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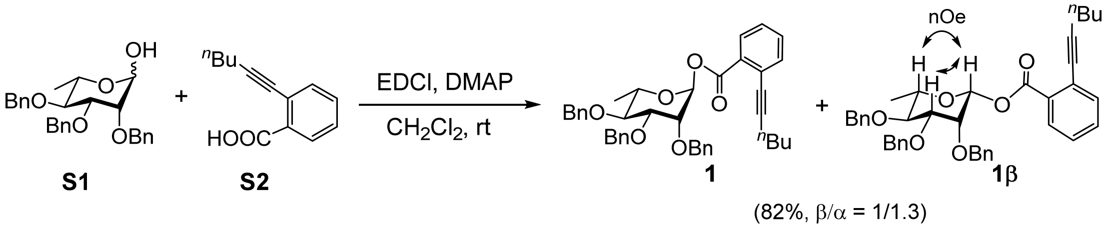
1. General Considerations

Commercial reagents were used without further purification unless specialized. Crushed 4Å or 5Å molecular sieves were activated through flame-drying under high vacuum immediately prior to use. Dry dichloromethane, diethyl ether, and chlorobenzene were obtained by mixing with 4Å molecular sieves for 2 days. Thin layer chromatography (TLC) was performed on precoated plates of Silica Gel HF254 (0.2 mm, Yantai, China). The TLC plates were visualized with UV light and/or by staining with ethanol/sulfuric acid (10%, v/v). Flash column chromatography was performed on Silica Gel H (10–40 μ, Yantai, China). ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Agilent 500 MHz or 600 MHz NMR spectrometer at 25 °C unless specialized. ^{1}H and ^{13}C NMR signals were calibrated to the residual proton and carbon resonance of the solvent ($CDCl_3$: $\delta_H = 0$ ppm (relative to tetramethylsilane); $\delta_C = 77.16$ ppm; CD_2Cl_2: $\delta_H = 5.3$ ppm, $\delta_C = 53.52$ ppm). High-resolution mass spectra were recorded with IonSpec 4.7 Tesla FTMS or APEXIII 7.0 TESLA FTMS. Optical rotations were measured on a Perkin–Elmer Model 241 MC polarimeter.

2. Preparation of Rhamnopyranosyl *ortho*-Hexynylbenzoates 1-5

2.1. 2,3,4-Tri-*O*-benzyl-L-rhamnopyranosyl *ortho*-hexynylbenzoate (1 and 1β)

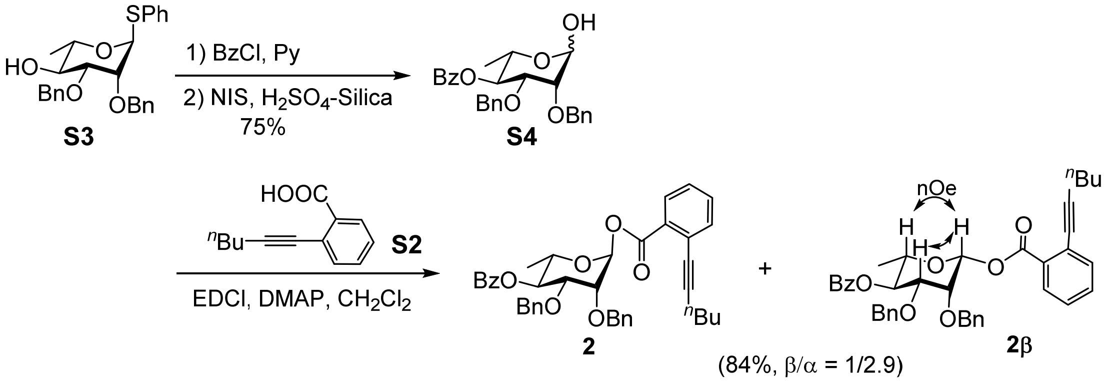


A solution of 2,3,4-tri-*O*-benzyl-L-rhamnopyranose (**S1**) (936 mg, 2.15 mmol), *ortho*-hexynylbenzoic acid (**S2**) (521 g, 2.58 mmol), 4-dimethylaminopyridine (DMAP) (52 mg, 0.43 mmol), and 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCI) (493 mg, 2.58 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 3 h, and was then diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, respectively, and was then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 20:1) to provide **1** (630 mg, 47%) and **1β** (468 mg, 35%) as colorless oil.

1: $[\alpha]_D^{20}$ = -27.3 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.79 (dd, *J* = 4.2, 3.7 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.46–7.40 (m, 3H), 7.36–7.24 (m, 14H), 6.41 (d, *J* = 1.7 Hz, 1H), 4.98 (d, *J* = 10.7 Hz, 1H), 4.84 (d, *J* = 12.3 Hz, 1H), 4.77 (d, *J* = 12.3 Hz, 1H), 4.67 (d, *J* = 10.7 Hz, 1H), 4.57 (s, 2H), 3.97 (ddd, *J* = 15.8, 9.5, 4.6 Hz, 2H), 3.91–3.85 (m, 1H), 3.73 (t, *J* = 9.5 Hz, 1H), 2.43 (qt, *J* = 17.0, 7.2 Hz, 2H), 1.58–1.50 (m, 2H), 1.43–1.38 (m, 2H), 1.37 (d, *J* = 6.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 164.55, 138.60, 138.28, 138.01, 135.05, 132.16, 130.77, 130.75, 128.53, 128.48, 128.47, 128.18, 127.92, 127.81, 127.79, 127.29, 125.10, 97.04, 92.79, 80.02, 79.74, 79.31, 75.76, 74.03, 72.75, 72.19, 71.13, 30.89, 22.17, 19.69, 18.22, 13.81; HRMS (MALDI) calcd for $C_{40}H_{42}O_6Na$ $[M+Na]^+$ 641.2874, found 641.2870.

1β: $[\alpha]_D^{20}$ = 20.9 (*c* 2.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.96–7.90 (m, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.45 (td, *J* = 7.6, 1.3 Hz, 1H), 7.42–7.36 (m, 2H), 7.36–7.17 (m, 14H), 5.85 (s, 1H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.92 (d, *J* = 12.3 Hz, 1H), 4.88 (d, *J* = 12.3 Hz, 1H), 4.68 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.09 (d, *J* = 2.5 Hz, 1H), 3.70 (t, *J* = 9.1 Hz, 1H), 3.65 (dd, *J* = 9.3, 2.7 Hz, 1H), 3.55 (dq, *J* = 8.9, 6.1 Hz, 1H), 2.46 (t, *J* = 7.2 Hz, 2H), 1.66–1.57 (m, 2H), 1.49 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.40 (d, *J* = 6.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 163.98, 138.44, 138.43, 138.15, 134.60, 132.23, 130.74, 130.51, 128.56, 128.54, 128.54, 128.52, 128.31, 128.25, 128.22, 127.88, 127.85, 127.74, 127.70, 127.14, 125.66, 97.12, 93.84, 82.41, 79.84, 79.15, 75.60, 74.50, 74.35, 73.07, 72.19, 30.80, 22.22, 19.69, 18.06, 13.81; HRMS (MALDI) calcd for $C_{40}H_{42}O_6Na$ $[M+Na]^+$ 641.2874, found 641.2874.

2.2. 2,3-Di-*O*-benzyl-4-*O*-benzoyl-L-rhamnopyranosyl *ortho*-hexynylbenzoate (2 and 2β)



To a solution of phenyl 2,3-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**S3**) (700 mg, 1.6 mmol) in pyridine (10 mL) was added BzCl (0.37 mL, 3.2 mmol) at 0 °C. The solution was stirred at 0 °C for 10 min and then at room temperature for further 5 h. The mixture was quenched with EtOH, and was then washed with H_2O and then extracted with EtOAc. The combined organic layer, being washed with a saturated solution of $CuSO_4$, aqueous HCl (0.5 M) and brine, respectively, was dried over Na_2SO_4, and concentrated in vacuum. The residue was used directly for the next step without purification.

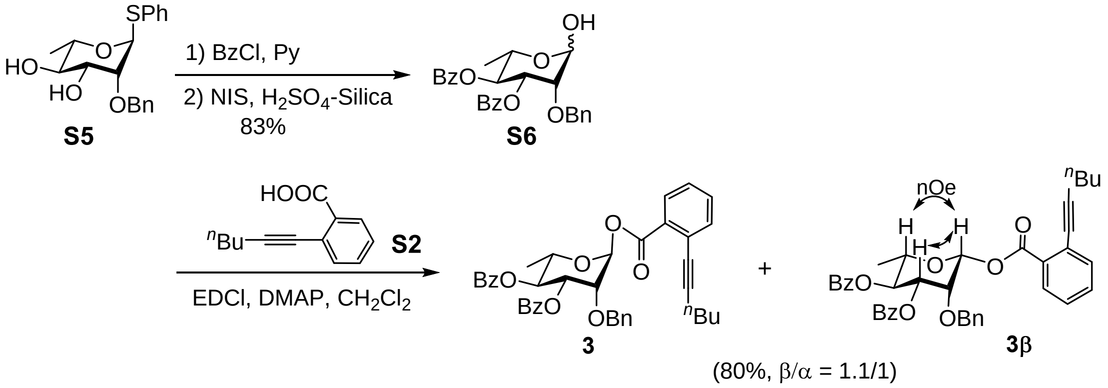
To a stirred mixture of the residue in CH_2Cl_2/H_2O (10:1, 7 mL) was added NIS (432 mg, 1.92 mmol) followed by H_2SO_4-Silica (160 mg) at 0 °C. The mixture was allowed to stir at 0 °C for 2.5 h until TLC showed complete conversion of the starting materials. The mixture was diluted with CH_2Cl_2 and was washed successively with aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and brine. The organic layer was collected, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to provide 2,3-di-*O*-benzyl-4-benzoyl-L-rhamnopyranose (**S4**) (540 mg, α/β = 2.5, 75% for two steps) as a colorless oil: $[\alpha]_D^{20} = 19.8$ (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.17–6.91 (m, 21H), 5.50 (t, $J = 9.7$ Hz, 1H), 5.44 (t, $J = 9.6$ Hz, 0.4H), 5.25 (d, $J = 1.4$ Hz, 1H), 5.13 (d, $J = 11.6$ Hz, 0.4H), 4.83 (d, $J = 12.4$ Hz, 1H), 4.73 (d, $J= 12.3$ Hz, 1.4H), 4.70–4.62 (m, 1H), 4.56 (d, $J = 12.3$ Hz, 1.4H), 4.45 (d, $J = 12.2$ Hz, 1H), 4.11 (dq, $J = 9.6, 6.3$ Hz, 1H), 3.99 (dd, $J = 9.6, 3.0$ Hz, 1H), 3.92 (dd, $J = 2.9, 1.4$ Hz, 0.4H), 3.87 (t, $J = 2.5$ Hz, 1H), 3.68 (dd, $J = 9.8, 2.8$ Hz, 0.4H), 3.56 (dq, $J = 9.5, 6.2$ Hz, 0.4H), 3.03 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.83, 165.80, 138.32, 138.12, 137.88, 137.54, 133.34, 133.14, 130.23, 129.98, 129.90, 129.89, 128.78, 128.57, 128.48, 128.34, 128.28, 128.16, 128.01, 127.93, 127.80, 127.78, 127.77, 127.63, 93.60, 93.36, 79.95, 76.67, 75.87, 75.05, 74.56, 73.79, 73.23, 73.17, 72.43, 71.92, 70.67, 67.25, 17.86, 17.72; HRMS (MALDI) calcd for $C_{37}H_{44}O_{10}$ $[M+Na]^+$ 471.1778, found 471.1776.

A solution of compound **S4** (820 mg, 1.83 mmol), *ortho*-hexynylbenzoic acid (**S2**) (555 mg, 2.75 mmol), 4-dimethylaminopyridine (DMAP) (45 mg, 0.37 mmol), and 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCl) (421 mg, 2.21 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 3 h, and was then diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, respectively, and was then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 20:1) to provide **2** (730 mg, 63%) and **2β** (240 mg, 21%) as colorless oil.

2: $[\alpha]_D^{20}$ = -15.7 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.05 (m, 19H), 6.44 (d, *J* = 2.0 Hz, 1H), 5.61 (t, *J* = 9.8 Hz, 1H), 4.83 (d, *J* = 1.9 Hz, 2H), 4.51 (d, *J* = 12.2 Hz, 1H), 4.37 (d, *J* = 12.2 Hz, 1H), 4.10 (dq, *J* = 9.9, 6.2 Hz, 1H), 4.02 (dd, *J* = 9.9, 3.1 Hz, 1H), 3.96 (dd, *J* = 3.1, 2.0 Hz, 1H), 2.54–2.31 (m, 2H), 1.66–1.53 (m, 2H), 1.53–1.38 (m, 2H), 1.29 (d, *J* = 6.2 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.74, 164.45, 137.87, 137.72, 135.01, 133.25, 132.23, 130.76, 130.63, 130.10, 129.88, 128.52, 128.49, 128.36, 128.19, 127.98, 127.91, 127.76, 127.37, 125.04, 96.73, 93.08, 79.77, 76.05, 73.54, 72.98, 72.96, 71.62, 70.16, 30.90, 22.20, 19.75, 17.86, 13.82; HRMS (MALDI) calcd for $C_{40}H_{40}O_7$ $[M+Na]^+$ 655.2666, found 655.2651.

2β: $[\alpha]_D^{20}$ = 63.8 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.04 (m, 20H), 5.92 (d, *J* = 1.1 Hz, 1H), 5.54 (t, *J* = 9.5 Hz, 1H), 4.91 (s, 2H), 4.55 (d, *J* = 12.4 Hz, 1H), 4.38 (d, *J* = 12.4 Hz, 1H), 4.12 (dd, *J* = 2.9, 1.1 Hz, 1H), 3.79–3.63 (m, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.67–1.56 (m, 2H), 1.54–1.42 (m, 2H), 1.33 (d, *J* = 6.2 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.71, 164.00, 138.18, 137.56, 134.64, 133.30, 132.36, 130.86, 130.32, 129.98, 129.94, 128.53, 128.45, 128.41, 128.33, 127.86, 127.84, 127.77, 127.21, 125.69, 97.19, 93.59, 79.15, 78.92, 74.40, 73.45, 73.01, 72.05, 71.59, 30.79, 22.22, 19.69, 17.78, 13.83; HRMS (MALDI) calcd for $C_{40}H_{40}O_7$ $[M+Na]^+$ 655.2666, found 655.2651.

2.3. 3,4-Di-*O*-benzoyl-2-*O*-benzyl-L-rhamnopyranosyl *ortho*-hexynylbenzoate (3 and 3β)



To a solution of phenyl 2-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**S5**) (268 mg, 0.774 mmol) in pyridine (5 mL) was added BzCl (0.37 mL, 3.2 mmol) at 0 °C. The solution was stirred at 0 °C for 10 min and then at room temperature for further 5 h. The mixture was quenched with EtOH, and was then washed with H_2O and then extracted with EtOAc. The combined organic layer, being washed with a saturated solution of $CuSO_4$, aqueous HCl (0.5 M), and brine, respectively, was dried over Na_2SO_4, and concentrated in vacuum. The residue was used directly for the next step without purification.

To a stirred mixture of the residue in CH_2Cl_2/H_2O (10:1, 3.5 mL) was added NIS (209 mg, 0.93 mmol) followed by H_2SO_4-Silica (77 mg) at 0 °C. The mixture was allowed to stir at 0 °C for 2.5 h until TLC showed complete conversion of the starting materials. The mixture was diluted with CH_2Cl_2 and was washed successively with aq $Na_2S_2O_3$, aq. $NaHCO_3$, and brine. The organic layer was collected, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to provide 3,4-di-*O*-benzoyl-2-*O*-benzyl-L-rhamnopyranose (**S6**) (297 mg, α/β = 4.0, 83% for two steps) as a colorless oil: $[\alpha]_D^{20} = 55.3$ (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04–7.11 (m, 18H), 5.76–5.53 (m, 2.2H), 5.39 (dd, J = 10.2, 3.0 Hz, 0.25H), 5.31

(d, *J* = 1.8 Hz, 1H), 4.93 (d, *J* = 11.4 Hz, 0.5H), 4.67 (d, *J* = 2.8 Hz, 2H), 4.56 (d, *J* = 11.5 Hz, 0.26H), 4.39–4.26 (m, 1H), 4.16 (dd, *J* = 3.0, 1.4 Hz, 0.25H), 4.10 (t, *J* = 2.3 Hz, 1H), 3.76 (dt, *J* = 9.6, 6.2 Hz, 0.5H), 1.35 (d, *J* = 6.2 Hz, 0.75H), 1.32 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.99, 165.89, 137.72, 137.27, 133.64, 133.41, 133.25, 129.96, 129.94, 129.82, 129.78, 129.72, 129.63, 129.49, 129.06, 128.82, 128.68, 128.55, 128.49, 128.42, 128.01, 127.90, 110.12, 93.47, 93.11, 75.97, 75.75, 74.79, 73.49, 72.09, 72.07, 71.38, 70.65, 67.02, 17.86, 17.75; HRMS (MALDI) calcd for $C_{27}H_{26}O_7$ $[M+Na]^+$ 485.1571, found 485.1568.

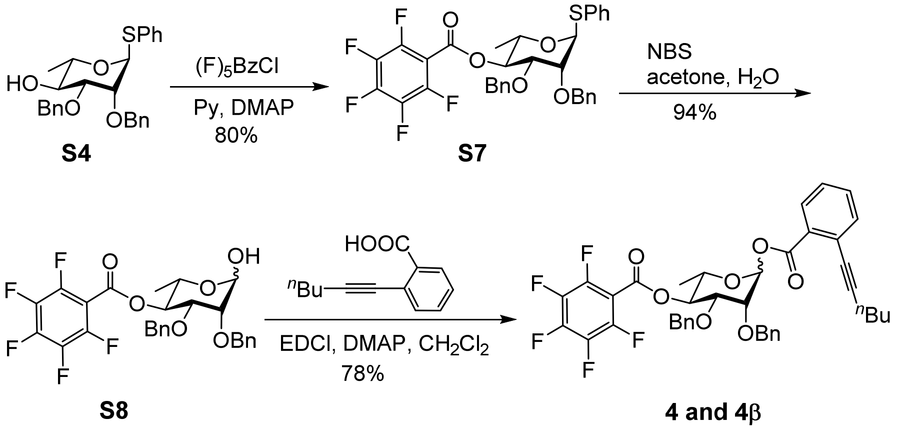
A solution of compound **S6** (294 mg, 0.64 mmol), *ortho*-hexynylbenzoic acid (**S2**) (154 mg, 0.76 mmol), 4-dimethylaminopyridine (DMAP) (16 mg, 0.13 mmol), and 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCl) (146 mg, 0.76 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 3 h, and was then diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, respectively, and was then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 20:1) to provide **3** (161 mg, 40%) and **3β** (169 mg, 40%) as colorless oil.

3: $[\alpha]_D^{20}$ = -1.3 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10–7.06 (m, 19H), 6.53 (d, *J* = 1.9 Hz, 1H), 5.80 (t, *J* = 10.0 Hz, 1H), 5.72 (dd, *J* = 10.3, 3.3 Hz, 1H), 4.82 (d, *J* = 12.2 Hz, 1H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.33 (dq, *J* = 9.7, 6.2 Hz, 1H), 4.21 (dd, *J* = 3.4, 1.9 Hz, 1H), 2.53 (td, *J* = 7.2, 1.2 Hz, 2H), 1.64 (dq, *J* = 8.7, 7.2 Hz, 2H), 1.55–1.44 (m, 2H), 1.37 (d, *J* = 6.2 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.89, 165.79, 164.56, 137.35, 135.11, 133.36, 132.35, 130.86, 130.57, 129.95, 129.80, 129.62, 129.48, 128.52, 128.48, 128.05, 127.97, 127.47, 125.28, 97.01, 92.47, 79.79, 74.91, 73.30, 71.82, 71.50, 69.86, 30.91, 22.25, 19.79, 17.89, 13.81; HRMS (MALDI) calcd for $C_{40}H_{38}O_8$ $[M+Na]^+$ 669.2459, found 669.2452.

3β: $[\alpha]_D^{20}$ = 52.8 (*c* 2.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–7.01 (m, 16H), 6.18 (s, 1H), 5.76 (t, *J* = 9.8 Hz, 1H), 5.40 (dd, *J* = 10.2, 3.0 Hz, 1H), 4.90 (d, *J* = 12.1

Hz, 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.38 (d, *J* = 3.3 Hz, 1H), 3.96 (dq, *J* = 12.1, 6.2 Hz, 1H), 2.51 (t, *J* = 7.1 Hz, 2H), 1.66 (q, *J* = 7.4 Hz, 2H), 1.59–1.47 (m, 2H), 1.43 (d, *J* = 6.4 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.84, 165.74, 163.88, 137.65, 134.56, 133.41, 133.39, 132.33, 130.65, 130.48, 130.00, 129.81, 129.50, 129.24, 128.53, 128.49, 128.29, 128.25, 127.78, 127.19, 125.72, 97.32, 93.19, 79.02, 75.21, 75.13, 73.97, 71.91, 71.34, 30.80, 22.24, 19.71, 17.76, 13.82; HRMS (MALDI) calcd for $C_{40}H_{38}O_8$ $[M+Na]^+$ 669.2459, found 669.2458.

2.4. 2,3-Di-*O*-benzyl-4-*O*-pentafluorobenzoyl-L-rhamnopyranosyl *ortho*-hexynylbenzoate (4 and 4β)



To a solution of phenyl 2,3-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**S4**) (325 mg, 0.75 mmol) in pyridine (5 mL) were added 4-dimethylaminopyridine (DMAP) (12 mg, 0.07 mmol) and pentafluorobenzoyl chloride (0.12 mL, 0.9 mmol) at 0 °C. The solution was stirred at 0 °C for 10 min and then at room temperature overnight. The mixture was quenched with EtOH, and was then washed with H_2O and then extracted with EtOAc. The combined organic layer, being washed with a saturated solution of $CuSO_4$ and brine, respectively, was dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 18:1) to afford phenyl 2,3-di-*O*-benzyl-4-*O*-pentafluorobenzoyl-1-thio-α-L-rhamnopyranoside (**S7**) (376 mg, 80%) as a colorless oil: $[\alpha]_D^{20}$ = -85.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.38 (m, 2H), 7.37–7.26 (m, 13H), 5.64–5.48 (m, 2H), 4.78–4.63 (m, 2H), 4.52 (q, *J* = 11.9 Hz, 2H), 4.32 (dq, *J* = 12.5, 6.2 Hz, 1H), 4.03 (s, 1H), 3.87 (dd, *J* = 9.7, 2.9 Hz, 1H), 1.34 (d, *J* = 6.2 Hz, 3H); ^{13}C

NMR (126 MHz, $CDCl_3$) δ 137.77, 137.75, 134.24, 131.36, 129.28, 128.55, 128.45, 128.11, 127.96, 127.85, 127.75, 127.65, 85.97, 76.02, 75.66, 72.52, 72.00, 67.79, 17.61; HRMS (ESI) calcd for $C_{33}H_{37}F_5O_5S$ $[M+Na]^+$ 653.1397, found 653.1398.

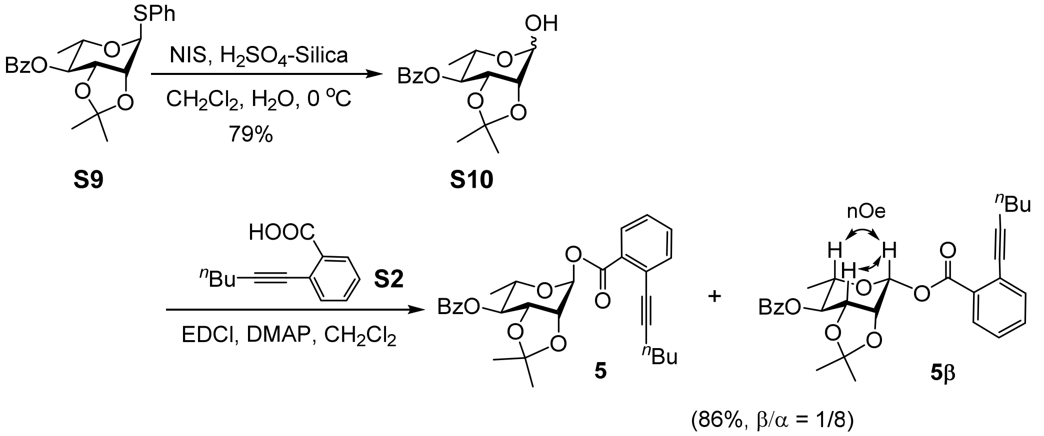
A solution of compound **S7** (355 mg, 0.563 mmol) in acetone (4.5 mL) and H_2O (0.5 mL) was added NBS (300 mg, 1.69 mmol). The mixture was stirred at room temperature for 3 h, and was then quenched with a saturated solution of $Na_2S_2O_3$. The mixture was extracted with EtOAc. The combined organic layer was washed with H_2O and brine, respectively, and was then dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether /EtOAc, 4:1) to afford 2,3-di-*O*-benzoyl-4-*O*-pentafluorobenzoyl-L-rhamnopyranose (**S8**) (284 mg, α/β = 11.2:1, 94%) as a colorless oil: HRMS (ESI) calcd for $C_{27}H_{23}F_5O_6$ $[M+Na]^+$ 561.1313, found 561.1309.

A solution of compound **S8** (264 mg, 0.5 mmol), *ortho*-hexynylbenzoic acid (**S2**) (120 mg, 0.6 mmol), 4-dimethylaminopyridine (DMAP) (12 mg, 0.1 mmol), and 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCl) (141 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 3 h, and was then diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, respectively, and was then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 20:1) to provide **4** (140 mg, 39%) and **4β** (140 mg, 39%) as colorless oil.

4: $[\alpha]_D^{20}$ = -13.8 (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.44–7.39 (m, 2H), 7.37–7.27 (m, 4H), 7.23 (s, 5H), 6.45 (d, *J* = 1.9 Hz, 1H), 5.62 (t, *J* = 9.9 Hz, 1H), 4.85–4.75 (m, 2H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.13 (dq, *J* = 10.0, 6.2 Hz, 1H), 4.03 (dd, *J* = 9.9, 3.1 Hz, 1H), 3.96–3.90 (m, 1H), 2.47–2.30 (m, 2H), 1.62–1.53 (m, 2H), 1.48–1.38 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.42, 158.07, 137.69, 137.64, 135.14, 132.32, 130.71, 130.56, 128.55, 128.39, 128.17, 128.00, 127.84, 127.68, 127.42, 125.02, 96.78, 92.78, 79.89, 76.36, 75.10, 73.40, 72.96, 71.75, 69.52, 30.89, 22.18, 19.64, 17.75, 13.72; HRMS (MALDI) calcd for $C_{40}H_{36}O_7F_5$ $[M+H]^+$ 723.2376, found 723.2360.

4β: $[\alpha]_D^{20} = 40.9$ (*c* 1.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.56 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.48 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.34–7.24 (m, 6H), 7.21 (dd, *J* = 5.0, 1.8 Hz, 3H), 5.92 (d, *J* = 0.7 Hz, 1H), 5.55 (t, *J* = 9.6 Hz, 1H), 4.94–4.85 (m, 2H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.13 (d, *J* = 2.2 Hz, 1H), 3.79–3.67 (m, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 1.68–1.60 (m, 2H), 1.56–1.45 (m, 2H), 1.40 (d, *J* = 6.2 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.95, 158.19, 138.04, 137.55, 134.64, 132.40, 130.80, 130.27, 128.45, 128.34, 128.29, 127.88, 127.79, 127.53, 127.21, 125.73, 97.25, 93.51, 79.59, 79.10, 75.04, 74.47, 73.53, 71.96, 71.47, 30.79, 22.22, 19.68, 17.67, 13.80; HRMS (MALDI) calcd for $C_{40}H_{36}O_7F_5$ $[M+H]^+$ 723.2376, found 723.2362.

2.5. 4-*O*-Benzoyl-2,3-*O*-isopropylidene-L-rhamnopyranosyl *ortho*-hexynylbenzoate (5 and 5β)



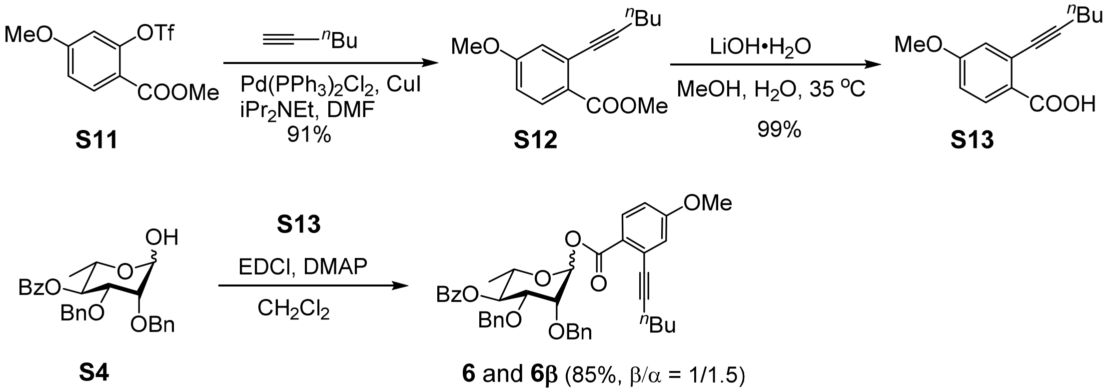
To a stirred mixture of compound **S9** (860 mg, 2 mmol) in CH_2Cl_2/H_2O (10:1, 10 mL) was added NIS (540 mg, 2.4 mmol) followed by H_2SO_4-Silica (200 mg) at 0 °C. The mixture was allowed to stir at 0 °C for 2.0 h until TLC showed complete conversion of the starting materials. The mixture was diluted with CH_2Cl_2 and was washed successively with aq $Na_2S_2O_3$, aq. $NaHCO_3$, and brine. The organic layer was collected, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc/CH_2Cl_2, 5:1:1) to provide 4-*O*-benzoyl-2,3-*O*-isopropylidene-L-rhamnopyranose (**S10**) (484 mg, 79% for two steps) as a white solid.

A solution of compound **S10** (460 mg, 1.5 mmol), *ortho*-hexynylbenzoic acid (**S2**) (362 mg, 1.8 mmol), 4-dimethylaminopyridine (DMAP) (37 mg, 0.3 mmol), and 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCl) (362 mg, 1.5 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 3 h, and was then diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, respectively, and was then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 20:1) to provide **5** (564 mg, 77%) and **5β** (70 mg, 9%) as colorless oil.

5: $[\alpha]_D^{20}$ = 6.2 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–7.29 (m, 9H), 6.63 (s, 1H), 5.23 (dd, *J* = 10.0, 7.9 Hz, 1H), 4.44 (dd, *J* = 7.9, 5.3 Hz, 1H), 4.38–4.31 (m, 1H), 4.13 (dq, *J* = 10.1, 6.3 Hz, 1H), 2.51 (t, *J* = 7.1 Hz, 2H), 1.71–1.57 (m, 6H), 1.56–1.41 (m, 2H), 1.37 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.79, 164.44, 135.00, 133.42, 132.27, 130.84, 130.83, 129.91, 129.78, 128.53, 127.49, 124.82, 110.59, 96.36, 92.00, 79.89, 75.70, 75.37, 74.48, 67.49, 30.96, 27.82, 26.62, 22.27, 19.84, 17.36, 13.81; HRMS (MALDI) calcd for $C_{29}H_{32}O_7$ $[M+Na]^+$ 515.2040, found 515.2033.

5β: $[\alpha]_D^{20}$ = 21.4 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–7.32 (m, 9H), 6.34 (d, *J* = 2.1 Hz, 1H), 5.42 (dd, *J* = 9.2, 6.0 Hz, 1H), 4.53–4.42 (m, 2H), 3.87 (dq, *J* = 9.2, 6.2 Hz, 1H), 2.48 (t, *J* = 7.1 Hz, 2H), 1.67–1.60 (m, 2H), 1.58 (s, 3H), 1.53–1.43 (m, 2H), 1.36 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.33, 163.72, 134.36, 133.18, 132.01, 130.65, 130.08, 129.63, 129.36, 128.28, 127.05, 125.39, 111.18, 96.80, 90.99, 78.88, 76.62, 73.88, 73.18, 71.13, 30.52, 26.92, 25.66, 21.91, 19.41, 18.26, 13.51; HRMS (MALDI) calcd for $C_{29}H_{32}O_7$ $[M+Na]^+$ 515.2040, found 515.2053.

2.6. 2,3-Di-*O*-benzyl-4-*O*-benzoyl-L-rhamnopyranosyl *2*-hexynyl-4-methoxybenzoate (6 and 6β)



To a degassed solution of $Pd(PPh_3)_2Cl_2$ (424 mg, 0.6 mmol), CuI (118 mg, 0.6 mmol), compound **S11** (1.8 g, 6 mmol), and *N*,*N*-diisopropylethylamine (3.5 mL) in DMF (25 mL) was added *n*-hexyne (1.24 mL, 10.5 mmol) introduced via a gastight syringe. After 24 h at room temperature, the reaction mixture was poured into a flask containing a saturated NH_4Cl solution (60 mL) and pentane (60 mL). After filtration, the organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (petroleum ether/EtOAc, 30:1) to afford methyl 4-methoxyl-2-(1-hexynyl)benzoate (**S12**) (1.35 g, 91%) as a light yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 1H), 6.99 (d, J = 2.6 Hz, 1H), 6.81 (dd, J = 8.8, 2.6 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.48 (t, J = 7.1 Hz, 2H), 1.69–1.56 (m, 2H), 1.56–1.42 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.53, 162.00, 132.49, 126.68, 118.82, 113.69, 96.08, 79.50, 55.52, 51.85, 30.85, 22.16, 19.60, 13.75; HRMS (ESI) calcd for $C_{15}H_{18}O_3$ $[M+H]^+$ 247.1329, found 247.1337.

To a flask containing LiOH monohydrate (856 mg) in methanol (80 mL) and H_2O (40 mL) was added a solution of **S12** (1.1 g, 4.5 mmol) in methanol (40 mL). The resulting mixture was heated at 35 °C for 48 h before it was allowed to cool to room temperature. Then, the flask was placed in an ice water bath. A dilute NH_4Cl solution at 0 °C was added until the pH of the solution became *ca*. 8. The solution was then treated dropwise diluted HCl (1.0 M) until the pH reached 4. At this point a white solid appeared, and was then diluted with CH_2Cl_2. The mixture was washed with H_2O

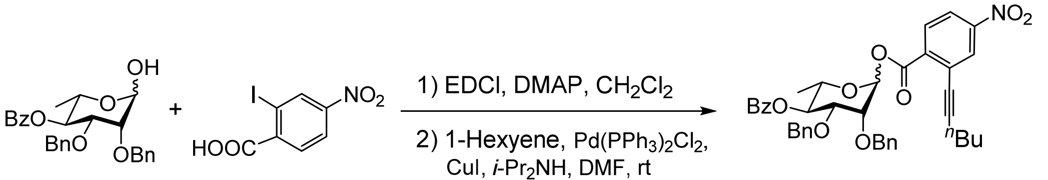
and brine, respectively, and was then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuum to provide 4-methoxy-2-(1-hexynyl)benzoic acid (**S13**) (975 mg, 93%) as a light yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 2.7 Hz, 1H), 6.88 (dd, J = 8.9, 2.7 Hz, 1H), 3.86 (s, 3H), 2.51 (t, J = 7.0 Hz, 2H), 1.74–1.61 (m, 2H), 1.58–1.46 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.18, 162.74, 133.64, 126.84, 123.10, 118.90, 114.03, 97.81, 79.31, 55.67, 30.64, 19.64; HRMS (ESI) calcd for $C_{14}H_{16}O_3$ $[M+H]^+$ 233.1177, found 233.1170.

A solution of rhamnopyranose **S4** (235 mg, 0.75 mmol), *ortho*-hexynylbenzoic acid (**S2**) (260 mg, 1.1 mmol), 4-dimethylaminopyridine (DMAP) (18 mg, 0.15 mmol), and 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCl) (157 mg, 0.9 mmol) in CH_2Cl_2 (6 mL) was stirred at room temperature for 3 h, and was then diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, respectively, and was then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 9:1) to provide **6** (198 mg, 34%) and **6β** (298 mg, 51%) as colorless oil.

6: $[\alpha]_D^{20}$ = -19.6 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.65–7.56 (m, 1H), 7.50–7.11 (m, 10H), 7.04 (d, J = 2.7 Hz, 1H), 6.87 (dd, J = 8.9, 2.6 Hz, 1H), 6.45 (d, J = 2.0 Hz, 1H), 5.62 (t, J = 9.9 Hz, 1H), 4.90–4.77 (m, 2H), 4.53 (d, J = 12.2 Hz, 1H), 4.39 (d, J = 12.2 Hz, 1H), 4.10 (dq, J = 9.9, 6.2 Hz, 1H), 4.03 (dd, J = 9.9, 3.1 Hz, 1H), 3.98–3.94 (m, 1H), 3.89 (s, 3H), 2.46 (qt, J = 17.0, 7.2 Hz, 2H), 1.67–1.58 (m, 2H), 1.54–1.42 (m, 2H), 1.30 (d, J = 6.2 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.76, 163.81, 162.53, 137.94, 137.77, 133.25, 132.91, 130.13, 129.90, 128.52, 128.50, 128.38, 128.19, 128.01, 127.89, 127.77, 127.29, 122.85, 119.40, 113.98, 96.80, 92.67, 79.89, 76.07, 73.55, 73.03, 72.91, 71.54, 70.07, 55.71, 30.91, 22.27, 19.80, 17.88, 13.85; HRMS (ESI) calcd for $C_{41}H_{43}O_8$ $[M+Na]^+$ 685.2774, found 685.2784.

6β: $[\alpha]_D^{20}$ = 62.9 (c 0.9, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.93 (m, 3H), 7.59 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.41 (dd, J = 6.6, 3.0 Hz, 2H), 7.25–7.12 (m, 8H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.80 (dd, *J* = 8.9, 2.7 Hz, 1H), 5.93 (d, *J* = 1.0 Hz, 1H), 5.55 (t, *J* = 9.5 Hz, 1H), 4.93 (s, 2H), 4.55 (d, *J* = 12.4 Hz, 1H), 4.38 (d, *J* = 12.4 Hz, 1H), 4.13 (d, *J* = 2.9 Hz, 1H), 3.85 (s, 3H), 3.77–3.68 (m, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.64 (dq, *J* = 8.6, 7.1 Hz, 2H), 1.56–1.44 (m, 2H), 1.34 (d, *J* = 6.2 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.73, 163.43, 162.67, 138.27, 137.63, 133.28, 133.16, 130.05, 129.96, 128.53, 128.45, 128.42, 128.41, 128.36, 128.35, 127.98, 127.85, 127.75, 122.50, 119.31, 113.60, 97.21, 93.41, 79.30, 78.99, 74.41, 73.59, 73.09, 72.04, 71.59, 55.67, 30.81, 22.28, 19.73, 17.80, 13.84; HRMS (ESI) calcd for $C_{41}H_{43}O_8$ $[M+Na]^+$ 685.2772, found 685.2784.

2.7. 2,3-Di-*O*-benzyl-4-*O*-benzoyl-L-rhamnopyranosyl 2-hexynyl-4-nitrobenzoate (7 and 7β)

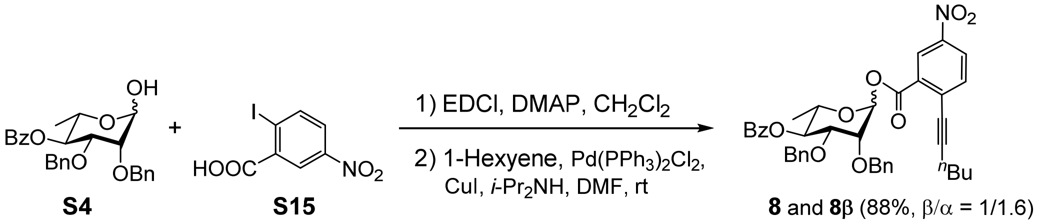


S4 **S14** **7** and **7β** (86%, β/α = 1/2.1)

A solution of 2,3-di-*O*-benzyl-4-*O*-benzoyl-L-rhamnopyranose (**S4**) (2.0 g, 4.5 mmol), 2-iodo-4-nitrobenzoic acid (**S14**) (1.57 g, 5.4 mmol), 4-dimethylaminopyridine (DMAP) (0.8 g, 6.7 mmol), and 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCl) (1.7 g, 8.9 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 6 h, and was then diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, respectively, and was then dried over Na_2SO_4. After filtration, the mixture was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 10:1) to provide a pale yellow foam (3.1 g, 96 %).

To a degassed solution of the foam (3.1 g, 4.3 mmol), $Pd(PPh_3)_2Cl_2$ (302 mg, 0.43 mmol), CuI (82 mg, 0.43 mmol), and *N*,*N*-diisopropylethylamine (2.0 mL) in DMF (80 mL) was added *n*-hexyne (0.88 mL, 7.7 mmol) introduced via a gastight syringe. After 24 h at room temperature, the reaction mixture was poured into a flask containing a saturated NH_4Cl solution (100 mL) and CH_2Cl_2 (100mL). After filtration, the organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (petroleum ether/EtOAc, 20:1) to afford **7** (1.7 g, 58%) and **7β** (0.8 g, 28%) as light yellow liquid. **7**: $[\alpha]_D^{20}$ = -26.8 (*c* 1.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.48–7.06 (m, 19H), 6.46 (d, *J* = 1.7 Hz, 1H), 5.64 (t, *J* = 9.6 Hz, 1H), 4.86 (s, 2H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 4.10 (dd, *J* = 9.7, 6.2 Hz, 1H), 4.03–3.93 (m, 2H), 2.57–2.36 (m, 2H), 1.63 (dd, *J* = 15.0, 7.3 Hz, 2H), 1.48 (dd, *J* = 15.0, 7.4 Hz, 2H), 1.33 (d, *J* = 6.2 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.66, 163.14, 149.63, 137.71, 137.64, 136.17, 133.35, 131.63, 129.98, 129.85, 129.38, 128.56, 128.53, 128.40, 128.19, 128.01, 127.97, 127.87, 126.57, 121.73, 100.17, 94.00, 78.07, 75.82, 73.44, 73.09, 72.84, 71.71, 70.47, 30.59, 22.21, 19.72, 17.87, 13.76; HRMS (ESI) calcd for $C_{40}H_{39}N_1O_9$ $[M+Na]^+$ 700.2517, found 700.2506. **7β**: $[\alpha]_D^{20}$ = 56.1 (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.2 Hz, 1H), 8.03 (dd, *J* = 9.3, 1.6 Hz, 3H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.66–7.57 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.43–7.34 (m, 2H), 7.25–7.14 (m, 8H), 5.95 (d, *J* = 1.0 Hz, 1H), 5.57 (t, *J* = 9.2 Hz, 1H), 4.90 (d, *J* = 12.3 Hz, 2H), 4.56 (d, *J* = 12.2 Hz, 2H), 4.15 (dd, *J* = 2.6, 0.9 Hz, 1H), 3.82–3.72 (m, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 1.72–1.58 (m, 2H), 1.56–1.45 (m, 2H), 1.37 (d, *J* = 6.3 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.65, 162.68, 149.68, 138.06, 137.50, 135.78, 133.37, 131.84, 129.92, 129.89, 128.94, 128.56, 128.51, 128.40, 128.37, 127.97, 127.90, 127.87, 127.25, 121.52, 100.71, 93.83, 78.80, 74.41, 73.50, 72.89, 72.17, 72.02, 30.44, 22.20, 19.68, 17.88, 14.32, 13.76; HRMS (ESI) calcd for $C_{40}H_{39}NO_9$ $[M+Na]^+$ 700.2523, found 700.2523.

2.8. 2,3-Di-*O*-benzyl-4-*O*-benzoyl-L-rhamnopyranosyl 2-hexynyl-5-nitrobenzoate (8 and 8β)



S4 **S15** **8** and **8β** (88%, β/α = 1/1.6)

A solution of rhamnopyranose **S4** (2.0 g, 4.5 mmol), 2-iodo-5-nitrobenzoic acid (**S15**) (1.57 g, 5.4 mmol), 4-dimethylaminopyridine (DMAP) (0.8 g, 6.7 mmol), and 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDCl) (1.7 g, 8.9 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 6 h, and was then diluted with CH_2Cl_2. The mixture was washed with saturated $NaHCO_3$ solution, H_2O, and brine, respectively, and was then dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 10:1) to provide a pale yellow foam (3.0 g, 93%).

To a degassed solution of the foam (2.2 g, 3.1 mmol), $Pd(PPh_3)_2Cl_2$ (218 mg, 0.31 mmol), CuI (117 mg, 0.61 mmol), and *N*,*N*-diisopropylethylamine (1.5 mL) in DMF (80 mL) was added *n*-hexyne (0.6 mL, 5.5 mmol) introduced via a gastight syringe. After 24 h at room temperature, the reaction mixture was poured into a flask containing a saturated NH_4Cl solution (100 mL) and CH_2Cl_2 (100 mL). After filtration, the organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (petroleum ether/EtOAc, 20:1) to afford **8** (1.2 g, 54%) and **8β** (0.7 g, 34%) as light yellow liquid.

8: $[\alpha]_D^{20}$ = -19.2 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77–6.92 (m, 21H), 6.44 (d, *J* = 1.9 Hz, 1H), 5.63 (s, 1H), 4.85 (d, *J* = 3.2 Hz, 2H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 12.2 Hz, 1H), 4.16–4.05 (m, 1H), 4.04–3.98 (m, 1H), 3.95 (d, *J* = 2.4 Hz, 1H), 2.49 (d, *J* = 13.4 Hz, 2H), 1.69–1.57 (m, 2H), 1.48 (d, *J* = 7.5 Hz, 2H), 1.32 (d, *J* = 6.2 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.71, 162.58, 146.15, 137.77, 137.62, 135.94, 133.33, 132.10, 131.56, 129.99, 129.92, 128.58, 128.55, 128.46, 128.21, 128.07, 128.02, 127.90, 126.39, 125.74, 103.87, 94.08, 78.88, 76.06, 73.59, 73.17, 72.84, 72.00, 70.48, 30.54, 22.23, 19.99, 17.93, 13.77; HRMS (ESI) calcd for $C_{40}H_{39}NO_9$ $[M+Na]^+$ 700.2517, found 700.2521.

8β: $[\alpha]_D^{20}$ = 33.4 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 2.4 Hz, 1H), 8.31 (dd, *J* = 8.6, 2.4 Hz, 1H), 8.11–7.96 (m, 2H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.64–7.57 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.45–7.40 (m, 2H), 7.25–7.09 (m, 9H), 5.93 (d, *J* = 1.0 Hz, 1H), 5.56 (t, *J* = 9.3 Hz, 1H), 4.97–4.87 (m, 2H), 4.55 (dd, *J* =

71.0, 12.3 Hz, 2H), 4.15 (d, *J* = 1.8 Hz, 1H), 3.76 (ddd, *J* = 9.7, 6.7, 3.0 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.70–1.60 (m, 2H), 1.54–1.43 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.67, 162.34, 146.03, 137.96, 137.54, 135.53, 133.37, 132.11, 131.74, 129.96, 128.58, 128.52, 128.42, 127.96, 127.91, 127.87, 126.56, 126.00, 104.42, 94.01, 78.85, 78.43, 74.53, 73.36, 72.96, 72.23, 71.89, 30.42, 22.25, 19.97, 17.87, 13.78; HRMS (ESI) calcd for $C_{40}H_{39}NO_9$ $[M+Na]^+$ 700.2523, found 700.2522.

3. Preparation of $AgBAr_4^F$

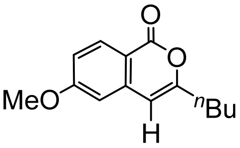
A 5 mL standard brown opening screw top vial was charged with $NaBAr_4^F$ (200 mg, 0.23 mmol), $AgNO_3$ (80 mg, 0.46 mmol), H_2O (1.0 mL), and Et_2O (1.0 mL). After stirring the mixture at room temperature for 30 min, the Et_2O layer was transferred to a 2.5 mL opening brown crew top vial using a syringe. Then, Et_2O was evaporated at room temperature to 0.5 mL to afford the solution of $AgBAr_4^F$ in Et_2O (0.45 M).

4. Typical procedure for the glycosylation with rhamnopyranosyl *ortho*-hexynylbenzoates using $Ph_3PAuCl/AgBAr_4^F$ as the catalyst

A mixture of the α-donor (~30 mg, 0.05 mmol), acceptor (0.1 mmol, 2.0 equiv), 5Å MS (100 mg), and Ph_3PAuCl (2.5 mg, 0.005 mmol) in PhCl (2 mL) was stirred for 30 min at the indicated temperature under argon atmosphere. A solution of $AgBAr_4^F$ in Et_2O (17 µL × 0.28 M, or 11 µL × 0.45 M, 0.005 mmol) was then added. Stirring was continued at the same temperature under argon atmosphere until the reaction was completed. Ph_3P (~6 mg) was added. The mixture was filtered through Celite. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to provide the coupled glycoside.

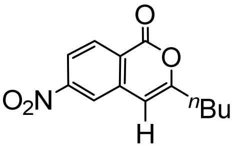
5. Characterization of the glycosylation products

Compound **6H**



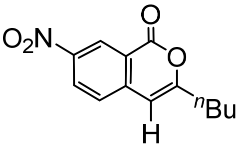
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.17 (d, J = 8.8 Hz, 1H), 6.98 (dd, J = 8.8, 2.5 Hz, 1H), 6.73 (d, J = 2.5 Hz, 1H), 6.19 (s, 1H), 3.90 (s, 3H), 2.51 (t, J = 7.6 Hz, 2H), 1.69 (p, J = 7.6 Hz, 2H), 1.44-1.37 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.79, 162.99, 159.08, 140.14, 131.85, 116.00, 113.43, 107.21, 103.04, 55.73, 33.41, 29.10, 22.26, 13.91; HRMS (EI) calcd for $C_{14}H_{16}O_3$ $[M]^+$ 232.1099, found 232.1099.

Compound **7H**



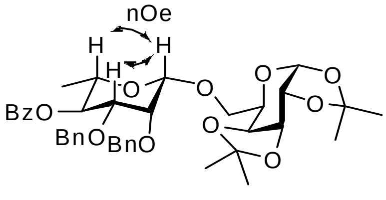
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.48–8.37 (m, 1H), 8.20 (dd, J = 7.5, 2.0 Hz, 2H), 6.38 (s, 1H), 2.60–2.54 (m, 2H), 1.71 (dt, J = 15.3, 7.6 Hz, 2H), 1.46–1.37 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 161.35, 161.09, 151.73, 138.82, 131.65, 124.19, 121.53, 120.32, 102.40, 33.43, 28.95, 22.24, 13.86; HRMS (EI) calcd for $C_{13}H_{13}NO_4$ $[M]^+$ 247.0845, found 247.0847.

Compound **8H**



^{1}H NMR (500 MHz, CDCl$_3$) δ 9.08 (d, J = 2.3 Hz, 1H), 8.47 (dd, J = 8.6, 2.4 Hz, 1H), 7.51 (d, J = 8.7 Hz, 2H), 6.37 (s, 1H), 2.70–2.53 (m, 2H), 1.72 (dt, J = 15.2, 7.6 Hz, 2H), 1.51–1.34 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.74, 161.24, 146.67, 129.05, 126.49, 125.82, 120.50, 102.35, 33.64, 28.93, 22.27, 13.86; HRMS (EI) calcd for $C_{13}H_{13}NO_4$ $[M]^+$ 247.0845, found 247.0845.

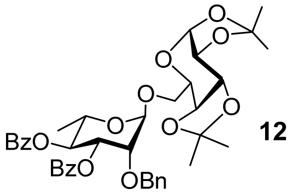
2,3-Di-*O*-benzyl-4-*O*-benzoyl-β-L-rhamnopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (11β)



11β

Compound **11β** was purified by silica gel column chromatography (petroleum ether/EtOAc, 7:1) as a colorless oil: $[\alpha]_D^{20}$ = 30.4 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04–6.99 (m, 9H), 5.51 (d, J = 5.0 Hz, 1H), 5.44 (t, J = 9.6 Hz, 1H), 4.92 (q, J = 12.6 Hz, 2H), 4.60 (dd, J = 8.0, 2.3 Hz, 1H), 4.49–4.40 (m, 2H), 4.31 (dd, J = 5.1, 2.3 Hz, 1H), 4.27–4.20 (m, 2H), 4.08 (ddd, J = 8.1, 5.7, 1.8 Hz, 1H), 4.00–3.86 (m, 2H), 3.73 (t, J= 9.0 Hz, 1H), 3.49 (ddd, J = 9.6, 6.9, 4.6 Hz, 2H), 1.55 (s, 3H), 1.45 (s, 3H), 1.33 (s, 4H), 1.33 (s, 3H), 1.28 (d, J= 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.68, 138.67, 137.78, 133.17, 130.15, 129.88, 128.69, 128.47, 128.33, 128.18, 127.70, 127.67, 127.54, 109.13, 108.70, 101.91, 96.39, 78.74, 73.98, 73.47, 73.21, 71.06, 70.98, 70.89, 70.69, 70.61, 67.95, 65.93, 26.29, 26.13, 25.06, 24.55, 17.73; HRMS (MALDI) calcd for $C_{39}H_{46}O_{11}$ $[M+Na]^+$ 713.2932, found 713.2938.

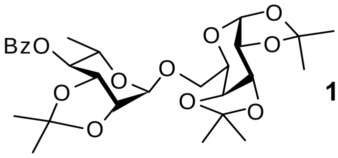
3,4-Di-*O*-benzoyl-2-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (12α)



12α

$[\alpha]_D^{20}$ = -14 (*c* 1.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08–6.97 (m, 13H), 5.65 (t, J = 9.9 Hz, 1H), 5.57–5.50 (m, 2H), 4.99 (d, J = 1.8 Hz, 1H), 4.73–4.51 (m, 3H), 4.33 (dt, J = 7.4, 2.1 Hz, 2H), 4.19 (dq, J = 9.8, 6.2 Hz, 1H), 4.09–3.99 (m, 2H), 3.91 (dd, J = 9.8, 6.8 Hz, 1H), 3.63 (dd, J = 9.8, 6.4 Hz, 1H), 1.56 (s, 3H), 1.44 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.29 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.76, 137.78, 133.20, 129.90, 129.75, 129.73, 129.65, 128.46, 128.44, 128.36, 127.95, 127.77, 109.29, 108.81, 97.91, 96.32, 75.73, 73.18, 72.34, 72.02, 70.99, 70.70, 66.83, 66.79, 65.51, 26.30, 26.11, 25.09, 24.54, 17.59; HRMS (ESI) calcd for $C_{39}H_{44}O_{12}$ $[M+Na]^+$ 727.2731, found 727.2724.

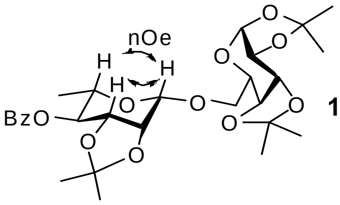
4-*O*-Benzoyl-2,3-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (13α)



13α

Compound **13α** was purified by silica gel column chromatography (petroleum ether/EtOAc, 7:1) as a colorless oil: $[\alpha]_D^{20}$ = -39.6 (*c* 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J*= 8.3, 1.4 Hz, 2H), 7.61–7.54 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 5.56 (d, *J* = 5.0 Hz, 1H), 5.18–5.04 (m, 2H), 4.64 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.41–4.21 (m, 4H), 4.01 (td, *J* = 6.4, 1.9 Hz, 1H), 3.97–1.90 (m, 2H), 3.67 (dd, *J* = 10.2, 6.7 Hz, 1H), 1.62 (s, 3H), 1.57 (s, 3H), 1.46 (s, 3H), 1.36 (d, *J* = 1.9 Hz, 9H), 1.22 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.87, 133.25, 130.04, 129.89, 128.48, 109.96, 109.50, 108.75, 97.25, 96.44, 76.09, 75.97, 75.29, 71.21, 70.79, 70.67, 66.69, 65.92, 64.33, 27.88, 26.55, 26.26, 26.13, 25.06, 24.65, 17.15; HRMS (MALDI) calcd for $C_{28}H_{38}O_{11}$ $[M+Na]^+$ 573.2306, found 573.2309.

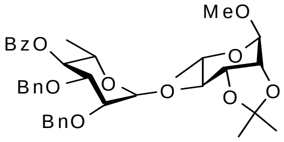
4-*O*-Benzoyl-2,3-*O*-isopropylidene-β-L-rhamnopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (13β)



13β

Compound **13β** was purified by silica gel column chromatography (petroleum ether/EtOAc, 7:1) as a colorless oil: $[\alpha]_D^{20}$ = 5.4 (*c* 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.61–7.54 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.52 (d, *J* = 5.0 Hz, 1H), 5.21 (dd, *J* = 9.5, 6.1 Hz, 1H), 4.90 (d, *J* = 1.6 Hz, 1H), 4.64 (dd, *J* = 8.0, 2.3 Hz, 1H), 4.40 (dd, *J* = 8.0, 1.8 Hz, 1H), 4.38–4.28 (m, 3H), 4.17–4.01 (m, 2H), 3.86 (dd, *J* = 10.0, 8.7 Hz, 1H), 3.61 (dq, *J* = 9.4, 6.2 Hz, 1H), 1.66 (s, 3H), 1.55 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.30 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) *δ* 165.71, 133.35, 129.90, 128.52, 111.36, 109.22, 108.73, 99.30, 96.42, 75.02, 74.64, 70.86, 70.70, 70.65, 70.45, 68.32, 65.66, 27.73, 26.48, 26.25, 26.18, 25.03, 24.68, 17.97; HRMS (MALDI) calcd for $C_{28}H_{38}O_{11}$ [M+Na]$^+$ 573.2306, found 573.2296.

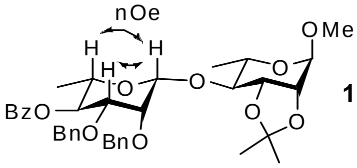
Methyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (14α)



14α

Compound **14α** was purified by silica gel column chromatography (petroleum ether/EtOAc, 7:1) as a colorless oil: $[\alpha]_D^{20}$ = -5.3 (*c* 0.5, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 8.04–7.08 (m, 10H), 5.50 (t, *J* = 9.7 Hz, 1H), 5.43 (d, *J* = 1.9 Hz, 1H), 4.87 (s, 1H), 4.84–4.75 (m, 2H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.39 (d, *J* = 12.2 Hz, 1H), 4.14–4.05 (m, 2H), 3.94–3.82 (m, 3H), 3.63 (dq, *J* = 9.8, 6.2 Hz, 1H), 3.49 (dd, *J* = 9.9, 6.8 Hz, 1H), 3.40 (s, 3H), 1.54 (s, 3H), 1.37 (s, 3H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) *δ* 165.78, 138.38, 138.16, 133.11, 130.31, 129.91, 128.47, 128.43, 128.29, 128.19, 127.73, 127.56, 109.66, 98.17, 97.72, 78.63, 78.56, 76.78, 76.20, 74.49, 73.68, 72.81, 71.61, 67.79, 64.11, 55.04, 28.12, 26.57, 18.03, 17.83; HRMS (MALDI) calcd for $C_{37}H_{44}O_{10}$ [M+Na]$^+$ 671.2827, found 671.2821.

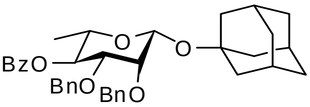
Methyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-β-L-rhamnopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (14β)



14β

Compound **14β** was purified by silica gel column chromatography (petroleum ether/EtOAc, 6:1) as a colorless oil: $[\alpha]_D^{20} = 42.3$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12–7.01 (m, 15H), 5.47 (t, *J* = 9.6 Hz, 1H), 4.98 (d, *J* = 12.6 Hz, 1H), 4.86 (d, *J* = 13.2 Hz, 2H), 4.64 (d, *J* = 0.9 Hz, 1H), 4.52–4.40 (m, 2H), 4.28 (d, *J* = 12.4 Hz, 1H), 4.13 (dd, *J* = 5.9, 0.8 Hz, 1H), 3.97 (dd, *J* = 2.9, 0.8 Hz, 1H), 3.75 (dq, *J* = 9.6, 6.3 Hz, 1H), 3.54 (ddd, *J* = 15.7, 9.6, 4.6 Hz, 2H), 3.46–3.34 (m, 4H), 1.52 (s, 3H), 1.34 (s, 3H), 1.31 (dd, *J* = 6.3, 5.3 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.73, 138.68, 137.91, 133.16, 130.26, 129.90, 128.55, 128.48, 128.25, 127.64, 127.57, 108.98, 101.34, 98.50, 82.96, 79.30, 76.75, 75.88, 74.01, 73.76, 73.61, 71.18, 71.10, 64.37, 55.03, 28.19, 26.28, 18.11, 17.73; HRMS (MALDI) calcd for $C_{37}H_{44}O_{10}$ $[M+Na]^+$ 671.2827, found 671.2815.

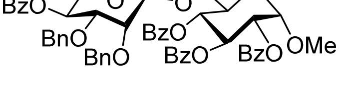
1-Adamantanyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-β-L-rhamnopyranoside (16β)



16β

Compound **16β** was purified by silica gel column chromatography (petroleum ether/EtOAc, 13:1) as a colorless oil: $[\alpha]_D^{20} = 59.4$ (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.02 (m, 15H), 5.42 (t, *J* = 9.6 Hz, 1H), 4.98 (q, *J* = 12.9 Hz, 2H), 4.70 (d, *J* = 1.0 Hz, 1H), 4.42 (d, *J* = 12.5 Hz, 1H), 4.19 (d, *J* = 12.5 Hz, 1H), 3.77 (d, *J* = 3.0 Hz, 1H), 3.56–3.44 (m, 2H), 2.15 (s, 3H), 1.92–1.74 (m, 6H), 1.68–1.56 (m, 6H), 1.27 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.71, 138.87, 137.95, 133.08, 130.29, 129.85, 128.76, 128.44, 128.27, 128.10, 127.60, 127.55, 127.41, 94.23, 79.23, 75.05, 74.44, 73.82, 73.69, 70.79, 70.48, 42.56, 36.40, 30.75, 18.08; HRMS (MALDI) calcd for $C_{37}H_{42}O_6$ $[M+Na]^+$ 605.2874, found 605.2876.

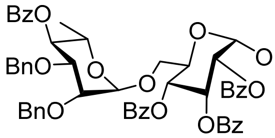
Methyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-β-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (17β)



17β

$[\alpha]_D^{20} = 118.6$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–7.98 (m, 6H), 7.96–7.90 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52 (q, *J* = 7.4 Hz, 2H), 7.49–7.35 (m, 10H), 7.31 (m, 6H), 7.17 (dt, *J* = 24.6, 7.2 Hz, 4H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.22 (t, *J* = 9.9 Hz, 1H), 5.68 (t, *J* = 9.8 Hz, 1H), 5.44 (t, *J* = 9.6 Hz, 1H), 5.29 (dd, *J* = 10.1, 3.6 Hz, 1H), 5.24 (d, *J* = 3.6 Hz, 1H), 4.87–4.68 (m, 2H), 4.51 (s, 1H), 4.41 (d, *J* = 12.5 Hz, 1H), 4.28 (dd, *J* = 9.8, 4.0 Hz, 1H), 4.25–4.18 (m, 2H), 3.85–3.78 (m, 2H), 3.54–3.46 (m, 5H), 1.28 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) *δ* 166.01, 165.93, 165.64, 165.34, 138.84, 137.84, 133.49, 133.19, 133.11, 130.19, 130.04, 129.95, 129.86, 129.77, 129.41, 129.34, 129.16, 129.13, 128.58, 128.53, 128.43, 128.39, 128.32, 128.29, 128.23, 128.17, 127.58, 127.38, 125.39, 101.77, 97.11, 78.76, 74.18, 73.76, 73.45, 72.29, 71.03, 70.73, 70.61, 70.53, 68.72, 68.67, 55.84, 17.67; HRMS (ESI) calcd for $C_{55}H_{52}O_{14}$ [M+NH$_4$]$^+$ 954.3701, found 954.3696.

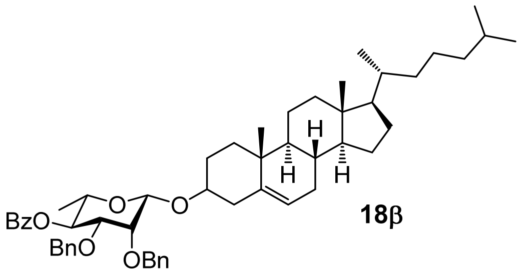
Methyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (17α)



17α

[α]$_D^{20}$ = 39.5 (*c* 0.5, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) *δ* 8.08–8.04 (m, 2H), 8.03–7.99 (m, 2H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.93–7.88 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.56–7.34 (m, 11H), 7.30 (m, 5H), 7.19 (m, 5H), 6.17 (t, *J* = 9.9 Hz, 1H), 5.61 (t, *J* = 9.9 Hz, 1H), 5.49 (t, *J* = 9.7 Hz, 1H), 5.29 (dd, *J* = 10.2, 3.6 Hz, 1H), 5.22 (d, *J* = 3.6 Hz, 1H), 4.79 (m, 3H), 4.49 (d, *J* = 12.2 Hz, 2H), 4.25–4.19 (m, 1H), 3.96 (d, *J* = 1.8 Hz, 1H), 3.94–3.85 (m, 3H), 3.62 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.40 (s, 3H), 1.19 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) *δ* 166.01, 165.94, 165.80, 165.36, 138.49, 138.20, 133.65, 133.54, 133.25, 133.11, 130.30, 130.07, 129.95, 129.91, 129.77, 129.38, 129.17, 129.04, 128.64, 128.57, 128.47, 128.42, 128.41, 128.31, 128.04, 127.85, 127.69, 127.61, 99.42, 97.14, 74.40, 73.58, 73.10, 72.18, 71.58, 70.61, 69.34, 69.00, 67.40, 66.28, 55.64, 17.70; HRMS (ESI) calcd for $C_{55}H_{52}O_{14}$ [M+NH$_4$]$^+$ 954.3701, found 954.3696.

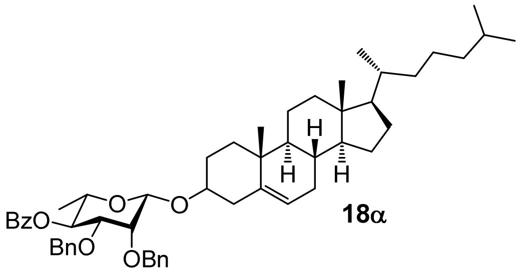
Cholestanyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-β-L-rhamnopyranoside (18β)



18β

$[\alpha]_D^{20}$ = 30.9 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.03–7.99 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.34–7.24 (m, 3H), 7.19–7.16 (m, 1H), 7.12 (t, *J* = 7.3 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 2H), 5.45 (t, *J* = 9.6 Hz, 1H), 5.37 (d, *J* = 5.2 Hz, 1H), 4.96 (d, *J* = 12.8 Hz, 2H), 4.55 (s, 1H), 4.45 (d, *J* = 12.5 Hz, 1H), 4.23 (d, *J* = 12.5 Hz, 1H), 3.89 (d, *J* = 2.9 Hz, 1H), 3.62–3.43 (m, 3H), 2.50 (dd, *J* = 13.5, 3.2 Hz, 1H), 2.41 (dd, *J* = 18.0, 6.8 Hz, 1H), 2.08–1.94 (m, 2H), 1.92–1.78 (m, 3H), 1.64–0.79 (m, 36H), 0.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 165.71, 140.94, 138.86, 137.95, 133.13, 130.31, 129.91, 128.71, 128.48, 128.33, 128.16, 127.69, 127.62, 127.48, 121.98, 99.37, 79.00, 78.60, 73.96, 73.88, 73.70, 70.92, 70.87, 56.95, 56.32, 50.34, 42.49, 40.32, 39.96, 39.67, 37.28, 36.89, 36.35, 35.93, 32.10, 32.05, 28.38, 28.25, 28.17, 24.44, 23.98, 22.97, 22.71, 21.25, 19.56, 18.89, 17.91, 12.03; HRMS (ESI) calcd for $C_{54}H_{72}O_6$ $[M+NH_4]^+$ 834.5673, found 834.5667.

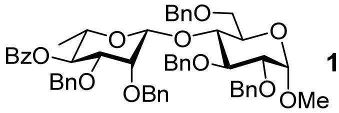
Cholestanyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-α-L-rhamnopyranoside (18α)



18α

$[\alpha]_D^{20}$ = -19.1 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.03 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.60–7.55 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.40–7.36 (m, 2H), 7.35–7.30 (m, 2H), 7.21–7.13 (m, 5H), 5.48 (t, *J* = 9.7 Hz, 1H), 5.36–5.32 (m, 1H), 4.95 (d, *J* = 1.7 Hz, 1H), 4.77 (d, *J* = 12.5 Hz, 2H), 4.52 (d, *J* = 12.1 Hz, 2H), 3.93 (dd, *J* = 9.7, 2.9 Hz, 2H), 3.80–3.77 (m, 1H), 3.45 (ddd, *J* = 15.8, 11.2, 4.5 Hz, 1H), 2.27–2.21 (m, 1H), 2.13 (t, *J* = 11.2 Hz, 1H), 2.00 (ddd, *J* = 19.4, 11.1, 6.8 Hz, 2H), 1.91–1.80 (m, 3H), 1.64–1.42 (m, 13H), 1.40–1.25 (m, 5H), 1.23 (d, J = 6.3 Hz, 3H), 1.20–1.04 (m, 8H), 1.03–0.97 (m, 5H), 0.96–0.90 (m, 4H), 0.87 (dd, J = 6.6, 2.3 Hz, 7H), 0.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.86, 140.53, 138.55, 138.37, 133.07, 130.40, 129.92, 128.48, 128.46, 128.31, 128.12, 127.75, 127.65, 127.52, 122.15, 96.90, 75.18, 74.03, 73.18, 71.95, 67.20, 56.88, 56.30, 50.29, 42.48, 39.92, 39.68, 38.63, 37.44, 36.90, 36.35, 35.95, 32.10, 32.06, 29.64, 28.39, 28.18, 24.46, 23.98, 22.98, 22.72, 21.22, 19.55, 18.88, 17.81, 12.02; HRMS (ESI) calcd for $C_{54}H_{72}O_6$ $[M+Na]^+$ 839.5227, found 839.5224.

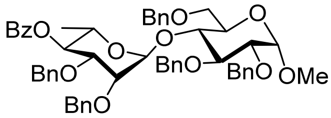
Methyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-β-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (19β)



19β

$[\alpha]_D^{20}$ = -23.2 (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.38–7.23 (m, 18H), 7.23–7.11 (m, 7H), 5.43 (t, J = 9.7 Hz, 1H), 5.06 (d, J = 1.5 Hz, 1H), 5.01 (d, J = 10.9 Hz, 1H), 4.77–4.38 (m, 11H), 4.08 (dq, J = 12.4, 6.1 Hz, 1H), 3.89–3.84 (m, 2H), 3.81 (t, J = 9.2 Hz, 1H), 3.77–3.74 (m, 1H), 3.68 (d, J = 9.4 Hz, 1H), 3.61–3.54 (m, 2H), 3.46 (dd, J = 11.2, 3.5 Hz, 1H), 3.39 (s, 3H), 0.95 (d, J = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.76, 138.77, 138.43, 138.14, 138.08, 137.96, 133.01, 130.31, 129.87, 128.59, 128.55, 128.48, 128.41, 128.35, 128.32, 128.31, 128.10, 128.04, 127.85, 127.83, 127.73, 127.70, 127.64, 127.57, 127.46, 98.33, 98.09, 80.39, 80.12, 75.46, 74.55, 74.47, 73.74, 73.65, 73.53, 72.85, 71.74, 70.25, 68.99, 67.77, 55.45, 29.84, 17.49; HRMS (ESI) calcd for $C_{55}H_{58}O_{11}$ $[M+NH_4]^+$ 912.4323, found 912.4319.

Methyl 2,3-di-*O*-benzyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (19α)



19α

$[\alpha]_D^{20}$ = 52.3 (c 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98–7.93 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 4H), 7.39–7.27 (m, 15H), 7.17 (dd, *J* = 15.5, 7.1 Hz, 4H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.3 Hz, 2H), 5.37 (t, *J* = 9.7 Hz, 1H), 4.99 (d, *J* = 11.6 Hz, 1H), 4.88–4.81 (m, 2H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.71–4.61 (m, 4H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.6 Hz, 1H), 4.26 (d, *J* = 12.2 Hz, 1H), 4.03 (d, *J* = 12.3 Hz, 1H), 3.94–3.84 (m, 2H), 3.83–3.68 (m, 4H), 3.56 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.46 (s, 3H), 3.39–3.32 (m, 1H), 3.21 (dd, *J* = 9.8, 2.8 Hz, 1H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.70, 139.03, 138.77, 138.69, 138.06, 137.89, 133.09, 130.21, 129.83, 128.62, 128.59, 128.57, 128.43, 128.32, 128.29, 128.26, 128.25, 128.11, 127.70, 127.59, 127.54, 127.46, 127.44, 102.46, 97.97, 82.10, 80.01, 79.64, 75.52, 73.85, 73.54, 73.47, 73.30, 73.23, 71.20, 70.86, 69.91, 69.04, 55.52, 17.67; HRMS (ESI) calcd for $C_{55}H_{58}O_{11}$ $[M+NH_4]^+$ 912.4323, found 912.4318.

6. NMR studies

6.1. Formation of 1-α-glycosyloxy-isochromenylium-4-gold(I) intermediate 6Cα

General procedure: A 5 mL standard opening screw top vial was charged with rhamnosyl *ortho*-hexynylbenzoate **6** (33 mg, 0.05 mmol) and heated at 60 °C for 5 min under high vacuum. The vial was allowed to cool to room temperature, and then filled with argon. After addition of CD_2Cl_2 (0.5 mL), the solution was transferred into an NMR tube which contained Ph_3PAuCl (25 mg, 0.05 mmol, 1.0 equiv). The mixture was then cooled down to -60 °C. A solution of $AgBAr_4^F$ in PhCl-*d5* (0.25 M, 100 μL × 2, 0.05 mmol) was added followed by vigorously shaking for 30 s at -60 °C. The ^1H, HSQC (50 min), as well as HMBC (20 min) and ^{13}C NMR (90 min) spectra were recorded successively at -42 °C or after warming up, using an Agilent 600 MHz NMR spectrometer.

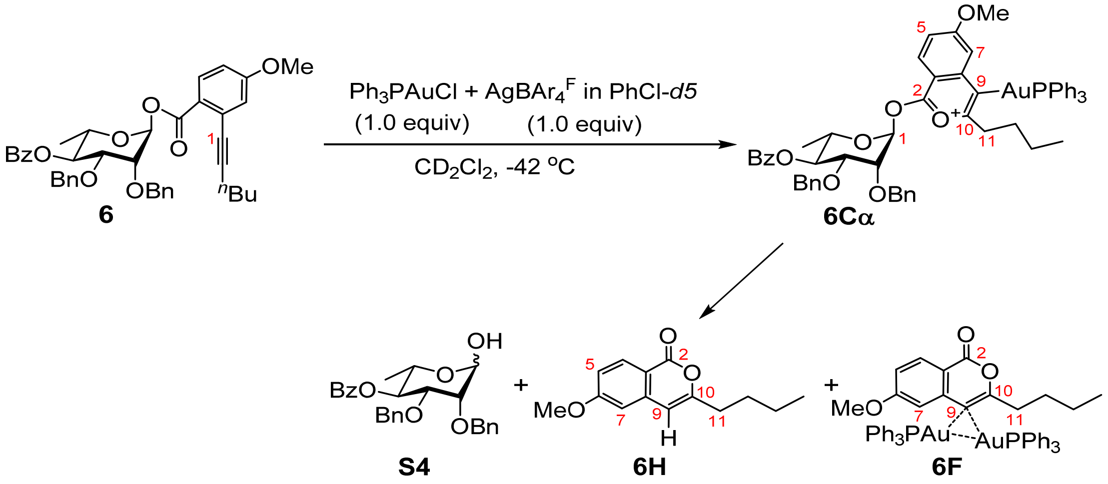


Figure S1. The ^1H NMR spectra after addition of $AgBAr_4^F$ (1.0 equiv) into a mixture of **6** and Ph_3PAuCl (1.0 equiv) in CD_2Cl_2 at -42 °C or after warming up to -32 °C. a: pure **6** at -42 °C; b: 2 min after addition of $AgBAr_4^F$ at -42 °C; c: 17 min after addition of $AgBAr_4^F$ at -42 °C; d: 22 min after addition of $AgBAr_4^F$ at -32 °C; e: 38 min after addition of $AgBAr_4^F$ at -32 °C; f: pure **6H** at 25 °C.

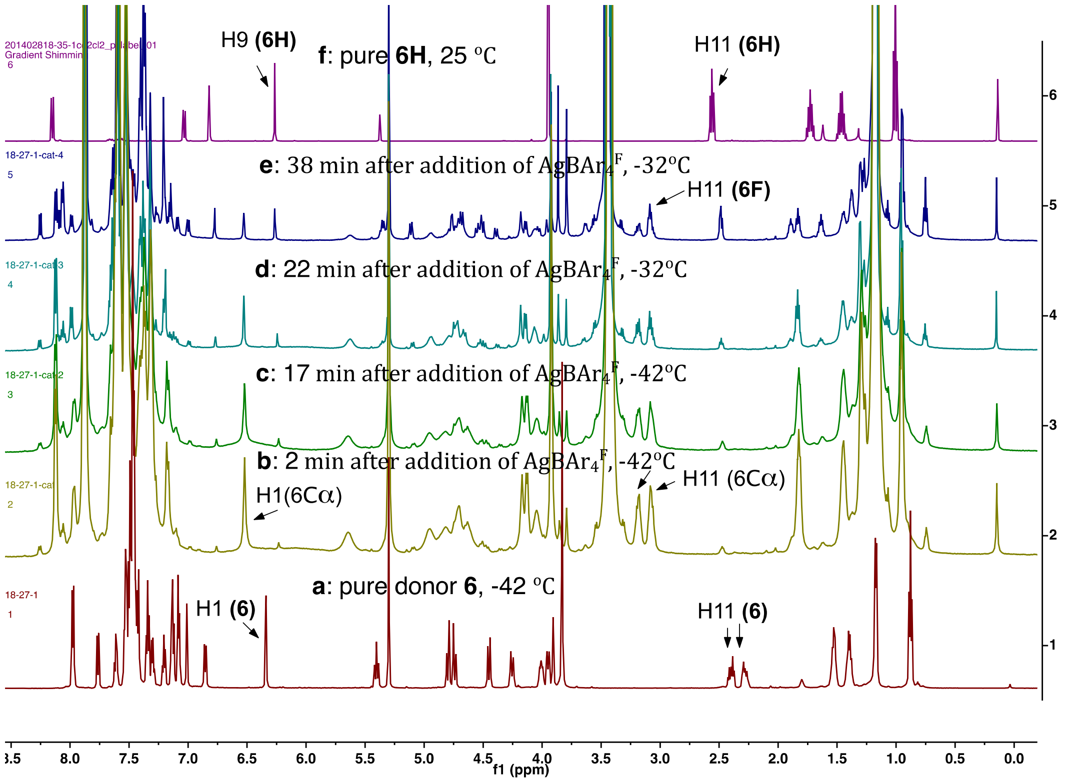
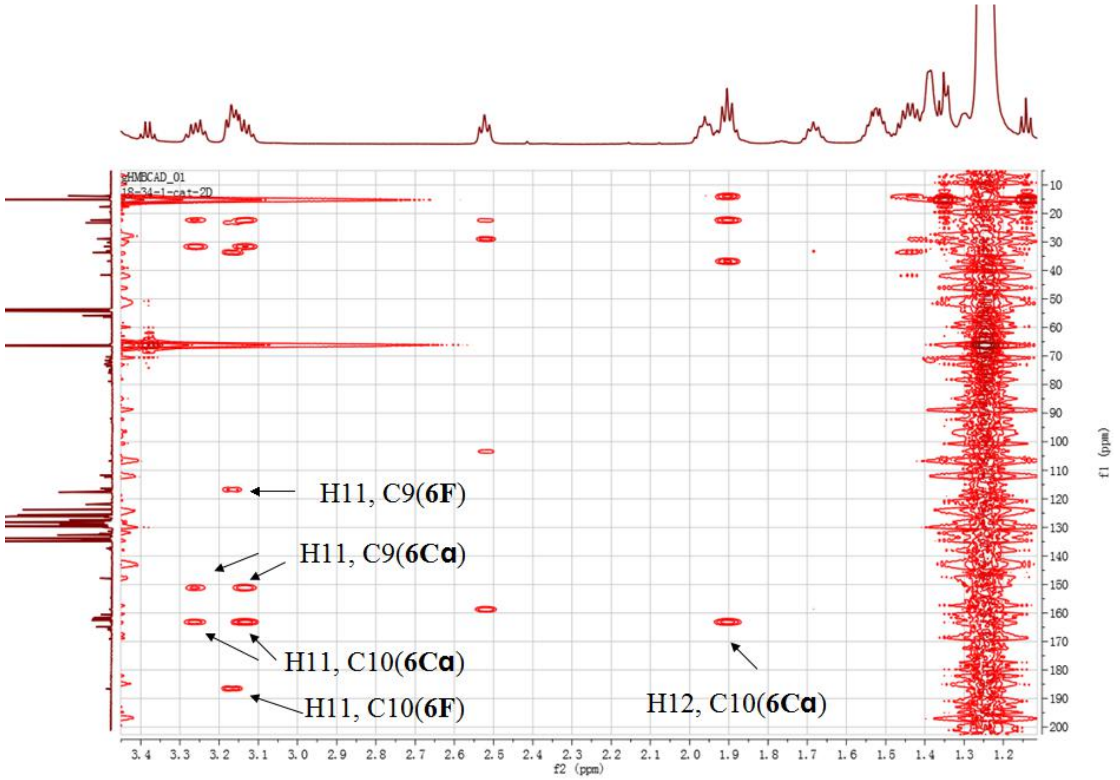


Figure S2. The regional HMBC spectra after addition of AgBAr$_4^F$ (1.0 equiv) into a mixture of **6** and Ph$_3$PAuCl (1.0 equiv) in CD$_2$Cl$_2$ at -42 °C.



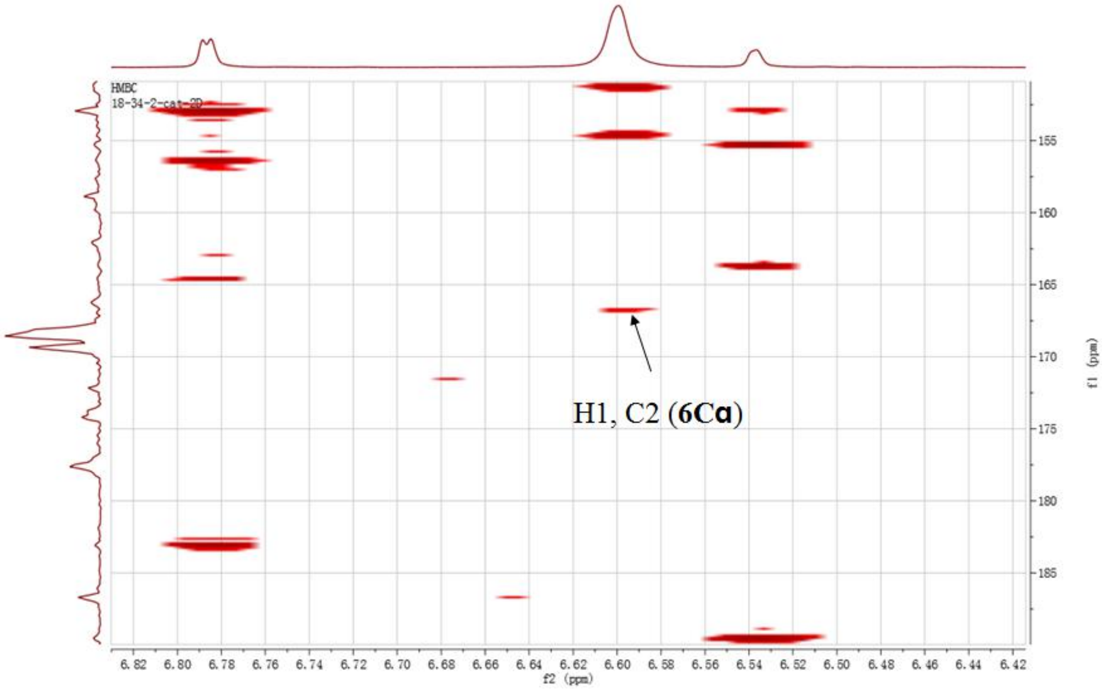


Table S1. ^{1}H (600 MHz), ^{13}C (150 MHz), HMBC NMR data assigned for compound **6Cα** in CD_2Cl_2 at -42 ^{o}C.

Position	Complex **6Cα**		
	δH (ppm)	δC (ppm), type	HMBC
1	6.61 (bs)	100.7, CH	H1 to C2
2	----	166.7, C	C2 to H1
9	----	151.2, C	C9 to H11
10		163.2, C	C10 to H11, H12
11	3.20	36.7, CH_2	H11 to C9, C10, C12
12	1.90	31.8, CH_2	H12 to C10

6.2. Formation of 1-α-glycosyloxy-isochromenylium-4-gold(I) intermediate 2Cα

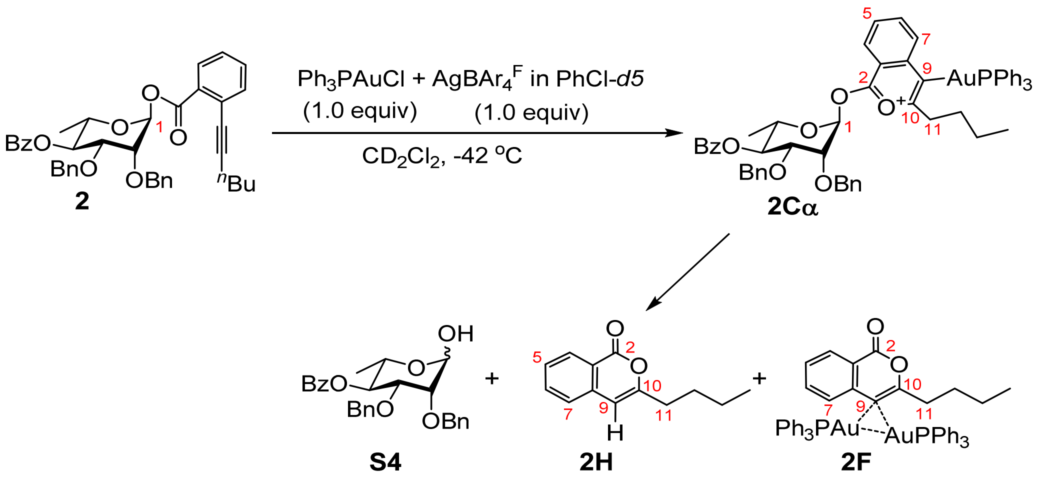
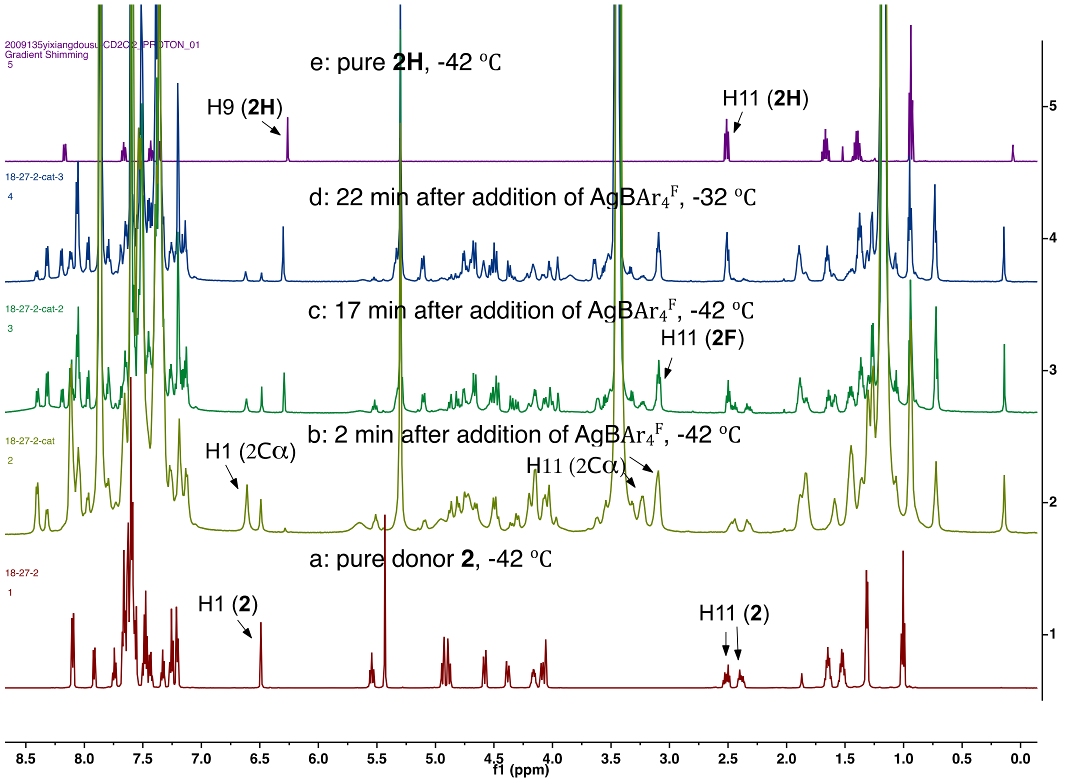


Figure S3. The ^{1}H NMR spectra after addition of $AgBAr_4^F$ (1.0 equiv) into a mixture of **2** and Ph_3PAuCl (1.0 equiv) in CD_2Cl_2 at -42 °C or after warming up to -32 °C. a: pure **2** at -42 °C; b: 2 min after addition of $AgBAr_4^F$ at -42 °C; c: 17 min after addition of $AgBAr_4^F$ at -42 °C; d: 22 min after addition of $AgBAr_4^F$ at -32 °C; e: pure **2H** at -42 °C.



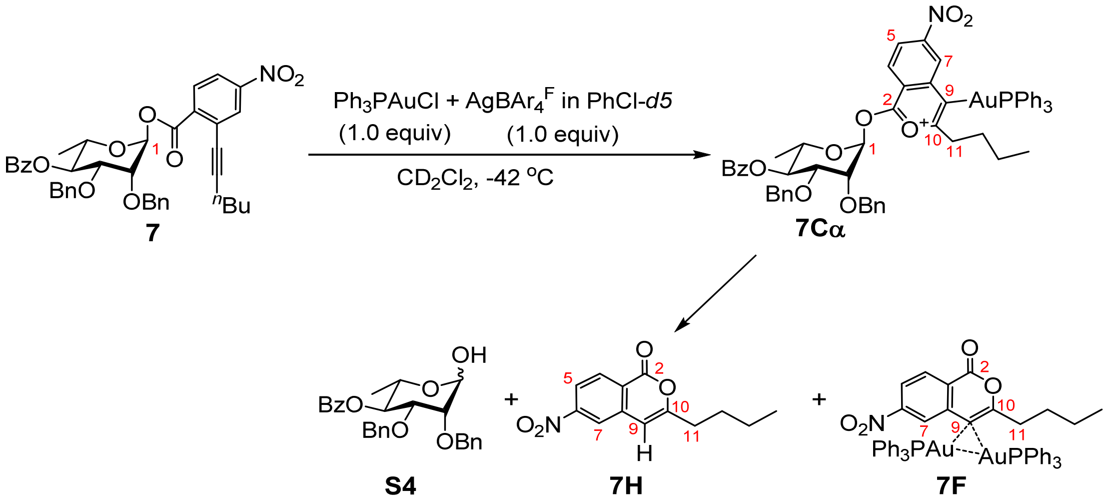
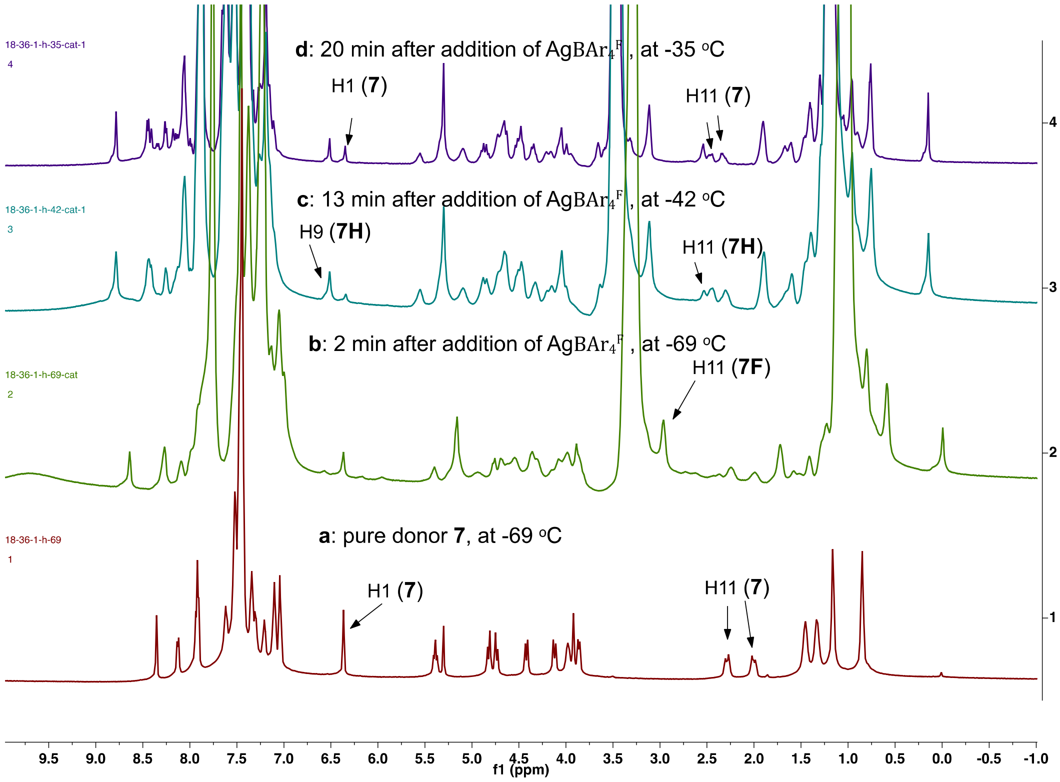
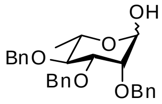
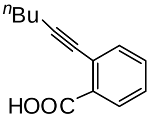
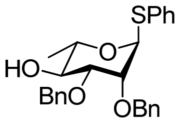
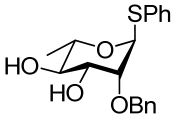
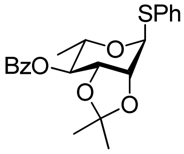
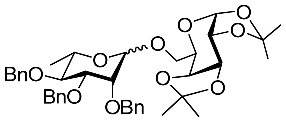
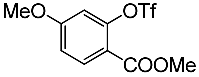
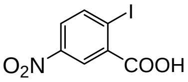


Figure S4. The ^{1}H NMR spectra after addition of AgBAr$_4^F$ (1.0 equiv) into a mixture of **7** and Ph$_3$PAuCl (1.0 equiv) in CD$_2$Cl$_2$ at -69 °C or after warming up. a: pure **7** at -69 °C; b: 2 min after addition of AgBAr$_4^F$ at -69 °C; c: 13 min after addition of AgBAr$_4^F$ at -42 °C; d: 20 min after addition of AgBAr$_4^F$ at -35 °C.

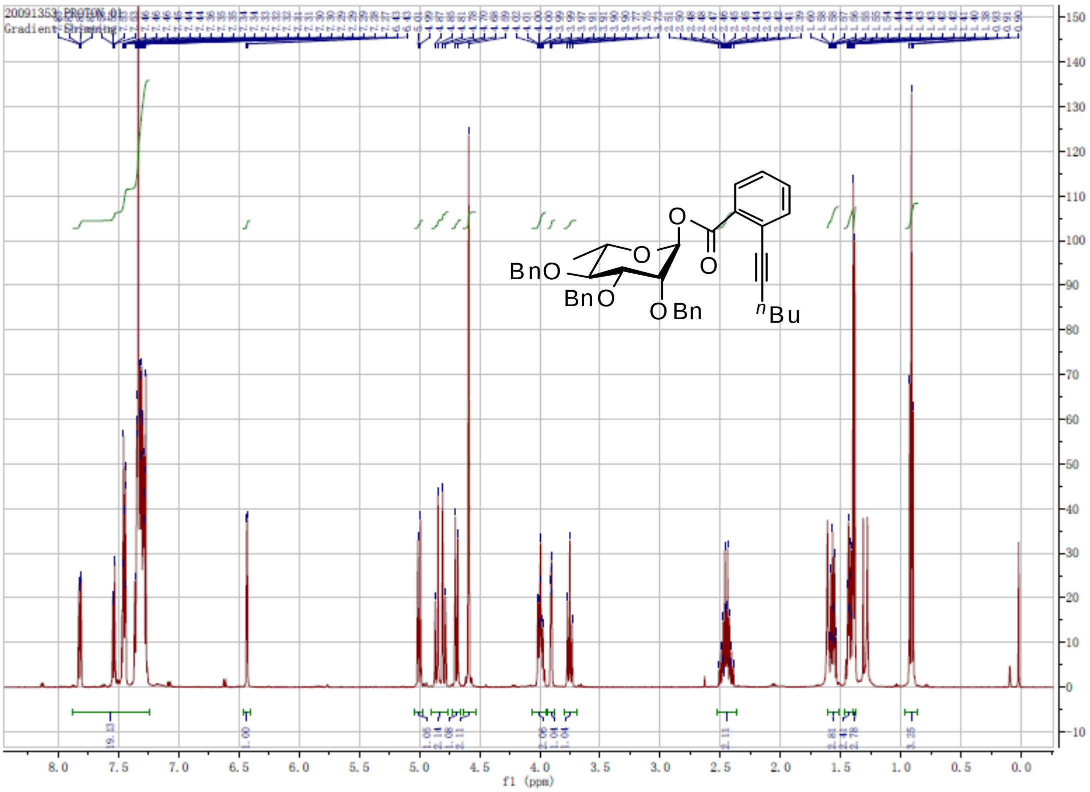


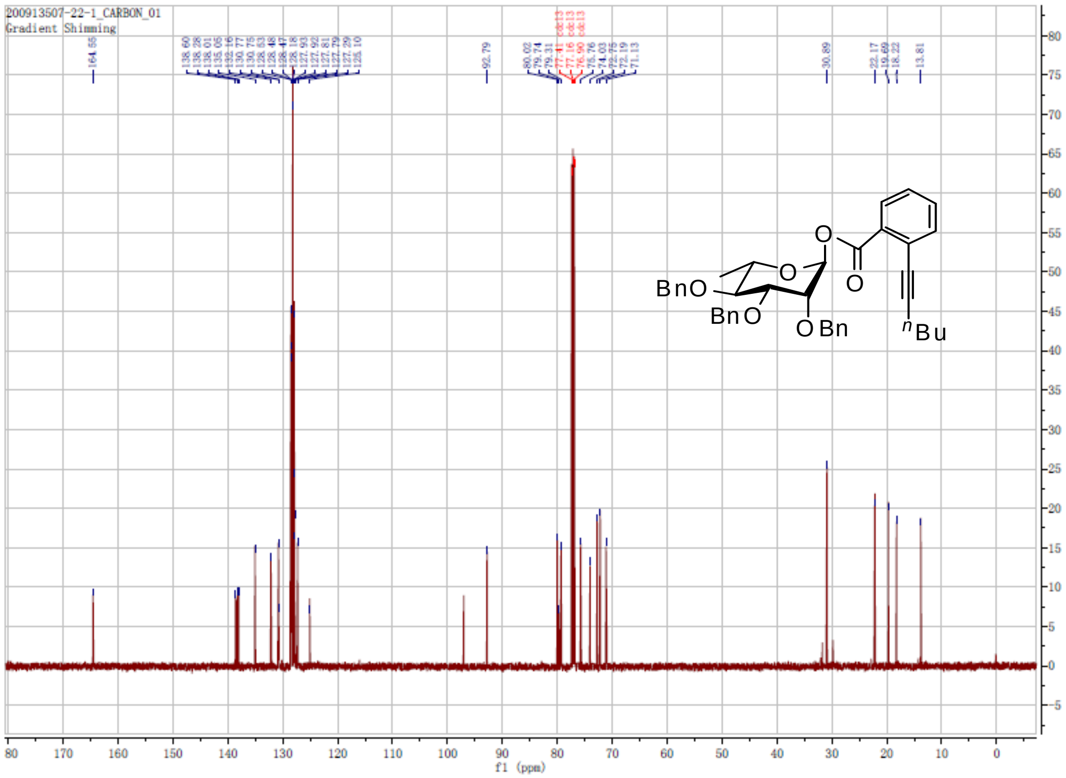
7. Known compounds

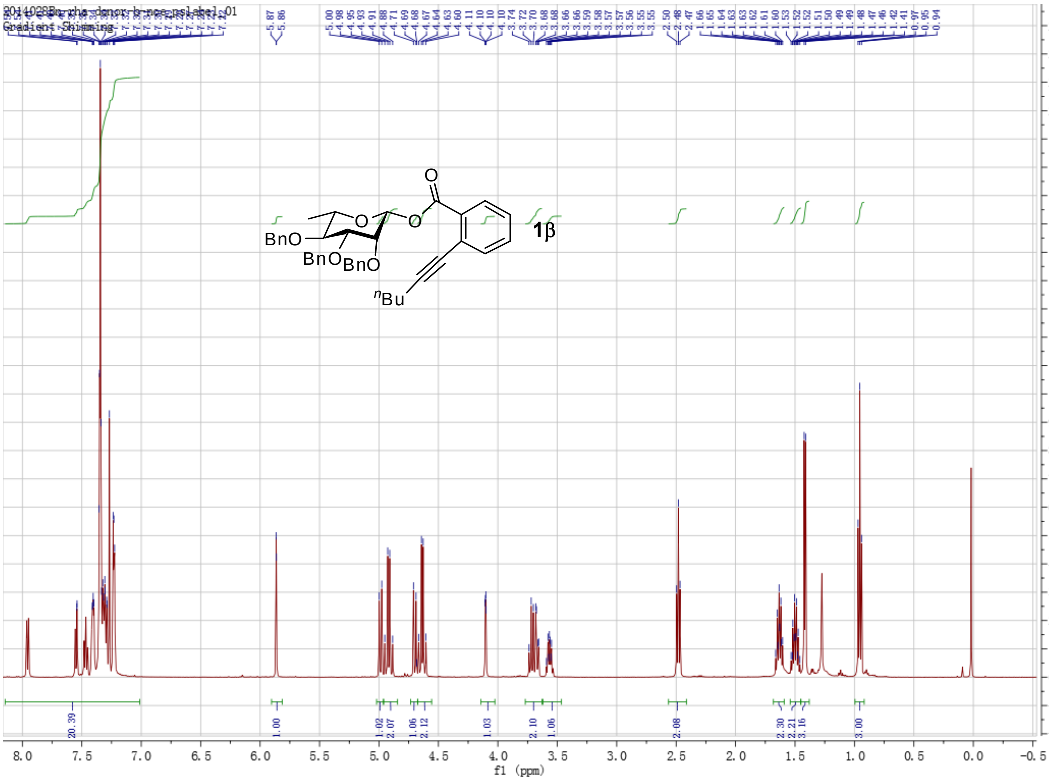
 **S1**	Somnath, D.; Bimalendu, R.; Balaram, M. *Carbohydr. Res.* **2006***, 341*, 2708-2713.
 **S2**	Li, Y.; Yang, X.; Liu, Y.; Zhu, C.; Yang, Y.; Yu, B. *Chem. Eur. J.* **2010**, *16*, 1871-1882.
 **S3**	Crich, D.; Vinogradova, O. *J. Org. Chem*. **2007**, *72*, 3581-3584.
 **S5**	Crich, D.; Vinogradova, O. *J. Org. Chem*. **2007**, *72*, 3581-3584.
 **S9**	Pozsgay, V. *Carbohydr. Res.* **1992**, *235*, 295-302.
 **10**	Mereyala, H.; Reddy, G. *Tetrahedron* **1991**, *47*, 6435-6448.
 **S11**	Matos, M.; Murphy, P. V. *J. Org. Chem*. **2007**, *72*, 1803-1806.
 **S15**	Monnereau, C.; Blart, E.; Montembault, V.; Fontaine, L.; Odobel, F. *Tetrahedron* **2005**, *61*, 10113-10121.

8 NMR Spectra of New Compounds

Compounds 1 and 1β:



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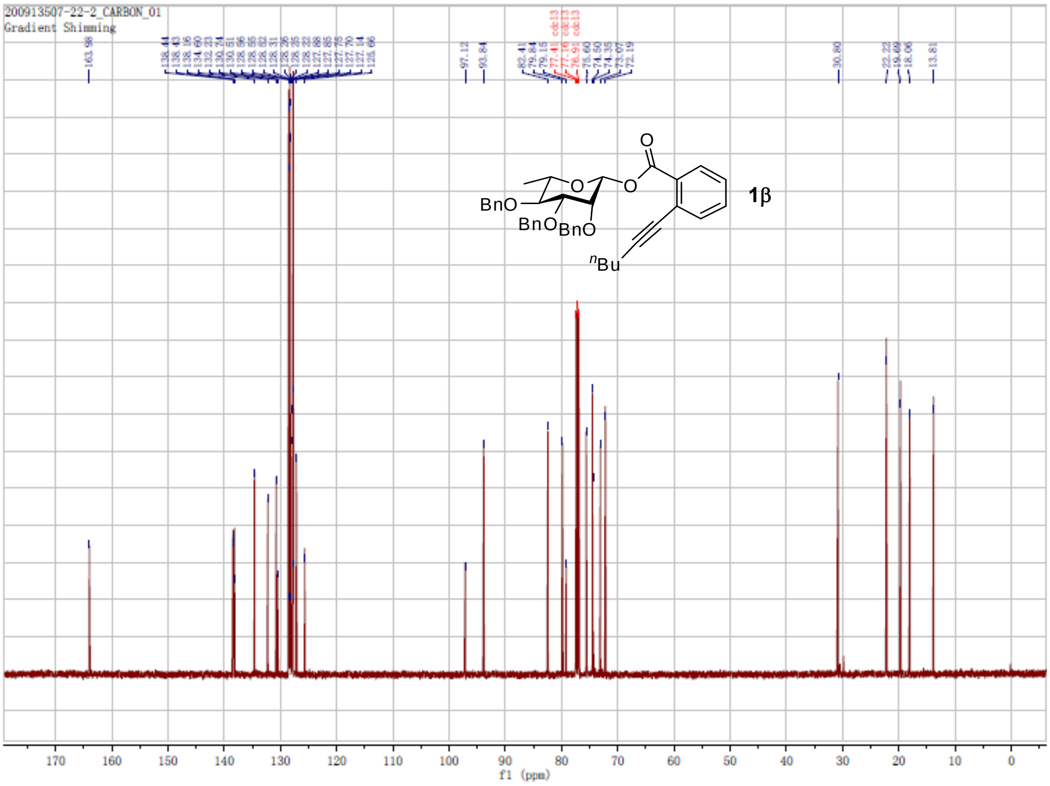
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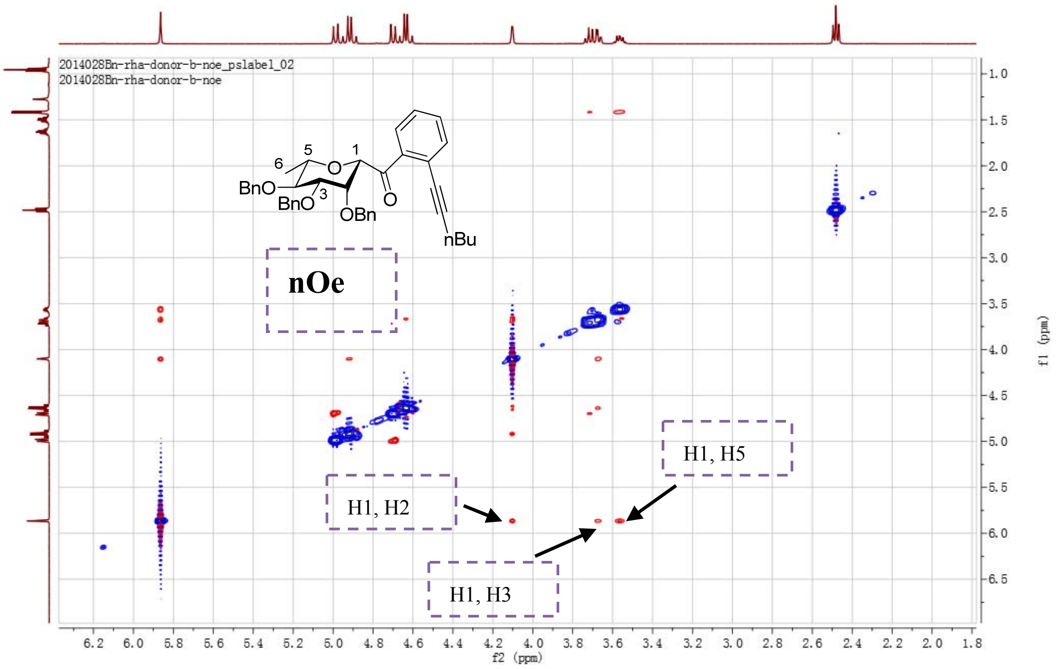
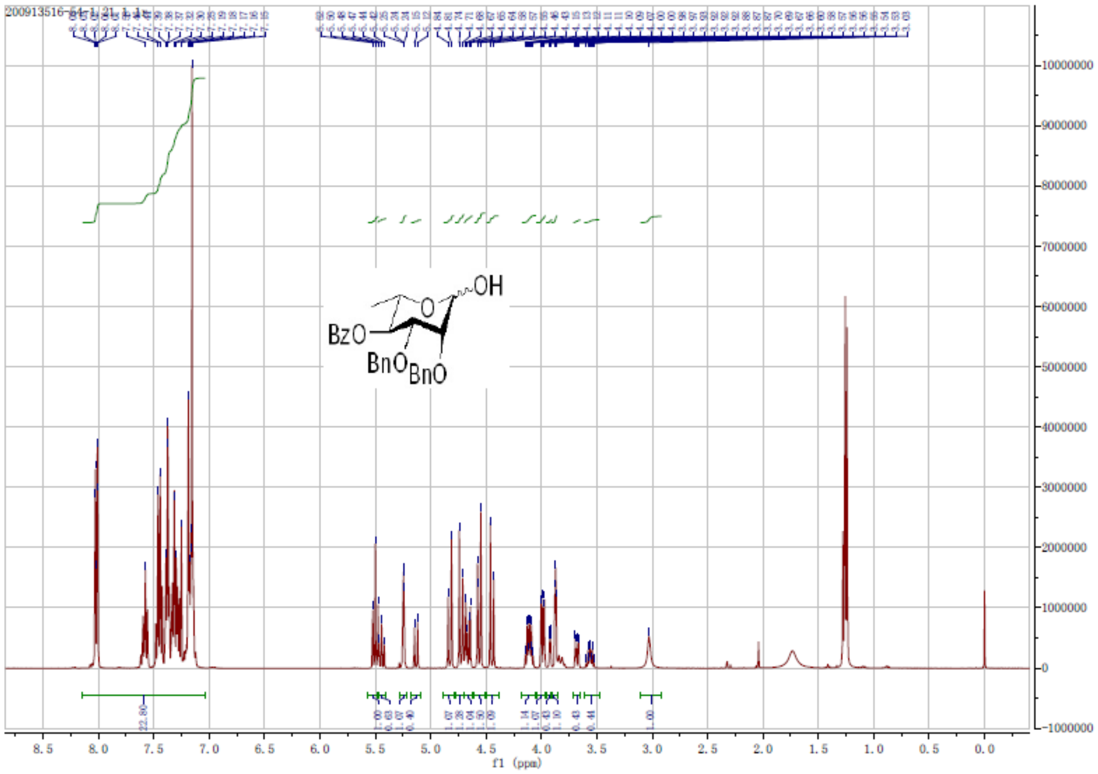
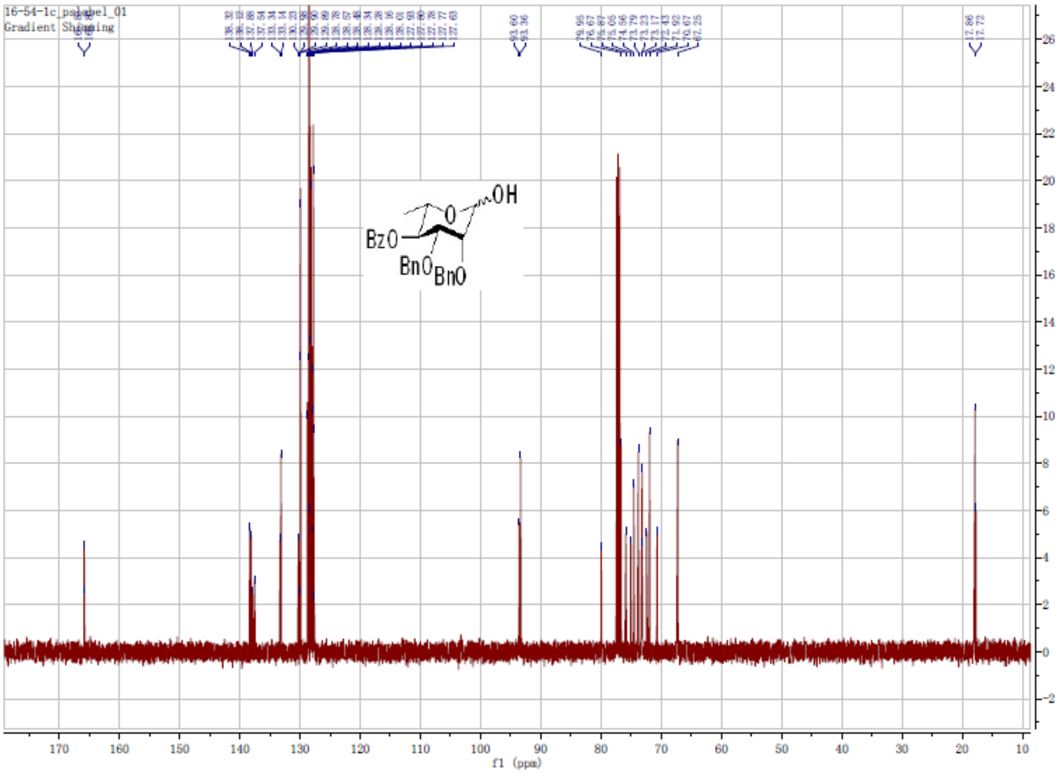
77.16 cdcl3
76.91 cdcl3
75.60
74.50
74.35
73.07
72.19
30.80
22.22
19.69
18.06
13.81
BnO
BnO
BnO
O
O
O
nBu
1β
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5

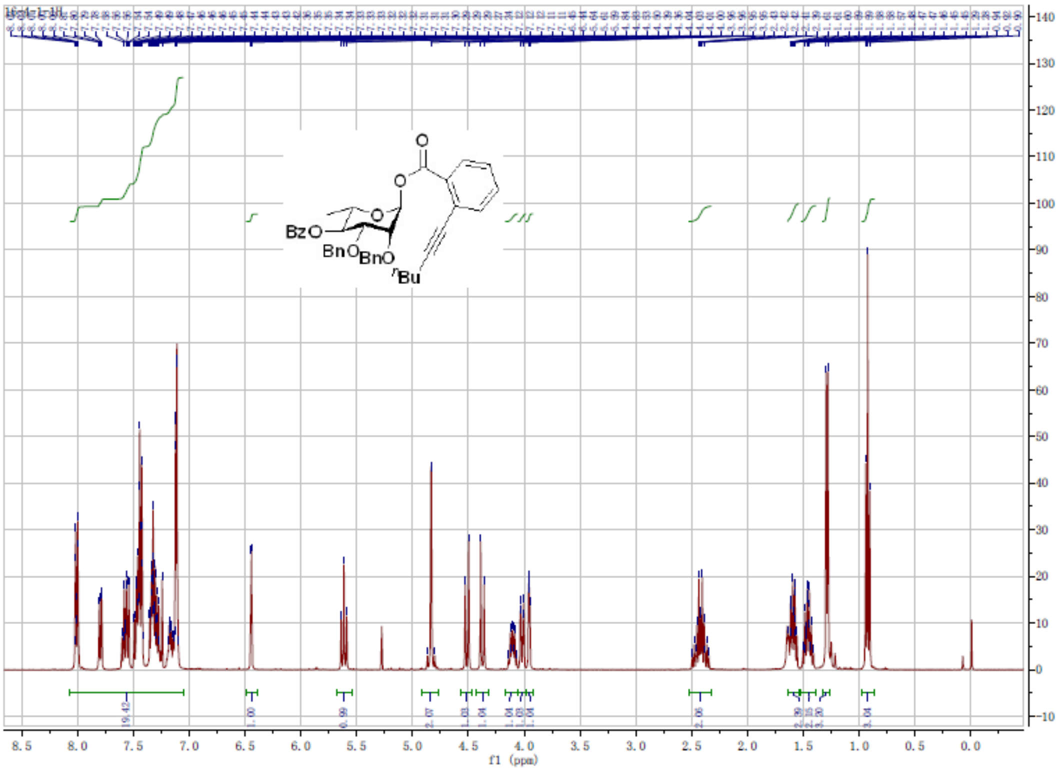

2014028Bn-rha-donor-b-noe_pslabel_02
2014028Bn-rha-donor-b-noe
BnO
BnO
OBn
O
nBu
1
3
5
6
nOe
H1, H2
H1, H3
H1, H5
f2 (ppm)
f1 (ppm)

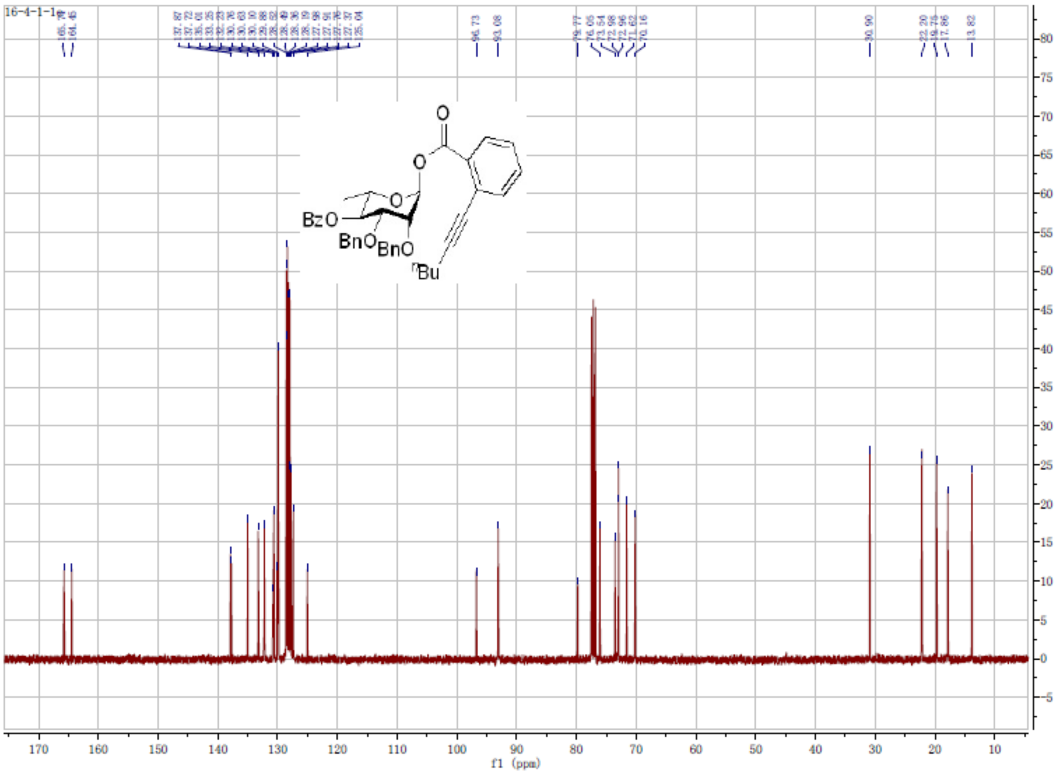
Compound S4:

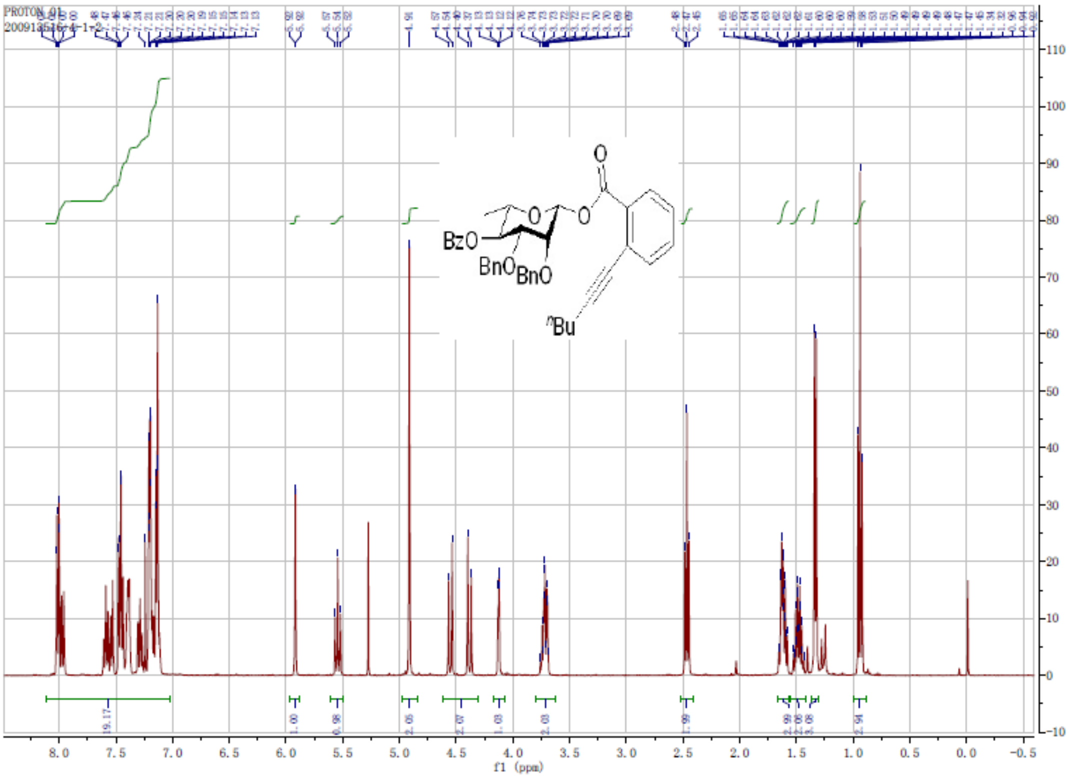

BzO
BnO
BnO
OH
f1 (ppm)

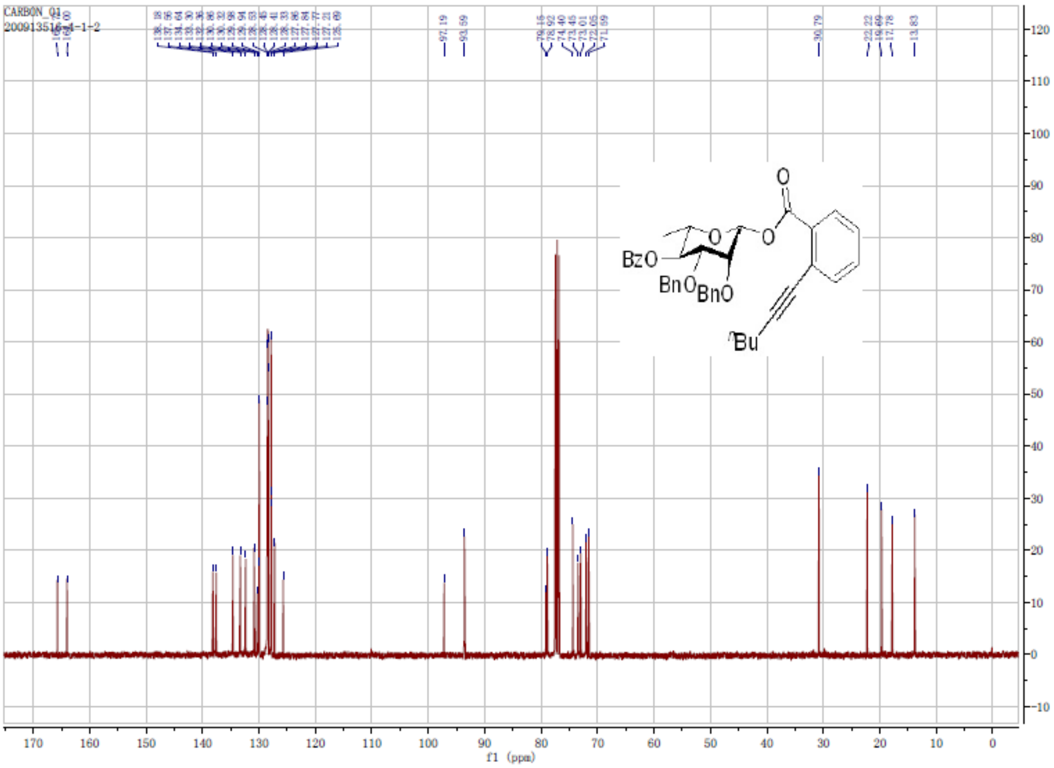


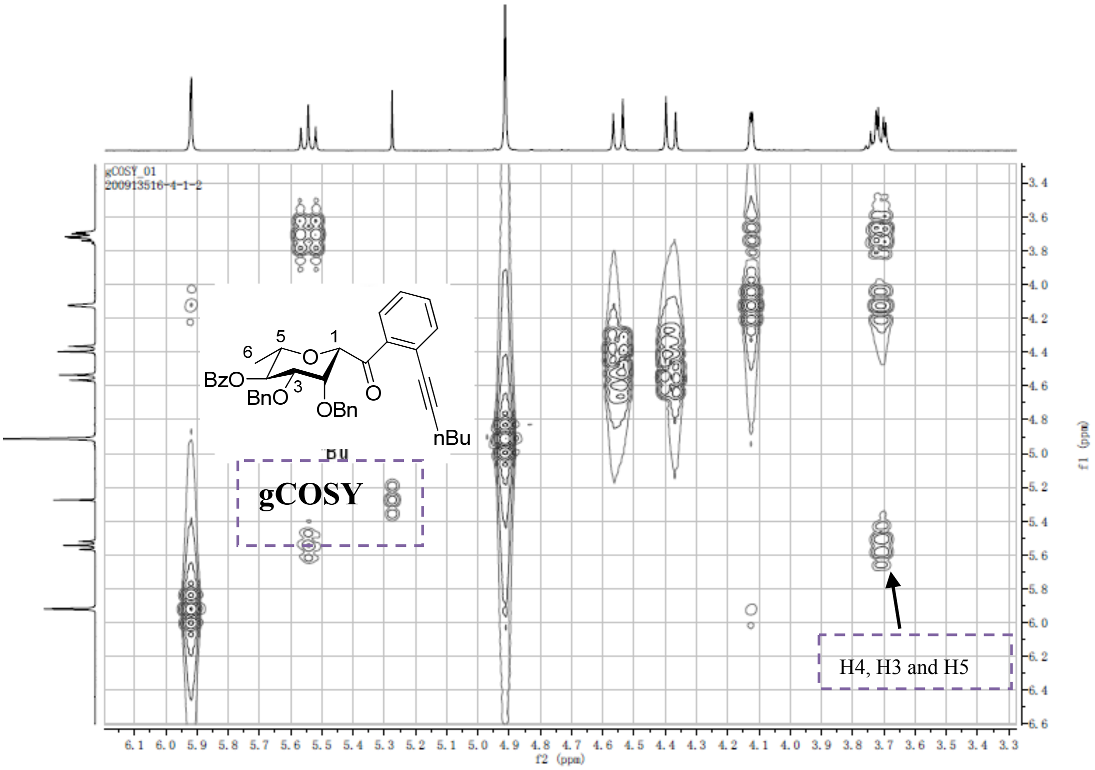
Compounds 2 and 2β:

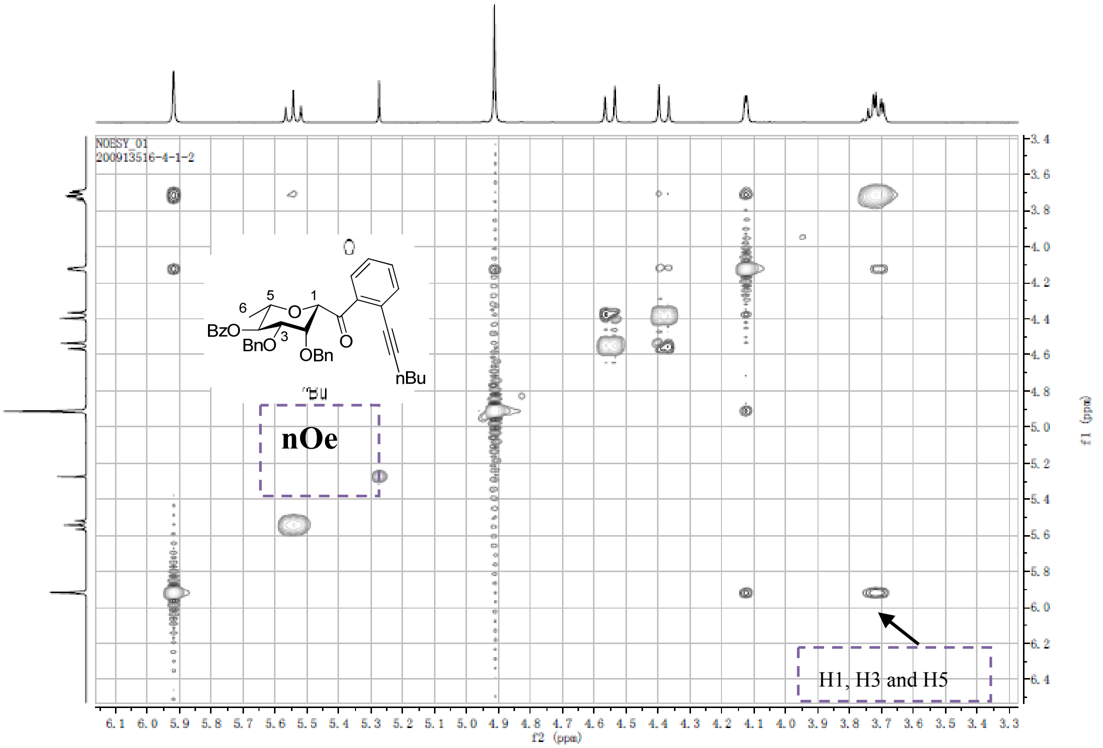



16-4-1-1
164.45
137.87
137.72
135.01
133.25
132.23
130.76
130.63
130.10
129.88
128.52
128.49
128.36
128.19
127.98
127.91
127.76
127.37
125.04
96.73
93.08
79.77
76.05
73.54
72.98
72.96
71.62
70.16
30.90
22.20
19.75
17.86
13.82
O
O
BzO
BnO
BnO
ⁿBu
f1 (ppm)

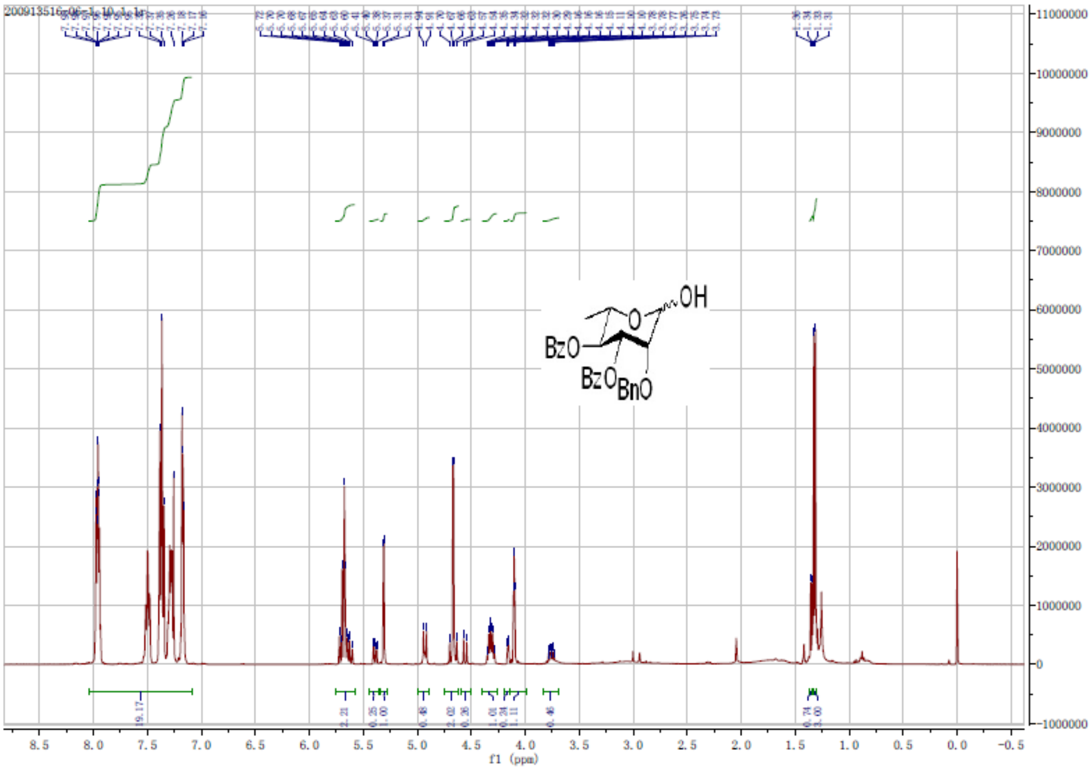

PROTON_01
20091316-4-1-2
5.92
5.92
5.57
5.54
5.52
4.91
2.48
2.47
2.45
O
O
BzO
BnO
BnO
ⁿBu
19.17
1.00
0.98
2.05
2.07
1.03
2.03
1.99
2.99
2.08
3.08
2.94
f1 (ppm)

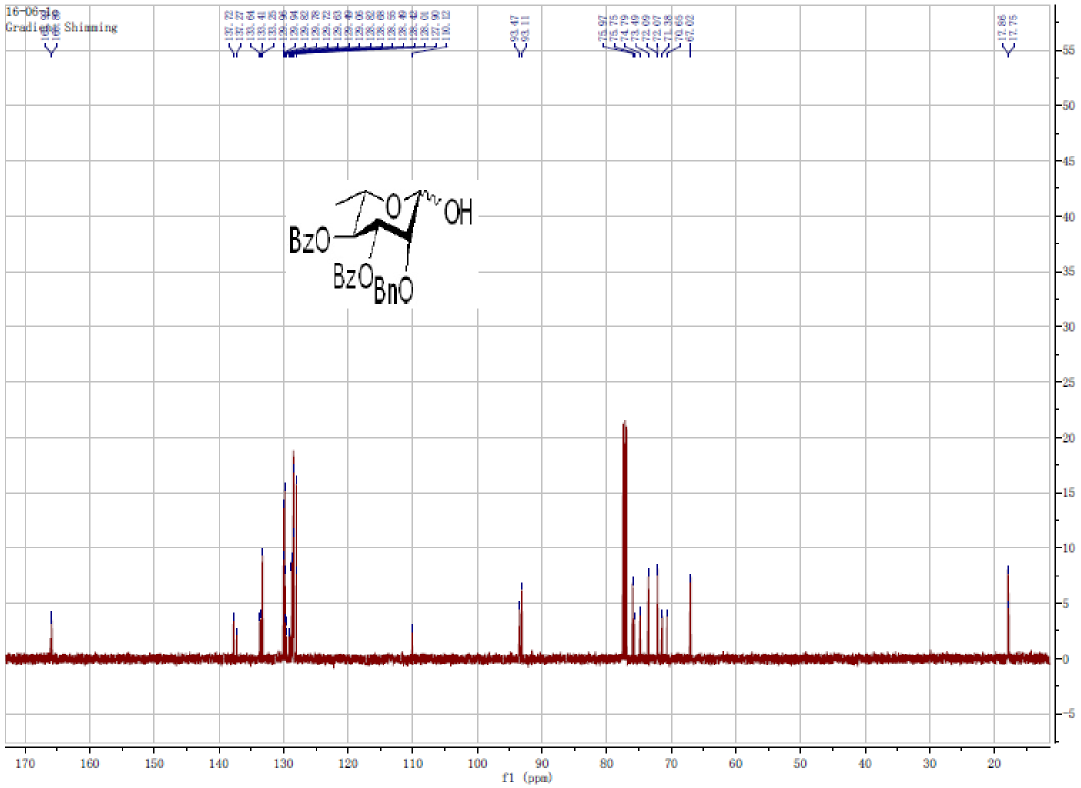

CARBON_01
200913516-4-1-2
164.00
138.18
137.56
134.64
133.30
132.36
130.86
130.32
129.98
129.94
128.53
128.45
128.41
128.33
127.86
127.84
127.77
127.21
125.69
97.19
93.59
79.16
78.92
74.40
73.45
73.01
72.05
71.59
30.79
22.22
19.69
17.78
13.83
BzO
BnO
BnO
O
O
O
ⁿBu
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


gCOSY_01
200913516-4-1-2
5
1
6
O
BzO
BnO
3
OBn
O
nBu
gCOSY
H4, H3 and H5
f2 (ppm)
f1 (ppm)
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6

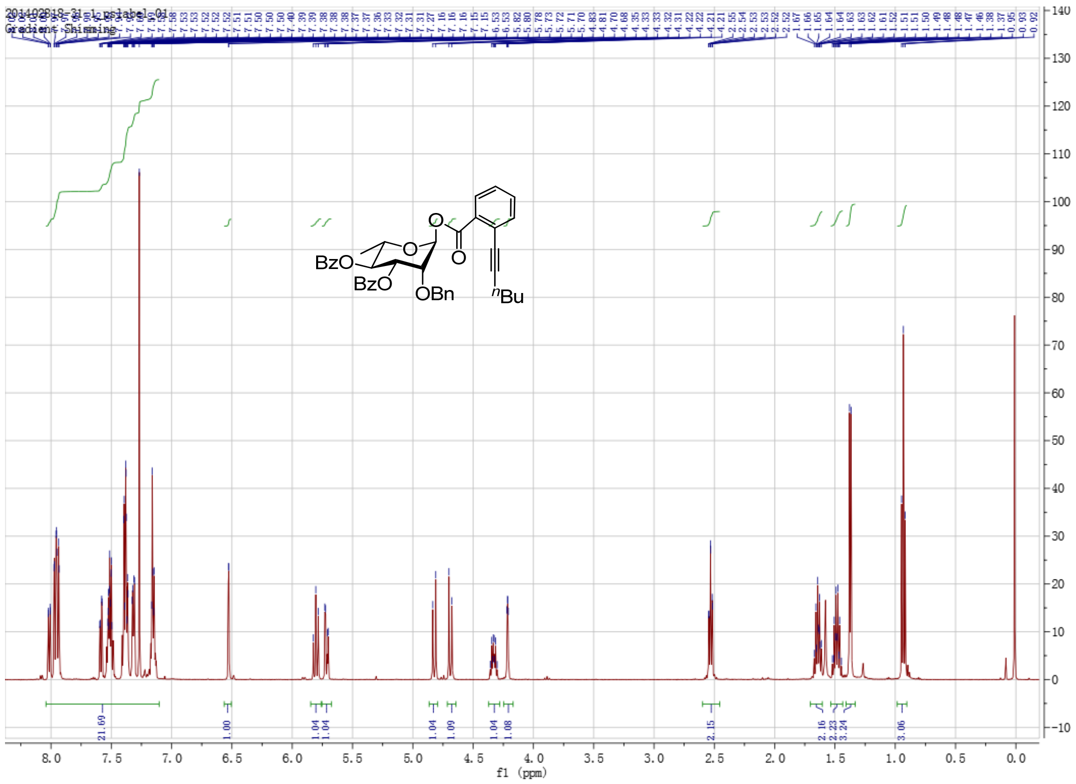

NOESY_01
200913516-4-1-2
6
5
1
O
BzO
BnO
3
OBn
O
nBu
nOe
H1, H3 and H5
f2 (ppm)
f1 (ppm)

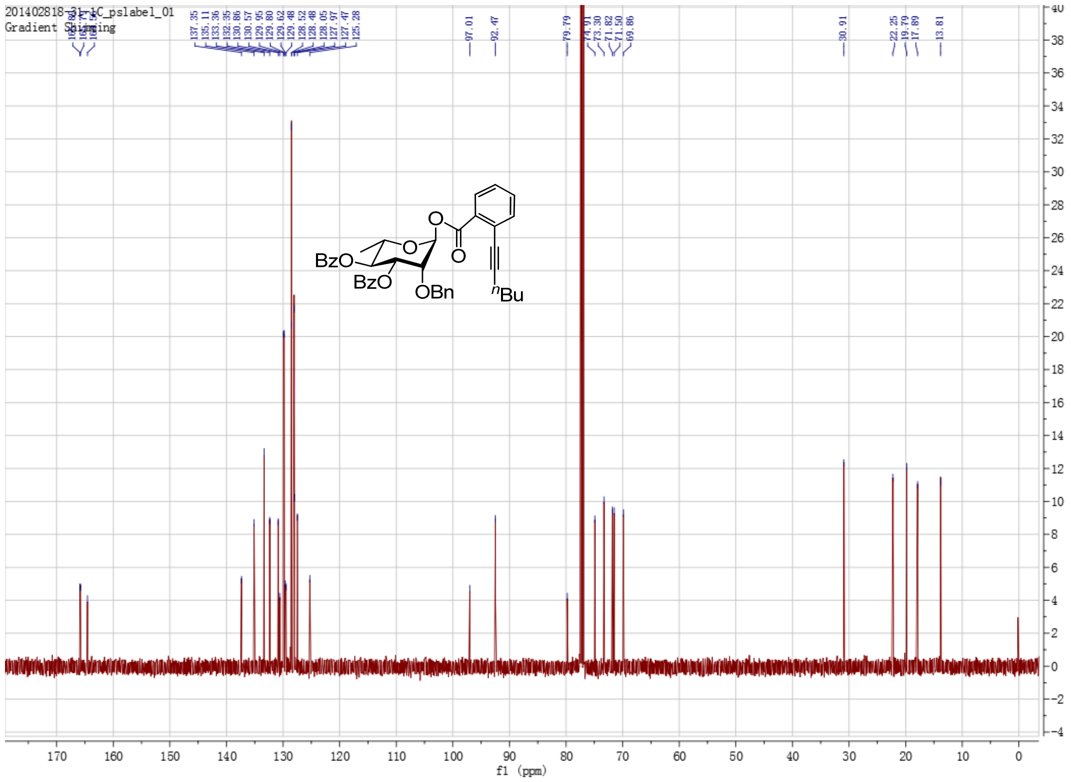
Compound S6:

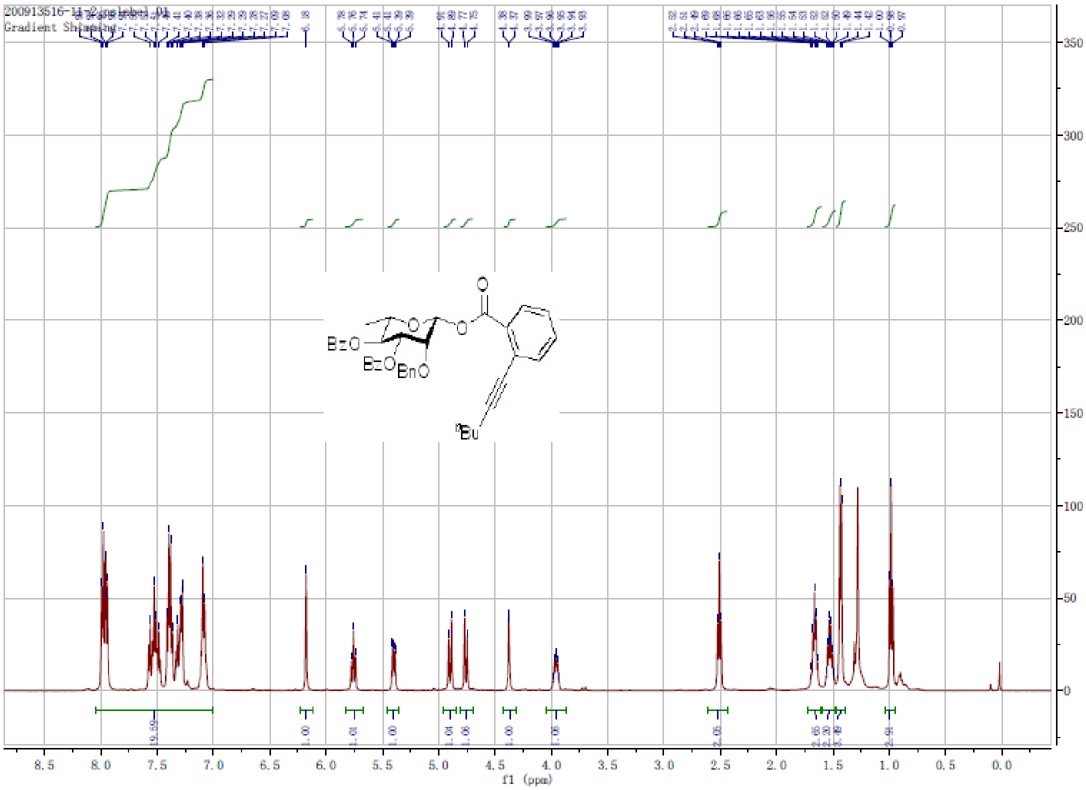

OH
O
BzO
BzO
BnO
19.17
2.21
0.25
1.00
0.48
2.02
0.26
1.01
0.24
1.11
0.46
0.74
3.00
f1 (ppm)

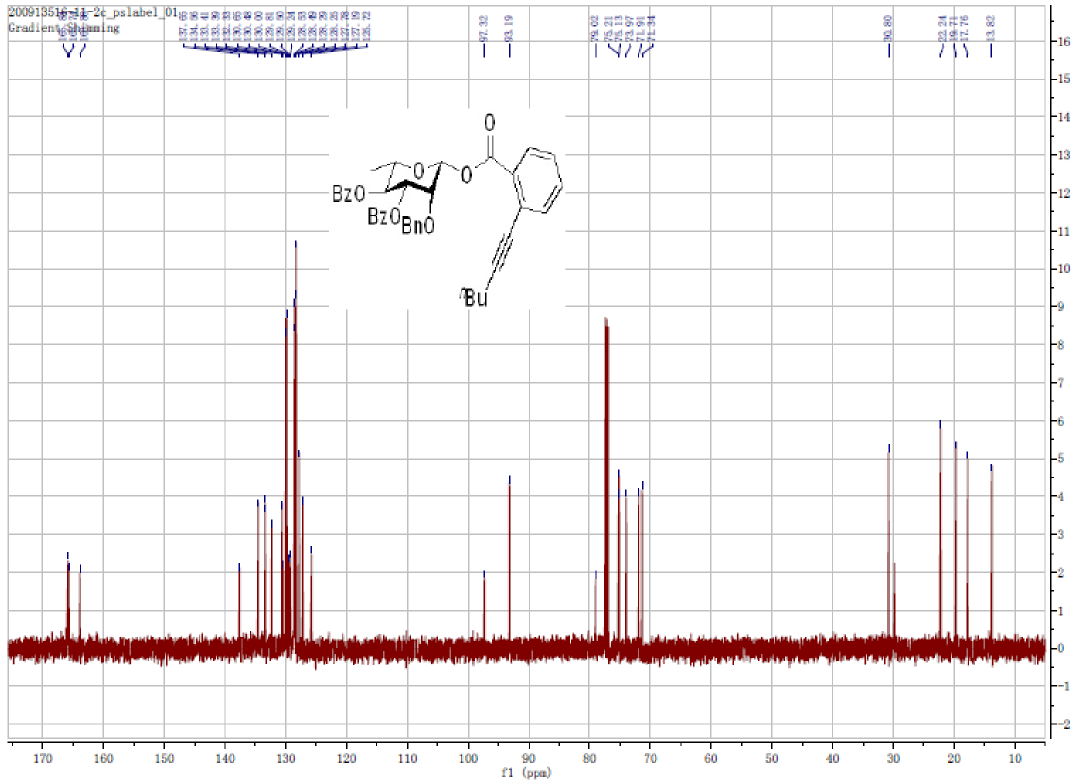


Compounds 3 and 3β:

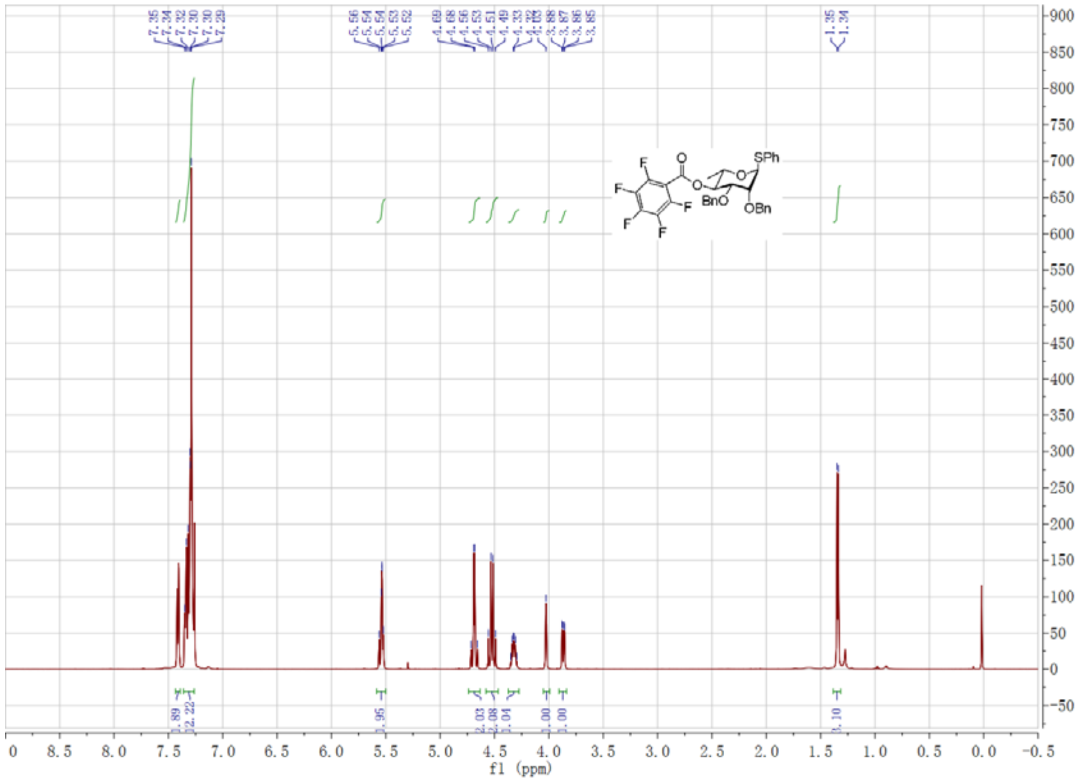


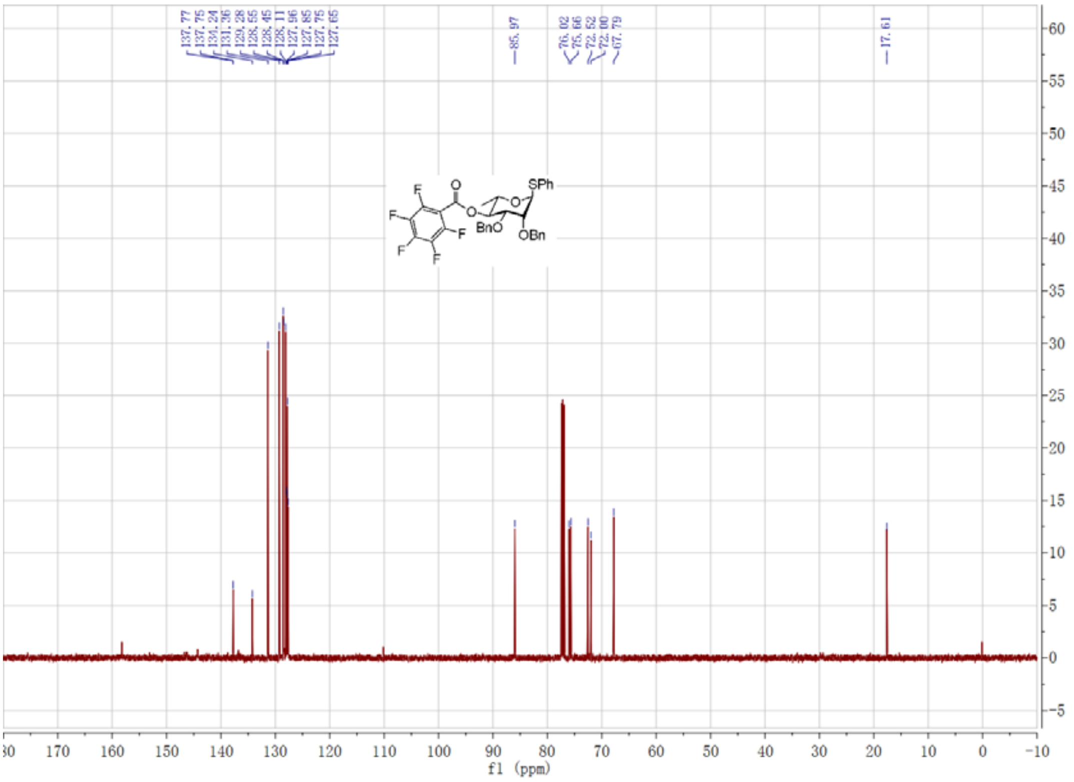

201402818-31-1C_pslabel_01
Gradient Shimming
137.35
135.11
133.36
132.35
130.86
130.57
129.95
129.80
129.62
129.48
128.52
128.48
128.05
127.97
127.47
125.28
97.01
92.47
79.79
74.91
73.30
71.82
71.50
69.86
30.91
22.25
19.70
17.89
13.81
BzO
BzO
O
O
O
OBn
^{n}Bu
f1 (ppm)


200913516-11-2_pslabel_01
Gradient Shimming
BzO
BzO
BnO
O
O
O
^{n}Bu
19.59
1.00
1.01
1.00
1.04
1.06
1.00
1.06
2.05
2.65
2.30
3.49
2.94
f1 (ppm)

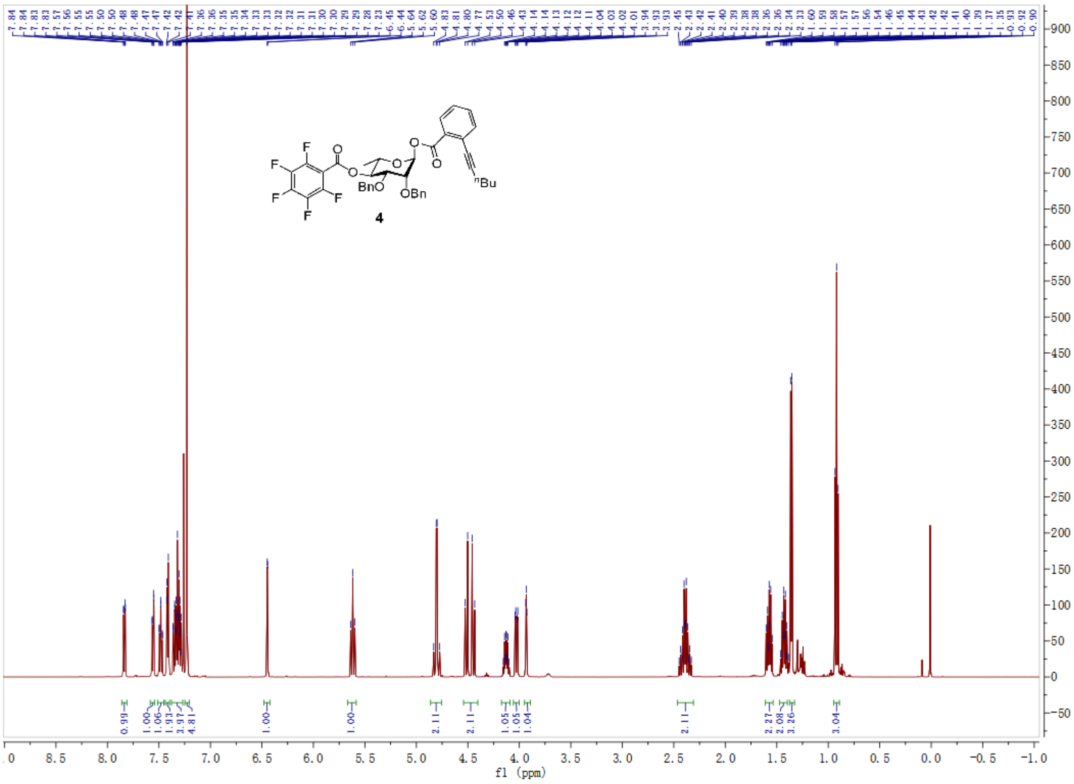

20091351б-11-2c_pslabel_01
Gradient Shimming
137.65
134.56
133.41
133.30
132.33
130.65
130.48
130.00
129.81
129.60
129.34
128.53
128.49
128.35
128.26
127.78
127.19
125.72
97.32
93.19
79.02
75.21
75.13
73.97
71.91
71.34
30.80
22.24
19.71
17.76
13.82
BzO
BzO
BnO
O
O
O
ⁿBu
f1 (ppm)

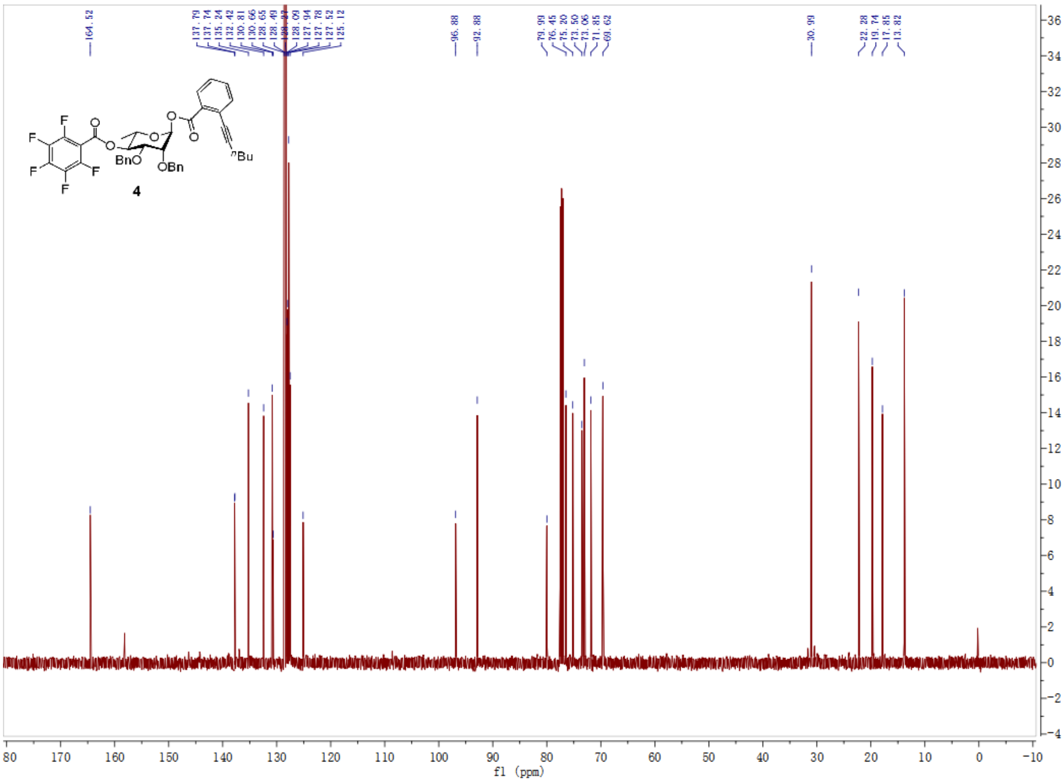
Compound S7:


7.35
7.34
7.32
7.30
7.30
7.29
5.56
5.54
5.54
5.53
5.52
4.69
4.68
4.56
4.53
4.51
4.49
4.33
4.32
4.03
3.88
3.87
3.86
3.85
1.35
1.34
1.89
22.22
0.95
2.03
2.08
1.04
1.00
3.00
3.10
SPh
F
F
F
F
F
O
O
BnO
OBn
f1 (ppm)

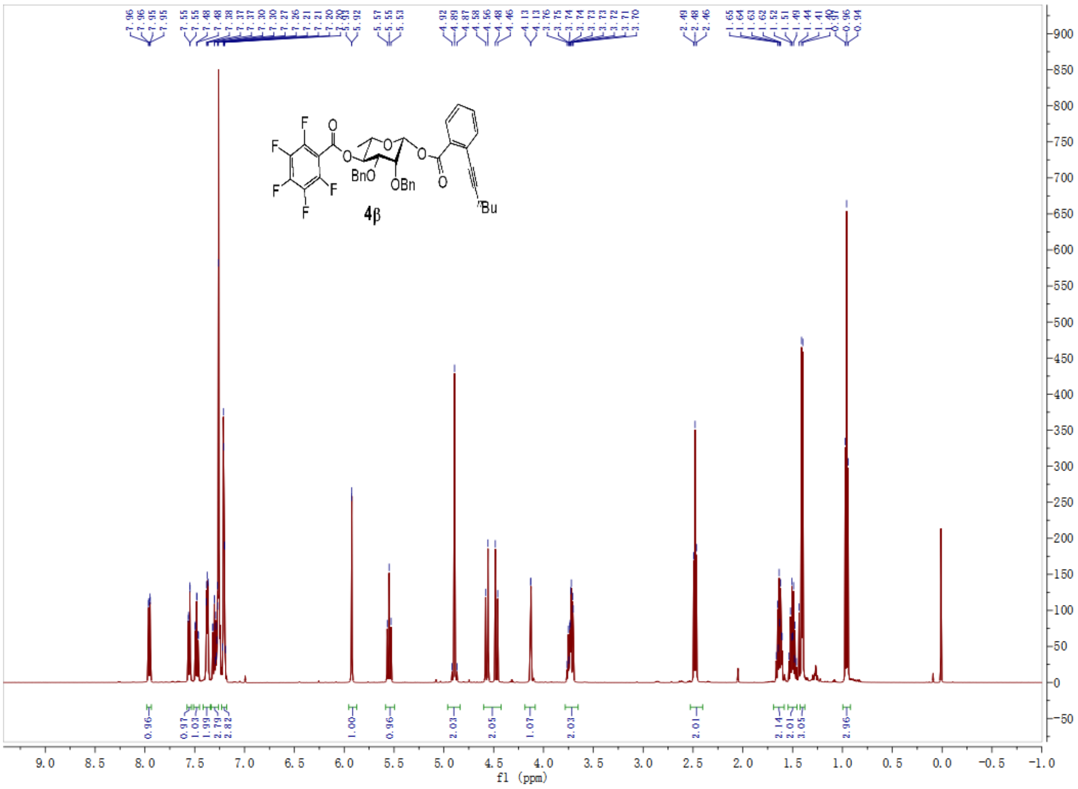


Compounds 4 and 4β:

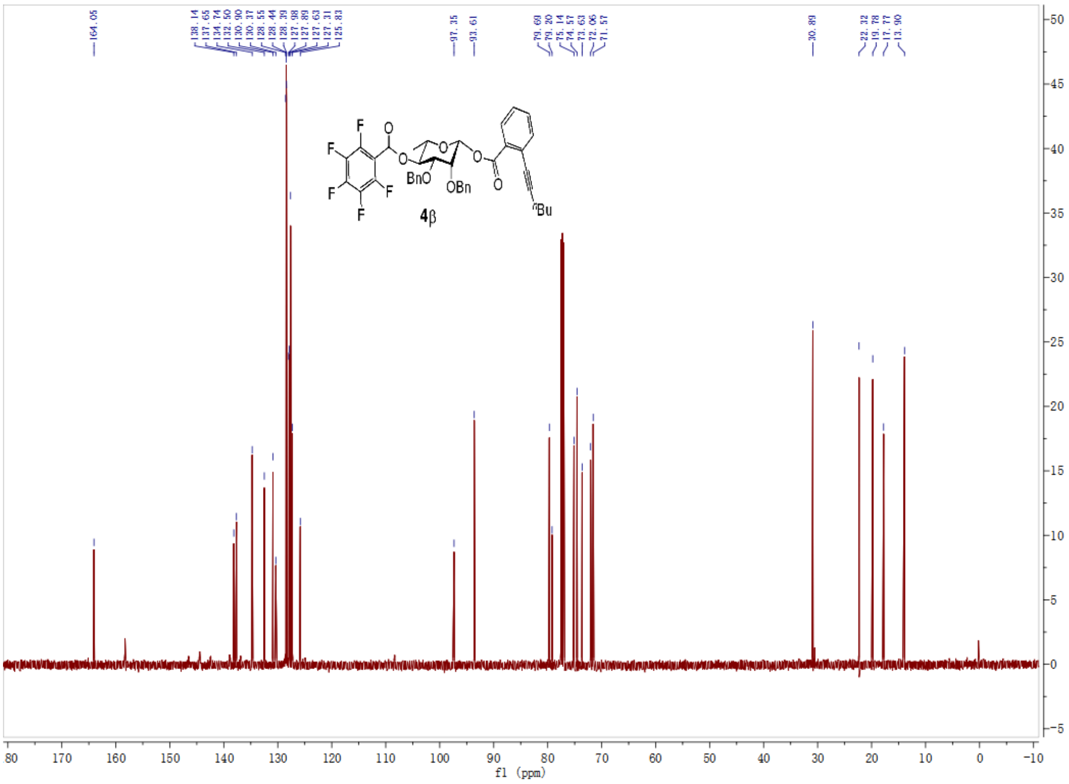


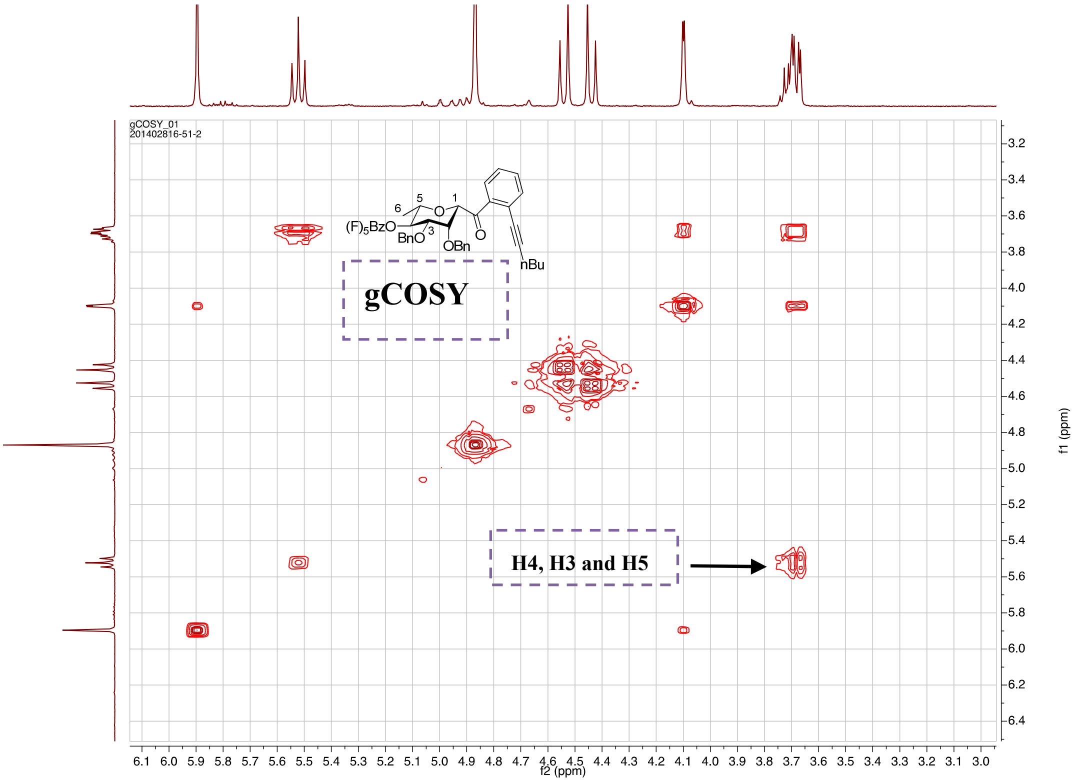

4

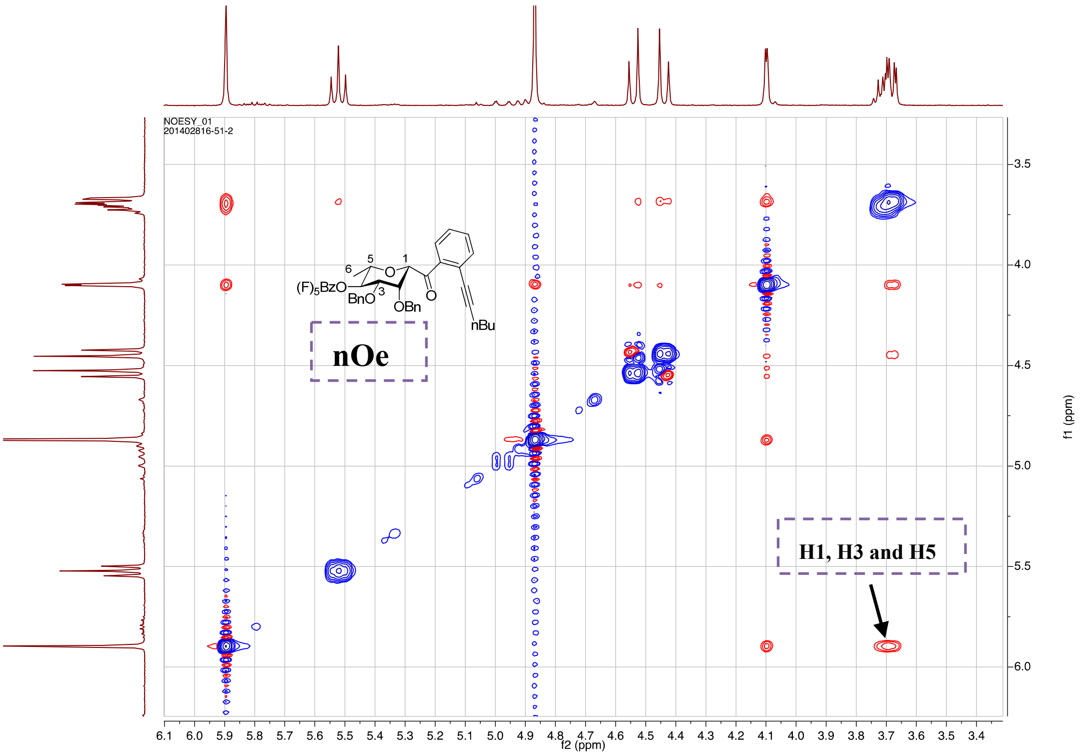
164.52
137.79 137.74 135.24 132.42 130.81 130.66 128.65 128.49 128.27 128.09 127.94 127.78 127.52 125.12
96.88
92.88
79.99 76.45 75.20 73.50 73.06 71.85 69.62
30.99
22.28 19.74 17.85 13.82
F
O
BnO
OBn
ⁿBu
36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 −2 −4
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


4β

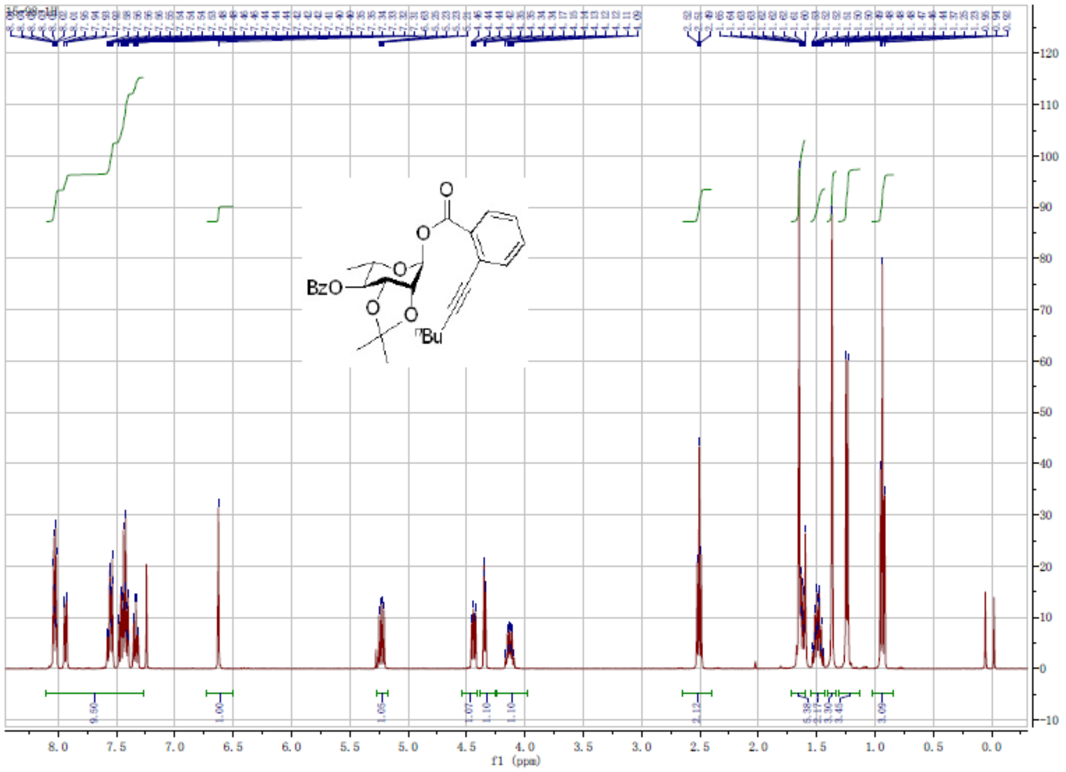
7.96 7.96 7.95 7.95
7.55 7.55 7.48 7.48 7.38 7.37 7.37 7.30 7.30 7.27 7.26 7.21 7.21 7.20 7.20 5.93 5.92
5.57 5.55 5.53
4.92 4.89 4.87 4.58 4.56 4.48 4.46
4.13 4.13 3.76 3.75 3.74 3.74 3.73 3.73 3.72 3.71 3.70
2.49 2.48 2.46
1.65 1.64 1.63 1.62 1.52 1.51 1.49 1.44 1.41 1.40 0.97 0.96 0.94
F
O
BnO
OBn
ⁿBu
0.96 0.97 1.03 1.99 2.79 2.82 1.00 0.96 2.03 2.05 1.07 2.03 2.01 2.14 2.01 3.05 2.96
900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 −50
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

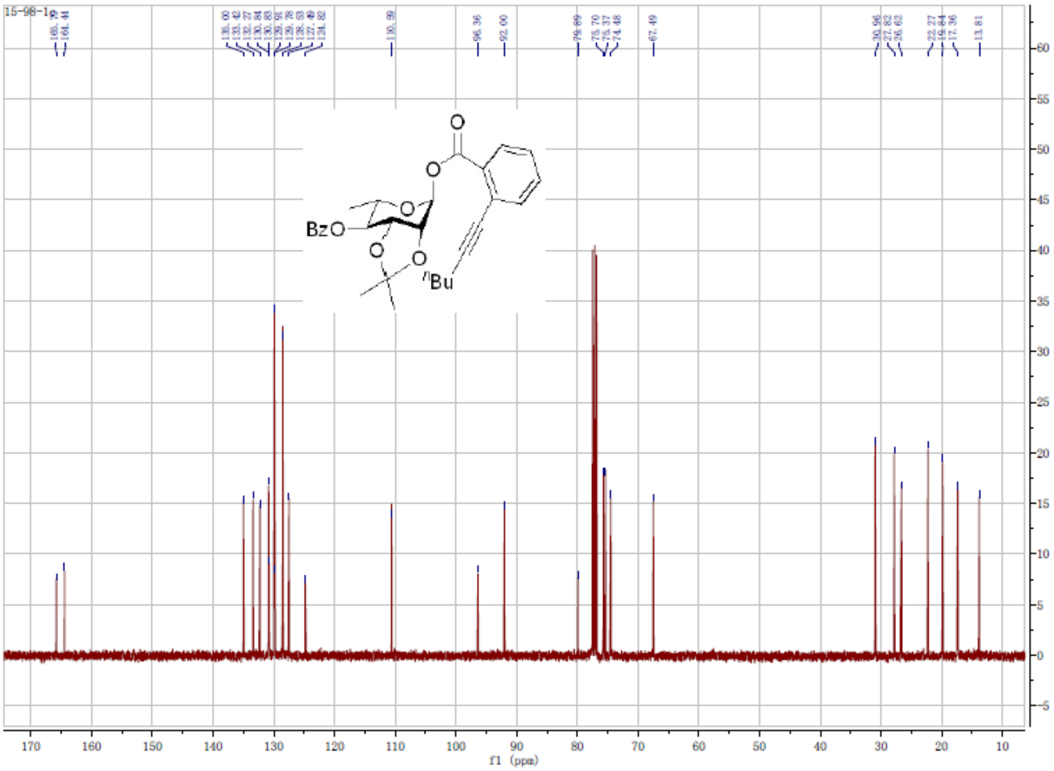

164.05
138.14
137.65
134.74
132.50
130.90
130.37
128.55
128.44
128.39
127.98
127.89
127.63
127.31
125.83
97.35
93.61
79.69
79.20
75.14
74.57
73.63
72.06
71.57
30.89
22.32
19.78
17.77
13.90
F
F
F
F
F
O
O
BnO
OBn
O
O
nBu
4β
f1 (ppm)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
50 45 40 35 30 25 20 15 10 5 0 -5

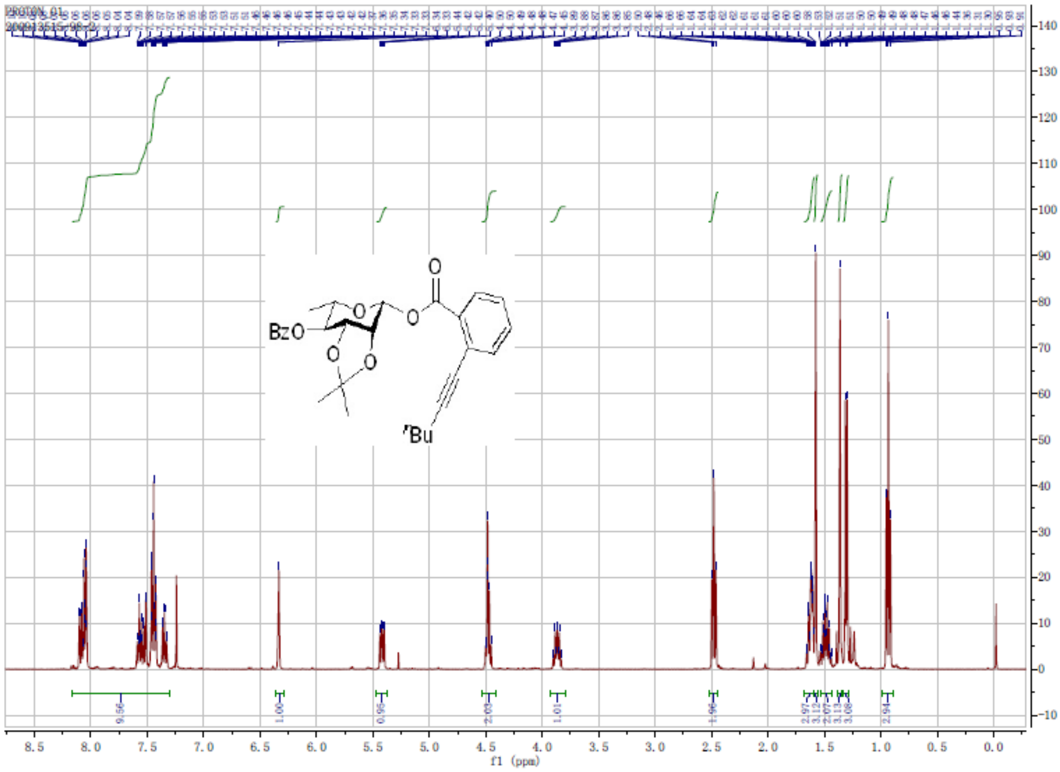

gCOSY_01
201402816-51-2
6
5
1
3
(F)5BzO
BnO
O
OBn
O
nBu
gCOSY
H4, H3 and H5
f2 (ppm)
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
f1 (ppm)
3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2 6.4

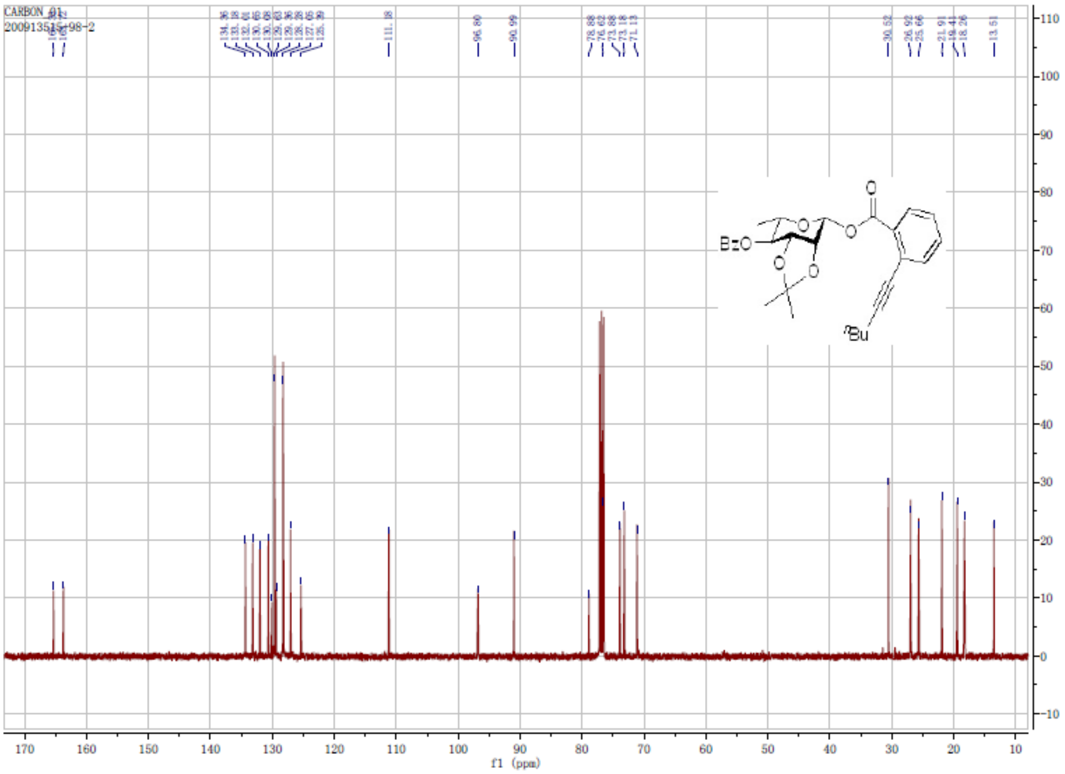


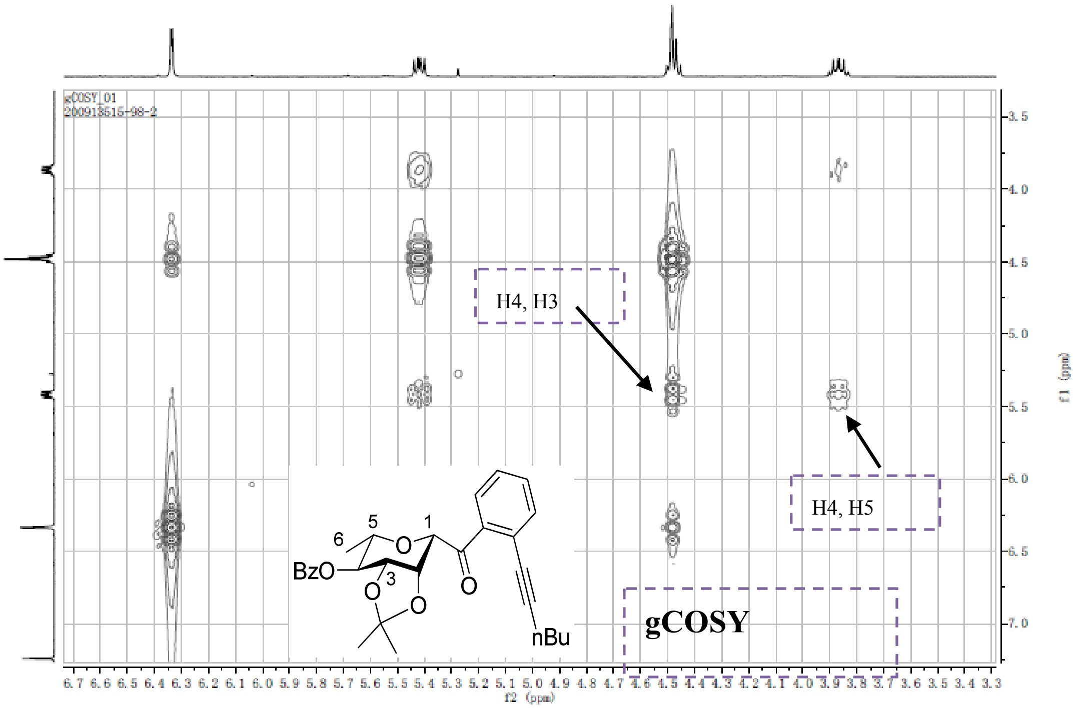
Compounds 5 and 5β:

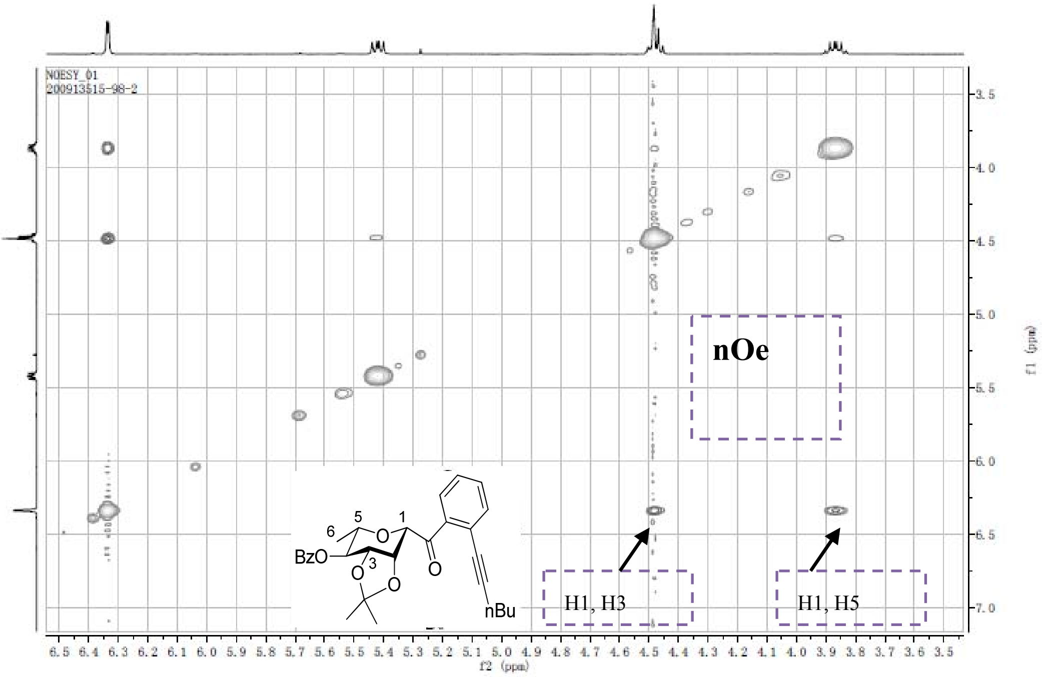



15-98-1c
165.79
164.44
135.00
133.42
132.27
130.84
130.83
129.91
129.78
128.53
127.49
124.82
110.99
96.36
92.00
79.89
75.70
75.37
74.48
67.49
30.96
27.82
26.62
22.27
19.84
17.36
13.81
BzO
O
O
O
O
O
nBu
f1 (ppm)

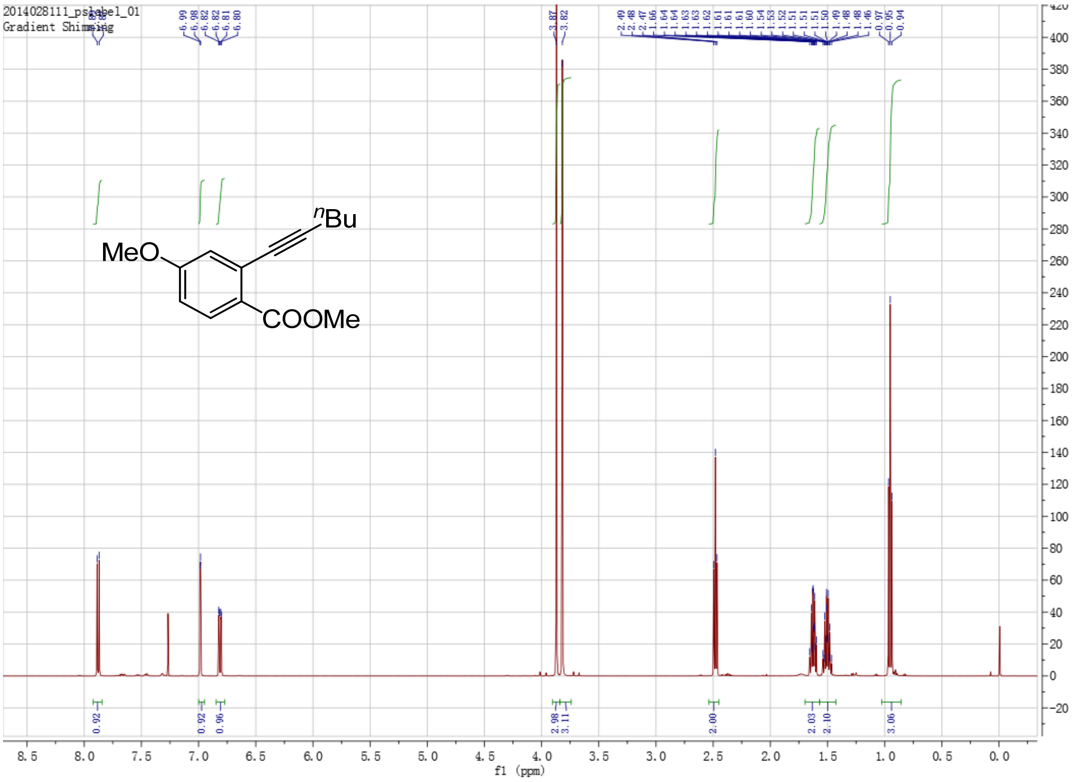

PROTON_01
BzO
O
O
O
O
O
nBu
9.56
1.00
0.95
2.03
1.01
1.96
2.97
3.12
2.07
3.11
3.08
2.94
f1 (ppm)

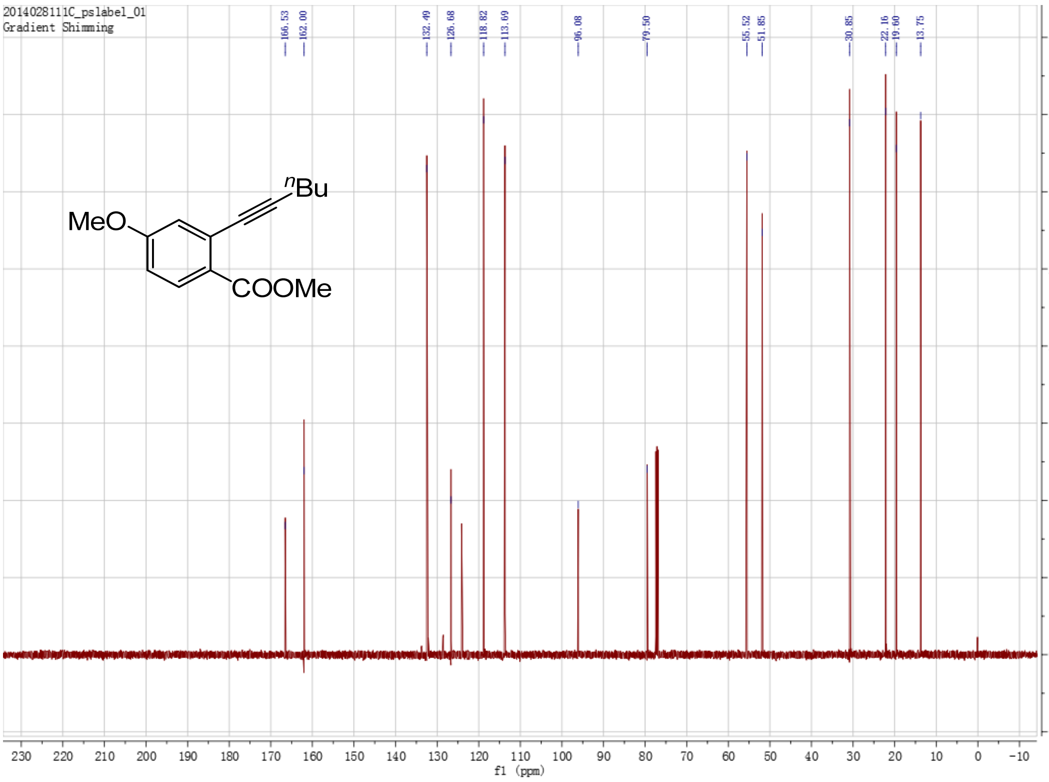

CARBON_01
200913515-98-2
134.36
133.18
132.61
130.65
111.18
96.80
90.99
78.88
76.62
73.88
73.18
71.13
30.52
26.92
25.66
21.91
19.41
18.26
13.51
BzO
O
O
O
O
nBu
f1 (ppm)


gCOSY_01
200913515-98-2
H4, H3
H4, H5
gCOSY
BzO
O
O
O
O
1
3
5
6
nBu
f2 (ppm)
f1 (ppm)

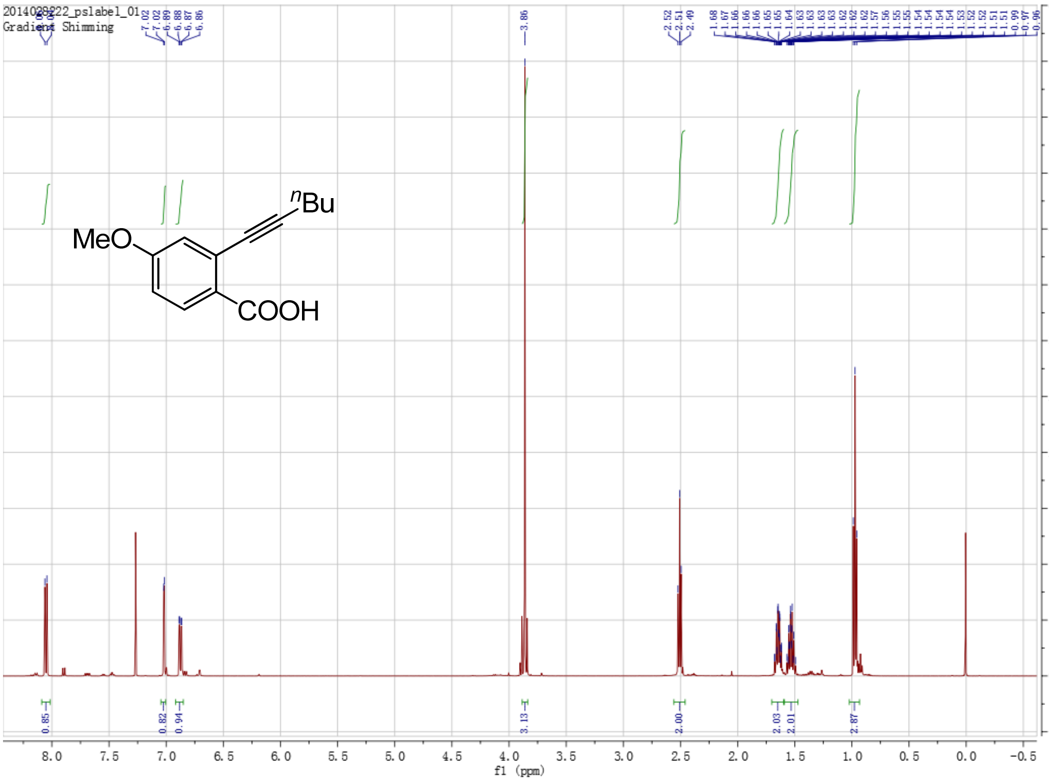


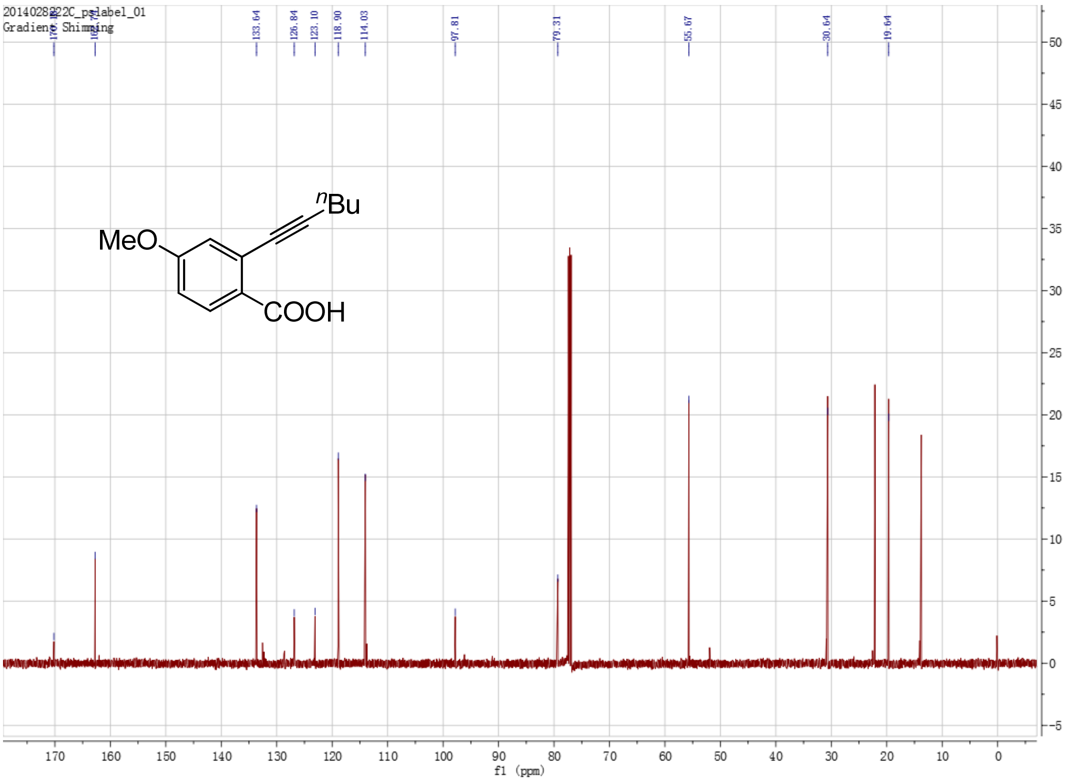
Compound S12:



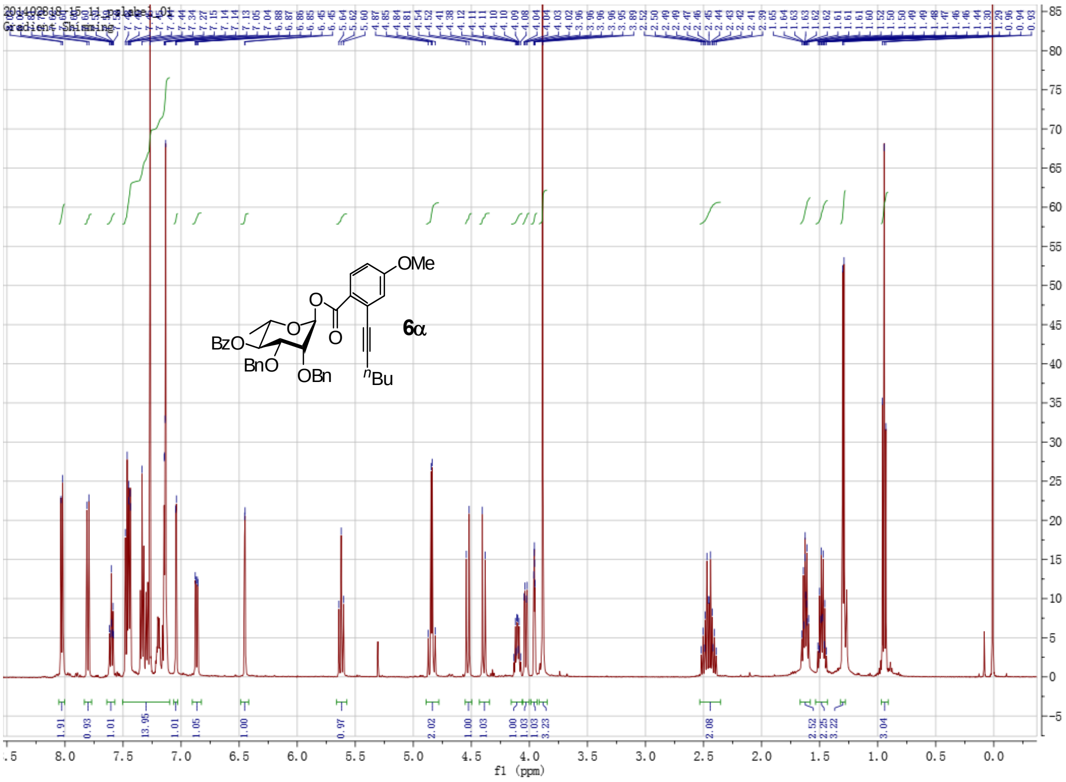


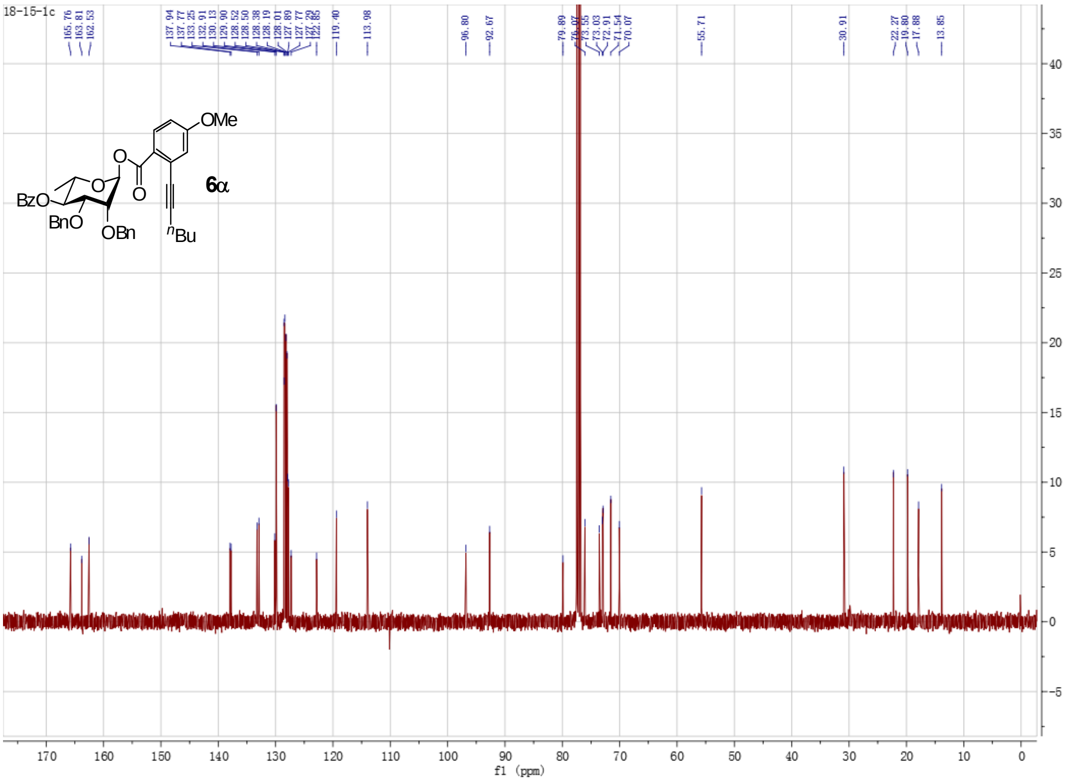
Compound S13:

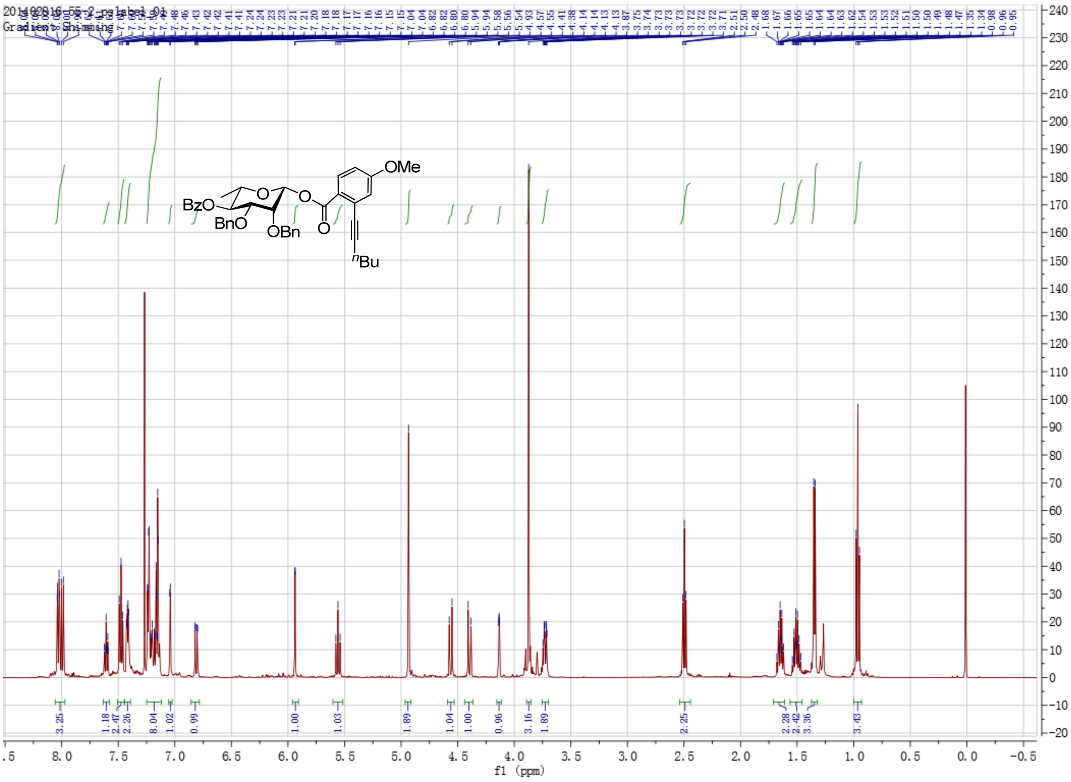


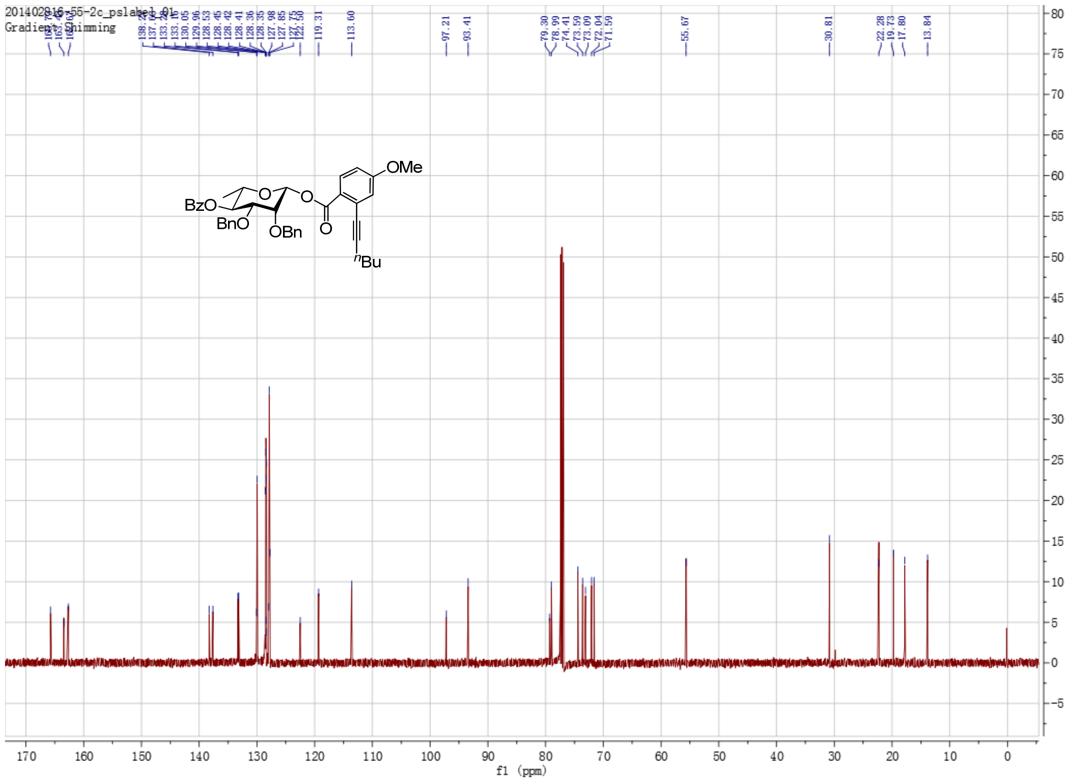


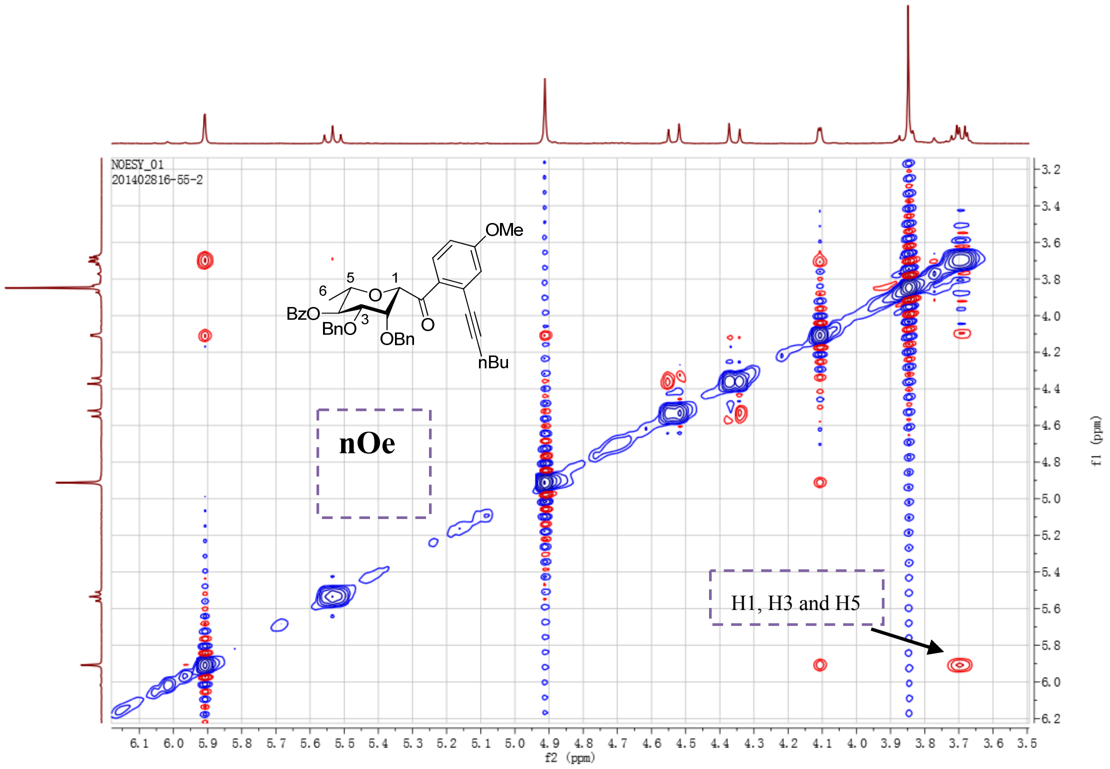
Compounds 6 and 6β:



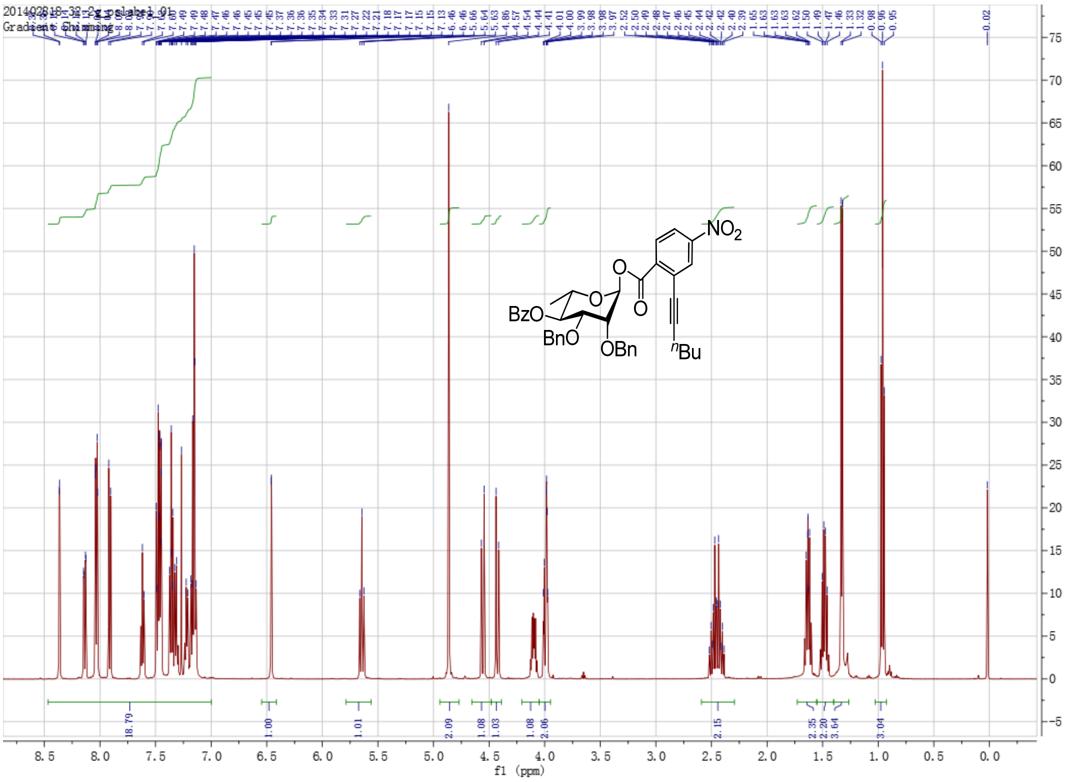

18-15-1c
165.76
163.81
162.53
137.94
137.77
133.25
132.91
130.13
129.90
128.52
128.50
128.38
128.19
128.01
127.89
127.77
127.29
122.85
119.40
113.98
96.80
92.67
79.89
76.97
73.55
73.03
72.91
71.54
70.07
55.71
30.91
22.27
19.80
17.88
13.85
OMe
O
O
O
BzO
BnO
OBn
O
6α
ⁿBu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
40
35
30
25
20
15
10
5
0
-5

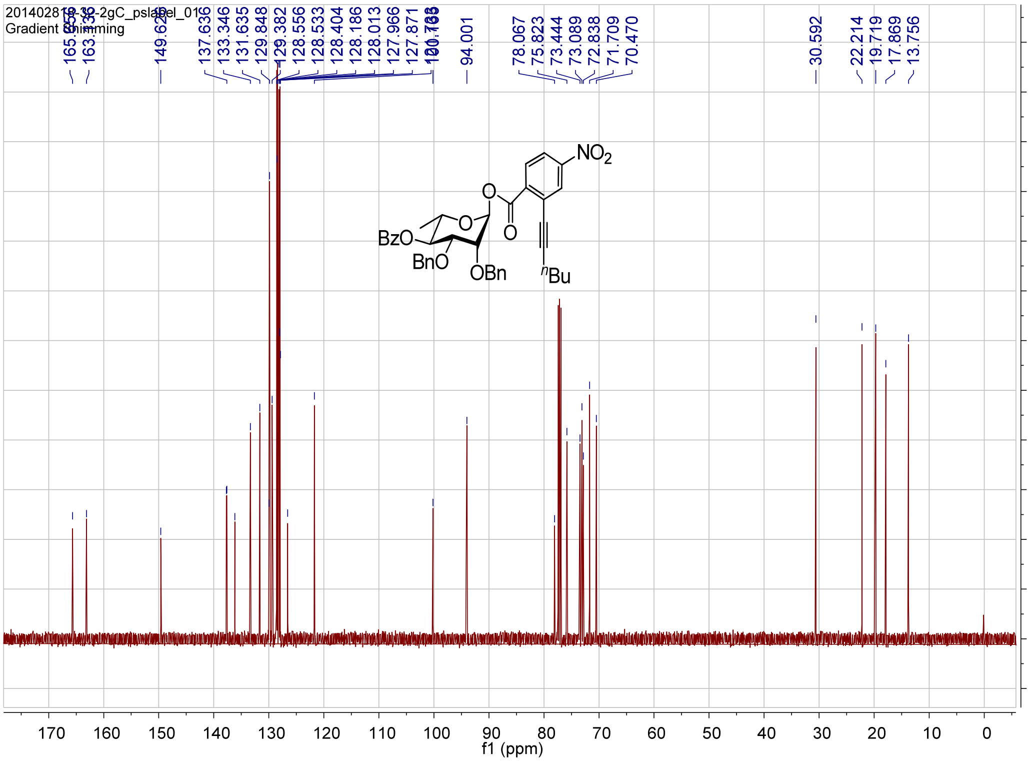

20140816-55-2_palabel_01
Gradient Shimming
7.48
7.46
7.43
7.42
7.42
7.41
7.41
7.24
7.24
7.23
7.23
7.21
7.21
7.20
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.04
7.04
6.82
6.82
6.80
6.80
5.94
5.94
5.58
5.56
5.54
4.93
4.57
4.55
4.41
4.38
4.14
4.14
4.13
4.13
3.87
3.75
3.74
3.73
3.73
3.73
3.72
3.72
3.72
3.71
2.51
2.50
2.48
1.68
1.67
1.66
1.65
1.65
1.64
1.64
1.63
1.62
1.54
1.53
1.53
1.52
1.51
1.50
1.50
1.49
1.48
1.47
1.35
1.34
0.98
0.96
0.95
OMe
BzO
O
O
BnO
OBn
O
ⁿBu
3.25
1.18
2.47
2.26
8.04
1.02
0.99
1.00
1.03
1.89
1.04
1.00
0.96
3.16
1.89
2.25
2.28
2.42
3.36
3.43
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

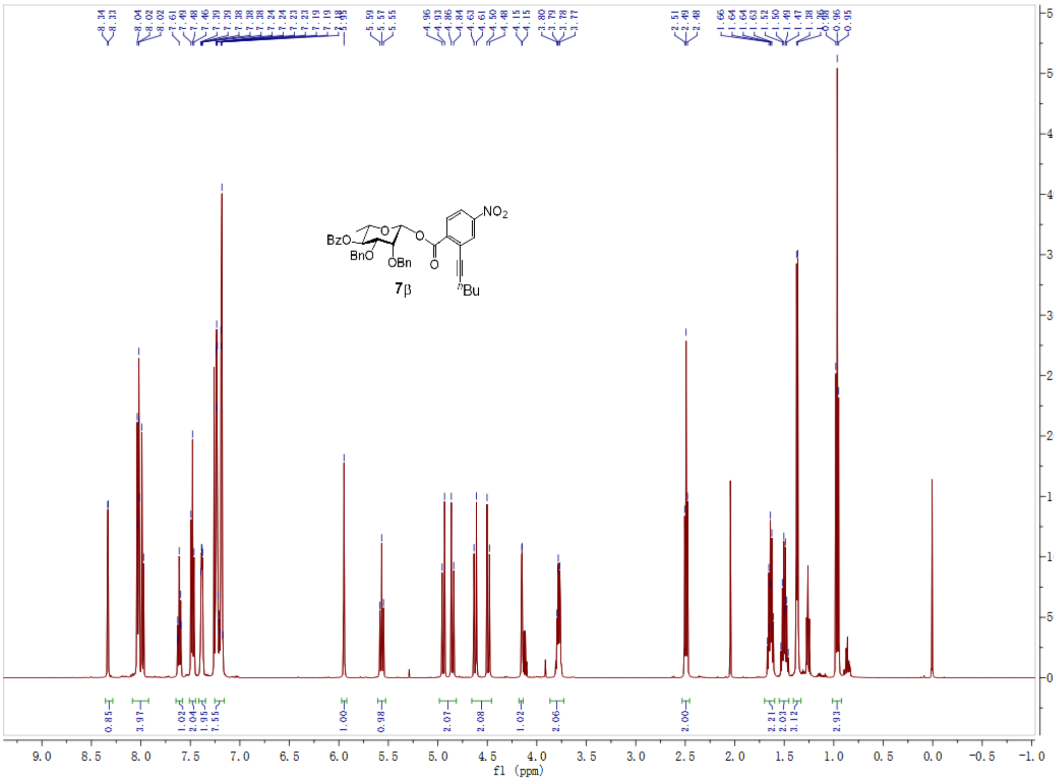

201402816-55-2c_pslabel_01
Gradient Shimming
138.22
137.65
133.28
133.15
130.05
129.96
128.53
128.45
128.42
128.41
128.36
128.35
127.98
127.85
127.75
122.50
119.31
113.60
97.21
93.41
79.30
78.99
74.41
73.59
73.09
72.04
71.59
55.67
30.81
22.28
19.73
17.80
13.84
OMe
BzO
O
O
BnO
OBn
O
^{n}Bu
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5

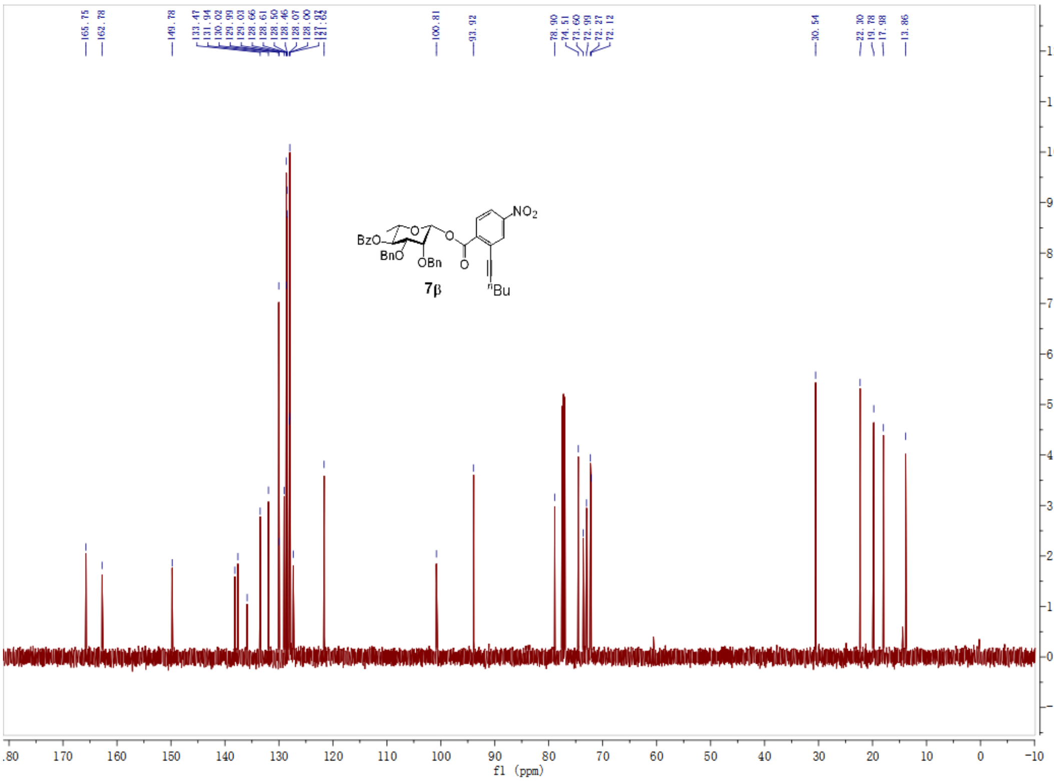

NOESY_01
201402816-55-2
OMe
5
1
6
O
BzO
3
BnO
OBn
O
nBu
nOe
H1, H3 and H5
f2 (ppm)
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
f1 (ppm)
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2

Compounds 7 and 7β:

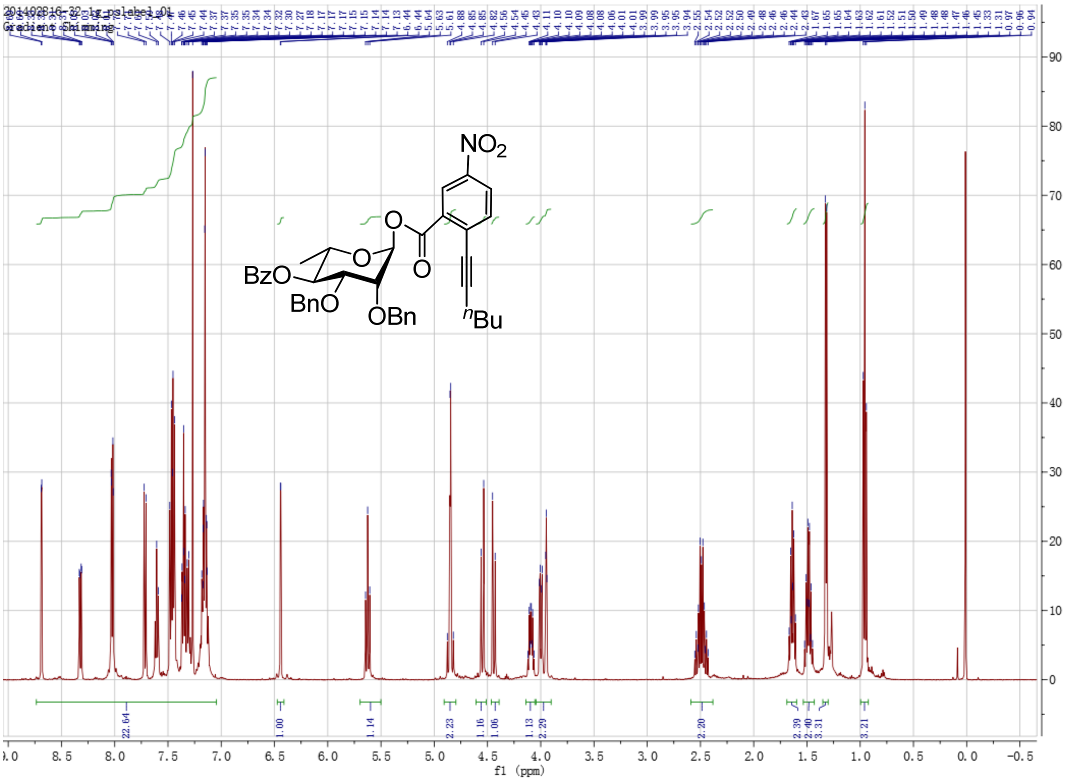


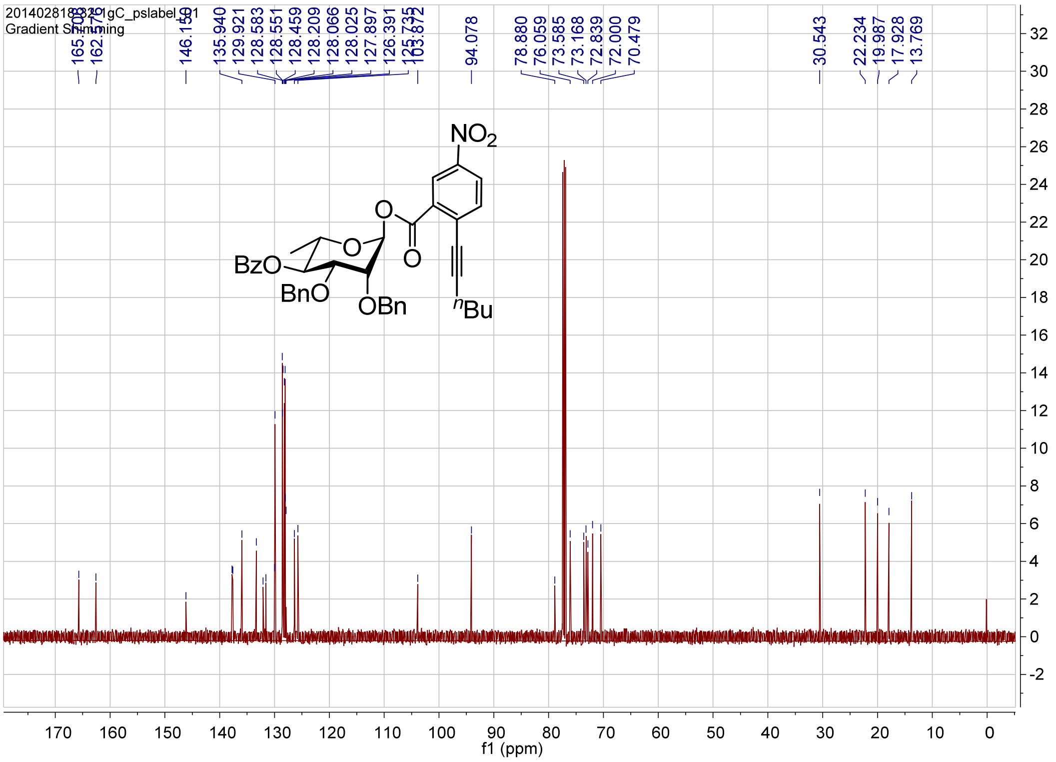


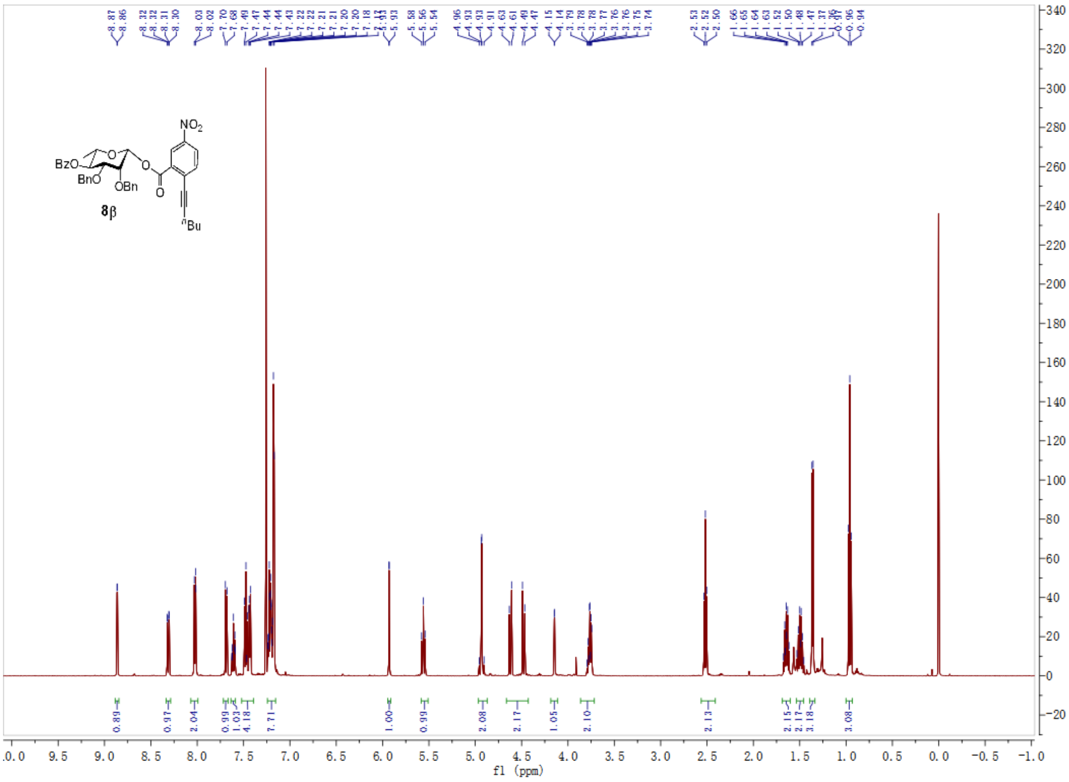

8.34
8.33
8.04
8.02
8.02
7.61
7.49
7.48
7.46
7.39
7.39
7.38
7.38
7.38
7.24
7.24
7.23
7.23
7.19
7.19
7.18
5.95
5.59
5.57
5.55
4.96
4.93
4.86
4.84
4.63
4.61
4.50
4.48
4.15
4.15
3.80
3.79
3.78
3.77
2.51
2.49
2.48
1.66
1.64
1.64
1.63
1.52
1.50
1.49
1.47
1.38
1.36
0.98
0.96
0.95
BzO
BnO
O
OBn
O
O
NO2
nBu
7β
0.85
3.97
1.02
2.04
1.95
7.55
1.00
0.98
2.07
2.08
1.02
2.06
2.00
2.21
2.03
3.12
2.93
550
500
450
400
350
300
250
200
150
100
50
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

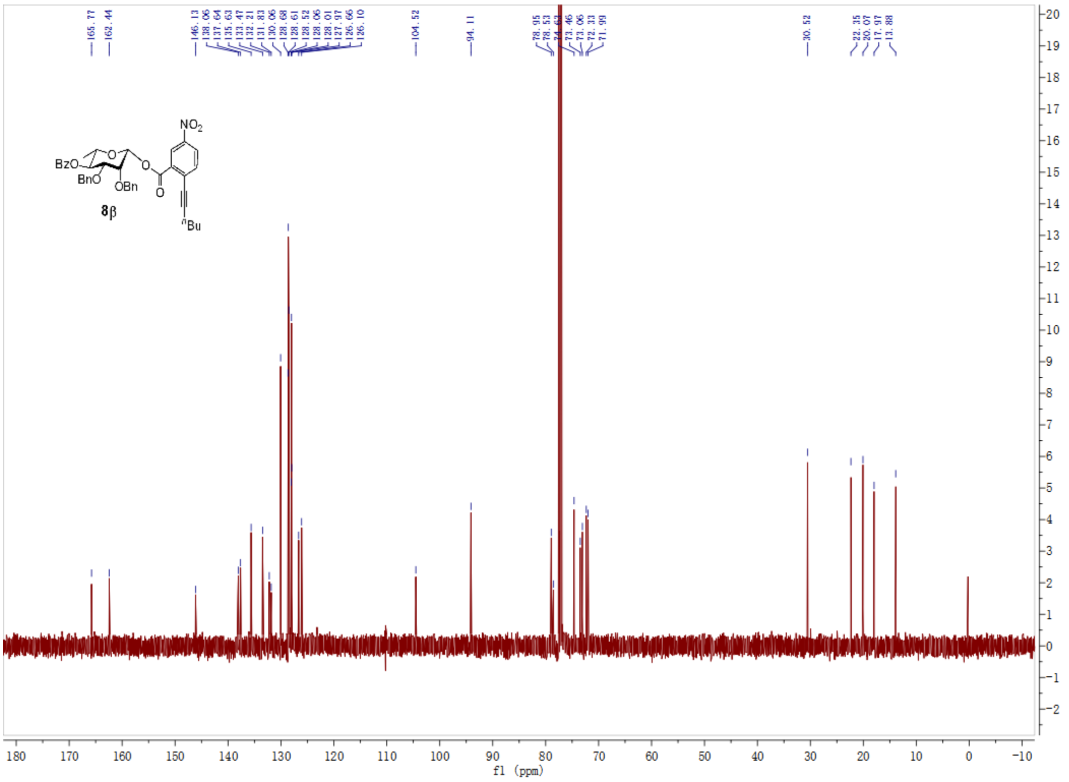

165.75
162.78
149.78
133.47
131.94
130.02
129.99
129.03
128.66
128.61
128.50
128.46
128.07
128.00
127.92
121.82
100.81
93.92
78.90
74.51
73.60
72.99
72.27
72.12
30.54
22.30
19.78
17.98
13.86
BzO
BnO
O
OBn
O
O
NO2
nBu
7β
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compounds 8 and 8β:

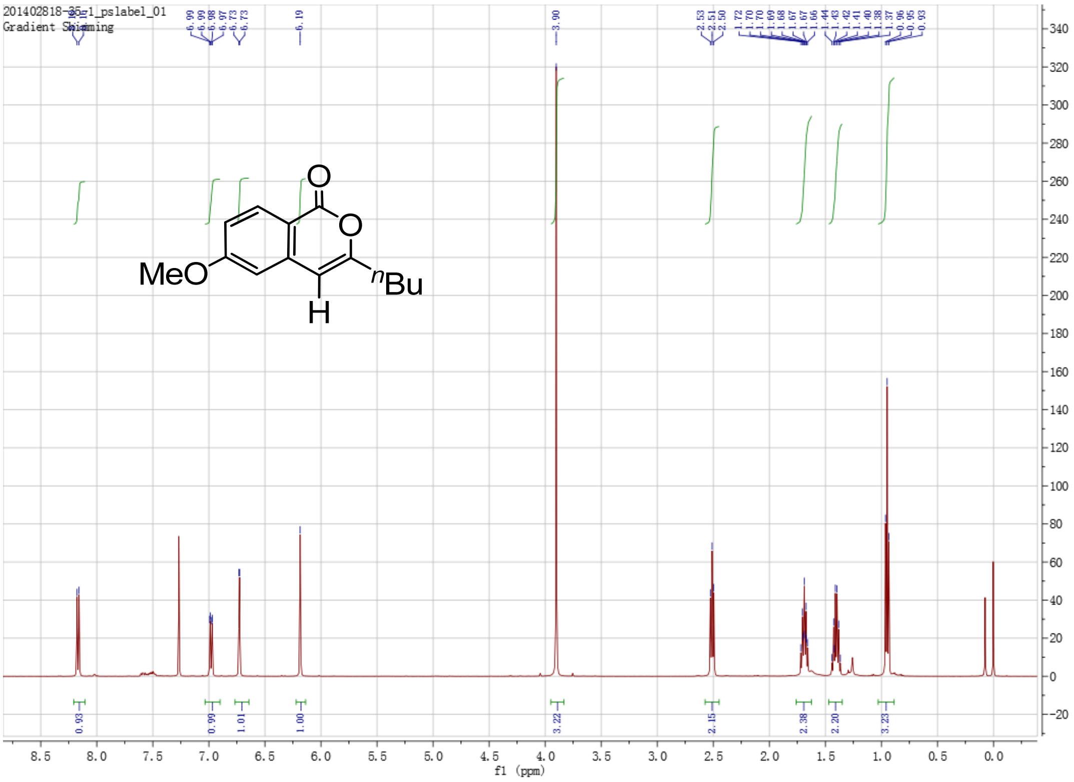


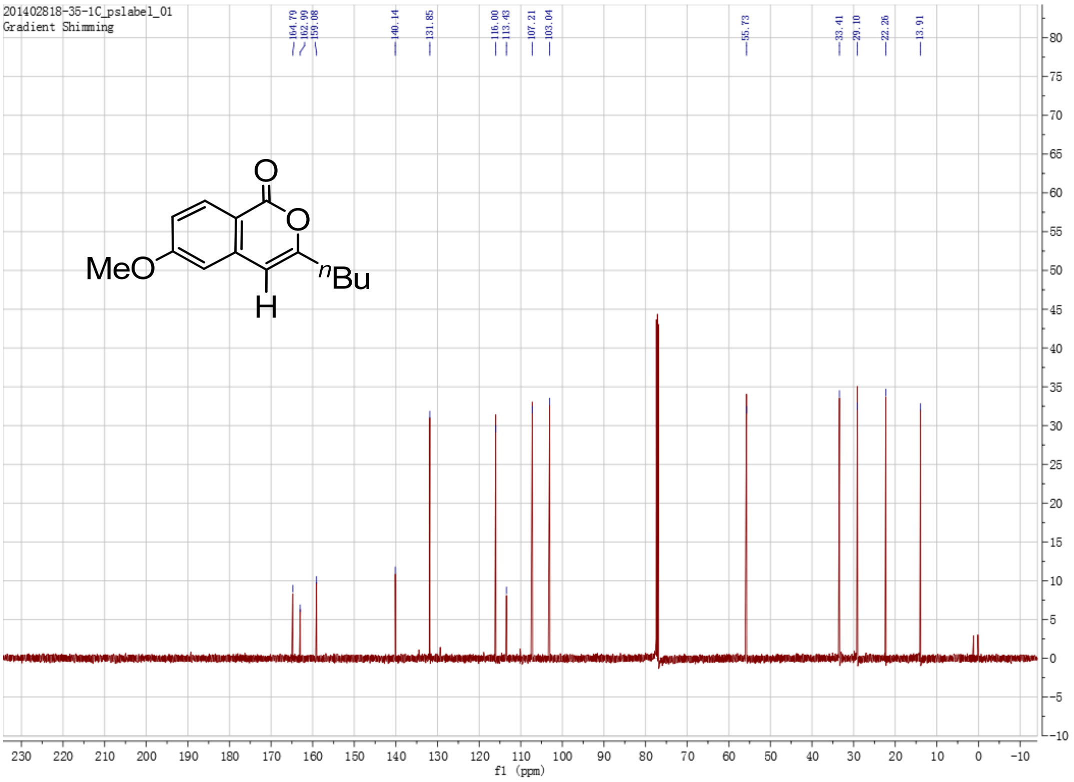



8.87
8.86
8.32
8.32
8.31
8.30
8.03
8.02
7.70
7.68
7.49
7.47
7.44
7.44
7.43
7.22
7.22
7.21
7.21
7.20
7.20
7.18
7.13
5.93
5.58
5.56
5.54
4.96
4.93
4.93
4.91
4.63
4.61
4.49
4.47
4.15
4.14
3.79
3.78
3.78
3.77
3.76
3.76
3.75
3.74
2.53
2.52
2.50
1.66
1.65
1.64
1.63
1.52
1.50
1.48
1.47
1.37
1.36
0.97
0.96
0.94
NO2
BzO
O
O
BnO
OBn
O
8β
nBu
0.89
0.97
2.04
0.99
1.03
4.18
7.71
1.00
0.99
2.08
2.17
1.05
2.10
2.13
2.15
2.17
3.18
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

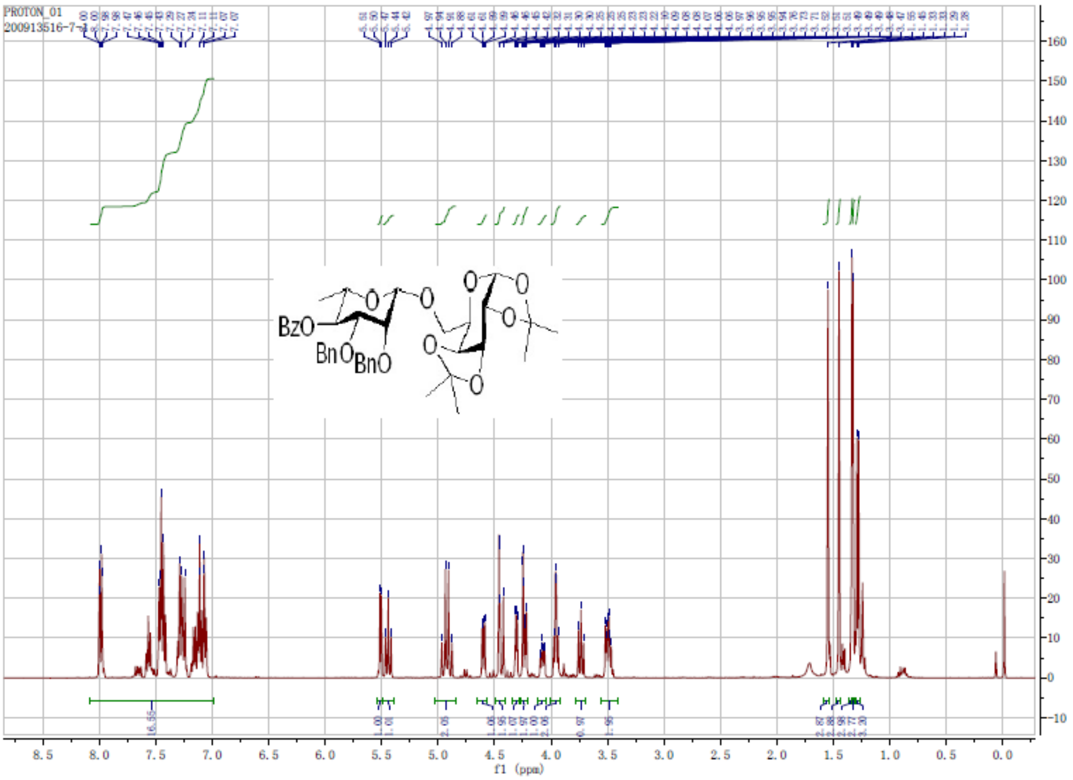

165.77
162.44
146.13
138.06
137.64
135.63
133.47
132.21
131.83
130.06
128.68
128.61
128.52
128.06
128.01
127.97
126.66
126.10
104.52
94.11
78.95
78.53
74.63
73.46
73.06
72.33
71.99
30.52
22.35
20.07
17.97
13.88
NO2
BzO
O
O
BnO
OBn
O
8β
nBu
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2

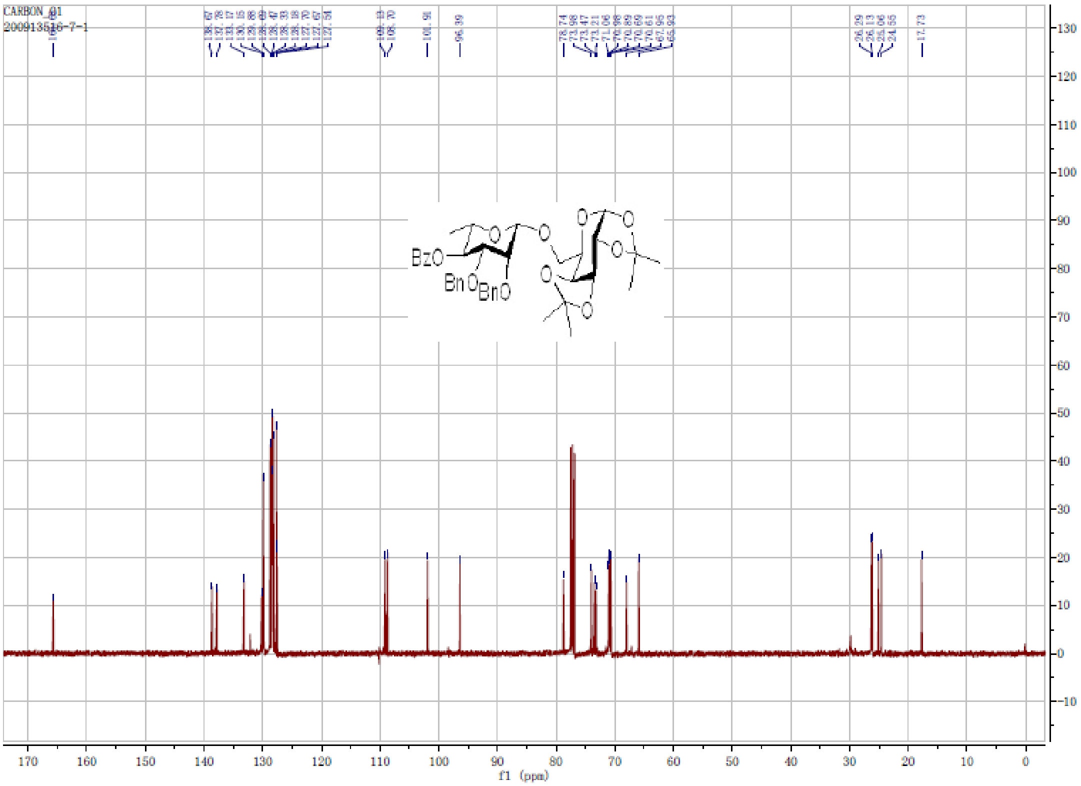
Compound 6H:

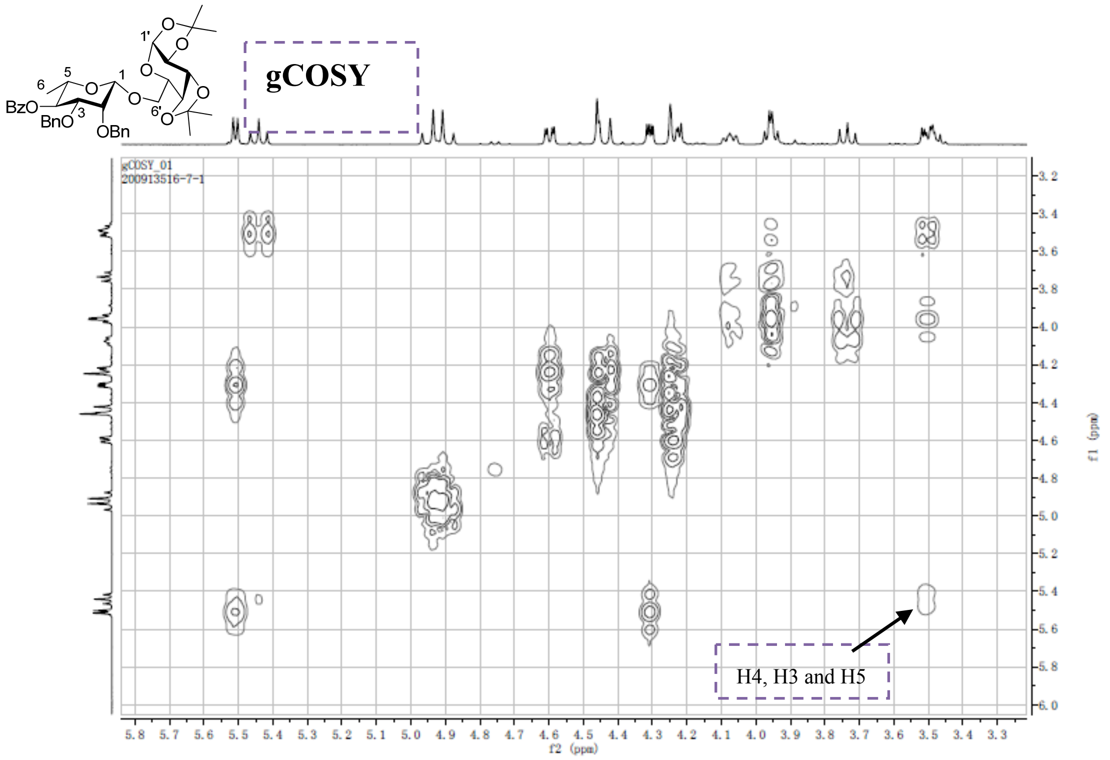

201402818-35-1_pslabel_01
Gradient Shimming
6.99
6.99
6.98
6.97
6.73
6.73
6.19
3.90
2.53
2.51
2.50
1.72
1.70
1.70
1.69
1.68
1.67
1.67
1.66
1.44
1.43
1.42
1.41
1.40
1.38
1.37
0.96
0.95
0.93
MeO
O
O
nBu
H
0.93
0.99
1.01
1.00
3.22
2.15
2.38
2.20
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
−20

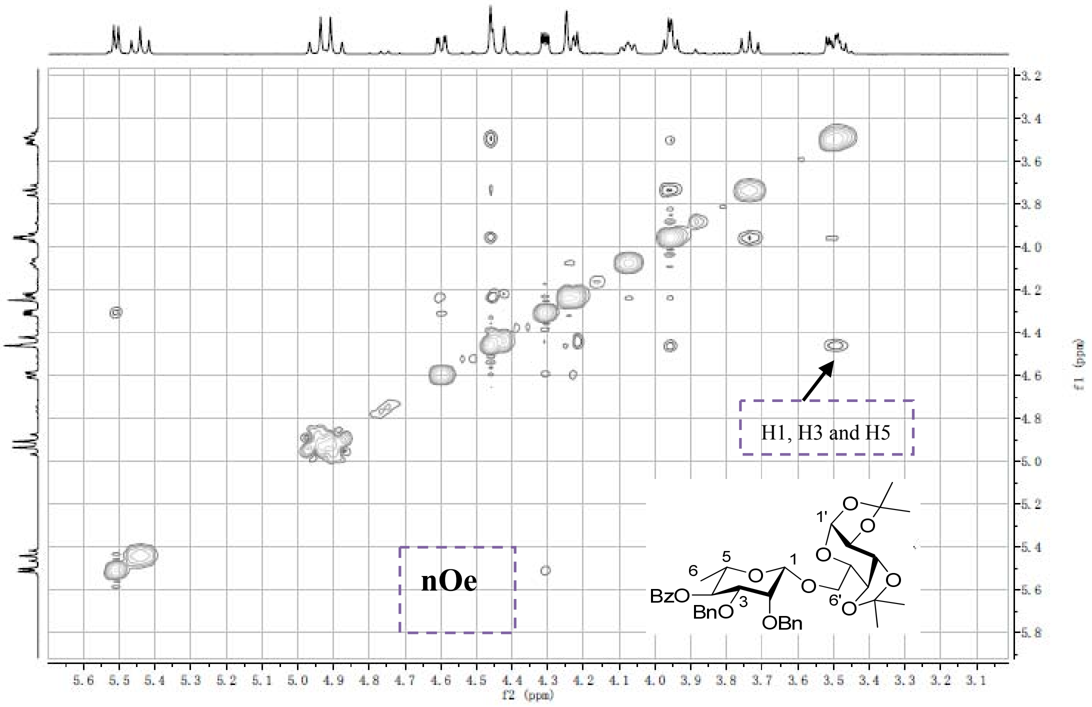

201402818-35-1C_pslabel_01
Gradient Shimming
164.79
162.99
159.08
140.14
131.85
116.00
113.43
107.21
103.04
55.73
33.41
29.10
22.26
13.91
MeO
O
O
nBu
H
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
−10

Compound 11β:

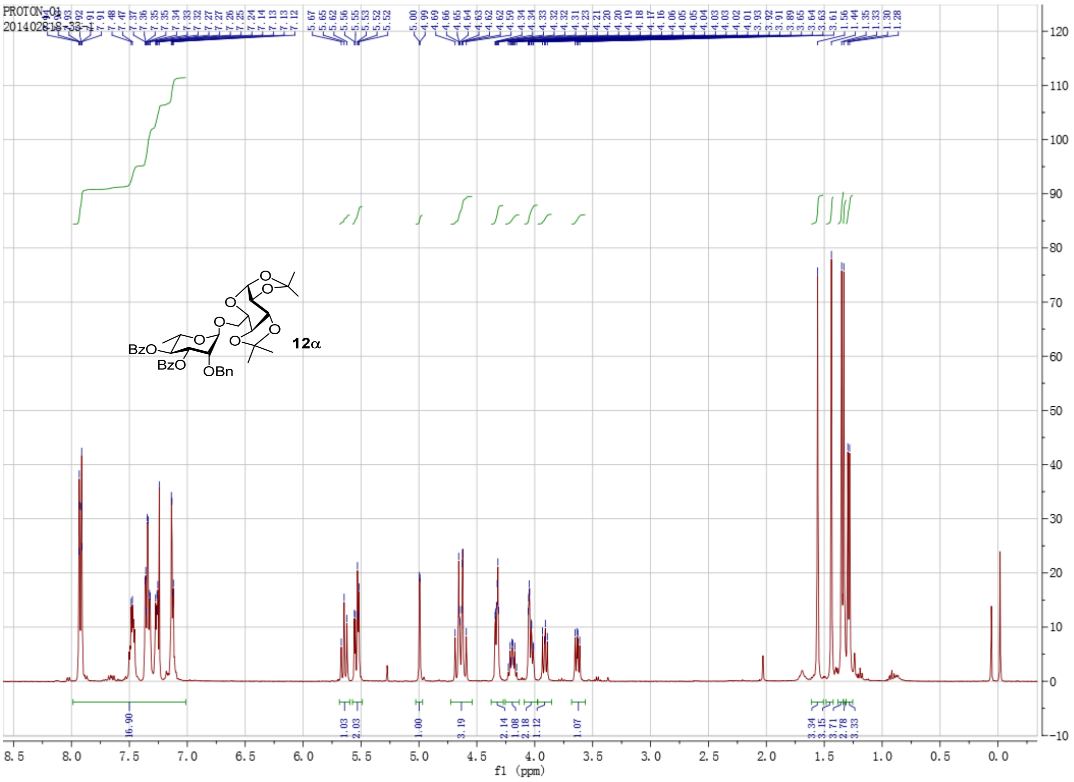


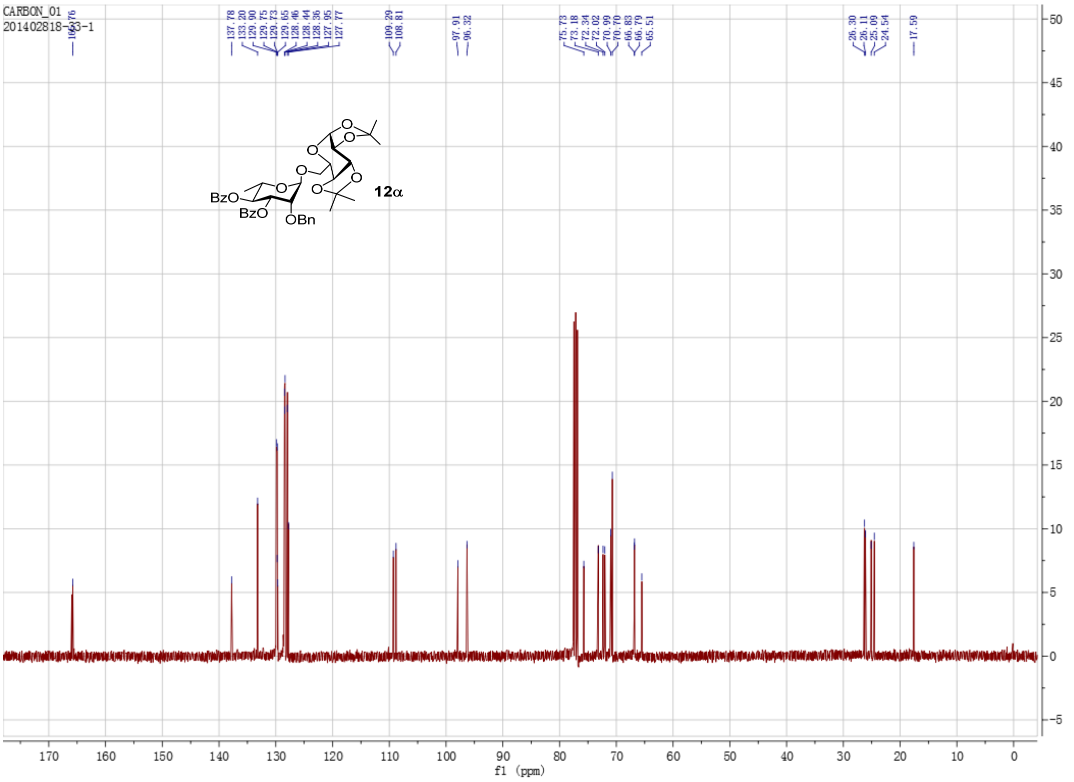


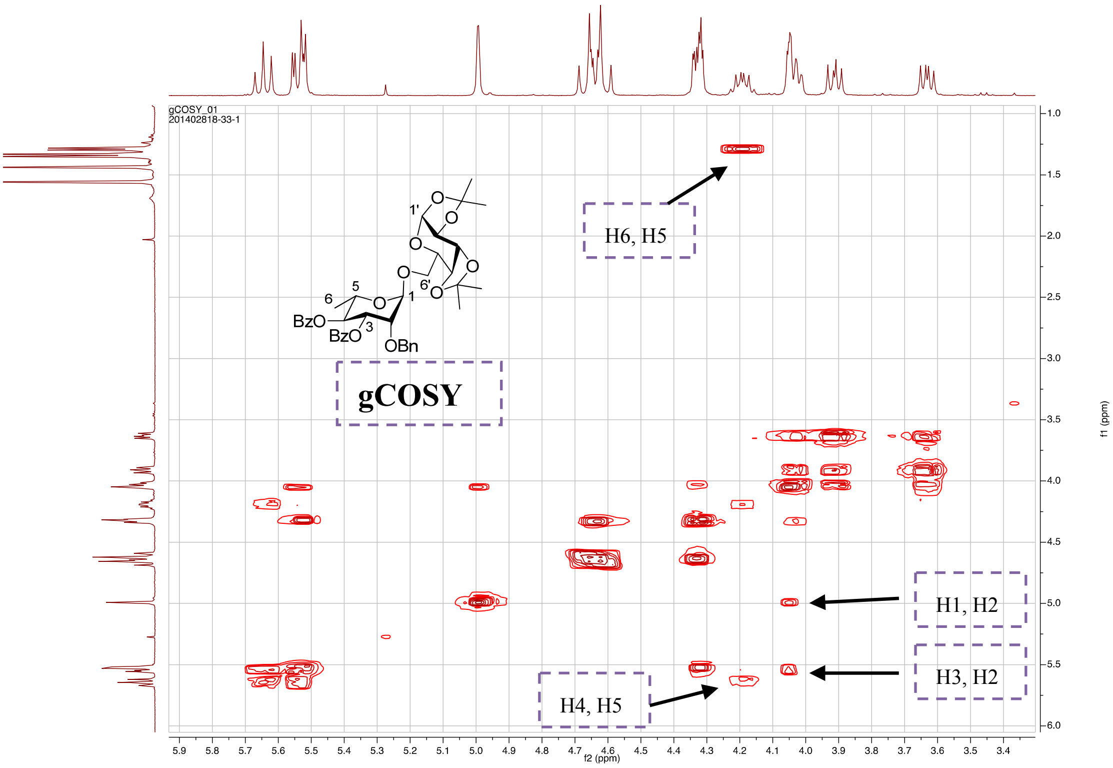

gCOSY
1'
5
6
1
BzO
BnO
3
OBn
6'
O
gCOSY_01
200913516-7-1
H4, H3 and H5
f2 (ppm)
f1 (ppm)
5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3
3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0

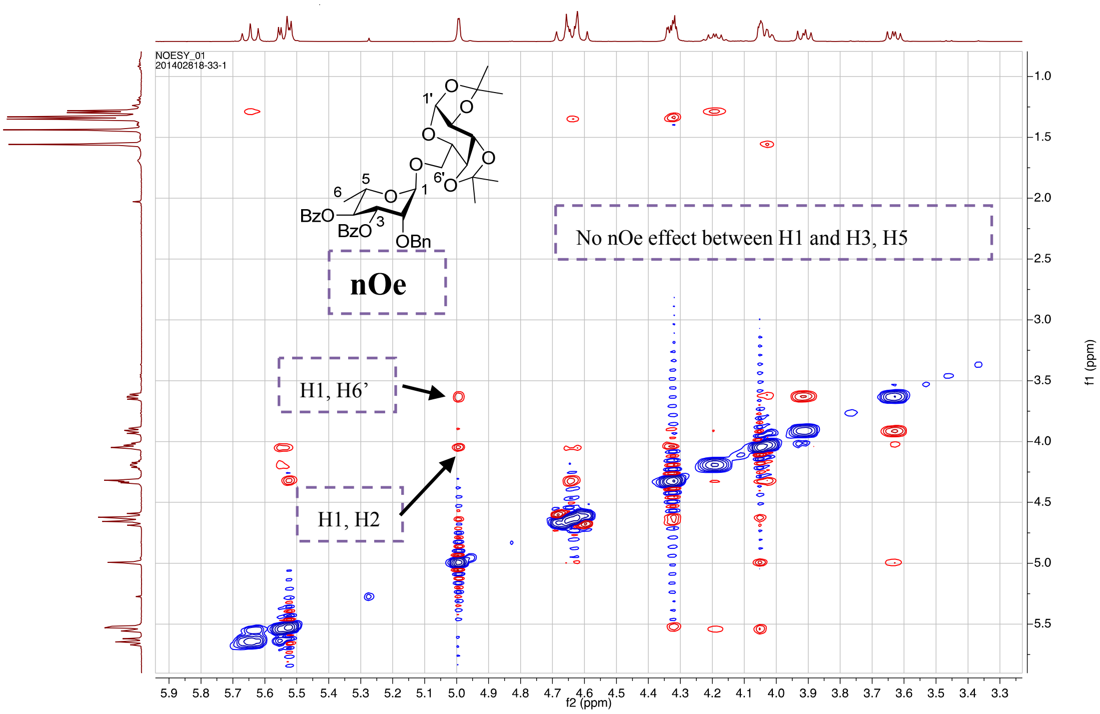

nOe
H1, H3 and H5
1'
5
6
1
BzO
BnO
3
OBn
6'
O
f2 (ppm)
f1 (ppm)
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8

Compound 12α:

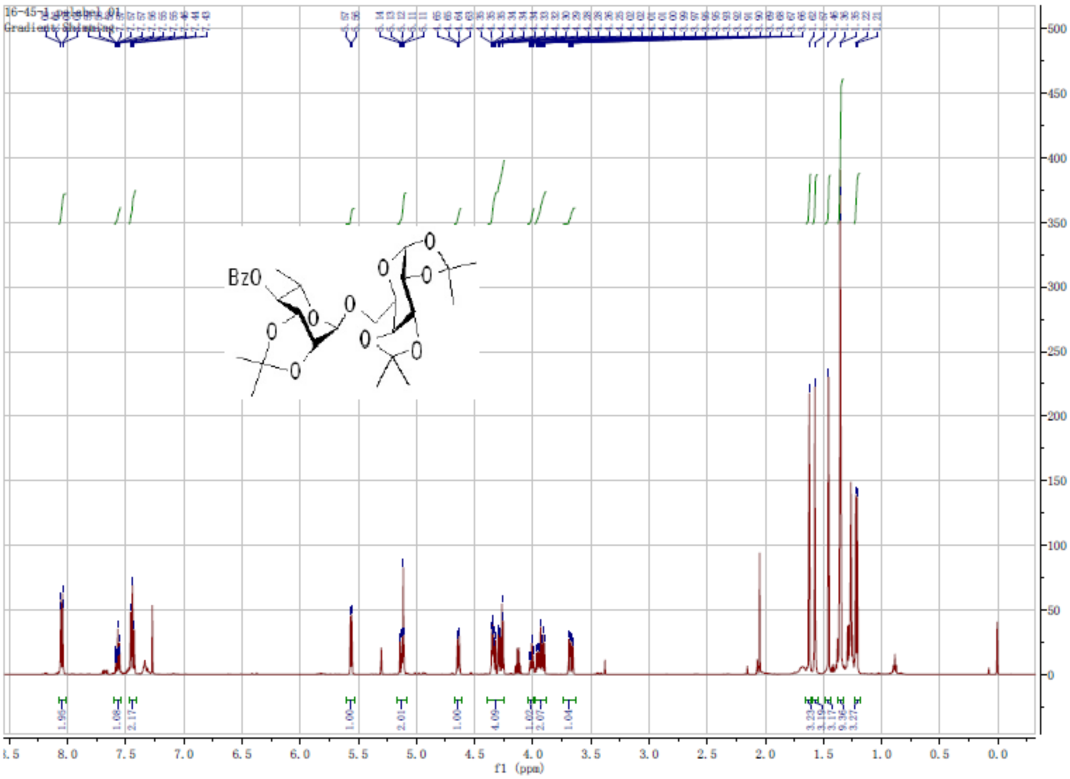


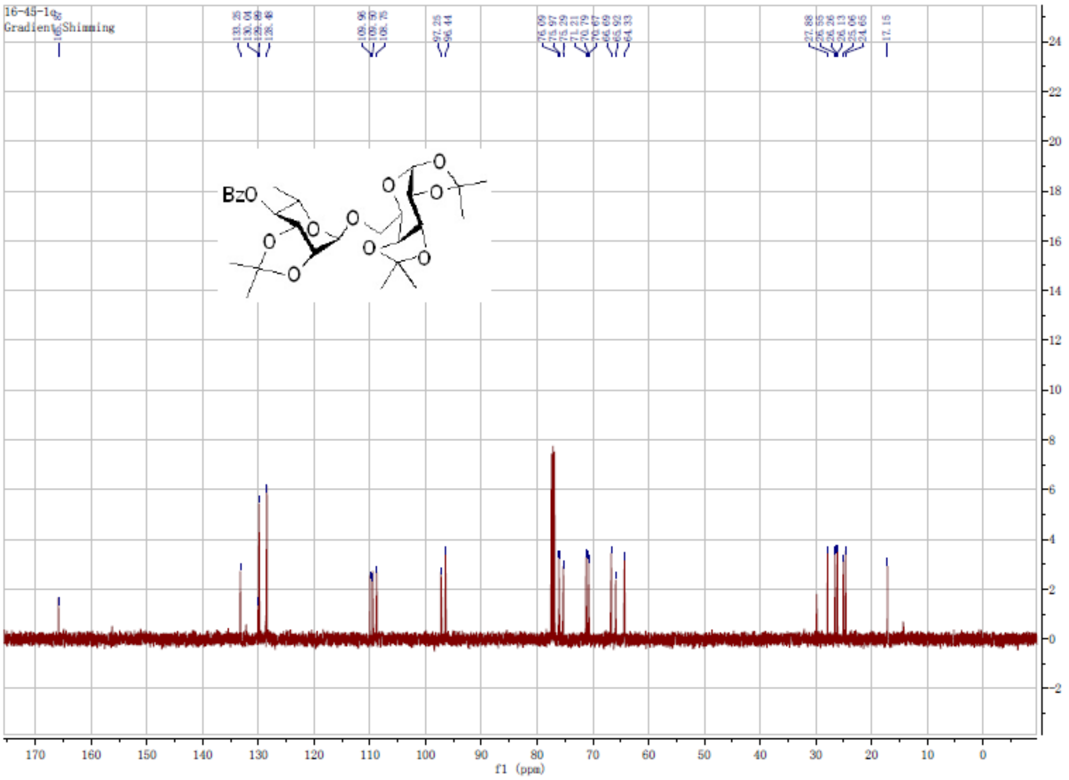


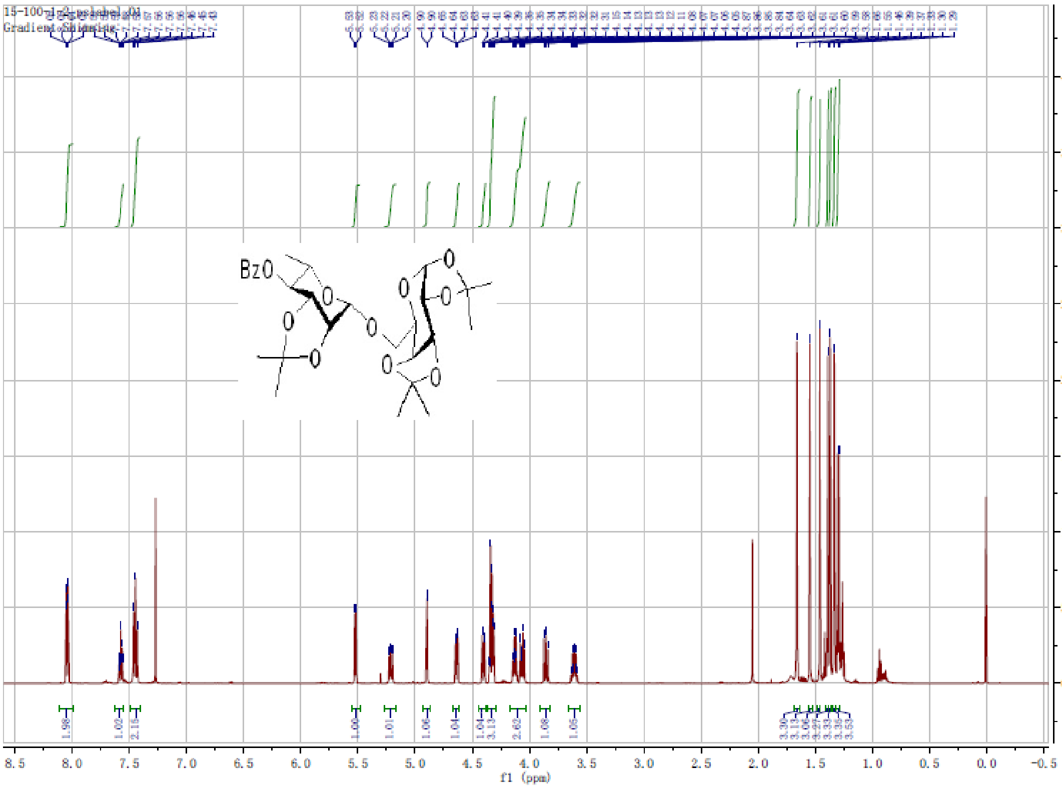

gCOSY_01
201402818-33-1
1'
6'
1
5
6
3
BzO
BzO
OBn
O
gCOSY
H6, H5
H1, H2
H3, H2
H4, H5
f2 (ppm)
f1 (ppm)

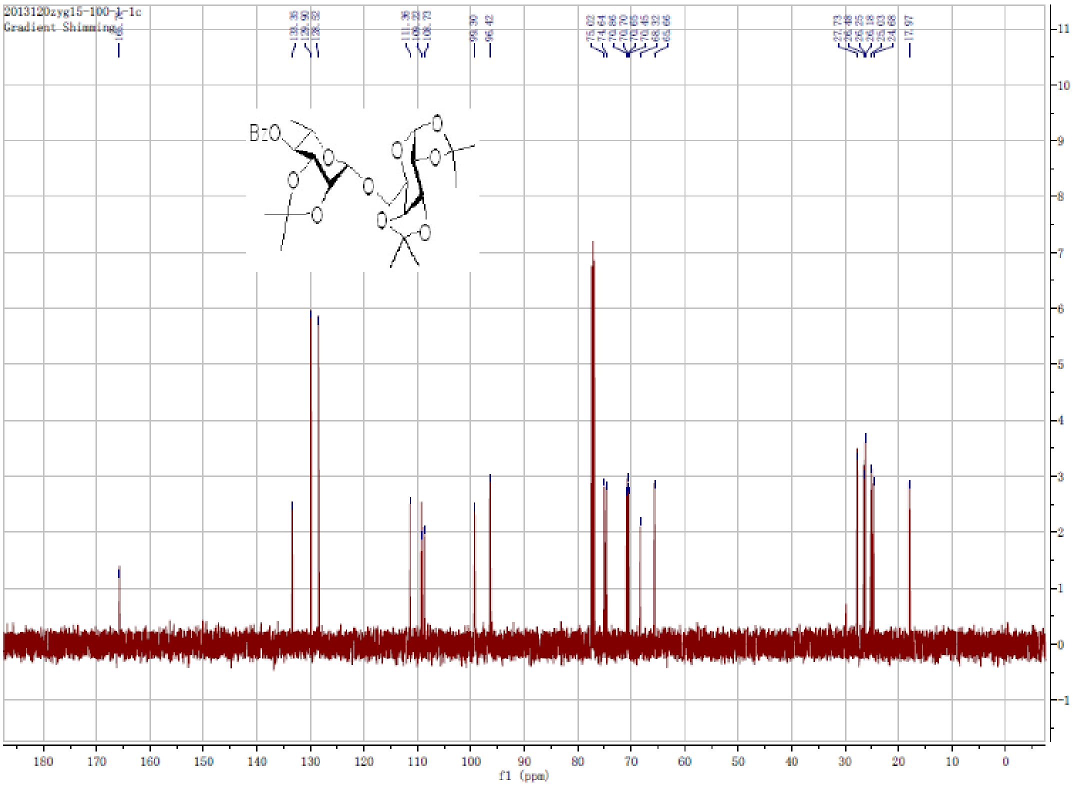

NOESY_01
201402818-33-1
1'
6'
1
5
6
3
BzO
BzO
OBn
O
nOe
No nOe effect between H1 and H3, H5
H1, H6'
H1, H2
f2 (ppm)
f1 (ppm)

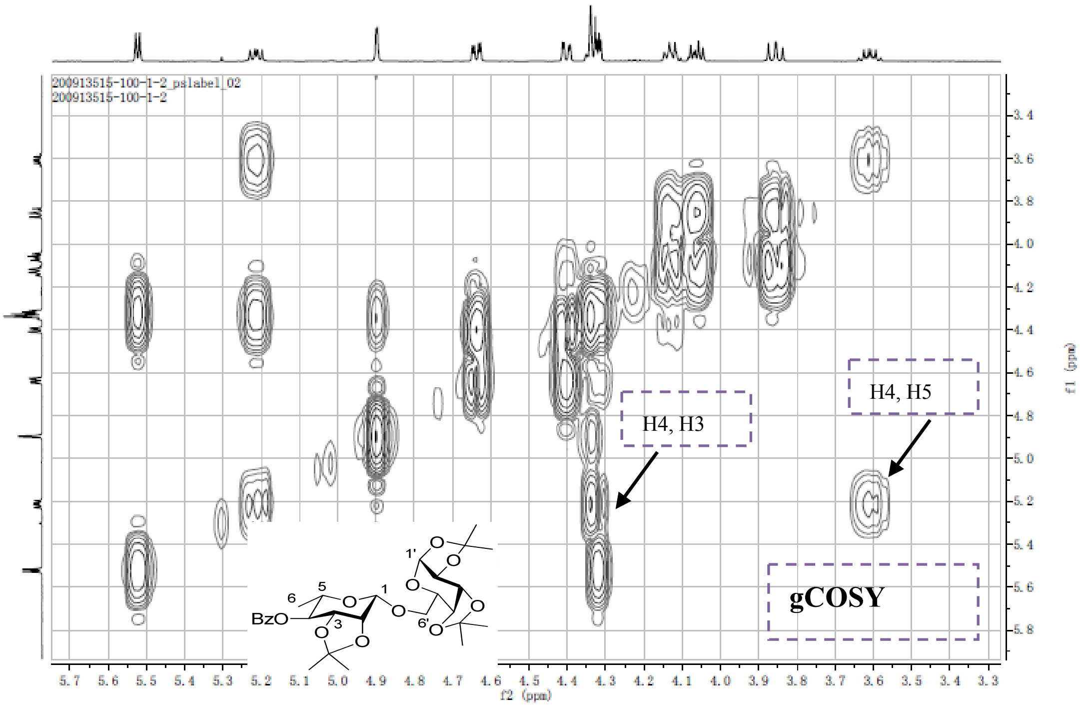
Compounds 13α and 13β:

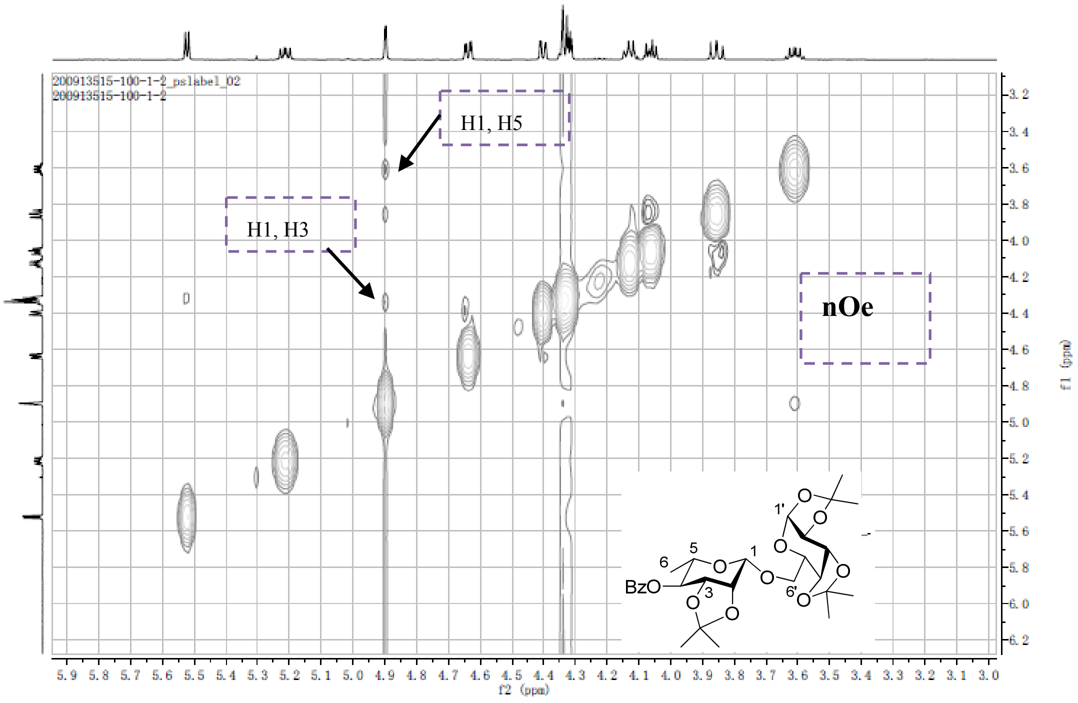




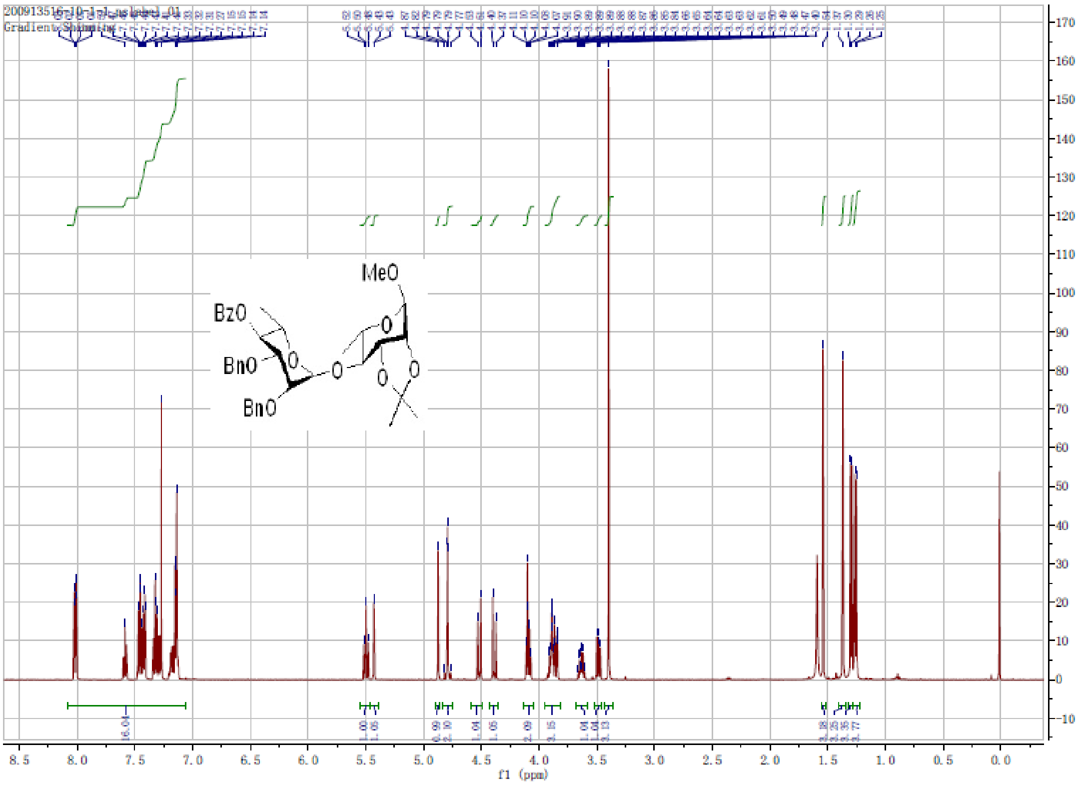

15-100-1-2-proton1.01
Gradient Shimming
BzO
O
1.98
1.02
2.15
1.00
1.01
1.06
1.04
1.04
3.13
2.62
1.08
1.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
400
350
300
250
200
150
100
50
0

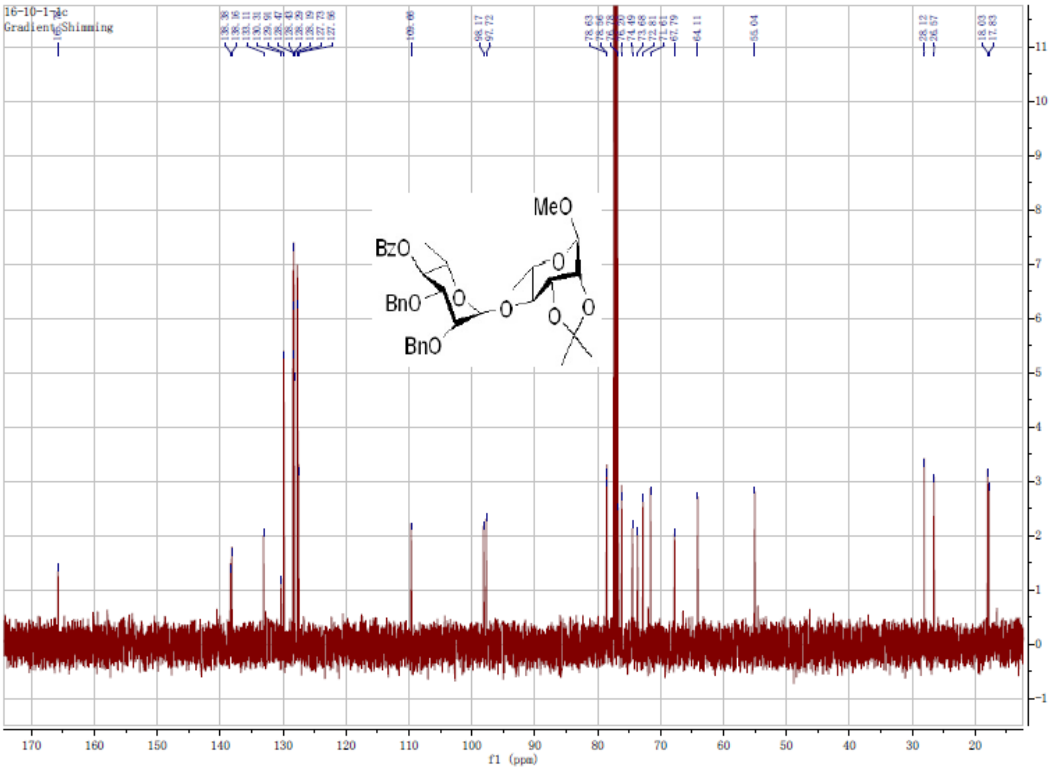

2013120zyg15-100-1-1c
Gradient Shimming
133.35
129.90
128.52
111.36
108.73
99.30
96.42
75.02
74.64
70.86
70.70
70.45
68.32
65.66
27.73
26.25
26.18
25.03
24.68
17.97
BzO
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
11
10
9
8
7
6
5
4
3
2
1
0
-1

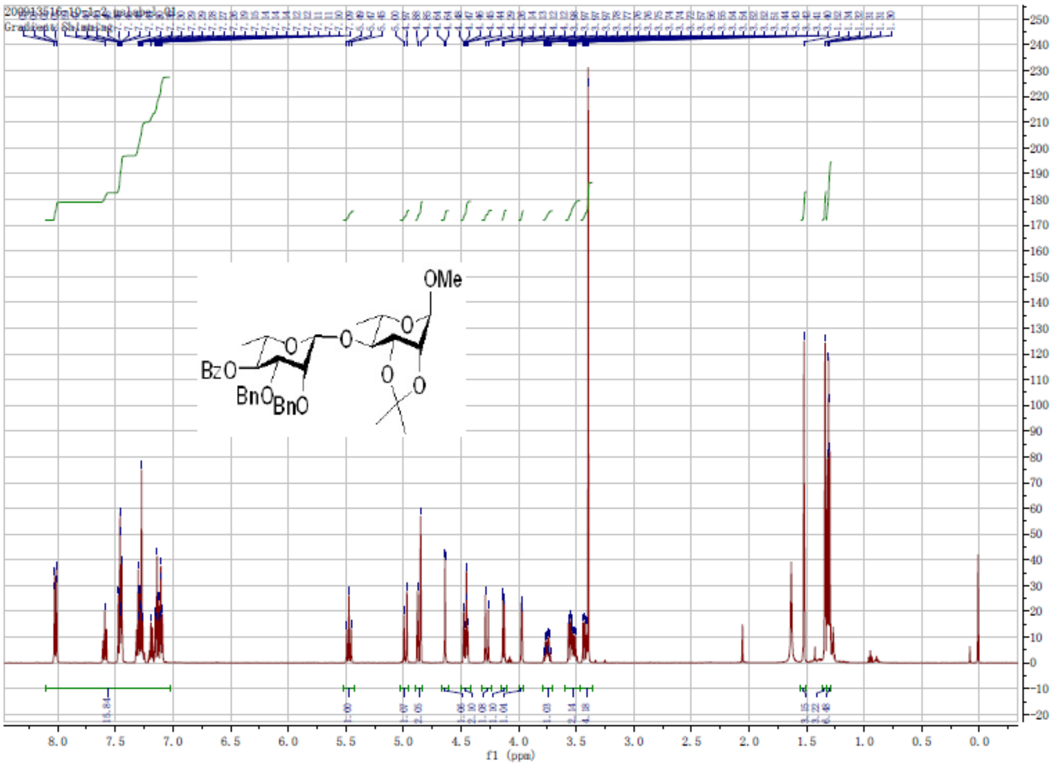

200913515-100-1-2_pslabel_02
200913515-100-1-2
H4, H3
H4, H5
gCOSY
BzO
6
5
3
1
1'
6'
O
f2 (ppm)
f1 (ppm)
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3
3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8

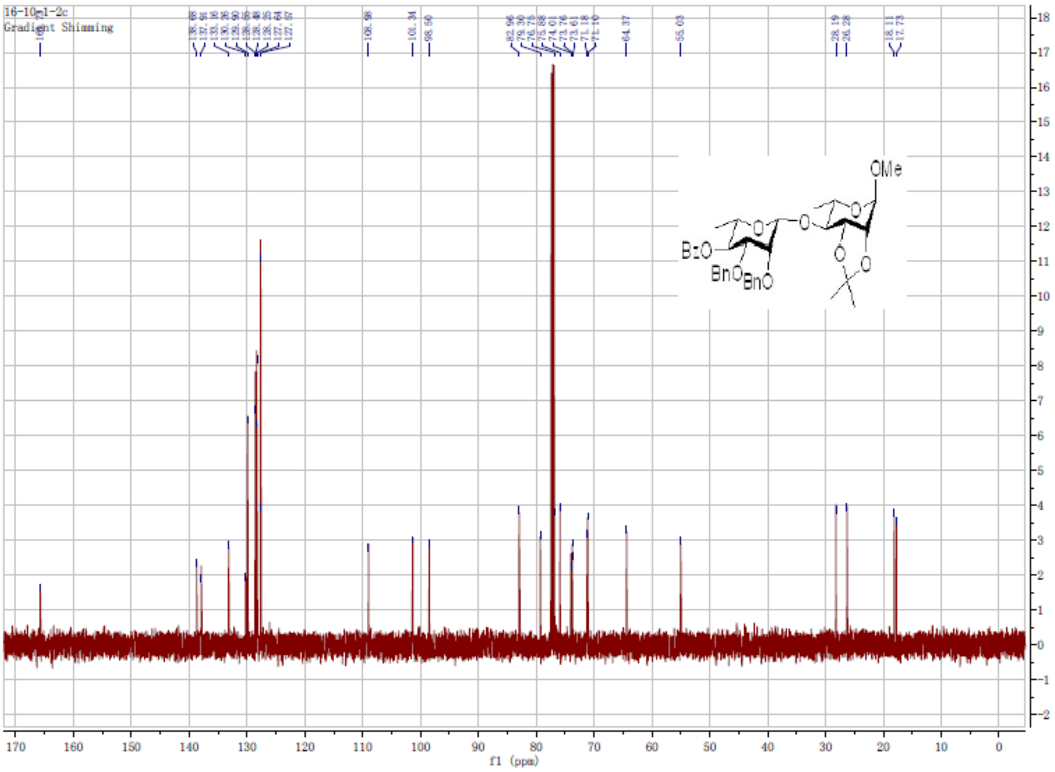

200913515-100-1-2_pslabel_02
200913515-100-1-2
H1, H5
H1, H3
nOe
BzO
6
5
3
1
1'
6'
O
f2 (ppm)
f1 (ppm)
5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2

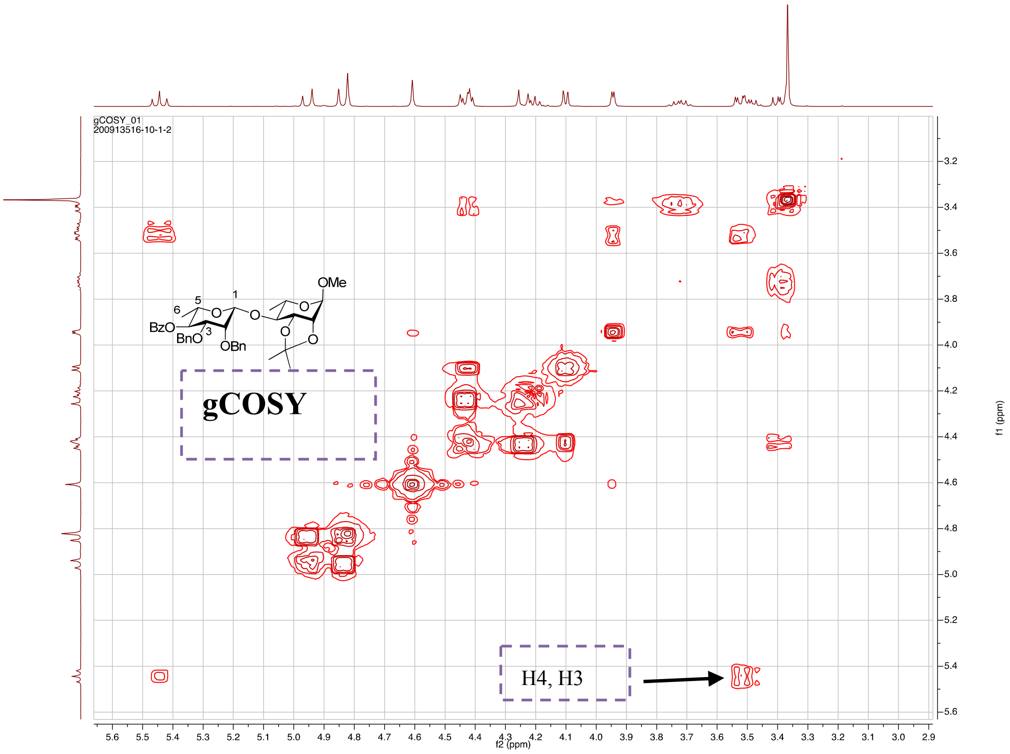
Compounds 14α and 14β:

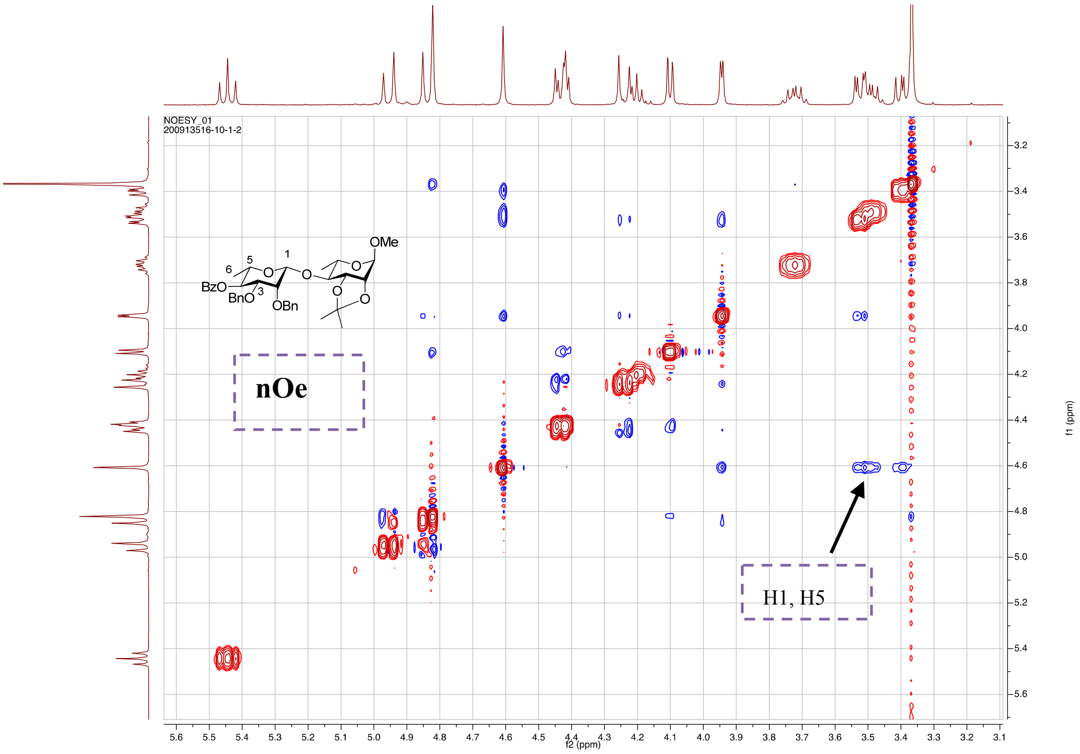




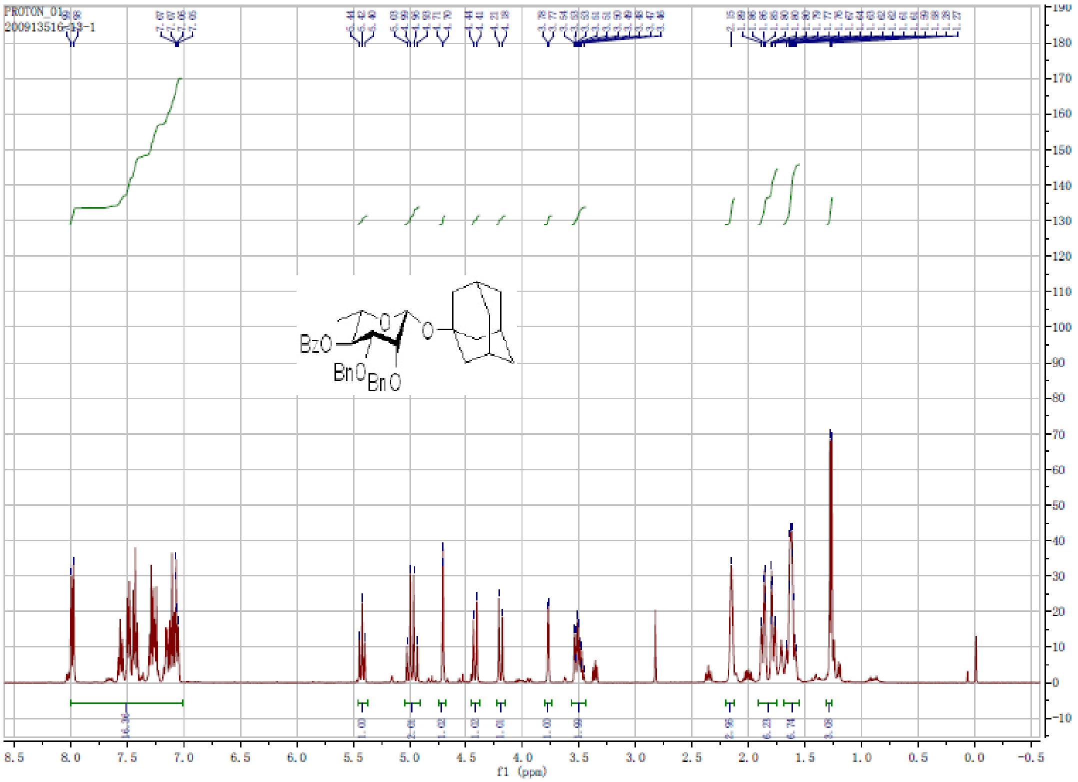

Gradient Shimming
OMe
BzO
BnO
BnO
O
15.84
1.00
1.07
2.05
1.06
2.10
1.08
1.10
1.04
1.03
2.14
4.18
3.15
3.22
6.48
f1 (ppm)

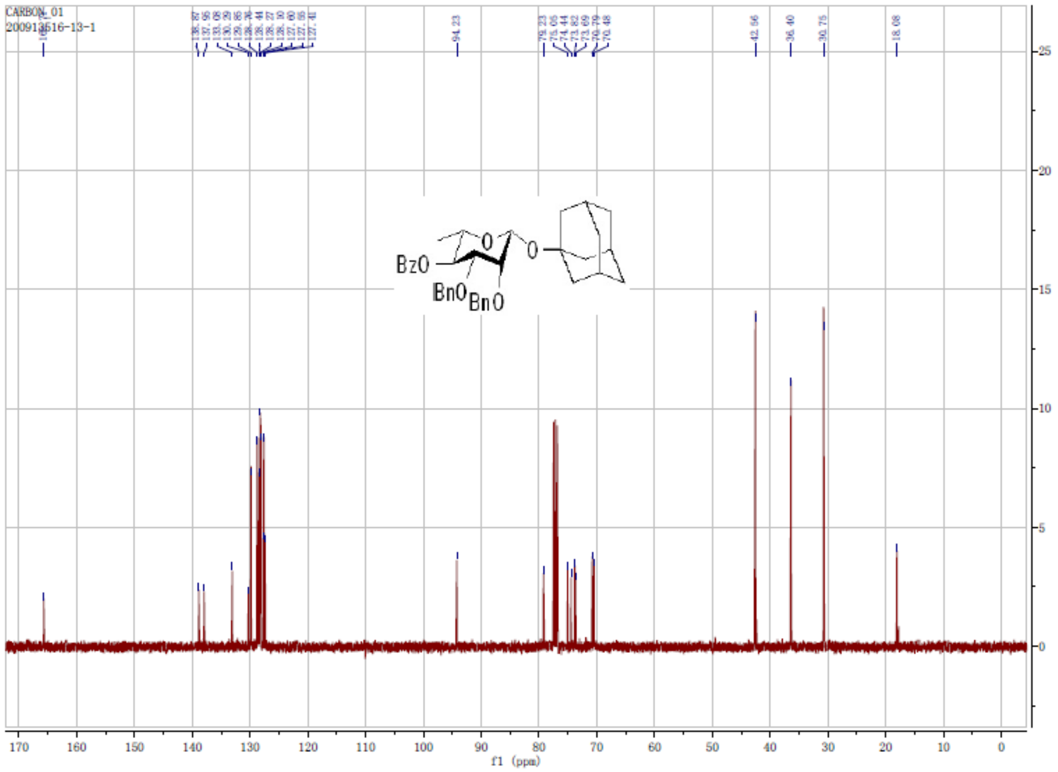

16-10-1-2c
Gradient Shimming
138.88
137.91
133.16
108.98
101.34
98.50
82.96
79.30
76.75
75.88
74.01
73.76
73.61
71.18
71.10
64.37
55.03
28.19
26.28
18.11
17.73
OMe
BzO
BnO
BnO
O
f1 (ppm)

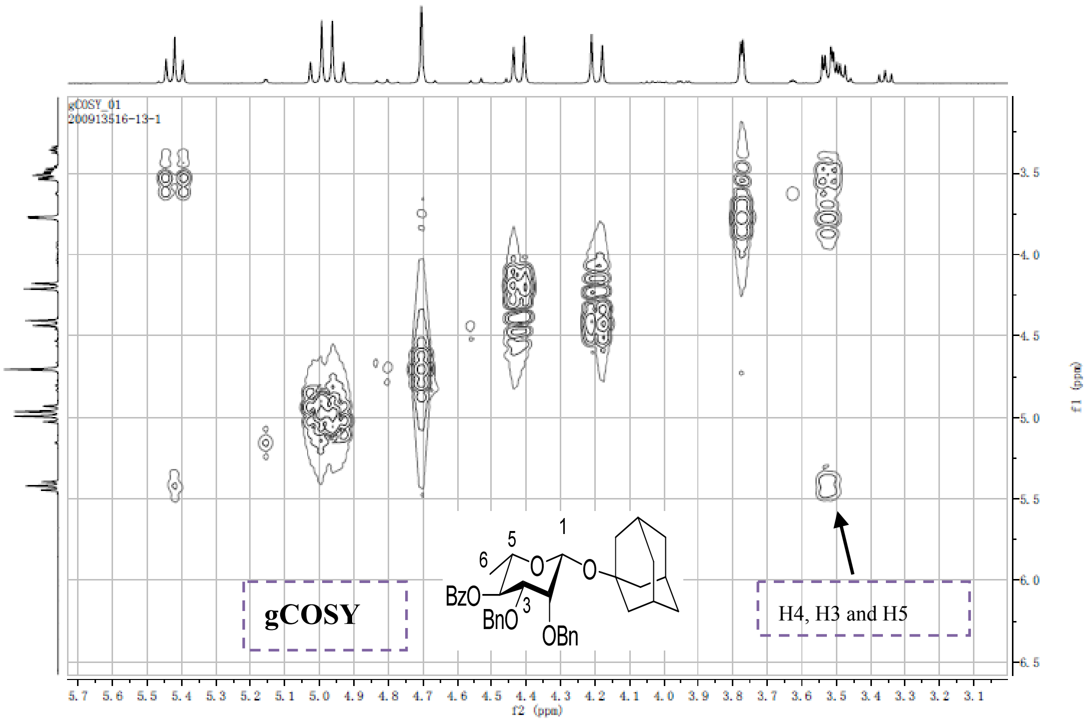

gCOSY_01
200913516-10-1-2
OMe
1
5
6
O
BzO
BnO
3
OBn
gCOSY
H4, H3
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9
f2 (ppm)
3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6
f1 (ppm)

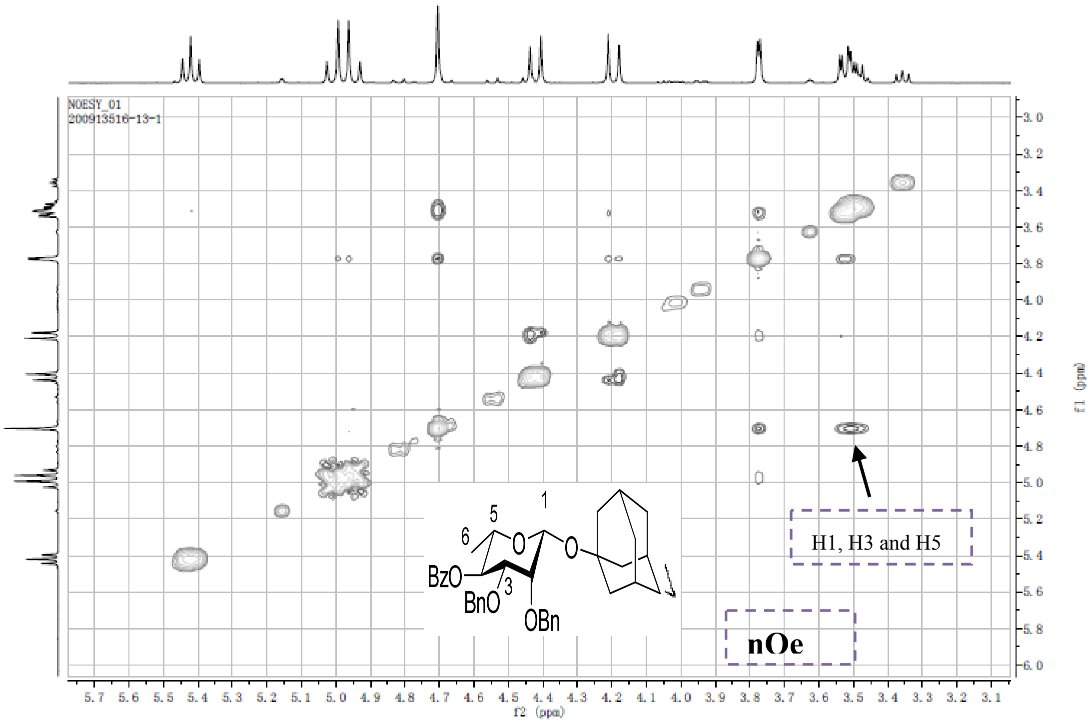

NOESY_01
200913516-10-1-2
OMe
1
5
6
O
BzO
BnO
3
OBn
nOe
H1, H5
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
f2 (ppm)
3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6
f1 (ppm)

Compound 16β:

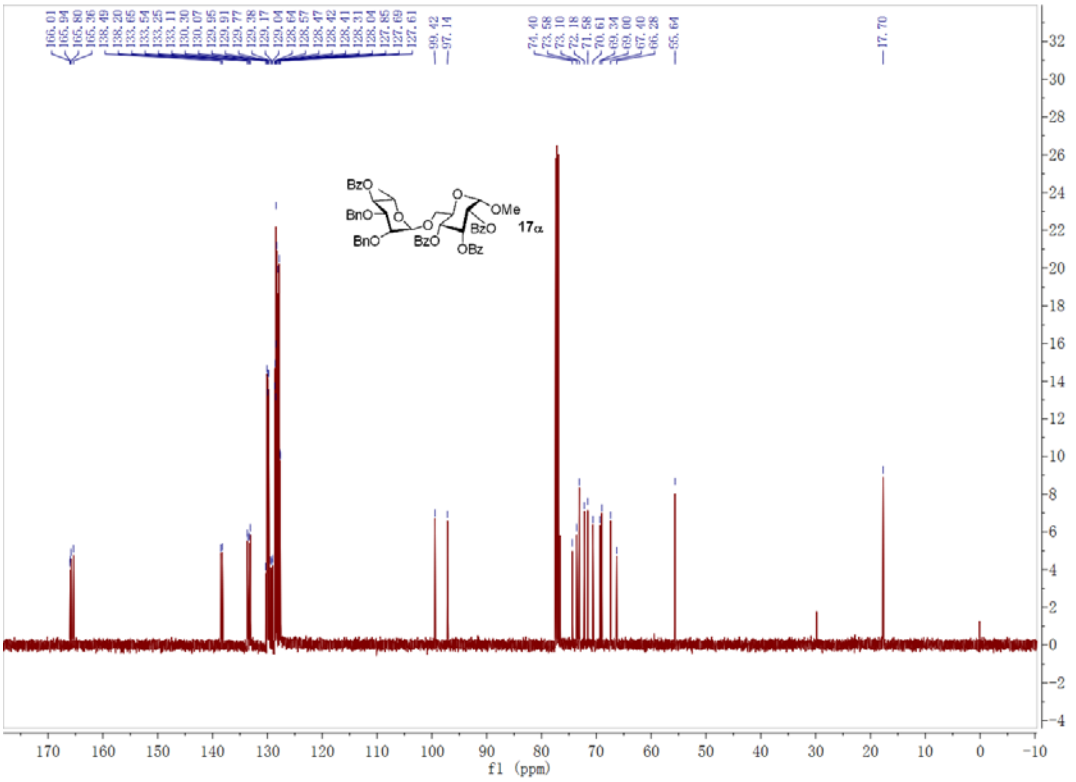


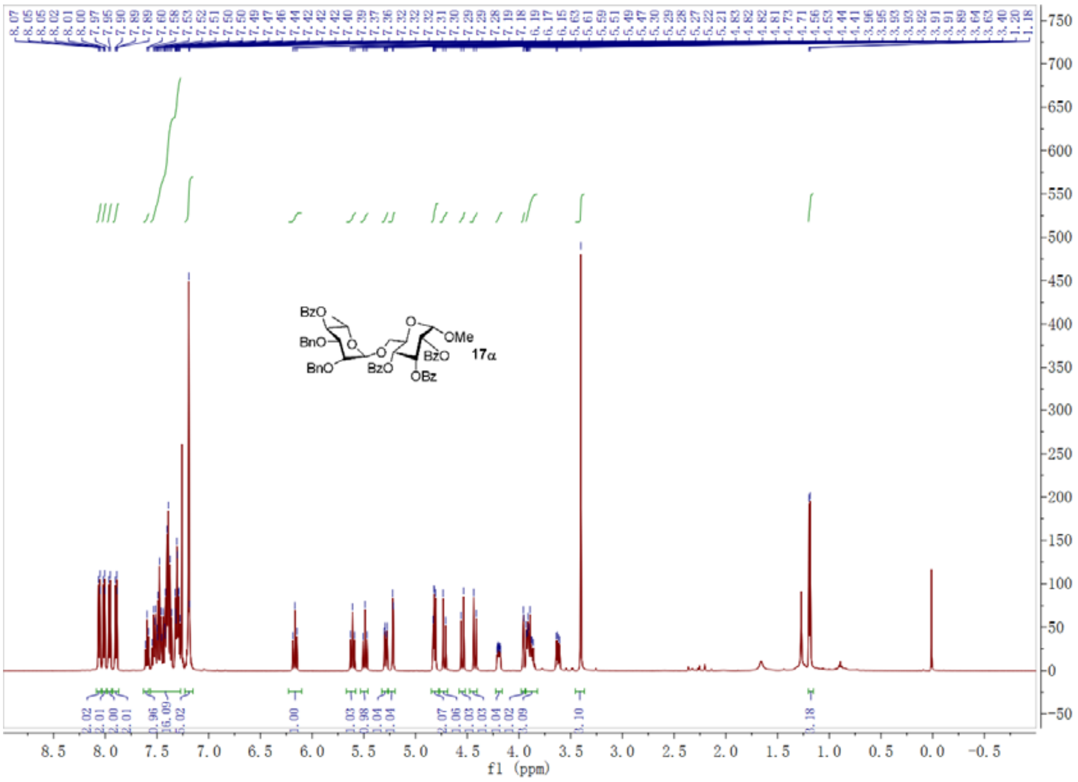


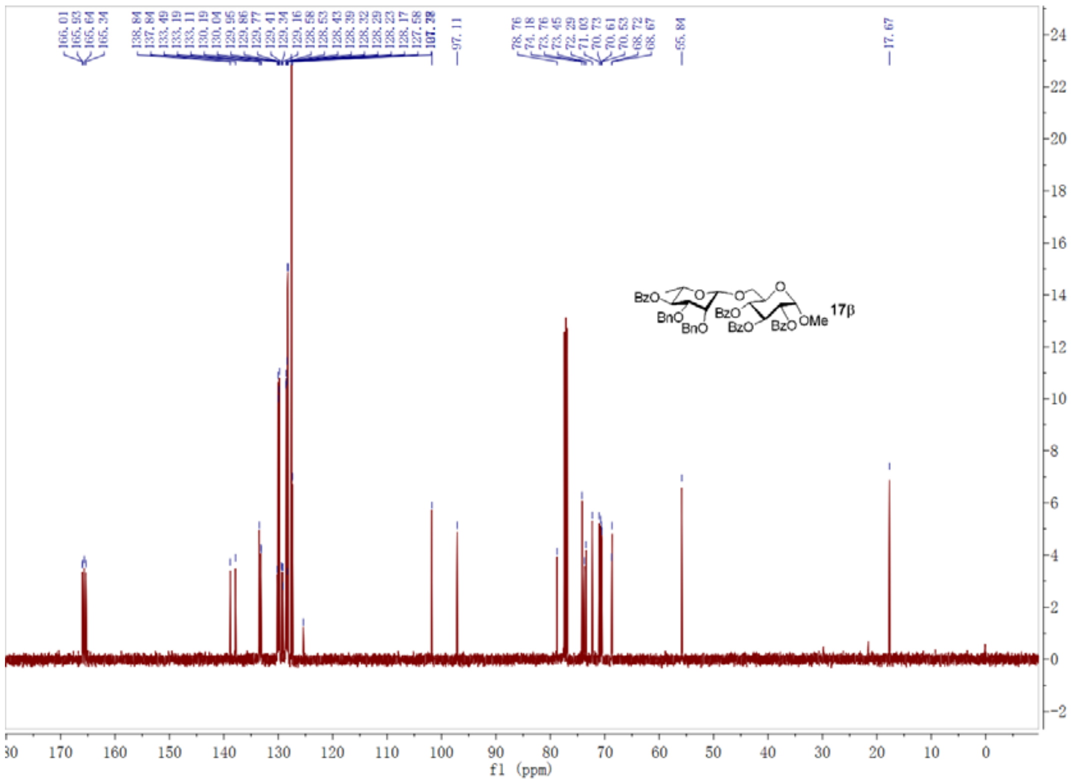

gCOSY_01
200913516-13-1
gCOSY
H4, H3 and H5
5
1
6
O
O
BzO
3
BnO
OBn
f2 (ppm)
f1 (ppm)
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
3.5 4.0 4.5 5.0 5.5 6.0 6.5

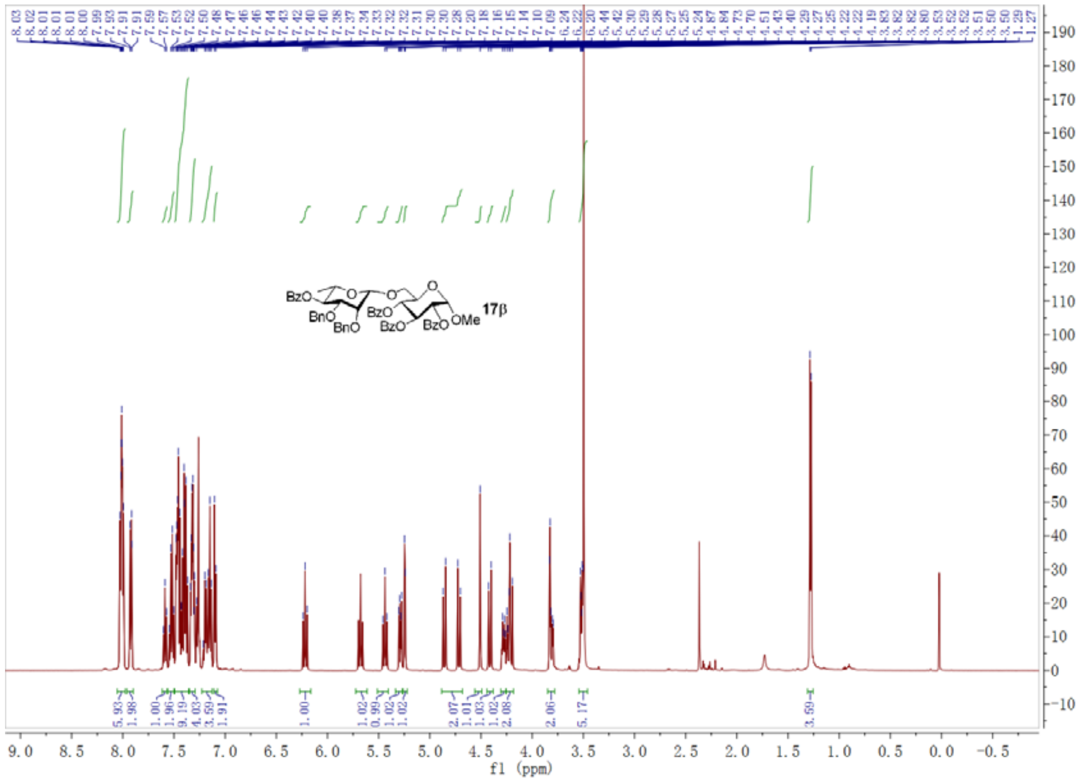

NOESY_01
200913516-13-1
H1, H3 and H5
nOe
5
1
6
O
O
BzO
3
BnO
OBn
f2 (ppm)
f1 (ppm)
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0

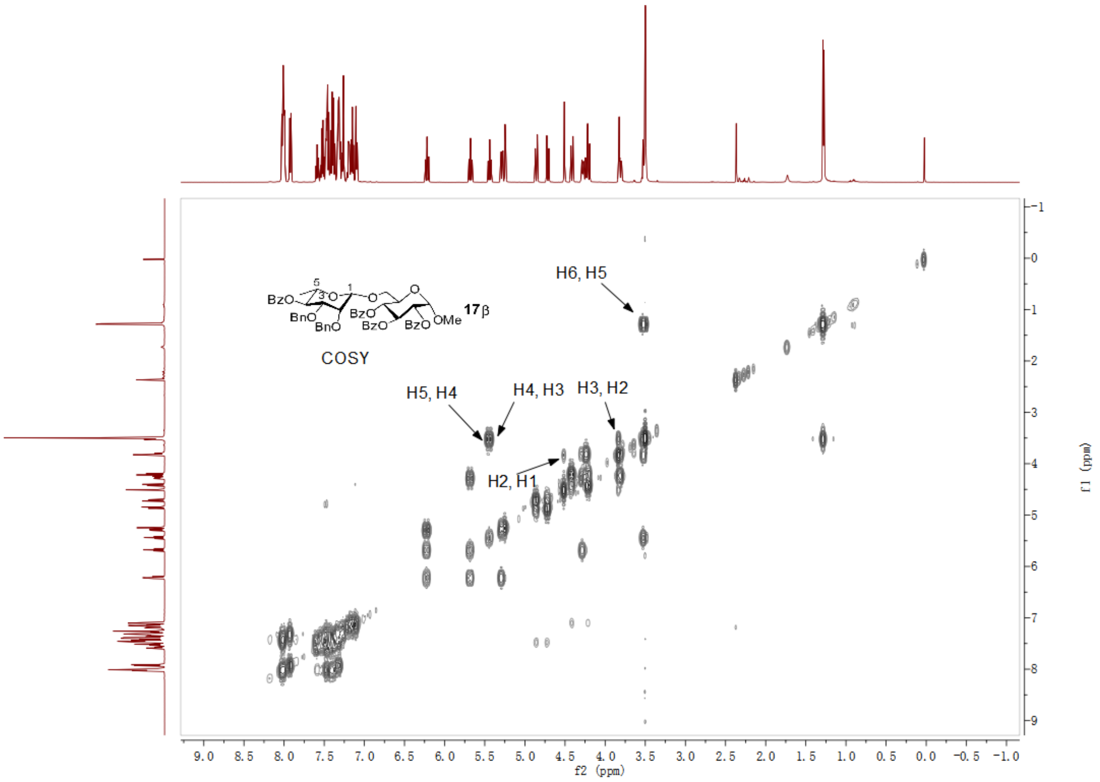
Compounds 17α and 17β:

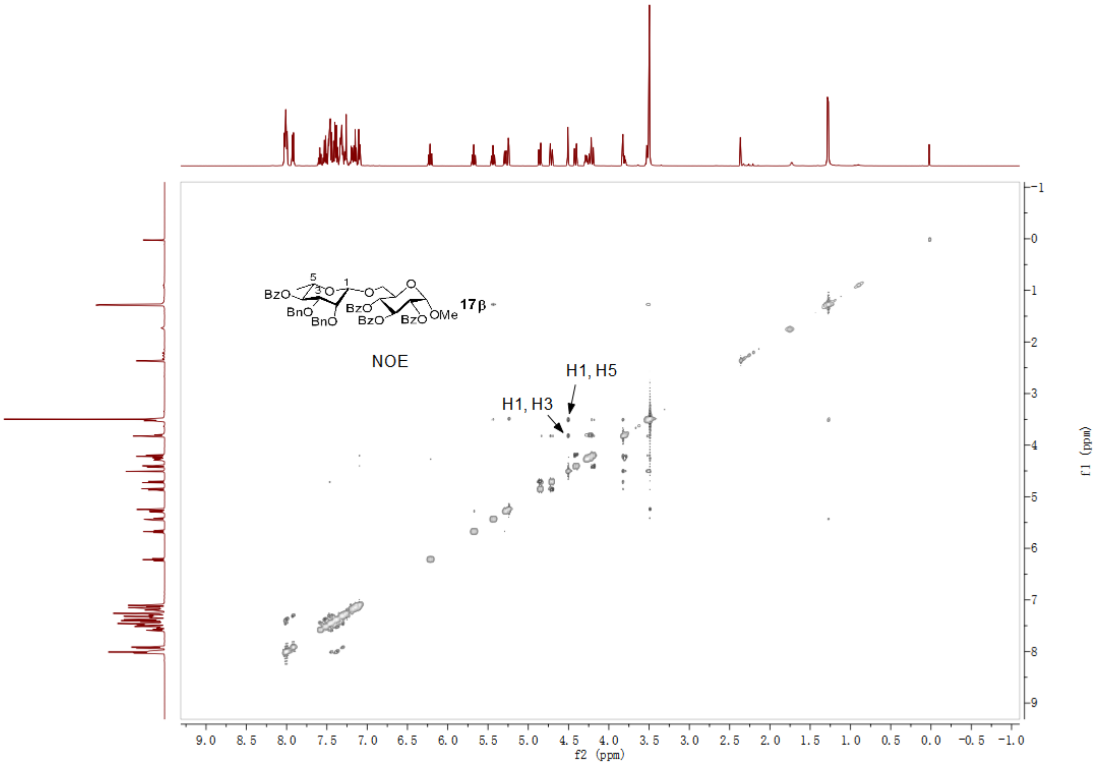




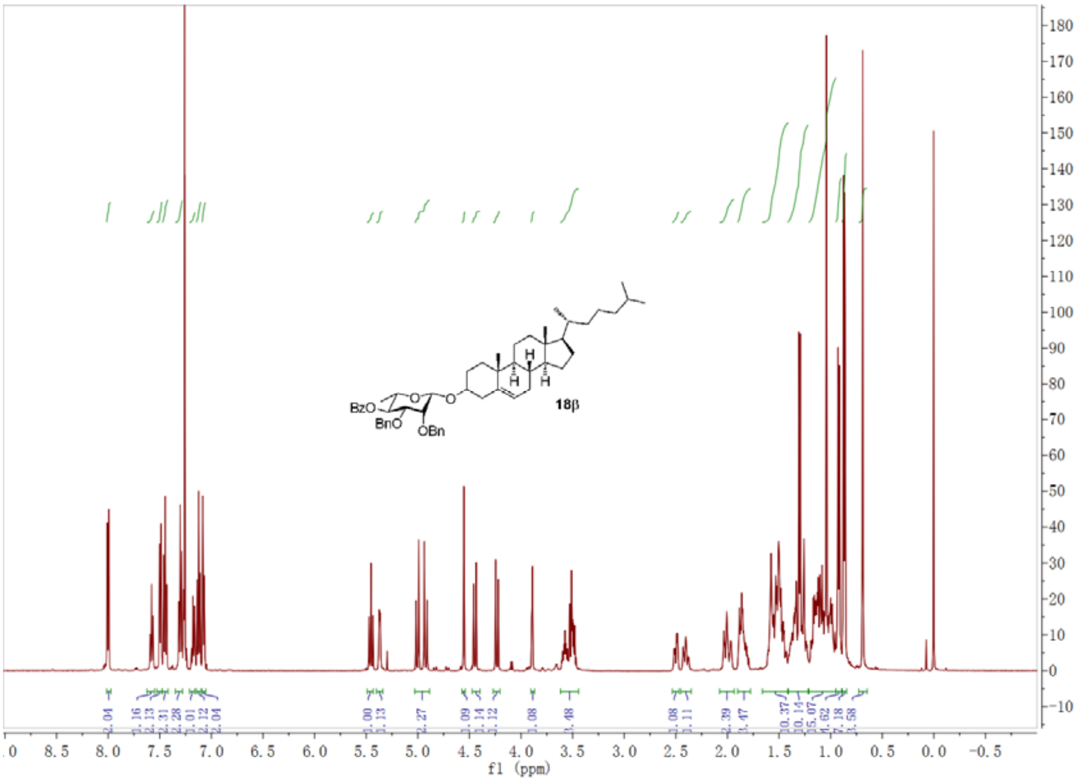

166.01
165.93
165.64
165.34
138.84
137.84
133.49
133.19
133.11
130.19
130.04
129.95
129.86
129.77
129.41
129.34
129.16
128.58
128.53
128.43
128.39
128.32
128.29
128.23
128.17
127.58
107.28
97.11
78.76
74.18
73.76
73.45
72.29
71.03
70.73
70.61
70.53
68.72
68.67
55.84
17.67
BzO
BnO
BnO
BzO
BzO
BzO
OMe
17β
24
22
20
18
16
14
12
10
8
6
4
2
0
−2
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

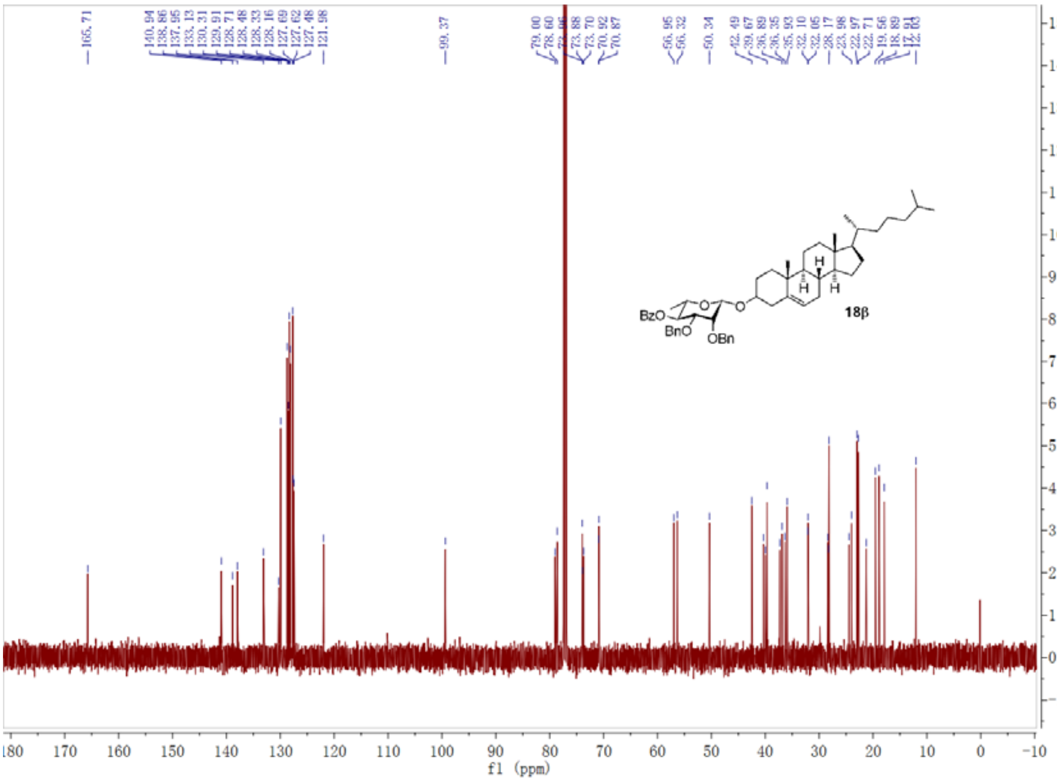

8.03
8.02
8.01
8.01
8.01
8.00
7.99
7.93
7.91
7.91
7.59
7.57
7.53
7.52
7.50
7.48
7.47
7.46
7.46
7.44
7.43
7.42
7.40
7.40
7.38
7.37
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.28
7.20
7.18
7.16
7.15
7.14
7.10
7.09
6.24
6.22
6.20
5.44
5.42
5.30
5.29
5.28
5.27
5.25
5.24
4.87
4.84
4.73
4.70
4.51
4.43
4.40
4.29
4.27
4.25
4.22
4.22
4.19
3.83
3.82
3.82
3.80
3.53
3.52
3.52
3.51
3.50
3.50
1.29
1.27
BzO
BnO
BnO
BzO
BzO
BzO
OMe
17β
5.93
1.98
1.00
1.96
9.19
4.03
3.59
1.91
1.00
1.02
0.99
1.02
1.02
2.07
1.01
1.03
1.02
2.08
2.06
5.17
3.59
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

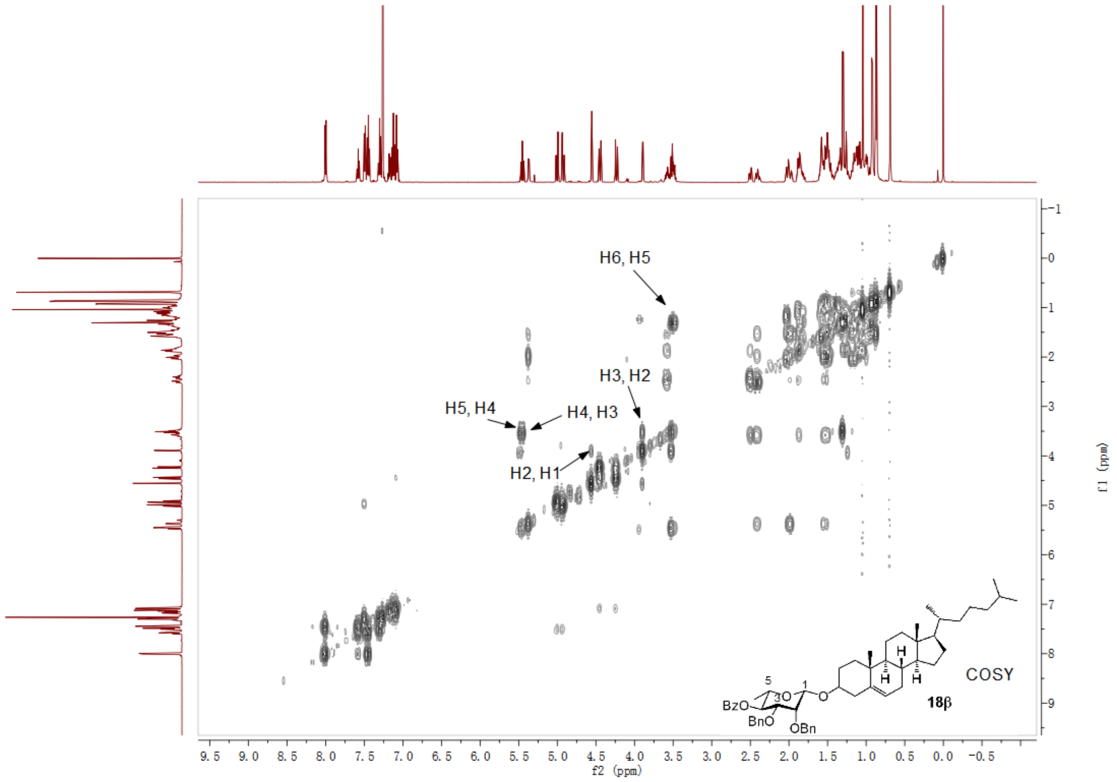

BzO
BnO
BnO
5
3
O
1
O
BzO
BzO
O
BzO
OMe
17β
COSY
H6, H5
H5, H4
H4, H3
H3, H2
H2, H1
f1 (ppm)
f2 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
0
1
2
3
4
5
6
7
8
9

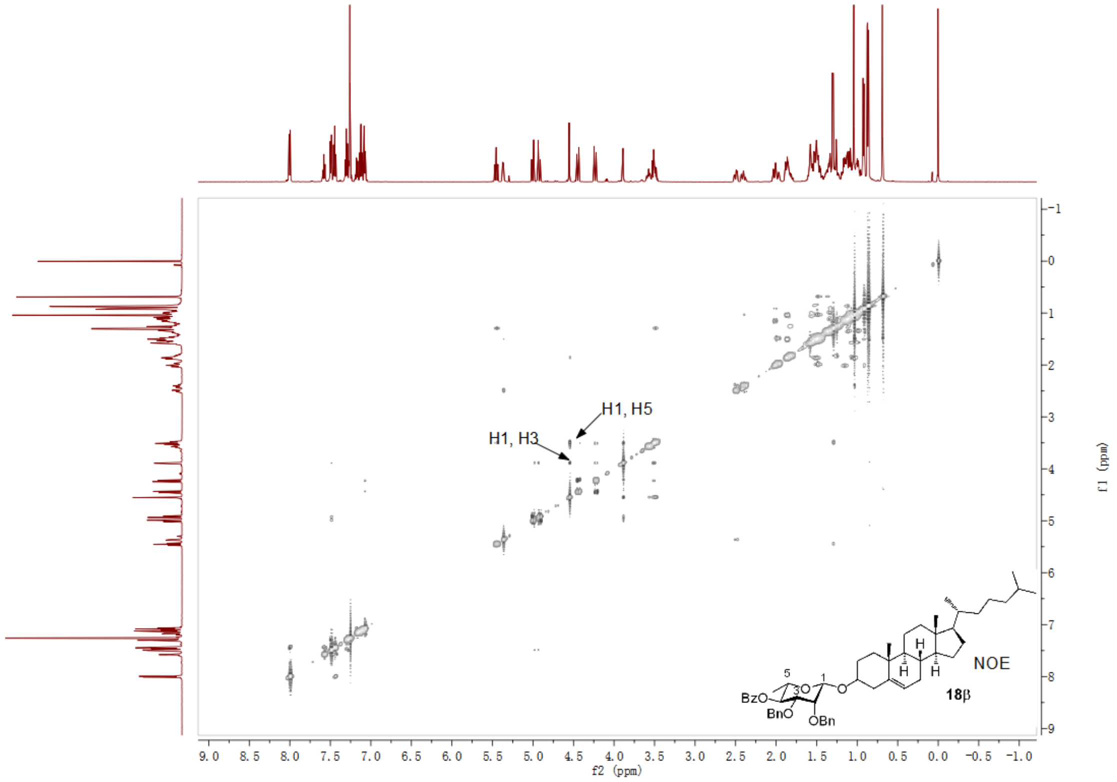

BzO
BnO
BnO
5
3
O
1
O
BzO
BzO
O
BzO
OMe
17β
NOE
H1, H5
H1, H3
f1 (ppm)
f2 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
0
1
2
3
4
5
6
7
8
9

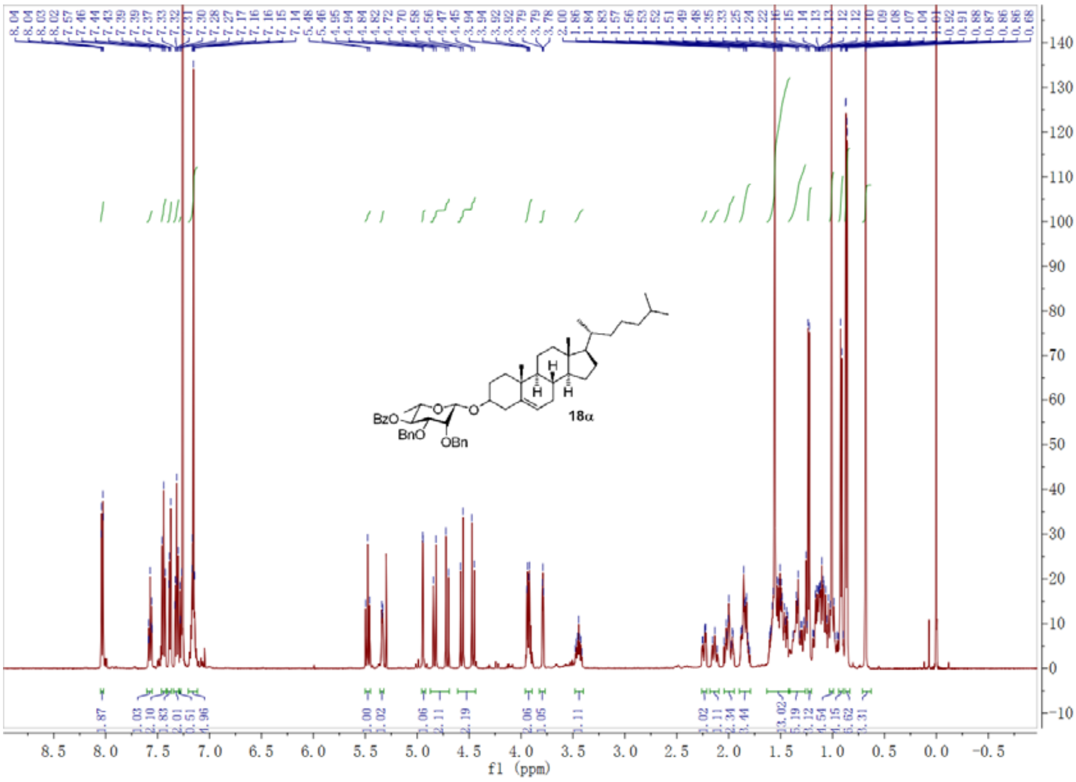
Compounds 18α and 18β:

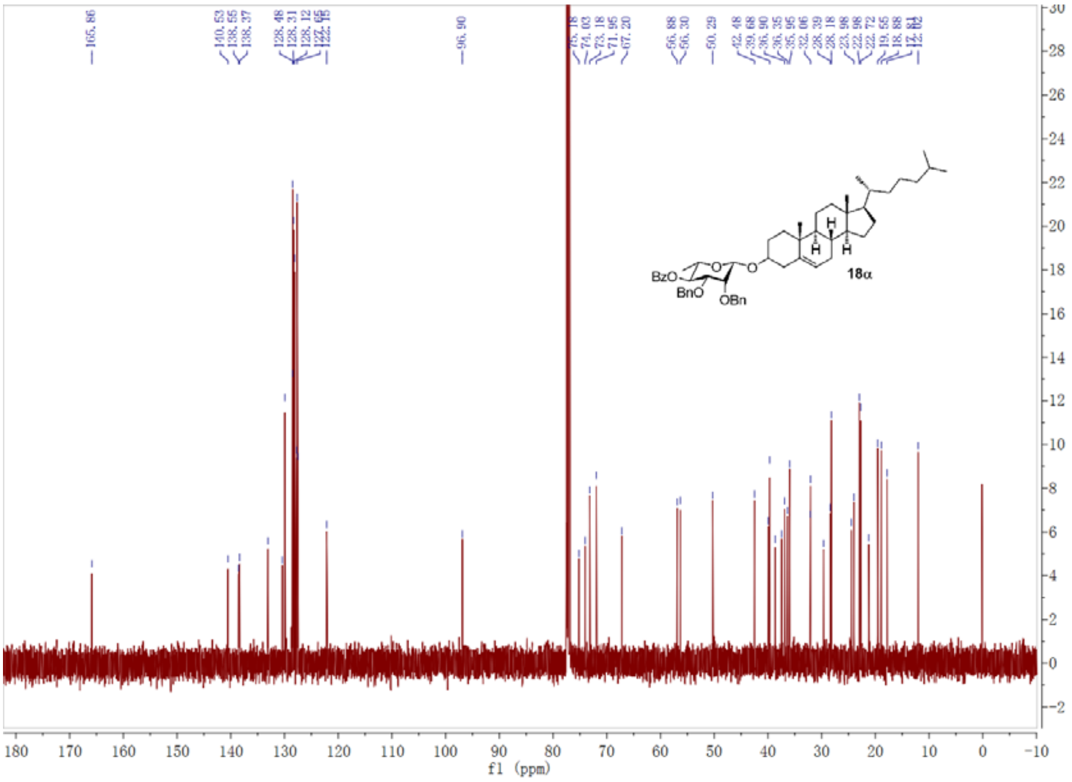




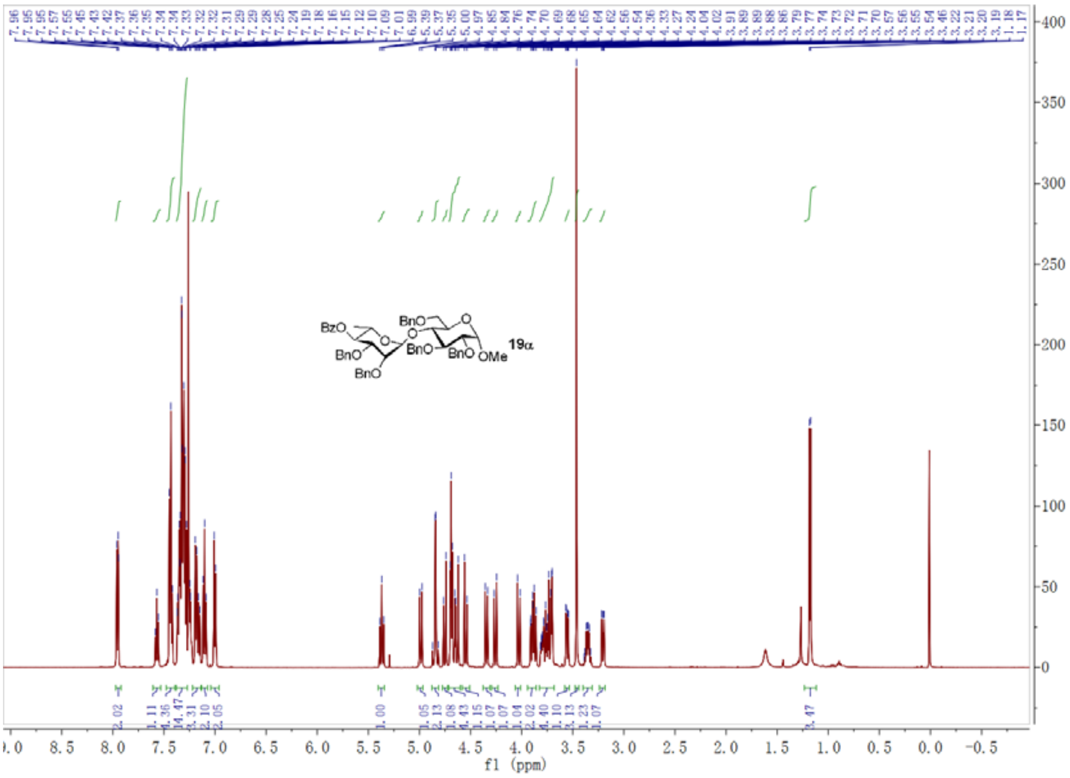

H6, H5
H3, H2
H5, H4
H4, H3
H2, H1
COSY
BzO
BnO
OBn
O
5
3
1
H
18β
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9
f1 (ppm)

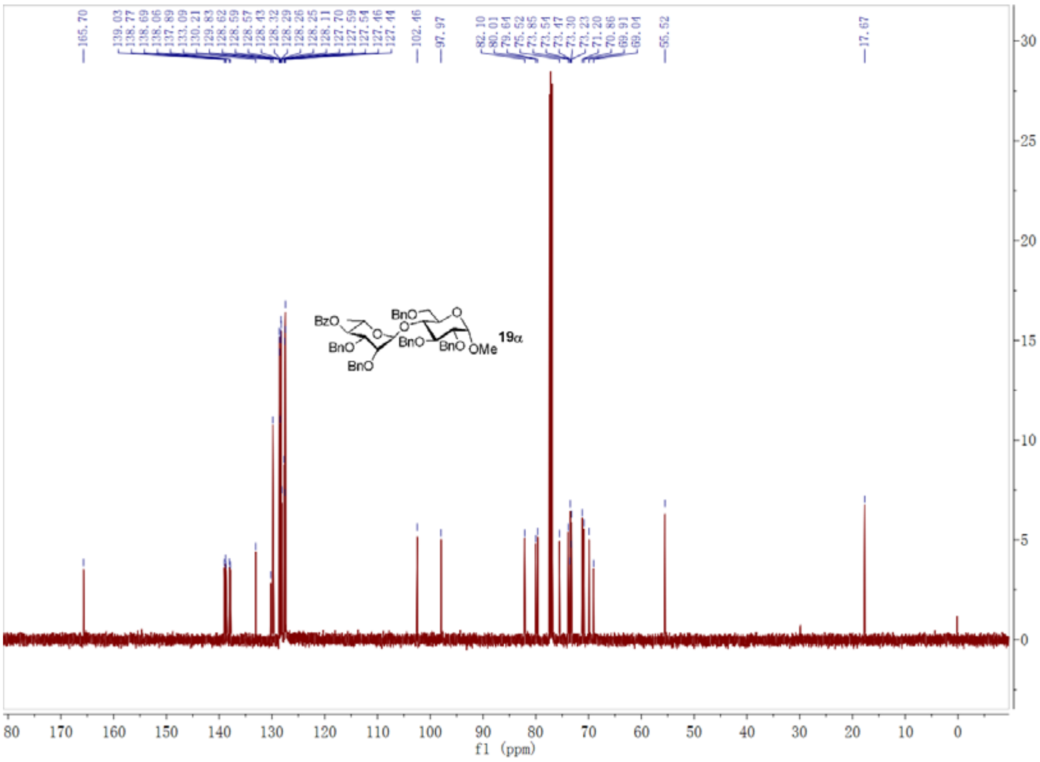

H1, H5
H1, H3
NOE
BzO
BnO
OBn
O
5
3
1
H
18β
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9
f1 (ppm)

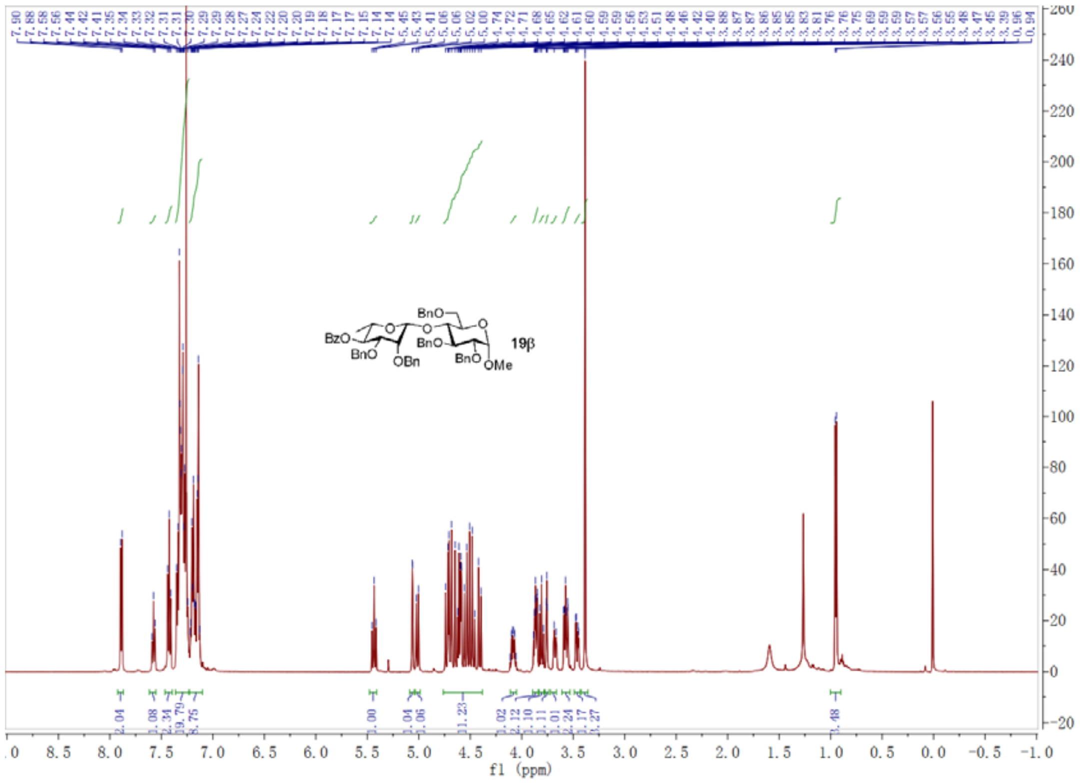

8.04
8.04
8.03
8.02
7.57
7.46
7.44
7.43
7.39
7.39
7.37
7.33
7.32
7.31
7.30
7.28
7.27
7.17
7.16
7.16
7.15
7.14
5.48
5.46
4.95
4.94
4.84
4.82
4.72
4.70
4.58
4.56
4.47
4.45
3.94
3.94
3.92
3.92
3.79
3.79
3.78
2.00
1.86
1.84
1.83
1.57
1.56
1.53
1.52
1.51
1.49
1.48
1.35
1.33
1.25
1.24
1.22
1.16
1.15
1.14
1.13
1.13
1.12
1.12
1.10
1.09
1.08
1.07
1.04
1.01
0.92
0.91
0.88
0.87
0.86
0.86
0.68
BzO
BnO
OBn
O
O
H
H
H
18α
f1 (ppm)

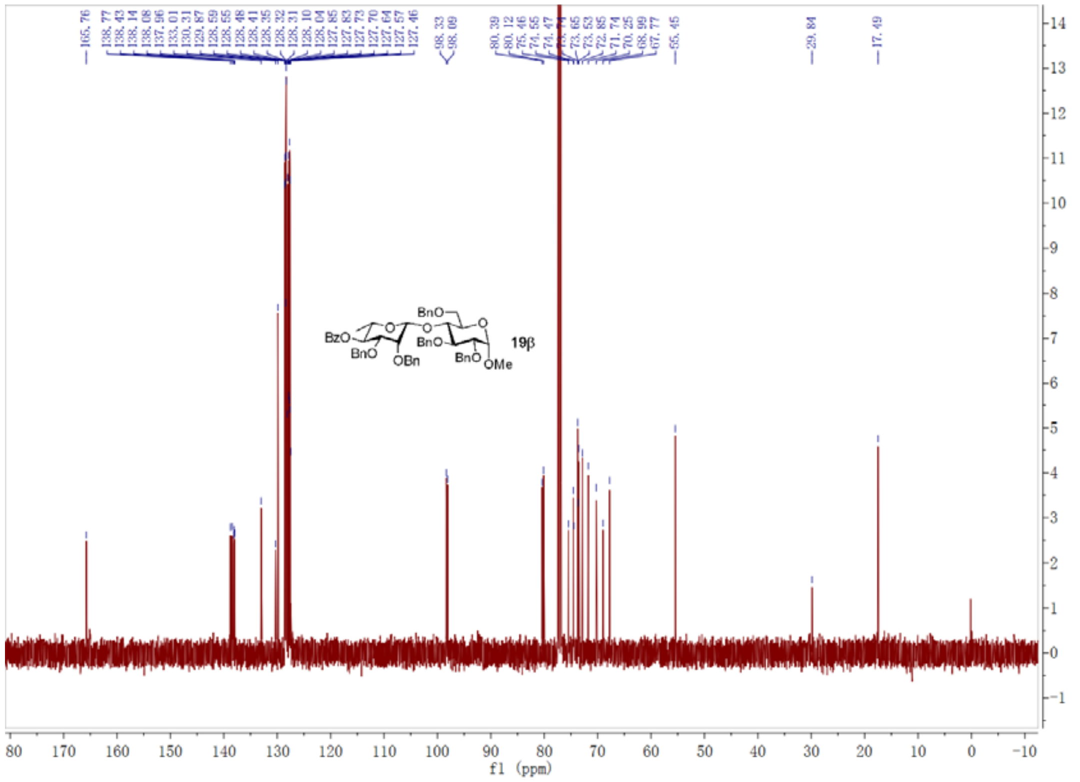

165.86
140.53
138.55
138.37
128.48
128.31
128.12
127.65
122.15
96.90
75.18
74.03
73.18
71.95
67.20
56.88
56.30
50.29
42.48
39.68
36.90
36.35
35.95
32.06
28.39
28.18
23.98
22.98
22.72
19.55
18.88
12.02
BzO
BnO
OBn
O
O
H
H
H
18α
f1 (ppm)

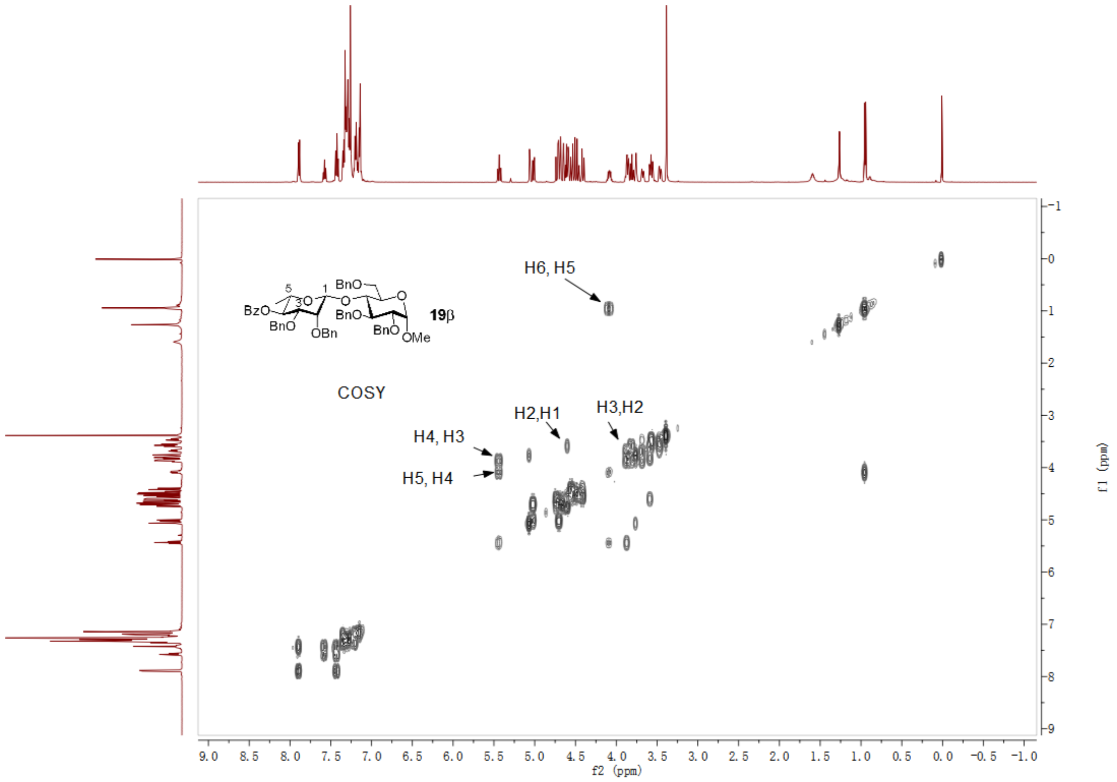
Compounds 19α and 19β:

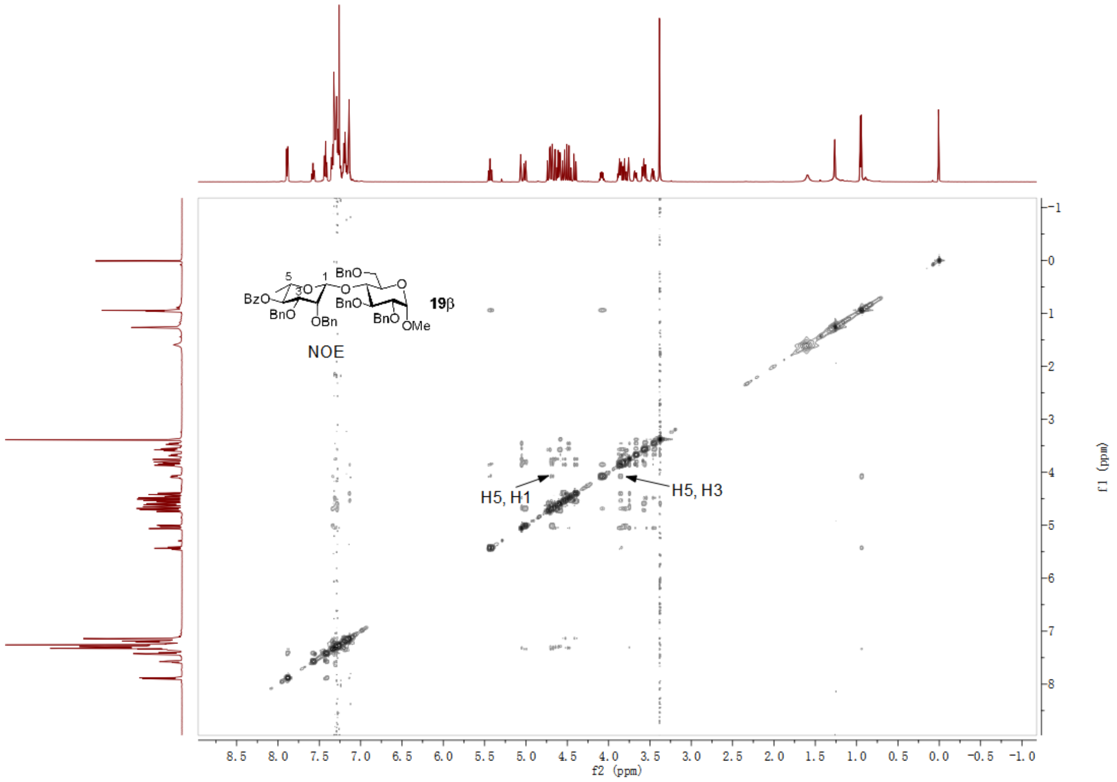





7.90 7.88 7.58 7.56 7.44 7.42 7.41 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.24 7.22 7.20 7.20 7.19 7.18 7.17 7.17 7.15 7.14 7.14 5.45 5.43 5.41 5.06 5.06 5.02 5.00 4.74 4.72 4.71 4.68 4.65 4.62 4.61 4.60 4.59 4.59 4.56 4.53 4.51 4.48 4.46 4.42 4.40 3.88 3.87 3.87 3.86 3.85 3.85 3.83 3.81 3.76 3.76 3.75 3.69 3.59 3.59 3.57 3.57 3.56 3.55 3.48 3.47 3.45 3.39 0.96 0.94
BzO
BnO
OBn
BnO
BnO
BnO
OMe
19β
2.04
1.08
2.34
19.79
8.75
1.00
1.04
1.06
11.23
1.02
2.12
1.10
1.11
1.01
2.24
1.17
3.27
3.48
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20


165.76
138.77 138.43 138.14 138.08 137.96 133.01 130.31 129.87 128.59 128.55 128.48 128.41 128.35 128.32 128.31 128.10 128.04 127.85 127.83 127.73 127.70 127.64 127.57 127.46
98.33 98.09
80.39 80.12 75.46 74.55 74.47 73.74 73.65 73.53 72.85 71.74 70.25 68.99 67.77
55.45
29.84
17.49
BzO
BnO
OBn
BnO
BnO
BnO
OMe
19β
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1


BzO
BnO
OBn
BnO
BnO
BnO
OMe
O
5
3
1
19β
COSY
H6, H5
H2,H1
H3,H2
H4, H3
H5, H4
f2 (ppm)
f1 (ppm)


BzO
BnO
OBn
BnO
BnO
BnO
OMe
O
5
3
1
19β
NOE
H5, H1
H5, H3
f2 (ppm)
f1 (ppm)