Supporting Information for

Hetero-bifunctional catalyst manipulates carbonyl and alkynyl reductions of conjugated alkynones in an aqueous medium

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Experimental

1). General

All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using the standard Schlenk techniques. Tetraethoxysilane (TEOS), 1,4-bis(triethoxy)silyl)ethane, cetyltrimethylammonium bromide (CTAB), fluorocarbon surfactant (FC-4: \( [\text{C}_3\text{F}_7\text{O(CF(CF}_3\text{)CF}_2\text{O}_2\text{CF(CF}_3\text{)}\text{CONH(CH}_2\text{)_3N}^+ (\text{C}_2\text{H}_5)_2\text{CH}_3]^- \)), 4-(2-(trimethoxysilyl)ethyl)benzene-1-sulfonyl chloride, Triethylenediamine (DABCO), 4-(methylphenylsulfonyl)-1,2-diphenylethlenediamine \(((S,S)-\text{TsDPEN})\), \((\text{MesityleneRuCl}_2)_2\) were purchased from Sigma-Aldrich Company Ltd and used as received.

2). Characterization

Ru and Pd loading amounts in the catalysts were analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna 550 spectrometer using KBr method. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV. Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000C ESCA system. A 200 μm diameter spot size was scanned using a monochromatized Aluminum Ka X-ray source (1486.6.6 eV) at 40 W and 15 kV with 58.7 eV pass energies. All the binding energies were calibrated by using the contaminant carbon \((\text{C}_{1s} = 284.6 \text{ eV})\) as a reference. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas \((S_{\text{BET}})\) of samples were determined from the linear parts of BET plots \((p/p_0 = 0.05-1.00)\). Solid state NMR experiments were explored on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with \(^1\text{H} \) frequency of 400.1 MHz, \(^{13}\text{C} \) frequency of 100.5 MHz, and \(^{29}\text{Si} \) frequency of 79.4 MHz with 4 mm rotor at two spinning frequency of 5.5 kHz and 8.0 kHz, TPPM decoupling is applied in the during acquisition period. \(^1\text{H} \) cross polarization in all solid state NMR experiments was employed using a contact time of 2 ms and the pulse lengths of 4μs.
Figure S1. FT-IR spectra of 4 and catalyst 5.

Figure S2. Small-angle powder XRD patterns of 4 and catalyst 5.
Table S1. Optimizing reaction conditions for the 5-catalysed enantioselective cascade reactions of (4-(phenylethynyl)phenyl)ethanone.

![Image of catalyst 5 catalyzing the reaction]

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Reaction conditions: Catalyst 5 (4.38 mol% of Pd based on ICP analysis), HCOO$_2$Na (1.0 mmol), alkynone (0.10 mmol), and 2.0 mL of solvent were added sequentially to a 10.0 mL round–bottom flask. Yields were determined by $^1$H–NMR analysis and ee values were determined by chiral HPLC analysis.
Figure 3. The HPLC analysis for chiral products. (Table 1 in manuscript: The selective ATH/reduction one-pot enantioselective cascade reductions of conjugated alkynones.)

7a. (S)-1-(4-phenethylphenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C). [Literature (Chem. Eur. J. 2010, 16, 6748): HPLC: Chiracel AD-H, eluent: n-hexane/2-propanol = 95/5, flow rate = 0.7 mL/min, detected at 254 nm, Retention time: 10.98 min (S), 12.16 min (R).]

Translation of Chinese to English is as follows:
7b. (S)-1-(4-(4-fluorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:
7c. (S)-1-(4-(3-fluorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).
7d. (S)-1-(4-(4-chlorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).
7e. (S)-4-(4-(1-hydroxyethyl)phenethyl)benzonitrile: (HPLC: Chiracel OD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 ℃).

Translation of Chinese to English is as follows:
7f. (S)-1-(4-(4-nitrophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:

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7g. (S)-1-(4-(4-methylphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:

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7h. (S)-1-(4-(3-methylphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C ).

Translation of Chinese to English is as follows:
7i. (S)-1-(4-(4-methoxyphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).
7j. (S)-1-(4-(3-methoxyphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:
7k. (S)-1-(3-phenethylphenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:

**Name** | **ReTime** [min] | **Peak** | **Area** | **Heigh** | **Area%**
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1 | 3322.600 | 32.600 | 1 | 26100.00 | 551980 | 95.3241
2 | 3325.100 | 25.100 | 2 | 477973 | 11049 | 1.6059
71. (S)-1-(3-(4-fluorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:

Translation of Chinese to English is as follows:
7m. (S)-1-(3-(3-fluorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 ºC).

Translation of Chinese to English is as follows:

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2 | 8373.650 | 10.650 | 2 | 991750 | 9.7000 | 19790 | 0.6275  

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7n. (S)-1-(3-(4-chlorophenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:
7o. (S)-1-(3-(4-methylphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).

**Translation of Chinese to English is as follows:**

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2 | 33.25 | 100 | 2 | 4777073 | 11049 | 1.6059
7p. (S)-1-(3-(3-methylphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:
7q. (S)-1-(3-(4-methoxyphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel AS-H, detected at 254 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 1.0 mL/min, 25 ℃).

Translation of Chinese to English is as follows:

**Name**

**ReTime [min]**

**Peak**

**Area**

**Heigh**

**Area%**

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7r. (S)-1-(3-(3-methoxyphenethyl)phenyl)ethan-1-ol: (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).
7s. (S)-1-(4-hexylphenyl)ethan-1-ol: (HPLC: Chiracel OD-H, detected at 215 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 ℃).

Translation of Chinese to English is as follows:
7t. (1S,1'S)-1,1'-(ethane-1,2-diylbis(4,1-phenylene))bis(ethan-1-ol): (HPLC: Chiracel OB-H, detected at 254 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 1.0 mL/min, 25 °C).

Translation of Chinese to English is as follows:
Figure 4. Reusability of catalyst 5 for the enantioselective cascade reductions of conjugated alkyrones.

Recycle 1

Recycle 2

Recycle 3

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Recycle 4

Recycle 5

Translation of Chinese to English is as follows:
Recycle 6

Recycle 7

Translation of Chinese to English is as follows:
Figure 5. The characterizations of chiral products (Table 1 in manuscript).

7a. *(S)*-1-(4-phenethylphenyl)ethan-1-ol. White solid, 99% yield, 97% ee. $[\alpha]_{D}^{25} = -25.891$ (c 0.216. CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 (dd, $J = 7.6$, 5.7 Hz, 4H), 7.21 (dt, $J = 8.2$, 5.5 Hz, 5H), 4.89 (q, $J = 6.4$ Hz, 1H), 2.94 (s, 4H), 1.88 (brs, 1H), 1.51 (d, $J = 6.6$z Hz, 3H). $^{13}$C[$^1$H] NMR (100 MHz, CDCl$_3$): $\delta$ 143.5, 141.8, 141.0, 128.6, 128.5, 128.4, 126.0, 125.5, 70.2, 37.9, 37.6, 25.1. HRMS (ESI): m/z [M+Na]$^+$ calculated for C$_{16}$H$_{18}$ONa$: 249.1250; found: 249.1251. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7a ($^1$H NMR, $^{13}$C NMR spectra).
7b. (S)-1-(4-(4-fluorophenethyl)phenyl)ethan-1-ol. White solid, 93% yield, 95% ee. [α]D25 = -29.648 (c 0.256, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.21 (t, J = 8.8 Hz, 2H), 7.12 – 6.99 (m, 4H), 6.88 (d, J = 8.6 Hz, 2H), 4.82 (q, J = 6.5 Hz, 1H), 2.82 (s, 4H), 1.70 (brs, 1H), 1.43 (d, J = 6.5 Hz, 3H). 13C{1H} NMR (100 MHz, CDCl3) δ 161.3 (d, J = 243 Hz), 143.5, 140.7, 137.3, 129.8, 128.6, 125.5, 114.9, 70.2, 37.6, 37.0, 25.1. HRMS (ESI): m/z [M+Na]+ calculated for C16H17FONa+: 267.1156; found: 267.1156. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7b (1H NMR, 13C NMR spectra).
7c. (S)-1-(4-(3-fluorophenethyl)phenyl)ethan-1-ol. Yellow liquid, 92% yield, 94% ee. $[\alpha]_D^{25} = -28.785$ (c 0.378, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 8.2$ Hz, 2H), 7.25 – 7.20 (m, 1H), 7.16 (d, $J = 8.2$ Hz, 2H), 6.94 (d, $J = 7.7$ Hz, 1H), 6.93 – 6.87 (m, 2H), 4.89 (q, $J = 6.5$ Hz, 1H), 2.91 (s, 4H), 1.79 (brs, 1H), 1.50 (d, $J = 6.2$ Hz, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 162.9 (d, $J = 245$ Hz), 144.2 (d, $J = 6.5$ Hz), 143.6, 140.6, 129.8 (d, $J = 8.7$ Hz), 128.5, 125.5, 124.1 (d, $J = 2.3$ Hz), 115.3 (d, $J = 20.9$ Hz), 112.8 (d, $J = 21.5$ Hz), 70.2, 37.6, 37.5, 37.2, 25.1. HRMS (ESI): m/z [M+Na]$^+$ calculated for C$_{16}$H$_{17}$FONa$: 267.1156; found: 267.1158. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7c ($^1$H NMR, $^{13}$C NMR spectra). (S)-1-(4-(3-fluorophenethyl)phenyl)ethan-1-ol.
7d. (S)-1-(4-(4-chlorophenethyl)phenyl)ethan-1-ol. White solid, 94% yield, 95% ee. $[\alpha]_D^{25} = -33.289$ (c 0.216, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.20 (m, 4H), 7.16 – 7.10 (m, 4H), 4.82 (qd, $J = 6.4$, 2.2 Hz, 1H), 2.86 – 2.85 (d, $J = 2.5$ Hz, 4H), 1.69 (brs, 1H), 1.43 (dd, $J = 6.7$, 2.4 Hz, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 143.5, 141.8, 141.1, 128.6, 128.5, 128.4, 126.0, 125.5, 70.3, 37.9, 37.6, 25.1. HRMS (ESI): m/z [M+Na]$^+$ calculated for C$_{16}$H$_{17}$ClONa$: 283.0860; found: 283.0861. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7d ($^1$H NMR, $^{13}$C NMR spectra).
7e. **(S)-4-(4-(1-hydroxyethyl)phenethyl)benzonitrile.** White solid, 91% yield, 94% ee. \( [\alpha]_D^{25} = -7.467 \) (c 0.214, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.56 (d, \( J = 8.2 \) Hz, 2H), 7.29 (d, \( J = 8.0 \) Hz, 2H), 7.25 (d, \( J = 8.0 \) Hz, 2H), 7.12 (d, \( J = 8.1 \) Hz, 2H), 4.89 (q, \( J = 6.5 \) Hz, 1H), 3.06 – 2.83 (m, 4H), 1.69 (brs, 1H), 1.49 (d, \( J = 6.5 \) Hz, 3H). \(^13\)C\(^{1}\)H NMR (100 MHz, CDCl₃) \( \delta \) 147.2, 143.8, 139.9, 132.2, 129.3, 128.5, 125.6, 119.0, 109.0, 70.2, 37.9, 36.8, 25.2. HRMS (ESI): m/z \([M+NH_4]^+\) calculated for C\(_{17}\)H\(_{21}\)N\(_2\)O\(^+\): 269.1650; found: 269.1648. HPLC (Chiralpak OD-H, detector: 215 nm, elute: Hexane/i-PrOH = 95/5, flow rate: 1.0 mL/min, 25 °C).

7e \( (^1\)H NMR, \(^13\)C NMR spectra).
7f. (S)-1-(4-(4-nitrophényl)phenyl)ethan-1-ol. Brown solid, 83% yield, 99% ee. $[\alpha]_D^{25} = -4.781$ (c 0.376, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 8.7$ Hz, 2H), 7.30 (d, $J = 7.2$ Hz, 4H), 7.13 (d, $J = 8.1$ Hz, 2H), 4.89 (q, $J = 6.5$ Hz, 1H), 3.03 – 2.94 (m, 4H), 1.70 (s, 1H), 1.49 (d, $J = 6.5$ Hz, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 149.3, 146.5, 143.9, 139.7, 129.3, 128.5, 123.6, 70.2, 37.6, 36.8, 25.2. HRMS (ESI): m/z [M+NH$_4$]$^+$ calculated for C$_{16}$H$_{21}$N$_2$O$_3$: 289.1548; found: 289.1547. HPLC (Chiralpak ODH, detector: 254 nm, elute: Hexane/i-PrOH = 96/4, flow rate: 1.0 mL/min, 25 °C).

7f ($^1$H NMR, $^{13}$C NMR spectra).
7g. (S)-1-(4-(4-methylphenethyl)phenyl)ethan-1-ol. White solid, 95% yield, 95% ee. [α]_D^{25} = -20.693 (c 0.222, CHCl_3). $^1$H NMR (400 MHz, Chloroform-d) δ 7.30 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 4.89 (d, J = 6.3 Hz, 1H), 3.80 (s, 3H), 2.87 (q, J = 2.9 Hz, 4H), 1.74 (brs, 1H), 1.50 (d, J = 6.7 Hz, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl_3) δ 143.4, 141.2, 138.7, 135.4, 129.0, 128.6, 128.3, 125.4, 70.3, 37.6, 37.4, 25.1, 21.0. HRMS (ESI): m/z [M+Na]^+ calculated for C_{17}H_{20}ONa: 263.1406; found: 263.1409. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7g ($^1$H NMR, $^{13}$C NMR spectra).
7h. (S)-1-(4-(3-methylphenethyl)phenyl)ethan-1-ol. White solid, 94% yield, 95% ee. [α]D25 = -37.333 (c 0.214, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.30 (dd, J = 8.3, 2.9 Hz, 2H), 7.20 (dd, J = 8.1, 2.8 Hz, 3H), 7.07 – 6.95 (m, 3H), 4.89 (qd, J = 6.5, 2.8 Hz, 1H), 2.90 (h, J = 3.4, 2.5 Hz, 4H), 2.34 (d, J = 3.1 Hz, 3H), 1.80 (brs, 1H), 1.53 – 1.44 (m, 3H). 13C{1H} NMR (100 MHz, CDCl3) δ 143.4, 141.7, 141.3, 137.9, 129.3, 128.6, 128.3, 126.7, 125.5, 125.4, 70.3, 37.9, 37.6, 25.1, 21.4. HRMS (ESI): m/z [M+Na]+ calculated for C17H20ONa+: 263.1406; found: 263.1407. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7h (1H NMR, 13C NMR spectra).
7i. (S)-1-(4-(4-methoxyphenethyl)phenyl)ethan-1-ol. White solid, 95% yield, 94% ee. [α]_D^{25} = -23.941 (c 0.292, CHCl₃). ^1H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 4.88 (q, J = 6.4 Hz, 1H), 3.80 (s, 3H), 2.88 (q, J = 3.0 Hz, 4H), 1.76 (brs, 1H), 1.50 (d, J = 6.6 Hz, 3H). ^13C(^1H) NMR (100 MHz, CDCl₃) δ 157.9, 143.4, 141.2, 133.9, 129.3, 128.6, 125.4, 113.8, 70.3, 55.3, 37.8, 37.0, 25.1. HRMS (ESI): m/z [M+Na]^+ calculated for C₁₇H₂₀O₂Na+: 279.1356; found: 279.1359. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7i (^1H NMR, ^13C NMR spectra).
7j. (S)-1-(4-(3-methoxyphenethyl)phenyl)ethan-1-ol. White solid, 92% yield, 95% ee. [α]_D^{25} = -39.207 (c 0.270, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, J = 8.2 Hz, 2H), 7.20 (dd, J = 7.8, 5.8 Hz, 3H), 6.84 – 6.72 (m, 3H), 4.88 (q, J = 6.5 Hz, 1H), 3.79 (s, 3H), 2.91 (s, 4H), 1.84 (brs, 1H), 1.50 (d, J = 6.5 Hz, 3H). ^13C{^1H} NMR (100 MHz, CDCl_3) δ 159.7, 143.5, 143.4, 141.0, 129.3, 128.6, 125.5, 120.9, 114.28, 111.3, 70.2, 55.2, 37.9, 37.4, 25.1. HRMS (ESI): m/z [M+Na]^+ calculated for C_{17}H_{20}O_2Na^+: 279.1356; found: 279.1361. HPLC (Chiralpak OB-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7j (^1H NMR, ^13C NMR spectra).
7k. (S)-1-(3-phenethylphenyl)ethan-1-ol. Yellow liquid, 93% yield, 95% ee. [α]D<sup>25</sup> = -21.766 (c 0.468, CHCl<sub>3</sub>). H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (q, J = 7.3 Hz, 3H), 7.22 (dd, J = 11.5, 7.5 Hz, 5H), 7.13 (d, J = 7.5 Hz, 1H), 4.87 (q, J = 6.5 Hz, 1H), 2.95 (s, 4H), 1.90 (s, 1H), 1.50 (d, J = 6.5 Hz, 3H). 13C(1H) NMR (100 MHz, CDCl<sub>3</sub>) δ 145.9, 142.1, 141.8, 128.6, 128.4, 127.6, 126.0, 125.6, 123.1, 70.5, 38.1, 38.0, 25.2. HRMS (ESI): m/z [M+Na]<sup>+</sup> calculated for C<sub>16</sub>H<sub>18</sub>ONa<sup>+</sup>: 249.1250; found: 249.1252. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7k (1H NMR, 13C NMR spectra).
**7l. (S)-1-(3-(4-fluorophenethyl)phenyl)ethan-1-ol.** Yellow liquid, 91% yield, 94% ee. \([\alpha]_D^{25} = -33.116\) (c 0.386, CHCl₃). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta 7.21\) (t, \(J = 7.5\) Hz, 1H), \(7.14\) (d, \(J = 7.6\) Hz, 1H), \(7.09\) (s, 1H), \(7.07 - 6.99\) (m, 3H), \(6.89\) (t, \(J = 8.7\) Hz, 2H), \(4.80\) (q, \(J = 6.4\) Hz, 1H), \(2.84\) (s, 4H), \(1.82\) (brs, 1H), \(1.41\) (d, \(J = 6.2\) Hz, 3H). \(^{13}\)C\(^{1}\)H NMR (100 MHz, CDCl₃) \(\delta 161.4\) (d, \(J = 245\) Hz), \(145.9\), \(141.7\), \(137.3\) (d, \(J = 3.2\) Hz), \(129.8\) (d, \(J = 7.4\) Hz), \(128.5\), \(127.6\), \(125.5\), \(123.1\), \(115.0\) (d, \(J = 21.5\) Hz), \(70.4\), \(38.1\), \(37.1\), \(25.2\). HRMS (ESI): m/z [M+Na]\(^+\) calculated for \(\text{C}_{16}\text{H}_{17}\text{FO}\text{Na}^+\): 267.1156; found: 267.1158. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/i-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

**7l (\(^1\)H NMR, \(^{13}\)C NMR spectra).**
7m. (S)-1-(3-(3-fluorophenethyl)phenyl)ethan-1-ol. Yellow liquid, 90% yield, 94% ee. \([\alpha]_D^{25} = -22.323\) (c 0.340, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.27 – 7.13 (m, 3H), 7.11 (s, 1H), 7.05 (d, \(J = 7.3\) Hz, 1H), 6.91 – 6.82 (m, 3H), 4.79 (q, \(J = 6.4\) Hz, 1H), 2.87 (s, 4H), 2.19 – 2.09 (m, 1H). 1.42 (d, \(J = 6.3\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.9 (d, \(J = 245\) Hz), 146.1, 144.2 (d, \(J = 7.2\) Hz), 141.5, 129.7 (d, \(J = 8.4\) Hz), 128.6, 127.5, 125.4, 124.2 (d, \(J = 2.7\) Hz), 123.2, 115.3 (d, \(J = 21.1\) Hz), 112.8 (d, \(J = 21.1\) Hz), 70.4, 37.6, 37.6, 25.2. HRMS (ESI): \(m/z\) [M+Na]\(^+\) calculated for C\(_{16}\)H\(_{17}\)FONa\(^+\): 267.1156; found: 267.1157. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/i-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7m \(^1\)H NMR, \(^13\)C NMR spectra.
7n. (S)-1-(3-(4-chlorophenethyl)phenyl)ethan-1-ol. Yellow liquid, 91% yield, 93% ee. [α]D²⁵ = -23.839 (c 0.310, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.26 (m, 3H), 7.21 (dt, J = 8.3, 5.9 Hz, 4H), 7.13 (d, J = 7.4 Hz, 1H), 4.87 (q, J = 6.4 Hz, 1H), 3.13 – 2.72 (m, 4H), 1.82 (brs, 1H), 1.49 (d, J = 6.5 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.9, 142.1, 141.7, 128.5, 128.4, 127.6, 126.0, 125.6, 123.1, 70.5, 38.0, 37.9, 25.2. HRMS (ESI): m/z [M+Na]+ calculated for C₁₆H₁₇ClONa⁺: 283.0860; found: 283.0862. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/i-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7n (¹H NMR, ¹³C NMR spectra).
7o. (S)-1-(3-(4-methylphenethyl)phenyl)ethan-1-ol. Yellow liquid, 92% yield, 96% ee. \([\alpha]_{D}^{25} = -24.845\) (c 0.410, CHCl\(_3\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.30\) (t, \(J = 7.5\) Hz, 1H), 7.22 (d, \(J = 9.2\) Hz, 2H), 7.15 – 7.10 (m, 5H), 4.88 (q, \(J = 6.4\) Hz, 1H), 2.97 – 2.88 (m, 4H), 2.36 (s, 3H), 1.93 (s, 1H), 1.50 (d, \(J = 6.2\) Hz, 3H). \(^1\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta 145.9, 142.2, 138.7, 135.4, 129.1, 128.6, 128.4, 127.6, 125.6, 123.1, 70.5, 38.2, 37.6, 25.2, 21.1. HRMS (ESI): m/z [M+Na]^+ calculated for C\(_{17}\)H\(_{20}\)O\(_{2}\)Na\(^+\): 263.1406; found: 263.1414. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/i-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7o (\(^1\)H NMR, \(^{13}\)C NMR spectra).
7p. (S)-1-(3-(3-methylphenethyl)phenyl)ethan-1-ol. Yellow liquid, 92% yield, 95% ee. $[\alpha]_D^{25} = -22.688$ (c 0.493, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 14.9$ Hz, 1H), 7.25 – 7.18 (m, 3H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.09 – 7.01 (m, 3H), 4.88 (q, $J = 6.6$ Hz, 1H), 2.93 (d, $J = 3.4$ Hz, 4H), 2.36 (s, 3H), 1.90 (brs, 1H), 1.51 (d, $J = 6.6$ Hz, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 145.9, 142.2, 141.7, 137.9, 129.3, 128.5, 128.3, 127.6, 126.7, 125.6, 125.5, 123.0, 70.5, 38.1, 38.0, 25.2, 21.4. HRMS (ESI): m/z [M+Na]$^+$ calculated for C$_{17}$H$_{20}$ONa$^+$: 263.1406; found: 263.1409. HPLC (Chiralpak OJ-H, detector: 254 nm, elute: Hexane/i-PrOH = 97/3, flow rate: 1.0 mL/min, 25 °C).

7p ($^1$H NMR, $^{13}$C NMR spectra).
7q. (S)-1-(3-(4-methoxyphenethyl)phenyl)ethan-1-ol. Yellow liquid, 92% yield, 96% ee.

$[\alpha]_D^{25} = -22.122$ (c 0.316, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (t, $J = 7.5$ Hz, 1H), 7.25 – 7.16 (m, 2H), 7.11 (d, $J = 8.6$ Hz, 3H), 6.85 (d, $J = 8.5$ Hz, 2H), 4.87 (q, $J = 6.5$ Hz, 1H), 3.80 (s, 3H), 2.95 – 2.86 (m, 4H), 2.03 (brs, 1H), 1.49 (d, $J = 6.3$ Hz, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ 157.9, 145.9, 142.1, 133.9, 129.4, 128.5, 127.6, 125.6, 123.0, 113.8, 70.4, 55.3, 38.3, 37.1, 25.2. HRMS (ESI): m/z [M+Na]$^+$ calculated for C$_{17}$H$_{20}$O$_2$Na$: 279.1356$; found: 279.1364. HPLC (Chiralpak AS-H, detector: 254 nm, elute: Hexane/i-PrOH = 96/4, flow rate: 1.0 mL/min, 25 °C).

7q ($^1$H NMR, $^{13}$C NMR spectra).
7r. (S)-1-(3-(3-methoxyphenethyl)phenyl)ethan-1-ol. Yellow liquid, 91% yield, 95% ee. 
\[^{[\alpha]}_D^{25} = -24.247\ (c\ 0.486,\ CHCl_3)\]. 
\[^{1}H\ NMR\ (400\ MHz,\ CDCl_3)\ \delta\ 7.23\ (t, J = 7.4\ Hz, 1H),\ 7.20 – 7.11\ (m, 3H),\ 7.10 – 7.04\ (m, 1H),\ 6.78 – 6.65\ (m, 3H),\ 4.80\ (q, J = 6.5\ Hz, 1H),\ 3.73\ (s, 3H),\ 2.98 – 2.76\ (m, 4H),\ 2.14\ (brs, 1H),\ 1.43\ (d, J = 6.2\ Hz, 3H).\ \[^{13}C\ NMR\ (100\ MHz,\ CDCl_3)\ \delta\ 159.6,\ 146.0,\ 143.4,\ 142.0,\ 129.4,\ 128.6,\ 127.6,\ 125.6,\ 123.1,\ 121.1,\ 114.4,\ 111.3,\ 70.4,\ 55.2,\ 38.0,\ 37.9,\ 25.2.\ HRMS\ (ESI):\ m/z\ [M+Na]^+\ calculated\ for\ C_{17}H_{20}O_{2}Na^+:\ 279.1356;\ found: 279.1364.\ HPLC\ (Chiralpak\ OJ-H,\ detector:\ 254\ nm,\ elute:\ Hexane/i-PrOH = 97/3\ flow\ rate: 1.0\ mL/min, 25 °C).

7r (\[^{1}H\ NMR,\ \[^{13}C\ NMR\ spectra\].)
7s. (S)-1-(4-hexylphenyl)ethan-1-ol. Colorless liquid, 86% yield, 97% ee. [α]D^25 = -5.707 (c 0.350, CHCl₃). \(^1\)H NMR (400 MHz, CHCl₃) δ 7.29 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 4.88 (q, J = 6.4 Hz, 1H), 2.66 – 2.57 (m, 2H), 1.68 (brs, 1H), 1.60 (ddd, J = 9.2, 4.6, 1.5 Hz, 2H), 1.49 (d, J = 6.4 Hz, 3H), 1.32 – 1.29 (m, 6H), 0.90 – 0.86 (m, 3H). \(^1^3\)C{\(^1\)H} NMR (100 MHz, CHCl₃) δ 143.0, 142.3, 128.5, 125.3, 70.3, 35.6, 31.7, 31.5, 29.0, 25.0, 22.6, 14.1. HRMS (ESI): m/z [M+NH₄]^+ calculated for C₁₄H₂₆N0: 224.2111; found: 224.2009. HPLC (Chiralpak OD-H, detector: 215 nm, elute: Hexane/i-PrOH = 98/2, flow rate: 1.0 mL/min, 25 °C).

7s. (\(^1\)H NMR, \(^1^3\)C NMR spectra).
7t. (1S,1'S)-1,1'-[(ethane-1,2-diylbis(4,1-phenylene))bis(ethan-1-ol)]. Colorless liquid, 86% yield, 99% ee, 21:1 dr. $[\alpha]_D^{25} = -9.939$ (c 0.422, CHCl$_3$). $^1$H NMR (400 MHz, CHCl$_3$) $\delta$ 7.30 (d, $J = 8.0$ Hz, 4H), 7.18 (d, $J = 8.0$ Hz, 4H), 4.93 – 4.85 (m, 2H), 2.89 (s, 4H), 1.77 (brs, 2H), 1.49 (d, $J = 9.3$ Hz, 6H). $^{13}$C($^1$H) NMR (101 MHz, Chloroform-d) $\delta$ 143.4, 141.0, 128.5, 125.5, 70.3, 37.5, 25.1. HRMS (ESI): m/z [M+NH$_4$]$^+$ calculated for C$_{18}$H$_{26}$NO$: 288.1960; found: 288.1958. (HPLC: Chiracel OB-H, detected at 254 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 1.0 mL/min, 25 °C).

7t. ($^1$H NMR, $^{13}$C NMR spectra).