Supporting Information

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1. General Information

Unless noted otherwise, all solvents were dried by filtration through a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Dimethylformamide was then vacuum-distilled freshly over calcium hydride and carefully freeze-pump-thawed. Reaction temperatures were reported as the temperatures of the bather surrounding the flasks or vials. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Sodium acetate was purchased from STREM, stored and used directly in the glovebox. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). Vials (15 x 45 mm 1 dram (4 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried and cooled in a desiccator prior to usage. Mass spectra were recorded on an Agilent 6530 LC Q-TOF mass spectrometer using electrospray ionization with fragmentation voltage set at 115 V and processed with an Agilent MassHunter Operating System. X-ray diffraction data were collected at 100(2) K on a Bruker-Nonius Kappa CCD or Agilent SuperNova AtlasS2 CCD. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film technique. Nuclear magnetic resonance spectra (1H NMR and 13C NMR) were recorded with a Bruker (400 MHz, 1H at 400 MHz, 13C at 101 MHz) or Bruker Model DMX 500 (500 MHz, 1H at 500 MHz, 13C at 126 MHz). Chemical shifts were reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ=0.00 ppm) and were referenced to residual solvent (CDCl3, δ=7.26 ppm (1H) and 77.00 ppm (13C)). All the 19F chemical shifts were not referenced. Coupling constants were reported in Hertz (Hz). Data for 1H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All other materials were obtained from Aldrich Chemical Company or Combi-blocks and were used as received.
2. Experimental Procedures and Characterization Data

2.1 Chiral Resolution of Ester Substituted NBE

\[
\text{NBE-CO}_2\text{H} \quad \text{Cl} = \text{COCl} \\
\text{DMF (cat.)} \quad \text{DCM, 0°C - rt.}
\]

To a solution of NBE-CO$_2$H (700 mg, 5.1 mmol, 1.0 equiv) and 1 drop of DMF in DCM (5 mL) was added oxalyl chloride (648 mg, 5.1 mmol, 1.0 equiv) dropwise at 0 °C.\(^1\) The reaction mixture was stirred at room temperature for another 1 h until the bubbling stopped. To another flame-dried round bottom flask was added sulfonamide (1.65g, 7.65 mmol, 1.5 equiv) and dry toluene (50 mL). Then NaH (3.06g, 76.5 mmol, 15 equiv) was added slowly to the flask and the reaction mixture was stirred at room temperature for another 30 min. After that, the generated acid chloride from the first flask was transferred into the second flask dropwise and the reaction mixture was stirred at room temperature until the reaction was completed. Then the reaction was quenched by 1M HCl and the aqueous lays was extracted by DCM for three times. The combined organic layers were dried over MgSO$_4$. Sulfonamide A and B were isolated via silica gel chromatography as a pair of diastereomers.

A: White solid (666 mg, 39%). R$_f$ = 0.4 (hexane/ethyl acetate = 5:1). Mp = 125.7 – 127.1 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.11 (d, $J = 3.4$ Hz, 1H), 4.06 (dd, $J = 7.7, 4.7$ Hz, 1H), 3.47 (d, $J = 13.6$ Hz, 1H), 3.37 (d, $J = 13.7$ Hz, 2H), 3.03 (s, 1H), 2.03 (dd, $J = 13.7, 7.7$ Hz, 1H), 1.99 – 1.84 (m, 4H), 1.79 – 1.65 (m, 2H), 1.61 (dt, $J = 8.6, 2.2$ Hz, 1H), 1.45 – 1.24 (m, 5H), 1.21 (s, 3H), 0.98 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.30, 148.53, 141.13, 65.84, 53.81, 49.80, 47.96, 47.82, 45.28, 43.72, 43.08, 38.49, 33.34, 26.65, 24.21, 24.03, 21.36, 20.06. IR (KBr): $\nu$ 2960,
2874, 1671, 1590, 1332, 1286, 1172, 1140, 754, 536 cm$^{-1}$. **HRMS** (ESI): Calculated for C$_{18}$H$_{26}$NO$_3$S (M+H$^+$): 336.1628, found: 336.1631.

**B**: White solid (652 mg, 38%) R$_f$ = 0.3 (hexane/ethyl acetate = 5:1). Mp = 169.2 – 170.0 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.91 (d, $J = 3.2$ Hz, 1H), 4.04 (dd, $J = 7.7$, 4.7 Hz, 1H), 3.49 (d, $J = 13.6$ Hz, 1H), 3.39 (d, $J = 13.6$ Hz, 1H), 3.23 (s, 1H), 3.08 (s, 1H), 2.05 – 1.91 (m, 3H), 1.90 – 1.83 (m, 2H), 1.76 (ttd, $J = 12.8$, 9.4, 3.6 Hz, 2H), 1.56 (dt, $J = 8.8$, 2.2 Hz, 1H), 1.41 (ddd, $J = 10.9$, 9.1, 2.3 Hz, 1H), 1.37 (s, 1H), 1.21 (s, 4H), 1.19 – 1.12 (m, 1H), 1.11 – 1.05 (m, 1H), 0.98 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.12, 148.31, 142.38, 65.78, 53.74, 48.07, 47.81, 46.72, 45.36, 44.34, 43.99, 38.65, 33.34, 26.64, 25.24, 25.20, 21.44, 20.05. IR (KBr): $\nu$ 2962, 2876, 1668, 1586, 1334, 1288, 1139, 1054, 748, 536 cm$^{-1}$. **HRMS** (ESI): Calculated for C$_{18}$H$_{26}$NO$_3$S (M+H$^+$): 336.1628, found: 336.1632.

### 2.2 General Procedure for Synthesis of Chiral NBEs

![Diagram](image)

To a solution (18 mL, H$_2$O/THF = 1:2) of sulfonamide (565 mg, 1.69 mmol, 1.0 equiv) was added LiOH • H$_2$O (354 mg, 8.42 mmol, 5.0 equiv). The reaction was stirred at 60 °C for 48 h until the reaction mixture became clear. Then the aqueous layer was washed by diethyl ether for two times and then acidified by 1 M hydrochloric acid until pH < 7. Then the reaction mixture was extracted by dichloromethane for three times and the combined organic layers were dried over MgSO$_4$. The solvent was removed under vacuum to afford the chiral NBE-CO$_2$H as a colorless oil, which was used directly in the next step without further purification.
To a solution of NBE-CO₂H (276 mg, 2.0 mmol, 1.0 equiv) in DCM (2 mL) with 1 drop of DMF was added oxalyl chloride (254 mg, 2.0 mmol, 1.0 equiv) dropwise at 0 °C. The reaction mixture was stirred at room temperature for another 1 h until the bubbling stopped. Then a mixture of the corresponding alcohol (6.0 mmol, 3.0 equiv) and pyridine (949.2 mg, 12.0 mmol, 6.0 equiv) was added dropwise and the reaction mixture was stirred at room temperature for another 3 h until the reaction was completed. The organic layer was washed with 1 M hydrochloric acid and then concentrated under vacuum. The corresponding ester substituted NBE was isolated by silica gel chromatography (hexane/Et₂O = 20:1) as a colorless oil.

N1*: Colorless oil (151 mg, 42%). Rᵣ = 0.6 (hexane/ethyl acetate = 20:1). ¹H NMR (500 MHz, CDCl₃) δ 6.88 (d, J = 3.2 Hz, 1H), 5.05 (hept, J = 6.1 Hz, 1H), 3.24 (s, 1H), 3.00 (s, 1H), 1.74 (th, J = 13.0, 3.3 Hz, 2H), 1.52 – 1.43 (m, 1H), 1.26 (dd, J = 6.3, 4.1 Hz, 6H), 1.18 (d, J = 8.7 Hz, 1H), 1.07 (dt, J = 7.4, 2.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 164.7, 146.4, 141.6, 67.3, 48.3, 43.6, 42.0, 24.8, 24.7, 22.1. IR (KBr): ν 2978, 2874, 1707, 1279, 1259, 1163, 1110, 1076, 753 cm⁻¹. HRMS (ESI): Calculated for C₁₁H₁₇O₂ (M+H⁺): 181.1223, found: 181.1219. Chiral HPLC (Chiralpak IC, hexane/isopropanol = 98:2, 0.5 mL/min, 230 nm): tminster = 12.308 min, tmajor = 12.778. [α]D = -139.6 (c = 0.53, dichloromethane, 21.0 °C) at 98% ee.

Racemic N1
Enantiomeric N1* 

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\text{N}^2: \text{Colorless oil (47%). } R_f = 0.5 \text{ (hexane/ethyl acetate = 20:1). }^1 H \text{ NMR (500 MHz, CDCl}_3\text{) } \delta 7.26 \text{ (d, } J = 3.1 \text{ Hz, 1H), 4.53 (q, } J = 7.0 \text{ Hz, 2H), 3.61 (s, 1H), 3.36 (s, 1H), 2.09 (dtt, } J = 15.1, 11.6, 7.6 \text{ Hz, 2H), 1.83 (d, } J = 8.5 \text{ Hz, 1H), 1.64 (t, } J = 7.1 \text{ Hz, 3H), 1.54 (d, } J = 8.6 \text{ Hz, 1H), 1.44 (tdt, } J = 7.6, 5.1, 2.3 \text{ Hz, 2H). }^13 C \text{ NMR (101 MHz, CDCl}_3\text{)}
\]
CDCl₃) δ 165.1, 146.8, 141.2, 60.2, 48.3, 43.6, 42.0, 24.8, 24.6, 14.5. IR (KBr): ν 2977, 2874, 1712, 1596, 1370, 1341, 1278, 1258, 1160, 1079, 753 cm⁻¹. HRMS (ESI): Calculated for C₁₀H₁₅O₂ (M+H⁺): 167.1067, found: 167.1061. [α]₀ = 155.6 (c = 0.32, dichloromethane, 22.0 °C).

N₃*: White solid (48%). Rₛ = 0.6 (hexane/ethyl acetate = 20:1). Mp = 52.0 – 54.0 °C. ¹H NMR (500 MHz, CDCl₃) δ 6.79 (d, J = 3.1 Hz, 1H), 3.19 (s, 1H), 2.98 (s, 1H), 1.78 – 1.68 (m, 2H), 1.48 (s, 10H), 1.16 (d, J = 8.5 Hz, 1H), 1.07 (qd, J = 8.5, 2.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 164.6, 145.6, 142.8, 80.0, 48.3, 43.5, 42.0, 28.4, 24.9, 24.7. IR (KBr): ν 2976, 2873, 1702, 1596, 1284, 1260, 1154, 1077, 756 cm⁻¹. HRMS (ESI): Calculated for C₁₂H₁₈O₂Na (M+Na⁺): 217.1199, found: 217.1184. [α]₀ = 148.9 (c = 0.91, dichloromethane, 22.0 °C).

N₄*: Colorless oil (50%, dr = 1:1). Rₛ = 0.5 (hexane/ethyl acetate = 20:1). ¹H NMR (500 MHz, CDCl₃) δ 6.89 (dd, J = 6.6, 3.2 Hz, 1H), 4.88 (h, J = 6.1, 5.7 Hz, 1H), 3.24 (s, 1H), 3.00 (s, 1H), 1.74 (tt, J = 9.6, 1.9 Hz, 2H), 1.68 – 1.60 (m, 1H), 1.48 (d, J = 8.5 Hz, 1H), 1.23 (dd, J = 6.3, 5.2 Hz, 4H), 1.20 – 1.16 (m, 1H), 1.11 – 1.04 (m, 2H), 0.90 (td, J = 7.5, 5.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.86, 164.83, 146.83, 146.45, 146.31, 141.64, 141.59, 71.85, 71.82, 48.28, 48.23, 43.57, 43.55, 42.04, 42.01, 29.08, 29.05, 24.83, 24.80, 24.67, 19.73, 19.67, 9.86, 9.85. IR (KBr): ν 2974, 1708, 1596, 1449, 1364, 1337, 1278, 1257, 1162, 933, 752 cm⁻¹. HRMS (ESI): Calculated for C₁₂H₁₉O₂ (M+H⁺): 195.1380, found: 195.1370. [α]₀ = -133.3 (c = 0.95, dichloromethane, 21.8 °C).
N5*: White solid (45%). \( R_f = 0.5 \) (hexane/ethyl acetate = 20:1). \( \text{Mp} = 60.2 - 60.8 \, ^\circ\text{C} \). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 6.79 (d, \( J = 3.2 \) Hz, 1H), 5.14 (dq, \( J = 6.0, 3.1 \) Hz, 1H), 3.16 (s, 1H), 2.92 (s, 1H), 1.80 (dtd, \( J = 12.5, 6.6, 6.0, 3.0 \) Hz, 2H), 1.71 – 1.60 (m, 6H), 1.58 – 1.47 (m, 2H), 1.40 (dt, \( J = 8.6, 2.1 \) Hz, 1H), 1.11 (d, \( J = 8.5 \) Hz, 1H), 1.04 – 0.96 (m, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 164.9, 146.3, 141.6, 76.6, 48.2, 43.5, 42.0, 32.9, 32.8, 24.8, 24.6, 23.91, 23.90. IR (KBr): \( \nu \) 2871, 1703, 1593, 1449, 1369, 1341, 1277, 1217, 1116, 1078, 879, 753 cm\(^{-1}\). HRMS (ESI): Calculated for \( \text{C}_{13}\text{H}_{19}\text{O}_2 \) (M+H\(^+\)): 207.1380, found: 207.1374. \([\alpha]_D = -130.1 \) (c = 0.99, dichloromethane, 22.0 \( ^\circ\text{C} \)).

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\text{NBE-CO}_2\text{H} \quad (138 \text{ mg, 1.0 mmol, 1.0 equiv), amine (1.1 mmol, 1.1 equiv), 1-ethyl-3-(3-}
\text{dimethylaminopropyl)carbodiimide hydrochloride (230 mg, 1.2 mmol, 1.2 equiv) and 4-dimethylaminopyridine}
\text{(12.2 mg, 0.1 mmol, 10 mol%) were dissolved in dichloromethane (5 mL). The reaction mixture was stirred at}
\text{room}
\text{temperature overnight. Then it was diluted with diethyl ether, washed with water and brine, dried over MgSO}_4
\text{, and}
\text{purified on silica gel chromatography (hexanes/ethyl acetate = 2:1) to afford the corresponding amide-derived}
\text{norbornene N7* and N8*.}
\]

N7*: Colorless oil (49%). \( R_f = 0.3 \) (hexane/ethyl acetate = 2:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.30 (d, \( J = 3.1 \) Hz, 1H), 3.65 – 3.33 (m, 4H), 3.26 (s, 1H), 2.99 (s, 1H), 1.99 – 1.76 (m, 4H), 1.71 (d, \( J = 6.0 \) Hz, 2H), 1.37 (d, \( J = 8.3 \) Hz, 1H), 1.29 – 1.20 (m, 1H), 1.15 – 1.00 (m, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 165.9, 144.4, 139.4, 48.4, 47.1, 46.3, 44.3, 43.8, 26.6, 25.3, 25.2, 24.2. IR (KBr): \( \nu \) 2968, 2871, 1722, 1612, 1577, 1426, 1341, 1311, 1166, 875, 748 cm\(^{-1}\). HRMS (ESI): Calculated for \( \text{C}_{12}\text{H}_{18}\text{NO} \) (M+H\(^+\)): 192.1383, found: 192.1374. \([\alpha]_D = 76.9 \) (c = 1.27, dichloromethane, 21.6 \( ^\circ\text{C} \)).
N8*: Colorless oil (50%). Rf = 0.3 (hexane/ethyl acetate = 2:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 6.10\) (d, \(J = 3.1\) Hz, 1H), 3.54 – 3.39 (m, 2H), 3.31 (dq, \(J = 14.1, 7.1\) Hz, 2H), 3.12 (s, 1H), 2.97 (s, 1H), 1.76 – 1.66 (m, 2H), 1.44 – 1.33 (m, 2H), 1.13 (t, \(J = 7.1\) Hz, 8H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 168.6, 143.2, 135.8, 47.4, 45.5, 43.5, 42.7, 39.4, 25.5, 25.4, 14.8, 13.0\). IR (KBr): \(\nu 2971, 2872, 1620, 1585, 1427, 1379, 1285, 1150, 1064, 812, 743\) cm\(^{-1}\). HRMS (ESI): Calculated for C\(_{12}\)H\(_{20}\)NO (M+H\(^+\)): 194.1539, found: 194.1535. [\(\alpha\)]\(_D\) = 125.7 (c = 0.97, dichloromethane, 22.0 °C).

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\text{To a solution of NBE-CO}_2\text{H (138 mg, 1.0 mmol, 1.0 equiv) in DCM (1 mL) with 1 drop of DMF was added oxalyl chloride (152 mg, 1.2 mmol, 1.2 equiv) dropwise at 0 °C. The reaction mixture was stirred at room temperature for another 1 h until the bubbling stopped. To another flame-dried round bottom flask was added 2-oxazolidinone (95.8 mg, 1.1 mmol, 1.1 equiv) and dry THF (10 mL). Then, \(n\)BuLi (0.81 mL, 1.6 M in hexane, 1.3 mmol, 1.3 equiv) was added dropwise to the flask at -78 °C and the reaction mixture was stirred at -78 °C for another 30 min. After that, the generated acyl chloride from the first flask was transferred into the second flask dropwise using dry THF. Then the reaction mixture was warmed to room temperature slowly and stirred for another 2 h. The reaction was quenched by 5 mL H\(_2\)O and the aqueous layers was extracted by ethyl acetate for three times. The combined organic layers were dried over MgSO\(_4\) and then purified by silica gel chromatography to afford N9*.}
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S9
N9*: White solid (48%). Rf = 0.2 (hexane/ethyl acetate = 2:1). Mp = 85.4 – 87.9 °C. \( ^1H \text{ NMR} \) (400 MHz, CDCl₃) δ 6.83 (d, \( J = 3.3 \) Hz, 1H), 4.41 – 4.27 (m, 2H), 4.02 (ddd, \( J = 10.9, 9.0, 7.9 \) Hz, 1H), 3.91 (ddd, \( J = 10.8, 8.6, 5.9 \) Hz, 1H), 3.21 (s, 1H), 3.03 (s, 1H), 1.76 – 1.64 (m, 2H), 1.55 (dt, \( J = 8.6, 2.1 \) Hz, 1H), 1.20 – 1.00 (m, 3H). \( ^{13}C \text{ NMR} \) (101 MHz, CDCl₃) δ 165.7, 153.3, 148.3, 140.1, 62.2, 47.3, 44.2, 44.0, 43.6, 25.10, 25.06. IR (KBr): \( \nu \) 2971, 2872, 1783, 1664, 1587, 1478, 1383, 1301, 1199, 1115, 1080, 1039, 987, 746, 698 cm\(^{-1}\). HRMS (ESI): Calculated for C₁₁H₁₄NO₃ (M+H⁺): 208.0968, found: 208.0966. \([\alpha]_D = -65.9 \) (c = 0.97, dichloromethane, 22.0 °C).

\[ \text{Image} \]

N10*: White solid (63%). Rf = 0.2 (hexane/ethyl acetate = 2:1). Mp = 105.9 – 107.2 °C. \( ^1H \text{ NMR} \) (400 MHz, CDCl₃) δ 7.33 – 7.27 (m, 3H), 7.19 – 7.13 (m, 2H), 6.89 (d, \( J = 3.0 \) Hz, 1H), 4.80 (tdd, \( J = 8.7, 5.1, 3.6 \) Hz, 1H), 4.25 (t, \( J = 8.6 \) Hz, 1H), 4.13 (dd, \( J = 8.9, 5.2 \) Hz, 1H), 3.32 – 3.21 (m, 2H), 3.11 (s, 1H), 2.83 (dd, \( J = 13.5, 8.9 \) Hz, 1H), 1.86 – 1.73 (m, 2H), 1.61 (dq, \( J = 6.4, 2.1 \) Hz, 1H), 1.28 – 1.18 (m, 2H), 1.17 – 1.10 (m, 1H). \( ^{13}C \text{ NMR} \) (101 MHz, CDCl₃) δ 166.0, 153.4, 148.9, 140.7, 135.4, 129.6, 129.0, 127.4, 66.3, 55.5, 47.1, 44.3, 44.0, 38.0, 25.3, 25.3. IR (KBr): \( \nu \) 2972, 2872, 1785, 1660, 1497, 1453, 1348, 1290, 1212, 1114, 746, 702 cm\(^{-1}\). HRMS (ESI): Calculated for C₁₈H₂₀NO₃ (M+H⁺): 298.1438, found: 298.1439. \([\alpha]_D = -7.5 \) (c = 0.99, dichloromethane, 22.0 °C).

\[ \text{Image} \]

N11*: White solid (47%). Rf = 0.2 (hexane/ethyl acetate = 2:1). Mp = 92.4 – 93.1 °C. \( ^1H \text{ NMR} \) (400 MHz, CDCl₃) δ 7.36 – 7.30 (m, 2H), 7.30 – 7.25 (m, 1H), 7.24 – 7.20 (m, 2H), 6.86 (d, \( J = 3.2 \) Hz, 1H), 4.64 (ddt, \( J = 9.6, 7.3, 3.6 \) Hz, 1H), 4.24 – 4.11 (m, 2H), 3.40 (dd, \( J = 13.4, 3.3 \) Hz, 1H), 3.32 (s, 1H), 3.09 (s, 1H), 2.80 (dd, \( J = 13.4, 9.6 \) Hz, 1H), 1.85 – 1.73 (m, 2H), 1.68 (dt, \( J = 8.6, 2.1 \) Hz, 1H), 1.28 – 1.10 (m, 3H). \( ^{13}C \text{ NMR} \) (101 MHz, CDCl₃) δ 165.7, 153.3, 147.6, 140.6, 135.6, 129.6, 129.0, 127.4, 66.3, 56.4, 47.7, 44.2, 44.1, 37.6, 25.1, 25.0. IR (KBr): \( \nu \) 2973, 1785.
1659, 1453, 1350, 1293, 1211, 1114, 1084, 745, 702 cm\(^{-1}\). **HRMS** (ESI): Calculated for C\(_{18}H_{20}NO_3\) (M+H\(^+\)):
298.1438, found: 298.1441. \([\alpha]_D = -128.7\) (c = 0.97, dichloromethane, 22.0 °C).

**N12\(^*\)**: White solid (61%). \(R_f = 0.3\) (hexane/ethyl acetate = 2:1). Mp = 84.1 – 86.2 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 6.88 (dt, \(J = 3.4, 1.0\) Hz, 1H), 4.56 (dt, \(J = 9.0, 4.7\) Hz, 1H), 4.30 (t, \(J = 8.9\) Hz, 1H), 4.15 (dd, \(J = 9.0, 4.9\) Hz, 1H), 3.24 (s, 1H), 3.09 (s, 1H), 2.27 (pd, \(J = 7.0, 4.4\) Hz, 1H), 1.83 – 1.70 (m, 2H), 1.60 (dt, \(J = 8.6, 2.1\) Hz, 1H), 1.22 – 1.15 (m, 2H), 1.12 – 1.05 (m, 1H), 0.87 (dd, \(J = 9.7, 7.0\) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 166.1, 153.9, 148.6, 140.9, 63.5, 58.4, 46.9, 44.4, 44.0, 28.8, 25.4, 25.3, 17.9, 15.2. IR (KBr): \(\nu\) 2965, 2873, 1783, 1665, 1587, 1485, 1388, 1363, 1289, 1203, 864, 764, 745 cm\(^{-1}\). **HRMS** (ESI): Calculated for C\(_{14}H_{20}NO_3\) (M+H\(^+\)): 250.1438, found: 250.1433. \([\alpha]_D = 37.2\) (c = 1.13, dichloromethane, 22.0 °C).

**N13\(^*\)**: White solid (54%). \(R_f = 0.3\) (hexane/ethyl acetate = 2:1). Mp = 85.5 – 89.4 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 6.81 (d, \(J = 3.3\) Hz, 1H), 4.45 (dt, \(J = 8.6, 4.3\) Hz, 1H), 4.28 (t, \(J = 8.7\) Hz, 1H), 4.17 (dd, \(J = 8.9, 4.5\) Hz, 1H), 3.28 (s, 1H), 3.05 (s, 1H), 2.42 (pd, \(J = 7.0, 4.1\) Hz, 1H), 1.82 – 1.66 (m, 3H), 1.24 (dd, \(J = 8.6, 1.1\) Hz, 1H), 1.19 – 1.11 (m, 2H), 0.90 (dd, \(J = 8.2, 7.0\) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 165.6, 154.0, 146.8, 141.1, 63.5, 59.0, 48.3, 44.2, 43.8, 28.4, 24.9, 24.8, 18.0, 15.0. IR (KBr): \(\nu\) 2965, 2672, 1783, 1672, 1589, 1465, 1387, 1341, 1293, 1201, 1079, 888, 766, 744 cm\(^{-1}\). **HRMS** (ESI): Calculated for C\(_{14}H_{20}NO_3\) (M+H\(^+\)): 250.1438, found: 250.1429. \([\alpha]_D = 132.5\) (c = 1.02, dichloromethane, 22.0 °C).

### 2.3 Enantioselective Transformation Using Chiral NBE-CO\(_2\)Pr (N1\(^*\))
A flame-dried 4.0 mL vial was charged with aryl iodide 1a (43.6 mg, 0.2 mmol, 1.0 equiv), NaOAc (24.6 mg, 0.3 mmol, 1.5 equiv) and RuPhos-Pd-G4 (8.5 mg, 0.01 mmol, 5 mol%). Then the vial was directly transferred into a nitrogen-filled glovebox without caps. After enantiomeric NBE-CO\textsubscript{2}iPr N1\textsuperscript{*} (7.2 mg, 0.04 mmol, 20 mol%) and 1,2-epoxyhexane (80 mg, 0.8 mmol, 4.0 equiv) was added to the vial, 2 mL of degassed DMF was added. Then the vial was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 120 °C for 24 hours. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with dichloromethane and diethyl ether, and the combined filtrate was concentrated. The residue was absorbed onto a small amount of silica gel and then purified by flash column chromatography on silica gel to give the desired product.

3aa\textsuperscript{*}: Pale yellow oil (68%). R\textsubscript{f} = 0.4 (hexane/ethyl acetate = 40:1). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.00 (d, \(J = 6.9\) Hz, 1H), 6.93 (ddq, \(J = 7.5, 1.5, 0.8\) Hz, 1H), 6.74 (t, \(J = 7.4\) Hz, 1H), 4.76 (dddd, \(J = 8.9, 7.8, 6.9, 6.2\) Hz, 1H), 3.28 (dd, \(J = 15.4, 8.9\) Hz, 1H), 2.86 (dd, \(J = 15.4, 7.8\) Hz, 1H), 2.22 (s, 3H), 1.93 – 1.79 (m, 1H), 1.73 – 1.62 (m, 1H), 1.55 – 1.34 (m, 4H), 0.95 (t, \(J = 7.1\) Hz, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 158.2, 129.2, 126.3, 122.4, 120.0, 119.6, 83.1, 36.0, 35.9, 27.7, 22.8, 15.4, 14.2. IR (KBr): \(\nu\) 3025, 2956, 2931, 2859, 1599, 1467, 1260, 759 cm\textsuperscript{-1}. HRMS (ESI): Calculated for C\textsubscript{13}H\textsubscript{19}O (M+H\textsuperscript{+}): 191.1430, found: 191.1428. Chiral HPLC (Chiralpak OD-H, hexane/isopropanol = 99:1, 0.5 mL/min, 230 nm): t\textsubscript{minor} = 11.161, t\textsubscript{major} = 10.094. 42% ee.

**Racemic 3aa**
Enantiomeric 3aa*
3ba*: Pale yellow oil (54%). \( R_f = 0.2 \) (hexane/ethyl acetate = 40:1). \(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.70 – 7.65 (m, 2H), 4.89 – 4.78 (m, 1H), 3.85 (s, 3H), 3.28 (dd, \( J = 15.5, 9.0 \) Hz, 1H), 2.85 (dd, \( J = 15.5, 7.7 \) Hz, 1H), 2.21 (s, 3H), 1.90 – 1.78 (m, 1H), 1.74 – 1.62 (m, 1H), 1.54 – 1.32 (m, 4H), 0.93 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \) 167.4, 162.4, 131.9, 126.6, 124.4, 122.2, 119.3, 84.4, 51.8, 36.0, 35.3, 27.6, 22.7, 15.3, 14.1. \( \text{IR (KBr): } \nu \) 2954, 2860, 1715, 1607, 1434, 1306, 1161, 954, 771 cm\(^{-1}\). \( \text{HRMS (ESI): Calculated for C}_{15}\text{H}_{21}\text{O}_{3} \) (M+H\(^{+}\)): 249.1485, found: 249.1492. \( \text{Chiral HPLC (Chiralpak OD-H, hexane/isopropanol = 99:1, 0.5 mL/min, 260 nm): } t_{\text{minor}} = 21.892, t_{\text{major}} = 14.268. \) 31% ee.

**Racemic 3ba**

**Enantiomeric 3ba**
3ab*: White solid (92%). Rf = 0.3 (hexane/ethyl acetate = 40:1). Mp = 77.8 – 78.6 °C. \textbf{\textit{1H NMR}} (400 MHz, CDCl$_3$) δ 7.35 – 7.25 (m, 2H), 7.04 (ddd, $J$ = 7.3, 1.4, 0.7 Hz, 1H), 7.03 – 6.91 (m, 4H), 6.79 (t, $J$ = 7.4 Hz, 1H), 5.15 (dddd, $J$ = 9.4, 7.0, 5.9, 5.3 Hz, 1H), 4.24 (dd, $J$ = 9.9, 5.9 Hz, 1H), 4.10 (dd, $J$ = 9.9, 5.3 Hz, 1H), 3.40 (ddd, $J$ = 15.7, 9.4 Hz, 1H), 3.17 (dd, $J$ = 15.7, 7.1 Hz, 1H), 2.23 (s, 3H). \textbf{\textit{13C NMR}} (101 MHz, CDCl$_3$) δ 158.8, 157.9, 129.6, 129.5, 125.4, 122.5, 121.2, 120.6, 120.0, 114.8, 80.2, 69.9, 32.9, 15.4. \textbf{\textit{IR}} (KBr): υ 3040, 2920, 2857, 1599, 1497, 1468, 1243, 1193, 1050, 754, 691 cm$^{-1}$. \textbf{HRMS} (ESI): Calculated for C$_{16}$H$_{17}$O$_2$ (M+H$^+$): 241.1223, found: 241.1221. 

\textbf{Chiral HPLC} (Chiralpak OD-H, hexane/isopropanol = 98:2, 0.5 mL/min, 230 nm): $t_{\text{minor}}$ = 23.912, $t_{\text{major}}$ = 34.968. 38% ee.

\textbf{Racemic 3ab}
Enantiomeric 3ab*

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Totals: 5819.32446 119.00621

3ac*: Yellow oil (78%). Rf = 0.2 (hexane/ethyl acetate = 40:1). $^1$H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 1.8, 0.9 Hz, 1H), 7.00 (d, J = 7.0 Hz, 1H), 6.94 (ddq, J = 7.5, 1.5, 0.8 Hz, 1H), 6.76 (t, J = 7.4 Hz, 1H), 6.38 – 6.32 (m, 2H), 4.94 (dddd, J = 9.4, 7.5, 6.3, 4.8 Hz, 1H), 4.65 – 4.52 (m, 2H), 3.73 (dd, J = 10.4, 6.3 Hz, 1H), 3.64 (dd, J = 10.4, 4.8 Hz, 1H), 3.26 (dd, J = 15.6, 9.4 Hz, 1H), 3.00 (dd, J = 15.6, 7.5 Hz, 1H), 2.23 (d, J = 0.6 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl₃) δ 158.0, 151.7, 143.0, 129.3, 125.6, 122.4, 120.4, 119.8, 110.4, 109.6, 81.2, 72.1, 65.4, 32.8, 15.4. IR (KBr): ν 3119, 3049, 2919, 2857, 1599, 1468, 1261, 1194, 1151, 1073, 920, 758, 600 cm⁻¹. HRMS (ESI):
Calculated for C15H17O3 (M+H⁺): 245.1172, found: 245.1174. **Chiral HPLC** (Chiralpak OD-H, hexane/isopropanol = 95:5, 0.5 mL/min, 230 nm): $t_{\text{minor}} = 27.530$, $t_{\text{major}} = 44.530$. 34% ee.

**Racemic 3ac**

![Chiral HPLC graph for racemic 3ac](image)

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**Totals:**

2.35776e4 370.92505

**Enantiomeric 3ac⁺**

![Chiral HPLC graph for enantiomeric 3ac⁺](image)
2.4 Matched/Mismatched Experiments for the Stereochemistry of NBE and Epoxide

A flame-dried 4.0 mL vial was charged with aryl iodide 1a (21.8 mg, 0.1 mmol, 1.0 equiv), NaOAc (12.3 mg, 0.15 mmol, 1.5 equiv) and RuPhos-Pd-G4 (8.5 mg, 0.01 mmol, 10 mol%). Then the vial was directly transferred into a nitrogen-filled glovebox without caps. After (+) or (−) NBE-CO$_2$iPr N1* (3.6 mg, 0.02 mmol, 20 mol%) and chiral epoxide (S)-2b (60 mg, 0.4 mmol, 4.0 equiv) were transferred to the vial, 1 mL of degassed DMF was added. Then the vial was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 120 °C. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with dichloromethane and diethyl ether, and the combined filtrate was concentrated. The residue was absorbed onto a small amount of silica gel and then purified by flash column chromatography on silica gel to give the desired product.
3. NMR Spectra
4. Crystallographic Data

Empirical formula \( \text{C}_{18}\text{H}_{25}\text{NO}_{3}\text{S} \)

Formula weight \( 335.45 \)

Temperature \( 100(2) \text{ K} \)

Wavelength \( 0.71073 \text{ Å} \)

Crystal system orthorhombic

Space group \( \text{P} \text{ 21 21 21} \)

Unit cell dimensions
\[ a = 7.8259(6) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 9.5135(8) \text{ Å} \quad \beta = 90^\circ. \]
\[ c = 22.6470(18) \text{ Å} \quad \gamma = 90^\circ. \]

Volume \( 1686.1(2) \text{ Å}^3 \)

\( Z \)

Density (calculated) \( 1.321 \text{ Mg/m}^3 \)

Absorption coefficient \( 0.207 \text{ mm}^{-1} \)

\( F(000) \)

Crystal size \( 0.510 \times 0.380 \times 0.320 \text{ mm}^3 \)

Theta range for data collection \( 2.754 \text{ to } 30.819^\circ. \)

Index ranges \(-11 \leq h \leq 11, -13 \leq k \leq 13, -32 \leq l \leq 32 \)

Reflections collected \( 60626 \)

Independent reflections \( 5259 [R(int) = 0.0409] \)

Completeness to theta = \( 25.242^\circ \) \( 99.9\% \)

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 1.00 and 0.912

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters \( 5259 / 0 / 214 \)

Goodness-of-fit on \( F^2 \) \( 1.044 \)

Final R indices \( [I>2\sigma(I)] \) \( R_1 = 0.0304, wR_2 = 0.0758 \)

R indices (all data) \( R_1 = 0.0350, wR_2 = 0.0771 \)

Absolute structure parameter \( 0.039(12) \)

Extinction coefficient n/a

Largest diff. peak and hole \( 0.295 \text{ and } -0.406 \text{ e.Å}^{-3} \)
Identification code LRH 2-21-2
Empirical formula C_{18}H_{25}NO_{3}S
Formula weight 335.45
Temperature/K 100.0
Crystal system monoclinic
Space group P2_1
a/Å 7.9608(8)
b/Å 9.0050(9)
c/Å 11.9856(12)
α/° 90
β/° 105.827(2)
γ/° 90
Volume/Å³ 826.64(14)
Z 2
ρ_{calc}/g/cm³ 1.348
μ/mm⁻¹ 0.211
F(000) 360.0
Crystal size/mm³ 0.1 × 0.06 × 0.05
Radiation MoKα (λ = 0.71073)
2Θ range for data collection/° 5.318 to 54.998
Index ranges -10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -15 ≤ l ≤ 14
Reflections collected 12941
Independent reflections 3792 [R_{int} = 0.0422, R_{sigma} = 0.0432]
Data/restraints/parameters 3792/1/210
Goodness-of-fit on F² 1.053
Final R indexes [I>=2σ (I)] R₁ = 0.0393, wR₂ = 0.0827
Final R indexes [all data] R₁ = 0.0478, wR₂ = 0.0864
Largest diff. peak/hole / e Å⁻³ 0.30/-0.27
Flack parameter 0.02(3)
5. Reference