Supporting Information
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Supporting Information

A Dramatic Base-Oriented Chemoselectivity of Palladium-Catalyzed Aerobic Cyclization: Synthesis of the Skeleton of Rubromycins and 2-Substituent Chromans

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(A) General Information

All reactions were carried out under oxygen atmosphere. MeOH used as solvent was distilled from magnesium methoxide. The $^1$H and $^{13}$C NMR data were recorded on a Mercury Plus-300 or a Bruker-400 MHz spectrometer at room temperature in CDCl$_3$ or DMSO-d$_6$ as solvent. Chemical shifts for protons are reported using residual CHCl$_3$ or DMSO as internal reference ($\delta = 7.27$ or 2.50 ppm). Carbon spectra were referenced to the shift of the $^{13}$C signal of CDCl$_3$ or DMSO ($\delta = 77.0$ or 39.5 ppm). Mass spectral (MS) data were obtained on a V.G.ZAB-HS mass spectrometer. High-resolution mass spectra (HRMS) date were obtained on a Bruker Daltonics APEX II 47e mass spectrometer. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC inspections were on silica gel GF254 plates. PdCl$_2$, CuCl$_2$ and Cs$_2$CO$_3$ were purchased from commercial suppliers and used without further treatment. 2-hydroxybenzaldehydes were commercial available.

(B) General Experimental Procedures for the Synthesis of Starting Material
A solution of LDA in THF (2.0 M, 1.2×10⁻³ ml, 2.4 mmol) was added dropwise to a solution of sulfone 13 (894 mg, 2.0 mmol) in THF (10 ml) at -80 °C. The resulting dark brown solution was stirred at -80 °C for 1 h whereupon a solution of 2-hydroxybenzaldehyde 12a (472 mg, 2.0 mmol) in THF (2 mL) was added via cannula. The mixture was stirred at -80 °C for a further 90 min and then warmed to r.t. and stirred for 30 min. The dark brown solution quenched with 20 mL of water. The aqueous layer was extracted with H₂O and Et₂O (25 mL×3). The combined organic extracts were washed with brine, dried (MgSO₄), and concentrated via rotary evaporation. The residue was purified by silica gel column chromatography with hexane-EtOAc (32:1) as eluent to afford 739 mg (79%) of olefin 14a as colorless oil.

A mixture of olefin 14a (936 mg, 2.0 mmol) and TBAF (1.512 g, 4.8 mmol) in 20 mL THF was stirred at room temperature. After the mixture had been stirred for 2 h, the mixture was extracted with EtOAc. The combined organic solution was washed with brine, dried over MgSO₄ and evaporated. The residue was purified by silica gel column chromatography with hexane-EtOAc (4:1) as eluent to afford 460 mg (96%) of the phenolic olefin 1a as a white solid.

Other precursors were generated in the same way as above from sulfone 13 and corresponding 2-hydroxybenzaldehydes.

(C) **Representative Procedures for Palladium-Catalyzed Wacker cyclization**

A three-necked flask was purged with oxygen gas and then was charged with PdCl₂ (3.5 mg, 0.02 mmol), CuCl₂ (5.4 mg, 0.04 mmol), 2-alkenyl phenol (0.20 mmol), MeOH (2 mL) and the mixture was magnetically stirred and heated at 60 °C for the appropriate reaction time (Table 3). Evaporation of the solvent and purification by flash column chromatography on silica gel (n-hexane/EtOAc, 8:1 v/v) gave the desired bisspiroketalts; yield: 36–71%.

(D) **Representative Procedures for Palladium-Catalyzed cyclization and conjugated addition**
Under oxygen, PdCl$_2$ (3.5 mg, 0.02 mmol), CuCl$_2$ (5.4 mg, 0.04 mmol) and Cs$_2$CO$_3$ (13mg, 0.04 mmol) were added to a stirred solution of 1 (0.20 mmol) in MeOH (2 mL). After the reaction mixture had been stirred at r.t. for the appropriate reaction time (Table 4), the solvent was removed and the residue purified by flash chromatography on silica gel (n-hexane/EtOAc, 8:1 v/v) to give the desired chromans (56-95%).

The relative configuration was determined by comparison the spectrum of 4h with literature, $^{[6c]}$ which showed that the products 4a-h from our reactions are syn.

(E) Characterization of the Products

$(E)$-2-(4-(2-hydroxyphenyl)but-3-enyl)phenol (1a)

Following procedure (B). White solid; $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 9.45 (s, 1H), 9.26 (s, 1H), 7.33-7.31 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H), 7.09-7.07 (dd, $J = 1.2$ Hz, 1H), 7.03-6.97 (m, 2H), 6.80-6.78 (dd, $J = 7.6$ Hz, $J = 0.8$ Hz, 2H), 6.75-6.69 (q, $J = 8.4$ Hz, 2H), 6.64-6.60 (d, $J = 16.0$ Hz, 1H), 6.29-6.22 (dt, $J = 16.0$ Hz, $J = 7.6$ Hz, 1H), 2.69-2.66 (t, $J = 7.2$ Hz, 2H), 2.45-2.40 (q, $J = 7.2$ Hz, 2H), $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 155.1, 154.1, 129.8, 127.7, 126.8, 126.1, 124.7, 124.1, 119.1, 118.8, 115.5, 114.8, 32.3, 29.9; HRMS (ESI) Calcd. for C$_{16}$H$_{15}$O$_2$ [M-H]$^-$ 239.1078, found 239.1084.

$(E)$-2-(4-(5-methyl-2-hydroxyphenyl)but-3-enyl)phenol (1b)

Following procedure (B). White solid; $^1$H NMR (400 MHz DMSO-d$_6$) $\delta$ 9.26 (s, 1H), 9.20 (s, 1H), 7.14-7.13 (d, $J = 1.6$ Hz, 1H), 7.09-7.07 (dd, $J = 1.2$ Hz, 1H), 7.01-6.97 (td, $J = 8.0$ Hz, $J = 1.6$ Hz, 1H), 6.82-6.79 (m, 2H), 6.73-6.68 (m, 2H), 6.62-6.58 (d, $J = 16.0$ Hz, 1H), 6.27-6.20 (dt, $J = 13.6$, $J = 6.8$, 1H), 2.69-2.66 (t, $J = 7.2$ Hz, 2H), 2.45-2.39 (q, $J = 7.2$ Hz, 2H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 155.1, 151.9, 129.8, 129.5, 128.1, 127.7, 126.8, 126.1, 124.7, 124.1, 119.1, 118.8, 115.5, 114.8, 33.3, 29.9, 20.2; HRMS (ESI) Calcd. for C$_{17}$H$_{17}$O$_2$ [M-H]$^-$ 253.1234, found 253.1241.

$(E)$-2-(4-(5-tert-butyl-2-hydroxyphenyl)but-3-enyl)phenol (1c)
Following procedure (B). White solid; $^1$H NMR (400 MHz DMSO-$d_6$) δ 9.25 (bs, 2H), 7.31-7.30 (d, $J = 2.4$ Hz, 1H), 7.10-7.07 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.04-6.97 (m, 2H), 6.80-6.78 (d, $J = 7.2$ Hz, 1H), 6.73-6.69 (m, 2H), 6.63-6.59 (d, $J = 16.4$ Hz, 1H), 6.32-6.24 (dt, $J = 16.0$ Hz, $J = 6.8$ Hz, 1H), 2.70-2.66 (t, $J = 7.2$ Hz, 2H), 2.45-2.39 (m, 2H), 1.24 (s, 9H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 155.1, 151.9, 141.0, 129.7, 129.5, 127.8, 126.7, 125.3, 124.4, 123.2, 122.7, 118.8, 115.1, 114.8, 33.6, 33.3, 31.4, 29.9; HRMS (ESI) Calcd. for C$_{20}$H$_{28}$O$_2$N [M+NH$_4$]$^+$ 314.2115, found 314.2113.

(E)-2-(4-(5-phenyl-2-hydroxyphenyl)but-3-enyl)phenol (1d)

Following procedure (B). White solid; $^1$H NMR (400 MHz DMSO-$d_6$) δ 9.68 (s, 1H), 9.28 (s, 1H), 7.62-7.59 (m, 3H), 7.42-7.34 (m, 2H), 7.32 (d, $J = 2.4$ Hz, 1H), 7.29-7.26 (t, $J = 7.6$ Hz, 1H), 7.11-7.09 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H), 7.01-6.97 (td, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 6.90-6.88 (d, $J = 8.4$ Hz, 1H), 6.80-6.78 (d, $J = 8.0$ Hz, 1H), 6.73-6.64 (m, 2H), 6.45-6.38(dt, $J = 16.0$ Hz, $J = 6.8$ Hz, 1H), 2.72-2.68 (t, $J = 7.6$ Hz, 2H), 2.48-2.42 (t, $J = 7.2$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 155.1, 153.9, 140.2, 131.1, 130.5, 129.8, 128.7, 127.7, 126.8, 126.4, 126.0, 124.6, 124.5, 124.4, 118.8, 116.0, 114.8, 33.4, 29.8; HRMS (ESI) Calcd. for C$_{22}$H$_{24}$O$_2$N [M+NH$_4$]$^+$ 334.1802, found 334.1805.

(E)-2-(4-(5-chloro-2-hydroxyphenyl)but-3-enyl)phenol (1e)

Following procedure (B). Yellow solid; $^1$H NMR (400 MHz DMSO-$d_6$) δ 9.80 (s, 1H), 9.27 (s, 1H), 7.35-7.34 (d, $J = 2.8$ Hz, 1H), 7.09-6.97 (m, 3H), 6.84-6.79 (m, 2H), 6.72-6.68 (m, 1H), 6.59-6.55 (d, $J = 16.0$ Hz, 1H), 6.42-6.30 (m, 1H), 2.70-2.64 (m, 2H), 2.46-2.40 (m, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 155.1, 153.0, 131.7, 129.8, 127.6, 127.1, 126.8, 126.1, 125.4, 123.5, 122.8, 118.8, 117.1, 114.9, 33.3, 29.7; HRMS (ESI) Calcd. for C$_{16}$H$_{14}$ClO$_2$ [M-H]$^-$ 273.0688, found 273.0694.

(E)-ethyl 4-hydroxy-3-(4-(2-hydroxyphenyl)but-1-enyl)benzoate (1f)
Following procedure (B). White solid; $^1$H NMR (400 MHz DMSO-$d_6$) δ 10.47 (bs, 1H), 9.28 (bs, 1H), 7.94-7.93 (d, $J = 2.4$ Hz, 1H), 7.67-7.65 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 1H), 7.09-7.07 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.01-6.97 (td, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 6.91-6.89 (d, $J = 8.8$ Hz, 1H), 6.80-6.78 (d, $J = 8.0$ Hz, 1H), 6.72-6.68 (td, $J = 7.2$ Hz, $J = 0.8$ Hz, 1H), 6.63-6.59 (d, $J = 16.0$ Hz, 1H), 6.63-6.29 (dt, $J = 16.0$ Hz, $J = 6.8$ Hz, 1H), 4.28-4.22 (q, $J = 7.2$ Hz, 2H), 2.70-2.67 (t, $J = 7.2$ Hz, 2H), 2.47-2.41 (q, $J = 7.2$ Hz, 2H), 1.31-1.27 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 165.6, 158.5, 155.1, 131.4, 129.8, 129.2, 127.6, 126.8, 124.3, 123.9, 120.7, 118.8, 115.5, 114.9, 60.1, 33.2, 29.7, 14.2; HRMS (ESI) Calcd. for C$_{19}$H$_{29}$O$_4$ [M-H]$^-$ 311.1289, found 311.1285.

(\textit{E})-2-(4-(2-hydroxy-3-methoxyphenyl)but-3-enyl)phenol (1g)

Following procedure (B). White solid; $^1$H NMR (400 MHz CDCl$_3$) δ 7.20-7.18 (d, $J = 7.2$ Hz, 1H), 7.14-7.09 (td, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H), 7.04-7.02 (d, $J = 7.6$ Hz, 1H), 6.93-6.89 (t, $J = 7.6$ Hz, 1H), 6.84-6.74 (m, 4H), 6.42-6.35 (dt, $J = 16.0$ Hz, $J = 7.2$ Hz, 1H), 5.94 (s, 1H), 4.97 (s, 1H), 3.89 (s, 3H), 2.85-2.81 (t, $J = 7.6$ Hz, 2H), 2.61-2.56 (q, $J = 7.2$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.4, 146.6, 142.6, 131.3, 130.2, 127.8, 127.1, 124.5, 124.0, 120.8, 119.4, 118.9, 115.3, 108.8, 56.0, 33.6, 30.1; HRMS (ESI) Calcd. for C$_{17}$H$_{17}$O$_3$ [M-H]$^-$ 269.1183, found 269.1189.

(\textit{E})-2-(4-(2-hydroxyphenyl)but-3-enyl)-6-methoxyphenol (1h)

Following procedure (B). Yellow solid; $^1$H NMR (400 MHz DMSO-$d_6$) δ 9.44 (s, 1H), 8.40 (s, 1H), 7.32-7.30 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H), 7.02-6.98 (m, 1H), 6.79-6.77 (d, $J = 7.6$ Hz, 2H), 6.74-6.65 (m, 3H), 6.62-6.58 (d, $J = 16.0$ Hz, 1H), 6.28-6.20 (dt, $J = 16.0$ Hz, $J = 6.8$ Hz, 1H), 3.77 (s, 3H), 2.69-2.65 (t, $J = 7.2$ Hz, 2H), 2.43-2.38 (dd, $J = 14.8$ Hz, $J = 7.2$ Hz, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 154.1, 147.2, 143.9, 129.7, 128.1, 127.6, 126.0, 124.7, 124.1, 121.8, 119.0, 118.5, 115.5, 109.5, 55.7, 33.3, 29.8; HRMS (ESI) Calcd. for C$_{17}$H$_{17}$O$_3$ [M-H]$^-$ 269.1183, found 269.1179.

(\textit{E})-2-(6-hydroxyhex-1-enyl)phenol (1i)
Following procedure (B). Colorless oil; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.34-7.31 (dd, $J$ = 7.2 Hz, 1H), 7.09-7.05 (td, $J$ = 8.0 Hz, $J$ = 1.2 Hz, 1H), 6.88-6.84 (td, $J$ = 7.6 Hz, $J$ = 0.8 Hz, 1H), 6.79-6.77 (dd, $J$ = 8.0 Hz, $J$ = 1.2 Hz, 1H), 6.64-6.61 (dd, $J$ = 15.6 Hz, 1H), 6.22-6.15 (m, 2H), 3.70-3.66 (t, $J$ = 6.4 Hz, 2H), 2.29-2.23 (qd, $J$ = 7.2 Hz, $J$ = 1.2 Hz, 2H), 1.87 (bs, 1H), 1.68-1.61 (m, 2H), 1.59-1.51 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.7, 132.1, 127.8, 127.0, 124.9, 124.5, 120.5, 115.7, 62.7, 33.0, 32.0, 25.3; HRMS (ESI) Calcd. for C$_{12}$H$_{15}$O$_2$ [M-H]$^-$ 191.1078, found 191.1083.

spiroketal 2a

Following representative procedure (C). White solid; Yield: 65%; Melting point: 126-128 °C; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.28-7.26 (d, $J$ = 7.2 Hz, 1H), 7.20-7.13 (m, 3H), 6.97-6.94 (t, $J$ = 7.6 Hz, 2H), 6.84-6.82 (d, $J$ = 7.6 Hz, 2H), 3.50-3.46 (d, $J$ = 16.8 Hz, 1H), 3.34-3.24 (m, 2H), 2.89-2.82 (ddd, $J$ = 16.4 Hz, $J$ = 6.0 Hz, $J$ = 2.4 Hz, 1H), 2.39-2.33 (ddd, $J$ = 13.2 Hz, $J$ = 6.0 Hz, $J$ = 2.4 Hz, 1H), 2.27-2.19 (td, $J$ = 13.2 Hz, $J$ = 6.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.8, 152.2, 129.1, 128.1, 127.4, 125.3, 124.8, 121.3, 121.0, 117.1, 109.8, 108.9, 41.8, 30.4, 21.8; HRMS (ESI) Calcd. for C$_{16}$H$_{15}$O$_2$ [M+H]$^+$ 239.1067, found 239.1068.

spiroketal 2b

Following representative procedure (C). White solid; Yield: 63%; Melting point: 115-117 °C; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.16-7.11 (m, 2H), 7.07 (s, 1H), 6.98-6.91 (m, 2H), 6.82-6.80 (d, $J$ = 8.0 Hz, 1H), 6.72-6.70 (d, $J$ = 8.4 Hz, 1H), 3.45-3.40 (d, $J$ = 16.4 Hz, 1H), 3.30-3.22 (m, 2H), 2.87-2.81 (ddd, $J$ = 16.4, $J$ = 6.0, $J$ = 2.8, 1H), 2.37-2.32 (m, 4H), 2.25-2.17 (td, $J$ = 12.8, $J$ = 6.0, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.7, 152.3, 130.4, 129.0, 128.4, 127.4, 125.4, 125.2, 121.3, 121.1, 117.1, 109.4, 109.0, 41.8, 30.3, 21.9, 20.8; HRMS (ESI) Calcd. for C$_{17}$H$_{16}$O$_2$Na [M+Na]$^+$ 275.1043, found 275.1046.

spiroketal 2c

Following representative procedure (C). Pale yellow solid; Yield: 60%; Melting point:
173-175 °C; 1H NMR (400 MHz CDCl3) δ 7.29 (s, 1H), 7.20-7.18 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.15-7.10 (q, J = 8.0 Hz, 2H), 6.95-6.91 (t, J = 7.6 Hz, 1H), 6.82-6.80 (d, J = 8.0 Hz, 1H), 6.75-6.73 (d, J = 8.8 Hz, 1H), 3.48-3.44 (d, J = 16.4 Hz, 1H), 3.33-3.22 (m, 2H), 2.86-2.80 (ddd, J = 16.4 Hz, J = 6.0 Hz, J = 2.8 Hz, 1H), 2.36-2.30 (ddd, J = 13.6 Hz, J = 6.0 Hz, J = 2.8 Hz, 1H), 2.25-2.17 (td, J = 12.8 Hz, J = 5.6 Hz, 1H), 1.33 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 155.6, 152.3, 144.1, 129.1, 127.4, 124.9, 124.8, 121.8, 121.4, 117.1, 109.1, 109.0, 42.0, 34.3, 31.7, 30.5, 21.9; HRMS (ESI) Calcd. for C20H23O2 [M+H]+ 295.1693, found 295.1690.

**spiroketal 2d**

Following representative procedure (C). Pale yellow solid; Yield: 50%; Melting point: 154-155 °C; 1H NMR (400 MHz CDCl3) δ 7.58-7.57 (d, J = 1.2 Hz, 2H), 7.55-7.49 (m, 4H), 7.35-7.31 (t, J = 7.2 Hz, 1H), 7.18-7.13 (m, 2H), 6.98-6.90 (td, J = 7.2 Hz, J = 0.8 Hz, 1H), 6.90-6.83 (dd, J = 18.0 Hz, J = 8.4 Hz, 2H), 3.55-3.51 (d, J = 16.4 Hz, 1H), 3.39-3.26 (m, 2H), 2.90-2.84 (ddd, J = 16.4 Hz, J = 5.6 Hz, J = 2.4 Hz, 1H), 2.41-2.36 (ddd, J = 13.6 Hz, J = 6.0 Hz, J = 2.4 Hz, 1H), 2.29-2.21 (td, J = 12.8 Hz, J = 6.0 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 157.5, 152.2, 141.2, 134.7, 129.1, 128.6, 127.5, 127.2, 126.8, 126.6, 126.0, 123.7, 121.3, 121.2, 117.1, 109.9, 109.4, 41.8, 30.4, 21.8; HRMS (ESI) Calcd. for C22H19O2 [M+H]+ 315.1380, found 315.1378.

**spiroketal 2e**

Following representative procedure (C). Pale yellow solid; Yield: 45%; Melting point: 127-129 °C; 1H NMR (400 MHz CDCl3) δ 7.21 (t, J = 1.2 Hz, 1H), 7.15-7.10 (m, 3H), 6.96-6.92 (td, J = 7.6 Hz, J = 0.8 Hz, 1H), 6.81-6.79 (s, J = 8.0 Hz, 1H), 6.73-6.71 (d, J = 8.8 Hz, 1H), 3.46-3.42 (d, J = 16.4 Hz, 1H), 3.31-3.20 (m, 2H), 2.87-2.81 (ddd, J = 16.8 Hz, J = 6.0 Hz, J = 2.4 Hz, 1H), 2.37-2.31 (ddd, J = 13.6 Hz, J = 6.0 Hz, J = 2.4 Hz, 1H), 2.25-2.16 (td, J = 13.2 Hz, J = 6.0 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 156.4, 152.0, 129.1, 128.0, 127.5, 127.2, 125.8, 124.9, 121.3, 121.2, 117.0, 110.8, 109.5, 41.7, 30.2, 21.7; Ms m/z (%) 272 (M+, 42), 165 (41), 131 (15), 107 (100), 77 (11).

**spiroketal 2f**

Following representative procedure (C). White solid; Yield: 36%; Melting point:
184-186 °C; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 8.14 (d, $J = 2.4$ Hz, 1H), 7.81-7.78 (dd, $J = 8.8$ Hz, 1H), 7.18-7.16 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.11-7.06 (td, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 6.91-6.88 (m, 1H), 6.81-6.79 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 2H), 4.39-4.34 (q, $J = 7.2$ Hz, 2H), 3.46-3.42 (d, $J = 15.6$ Hz, 1H), 3.31-3.20 (m, 2H), 2.37-2.31 (ddd, $J = 13.2$ Hz, $J = 6.0$ Hz $J = 2.4$ Hz, 1H), 2.25-2.18 (td, $J = 12.8$ Hz, $J = 6.0$ Hz, 1H), 1.42-1.38 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.5, 156.4, 153.5, 132.3, 131.7, 130.2, 129.3, 129.2, 128.1, 126.9, 124.2, 123.5, 120.9, 119.1, 118.3, 109.5, 41.7, 30.3, 21.8; HRMS (ESI) Calcd. for C$_{19}$H$_{19}$O$_4$ [M+H]$^+$ 311.1278, found 311.1280.

**spiroketal 2g**

Following representative procedure (C). White solid; Yield: 71%; Melting point: 134-136 °C; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.13-7.09 (t, $J = 7.6$ Hz, 2H), 6.93-6.86 (m, 3H), 6.80-6.78 (m, 2H), 3.83 (m, 3H), 3.48-3.44 (d, $J = 16.4$ Hz, 1H), 3.34-3.26 (m, 2H), 2.86-2.79 (ddd, $J = 16.4$ Hz, $J = 5.6$ Hz, $J = 3.2$ Hz, 1H), 2.41-2.36 (ddd, $J = 13.2$ Hz, $J = 5.6$ Hz, $J = 3.2$ Hz, 1H), 2.24-2.16 (td, $J = 13.2$ Hz, $J = 5.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.2, 146.2, 144.3, 129.0, 127.4, 126.5, 121.6, 121.4, 121.0, 117.0, 117.0, 111.6, 109.5, 56.0, 42.2, 30.4, 21.9; HRMS (ESI) Calcd. for C$_{17}$H$_{15}$O$_3$ [M-H]$^-$ 267.1027, found 267.1023.

**2-(2-(benzofuran-2-yl)ethyl)phenol (3a)**

Following representative procedure (C). White solid; Yield: 28%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.50-7.44 (dd, $J = 12.8$ Hz, $J = 8.0$ Hz, 2H), 7.26-7.10 (m, 4H), 6.90-6.86 (t, $J = 7.6$ Hz, 1H), 6.77-6.75 (d, $J = 8.0$ Hz, 1H), 6.40 (s, 1H), 4.81 (s, 1H), 3.15-3.06 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.6, 154.6, 153.4, 130.3, 128.9, 127.5, 127.0, 123.2, 122.4, 120.9, 120.2, 115.2, 110.7, 102.3, 28.6, 28.4.

**2-(2-(5-methylbenzofuran-2-yl)ethyl)phenol (3b)**

Following representative procedure (C). White solid; Yield: 27%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.37-7.35 (d, $J = 8.0$ Hz, 1H), 7.30 (s, 1H), 7.18 (d, $J = 1.2$ Hz, 1H), 7.15 (d, $J = 1.6$ Hz, 1H), 7.13-7.11 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz 1H), 7.08-7.06 (dd, $J = 8.0$ Hz, $J = 1.2$ Hz, 1H), 6.92-6.89 (t, $J = 7.2$ Hz, 1H), 6.77-6.75 (d, $J = 8.0$ Hz, 1H), 6.35 (s, 1H), 5.02 (s, 1H), 3.12 (s, 4H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.7, 153.4, 153.0, 131.7, 130.2, 129.0, 127.5, 127.1, 124.3, 120.8, 120.2, 115.3, 110.1,
2-(2-(5-tert-butylbenzofuran-2-yl)ethyl)phenol (3c)

Following representative procedure (C). Yellow solid; Yield: 25%; $^1$H NMR (400 MHz CDCl$_3$) δ 7.51 (d, $J = 2.0$ Hz, 1H), 7.40-7.38 (d, $J = 8.4$ Hz, 1H), 7.32-7.30 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 1H), 7.18-7.16 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.14-7.10 (td, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 6.91-6.87 (td, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H), 6.77-6.75 (dd, $J = 7.6$ Hz, $J = 0.8$ Hz, 1H) 6.38 (s, 1H), 4.89 (s, 1H), 3.15-3.06 (m, 4H), 1.40 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.7, 153.5, 152.8, 145.5, 130.3, 128.6, 127.5, 127.1, 121.0, 120.9, 116.6, 115.3, 109.9, 102.4, 34.6, 31.8, 28.7, 28.4.

2-(2-(5-phenylbenzofuran-2-yl)ethyl)phenol (3d)

Following representative procedure (C). Pale yellow solid; Yield: 32%; $^1$H NMR (400 MHz CDCl$_3$) δ 7.71 (d, $J = 1.2$ Hz, 1H), 7.67-7.65 (d, $J = 7.2$ Hz, 2H), 7.55-7.47 (m, 4H), 7.40-7.36 (t, $J = 7.2$ Hz, 1H), 7.20-7.13 (m, 2H), 6.94-6.90 (t, $J = 7.6$ Hz, 1H), 6.79-6.77 (d, $J = 8.0$ Hz, 1H), 6.47 (s, 1H), 4.96 (s, 1H), 3.20-3.11 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.4, 154.2, 153.4, 141.8, 136.1, 136.1, 130.3, 129.4, 128.6, 127.5, 127.3, 127.0, 122.8, 120.9, 118.8, 115.3, 110.8, 102.5, 28.7, 28.4.

2-(2-(5-chlorobenzofuran-2-yl)ethyl)phenol (3e)

Following representative procedure (C). White solid; Yield: 42%; $^1$H NMR (400 MHz CDCl$_3$) δ 7.43 (d, $J = 2.0$ Hz, 1H), 7.35-7.33 (d, $J = 8.8$ Hz, 1H), 7.18-7.16 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 1H), 7.13-7.09 (t, $J = 7.6$ Hz, 2H), 6.89-6.85 (m, 1H), 6.76-6.74 (d, $J = 7.6$ Hz, 1H), 6.33 (s, 1H), 4.74 (s, 1H), 3.11-3.05 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.3, 153.4, 153.0, 130.3, 127.9, 127.6, 126.8, 123.3, 120.9, 119.9, 115.2, 111.6, 102.0, 28.6, 28.3.

ethyl 2-(2-hydroxyphenethyl)benzofuran-5-carboxylate (3f)

Following representative procedure (C). Yellow solid; Yield: 28%; $^1$H NMR (400 MHz CDCl$_3$) δ 8.22-8.21 (d, $J = 1.6$ Hz, 1H), 7.98-7.95 (dd, $J = 8.8$ Hz, $J = 1.6$ Hz,
1H), 7.45-7.43(d, J = 8.8 Hz, 1H), 7.13-7.08 (m, 2H), 6.88-6.84 (td, J = 7.2 Hz, J = 1.2 Hz, 1H), 6.79-6.77 (d, J = 8.0 Hz, 1H), 6.44 (s, 1H), 5.30 (s 1H), 4.43-4.38 (q, J = 7.2 Hz, 2H), 3.15-3.07 (m, 4H), 1.44-1.40 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl₃) δ 167.2, 160.3, 157.3, 153.6, 130.2, 128.9, 127.6, 126.9, 125.1, 125.0, 122.6, 120.8, 115.2, 110.5, 102.6, 60.9, 28.6, 28.3, 14.3.

2-(2-(7-methoxybenzofuran-2-yl)ethyl)phenol (3g)

Following representative procedure (C). White solid; Yield: 22%; $^1$H NMR (400 MHz CDCl₃) δ 7.15-7.08 (m, 4H), 6.89-6.85 (m, 1H), 6.78-6.75 (m, 2H), 6.39 (s, 1H), 5.00 (s, 1H), 4.03 (s 3H), 3.16-3.07 (m, 4H); $^{13}$C NMR (100 MHz, CDCl₃) δ 158.8, 153.5, 144.9, 143.7, 130.5, 127.5, 127.0, 123.0, 120.8, 115.3, 112.8, 105.5, 102.6, 55.9, 28.5, 28.4.

2-(2-(benzofuran-2-yl)ethyl)-6-methoxyphenol (3h)

Following representative procedure (C). White solid; Yield: 47%; $^1$H NMR (400 MHz CDCl₃) δ 7.49-7.43 (m, 2H), 7.24-7.16 (m, 2H), 6.77 (s, 3H), 6.42 (s, 1H), 5.76 (s, 1H), 3.90 (s, 3H), 3.11 (s, 4H); $^{13}$C NMR (100 MHz, CDCl₃) δ 159.0, 154.6, 146.3, 143.6, 129.0, 126.6, 123.0, 122.3, 122.2, 120.2, 119.3, 110.7, 108.7, 102.0, 55.9, 28.4, 28.2; Ms m/z (%) 268 (M⁺, 82), 253 (5), 137 (100), 131 (59), 77 (9).

2-(chroman-2-yl(methoxy)methyl)phenol (4a)

Following representative procedure (D). Colorless oil; Yield: 89%; $^1$H NMR (400 MHz CDCl₃) δ 7.76 (s, 1H), 7.25-7.20 (m, 1H), 7.09-7.05 (m, 2H), 7.00-6.98 (d, J = 7.6 Hz, 1H), 6.92-6.79 (m, 4H), 4.50-4.48 (d, J = 6.0 Hz, 1H), 4.39-4.34 (m, 1H), 3.48 (s, 3H), 2.81-2.65 (m, 2H), 1.83- 1.75 (m, 1H), 1.73-1.61 (m, 2H); $^{13}$C NMR (100 MHz, CDCl₃) δ 155.7, 154.0, 129.6, 129.4, 129.3, 127.2, 121.7, 121.5, 120.5, 119.8, 117.2, 116.8, 86.6, 77.7, 58.0, 24.2, 23.6; HRMS (ESI) Calcd. for C₁₇H₂₃O₃N $[M+NH₄]^+$ 288.1594, found 288.1592.

2-(chroman-2-yl(methoxy)methyl)-4-methylphenol (4b)
Following representative procedure (D). Colorless oil; Yield: 90%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.55 (s, 1H), 7.11-7.01 (m, 3H), 6.89-6.81 (m, 4H), 4.46-4.44 (d, $J = 6.0$ Hz, 1H), 4.40-4.36 (m, 1H), 3.50 (s, 3H), 2.84-2.68 (m, 2H), 2.28 (s, 3H), 1.86-1.79 (m, 1H), 1.77-1.67 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.1, 153.4, 130.2, 129.8, 129.3, 129.0, 127.2, 121.8, 121.2, 120.5, 117.0, 116.8, 86.7, 77.7, 58.0, 25.6, 24.3, 23.7; HRMS (ESI) Calcd. for C$_{18}$H$_{24}$O$_3$N [M+NH$_4$]$^+$ 302.1751, found 302.1755.

4-tert-butyl-2-(chroman-2-yl(methoxy)methyl)phenol (4c)

Following representative procedure (D). Colorless oil; Yield: 89%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.63 (s, 1H), 7.26-7.22 (m, 1H), 7.11-7.01 (m, 3H), 6.89-6.81 (m, 3H), 4.50-4.49 (d, $J = 6.4$ Hz, 1H), 4.41-4.36 (m, 1H), 3.52 (s, 3H), 2.84-2.68 (m, 2H), 1.86-1.80 (m, 1H), 1.79-1.65 (m, 1H), 1.30 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.0, 153.3, 142.5, 129.3, 127.3, 126.4, 126.2, 121.8, 120.6, 120.4, 116.8, 116.5, 87.0, 77.7, 58.1, 33.9, 31.5, 24.2, 23.5; HRMS (ESI) Calcd. for C$_{21}$H$_{26}$O$_3$Na [M+Na]$^+$ 349.1774, found 349.1780.

4-phenyl-2-(chroman-2-yl(methoxy)methyl)phenol (4d)

Following representative procedure (D). Colorless oil; Yield: 85%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.85 (s, 1H), 7.57-7.55 (dd, $J = 8.0$ Hz, $J = 1.2$ Hz, 2H), 7.51-7.49 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1H), 7.46-7.42 (t, $J = 8.0$ Hz, 2H), 7.34-7.31 (m, 2H), 7.13-7.09 (t, $J = 8.0$ Hz, 1H), 7.04-7.00 (t, $J = 6.8$ Hz, 2H), 6.92-6.84 (m, 2H), 4.60-4.58 (d, $J = 5.6$ Hz, 1H), 4.46-4.40 (m, 1H), 3.56 (s, 3H), 2.87-2.70 (m, 2H), 1.92-1.87 (m, 1H), 1.84-1.74 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.3, 153.9, 140.5, 133.1, 129.4, 128.7, 128.4, 128.0, 127.3, 126.7, 126.6, 126.6, 121.8, 121.7, 120.5, 117.7, 116.8, 86.6, 77.8, 58.2, 24.3, 23.6; HRMS (ESI) Calcd. for C$_{23}$H$_{21}$O$_3$ [M-H]$^-$ 345.1496, found 345.1506.
4-chloro-2-(chroman-2-yl(methoxy)methyl)phenol (4e)

Following representative procedure (D). Yellow oil; Yield: 88%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.75 (s, 1H), 7.20-7.17 (dd, $J$ = 8.4 Hz, $J$ = 2.4 Hz, 1H), 7.11-7.08 (m, 2H), 7.03-7.02 (d, $J$ = 6.8 Hz, 1H), 6.87-6.82 (m, 3H), 4.49-4.48 (d, $J$ = 6.0 Hz, 1H), 4.39-4.34 (m, 1H), 3.50 (s, 3H), 3.49-2.27 (m, 2H), 1.92-1.87 (m, 1H), 1.79-1.59 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.4, 153.8, 129.4, 129.4, 128.7, 127.3, 124.7, 123.4, 121.7, 120.7, 118.7, 116.7, 85.4, 77.8, 58.3, 24.2, 23.3; HRMS (ESI) Calcd. for C$_{17}$H$_{17}$ClO$_3$Na [M+Na]$^+$ 327.0758, found 327.0765.

ethyl 3-(chroman-2-yl(methoxy)methyl)-4-hydroxybenzoate (4f)

Following representative procedure (D). Pale yellow oil; Yield: 56%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 8.33 (s, 1H), 7.96-7.93 (dd, $J$ = 8.8 Hz, $J$ = 2.0 Hz, 1H), 7.83 (d, $J$ = 2.4 Hz, 1H), 7.11-7.07 (t, $J$ = 8.8 Hz, 1H), 7.03-7.01 (d, $J$ = 7.2 Hz, 1H), 6.96-6.94 (d, $J$ = 8.4 Hz, 1H), 6.87-6.83 (m, 2H), 4.55-4.54 (d, $J$ = 4.8 Hz, 1H), 4.38-4.33 (m, 3H), 3.50 (s, 3H), 2.86-2.70 (m, 2H), 1.90-1.66 (m, 2H), 1.41-1.37 (t, $J$ = 7.2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.2, 160.1, 153.9, 131.5, 131.4, 129.3, 127.3, 122.2, 121.7, 121.5, 120.6, 117.2, 116.8, 86.4, 77.9, 60.7, 58.3, 24.3, 23.7, 14.3; HRMS (ESI) Calcd. for C$_{20}$H$_{26}$O$_5$N [M+NH$_4$]$^+$ 360.1805, found 360.1808.

2-(chroman-2-yl(methoxy)methyl)-6-methoxyphenol (4g)

Following representative procedure (D). Colorless oil; Yield: 95%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.10-7.06 (t, $J$ = 7.2 Hz, 1H), 7.01-7.00 (d, $J$ = 7.6 Hz, 1H), 6.92-6.80 (m, 5H), 6.70 (s, 1H), 4.72-4.70 (d, $J$ = 7.2 Hz, 1H), 4.36-4.31 (q, $J$ = 6.8 Hz, 1H), 3.91 (s, 3H), 3.41 (s, 3H), 2.75-2.71 (m, 2H), 1.79-1.74 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.3, 147.2, 144.5, 129.2, 127.1, 123.2, 121.9, 120.6, 120.1, 119.7, 117.0, 110.5, 82.2, 78.1, 57.6, 55.9, 24.3, 23.5; HRMS (ESI) Calcd. for C$_{18}$H$_{24}$O$_4$N $[M+NH_3]^+$ 318.1700, found 318.1708.
2-(methoxy(tetrahydro-2H-pyran-2-yl)methyl)phenol (4i)

Following representative procedure (D). Colorless oil; Yield: 89%; $^1$H NMR (400 MHz CDCl$_3$) $\delta$ 7.96 (s, 1H), 7.24-7.19 (m, 1H), 7.05-7.00 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 6.92-6.84 (m, 2H), 4.24-4.23 (d, $J = 5.6$ Hz, 1H), 4.12-4.08 (m, 1H), 3.73-3.69 (m, 1H), 3.52-3.46 (td, $J = 11.6$ Hz, $J = 2.8$ Hz, 1H), 3.38 (s, 3H), 1.81-1.78 (m, 1H), 1.61-1.33 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.5, 129.6, 129.4, 122.7, 119.6, 117.3, 86.9, 79.8, 68.9, 57.7, 27.7, 25.6, 22.8; HRMS (ESI) Calcd. for C$_{13}$H$_{18}$O$_3$Na $[M+Na]^+$ 245.1148, found 245.1142.

These data is consistent the literature which reported a absolute syn product (K. H. Jensen, T. P. Pathak, Y. Zhang, M. S. Sigman, J. Am. Chem. Soc. 2009, 131, 17074-17075), from which we make sure of the relative configuration of our products. The data of literature compound was listed:

2-((R)-methoxy((R)-tetrahydro-2H-pyran-2-yl)methyl)phenol:

White solid. Mp = 98-103 °C. [\alpha]$_{20}$ = -14.0° (c = 0.28, CHCl$_3$), $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 (s, 1H), 7.22 (ddd, $J = 7.7$ Hz, $J = 7.7$ Hz, $J = 1.7$ Hz, 1H), 7.03 (dd, $J = 7.5$ Hz, $J = 1.7$ Hz, 1H), 6.91-6.83 (m, 2H), 4.23 (d, $J = 5.6$ Hz, 1H), 4.16-4.05 (m, 1H), 3.75-3.68 (m, 1H), 3.49 (ddd, $J = 11.5$ Hz, $J = 11.5$ Hz, $J = 2.7$ Hz, 1H), 3.38 (s, 3H), 1.85-1.75 (m, 1H), 1.65-1.15 (m, 5H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 155.8, 129.9, 129.7, 122.9, 119.9, 117.6, 87.3, 80.0, 69.1, 57.9, 28.1, 25.9, 23.1. IR 3326, 2937, 2855, 1506, 1457, 1241, 1082, 756 cm$^{-1}$. HRMS C$_{13}$H$_{18}$O$_3$ [M+Na]$^+$ calcd. 245.1148, obsvd. 245.1152.
(F) $^1$H and $^{13}$C NMR Spectra