Supplementary data for

Catalytic asymmetric 1,6-conjugate addition of *in situ* generated *para*-quinone methides with tritylthiol

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**Contents:**

General information...........................................................................................................................................1

General procedure for the preparation of *para*-quinone methide precursors 1 .................................2

Characterization data of sulfone 1a–p...........................................................................................................2

General procedure for the phase-transfer catalyzed 1,6-conjugate addition ............................................7

Characterization data of chiral thioethers 2a–q..........................................................................................7

Determination of the absolute configuration of compound 2f.................................................................14

Procedure for the transformation of chiral thioether 2a into chiral thiol 4..............................................16

Reference .......................................................................................................................................................17

Copies of NMR spectra for new compounds.............................................................................................18

Copies of HPLC charts of chiral thioethers 2a–q and chiral thiol 4 .........................................................51
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 Avance III spectrometer operating at 400 MHz ($^1$H NMR) or 100 MHz ($^{13}$C NMR). Chemical shifts were reported in ppm downfield and referenced as follows: $^1$H: residual internal CHCl$_3$ (δ 7.26 ppm); $^{13}$C: internal CDCl$_3$ (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 XtaLAB mini (600 W, SHINE, CCD, 75 mm, 0.1 electrons/pixel/sec). Optical rotations were determined using an Autopol IV automatic polarimeter. HPLC analyses were carried out on a Hewlett Packard Model HP 1200 instrument.

Materials: Dichloromethane (CH$_2$Cl$_2$) was distilled from CaH$_2$ prior to use. Toluene and tetrahydrofuran (THF) were distilled from sodium/benzophenone. Methyl tert-butyl ether (MTBE, 99.8%) was purchased from J&K Scientific (Beijing, China). Binaphthyl-modified chiral ammonium salt B and tritylthiol were purchased from TCI (Shanghai) Development Co., Ltd. Cinchona alkaloid-derived chiral ammonium salts A were synthesized according and in analogy to literature-known methods.¹
General procedure for the preparation of para-quinone methide precursors 1

\[
\begin{array}{c}
\text{S1} \quad \text{Ar} \quad \text{HO} \\
\text{RMgBr} \\
\text{S2} \quad \text{Ar} \quad \text{HO} \\
\text{R} \\
\text{Ts} \\
\text{p-TolSO}_2\text{Na} \\
\text{p-TsOH} \\
\text{1} \\
\end{array}
\]

To a solution of aryl magnesium bromide (30.0 mmol) in anhydrous THF (60 mL) was added a solution of substituted 4-hydroxybenzaldehyde S1 (10.0 mmol) in anhydrous THF (30 mL) dropwise at room temperature. After being stirred for 1 h, the reaction mixture was quenched with saturated NH₄Cl aqueous solution (20 mL) and extracted with CH₂Cl₂ (40 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, then concentrated under vacuum to afford crude 4-(hydroxymethyl)phenol S2, which was used directly in next step without further purification.

To a mixture of sodium p-toluenesulfinate tetrahydrate (10.0 mmol) and p-toluenesulfonic acid monohydrate (p-TsOH, 15.0 mmol) in CH₂Cl₂ (20 mL) was added a solution of S2 in CH₂Cl₂ (30 mL) at room temperature. The resulting suspension was stirred for 2 h, then quenched by adjusting to pH 8 with saturated Na₂CO₃ aqueous solution. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (40 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, concentrated under vacuum and purified by recrystallization from petroleum ether and ethyl acetate to afford the corresponding sulfone 1.

Characterization data of sulfone 1a–p

2,6-dimethyl-4-(phenyl(tosyl)methyl)phenol (1a)

White solid, mp 212–215 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.50–7.47 (m, 4H, Ar-H), 7.30–7.27 (m, 3H, Ar-H), 7.16–7.14 (m, 4H, Ar-H), 5.14 (s, 1H, CH), 4.77 (br, 1H, OH), 2.36 (s, 3H, CH₃), 2.19 (s, 6H, CH₃). ¹³C NMR (CDCl₃, 100 MHz) δ 152.7, 144.3, 135.5, 133.7, 130.2, 129.9, 129.2, 129.1, 128.6, 128.4, 124.2, 123.4, 76.1, 21.6, 16.0. HRMS (ESI) m/z calcd. for C₂₂H₂₂NaO₃S⁺ 389.1182, found 389.1183 [M+Na]⁺.

2,6-dimethyl-4-(p-tolyl(tosyl)methyl)phenol (1b)

White solid, mp 199–201 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (d, J = 8.4 Hz, 2H, Ar-H), 7.36 (d, J = 8.0 Hz, 2H, Ar-H), 7.15 (d, J = 8.0 Hz, 2H, Ar-H), 7.12 (s, 2H, Ar-H), 7.09 (d, J = 8.0 Hz, 2H, Ar-H), 5.11 (s, 1H, CH), 4.82 (br, 1H, OH), 2.36 (s, 3H, CH₃), 2.30 (s, 3H, CH₃), 2.17 (s, 6H, CH₃). ¹³C NMR (CDCl₃, 100 MHz) δ 152.6, 144.3, 135.5, 133.7, 130.2, 129.9, 129.2, 129.1, 128.6, 128.4, 124.2, 123.4, 76.1, 21.6, 16.0. HRMS (ESI)
m/z calcd. for C23H24NaO3S+ 403.1338, found 403.1343 [M+Na]+.

4-((4-methoxyphenyl)(tosyl)methyl)-2,6-dimethylphenol (1c)

White solid, mp 195−197 °C. 1H NMR (CDCl3, 400 MHz) δ 7.49 (d, J = 8.0 Hz, 2H, Ar-H), 7.39 (d, J = 8.4 Hz, 2H, Ar-H), 7.16 (d, J = 8.0 Hz, 2H, Ar-H), 7.13 (s, 2H, Ar-H), 6.81 (d, J = 8.8 Hz, 2H, Ar-H), 5.11 (s, 1H, CH), 3.77 (s, 3H, CH3), 2.36 (s, 3H, CH3), 2.17 (s, 6H, CH3). 13C NMR (CDCl3, 100 MHz) δ 159.6, 152.7, 144.2, 135.5, 131.1, 130.1, 129.2, 129.1, 125.6, 124.4, 123.4, 114.0, 75.4, 55.3, 21.6, 16.1. HRMS (ESI) m/z calcd. for C23H24NaO3S+ 419.1288, found 419.1283 [M+Na]+.

4-((4-(tert-butyl)phenyl)(tosyl)methyl)-2,6-dimethylphenol (1d)

White solid, mp 199−201 °C. 1H NMR (CDCl3, 400 MHz) δ 7.49 (d, J = 8.4 Hz, 2H, Ar-H), 7.41 (d, J = 8.4 Hz, 2H, Ar-H), 7.30 (d, J = 8.4 Hz, 2H, Ar-H), 7.13−7.12 (m, 4H, Ar-H), 5.12 (s, 1H, CH), 5.00 (br, 1H, OH), 2.34 (s, 3H, CH3), 2.15 (s, 6H, CH3), 1.27 (s, 9H, C(CH3)3). 13C NMR (CDCl3, 100 MHz) δ 152.7, 151.4, 144.2, 135.6, 130.4, 130.2, 129.6, 129.1, 125.6, 124.3, 123.4, 75.9, 34.6, 31.3, 21.6, 16.0. HRMS (ESI) m/z calcd. for C26H30NaO3S+ 445.1808, found 445.1797 [M+Na]+.

4-((4-fluorophenyl)(tosyl)methyl)-2,6-dimethylphenol (1e)

White solid, mp 189−191 °C. 1H NMR (CDCl3, 400 MHz) δ 7.50−7.44 (m, 4H, Ar-H), 7.17 (d, J = 8.0 Hz, 2H, Ar-H), 7.11 (s, 2H, Ar-H), 6.98 (t, J = 8.8 Hz, 2H, Ar-H), 5.14 (s, 1H, CH), 4.88 (s, 1H, OH), 2.37 (s, 3H, CH3), 2.18 (s, 6H, CH3). 13C NMR (CDCl3, 100 MHz) δ 162.7 (d, J = 249 Hz), 152.8, 144.5, 135.3, 131.7 (d, J = 8.3 Hz), 130.1, 129.6 (d, J = 3.3 Hz), 129.3, 129.1, 123.9, 123.5, 115.6 (d, J = 21.7 Hz), 75.2, 21.6, 16.0. HRMS (ESI) m/z calcd. for C22H21FNaO3S+ 407.1088, found 407.1088 [M+Na]+.

2,6-dimethyl-4-(tosyl(4-(trifluoromethyl)phenyl)methyl)phenol (1f)

White solid, mp 198−201 °C. 1H NMR (CDCl3, 400 MHz) δ 7.67 (d, J = 8.4 Hz, 2H, Ar-H), 7.58 (d, J = 8.4 Hz, 2H, Ar-H), 7.52 (d, J = 8.0 Hz, 2H, Ar-H), 7.21 (d, J = 8.4 Hz, 2H, Ar-H), 7.11 (s, 2H, Ar-H), 5.22 (s, 1H, CH), 4.88 (s, 1H, OH), 2.41 (s, 3H, CH3), 2.21 (s, 6H, CH3). 13C NMR (DMSO-d6, 100 MHz) δ 154.0, 144.8, 139.5, 135.8, 131.0, 130.2, 129.8, 129.1 (q, J = 32.0 Hz), 129.0, 125.8 (q, J = 3.6 Hz), 124.8, 124.6 (q, J = 273 Hz), 123.4, 72.5, 21.5, 17.2. HRMS (ESI) m/z calcd. for C22H21F3NaO3S+ 457.1056, found 457.1058 [M+Na]+.
2,6-dimethyl-4-(o-tolyl(tosyl)methyl)phenol (1g)

White solid, mp 175–177 °C. \( ^1H \text{NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \) 8.15 (d, \( J = 8.0 \) Hz, 1H, Ar-H), 7.50 (d, \( J = 8.0 \) Hz, 2H, Ar-H), 7.25 (t, \( J = 7.6 \) Hz, 1H, Ar-H), 7.15–7.10 (m, 3H, Ar-H), 7.06 (s, 2H, Ar-H), 6.99 (d, \( J = 7.6 \) Hz, 1H, Ar-H), 5.47 (s, 1H, CH), 5.25 (br, 1H, OH), 2.31 (s, 3H, CH\(_3\)), 2.10 (s, 6H, CH\(_3\)), 2.04 (s, 3H, CH\(_3\)). \( ^{13}C \text{NMR} \) (CDCl\(_3\), 100 MHz) \( \delta \) 153.0, 144.4, 136.7, 135.8, 132.4, 130.7, 130.6, 129.3, 129.0, 128.9, 128.3, 126.4, 123.7, 123.4, 71.0, 21.6, 19.8, 16.1. \( \text{HRMS (ESI)} \) m/z calcd. for C\(_{23}\)H\(_{24}\)NaO\(_3\)S\(^+\) 403.1338, found 403.1338 [M+Na]\(^+\).

2,6-dimethyl-4-(tosyl(2-(trifluoromethyl)phenyl)methyl)phenol (1h)

White solid, mp 198–201 °C. \( ^1H \text{NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \) 8.57 (d, \( J = 8.0 \) Hz, 1H, Ar-H), 7.67 (t, \( J = 7.6 \) Hz, 1H, Ar-H), 7.51 (d, \( J = 7.6 \) Hz, 2H, Ar-H), 7.40 (t, \( J = 7.6 \) Hz, 1H, Ar-H), 7.16 (d, \( J = 7.6 \) Hz, 2H, Ar-H), 7.10 (s, 2H, Ar-H), 5.62 (s, 1H, CH), 4.87 (br, 1H, OH), 2.35 (s, 3H, CH\(_3\)), 2.16 (s, 6H, CH\(_3\)). \( ^{13}C \text{NMR} \) (DMSO-d\(_6\), 100 MHz) \( \delta \) 154.4, 145.2, 135.4, 133.2, 132.5, 131.1, 130.4, 130.0, 129.4, 129.1, 128.0 (q, \( J = 29.3 \) Hz), 126.8 (q, \( J = 5.8 \) Hz), 124.9, 124.4 (q, \( J = 276 \) Hz), 121.9, 70.1, 21.4, 17.1. \( \text{HRMS (ESI)} \) m/z calcd. for C\(_{23}\)H\(_{21}\)F\(_3\)NaO\(_3\)S\(^+\) 457.1056, found 457.1058 [M+Na]\(^+\).

2,6-dimethyl-4-(m-tolyl(tosyl)methyl)phenol (1i)

White solid, mp 165–168 °C. \( ^1H \text{NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \) 7.53 (d, \( J = 8.4 \) Hz, 2H, Ar-H), 7.35 (d, \( J = 7.6 \) Hz, 1H, Ar-H), 7.28 (s, 1H, Ar-H), 7.22–7.10 (m, 6H, Ar-H), 5.14 (s, 1H, CH), 4.93 (s, 1H, OH), 2.39 (s, 3H, CH\(_3\)), 2.31 (s, 3H, CH\(_3\)), 2.20 (s, 6H, CH\(_3\)). \( ^{13}C \text{NMR} \) (CDCl\(_3\), 100 MHz) \( \delta \) 152.7, 144.2, 138.2, 135.6, 133.2, 132.5, 131.1, 130.4, 130.0, 129.4, 129.1, 76.1, 21.6, 21.4, 16.0. \( \text{HRMS (ESI)} \) m/z calcd. for C\(_{23}\)H\(_{24}\)NaO\(_3\)S\(^+\) 403.1338, found 403.1338 [M+Na]\(^+\).

2,6-dimethyl-4-(tosyl(3-(trifluoromethyl)phenyl)methyl)phenol (1j)

White solid, mp 199–202 °C. \( ^1H \text{NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \) 7.82 (d, \( J = 7.6 \) Hz, 1H, Ar-H), 7.55–7.43 (m, 5H, Ar-H), 7.18 (d, \( J = 7.6 \) Hz, 2H, Ar-H), 7.12 (s, 2H, Ar-H), 5.19 (s, 1H, CH), 4.83 (br, 1H, OH), 2.38 (s, 3H, CH\(_3\)), 2.20 (s, 6H, CH\(_3\)). \( ^{13}C \text{NMR} \) (DMSO-d\(_6\), 100 MHz) \( \delta \) 154.0, 144.8, 136.1, 135.6, 133.9, 130.1, 130.0, 129.8, 129.5 (q, \( J = 31.8 \) Hz), 128.9, 127.1 (q, \( J = 3.7 \) Hz), 125.3 (q, \( J = 3.6 \) Hz), 124.9, 124.4 (q, \( J = 273 \) Hz), 123.4, 72.5, 21.4, 17.1. \( \text{HRMS (ESI)} \) m/z calcd. for C\(_{23}\)H\(_{21}\)F\(_3\)NaO\(_3\)S\(^+\) 457.1056, found 457.1058 [M+Na]\(^+\).
2,6-dimethyl-4-(naphthalen-1-yl(tosyl)methyl)phenol (1k)

White solid, mp 197–200 °C. \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.48 (d, \(J = 7.2\) Hz, 1H, Ar-H), 7.83–7.80 (m, 3H, Ar-H), 7.60–7.56 (m, 3H, Ar-H), 7.42–7.40 (m, 2H, Ar-H), 7.12 (d, \(J = 8.4\) Hz, 2H, Ar-H), 7.10 (s, 2H, Ar-H), 6.11 (s, 1H, CH), 4.80 (s, 1H, OH), 2.33 (s, 3H, CH\(_3\)), 2.16 (s, 6H, CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 152.7, 144.3, 135.9, 134.0, 131.5, 130.7, 129.6, 129.2, 129.1, 128.9, 127.2, 126.6, 125.5, 125.3, 124.1, 123.2, 122.1, 70.4, 21.5, 15.9. HRMS (ESI) \(m/z\) calcd. for C\(_{26}\)H\(_{24}\)NaO\(_3\)S\(^{+}\) 439.1338, found 439.1329 [M+Na]\(^{+}\).

2,6-dimethyl-4-(naphthalen-2-yl(tosyl)methyl)phenol (1l)

White solid, mp 203–205 °C. \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.00 (s, 1H, Ar-H), 7.82–7.79 (m, 3H, Ar-H), 7.66 (dd, \(J = 8.8, 2.0\) Hz, 1H, Ar-H), 7.55 (d, \(J = 8.4\) Hz, 2H, Ar-H), 7.50–7.48 (m, 2H, Ar-H), 7.21 (s, 2H, Ar-H), 7.15 (d, \(J = 8.0\) Hz, 2H, Ar-H), 5.36 (s, 1H, CH), 4.78 (s, 1H, OH), 2.36 (s, 3H, CH\(_3\)), 2.22 (s, 6H, CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 152.7, 144.3, 135.6, 133.1, 133.0, 131.3, 130.3, 129.3, 129.2, 128.3, 128.2, 127.6, 127.0, 126.5, 126.3, 124.3, 123.4, 76.1, 21.5, 16.0. HRMS (ESI) \(m/z\) calcd. for C\(_{26}\)H\(_{24}\)NaO\(_3\)S\(^{+}\) 439.1338, found 439.1329 [M+Na]\(^{+}\).

4-(cyclohexyl(tosyl)methyl)-2,6-dimethylphenol (1m)

White solid, mp 140–142 °C. \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.37 (d, \(J = 7.6\) Hz, 2H, Ar-H), 7.09 (d, \(J = 7.6\) Hz, 2H, Ar-H), 6.71 (s, 2H, Ar-H), 4.77 (s, 1H, OH), 3.74 (d, \(J = 7.6\) Hz, 1H, CH), 2.50–2.42 (m, 1H, CH), 2.33 (s, 3H, CH\(_3\)), 2.11 (s, 6H, CH\(_3\)), 1.80–1.74 (m, 2H, CH\(_2\)), 1.67–1.60 (m, 2H, CH\(_2\)), 1.37–1.07 (m, 5H, CH\(_2\)), 0.98–0.89 (m, 1H, CH\(_2\)). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 154.8, 144.5, 135.2, 133.5, 132.6, 129.9, 129.3, 128.9, 128.5, 124.0, 122.8, 76.6, 38.1, 32.4, 30.6, 26.2, 26.2, 26.0, 21.5, 15.9. HRMS (ESI) \(m/z\) calcd. for C\(_{22}\)H\(_{28}\)NaO\(_3\)S\(^{+}\) 395.1651, found 395.1651 [M+Na]\(^{+}\).

2-methyl-4-(phenyl(tosyl)methyl)phenol (1n)

White solid, mp 158–160 °C. \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.52 (d, \(J = 8.0\) Hz, 4H, Ar-H), 7.31–7.24 (m, 4H, Ar-H), 7.16 (d, \(J = 8.0\) Hz, 2H, Ar-H), 6.64 (d, \(J = 8.0\) Hz, 1H, Ar-H), 6.13 (s, 1H, Ar-H), 5.25 (s, 1H, CH), 2.36 (s, 3H, CH\(_3\)), 2.17 (s, 3H, CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 154.8, 144.5, 135.2, 133.5, 132.6, 129.9, 129.3, 128.7, 128.7, 128.5, 124.6, 123.9, 115.4, 76.2, 21.6, 16.0. HRMS (ESI) \(m/z\) calcd. for C\(_{21}\)H\(_{26}\)NaO\(_3\)S\(^{+}\) 375.1025, found 375.1031 [M+Na]\(^{+}\).
2-methyl-4-(p-tolyl(tosyl)methyl)phenol (1o)

Pale yellow solid, mp 124−126 °C. \( ^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \)

- 7.42 (d, \( J = 7.6 \) Hz, 2H, Ar-H), 7.30 (d, \( J = 7.6 \) Hz, 2H, Ar-H),
- 7.15−7.13 (m, 2H, Ar-H), 7.08 (d, \( J = 7.6 \) Hz, 2H, Ar-H), 7.02 (d, \( J = 7.6 \) Hz, 2H, Ar-H), 6.56 (d, \( J = 8.0 \) Hz, 1H, Ar-H), 5.34 (s, 1H), 5.08 (s, 1H), 2.29 (s, 3H, CH\(_3\)), 2.23 (s, 3H, CH\(_3\)), 2.09 (s, 3H, CH\(_3\)).

\( ^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \)

- 154.4, 144.3, 138.4, 135.4, 132.6, 130.4, 129.7, 129.4, 129.3, 129.1, 128.7, 124.7, 124.3, 115.2, 75.8, 21.6, 21.2, 15.9. HRMS (ESI) \( m/z \) calcd. for C\(_{22}\)H\(_{22}\)NaO\(_3\)S\(^+\) 389.1182, found 389.1146 [M+Na]\(^+\).

4-((4-methoxyphenyl)(tosyl)methyl)-2-methylphenol (1p)

Light pink solid, mp 118−120 °C. \( ^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \)

- 7.49 (d, \( J = 8.0 \) Hz, 2H, Ar-H), 7.39 (d, \( J = 8.4 \) Hz, 2H, Ar-H),
- 7.22−7.20 (m, 2H, Ar-H), 7.15 (d, \( J = 7.6 \) Hz, 2H, Ar-H), 6.81 (d, \( J = 8.4 \) Hz, 2H, Ar-H), 6.62 (d, \( J = 8.0 \) Hz, 1H, Ar-H), 5.15 (s, 1H, CH), 3.76 (s, 3H, CH\(_3\)), 2.36 (s, 3H, CH\(_3\)), 2.16 (s, 3H, CH\(_3\)). \( ^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \)

- 159.7, 154.6, 144.4, 135.3, 132.5, 131.2, 129.3, 129.0, 128.6, 125.4, 124.4, 115.3, 114.0, 75.5, 55.3, 21.6, 15.9. HRMS (ESI) \( m/z \) calcd. for C\(_{22}\)H\(_{22}\)NaO\(_4\)S\(^+\) 405.1131, found 405.1123 [M+Na]\(^+\).
General procedure for the phase-transfer catalyzed 1,6-conjugate addition

To a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 4-(tosylmethyl)phenol 1 (0.2 mmol), tritylthiol (0.24 mmol), catalyst B (0.002 mmol), saturated aqueous solution of Na$_2$CO$_3$ (2.0 mL) and MTBE (1 mL). The reaction mixture was stirred vigorously at room temperature until it became completely clear, which indicating a full conversion of 1.

For work-up, the mixture was diluted with water (10 mL) and extracted with CH$_2$Cl$_2$ (20 mL × 3). The combined organic layers were washed with saturate NH$_4$Cl aqueous solution (20 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The residue was subjected to flash chromatography on silica gel to afford the desired product 2.

Characterization data of chiral thioethers 2a–q

(R)-2,6-dimethyl-4-(phenyl(tritylthio)methyl)phenol (2a)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R$_f$ = 0.6), 95 mg, 98% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] $t_R$ = 7.7 min (major) and 9.8 min (minor) as 96% ee; [$\alpha$]$_D^{25}$ = +29.2 (c 1.0, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.33 (d, $J$ = 7.2 Hz, 6H, Ar-H), 7.16−7.08 (m, 14H, Ar-H), 6.67 (s, 2H, Ar-H), 4.43 (br, 1H, OH), 4.39 (s, 1H, CH), 2.12 (s, 6H, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 150.8, 144.5, 143.6, 134.8, 130.1, 128.2, 128.1, 127.9, 127.7, 126.6, 126.3, 122.7, 69.8, 54.3, 16.0. HRMS (ESI) m/z calcd. for C$_{34}$H$_{30}$NaOS$^+$ 509.1910, found 509.1914 [M+Na]$^+$.

(R)-2,6-dimethyl-4-(p-tolyl(tritylthio)methyl)phenol (2b)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R$_f$ = 0.6), 95 mg, 95% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 0.7 mL/min flow rate] $t_R$ = 8.6 min (major) and 10.0 min (minor) as 97% ee; [$\alpha$]$_D^{25}$ = −15.0 (c 1.0, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.33 (d, $J$ = 6.4 Hz, 6H, Ar-H), 7.13−7.12 (m, 9H, Ar-H), 7.02 (d, $J$ = 7.6 Hz, 2H, Ar-H), 6.96 (d, $J$ = 7.6 Hz, 2H, Ar-H), 6.63 (s, 2H, Ar-H), 4.40 (s, 1H), 4.36 (s, 1H), 2.25 (s, 3H, CH$_3$), 2.09 (s, 6H, CH$_3$). $^{13}$C
NMR (CDCl$_3$, 100 MHz) δ 150.7, 144.6, 140.7, 135.9, 135.0, 130.1, 129.0, 128.1, 127.8, 127.7, 126.6, 122.6, 69.7, 54.1, 21.1, 16.0. HRMS (ESI) m/z calcd. for C$_{35}$H$_{32}$NaO$_2$S$^+$ 523.2066, found 523.2072 [M+Na]$^+$. 

(R)-4-((4-methoxyphenyl)(tritylthio)methyl)-2,6-dimethylphenol (2c) 

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R$_f$ = 0.65), 88 mg, 85% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK IA column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] t$_R$ = 10.0 min (major) and 11.9 min (minor) as 97% ee; [α]$_D^{25}$ = −11.8 (c 1.0, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.34 (d, $J$ = 7.6 Hz, 6H, Ar-H), 7.15−7.08 (m, 9H, Ar-H), 7.04 (d, $J$ = 8.4 Hz, 2H, Ar-H), 6.68 (d, $J$ = 8.4 Hz, 2H, Ar-H), 6.64 (s, 2H, Ar-H), 4.49 (br, 1H, OH), 4.36 (s, 1H, CH$_3$), 3.71 (s, 3H, CH$_3$), 2.09 (s, 6H, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 158.1, 150.7, 144.6, 135.9, 135.1, 130.1, 129.0, 128.1, 127.7, 126.6, 113.7, 69.7, 55.4, 53.7, 16.1. HRMS (ESI) m/z calcd. for C$_{35}$H$_{32}$NaO$_2$S$^+$ 539.2015, found 539.2016 [M+Na]$^+$. 

(R)-4-((4-(tert-butyl)phenyl)(tritylthio)methyl)-2,6-dimethylphenol (2d) 

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R$_f$ = 0.6), 103 mg, 95% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK IA column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 98:2, λ 230 nm, 1.0 mL/min flow rate] t$_R$ = 9.8 min (major) and 12.1 min (minor) as 95% ee; [α]$_D^{25}$ = −18.6 (c 1.0, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.33−7.31 (m, 6H, Ar-H), 7.15−7.08 (m, 11H, Ar-H), 7.03 (d, $J$ = 8.4 Hz, 2H, Ar-H), 6.69 (s, 2H, Ar-H), 4.41 (s, 1H), 4.37 (s, 1H), 2.11 (s, 6H, CH$_3$), 1.26 (s, 9H, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 150.7, 148.9, 144.5, 140.4, 134.9, 130.1, 128.1, 127.6, 127.4, 126.5, 125.2, 122.6, 69.6, 54.0, 34.4, 31.4, 16.0. HRMS (ESI) m/z calcd. for C$_{38}$H$_{38}$NaOS$^+$ 565.2536, found 565.2535 [M+Na]$^+$. 

(R)-4-((4-fluorophenyl)(tritylthio)methyl)-2,6-dimethylphenol (2e) 

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R$_f$ = 0.6), 91 mg, 90% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK IA column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] t$_R$ = 8.1 min (major) and 9.4 min (minor) as 95% ee; [α]$_D^{25}$ = +89.6 (c 1.0, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.26 (d, $J$ = 5.6 Hz, 6H, Ar-H), 7.07−6.96 (m, 11H, Ar-H), 6.71 (t, $J$ = 8.0 Hz, 2H, Ar-H), 6.60 (s, 2H, Ar-H), 4.40 (s, 1H), 4.32 (s, 1H), 3.61 (s, 3H, CH$_3$) 

58
2.05 (s, 6H, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 161.3 (d, $J = 246$ Hz), 150.9, 144.4, 139.3 (d, $J = 3.2$ Hz), 134.7, 130.0, 129.4 (d, $J = 8.1$ Hz), 128.0, 127.7, 126.6, 122.8, 114.8 (d, $J = 21.5$ Hz), 69.7, 53.5, 15.9. HRMS (ESI) m/z calcd. for C$_{34}$H$_{29}$FNaOS$^+$ 527.1815, found 527.1815 [M+Na]$^+$. 

$(R)$-2,6-dimethyl-4-((4-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2f)

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R$_f$ = 0.5), mp 162−164 °C, 100 mg, 90% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] $t_R$ = 5.8 min (major) and 7.0 min (minor) as 92% ee; $[\alpha]_{D}^{25}$ = +99.0 (c 1.0, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.35−7.30 (m, 8H, Ar-H), 7.16−7.10 (m, 11H, Ar-H), 6.73 (s, 2H, Ar-H), 4.55 (s, 1H), 4.48 (s, 1H), 2.14 (s, 6H, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 151.2, 147.5, 144.2, 133.9, 129.9, 128.3 (q, $J = 32.2$ Hz), 128.1, 128.0, 127.8, 126.7, 125.0 (q, $J = 3.7$ Hz), 124.3 (q, $J = 273$ Hz), 123.1, 69.8, 53.8, 16.0. HRMS (ESI) m/z calcd. for C$_{35}$H$_{29}$F$_3$NaOS$^+$ 577.1783, found 577.1786 [M+Na]$^+$. 

$(S)$-2,6-dimethyl-4-(o-tolyl(tritylthio)methyl)phenol (2g)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R$_f$ = 0.6), 90 mg, 90% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] $t_R$ = 5.6 min (major) and 6.8 min (minor) as 97% ee; $[\alpha]_{D}^{25}$ = +140.2 (c 1.0, CH$_2$Cl$_2$). $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.77 (d, $J = 7.6$ Hz, 1H, Ar-H), 7.33 (dd, $J = 7.6$, 1.6 Hz, 6H, Ar-H), 7.14−7.12 (m, 10H, Ar-H), 7.01 (t, $J = 7.6$ Hz, 1H, Ar-H), 6.86 (d, $J = 7.2$ Hz, 1H, Ar-H), 6.59 (s, 2H, Ar-H), 4.62 (s, 1H), 4.42 (s, 1H), 2.10 (s, 6H, CH$_3$), 1.82 (s, 3H, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 150.7, 144.6, 141.3, 134.6, 133.9, 130.0, 129.9, 129.0, 128.3, 127.6, 126.6, 126.3, 125.9, 122.7, 70.0, 50.4, 19.5, 16.0. HRMS (ESI) m/z calcd. for C$_{35}$H$_{32}$NaOS$^+$ 523.2066, found 523.2066 [M+Na]$^+$. 

$(S)$-2,6-dimethyl-4-((2-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2h)

Obtained as a white foamy solid after column chromatography...
(petroleum ether/ethyl acetate = 5:1, Rf = 0.5), 105 mg, 95% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 98:2, λ 230 nm, 1.0 mL/min flow rate] tR = 11.4 min (major) and 14.5 min (minor) as 93% ee; [α]D25 = +84.6 (c 1.0, CH2Cl2). 1H NMR (CDCl3, 400 MHz) δ 8.06 (d, J = 7.6 Hz, 1H, Ar-H), 7.39–7.25 (m, 8H, Ar-H), 7.14–7.02 (m, 10H, Ar-H), 6.42 (s, 2H, Ar-H), 5.04 (s, 1H), 4.37 (s, 1H), 1.98 (s, 6H, CH3). 13C NMR (CDCl3, 100 MHz) δ 151.0, 144.2, 141.1, 133.8, 131.7, 131.6, 130.0, 128.1, 127.7, 126.9 (q, J = 29.8 Hz), 126.7, 126.6, 125.9 (q, J = 6.0 Hz), 124.2 (q, J = 276 Hz), 122.8, 70.1, 49.3, 16.1. HRMS (ESI) m/z calcd. for C35H29F3NaOS+ 577.1783, found 577.1786 [M+Na]+.

(R)-2,6-dimethyl-4-(m-tolyl(tritylthio)methyl)phenol (2i)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, Rf = 0.6), 95 mg, 95% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 98:2, λ 230 nm, 1.0 mL/min flow rate] tR = 9.5 min (major) and 11.1 min (minor) as 97% ee; [α]D25 = +33.6 (c 1.0, CH2Cl2). 1H NMR (CDCl3, 400 MHz) δ 7.33 (dd, J = 8.0, 1.6 Hz, 6H, Ar-H), 7.16–7.09 (m, 9H, Ar-H), 7.03 (t, J = 7.6 Hz, 1H, Ar-H), 6.95 (d, J = 7.6 Hz, 1H, Ar-H), 6.85 (d, J = 7.2 Hz, 1H, Ar-H), 6.83 (s, 1H, Ar-H), 6.80 (2H, Ar-H), 6.68 (s, 2H, Ar-H), 4.42 (s, 1H), 4.37 (s, 1H), 2.22 (s, 3H, CH3), 2.12 (s, 6H, CH3). 13C NMR (CDCl3, 100 MHz) δ 150.7, 144.5, 143.4, 137.6, 134.9, 130.0, 128.5, 128.1, 128.0, 127.6, 127.0, 126.5, 124.9, 122.6, 69.6, 54.3, 21.4, 15.9. HRMS (ESI) m/z calcd. for C35H32F3NaOS+ 523.2066, found 523.2063 [M+Na]+.

(R)-2,6-dimethyl-4-((3-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2j)

Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate = 5:1, Rf = 0.5), mp 174–176 °C, 106 mg, 96% yield. The enantioselectivity was determined by HPLC using a CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 98:2, λ 230 nm, 1.0 mL/min flow rate] tR = 13.4 min (minor) and 15.9 min (major) as 88% ee; [α]D25 = +151.2 (c 1.0, CH2Cl2). 1H NMR (CDCl3, 400 MHz) δ 7.41 (d, J = 6.8 Hz, 6H, Ar-H), 7.36–7.33 (m, 2H, Ar-H), 7.28–7.14 (m, 11H, Ar-H), 6.82 (2H, Ar-H), 4.58 (s, 1H), 4.54 (s, 1H), 2.22 (s, 6H, CH3). 13C NMR (CDCl3, 100 MHz) δ 151.2, 144.3, 144.1, 134.1, 131.3, 129.9, 128.5, 127.9, 127.8, 126.8, 124.5 (q, J = 3.8 Hz), 124.1 (q, J = 274 Hz), 123.2, 122.9 (q, J = 3.7 Hz), 69.7, 53.8, 16.0. HRMS (ESI) m/z calcd. for C35H29F3NaOS+ 577.1783, found 577.1786 [M+Na]+.

(S)-2,6-dimethyl-4-(naphthalen-1-yl(tritylthio)methyl)phenol (2k)
Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R<sub>f</sub> = 0.6), 100 mg, 93% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] t<sub>R</sub> = 6.7 min (major) and 8.8 min (minor) as 96% ee; [α]<sub>D</sub><sup>25</sup> = +108.4 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

1<sup>H</sup> NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.71 (d, J = 8.0 Hz, 1H, Ar-H), 7.62−7.57 (m, 2H, Ar-H), 7.37−7.21 (m, 10H, Ar-H), 7.07−7.02 (m, 9H, Ar-H), 6.77 (s, 2H, Ar-H), 5.28 (s, 1H), 4.43 (s, 1H), 2.08 (s, 6H, CH<sub>3</sub>).

13<sup>C</sup> NMR (CDCl<sub>3</sub>, 100 MHz) δ 150.9, 144.5, 138.5, 134.0, 133.8, 130.5, 130.0, 128.6, 128.2, 127.6, 127.2, 127.0, 126.5, 125.6, 125.3, 125.1, 123.6, 122.8, 69.9, 50.1, 16.0.

HRMS (ESI) m/z calcd. for C<sub>38</sub>H<sub>32</sub>NaOS<sup>+</sup> 559.2066, found 559.2072 [M+Na]<sup>+</sup>.

(R)-2,6-dimethyl-4-(naphthalen-2-yl(tritylthio)methyl)phenol (2l)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R<sub>f</sub> = 0.6), 104 mg, 97% yield. The enantioselectivity was determined by HPLC using a CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] t<sub>R</sub> = 9.4 min (minor) and 10.8 min (major) as 94% ee; [α]<sub>D</sub><sup>25</sup> = −20.8 (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

1<sup>H</sup> NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.69 (d, J = 7.2 Hz, 1H, Ar-H), 7.64−7.59 (m, 2H, Ar-H), 7.42−7.35 (m, 9H, Ar-H), 7.29 (d, J = 8.8 Hz, 1H, Ar-H), 7.11−7.03 (m, 9H, Ar-H), 6.75 (s, 2H, Ar-H), 4.60 (s, 1H), 4.45 (s, 1H), 2.10 (s, 6H, CH<sub>3</sub>).

13<sup>C</sup> NMR (CDCl<sub>3</sub>, 100 MHz) δ 150.9, 144.5, 134.7, 133.3, 132.2, 130.1, 128.3, 127.9, 127.7, 127.5, 126.6, 126.2, 125.9, 125.5, 122.8, 69.8, 54.5, 16.0. HRMS (ESI) m/z calcd. for C<sub>38</sub>H<sub>32</sub>NaOS<sup>+</sup> 559.2066, found 559.2065 [M+Na]<sup>+</sup>.

(R)-4-(cyclohexyl(tritylthio)methyl)-2,6-dimethylphenol (2m)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, R<sub>f</sub> = 0.5), 94 mg, 95% yield. The enantioselectivity was determined by HPLC using a CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 98:2, λ 230 nm, 1.0 mL/min flow rate] t<sub>R</sub> = 22.6 min (major) and 27.5 min (minor) as 90% ee.

1<sup>H</sup> NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.36 (d, J = 6.8 Hz, 6H, Ar-H), 7.20−7.15 (m, 9H, Ar-H), 6.52 (s, 2H, Ar-H), 4.48 (s, 1H, OH), 3.03 (d, J = 5.2 Hz, 1H, CH), 2.17 (s, 6H, CH<sub>3</sub>), 1.70−1.67 (m, 1H, CH), 1.62−1.47 (m, 4H, CH<sub>2</sub>), 1.05−0.96 (m, 2H, CH<sub>2</sub>), 0.92−0.87 (m, 2H, CH<sub>2</sub>), 0.81−0.71 (m, 1H, CH<sub>3</sub>), 0.61−0.52 (m, 1H, CH<sub>3</sub>).

13<sup>C</sup> NMR (CDCl<sub>3</sub>, 100 MHz) δ 150.4, 145.0, 133.2, 130.0, 129.4, 127.5, 126.4, 121.6, 68.5, 55.8, 44.3, 32.1, 29.2, 27.0, 26.6, 26.2, 16.0. HRMS (ESI) m/z calcd. for C<sub>34</sub>H<sub>36</sub>NaOS<sup>+</sup> 515.2379, found 515.2366 [M+Na]<sup>+</sup>.
(R)-2-methyl-4-(phenyl(tritylthio)methyl)phenol (2n)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, Rf = 0.6), 85 mg, 90% yield. The enantioselectivity was determined by HPLC using a CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] tR = 12.6 min (major) and 18.1 min (minor) as 83% ee; [α]D25 = +26.6 (c 1.0, CH2Cl2).1H NMR (CDCl3, 400 MHz) δ 7.35 (dd, J = 8.0, 1.6 Hz, 6H, Ar-H), 7.18−7.09 (m, 14H, Ar-H), 6.85−6.80 (m, 2H, Ar-H), 6.55 (d, J = 8.0 Hz, 1H, Ar-H), 4.51 (s, 1H), 4.42 (s, 1H), 2.13 (s, 3H, CH3).13C NMR (CDCl3, 100 MHz) δ 152.3, 144.4, 143.5, 135.5, 130.6, 130.0, 128.2, 127.9, 127.6, 126.6, 126.3, 123.3, 114.7, 69.7, 54.2, 15.7. HRMS (ESI) m/z calcd. for C33H28NaOS+ 495.1753, found 495.1752 [M+Na]+.

(R)-2-methyl-4-(p-tolyl(tritylthio)methyl)phenol (2o)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, Rf = 0.6), 88 mg, 90% yield. The enantioselectivity was determined by HPLC using a CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] tR = 16.7 min (major) and 20.0 min (minor) as 83% ee; [α]D25 = −15.6 (c 1.0, CH2Cl2).1H NMR (CDCl3, 400 MHz) δ 7.33 (d, J = 7.2 Hz, 6H, Ar-H), 7.14−7.09 (m, 9H, Ar-H), 7.02−6.95 (m, 4H, Ar-H), 6.80 (d, J = 8.0 Hz, 1H, Ar-H), 6.75 (s, 1H, Ar-H), 6.50 (d, J = 8.0 Hz, 1H, Ar-H), 4.53 (s, 1H), 4.38 (s, 1H), 2.25 (s, 3H, CH3), 2.09 (s, 3H, CH3).13C NMR (CDCl3, 100 MHz) δ 152.2, 144.5, 140.6, 135.9, 135.6, 130.6, 130.0, 129.0, 127.7, 127.6, 126.5, 123.2, 114.6, 69.7, 53.9, 21.1, 15.8. HRMS (ESI) m/z calcd. for C34H30NaOS+ 509.1910, found 509.1893 [M+Na]+.

(R)-4-((4-methoxyphenyl)(tritylthio)methyl)-2-methylphenol (2p)

Obtained as a white foamy solid after column chromatography (petroleum ether/ethyl acetate = 5:1, Rf = 0.65), 92 mg, 91% yield. The enantioselectivity was determined by HPLC using a CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 98:2, λ 230 nm, 1.0 mL/min flow rate] tR = 22.5 min (major) and 29.2 min (minor) as 90% ee; [α]D25 = −14.4 (c 1.0, CH2Cl2).1H NMR (CDCl3, 400 MHz) δ 7.39 (dd, J = 8.4, 1.6 Hz, 6H, Ar-H), 7.22−7.17 (m, 9H, Ar-H), 7.08 (d, J = 8.4 Hz, 2H, Ar-H), 6.87−6.82 (m, 2H, Ar-H), 6.74 (d, J = 8.4 Hz, 2H, Ar-H), 6.57 (d, J = 8.4 Hz, 1H, Ar-H), 4.65 (s, 1H), 4.44 (s, 1H), 3.78 (s, 3H, CH3), 2.16 (s, 3H, CH3).13C NMR (CDCl3, 100 MHz) δ 158.0, 152.3, 144.5, 140.6, 135.9, 135.6, 130.6, 130.0, 129.0, 127.7, 127.6, 126.5, 123.2, 114.6, 69.7, 55.3, 53.6, 15.8. HRMS

512
(ESI) m/z calcd. for C$_{34}$H$_{30}$NaO$_2$S$^+$ 525.1859, found 525.1875 [M$^+$Na]$^+$.  

(R)-4-(phenyl(tritylthio)methyl)phenol (2q)

Obtained as a colorless oil after column chromatography (petroleum ether/ethyl acetate 5:1, R$_f$ = 0.5), 78 mg, 85% yield. The enantioselectivity was determined by HPLC using a CHIRALPAK AS column (25 cm × 0.46 cm ID), [hexane/isopropanol = 95:5, λ 230 nm, 1.0 mL/min flow rate] $t_R$ = 21.8 min (major) and 28.2 min (minor) as 52% ee; [α]$_{D}^{25}$ = +11.6 (c 1.0, CH$_2$Cl$_2$). 

$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.33 (dd, $J$ = 8.0, 1.6 Hz, 6H, Ar-H), 7.17−7.07 (m, 14H, Ar-H), 6.97 (d, $J$ = 8.4 Hz, 2H, Ar-H), 6.59 (d, $J$ = 8.4 Hz, 2H, Ar-H), 4.63 (br, 1H, OH), 4.42 (s, 1H, CH).
Determination of the absolute configuration of compound 2f

The single crystal of 2f was grown from its petroleum ether solution using a slow evaporation method. After single crystal X-ray analysis, the absolute configuration was unambiguously determined as $R$.

Supplementary Table 1. Crystallographic data and structure refinement for 2f

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<td>Completeness</td>
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<tr>
<td>Max. and min. transmission</td>
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<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
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<tr>
<td>Final R indices [$I&gt;2\sigma(I)$]</td>
<td>$R_1 = 0.0302, wR_2 = 0.0737$</td>
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<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0348, wR_2 = 0.0759$</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.204 and $-0.243$ e/Å$^3$</td>
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</table>
Procedure for the transformation of chiral thioether 2a into chiral thiol 4

At 0 °C, to a solution of 2a (243 mg, 0.5 mmol) in CH₂Cl₂ (5 mL) was added pyridine (80 μL, 1 mmol) and Tf₂O (100 μL, 0.6 mmol) in turns. The resulting mixture was allowed to warm to room temperature and was stirred for 12 h. After removal of the solvent, the residue was diluted with ethyl acetate (20 mL), washed with 1N HCl aqueous solution (10 mL) and saturated brine (10 mL). The organic layer was dried over anhydrous Na₂SO₄, concentrated under vacuum to afford 3, which was used directly in next step without further purification.

Under argon atmosphere, to a solution of 3 (75 mg, 0.12 mmol) in CH₂Cl₂ (2 mL) was added trifluoroacetic acid (TFA, 50 μL, 0.65 mmol) and triethylsilane (Et₃SiH, 32 μL, 0.2 mmol) at room temperature. After being stirred for 0.5 h, the reaction mixture was quenched with saturated NaHCO₃ aqueous solution (5 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, concentrated under vacuum and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, Rf = 0.7) to afford (R)-4-(mercapto(phenyl)methyl)-2,6-dimethylphenyl trifluoromethanesulfonate 4 (36 mg, 0.96 mmol) as a colorless oil in 80% yield. The enantioselectivity was determined by HPLC using a CHIRALCEL OD-H column (25 cm × 0.46 cm ID), [hexane/iso-propanol = 98:2, λ = 230 nm, 1.0 mL/min flow rate] tᵣ = 6.6 min (major) and 7.2 min (minor) as 95% ee; [α]D²⁵ = −4.8 (c 1.0, CH₂Cl₂). ¹H NMR (CDCl₃, 400 MHz) δ 7.32−7.19 (m, 5H, Ar-H), 7.08 (s, 2H, Ar-H), 5.29 (d, J = 4.4 Hz, 1H, CH), 2.28 (s, 6H, CH₃), 2.21 (d, J = 4.4 Hz, 1H, SH). ¹³C NMR (CDCl₃, 100 MHz) δ 145.8, 143.2, 142.6, 131.7, 129.2, 128.8, 127.7, 127.5, 118.6 (q, J = 321 Hz), 47.0, 17.3. HRMS (ESI) m/z calcd. for C₁₆H₁₄F₃O₃S₂⁻ 375.0342, found 375.0338 [M+Na]⁺.
Reference


3 The CIF file was deposited at the Cambridge Crystallographic Data Center (CCDC 1540101) and contains the supplementary crystallographic data for this article. The data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
Copies of NMR spectra for new compounds

2,6-dimethyl-4-(phenyl(tosyl)methyl)phenol (1a)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
2,6-dimethyl-4-((p-tolyl(tosyl)methyl)phenol (1b)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
4-((4-methoxyphenyl)(tosyl)methyl)-2,6-dimethylphenol (1c)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
4-((4-(tert-butyl)phenyl)(tosyl)methyl)-2,6-dimethylphenol (1d)

\[
\begin{align*}
&\text{H NMR (CDCl}_3, 400 MHz) \\
&\text{C NMR (CDCl}_3, 100 MHz)
\end{align*}
\]

\[
\begin{align*}
&\text{H NMR (CDCl}_3, 400 MHz) \\
&\text{C NMR (CDCl}_3, 100 MHz)
\end{align*}
\]
4-((4-fluorophenyl)(tosyl)methyl)-2,6-dimethylphenol (1e)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
2,6-dimethyl-4-(tosyl(4-(trifluoromethyl)phenyl)methyl)phenol (1f)

**1H NMR (CDCl₃, 400 MHz)**

**13C NMR (DMSO-$_d_6$, 100 MHz)**
2,6-dimethyl-4-(o-tolyl(tosyl)methyl)phenol (1g)

$^{1}H$ NMR (CDCl$_3$, 400 MHz)

$^{13}C$ NMR (CDCl$_3$, 100 MHz)
2,6-dimethyl-4-(tosyl(2-(trifluoromethyl)phenyl)methyl)phenol (1h)

$\text{H NMR (CDCl}_3, 400 \text{ MHz)}$

$\text{C NMR (DMSO-}d_6, 100 \text{ MHz)}$

S25
2,6-dimethyl-4-\((m\)-tolyl(tosyl)methyl\)phenol (1i)

\[^1\text{H}\text{NMR}\] (CDCl\(_3\), 400 MHz)

\[^{13}\text{C}\text{NMR}\] (CDCl\(_3\), 100 MHz)
2,6-dimethyl-4-(tosyl(3-(trifluoromethyl)phenyl)methyl)phenol (1j)

$\textbf{1}^1\text{H NMR (CDCl}_3, 400 \text{ MHz)}$

$\textbf{1}^{13}\text{C NMR (DMSO-}d_6, 100 \text{ MHz)}$
2,6-dimethyl-4-(naphthalen-1-yl(tosyl)methyl)phenol (1k)

**1H NMR (CDCl₃, 400 MHz)**

**13C NMR (CDCl₃, 100 MHz)**
2,6-dimethyl-4-(naphthalen-2-yl(tosyl)methyl)phenol (1l)

\[ \text{1H NMR (CDCl}_3, 400 MHz) \]

\[ \text{13C NMR (CDCl}_3, 100 MHz) \]
4-(cyclohexyl(tosyl)methyl)-2,6-dimethylphenol (1m)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
2-methyl-4-(phenyl(tosyl)methyl)phenol (1n)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
2-methyl-4-(p-tolyI(tosyl)methyl)phenol (1o)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
4-((4-methoxyphenyl)(tosyl)methyl)-2-methylphenol (1p)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(R)-2,6-dimethyl-4-(phenyl(tritylthio)methyl)phenol (2a)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(R)-2,6-dimethyl-4-(p-tolyl(tritylthio)methyl)phenol (2b)

\[ \text{H NMR (CDCl}_3, 400 \text{ MHz)} \]

\[ \text{C NMR (CDCl}_3, 100 \text{ MHz)} \]

\[ \text{13C NMR (CDCl}_3, 100 \text{ MHz)} \]
(R)-4-((4-methoxyphenyl)(tritylthio)methyl)-2,6-dimethylphenol (2c)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
"(R)-4-((4-(tert-butyl)phenyl)(tritylthio)methyl)-2,6-dimethylphenol (2d)"

\[
\text{HO} \quad \text{Me} \\
\text{Me} \quad \text{tBu} \\
\text{SCPh}_3 \quad 2d
\]

$\text{H NMR (CDCl}_3, 400 \text{ MHz)}$

\[
\text{ppm (H)}
\]

\[
\text{13C NMR (CDCl}_3, 100 \text{ MHz)}
\]

\[
\text{ppm (C)}
\]
(R)-4-((4-fluorophenyl)(tritylthio)methyl)-2,6-dimethylphenol (2e)

\[ \text{S38} \]

\[ \text{R}-4-((4\text{-fluorophenyl})(\text{tritylthio})\text{methyl})-2,6\text{-dimethylphenol (2e)} \]

**\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz)**

\[ \text{HO} \]
\[ \text{Me} \]
\[ \text{Me} \]
\[ \text{F} \]
\[ \text{SCPh} \]
\[ \text{3} \]

\[ \text{2e} \]

**\(^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz)**

\[ \text{CDCl}_3 \]

\[ \text{Me} \]
\[ \text{Me} \]
\[ \text{F} \]
\[ \text{SCPh}_3 \]

\[ \text{2e} \]
(R)-2,6-dimethyl-4-((4-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2f)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(S)-2,6-dimethyl-4-(o-tolyl(tritylthio)methyl)phenol (2g)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(S)-2,6-dimethyl-4-((2-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2h)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(R)-2,6-dimethyl-4-(m-tolyl(tritylthio)methyl)phenol (2i)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(R)-2,6-dimethyl-4-((3-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2j)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(S)-2,6-dimethyl-4-(naphthalen-1-yl(tritylthio)methyl)phenol (2k)

$^{1}H$ NMR (CDCl$_3$, 400 MHz)

$^{13}C$ NMR (CDCl$_3$, 100 MHz)
(R)-2,6-dimethyl-4-(naphthalen-2-yl(tritylthio)methyl)phenol (2l)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(R)-4-(cyclohexyl(tritylthio)methyl)-2,6-dimethylphenol (2m)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(R)-2-methyl-4-(phenyl(tritylthio)methyl)phenol (2n)

$^{1}H$ NMR (CDCl$_3$, 400 MHz)

$^{13}C$ NMR (CDCl$_3$, 100 MHz)
(R)-2-methyl-4-(p-tolyl(tritylthio)methyl)phenol (2o)

**1H NMR (CDCl₃, 400 MHz)**

**13C NMR (CDCl₃, 100 MHz)**
(R)-4-((4-methoxyphenyl)(tritylthio)methyl)-2-methylphenol (2p)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
(R)-4-(mercapto(phenyl)methyl)-2,6-dimethylphenyl trifluoromethanesulfonate (4)

$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
Copies of HPLC charts of chiral thioethers 2a–q and chiral thiol 4

(rac)-2,6-dimethyl-4-(phenyl(tritylthio)methyl)phenol

(R)-2,6-dimethyl-4-(phenyl(tritylthio)methyl)phenol (2a)
(rac)-2,6-dimethyl-4-(p-tolyl(tritylthio)methyl)phenol

(Signal 1: VWD1 A, Wavelength=230 nm)

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<th>Area [mAU]</th>
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(R)-2,6-dimethyl-4-(p-tolyl(tritylthio)methyl)phenol (2b)

(Signal 1: VWD1 A, Wavelength=230 nm)

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(rac)-4-((4-methoxyphenyl)(tritylthio)methyl)-2,6-dimethylphenol

\[
\begin{align*}
\text{Signal 1: VWD1 A, Wavelength=230 nm} \\
\text{Peak RetTime Type Width Area Height Area %} \\
\hline \\
1 & 10.253 & VV & 0.4659 & 1.9495e4 & 610.27269 & 49.8227 & \\
2 & 12.278 & VB & 0.5052 & 1.9634e4 & 568.02246 & 50.1773 & \\
\end{align*}
\]

(R)-4-((4-methoxyphenyl)(tritylthio)methyl)-2,6-dimethylphenol (2c)

\[
\begin{align*}
\text{Signal 1: VWD1 A, Wavelength=230 nm} \\
\text{Peak RetTime Type Width Area Height Area %} \\
\hline \\
1 & 9.966 & BV & 0.3309 & 2.7524e4 & 1243.97595 & 98.2708 & \\
2 & 11.928 & VB & 0.4245 & 484.34882 & 16.76044 & 1.7292 & \\
\end{align*}
\]
(rac)-4-((4-(tert-butyl)phenyl)(tritylthio)methyl)-2,6-dimethylphenol

(S)-4-((4-(tert-butyl)phenyl)(tritylthio)methyl)-2,6-dimethylphenol (2d)

(R)-4-((4-(tert-butyl)phenyl)(tritylthio)methyl)-2,6-dimethylphenol (2d)
(rac)-4-((4-fluorophenyl)(tritylthio)methyl)-2,6-dimethylphenol

Signal 1: VWD1 A, Wavelength=230 nm

| Peak RetTime Type Width Area  Height Area |
|---|---|---|---|---|---|
| 1 | 8.112 | 0.3219 | 3.13788e4 | 1435.93005 | 49.5286 |
| 2 | 9.344 | 0.3563 | 3.19762e4 | 1329.54529 | 50.4714 |

(R)-4-((4-fluorophenyl)(tritylthio)methyl)-2,6-dimethylphenol (2e)

Signal 1: VWD1 A, Wavelength=230 nm

| Peak RetTime Type Width Area  Height Area |
|---|---|---|---|---|
| 1 | 8.117 | 0.2964 | 3.84530e4 | 1930.87268 | 97.2984 |
| 2 | 9.376 | 0.3222 | 1067.67859 | 49.36447 | 2.7016 |
(rac)-2,6-dimethyl-4-((4-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol

(R)-2,6-dimethyl-4-((4-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2f)
(rac)-2,6-dimethyl-4-((o-tolyl(tritylthio)methyl)phenol

(S)-2,6-dimethyl-4-((o-tolyl(tritylthio)methyl)phenol (2g)

Signal 1: VWD1 A, Wavelength=230 nm

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<th>Type</th>
<th>Width (min)</th>
<th>Area (mAU s)</th>
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Signal 1: VWD1 A, Wavelength=230 nm

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(rac)-2,6-dimethyl-4-((2-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol

(S)-2,6-dimethyl-4-((2-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2h)
(rac)-2,6-dimethyl-4-(m-tolyl(tritylthio)methyl)phenol

Signal 1: VWD1 A, Wavelength=230 nm

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(R)-2,6-dimethyl-4-(m-tolyl(tritylthio)methyl)phenol (2i)

Signal 1: VWD1 A, Wavelength=230 nm

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(rac)-2,6-dimethyl-4-((3-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol

![Graph](image1)

<table>
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(R)-2,6-dimethyl-4-((3-(trifluoromethyl)phenyl)(tritylthio)methyl)phenol (2j)

![Graph](image2)

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<th>Area <strong>%</strong></th>
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</table>
(rac)-2,6-dimethyl-4-(naphthalen-1-yl(tritylthio)methyl)phenol

![Graph](image_url)

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(S)-2,6-dimethyl-4-(naphthalen-1-yl(tritylthio)methyl)phenol (2k)

![Graph](image_url)

<table>
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(rac)-2,6-dimethyl-4-(naphthalen-2-yl(thiophenyl)methyl)phenol

Signal 1: VWD1 A, Wavelength=230 nm

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

1 9.343 VV 0.4706 2.4754e4 804.03076 49.4193
2 10.894 VB 0.6679 2.5286e4 574.47363 50.5807

(R)-2,6-dimethyl-4-(naphthalen-2-yl(tritylthio)methyl)phenol (2l)

Signal 1: VWD1 A, Wavelength=230 nm

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

1 9.363 BV 0.4647 2581.07544 84.71452 3.0992
2 10.755 VB 0.6336 8.0701e4 1906.69055 96.9008
(rac)-4-(cyclohexyl(tritylthio)methyl)-2,6-dimethylphenol

Signal 1: VwD1 A, Wavelength=230 nm

<table>
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<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>23.610</td>
<td>VV</td>
<td>1.0628</td>
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<td>44.06628</td>
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<td>2</td>
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<td>1.2349</td>
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(R)-4-(cyclohexyl(tritylthio)methyl)-2,6-dimethylphenol (2m)

Signal 1: VwD1 A, Wavelength=230 nm

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<th>Peak</th>
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<tbody>
<tr>
<td>1</td>
<td>22.645</td>
<td>VV</td>
<td>0.9432</td>
<td>1.74221e5</td>
<td>2182.03223</td>
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(rac)-2-methyl-4-(phenyl(tritylthio)methyl)phenol

Signal 1: VWD A, Wavelength=230 nm

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
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<td>1.1290</td>
<td>9045.09180</td>
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(R)-2-methyl-4-(phenyl(tritylthio)methyl)phenol (2n)

Signal 1: VWD A, Wavelength=230 nm

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<th>Peak RetTime</th>
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<th>Area %</th>
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<td>6.18146e4</td>
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<td>1.0541</td>
<td>5667.50195</td>
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(rac)-2-methyl-4-(p-tolyl(tritylthio)methyl)phenol

(R)-2-methyl-4-(p-tolyl(tritylthio)methyl)phenol (2o)
(rac)-4-((4-methoxyphenyl)(tritylthio)methyl)-2-methylphenol

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type Width Area Height Area %
# [min] [min] mAU *s [mAU ] %
---|-----|------|-----|-----|-----|-----|
1  23.958 BB  1.2077 1.00330e4  105.58058  49.5616
2  30.326 VB  1.6214 1.02104e4  74.47016  50.4384

(R)-4-((4-methoxyphenyl)(tritylthio)methyl)-2-methylphenol (2p)

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type Width Area Height Area %
# [min] [min] mAU *s [mAU ] %
---|-----|------|-----|-----|-----|-----|
1  22.501 BB  1.3022 1.00930e5  1051.12402  94.7446
2  29.195 BB  1.5454 5598.58293  42.87058  5.2554
(rac)-4-(phenyl(tritylthio)methyl)phenol

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type Width Area Height Area %
---------------------------------------------
# [min] [min] mAU *s [mAU ] %
---------------------------------------------
1 21.854 BB 1.5847 1.92960e4 160.66270 50.5852
2 28.016 BB 1.8417 1.88495e4 122.30628 49.4148

(R)-4-(phenyl(tritylthio)methyl)phenol (2q)

Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type Width Area Height Area %
---------------------------------------------
# [min] [min] mAU *s [mAU ] %
---------------------------------------------
1 21.800 BB 1.6078 2.10132e4 175.34082 76.0852
2 28.246 BB 1.6619 6604.76611 46.77528 23.9148
(rac)-4-(mercapto(phenyl)methyl)-2,6-dimethylphenyl trifluoromethanesulfonate

Signal 1: VWD1 A, Wavelength=230 nm

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<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
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<td>s[mAU]</td>
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<tr>
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<td>0.218</td>
<td>4717.13916</td>
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(R)-4-(mercapto(phenyl)methyl)-2,6-dimethylphenyl trifluoromethanesulfonate (4)

Signal 1: VWD1 A, Wavelength=230 nm

<table>
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<tr>
<th>Peak</th>
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<th>Type</th>
<th>Width</th>
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<td>s[mAU]</td>
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