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Supporting Information

Chiral polycyclic benzosultams from photocatalytic diastereo- and enantioselective benzylic C-H functionalization

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Supplementary Methods

1. General Information

Synthesis of the substrates were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Visible-light photocatalytic reactions were performed in 10 mL Schlenk tubes at the indicated temperature under an atmosphere of argon and under irradiation with a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm; commercial supplier: Hong Chang Lighting Co. Ltd., website: http://hongchang-led.taobao.com) . 1a–1f¹, 2a–2s^{2–5} and 6a–6f^{2–5} were synthesized according to the published procedures.

All other reagents were purchased from commercial suppliers (TCI, Aldrich, Alfa, Strem, Energy Chemical, Adamas-beta[®] and J&K) and used without further purification. Flash column chromatography were performed with silica gel (300–400 mesh, pH = 6.7-7.0). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM (500 MHz) or Bruker AM (600 MHz) spectrometer at ambient temperature. NMR standards were used as follows: CDCl₃ = 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. Diastereomeric and enantiomeric excess of the products were determined by HPLC analysis on chiral stationary phases. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 T FT-MS and Agilent 1290-G6545XT QTOF instrument using ESI technique. X-ray diffraction data were recorded on a XtaLAB Synergy fourcircle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 293 K, 193 K, 100 K. Emission spectra were recorded on a Hitachi F-7000.

2. Synthesis of the Substrates and Racemic Products

2.1 Synthesis of the Substrates

Substrates 1d, 2c, 2d, 2g, 2h, 2i and 2k-2o were prepared by published procedures and other substrates are same as reported in literatures¹⁻⁵.

Synthesis of neopentyl benzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (1d)



Scheme S1. Synthetic route to **1d**.Neopentyl 2-(2-hydroxyphenyl)-2-oxoacetate was synthesized according to a modified procedure¹. To a solution of neopentyl 2-(2-hydroxyphenyl)-2-oxoacetate (**S1d**, 6.56 g, 27.8 mmol, 1 equiv.) in 50.0 mL of *N*,*N*-Dimethylaniline (DMA), NH₂SO₂Cl (11.2 g, 97.1 mmol, 3.5 equiv.) was quickly added. The mixture was stirred for 1 h, then NaH (60% in mineral oil, 3.88 g, 97.1 mmol, 3.5 equiv.) was added in 3 potions in 2 h. The resulting suspension was stirred at room temperature for 2 h, then heated to 50 °C and stirred for additional 12 h. The reaction was quenched by the addition of 50 mL of H₂O, extracted with diethyl ether (Et₂O, 50 mL × 3). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether / ethyl acetate (EtOAc) = 10:1) to afford **1d** as a white solid (5.3 g, 19.7 mmol, yield: 71%).

neopentyl benzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (1d)



¹H NMR (500 MHz, CDCl₃) δ 7.97 (dd, J = 8.0, 1.6 Hz, 1H), 7.79 (ddd, J = 8.7, 7.5,

1.5 Hz, 1H), 7.43 (td, J = 7.8, 1.2 Hz, 1H), 7.36 (dd, J = 8.4, 1.1 Hz, 1H), 4.16 (s, 2H),
1.04 (s, 9H).
¹³C NMR (126 MHz, CDCl₃) δ 165.32, 160.98, 154.82, 138.04, 130.06, 126.25, 119.20,
113.66, 31.74, 26.28.
IR (film): v (cm⁻¹) 3411, 2964, 1740, 1598, 1556, 1402, 1231, 1190, 1018, 935, 863,
755, 610, 569.

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{30}N_2NaO_{10}S_2$ (2M+Na)⁺: 617.1234, found: 617.1228.

Synthesis of (3-chloropropyl)benzene derivatives 2c and 2d



Scheme S2. Synthetic route to substrates 2c and 2d.

To a stirring solution of **S2c** or **S2d** (10.0 mmol) in anhydrous THF (50 mL) at 0 °C was added LiAlH₄ (0.76 g, 20.0 mmol) in portions. The mixture was heated, and then refluxed at 70 °C for 5 h in Ar. After cooling down in ice-bath, water was added carefully until H₂ evolvement ceased. The suspension was filtered through celite, and the filtrate was collected, concentrated to dryness to give the crude alcohol derivate (**S3c** or **S3d**).

Subsequently, a flame-dried flask equipped with a stir bar was charged with crude **S3c** or **S3d** (10 mmol) and CCl₄ (3.23 g, 21.0 mmol) under argon. Anhydrous CH₂Cl₂ (100 mL) was added and the mixture was placed in an ice bath and stirred for 10 minutes at 0 °C. PPh₃ (5.24 g, 20.0 mmol) was added dropwise at 0 °C. The ice bath was then removed, and the mixture was stirred at room temperature for 12 h. The reaction was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (petroleum ether/ EtOAc=10:1) to give pure alkyl chloride (**2c** or **2d**).

1-(3-chloropropyl)-4-isopropylbenzene



According to the 2-step procedure, **2c** was obtained as a colorless oil (0.82 g, 4.2 mmol, overall yield: 42%).

¹H NMR (500 MHz, CDCl₃) δ 7.19 – 7.04 (m, 4H), 3.51 (t, *J* = 6.5 Hz, 2H), 2.87 (s, 1H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.06 (dq, *J* = 8.3, 6.6 Hz, 2H), 1.23 (d, *J* = 7.0 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 146.63, 137.94, 128.42, 126.47, 44.27, 34.05, 33.68, 32.31, 24.02.

IR (film): v (cm⁻¹) 3359, 2955, 2931, 1903, 1479, 1611, 1512, 1492, 1469, 1409, 1309, 1239, 1177, 1016, 966, 833, 738, 649, 575.

HRMS (ESI-TOF, m/z) calcd for C₁₂H₁₈Cl (M+H)⁺: 197.1092, found: 197.1082.

1,4-bis(3-chloropropyl)benzene



According to the 2-step procedure, **2d** was obtained as a white solid (0.83 g, 3.6 mmol, overall yield: 36%).

¹H NMR (500 MHz, CDCl₃) δ 7.13 (s, 4H), 3.53 (t, *J* = 6.5 Hz, 4H), 2.75 (dd, *J* = 8.1,

6.8 Hz, 4H), 2.08 (dq, *J* = 8.4, 6.5 Hz, 4H).

¹³C NMR (151 MHz, CDCl₃) δ 139.16, 128.29, 61.90, 34.06, 31.49.

IR (film): v (cm⁻¹) 3336, 2936, 2862, 1654, 1513, 1451, 1158, 1057, 843, 913, 804.

HRMS (ESI, m/z) calcd for C₁₂H₁₆Cl₂Na (M+Na)⁺: 253.0521, found: 253.0519.

Synthesis of (3-chloropropyl)benzene derivatives 2g and 2h



Scheme S3. Synthetic route to substrates 2g and 2h.

A 100 mL round bottom flask was charged with copper (I) iodide (0.19 g, 1.0 mmol), picolinic acid (0.25 g, 2.0 mmol), 3-(4-hydroxyphenyl)propanoic acid (**S4**, 1.99 g, 12 mmol), aryl iodide (**S5g** or **S5h**, 10 mmol), potassium phosphate (4.25 g, 20 mmol) and DMSO (30 mL). The reaction mixture in an argon atmosphere was stirred at 100 °C until complete reaction, then cooled and diluted with a saturated aqueous solution of ammonium chloride (20 mL) and water (20 mL). The resulting mixture was extracted with methylene chloride (100 mL \times 2). The combined organic extracts were washed with a 5% aqueous solution of potassium hydroxide (20 mL), brine (20 mL), dried over anhydrous sodium sulfate, and concentrated to dryness. The residue was purified by flash column chromatography to give the carboxylic acid (**S6g** or **S6h**).

To the stirring solution of **S6g** or **S6h** (10 mmol) in 50 mL anhydrous THF at 0 °C was added LiAlH₄ (0.76 g, 20 mmol) in portions. The solution was warmed to room temperature and refluxed at 70 °C for 12 h in argon. After cooling down in ice-bath, water was added carefully until H₂ evolvement ceased. The resulting mixture was filtered through celite, and the filtrate was evaporated under reduced pressure to yield the corresponding alcohol (**S7g** or **S7h**).

A flame-dried flask equipped with a stir bar was charged with S7g or S7h (10 mmol)

and CCl₄ (3.23 g, 21 mmol) under argon. Anhydrous CH₂Cl₂ (100 mL) was added, and the mixture was stirred at 0 °C for 10 minutes. PPh₃ (5.24 g, 20 mmol) was added dropwise at 0 °C. The ice bath was removed, and the reaction stirred for 12 h at room temperature, then concentrated under reduced pressure. The residue was purified by silica gel chromatography to afford the product (**2g** or **2h**).

1-(3-chloropropyl)-4-phenoxybenzene



According to the 3-step procedure, **2g** was obtained as a white solid (0.62 g, 2.5 mmol, overall yield: 25%).

¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.30 (m, 2H), 7.20 – 7.15 (m, 2H), 7.14 – 7.07 (m, 1H), 7.05 – 6.99 (m, 2H), 7.00 – 6.94 (m, 2H), 3.55 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.10 (dq, *J* = 8.4, 6.5 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 157.47, 155.43, 135.56, 129.73, 129.67, 123.01, 119.05, 118.59, 44.12, 34.07, 31.97.

IR (film): v (cm⁻¹) 3414, 2929, 2433, 1891, 1590, 1506, 1489, 1238, 1166, 1101, 1072, 1022, 972, 871, 754, 691, 555.

HRMS (ESI-TOF, m/z) calcd for C₁₅H₁₅ClNaO (M+Na)⁺: 269.0704, found: 269.0715.

1-(tert-butyl)-4-(4-(3-chloropropyl)phenoxy)benzene



According to the 3-step procedure, **2h** was obtained as a white solid (8.2 g, 2.8 mmol, overall yield: 28%).

¹H NMR (600 MHz, CDCl₃) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.95 (dd, *J* = 8.7, 7.6 Hz, 4H), 3.55 (t, *J* = 6.5 Hz, 2H), 2.77 (d, *J* = 7.5 Hz, 2H), 2.12 – 2.07 (m, 2H), 1.34 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 155.78, 154.93, 145.90, 135.23, 129.65, 126.47, 118.79, 118.16, 44.13, 34.25, 34.09, 31.96, 31.47.

IR (film): v (cm⁻¹) 3412, 2961, 2404, 2041, 1891, 1772, 1599, 1505, 1461, 1393, 1242, 1173, 1109, 1014, 972, 876, 831, 725, 653, 547.

HRMS (ESI-TOF, m/z) calcd for C₁₉H₂₃ClNaO (M+Na)⁺: 325.1330, found: 325.1341.

Synthesis of (3-chloropropyl)benzene derivative 2i



Scheme S4. Synthetic route to substrate 2i.

A mixture of 3-(4-hydroxyphenyl)propanoic acid (S4, 1.66 g, 10 mmol), *tert*butyldimethylsilyl chloride (S8, 1.81 g, 12 mmol) and imidazole (1.70 g, 25 mmol) in DMF (10 mL) was stirred at room temperature for 12 h. The resulting mixture was filtered through celite, and the filtrate was concentrated to dryness under reduced pressure to yield the crude carboxylic acid (S9).

To the stirring solution of 3-(4-((tert-butyldimethylsilyl)oxy)phenyl)propanoic acid (**S9**, 2.80 g, 10 mmol) in anhydrous THF (50 mL) at 0 °C was added LiAlH₄ (0.76 g, 20 mmol) in portions. The mixture was warmed to room temperature, and then refluxed at 70 °C for 5 h in argon. After cooling down in ice-bath, water was added carefully until H₂ evolvement ceased. The resulting mixture was filtered through celite, and the filtrate was concentrated to dryness under reduced pressure to yield the crude alcohol (**S10**).

A flame-dried flask equipped with a stir bar was charged with crude 3-(4-((tert-

butyldimethylsilyl)oxy)phenyl)propan-1-ol (**S10**, 2.67 g, 10 mmol) and CCl₄ (3.23 g, 21 mmol) under argon. Anhydrous CH₂Cl₂ (100 mL) was added. The mixture under argon was stirred at 0 °C for 10 minutes. PPh₃ (5.24 g, 20 mmol) was added dropwise at 0 °C. The ice bath was removed and the reaction was stirred at room temperature for 12 h. The resulting mixture was concentrated to dryness, and the residue was purified by silica gel chromatography to afford product **2i** as a white solid (4.00 g, 1.16 mmol, overall yield: 41%).

tert-butyl(4-(3-chloropropyl)phenoxy)dimethylsilane



¹H NMR (500 MHz, CDCl₃) δ 7.13 – 6.96 (m, 2H), 6.86 – 6.67 (m, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.72 (d, *J* = 7.4 Hz, 2H), 2.06 (dd, *J* = 8.0, 6.6 Hz, 2H), 1.01 (s, 9H), 0.21 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 153.89, 133.25, 129.35, 119.97, 44.17, 34.18, 31.90, 25.67, 18.16, -4.46.

IR (film): v (cm⁻¹) 3410, 2956, 1885, 1610, 1510, 1472, 1362, 1258, 1169, 1099, 915, 839, 780, 688, 534.

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{25}CINaOSi$ (M+Na)⁺: 307.1255, found: 307.1231.

Synthesis of (3-chloropropyl)benzene derivatives 2k-2o



Scheme S5. Synthetic route to the Substrates 2k–2o.

A mixture of **S11k–S11o** (21 mmol), 3-(4-hydroxyphenyl)propanoic acid (**S4**, 1.67 g, 10 mmol) and K_2CO_3 (3.04 g, 22 mmol) in Acetone (50 mL) was stirred at 80 °C for 12 h. The resulting mixture was filtered through celite, and the filtrate was concentrated to dryness under reduced pressure to yield the crude product **S12k–S12o**.

To the stirring solution of **S12k–S12o** (10 mmol) in anhydrous THF (50 mL) at 0 °C was added LiAlH₄ (0.76 g, 20 mmol) in portions. The mixture was warmed to room temperature, and then refluxed at 70 °C for 5 h in argon. After cooling down in ice-bath, water was added carefully until H₂ evolvement ceased. The resulting mixture was filtered through celite, and the filtrate was concentrated to dryness under reduced pressure to yield the crude **S13k–S13o**.

A flame-dried flask equipped with a stir bar was charged with crude **S13k–S13o** (10 mmol), CCl₄ (3.23 g, 21 mmol), anhydrous CH₂Cl₂ (100 mL). The mixture under argon was stirred at 0 °C for 10 minutes. PPh₃ (5.24 g, 20 mmol) was added dropwise at 0 °C. The ice bath was removed and the reaction was stirred at room temperature for 12 h. The resulting mixture was concentrated to dryness, and the residue was purified by silica gel chromatography to afford product 2k-2o.

4-((4-(3-chloropropyl)phenoxy)methyl)-1,1'-biphenyl



According to the 3-step procedure, **2k** was obtained as a white solid (0.97 g, 2.9 mmol, overall yield: 29%).

¹H NMR (600 MHz, CDCl₃) δ 7.65 – 7.58 (m, 4H), 7.53 – 7.49 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.16 – 7.11 (m, 2H), 6.97 – 6.92 (m, 2H), 5.09 (s, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.06 (dq, *J* = 8.2, 6.6 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 157.21, 140.91, 140.78, 136.11, 133.04, 129.49, 128.77, 127.94, 127.34, 127.10, 114.85, 69.80, 44.21, 34.18, 31.82.

IR (film): v (cm⁻¹) 3357, 2929, 2339, 1912, 1609, 1580, 1511, 1445, 1407, 1382, 1240, 1177, 1110, 1075, 1010, 911, 878, 750, 652, 551.

HRMS (ESI-TOF, m/z) calcd for C₂₂H₂₁ClNaO (M+Na)⁺: 359.1173, found: 359.1163.

1-(3-chloropropyl)-4-((4-fluorobenzyl)oxy)benzene



According to the 3-step procedure, **2l** was obtained as a white solid (0.50 g, 1.8 mmol, overall yield: 18%).

¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.38 (m, 2H), 7.15 – 7.10 (m, 2H), 7.11 – 7.04 (m, 2H), 6.93 – 6.88 (m, 2H), 5.01 (s, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.11 – 2.01 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 162.46 (d, J_{C-F} = 246.1 Hz), 157.03, 133.17, 132.86 (d, J = 3.2 Hz), 129.50, 129.28 (d, J = 8.2 Hz), 115.44 (d, J = 21.4 Hz), 114.84, 69.37, 44.17, 34.16, 31.81.

IR (film): v (cm⁻¹) 3422, 2929, 1885, 1609, 1512, 1463, 1378, 1297, 1226, 1176, 1014,

872, 825, 762, 650, 576.

HRMS (ESI-TOF, m/z) calcd for C₁₆H₁₇ClFO (M+H)⁺: 279.0946, found: 279.0952.

1-chloro-4-((4-(3-chloropropyl)phenoxy)methyl)benzene



According to the 3-step procedure, **2m** was obtained as a white solid (0.91 g, 3.1 mmol, overall yield: 31%).

¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, J = 1.1 Hz, 4H), 7.11 (d, J = 8.6 Hz, 2H), 6.95 – 6.86 (m, 2H), 5.01 (s, 2H), 3.52 (t, J = 6.5 Hz, 2H), 2.73 (t, J = 7.4 Hz, 2H), 2.10 – 2.01 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.95, 135.65, 133.69, 133.25, 129.52, 128.73, 114.85, 69.26, 44.17, 34.16, 31.81.

IR (film): v (cm⁻¹) 3359, 2931, 1903, 1611, 1512, 1409, 1381, 1239, 1177, 1016, 966, 814, 738, 649, 575.

HRMS (ESI-TOF, m/z) calcd for C₁₆H₁₆C₁₂NaO (M+Na)⁺: 317.0470, found: 317.0488.

1-bromo-4-((4-(3-chloropropyl)phenoxy)methyl)benzene



According to the 3-step procedure, **2n** was obtained as a white solid (0.95 g, 2.8 mmol, overall yield: 28%).

¹H NMR (500 MHz, CDCl₃) δ 7.53 – 7.48 (m, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.14 – 7.09 (m, 2H), 6.91 – 6.86 (m, 2H), 5.00 (s, 2H), 3.38 (t, J = 6.6 Hz, 2H), 2.72 (t, J = 7.3 Hz, 2H), 2.13 (m, J = 6.8 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 156.95, 136.17, 133.10, 131.68, 129.53 (d, *J* = 2.3 Hz), 129.03, 121.79, 114.86, 69.28, 34.29, 33.08, 33.02.

IR (film): v (cm⁻¹) 3362, 2929, 1903, 1653, 1610, 1512, 1405, 1382, 1243, 1176, 1019,

965, 874, 737, 648, 562.

HRMS (ESI-TOF, m/z) calcd for C₁₆H₁₇BrClO (M+H)⁺: 339.0146, found: 339.0144.

1-(3-chloropropyl)-4-((4-(trifluoromethyl)benzyl)oxy)benzene



According to the 3-step procedure, **20** was obtained as a white solid (1.20 g, 3.7 mmol, overall yield: 37%).

¹H NMR (500 MHz, CDCl₃) δ 7.48 – 7.42 (m, 1H), 7.22 (d, J = 8.1 Hz, 1H), 7.14 – 7.09 (m, 1H), 6.94 – 6.87 (m, 2H), 5.03 (s, 1H), 3.51 (t, J = 6.5 Hz, 1H), 2.72 (t, J = 7.4 Hz, 1H), 2.04 (dq, J = 8.2, 6.5 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 156.94, 148.82, 135.86, 133.31, 129.54, 128.79, 121.07, 114.81, 69.13, 44.15, 34.15, 31.81.

IR (film): v (cm⁻¹) 3032, 2934, 2867, 2477, 1902, 1612, 1512, 1462, 1380, 1262, 1175, 1107, 1018, 972, 829, 721, 652, 619.

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{17}ClF_3O$ (M+H)⁺: 329.0915, found: 329.0927.

2.2 Synthesis of the Racemic Compounds

2.2.1 Synthesis of Racemic Compounds rac-3a-3x.



Scheme S6. Synthesis of the racemic reference compounds rac-3a-3x

Preparation of a 0.01 M Solution of Racemic Metal Catalyst [*rac*-L1-Ni] in CHCl₃: A solution of nickel bromide (4.4 mg, 0.020 mmol) and a racemic ligand (*rac*-L1, 7.4 mg, 0.022 mmol) in CHCl₃ (4.0 mL) was stirred at 70 °C for 1 h, which was used freshly

for the following photochemical reactions.

General procedure A. A dried 10 mL Schlenk tube was charged with 1a–1f (0.20 mmol), 2a–2s (0.60 mmol), PC1 (3.40 mg, 0.010 mmol), a racemic catalyst [*rac*-L1-Ni] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for the 10–29 h (monitored by TLC analysis), the reaction mixture was concentrated to dryness, and the residue was purified by flash chromatography on silica gel (eluted with PE:EtOAc = 10:1) to afford racemic product *rac*-3a–3x as HPLC reference for the determination of diastereomeric and enantiomeric excess.

2.2.2 Synthesis of the Racemic Compounds rac-7a-7k.



Scheme S7. Synthesis of the racemic reference compounds rac-7a-7k

Preparation of a 0.01 M Solution of Racemic Metal Catalyst [*rac***-L1-Ni**] **in CHCl**₃: A solution of nickel bromide (4.4 mg, 0.020 mmol) and a racemic ligand (*rac***-L1**, 7.4 mg, 0.022 mmol) in CHCl₃ (4.0 mL) was stirred at 70 °C for 1 h, which was used freshly for the following photochemical reactions.

General procedure B. A dried 10 mL Schlenk tube was charged with 1a–1f (0.20 mmol), 6a–6f (0.60 mmol), PC1 (3.40 mg, 0.010 mmol), racemic catalyst [*rac*-L1-Ni] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for the 24–96 h (monitored by TLC analysis), the reaction mixture was concentrated to dryness, and the residue was purified by flash chromatography on silica gel (eluted with PE:EtOAc = 10:1) to afford racemic product 7a–7k as HPLC reference for the determination of diastereomeric enantiomeric excess.

3. Photocatalytic Diastereo- and Enantioselective C-H

Functionalization/Cyclization Cascade Reactions

3.1 Reaction Optimization

Preparation of a 0.01 M Solution of the Non Racemic Metal Catalyst [L*-M] in CHCl₃:

A solution of metal salt (0.020 mmol) and a chiral ligand (L1–L7, 0.022 mmol) in CHCl₃ (4.0 mL) was stirred at 70 °C for 1 h, which was used freshly for the following photochemical reactions.

General Procedure for Reaction Optimization: A dried 10 mL Schlenk tube was charged with (3-chloropropyl)benzene (1a, 0.20 mmol), 2a (0.60 mmol), photocatalyst (PC1–PC3, 0.010 mmol), metal catalyst [L*-M] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at the indicated temperature for the indicated time, the reaction mixture was concentrated to dryness. The conversion was determined by ¹H NMR analysis of the crude productand *ee* value was determined by chiral HPLC chromatography using a Daicel Chiralpak AD-H column. *dr* value was determined by ¹H NMR and chiral HPLC chromatography using a Daicel Chiralpak AD-H column. *dr* value was determined by which were consistent with each other.

Table S1. Optimization of reaction conditions.



PC1

Ο



Br HO Br Br Br Br Br Br Br

entry	metal salt	ligand	solvent	HAT	Т	t	conv.	dr	ee
				PC	(°C)	(h)	$(\%)^{b}$		(%)°
1	Ni(ClO ₄) ₂ ·6H ₂ O	L1	CHCl ₃	PC1	20	20	72	7:1	91/91
2	$Cu(ClO_4)_2 \cdot 6H_2O$	L1	CHCl ₃	PC1	20	20	73	3:1	-19/-19
3	$Co(ClO_4)_2 \cdot 6H_2O$	L1	CHCl ₃	PC1	20	20	67	9:1	84/84
4	Mg(ClO ₄) ₂	L1	CHCl ₃	PC1	20	20	trace	n.a.	n.a.
5	$Zn(ClO_4)_2$	L1	CHCl ₃	PC1	20	20	13	n.d.	n.d.
6	Ni(acac) ₂	L1	CHCl ₃	PC1	20	20	67	4:1	79/84
7	NiCl ₂	L1	CHCl ₃	PC1	20	20	73	6:1	93/92
8	NiBr ₂	L1	CHCl ₃	PC1	20	20	70	8:1	93/74
9	Ni(NO ₃) ₂	L1	CHCl ₃	PC1	20	20	68	12:1	94/92
10	Ni(OAc) ₂	L1	CHCl ₃	PC1	20	20	60	18:1	91/91
11	Ni(BF ₄) ₂	L1	CHCl ₃	PC1	20	20	80	2:1	47/51
12	NiBr ₂	L1	CHCl ₃	PC2	20	20	0	n.a.	n.a.
13	NiBr ₂	L1	CHCl ₃	PC3	20	20	0	n.a.	n.a.

14	NiBr ₂	L2	CHCl ₃	PC1	20	20	60	2:1	66/45
15	NiBr ₂	L3	CHCl ₃	PC1	20	20	39	8:1	1/5
16	NiBr ₂	L4	CHCl ₃	PC1	20	20	trace	n.d.	n.d.
17	NiBr ₂	L5	CHCl ₃	PC1	20	20	39	12:1	92/91
18	NiBr ₂	L6	CHCl ₃	PC1	20	20	61	10:1	23/7
19	NiBr ₂	L7	CHCl ₃	PC1	20	20	56	8:1	5/1
20	NiBr ₂	L1	CHCl ₃	PC1	20	43	54	5:1	74/88
21	NiBr ₂	L1	CHCl ₃	none	20	20	0	n.a.	n.a.
22	None	none	CHCl ₃	PC1	20	20	trace	n.d.	n.d.
23 ^{<i>d</i>}	NiBr ₂	L1	CHCl ₃	PC1	20	20	0	n.a.	n.a.
24 ^e	NiBr ₂	L1	CHCl ₃	PC1	20	20	0	n.a.	n.a.
25	NiBr ₂	L1	DCM	PC1	20	20	67	8:1	89/88
26	NiBr ₂	L1	DCE	PC1	20	20	90	2:1	89/86
27	NiBr ₂	L1	MeCN	PC1	20	20	0	n.a.	n.a.
28	NiBr ₂	L1	MeOH	PC1	20	20	0	n.a.	n.a.

^{*a*}Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), metal salt (10 mol%), ligand (11 mol%), Na₂CO₃(31.8 mg, 0.30 mmol), CHCl₃ (4.0 mL), indicated temperature, 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm), under argon. ^{*b*} conversion and *dr* determined by ¹H-NMR. ^{*c*}*ee* value determined by chiral HPLC. ^{*d*} in the dark. ^{*e*} in air. n.a. = not applicable. n.d. = not determined.

3.2 Substrate Scope for the Reaction of *N*-Sulfonylimines and (3-Chloropropyl)benzene Derivatives

Preparation of a 0.01 M Solution of the *Non-Racemic* Nickel Catalyst [L1-Ni] in CHCl₃: A solution of nickel bromide (4.4 mg, 0.020 mmol) and a *non-racemic* ligand L1 (7.4 mg, 0.022 mmol) in CHCl₃ (4.0 mL) was stirred at 70 °C for 1 h, which was used freshly for the following photochemical reactions.



Scheme S8. Photocatalytic asymmetric C-H functionalization/cyclization cascade reactions to *non-racemic* products **3a–3x**.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2a** (92.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 20 h, the reaction mixture was concentrated to dryness, and the residue was purified by flash chromatography on silica gel (eluted with PE:CH₃CO₂H = 50:1) to afford product **3a** as a colorless oil (45.5 mg, 0.12 mmol, 61% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak AD-H column, *dr* = 8:1 by ¹H NMR, *ee* = 93/74% (HPLC: AD-H, 220 nm, *n*-hexane:isopropanol = 97:3, flow rate: 0.5 mL/min, 30 °C, t_r(minor) = 31.2 min, t_r(major) = 57.2 min). [α]_D²³ = +34.7° (*c* = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.61 (dd, J = 8.0, 1.6 Hz, 0.14H), 7.40 – 7.35 (m, 0.51H), 7.35 (td, J = 3.5, 1.4 Hz, 0.34H), 7.33 (dd, J = 6.7, 2.0 Hz, 0.96H), 7.32 – 7.26 (m, 1.77H), 7.22 (ddd, J = 8.3, 7.3, 1.6 Hz, 0.94H), 7.03 (dd, J = 8.2, 1.3 Hz, 0.20H), 6.97 (td, J = 7.9, 1.5 Hz, 2.67H), 6.73 (ddd, J = 8.5, 7.4, 1.4 Hz, 0.88H), 6.09 (dd, J = 8.1, 1.6 Hz, 0.90H), 4.42 – 4.29 (m, 2.75H), 4.08 (ddd, J = 9.8, 7.2, 2.9 Hz, 0.17H), 4.01 – 3.94 (m, 0.98H), 3.89 (td, J = 10.3, 6.9 Hz, 0.94H), 3.79 (dd, J = 10.1, 6.8 Hz, 0.15H), 3.64 (td, J = 9.6, 6.5 Hz, 0.14H), 2.57 (dtd, J = 12.7, 9.9, 7.2 Hz, 0.16H), 2.28 – 2.15 (m, 2.01H), 1.33 (t, J = 7.1 Hz, 2.69H), 1.04 (t, J = 7.1 Hz, 0.33H). ¹³C NMR (151 MHz, CDCl₃) δ 170.22, 151.88, 134.84, 131.81, 129.85, 128.93, 128.54, 128.47, 123.14, 118.26, 116.75, 76.21, 62.82, 55.73, 49.25, 28.11, 14.05. IR (film): v (cm⁻¹) 3423, 2029, 1739, 1638, 1401, 1202, 1175, 1025, 760, 639, 564. HRMS (ESI-TOF, m/z) calcd for C₁₉H₁₉NNaO₅S (M+Na)⁺: 396.0876, found: 396.0875.



Dimeric compound **5** was isolated as a side-product (white solid, 29.8 mg, 0.040 mmol, 20% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.93 (dd, J = 8.0, 1.6 Hz, 2H), 7.44 (td, J = 7.7, 1.6 Hz, 2H), 7.42 – 7.39 (m, 4H), 7.39 – 7.36 (m, 2H), 7.34 (dd, J = 10.3, 7.2 Hz, 4H), 7.11 (dd, J = 8.1, 1.4 Hz, 2H), 6.27 (s, 2H), 4.22 – 4.16 (m, 2H), 4.03 (t, J = 7.2 Hz, 4H), 3.51 (ddd, J = 11.0, 4.7, 3.4 Hz, 2H), 3.04 (td, J = 11.5, 3.3 Hz, 2H), 2.50 (ddt, J = 15.4, 12.2, 3.4 Hz, 2H), 2.09 – 2.00 (m, 2H), 1.17 (t, J = 7.1 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 169.50, 150.99, 135.16, 130.95, 130.02, 128.96, 128.68, 128.46, 126.32, 119.93, 119.42, 71.43, 64.07, 49.73, 43.04, 31.85, 13.75.

IR (film): v (cm⁻¹) 2921, 2331, 1735, 1661, 1506, 1458, 1253, 1112, 1023, 902, 860, 735, 641, 562.

HRMS (ESI-TOF, m/z) calcd for $C_{38}H_{38}N_2NaO_{10}S_2$ (M+Na)⁺: 769.1860, found: 769.1862.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2b** (126.0 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 14 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3b** as a colorless oil (54.1 mg, 0.126 mmol, 63% yield). Enantiomeric excess were established by HPLC analysis using a Guangzhou FLM Scientific Instrument Co.Ltd FMG-AC5-B01-NFC Chiralpak column, *dr* > 20:1 by ¹H NMR, *ee* = 92/63% (HPLC: FMG-AC5-B01-NFC, 240 nm, *n*-hexane:isopropanol = 97:3, flow rate: 0.5 mL/min, 30 °C, t_r(minor) = 26.3 min, t_r(major) = 36.2 min). [α]_D²³ = +48.4° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.28 (m, 2H), 7.21 (ddd, J = 8.7, 7.3, 1.6 Hz, 1H), 6.96 (dd, J = 8.3, 1.3 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.70 (td, J = 7.7, 1.3 Hz, 1H), 6.06 (dd, J = 8.1, 1.6 Hz, 1H), 4.37 (m, J = 14.2, 7.1, 3.5 Hz, 2H), 4.33 – 4.26 (m, 1H), 3.95 (ddd, J = 11.0, 8.1, 2.9 Hz, 1H), 3.92 – 3.82 (m, 1H), 2.19 (ddd, J = 11.9, 5.3, 2.2 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.32 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 170.25, 151.92, 151.78, 131.97, 131.57, 129.77, 128.62, 125.38, 123.02, 118.16, 116.75, 76.19, 62.75, 55.41, 34.59, 28.07, 14.07.
IR (film): v (cm⁻¹) 3428, 1637, 1403, 1176, 797, 639,572.

HRMS (ESI-TOF, m/z) calcd for C₂₃H₂₈NO₅S (M+H)⁺: 430.1683, found: 430.1688.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2c** (117.7 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 18 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3c** as a colorless oil (34.9 mg, 0.0840 mmol, 42% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak AD-H column, *dr* = 3.9:1 by ¹H NMR, *ee* = 98/93% (HPLC: AD-H, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 7.7 min, t_r(major) = 10.5 min). [α]_D²³ = +20.0° (*c* = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.63 (dd, J = 8.0, 1.6 Hz, 0.25H), 7.34 (m, J = 8.4, 7.3, 1.7 Hz, 0.37H), 7.24 (d, J = 1.6 Hz, 2.08H), 7.15 (d, J = 7.9 Hz, 1.44H), 7.02 (dd, J = 8.2, 1.3 Hz, 0.27H), 6.97 (dd, J = 8.2, 1.3 Hz, 0.71H), 6.87 (d, J = 7.9 Hz, 1.42H), 6.77 – 6.64 (m, 0.70H), 6.07 (dd, J = 8.1, 1.6 Hz, 0.67H), 4.47 – 4.21 (m, 2.21H), 4.07 (m, 0.26H), 3.95 (ddd, J = 11.0, 8.6, 2.2 Hz, 0.97H), 3.88 (td, J = 10.4, 7.0 Hz, 0.93H), 3.77 (dd, J = 10.3, 6.8 Hz, 0.23H), 3.62 (td, J = 9.6, 6.4 Hz, 0.21H), 2.91 (p, J = 6.8 Hz, 0.94H), 2.55 (ddt, J = 12.7, 10.0, 5.0 Hz, 0.22H), 2.32 – 2.05 (m, 1.78H), 1.34 (t, J = 7.1 Hz, 2.57H), 1.26 (d, J = 2.5 Hz, 2.96H), 1.25 (d, J = 2.4 Hz, 2.72H), 1.01 (t, J = 7.1 Hz, 0.66H).

¹³C NMR (151 MHz, CDCl₃) δ 170.25, 151.90, 149.45, 149.30, 131.97, 129.77, 128.87, 126.53, 123.03, 118.16, 116.72, 76.18, 62.76, 55.49, 49.25, 33.76, 28.07, 23.93, 14.06. IR (film): v (cm⁻¹) 2961, 1741, 1576, 1482, 1403, 1205, 1175, 1109, 1021, 912, 865, 760, 664, 603.

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{25}NNaO_5S$ (M+Na)⁺: 438.1346, found: S23

438.1338.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2d** (138.0 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 17 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3d** as a yellow oil (60.2 mg, 0.134 mmol, 67% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IA column, *dr* = 19:1 by ¹H NMR, *ee* = 92/94% (HPLC: IA, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 0.5 mL/min, 30 °C, t_r(minor) = 19.3 min, t_r(major) = 27.6 min). [α]_D²³ = +14.1° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.22 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 7.12 (d, J = 7.9 Hz, 2H), 6.97 (dd, J = 8.3, 1.3 Hz, 1H), 6.88 (d, J = 7.8 Hz, 2H), 6.72 (ddd, J = 8.4, 7.4, 1.4 Hz, 1H), 6.09 (dd, J = 8.1, 1.7 Hz, 1H), 4.42 – 4.25 (m, 3H), 3.96 (ddd, J = 11.1, 8.8, 2.5 Hz, 1H), 3.88 (td, J = 10.3, 6.9 Hz, 1H), 3.51 (td, J = 6.5, 1.2 Hz, 2H), 2.79 (t, J = 7.4 Hz, 2H), 2.19 (dddd, J = 25.5, 12.8, 8.9, 2.6 Hz, 2H), 2.08 (dq, J = 8.9, 6.9 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.20, 151.86, 141.08, 132.61, 131.78, 129.81, 129.04,
128.66, 123.04, 118.22, 116.76, 76.14, 62.77, 55.45, 49.25, 43.93, 33.79, 32.29, 28.14,
14.03.

IR (film): v (cm⁻¹) 3437, 2918, 1740, 1617, 1445, 1401, 1224, 1174, 1109, 1045, 914, 859, 760, 602, 565.

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{24}CINNaO_5S$ (M+Na)⁺: 472.0956, found: S24

472.0942.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2e** (138.1 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 19 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3e** as a white solid (73.3 mg, 0.164 mmol, 82% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IF column, *dr* = 1.8:1 by ¹H NMR, *ee* = 96/94% (HPLC: IF, 220 nm, *n*-hexane:isopropanol = 95:5, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 23.3 min, t_r(major) = 29.9 min). [α]_D²³ = +42.1° (*c* = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.71 (dt, J = 8.0, 1.9 Hz, 0.41H), 7.65 (ddt, J = 8.5, 4.4, 2.3 Hz, 2.75H), 7.61 – 7.56 (m, 1.29H), 7.53 – 7.47 (m, 2.06H), 7.42 (dddd, J = 22.4, 15.4, 8.2, 1.7 Hz, 2.15H), 7.33 – 7.23 (m, 1.09H), 7.12 – 7.05 (m, 1.63H), 7.02 (dd, J = 8.3, 1.3 Hz, 0.63H), 6.83 – 6.75 (m, 0.63H), 6.27 (dt, J = 8.2, 1.8 Hz, 0.63H), 4.50 – 4.33 (m, 1.97H), 4.13 (ddd, J = 9.7, 7.2, 2.8 Hz, 0.38H), 4.09 – 3.99 (m, 1.02H), 3.94 (dtt, J = 10.4, 6.9, 4.0 Hz, 1.01H), 3.88 (dd, J = 10.1, 6.8 Hz, 0.37H), 3.69 (td, J = 9.5, 6.5 Hz, 0.37H), 2.64 (dtd, J = 12.6, 9.8, 7.2 Hz, 0.37H), 2.37 – 2.18 (m, 1.69H), 1.39 (t, J = 7.1 Hz, 1.92H), 1.09 (t, J = 7.1 Hz, 1.07H).

¹³C NMR (151 MHz, CDCl₃) δ 170.17, 168.16, 151.84, 149.30, 141.32, 141.15, 140.18, 140.04, 135.58, 133.74, 131.82, 130.52, 129.87, 129.64, 129.56, 129.35, 128.84, 127.63, 127.25, 127.01, 126.97, 126.92, 124.94, 123.18, 122.62, 118.54, 118.23, 116.70, 76.15, 62.80, 62.22, 60.72, 55.45, 50.35, 49.22, 31.31, 28.16, 14.03, 13.60.

IR (film): v (cm⁻¹) 3409, 2918, 1740, 1637, 1617, 1485, 1403, 1258, 1174, 912, 852, 765, 697, 535.

HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{23}NNaO_5S$ (M+Na)⁺: 472.1189, found: 472.1179.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2f** (110.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 14 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3f** as a yellow solid (58.9 mg, 0.146 mmol, 73% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak ID column, *dr* = 8:1 by ¹H NMR, *ee* = 90/87% (HPLC: ID, 240 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 24.9 min, t_r(major) = 40.5 min). [α]_D²³ = +10.2° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.59 (dd, J = 8.0, 1.7 Hz, 0.12H), 7.33 (ddd, J = 8.4, 7.3, 1.7 Hz, 0.20H), 7.27 – 7.17 (m, 1.30H), 7.02 (dd, J = 8.2, 1.3 Hz, 0.14H), 6.97 (dd, J = 8.2, 1.4 Hz, 0.82H), 6.93 – 6.89 (m, 0.28H), 6.87 (d, J = 8.7 Hz, 1.63H), 6.84 – 6.80 (m, 1.61H), 6.77 (ddd, J = 8.4, 7.3, 1.4 Hz, 0.83H), 6.15 (dd, J = 8.1, 1.6 Hz, 0.81H), 4.47 – 4.17 (m, 2.55H), 4.07 – 3.96 (m, 0.23H), 3.96 – 3.84 (m, 1.71H), 3.82 (d, J = 2.9 Hz, 2.78H), 3.78 – 3.70 (m, 0.17H), 3.60 (td, J = 9.7, 6.3 Hz, 0.13H), 2.53 (dtd, J = 12.5, 10.2, 7.2 Hz, 0.12H), 2.27 – 1.99 (m, 2.01H), 1.32 (t, J = 7.1 Hz, 2.80H), 1.08 (t, J = 7.1 Hz, 0.33H).

¹³C NMR (126 MHz, CDCl₃) δ 170.23, 159.60, 151.89, 131.93, 129.99, 129.78, 126.52,

123.09, 118.15, 116.70, 113.83, 62.70, 55.25, 55.19, 49.15, 28.24, 14.01.

IR (film): v (cm⁻¹) 3412, 2930, 1740, 1613, 1577, 1482, 1254, 1174, 1029, 863, 762, 604, 563.

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{21}NNaO_6S$ (M+Na)⁺: 426.0982, found: 426.0979.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2g** (147.6 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp (λ_{max} = 455 nm). After being stirred at 20 °C for 16 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3g** as a yellow oil (69.8 mg, 0.150 mmol, 75% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak OZH column, *dr* > 20:1 by ¹H NMR, *ee* = 96/62% (HPLC: OZ-H, 240 nm, *n*-hexane:isopropanol = 90:10, flow rate: 0.50 mL/min, 30 °C, t_r(minor) = 35.9 min, t_r(major) = 72.5 min). [α]_D²³ = +12.2° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.33 (m, 2H), 7.25 (d, J = 7.3 Hz, 1H), 7.13 (s, 1H), 7.04 – 6.88 (m, 7H), 6.84 – 6.77 (m, 1H), 6.22 (dd, J = 8.1, 1.6 Hz, 1H), 4.45 – 4.20 (m, 3H), 3.96 (ddd, J = 11.1, 9.0, 2.3 Hz, 1H), 3.88 (td, J = 10.3, 6.8 Hz, 1H), 2.27 – 2.09 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.19, 157.47, 156.72, 151.92, 131.81, 130.29, 129.87, 129.84, 129.50, 123.66, 123.15, 118.99, 118.62, 118.32, 116.83, 76.15, 62.79, 55.24, 49.27, 28.41, 14.03.

IR (film): v (cm⁻¹) 3469, 1735, 1617, 1508, 1488, 1231, 1174, 1023, 912, 861, 762, 694,

597, 542.

HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{23}NNaO_6S$ (M+Na)⁺: 488.1138, found: 488.1134.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2h** (181.3 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp (λ_{max} = 455 nm). After being stirred at 20 °C for 17 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3h** as a white solid (75.1 mg, 0.144 mmol, 72% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IA column, *dr* > 20:1 by ¹H NMR, *ee* = 92/47% (HPLC: IA, 240 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 13.9 min, t_r(major) = 18.8 min). [α]_D²³ = +42.6° (*c* = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.38 – 7.36 (m, 2H), 7.25 – 7.22 (m, 1H), 7.00 – 6.96 (m, 1H), 6.96 – 6.87 (m, 6H), 6.81 (ddd, J = 8.4, 7.4, 1.3 Hz, 1H), 6.21 (dd, J = 8.1, 1.6 Hz, 1H), 4.41 – 4.27 (m, 3H), 4.00 – 3.84 (m, 2H), 2.22 (dddd, J = 12.4, 6.7, 5.6, 2.2 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.33 (d, J = 4.0 Hz, 12H).

¹³C NMR (151 MHz, CDCl₃) δ 170.20, 157.81, 154.14, 151.92, 146.66, 131.85, 130.21, 129.88, 129.05, 126.66, 123.16, 118.58, 118.35, 118.31, 116.76, 76.13, 62.80, 55.22, 49.24, 34.34, 31.46, 28.35, 14.06.

IR (film): v (cm⁻¹) 3460, 2961, 2375, 1958, 1740, 1576, 1402, 1365, 1243, 1109, 912, 854, 705, 656, 505.

HRMS (ESI-TOF, m/z) calcd for C₂₉H₃₂NO₆S (M+H)⁺: 522.1945, found: 522.1937.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2i** (170.5 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 29 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3i** as a white solid (65.4 mg, 0.130 mmol, 65% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IC column, *dr* > 20:1 by ¹H NMR, *ee* = 97/95% (HPLC: IC, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 44.1 min, t_r(major) = 66.8 min). [α]_D²³ = +46.8° (*c* = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.22 (ddd, J = 8.2, 7.3, 1.6 Hz, 1H), 6.97 (dd, J = 8.3, 1.3 Hz, 1H), 6.81 (d, J = 8.4 Hz, 2H), 6.79 – 6.75 (m, 2H), 6.74 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 6.12 (dd, J = 8.1, 1.6 Hz, 1H), 4.41 – 4.21 (m, 3H), 3.98 – 3.81 (m, 2H), 2.27 – 2.00 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 0.99 (s, 9H), 0.20 (s, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 170.27, 155.91, 151.94, 131.96, 129.95, 129.79, 127.38, 123.04, 120.25, 118.20, 116.75, 76.13, 62.74, 55.27, 49.24, 28.21, 25.67, 18.30, 14.05, -0.02.

IR (film): v (cm⁻¹) 3406, 2929, 2933, 1742, 1616, 1512, 1405, 1262, 1173, 1015, 908, 836, 779, 601, 533.

HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{33}NNaO_6SSi$ (M+Na)⁺: 526.1690, found: 526.1677.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.2 mmol), **2j** (156.1 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 16 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3j** as a white solid (67.0 mg, 0.146 mmol, 73% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IF column, *dr* = 4.4:1 by ¹H NMR, *ee* = 96/95% (HPLC: IF, 240 nm, *n*-hexane:isopropanol = 90:10, flow rate: 0.50 mL/min, 30 °C, t_r(minor) = 36.1 min, t_r(major) = 49.3 min). [α]_D²³ = +56.8° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.59 (dd, J = 8.1, 1.6 Hz, 0.22H), 7.45 – 7.35 (m, 3.88H), 7.36 – 7.29 (m, 1.23H), 7.26 – 7.17 (m, 1.60H), 7.19 – 7.12 (m, 0.29H), 7.00 (dd, J = 8.3, 1.3 Hz, 0.31H), 6.98 (s, 1.18H), 6.92 – 6.82 (m, 3.01H), 6.73 (td, J = 7.8, 7.4, 1.3 Hz, 0.73H), 6.13 (dd, J = 8.2, 1.6 Hz, 0.73H), 5.07 (d, J = 3.8 Hz, 1.80H), 4.42 – 4.17 (m, 2.38H), 4.07 – 3.94 (m, 0.48H), 3.96 – 3.80 (m, 1.64H), 3.72 (dd, J = 10.5, 6.8 Hz, 0.22H), 3.58 (td, J = 9.6, 6.3 Hz, 0.21H), 2.51 (dtd, J = 12.7, 10.2, 7.2 Hz, 0.20H), 2.34 (s, 0.25H), 2.23 – 2.04 (m, 1.66H), 1.31 (t, J = 7.1 Hz, 2.44H), 1.04 (t, J = 7.1 Hz, 0.56H).

¹³C NMR (126 MHz, CDCl₃) δ 170.19, 158.71, 151.87, 136.57, 131.92, 129.99, 129.76, 128.55, 128.01, 127.41, 126.82, 123.07, 118.12, 116.67, 114.82, 76.07, 69.96, 62.67, 55.18, 49.15, 28.20, 14.00.

IR (film): v (cm⁻¹) 3416, 2919, 2933, 1740, 1611, 1578, 1402, 1248, 1026, 913, 862, 761, 663, 558.

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{25}NNaO_6S$ (M+Na)⁺: 502.1295, found: S30

502.1306.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.2 mmol), **2k** (201.7 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 15 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3k** as a white solid (87.7 mg, 0.158 mmol, 79% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IF column, *dr* = 16:1 by ¹H NMR, *ee* = 97/99% (HPLC: IF, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 27.4 min, t_r(major) = 31.2 min). [α]_D²³ = +42.2° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.64 – 7.59 (m, 4H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.21 (ddd, *J* = 8.6, 7.4, 1.6 Hz, 1H), 6.97 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.74 (td, *J* = 7.8, 1.3 Hz, 1H), 6.14 (dd, *J* = 8.1, 1.6 Hz, 1H), 5.12 (s, 2H), 4.44 – 4.21 (m, 3H), 3.98 – 3.82 (m, 2H), 2.15 (d, *J* = 30.4 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.22, 158.72, 151.90, 141.06, 140.62, 135.56, 131.94,
130.04, 129.79, 128.79, 127.96, 127.42, 127.34, 127.05, 126.87, 123.10, 118.17,
116.68, 114.86, 76.09, 69.76, 62.72, 55.20, 49.17, 28.22, 14.04.

IR (film): v (cm⁻¹) 3422, 2923, 1739, 1611, 1513, 1486, 1249, 1025, 912, 864, 761, 601, 559.

HRMS (ESI-TOF, m/z) calcd for $C_{32}H_{29}NNaO_6S$ (M+Na)⁺: 578.1608, found: 578.1602.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2l** (166.9 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 16 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3l** as a white solid (73.6 mg, 0.148 mmol, 74% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IF column, *dr* = 4:1 by ¹H NMR, *ee* = 93/64% (HPLC: IF, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 19.8 min, t_r(major) = 25.0 min). [α]_D²³ = +26.3° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.59 (dd, J = 8.1, 1.6 Hz, 0.35H), 7.41 (dd, J = 8.4, 5.4 Hz, 1.88H), 7.32 (td, J = 7.7, 1.7 Hz, 0.39H), 7.28 – 7.18 (m, 1.60H), 7.07 (t, J = 8.6 Hz, 1.74H), 7.01 (dd, J = 8.2, 1.3 Hz, 0.42H), 6.97 – 6.95 (m, 0.91H), 6.88 (s, 3.18H), 6.77 – 6.70 (m, 0.79H), 6.14 (dd, J = 8.2, 1.6 Hz, 0.75H), 5.03 (d, J = 4.1 Hz, 1.94H), 4.42 – 4.23 (m, 2.48H), 4.08 – 3.95 (m, 0.55H), 3.95 – 3.82 (m, 1.73H), 3.74 (dd, J = 10.5, 6.8 Hz, 0.26H), 3.59 (td, J = 9.6, 6.3 Hz, 0.21H), 2.68 – 2.31 (m, 0.22H), 2.23 – 2.08 (m, 1.69H), 1.31 (t, J = 7.1 Hz, 2.43H), 1.06 (t, J = 7.1 Hz, 0.60H).

¹³C NMR (126 MHz, CDCl₃) δ 170.28, 158.63, 151.97, 131.99, 130.14, 129.89, 129.44, 129.38, 127.08, 123.17, 118.25, 116.76, 115.64, 115.47, 114.87, 76.16, 69.38, 62.79, 55.25, 49.24, 28.31, 14.10.

IR (film): v (cm⁻¹) 3450, 2980, 1739, 1610, 1514, 1402, 1226, 1174, 1021, 912, 829, 761, 601, 562.

HRMS (ESI-TOF, m/z) calcd for C₂₆H₂₅FNO₆S (M+H)⁺: 498.1381, found: 498.1398.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2m** (176.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 16 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3m** as a white solid (79.0 mg, 0.154 mmol, 77% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IF column, *dr* = 4.4:1 by ¹H NMR, *ee* = 94/52% (HPLC: IF, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 20.7 min, t_r(major) = 26.0 min). [α]_D²³ = +41.0° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.58 (dd, J = 8.0, 1.7 Hz, 0.23H), 7.36 (s, 4.28H), 7.25 - 7.18 (m, 1.28H), 7.07 - 6.96 (m, 0.36H), 6.98 - 6.93 (m, 1.15H), 6.87 (s, 3.12H), 6.77 - 6.70 (m, 0.82H), 6.13 (dd, J = 8.1, 1.6 Hz, 0.80H), 5.04 (d, J = 4.3 Hz, 2.07H), 4.40 - 4.22 (m, 2.54H), 4.07 - 3.95 (m, 0.45H), 3.93 (ddd, J = 11.1, 8.9, 2.0 Hz, 0.84H), 3.91 - 3.82 (m, 0.90H), 3.73 (dd, J = 10.5, 6.8 Hz, 0.21H), 3.59 (td, J = 9.6, 6.4 Hz, 0.19H), 3.53 - 3.37 (m, 0.10H), 2.51 (dtd, J = 12.5, 10.1, 7.2 Hz, 0.18H), 2.24 - 2.06 (m, 1.81H), 1.31 (t, J = 7.1 Hz, 2.44H), 1.05 (t, J = 7.1 Hz, 0.55H).

¹³C NMR (126 MHz, CDCl₃) δ 170.17, 158.43, 151.86, 135.10, 133.79, 131.86, 130.31, 129.54, 128.74, 128.72, 127.07, 123.07, 118.17, 116.66, 114.78, 76.05, 69.15, 62.70, 55.14, 49.14, 28.21, 14.01.

IR (film): v (cm⁻¹) 3459, 2982, 1740, 1610, 1514, 1401, 1248, 1174, 1015, 912, 865, 761, 664, 565.

HRMS (ESI-TOF, m/z) calcd for C₂₆H₂₅ClNO₆S (M+H)⁺: 514.1086, found: 514.1077.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2n** (202.8 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 16 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3n** as a white solid (79.1 mg, 0.142 mmol, 71% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IF column, *dr* = 4.5:1 by ¹H NMR, *ee* = 62/62% (HPLC: IF, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 0.50 mL/min, 30 °C, t_r(minor) = 44.2 min, t_r(major) = 55.4 min). [α]_D²³ = +36.8° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.58 (dd, J = 8.0, 1.6 Hz, 0.28H), 7.52 (d, J = 8.1 Hz, 1.91H), 7.31 (d, J = 8.1 Hz, 2.36H), 7.23 (td, J = 8.5, 8.0, 3.0 Hz, 1.57H), 7.05 – 6.99 (m, 0.34H), 6.99 – 6.95 (m, 1.05H), 6.87 (s, 3.09H), 6.78 – 6.70 (m, 0.82H), 6.13 (dd, J = 8.1, 1.6 Hz, 0.78H), 5.02 (s, 1.95H), 4.31 (s, 2.61H), 3.96 – 3.83 (m, 1.77H), 3.74 (dd, J = 10.4, 6.8 Hz, 0.24H), 3.60 (td, J = 9.6, 6.3 Hz, 0.23H), 2.52 (dtd, J = 12.6, 10.2, 7.2 Hz, 0.22H), 2.22 – 2.07 (m, 1.74H), 1.32 (t, J = 7.1 Hz, 2.53H), 1.06 (t, J = 7.1 Hz, 0.56H).

¹³C NMR (126 MHz, CDCl₃) δ 170.21, 158.43, 151.90, 135.64, 131.88, 131.72, 130.08, 129.82, 129.05, 127.14, 123.10, 121.97, 118.22, 116.69, 114.82, 76.08, 69.22, 62.74, 55.16, 49.17, 28.26, 14.04.

IR (film): v (cm⁻¹) 3417, 2917, 1738, 1616, 1513, 1403, 1230, 1174, 1024, 865, 768, 665, 576.

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{24}BrKNO_6S$ (M+K)⁺: 598.0124, found: 598.0117.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2o** (196.9 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 16 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3o** as a white solid (74.4 mg, 0.136 mmol, 68% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak OX-H column, *dr* = 5.4:1 by ¹H NMR, *ee* = 95/97% (HPLC: OX-H, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 22.1 min, t_r(major) = 54.0 min). [α]_D²³ = +41.4° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.59 (dd, J = 8.0, 1.7 Hz, 0.17H), 7.52 – 7.41 (m, 1.95H), 7.33 (ddd, J = 8.4, 7.3, 1.7 Hz, 0.24H), 7.29 – 7.18 (m, 3.39H), 7.07 – 6.98 (m, 0.22H), 6.97 (dd, J = 8.2, 1.3 Hz, 1.12H), 6.88 (s, 3.20H), 6.74 (m, J = 8.4, 7.4, 1.4 Hz, 0.84H), 6.13 (dd, J = 8.1, 1.6 Hz, 0.78H), 5.08 (d, J = 3.7 Hz, 1.97H), 4.48 – 4.21 (m, 2.46H), 4.11 – 3.96 (m, 0.39H), 3.96 – 3.81 (m, 1.68H), 3.75 (dd, J = 10.5, 6.8 Hz, 0.17H), 3.61 (td, J = 9.6, 6.3 Hz, 0.16H), 2.53 (dtd, J = 12.6, 10.1, 7.2 Hz, 0.16H), 2.28 – 2.00 (m, 1.79H), 1.32 (t, J = 7.1 Hz, 2.56H), 1.06 (t, J = 7.2 Hz, 0.46H).

¹³C NMR (126 MHz, CDCl₃) δ 170.22, 158.45, 151.92, 148.90, 135.34, 131.89, 130.12, 129.82, 128.83, 127.20, 123.09, 121.12, 118.23, 116.70, 114.77, 76.09, 69.07, 62.75, 55.18, 49.18, 28.27, 14.04.

IR (film): v (cm⁻¹) 3440, 2920, 2340, 1740, 1612, 1514, 1403, 1256, 1173, 1020, 910, 831, 761, 661, 535.

HRMS (ESI-TOF, m/z) calcd for $C_{27}H_{24}F_3NNaO_6S$ (M+Na)⁺: 570.1169, found: 570.1167.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2p** (112.8 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 23 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3p** as a yellow solid (53.7 mg, 0.132 mmol, 66% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak ID column, *dr* = 8:1 by ¹H NMR, *ee* = 75/71% (HPLC: ID, 240 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 14.6 min, t_r(major) = 21.4 min). [α]_D²³ = +22.6° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.56 (dd, J = 8.0, 1.7 Hz, 0.12H), 7.39 – 7.31 (m, 0.46H), 7.29 – 7.23 (m, 2.83H), 7.06 – 7.01 (m, 0.17H), 6.99 (dd, J = 8.2, 1.3 Hz, 0.89H), 6.93 – 6.85 (m, 1.63H), 6.80 (ddd, J = 8.5, 7.4, 1.3 Hz, 0.83H), 6.18 (dd, J = 8.1, 1.5 Hz, 0.79H), 4.44 – 4.23 (m, 2.67H), 4.10 – 4.02 (m, 0.18H), 4.02 – 3.94 (m, 0.96H), 3.93 – 3.83 (m, 1.00H), 3.80 – 3.72 (m, 0.17H), 3.64 (td, J = 9.5, 6.6 Hz, 0.14H), 2.50 (dtd, J= 12.7, 9.7, 7.3 Hz, 0.13H), 2.22 (dd, J = 6.3, 1.9 Hz, 1.02H), 2.14 (d, J = 12.3 Hz, 0.92H), 1.32 (t, J = 7.1 Hz, 2.64H), 1.07 (t, J = 7.2 Hz, 0.33H).

¹³C NMR (126 MHz, CDCl₃) δ 170.09, 151.85, 134.40, 133.59, 131.53, 130.25, 130.03, 128.72, 123.36, 118.47, 116.69, 76.08, 62.93, 55.11, 49.21, 28.38, 14.03.

IR (film): v (cm⁻¹) 3413, 1740, 1637, 1617, 1494, 1402, 1225, 1174, 1026, 853, 756, 607, 536.

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{18}CINNaO_5S$ (M+Na)⁺: 430.0486, found: 430.0483.


A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2q** (139.2 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 25 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3q** as a yellow solid (60.4 mg, 0.134 mmol, 67% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak ID column, *dr* > 20:1 by ¹H NMR, *ee* = 72/76% (HPLC: IF, 240 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 15.4 min, t_r(major) = 22.0 min). [α]_D²³ = +44.2° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.39 (m, 2H), 7.26 – 7.22 (m, 1H), 6.99 (dd, J = 8.3, 1.3 Hz, 1H), 6.86 – 6.78 (m, 3H), 6.19 (dd, J = 8.1, 1.6 Hz, 1H), 4.41 – 4.29 (m, 2H), 4.26 (dd, J = 12.1, 5.6 Hz, 1H), 3.97 (ddd, J = 11.2, 9.0, 2.4 Hz, 1H), 3.88 (td, J = 10.3, 6.8 Hz, 1H), 2.23 (dddd, J = 12.5, 6.8, 5.7, 2.4 Hz, 1H), 2.13 (tt, J = 12.4, 9.4 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.06, 151.84, 134.11, 131.68, 131.51, 130.57, 130.04,
123.38, 122.51, 118.48, 116.69, 76.02, 62.93, 55.17, 49.20, 28.33, 14.03.

IR (film): v (cm⁻¹) 3420, 1738, 1629, 1484, 1402, 1226, 1175, 1107, 1010, 849, 821, 760, 664, 468.

HRMS (ESI-TOF, m/z) calcd for C₁₉H₁₉BrNO₅S (M+H)⁺: 452.0162, found: 452.0157.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2r** (122.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 15 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3r** as a white solid (70.2 mg, 0.166 mmol, 83% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IF column, *dr* = 2.2:1 by ¹H NMR, *ee* = 96/96% (HPLC: IF, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 0.50 mL/min, 30 °C, t_r(minor) = 28.0 min, t_r(major) = 34.5 min). [α]_D²³ = +23.6° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J* = 8.4 Hz, 0.71H), 7.93 – 7.86 (m, 1.30H), 7.84 (dd, *J* = 11.6, 8.1 Hz, 0.98H), 7.68 (d, *J* = 7.3 Hz, 0.31H), 7.59 – 7.46 (m, 2.59H), 7.32 (td, *J* = 7.8, 1.6 Hz, 0.34H), 7.29 – 7.23 (m, 0.79H), 7.18 (td, *J* = 7.8, 7.4, 1.6 Hz, 0.72H), 7.10 – 7.05 (m, 0.31H), 7.04 (dd, *J* = 8.3, 1.3 Hz, 0.28H), 6.96 (dd, *J* = 8.3, 1.3 Hz, 0.65H), 6.80 (d, *J* = 7.3 Hz, 0.71H), 6.63 – 6.57 (m, 0.68H), 5.81 (dd, *J* = 8.0, 1.6 Hz, 0.69H), 5.10 (dd, *J* = 12.2, 5.4 Hz, 0.71H), 4.79 (t, *J* = 7.6 Hz, 0.27H), 4.22 (qd, *J* = 7.1, 3.0 Hz, 1.43H), 4.15 (ddd, *J* = 9.8, 7.3, 4.3 Hz, 0.34H), 4.09 (ddd, *J* = 10.8, 8.7, 2.1 Hz, 0.70H), 3.97 (td, *J* = 10.5, 6.4 Hz, 0.71H), 3.88 – 3.71 (m, 0.88H), 2.53 (dq, *J* = 12.7, 7.9 Hz, 0.29H), 2.43 – 2.32 (m, 0.99H), 2.27 (dtd, *J* = 12.3, 6.0, 2.1 Hz, 0.75H), 1.14 (t, *J* = 7.1 Hz, 2.05H), 0.86 (t, *J* = 7.1 Hz, 0.93H).

¹³C NMR (126 MHz, CDCl₃) δ 170.33, 151.97, 133.80, 133.09, 132.33, 131.22, 130.92, 129.85, 129.25, 129.15, 127.74, 126.68, 126.09, 124.64, 122.60 (d, *J* = 9.6 Hz), 118.18, 116.83, 75.88, 62.96, 50.75, 49.24, 30.28, 13.72.

IR (film): v (cm⁻¹) 3408, 2919, 1958, 1735, 1637, 1617, 1399, 1178, 1020, 875, 752, 610, 538.

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{21}NNaO_5S$ (M+Na)⁺: 446.1033, found: 446.1028.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2s** (96.0 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 17 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3s** as a yellow solid (50.8 mg, 0.134 mmol, 67% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IE column, *dr* > 20:1 by ¹H NMR, *ee* = 96/94% (HPLC: IE, 240 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 22.8 min, t_r(major) = 29.5 min). [α]_D²³ = +45.3° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.22 (m, 2H), 7.00 – 6.93 (m, 2H), 6.84 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 6.72 (dd, J = 3.6, 1.1 Hz, 1H), 6.35 (dd, J = 8.1, 1.6 Hz, 1H), 4.57 (dd, J = 11.6, 5.7 Hz, 1H), 4.36 (qd, J = 7.1, 2.2 Hz, 2H), 3.90 (dddd, J = 17.5, 10.6, 9.2, 7.2 Hz, 2H), 2.38 (m, J = 12.7, 7.0, 5.8, 3.1 Hz, 1H), 2.16 – 2.04 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 169.82, 151.75, 138.08, 130.88, 129.98, 127.11, 127.07, 125.63, 123.59, 118.30, 116.72, 76.20, 62.96, 51.30, 49.17, 29.72, 14.01.

IR (film): v (cm⁻¹) 3408, 1742, 1616, 1404, 1204, 1174, 1110, 1022, 864, 762, 665, 617, 501.

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{17}NNaO_5S_2$ (M+Na)⁺: 402.0440, found: 402.0437.



A dried 10 mL Schlenk tube was charged with **1b** (48.2 mg, 0.20 mmol), **2a** (92.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 17 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3t** as a colorless oil (38.1 mg, 0.106 mmol, 53% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IA column, *dr* = 18:1 by ¹H NMR, *ee* = 88/79% (HPLC: IA, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 0.50 mL/min, 30 °C, t_r(minor) = 17.0 min, t_r(major) = 26.9 min). [α]_D²³ = +53.2° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.31 (ddd, *J* = 14.4, 7.8, 6.2 Hz, 3H), 7.22 (ddd, *J* = 8.7, 7.4, 1.6 Hz, 1H), 7.01 – 6.91 (m, 3H), 6.73 (td, *J* = 7.7, 7.2, 1.3 Hz, 1H), 6.09 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.33 (dd, *J* = 12.1, 5.9 Hz, 1H), 3.97 (ddd, *J* = 11.2, 8.8, 2.6 Hz, 1H), 3.88 (s, 4H), 2.28 – 2.15 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 170.85, 151.87, 134.79, 131.69, 129.93, 128.89, 128.59, 128.48, 123.26, 118.28, 116.69, 76.25, 55.83, 53.55, 49.28, 28.11.

IR (film): v (cm⁻¹) 3463, 2918, 2332, 1958, 1742, 1617, 1402, 1259, 1173, 1045, 904, 849, 764, 620, 542.

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{17}NNaO_5S$ (M+Na)⁺: 382.0720, found: 382.0717.



A dried 10 mL Schlenk tube was charged with **1c** (53.8 mg, 0.20 mmol), **2a** (92.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp (λ_{max} = 455 nm). After being stirred at 20 °C for 17 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3u** as a colorless oil (44.1 mg, 0.114 mmol, 57% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IE column, *dr* > 20:1 by ¹H NMR, *ee* = 92/65% (HPLC: IE, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 0.50 mL/min, 30 °C, t_r(minor) = 43.4 min, t_r(major) = 54.7 min). [α]_D²³ = +41.1° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.27 (m, 3H), 7.21 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 7.04 – 6.85 (m, 3H), 6.72 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 6.10 (dd, J = 8.1, 1.6 Hz, 1H), 4.36 – 4.25 (m, 2H), 4.21 (dt, J = 10.6, 6.6 Hz, 1H), 3.97 (ddd, J = 11.2, 8.8, 2.6 Hz, 1H), 3.89 (td, J = 10.3, 6.9 Hz, 1H), 2.32 – 2.11 (m, 2H), 1.71 (h, J = 7.2 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.34, 151.87, 134.90, 131.75, 129.84, 128.92, 128.55, 128.46, 123.12, 118.28, 116.82, 76.32, 68.39, 55.80, 49.27, 28.13, 21.79, 10.38.

IR (film): v (cm⁻¹) 3416, 2921, 1958, 1740, 1634, 1559, 1403, 1259, 1174, 1015, 905, 849, 795, 624, 518.

HRMS (ESI-TOF, m/z) calcd for C₂₀H₂₁KNO₅S (M+K)⁺: 427.0806, found: 427.0811.



A dried 10 mL Schlenk tube was charged with 1d (59.4 mg, 0.20 mmol), 2a (92.4 mg, 0.60 mmol), PC1 (3.4 mg, 0.010 mmol), chiral nickel catalyst [L1-Ni] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp (λ_{max} = 455 nm). After being stirred at 20 °C for 27 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3v** as a colorless oil (64.8 mg, 0.150 mmol, 78% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IE column, *dr* = 6:1 by ¹H NMR, *ee* = 97/94% (HPLC: IE, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 14.7 min, t_r(major) = 20.8 min). [α]_D²³ = +32.7° (*c* = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.59 (dd, J = 8.1, 1.7 Hz, 0.17H), 7.42 – 7.33 (m, 1.07H), 7.33 – 7.25 (m, 2.53H), 7.24 – 7.19 (m, 1.01H), 7.03 (dd, J = 8.3, 1.3 Hz, 0.26H), 6.97 (dt, J = 8.2, 1.7 Hz, 2.32H), 6.73 (ddd, J = 8.3, 7.3, 1.3 Hz, 0.79H), 6.11 (dd, J = 8.1, 1.6 Hz, 0.78H), 4.35 (dd, J = 12.0, 5.9 Hz, 0.82H), 4.08 (ddd, J = 9.5, 7.2, 2.4 Hz, 0.26H), 4.00 – 3.95 (m, 1.56H), 3.94 – 3.85 (m, 1.65H), 3.78 (dd, J = 10.8, 6.7 Hz, 0.18H), 3.64 (td, J = 9.7, 6.2 Hz, 0.17H), 3.57 – 3.45 (m, 0.34H), 2.58 (dtd, J = 12.6, 10.4, 7.2 Hz, 0.19H), 2.31 – 2.13 (m, 1.83H), 0.87 (s, 7.62H), 0.76 (s, 1.26H). ¹³C NMR (126 MHz, CDCl₃) δ 170.37, 151.84, 135.06, 131.65, 129.79, 128.86, 128.55, 128.42, 123.07, 118.29, 116.97, 76.48, 76.20, 55.91, 49.33, 31.30, 28.18, 26.32. IR (film): v (cm⁻¹) 3449, 2960, 2314, 1958, 1739, 1614, 1576, 1481, 1402, 1224, 1176, 1026, 911, 852, 762, 625, 563.

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{25}NNaO_5S$ (M+Na)⁺: 438.1346, found: 438.1341.



A dried 10 mL Schlenk tube was charged with **1e** (57.8 mg, 0.20 mmol), **2a** (92.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 18 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3w** as a colorless oil (44.0 mg, 0.108 mmol, 54% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IE column, *dr* = 4.5:1 by ¹H NMR, *ee* = 82/75% (HPLC: IE, 220 nm, *n*-hexane:isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 24.9 min, t_r(major) = 37.0 min). [α]_D²³ = +20.2° (*c* = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.54 – 7.48 (m, 0.23H), 7.40 – 7.33 (m, 1.59H), 7.33 – 7.27 (m, 1.98H), 7.21 (dd, J = 8.6, 2.2 Hz, 0.21H), 7.06 (d, J = 2.2 Hz, 0.20H), 7.00 (d, J = 2.2 Hz, 0.77H), 6.98 – 6.93 (m, 1.55H), 6.71 (dd, J = 8.7, 2.2 Hz, 0.77H), 5.97 (d, J = 8.7 Hz, 0.77H), 4.52 (dd, J = 9.7, 7.2 Hz, 0.10H), 4.43 – 4.25 (m, 2.44H), 4.08 (ddd, J = 9.7, 7.2, 2.7 Hz, 0.22H), 3.96 (ddd, J = 11.0, 9.0, 1.8 Hz, 0.86H), 3.92 – 3.87 (m, 0.96H), 3.72 (dd, J = 10.4, 6.7 Hz, 0.20H), 3.63 (td, J = 9.6, 6.4 Hz, 0.19H), 2.58 (dtd, J = 12.7, 10.1, 7.2 Hz, 0.19H), 2.27 – 2.16 (m, 1.67H), 1.34 (t, J = 7.1 Hz, 2.43H), 1.05 (t, J = 7.1 Hz, 0.54H).

¹³C NMR (151 MHz, CDCl₃) δ 169.85, 152.22, 135.34, 134.29, 132.77, 128.88, 128.73, 128.71, 123.49, 118.53, 115.26, 75.94, 63.00, 55.74, 49.32, 27.98, 14.04.

IR (film): v (cm⁻¹) 3429, 2918, 1739, 1618, 1540, 1407, 1181, 1014, 903, 799,701, 628, 563.

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{18}CINNaO_5S$ (M+Na)⁺: 430.0486, found: 430.0478.



A dried 10 mL Schlenk tube was charged with **1f** (57.0 mg, 0.20 mmol), **2a** (92.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 17 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE:CH₃COOH = 50:1) to afford product **3x** as a white solid (54.8 mg, 0.136 mmol, 68% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IA column, *dr* = 2.6:1 by ¹H NMR, *ee* = 77/84% (HPLC: IA, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 0.50 mL/min, 30 °C, t_r(minor) = 19.3 min, t_r(major) = 27.6 min). [α]_D²³ = +42.6° (*c* = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, J = 8.9 Hz, 0.29H), 7.43 – 7.25 (m, 3.73H), 6.97 (d, J = 7.1 Hz, 1.38H), 6.80 (dd, J = 8.9, 2.7 Hz, 0.28H), 6.54 (d, J = 2.6 Hz, 0.28H), 6.49 (d, J = 2.6 Hz, 0.65H), 6.29 (dd, J = 9.0, 2.7 Hz, 0.67H), 5.94 (d, J = 8.9 Hz, 0.66H), 4.32 (s, 2.09H), 4.07 (ddd, J = 9.9, 7.2, 3.0 Hz, 0.28H), 3.94 (ddd, J = 11.0, 6.6, 4.0 Hz, 0.99H), 3.90 – 3.82 (m, 0.94H), 3.81 (s, 0.92H), 3.73 (s, 2.39H), 3.64 (td, J = 9.4, 6.6 Hz, 0.29H), 2.54 (dtd, J = 12.5, 9.6, 7.2 Hz, 0.26H), 2.21 (dtd, J = 9.6, 7.3, 6.4, 3.6 Hz, 1.70H), 1.33 (t, J = 7.1 Hz, 2.16H), 1.02 (t, J = 7.1 Hz, 0.83H).

¹³C NMR (151 MHz, CDCl₃) δ 170.46, 160.37, 152.73, 134.70, 132.51, 128.97, 128.51, 128.45, 110.11, 102.95, 102.91, 75.81, 62.70, 55.60, 55.43, 49.22, 27.91, 14.05.

IR (film): v (cm⁻¹) 3418, 2919, 1739, 1623, 1573, 1402, 1294, 1110, 1031, 965, 804, 740, 620, 581.

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{21}NNaO_6S$ (M+Na)⁺: 426.0982, found: 426.0976.

3.3 Substrate Scope for the Reaction of *N*-Sulfonylimines and *O*-Methylbenzyl Chloride Derivatives

Preparation of a 0.01 M Solution of the Non Racemic Nickel Catalyst [L1-Ni] in CHCl₃ : A solution of nickel bromide (4.4 mg, 0.020 mmol) and a chiral ligand (L1, 7.4 mg, 0.022 mmol) in CHCl₃ (4.0 mL) was stirred at 70 °C for 1 h, which was used freshly for the following photochemical reactions.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 2.0 mmol), **6a** (84.0 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 42 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **7a** as a colorless oil (48.8 mg, 0.136 mmol, 68% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak ODH column, *ee* = 91% (HPLC: OD-H, 220 nm, *n*-hexane:isopropanol = 97:3, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 18.8 min, t_r(major) = 29.3 min). [α]_D²³ = -55.2° (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃) δ 7.60 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.15 (m, 4H), 7.12 – 7.03 (m, 1H), 6.93 (dd, *J* = 8.1, 1.4 Hz, 1H), 4.84 (d, *J* = 15.5 Hz, 1H), 4.69 (d, *J* = 15.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.65 (d, *J* = 15.2 Hz, 1H), 3.47 (d, *J* = 15.2 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.09, 150.00, 132.29, 131.68, 130.01, 128.62, 127.93, 127.88, 127.45, 125.79, 125.25, 121.56, 118.73, 68.10, 62.62, 47.10, 40.58, 13.84.
IR (film): v (cm⁻¹) 2921, 2330, 1738, 1577, 1485, 1397, 1205, 1117, 1028, 928, 861,

757, 612, 564.

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{17}NNaO_5S$ (M+Na)⁺: 382.0720, found: 382.0715.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 2.0 mmol), **6b** (92.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 24 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **7b** as a white solid (47.8 mg, 0.128 mmol, 64% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak AD-H column, *ee* = 89% (HPLC: AD-H, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 9.9 min, t_r(major) = 12.4 min). [α]_D²³ = -82.8° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.63 (dd, J = 7.9, 1.6 Hz, 1H), 7.30 (ddd, J = 8.2, 7.3, 1.6 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.11 – 7.02 (m, 2H), 6.98 – 6.91 (m, 2H), 4.89 (d, J = 15.8 Hz, 1H), 4.60 (d, J = 15.8 Hz, 1H), 4.18 (qd, J = 7.1, 1.9 Hz, 2H), 3.64 (d, J = 15.2 Hz, 1H), 3.47 (d, J = 15.2 Hz, 1H), 2.29 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.78, 149.74, 134.09, 131.22, 130.29, 130.06, 129.00, 128.39, 127.32, 125.88, 125.40, 121.78, 118.80, 67.72, 62.57, 44.44, 40.80, 18.51, 13.84.

IR (film): v (cm⁻¹) 2924, 2338, 1742, 1597, 1451, 1401, 1241, 1177, 1031, 1001, 919, 867, 760, 664, 554.

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{19}NNaO_5S$ (M+Na)⁺: 396.0876, found: 396.0871.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 2.0 mmol), **6c** (102.0 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 24 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **7c** as a white solid (49.0 mg, 0.126 mmol, 63% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak AD-H column, *ee* = 83% (HPLC: AD-H, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 12.8 min, t_r(major) = 15.2 min). [α]_D²³ = -64.7° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.61 (dd, J = 8.0, 1.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.22 – 7.18 (m, 1H), 7.14 (t, J = 7.9 Hz, 1H), 6.92 (dd, J = 8.2, 1.3 Hz, 1H), 6.79 – 6.73 (m, 1H), 6.70 (d, J = 8.2 Hz, 1H), 4.82 (d, J = 15.7 Hz, 1H), 4.64 (d, J = 15.7 Hz, 1H), 4.19 (qd, J = 7.1, 4.6 Hz, 2H), 3.78 (s, 3H), 3.65 (d, J = 15.8 Hz, 1H), 3.51 (d, J = 15.8 Hz, 1H), 1.17 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 170.04, 156.25, 149.86, 133.21, 129.92, 128.60, 127.90, 125.09, 121.81, 120.30, 118.52, 117.85, 109.23, 68.06, 62.52, 55.47, 46.70, 33.05, 13.81.

IR (film): v (cm⁻¹) 2935, 1740, 1577, 1596, 1484, 1343, 1271, 1176, 1030, 903, 865, 771, 663.

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{19}NNaO_6S$ (M+Na)⁺: 412.0825, found: 412.0823.

S47



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 2.0 mmol), **6d** (130.8 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 24 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **7d** as a white solid (66.4 mg, 0.152 mmol, 76% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak AD-H column, *ee* = 76% (HPLC: AD-H, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 15.2 min, t_r(major) = 31.2 min). [α] D²³ = -66.7° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.55 (dd, J = 8.0, 1.5 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.26 – 7.21 (m, 1H), 7.00 – 6.94 (m, 2H), 4.82 (d, J = 15.9 Hz, 1H), 4.64 (d, J = 15.9 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.60 (d, J = 15.4 Hz, 1H), 3.43 (d, J = 15.4 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.74, 149.85, 134.11, 131.00, 130.69, 130.24, 129.62, 128.80, 128.32, 125.47, 121.39, 121.04, 118.94, 67.91, 62.83, 46.38, 39.70, 13.87. IR (film): v (cm⁻¹) 2935, 2841, 2330, 1740, 1577, 1595, 1484, 1400, 1271, 1176, 1073, 903, 865, 771, 663.

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{16}BrNNaO_5S$ (M+Na)⁺: 461.9804, found: 461.9797.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 2.0 mmol), **6e** (92.4 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 46 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **6e** as a colourless oil (48.1 mg, 0.134 mmol, 67% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IC column, *dr* > 20:1 by ¹H NMR, *ee* = 91% (HPLC: IC, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 30 °C, t_r(minor) = 14.2 min, t_r(major) = 19.7 min). [α]_D²³ = -32.3° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.83 (dd, J = 8.0, 1.5 Hz, 1H), 7.40 (td, J = 7.7, 1.3 Hz, 1H), 7.32 (td, J = 7.6, 7.2, 1.1 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.14 (td, J = 6.9, 1.6 Hz, 2H), 7.11 (dd, J = 8.2, 1.2 Hz, 1H), 4.98 (d, J = 14.6 Hz, 1H), 4.86 (d, J = 14.7 Hz, 1H), 4.07 – 3.97 (m, 2H), 3.77 (q, J = 7.0 Hz, 1H), 1.01 (d, J = 7.0 Hz, 3H), 0.97 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.25, 150.02, 136.59, 130.40, 129.32, 128.47, 127.52, 127.40, 127.30, 126.20, 126.11, 121.51, 119.15, 70.96, 62.32, 45.94, 45.71, 17.96, 13.64.

IR (film): v (cm⁻¹) 2975, 2316, 1733, 1670, 1582, 1456, 1383, 1236, 1176, 1059, 907, 820, 712, 660, 555.

HRMS (ESI-TOF, m/z) calcd for $C_{38}H_{38}N_2NaO_{10}S_2$ (2M+Na)⁺: 769.1860, found: 769.1857.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 2.0 mmol), **6f** (129.6 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 42 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **7f** as a white solid (66.1 mg, 0.152 mmol, 76% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IC column, *dr* > 20:1 by ¹H NMR, *ee* = 83% (HPLC: IC, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 12.9 min, t_r(major) = 14.3 min). [α]_D²³ = +79.4° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.77 (dd, J = 8.0, 1.6 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.16 – 7.12 (m, 2H), 7.08 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.92 (dt, J = 14.8, 7.2 Hz, 3H), 6.65 (dd, J = 25.2, 7.6 Hz, 3H), 5.18 (d, J = 15.1 Hz, 1H), 4.91 – 4.74 (m, 2H), 4.18 – 3.98 (m, 2H), 1.01 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 168.45, 149.31, 138.10, 134.41, 130.32, 129.90, 129.48, 129.17, 127.62, 127.59, 127.47, 127.13, 127.09, 125.98, 125.83, 121.22, 118.98, 71.59, 62.71, 55.74, 45.70, 13.74.

IR (film): v (cm⁻¹) 2925, 1731, 1583, 1487, 1381, 1230, 1176, 1088, 971, 886, 701, 670, 590.

HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{21}NNaO_5S$ (M+Na)⁺: 458.1033, found: 458.1038.



A dried 10 mL Schlenk tube was charged with **1b** (51.0 mg, 2.0 mmol), **6e** (129.6 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 42 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **7g** as a colorless oil (46.0 mg, 0.128 mmol, 64% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IG column, *dr* > 20:1 by ¹H NMR, *ee* = 99% (HPLC: IG, 220 nm, *n*-hexane:isopropanol = 99:1, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 29.5 min, t_r(major) = 42.3 min). [α]_D²³ = +46.4° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.41 (ddd, *J* = 8.2, 7.4, 1.6 Hz, 1H), 7.32 (ddd, *J* = 8.1, 7.4, 1.3 Hz, 1H), 7.24 (td, *J* = 6.6, 1.7 Hz, 2H), 7.17 – 7.09 (m, 3H), 4.99 (d, *J* = 14.7 Hz, 1H), 4.84 (d, *J* = 14.8 Hz, 1H), 3.78 (q, *J* = 7.0 Hz, 1H), 3.58 (s, 3H), 1.01 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.87, 149.98, 136.54, 130.48, 129.07, 128.45, 127.43, 127.38, 126.31, 126.15, 121.44, 119.22, 71.06, 53.17, 45.81, 45.49, 18.03.
IR (film): v (cm⁻¹) 2922, 1734, 1654, 1451, 1382, 1176, 1084, 864, 806, 769.
HRMS (ESI-TOF, m/z) calcd for C₁₈H₁₇NNaO₅S (M+Na)⁺: 382.0720, found: 382.0717.



A dried 10 mL Schlenk tube was charged with 1c (51.0 mg, 2.0 mmol), 6e (129.6 mg,

0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 42 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **7h** as a colorless solid (54.2 mg, 0.140 mmol, 70% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IG column, *dr* > 20:1 by ¹H NMR, *ee* = 94% (HPLC: IG, 220 nm, *n*-hexane:isopropanol = 95:5, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 12.9 min, t_r(major) = 17.0 min). [α]_D²³ = +35.8° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.82 (dd, J = 8.0, 1.6 Hz, 1H), 7.40 (ddd, J = 8.4, 7.5, 1.6 Hz, 1H), 7.32 (td, J = 7.7, 1.3 Hz, 1H), 7.23 (qd, J = 7.1, 1.6 Hz, 2H), 7.18 – 7.07 (m, 3H), 4.98 (d, J = 14.7 Hz, 1H), 4.86 (d, J = 14.6 Hz, 1H), 3.92 (qt, J = 10.7, 6.5 Hz, 2H), 3.78 (q, J = 7.0 Hz, 1H), 1.46 – 1.35 (m, 2H), 1.01 (d, J = 7.0 Hz, 3H), 0.74 (t, J = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.40, 150.00, 136.61, 130.40, 129.23, 128.46, 127.51, 127.38, 127.32, 126.20, 126.12, 121.59, 119.16, 71.02, 68.03, 45.90, 45.55, 21.65, 18.03, 10.24.

IR (film): v (cm⁻¹) 2970, 2933, 1734, 1582, 1485, 1456, 1384, 1232, 1178, 1129, 1085, 987, 866, 770, 664.

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{21}NNaO_5S$ (M+Na)⁺: 410.1033, found: 410.1030.



A dried 10 mL Schlenk tube was charged with **1d** (51.0 mg, 2.0 mmol), **6e** (129.6 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freeze-

pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 42 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product 7i as a colorless oil (54.8 mg, 0.132 mmol, 66% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IG column, *dr* > 20:1 by ¹H NMR, *ee* = 97% (HPLC: IG, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 6.8 min, t_r(major) = 7.6 min). [α]_D²³ = +34.2° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.82 (dd, J = 8.0, 1.6 Hz, 1H), 7.41 (td, J = 7.8, 1.6 Hz, 1H), 7.32 (td, J = 7.7, 1.3 Hz, 1H), 7.23 (tt, J = 7.4, 5.6 Hz, 2H), 7.18 – 7.09 (m, 3H), 4.99 (d, J = 14.6 Hz, 1H), 4.87 (d, J = 14.7 Hz, 1H), 3.80 (q, J = 7.0 Hz, 1H), 3.71 (d, J = 10.6 Hz, 1H), 3.54 (d, J = 10.6 Hz, 1H), 1.03 (d, J = 7.0 Hz, 3H), 0.78 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 169.55, 150.04, 136.67, 130.43, 129.16, 128.51, 127.52, 127.38, 126.23, 126.19, 121.71, 119.23, 76.09, 71.10, 45.92, 45.43, 31.17, 26.23, 18.02. IR (film): v (cm⁻¹) 2921, 1734, 1484, 1458, 1354, 1243, 1177, 1135, 1087, 1038, 993, 868, 752, 666.

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{25}NNaO_5S$ (M+Na)⁺: 438.1346, found: 438.1348.



A dried 10 mL Schlenk tube was charged with **1e** (51.0 mg, 2.0 mmol), **6e** (129.6 mg, 0.60 mmol), **PC1** (3.4 mg, 0.010 mmol), chiral nickel catalyst [**L1-Ni**] in CHCl₃ (4.0 mL) and Na₂CO₃ (31.8 mg, 0.30 mmol). The mixture was degassed *via* three freezepump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 42 h, the reaction mixture was concentrated, then purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford product **7j** as a colorless oil (61.9 mg, 0.152 mmol, 76% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak IG column, dr > 20:1 by ¹H NMR, ee = 98% (HPLC: IG, 220 nm, *n*-hexane:isopropanol = 99:1, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 15.4 min, t_r(major) = 25.1 min). [α]_D²³ = +39.1° (c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.80 (d, J = 8.6 Hz, 1H), 7.30 (dd, J = 8.6, 2.2 Hz, 1H), 7.26 - 7.20 (m, 2H), 7.18 - 7.08 (m, 3H), 4.99 - 4.91 (m, 1H), 4.87 (d, J = 14.6 Hz, 1H), 4.02 (t, J = 7.1 Hz, 2H), 3.72 (q, J = 7.0 Hz, 1H), 1.01 (d, J = 7.0 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.13, 150.28, 136.11, 135.76, 129.26, 128.78, 128.37, 127.56, 127.43, 126.51, 126.11, 120.12, 119.41, 70.62, 62.48, 46.11, 45.89, 17.89, 13.61.

IR (film): v (cm⁻¹) 2976, 1733, 1605, 1571, 1484, 1387, 1246, 1182, 1141, 1090, 901, 816, 724, 664.

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{18}CINaNO_5S$ (M+Na)⁺: 430.0492, found: 430.0478.

3.4 Configuration Assignment of the Chiral Products

Relative and absolute configuration of the major enantiomer of product 3a was assigned as (1*S*, 10b*S*) by its crystal structure (CCDC no. 2105105).Other products (3b-3x) were assigned as (1*S*, 10b*S*) in analogy.

Absolute configuration of the major enantiomer of product 7c was assigned as S by its crystal structure (CCDC no. 21052806). Other products (7a, 7b, 7d) were assigned as S in analogy.

Relative and absolute configuration of the major enantiomer of product 7f was assigned as (13*R*, 13a*S*) by its crystal structure (CCDC no. 2105071). Other products (7e, 7g–8e) were assigned as (13*R*, 13a*S*) in analogy.

3.5 Set-up of the Photoreactions



Figure S1. Reaction set up in a constant low temperature box.

3.6 Unsuccessful Substrates

• unreactive substrates



• substrates giving complex mixture



Under the standard conditions, secondary and tertiary chlorides, such as (3-chlorobutyl)benzene and (3-chloro-3-methylbutyl)benzene were found to be unreactive substrates.

Under the standard conditions, chlorine-substituent benzylic substrates containing a longer or shorter side chain, such as (2-chloroethyl)benzene and (4-chlorobutyl)benzene, failed in the reaction to construct 4- or 6-membered rings and gave very complex mixture.

4. A Synthetic Transformation of Product 7e



Scheme S9. A synthetic transformation of product 7e.

To a stirring solution of **7e** (37.3 mg, 0.10 mmol) in anhydrous THF (5 mL) at 0 °C was added LiAlH₄ (22.8 mg, 0.60 mmol) in portions. The mixture was warmed to room temperature, then heated attrefluxed for 12 h in argon. After cooling down in ice-bath, water was added carefully until H₂ evolvement ceased. The resulting mixture was filtered through celite, and the filtrate was collected, concentrated to dryness under reduced pressure to give **8e** as a white solid (23.9 mg, 0.089 mmol, 89% yield). Enantiomeric excess were established by HPLC analysis using a Chiralpak ID column, dr > 20:1 by ¹H NMR, ee = 97% (HPLC: ID, 220 nm, *n*-hexane:isopropanol = 90:10, flow rate: 1.0 mL/min, 25 °C, t_r(minor) = 32.0 min, t_r(major) = 35.7 min). [α]_D²³ = - 39.5°(c = 1.0, CH₂Cl₂).

¹H NMR (600 MHz, CDCl₃) δ 7.24 – 7.13 (m, 4H), 7.09 (ddd, *J* = 22.5, 7.8, 1.8 Hz, 2H), 6.89 – 6.82 (m, 2H), 4.19 (d, *J* = 4.0 Hz, 2H), 3.81 (d, *J* = 11.7 Hz, 1H), 3.71 (d, *J* = 11.8 Hz, 1H), 3.15 (q, *J* = 7.1 Hz, 1H), 1.20 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 160.28, 139.19, 131.99, 129.26, 129.11, 127.16, 127.00, 126.52, 125.82, 123.21, 118.89, 118.23, 65.84, 64.86, 42.84, 19.47. IR (film): v (cm⁻¹) 2930, 1609, 1585, 1492, 1458, 1411, 1351, 1282, 1155, 1067, 972, 848, 813, 757, 664.

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{19}NNaO_2$ (M+Na)⁺: 292.1308, found: 292.1303.

5. Mechanistic Investigations

Radical Trapping Experiments



Scheme S10. A photochemical reaction in the presence of ethyl 2-((phenylsulfonyl)methyl)acrylate.



A dried 10 mL Schlenk tube was charged with **1a** (51.0 mg, 0.20 mmol), **2a** (92.4 mg, 0.60 mmol), ethyl 2-((phenylsulfonyl)methyl)acrylate(101.6 mg, 0.40 mmol), **PC1**

(3.40 mg, 0.010 mmol), Na₂CO₃ (31.8 mg, 0.30 mmol) and chiral nickel catalyst **[L1-Ni]** in CHCl₃ (4 mL). The mixture was degassed *via* three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp ($\lambda_{max} = 455$ nm). After being stirred at 20 °C for 18 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (eluted with PE: EtOAc = 10:1) to afford compound **4** as a white solid (29.8 mg, 0.11 mmol, 56% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.29 (t, J = 7.6 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.17 – 7.13 (m, 2H), 6.08 (d, J = 1.5 Hz, 1H), 5.34 (q, J = 1.3 Hz, 1H), 4.18 (qd, J = 7.1, 1.6 Hz, 2H), 3.46 – 3.36 (m, 1H), 3.29 – 3.20 (m, 1H), 3.12 – 3.04 (m, 1H), 2.69 – 2.64 (m, 1H), 2.62 – 2.56 (m, 1H), 2.18 – 2.11 (m, 1H), 2.06 – 1.99 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 167.01, 142.80, 138.31, 128.54, 127.71, 126.73, 126.64, 60.68, 42.97, 41.95, 39.05, 38.55, 14.18.

IR (film): v (cm⁻¹) 2934, 2329, 1716, 1629, 1543, 1494, 1453, 1368, 1189, 1026, 945, 855, 763, 701, 604, 572.

HRMS (ESI-TOF, m/z) calcd for $C_{30}H_{38}Cl_2NaO_4$ (2M+Na)⁺: 555.2039, found: 555.2034.

6. Chiral Chromatography

6.1 Determination of Diastereo- and Enantioselectivities of the Photocatalytic Reactions

Optical purities of the compounds 3a-3x, 7a-7k and 8e were determined with a Daicel Chiralpak column (AD-H, OZ-H, OX-H, IA, IC, ID, IE, IF, IG or Chiralpak FMG-AC5-B01-NFC HPLC column purchased from Guangzhou FLM Scientific Instrument Co.Ltd) on an Agilent 1260 Series HPLC System. The column temperature was 30 °C or 25 °C and UV-absorption was measured at 220 nm or 240 nm.





Figure S4. HPLC trace for the racemic reference *rac*-3a, and *non-racemic* product 3a.



Figure S5. HPLC trace for the racemic reference *rac-*3b, and *non-racemic* product 3b.



Figure S6. HPLC trace for the racemic reference *rac*-3c, and *non-racemic* product 3c.



Figure S7. HPLC trace for the racemic reference *rac-3d*, and *non-racemic* product 3d.



Figure S8. HPLC trace for the racemic reference *rac*-3e, and *non-racemic* product 3e.



Figure S9. HPLC trace for the racemic reference rac-3f, and non-racemic product 3f.



Figure S10. HPLC trace for the racemic reference *rac*-3g, and *non-racemic* product 3g.



Figure S11. HPLC trace for the racemic reference *rac*-3h, and *non-racemic* product 3h.



Figure S12. HPLC trace for the racemic reference rac-3i, and non-racemic product 3i.



Figure S13. HPLC trace for the racemic reference rac-3j, and non-racemic product 3j.



Figure S14. HPLC trace for the racemic reference *rac*-3k, and *non-racemic* product 3k.



Figure S15. HPLC trace for the racemic reference rac-31, and non-racemic product 31.



Figure S16. HPLC trace for the racemic reference *rac*-3m, and *non-racemic* product 3m.


Figure S17. HPLC trace for the racemic reference *rac*-3n, and *non-racemic* product 3n.



Figure S18 HPLC trace for the racemic reference rac-30, and non-racemic product 30.



Figure S19. HPLC trace for the racemic reference *rac*-3p, and *non-racemic* product 3p.



Figure S20. HPLC trace for the racemic reference *rac*-3q, and *non-racemic* product 3q.



Figure S21. HPLC trace for the racemic reference *rac*-3r, and *non-racemic* product 3r.



Figure S22. HPLC trace for the racemic reference *rac-3s*, and *non-racemic* product 3s.



Figure S23. HPLC trace for the racemic reference rac-3t, and non-racemic product 3t.



Figure S24. HPLC trace for the racemic reference *rac*-3u, and *non-racemic* product 3u.



Figure S25. HPLC trace for the racemic reference *rac*-3v, and *non-racemic* product 3v.



Figure S26. HPLC trace for the racemic reference *rac*-3w, and *non-racemic* product 3w



Figure S27. HPLC trace for the racemic reference *rac*-3x, and *non-racemic* product 3x.



Figure S28. HPLC trace for the racemic reference *rac*-7a, and *non-racemic* product 7a.



Figure S29. HPLC trace for the racemic reference *rac-*7b, and *non-racemic* product 7b.



Figure S30. HPLC trace for the racemic reference *rac*-7c, and *non-racemic* product 7c.



Figure S31. HPLC trace for the racemic reference *rac*-7d, and *non-racemic* product 7d.



Figure S32. HPLC trace for the racemic reference *rac*-7e, and *non-racemic* product 7e.



Figure S33. HPLC trace for the racemic reference rac-7f, and non-racemic product 7f.



Figure S34. HPLC trace for the racemic reference *rac*-7g, and *non-racemic* product 7g.



Figure S35. HPLC trace for the racemic reference *rac*-7h, and *non-racemic* product 7h.



Figure S36. HPLC trace for the racemic reference *rac*-7i, and *non-racemic* product 7i.



Figure S37. HPLC trace for the racemic reference rac-7j, and non-racemic product 7j.

6.2 Determination of Diastereo- and Enantiopurities of the Transformation Product



Figure S38. HPLC trace for the racemic reference rac-8e, and non-racemic product 8e.

7. X-Ray Diffraction

7.1 Crystal Structure of Product 3a

Crystallization procedure. A solution of product **3a** (37.3 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL). Single crystals were obtained after evaporation under ambient conditions for 3 days.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 193.15 K. Data reduction and absorption correction were applied by using the multi-scan program. The structures were determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on **Figure S40**. Crystallographic data for **3a** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2105105.



Figure S39. Ortep drawing of compound 3a with thermal ellipsoids.

7.2 Crystal Structure of Product 7c

Crystallization procedure. A solution of product **7c** (38.9 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL). Single crystals were obtained after evaporation under ambient conditions for 3 days.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 293 K. Data

reduction and absorption correction were applied by using the multi-scan program. The structures were determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on **Figure S41**. Crystallographic data for **7c** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2105280.



Figure S40. Ortep drawing of compound 7c with thermal ellipsoids.

7.3 Crystal Structure of Product 7f

Crystallization procedure. A solution of product **7f** (43.5 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL). Single crystals were obtained after evaporation under ambient conditions for 3 days.

Data collection and solution. Data was collected on a XtaLAB Synergy four-circle diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54184$ Å) at 100.0 K. Data reduction and absorption correction were applied by using the multi-scan program. The structures were determined and refined using full-matrix least-squares based on F^2 with SHELXT and SHELXL within Olex2. The structure is shown on **Figure S42**. Crystallographic data for **7f** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2105071.



Figure S41. Ortep drawing of compound 7f with thermal ellipsoids.

Table S2. Data collection and refinement statistics for the compounds 3a, 7c and 7f.

	3a	7c	7f
Empirical	$C_{19}H_{19}NO_5S$	$C_{19}H_{19}NO_6S$	$C_{24}H_{21}NO_5S$
formula			
Formula weight	373.41	389.41	435.48
Temperature (K)	193.15	293(2)	100.0(3)
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group Cell	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
dimensions			
a, b, c (A)	8.8137,	7.4466,	8.51370,
	13.8729,	15.4504,	14.8988,
	14.1426	15.8556	15.9015
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 90, 90
Volume (Å ³)	1729.24(8)	1824.22(13)	2017.01(4)
Z	4	4	4
Density	1.434	1.418	1.434
(calculated, mg/m ³) Absorption coefficient	1.939	1.905	1.752
(mm ⁻¹)			
F(000)	784.0	816.0	912.0
Crystal size	0.3 imes 0.2 imes	0.1 imes 0.1 imes	0.1 imes 0.1 imes
(mm^3)	0.1	0.1	0.1

Theta range	4.465 to	3.995 to	4.066 to
for data	62.129	62.367	75.253
collection/°			
Index ranges	$-9 \le h \le 10, -$	$-8 \le h \le 8, -17$	$-10 \le h \le 10$,
	$15 \le k \le 13, -$	\leq k \leq 17, -17	$-18 \le k \le 17$,
	$16 \le l \le 16$	$\leq l \leq 18$	$-15 \le 1 \le 19$
Reflections collected	9479	22343	10555
Independent	2685 [$R_{int} =$	2867 [$R_{int} =$	3923 [$R_{int} =$
reflections	0.0410,	0.0899,	0.0385,
	$R_{\rm sigma} =$	$R_{\rm sigma} =$	$R_{\rm sigma} =$
	0.0347]	0.0461]	0.0422]
Completeness	100 %	100 %	100 %
Absorption correction	multi-scan	multi-scan	multi-scan
Refinement	Full-matrix	Full-matrix	Full-matrix
method	least-squares on F^2	least-squares on F^2	least-squares on F^2
Data /	2685/0/236	2867/0/246	3923/0/281
restraints /			
parameters			
Goodness-of-	1.061	1.112	1.053
fit on F^2			
Final R	$R_1 = 0.0437,$	D1 0.0415	$R_1 = 0.0293,$
indices	$wR_2 = 0.1200$	RI = 0.0415,	$wR_2 = 0.0733$
[I>=2σ (I)]		$wR_2 = 0.09/9$	
R indices (all	$R_1 = 0.0444,$	R1 = 0.0495,	$R_1 = 0.0325,$
data)	$wR_2 = 0.1209$	$wR_2 = 0.1037$	$wR_2 = 0.0743$
Flack	0.022(14)	0.029(16)	0.005(0)
parameter			-0.003(9)
Largest diff.	0.73 and -0.27	0.18 and -0.32	0.21 and -
peak and hole			0.31

(e.Å-3)

8. DFT Calculation

All the geometry optimizations were performed by Gaussian 16 package⁷ at the (U)B3LYP⁸ level using the effective core potential SDD⁹ for Ni atom and the 6-31G(d) for the other atoms. The relative Gibbs free energy (ΔG) was the outcome of the formula $\Delta G = \Delta E + \Delta G_{ZPE}$, where ΔG_{ZPE} is the Gibbs free energy correction acquired from the B3LYP/6-31G(d)/SDD method and the electronic energy ΔE was obtained from single-point energies calculations at the B3LYP/6-311+G(d,p)/SDD level. The SMD solvation model¹⁰ was used to simulate the solvent effect, and the standard parameter for trichloromethane (ϵ =4.7113) was used for the single-point energy calculations. Vibrational frequency calculations were carried out at the same level to confirm that whether the structure is a minimum (no imaginary frequency). Optimized structures were visualized by the *CYLview* program.¹¹



Scheme S11. A proposed out-sphere mechanism I (Major pathway proposed in the main text)



Scheme S12. The Gibbs energy profiles for the reaction forming V-2 at the B3LYP/6-311+G(d,p)/SDD//B3LYP/6-31G(d)/SDD level. The Gibbs free energies are given in kcal mol⁻¹.



Figure S43. Structural parameters of compounds V and VI at B3LYP/6-31G(d)/SDD level. Bond length (black) are in Å. Hydrogen atoms and substituents are omitted for clarity in 3D structure.

Results: As shown in Scheme 12 and Figure S43, the calculation results show that a key step in the proposed reaction **mechanism I** is thermodynamically favored. The reaction is exergonic, with an ΔG value of 9.9 kcal mol⁻¹ in triplet state. In contrast, the calculation results show that the ΔG value is +0.8 kcal mol⁻¹ in open-shell singlet state.

(a) photocatalytic cycle



Scheme S13. An alternative mechanism II going through an organometallic pathway

G

D

CO₂M

3



Scheme S14. The Gibbs energy profiles for the reaction forming F at the B3LYP/6-

311+G(d,p)/SDD//B3LYP/6-31G(d)/SDD level. The Gibbs free energies are given in kcal mol⁻¹.

Results: As shown in Scheme S14, the calculation results show that a key step in the proposed reaction **mechanism II** is thermodynamically unfavored. The reaction is endergonic, with an ΔG value of 80.4 kcal mol⁻¹ in triplet state.

Cartesian Coordinates

	I				Н	5.34383200	0.70117100	-2.70368400
B3LYP/6-31G(d)~SDD				С	5.78969200	1.14906600	0.65344000	
E = -809.132389 a.u.				Н	6.56390600	1.35739700	1.38514100	
	С	2.40635200	-1.54848600	-0.14774500	С	6.12086000	1.03359200	-0.70138100
	С	1.18856400	-0.91115400	-0.33883400	Н	7.15032900	1.14863400	-1.02580000
	С	1.06513300	0.50151200	-0.18500700	С	1.74481000	-0.38167100	4.06685900
	С	2.24524800	1.22010500	0.17233800	Н	0.98138100	0.31806700	4.41358100
	С	3.45637300	0.57336200	0.35968300	Н	1.30896900	-1.37452000	3.93635400
	С	3.54957200	-0.81716900	0.20201700	0	-4.81510400	0.56374400	0.66574500
	Н	2.47123200	-2.62647000	-0.27120400	0	-2.79914600	-3.21459900	-1.44766100
	Н	0.31749900	-1.50036000	-0.60929900	Ν	-2.58325100	0.56285400	0.59658100
	Н	2.18013400	2.29861300	0.29568200	Ν	-1.38392600	-1.69866900	-0.61825900
	Н	4.33785400	1.14859300	0.63078600	С	-2.91285000	1.82522300	1.32290900
	Н	4.49934000	-1.32304600	0.34960500	С	-4.45687100	1.87471600	1.20024800
	С	-0.15274700	1.20044500	-0.37046900	Н	-4.97511200	1.99597700	2.15160900
	С	-1.47777400	0.58744100	-0.71411300	Н	-4.80534400	2.62569800	0.48727400
	Н	-2.07427500	1.28994100	-1.30787700	С	-3.68119600	-0.04592300	0.30762300
	Н	-1.36216300	-0.31973100	-1.31718100	С	-3.89360900	-1.37461700	-0.38974100
	С	-2.26141200	0.23810700	0.55964000	С	-4.74250900	-1.12484500	-1.67139700
	Н	-2.45245000	1.12267500	1.16994300	С	-4.66653000	-2.31629100	0.58045100
	Н	-1.73357000	-0.50313400	1.16200800	С	-2.60595300	-2.06324300	-0.79974000
	Cl	-3.89181000	-0.47806000	0.16883700	С	-1.48746400	-3.77513800	-1.75865100
	Н	-0.13868100	2.27495100	-0.19775200	Н	-1.44681700	-3.93198800	-2.83730400
					Н	-1.40927100	-4.73244200	-1.24002600
					С	-0.48072400	-2.71048900	-1.24455500
	IV				С	0.56577300	-3.23288100	-0.28041200
	B3L	YP/6-31G(d)~S	DD		С	0.19556200	-3.85260900	0.92203600
	E = -	-2420.410229 a	.u.		С	1.92420400	-3.11321000	-0.59610400
	S	1.38809900	1.06159800	-1.99502200	С	1.16806800	-4.34515600	1.79186600
	0	2.85846900	0.32388200	-2.18804100	Н	-0.85568600	-3.95254300	1.18391600
	0	2.31284800	0.07420200	2.81874000	С	2.89928900	-3.60886400	0.27335900
	0	1.56127100	2.49829900	-2.10293000	Н	2.22120800	-2.63196200	-1.52476400
	0	0.46598900	0.33857500	-2.85760300	С	2.52304900	-4.22546800	1.46747000
	0	0.25183000	-0.03663700	1.89897600	Н	0.86950600	-4.83093000	2.71663100
	N	1.04194700	0.60547900	-0.43208900	Н	3.94979400	-3.51634300	0.01373200
	С	1.48937700	0.18932700	1.78560800	Н	3.28014800	-4.61769700	2.14037200
	С	2.04410400	0.56052200	0.49746300	С	-2.17556800	3.02483700	0.76641700
	С	3.43991900	0.74185800	0.14650600	С	-2.23827500	3.33944100	-0.59973100
	С	3.81249300	0.64721600	-1.21662400	С	-1.41762700	3.83490600	1.61975300
	С	4.47295900	1.00857500	1.07389700	С	-1.54489800	4.43987800	-1.10231800
	Н	4.22809700	1.10972000	2.12245100	Н	-2.82308100	2.72162000	-1.27810100
	С	5.12361800	0.78616000	-1.64505600	С	-0.73271400	4.94399300	1.11828000

Η	-1.36555100	3.60064900	2.68069700
С	-0.79223500	5.24483800	-0.24299800
Н	-1.58892400	4.66729400	-2.16299000
Н	-0.15174800	5.56858800	1.79051300
Н	-0.25265100	6.10123100	-0.63583700
Н	0.01839400	-2.21138300	-2.08005600
Н	-2.61256900	1.67778600	2.36602200
Н	-4.09207900	-2.50258200	1.49398400
Н	-5.61974600	-1.85921500	0.85389000
Н	-4.94797000	-2.07607300	-2.16602200
Н	-4.21516300	-0.47225300	-2.37521000
Н	2.58223300	-0.41440800	4.76217600
Н	-5.68897700	-0.65458100	-1.39743000
Н	-4.85963700	-3.27049200	0.08595000
Ni	-0.71850900	0.03429200	0.12746400

V

B3I	B3LYP/6-31G(d)~SDD					
E =	-3229.566934 a	ı.u.				
S	0.63850000	-0.25486800	-1.93066400			
0	2.22702600	-0.41641200	-2.30460300			
0	2.24542600	0.34092100	2.79784400			
0	0.21533500	1.10584100	-2.29307400			
0	-0.03138000	-1.36451900	-2.60154700			
0	0.19049600	0.64867100	2.01033400			
Ν	0.60149000	-0.44778600	-0.29807800			
С	1.35833800	0.26793300	1.83393900			
С	1.84015100	-0.39868000	0.52433900			
С	2.98017500	0.40197600	-0.14535400			
С	3.10966300	0.34955700	-1.53979300			
С	3.97040700	1.11084400	0.55044600			
Н	3.93565500	1.17109000	1.62974300			
С	4.14072900	0.97705200	-2.22931100			
Н	4.17237200	0.89322800	-3.31026500			
С	5.02224200	1.73599000	-0.12081500			
Н	5.77485900	2.27002200	0.45120400			
С	5.11115900	1.67208000	-1.51150000			
Н	5.92972500	2.15532800	-2.03602500			
С	1.82554400	0.90585200	4.07126100			
Н	2.70456600	0.83500800	4.70900600			
Н	1.52628800	1.94464700	3.92514000			
0	-3.01112000	4.02407200	-0.23431700			
0	-3.92026000	-0.03653400	-2.49850200			

Ν	-1.70628600	2.31327000	0.36995600
Ν	-2.52734500	-0.18408900	-0.76060300
С	-1.30251300	3.40760000	1.29773400
С	-2.28595300	4.55029600	0.91099100
Н	-3.02166300	4.77789800	1.68557600
Н	-1.78299500	5.46389600	0.59273100
С	-2.62641900	2.76170500	-0.42025800
С	-3.33045200	2.08274800	-1.57832000
С	-2.71407600	2.62772200	-2.90447500
С	-4.84621900	2.43321000	-1.52515700
С	-3.20108400	0.57456900	-1.56089400
С	-3.60168200	-1.46121600	-2.42943800
Н	-2.96755700	-1.69047500	-3.28833200
Н	-4.54166400	-2.00966000	-2.48067700
С	-2.85625800	-1.60688700	-1.07928900
С	-3.66582300	-2.26720500	0.02234800
С	-4.72656600	-1.60356100	0.65687300
С	-3.39308900	-3.59565800	0.36967100
С	-5.49450900	-2.25699500	1.62055000
Н	-4.95995800	-0.57342000	0.39957000
С	-4.16367400	-4.25195600	1.33132400
Н	-2.57555600	-4.12407900	-0.11445700
С	-5.21507300	-3.58364000	1.95891700
Н	-6.31327100	-1.73225400	2.10476700
Н	-3.93348600	-5.27992600	1.59356800
Н	-5.81345000	-4.09160300	2.70948100
С	0.15139900	3.82835700	1.18556700
С	0.85352900	3.77056200	-0.02436900
С	0.76855000	4.39244400	2.31166800
С	2.15443400	4.27419600	-0.10251900
Н	0.40388100	3.31454300	-0.90116100
С	2.06456200	4.90414100	2.22805800
Н	0.22626900	4.44916700	3.25395000
С	2.75960600	4.84651900	1.01766400
Н	2.69504100	4.21251700	-1.04211700
Н	2.52713900	5.35010700	3.10410700
Н	3.76770000	5.24475800	0.94903400
Н	-1.92099400	-2.14699400	-1.23363400
Н	-1.49555100	3.06733800	2.31947800
Н	-5.30562300	2.09047700	-0.59178300
Н	-4.97638000	3.51378300	-1.59852700
Н	-3.26398500	2.20825100	-3.75037300
Н	-1.66120200	2.35040500	-2.99181500
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-0.94566100

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Н	-1.62691800	-1.62778200	3.61340400
Cl	-0.62932600	-3.43860000	-0.15259500

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10. ¹H and ¹³C NMR Spectrum

















3.51 3.51 3.51 3.51 2.73 2.73 2.05 2.05 2.05 2.05 2.05







3.40 3.37 3.37 3.37 3.37 3.37 2.15 2.15 2.15 2.15 2.13 2.10 2.10

¹H NMR CDCl₃









 $\begin{array}{c} -2.223339 \\ -2.223339 \\ -2.223339 \\ -2.2339 \\ -2.2339 \\ -2.2339 \\ -2.2$
































































3.3.5.558







190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)





S155



S156