De Novo Asymmetric Syntheses of SL0101 and Its Analogues via a Palladium-Catalyzed Glycosylation

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Supporting Information

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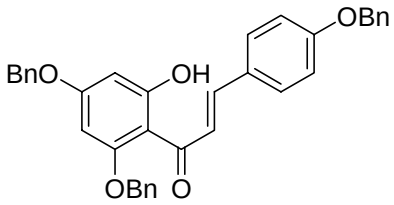
Section A: General Information:

General methods and materials: ^{1}H and ^{13}C spectra were recorded on Joel 270 and Varian 600 spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) or CD_3OD (δ 4.78 ppm) or acetone-d_6 (δ 2.05 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) or CD_3OD (δ 49.0 ppm) or acetone-d_6 (δ 29.92 ppm) for ^{13}C. Optical rotations were measured with a Jasco DIP-370 digital polarimeter in the solvent specified. Infrared (IR) spectra were obtained on a prospect MIDAC FT-IR spectrometer. Flash column chromatography was performed on ICN reagent 60 (60-200 mesh) silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates (Whatman K6F 60, F254) and visualized by quenching of fluorescence and by charring after treatment with panisaldehyde or phosphomolybdic acid or potassium permanganate stain. R_f values were obtained by elution in the stated solvent ratios (v/v). Ether, THF, methylene chloride and triethylamine were dried by passing through activated alumina (8 x 14 mesh) column with Argon gas pressure. Commercial reagents were used without purification unless otherwise noted. Air and/or moisture-sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven/flamed-dried glassware and standard syringe/septa techniques.

Section B: Experimental Procedures:

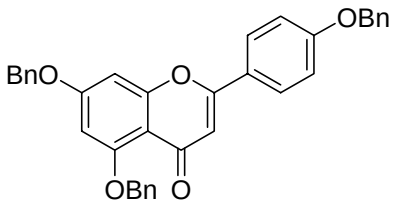
(*E*)-1-(2,4-bis(benzyloxy)-6-hydroxyphenyl)-3-(4-(benzyloxy)phenyl)prop-2-en-1-one (14)



To a solution of 4.0 g 4', 5, 7-trihydroxyflavanone **6** (14.7 mmol) in 50 mL acetone was added 5.3 mL BnBr (44.4 mmol) and 12.2 g K_2CO_3 (88.2 mmol). The reaction mixture was heated under reflux for 6 hours, then cooled down to room temperature. The mixture was concentrated under reduced pressure to give a residue which was then partitioned between 150 mL EtOAc and 80 mL H_2O. The water layer was extracted by EtOAc (100 mL × 3). The organic layer was pooled, then washed by saturated brine, dried over Na_2SO_4 and concentrated under reduced pressure to give a crude product. Recrystallization and further chromatograph for the mother liquid eluting with hexane-EtOAc (6:1) gave pure phenol **14** (6 g, 75%):[1] Yellow solid; R_f = 0.51 (3:1 (v/v) hexane/EtOAc); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.75 (dd, *J* = 15.6, 15.3 Hz, 2H), 7.53-7.30 (m, 15H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.22 (d, *J* = 2.5 Hz, 1H), 6.17 (d, *J* = 2.5 Hz, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 5.10 (s, 2H), 5.08 (s, 2H), 5.05 (s, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 192.6, 168.8, 165.1, 161.7, 160.3, 142.7, 136.5, 135.9, 135.5, 130.1, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.3, 128.1, 127.7, 127.4, 125.2, 115.0, 106.3, 95.0, 92.5, 71.4, 70.3, 70.0.

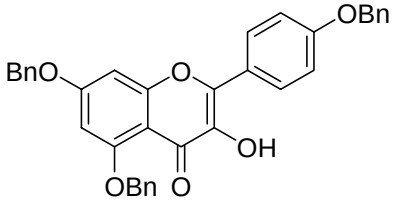
[1] These known compounds were characterized based on the comparison of ^{1}H and ^{13}C NMR data with the published ones: Maloney, D. J.; Hecht, S. M. *Org. Lett.* **2005**, *7*, 1097-1099.

5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-4H-chromen-4-one (15)



2.76 g phenol **14** (5.09 mmol) was dissolved in 6 mL dry DMSO, and a catalytic amount of I_2 (41 mg, 0.16 mmol) was added into the solution. The reaction mixture was heated to 110 °C and kept stirring at this temperature for 24 hours. Then it was cooled down to the room temperature. 10 mL saturated $NaHCO_3$ was added to quench the reaction. The water layer was extracted with EtOAc (30 mL × 3). The organic layer was pooled, then washed by 10 mL saturated brine, dried over Na_2SO_4, and concentrated the organic layer under reduced pressure to give a crude product. Chromatograph eluting with hexane-EtOAc (2:1) afforded desired flavone **15** (2.10 g, 76%): Yellow solid; R_f = 0.20 (2:1 (v/v) Hexane/EtOAc); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.81 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.46-7.28 (m, 13H), 7.07 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 1.8 Hz, 1H), 6.58 (s, 1H), 6.49 (d, J = 2.4 Hz, 1H), 5.23 (s, 2H), 5.14 (s, 2H), 5.11 (s, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 177.3, 162.8, 161.1, 160.6, 159.6, 136.4, 136.2, 135.7, 128.7, 128.6, 128.5, 128.4, 128.2, 127.6, 127.4, 126.5, 124.0, 118.0, 115.2, 109.7, 107.7, 98.3, 94.2, 70.7, 70.4, 70.1.

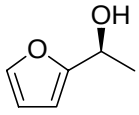
5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-hydroxy-4H-chromen-4-one (3)



150 mL solution of freshly generated DMDO in acetone (~ 0.1 M) was dried by 3 Å MS at -20 °C under the protection of argon, and into this solution was added a solution

of 2.3 g flavone **15** (4.26 mmol) in 20 mL dry CH_2Cl_2 at this temperature via a cannula. Then allow it warm up to 0 ^oC and keep stirring at 0 ^oC overnight. The solvent was evaporated under reduced pressure to give brown-yellowish solid, which was then redissolved in 20 mL CH_2Cl_2. Into this solution was added 2 mg $TsOH{\cdot}H_2O$ and it was then kept stirring at room temperature for 1 hour. The reaction mixture was concentrated under reduced pressure to a residue, which was then subjected to chromatograph. Elution with hexane-EtOAc (5:1) gave perbenzylated flavonol **3** (1.2 g, 50%) and elution with hexane-EtOAc (2:1) recovered 0.7 g starting material. Perbenzylated flavonol **3**: Yellow solid; R_f = 0.35 (3:1 (v/v) Hexane/EtOAc); ^1H NMR ($CDCl_3$, 600 MHz) δ 8.17 (d, J = 9.6 Hz, 2H), 7.61 (d, J = 7.2 Hz, 2H), 7.47-7.30 (m, 13H), 7.10 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 1.8 Hz, 1H), 6.49 (d, J = 1.8 Hz, 1H), 5.24 (s, 2H), 5.15 (s, 2H), 5.12 (s, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 171.8, 163.2, 159.8, 159.4, 158,7, 142.2, 137.6, 136.5, 136.2, 135.6, 128.9, 128.8, 128.6, 128.5, 128.1, 127.8, 127.6, 127.5, 126.7, 123.8, 114.9, 106.8, 97.6, 93.7, 70.7, 70.6, 70.0.

(*S*)-1-(furan-2-yl)ethanol (16)[2]

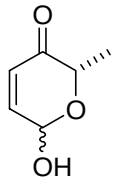


To a solution of 15 g acylfuran **5** (136.4 mmol) in 20 mL CH_2Cl_2 was added a prepared solution of formic acid/triethylamine (40 mL, 2:1(mol/mol)) and Noyori asymmetric transfer hydrogenation catalyst (*R*)-Ru(η^6-mesitylene)-(*S*, *S*)-TsDPEN (0.2 g, 0.25 mol%). The resulting solution was stirred at room temperature for 24 h. Then it was diluted with water (90 mL) and extracted with Et_2O (200 mL x 3). The

[2] Ohkuma, T.; Koizumi, M.; Yoshida, M.; Noyori R. *Org. Lett.,* **2000**, *2*, 1749-1751.

pooled organic layer was washed with 50 mL saturated $NaHCO_3$, 50 mL saturated brine, dried over Na_2SO_4 and then concentrated under reduced pressure to give a residue. Flush chromatograph on silica gel eluting with hexane-Et_2O (1:1) gave furan alcohol **16** (14 g, 92%):3 Colorless oil; R_f = 0.45 (7:3 (v/v) Hexane/EtOAc); $[\alpha]_D^{25}$ = +21^o (c = 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz $CDCl_3$) δ 7.30 (d, *J* = 1.8, 1H), 6.26 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.15 (d, *J* = 3.0, 1H), 4.78 (dq, *J* = 6.6, 6.6 Hz, 1H), 3.11 (s, 1H), 1.46 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 141.6, 109.9, 104.9, 63.3, 21.1.

(2*S*, 6*R*)-6-hydroxy-2-methyl-2H-pyran-3(6H)-one (17)

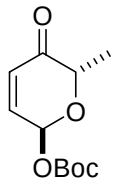


To a solution of 14 g furan alcohol **16** (125 mmol) in 416 mL THF-H_2O (3:1) was added 21 g $NaHCO_3$ (250 mmol), 17 g NaOAc•3H_2O (125 mmol), and 22.3 g NBS (125 mmol) at 0 ^{o}C. The reaction mixture was kept stirring at this temperature for 1 hour, then at 0 ^{o}C 200 mL saturated $NaHCO_3$ was added to quench the reaction. The reaction mixture was directly extracted with Et_2O (300 mL × 3) and the organic layer was pooled, washed by 100 mL saturated brine, dried over Na_2SO_4 and then concentrated reduced pressure to give a residue, which was rapidly subjected to flush chromatography on silica gel. Elution with hexane-EtOAc (1:1) afforded pyranone alcohol **17** (14.4 g, 90 %): White solid; R_f = 0.25 (7:3 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ = +44^o (c = 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) major isomer δ 6.82 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.96 (d, *J* = 10.2, 1H), 5.48 (d, *J* = 3.0 Hz, 1H), 3.99 (q, *J* = 7.2 Hz,

[3] These known compounds were characterized based on the comparison with authentic sample that our group prepared before: (a) Guo, H.; O'Doherty, G. A. *Org. Lett.* **2005**, *7*, 3921-3924. (b) Li, M.; Scott, J. G.; O'Doherty, G. A. *Tetrahedron Lett*. **2004**, *45*, 1005-1009.

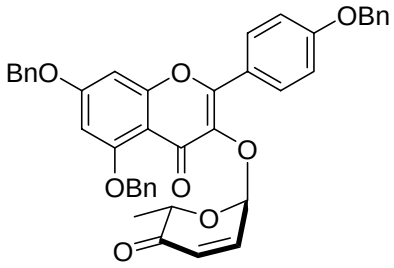
1H), 1.23 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) major isomer δ 197.6, 145.3, 126.6, 87.2, 74.8, 15.1.

(2*S*,6*S*)-*t*-butyl -5,6-dihydro-6-methyl-5-oxo-2H-pyran-2-yl carbonate (5)



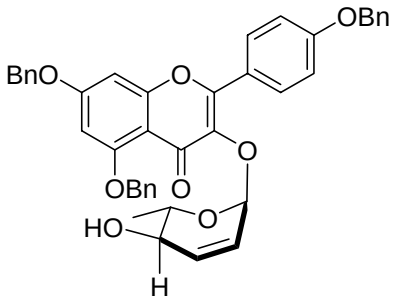
To a solution of 7.4 g pyranone alcohol **17** (57.8 mmol) in 80 mL CH_2Cl_2 was added 528 mg DMAP (4.33 mmol) at -78 ^oC. A pre-cooled solution of 25.2 g $(Boc)_2O$ (115.6 mmol) in 30 mL CH_2Cl_2 was dropwised into the reaction mixture via a cannula. The reaction mixture was stirred at -78 ^oC for 12 hours. The reaction was quenched by 100 mL saturated $NaHCO_3$ and then extracted with Et_2O (300 mL × 3). The organic layers were pooled, then washed by 70 mL saturated NaCl, dried over Na_2SO_4 and concentrated under reduced pressure to give a residue. Flush chromatograph on silica gel eluting with hexane-Et_2O (100:7) gave Boc protected α-pyranone **5** (7.8 g, 60%). Elution with hexane-Et_2O (10:1) gave β-isomer (2.5g, 19%). α-pyranone **5**: R_f = 0.60 (7:3 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ = +98^o (c = 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (dd, J = 10.2, 3.6 Hz, 1H), 6.22 (d, J = 3.6 Hz, 1H), 6.09 (d, J = 10.2 Hz, 1H), 4.53 (q, J = 6.6 Hz, 1H), 1.40 (s, 9H), 1.28 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150.8 MHz, CDCl3) δ 195.5, 151.7, 140.9, 128.2, 89.1, 83.3, 72.0, 27.5, 15.1;

3-((2*S*,6*S*)-5,6-dihydro-6-methyl-5-oxo-2H-pyran-2-yloxy)-5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-4H-chromen-4-one (2)



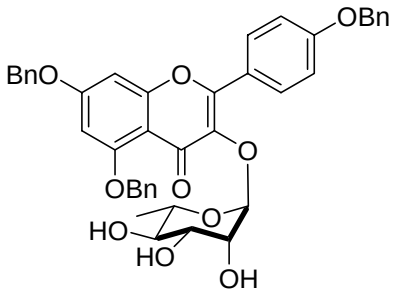
To a solution of 875 mg perbenzylated flavonol **3** (1.6 mmol) and 537 mg pyranone **4** (2.4 mmol) in 8 mL CH_2Cl_2 was added a solution of 41 mg $Pd_2(DBA)_3{\cdot}CHCl_3$ (0.04 mmol) and 41 mg PPh_3 (0.16 mmol) in 1 mL CH_2Cl_2 at 0 ^oC. The reaction mixture was stirred at 0 ^oC for 3 hours and then quenched by 15 mL saturated $NaHCO_3$, followed by extraction with Et_2O (25 mL × 3). The organic layer was pooled, then washed by 15 mL saturated NaCl, dried over Na_2SO_4 and concentrated under reduced pressure to give crude product. Chromatograph on silica gel, eluting with hexane-EtOAc (3:1) gave glycosylated pyranone **2** (888 mg, 85%): Yellow solid, mp: 75-77 ^oC; R_f = 0.50 (2:1 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -63° (*c* 0.93, $CHCl_3$); IR (thin film, cm^{-1}) 3063, 2921, 1699, 1636, 1607, 1574, 1509, 1454, 1375, 1355, 1300, 1252, 1198, 1178, 1162, 1103, 1013, 937. ^1H NMR ($CDCl_3$, 600 MHz) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.46-7.29 (m, 13H), 7.27 (dd, *J* = 10.2, 3.6 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.58 (d, *J* = 1.8 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 5.92 (d, *J* = 3.6 Hz, 1H), 5.27 (s, 2H), 5.15 (s, 2H), 5.08 (d, *J* = 12 Hz, 2H), 4.02 (q, *J* = 6.0 Hz, 1H), 0.93 (d, *J* = 6.6Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 196.7, 173.3, 163.0, 160.4, 159.8, 159.0, 154.9, 143.1, 137.6, 136.3, 136.2, 135.6, 130.4, 128.8, 128.7, 128.6, 128.4, 128.2, 127.7, 127.6, 127.4, 126.6, 123.2, 114.7, 109.9, 98.3, 94.3, 94.0, 71.5, 70.8, 70.5, 70.1, 14.6; HRMS (CI): calcd. for $[C_{42}H_{34}O_8 + Na]^+$: 689.2146, Found: 689.2153.

3-((2*S*,5*R*,6*S*)-5,6-dihydro-5-hydroxy-6-methyl-2H-pyran-2-yloxy)-5,7 bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-4H-chromen-4-one (7)



A solution of 87 mg pyranone **2** (0.13 mmol) in 3.5 mL CH_2Cl_2-MeOH (5:1) was cooled down to -78 ^oC, then 10 mg $NaBH_4$ (0.26 mmol) was added in. The reaction mixture was kept stirring at -78 ^oC for 3 hours. The reaction was then quenched by 2 mL saturated $NaHCO_3$, followed by extraction with Et_2O (10 mL × 3). The organic layer was washed by 2 mL saturated NaCl, dried over Na_2SO_4, and concentrated under reduced pressure to give crude product. Crude ^{1}H-NMR showed a dr > 20:1. Chromatograph on silica gel eluting with hexane-EtOAc (2:1) gave allylic alcohol **7** (63 mg, 73%): Amorphous yellow solid; R_f = 0.29 (1:1 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -83° (*c* 0.85, $CHCl_3$); IR (thin film, cm^{-1}) 3361, 2927, 1604, 1509, 1453, 1354, 1298, 1251, 1176, 1098, 1013, 916; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.45-7.27 (m, 13H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 6.20 (ddd, *J* = 10.2, 2.4, 2.4 Hz, 1H), 5.97 (d, *J* = 10.2 Hz, 1H), 5.60 (s, 1H), 5.26 (s, 2H), 5.15 (s, 2H), 5.07 (d, *J* = 12 Hz, 2H), 3.74 (dd, *J* = 7.2, 6.6 Hz, 1H), 3.31 (dq, *J* = 8.4, 6.0 Hz, 1H), 0.71 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 173.8, 162.8, 160.3, 159.9, 159.0, 154.8, 138.3, 136.5, 136.4, 135.7, 133.9, 130.7, 128.8, 128.7, 128.6, 128.5, 128.2, 127.8, 127.7, 127.5, 126.7, 126.6, 123.8, 114.6, 110.2, 98.3, 95.7, 94.0, 70.8, 70.5, 70.1, 69.6, 69.4, 17.0; HRMS (CI): calcd. for $[C_{42}H_{36}O_8 + Na]^+$: 691.2302, Found: 691.2296.

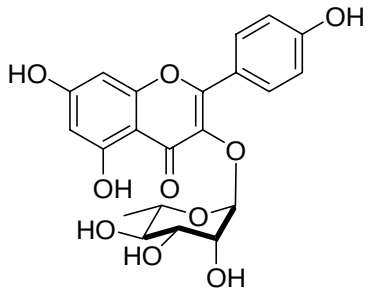
5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(*α*-L-rhamnopyranosyloxy)-4H-chromen-4-one (8)



A solution of 80 mg allylic alcohol **7** (0.12 mmol) in 2 mL acetone-*t*-BuOH (1:1) was cooled down to 0 ^{o}C. To the solution was added 0.5 mL NMO-H_2O (w/w 1:1), and then catalytic amount of crystalline OsO_4 was added into the mixture when stirring. The reaction mixture was kept stirring at 0 ^{o}C for 3 hours. The reaction mixture was then quenched by 0.5 mL saturated $Na_2S_2O_3$. After stirring for another 5 hours, all the staff was passed through a small pad of celite and silica gel, washed by EtOAc-MeOH (1:1) (10 mL × 3). The organic effluent was dried by Na_2SO_4, and concentrated under reduced pressure to give crude prodcut. Chromatograph on silica gel eluting with Et_2O-MeOH (20:1) gave triol **8** (80 mg, 96%): White solid, mp: 105-107 ^{o}C; R_f = 0.56 (10:1 (v/v) Et_2O/MeOH); $[\alpha]_D^{25}$ -112° (*c* 1.3, MeOH); IR (thin film, cm^{-1}) 3418 (broad), 2924, 1606, 1506, 1453, 1354, 1299, 1255, 1177, 1141, 1102, 1058, 998, 953; ^{1}H NMR (acetone-d_6, 600 MHz) δ 7.91 (d, *J* = 9.0 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 4H) 7.43-39 (m, 6H), 7.38-7.29 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 1.8 Hz, 1H), 6.67 (d, *J* = 2.4 Hz, 1H), 5.57 (d, *J* = 1.8 Hz, 1H), 5.29 (d, *J* = 13.2 Hz, 1H), 5.28 (d, *J* = 13.2 Hz, 1H), 5.24 (s, 2H), 5.23(s, 2H), 4.28 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.70 (dd, *J* = 9.0, 3.6 Hz, 1H), 3.33 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.21 (dq, *J* = 9.6, 6.0 Hz, 1H), 2.91 (brs, 1H), 0.87 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (acetone-d_6, 150 MHz) δ 173.5, 164.1, 161.5, 160.8, 159.8, 154.8, 138.4, 138.1, 138.0, 137.4, 131.4, 129.5, 129.4, 129.3, 129.1, 128.9, 128.7, 128.5, 128.4, 127.9, 124.4, 115.7,

110.6, 102.2, 98.9, 95.1, 73.2, 72.2, 71.5, 71.4, 71.3, 71.2, 70.8, 17.9; HRMS (ESI) calcd for $[C_{42}H_{38}O_{10} + H]^+$: 703.2543, Found: 703.2537.

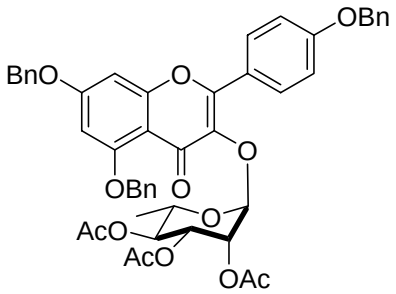
Kaempferol-3-*α*-L-rhamnoside (1b)



A solution of 50 mg triol **8** (0.07 mmol) in 2 mL THF-EtOH (1:1) was added 20 mg Pearlman's catalyst (Pd-C, 10%). The solution was degassed using vacuum at -90 °C and refilling with H_2. This procedure was repeated three times, then the bath was removed. The reaction was warmed up to room temperature and stirred under a H_2 atmosphere for 3 hours. The reaction mixture was loaded onto silica gel and elution with Et_2O-MeOH (20:1) gave kaempferol-3-α-L-rhamnoside (**1b**) (24mg, 80%):[4] Pale yellow solid, mp: 140-142 °C; R_f = 0.71 (5:1 (v/v) Et_2O/MeOH); $[\alpha]_D^{25}$ -96° (*c* 1.3, MeOH); IR (thin film, cm^{-1}) 3259 (broad), 2924, 2855, 1653, 1607, 1442, 1360, 1251, 1207, 1172, 1057, 996; ^1H NMR (CD_3OD, 600 MHz) δ 7.72 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.30 (d, *J* = 2.4 Hz, 1H), 6.13 (d, *J* = 1.8 Hz, 1H), 5.33 (d, *J* = 1.8 Hz, 1H), 4.18 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.67 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.30-3.27 (m, 4H), 0.88 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (CD_3OD, 150 MHz) δ 179.5, 163.2, 161.6, 159.1, 158.7, 136.1, 131.9, 122.7, 116.6, 105.5, 103.5, 100.4, 95.2, 73.2, 72.2, 72.2, 71.9, 17.6; HRMS (ESI) calcd for $[C_{21}H_{20}O_{10} + Na]^+$: 455.0954, Found: 455.0949.

[4] (a) Matthes, H. W. D.; Luu, B.; Ourisson, G. *Phytochemistry* **1980**, *19*, 2643-2650. (b) Kaouadji, M. *Phytochemistry* **1990**, *29*, 2295-2297. (c) Masuda, T.; Jitoe, A.; Kato, S.; Nakatani, N. *Phytochemistry* **1991**, *30*, 2391-2392. (d) Deng, J.-Z.; Marshall, R.; Jones, S. H.; Johnson, R. K.; Hecht, S. M. *J. Nat. Prod.* **2002**, *65*, 1930-1932.

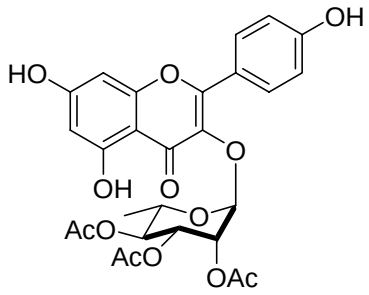
5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(2,3,4-*O*-triacetyl-*α*-L-rhamnopyranoyloxy)-4H-chromen-4-one (9)



A solution of 63 mg triol **8** (0.09 mmol) in 2.5 mL CH_2Cl_2 was cooled down to 0 ^oC, then sequentially 0.4 mL pyridine, catalytic amount of DMAP and 0.4 mL Ac_2O were added. The reaction mixture was stirred at 0 ^oC overnight. The reaction mixture was diluted by 15 mL Et_2O and then the reaction was quenched by 1.5 mL H_2O, the organic layer was washed by 2 mL saturated $NaHCO_3$, 2 mL saturated NaCl, dried over Na_2SO_4, and concentrated under reduced pressure to give a residue which was subjected to chromatograph on silica gel. Elution with hexane-EtOAc (2:1) afforded triacetate **9** (63 mg, 86%): White solid, mp: 90-92 ^oC; R_f = 0.58 (1:1 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -175° (*c* 1.3, $CHCl_3$); IR (thin film, cm^{-1}) 3035, 2982, 2938, 1746, 1632, 1605, 1574, 1509, 1498, 1486, 1453, 1432, 1368, 1298, 1247, 1217, 1174, 1136, 1101, 1044, 1019, 968; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.86 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.46-7.27 (m, 13H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 5.73 (d, *J* = 1.8 Hz, 1H), 5.72 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.32 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.26 (s, 2H), 5.15 (s, 2H), 5.08 (s, 2H), 4.92 (dd, *J* = 10.2, 9.6 Hz, 1H), 3.37 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.11 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 0.85 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 172.9, 169.9, 169.8, 169.5, 162.9, 160.6, 159.9, 158.8, 154.2, 136.5, 136.4, 136.3, 135.6, 130.4, 128.8, 128.7, 128.6, 128.4, 128.2, 127.7, 127.5, 127.4, 126.6, 123.1, 114.9, 110.1, 98.4, 97.9,

94.0, 70.8, 70.7, 70.5, 70.2, 69.3, 69.1, 68.1, 20.9, 20.8, 20.7, 17.1; HRMS (ESI) calcd for $[C_{48}H_{44}O_{13} + Na]^+$: 851.2679, Found: 851.2678.

Kaempferol-3-*α*-L-3'',4'',5''-*O*-triacetylrhamnoside (1c)

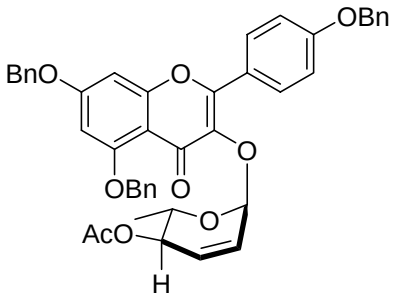


To a solution of 60 mg triacetate **9** (0.07 mmol) in 3 mL THF-EtOH (1:1) was added 30 mg Pearlman's catalyst (Pd-C, 10%). The reaction mixture was degassed using vacuum at -90 ^oC and refilling with H_2. This procedure was repeated three times, then the bath was removed and the reaction was warmed up to room temperature. The reaction mixture was stirred under a H_2 atmosphere for 3 hours. The reaction mixture was loaded onto silica gel and elution with hexane-EtOAc (1:1) gave kaempferol-3-α-L-3'',4'',5''-*O*-triacetylrhamnoside (**1c**) (35 mg, 86%):[5] Yellow solid, mp: 152-154 ^oC; R_f = 0.42 (1:2 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -128° (*c* 1.4, $CHCl_3$); IR (thin film, cm^{-1}) 3372 (broad), 2982, 1749, 1654, 1609, 1504, 1364, 1207, 1174, 1085, 1043, 971; ^1H NMR ($CDCl_3$, 600 MHz) δ 12.5 (s, 1H), 7.77 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 1.8 Hz, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 5.62 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.55 (d, *J* = 1.8 Hz, 1H), 5.32 (dd, *J* = 10.2, 3.6 Hz, 1H), 4.97 (dd, *J* = 10.2, 9.6 Hz, 1H), 3.54 (dq, *J* = 10.2, 6.0 Hz, 1H), 2.13 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 0.94 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 177.9, 170.8, 170.3, 170.1, 162.5, 162.1, 158.6, 157.4, 156.9, 134.1, 130.7, 122.1, 115.7, 105.7, 99.3, 98.2, 94.1, 70.4,

[5] Usia, T.; Iwata, H.; Hiratsuka, A.; Watabe, T.; Kadota, S.; Tezuka, Y. *J. Nat. Prod.* **2004**, *67*, 1079-1083.

69.4, 69.2, 68.4, 20.9, 20.8, 20.7, 17.1; HRMS (ESI) calcd for $[C_{27}H_{26}O_{13} + Na]^+$: 581.1271, Found: 581.1266.

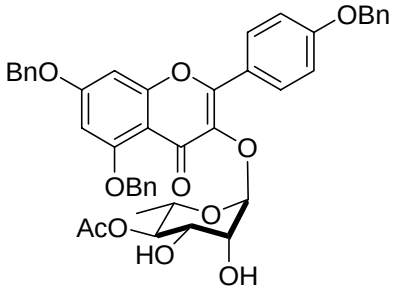
6-(5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-4-oxo-4H-chromen-3-yloxy)-3,6-dihydro-2-methyl-2H-pyran-3-yl acetate (10)



A solution of 210 mg pyranone **2** (0.32 mmol) in 3.5 mL CH_2Cl_2-MeOH (5:1) was cooled down to -78 ^oC, then 25 mg $NaBH_4$ (0.64 mmol) was added. The reaction mixture was stirred at -78 ^oC for 3 hours. Then the reaction was quenched by 3 mL saturated $NaHCO_3$, followed by extraction with Et_2O (15 mL × 3). The organic layer was washed by 3 mL saturated NaCl, dried over Na_2SO_4, and concentrated under reduced pressure to give a residue. All residual solvent was removed by applying a high vacuum produced by oil pump for half an hour. The dry residue was redissolved in CH_2Cl_2 and cooled down to 0 ^oC. To the solution was added 0.4 mL pyridine, catalytic amount of DMAP, and 0.3 mL Ac_2O. After stirring for 1 hour, the mixture was diluted by 20 mL Et_2O. The organic layer was sequentially washed with 2 mL H_2O, 2 mL saturated $NaHCO_3$, 2 mL saturated brine, dried over Na_2SO_4 and then concentrated under reduced pressure to afford crude product. Chromatograph on silica gel eluting with hexane-EtOAc (5:1) gave pure acetate **10** (156 mg, 70%): Amorphous yellow solid; R_f = 0.52 (3:2 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -146° (*c* 1.1, $CHCl_3$); IR (thin film, cm^{-1}) 3052, 2927, 1736, 1636, 1608, 1509, 1454, 1375, 1355, 1298, 1240, 1178, 1104, 1023, 936; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.96 (d, *J* = 9.0 Hz,

2H), 7.55 (d, J = 7.2 Hz, 2H), 7.47-7.27 (m, 13H), 7.09 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 2.4 Hz, 1H), 6.44 (d, J = 2.4 Hz, 1H), 6.20 (ddd, J = 10.2, 2.4, 2.4 Hz, 1H), 5.90 (d, J = 10.2 Hz, 1H), 5.60 (brs, 1H), 5.27 (s, 2H), 5.17 (s, 2H), 5.08 (d, J = 11.4 Hz, 1H), 5.07 (d, J = 11.4 Hz, 1H), 4.96 (ddd, J = 9.6, 1.8, 1.8 Hz, 1H), 3.60 (dq, J = 9.6, 6.6 Hz, 1H), 2.08 (s, 3H), 0.61 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.5, 170.3, 162.8, 160.2, 159.8, 154.5, 138.4, 136.5, 136.4, 135.7, 130.6, 130.3, 128.7, 128.6, 128.6, 128.5, 128.4, 128.1, 127.6, 127.5, 127.3, 126.6, 123.8, 114.5, 110.0, 98.2, 95.8, 94.0, 70.8, 70.7, 70.4, 70.1, 66.5, 21.1, 17.0; HRMS (CI): calcd. for $[C_{44}H_{38}O_9 + Na]^+$: 733.2408, Found: 733.2405.

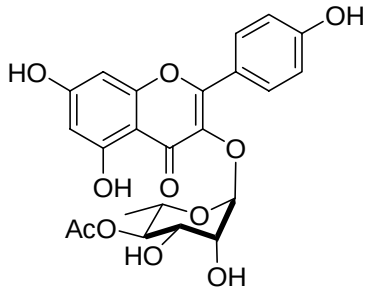
5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(4-*O*-acetyl-*α*-L-rhamnopyranoyloxy)-4H-chromen-4-one (11)



A solution of 142 mg acetate (**10**) (0.20 mmol) in 3 mL acetone-*t*-BuOH (1:1) was cooled down to 0 ^{o}C. To the solution was added 1 mL NMO-H_2O (w/w 1:1), and a catalytic amount (~ 5 mg) of crystalline OsO_4 was added into the mixture. The reaction mixture was stirred at 0 ^{o}C for 24 hours. The reaction was quenched with 1 mL saturated $Na_2S_2O_3$ (aq.) and stirred overnight. Then the mixture was passed through a small pad of celite and silica gel, washed with EtOAc-MeOH (1:1) (15 mL × 3), the organic solution was dried over Na_2SO_4, and concentrated under reduced pressure to give a residue. Chromatograph on silica gel eluting with hexane-EtOAc (2:3) gave diol **11** (115 mg, 77%): Pale yellow solid, mp: 90.5-92.5 ^{o}C; R_f = 0.67

(10:1 (v/v) Et_2O/MeOH); $[\alpha]_D^{25}$ -116 (*c* 0.8, $CHCl_3$); IR (thin film, cm^{-1}) 3424 (broad), 3066, 3035, 2928, 1741, 1605, 1574, 1509, 1498, 1486, 1454, 1375, 1354, 1299, 1251, 1199, 1177, 1144, 1102, 1049, 1004, 955; ^{1}H NMR (acetone-d_6, 600 MHz) δ 7.82 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.46-7.27 (m, 13H), 7.09 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 5.51 (d, *J* = 1.8 Hz, 1H), 5.27 (s, 2H), 5.15 (s, 2H), 5.07 (s, 2H), 4.78 (dd, *J* = 9.6, 9.0 Hz, 1H), 4.51 (ddd, *J* = 3.6, 3.6, 2.4 Hz, 1H), 3.93 (ddd, *J* = 8.4, 7.8, 3.0 Hz, 1H), 3.45 (d, *J* = 4.2 Hz, 1H), 3.40 (dq, *J* = 9.6, 6.6 Hz, 1H), 2.91 (d, *J* = 7.8 Hz, 1H), 2.05 (s, 3H), 0.81 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (acetone-d_6, 150 MHz) δ 173.5, 171.2, 163.0, 160.5, 159.8, 158.9, 154.6, 137.8, 136.4, 136.3, 135.6, 130.5, 128.8, 128.7, 128.6, 128.4, 128.2, 127.8, 127.6, 127.3, 126.8, 123.3, 114.7, 109.9, 101.4, 98.4, 94.0, 74.7, 70.8, 70.7, 70.5, 70.2, 69.9, 67.8, 21.0, 17.1; HRMS (ESI) calcd for $[C_{44}H_{40}O_{11} + H]^+$: 745.2649, Found: 745.2642.

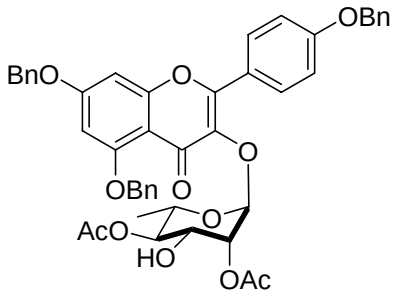
Kaempferol-3-*α*-L-4''-*O*-acetylrhamnoside (1d)



To a solution of 54.8 mg diol **11** (0.07 mmol) in 3 mL THF-EtOH (1:1) was added 30 mg Pearlman's catalyst (Pd-C, 10%). The reaction mixture was degassed using vacuum at -90 ^oC and refilling with H_2. This procedure was repeated three times, then the bath was removed and the reaction was warmed up to room temperature. The reaction mixture was stirred under a H_2 atmosphere for 3 hours. The reaction mixture was loaded onto silica gel and elution with hexane-EtOAc (1:2) to give kaempferol-3-α-L-4''-*O*-acetylrhamnoside (**1d**) (30 mg, 87%):[4c] Yellow solid, mp: 150-152 ^oC; R_f =

0.18 (1:3 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -145° (*c* 1.3, MeOH); IR (thin film, cm^{-1}) 3317 (broad), 2927, 1721, 1651, 1607, 1500, 1446, 1359, 1253, 1207, 1172, 1141, 1085, 1047, 1004, 970, 952; ^{1}H NMR (acetone-d_6, 600 MHz) δ 7.84 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.47 (d, *J* = 1.8 Hz, 1H), 6.28 (d, *J* = 1.8 Hz, 1H), 5.53 (d, *J* = 1.2 Hz, 1H), 4.82 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.23 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.85 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40 (dq, *J* = 9.6, 6.0 Hz, 1H), 2.87 (brs, 1H), 1.97 (s, 3H), 0.78 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (acetone-d_6, 150 MHz) δ 179.3, 170.9, 165.1, 163.1, 161.1, 158.7, 158.2, 135.7, 131.8, 122.5, 116.4, 105.9, 102.4, 99.6, 94.7, 74.6, 71.5, 69.8, 69.1, 21.0, 17.6; HRMS (ESI) calcd for $[C_{23}H_{22}O_{11} + Na]^+$: 497.1060, Found: 497.1054.

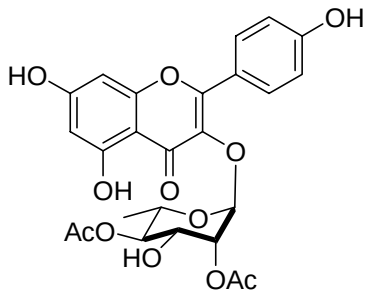
5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(2,4-*O*-triacetyl-*α*-L-rhamnopyranoyloxy)-4H-chromen-4-one (12)



To a solution of 75 mg diol **11** (0.10 mmol) in 1.6 mL CH_2Cl_2 was added 0.6 mg (3 μmol) *p*-TsOH·H_2O, 38 μL trimethylorthoacetate (0.30 mmol) at 0 °C. After stirring at 0 °C for 15 min, 0.5 mL 90% HOAc (aq.) was added and the reaction mixture was stirred for another 15 min. The reaction mixture was diluted with 25 mL EtOAc and washed at 0 °C by 3 mL saturated $NaHCO_3$ two times, then it was washed by 3 mL saturated brine, and dried over Na_2SO_4. The organic layer was concentrated under reduced pressure to give crude product, which was then subjected to chromatograph on silica gel. Elution with hexane-EtOAc (1:1) gave diacetate **12** (78 mg, 99%):

White solid, mp: 99.5-101.5 ^{o}C; R_f = 0.58 (1:2 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -115° (*c* 1.1, $CHCl_3$); IR (thin film, cm^{-1}) 3430 (broad), 3032, 2927, 1741, 1628, 1604, 1575, 1509, 1499, 1486, 1453, 1433, 1373, 1299, 1225, 1196, 1174, 1136, 1099, 1047, 1017, 963; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.81 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.46-7.27 (m, 13H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 5.57 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.26 (s, 2H), 5.16 (s, 2H), 5.07 (s, 2H), 4.76 (dd, *J* = 10.2, 9.6 Hz, 1H), 4.11 (ddd, *J* = 9.6, 6.6, 3.0 Hz, 1H), 3.50 (dq, *J* = 10.2, 6.6 Hz, 1H), 2.28 (d, *J* = 6.6 Hz, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 0.89 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.0, 171.2, 170.5, 162.9, 160.6, 159.9, 158.8, 154.3, 136.9, 136.3, 135.6, 130.3, 128.8, 128.7, 128.6, 128.4, 128.2, 127.7, 127.6, 127.3, 126.7, 123.1, 114.9, 110.0, 98.4, 98.3, 94.0, 74.1, 72.1, 70.8, 70.5, 70.2, 68.8, 67.9, 21.0, 20.9, 17.1; HRMS (ESI) calcd for $[C_{46}H_{42}O_{12} + Na]^+$: 809.2574, Found: 809.2567.

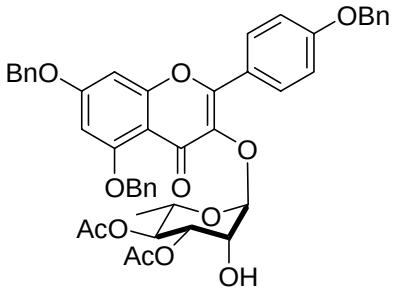
Kaempferol-3-*α*-L-2'',4''-*O*-diacetylrhamnoside (1e)



To a solution of 66.8 mg diacetate **12** (0.08 mmol) in 3 mL THF-EtOH (1:1) was added 30 mg Pearlman's catalyst (Pd-C, 10%). The reaction mixture was degassed using vacuum at -90 ^{o}C and refilling with H_2. This procedure was repeated three times, then the bath was removed and the reaction was warmed up to room temperature. The reaction mixture was stirred under a H_2 atmosphere for 3 hours. The reaction mixture was loaded onto silica gel and elution with hexane-EtOAc (2:3) to give kaempferol-3-

α-L-2'',4''-*O*-diacetylrhamnoside (**1e**) (38 mg, 88%):[6] Yellow solid, mp: 127-129 °C; R_f = 0.24 (1:2 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -93° (*c* 0.96, MeOH); IR (thin film, cm^{-1}) 3311 (broad), 2925, 1721, 1653, 1608, 1502, 1445, 1362, 1205, 1171, 1144, 1129, 1085, 1047, 1007, 970; ^{1}H NMR (acetone-d_6, 600 MHz) δ 7.85 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 1.8 Hz, 1H), 6.28 (d, *J* = 1.8 Hz, 1H), 5.60 (s, 1H), 5.47 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.76 (dd, *J* = 10.2, 9.6 Hz, 1H), 4.04 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.38 (dq, *J* = 10.2, 6.0 Hz, 1H), 2.06 (s, 3H), 1.99 (s, 3H), 0.81 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (acetone-d_6, 150 MHz) δ 179.0, 170.8, 170.3, 165.2, 163.0, 161.2, 158.8, 158.1, 134.8, 131.8, 122.3, 116.5, 105.8, 99.7, 99.3, 94.7, 74.4, 72.4, 69.2, 68.0, 21.0, 20.9, 17.7; HRMS (ESI) calcd for $[C_{25}H_{24}O_{12} + Na]^+$: 539.1166, Found: 539.1159.

5,7-bis(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(3,4-*O*-triacetyl-*α*-L-rhamnopyranoyloxy)-4H-chromen-4-one (13)

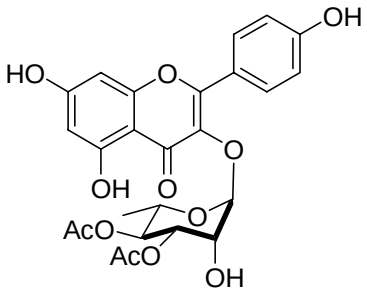


To a solution of 50 mg diacetate **12** (0.064 mmol) in 4 mL toluene was added a solution of 10 μl DBU in 1 mL toluene at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour, then diluted with 20 mL Et_2O-EtOAc (1:1). The mixture was sequentially washed with 2 mL saturated NH_4Cl, 2 mL saturated $NaHCO_3$, dried over Na_2SO_4. The organic layer was concentrated under reduced pressure to give a residue. Crude ^{1}H-NMR showed this residue contains 64% diacetate **13** *vs.* 36% diacetate **12**.

[6] Nakatani, N.; Jitoe, A.; Masuda, T. *Agric. Biol. Chem.* **1991**, *55(2)*, 455-460.

Chromatograph on silica gel eluting with hexane-EtOAc (1.6:1) gave desired diacetate **13** (31 mg, 62%) and further elution with hexane-EtOAc (1.4:1) gave 17 mg (34%) starting material **12** back. Diacetate **13** : White solid, mp: 93-95 ^{o}C; R_f = 0.59 (2:3 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -151° (*c* 1.3, $CHCl_3$); IR (thin film, cm^{-1}) 3394 (broad), 3064, 2924, 1741, 1604, 1509, 1453, 1432, 1369, 1353, 1296, 1249, 1222, 1172, 1100, 1043, 1004, 958; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.46-7.27 (m, 13H), 7.12 (d, *J* = 9.0 Hz, 2H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 5.53 (d, *J* = 2.4 Hz, 1H), 5.31 (dd, *J* = 9.0, 3.0 Hz, 1H), 5.26 (s, 2H), 5.15 (s, 2H), 5.08 (s, 2H), 4.98 (dd, *J* = 9.6, 9.0 Hz, 1H), 4.57 (ddd, *J* = 6.6, 3.6 Hz, 1H), 3.46 (dq, *J* = 9.6, 6.6 Hz, 1H), 2.87 (brs, 1H), 2.07 (s, 3H), 1.99 (s, 3H), 0.82 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.3, 169.9, 169.8, 163.0, 160.5, 159.9, 158.9, 154.5, 137.6, 136.4, 136.3, 135.6, 130.5, 128.8, 128.7, 128.6, 128.4, 128.2, 127.7, 127.6, 127.3, 126.7, 123.2, 114.8, 109.9, 101.9, 98.3, 94.0, 74.7, 71.2, 70.8, 70.5, 70.1, 69.5, 67.9, 20.9, 20.8, 17.2; HRMS (ESI) calcd for $[C_{46}H_{42}O_{12} + Na]^+$: 809.2574, Found: 809.2569.

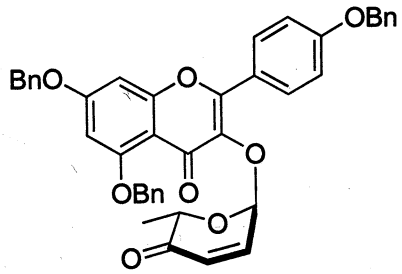
SL0101 (1a)



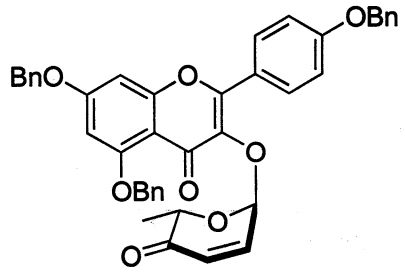
To a solution of 46 mg diacetate **13** (0.058 mmol) in 2.5 mL THF-EtOH (1:1) was added 25 mg Pearlman's catalyst (Pd-C, 10%). The reaction mixture was degassed using vacuum at -90 ^{o}C and refilling with H_2. This procedure was repeated three times, then the bath was removed and the reaction was warmed up to room temperature. The

reaction mixture was stirred under a H_2 atmosphere for 3 hours. The reaction mixture was loaded onto silica gel and elution with hexane-EtOAc (2:3) to give SL0101 (**1a**) (28 mg, 91%):[1,4a,6] Yellow solid, mp: 147-149 ^{o}C; R_f = 0.26 (1:2 (v/v) hexane/EtOAc); $[\alpha]_D^{25}$ -163° (*c* 1.6, MeOH); IR (thin film, cm^{-1}) 3211 (broad), 2980, 2930, 1722, 1650, 1607, 1502, 1444, 1361, 1206, 1171, 1045, 1005, 970; ^{1}H NMR (acetone-d_6, 600 MHz) δ 7.86 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.48 (d, *J* = 1.8 Hz, 1H), 6.28 (d, *J* = 1.8 Hz, 1H), 5.56 (d, *J* = 1.8 Hz, 1H), 5.17 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.07 (dd, *J* = 10.2, 9.6 Hz, 1H), 4.42 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.49 (dq, *J* = 9.6, 6.0 Hz, 1H), 2.02 (s, 3H), 1.96 (s, 3H), 0.82 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (acetone-d_6, 150 MHz) δ 179.2, 170.7, 170.4, 165.1, 163.0, 161.1, 158.7, 158.2, 135.5, 131.8, 122.4, 116.5, 105.8, 102.2, 99.7, 99.6, 94.7, 72.3, 71.2, 69.3, 69.2, 21.0, 20.8, 17.6; HRMS (ESI) calcd for $[C_{25}H_{24}O_{12} + Na]^+$: 539.1166, Found: 539.1161.

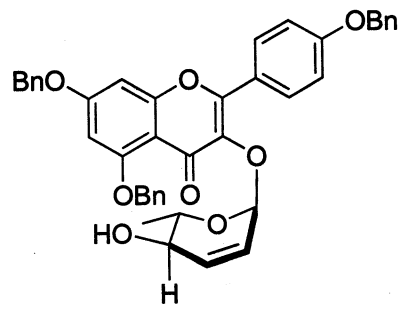
Section C: ^{1}H and ^{13}C NMR Spectra



^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 150 MHz)

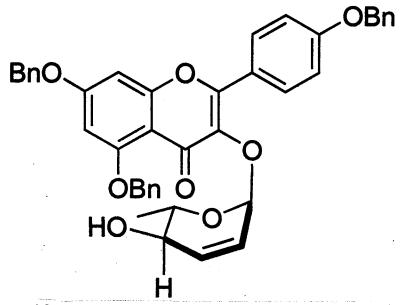


^{1}H NMR ($CDCl_3$, 270 MHz)

12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 −1.0 −2.0

8.1560 7.9636 7.9306 7.4322 7.4093 7.4011 7.3791 7.2600 6.5655 6.5582 6.4400 6.1835 5.9929 5.9554 5.5852 5.2700 5.1564 5.0694 4.1349 4.1083 3.7437 3.7144 3.3296 3.3076 3.2975 2.6159 2.0469 1.6282 1.4285 1.2599 0.9090 0.7029 0.6800 0.0726

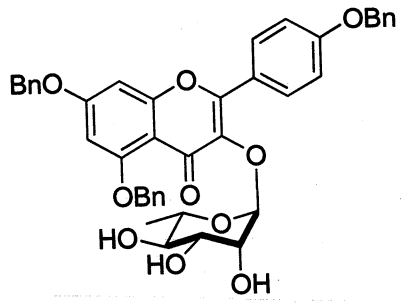
X : parts per Million : 1H



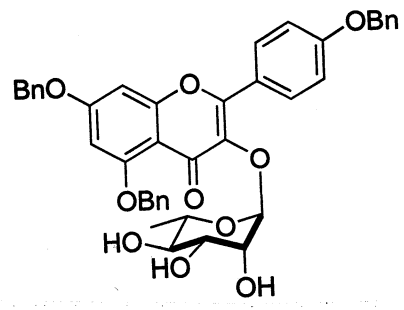
^{13}C NMR ($CDCl_3$, 67.5 MHz)

162.8380
160.2635
159.8510
159.0259
154.8013
130.7142
128.8273
128.7586
128.6898
127.6814
127.4599
126.7418
114.5875
98.3079
95.7334
94.0145
77.5669
77.1009
76.6272
70.8136
69.4538
17.0169

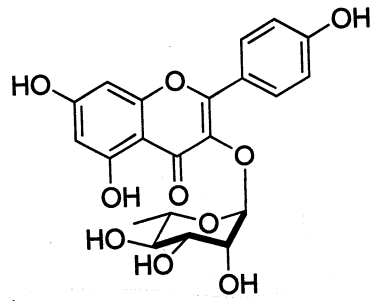
X : parts per Million : 13C



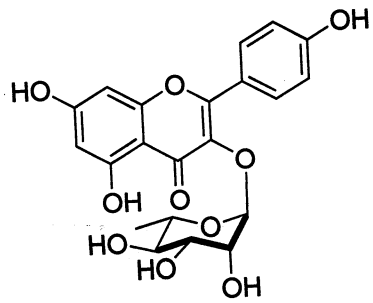
^{1}H NMR (acetone-d_6, 600 MHz)



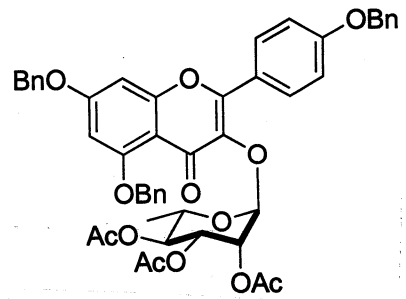
^{13}C NMR (acetone-d_6, 150 MHz)



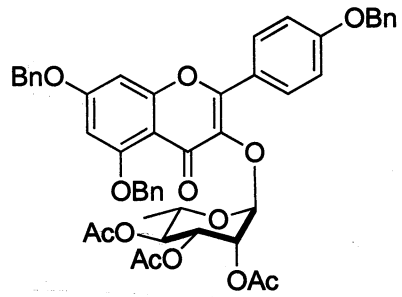
^{1}H NMR (CD_3OD, 600 MHz)



^{13}C NMR (CD_3OD, 150 MHz)

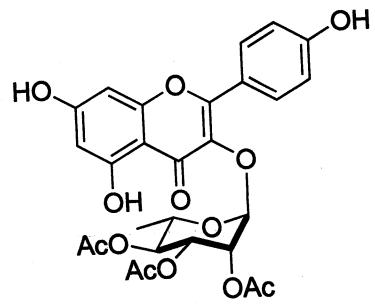


^{1}H NMR ($CDCl_3$, 600 MHz)

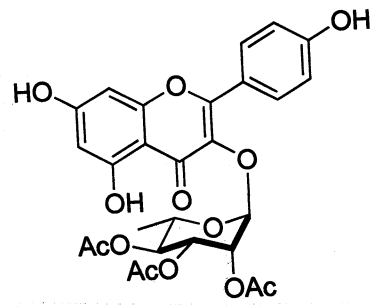


^{13}C NMR ($CDCl_3$, 150 MHz)

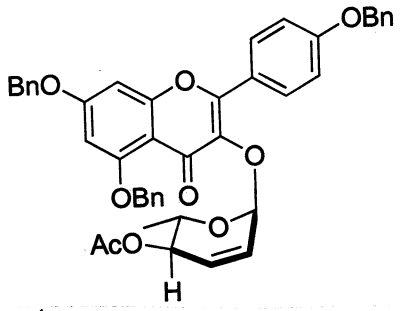
200 180 160 140 120 100 80 60 40 20 0 -20 ppm



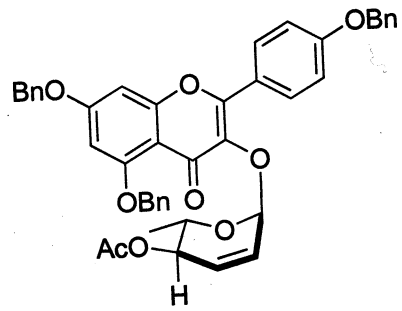
^{1}H NMR ($CDCl_3$, 600 MHz)



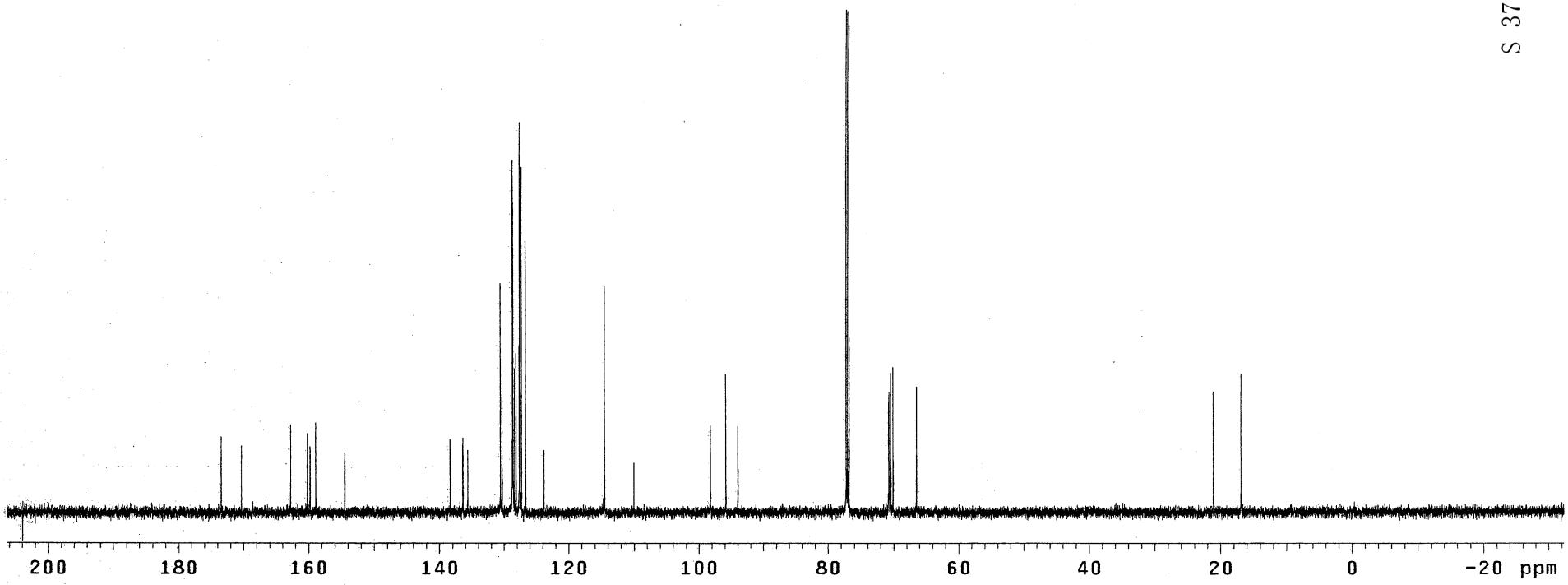
^{13}C NMR ($CDCl_3$, 150 MHz)

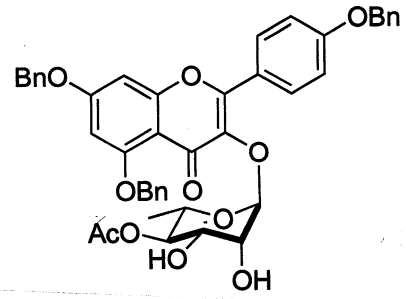


^{1}H NMR ($CDCl_3$, 600 MHz)

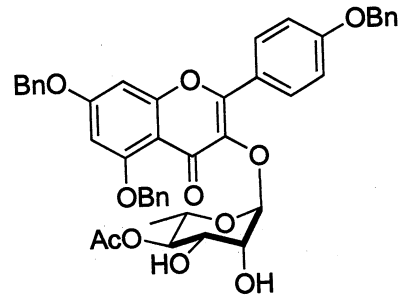


^{13}C NMR ($CDCl_3$, 150 MHz)



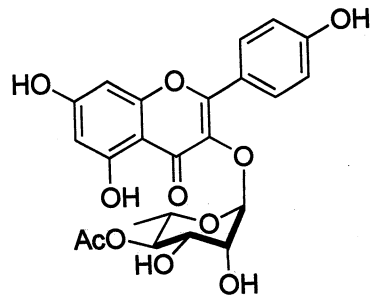


^{1}H NMR ($CDCl_3$, 600 MHz)

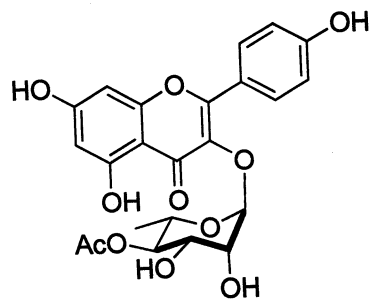


^{13}C NMR ($CDCl_3$, 150 MHz)

200 180 160 140 120 100 80 60 40 20 0 ppm

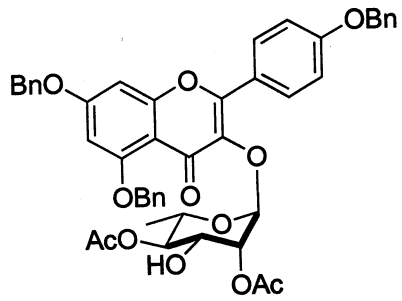


^{1}H NMR (acetone-d_6, 600 MHz)

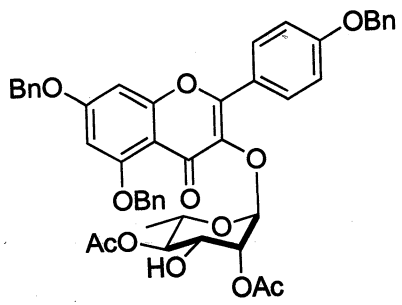


^{13}C NMR (acetone-d_6, 150 MHz)

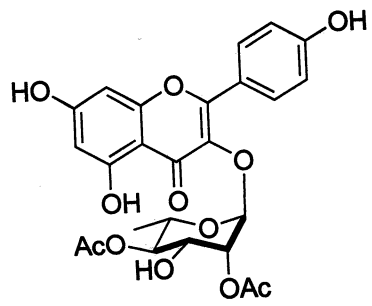
200 180 160 140 120 100 80 60 40 20 0 -20 ppm



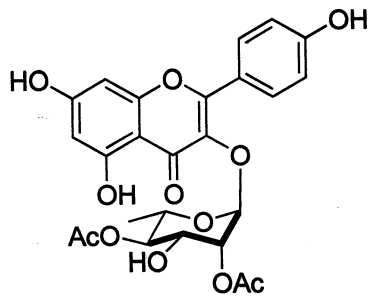
^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 150 MHz)

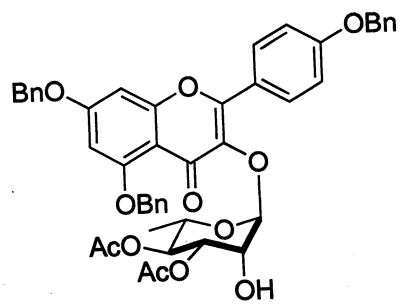


^{1}H NMR (acetone-d_6, 600 MHz)

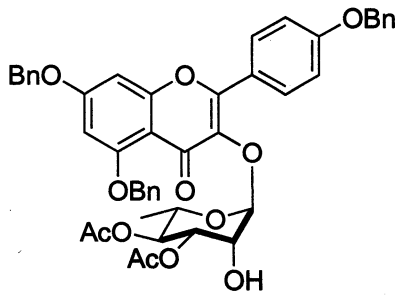


^{13}C NMR (acetone-d_6, 150 MHz)

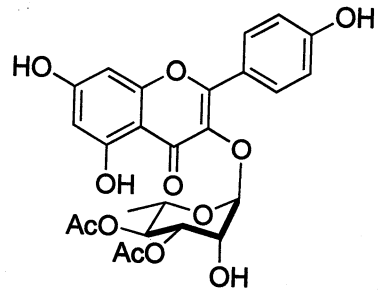
200 180 160 140 120 100 80 60 40 20 0 -20 ppm



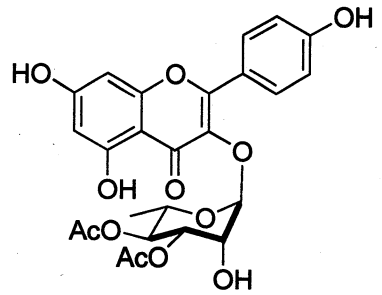
^{1}H NMR ($CDCl_3$, 600 MHz)



^{13}C NMR ($CDCl_3$, 150 MHz)



^{1}H NMR (acetone-d_6, 600 MHz)



^{13}C NMR (acetone-d_6, 150 MHz)