Supporting Information for

Highly Efficient Synthesis of Flavonol 5-O-glycosides with Glycosyl ortho-Akynylbenzoates as Donors

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3,7,3',4'-Tetra-\textit{O-}\textit{tert}-butyldimethylsilyl-quercetin (3)

To a suspension of quercetin (1 g, 3.3 mmol) in dry CH$_2$Cl$_2$ (10 mL) was added TBSCl (2.80 g, 19 mmol) and DBU (3 mL, 20 mmol) at room temperature. Then the reaction mixture was stirred for another 5 h, at which time TLC showed that all starting material was consumed. Ethyl acetate (100 mL) was added to dilute the reaction mixture, and the mixture was washed successively with water, saturated NaCl solution and dried over Na$_2$SO$_4$. Filtration and concentration under reduced pressure to afford the crude product, which was further purified by silica gel chromatography (eluent system: PE : EA = 15 : 1) to afford the fully TBS protected quercetin.

The above obtained intermediate was dissolved in CH$_2$Cl$_2$/H$_2$O (v/v = 10 : 1, 10 mL), to which catalytic amount I$_2$ was added. Then the reaction mixture was heated to reflux for 3 hours, at which time TLC showed that all starting material was consumed. General procedure was adopted to get 3 (1.8 g, 70 %) as light-yellow solid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.68 (s, 1 H), 7.46 (m, 1 H), 7.35 (m, 1 H), 6.91 (d, $J = 8.4$ Hz, 1 H), 1.01 (s, 9 H), 1.00 (s, 9 H), 0.99 (s, 9 H), 0.84 (s, 9 H), 0.26 (s, 6 H), 0.23 (s, 6 H), 0.21 (s, 6 H), 0.12 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 178.2, 161.8 (2 C), 156.4, 153.2, 149.2, 146.8, 135.6, 124.4, 123.2, 121.8, 120.8, 106.1, 102.9, 98.2, 25.9 (2 C), 25.7, 25.6, 18.6, 18.4, 18.3, -4.0, -4.1, -4.2, -4.4; HRMS (ESI) calcd for C$_{39}$H$_{67}$O$_7$Si$_4$ [M+H]$^+$ 759.3958, found 759.3959.

3,7,4'-Tri-\textit{O-hexanoyl}-kaempferol (5)

To a suspension of kaempferol (2.3 g, 8 mmol) and Et$_3$N (3.7 mL) in dry acetone (100 mL) was added hexanoyl chloride (3.66 mL, 26.4 mmol) dropwise at 0 °C. After hexanoyl chloride addition completed, the temperature was raised to rt, and the stirring was continued for another 3 h. Ice water (10 mL) was added to quench the reaction and the acetone was removed under reduced pressure, the resultant reaction mixture was diluted with ethyl acetate and washed with 1 N HCl, saturated Na$_2$CO$_3$ and NaCl successively, then dried over Na$_2$SO$_4$. Filtration and concentration under reduced pressure afforded the crude product which was further purified by silica gel chromatography (eluent system: PE : EA = 13 : 1) to give 5 (3.1 g, 68%) as light-yellow solid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.17 (s, 1 H), 7.88 (dd, $J = 2.0$, 6.8 Hz, 1 H).
Hz, 2 H), 7.26 (dd, J = 2.0, 6.8 Hz, 2 H), 6.84 (d, J = 2.0 Hz, 1 H), 6.58 (d, J = 2.0 Hz, 1 H), 2.63-2.56 (m, 6 H), 1.80-1.74 (m, 6 H), 1.41-1.33 (m, 12 H), 0.96-0.88 (m, 9 H); 13C NMR (100 MHz, CDCl3) δ 176.3, 171.7, 171.1, 170.6, 161.7, 156.5, 156.4, 156.0, 153.2, 132.0, 129.7, 126.7, 122.0, 108.7, 105.4, 101.0, 34.3, 33.7, 31.2, 31.1, 31.0, 24.5, 24.4 (2 C), 22.3, 22.2 (2 C), 13.9, 13.8; HRMS (ESI) calcd for C33H40O9Na [M+Na]+ 603.2565, found 603.2562.

3,7,4'-Tri-O-tert-butyldimethylsilyl-5-O-(2''''-O-benzoyl-β-D-glucopyranosyl)-kaempferol (10)

To a suspension of acceptor 2 (63 mg, 0.1 mmol), donor 6 (115 mg, 0.15 mmol), and activated powdered 4Å MS in dry CH2Cl2 (3 mL) was added PPh3AuNTf2 (22 mg, 0.03 mmol) under the protection of N2. The reaction mixture was then stirred at 30 °C overnight. Filtration and concentration under reduced pressure gave the crude product which was further purified by silica gel chromatography (eluent system: PE : EA = 15 : 1) to furnish 10 (103 mg, 90%), as a white solid: [α]28D 6.0 (c 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.07 (d, J = 7.2 Hz, 2 H), 7.93-7.87 (m, 6 H), 7.82 (d, J = 8.8 Hz, 2 H), 7.52-7.28 (m, 12 H), 6.91 (d, J = 8.8 Hz, 2 H), 6.62 (d, J = 2.4 Hz, 1 H), 6.61 (d, J = 2.4 Hz, 1 H), 6.04-5.95 (m, 2 H), 5.86 (t, J = 9.2 Hz, 1 H), 5.71 (d, J = 6.8 Hz, 1 H), 4.61 (dd, J = 3.1, 12.4 Hz, 1 H), 4.50 (dd, J = 4.7, 12.0 Hz, 1 H), 4.23 (m, 1 H), 1.00 (s, 9 H), 0.95 (s, 9 H), 0.75 (s, 9 H), 0.23 (s, 6 H), 0.22 (s, 3 H), 0.21 (s, 3 H), 0.01 (d, J = 4.0 Hz, 3 H); 13C NMR (100 MHz, CDCl3) δ 172.5, 166.0, 165.8, 165.2, 165.1, 159.3, 157.6, 157.1, 155.9, 149.5, 137.7, 133.4, 133.1, 133.0, 132.8, 130.1, 129.8 (2 C), 129.7, 129.6, 129.5, 128.9, 128.8, 128.4, 128.3, 128.1, 124.6, 119.8, 110.8, 109.6, 103.9, 99.9, 73.1, 72.4, 72.0, 69.6, 65.5, 63.0, 25.8, 25.6, 25.5, 18.7, 18.3, 18.2, 1.0, -3.9, -4.0, -4.4; HRMS (ESI) calcd for C67H78O15Si3Na [M+Na]+ 1229.4541, found 1229.4542.

3,7,4'-Tri-O-tert-butyldimethylsilyl-5-O-(2''''',4''''',6''''-tetra-O-benzoyl-β-D-glucopyranosyl)-kaempferol (11)

Similar procedure as that used for the synthesis of 10 was adopted to give 11 (121 mg, 90%) as a white solid: [α]28D -0.1 (c 2.7, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.08 (d, J = 8.0 Hz, 2 H), 7.91-7.88 (m, 4 H), 7.84 (d, J = 8.8 Hz, 2 H), 7.62 (d, J =
8.0 Hz, 2 H), 7.56-7.19 (m, 15 H), 7.14 (t, \( J = 7.6 \) Hz, 2 H), 6.92 (d, \( J = 8.8 \) Hz, 2 H), 6.67 (d, \( J = 2.4 \) Hz, 1 H), 6.64 (d, \( J = 2.4 \) Hz, 1 H), 6.01-5.86 (m, 3 H), 5.69 (d, \( J = 7.2 \) Hz, 1 H), 3.93-3.89 (m, 15 H), 3.83 (d, \( J = 2.8 \) Hz, 2 H), 1.01 (s, 9 H), 0.98 (s, 9 H), 0.94 (s, 9 H), 0.75 (s, 9 H), 0.23 (s, 6 H), 0.19 (s, 3 H), 0.18 (s, 3 H), 0.07 (s, 3 H), -0.04 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.6, 166.0, 165.2, 164.9, 159.4, 157.6, 157.0, 156.4, 149.4, 137.7, 135.6, 135.4, 133.1, 133.0, 132.9, 132.7, 132.6, 130.2, 129.8 (2 C), 129.5, 129.4, 129.3, 129.1, 128.3, 128.2, 128.1, 127.6, 127.5, 124.6, 119.8, 110.8, 109.3, 103.5, 100.1, 75.2, 73.6, 72.0, 68.9, 62.2, 26.5, 25.8, 25.7, 25.5, 19.0, 18.7, 18.3, 18.2, -4.0 (2 C), -4.4 (3 C); HRMS (ESI) calcd for C\(_{76}\)H\(_{92}\)O\(_{14}\)Si\(_4\)Na [M+Na]\(^{+}\) 1363.5456, found 1363.5458.

3,7,4'-Tri-O-tert-butyldimethylsilyl-5-O-(2'',3'',4'',6''-tetra-O-benzoyl-β-D-galactopyranosyl)-kaempferol (12)

Similar procedure as that used for the synthesis of 10 was adopted to give 12 (120 mg, 99%) as a white solid: \([\alpha]^{28}_D\) 47.6 (c 1.6, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.14 (d, \( J = 7.2 \) Hz, 2 H), 8.06 (d, \( J = 7.2 \) Hz, 2 H), 7.94 (d, \( J = 7.6 \) Hz, 2 H), 7.84 (d, \( J = 7.2 \) Hz, 2 H), 7.82 (d, \( J = 8.8 \) Hz, 2 H), 7.65 (t, \( J = 7.2 \) Hz, 1 H), 7.54-7.24 (m, 11 H), 6.91 (d, \( J = 8.8 \) Hz, 2 H), 6.70 (d, \( J = 2.2 \) Hz, 1 H), 6.63 (d, \( J = 2.2 \) Hz, 1 H), 6.27 (dd, \( J = 8.0 \), 10.4 Hz, 1 H), 6.08 (d, \( J = 3.2 \) Hz, 1 H), 5.70 (dd, \( J = 3.8 \), 10.4 Hz, 1 H), 5.65 (d, \( J = 8.0 \) Hz, 1 H), 4.68-4.62 (m, 1 H), 4.44-4.38 (m, 2 H), 1.00 (s, 9 H), 0.98 (s, 3 H), 0.74 (s, 9 H), 0.26 (s, 6 H), 0.22 (s, 6 H), 0.07 (s, 3 H), -0.10 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.5, 165.9, 165.6, 165.3, 159.4, 157.6, 157.1, 156.4, 149.4, 137.7, 133.5, 133.2 (2 C), 132.8, 130.2, 130.1, 129.8, 129.7, 129.3, 129.1, 128.8, 128.6, 128.4 (2 C), 128.2, 128.1, 124.6, 119.8, 110.7, 109.6, 103.8, 100.6, 71.9, 71.6, 69.4, 68.0, 61.7, 25.8, 25.7, 25.6, 18.7, 18.3, 18.2, -3.9, -4.1, -4.3 (2 C), -4.4; HRMS (ESI) calcd for C\(_{67}\)H\(_{78}\)O\(_{15}\)Si\(_3\)Na [M+H]\(^{+}\) 1207.4721, found 1207.4726.

3,7,4'-Tri-O-tert-butyldimethylsilyl-5-O-(2'',3'',4''-tri-O-benzoyl-α-L-rhamnopyranosyl)-kaempferol (13)

Similar procedure as that used for the synthesis of 10 was adopted to give 13 (73 mg, 72%) as a white solid: \([\alpha]^{28}_D\) 17.9 (c 1.5, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.17 (d, \( J = 7.2 \) Hz, 2 H), 8.05 (d, \( J = 7.2 \) Hz, 2 H), 7.93 (d, \( J = 8.8 \) Hz, 2 H), 7.89 (d,
J = 7.2 Hz, 2 H), 7.63 (t, J = 7.2 Hz, 1 H), 7.54-7.50 (m, 3 H), 7.44-7.36 (m, 3 H), 7.29-7.25 (m, 2 H), 6.95 (d, J = 8.8 Hz, 2 H), 6.62 (d, J = 2.0 Hz, 1 H), 6.54 (d, J = 2.0 Hz, 1 H), 6.53 (dd, J = 3.4, 10.0 Hz, 1 H), 6.13-6.12 (m, 1 H), 5.89 (s, 1 H), 5.81 (t, J = 10.0 Hz, 1 H), 4.55-4.51 (m, 1 H), 1.33 (d, J = 6.4 Hz, 3 H), 1.01 (s, 9 H), 1.007 (s, 9 H), 0.36 (s, 3 H), 0.31 (s, 3 H), 0.294 (s, 3 H), 0.291 (s, 3 H), 0.24 (s, 6 H);

13C NMR (100 MHz, CDCl3) δ 172.7, 166.0, 165.5, 164.9, 159.7, 157.9, 157.1, 155.5, 149.1, 138.0, 133.4, 133.2, 132.8, 130.1, 130.0, 129.9, 129.7, 129.6, 129.5, 129.4, 128.6, 128.3, 128.2, 124.6, 119.8, 110.2, 105.3, 102.6, 96.1, 72.0, 70.7, 69.7, 68.2, 26.0, 25.7 (2 C), 25.6, 19.0, 18.3, 18.2, 17.6, -3.4 (2 C), -4.3, -4.4 (2 C).

HRMS (MALDI) calcd for C60H75O13Si3 [M+H]+ 1087.4783, found 1087.4510.

3,7,3’,4’-Tetra-O-tert-butyldimethylsilyl-5-O-(2”,3”,4”,6”-tetra-O-benzoyl-β-D-glucopyranosyl)-quercetin (14)

Similar procedure as that used for the synthesis of 10 was adopted to give 14 (125 mg, 93%) as a white solid: \([\alpha]^{28}_D \) 7.3 (c 1.7, CHCl3); \(^1\)H NMR (400 MHz, CDCl3) δ 8.08 (d, J = 7.2 Hz, 2 H), 7.92 (d, J = 6.5 Hz, 2 H), 7.88 (d, J = 7.2 Hz, 2 H), 7.52-7.41 (m, 5 H), 7.37-7.26 (m, 9 H), 6.88 (d, J = 8.4 Hz, 2 H), 6.62 (d, J = 2.2 Hz, 1 H), 6.56 (d, J = 2.2 Hz, 1 H), 6.04-5.93 (m, 2 H), 5.85 (t, J = 9.6 Hz, 1 H), 5.71 (d, J = 7.2 Hz, 1 H), 4.96 (dd, J = 3.2, 12.0 Hz, 1 H), 4.49 (dd, J = 4.8, 12.0 Hz, 1 H), 4.22-4.17 (m, 1 H), 1.0 (s, 9 H), 0.99 (s, 9 H), 0.94 (s, 9 H), 0.73 (s, 9 H), 0.223 (s, 3 H), 0.218 (s, 3 H), 0.21 (s, 3 H), 0.20 (s, 6 H), 0.198 (s, 3 H), -0.01 (s, 3 H), -0.02 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl3) δ 172.6, 166.0, 165.8, 165.2, 165.1, 159.3, 157.6, 155.9, 159.6, 148.6, 146.6, 137.6, 133.3, 133.1, 133.0, 132.8, 130.1, 129.8 (2 C), 129.7, 129.6, 129.5, 128.9, 128.8, 128.3, 128.2, 128.1, 124.7, 123.0, 121.4, 120.7, 110.9, 109.9, 103.8, 100.0, 73.1, 72.4, 72.0, 69.6, 62.9, 62.9, 25.9, 25.7, 25.5, 15.6, 18.5, 18.4, 18.2, -4.0, -4.1 (2 C), -4.2 (3 C), -4.4 (2 C); HRMS (ESI) calcd for C73H92O16Si4Na [M+Na]+ 1359.5355, found 1359.5361.

3,7,3’,4’-Tetra-O-tert-butyldimethylsilyl-5-O-(2”,3”,4”-tri-O-benzoyl-6-O-tert-butyldiphenylsilyl-β-D-glucopyranosyl)-quercetin (15)

Similar procedure as that used for the synthesis of 10 was adopted to give 15 (121 mg, 90%) as a white solid: \([\alpha]^{28}_D \) -0.1 (c 2.7, CHCl3); \(^1\)H NMR (400 MHz, CDCl3) δ
8.08 (d, J = 7.6 Hz, 2 H), 7.90 (d, J = 8.0 Hz, 4 H), 7.61 (d, J = 6.8 Hz, 2 H),
7.55-7.24 (m, 15 H), 7.20 (t, J = 7.2 Hz, 2 H), 7.15 (t, J = 7.6 Hz, 2 H), 6.89 (d, J =
8.4 Hz, 1 H), 6.67 (d, J = 2.1 Hz, 1 H), 6.60 (d, J = 2.1 Hz, 1 H), 5.99-5.92 (m, 2 H),
5.88 (t, J = 9.2 Hz, 1 H), 5.69 (d, J = 7.2 Hz, 1 H), 3.91 (m, 1 H), 3.82 (d, J = 2.5 Hz, 1 H),
1.00 (s, 9 H), 0.99 (s, 9 H), 0.97 (s, 9 H), 0.94 (s, 9 H), 0.74 (s, 9 H), 0.22 (s, 6 H), 0.20 (s, 6 H), 0.19 (s, 3 H), 0.188 (s, 3 H), 0.04 (s, 3 H), -0.05 (s, 3 H);

13C NMR (100 MHz, CDCl3) δ 172.6, 166.0, 165.2, 164.9, 159.4, 157.6, 156.4, 149.5, 148.6,
146.6, 137.7, 135.6, 135.4, 133.1, 133.0 (2 C), 132.7, 132.6, 130.2, 129.8 (3 C), 129.5,
129.4 (2 C), 129.1, 128.3, 128.2, 128.0, 127.6, 127.5, 124.8, 123.0, 121.4, 120.7,
110.9, 109.5, 103.5, 100.2, 75.2, 73.6, 72.1, 69.0, 62.2, 26.5, 25.9, 25.8, 25.5, 19.0,
18.7, 18.6, 18.4, 18.2, -4.1 (3 C), -4.2, -4.3, -4.4; HRMS (ESI) calcd for C76H92O14Si4Na [M+Na]⁺ 1363.5456, found 1363.5458.

3,7,3',4’-Tetra-O-tert-butyldimethylsilyl-5-O-(2”',3”',4”',6”'-tetra-O-benzoyl-β-D-galactopyranosyl)-quercetin (16)

Similar procedure as that used for the synthesis of 10 was adopted to give 16 (87 mg, 70%) as a white solid: [α]²⁸D 41.7 (c 1.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, J = 7.2 Hz, 2 H), 8.06 (d, J = 7.2 Hz, 2 H), 7.94 (d, J = 7.2 Hz, 7.84 (d, J =
7.2 Hz, 2 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.54-7.24 (m, 13 H), 6.88 (d, J = 8.4 Hz, 1 H),
6.70 (d, J = 2.2 Hz, 1 H), 6.58 (d, J = 2.2 Hz, 1 H), 6.25 (dd, J = 8.0 Hz, 1 H),
6.07 (d, J = 3.3 Hz, 1 H), 5.70 (dd, J = 3.4, 10.4 Hz, 1 H), 5.65 (d, J = 8.0 Hz, 1 H),
4.66-4.61 (m, 1 H), 4.44-4.37 (m, 1 H), 1.00 (s, 9 H), 0.998 (s, 9 H), 0.990 (s, 9 H),
0.98 (s, 9 H), 0.72 (s, 9 H), 0.26 (d, J = 1.8 Hz, 6 H), 0.22 (s, 6 H), 0.20 (s, 6 H), 0.03 (s, 3 H), -0.12 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 172.6, 165.9, 165.6, 165.3,
159.4, 157.6, 156.3, 149.6, 148.6, 146.6, 137.7, 133.5, 133.2 (2 C), 132.8, 130.1,
130.0, 129.8 (2 C), 129.7, 129.3, 129.2, 129.1, 128.8, 128.6, 128.5, 128.4 (2 C), 128.3
(2 C), 128.1, 126.3, 124.7, 123.0, 121.4, 120.7, 110.8, 109.3, 103.7, 100.6, 71.9, 71.6,
69.5, 68.0, 61.7, 25.9, 25.7, 25.6, 18.7, 18.6, 18.4, 18.3, -4.1, -4.2 (2 C), -4.3 (2 C);
HRMS (ESI) calcd for C73H92O16Si4 [M+H]⁺ 1338.5560, found 1338.5561.

3,7,3’,4’-Tetra-O-tert-butyldimethylsilyl-5-O-(2”’,3”’,4”’-tri-O-benzoyl-α-L-rhamnopyranosyl)-quercetin (17)
Similar procedure as that used for the synthesis of \textbf{10} was adopted to give \textbf{17} (120 mg, 99\%) as a white solid:  $\left[\alpha\right]_{D}^{28} 7.7$ (c 1.9, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J = 7.2$ Hz, 2 H), 8.04 (d, $J = 7.2$ Hz, 2 H), 7.88 (d, $J = 7.2$ Hz, 2 H), 7.64 (t, $J = 7.2$ Hz, 1 H), 7.56-7.49 (m, 4 H), 7.43-7.36 (m, 4 H), 7.28 (t, $J = 8.0$ Hz, 2 H), 6.92 (d, $J = 8.4$ Hz, 1 H), 6.58 (d, $J = 2.0$ Hz, 1 H), 6.54 (d, $J = 2.0$ Hz, 1 H), 6.52 (dd, $J = 3.4$, 10.0 Hz, 1 H), 6.12 (m, 1 H), 5.88 (bs, 1 H), 5.80 (t, $J = 6.0$ Hz, 1 H), 4.56-4.52 (m, 1 H), 1.02 (s, 9 H), 1.01 (s, 18 H), 0.83 (s, 9 H), 0.33 (s, 3 H), 0.29 (s, 6 H), 0.28 (s, 3 H), 0.24 (s, 6 H), 0.23 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.8, 166.0, 165.5, 164.9, 159.7, 157.9, 155.6, 149.2, 148.6, 146.6, 138.0, 133.4, 133.2, 132.8, 130.0 (2 C), 129.7, 129.6 (2 C), 129.4, 128.6, 128.3, 128.1, 124.8, 123.0, 121.3, 120.7, 110.2, 105.2, 96.1, 72.0, 70.7, 69.7, 68.2, 26.0, 25.9, 25.6, 19.0, 18.6, 18.5, 18.3, 17.6, -3.5, -3.6, -4.0 (2 C), -4.1, -4.2, -4.3, -4.4; HRMS (ESI) calcd for C$_{66}$H$_{89}$O$_{14}$Si$_4$Na $[M+Na]^+$ 1217.5324, found 1217.5314.

3,7,4'-Tri-O-benzyl-5-O-(2",3",4",6"-tetra-O-benzoyl-β-D-glucopyranosyl)-kaempferol (\textbf{18})

Similar procedure as that used for the synthesis of \textbf{10} was adopted to give \textbf{18} (108 mg, 87\%) as a white solid:  $\left[\alpha\right]_{D}^{28} 9.0$ (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J = 7.2$ Hz, 2 H), 7.98-7.89 (m, 6 H), 7.53-7.20 (m, 29 H), 6.99 (d, $J = 12.8$ Hz, 2 H), 6.84 (d, $J = 2.3$ Hz, 1 H), 6.64 (d, $J = 2.3$ Hz, 1 H), 6.07 (t, $J = 9.2$ Hz, 1 H), 6.00 (dd, $J = 7.2$, 9.2 Hz, 1 H), 5.86 (t, $J = 9.6$ Hz, 1 H), 5.70 (d, $J = 7.2$ Hz, 1 H), 5.12 (s, 2 H), 5.06 (s, 2 H), 4.77 (d, $J = 10.8$ Hz, 1 H), 4.72 (dd, $J = 2.9$, 12.0 Hz, 1 H), 4.70 (d, $J = 10.8$ Hz, 1 H), 4.52 (dd, $J = 5.6$, 12.0 Hz, 1 H), 4.31-4.26 (m, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.6, 166.0, 165.8, 165.3, 165.2, 162.0, 160.2, 157.8, 156.6, 153.3, 139.2, 137.0, 136.4, 135.6, 133.4, 133.1, 132.9, 132.7, 130.1, 130.0, 129.8 (2 C), 129.6, 129.4, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2 (2 C), 128.1, 128.0 (2 C), 127.8, 127.4 (2 C), 123.4, 114.5, 111.0, 104.7, 100.2, 97.6, 73.3, 72.8, 72.6, 71.8, 70.4, 70.0, 69.5, 62.8. HRMS (MALDI) calcd for C$_{70}$H$_{55}$O$_{15}$ [M+H]$^+$ 1135.1688, found 1135.3535.

3,7,4'-Tri-O-benzyl-5-O-(2",3",4")-tri-O-benzoyl-6-O-tert-butyldiphenylsilyl-β-D-glucopyranosyl)-kaempferol (\textbf{19})
Similar procedure as that used for the synthesis of 10 was adopted to give 19 (87 mg, 69%) as a white solide: $[\alpha]_{D}^{28} 6.1$ (c 1.4, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J = 7.6$ Hz, 2 H), 7.93 (dd, $J = 8.0, 8.4$ Hz, 6 H), 7.65 (d, $J = 7.2$ Hz, 2 H), 7.56 (d, $J = 7.2$ Hz, 3 H), 7.46-7.13 (m, 29 H), 6.99 (d, $J = 8.9$ Hz, 2 H), 6.92 (d, $J = 1.8$ Hz, 1 H), 6.71 (d, $J = 1.8$ Hz, 1 H), 6.02-5.95 (m, 2 H), 5.81 (t, $J = 9.6$ Hz, 1 H), 5.65 (d, $J = 6.8$ Hz, 1 H), 5.12 (s, 2 H), 5.02 (s, 2 H), 4.74 (AB, 2 H), 3.98 (m, 1 H), 3.89-3.82 (m, 2 H), 0.97 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.6, 165.9, 165.4, 164.9, 162.2, 160.2, 158.0, 157.1, 153.2, 139.3, 137.1, 136.5, 135.6, 135.5, 135.4, 133.2, 133.0, 132.9, 132.8, 132.6, 130.1, 130.0, 129.9, 129.8, 129.5, 129.2, 129.1, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0 (2 C), 127.8, 127.6 (2 C), 127.4, 123.5, 114.5, 111.2, 105.3, 100.7, 97.2, 75.5, 73.3, 71.9, 70.4, 70.0, 69.1, 62.5, 26.5, 19.0; HRMS (ESI) calcd for C$_{79}$H$_{68}$O$_{14}$SiNa [M+Na]$^+$ 1291.4271, found 1291.4280.

3,7,4'-Tri-O-benzyl-5-O-(2'',3'',4'',6''-tetra-O-benzoyl-β-D-galactopyranosyl)-kaempferol (20)

Similar procedure as that used for the synthesis of 10 was adopted to give 20 (123 mg, 99%) as a white solide: $[\alpha]_{D}^{28} 70.8$ (c 1.8, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 7.2$ Hz, 2 H), 8.05 (d, $J = 7.2$ Hz, 2 H), 8.00 (d, $J = 7.2$ Hz, 2 H), 7.91 (d, $J = 8.8$ Hz, 2 H), 7.86 (d, $J = 7.2$ Hz, 2 H), 7.64 (t, $J = 7.4$ Hz, 1 H), 7.51-7.14 (m, 22 H), 6.98 (d, $J = 9.0$ Hz, 2 H), 6.95 (d, $J = 2.3$ Hz, 1 H), 6.68 (d, $J = 2.3$ Hz, 1 H), 6.34 (dd, $J = 8.0, 10.4$ Hz, 1 H), 6.09 (d, $J = 2.9$ Hz, 1 H), 5.74 (dd, $J = 3.4, 10.4$ Hz, 1 H), 5.60 (d, $J = 8.0$ Hz, 1 H), 5.11 (s, 2 H), 5.09 (s, 2 H), 4.71 (dd, $J = 4.2, 11.2$ Hz, 1 H), 4.62 (AB, 2 H), 4.52-4.45 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.6, 166.0, 165.6, 165.4, 162.1, 160.1, 157.9, 157.3, 153.2, 139.3, 137.0, 136.4, 135.6, 133.6, 133.2, 133.1, 132.6, 130.0 (2 C), 129.9, 129.8, 129.7, 129.3, 128.9, 128.7 (2 C), 128.6, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 123.4, 114.5, 111.0, 104.6, 101.3, 97.3, 73.2, 71.9, 70.4, 70.0, 69.2, 68.1, 62.4; HRMS (ESI) calcd for C$_{70}$H$_{64}$O$_{15}$ [M+H]$^+$ 1135.3535, found 1135.3527.

3,7,4'-Tri-O-benzyl-2''',3''',4'''-tri-O-benzoyl-α-L-rhamnopyranosyl)-kaempferol (21)

Similar procedure as that used for the synthesis of 10 was adopted to give 21 (100 mg,
99%) as a white solid: \([\alpha]^D_{22.3} 22.3 (c 0.6, \text{CHCl}_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.17 (d, \(J = 7.6\) Hz, 2 H), 8.05 (d, \(J = 7.6\) Hz, 2 H), 8.00 (d, \(J = 8.4\) Hz, 2 H), 7.89 (d, \(J = 7.6\) Hz, 2 H), 7.64 (t, \(J = 7.2\) Hz, 1 H), 7.53-7.26 (m, 23 H), 7.03 (d, \(J = 8.4\) Hz, 2 H), 6.80 (s, 1 H), 6.72 (s, 1 H), 6.43 (dd, \(J = 3.4, 10.4\) Hz, 1 H), 6.14 (s, 1 H), 5.92 (s, 1 H), 5.84 (t, \(J = 10.0\) Hz, 1 H), 5.22-5.10 (m, 6 H), 4.61-4.58 (m, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 173.2, 166.0, 165.4, 165.2, 162.4, 160.2, 158.4, 156.2, 153.7, 139.6, 137.0, 136.5, 135.7, 133.4, 133.2, 132.9, 130.2, 030.0, 129.9, 129.7, 129.5, 129.4, 129.3, 129.1, 128.7, 128.6 (2 C), 128.4, 128.2, 128.1, 127.9, 127.5 (2 C), 123.5, 114.6, 110.7, 101.4, 96.6, 96.5, 74.0, 71.9, 70.7, 70.5, 70.0, 69.9, 68.4; HRMS (ESI) calcd for C\(_{63}\)H\(_{50}\)O\(_{13}\)Na \([M+Na]^+\) 1037.3144, found 1037.3140.

3,7,4'-Tri-O-hexanoyl-5-O-(2'''',3'''',4'''',6''''-tetra-O-benzoyl-\(\beta\)-D-glucopyranosyl)-kaempferol (22)

Similar procedure as that used for the synthesis of 10 was adopted to give 22 (115 mg, 99%) as a white solid: \([\alpha]^D_{11} 11 (c 1.3, \text{CHCl}_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01-7.90 (m, 8 H), 7.80 (d, \(J = 8.8\) Hz, 2 H), 7.54-7.43 (m, 4 H), 7.40-7.30 (m, 8 H), 7.21 (d, \(J = 8.8\) Hz, 2 H), 7.08 (d, \(J = 2.1\) Hz, 1 H), 6.96 (d, \(J = 2.1\) Hz, 1 H); 6.03 (t, \(J = 9.2\) Hz, 1 H), 5.94 (dd, \(J = 7.2, 8.8\) Hz, 1 H), 5.82 (t, \(J = 9.2\) Hz, 1 H), 5.64 (d, \(J = 7.2\) Hz, 1 H), 4.73 (dd, \(J = 3.2, 12.0\) Hz, 1 H), 4.50 (dd, \(J = 5.6, 12.4\) Hz, 1 H), 4.33 (m, 1 H), 2.60 (t, \(J = 7.6\) Hz, 2 H), 2.46-2.41 (m, 4 H), 1.79-1.60 (m, 6 H), 1.43-1.28 (m, 12 H), 0.95-0.88 (m, 9 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.7, 170.9, 170.4, 169.4, 166.0, 165.8, 165.3, 165.1, 157.1, 156.5, 154.2, 153.3, 152.7, 134.1, 133.4, 133.2, 133.0, 132.7, 130.0, 129.9, 129.8, 129.7, 129.5, 129.4, 128.9, 128.8, 128.4, 128.3 (2 C), 128.0, 127.1, 121.8, 113.8, 109.5, 106.5, 100.0, 72.7, 71.7, 69.4, 62.9, 34.3, 34.2, 33.7, 31.2, 31.1, 24.5, 24.3, 24.2, 22.3, 13.9; HRMS (ESI) calcd for C\(_{67}\)H\(_{66}\)O\(_{18}\)Na \([M+Na]^+\) 1181.4141, found 1181.4148.

3,7,4'-Tri-O-hexanoyl-5-O-(2''',3''',4''''-tri-O-benzoyl-6-O-tert-butyldiphenylsilyl-\(\beta\)-D-glucopyranosyl)-kaempferol (23)

Similar procedure as that used for the synthesis of 10 was adopted to give 23 (127 mg, 98%) as a white solid: \([\alpha]^D_{14.7} 14.7 (c 1.36, \text{CHCl}_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, \(J = 7.2\) Hz, 2 H), 7.90-7.86 (m, 4 H), 7.81 (d, \(J = 8.8\) Hz, 2 H), 7.57-7.27 (m,
14 H), 7.25-7.18 (m, 5 H), 7.16 (d, J = 2.2 Hz, 1 H), 7.03 (d, J = 2.2 Hz, 1 H),
5.95-5.93 (m, 2 H), 5.78-5.73 (m, 1 H), 5.61 (d, J = 7.2 Hz, 1 H), 4.05-4.01 (m, 1 H),
6.90-3.82 (m, 2 H), 2.60 (t, J = 3.4 Hz, 2 H), 2.46-2.40 (m, 4 H), 1.81-1.74 (m, 2 H),
1.70-1.60 (m, 4 H), 1.42-1.26 (m, 12 H), 0.96-0.86 (m, 9 H); 13C NMR (100 MHz, CDCl3) δ 171.7, 170.9, 170.4, 169.4, 165.9, 165.4, 164.9, 157.2, 157.1, 154.2, 153.2,
152.7, 135.5, 135.4, 134.1, 133.2, 133.0, 132.8, 132.5, 130.0, 129.9 (2 C), 129.8,
129.6, 129.4, 129.2, 129.0, 128.3, 128.2, 128.0, 127.6, 127.1, 121.8, 113.8, 109.3,
106.4, 100.5, 73.1, 71.7, 68.9, 62.5, 34.3 (2 C), 33.7, 31.2 (2 C), 31.1, 26.6, 24.5, 24.2,
22.2 (2 C), 19.1, 13.9, 13.8 (2 C); HRMS (MALDI) calcd for C76H80O17Si3Na [M+Na]+ 1315.5057.

3,7,4’-Tri-O-hexanoyl-5-O-(2”,3”,4”,6”-tetra-O-benzoyl-β-D-galactopyranosyl)-kaempferol (24)

Similar procedure as that used for the synthesis of 10 was adopted to give 24 (115 mg, 99%) as a white solide: [α]D 28 66.3 (c 2.4, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.13 (d, J = 7.2 Hz, 2 H), 8.01 (dd, J = 7.2, 8.8 Hz, 4 H), 7.85 (d, J = 7.2 Hz, 2 H), 7.79 (d, J = 8.8 Hz, 2 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.58-7.25 (m, 11 H), 7.20 (d, J = 8.8 Hz, 2 H), 7.12 (d, J = 2.1 Hz, 1 H), 7.03 (d, J = 2.0 Hz, 1 H), 6.27 (dd, J = 8.0, 10.3 Hz, 1 H), 6.07 (d, J = 3.2 Hz, 1 H), 4.68 (dd, J = 6.8, 11.1 Hz, 1 H), 4.55-4.47 (m, 2 H), 2.59 (t, J = 7.6 Hz, 2 H), 2.44-2.37 (m, 4 H), 1.78-1.57 (m, 6 H), 1.40-1.28 (m, 12 H), 0.95-0.88 (m, 9 H); 13C NMR (100 MHz, CDCl3) δ 171.7, 171.0, 170.4, 169.3, 166.0, 165.6, 165.5, 157.1 (2 C), 154.2, 153.3, 152.7, 134.1, 133.6, 133.2 (2 C), 132.6, 130.1, 130.0, 129.8 (2 C), 129.4, 128.9, 128.7, 128.6, 128.4, 128.3, 128.0, 127.0, 121.8, 113.7, 109.1, 106.6, 101.0, 71.9, 71.6, 69.1, 68.0, 62.2, 34.3, 34.2, 33.6, 31.2 (2 C), 31.1, 24.5, 24.2 (2 C), 22.2, 13.4; HRMS (ESI) calcd for C67H66O18Na [M+Na]+ 1181.4146, found 1181.4140.

3,7,4’-Tri-O-hexanoyl-2”,”3”,4”-tri-O-benzoyl-α-L-rhamnopyranosyl)-kaempferol 1 (25)

Similar procedure as that used for the synthesis of 10 was adopted to give 25 (85 mg, 82%) as a white solide: [α]D 28 15.9 (c 0.9, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.15 (d, J = 7.2 Hz, 2 H), 8.04 (d, J = 7.6 Hz, 2 H), 7.90 (t, J = 5.8, 8.4 Hz, 4 H), 7.64
(t, J = 7.4 Hz, 1 H), 7.54-7.49 (m, 3 H), 7.44-7.37 (m, 3 H), 7.29-7.24 (m, 4 H), 7.10 (d, J = 1.8 Hz, 1 H), 6.94 (d, J = 1.8 Hz, 1 H), 6.36 (dd, J = 3.3, 10.1 Hz, 1 H), 6.05 (s, 1 H), 5.89 (s, 1 H), 5.81 (t, J = 10.0 Hz, 1 H), 4.44-4.38 (m, 1 H), 2.68 (t, J = 7.2 Hz, 2 H), 2.62 (td, J = 3.3, 7.6 Hz, 4 H), 1.80 (dd, J = 7.2, 14.4 Hz, 6 H), 1.35 (d, J = 6.2 Hz, 3 H), 0.96 (dd, J = 6.8, 13.0 Hz, 6 H), 0.86 (t, J = 6.8 Hz, 3 H);

13C NMR (100 MHz, CDCl3) δ 171.7, 171.0 (2 C), 165.9, 165.4, 165.0, 157.6, 156.1, 154.6, 153.6, 153.2, 134.2, 133.5, 133.2, 132.8, 129.9, 129.7, 129.5, 129.4, 129.3 (2 C), 128.6, 128.3, 128.2, 127.1, 121.9, 113.1, 105.7, 105.4, 96.3, 71.6, 70.6, 69.7, 68.3, 34.3, 33.9, 31.2 (2 C), 31.1, 24.5, 24.4 (2 C), 22.3, 22.2, 17.6, 13.8 (3 C); HRMS (ESI) calcd for C60H62O16Na [M+Na]+ 1061.3934, found 1061.3930.

3,7,4'-Tri-O-hexanoyl-5-O-(2'',3'',4''-tri-O-benzoyl-β-D-glucopyranosyl)-kaempferol (26)

To a solution of 23 (70 mg, 0.06 mmol) in THF (2 mL) was added HOAc (0.02 mL, 0.36 mmol) and TBAF (1 mmol/ml in THF, 0.18 mL, 0.18 mmol) at 0 °C. Then the reaction mixture was warmed to room temperature and stirred overnight. Ethyl acetate (20 mL) was added and the solution was washed with water, saturated NaHCO3 and brine successively, and then dried over Na2SO4. Filtration and concentration under reduced pressure to afford the crude product which was further purified by silica gel chromatography (eluent system: PE : EA = 4 : 1) to afford 26 (32 mg, 57%) as a white solid: [α]28D -9.6 (c 1.1, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.01 (d, J = 7.2 Hz, 2 H), 7.99 (d, J = 7.6 Hz, 2 H), 7.90 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 8.4 Hz, 2 H), 7.55-7.28 (m, 9 H), 7.22 (d, J = 8.4 Hz, 2 H), 7.08 (d, J = 2.1 Hz, 1 H), 7.03 (d, J = 2.1 Hz, 1 H), 6.05 (t, J = 9.2 Hz, 1 H), 5.95 (dd, J = 7.2, 9.6 Hz, 1 H), 5.62 (d, J = 7.6 Hz, 1 H), 5.62 (dd, J = 7.6, 9.6 Hz, 1 H), 3.98-3.95 (m, 1 H), 3.88-3.80 (m, 2 H), 2.60 (t, J = 7.6 Hz, 4 H), 2.48 (t, J = 7.6 Hz, 2 H), 1.79-1.72 (m, 4 H), 1.69-1.62 (m, 2 H), 1.40-1.29 (m, 12 H), 0.95-0.89 (m, 9 H); 13C NMR (100 MHz, CDCl3) δ 171.7, 171.2, 170.5, 169.6, 165.8, 165.7, 165.2, 157.2, 156.3, 154.1, 153.4, 152.8, 134.1, 133.5, 133.2, 132.7, 129.9 (2 C), 129.8, 129.7, 129.4, 128.9, 128.7, 128.4, 128.2, 128.0, 127.0, 121.8, 76.0, 72.5, 71.7, 69.8, 61.7, 34.3 (2 C), 33.7, 31.2, 31.1, 24.4, 24.3, 24.2, 22.2, 13.9, 13.8. HRMS (MALDI) calcd for C60H60O17 [M+H]+ 1055.4040, found
3,7,4’-Tri-O-hexanoyl-5-O-[2”’,3”’,4”’-tri-O-benzoyl-6”’-O-(2”’,3”’,4”’-tri-O-benzyll-α-L-rhamnopyranonyl)-β-D-glucopyranosyl]-kaempferol (27)

Similar procedure as that used for the synthesis of 10 was adopted to give 27 (36 mg, 82%) as a white solid: [α]D 28 33.0 (c 0.57, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.03 (dd, J = 7.2, 7.6 Hz, 6 H), 7.95 (t, J = 8.0 Hz, 4 H), 7.78 (d, J = 8.8 Hz, 4 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.52-7.30 (m, 15 H), 7.23-7.17 (m, 4 H), 7.08 (d, J = 1.8 Hz, 1 H), 7.05 (s, 1 H), 6.05 (t, J = 9.2 Hz, 1 H), 5.94 (dd, J = 7.2, 9.2 Hz, 1 H), 5.72-5.54 (m, 5 H), 4.98 (s, 1 H), 4.30 (t, J = 6.8 Hz, 1 H), 4.10-3.90 (m, 3 H), 2.60 (t, J = 7.6 Hz, 2 H), 2.46-2.39 (m, 4 H), 1.81-1.73 (m, 2 H), 1.67-1.53 (m, 4 H), 1.43-1.18 (m, 15 H), 0.96-0.88 (m, 6 H), 0.82 (t, J = 7.2 Hz, 3 H); 13C NMR (100 MHz, CDCl3) δ 171.8, 171.1, 170.4, 169.5, 165.7, 165.3, 165.1 (2 C), 157.2, 156.4, 154.3, 153.3, 152.7, 134.1, 133.5, 133.3, 133.2, 133.1, 132.9, 132.7, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.3, 128.9, 128.8, 128.5 (2 C), 128.4, 128.3, 128.2, 128.0, 127.2, 121.8, 113.8, 109.8, 106.8, 100.2, 98.1, 74.4, 72.5, 71.7 (2 C), 70.4, 69.9, 69.7, 67.2, 66.9, 34.4, 34.1, 33.7, 31.2, 31.0, 29.7, 24.5, 24.2 (2 C), 22.3, 22.2, 17.5, 13.9 (2 C), 13.8. HRMS (MALDI) calcd for C87H85O24 [M+H]+ 1513.5419, found 1513.5425.

3,7,4’-Tri-O-benzyl-5-O-(2”’,3”’,4”’-tri-O-benzoyl)-β-D-glucopyranosyl]-kaempferol (29)

Similar procedure as that used for the synthesis of 26 was adopted to give 29 (130 mg, 99%) as a white solid: [α]D 28 4.7 (c 1.2, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.06 (t, J = 7.6 Hz, 4 H), 7.96 (dd, J = 6.4, 8.0 Hz, 4 H), 7.60 (t, J = 7.2 Hz, 1 H), 7.46-7.24 (m, 23 H), 7.01 (d, J = 8.4 Hz, 2 H), 6.87 (s, 1 H), 6.68 (d, J = 10.4 Hz, 1 H), 6.09-6.02 (m, 2 H), 5.76-5.69 (m, 2 H), 5.13 (s, 4 H), 4.74 (s, 2 H), 4.03 (s, 1 H), 3.94 (s, 2 H); 13C NMR (100 MHz, CDCl3) δ 172.7, 165.9, 165.6, 165.0, 162.3, 160.0, 157.6, 157.4, 152.9, 139.2, 136.9, 136.4, 135.8, 133.3, 133.0, 132.6, 129.9, 129.8 (2 C), 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.3, 123.2, 114.3, 110.3, 102.1, 100.5, 97.0, 76.7, 76.0, 73.3, 73.0, 71.6, 70.4, 69.8, 69.7, 61.5; HRMS (ESI) calcd for C63H51O14Na [M+Na]+ 1053.3093, found 1053.3104.
-α-L-rhamnopyranonyl)-β-D-glucopyranosyl]-kaempferol (30)

Similar procedure as that used for the synthesis of 10 was adopted to give 27 (106 mg, 67%) as a white solid: [α]$_D^{28} = 21.5$ (c 1.2, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.1 (d, $J = 7.2$ Hz, 2 H), 8.03 (dd, $J = 7.6$, 8.4 Hz, 4 H), 7.94 (d, $J = 7.6$ Hz, 4 H), 7.87 (d, $J = 8.8$ Hz, 2 H), 7.87 (d, $J = 7.2$ Hz, 2 H), 7.57-7.18 (m, 33 H), 6.97 (d, $J = 8.8$ Hz, 2 H), 6.91 (d, $J = 2.0$ Hz, 1 H), 6.49 (d, $J = 2.0$ Hz, 1 H), 6.09 (t, $J = 9.2$ Hz, 1 H), 6.00 (dd, $J = 7.2$, 9.2 Hz, 1 H), 5.75-5.54 (m, 5 H), 5.11 (s, 2 H), 5.10 (AB, 2 H), 4.99 (s, 1 H), 4.80 (AB, 2 H), 4.31-4.25 (m, 1 H), 4.11-4.02 (m, 1 H), 4.02-3.91 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.7, 165.7, 165.3, 165.1, 162.1, 160.1, 157.8, 156.4, 153.3, 139.2, 137.0, 136.4, 135.8, 133.4, 133.2 (2 C), 133.1, 132.8, 132.7, 130.1, 130.0, 129.9 (2 C), 129.8, 129.7, 129.6, 129.4, 129.2, 128.9, 128.8, 128.7, 128.6 (2 C), 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 127.3, 123.4, 114.4, 111.1, 105.2, 100.2, 98.0, 97.7, 74.4, 73.3, 72.6, 71.8, 71.7, 70.4, 69.9, 69.8 (2 C), 66.9 (2 C); HRMS (ESI) calcd for C$_{90}$H$_{73}$O$_{21}$ [M+H]$^+$ 1489.4639, found 1489.4647.

3,7,4′-Tri-O-acetyl-5-O-[2′′,3′′,4′′-tri-O-acetyl-6′′-O-(2′′′,3′′′,4′′′-tri-O-acetyl-α-L-rhamnopyranonyl)-β-D-glucopyranosyl]-kaempferol (28)

To a solution of 30 in MeOH (5 mL) and THF (5 mL) was added NaOMe (in MeOH solution). The reaction mixture was stirred at room temperature for 6 hours, then $^4$H resin was added to quench the reaction. Filtration and concentration to get the crude deacylated intermediate which was not purified for the next hydrogenolysis step.

The above obtained intermediate was dissolved in ethyl acetate (2 mL) and ethanol (2 mL), to which 10% Pd/C was added. The reaction flask was evacuate and then refilled with H$_2$. After repeating this process three times, the mixture was stirred at room temperature for another 24 hours. Filtration and concentration yield the crude 28a which was put directly to next acetylation step.

To a solution of 28a in dry pyridine (1 mL) was added Ac$_2$O (1 mL) dropwise at 0 °C. Then the addition was completed, the temperature was raised to room temperature.

The stirring was continued for another 36 hours, at which time TLC showed that the starting material disappeared and one new compound was formed. Ethyl acetate (30 mL) was added to dilute the reaction mixture, the solution was washed with 1 N HCl,
saturated NaHCO$_3$, and brine successively and then dried over Na$_2$SO$_4$. Filtration and concentration under reduced pressure to give the crude product which was further purified by silica gel chromatography (eluent system: PE : EA = 2 : 1) to afford 30 (20 mg, 99%) as a white solid: $[\alpha]^{28}_{D}$ -129.0 (c 0.25, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.8$ Hz, 2 H), 7.25 (d, $J = 8.8$ Hz, 2 H), 7.15 (d, $J = 2.0$ Hz, 1 H), 6.92 (d, $J = 2.0$ Hz, 1 H), 5.43 (dd, $J = 7.8$, 9.4 Hz, 1 H), 5.32 (dd, $J = 9.3$, 11.0 Hz, 1 H), 5.24-5.21 (m, 2 H), 5.15 (d, $J = 7.7$ Hz, 1 H), 5.13 (t, $J = 10.0$ Hz, 1 H), 5.06 (t, $J = 9.8$ Hz, 1 H), 4.74 (s, 1 H), 3.93-3.89 (m, 1 H), 3.85 (dd, $J = 5.6$, 9.7 Hz, 1 H), 3.80 (d, $J = 11.4$ Hz, 1 H), 3.71 (dd, $J = 6.0$, 11.6 Hz, 1 H), 2.34 (s, 3 H), 2.33 (s, 3 H), 2.31 (s, 3 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 1.97 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.3, 170.0, 169.8 (2 C), 169.5, 169.4, 168.9, 168.2, 167.9, 157.4, 157.2, 154.4, 153.3, 152.7, 134.3, 129.5, 127.1, 122.0, 113.3, 107.8, 106.2, 100.5, 98.0, 77.2, 73.5, 72.4, 70.8, 70.5, 69.3, 69.1, 69.0, 66.6, 21.1, 20.8, 20.7, 20.6 (2 C), 17.3; HRMS (ESI) calcd for C$_{45}$H$_{49}$O$_{24}$ [M+H]$^+$ 973.2613, found 973.2626.

**Key correlations in compound 28:**

![Figure 1. Key HMBC and NOE correlations in 28](image-url)
Parameter | Value
--- | ---
Solvent | CDCl3
Spectrometer Frequency | 400.13
Nucleus | 1H
Parameter | Value
---|---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value (f2, f1)
--- | ---
1 Solvent | CDCl3
2 Experiment | 2D-HMBC
3 Spectrometer Frequency | (400.13, 100.61)
4 Nucleus | (1H, 13C)
Parameter | Value (f2, f1)
---|---
1 Solvent | CDCl3
2 Experiment | 2D-NOESY
3 Spectrometer Frequency | (400.13, 400.13)
4 Nucleus | (1H, 1H)

TBSO

OTBS

OH

O

TBS

2
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![Chemical Structure Diagram](image)
Parameter | Value
--- | ---
Solvent | CDCl$_3$
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value
---|---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | IH
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Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D-DEPT-135
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value (f2, f1)
--- | ---
1 Solvent | CDCl3
2 Experiment | 2D-COSY
3 Spectrometer Frequency | (400.13, 400.13)
4 Nucleus | (1H, 1H)
Parameter | Value (f2, f1)
--- | ---
1 Solvent | CDCl3
2 Experiment | 2D-HMBC
3 Spectrometer Frequency | (400.13, 100.61)
4 Nucleus | (1H, 13C)

{12.583, 98.519}
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | H

![Chemical Structure Image]

**Compound Structure**

![NMR Spectrum](Image)
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C

![Chemical Structure](image)
Solvent: CDCl₃
Experiment: 1D-DEPT-135
Spectrometer Frequency: 100.61 MHz
Nucleus: 13C
Parameter | Value (f2, f1)
--- | ---
1. Solvent | CDCl3
2. Experiment | 2D-COSY
3. Spectrometer Frequency | (400.13, 400.13)
4. Nucleus | (1H, 1H)
Parameter | Value (f2, f1)
--- | ---
1 Solvent | CDCl3
2 Experiment | 2D-HMBC
3 Spectrometer Frequency | (400.13, 100.61)
4 Nucleus | (1H, 13C)

Parameter Value (f2, f1)

1 Solvent | CDCl3
2 Experiment | 2D-HMBC
3 Spectrometer Frequency | (400.13, 100.61)
4 Nucleus | (1H, 13C)
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | 1H
Parameter | Value
---|---
Solvent | CDCl₃
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
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![Chemical Structure Image](image)
Parameter | Value (\(f_2, f_1\))
--- | ---
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2 Experiment | 2D-NOESY
3 Spectrometer Frequency | \(400.13, 400.13\)
4 Nucleus | \(\text{H}, \text{H}\)
Parameter | Value
--- | ---
Solvent | CDCl₃
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
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**Diagram:**

The diagram shows a molecular structure labeled as 12 with various atoms and groups labeled, such as TBSO, OBz, BzO, and others. The spectrum is labeled as 1D, and the solvent is CDCl3.
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | 1H
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C

13C NMR spectrum of compound 13.
Parameter | Value
---|---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | 1H

![NMR Spectrum](image)

**Compound 14**

- TBSO
- O
- OBz
- B2O
- OBz
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter: Solvent
Value: CDCl₃

Parameter: Experiment
Value: 1D

Parameter: Spectrometer Frequency
Value: 400.13 MHz

Parameter: Nucleus
Value: ¹H
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value
---|---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter  Value
Solvent   CDCl3
Experiment  1D
Spectrometer Frequency  400.13
Nucleus    1H
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
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![Chemical structure diagram](image)
Parameter | Value
--- | ---
Solvent | CDCl₃
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value
---|---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13 MHz
Nucleus | 1H
Parameter | Value
---|---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
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Parameter values for 1H NMR spectra:

- f1 (ppm):
  - 0.8852
  - 0.9549
  - 1.2558
  - 1.2805
  - 1.4326
  - 1.5972
  - 1.7882
  - 2.0487
  - 2.7972
  - 2.3972
  - 1.9105
  - 1.2588
  - 0.9582

Molecular structure and spectra for compound 22.
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![Chemical Structure](image)

![NMR Spectrum](image)
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Parameter | Value
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Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
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![Chemical Structure](image)
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C

![Chemical Structure Image]

![Chemical Structure Image]
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | H

![Chemical Structure Image]

**Compound 25**
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![NMR Spectrum](image)
Parameter | Value
--- | ---
Solvent | CDCl₃
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | 1H
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Parameter | Value
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Solvent | CDCl₃
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | 1H
Parameter | Value
---|---
Solvent | CDC13
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | 1H
Parameter | Value
--- | ---
Solvent | CDCl₃
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | ¹³C
Parameter | Value
---|---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 400.13
Nucleus | 1H
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D
Spectrometer Frequency | 100.61 MHz
Nucleus | 13C
Parameter | Value
--- | ---
Solvent | CDCl3
Experiment | 1D-DEPT-135
Spectrometer Frequency | 100.61
Nucleus | 13C
Parameter | Value (f2, f1)
---|---
1 Solvent | CDCl3
2 Experiment | 2D-HSQC
3 Spectrometer Frequency | (400.13, 100.61)
4 Nucleus | (1H, 13C)
Parameter | Value (f₂, f₁)
---|---
1 Solvent | CDCl₃
2 Experiment | 2D-HMBC
3 Spectrometer Frequency | (400.13, 100.61)
4 Nucleus | (¹H, ¹³C)
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (f2, f1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Solvent</td>
<td>CDCl3</td>
</tr>
<tr>
<td>2 Experiment</td>
<td>2D-NOESY</td>
</tr>
<tr>
<td>3 Spectrometer Frequency</td>
<td>(400.13, 400.13)</td>
</tr>
<tr>
<td>4 Nucleus</td>
<td>(1H, 1H)</td>
</tr>
</tbody>
</table>

![Chemical Structure](image)