supplementary information for

Organocatalytic asymmetric synthesis of β,β-diaryl ketones via one-pot tandem dehydration/1,6-addition/decarboxylation transformation of β-keto acids and 4-hydroxybenzyl alcohols

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General information

Thin-layer chromatography (TLC) was performed on precoated GF254 silica gel plates (Qingdao Marine Chemical Inc.) and compounds were visualized with a UV light at 254nm. Flash chromatography separations were carried out using silica gel (200–300 mesh, Qingdao Marine Chemical Inc.). NMR spectra were recorded on a Bruker AV 400 MHz instrument at 400 MHz (¹H NMR), 100 MHz (¹³C NMR), and 376 MHz (¹⁹F NMR). Chemical shifts were reported in ppm downfield and referenced as follows: ¹H: residual internal CHCl₃ (δ 7.26 ppm) or DMSO-*d*₆ (δ 2.50 ppm); ¹³C: internal CDCl₃ (δ 77.2 ppm) or DMSO-*d*₆ (δ 39.5 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets) and br (broad signal). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were recorded on a Bruker microTOF-QII Instrument. Melting points were measured on a SGW X-4A digital melting point apparatus and are uncorrected. X-ray crystallographic analyses were conducted on a Bruker APEX-II CCD instrument. Optical rotations were determined using an Autopol IV automatic polarimeter. HPLC analyses were carried out on an Agilent HP 1200 series HPLC apparatus or on a Shimadzu Prominence-I LC-2030C 3D liquid chromatograph.

Materials: Dichloromethane (CH₂Cl₂) was distilled from CaH₂ prior to use. Tetrahydrofuran, toluene and *p*-xylene were distilled from sodium/benzophenone. Other solvents were used directly without further purification. β -Keto acids (1),¹ 4-hydroxybenzyl alcohols (2),² and chiral phosphoric acids (3)³ were synthesized according and in analogy to the literature-known methods.

General procedure for the enantioselective dehydration/1,6-addition/ decarboxylation transformation



To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with β -keto acid 1 (0.26 mmol), 4-hydroxybenzyl alcohol 2 (0.2 mmol), chiral phosphoric acid (*S*)-**3h** (0.04 mmol) and *p*-xylene (1.6 mL). The resulting mixture was placed in a low-temperature circulator to maintain the temperature at 13 °C and stirred until the complete conversion of **2** (monitored by TLC). Then the mixture was allowed to warm to room temperature, Et₃N (0.25 mL) was added and stirring was commenced for 5 minutes. The resulting clear solution was washed with 1 N HCl (1 × 5 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was subjected to flash chromatography on silica gel to afford the corresponding product **4**.

Characterization data for chiral ketones 4

(*R*)-3-(4-hydroxyphenyl)-1,3-diphenylpropan-1-one (4a)⁴

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.4$), 51.4 mg, 85% yield. m.p. 85–87 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 16.3 min (minor) and 22.4 min (major) as 96% ee; $[\alpha]_D^{20}$ = +3.5 (c 0.57, CH₃OH). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.54 (d, *J* = 7.3 Hz, 1H, Ar-H), 7.45 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.29–7.21 (m, 4H, Ar-H), 7.21–7.13 (m, 1H, Ar-H), 7.11 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.74–6.65 (m, 2H, Ar-H), 4.94 (s, 1H, OH), 4.75 (t, *J* = 7.3 Hz, 1H, CH), 3.70 (d, *J* = 7.4 Hz, 2H, CH₂).

(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(p-tolyl)propan-1-one (4b)

Constained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 63.3 mg, > 99% yield. m.p. 148–149 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 16.6 min (minor) and 18.8 min (major) as 89% ee; $[\alpha]_D^{20} = -4.6$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 7.8 Hz, 2H, Ar-H), 7.29–7.18 (m, 6H, Ar-H), 7.16–7.12 (m, 1H, Ar-H), 7.07 (d, J = 7.9 Hz, 2H, Ar-H), 6.66 (d, J = 7.9 Hz, 2H, Ar-H), 5.49 (s, 1H, OH), 4.73 (t, J = 7.2 Hz, 1H, CH), 3.65 (d, J = 3.4 Hz, 2H, CH₂), 2.38 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 198.6, 154.3, 144.7, 144.2, 136.2, 134.7, 129.4, 129.1, 128.7, 128.4, 127.9, 126.4, 115.6, 45.5, 45.0, 21.8. HRMS (ESI) *m*/*z* calcd. for C₂₂H₂₀NaO₂⁺ 339.1356, found 339.1361 [*M*+Na]⁺.

(*R*)-3-(4-hydroxyphenyl)-3-phenyl-1-(*m*-tolyl)propan-1-one (4c)

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 63.3 mg, > 99% yield. m.p. 90–92 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 12.9 min (minor) and 17.5 min (major) as 84% ee; $[\alpha]_D^{20}$ = +1.4 (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.75–7.71 (m, 2H, Ar-H), 7.38–7.20 (m, 6H, Ar-H), 7.19–7.11 (m, 1H, Ar-H), 7.07 (d, *J* = 7.9 Hz, 2H, Ar-H), 6.67 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.61 (br, 1H, OH), 4.73 (t, *J* = 7.4 Hz, 1H, CH), 3.67 (dd, *J* = 7.4, 3.3 Hz, 2H, CH₂), 2.36 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 199.2, 154.3, 144.7, 138.6, 137.1, 136.1, 134.1, 129.0, 128.8, 128.6, 128.6, 127.9, 126.4, 125.5, 115.6, 45.4, 45.2, 21.5. HRMS (ESI) *m/z* calcd. for C₂₂H₂₀NaO₂⁺ 339.1356, found 339.1362 [*M*+Na]⁺.

(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(o-tolyl)propan-1-one (4d)

Obtained as a yellow oil after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 63.2 mg, > 99% yield. The enantioselectivity was determined by HPLC using a Daicel CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_R = 19.5$ min (minor) and 22.9 min (major) as 82% ee; $[\alpha]_D^{20} = +1.2$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, J = 7.8, 2.8 Hz, 1H, Ar-H), 7.25–7.23 (m, 1H, Ar-H), 7.21–7.15 (m, 7H, Ar-H), 7.05 (d, J = 7.9 Hz, 2H, Ar-H), 6.68 (d, J = 8.6 Hz, 2H, Ar-H), 5.41 (br, 1H, OH), 4.64 (t, J = 7.6 Hz, 1H, CH), 3.59 (d, J = 7.6 Hz, 2H, CH₂), 2.20 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 203.5, 154.2, 144.2, 138.4, 137.9, 135.8, 131.9, 131.2, 129.0, 128.6, 128.0, 127.7, 126.4, 125.6, 115.4, 48.1, 45.9, 20.6. HRMS (ESI) *m/z* calcd. for C₂₂H₂₀NaO₂⁺ 339.1356, found 339.1364 [*M*+Na]⁺.

(R)-1-(2,4-dimethylphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4e)



Obtained as a yellow oil after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 66.0 mg, > 99% yield. The enantioselectivity was determined by HPLC using a Daicel

CHIRALPAK AD-H column (25 cm \times 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm,

1.0 mL/min flow rate] $t_{\rm R} = 21.3$ min (minor) and 27.4 min (major) as 87% ee; $[\alpha]_{\rm D}^{20} = +0.6$ (c 1.0, CH₂Cl₂). ¹**H NMR** (400 MHz, CDCl₃) δ 7.49 (d, J = 7.8 Hz, 1H, Ar-H), 7.26–7.13 (m, 5H, Ar-H), 7.07–6.97 (m, 4H, Ar-H), 6.66 (d, J = 8.5 Hz, 2H, Ar-H), 5.64 (br, 1H, OH), 4.63 (t, J = 7.7 Hz, 1H, CH), 3.58 (d, J = 7.7 Hz, 2H, CH₂), 2.32 (s, 3H, CH₃), 2.21 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 202.9, 154.3, 144.4, 141.9, 138.5, 135.8, 135.3, 132.8, 129.0, 128.6, 128.5, 127.7, 126.3, 126.3, 115.4, 47.8, 46.0, 21.4, 20.9. **HRMS** (ESI) *m/z* calcd. for C₂₃H₂₂NaO₂⁺ 353.1512, found 339.1519 [*M*+Na]⁺.

(R)-1-(4-ethylphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4f)

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.5$), 66.1 mg, > 99% yield. m.p. Et 137–138 °C. The enantioselectivity was determined by HPLC

using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 14.5 min (minor) and 18.8 min (major) as 91% ee; $[\alpha]_{\rm D}^{20}$ = +1.6 (c 1.0, CH₂Cl₂). ¹**H NMR** (400 MHz, CDCl₃) δ 7.85 (d, J = 8.3 Hz, 2H, Ar-H), 7.28–7.22 (m, 6H, Ar-H), 7.19–7.11 (m, 1H, Ar-H), 7.07 (d, J = 8.5 Hz, 2H, Ar-H), 6.66 (d, J = 8.6 Hz, 2H, Ar-H), 5.54 (br, 1H, OH), 4.73 (t, J = 7.4 Hz, 1H, CH), 3.67 (dd, J = 7.4, 4.1 Hz, 2H, CH₂), 2.68 (q, J = 7.6 Hz, 2H, CH₂), 1.24 (t, J = 7.6 Hz, 3H, CH₃). ¹³C **NMR** (100 MHz, CDCl₃) δ 198.7, 154.3, 150.3, 144.7, 136.1, 134.8, 129.0, 128.6, 128.5, 128.3, 127.9, 126.4, 115.6, 45.5, 45.0, 29.1, 15.3. **HRMS** (ESI) *m/z* calcd. for C₂₃H₂₂NaO₂⁺ 353.1512, found 339.1513 [*M*+Na]⁺.

(R)-3-(4-hydroxyphenyl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (4g)

Ph O HO

OMe

Ph

HO

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.35$), 66.5 mg, > 99% yield. m.p. 177–178 °C. The enantioselectivity was determined

by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 31.5 min (minor) and 36.4 min (major) as 93% ee; $[\alpha]_{\rm D}^{20}$ = +1.0 (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, DMSO- d_6) δ 9.16 (s, 1H, OH), 7.98 (d, J = 8.9 Hz, 2H, Ar-H), 7.32 (d, J = 7.3 Hz, 2H, Ar-H), 7.23 (t, J = 7.6 Hz, 2H, Ar-H), 7.16–7.07 (m, 3H, Ar-H), 7.01 (d, J = 8.8 Hz, 2H, Ar-H), 6.63 (d, J = 8.5 Hz, 2H, Ar-H), 4.54 (t, J = 7.5 Hz, 1H, CH), 3.83 (s, 3H, CH₃), 3.72 (dd, J = 7.5, 3.2 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 197.1, 163.7, 154.2, 144.8, 136.5, 130.5, 130.3, 129.1, 128.7, 127.9, 126.4, 115.5, 113.9, 55.6, 45.5, 44.7. HRMS (ESI) *m*/*z* calcd. for C₂₂H₂₀NaO₃⁺ 355.1304, found 355.1312 [*M*+Na]⁺.

(R)-1-(3,4-dimethoxyphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4h)

OMe HO OMe

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.3$), 72.6 mg, > 99% yield. m.p. 68-70 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm \times 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 51.9 min (minor) and 63.0 min (major) as 92% ee; $[\alpha]_D^{20} = +0.8$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ

7.59 (dd, *J* = 8.4, 2.0 Hz, 1H, Ar-H), 7.45 (d, *J* = 2.1 Hz, 1H, Ar-H), 7.29–7.21 (m, 4H, Ar-H), 7.19–7.12 (m, 1H, Ar-H), 7.09 (d, J = 8.6 Hz, 2H, Ar-H), 6.86 (d, J = 8.5 Hz, 1H, Ar-H), 6.69 (d, J = 8.6 Hz, 2H, Ar-H), 5.44 (s, 1H, OH), 4.73 (t, J = 7.4 Hz, 1H, CH), 3.92 (s, 3H, CH₃), 3.86 (s, 3H, CH₃), 3.65 (dd, J = 7.4, 3.2 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 154.3, 153.5, 149.2, 144.7, 136.2, 130.4, 129.1, 128.7, 127.9, 126.4, 122.9, 115.5, 110.5, 110.1, 56.2, 56.1, 45.7, 44.6. **HRMS** (ESI) m/z calcd. for $C_{23}H_{22}NaO_4^+$ 385.1410, found 385.1419 $[M+Na]^+$.

(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(2,4,6-trimethoxyphenyl)propan-1-one (4i)

Obtained as a white solid after column chromatography Ph Q OMe (petroleum ether/ethyl acetate = 2:1, $R_f = 0.3$), 78.5 mg, > 99% MeO HO OMe yield. m.p. 75-77 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm \times 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 36.5 min (major) and 44.5 min (minor) as 87% ee; $[\alpha]_D^{20} = -0.4$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.21 (m, 4H, Ar-H), 7.18–7.15 (m, 1H, Ar-H), 7.07 (d, J = 8.5 Hz, 2H, Ar-H), 6.69 (d, J = 8.4 Hz, 2H, Ar-H), 6.06 (s, 2H, Ar-H), 5.98 (s, 1H, OH), 4.61 (t, J = 7.6 Hz, 1H, CH), 3.83 (s, 3H, CH₃), 3.64 (s, 6H, CH₃), 3.53 (dd, J = 7.6, 2.3 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) & 202.9, 162.5, 158.4, 154.2, 144.9, 136.0, 129.1, 128.2, 127.9, 126.0, 115.2, 113.0, 90.5, 55.7, 55.4, 51.2, 45.5. HRMS (ESI) m/z calcd. for C₂₄H₂₅O₅⁺ 393.1697, found 393.1700 $[M+H]^+$.

(R)-1-(4-fluorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4j)

Obtained as a white solid after column chromatography (petroleum Ph Q ether/ethyl acetate = 2:1, $R_f = 0.35$), 64.0 mg, > 99% yield. m.p. 116-117 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm \times 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R} = 18.9$ min (minor) and 24.8 min (major) as 76% ee; $[\alpha]_{\rm D}^{20}$ = +1.8 (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (t, J = 6.9 Hz, 2H, Ar-H), 7.29– 7.19 (m, 4H), 7.18–7.12 (m, 1H, Ar-H), 7.11–7.02 (m, 4H, Ar-H), 6.67 (d, J = 8.1 Hz, 2H,

Ar-H), 5.55 (s, 1H, OH), 4.71 (t, J = 7.6 Hz, 1H, CH), 3.65 (d, J = 7.4 Hz, 2H, CH₂). ¹⁹F NMR (376 MHz, CDCl₃) δ –104.8. ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 165.9 (d, J = 255.3 Hz), 154.4, 144.5, 136.0, 133.5 (d, J = 3.6 Hz), 130.9 (d, J = 9.7 Hz), 129.0, 128.7, 127.8, 126.5, 115.9 (d, J = 21.7 Hz), 115.6, 45.5, 45.0. HRMS (ESI) *m*/*z* calcd. for C₂₁H₁₇FNaO₂⁺ 343.1105, found 343.1111 [*M*+Na]⁺.

(R)-1-(3-fluorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4k)

Obtained as a yellow oil after column chromatography (petroleum therefore the enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 15.0 min (minor) and 22.4 min (major) as 74% ee; $[\alpha]_D^{20}$ = +1.8 (c 1.0, CH₂Cl₂). ¹**H NMR** (400 MHz, CDCl₃) δ 7.69 (d, J = 7.8 Hz, 1H, Ar-H), 7.58 (dt, J = 9.5, 2.0 Hz, 1H, Ar-H), 7.40 (td, J = 8.0, 5.6 Hz, 1H, Ar-H), 7.30–7.19 (m, 5H, Ar-H), 7.21–7.12 (m, 1H, Ar-H), 7.08 (d, J = 8.5 Hz, 2H, Ar-H), 6.69 (d, J = 8.5 Hz, 2H, Ar-H), 5.36 (br, 1H, OH), 4.72 (t, J = 7.3 Hz, 1H, CH), 3.66 (d, J = 7.2 Hz, 2H, CH₂). ¹⁹**F NMR** (376 MHz, CDCl₃) δ –111.6. ¹³**C NMR** (100 MHz, CDCl₃) δ 197.6, 163.0 (d, J = 248.2 Hz), 154.3, 144.3, 139.2 (d, J = 6.1 Hz), 136.0, 130.4 (d, J = 7.6 Hz), 129.0, 128.7, 127.8, 126.6, 124.0 (d, J = 2.9 Hz), 120.3 (d, J = 21.5 Hz), 115.6, 115.0 (d, J = 23.2 Hz), 45.4, 45.2. **HRMS** (ESI) *m/z* calcd. for C₂₁H₁₇FNaO₂⁺ 343.1105, found 343.1110 [*M*+Na]⁺.

(R)-1-(4-chlorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (41)

Ph O HO Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 67.4 mg, > 99% yield. m.p. 119–121 °C. The enantioselectivity was determined by HPLC

using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 19.4 min (minor) and 29.8 min (major) as 77% ee; $[\alpha]_{\rm D}^{20}$ = +1.2 (c 1.0, CH₂Cl₂). ¹**H NMR** (400 MHz, CDCl₃) δ 7.84 (d, J = 8.5 Hz, 2H, Ar-H), 7.40 (d, J = 8.6 Hz, 2H, Ar-H), 7.31–7.20 (m, 4H, Ar-H), 7.19–7.12 (m, 1H, Ar-H), 7.08 (d, J = 8.5 Hz, 2H, Ar-H), 6.69 (d, J = 8.5 Hz, 2H, Ar-H), 4.71 (t, J = 7.4 Hz, 1H, CH), 3.65 (dd, J = 7.4, 1.5 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 154.3, 144.4, 139.8, 136.1, 135.5, 129.7, 129.1, 129.0, 128.7, 127.8, 126.6, 115.6, 45.5, 45.1. **HRMS** (ESI) *m/z* calcd. for C₂₁H₁₇ClNaO₂⁺ 359.0809, found 359.0813 [*M*+Na]⁺.

(*R*)-1-(4-bromophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4m)

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.4$), 76.3 mg, > 99% yield. m.p. 105-107 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm \times 0.46 cm ID), [hexane/iso-propanol =

90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 21.6 min (minor) and 34.0 min (major) as 83% ee; $\left[\alpha\right]_{D}^{20} = +1.0$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 8.6 Hz, 2H, Ar-H), 7.57 (d, J = 8.6 Hz, 2H, Ar-H), 7.30–7.20 (m, 4H, Ar-H), 7.19–7.13 (m, 1H, Ar-H), 7.09 (d, J = 8.5 Hz, 2H, Ar-H), 6.70 (d, J = 8.6 Hz, 2H, Ar-H), 4.98 (br, 1H, OH), 4.72 (t, J = 7.3 Hz, 1H, CH), 3.65 (d, J = 7.5 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 197.5, 154.1, 144.2, 136.1, 135.8, 131.9, 129.6, 128.9, 128.6, 128.3, 127.7, 126.4, 115.4, 45.3, 44.9. HRMS (ESI) m/z calcd. for C₂₁H₁₇BrNaO₂⁺ 403.0304, found 403.0316 [M+Na]⁺.

(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(thiophen-2-yl)propan-1-one (4n)

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.5), 61.7 mg, > 99% yield. m.p. 101-103 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm \times 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 21.5 min (minor) and 24.3 min (major) as 88% ee; $[\alpha]_{\rm D}^{20}$ = +4.4 (c 1.0, CH₂Cl₂). ¹**H NMR** (400 MHz, CDCl₃) δ 7.70 (dd, J = 3.8, 1.2 Hz, 1H, Ar-H), 7.59 (dd, J = 4.9, 1.2 Hz, 1H, Ar-H), 7.29–7.20 (m, 4H, Ar-H), 7.20–7.12 (m, 1H, Ar-H), 7.12–7.03 (m, 3H, Ar-H), 6.69 (d, J = 8.6 Hz, 2H, Ar-H), 5.31 (s, 1H, OH), 4.73 (t, J = 7.5 Hz, 1H, CH), 3.61 (dd, J = 7.5, 3.6 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 191.5, 154.2, 144.3, 144.2, 135.8, 133.9, 132.0, 129.0, 128.6, 128.1, 127.7, 126.4, 115.5, 45.8, 45.5. HRMS (ESI) m/z calcd. for C₁₉H₁₆NaO₂S⁺ 331.0763, found 331.0771 [M+Na]⁺.

(*R*)-1-(4-hydroxyphenyl)-1,5-diphenylpentan-3-one (40)

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 66.1 mg, > 99% yield. m.p. 98-100 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 23.4 min (major) and 57.2 min (minor) as 79% ee; $[\alpha]_D^{20} = +0.2$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.20 (m, 4H, Ar-H), 7.19–7.12 (m, 4H, Ar-H), 7.09–6.99 (m, 4H, Ar-H), 6.69 (d, J = 8.6 Hz, 2H, Ar-H), 5.19 (s, 1H, OH), 4.52 (t, *J* = 7.6 Hz, 1H, CH), 3.10 (dd, *J* = 7.7, 2.7 Hz, 2H, CH₂), 2.78 (t, J = 7.5 Hz, 2H, CH₂), 2.64 (t, J = 7.4 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) § 208.7, 154.3, 144.3, 141.0, 136.1, 129.0, 128.7, 128.6, 128.4, 127.7, 126.5, 126.2, 115.6, 49.5, 45.4, 45.2, 29.6. **HRMS** (ESI) m/z calcd. for C₂₃H₂₂NaO₂⁺ 353.1512, found 353.1517 $[M+Na]^+$.

(*R*)-1-cyclohexyl-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4p)

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.5$), 61.7 mg, > 99% yield. m.p. 112– 114 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 8.6 min (minor) and 10.0 min (major) as 77% ee; $[\alpha]_D^{20}$ = +2.6 (c 1.0, CH₂Cl₂). ¹**H NMR** (400 MHz, CDCl₃) δ 7.27–7.23 (m, 2H, Ar-H), 7.22–7.10 (m, 3H, Ar-H), 7.05 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.68 (d, *J* = 8.6 Hz, 2H, Ar-H), 5.42 (s, 1H, OH), 4.54 (t, *J* = 7.5 Hz, 1H, CH), 3.15 (dd, *J* = 7.5, 5.5 Hz, 2H, CH₂), 2.32–2.20 (m, 1H, CH), 1.83–1.68 (m, 4H, CH₂), 1.65–1.54 (m, 1H, CH₂), 1.31–1.06 (m, 5H, CH₂). ¹³**C NMR** (100 MHz, CDCl₃) δ 212.9, 154.3, 144.7, 136.2, 129.0, 128.6, 127.8, 126.4, 115.5, 51.4, 47.3, 45.1, 28.3, 28.3, 25.9, 25.7, 25.7. **HRMS** (ESI) *m/z* calcd. for C₂₁H₂₄NaO₂⁺ 331.1668, found 331.1677 [*M*+Na]⁺.

(R)-1-(4-hydroxyphenyl)-1-phenylpentan-3-one (4q)

HO Ph O

(petroleum ether/ethyl acetate = 2:1, $R_f = 0.4$), 51.3 mg, > 99% yield. The enantioselectivity was determined by HPLC using a Daicel

Obtained as a yellow oily liquid after column chromatography

CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 16.0 min (minor) and 24.2 min (major) as 50% ee; $[\alpha]_{\rm D}^{20}$ = -5.6 (c 1.0, CH₂Cl₂). ¹**H NMR** (400 MHz, CDCl₃) δ 7.31–7.27 (m, 2H, Ar-H), 7.23–7.15 (m, 3H, Ar-H), 7.08 (d, *J* = 8.0 Hz, 2H, Ar-H), 6.73 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.04 (br, 1H, OH), 4.56 (t, *J* = 7.7 Hz, 1H, CH), 3.18–3.14 (m, 2H, CH₂), 2.38 (q, *J* = 7.8 Hz, 2H, CH₂), 0.99 (t, *J* = 7.8 Hz, 3H, CH₃). ¹³**C NMR** (100 MHz, CDCl₃) δ 211.2, 154.5, 144.4, 135.7, 128.9, 128.7, 127.7, 126.5, 115.6, 48.9, 45.5, 36.9, 7.7. **HRMS** (ESI) *m/z* calcd. for C₁₇H₁₉O₂⁺ 255.1380, found 255.1386 [*M*+H]⁺.

(R)-3-(4-hydroxyphenyl)-1-phenyl-3-(p-tolyl)propan-1-one (4a')



Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.5$), 63.3 mg, > 99% yield. m.p. 98–100 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_R = 13.1$

min (minor) and 16.9 min (major) as 88% ee; $[\alpha]_D^{20} = +6.0$ (c 0.1, CH₂Cl₂). ¹H NMR (400

MHz, CDCl₃) δ 7.91 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.59–7.48 (m, 1H, Ar-H), 7.42 (t, *J* = 7.3 Hz, 2H, Ar-H), 7.17–6.97 (m, 6H, Ar-H), 6.66 (d, J = 7.4 Hz, 2H, Ar-H), 5.72 (br, 1H, OH), 4.68 (t, J = 7.0 Hz, 1H, CH), 3.67 (d, J = 7.1 Hz, 2H, CH₂), 2.26 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) & 199.2, 154.3, 141.6, 137.1, 136.3, 135.9, 133.3, 129.3, 129.0, 128.7, 128.3, 127.7, 115.6, 45.2, 45.2, 21.1. HRMS (ESI) m/z calcd. for C₂₂H₂₀NaO₂⁺ 339.1356, found 339.1367 [*M*+Na]⁺.

(R)-3-(4-hydroxyphenyl)-1-phenyl-3-(m-tolyl)propan-1-one (4b')

Obtained as a yellow oil after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.5$), 63.3 mg, > 99% yield. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm \times 0.46 ID), cm

Obtained as a yellow oil after column chromatography (petroleum

[hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 13.1 min (minor) and 18.2 min (major) as 82% ee; $[\alpha]_D^{20} = +4.8$ (c 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 7.8 Hz, 2H, Ar-H), 7.59–7.49 (m, 1H, Ar-H), 7.47–7.39 (m, 2H, Ar-H), 7.18–6.96 (m, 6H, Ar-H), 6.69 (d, J = 8.6 Hz, 2H, Ar-H), 5.16 (br, 1H, OH), 4.70 (t, J = 7.4 Hz, 1H, CH), 3.68 (dd, J = 7.4, 5.8 Hz, 2H, CH₂), 2.28 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 154.2, 144.6, 138.2, 137.2, 136.4, 133.3, 129.1, 128.7, 128.6, 128.2, 127.3, 124.7, 115.5, 45.4, 45.1, 21.6. **HRMS** (ESI) *m/z* calcd. for C₂₂H₂₀NaO₂⁺ 339.1356, found 339.1363 [*M*+Na]⁺.

(*R*)-3-(4-hydroxyphenyl)-1-phenyl-3-(*o*-tolyl)propan-1-one (4c')



ether/ethyl acetate = 2:1, $R_f = 0.5$), 63.2 mg, > 99% yield. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm \times 0.46 ID), cm [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 12.8 min (minor) and 20.1 min (major) as 72% ee; $[\alpha]_D^{20} = +36.0$ (c 0.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 7.5 Hz, 2H, Ar-H), 7.57–7.49 (m, 1H, Ar-H), 7.47–7.39 (m, 2H, Ar-H), 7.26–7.20 (m, 1H, Ar-H), 7.19–7.06 (m, 3H), 7.02 (d, J = 8.0 Hz, 2H, Ar-H), 6.65 (d, J = 8.0 Hz, 2H, Ar-H), 5.39 (br, 1H, OH), 4.92 (t, J = 7.3 Hz, 1H, CH), 3.66 (d, J = 7.3 Hz, 2H, CH₂), 2.29 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 154.2, 142.2, 137.2, 136.5, 135.7, 133.3, 130.9, 129.3, 128.8, 128.2, 126.4, 126.4, 126.1, 115.5, 45.3, 41.4, 20.0. HRMS (ESI) m/z calcd. for C₂₂H₂₀NaO₂⁺ 339.1356, found 339.1363 [*M*+Na]⁺.

(R)-3-([1,1'-biphenyl]-4-yl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4d')



Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 75.6 mg, > 99% yield. m.p. 144–146 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_R = 54.8$

min (minor) and 59.7 min (major) as 89% ee; $[\alpha]_D^{20} = +13.0$ (c 1.0, ethyl acetate). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.5 Hz, 2H, Ar-H), 7.60–7.38 (m, 9H, Ar-H), 7.36–7.29 (m, 3H, Ar-H), 7.18 (d, J = 7.5 Hz, 2H, Ar-H), 6.77 (d, J = 7.6 Hz, 2H, Ar-H), 4.87–4.78 (m, 2H, OH and CH), 3.76 (d, J = 7.6 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 154.1, 143.6, 140.9, 139.2, 137.1, 136.3, 133.2, 129.0, 128.7, 128.6, 128.1, 127.3, 127.1, 127.1, 127.0, 115.5, 45.0, 44.9. HRMS (ESI) *m/z* calcd. for C₂₇H₂₂NaO₂⁺ 401.1512, found 401.1518 [*M*+Na]⁺.

(S)-3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (4e')



Obtained as a yellow oil after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.35$), 66.5 mg, > 99% yield. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 22.4

min (minor) and 26.4 min (major) as 83% ee; $[\alpha]_D^{20} = +4.0$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.5 Hz, 2H, Ar-H), 7.52 (t, J = 7.6 Hz, 1H, Ar-H), 7.40 (t, J = 7.3 Hz, 2H, Ar-H), 7.13 (d, J = 7.9 Hz, 2H, Ar-H), 7.04 (d, J = 7.8 Hz, 2H, Ar-H), 6.79 (d, J = 7.9 Hz, 2H, Ar-H), 6.66 (d, J = 7.9 Hz, 2H, Ar-H), 6.04 (s, 1H, OH), 4.67 (t, J = 7.3 Hz, 1H, CH), 3.72 (s, 3H, CH₃), 3.65 (d, J = 7.2 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 199.4, 158.0. 154.4, 137.1, 136.8, 136.3, 133.3, 128.9, 128.8, 128.7, 128.2, 115.6, 114.1, 55.3, 45.3, 44.7. HRMS (ESI) m/z calcd. for C₂₂H₂₀NaO₃⁺ 355.1304, found 355.1313 [M+Na]⁺.

(S)-3-(4-hydroxyphenyl)-3-(3-methoxyphenyl)-1-phenylpropan-1-one (4f')



Obtained as a yellow oil after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.35$), 66.5 mg, > 99% yield. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID),

[hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 22.6 min (minor) and 34.3 min (major) as 77% ee; $[\alpha]_{\rm D}^{20}$ = +4.6 (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ

7.92 (d, J = 7.2 Hz, 2H, Ar-H), 7.58–7.51 (m, 1H, Ar-H), 7.68–7.38 (m, 2H, Ar-H), 7.18 (t, J = 7.9 Hz, 1H, Ar-H), 7.10 (d, J = 8.5 Hz, 2H, Ar-H), 6.84 (d, J = 7.7 Hz, 1H, Ar-H), 6.79 (s, 1H, Ar-H), 6.74–6.63 (m, 3H, Ar-H), 5.19 (br, 1H, OH), 4.71 (t, J = 7.3 Hz, 1H, CH), 3.74 (s, 3H, CH₃), 3.68 (d, J = 7.4 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 198.5, 159.7, 154.2, 146.2, 137.1, 136.0, 133.1, 129.5, 128.9, 128.6, 128.1, 120.1, 115.4, 114.0, 111.3, 55.2, 45.3, 44.9. HRMS (ESI) *m*/*z* calcd. for C₂₂H₂₀NaO₃⁺ 355.1304, found 355.1313 [*M*+Na]⁺.

(S)-3-(4-hydroxyphenyl)-3-(2-methoxyphenyl)-1-phenylpropan-1-one (4g')



Obtained as a yellow oil after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.35$), 61.2 mg, 92% yield. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID),

[hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 21.8 min (minor) and 32.7 min (major) as 78% ee; $[\alpha]_{\rm D}^{20}$ = +5.2 (c 1.0, CH₂Cl₂). ¹**H NMR** (400 MHz, CDCl₃) δ 7.92 (d, J = 7.5 Hz, 2H, Ar-H), 7.57–7.51 (m, 1H, Ar-H), 7.47–7.38 (m, 2H, Ar-H), 7.18 (t, J= 7.6 Hz, 1H, Ar-H), 7.10 (d, J = 7.5 Hz, 2H, Ar-H), 6.84 (d, J = 7.6 Hz, 1H, Ar-H), 6.79 (s, 1H, Ar-H), 6.74–6.66 (m, 3H, Ar-H), 5.24 (br, 1H, OH), 4.71 (t, J = 7.1 Hz, 1H, CH), 3.74 (s, 3H, CH₃), 3.68 (d, J = 7.2 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 198.7, 159.8, 154.3, 146.3, 137.2, 136.1, 133.3, 129.7, 129.1, 128.8, 128.2, 120.3, 115.6, 114.1, 111.4, 55.3, 45.4, 45.1. HRMS (ESI) *m/z* calcd. for C₂₂H₂₀NaO₃⁺ 355.1304, found 355.1311 [*M*+Na]⁺.

(R)-3-(4-hydroxyphenyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (4h')



Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.3$), 74.0 mg, > 99% yield. m.p. 182–183 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 16.3

min (minor) and 21.8 min (major) as 87% ee; $[\alpha]_D^{20} = +6.7$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 7.6 Hz, 2H, Ar-H), 7.60–7.49 (m, 3H, Ar-H), 7.48–7.42 (m, 2H, Ar-H), 7.36 (d, J = 8.0 Hz, 2H, Ar-H), 7.10 (d, J = 8.1 Hz, 2H, Ar-H), 6.74 (d, J = 8.1 Hz, 2H, Ar-H), 4.95 (s, 1H, OH), 4.82 (t, J = 7.4 Hz, 1H, CH), 3.72 (d, J = 7.3 Hz, 2H, CH₂). ¹⁹F NMR (376 MHz, CDCl₃) δ –62.4. ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 154.3, 148.5, 136.8, 135.4, 133.4, 129.0, 128.7, 128.6 (q, J = 32.2 Hz), 128.1, 128.1, 125.5 (q, J = 3.7 Hz), 124.2 (q, J = 270 Hz), 115.6, 45.0, 44.6. HRMS (ESI) *m*/*z* calcd. for C₂₂H₁₇F₃NaO₂⁺ 393.1073, found 393.1080 [*M*+Na]⁺.

(S)-3-(4-fluorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4i')



Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.35$), 64.0 mg, > 99% yield. m.p. 95–96 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 16.7

min (minor) and 21.0 min (major) as 83% ee; $[\alpha]_D^{20} = +1.2$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 7.7 Hz, 2H, Ar-H), 7.57–7.49 (m, 1H, Ar-H), 7.47–7.39 (m, 2H, Ar-H), 7.21–7.12 (m, 2H, Ar-H), 7.05 (d, J = 7.5 Hz, 2H, Ar-H), 6.92 (t, J = 8.0 Hz, 2H, Ar-H), 6.69 (d, J = 7.4 Hz, 2H, Ar-H), 5.76 (br, 1H, OH), 4.71 (t, J = 7.5 Hz, 1H, CH), 3.66 (d, J = 7.4 Hz, 2H, CH₂). ¹⁹F NMR (376 MHz, CDCl₃) δ –116.8. ¹³C NMR (100 MHz, CDCl₃) δ 198.3, 161.5 (d, J = 244.5 Hz), 154.3, 140.3 (d, J = 3.2 Hz), 137.1, 136.4, 133.3, 129.3 (d, J = 7.9 Hz), 129.0, 128.8, 128.2, 115.6, 115.5 (d, J = 21.2 Hz), 45.2, 44.6. HRMS (ESI) *m/z* calcd. for C₂₁H₁₇FNaO₂⁺ 343.1105, found 343.1111 [*M*+Na]⁺.

(S)-3-(3-fluorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4j')

Obtained as a yellow oil after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.35$), 64.0 mg, > 99% yield. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), HO [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 16.3 min (minor) and 24.5 min (major) as 73% ee; $[\alpha]_D^{20} = +1.3$ (c 0.3, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.55 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.44 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.25–7.14 (m, 1H, Ar-H), 7.09 (d, J = 8.5 Hz, 2H, Ar-H), 7.03 (d, J = 7.7 Hz, 1H, Ar-H), 6.93 (d, J = 10.2 Hz, 1H, Ar-H), 6.85 (td, J = 8.3, 1.9 Hz, 1H, Ar-H), 6.72 (d, J = 8.5 Hz, 2H)Ar-H), 5.16 (br, 1H, OH), 4.75 (t, J = 7.3 Hz, 1H, CH), 3.68 (d, J = 7.4 Hz, 2H, CH₂). ¹⁹F **NMR** (376 MHz, CDCl₃) δ –113.0. ¹³C **NMR** (100 MHz, CDCl₃) δ 198.3, 163.1 (d, J = 245.8 Hz), 154.5, 147.3 (d, J = 6.7 Hz), 137.0, 135.7, 133.4, 130.1 (d, J = 8.4 Hz), 129.1, 128.8, 128.2, 123.5 (d, J = 2.8 Hz), 115.7, 114.8 (d, J = 21.5 Hz), 113.4 (d, J = 20.9 Hz), 45.1, 45.1, 44.9. **HRMS** (ESI) m/z calcd. for C₂₁H₁₇FNaO₂⁺ 343.1105, found 343.1113 [M+Na]⁺.

(S)-3-(4-chlorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4k')



Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.4$), 67.3 mg, > 99% yield. m.p. 94–96 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 18.3

min (minor) and 23.2 min (major) as 90% ee; $[\alpha]_D^{20} = +3.6$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 7.4 Hz, 2H, Ar-H), 7.62–7.55 (m, 1H, Ar-H), 7.48 (t, J = 7.7 Hz, 2H, Ar-H), 7.29–7.16 (m, 4H, Ar-H), 7.11 (d, J = 8.5 Hz, 2H, Ar-H), 6.75 (d, J = 8.5 Hz, 2H, Ar-H), 5.31 (s, 1H, OH), 4.76 (t, J = 7.3 Hz, 1H, CH), 3.70 (d, J = 7.4 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 198.6, 154.5, 143.1, 137.0, 135.8, 133.5, 132.2, 129.2, 129.0, 128.8, 128.8, 128.2, 115.7, 45.0, 44.8. HRMS (ESI) *m/z* calcd. for C₂₁H₁₇ClNaO₂⁺ 359.0809, found 359.0812 [*M*+Na]⁺.

(S)-3-(4-hydroxyphenyl)-3-(naphthalen-1-yl)-1-phenylpropan-1-one (4l')

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 70.5 mg, > 99% yield. m.p. 63–65 °C. The enantioselectivity was determined by HPLC using a Daicel HO CHIRALCEL OD-H column (25 cm \times 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 26.4 min (minor) and 30.5 min (major) as 83% ee; $[\alpha]_D^{20} = +136$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 6.5 Hz, 1H, Ar-H), 7.90 (d, J = 7.7 Hz, 2H, Ar-H), 7.79 (d, J = 7.3 Hz, 1H, Ar-H), 7.69 (d, J = 8.0 Hz, 1H, Ar-H), 7.52–7.46 (m, 1H, Ar-H), 7.44–7.26 (m, 6H, Ar-H), 7.05 (d, J = 8.0 Hz, 2H, Ar-H), 6.59 (d, J = 7.7 Hz, 2H, Ar-H), 5.72 (s, 1H, OH), 5.55 (t, J = 7.4 Hz, 1H, CH), 3.83–3.73 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 199.2, 154.3, 140.1, 137.1, 135.7, 134.3, 133.4, 131.6, 129.2, 128.9, 128.8, 128.3, 127.4, 126.3, 125.7, 125.4, 124.4, 123.9, 115.6, 45.4, 40.9. HRMS (ESI) m/z calcd. for C₂₅H₂₀NaO₂⁺ 375.1355, found 375.1357 $[M+Na]^+$.

(S)-3-(4-hydroxyphenyl)-3-(naphthalen-2-yl)-1-phenylpropan-1-one (4m')



Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 2:1, $R_f = 0.45$), 70.5 mg, > 99% yield. m.p. 60–62 °C. The enantioselectivity was determined by HPLC using a Daicel CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] t_R = 20.8

min (minor) and 30.5 min (major) as 83% ee; $[\alpha]_D^{20} = +102$ (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.6 Hz, 2H, Ar-H), 7.76–7.60 (m, 4H, Ar-H), 7.53–7.45 (m, 1H,

Ar-H), 7.43–7.25 (m, 5H, Ar-H), 7.05 (d, J = 7.9 Hz, 2H, Ar-H), 6.63 (d, J = 7.9 Hz, 2H, Ar-H), 6.12 (br, 1H, OH), 4.86 (t, J = 7.5 Hz, 1H, CH), 3.75 (d, J = 7.4 Hz, 2H, CH₂). ¹³C **NMR** (100 MHz, CDCl₃) δ 199.3, 154.5, 142.0, 137.0, 135.7, 133.6, 133.4, 132.3, 129.1, 128.8, 128.3, 128.3, 127.9, 127.7, 126.8, 126.1, 125.7, 125.6, 115.6, 45.5, 45.0. **HRMS** (ESI) *m/z* calcd. for C₂₅H₂₀NaO₂⁺ 375.1355, found 375.1357 [*M*+Na]⁺.

Procedure for the gram scale experiment



To a 50 mL Schlenk flask equipped with a magnetic stir bar was charged with 4-hydroxybenzyl alcohol **2a** (0.60 g, 3.0 mmol), chiral phosphoric acid (*S*)-**3h** (0.45 g, 0.6 mmol) and *p*-xylene (25 mL). The resulting mixture was placed in a low-temperature circulator to maintain the temperature at 13 °C and stirred for 15 minutes, then β -keto acid **1g** (0.76g, 3.9 mmol) was added to the mixture and stirring was continued until the complete conversion of **2a** (monitored by TLC). The mixture was allowed to warm to room temperature, Et₃N (4.0 mL) was added and stirring was commenced for 30 minutes. The resulting clear solution was washed with 1 N HCl (3 × 15 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was subjected to flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 2:1, R_f = 0.35) to afford the corresponding product **4g** in quantitative yield (1.0 g) with 93% ee.

The catalyst (S)-**3h** was also recovered in 98% yield (0.44 g) by flash chromatography (eluting with $CH_2Cl_2/CH_3OH = 20:1$, $R_f = 0.5$) from the reaction crude.

Procedure for recycling the chiral phosphoric acid catalyst

After standard workup, the residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1, v/v). When the chiral ketone product was off the column, the eluting solvent was changed to CH_2Cl_2/CH_3OH (20:1, v/v), which allowed the chiral phosphoric acid to elute from the column. The recovered catalyst was then reused for subsequent reactions without further purification.

To test its efficiency, the above procedure was applied to the reaction of **1g** with **2a** and was repeated three times. The results obtained are shown below:



Procedure for the synthesis of chiral β,β-diaryl propionic acid 6



A mixture of **4g** (167 mg, 0.5 mmol), *meta*-chloroperoxybenzoic acid (*m*CPBA, 2.0 mmol), TFA (1.0 mmol) in CH₂Cl₂ (10 mL) was stirred at room temperature. Upon completion of the reaction (monitored by TLC), the mixture was diluted with CH₂Cl₂ (20 mL), washed with saturated aqueous Na₂SO₃ (1 × 30 mL) and saturated aqueous NaHCO₃ (1 × 30 mL). The resulting organic layer was dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 2:1, R_f = 0.55) to give **5**.

4-methoxyphenyl (R)-3-(4-hydroxypheyl)-3-phenylpropanoate (5)

Obtained as a white solid, 139.5 mg, 80% yield. m.p. 131–132 °C. The enantioselectivity was determined by HPLC using a CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 90:10, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 60.7 min (minor) and 64.9min (major) as 94% ee; $[\alpha]_{\rm D}^{20}$ = +0.2 (c 1.0, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.27 (m, 5H, Ar-H), 7.19 (d, J = 8.4 Hz, 2H, Ar-H), 6.87–6.75 (m, 4H, Ar-H), 6.71 (d, J = 8.0 Hz, 2H, Ar-H), 4.88 (br, 1H, OH), 4.61 (t, J = 8.2 Hz, 1H, CH), 3.78 (s, 3H, CH₃), 3.26 (d, J = 8.3 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 157.4, 154.4, 144.2, 143.6, 135.5, 129.1, 128.8, 127.8, 126.8, 122.3, 115.6, 114.6, 55.7, 46.7, 41.3. HRMS (ESI) *m/z* calcd. for C₂₂H₂₀NaO₄⁺ 371.1254, found 371.1263 [*M*+Na]⁺.



A suspension of **5** (139.5 mg, 0.4 mmol) in aqueous NaOH (1 N, 10 mL) was stirred at room temperature overnight. Then concentrated hydrochloric acid was added carefully with stirring until the pH reached 2. The mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was dissolved in saturated Na₂CO₃ aqueous solution (15 mL) and washed with ether (3×10 mL). The residual aqueous layer was acidified to pH 2 with concentrated hydrochloric acid. The mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous Na₂SO₄. **6** was obtained after evaporation of the solvent under vacuum.

(*R*)-3-(4-hydroxyphenyl)-3-phenylpropanoic acid (6)⁵

Obtained as a white solid, 68.7 mg, 71% yield. m.p. 169–171 °C. $[\alpha]_D{}^{20} = -6.4$ (c 1.0, CH₃OH). ¹H NMR (400 MHz, methanol- d_4) δ 7.29–7.21 (m, 4H, Ar-H), 7.17–7.14 (m, 1H, Ar-H), 7.08 (d, J = 8.6 Hz, 2H, Ar-H), 6.70 (d, J = 8.6 Hz, 2H, Ar-H), 4.41 (t, J = 8.0 Hz, 1H, CH), 2.99 (d, J = 7.9 Hz, 2H, CH₂).

Procedure for the enantioselective dehydration/1,10-addition/decarboxylation transformation



To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.26 mmol), **8**⁶ (0.2 mmol), (*S*)-**3h** (0.04 mmol) and *p*-xylene (1.6 mL). The resulting mixture was placed in a low-temperature circulator to maintain the temperature at 13 °C and stirred until the complete conversion of **8** (monitored by TLC). Then the mixture was allowed to warm to room temperature, Et₃N (0.25 mL) was added and stirring was commenced for 5 minutes. The resulting clear solution was washed with 1 N HCl (1 × 5 mL), dried over anhydrous Na₂SO₄, and concentrated under vacuum. The residue was subjected to flash chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 2:1, $R_f = 0.4$) to afford **9**.

(-)-3-(4'-hydroxy-[1,1'-biphenyl]-4-yl)-1,3-diphenylpropan-1-one (9)

Obtained as a white solid, 71.9 mg, 95% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AS column (25 cm × 0.46 cm ID), [hexane/*iso*-propanol = 91:9, λ 254 nm, 1.0 mL/min flow rate] $t_{\rm R}$ = 81.6 min (minor) and 93.6 min (major) as 11% ee; $[\alpha]_{\rm D}^{20} = -2.9$ (c 0.7, CH₃OH). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 7.2 Hz, 2H, Ar-H), 7.60–7.53 (m, 1H, Ar-H), 7.49–7.34 (m, 6H, Ar-H), 7.35–7.27 (m, 6H, Ar-H), 7.23–7.16 (m, 1H, Ar-H), 6.82 (d, J = 8.6 Hz, 2H, Ar-H), 5.22 (br, 1H, OH), 4.85 (t, J = 7.3 Hz, 1H, CH), 3.85–3.72 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 198.6, 155.2, 144.2, 142.4, 138.9, 137.0, 133.4, 133.2, 128.7, 128.6, 128.2, 128.1, 127.8, 126.8, 126.5, 115.6, 45.7, 44.8. HRMS (ESI) *m/z* calcd. for C₂₇H₂₂NaO₂⁺ 401.1512, found 401.1513 [*M*+Na]⁺.

X-Ray crystal data for compound 4k', 6 and 7

The single crystal of compound $4\mathbf{k'}$ was grown from its solution in the mixture of ethyl acetate/petroleum ether using a slow evaporation method. After single crystal analysis, the absolute configuration of the chiral carbon center in $4\mathbf{k'}$ was established as *S*.



Supplementary Table 1. Crystallographic data and structure refinement for 4k'

CCDC Number	1982314		
Empirical formula	C21 H17 Cl O2		
Formula weight	336.80		
Temperature	170 K		
Radiation	MoK\a		
Wavelength	0.71073 Å		
Crystal system	orthorhombic		
Space group	P 21 21 21		
Unit cell dimensions	a = 5.339(4) Å $alpha = 90$ deg. $b = 15.845(10)$ Å $beta = 90$ deg. $c = 23.929(14)$ Å $gamma = 90$ deg.		
Volume	2024(2) Å ³		
Z	4		
Calculated density	1.105 g/cm ³		
Absorption coefficient	0.197 mm ⁻¹		
F(000)	704.0		
Crystal size	0.15×0.08×0.05 mm ³		
Theta range for data collection	5.142 to 50.170 deg.		
Limiting indices	$-6 \le h \le 4$ $-18 \le k \le 17$		

	$-28 \le 1 \le 28$
Reflections collected / unique	5498 / 3363 [R(int) = 0.0619]
Data / restraints / parameters	3363 / 0 / 218
Goodness-of-fit on F ²	0.942
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1183
R indices (all data)	R1 = 0.1358, wR2 = 0.1483
Largest diff. peak and hole	0.18 and -0.18 e/Å ³
Flack parameter	-0.11(11)

The single crystal of compound **6** was grown from its solution in the mixture of ethyl acetate/petroleum ether using a slow evaporation method. After single crystal analysis, the absolute configuration of the chiral carbon center in **6** was established as R.



Supplementary Table 2. Crystallographic data and structure refinement for ${\bf 6}$

CCDC Number	2009297
Empirical formula	C15 H14 O3
Formula weight	242.26
Temperature	170 K
Radiation	CuK\a
Wavelength	1.54178 Å
Crystal system	orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 5.8696(4) Å $alpha = 90$ deg. $b = 10.0626(8)$ Å $beta = 90$ deg. $c = 20.1420(16)$ Å $gamma = 90$ deg.
Volume	1189.66(16) Å ³

Z	4
Calculated density	1.353 g/cm ³
Absorption coefficient	0.763 mm ⁻¹
F(000)	512.0
Crystal size	0.15×0.08×0.05 mm ³
Theta range for data collection	4.390 to 74.833 deg.
Limiting indices	$-6 \le h \le 7$ $-12 \le k \le 12$ $-25 \le 1 \le 24$
Reflections collected / unique	16116 / 2447 [R(int) = 0.0611]
Data / restraints / parameters	2447 / 0 / 165
Goodness-of-fit on F ²	1.114
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0918
R indices (all data)	R1 = 0.0417, wR2 = 0.0942
Largest diff. peak and hole	0.17 and -0.23 e/Å ³
Flack parameter	0.06(11)

The single crystal of compound 7 was grown from its solution in the mixture of CH_2Cl_2 /petroleum ether using a slow evaporation method at -20 °C.. After single crystal analysis, the structure of 7 was unambiguously determined.



Supplementary Table 3. Crystallographic data and structure refinement for 7

CCDC Number	1982315
Empirical formula	C22 H17 Cl O4
Formula weight	380.80
Temperature	150 K

Radiation	MoK\a		
Wavelength	0.71073 Å		
Crystal system	orthorhombic		
Space group	P 21 21 21		
Unit cell dimensions	a = 5.6683(8) Å $alpha = 90$ deg. $b = 12.2650(19)$ Å $beta = 90$ deg. $c = 32.881(5)$ Å $gamma = 90$ deg.		
Volume	2285.9(6) Å ³		
Z	4		
Calculated density	1.106 g/cm ³		
Absorption coefficient	0.188 mm ⁻¹		
F(000)	792.0		
	0.25×0.15×0.12 mm ³		
Crystal size	0.25×0.15×0.12 mm ³		
Crystal size Theta range for data collection	0.25×0.15×0.12 mm ³ 4.956 to 51.354 deg.		
Crystal size Theta range for data collection Limiting indices	$0.25 \times 0.15 \times 0.12 \text{ mm}^{3}$ $4.956 \text{ to } 51.354 \text{ deg.}$ $-6 \le h \le 6$ $-14 \le k \le 13$ $-40 \le 1 \le 39$		
Crystal size Theta range for data collection Limiting indices Reflections collected / unique	$0.25 \times 0.15 \times 0.12 \text{ mm}^{3}$ $4.956 \text{ to } 51.354 \text{ deg.}$ $-6 \le h \le 6$ $-14 \le k \le 13$ $-40 \le 1 \le 39$ $14538 / 4261 [\text{R(int)} = 0.0908]$		
Crystal size Theta range for data collection Limiting indices Reflections collected / unique Data / restraints / parameters	$0.25 \times 0.15 \times 0.12 \text{ mm}^{3}$ $4.956 \text{ to } 51.354 \text{ deg.}$ $-6 \le h \le 6$ $-14 \le k \le 13$ $-40 \le 1 \le 39$ $14538 / 4261 [R(\text{int}) = 0.0908]$ $4261 / 0 / 246$		
Crystal size Theta range for data collection Limiting indices Reflections collected / unique Data / restraints / parameters Goodness-of-fit on F ²	$0.25 \times 0.15 \times 0.12 \text{ mm}^{3}$ $4.956 \text{ to } 51.354 \text{ deg.}$ $-6 \le h \le 6$ $-14 \le k \le 13$ $-40 \le 1 \le 39$ $14538 / 4261 [R(\text{int}) = 0.0908]$ $4261 / 0 / 246$ 0.962		
Crystal sizeTheta range for data collectionLimiting indicesReflections collected / uniqueData / restraints / parametersGoodness-of-fit on F ² Final R indices [I>2sigma(I)]	$0.25 \times 0.15 \times 0.12 \text{ mm}^{3}$ $4.956 \text{ to } 51.354 \text{ deg.}$ $-6 \le h \le 6$ $-14 \le k \le 13$ $-40 \le 1 \le 39$ $14538 / 4261 [R(\text{int}) = 0.0908]$ $4261 / 0 / 246$ 0.962 $R1 = 0.0560, \text{ wR2} = 0.1153$		
Crystal sizeTheta range for data collectionLimiting indicesReflections collected / uniqueData / restraints / parametersGoodness-of-fit on F2Final R indices [I>2sigma(I)]R indices (all data)	$0.25 \times 0.15 \times 0.12 \text{ mm}^{3}$ $4.956 \text{ to } 51.354 \text{ deg.}$ $-6 \le h \le 6$ $-14 \le k \le 13$ $-40 \le 1 \le 39$ $14538 / 4261 [R(\text{int}) = 0.0908]$ $4261 / 0 / 246$ 0.962 $R1 = 0.0560, \text{ wR2} = 0.1153$ $R1 = 0.1022, \text{ wR2} = 0.1310$		
Crystal sizeTheta range for data collectionLimiting indicesReflections collected / uniqueData / restraints / parametersGoodness-of-fit on F2Final R indices [I>2sigma(I)]R indices (all data)Largest diff. peak and hole	$0.25 \times 0.15 \times 0.12 \text{ mm}^{3}$ $4.956 \text{ to } 51.354 \text{ deg.}$ $-6 \le h \le 6$ $-14 \le k \le 13$ $-40 \le 1 \le 39$ $14538 / 4261 [R(\text{int}) = 0.0908]$ $4261 / 0 / 246$ 0.962 $R1 = 0.0560, \text{ wR2} = 0.1153$ $R1 = 0.1022, \text{ wR2} = 0.1310$ $0.20 \text{ and } -0.24 \text{ e/Å}^{3}$		

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Copies of NMR spectra for new compounds

(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(p-tolyl)propan-1-one (4b)



(*R*)-3-(4-hydroxyphenyl)-3-phenyl-1-(*m*-tolyl)propan-1-one (4c)

¹H NMR (400 MHz, CDCl₃)





(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(o-tolyl)propan-1-one (4d)

¹H NMR (400 MHz, CDCl₃)

-2.20- 4.66 - 4.64 - 4.62 3.60 Ρh Ö Мe 7.25 7.23 7.23 7.23 7.21 7.21 7.21 7.19 7.19 7.17 7.17 7.17 7.17 7.16 6.69 6.69 HO 4d 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 fl (ppm) .03 80.1 0.98 1.00 3.02 1.98 7.20 2.0 2.0

 $11.5\ 11.0\ 10.5\ 10.0\ 9.5\ 9.0\ 8.5\ 8.0\ 7.5\ 7.0\ 6.5\ 6.0\ 5.5\ 5.0\ 4.5\ 4.0\ 3.5\ 3.0\ 2.5\ 2.0\ 1.5\ 1.0\ 0.5\ 0.0\ -0.5\ -1.0\ -1.5\ -2\ fl\ (ppm)$





(R)-1-(2,4-dimethylphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4e)

¹H NMR (400 MHz, CDCl₃)











(R)-3-(4-hydroxyphenyl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (4g)

¹H NMR (400 MHz, DMSO-*d*₆)



 $11.5\ 11.0\ 10.5\ 10.0\ 9.5\ 9.0\ 8.5\ 8.0\ 7.5\ 7.0\ 6.5\ 6.0\ 5.5\ 5.0\ 4.5\ 4.0\ 3.5\ 3.0\ 2.5\ 2.0\ 1.5\ 1.0\ 0.5\ 0.0\ -0.5\ -1.0\ -1.5\ -2\ fl\ (ppm)$







11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2 fl (ppm)



(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(2,4,6-trimethoxyphenyl)propan-1-one (4i)

¹H NMR (400 MHz, CDCl₃)



 $11.5\ 11.0\ 10.5\ 10.0\ 9.5\ 9.0\ 8.5\ 8.0\ 7.5\ 7.0\ 6.5\ 6.0\ 5.5\ 5.0\ 4.5\ 4.0\ 3.5\ 3.0\ 2.5\ 2.0\ 1.5\ 1.0\ 0.5\ 0.0\ -0.5\ -1.0\ -1.5\ -2\ fl\ (ppm)$

- 202.93	~ 162.50 - 158.41 ~ 154.24 144.90 135.97 135.97 127.88 ~ 125.97	× 115.16 × 113.01	- 90.53	$\begin{cases} 55.66 \\ 55.42 \\ 51.15 \\ 242.46 \end{cases}$
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(R)-1-(4-fluorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4j)

¹H NMR (400 MHz, CDCl₃)



2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2 fl (ppm)



(R)-1-(3-fluorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4k)

¹H NMR (400 MHz, CDCl₃)



 $11.5\ 11.0\ 10.5\ 10.0\ 9.5\ 9.0\ 8.5\ 8.0\ 7.5\ 7.0\ 6.5\ 6.0\ 5.5\ 5.0\ 4.5\ 4.0\ 3.5\ 3.0\ 2.5\ 2.0\ 1.5\ 1.0\ 0.5\ 0.0\ -0.5\ -1.0\ -1.5\ -2\ fl\ (ppm)$



(R)-1-(4-chlorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4l)

¹H NMR (400 MHz, CDCl₃)

-3.66 -3.66 3.64 -3.64





(R)-1-(4-bromophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4m)

¹H NMR (400 MHz, CDCl₃)



 $11.5\ 11.0\ 10.5\ 10.0\ 9.5\ 9.0\ 8.5\ 8.0\ 7.5\ 7.0\ 6.5\ 6.0\ 5.5\ 5.0\ 4.5\ 4.0\ 3.5\ 3.0\ 2.5\ 2.0\ 1.5\ 1.0\ 0.5\ 0.0\ -0.5\ -1.0\ -1.5\ -2\ fl\ (ppm)$



(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(thiophen-2-yl)propan-1-one (4n)

¹H NMR (400 MHz, CDCl₃)

 $\begin{array}{c} 7.71\\ 7.70\\ 7.70\\ 7.70\\ 7.70\\ 7.70\\ 7.71\\ 7.72\\ 7.71\\ 7.72\\ 7.71\\ 7.72\\$



 $11.5\ 11.0\ 10.5\ 10.0\ 9.5\ 9.0\ 8.5\ 8.0\ 7.5\ 7.0\ 6.5\ 6.0\ 5.5\ 5.0\ 4.5\ 4.0\ 3.5\ 3.0\ 2.5\ 2.0\ 1.5\ 1.0\ 0.5\ 0.0\ -0.5\ -1.0\ -1.5\ -2\ fl\ (ppm)$


(*R*)-1-(4-hydroxyphenyl)-1,5-diphenylpentan-3-one (40)







(R)-1-cyclohexyl-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4p)

¹H NMR (400 MHz, CDCl₃)

 $\begin{array}{c} 7.7.7\\ 7.7.7\\ 7.7.1\\ 7.$



 $11.5\ 11.0\ 10.5\ 10.0\ 9.5\ 9.0\ 8.5\ 8.0\ 7.5\ 7.0\ 6.5\ 6.0\ 5.5\ 5.0\ 4.5\ 4.0\ 3.5\ 3.0\ 2.5\ 2.0\ 1.5\ 1.0\ 0.5\ 0.0\ -0.5\ -1.0\ -1.5\ -2\ fl\ (ppm)$

- 212.87	-124.26 144.66 136.24 128.99 128.60 127.78 126.38	- 115.50	√ 51.44 √ 47.25 √ 45.05	$\int_{25.73}^{28.31} \sum_{25.73}^{28.25} \sum_{25.73}^{25.73}$
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(R)-1-(4-hydroxyphenyl)-1-phenylpentan-3-one (4q)

¹H NMR (400 MHz, CDCl₃)





-211.20 -154.50 -154.50 135.72 135.72 122.65 -115.59 -115.59	∠48.89 -45.51 ∠36.88	
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(R)-3-(4-hydroxyphenyl)-1-phenyl-3-(p-tolyl)propan-1-one (4a')

¹H NMR (400 MHz, CDCl₃)



ii (ppm)



(S)-3-(4-hydroxyphenyl)-1-phenyl-3-(m-tolyl)propan-1-one (4b')

¹H NMR (400 MHz, CDCl₃)



0

 $12.5\,12.0\,11.5\,11.0\,10.5\,10.0\,\,9.5\,\,9.0\,\,8.5\,\,8.0\,\,7.5\,\,7.0\,\,6.5\,\,6.0\,\,5.5\,\,5.0\,\,4.5\,\,4.0\,\,3.5\,\,3.0\,\,2.5\,\,2.0\,\,1.5\,\,1.0\,\,0.5\,\,0.0\,\,-0.5\,\,-1.0\,\,-1.5\,\,11\,\,(ppm)$



(S)-3-(4-hydroxyphenyl)-1-phenyl-3-(o-tolyl)propan-1-one (4c')

¹H NMR (400 MHz, CDCl₃)





(R)-3-([1,1'-biphenyl]-4-yl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4d')



11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2 fl (ppm)



(S)-3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (4e')







(S)-3-(4-hydroxyphenyl)-3-(3-methoxyphenyl)-1-phenylpropan-1-one (4f')



11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2 fl (ppm)



(S)-3-(4-hydroxyphenyl)-3-(2-methoxyphenyl)-1-phenylpropan-1-one (4g')





(*R*)-3-(4-hydroxyphenyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (4h') ¹H NMR (400 MHz, CDCl₃)





(S)-3-(4-fluorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4i')

¹H NMR (400 MHz, CDCl₃)





(S)-3-(3-fluorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4j')

¹H NMR (400 MHz, CDCl₃)





11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 fl (ppm)



(S)-3-(4-chlorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4k')



11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2 fl (ppm)







(S)-3-(4-hydroxyphenyl)-3-(naphthalen-2-yl)-1-phenylpropan-1-one (4m')

¹H NMR (400 MHz, CDCl₃)



2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 fl (ppm)



4-methoxyphenyl (R)-3-(4-hydroxyphenyl)-3-phenylpropanoate (5)

¹H NMR (CDCl₃, 400 MHz)







(-)-3-(4'-hydroxy-[1,1'-biphenyl]-4-yl)-1,3-diphenylpropan-1-one (9)

¹H NMR (CDCl₃, 400 MHz)







Copies of HPLC charts of chiral compounds (*rac*)-3-(4-hydroxyphenyl)-1,3-diphenylpropan-1-one



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	15.814	8024.1	204.3	0.5963	0.495	49.915
2	22.788	8051.3	152.2	0.8131	0.589	50.085

(R)-3-(4-hydroxyphenyl)-1,3-diphenylpropan-1-one (4a)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	16.291	459.8	11.7	0.5996	0.719	1.869
2	22.377	24133.9	447.8	0.8077	0.441	98.131

(rac)-3-(4-hydroxyphenyl)-3-phenyl-1-(p-tolyl)propan-1-one



I	reak#	Ket. lime	Area	Reight	Tidth(50%)	Area»
I	1	16, 153	170641406	3751267	0.613	51.153
	2	18, 806	162945601	3180268	0.735	48.847

(*R*)-3-(4-hydroxyphenyl)-3-phenyl-1-(*p*-tolyl)propan-1-one (4b)



Peak#	Ret. Time	Area	Height	Width (50%)	Area%
1	16.587	3938005	82754	0.719	5, 491
2	18, 781	67776213	1234249	0.837	94.509





Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	12.877	10455.7	337.5	0.5163	0.62	50.084
2	17.854	10420.4	243.0	0.6603	0.61	49.916

(*R*)-3-(4-hydroxyphenyl)-3-phenyl-1-(*m*-tolyl)propan-1-one (4c)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	12.926	2094.2	69.3	0.4628	0.731	7.916
2	17.549	24360.5	547.5	0.6811	0.510	92.084





(*R*)-3-(4-hydroxyphenyl)-3-phenyl-1-(*o*-tolyl)propan-1-one (4d)



Peak#	Ret. Time	Area	Height	Width (50%)	Ar e a %
1	19.547	17702111	335648	0. 795	9.033
2	22, 942	178279606	3077958	0. 776	90.967

(rac)-1-(2,4-dimethylphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one



(*R*)-1-(2,4-dimethylphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4e)



Peak#	Ret. Time	Area	Height	Width (50%)	Area%
1	21.347	27078036	453894	0.897	6.461
2	27.429	392014230	3996841	1.413	93, 539



(rac)-1-(4-ethylphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one

Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	14.365	4540.9	113.4	0.6051	0.560	49.891
2	19.276	4560.7	96.4	0.7298	0.726	50.109

(R)-1-(4-ethylphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4f)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	14.470	1959.1	48.0	0.6181	0.624	4.643
2	18.836	40232.7	806.8	0.7578	0.507	95.357

(rac)-3-(4-hydroxyphenyl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one



(R)-3-(4-hydroxyphenyl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one (4g)



Peak#	Ret. Time	Area	Height	Width (50%)	Area%
1	31.511	1908099	19375	1.488	3.510
2	36.400	52457229	471363	1.685	96.490





#	[min]	mAu*s	[mAu]	[min]	,	%
1	49.665	20542.2	124.5	2.3244	0.326	49.998
2	64.560	20544.2	93.0	3.0389	0.334	50.002

(R)-1-(3,4-dimethoxyphenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4h)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	51.884	1613.7	11.0	2.1069	0.573	3.970
2	62.991	39037.1	167.7	3.1095	0.280	96.030



(rac)-3-(4-hydroxyphenyl)-3-phenyl-1-(2,4,6-trimethoxyphenyl)propan-1-one



1951.2

2

43.907



14.6

1.9423

0.537

51.747

Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	36.506	8082.3	62.6	1.8955	0.364	93.651
2	44.456	547.9	4.3	1.8371	0.622	6.349



(rac)-1-(4-fluorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one







(rac)-1-(3-fluorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one

Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	14.933	3751.9	114.1	0.5076	0.657	49.324
2	22.691	3854.7	73.7	0.8041	0.626	50.676

(*R*)-1-(3-fluorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4k)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	15.024	1740.4	54.5	0.4923	0.721	13.099
2	22.366	11546.7	209.8	0.8381	0.478	86.901



(rac)-1-(4-chlorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one

Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	19.347	8666.9	190.1	0.7039	0.675	49.842
2	30.505	8721.7	120.4	1.1088	0.705	50.158

(R)-1-(4-chlorophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4l)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	19.407	5116.1	112.3	0.6994	0.719	11.450
2	29.819	39565.8	528.4	1.1535	0.518	88.550



(rac)-1-(4-bromophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one

Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	21.503	7429.3	142.4	0.8065	0.685	49.937
2	35.011	7448.1	87.6	1.3197	0.729	50.063

(R)-1-(4-bromophenyl)-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4m)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	21.557	7248.6	136.8	0.8142	0.705	8.297
2	33.954	80114.7	857.4	1.3922	0.419	91.703



(rac)-3-(4-hydroxyphenyl)-3-phenyl-1-(thiophen-2-yl)propan-1-one

Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	21.096	17798.3	316.3	0.8405	0.419	51.113
2	24.527	17023.1	292.9	0.8821	0.545	48.887

(R)-3-(4-hydroxyphenyl)-3-phenyl-1-(thiophen-2-yl)propan-1-one (4n)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	21.544	2051.2	40.3	0.7754	0.603	6.031
2	24.268	31959.4	542.9	0.8928	0.483	93.969

(rac)-1-(4-hydroxyphenyl)-1,5-diphenylpentan-3-one



(R)-1-(4-hydroxyphenyl)-1,5-diphenylpentan-3-one (40)





Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	23.390	657.0	20.5	0.5003	0.930	10.463
2	57.164	5622.3	60.3	1.3925	2.193	89.537

(rac)-1-cyclohexyl-3-(4-hydroxyphenyl)-3-phenylpropan-1-one



feak #	[min]	mAu*s	[mAu]	[min]	3	%
1	8.670	489.2	27.4	0.2762	0.771	50.199
2	10.238	501.0	22.8	0.3428	0.754	49.801

(R)-1-cyclohexyl-3-(4-hydroxyphenyl)-3-phenylpropan-1-one (4p)



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	8.566	302.9	17.7	0.2631	0.788	11.674
2	9.983	2291.7	104.8	0.3372	0.602	88.326



(rac)-1-(4-hydroxyphenyl)-1-phenylpentan-3-one







(rac)-3-(4-hydroxyphenyl)-1-phenyl-3-(p-tolyl)propan-1-one



16.937



1764473

49262

0.553

94.073


(rac)-3-(4-hydroxyphenyl)-1-phenyl-3-(m-tolyl)propan-1-one

Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	12.947	12265.8	388.5	0.4804	0.519	49.755
2	18.497	12386.6	278.0	0.6856	0.570	50.245

(R)-3-(4-hydroxyphenyl)-1-phenyl-3-(*m*-tolyl)propan-1-one (4b')



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	13.058	2385.3	78.1	0.4684	0.657	9.192
2	18.203	23564.7	503.1	0.7102	0.471	90.808





(*R*)-3-(4-hydroxyphenyl)-1-phenyl-3-(*o*-tolyl)propan-1-one (4c')





(rac)-3-([1,1'-biphenyl]-4-yl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one







(rac)-3-(4-hydroxyphenyl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one









Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	22.160	4379.6	79.9	0.8438	0.608	49.934
2	34.798	4391.3	50.5	1.3383	0.593	50.066

(S)-3-(4-hydroxyphenyl)-3-(3-methoxyphenyl)-1-phenylpropan-1-one (4f')





Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	22.641	4127.3	73.2	0.8635	0.611	11.440
2	34.309	31952.0	306.6	1.5519	0.332	88.560



(rac)-3-(4-hydroxyphenyl)-3-(2-methoxyphenyl)-1-phenylpropan-1-one

(S)-3-(4-hydroxyphenyl)-3-(2-methoxyphenyl)-1-phenylpropan-1-one (4g')



峰号	保留时间	面枳	高度	峰茂(高度	面积\$
1	21,846	3823743	73979	0, 781	10,904
2	32,679	31244997	331204	1.458	89.096



(rac)-3-(4-hydroxyphenyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one







(rac)-3-(4-fluorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one





(rac)-3-(3-fluorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	16.231	4366.8	102.8	0.6338	0.505	50.941
2	24.952	4205.5	72.1	0.9718	0.849	49.059

(S)-3-(3-fluorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (4j')



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	16.259	2429.3	64.2	0.5777	0.605	13.487
2	24.522	15583.4	273.2	0.8755	0.545	86.513



(rac)-3-(4-chlorophenyl)-3-(4-hydroxyphenyl)-1-phenylpropan-1-one









(S)-3-(4-hydroxyphenyl)-3-(naphthalen-1-yl)-1-phenylpropan-1-one (4l')



Peak#	Ret. Time	Area	Height	Width (50%)	Ar e a %
1	26.411	4968901	57007	1.326	8.617
2	30, 502	52696503	501625	1.612	91.383



(rac)-3-(4-hydroxyphenyl)-3-(naphthalen-2-yl)-1-phenylpropan-1-one

峰号	保留时间	面积	高度	峰宽(高度	面积\$
1	20, 624	15514468	290960	0, 806	49,843
2	30.681	15612233	204621	1.174	50.157

(S)-3-(4-hydroxyphenyl)-3-(naphthalen-2-yl)-1-phenylpropan-1-one (4m')



4-methoxyphenyl (rac)-3-(4-hydroxyphenyl)-3-phenylpropanoate



Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	60.066	1631.2	11.1	2.0740	0.543	50.898
2	67.220	1573.6	8.8	2.4441	0.431	49.102

4-methoxyphenyl (R)-3-(4-hydroxyphenyl)-3-phenylpropanoate (5)





Peak #	Ret. Time [min]	Area mAu*s	Height [mAu]	Width [min]	S	Area %
1	60.692	217.0	1.7	1.5047	0.875	3.180
2	64.922	6605.8	33.3	2.6586	0.282	96.820



