Electronic Supplementary Information

Chiral Nickel DBFOX Complex as the Bifunctional Catalyst for Visible-Light-Promoted Asymmetric Photoredox Reaction

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1. General Information

Synthesis of the substrates were carried out under an atmosphere of argon with magnetic stirring unless stated otherwise. Visible-light-induced catalytic reactions were performed in 10 mL Schlenk tubes at 25 °C under an atmosphere of argon and under irradiation with a 24 W blue LEDs lamp ($\lambda_{\text{max}} = 450$ nm; commercial supplier: Hong Chang Lighting Co. Ltd., website: http://hongchang-led.taobao.com). Solvents were distilled under argon from calcium hydride (CH$_3$CN, CH$_2$Cl$_2$) or sodium/benzophenone (THF, toluene). α,β-Unsaturated N-acyl pyrazole 1c, e–p,1 crotonyl oxazolidinone 1a,2 α,β-unsaturated 2-imidazole 1b,3 α,β-unsaturated 1,2-dione 1d,4 tertiary α-silylamines 2a–l,5 secondary α-silylamines 2m–r5,6 and bisoxazoline ligands L1–47 were synthesized according to the published procedures. All others reagents were purchased from commercial suppliers (TCI, Aldrich, Alfa and J&K) and used without further purification. Flash column chromatography was performed with silica gel (300-400 mesh, pH = 6.7–7.0). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM (400 MHz) or Bruker AM (500 MHz) or Bruker AM (850 MHz) spectrometer at ambient temperature. NMR standards were used as follows: CDCl$_3$ = 7.26 ppm ($^1$H NMR), 77.0 ppm ($^{13}$C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-7000 Fluorescent Spectrophotometer. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 T FT-MS instrument using ESI technique. Optical rotations were measured on Anton Paar MCP 500 polarimeter at concentrations of 1.0 g/100 mL. UV/vis absorption spectra were recorded on a Shimadzu UV-2550 in a 10.0 mm quartz cuvette. Cyclic voltammetry studies were carried out on a Princeton Applied Research PARSTAT 263A potentiostat offering compliance voltage up to ± 100 V (available at the counter electrode), scan range of ± 10 V and current range of ± 2 A. Enantiomeric excess of the products were determined by HPLC analysis on chiral stationary phases.
2. Synthesis of the Substrates and Racemic Reference Products

2.1 Synthesis of the Substrates

1) \(\alpha,\beta\)-Unsaturated \(N\)-acyl pyrazole 1c, e–p were prepared according to published procedures.\(^1\)

![Scheme S1. Synthetic route to \(\alpha,\beta\)-unsaturated \(N\)-acyl pyrazole 1c, e–p.](imagedesc)

**General procedure.** To a solution of \(\alpha,\beta\)-unsaturated carboxylic acid \(S1c\), e–p (6.5 mmol) and 3,5-dimethyl-1H-pyrazole (\(S2\), 692 mg, 7.2 mmol) in dichloromethane (15 mL) at 0 °C, \(N\)-(3-dimethylaminopropyl)-\(N\)'-ethylcarbodiimide hydrochloride (EDC·HCl, 1246 mg, 7.2 mmol) and 4-dimethylaminopyridine (DMAP, 7.9 mg, 0.065 mmol) were added. The resulting mixture was stirred at 0 °C for 30 min, then gradually warmed to room temperature, and stirred for additional 12 h. The resulting mixture was concentrated to dryness. The residue was purified by column chromatography on silica gel (eluted with a mixture of petroleum (PE) and ethyl acetate(EtOAc)) to afford pure product 1c, e–p. The analytic data of the products were consistent with the reported literature.\(^1\) The new compound 1o was synthesized and characterized as shown below.

![1o](imagedesc)

According to the general procedure, \(\alpha,\beta\)-unsaturated carboxylic acid \(S1o\) (897 g, 6.5 mmol) was converted to corresponding \(\alpha,\beta\)-unsaturated \(N\)-acyl pyrazole 1o (1053 mg, 4.9 mmol, 74%) as a white solid.
$^1$H NMR (500 MHz, CDCl$_3$): δ 7.83–7.69 (m, 2H), 7.62 (d, $J$ = 15.8 Hz, 1H), 7.44 (s, 1H), 6.76 (s, 1H), 5.99 (s, 1H), 2.60 (s, 3H), 2.28 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 165.6, 152.0, 145.4, 144.5, 136.2, 123.4, 117.7, 111.5, 108.1, 14.8, 14.0.

IR (film): ν (cm$^{-1}$) 3117, 2925, 1689, 1625, 1375, 1349, 1276, 1239, 1160, 1012, 967, 872, 842, 830, 790, 675, 613, 594, 575.

HRMS (ESI, m/z) calcd for C$_{12}$H$_{12}$N$_2$NaO$_2$ (M+Na)$^+$: 239.0796, found: 239.0790.

2) Tertiary α-silylamines 2a–l were prepared according to published procedures.$^5$

![Scheme S2. Synthetic route to tertiary α-silylamines 2a–l.](image)

**General procedure.** To a solution of tertiary amine 3a–l (9.3 mmol) in dry THF (31 mL) at -78 °C under argon was added dropwise a solution of n-BuLi in hexanes (1.6 M, 6.4 mL, 10.2 mmol). The solution was then allowed to warm to room temperature and stirred for 24 h. (Iodomethyl)trimethylsilane (1.5 mL, 10.2 mmol) was added dropwise. The resulting solution was stirred for additional 12 h, then quenched with a saturate solution of NH$_4$Cl in water (10 mL). The mixture was extracted with diethyl ether (3 x 20 mL). The combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The residue was subjected to silica gel chromatography (eluted with PE:EtOAc = 50:1) to afford product 2a–l. The analytic data of the products were consistent with the reported literature.$^5$ The new compound 2k and 2l were synthesized and characterized as shown below.
According to the general procedure, 3-bromo-N,N-dimethylaniline (S3k, 1731 mg, 9.3 mmol) was converted to corresponding tertiary α-silylamines 2k (1978 mg, 7.3 mmol, 78%) as a yellow liquid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.02 (t, $J = 8.1$ Hz, 1H), 6.80–6.62 (m, 2H), 6.54 (d, $J = 8.4$ Hz, 1H), 2.92 (s, 3H), 2.84 (s, 2H), 0.09 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 151.5, 130.2, 123.5, 117.8, 114.4, 110.3, 44.1, 40.3, -1.0.

IR (film): $\nu$ (cm$^{-1}$) 2959, 2897, 1590, 1551, 1493, 1365, 1260, 1232, 1073, 1018, 982, 854, 820, 795, 754, 593, 680.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{19}$BrNSi (M+H)$^+$: 272.0470, found: 272.0463.

According to the general procedure, N-ethyl-N,4-dimethylaniline (S3l, 1256 mg, 9.3 mmol) was converted to corresponding tertiary α-silylamines 2l (1326 mg, 6.0 mmol, 65%) as a yellow liquid.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.00 (d, $J = 8.1$ Hz, 2H), 6.58 (d, $J = 8.1$ Hz, 2H), 2.76 (s, 2H), 2.24 (s, 3H), 1.09 (t, $J = 7.0$ Hz, 3H), 0.08 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 147.3, 129.6, 124.2, 112.7, 46.9, 41.5, 20.3, 10.8, -1.1.

IR (film): $\nu$ (cm$^{-1}$) 3095, 3007, 2955, 2920, 2867, 1618, 1567, 1519, 1372, 1348, 1247, 1216, 1191, 1169, 1110, 1067, 984, 908, 850, 799, 760, 693, 505.

HRMS (ESI, m/z) calcd for C$_{13}$H$_{24}$NSi (M+H)$^+$: 222.1678, found: 222.1673.
3) Secondary α-silylamines 2m–r were prepared according to published procedure.\textsuperscript{5,6}

\textbf{Scheme S3.} Synthetic route to secondary α-silylamines 2m–r.

\textbf{General procedure.} To a solution of (iodomethyl)trimethylsilane (1006 mg, 4.7 mmol) in toluene (5.0 mL), aniline S3m–r (24 mmol) was added dropwise. The reaction mixture was stirred at 130 °C for 12 h, then allowed to cool to room temperature, quenched with water (5 mL) and extracted with Et₂O (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel (eluted with PE:EtOAc = 50:1) to afford secondary α-silylamines 2m–r. The analytic data of the products were consistent with the reported literature.\textsuperscript{5,6} The new compounds 2o, 2q and 2r were synthesized and characterized as shown below.

According to the general procedure, the reaction of 3-chloroaniline (S3o, 3061 mg, 24 mmol) with (iodomethyl)trimethylsilane (1006 mg, 4.7 mmol) afforded secondary α-silylamines 2o (403 mg, 1.89 mmol, 40%) as a yellow liquid.

\textsuperscript{1}H NMR (400 MHz, CDCl₃): δ 7.08–7.03 (m, 1H), 6.66–6.61 (m, 2H), 6.53–6.49 (m, 1H), 3.53 (s, 1H), 2.47 (s, 2H), 0.14 (s, 9H).

\textsuperscript{13}C NMR (101 MHz, CDCl₃) δ 151.8, 135.2, 130.1, 116.9, 112.2, 111.1, 33.7, -2.6.

IR(film): ν(cm⁻¹) 3420, 3055, 2953, 2894, 1629, 1601, 1529, 1400, 1310, 1261, 829, 804, 741, 702, 472.

HRMS (ESI, m/z) calcd for C₁₀H₁₇ClNSi (M+H)+: 214.0818, found: 214.0813.
According to the general procedure, the reaction of 3-fluoroaniline (S3q, 2667 mg, 24 mmol) with (iodomethyl)trimethylsilane (1006 mg, 4.7 mmol) afforded secondary α-silylamines 2q (387 mg, 1.96 mmol, 42%) as a yellow liquid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.16–7.03 (m, 1H), 6.51–6.30 (m, 3H), 3.62 (s, 1H), 2.48 (s, 2H), 0.15 (s, 10H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 130.1, 108.6, 103.5, 103.3, 99.2, 98.94, 33.7, -2.3.

IR(film): ν(cm$^{-1}$) 3416, 3048, 2950, 2894, 163, 1601, 1519, 1398, 1300, 1261, 829, 804, 739, 701475.

HRMS (ESI, m/z) calcd for C$_{10}$H$_{17}$FNSi (M+H)$^+$: 198.1114, found: 198.1109.

According to the general procedure, the reaction of naphthalen-2-amine (S3r, 3432 mg, 24 mmol) with (iodomethyl)trimethylsilane (1006 mg, 4.7 mmol) afforded secondary α-silylamines 2r (204 mg, 0.89 mmol, 19%) as a yellow liquid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.69–7.58 (m, 3H), 7.35 (t, $J$ = 7.6 Hz, 1H), 7.18 (t, $J$ = 7.4 Hz, 1H), 6.91 (d, $J$ = 8.6 Hz, 2H), 3.70 (s, 1H), 2.62 (s, 2H), 0.15 (s, 9H).

IR(film): ν(cm$^{-1}$) 3416, 3052, 2953, 2894, 1629, 1601, 1519, 1398, 1300, 1261, 829, 804, 741, 702, 470.

HRMS (ESI, m/z) calcd for C$_{14}$H$_{20}$NSi (M+H)$^+$: 230.1365, found: 230.1363.
2.2 Synthesis of the Racemic Products as References

1) Preparation of 125 mM stock solution of the racemic catalyst [Ni(ClO₄)₂·6H₂O/rac-L₁] in THF.

A solution of Ni(ClO₄)₂·6H₂O (73 mg, 0.20 mmol) and racemic DBFOX ligand rac-L₁ (110 mg, 0.24 mmol) in THF (1.6 mL) was stirred at 30 °C for 1 h, which was used directly for the catalytic reactions.

2) Synthesis of racemic reference compounds rac-3a–z, 3za (reaction with tertiary α-silylamines).

![Scheme S4. Synthesis of racemic reference compounds rac-3a–z, 3za.](image)

**General procedure.** A dried 10 mL Schlenk tube was charged with 1a–p (0.10 mmol), 2a–l (58.0 mg, 0.30 mmol), racemic catalyst Ni(ClO₄)₂·6H₂O/rac-L₁ (80 μL taken from the 125 mM stock solution), and THF (420 μL). 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. After being stirred at 25 °C for the 8–16 h (monitored by TLC analysis), the reaction mixture was concentrated and then purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford racemic product rac-3a–z, 3za as HPLC reference for the determination of enantiomeric excess.
3) Synthesis of racemic reference compounds rac-3zb–zg (reaction with secondary α-silylamines).

**Scheme S5.** Synthesis of racemic reference compounds rac-3zb–zg.

**General procedure.** A dried 10 mL Schlenk tube was charged with 1c (24.6 mg, 0.15 mmol), 2m–r (0.10 mmol), racemic catalyst Ni(ClO₄)₂·6H₂O/rac-L1 (80 μL taken from the 125 mM stock solution), and THF (420 μL). 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. After being stirred at 25 °C for 12 h, the mixture was concentrated and then purified by flash chromatography on silica gel (PE/EtOAc = 40:1 to 5:1) to afford racemic product rac-3zb–zg as HPLC reference for the determination of enantiomeric excess.
3. Nickel-Catalyzed Asymmetric Photoredox Reactions

3.1 Optimization of the Reaction Conditions

*Preparation of 125 mM stock solutions in THF of the non-racemic metal catalyst (metal salt/L1–4).* A solution of metal salt (0.050 mmol) and chiral ligand L1–4 (0.060 mmol) in THF (0.40 mL) was stirred at 30 °C for 1 h, which was used directly for the catalytic reactions.

**Table S1.** Optimization of reaction conditions.

| entry | metal salt | L* | solv. | subs. | light source | t (h) | product conv. | ee (%) |
|-------|------------|----|-------|-------|--------------|------|--------------|-------|
| 1     | Ni(ClO₄)₂ | L1 | THF   | 1a    | CFL 23 W     | 12   | 3a           | 0 n.a |
| 2     | Ni(ClO₄)₂ | L1 | THF   | 1b    | CFL 23 W     | 12   | 3b           | 22 78 |
| 3     | Ni(ClO₄)₂ | L1 | THF   | 1c    | CFL 23 W     | 6    | 3c           | 95 91 |
| 4     | Ni(ClO₄)₂ | L1 | THF   | 1d    | CFL 23 W     | 12   | 3d           | 0 n.a |
| 5     | Ni(ClO₄)₂ | L2 | THF   | 1c    | CFL 23 W     | 12   | 3c           | 23 0  |
| 6     | Ni(ClO₄)₂ | L3 | THF   | 1c    | CFL 23 W     | 12   | 3c           | 21 n.d|
| 7     | Ni(ClO₄)₂ | L4 | THF   | 1c    | CFL 23 W     | 12   | 3c           | 0 n.a |
| 8     | Ni(ClO₄)₂ | L1 | CH₂Cl₂| 1c    | CFL 23 W     | 6    | 3c           | 0 n.a |
| 9     | Ni(ClO₄)₂ | L1 | MeOH  | 1c    | CFL 23 W     | 6    | 3c           | 0 n.a |
| 10    | Ni(ClO₄)₂ | L1 | CF₃Ph | 1c    | CFL 23 W     | 6    | 3c           | 0 n.a |
| Entry | Catalyst | Solvent | Light Source | W | % Conversion |
|-------|----------|---------|--------------|---|--------------|
| 11    | Ni(ClO₄)₂ | L₁ | CH₃CN | 6 | 57 66 |
| 12    | Ni(ClO₄)₂ | L₁ | NMP | 6 | 3c 0 n.a. |
| 13    | Ni(ClO₄)₂ | L₁ | CH₃NO₂ | 6 | 3c 0 n.a. |
| 14    | Ni(ClO₄)₂ | L₁ | THF | 12 | 3c 95 91 |
| 15    | Ni(ClO₄)₂ | L₁ | THF | blue LEDs | 3 | 3c 95 91 |
| 16    | Ni(ClO₄)₂ | L₁ | THF | red LEDs | 12 | 3c 0 n.a. |
| 17    | Ni(ClO₄)₂ | L₁ | THF | yellow LEDs | 12 | 3c 0 n.a. |
| 18    | Ni(ClO₄)₂ | L₁ | THF | UV 365 nm | 6 | 3c 90 91 |
| 19    | Mg(OTf)₂ | L₁ | THF | blue LEDs | 12 | 3c 0 n.a. |
| 20    | Ni(COD)₂ | L₁ | THF | blue LEDs | 12 | 3c 0 n.a. |
| 21    | none | L₁ | THF | blue LEDs | 12 | 3c 0 n.a. |
| 22    | Ni(ClO₄)₂ | none | THF | blue LEDs | 12 | 3c 0 n.a. |
| 23    | Ni(ClO₄)₂ | L₁ | THF | none | 12 | 3c <5 n.a. |
| 24<sup>c</sup> | Ni(ClO₄)₂ | L₁ | THF | blue LEDs | 12 | 3c 0 n.a. |
| 25<sup>d</sup> | Ni(ClO₄)₂ | L₁ | THF | blue LEDs | 12 | 3c 0 n.a. |
| 26<sup>e</sup> | Ni(ClO₄)₂ | L₁ | THF | blue LEDs | 12 | 3c 0 n.a. |

<sup>a</sup> conversion determined by ¹H-NMR. <sup>b</sup> ee value determined by chiral HPLC. <sup>c</sup> reaction performed in air. <sup>d</sup> reaction performed in the presence of 1 equiv. TEMPO. <sup>e</sup> reaction performed in the presence of 3 equiv. BHT. n.d. = not determined, n. a. = not applicable.

**General Procedure.**

For entries 1–20: A dried 10 mL Schlenk tube was charged with 1a–d (0.10 mmol), 2a (58.0 mg, 0.30 mmol), metal catalyst (metal salt/L₁–4, 80 μL taken from the 125 mM stock solution in the indicated solvent), and the indicated solvent (420 μL). The mixture was degassed via three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from the indicated light source. After being stirred at 25 °C for the indicated time, the reaction mixture was concentrated to dryness. The conversion was
determined by $^1$H NMR analysis of the crude product, and ee value was determined by chiral HPLC chromatography using a Daicel Chiralpak OJ column.

For entries 21–26: The nickel-catalyzed photoredox reactions were performed at the standard conditions (entry 15) with the indicated variations. After being stirred in air at 25 °C for the indicated time, the reaction mixture was concentrated to dryness. The conversion was determined by $^1$H NMR analysis of the crude product, and ee value was determined by chiral HPLC chromatography using a Daicel Chiralpak OJ column.

3.2 Substrate Scope

1) Reaction with tertiary α-silylamines

**General Procedure.** A dried 10 mL Schlenk tube was charged with 1c, e–p (0.20 mmol), 2a–l (0.60 mmol), chiral nickel catalyst Ni(ClO$_4$)$_2$·6H$_2$O /L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for the indicated time, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH$_2$Cl$_2$ = 10:1 to 2:1) to afford non-racemic product 3c, e–z, za.

![Scheme S6. Nickel-catalyzed asymmetric photoredox reaction to non-racemic products 3c, e–z, za.](image)
A dried 10 mL Schlenk tube was charged with 1c (32.4 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L₁ (160 μL taken from the 125 M stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 8 h the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3c as a light yellow liquid (43.1 mg, 0.151 mmol, yield: 76%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 91% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, tᵣ(major) = 32.4 min, tᵣ(minor) = 17.8 min. [α]D²³ = -8.33° (c = 1.0, CH₂Cl₂).

1H NMR (500 MHz, CDCl₃): δ 7.22 (t, J = 1.6 Hz, 2H), 6.74 (d, J = 8.3 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 5.93 (s, 1H), 3.37 (dd, J = 14.4, 7.1 Hz, 1H), 3.20 (dd, J = 16.2, 6.0 Hz, 1H), 3.13 (dd, J = 14.4, 7.9 Hz, 1H), 2.95 (s, 4H), 2.68 (m, 1H), 2.52 (s, 3H), 2.23 (s, 3H), 1.05 (d, J = 6.7 Hz, 3H).

13C NMR (126 MHz, CDCl₃): δ 173.2, 151.8, 149.8, 144.1, 129.2, 116.3, 112.4, 111.1, 59.3, 40.2, 39.5, 29.5, 18.2, 14.7, 13.9.

IR (film): ν (cm⁻¹) 3025, 2962, 2926, 2655, 1724, 1599, 1506, 1454, 1411, 1376, 1337, 1260, 1224, 1194, 1080, 1033, 963, 863, 800, 747, 693, 661, 520.

HRMS (ESI, m/z) calcd for C₁₇H₂₃N₃NaO (M+Na)⁺: 308.1738, found: 308.1733.

A dried 10 mL Schlenk tube was charged with 1e (35.6 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L₁ (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3e as a light yellow oil (48.6 mg, 0.162 mmol, yield: 81%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 96% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, tᵣ(major) = 22.5 min, tᵣ(minor) = 12.3 min. [α]D23 = -9.9° (c = 1.0, CH₂Cl₂).

1H NMR (500 MHz, CDCl₃): δ 7.23–7.17 (m, 2H), 6.73 (d, 2H), 6.67 (t, J = 7.2 Hz, 1H), 5.91 (d, J = 1.1 Hz, 1H), 3.31 (dd, J = 14.5, 7.8 Hz, 1H), 3.22 (dd, J = 14.5, 7.5 Hz, 1H), 3.15 (dd, J = 16.5, 7.2 Hz, 1H), 3.06 (dd, J = 16.5, 6.0 Hz, 1H), 2.91 (s, 3H), 2.59–2.52 (m, 1H), 2.49 (s, 3H), 2.21 (s, 3H), 1.60–1.51 (m, 1H), 1.46–1.37 (m, 1H), 0.98 (t, J = 7.5 Hz, 3H).

13C NMR (126 MHz, CDCl₃): δ 173.5, 151.7, 150.0, 144.0, 129.1, 116.3, 112.5, 111.1, 57.4, 39.4, 37.4, 35.8, 25.1, 14.7, 13.9, 11.4.

IR (film): ν (cm⁻¹) 2962, 2926, 1958, 1724, 1599, 1505, 1411, 1377, 1343, 1261, 1094, 1020, 962, 855, 800, 746, 691, 516.

HRMS (ESI, m/z) calcd for C₁₈H₂₅N₃NaO (M+Na)⁺: 322.1895, found: 322.1889.

A dried 10 mL Schlenk tube was charged with 1f (38.4 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3f as a light yellow oil (50.1 mg, 0.160 mmol, yield: 80%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 95% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, tᵣ(major) = 15.7 min, tᵣ(minor) = 10.3 min. [α]D23 = -7.03° (c = 1.0, CH₂Cl₂).
1H NMR (500 MHz, CDCl3): δ 7.19 (t, J = 7.7 Hz, 2H), 6.72 (d, J = 8.2 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 5.90 (s, 1H), 3.30 (dd, J = 14.4, 7.9 Hz, 1H), 3.24–3.12 (m, 2H), 3.05 (dd, J = 16.5, 5.9 Hz, 1H), 2.90 (s, 3H), 2.65–2.59 (m, 1H), 2.49 (s, 3H), 2.21 (s, 3H), 1.48–1.42 (m, 2H), 1.40–1.35 (m, 2H), 0.91 (t, J = 6.5 Hz, 3H).

13C NMR (126 MHz, CDCl3): δ 173.5, 151.7, 150.0, 144.0, 129.1, 116.3, 112.6, 111.1, 57.8, 39.4, 37.9, 34.9, 34.1, 20.2, 14.7, 14.5, 13.9.

IR (film): ν (cm⁻¹) 3432, 2960, 2926, 2915, 1723, 1599, 1505, 1410, 1401, 1338, 1260, 1092, 1025, 961, 799, 746, 691.

HRMS (ESI, m/z) calcd for C19H27N3NaO (M+Na)⁺: 336.2051, found: 336.2046.

A dried 10 mL Schlenk tube was charged with 1g (46.4 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO4)2·6H2O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH2Cl2 = 10:1 to 2:1) to afford product 3g as a colorless oil (51.0 mg, 0.144 mmol, yield: 72%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 99% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, t₁(major) = 10.0 min, t₁(minor) = 8.8 min. [α]D23 = -8.31° (c = 1.0, CH2Cl2).

1H NMR (500 MHz, CDCl3): δ 7.20–7.15 (m, 2H), 6.70 (d, J = 8.2 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 5.88 (s, 1H), 3.27 (d, J = 7.8 Hz, 2H), 3.12 (dd, J = 16.5, 8.0 Hz, 1H), 3.03 (dd, J = 16.5, 5.2 Hz, 1H), 2.84 (s, 3H), 2.61–2.52 (m, 1H), 2.45 (s, 3H), 2.19 (s, 3H), 1.81–1.61 (m, 7H), 1.55–1.45 (m, 1H), 1.22–1.16 (m, 3H).

13C NMR (126 MHz, CDCl3): δ 173.8, 151.5, 150.2, 143.9, 129.0, 116.4, 112.7, 111.0, 55.3, 39.4, 39.3, 39.2, 34.9, 30.8, 29.3, 27.0, 26.9, 26.8, 14.7, 13.9.
IR (film): ν (cm⁻¹) 3059, 3024, 2961, 2924, 2851, 1723, 1599, 1506, 1448, 1411, 1376, 1339, 1260, 1193, 1172, 1103, 1033, 994, 962, 855, 801, 747, 692, 586, 520.

HRMS (ESI, m/z) calcd for C_{22}H_{31}N_{3}NaO (M+Na)^+: 376.2364, found: 376.2359.

A dried 10 mL Schlenk tube was charged with 1h (41.2 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3h as a light yellow oil (49.8 mg, 0.158 mmol, yield: 79%).

Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 96% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, t( major) = 11.5 min, t(minor) = 9.1 min. [α]D²³ = -9.46° (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃): δ 7.20 (t, J = 6.9 Hz, 2H), 6.72 (d, J = 8.2 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 5.91 (s, 1H), 3.31 (dd, J = 14.4, 7.9 Hz, 1H), 3.24–3.12 (m, 2H), 3.05 (dd, J = 16.4, 5.8 Hz, 1H), 2.90 (s, 3H), 2.65–2.56 (m, 1H), 2.49 (s, 3H), 2.21 (s, 3H), 1.53–1.45 (m, 5H), 0.89 (t, J = 7.0 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 173.5, 151.6, 150.0, 144.0, 129.1, 116.3, 112.6, 111.0, 57.8, 39.4, 34.3, 32.3, 29.2, 23.1, 14.7, 14.2, 13.9.

IR (film): ν (cm⁻¹) 2957, 2927, 2856, 1724, 1601, 1506, 1453, 1411, 1392, 1342, 1260, 1095, 1033, 992, 962, 800, 747, 654.

HRMS (ESI, m/z) calcd for C_{20}H_{29}N_{3}NaO (M+Na)^+: 350.2208, found: 350.2201.
A dried 10 mL Schlenk tube was charged with 1i (38.8 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3i as a yellow oil (45.5 mg, 0.144 mmol, yield: 72%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 93% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 95:5, flow rate: 0.5 mL/min, 30 °C, t_r(major) = 11.6 min, t_r(minor) = 14.4 min. [α]D⁰²³ = 9.70° (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃): δ 7.23 (t, J = 8.3 Hz, 2H), 6.76 (d, J = 8.2 Hz, 2H), 6.69 (t, J = 7.2 Hz, 1H), 5.95 (s, 1H), 4.29–4.20 (m, 1H), 3.65–3.46 (m, 3H), 3.46–3.36 (m, 2H), 3.23 (dd, J = 16.1, 5.7 Hz, 1H), 3.02 (s, 3H), 2.54 (s, 3H), 2.23 (s, 3H), 1.09 (t, J = 7.0 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 171.9, 152.1, 149.4, 144.1, 129.2, 116.3, 112.2, 111.3, 74.7, 66.2, 57.5, 39.7, 39.4, 15.8, 14.6, 13.9.

IR (film): ν (cm⁻¹) 2963, 2926, 1723, 1599, 1506, 1480, 1445, 1410, 1377, 1340, 1261, 1194, 1109, 1033, 962, 864, 801, 744, 692, 669, 509.

HRMS (ESI, m/z) calcd for C₁₈H₂₅N₃NaO₂ (M+Na)+: 338.1844, found: 338.1838.

A dried 10 mL Schlenk tube was charged with 1j (43.6 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3j as a yellow oil (45.5 mg, 0.144 mmol, yield: 72%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 93% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 95:5, flow rate: 0.5 mL/min, 30 °C, t_r(major) = 11.6 min, t_r(minor) = 14.4 min. [α]D⁰²³ = 9.70° (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃): δ 7.23 (t, J = 8.3 Hz, 2H), 6.76 (d, J = 8.2 Hz, 2H), 6.69 (t, J = 7.2 Hz, 1H), 5.95 (s, 1H), 4.29–4.20 (m, 1H), 3.65–3.46 (m, 3H), 3.46–3.36 (m, 2H), 3.23 (dd, J = 16.1, 5.7 Hz, 1H), 3.02 (s, 3H), 2.54 (s, 3H), 2.23 (s, 3H), 1.09 (t, J = 7.0 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 171.9, 152.1, 149.4, 144.1, 129.2, 116.3, 112.2, 111.3, 74.7, 66.2, 57.5, 39.7, 39.4, 15.8, 14.6, 13.9.

IR (film): ν (cm⁻¹) 2963, 2926, 1723, 1599, 1506, 1480, 1445, 1410, 1377, 1340, 1261, 1194, 1109, 1033, 962, 864, 801, 744, 692, 669, 509.

HRMS (ESI, m/z) calcd for C₁₈H₂₅N₃NaO₂ (M+Na)+: 338.1844, found: 338.1838.
cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3j as a white powder (46.6 mg, 0.137 mmol, yield: 68%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 1%, 16:1 dr (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 99:1, flow rate: 0.5 mL/min, 30 °C, tᵢ(3j, major) = 10.7 min, tᵢ(3j, minor) = 11.0 min, tᵢ(3j', major) = 12.5 min, tᵢ(3j', minor) = 13.5 min.

Analytic data of the major diastereomer 3j:

¹H NMR (500 MHz, CDCl₃): δ 7.16–7.12 (m, 1H), 6.99 (d, J = 6.4 Hz, 1H), 6.72 (s, 1H), 6.67–6.61 (m, 1H), 6.05 (s, 1H), 5.74 (d, J = 8.1 Hz, 1H), 3.56–3.49 (m, 1H), 3.49–3.40 (m, 1H), 3.27 (dd, J = 11.5, 8.6 Hz, 1H), 2.95 (s, 3H), 2.53 (s, 3H), 2.30 (s, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 173.6, 153.0, 146.7, 145.0, 128.7, 128.5, 119.2, 118.1, 112.5, 86.1, 47.9, 41.4, 40.3, 39.7, 29.9, 14.7, 14.1.

IR (film): ν (cm⁻¹) 2962, 2924, 2853, 1727, 1602, 1587, 1503, 1455, 1400, 1379, 1352, 1285, 1112, 1025, 962, 801, 751, 684, 600, 462.

HRMS (ESI, m/z) calcd for C₁₇H₁₈F₃N₃NaO (M+Na)⁺: 360.1297, found: 360.1293.

A dried 10 mL Schlenk tube was charged with 1k (41.6 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 16 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 15:1 to 10:1) to afford product 3k as a colorless oil (37.6 mg, 0.115 mmol, yield: 57%). Enantiomeric
excess was established by HPLC analysis using a Chiralpak OD-H column, \( ee = 1\% \), 32:1 dr (HPLC: OD-H, 220 nm, \( n\)-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, \( t_r(3k, \text{major}) = 13.5 \text{ min}, t_r(3k, \text{minor}) = 14.0 \text{ min}, t_r(3k', \text{major}) = 16.4 \text{ min, } t_r(3k', \text{minor}) = 45.4 \text{ min.} \)

**Analytic data of the major diastereomer 3k:**

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta 7.15–7.07 \text{ (m, 1H)}, 6.87 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, 6.66 \text{ (d, } J = 8.3 \text{ Hz, 1H)}, 6.60 \text{ (t, } J = 7.4 \text{ Hz, 1H)}, 6.03 \text{ (s, 1H)}, 5.70 \text{ (d, } J = 7.4 \text{ Hz, 1H)}, 3.69–3.60 \text{ (m, 4H)}, 3.56–3.50 \text{ (m, 1H)}, 3.44 \text{ (dd, } J = 11.3, 7.9 \text{ Hz, 1H)}, 2.94 \text{ (s, 3H)}, 2.55 \text{ (s, 3H)}, 2.28 \text{ (s, 3H)}. \)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta 174.5, 172.6, 152.7, 146.3, 144.7, 128.7, 128.4, 119.3, 117.3, 111.9, 100.1, 52.4, 50.5, 43.4, 41.9, 39.5, 29.9, 14.8. \)

IR (film): \( \nu (\text{cm}^{-1}) \) 2962, 2924, 1729, 1602, 1587, 1508, 1455, 1405, 1379, 1352, 1285, 1122, 1028, 962, 801, 753, 684, 605, 460.

HRMS (ESI, m/z) calcd for C\(_{18}\)H\(_{21}\)N\(_3\)NaO\(_3\) (M+Na\(^+\)): 350.1481, found: 350.1476.

A dried 10 mL Schlenk tube was charged with \( 1l \) (45.2 mg, 0.20 mmol), \( 2a \) (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO\(_4\))\(_2\)·6H\(_2\)O/\( L1 \) (160 \( \mu \)L taken from the 125 mM stock solution in THF), and THF (840 \( \mu \)L). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (\( n\)-hexane/EtOAc = 30:1 to 10:1) to afford product \( 3l \) (38.2 mg, 0.110 mmol, yield: 55%) as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, \( ee = 90\% \) (HPLC: OJ, 254 nm, \( n\)-hexane/isopropanol = 95:5, flow rate: 1 mL/min, 30 °C, \( t_r(\text{major}) = 32.4 \text{ min, } t_r(\text{minor}) = 15.1 \text{ min.} \) \( [\alpha]_D^{23} = 68.75° \) (c = 1.0, CH\(_2\)Cl\(_2\)).
$^1$H NMR (500 MHz, CDCl$_3$): δ 7.30–7.25 (m, 4H), 7.23–7.18 (m, 3H), 6.73–6.65 (m, 3H), 5.88 (s, 1H), 3.88–3.78 (m, 1H), 3.73 (dd, $J = 14.5, 7.2$ Hz, 1H), 3.58–3.47 (m, 2H), 3.36 (dd, $J = 14.5, 8.0$ Hz, 1H), 2.67 (s, 3H), 2.43 (s, 3H), 2.22 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 172.3, 151.9, 149.2, 144.1, 142.6, 129.2, 128.6, 128.1, 126.9, 116.4, 112.4, 111.1, 59.7, 40.2, 39.6, 38.8, 14.6, 13.9.

IR (film): ν (cm$^{-1}$) 3027, 2926, 2805, 1724, 1599, 1506, 1453, 1410, 1385, 1351, 1250, 1117, 1034, 993, 962, 868, 802, 747, 699, 605, 518.

HRMS (ESI, m/z) calcd for C$_{22}$H$_{25}$N$_3$NaO (M+Na)$^+$: 370.1895, found: 370.1889.

A dried 10 mL Schlenk tube was charged with 1m (48.1 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO$_4$)$_2$·6H$_2$O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 30:1 to 10:1) to afford product 3m as a colorless oil (50.9 mg, 0.141 mmol, yield: 70%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 90% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.8 mL/min, 30 °C, $t_{(major)}$ = 37.7 min, $t_{(minor)}$ = 22.6 min, [α]$_D^{23}$ = -69.30° (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.23 (t, $J = 8.6$ Hz, 2H), 7.18 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 6.71 (dd, $J = 18.1, 7.7$ Hz, 3H), 5.90 (s, 1H), 3.86–3.77 (m, 1H), 3.71 (dd, $J = 14.5, 7.4$ Hz, 1H), 3.58–3.47 (m, 2H), 3.36 (dd, $J = 14.4, 7.8$ Hz, 1H), 2.70 (s, 3H), 2.44 (s, 3H), 2.32 (s, 3H), 2.23 (s, 3H).
\(^{13}\text{C NMR} \ (126 \text{ MHz, CDCl}_3): \ \delta \ 172.4, 151.8, 149.3, 144.1, 139.5, 136.4, 129.3, 129.2, 127.9, 116.3, 112.4, 111.1, 66.0, 59.8, 39.8, 38.9, 21.2, 14.6, 13.9.\)

IR (film): \(\nu \ (\text{cm}^{-1}) \ 3021, 2962, 2810, 1723, 1514, 1504, 1411, 1376, 1345, 1261, 1095, 1020, 962, 864, 800, 746, 691.\)

HRMS (ESI, \(m/z\)) calcd for \(\text{C}_{23}\text{H}_{27}\text{N}_3\text{NaO} \ (\text{M+Na})^+: \ 384.2051\), found: 384.2046.

A dried 10 mL Schlenk tube was charged with \(1\text{n} \ (51.3 \text{ mg, 0.20 mmol})\), \(2\text{a} \ (116 \text{ mg, 0.60 mmol})\), chiral nickel catalyst \(\text{Ni(ClO}_4)_2\cdot 6\text{H}_2\text{O/L1} \ (160 \mu\text{L taken from the 125 mM stock solution in THF}) \) in THF (840 \(\mu\text{L})\). The mixture was degassed \(\text{via}\) three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (\(n\)-hexane/EtOAc = 30:1 to 10:1) to afford product \(3\text{n}\) as a colorless oil (38.3 mg, 0.101 mmol, yield: 51%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, \(ee = 80\% \ (\text{HPLC: OJ, 254 nm, n}}\)-hexane/isopropanol = 95:5, flow rate: 0.8 mL/min, 30 °C, \(t_1\text{(major)} = 39.8 \text{ min, } t_1\text{(minor)} = 27.9 \text{ min}. \ [\alpha]_D^{23} = -37.80^\circ \ (c = 1.0, \text{CH}_2\text{Cl}_2).\)

\(^{1}\text{H NMR} \ (500 \text{ MHz, CDCl}_3): \ \delta \ 7.24–7.17 \ (m, 4\text{H}), 6.83 \ (d, J = 8.4 \text{ Hz, 2H}), 6.70 \ (t, J = 8.1 \text{ Hz, 3H}), 5.90 \ (s, 1\text{H}), 3.78 \ (s, 4\text{H}), 3.71 \ (dd, J = 14.4, 7.2 \text{ Hz, 1H}), 3.56–3.44 \ (m, 2\text{H}), 3.32 \ (dd, J = 14.4, 7.9 \text{ Hz, 1H}), 2.68 \ (s, 3\text{H}), 2.44 \ (s, 3\text{H}), 2.23 \ (s, 3\text{H}).\)

\(^{13}\text{C NMR} \ (126 \text{ MHz, CDCl}_3): \ \delta \ 172.4, 158.5, 151.9, 149.2, 144.1, 134.6, 129.2, 129.0, 116.3, 114.0, 112.3, 111.1, 59.8, 55.3, 39.6, 39.4, 39.0, 14.6, 13.9.\)

IR (film): \(\nu \ (\text{cm}^{-1}) \ 2961, 2925, 2820, 1722, 1598, 1505, 1453, 1410, 1376, 1351, 1259, 1177, 1096, 1033, 962, 863, 800, 747, 692, 586, 547.\)

HRMS (ESI, \(m/z\)) calcd for \(\text{C}_{23}\text{H}_{27}\text{N}_3\text{NaO}_2 \ (\text{M+Na})^+: \ 400.2001\), found: 400.1995.
A dried 10 mL Schlenk tube was charged with 1o (48.8 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 30:1 to 10:1) to afford product 3o as a colorless oil (33.6 mg, 0.092 mmol, yield: 47%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 89% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 95:5, flow rate: 0.8 mL/min, 30 °C, t_r(major) = 18.9 min, t_r(minor) = 16.4 min. [α]D²³ = 40.03° (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃): δ 7.25–7.20 (m, 4H), 7.04–6.92 (m, 2H), 6.75–6.64 (m, 3H), 5.91 (d, J = 1.1 Hz, 1H), 3.87–3.78 (m, 1H), 3.73 (dd, J = 14.4, 6.9 Hz, 1H), 3.58–3.45 (m, 2H), 3.33 (dd, J = 14.4, 8.2 Hz, 1H), 2.68 (s, 3H), 2.45 (d, J = 45.3 Hz, 3H), 2.23 (s, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 172.2, 161.9 (J_C–F = 251.6 Hz), 152.0, 149.1, 144.1, 129.5, 129.4, 116.5, 115.5, 115.4, 112.3, 111.2, 59.7, 39.6, 39.5, 38.9, 14.6, 13.9.

IR (film): ν (cm⁻¹) 2962, 2895, 2801, 1722, 1598, 1505, 1410, 1377, 1353, 1261, 1223, 1096, 1020, 961, 864, 800, 747, 692.

HRMS (ESI, m/z) calcd for C₂₂H₂₄F₃N₃O (M+Na⁺): 388.1801, found: 388.1791.
A dried 10 mL Schlenk tube was charged with 1p (43.2 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 30:1 to 10:1) to afford product 3p as a colorless oil (44.0 mg, 0.122 mmol, yield: 65%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 92% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.8 mL/min, 30 °C, t_r(major) = 26.6 min, t_r(minor) = 23.3 min. [α]D²³ = 19.89° (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃): δ 7.36 (s, 1H), 7.29 (s, 1H), 7.23 (t, J = 8.7 Hz, 2H), 6.75–6.67 (m, 3H), 6.39 (s, 1H), 5.92 (s, 1H), 3.80 (m 1H), 3.64 (dd, J = 14.4, 7.5 Hz, 1H), 3.48–3.32 (m, 3H), 2.84 (s, 3H), 2.48 (s, 3H), 2.23 (s, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 172.3, 152.0, 149.3, 143.1, 139.6, 129.2, 126.0, 116.5, 112.5, 111.2, 109.9, 58.8, 39.6, 38.7, 31.2, 14.6, 13.9.

IR (film): ν (cm⁻¹) 2971, 2926, 1870, 1723, 1509, 1506, 1437, 1376, 1360, 1357, 1259, 1193, 1158, 1027, 991, 962, 928, 873, 798, 748, 693, 600.

HRMS (ESI, m/z) calcd for C₂₀H₂₃N₃NaO₂ (M+Na)⁺: 360.1688, found: 360.1683.

A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2b (133 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock
solution in THF) in THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3q as a colorless oil (40.7 mg, 0.136 mmol, yield: 68%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 94% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.3 mL/min, 30 °C, t₁(major) = 34.5 min, t₁(minor) = 21.2 min. [α]₀²³ = -8.14° (c = 1.0, CH₂Cl₂).

³H NMR (500 MHz, CDCl₃): δ 7.20 (t, J = 7.7 Hz, 2H), 6.73 (d, J = 8.2 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 5.93 (s, 1H), 3.45–3.35 (m, 2H), 3.28 (dd, J = 14.5, 7.2 Hz, 1H), 3.20 (dd, J = 16.2, 5.8 Hz, 1H), 3.11 (dd, J = 14.5, 7.9 Hz, 1H), 2.95 (dd, J = 16.2, 7.7 Hz, 1H), 2.71–2.61 (m, 1H), 2.52 (s, 3H), 2.22 (s, 3H), 1.12 (t, J = 7.0 Hz, 3H), 1.05 (d, J = 6.6 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 173.3, 151.8, 148.4, 144.1, 129.3, 116.0, 112.8, 111.1, 56.7, 45.9, 40.3, 29.3, 18.2, 14.7, 13.9, 11.6.

IR (film): v (cm⁻¹) 2960, 2923, 2690, 1718, 1595, 1504, 1483, 1456, 1412, 1384, 1330, 1310, 1259, 1215, 1188, 1089, 1019, 964, 798, 745, 695.

HRMS (ESI, m/z) calcd for C₁₈H₂₅N₃NaO (M+Na⁺): 322.1895, found: 322.1892.

A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2c (133 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 15 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3r as a colourless oil (20.0 mg, 0.064 mmol, yield: 32%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 89% (HPLC: OJ,
254 nm, *n*-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, t_{(major)} = 14.2 min, t_{(minor)} = 9.0 min. [α]_{D}^{23} = -6.53° (c = 1.0, CH_{2}Cl_{2}).

{^1}H NMR (500 MHz, CDCl_{3}): δ 7.20 (t, J = 7.7 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 5.93 (s, 1H), 4.02–3.90 (m, 1H), 3.22 (dd, J = 16.2, 5.4 Hz, 1H), 3.07 (dd, J = 14.2, 7.0 Hz, 1H), 2.98–2.82 (m, 2H), 2.52 (s, 3H), 2.21 (s, 3H), 1.14 (t, J = 6.8 Hz, 6H), 0.99 (d, J = 6.7 Hz, 3H).

{^{13}}C NMR (214 MHz, CDCl_{3}): δ 173.6, 151.7, 149.8, 144.0, 128.9, 118.1, 117.3, 111.0, 49.4, 40.7, 29.9, 28.2, 20.2, 20.1, 18.3, 14.8, 13.9.

IR (film): ν (cm⁻¹) 2962, 2925, 2853, 1726, 1598, 1496, 1456, 1411, 1377, 1362, 1338, 1260, 1183, 1082, 1019, 963, 800, 748, 695.

HRMS (ESI, m/z) calcd for C_{19}H_{27}N_{3}NaO (M+Na)^+: 336.2051, found: 336.2051.

A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2d (153 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO_{4})_{2}·6H_{2}O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 16 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (*n*-hexane/CH_{2}Cl_{2} = 10:1 to 2:1) to afford product 3s as a colorless oil (59.0 mg, 0.170 mmol, yield: 85%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 95% (HPLC: OJ, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, t_{(major)} = 15.3 min, t_{(minor)} = 13.3 min. [α]_{D}^{23} = -11.92° (c = 1.0, CH_{2}Cl_{2}).

{^1}H NMR (500 MHz, CDCl_{3}): δ 7.26 (t, J = 1.5 Hz, 4H), 7.02 (d, J = 8.0 Hz, 4H), 6.95–6.91 (m, 2H), 5.93 (s, 1H), 3.79 (dd, J = 14.5, 6.7 Hz, 1H), 3.57 (dd, J = 14.5, 8.2 Hz, 1H), 3.26 (dd, J = 16.2, 5.5 Hz, 1H), 3.05–2.93 (m, 1H), 2.71–2.61 (m, 1H), 2.52 (s, 3H), 2.21 (s, 3H), 1.07 (d, 3H).
13C NMR (126 MHz, CDCl₃): δ 173.2, 156.6, 151.9, 148.9, 144.1, 129.3, 121.5, 111.2, 58.6, 40.3, 29.3, 18.2, 14.7, 13.9.

IR (film): ν (cm⁻¹) 2962, 2927, 2854, 1724, 1588, 1495, 1411, 1376, 1337, 1261, 1093, 1020, 863, 800, 748, 695, 672.

HRMS (ESI, m/z) calcd for C₂₂H₂₅N₃NaO (M+Na)⁺: 370.1895, found: 370.1890.

A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2e (131 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L₁ (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 15 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3t as a colorless oil (47.9 mg, 0.154 mmol, yield: 71%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 89% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, tᵣ(major) = 17.8 min, tᵣ(minor) = 12.9 min. [α]D²³ = -11.72° (c = 1.0, CH₂Cl₂).

1H NMR (500 MHz, CDCl₃): δ 7.08–6.98 (m, 1H), 6.92 (d, J = 7.4 Hz, 1H), 6.66 (d, J = 8.3 Hz, 1H), 6.55 (t, J = 7.3 Hz, 1H), 5.94 (s, 1H), 3.36–3.24 (m, 3H), 3.21 (dd, J = 16.2, 5.8 Hz, 1H), 3.04 (dd, J = 14.5, 8.0 Hz, 1H), 2.95 (dd, J = 16.2, 7.8 Hz, 1H), 2.74 (t, J = 6.4 Hz, 2H), 2.71– 2.63 (m, 1H), 2.52 (s, 3H), 2.23 (s, 3H), 1.98–1.85 (m, 2H), 1.06 (d, J = 6.7 Hz, 3H).

13C NMR (126 MHz, CDCl₃): δ 173.3, 151.8 146.0, 144.1, 129.2, 127.2, 124.1, 122.3, 115.7, 111.1, 58.3, 51.0, 40.2, 29.2, 28.3, 22.3, 18.2, 14.7, 13.9.

IR (film): ν (cm⁻¹) 3408, 3016, 2961, 2842, 1723, 1602, 1583, 1504, 1455, 1410, 1377, 1338, 1309, 1262, 1207, 1097, 1058, 1016, 963, 938, 871, 800, 744, 717, 662.

HRMS (ESI, m/z) calcd for C₁₉H₂₅N₃NaO (M+Na)⁺: 334.1895, found: 334.1886.
A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2f (124 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3u as a red oil (51.6 mg, 0.172 mmol, yield: 86%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 89% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, t₁(major) = 32.1 min, t₁(minor) = 18.4 min. [α]D23 = -9.46° (c = 1.0, CH₂Cl₂).

¹H NMR (500 MHz, CDCl₃): δ 7.02 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 5.93 (s, 1H), 3.31 (dd, J = 14.3, 7.2 Hz, 1H), 3.20 (dd, J = 16.2, 6.0 Hz, 1H), 3.08 (dd, J = 14.3, 7.8 Hz, 1H), 2.98–2.92 (m, 1H), 2.91 (s, 3H), 2.70–2.62 (m, 1H), 2.52 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H), 1.04 (d, J = 6.7 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 173.3, 151.7, 147.9, 144.0, 129.7, 125.6, 112.8, 111.1, 59.7, 40.2, 39.6, 29.5, 20.3, 18.3, 14.7, 13.9.

IR (film): ν (cm⁻¹) 2962, 2926, 2869, 1725, 1618, 1582, 1521, 1454, 1411, 1376, 1335, 1080, 1017, 963, 937, 800, 746, 651.

HRMS (ESI, m/z) calcd for C₁₈H₂₅N₃NaO (M+Na)⁺: 322.1895, found: 322.1886.
solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH$_2$Cl$_2$ = 10:1 to 2:1) to afford product 3v as a colorless oil (35.2 mg, 0.117 mmol, yield: 59%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 90% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, $t_r$(major) = 21.4 min, $t_r$(minor) = 13.2 min. [$\alpha$]$_D^{23}$ = -28.49° (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.11 (t, $J$ = 7.7 Hz, 1H), 6.60–6.49 (m, 3H), 5.94 (s, 1H), 3.36 (dd, $J$ = 14.4, 7.1 Hz, 1H), 3.20 (dd, $J$ = 16.2, 6.1 Hz, 1H), 3.12 (dd, $J$ = 14.4, 7.9 Hz, 1H), 2.99–2.93 (m, 4H), 2.68 (m, 1H), 2.53 (s, 3H), 2.32 (s, 3H), 2.23 (s, 3H), 1.05 (d, $J$ = 6.7 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 173.2, 151.8, 149.9, 144.0, 138.8, 129.0, 117.2, 113.2, 111.1, 109.7, 59.2, 40.2, 39.5, 29.5, 22.1, 18.2, 14.7, 13.9.

IR (film): ν (cm$^{-1}$) 3043, 2926, 2871, 1720, 1601, 1581, 1498, 1411, 1337, 1262, 1178, 1138, 1081, 996, 963, 937, 834, 800, 766, 746, 693, 659.

HRMS (ESI, m/z) calcd for C$_{18}$H$_{25}$N$_3$NaO (M+Na)$^+$: 322.1895, found: 322.1895.

A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2i (134 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO$_4$)$_2$·6H$_2$O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH$_2$Cl$_2$ = 10:1 to 2:1) to afford product 3x as a red oil (32.3 mg, 0.102 mmol, yield: 51%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 87% (HPLC: OJ, 254 nm,
$n$-hexane/isopropanol = 90:10, flow rate: 0.5 mL/min, 30 °C, $t_r$(major) = 14.9 min, $t_r$(minor) = 8.6 min. $[\alpha]_D^{23} = -2.45^\circ$ (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (500 MHz, CDCl$_3$): δ 6.83–6.79 (m, 2H), 6.73–6.69 (m, 2H), 5.92 (s, 1H), 3.75 (s, 3H), 3.26–3.18 (m, 2H), 3.05–2.99 (m, 1H), 2.97–2.89 (m, 1H), 2.86 (s, 3H), 2.68–2.60 (m, 1H), 2.51 (s, 3H), 2.22 (s, 3H), 1.03 (d, $J$ = 6.7, 1.3 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 173.3, 151.7, 145.1, 144.0, 114.8, 114.6, 111.1, 60.6, 56.0, 40.3, 40.0, 29.5, 18.3, 14.7, 13.9.

IR (film): ν (cm$^{-1}$) 2961, 2928, 2873, 1723, 1615, 1580, 1513, 1461, 1411, 1377, 1336, 1259, 1180, 1078, 1038, 963, 937, 804, 746, 701.

HRMS (ESI, m/z) calcd for C$_{18}$H$_{25}$N$_3$NaO$_2$ (M+Na)$^+$: 338.1844, found: 338.1840.

A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2j (127 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO$_4$)$_2$·6H$_2$O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel ($n$-hexane/CH$_2$Cl$_2$ = 10:1 to 2:1) to afford product 3y as a colourless oil (46.0 mg, 0.152 mmol, yield: 76%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 90% (HPLC: OJ, 254 nm, $n$-hexane/isopropanol = 98:2, flow rate: 0.5 mL/min, 30 °C, $t_r$(major) = 20.7 min, $t_r$(minor) = 15.9 min. $[\alpha]_D^{23} = -14.43^\circ$ (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (500 MHz, CDCl$_3$): δ 6.90 (t, $J$ = 8.7 Hz, 2H), 6.65 (dd, $J$ = 9.2, 4.2 Hz, 2H), 5.92 (s, 1H), 3.29 (dd, $J$ = 14.3, 7.3 Hz, 1H), 3.20 (dd, $J$ = 16.2, 6.3 Hz, 1H), 3.05 (dd, $J$ = 14.3, 7.7 Hz, 1H), 2.92 (dd, $J$ = 16.2, 7.3 Hz, 1H), 2.89 (s, 3H), 2.65 (dq, $J$ = 14.0, 7.0 Hz, 1H), 2.51 (s, 3H), 2.21 (s, 3H), 1.04 (d, $J$ = 6.7 Hz, 3H).
$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 173.2, 155.4 ($J_{C-F} = 235.2$ Hz), 151.8, 146.7, 144.0, 115.3, 113.6, 111.1, 60.1, 40.2, 40.0, 29.5, 18.3, 14.7, 13.9.

IR (film): $\nu$ (cm$^{-1}$) 2962, 2930, 2875, 1723, 1582, 1512, 1411, 1376, 1336, 1261, 1227, 1094, 1020, 865, 800, 704.

HRMS (ESI, m/z) calcd for C$_{17}$H$_{22}$FN$_3$NaO (M+Na)$^+$: 326.1644, found: 326.1633.

A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2k (163 mg, 0.60 mmol), and chiral nickel catalyst Ni(ClO$_4$)$_2$·6H$_2$O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 15 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel ($n$-hexane/CH$_2$Cl$_2$ = 10:1 to 2:1) to afford product 3z as a colorless oil (46.4 mg, 0.128 mmol, yield: 64%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 92% (HPLC: OJ, 254 nm, $n$-hexane/isopropanol = 98:2, flow rate 0.5 mL/min, 30 °C, $t_r$(major) = 17.2 min, $t_r$(minor) = 14.2 min. $[\alpha]_D^{23} = -5.82^\circ$ (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.03 (t, $J = 8.0$ Hz, 1H), 6.81 (s, 1H), 6.76 (d, $J = 7.8$ Hz, 1H), 6.64 (d, $J = 8.3$ Hz, 1H), 5.92 (s, 1H), 3.36 (dd, $J = 14.5$, 7.1 Hz, 1H), 3.22–3.04 (m, 2H), 2.98–2.85 (m, 4H), 2.71–2.60 (m, 1H), 2.51 (s, 3H), 2.21 (s, 3H), 1.03 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 173.0, 151.9, 150.9, 144.1, 130.3, 123.5, 118.9, 115.0, 111.2, 110.9, 58.9, 40.1, 39.6, 29.4, 18.2, 14.7, 14.0.

IR (film): $\nu$ (cm$^{-1}$) 2962, 2915, 1867, 1721, 1591, 1493, 1410, 1375, 1336, 1261, 1095, 1020, 985, 962, 821, 800, 790, 721, 704, 698.

HRMS (ESI, m/z) calcd for C$_{17}$H$_{22}$BrN$_3$NaO (M+Na)$^+$: 386.0843, found: 386.0835.
A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2l (133 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 10 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH₂Cl₂ = 10:1 to 2:1) to afford product 3za as a red oil (44.0 mg, 0.142 mmol, yield: 71%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 90% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 98:2, flow rate 0.5 mL/min, 30 °C, t_major = 20.4 min, t_minor = 16.9 min. [α]D23 = -10.45° (c = 1.0, CH₂Cl₂).

1H NMR (500 MHz, CDCl₃): δ 7.01 (d, J = 8.3 Hz, 2H), 6.66 (d, J = 8.3 Hz, 2H), 5.93 (s, 1H), 3.41–3.29 (m, 2H), 3.29–3.15 (m, 2H), 3.07 (dd, J = 14.3, 7.7 Hz, 1H), 2.94 (dd, J = 16.2, 7.8 Hz, 1H), 2.71–2.60 (m, 1H), 2.52 (s, 3H), 2.23 (d, J = 7.5 Hz, 6H), 1.09 (t, J = 7.0 Hz, 3H), 1.04 (d, J = 6.7 Hz, 3H).

13C NMR (126 MHz, CDCl₃): δ 173.4, 151.7, 146.3, 144.1, 129.8, 125.3, 113.3, 111.1, 57.0, 46.1, 40.3, 29.3, 20.3, 18.2, 14.7, 13.9, 11.5.

IR (film): ν (cm⁻¹) 2962, 2925, 2869, 1724, 1617, 1581, 1519, 1455, 1411, 1376, 1336, 1260, 1172, 1092, 1018, 963, 937, 800, 746, 698.

HRMS (ESI, m/z) calcd for C₁₉H₂₇N₃NaO (M+Na)⁺: 336.2051, found: 336.2043.
2) Reaction with secondary α-silylamines

$$\begin{align*}
\text{1c} + \text{2m–r} &\xrightarrow{\text{Ni(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O/L1}} \text{3zb–zg} \\
\text{THF, argon, 25°C} &\xrightarrow{24 \text{ W blue LEDs}}
\end{align*}$$

Scheme S7. Nickel-catalyzed asymmetric photoredox reaction to non-racemic products 3zb–zg.

**General Procedure.** A dried 10 mL Schlenk tube was charged with 1c (49.2 mg, 0.30 mmol), 2m–r (0.20 mmol), chiral nickel catalyst Ni(ClO4)2·6H2O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 20:1 to 5:1) to afford non-racemic product 3zb–zg. Enantiomeric excess was established by HPLC analysis.

A dried 10 mL Schlenk tube was charged with 1c (49.2 mg, 0.30 mmol), 2m (36.0 mg, 0.20 mmol), and chiral nickel catalyst Ni(ClO4)2·6H2O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 20:1 to 5:1) to afford product 3zb as a colorless oil (22.1 mg, 0.126 mmol, yield: 63%). Enantiomeric excess was established by HPLC analysis using a Chiralpak OJ column, ee = 91% (HPLC: OJ, 254 nm, n-hexane/isopropanol = 95:5, flow rate 0.5 mL/min, 30 °C, t1/2(major) = 32.3 min,
tr(minor) = 30.8 min. [α]D23 = -2.18° (c = 1.0, CH₂Cl₂). Other analytic data of 3zb are consistent with the literature.⁵

³¹H NMR (500 MHz, CDCl₃): δ 7.62–7.57 (m, 2H), 7.35 (t, J = 8.7 Hz, 2H), 7.16–7.11 (m, 1H), 3.94 (dd, J = 9.4, 7.5 Hz, 1H), 3.45 (dd, J = 9.4, 6.3 Hz, 1H), 2.75 (dd, J = 16.7, 8.3 Hz, 1H), 2.62–2.50 (m, J = 7.1 Hz, 1H), 2.26 (dd, J = 16.8, 7.5 Hz, 1H), 1.21 (d, J = 6.8 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 173.9, 139.6, 128.9, 124.6, 120.1, 56.0, 41.1, 26.5, 19.6.

A dried 10 mL Schlenk tube was charged with 1c (49.2 mg, 0.30 mmol), 2n (43 mg, 0.20 mmol), and chiral nickel catalyst Ni(ClO₄)₂·6H₂O (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 20:1 to 5:1) to afford product 3zc as a colorless oil (31.1 mg, 0.134 mmol, yield: 67%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 93% (HPLC: IC, 254 nm, n-hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 30 °C, tᵣ(major) = 27.8 min, tᵣ(minor) = 25.6 min. [α]D23 = -4.57° (c = 1.0, CH₂Cl₂).

³¹H NMR (500 MHz, CDCl₃): δ 7.59–7.53 (m, 2H), 7.35–7.28 (m, 2H), 3.91 (dd, J = 9.4, 7.6 Hz, 1H), 3.41 (dd, J = 9.4, 6.4 Hz, 1H), 2.75 (dd, J = 16.8, 8.4 Hz, 1H), 2.62–2.51 (m, J = 7.0 Hz, 1H), 2.25 (dd, J = 16.9, 7.5 Hz, 1H), 1.21 (d, J = 6.7 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 174.0, 138.2, 129.6, 128.9, 121.0, 55.9, 41.0, 26.4, 19.6.

IR (film): ν (cm⁻¹) 2962, 2925, 2863, 1687, 1650, 1592, 1496, 1451, 1416, 1391, 1352, 1260, 1222, 1092, 1019, 810, 799, 703.

HRMS (ESI, m/z) calcd for C₁₁H₁₂ClINaO (M+Na)⁺: 232.0505, found: 232.0498.
A dried 10 mL Schlenk tube was charged with \textbf{1c} (49.2 mg, 0.30 mmol), \textbf{2o} (43 mg, 0.20 mmol), and chiral nickel catalyst Ni(ClO$_4$)$_2$·6H$_2$O (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). The mixture was degassed \textit{via} three freeze-pump-thaw cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH$_2$Cl$_2$ = 20:1 to 5:1) to afford product \textbf{3zd} as a colorless oil (33 mg, 0.158 mmol, yield: 79%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 93% (HPLC: IC, 220 nm, n-hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 30 °C, t$_r$(major) = 24.9 min, t$_r$(minor) = 22.1 min. $[\alpha]_D^{23}$ = -2.73° (c = 1.0, CH$_2$Cl$_2$).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.23–7.09 (m, 1H), 7.01–6.79 (m, 2H), 6.79–6.69 (m, 1H), 3.63–3.48 (m, 1H), 3.15–2.99 (m, 1H), 2.45–2.33 (m, 1H), 2.29–2.12 (m, 1H), 1.99–1.80 (m, 1H), 0.83 (d, $J$ = 2.6 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 174.0, 140.8, 134.7, 129.9, 124.5, 119.9, 117.8, 55.8, 41.1, 26.4, 19.6.

IR (film): ν (cm$^{-1}$) 2962, 2925, 2863, 1687, 1650, 1592, 1496, 1451, 1416, 1391, 1352, 1260, 1222, 1092, 1019, 810, 799, 703.

HRMS (ESI, m/z) calcd for C$_{11}$H$_{12}$ClNNaO (M+Na)$^+$: 232.0505, found: 232.0498.

A dried 10 mL Schlenk tube was charged with \textbf{1c} (49.2 mg, 0.3 mmol), \textbf{2p} (43 mg, 0.20 mmol), and chiral nickel catalyst Ni(ClO$_4$)$_2$·6H$_2$O (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). The mixture was degassed \textit{via} three freeze-pump-thaw...
cycles. The Schlenk tube was positioned approximately 5 cm away from a 24 W blue LEDs lamp. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 20:1 to 5:1) to afford product 3ze as a colorless oil (28.2 mg, 0.146 mmol, yield: 73%). Enantiomeric excess was established by HPLC analysis using a Chiralpak ODH column, ee = 91% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 98:2, flow rate 0.8 mL/min, 30 °C, t_r(major) = 25.3 min, t_r(minor) = 23.8 min. [α]_D^{23} = -3.88° (c = 1.0, CH_2Cl_2).

^1 H NMR (500 MHz, CDCl_3): δ 7.58–7.52 (m, 2H), 7.08–7.00 (m, 2H), 3.91 (dd, J = 9.4, 7.6 Hz, 1H), 3.42 (dd, J = 9.4, 6.4 Hz, 1H), 2.75 (dd, J = 16.8, 8.4 Hz, 1H), 2.64–2.49 (m, 1H), 2.25 (dd, 1H), 1.21 (d, J = 6.7 Hz, 3H).

^13 C NMR (126 MHz, CDCl_3): δ 173.8, 159.6 (J_C–F = 239.0 Hz), 135.8, 121.8, 115.5, 56.3, 40.9, 26.5, 19.6.

IR (film): ν (cm⁻¹) 2962, 2926, 2865, 1696, 1509, 1483, 1425, 1394, 1351, 1296, 1313, 1260, 1221, 1159, 1096, 1015, 817, 801, 702.

HRMS (ESI, m/z) calcd for C_{11}H_{12}FNNaO (M+Na)^+: 216.0800, found: 216.0794.

A dried 10 mL Schlenk tube was charged with 1c (49.2 mg, 0.3 mmol), 2q (39.4mg, 0.20 mmol), and chiral nickel catalyst Ni(ClO_4)_{2}·6H_2O (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/CH_2Cl_2 = 20:1 to 5:1) to afford product 3zf as a colorless oil (31.1 mg, 0.161 mmol, yield: 80%). Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 91% (HPLC: IC, 220 nm, n-hexane/isopropanol = 90:10, flow rate 1.0 mL/min, 30 °C, t_r(major) = 26.0 min, t_r(minor) = 22.7 min. [α]_D^{23} = -2.66° (c = 1.0, CH_2Cl_2).
$^1$H NMR (400 MHz, CDCl₃): δ 7.54–7.44 (m, 1H), 7.35–7.22 (m, 2H), 6.87–6.76 (m, 1H), 3.95–3.86 (m, 1H), 3.45–3.34 (m, 1H), 2.79–2.68 (m, 1H), 2.61–2.46 (m, 1H), 2.32–2.16 (m, 1H), 1.20 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl₃): δ 174.1, 130.0 ($J_{C–F} = 9.1$ Hz), 114.9 ($J_{C–F} = 3.0$ Hz), 111.2, 111.0, 107.4, 107.2, 55.9, 41.2, 26.3, 19.6.

IR (film): ν (cm⁻¹) 2962, 2926, 2865, 1696, 1509, 1483, 1425, 1394, 1351, 1296, 1313, 1260, 1221, 1159, 1096, 1015, 817, 801, 702.

HRMS (ESI, m/z) calcd for C₁₁H₁₂FNNaO (M+Na)+: 216.0800, found: 216.0796.

A dried 10 mL Schlenk tube was charged with 1c (49.2 mg, 0.30 mmol), 2r (43 mg, 0.20 mmol), and chiral nickel catalyst Ni(ClO₄)₂·6H₂O (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 20:1 to 5:1) to afford product 3zg as a colorless oil (30.2 mg, 0.134 mmol, yield: 67%). Enantiomeric excess was established by HPLC analysis using a Chiralpak ODH column, ee = 92% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 95:5, flow rate 1.0 mL/min, 30 °C, tᵣ(major) = 35.6 min, tᵣ(minor) = 30.0 min. [α]D²³ = -2.21° (c = 1.0, CH₂Cl₂).

$^1$H NMR (500 MHz, CDCl₃): δ 7.97 (dd, $J = 8.9$, 2.3 Hz, 1H), 7.88–7.77 (m, 4H), 7.50–7.38 (m, 2H), 4.07 (dd, $J = 9.4$, 7.6 Hz, 1H), 3.58 (dd, $J = 9.4$, 6.4 Hz, 1H), 2.81 (dd, $J = 16.8$, 8.4 Hz, 1H), 2.67–2.58 (m, 1H), 2.32 (dd, $J = 16.8$, 7.5 Hz, 1H), 1.27–1.25 (m, 3H).

$^{13}$C NMR (126 MHz, CDCl₃): δ 174.1, 137.4, 133.7, 130.8, 128.7, 127.8, 127.7, 126.5, 125.3, 120.0, 116.9, 56.3, 41.3, 26.6, 19.7.
IR (film): ν (cm⁻¹) 2962, 2923, 2852, 1693, 1597, 1469, 1397, 1337, 1310, 1260, 1216, 1094, 1019, 800, 746, 721, 709.

HRMS (ESI, m/z) calcld for C₁₅H₁₅NNaO (M+Na)+: 248.1051, found: 248.1043.

3.3 Set-up of the Photoreactions and Emission Spectra of the Light Source

Fig. S1 Reaction set-up of the photochemical catalysis in a constant temperature cabinet.

Fig. S2 Emission spectra of the light source (maxium emission at λ = 455 nm).
4. Synthetic Transformation and Absolute Configuration Assignment of the Products

4.1 Transformation of Product 3r to Its Alcohol Derivative (S)-5

![Scheme S8](image)

To a solution of 3s (46.0 mg, 0.146 mmol, product of the asymmetric photoredox reaction, 95% ee) in THF/H₂O (4/1, 1.5 mL) at 0 °C was added NaBH₄ (56.0 mg, 1.5 mmol). The reaction mixture was stirred at room temperature overnight. The reaction was quenched with aqueous 2 N HCl (1.0 mL) at room temperature and extracted with DCM (4 x 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/n-hexane = 1:5) to afford 5 (35.0 mg, 0.146 mmol, yield: 94%) as a colorless oil.

Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 254 nm, n-hexane/isopropanol = 98:2, flow rate 0.5 mL/min, 30 °C, tᵣ(major) = 42.8 min, tᵣ(minor) = 39.3 min. [α]D²³ = -7.05° (c = 1, CH₂Cl₂). The absolute configuration of product 5 was assigned as S by comparison of its optical rotation with the published literature.⁵

¹H NMR (500 MHz, CDCl₃): δ 7.18 (t, J = 7.8 Hz, 4H), 6.92 (d, J = 8.1 Hz, 4H), 6.87 (t, J = 7.3 Hz, 2H), 3.70–3.61 (m, 1H), 3.62–3.53 (m, 2H), 3.45 (dd, 1H), 2.04–1.91 (m, 1H), 1.77–1.69 (m, 1H), 1.40–1.28 (m, 2H), 0.92 (d, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 148.8, 129.2 121.3, 121.3, 61.1, 59.1, 37.7, 29.0, 18.0.

Other analytic data of 5 are consistent with the literature.⁵
4.2 Absolute Configuration Assignment of the Products

The absolute configuration of the ester derivative 5 (95% ee, synthesized from the asymmetric photoredox product 3s) was assigned as S by comparison of its optical rotation with the published literature. Accordingly, asymmetric photoredox product 3s and all other products were assigned as S in analogy.
5. Mechanistic Studies

5.1 Uv/Vis-Absorption Spectra

Fig. S3 Uv-Vis spectra of substrate 1c, 2a, chiral ligand L1, nickel catalyst Ni-L1, potential intermediate complex Ni-L1-1c, and Ni-L1-1c + 2a (1eq) in THF (0.020 M).

Preparation of the samples for Uv-Vis spectra measurement.

1c in THF (0.020 M): α,β-Unsaturated N-acyl pyrazole 1c (16.4 mg, 0.10 mmol) was dissolved in distilled THF (5 mL). The solution was used freshly for Uv-vis spectra measurement.

2a in THF (0.020 M): Tertiary α-silylamine 2a (19.3 mg, 0.10 mmol) was dissolved in distilled THF (5 mL). The solution was used freshly for Uv-vis spectra measurement.

L1 in THF (0.020 M): DBFOX ligand L1 (45.9 mg, 0.10 mmol) was dissolved in distilled THF (5 mL). The solution was used freshly for Uv-vis spectra measurement.

Ni-L1 in THF (0.020 M): A solution of Ni(ClO₄)₂·6H₂O (36.6 mg, 0.10 mmol) and DBFOX ligand L1 (45.9 mg, 0.10 mmol) in THF (5 mL) was stirred at 30 °C for 1 h. The solution was used freshly for Uv-vis spectra measurement.
Ni-L1-1c in THF (0.020 M): A solution of Ni(ClO₄)₂·6H₂O (36.6 mg, 0.10 mmol) and DBFOX ligand L1 (45.9 mg, 0.10 mmol) in THF (5 mL) was stirred at 30 °C for 1 h, then α,β-unsaturated N-acyl pyrazole 1c (16.4 mg, 0.1 mmol) was added. The resulting mixture was heated at 30 °C for additional 1 h. The solution was used freshly for Uv-vis spectra measurement.

[Ni-L1-1c + 2a (1eq)] in THF (0.020 M): A solution of Ni(ClO₄)₂·6H₂O (36.6 mg, 0.1 mmol) and DBFOX ligand L1 (45.9 mg, 0.10 mmol) in THF (5 mL) was stirred at 30 °C for 1 h, then α,β-Unsaturated N-acyl pyrazole 1c (16.4 mg, 0.10 mmol) was added. The resulting mixture was heated at 30 °C for additional 1 h. Tertiary α-silylamine 2a (19.3 mg, 0.10 mmol) was added. The solution was used freshly for Uv-vis spectra measurement.

Remarks: All of the individual chiral ligand L1, substrate 1c and 2a had no obvious absorption in the visible light region. However, chiral nickel catalyst Ni-L1 and potential intermediate Ni-L1-1c exhibited significant absorption enhancement in the range of 400–450 nm. The broad peak at ~600 nm was probably attributed to the nickel.

Fig. S4 I: Substrate 1c in THF (0.030 M). II: substrate 2a in THF (0.030 M). III: Ni-L1 in THF (0.030 M). IV: Ni-L1-1c in THF (0.030 M).
5.2 Luminescence Emission Behaviors of the Nickel Complexes

Emission intensities were recorded on a Spectra Max M5 microplate reader in a 10.0 mm quartz cuvette. Nickel catalyst Ni-L1 (generated in situ by mixing NiClO₄·6H₂O and L1 in a 1:1 ratio in THF at 30 °C for 1 h) and potential intermediate complex Ni-L1-1c (generated in situ by mixing NiClO₄·6H₂O, L1 and 1c in a 1:1:1 ratio in THF at 30 °C for 1 h) were excited at 390 nm (λ_max_abs). The concentration of nickel complex was 5 mM in THF.

![Graph showing luminescence emission spectra](https://example.com/graph.png)

**Fig. S5** Luminescence emission spectra, and the THF solution of nickel catalyst Ni-L1 in the dark or light.

5.3 Cyclic Voltammetry Analysis

Voltammetric experiments were conducted with a computer controlled Princeton Applied Research PARSTAT 263A containing Pt electrode working electrode, SCE reference electrode, Pt wire auxiliary electrode.

All solutions used for the voltammetric experiments were deoxygenated by purging with high purity argon gas and measurements were performed in a Faraday cage at room temperature (22 ± 2 °C). HPLC purity acetonitrile (CH₃CN) was purchased from OCEANPAK. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (nBu₄NPF₆), was purchased from commercial suppliers Aldrich.
Fig. S6 Cyclic voltammogram of a solution of substrate 2a (0.030 M) and TBAPF₆ (0.10 M) in CH₃CN. Sweep rate: 20 mV/s. Pt electrode working electrode, SCE reference electrode, Pt wire auxiliary electrode. Irreversible oxidation. $E_p^A = +0.60$ V.

Fig. S7 Cyclic voltammogram of a solution of 1c (0.030 M) and TBAPF₆ (0.10 M) in CH₃CN. Sweep rate: 20 mV/s. Pt electrode working electrode, SCE reference electrode, Pt wire auxiliary electrode. No observation of reduction peaks in the region of -1.5–1.5 V.
**Fig. S8** Cyclic voltammogram of a solution of nickel catalyst Ni-L1 (generated *in situ* by mixing NiClO₄·6H₂O and L1 in a 1:1 ratio in THF (0.030 M) at 30 °C for 1 h) and TBAPF₆ (0.10 M) in CH₃CN. Sweep rate: 20 mV/s. Pt electrode working electrode, SCE reference electrode, Pt wire auxiliary electrode. Irreversible reduction. $E_{\text{p}C} = -1.35$ V.

**Fig. S9** Cyclic voltammogram of a solution of potential intermediate complex Ni-L1-1c (generated *in situ* by mixing NiClO₄·6H₂O, L1 and 1c in a 1:1:1 ratio in THF (0.030 M) at 30 °C
for 1 h) and TBAPF₆ (0.10 M) in CH₃CN. Sweep rate: 20 mV/s. Pt electrode working electrode, SCE reference electrode, Pt wire auxiliary electrode. Irreversible reduction. \( E_p^C = -0.65 \) V.

**Remarks:** Cyclic voltammetry of \( \alpha \)-silylamine 2a exhibited an irreversible oxidation at +0.60 V (\( E_{ox(2a^+/2a)} \)). That of \( \alpha,\beta \)-Unsaturated N-acyl pyrazole 1c didn’t show any reduction peak between -1.5–1.5 V. Cyclic voltammetry of nickel catalyst Ni-L1 and potential intermediate Ni-L1-1c showed reductive peaks at -1.35 and -0.65 V, respectively. These observations indicated that the direct electron transfer from 2a to 1c, or the nickel complexes Ni-L1, Ni-L1-1c would not occur without excitation.

### 5.4 Isolation of a Side Product

![Scheme S9](image)

**Scheme S9.** Isolation of the further cyclized side-product 3l'.

A dried 10 mL Schlenk tube was charged with 1l (45.2 mg, 0.20 mmol), 2a (116 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock solution in THF), and THF (840 μL). 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. After being stirred at 25 °C for 20 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc = 30:1 to 10:1) to afford product 3l (38.2 mg, 0.110 mmol, yield: 55%) as a colorless oil. Meanwhile, cyclized product 3l' (1.98 mg, 0.0060 mmol, yield: 3%) was isolated as a yellow oil. Enantiomeric excess of 3l' was established by HPLC analysis using a Chiralpak ODH column, \( ee = 1\%\), 18:1 \( dr \) (HPLC: O-DH, 254 nm, n-hexane/isopropanol = 98:2, flow rate 0.5mL/min, 30 °C, \( t_r(3l, \text{major}) = 11.0 \) min, \( t_r(3l, \text{minor}) = 12.5 \) min, \( t_r(3l', \text{major}) = 18.8 \) min, \( t_r(3l', \text{minor}) = 24.8 \) min.
Analytic data of 3l’

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.33–7.27 (m, 2H), 7.25–7.21 (m, 2H), 7.21–7.10 (m, 2H), 6.82 (d, $J = 7.5$, 1.3 Hz, 1H), 6.70 (d, $J = 8.4$, 1.1 Hz, 1H), 6.58 (t, $J = 7.4$ Hz, 1H), 5.94 (s, 1H), 5.69 (d, $J = 8.2$ Hz, 1H), 3.72–3.62 (m, 1H), 3.52 (dd, $J = 11.5$, 4.1 Hz, 1H), 3.39 (dd, $J = 11.5$, 8.5 Hz, 1H), 2.96 (s, 3H), 2.45 (s, 3H), 2.23 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 174.8, 152.3, 146.3, 144.4, 142.0, 128.6, 128.6, 128.3, 127.9, 126.9, 120.3, 116.7, 111.7, 111.5, 55.5, 47.5, 41.7, 39.3, 14.7, 14.0.

IR (film): ν (cm$^{-1}$) 3061, 3028, 2962, 2924, 2852, 1721, 1601, 1584, 1479, 1452, 1410, 1375, 1349, 1262, 1027, 962, 920, 872, 801, 747, 699.

HRMS (ESI, m/z) calcd for C$_{22}$H$_{23}$N$_3$NaO (M+Na)$^+$: 368.1738, found: 368.1729.

HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak ODH (250 x 4.6 mm)
Mobile phase: n-hexane/isopropanol = 98:2
Flow rate: 0.5 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

rac-3l’

3% yield
18:1 dr, 1% ee
Fig. S10 HPLC trace for the racemic reference rac-3l', and non-racemic product 3l' generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.

Remarks: In some of the catalytic reactions, such cyclized products were isolated in a very low yield and with almost no enantiomer excess. Observation of the side-products, which were most likely generated through uncatalyzed background radical additions, further supported the radical mechanism.

5.5 Light-Dark Interval Experiments

The light-dark interval experiments were performed according the general catalysis procedure with 0.10 mmol substrate 1c. The conversion was determined by 1H NMR analysis of an aliquot from the reaction mixture. An aliquot was taken out of the reaction system via syringe for every 40 min until complete conversion was achieved. The whole process was performed under argon with Schlenk line. The NMR spectra shown below demonstrate that no significant byproducts are formed in this photoredox reaction.
**Fig. S11** From the top to bottom, $^1$H NMR (400 MHz, in CDCl$_3$) spectra of 1c, 3c (both as reference) and the crude product from the light-dark interval experiments. Conversion was inferred by area integration ratio (signals A and B).

### 5.6 Luminescence Quenching Experiments

Emission intensities were recorded on a Spectra Max M5 microplate reader in a 10.0 mm quartz cuvette. Nickel catalyst Ni-L1 (generated *in situ* by mixing NiClO$_4$·6H$_2$O and L1 in a 1:1 ratio in THF at 30 °C for 1 h) and potential intermediate complex Ni-L1-1c (generated *in situ* by mixing NiClO$_4$·6H$_2$O, L1 and 1c in a 1:1:1 ratio in THF at 30 °C for 1 h) were excited at 390 nm (absorption maximum) and the emissions were measured at 430 nm (emission maximum). The concentration of nickle complex was 5 mM in THF. The concentration of the quencher ($\alpha$-silylamine 2a) was 10 mM in THF. For each quenching experiment, 2a were titrated to a solution (5 mL) of the nickle complex in a quartz glass bottle. The addition of 2a refers to an increase of the quencher concentration of 25 mM. After degassing with an argon stream for 5 minutes, the emission intensity was collected.
**Fig. S12** Emission quenching of nickel catalyst Ni-L1 in THF (5 mM) in the presence of increasing amounts of α-silylamine 2a.

**Fig. S13** Emission quenching of potential intermediate complex Ni-L1-1c in THF (5 mM) in the presence of increasing amounts of α-silylamine 2a.
5.7 Photostability Test of α-Silylamine 2a

To exclude the homolytic cleavage pathway, the stability of α-silylamine 2a under the light source using in the catalysis was tested. Accordingly, 2a (10 mg) was dissolved in deuterium tetrahydrofuran (0.5 mL) in a NMR tube under argon atmosphere. The sample was
positioned approximately 5 cm away from a 24 W blue LEDs lamp and measured by $^1$H NMR after 4, 8, 12 and 24 h.

**Conclusion:** Under irradiation with a 24 W blue LEDs lamp for 24 h, no obvious decomposition of $\alpha$-silylamine 2a was observed.

![Fig. S16 $^1$H NMR (400 MHz, THF-$d_8$) spectra of 2a under irradiation with a 24 W blue LEDs lamp at different time courses.](image)

**5.8 Evaluation of the Excited State Potential of the Nickel Complexes**

Using the data collected from the cyclic voltammetry studies (section 5.3) and emission spectra (section 5.6) of the nickel catalyst Ni-L1 and potential intermediate complex Ni-L1-1c, we could estimate the redox potential of the excited complex employing the following Equation 1:

$$E(I^*/I^-) = E(I/I^-) + E_{0,0}(I^*/I)$$  Eq. 1
The irreversible reduction potentials \( (E_p) \) of \textbf{Ni-L1} and \textbf{Ni-L1-1c} were used for \( E(I^*/I^-) \). \( E_{0,0}(I^*/I^-) \), the excited state energy of the complex, was estimated spectroscopically from the luminescence peak (Figure S12, 13) recorded in THF, according to ref 8.

For nickel catalyst \textbf{Ni-L1}, \( E_p \), which provides \( E([\text{Ni-L1}]/[\text{Ni-L1}^-]) \), is -1.35 V (Fig. S8). The position of luminescence peak corresponds to 430 nm (Figure S12), which translates into an \( E_{0,0}([\text{Ni-L1}]*/[\text{Ni-L1}]) \) of 2.88 eV.

\[
E([\text{Ni-L1}]*/[\text{Ni-L1}^-]) = -1.35 + 2.88 = +1.53 \text{ V (vs SCE)}
\]

For potential intermediate complex \textbf{Ni-L1-1c}, \( E_p \), which provides \( E([\text{Ni-L1-1c}]/[\text{Ni-L1-1c}^-]) \), is -0.65 V (Fig. S9). The position of luminescence peak corresponds to 430 nm (Figure S13), which translates into an \( E_{0,0}([\text{Ni-L1-1c}]*/[\text{Ni-L1-1c}]) \) of 2.88 eV.

\[
E([\text{Ni-L1-1c}]*/[\text{Ni-L1-1c}^-]) = -0.65 + 2.88 = +2.23 \text{ V (vs SCE)}
\]

### 5.9 Radical Trapping Experiments

![Scheme S11](image)

\textbf{Scheme S11}. Radical trapping by ethyl 2-((phenylsulfonyl)methyl)acrylate.

A dried 10 mL Schlenk tube was charged with \textbf{1c} (32.8 mg, 0.20 mmol), \textbf{2d} (153 mg, 0.60 mmol), chiral nickel catalyst \textbf{Ni(ClO}_4)_2·6H}_2O/\textbf{L1} (800 μL taken from the 125 mM stock
solution in THF), ethyl 2-((phenylsulfonyl)methyl)acrylate (152 mg, 0.60 mmol) and THF (200 μL). 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. After being stirred at 25 °C for 16 h, the reaction mixture was concentrated to dryness. The residue was purified by flash chromatography on silica gel (n-hexane/EtOAc= 15:1 to 10:1) to afford product 3s as a colorless oil (9.0 mg, 0.026 mmol, yield: 13%) and product 4 as a colorless oil (118.6 mg, 0.402 mmol, yield based on 2d: 67%) 

\(^1\)H NMR (500 MHz, CDCl₃): δ 7.31–7.26 (m, 4H), 7.07 (d, J = 8.0 Hz, 4H), 6.98 (t, J = 7.4 Hz, 2H), 6.24 (s, 1H), 5.59 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.98–3.85 (m, 2H), 2.78–2.65 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H).

\(^{13}\)C NMR (126 MHz, CDCl₃) δ 167.1, 147.8, 138.2, 129.4, 127.1, 121.4, 121.1, 118.0, 61.0, 51.9, 30.6, 14.4.

IR (film): ν (cm⁻¹) 3052, 3049, 3010, 1702, 1587, 1508, 1455, 1405, 1379, 1352, 1285, 1112, 1028, 962, 801, 753, 684, 605, 460.

HRMS (ESI, m/z) calcd for C₁₉H₂₁NNaO₂ (M+Na)⁺: 318.1470, found: 318.1463

Scheme S12. Radical trapping by TEMPO.

A dried 10 mL Schlenk tube was charged with 1c (32.8 mg, 0.20 mmol), 2d (153 mg, 0.60 mmol), chiral nickel catalyst Ni(ClO₄)₂·6H₂O/L1 (160 μL taken from the 125 mM stock
solution in THF), TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, 15.6 mg, 1.0 mmol) and THF (840 μL). 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. After being stirred at 25 °C for 12 h, the reaction mixture was tested directly with FT-MS instrument using ESI technique. 3s was not generated while the coupling product 4’ was observed in HRMS (ESI, m/z). Calcd for C_{22}H_{31}N_{2}O (M+H)^+: 339.2436, found: 339.2424.

**Fig. S17** HRMS spectra of the reaction solution of the radical trapping experiment.
5.10 An Alternative Radical Coupling Mechanism

A radical coupling pathway involving a nickel enolate radical could not be completely excluded. Accordingly, N-acyl pyrazole substrate 1 underwent fast ligand exchange with the chiral nickel catalyst and afforded the intermediate complex A. Under irradiation of visible light, its excited state B single-electronically oxidized α-silylamine 2, and generate the nickel enolate radical C and silylamine cation radical D. Actually, SET between tertiary α-silylamines and uncoordinated α,β-unsaturated carbonyl compounds under Uv light has been established by Mariano et al.9 Subsequent desilylation of D led to formation of the nucleophilic α-amino radical E, followed by a radical coupling with the nickel enolate radical C, and the neutral complex F. Finally, silylation of F and further hydrolysis afforded the final product 3 and release intermediate A for the next catalytic cycle.

Scheme S13. An alternative radical coupling mechanism

5.11 Quantum Yield Measurement

The quantum yield (Φ) of the photochemical reaction was measured according to the procedure reported by Melchiorre et al.10
First, a ferrioxalate actinometer solution was first prepared according to the literature,\textsuperscript{11} and used for determination of photon flux of the light source. Under irradiation, the ferrioxalate actinometer solution undergoes decomposition from ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed.

**Preparation of the stock solutions:**

- **Potassium ferrioxalate solution:** potassium ferrioxalate (294.8 mg) and sulfuric acid (139 μL) were added to deionized water in a 50 mL volumetric flask (filled with deionized water to the mark).
- **Phenanthroline solution:** 1,10-phenanthroline (100 mg) was added to deionized water in a 50 mL volumetric flask (filled with deionized water to the mark).
- **Buffer solution:** sodium acetate (2.47 g) and sulfuric acid (0.5 mL) were added to deionized water in a 50 mL volumetric flask (filled with deionized water to the mark).
- **Model reaction solution:** \(\alpha,\beta\)-unsaturated \(N\)-acyl pyrazole \(1c\) (16.4 mg, 1.0 mmol), tertiary \(\alpha\)-silylamine \(2f\) (3.0 mmol) and chiral nickel catalyst \(\text{Ni(ClO}_4\text{)}_2\cdot6\text{H}_2\text{O}/\text{L1}\) (0.10 mmol, 80 μL taken from the 125 mM stock solution in THF) were sequentially added to a 5 mL volumetric flask and filled to the mark with HPLC-grade tetrafuran. Note: all the stock solutions were prepared and stored in the dark.

**Actinometry measurements:**

The actinometer solution (potassium ferrioxalate in water, 1.0 mL) and the model reaction solution (\(1c\) with \(2f\) catalyzed by chiral nickel catalyst in THF, 1.0 mL) were added to two identical Schlenk tubes (diameter = 12 mm) respectively. The Schlenk tubes were placed 5 cm away from the light source. They were irradiated together with a 24 W blue LEDs Lamp operating without stirring. This procedure was repeated 4 times, quenching the two reactions after different time intervals: 45 sec, 60 sec, 75 sec, and 90 sec for the actinometry solution; 30 min, 60 min, 90 min, and 120 min for the model reaction. After irradiation, the actinometer solution was removed and placed in a 10 mL volumetric flask containing 1,10-phenanthroline solution (0.5 mL) and buffer solution (2 mL). This flask was filled to the mark with deionized water. The UV-Vis spectra of the complexed actinometer samples were
recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm (Fig. S18).

![UV-Vis spectra](image)

**Fig. S18** UV-Vis spectra of the complexed actinometer samples at each time interval (45 sec, 60 sec, 75 sec, and 90 sec).

**Calculation of photon flux of the light source:**

Moles of Fe$^{2+}$ formed for each sample is determined using Beers’ Law (Eq. 2):

$$\text{Moles of Fe}(II) = \frac{V_1 \times V_3 \times \Delta A(510 \text{ nm})}{10^3 \times V_2 \times \lambda \times \epsilon(510 \text{ nm})} \quad \text{(Eq. 2)}$$

V1 is the irradiated volume (1.0 mL), V2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1.0 mL), V3 is the final volume after complexation with phenanthroline (10 mL), $\lambda$ is the optical path-length of the irradiation cell (1.0 cm), $\Delta A(510 \text{ nm})$ is the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\epsilon(510 \text{ nm})$ is the extinction coefficient the complex Fe(phen)$_3^{2+}$ at 510 nm (11100 L mol$^{-1}$ cm$^{-1}$).

The moles of Fe$^{2+}$ formed (x) are plotted as a function of time (t) (Fig. S19).
Fig. S19 The moles of Fe^{2+} formed (x) versus time (t).

The slope of this line was correlated to the moles of incident photons by unit of time \( q_{0,n,p} \) by the use of the following Eq. 3:

\[
\Phi(\lambda) = \frac{dx/dt}{q_{0,n,p}[1-10^{-A(\lambda)}]} \quad (\text{Eq. } 3)
\]

dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield \( \Phi \) for Fe^{2+} at 400 nm is 1.13,\(^{12} \) \([1-10^{-A(\lambda)}] \) is the ratio of absorbed photons by the solution, and \( A(\lambda) \) is the absorbance of the actinometer at the wavelength used to carry out the experiments (400 nm). The absorbance at 400 nm \( A(400) \) was measured using a Shimadzu UV-2550 UV-Vis spectrophotometer in a 10 mm path quartz cuvette, obtaining an absorbance of 2.52.

Accordingly, \( q_{0,n,p} \), which is the photon flux, was determined to be \( 1.61 \times 10^{-8} \) einstein \( s^{-1} \).

**Calculation of quantum yield of the photochemical reaction:**

The moles of product 3u formed for the model reaction were determined by \(^1\)H NMR. The moles of product per unit of time are related to the number of photons absorbed. The photons absorbed are correlated to the number of incident photons by the use of Eq. 3.
Accordingly, if we plot the moles of product (x) versus the moles of incident photons \( (q_{n,p}^0 \cdot dt) \), the slope is equal to: \( \Phi \cdot (1 - 10^{-A(400 \text{ nm})}) \), where \( \Phi \) is the quantum yield to be determined and \( A(400 \text{ nm}) \) is the absorption of the reaction under study (Fig. S20). 

\( A(400 \text{ nm}) \) was measured using a Shimadzu UV-2550 UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 1.69 was determined for the model reaction mixture.

\[ y = 0.5906x + 7.6 \times 10^{-6} \]
\[ R^2 = 0.9017 \]

**Fig. S20** The moles of product (x) versus the moles of incident photons (\( q_{n,p}^0 \cdot dt \)).

The quantum yield (\( \Phi \)) of the photochemical reaction of 1c with tertiary \( \alpha \)-silylamines 2f catalyzed by chiral nickel catalyst Ni(ClO\(_4\))\(_2\)·6H\(_2\)O / L1 was calculated to be 0.59.

### 5.12 Estimating the lifetime of the excited state of nickel complex Ni-L1

Estimating the lifetime of the excited state of nickel complex Ni-L1 was based on the ultrafast transient absorption spectroscopic techniques. The luminescence decays were measured on an Edingburg FLS980 spectrometer. The sample compartment was home-built and designed as 10x10 mm cuvettes in 90° geometry between excitation and detection. Temperature was set to 25 °C. The solution of Ni-L1 in THF (0.020 M) was excited at 378 nm. All decay traces were fitted by iterative reconvolution with an experimental instrument response function recorded directly after decay acquisition.
Fig. S21 Luminescence decays of nickel complex Ni-L1 (0.020 M) detected at 25°C after excitation at 378 nm. Detection was at the wavelengths of the emission band maxima.

**Fit Results**

Fit: \( A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3) \)

- Decay Scan: \( \geq 2 \text{ ex 377} \)
- File location: \( \geq C:\text{Data\gongle\shenxiang\2 ex 377.6nm em 430nm delay time.FL} \)
- Range (ch): \( \geq 60 \text{ to } 2047 \)
- Peak Count: \( \geq 4959 \text{ in channel 73} \)
- Total Count: \( \geq 294477 \)
- Time Calibration: \( \geq 0.049 \text{ ns/ch} \)
- Total Experiment Time: \( \geq 241.93 \text{ s} \)
- Fit Range (ch): \( \geq 74 \text{ to } 1704 \)

| Parameter | Value     | Std. Dev. | Rel % |
|-----------|-----------|-----------|-------|
| \( \tau_1 \) | 1.410E-009 s | 1.9752E-011 s |       |
| \( \tau_2 \) | 3.787E-009 s | 1.9585E-010 s |       |
| \( \tau_3 \) | 1.503E-008 s | 1.7116E-009 s |       |
| B1        | 4974.320     | 69.3200    | 67.80 |
| B2        | 739.024      | 71.3417    | 27.06 |
| B3        | 35.354       | 7.6043     | 5.14  |
| A         | 3.061       |           |       |
| \( \chi^2 \) | 1.344       |           |       |
\[ \tau = \frac{(\tau_1^2 \times B_1 + \tau_2^2 \times B_2 + \tau_3^2 \times B_3)}{(\tau_1 \times B_1 + \tau_2 \times B_2 + \tau_3 \times B_3)} \]

\[ \tau = \frac{[(1.41 \times 10^{-9})^2 \times 4974.32 + (3.79 \times 10^{-9})^2 \times 739.02 + (1.50 \times 10^{-9})^2 \times 35.35]}{(1.41 \times 10^{-9} \times 4974.32 + 3.79 \times 10^{-9} \times 739.02 + 1.50 \times 10^{-9} \times 35.35)} \]

\[ \tau = 2.75 \text{ ns} \]

**Remarks:** According to the luminescence decays experiment, lifetime of the excited state of nickel complex Ni-L1 can be estimated as \( 1 \times 10^{-9} \) - \( 1 \times 10^{-8} \) s, which is comparable to that of a NiII complex reported as a potential photoredox catalyst by Bach and Hess very recently.\(^\text{13}\)
6. Chiral Chromatography

6.1 Determination of Enantioselectivities of the Photoredox Reactions

Optical purities of the compounds 3c, e–z, za and 3zb–zg were determined with a Daicel Chiralpak OJ, OD-H or IC HPLC column on an Agilent 1260 Series HPLC System. The column temperature was 30 °C and UV-absorption was measured at 254 nm.

Fig. S22 HPLC trace for the racemic reference rac-3c, and non-racemic product 3c generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S23 HPLC trace for the racemic reference rac-3e, and non-racemic product 3e generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S24** HPLC trace for the racemic reference \textit{rac-3f}, and non-racemic product \textit{3f} generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S25** HPLC trace for the racemic reference \textit{rac-3g}, and non-racemic product \textit{3g} generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S26 HPLC trace for the racemic reference rac-3h, and non-racemic product 3h generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S27** HPLC trace for the racemic reference *rac-3i*, and non-racemic product *3i* generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S28** HPLC trace for the racemic reference rac-3j, and product 3j generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S29 HPLC trace for the racemic reference rac-3k, and non-racemic product 3k generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S30 HPLC trace for the racemic reference rac-3l, and non-racemic product 3l generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S31 HPLC trace for the racemic reference rac-3m, and non-racemic product 3m generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S32** HPLC trace for the racemic reference *rac-3n*, and non-racemic product *3n* generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.

| #  | [min] | [min] | [mAU*s] | [mAU]   | %      |
|----|-------|-------|---------|---------|--------|
| 1  | 27.939| 1.4506| 1767.86450| 20.31202| 9.9773 |
| 2  | 39.839| 2.3492| 1.59510e4 | 113.16592| 90.0227|
Fig. S33 HPLC trace for the racemic reference rac-3o, and non-racemic product 3o generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S34 HPLC trace for the racemic reference *rac-3p*, and non-racemic product *3p* generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
HPLC: Agilent 1260 Series HPLC system
Column: Daicel Chiralpak OJ (250 x 4.6 mm)
Mobile phase: n-hexane/isopropanol = 98:2
Flow rate: 0.3 mL/min
Column temperature: 30 °C
Detection: UV-absorption at 254 nm

*Fig. S35* HPLC trace for the racemic reference *rac-3q*, and non-racemic product *3q* generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S36 HPLC trace for the racemic reference rac-3r, and non-racemic product 3r generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S37  HPLC trace for the racemic reference rac-3s, and non-racemic product 3s generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S38** HPLC trace for the racemic reference *rac*-3t, and non-racemic product 3t generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S39 HPLC trace for the racemic reference rac-3u, and non-racemic product 3u generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S40 HPLC trace for the racemic reference *rac-*3v, and non-racemic product 3v generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S41 HPLC trace for the racemic reference *rac-3x*, and non-racemic product *3x* generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S42 HPLC trace for the racemic reference rac-3y, and non-racemic product 3y generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S43** HPLC trace for the racemic reference *rac-3z*, and non-racemic product *3z* generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.

|   | [min] | [min] | [mAU*s] | [mAU] | %     |
|---|-------|-------|---------|-------|-------|
| 1 | 14.214| 0.4704| 263.31683| 8.69169| 3.7626 |
| 2 | 17.207| 0.5609| 6734.90332| 184.94110| 96.2374 |
Fig. S44 HPLC trace for the racemic reference rac-3za, and non-racemic product 3za generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S45 HPLC trace for the racemic reference rac-3zb, and non-racemic product 3zb generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S46 HPLC trace for the racemic reference \textit{rac-3zc}, and non-racemic product \textit{3zc} generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S47** HPLC trace for the racemic reference *rac-3zd*, and non-racemic product *3zd* generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
**Fig. S48** HPLC trace for the racemic reference \textit{rac-3ze}, and non-racemic product \textit{3ze} generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S49 HPLC trace for the racemic reference rac-3zf, and non-racemic product 3zf generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
Fig. S50 HPLC trace for the racemic reference rac-3zg, and non-racemic product 3zg generated from the asymmetric photoredox reaction catalyzed by the chiral nickel catalyst.
6.2 Determination of Enantiopurity of the Transformation Product 5

Optical purities of the compound 5 were determined with a Daicel Chiralpak OJ column on an Agilent 1260 Series HPLC System. The column temperature was 30 °C and UV-absorption was measured at 254 nm.

**Fig. S51** HPLC trace for the racemic reference *rac-5*, and non-racemic product *(S)-5*. 
7. References

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8. $^1$H and $^{13}$C NMR Spectrum
$^1$H NMR
500 MHz
CDCl$_3$

$^{13}$C NMR
126 MHz
CDCl$_3$
$^1$H NMR
400 MHz
CDCl$_3$
$^1$H NMR
500 MHz
CDCl$_3$

$^{13}$C NMR
126 MHz
CDCl$_3$
$^1$H NMR
500 MHz
CDCl$_3$

$^{13}$C NMR
126 MHz
CDCl$_3$
$^1$H NMR
500 MHz
CD$_2$OD

$^{13}$C NMR
126 MHz
CD$_2$OD
