Supplementary Information:

Enantioselective iridium-catalyzed hydrogenation of β,β-disubstituted nitroalkenes

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S1
General Information. Unless otherwise noted, all reactions and manipulations were performed in an argon-filled glovebox (VAC DRI-LAB HE 493) or using standard Schlenk techniques. Melting points were measured on a RY-I apparatus and uncorrected. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz ($^1$H NMR), 100 MHz ($^{13}$C NMR) and 162 MHz ($^{31}$P NMR) in CDCl$_3$. Chemical shifts were reported in ppm down field from internal Me$_4$Si and external 85% H$_3$PO$_4$, respectively. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. HRMS were recorded on IonSpec FT-ICR mass spectrometer with ESI or MALDI resource. Enantiomeric excesses of the asymmetric hydrogenation products were determined by chiral GC, HPLC or SFC. GC analyses were performed using a Hewlett Packard Model HP 6890 Series instruments. HPLC analyses were performed using a Hewlett Packard Model HP 1100 instruments. SFC analyses were performed using a Mettler-Toledo Model Analytix SFC. Anhydrous THF and toluene were distilled from sodium benzophenone ketyl, anhydrous CH$_2$Cl$_2$, NEt$_3$ and DCE were freshly distilled from calcium hydride under nitrogen atmosphere. Absolute MeOH were distilled from magnesium under nitrogen atmosphere. Hydrogen gas (99.999%) was purchased from Boc Gas Inc., Tianjin.
1. Preparation and Analytical Data of Iridium/SprioBAPs Complexes

(R)-(7'-(diphenylphosphanyl)-1,1'-spirobiinane-7-yl)propan-2-amine [(R)-6g]¹

A suspension of CeCl₃ (369 mg, 1.5 mmol) in THF (2 mL) in a dry Schlenk tube was stirred at 25 °C for 1 h. MeLi (0.5 mL of a 3 M solution in CH₂Cl₂, 1.5 mmol) was added to the above suspension and cooled with a dry ice/acetone bath and stirred for 1 h. A solution of (R)-5g² (86 mg, 0.2 mmol) in THF (2 mL) was added to the resulting mixture and stirred at −40 °C for 6 h. The reaction was quenched with 2N NaOH (1 mL) at −40 °C, spontaneously warmed to room temperature, and then filtered with a Celite. The solids were washed several times with CH₂Cl₂, and the aqueous layer of the filtrates was extracted twice with CH₂Cl₂. The combined organic phases were dried and concentrated. After removal of solvent under reduced pressure, the residue was chromatographed on a silica gel column with petroleum ether/ethyl acetate (20:1 in volume) and 1% Et₃N as additive to afford (R)-6g (44 mg, 48%) as a white solid. mp: 169 – 171 °C. [α]D³⁰ +152 (c 1.0, CH₂Cl₂).¹ ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.19 (m, 8H, Ar-H), 7.15 – 7.06 (m, 6H, Ar-H), 7.04 – 6.98 (m, 2H, Ar-H), 3.08 – 3.05 (m, 2H, CH₂), 2.97 – 2.88 (m, 1H, CH₂), 2.83 – 2.70 (m, 2H, CH₂), 2.32 – 2.26 (m, 1H, CH₂), 2.12 – 2.00 (m, 2H, CH₂), 1.60 (brs, 2H, NH₂), 1.24 (s, 3H, CH₃), 1.14 (s, 3H, CH₃). ³¹P NMR (162 MHz, CDCl₃) δ −20.2 (s). ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 159.3, 147.33, 147.30, 146.40, 146.38, 145.0, 144.9, 142.6, 142.5, 138.9, 138.7, 137.0, 136.8, 134.14, 134.12, 134.0, 133.8, 133.7, 133.5, 131.5, 131.3, 128.34, 128.28, 128.2, 128.09, 128.07, 128.0, 127.7, 126.7, 126.4, 125.9, 122.5, 64.64, 64.60, 55.3, 40.9, 40.9, 39.7, 35.6, 35.0, 31.1, 30.4. HRMS (MALDI) calcd for [C₃₁H₂₉NP, M–CH₃]⁺: 446.2032, Found 446.2116.
(R)-(7'-di(3,5-tert-butylphenyl)-phosphion)-1,1'-spirobiinane-7-yl)propan-2-amine [(R)-6d]

White solid, mp: 75 – 77 °C. [α]D²⁹ +102 (c 1.5, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.13 (m, 4H, Ar-H), 7.08 – 7.02 (m, 4H, Ar-H), 6.92 – 6.90 (m, 2H, Ar-H), 6.70 – 6.68 (m, 2H, Ar-H), 3.06 – 3.04 (m, 2H, CH₂), 2.97–2.84 (m, 2H, CH₂), 2.75 – 2.67 (m, 1H, CH₂), 2.30 – 2.19 (m, 2H, CH₂), 2.12 – 2.08 (m, 1H, CH₂), 1.18 (s, 3H, CH₃), 1.16 (s, 20H, CH₃ and NH₂), 1.12 (s, 18H, CH₃), 0.92 (s, 3H, CH₃). ³¹P NMR (162 MHz, CDCl₃) δ −18.0 (s).

¹³C NMR (100 MHz, CDCl₃) δ 159.4, 159.1, 150.4, 150.3, 149.9, 149.8, 147.2, 146.6, 146.5, 145.1, 142.0, 141.9, 138.4, 138.2, 135.5, 135.4, 134.5, 132.1, 131.8, 128.4, 128.2, 127.7, 127.6, 127.5, 126.7, 126.0, 125.7, 122.5, 122.3, 121.4, 81.5, 81.0, 68.5, 68.4, 64.60, 64.57, 55.3, 41.0, 40.9, 39.7, 35.5, 34.8, 34.7, 34.3, 31.3, 31.2, 30.3. HRMS (MALDI) calcd for [C₄₇H₆₁NP, M–CH₃]⁺: 670.4536, Found 670.4620.

(S)-(7'-di(3,5-tert-butylphenyl)-phosphion)-1,1'-spirobiinane-7-yl)diphenylmethanamine [(S)-6f]

White solid, mp: 92 – 94 °C. [α]D³⁰ −146 (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (m, 3H, Ar-H), 7.26 (m, 4H, Ar-H), 7.21 (m, 3H, Ar-H), 7.15 – 7.06 (m, 3H, Ar-H), 6.93 – 6.91 (m, 2H, Ar-H), 6.83 – 6.81 (m, 2H, Ar-H), 6.76 – 6.75 (m, 1H, Ar-H), 3.07 – 3.00 (m, 2H, CH₂), 2.88 – 2.79 (m, 1H, CH₂), 2.50 – 2.44 (m, 1H, CH₂), 2.31 (m, 1H, CH₂), 2.16 – 1.98 (m, 3H, CH₂), 1.20 (s, 18H, CH₃), 1.17 (s, 18H, CH₃). ³¹P NMR (162 MHz, CDCl₃) δ −16.4 (s). ¹³C NMR (100 MHz, CDCl₃) δ 176.6, 156.4, 156.1, 150.14, 150.08, 150.02, 149.96, 147.1, 147.0, 146.22, 146.19, 143.3, 143.2, 140.3, 137.8, 137.7, 137.2, 135.9, 135.8, 134.0, 133.1, 132.8, 129.9, 128.5, 127.9, 127.8, 127.7, 127.6, 127.2, 127.0, 126.7, 125.7, 124.9, 122.3, 121.5, 62.6, 62.6, 41.5, 41.4, 40.4, 34.8, 34.7, 31.35, 31.30, 30.7, 29.7. HRMS (MALDI) calcd for [C₅₂H₆₃NP, M–C₆H₅]⁺: 732.4693, Found 732.4925.
To a solution of (R)-5e (134 mg, 0.2 mmol) in Et₂O (5 mL) was added a 3 M EtMgBr in Et₂O (0.2 ml, 0.6 mmol). After stirred for 40 min, Ti(O-i-Pr)₄ (57 mg, 0.2 mmol) was added successively at room temperature. The resulted mixture heated under reflux and monitored by TLC for full conversion (about 10 h). A solution of NaOH (2N, 1 mL) was added, and the mixture was filtered with Celite. The solids were washed several times with CH₂Cl₂, and the aqueous layer of the filtrates was extracted twice with CH₂Cl₂. The combined organic phases were dried and concentrated. The residue was chromatographed on a silica gel column with petroleum ether/EtOAc (20:1 in volume) and 1% Et₃N as additive to afford (R)-2e (113 mg, 81%) as a white solid. mp: 84 – 86 °C. [α]₃⁰⁺122 (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.10 (m, 7H, Ar-H), 7.01 – 6.99 (m, 1H, Ar-H), 6.83 – 6.80 (m, 4 H, Ar-H), 3.05 – 2.97 (m, 4H, CH₂), 2.57 – 2.49 (m, 1H, CH₂), 2.41 – 2.32 (m, 1H, CH₂), 2.26 – 1.86 (m, 5H, CH₂), 1.33 – 1.01 (m, 42H, CH₃ & CH₂ & NH₂), 0.80 (t, J = 7.2 Hz, 3H, CH₃). ³¹P NMR (162 MHz, CDCl₃) δ –16.8 (s). ¹³C NMR (100 MHz, CDCl₃) δ 182.4, 155.8, 155.7, 150.03, 149.97, 149.9, 146.2, 146.1, 146.06, 143.55, 143.48, 139.7, 137.9, 137.8, 136.0, 135.8, 134.0, 133.5, 133.2, 128.1, 127.9, 127.8, 127.6, 126.99, 126.95, 125.5, 125.2, 124.5, 122.2, 121.5, 62.89, 62.86, 41.72, 41.66, 41.4, 34.7, 32.7, 31.3, 30.9, 9.7. HRMS (MALDI) calcd for [C₄₈H₆₃NP, M–C₂H₅]⁺: 684.4693, Found 684.4698.
To a mixture of (\(R\))-6g (125 mg, 0.271 mmol), [Ir(COD)Cl]_2 (100 mg, 0.149 mmol) and NaBAR\(_F\)-3H\(_2\)O (313 mg, 0.325 mmol) in a Schlenk tube under argon atmosphere, CH\(_2\)Cl\(_2\) (2 mL) was introduced. The resulting suspension was heated to 45 °C until the TLC analysis showed no free ligand existed. After cooling to room temperature, the mixture was concentrated under reduced pressure and the residue was purified by a flash column chromatography on silica gel with CH\(_2\)Cl\(_2\)/petroleum ether (1:1 in volume) to offer (\(R\))-4g (407 mg, 86%) as an orange-yellow solid.

\[
\text{mp: 172 – 174 °C. } [\alpha]_D^{30} -112 (c 1.0, \text{CH}_2\text{Cl}_2).
\]
\[
^1H \text{ NMR (400 MHz, CDCl}_3) \delta 8.15 (d, J = 7.6 Hz, 1H), 7.80 – 7.73 (m, 9H), 7.53 – 7.43 (m, 8H), 7.39 – 7.25 (m, 6H), 7.17 (t, J = 8.4 Hz, 2H), 6.80 (t, J = 8.8 Hz, 2H), 4.20 – 4.18 (m, 1H), 3.68 – 3.26 (m, 4H), 3.04 – 3.02 (m, 2H), 2.94 – 2.85 (m, 2H), 2.37 – 2.21 (m, 3H), 2.15 – 2.12 (m, 2H), 1.91 (s, 3H), 1.68 – 1.61 (m, 2H), 1.46 (s, 3H), 1.41 – 1.26 (m, 4H), 0.98 – 0.86 (m, 2H). \]
\[
^{31}P \text{ NMR (162 MHz, CDCl}_3) \delta 13.5 (s).
\]
\[
^{13}C \text{ NMR (100 MHz, CDCl}_3) \delta 162.4, 161.9, 161.4, 160.9, 152.7, 152.6, 147.0, 146.9, 146.0, 145.6, 135.1, 135.0, 134.9, 134.8, 133.9, 133.4, 132.3, 131.6, 131.5, 129.9, 129.8, 129.7, 129.6, 129.3, 129.2, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.0, 127.7, 127.3, 126.1, 125.9, 125.0, 124.7, 123.2, 120.5, 117.5, 65.0, 60.4, 38.2, 38.1, 35.6, 32.4, 30.4, 29.6. \]
HRMS (MALDI) calcd for [C\(_{40}\)H\(_{44}\)IrNP, M\(^+\): 762.2835, Found 762.2840.

(\(R\)-4d)

Orange-yellow solid, mp: 84 – 86 °C. [\(\alpha\)]\(_D\)\(^{29}\) +80 (c 1.0, CH\(_2\)Cl\(_2\)).
\[
^1H \text{ NMR (400 MHz, CDCl}_3) \delta 8.07 (m, 2H), 7.84 (m, 2H), 7.64 (m, 9H), 7.45 – 7.30 (m, 10H), 7.19 (m, 1H), 6.68 (m, 2H), 6.50 – 6.48 (m, 2H), 4.17 – 4.05 (m, 1H), 3.70 – 3.45 (m, 3H), 3.11 – 2.73 (m, 5H), 2.37 – 1.97 (m, 6H), 1.85 (s, 3H, CH\(_3\)), 1.67 (m, 1H), 1.48 (m, 2H), 1.41 (s, 3H, CH\(_3\)), 1.26 (m, 4H) 1.11 (s, 36H). \]
\[
^{31}P \text{ NMR (162 MHz, CDCl}_3) \delta 15.7 (s). \]
\[
^{13}C \text{ NMR (100 MHz, CDCl}_3) \delta 162.5, 162.0, 161.5, 161.0, 152.6, 152.5, 151.1, 146.9, 146.8, 146.0, 145.6, 135.2, 134.8, 133.6, 133.1, 129.5, 129.4, 129.1, 129.0, 128.8, 128.4, 128.1, 128.0, 127.7, 126.9, 126.4, 126.2, 125.9, 125.2, 124.9, 123.4, 123.2, 120.5, 117.5, 71.0, 70.0, 65.7, 65.0, 60.4, 37.9, 37.8, 37.1, 35.6, 35.0, 34.9, 32.3, 32.0, 31.1, 30.6, 30.3, 30.1, 29.7, 29.6, 29.4, 27.1, 26.9, 22.7, 19.7, 19.2, 14.1. \]
HRMS (MALDI) calcd for [C\(_{56}\)H\(_{76}\)IrNP, M\(^+\): 986.5339, Found 986.5347.
**Orange-yellow solid, mp: 118 – 120 °C. [α]D<sup>29</sup> = 96 (c 1.3, CH<sub>2</sub>Cl<sub>2</sub>).**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (m, 9H), 7.54 – 7.48 (m, 3H), 7.40 – 7.34 (m, 6H), 7.26 – 7.17 (m, 2H), 7.06 – 6.93 (m, 2H), 6.49 – 6.46 (m, 2H), 3.89 (m, 1H), 3.25 – 3.24 (m, 2H), 2.87 – 2.71 (m, 3H), 2.38 – 2.10 (m, 7H), 1.89 – 1.80 (m, 1H), 1.68 – 1.60 (m, 2H), 1.49 – 1.48 (m, 2H), 1.39 – 1.34 (m, 2H), 1.24 – 1.17 (m, 5H), 1.14 (s, 18H), 1.09 (s, 18H), 0.81 – 0.78 (m, 2H), 0.74 (m, J = 7.6 Hz, 3H), 0.49 – 0.41 (m, 2H).**

**<sup>3</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 14.6 (s).**

**<sup>1</sup>3C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.4, 162.5, 162.0, 161.5, 161.0, 152.5, 152.4, 150.8, 150.7, 147.9, 147.8, 146.6, 146.5, 145.2, 141.0, 134.8, 132.7, 132.6, 132.1, 130.3, 129.0, 128.9, 128.7, 128.6, 128.4, 128.2, 128.0, 126.9, 126.8, 126.3, 125.9, 124.5, 123.7, 123.2, 120.5, 117.4, 75.3, 73.3, 70.3, 67.8, 67.5, 62.8, 41.0, 35.8, 35.0, 34.9, 33.1, 33.0, 31.14, 31.08, 30.5, 30.4, 30.1, 30.0, 29.7, 28.31, 28.27, 9.0. HRMS (MALDI) calced for [C<sub>56</sub>H<sub>75</sub>IrNP, M]⁺: 985.5261, Found 985.5260.

**Orange-yellow solid, mp: 96 – 98 °C. [α]D<sup>30</sup> = +120 (c 1.6, CH<sub>2</sub>Cl<sub>2</sub>).**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.17 (m, 1H), 8.00 – 7.99 (m, 1H), 7.77 – 7.71 (m, 10H), 7.56 – 7.47 (m, 10H), 7.36 – 7.18 (m, 8H), 6.69 – 6.67 (m, 2H), 6.55 – 6.53 (m, 2H), 4.30 – 4.24 (m, 1H), 4.12 – 4.04 (m, 2H), 3.54 (m, 1H), 3.32 – 3.31 (m, 1H), 2.78 – 2.74 (m, 1H), 2.60 – 2.56 (m, 1H), 2.40 – 2.36 (m, 2H), 2.13 – 2.03 (m, 4H), 1.88 (m, 1H), 1.67 – 1.59 (m, 4H), 1.25 (s, 18H), 1.17 (s, 18H).**

**<sup>3</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 15.4 (s).**

**<sup>1</sup>3C NMR (100 MHz, CDCl<sub>3</sub>) δ 184.0, 162.4, 162.0, 161.5, 161.1, 152.4, 152.3, 150.6, 148.7, 148.6, 147.3, 145.8, 141.6, 136.9, 134.8, 133.8, 132.8, 132.3, 132.2, 129.2, 129.0, 128.7, 128.6, 128.3, 128.0, 127.8, 127.6, 126.6, 126.3, 125.9, 125.8, 124.9, 123.6, 123.2, 120.5, 117.4, 74.4, 74.1, 71.5, 66.5, 66.3, 62.6, 38.8, 35.0, 34.9, 34.8, 33.1, 33.0, 31.1, 30.5, 30.3, 30.1, 28.8, 28.7. HRMS (MALDI) calced for [C<sub>66</sub>H<sub>80</sub>IrNP, M]⁺: 1110.5652, Found 1110.5549.
X-Ray Diffraction Analysis of (R)-4g

Table S1. Crystal data and structure refinement for (R)-4g

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<th>Value</th>
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<tr>
<td>Temperature</td>
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<td>Wavelength</td>
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<tr>
<td></td>
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<tr>
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<tr>
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</tr>
<tr>
<td>Limiting indices</td>
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</tr>
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Reflections collected / unique: 45814 / 15920 [R(int) = 0.0189]
Completeness to theta = 27.52: 99.7%
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.7120 and 0.6422
Refinement method: Full-matrix least-squares on F^2
Data / restraints / parameters: 15920 / 186 / 1039
Goodness-of-fit on F^2: 0.705
Final R indices [I>2sigma(I)]: R_1 = 0.0151, wR_2 = 0.0312
R indices (all data): R_1 = 0.0170, wR_2 = 0.0314
Absolute structure parameter: -0.0099(18)
Largest diff. peak and hole: 0.519 and -0.365 e.Å^3

2. Preparation and Analytical Data of Hydrogenation Substrates

(a) Synthesis of (E)-β-aryl-β-methyl nitroalkenes^4

![Chemical Structure](image)

Acetic acid (120 mmol) was added to a suspension of α-methylstyrene (10 mmol), NaNO_2 (100 mmol) and cerium(IV) ammonium nitrate (CAN, 10 mmol) in CHCl_3 (100 mL) and the mixture was sonicated in a sealed flask connected to a bubbler until the reaction reached completion as judged by TLC (30–60 min). CHCl_3 (100 mL) was added and solution was washed with saturated NaHCO_3 and water and then dried (anhydride MgSO_4). The solvent was evaporated and the product (E)-1 was purified by flash chromatography on silica gel with petroleum ether/EtOAc (20:1 in volume) as eluent. The product could be further purified by distillation under vacuum if needed.

(b) Synthesis of β-alkyl-β-methyl nitroalkenes^5

![Chemical Structure](image)

To an oven-dried Schlenk tube charged with a magnetic stir-bar was added AgNO_2 (30 mmol), TEMPO (4 mmol), and dried 4 Å molecular sieves (1 g) under nitrogen atmosphere. The olefin (10 mmol) and solvent (DCE, 20 mL) were added by microliter syringe and laboratory syringe
respectively. The tube was placed in a preheated oil bath at 70 °C and the reaction mixture was stirred vigorously and reached completion as judged by TLC. Then the reaction mixture was cooled to room temperature, filtered through a celite bed filter with ethyl acetate as the washing solvent. Finally organic extract was concentrated and was purified by flash chromatography on silica gel with petroleum ether/EtOAc (20:1 in volume) as eluent.

(E)-(1-nitroprop-1-en-2-yl)benzene (1a)

\[
\begin{align*}
\text{Me} & \end{align*}
\]
Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.42 (m, 5H, Ar-H), 7.31 (q, $J = 1.6$ Hz, 1H, CH), 2.65 (d, $J = 1.6$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.9, 138.3, 136.3, 130.3, 129.0, 126.8, 18.6.

(E)-1-methyl-4-(1-nitroprop-1-en-2-yl)benzene (1b)

\[
\begin{align*}
\text{Me} & \end{align*}
\]
Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.35 (m, 2H, Ar-H), 7.33 – 7.32 (m, 1H, CH), 7.25 – 7.23 (m, 2H, Ar-H), 2.64 (d, $J = 1.2$ Hz, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.0, 140.9, 135.8, 135.3, 129.7, 126.8, 21.3, 18.4.

(E)-1-methoxy-4-(1-nitroprop-1-en-2-yl)benzene (1c)

\[
\begin{align*}
\text{MeO} & \end{align*}
\]
Pale yellow solid, mp: 32 – 34 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.42 (m, 2H, Ar-H), 7.34 – 7.34 (m, 1H, CH), 6.96 – 6.94 (m, 2H, Ar-H), 3.85 (s, 3H, OCH$_3$), 2.64 (d, $J = 0.8$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.5, 149.7, 135.0, 130.1, 128.4, 114.4, 55.4, 18.2.

(E)-1-chloro-4-(1-nitroprop-1-en-2-yl)benzene (1d)

\[
\begin{align*}
\text{Cl} & \end{align*}
\]
Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.38 (m, 4H, Ar-H), 7.29 – 7.28 (m, 1H, CH), 2.62 (d, $J = 1.2$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.5, 136.6, 136.4, 129.3, 128.1, 18.4.

(E)-1-fluoro-4-(1-nitroprop-1-en-2-yl)benzene (1e)

\[
\begin{align*}
\text{F} & \end{align*}
\]
Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.43 (m, 2H, Ar-H), 7.29 – 7.28 (m, 1H, CH), 7.16 – 7.10 (m, 2H, Ar-H), 2.63 (d, $J = 1.2$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.0 (d, $J_{CF} = 250$ Hz), 148.7, 136.2, 134.3 (d, $J_{CF} = 3.5$ Hz), 128.8 (d, $J_{CF} = 8.6$ Hz), 116.2 (d, $J_{CF} = 22$Hz), 18.6.
(E)-methyl 4-(1-nitroprop-1-en-2-yl)benzoate (1f)

Yellow solid, mp: 98 – 100 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 – 8.08 (m, 2H, Ar-H), 7.52 – 7.50 (m, 2H, Ar-H), 7.31 (d, $J=1.2$ Hz, 1H, CH), 3.94 (s, 3H, COOCH$_3$), 2.64 (d, $J=1.2$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.1, 148.5, 142.5, 137.1, 131.7, 130.2, 126.8, 52.4, 18.4. HRMS (ESI) calcd for [C$_{11}$H$_{11}$NO$_4$Na, M+Na]$^+$: 244.0580, Found 244.0582.

(E)-4-(1-nitroprop-1-en-2-yl)benzonitrile (1g)

Pale yellow solid, mp: 54 – 56 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.72 (m, 2H, Ar-H), 7.57 – 7.55 (m, 2H, Ar-H), 7.28 – 7.27 (m, 1H, CH), 2.62 (d, $J=1.2$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.3, 142.6, 137.5, 132.7, 127.5, 117.9, 113.8, 18.2. HRMS (ESI) calcd for [C$_{10}$H$_7$N$_2$O$_2$, M–H]$^-$: 187.0411, Found 187.0512.

(E)-1-nitro-4-(1-nitroprop-1-en-2-yl)benzene (1h)

Yellow solid, mp: 106 – 108 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.31 – 8.29 (m, 2H, Ar-H), 7.64 – 7.62 (m, 2H, Ar-H), 7.30 (d, $J=1.6$ Hz, 1H, CH), 2.65 (d, $J=1.2$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.7, 146.94, 146.90, 144.5, 137.8, 127.9, 124.2, 18.5. HRMS (ESI) calcd for [C$_9$H$_8$N$_2$O$_2$, M–H]$^-$: 207.0411, Found 207.0411.

(E)-1-methoxy-3-(1-nitroprop-1-en-2-yl)benzene (1i)$^4$

Pale yellow solid, mp: 48 – 50 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.29 (m, 2H, Ar-H and CH), 7.03 – 6.94 (m, 3H, Ar-H), 3.84 (s, 3H, OCH$_3$), 2.61 (d, $J=1.6$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.8, 149.8, 139.6, 136.3, 130.0, 119.1, 115.5, 112.6, 55.3, 18.5.

(E)-1-chloro-3-(1-nitroprop-1-en-2-yl)benzene (1j)$^6$

Pale yellow solid, mp: 62 – 64 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.42 (m, 2H, Ar-H), 7.40 – 7.31 (m, 2H, Ar-H), 7.27 (q, $J=1.6$ Hz, 1H, CH), 2.61 (d, $J=1.6$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.2, 140.0, 136.8, 135.1, 130.29, 130.27, 127.0, 124.9, 18.4.
(E)-6-(1-nitroprop-1-en-2-yl)-1,2,3,4-tetrahydronaphthalene (1k)

Pale yellow solid, mp: 60 – 62 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.32 (m, 1H, Ar-H), 7.20 – 7.11 (m, 3H, Ar-H&CH), 2.80 (t, \(J = 6.3\) Hz, 4H, CH\(_2\)), 2.63 (d, \(J = 1.2\) Hz, 3H, CH\(_3\)), 1.84 – 1.80 (m, 4H, CH\(_2\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.4, 140.3, 137.9, 135.6, 135.3, 129.8, 127.6, 123.9, 29.4, 29.2, 22.91, 22.86, 18.4. HRMS (ESI) calcd for \([C_{13}H_{15}NO_2Na, M^+Na]^+\): 240.0995, Found 240.0998.

(E)-2-(1-nitroprop-1-en-2-yl)naphthalene (1l)

Yellow solid, mp: 76 – 78 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 – 7.95 (m, 1H, Ar-H), 7.91 – 7.86 (m, 3H, Ar-H), 7.59 – 7.51 (m, 3H, Ar-H), 7.45 (q, \(J = 1.2\) Hz, 1H, CH), 2.75 (d, \(J = 1.6\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.8, 136.6, 135.4, 133.9, 133.0, 128.9, 128.6, 127.7, 127.5, 127.0, 123.6, 18.5.

(E)-5-(1-nitroprop-1-en-2-yl)benzo[d][1,3]dioxole (1m)

Pale yellow solid, mp: 124 – 126 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29 (m, 1H, CH), 7.00 (dd, \(J = 8.0, 1.6\) Hz, 1H, Ar-H), 6.93 (d, \(J = 1.6\) Hz, 1H, Ar-H), 6.84 (d, \(J = 8.0\) Hz, 1H, Ar-H), 6.03 (s, 2H, CH\(_2\)), 2.61 (d, \(J = 1.2\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.7, 149.6, 148.4, 135.5, 132.1, 121.5, 108.7, 107.0, 101.8, 18.5. HRMS (ESI) calcd for \([C_{10}H_9NO_4Na, M^+Na]^+\): 230.0424, Found 230.0428.

(3-methyl-4-nitrobut-3-en-1-yl)benzene (1o)

Yellow liquid. E-isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.29 (m, 2H, Ar-H), 7.26 – 7.21 (m, 2H, Ar-H), 7.17 – 7.15 (m, 1H, Ar-H), 6.90 – 6.89 (m, 1H, CH), 2.84 (t, \(J = 7.2\) Hz, 2H, CH\(_2\)), 2.50 (t, \(J = 7.2\) Hz, 2H, CH\(_2\)), 2.30 (d, \(J = 1.6\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.0, 139.7, 135.6, 128.6, 128.2, 126.5, 39.7, 33.4, 18.7. HRMS (ESI) calcd for \([C_{11}H_{14}NO_2, M^+H]^+\): 192.1019, Found 192.1031.

Z-isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.29 (m, 2H, Ar-H), 7.26 – 7.21 (m, 2H, Ar-H), 7.17 – 7.15 (m, 1H, Ar-H), 6.97 (m, 1H, CH), 2.96 – 2.93 (m, 2H, CH\(_2\)), 2.88 – 2.86 (m, 2H, CH\(_2\)), 1.89 (d, \(J = 1.6\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.8, 140.4, 135.2, 128.5, 128.3, 126.3, 35.1, 33.7, 22.6.
2-(3-methyl-4-nitrobut-3-en-1-yl)naphthalene (1p)

Yellow solid. E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 – 7.77 (m, 3H, Ar-H), 7.61 (m, 1H, Ar-H), 7.50 – 7.44 (m, 2H, Ar-H), 7.29 (d, $J = 8.4$ Hz, 1H, Ar-H), 6.94 (m, 1H, CH), 3.00 (t, $J = 7.6$ Hz, 2H, CH$_2$), 2.59 (t, $J = 7.2$ Hz, 2H, CH$_2$), 2.33 (d, $J = 0.8$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.0, 137.2, 135.5, 133.4, 132.1, 128.2, 127.5, 127.3, 126.5, 126.4, 126.1, 125.5, 39.4, 33.4, 18.6. HRMS (ESI) calcd for [C$_{15}$H$_{16}$NO$_2$, M+H]$^+$: 242.1176, Found 242.0953.

Z-isomer: $\delta$ 7.83 – 7.77 (m, 3H, Ar-H), 7.61 (m, 1H, Ar-H), 7.50 – 7.44 (m, 2H, Ar-H), 7.31 – 7.28 (m, 1H, Ar-H), 6.99 (m, 1H, CH), 3.03 – 3.00 (m, 4H, CH$_2$), 1.91 (m, 3H, CH$_3$).

5-(3-methyl-4-nitrobut-3-en-1-yl)benzo[d][1,3]dioxole (1q)

Pale yellow solid. E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.88 (m, 1H, CH), 6.73 (d, $J = 7.6$ Hz, 1H, Ar-H), 6.64 (s, 1H, Ar-H), 6.59 (d, $J = 7.6$ Hz, 1H, Ar-H), 5.93 (s, 2H, CH$_2$), 2.75 (t, $J = 7.6$ Hz, 2H, CH$_2$), 2.44 (t, $J = 7.6$ Hz, 2H, CH$_2$), 2.27 (m, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.9, 147.8, 146.1, 135.6, 133.4, 121.0, 108.5, 108.3, 100.9, 40.0, 33.1, 18.6. HRMS (ESI) calcd for [C$_{12}$H$_{13}$NO$_4$Na, M+Na]$^+$: 258.0737, Found 258.0729.

Z-isomer: $\delta$ 6.96 (m, 1H, CH), 6.73 (d, $J = 7.6$ Hz, 1H, Ar-H), 6.68 (d, $J = 8.0$ Hz, 1H, Ar-H), 6.64 (s, 1H, Ar-H), 5.93 (s, 2H, CH$_2$), 2.88 (t, $J = 7.2$ Hz, 2H, CH$_2$), 2.77 (t, $J = 7.2$ Hz, 2H, CH$_2$), 1.89 (m, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) 152.7, 147.6, 146.0, 135.2, 134.2, 121.1, 108.8, 108.2, 35.4, 33.5, 22.7.

(4-methyl-5-nitropent-4-en-1-yl)benzene (1r)

Yellow liquid. E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.27 (m, 2H, Ar-H), 7.23 – 7.16 (m, 3H, Ar-H), 6.94 – 6.93 (m, 1H, CH), 2.64 (t, $J = 7.6$ Hz, 2H, CH$_2$), 2.23 (d, $J = 1.2$ Hz, 3H, CH$_3$), 2.20 – 2.18 (m, 2H, CH$_2$), 1.85 (t, $J = 7.6$ Hz, 2H, CH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.9, 140.9, 135.3, 128.5, 128.3, 126.2, 37.3, 35.1, 28.6, 18.5. HRMS (ESI) calcd for [C$_{12}$H$_{15}$NO$_2$Na, M+Na]$^+$: 228.0995, Found 228.0985.

Z-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.27 (m, 2H, Ar-H), 7.23 – 7.16 (m, 3H, Ar-H), 6.94 – 6.93 (m, 1H, CH), 2.73 – 2.65 (m, 4H, CH$_2$), 1.90 (d, $J = 1.6$ Hz, 1H, CH$_3$), 1.89 – 1.81 (m,
2H, CH$_2$)$_{13}$C NMR (100 MHz, CDCl$_3$) δ 153.2, 141.4, 135.0, 128.4, 128.3, 126.0, 35.9, 32.6, 29.1, 22.2.

**(E)-3-(3-methyl-4-nitrobut-3-en-1-yl)-1-tosyl-1H-indole (1s)**

![Chemical structure](image)

White solid, mp: 136 – 138 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.71 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.44 (d, $J = 8.0$ Hz, 1H, Ar-H), 7.36 – 7.32 (m, 2H, Ar-H), 7.27 – 7.23 (m, 1H, Ar-H), 7.21 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.81 (m, 1H, CH), 2.90 (t, $J = 7.6$ Hz, 2H, CH$_2$), 2.56 (t, $J = 7.6$ Hz, 2H, CH$_2$), 2.34 (s, 3H, CH$_3$), 2.27 (m, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.4, 145.0, 135.7, 135.3, 135.0, 130.2, 129.9, 126.6, 125.0, 123.2, 123.0, 119.0, 113.9, 37.1, 22.6, 21.5, 18.5. HRMS (ESI) calcd for [C$_{20}$H$_{20}$N$_2$O$_4$SNa, M+Na]$^+$: 407.1036, Found 407.1086.

**2-methyl-1-nitrohex-1-ene (1t)**$^7$

![Chemical structure](image)

Yellow liquid. $E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 6.94 (m, 1H, CH), 2.23 (m, 3H, CH$_3$), 2.18 (t, $J = 8.0$ Hz, 2H, CH$_2$), 1.54 – 1.44 (m, 2H, CH$_2$), 1.42 – 1.29 (m, 2H, CH$_2$), 0.95 – 0.89 (m, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.6, 135.1, 37.7, 29.1, 22.8, 22.2, 13.7.

$Z$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 6.91 (m, 1H, CH), 2.63 (t, $J = 8.0$ Hz, 2H, CH$_2$), 1.91 (m, 3H, CH$_3$), 1.54 – 1.44 (m, 2H, CH$_2$), 1.42 – 1.29 (m, 2H, CH$_2$), 0.95 – 0.89 (m, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.9, 134.7, 32.6, 29.6, 22.3, 18.5, 13.7.

**2,3-dimethyl-1-nitrobut-1-ene (1u)**$^7$

![Chemical structure](image)

Yellow liquid. $E$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 6.96 (m, 1H, CH), 2.49 – 2.39 (m, 1H, CH), 2.20 (d, $J = 1.6$ Hz, 3H, CH$_3$), 1.12 (d, $J = 6.8$ Hz, 6H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.4, 134.4, 35.9, 20.4, 16.1.

$Z$-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 6.84 (m, 1H, CH), 3.87 – 3.78 (m, 1H, CH), 1.82 (d, $J = 1.6$ Hz, 3H, CH$_3$), 1.09 (d, $J = 6.8$ Hz, 6H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.4, 134.4, 28.6, 20.0, 16.4.
(1-nitroprop-1-en-2-yl)cyclohexane (1v)

Yellow liquid. E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.93 (m, 1H, CH), 2.20 (d, $J$ = 0.8 Hz, 3H, CH$_3$), 1.84 – 1.68 (m, 6H, Cy), 1.43 – 1.08 (m, 5H, Cy). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.8, 134.7, 46.4, 30.8, 26.0, 25.8, 17.1.

Z-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.84 (m, 1H, CH), 2.08 – 2.02 (m, 4H, CH & CH$_3$), 1.84 – 1.68 (m, 5H, Cy), 1.43 – 1.08 (m, 5H, Cy). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.8, 133.9, 39.4, 31.9, 30.2, 25.7, 17.9.

2-(3-methyl-4-nitrobut-3-en-1-yl)isoindoline-1,3-dione (1w)

White solid. E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 – 7.82 (m, 2H, Ar-H), 7.74 – 7.72 (m, 2H, Ar-H), 6.89 (m, 1H, CH), 3.90 (t, $J$ = 6.8 Hz, 2H, CH$_2$), 2.56 (t, $J$ = 6.8 Hz, 2H), 2.34 (d, $J$ = 1.2 Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9, 148.7, 136.3, 134.2, 131.6, 123.4, 36.5, 35.2, 18.2.

HRMS (ESI) calcd for [C$_{13}$H$_{12}$N$_2$O$_4$Na, M+Na]$^+$: 283.0689, Found 283.0732.

Z-isomer: $\delta$ 7.85 – 7.82 (m, 2H, Ar-H), 7.74 – 7.72 (m, 2H, Ar-H), 6.93 (m, 1H, CH), 3.97 (t, $J$ = 6.8 Hz, 2H, CH$_2$), 2.99 (t, $J$ = 6.4 Hz, 2H, CH$_2$), 2.02 (m, 1H, CH$_3$).

3. General Procedures for Asymmetric Hydrogenation

3.1 Asymmetric hydrogenation of (E)-β-aryl-β-methyl-nitroalkenes

To a hydrogenation tube was charged with a stir bar, (E)-β-aryl-β-methyl nitroalkenes 1 (0.5 mmol), catalyst (S)-4d (4.6 mg, 0.0025mmol) in an argon-filled glovebox. Then 1.5 mL MeOH, 0.5 mL CF$_3$CH$_2$OH, and Et$_3$N (70 uL, 0.5 mmol) was injected into the hydrogenation tube by a syringe with stirring. The hydrogenation tube was put into an autoclave. The autoclave was sealed, purged with hydrogen for 3 times, and finally charged with hydrogen to 20 atm. The reaction mixture was stirred at 10 ºC for specified time before releasing the hydrogen. The solution was
concentrated and passed through a short column of silica gel to remove the metal complex. The product was analyzed by $^1$H NMR spectroscopy for conversion and chiral HPLC or SFC for ee values.

3.2 Asymmetric hydrogenation of $\beta$-alkyl-$\beta$-methyl-nitroalkenes

\[
\begin{array}{c}
\text{Alkyl} \quad \text{Me} \\
\begin{array}{c}
\underline{\text{NO}_2} \quad + \\
\text{H}_2 \quad (50 \text{ atm})
\end{array}
\end{array}
\xrightarrow{2 \text{ mol} \% \,(R)-4d}
\begin{array}{c}
\text{Alkyl} \quad \text{Me} \\
\begin{array}{c}
\begin{array}{c}
\underline{\text{NO}_2} \\
\end{array}
\end{array}
\end{array}
\]

To a hydrogenation tube was charged with a stir bar, $\beta$-alkyl-$\beta$-methyl nitroalkenes 1 (0.25 mmol), catalyst $(R)$-4d (9.3 mg, 0.005mmol) in an argon-filled glovebox. Then 2 mL MeOH and Et$_3$N (35 uL, 0.25 mmol) was injected into the hydrogenation tube by a syringe with stirring. The hydrogenation tube was put into an autoclave. The autoclave was sealed, purged with hydrogen for 3 times, and finally charged with hydrogen to 50 atm. The reaction mixture was stirred at 10 °C for specified time before releasing the hydrogen. The solution was concentrated and passed through a short column of silica gel to remove the metal complex. The product was analyzed by NMR spectroscopy for conversion and chiral GC, HPLC or SFC for ee values.

Table S2. Asymmetric hydrogenation of (3-methyl-4-nitro-3-en-1-yl)benzene (1o)$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>$P_{H_2}$ (atm)</th>
<th>Conv.$^b$</th>
<th>ee (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(R)$-4a</td>
<td>50</td>
<td>24%</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>$(R)$-4b</td>
<td>50</td>
<td>32%</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>$(R)$-4c</td>
<td>50</td>
<td>36%</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>$(R)$-4d</td>
<td>50</td>
<td>100%</td>
<td>90</td>
</tr>
</tbody>
</table>

$^a$ Table S2 contains the results of the asymmetric hydrogenation of (3-methyl-4-nitro-3-en-1-yl)benzene (1o) using different catalysts. $^b$ Conversion is given as a percentage of the reaction completion. $^c$ Enantiomeric excess (ee) values are reported for each experiment.
|  | (R)-4e | 50 | 100% | 67 |
|  | (S)-4f | 50 | 65% | 13 |
|  | (R)-4d | 20 | 95% | 86 |
|  | (R)-4d | 80 | 100% | 84 |
|  | (R)-4d | 50 | 100% | 91 |

\(^a\) Reaction conditions: 0.125 mmol scale, [substrate] = 0.0625 mol/L in MeOH and CF\(_3\)CH\(_2\)OH, substrate to catalyst is 50, 1 equiv Et\(_3\)N. BAr\(_F\) = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. \(^b\) Determined by \(^1\)H NMR. \(^c\) Determined by HPLC using a Chiralcel OJ-H column. \(^d\) Used MeOH as solvent.

### 3.3 Deuterium experiments

#### 3.3.1 Deuterium experiments of the hydrogenation of 1b

![Image of reaction](image)

To a hydrogenation tube was charged with a stir bar, 1b (0.5 mmol), catalyst (S)-4d (4.6 mg, 0.0025 mmol) in an argon-filled glovebox. Then 2 mL CD\(_3\)OD and Et\(_3\)N (70 \(\mu\)L, 0.5 mmol) was injected into the hydrogenation tube by a syringe with stirring. The hydrogenation tube was put into an autoclave. The autoclave was sealed, purged with deuterium gas for 3 times, and finally charged with deuterium gas to 20 atm. The reaction mixture was stirred at 45 °C for 3 h before releasing the deuterium gas. The solution was concentrated and the product was analyzed by NMR spectroscopy. 2b-d, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.16 – 7.10 (m, 4H, Ar-H), 2.34 (s, 3H, CH\(_3\)), 1.34 (s, 1.44H).

#### 3.3.2 Deuterium experiments of the hydrogenation of 1q

![Image of reaction](image)
To a hydrogenation tube was charged with a stir bar, 1q (0.25 mmol), catalyst (R)-4d (9.2 mg, 0.005 mmol) in an argon-filled glovebox. Then 2 mL CD$_3$OD and Et$_3$N (35 uL, 0.25 mmol) was injected into the hydrogenation tube by a syringe with stirring. The hydrogenation tube was put into an autoclave. The hydrogenation tube was put into an autoclave. The autoclave was sealed, purged with deuterium gas for 3 times, and finally charged with deuterium gas to 50 atm. The reaction mixture was stirred at 45 °C for 20 h before releasing the deuterium gas. The solution was concentrated and the product was analyzed by NMR spectroscopy. 2q-d, $^1$H NMR (400 MHz, CDCl$_3$) δ 6.75 – 6.72 (m, 1H, Ar-H), 6.65 – 6.60 (m, 2H, Ar-H), 5.93 (s, 2H, CH$_2$), 2.68 – 2.60 (m, 1H, CH$_2$), 2.57 – 2.50 (m, 1H, CH$_2$), 1.73 – 1.63 (m, 1H, CH$_2$), 1.55 – 1.49 (m, 1H, CH$_2$), 1.04 (s, 1.5H).

4. Analytical Data of Hydrogenation Products

(S)-(1-nitropropan-2-yl)benzene (2a)$^{4a}$

Yield: 98%, colorless oil. 94% ee, $[\alpha]_D^{23}$ $-58.0$ (c 1.0, CH$_2$Cl$_2$), Chiralcel OD-H column (25 cm × 0.46 cm ID), n-hexane/2-propanol = 98:2, 1.0 mL/min, 220 nm UV detector, $t_R$ = 14.09 min (minor) and $t_R$ = 20.25 min (major). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36–7.32 (m, 2H, Ar-H), 7.28–7.21 (m, 3H, Ar-H), 4.57–4.45 (m, 2H, CH$_2$), 3.67–3.58 (m, 1H, CH), 1.38 (d, $J$ = 7.2 Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.8, 128.9, 127.5, 126.9, 81.8, 38.6, 18.7.

(-)-1-methyl-4-(1-nitropropan-2-yl)benzene (2b)$^{4b}$

Yield: 96%, colorless oil. 93% ee, $[\alpha]_D^{23}$ $-60.0$ (c 1.0, CH$_2$Cl$_2$), Chiralcel OJ-H column (25 cm × 0.46 cm ID), n-hexane/2-propanol = 97:3, 1.0 mL/min, 220 nm UV detector, $t_R$ = 12.13 min (minor) and $t_R$ = 13.80 min (major). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 – 7.10 (m, 4H, Ar-H), 4.55 – 4.44 (m, 2H, CH$_2$), 3.65 – 3.55 (m, 1H, CH), 2.33 (s, 3H, CH$_3$), 1.36 (d, $J$ = 7.2 Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.8, 137.2, 129.6, 126.7, 82.0, 38.3, 21.0, 18.7.
(-)-1-methoxy-4-(1-nitropropan-2-yl)benzene (2c)<sup>4b</sup>

Yield: 95%, colorless oil, 91% ee, [α]<sub>D</sub><sup>23</sup> = –60.5 (c 0.8, CH<sub>2</sub>Cl<sub>2</sub>), Chiralcel OJ-H column (25 cm × 0.46 cm ID), <i>n</i>-hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detector, <i>t</i><sub>R</sub> = 24.04 min (minor) and <i>t</i><sub>R</sub> = 27.27 min (major).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.17 – 7.13 (m, 2H, Ar-<i>H</i>), 6.89 – 6.86 (m, 2H, Ar-<i>H</i>), 4.53 – 4.43 (m, 2H, CH<sub>2</sub>), 3.79 (s, 3H, OCH<sub>3</sub>), 3.64 – 3.54 (m, 1H, CH), 1.36 (d, <i>J</i> = 6.8 Hz, 3H, CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.9, 132.8, 127.9, 114.3, 82.1, 55.2, 37.9, 18.8.

(-)-1-chloro-4-(1-nitropropan-2-yl)benzene (2d)<sup>4b</sup>

Yield: 99%, colorless oil, 97% ee, [α]<sub>D</sub><sup>26</sup> = –51.0 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>), Chiralcel OJ-H column (25 cm × 0.46 cm ID), <i>n</i>-hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detector, <i>t</i><sub>R</sub> = 16.66 min (minor) and <i>t</i><sub>R</sub> = 21.97 min (major).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.30 (m, 2H, Ar-<i>H</i>), 7.18 – 7.16 (m, 2H, Ar-<i>H</i>), 4.54 – 4.45 (m, 2H, CH<sub>2</sub>), 3.65 – 3.59 (m, 1H, CH), 1.37 (d, <i>J</i> = 6.8 Hz, 3H, CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.4, 133.4, 129.1, 128.3, 81.5, 38.1, 18.7.

(-)-1-fluoro-4-(1-nitropropan-2-yl)benzene (2e)<sup>4b</sup>

Yield: 96%, colorless oil, 96% ee, [α]<sub>D</sub><sup>26</sup> = –57.6 (c 1.3, CH<sub>2</sub>Cl<sub>2</sub>), Chiralcel OJ-H column (25 cm × 0.46 cm ID), <i>n</i>-hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detector, <i>t</i><sub>R</sub> = 15.22 min (minor) and <i>t</i><sub>R</sub> = 17.26 min (major).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 – 7.17 (m, 2H, Ar-<i>H</i>), 7.06 – 7.00 (m, 2H, Ar-<i>H</i>), 4.54 – 4.45 (m, 2H, CH<sub>2</sub>), 3.68 – 3.59 (m, 1H, CH), 1.37 (d, <i>J</i> = 6.8 Hz, 3H, CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.1 (d, <i>J</i> = 245 Hz, CF), 136.5, 128.5 (d, <i>J</i> = 8 Hz), 115.8 (d, <i>J</i> = 21 Hz), 81.8, 38.0, 18.8.

(-)-methyl-4-(1-nitropropan-2-yl)benzoate (2f)

Yield: 98%, colorless oil, 98% ee, [α]<sub>D</sub><sup>22</sup> = –125.4 (c 2.7, CH<sub>2</sub>Cl<sub>2</sub>), Chiralcel OJ-H column (25 cm × 0.46 cm ID), <i>n</i>-hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detector, <i>t</i><sub>R</sub> = 54.76 min (major) and
$t_R = 59.77$ min (minor). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.30 (d, $J = 8.4$ Hz, 2H, Ar-H), 4.59 – 4.49 (m, 2H, CH$_2$), 3.90 (s, 3H, COOCH$_3$), 3.74 – 3.65 (m, 1H, CH), 1.39 (d, $J = 6.8$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.6, 146.0, 130.2, 129.5, 127.0, 81.2, 52.1, 38.5, 18.6. HRMS (ESI) calcd for [C$_{11}$H$_{13}$NO$_4$Na, M+Na$^+$]: 246.0737, Found 246.0740.

(-)-4-(1-nitropropan-2-yl)benzonitrile (2g)

Yield: 94%, colorless oil. 97% ee, $[\alpha]_D^{22}$ $-8.8$ (c 0.2, CH$_2$Cl$_2$), SFC Chiralcel OJ-H column (25 cm x 0.46 cm ID), sc CO$_2$/2-propanol = 95:5, 1.0 mL/min, column backpressure = 100 bar, 220 nm UV detector, $t_R = 14.79$ min (minor) and $t_R = 15.81$ min (major). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.35 (d, $J = 8.4$ Hz, 2H, Ar-H), 4.59 – 4.50 (m, 2H, CH$_2$), 3.75 – 3.66 (m, 1H, CH), 1.39 (d, $J = 6.8$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.2, 132.8, 127.8, 118.4, 111.6, 80.8, 38.5, 18.5. HRMS (ESI) calcd for [C$_{10}$H$_9$N$_2$O$_2$, M–H$^-$]: 189.0670, Found 189.0669.

(-)-1-nitro-4-(1-nitropropan-2-yl)benzene (2h)

Yield: 93%, yellow solid. mp: 36 – 38 °C. 98% ee, $[\alpha]_D^{22}$ $-14.2$ (c 0.4, CH$_2$Cl$_2$), SFC Chiralpak AS-H column (25 cm x 0.46 cm ID), sc CO$_2$/2-propanol = 98:2, 0.8 mL/min, column backpressure = 100 bar, 254 nm UV detector, $t_R = 33.73$ min (minor) and $t_R = 34.79$ min (major). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.42 (d, $J = 8.8$ Hz, 2H, Ar-H), 4.62 – 4.54 (m, 2H, CH$_2$), 3.82 – 3.73 (m, 1H, CH), 1.42 (d, $J = 6.8$ Hz, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.3, 147.3, 127.9, 124.2, 80.8, 38.4, 18.6. HRMS (ESI) calcd for [C$_{9}$H$_{9}$N$_2$O$_4$, M–H$^-$]: 209.0568, Found 209.0566.

(-)-1-methoxy-3-(1-nitropropan-2-yl)benzene (2i)$^{4b}$

Yield: 98%, colorless oil. 94% ee, $[\alpha]_D^{23}$ $-55.2$ (c 1.0, CH$_2$Cl$_2$), Chiralcel OJ-H column (25 cm x 0.46 cm ID), n-hexane/2-propanol = 97:3, 1.0 mL/min, 220 nm UV detector, $t_R = 24.35$ min (minor) and $t_R = 25.99$ min (major). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 – 7.24 (m, 1H, Ar-H), 6.83 – 6.80 (m, 2H, Ar-H), 6.77 – 6.76 (m, 1H, Ar-H), 4.55 (dd, $J = 12.0$, 7.2 Hz, 1H, CH$_3$), 4.47 (dd, $J = 12.0$, 8.0 Hz, 1H,
\(\text{CH}_3\), 3.81 (s, 3H, OCH\(_3\)), 3.65 – 3.56 (m, 1H, CH), 1.37 (d, \(J = 6.8\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.9, 142.5, 129.9, 119.1, 113.0, 112.5, 81.7, 55.2, 38.6, 18.6.

(-)-1-chloro-3-(1-nitropropan-2-yl)benzene (2j)

\[
\text{\begin{array}{c}
\text{Cl} \\
\text{Me} \\
\text{NO}_2
\end{array}}
\]

Yield: 98%, colorless oil. 95% ee, \([\alpha]_D^{23} -51.8 (c 1.0, \text{CH}_2\text{Cl}_2)\), Chiralcel OJ-H column (25 cm \(\times\) 0.46 cm ID), \(n\)-hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detector, \(t_R = 20.31\) min (minor) and \(t_R = 25.07\) min (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.22 (m, 3H, Ar-\(H\)), 7.13 – 7.10 (m, 1H, Ar-\(H\)), 4.56 (dd, \(J = 12.4, 7.6\) Hz, 1H, CH\(_2\)), 4.48 (dd, \(J = 12.4, 8.0\) Hz, 1H, CH\(_2\)), 3.67 – 3.58 (m, 1H, CH), 1.38 (d, \(J = 7.2\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.9, 134.7, 130.2, 127.8, 127.1, 125.2, 81.3, 38.3, 18.6.

(-)-6-(1-nitropropan-2-yl)-1,2,3,4-tetrahydronaphthalene (2k)

\[
\text{\begin{array}{c}
\text{Me} \\
\text{NO}_2
\end{array}}
\]

Yield: 98%, colorless oil. 92% ee, \([\alpha]_D^{26} -54.6 (c 1.0, \text{CH}_2\text{Cl}_2)\), Chiralcel OD-H column (25 cm \(\times\) 0.46 cm ID), \(n\)-hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detector, \(t_R = 7.64\) min (minor) and \(t_R = 13.22\) min (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.05 – 7.03 (m, 1H, Ar-\(H\)), 6.96 – 6.92 (m, 2H, Ar-\(H\)), 4.54 (dd, \(J = 12.0, 7.2\) Hz, 1H, CH\(_2\)), 4.46 (dd, \(J = 12.0, 8.8\) Hz, 1H, CH\(_2\)), 3.61 – 3.52 (m, 1H, CH), 2.75 – 2.74 (m, 4H, CH\(_2\)), 1.80 – 1.78 (m, 4H, CH\(_2\)), 1.36 (d, \(J = 6.8\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.9, 137.7, 136.5, 129.7, 127.6, 123.8, 82.0, 38.3, 29.4, 29.0, 23.09, 23.07, 18.8. HRMS (ESI) calcd for [C\(_{13}\)H\(_{17}\)NO\(_2\)Na, M+Na\(^+\)]: 242.1151, Found 242.1152.

(-)-2-(1-nitropropan-2-yl)naphthalene (2l)

\[
\text{\begin{array}{c}
\text{Me} \\
\text{NO}_2
\end{array}}
\]

Yield: 97%, white solid. mp: 92 – 94 °C. 95% ee, \([\alpha]_D^{26} -64.4 (c 1.0, \text{CH}_2\text{Cl}_2)\), Chiralcel OD-H column (25 cm \(\times\) 0.46 cm ID), \(n\)-hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detector, \(t_R = 25.54\) min (minor) and \(t_R = 33.14\) min (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 – 7.80 (m, 3H, Ar-\(H\)), 7.68 (m, 1H, Ar-\(H\)), 7.52 – 7.45 (m, 2H, Ar-\(H\)), 7.36 (dd, \(J = 8.5, 2.0\) Hz, 1H, Ar-\(H\)), 4.66 (dd, \(J = 12.0, 7.2\) Hz, 1H, CH\(_2\)), 4.58 (dd, \(J = 12.0, 8.4\) Hz, 1H, CH\(_2\)), 3.86 – 3.77 (m, 1H, CH), 1.48 (d, \(J\)
= 7.2 Hz, 3H, CH₃).¹³C NMR (100 MHz, CDCl₃) δ 138.2, 133.5, 132.7, 128.8, 127.73, 127.66, 126.4, 126.1, 125.8, 124.8, 81.8, 38.8, 18.8.

(-)-5-(1-nitropropan-2-yl)benzo[d][1,3]dioxole (2m)

Yield: 97%, colorless oil. 93% ee, [α]D²⁻⁻⁵.70 (c 1.0, CH₂Cl₂), Chiralcel OJ-H column (25 cm x 0.46 cm ID), n-hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detector, tᵣ = 31.83 min for (minor) and tᵣ = 34.82 min (major).¹H NMR (400 MHz, CDCl₃) δ 6.77 – 6.75 (m, 1H, Ar-H), 6.71 – 6.67 (m, 2H, Ar-H), 5.95 (s, 2H), 4.51 – 4.41 (m, 2H, CH₂), 3.60 – 3.51 (m, 1H, CH), 1.34 (d, J = 7.2 Hz, 3H, CH₃).¹³C NMR (100 MHz, CDCl₃) δ 148.1, 146.9, 134.6, 120.1, 108.6, 101.1, 82.0, 38.5, 18.9.


(+)-(3-methyl-4-nitrobutyl)benzene (2o)

Yield: 92%, colorless oil. 91% ee, [α]D²⁸⁺⁺20.7 (c 2.2, CH₂Cl₂), Chiralcel OJ-H column (25 cm x 0.46 cm ID), n-hexane/2-propanol = 98:2, 1.0 mL/min, 210 nm UV detector, tᵣ = 21.55 min (major) and tᵣ = 23.70 min (minor).¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.18 (m, 2H, Ar-H), 7.12 – 7.07 (m, 3H, Ar-H), 4.23 (dd, J = 11.6, 6.0 Hz, 1H, CH₂), 4.11 (dd, J = 11.6, 7.6 Hz, 1H, CH₂), 2.58 – 2.65 (m, 1H, CH₂), 2.55 – 2.48 (m, 1H, CH₂), 2.29 – 2.21 (m, 1H, CH), 1.67 – 1.58 (m, 1H, CH₂), 1.52 – 1.43 (m, 1H, CH₂), 0.97 (d, J = 6.8 Hz, 3H).¹³C NMR (100 MHz, CDCl₃) δ 141.1, 128.4, 128.2, 126.0, 81.3, 35.3, 32.7, 32.2, 17.0. HRMS (ESI) calcd for [C₁₁H₁₅NO₂Na, M⁺Na]⁺: 216.0995, Found 216.0987.

(+)-2-(3-methyl-4-nitrobutyl)naphthalene (2p)

Yield: 90%, colorless oil. 85% ee, [α]D³¹⁺⁺22.2 (c 2.4, CH₂Cl₂), Chiralcel OD-H column (25 cm x 0.46 cm ID), n-hexane/2-propanol = 95:5, 1.0 mL/min, 210 nm UV detector, tᵣ = 17.08 min (minor) and tᵣ = 19.18 min (major).¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.78 (m, 3H, Ar-H), 7.62 (s, 1H, Ar-H), 7.49 – 7.42 (m, 2H, Ar-H), 7.32 (d, J = 8.4 Hz, 1H, Ar-H), 4.38 (dd, J = 11.6, 6.0 Hz, 1H, CH₂), 4.26 (dd, J = 11.6, 8.0 Hz, 1H, CH₂), 2.93 – 2.86 (m, 1H, CH₂), 2.83 – 2.75 (m, 1H, CH₂), 2.46 – 2.34 (m, 1H, CH), 1.87 – 1.79 (m, 1H, CH₂), 1.72 – 1.63 (m, 1H, CH₂), 1.12 (d, J = 6.8 Hz, S22
3H, CH3). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 138.6, 133.5, 131.9, 128.0, 127.5, 127.3, 126.9, 126.2, 125.9, 125.2, 81.2, 35.0, 32.7, 32.1, 16.9. HRMS (ESI) calcd for [C\(_{15}\)H\(_{18}\)NO\(_2\), M+H]\(^+\): 244.1332, Found 244.1103.

\(\text{(+)-5-(3-methyl-4-nitrobutyl)benzod[1,3]dioxole (2q)}\)

Yield: 97%, colorless oil. 85% ee, \([\alpha]_D^{31}\) +24.0 (c 2.1, CH\(_2\)Cl\(_2\)), Chiralcel OD-H column (25 cm × 0.46 cm ID), n-hexane/2-propanol = 95:5, 1.0 mL/min, 210 nm UV detector, \(t_R = 19.82\) min (minor) and \(t_R = 21.75\) min (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 6.73 (d, \(J = 7.6\) Hz, 1H, Ar-H), 6.65 (s, 1H, Ar-H), 6.61 (d, \(J = 8.0\) Hz, 1H, Ar-H), 5.92 (s, 2H, CH\(_2\)), 4.33 (dd, \(J = 11.6, 6.4\) Hz, 1H, CH\(_2\)), 4.22 (dd, \(J = 11.6, 8.0\) Hz, 1H, CH\(_2\)), 2.68 – 2.60 (m, 1H, CH\(_2\)), 2.58 – 2.50 (m, 1H, CH\(_2\)), 2.40 – 2.28 (m, 1H, CH), 1.72 – 1.63 (m, 1H, CH\(_2\)), 1.58 – 1.49 (m, 1H, CH\(_2\)), 1.07 (d, \(J = 6.8\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 147.7, 145.8, 134.9, 121.0, 108.6, 108.2, 100.8, 81.4, 35.6, 32.5, 32.1, 17.0. HRMS (ESI) calcd for [C\(_{12}\)H\(_{16}\)NO\(_2\), M+H]\(^+\): 238.1074, Found 238.1093.

\(\text{(+)-4-methyl-5-nitropentyl} - 1\text{-tosyl-1H-indole (2r)}\)

Yield: 91%, colorless oil. 85% ee, \([\alpha]_D^{29}\) +12.2 (c 2.0, CH\(_2\)Cl\(_2\)), Chiralpad AS-H column (25 cm × 0.46 cm ID), n-hexane/2-propanol = 98:2, 1.0 mL/min, 210 nm UV detector, \(t_R = 7.07\) min (minor) and \(t_R = 7.40\) min (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.29 – 7.26 (m, 2H, Ar-H), 7.23 – 7.15 (m, 3H, Ar-H), 4.28 (dd, \(J = 11.6, 6.4\) Hz, 1H, CH\(_2\)), 4.15 (dd, \(J = 11.6, 8.0\) Hz, 1H, CH\(_2\)), 2.66 – 2.55 (m, 2H, CH\(_2\)), 2.39 – 2.27 (m, 1H, CH), 1.75 – 1.56 (m, 2H, CH\(_2\)), 1.46 – 1.37 (m, 1H, CH\(_2\)), 1.33 – 1.24 (m, 1H, CH\(_2\)), 1.00 (d, \(J = 6.8\) Hz, 3H, CH\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 141.8, 128.32, 128.27, 125.8, 81.5, 35.7, 33.2, 32.6, 28.3, 17.0. HRMS (ESI) calcd for [C\(_{12}\)H\(_{17}\)NO\(_2\)Na, M+Na]\(^+\): 230.1151, Found 230.1141.

\(\text{(+)-3-(3-methyl-4-nitrobutyl)-1-tosyl-1H-indole (2s)}\)

Yield: 91%, white solid, mp: 80 – 82 °C. 77% ee, \([\alpha]_D^{33}\) +13.2 (c 1.0, CH\(_2\)Cl\(_2\)), Chiralpad AD-H column (25 cm × 0.46 cm ID), n-hexane/2-propanol = 85:15, 1.0 mL/min, 220 nm UV detector, \(t_R = 15.15\) min (minor) and \(t_R = 17.80\) min (major). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.98 (d, \(J = 8.0\) Hz, 1H, Ar-H), 7.74 (d, \(J = 7.6\) Hz, 2H, Ar-H), 7.45 (d, \(J = 7.6\) Hz, 1H, Ar-H), 7.33 – 7.29 (m, 2H, Ar-H), 7.24 (d,
J = 8.0 Hz, 1H, Ar-H), 7.20 (d, J = 8.0 Hz, 2H, Ar-H), 4.34 (dd, J = 11.6, 6.4 Hz, 1H, CH₂), 4.23 (dd, J = 11.2, 7.6 Hz, 1H, CH₂), 2.80 – 2.64 (m, 2H, CH₂), 2.40 – 2.35 (m, 1H, CH), 2.31 (s, 3H, CH₃), 1.83 – 1.74 (m, 1H, CH₂), 1.68 – 1.59 (m, 1H, CH), 1.08 (d, J = 6.4 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 135.3, 135.1, 130.6, 129.8, 126.7, 124.7, 123.0, 122.6, 122.0, 119.2, 113.8, 81.2, 76.7, 32.7, 32.3, 21.9, 21.5, 17.0. HRMS (ESI) calcd for [C₂₀H₂₂N₂O₄SNa⁺]: 409.1192, Found 409.1245.

(+) -2-methyl-1-nitroheptane (2t)⁹

Yield: 92%, colorless oil. 80% ee, [α]²⁰ D +5.2 (c 1.2, CH₂Cl₂), GC condition: Coating CP Chirasil-DEX CB, CP7502, dᵣ = 0.25 μm, 0.25 mm i.d. x 25 m, carrier gas: N₂ (0.8 mL/min), inject temperature: 230 °C, initial temperature: 50 °C, hold 30 min then temperature programmed, programming rate: 1.0 °C /min, final temperature: 190 °C. tᵣ = 77.74 min (minor) and tᵣ = 78.24 min (major). ¹H NMR (400 MHz, CDCl₃) δ 4.31 (dd, J = 11.6, 6.4 Hz, 1H, CH₂), 4.17 (dd, J = 11.6, 9.0 Hz, 1H, CH₂), 2.35 – 2.27 (m, 1H, CH), 1.40 – 1.24 (m, 6H, CH₂), 1.00 (d, J = 6.8 Hz, 3H, CH₃), 0.90 (t, J = 6.8 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 81.7, 33.4, 32.7, 28.6, 22.6, 17.1, 13.9.

(+) -2,3-dimethyl-1-nitrobutane (2u)

Yield: 88%, colorless oil. 90% ee, [α]²⁰ D +9.4 (c 1.0, CH₂Cl₂), GC condition: Coating CP Chirasil-DEX CB, β225, dᵣ = 0.25 μm, 0.25 mm i.d. x 25 m, carrier gas: N₂ (1.0 mL/min), inject temperature: 230 °C, initial temperature: 50 °C, hold 20 min then temperature programmed, programming rate: 1.0 °C /min, final temperature: 200 °C. tᵣ = 75.66 min (minor) and tᵣ = 75.83 min (major). ¹H NMR (400 MHz, CDCl₃) δ 4.39 (dd, J = 11.6, 5.6 Hz, 1H, CH₂), 4.17 (dd, J = 11.6, 9.0 Hz, 1H, CH₂), 2.30 – 2.20 (m, 1H, CH), 1.72 – 1.64 (m, 1H, CH), 0.95 (t, J = 6.8 Hz, 6H, CH₃), 0.90 (d, J = 6.8 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 80.2, 38.2, 30.1, 19.8, 18.0, 13.3.

(+) -(1-nitropropan-2-y) cyclohexane (2v)

Yield: 90%, colorless oil. 95% ee, [α]²⁰ D +12.8 (c 1.4, CH₂Cl₂), GC condition: Coating CP Chirasil-DEX CB, CP7502, dᵣ = 0.25 μm, 0.25 mm i.d. x 25 m, carrier gas: N₂ (0.8 mL/min), inject temperature: 230 °C, initial temperature: 40
S, hold 30 min then temperature programmed, programming rate: 0.6 °C /min, final temperature:
190 °C. \( t_R = 157.49 \) min (minor) and \( t_R = 158.18 \) min (major).\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 4.41 (dd, \( J = 11.6, 6.0 \) Hz, 1H, CH\(_2\)), 4.17 (dd, \( J = 11.6, 8.8 \) Hz, 1H, CH\(_2\)), 2.27 – 2.17 (m, 1H, CH), 1.77 – 1.74 (m, 2H, CH\(_2\)), 1.68 – 1.63 (m, 3H, CH\(_2\) and CH), 1.34 – 1.12 (m, 4H, CH\(_2\)), 1.11 – 0.99 (m, 2H, CH\(_2\)), 0.96 (d, \( J = 6.8 \) Hz, 3H).\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 80.2, 40.4, 37.8, 30.2, 28.7, 26.4, 26.3, 26.2, 14.0.

\((-\))-(3-methyl-4-nitrobutyl)isoindole-1,3-dione (2w)

Yield: 96%, white solid, mp: 76 – 78 °C. 84% ee, \([\alpha]_D^{27} +18.4 \) (c 2.1, CH\(_2\)Cl\(_2\)), SFC Chiralcel OD column (25 cm × 0.46 cm ID), sc CO\(_2\)/2-propanol = 90:10, 1.0 mL/min, column backpressure = 100 bar, 220 nm UV detector, \( t_R = 15.17 \) min (major) and \( t_R = 16.73 \) min (minor). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.84 – 7.82 (m, 2H, Ar-H), 7.72 – 7.71 (m, 2H, Ar-H), 4.41 (dd, \( J = 12.0, 5.6 \) Hz, 1H, CH\(_2\)), 4.29 (dd, \( J = 11.6, 8.0 \) Hz, 1H, CH\(_2\)), 3.75 (t, \( J = 6.8 \) Hz, 2H, CH\(_2\)), 2.36 – 2.28 (m, 1H, CH), 1.84 – 1.74 (m, 1H, CH\(_2\)), 1.68 – 1.59 (m, 1H, CH\(_2\)), 1.11 (d, \( J = 6.8 \) Hz, 3H, CH\(_3\)).\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.2, 134.1, 131.9, 123.3, 80.8, 35.2, 32.3, 30.2, 17.0. HRMS (ESI) calcd for [C\(_{13}\)H\(_{14}\)N\(_2\)O\(_4\)Na, M+Na]\(^+\): 285.0846, Found 285.0859.
5. NMR Spectra for New Compounds

(R)-(7'-(diphenylphosphanyloxy)-1,1'-spirobiinane-7-yl)propan-2-amine (6g)
(R)-(7'-Di(3,5-tert-butylphenyl)-phosphion)-1,1'-spiropinane-7-yl)propan-2-amine (6d)
(R)-(7'-Di(3,5-tert-butylphenyl)-phosphion)-1,1'-spirobiinane-7-yl)pntan-3-amine (6e)
(S)-(7'-Di(3,5-tert-butylphenyl)-phosphion)-1,1'-spirobiinane-7-yl)diphenylmethanamine

(6f)
(E)-(1-nitroprop-1-en-2-yl)benzene (1a)
(E)-1-methyl-4-(1-nitroprop-1-en-2-yl)benzene (1b)
(E)-1-methoxy-4-(1-nitroprop-1-en-2-yl)benzene (1c)
(E)-1-chloro-4-(1-nitroprop-1-en-2-yl)benzene (1d)
(E)-1-fluoro-4-(1-nitroprop-1-en-2-yl)benzene (1e)
(E)-methyl 4-((1-nitroprop-1-en-2-yl)benzoate (1f)
(E)-4-(1-nitroprop-1-en-2-yl)benzonitrile (1g)
(E)-1-nitro-4-(1-nitroprop-1-en-2-yl)benzene (1h)
(E)-1-methoxy-3-(1-nitroprop-1-en-2-yl)benzene (1i)
(E)-1-chloro-3-(1-nitroprop-1-en-2-yl)benzene (1j)
(E)-6-(1-nitroprop-1-en-2-yl)-1,2,3,4-tetrahydronaphthalene (1k)
(E)-2-(1-nitroprop-1-en-2-yl)naphthalene (II)
(E)-5-(1-nitroprop-1-en-2-yl)benzo[d][1,3]dioxole (1m)
(3-methyl-4-nitrobut-3-en-1-yl)benzene (1o)
2-(3-methyl-4-nitrobut-3-en-1-yl)naphthalene (1p)
5-(3-methyl-4-nitrobupro-3-en-1-yl)benzo[d][1,3]dioxole (1q)
(4-methyl-5-nitropent-4-en-1-yl)benzene (1r)
(E)-3-(3-methyl-4-nitrobut-3-en-1-yl)-1-tosyl-1H-indole (1s)
2-methyl-1-nitrohex-1-ene (1t)
2,3-dimethyl-1-nitrobut-1-ene (1u)
(1-nitroprop-1-en-2-yl)cyclohexane (1v)
2-(3-methyl-4-nitrobut-3-en-1-yl)isoindoline-1,3-dione (1w)
(-)-(1-nitropropan-2-yl)benzene (2a)
(-)-1-methoxy-4-(1-nitropropan-2-yl)benzene (2c)
(-)-1-fluoro-4-(1-nitropropan-2-yl)benzene (2e)

Parameter | Value
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2 Title | ypb-14-169-F-15C/12-P-1
3 Comment | 1M0720
4 Origin | Bruker BioSpin GmbH
5 Owner | common
6 Site | spectrometer
7 Author | dkm
8 Solvent | CDC13
9 Temperature | 293.6
10 Pulse Sequence | npp9
11 Experiment | 10
12 Number of scans | 6
13 Number of scans | 6
14 Havrany Gain | 200
15 Relaxation Delay | 0.0000
16 Pulse Width | 12.0000
17 Acquisition | 0.0000
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19 Acquisition | 0.0000
20 Acquisition | 0.0000
21 Spectral Width | 2.517 Hz
22 Lowest Frequency | -1.8377 Hz
23 Nuclear | 13C
24 Acquired Size | 244720
25 Spectral Size | 80336

Parameter | Value
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1 Data File Name | 2e/D ata/NMR/201506/ypb-14-169-F-15C/12-P-1
2 Title | ypb-14-169-F-15C/12-P-1
3 Comment | 1M0720
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6 Site | spectrometer
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8 Solvent | CDC13
9 Temperature | 293.6
10 Pulse Sequence | npp9
11 Experiment | 10
12 Number of scans | 6
13 Number of scans | 6
14 Havrany Gain | 200
15 Relaxation Delay | 0.0000
16 Pulse Width | 12.0000
17 Acquisition | 0.0000
18 Acquisition | 0.0000
19 Acquisition | 0.0000
20 Acquisition | 0.0000
21 Spectral Width | 2.517 Hz
22 Lowest Frequency | -1.8377 Hz
23 Nuclear | 13C
24 Acquired Size | 244720
25 Spectral Size | 80336
(-)-methyl 4-(1-nitropropan-2-yl)benzoate (2f)
(−)-4-(1-nitropropan-2-yl)benzonitrile (2g)
(-)-1-chloro-3-(1-nitropropan-2-yl)benzene (2j)
(-)-2-(1-nitropropan-2-yl)naphthalene (2l)
(+)-(3-methyl-4-nitrobutyl)benzene (2o)
(+)-5-(3-methyl-4-nitrobutyl)benzo[d][1,3]dioxole (2q)
(+)-(4-methyl-5-nitropentyl)benzene (2r)
(+)-3-(3-methyl-4-nitrobutyl)-1-tosyl-1H-indole (2s)
(+)-2-methyl-1-nitroheptane (2t)
(+)-(1-nitropropan-2-yl)cyclohexane (2v)
(+)-2-(3-methyl-4-nitrobutyl)isoindoline-1,3-dione (2w)
1-methyl-4-(1-nitropropan-2-yl)benzene (2b-d)

5-(3-methyl-4-nitrobutyl)benzo[d][1,3]dioxole (2p-d)
6. GC, HPLC or SFC Charts of Hydrogenation Products

(1-nitropropan-2-yl)benzene (2a)
1-methyl-4-(1-nitropropan-2-yl)benzene (2b)

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1-methoxy-4-(1-nitropropan-2-yl)benzene (2c)
1-chloro-4-(1-nitropropan-2-yl)benzene (2d)
1-fluoro-4-(1-nitropropan-2-yl)benzene (2e)

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %

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Methyl 4-(1-nitropropan-2-yl)benzoate (2f)

**Chemical Structure**

![Chemical Structure Image]

**HPLC Analysis**

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4-(1-nitropropan-2-yl)benzonitrile (2g)

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# [min] [min] mAU *s [mAU ]
1 14.786 BB 0.2599 41.94287 2.37471 1.3793
2 15.808 BB 0.2895 2998.93623 159.28508 98.6207
1-nitro-4-(1-nitropropan-2-yl)benzene (2h)

![Graph of 1-nitro-4-(1-nitropropan-2-yl)benzene](image)

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1-methoxy-3-(1-nitropropan-2-yl)benzene (2i)
1-chloro-3-(1-nitropropan-2-yl)benzene (2j)

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6-(1-nitropropan-2-yl)-1,2,3,4-tetrahydronaphthalene (2k)
2-(1-nitropropan-2-yl)naphthalene (21)

![Chemical Structure of 2-(1-nitropropan-2-yl)naphthalene](image)

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5-(1-nitropropan-2-yl)benzo[d][1,3]dioxole (2m)
(3-methyl-4-nitrobutyl)benzene (2o)

Peak | RetTime | Type | Width | Area | Height | Area |
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1    | 21.546  | BB   | 0.6489| 3.1955e4 | 756.38763 | 95.4596 |
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2-(3-methyl-4-nitrobutyl)naphthalene (2p)

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5-(3-methyl-4-nitrobutyl)benzo[d][1,3]dioxole (2q)

![Chemical Structure](image)

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(4-methyl-5-nitropentyl)benzene (2r)

**Peaks Table**

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3-(3-methyl-4-nitrobutyl)-1-tosyl-1H-indole (2s)
2-methyl-1-nitroheptane (2t)

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2,3-dimethyl-1-nitrobutane (2u)

\[
\begin{align*}
\text{(t-)} & \quad \text{Me} & \quad \text{Me} & \quad \text{NO}_2 \\
\text{(+) & \quad \text{Me} & \quad \text{Me} & \quad \text{NO}_2}
\end{align*}
\]

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(1-nitropropan-2-yl)cyclohexane (2v)

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1 157.485 BV 0.2523 15.22097 9.13826e-1 2.42731
2 158.178 VB 0.5204 611.85028 15.11144 97.57269
2-(3-methyl-4-nitrobutyl)isoindoline-1,3-dione (2w)

Peak RetTime Type Width Area Height Area
# [min] [min] mAU *s [mAU ] %
1 15.168 VV 0.3581 4.20153e4 1840.01318 92.2194
2 16.730 VB 0.3740 3544.86597 147.25780 7.7806
7. References