Supporting Information

Brønsted acid-catalysed intramolecular ring opening of 2-(aryloxymethyl)-3-aryloxiranes leading to trans-4-arylchroman-3-ols: scope and limitations

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1 General information

All dry reactions were carried out under nitrogen in oven-dried glassware using standard gas-light syringes, cannulas, and septa. Commercial reagents were used without further purification unless otherwise stated. Progress of reactions was monitored by TLC on precoated Merck silica gel plates (60F-254). Visualization of reactants and products was accomplished with UV light. Column chromatography was performed over silica gel (60–120 mesh) procured from Merck using freshly distilled solvents. Melting points were determined with a Buchi-545 apparatus. Perkin Elmer 20 analyzer was utilized for elemental analysis of all compounds. $^1$H NMR and $^{13}$C NMR spectra were run on a JEOL 400 MHz spectrometer in CDCl$_3$ as solvent. Tetramethylsilane (0.00 ppm) served as an internal standard in $^1$H NMR and CDCl$_3$ (77.0 ppm) in $^{13}$C NMR. All spectra were recorded at 25 ºC. Coupling constants (J values) are given in hertz (Hz). Chemical shifts are expressed in parts per million (ppm).

2 Preparation of starting materials:

Starting materials 5a, 5b, 5e, 5g, 5h, 5j, 5k, 5l, and 5m were prepared according to literature procedures$^{1-3}$ whereas the syntheses of 5c, 5d, 5f, 5i, 5n, 5o, and 5p are described below. Enantiomerically pure [(2S,3S)-2-((3,5-dimethoxyphenoxy)methyl)-3-phenyloxirane] 5b and (3S,4R)-4-(4-bromophenyl)-5,7-dimethoxychroman-3-ol 5m were also prepared according to the literature procedures.$^2$

Preparation of racemic 2-((3,4,5-trimethoxyphenoxy)methyl)-3-phenyloxirane 5c:

To a stirred suspension of sodium hydride (25 mg, 1.07 mmol,) in DMF (3 mL), a solution of 3,4,5-trimethoxyphenol (130 mg, 0.70 mmol) in dry DMF (5 mL) was added at 0 ºC under N$_2$ atmosphere. The resulting mixture was stirred for 5 min, and a solution of racemic (3-phenyloxiran-2-yl)methyl 4-methylbenzenesulfonate$^2$ (0.23 g, 0.76 mmol) in DMF (5 mL) was added dropwise. The solution was stirred for an additional 10 h at 0 ºC. The reaction was terminated by the addition of 10% aqueous ammonium chloride (10 mL) and diethyl
ether (50 mL) was added. The organic layer was separated, washed by brine (50 mL), dried over anhyd. Na$_2$SO$_4$, and filtered. Evaporation of the solvent under reduced pressure gave the crude product which was subjected to silica gel column chromatography using hexane:EtOAc (90:10/80:20) as eluent to get the title compound 5c (170 mg, 74%) as a colourless gum. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.39-7.29 (m, 5H), 6.22 (s, 2H), 4.29 (dd, $J$ = 3.1 and 11.1 Hz, 1H), 4.11 (dd, $J$ = 5.2 and 11.2 Hz, 1H), 3.91 (d, $J$ = 2.0 Hz, 1H), 3.84 (s, 6H), 3.79 (s, 3H), 3.40-3.38 (m, 1H). Anal. Calcd for C$_{18}$H$_{20}$O$_5$: C, 68.34; H, 6.37. Found: C, 68.22; H, 6.44.

2-((3,4-Dimethoxyphenoxy)methyl)-3-phenyloxirane 5d:

Starting from 3,4-dimethoxyphenol (150 mg, 0.97 mmol), the title compound was prepared in the same manner as that described for 5c. After the usual work-up, the title compound was 5d (225 mg, 81%) was obtained as a colourless semi-solid in the pure form which was used for the next step without further purification and characterisation.

2-((Naphthalen-1-yloxy)methyl)-3-phenyloxirane 5i:

Starting from 1-naphthol (0.15 g, 1.04 mmol), the title compound was prepared in the same manner as that described for 5c. Silica gel column chromatography of the crude product using hexane:EtOAc (98:2/90:10) as eluent furnished the title compound 5i (0.23 g, 80%) as a colourless semi-solid. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.24 (d, $J$ = 8.5 Hz, 1H), 7.73 (d, $J$ = 6.5 Hz, 1H), 7.44-7.38 (m, 3H), 7.31-7.17 (m, 6H), 6.77 (d, $J$ = 7.5 Hz, 1H), 4.42 (dd, $J$ = 2.0 and 11.0 Hz, 1H), 4.25 (dd, $J$ = 5.0 and 11.0 Hz, 1H), 3.94 (d, $J$ = 2.0 Hz, 1H), 3.48-3.37 (m, 1H). Anal. Calcd for C$_{19}$H$_{16}$O$_2$: C, 82.58; H, 5.84. Found: C, 82.66; H, 5.76.

2-(4-Bromophenyl)-3-((3,5-dimethylphenoxy)methyl)oxirane 5n:

Starting from 3,5-dimethylphenol (0.11 g, 0.90 mmol), the title compound was prepared in the same manner as that described for 5c. After the usual work-up, the title compound was 5n (0.25 g, 83%) was obtained as a as a light
yellow liquid in the pure form which was used for the next step without further purification and characterisation.

2-(4-Bromophenyl)-3-((3,4-dimethoxyphenoxy)methyl)oxirane 5o:

Starting from 3,4-dimethoxyphenol (0.11 g, 0.71 mmol), the title compound was prepared in the same manner as that described for 5c. Silica gel column chromatography of the crude product using hexane:EtOAc (98:2/80:20) as eluent furnished the title compound 5o (0.19 g, 73%) as a white solid. M.P.: 122-123°C. ¹H NMR (500 MHz, CDCl₃): δ 7.39 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 9.0 Hz, 1H), 6.49 (d, J = 2.5 Hz, 1H), 6.34 (dd, J = 3.0 and 9.0 Hz, 1H), 4.18 (dd, J = 3.0 and 11.0 Hz, 1H), 4.01 (dd, J = 4.5 and 11.0 Hz, 1H), 3.79-3.75 (m, 7H), 3.24 (d, J = 1.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 152.9, 149.9, 144.0, 135.6, 131.7, 127.3, 122.3, 111.6, 104.0, 101.2, 68.2, 60.4, 56.4, 55.8, 55.7. Anal. Calcd for C₁₇H₁₇BrO₄: C, 55.91; H, 4.69. Found: C, 55.88; H, 4.62.

2-(4-Bromophenyl)-3-((naphthalen-1-yloxy)methyl)oxirane 5p:

Starting from 1-naphthol (0.15 g, 1.04 mmol), the title compound was prepared in the same manner as that described for 5c. Silica gel column chromatography of the crude product using hexane:EtOAc (98:2/90:10) as eluent furnished the title compound 5p (0.28 g, 76%) as a white solid. M.P.: 144-145°C. ¹H NMR (400 MHz, CDCl₃): δ 8.30-8.27 (m, 1H), 7.80 (d, J = 2.3 Hz, 1H), 7.51-7.45 (m, 5H), 7.36 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 7.8 Hz, 1H), 4.48 (dd, J = 3.2 and 11.0 Hz, 1H), 4.31 (dd, J = 5.0 and 11.0 Hz, 1H), 3.97 (d, J = 1.8 Hz, 1H), 3.48-3.45 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 154.1, 135.7, 134.6, 131.7, 127.5, 127.4, 126.6, 125.7, 125.6, 125.4, 122.3, 121.9, 121.0, 105.1, 67.9, 60.3, 55.8. Anal. Calcd for C₁₉H₁₅BrO₂: C, 64.24; H, 4.26. Found: C, 64.29; H, 4.34.

3 Synthesis of racemic trans-4-arylchroman-3-ols:

trans-5,7-Dimethyl-4-phenylchroman-3-ol 6a:
TsOH.H₂O (0.0074 g, 0.039 mmol) was added to a solution of compound 5a (50 mg, 0.196 mmol) in toluene (5 mL) and the resulting solution was heated at 70°C for 30 min. After cooling, EtOAc (50 mL) was added to the reaction mixture, and then the whole mixture was poured in a beaker containing saturated aq. NaHCO₃ solution (25 mL) with vigorous stirring. The combined organic layers were washed with brine (50 mL) and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure. Purification of the crude product by silica gel column chromatography (5-12% ethyl acetate in hexane) afforded compound 7a (45 mg, 90%) as a white solid. M.P.: 125-126°C.

1H NMR (400 MHz, CDCl₃): δ 7.29-7.25 (m, J = 7.2 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 7.2 Hz, 2H), 6.66 (s, 1H), 6.64 (s, 1H), 4.13 (m, 1H), 4.05-4.04 (m, 1H), 4.01-3.96 (m, 2H), 2.28 (s, 4H), 1.88 (s, 3H).

13C NMR (100 MHz, CDCl₃): δ 153.8, 142.6, 139.2, 138.0, 128.7, 128.5, 126.7, 124.5, 116.0, 114.9, 69.9, 64.4, 46.5, 21.1, 18.9. Anal. Calcd for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.36; H, 7.19.

trans-5,7-Dimethoxy-4-phenylchroman-3-ol 6b and its (3S, 4R) isomer:

Starting from 5b (50 mg, 0.17 mmol), the title compound was prepared in the same manner as that described for 6a. Silica gel column chromatography of the crude product (5-12% ethyl acetate in hexane) furnished the title compound 6b (44 mg, 88%) as a white solid. M.P.: 101-112°C. Compound 6b in the enantiomerically pure form [(3S,4R)-5,7-Dimethoxy-4-phenylchroman-3-ol] was also similarly synthesised from [(2S,3S)-2-((3,5-dimethoxyphenoxy)methyl)-3-phenyloxirane]. [α]D²⁷ = +51.5 (c = 1.0 in CHCl₃). Literature: [α]D²⁰ = +53.0 (c = 1.0 in CHCl₃)² and [α]D²⁷ = +52.3 (c = 1.1 in CHCl₃)³. ¹H NMR (400 MHz, CDCl₃): δ 7.27-7.24 (m, 2H), 7.19-7.16 (m, 1H), 7.08 (d, J = 7.3 Hz), 6.15 (d, J = 2.3 Hz, 1H), 6.08 (d, J = 2.3 Hz, 1H), 4.22 (m, 1H), 4.02-3.92 (m, 3H), 3.78 (s, 3H), 3.55 (s, 3H), 2.1 (bs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 60.2, 159.6, 154.9, 143.3, 128.3, 128.0, 126.3, 101.6, 92.8, 92.3, 69.2, 64.9, 55.4, 55.2, 43.2. Anal. Calcd for C₁₇H₁₈O₄: C, 71.31; H, 6.34. Found: C, 71.40; H, 6.36.
	rans-5,6,7-Trimethoxy-4-phenylchroman-3-ol 6c:
Starting from **5c** (50 mg, 0.158 mmol), the title compound was prepared in the same manner as that described for **6a**. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound **6c** (38.5 mg, 77%) as a white semi-solid. ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.26 (m, 3H), 7.11 (d, J = 7.3 Hz, 2H), 6.31 (s, 1H), 4.23 (m, 1H), 3.99 (m, 3H), 3.83 (s, 3H), 3.74 (s, 3H), 3.40 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 153.2, 149.8, 143.8, 136.6, 128.3, 128.1, 126.5, 106.9, 95.5, 69.1, 64.9, 60.6, 60.1, 55.7, 44.1. Anal. Calcd for C₁₈H₂₀O₅: C, 68.34; H, 6.37. Found: C, 68.41; H, 6.39.

**trans-6,7-Dimethoxy-4-phenylchroman-3-ol 6d:**

Starting from **5d** (50 mg, 0.17 mmol), the title compound was prepared in the same manner as that described for **6a**. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound **6d** (0.0375 g, 75%) as a white solid. M.P.: 118-119 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.35-7.19 (m, 3H), 7.14 (d, J = 7.5 Hz, 2H), 6.49 (s, 1H), 6.33 (s, 1H), 4.09-4.06 (m, 1H), 4.03 (d, J = 2.0 Hz, 2H), 3.98-3.93 (m, 1H), 3.88 (s, 3H), 3.65 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 148.9, 147.9, 143.8, 142.8, 128.9, 128.5, 126.8, 113.1, 111.9, 100.2, 69.9, 66.2, 56.2, 55.7, 49.3. Anal. Calcd for C₁₇H₁₈O₄: C, 71.31; H, 6.34. Found: C, 71.25; H, 6.42.

**trans-6-Methoxy-4-phenylchroman-3-ol 6e:**

Starting from **5e** (50 mg, 0.195 mmol), the title compound was prepared in the same manner as that described for **6e**. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound **6e** (40 mg, 80%) as a white solid. M.P.: 114-115 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.32 (m, 2H), 7.30-7.25 (m, 1H), 7.18-7.16 (m, 2H), 6.89 (d, J = 9.1 Hz, 1H), 6.79 (dd, J = 3.0, 9.1 Hz, 1H), 6.42 (d, J = 2.9 Hz, 1H), 4.15 (d, J = 10.5 Hz, 1H), 4.09-4.12 (m, 2H), 4.03-4.06 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 153.9, 148.0, 142.5, 129.0, 128.6, 128.9, 122.5, 117.2, 115.2, 114.6, 69.7, 66.5, 55.5, 50.2. Anal. Calcd for C₁₆H₁₆O₃: C, 74.98; H, 6.29. Found: C, 74.91; H, 6.22.

**trans-6-Methyl-4-phenylchroman-3-ol 6f:**
Starting from 5f (50 mg, 0.208 mmol), the title compound was prepared in the same manner as that described for 6a. Silica gel column chromatography of the crude product (5-15% ethyl acetate in hexane) furnished the title compound 6f (36 mg, 72%) as a white solid. M.P.: 102-103 °C. 1H NMR (400 MHz, CDCl3):  δ 7.35-7.11 (m, 5H), 6.98-6.95 (m, 1H), 6.81 (d, J = 8.5 Hz, 1H), 6.67 (br. s, 1H), 4.15-4.04 (m, 3H), 3.998-3.95 (m, 1H), 2.17 (s, 3H), 2.01 (bs, 1H). 13C NMR (100 MHz, CDCl3): δ 151.8, 142.7, 131.4, 130.2, 129.1, 128.9, 128.6, 126.9, 121.5, 116.3, 69.8, 66.5, 50.1, 20.4. Anal. Calcd for C16H16O2: C, 79.97; H, 6.71. Found: C, 79.92; H, 6.78.

trans-6-(tert-Butyl)-4-phenylchroman-3-ol 6g: 3

Starting from 5g (50 mg, 0.208 mmol), the title compound was prepared in the same manner as that described for 6a. Purification of the crude product by silica gel column chromatography (5-15% ethyl acetate in hexane) furnished compound 6g (0.035 g, 70%) as a white solid. M.P.: 108-109 oC. 1H NMR (400 MHz, CDCl3): δ 7.35-7.21 (m, 4H), 7.14 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.15-4.08 (m, 3H), 4.08-3.99 (m, 1H), 1.98 (bs, 1H), 1.19 (s, 9H). 13C NMR (100 MHz, CDCl3): δ 151.8, 144.1, 128.7, 128.1, 127.9, 125.3, 120.8, 116.0, 70.1, 66.5, 50.2, 34.1, 31.1. Anal.Calced for C19H22O2: C, 80.52; H, 7.59. Found: C, 80.57; H, 7.53.

trans-1-Phenyl-2,3-dihydro-1H-benzo[f]chromen-2-ol 6h: 3

Starting from compound 5h (50 mg, 0.18 mmol), the title compound was prepared in the same manner as that described for 6a. Purification of the crude product by silica gel column chromatography (5-15% ethyl acetate in hexane) furnished compound 6a (35 mg, 70%) as a white solid. M.P.: 119-120 oC. 1H NMR (400 MHz, CDCl3): δ 7.77-7.73 (m, 2H), 7.48–7.45 (m, 1H), 7.30-7.15 (m, 8H), 4.68 (br s, 1H), 4.22–4.14 (m, 3H), 2.30 (br s, 1H). 13C NMR (100 MHz, CDCl3): δ 151.7, 143.0, 133.4, 129.8, 129.3, 128.5, 126.8, 126.7, 123.5, 122.9, 118.5, 111.7, 69.7, 64.8, 45.9. Anal.Calced for C19H16O2: C, 82.58; H, 5.84. Found: C, 82.66; H, 5.89.

trans-4-Phenyl-3,4-dihydro-2H-benzo[h]chromen-3-ol 6i:
Starting from compound $5i$ (50 mg, 0.18 mmol), the title compound was prepared in the same manner as that described for $6a$. Purification of the crude product by silica gel column chromatography (5-15% ethyl acetate in hexane) furnished compound $6i$ (37.5 mg, 75%) as a white solid. M.P.: 130-131°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.25-8.23 (m, 1H), 7.72-7.70 (m, 1H), 7.48-7.42 (m, 2H), 7.31-7.08 (m, 6H), 6.89 (d, $J = 8.5$ Hz, 2H), 4.24-4.21 (m, 1H), 4.14-4.05 (m, 3H), 2.38 (bs, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.3, 142.8, 133.6, 129.2, 128.7, 128.5, 127.4, 127.0, 126.3, 125.6, 124.8, 121.8, 120.8, 115.2, 69.9, 66.7, 50.1. Anal.Calcd for C$_{19}$H$_{16}$O$_2$: C, 82.58; H, 5.84. Found: C, 82.52; H, 5.89.

**trans-4-Phenylchroman-3-ol $6j$:**

Starting from compound $5j$ (50 mg, 0.22 mmol), the title compound was prepared in the same manner as that described for $6a$. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound $6j$ (27 mg, 54%) as a white solid. M.P.: 122-123°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35-7.13 (m, 6H), 6.92-6.84 (m, 3H), 4.18 (dd, $J = 2.1$, 11.0 Hz, 1H), 4.09 (m, 2H), 4.02-3.98 (m, 1H), 2.08 (br s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.1, 142.6, 131.3, 129.1, 128.5, 128.2, 127.1, 122.1, 121.2, 116.6, 69.7, 66.7, 50.1. Anal.Calcd for C$_{15}$H$_{14}$O$_2$: C, 79.62; H, 6.24. Found: C, 79.68; H, 6.19.

**trans-6-Iodo-4-phenylchroman-3-ol $6k$:**

Starting from compound $5j$ (50 mg, 0.14 mmol), the title compound was prepared in the same manner as that described for $6a$. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound $6j$ (25 mg, 50%) as a white solid. M.P.: 108-109°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.49-7.12 (m, 7H), 6.72 (d, $J = 8.5$ Hz, 1H), 4.18 (d, $J = 2.1$, 11.0 Hz, 1H), 4.12-3.98 (m, 3H), 2.10 (br s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.3, 141.9, 139.8, 137.1, 129.0, 129.0, 127.5, 124.8, 119.0, 83.5, 69.4, 66.5, 49.9. Anal.Calcd for C$_{15}$H$_{13}$IO$_2$: C, 51.16; H, 3.72. Found: C, 51.26; H, 3.76.
**trans-6-Bromo-4-phenylchroman-3-ol 6l:**

Starting from compound 5j (50 mg, 0.16 mmol), the title compound was prepared in the same manner as that described for 6a. Purification of the crude product by silica gel column chromatography (5-15 \% ethyl acetate in hexane) furnished compound 6j (22.5 mg, 45\%) as a white solid. M.P.: 118-119°C. ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.19 (m, 4H), 7.07 (d, J = 7.5 Hz, 2H), 6.76 (d, J = 8.8 Hz, 1H), 4.18 (d, J = 2.1, 10.9 Hz, 1H), 4.11-3.97 (m, 3H), 1.58 (br s, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 154.3, 141.9, 139.8, 137.1, 129.0, 129.0, 127.5, 124.8, 119.0, 83.5, 69.4, 66.5, 49.9. Anal.Calcd for C₁₅H₁₃BrO₂: C, 59.04; H, 4.29. Found: C, 59.10; H, 4.21.

**trans-4-(4-bromophenyl)-5,7-dimethoxychroman-3-ol 6m and its (3S, 4R) isomer:**

Starting from compound 5m (50 mg, 0.136 mmol), the title compound was prepared in the same manner as that described for 6a. Purification of the crude product by silica gel column chromatography (5-15 \% ethyl acetate in hexane) furnished compound 6m (42 mg, 84\%) as a white solid. M.P.: 76-77°C. Compound 6m in the enantiomerically pure form (3S,4R)-4-(4-bromophenyl)-5,7-dimethoxychroman-3-ol was also similarly synthesised from [(2S,3S)-2-(4-bromophenyl)-3-((3,5-dimethoxyphenoxy)methyl)oxirane]. [α]D²⁷ = +33.8 (c = 0.5 in CHCl₃). Literature: [α]D²⁷ = +35.2 (c = 0.5 in CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 6.14 (d, J = 2.3 Hz, 1H), 6.08 (d, J = 2.3 Hz, 1H), 4.16 (m, 1H), 4.02-3.95 (m, 2H), 3.89 (d, J = 11.1 Hz, 1H), 3.78 (s, 3H), 3.56 (s, 3H), 2.30 (bs, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 160.4, 159.5, 155.0, 142.5, 131.4, 129.7, 120.2, 101.3, 92.9, 92.4, 69.0, 64.9, 55.4, 55.3, 42.8. Anal.Calcd for C₁₇H₁₇BrO₄: C, 55.91; H, 4.69. Found: C, 55.99; H, 4.61.

**trans-(3S,4R)-4-(4-bromophenyl)-5,7-dimethylchroman-3-ol 6n:**

Starting from compound 5m (50 mg, 0.15 mmol), the title compound was prepared in the same manner as that described for 6a. Purification of the crude product by silica gel column chromatography (5-15 \% ethyl acetate in hexane) furnished compound 6n (43 mg, 86\%) as a white solid.
M.P.: 86-87°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38 (d, $J = 8.7$ Hz, 2H), 6.94 (d, $J = 8.7$ Hz, 2H), 6.64 (d, $J = 6.8$ Hz, 1H), 4.07 (m, 1H), 4.03-3.99 (m, 2H), 3.92-88 (m, 1H), 2.28 (s, 3H), 1.97 (bs, 1H), 1.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.7, 141.7, 139.1, 138.4, 131.9, 130.3, 124.7, 115.5, 115.08, 69.7, 64.3, 46.0, 21.2, 18.9. Anal.Calcd for C$_{17}$H$_{17}$BrO$_2$: C, 61.28; H, 5.14. Found: C, 61.37; H, 5.31.

**trans-4-(4-bromophenyl)-6,7-dimethoxychroman-3-ol 6o:**

Starting from compound 5o (50 mg, 0.136 mmol), the title compound was prepared in the same manner as that described for 6a. Purification of the crude product by silica gel column chromatography (5-15 % ethyl acetate in hexane) furnished compound 6o (35 mg, 69%) as a white solid. M.P.: 89-90°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 (d, $J = 8.3$ Hz, 2H), 7.03 (d, $J = 8.3$ Hz, 2H), 6.49 (s, 1H), 6.29 (s, 1H), 4.06 (d, $J = 10.1$ Hz, 1H), 4.01-3.99 (m, 3H), 3.86 (s, 3H), 3.68 (s, 3H), 1.83 (bs, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.9, 144.1, 141.9, 131.7, 130.6, 120.9, 112.8, 111.3, 100.3, 69.8, 66.2, 56.2, 55.8, 48.9. Anal.Calcd for C$_{17}$H$_{17}$BrO$_2$: C, 55.91; H, 4.69. Found: C, 55.97; H, 4.78.

**trans-4-(4-Bromophenyl)-3,4-dihydro-2H-benzo[h]chromen-3-ol 6p:**

Starting from 5p (50 mg, 0.14 mmol), the title compound was prepared in the same manner as that described for 6a. Silica gel column chromatography of the crude product (5-12% ethyl acetate in hexane) furnished the title compound 6p (33 mg, 66%) as a white solid. M.P.: 128-129°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.26-8.23 (m, 1H), 7.77-7.75 (m, 1H), 7.51-7.47 (m, 2H), 7.42 (d, $J = 8.7$ Hz, 2H), 7.35 (d, $J = 8.7$ Hz, 1H), 7.01 (d, $J = 8.3$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 1H), 4.28-4.21 (m, 1H), 4.23-4.11 (m, 3H), 2.43 (bs, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.3, 141.9, 133.6, 131.8, 130.8, 128.2, 127.4, 126.5, 125.7, 124.8, 121.8, 121.1, 114.7, 69.8, 66.7, 49.5. Anal. Calcd for C$_{19}$H$_{15}$BrO$_2$: C, 64.24; H, 4.26. Found: C, 64.29; H, 4.38.

4 References


4 Copies of $^1$H and $^{13}$C NMR spectra for *trans*-4-aryl-chroman-3-ols

$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6a.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6a.
$\text{H NMR (400 MHz, CDCl}_3\text{)}$ spectrum of compound 6b.

$\text{C NMR (100 MHz, CDCl}_3\text{)}$ spectrum of compound 6b.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6c.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6c.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6d.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6d.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6e.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6e.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6g.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6g.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6h.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6h.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6i.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6i.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6j.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6j.
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H NMR (400 MHz, CDCl₃) spectrum of compound 6m.

C NMR (100 MHz, CDCl₃) spectrum of compound 6m.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6n.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6n.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6o.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6o.
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 6p.

$^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 6p.