Novel route for the construction of chroman ring system using cross coupling between benzylic- and aliphatic- alcohols in the presence of NaHSO$_4$/SiO$_2$

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Experimental Section
General
Melting points were determined on Büchi Melting Point B-540. NMR spectra were recorded on a JEOL ECX 400 spectrometer. Tetramethylsilane (δ = 0) was used as an internal standard for $^1$H NMR and CDCl$_3$ (δ = 77.0) for $^{13}$C NMR. Mass analysis were performed on a Agilent G1969 LC/MDS TOF. IR spectra were recorded on a JASCO FT/IR-6100. Elemental analyses were performed on a J Science Lab. micro corder JM-10.

Preparation of NaHSO$_4$/SiO$_2$: SiO$_2$ [Wakogel C-200 (Wako Pure Chemical Ind. Ltd.), 10 g] was added to a solution of NaHSO$_4$·H$_2$O (30 mmol, 4.14 g) in distilled water, and the mixture was stirred at room temperature for 0.5 h. The water was removed by rotary evaporator under reduced pressure, and the resulting reagent was dried in vacuo (10 mmHg) at 120 °C for 5 h.

Preparation of alcohols: Alcohols were prepared according to reported method.$^1$

Typical procedure for the construction of chlomans: A mixture of 1 (2 mmol), 2 (4 or 15 mmol) and NaHSO$_4$/SiO$_2$ (2.1 mmol/g, 1.0 or 2.0g) in DCE (10 mL) was stirred at 80 °C for 2 h, and then the used supported reagent was removed by filtration. The filtrate was evaporated to leave crude product, which was purified by column chromatography (hexane/chloroform) to obtain substituted chlomans 3.
$o$-Hydroxybenzhydrol (1a) ²

White solid; $^1$H NMR (400 MHz, CDCl₃) $\delta$ 3.09 (d, $J=3.4$ Hz, 1H), 5.97 (d, $J=3.4$ Hz, 1H), 6.78-6.88 (m, 3H), 7.15-7.20 (m, 1H), 7.28-7.38 (m, 5H), 7.92 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 76.9, 117.2, 119.9, 126.6, 126.8, 128.2, 128.7, 129.3, 141.8, 155.4.

2-Hydroxy-5-methylbenzhydrol (1b) ³

White solid; $^1$H NMR (400 MHz, CDCl₃) $\delta$ 2.19 (s, 3H), 3.02 (d, $J=3.4$ Hz, 1H), 5.92 (d, $J=3.4$ Hz, 1H), 6.67 (d, $J=1.8$ Hz, 1H), 6.77 (d, $J=8.2$ Hz, 1H), 6.97 (dd, $J=1.8$, 8.2 Hz, 1H), 7.27-7.39 (m, 5H), 7.68 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 20.4, 76.8, 116.9, 126.4, 126.7, 128.1, 128.6, 129.1, 129.6, 141.9, 152.8.

2-Hydroxy-5-methoxybenzhydrol (1c) ³

White solid; $^1$H NMR (400 MHz, CDCl₃) $\delta$ 3.16 (d, $J=3.5$ Hz, 1H), 3.67 (s, 3H), 5.90 (d, $J=3.5$ Hz, 1H), 6.43 (d, $J=3.0$ Hz, 1H), 6.72 (dd, $J=3.0$, 8.8 Hz, 1H), 6.80 (d, $J=8.8$ Hz, 1H), 7.28-7.39 (m, 5H), 7.47 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 55.7, 76.7, 113.9, 114.0, 117.7, 126.8, 127.5, 128.2, 128.7, 141.6, 149.1, 152.8.

5-Bromo-2-hydroxybenzhydrol (1d) ⁴

White solid; $^1$H NMR (400 MHz, CDCl₃) $\delta$ 3.33 (brs, 1H), 5.85 (s, 1H), 6.69 (d, $J=8.6$ Hz, 1H), 7.68-7.78 (m, 3H), 7.92 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 20.4, 76.8, 116.9, 126.4, 126.7, 128.1, 128.6, 129.1, 129.6, 141.9, 152.8.
Hz, 1H), 6.94 (d, J = 2.5 Hz, 1H), 7.23 (dd, J = 8.6, 2.5 Hz, 1H), 7.28-7.37 (m, 5H), 8.06 (brs, 1H); \(^1\)C NMR(100 MHz, CDCl\(_3\)) \(\delta\) 76.3, 112.0, 118.9, 126.7, 128.5, 128.6, 128.8, 130.7, 131.9, 141.0, 154.3.

2-Hydroxy-4-methoxybenzhydrol(1e)

[Diagram of 2-Hydroxy-4-methoxybenzhydrol]

Yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.39 (brs, 1H), 3.71 (s, 3H), 5.89 (s, 1H), 6.33 (dd, J = 8.5, 2.5 Hz, 1H), 6.43 (d, J = 2.5 Hz, 1H), 6.67 (d, J = 8.5 Hz, 1H), 7.23-7.34 (m, 5H), 8.15 (brs, 1H); \(^1\)C NMR(100 MHz, CDCl\(_3\)) \(\delta\) 55.2, 76.3, 102.5, 105.8, 119.3, 126.7, 128.0, 128.9, 142.1, 156.6, 160.4.

4-Benzyloxy-2-hydroxybenzhydrol(1f)

[Diagram of 4-Benzyloxy-2-hydroxybenzhydrol]

White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.89 (d, J = 2.9 Hz, 1H), 4.99 (s, 2H), 5.93 (d, J = 2.9 Hz, 1H), 6.42 (dd, J = 8.5, 2.5 Hz, 1H), 6.54 (d, J = 2.5 Hz, 1H), 6.69 (d, J = 8.5 Hz, 1H), 7.28-7.41 (m, 5H), 8.00 (s, 1H); \(^1\)C NMR(100 MHz, CDCl\(_3\)) \(\delta\) 69.9, 76.5, 103.4, 106.7, 119.4, 126.8, 127.5, 127.9, 128.1, 128.5, 128.6, 129.0, 136.8, 141.9, 156.6, 159.7.

3,5-dibromo-2-hydroxybenzhydrol(1g)

[Diagram of 3,5-dibromo-2-hydroxybenzhydrol]

White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.78 (d, J = 3.8 Hz, 1H), 6.02 (d, J = 3.8 Hz, 1H), 7.23 (d, J = 2.2 Hz, 1H), 7.25 (s, 1H), 7.30-7.40 (m, 5H), 7.55 (d, J = 2.2 Hz, 1H); \(^1\)C NMR(100 MHz, CDCl\(_3\)) \(\delta\) 74.2, 111.7, 112.3, 126.7, 128.4, 128.8, 129.9, 130.9, 133.7, 141.1, 149.9.

1-(2-hydroxyphenyl)-1-ethanol(1h)

[Diagram of 1-(2-hydroxyphenyl)-1-ethanol]
1-(2-hydroxy-5-methylphenyl)-1-ethanol (1i)

White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.53 (d, $J = 6.6$ Hz, 3H), 2.23 (s, 3H), 3.02 (d, $J = 3.8$ Hz, 1H), 4.96 (dq, $J = 6.6$, 3.8 Hz, 1H), 6.73 (d, $J = 8.2$ Hz, 1H), 6.76 (d, $J = 2.0$ Hz, 1H), 6.94 (dd, $J = 8.2$, 2.0 Hz, 1H), 7.85 (s, 1H); $^{13}$C NMR(100 MHz, CDCl$_3$) $\delta$ 20.4, 23.4, 71.4, 116.7, 126.9, 128.2, 129.0, 129.2, 152.7.

1-(5-bromo-2-hydroxyphenyl)-1-ethanol (1j)

White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.58 (d, $J = 6.6$ Hz, 3H), 2.56 (d, $J = 4.1$ Hz, 1H), 5.03 (dq, $J = 6.6$, 4.1 Hz, 1H), 6.75 (d, $J = 8.7$ Hz, 1H), 7.10 (d, $J = 2.3$ Hz, 1H), 7.26 (dd, $J = 8.7$, 2.3 Hz, 1H), 7.98 (s, 1H); $^{13}$C NMR(400 MHz, CDCl$_3$) $\delta$ 23.4, 71.2, 111.7, 119.0, 129.1, 130.2, 131.6, 154.6.

(2-Hydroxyphenyl)thiophen-2-ylmethanol (1k)

Lime green solid; m.p. 100-101 °C($n$-hexane/ethyl acetate); $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 6.00 (d, $J = 4.1$ Hz, 1H), 6.19 (d, $J = 4.1$ Hz, 1H), 6.78-6.82 (m, 3H), 6.88 (dd, $J = 5.0$, 1.3 Hz, 1H), 7.06 (dt, $J = 7.7$, 1.7 Hz, 1H), 7.30 (dd, $J = 5.0$, 1.3 Hz, 1H), 7.41 (dd, $J = 8.0$, 1.6 Hz, 1H), 9.49 (s, 1H); $^{13}$C NMR(100 MHz, DMSO-$d_6$) $\delta$ 64.7,
2,2-dimethyl-4-phenylchroman(3aa)\(^7\)

White solid; m.p. 118-120 °C (methanol); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.36 (s, 3H), 1.45 (s, 3H) 1.96-2.07 (m, 2H), 4.09 (dd, \(J = 11.8, 6.8\) Hz, 1H), 6.73-6.74 (m, 2H), (6.82-6.84 (m, 1H), 7.07-7.33 (m, 6H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 24.3, 30.0, 40.0, 43.6, 74.6, 117.3, 119.8, 124.6, 126.6, 127.7, 128.6, 128.8, 129.8, 145.1, 154.1; IR (neat): 3034, 2970, 2934, 1579, 1478, 1448, 1375, 1300, 1253, 1118, 1026, 993, 913, 831, 748, 701, 618, 543 cm\(^{-1}\); HRMS (TOF-CI): \(m/z\) [M+H]\(^+\) calcd. for C\(_{17}\)H\(_{19}\)O: 239.1435; found: 239.1438.

2,2,4-triphenylchroman(3ab)\(^8\)

White solid; m.p. 164-166 °C (methanol); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.62 (dd, \(J = 13.8, 12.6\) Hz, 1H), 3.10 (dd, \(J = 13.8, 5.4\) Hz, 1H), 3.89 (dd, \(J = 12.6, 5.4\) Hz, 1H), 6.60-6.30 (m, 1H), 6.70-6.74 (m, 1H), 7.12-7.34 (m, 13H), 7.48-7.52 (m, 4H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 40.1, 42.0, 81.8, 117.2, 120.4, 125.3, 125.7, 126.3, 126.8, 127.1, 127.3, 127.8, 128.2, 128.6, 128.8, 129.6, 143.5, 144.3, 145.7, 154.1; IR (neat): 3058, 1580, 1484, 1444, 1301, 1225, 1105, 1064, 1019, 914, 852, 754, 695, 583, 548 cm\(^{-1}\); HRMS (TOF-CI): \(m/z\) [M+H]\(^+\) calcd. for C\(_{27}\)H\(_{23}\)O: 363.1748; found: 363.1756.

6-methyl-2,2,4-triphenylchroman(3bb)

White solid; m.p. 173-175 °C (methanol); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.08 (s, 3H), 2.60 (dd, \(J = 13.9, 12.6\) Hz, 1H), 3.06 (dd, \(J = 13.9, 5.4\) Hz, 1H), 3.86 (dd, \(J = 12.6, 5.4\) Hz, 1H), 6.60-6.30 (m, 1H), 6.70-6.74 (m, 1H), 7.12-7.34 (m, 13H), 7.48-7.52 (m, 4H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 24.3, 30.0, 40.0, 43.6, 74.6, 117.3, 119.8, 124.6, 126.6, 127.7, 128.6, 128.8, 129.8, 145.1, 154.1; IR (neat): 3034, 2970, 2934, 1579, 1478, 1448, 1375, 1300, 1253, 1118, 1026, 993, 913, 831, 748, 701, 618, 543 cm\(^{-1}\); HRMS (TOF-CI): \(m/z\) [M+H]\(^+\) calcd. for C\(_{17}\)H\(_{19}\)O: 239.1435; found: 239.1438.
Hz, 1H), 6.42 (s, 1H), 6.95 (dd, \( J = 8.2, 2.3 \) Hz, 1H), 7.03 (d, \( J = 8.2 \) Hz, 1H), 7.18-7.34 (m, 11H) 7.47-7.52 (m, 4H); 13C NMR(100 MHz, CDCl3) δ 20.5, 40.1, 42.2, 81.6, 117.0, 124.8, 125.6, 126.3, 126.7, 127.0, 127.3, 128.2, 128.5, 128.6 (overlap), 128.8, 129.5, 129.7, 143.5, 144.5, 145.8, 152.0; IR(neat):3057, 2920, 1591, 1487, 1445, 1233, 1231, 1110, 1061, 1007, 920, 846, 805, 784, 748, 732, 695, 628, 585, 539 cm⁻¹; HRMS (TOF-CI): m/z [M+H]⁺ calcd. for C28H25O: 377.1905; found: 377.1896; Anal. calcd. for C28H24O: C, 89.33; H, 6.43. found C, 89.58; H, 6.15.

6-methoxy-2,2,4-triphenylchroman(3cb)

White solid; m.p. 106-108 °C(methanol); ¹H NMR (400 MHz, CDCl3) δ 2.59 (dd, \( J = 13.9, 12.6 \) Hz, 1H), 3.08 (dd, \( J = 13.9, 5.4 \) Hz, 1H), 3.52 (s, 3H), 3.87 (dd, \( J = 12.6, 5.4 \) Hz, 1H), 6.15 (d, \( J = 3.0 \) Hz, 1H), 6.73 (dd, \( J = 3.0, 1.0 \) Hz, 1H), 7.07 (d, \( J = 8.9 \) Hz, 1H), 7.17-7.33 (m, 11H), 7.47-7.52 (m, 4H); ¹³C NMR(100 MHz, CDCl3) δ 40.4, 42.0, 55.4, 81.5, 113.8, 114.1, 117.8, 125.6, 125.8, 126.3, 126.8, 127.0, 127.2, 128.2, 128.6, 128.8, 143.4, 144.2, 145.8, 148.2, 153.2; IR(neat):3055, 2827, 1604, 1489, 1451, 1417, 1252, 1211, 1155, 1100, 1036, 950, 912, 859, 809, 755, 698, 588, 512 cm⁻¹; HRMS (TOF-CI): m/z [M] calcd. for C28H24O2: 392.1776; found: 392.1777; Anal. calcd. for C28H24O2: C, 85.68; H, 6.16. found C, 85.77; H, 6.16.

6-Bromo-2,2,4-triphenylchroman(3db)

White solid; m.p. 158-160 °C(methanol); ¹H NMR (400 MHz, CDCl3) δ 2.59 (dd, \( J = 14.0, 12.7 \) Hz, 1H), 3.08 (dd, \( J = 14.0, 5.5 \) Hz, 1H), 3.85 (dd, \( J = 12.7, 5.5 \) Hz, 1H), 6.74 (d, \( J = 2.3 \) Hz, 1H), 7.02 (d, \( J = 8.7 \) Hz, 1H), 7.15-7.35 (m, 12H) 7.45-7.48 (m, 4H); ¹³C NMR(100 MHz, CDCl3) δ 40.1, 41.6, 82.2, 112.7, 119.1, 125.6, 126.1, 127.1, 127.3, 127.5, 127.6, 128.3, 128.7, 128.8, 130.8, 132.1, 143.0, 143.4, 145.2, 153.3; IR(neat):3056, 1592, 1469, 1396, 1240, 1203, 1110, 1062, 1007, 915, 877, 842, 811, 777, 754, 694, 585, 542 cm⁻¹; HRMS (TOF-CI): m/z [M] calcd. for C27H21BrO: 440.0775; found: 440.0776; Anal. calcd. for C27H21BrO: C, 73.48; H, 4.80. found
C, 73.68; H, 4.71.

7-Methoxy-2,2,4-triphenylchroman (3eb)

White solid; m.p. 148-149 °C (methanol); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.59 (dd, $J = 13.8, 12.6$ Hz, 1H), 3.07 (dd, $J = 13.8, 5.4$ Hz, 1H), 3.78 (s, 3H), 3.88 (dd, $J = 12.6, 5.4$ Hz, 1H), 6.33 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.51 (d, $J = 8.6$ Hz, 1H), 6.7 (d, $J = 2.6$ Hz, 1H), 7.16-7.35 (m, 11 H) 7.47-7.52 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 39.5, 42.2, 55.3, 82.1, 101.7, 107.4, 117.6, 125.7, 126.3, 126.7, 127.1, 127.3, 128.2, 128.6 (overlap), 128.7, 130.2, 143.4, 144.6, 145.6, 155.0, 159.3; IR (neat): 2969, 1611, 1580, 1495, 1444, 1410, 1318, 1258, 1195, 1158, 1101, 1058, 1033, 1018, 966, 910, 835, 772, 734, 696, 627, 594, 556, 518 cm$^{-1}$; HRMS (TOF-CI): m/z [M+H]$^+$ calcd. for C$_{28}$H$_{25}$O$_2$: 393.1854; found: 393.1851; Anal. calcd. for C$_{28}$H$_{24}$O$_2$: C, 85.68; H, 6.16. found C, 85.88; H, 6.02.

7-Benzylxy-2,2,4-triphenylchroman (3fb)

White solid; m.p. 129-131 °C (methanol) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.59 (dd, $J = 13.8, 12.6$ Hz, 1H), 3.06 (dd, $J = 13.8, 5.4$ Hz, 1H), 3.80 (dd, $J = 12.6, 5.4$ Hz, 1H), 5.01 (d, $J = 11.7$ Hz, 1H), 5.06 (d, $J = 11.7$ Hz, 1H), 6.40 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.51 (d, $J = 8.6$ Hz, 1H), 6.79 (d, $J = 2.6$ Hz, 1H), 7.16-7.51 (m, 20H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 39.5, 42.1, 70.0, 82.1, 102.7, 108.2, 117.9, 125.7, 126.3, 126.7, 127.1, 127.3, 127.6, 127.9, 128.2, 128.5, 128.6 (overlap), 128.7, 130.2, 137.0 143.4, 144.5, 145.6, 154.9, 158.6; IR (neat): 3028, 1612, 1580, 1496, 1448, 1315, 1252, 1160, 1119, 1058, 1018, 909, 834, 746, 696, 620, 589, 527 cm$^{-1}$; HRMS (TOF-CI): m/z [M+H]$^+$ calcd. for C$_{34}$H$_{29}$O$_2$: 469.2162; found: 469.2155; Anal. calcd. for C$_{34}$H$_{28}$O$_2$: C, 87.15; H, 6.02. found C, 87.13; H, 5.94.
6,8-Dibromo-2,2,4-triphenylchroman (3gb)

White solid; m.p. 166-167 °C (ethanol); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.55 (dd, \(J = 14.1, 12.6\) Hz, 1H), 3.21 (dd, \(J = 14.1, 5.5\) Hz, 1H), 3.93 (dd, \(J = 14.1, 12.6\) Hz, 1H), 6.69 (d, \(J = 2.4\) Hz, 1H), 7.13-7.35 (m, 11H), 7.48-7.60 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 40.3, 41.2, 83.4, 112.5, 112.6, 125.0, 125.6, 127.3, 127.4, 127.5, 128.4, 128.6, 128.9, 129.0 (overlap), 131.4, 133.6, 142.7, 142.9, 144.9, 149.8; IR (neat): 3074, 3032, 1490, 1440, 1248, 1153, 1114, 1058, 1015, 941, 862, 771, 741, 695, 582 cm\(^{-1}\); HRMS (TOF-CI): \(m/z\) [M] calcd. for C\(_{27}\)H\(_{20}\)Br\(_2\)O: 517.9880; found: 517.9872; Anal. calcd. for C\(_{27}\)H\(_{20}\)Br\(_2\)O: C, 62.33; H, 3.87. found C, 62.45; H, 3.77.

4-methyl-2,2-diphenylchroman (3hb)

oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.34 (d, \(J = 6.8\) Hz, 3H), 2.18 (dd, \(J = 13.6, 12.1\) Hz, 1H), 2.69-2.79 (m, 1H), 2.87 (dd, \(J = 13.6, 5.3\) Hz, 1H), 6.83-6.87 (m, 1H), 7.06-7.33 (m, 9H), 7.42-7.48 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 19.9, 26.6, 41.5, 81.6, 117.1, 120.4, 125.8, 126.4, 126.9, 127.2, 127.4, 128.2, 128.4, 143.7, 146.1, 153.5; IR (neat): 3030, 2959, 1581, 1486, 1447, 1297, 1226, 1116, 1060, 1027, 986, 907, 843, 750, 695, 603 cm\(^{-1}\); HRMS (TOF-CI): \(m/z\) [M+H]\(^+\) calcd. for C\(_{22}\)H\(_{21}\)O: 301.1592; found: 301.1588.

4,6-Dimethyl-2,2-diphenylchroman (3ib)

White solid; m.p. 135-137 °C \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.31 (d, \(J = 6.8\) Hz, 3H), 2.15 (d, \(J = 13.6, 12.1\) Hz, 1H), 2.21 (s, 3H) 2.66-2.75 (m, 1H), 2.84 (dd, \(J = 13.6, 5.3\) Hz, 1H), 6.90-6.98 (m, 3H), 7.12-7.30 (m, 6H), 7.42-7.46 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 19.9, 20.7, 26.6, 41.6, 81.4, 116.9, 125.7, 126.4, 126.5, 126.9, 127.2, 127.3,
6-Bromo-4-methyl-2,2-diphenylchroman(3jb)

White solid; m.p. 146-147 °C. \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.32 (d, \(J = 6.8\) Hz, 3H), 2.15 (dd, \(J = 13.7, 12.2\) Hz, 1H), 2.67-2.77 (m, 1H), 2.87 (dd, \(J = 13.7, 5.3\) Hz, 1H), 6.93-6.96 (m, 1H), 7.18-7.33 (m, 8H), 7.39-7.45 (m, 4H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 19.8, 26.7, 41.0, 82.0, 112.7, 119.0, 125.7, 126.3, 127.1, 127.4, 128.2, 128.5, 129.1, 129.8, 130.3, 143.2, 145.6, 152.7; IR (neat): 3058, 2871, 1572, 1473, 1397, 1321, 1218, 1180, 1122, 1094, 1056, 982, 899, 824, 761, 727, 696, 670, 603, 512 cm\(^{-1}\); HRMS (TOF-CI): \(m/z\) [M] calcd. for C\(_{23}\)H\(_{22}\)O: 314.1670; found: 314.1671. Anal. calcd. for C\(_{23}\)H\(_{22}\)O: C, 87.86; H, 7.05. found C, 87.81; H, 7.00.

2-methyl-2,4-diphenylchroman(3ac)\(^9\)

White solid. \(^1^H\) NMR (400 MHz, CDCl\(_3\)) cis-isomer \(\delta\) 1.70 (s, 3H), 2.20 (dd, \(J = 13.8, 12.1\) Hz, 1H), 2.38 (dd, \(J = 13.8, 5.9\) Hz, 1H), 4.24 (dd, \(J = 12.1, 5.9\) Hz, 1H), 6.54-7.55 (m, 14H); trans-isomer \(\delta\) 1.67 (s, 3H), 2.29 (dd, \(J = 13.7, 12.9\) Hz, 1H), 2.68 (dd, \(J = 13.7, 5.3\) Hz, 1H), 3.58 (dd, \(J = 12.9, 5.3\) Hz, 1H), 6.53-7.55 (m, 14H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)) See spectrum; IR (neat): 3033, 2935, 1578, 1484, 1444, 1379, 1301, 1241, 1181, 1113, 1062, 1036, 945, 911, 811, 755, 695, 549, 488 cm\(^{-1}\); HRMS (TOF-CI): \(m/z\) [M+H]\(^+\) calcd. for C\(_{22}\)H\(_{21}\)O: 301.1592; found: 301.1601; Anal. calcd. for C\(_{22}\)H\(_{20}\)O: C, 87.96; H, 6.71. found C, 88.08; H, 6.54.

3-Acetyl-6-bromo-2,2-dimethyl-4-phenylchroman(3df)
White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.33 (s, 3H), 1.46 (s, 3H), 1.79 (s, 3H), 3.26 (d, $J = 12.2$ Hz, 1H), 4.24 (d, $J = 12.2$ Hz, 1H), 6.73 (d, $J = 8.7$ Hz, 1H), 6.82 (d, $J = 2.3$ Hz, 1H), 7.08-7.11 (m, 2H), 7.20 (dd, $J = 8.7$, 2.3 Hz, 1H), 7.25-7.32 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.1, 28.3, 34.6, 43.6, 61.9, 76.0, 112.6, 119.1, 127.0, 127.3, 128.9, 129.0, 130.9, 132.2, 141.7, 152.2, 209.5; HRMS (TOF-CI): $m/z$ [M] calcd. for C$_{19}$H$_{19}$BrO$_2$: 358.0562; found: 358.0559; IR(neat): 3027, 2923, 2284, 1705, 1575, 1472, 1349, 1284, 1252, 1222, 1176, 1118, 1069, 1024, 946, 907, 873, 822, 750, 697, 673, 598, 539 cm$^{-1}$; Anal. calcd. for C$_{19}$H$_{19}$BrO$_2$: C, 63.52; H, 5.33. found C, 63.53; H, 5.32.

Yellow oil; HRMS (TOF-CI): $m/z$ [M] calcd. for C$_{19}$H$_{19}$BrO$_2$: 358.0562; found: 358.0557; IR(neat): 3027, 2925, 1709, 1570, 1471, 1402, 1358, 1248, 1180, 1116, 1073, 947, 913, 880, 815, 752, 699, 635, 594, 542 cm$^{-1}$; HRMS (TOF-CI): $m/z$ [M+H]$^+$ calcd. for C$_{18}$H$_{21}$O: 253.1592; found: 253.1591; Anal. calcd. for C$_{18}$H$_{20}$O: C, 85.67; H, 7.99. found C, 86.06; H, 8.15.
2,6-dimethyl-2,4-diphenylchroman (3bc)

White solid; $^1$H NMR (400 MHz, CDCl$_3$) cis-isomer δ 1.68 (s, 3H), 2.18 (dd, $J = 13.7$, 12.0 Hz, 1H), 2.15 (s, 3H), 2.35 (dd, $J = 13.7$, 6.0 Hz, 1H), 4.20 (dd, $J = 12.0$, 6.0 Hz, 1H), 6.60 (s, 1H), 6.90-7.54 (m, 12H); trans-isomer δ 1.65 (s, 3H), 2.05 (s, 3H), 2.27 (dd, $J = 13.6$, 12.8 Hz, 1H), 2.66 (dd, $J = 13.6$, 5.3 Hz, 1H), 3.55 (dd, $J = 12.8$, 5.3 Hz, 1H), 6.36 (s, 1H), 6.90-7.54 (m, 12H); $^{13}$C NMR (400 MHz, CDCl$_3$) See spectrum; IR(neat): 3027, 2965, 2919, 1591, 1487, 1446, 1371, 1235, 1178, 1121, 1066, 1026, 950, 916, 814, 768, 700, 566, 540, 491 cm$^{-1}$; HRMS (TOF-CI): m/z [M+H]$^+$ calcd. for C$_{23}$H$_{23}$O: 315.1748; found: 315.1751; Anal. calcd. for C$_{23}$H$_{22}$O: C, 87.86; H, 7.05. found C, 88.09; H, 7.15.

6-Methoxy-2,2,4-diphenylchroman (3ca)

White solid; m.p. 72-75 °C(methanol); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.33 (s, 3H), 1.43 (s, 3H), 1.96 (dd, $J = 13.6$, 11.4 Hz, 1H) 2.02 (dd, $J = 13.6$, 6.8 Hz, 1H), 3.59 (s, 3H), 4.05 (dd, $J = 11.4$, 6.8 Hz, 1H), 6.29 (d, $J = 2.8$ Hz, 1H), 6.69 (dd, $J = 8.9$, 2.8 Hz, 1H), 6.77 (d, $J = 8.9$ Hz, 1H) 7.19-7.33 (m, 5H); $^{13}$C NMR (400 MHz, CDCl$_3$) δ 24.0, 29.9, 40.3, 43.6, 55.6, 74.2, 113.7, 114.5, 117.7, 125.1, 126.6, 128.6, 128.7, 144.9, 148.1, 152.9; IR(neat): 3038, 2942, 2830, 2169, 2031, 1610, 1487, 1428, 1375, 1255, 1194, 1147, 1112, 1035, 916, 875, 806, 762, 727, 702, 624, 552 cm$^{-1}$; HRMS (TOF-CI): m/z [M] calcd. for C$_{18}$H$_{26}$O$_2$: 268.1463; found: 268.1465; Anal. calcd. for C$_{18}$H$_{26}$O$_2$: C, 80.56; H, 7.51. found C, 80.82; H, 7.64.

6-methoxy-2-methyl-2,4-diphenylchroman (3cc)
White solid; $^1$H NMR (400 MHz, CDCl$_3$) cis-isomer δ 1.64 (s, 3H), 2.17 (dd, $J = 13.6$, 12.1 Hz, 1H), 2.36 (dd, $J = 13.6$, 6.0 Hz, 1H), 3.51 (s, 3H), 4.20 (dd, $J = 12.1$, 6.0 Hz, 1H), 6.34 (d, $J = 3.0$ Hz 1H), 6.76 (dd, $J = 8.9$, 3.0 Hz 1H), 6.95 (d, $J = 8.9$ Hz 1H), 7.12-7.53 (m, 10H); trans-isomer δ 1.67 (s, 3H), 2.27 (dd, $J = 13.7$, 13.0 Hz, 1H), 2.67 (dd, $J = 13.7$, 5.4 Hz, 1H), 3.57 (dd, $J = 13.0$, 5.4 Hz, 1H), 6.10 (d, $J = 3.0$ Hz 1H), 6.72 (dd, $J = 8.9$, 3.0 Hz, 1H), 6.97 (d, $J = 8.9$ Hz 1H), 7.12-7.53 (m, 10H); $^{13}$C NMR(100 MHz, CDCl$_3$) See spectrum; IR(neat):3038, 2942, 2830, 2169, 2031, 1610, 1487, 1428, 1375, 1255, 1194, 1147, 1112, 1035, 916, 875, 806, 762, 727, 702, 624, 552 cm$^{-1}$; HRMS (TOF-CI): m/z [M] calcd. for C$_{23}$H$_{22}$O$_2$: 330.1619; found:330.1616; Anal. calcd. for C$_{23}$H$_{22}$O$_2$: C,83.60; H, 6.71. found C,83.89; H, 6.78.

6-Bromo-2,2,-dimethyl-4-phenylchroman (3da)

White solid; m.p. 78-79 °C(methanol); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.33 (s, 3H), 1.43 (s, 3H), 1.96 (dd, $J = 13.7$, 12.3 Hz, 1H), 2.02 (dd, $J = 13.7$, 6.4 Hz, 1H), 4.04 (dd, $J = 12.3$, 6.4 Hz, 1H), 6.71 (d, $J = 8.7$ Hz, 1H), 6.85 (d, $J = 2.5$ Hz, 1H), 7.15-7.35 (m, 6H); $^{13}$C NMR(100 MHz, CDCl$_3$) δ 24.1, 29.8, 39.9, 43.1, 75.0, 111.9, 119.2, 126.8, 126.9, 128.6, 128.8, 130.7, 132.2, 144.1, 153.2; IR(neat):3060, 2975, 1563, 1462, 1390, 1253, 1186, 1117, 1076, 909, 877, 802, 752, 698, 660, 609, 542 cm$^{-1}$; HRMS (TOF-CI): m/z [M] calcd. for C$_{17}$H$_{17}$BrO: 316.0462; found: 316.0460; Anal. calcd. for C$_{17}$H$_{17}$BrO: C,64.37; H, 5.40. found C,64.55; H, 5.37.

6-Bromo-2-methyl-2,4-diphenylchroman (3dc)

White solid; $^1$H NMR (400 MHz, CDCl$_3$) cis-isomer δ 1.68 (s, 3H), 2.17 (dd, $J = 13.7$, 12.2 Hz, 1H), 2.37 (dd, $J = 13.7$, 6.0 Hz, 1H), 4.20 (dd, $J = 12.2$, 6.0 Hz, 1H), 6.67-7.52 (m, 13H); trans-isomer δ 1.66 (s, 3H), 2.26 (dd, $J = 13.8$, 12.8 Hz, 1H), 2.67 (dd, $J =$
13.8, 5.3 Hz, 1H), 3.55 (dd, J = 12.8, 5.3 Hz, 1H), 6.67 (d, J = 2.5 Hz, 1H), 6.89-7.52 (m, 12H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) spectrum; IR (neat): 3028, 2970, 2924, 1575, 1469, 1397, 1248, 1166, 1119, 1063, 1027, 950, 889, 814, 768, 699, 619, 566, 535, 490 cm\(^{-1}\); HRMS (TOF-CI): m/z [M] calcd. for C\(_{22}\)H\(_{19}\)BrO: 378.0619; found: 378.0613; Anal. calcd. for C\(_{22}\)H\(_{19}\)BrO: C, 69.67; H, 5.05. found C, 70.04; H, 5.00.

6,8-Dibromo-2,2-dimethyl-4-phenylchroman (3ga)

White solid; m.p. 130-131 °C (methanol); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.35 (s, 3H), 1.51 (s, 3H), 1.99 (dd, J = 13.8, 12.1 Hz, 1H), 2.06 (dd, J = 13.8, 6.6 Hz, 1H), 4.06 (dd, J = 12.1, 6.6 Hz, 1H), 6.80 (d, J = 2.3 Hz, 1H), 7.15-7.36 (m, 5H), 7.50 (d, J = 2.3 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 24.3, 29.6, 40.2, 43.0, 76.5, 111.5, 112.5, 127.1, 128.1, 128.6, 128.9, 131.5, 133.6, 143.5, 150.2; IR (neat): 3067, 2975, 1546, 1491, 1436, 1263, 1224, 1179, 1150, 1118, 912, 866, 800, 763, 701, 615, 557 cm\(^{-1}\); HRMS (TOF-CI): m/z [M] calcd. for C\(_{17}\)H\(_{16}\)Br\(_2\)O: 393.9567; found: 393.9577; Anal. calcd. for C\(_{17}\)H\(_{16}\)Br\(_2\)O: C, 51.55; H, 4.07. found C, 51.60; H, 4.08.

6,8-Dibromo-2-methyl-2,4-diphenylchroman (3ge)

White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) cis-isomer \(\delta\) 1.67 (s, 3H), 2.19 (dd, J = 13.8, 12.3 Hz, 1H), 2.47 (dd, J = 13.8, 6.0 Hz, 1H), 4.23 (dd, J = 12.3, 6.0 Hz, 1H), 6.86 (dd, J = 2.4 Hz, 1H), 7.10-7.59 (m, 11H); trans-isomer \(\delta\) 1.71 (s, 3H), 2.30 (dd, J = 14.0, 12.8 Hz, 1H), 2.74 (dd, J = 14.0, 5.6 Hz, 1H), 3.63 (dd, J = 12.8, 5.6 Hz, 1H), 6.63 (d, J = 2.4 Hz, 1H), 7.10-7.59 (m, 11H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) See spectrum; IR (neat): 3065, 3028, 2968, 1552, 1492, 1437, 1248, 1151, 1063, 1025, 951, 915, 861, 758, 695, 620, 577, 552, 515 cm\(^{-1}\); HRMS (TOF-CI): m/z [M] calcd. for C\(_{22}\)H\(_{18}\)Br\(_2\)O:
2,2-diphenyl-4-(2-thienyl)chroman(3kb)

White solid; m.p. 200-201 °C(methanol); $^1$H NMR (400 MHz, CDCl$_3$) δ 2.72 (dd, $J =$ 13.8, 12.6 Hz, 1H), 3.21 (dd, $J =$ 13.8, 5.2 Hz, 1H), 4.23 (dd, $J =$ 12.6, 5.2 Hz, 1H), 6.74-6.82 (m, 2H), 6.92-6.97 (m, 2H), 7.10-7.35 (m, 9H), 7.49-7.51 (m, 4H); $^{13}$C NMR(100 MHz, CDCl$_3$) δ 35.2, 42.4, 81.9, 117.2, 120.5, 124.2, 124.8, 125.7, 125.9, 126.3, 126.5, 127.2, 127.4, 128.2, 128.3, 128.7, 129.0, 143.1, 145.4, 147.2, 153.4; IR(neat): 3067, 1578, 1482, 1443, 1298, 1272, 1224, 1103, 1062, 1011, 915, 842, 759, 698, 644, 620, 583, 535 cm$^{-1}$; HRMS (TOF-Cl): m/z [M] calcd. for C$_{25}$H$_{20}$OS: 368.1234.

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X: parts per Million: 1H
X: parts per Million : 1H
3cb
3db
3ib