Supporting Information for

Collective Total Synthesis of Chartreusin Derivatives and Bioactivity Investigations

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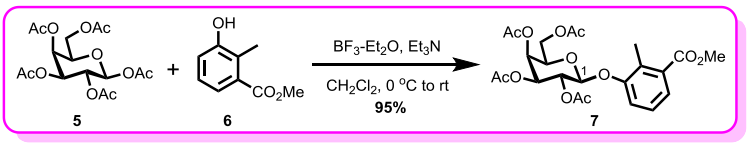
General Comments:

All reactions were monitored by thin-layer chromatography over silica-gel-coated TLC plates (Yantai Chemical Industry Research Institute). The spots on TLC were visualized either by UV light (254 nm) or by warming 5% H_2SO_4 (5% H_2SO_4 in ethanol) sprayed plates on a hot plate. Flash column chromatography was performed using silica gel (Qingdao Marine Chemical Inc., China), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden). NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) or AVANCE NEO Ascend 600 (600 MHz). Optical rotations were measured at 20 ℃ with a Rudolph Autopol IV automatic polarimeter using a quartz cell with 2 mL capacity and a 1 dm path length. Concentrations (*c*) are given in g/100 mL. High resolution mass spectra were recorded on a Bruker micrOTOF II spectrometer using electrospray ionization (ESI).

All solvents were processed under conventional way before using, and all reagents were purchased from Adamas and used without further purification.

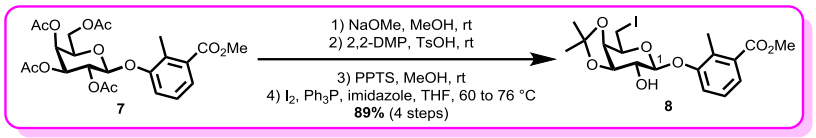
Methyl 2-methyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-benzoate (7)



To a solution of peracetylated galactose **5** (5.00 g, 12.81 mmol) and methyl 2-methyl-3-hydroxyl-benzoate **6**[S1] (3.19 g, 19.20 mmol) and Et_3N (0.9 mL, 6.40 mmol) in dry CH_2Cl_2 (36.0 mL) was added $BF_3 \cdot Et_2O$ (4.0 mL, 32.02 mmol) dropwise at 0 °C under N_2 atmosphere. The reaction mixture was then gradually warmed up to room temperature, and the stirring was continued for another 16 h, at which time TLC showed that all the starting materials disappeared. The reaction was quenched by Et_3N, which was followed by evaporation to remove all volatile solvent to give a residue. The resulting residue was purified by silica gel column chromatograghy (PE/EA = 3 : 1) to afford **7** (6.03 g, 95%) as a colorless syrup: $[\alpha]_D^{25}$ = -9.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 1 H), 7.19-7.14 (m, 2 H), 5.55 (dd, *J* = 10.4, 8.0 Hz, 1 H, H-2), 5.45 (d, *J* = 3.6 Hz, 1 H, H-4), 5.10 (dd, *J* = 10.4, 3.2 Hz, 1 H, H-3), 4.96 (d, *J* =

8.0 Hz, 1 H, H-1), 4.23 (dd, *J* = 11.2, 6.8 Hz, 1 H, H-6), 4.15 (dd, *J* = 11.2, 6.8 Hz, 1 H, H-6), 4.07-4.04 (m, 1 H, H-5), 3.87 (s, 3 H, -CO_2CH_3), 2.36 (s, 3 H, Ar-CH_3), 2.18 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.00 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.3, 170.2, 169.4, 168.1, 155.7, 132.1, 129.9, 126.2, 125.0, 118.8, 100.2 (C-1), 71.1, 70.8, 68.6, 67.0, 61.4, 52.1, 20.8, 20.7 (3 C), 12.8; HRMS (ESI) m/z calcd for $C_{23}H_{29}O_{12}$ $[M + H]^+$: 497.1654, found: 497.1655.

Methyl 2-methyl-3-*O*-(3,4-*O*-isopropylidene-6-deoxy-6-iodo-β-D-galactopyranosyl)-benzoate (8)



To a solution of **7** (2.70 g, 5.44 mmol) in absolute MeOH (150.0 mL) was added NaOMe (29 mg, 0.54 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 1 h, when TLC shown that the reaction reached to completion. AcOH was added to quench the reaction before evaporation *in vacuo* was adopted to remove all volatile solvent. After co-evaporation with toluene for three times, the resulting crude product was put to the next step without further purification.

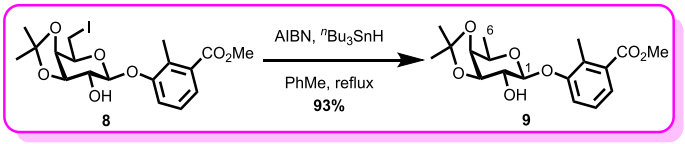
To the obtained tetraol intermediate was added 2,2-dimethoxypropane (18.0 mL) and TsOH (91 mg, 0.54 mmol) at room temperature under N_2 atmosphere. The resulting mixture was stirred at the same temperature for 2 h, at which time TLC showed the reaction reached completion. Et_3N was added to quench the reaction before evaporation *in vacuo* was adopted to remove all volatile solvent. The resulting crude product was put to the next step without further purification.

The obtained crude product was then dissolved in MeOH (18.0 mL), to which PPTS (142 mg, 0.57 mmol) was added at room temperature. The stirring was continued at the same temperature for 20 min before Et_3N was added to quench the reaction. The mixture was concentrated *in vacuo* and diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layers was dried over anhydrous Na_2SO_4.

Filtration was followed by concentration under reduced pressure delivered a residue, which was put to the next step without further purification.

To the above obtained diol intermediate in dry THF (40.0 mL) were added PPh_3 (1.99 g, 7.56 mmol) and imidazole (667 mg, 9.80 mmol) successively at room temperature under N_2 atmosphere. The reaction mixture was then gradually warmed up to 60 °C. After being stirred for another 10 min at the same temperature, I_2 (1.92 g, 7.56 mmol, in 14.0 mL dry THF) was added dropwise. Upon completion of I_2, the reaction mixture was then heated to reflux and was stirred overnight. After completion of the reaction (monitored by TLC), EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with saturated aqueous $Na_2S_2O_3$, H_2O and brine, and the combined organic layers was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to afford **8** (2.31 g, 89% yield for 4 steps) as a white foam: $[\alpha]_D^{25}$ = +7.5 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.32 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 4.66 (d, *J* = 8.0 Hz, 1 H, H-1), 4.32 (dd, *J* = 5.6, 2.4 Hz, 1 H, H-4), 4.16 (dd, *J* = 7.2, 5.6 Hz, 1 H, H-3), 3.99 (ddd, *J* = 8.0, 6.0, 2.4 Hz, 1 H, H-5), 3.89-3.84 (m, 4 H), 3.47-3.34 (m, 2 H, H-6), 2.99 (d, *J* = 3.6 Hz, 1 H, C2-OH), 2.46 (s, 3 H), 1.55 (s, 3 H), 1.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 155.7, 131.8, 130.0, 126.3, 125.0, 120.0, 110.5, 101.6 (C-1), 78.9, 74.1, 74.0, 73.1, 52.1, 28.1, 26.3, 13.3, 1.5; HRMS (ESI) m/z calcd for $C_{18}H_{24}IO_7$ $[M + H]^+$: 479.0561, found: 479.0563.

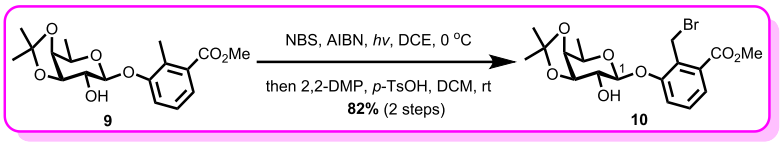
Methyl 2-methyl-3-*O*-(3,4-*O*-isopropylidene-β-D-fucopyranosyl)-benzoate (9)



To a solution of **8** (2.19 g, 4.58 mmol) in dry PhMe (46.0 mL) were added ^{n}Bn$_3$SnH (2.5 mL, 9.16 mmol) and AIBN (150 mg, 0.92 mmol) successively at room temperature under N_2 atmosphere. The resulting mixture was heated to reflux for 3 h, when TLC showed that the reaction reached completion. After cooling down to room temperature,

the solvent was removed *in vacuo* to give the crude product, which was further purified by silica gel column chromatography (PE/EA= 2 : 1) to give **9** (1.50 g, 93%) as a white solid: $[\alpha]_D^{25}$ = -6.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 7.45 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.28 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.22 (t, *J* = 8.0 Hz, 1 H), 4.88 (d, *J* = 8.0 Hz, 1 H, H-1), 4.73 (d, *J* = 4.8 Hz, 1 H), 4.22-4.10 (m, 3 H), 3.85 (s, 3 H), 3.78-3.74 (m, 1 H), 2.44 (s, 3 H), 1.48 (s, 3 H, H-6), 1.35 (d, *J* = 6.4 Hz, 3 H), 1.32 (s, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.6, 157.1, 132.8, 129.9, 127.0, 124.3, 119.3, 109.7, 102.0 (C-1), 80.6, 77.0, 73.6, 69.5, 52.2, 28.6, 26.6, 17.0, 13.2; HRMS (ESI) m/z calcd for $C_{18}H_{25}O_7$ $[M + H]^+$: 353.1595, found: 353.1589.

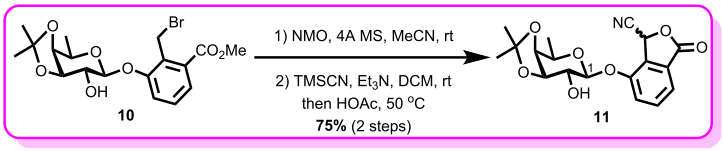
Methyl 2-bromomethyl-3-*O*-(3,4-*O*-isopropylidene-β-D-fucopyranosyl)-benzoate (10)



To a solution of **9** (420 mg, 1.19 mmol) in dry DCE (23.8 mL) were added NBS (228 mg, 1.28 mmol) and AIBN (19 mg, 0.12 mmol) successively under N_2 atmosphere at room temperature. The resulting mixture was cooled to 0 °C and stirred under the irradiation of UV Identification Lamp (365 nm) for 30 min before Et_3N was added to quench the reaction. The mixture was evaporated to remove all volatile solvent to give a residue. The resulting residue was dissolved in 2,2-dimethoxypropane/CH_2Cl_2 (10 mL, v/v = 1 : 1), to which *p*-TsOH (4.1 mg, 0.024 mmol) was added at room temperature. The reaction mixture was stirred for 20 min at this temperature, when TLC showed that the reaction reached to completion. Et_3N was added to quench the reaction before evaporation *in vacuo* was adopted to remove all volatile solvent. The resulting crude product was further purified by silica gel column chromatography (PE/EA= 2 : 1) to furnish **10** (422 mg, 82%) as a white solid: $[\alpha]_D^{25}$ = +15.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 7.20 (dd, *J* = 8.0, 1.2 Hz, 1 H), 5.28 (d, *J* = 9.2 Hz, 1 H, -CH_2-Br), 4.86 (d, *J* = 9.2 Hz, 1 H, -CH_2-Br), 4.81 (d, *J* = 8.0 Hz, 1 H, H-1), 4.18 (dd, *J* = 7.2, 5.2 Hz, 1 H), 4.12-4.04 (m, 2 H),

3.96-3.93 (m, 4 H), 3.10 (br s, 1 H), 1.60 (s, 3 H), 1.49 (d, J = 6.4 Hz, 3 H), 1.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 156.3, 130.6, 129.7, 128.2, 125.1, 118.5, 110.3, 101.4 (C-1), 78.6, 76.0, 73.4, 69.7, 52.6, 27.0, 26.5, 25.3, 16.8; HRMS (ESI) m/z calcd for $C_{18}H_{24}BrO_7$ $[M + H]^+$: 431.0700, found: 431.0705.

4-*O*-(3,4-*O*-Isopropylidene-β-D-fucopyranosyl)-3-cyanoisobenzofuran-1(3*H*)-one (11)



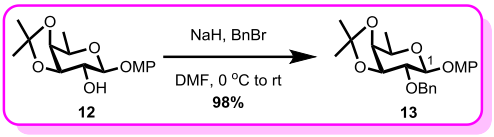
To a solution of **10** (400 mg, 0.93 mmol) in dry MeCN (18.5 mL) was added activated 4 Å molecular sieves (1.85 g). The suspension was stirred at room temperature for 10 min before NMO (346 mg, 2.97 mmol) was added. The resulting mixture was stirred at the same temperature for another 40 min, at which time TLC showed the reaction reached completion. Filtration was followed by concentration under reduced pressure delivered a residue, which was put to the next step without further purification.

The above obtained residue was dissolved in dry CH_2Cl_2 (18.5 mL), to which Et_3N (52 μL, 0.37 mmol) and TMSCN (187 μL, 1.49 mmol) were added at room temperature. The reaction was stirred for 1 h at the same temperature, when TLC showed that the reaction reached to completion. The solvent was removed *in vacuo* to give the crude product, which was put to the next step after co-evaporation with toluene for 3 times.

The above obtained intermediate was dissolved in AcOH (9.0 mL) at room temperature. The mixture was allowed to warm to 50 ℃ and the stirring was continued at this temperature for 24 h, when TLC showed that the reaction reached to completion. After cooling down to room temperature, the solvent was removed *in vacuo* to give the crude product, which was further purified by silica gel column chromatography (PE/EA= 3 : 2 to 1 : 1) to give **11** (251 mg, 75% yield for 2 steps) as an inseparable mixture of stereomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.59 (m, 8 H), 7.39-7.34 (m, 4 H), 6.21 (s, 1 H, -CH-CN), 6.07 (s, 3 H, -CH-CN), 4.96 (d, J = 7.2 Hz, 3 H, H-1), 4.88 (d, J = 7.6 Hz, 1 H, H-1), 4.19-4.07 (m, 12 H), 3.91-3.86 (m, 4 H), 3.10 (s, 3 H), 1.57 (s, 12

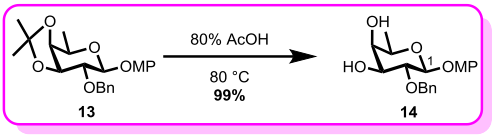
H), 1.47-1.45 (m, 12 H), 1.37 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.3, 152.3, 152.1, 133.6, 133.3, 130.4, 126.3, 126.2, 121.5, 120.6, 120.2, 120.1, 114.0 (-CN), 113.3 (-CN), 110.4 (2 C), 101.2 (C-1), 100.9 (C-1), 79.1, 78.5, 76.0, 75.8, 73.0, 72.7, 69.9, 69.8, 64.4 (Ar-CH-), 64.1(Ar-CH-), 28.3, 26.4, 16.7 (2 C); HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_7Na$ $[M + Na]^+$: 384.1054, found: 384.1048.

4-Methoxyphenyl 2-*O*-benzyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (13)



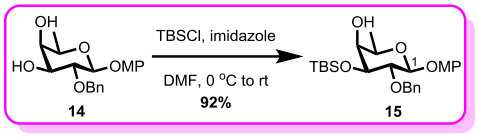
To a solution of **12**[S2] (1.00 g, 3.22 mmol) and BnBr (760 μL, 6.44 mmol) in dry DMF (17.0 mL) at 0 ℃ was added NaH (60% dispersed in mineral oil, 387 mg, 9.67 mmol) in three batches. The reaction mixture was then gradually warmed to room temperature, and the stirring was continued for 3 h, at which time TLC showed that all the starting materials disappeared. The reaction was quenched by MeOH and saturated aqueous NH_4Cl at 0 °C. The resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 6 : 1) to give **13** (1.27 g, 98%) as a white solid: $[\alpha]_D^{25}$ = +50.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.42 (m, 2 H), 7.36-7.32 (m, 2 H), 7.29-7.26 (m, 1 H), 7.03-6.99 (m, 2 H), 6.85-6.81 (m, 2 H), 4.94 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.90 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 4.79 (d, *J* = 8.0 Hz, 1 H, H-1), 4.23 (dd, *J* = 5.6, 6.8 Hz, 1 H, H-3), 4.05 (dd, *J* = 2.0, 5.2 Hz, 1 H, H-4), 3.95 (dq, *J* = 2.0, 6.8 Hz, 1 H, H-5), 3.78 (s, 3 H, -OCH_3), 3.65 (t, *J* = 7.6 Hz, 1 H, H-2), 1.44 (d, *J* = 6.8 Hz, 3 H, H-6), 1.43 (s, 3 H), 1.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 151.6, 138.3, 128.4, 128.3, 127.7, 118.7, 114.6, 109.9, 102.2 (C-1), 79.3, 79.2, 76.4, 73.8, 69.0, 55.8, 28.0, 26.5, 16.8; HRMS (ESI) $[M + Na]^+$ calcd for $C_{23}H_{28}O_6Na$: 423.1778, found: 423.1770.

4-methoxyphenyl 2-*O*-benzyl-β-D-fucopyranoside (14)



The compound **13** (30.60 g, 76.4 mmol) was dissolved in 80% HOAc (250.0 mL) at room temperature. The mixture was allowed to warm to 80 °C and stirred at the same temperature for 45 min, when TLC showed that the reaction reached to completion. After being cooled down to room temperature, the solvent was removed *in vacuo* to give the crude product, which was further purified by silica gel column chromatography (PE/EA = 1 : 3) to give **14** (27.20 g, 99%) as a white solid: $[\alpha]_D^{25}$ = +36.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5 H), 7.02 (d, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 5.05 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.83 (d, *J* = 7.2 Hz, 1 H, H-1), 4.77 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 3.76 (s, 3 H, -OCH_3), 3.74-3.70 (m, 2 H), 3.67-3.60 (m, 2 H), 2.75 (br s, 2 H, C3,4-OH), 1.34 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.5, 138.4, 128.6, 128.3, 128.0, 118.5, 114.6, 102.8 (C-1), 78.9, 74.9, 73.5, 71.3 (2 C), 70.6 (2 C), 55.7 (2 C), 16.4; HRMS (ESI) $[M + Na]^+$ calcd for $C_{20}H_{24}O_6Na$: 383.1465, found: 383.1455.

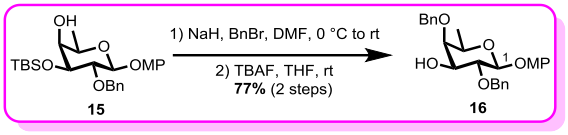
4-Methoxyphenyl 2-*O*-benzyl-3-*O*-*tert*-butlyldimethylsilyl-β-D-fucopyranoside (15)



To a solution of **14** (21.00 g, 58.27 mmol) and imidazole (15.90 g, 233.55 mmol) in dry DMF (117.0 mL) at 0 ℃ was added TBSCl (17.60 g, 116.77 mmol) in three batches. The reaction mixture was then gradually warmed up to room temperature, and the stirring was continued for 5.5 h, at which time TLC showed that all the starting materials disappeared. The reaction was quenched by MeOH at 0 °C. The resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 7 : 1) to give **15** (25.41 g, 92%) as a

white solid: $[\alpha]_D^{25}$ = +3.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 5 H), 7.01-6.97 (m, 2 H), 6.83-6.79 (m, 2 H), 5.03 (d, *J* = 10.8 Hz, 1 H, Ar-CH_2-), 4.83 (d, *J* = 7.2 Hz, 1 H, H-1), 4.73 (d, *J* = 10.8 Hz, 1 H, Ar-CH_2-), 3.77 (s, 3 H, -OCH_3), 3.75-3.63 (m, 3 H), 3.62 (d, *J* = 3.6 Hz, 1 H), 2.50 (brs, 1 H, C4-OH), 1.41 (d, *J* = 6.4 Hz, 3 H, H-6), 0.93 (s, 9 H), 0.09 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.7, 138.6, 128.4, 128.2, 127.7, 118.7, 114.6, 103.0 (C-1), 79.2, 75.3, 74.8, 72.4, 70.1, 55.8, 25.9, 18.2, 16.6, -4.3, -4.7; HRMS (ESI) m/z calcd for $C_{26}H_{39}O_6Si$ $[M + H]^+$: 475.2510, found: 475.2509.

4-Methoxyphenyl 2,4-di-*O*-benzyl-β-D-fucopyranoside (16)

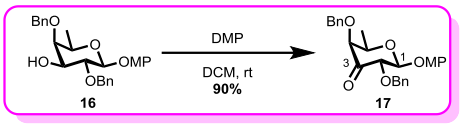


To a solution of **15** (25.40 g, 53.51 mmol) and BnBr (12.7 mL, 106.92 mmol) in dry DMF (134.0 mL) at 0 ℃ was added NaH (60% dispersed in mineral oil, 6.40 g, 160.51 mmol) in three batches. The reaction mixture was then gradually warmed up to room temperature, and the stirring was continued for 7 h, at which time TLC showed that all the starting materials disappeared. The reaction was quenched by MeOH and saturated aqueous NH_4Cl at 0 ^oC. The resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was put to the next step without further purification.

The above obtained intermediate was dissolved in THF (267.0 mL), to which TBAF (28.00 g, 107.09 mmol) was added at room temperature. The mixture was stirred at the same temperature for 7 h, when TLC showed that the reaction reached to completion. The resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to give **16** (18.61 g, 77% yield for 2 steps) as a white solid: $[\alpha]_D^{25}$ = -1.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400

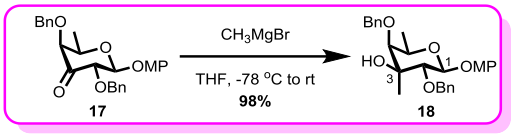
MHz, $CDCl_3$) δ 7.40-7.28 (m, 10 H), 7.04-7.00 (m, 2 H), 6.84-6.80 (m, 2 H), 5.08 (d, *J* = 11.2 Hz, 1 H), 4.87-4.74 (m, 4 H), 3.84 (dd, *J* = 7.6, 10.0 Hz, 1 H), 3.78 (s, 3 H), 3.74 (dd, *J* = 2.8, 8.8 Hz, 1 H), 3.69 (dd, *J* = 6.4, 13.2 Hz, 1 H), 3.63 (d, *J* = 3.2 Hz, 1 H), 1.94 (br s, 1 H), 1.30 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.7, 138.5, 128.7, 128.5, 128.4, 128.0, 127.9, 118.6, 114.6, 103.0 (C-1), 79.3, 78.4, 75.6, 75.0, 74.5, 71.0, 55.8, 17.1; HRMS (ESI) m/z calcd for $C_{27}H_{34}NO_6$ $[M + NH_4]^+$: 468.2381, found: 468.2387.

4-Methoxyphenyl 2,4-di-*O*-benzyl-β-D-fucopyrano-3-uloside (17)



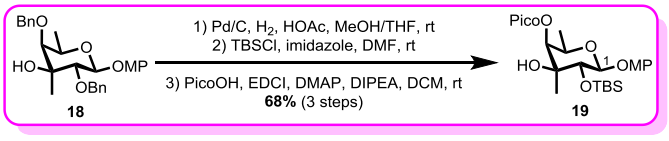
To a solution of **16** (5.80 g, 12.87 mmol) in dry CH_2Cl_2 (374.0 mL) was added Dess-Martin periodinane (8.21 g, 19.36 mmol) in three batches at room temperature. The mixture was stirred at the same temperature for 35 min, when TLC showed that the reaction reached completion. The resulting mixture was diluted with CH_2Cl_2, washed successively with saturated aqueous $Na_2S_2O_3$, $NaHCO_3$ and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 5 : 1 to 3 : 1) to give **17** (5.20 g, 90%) as a white solid: $[\alpha]_D^{25}$ = -42.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2 H), 7.34-7.21 (m, 8 H), 7.05-7.01 (m, 2 H), 6.82-6.78 (m, 2 H), 4.95 (d, *J* = 7.6 Hz, 1 H, H-1), 4.78 (dd, *J* = 11.6, 14.4 Hz, 2 H, Ar-CH_2-), 4.57 (d, *J* = 7.6 Hz, 1 H, H-2), 4.48 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.35 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 3.73-3.69 (m, 4 H), 3.66 (d, *J* = 1.6 Hz, 1 H, H-4), 1.36 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2 (C-3), 155.6, 151.1, 137.3, 136.5, 128.5, 128.4 (2 C), 128.2, 128.0, 119.0, 114.5, 103.4 (C-1), 83.1, 81.7, 73.6, 72.2, 71.2, 55.6, 15.9; HRMS (ESI) m/z calcd for $C_{27}H_{28}O_6Na$ $[M + Na]^+$: 471.1778, found: 471.1788.

4-Methoxyphenyl 2,4-di-*O*-benzyl-3-*C*-methyl-β-D-fucopyranoside (18)



To a solution of **17** (5.20 g, 11.59 mmol) in dry THF (168.0 mL) was added CH_3MgBr (7.7 mL, 23.10 mmol, 3 M in THF) dropwise at -78 ℃ under N_2 atmosphere. The reaction was stirred at the same temperature for 30 min, which was followed by warming up to room temperature and continuous stirring at the same temperature for another 2 h. After completion of the reaction (monitored by TLC), EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with aturated aqueous NH_4Cl, and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 5 : 1) to afford **18** (5.30 g, 98%) as a white foam: $[\alpha]_D^{25}$ = +11.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.24 (m, 10 H), 7.03-6.99 (m, 2 H), 6.82-6.78 (m, 2 H), 4.98 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.85-4.80 (m, 3 H), 4.72 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 3.93 (dq, *J* = 1.2, 6.4 Hz, 1 H, H-5), 3.76 (s, 3 H, -OCH_3), 3.70 (d, *J* = 8.0 Hz, 1 H, H-2), 3.25 (d, *J* = 1.2 Hz, 1 H, H-4), 2.33 (brs, 1 H, C3-OH), 1.36 (d, *J* = 6.4 Hz, 3 H, H-6), 1.31 (s, 3 H, C3-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 152.0, 138.9, 137.9, 128.7, 128.4, 128.2 (2 C), 128.0, 127.6, 118.7, 114.5, 102.2 (C-1), 85.5, 81.9, 76.7, 75.4, 75.0, 69.7, 55.8, 19.7, 17.6; HRMS (ESI) m/z calcd for $C_{28}H_{32}O_6Na$ $[M + Na]^+$: 487.2091, found: 487.2102.

4-Methoxyphenyl 2-*O*-*tert*-butyldimethylsilyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranoside (19)



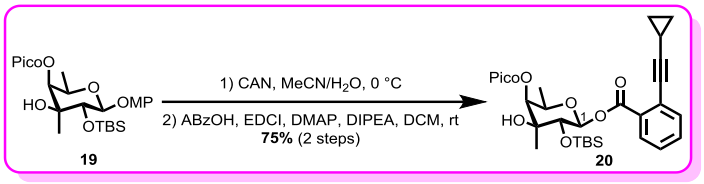
To a solution of **18** (1.00 g, 2.15 mmol) in MeOH/THF (42.0 mL, v/v = 1 : 1) was added HOAc (189 μL) and Pd/C (10 wt% on carbon, 245 mg) successively at room temperature. The resulting mixture was degassed at -78 °C (evacuated under reduced

pressure and refilled with H_2, and this process was repeated for 3 times), then was warmed to room temperature. The stirring was continued at the same temperature for 6 h, when TLC showed that the reaction reached completion. Filtration through a pad of Celite/silica gel was followed by concentration under reduced pressure delivered the intermediate which was put to the next step without further characterization.

The obtained intermediate and imidazole (866 mg, 12.72 mmol) were then dissolved in dry DMF (7.2 mL), to which TBSCl (1.92 g, 12.72 mmol) was added in three batches at 0 □. The reaction was stirred at room temperature over night, when TLC showed that the reaction reached completion. The reaction was then quenched by MeOH and the resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to afford the crude intermediate, which was put to the next step without further characterization.

To a solution of the above obtained intermediate in dry CH_2Cl_2 (7.2 mL), picolinic acid (346 mg, 2.80 mmol), EDCI (984 mg, 5.13 mmol), DMAP (551 mg, 4.51 mmol), and DIPEA (1.5 mL, 8.61 mmol) were added successively at room temperature under N_2 atmosphere. The reaction mixture was stirred at the same temperature for 3 h before the reaction had reached completion as monitored by TLC, then the solvent was removed *in vacuo* to give a residue, which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to give **19** (736 mg, 68% yield for 3 steps) as a white foam: $[\alpha]_D^{25}$ = -21.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (dq, *J* = 0.8, 1.6 Hz, 1 H), 8.16 (dt, *J* = 1.2, 8.0 Hz, 1 H), 7.90 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.52 (ddd, *J* = 1.2, 4.8, 7.6 Hz, 1 H), 7.02-6.98 (m, 2 H), 6.84-6.80 (m, 2 H), 5.15 (d, *J* = 1.2 Hz, 1 H, H-4), 4.87 (d, *J* = 8.0 Hz, 1 H, H-1), 4.14 (dq, *J* = 1.2, 6.4 Hz, 1 H, H-5), 4.07 (d, *J* = 8.0 Hz, 1 H, H-2), 3.77 (s, 3 H, -OCH_3), 1.43 (s, 3 H, C3-CH_3), 1.30 (d, *J* = 6.4 Hz, 3 H, H-6), 0.91 (s, 9 H), 0.19 (s, 3 H), 0.17 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 155.1, 151.6, 150.0, 147.9, 137.4, 127.3, 125.4, 117.9, 114.6, 101.2 (C-1), 79.6, 74.9, 74.4, 68.8, 55.8, 26.1, 20.0, 18.5, 17.2, -4.0, -4.6; HRMS (ESI) m/z calcd for $C_{26}H_{38}NO_7Si$ $[M + H]^+$: 504.2412, found: 504.2410.

2-*O*-*tert*-Butyldimethylsilyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (20)

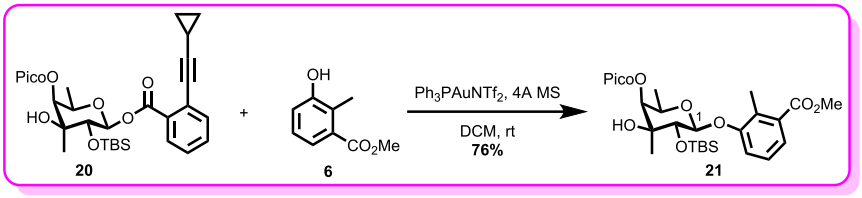


To a solution of **19** (198 mg, 0.39 mmol) in MeCN/H_2O (7.8 mL, v/v = 3 : 2) was added CAN (617 mg, 1.13 mmol) at 0 °C in three batches. The reaction was stirred for 20 min at the same temperature, then EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with ice water, saturated aqueous $NaHCO_3$, $Na_2S_2O_3$, and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 2 : 1 to 1 : 1) to give hemiacetal intermediate (137 mg, 88%) as a light yellow foam. The resulting lactol intermediate was directly put into the next step without further characterization.

To a solution of the above obtained hemiacetal intermediate (137 mg, 0.345 mmol) in dry CH_2Cl_2 (1.2 mL) were added ABzOH (76 mg, 0.41 mmol), EDCI (154 mg, 0.80 mmol), DMAP (89 mg, 0.73 mmol), and DIPEA (249 μL, 1.43 mmol) successively at room temperature under N_2 atmosphere. The reaction was stirred at the same temperature for 2 h, which was followed by solvent evaporation *in vacuo* to give the crude product that was further purified by silica gel column chromatography (PE/EA = 4 : 1 to 2 : 1) to give **20** (166 mg, 85%) as a white foam: $[\alpha]_D^{25}$ = -30.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dt, *J* = 1.2, 4.4 Hz, 1 H), 8.15 (dt, *J* = 0.8, 8.0 Hz, 1 H), 8.03 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.91 (td, *J* = 2.0, 8.0 Hz, 1 H), 7.54 (ddd, *J* = 1.2, 4.8, 7.6 Hz, 1 H), 7.49 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.44 (td, *J* = 1.2, 7.2 Hz, 1 H), 7.31 (td, *J* = 1.2, 7.6 Hz, 1 H), 5.88 (d, *J* = 8.4 Hz, 1 H, H-1), 5.14 (d, *J* = 1.2 Hz, 1 H, H-4), 4.24 (ddd, *J* = 1.2, 6.0, 12.4 Hz, 1 H, H-5), 4.12 (d, *J* = 8.0 Hz, 1 H, H-2), 1.55-1.48 (m, 1 H), 1.47 (s, 3 H, C3-CH_3), 1.30 (d, *J* = 6.4 Hz, 3 H, H-6), 0.90-0.80 (m, 4 H), 0.79 (s, 9 H), 0.13 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.6, 149.9,

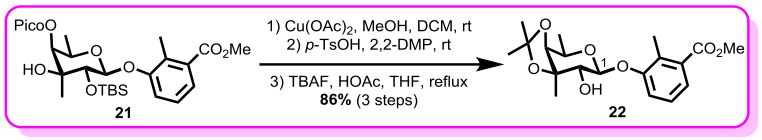
148.1, 137.4, 134.4, 132.1, 130.9, 130.7, 127.3, 126.9, 125.6, 125.4, 100.1, 94.2 (C-1), 80.0, 74.7, 74.6, 74.0, 69.8, 25.9, 19.8, 18.3, 17.1, 9.1, 9.0, 0.8, -4.4, -4.6; HRMS (ESI) m/z calcd for $C_{31}H_{40}NO_7Si$ $[M + H]^+$: 566.2569, found: 566.2578.

Methyl 2-methyl-3-*O*-[2-*O*-*tert*-butyldimethylsilyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranosyl]-benzoate (21)



To a stirred solution of glycosyl donor **20** (95 mg, 0.17 mmol) and acceptor **6** (28 mg, 0.17 mmol) in dry CH_2Cl_2 (3.4 mL) was added activated 4 Å molecular sieves (340 mg) at room temperature under N_2 atmosphere. The resulting suspension was stirred at the same temperature for 1 h before $Ph_3PAuNTf_2$ (25 mg, 0.034 mmol) was added at the same temperature. The resulting mixture was stirred at the same temperature for another 80 min, before filtration was conducted to remove 4 Å molecular sieves. Concentration under reduced pressure yielded the crude product, which was further purified by silica gel column chromatography (PE/EA = 4 : 1 to 3 : 1) to furnish **21** (70 mg, 76%) as a white foam: $[\alpha]_D^{25}$ = +8.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (dq, *J* = 0.8, 4.8 Hz, 1 H), 8.15 (dt, *J* = 1.2, 8.0 Hz, 1 H), 7.94 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.56-7.51 (m, 2 H), 7.21-7.13 (m, 2 H), 5.14 (d, *J* = 0.8 Hz, 1 H, H-4), 5.01 (d, *J* = 8.0 Hz, 1 H, H-1), 4.16 (d, *J* = 7.6 Hz, 1 H, H-2), 4.09 (qd, *J* = 1.2, 6.4 Hz, 1 H, H-5), 3.88 (s, 3 H, $-CO_2CH_3$), 2.53 (s, 3 H, Ar-CH_3), 1.45 (s, 3 H, C3-CH_3), 1.25 (d, *J* = 6.4 Hz, 3 H, H-6), 0.90 (s, 9 H), 0.21 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 165.4, 155.7, 149.9, 147.8, 137.7, 132.0, 130.4, 127.4, 126.0, 125.5, 124.4, 119.1, 100.7 (C-1), 79.9, 75.0, 74.5, 69.0, 52.1, 26.1, 20.1, 18.6, 17.2, 13.8, -4.3, -4.5; HRMS (ESI) m/z calcd for $C_{28}H_{40}NO_8Si$ $[M + H]^+$: 546.2518, found: 546.2517.

Methyl 2-methyl-3-*O*-(3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-benzoate (22)

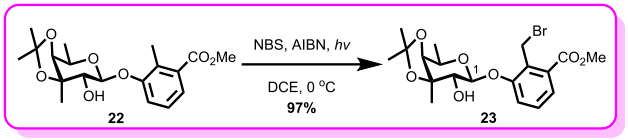


To a solution of **21** (300 mg, 0.55 mmol) in CH_2Cl_2 (10.6 mL) was added $Cu(OAc)_2$ (144 mg, 0.72 mmol) and MeOH (1.5 mL) successively at room temperature. The reaction was stirred for 2 h at the same temperature, then EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with H_2O, saturated aqueous NH_4Cl and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered the intermediate which was put to the next step without further purification.

The above obtained intermediate was dissolved in 2,2-dimethoxypropane (5.0 mL), to which *p*-TsOH (18 mg, 0.11 mmol) was added at room temperature. The reaction was stirred for 30 min at the same temperature, before Et_3N was added to quench the reaction. Evaporation *in vacuo* was adopted to remove all volatile solvent, and the resulting intermediate was put to the next step without further purification.

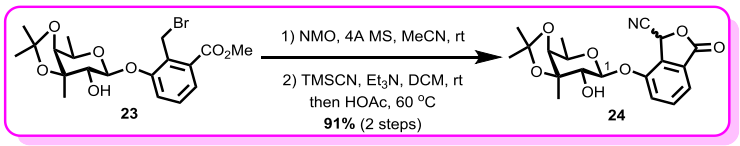
To a solution of the above obtained intermediate in THF (5.3 mL) were added HOAc (383 μL, 6.36 mmol) and TBAF (1.66 g, 6.36 mmol) successively at room temperature. The resulting mixture was heated to reflux for 18 h, when TLC showed that the reaction reached completion. The solvent was removed *in vacuo* to give a residue, which was further purified by silica gel column chromatography (PE/EA = 10 : 1 to 5 : 1) to give **22** (173 mg, 86% yield for 3 steps) as a white solid: $[\alpha]_D^{25}$ = -34.2 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 2.0, 7.2 Hz, 1 H), 7.22-7.16 (m, 2 H), 4.70 (d, *J* = 8.4 Hz, 1 H, H-1), 4.03 (dt, *J* = 0.8, 2.0, 8.4 Hz, 1 H, H-2), 3.98 (dq, *J* = 2.0, 6.4 Hz, 1 H, H-5), 3.89 (s, 3 H, -CO_2CH_3), 3.70 (d, *J* = 2.0 Hz, 1 H, H-4), 2.48 (s, 3 H, Ar-CH_3), 2.38 (d, *J* = 2.8 Hz, 1 H, C2-OH), 1.59 (s, 3 H), 1.45 (d, *J* = 6.4 Hz, 3 H, H-6), 1.40 (s, 3 H,), 1.38 (s, 3 H, C3-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 156.1, 132.0, 130.1, 126.3, 124.8, 119.4, 109.2, 101.3 (C-1), 82.1, 81.6, 75.0, 68.5, 52.2, 28.5, 27.2, 17.5, 17.1, 13.4; HRMS (ESI) m/z calcd for $C_{19}H_{27}O_7$ $[M + H]^+$: 367.1752, found: 367.1753.

Methyl 2-bromomethyl-3-*O*-(3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-benzoate (23)



To a solution of **22** (235 mg, 0.64 mmol) in dry DCE (12.8 mL) was added NBS (122 mg, 0.71 mmol) and AIBN (10 mg, 0.064 mmol) successively under N_2 atmosphere at room temperature. The resulting mixture was cooled to 0 °C and stirred under the irradiation of UV Identification Lamp (365 nm) for 15 min, at which time TLC showed that all the starting materials disappeared. The reaction was then quenched by Et_3N, which was followed by evaporation under reduced pressure to remove all volatile solvent to give a residue. The resulting residue was further purified by silica gel column chromatography (PE/EA = 4 : 1) to give **23** (276 mg, 97%) as a white solid: $[\alpha]_D^{25}$ = +32.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 2.8, 7.6 Hz, 1 H), 7.38 (td, *J* = 3.2, 8.0 Hz, 1 H), 7.25-7.23 (m, 1 H), 5.31 (d, *J* = 9.2 Hz, 1 H, -CH_2Br), 4.88 (d, *J* = 9.2 Hz, 1 H, -CH_2Br), 4.82 (d, *J* = 8.4 Hz, 1 H, H-1), 4.10-4.02 (m, 2 H, H-2, H-5), 3.94 (s, 3 H, -CO_2CH_3), 3.73 (s, 1 H, H-4), 3.00 (brs, 1 H, C2-OH), 1.62 (s, 3 H), 1.49 (d, *J* = 6.0 Hz, 3 H, H-6), 1.41-1.40 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 156.3, 130.6, 129.7, 128.1, 125.1, 118.5, 109.3, 100.9 (C-1), 81.9, 81.4, 74.8, 68.7, 52.6, 28.5, 27.2, 25.3, 17.6, 17.1; HRMS (ESI) m/z calcd for $C_{19}H_{25}BrO_7Na$ [M + Na]$^+$: 467.0676, found: 467.0677.

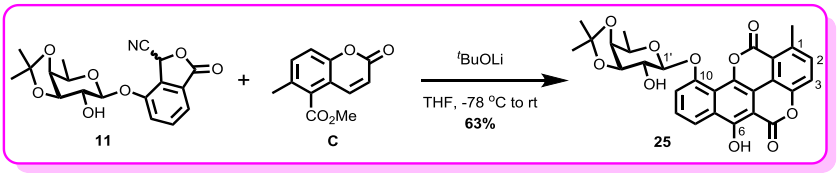
4-*O*-(3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-3-cyanoisobenzofuran-1(3*H*)-one (24)



Similar procedures as that used for the synthesis of **11** were adopted to convert **23** (276 mg, 0.62 mmol) to **24** (211 mg, 91% yield for 2 steps) as an inseparable mixture of

stereomers: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.77-7.72 (m, 1.9 H), 7.69-7.58 (m, 3.8 H), 6.54 (s, 0.9 H, -CHCN), 6.52 (s, 1 H, -CHCN), 5.20-5.15 (m, 1.9 H, H-1), 4.91 (t, *J* = 3.6 Hz, 1 H, C2-OH), 4.35-4.26 (m, 2.8 H), 3.98-3.93 (m, 1.9 H, H-2), 3.85-3.84 (m, 1.9 H), 1.46 (s, 5.7 H), 1.40-1.38 (d, *J* = 3.1 Hz, 11.4 H), 1.34 (s, 5.7 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.2, 153.4, 153.3, 134.1 (2 C), 131.9, 131.1, 127.0, 126.9, 122.6, 121.3, 120.0, 119.5, 115.0, 114.6, 109.0, 101.4 (C-1), 101.0 (C-1), 82.7, 82.6, 82.5, 74.8, 74.7, 69.0, 68.9, 65.4 (Ar-CH-), 65.3 (Ar-CH-), 28.7 (2 C), 27.4, 27.3, 17.8, 17.2; HRMS (ESI) m/z calcd for $C_{19}H_{22}NO_7$ $[M + H]^+$: 376.1391, found: 376.1390.

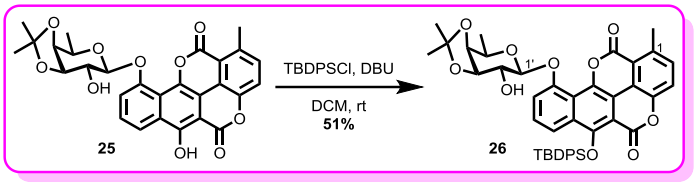
Chartarin 3,4-*O*-isopropylidene-β-D-fucopyranoside (25)



To a solution of **11** (20 mg, 0.055 mmol) and **C** (12 mg, 0.055 mmol) in dry THF (1.2 mL) was treated dropwise with *t*-BuOLi (61 μL, 0.061 mmol, 1 M in THF) at -78 □ under N_2 atmosphere. The reaction mixture was stirred at the same temperature for 30 min and then warmed up to room temperature. After being stirred at room temperature for 4 h, EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with saturated aqueous NH_4Cl, H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (DCM/EA = 5 : 1) to give **25** (18 mg, 63%) as a yellow solid: $[\alpha]_D^{25}$ = -64.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1 H, C6-OH), 7.97 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.53 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.47-7.41 (m, 3 H), 4.83 (d, *J* = 8.4 Hz, 1 H, H-1'), 4.32 (d, *J* = 3.6 Hz, 1 H, C2'-OH), 4.26 (dd, *J* = 5.2, 7.6 Hz, 1 H, H-3'), 4.16-4.11 (m, 2 H, H-2', H-4'), 4.00 (td, *J* = 3.6, 8.0 Hz, 1 H, H-5'), 2.79 (s, 3 H, C1-CH_3), 1.67 (s, 3 H), 1.57 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 159.5, 157.1, 154.4, 146.5, 140.3, 137.6, 133.1, 128.2, 126.1, 121.4, 119.4, 118.7, 118.5, 118.0, 117.0, 110.0, 108.5, 103.5 (C-1'), 96.1,

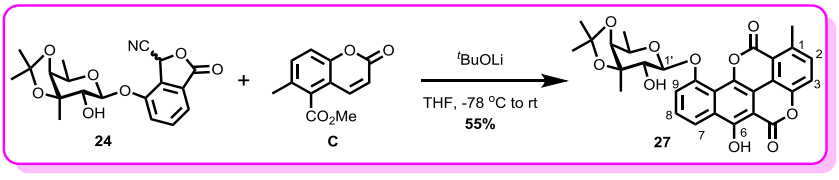
78.8, 76.1, 73.3, 69.6, 28.6, 26.6, 22.2, 17.0; HRMS (ESI) m/z calcd for $C_{28}H_{24}O_{10}Na$ $[M + Na]^+$: 543.1261, found: 543.1259.

6-*O*-*tert*-Butyldiphenylsilyl chartarin 3,4-*O*-isopropylidene-β-D-fucopyranoside (26)



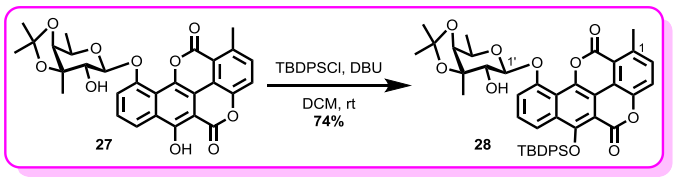
To a solution of **25** (80 mg, 0.15 mmol) in dry CH_2Cl_2 (1.5 mL) was added DBU (124 μL, 0.46 mmol) and TBDPSCl (208 μL, 0.46 mmol) successively at room temperature. The mixture was stirred at the same temperature for 30 min, at which time TLC shown that the reaction reached to completion. The reaction mixture was directly purified by silica gel column chromatography (PE/EA = 3 : 1 to 1 : 1) to give **25** (22 mg) and **26** (60 mg, 51%, brsm 79%) as a yellow solid: $[\alpha]_D^{25}$ = -15.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 1.2, 8.4 Hz, 1 H), 7.73-7.70 (m, 2 H), 7.66-7.63 (m, 3 H), 7.51 (t, *J* = 8.4 Hz, 1 H), 7.39-7.24 (m, 8 H), 4.95 (d, *J* = 8.0 Hz, 1 H, H-1'), 4.71 (brs, 1 H, C2'-OH), 4.27 (dd, *J* = 4.8, 7.6 Hz, 1 H, H-3'), 4.20-4.13 (m, 3 H, H-2', H-4', H-5'), 2.85 (s, 3 H, C1-CH_3), 1.66 (s, 3 H), 1.59 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.43 (s, 3 H), 1.13 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 157.1, 154.9, 153.3, 147.1, 139.9, 139.2, 135.3 (2 C), 133.0, 132.7, 132.6, 131.0, 129.8, 129.7, 127.9, 127.5 (2 C), 120.9, 120.4, 119.5, 118.9, 117.1, 117.0, 110.4, 110.1, 104.5, 103.8 (C-1'), 78.9, 76.2, 73.4, 69.8, 28.5, 27.2, 26.6, 22.2, 21.1, 17.0; HRMS (ESI) m/z calcd for $C_{44}H_{43}O_{10}Si$ $[M + H]^+$: 759.2620, found: 759.2621.

Chartarin 10-*O*-(3-*C*-methyl-3,4-*O*-isopropylidene)-β-D-fucopyranoside (27)



Similar procedures as those used for the synthesis of **25** was adopted to convert **24** (30 mg, 0.080 mmol) and **C** (17 mg, 0.080 mmol) to **27** (23 mg, 55%) as a yellow solid: $[\alpha]_D^{25}$ = -87.0 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 1 H, C6-OH), 8.16 (d, *J* = 8.4 Hz, 1 H, H-7), 7.68 (d, *J* = 7.6 Hz, 1 H, H-9), 7.59 (t, *J* = 8.0 Hz, 1 H, H-8), 7.54 (d, *J* = 8.4 Hz, 1 H, H-3), 7.48 (d, *J* = 8.4 Hz, 1 H, H-2), 4.91 (d, *J* = 8.0 Hz, 1 H, H-1'), 4.32 (brs, 1 H, C2'-OH), 4.24 (d, *J* = 8.4 Hz, 1 H, H-2'), 4.16 (qd, *J* = 2.0, 6.8 Hz, 1 H, H-5'), 3.77 (d, *J* = 2.0 Hz, 1 H, H-4'), 2.85 (s, 3 H, C1-CH_3), 1.68 (s, 3 H), 1.58 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.46 (s, 3 H), 1.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 159.8, 157.5, 154.9, 146.7, 140.4, 138.1, 133.2, 128.4, 126.6, 121.5, 119.8, 118.9 (2 C), 117.8, 117.3, 109.1, 108.8, 103.3 (C-1'), 96.4, 82.1, 81.6, 74.8, 68.8, 28.7, 27.3, 22.2, 17.6, 17.3; HRMS (ESI) m/z calcd for $C_{29}H_{26}O_{10}Na$ $[M + Na]^+$: 557.1418, found: 557.1414.

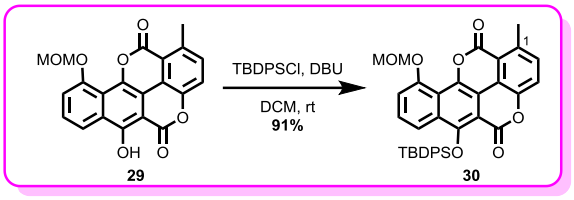
6-*O*-*tert*-Butyldiphenylsilyl chartarin 10-*O*-(3-*C*-methyl-3,4-*O*-isopropylidene)-β-D-fucopyranoside (28)



Similar procedure as that used for the synthesis of **26** was adopted to convert **27** (47 mg, 0.088 mmol) to **28** (50 mg, 74%, brsm 99%) as a yellow solid: $[\alpha]_D^{25}$ = -26.5 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 1.6, 8.0 Hz, 2 H), 7.67-7.63 (m, 3 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 7.39-7.23 (m, 8 H), 4.98 (d, *J* = 8.4 Hz, 1 H, H-1'), 4.61 (brs, 1 H, C2'-OH), 4.31 (d, *J* = 8.4 Hz, 1 H, H-2'), 4.18-4.13 (m, 1 H, H-5'), 3.78 (d, *J* = 2.0 Hz, 1 H, H-4'), 2.85 (s, 3 H, C1-CH_3), 1.66 (s, 3 H), 1.58 (d, *J* = 6.8 Hz, 3 H, H-6'), 1.46 (s, 3 H), 1.44 (s, 3 H), 1.13 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 157.1, 155.0, 153.3, 147.1, 140.0, 139.2, 135.3 (2 C), 133.0, 132.7, 132.6, 131.0, 129.8, 129.7, 127.9, 127.5 (2 C), 120.9, 120.2, 119.5, 118.9, 117.0, 116.5, 110.4, 109.1, 104.5, 103.3 (C-1'), 82.1, 81.6, 74.8, 68.8, 28.7, 27.3, 27.2, 22.2, 21.1, 17.5, 17.3; HRMS (ESI) m/z calcd for $C_{45}H_{45}O_{10}Si$ $[M + H]^+$: 773.2777, found:

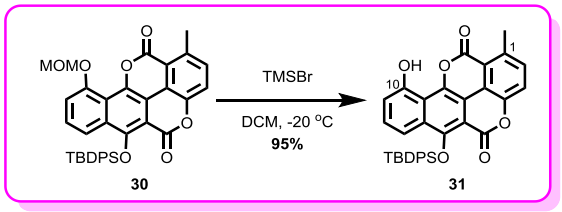
773.2374.

6-*O-tert*-Butyldiphenylsilyl-10-*O*-methoxymethyl chartarin (30)



To a stirred solution of **29**[S3] (150 mg, 0.40 mmol) in dry DCM (8.0 mL) was added DBU (118 μL, 0.79 mmol) at room temperature under N_2 atmosphere. After being stirred for 5 min at the same temperature, TBDPSCl (206 μL, 0.79 mmol) was added under N_2 atmosphere. The resulting suspension was stirred at room temperature for 3 h and then was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 6 : 1) to afford compound **30** (223 mg, 91%) as a yellow powder: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1 H), 7.71-7.70 (m, 4 H), 7.55 (td, *J* = 1.6, 8.0 Hz, 1 H), 7.42-7.23 (m, 9 H), 5.50 (s, 2 H, -OCH_2O-), 3.73 (s, 3 H, -OCH_3), 2.86 (s, 3 H, C1-CH_3), 1.14 (s, 9 H, -Si^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 157.3, 154.1, 153.2, 147.0, 140.5, 138.9, 135.2, 132.9, 132.8, 131.3, 129.7, 127.8, 127.5, 120.5, 119.5 (3 C), 117.4, 116.2, 110.2, 104.3, 96.2, 57.0, 27.2, 22.5, 21.1; HRMS (ESI) $[M + Na]^+$ calcd for $C_{37}H_{32}SiO_7Na$: 639.1810, found: 639.1800.

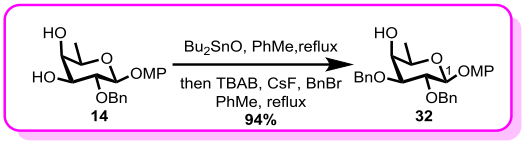
6-*O-tert*-Butyldiphenylsilyl chartarin (31)



To a stirred solution of **30** (649 mg, 1.05 mmol) in dry DCM (26.3 mL) was added TMSBr (0.56 mL, 4.21 mmol) at -20 °C under N_2 atmosphere. The resulting suspension was stirred at the same temperature for 20 min before saturated aqueous $NaHCO_3$ was added to quench the reaction. The resulting mixture was washed successively with

saturated aqueous $NaHCO_3$ and brine, and was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration *in vacuo* to give the crude product, which was further purified by silica gel column chromatography (PE/EA = 7 : 1) to furnish **31** (574 mg, 95%) as a yellow powder: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (brs, 1 H, C10-OH), 8.22 (dd, *J* = 2.0, 8.4 Hz, 1 H), 7.71-7.69 (m, 4 H), 7.51 (td, *J* = 2.4, 8.0 Hz, 1 H), 7.37-7.20 (m, 9 H), 2.82 (s, 3 H, C1-CH_3), 1.13 (s, 9 H, -Si^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 156.9, 154.0, 153.7, 147.1, 140.6, 139.5, 135.2, 133.0, 132.8, 130.7, 129.7, 128.9, 127.5, 121.3, 119.2, 117.7, 116.5 (2 C), 115.8, 108.9, 103.5, 27.1, 22.5, 21.1; HRMS (ESI) $[M + Na]^+$ calcd for $C_{35}H_{28}SiO_6Na$: 595.1547, found: 595.1550.

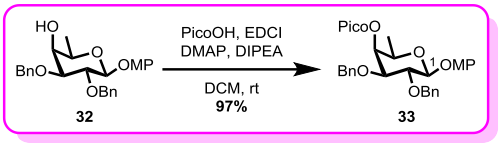
4-Methoxyphenyl 2,3-di-*O*-benzyl-β-D-fucopyranoside (32)



To a stirred solution of the **14** (700 mg, 1.94 mmol) in dry toluene (19.0 mL) was added Bu_2SnO (532 mg, 2.14 mmol) at room temperature. The reaction mixture was then heated to 120 °C and the stirring was continued for 4 h. After being cooled down to room temperature, the solvent was removed *in vacuo* to give a residue. The obtained residue was then dissolved in dry toluene (19.0 mL), to which BnBr (250 μL, 2.14 mmol), TBAB (664 mg, 2.06 mmol) and CsF (295 mg, 1.94 mmol) were added successively under N_2 atmosphere. The resulting mixture was stirred for another 4 h at 120 °C, which was then cooled to the room temperature and diluted with ethyl acetate. After being washed with water and brine successively, the solution was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to give the crude product, which was further purified by silica gel column chromatography (PE/EA = 4 : 1) to provide **32** (821 mg, 94%) as a white solid: $[\alpha]_D^{25}$ = +4.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 10 H), 7.05-7.03 (m, 2 H), 6.85-6.83 (m, 2 H), 5.03 (d, *J* = 10.8 Hz, 1 H, Ar-CH_2-), 4.85-4.83 (m, 2 H, H-1, Ar-CH_2-), 4.79 (t, *J* = 12.0 Hz, 2 H, Ar-CH_2-), 3.90-3.86 (m, 1 H), 3.81-3.78 (m, 4 H), 3.65-3.57 (m, 2 H), 2.49 (s, 1 H, C4-OH), 1.40 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz,

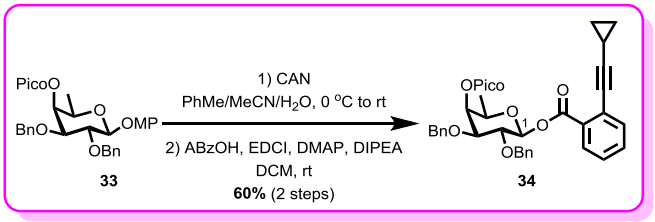
$CDCl_3$) δ 155.4, 151.7, 138.6, 138.0, 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 118.8, 114.6, 103.0 (C-1), 81.0, 78.6, 75.5, 72.6, 70.3, 69.5, 55.8, 16.6; HRMS (ESI) $[M + Na]^+$ calcd for $C_{27}H_{30}O_6Na$: 473.1935, found: 473.1943.

4-Methoxyphenyl 2,3-di-*O*-benzyl-4-*O*-picolinyl-β-D-fucopyranoside (33)



To a solution of **32** (795 mg, 1.76 mmol) in dry DCM (8.8 mL) was added PicoOH (391 mg, 3.18 mmol), EDCI (1.22 g, 6.36 mmol), DMAP (647 mg, 5.30 mmol), and DIPEA (1.8 mL, 10.33 mmol) successively, the resulting solution was stirred at room temperature overnight. Then the mixture was concentrated *in vacuo* and purified by silica gel column chromatography (PE/EA = 2 : 1) to deliver **33** (952 mg, 97%) as a colorless oil: $[\alpha]_D^{25}$ = +48.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 2.0, 4.4 Hz, 1 H), 8.20 (d, *J* = 7.6 Hz, 1 H), 7.84-7.79 (m, 1 H), 7.48-7.43 (m, 1 H), 7.37-7.22 (m, 10 H), 7.08 (dd, *J* = 2.0, 9.2 Hz, 2 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 5.69 (d, *J* = 3.2 Hz, 1 H, H-4), 5.02 (d, *J* = 10.8 Hz, 1 H, Ar-CH_2-), 4.96 (d, *J* = 7.6 Hz, 1 H, H-1), 4.86-4.82 (m, 2 H, Ar-CH_2-), 4.63 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 3.98-3.93 (m, 1 H), 3.89 (dd, *J* = 6.4, 13.2 Hz, 1 H, H-5), 3.79-3.75 (m, 4 H), 1.33 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 155.3, 151.6, 150.2, 147.4, 138.4, 137.6, 137.1, 128.3 (2 C), 128.1 (2 C), 127.7 (2 C), 127.1, 125.6, 118.5, 114.5, 102.9 (C-1), 79.2, 78.6, 75.5, 72.2, 71.1, 69.4, 55.6, 16.6; HRMS (ESI) $[M + H]^+$ calcd for $C_{33}H_{34}NO_7$: 556.2330, found: 556.2326.

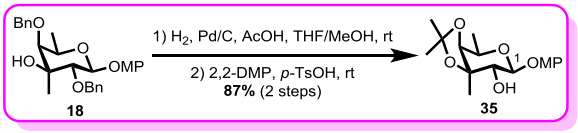
2,3-di-*O*-Benzyl-4-*O*-picoloyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (34)



To a solution of **33** (837 mg, 1.51 mmol) in PhMe/MeCN/H_2O (50.4 mL, v/v/v = 2 : 3 : 2) was added CAN (2.48 g, 4.53 mmol) portionwise under 0 °C, then the resulting mixture was warmed to room temperature and the stirring was continued for 30 min, which was followed by addition of ethyl acetate to dilute the mixture. The resulting solution was washed successively with ice water, saturated aqueous $NaHCO_3$, and brine, and was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to afford the crude product, which was further purified by silica gel column chromatography (PE/EA = 1 : 1) to provide the hemiacetal intermediate (454 mg, 67%) as a light yellow solid, which was put to the next step directly without detailed characterization.

The above obtained lactol was dissolved in dry DCM (5.0 mL), to which *o*-cycolpropylethynylbenzoic acid (226 mg, 1.21 mmol), EDCI (465 mg, 2.42 mmol), DMAP (247 mg, 2.02 mmol), and DIPEA (0.70 mL, 4.04 mmol) were added under N_2 atmosphere at room temperature. The resulting solution was stirred at the same temperature until TLC showed the complete consumption of the starting material. After being diluted with ethyl acetate, the reaction mixture was successively washed with 1N HCl, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous Na_2SO_4. Filtration combined with concentration under reduced pressure afforded a residue, which was purified by silica gel column chromatography (PE/EA = 3 : 1) to deliver compound **34** (555 mg, 89%) exclusively as a white foam: $[\alpha]_D^{25}$ = +47.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 10.8 Hz, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 7.88 (td, *J* = 1.6, 8.0 Hz, 1 H), 7.52-7.49 (m, 2 H), 7.46-7.43 (m, 1 H), 7.35-7.21 (m, 11 H), 5.95 (d, *J* = 8.0 Hz, 1 H, H-1), 5.73 (d, *J* = 3.6 Hz, 1 H, H-4), 4.87-4.80 (m, 3 H, Ar-CH_2-), 4.64 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 4.06-3.97 (m, 2 H, H-5, H-2), 3.89 (dd, *J* = 3.2, 9.6 Hz, 1 H, H-3), 1.56-1.49 (m, 1 H), 1.33 (d, *J* = 6.4 Hz, 3 H, H-6), 0.93-0.84 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.1, 150.3, 147.6, 138.1, 137.6, 137.1, 134.5, 132.2, 130.8, 130.5, 128.5, 128.3 (2 C), 128.1, 127.9, 127.7, 127.2, 127.1, 125.6, 125.6, 100.2, 94.6 (C-1), 79.9, 75.4, 74.6, 72.4, 71.3, 70.5, 16.5, 9.1, 0.9; HRMS (ESI) $[M + Na]^+$ calcd for $C_{38}H_{35}NO_7Na$: 640.2306, found: 640.2312.

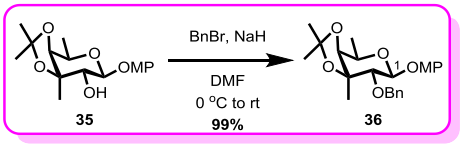
4-Methoxyphenyl 3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (35)



To a solution of **18** (5.30 g, 11.41 mmol) in MeOH/THF (226.0 mL, v/v = 1 : 1) was added HOAc (1.0 mL) and Pd/C (10 wt% on carbon, 1.30 g) successively at room temperature. The resulting mixture was degassed at -78 °C (evacuated under reduced pressure and refilled with H_2, and this process was repeated for 3 times), then was warmed up to room temperature. The black suspension was then stirred over night at the same temperature, before all black solids were removed by filtration through a pad of Celite/silica gel. The filtrate was concentrated *in vacuo* and the resulting residue was put to the next step without further purification.

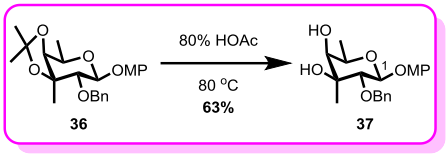
The above obtained intermediate was dissolved in 2,2-dimethoxypropane (30.0 mL), to which *p*-TsOH (98 mg, 0.57 mmol) was added at room temperature. The reaction mixture was stirred for 1 h at the same temperature, before Et_3N was added to quench the reaction. Evaporation under reduced pressure provided the crude product, which was purified by silica gel column chromatography (PE/EA = 3 : 1) to give **35** (3.20 g, 87% yield for 2 steps) as a white solid: $[\alpha]_D^{25}$ = -29.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.03-6.99 (m, 2 H), 6.84-6.80 (m, 2 H), 4.63 (d, *J* = 8.4 Hz, 1 H, H-1), 3.93-3.88 (m, 2 H, H-2, H-5), 3.77 (s, 3 H, -OCH_3), 3.67 (d, *J* = 2.0 Hz, 1 H, H-4), 2.51-2.48 (m, 1 H, C2-OH), 1.57 (s, 3 H), 1.44 (d, *J* = 6.4 Hz, 3 H, H-6), 1.39 (s, 3 H), 1.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 151.4, 118.9, 114.6, 109.1, 101.7 (C-1), 82.1, 81.5, 74.9, 68.4, 55.8, 28.5, 27.2, 17.5, 17.1; HRMS (ESI) m/z calcd for $C_{17}H_{25}O_6$ $[M + H]^+$: 325.1646, found:325.1654.

4-Methoxyphenyl 2-*O*-benzyl-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (36)



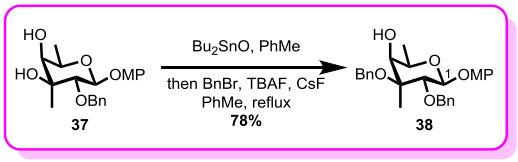
Similar procedure as that used for the synthesis of **13** was adopted to convert **35** (762 mg, 2.35 mmol) to **36** (964 mg, 99%) as colorless oil: $[\alpha]_D^{25}$ = +21.5 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 1.6, 8.4 Hz, 1 H), 7.35-7.31 (m, 2 H), 7.28-7.24 (m, 2 H), 7.03-6.99 (m, 2 H), 6.84-6.80 (m, 2 H), 4.93 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.89 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 4.74 (d, *J* = 8.4 Hz, 1 H, H-1), 3.92 (qd, *J* = 2.0, 6.4, Hz, 1 H, H-5), 3.77 (s, 3 H, -OCH_3), 3.76 (d, *J* = 8.4 Hz, 1 H, H-2), 3.65 (d, *J* = 2.0 Hz, 1 H, H-4), 1.43-1.41 (m, 6 H), 1.39 (s, 3 H), 1.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 151.9, 138.7, 128.3, 128.2, 127.6, 118.9, 114.6, 108.9, 102.0 (C-1), 82.4 (2 C), 81.3, 74.5, 68.0, 55.8, 28.3, 27.3, 18.5, 17.1; HRMS (ESI) $[M + Na]^+$ calcd for $C_{24}H_{30}O_6Na$: 437.1935, found: 437.1929.

4-Methoxyphenyl 2-*O*-benzyl-3-*C*-methyl-β-D-fucopyranoside (37)



Similar procedures as that used for the synthesis of **14** was adopted to convert **36** (1.19 g, 2.87 mmol) to **37** (676 mg, 63%) as colorless oil: $[\alpha]_D^{25}$ = +16.9 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.27 (m, 5 H), 7.05-7.01 (m, 2 H), 6.85-6.81 (m, 2 H), 5.04 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.86-4.82 (m, 2 H, H-1, Ar-CH_2-), 3.92 (qd, *J* = 1.2, 6.4 Hz, 1 H, H-5), 3.78 (s, 3 H, -OCH_3), 3.73 (d, *J* = 8.0 Hz, 1 H, H-2), 3.37 (d, *J* = 0.8 Hz, 1 H, H-4), 2.61 (brs, 2 H, C3,4-OH), 1.37 (d, *J* = 6.4 Hz, 3 H, H-6), 1.30 (s, 3 H, C3-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 151.7, 138.8, 128.5, 128.0, 127.8, 118.7, 114.6, 102.4 (C-1), 81.3, 76.7, 75.2, 74.7, 69.4, 55.8, 19.7, 17.0; HRMS (ESI) $[M + Na]^+$ calcd for $C_{21}H_{26}O_6Na$: 397.1621, found: 397.1615.

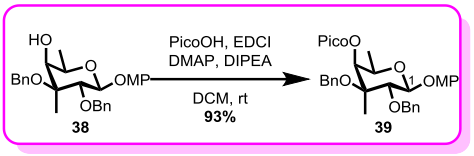
4-Methoxyphenyl 2,3-di-*O*-benzyl-3-*C*-methyl-β-D-fucopyranoside (38)



Similar procedures as that used for the synthesis of **32** was adopted to convert **37** (314

mg, 0.84 mmol) to **38** (303 mg, 78%) as colorless oil: $[\alpha]_D^{25}$ = +42.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 10 H), 7.05-7.00 (m, 2 H), 6.83-6.79 (m, 2 H), 5.03 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.90 (d, *J* = 8.0 Hz, 1 H, H-1), 4.81 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.67 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.62 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 3.90 (d, *J* = 8.0 Hz, 1 H, H-2), 3.86-3.81 (m, 1 H, H-5), 3.76 (s, 3 H, -OCH_3), 3.61 (d, *J* = 1.2 Hz, 1 H, H-4), 2.95 (brs, 1 H, C4-OH), 1.45 (s, 3 H, C3-CH_3), 1.42 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.9, 138.9, 138.6, 128.6, 128.3, 127.9, 127.7, 127.6, 127.5, 118.9, 114.6, 102.3 (C-1), 81.1, 79.8, 75.2, 74.2, 69.4, 64.4, 55.8, 17.1, 15.9; HRMS (ESI) $[M + Na]^+$ calcd for $C_{28}H_{32}O_6Na$: 487.2091, found: 487.2086.

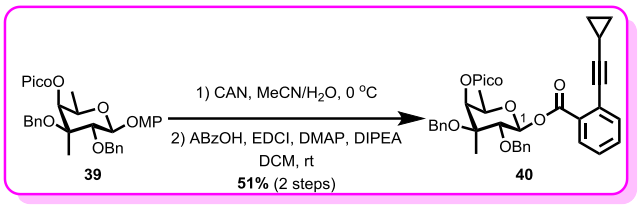
4-Methoxyphenyl 2,3-di-*O*-benzyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranoside (39)



Similar procedure as that used for synthesis of **33** from **32** was applied to convert **38** (568 mg, 1.22 mmol) to **39** under the combined effect of PicoOH (181 mg, 1.46 mmol), EDCI (563 mg, 2.93 mmol), DMAP (300 mg, 2.45 mmol), and DIPEA (850 μL, 4.89 mmol). After purified by silica gel column chromatography (PE/EA = 2 : 1), compound **39** (648 mg, 93%) was obtained as a white foam: $[\alpha]_D^{25}$ = +55.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (dq, *J* = 0.8, 1.6 Hz, 1 H), 8.08 (dt, *J* = 1.2, 8.0 Hz, 1 H), 7.74 (td, *J* = 2.0, 8.0 Hz, 1 H), 7.40-7.36 (m, 3 H), 7.30-7.22 (m, 3 H), 7.19-7.16 (m, 2 H), 7.14-7.06 (m, 5 H), 6.85-6.81 (m, 2 H), 5.49 (s, 1 H, H-4), 5.06 (d, *J* = 8.0 Hz, 1 H, H-1), 5.01 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.89 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.60 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.52 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.09-4.05 (m, 1 H, H-5), 4.03 (d, *J* = 8.0 Hz, 1 H, H-2), 3.73 (s, 3 H, -OCH_3), 1.55 (s, 3 H, C3-CH_3), 1.32 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 155.2, 151.8, 150.0, 147.5, 138.7, 138.5, 136.8, 128.1, 127.9, 127.8, 127.4, 127.2, 127.0, 126.8, 125.5, 118.5, 114.4, 102.0 (C-1), 80.9, 78.6, 75.3, 75.0, 68.8, 64.0, 55.5, 17.1, 16.2; HRMS

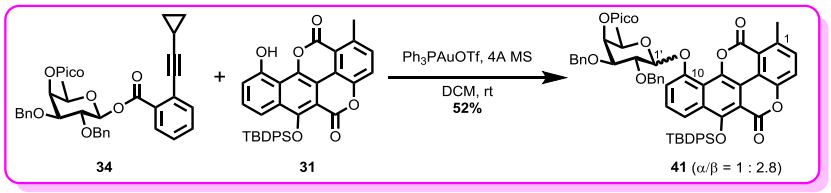
(ESI) $[M + Na]^+$ calcd for $C_{34}H_{35}NO_7Na$: 592.2306, found: 592.2298.

2,3-di-*O*-Benzyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (40)



Similar procedures as those used for the synthesis of **20** from **19** were applied to convert **39** (386 mg, 0.68 mmol) to **40** (219 mg, 51% over 2 steps) as a white foam: $[\alpha]_D^{25}$ = +46.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.79-8.77 (m, 1 H), 8.07 (dt, *J* = 1.2, 8.0 Hz, 1 H), 7.97 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.80 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.52 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.47-7.41 (m, 2 H), 7.30-7.27 (m, 1 H), 7.23-7.16 (m, 7 H), 7.14-7.10 (m, 3 H), 6.09 (d, *J* = 8.4 Hz, 1 H, H-1), 5.54 (d, *J* = 1.2 Hz, 1 H, H-4), 4.86 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.82 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.63 (d, *J* = 10.8 Hz, 1 H, Ar-CH_2-), 4.52 (d, *J* = 10.8 Hz, 1 H, Ar-CH_2-), 4.24-4.19 (m, 1 H, H-5), 4.09 (d, *J* = 8.4 Hz, 1 H, H-2), 1.65 (s, 3 H, C3-CH_3), 1.55-1.49 (m, 1 H), 1.32 (d, *J* = 6.4 Hz, 1 H, H-6), 0.93-0.82 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 163.2, 149.1, 146.7, 137.5, 137.3, 135.9, 133.4, 131.1, 129.7, 129.6, 127.2, 127.1, 126.9, 126.5, 126.4, 126.1, 126.0, 125.9, 124.5 (2 C), 99.1 (C-1), 92.6, 78.9, 78.8, 78.3, 74.2, 74.0 (2 C), 73.6, 68.8 (2 C), 63.1, 16.0, 15.2, 8.0, -0.2; HRMS (ESI) $[M + Na]^+$ calcd for $C_{39}H_{37}NO_7Na$: 654.2462, found: 654.2454.

6-*O*-*tert*-Butyldiphenylsilyl chartarin 10-*O*-(2,3-di-*O*-benzyl-4-*O*-picoloyl)-D-fucopyranoside (41)

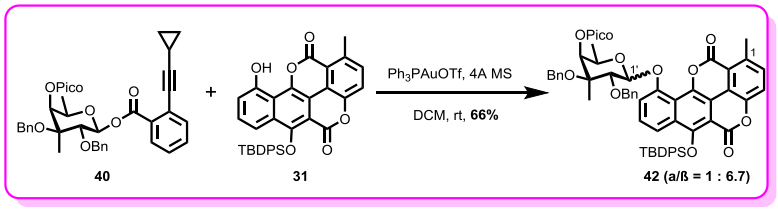


Preparation of $Ph_3PAuOTf$ solution: To a stirred suspension of Ph_3PAuCl (25 mg,

0.050 mmol) and activated 4 Å molecular sieves (50 mg) in dry DCM (0.5 mL) was added AgOTf (13 mg, 0.050 mmol) at room temperature under N_2 atmosphere. The mixture was stirred at the same temperature for 15 min, then the resulting mixture was stood for 5 minutes, and then the supernatant was drawn with a syringe.

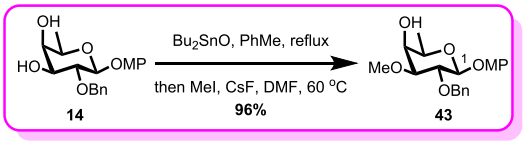
To a stirred solution of glycosyl donor **34** (22 mg, 0.035 mmol) and chartarin acceptor **31** (10 mg, 0.017 mmol) in dry DCM (1.7 mL) was added freshly activated 4 Å molecular sieves (170 mg) at room temperature under N_2 atmosphere. The suspension was stirred at the same temperature for 1 h before $Ph_3PAuOTf$ (70 μL, 0.0070 mmol) was added dropwise at the same temperature. The resulting mixture was then stirred at room temperature for 18 h. Filtration and concentration under reduced pressure gave the crude product, which was further purified by silica gel column chromatography (PhMe/EA = 9 : 1 to 6 :1) to provide **41** (9.1 mg, 52%, α/β = 1 : 2.8) as a α/β mixture. An aliquot of pure **41β** was obtained as a yellow solid: $[\alpha]_D^{25}$ = +11.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1 H), 8.47-8.42 (m, 2 H), 7.95 (s, 1 H), 7.76 (d, *J* = 7.2 Hz, 2 H), 7.68 (d, *J* = 7.2 Hz, 1 H), 7.57-7.53 (m, 2 H), 7.40-7.26 (m, 11 H), 7.25-7.22 (m, 3 H), 7.16-7.14 (m, 2 H), 7.02-6.99 (m, 3 H), 5.81 (s, 1 H, H-4'), 5.47 (d, *J* = 7.6 Hz, 1 H, H-1'), 5.32 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 5.13 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 4.90 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 4.68 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.52 (t, *J* = 8.4 Hz, 1 H, H-2'), 4.11 (dd, *J* = 7.2, 14.0 Hz, 1 H, H-5'), 3.93 (d, *J* = 9.6 Hz, 1 H, H-3'), 2.81 (s, 3 H, C1-CH_3), 1.40 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.14 (s, 9 H, -Si^{t}Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 157.4, 154.0, 153.0, 150.4, 147.0, 140.7, 139.4, 138.6, 137.7, 135.3 (2 C), 132.9, 132.7 (2 C), 131.3, 129.7, 128.5, 128.2, 128.0, 127.9, 127.6, 127.5 (2 C), 127.2, 127.1, 126.4, 120.3, 119.5, 119.4, 118.9, 117.5, 113.6, 110.3, 104.5, 100.8 (C-1'), 79.5, 79.3, 75.8, 72.2, 71.4, 69.9, 27.2, 22.5, 21.2, 16.9; HRMS (ESI) $[M + H]^+$ calcd for $C_{61}H_{54}NSiO_{11}$: 1004.3461, found: 1004.3456.

6-*O*-*tert*-Butyldiphenylsilyl chartarin 10-*O*-(2,3-di-*O*-benzyl-3-*C*-methyl-4-*O*-picoloyl)-D-fucopyranoside (42)



Similar procedure as that used for the synthesis of **41** was adopted to mediate the coupling between donor **40** (66 mg, 0.10 mmol) and the chartarin acceptor **31** (30 mg, 0.052 mmol) to provide **42** (35 mg, 66%, α/β = 1 : 6.7) as a α/β mixture. An aliquot of pure **42β** was obtained as a yellow solid: $[\alpha]_D^{25}$ = +1.6 (*c* 0.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.8 Hz, 1 H), 8.43 (dd, *J* = 3.0, 8.4 Hz, 2 H), 7.95 (dd, *J* = 4.8, 6.0 Hz, 1 H), 7.75 (dd, *J* = 1.8, 8.4 Hz, 2 H), 7.68 (dd, *J* = 1.2, 7.8 Hz, 2 H), 7.57-7.52 (m, 2 H), 7.47 (d, *J* = 7.8 Hz, 1 H), 7.38 (m, 6 H), 7.25-7.19 (m, 4 H), 7.16-7.11 (m, 5 H), 6.95-6.89 (m, 3 H), 5.64 (s, 1 H, H-4'), 5.54 (d, *J* = 7.8 Hz, 1 H, H-1'), 5.30 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 5.13 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.63 (d, *J* = 11.4 Hz, 1 H, Ar-CH_2-), 4.55-4.52 (m, 2 H, H-2', Ar-CH_2-), 4.32 (dd, *J* = 6.0, 12.6 Hz, 1 H, H-5'), 2.80 (s, 3 H, C1-CH_3), 1.66 (s, 3 H, C3'-CH_3), 1.40 (d, *J* = 6.6 Hz, 3 H, H-6'), 1.14 (s, 9 H, -Si^{t}Bu); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 157.4, 154.5, 153.0, 150.3, 147.0, 140.7, 139.7, 138.6 (2 C), 135.3 (2 C), 132.9, 132.8, 132.7, 131.3, 129.7, 128.3, 127.8, 127.7, 127.6, 127.5 (2 C), 127.3, 126.8, 126.7, 126.6, 120.3, 119.5 (2 C), 118.9, 117.5, 113.8, 110.3, 104.5, 100.3 (C-1'), 81.8, 79.1, 75.8, 75.5, 69.3, 64.3, 27.2, 22.5, 21.2, 17.5, 16.8; HRMS (ESI) $[M + H]^+$ calcd for $C_{62}H_{56}NSiO_{11}$: 1018.3617, found: 1018.3610.

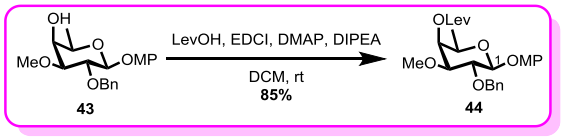
4-Methoxyphenyl 2-*O*-benzyl-3-*O*-methyl-β-D-fucopyranoside (43)



To a solution of the **14** (4.79 g, 13.29 mmol) in dry PhMe (66.5 mL) was added Bu_2SnO (3.64 g, 14.62 mmol) at room temperature under N_2 atmosphere.The reaction mixture was then refluxed for 4 h. After being cooled down to room temperature, the solvent

was removed *in vacuo* to give a residue. The obtained residue and CsF (4.04 g, 26.60 mmol) were then dissolved in dry DMF (66.5 mL), to which MeI (1.7 mL, 27.31 mmol) was added under N_2 atmosphere at room temperature. The mixture was allowed to warm to 60 ℃ and be stirred at the same temperature overnight. After completion of the reaction (monitored by TLC), ethyl acetate was added to dilute the reaction mixture. The resulting mixture was washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 2 : 1) to give **43** (4.76 g, 96%) as a light yellow solid: $[\alpha]_D^{25}$ = +2.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.27 (m, 5 H), 7.07-7.03 (m, 2 H), 6.87-6.82 (m, 2 H), 5.01 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.86-4.81 (m, 2 H, H-1, Ar-CH_2-), 3.86 (d, *J* = 3.2 Hz, 1 H, H-4), 3.83-3.77 (m, 4 H, H-3, Ar-OCH_3), 3.66 (dd, *J* = 6.4, 12.8 Hz, 1 H, H-5), 3.55 (s, 3 H, C3-OCH_3), 3.36 (dd, *J* = 3.6, 9.6 Hz, 1 H, H-3), 2.56 (brs, 1 H, C4-OH), 1.42 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 151.6, 138.6, 128.3, 128.0, 127.6, 118.6, 114.5, 102.8 (C-1), 83.2, 78.5, 75.2, 70.3, 68.6, 58.2, 55.6, 16.5; HRMS (ESI) $[M + Na]^+$ calcd for $C_{21}H_{26}O_6Na$: 397.1622, found: 397.1615.

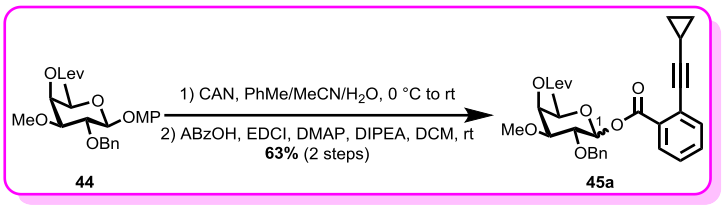
4-Methoxyphenyl 2-*O*-benzyl-3-*O*-methyl-4-*O*-levulinoyl-β-D-fucopyranoside (44)



To a solution of the **43** (640 mg, 1.71 mmol), EDCI (772 mg, 4.03 mmol), and DMAP (432 mg, 3.54 mmol) in dry CH_2Cl_2 (8.5 mL) was added LevOH (228 μL, 2.22 mmol) and DIPEA (1.2 mL, 6.84 mmol) at room temperature under N_2 atmosphere. The resulting mixture was stirred at the same temperature for 2 days. After completion of the reaction (monitored by TLC), the solvent was removed *in vacuo* to give a residue, which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to give **44** (684 mg, 85%) as a light yellow syrup: $[\alpha]_D^{25}$ = +1.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 5 H), 7.04-6.99 (m, 2 H), 6.84-6.80 (m, 2 H), 5.33 (dd, *J*

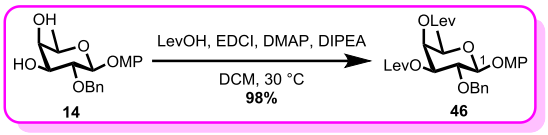
= 0.8, 3.2 Hz, 1 H, H-4), 4.96 (d, *J* = 10.8 Hz, 1 H, Ar-CH_2-), 4.86 (d, *J* = 7.6 Hz, 1 H, H-1), 4.83 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 3.77 (s, 3 H, Ar-OCH_3), 3.76-3.70 (m, 2 H, H-2, H-5), 3.44 (s, 3 H, C3-OCH_3), 3.40 (dd, *J* = 3.6, 9.6 Hz, 1 H, H-3), 2.88-2.65 (m, 4 H, -CH_2CH_2-), 2.20 (s, 3 H, -$COCH_3$), 1.27 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 172.6, 155.4, 151.7, 138.7, 128.4, 128.1, 127.8, 118.6, 114.6, 102.9 (C-1), 81.9, 78.6, 75.4, 69.4 (2 C), 58.3, 55.8, 38.2, 30.0, 28.2, 16.6; HRMS (ESI) $[M + Na]^+$ calcd for $C_{26}H_{32}O_8Na$: 495.1989, found: 495.1984.

2-*O*-Benzyl-3-*O*-methyl-4-*O*-levulinoyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (45a)



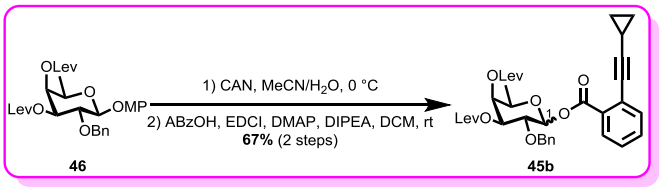
Similar procedures as that used for the synthesis of **20** was adopted to convert **44** (1.75 g, 3.70 mmol) to **45a** (1.26 g, 63% yield for 2 steps) as a α/β mixture. Pure **45aβ** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = -6.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.6 Hz, 1 H), 7.51 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.45 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.30-7.27 (m, 1 H), 7.24-7.18 (m, 5 H), 5.86 (d, *J* = 8.0 Hz, 1 H, H-1), 5.36 (dd, *J* = 1.2, 3.6 Hz, 1 H, H-4), 4.81 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 4.76 (d, *J* = 11.2 Hz, 1 H, Ar-CH_2-), 3.91-3.87 (m, 1 H, H-5), 3.78 (dd, *J* = 8.0, 9.6 Hz, 1 H, H-2), 3.49 (dd, *J* = 3.6, 9.6 Hz, 1 H, H-3), 3.44 (s, 3 H, -OCH_3), 2.89-2.68 (m, 4 H, -$COCH_2CH_2CO$-), 2.21 (s, 3 H, -$COCH_3$), 1.56-1.49 (m, 1 H), 1.25 (d, *J* = 6.4 Hz, 3 H, H-6), 0.92-0.88 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 172.6, 164.2, 138.4, 134.5, 132.2, 130.9, 130.5, 128.4, 128.0, 127.7, 127.0, 125.6, 100.2, 94.5 (C-1), 82.4, 75.3, 74.7, 70.4, 69.5, 58.2 (2 C), 38.2, 30.0, 28.1, 16.4, 9.0, 0.9; HRMS (ESI) $[M + Na]^+$ calcd for $C_{31}H_{34}O_8Na$: 557.2146, found: 557.2141.

4-Methoxyphenyl 2-*O*-benzyl-3,4-di-*O*-levulinoyl-β-D-fucopyranoside (46)



Similar procedure as that used for synthesis of **44** was applied to convert **14** (4.90 g, 13.60 mmol) to **46** under the combined effect of EDCI (12.52 g, 65.31 mmol), DMAP (3.32 g, 27.18 mmol), LevOH (3.2 mL, 32.64 mmol), as well as DIPEA (9.5 mL, 54.40 mmol) in dry CH_2Cl_2 (68.0 mL) at room temperature. Compound **46** (7.39 g, 98%), purified by silica gel column chromatography (PE/EA = 3 : 2), was obtained as a light yellow syrup: $[\alpha]_D^{25}$ = +29.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 4 H), 7.29-7.26 (m, 1 H), 7.05-7.00 (m, 2 H), 6.85-6.81 (m, 2 H), 5.25 (d, *J* = 3.6 Hz, 1 H, H-4), 5.04 (dd, *J* = 3.6, 10.4 Hz, 1 H, H-3), 4.97-4.92 (m, 2 H, Ar-CH_2-, H-1), 4.78 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 3.88-3.83 (m, 2 H, H-2, H-5), 3.77 (s, 3 H, -OCH_3), 2.79-2.62 (m, 6 H), 2.60-2.44 (m, 2 H), 2.19 (s, 3 H), 2.17 (s, 3 H), 1.24 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 206.2, 172.4, 172.1, 155.5, 151.5, 138.2, 128.4, 128.1, 127.8, 118.6, 114.6, 102.9 (C-1), 76.2, 75.0, 73.1, 70.7, 69.2, 55.7, 37.9, 37.8, 29.9, 29.8, 27.9 (2 C), 16.3; HRMS (ESI) $[M + Na]^+$ calcd for $C_{30}H_{36}O_{10}Na$: 579.2201, found: 579.2197.

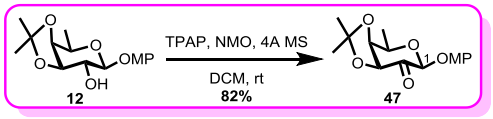
2-*O*-Benzyl-3,4-di-*O*-levulinoyl-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (45b)



Similar procedures as those used for synthesis of **20** were applied to convert **46** (7.39 g, 13.28 mmol) to **45b** (5.52 g, 67% yield for 2 steps, α/β = 1: 3.9) as a α/β mixture. Pure **45bα** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +74.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.50 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.44 (td, *J* = 1.2, 7.2 Hz, 1 H), 7.30-7.24 (m, 5 H), 6.64 (d, *J* = 3.6 Hz, 1 H, H-1), 5.44-5.37 (m, 2 H, H-3, H-4), 4.74 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.65 (d, *J* = 12.0 Hz, 1 H,

Ar-CH_2-), 4.49 (dd, *J* = 6.4, 13.2 Hz, 1 H, H-5), 4.04 (dd, *J* = 3.6, 10.0 Hz, 1 H, H-2), 2.80-2.45 (m, 8 H), 2.18 (s, 3 H), 2.16 (s, 3 H), 1.60-1.54 (m, 1 H), 1.16 (d, *J* = 6.4 Hz, 3 H, H-6), 0.91-0.79 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 206.2, 172.5, 172.2, 164.8, 137.8, 134.9, 132.1, 131.0 (2 C), 128.5, 128.0 (2 C), 127.3, 125.0, 99.7, 91.3 (C-1), 75.0, 73.1, 72.4, 71.3, 70.7, 67.6, 38.0, 37.9, 30.0, 29.9, 28.0, 27.9, 16.2, 9.1, 0.7; HRMS (ESI) $[M + Na]^+$ calcd for $C_{35}H_{38}O_{10}Na$: 641.2357, found: 641.2349. Pure **45bβ** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +18.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.52 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.47 (td, *J* = 1.2, 7.6 Hz, 1 H), 7.31 (td, *J* = 1.2, 7.6 Hz, 1 H), 7.24-7.19 (m, 1 H), 5.92 (d, *J* = 8.0 Hz, 1 H, H-1), 5.28 (d, *J* = 1.2, 3.6 Hz, 1 H, H-4), 5.10 (dd, *J* = 3.6, 10.0 Hz, 1 H, H-3), 4.76 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 4.71 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 4.01-3.97 (m, 1 H, H-5), 3.94 (dd, *J* = 8.0, 10.0 Hz, 1 H, H-2), 2.83-2.63 (m, 6 H), 2.59-2.44 (m, 2 H), 2.20 (s, 3 H), 2.17 (s, 3 H), 1.56-1.50 (m, 1 H), 1.23 (d, *J* = 6.4 Hz, 3 H, H-6), 0.92-0.89 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 206.2, 172.5, 172.1, 164.0, 137.9, 134.5, 132.3, 130.8, 130.4, 128.4, 128.0, 127.9, 127.0, 125.7, 100.3, 94.6 (C-1), 75.5, 75.0, 74.6, 73.7, 70.9, 70.2, 38.0, 37.9, 30.0, 29.9, 28.0, 27.9, 16.2, 9.1(2 C), 0.9; HRMS (ESI) $[M + Na]^+$ calcd for $C_{35}H_{38}O_{10}Na$: 641.2357, found: 641.2349.

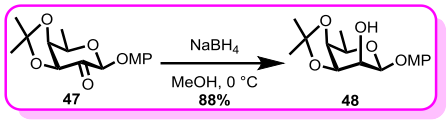
4-Methoxyphenyl 3,4-*O*-isopropylidene-β-D-fucopyrano-2-uloside (47)



To a solution of **12** (3.00 g, 9.67 mmol) in dry CH_2Cl_2 (96.7 mL) was added activated 4 Å molecular sieves (3.20 g) and NMO (1.92 g, 16.39 mmol) under N_2 atmosphere at room temperature. The mixture was stirred at the same temperature for 30 min before TPAP (169 mg, 0.48 mmol) was added. The resulting mixture was then stirred for another 2.5 h at this temperature. After completion of the reaction (monitored by TLC), filtration was followed by concentration under reduced pressure to yield the crude product, which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to furnish **47** (2.44 g, 82%) as a light yellow foam: $[\alpha]_D^{25}$ = -15.3 (*c* 2.0, $CHCl_3$); ^{1}H

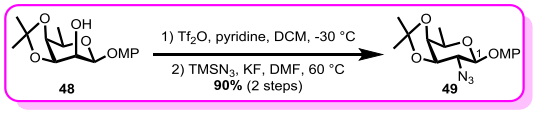
NMR (400 MHz, $CDCl_3$) δ 7.05-7.01 (m, 2 H), 6.84-6.80 (m, 2 H), 5.25 (s, 1 H, H-1), 4.55 (d, *J* = 6.0 Hz, 1 H, H-3), 4.50 (dd, *J* = 2.0, 6.0 Hz, 1 H, H-4), 4.29 (qd, *J* = 2.0, 6.8 Hz, 1 H, H-5), 3.76 (s, 3 H, -OCH_3), 1.49-1.48 (m, 6 H), 1.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9 (C-2), 155.8, 150.6, 118.9, 114.7, 111.4, 98.6 (C-1), 80.5, 77.8, 69.5, 55.7, 27.3, 26.2, 16.6; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_6$ $[M + H]^+$: 309.1333, found: 309.1339.

4-Methoxyphenyl 3,4-*O*-isopropylidene-6-deoxy-β-D-talopyranoside (48)



To a solution of **47** (1.92 g, 6.23 mmol) in dry MeOH (63.2 mL) was added $NaBH_4$ (952 mg, 25.17 mmol) under N_2 atmosphere at 0 □. The mixture was stirred at the same temperature for 30 min before H_2O was added to quench the reaction. The resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to give **48** (1.73 g, 88%) as a white solid: $[\alpha]_D^{25}$ = -21.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03-6.99 (m, 2 H), 6.84-6.80 (m, 2 H), 5.05 (d, *J* = 2.4 Hz, 1 H, H-1), 4.39 (dd, *J* = 4.8, 6.8 Hz, 1 H, H-3), 4.17 (dd, *J* = 2.4, 6.8 Hz, 1 H, H-2), 3.95-3.88 (m, 2 H, H-5, H-4), 3.77 (s, 3 H, -OCH_3), 2.65 (d, *J* = 9.6 Hz, 1 H, C2-OH), 1.62 (s, 3 H), 1.42 (d, *J* = 6.8 Hz, 3 H, H-6), 1.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.6, 118.8, 114.6, 110.2, 99.1 (C-1), 74.5, 73.3, 68.2, 66.5, 55.8, 25.7, 25.3, 17.2; HRMS (ESI) m/z calcd for $C_{16}H_{22}O_6Na$ $[M + Na]^+$: 333.1308, found: 333.1303.

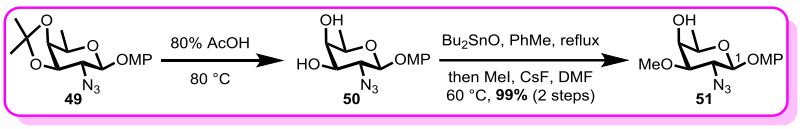
4-Methoxyphenyl 2-deoxy-2-azido-3,4-*O*-isopropylidene-β-D-fucopyranoside (49)



To a stirred solution of **48** (2.52 g, 8.12 mmol) and pyridine (6.5 mL, 80.37 mmol) in dry CH_2Cl_2 (81.0 mL) was added Tf_2O (4.1 mL, 24.36 mmol) dropwise at -30 °C under N_2 atmosphere. The mixture was stirred at the same temperature for 50 min before H_2O was added to quench the reaction. The resulting mixture was diluted with EtOAc, washed successively with 1N HCl, H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to afford the intermediate, which was used to the next step without further purification.

To a solution of the above obtained intermediate and KF (1.15 g, 19.79 mmol) in dry DMF (27.0 mL) was added $TMSN_3$ (2.2 mL, 16.73 mmol) at 0 °C under N_2 atmosphere. The mixture was allowed to warm to 60 °C and stirred at the same temperature over night. After completion of the reaction (monitored by TLC), EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver a residue, which was further purified by silica gel column chromatography (PE/EA = 8 : 1) to give **49** (2.45 g, 90% yield for 2 steps) as a white solid: $[\alpha]_D^{25}$ = +109.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-7.00 (m, 2 H), 6.85-6.81 (m, 1 H), 4.67 (d, *J* = 8.4 Hz, 1 H, H-1), 4.01 (dd, *J* = 2.4, 5.6 Hz, 1 H, H-4), 3.96-3.93 (m, 2 H, H-3, H-5), 3.78 (s, 3 H, -OCH_3), 3.66 (t, *J* = 8.4 Hz, 1 H, H-2), 1.60 (s, 3 H), 1.47 (d, *J* = 6.4 Hz, 3 H, H-6), 1.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 151.2, 118.7, 114.7, 110.5, 101.4 (C-1), 75.5, 69.3, 65.0, 55.8, 55.7, 28.4, 26.4, 16.8; HRMS (ESI) m/z calcd for $C_{16}H_{22}N_3O_5$ [M + H]$^+$: 336.1554, found: 336.1556.

4-Methoxyphenyl 2-azido-2-deoxy-3-*O*-methyl-β-D-fucopyranoside (51)

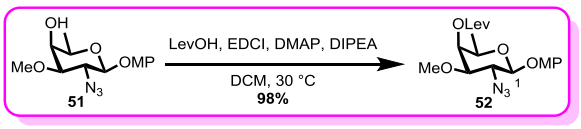


Compound **49** (1.60 g, 4.77 mmol) was dissolved in 80% HOAc (50.0 mL) at room temperature. The mixture was allowed to warm to 80 °C and stirred at the same

temperature for 25 min, when TLC showed that the reaction reached completion. After cooling down to room temperature, the solvent was removed *in vacuo* to give the diol intermediate **50** which was put to the next step without further purification.

The obtained diol intermediate and Bu_2SnO (1.31 g, 5.25 mmol) were then dissolved in dry toluene (24.0 mL). The reaction mixture was then heated to reflux for 4 h. After being cooled down to room temperature, the solvent was removed *in vacuo* to give a residue. The thus obtained residue and CsF (1.47 g, 9.68 mmol) were then dissolved in dry DMF (24.0 mL), to which MeI (592 μL, 9.51 mmol) were added under N_2 atmosphere at room temperature. The mixture was allowed to warm to 60 °C and stirred at this temperature over night. After completion of the reaction (monitored by TLC), EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 2 : 1) to give **51** (1.46 g, 99% yield for 2 steps) as a white solid: $[\alpha]_D^{25}$ = +62.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-7.02 (m, 2 H), 6.85-6.81 (m, 2 H), 4.68 (d, *J* = 8.0 Hz, 1 H, H-1), 3.87-3.85 (m, 1 H, H-4), 3.80-3.75 (m, 4 H, Ar-OCH_3, H-2), 3.65-3.61 (m, 1 H, H-5), 3.53 (s, 3 H, C3-OCH_3), 3.16 (dd, *J* = 3.2, 10.4 Hz, 1 H, H-3), 2.32 (s, 1 H, C4-OH), 1.42 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 151.3, 118.9, 114.7, 101.8 (C-1), 81.9, 70.6, 67.4, 62.2, 57.8, 55.8, 16.6; HRMS (ESI) m/z calcd for $C_{14}H_{20}N_3O_5$ $[M + H]^+$: 310.1398, found: 310.1400.

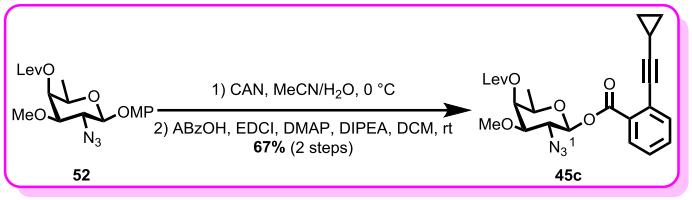
4-Methoxyphenyl 2-azido-2-deoxy-3-*O*-methyl-4-*O*-levulinoyl-β-D-fucopyranoside (52)



Similar procedure as that used for synthesis of **44** was adopted to convert **51** (500 mg, 1.62 mmol) to **52** under the combined effects of EDCI (1.09 g, 5.71 mmol), DMAP

(612 mg, 5.00 mmol), LevOH (298 μL, 2.91 mmol), and DIPEA (1.7 mL, 9.70 mmol) in dry CH_2Cl_2 (5.4 mL) at 30 □. After purified by silica gel column chromatography (PE/EA = 3 : 1 to 2 : 1), **52** (645 mg, 98%) was obtained as a light yellow syrup: $[\alpha]_D^{25}$ = +20.4 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-7.00 (m, 2 H), 6.84-6.80 (m, 2 H), 5.29 (dd, *J* = 1.2, 3.6 Hz, 1 H, H-4), 4.69 (d, *J* = 8.0 Hz, 1 H, H-1), 3.76-3.69 (m, 5 H, Ar-OCH_3, H-2, H-5), 3.40 (s, 3 H, C3-OCH_3), 3.20 (dd, *J* = 3.2, 10.0 Hz, 1 H, H-3), 2.87-2.63 (m, 4 H, -CH_2CH_2-), 2.19 (s, 3 H, -$COCH_3$), 1.27 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 172.5, 155.7, 151.3, 118.7, 114.7, 101.7 (C-1), 80.3, 69.6, 68.0, 62.4, 57.8, 55.7, 38.1, 29.9, 28.0, 16.5; HRMS (ESI) m/z calcd for $C_{19}H_{26}N_3O_7$ $[M + H]^+$: 408.1766, found: 408.1757.

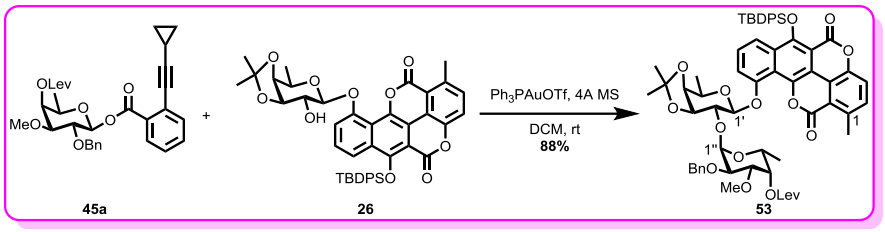
2-Azido-2-deoxy-3-*O*-methyl-4-*O*-levulinoyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (45c)



Similar procedures as those used for the synthesis of **20** was adopted to convert **52** (600 mg, 1.47 mmol) to **45c** (467 mg, 67% yield for 2 steps) as a light yellow syrup: $[\alpha]_D^{25}$ = -22.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.51 (dd, *J* = 1.6, 7.6 Hz, 1 H), 7.46 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.33 (td, *J* = 1.6, 7.6 Hz, 1 H), 5.68 (d, *J* = 8.8 Hz, 1 H, H-1), 5.33 (dd, *J* = 0.8, 3.2 Hz, 1 H, H-4), 3.89-3.84 (m, 1 H, H-5), 3.80 (dd, *J* = 8.8, 10.4 Hz, 1 H, H-2), 3.43 (s, 3 H, -OCH_3), 3.35 (dd, *J* = 3.6, 10.4 Hz, 1 H, H-3), 2.89-2.64 (m, 4 H, -CH_2CH_2-), 2.19 (s, 3 H, -$COCH_3$), 1.56-1.49 (m, 1 H), 1.25 (d, *J* = 6.4 Hz, 3 H, H-6), 0.91-0.89 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 172.5, 163.9, 134.5, 132.5, 130.9, 130.0, 127.1, 125.6, 100.3, 93.4 (C-1), 80.9, 74.6, 70.6, 68.1, 61.5, 57.9, 38.1, 29.9, 28.0, 16.4, 9.0, 0.8; HRMS (ESI) m/z calcd for $C_{24}H_{28}N_3O_7$ $[M + H]^+$: 470.1922, found: 470.1921.

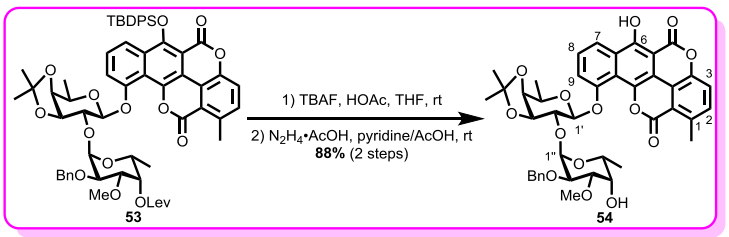
6-*O*-*tert*-Butyldiphenylsilyl chartarin 10-*O*-[2-*O*-benzyl-3-*O*-methyl-4-*O*-

levulinoyl-α-D-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene]-β-D-fucopyranoside (53)



Similar procedure as that used for the synthesis of **41** was adopted to perform the coupling between donor **45a** (105 mg, 0.20 mmol) and acceptor **26** (60 mg, 0.079 mmol), furnishing **53** (77 mg, 88%) as a yellow solid: $[\alpha]_D^{25}$ = +20.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.4 Hz, 1 H), 7.69-7.64 (m, 4 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.36-7.30 (m, 3 H), 7.27-7.19 (m, 6 H), 6.84-6.79 (m, 1 H), 6.62-6.57 (m, 4 H), 6.16 (d, *J* = 2.8 Hz, 1 H, H-1''), 5.44 (d, *J* = 7.2 Hz, 1 H, H-1'), 5.40-5.39 (m, 1 H, H-4''), 4.50 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.45-4.35 (m, 3 H, H-2', H-3', H-5''), 4.32 (d, *J* = 11.6 Hz, 1 H, Ar-CH_2-), 4.17 (dd, *J* = 2.4, 5.2 Hz, 1 H, H-4'), 4.12 (qd, *J* = 2.0, 6.4 Hz, 1 H, H-5'), 3.76-3.69 (m, 2 H, H-2'', H-3''), 3.34 (s, 3 H, -OCH_3), 2.86 (s, 3 H, C1-CH_3), 2.80-2.69 (m, 4 H, -CH_2CH_2-), 2.20 (s, 3 H, -$COCH_3$), 1.44-1.42 (m, 9 H), 1.25 (d, *J* = 6.4 Hz, 3 H), 1.14 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 172.6, 158.6, 157.3, 153.3, 152.8, 146.8, 140.7, 138.7, 138.3, 135.2, 132.9 (2 C), 132.7, 131.3, 129.6 (2 C), 127.6, 127.4 (2 C), 126.8, 126.4, 120.3, 119.6, 119.3 (2 C), 117.4, 114.5, 110.3, 110.1, 104.4, 99.4 (C-1''), 98.3 (C-1'), 78.9, 78.3, 76.7, 76.4, 75.8, 72.8, 71.0, 69.4, 64.8, 57.6, 38.2, 30.1, 28.4, 27.2, 27.1, 26.8, 22.6, 21.1, 16.7, 16.4; HRMS (ESI) m/z calcd for $C_{63}H_{66}O_{16}SiNa$ $[M + Na]^+$: 1129.4012, found: 1129.4415.

Chartarin 10-*O*-[2-*O*-benzyl-3-*O*-methyl-α-D-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene]-β-D-fucopyranoside (54)

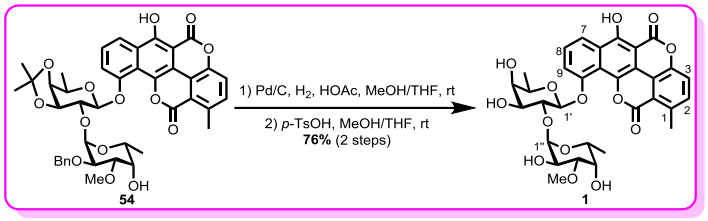


To a solution of **53** (65 mg, 0.059 mmol) in THF (2.0 mL) were added HOAc (10 μL, 0.18 mmol) and TBAF (89 μL, 1 M in THF, 0.088 mmol) successively at room temperature. The mixture was stirred at the same temperature for 10 min, when TLC showed that the reaction reached to completion. The resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver the intermediate which was put to the next step without further purification.

The above obtained intermediate was then dissolved in pyridine/HOAc (2.0 mL, v/v = 3 : 2), to which N_2H_4•HOAc (52 mg, 0.56 mmol) was added at room temperature. The reaction mixture was stirred at the same temperature for 4 h, at which time TLC showed that all the starting materials disappeared. After quenched by acetone, the resulting mixture was diluted with EtOAc, washed successively with 1N HCl, H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to yield a residue, which was further purified by silica gel column chromatography (DCM/EA = 8 : 1 to 5 : 1) to give **54** (40 mg, 88% yield for 2 steps) as a yellow solid: $[\alpha]_D^{25}$ = +33.8 (*c* 0.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.64 (brs, 1 H, C6-OH), 8.26 (d, *J* = 8.4 Hz, 1 H, H-7), 7.63 (t, *J* = 8.6 Hz, 1 H, H-8), 7.51 (d, *J* = 8.4 Hz, 1 H, H-3), 7.48 (d, *J* = 8.4 Hz, 1 H, H-2), 7.29 (d, *J* = 7.8 Hz, 1 H, H-9), 6.83 (t, *J* = 7.8 Hz, 1 H), 6.61 (t, *J* = 7.8 Hz, 2 H), 6.49 (d, *J* = 7.8 Hz, 2 H), 6.08 (d, *J* = 3.6 Hz, 1 H, H-1''), 5.38 (d, *J* = 7.2 Hz, 1 H, H-1'), 4.44 (d, *J* = 11.4 Hz, 1 H, Ar-CH_2-), 4.39-4.34 (m, 3 H, H-2', H-3', H-5''), 4.23 (d, *J* = 11.4 Hz, 1 H, Ar-CH_2-), 4.17 (dd, *J* = 2.4, 5.4 Hz, 1 H, H-4'), 4.11-4.08 (m, 1 H, H-5'), 3.96 (d, *J* = 3.0 Hz, 1 H, H-4''), 3.75 (dd, *J* = 4.2, 10.2 Hz, 1 H, H-2''), 3.65 (dd, *J* = 3.0, 9.6 Hz, 1 H, H-3''), 3.43 (s, 3 H, -OCH_3), 2.90 (s, 3 H, C1-CH_3), 1.71 (s, 3 H), 1.45 (d, *J* = 6.6 Hz, 3 H), 1.43 (s, 3 H), 1.41 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 158.8, 157.4, 153.5, 146.5, 140.3, 139.0, 138.2, 133.0, 127.9, 127.6, 127.2, 126.6, 126.1, 120.9, 120.0, 119.5, 118.4, 117.9, 115.4, 110.3, 108.8, 99.6 (C-1'), 98.2 (C-1''), 96.7, 80.0, 78.9, 76.7, 76.4, 75.8, 72.7, 69.8, 69.4, 65.5, 57.7, 28.4, 26.8, 22.6, 16.8, 16.4;

HRMS (ESI) m/z calcd for $C_{42}H_{43}O_{14}$ $[M + H]^+$: 771.2648, found: 771.2639.

Chartreusin (1)

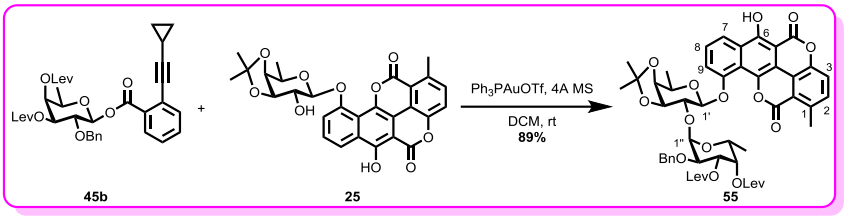


To a solution of **54** (40 mg, 0.052 mmol) in MeOH/THF (2.0 mL, v/v = 1 : 1) was added HOAc (2 drops) and Pd/C (10 wt% on carbon, 15 mg) successively at room temperature. The resulting mixture was degassed at -78 ^oC (evacuated under reduced pressure and refilled with H_2, and this process was repeated for 3 times), then was warmed up to room temperature. The reaction mixture was stirred over night at room temperature, when TLC showed that the reaction reached to completion. Filtration through a pad of Celite/silica gel was followed by concentration under reduced pressure to give the intermediate which was put to the next step without further purification.

The above obtained intermediate was then dissolved in MeOH/THF (2.0 mL, v/v = 1 : 1), to which *p*-TsOH (8.3 mg, 0.048 mmol) was added at room temperature. The reacton mixture was stirred over night at the same temperature, at which time TLC showed that all the starting materials disappeared. Et_3N was added to quench the reaction before evaporation under reduced pressure was adopted to remove all volatile solvent. The resulting crude product was purified by silica gel column chromatography (DCM/MeOH = 20 : 1) to give **1** (25 mg, 76% yield for 2 steps) as a yellow solid: $[\alpha]_D^{25}$ = -90.7 (*c* 0.5, $CHCl_3$); ^1H NMR (600 MHz, pyridine-d_5) δ 8.35 (d, *J* = 7.8 Hz, 1 H, H-7), 7.76 (d, *J* = 7.8 Hz, 1 H, H-9), 7.66 (td, *J* = 1.2, 7.8 Hz, 1 H, H-8), 7.45 (dd, *J* = 1.2, 8.4 Hz, 1 H, H-3), 7.33 (d, *J* = 7.8 Hz, 1 H, H-2), 6.56 (d, *J* = 4.2 Hz, 1 H, H-1''), 5.82 (d, *J* = 7.2 Hz, 1 H, H-1'), 5.08 (t, *J* = 8.4 Hz, 1 H, H-2'), 5.04 (q, *J* = 6.3 Hz, 1 H, H-5''), 4.57 (dd, *J* = 4.0, 9.9 Hz, 1 H, H-2''), 4.35 (dd, *J* = 3.4, 9.9 Hz, 1 H, H-3'), 4.22 (d, *J* = 3.6 Hz, 1 H, H-4'), 4.16 (t, *J* = 2.1 Hz, 1 H, H-4''), 4.13 (q, *J* = 6.0 Hz, 1 H, H-5'), 3.87 (dt, *J* = 2.4, 10.2 Hz, 1 H, H-3''), 3.34 (s, 3 H, -OCH_3), 2.73 (s, 3 H, C1-CH_3), 1.59

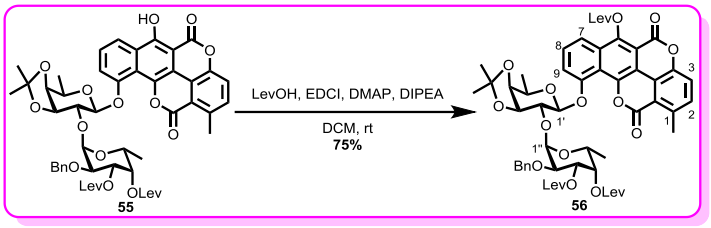
(d, J = 6.0 Hz, 6 H, H-6', H-6"); ^{13}C NMR (150 MHz, pyridine-d_5) δ 165.1, 159.5, 157.3, 155.4, 147.1, 139.9, 139.8, 133.4 (C-2), 128.8 (C-8), 127.6, 121.1 (C-3), 120.4, 119.6, 118.4, 117.9 (C-7), 115.4 (C-9), 109.4, 102.3 (C-1"), 101.5 (C-1'), 97.7, 82.0 (C-3"), 80.6 (C-2'), 74.6 (C-3'), 73.0 (C-4'), 72.2 (C-5'), 69.7 (C-4"), 69.4 (C-2"), 67.8 (C-5"), 57.1 (C3"-OCH_3), 22.4 (C1-CH_3), 17.5 (C-6', C-6"); HRMS (ESI) m/z calcd for $C_{32}H_{33}O_{14}$ [M + H]$^+$: 641.1865, found: 641.1851.

Chartarin 10-*O*-[2-*O*-benzyl-3,4-di-*O*-levulinoyl-α-D-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene]-β-D-fucopyranoside (55)



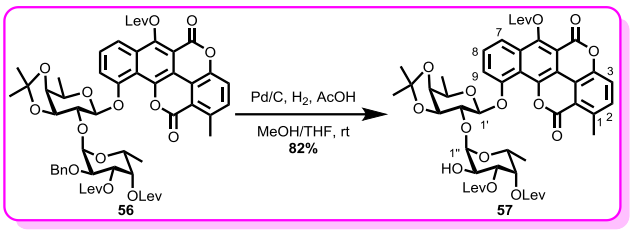
Similar procedure as that used for the synthesis of **41** was adopted to mediate the coupling between **45b** (143 mg, 0.23 mmol) and acceptor **25** (40 mg, 0.077 mmol) to **55** (65 mg, 89%) as a yellow solid: $[\alpha]_D^{25}$ = +16.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.58 (s, 1 H, C6-OH), 8.22 (dd, J = 0.8, 8.4 Hz, 1 H, H-7), 7.61 (t, J = 8.4 Hz, 1 H, H-8), 7.47 (d, J = 8.4 Hz, 1 H, H-3), 7.39 (d, J = 8.4 Hz, 1 H, H-2), 7.27-7.25 (m, 1 H, H-9), 6.83-6.78 (m, 1 H), 6.62 (t, J = 7.6 Hz, 2 H), 6.43 (dd, J = 1.2, 7.6 Hz, 2 H), 6.14 (d, J = 4.0 Hz, 1 H, H-1"), 5.34-5.29 (m, 3 H, H-1', H-3", H-4"), 4.54-4.49 (m, 1 H, H-5"), 4.36-4.28 (m, 3 H, H-2', H-3', Ar-CH_2-), 4.19-4.14 (m, 2 H, Ar-CH_2-, H-4'), 4.14-4.08 (m, 1 H, H-5'), 3.84 (dd, J = 3.6, 10.0 Hz, 1 H, H-2"), 2.92 (s, 3 H, C6-CH_3), 2.76-2.56 (m, 6 H), 2.42-2.37 (m, 2 H), 2.18 (s, 3 H), 2.04 (s, 3 H), 1.69 (s, 3 H), 1.46 (d, J = 6.4 Hz, 3 H, H-6'), 1.41 (s, 3 H), 1.21 (d, J = 6.4 Hz, 3 H, H-6"); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 206.4, 172.4, 172.0, 164.6, 158.7, 157.3, 153.3, 146.3, 140.0, 138.7, 137.6, 133.1, 127.9, 127.5, 127.0, 126.6, 125.9, 120.8, 119.7, 119.1, 118.2, 117.6, 115.2, 110.1, 108.4, 99.1 (C-1'), 98.3 (C-1"), 96.4, 78.8, 77.3, 76.4, 73.9, 72.3, 72.0, 70.6, 69.3, 64.5 38.0, 37.9, 30.0, 29.8, 28.4, 28.0 (2 C), 26.7, 22.5, 16.7, 16.0; HRMS (ESI) m/z calcd for $C_{51}H_{52}O_{18}Na$ [M + Na]$^+$: 975.3046, found: 975.3034.

6-*O*-Levulinoyl chartarin 10-*O*-[2-*O*-benzyl-3,4-di-*O*-levulinoyl-α-D-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene]-β-D-fucopyranoside (56)



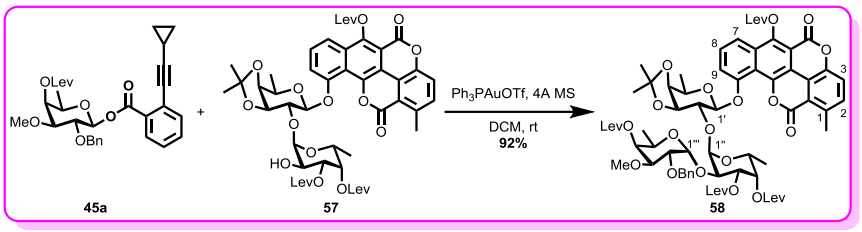
Similar procedure as that used for the synthesis of **44** was applied to convert **55** (110 mg, 0.12 mmol) to **56** under the combined effects of EDCI (78 mg, 0.41 mmol), DMAP (44 mg, 0.35 mmol), LevOH (21 μL, 0.22 mmol), and DIPEA (61 μL, 0.35 mmol) in dry CH_2Cl_2 (4.6 mL) at room temperature. After purification by silica gel column chromatography (DCM/EA = 5 : 1), **56** (91 mg, 75%) was obtained as a yellow solid: $[\alpha]_D^{25}$ = +32.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1 H, H-7), 7.68 (t, *J* = 7.8 Hz, 1 H, H-8), 7.53-7.50 (m, 2 H, H-3, H-2), 7.26-7.24 (m, 1 H, H-9), 6.82 (t, *J* = 7.2 Hz, 1 H), 6.63 (t, *J* = 7.2 Hz, 2 H), 6.53-6.52 (m, 2 H), 6.14 (d, *J* = 3.6 Hz, 1 H, H-1"), 5.38-5.35 (m, 2 H, H-1', H-3"), 5.33-5.32 (m, 1 H, H-5"), 4.56 (dd, *J* = 6.0, 12.6 Hz, 1 H, H-5"), 4.39-4.31 (m, 4 H, H-2', H-3', Ar-CH_2-), 4.15 (dd, *J* = 2.4, 5.4 Hz, 1 H, H-4'), 4.08 (qd, *J* = 1.8, 6.6 Hz, 1 H, H-5'), 3.89 (dd, *J* = 3.6, 10.8 Hz, 1 H, H-2"), 3.18-3.04 (m, 4 H), 2.93 (s, 3 H, C1-CH_3), 2.82-2.58 (m, 6 H), 2.49-2.40 (m, 2 H), 2.27 (s, 3 H, -$COCH_3$), 2.20 (s, 3 H, -$COCH_3$), 2.08 (s, 3 H, -$COCH_3$), 1.68 (s, 3 H), 1.41 (s, 3 H), 1.40 (d, *J* = 6.6 Hz, 3 H, H-6'), 1.22 (d, *J* = 6.6 Hz, 3 H, H-6"); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.8, 206.5 (2 C), 172.5, 172.1, 171.3, 158.4, 156.9, 146.9, 146.2, 144.5, 139.6, 137.7, 133.3, 130.9, 129.5, 127.7, 127.0, 126.1, 121.0, 119.1, 118.9, 117.9, 117.3, 115.1, 110.5, 110.2, 108.0, 99.4 (C-1'), 98.3 (C-1"), 78.8, 77.4, 76.4, 74.1, 72.4, 70.8, 69.5, 64.6, 38.2, 38.1, 38.0, 30.1, 30.0, 29.9, 28.5, 28.3, 28.1 (2 C), 26.7, 22.6, 16.7, 16.1; HRMS (ESI) m/z calcd for $C_{56}H_{58}O_{20}Na$ $[M + Na]^+$: 1073.3413, found: 1073.3396.

6-*O*-Levulinoyl chartarin 10-*O*-[3,4-di-*O*-levulinoyl-α-D-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene]-β-D-fucopyranoside (57)



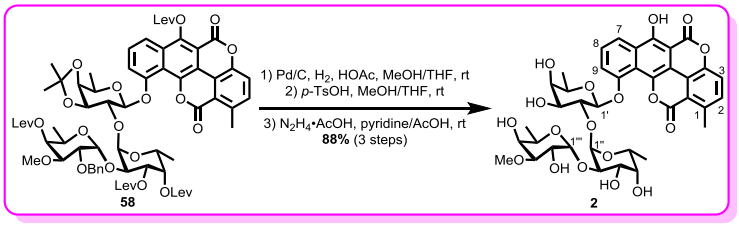
To a solution of **56** (81 mg, 0.077 mmol) in MeOH/THF (8.0 mL, v/v = 1 : 1) was added HOAc (3 drops) and Pd/C (10 wt% on carbon, 40 mg) successively at room temperature. The resulting suspension was degassed at -78 °C (evacuated under reduced pressure and refilled with H_2, and this process was repeated for 3 times), then was warmed to room temperature. The black suspension was stirred at the same temperature for 6 h, when TLC showed that the reaction reached to completion. Filtration through a pad of Celite/silica gel was followed by concentration under reduced pressure to yield the crude product, which was further purified by silica gel column chromatography (PE/EA = 1 : 3) to furnish **57** (61 mg, 82%) as a yellow solid: $[\alpha]_D^{25}$ = +15.1 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1 H, H-7), 7.74 (td, *J* = 2.0, 8.4 Hz, 1 H, H-8), 7.56-7.50 (m, 2 H, H-3, H-2), 7.33 (d, *J* = 6.8 Hz, 1 H, H-9), 6.03 (s, 1 H, H-1''), 5.23 (s, 1 H, H-4''), 5.20 (d, *J* = 7.6 Hz, 1 H, H-1'), 5.11 (d, *J* = 10.4 Hz, 1 H, H-3''), 4.45 (dd, *J* = 5.6, 12.4 Hz, 1 H, H-5''), 4.28-4.22 (m, 2 H, H-2', H-3'), 4.16-4.11 (m, 2 H, H-4'. H-5'), 3.85 (s, 1 H, H-2''), 3.17-3.03 (m, 4 H), 2.92 (s, 3 H, C1-CH_3), 2.78-2.73 (m, 2 H), 2.68-2.60 (m, 4 H), 2.60-2.39 (m, 2 H), 2.25 (s, 3 H, -$COCH_3$), 2.18 (s, 3 H, -$COCH_3$), 2.08 (s, 3 H, -$COCH_3$), 1.68 (s, 3 H), 1.46 (d, *J* = 7.2 Hz, 3 H, H-6'), 1.41 (s, 3 H), 1.20 (d, *J* = 6.0 Hz, 3 H, H-6''); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 206.7, 206.4, 172.7, 172.5, 171.4, 158.8, 156.9, 147.0, 146.3, 144.3, 139.8, 133.4, 130.9, 129.5, 121.1, 119.1, 118.4, 117.4, 110.9, 110.3, 108.1, 100.6 (C-1''), 100.1, 99.6 (C-1'), 79.0, 78.6, 76.6, 72.0, 71.8, 69.8, 67.2, 65.2, 38.2, 38.0 (2 C), 30.0 (2 C), 29.9, 28.5, 28.4, 28.1, 28.0, 26.7, 22.6, 16.6, 16.1; HRMS (ESI) m/z calcd for $C_{49}H_{53}O_{20}$ $[M + H]^+$: 961.3125, found: 961.3123.

6-*O*-Levulinoyl chartarin 10-*O*-[2-*O*-benzyl-3-*O*-methyl-4-*O*-levulinoyl-α-D-fucopyranosyl-(1→2)-3,4-di-*O*-levulinoyl-α-D-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene]-β-D-fucopyranoside (58)



Similar procedure as that used for the synthesis of **41** was adopted to mediate the coupling between donor **45a** (257 mg, 0.48 mmol) and acceptor **57** (77 mg, 0.080 mmol) to **58** (96 mg, 92%) as a light yellow solid: $[\alpha]_D^{25}$ = +25.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1 H, H-7), 7.61 (t, *J* = 8.4 Hz, 1 H, H-8), 7.55 (dd, *J* = 8.4, 14.8 Hz, 2 H, H-3, H-2), 7.32-7.28 (m, 2 H), 7.24-7.19 (m, 3 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 6.31 (d, *J* = 4.0 Hz, 1 H, H-1''), 5.39 (dd, *J* = 3.6, 10.8 Hz, 1 H, H-3''), 5.27 (d, *J* = 3.6 Hz, 1 H, H-4''), 5.14 (d, *J* = 3.6 Hz, 1 H, H-1'''), 5.04 (d, *J* = 3.2 Hz, 1 H, H-4'''), 4.57-4.50 (m, 2 H, H-1', H-5''), 4.29-4.25 (m, 1 H, H-2'), 4.23 (d, *J* = 12.0 Hz, 1 H, Ar-CH_2-), 4.12 (t, *J* = 5.2 Hz, 1 H, H-3'), 4.00 (dd, *J* = 1.6, 6.0 Hz, 1 H, H-4'), 3.91 (dd, *J* = 2.8, 10.0 Hz, 1 H, H-2''), 3.75-3.73 (m, 1 H, H-5'''), 3.52 (dd, *J* = 3.2, 10.0 Hz, 2 H, H-5', H-3'''), 3.34 (d, *J* = 12.4 Hz, 1 H, Ar-CH_2-), 3.17-3.04 (m, 7 H, -CH_2CH_2-, -OCH_3), 2.93 (s, 3 H, C1-CH_3), 2.87-2.65 (m, 6 H, -CH_2CH_2-), 2.61-2.54 (m, 2 H, -CH_2CH_2-), 2.47-2.28 (m, 8 H, -CH_2CH_2-, H-2''', -$COCH_3$), 2.21 (s, 3 H, -$COCH_3$), 2.15 (s, 3 H, -$COCH_3$), 2.08 (s, 3 H, -$COCH_3$), 1.64 (s, 3 H), 1.40 (s, 3 H), 1.36 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.24 (d, *J* = 6.4 Hz, 3 H, H-6''), 0.32 (s, 3 H, H-6'''); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 206.3, 206.2, 172.5, 172.0, 158.5, 157.0, 153.5, 146.9, 146.1, 144.3, 139.9, 139.5, 133.3, 130.6, 129.5, 128.0, 126.9, 126.8, 121.0, 119.1, 118.0 (2 C), 114.8, 111.3, 110.1, 108.1, 99.8 (C-1'), 95.8 (C-1''), 92.4 (C-1'''), 78.9, 76.4, 76.2, 75.8, 75.0, 71.9, 70.6, 70.0, 69.9, 69.0, 67.4, 64.6, 64.1, 56.8, 38.2, 38.0 (2 C), 37.8, 30.1, 30.0, 29.8, 28.5, 28.4, 28.1, 27.9, 27.6, 26.6, 22.6, 16.6, 16.3, 15.0; HRMS (ESI) m/z calcd for $C_{68}H_{76}O_{26}Na$ $[M + Na]^+$: 1331.4517, found: 1331.4496.

D329C (2)



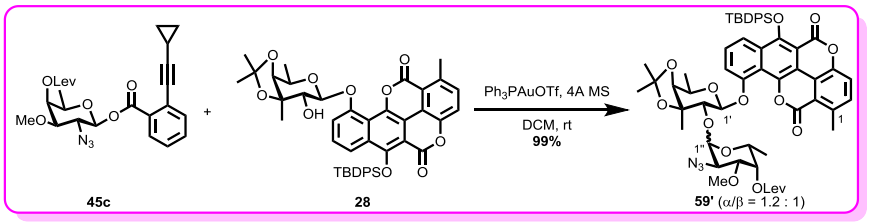
To a solution of **58** (19 mg, 0.015 mmol) in MeOH/THF (3.0 mL, v/v = 1 : 1) was added HOAc (2 drops) and Pd/C (10 wt% on carbon, 15 mg) successively at room temperature. The resulting mixture was degassed at -78 ^{o}C (evacuated under reduced pressure and refilled with H_2, and this process was repeated for 3 times), then was warmed to room temperature. The resulting black suspension was stirred at the same temperature for 17 h, when TLC showed that the reaction reached to completion. Filtration through a pad of Celite/silica gel was followed by concentration under reduced pressure to deliver the intermediate, which was put to the next step without further purification.

The above obtained intermediate was then dissolved in MeOH/THF (2.9 mL, v/v = 1 : 1), to which *p*-TsOH (13 mg, 0.075 mmol) was added at room temperature. The resulting mixture was stirred at the same temperature for 4 h, at which time TLC showed that all the starting materials disappeared. The reaction was then quenched by Et_3N; the resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivering the intermediate, which was put to the next step without further purification.

The above obtained intermediate was then dissolved in pyridine/HOAc (2.0 mL, v/v = 3 : 2), to which N_2H_4•HOAc (31 mg, 0.34 mmol) was added at room temperature. The resulting mixture was stirred at the same temperature for 24 h. Acetone was added to quench the reaction, which was followed by evaporation under reduced pressure. The resulting crude product was purified by silica gel column chromatography ($CHCl_3$/MeOH = 6 : 1) to give **2** (10 mg, 88% yield for 3 steps) as a yellow solid: $[\alpha]_D^{25}$ = -12.0 (*c* 0.1, MeOH); ^{1}H NMR (400 MHz, pyridine-d_5) δ 8.29 (d, *J* = 8.0 Hz, 1 H, H-7), 7.95 (d, *J* = 8.0 Hz, 1 H, H-9), 7.63 (t, *J* = 8.0 Hz, 1 H, H-8), 7.46 (d, *J* = 8.0 Hz, 1 H, H-3), 7.34 (d, *J* = 8.4 Hz, 1 H, H-2), 6.61 (d, *J* = 3.6 Hz, 1 H, H-1"), 6.00 (d, *J* = 7.6

Hz, 1 H, H-1'), 5.59 (d, *J* = 4.0 Hz, 1 H, H-1'''), 5.20 (qd, *J* = 1.6, 6.0 Hz, 1 H, H-5''), 5.14 (dd, *J* = 9.6, 7.6 Hz, 1 H, H-2'), 4.63 (dd, *J* = 3.6, 10.0 Hz, 1 H, H-3''), 4.57 (dd, *J* = 3.6, 10.0 Hz, 1 H, H-2''), 4.31 (q, *J* = 6.4 Hz, 1 H, H-5'''), 4.26 (dd, *J* = 3.6, 9.6 Hz, 1 H, H-3'), 4.11 (dd, *J* = 1.4, 3.2 Hz, 1 H, H-4''), 4.08 (d, *J* = 3.6 Hz, 1 H, H-4'), 3.99 (q, *J* = 6.4 Hz, 1 H, H-5'), 3.76 (d, *J* = 3.2 Hz, 1 H, H-4'''), 3.58 (dd, *J* = 3.2, 10.0 Hz, 1 H, H-3'''), 3.43 (dd, *J* = 3.6, 8.8 Hz, 1 H, H-2'''), 3.21 (s, 3 H, C3'''-CH_3), 2.80 (s, 3 H, C1-CH_3), 1.47 (d, *J* = 6.4 Hz, 6 H, H-6', H-6''), 0.90 (d, *J* = 6.4 Hz, 3 H, H-6'''); ^{13}C NMR (100 MHz, pyridine-d_5) δ 165.1, 159.3, 154.3, 147.3, 139.6, 132.9 (C-2), 128.4 (C-8), 120.8, 120.7 (C-3), 119.9, 118.9, 118.1 (C-7), 116.6 (C-9), 109.8, 100.9 (C-1'), 97.7, 97.0 (C-1''), 96.4 (C-1'''), 81.4 (C-3'''), 78.1 (C-2'), 73.9 (C-2''), 73.8 (C-3'), 73.5, (C-4'') 73.0 (C-4'), 71.7 (C-5'), 70.1 (C-3''), 69.0 (C-4'''), 68.6 (C-2'''), 67.2 (C-5''), 66.9 (C-5), 56.7 (C3'''-OCH_3), 22.1 (C1-CH_3), 17.1 (C-5''), 17.0 (C-5'), 16.3 (C-6'''); HRMS (ESI) m/z calcd for $C_{38}H_{43}O_{18}$ $[M + H]^+$: 787.2444, found: 787.2447.

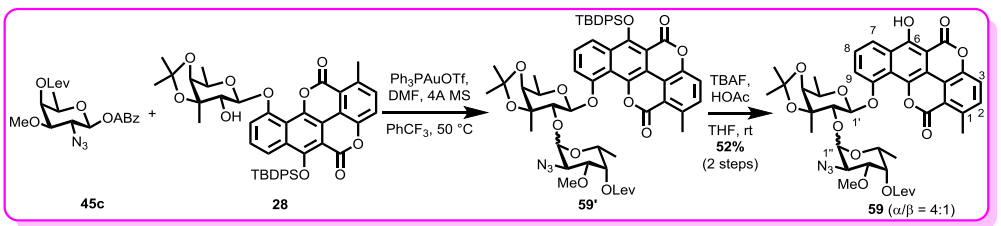
6-*O*-*tert*-Butyldiphenylsilyl chartarin 10-*O*-[2-azide-2-deoxy-3-*O*-methyl-4-*O*-levulinoyl-D-fucopyranosyl-(1→2)-3-*C*-methyl-3,4-*O*-isopropylidene]-β-D-fucopyranoside (59')



Similar procedure as that used for the synthesis of **41** was adopted to mediate the coupling between donor **45c** (18 mg, 0.038 mmol) and acceptor **28** (5.0 mg, 0.0065 mmol) to furnish **59'** (7.0 mg, 99%, α/β = 1.2 : 1) as a α/β mixture. Pure **59'α** was obtained as a yellow solid: $[\alpha]_D^{25}$ = +12.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1 H), 7.71-7.67 (m, 4 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 7.37-7.27 (m, 8 H), 7.25-7.22 (m, 1 H), 6.29 (d, *J* = 3.6 Hz, 1 H, H-1''), 5.39 (dd, *J* = 1.6, 3.6 Hz, 1 H, H-4''), 5.22 (d, *J* = 8.4 Hz, 1 H, H-1'), 4.40-4.33 (m, 2 H, H-2', H-5''), 4.15-4.10 (m, 1 H, H-5'), 3.77 (d, *J* = 2.0 Hz, 1 H, H-4'), 3.64 (dd, *J* = 2.8, 10.8 Hz, 1 H, H-3''), 3.32 (s,

3 H, -OCH_3), 3.25 (dd, *J* = 3.6, 11.2 Hz, 1 H, H-2''), 2.86 (s, 3 H, C1-CH_3), 2.79-2.58 (m, 4 H, -CH_2CH_2-), 2.18 (s, 3 H, -$COCH_3$), 1.71 (s, 3 H), 1.49 (d, *J* = 6.8 Hz, 3 H, H-6'), 1.46 (s, 3 H, C3'-CH_3), 1.43 (s, 3 H), 1.24 (d, *J* = 6.4 Hz, 3 H, H-6''), 1.12 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 172.5, 159.2, 157.4, 154.2, 153.0, 147.0, 140.7, 138.7, 135.3 (2 C), 132.8 (2 C), 132.7, 131.3, 129.7, 127.5 (2 C), 120.4, 119.8, 119.5, 118.8, 117.4, 113.9, 110.2, 109.4, 104.6 (C-1''), 100.2 (C-1'), 99.7, 82.4, 81.6, 79.7, 75.8, 69.7, 68.5, 65.4, 59.4, 57.2, 38.2, 30.0, 28.7, 28.1, 27.5, 27.2, 22.7, 21.2, 18.3, 17.1, 16.4; HRMS (ESI) m/z calcd for $C_{57}H_{61}N_3O_{15}SiNa$ $[M + Na]^+$: 1078.3764, found: 1078.3761. Pure **59'β** was also obtained as a yellow solid: $[\alpha]_D^{25}$ = -35.8 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1 H), 7.70-7.67 (m, 4 H), 7.52 (t, *J* = 8.2 Hz, 1 H), 7.42-7.32 (m, 5 H), 7.29-7.25 (m, 4 H), 5.49 (d, *J* = 7.2 Hz, 1 H, H-1'), 5.18 (d, *J* = 8.0 Hz, 1 H, H-1''), 4.99 (d, *J* = 3.2 Hz, 1 H, H-4''), 4.62 (d, *J* = 6.8 Hz, 1 H, H-2'), 4.12-4.07 (m, 1 H, H-5'), 3.79 (d, *J* = 2.0 Hz, 1 H, H-4'), 3.36-3.27 (m, 2 H, H-2'', H-5''), 3.34 (s, 3 H, -OCH_3), 3.18 (dd, *J* = 3.4, 10.4 Hz, 1 H, H-3''), 2.86 (s, 3 H, C1-CH_3), 2.76-2.49 (m, 4 H, -CH_2CH_2-), 2.11 (s, 3 H, -$COCH_3$), 1.69 (s, 3 H), 1.56 (s, 3 H, C3'-CH_3), 1.45 (s, 3 H), 1.43 (d, *J* = 6.8 Hz, 3 H, H-6'), 1.12 (s, 9 H), 0.50 (d, *J* = 6.4 Hz, 3 H, H-6''); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 172.6, 159.2, 157.3, 153.3 (2 C), 147.1, 140.6, 138.8, 135.3, 135.2, 132.9, 132.8, 131.3, 129.7, 127.7, 127.5, 120.6, 119.7, 119.4 (2 C), 117.3, 115.7, 109.9, 109.7, 104.2, 102.6 (H-1''), 99.1 (C-1'), 82.3, 82.0, 81.5, 80.5, 69.0, 68.3 (2 C), 64.3, 57.9, 38.0, 29.9, 27.9 (2 C), 27.6, 27.2, 22.6, 21.2, 19.8, 17.2, 15.9; HRMS (ESI) m/z calcd for $C_{57}H_{61}N_3O_{15}SiNa$ $[M + Na]^+$: 1078.3764, found: 1078.3761.

Chartarin 10-*O*-[2-azide-2-deoxy-3-*O*-methyl-4-*O*-levulinoyl-D-fucopyranosyl-(1→2)-3-*C*-methyl-3,4-*O*-isopropylidene]-β-D-fucopyranoside (59)

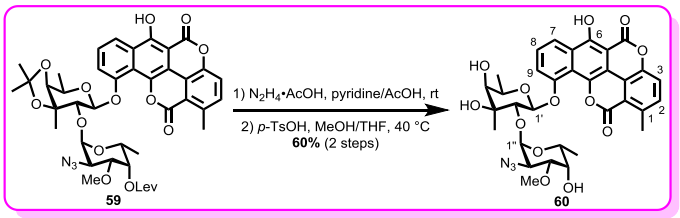


To a stirred solution of glycosyl donor **45c** (120 mg, 0.26 mmol), acceptor **28** (33 mg, 0.043 mmol) and DMF (119 μL, 1.54 mmol) in dry $PhCF_3$ (4.5 mL) was added activated 4 Å molecular sieves (510 mg) at room temperature under N_2 atmosphere. The resulting mixture was stirred at the same temperature for 1 h before $Ph_3PAuOTf$ (512 μL, 0.2 M in CH_2Cl_2, 0.10 mmol) was added. The reaction mixture was then heated to 50 □, and was stirred over night, when TLC showed that all glycosyl donor disappeared. Filtration was followed by concentration under reduced pressure to yield the crude product **59'**.

To a solution of the above obtained crude product in THF (3.0 mL) was added HOAc (7.3 μL, 0.13 mmol) and TBAF (64 μL, 1 M in THF, 0.064 mmol) successively at room temperature. The resulting mixture was stirred at the same temperature for 10 min, when TLC showed that the reaction reached to completion. The solvent was removed *in vacuo* to give a residue, which was further purified by silica gel column chromatography (DCM/EA = 15 : 1) to give **59** (18 mg, 52% yield for 2 steps, α/β = 4 : 1) as a α/β mixture. Pure **59α** was obtained as a yellow syrup: $[\alpha]_D^{25}$ = +68.8 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1 H, C6-OH), 8.31 (d, *J* = 8.0 Hz, 1 H, H-7), 7.67 (t, *J* = 8.4 Hz, 1 H, H-8), 7.56 (d, *J* = 8.0 Hz, 1 H, H-3), 7.49 (d, *J* = 8.4 Hz, 1 H, H-2), 7.39 (d, *J* = 8.0 Hz, 1 H, H-9), 6.31 (d, *J* = 3.6 Hz, 1 H, H-1"), 5.39 (dd, *J* = 1.2, 3.2 Hz, 1 H, H-4"), 5.23 (d, *J* = 8.8 Hz, 1 H, H-1'), 4.39-4.33 (m, 2 H, H-2', H-5"), 4.16-4.11 (m, 1 H, H-5'), 3.77 (d, *J* = 1.6 Hz, 1 H, H-4'), 3.64 (dd, *J* = 3.2, 10.8 Hz, 1 H, H-3"), 3.30 (s, 3 H, -OCH_3), 3.22 (dd, *J* = 3.6, 11.2 Hz, 1 H, H-2"), 2.91 (s, 3 H, C1-CH_3), 2.78-2.72 (m, 2 H), 2.69-2.58 (m, 2 H), 2.19 (s, 3 H, -$COCH_3$), 1.70 (s, 3 H), 1.49 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.46 (s, 3 H, C3'-CH_3), 1.43 (s, 3 H), 1.25 (d, *J* = 6.4 Hz, 3 H, H-6"); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 172.5, 165.1, 159.3, 157.6, 154.3, 146.7, 140.1, 139.1, 133.0, 128.1, 127.2, 121.0, 120.3, 119.2, 118.5, 117.9, 115.0, 109.4, 108.9, 100.3 (C-1"), 100.1, 99.6 (C-1'), 96.8, 82.4, 81.6, 79.7, 75.6, 69.7, 68.5, 65.4, 59.3, 57.2, 38.2, 30.0, 28.7, 28.1, 27.5, 22.7, 18.3, 17.1, 16.4; HRMS (ESI) m/z calcd for $C_{41}H_{44}N_3O_{15}$ $[M + H]^+$: 818.2767, found: 818.2761. Pure **59β** was also obtained as a yellow solid: $[\alpha]_D^{25}$ = +33.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1 H, C6-OH), 8.27 (d, *J* = 8.4 Hz, 1 H, H-7), 7.64 (t, *J* = 8.2 Hz, 1 H, H-8), 7.56-7.49

(m, 3 H, H-2, H-3, H-9), 5.49 (d, *J* = 7.2 Hz, 1 H, H-1'), 5.11 (d, *J* = 8.0 Hz, 1 H, H-1''), 4.99 (d, *J* = 3.2 Hz, 1 H, H-4''), 4.62 (d, *J* = 7.2 Hz, 1 H, H-1'), 4.09 (q, *J* = 6.8 Hz, 1 H, H-5'), 3.79 (d, *J* = 2.0 Hz, 1 H, H-4'), 3.33 (s, 3 H, -OCH_3), 3.33-3.26 (m, 2 H, H-2'', H-5''), 3.17 (dd, *J* = 3.4, 10.2 Hz, 1 H, H-3''), 2.91 (s, 3 H, C1-CH_3), 2.76-2.68 (m, 1 H), 2.64-2.57 (m, 1 H), 2.53-2.45 (m, 2 H), 2.11 (s, 3 H, -$COCH_3$), 1.67 (s, 3 H), 1.56 (s, 3 H, C3'-CH_3), 1.44 (s, 3 H), 1.42 (d, *J* = 6.4 Hz, 3 H, H-6'), 0.52 (d, *J* = 6.4 Hz, 3 H, H-6''); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 172.5, 164.9, 159.2, 157.7, 153.3, 146.7, 140.1, 139.0, 133.1, 128.2, 127.2, 121.2, 120.1, 120.0, 118.5, 117.9, 117.6, 109.6, 108.5, 102.2 (C-1''), 99.3 (C-1'), 96.4, 82.3, 81.6, 81.2, 80.5, 69.0, 68.4, 68.2, 64.1, 57.9, 38.0, 29.9, 27.9, 27.6, 22.6, 19.7, 17.2, 16.0; HRMS (ESI) m/z calcd for $C_{41}H_{44}N_3O_{15}$ $[M + H]^+$: 818.2767, found: 818.2762.

Chartarin 10-*O*-[2-azide-2-deoxy-3-*O*-methyl-4-*O*-levulinoyl-α-D-fucopyranosyl-(1→2)-3-*C*-methyl]-β-D-fucopyranoside (60)

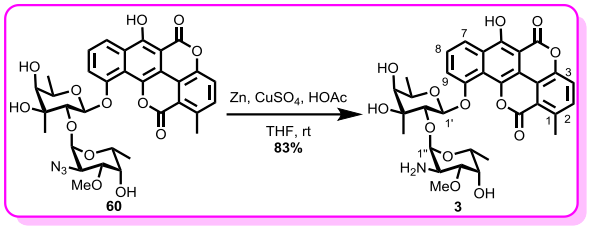


To a solution of **59** (12 mg, 0.015 mmol) in pyridine/HOAc (2.0 mL, v/v = 3 : 2) was added N_2H_4•HOAc (5.4 mg, 0.058 mmol) at room temperature. The resultant mixture was stirred at the same temperature for 2 h, when TLC showed that the reaction reached to completion. After quenched by acetone, the resulting mixture was diluted with EtOAc, washed successively with 1N HCl, H_2O, and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver the intermediate, which was put to the next step without further purification.

The above obtained intermediate was then dissolved in MeOH/THF (2.0 mL, v/v = 1 : 1), to which *p*-TsOH (8.3 mg, 0.048 mmol) was added at room temperature. The resulting mixture was heated to 40 ℃ and stirred at the same temperature for 8 h before

Et_3N was added to quench the reaction. Evaporation under reduced pressure afforded a residue, which was further purified by silica gel column chromatography (DCM/MeOH = 50 : 1) to give **60** (6.0 mg, 60% yield for 2 steps) as a yellow solid: $[\alpha]_D^{25}$ = +32.0 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1 H, C6-OH), 8.23 (d, *J* = 8.4 Hz, 1 H, H-7), 7.64 (t, *J* = 8.2 Hz, 1 H, H-8), 7.51-7.49 (m, 2 H, H-3, H-9), 7.38 (d, *J* = 8.4 Hz, 1 H, H-2), 5.90 (d, *J* = 4.0 Hz, 1 H, H-1''), 5.39 (d, *J* = 7.6 Hz, 1 H, H-1'), 4.44 (q, *J* = 6.4 Hz, 1 H, H-5''), 4.31 (d, *J* = 7.6 Hz, 1 H, H-2'), 4.04 (q, *J* = 6.4 Hz, 1 H, H-5'), 4.00 (d, *J* = 2.4 Hz, 1 H, H-4''), 3.62 (dd, *J* = 3.2, 10.8 Hz, 1 H, H-3''), 3.48 (s, 1 H, H-4'), 3.45 (s, 3 H, -OCH_3), 3.32 (dd, *J* = 10.8, 3.8 Hz, 1 H, H-2''), 2.76 (s, 3 H, C1-CH_3), 1.38 (d, *J* = 6.4 Hz, 3 H, H-6''), 1.37 (s, 3 H, C3'-CH_3), 1.34 (d, *J* = 6.4 Hz, 3 H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 159.5, 157.5, 153.5, 146.5, 140.2, 138.7, 132.9 (C-2), 128.1 (C-8), 127.0, 121.0 (2 C, C-3), 119.9, 118.9 (C-7), 117.7, 116.8 (C-9), 108.8, 100.5 (C-1''), 100.3 (C-1'), 96.5, 81.6 (C-2'), 77.3 (C-4'), 77.1 (C-3''), 73.8 (C-3'), 69.6 (C-5'), 68.4 (C-4''), 66.6 (C-5''), 58.8 (C-2''), 57.1 (C3''-OCH_3), 22.3 (C1-CH_3), 19.5 (C3'-CH_3), 17.1 (C-6'), 16.4 (C-6''); HRMS (ESI) m/z calcd for $C_{33}H_{33}N_3O_{13}Na$ $[M + Na]^+$: 702.1905, found: 702.1896.

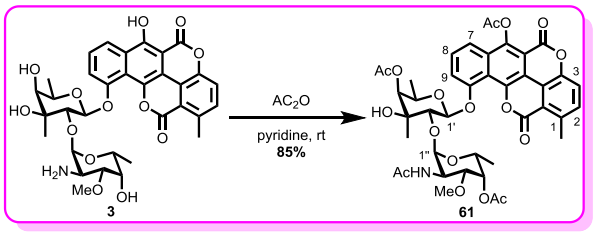
Elsamicin A (3)



To a solution of **60** (10 mg, 0.015 mmol) and AcOH (83 μL, 1.45 mmol) in THF (2.5 mL) was added Zn power (57 mg, 0.88 mmol) and $CuSO_4$ (23 mg, 0.15 mmol) successively at room temperature under N_2 atmosphere. The reaction mixture was stirred for 5.5 h at the same temperature. After completion of the reaction (monitored by TLC), filtration was followed by concentration under reduced pressure to yield a yellow solid, which was further purified by silica gel column chromatography (DCM/MeOH = 6 : 1) and C18 reversed-phase chromatography (NH_4OAc (0.1 M, pH

4.0)/MeCN = 1 : 1) to furnish **3** (8.0 mg, 83%) as a yellow solid: $[\alpha]_D$ = +90.2 (*c* 0.5, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.65 (brs, 1 H, H-7), 7.31 (brs, 2 H, H-9), 7.27 (brs, 1 H, H-8), 7.06 (brs, 1 H, H-2), 6.59 (brs, 1 H, H-3), 5.86 (s, 1 H, H-1''), 5.60 (d, *J* = 7.2 Hz, 1 H, H-1'), 4.50 (q, *J* = 6.7 Hz, 1 H, H-5''), 4.15 (d, *J* = 7.6 Hz, 1 H, H-2'), 4.11-4.08 (m, 2 H, H-5', H-4''), 3.72 (d, *J* = 10.8 Hz, 1 H, H-3''), 3.65 (d, *J* = 11.6 Hz, 1 H, H-2''), 3.48 (s, 3 H, -OCH_3), 3.44 (s, 1 H, H-4'), 2.47 (s, 3 H, C1-CH_3), 1.43 (s, 3 H, C3'-CH_3), 1.39 (d, *J* = 6.4 Hz, 3 H, H-6''), 1.27 (d, *J* = 6.0 Hz, 3 H, H-6'); ^{13}C NMR (150 MHz, CD_3OD) δ 163.3, 161.0, 152.4, 147.2, 139.8, 135.9, 133.9 (C-2), 130.8, 127.5 (C-8, C-9), 121.0 (C-3), 120.4, 120.3 (2 C, C-7), 117.4, 110.4, 99.7 (C-1''), 98.8 (C-1'), 94.7, 82.6 (C-2'), 78.4 (C-3''), 78.3 (C-4'), 74.9 (C-3'), 71.2 (C-5'), 68.7 (C-5''), 67.6 (C-4''), 56.2 (-OCH_3), 51.3 (C-2''), 22.3 (C1-CH_3), 19.8 (C3'-CH_3), 17.2 (C-6'), 16.8 (C-6''); HRMS (ESI) m/z calcd for $C_{33}H_{36}NO_{13}$ $[M + H]^+$: 654.2181, found: 654.2183.

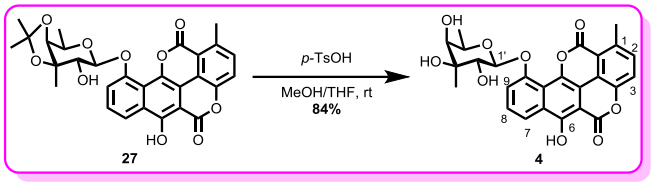
Acetylated elsamicin A (61)



To a solution of **3** (6 mg, 0.0092 mmol) in dry pyridine (0.5 mL) was added Ac_2O (0.5 mL, 5.29 mmol) at room temperature. The mixture was stirred at the same temperature for 9 h, when TLC shown that the reaction reached to completion. The resulting mixture was diluted with EtOAc, washed successively with 1N HCl, H_2O, saturated aqueous Na_2HCO_3, and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to give a residue, which was further purified by silica gel column chromatography ($CHCl_3$/MeOH = 50 : 1) to give **61** (6.4 mg, 85%) as a yellow solid: $[\alpha]_D^{25}$ = -12.0 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1 H, H-7), 7.67 (t, *J* = 8.0 Hz, 1 H, H-8), 7.57-7.52 (m, 2 H, H-2, H-3), 7.39 (d, *J* = 6.8 Hz, 1 H, H-9), 5.89 (brs, 1 H, H-1''), 5.40 (d,

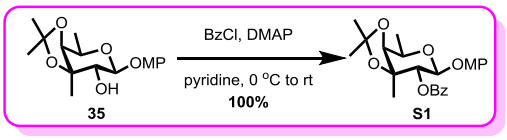
J = 10.8 Hz, 1 H, H-1'), 5.39 (s, 1 H, H-4''), 5.02 (s, 1 H, H-4'), 4.42-4.37 (m, 2 H, H-2'', H-5''), 4.24 (brs, 1 H, H-2'), 4.12 (brs, 1 H, H-5'), 3.40 (brs, 1 H, H-3''), 3.25 (s, 3 H, -OCH_3), 2.94 (s, 3 H, C6-OAc), 2.61 (s, 3 H, C1-CH_3), 2.25 (s, 3 H, C4''-OAc), 2.16 (s, 3 H, C4'-OAc), 1.47 (s, 3 H, C3'-CH_3), 1.22 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.20 (d, *J* = 6.8 Hz, 3 H, H-6''), 0.77 (brs, 3 H, C2''-NHAc); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.8, 169.0 158.5, 156.6, 146.8, 145.7, 144.0, 139.7, 133.5, 130.5, 128.7, 121.0, 118.7, 117.3, 111.4, 108.6, 100.9 (C-1''), 98.3 (C-1'), 81.7, 72.3, 69.3, 68.4, 66.3, 56.9, 48.2, 22.4, 22.1, 21.0, 20.9, 20.8, 20.1, 16.7, 16.5; HRMS (ESI) m/z calcd for $C_{41}H_{43}NO_{17}Na$ $[M + Na]^+$: 844.2423, found: 844.2418.

Elsamicin B (4)



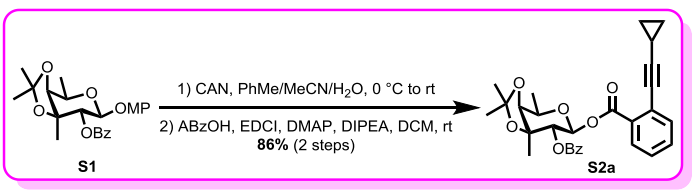
To a solution of **27** (5.0 mg, 0.0094 mmol) in MeOH/THF (1.0 mL, v/v = 1 : 1) was added *p*-TsOH (3 mg, 0.017 mmol) at room temperature. The resultant mixture was stirred at the same temperature for 6 h before Et_3N was added to quench the reaction. Evaporation under reduced pressure afforded a residue, which was further purified by silica gel column chromatography (DCM/MeOH = 20 : 1) to give **4** (3.9 mg, 84%) as a yellow solid: $[\alpha]_D^{25}$ = -12.6 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.39 (s, 1 H, C6-OH), 8.00 (d, *J* = 8.0 Hz, 1 H, H-7), 7.71-7.56 (m, 4 H, H-8, H-9, H-2, H-3), 5.13 (d, *J* = 7.6 Hz, 1 H, H-1'), 4.74 (d, *J* = 4.4 Hz, 1 H, C4'-OH), 4.64 (s, 1 H, C3'-OH), 4.18 (d, *J* = 4.4 Hz, 1 H, C2'-OH), 4.12 (q, *J* = 6.4 Hz, 1 H, H-5'), 3.99 (dd, *J* = 4.0, 8.0 Hz, 1 H, H-2'), 3.27 (d, *J* = 3.2 Hz, 1 H, H-4'), 2.75 (s, 3 H, C1-CH_3), 1.26 (d, *J* = 6.0 Hz, 3 H, H-6'), 1.24 (s, 3 H, C3'-CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.5, 158.7, 155.5, 154.2, 146.2, 138.6, 137.9, 133.1 (C-2), 128.6 (C-8), 125.9, 121.0 (C-3), 119.2, 117.7, 116.8 (C-7), 116.7, 115.8 (C-9), 108.4, 101.3 (C-1'), 96.7, 75.7 (C-4'), 73.1 (C-3'), 72.8 (C-2'), 69.3 (C-5'), 21.5 (C1-CH_3), 19.1 (C3'-CH_3), 17.1 (C-6'); HRMS (ESI) m/z calcd for $C_{26}H_{22}O_{10}Na$ $[M + Na]^+$: 517.1105, found: 517.1104.

4-Methoxyphenyl 2-*O*-benzoyl-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (S1)



To a stirred solution of **35** (600 mg, 1.85 mmol) and DMAP (225 mg, 1.85 mmol) in dry pyridine (12.3 mL) was added BzCl (624 μL, 5.38 mmol) dropwise at 0 °C under N_2 atmosphere. The reaction mixture was then gradually warmed up to room temperature and stirred overnight, at which time TLC showed that all the starting materials disappeared. After quenched by MeOH in 0 °C, the resulting mixture was diluted with EtOAc, washed successively with 1N HCl, H_2O, and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration followed by concentration under reduced pressure delivered a residue, which was further purified by silica gel column chromatography (PE/EA = 7 : 1) to afford **S1** (794 mg, 100%) as a white solid: $[\alpha]_D^{25}$ = +38.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2 H), 7.58-7.54 (m, 1 H), 7.45-7.41 (m, 2 H), 6.91-6.87 (m, 2 H), 6.76-6.72 (m, 2 H), 5.65 (d, *J* = 8.8 Hz, 1 H), 4.86 (d, *J* = 8.4 Hz, 1 H), 4.04 (qd, *J* = 2.0, 6.8 Hz, 1 H), 3.75-3.73 (m, 4 H), 1.71 (s, 3 H), 1.51 (d, *J* = 6.8 Hz, 3 H), 1.48 (s, 3 H), 1.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 155.6, 151.8, 133.1, 130.2, 129.9, 128.5, 119.1, 114.5, 109.6, 100.6, 82.4, 81.0, 74.7, 68.4, 55.7, 28.0, 27.3, 18.4, 17.1; HRMS (ESI) m/z calcd for $C_{24}H_{28}O_7Na$ $[M + Na]^+$: 451.1727, found: 451.1721.

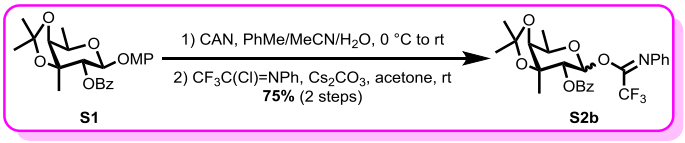
2-*O*-Benzoyl-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S2a)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S1** (100 mg, 0.23 mmol) to **S2a** (99 mg, 86% yield for 2 steps) as a white solid: $[\alpha]_D^{25}$ =

+50.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 8.05-8.01 (m, 2 H), 7.79 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.63-7.59 (m, 1 H), 7.50-7.42 (m, 4 H), 7.33-7.28 (m, 1 H), 5.98 (d, *J* = 8.8 Hz, 1 H, H-1), 5.66 (d, *J* = 9.2 Hz, 1 H, H-2), 4.36 (dq, *J* = 1.6, 6.4 Hz, 1 H, H-5), 3.97 (d, *J* = 2.0 Hz, 1 H, H-4), 1.61 (s, 6 H), 1.55-1.48 (m, 1 H), 1.43 (d, *J* = 6.8 Hz, 3 H, H-6), 1.37 (s, 3 H), 0.94-0.87 (m, 2 H), 0.86-0.79 (m, 2 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 165.9, 164.3, 134.9, 134.2, 133.3, 131.1 (2 C), 130.7, 130.3, 129.5, 128.0, 126.1, 109.7, 100.9, 92.9 (C-1), 82.9, 81.7, 74.9, 74.8, 69.8, 28.3, 27.4, 18.1, 17.1, 9.2 (2 C), 1.1; HRMS (ESI) m/z calcd for $C_{29}H_{30}O_7Na$ $[M + Na]^+$: 513.1884, found: 513.1877.

2-*O*-Benzoyl-3-*C*-methyl-3,4-*O*-isopropylidene-D-fucopyranosyl *N*-phenyltrifluoroacetimidate (S2b)

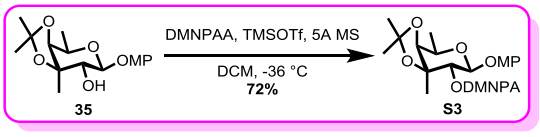


To a solution of **S1** (200 mg, 0.47 mmol) in PhMe/MeCN/H_2O (18.6 mL, v/v/v = 2 : 3 : 2) was added CAN (756 mg, 1.38 mmol) in three batches at 0 °C. The resultant mixture was stirred at the same temperature for 10 min and then warmed up to room temperature. After being stirred at the same temperature for another 45 min, EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with ice water, saturated aqueous $NaHCO_3$ and brine, and the combined organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to give a residue, which was further purified by silica gel column chromatography (PE/EA = 3 : 1) to give the hemiacetal intermediate (140 mg, 93%) as a yellow syrup.

To a solution of the above obtained hemiacetal intermediate (70 mg, 0.22 mmol) and Cs_2CO_3 (64 mg, 0.87 mmol) in acetone (2.2 mL) was added $CF_3C(Cl)$=NPh (32 μL, 0.33 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 9 h. After the completion of the reaction (monitored by TLC), filtration was followed by concentration under reduced pressure to yield the crude product, which

was further purified by silica gel column chromatography (PE/EA/Et_3N = 30 : 1 : 1%) to furnish **S2b** (87 mg, 81%, α/β = 1 : 2.5) as a α/β mixture. Pure **S2bα** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +39.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 8.11-8.09 (m, 2 H), 7.75-7.71 (m, 1 H), 7.61-7.57 (m, 2 H), 7.21-7.17 (m, 2 H), 7.06-7.02 (m, 1 H), 6.57-6.48 (m, 3 H, H-1), 5.53 (d, *J* = 3.2 Hz, 1 H, H-2), 4.48 (d, *J* = 7.2 Hz, 1 H, H-5), 4.08 (d, *J* = 2.0 Hz, 1 H, H-4), 1.64 (s, 3 H), 1.50 (s, 3 H), 1.41 (d, *J* = 6.8 Hz, 3 H, H-6), 1.38 (s, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 166.0, 144.4, 134.6, 130.5, 130.4, 129.7, 129.5, 125.0, 119.9, 109.7, 94.1 (C-1), 82.3, 79.2, 73.0, 67.1, 28.2, 27.5, 20.0, 17.0; HRMS (ESI) m/z calcd for $C_{25}H_{26}F_3NO_6Na$ $[M + Na]^+$: 516.1604, found: 516.1595. Pure **S2bβ** was obtained as a white solid: $[\alpha]_D^{25}$ = +86.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 1.2, 8.0 Hz, 2 H), 7.61-7.57 (m, 1 H), 7.48-7.44 (m, 2 H), 7.29-7.25 (m, 2 H), 7.11-7.07 (m, 1 H), 6.76-6.74 (m, 2 H), 5.80 (brs, 1 H, H-1), 5.63 (d, *J* = 8.0 Hz, 1 H, H-2), 3.99 (brs, 1 H, H-5), 3.71 (s, 1 H, H-4), 1.68 (s, 3 H), 1.47 (d, *J* = 6.4 Hz, 3 H, H-6), 1.38 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.0, 143.6, 133.4, 129.9, 129.8, 128.8, 128.6, 124.5, 119.4, 109.8, 94.6 (C-1), 82.2, 80.9, 73.8, 69.5, 27.9, 27.3, 18.3, 16.9; HRMS (ESI) m/z calcd for $C_{25}H_{26}F_3NO_6Na$ $[M + Na]^+$: 516.1604, found: 516.1595.

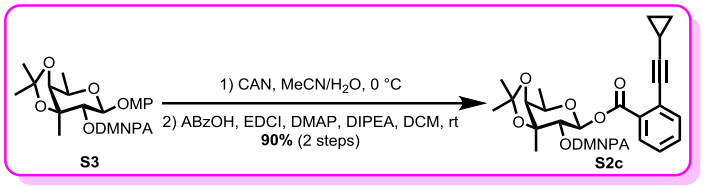
4-Methoxyphenyl 2-*O*-[2,2-dimethyl-2-(*ortho*-nitrophenyl)acetyl]-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (S3)



To a solution of **35** (200 mg, 0.62 mmol) and DMNPAA (460 mg, 1.15 mmol) in dry CH_2Cl_2 (6.2 mL) was added TMSOTf (520 μL, 2.87 mmol) dropwise at -36 °C in the presence of 5 Å molecular sieves (240 mg) under N_2 atmosphere. The resulting reaction mixture was stirred at the same temperature for another 65 min, at which time TLC showed the disappearance of all starting material. Et_3N (0.6 mL) was added to quench the reaction, the reaction mixture was then diluted with ethyl acetate. Washing with saturated aqueous $NaHCO_3$, brine successively, the organic phase was then dried over

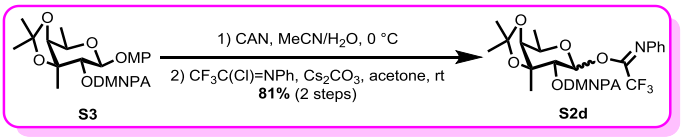
anhydrous Na_2SO_4. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (PhMe/EA = 20 : 1) to deliver **S3** (229 mg, 72%) as a colorless syrup: $[\alpha]_D^{25}$ = +34.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1 H), 7.58-7.53 (m, 2 H), 7.40-7.36 (m, 1 H), 6.95-6.91 (m, 2 H), 6.82-6.77 (m, 2 H), 5.38 (d, *J* = 8.4 Hz, 1 H), 4.74 (d, *J* = 8.4 Hz, 1 H), 3.93-3.88 (m, 1 H), 3.77 (s, 3 H), 3.63 (d, *J* = 1.6 Hz, 1 H), 1.71 (s, 3 H), 1.68 (s, 3 H), 1.63 (s, 3 H), 1.44 (d, *J* = 6.4 Hz, 3 H), 1.37 (s, 3 H), 1.18 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 155.2, 151.4, 148.9, 138.9, 133.0, 128.5, 127.9, 125.7, 118.1, 114.5, 109.5, 99.0, 82.4, 80.6, 74.3, 68.2, 55.8, 47.2, 27.9, 27.5, 27.2, 27.0, 17.8, 17.1; HRMS (ESI) m/z calcd for $C_{27}H_{33}NO_9Na$ $[M + Na]^+$: 538.2047, found: 538.2038.

2-*O*-[2,2-dimethyl-2-(*ortho*-nitrophenyl)acetyl]-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S2c)



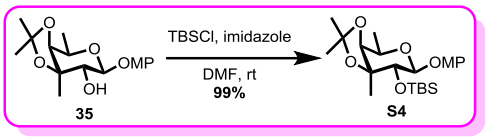
Similar procedures as those used for the synthesis of **20** were adopted to convert **S3** (112 mg, 0.22 mmol) to **S2c** (114 mg, 90% yield for 2 steps) as a light yellow syrup: $[\alpha]_D^{25}$ = +39.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 1.2, 6.4 Hz, 1 H), 7.83 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.52 (td, *J* = 1.2, 7.8 Hz, 1 H), 7.48 (td, *J* = 1.2, 8.4 Hz, 2 H), 7.43 (td, *J* = 1.2, 7.2 Hz, 1 H), 7.37-7.35 (m, 1 H), 7.29-7.26 (m, 1 H), 5.74 (d, *J* = 9.0 Hz, 1 H, H-1), 5.42 (d, *J* = 9.0 Hz, 1 H, H-2), 4.04 (qd, *J* = 1.8, 6.6 Hz, 1 H, H-5), 3.64 (d, *J* = 1.8 Hz, 1 H, H-4), 1.64 (s, 3 H), 1.57-1.54 (m, 1 H), 1.53 (s, 3 H), 1.48 (s, 3 H), 1.42 (d, *J* = 6.6 Hz, 3 H, H-6), 1.38 (s, 3 H), 1.19 (s, 3 H), 0.93-0.89 (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.2, 163.9, 148.7, 138.6, 134.5, 133.0, 132.5, 131.7, 129.6, 128.3, 127.9, 127.2, 125.9, 125.7, 109.5, 100.3, 91.7 (C-1), 82.4, 80.7, 74.8, 73.6, 69.2, 46.9, 28.0, 27.5, 26.9, 26.8, 17.6, 16.9, 9.1, 0.9; HRMS (ESI) m/z calcd for $C_{32}H_{35}NO_9Na$ $[M + Na]^+$: 600.2204, found: 600.2196.

2-*O*-[2,2-dimethyl-2-(*ortho*-nitrophenyl)acetyl]-3-*C*-methyl-3,4-*O*-isopropylidene-D-fucopyranosyl *N*-phenyltrifluoroacetimidate (S2d)



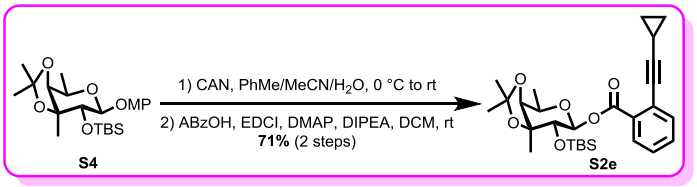
Similar procedures as that used for the synthesis of **S2b** were adopted to convert **S3** (112 mg, 0.22 mmol) to **S2d** (102 mg, 81% yield for 2 steps, α/β = 1 : 4.2) as a α/β mixture. Pure **S2dα** was obtained as a light yellow syrup: $[\alpha]_D^{25}$ = +20.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, acetone-d_6) δ 8.04 (dd, *J* = 1.2, 7.8 Hz, 1 H), 7.86 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.81 (td, *J* = 1.2, 7.2 Hz, 1 H), 7.61 (td, *J* = 1.2, 7.8 Hz, 1 H), 7.35-7.32 (m, 2 H), 7.14-7.11 (m, 1 H), 6.91 (d, *J* = 7.2 Hz, 2 H), 6.25 (brs, 1 H, H-1), 5.16 (s, 1 H, H-2), 4.29-4.26 (m, 1 H, H-5), 3.93 (d, *J* = 1.8 Hz, 1 H, H-4), 1.76 (s, 3 H), 1.68 (s, 3 H), 1.45 (s, 3 H), 1.34 (d, *J* = 6.6 Hz, 3 H, H-6), 1.34 (s, 3 H), 1.31 (s, 3 H); ^{13}C NMR (150 MHz, acetone-d_6) δ 175.5, 149.3, 144.8, 139.5, 134.7, 129.6, 129.5, 129.2, 126.5, 125.0, 120.1, 109.3, 93.6 (C-1), 82.2, 79.0, 73.2, 66.3, 47.4, 28.3, 27.5, 27.4, 27.0, 19.1, 17.0; HRMS (ESI) m/z calcd for $C_{28}H_{31}F_3N_2O_8Na$ $[M + Na]^+$: 603.1925, found: 603.1921. Pure **S2dβ** was obtained as a white foam: $[\alpha]_D^{25}$ = -12.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 8.04 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.84 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.79 (td, *J* = 1.6, 8.0 Hz, 1 H), 7.62 (td, *J* = 1.6, 8.0 Hz, 1 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.16 (t, *J* = 7.6 Hz, 1 H), 6.89 (d, *J* = 7.6 Hz, 2 H), 5.60 (brs, 1 H, H-1), 5.24 (s, 1 H, H-2), 4.02 (brs, 1 H, H-5), 3.74 (s, 1 H, H-4), 1.72 (s, 3 H), 1.70 (s, 3 H), 1.50 (s, 3 H), 1.33 (d, *J* = 6.4 Hz, 3 H, H-6), 1.30 (s, 3 H), 1.07 (brs, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 174.3, 149.6, 144.6, 139.2, 134.3, 129.7, 129.6, 129.1, 126.3, 125.2, 120.1, 109.6, 95.1 (C-1), 82.5, 81.3, 74.3, 69.6, 47.6, 28.1, 27.4 (2 C), 17.6, 16.9; HRMS (ESI) m/z calcd for $C_{28}H_{31}F_3N_2O_8Na$ $[M + Na]^+$: 603.1925, found: 603.1920.

4-Methoxyphenyl 2-*O*-tert-butyldimethylsilyl-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (S4)



To a solution of **35** (300 mg, 0.92 mmol) and imidazole (372 mg, 5.46 mmol) in dry DMF (3.1 mL) was added TBSCl (827 mg, 5.49 mmol) in three batches at room temperature. The reaction mixture was stirred at the same temperature over night, when TLC shown that the reaction reached to completion. The reaction was quenched by MeOH at 0 °C. The resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and the organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure delivering a residue, which was further purified by silica gel column chromatography (PE/EA = 20 : 1) to give **S4** (405 mg, 99%) as a white solid: $[\alpha]_D^{25}$ = -24.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98-6.94 (m, 2 H), 6.83-6.79 (m, 2 H), 4.61 (d, *J* = 8.4 Hz, 1 H), 3.92-3.87 (m, 2 H), 3.77 (s, 3 H), 3.68 (d, *J* = 2.0 Hz, 1 H), 1.55 (s, 3 H), 1.42 (d, *J* = 6.4 Hz, 3 H), 1.38 (s, 3 H), 1.31 (s, 3 H), 0.91 (s, 9 H), 0.18 (s, 3 H), 0.14 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 151.8, 118.2, 114.5, 108.7, 101.3, 82.6, 82.3, 75.9, 68.0, 55.8, 28.5, 27.4, 26.1, 18.5, 18.4, 17.1, -4.1, -4.4; HRMS (ESI) m/z calcd for $C_{23}H_{38}O_6SiNa$ $[M + Na]^+$: 461.2330, found: 461.2324.

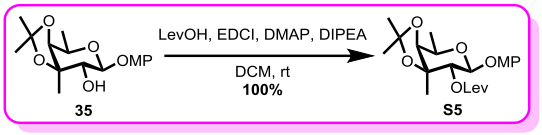
2-*O*-*tert*-Butyldimethylsilyl-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S2e)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S4** (539 mg, 1.23 mmol) to **S2e** (440 mg, 71% yield for 2 steps) as a colorless syrup: $[\alpha]_D^{25}$ = -42.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.49 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.43 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.29-7.27 (m, 1 H), 5.67 (d, *J* = 8.8 Hz, 1 H, H-1), 4.06 (qd, *J* = 2.0, 6.4 Hz, 1 H, H-5), 3.94 (d, *J* = 8.4 Hz, 1 H,

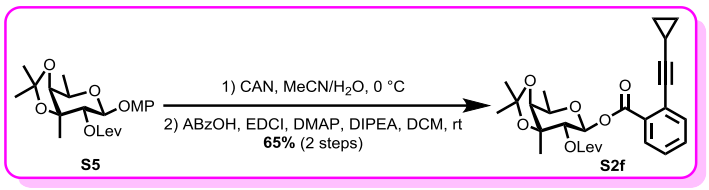
H-2), 3.70 (d, J = 2.0 Hz, 1 H, H-4), 1.56 (s, 3 H), 1.53-1.49 (m, 1 H), 1.41 (d, J = 6.4 Hz, 3 H, H-6), 1.38 (s, 3 H), 1.34 (s, 3 H), 0.93-0.86 (m, 4 H), 0.76 (s, 9 H), 0.12 (s, 3 H), -0.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 134.3, 132.0, 131.0, 130.9, 126.8, 125.4, 108.7, 100.0, 94.0 (C-1), 82.6, 82.4, 75.0, 74.6, 69.0, 28.5, 27.3, 25.8, 18.2 (2 C), 17.0, 9.0, 8.9, 0.8, -4.3, -4.8; HRMS (ESI) m/z calcd for $C_{28}H_{40}O_6SiNa$ [M + Na]$^+$: 523.2486, found: 523.2483.

4-Methoxyphenyl 2-*O*-levulinoyl-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (S5)



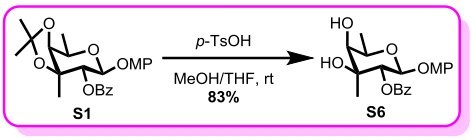
Similar procedure as that used for the synthesis of **44** was applied to convert **35** (200 mg, 0.62 mmol) to **S5** under the combined effects of EDCI (417 mg, 2.18 mmol), LevOH (114 μL, 1.11 mmol), DIPEA (650 μL, 3.70 mmol), and DMAP (234 mg, 1.92 mmol) in dry CH_2Cl_2 (2.1 mL) at room temperature. After purification by silica gel column chromatography (PE/EA = 3 : 1), **S5** (260 mg, 100%) was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +20.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-6.96 (m, 2 H), 6.83-6.79 (m, 2 H), 5.37 (d, J = 8.4 Hz, 1 H), 4.71 (d, J = 8.8 Hz, 1 H), 3.96 (qd, J = 2.0, 6.4 Hz, 1 H), 3.76 (s, 3 H), 3.67 (d, J = 2.0 Hz, 1 H), 2.89-2.59 (m, 1 H), 2.17 (s, 3 H), 1.61 (s, 3 H), 1.46 (d, J = 6.4 Hz, 3 H), 1.37 (s, 3 H), 1.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 171.6, 155.5, 151.8, 118.9, 114.6, 109.5, 100.1, 82.3, 80.7, 74.4, 68.3, 55.8, 38.1, 30.0, 28.0, 27.9, 27.3, 18.2, 17.1; HRMS (ESI) m/z calcd for $C_{22}H_{30}O_8Na$ [M + Na]$^+$: 445.1833, found: 445.1828.

2-*O*-levulinoyl-3-*C*-methyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S2f)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S5** (252 mg, 0.60 mmol) to **S2f** (187 mg, 65% yield for 2 steps) as a light yellow syrup: $[\alpha]_D^{25}$ = -4.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.48 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.43 (td, *J* = 1.2, 7.2 Hz, 1 H), 7.31-7.26 (m, 1 H), 5.77 (d, *J* = 8.8 Hz, 1 H, H-1), 5.41 (d, *J* = 9.2 Hz, 1 H, H-2), 4.10 (qd, *J* = 2.0, 6.4 Hz, 1 H, H-5), 3.70 (d, *J* = 1.6 Hz, 1 H, H-4), 2.69-2.59 (m, 2 H), 2.55-2.51 (m, 2 H), 2.04 (s, 3 H), 1.61 (s, 3 H), 1.56-1.49 (m, 1 H), 1.43 (d, *J* = 6.4 Hz, 3 H, H-6), 1.40 (s, 3 H), 1.37 (s, 3 H), 0.90-0.88 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 171.6, 163.9, 134.5, 132.4, 131.2, 129.7, 127.2, 125.8, 109.5, 100.4, 91.8 (C-1), 82.3, 80.7, 74.6, 73.6, 69.2, 38.1, 29.7, 28.1, 27.9, 27.2, 18.0, 16.9, 9.1 (2 C), 0.8; HRMS (ESI) m/z calcd for $C_{27}H_{32}O_8Na$ $[M + Na]^+$: 507.1989, found: 507.1988.

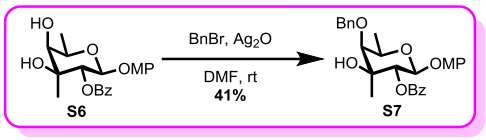
4-Methoxyphenyl 2-*O*-benzoyl-3-*C*-methyl-β-D-fucopyranoside (S6)



To a solution of **S1** (570 mg, 1.33 mmol) in MeOH/THF (13.3 mL, v/v = 1 : 1) was added *p*-TsOH (114 mg, 0.66 mmol) at room temperature. The mixture was stirred at the same temperature for 28 h before Et_3N was added to quench the reaction. Evaporation under reduced pressure afforded a residue, which was further purified by silica gel column chromatography (PE/EA = 6 : 1 to 2 : 1) to give diol **S6** (427 mg, 83%,) as a white foam: $[\alpha]_D^{25}$ = +25.5 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2 H), 7.61-7.56 (m, 1 H), 7.47-7.43 (m, 2 H), 6.97-6.92 (m, 2 H), 6.79-6.75 (m, 2 H), 5.41 (d, *J* = 8.4 Hz, 1 H), 5.00 (d, *J* = 8.0 Hz, 1 H), 3.99 (qd, *J* = 6.8, 1.2 Hz, 1 H), 3.74 (s, 3 H), 3.48 (d, *J* = 1.2 Hz, 1 H), 3.02 (brs, 2 H), 1.43 (d, *J* = 6.4 Hz, 3 H), 1.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 155.6, 151.7, 133.6, 130.0,

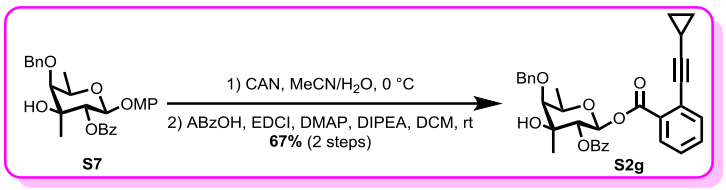
129.7, 128.6, 119.1, 114.6, 100.5, 76.8, 76.1, 74.2, 69.8, 55.7, 19.5, 17.0; HRMS (ESI) m/z calcd for $C_{21}H_{24}O_7Na$ $[M + Na]^+$: 411.1414, found: 411.1418.

4-Methoxyphenyl 2-*O*-benzoyl-3-*C*-methyl-4-*O*-benzyl-β-D-fucopyranoside (S7)



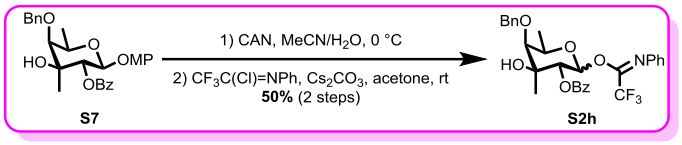
The diol **S6** (286 mg, 0.74 mmol) and TBAI (57 mg, 0.15 mmol) were dissolved in dry DMF (5.7 mL), to which BnBr (547 μL, 4.60 mmol) was added at room temperature. The mixture was stirred at the same temperature for 15 min before Ag_2O (1.06 g, 4.57 mmol) was added at room temperature. The stirring was continued at the same temperature for another 5.5 h before MeOH was added to quench the reaction. The resulting mixture was filtered and the filtrate was diluted with EtOAc. The resulting solution was washed successively with H_2O and brine, and the organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver a residue, which was further purified by silica gel column chromatography (PE/EA = 6 : 1 to 2 : 1) to give **S7** (144 mg, 41%) as a light yellow solid: $[\alpha]_D^{25}$ = +29.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 1.2, 8.4 Hz, 2 H), 7.58-7.55 (m, 1 H), 7.45-7.43 (m, 4 H), 7.40-7.37 (m, 2 H), 7.34-7.31 (m, 2 H), 6.77-6.74 (m, 2 H), 5.51 (d, *J* = 7.8 Hz, 1 H), 5.00 (d, *J* = 7.8 Hz, 1 H), 4.86 (d, *J* = 11.4 Hz, 1 H), 4.81 (d, *J* = 11.4 Hz, 1 H), 4.02 (qd, *J* = 1.2, 6.0 Hz, 1 H), 3.74 (s, 3 H), 3.34 (d, *J* = 1.2 Hz, 1 H), 1.41 (d, *J* = 6.0 Hz, 3 H), 1.40 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 155.5, 151.9, 137.7, 133.3, 130.1, 129.9, 128.7, 128.5, 128.2, 128.1, 119.0, 114.5, 100.4, 85.4, 76.9, 75.4, 74.4, 70.2, 55.7, 19.4, 17.5; HRMS (ESI) m/z calcd for $C_{28}H_{30}O_7Na$ $[M + Na]^+$: 501.1884, found: 501.1885.

2-*O*-Benzoyl-3-*C*-methyl-4-*O*-benzyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S2g)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S7** (60 mg, 0.13 mmol) to **S2g** (46 mg, 67% yield for 2 steps) as a colorless syrup: $[\alpha]_D^{25}$ = +56.3 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.45-7.32 (m, 9 H), 7.21 (t, *J* = 7.6 Hz, 1 H), 6.11 (d, *J* = 8.4 Hz, 1 H, H-1), 5.57 (d, *J* = 8.4 Hz, 1 H, H-2), 4.86 (d, *J* = 11.6 Hz, 1 H), 4.80 (d, *J* = 11.2 Hz, 1 H), 4.15 (q, *J* = 6.4 Hz, 1 H, H-5), 3.37 (s, 1 H, H-4), 2.93 (s, 1 H, C3-OH), 1.54-1.47 (m, 4 H), 1.39 (d, *J* = 6.4 Hz, 3 H, H-6), 0.90-0.82 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 164.1, 137.6, 134.4, 133.3, 132.3, 131.1, 129.9, 129.7, 129.6, 128.7, 128.5, 128.3, 128.2, 127.1, 125.6, 100.3, 92.0 (C-1), 85.4, 77.0, 74.6, 74.5, 74.4, 71.1, 19.2, 17.2, 9.1, 9.0, 0.8; HRMS (ESI) m/z calcd for $C_{33}H_{32}O_7Na$ $[M + Na]^+$: 563.2040, found: 563.2038.

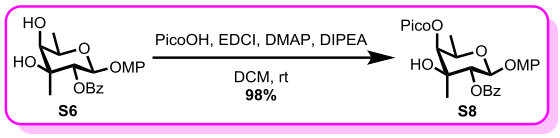
2-*O*-Benzoyl-3-*C*-methyl-4-*O*-benzyl-D-fucopyranosyl *N*-phenyltrifluoroacetimidate (S2h)



Similar procedures as those used for the synthesis of **S2b** were adopted to convert **S7** (60 mg, 0.13 mmol) to **S2h** (34 mg, 50% yield for 2 steps, α/β = 1 : 4.7) as a α/β mixture. Pure **S2hα** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +98.9 (*c* 0.25, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 8.10-8.09 (m, 2 H), 7.75-7.71 (m, 1 H), 7.59 (t, *J* = 7.6 Hz, 2 H), 7.48-7.46 (m, 2 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.32-7.28 (m, 1 H), 7.15 (t, *J* = 8.0 Hz, 2 H), 7.02-6.99 (m, 1 H), 6.60 (brs, 1 H, H-1), 6.43 (brs, 2 H), 5.57 (s, 1 H, H-2), 5.09 (d, *J* = 11.2 Hz, 1 H), 4.72 (d, *J* = 11.2 Hz, 1 H), 4.43 (s, 1 H, H-5), 4.38 (s, 1 H, H-4), 3.62 (s, 1 H), 1.68 (s, 3 H), 1.31 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, acetone-d_6) δ 166.3, 144.5, 139.8, 134.4, 130.8, 130.5, 129.6, 129.5, 129.1, 128.9, 128.4, 124.9,

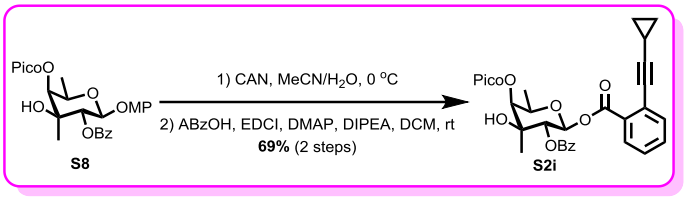
119.9, 100.9 (C-1), 85.6, 76.9, 73.5, 72.9, 70.0, 21.8, 17.3; HRMS (ESI) m/z calcd for $C_{29}H_{28}F_3NO_6Na$ $[M + Na]^+$: 566.1761, found: 566.1759. Pure **S2hβ** was obtained as a white solid: $[\alpha]_D^{25}$ = +68.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, acetone-d_6) δ 8.09 (d, *J* = 7.6 Hz, 2 H), 7.71-7.67 (m, 1 H), 7.58 (td, *J* = 2.4, 8.0 Hz, 2 H), 7.50-7.48 (m, 2 H), 7.40-7.29 (m, 5 H), 7.14 (t, *J* = 7.6 Hz, 1 H), 6.77 (brs, 2 H), 6.03 (brs, 1 H, H-1), 5.58 (s, 1 H), 5.06 (d, *J* = 11.2 Hz, 1 H), 4.73 (d, *J* = 11.2 Hz, 1 H), 4.18 (s, 1 H), 3.48 (s, 1 H), 1.45 (s, 3 H), 1.30 (d, *J* = 5.6 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 165.8, 144.5, 139.7, 134.1, 131.0, 130.4, 129.6, 129.5, 129.1, 128.9, 128.4, 125.1, 120.0, 96.3, 85.4, 76.9, 75.1, 75.0, 72.1, 20.3, 17.2; HRMS (ESI) m/z calcd for $C_{29}H_{28}F_3NO_6Na$ $[M + Na]^+$: 566.1761, found: 566.1758.

4-Methoxyphenyl 2-*O*-benzoyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranoside (S8)



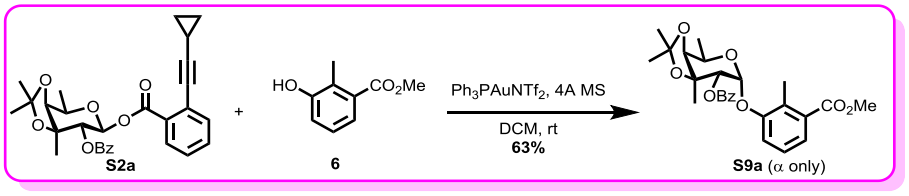
Similar procedure as that used for the synthesis of **33** was adopted to convert **S6** (100 mg, 0.26 mmol) to **S8** under the combined effects of PicoOH (55 mg, 0.45 mmol), EDCI (157 mg, 0.82 mmol), DMAP (88 mg, 0.72 mmol), as well as DIPEA (250 μL, 1.44 mmol) in dry CH_2Cl_2 (1.3 mL) at room temperature. After purification by silica gel column chromatography (PE/EA = 3 : 2), **S8** (124 mg, 98%) was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +58.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 1.6, 5.2 Hz, 1 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 8.08 (dd, *J* = 1.2, 8.4 Hz, 2 H), 7.91 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.61-7.56 (m, 1 H), 7.57 (ddd, *J* = 1.2, 4.8, 7.6 Hz, 1 H), 7.47-7.43 (m, 2 H), 6.97-6.93 (m, 2 H), 6.79-6.75 (m, 2 H), 5.70 (d, *J* = 8.0 Hz, 1 H), 5.28 (d, *J* = 1.2 Hz, 1 H), 5.14 (d, *J* = 8.4 Hz, 1 H), 4.23-4.19 (m, 1 H), 3.74 (s, 3 H), 1.55 (s, 3 H), 1.36 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 164.8, 155.7, 151.7, 150.2, 147.5, 137.5, 133.5, 130.0, 129.8, 128.6, 127.4, 125.7, 119.0, 114.6, 100.5, 79.2, 75.0, 73.3, 69.5, 55.7, 20.0, 17.3; HRMS (ESI) m/z calcd for $C_{27}H_{27}NO_8Na$ $[M + Na]^+$: 516.1629, found: 516.1626.

2-*O*-Benzoyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S2i)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S8** (99 mg, 0.20 mmol) to **S2i** (77 mg, 69% yield for 2 steps) as a white solid: $[\alpha]_D^{25}$ = +85.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 1 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 8.00 (d, *J* = 7.6 Hz, 2 H), 7.93-7.89 (m, 2 H), 7.55-7.51 (m, 2 H), 7.43-7.34 (m, 4 H), 7.23-7.19 (m, 1 H), 6.23 (dd, *J* = 1.6, 8.8 Hz, 1 H, H-1), 5.77 (d, *J* = 8.4 Hz, 1 H, H-2), 5.28 (s, 1 H, H-4), 4.36 (dd, *J* = 6.4, 13.2 Hz, 1 H, H-5), 1.63 (s, 3 H), 1.55-1.49 (m, 1 H), 1.35 (d, *J* = 6.4 Hz, 3 H, H-6), 0.89-0.87 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 165.0, 164.0, 150.1, 147.6, 137.5, 134.5, 133.6, 132.4, 131.0, 130.0, 129.6, 129.3, 128.6, 127.4, 127.1, 125.8, 125.7, 100.4, 92.0 (C-1), 79.3, 74.5, 74.1, 73.6, 70.4, 19.9, 17.1, 9.1 (2 C), 0.8; HRMS (ESI) m/z calcd for $C_{32}H_{29}NO_8Na$ $[M + Na]^+$: 578.1785, found: 578.1787.

Methyl 2-methyl-3-*O*-(2-*O*-benzoyl-3-*C*-methyl-3,4-*O*-isopropylidene-α-D-fucopyranosyl)-benzoate (S9a)



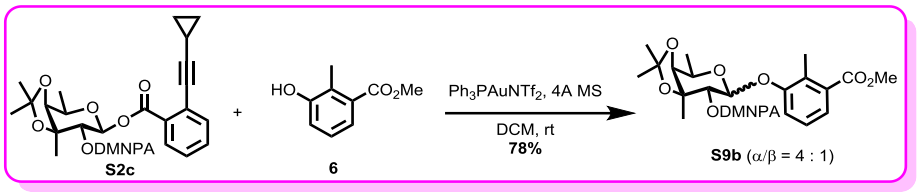
Similar procedure as that used for the synthesis of **21** was adopted to mediate the coupling between **S2a** (50 mg, 0.10 mmol) and acceptor **6** (17 mg, 0.10 mmol), furnishing **S9a** (30 mg, 63%) α-stereoselectively as a white solid: $[\alpha]_D^{25}$ = +130.1 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2 H), 7.58-7.53 (m, 1 H), 7.48-7.41 (m, 3 H), 7.36 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 5.59 (d, *J* = 4.0 Hz, 1 H, H-1), 5.54 (d, *J* = 4.0 Hz, 1 H, H-2), 4.33 (qd, *J* = 2.0, 6.4 Hz, 1 H, H-

5), 3.87-3.85 (m, 4 H, H-4, -CO_2CH_3), 2.46 (s, 3 H, Ar-CH_3), 1.79 (s, 3 H), 1.62 (s, 3 H), 1.43 (d, J = 5.6 Hz, 3 H, H-6), 1.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.8, 156.1, 133.5, 131.8, 129.9, 129.7, 129.2, 128.6, 126.6, 124.1, 118.1, 109.2, 96.2 (C-1), 82.3 (2 C), 79.2, 73.5, 63.8, 52.1, 28.1, 27.4, 20.1, 16.9, 13.3; HRMS (ESI) m/z calcd for $C_{26}H_{30}O_8Na$ $[M + Na]^+$: 493.1833, found: 493.1832.

Methyl 2-methyl-3-*O*-(2-*O*-benzoyl-3-*C*-methyl-3,4-*O*-isopropylidene-D-fucopyranosyl)-benzoate (S9a)

To a stirred solution of glycosyl donor **S2b** (55 mg, 0.11 mmol) and acceptor **6** (19 mg, 0.11 mmol) in dry CH_2Cl_2 (2.2 mL) was added activated 4 Å molecular sieves (220 mg) at room temperature under N_2 atmosphere. The resulting suspension was stirred at the same temperature for 1 h before TBSOTf (5.1 μL, 0.022 mmol) was added at 0 ºC. The reaction mixture was stirred at the same temperature overnight, at which time TLC showed that all the starting materials disappeared. The reaction was then quenched by Et_3N. Filtration was followed by concentration under reduced pressure to yield the crude product, which was further purified by silica gel column chromatography (PE/EA = 10 : 1) to furnish **S9a** (40 mg, 77%, α/β = 4.7 : 1) as a α/β mixture. Pure **S9aβ** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +8.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 2.8, 8.0 Hz, 2 H), 7.57-7.53 (m, 1 H), 7.48-7.40 (m, 3 H), 7.22 (dd, J = 2.0, 8.0 Hz, 1 H), 7.17-7.12 (m, 1 H), 5.77 (d, J = 8.4 Hz, 1 H, H-2), 4.93 (d, J = 8.4 Hz, 1 H, H-1), 4.10 (q, J = 6.8 Hz, 1 H, H-5), 3.81 (s, 3 H, -CO_2CH_3), 3.77 (d, J = 2.8 Hz, 1 H, H-4), 2.16 (s, 3H, Ar-CH_3), 1.71 (s, 3 H), 1.52 (d, J = 6.4 Hz, 3 H, H-6), 1.51 (s, 3 H), 1.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.4, 156.2, 133.3, 131.9, 130.1, 130.0, 129.8, 128.5, 126.1, 124.5, 118.7, 109.7, 99.4 (C-1), 82.3, 80.9, 74.2, 68.5, 52.1, 28.0, 27.3, 18.3, 17.1, 12.8; HRMS (ESI) m/z calcd for $C_{26}H_{30}O_8Na$ $[M + Na]^+$: 493.1833, found: 493.1830.

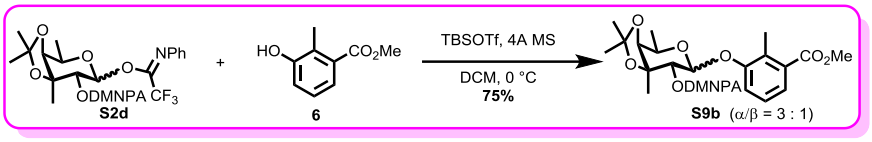
Methyl 2-methyl-3-*O*-{2-*O*-[2,2-dimethyl-2-(*ortho*-nitrophenyl)acetyl]-3-*C*-methyl-3,4-*O*-isopropylidene}-D-fucopyranosyl-benzoate (S9b)



Similar procedure as that used for the synthesis of **21** was adopted to mediate the coupling between **S2c** (40 mg, 0.069 mmol) and **6** (12 mg, 0.069 mmol) to furnish **S9b** (30 mg, 78%, α/β = 4 : 1) as a α/β mixture. Pure **S9bα** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +49.9 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1 H), 7.58-7.57 (m, 2H), 7.47 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.37-7.33 (m, 1 H), 7.28-7.25 (m, 1 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 5.52 (d, *J* = 3.6 Hz, 1 H, H-1), 5.34 (d, *J* = 4.0 Hz, 1 H, H-2), 4.16 (qd, *J* = 2.0, 6.8 Hz, 1 H, H-5), 3.89 (s, 3 H, -CO_2CH_3), 3.71 (d, *J* = 2.0 Hz, 1 H, H-4), 2.12 (s, 3 H, Ar-CH_3), 1.69 (s, 3 H), 1.59 (s, 3 H), 1.58 (s, 3 H), 1.42 (s, 3 H), 1.37 (s, 3 H), 1.34 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 168.4, 155.8, 148.3, 138.9, 133.4, 131.5, 128.4, 128.0, 126.5, 125.9, 123.5, 116.9, 108.9, 95.4 (C-1), 82.1, 78.8, 73.1, 63.7, 52.1, 46.6, 28.0, 27.4 (2 C), 26.7, 19.4, 16.9, 13.2; HRMS (ESI) m/z calcd for $C_{29}H_{35}NO_{10}Na$ $[M + Na]^+$: 580.2153, found: 580.2150. Pure **S9bβ** was also obtained as a colorless syrup: $[\alpha]_D^{25}$ = +171.6 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1 H), 7.54-7.53 (m, 2 H), 7.51 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.41-7.36 (m, 1 H), 7.17 (t, *J* = 8.0 Hz, 1 H), 6.98 (d, *J* = 8.0 Hz, 1 H), 5.47 (d, *J* = 8.4 Hz, 1 H, H-2), 4.92 (d, *J* = 8.4 Hz, 1 H, H-1), 3.94-3.88 (m, 4 H, H-5, -CO_2CH_3), 3.65 (d, *J* = 2.0 Hz, 1 H, H-4), 2.41 (s, 3 H, Ar-CH_3), 1.68 (s, 3 H), 1.65 (s, 3 H), 1.64 (s, 3 H), 1.41 (d, *J* = 6.4 Hz, 3 H, H-6), 1.39 (s, 3 H), 1.18 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 168.4, 155.2, 149.0, 138.8, 133.0, 132.1, 130.1, 128.6, 127.9, 125.9, 125.7, 124.1, 117.4, 109.7, 97.5 (C-1), 82.4, 80.5, 74.3, 68.3, 52.1, 47.2, 28.0, 27.6, 27.1 (2 C), 18.0, 17.0, 13.4; HRMS (ESI) m/z calcd for $C_{29}H_{35}NO_{10}Na$ $[M + Na]^+$: 580.2153, found: 580.2148.

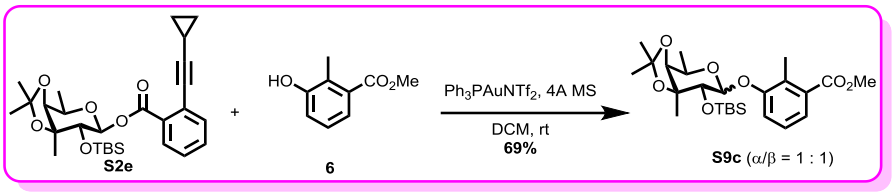
Methyl 2-methyl-3-*O*-{2-*O*-[2,2-dimethyl-2-(*ortho*-nitrophenyl)acetyl]-3-*C*-

methyl-3,4-*O*-isopropylidene}-D-fucopyranosyl-benzoate (S9b)



Similar procedure as that used for the synthesis of **S9a** from **S2b** was adopted to mediate the coupling between **S2d** (39 mg, 0.067 mmol) and **6** (11 mg, 0.067 mmol) to afford **S9b** (28 mg, 75%, α/β = 3 : 1) as a α/β mixture.

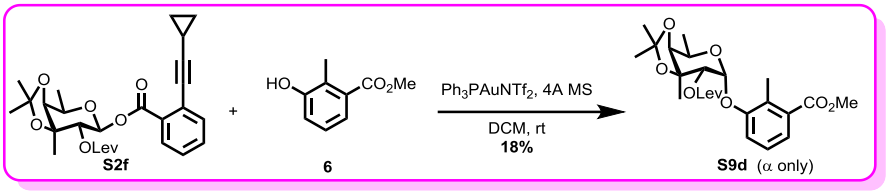
Methyl 2-methyl-3-*O*-(2-*O*-*tert*-butyldimethylsilyl-3-*C*-methyl-3,4-*O*-isopropylidene-D-fucopyranosyl)-benzoate (S9c)



Similar procedure as that used for the synthesis of **21** was adopted to mediate the coupling between **S2e** (100 mg, 0.20 mmol) and **6** (33 mg, 0.20 mmol), delivering **S9c** (66 mg, 69%, α/β = 1 : 1) as a α/β mixture. Pure **S9cα** was obtained as a white solid: $[\alpha]_D^{25}$ = +126.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 1 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 5.20 (d, *J* = 3.6 Hz, 1 H, H-1), 4.20 (qd, *J* = 2.0, 2.8 Hz, 1 H, H-5), 4.04 (d, *J* = 4.0 Hz, 1 H, H-2), 3.89 (s, 3 H, -CO_2CH_3), 3.77 (d, *J* = 2.0 Hz, 1 H, H-4), 2.47 (s, 3H, Ar-CH_3), 1.54 (s, 6 H), 1.39 (s, 3 H), 1.34 (d, *J* = 6.7 Hz, 3 H, H-6), 0.84 (s, 9 H), 0.13 (s, 3 H), -0.02 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 156.7, 131.8, 129.3, 126.4, 123.5, 117.5, 108.3, 99.1 (C-1), 81.9, 81.0, 73.7, 63.5, 52.1, 28.6, 27.3, 25.8, 19.6, 18.1, 16.9, 13.4, -4.4, -4.7; HRMS (ESI) m/z calcd for $C_{25}H_{40}O_7SiNa$ $[M + Na]^+$: 503.2435, found: 503.2425. Pure **S9cβ** was obtained as a white solid: $[\alpha]_D^{25}$ = -10.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 7.08 (dd, *J* = 1.2, 8.4 Hz, 1 H), 4.76 (d, *J* = 8.0 Hz, 1 H, H-1), 3.98 (d, *J* = 8.0 Hz, 1 H, H-2), 3.88 (s, 3 H, -CO_2CH_3), 3.87-3.82 (m, 1 H, H-5), 3.69 (d, *J* = 1.6 Hz, 1 H, H-4), 2.49 (s, 3 H, Ar-CH_3), 1.57 (s, 3 H), 1.38 (s, 3 H), 1.36 (d, *J* = 6.4 Hz, 3 H, H-6), 1.34 (s, 3 H), 0.89 (s, 9 H), 0.20 (s,

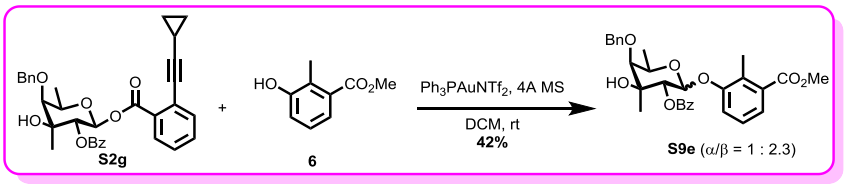
3 H), 0.09 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 155.9, 132.0, 130.5, 125.9, 124.2, 119.2, 108.8, 100.7 (C-1), 82.6, 82.4, 75.9, 68.2, 52.1, 28.5, 27.4, 26.1, 18.6, 18.5, 17.0, 13.8, -4.2, -4.4; HRMS (ESI) m/z calcd for $C_{25}H_{40}O_7SiNa$ $[M + Na]^+$: 503.2435, found: 503.2430.

Methyl 2-methyl-3-*O*-(2-*O*-levulinoyl-3-*C*-methyl-3,4-*O*-isopropylidene-α-D-fucopyranosyl)-benzoate (S9d)



Similar procedure as that used for the synthesis of **21** was adopted to mediate the coupling between **S2f** (40 mg, 0.083 mmol) and acceptor **6** (14 mg, 0.083 mmol), providing **S9d** (7.0 mg, 18%) α-stereoselectively as a colorless syrup: $[\alpha]_D^{25}$ = +122.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.32 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.21 (t, *J* = 8.0 Hz, 1 H), 5.45 (d, *J* = 4.0 Hz, 1 H, H-1), 5.28 (d, *J* = 3.6 Hz, 1 H, H-2), 4.28 (qd, *J* = 2.0, 6.8 Hz, 1 H, H-4), 3.89 (s, 3 H, $-CO_2CH_3$), 3.79 (d, *J* = 2.0 Hz, 1 H, H-4), 2.80-2.59 (m, 4 H), 2.46 (s, 3 H, Ar-CH_3), 2.12 (s, 3 H), 1.62 (s, 3 H), 1.56 (s, 3 H), 1.39 (s, 3 H), 1.38 (d, *J* = 6.8 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 172.2, 168.4, 156.1, 131.9, 129.2, 126.6, 124.1, 118.2, 109.1, 96.1 (C-1), 82.2, 79.0, 73.3, 63.8, 52.2, 38.1, 29.8, 28.1, 27.4, 27.1, 19.9, 16.9, 13.3; HRMS (ESI) m/z calcd for $C_{24}H_{32}O_9Na$ $[M + Na]^+$: 487.1938, found: 487.1934.

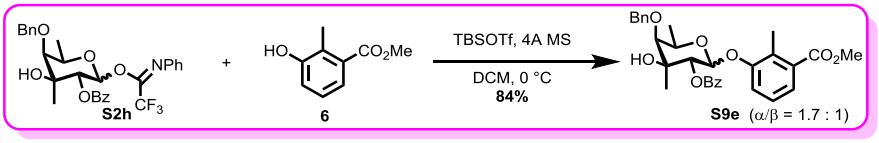
Methyl 2-methyl-3-*O*-(2-*O*-benzoyl-3-*C*-methyl-4-*O*-benzyl-D-fucopyranosyl)-benzoate (S9e)



Similar procedure as that used for the synthesis of **21** was adopted to mediate the

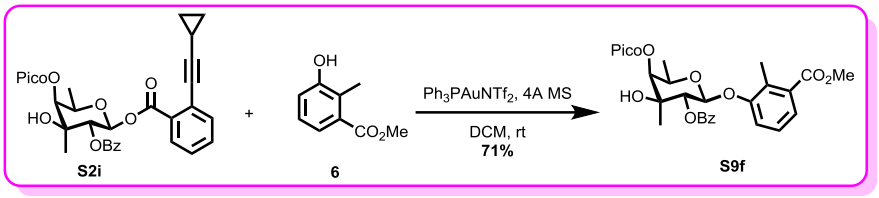
coupling between **S2g** (36 mg, 0.067 mmol) and acceptor **6** (11 mg, 0.067 mmol) to afford **S9e** (14 mg, 42%, α/β = 1 : 2.3) as a α/β mixture. Pure **S9eα** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +137.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2 H), 7.58-7.54 (m, 1 H), 7.48-7.32 (m, 9 H), 7.18 (t, *J* = 8.0 Hz, 1 H), 5.66 (d, *J* = 4.4 Hz, 1 H, H-1), 5.46 (d, *J* = 4.4 Hz, 1 H, H-2), 4.88 (d, *J* = 11.6 Hz, 1 H), 4.81 (d, *J* = 11.6 Hz, 1 H), 4.39 (q, *J* = 6.4 Hz, 1 H, H-5), 3.86 (s, 3 H, -CO_2CH_3), 3.45 (d, *J* = 1.2 Hz, 1 H, H-4), 2.49 (s, 3 H, Ar-CH_3), 1.74 (s, 3 H), 1.35 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 166.4, 156.3, 137.6, 133.5, 131.8, 129.9, 129.8, 129.3, 128.8, 128.6, 128.3, 128.2, 126.5, 123.9, 118.1, 96.5 (C-1), 85.9, 77.0, 73.5, 72.6, 66.6, 52.1, 20.9, 17.3, 13.3; HRMS (ESI) m/z calcd for $C_{30}H_{32}O_8Na$ [M + Na]$^+$: 543.1989, found: 543.1989. Pure **S9eβ** was also obtained as a colorless syrup: $[\alpha]_D^{25}$ = +12.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2 H), 7.57-7.53 (m, 1 H), 7.48 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.45-7.31 (m, 7 H), 7.27 (d, *J* = 1.2 Hz, 1 H), 7.27-7.25 (m, 1 H), 7.17 (t, *J* = 8.0 Hz, 1 H), 5.64 (d, *J* = 8.0 Hz, 1 H, H-2), 5.06 (d, *J* = 8.4 Hz, 1 H, H-1), 4.88 (d, *J* = 11.6 Hz, 1 H), 4.81 (d, *J* = 11.2 Hz, 1 H), 4.09-4.04 (m, 1 H, H-5), 3.81 (s, 3 H, -CO_2CH_3), 3.37 (d, *J* = 1.2 Hz, 1 H, H-4), 2.87 (d, *J* = 1.2 Hz, 1 H, C3-OH), 2.18 (s, 3 H, Ar-CH_3), 1.43 (s, 3 H), 1.42 (d, *J* = 6.4 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 166.3, 156.3, 137.6, 133.3, 131.9, 130.1, 129.9 (2 C), 128.8, 128.6, 128.3, 128.2, 126.1, 124.4, 118.8, 99.6 (C-1), 85.4, 77.0, 74.9, 74.3, 70.3, 52.1, 19.3, 17.5, 12.9; HRMS (ESI) m/z calcd for $C_{30}H_{32}O_8Na$ [M + Na]$^+$: 543.1989, found: 543.1989.

Methyl 2-methyl-3-*O*-(2-*O*-benzoyl-3-*C*-methyl-4-*O*-benzyl-D-fucopyranosyl)-benzoate (S9e)



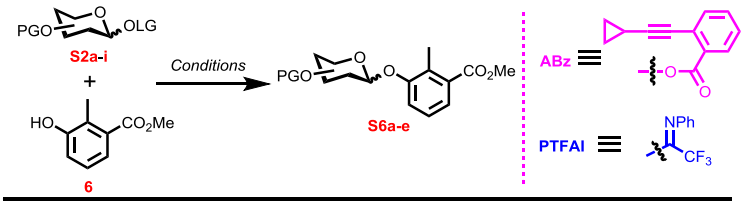
Similar procedure as that used for the synthesis of **S9a** from **S2b** was adopted to mediate the coupling between **S2h** (40 mg, 0.074 mmol) and **6** (12 mg, 0.074 mmol), furnishing **S9e** (32 mg, 84%, α/β = 1.7 : 1) as a α/β mixture.

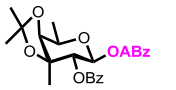
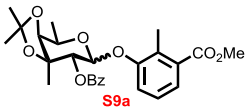
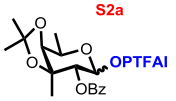
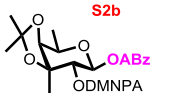
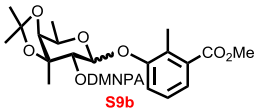
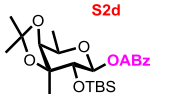
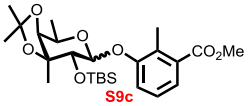
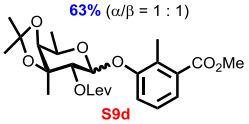
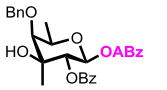
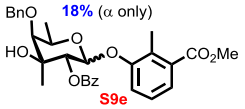
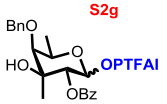
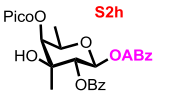
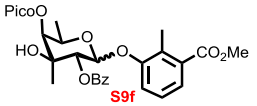
Methyl 2-methyl-3-*O*-(2-*O*-benzoyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranosyl)-benzoate (S9f)



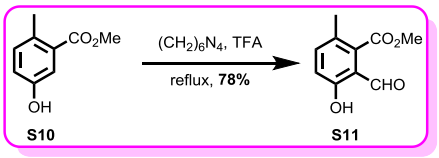
Similar procedure as that used for the synthesis of **21** was adopted to mediate the coupling between **S2i** (118 mg, 0.21 mmol) and **6** (35 mg, 0.21 mmol) to provide **S9f** (80 mg, 71%) β-selectively as a white foam: $[\alpha]_D^{25}$ = +47.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (t, *J* = 3.2 Hz, 1 H), 8.26 (d, *J* = 8.0 Hz, 1 H), 8.03 (d, *J* = 7.6 Hz, 2 H), 7.94-7.90 (m, 1 H), 7.56-7.57 (m, 2 H), 7.51-7.48 (m, 1 H), 7.45 (td, *J* = 2.4, 8.0 Hz, 2 H), 7.28-7.26 (m, 1 H), 7.20 (td, *J* = 2.4, 8.0 Hz, 1 H), 5.80 (d, *J* = 8.0 Hz, 1 H, H-2), 5.30 (d, *J* = 2.4 Hz, 1 H, H-4), 5.17 (d, *J* = 8.0 Hz, 1 H, H-1), 4.28-4.23 (m, 1 H, H-5), 3.82 (s, 3 H, $-CO_2CH_3$), 2.20 (s, 3 H, Ar-CH_3), 1.57 (s, 3 H), 1.37 (d, *J* = 5.2 Hz, 3 H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 166.5, 164.8, 156.1, 150.0, 147.0, 138.1, 133.7, 132.0, 130.0, 129.9, 129.5, 128.7, 127.8, 126.2, 125.9, 124.7, 118.8, 99.7 (C-1), 79.3, 74.4, 73.3, 69.6, 52.1, 20.0, 17.3, 12.9; HRMS (ESI) m/z calcd for $C_{29}H_{29}NO_9Na$ $[M + Na]^+$: 558.1734, found: 558.1734.

Table S1. Glycosylation of **6** with various 3-*C*-methyl-branched D-fucosyl donors.



Entry	Donors	Conditions	Product (yield and α/β ratio)
1	 S2a	$Ph_3PAuNTf_2$ (0.2 eq), 4A MS DCM, rt	 S9a 63% (α only)
2	 S2a	TBSOTf (0.2 eq), 4A MS DCM, 0 °C	S9a 77% (α/β = 4.7 : 1)
3	 S2b	$Ph_3PAuNTf_2$ (0.2 eq), 4A MS DCM, rt	 S9b 78% (α/β = 4 : 1)
4	 S2c	TBSOTf (0.2 eq), 4A MS DCM, 0 °C	S9b 75% (α/β = 3 : 1)
5	 S2d	$Ph_3PAuNTf_2$ (0.2 eq), 4A MS DCM, rt	 S9c 63% (α/β = 1 : 1)
6	 S2e	$Ph_3PAuNTf_2$ (0.2 eq), 4A MS DCM, rt	 S9d 18% (α only)
7	 S2f	$Ph_3PAuNTf_2$ (0.2 eq), 4A MS DCM, rt	 S9e 42% (α/β = 1 : 2.3)
8	 S2g	TBSOTf (0.2 eq), 4A MS DCM, 0 °C	S9e 84% (α/β = 1.7 : 1)
9	 S2h S2i	$Ph_3PAuNTf_2$ (0.2 eq), 4A MS DCM, rt	 S9f 71% (β only)

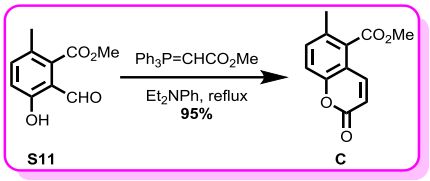
Methyl 2-formyl-3-hydroxy-6-methyl benzoate (S11)



To a solution of **S10**[S4] (1.0 g, 6.02 mmol) in TFA (20.0 mL) at room temperature was added $(CH_2)_6N_4$ (886 mg, 6.32 mmol) in three batches. The resulting mixture was heated to reflux for 1 h, when TLC showed that the reaction reached to completion. The

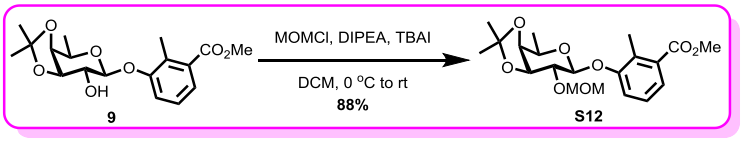
resulting mixture was diluted with EtOAc, washed successively with H_2O, saturated aqueous $NaHCO_3$ and brine, and the organic layer was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver a residue, which was further purified by silica gel column chromatography (PE/EA = 10 : 1) to give **S11**[S4] (911 mg, 78%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (d, *J* = 1.6 Hz, 1 H), 9.92 (d, *J* = 1.6 Hz, 1 H), 7.38 (dd, *J* = 1.6, 8.8 Hz, 1 H), 7.00 (dd, *J* = 1.6, 8.8 Hz, 1 H), 3.98 (s, 3 H), 2.29 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 168.0, 160.6, 139.2, 136.2, 126.9, 119.7 (2 C), 116.9, 52.8, 18.8.

5-Methoxycarbonyl-6-methyl-2*H*-chromen-2-one (C)



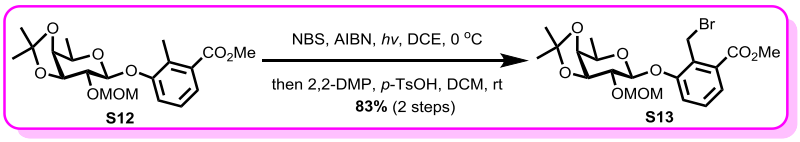
To a solution of **S11** (3.28 g, 16.89 mmol) in Et_2NPh (84.0 mL) at room temperature was added $Ph_3P{=}CHCO_2Me$ (6.47 g, 19.35 mmol). The resulting mixture was heated to reflux for 25 min, when TLC showed that the reaction reached to completion. The resulting mixture was diluted with EtOAc, washed successively with H_2O, 1N HCl, saturated aqueous $NaHCO_3$ and brine, and the organic layer was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver a residue, which was further purified by silica gel column chromatography (PE/EA = 10 : 1) to give **C**[S4] (3.50 g, 95%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.6 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.32 (d, *J* = 8.8 Hz, 1 H), 6.46 (d, *J* = 10.0 Hz, 1 H), 4.00 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 160.1, 152.5, 140.9, 134.1, 132.7, 130.8, 118.7, 117.6, 116.6, 52.8, 19.9.

Methyl 2-methyl-3-*O*-(2-*O*-methoxymethyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-benzoate (S12)



To a solution of **9** (250 mg, 0.71 mmol) and DIPEA (1.2 mL, 7.09 mmol) in dry DCM (3.5 mL) was added MOMCl (388 μL, 5.11 mmol) dropwise and TBAI (655 mg, 1.77 mmol) successively at 0 °C. The reaction mixture was then gradually warmed up to room temperature, and stirred at the same temperature overnight. EtOAc was added to dilute the reaction mixture. The resulting mixture was washed successively with saturated aqueous $NaHCO_3$ and brine, and then the organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver a residue, which was further purified by silica gel column chromatography (PE/EA = 4 : 1) to afford **S12** (247 mg, 88%) as a yellow syrup: $[\alpha]_D^{25}$ = +46.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.46 (dd, *J* = 2.4, 6.8 Hz, 1 H), 7.27-7.21 (m, 2 H), 5.02 (d, *J* = 8.0 Hz, 1 H), 4.97 (d, *J* = 6.4 Hz, 1 H), 4.80 (d, *J* = 6.4 Hz, 1 H), 4.25-4.17 (m, 3 H), 3.88-3.84 (m, 4 H), 3.42 (s, 3 H), 2.43 (s, 3 H), 1.53 (s, 3 H), 1.35 (d, *J* = 6.4 Hz, 3 H), 1.34 (s, 3 H); ^{13}C NMR (150 MHz, acetone-d_6) δ 168.5, 156.8, 133.0, 129.5, 127.1, 124.5, 119.2, 100.8, 96.9, 79.7, 77.3, 76.7, 69.5, 55.7, 52.2, 28.3, 26.7, 16.9, 13.4; HRMS (ESI) m/z calcd for $C_{20}H_{28}O_8Na$ $[M + Na]^+$: 419.1676, found: 419.1675.

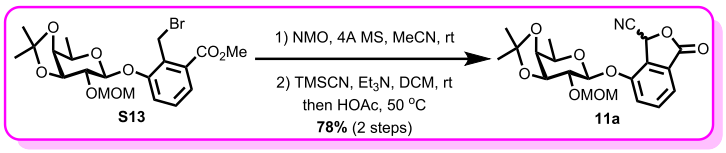
Methyl 2-bromomethyl-3-*O*-(2-*O*-methoxymethyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-benzoate (S13)



Similar procedures as those used for the synthesis of **10** were adopted to convert **S12** (174 mg, 0.44 mmol) to **S13** (173 mg, 83% yield for 2 steps) as a colorless syrup: $[\alpha]_D^{25}$ = +41.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 1.4, 7.6 Hz, 1 H), 7.44-7.38 (m, 2 H), 5.16 (d, *J* = 9.0 Hz, 1 H), 5.14 (d, *J* = 7.8 Hz, 1 H), 5.09 (d, *J* = 9.0 Hz, 1 H), 5.03 (d, *J* = 6.0 Hz, 1 H), 4.84 (d, *J* = 6.0 Hz, 1 H), 4.26 (dd, *J* = 5.4, 7.2 Hz,

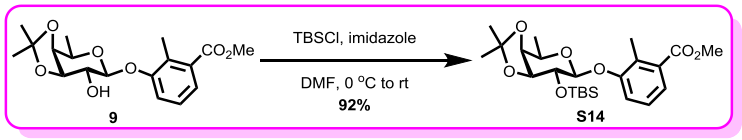
1 H), 4.25-4.21 (m, 1 H), 4.20 (dd, *J* = 1.8, 5.4 Hz, 1 H), 3.91-3.89 (m, 4 H), 3.43 (s, 3 H), 1.54 (s, 3 H), 1.35 (d, *J* = 6.6 Hz, 3 H), 1.34 (s, 3 H); ^{13}C NMR (150 MHz, acetone-d_6) δ 167.5, 156.5, 132.1, 130.4, 129.3, 125.5, 120.5, 110.1, 100.8, 97.2, 79.6, 77.2, 76.8, 69.7, 55.8, 52.6, 28.3, 26.7, 25.0, 16.8; HRMS (ESI) m/z calcd for $C_{20}H_{27}BrO_8Na$ $[M + Na]^+$: 497.0781, found: 497.0781.

4-*O*-(2-*O*-Methoxymethyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-3-cyanoisobenzofuran-1(3*H*)-one (11a)



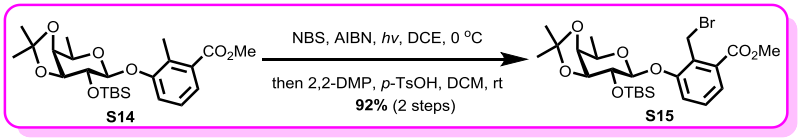
Similar procedures as those used for the synthesis of **11** was adopted to convert **S13** (154 mg, 0.32 mmol) to **11a** (103 mg, 78% yield for 2 steps) as an inseparable mixture of epimers: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.78 (t, *J* = 7.8 Hz, 2.9 H), 7.64-7.61 (m, 5.8 H), 6.65 (s, 1.9 H, -CHCN), 6.56 (s, 1 H, -CHCN), 5.38 (d, *J* = 8.0 Hz, 1.9 H, H-1), 5.30 (d, *J* = 8.4 Hz, 1 H, H-1), 5.04 (d, *J* = 6.4 Hz, 1.9 H), 4.93 (d, *J* = 6.4 Hz, 1 H), 4.87 (d, *J* = 6.4 Hz, 1 H), 4.73 (d, *J* = 6.4 Hz, 1.9 H), 4.38-4.31 (m, 3 H), 4.29-4.22 (m, 5.7 H), 3.92 (dd, *J* = 7.2, 8.4 Hz, 1 H), 3.87 (dd, *J* = 7.2, 8.4 Hz, 1.9 H), 3.43 (s, 3 H), 3.41 (s, 5.7 H), 1.53 (s, 8.7 H), 1.40 (d, *J* = 6.4 Hz, 3 H), 1.38 (d, *J* = 6.8 Hz, 5.7 H), 1.35 (s, 8.7 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.2, 168.1, 153.0, 152.7, 134.2, 134.1, 131.3, 131.0, 127.2, 127.1, 121.7, 121.5, 120.0, 119.9, 115.0, 114.4, 110.2, 110.1, 100.5, 100.2, 97.6, 97.2, 79.5, 79.3, 77.2 (2 C), 76.8, 76.4, 69.9, 65.4, 65.2, 55.7, 55.6, 28.3, 28.2, 26.7, 16.8 (2 C); HRMS (ESI) m/z calcd for $C_{20}H_{23}NO_8Na$ $[M + Na]^+$: 428.1316, found: 428.1316.

Methyl 2-methyl-3-*O*-(2-*O*-*tert*-butyldimethylsilyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-benzoate (S14)



To a solution of **9** (250 mg, 0.71 mmol) and imidazole (145 mg, 2.13 mmol) in dry DMF (3.5 mL) at 0 °C was added TBSCl (321 mg, 2.13 mmol). The reaction mixture was then gradually warmed up to room temperature, and the stirring was continued for 4 h, at which time TLC showed that all the starting materials disappeared. The reaction was quenched by MeOH at 0 ºC. The resulting mixture was diluted with EtOAc, washed successively with H_2O and brine, and then the organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver a residue, which was further purified by silica gel column chromatography (PE/EA = 30 : 1) to give **S14** (303 mg, 92%) as a colorless syrup: $[\alpha]_D^{25}$ = +16.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.48-7.44 (m, 1 H), 7.26-7.22 (m, 2 H), 5.03 (d, *J* = 8.0 Hz, 1 H), 4.19-4.13 (m, 3 H), 3.85 (s, 3 H), 3.81 (dd, *J* = 6.4, 7.6 Hz, 1 H), 2.47 (s, 3 H), 1.53 (s, 3 H), 1.34 (s, 3 H), 1.31 (d, *J* = 6.4 Hz, 3 H), 0.90 (s, 9 H), 0.22 (s, 3 H), 0.13 (s, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.5, 156.6, 133.0, 129.7, 127.0, 124.3, 119.2, 110.0, 100.9, 81.6, 77.3, 75.5, 69.5, 52.2, 28.6, 26.6, 26.2, 18.7, 16.9, 13.7, -4.1, -4.3; HRMS (ESI) m/z calcd for $C_{24}H_{38}O_7SiNa$ $[M + Na]^+$: 489.2279, found: 489.2275.

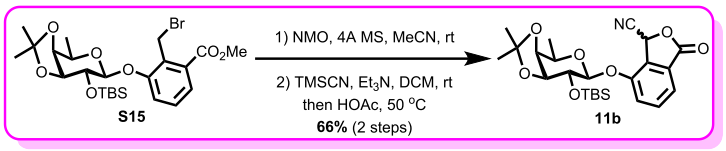
Methyl 2-bromomethyl-3-*O*-(2-*O*-tert-butyldimethylsilyl-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-benzoate (S15)



Similar procedures as those used for the synthesis of **10** were adopted to convert **S14** (276 mg, 0.59 mmol) to **S15** (298 mg, 92% yield for 2 steps) as a colorless syrup: $[\alpha]_D^{25}$ = +18.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.60 (dd, *J* = 1.6, 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.37 (dd, *J* = 1.2, 8.4 Hz, 1 H), 5.18-5.13 (m, 2 H), 5.11 (d, *J* = 7.6 Hz, 1 H), 4.21-4.14 (m, 3 H), 3.91 (s, 3 H), 3.87 (dd, *J* = 6.0, 8.0 Hz, 1 H), 1.53 (s, 3 H), 1.35 (s, 3 H), 1.31 (d, *J* = 6.4 Hz, 3 H), 0.91 (s, 9 H), 0.24 (s, 3 H), 0.16 (s, 3 H); ^{13}C NMR (150 MHz, acetone-d_6) δ 167.6, 156.7, 132.2, 130.3, 129.9, 125.6, 121.1, 110.0, 101.9, 81.3, 77.2, 75.3, 69.7, 52.6, 28.5, 26.6, 26.3, 25.1, 18.8, 16.8, -4.1,

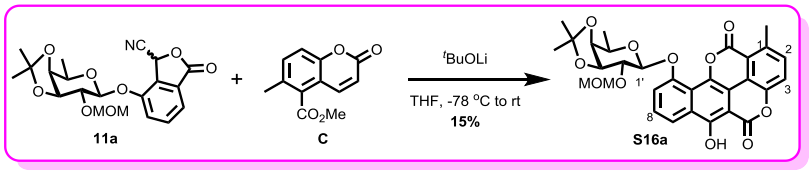
-4.3; HRMS (ESI) m/z calcd for $C_{24}H_{37}BrO_7SiNa$ [M + Na]$^+$: 567.1384, found: 567.1381.

4-*O*-(2-*O*-*tert*-Butyldimethylsily-3,4-*O*-isopropylidene-β-D-fucopyranosyl)-3-cyanoisobenzofuran-1(3*H*)-one (11b)



Similar procedures as those used for the synthesis of **11** were adopted to convert **S15** (276 mg, 0.51 mmol) to **11b** (160 mg, 66% yield for 2 steps) as a inseparable mixture of epimers: ^{1}H NMR (400 MHz, acetone-d_6) δ 7.81 (m, 2 H), 7.68 (d, J = 7.6 Hz, 2 H), 7.60 (d, J = 7.6 Hz, 2 H), 6.54 (s, 1 H, -CHCN), 6.38 (s, 1 H, -CHCN), 5.34 (d, J = 8.0 Hz, 1 H, H-1), 5.30 (d, J = 7.2 Hz, 1 H, H-1), 4.39 (qd, J = 2.0, 6.8 Hz, 1 H), 4.25 (dd, J = 2.0, 5.6 Hz, 1 H), 4.21-4.14 (m, 4 H), 3.89-3.84 (m, 2 H), 1.52 (s, 6 H), 1.36-1.34 (m, 9 H), 1.32 (d, J = 6.8 Hz, 3 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.25 (s, 3 H), 0.21 (s, 6 H), 0.13 (s, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 168.1 (2 C), 153.3, 152.8, 134.2, 134.1, 133.2, 130.4, 127.3, 124.2, 121.0, 120.9, 119.5, 114.8, 114.3, 110.2, 110.1, 102.6, 99.8, 81.5, 81.0, 77.2, 77.0, 75.1 (2 C), 70.0, 65.6, 65.3, 28.5, 28.4, 26.6, 26.5, 26.3, 26.2, 18.7, 16.8, -4.1, -4.3 (3 C); HRMS (ESI) m/z calcd for $C_{24}H_{33}NO_7SiNa$ [M + Na]$^+$: 498.1918, found: 498.1913.

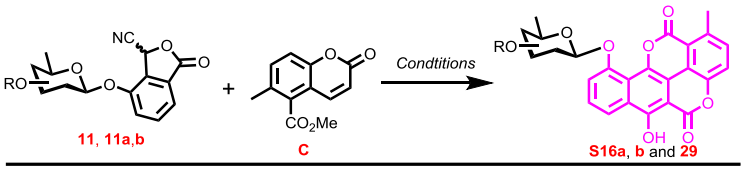
Chartarin 10-*O*-(2-*O*-methoxymethyl-3,4-*O*-isopropylidene)-β-D-fucopyranoside (S16a)

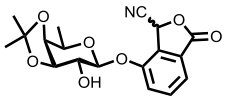
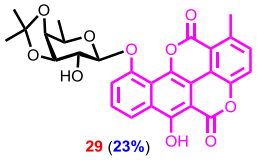
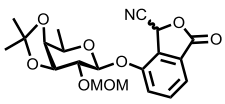
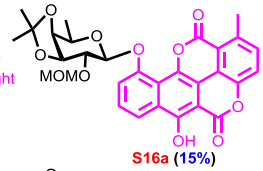
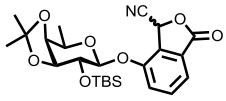
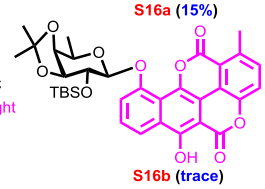


To a solution of **11a** (20 mg, 0.049 mmol) and **C** (11 mg, 0.049 mmol) in dry THF (1.0 mL) was added *t*-BuOLi (54 μL, 0.054 mmol, 1 M in THF) at -78 °C under N_2 atmosphere. The reaction mixture was stirred at the same temperature for 30 min and

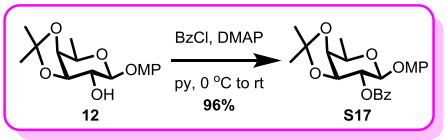
then warmed up to room temperature. The stirring was continued overnight before ethyl acetate was added to dilute the reaction mixture. The resulting mixture was washed successively with saturated aqueous NH_4Cl, H_2O, and brine, and then the organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to afford a residue, which was further purified by silica gel column chromatography (DCM/EA = 15 : 1) to give **S16a** (4.2 mg, 15%) as a yellow solid: $[\alpha]_D^{25}$ = +16.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1 H, C6-OH), 8.27 (dd, *J* = 0.8, 8.4 Hz, 1 H, H-7), 7.65 (t, *J* = 8.0 Hz, 1 H, H-8), 7.52-7.46 (m, 2 H, H-3, H-2), 7.35 (dd, *J* = 1.2, 8.4 Hz, 1 H, H-9), 5.38 (d, *J* = 6.0 Hz, 1 H), 5.24 (d, *J* = 7.6 Hz, 1 H, H-1'), 4.96 (d, *J* = 6.0 Hz, 1 H), 4.36-4.33 (m, 1 H, H-3'), 4.27 (dd, *J* = 6.4, 7.2 Hz, 1 H, H-2'), 4.18 (dd, *J* = 2.4, 5.6 Hz, 1 H, H-4'), 4.15 (qd, *J* = 2.0, 6.4 Hz, 1 H, H-5'), 3.47 (s, 3 H), 2.90 (s, 3 H, Ar-CH_3), 1.68 (s, 3 H), 1.48 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 158.9, 157.5, 153.6, 146.6, 140.3, 139.1, 133.0, 128.1, 127.1, 120.9, 120.0, 119.5, 118.4, 118.0, 115.8, 110.3, 108.8, 99.7, 98.4, 96.6, 78.8, 77.8, 76.2, 69.2, 56.0, 28.0, 26.5, 22.6, 16.9; HRMS (ESI) m/z calcd for $C_{30}H_{28}O_{11}Na$ $[M + Na]^+$: 587.1524, found: 587.1520.

Table S2. Optimization of the key Hauser-Kraus annulation reaction.



Entry	Phthalide	Conditions	Product (yield%)
1		^{t}BuOLi (**3.0 eq**), -78 °C 30 min then rt 2 h	
2	**11**		**29** (**23%**)
3	**11**	^{t}BuOLi (**4.5 eq**), -78 °C 30 min then rt 4 h	**29** (**4%**)
4	**11**	^{t}BuOLi (**1.5 eq**), -78 °C 30 min then rt 2 h	**29** (**31%**)
5	**11**	^{t}BuOLi (**1.5 eq**), -78 °C 1 h then rt 30 min	**29** (**16%**)
6	**11**	^{t}BuOLi (**1.5 eq**) was added at -78 °C, then rt 4 h	**29** (**32%**)
7	**11**	LiHMDS (**1.5 eq**) was added at -78 °C, then rt 3.5 h	**29** (**26%**)
8	**11**	^{t}BuOLi (**1.1 eq**), -78 °C 30 min then rt 4 h	**29** (**63%**)
9	**11**	^{t}BuOLi (**1.1 eq**), LiCl (0.2 eq) -78 °C 30 min then rt over night	**29** (**38%**)
10	**11**	^{t}BuOLi (**1.1 eq**) rt over night	**29** (**36%**)
11	 **11a**	^{t}BuOLi (**1.1 eq**), -78 °C 30 min then rt over night	 **S16a** (**15%**)
12	 **11b**	^{t}BuOLi (**1.1 eq**), -78 °C 30 min then rt over night	 **S16b** (**trace**)

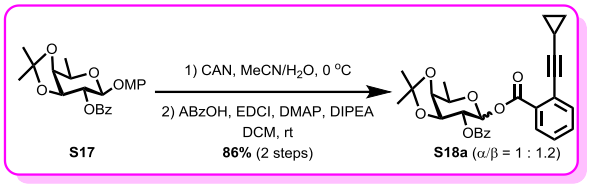
4-Methoxyphenyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (S17)



Similar procedure as that used for the synthesis of **S1** was applied to convert **12** (1.00 g, 3.22 mmol) to **S17** under the combined effects of DMAP (197 mg, 1.61 mmol) and BzCl (750 μL, 6.44 mmol) in dry pyridine (16.1 mL). After purification by silica gel

column chromatography (PE/EA = 8 : 1 to 6 :1), **S17** (1.28 g, 96%) was obtained as a white solid: $[\alpha]_D^{25}$ = +25.5 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2 H), 7.58-7.54 (m, 1 H), 7.45-7.41 (m, 2 H), 6.92 (dd, *J* = 1.6, 8.8 Hz, 2 H), 6.78-6.74 (m, 2 H), 5.47-5.43 (m, 1 H), 4.94 (d, *J* = 8.0 Hz, 1 H), 4.39-4.36 (m, 1 H), 4.15-4.13 (m, 1 H), 4.08-4.02 (m, 1 H), 3.73 (s, 3 H), 1.68 (s, 3 H), 1.51 (d, *J* = 6.4 Hz, 3 H), 1.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 155.5, 151.6, 133.2, 130.1, 130.0, 128.5, 119.0, 114.5, 110.6, 100.5, 76.5, 73.5, 69.3, 55.8, 27.9, 26.5, 16.8; HRMS (ESI) $[M + Na]^+$ calcd for $C_{23}H_{26}O_7Na$: 437.1571, found: 437.1563.

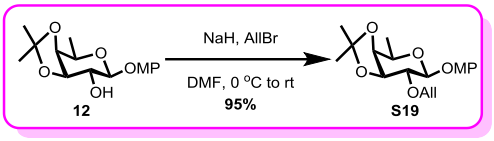
2-*O*-Benzoyl-3,4-*O*-isopropylidene-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S18a)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S17** (205 mg, 0.49 mmol) to **S18a** (201 mg, 86% yield for 2 steps, α/β = 1 : 1.2) as a α/β mixture. An aliquot of pure **S18aα** was obtained as a white foam: $[\alpha]_D^{25}$ = +102.2 (*c* 0.25, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.54-7.49 (m, 2 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.40-7.36 (m, 2 H), 7.33-7.28 (m, 1 H), 6.59-6.58 (m, 1 H, H-1), 5.49-5.46 (m, 1 H, H-2), 4.74 (t, *J* = 6.4 Hz, 1 H, H-3), 4.51 (q, *J* = 6.8 Hz, 1 H, H-5), 4.28-4.26 (m, 1 H, H-4), 1.63 (s, 3 H), 1.47-1.41 (m, 4 H), 1.39 (s, 3 H), 0.89-0.82 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.5, 134.9, 133.3, 132.2, 131.0, 130.8, 130.0, 129.6, 128.5, 127.3, 125.0, 110.0, 99.7, 90.9 (C-1), 76.0, 74.9, 73.6, 70.8, 66.5, 28.1, 26.5, 16.6, 9.1, 0.9; HRMS (ESI) $[M + H]^+$ calcd for $C_{28}H_{29}O_7$: 477.1908, found: 477.1915; An aliquot of pure **S18aβ** was also obtained as a white foam: $[\alpha]_D^{25}$ = +59.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.52-7.49 (m, 1 H), 7.42-7.34 (m, 4 H), 7.24 (t, *J* = 7.6 Hz, 1 H), 5.97 (dd, *J* = 2.0, 8.8 Hz, 1 H, H-1), 5.55-5.51 (m, 1 H, H-2), 4.45 (ddd, *J* = 2.0, 5.2, 7.2 Hz, 1 H, H-3), 4.23-4.16 (m, 2 H, H-5, H-4), 1.68 (s,

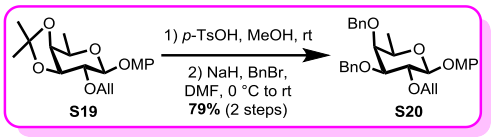
3 H), 1.55-1.48 (m, 4 H), 1.39 (s, 3 H), 0.89-0.88 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.9, 134.4, 133.3, 132.4, 131.1, 129.9, 129.7, 129.6, 128.4, 127.1, 125.6, 110.6, 100.3, 92.2 (C-1), 77.2, 76.5, 74.5, 72.4, 70.2, 27.9, 26.4, 16.6, 9.1, 0.8; HRMS (ESI) $[M + H]^+$ calcd for $C_{28}H_{29}O_7$: 477.1908, found: 477.1913.

4-Methoxyphenyl 2-*O*-allyl-3,4-*O*-isopropylidene-β-D-fucopyranoside (S19)



To a stirred solution of **12** (1.00 g, 3.22 mmol) in dry DMF (6.4 mL), NaH (60% dispersed in mineral oil, 387 mg, 9.67 mmol) was added portionwise at 0 °C. After the addition was completed, to the resulting suspension AllBr (557 μL, 6.44 mmol) was added slowly at the same temperature. The reaction mixture was then gradually warmed up to room temperature and the stirring was continued for 45 min. Then MeOH and saturated aqueous NH_4Cl were successively added to quench the reaction, which was followed by addition of ethyl acetate to dilute the reaction mixture. The resulting mixture was washed successively with water and brine, and was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to give the crude product, which was further purified by silica gel column chromatography (PE/EA = 10 : 1) to furnish **S19** (1.07 g, 95%) as a white solid: $[\alpha]_D^{25}$ = +19.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.01-6.97(m, 2 H), 6.87-6.83 (m, 2 H), 5.99-5.89 (m, 1 H), 5.36 (dq, *J* = 2.0, 17.6 Hz, 1 H), 5.15 (dq, *J* = 1.2, 10.4 Hz, 1 H), 4.82 (d, *J* = 8.0 Hz, 1 H), 4.38-4.28 (m, 2 H), 4.17-4.08 (m, 3 H), 3.75 (s, 3 H), 3.49 (dd, *J* = 6.8, 8.4 Hz, 1 H), 1.50 (s, 3 H), 1.35 (d, *J* = 6.8 Hz, 3 H), 1.32 (s, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 156.0, 152.5, 136.6, 118.7, 116.3, 115.3, 109.9, 102.2, 80.5, 80.0, 77.2, 73.0, 69.3, 55.8, 28.4, 26.6, 17.0; HRMS (ESI) $[M + Na]^+$ calcd for $C_{19}H_{26}O_6Na$: 373.1621, found: 373.1612.

4-Methoxyphenyl 2-*O*-allyl-3,4-di-*O*-benzyl-β-D-fucopyranoside (S20)

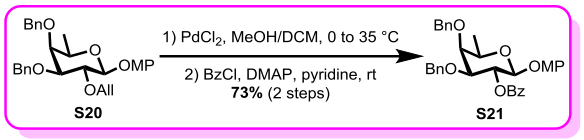


To a suspension of **S19** (1.07 g, 3.05 mmol) in MeOH (15.2 mL) was added TsOH (105 mg, 0.61 mmol) at room temperature. The reaction mixture was stirred at that temperature for 45 min before Et_3N was added to quench the reaction. Concentration at reduced pressure yielded a residue, which was purified by silica gel column chromatography (PE/EA = 1 : 1 to 1 : 2) to afford the deisopropylidenated intermediate (764 mg, 81%) as a white solid, which was put to the next step directly without further characterization.

To a stirred solution of the above obtained intermediate (764 mg, 2.46 mmol) in dry DMF (13.0 mL) was added NaH (60% dispersed in mineral oil, 295 mg, 7.38 mmol) portionwise at 0 °C. After the addition was completed, to the reaction mixture BnBr (584 μL, 4.92 mmol) was added slowly at the same temperature. The resulting reaction mixture was then gradually warmed up to room temperature and the stirring was continued for another 3 h, at which time TLC showed that a major product was formed. Then MeOH and saturated aqueous NH_4Cl were successively added to quench the reaction; ethyl acetate was added to dilute the reaction mixture. The resulting mixture was washed successively with water and brine, and then dried over anhydrous Na_2SO_4. Filtration was followed by concentration at reduced pressure to give the crude product, which was further purified by silica gel column chromatography (PE/EA = 9 : 1) to furnish **S20** (1.18 g, 98%) as a white solid: $[\alpha]_D^{25}$ = -21.9 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.24 (m, 10 H), 7.01 (d, *J* = 9.2 Hz, 2 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 6.04-5.95 (m, 1 H), 5.32-5.28 (m, 1 H), 5.17 (d, *J* = 10.4 Hz, 1 H), 5.01 (d, *J* = 12.0 Hz, 1 H), 4.85 (d, *J* = 12.0 Hz, 1 H), 4.75-4.69 (m, 3 H), 4.50 (dd, *J* = 5.6, 12.4 Hz, 1 H), 4.37 (dd, *J* = 5.6, 12.4 Hz, 1 H), 3.95 (dd, *J* = 7.6, 13.6 Hz, 1 H), 3.75 (s, 3 H), 3.58 (d, *J* = 2.8 Hz, 1 H), 3.54-3.50 (m, 2 H), 1.21 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 152.0, 138.7 (2 C), 135.4, 128.5 (2 C), 128.3, 127.7 (2 C), 118.7, 116.8, 114.5, 103.3, 82.4, 79.0, 76.4, 74.7, 74.1, 73.4, 70.7, 55.8, 17.1; HRMS (ESI) [M +

Na]$^+$ calcd for $C_{30}H_{34}O_6Na$: 513.2248, found:513.2233.

4-Methoxyphenyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-fucopyranoside (S21)

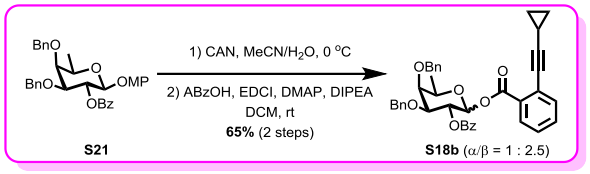


To a stirred solution of **S20** (158 mg, 0.32 mmol) in DCM/MeOH (8.0 mL, v/v = 1 : 3) was added $PdCl_2$ (14 mg, 0.079 mmol) at 0 °C. Then the reaction mixture was warmed up to 35 °C and was stirred for 30 min. Filtration through a pad of Celit/silica gel and concentration at reduced pressure yielded a residue, which was purified by silica gel column chromatography (PE/EA = 8 : 1 to 6 :1) to deliver the deallylated intermediate (119 mg, 82%) as a white solid, which was put to the next step directly without further characterization.

To a stirred solution of above obtained intermediate (119 mg, 0.26 mmol) and DMAP (16 mg, 0.13 mmol) in dry pyridine (1.3 mL) was added BzCl (46 μL, 0.40 mmol) slowly at 0 °C. The reaction mixture was then warmed up to the room temperature and the stirring was continued for 1 h. Then ethyl acetate was added to dilute the reaction mixture. The resulting mixture was washed successively with 1N HCl, saturated aqueous $NaHCO_3$ and brine, and was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to give the crude product, which was further purified by silica gel column chromatography (PE/EA = 6 : 1) to deliver **S21** (130 mg, 89%) as a white solid: $[\alpha]_D^{25}$ = +26.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 7.45-7.40 (m, 4 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.29-7.25 (m, 1 H), 7.20-7.14 (m, 5 H), 6.90-6.88 (m, 2 H), 6.71 (d, *J* = 8.4 Hz, 2 H), 5.89 (t, *J* = 9.2 Hz, 1 H), 5.08 (d, *J* = 12.0 Hz, 1 H), 4.92 (d, *J* = 7.6 Hz, 1 H), 4.76 (d, *J* = 12.0 Hz, 1 H), 4.69 (d, *J* = 12.0 Hz, 1 H), 4.55 (d, *J* = 12.0 Hz, 1 H), 3.73-3.69 (m, 5 H), 3.67 (q, *J* = 6.4 Hz, 1 H), 1.30 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 155.3, 151.8, 138.4, 137.7, 133.1, 130.3, 129.9, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8 (2 C), 119.0, 114.4, 101.4, 80.3, 75.0, 74.6, 72.1, 71.9,

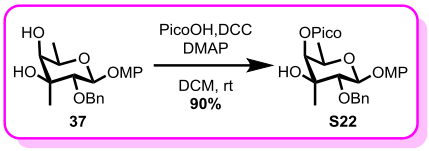
71.1, 55.7, 17.1; HRMS (ESI) $[M + Na]^+$ calcd for $C_{34}H_{34}O_7Na$: 577.2197, found: 577.2190.

2-*O*-Benzoyl-3,4-di-*O*-benzyl-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S18b)



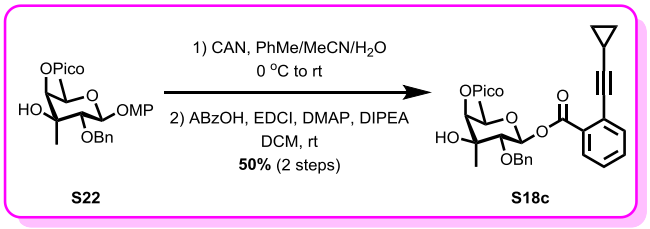
Similar procedures as those used for the synthesis of **20** were adopted to convert **S21** (333 mg, 0.60 mmol) to **S18b** (242 mg, 65% yield for 2 steps, α/β = 1 : 2.5) as a α/β mixture. An aliquot of pure **S18bα** was obtained as a white solid: $[\alpha]_D^{25}$ = +93.0 (*c* 0.5, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.53-7.48 (m, 2 H), 7.46-7.40 (m, 3 H), 7.38 (t, *J* = 7.6 Hz, 4 H), 7.32-7.24 (m, 7 H), 6.71 (d, *J* = 3.6 Hz, 1 H, H-1), 5.94 (dd, *J* = 10.8, 13.6 Hz, 1 H, H-2), 5.09 (d, *J* = 11.6 Hz, 1 H), 4.76-4.67 (m, 3 H), 4.30-4.25 (m, 2 H), 3.86 (s, 1 H, H-1), 1.32-1.25 (m, 4 H), 0.81-0.73 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 164.3, 138.3, 138.1, 134.8, 133.1, 132.0, 131.4, 130.5, 129.9, 128.6, 128.5 (2 C), 128.4, 127.9, 127.8 (2 C), 127.2, 125.0, 99.7, 91.8 (C-1), 77.1, 76.8, 75.1, 74.8, 72.6, 70.0 (2 C), 17.0, 9.1, 0.8; HRMS (ESI) $[M + Na]^+$ calcd for $C_{39}H_{36}O_7Na$: 639.2353, found:639.2343. An aliquot of pure **S18bβ** was also obtained as a white solid: $[\alpha]_D^{25}$ = +38.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 3 H), 7.54 (t, *J* = 7.2 Hz, 1 H), 7.43-7.16 (m, 15 H), 5.97-5.90 (m, 2 H, H-1, H-2), 5.08 (d, *J* = 11.6 Hz, 1 H), 4.76 (d, *J* = 12.0 Hz, 1 H), 4.71 (d, *J* = 12.4 Hz, 1 H), 4.58 (d, *J* = 12.4 Hz, 1 H), 3.81- 3.75 (m, 3 H), 1.51-1.44 (m, 1 H), 1.29 (d, *J* = 6.4 Hz, 3 H), 0.86-0.82 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 164.0, 138.3, 137.6, 134.3, 133.2, 132.3, 131.3, 129.9, 129.8 (2 C), 128.7, 128.5, 128.4 (2 C), 128.0, 127.9 (2 C), 127.1, 125.6, 100.2, 93.1 (C-1), 80.4, 75.2, 74.8, 74.6, 72.3, 72.1, 70.8, 16.9, 9.0 (2 C), 0.8; HRMS (ESI) $[M + Na]^+$ calcd for $C_{39}H_{36}O_7Na$: 639.2353, found:639.2344.

4-Methoxyphenyl 2-*O*-benzyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranoside (S22)



To a solution of **37** (90 mg, 0.24 mmol) in dry DCM (1.2 mL) was added PicoOH (53 mg, 0.43 mmol), DCC (149 mg, 0.72 mmol) and DMAP (8.8 mg, 0.072 mmol), the resulting solution was stirred at room temperature for 6.5 h. Filtration was followed by concentration under reduced pressure to afford the crude product, which was further purified by silica gel column chromatography (PE/EA = 3 : 1 to 1 : 1) to deliver compound **S22** (103 mg, 90%) as a white foam: $[\alpha]_D^{25}$ = +32.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75-8.74 (m, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H), 7.86 (td, *J* = 2.0, 8.0 Hz, 1 H), 7.50 (ddd, *J* = 1.2, 4.8, 7.6 Hz, 1 H), 7.41-7.39 (m, 2 H), 7.33 (t, *J* = 6.8 Hz, 2 H), 7.27 (t, *J* = 3.6 Hz, 1 H), 7.07-7.03 (m, 2 H), 6.85-6.81 (m, 2 H), 5.17 (s, 1 H), 5.06 (d, *J* = 11.2 Hz, 1 H), 4.98 (d, *J* = 8.0 Hz, 1 H), 4.89 (d, *J* = 11.6 Hz, 1 H), 4.13-4.08 (m, 1 H), 3.97 (d, *J* = 8.4 Hz, 1 H), 3.77 (s, 3 H), 1.47 (s, 3 H), 1.30 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 155.4, 151.8, 149.9, 147.6, 138.7, 137.3, 128.4, 128.0, 127.7, 127.2, 125.6, 118.7, 114.6, 102.3, 80.8, 79.0, 75.3, 73.9, 69.0, 55.7, 20.4, 17.1; HRMS (ESI) $[M + Na]^+$ calcd for $C_{27}H_{29}NO_7Na$: 502.1836, found: 502.1837.

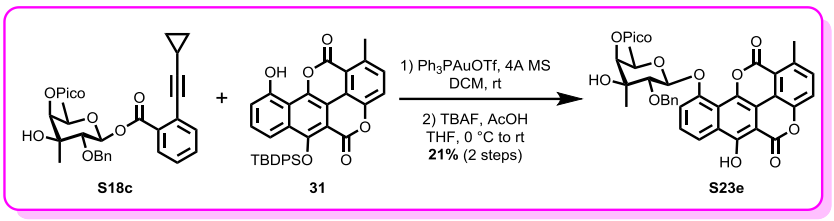
2-*O*-Benzyl-3-*C*-methyl-4-*O*-picoloyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S18c)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S22** (604 mg, 1.26 mmol) to **S18c** (344 mg, 50% yield for 2 steps) as a white foam: $[\alpha]_D^{25}$ = +11.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77-8.76 (m, 1 H), 8.13-8.11 (m, 1 H), 7.99-7.97 (m, 1 H), 7.89 (t, *J* = 7.6 Hz, 1 H), 7.52-7.50 (m, 2 H), 7.46 (t, *J* =

7.6 Hz, 1 H), 7.32-7.21 (m, 6 H), 5.99 (d, J = 8.4 Hz, 1 H, H-1), 5.16 (s, 1 H, H-4), 4.87 (t, J = 12.8 Hz, 2 H), 4.26 (q, J = 6.4 Hz, 1 H, H-5), 4.00 (d, J = 8.4 Hz, 1 H, H-3), 1.54-1.50 (m, 4 H), 1.30 (d, J = 5.2 Hz, 3 H, H-6), 0.92-0.82 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.3, 150.0, 147.9, 138.3, 137.3, 134.5, 132.2, 130.8, 130.5, 128.4, 128.0, 127.7, 127.2, 127.0, 125.6, 125.5, 100.2, 93.9 (C-1), 80.1, 79.4, 75.3, 74.7, 74.6, 69.8, 20.3, 17.0, 9.0, 0.9; HRMS (ESI) $[M + Na]^+$ calcd for $C_{32}H_{31}NO_7Na$: 564.1993, found: 564.1984.

Chartarin 10-*O*-(2-*O*-benzyl-3-*C*-methyl-4-*O*-picoloyl)-β-D-fucopyranoside (S23e)

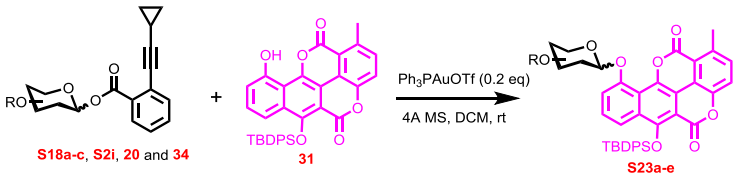


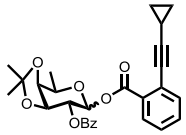
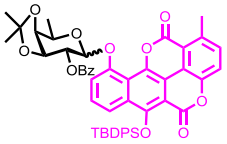
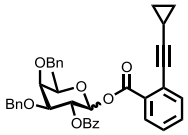
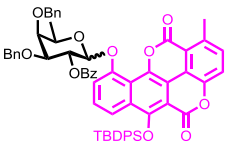
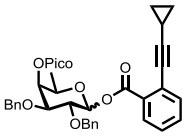
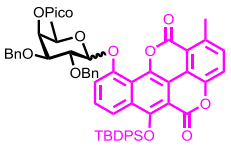
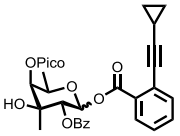
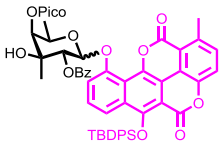
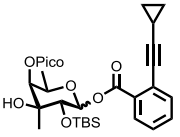
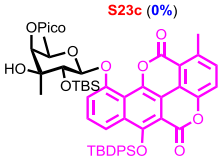
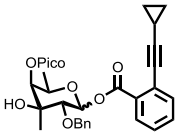
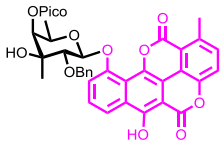
To a stirred solution of glycosyl donor **S18c** (38 mg, 0.070 mmol) and acceptor **31** (20 mg, 0.035 mmol) in dry DCM (5.2 mL) was added activated 4 Å molecular sieves (350 mg) at room temperature under N_2 atmosphere. The mixture was stirred at the same temperature for 1 h before $Ph_3PAuOTf$ (0.2 M in dry dichloromethane, 70 μL, 0.014 mmol) was added at room temperature. The resulting mixture was stirred at the same temperature for 24 h. Filtration was followed by concentration under reduced pressure to yield the crude glycosylation product.

To a solution of the above obtained intermediate in THF (5.2 mL) were added HOAc (8 μL, 0.14 mmol) and TBAF (70 μL, 1 M in THF, 0.070 mmol) successively at 0 °C. Then the mixture was warmed to room temperature and was stirred for 10 min, at which time TLC showed that the reaction reached to completion. The solvent was removed *in vacuo* to give a residue, which was further purified by silica gel column chromatography (PE/EA = 3 : 2 to 1 : 2) to give **S23e** (5.1 mg, 21% yield for 2 steps) β-selectively as a yellow solid: $[\alpha]_D^{25}$ = +20.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1 H, C6-OH), 8.85 (d, J = 4.4 Hz, 1 H), 8.36 (d, J = 8.0 Hz, 1 H), 8.28 (dd, J = 0.8, 8.0 Hz, 1H), 7.98 (t, J = 7.6 Hz, 1 H), 7.68 (t, J = 8.0 Hz, 1 H), 7.56-

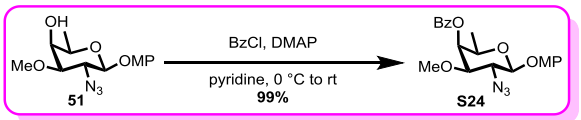
7.45 (m, 4 H), 7.20-7.17 (m, 2 H), 7.01-6.93 (m, 3 H), 5.46 (d, *J* = 7.6 Hz, 1 H, H-1'), 5.31 (d, *J* = 1.2 Hz, 1 H, H-4'), 5.29 (d, *J* = 12.0 Hz, 1 H), 5.18 (d, *J* = 12.4 Hz, 1 H), 4.53 (d, *J* = 7.7 Hz, 1 H, H-2'), 4.34 (q, *J* = 6.0 Hz, 1 H, H-5'), 2.86 (s, 3 H, C1-CH_3), 1.58 (s, 3 H, C3'-CH_3), 1.37 (d, *J* = 6.4 Hz, 3 H, H-6'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 165.0, 159.2, 157.6, 154.3, 150.1, 147.5, 146.6, 140.0, 139.5, 139.0, 137.8, 132.9, 128.2, 128.0, 127.4, 127.1, 127.0, 126.9, 126.1, 120.9, 120.1, 119.3, 118.2, 117.9, 115.0, 108.9, 100.4, 96.6 (C-1), 82.0, 78.9, 75.6, 74.3, 69.5, 22.5, 20.8, 17.4; HRMS (ESI) [M + Na]$^+$ calcd for $C_{39}H_{31}NO_{11}Na$: 712.1789, found: 712.1799.

Table S3. Optimization of the direct construction of chartarin 10-*O*-glycosidic linkages.



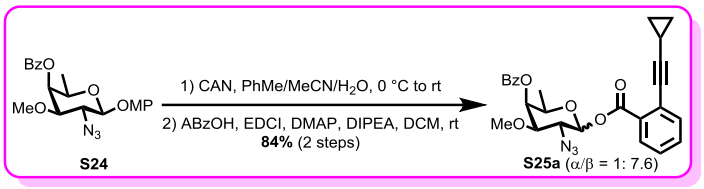
Entry	Donor	Product (yield and α/β ratio)
1	 S18a	 S23a (0%)
2	 S18b	 S23b (0%)
3	 34	 41 (52%, α/β = 1 : 2.8)
4	 S2i	 S23c (0%)
5	 20	 S23d (0%)
6	 S18c	 S23e (21%, β only)

4-Methoxyphenyl 2-deoxy-2-azido-3-*O*-methyl-4-*O*-benzoyl-β-D-fucopyranoside (S24)



Similar procedure as that used for the synthesis of **S1** was applied to convert **51** (500 mg, 1.62 mmol) to **S24** under the effects of DMAP (198 mg, 1.62 mmol) and BzCl (563 μL, 4.85 mmol) in dry pyridine (8.1 mL) under N_2 atmosphere. After purified by silica gel column chromatography (PE/EA = 6 : 1), **S24** (663 mg, 99%) was obtained as a colorless syrup: $[\alpha]_D^{25}$ = +48.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2 H), 7.62-7.58 (m, 1 H), 7.50-7.46 (m, 2 H), 7.11-7.07 (m, 2 H), 6.88-6.84 (m, 2 H), 5.57 (dd, *J* = 1.2, 3.6 Hz, 1 H), 4.79 (d, *J* = 8.0 Hz, 1 H), 3.91-3.84 (m, 2 H), 3.79 (s, 3 H), 3.48 (s, 3 H), 3.34 (dd, *J* = 3.2, 10.0 Hz, 1 H), 1.33 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 155.8, 151.3, 133.6, 130.2, 129.5, 128.6, 118.8, 114.7, 101.9, 80.7, 69.9, 68.4, 62.5, 58.0, 55.8, 16.8; HRMS (ESI) m/z calcd for $C_{21}H_{23}N_3O_6Na$ $[M + Na]^+$: 436.1479, found: 436.1477.

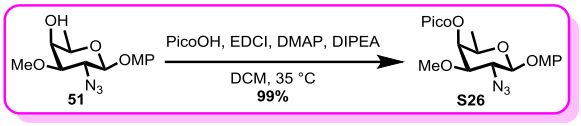
2-Deoxy-2-azido-3-*O*-methyl-4-*O*-benzoyl-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S25a)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S24** (650 mg, 1.57 mmol) to **S25a** (625 mg, 84% yield for 2 steps, α/β = 1 : 7.6) as a α/β mixture. Pure **S25aα** was obtained as a white solid: $[\alpha]_D^{25}$ = +149.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.11 (m, 2 H), 7.99 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.64-7.60 (m, 1 H), 7.54-7.45 (m, 4 H), 7.38 (td, *J* = 1.6, 7.6 Hz, 1 H), 6.58 (d, *J* = 2.4 Hz, 1 H, H-1), 5.72 (dd, *J* = 1.6, 2.4 Hz, 1 H, H-4), 4.49-4.44 (m, 1 H, H-5), 4.07-4.01 (m, 2 H, H-2, H-3), 3.53 (s, 3 H), 1.54-1.47 (m, 1 H), 1.26 (d, *J* = 6.4 Hz, 3 H, H-6), 0.99-0.87 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 164.6, 135.0, 133.6, 132.3, 130.9 (2 C), 130.1, 129.5, 128.7, 127.5, 124.9, 99.5, 91.9 (C-1), 77.6, 75.2, 69.2, 68.3, 59.0, 57.4, 16.6, 9.2 (2 C), 0.9; HRMS (ESI) m/z calcd for $C_{26}H_{25}N_3O_6Na$ $[M + Na]^+$: 498.1635, found: 498.1630. Pure **S25aβ** was obtained as a white foam: $[\alpha]_D^{25}$ = +14.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.2 Hz, 2 H), 8.08 (dd, *J* =

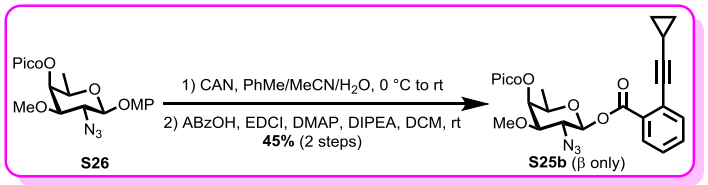
1.2, 8.0 Hz, 1 H), 7.63-7.59 (m, 1 H), 7.53-7.44 (m, 4 H), 7.37 (td, *J* = 1.6, 8.0 Hz, 1 H), 5.77 (d, *J* = 8.8 Hz, 1 H, H-1), 5.61 (d, *J* = 3.2 Hz, 1 H, H-4), 4.02 (q, *J* = 6.4 Hz, 1 H, H-5), 3.94 (dd, *J* = 8.4, 10.0 Hz, 1 H, H-2), 3.51 (s, 3 H), 3.49 (dd, *J* = 3.6, 10.0 Hz, 1 H, H-3), 1.57-1.50 (m, 1 H), 1.31 (d, *J* = 6.4 Hz, 3 H, H-6), 0.93-0.86 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 164.1, 134.6, 133.6, 132.5, 131.0, 130.1, 129.6, 128.6, 127.2, 125.7, 100.3, 93.5 (C-1), 81.3, 74.6, 70.9, 68.4, 61.8, 58.1, 16.5, 9.1 (2 C), 0.9; HRMS (ESI) m/z calcd for $C_{26}H_{25}N_3O_6Na$ $[M + Na]^+$: 498.1635, found: 498.1629.

4-Methoxyphenyl 2-deoxy-2-azido-3-*O*-methyl-4-*O*-picoloyl-β-D-fucopyranoside (S26)



Similar procedure as that used for the synthesis of **33** was adopted to convert **51** (200 mg, 0.65 mmol) to **S26** (265 mg, 99%) as a white foam: $[\alpha]_D^{25}$ = +40.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.83 (d, *J* = 4.4 Hz, 1 H), 8.21 (d, *J* = 8.0 Hz, 1 H), 7.90 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.54 (ddd, *J* = 1.2, 4.8, 8.0 Hz, 1 H), 7.09-7.05 (m, 2 H), 6.87-6.82 (m, 2 H), 5.65 (d, *J* = 3.6 Hz, 1 H), 4.79 (d, *J* = 8.0 Hz, 1 H), 3.91-3.86 (m, 2 H), 3.78 (s, 3 H), 3.49 (s, 3 H), 3.35 (dd, *J* = 3.2, 10.0 Hz, 1 H), 1.35 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 164.2, 155.8, 151.3, 150.4, 147.2, 137.4, 127.4, 125.7, 118.8, 114.7, 101.9, 80.5, 69.8, 69.3, 62.5, 58.2, 55.8, 16.8; HRMS (ESI) m/z calcd for $C_{20}H_{22}N_4O_6Na$ $[M + Na]^+$: 437.1431, found: 437.1431.

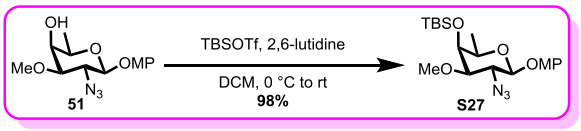
2-Deoxy-2-azido-3-*O*-methyl-4-*O*-picoloyl-β-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S25b)



Similar procedures as those used for the synthesis of **20** were adopted to convert **S26**

(265 mg, 0.64 mmol) to **S25b** (139 mg, 45% yield for 2 steps) β-selectively as a light yellow foam: $[\alpha]_D^{25}$ = +10.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81-8.79 (m, 1 H), 8.17 (d, *J* = 7.6 Hz, 1 H), 8.04 (dd, *J* = 1.2, 7.6 Hz, 1 H), 7.88 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.51-7.48 (m, 2 H), 7.46 (td, *J* = 1.2, 7.2 Hz, 1 H), 7.34 (td, *J* = 1.6, 7.6 Hz, 1 H), 5.76 (d, *J* = 8.8 Hz, 1 H, H-1), 5.67 (dd, *J* = 1.2, 3.6 Hz, 1 H, H-4), 4.03-3.95 (m, 1H, H-5), 3.93 (dd, *J* = 8.8, 10.4 Hz, 1 H, H-2), 3.50-3.46 (m, 4 H, -OCH_3, H-3), 1.55-1.49 (m, 1 H), 1.31 (d, *J* = 6.4 Hz, 3 H, H-6), 0.91-0.83 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 163.9, 150.4, 147.4, 137.1, 134.5, 132.5, 130.9, 130.0, 127.3, 127.1, 125.6, 125.5, 100.3, 93.4 (C-1), 81.1, 74.5, 70.7, 69.3, 61.6, 58.2, 16.5, 9.0 (2 C), 0.8; HRMS (ESI) m/z calcd for $C_{25}H_{25}N_4O_6$ $[M + H]^+$: 477.1769, found: 477.1769.

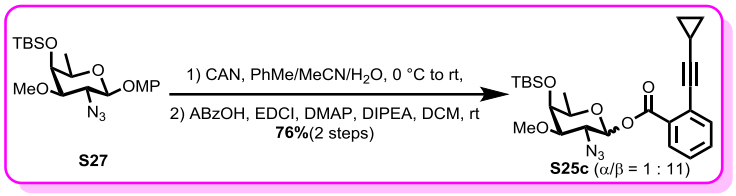
4-Methoxyphenyl 2-deoxy-2-azido-3-*O*-methyl-4-*O*-*tert*-butyldimethylsilyl-β-D-fucopyranoside (S27)



To a stirred solution of **51** (200 mg, 0.65 mmol) in dry CH_2Cl_2 (3.2 mL) was added 2,6-lutidine (224 μL, 1.92 mmol) and TBSOTf (296 μL, 1.29 mmol) successively at 0 °C under N_2 atmosphere. The reaction mixture was then gradually warmed up to room temperature, and the stirring was continued overnight, at which time TLC showed that all the starting materials disappeared. The resulting mixture was diluted with EtOAc, washed successively with 1N HCl, H_2O, saturated aqueous $NaHCO_3$ and brine, and then the organic layer was dried over anhydrous Na_2SO_4. Filtration was followed by concentration under reduced pressure to deliver a residue, which was further purified by silica gel column chromatography (PE/EA = 20 : 1) to give **S27** (269 mg, 98%) as a white solid. $[\alpha]_D^{25}$ = +18.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-7.02 (m, 2 H), 6.84-6.79 (m, 2 H), 4.66 (d, *J* = 8.0 Hz, 1 H), 3.84-3.80 (m, 2 H), 3.77 (s, 3 H), 3.59-3.54 (m, 1 H), 3.47 (s, 3 H), 2.99 (dd, *J* = 2.8, 10.4 Hz, 1 H), 1.32 (d, *J* = 6.4 Hz, 3 H), 0.95 (s, 9 H), 0.14 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 151.5, 118.6, 114.6, 102.0, 83.1, 71.6, 69.6, 62.1, 58.6, 55.8, 26.2, 18.7, 17.6, -4.0, -4.5;

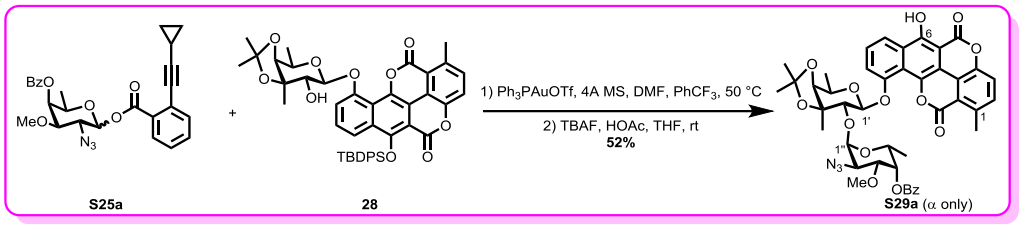
HRMS (ESI) m/z calcd for $C_{20}H_{33}N_3O_5SiNa$ $[M + Na]^+$: 446.2081, found: 446.2079.

2-Deoxy-2-azido-3-*O*-methyl-4-*O*-*tert*-butyldimethylsilyl-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (S25c)



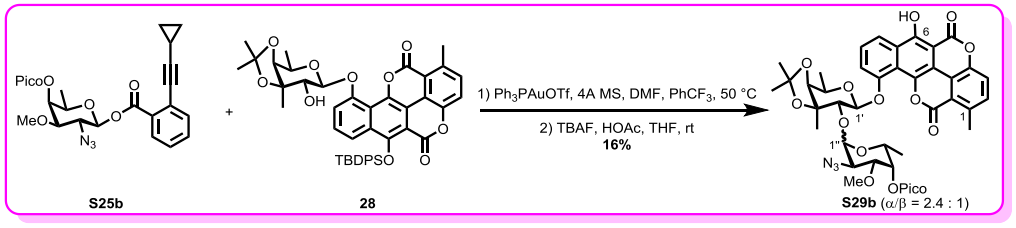
Similar procedures as that used for the synthesis of **20** were adopted to convert **S27** (237 mg, 0.56 mmol) to **S25c** (211 mg, 76% yield for 2 steps, α/β = 1 : 11) as a α/β mixture. Pure **S25cα** was obtained as a white solid: $[\alpha]_D^{25}$ = +127.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.45-7.41 (m, 1 H), 7.34-7.30 (m, 1 H), 6.45 (d, *J* = 3.6 Hz, 1 H, H-1), 4.15 (q, *J* = 6.8 Hz, 1 H, H-5), 3.98-3.94 (m, 2 H, H-2, H-4), 3.74-3.70 (m, 1 H, H-3), 3.52 (s, 3 H), 1.50-1.43 (m, 1 H), 1.24 (d, *J* = 6.4 Hz, 3 H, H-6), 0.94 (s, 9 H), 0.92-0.86 (m, 4 H), 0.14 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 134.8, 132.1, 131.3, 130.7, 127.3, 124.9, 99.5, 92.3 (C-1), 79.9, 75.0, 70.2, 58.6, 57.8, 26.1, 18.7, 17.5, 9.2, 9.1, 0.9, -3.9, -4.6; HRMS (ESI) m/z calcd for $C_{25}H_{36}N_3O_5Si$ $[M + H]^+$: 486.2419, found: 486.2421. Pure **S25cβ** was obtained as a colorless syrup: $[\alpha]_D^{25}$ = -39.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.49 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.45 (td, *J* = 1.6, 7.6 Hz, 1 H), 7.33 (td, *J* = 1.6, 8.0 Hz, 1 H), 5.65 (d, *J* = 8.4 Hz, 1 H, H-1), 3.86-3.82 (m, 2 H, H-3, H-4), 3.70-3.65 (m, 1 H, H-5), 3.50 (s, 3 H), 3.14 (dd, *J* = 2.4, 10.0 Hz, 1 H, H-2), 1.55-1.49 (m, 1 H), 1.29 (d, *J* = 6.4 Hz, 3 H, H-6), 0.95 (s, 9 H), 0.90 (d, *J* = 6.8 Hz, 4 H), 0.14 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 134.5, 132.3, 131.1, 130.4, 127.1, 125.6, 100.1, 93.8 (C-1), 83.7, 74.7, 72.6, 69.7, 61.5, 58.6, 26.2, 18.7, 17.3, 9.1, 9.0, 0.9, -4.0, -4.5; HRMS (ESI) m/z calcd for $C_{25}H_{36}N_3O_5Si$ $[M + H]^+$: 486.2419, found: 486.2422.

Chartarin 10-*O*-[2-deoxy-2-azido-3-*O*-methyl-4-*O*-picolinyl-α-D-fucopyranosyl-(1→2)-3-*C*-methyl-3,4-*O*-isopropylidene]-β-D-fucopyranoside (S29a)



Similar procedures as those used for the synthesis of **59** were adopted to mediate the coupling between **S25a** (55 mg, 0.12 mmol) and **28** (15 mg, 0.019 mmol) to provide **S29a** (8.3 mg, 52% for 2 steps) α-stereoselectively as a yellow solid after desilylation: $[\alpha]_D^{25}$ = +45.6 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1 H, C6-OH), 8.32 (d, *J* = 8.0 Hz, 1 H), 8.12-8.09 (m, 2 H), 7.66 (d, *J* = 8.2 Hz, 1 H), 7.60-7.54 (m, 2 H), 7.49 (d, *J* = 8.4 Hz, 1 H), 7.45-7.40 (m, 3 H), 6.51 (d, *J* = 3.6 Hz, 1 H, H-1"), 5.64 (d, *J* = 2.8 Hz, 1 H, H-4"), 5.24 (d, *J* = 8.8 Hz, 1 H, H-1'), 4.48 (q, *J* = 6.4 Hz, 1 H, H-5"), 4.42 (d, *J* = 8.8 Hz, 1 H, H-2'), 4.17 (qd, *J* = 1.6, 6.4 Hz, 1 H, H-5'), 3.80 (d, *J* = 1.6 Hz, 1 H, H-4'), 3.74 (dd, *J* = 3.0, 11.0 Hz, 1 H, H-3"), 3.39 (dd, *J* = 3.8, 11.0 Hz, 1 H, H-2"), 3.37 (s, 3 H), 2.99 (s, 3 H, C1-CH_3), 1.71 (s, 3 H), 1.51 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.50 (s, 3 H), 1.44 (s, 3 H), 1.30 (d, *J* = 6.4 Hz, 3 H, H-6"); ^{13}C NMR (100 Hz, $CDCl_3$) δ 166.2, 165.1, 159.5, 157.6, 154.4, 146.7, 140.0, 133.3 (2 C), 130.1, 129.9, 128.5, 128.2, 127.3, 126.2, 121.1, 119.1, 118.5, 117.9, 115.1, 109.4, 107.8, 100.3 (C-1"), 99.8 (C-1'), 96.8, 82.4, 81.7, 79.6, 75.9, 70.1, 68.6, 65.7, 59.4, 57.3, 28.8, 27.5, 22.7, 18.3, 17.1, 16.7; HRMS (ESI) m/z calcd for $C_{43}H_{41}N_3O_{14}Na$ $[M + Na]^+$: 846.2481, found: 846.2482.

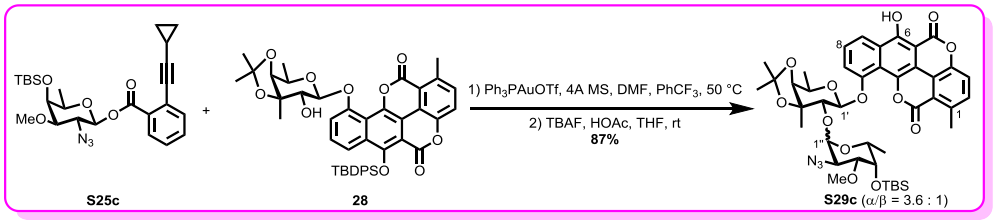
Chartarin 10-*O*-[2-deoxy-2-azido-3-*O*-methyl-4-*O*-picoloyl-D-fucopyranosyl-(1→2)-3-*C*-methyl-3,4-*O*-isopropylidene]-β-D-fucopyranoside (S29b)



Similar procedures as those used for the synthesis of **59** were adopted to mediate the coupling between **S25b** (55 mg, 0.12 mmol) and acceptor **28** (15 mg, 0.019 mmol) to

provide **S29b** (2.6 mg, 16%, α/β = 2.4 : 1) as a α/β mixture after desilylation. Pure **S29bα** was obtained as a yellow solid: $[\alpha]_D^{25}$ = +46.8 (*c* 0.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.74 (s, 1 H, C6-OH), 8.81 (s, 1 H), 8.31 (d, *J* = 8.4 Hz, 1 H), 8.17 (d, *J* = 7.8 Hz, 1 H), 7.82 (t, *J* = 7.5 Hz, 1 H), 7.66 (t, *J* = 8.1 Hz, 1 H), 7.54 (d, *J* = 8.4 Hz, 1 H), 7.51 (brs, 1 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 7.39 (d, *J* = 7.8 Hz, 1 H), 6.47 (d, *J* = 3.6 Hz, 1 H, H-1"), 5.73 (d, *J* = 3.6 Hz, 1 H, H-4"), 5.25 (d, *J* = 9.0 Hz, 1 H, H-1'), 4.51 (q, *J* = 6.3 Hz, 1 H, H-5"), 4.42(d, *J* = 8.4 Hz, 1 H, H-2'), 4.16 (qd, *J* = 1.8, 6.6 Hz, 1 H, H-5'), 3.80 (d, *J* = 1.8 Hz, 1 H, H-4'), 3.75 (dd, *J* = 3.0, 10.8 Hz, 1 H, H-3"), 3.39 (dd, *J* = 3.0, 10.8 Hz, 1 H, H-2"), 3.39 (s, 3 H), 2.96 (s, 3 H, C1-CH_3), 1.71 (s, 3 H), 1.50 (d, *J* = 6.4 Hz, 3 H, H-6'), 1.50 (s, 3 H), 1.44 (s, 3 H), 1.32 (d, *J* = 6.4 Hz, 3 H, H-6"); ^{13}C NMR (150 Hz, $CDCl_3$) δ 165.0, 159.5, 157.6, 154.3, 150.4, 146.7, 139.9, 139.1, 137.2, 133.0, 128.2, 127.2, 125.5, 121.1, 120.3, 119.1, 118.6, 117.9, 115.1, 109.5, 108.9, 100.3 (C-1"), 99.6 (C-1'), 96.7, 82.4, 81.7, 79.7, 75.9, 71.0, 68.6, 65.5, 59.3, 57.4, 28.8, 27.5, 22.7, 18.3, 17.0, 16.6; HRMS (ESI) m/z calcd for $C_{42}H_{40}N_4O_{14}Na$ $[M + Na]^+$: 847.2433, found: 847.2432.

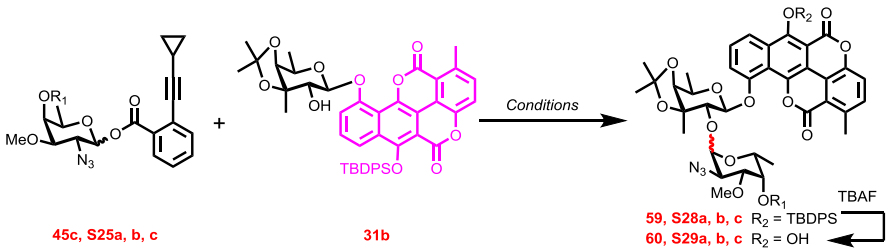
Chartarin 10-*O*-[2-deoxy-2-azido-3-*O*-methyl-4-*O*-*tert*-butyldimethylsilyl-D-fucopyranosyl-(1→2)-3-*C*-methyl-3,4-*O*-isopropylidene]-β-D-fucopyranoside (S29c)



Similar procedures as those used for the synthesis of **59** were adopted to mediate the coupling between **S25c** (76 mg, 0.16 mmol) and acceptor **28** (20 mg, 0.026 mmol) to **S29c** (19 mg, 87%, α/β = 3.6 : 1) after desilylation as a α/β mixture. Pure **S29cα** was obtained as a yellow solid: $[\alpha]_D^{25}$ = -10.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1 H, C6-OH), 8.30 (dd, *J* = 1.2, 8.4 Hz, 1 H, H-7), 7.64 (t, *J* = 8.2 Hz, 1 H, H-8), 7.53 (d, *J* = 8.3 Hz, 1 H, H-3), 7.45 (dd, *J* = 0.8, 8.3 Hz, 1 H, H-2), 7.37 (dd, *J* =

1.1, 8.2 Hz, 1 H, H-9), 6.26 (d, *J* = 3.6 Hz, 1 H, H-1''), 5.18 (d, *J* = 8.6 Hz, 1 H, H-1'), 4.36 (d, *J* = 8.6 Hz, 1 H, H-2'), 4.13 (dd, *J* = 2.0, 6.6 Hz, 2 H, H-5', H-5''), 3.94-3.88 (m, 1 H, H-4''), 3.76 (d, *J* = 1.9 Hz, 1 H, H-4'), 3.46 (dd, *J* = 2.6, 11.0 Hz, 1 H, H-3''), 3.32 (s, 3 H), 3.26 (dd, *J* = 3.5, 10.9 Hz, 1 H, H-2''), 2.86 (s, 3 H, C1-CH_3), 1.71 (s, 3 H), 1.50 (d, *J* = 6.6 Hz, 3 H), 1.43 (d, *J* = 7.2 Hz, 6 H), 1.27 (d, *J* = 6.4 Hz, 3 H), 0.89 (s, 9 H), 0.06 (s, 3 H), 0.01 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 159.1, 157.4, 154.6, 146.6, 140.3, 139.1, 132.8, 128.1, 127.1, 120.9, 120.2, 119.1, 118.4, 117.9, 115.0, 109.3, 108.8, 100.5 (C-1''), 100.1 (C-1'), 96.8, 82.4, 81.8, 79.2, 78.2, 70.6, 68.5, 67.6, 59.0, 57.5, 28.8, 27.5, 26.2, 22.6, 18.6, 18.3, 17.5, 17.1, -4.0, -4.4; HRMS (ESI) m/z calcd for $C_{42}H_{51}N_3O_{13}SiNa$ $[M + Na]^+$: 856.3083, found: 856.3083.

Table S4. Optimization of glycosylation reactions with 2-OH of 3-*C*-methyl-branched-β-fucoside as acceptor.



45c, S25a, b, c 31b

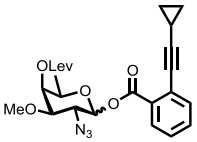
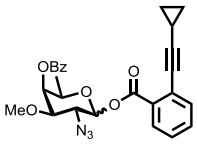
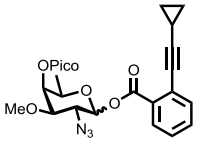
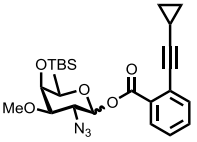
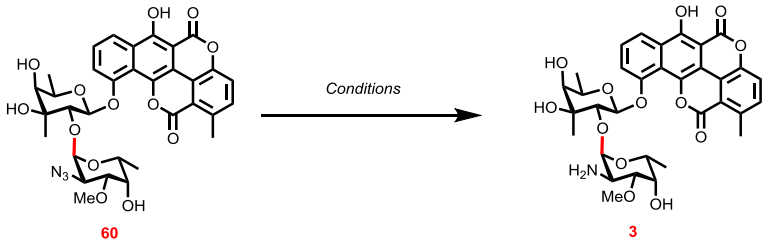
Entry	Donor	Conditions	Product (yield (%), α/β ratio)
1	 **45c** (β only)	PPh_3AuOTf (0.2 eq), DCM, rt	**59** 99%, 1.2 : 1
2		PPh_3AuOTf (0.2 eq), DMF (6 eq), DCM, rt	**59** 12%, 3 : 1
3		PPh_3AuOTf (0.4 eq), DMF (6 eq), DCM, rt	**59** 50%, 3 : 1
4		PPh_3AuOTf (0.4 eq), $PhCF_3$, rt	**59** 82%, 1.8 : 1
5		PPh_3AuOTf (0.4 eq), DMF (6 eq), $PhCF_3$, rt	**60** 10%, 4 : 1
6		PPh_3AuOTf (0.4 eq), DMF (6 eq), $PhCF_3$, 50 °C	**60** 52%, 4 : 1
7		PPh_3AuOTf (0.4 eq), DMF (6 eq), $PhCF_3$, 80 °C	**60** 20%, 3 : 1
8	 **S25a** (α/β = 1 : 7.6)	PPh_3AuOTf (0.4 eq), DMF (6 eq), $PhCF_3$, 50 °C	**S29a** 52%, α only
9	 **S25b** (β only)	PPh_3AuOTf (0.4 eq), DMF (6 eq), $PhCF_3$, 50 °C	**S29b** 16%, 2.4 : 1
10	 **S25c** (α/β = 1 : 11)	PPh_3AuOTf (0.4 eq), DMF (6 eq), $PhCF_3$, 50 °C	**S29c** 87%, 3.6 : 1

Table S5. Optimization of reduction of N_3 in **60**.



60 3

Entry	Conditions	Result (%)
1	Ph_3P, H_2O, Et_3N, THF, 60 °C	N,P-ylide was formed
2	10% Pd/C, H_2, THF/^{t}BuOH, rt	complex
3	10% Pd/C, H_2, DCM/^{t}BuOH, rt	complex
4	Raney Ni, H_2, THF/MeOH, rt	complex
5	1,3-propanedithiol, Et_3N, THF/H_2O, rt to 55 °C	below 50%
6	Zn, HOAc, rt	below 30%
7	Zn, $CuSO_4$, HOAc, THF, rt	83%

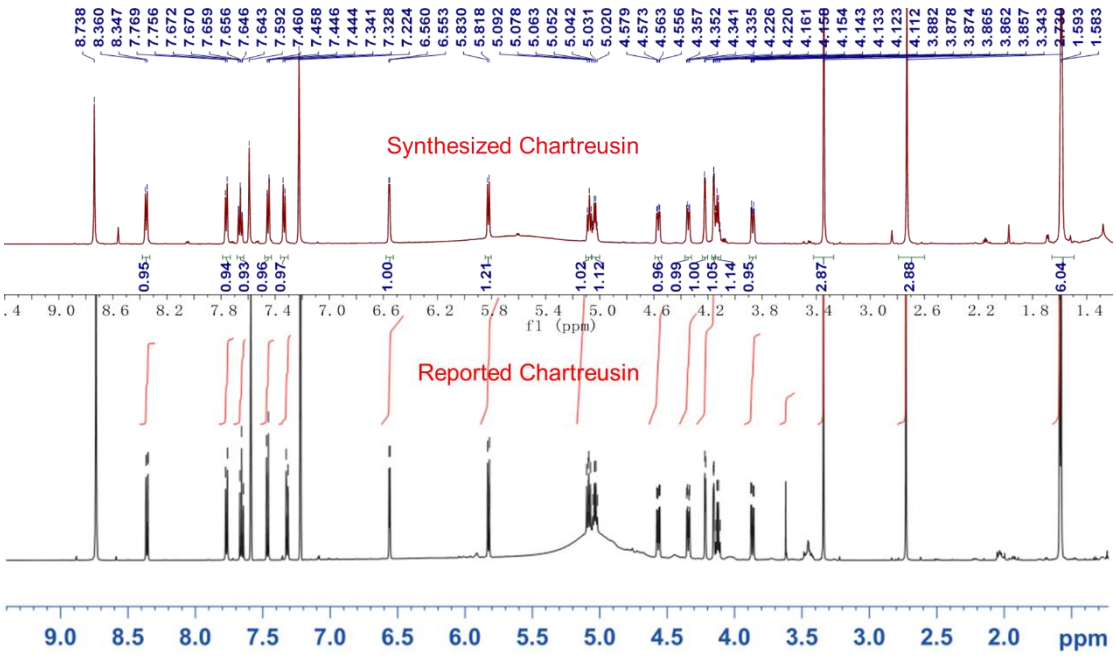


Figure S1. Comparison of the ^{1}H NMR spectrum of the synthetic Chartreusin (**1**) with that of the natural product. [S5]

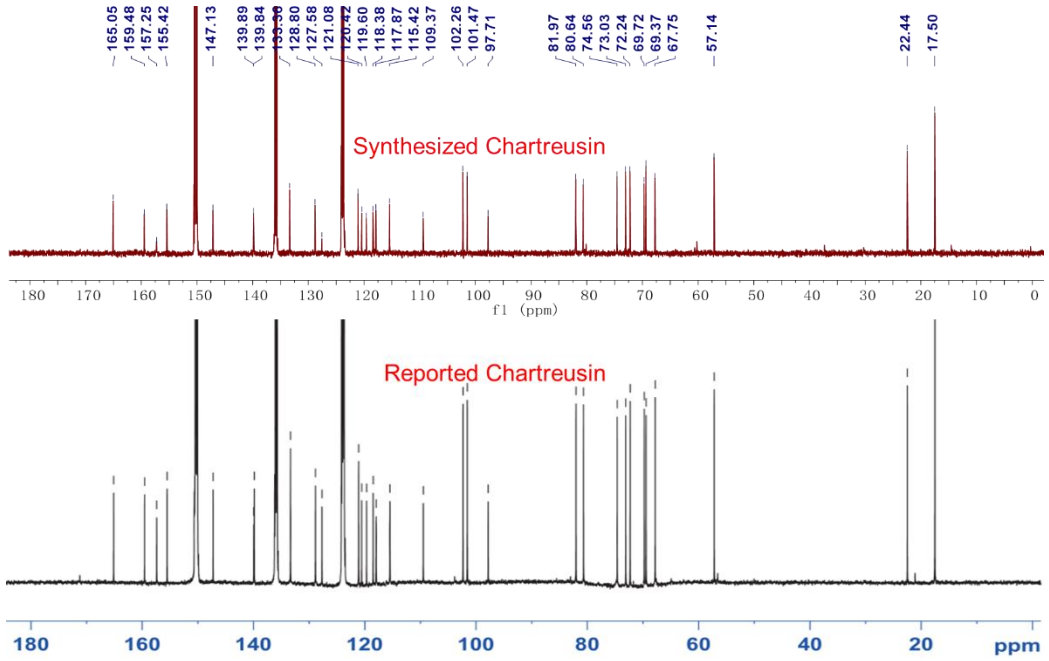


Figure S2. Comparison of the ^{13}C NMR spectrum of the synthetic Chartreusin (**1**) with that of the natural product. [S5]

Table S6. Comparison of the ^{1}H NMR data of the synthetic Chartreusin (**1**) with those of the natural product.[S5]

Position	**Reported** ^{1}H NMR (600 MHz, pyridine-d_5) δ [ppm, mult, *J* (Hz)]	**Synthetic** ^{1}H NMR (600 MHz, pyridine-d_5) δ [ppm, mult, *J* (Hz)]	Δδ (ppm)
1-CH_3	2.73 (s, 3H)	2.73 (s, 3H)	0
2	7.32 (d, 8.8 Hz, 1H)	7.33 (d, 7.8 Hz, 1H)	0.01
3	7.47 (d, 8.3 Hz, 1H)	7.45 (dd, 8.4, 1.2 Hz, 1H)	-0.02
7	8.36 (dd, 8.3, 0.6 Hz, 1H)	8.35 (d, 7.8 Hz, 1H)	-0.01
8	7.66 (t, 8.1 Hz, 1H)	7.66 (td, 7.8, 1.2 Hz, 1H)	0
9	7.77 (d, 7.8 Hz, 1H)	7.76 (td, 7.8, 1.2 Hz, 1H)	-0.01
1'	5.83 (d, 4.1 Hz, 1H))	5.82 (d, 7.2 Hz, 1H)	-0.01
2'	5.08 (dd, 9.5, 7.7 Hz, 1H)	5.08 (t, 8.4 Hz, 1H)	0
3'	4.34 (dd, 9.6, 3.5 Hz, 1H)	4.35 (dd, 9.9, 3.4 Hz, 1H),	0.01
4'	4.22 (d, 3.4 Hz, 1H)	4.22 (d, 3.6 Hz, 1H)	0
5'	4.12 (q, 6.5 Hz, 1H)	4.13 (q, 6.0 Hz, 1H)	0.01
5'-CH_3	1.58 (d, 6.5 Hz, 3H)	1.59 (d, 6.0 Hz, 3H)	0.01
1"	6.56 (d, 4.1 Hz, 1H)	6.56 (d, 4.2 Hz, 1H)	0
2"	4.57 (dd, 10.0, 4.1 Hz, 1H)	4.57 (dd, 9.9, 4.0 Hz, 1H)	0
3"	3.87 (dd, 10.1, 3.1 Hz, 1H)	3.87 (dt, 10.2, 2.4 Hz, 1H)	0
3"-OMe	3.34 (s, 3H)	3.34 (s, 3H)	0
4"	4.16 (d, 1.7 Hz, 1H)	4.16 (t, 2.1 Hz, 1H)	0
5"	5.03 (dq, 6.3, 0.9 Hz, 1H)	5.04 (q, 6.3 Hz, 1H)	0.01
5"-CH_3	1.59 (d, 6.5 Hz, 3H)	1.59 (d, 6.0 Hz, 3H)	0

Table S7. Comparison of the ^{13}C NMR data of the synthetic Chartreusin (**1**) with those of the natural product. [S5]

Position	**Reported** ^{13}C NMR (150 MHz, pyridine-d_5)	**Synthetic** ^{13}C NMR (150 MHz, pyridine-d_5)	Δδ (ppm)
1	139.8	139.8	0

1-CH_3	22.5	22.4	-0.1
2	133.2	133.4	0.2
3	121.1	121.1	0
3a	147.2	147.1	-0.1
3a[1]	120.5	120.4	-0.1
5	165.1	165.1	0
5a	97.8	97.7	-0.1
5a[1]	109.5	109.4	-0.1
6	159.5	159.5	0
6a	127.7	127.6	-0.1
7	117.9	117.9	0
8	128.8	128.8	0
9	115.5	115.4	-0.1
10	155.5	155.4	-0.1
10a	119.7	119.6	-0.1
10b	139.9	139.9	0
12	157.4	157.3	-0.1
12a	118.5	118.4	-0.1
1'	101.6	101.5	-0.1
2'	80.7	80.6	-0.1
3'	74.6	74.6	0
4'	73.1	73.0	-0.1
5'	72.3	72.2	-0.1
5'-CH_3	17.5	17.5	0
1"	102.3	102.3	0
2"	69.4	69.4	0
3"	82.0	82.0	0
3"-OMe	57.2	57.1	-0.1
4"	69.7	69.7	0
5"	67.8	67.8	0
5"-CH_3	17.5	17.5	0

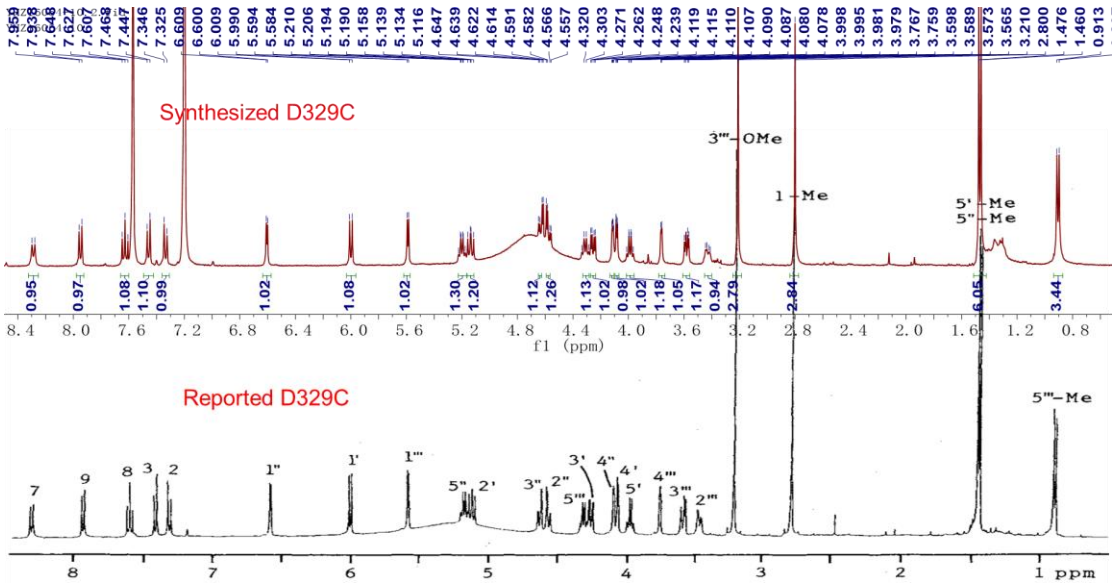


Figure S3. Comparison of the ^{1}H NMR spectrum of the synthetic D329C (**2**) with that of the natural product.[S6]

Table S8. Comparison of the ^{1}H NMR data of the synthetic D329C (**2**) with those of the natural product.[S6]

Position	**Reported** ^{1}H NMR (400 MHz, pyridine -d_5, 60 □) δ [ppm, mult, *J* (Hz)]	**Synthetic** ^{1}H NMR (400 MHz, pyridine -d_5, 60 □) δ [ppm, mult, *J* (Hz)]	Δδ (ppm)
1-CH_3	2.80 (s, 3H)	2.80 (s, 3H)	0
2	7.30 (d, 8.3 Hz, 1H)	7.34 (d, 8.4 Hz, 1H)	0.04
3	7.41 (d, 8.3 Hz, 1H)	7.46 (d, 8.0 Hz, 1H)	0.05
7	8.36 (br d, 8.0 Hz, 1H)	8.29 (d, 8.0 Hz, 1H),	-0.07
8	7.59 (t, 7.2 Hz, 1H)	7.63 (t, 8.0 Hz, 1H),	0.04
9	7.94 (d, 7.8 Hz, 1H)	7.95 (d, 8.0 Hz, 1H),	0.01
1'	6.01 (d, 7.7 Hz, 1H)	6.00 (d, 7.6 Hz, 1H)	-0.01
2'	5.14 (dd, 9.5, 7.7 Hz, 1H)	5.14 (dd, 9.6, 7.6 Hz, 1H),	0
3'	4.27 (dd, 9.5, 3.6 Hz, 1H)	4.25 (dd, 9.4, 3.6 Hz, 1H)	-0.02
4'	4.07 (d, 3.6 Hz, 1H)	4.08 (d, 3.6 Hz, 1H)	0.01
5'	3.97 (q, 6.4 Hz, 1H)	3.99 (q, 6.4 Hz, 1H)	0.02

5'-CH_3	1.44 (d, 6.4 Hz, 3H)	1.47 (d, 6.4 Hz, 3H)	0.03
1"	6.59 (d, 3.6 Hz, 1H)	6.61 (d, 3.6 Hz, 1H)	0.02
2"	4.59 (dd, 10.0, 3.6 Hz, 1H)	4.57 (dd, 10.0, 3.7 Hz, 1H)	-0.02
3"	4.66 (dd, 10.0, 3.4 Hz, 1H)	4.63 (dd, 10.0, 3.6 Hz, 1H)	-0.03
4"	4.11 (d, 3.4 Hz, 1H)	4.11 (dd, 3.2, 1.4 Hz, 1H)	0
5"	5.20 (q, 6.6 Hz, 1H)	5.20 (qd, 6.0, 1.6 Hz, 1H)	0
5"-CH_3	1.46 (d, 6.6 Hz, 3H)	1.47 (d, 6.4 Hz, 3H)	0.01
1"'	5.60 (d, 3.7 Hz, 1H)	5.59 (d, 4.0 Hz, 1H)	-0.01
2"'	3.53 (br d, 1H)	3.43 (dd, 8.8, 3.6 Hz, 1H)	-0.1
3"'	3.61 (dd, 9.8, 2.7 Hz, 3H)	3.58 (dd, 10.0, 3.2 Hz, 1H)	-0.03
3"'-OMe	3.58 (s, 3H)	3.21 (s, 3H)	-0.37
4"'	3.78 (d, 2.7 Hz, 1H)	3.76 (d, 3.2 Hz, 2H)	-0.02
5"'	4.35 (q, 6.3 Hz, 1H)	4.31 (q, 6.5 Hz, 1H)	-0.04
5"'-CH_3	0.94 (d, 6.3 Hz, 3H)	0.90 (d, 6.4 Hz, 3H)	-0.04

Table S9. Comparison of the ^{13}C NMR data of the synthetic D329C (**2**) with those of the natural product.[S6]

Position	**Reported** ^{13}C NMR (100 MHz, pyridine-d_5, 60 □)	**Synthetic** ^{13}C NMR (100 MHz, pyridine-d_5, 60 □)	Δδ (ppm)
1-CH_3	22.1	22.1	0
2	132.8	132.9	0.1
3	120.5	120.7	0.2
7	118.3	118.1	-0.2
8	128.1	128.4	0.3
9	116.6	116.6	0
1'	100.9	100.9	0
2'	78.0	78.1	0.1
3'	73.7	73.8	0.1
4'	73.0	73.0	0
5'	71.7	71.7	0

5'-CH_3	17.0	17.0	0
1''	96.9	97.0	0.1
2''	73.8	73.9	0.1
3''	70.0	70.1	0.1
4''	73.5	73.5	0
5''	67.2	67.2	0
5''-CH_3	17.0	17.1	0.1
1'''	96.4	96.4	0
2'''	68.5	68.6	0.1
3'''	81.4	81.4	0
3'''-OMe	56.7	56.7	0
4'''	69.0	69.0	0
5'''	67.0	66.9	-0.1
5'''-CH_3	16.3	16.3	0

Table S10. ^{1}H and ^{13}C NMR data of Elsamicin A (**3**).

	Position	1H NMR (400 MHz, CD_3OD) δ [ppm, mult, J (Hz)]	13C NMR (150 MHz, CD_3OD) δ [ppm]
Aglycone	1-CH_3	2.47 (s, 3H)	22.3
	2	7.06 (brs, 1H)	133.9
	3	6.59 (brs, 1H)	121.0
	7	7.65 (brs, 1H)	120.3
	8	7.27 (brs, 1H)	127.5
	9	7.31 (brs, 1H)	127.5
Sugar	1'	5.60 (d, 7.2 Hz, 1H)	98.8
	2'	4.15 (d, 7.6 Hz, 1H)	82.6
	3'	------	74.9
	3'-CH3	1.43 (s, 3H)	19.8
	4'	3.44 (s, 1H)	78.3
	5'	4.11-4.08 (m, 1H)	71.2
	5'-CH_3	1.27 (d, 6.0 Hz, 3H)	17.2

	1"	5.86 (s, 1H)	99.7
	2"	3.65 (d, 11.6 Hz, 1H)	51.3
	3"	3.72 (d, 10.8 Hz, 1H)	78.4
	3"-OCH_3	3.48 (s, 3H)	56.2
	4"	4.08 (s, 1H)	67.6
	5"	4.50 (q, 6.7 Hz, 1H)	68.7
	5"-CH_3	1.39 (d, 6.4 Hz, 3H)	16.8

Table S11. Comparison of the ^{1}H NMR data of the synthetic *N, O*-tetra-acetylated Elsamicin A (**61**) with those reported in literature.[S7]

Position	**Reported** ^{1}H NMR (360 MHz, pyridine-d_5) δ [ppm, mult, *J* (Hz)]	**Synthetic** ^{1}H NMR (400 MHz, pyridine-d_5) δ [ppm, mult, *J* (Hz)]	Δδ (ppm)
1-CH_3	2.61 (s, 3H)	2.61 (s, 3H)	0
2	7.78 (d, 8.9 Hz, 1H)	7.57-7.52 (m, 2H)	
3	7.53 (d, 8.9 Hz, 1H)		
6-OAc	2.95 (s, 3H)	2.94 (s, 3H)	-0.01
7	7.95 (d, 8.5 Hz, 1H)	7.95 (d, 8.0 Hz, 1H)	0
8	7.68 (t, 8.5 Hz, 1H)	7.67 (t, 8.0 Hz, 1H)	-0.01
9	7.40 (br d, 1H)	7.39 (d, 6.8 Hz, 1 H)	-0.01
1'	5.42 (d, 8.2 Hz, 1H))	5.40 (d, *J* = 10.8 Hz, 1H)	-0.02
2'	4.25 (br d, 1H)	4.24 (br s, 1H)	-0.01
3'-CH_3	1.48 (s, 3H)	1.47 (s, 3H),	0
4'	5.02 (s, 1H)	5.02 (s, 1H)	0
5'	4.13 (br s, 1H)	4.12 (br s, 1H)	-0.01
5'-CH_3	1.21 (d, 6.4 Hz, 3H)	1.22 (d, 6.4 Hz, 3H)	0.01
1"	5.90 (d, 3.2 Hz, 1H)	5.89 (br s, 1H)	-0.01
2"	4.38-4.42 (m, 1H)	4.37-4.42 (m, 1H)	0
2"-NHAc	0.78 (br s, 3H)	0.77 (br s, 3H)	-0.01
3"	3.40 (br s, 1H)	3.40 (br s, 1H)	0

3''-OMe	3.25 (s, 3H)	3.25 (s, 3H)	0
4''	5.40 (s, 1H)	5.39 (s, 1H)	-0.01
5''	4.38-4.42 (m, 1H)	4.37-4.42 (m, 1H)	0
5''-CH_3	1.21 (d, 6.4 Hz, 3H)	1.20 (d, 6.8 Hz, 3H)	-0.01
4'-OAc 4''-OAc	2.16 (s, 3H) 2.25 (s 3H)	2.16 (s, 3H) 2.25 (s, 3H)	0 0

Table S12. ^{1}H and ^{13}C NMR data of Elsamicin B (**4**).

	Position	^{1}H NMR (400 MHz, DMSO-d_6) δ [ppm, mult, *J* (Hz)]	^{13}C NMR (100 MHz, DMSO-d_6) δ [ppm]
Aglycone	1-CH_3	2.75 (s, 3H)	21.5
	2	7.71-7.56 (m, 1H)	133.1
	3	7.71-7.56 (m, 1H)	121.0
	6-OH	11.39 (s, 1H)	------
	7	8.00 (d, 8.0 Hz, 1H)	116.8
	8	7.71-7.56 (m, 1H)	128.6
	9	7.71-7.56 (m, 1H)	115.8
Sugar	1'	5.13 (d, 7.6 Hz, 1H)	101.3
	2'	3.99 (dd, 8.0, 4.0 Hz, 1H)	72.8
	2'-OH	4.18 (d, 4.4 Hz, 1H)	------
	3'-OH	4.64 (s, 1H)	------
	3'-CH_3	1.24 (s, 3H)	19.1
	4'	3.27 (d, 3.2 Hz, 1H)	75.7
	4'-OH	4.74 (d, 4.4 Hz, 1H)	------
	5'	4.12 (q, 6.4 Hz, 1H)	69.3
	5'-CH_3	1.26 (d, 6.0 Hz, 3H)	17.1

Evaluation of the cytotoxic activities of 1-4

Each cell line was seeded into a separate 96-well plate to ensure that the effects of the drugs were assessed individually. 100 μL of cell suspension was added to each well and cells were attached after 24 hours in the incubator. Elsamicin A, Elsamicin B,

Chartreusin, and D329C were prepared as 10 mM stock solutions in dimethyl sulfoxide (DMSO). Working solutions were diluted in supplemented DMEM to create five concentration gradients. In each 96-well plate, four wells were designated as negative controls (untreated), and the remaining wells received 100 μL of each drug concentration, resulting in a total of four wells per drug concentration. After 48 hours of drug exposure, 10 μL of CCK-8 reagent was added to each well and incubated for 2 hours at 37°C. The absorbance at 450 nm was measured using a microplate reader. The absorbance values were normalized to the negative control wells to calculate the relative cell viability for each drug concentration. The half-maximal inhibitory concentration (IC50) for each drug was determined using non-linear regression analysis.

RNA-seq analysis

ES-2 cells were cultured using the above cell culture method and inoculated into six-well plates at 2 mL of cell suspension per well. Cells were allowed to attach overnight under standard culture conditions. After attachment, Chartreusin, Elsamicin A, and Elsamicin B, at predetermined concentrations (based on IC50) were added to the corresponding wells. Each drug was tested in triplicate and three wells were left in each plate as control. The plates were incubated for 24 hours after treatment to allow the drugs to act. Following drug treatment, RNA was extracted by the Trizol method and the quality of RNA was assessed. RNA-seq library construction was performed using the extracted total RNA, and sequencing was performed using the Illumina Novaseq-PE150 platform to obtain and analyze the sequencing data.

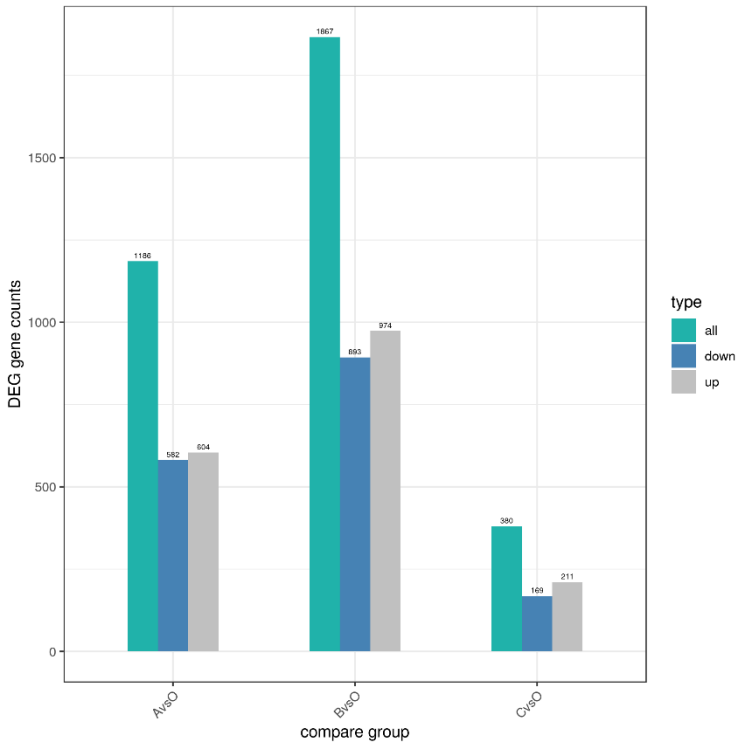


Figure S4. Gene numbers of ES-21 cells influenced by chartreusin (C), elsamicin A, and B.

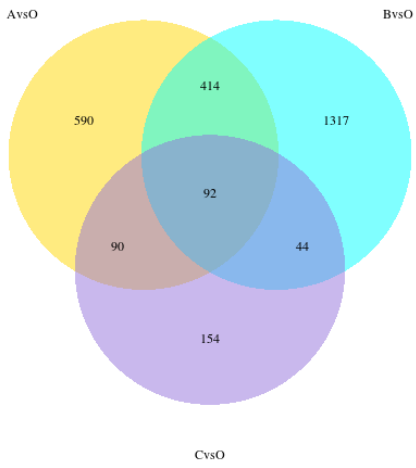


Figure S5. Venn diagram showing a number of genes significantly up- or downregulated greater than 1.5 fold ($p < 0.05$) following treatment with compounds **1**, **3**, and **4**. The yellow circle represents the number of influenced genes by elsamicin A relative to blank control, the light blue circle means the number of influenced genes of ES-2 cells induced by elsamicin B, and the lavender circle means the number of influenced genes of ES-2 cells induced by chartreusin.

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