Supplementary Information

for

Magnesium dicarboxylates promote the prenylation of phenolics
that is extended to the total synthesis of icaritin

Jichao Zhang,¹,² Wei Xiong,³ Yongju Wen,³ Xuewen Fu,³ Xiaoxia Lu,³
Guolin Zhang³ and Chun Wang*³

¹Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, China.
²University of Chinese Academy of Sciences, Beijing 100049, China.

*E-mail: wangchun@cib.ac.cn

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1. Synthesis and Characterization of Magnesium Dicarboxylates

FT-IR Spectra

Fig. S1A FT-IR Spectra of (a) malonate and (b) Magnesium malonate 4a

Fig. S1B FT-IR Spectra of (a) succinate and (b) Magnesium succinate 4b
Fig. S1C FT-IR Spectra of (a) glutarate and (b) Magnesium glutarate 4c

Fig. S1D FT-IR Spectra of (a) adipate and (b) Magnesium adipate 4d
Fig. S1E FT-IR Spectra of (a) phthalate and (b) Magnesium phthalate 4e

Fig. S1F FT-IR Spectra of (a) succinate and (b) Zinc succinate 4f
Thermal Gravity Analysis

![TGA and DTG curves for 4b](image)

**Fig. S2** Thermal Gravity Analysis Curves of 4b (a) TGA and (b) DTG

2. Synthetic Procedures and Characterization Data of the Compounds

**1-(2,6-dihydroxy-3-(3-methylbut-2-en-1-yl)phenyl)ethan-1-one (3ba)**

![Molecular structure of 3ba](image)

Obtained in MeCN with yield: 48% (0.211 g). White solid, mp: 79-80 °C.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 13.31 (s, 1H), 10.79 - 10.52 (m, 1H), 7.13 (d, $J$ = 8.3 Hz, 1H), 6.37 (d, $J$ = 8.4 Hz, 1H), 5.22 (m, 1H), 3.13 (d, $J$ = 7.3 Hz, 2H), 2.65 (s, 3H), 1.70 (s, 3H), 1.65 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 205.94, 161.04, 159.22, 136.57, 131.90, 123.08, 119.30, 110.17, 106.47, 33.72, 27.30, 25.96, 18.04. HRMS-ESI (m/z) calcd for C$_{13}$H$_{17}$O$_3$ ([M+H]$^+$): 221.1178; found: 221.1174.

**2-(3-methylbut-2-en-1-yl)phenol (3ca$_1$) (known compound)$^{[1]}$**

![Molecular structure of 3ca$_1$](image)

Obtained in MeCN with yield: 27% (0.120 g). White solid, mp: 124-126 °C.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.47 (s, 1H), 10.65 (s, 1H), 7.53 (s, 1H), 6.30 (s, 1H), 5.33 - 5.13 (m, 1H), 3.16 (d, $J$ = 7.2 Hz, 2H), 2.50 (s, 3H),
1.72 (s, 3H), 1.65 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 202.86, 163.23, 162.85, 132.61, 131.86, 123.16, 120.63, 113.01, 102.42, 27.96, 26.83, 25.96, 18.13. HRMS-ESI (m/z) calcd for C$_{13}$H$_{17}$O$_3$ ([M+H]$^+$): 221.1178; found: 221.1172.

1-(2,4-dihydroxy-3-(3-methylbut-2-en-1-yl)phenyl)ethan-1-one (3ca$_2$)

Obtained in MeCN with yield: 25% (0.110 g). White solid, mp: 153-154 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.05 (s, 1H), 10.55 (s, 1H), 7.64 (d, $J = 8.8$ Hz, 1H), 6.44 (d, $J = 8.8$ Hz, 1H), 5.18 – 5.12 (m, 1H), 3.20 (d, $J = 7.2$ Hz, 2H), 1.71 (s, 3H), 1.61 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 203.64, 162.68, 162.45, 131.18, 130.95, 122.74, 114.63, 112.91, 107.80, 26.57, 25.94, 21.61, 18.15. HRMS-ESI (m/z) calcd for C$_{13}$H$_{15}$O$_3$ ([M-H]$^-$): 219.1027; found: 219.1029.

$E$-1-(2,4-dihydroxy-3-(3-methylbut-2-en-1-yl)-phenyl)-3(4-hydroxyphenyl)prop-2-en-1-one (3da$_1$) (known compound)$^{[2]}$

Obtained in MeCN with yield: 22% (0.140 g). Yellow solid, mp: 168-170 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.49 (s, 1H), 10.68 (s, 1H), 10.15 (s, 1H), 7.98 (s, 1H), 7.86 – 7.64 (m, 4H), 6.95 – 6.75 (m, 2H), 6.33 (s, 1H), 5.37 – 5.06 (m, 1H), 3.22 (d, $J = 7.1$ Hz, 2H), 1.72 (s, 3H), 1.68 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 191.78, 164.50, 163.41, 160.68, 144.47, 132.13, 131.64, 131.22, 126.25, 123.87, 120.92, 117.99, 116.29, 113.15, 102.74, 28.43, 25.95, 18.25. HRMS-ESI (m/z) calcd for C$_{20}$H$_{21}$O$_4$ ([M+H]$^+$): 325.1440; found: 325.1431.

(E)-1-(2,4-dihydroxy-3-(3-methylbut-2-en-1-yl)phenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one (3da$_2$)

Obtained in MeCN with yield: 18% (0.115 g). Yellow solid, mp: 154-156 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 14.02 (s, 1H), 10.57 (s, 1H), 10.16 (s, 1H), 8.05 (d, $J = 9.0$ Hz, 1H), 7.76 (s, 4H), 6.95 – 6.75 (m, 2H), 6.48 (d, $J = 8.9$ Hz, 1H), 5.20 – 5.16 (m, 1H), 3.24 (d, $J = 7.2$ Hz, 2H), 1.73 (s, 3H), 1.62 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 192.21, 164.00, 162.73, 160.69, 144.59, 131.66, 130.92, 130.27,
126.23, 122.82, 117.82, 116.30, 114.90, 113.16, 107.76, 25.96, 21.74, 18.19. HRMS-ESI (m/z) calcd for C_{20}H_{20}NaO_{4} ([M+Na]^+): 347.1259; found: 347.1250.

2-(3-methylbut-2-en-1-yl)benzene-1,3,5-triol (3ea) (known compound)[3]

![Chemical structure of 2-(3-methylbut-2-en-1-yl)benzene-1,3,5-triol (3ea)]

Obtained in DMF with yield: 71% (0.275 g). Light yellow solid, mp: 96-97 °C. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 8.82 (s, 2H), 8.72 (s, 1H), 5.76 (s, 2H), 5.12 (m, 1H), 3.04 (d, \(J = 7.1\) Hz, 2H), 1.67 (s, 3H), 1.59 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 156.66, 156.17, 128.84, 125.10, 105.67, 94.53, 25.99, 22.00, 18.09. HRMS-ESI (m/z) calcd for C\(_{11}\)H\(_{14}\)O\(_3\)Na ([M+Na]^+): 217.0841; found: 217.1064.

5-(hydroxymethyl)-4-(3-methylbut-2-en-1-yl)benzene-1,3-diol (3fa)

![Chemical structure of 5-(hydroxymethyl)-4-(3-methylbut-2-en-1-yl)benzene-1,3-diol (3fa)]

Obtained in DMF with yield: 59% (0.246 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 8.98 (s, 1H), 8.87 (s, 1H), 6.32 (d, \(J = 2.5\) Hz, 1H), 6.16 (d, \(J = 2.5\) Hz, 1H), 5.05-4.95 (m, 1H), 4.91 (t, \(J = 5.5\) Hz, 1H), 4.35 (d, \(J = 5.4\) Hz, 2H), 3.11 (d, \(J = 6.9\) Hz, 2H), 1.69 (s, 3H), 1.61 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 156.04, 155.79, 142.31, 129.50, 124.62, 115.37, 105.50, 101.20, 61.18, 25.99, 23.77, 18.12. HRMS-ESI (m/z) calcd for C\(_{12}\)H\(_{16}\)O\(_3\)Na ([M+Na]^+): 231.0997; found: 231.1009.

4-(3-methylbut-2-en-1-yl)benzene-1,3-diol (3ga\(_1\)) (known compound)[4]

![Chemical structure of 4-(3-methylbut-2-en-1-yl)benzene-1,3-diol (3ga\(_1\))]  

Obtained in DMF with yield: 45% (0.160 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 9.03 (s, 2H), 6.75 (d, \(J = 8.2\) Hz, 1H), 6.26 (d, \(J = 2.5\) Hz, 1H), 6.13 (dd, \(J = 8.1, 2.4\) Hz, 1H), 5.27-5.17 (m, 1H), 3.08 (d, \(J = 7.5\) Hz, 2H), 1.67 (s, 3H), 1.64 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 156.40, 129.92, 124.18, 118.31, 106.36, 102.82, 27.77, 25.99, 18.01. HRMS-ESI (m/z) calcd for C\(_{11}\)H\(_{15}\)O\(_2\) ([M+H]^+): 179.1072; found: 179.1072.

2-(3-methylbut-2-en-1-yl)benzene-1,3-diol (3ga\(_2\))

![Chemical structure of 2-(3-methylbut-2-en-1-yl)benzene-1,3-diol (3ga\(_2\))]  

Obtained in DMF with yield: 12% (0.041 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 9.02 (s, 2H), 6.73 (t, \(J = 8.0\) Hz, 1H), 6.24 (d, \(J = 8.0\) Hz, 2H), 5.22 – 5.10 (m, 1H), 3.16 (d, \(J = 7.4\) Hz, 2H), 1.70 (s, 3H), 1.60 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 156.40, 129.68, 126.45, 124.13, 114.63, 106.61, 25.99, 22.44, 18.17. HRMS-ESI (m/z) calcd for C\(_{11}\)H\(_{15}\)O\(_2\) ([M+H]^+): 179.1072; found: 179.1065.
2-(3-methylbut-2-en-1-yl)benzene-1,4-diol (3ha) (known compound)\(^{[5]}\)

Obtained in DMF with yield: 53% (0.188 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.52 (d, \(J = 3.7\) Hz, 2H), 6.56 (d, \(J = 8.5\) Hz, 1H), 6.44 (d, \(J = 3.0\) Hz, 1H), 6.37 (dd, \(J = 8.5, 3.0\) Hz, 1H), 5.24 (m, 1H), 3.13 (d, \(J = 7.4\) Hz, 2H), 1.69 (s, 3H), 1.65 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 150.16, 147.67, 131.57, 128.49, 123.42, 116.34, 115.78, 113.16, 28.44, 26.01, 18.06. HRMS-ESI (m/z) calcd for C\(_{11}\)H\(_{15}\)O\(_2\) ([M+H]: 179.1072; found: 179.1071.

2-(3-methylbut-2-en-1-yl)phenol (3ia')

Obtained in MeCN with yield: 14% (0.045 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.25 (s, 1H), 6.99 (m, 2H), 6.76 (m, 1H), 6.70 (m, 1H), 5.27 (m, 1H), 3.20 (d, \(J = 7.4\) Hz, 2H), 1.70 (s, 3H), 1.67 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 155.30, 131.55, 129.69, 127.83, 127.07, 123.39, 119.32, 115.24, 28.43, 26.00, 18.08. HRMS-ESI (m/z) calcd for C\(_{11}\)H\(_{13}\)O ([M+H]: 163.1123; found: 163.1195.

4-(3-methylbut-2-en-1-yl)phenol (3ia'')

Obtained in MeCN with yield: 44% (0.143 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.12 (s, 1H), 6.94 (d, \(J = 8.3\) Hz, 2H), 6.65 (d, \(J = 8.4\) Hz, 2H), 5.28 – 5.21 (m, 1H), 3.18 (d, \(J = 7.4\) Hz, 2H), 1.69 (s, 3H), 1.67 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 155.73, 131.81, 129.41, 124.49, 119.53, 32.29, 25.97, 18.08. HRMS-ESI (m/z) calcd for C\(_{11}\)H\(_{13}\)O ([M-H]: 161.0972; found: 161.0969.

5-(3-methylbut-2-en-1-yl)benzo[d][1,3]dioxol-4-ol (3ja)

Obtained in MeCN with yield: 49% (0.200 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.98 (s, 1H), 6.56 (s, 1H), 6.41 (s, 1H), 5.84 (s, 2H), 5.31 – 5.16 (m, 1H), 3.11 (d, \(J = 7.4\) Hz, 2H), 1.68 (s, 3H), 1.65 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 149.49, 145.63, 139.95, 131.45, 123.69, 119.52, 109.21, 100.74, 97.94, 28.16, 25.97, 18.06. HRMS-ESI (m/z) calcd for C\(_{12}\)H\(_{15}\)O\(_3\) ([M+H]: 207.1021; found: 207.1031.
3-(3-methylbut-2-en-1-yl)benzene-1,2-diol (3ka')

Obtained in MeCN with yield: 18% (0.064 g). Colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.16 (s, 1H), 8.09 (s, 1H), 6.60 (dd, $J = 7.6$, 2.0 Hz, 1H), 6.52 (t, $J = 7.6$ Hz, 1H), 6.48 (dd, $J = 5.8$, 2.7 Hz, 1H), 5.27 – 5.23 (m, 1H), 3.19 (d, $J = 7.4$ Hz, 2H), 1.67 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 145.31, 143.29, 131.26, 128.60, 123.61, 120.21, 119.07, 113.40, 28.53, 26.00, 18.08. HRMS-ESI (m/z) calcd for C$_{11}$H$_{13}$O$_2$ ([M-H]$: 177.0921$; found: 177.0912.

4-(3-methylbut-2-en-1-yl)benzene-1,2-diol (3ka'')

Obtained in MeCN with yield: 43% (0.152 g). Colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.70 (s, 1H), 8.57 (s, 1H), 6.61 (d, $J = 7.9$ Hz, 1H), 6.53 (d, $J = 2.1$ Hz, 1H), 6.39 (dd, $J = 8.0$, 2.1 Hz, 1H), 5.28 – 5.20 (m, 1H), 3.11 (d, $J = 7.4$ Hz, 2H), 1.69 (s, 3H), 1.66 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 145.50, 143.59, 132.50, 131.27, 124.53, 119.12, 116.00, 115.88, 33.49, 26.00, 18.06. HRMS-ESI (m/z) calcd for C$_{11}$H$_{14}$NaO$_2$ ([M+Na]$^+$): 201.0891$; found: 201.0886.

1-(2-hydroxy-5-(3-methylbut-2-en-1-yl)phenyl)ethan-1-one (3la)

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.78 (s, 1H), 7.66 (d, $J = 2.2$ Hz, 1H), 7.32 (dd, $J = 8.5$, 2.3 Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 5.31 – 5.26 (m, 1H), 3.28 (d, $J = 7.4$ Hz, 2H), 2.63 (s, 3H), 1.71 (s, 3H), 1.70 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 204.80, 159.40, 136.72, 132.44, 132.38, 130.72, 123.73, 120.57, 118.05, 33.08, 28.13, 25.96, 18.18. HRMS-ESI (m/z) calcd for C$_{13}$H$_{16}$NaO$_2$ ([M+Na]$^+$): 227.1048; found: 227.1043.

2-methoxy-6-(3-methylbut-2-en-1-yl)phenol (3ma') (known compound)$^{[6]}$

Obtained in MeCN with yield: 30% (0.115 g). Colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.66 (s, 1H), 6.78 – 6.62 (m, 2H), 6.54 (d, $J = 8.0$ Hz, 1H), 5.27 (t, $J = 7.5$ Hz, 1H), 3.73 (s, 3H), 3.19 (d, $J = 7.3$ Hz, 2H), 1.70 (s, 3H), 1.67 (s, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 147.88, 144.92, 132.54, 132.38, 130.72, 123.73, 120.57, 118.05, 33.08, 28.13, 25.96, 18.18. HRMS-ESI (m/z) calcd for C$_{12}$H$_{16}$NaO$_2$ ([M+Na]$^+$): 215.1048; found: 215.1063.
2-methoxy-4-(3-methylbut-2-en-1-yl)phenol (3ma"") (known compound)[7]

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\[\text{2-methoxy-4-(3-methylbut-2-en-1-yl)phenol (3ma"") (known compound)[7]}\]
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Obtained in MeCN with yield: 16\% (0.060 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.81 (s, 1H), 6.79 (d, \(J = 8.1\) Hz, 1H), 6.57 (d, \(J = 2.1\) Hz, 1H), 6.52 (dd, \(J = 8.1, 2.2\) Hz, 1H), 5.33 (t, \(J = 4.9\) Hz, 1H), 3.71 (s, 3H), 3.15 (d, \(J = 7.5\) Hz, 2H), 1.69 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 146.87, 146.19, 134.39, 131.59, 124.26, 118.96, 116.01, 112.86, 56.19, 33.46, 25.98, 18.08. HRMS-ESI (m/z) calcd for C\(_{12}\)H\(_{16}\)O\(_2\) ([M+Na\(^+\]): 215.1048; found: 215.1063.

4-methoxy-2-(3-methylbut-2-en-1-yl)phenol (3na)

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\[\text{4-methoxy-2-(3-methylbut-2-en-1-yl)phenol (3na)}\]
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Obtained in MeCN with yield: 35\% (0.135 g). Colorless oil. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.80 (s, 1H), 6.68 (d, \(J = 8.3\) Hz, 1H), 6.61–6.52 (m, 2H), 5.30–5.23 (m, 1H), 3.63 (s, 3H), 3.17 (d, \(J = 7.3\) Hz, 2H), 1.69 (s, 3H), 1.66 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 152.53, 149.10, 131.75, 128.81, 123.24, 115.62, 111.61, 55.68, 28.64, 25.98, 18.10. HRMS-ESI (m/z) calcd for C\(_{12}\)H\(_{15}\)O\(_2\) ([M-H]: 191.1078; found: 191.1064.

1-(2,4-dihydroxy-6-((3-methylbut-2-en-1-yl)oxy)phenyl)ethan-1-one (5aa)

(known compound)[8]

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\[\text{1-(2,4-dihydroxy-6-((3-methylbut-2-en-1-yl)oxy)phenyl)ethan-1-one (5aa)}\]
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Obtained in K\(_2\)CO\(_3\)/acetone with yield: 28\% (0.132 g). White solid, mp: 106-107 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 13.84 (s, 1H), 10.60 (s, 1H), 5.99 (d, \(J = 2.3\) Hz, 1H), 5.86 (d, \(J = 2.1\) Hz, 1H), 5.49 (t, \(J = 6.7\) Hz, 1H), 4.57 (d, \(J = 6.6\) Hz, 2H), 1.77 (s, 3H), 1.72 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 202.70, 166.76, 165.50, 162.94, 138.35, 119.44, 105.18, 95.95, 92.65, 65.84, 33.15, 25.89, 18.52. HRMS-ESI (m/z) calcd for C\(_{13}\)H\(_{16}\)O\(_4\)Na ([M+Na\(^+\]): 259.0946; found: 259.0938.

1-(2,4-dihydroxy-6-((3-methylbut-2-en-1-yl)oxy)phenyl)ethan-1-one (5aa')

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\[\text{1-(2,4-dihydroxy-6-((3-methylbut-2-en-1-yl)oxy)phenyl)ethan-1-one (5aa')}\]
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\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.30 (s, 2H), 5.94 (s, 2H), 5.38 (t, \(J = 1.6\) Hz, 1H), 4.52 (d, \(J = 6.8\) Hz, 2H), 2.58 (s, 3H), 1.74 (s, 3H), 1.70 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 203.44, 166.75, 164.50, 162.94, 138.21, 119.67, 105.19, 94.11, 92.65, 65.03, 32.94, 25.89, 18.48. HRMS-ESI (m/z) calcd for C\(_{13}\)H\(_{16}\)O\(_4\)Na ([M+Na\(^+\]): 259.0946; found: 259.0938.
To the solution of 1g (0.220 g, 2.0 mmol ) in dry acetone (10 mL) was added prenyl bromide 2a (0.28 mL, 2.4 mmol) at 0 °C. Then, NaOH (0.160 g, 4.0 mmol) was added and the mixture was stirred for 3 h at room temperature under argon. Then, the reaction was stirred for 3 h at room temperature under argon. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into ice-cold water. The resulted solution was adjusted to PH=7.0 with 1M HCl (aq) and extracted with ethyl acetate. The organic phase was washed with water (3×10) and dried over anhydrous Na₂SO₄. After removing of the solvents, the residue was purified by flash silica gel column chromatography with petroleum ether-ethyl acetate (10:1, v/v) to give the product 5ga. Yield: 61% (0.217 g). Colorless oil. ¹H NMR (400 MHz, DMSO-d₆) δ 9.40 (s, 1H), 7.03 (t, J = 8.0 Hz, 1H), 6.41 – 6.29 (m, 3H), 5.40 (m, 1H), 4.44 (d, J = 6.6 Hz, 2H), 1.74 (s, 3H), 1.69 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 160.12, 159.01, 137.13, 130.21, 120.59, 108.16, 105.67, 102.31, 64.50, 25.87, 18.43. HRMS-ESI (m/z) calcd for C₁₁H₁₅O₂ ([M+H]⁺): 179.1072; found: 179.1063.

1-(5,7-dihydroxy-2,2-dimethylchroman-8-yl)ethan-1-one (6aa) (known compound) [⁹]

Obtained in MeCN with yield: 25% (0.118 g). White solid, mp: 147-148 °C. ¹H NMR (400 MHz, DMSO-d₆) δ 14.11 (s, 1H), 10.62 (s, 1H), 5.80 (s, 1H), 2.57 (s, 3H), 2.45 (t, J = 6.7 Hz, 2H), 1.72 (t, J = 6.8 Hz, 2H), 1.26 (s, 6H). ¹³C NMR (101 MHz, DMSO-d₆) δ 203.30, 163.63, 160.82, 160.35, 104.56, 99.99, 95.19, 76.09, 32.88, 31.88, 26.82, 16.14. HRMS-ESI (m/z) calcd for C₁₃H₁₅O₄ ([M+H]⁺): 237.1127; found: 237.1113.

2,2-dimethylchromane-5,7-diol (6ea) (known compound) [¹⁰]
Obtained in MeCN with yield: 33% (0.128 g). Colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.11 (s, 1H), 8.85 (s, 1H), 5.84 (d, $J = 2.3$ Hz, 1H), 5.60 (d, $J = 2.3$ Hz, 1H), 2.40 (t, $J = 6.8$ Hz, 2H), 1.64 (t, $J = 6.8$ Hz, 2H), 1.21 (s, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 156.79, 156.41, 155.27, 99.55, 95.06, 94.93, 73.77, 32.53, 26.88, 16.88. HRMS-ESI (m/z) calcd for C$_{13}$H$_{13}$O$_3$ ([M-H]): 193.0870; found: 193.0867.

5-(hydroxymethyl)-2,2-dimethylchroman-7-ol (6fa)

Obtained in MeCN with yield: 26% (0.108 g). Colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.99 (s, 1H), 6.40 (d, $J = 2.5$ Hz, 1H), 5.99 (d, $J = 2.5$ Hz, 1H), 4.96 (t, $J = 5.5$ Hz, 1H), 4.36 (d, $J = 5.5$ Hz, 2H), 2.50–2.44 (m, 2H), 1.70 (s, 2H), 1.22 (s, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 156.44, 154.40, 142.12, 109.00, 106.68, 102.11, 73.53, 61.11, 32.69, 26.87, 18.24. HRMS-ESI (m/z) calcd for C$_{12}$H$_{15}$O$_3$ ([M-H]): 207.1027; found: 207.1046.

2,2-dimethylchroman-7-ol (6ga) (known compound)$^{[10]}$

Obtained in MeCN with yield: 11% (0.040 g). Colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.07 (s, 1H), 6.82 (d, $J = 8.2$ Hz, 1H), 6.25 (dd, $J = 8.2, 2.5$ Hz, 1H), 6.11 (d, $J = 2.4$ Hz, 1H), 2.59 (t, $J = 6.7$ Hz, 2H), 1.69 (t, $J = 6.6$ Hz, 2H), 1.24 (s, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 156.96, 154.65, 130.20, 111.54, 107.91, 115.56, 114.66, 74.12, 32.93, 27.03, 21.59. HRMS-ESI (m/z) calcd for C$_{11}$H$_{15}$O$_2$ ([M+H]$^+$): 179.1072; found: 179.1071.

2,2-dimethylchroman-6-ol (6ha) (known compound)$^{[10]}$

Obtained in MeCN with yield: 21% (0.075 g). Colorless oil. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.69 (s, 1H), 6.63–6.37 (m, 3H), 2.63 (t, $J = 6.8$ Hz, 2H), 1.68 (t, $J = 6.8$ Hz, 2H), 1.22 (s, 6H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 150.55, 146.59, 121.59, 117.49, 115.56, 114.66, 73.55, 32.74, 26.95, 22.53. HRMS-ESI (m/z) calcd for C$_{11}$H$_{15}$O$_2$ ([M+H]$^+$): 179.1072; found: 179.1068.
4-benzylbenzene-1,3-diol (10) (known compound)\(^{[11]}\) and 2-benzylbenzene-1,3-diol (11)

Scheme S2 The reaction of 1g with BnBr in the presence of 4b

Phenols 1g (2.0 mmol, 1.0 equiv) and 4b (2.0 mmol, 1.0 equiv) were sequentially added in DMF (10 mL) and stirred at room temperature for 5 min. Then, benzyl bromide (2.4 mmol, 1.2 equiv) was dropwise added and the mixture was stirred at 60 °C for 96 h under argon. After cooling to room temperature, the mixture was poured into ice-cold water and extracted with ethyl acetate. The organic layer was washed with water (3×10) and dried with anhydrous Na₂SO₄. After removing of the solvent, the crude product was further purified by reversed-phase column chromatography with MeOH-H₂O (70%, v/v) to afford C-benzylated phenols 10 and 11 (5:1, mol/mol).

10: Yield: 60% (0.240 g). White solid, mp: 75-76 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.21 (s, 1H), 9.04 (s, 1H), 7.28 – 7.20 (m, 2H), 7.20 – 7.15 (m, 2H), 7.13 (m, 1H), 6.79 (d, \(J = 8.1\) Hz, 1H), 6.30 (d, \(J = 2.4\) Hz, 1H), 6.15 (dd, \(J = 8.1, 2.4\) Hz, 1H), 3.74 (s, 2H). \(^1\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 157.01, 156.07, 142.50, 131.09, 128.95, 128.50, 125.86, 118.39, 106.53, 102.88, 35.11. HRMS-ESI (m/z) calcd for C\(_{13}\)H\(_{11}\)O\(_2\) ([M-H]): 199.0759; found: 199.0748.

11: Yield: 12% (0.048 g). White solid, mp: 117-118 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 9.19 (s, 2H), 7.27 – 7.14 (m, 4H), 7.09 (d, \(J = 6.8\) Hz, 1H), 6.80 (t, \(J = 8.0\) Hz, 1H), 6.30 (d, \(J = 8.0\) Hz, 2H), 3.82 (s, 2H). \(^1\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 156.64, 142.37, 128.85, 128.24, 127.15, 125.61, 114.43, 106.66, 28.88. HRMS-ESI (m/z) calcd for C\(_{13}\)H\(_{11}\)O\(_2\) ([M-H]): 199.0759; found: 199.0747.

\((E)\)-1-(2-hydroxy-4,6-bis(methoxymethoxy)-3-(3-methylbut-2-en-1-yl)phenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (15)

Scheme S3 The reaction of 12 and p-anisaldehyde promoted by pyrrolidine in MeOH
To the solution of 12 (0.320 g, 1.0 mmol) in MeOH (10 mL) was added p-anisaldehyde (0.13 mL, 1.1 mmol) at room temperature. Then, the reaction temperature was raised to 50 °C and stirred for 16 h under an atmospheric condition. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into ice-cold water. The obtained solution was adjusted to pH=7.0 with 1M HCl (aq) and extracted with ethyl acetate. The organic layer was washed with water (3×10) and dried with anhydrous Na₂SO₄. After removing of solvent, the residue obtained was purified over flash column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as the eluent to give 15. Yield: 75% (0.330 g). Yellow solid. ¹H NMR (400 MHz, DMSO-d₆) δ 13.78 (s, 1H), 7.87 – 7.64 (m, 4H), 7.12 – 6.95 (m, 2H), 6.40 (s, 1H), 5.33 (d, J = 19.0 Hz, 4H), 5.13 (t, J = 1.5 Hz, 1H), 3.82 (s, 3H), 3.42 (s, 3H), 3.40 (s, 3H), 3.22 (d, J = 7.2 Hz, 2H), 1.72 (s, 3H), 1.60 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 193.22, 162.82, 161.81, 160.65, 158.22, 143.13, 130.99, 130.83, 127.84, 125.18, 122.90, 115.09, 110.92, 107.51, 95.67, 94.16, 92.83, 57.02, 56.50, 55.84, 25.94, 21.70, 18.09. HRMS-ESI (m/z) calcd for C₂₅H₃₁O₇ ([M+H]⁺): 443.2070; found: 443.2056.
3. References


4. NMR Spectra of All Compounds

$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3aa

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3aa
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ba

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3ba
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ca$_1$

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3ca$_1$
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ca$_2$

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3ca$_2$
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of $3\text{da}_1$

$^{13}$C\{$^1$H\} NMR (101 MHz, DMSO-$d_6$) spectrum of $3\text{da}_1$
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3da$_2$

$^{13}$C$[^1]$H NMR (101 MHz, DMSO-$d_6$) spectrum of 3da$_2$
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ea

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3ea
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3fa

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3fa
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ga$_1$

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3ga$_1$
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ga$_2$

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3ga$_2$
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ha

$^{13}$C$^1$H NMR (101 MHz, DMSO-$d_6$) spectrum of 3ha
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ia'

$^{13}$C{$^1$H} NMR (101 MHz, DMSO-$d_6$) spectrum of 3ia'
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ia

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3ia
\( ^1H \text{NMR (400 MHz, DMSO-}d_6 \text{)} \text{ spectrum of 3ja} \)

\( ^{13}C\{^1H\} \text{NMR (101 MHz, DMSO-}d_6 \text{)} \text{ spectrum of 3ja} \)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ka'

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3ka'
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ka''

$^{13}$C$\{^1$H$\}$ NMR (101 MHz, DMSO-$d_6$) spectrum of 3ka''
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3la

$^{13}$C\($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3la
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ma'$

$^{13}$C{$^1$H} NMR (101 MHz, DMSO-$d_6$) spectrum of 3ma'$
$^1$H NMR (400 MHz, DMSO-\textit{d}_6) spectrum of 3ma$	extsuperscript{''}$

$^{13}$C\{$^1$H}\ NMR (101 MHz, DMSO-\textit{d}_6) spectrum of 3ma$	extsuperscript{''}$
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3na

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 3na
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 5aa

$^{13}$C{$^1$H} NMR (101 MHz, DMSO-$d_6$) spectrum of 5aa
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of a mixture of 5aa and 5aa' (5:1)

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of a mixture of 5aa and 5aa' (5:1)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 5ga

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 5ga
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 6aa

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 6aa
$^{1}H$ NMR (400 MHz, DMSO-$d_6$) spectrum of 6ea

$^{13}C\{^1H\}$ NMR (101 MHz, DMSO-$d_6$) spectrum of 6ea
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 6fa

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 6fa
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 6ga

$^{13}$C{$^1$H} NMR (101 MHz, DMSO-$d_6$) spectrum of 6ga
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 6ha

$^{13}$C-$^1$H NMR (101 MHz, DMSO-$d_6$) spectrum of 6ha
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 10

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 10
\[ ^1H \text{NMR (400 MHz, DMSO-}d_6\text{) spectrum of 11} \]

\[ ^{13}C\{^1H\} \text{NMR (101 MHz, DMSO-}d_6\text{) spectrum of 11} \]
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 12

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 12
$^1$H NMR (400 MHz, CDCl$_3$) spectrum of 13

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) spectrum of 13
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 14

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 14
HMBC NMR of compound 14 in DMSO-$d_6$
$^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 15

$^{13}$C($^1$H) NMR (101 MHz, DMSO-$d_6$) spectrum of 15