Supporting Information

Photochemical Asymmetric Nickel-Catalyzed Acyl Cross-Coupling

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A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for $^1$H or at 100 MHz and 125 MHz for $^{13}$C, respectively. High temperature NMRs were recorded at 328 K in CDCl$_3$ in a 500 MHz spectrometer. The chemical shifts (δ) for $^1$H and $^{13}$C are given in ppm relative to residual signals of the solvents (CHCl$_3$; @ 7.26 ppm $^1$H NMR, 77.36 ppm $^{13}$C NMR). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad signal.

High-resolution mass spectra (HRMS) were obtained from the ICIQ High Resolution Mass Spectrometry Unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization. Optical rotations were measured on a Polarimeter Jasco P-1030 and are reported as follows: $[\alpha]_D$ (c in g per 100 mL, solvent).

UV-vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D2 and W light sources. Cyclic voltammetry studies were carried out on a Princeton Applied Research PARSTAT 2273 potentiostat offering compliance voltage up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 2 A current range.

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General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques, unless otherwise stated. Synthesis grade solvents were used as purchased. Anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GP254, 0.25 mm) were used, using UV light as the visualizing agent and either phosphomolybdc acid in EtOH, dinitrophenylhydrazine in EtOH/H$_2$O or basic aqueous potassium permanganate (KMnO$_4$), and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator (in vacuo at 40 ºC, ~5 mbar).

In order to get consistent results, the nickel dibromide (NiBr$_2$) pre-catalyst was weighted and pre-dosed within a glove-box.

Determination of Enantiomeric Purity: UPC$_2$ analysis on chiral stationary phase was performed on a Waters Acquity instrument using a IC, CEL1, IE and AMY1 chiral columns. The exact conditions for the analyses are specified within the characterisation section. UPC$_2$ traces were compared to racemic samples prepared by running the reaction in the presence of a catalytic amount (12 mol%) of 2,2'-bipyridyl, which is commercially available form Sigma Aldrich.

Materials: Commercial grade reagents and solvents were purchased at the highest commercial quality from Sigma Aldrich, Fluka, Acros Organics, Fluorochem or Alfa Aesar and used as received, unless otherwise stated. All the ligand tested were purchased from Sigma Aldrich or Fluorochem. The chiral ligand 1 (L1) was purchased from Fluorochem. The nickel sources employed in the scope (NiCl$_2$ and NiBr$_2$) were purchased from Sigma Aldrich. Aldehydes precursor for the 4-alkyl-1,4-dihydropyridine derivatives 1h-o were prepared according to known literature procedures.[1]
B. Substrate Synthesis

B.1 Synthesis of the 4-alkyl-1,4-Dihydropyridines 1

4-alkyl-1,4-dihydropyridines 1 were synthesized using procedures reported in the literature.\[^{[2]}\] The following 4-alkyl-1,4-dihydropyridines were prepared from the corresponding aldehydes using the General procedure 1 in the Scheme S1:

![Scheme S1 Preparation of 4-alkyl 1,4-dihydropyridines.](image)

**General procedure 1:** In accordance to a reported procedure,\[^{[2]}\] ethyl-3-aminocrotonate (1 Equiv.) and ethylene glycol (2.5 M) were added to a flask under nitrogen. Next, ethyl acetooacetate (1 Equiv.) was added followed by the sequential addition of aldehyde (1 Equiv.) and tetrabutylammonium hydrogen sulfate (12 mol%). The resulting solution was heated up to 80 °C and stirred for 4 h, then cooled to ambient temperature and diluted with ethyl acetate. Brine was added and the mixture was extracted using ethyl acetate (3 x 50 mL). The organic layers were combined, dried (MgSO\(_4\)), and concentrated. The crude material was purified by flash column chromatography to furnish the desired 4-alkyl-1,4-dihydropyridine 1.

**Diethyl 4-(1-(1H-indol-1-yl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1a)**

Prepared according to the General Procedure 1 using 2-(1H-indol-1-yl)propanol (0,70 g, 4 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (0,66 g, 41% yield) as a yellow solid. The product was stored at -30 °C.

\(^{1}H\) NMR (400 MHz, Chloroform-d) \(\delta\) 7.53 (dt, \(J = 7.8, 1.0\) Hz, 1H), 7.41 (dd, \(J = 8.5, 1.0\) Hz, 1H), 7.13 (ddd, \(J = 8.3, 7.0, 1.2\) Hz, 1H), 7.04 – 6.99 (m, 2H), 6.39 (dd, \(J = 3.3, 0.8\) Hz, 1H), 5.43 (s, 1H), 4.65 – 4.56 (m, 1H), 4.53 (d, \(J = 4.0\) Hz, 1H), 4.19 (q, \(J = 7.1\) Hz, 2H), 3.99 (dq, \(J = 10.7, 7.1\) Hz, 1H), 3.67 (dq, \(J = 10.7, 7.1\) Hz, 1H), 2.20 (s, 3H), 1.94 (s, 3H), 1.44 (d, \(J = 7.2\) Hz, 3H), 1.34 (t, \(J = 7.1\) Hz, 3H), 0.93 (t, \(J = 7.1\) Hz, 3H).

\(^{13}C\) NMR (101 MHz, Chloroform-d) \(\delta\) 168.26, 167.99, 146.96, 146.42, 137.32, 128.51, 125.80, 121.15, 120.71, 119.24, 110.30, 100.48, 99.70, 99.29, 60.29, 60.25, 55.78, 39.46, 19.90, 19.21, 16.20, 14.76, 14.11.

HRMS (ESI) Exact mass calculated for C\(_{23}\)H\(_{29}\)N\(_{2}\)O\(_{4}\) [M+H]: 397.2049, found: 397.2122.

**Diethyl 4-(1-(5-fluoro-1H-indol-1-yl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1b)**

Prepared according to the General Procedure 1 using 2-(5-fluoro-1H-indol-1-yl)propanol (0,58 g, 3mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (0,71 g, 57% yield) as a yellow solid. The product was stored at -30 °C.

\(^{1}H\) NMR (400 MHz, Chloroform-d) \(\delta\) 7.36 (dd, \(J = 9.0, 4.4\) Hz, 1H), 7.18 (dd, \(J = 9.7, 2.5\) Hz, 1H), 7.06 (d, \(J = 3.2\) Hz, 1H), 6.89 (td, \(J = 9.1, 2.5\) Hz, 1H), 6.34 (dd, \(J = 3.2, 0.8\) Hz, 1H), 5.44 (s, 1H), 4.60 – 4.49 (m, 2H), 4.20 (q, \(J = 7.1\) Hz, 2H), 3.97 (dq, \(J = 10.8, 7.1\) Hz, 1H), 3.63 (dq, \(J = 10.7, 7.1\) Hz, 1H), 2.21 (s, 3H), 1.99 (s, 3H), 1.43 (d, \(J = 6.9\) Hz, 3H), 1.34 (t, \(J = 7.1\) Hz, 3H), 0.93 (t, \(J = 7.1\) Hz, 3H).

\(^{13}C\) NMR (101 MHz, Chloroform-d) \(\delta\) 168.19, 167.93, 159.06-159.73 (d, \(^{1}J_{CF} = 233.2\) Hz), 146.93, 146.33, 133.94, 128.66-128.56 (d, \(^{1}J_{CF} = 10.1\) Hz), 127.35, 110.93-110.83 (d, \(^{2}J_{CF} = 9.7\) Hz), 109.60-109.34 (d, \(^{2}J_{CF} = 9.7\) Hz), 105.34-105.11 (d, \(^{2}J_{CF} = 23.0\) Hz), 100.52-100.48 (d, \(^{4}J_{CF} = 4.6\) Hz), 99.61, 99.34, 60.36, 60.29, 56.09, 39.50, 19.97, 19.28, 16.03, 14.77, 14.12.

HRMS (ESI) Exact mass calculated for C\(_{23}\)H\(_{29}\)N\(_{2}\)O\(_{4}\) [M+Na]^+: 437.1954 found: 437.1829.
Diethyl 4-(1-(5-chloro-1H-indol-1-yl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1c)
Prepared according to the General procedure 1 using 2-(5-chloro-1H-indol-1-yl)propanal (1.14 g, 5.50 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (1.91 g, 81% yield) as a yellow solid. The product was stored at -30 °C.

$^1$H NMR (400 MHz, Chloroform-d), 7.50 (d, J = 2.1, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.09 (dd, J = 8.8, 2.1 Hz, 1H), 7.05 (d, J = 3.2 Hz, 1H), 6.33 (dd, J = 3.2, 0.8 Hz, 1H), 5.41 (s, 1H), 4.55 (m, 1H), 4.51 (d, J = 4.0 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.98 (dq, J = 10.7, 7.1 Hz, 1H), 3.66 (dq, J = 10.7, 7.1 Hz, 1H), 2.20 (s, 3H), 1.99 (s, 3H), 1.43 (d, J = 7.0 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (125 MHz, Chloroform-d) δ 168.15, 167.90, 135.73, 129.48, 127.14, 124.88, 121.41, 120.02, 111.32, 100.22, 99.62, 99.30, 60.38, 60.33, 56.10, 39.52, 19.97, 19.33, 16.10, 14.77, 14.14.

HRMS (ESI) Exact mass calculated for C$_{23}$H$_{23}$ClN$_{3}$O$_{4}$ [M+H]$^+$: 431.1659; found: 431.1732.

Diethyl 2,6-dimethyl-4-(1-(3-methyl-1H-indol-1-yl)ethyl)-1,4-dihydropyridine-3,5-dicarboxylate (1d)
Prepared according to the General procedure 1 using 2-(3-methyl-1H-indol-1-yl)propanal (1.93 g, 7.6 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (2.3 g, 63% yield) as a yellow solid. The product was stored at -30 °C.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.68 (d, J = 2.0, 1H), 7.33 (m, 1H), 7.23 (dd, J = 8.8, 1.9 Hz, 1H), 7.05 (d, J = 3.3 Hz, 1H), 6.35 (d, J = 3.2, 1H), 5.45 (s, 1H), 4.60 – 4.49 (m, 2H), 4.21 (q, J = 7.1 Hz, 2H), 4.01 (dq, J = 10.7, 7.1 Hz, 1H), 3.68 (dq, J = 10.7, 7.1 Hz, 1H), 2.22 (s, 3H), 2.01 (s, 3H), 1.46 (d, J = 6.9 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H), 0.98 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 168.14, 167.89, 146.96, 146.39, 135.98, 130.19, 127.00, 123.94, 123.13, 112.47, 111.79, 100.14, 99.60, 99.27, 60.38, 60.33, 55.09, 39.50, 19.96, 19.32, 16.09, 14.76, 14.13.

HRMS (ESI) Exact mass calculated for C$_{22}$H$_{25}$BrN$_{2}$O$_{4}$ [M+H]$^+$: 475.1154, found: 475.1227.

Diethyl 2,6-dimethyl-4-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)ethyl)-1,4-dihydropyridine-3,5-dicarboxylate (1e)
Prepared according to the General procedure 1 using 2-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)propanal (0.94 g, 4 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (0.63 g, 34% yield) as a yellow solid. The product was stored at -30 °C.

The product was observed as a complex mixture of rotamers. Recording the spectrum at high temperature didn’t resolve the observed complexity;

$^1$H NMR (500 MHz, T$_s$ = 328 K, Chloroform-d) δ 7.69 – 7.62 (m, 0.8 H), 7.39 (dd, J = 7.6, 1.3 Hz, 0.8 H), 7.36 (d, J = 7.7 Hz, 0.3H), 7.12 – 6.92 (m, 3H), 6.03 (br s, J = 1.1 H), 4.83 (d, J = 9.3 Hz, 0.75 Hz), 4.59 (d, J = 8.1 Hz, 0.22 H), 4.42 (dq, J = 18.4, 7.3 Hz, 0.29 H), 4.35 – 4.28 (m, 0.8 H), 4.24 (m, 0.8 H), 4.06 (dq, J = 10.7, 7.1 Hz, 0.2 H), 4.00 – 3.82 (m, 1.5 H), 3.55 (dq, J = 10.6, 7.1 Hz, 0.7H), 2.84 (m, 1H), 2.72 – 2.39 (m, 3H), 2.36 (s, 3H), 2.03 – 1.66 (m, 5H), 1.52 (d, J = 7.3 Hz, 2.3 H), 1.48 (d, J = 7.3 Hz, 0.77 H), 1.44 (t, J = 7.1 Hz, 3H), 1.13 – 1.07 (m, 1H), 0.68 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (125 MHz, T$_s$ = 328 K Chloroform-d) δ 168.38, 168.12, 167.50, 167.34, 146.41, 143.94, 138.06, 136.26, 135.94, 135.44, 128.73, 127.31, 120.33, 120.04, 118.26, 117.75, 117.44, 112.82, 110.50, 109.19, 108.92, 103.41, 100.69, 101.67, 100.54, 60.30, 60.14, 60.04, 59.63, 55.18, 55.00, 38.66, 37.38, 25.86, 24.38, 23.90, 23.51, 23.21, 23.01, 21.76, 21.39, 19.94, 19.61, 18.98, 16.88, 16.16, 14.78, 14.49, 14.30, 13.76.

HRMS (ESI) Exact mass calculated for C$_{27}$H$_{25}$N$_{2}$O$_{4}$ [M+H]$^+$: 451.2518, found: 451.2591.

Diethyl 4-(1-(9H-carbazol-9-yl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1f)
Prepared according to the General procedure 1 using 2-(9H-carbazol-9-yl)propanal (0.67g, 3 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (0.45 g, 34% yield) as a yellow solid. The product was stored at -30 °C.

S5
**Diethyl 2, 6-dimethyl-4-(1-phenylethyl)-1,4-dihydropyridine-3,5-dicarboxylate (1g)**

Prepared according to the General procedure 1 using 2-phenylpropanal (1.36 g, 10.1 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (2.17 g, 60% yield) as a pale yellow solid. The product was stored at -30 °C.

**HRMS (ESI)** Exact mass calculated for C$_{22}$H$_{23}$NO$_4$ [M+Na]$^+$: 469.2205, found: 469.2098.

**1H NMR** (300 MHz, Chloroform-d) δ 8.03 (app. t, J = 8.2, 1.1 Hz, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.45 – 7.29 (m, 2H), 7.15 (m, 3H), 5.74 (s, 1H), 4.88 (d, J = 8.3 Hz, 1H), 4.58 (p, J = 7.4 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.60 (dq, J = 10.8, 7.2 Hz, 1H), 3.15 (dq, J = 10.7, 7.1 Hz, 1H), 2.22 (s, 3H), 2.03 (s, 3H), 1.64 (d, J = 7.3 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H), 0.78 (t, J = 7.1 Hz, 3H).

**13C NMR** (101 MHz, Chloroform-d) δ 168.13, 167.23, 146.60, 145.19, 142.03, 139.99, 125.46, 125.17, 123.98, 122.78, 120.18, 120.08, 118.72, 118.65, 113.16, 108.94, 102.24, 100.83, 60.35, 59.67, 55.22, 37.67, 19.88, 19.24, 15.91, 14.74, 14.00.

**Diethyl 2, 6-dimethyl-4-(1-phenylpropyl)-1,4-dihydropyridine-3,5-dicarboxylate (1h)**

Prepared according to the General procedure 1 using 2-phenylbutanal (2.62 g, 17.7 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (1.93 g, 30% yield) as a pale yellow solid. The product was stored at -30 °C.

**HRMS (ESI)** Exact mass calculated for C$_{22}$H$_{23}$NO$_4$ [M+Na]$^+$: 384.2180.

**1H NMR** 1H NMR (400 MHz, Chloroform-d) δ 7.19 – 7.08 (m, 3H), 7.06 – 6.96 (m, 2H), 5.13 (s, 1H), 4.33 (d, J = 4.6 Hz, 1H), 4.18 – 4.00 (m, 4H), 2.42 (dt, J = 10.1, 5.2 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 1.75 – 1.53 (m, 2H), 1.27 (td, J = 7.1, 4.8 Hz, 6H), 0.76 (t, J = 7.3 Hz, 3H);

**13C NMR** 13C NMR (101 MHz, Chloroform-d) δ 168.95, 168.52, 145.55, 145.46, 142.49, 129.64, 127.20, 126.09, 101.56, 100.87, 59.93, 59.88, 55.02, 39.01, 23.27, 19.49, 14.69, 14.66, 12.92.

**Diethyl 2, 6-dimethyl-4-(1-phenylbutyl)-1,4-dihydropyridine-3,5-dicarboxylate (1i)**

Prepared according to the General procedure 1 using 2-phenylpentanal (0.57 g, 3.52 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (0.75 g, 55% yield) as a yellow oil. The product was stored at -30 °C.

**HRMS (ESI)** Exact mass calculated for C$_{22}$H$_{25}$NO$_4$ [M-H]: 370.2096, found: 370.2024.

**1H NMR** (400 MHz, Chloroform-d) δ 7.19 – 7.08 (m, 3H), 7.06 – 6.96 (m, 2H), 5.11 (s, 1H), 4.31 (d, J = 4.6 Hz, 1H), 4.17 – 4.01 (m, 4H), 2.57 – 2.50 (m, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 1.61 – 1.54 (m, 2H), 1.28 (td, J = 7.1, 4.8 Hz, 6H), 1.21 – 1.09 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H);

**13C NMR** 13C NMR (101 MHz, Chloroform-d) δ 169.01, 168.50, 145.56, 145.43, 142.67, 129.64, 127.16, 126.07, 101.56, 100.80, 59.95, 59.89, 52.69, 39.21, 32.77, 21.24, 19.47, 14.71, 14.66, 14.54.

**Diethyl 2, 6-dimethyl-4-(1-phenylpentyl)-1,4-dihydropyridine-3,5-dicarboxylate (1j)**

Prepared according to the General procedure 1 using 2-phenylhexanal (2 g, 11.3 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (2.2 g, 49% yield) as a yellow oil. The product was stored at -30 °C.

**1H NMR** (400 MHz, Chloroform-d) δ 7.18 – 7.08 (m, 3H), 7.03 – 6.95 (m, 2H), 5.28 (s, 1H), 4.30 (d, J = 4.6 Hz, 1H), 4.16 – 3.98 (m, 4H), 2.51 (m, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 1.67 – 1.56 (m, 2H), 1.27 (td, J = 7.1, 3.6 Hz, 6H), 1.24 (s, 2H), 1.16 – 1.02 (m, 2H), 0.79 (t, J = 7.2 Hz, 3H)
Diethyl 2,6-dimethyl-4-(1-(naphthalen-2-yl)ethyl)-1,4-dihydropyridine-3,5-dicarboxylate (I)

Prepared according to the General procedure 1 using 2-(naphthalen-2-yl)propanal (2.4 g, 13 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (1.76 g, 33% yield) as a pale yellow solid. The product was stored at -30 °C.

\[ \text{Diethyl 2,6-dimethyl-4-(1-(naphthalen-2-yl)ethyl)-1,4-dihydropyridine-3,5-dicarboxylate (I)} \]

HRMS (ESI) Exact mass calculated for C_{32}H_{32}NO_{14} [M-H]: 398.2409, found: 398.2337.

Diethyl 4-(1-(methoxyphenyl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (II)

Prepared according to the General procedure 1 using 2-(methoxyphenyl)propanal (2.3 g, 14 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (4.5 g, 83% yield) as yellow oil. The product was stored at -30 °C.

\[ \text{Diethyl 4-(1-(methoxyphenyl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (II)} \]

HRMS (ESI) Exact mass calculated for C_{28}H_{28}NO_{14} [M-H]: 406.2096 found: 406.2024.

Diethyl 2,6-dimethyl-4-(1-(p-toly)-ethyl)-1,4-dihydropyridine-3,5-dicarboxylate (1m)

Prepared according to the General procedure 1 using 2-(p-toly)propanal (2g, 14mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (2 g, 39% yield) as a pale yellow solid. The product was stored at -30 °C.

\[ \text{Diethyl 2,6-dimethyl-4-(1-(p-toly)-ethyl)-1,4-dihydropyridine-3,5-dicarboxylate (1m)} \]

HRMS (ESI) Exact mass calculated for C_{22}H_{22}NO_{14} [M-H]: 386.2045, found: 386.1973.

Diethyl 4-(1-(4-chlorophenyl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1n)

Prepared according to the General procedure 1 using 2-(4-chlorophenyl)propanal (1.73 g, 10.3 mmol). The crude material was purified by flash column chromatography (cyclohexane/ EtOAc 95:5) to give the corresponding product (1.19 g, 30% yield) as a yellow oil. The product was stored at -30 °C.

\[ \text{Diethyl 4-(1-(4-chlorophenyl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1n)} \]

HRMS (ESI) Exact mass calculated for C_{22}H_{22}NO_{14} [M-H]: 370.2096, found: 370.2024.
HRMS (ESI) Exact mass calculated for C_{21}H_{26}ClNNaO_4 [M+Na]^+: 414.1550, found: 414.1443.

**Diethyl 4-(1-(4-bromophenyl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1o)**

Prepared according to the General procedure 1 using 2-(4-bromophenyl)propanal (0.40 g, 1.9 mmol). The crude material was purified by flash column chromatography (cyclohexane/EtOAc 95:5) to give the corresponding product (0.39 g, 48% yield) as a yellow solid. The product was stored at -30 °C.

^1H NMR (400 MHz, Chloroform-d). δ 7.33 – 7.27 (m, 2H), 7.00 – 6.93 (m, 2H), 5.38 (s, 1H), 4.24 (d, J = 4.9 Hz, 1H), 4.13 – 3.99 (m, 3H), 3.97 – 3.87 (m, 1H), 2.77 – 2.67 (m, 1H), 2.19 (s, 6H), 1.27 (td, J = 7.1, 0.7 Hz, 3H), 1.23 – 1.16 (t, 7 Hz, 3H), 1.13 (d, J = 7.2 Hz, 3H).

^13C NMR (101 MHz, Chloroform-d). δ 168.60, 168.51, 143.52, 130.56, 130.47, 120.00, 101.16, 101.06, 60.01 (d, J = 1.4 Hz), 45.82, 40.37, 19.65, 19.50, 15.77, 14.69, 14.58.

HRMS (ESI) Exact mass calculated for C_{21}H_{26}BrNNaO_4 [M+Na]^+: 458.1045, found: 458.0937.

**B.2 Synthesis of the Symmetrical Anhydrides 2**

The following anhydrides were prepared from the corresponding acids using the procedure detailed in the Scheme S2:

**Scheme S2 Preparation of the symmetrical anhydrides**

**General Procedure 2:** In accordance to a reported procedure,^1[3] DCC (0.50-0.55 Equiv.) was added to a solution of the appropriate carboxylic acid (1 Equiv.) in toluene (0.3 M). The solution was stirred at room temperature for 15 min. The suspension was filtered and concentrated under vacuum to give the crude product, which was used without further purification.

**5-chloropentanoic anhydride (2b)**

Prepared according to the General procedure 2 using 5-chloropentanoic acid (1.3 g, 9.5 mmol). The product was obtained as a brown oil (1.4 g, 60% yield). The product was stored at -30 °C.

^1H NMR (300 MHz, Chloroform-d). δ 3.60 – 3.51 (m, 2H), 2.56 – 2.46 (m, 2H), 1.91 – 1.77 (m, 4H).

^13C NMR (75 MHz, Chloroform-d). δ 168.93, 44.30, 34.42, 31.48, 21.57.

HRMS (ESI) Exact mass calculated for C_{10}H_{16}Cl_2NaO_3 [M+Na]^+: 277.0471, found: 277.0369.

**5-oxo-5-phenylpentanoic anhydride (2c)**

Prepared according to the General procedure 2 using 5-oxo-5-phenylpentanoic acid (2.45 g, 12.8 mmol). The product was obtained as a grey powder (2.05 g, 44% yield). The product was stored at -30 °C.

^1H NMR (500 MHz, Chloroform-d). δ 7.98 – 7.94 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.43 (m, 2H), 3.09 (t, J = 7.0 Hz, 2H), 2.60 (t, J = 7.0 Hz, 2H), 2.11 (p, J = 7.0 Hz, 2H).

^13C NMR (125 MHz, Chloroform-d). δ 199.39, 169.45, 137.00, 133.55, 128.98, 128.35, 37.21, 34.60, 18.88.

HRMS (ESI) Exact mass calculated for C_{22}H_{22}NaO_5 [M+Na]^+: 389.1467, found: 389.1359.

**4-phenylbutanoic anhydride (2d)**

Prepared according to the General procedure 2 using 4-phenylbutanoic acid (2.45 g, 15 mmol). The product was obtained as a white solid (2.27 g, 49% yield). The product was stored at -30 °C.

^1H NMR (500 MHz, Chloroform-d). δ 7.33 – 7.27 (m, 2H), 7.23 – 7.14 (m, 3H), 2.69 (t, J = 7.6 Hz, 2H), 2.45 (t, J = 7.4 Hz, 2H), 2.04 – 1.95 (p, J = 7.0 Hz, 2H).
**5-oxohexanoic anhydride (2e)**

Prepared according to the General procedure 2 using 5-oxohexanoic acid (1 g, 7.6 mmol). The product was obtained as a brown oil (1.2 g, 65% yield).

The product was stored at -30 °C.

1H NMR (300 MHz, Chloroform-d) δ 2.55 (t, J = 7.0 Hz, 2H), 2.49 (t, J = 7.1 Hz, 2H), 2.14 (s, 3H), 1.91 (p, J = 7.0 Hz, 2H).

13C NMR (75 MHz, Chloroform-d) δ 207.86, 169.26, 42.05, 34.32, 30.21, 18.27.

HRMS (ESI) Exact mass calculated for C_{12}H_{18}NaO_{5} [M+Na]^+ : 265.1150, found: 265.1046.

3-phenylpropanoic anhydride (2f)

Prepared according to the General procedure 2 using 3-phenylpropanoic acid (0.400 g, 2.66 mmol). The product was obtained as a withe solid (0.37 g, 50 % yield). The product was stored at -30 °C.

The compound displayed spectroscopic data consistent with those reported previously.[4]

1H NMR (400 MHz, Chloroform-d) δ 7.30 (m, 1H), 7.25 – 7.17 (m, 2H), 2.96 (t, J = 7.7 Hz, 1H), 2.78 – 2.71 (t, J = 7.8 Hz, 1H).

13C NMR (101 MHz, Chloroform-d) δ 168.86, 139.92, 128.98, 128.64, 126.90, 37.18, 30.54.

3-(3-methoxyphenyl)propanoic anhydride (2g)

Prepared according to the General procedure 2 using 3-(3-methoxyphenyl)propanoic acid (0.54 g, 3 mmol). The product was obtained as a colorless oil (0.37 g, 36% yield). The product was stored at -30 °C.

1H NMR (500 MHz, Chloroform-d) δ 6.41 (s, 2H), 3.84 (s, 6H), 3.81 (s, 3H), 2.91 (t, J = 7.5 Hz, 2H), 2.74 (m, 2H).

13C NMR (125 MHz, Chloroform-d) δ 168.84, 153.61, 136.97, 135.63, 105.61, 100.29, 61.12, 56.40, 37.33, 30.90.

3-(3,4,5-trimethoxyphenyl)propanoic anhydride (2h)

Prepared according to the General procedure 2 using 3-(3,4,5-trimethoxyphenyl)propanoic acid (0.72 g, 3 mmol). The product was obtained as a colorless oil (0.53 g, 76% yield). The product was stored at -30 °C.

1H NMR (500 MHz, Chloroform-d) δ 6.41 (s, 2H), 3.84 (s, 6H), 3.81 (s, 3H), 2.91 (t, J = 7.5 Hz, 2H), 2.74 (m, 2H).

13C NMR (125 MHz, Chloroform-d) δ 168.84, 153.61, 136.97, 135.63, 105.61, 100.29, 61.12, 56.40, 37.33, 30.90.

**Hept-6-enolic anhydride (2i)**

Prepared according to the General procedure 2 using hept-6-enolic acid (0.38 g, 3 mmol). The product was obtained as a colorless oil (0.3 g, 84% yield). The product was stored at -30 °C. The compound displayed spectroscopic data consistent with those reported previously.[5]

1H NMR (500 MHz, Chloroform-d) δ 5.79 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.07 – 4.91 (m, 2H), 2.46 (t, J = 7.4 Hz, 2H), 2.13 – 2.03 (m, 2H), 1.74 – 1.62 (m, 2H), 1.51 – 1.41 (m, 2H).

13C NMR (125 MHz, Chloroform-d) δ 169.76, 138.43, 115.28, 35.43, 33.57, 28.35, 23.97.
B.2 Synthesis of the Aldehydes needed for the Preparation of 1

The following aldehydes were prepared according to the conditions reported in Scheme S3:

**Scheme S3** Preparation of α-amino aldehydes.

**General Procedure 3:** In a flask containing a solution of the indole (1 equiv.) in DMF (1.7 M), NaH (1.1 equiv.) was added. After evolution of the gas was over, the suspension was kept at 0 ºC and methyl 2-bromopropionate (1.25 equiv.) was added. The reaction was stirred overnight and then diluted with water and extracted with DCM. The organic phase was dried and concentrated in vacuo. The crude material was purified by flash column chromatography to furnish the desired α-amino ester.

To a cooled (-78 ºC) solution of the α-amino ester in ether (0.33 M) was slowly added via a syringe DIBAL-H (1 M in hexane) (1,2 equiv). The mixture was stirred -78 ºC for 4.5 hours, after which MeOH (2 equiv) was added to quench the unreacted DIBAL-H. A saturated solution of Rochelle’s salt (sodium potassium tartrate) was added to the reaction and stirred for 30 minutes. The crude was extracted with ether and the organic phase was dried over magnesium sulphate and evaporated. The crude material was purified by flash column chromatography to furnish the desired α-amino aldehyde.

**Aldehyde-1a**
Prepared according to the General Procedure 3. The crude material was purified by flash column chromatography (95:5 hexane/EtOAc) to give the corresponding product as a yellow oil (61% yield measured for the reduction step).

$^1$H NMR (400 MHz, Chloroform-d) δ 9.70 (d, J = 0.8 Hz, 1H), 7.76 – 7.56 (m, 1H), 7.30 – 7.16 (m, 4H), 6.6 (dd, J = 3.3, 0.8 Hz, 1H), 4.98 (q, J = 7.3 Hz, 1H), 1.74 (dd, J = 7.3, 0.6 Hz, 3H).

**Aldehyde-1b**
Prepared according to the General procedure 3. The crude material was purified by flash column chromatography (95:5 hexane/EtOAc) to give the corresponding product as a yellow oil (44% yield measured for the reduction step).

$^1$H NMR (300 MHz, Chloroform-d) δ 9.64 (s, 1H), 7.30 (dd, J = 9.5, 2.5 Hz, 1H), 7.16 (dd, J = 14.4, 3.8 Hz, 2H), 6.97 (td, J = 9.0, 2.5 Hz, 1H), 6.58 (d, J = 2.8 Hz, 1H), 4.90 (q, J = 7.3 Hz, 1H), 1.71 (d, J = 7.3 Hz, 3H).

**Aldehyde-1c**
Prepared according to the General procedure 3. The crude material was purified by flash column chromatography (95:5 hexane/EtOAc) to give the corresponding product as a yellow oil (63% yield measured for the reduction step).

$^1$H NMR (400 MHz, Chloroform-d) δ 9.67 (d, J = 0.8 Hz, 1H), 7.65 (dd, J = 1.7, 0.9 Hz, 1H), 7.19 (dd, J = 2.5, 0.7 Hz, 3H), 6.59 (d, J = 3.3 Hz, 1H), 4.94 (qd, J = 7.3, 0.9 Hz, 1H), 1.74 (d, J = 7.3 Hz, 3H).

**Aldehyde-1d**
Prepared according to the General Procedure 3. The crude material was purified by flash column chromatography (95:5 hexane/EtOAc) to give the corresponding product as a yellow oil (57% yield measured for the reduction step).

$^1$H NMR (400 MHz, Chloroform-d) δ 9.65 (d, J = 0.9 Hz, 1H), 7.80 (dd, J = 1.9, 0.6 Hz, 1H), 7.31 (dd, J = 8.8, 1.9, 1H), 7.19 – 7.08 (m, 2H), 6.57 (dd, J = 3.3, 0.9 Hz, 1H), 5.01 – 4.82 (t, 7.3 Hz, 1H), 1.72 (d, J = 7.3 Hz, 3H).
Prepared according to the General Procedure 3. The crude material was purified by flash column chromatography (95:5 hexane/EtOAc) to give the corresponding product as a yellow oil (25% yield measured for the reduction step).

**Aldehyde-1e**

1H NMR (400 MHz, Chloroform-d) δ 9.88 (s, 1H), 7.59 – 7.43 (m, 2H), 7.19 – 7.02 (m, 3H), 4.85 (q, J = 7.1 Hz, 1H), 2.81 – 2.56 (m, 4H), 2.06 – 1.83 (m, 4H), 1.63 (d, J = 7.1 Hz, 3H).

**Aldehyde-1f**

Prepared according to the General Procedure 3. The crude material was purified by flash column chromatography (95:5 hexane/EtOAc) to give the corresponding product as a yellow oil (40% yield measured for the reduction step).

1H NMR (500 MHz, Chloroform-d) δ 9.96 (s, 1H), 8.21 – 8.08 (m, 2H), 7.52 – 7.23 (m, 6H), 5.42 (q, J = 7.2 Hz, 1H), 1.84 (dd, J = 7.3, 0.9 Hz, 3H).
C. Experimental Procedure

C.1 General Procedures for the Photochemical Synthesis of α-amino and α-aryl ketones.

**Scheme S4** Photochemical Synthesis of α-Amino and α-Aryl Ketones.

**General Procedure 4:** To a vial containing 10 mol% of the nickel salt pre-catalyst (NiCl₂ or NiBr₂) was added a solution of the chiral ligand L1 (0.12 mol%) in THF (0.6 mL). The colored solution was added into a Schlenk tube containing the 4-alkyl dihydropyridine 1 (1 Equiv.), anhydride 2 (2 Equiv.), and lutidine (1 Equiv.). The mixture was placed under an atmosphere of argon, cooled to −78 °C, and degassed via vacuum evacuation (5 min), backfilled with argon, and warmed to room temperature. The freeze-pump-thaw cycle was repeated three times, and then the Schlenk tube was sealed with Parafilm and placed into a 3D-printed plastic support mounted on an aluminum block fitted with a 405 nm high-power single LED (λ = 405 nm, the full setup is detailed in Figure S1). The irradiance was fixed at 75 ± 3 mW/cm² (1200 μA), as controlled by an external power supply and measured using a photodiode light detector at the start of each reaction. The temperature was kept constant at +10 °C with a chiller connected to the irradiation plate (temperature measured within the reaction vial with a thermometer). The reaction was stirred for 18–48 hours, then the crude was filtered on a plug of silica using ethyl acetate as eluent, and the solvent evaporated. The crude mixture was purified on silica gel to furnish the chiral product.

**Figure S1.** Detailed set-up and illumination system. The light source for illuminating the reaction vessel consisted in a 405 nm high-power single LED (OCU-440 UE420-X-T) purchased from OSA OPTO.
C.2 Characterization of Products

(S)-2-(1H-indol-1-yl)hexan-3-one (3a)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (79 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48 h. The crude material was purified by flash chromatography (hexane/dichloromethane 9:1) to give product 3a (12 mg, 56% yield) as a yellow oil. The enantiomeric excess was determined by UPC² analysis using a CEL1 chiral column: after 1 min of 100% CO₂, gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 2.7 \text{ min}, \tau_{\text{major}} = 2.8 \text{ min (75% ee)}; \quad [\alpha]_{D}^{26} = \text{--144.5 (c = 0.5, CH}_{2}\text{Cl}_2, 75 \% \text{ ee).} \)

1H NMR (400 MHz, Chloroform-d) \( \delta \) 7.64 (dt, \( J = 7.9, 1.0 \text{ Hz, 1H} \)), 7.26 – 7.18 (m, 2H), 7.15 – 7.10 (m, 2H), 6.59 (dd, \( J = 3.3, 0.8 \text{ Hz, 1H} \)), 4.97 (q, \( J = 7.2 \text{ Hz, 1H} \)), 2.22 – 2.04 (m, 2H), 1.69 (d, \( J = 7.2 \text{ Hz, 3H} \)), 1.47 (h, \( J = 7.3 \text{ Hz, 2H} \)), 0.74 (t, \( J = 7.4 \text{ Hz, 3H} \)).

13C NMR (101 MHz, Chloroform-d) \( \delta \) 209.05, 136.35, 129.18, 125.48, 122.47, 121.60, 120.38, 109.46, 103.22, 60.29, 40.29, 17.12, 16.28, 13.85.

(S)-2-(5-fluoro-1H-indol-1-yl)hexan-3-one (3b)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (83 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48 h. The crude material was purified by flash chromatography (hexane/dichloromethane 9:1) to give product 3b (10 mg, 43% yield) as a yellow oil. The enantiomeric excess was determined by UPC² analysis using a CEL1 chiral column: after 1 min of 100% CO₂, gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 2.4 \text{ min, \tau_{\text{major}} = 2.5 \text{ min (81% ee); [\alpha]_{D}^{26} = -96.7 (c = 0.44, \text{CH}_{2}\text{Cl}_2, 81 \% \text{ ee).}} \)

1H NMR (400 MHz, Chloroform-d) \( \delta \) 7.29 (dd, \( J = 9.4, 2.5 \text{ Hz, 1H} \)), 7.20 (d, \( J = 3.2 \text{ Hz, 1H} \)), 7.15 (dd, \( J = 8.9, 4.2 \text{ Hz, 1H} \)), 7.00 – 6.92 (td, \( J = 9.1, 2.5 \text{ Hz, 1H} \)), 6.56 (dd, \( J = 3.2, 0.8 \text{ Hz, 1H} \)), 4.94 (q, \( J = 7.2 \text{ Hz, 1H} \)), 2.24 – 2.03 (m, 2H), 1.70 (d, \( J = 7.2 \text{ Hz, 3H} \)), 1.49 (sextet, \( J = 7.3 \text{ Hz, 2H} \)), 0.76 (t, \( J = 7.4 \text{ Hz, 3H} \)).

13C NMR (101 MHz, Chloroform-d) \( \delta \) 208.69, 158.41 (d, \( ^{1}J_{CF} = 235.0 \text{ Hz, 1H} \)), 132.97, 129.52 (d, \( ^{3}J_{CF} = 10.1 \text{ Hz, 1H} \)), 127.15, 110.87 (d, \( ^{2}J_{CF} = 26.4 \text{ Hz, 1H} \)), 110.11 (d, \( ^{3}J_{CF} = 9.7 \text{ Hz, 1H} \)), 106.40 (d, \( ^{2}J_{CF} = 23.4 \text{ Hz, 1H} \)), 103.16 (d, long range \( J = 4.7 \text{ Hz, 1H} \)), 60.64, 40.22, 17.13, 16.27, 13.86.

19F NMR (376 MHz, Chloroform-d) \( \delta \) -124.64.

(S)-2-(5-chloro-1H-indol-1-yl)hexan-3-one (3c)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (86 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48 h. The crude material was purified by flash chromatography (hexane/dichloromethane 9:1) to give product 3c (16 mg, 64% yield) as a yellow oil. The enantiomeric excess was determined by UPC² analysis using a CEL1 chiral column: after 1 min of 100% CO₂, gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 2.70 \text{ min, \tau_{\text{major}} = 2.9 \text{ min (78% ee); [\alpha]_{D}^{26} = -74.7 (c = 0.91, \text{CH}_{2}\text{Cl}_2, 78 \% \text{ ee).}} \)

1H NMR (300 MHz, Chloroform-d) \( \delta \) 7.61 (m, 1H), 7.20 – 7.14 (m, 3H), 6.54 (d, \( J = 3.3 \text{ Hz, 1H} \)), 4.94 (q, \( J = 7.2 \text{ Hz, 1H} \)), 2.25 – 2.01 (m, 2H), 1.70 (d, \( J = 7.2 \text{ Hz, 3H} \)), 1.48 (sextet, \( J = 7.4 \text{ Hz, 2H} \)), 0.76 (t, \( J = 7.4 \text{ Hz, 3H} \)).

13C NMR (101 MHz, Chloroform-d) \( \delta \) 208.45, 134.75, 130.20, 126.90, 126.12, 122.77, 121.00, 110.48, 102.87, 60.53, 40.31, 17.12, 16.26, 13.85.

HRMS (ESI) Exact mass calculated for [M+Na]+: 272.0920, found: 272.0813.
(S)-2-(3-methyl-1H-indol-1-yl)hexan-3-one (3d)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (95 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3d (13 mg, 44 % yield) as a pale yellow oil. The enantiomeric excess was determined by UPC₂ analysis using a CEL1 chiral column: after 1 min of 100% CO₂ gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 2.9 \text{ min, } \tau_{\text{major}} = 3.2 \text{ min (78 % ee); [}\alpha]\text{d}^{26} = -79.8 \) (c = 0.6, CH₂Cl₂, 78% ee).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta 7.78 \) (d, \( J = 1.9 \text{ Hz, } 1H \)), \( 7.33 – 7.24 \) (m, 1H), \( 7.19 – 7.08 \) (m, 2H), 6.54 (dd, \( J = 3.4, 0.8 \text{ Hz, } 1H \)), \( 4.94 \) (q, \( J = 7.2 \text{ Hz, } 1H \)), \( 2.23 – 2.04 \) (m, 2H), \( 1.70 \) (d, \( J = 7.2 \text{ Hz, } 3H \)), 1.49 (p, \( J = 7.3 \text{ Hz, } 2H \)), 0.76 (t, \( J = 7.4 \text{ Hz, } 3H \)).

\(^13\)C NMR (101 MHz, Chloroform-d) \( \delta 208.39, 135.03, 130.87, 126.75, 125.32, 124.13, 113.66, 110.92, 102.80, 60.51, 40.33, 17.13, 16.26, 13.86.

(S)-2-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)hexan-3-one (3e)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (90 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3e (23 mg, 85 % yield) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC3 column, 98:02 hexane/isopropanol flow rate 1.3 mL/min, 20ºC: \( \tau_{\text{minor}} = 9.0 \text{ min, } \tau_{\text{major}} = 9.3 \text{ min (46% ee); [}\alpha]\text{d}^{26} = -47.9 \) (c = 0.7, CH₂Cl₂, 40% ee).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta 7.54 – 7.45 \) (m, 1H), \( 7.17 – 7.03 \) (m, 3H), 4.81 (q, \( J = 7.0 \text{ Hz, } 1H \)), \( 2.84 – 2.56 \) (m, 4H), \( 2.24 – 2.04 \) (m, 2H), \( 2.03 – 1.80 \) (m, 4H), 1.60 (d, \( J = 7.1 \text{ Hz, } 3H \)), 1.55 – 1.42 (m, 2H), 0.81 – 0.74 (t, \( J = 7.4 \text{ Hz, } 3H \)).

\(^13\)C NMR (101 MHz, Chloroform-d) \( \delta 209.33, 135.59, 135.11, 128.47, 121.55, 119.56, 118.43, 111.42, 109.72, 58.73, 41.06, 23.72, 23.35, 23.06, 21.40, 17.34, 15.03, 13.94.

HRMS (ESI) Exact mass calculated for [M+Na]⁺: 292.1779, found: 292.1674.

(S)-2-(9H-carbazol-9-yl)hexan-3-one (3f)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (89 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3f (17 mg, 64 % yield) as a pale yellow oil. The enantiomeric excess was determined by UPC₂ analysis using a CEL1 chiral column: after 1 min of 100% CO₂ gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 3.9 \text{ min, } \tau_{\text{major}} = 4.0 \text{ min (47 % ee); [}\alpha]\text{d}^{26} = -74.2 \) (c = 0.7, CH₂Cl₂, 47% ee).

\(^1\)H NMR (300 MHz, Chloroform-d) \( \delta 8.17 – 8.09 \) (m, 2H), \( 7.45 \) (dd, \( J = 8.3, 7.1, 1.2 \text{ Hz, } 2H \)), \( 7.32 – 7.23 \) (m, 4H), 5.18 (q, \( J = 7.0 \text{ Hz, } 1H \)), \( 2.32 – 2.02 \) (m, 2H), 1.68 (d, \( J = 7.0 \text{ Hz, } 3H \)), 1.55 – 1.39 (m, 2H), 0.70 (t, \( J = 7.4 \text{ Hz, } 3H \)).

\(^13\)C NMR (101 MHz, Chloroform-d) \( \delta 209.26, 139.87, 126.41, 123.91, 120.96, 120.02, 109.28, 58.70, 41.18, 17.38, 13.86, 13.68.

HRMS (ESI) Exact mass calculated for [M+H]⁺: 266.1466, found: 266.1551.
(S)-7-chloro-2-(1H-indol-1-yl)heptan-3-one (3g)

Prepared according to the General procedure 4 using the corresponding anhydride (25 mg, 0.1 mmol), 2,6-lutidine (12 μL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (79 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3g (13 mg, 50% yield) as a pale yellow oil. The enantiomeric excess was determined by UPC² analysis using a CEL1 chiral column: after 1 min of 100% CO₂ gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. τ₂min,τ = 3.2 min, τmajor = 3.4 min (73% ee); [α]D²⁶ = -59.5 (c = 0.65, CH₂Cl₂, 73% ee).

1H NMR (400 MHz, Chloroform-d) δ 7.65 (dt, J = 7.8, 1.0 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.18 – 7.10 (m, 2H), 6.60 (d, J = 3.2, 1H), 4.98 (q, J = 7.2 Hz, 1H), 3.40 – 3.32 (m, 2H), 2.25 – 2.08 (m, 2H), 1.70 (d, J = 7.2 Hz, 3H), 1.64-1.50 (m, 4H).

13C NMR (101 MHz, Chloroform-d) δ 208.50, 136.32, 129.23, 125.39, 122.61, 121.71, 120.52, 109.41, 103.46, 60.35, 44.77, 37.32, 31.94, 20.96, 16.23.

(S)-6-(1H-indol-1-yl)-1-phenylheptane-1,5-dione (3h)

Prepared according to the General Procedure 4 using the corresponding anhydride (25 mg, 0.1 mmol), 2,6-lutidine (12 μL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (79 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3h (15 mg, 47% yield) as a pale yellow oil. The enantiomeric excess was determined by UPC² analysis using a CEL1 chiral column: after 1 min of 100% CO₂ gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. τ₂min = 4.4 min, τmajor = 4.8 min (79% ee); [α]D²⁶ = -58.4 (c = 0.75, CH₂Cl₂, 79% ee).

1H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.76 (m, 2H), 7.62 (dt, J = 7.8, 1.0 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.44 – 7.36 (m, 2H), 7.25 (m, 1H), 7.19 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.14 (d, J = 3.3 Hz, 1H), 7.11 (dd, J = 7.9, 6.8, 1.2 Hz, 1H), 6.57 (dd, J = 3.3, 0.9 Hz, 1H), 5.00 (q, J = 7.2 Hz, 1H), 2.76 (td, J = 7.0, 1.9 Hz, 2H), 2.28 (m, 2H), 1.89 (p, J = 7.0 Hz, 2H), 1.71 (d, J = 7.2 Hz, 3H).

13C NMR (101 MHz, Chloroform-d) δ 208.59, 199.78, 137.01, 136.28, 133.37, 129.23, 128.87, 128.31, 125.53, 122.55, 121.67, 120.45, 109.52, 103.38, 60.43, 37.48, 37.36, 18.19, 16.18.

(S)-2-(1H-indol-1-yl)-6-phenylhexan-3-one (3i)

Prepared according to the General Procedure 4 using the corresponding anhydride (25 mg, 0.1 mmol), 2,6-lutidine (12 μL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (79 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3i (14 mg, 48% yield) as a pale yellow oil. The enantiomeric excess was determined by UPC² analysis using a CEL1 chiral column: after 1 min of 100% CO₂ gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. τ₂min = 3.9 min, τmajor = 4.1 min (80% ee); [α]D²⁶ = -53.9 (c = 0.7, CH₂Cl₂, 80% ee).

1H NMR (400 MHz, Chloroform-d) δ 7.67 (dt, J = 7.8, 1.1 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.18 – 7.11 (m, 3H), 7.03 – 6.98 (m, 2H), 6.60 (d, J = 3.3 Hz, 1H), 4.96 (q, J = 7.2 Hz, 1H), 2.43 (tt, J = 13.8, 6.8 Hz, 2H), 2.28 – 2.10 (m, 2H), 1.79 (p, J = 7.4 Hz, 2H), 1.69 (d, J = 7.2 Hz, 3H).

13C NMR (101 MHz, Chloroform-d) δ 208.74, 141.67, 136.36, 129.22, 128.68 (d, J = 4.6 Hz), 126.25, 125.44, 122.53, 121.65, 120.43, 109.47, 103.33, 60.29, 37.62, 35.13, 25.15, 16.27.

(S)-7-(1H-indol-1-yl)octan-2,6-dione (3j)

Prepared according to the General Procedure 4 using the corresponding anhydride (25 mg, 0.1 mmol), 2,6-lutidine (12 μL, 0.1 mmol), NiCl₂ (1.3 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (79 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3j (16 mg, 61% yield) as a pale...
yellow oil. The enantiomeric excess was determined by UPC\textsuperscript{2} analysis using a CEL\textsuperscript{1} chiral column: after 1 min of 100\% CO\textsubscript{2}, gradient up to 60:40 CO\textsubscript{2}/acetoniitrite over 5 minutes, flow rate 2 mL/min. $\tau_{\text{min}}$= 3.40 min, $\tau_{\text{major}}$ = 3.5 min (75\% ee); [a]$_D$\textsuperscript{26} = 51.9 (c = 0.8, CH\textsubscript{2}Cl\textsubscript{2}, 75\% ee).

$^1$H NMR (400 MHz, Chloroform-d) \(\delta\) 7.62 (dt, $J$ = 7.8, 1.0 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.14 – 7.07 (m, 2H), 6.57 (dd, $J$ = 3.3, 0.7 Hz, 1H), 4.96 (q, $J$ = 7.2 Hz, 1H), 2.22 (td, $J$ = 7.0, 3.1 Hz, 2H), 2.16 (q, $J$ = 6.9 Hz, 2H), 1.96 (s, 3H), 1.73-1.64 (app m: q, $J$ = 7.1 Hz, 2H; d, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) \(\delta\) 208.51, 208.42, 136.28, 129.24, 125.50, 122.55, 121.67, 120.47, 109.49, 103.38, 60.35, 42.45, 37.19, 30.08, 17.64, 16.16.

(S)-4-(1H-indol-1-yl)-1-phenylpentan-3-one (3k)

Prepared according to the General Procedure 4 using the corresponding anhydride (25 mg, 0.1 mmol), 2,6-lutidine (12 \(\mu\)L, 0.1 mmol), NiCl\textsubscript{2} (1.3 mg, 10 mol\%), ligand L\textsubscript{1} (4.0 mg, 12 mol\%), the corresponding dihydropyridine (79 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3k (14 mg, 51\% yield) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpack IC3 column, 98:02 hexane/isopropanol flow rate 1.3 mL/min, 20°C. $\tau_{\text{min}}$ = 11.4 min, $\tau_{\text{major}}$ = 12.8 min (80\% ee); [a]$_D$\textsuperscript{26} = -55.5 (c = 0.7, CH\textsubscript{2}Cl\textsubscript{2}, 80\% ee).

$^1$H NMR (400 MHz, Chloroform-d) \(\delta\) 7.65 (dt, $J$ = 7.7, 1.0 Hz, 1H), 7.24 – 7.11 (m, 6H), 7.08 (d, $J$ = 3.3 Hz, 1H), 7.03 – 6.98 (m, 2H), 6.59 (dd, $J$ = 3.3, 0.7 Hz, 1H), 4.93 (q, $J$ = 7.2 Hz, 1H), 2.81 – 2.75 (t, $J$ = 7.9 Hz, 2H), 2.58 – 2.39 (m, 2H), 1.66 (d, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) \(\delta\) 208.20, 140.86, 136.32, 129.21, 128.78, 128.64, 126.50, 125.43, 122.55, 121.65, 120.45, 109.42, 103.39, 60.52, 40.04, 29.93, 16.13.

(S)-4-(1H-indol-1-yl)-1-(3-methoxyphenyl)pentan-3-one (3l)

Prepared according to the General Procedure 4 using the corresponding anhydride (25 mg, 0.1 mmol), 2,6-lutidine (12 \(\mu\)L, 0.1 mmol), NiCl\textsubscript{2} (1.3 mg, 10 mol\%), ligand L\textsubscript{1} (4.0 mg, 12 mol\%), the corresponding dihydropyridine (79 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 48h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 3l (15 mg, 49\% yield) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpack IC3 column, 98:02 hexane/isopropanol flow rate 1.3 mL/min, 20°C. $\tau_{\text{min}}$ = 16.8 min, $\tau_{\text{major}}$ = 18.0 min (82\% ee); [a]$_D$\textsuperscript{26} = -49.77 (c = 0.75, CH\textsubscript{2}Cl\textsubscript{2}, 82\% ee).

$^1$H NMR (400 MHz, Chloroform-d) \(\delta\) 7.67 (dt, $J$ = 7.8, 1.0 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.19 – 7.09 (m, 3H), 6.72 (ddd, $J$ = 8.3, 2.6, 1.0 Hz, 1H), 6.65 – 6.59 (m, 2H), 6.58 – 6.54 (m, 1H), 4.95 (q, $J$ = 7.2 Hz, 1H), 3.75 (s, 3H), 2.77 (td, $J$ = 7.2, 6.6, 1.7 Hz, 2H), 2.60 – 2.42 (m, 2H), 1.69 (d, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) \(\delta\) 208.22, 159.95, 142.45, 136.30, 129.75, 129.19, 125.44, 122.53, 121.63, 120.96, 120.44, 114.29, 111.94, 109.41, 103.37, 60.50, 55.43, 39.98, 30.01, 16.12.

(R)-2-phenylhexan-3-one (4a)

Prepared according to the General Procedure 4 using butyric anhydride (16 \(\mu\)L, 0.1 mmol), 2,6-lutidine (12 \(\mu\)L, 0.1 mmol), NiBr\textsubscript{2} (2.2 mg, 10 mol\%), ligand L\textsubscript{1} (4.0 mg, 12 mol\%), the corresponding dihydropyridine (71 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4a (23 mg, 66\% yield) as a pale yellow oil that displayed spectroscopic data consistent with those reported previously.\textsuperscript{[6]} The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpack IC3 column, 98.2 hexane/isopropanol flow rate 1 mL/min, 20 °C, 280 nm. $\tau_{\text{min}}$ = 6.7 min, $\tau_{\text{major}}$ = 7.5 min (95\% ee); [a]$_D$\textsuperscript{26} = -172.7 (c = 0.65, CH\textsubscript{2}Cl\textsubscript{2}, 95\% ee).

$^1$H NMR (400 MHz, Chloroform-d) \(\delta\) 7.36 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.24 – 7.17 (m, 2H), 3.74 (q, $J$ = 7.0 Hz, 1H), 2.36 – 2.28 (t, $J$ = 7.3 Hz 2H), 1.56 – 1.42 (m, 2H), 1.39 (d, $J$ = 7.2 Hz, 3H), 0.79 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) \(\delta\) 211.28, 141.10, 129.20, 128.23, 127.40, 53.31, 43.32, 17.78, 17.62, 13.94.
(R)-3-phenylheptan-4-one (4b)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), ligand L1 (4.0 mg, 12 mol%), the corresponding dihydropyridine (77 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4b (19 mg, 51% yield) as a pale yellow oil that displayed spectroscopic data consistent with those reported previously.[7] The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpack IC3 column, 98:2 hexane/isopropanol flow rate 1 mL/min, 20 ºC, 215 nm. τ\text{minor} = 6.0 min, τ\text{major} = 6.4 min (90% ee); [α]D²⁶ = -31.6 (c = 0.2, CH₂Cl₂, 90% ee).

¹H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 7.21 (m, 2H), 3.52 (t, J = 7.4 Hz, 1H), 2.37 – 2.29 (m, 2H), 2.13 – 1.98 (m, 1H), 1.70 (m, 1H), 1.57 – 1.41 (m, 2H), 0.80 (m, 6H).

¹³C NMR (101 MHz, Chloroform-d) δ 211.05, 139.66, 129.10, 128.62, 127.38, 59.39, 44.17, 32.20, 30.09, 29.63, 21.05.

HRMS (ESI) Exact mass calculated for [M+H]⁺: 205.1514, found: 205.1582

(R)-5-phenyloctan-4-one (4c)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), the corresponding dihydropyridine (77 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4c (20 mg, 48% yield) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpack IC3 column, 98:2 hexane/isopropanol flow rate 1 mL/min, 20 ºC, 230 nm. τ\text{minor} = 5.6 min, τ\text{major} = 6.3 min (92% ee); [α]D²⁶ = -100.7 (c = 0.25, CH₂Cl₂, 92 % ee).

¹H NMR (400 MHz, Chloroform-d) δ. 7.34 – 7.28 (m, 2H), 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 3.62 (t, J = 7.4 Hz, 1H), 2.37 – 2.28 (t, J = 7.6 Hz , 2H), 2.00 (m, 1H), 1.67 (, 1H), 1.54 – 1.39 (m, 2H), 1.25 – 1.10 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H), 0.79 (t, J = 7.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 211.03, 139.46, 129.12, 128.68, 127.44, 61.17, 44.23, 25.63, 17.53, 13.95, 12.50.

HRMS (ESI) Exact mass calculated for [M+H]⁺: 205.1514, found: 205.1582

(R)-5-phenylnonan-4-one (4d)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), ligand L1 (4.0 mg, 12 mol%), the corresponding dihydropyridine (80 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4d (18 mg, 42% yield) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpack IC3 column, 98:2 hexane/isopropanol flow rate 1 mL/min, 20 ºC, 215 nm. τ\text{minor} = 5.3 min, τ\text{major} = 6.0 min (94% ee); [α]D²⁶ = -104.5 (c = 0.3, CH₂Cl₂, 94% ee).

¹H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 7.23 – 7.17 (m, 2H), 3.60 (t, J = 7.4 Hz, 1H), 2.33 (td, J = 7.1, 0.9 Hz, 2H), 2.03 (m, 1H), 1.68 (m, 1H), 1.56 – 1.42 (m, 2H), 1.37 – 1.23 (m, 2H), 1.22 – 1.06 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H), 0.79 (t, J = 7.4 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 211.05, 139.66, 129.10, 128.62, 127.38, 59.39, 44.17, 32.20, 30.09, 22.98, 17.52, 14.26, 13.93.

HRMS (ESI) Exact mass calculated for [M+Na]⁺: 241.1670, found: 241.1557

(R)-5-(napthalen-2-yl)octan-4-one (4e)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), ligand L1 (4.0 mg, 12 mol%), the corresponding dihydropyridine (82 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4e (19 mg, 42% yield) as a pale yellow oil.

[7]
The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpack IC3 column, 98:2 hexane/isopropanol flow rate 1 mL/min, 20°C, 230 nm. \( \tau_{\text{minor}} = 9.4 \) min, \( \tau_{\text{major}} = 10.3 \) min (84% ee); [\( \alpha \)]=26 = -154.9 (c = 0.5, CH\(_2\)Cl\(_2\), 84% ee).

\(^{1}H\) NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.86 – 7.78 (m, 3H), 7.71 – 7.66 (m, 1H), 7.52 – 7.43 (m, 2H), 7.33 (dd, \( J = 8.5, 1.8 \) Hz, 1H), 3.92 (q, \( J = 7.0 \) Hz, 1H), 2.36 (t, \( J = 7.3 \) Hz, 2H), 1.61 – 1.50 (m, 2H), 1.48 (d, \( J = 6.9 \) Hz, 4H), 0.79 (t, \( J = 7.4 \) Hz, 3H).

\(^{13}C\) NMR (101 MHz, Chloroform-\( d \)) \( \delta \) 211.24, 138.62, 133.97, 132.87, 128.97, 128.03 (d, \( J = 1.5 \) Hz), 126.99, 126.61, 126.26, 126.19, 53.43, 43.44, 17.83, 17.62, 13.95.

**HRMS (ESI)** Exact mass calculated for [M+Na]: 229.1306, found: 229.1256.

**HRMS (ESI)** Exact mass calculated for [M+Na]: 213.1357, found: 213.1256.

**HRMS (ESI)** Exact mass calculated for [M+Na]: 213.1357, found: 213.1256.

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**HRMS (ESI)** Exact mass calculated for [M+Na]: 213.1357, found: 213.1256.

**HRMS (ESI)** Exact mass calculated for [M+Na]: 213.1357, found: 213.1256.
(R)-2-(4-bromophenyl)hexan-3-one (4i)

Prepared according to the General Procedure 4 using butyric anhydride (16 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (78 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4i (14 mg, 55% yield) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpack IC3 column, 100% hexane flow rate 1 mL/min, 20°C, 230 nm. \( \tau_{\text{minor}} = 20.9 \text{ min} \) \( \tau_{\text{major}} = 21.9 \text{ min} \) (90% ee); \( [\alpha]_D^{26} = -98.3 \text{ (c = 0.6, CH}_2\text{Cl}_2, 90\% \text{ ee) } \).

\[ ^1\text{H NMR} \ (400 \text{ MHz, Chloroform-}d) \delta 7.48 - 7.42 \text{ (m, 2H)}, 7.12 - 7.06 \text{ (m, 2H), 3.71 (q, } J = 7.0 \text{ Hz, 1H), 2.32 (t, } J = 7.3 \text{ Hz, 2H), 1.54 - 1.44 \text{ (m, 2H), 1.36 (d, } J = 7.0 \text{ Hz, 3H), 0.80 (t, } J = 7.4 \text{ Hz, 3H).} \]

\[ ^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-}d) \delta 210.64, 140.05, 132.32, 129.93, 121.40, 52.65, 43.44, 17.80, 17.56, 13.94. \]

(R)-2-phenylpentan-3-one (4j)

Prepared according to the General Procedure 4 using the corresponding anhydride (13 µL, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), the corresponding dihydropyridine (72 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4j (11 mg, 66% yield) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpack IC3 column, 98:02 hexane/isopropanol flow rate 1.0 mL/min, 20°C, \( \tau_{\text{minor}} = 7.7 \text{ min} \) \( \tau_{\text{major}} = 8.6 \text{ min} \) (93% ee); \( [\alpha]_D^{26} = -85 \text{ (c = 0.5, CH}_2\text{Cl}_2, 93\% \text{ ee) } \), Lit for R isomer: \( [\alpha]_D^{26} = -76 \text{ (c = 1.2, CHCl}_3, \text{ for 93% ee).} \)

\[ [\alpha]_D^{21} = -42 \text{ (c = 1.0, CHCl}_3, \text{ for 73% ee, R isomer);} \]

\[ [\alpha]_D^{26} = -225.9 \text{ (c = 0.57, CHCl}_3, \text{ for 91% ee).} \]

\[ ^1\text{H NMR} \ (400 \text{ MHz, Chloroform-}d) \delta 7.36 - 7.29 \text{ (m, 2H), 7.28 - 7.18 \text{ (m, 3H), 3.76 (q, } J = 7.0 \text{ Hz, 1H), 2.38 (dq, } J = 8.6, 7.3 \text{ Hz, 2H), 1.39 (d, } J = 6.9 \text{ Hz, 3H), 0.96 (t, } J = 7.3 \text{ Hz, 3H).} \]

\[ ^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-}d) \delta 211.89, 141.27, 129.22, 128.17, 127.40, 53.05, 34.59, 17.86, 8.32. \]

(R)-2-phenylnon-8-en-3-one (4k)

Prepared according to the General Procedure 4 using the corresponding anhydride (24 mg, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), the corresponding dihydropyridine (72 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4k (13 mg, 58% yield) as a pale yellow oil. The enantiomeric excess was determined by UPC² analysis using an AMY1 chiral column: after 1 min of 100% \text{CO}_2, gradient up to 60:40 \text{CO}_2/acetonitrile over 5 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 2.0 \text{ min} \) \( \tau_{\text{major}} = 2.10 \text{ min} \) (92% ee); \( [\alpha]_D^{26} = -128.4 \text{ (c = 0.75, CH}_2\text{Cl}_2, 92\% \text{ ee) } \).

\[ ^1\text{H NMR} \ (400 \text{ MHz, Chloroform-}d) \delta 7.38 - 7.32 \text{ (m, 2H), 7.31 - 7.27 \text{ (m, 1H), 7.26 - 7.20 \text{ (m, 2H), 5.75 (ddt, } J = 16.9, 10.2, 6.7 \text{ Hz, 1H), 5.05 - 4.80 \text{ (m, 2H), 3.77 (q, } J = 7.0 \text{ Hz, 1H), 2.46 - 2.29 \text{ (m, 2H), 2.05 - 1.91 \text{ (m, 2H), 1.59 - 1.46 \text{ (m, 2H), 1.41 (d, } J = 6.9 \text{ Hz, 3H), 1.34 - 1.20 \text{ (m, 2H).} \}

\[ ^{13}\text{C NMR} \ (101 \text{ MHz, Chloroform-}d) \delta 211.15, 141.08, 138.85, 129.23, 128.22, 127.43, 114.85, 53.33, 41.13, 33.76, 28.59, 23.64, 17.78. \]

HRMS (ESI) Exact mass calculated for [M+Na]⁺: 239.1514, found: 239.1409

(R)-1,4-diphenylpentan-3-one (4l)

Prepared according to the General Procedure 4 using the corresponding anhydride (24 mg, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), the corresponding dihydropyridine (72 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4l (18 mg, 75% yield) as a pale yellow oil.
The enantiomeric excess was determined by UPC² analysis using a IE3 chiral column: after 1 min of 100% CO₂, gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 3.5 \text{ min} \), \( \tau_{\text{major}} = 3.7 \text{ min (90\% ee)} \); \( [\alpha]_D^{26} = -407.4 \) (c = 0.2, CH₂Cl₂, 90\% ee).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.30 (m, 2H), 7.27 – 7.18 (m, 3H), 7.18 – 7.12 (m, 3H), 7.09 – 7.03 (m, 2H), 3.70 (q, \( J = 6.9 \text{ Hz, } 1H \)), 2.92 – 2.70 (m, 2H), 2.70 – 2.57 (m, 2H), 1.37 (d, \( J = 6.9 \text{ Hz, } 3H \)).

\(^13\)C NMR (101 MHz, Chloroform-d) \( \delta \) 210.19, 141.38, 140.80, 129.27, 128.72, 128.60, 128.21, 127.47, 126.33, 53.54, 42.91, 30.31, 17.65.

(R)-1-(3-methoxyphenyl)-4-phenylpentan-3-one (4m)

Prepared according to the General procedure 4 using the corresponding anhydride (34 mg, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (72 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4m (19 mg, 71\% yield) as a pale yellow oil. The enantiomeric excess was determined by UPC² analysis using a IE3 chiral column: after 1 min of 100\% CO₂, gradient up to 60:40 CO₂/acetonitrile over 5 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 4.1 \text{ min} \), \( \tau_{\text{major}} = 4.2 \text{ min (94\% ee)} \); \( [\alpha]_D^{26} = -105.9 \) (c = 0.85, CH₂Cl₂, 94\% ee).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 7.21 – 7.13 (m, 2H), 6.73 (dd, \( J = 8.3, 2.6, 1H \)), 6.68 (d, \( J = 7.5, 1H \)), 6.64 (m, 1H), 3.78 (s, 3H), 3.74 (q, \( J = 7.0 \text{ Hz, } 1H \)), 2.92 – 2.72 (m, 2H), 2.72 – 2.59 (m, 2H), 1.41 (d, \( J = 7.0 \text{ Hz, } 3H \)).

\(^13\)C NMR (101 MHz, Chloroform-d) \( \delta \) 210.17, 159.94, 143.01, 140.77, 129.69, 129.26, 128.20, 127.47, 120.97, 114.33, 111.68, 55.44, 53.53, 42.83, 30.35, 17.66.

HRMS (ESI) Exact mass calculated for [M+Na]+: 291.1463, found: 291.1351.

(R)-4-phenyl-1-(3,4,5-trimethoxyphenyl)pentan-3-one (4n)

Prepared according to the General Procedure 4 using the corresponding anhydride (51 mg, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (72 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/ethyl acetate 9:1) to give the product 4n (22 mg, 67\% yield) as a pale yellow oil. The enantiomeric excess was determined by UPC² analysis using a IE3 chiral column: isocratic 89:11 CO₂/isopropanol over 9 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 7.9 \text{ min} \), \( \tau_{\text{major}} = 8.6 \text{ min (95\% ee)} \); \( [\alpha]_D^{26} = -85.2 \) (c = 1.10, CH₂Cl₂, 95\% ee).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.34 – 7.20 (m, 3H), 7.17 – 7.10 (m, 2H), 6.26 (s, 2H), 3.80 (s, 3H), 3.78 (s, 6H), 3.71 (q, \( J = 6.9 \text{ Hz, } 1H \)), 2.86 – 2.57 (m, 4H), 1.38 (d, \( J = 7.0 \text{ Hz, } 3H \)).

\(^13\)C NMR (101 MHz, Chloroform-d) \( \delta \) 210.10, 153.39, 140.66, 137.15, 136.55, 129.22, 128.20, 127.47, 110.56, 61.14, 56.35, 53.86, 42.99, 30.67, 17.68.

(R)-7-phenyloctane-2,6-dione (4o)

Prepared according to the General Procedure 4 using the corresponding anhydride (24 mg, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr₂ (2.2 mg, 10 mol%), ligand L₁ (4.0 mg, 12 mol%), the corresponding dihydropyridine (72 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give product 4o (15 mg, 67\% yield) as a pale yellow oil. The enantiomeric excess was determined by UPC² analysis using a IE3 chiral column: isocratic 90:10 CO₂/acetonitrile over 9 minutes, flow rate 2 mL/min. \( \tau_{\text{minor}} = 1.9 \text{ min} \), \( \tau_{\text{major}} = 2.1 \text{ min (94\% ee)} \); \( [\alpha]_D^{26} = -192.4 \) (c = 0.55, CH₂Cl₂, 94\% ee).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.35 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.17 (m, 2H), 3.74 (q, \( J = 7.0 \text{ Hz, } 1H \)), 2.39 (t, \( J = 7.0 \text{ Hz, } 2H \)), 2.36 – 2.22 (m, 2H), 2.03 (s, 3H), 1.76 (m, 2H), 1.38 (d, \( J = 7.0 \text{ Hz, } 3H \)).

\(^13\)C NMR (101 MHz, Chloroform-d) \( \delta \) 210.63, 208.67, 140.79, 129.28, 128.19, 127.52, 53.33, 42.66, 40.05, 30.11, 18.10, 17.62.
(R)-7-chloro-2-phenylheptan-3-one (4p)

Prepared according to the General Procedure 4 using the corresponding anhydride (25 mg, 0.1 mmol), 2,6-lutidine (12 µL, 0.1 mmol), NiBr$_2$ (2.2 mg, 10 mol%), ligand L1 (4.0 mg, 12 mol%), the corresponding dihydropyridine (72 mg, 0.2 mmol) and tetrahydrofuran (0.6 mL). Reaction time: 18 h. The crude material was purified by flash column chromatography (hexane/dichloromethane 9:1) to give the product 4p (19 mg, 83% yield) as a pale yellow oil. The enantiomeric excess was determined by UPC$_2$ analysis using a IE3 chiral column: after 1 min of 100% CO$_2$, gradient up to 60:40 CO$_2$/acetonitrile over 5 minutes, flow rate 2 mL/min. $\tau_{\text{minor}}$ = 2.0 min, $\tau_{\text{major}}$ = 2.2 min (88% ee); $\alpha_D^{26} = -88.8$ (c = 1.2, CH$_2$Cl$_2$, 88% ee).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.37 – 7.29 (m, 2H), 7.29 – 7.23 (m, 1H), 7.23 – 7.16 (m, 2H), 3.75 (q, $J$ = 6.9 Hz, 1H), 3.41 (m, 2H), 2.49 – 2.27 (m, 2H), 1.73 – 1.54 (m, 4H), 1.39 (d, $J$ = 7.0 Hz, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 210.51, 140.87, 129.31, 128.18, 127.55, 53.38, 44.89, 40.20, 32.07, 21.39, 17.69.

D. Assignment of Absolute Configuration

(R)-2-phenylpentan-3-one (4j)

$\alpha_D^{20} = -85$ (c = 0.5, CH$_2$Cl$_2$, 93% ee), Lit for R isomer: $\alpha_D^{26} = -76$ (c = 1.2, CHCl$_3$, for 93% ee). $\alpha_D^{21} = -42$ (c = 1.0, CHCl$_3$, for 73% ee, R isomer). $\alpha_D^{25} = -225.9$ (c = 0.57, CHCl$_3$, for 91% ee).
E. Evaluation of the Excited State Potential of 1a and 1g

E.1 UV-vis Absorption Spectra of 1a and 1g

Solutions of 1a ([1a] = 3 mM in dry CH$_3$CN) were introduced into a 1 cm path length quartz cuvette equipped with a Teflon$^\text{®}$ septum. The solution was analyzed using a Shimadzu 2401PC UV-Vis spectrophotometer.

![Figure S2. Absorption spectra of diethyl 4-((1H-indol-1-yl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate 1a ([1a] = 3 mM in CH$_3$CN): $\lambda_{\text{max}}$ = 341 nm. The tail wavelength of absorption was considered at 418 nm.](image1)

Solutions of 1g ([1g] = 3 mM in dry CH$_3$CN) were introduced to a 1 cm path length quartz cuvette equipped with a Teflon$^\text{®}$ septum. The solution was analyzed using a Shimadzu 2401PC UV-Vis spectrophotometer.

![Figure S3. Absorption spectra of diethyl 4-((1H-indol-1-yl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate 1g ([1g] = 3 mM in CH$_3$CN): $\lambda_{\text{max}}$ = 337 nm. The tail wavelength of absorption was considered at 420 nm.](image2)
E.2 Cyclic Voltammetry Study

**Figure S4.** Cyclic voltammogram of 1a [0.02 M] in [0.1 M] TBAPF$_6$ in CH$_3$CN. Sweep rate: 200 mV/s. Pt electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible oxidation. 

$E_{pA} = E_{ox}(1a^+ / 1a) = +1.3$ V; $E_{pA}$ is the anodic peak potential, while $E_{ox}$ value describes the electrochemical properties of 1a.

**Figure S5.** Cyclic voltammogram of 1g [0.02 M] in [0.1 M] TBAPF$_6$ in CH$_3$CN. Sweep rate: 200 mV/s. Glassy-carbon electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible oxidation. 

$E_{pA} = E_{ox}(1g^+ / 1g) = +1.3$ V; $E_{pA}$ is the anodic peak potential, while $E_{ox}$ value describes the electrochemical properties of 1g.
E.3 Evaluation of the Excited State Potential of 1a and 1c

Using the data collected from the absorption spectra studies (Section E.1) and the cyclic voltammetry (Section E.2) of the 4-alkyl-1,4-dihydropyridines 1a and 1g, we could estimate the redox potential of the excited compounds (1*) employing the following Equation 1:[10]

$$E(1^*/1^*) = E(1^*/1) - E_{0.0}(1^*/1)$$  \[ Eq. 1 \]

DHP 1a - Since the electrochemical oxidation of the DHP 1a is irreversible (Figure S4), the irreversible peak potential $E_{p, \text{Anode}}$ was used for $E(1a^*/1a)$. $E_{0.0}(1a^*/1a)$, which is the excited state energy of the 4-alkyl-1,4-dihydropyridine 1a, was estimated spectroscopically from the position of the long wavelength tail of the absorption spectrum recorded in acetonitrile (418 nm, Figures S2), the solvent used for the electrochemical analysis.

For the DHP 1a, the $E_{p, \text{Anode}}$, which provides the $E(1a^*/1a)$, is 1.3 V (Figures S4), while the position of the long wavelength tail of the absorption spectrum corresponds to 418 nm (Figures S2), which translates into an $E_{0.0}(1a^*/1a^*)$ of 2.96 eV.

$$E(1a^*/1a^*) = 1.3 - 2.96 = -1.66 \text{ V (vs Ag/AgCl)}$$

DHP 1g - Equation 1 was applied. Since the electrochemical oxidation of the DHP 1g is irreversible (Figure S5), the irreversible peak potential $E_{p, \text{Anode}}$ was used for $E(1g^*/1g)$. $E_{0.0}(1g^*/1g)$, which is the excited state energy of 1g was estimated spectroscopically from the position of the long wavelength tail of the absorption spectrum recorded in acetonitrile (420 nm, Figures S3), the solvent used for the electrochemical analysis.

For the DHP 1g, the $E_{p, \text{Anode}}$, which provides the $E(1g^*/1g)$, is 1.3 V (Figures S4), while the position of the long wavelength tail of the absorption spectrum corresponds to 420 nm (Figures S2), which translates into an $E_{0.0}(1g^*/1g^*)$ of 2.95 eV.

$$E(1g^*/1g^*) = 1.3 - 2.95 = -1.65 \text{ V (vs Ag/AgCl)}$$
F. Characterization of Selected Compounds

F.1 UV-vis Absorption Spectra of 1e, 1f and 3f

Solutions of 1e ([1e] = 3 mM in dry CH₃CN) were introduced into a 1 cm path length quartz cuvette equipped with a Teflon® septum. The solution was analyzed using a Shimadzu 2401PC UV-Vis spectrophotometer.

Figure S6. Absorption spectra of diethyl 2,6-dimethyl-4-(1-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)ethyl)-1,4-dihydropyridine-3,5-dicarboxylate 1e ([1e] = 3 mM in CH₃CN): λ_max = 294 nm. The tail wavelength of absorption was considered at 413 nm.

Solutions of 1f ([1f] = 3 mM in dry CH₃CN) were introduced into a 1 cm path length quartz cuvette equipped with a Teflon® septum. The solution was analyzed using a Shimadzu 2401PC UV-Vis spectrophotometer.

Figure S7. Absorption spectra of diethyl 4-(1-(9H-carbazol-9-yl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate 1f ([1f] = 3 mM in CH₃CN): λ_max = 329 nm. The tail wavelength of absorption was considered at 410 nm.
Solutions of 3f ([3f] = 3 mM in dry CH₃CN) were introduced into a 1 cm path length quartz cuvette equipped with a Teflon® septum. The solution was analyzed using a Shimadzu 2401PC UV-Vis spectrophotometer.

**Figure S8.** Absorption spectra of (S)-2-(9H-carbazol-9-yl)hexan-3-one 3f ([3f] = 3 mM in CH₃CN): The tail wavelength of absorption was considered at 360 nm.

Solutions of 1e, 1f, 3f, 9-methyl-2,3,4,9-tetrahydro-1H-carbazole (NMe-THCbz) and 9-methyl-9H-carbazole (NMe-Cbz) (Concentration = 0.5 mM in dry CH₃CN) were introduced into a 1 cm path length quartz cuvette equipped with a Teflon® septum. The solution was analyzed using a Shimadzu 2401PC UV-Vis spectrophotometer.

**Figure S9.** Combined absorption spectra of 1e, 1f, 3f, 9-methyl-2,3,4,9-tetrahydro-1H-carbazole (NMe-THCbz) and 9-methyl-9H-carbazole (NMe-Cbz).
F.2 Cyclic Voltammetry Study of 1e, 1f and 3f

**Figure S10.** Cyclic voltammogram of 1e [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Sweep rate: 30 mV/s. Pt electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible oxidation. 

\[ E_{\text{pa}}^\Delta = E_{\text{ox}}(1e^+/1e) = +1.0 \text{ V}; \]

\[ E_{\text{pa}}^\text{ox} \text{ is the anodic peak potential, while } E_{\text{ox}} \text{ value describes the electrochemical properties of 1e.} \]

**Figure S11.** Cyclic voltammogram of 1f [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Sweep rate: 200 mV/s. Pt electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible oxidation.

\[ E_{\text{pa}}^{\text{ox}} \approx E_{\text{pa}} = +1.53 \text{ V}; E_{\text{pc}}^{\text{red}} \approx E_{\text{pc}} = +1.31 \text{ V}; \]

\[ E_{\text{pa}}^{\text{ox}} \text{ is the anodic peak potential, while and } E_{\text{pc}} \text{ is the cathodic peak potential. } E_{\text{pa}}^{\text{ox}} \text{ and } E_{\text{pc}}^{\text{red}} \text{ values describe the electrochemical properties of 1f.} \]
Figure S12. Cyclic voltammogram of 3f [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Sweep rate: 200 mV/s. Pt electrode working electrode, Ag/AgCl (NaCl saturated) reference electrode, Pt wire auxiliary electrode. Irreversible oxidation. E⁰_pox = E_poa = +1.46 V; E⁰_pred = E_poc = +1.20 V; E_poa is the anodic peak potential, while E_poc is the cathodic peak potential. E_pox and E_pred values describe the electrochemical properties of 3f.

G. Unsuccessful substrates in the Photochemical Asymmetric Cross-Coupling

Figure S13. List of unsuccessful substrates in the photochemical asymmetric cross-coupling
H. References

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I. NMR spectra

$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^{1}H$ NMR 400 MHz, Chloroform-d

$^{13}C$ NMR 101 MHz, Chloroform-d
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 500 MHz, T = 328 K, Chloroform-$d$

$^{13}$C NMR 500 MHz, T = 328 K, Chloroform-$d$
$^{2}$H NMR 300 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^2$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^2$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^2$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^2$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^2$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^13$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 300 MHz, Chloroform-$d$

$^{13}$C NMR 75 MHz, Chloroform-$d$
$^1$H NMR 500 MHz, Chloroform-$d$

$^1$C NMR 125 MHz, Chloroform-$d$
\[^1\text{H} \text{NMR} \; 500 \text{ MHz, Chloroform-}d\]

\[^1\text{C} \text{NMR} \; 125 \text{ MHz, Chloroform-}d\]
$^{1}H$ NMR 300 MHz, Chloroform-$d$

$^{13}C$ NMR 75 MHz, Chloroform-$d$
$^{1}H$ NMR 400 MHz, Chloroform-$d$

$^{13}C$ NMR 101 MHz, Chloroform-$d$
$^1$H NMR 500 MHz, Chloroform-d

$^{13}$C NMR 125 MHz, Chloroform-d
\textsuperscript{1}H NMR 400 MHz, Chloroform-\textit{d}

\textsuperscript{13}C NMR 125 MHz, Chloroform-\textit{d}
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 125 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 125 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^{19}$F NMR 376 MHz, Chloroform-$d$
$^1$H NMR 300 MHz, Chloroform-$d$

$^{13}$C NMR 75 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 300 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^{1}H\text{ NMR 400 MHz, Chloroform-}d$

$^{13}C\text{ NMR 101 MHz, Chloroform-}d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
$^{13}$C NMR 101 MHz, Chloroform-$d$

$^1$H NMR 400 MHz, Chloroform-$d$
$\text{C NMR 101 MHz, Chloroform-}\text{d}$

$\text{H NMR 400 MHz, Chloroform-}\text{d}$
$^{13}$C NMR 101 MHz, Chloroform-d

$^1$H NMR 400 MHz, Chloroform-d
$^{13}$C NMR 101 MHz, Chloroform-$d$

$^1$H NMR 400 MHz, Chloroform-$d$
$^{13}$C NMR 101 MHz, Chloroform-$d$

$^1$H NMR 400 MHz, Chloroform-$d$
$^{13}$C NMR 101 MHz, Chloroform-$d$

$^1$H NMR 400 MHz, Chloroform-$d$
$\text{Ph} - \text{O} - \text{Me}$

$\text{C NMR 101 MHz, Chloroform-}d$

$\text{H NMR 400 MHz, Chloroform-}d$

$\text{1}^3\text{C NMR 101 MHz, Chloroform-}d$

$\text{1}^1\text{H NMR 400 MHz, Chloroform-}d$
$^{13}$C NMR 101 MHz, Chloroform-$d$

$^1$H NMR 400 MHz, Chloroform-$d$
$^{13}$C NMR 101 MHz, Chloroform-$d$

$^1$H NMR 400 MHz, Chloroform-$d$
$^{13}$C NMR 101 MHz, Chloroform-$d$
$^1$H NMR 400 MHz, Chloroform-$d$

$^{13}$C NMR 101 MHz, Chloroform-$d$
J. HPLC and UPC$^2$ Trace

**Conditions:** UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, curve 6), flow rate 2 mL/min, $\lambda = 210$ nm
**Conditions:** UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, curve 6), flow rate 2 mL/min, $\lambda = 210$ nm
Conditions: UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, curve 6), flow rate 2 mL/min, \( \lambda = 210 \text{ nm} \)
Conditions: UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, curve 6, flow rate 2 mL/min, $\lambda = 210$ nm
**Conditions:** HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1.3 mL/min, $\lambda = 360$ nm

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|-------|
| #                | [min] | [min] | [mAU*s] | [mAU] |
| 1                | 4.809 | VV   | 0.0918 | 7314.16357 | 1223.10950 | 49.8744 |
| 2                | 5.220 | VB   | 0.1024 | 7351.00586 | 1094.07458 | 50.1256 |

| Peak RetTime Type | Width | Area | Height | Area % |
|------------------|-------|------|--------|-------|
| #                | [min] | [min] | [mAU*s] | [mAU] |
| 1                | 4.907 | MM   | 0.0986 | 2876.45898 | 486.39020 | 26.7300 |
| 2                | 5.334 | MM   | 0.1135 | 7884.69629 | 1158.24109 | 73.2700 |
**Conditions:** UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, curve 6), flow rate 2 mL/min, $\lambda = 210$ nm
UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40
CO2:acetonitrile over 5 min, curve 6), flow rate 2 mL/min, $\lambda = 210$ nm
UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, curve 6), flow rate 2 mL/min, $\lambda = 210$ nm
UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, curve 6), flow rate 2 mL/min, $\lambda = 210$ nm
UPC2 Daicel Chiralpak CEL1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, curve 6), flow rate 2 mL/min, $\lambda = 210$ nm
**Conditions:** HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1.3 mL/min, $\lambda = 254$ nm
Conditions: HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1.3 mL/min, λ = 280 nm

Peak RetTime Type Width Area Height Area %
1 16.290 BB 0.3634 6565.85156 268.36041 49.9621
2 17.770 BB 0.4290 6575.81494 227.65619 50.0379
HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1 mL/min, λ = 360 nm

| # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---|---------------|------|-------------|--------------|--------------|----------|
| 1 | 6.770 | BB | 0.1054 | 123.69100 | 18.16771 | 50.0008 |
| 2 | 7.532 | BB | 0.1147 | 123.68684 | 16.65265 | 49.9992 |

Peak RetTime Type Width Area Height Area
| # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|---|---------------|------|-------------|--------------|--------------|----------|
| 1 | 6.744 | BV | 0.1020 | 58.19639 | 8.70219 | 2.3320 |
| 2 | 7.505 | MM | 0.1214 | 2437.33057 | 334.57257 | 97.6680 |
HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1 mL/min, λ = 215 nm

| # | RetTime [min] | Width [min] | Area [mAU*sec] | Height [mAU] | Area [%] |
|---|---------------|-------------|----------------|--------------|---------|
| 1 | 6.144 MM | 0.1305 | 4882.72021 | 623.63599 | 50.5596 |
| 2 | 6.631 MM | 0.1822 | 4774.62891 | 436.82913 | 49.4404 |

| # | RetTime [min] | Width [min] | Area [mAU*sec] | Height [mAU] | Area [%] |
|---|---------------|-------------|----------------|--------------|---------|
| 1 | 5.577 MM | 0.1106 | 50.69938 | 7.64201 | 5.2063 |
| 2 | 5.891 MM | 0.1031 | 923.11450 | 149.16211 | 94.7937 |
HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1 mL/min, $\lambda = 215$ nm
HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1 mL/min, λ = 360 nm

| Peak | RetTime | Type | Width | Area  | Height | Area % |
|------|---------|------|-------|-------|--------|--------|
| 1    | 5.658   | MM   | 0.1059| 5751.49756 | 905.02155 | 49.7665 |
| 2    | 6.476   | MM   | 0.1302| 5805.46777 | 743.20251 | 50.2335 |

| Peak | RetTime | Type | Width | Area  | Height | Area % |
|------|---------|------|-------|-------|--------|--------|
| 1    | 5.347   | BB   | 0.0919| 53.98615 | 9.00560 | 2.9777 |
| 2    | 6.092   | BB   | 0.1170| 1759.04346 | 230.46873 | 97.0223 |
HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1 mL/min, \( \lambda = 254 \text{ nm} \)

### Peak RetTime Type Width Area Height Area %

|    | [min] | [min]  | [mAU*s] | [mAU]   |          |
|----|-------|--------|---------|---------|----------|
| 1  | 9.520 | BB     | 0.1775  | 607.15808 | 52.25922  | 49.6695  |
| 2  | 10.834| BB     | 0.2396  | 615.23730 | 39.53337  | 50.3305  |

### Peak RetTime Type Width Area Height Area %

|    | [min] | [min]  | [mAU*s] | [mAU]   |          |
|----|-------|--------|---------|---------|----------|
| 1  | 9.412 | BB     | 0.1512  | 46.55208 | 4.79988  | 6.8057   |
| 2  | 10.382| BB     | 0.1653  | 637.46692 | 59.35485 | 93.1943  |
HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1 mL/min, \( \lambda = 360 \text{ nm} \)

### Peak RetTime Type Width Area Height Area %

| # | [min] | [min] | [mAU*s] | [mAU] | %     |
|---|-------|-------|---------|-------|-------|
| 1 | 13.063| BB    | 0.1990  | 76.99632| 5.94854| 50.6770 |
| 2 | 14.037| MM    | 0.2439  | 74.93908| 5.12061| 49.3230 |

### Peak RetTime Type Width Area Height Area %

| # | [min] | [min] | [mAU*s] | [mAU] | %     |
|---|-------|-------|---------|-------|-------|
| 1 | 12.397| BB    | 0.1963  | 114.91766| 9.04206| 2.8303  |
| 2 | 13.298| MM    | 0.2379  | 3945.33350| 276.42804| 97.1697 |
HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1 mL/min, λ = 360 nm

HPLC Daicel Chiralpak ID-3 column, 20 °C, 100% hexane, flow rate: 1 mL/min, λ = 360 nm
HPLC Daicel Chiralpak ID-3 column, 20 °C, 100% hexane, flow rate: 1 mL/min, $\lambda = 360$ nm
| Peak | RetTime | Type | Width | Area | Height | Area % |
|------|---------|------|-------|------|--------|-------|
| 1    | 21.988  | MM   | 0.6859| 30.71531| 7.46382e-1 | 49.8115 |
| 2    | 23.485  | MM   | 0.7098| 30.94781| 7.26698e-1 | 50.1885 |

| Peak | RetTime | Type | Width | Area | Height | Area % |
|------|---------|------|-------|------|--------|-------|
| 1    | 20.950  | MM   | 0.5163| 370.39713| 11.95617 | 5.1678  |
| 2    | 21.917  | MM   | 0.8421| 6796.98047| 134.51663 | 94.8322 |
Conditions: HPLC Daicel Chiralpak IC-3 column, 20 °C, 98:02 hexane/i-PrOH, flow rate: 1 mL/min, λ = 360 nm
**Conditions:** UPC2 (Daicel Chiralpak AMY1 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, flow rate 2 mL/min, λ = 210 nm)
Conditions: UPC2 (Daicel Chiralpak IE3 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, flow rate 2 mL/min, \( \lambda = 210 \text{ nm} \))
Conditions: UPC2 Daicel Chiralpak IE3 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, flow rate 2 mL/min, $\lambda = 210$ nm.
**Conditions:** UPC2 Daicel Chiralpak IE3 gradient 89:11 CO2:isopropanol over 9 min, flow rate 2 mL/min, \( \lambda = 210 \) nm.
**Conditions:** UPC2 Daicel Chiralpak IE3 isocratic 90:10 CO2:acetonitrile over 9 min, flow rate 2 mL/min, $\lambda = 210$ nm
Conditions: UPC2 Daicel Chiralpak IE3 gradient 100% CO2 for 1 min, then gradient up to 60:40 CO2:acetonitrile over 5 min, flow rate 2 mL/min, $\lambda = 210$ nm