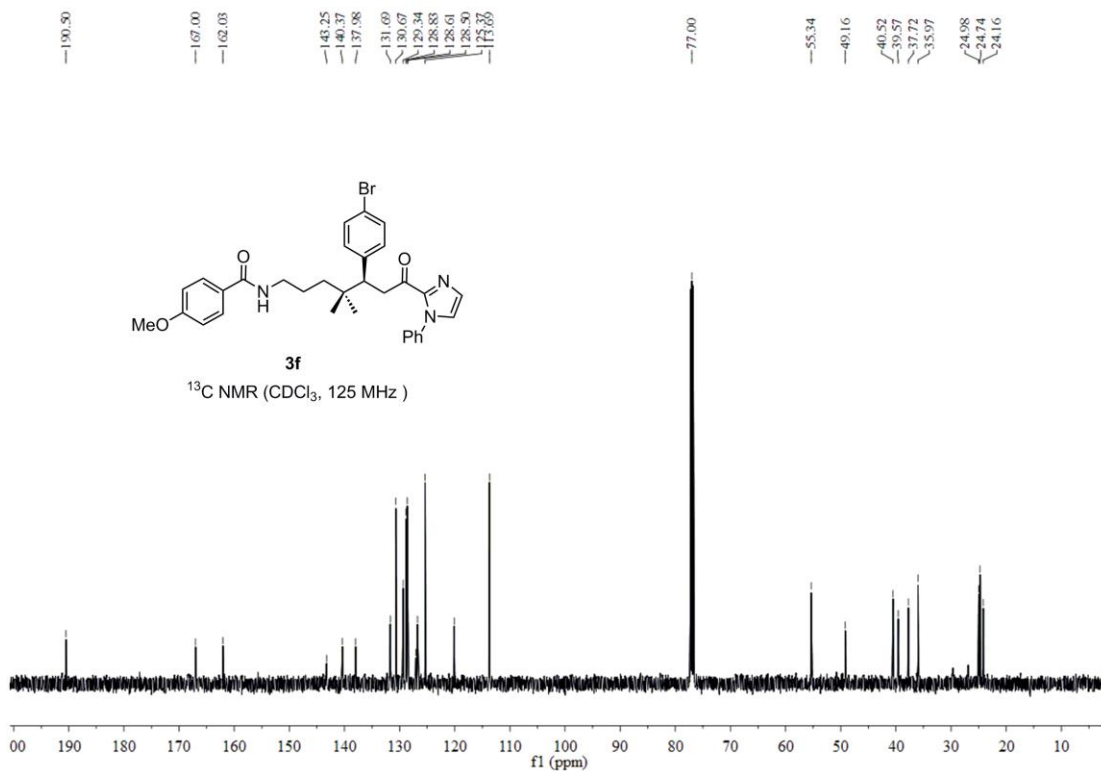
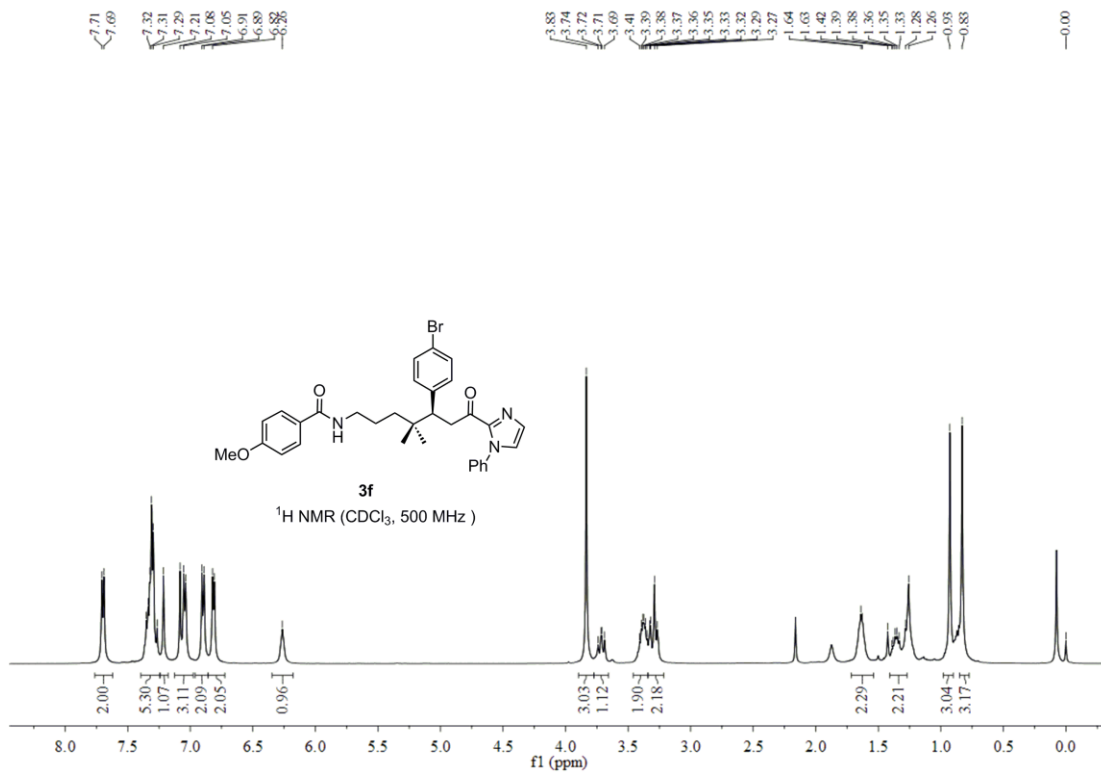


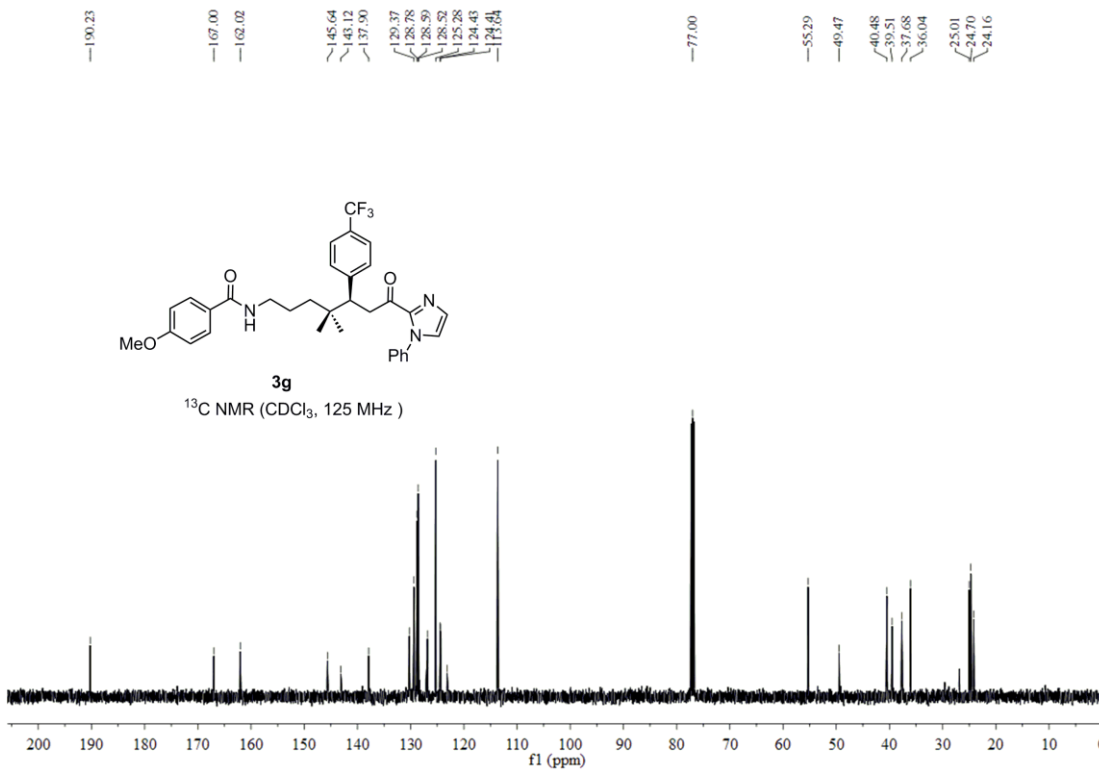
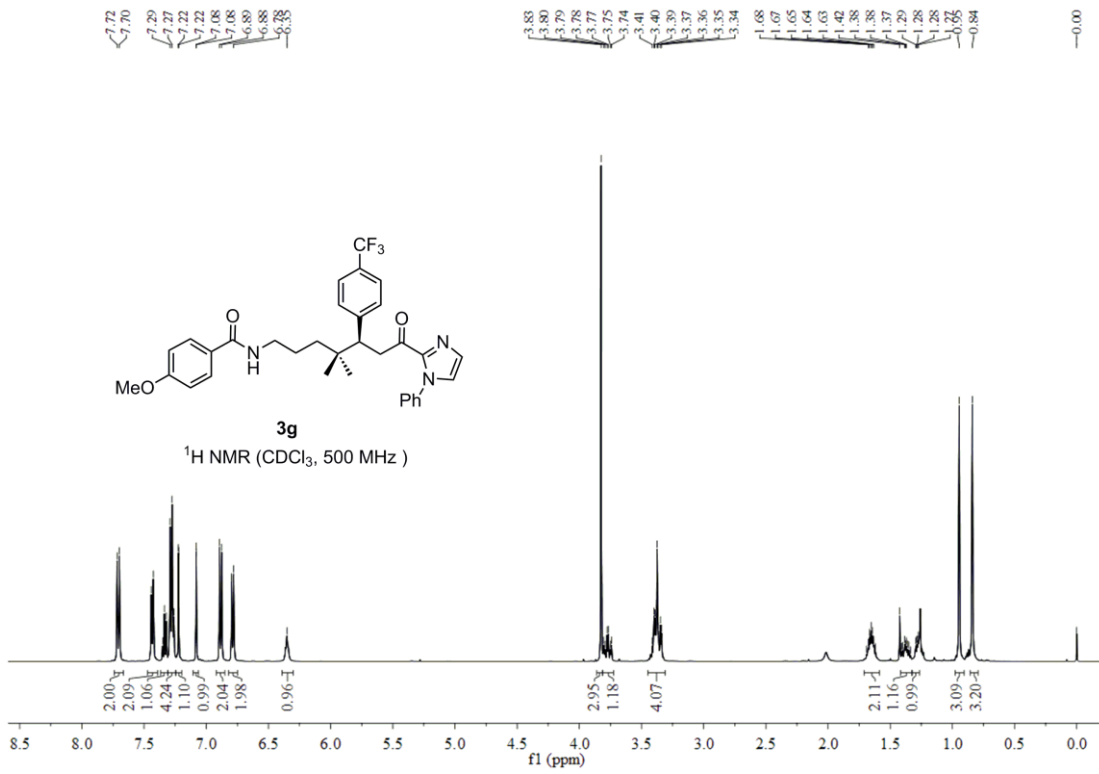


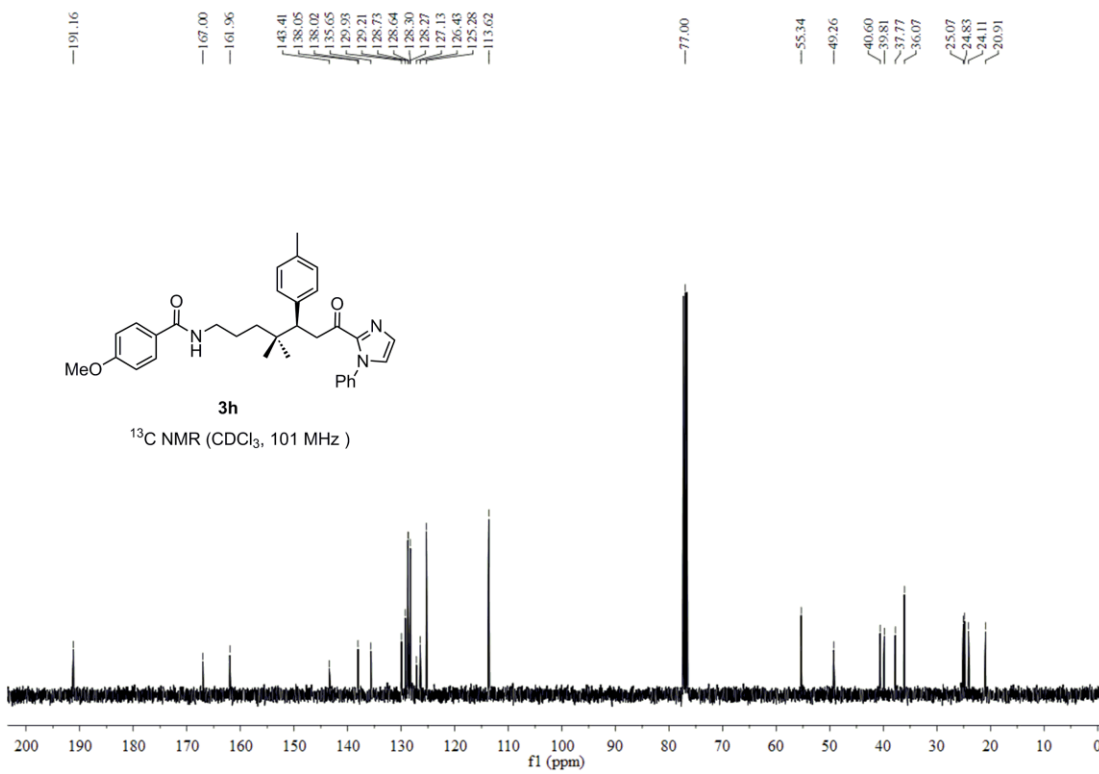
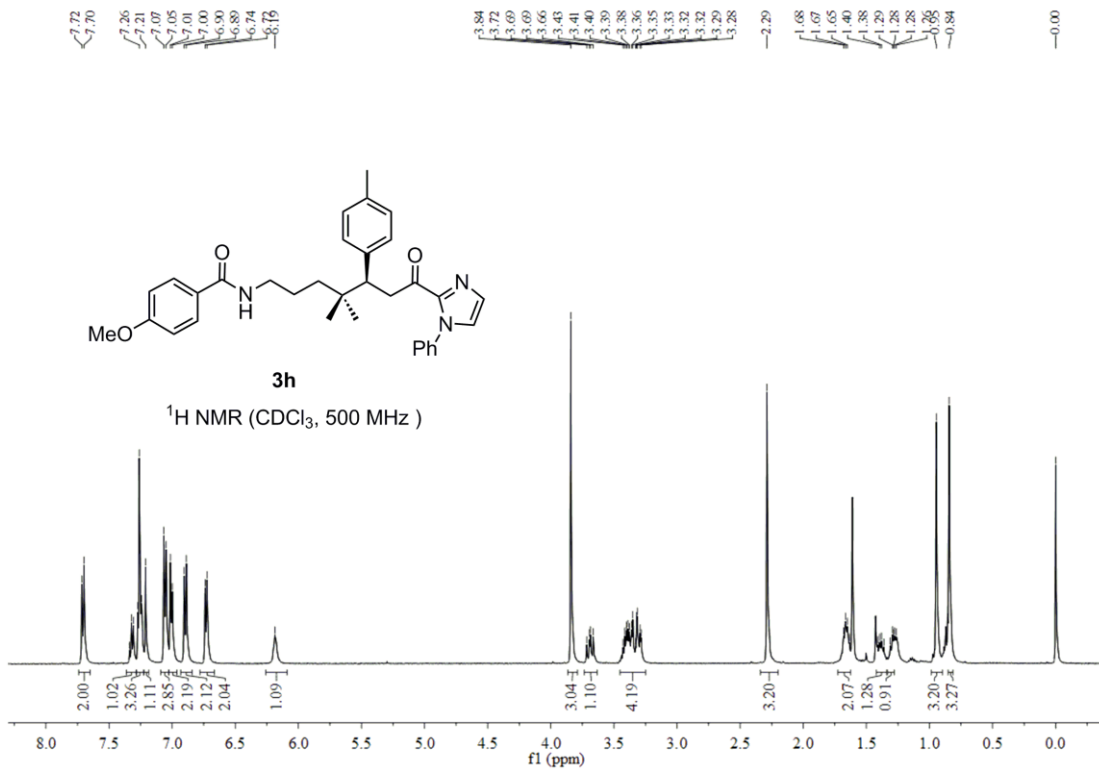


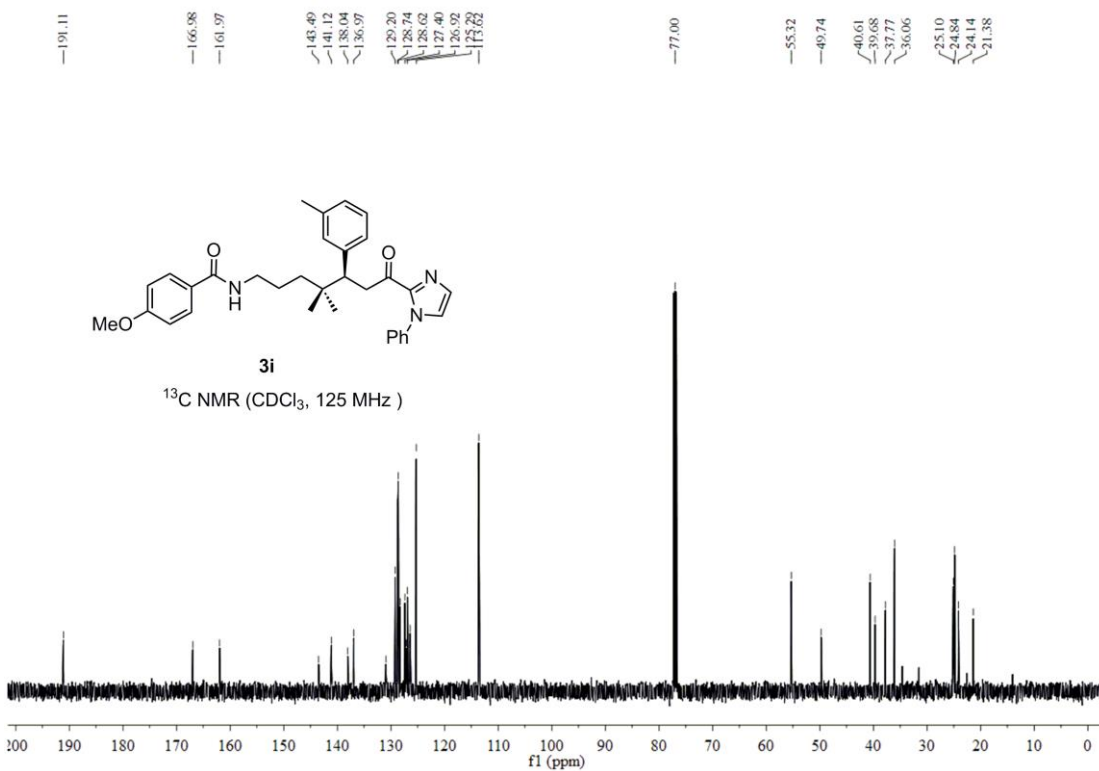
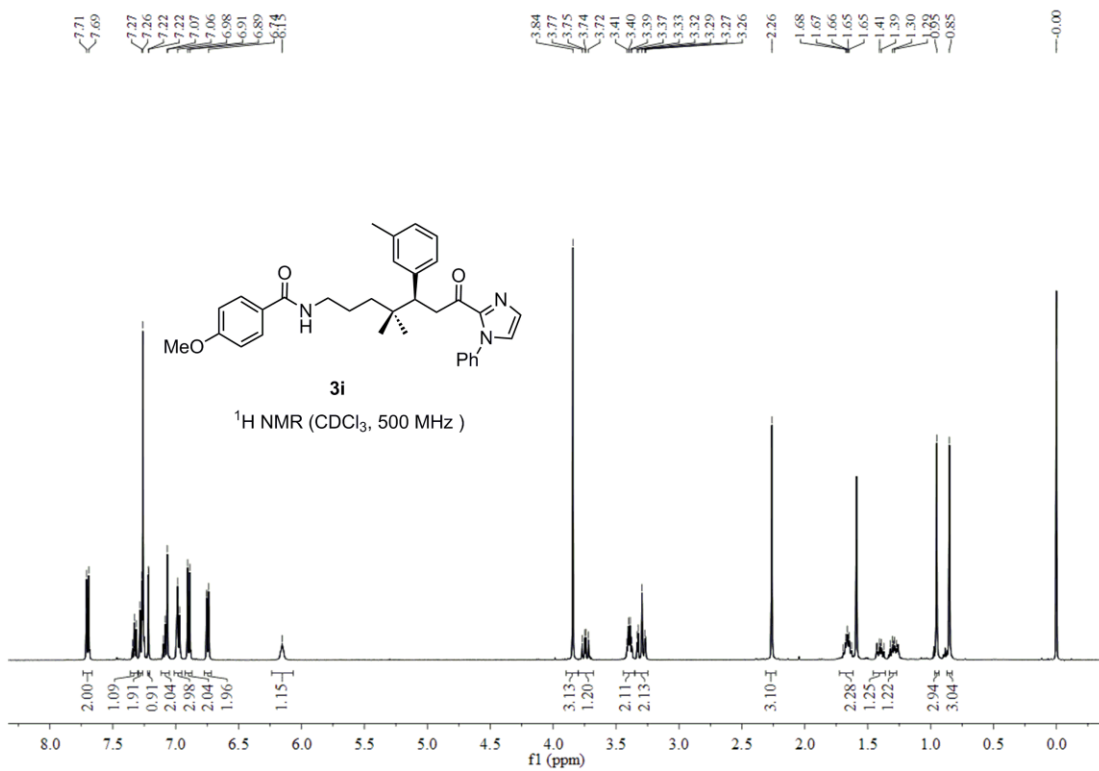


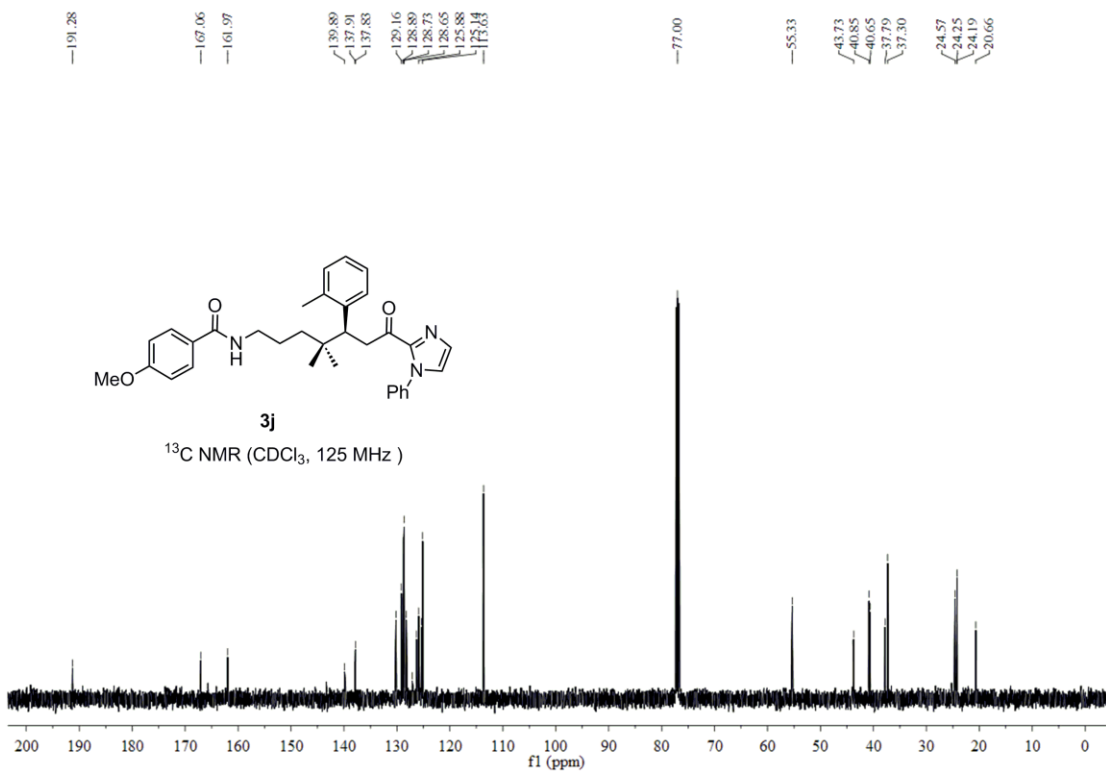
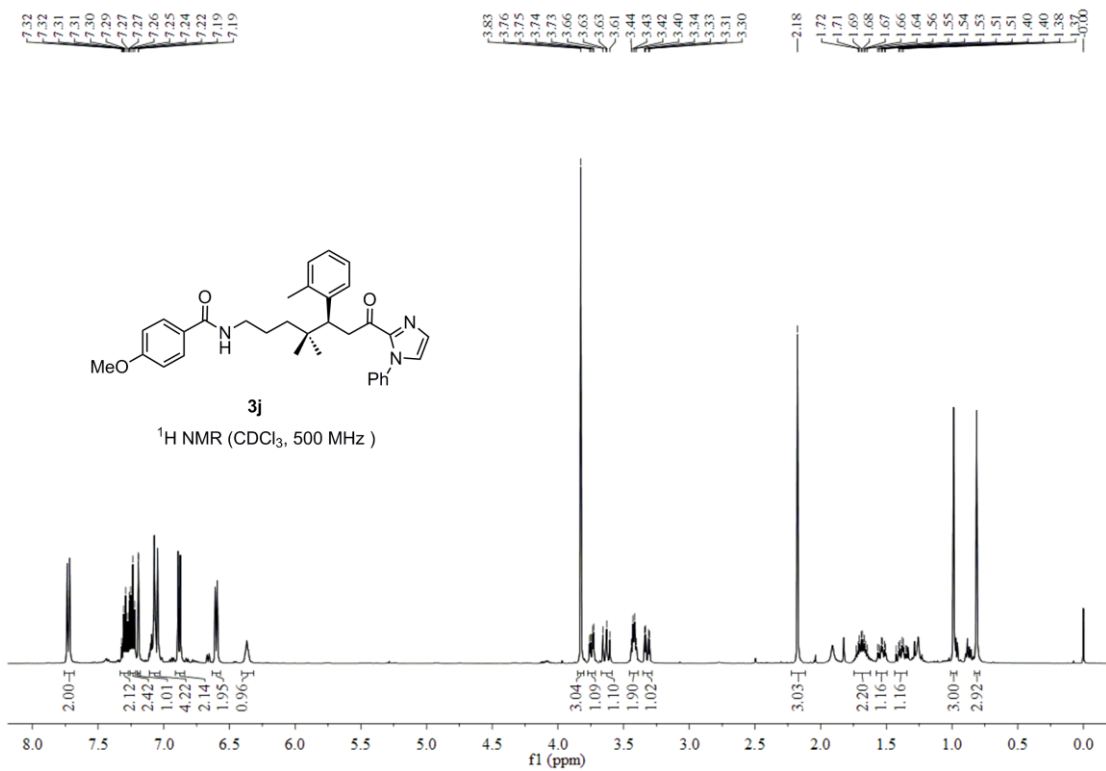


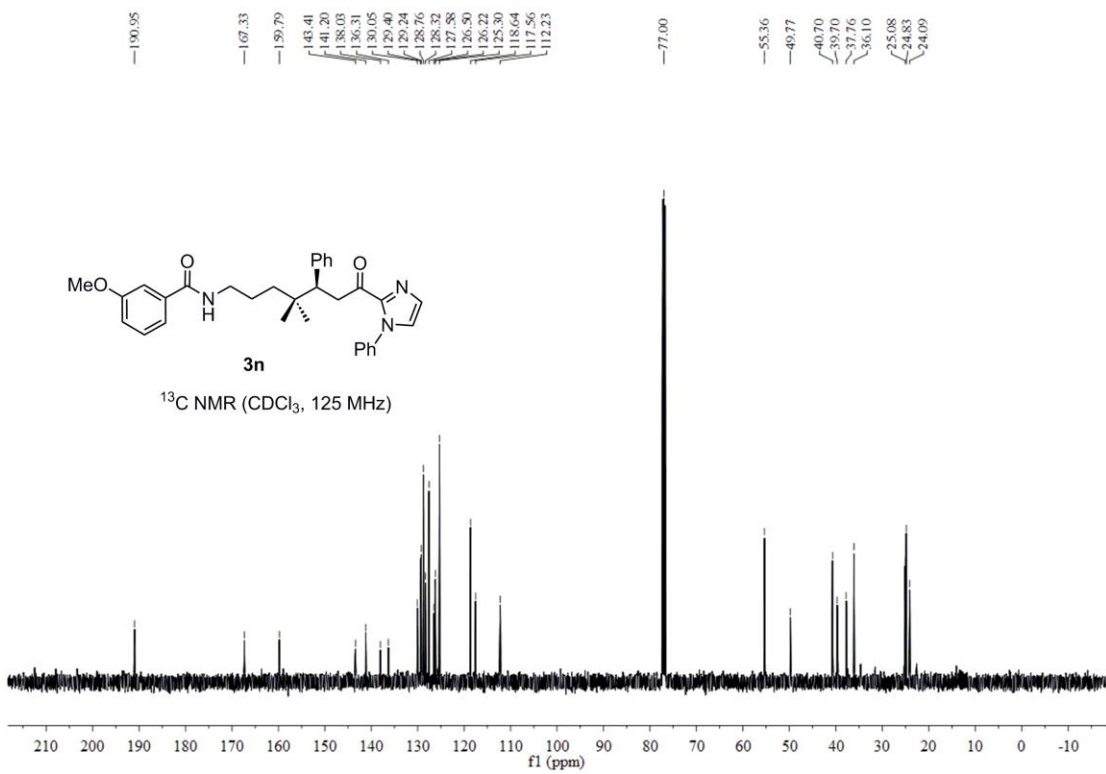
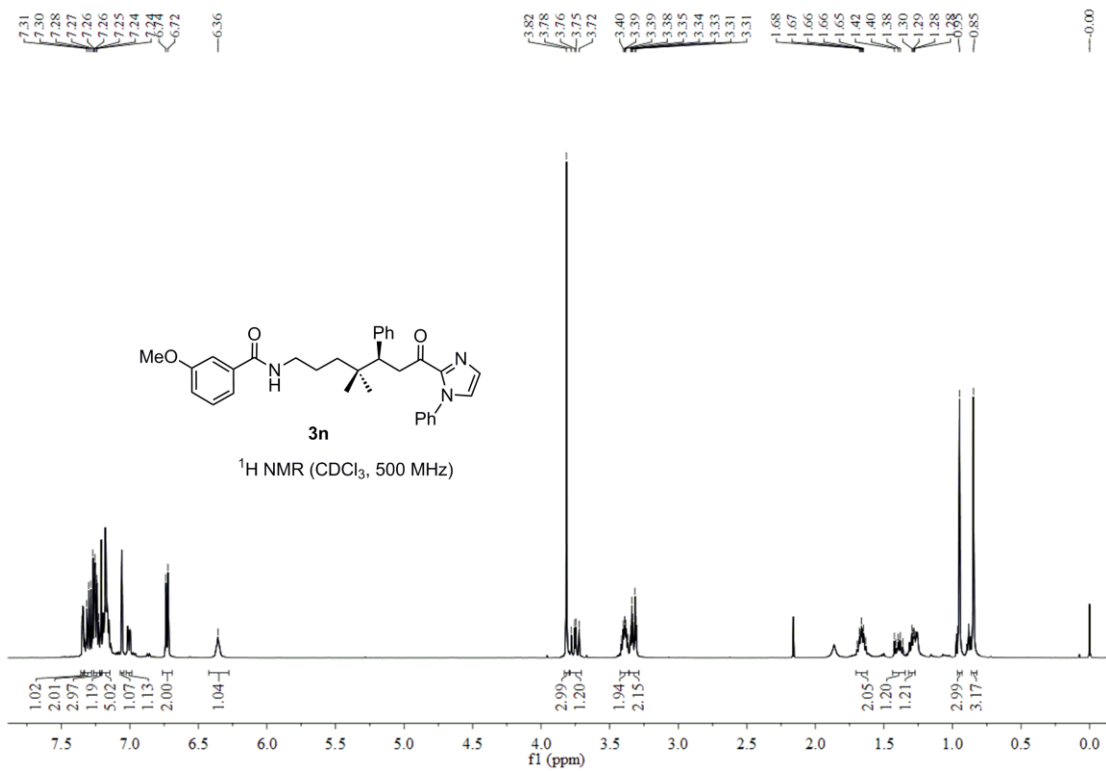


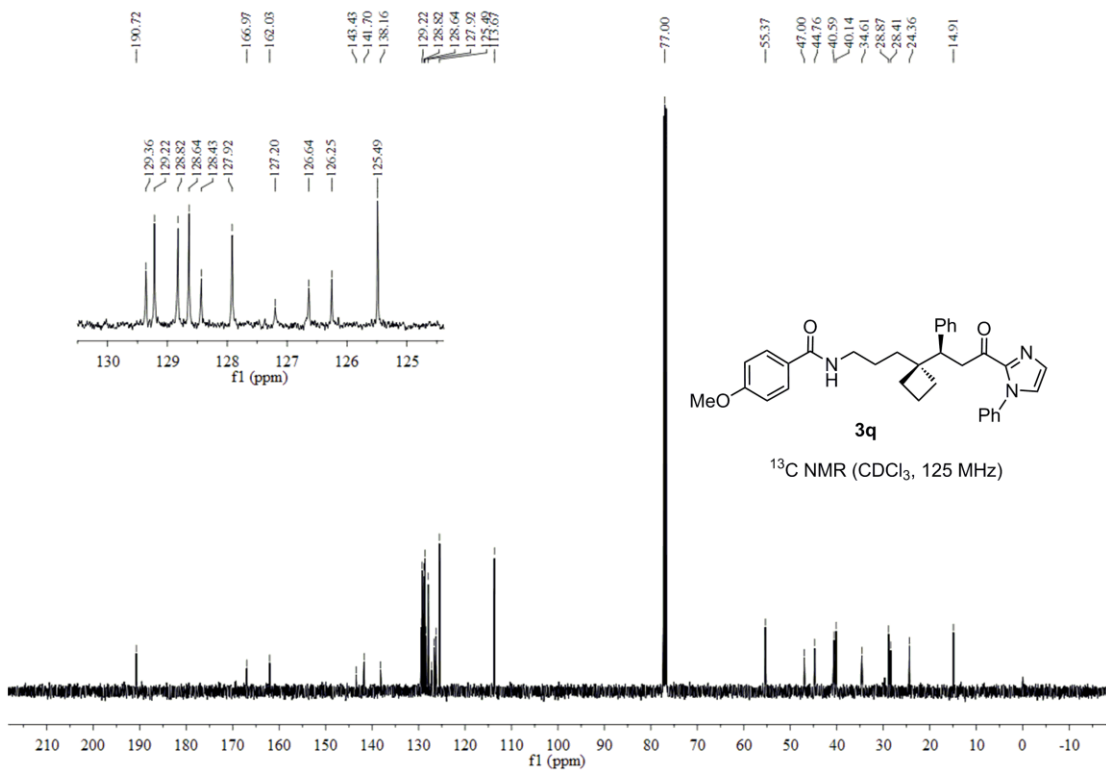
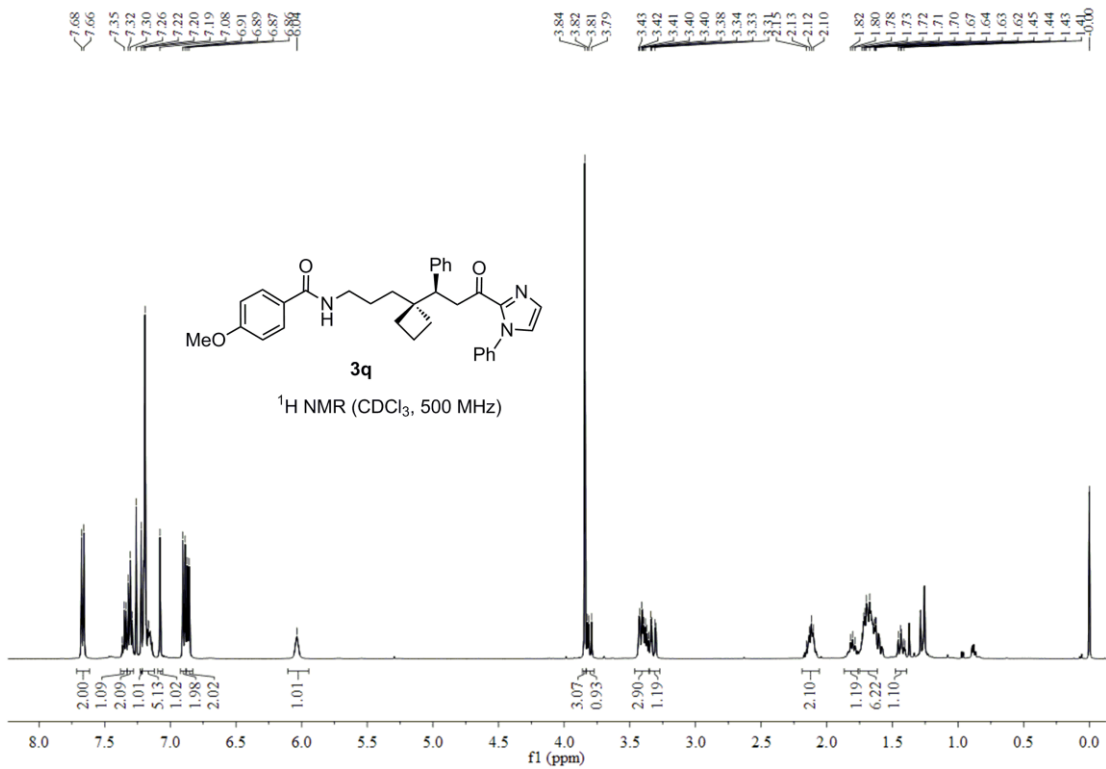


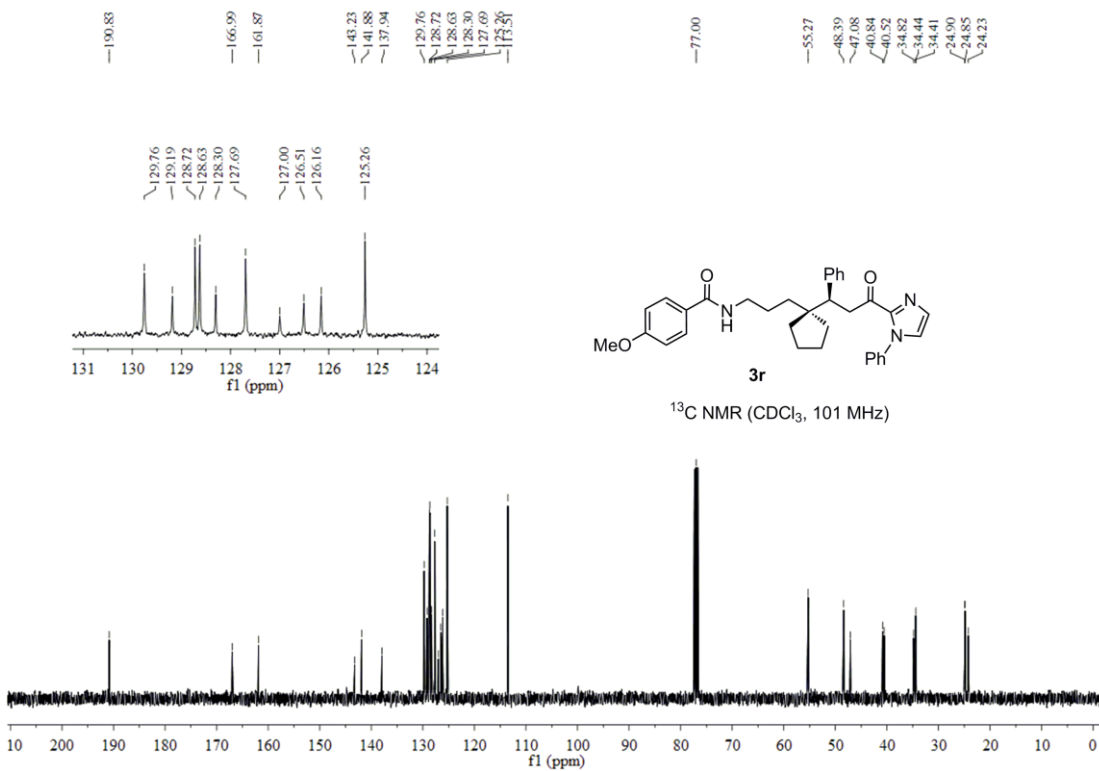
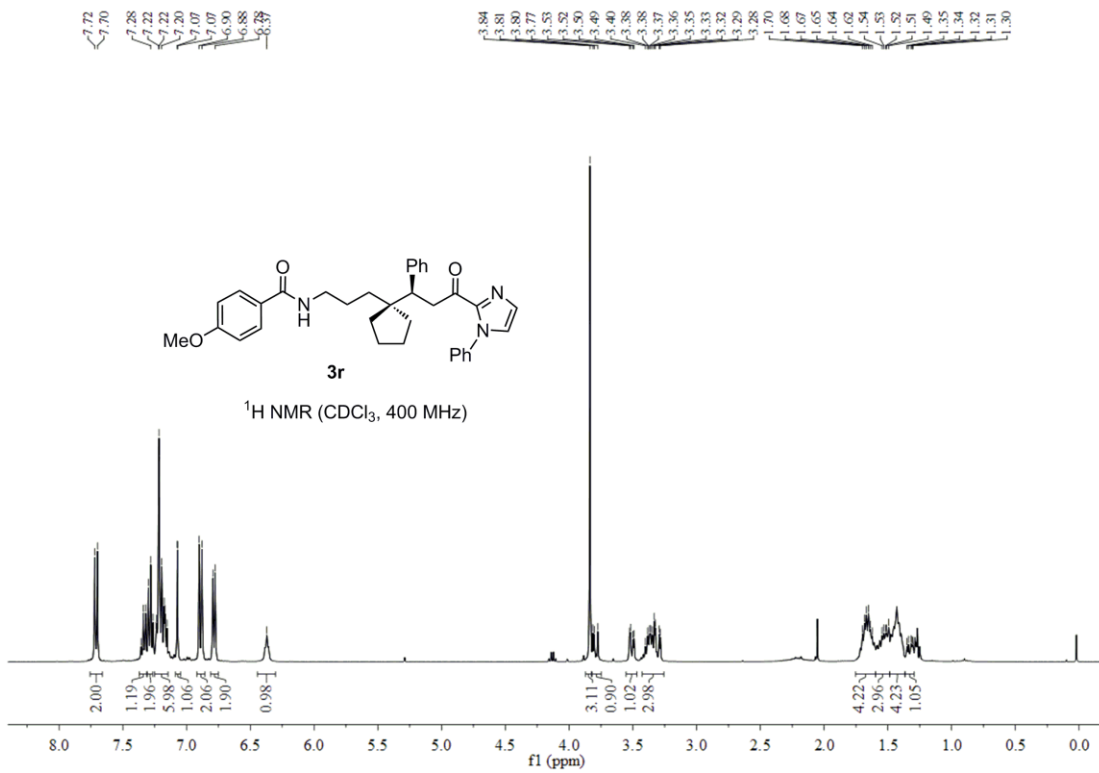


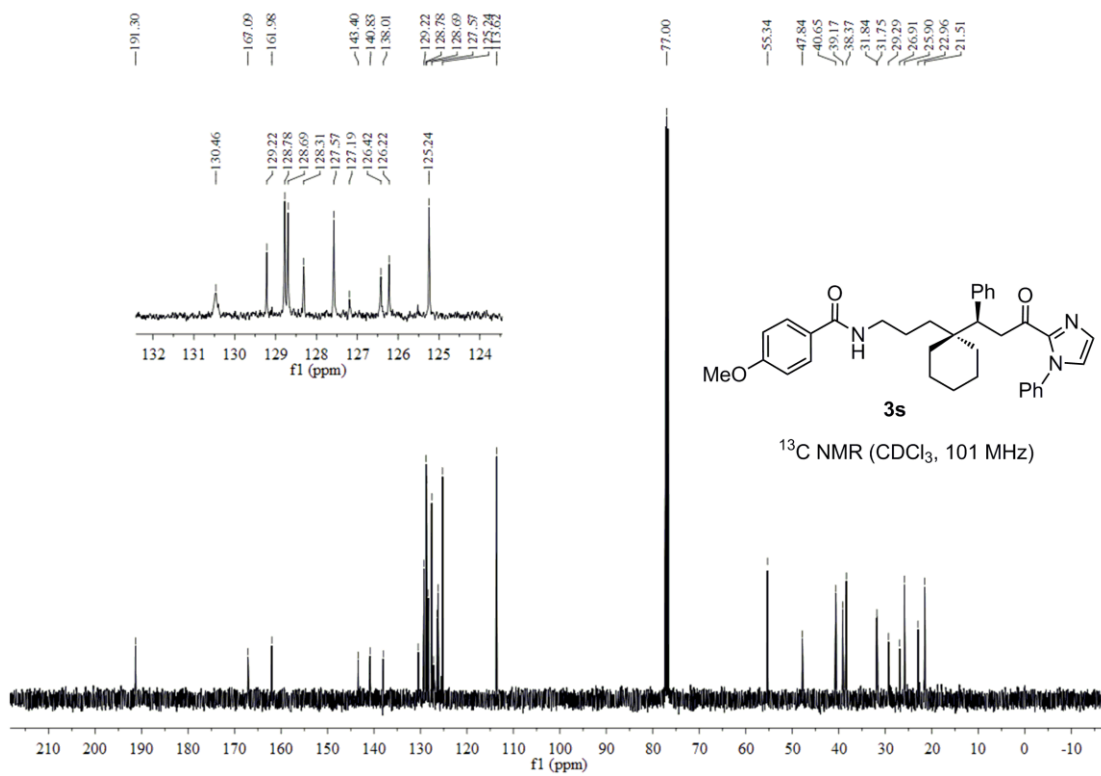
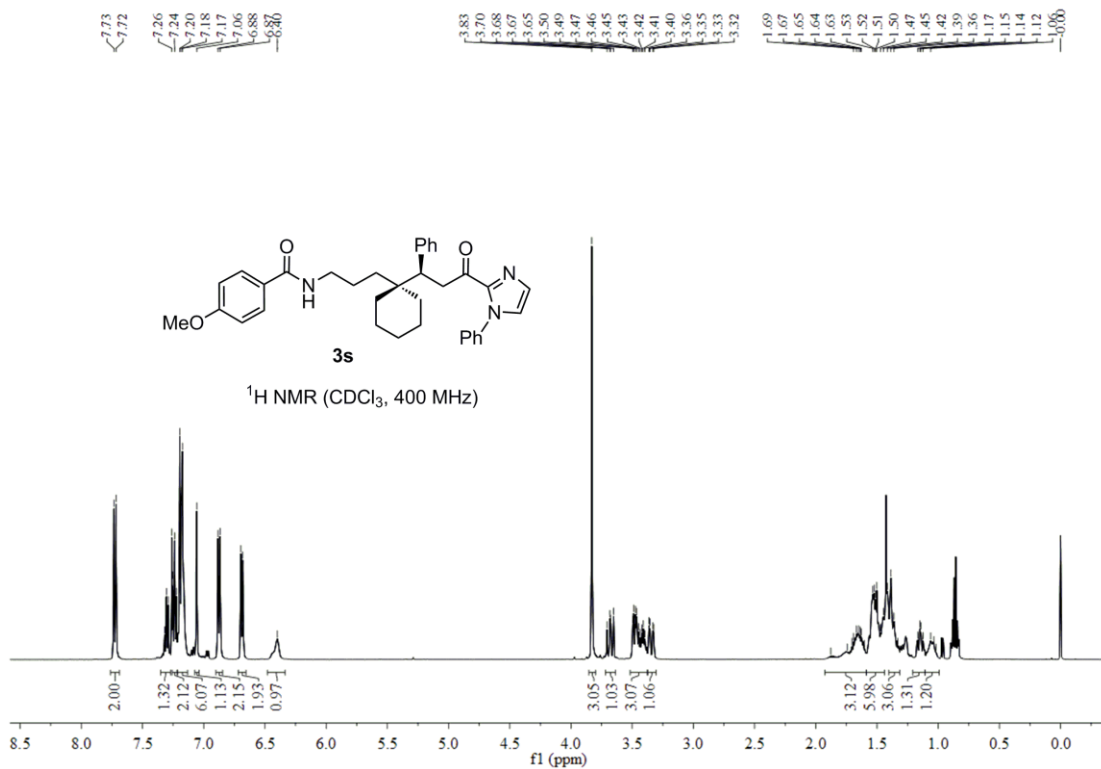


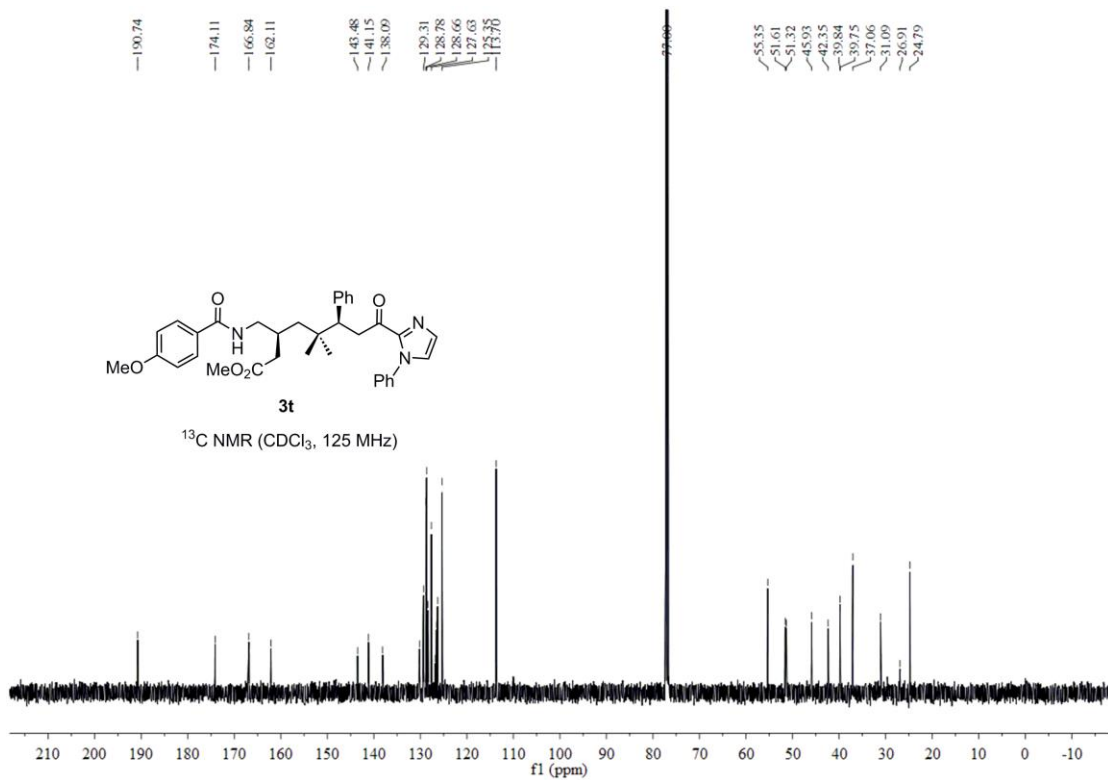
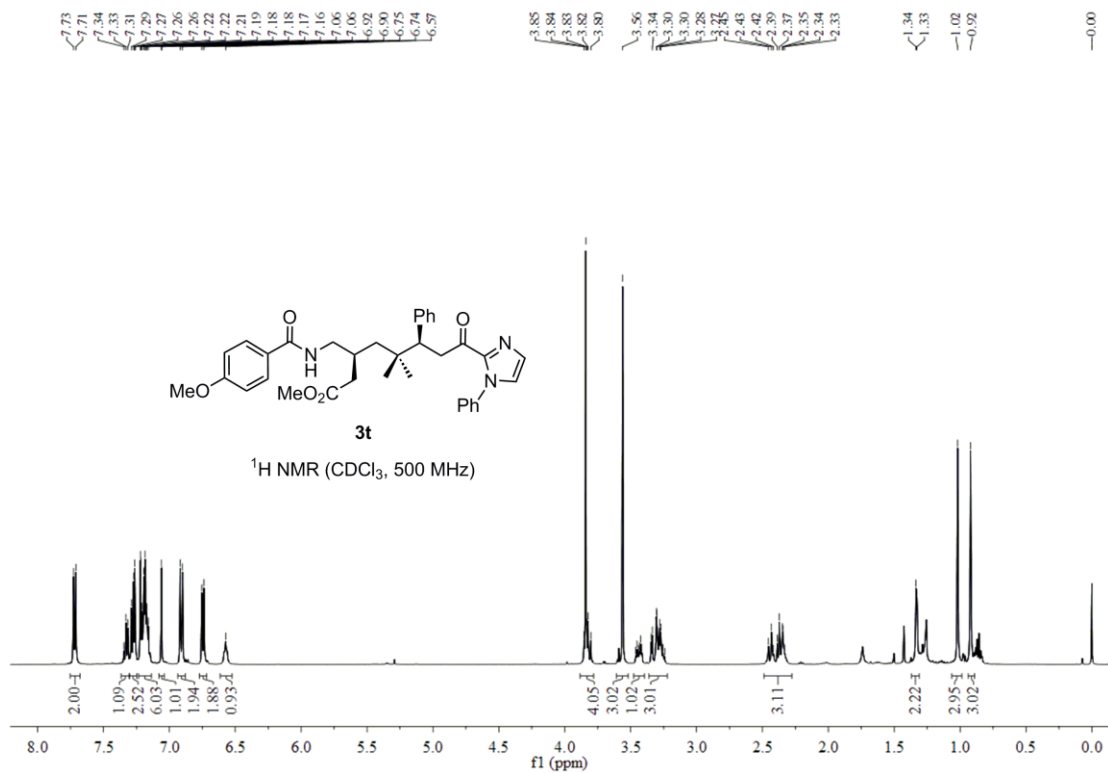


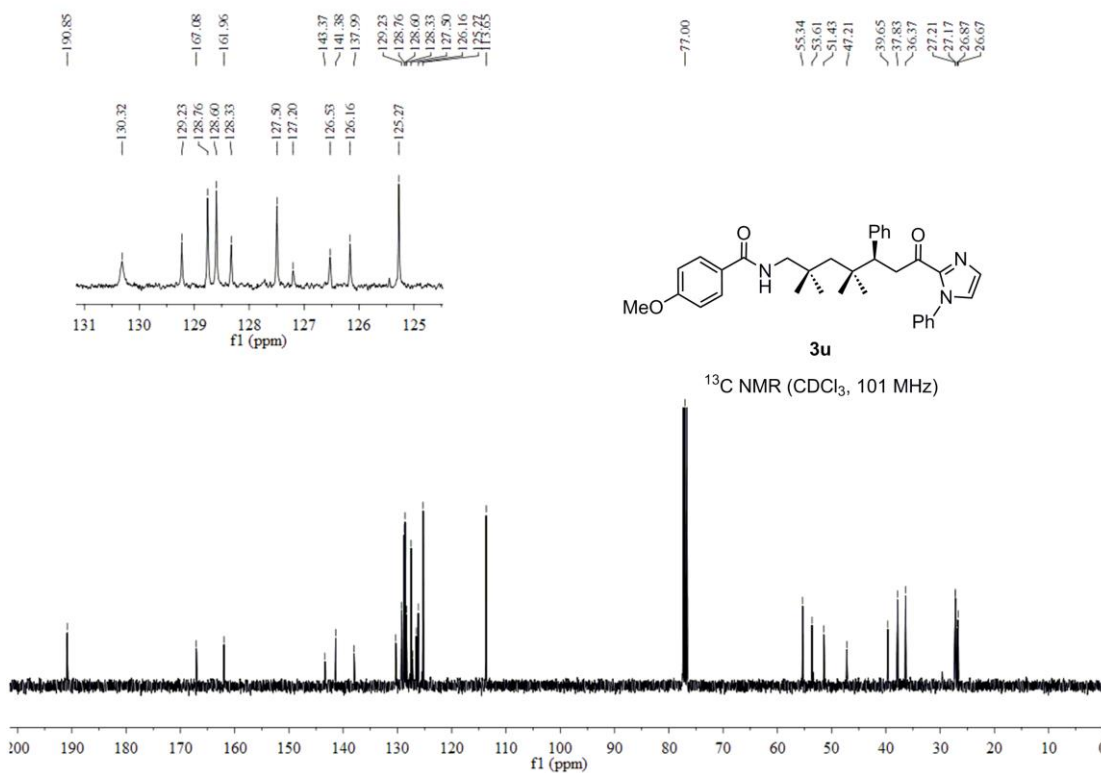
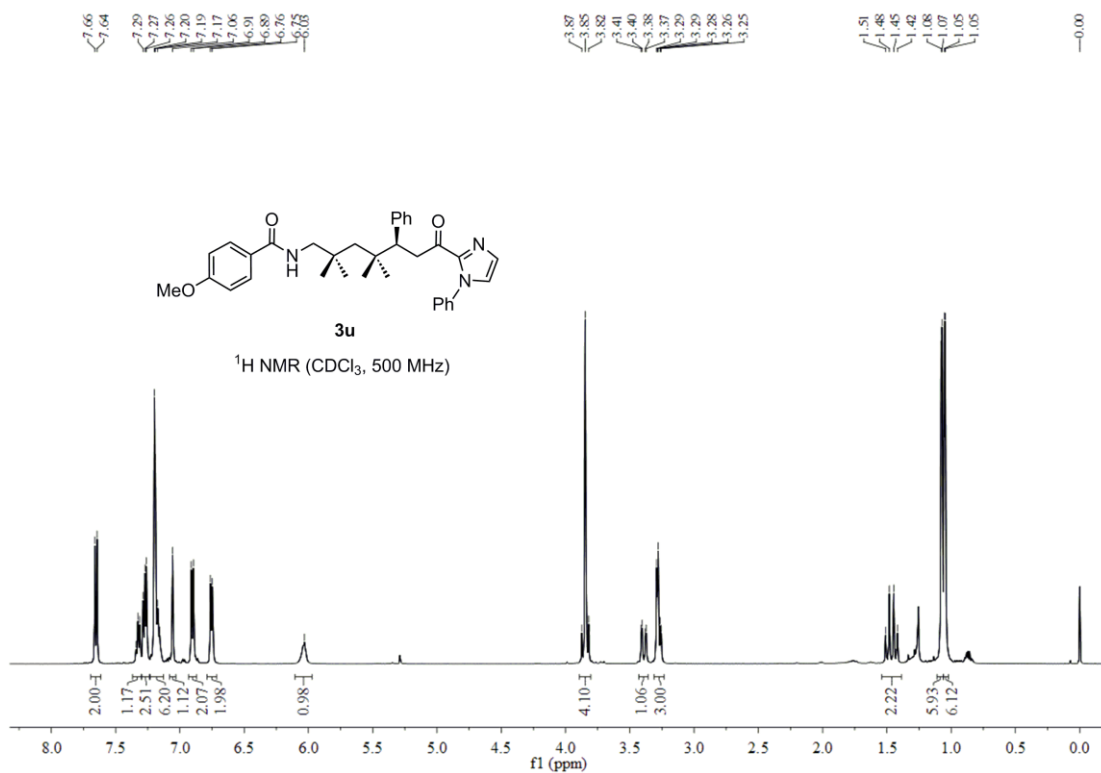


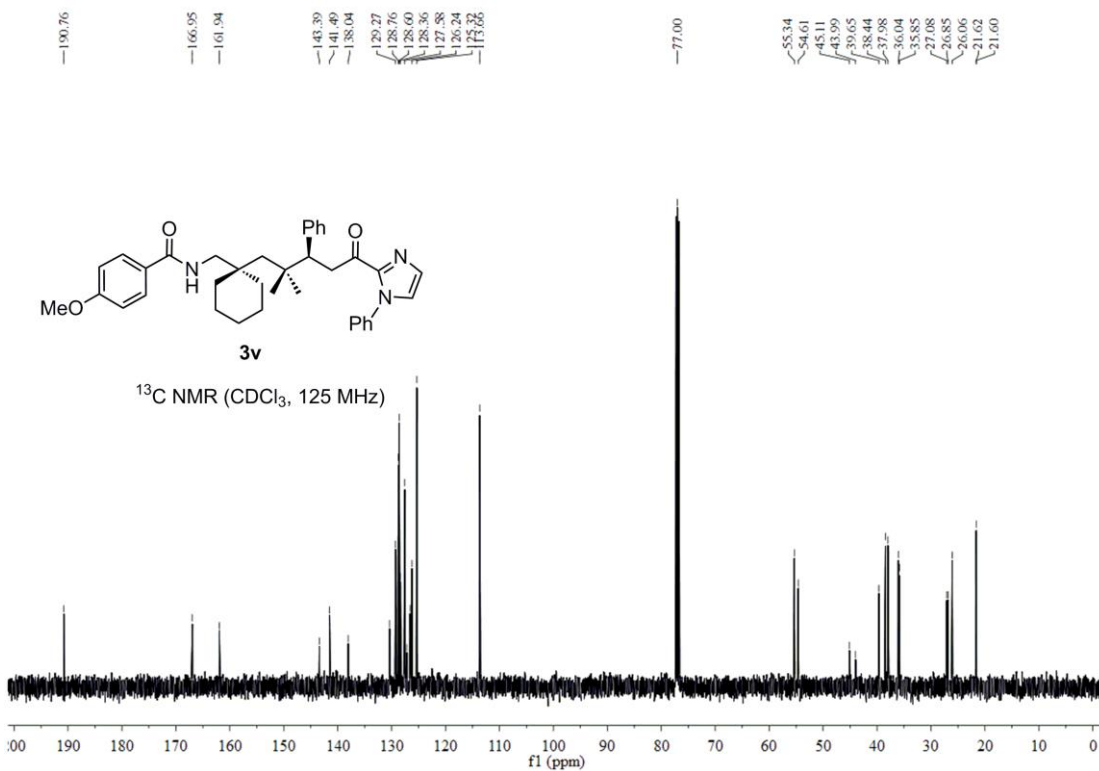
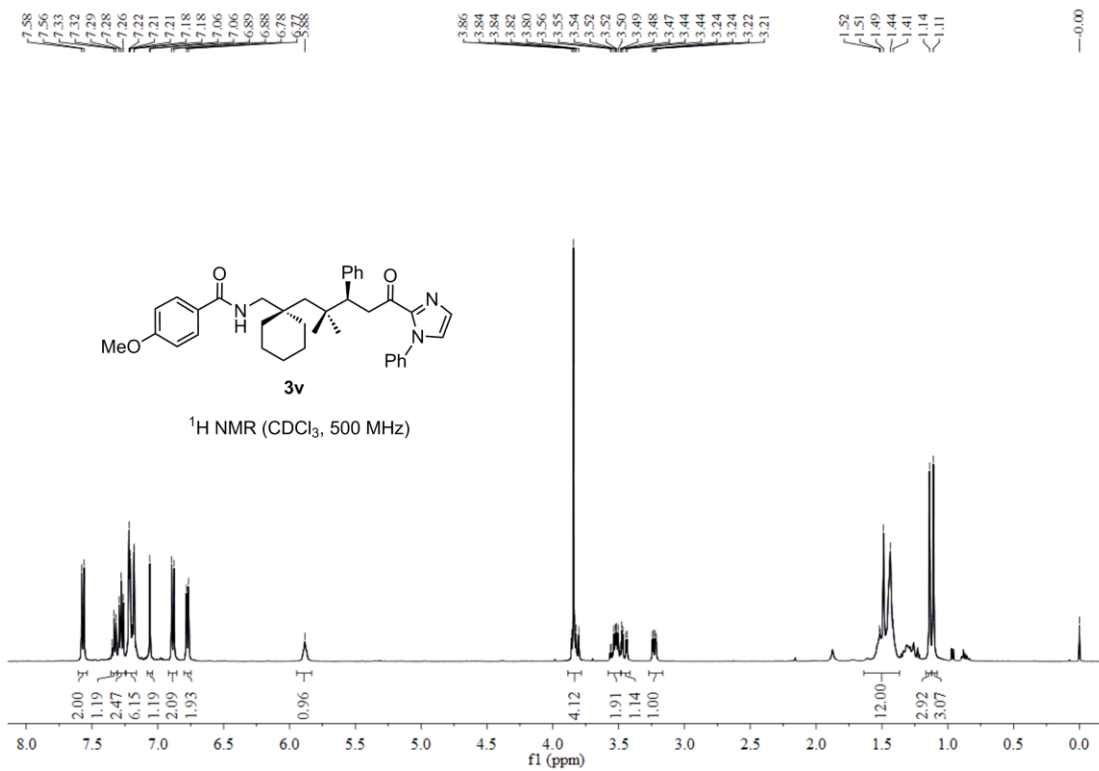


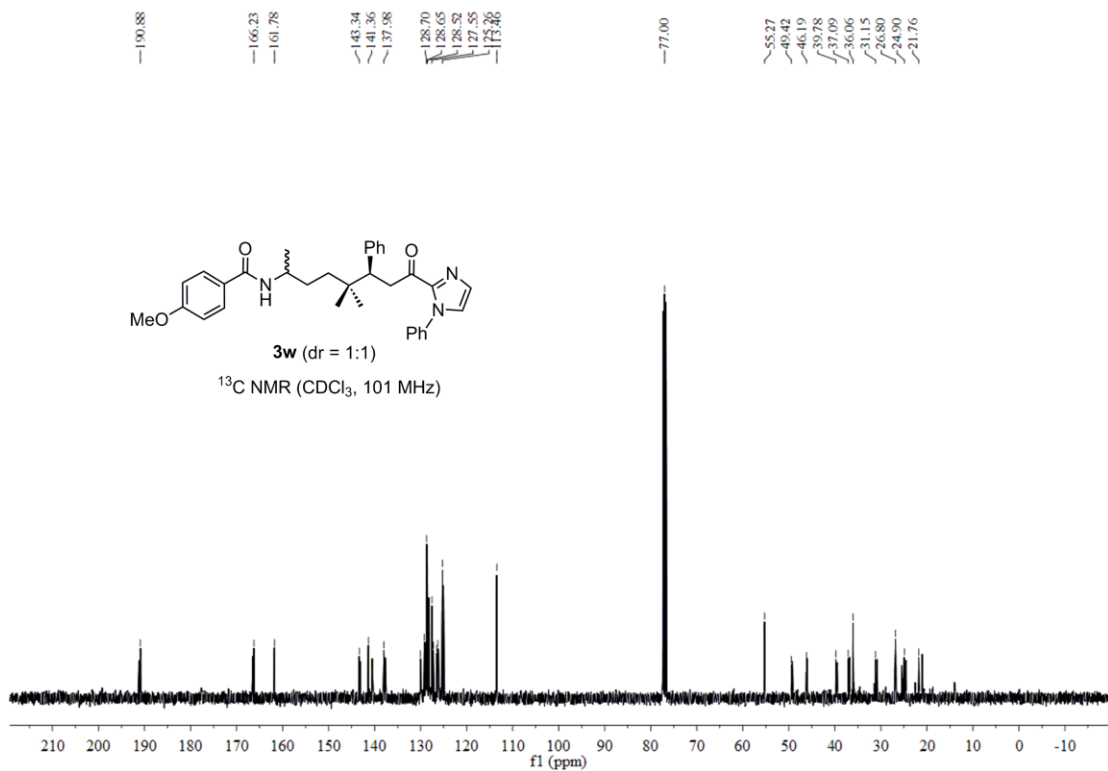
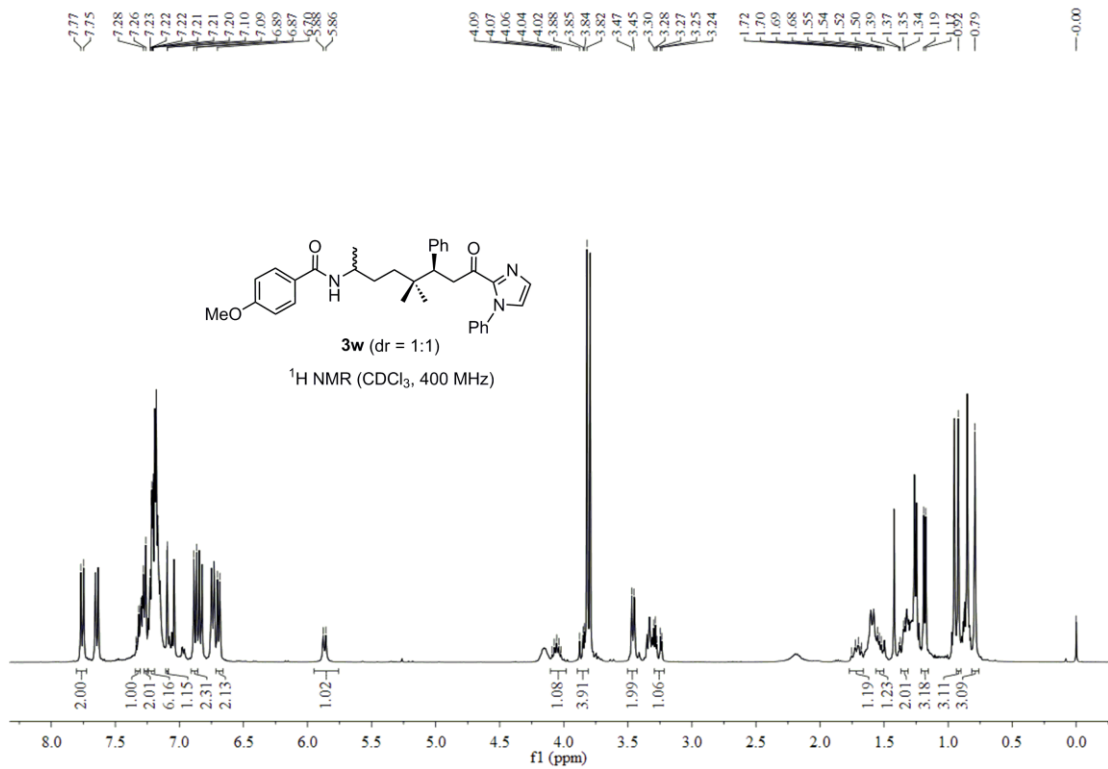


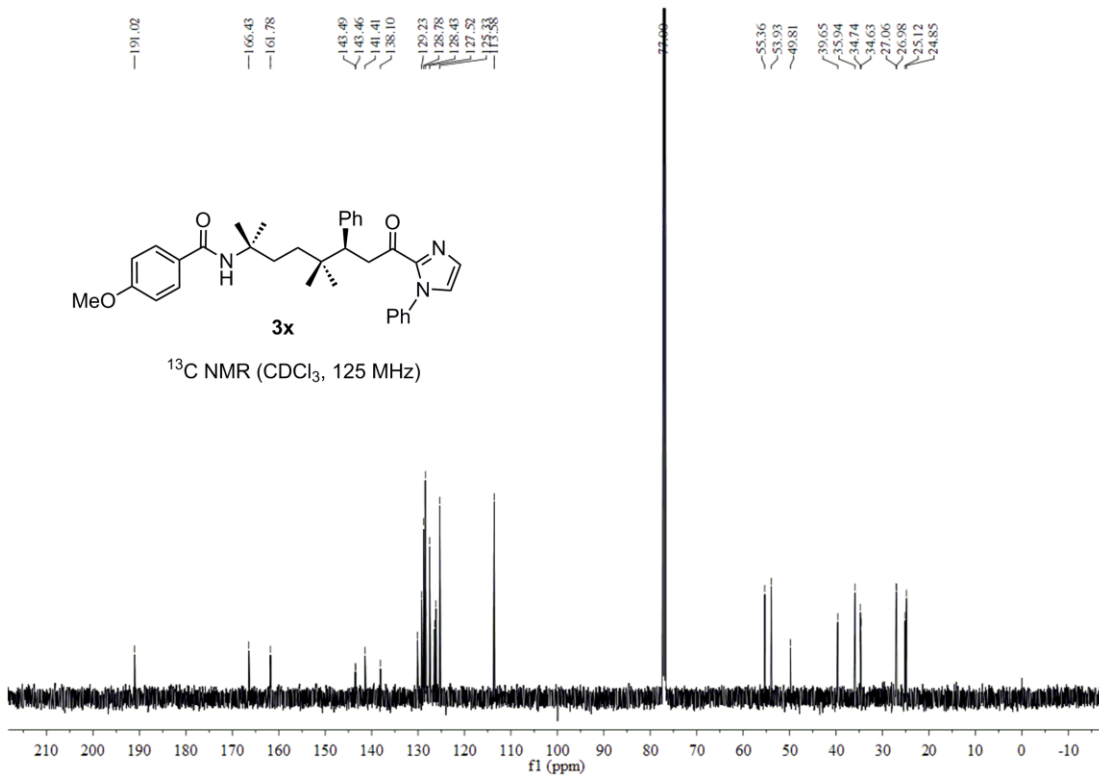
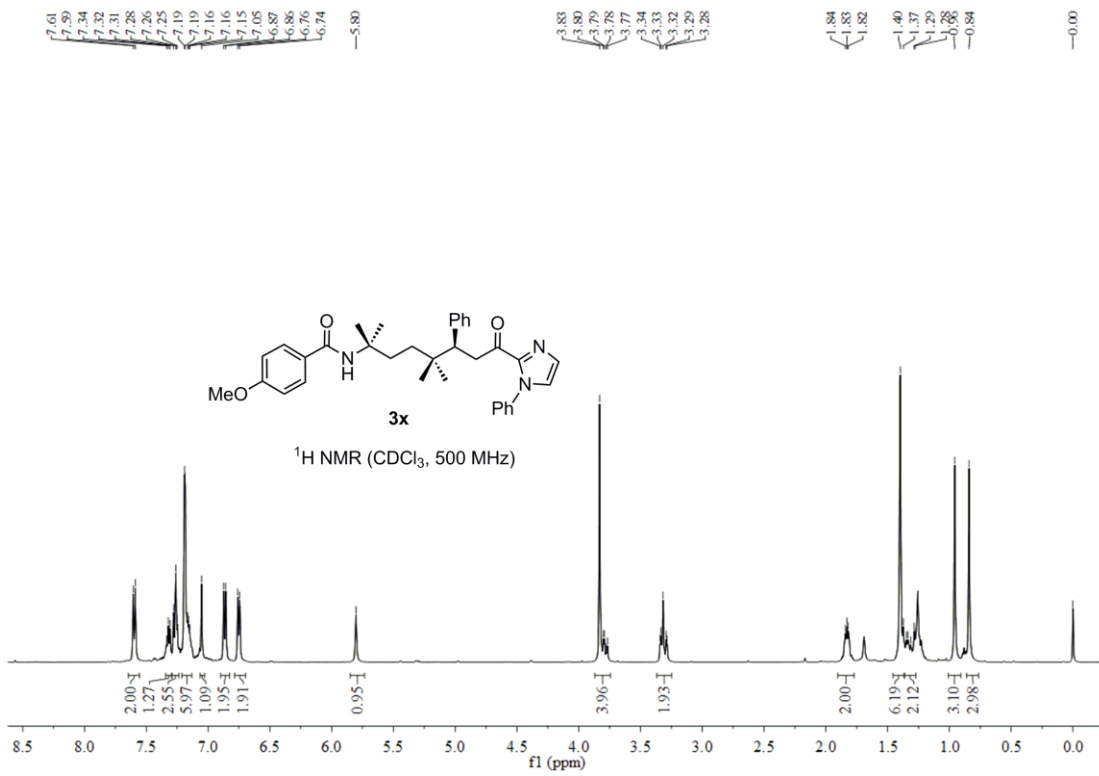


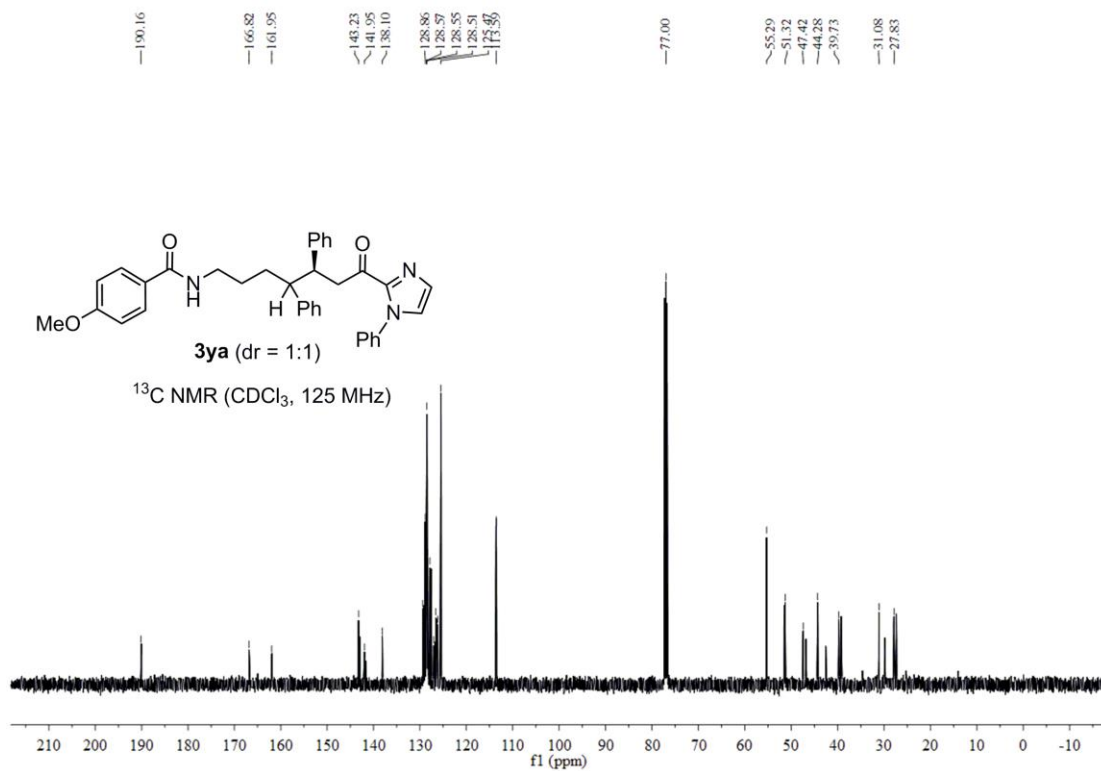
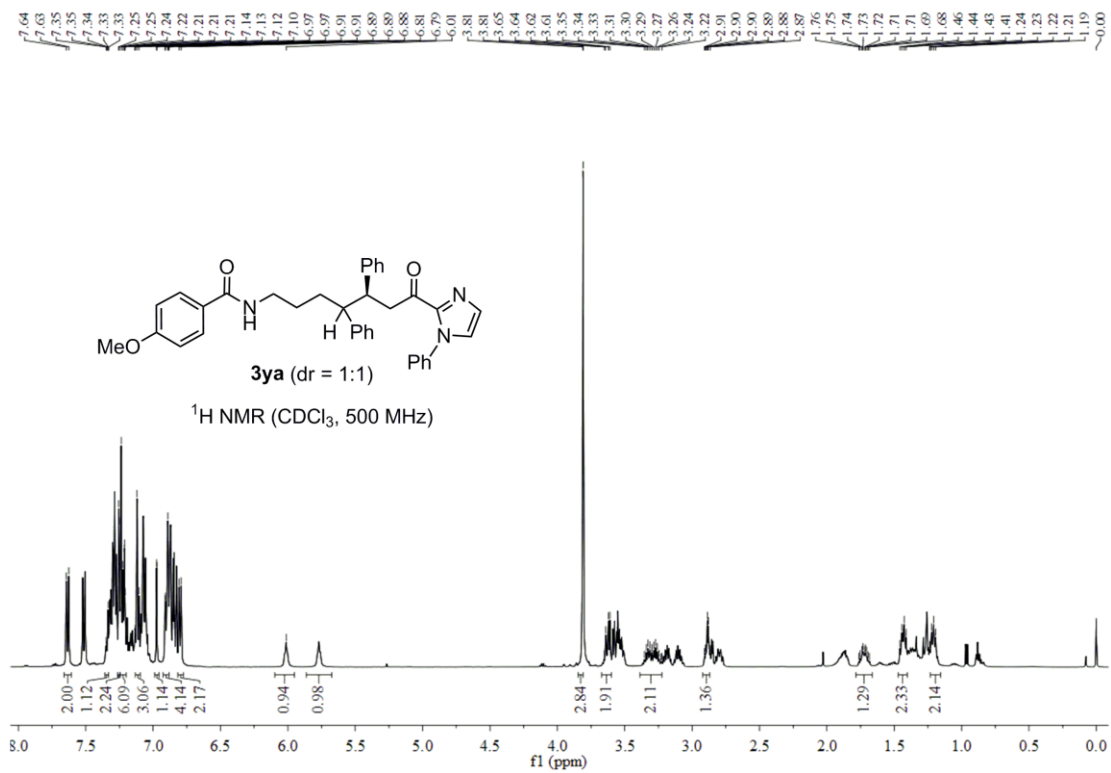


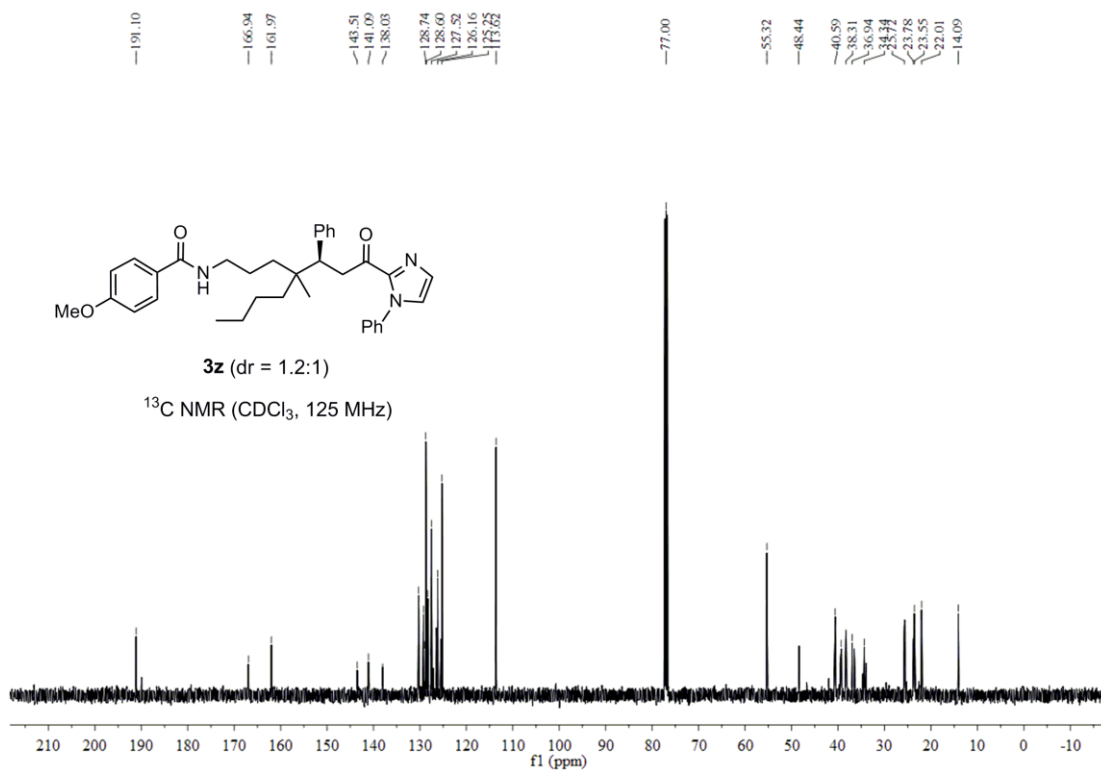
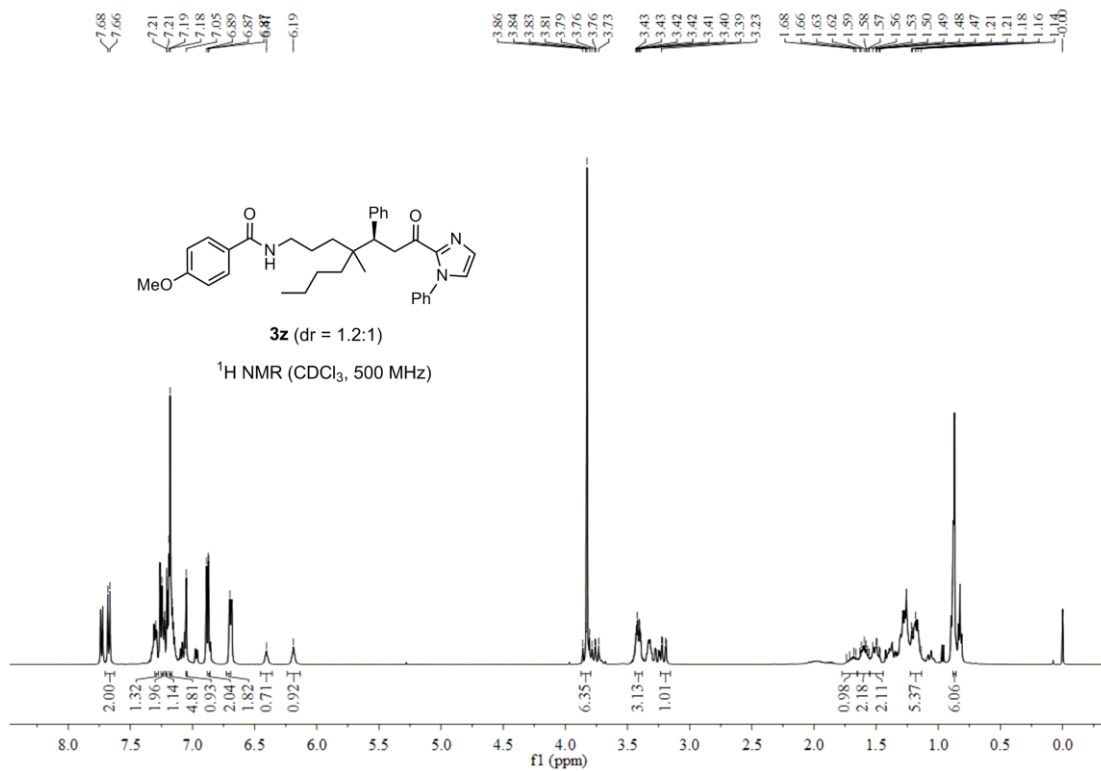


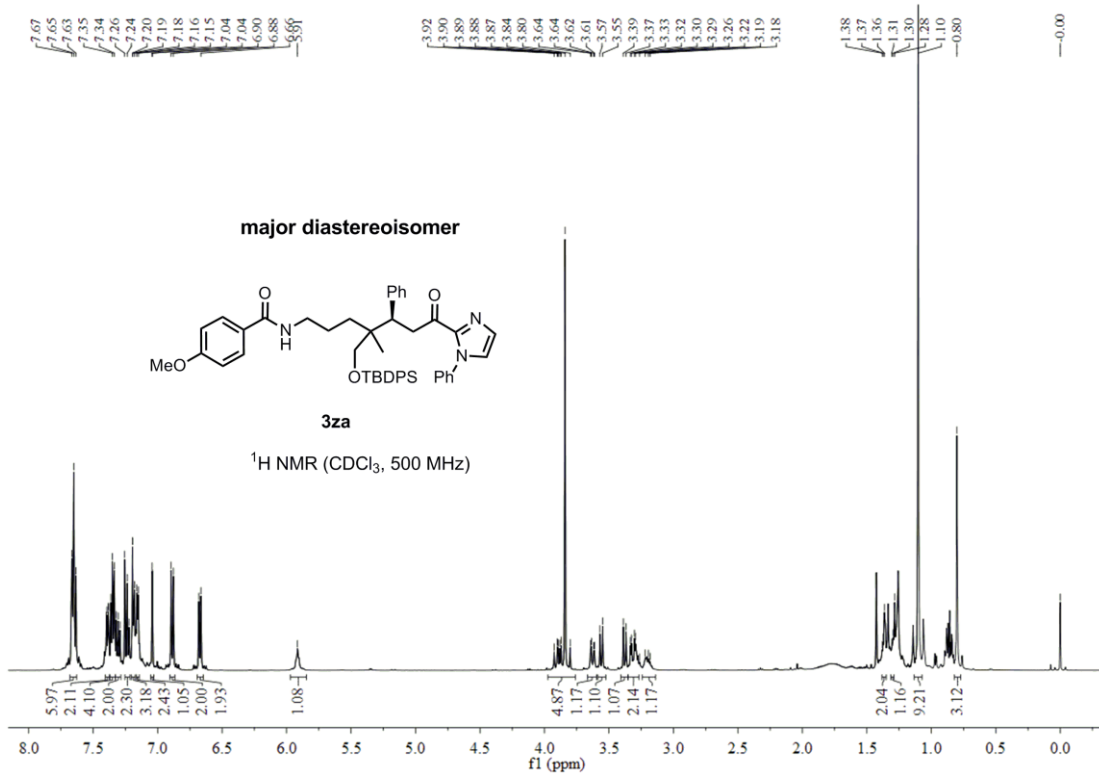
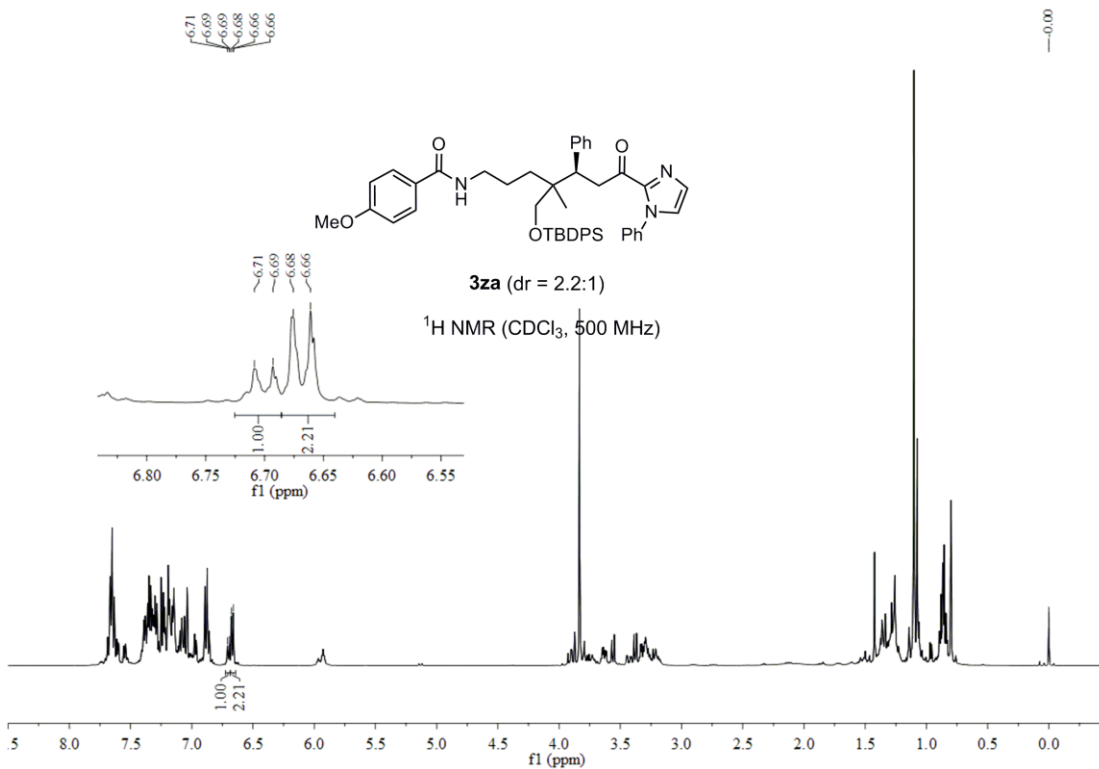


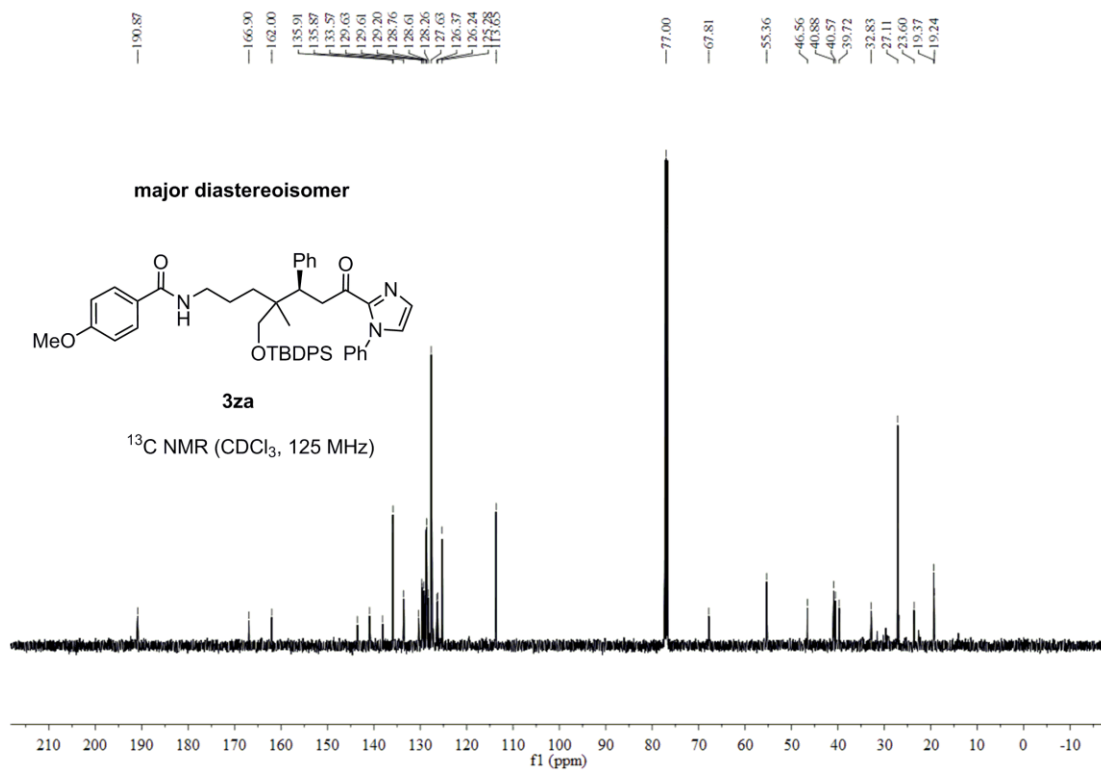


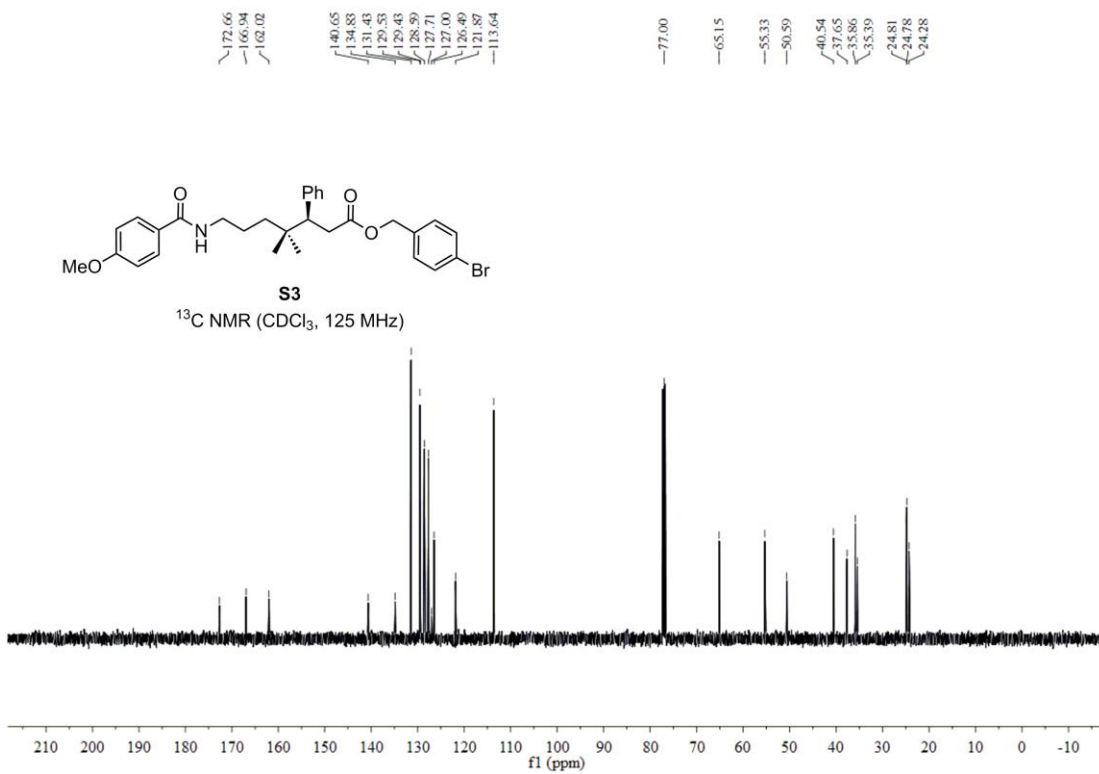
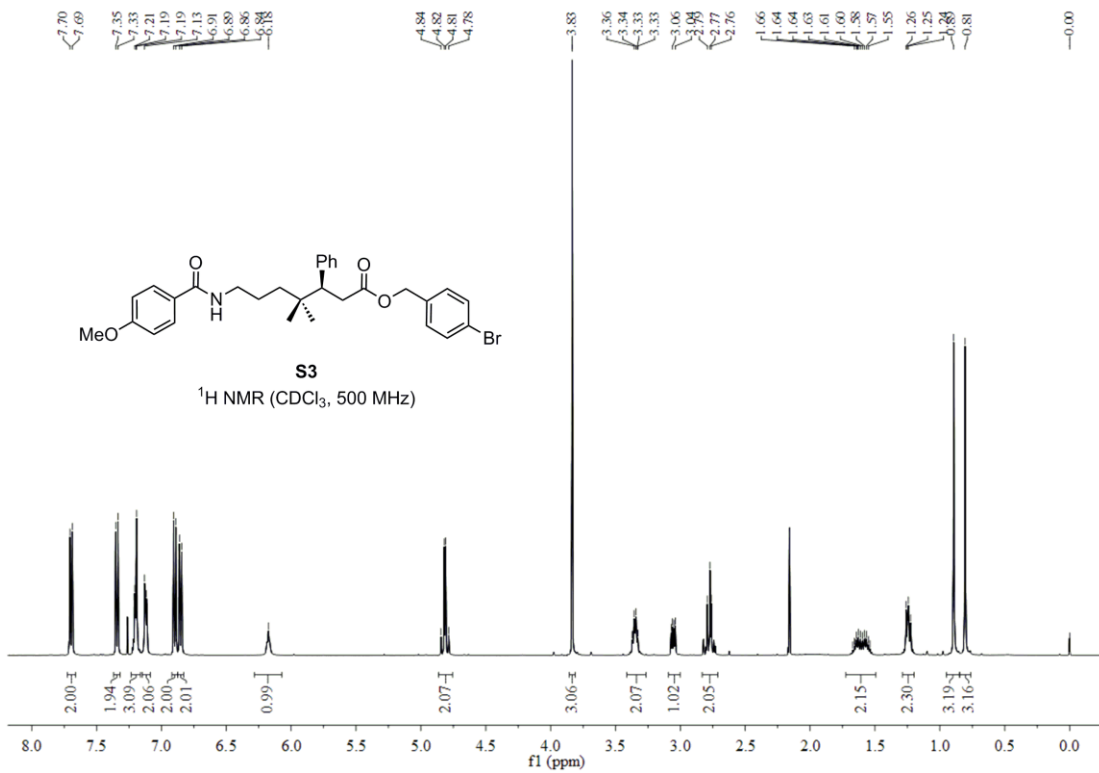






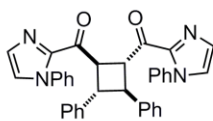






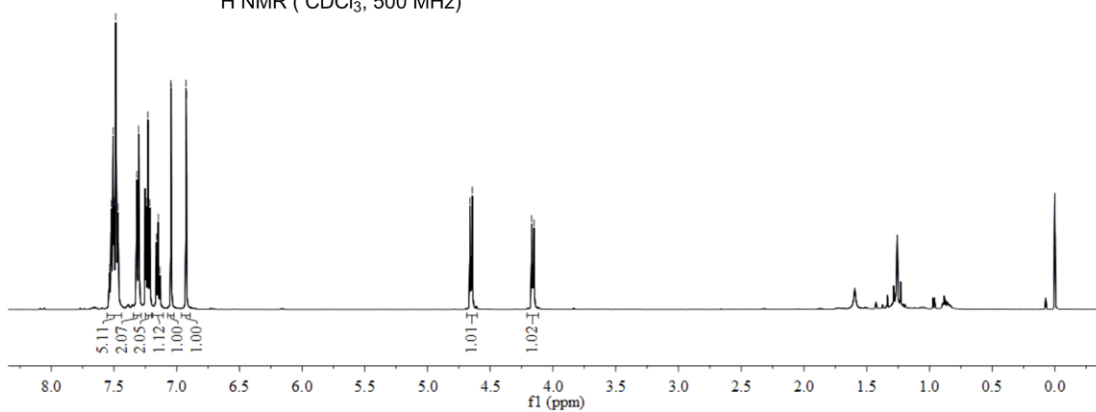
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.47
7.32
7.30
7.24
7.23
7.21
7.16
7.15
7.04
7.04
6.92
4.86
4.65
4.64
4.17
4.16
4.16
4.15

—0.00



S6

¹H NMR (CDCl₃, 500 MHz)



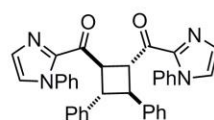
—188.87

143.08
141.97
138.47
129.36
129.06
128.67
128.33
127.28
126.71
126.54
125.82

—77.00

—50.51

—43.23



S6

¹³C NMR (CDCl₃, 125 MHz)

