Supporting Information

Friedel-Crafts Alkylation of Arenes with Epoxides Promoted by Fluorinated Alcohols or Water

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General information: All reactions were carried out in aerial atmosphere. Water was purchased from Watson’s or from Milli-Q® Ultrapure Water Purification System. 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) were used as received from Acros®. Substrates were synthesized according to the known procedures. Flash column chromatography was performed using the indicated solvent system on Qingdao–Haiyang® silica gel (200–300 mesh). All of the compounds were characterized by $^1$H NMR and $^{13}$C NMR. $^1$H NMR spectra were recorded at 300 MHz, 400 MHz or 600 MHz NMR machine; $^{13}$C NMR spectra were recorded at 75 MHz, 100 MHz or 150 MHz NMR machine. Peaks recorded are relative to the internal standards: TMS ($\delta = 0.00$) for $^1$H NMR and CDCl$_3$ ($\delta = 77.00$) for $^{13}$C NMR spectra. Optical rotations were measured on a Perkin Elmer 341 MC polarimeter. High resolution mass spectral analyses (HRMS) were performed on high resolution ESI–FTICR mass spectrometer (Varian 7.0 T).

General procedure for the preparation of starting materials.

$(2R,3R)$-2-((3,5-Dimethoxyphenoxy)methyl)-3-phenyloxirane (Table 2, entry 1, starting material la)\(^1\)

A solution of 3,5-dimethoxyphenol (0.32 mmol, 49 mg) in DMF (2 mL) was added via syringe to a suspension of sodium hydride (0.53 mmol, 13 mg) in DMF (2 mL) at 0°C under N$_2$. The mixture was stirred until gas evolution ceased, and a solution of enantiomerically pure (ee > 99%) [(2$R$,3$R$)-3-phenyloxiran-2-yl]methyl 4-methylbenzenesulfonate] (0.35 mmol, 106 mg) in DMF (2 mL) was added via syringe to the mixture. The solution was stirred for ca. 48 h at 0°C. The reaction mixture was suspended in MeOH (2.5 mL) and brine (30 mL) and extracted with Et$_2$O (4 × 8 mL). The residual oil was purified by column chromatography on silica gel using hexane: EtOAc (95:5) as eluent to afford the product (78 mg, 85%) as colorless oil. [$\alpha$]$_D$$^{20}$ = $^{+}54.0$ ($c$ = 1.0 in CHCl$_3$), liter.: [$\alpha$]$_D$$^{27}$ = $^{+}52.6$ ($c$ = 1.2 in CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 3.42 (br s, 1H), 3.80 (s, 6H), 3.94 (d, $J$ = 2.1 Hz, 1H), 4.11 (dd, $J$ = 5.4, 10.8 Hz, 1H), 6.16 (br s, 1H), 6.18 (br s, 2H), 7.33–7.39 (m, 5H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 55.2, 56.2, 60.0, 67.9, 93.4, 93.5, 125.6, 128.3, 128.4, 136.4, 160.2, 161.5; HRMS (ESI): $m/z$ calcld for C$_{17}$H$_{19}$O$_4$: 287.1283; found: 287.1287 [M+H]$^+$. 

Characterization data of aryloxymethyloxiranes in table 2

$(2R,3R)$-2-[(4-Methoxyphenoxy)methyl]-3-phenyloxirane (Table 2, entry 2, starting material 1b)\(^1\)

The general procedure was applied to 4-methoxyphenol to afford the product (70 mg, 85%) as a white solid: m.p. = 100–101 °C; [$\alpha$]$_D$$^{20}$ = $^{+}47.5$ ($c$ = 1.0 in CHCl$_3$), liter.: [$\alpha$]$_D$$^{27}$ = $^{+}48.3$ ($c$ = 1.0 in CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 3.35–3.39 (m, 1H), 3.76 (s, 3H), 3.88–3.90 (m, 1H), 4.08 (dd, $J$ = 5.1, 11.0 Hz, 1H), 4.26 (dd, $J$ = 3.1, 11.0 Hz, 1H), 6.16–6.91 (m, 4H), 7.26–7.38 (m, 5H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 55.2, 56.2, 60.0, 67.9, 93.4, 93.5, 125.6, 128.3, 128.4, 136.4, 160.2, 161.5; HRMS (ESI): $m/z$ calcld for C$_{16}$H$_{16}$O$_3$: 279.0997; found: 279.0994 [M+Na]$^+$. 

Characterization data of aryloxymethyloxiranes in table 2

$(2R,3R)$-2-[(4-Methoxyphenoxy)methyl]-3-phenyloxirane (Table 2, entry 2, starting material 1b)\(^1\)

The general procedure was applied to 4-methoxyphenol to afford the product (70 mg, 85%) as a white solid: m.p. = 100–101 °C; [$\alpha$]$_D$$^{20}$ = $^{+}47.5$ ($c$ = 1.0 in CHCl$_3$), liter.: [$\alpha$]$_D$$^{27}$ = $^{+}48.3$ ($c$ = 1.0 in CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 3.35–3.39 (m, 1H), 3.76 (s, 3H), 3.88–3.90 (m, 1H), 4.08 (dd, $J$ = 5.1, 11.0 Hz, 1H), 4.26 (dd, $J$ = 3.1, 11.0 Hz, 1H), 6.16–6.91 (m, 4H), 7.26–7.38 (m, 5H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 55.7, 56.4, 60.4, 68.7, 114.7, 115.8, 125.7, 128.4, 128.6, 136.6, 152.7, 154.3; HRMS (ESI): $m/z$ calcld for C$_{16}$H$_{16}$O$_3$: 279.0997; found: 279.0994 [M+Na]$^+$. 

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(2R,3R)-2-[(4-tert-butylphenoxy)methyl]-3-phenyloxirane (Table 2, entry 3, starting material 1c)

The general procedure was applied to 4-tert-butylphenol to afford the product (72 mg, 80%) as a white solid: m.p. = 126–127 °C; [α]D20 = +53.3 (c = 1.0 in CHCl3), lit.: [α]D27 = +54.2 (c = 0.8 in CHCl3); 1H NMR (600 MHz, CDCl3): δ = 1.30 (s, 9H), 3.39–3.41 (m, 1H), 3.91 (d, J = 2.4 Hz, 1H), 4.14 (dd, J = 5.1, 11.1 Hz, 1H), 4.31 (dd, J = 3.3, 11.1 Hz, 1H), 6.88–6.90 (m, 2H) 7.29–7.37 (m, 7H); 13C NMR (150 MHz, CDCl3): δ = 31.5, 34.1, 56.4, 60.3, 68.0, 114.2, 125.7, 126.3, 128.4, 128.5, 136.6, 144.0, 156.2; HRMS (ESI): m/z calcd for C19H22NaO2: 305.1517; found: 305.1520 [M+Na]+.

(2R,3R)-2-(phenoxymethyl)-3-phenyloxirane (Table 2, entry 4, starting material 1d)

The general procedure was applied to phenol to afford the product (58 mg, 80%) as a white solid: m.p. = 100–101 °C; [α]D20 = +44.5 (c = 1.0 in CHCl3), lit.: [α]D24 = +45.6 (c = 1.0 in CHCl3); 1H NMR (400 MHz, CDCl3): δ = 3.39–3.42 (m, 1H), 3.91 (d, J = 2.1 Hz, 1H), 4.14 (dd, J = 5.0, 11.1 Hz, 1H), 4.32 (dd, J = 3.3, 11.1 Hz, 1H), 6.94–7.0 (m, 3H), 7.27–7.38 (m, 7H); 13C NMR (150 MHz, CDCl3): δ = 56.4, 60.3, 67.9, 114.7, 121.3, 125.7, 128.4, 128.6, 129.6, 136.5, 158.5; HRMS (ESI): m/z calcd for C15H14NaO2: 249.0891; found: 249.0887 [M+Na]+.

(2R,3R)-2-((4-bromophenoxy)methyl)-3-phenyloxirane (Table 2, entry 5, starting material 1e)

The general procedure was applied to 4-bromophenol to afford the product (86 mg, 89%) as a white solid: m.p. = 117–118 °C; [α]D20 = +46.0 (c = 1.0 in CHCl3); 1H NMR (600 MHz, CDCl3): δ = 3.39–3.41 (m, 1H), 3.92 (d, J = 2.4 Hz, 1H), 4.10 (dd, J = 5.4, 10.8 Hz, 1H), 4.32 (dd, J = 3.0, 10.8 Hz, 1H), 6.83–6.86 (m, 2H), 7.34–7.40 (m, 5H); 13C NMR (150 MHz, CDCl3): δ = 56.2, 60.0, 68.1, 83.5, 117.1, 125.7, 128.5, 128.6, 132.3, 136.3, 157.6; HRMS (ESI): m/z calcd for C15H13BrNaO2: 326.9997; found: 326.9991 [M+Na]+.

(2R,3R)-2-((4-iodophenoxy)methyl)-3-phenyloxirane (Table 2, entry 6, starting material 1f)

The general procedure was applied to 4-iodophenol to afford the product (84 mg, 75%) as a white solid: m.p. = 95–96 °C; [α]D20 = +42.0 (c = 1.0 in CHCl3), lit.: [α]D27 = +45.6 (c = 1.0 in CHCl3); 1H NMR (600 MHz, CDCl3): δ = 3.39 (br s, 1H), 3.91 (br s, 1H), 4.07 (dd, J = 4.8, 10.8 Hz, 1H), 4.31 (dd, J = 1.8, 10.8 Hz, 1H), 6.74 (d, J = 8.4 Hz, 2H), 7.30–7.37 (m, 5H) 7.58 (d, J = 3.6 Hz, 2H); 13C NMR (150 MHz, CDCl3): δ = 56.3, 60.0, 68.1, 83.5, 117.1, 125.7, 128.5, 128.6, 136.3, 158.3; HRMS (ESI): m/z calcd for C15H13INaO2: 374.9858; found: 374.9852 [M+Na]+.

(2R,3R)-2-[(naphthalen-2-yloxy)methyl]-3-phenyloxirane (Table 2, entry 7, starting material 1g)

The general procedure was applied to naphthalene-2-ol to afford the product (71 mg, 80%) as a white solid: m.p. = 108–109 °C; [α]D20 = +26.7 (c = 1.0 in CHCl3); 1H NMR (400 MHz, CDCl3): δ = 3.48 (m, 1H), 3.99 (d, J = 3.0 Hz, 1H), 4.25 (dd, J = 7.8, 16.8 Hz, 1H), 4.46 (dd, J = 4.5, 16.5 Hz, 1H), 7.18–7.23 (m, 6H), 7.44–7.47 (m, 1H), 7.45 (m, 1H), 7.7–7.80 (m, 3H);
$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 56.4, 60.2, 67.9, 107.0, 118.8, 123.9, 125.7, 126.5, 126.8, 127.7, 128.4, 128.6, 129.2, 129.6, 134.4, 136.5, 156.4; HRMS (ESI): $m/z$ calcd for C$_{19}$H$_{17}$O$_2$: 277.1229; found: 277.1233 [M+H]$^+$. 

(2R,3R)-2-[(6-bromonaphthalen-2-yloxy)methyl]-3-phenyloxirane (Table 2, entry 8, starting material 1h)

The general procedure was applied to 6-bromonaphthalen-2-ol to afford the product (101 mg, 89%) as a white solid: m.p. = 123–124 °C; $\alpha$ D$^{20} = +31.1$ (c = 1.0 in CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 3.49 (m, 1H), 3.99 (br s, 1H), 4.26 (dd, $J$ = 4.8, 11.1 Hz), 4.47 (dd, $J$ = 2.4, 10.8 Hz, 1H), 7.17 (s, 1H), 7.25 (dd, $J$ = 1.8, 8.7 Hz, 1H), 7.34–7.41 (m, 5H), 7.53 (d, $J$ = 9.0 Hz, 1H), 7.62 (d, $J$ = 8.4 Hz, 1H), 7.69 (d, $J$ = 9.0 Hz, 1H), 7.95 (s, 1H); $^13$C NMR (150 MHz, CDCl$_3$): $\delta$ = 56.4, 60.1. 68.1, 107.1, 117.4, 119.8, 125.7, 128.4, 128.5, 128.6, 128.7, 129.8, 130.3, 132.9, 136.4, 156.7; HRMS (ESI): $m/z$ calcd for C$_{19}$H$_{16}$BrO$_2$: 355.0334; found: 355.0326 [M+H]$^+$. 

2-[(3,5-dimethoxyphenoxy)phenylmethyl]oxirane (Table 2, entry 9, starting material 1i)

$^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 2.79–2.84 (m, 2H), 3.31-3.34 (m, 1H), 3.70 (s, 6H), 5.10 (d, $J$ = 6.0 Hz), 6.10 (d, $J$ = 6.0 Hz), 6.03 (t, $J$ = 3.0 Hz), 6.06 (d, $J$ = 3.6 Hz), 7.30–7.42 (m, 5H); $^13$C NMR (150 MHz, CDCl$_3$): $\delta$ = 45.0, 54.3, 55.2, 79.1, 93.5, 94.9, 126.7, 128.4, 128.7, 137.4, 159.4, 161.3; HRMS (ESI): $m/z$ calcd for C$_{17}$H$_{19}$O$_4$: 287.1283; found: 287.1276 [M+H]$^+$. 

3-[(3,5-dimethoxyphenoxy)methyl]-2,2-dimethyloxirane (Table 2, entry 10, starting material 1j)

The general procedure which using racemic (3,3-dimethyloxiran-2-yl)methyl 4-methylbenzenesulfonate 4, 5 was applied to 3,5-dimethoxyphenol afford the product (65 mg, 85%) as a white solid: $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 1.35 (s, 3H), 1.38 (s, 3H), 3.12 (t, $J$ = 1.8 Hz, 1H), 3.76 (s, 3H), 3.85–3.93 (m, 3H), 4.15 (br s, 1H), 6.00 (d, $J$ = 1.2 Hz, 1H), 6.07 (d, $J$ = 1.2 Hz, 1H), 7.00 (d, $J$ = 7.2 Hz, 2H), 7.20 (t, $J$ = 7.2 Hz, 1H), 7.17 (t, $J$ = 7.2 Hz, 2H), $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 18.9, 24.6, 55.3, 58.2, 61.1, 67.0, 93.3, 93.5, 160.4, 161.5; HRMS (ESI): $m/z$ calcd for C$_{13}$H$_{19}$O$_4$: 239.1283; found: 239.1281 [M+H]$^+$. 

General procedure for the preparation of product in hexafluoroisopropanol.

(3S,4R)-5,7-dimethoxy-4-phenylchroman-3-ol (Table 2, entry 1, product 2a)

The starting material of (2R,3R)-2-[(3,5-dimethoxyphenoxy)methyl]-3-phenyloxirane 1a (43 mg, 0.15 mmol) was dissolved in 5mL of hexafluoroisopropanol and was refluxed under ambient pressure, The solvent of reaction mixture was removed under reduced pressure. The residue was underwent column chromatography on silica gel using hexane: EtOAc (80:20) as eluent to afford 2a (43 mg, >99%) as a colorless oil. $\alpha$ D$^{20} = +53.0$ (c = 1.0 in CHCl$_3$), liter.: $\alpha$ D$^{27} = +52.3$ (c = 1.1 in CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 2.26 (br s, 1H), 3.47 (s, 3H), 3.70 (s, 3H), 3.85–3.93 (m, 3H), 4.15 (br s, 1H), 6.00 (d, $J$ = 1.2 Hz, 1H), 6.07 (d, $J$ = 1.2 Hz, 1H), 7.00 (d, $J$ = 7.2 Hz, 2H), 7.20 (t, $J$ = 7.2 Hz, 1H), 7.17 (t, $J$ = 7.2 Hz, 2H), $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 43.4, 55.2, 55.4, 65.3, 69.3, 92.5, 93.0, 101.9, 126.3, 128.0, 128.3, 143.5, 155.1, 159.7, 160.3; HRMS (ESI): $m/z$ calcd for C$_{19}$H$_{15}$O$_4$: 287.1283; found: 287.1287 [M+H]$^+$. 

Supplementary Material (ESI) for Chemical Communications
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(3S,4R)-6-methoxy-4-phenylchroman-3-ol (Table 2, entry 2, product 2b) \(^1\)

The general procedure was applied to \(1b\) to afford \(2b\) (37 mg, 96%) as a white solid: \([\alpha]_D^{20} = +3.5 (c = 1.0 \text{ in CHCl}_3)\), \(\text{litr.}: \ [\alpha]_D^{28} = +3.4 (c = 1.0 \text{ in CHCl}_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 2.15 \text{ (br s, 1H)}, 3.65 \text{ (s, 3H)}, 3.97 \text{ (m, 1H)}, 4.07–4.10 \text{ (m, 2H)}, 4.15 \text{ (dd, } J = 1.2, 10.2 \text{ Hz, 1H)}, 6.41 \text{ (d, } J = 2.4 \text{ Hz, 1H)}, 6.78 \text{ (dd, } J = 3.0, 8.7 \text{ Hz, 1H)}, 6.88 \text{ (d, } J = 9.0 \text{ Hz, 1H)}, 7.16–7.17 \text{ (m, 2H)}, 7.26–7.29 \text{ (m, 1H)}, 7.33–7.36 \text{ (m, 2H)}; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 50.4, 55.6, 66.6, 69.9, 114.7, 115.4, 117.3, 122.6, 127.1, 128.7, 129.1, 142.5, 148.2, 154.1; \) HRMS (ESI): \(m/z\) calcd for C\(_{16}\)H\(_{16}\)NaO\(_3\): 279.0997; found: 279.0997 [M+Na]\(^+\).

(3S,4R)-6-tert-butyl-4-phenylchroman-3-ol (Table 2, entry 3, product 2c) \(^1\)

The general procedure was applied to \(1c\) to afford \(2c\) (42 mg, 99%) as a white solid: \([\alpha]_D^{20} = +206.0 (c = 1.0 \text{ in CHCl}_3)\), \(\text{litr.}: \ [\alpha]_D^{26} = +204.2 (c = 1.0 \text{ in CHCl}_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 1.20 \text{ (s, 9H)}, 1.85 \text{ (br s)}, 3.99–4.02 \text{ (m, 1H)}, 4.09–4.15 \text{ (m, 3H)}, 6.87 \text{ (d, } J = 7.2 \text{ Hz, 1H)}, 6.88 \text{ (s, 1H)}, 7.12–7.15 \text{ (m, 2H)}, 7.21 \text{ (dd, } J = 2.4, 9.0 \text{ Hz, 1H)}, 7.25–7.27 \text{ (m, 1H)}, 7.32–7.34 \text{ (m, 2H)}; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 31.4, 34.0, 50.2, 66.4, 70.0, 115.9, 120.8, 125.3, 126.9, 128.1, 128.6, 129.1, 142.8, 144.0, 151.8; \) HRMS (ESI): \(m/z\) calcd for C\(_{19}\)H\(_{22}\)NaO\(_2\): 305.1517; found: 305.1515 [M+Na]\(^+\).

(3S,4R)-4-phenylchroman-3-ol (Table 2, entry 4, product 2d) \(^1\)

The general procedure was applied to \(1d\) to afford \(2d\) (30 mg, 88%) as a white solid: \([\alpha]_D^{20} = −34.0 (c = 1.0 \text{ in CHCl}_3)\), \(\text{litr.}: \ [\alpha]_D^{27} = −33.9 (c = 1.0 \text{ in CHCl}_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 2.12 \text{ (br s, 1H)}, 4.03–4.06 \text{ (m, 1H)}, 4.12 \text{ (br s, 2H)}, 4.22 \text{ (dd, } J = 1.2, 10.8 \text{ Hz, 1H)}, 6.89 \text{ (d, } J = 4.2 \text{ Hz, 2H)}, 6.96 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 7.16 \text{ (d, } J = 7.2 \text{ Hz, 2H)}, 7.18–7.21 \text{ (m, 1H)}, 7.28–7.29 \text{ (m, 1H)}, 7.34–7.36 \text{ (m, 2H)}; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 50.2, 66.8, 69.8, 116.6, 121.3, 122.1, 127.1, 128.2, 128.8, 129.1, 131.3, 142.5, 154.1; \) HRMS (ESI): \(m/z\) calcd for C\(_{15}\)H\(_{14}\)NaO\(_2\): 249.0891; found: 249.0887 [M+Na]\(^+\).

(3S,4R)-6-bromo-4-phenylchroman-3-ol (Table 2, entry 5, product 2e)

The general procedure was applied to \(1e\) to afford \(2e\) (40 mg, 87%) as a white solid: m.p. = 120–121\(^\circ\)C; \([\alpha]_D^{20} = +33.9 (c = 1.0 \text{ in CHCl}_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta = 1.50 \text{ (br s, 1H)}, 3.95 \text{ (m, 1H)}, 4.00 \text{ (d, } J = 4.8 \text{ Hz, 1H)}, 4.04 \text{ (dd, } J = 2.4, 5.4 \text{ Hz, 1H)}, 4.11 \text{ (dd, } J = 2.4, 10.8 \text{ Hz, 1H)}, 6.76 \text{ (d, } J = 9.0 \text{ Hz, 1H)}, 7.05 \text{ (d, } J = 7.2 \text{ Hz, 2H)}, 7.21–7.30 \text{ (m, 4H)}; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta = 50.0, 66.8, 69.3, 113.3, 118.5, 124.3, 127.4, 128.9, 129.0, 131.2, 133.6, 141.7, 153.2; \) Chiral HPLC: AD-H (heptane/isopropanol = 85/15, 0.8 mL/min\(^1\)) UV at 254 nm, t (major) = 9.1 min, t (minor) = 9.7 min, ee > 99%; HRMS (ESI): \(m/z\) calcd for C\(_{15}\)H\(_{13}\)BrNaO\(_2\): 326.9997; found: 326.9991 [M+H]\(^+\).
The general procedure was applied to \( \textit{1f} \) to afford \( \textit{2f} \) (46 mg, 88\%) as a white solid: \([\alpha]_{D}^{20} = +14.9\) (c = 1.0 in CHCl\(_3\)); \(1^H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 2.10\) (br s, 1H), 4.01–4.04 (m, 1H), 4.07–4.10 (m, 2H), 4.18 (dd, \(J = 1.8, 10.8\) Hz, 1H), 6.73 (d, \(J = 8.4\) Hz, 1H), 7.13–7.48 (m, 7H); \(13^C\) NMR (150 MHz, CDCl\(_3\)): \(\delta = 49.8, 66.7, 69.3, 83.3, 119.0, 124.8, 127.4, 128.9, 129.0, 137.1, 139.7, 141.8, 154.1\); HRMS (ESI): \(m/z\) calcd for C\(_{15}\)H\(_{13}\)INaO\(_2\): 374.9858; found: 374.9852 \([\text{M+Na}]^+\).

\[(3S,4R)-6\text{-iodo-4-phenylchroman-3-ol (Table 2, entry 6, product 2f)}\]

The general procedure was applied to \( \textit{1g} \) to afford \( \textit{2g} \) (38 mg, 91\%) as a white solid: \([\alpha]_{D}^{20} = -88.7\) (c = 1.0 in CHCl\(_3\)); \(1^H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 2.00\) (br s, 1H), 4.06–4.07 (m, 2H), 4.14–4.15 (m, 1H), 4.59 (br s, 1H), 7.08–7.14 (m, 4H), 7.18–7.22 (m, 4H), 7.38–7.40 (m, 1H), 7.49–7.54 (m, 2H), 7.63–7.67 (m, 2H), 7.81 (br s, 1H), 7.93 (d, \(J = 8.4\) Hz, 1H), 8.03 (br s, 1H), 8.07–8.10 (m, 2H); HRMS (ESI): \(m/z\) calcd for C\(_{25}\)H\(_{22}\)INaO\(_2\): 412.0000; found: 412.0000 \([\text{M+Na}]^+\).
7.66–7.69 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 45.9, 64.8, 69.7, 111.7, 118.5, 122.9, 123.5, 126.7, 126.8, 128.5, 129.3, 129.8, 133.4, 143.0, 151.7; HRMS (ESI): $m/z$ calcd for C$_{19}$H$_{17}$O$_2$: 277.1229; found: 277.1233 [M+H]$^+$. The observed optical rotation of compound 2g can not match with the reported value. We performed the chiral HPLC analysis of this sample and the result indicated that the enantiomeric excess value of the product is 99%ee. Chiral HPLC: AD-H (heptane/isopropanol = 85/15, 0.8 mL/min$^{-1}$, UV at 254 nm, t (major) = 13.4 min, t (minor) = 23.3 min, ee > 99%

(1R,2S)-8-bromo-1-phenyl-2, 3-dihydro-1H-benzo[f]chromen-2-ol (Table 2, entry 8,
product 2h)
The general procedure was applied to afford 2h (51mg, 96%) as a white solid: m.p. = 138–139 °C; [α]D20 = −49.5 (c = 1.0 in CHCl3); 1H NMR (600 MHz, CDCl3): δ = 2.30 (br s, 1H), 4.03 (br s, 2H), 4.09 (dd, J = 3.6, 6.6 Hz, 2H), 4.79 (d, J = 1.2, 1H), 7.02 (d, J = 10.8 Hz, 2H), 7.08–7.20 (m, 4H), 7.22 (s, 1H), 7.54 (d, J = 13 Hz, 1H), 7.81 (s, 1H); 13C NMR (150 MHz, CDCl3): δ = 45.8, 64.8, 69.5, 112.2, 117.2, 119.7, 124.7, 127.0, 128.3, 128.4, 128.9, 129.8, 130.4, 131.0, 131.9, 142.6, 151.9; Chiral HPLC: AD-H (heptane/isopropanol = 85/15, 0.8 mL/min, UV at 254 nm, t (major) = 16.2 min, t (minor) = 29.2 min, ee > 99%; HRMS (ESI): m/z calc'd for C19H16BrO2: 355.0334; found: 355.0324 [M+H]+.

<Chromatogram>

5,7-dimethoxy-2-phenylchroman-3-ol (Table 2, entry 9, product 2i)
The general procedure was applied to afford 2i (22 mg, 51%) as a colorless oil: 1H NMR (400 MHz, CDCl3): δ = 1.73 (br s, 1H), 2.62 (dd, J = 8.4, 16.4 Hz, 1H), 2.99 (dd, J = 5.6, 16.4 Hz, 1H), 3.76 (s, 3H), 3.80 (s, 3H), 4.10 (dd, J = 8.0, 13.6 Hz, 1H), 4.78 (d, J = 8.0 Hz, 1H), 6.13 (dd, J = 2.0, 16.0 Hz, 2H), 7.36–7.44 (m, 5H); 13C NMR (100 MHz, CDCl3): δ = 27.2,
5.7-dimethoxy-4,4-dimethylchroman-3-ol (Table 2, entry 10, product 2j)
The general procedure was applied to 1j to afford 2j (19 mg, 52%) as a white solid: m.p. = 83–84 °C; 1H NMR (400 MHz, CDCl3): δ = 1.35 (s, 3H), 1.45 (s, 3H), 1.90 (br s, 1H), 3.56 (dd, J = 1.6, 4.4 Hz, 1H), 3.75 (s, 3H), 3.78 (s, 3H), 4.05–4.13 (m, 2H), 6.06 (d, J = 2.4 Hz, 1H), 6.10 (d, J = 2.4 Hz); 13C NMR (100 MHz, CDCl3): δ = 22.8, 27.5, 35.6, 55.1, 55.2, 66.4, 74.9, 99.4, 99.6, 110.6, 154.7, 159.2, 160.7; HRMS (ESI): m/z calcd for C17H19O4: 287.1283; found: 287.1272 [M+H]+.

General procedure for intermolecular ring-opening of epoxides
(R)-2-(2,4,6-trimethoxyphenyl)-2-phenylethanol (Table 3, product 3a)
1,3,5-Trimethoxybenzene (5 mmol, 840 mg) and (R)-styrene oxide (1 mmol, 120 mg) were dissolved in 5 mL of hexafluoroisopropanol and was refluxed at ambient pressure for 30 minutes. Purified the desired product by column chromatography on silica gel using hexane: EtOAc (90:20) as eluent to afford 3a (176 mg, 61%) as a white solid: m.p. = 80–81 °C; [α]D20 = +19.3 (c = 1.0 in CHCl3); 1H NMR (400 MHz, CDCl3): δ = 1.94 (br s, 1H), 3.71 (s, 6H), 3.77 (s, 3H), 4.27 (d, J = 7.2 Hz, 2H), 4.80 (t, J = 7.2 Hz, 1H), 6.13 (s, 2H), 7.11–7.31 (m, 5H); 13C NMR (100 MHz, CDCl3): δ = 43.1, 55.2, 55.6, 64.7, 91.1, 110.4, 125.6, 127.9, 128.0, 142.4, 159.3, 160.0; Chiral HPLC: OD-H (heptane/isopropanol = 90/10, 0.4 mL/min−1, UV at 254 nm, t (minor) = 31.0 min, t (major) = 34.5 min, ee = 95%; HRMS (ESI): m/z calcd for C12H18NaO4: 249.1103; found: 249.1105 [M+Na]+.

<Chromatogram>
The observed enantiomeric excess value of the product is 94.5%. We think the enantiomeric purity of (R)-styrene oxide (purity>98.5%, purchased from Acros Organics Co.) we have could be lower than 98.5%. Because we do not have the special chiral GC column (Chiraldex \(\gamma\)-TA column) which is used to separate (R)- and (S)- styrene oxide. We did a parallel experiment to establish the real enantiomeric purity of this (R)-styrene oxide. The reaction between (R)-styrene oxide and indole in refluxing TFE is stereospecific as reported by Professor Mayr’s group (Scheme 1). We carried this reaction using the (R)-styrene oxide we have at the identical reaction condition. The ee value of the reaction product is 94.3%, similar with our previous observation. This showed that the reaction between 1,3,5-trimethoxybenzene and (R)-styrene oxide is stereospecific. The observed 94.5% enantiomeric excess value of the product is because the enantiomeric excess value of (R)-styrene oxide we have is 94.5%.

**Scheme 1**

\[
\begin{align*}
\text{(R)-styrene oxide} & \quad \xrightarrow{\text{TFE, 80°C, 4h}} \quad \text{product} \\
67\% (99\% \text{ ee}) & \\
\end{align*}
\]
2-(1,1,1,3,3,3-hexafluoropropan-2-yloxy)-2-phenylethanol

Using hexane: EtOAc (90:10) as eluent to afford the byproduct (86 mg, 30%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.35 (dd, $J$ = 5.0 Hz, 1H), 3.66–3.72 (m, 1H), 3.89–3.95 (m, 1H), 4.10–4.21 (m, 1H), 4.85 (dd, $J$ = 3.8 Hz, 1H), 7.32–7.35 (m, 2H), 7.39–7.41 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 66.6, 72.5, 72.9, 73.2, 73.5, 73.8, 86.1, 119.6, 120.59, 122.35, 123.43, 127.7, 128.9, 129.6, 134.8; MS (ESI): m/z calcd for C$_{11}$H$_{10}$F$_6$O$_2$: 288.0; found: 286.8 [M-H]$^-$. 

2-(2,3,4-trimethoxy-6-methylphenyl)-2-phenylethanol (Table 3, product 3b)

The general procedure was applied to 1,2,3-trimethoxy-5-methylbenzene to afford (76 mg, 50%) the product as a white solid: m.p. = 60–61 ºC; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.18 (br s, 1H), 2.22 (s, 3H), 3.33 (s, 3H), 3.74 (s, 3H), 3.77 (s, 3H), 4.21 (dd, $J$ = 6.4, 10.6 Hz, 1H), 4.28 (dd, $J$ = 6.4, 10.6 Hz, 1H), 4.43 (dd, $J$ = 6.4, 10.6 Hz, 1H), 6.46 (s, 1H), 7.10 (t, $J$ = 6.8 Hz, 1H), 7.16–7.23 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.1, 46.6, 55.8, 60.2, 60.5, 64.6, 109.8, 125.3, 125.9, 126.1, 127.6, 128.2, 129.0, 132.7, 140.6, 142.4, 151.9, 152.6; HRMS (ES+): m/z calcd for C$_{18}$H$_{22}$NaO$_4$: 325.1416; found: 325.1415 [M+Na]$^+$. 

2-(2,5-dimethoxyphenyl)-2-phenylethanol (Table 3, product 3c)

The general procedure was applied to 1,4-dimethoxybenzene to afford the product (45 mg, 35%) as a colorless oil: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.61 (br s, 1H), 3.66 (s, 3H), 3.67 (s, 3H), 4.05 (d, $J$ = 4.8 Hz, 2H), 4.56 (t, $J$ = 7.2 Hz, 1H), 6.64–6.74 (m, 3H), 7.14–7.23 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 46.5, 55.6, 56.1, 65.4, 111.2, 111.8, 115.3, 126.6, 128.4, 128.5, 131.2, 141.1, 151.7, 153.6; HRMS (ESI): m/z calcd for C$_{16}$H$_{18}$NaO$_3$: 281.1154; found: 281.1156 [M+Na]$^+$. 

2-(4-methoxyphenyl)-2-phenylethanol (Table 3, product 3d)

The general procedure was applied to anisole to afford the product (17 mg, 15%) as a colorless oil: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.54 (br s, 1H), 3.70 (s, 3H), 4.04–4.11 (m, 3H), 6.79 (d, $J$ = 8.0 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 7.13–7.18 (m, 3H), 7.23 (d, $J$ = 7.2 Hz, 

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2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 52.8, 55.2, 66.2, 114.1, 126.7, 128.2, 128.6, 129.2, 133.4, 141.7, 158.4; HRMS (ESI): $m/z$ calcd for C$_{15}$H$_{16}$NaO$_2$: 251.1048; found: 251.1036 [M+Na]$^+$. 

1-(2,4,6-trimethoxyphenyl)propan-2-ol (Table 3, product 3e)$^2$

1,3,5-Trimethoxybenzene (1 mmol, 168 mg) and 2-methyloxirane (2 mmol, 116mg) were dissolved in 5 mL of hexafluoroisopropanol and was refluxed at ambient pressure for 48 hours. The solvent was removed under reduced pressure. The desired product was purified by column chromatography on silica gel using hexane: EtOAc (90: 20) as eluent to afford 4 (65 mg, 29%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.19 (d, $J$ = 6.0 Hz, 3H), 2.35 (br s, 1H), 2.72–2.84 (2H), 3.81 (s, 6H), 3.82 (s, 3H), 3.93–4.00 (m, 1H), 6.15 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 23.0, 32.0, 55.3, 55.6, 68.6, 90.6, 107.6, 159.0, 159.7.

References

1 R. Marcos, C. Rodríguez-Escrich, C. Herrerías, M. A. Pericàs, J. Am. Chem. Soc., 2008, 130, 16838-16839 (Note: enantiomer was synthesized).
This page contains two NMR spectra. The upper spectrum is labeled as 
$^1$H, 600MHz, CDCl$_3$ and shows proton signals. The lower spectrum is labeled as 
$^{13}$C, 150MHz, CDCl$_3$ and shows carbon signals. The spectra are used to identify and assign the chemical shifts of both protons and carbons in the molecule.
Supplementary Material (ESI) for Chemical Communications
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$^1$H, 400MHz, CDCl$_3$

$^{13}$C, 150MHz, CDCl$_3$

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

\[13^C, 100\text{MHz, CDCl}_3\]
OH
Ph
1H, CDCl₃, 400MHz

3b

CH₃
OMe
MeO
OMe

13C, 100MHz, CDCl₃

ppm (t1)
$^{1}H$, CDCl$_3$, 400MHz

$^{13}C$, 100MHz, CDCl$_3$