Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis and antiproliferative activities of OSW-1 analogues bearing 2-acylamino-xylose residues

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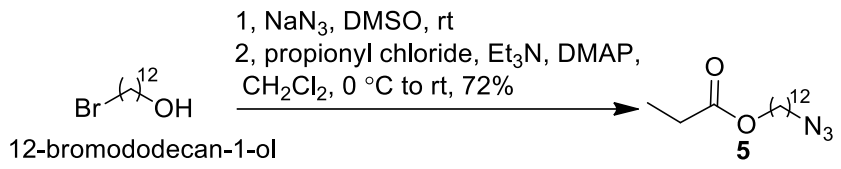
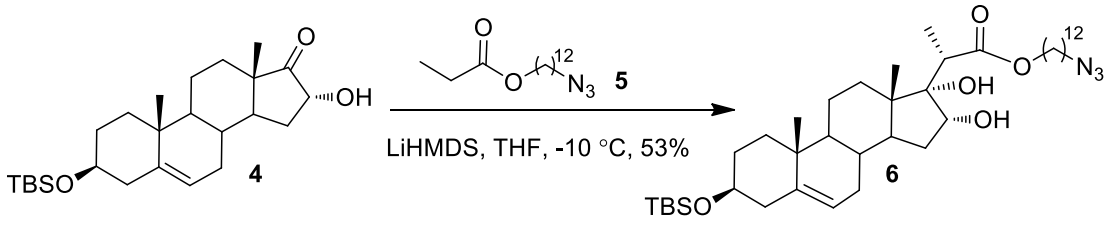
General remarks for the synthesis. All reactions were carried out with regular solvents in glassware, unless otherwise noted. The chemicals were reagent grade as supplied. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compound spots were visualized by UV light (254 nm) and by heating with a solution with 10% H_2SO_4 in ethanol. Flash column chromatography was performed on regular silica gel, unless otherwise noted. High Performance Liquid Chromatography was run on Agilent 1100. NMR spectra were referenced using Me_4Si (0 ppm), residual $CHCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm), CH_3OH (^{1}H NMR δ = 3.31 ppm, ^{13}C NMR δ = 49.00 ppm), Peak and coupling constant assignments are based on ^{1}H NMR, COSY, HSQC, HMBC and NOESY. Splitting patterns were indicated as s (singlet), d (doublet), t (triplet), q (quartet), and br s (broad singlet) for ^{1}H NMR data. ESI-MS, MALDI-MS and DART-MS were run on Bruker maXis 4G, Thermo Fisher Scientific LTQ FT Ultra and Applied Biosystems 4700 Proteomics Analyzer 72020, respectively. Optical rotations were measured using an Anton Paar MCP polarimeter.



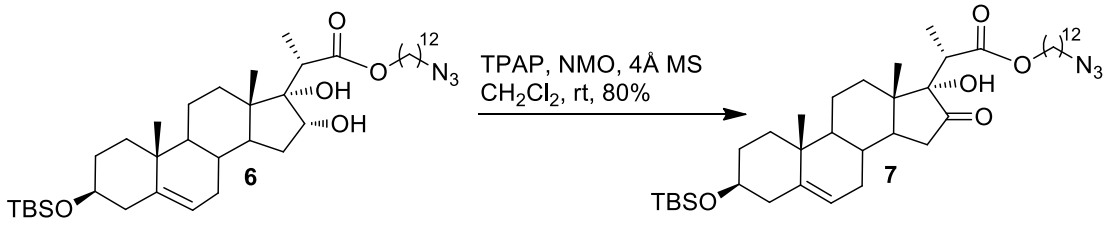
Ester **5.** To a solution of 12-bromododecan-1-ol (10 g, 37.7 mmol) in DMSO (60 mL) was added slowly NaN_3 (4.9 g, 75.4 mmol) at room temperature. After stirring for 24 h, the reaction mixture was then poured into cooled water, and extracted with Et_2O. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 10:1) to afford 12-azidododecan-1-ol[S1] (6.53 g) as a white solid.

To a cooled solution (0 ºC) of 12-azidododecan-1-ol[S1] (6.53 g, 28.7 mmol) in dry CH_2Cl_2 (60 mL) were added sequentially DMAP (0.17 g, 1.44 mmol), Et_3N (7.98 mL, 57.4 mmol), and propionyl chloride (3.26 mL, 37.3 mmol); and then the reaction mixture was allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was then poured into cooled saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 15:1) to afford **5** (7.73 g, 72% over two steps) as a colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.31 (q, *J* = 7.6 Hz, 2H), 1.63–1.56 (m, 4H), 1.38–1.26 (m, 16H), 1.13 (t, J = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 64.6, 51.6, 29.63, 29.61, 29.58, 29.4, 29.3, 29.0, 28.8, 27.8, 26.8, 26.0, 9.3; HR-ESI calcd for $C_{15}H_{29}N_3O_2Na$ $[M + Na]^+$ 306.2152, found 306.2149.



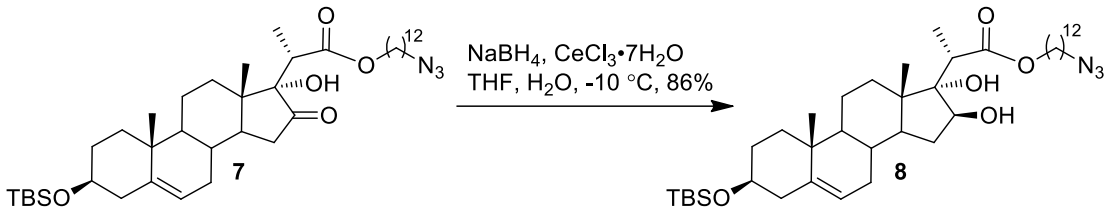
Diol **6**. To a cooled solution (–20 ºC) of 12-azidododecyl propionate **5** (8.13 g, 28.7 mmol) in dry

THF (200 mL) was slowly added LiHMDS (57.4 mL, 1 M /THF) under Ar, and another solution of **4** (2.0 g, 4.78 mmol) in dry THF (40 mL) was then added immediately. After being stirred at –20 °C for 1 h, the reaction mixture was poured into saturated aqueous NH_4Cl, and extracted with EtOAc. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 15:1) to afford **6** (1.77 g, 53%) as a white solid: $[\alpha]_D^{25}$ = –41.4 (*c* = 0.77 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.29 (d, *J* = 5.2 Hz, 1H), 4.17–4.14 (m, 1H), 4.11–4.02 (m, 2H), 3.55 (s, 1H), 3.50–3.44 (m, 1H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.80–2.76 (m, 2H), 2.27–2.22 (m, 1H), 2.17–2.14 (m, 1H), 0.98 (s, 3H), 0.88 (s, 9H), 0.79 (s, 3H), 0.05 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.4, 141.6, 121.0, 81.9, 76.6, 72.7, 65.4, 51.6, 49.6, 48.6, 48.3, 45.0, 42.9, 37.3, 36.6, 35.2, 32.5, 32.2, 31.89, 31.86, 29.63, 29.61, 29.59, 29.32, 29.28, 29.0, 28.5, 26.8, 26.1, 26.0, 20.4, 19.5, 18.4, 14.8, 12.9, -4.5; HR-ESI calcd for $C_{40}H_{71}N_3O_5SiNa$ $[M + Na]^+$ 724.5055, found 724.5060.

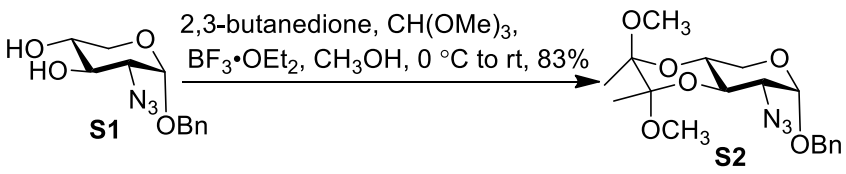


Ketone **7.** A suspension of tetrapropylammonium perruthenate (0.23 g, 0.66 mmol), *N*-methylmorpholine *N*-oxide (1.18 g, 10.1 mmol), and 4 Å molecular sieves (0.3 g) in dry CH_2Cl_2 (20 mL) was added to a solution of **6** (1.77 g, 2.52 mmol) in dry CH_2Cl_2 (20 mL) at room temperature. After being stirred at room temperature for 13 h, the mixture was diluted with CH_2Cl_2, and then filtered through a pad of silica gel and eluted with CH_2Cl_2. The filtrates were concentrated in vacuo to give a residue, which was purified by a flash column chromatography (petroleum ether-EtOAc, 40:1) to afford **7** (1.41 g, 80%) as a white solid: $[\alpha]_D^{25}$ = –89.5 (*c* = 1.10 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (d, *J* = 5.1 Hz, 1H), 5.24 (s, 1H), 4.22–4.09 (m, 2H), 3.53–3.45 (m, 1H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.55 (q, *J* = 7.1 Hz, 1H), 2.37 (dd, *J* = 18.6, 8.0 Hz, 1H), 2.29–2.15 (m, 3H), 2.06–2.00 (m, 1H), 1.02 (s, 3H), 0.88 (s, 9H), 0.77 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.6, 179.0, 141.7, 120.6, 82.7, 72.6, 65.4, 51.6, 49.5, 45.3,

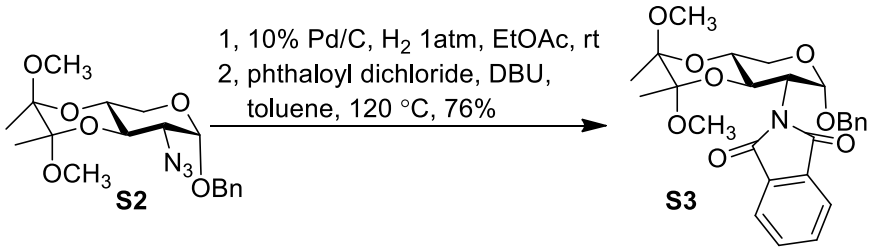
45.1, 42.9, 38.7, 37.2, 36.8, 36.0, 32.1, 32.0, 31.2, 30.5, 29.64, 29.61, 29.59, 29.34, 29.28, 29.0, 28.5, 26.8, 26.1, 26.0, 20.3, 19.6, 18.4, 13.9, 12.8, -4.5; HR-ESI calcd for $C_{40}H_{70}N_3O_5Si$ $[M + H]^+$ 700.5079, found 700.5078.



Diol **8**. A suspension of **7** (1.41 g, 2.01 mmol), $CeCl_3 \cdot 7H_2O$ (1.12 g, 3.02 mmol), and $NaBH_4$ (0.46 g, 12.1 mmol) in THF and H_2O (151.5 mL, v/v, 100:1) was stirred at –10 °C for 0.5 h. The mixture was then cooled to –78 °C and quenched with methanol. After being stirred 0.5 h, water was added, and then the reaction mixture was poured into cooled diluted HCl (1M), extracted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 20:1) to afford **8** (1.41 g, 86%) as a white solid: $[\alpha]_D^{25}$ = –31.8 (*c* = 0.83 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (d, *J* = 5.1 Hz, 1H), 4.48 (dd, *J* = 7.9, 4.7 Hz, 1H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.51–3.43 (m, 1H), 3.24 (t, *J* = 7.0 Hz, 2H), 2.72 (q, *J* = 7.7 Hz, 1H), 2.36–2.22 (m, 2H), 2.19–2.14 (m, 1H), 2.03–1.98 (m, 1H), 1.01 (s, 3H), 0.88 (s, 9H), 0.79 (s, 3H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 141.6, 120.6, 88.5, 86.7, 72.5, 63.2, 51.6, 50.8, 49.9, 46.2, 42.8, 40.1, 37.5, 36.8, 32.9, 32.6, 32.1, 32.0, 31.8, 30.4, 29.7, 29.64, 29.62, 29.58, 29.53, 29.3, 29.0, 26.8, 26.0, 25.9, 20.1, 19.6, 18.4, 14.3, 13.1, -4.5; HR-ESI calcd for $C_{40}H_{71}N_3O_5SiNa$ $[M + Na]^+$ 724.5055, found 724.5051.



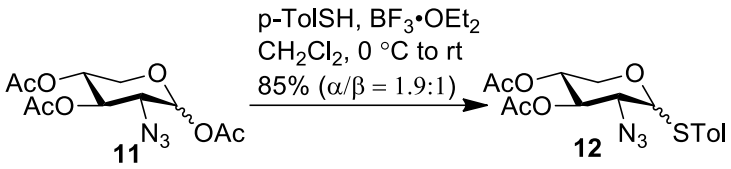
Compound **S2.** To a cooled solution (0 °C) of **S1**[S2] [S3] (3.61 g, 13.6 mmol) in methanol (60 mL) were added sequentially 2,3-butanedione (1.31 mL, 15.0 mmol), trimethyl orthoformate (4.91 mL, 44.9 mmol), and boron trifluoride etherate (3.36 mL, 27.2 mmol), then the reaction mixture was allowed to warm to room temperature. After being stirred under Ar at room temperature for 48 h, the mixture was then cooled to 0 °C and quenched with Et_3N. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 6:1) to afford **S2** (4.27 g, 83%) as a white foam: $[\alpha]_D^{25}$ = 280.8 (*c* = 0.97 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.34 (m, 4H), 7.32–7.30 (m, 1H), 4.92 (d, *J* = 3.6 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.25 (dd, *J* = 10.7, 9.6 Hz, 1H), 3.84–3.80 (m, 1H), 3.77–3.73 (m, 1H), 3.61 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.36 (s, 3H), 3.28 (s, 3H), 3.27–3.25 (m, 1H), 1.35 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.7, 128.6, 128.2, 128.1, 100.4, 100.0, 97.4, 69.6, 67.8, 67.0, 60.2, 60.1, 48.6, 48.2, 18.0, 17.8; HR-ESI calcd for $C_{18}H_{25}N_3O_6Na$ $[M + Na]^+$ 402.1636, found 402.1641.



Compound **S3.** A suspension of **S2** (4.27 g, 11.3 mmol) and 10% Pd/C (2 g) in EtOAc (60 mL) was stirred at room temperature under H_2 atmosphere (1 atm) for 6 h and then filtered. The filtrates were concentrated in vacuo. The residue was purified by a flash column chromatography (petroleum ether-EtOAc, 4:1) to afford an amine as a white solid (3.41 g).

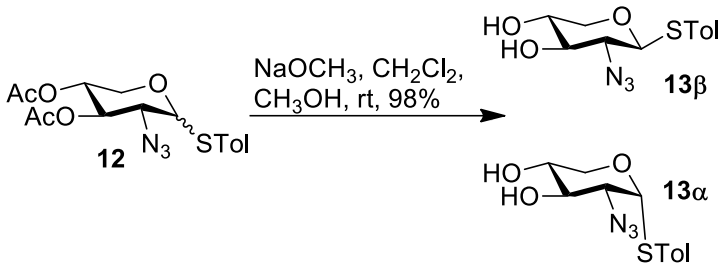
To a solution of the amine above (3.41 g, 9.65 mmol) in toluene (60 mL) were added DBU (7.21 mL, 48.3 mmol) and phthaloyl dichloride (5.56 mL, 38.6 mmol) sequentially at room temperature. The reaction mixture was heated at 120 °C for 8 h. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with H_2O,

saturated aqueous $NaHCO_3$ and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 5:1) to afford **S3** (4.41 g, 75%, over two steps) as a white foam: $[\alpha]_D^{25}$ = 182.6 (*c* = 0.29 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (br s, 2H), 7.72–7.70 (m, 2H), 7.13–7.11 (m, 2H), 7.07–7.03 (m, 3H), 5.41 (dd, *J* = 11.6, 9.5 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 4.72 (d, *J* = 12.6 Hz, 1H), 4.40–4.39 (m, 1H), 4.38–4.37 (m, 1H), 3.93–3.90 (m, 1H), 3.84 (ddd, *J* = 11.0, 9.6, 4.6 Hz, 1H), 3.67 (dd, *J* = 10.2, 4.6 Hz, 1H), 3.32 (s, 3H), 3.29 (s, 3H), 1.31 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.3, 134.0, 128.3, 127.5, 127.4, 123.3, 100.4, 100.1, 97.3, 69.5, 68.6, 64.1, 60.8, 54.30, 49.4, 48.2, 18.0, 17.9; HR-ESI calcd for $C_{26}H_{29}NO_8Na$ $[M + Na]^+$ 506.1785, found 506.1788.



Compound **12**. To a cooled solution (0 °C) of **11**[S4] (3.40 g, 11.3 mmol) and *p*-toluenethiol (2.10 g, 16.9 mmol) in dry CH_2Cl_2 (50 mL) was added slowly boron trifluoride etherate (2.80 mL, 22.6 mmol), and then the reaction mixture was allowed to warm to room temperature. After being stirred under Ar at room temperature for 10 h, the mixture was then cooled to 0 °C and quenched with Et_3N. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 5:1) to afford an inseparable mixture of thioglycosides **12α/12β** (3.51 g, 85%, α/β=1.9/1) as white solids. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 0.7H), 7.38 (d, *J* = 8.1 Hz, 1.3H), 7.17 (d, *J* = 7.9 Hz, 0.7H), 7.13 (d, *J* = 7.9 Hz, 1.3H), 5.44 (d, *J* = 5.0 Hz, 0.65H), 5.32–5.29 (m, 0.65H), 5.08–5.05 (m, 0.35H), 4.94 (ddd, *J* = 9.6, 8.6, 5.5 Hz, 0.65H), 4.87–4.82 (m, 0.35H), 4.43 (d, *J* = 9.5 Hz, 0.35H), 4.19–4.15 (m, 1.0H), 3.93 (dd, *J* = 9.6, 5.0 Hz, 0.65H), 3.85 (dd, *J* = 11.6, 5.5 Hz, 0.65H), 3.35–3.31 (m, 0.7H), 2.37 (s, 1.05H), 2.33 (s, 1.95H), 2.11 (s, 1.95H), 2.08 (s, 1.05H), 2.07 (s, 2.0H), 2.01 (s,

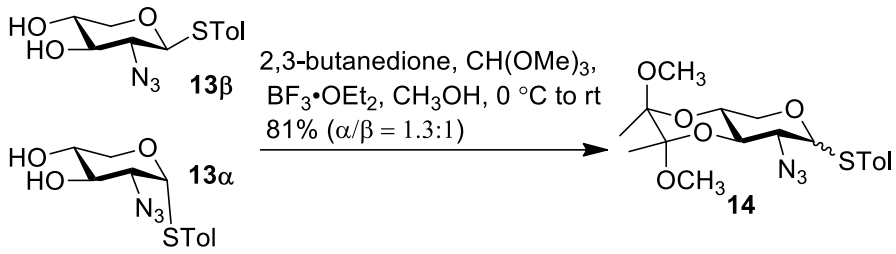
1.0H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 170.1, 169.9, 169.8, 139.4, 138.5, 134.6, 132.8, 130.12, 130.09, 129.2, 126.6, 87.4, 86.7, 73.8, 71.1, 69.1, 68.7, 66.5, 62.4, 61.6, 60.6, 21.4, 21.3, 20.88, 20.86, 20.81; HR-ESI calcd for $C_{16}H_{19}N_3O_5SNa$ $[M + Na]^+$ 388.0938, found 388.0945.



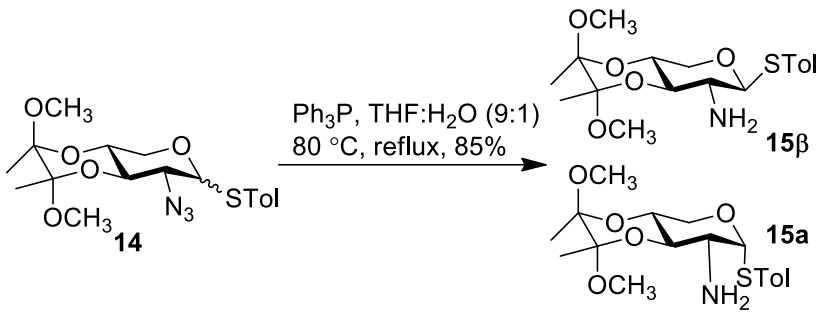
Compound **13**. To a solution of **12** (3.51 g, 9.60 mmol) in MeOH and CH_2Cl_2 (60 mL, v/v, 5:1) was added NaOMe (0.11 g, 1.96 mmol) at room temperature. After the mixture was stirred for 10 h, the reaction was quenched with water. The reaction mixture was concentrated in vacuo to give a residue, which was purified by a flash column chromatography (petroleum ether-EtOAc, 1:1) to afford a mixture of the α/β thioglycosides **13α/13β** (2.64 g, 98%, α/β=1.9/1) as white solids. The α- and β-anomers of **13** could be partially separated.

Compound **13α**: a white solid; $[\alpha]_D^{25}$ = 210.8 (*c* = 0.42 in CH_3OH);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.47 (d, *J* = 4.5 Hz, 1H), 4.11–4.07 (m, 1H), 3.81 (dd, *J* = 11.5, 5.3 Hz, 1H), 3.83–3.77 (m, 2H), 3.74–3.70 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 132.9, 130.1, 129.6, 88.2, 73.7, 70.7, 64.0, 62.6, 21.3; HR-ESI calcd for $C_{12}H_{15}N_3O_3SNa$ $[M + Na]^+$ 304.0726, found 304.0734.

Compound **13β**: a white solid; $[\alpha]_D^{25}$ = –68.2 (*c* = 0.57 in CH_3OH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46–7.45 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.38 (d, *J* = 9.9 Hz, 1H), 4.06 (dd, *J* = 11.5, 5.3 Hz, 1H), 3.63 (ddd, *J* = 10.3, 9.0, 5.3 Hz, 1H), 3.41–3.38 (m, 1H), 3.23–3.19 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.0, 134.0, 130.0, 127.5, 87.6, 77.5, 69.5, 69.4, 65.0, 21.3; HR-ESI calcd for $C_{12}H_{15}N_3O_3SNa$ $[M + Na]^+$ 304.0726, found 304.0731.



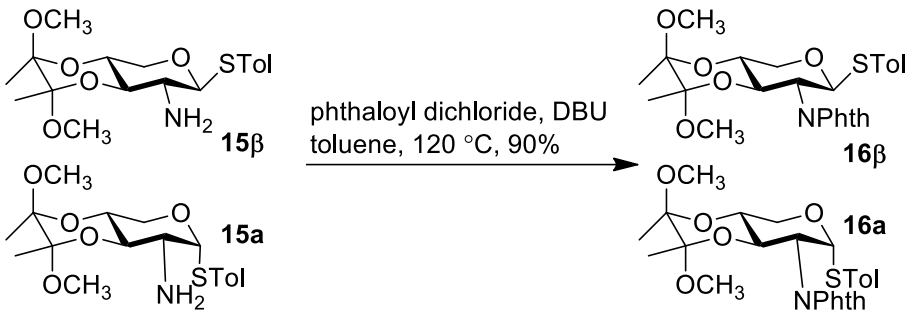
Compound **14**. To a cooled solution (0 ºC) of thioglycosides **13** (7.34 g, 26.1 mmol, α/β) in methanol (300 mL) were added sequentially 2,3-butanedione (2.51 mL, 28.7 mmol), trimethyl orthoformate (9.14 mL, 86.1 mmol), and boron trifluoride etherate (6.44 mL, 52.2 mmol), then the reaction mixture was allowed to warm to room temperature. After being stirred under Ar at room temperature for 48 h, the mixture was then cooled to 0 ºC and quenched with Et_3N. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 6:1) to afford an inseparable mixture of the α/β bisacetal **14α/14β** (8.35 g, 81%, α/β=1.3/1) as white solids, which were directly used for next step. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 0.85H), 7.37 (d, *J* = 8.1 Hz, 1.15H), 7.14 (d, *J* = 7.9 Hz, 0.85H), 7.12 (d, *J* = 7.9 Hz, 1.15H), 5.45 (d, *J* = 5.3 Hz, 0.57H), 4.28 (d, *J* = 9.8 Hz, 0.43H), 4.20–4.17 (m, 0.57H), 4.00 (dd, *J* = 10.7, 9.5 Hz, 0.57H), 3.96 (dd, *J* = 10.9, 4.6 Hz, 0.44H), 3.92 (dd, *J* = 10.8, 5.3 Hz, 0.56H), 3.83 (ddd, *J* = 10.9, 9.5, 5.2 Hz, 0.57H), 3.70–3.63 (m, 1.43H), 3.39–3.37 (m, 2.13H), 3.36–3.33 (m, 0.43H), 3.32 (s, 1.3H), 3.29 (s, 1.7H), 3.25 (s, 1.3H), 2.36 (s, 1.3H), 2.32 (s, 1.7H), 1.36 (s, 1.7H), 1.33 (s, 1.3H), 1.32 (s, 1.7H), 1.27 (s, 1.3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 138.2, 134.8, 132.8, 130.0, 129.9, 126.7, 100.6, 100.4, 100.0, 99.8, 88.7, 87.3, 73.8, 70.3, 68.0, 67.0, 65.9, 61.3, 60.9, 60.7, 48.5, 48.29, 48.28, 48.22, 21.4, 21.3, 17.9, 17.8, 17.7, 17.6; HR-ESI calcd for $C_{18}H_{25}N_3O_5SNa$ $[M + Na]^+$ 418.1407, found 418.1406.



Compound **15**. To a solution of **14** (2.30 g, 5.82 mmol, α/β) in THF and H_2O (60 mL, v/v, 9:1) was added triphenylphosphine (3.05 g, 11.6 mmol) at room temperature. The reaction mixture was heated at 80 ºC for 2 h. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with H_2O and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 2:1) to afford a mixture of the α/β compound **15α/15β** (1.82 g, 85%, α/β=1.5/1) as white solids. The α- and β-anomers of **15** could be partially separated.

Compound **15 α:** a white solid; $[\alpha]_D^{25}$ = 365.5 (*c* = 0.59 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 5.45 (d, *J* = 5.0 Hz, 1H), 4.19–4.16 (m, 1H), 3.75 (ddd, *J* = 10.7, 9.6, 5.2 Hz, 1H), 3.69 (dd, *J* = 10.7, 5.2 Hz, 1H), 3.58–3.55 (m, 1H), 3.31 (s, 3H), 3.29–3.25 (m, 4H), 2.31 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.8, 132.6, 130.8, 130.0, 100.2, 99.7, 92.6, 72.1, 67.2, 61.4, 54.3, 48.2, 48.1, 21.2, 18.0, 17.8; HR-ESI calcd for $C_{18}H_{28}NO_5S$ $[M + H]^+$ 370.1683, found 370.1688.

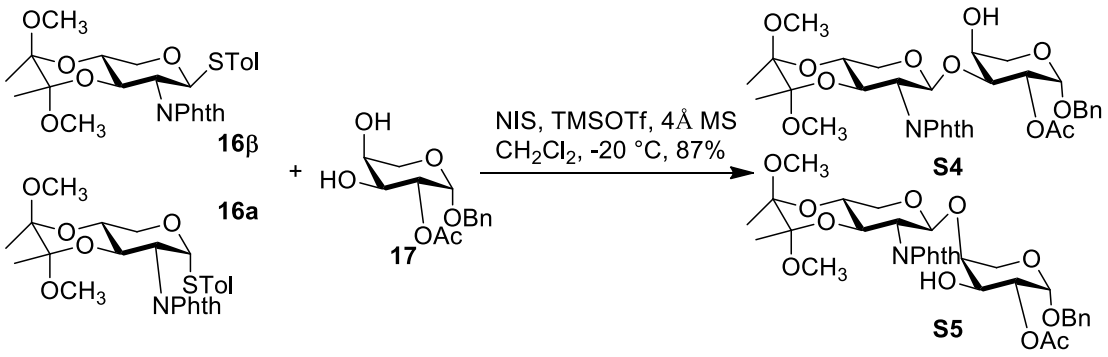
Compound **15 β:** a white solid; $[\alpha]_D^{25}$ = 135.5 (*c* = 0.97 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.36 (d, *J* = 9.4 Hz, 1H), 3.97 (dd, *J* = 10.8, 4.9 Hz, 1H), 3.72–3.68 (m, 1H), 3.56–3.52 (m, 1H), 3.44–3.41 (m, 1H), 3.28 (s, 3H), 3.24 (s, 3H), 2.85–2.82 (m, 1H), 2.33 (s, 3H), 1.31 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.7, 133.9, 129.9, 127.8, 100.0, 99.5, 90.5, 74.4, 68.2, 66.0, 53.1, 48.2, 48.1, 21.3, 17.9, 17.7; HR-ESI calcd for $C_{18}H_{28}NO_5S$ $[M + H]^+$ 370.1683, found 370.1686.



Compound **16**. To a solution of **15** (1.20 g, 3.25 mmol, α/β) in toluene (60 mL) were added DBU (2.43 mL, 16.3 mmol) and phthaloyl dichloride (1.87 mL, 13.0 mmol) sequentially at room temperature. The reaction mixture was heated at 120 °C for 8 h. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with H_2O, saturated aqueous $NaHCO_3$ and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 2:1) to afford a mixture of the α/β compound **16α/16β** (1.45 g, 90%, α/β=2.3/1) as white foams. The α- and β-anomers of **16** could be partially separated.

Compound **16 α:** a white foam; $[\alpha]_D^{25}$ = 206.6 (*c* = 0.95 in $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD) δ 7.90–7.89 (m, 2H), 7.86–7.84 (m, 2H), 7.24–7.22 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 5.48 (d, *J* = 5.4 Hz, 1H), 5.14 (dd, *J* = 11.8, 9.5 Hz, 1H), 4.59 (dd, *J* = 11.8, 5.4 Hz, 1H), 4.25–4.22 (m, 1H), 3.82 (ddd, *J* = 10.9, 9.6, 4.9 Hz, 1H), 3.72 (dd, *J* = 10.8, 4.9 Hz, 1H), 3.32(s, 3H), 3.29 (s, 3H), 2.27 (s, 3H), 1.31 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 139.1, 136.0, 135.7, 133.6, 131.7, 130.8, 124.4, 101.9, 101.4, 90.5, 70.1, 66.0, 61.7, 55.3, 50.0, 49.6, 48.4, 21.0, 18.1; HR-ESI calcd for $C_{26}H_{29}NO_7SNa$ $[M + Na]^+$ 522.1557, found 522.1560.

Compound **16 β:** a white foam; $[\alpha]_D^{25}$ = 233.7 (*c* = 0.20 in $CHCl_3$); ^{1}H NMR (600 MHz, CD_3OD) δ 7.93–7.92 (m, 1H), 7.88–7.85 (m, 3H), 7.24–7.23 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 5.45 (d, *J* = 10.2 Hz, 1H), 4.49 (dd, *J* = 10.9, 9.6 Hz, 1H), 4.17–4.14 (m, 1H), 4.00 (dd, *J* = 10.9, 5.0 Hz, 1H), 3.75 (ddd, *J* = 10.6, 9.6, 5.0 Hz, 1H), 3.53–3.49 (m, 1H), 3.27 (s, 3H), 2.98 (s, 3H), 2.29 (s, 3H), 1.24 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 169.6, 168.8, 139.7, 136.0, 135.9, 134.2, 132.7, 132.6, 130.7, 129.7, 124.7, 124.3, 101.5, 101.0, 86.7, 69.7, 69.1, 68.7, 54.5, 48.3, 48.2, 21.1, 18.0, 17.9; HR-ESI calcd for $C_{26}H_{33}N_2O_7S$ $[M + NH_4]^+$ 517.2003, found 517.2007.

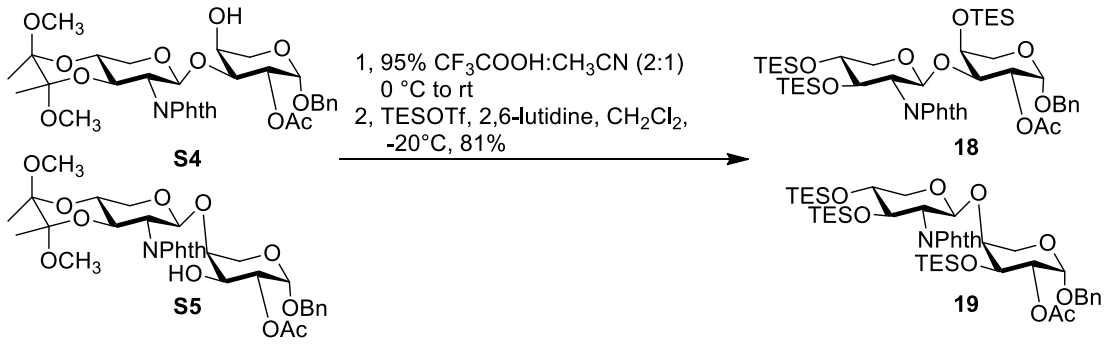


Compound disaccharide **S4** and **S5.** A suspension of donor **16** (0.99 g, 1.98 mmol, α/β), acceptor **17** (0.61 g, 2.18 mmol) and 4 Å MS (1.0 g) in dry CH_2Cl_2 (50 mL) was stirred at room temperature for 15 min and then cooled to –20 °C. *N*-Iodosuccinimide (0.53 g, 2.38 mmol) and a solution of TMSOTf (4.95 mL, 0.02 M) in dry CH_2Cl_2 were added sequentially. The stirring continued for 1 h at –20 °C and the reaction was quenched with Et_3N. The mixture was filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether-EtOAc, 1.5:1) to provide a mixture of the (1→3)-linked disaccharide **S4** and (1→4)-linked disaccharide **S5** (1.13 g, 87%) as white foams, which could be partially separated.

Compound **S4:** a white foam; $[\alpha]_D^{25}$ = 214.5 (*c* = 0.33 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.9, 1.5 Hz, 1H), 7.81 (dd, *J* = 5.9, 1.8 Hz, 1H), 7.76–7.71 (m, 2H), 7.32–7.27 (m, 3H), 7.25–7.24 (m, 2H), 5.26 (d, *J* = 8.2 Hz, 1H), 4.94 (d, *J* = 3.7 Hz, 1H), 4.87 (dd, *J* = 9.8, 3.8 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.61 (dd, *J* = 11.4, 9.6 Hz, 1H), 4.41 (d, *J* = 12.3 Hz, 1H), 4.23 (dd, *J* = 11.4, 8.2 Hz, 1H), 4.07 (br s, 1H), 4.05 (dd, *J* = 9.8, 3.5 Hz, 1H), 3.94 (dd, *J* = 11.1, 4.9 Hz, 1H), 3.86–3.85 (m, 1H), 3.84–3.82 (m, 1H), 3.73 (dd, *J* = 12.7, 1.9 Hz, 1H), 3.59–3.56 (m, 1H), 3.27 (s, 3H), 3.05 (s, 3H), 1.55 (s, 3H), 1.28 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.0, 168.3, 167.6, 137.3, 134.5, 134.3, 131.8, 131.6, 128.6, 128.1, 128.0, 124.0, 123.2, 100.18, 100.15, 99.8, 95.5, 75.5, 70.0, 69.5, 69.1, 67.5, 66.5, 64.4, 61.5, 54.0, 48.2, 48.1, 20.2, 17.8, 17.7; HR-ESI calcd for $C_{33}H_{43}N_2O_{13}$ $[M + NH_4]^+$675.2760, found 675.2769.

Compound **S5:** a white foam; $[\alpha]_D^{25}$ = 213.0 (*c* = 0.34 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 6.0 Hz, 1H), 7.81 (d, *J* = 6.0 Hz, 1H), 7.72–7.70 (m, 2H), 7.31–7.27 (m, 5H), 5.25 (d, *J* = 8.2 Hz, 1H), 4.99 (d, *J* = 3.6 Hz, 1H), 4.74 (dd, *J* = 9.9, 3.6 Hz, 1H), 4.67–4.63 (m, 2H), 4.45 (d, *J* = 12.3 Hz, 1H), 4.35 (dd, *J* = 11.4, 8.2 Hz, 1H), 3.99 (dd, *J* = 11.0, 4.9 Hz, 1H), 3.91–3.86 (m,

3H), 3.85–3.83 (m, 1H), 3.77–3.75 (m, 1H), 3.61–3.58 (m, 1H), 3.26 (s, 3H), 3.06 (s, 3H), 1.93 (s, 3H), 1.27 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 168.8, 168.0, 137.4, 134.20, 134.16, 131.8, 131.7, 128.5, 128.0, 127.9, 124.1, 123.2, 101.1, 100.1, 99.8, 95.8, 78.7, 71.8, 69.6, 67.38, 67.35, 66.7, 64.5, 61.9, 54.1, 48.2, 48.1, 20.9, 17.8, 17.7; HR-ESI calcd for $C_{33}H_{43}N_2O_{13}$ $[M + NH_4]^+$675.2760, found 675.2773.



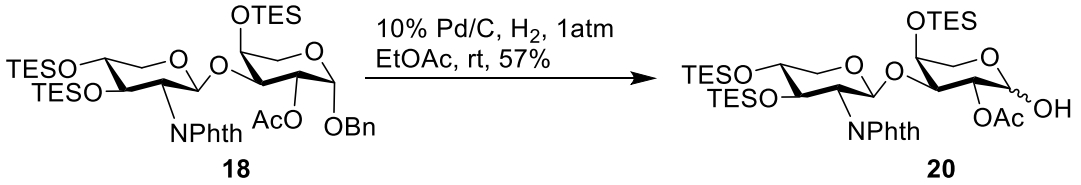
Compound disaccharide **18** and **19.** To a cooled solution (0 °C) of a mixture of the disaccharide **S4** and **S5** (1.13 g, 1.72 mmol) in CH_3CN (20 mL) was added slowly a solution of CF_3COOH and H_2O (40 mL, v/v, 19:1), and then the reaction mixture was allowed to warm to room temperature. After being stirred at room temperature for 2 h, the reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with H_2O, saturated aqueous $NaHCO_3$ and brine, respectively, dried over Na_2SO_4. After evaporation of the solvent, the residue was directly used for next step.

To a cooled solution (–20 °C) of the residue above in dry CH_2Cl_2 (60 mL) were added sequentially 2,6-lutidine (0.80 mL, 6.88 mmol) and TESOTf (1.36 mL, 6.02 mmol). After being stirred under Ar at –20 °C for 1 h, the mixture was quenched with Et_3N. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with diluted HCl (1M), saturated aqueous $NaHCO_3$ and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 8:1 to 6:1) to afford disaccharide **18** (0.41 g, 27% over two steps) and **19** (0.83 g, 55% over two steps) as pale yellow syrups.

Compound **18:** a pale yellow syrup; $[\alpha]_D^{25}$ = 71.4 (*c* = 0.69 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83–7.77 (m, 2H), 7.72–7.70 (m, 2H), 7.34–7.31 (m, 2H), 7.29–7.26 (m, 3H), 5.26 (d, *J* = 8.4 Hz, 1H), 4.98 (d, *J* = 3.7 Hz, 1H), 4.84 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.64 (d, *J* = 12.3 Hz, 1H),

4.41 (d, *J* = 12.3 Hz, 1H), 4.27 (dd, *J* = 10.4, 8.1 Hz, 1H), 4.05–4.00 (m, 3H), 3.90 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.80–3.78 (m, 1H), 3.67 (ddd, *J* = 10.5, 8.1, 5.3 Hz, 1H), 3.44 (dd, *J* = 12.0, 2.3 Hz, 1H), 3.34–3.30 (m, 1H), 1.83 (s, 3H), 1.00–0.97 (m, 9H), 0.94–0.91 (m, 9H), 0.74–0.72 (m, 9H), 0.67–0.58 (m, 12H), 0.44–0.38 (m, 3H), 0.33–0.27 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 168.7, 167.4, 137.6, 134.2, 134.1, 132.1, 131.8, 128.5, 128.00, 127.96, 123.6, 122.8, 99.6, 95.7, 73.6, 73.54, 73.51, 71.1, 70.8, 69.4, 66.3, 64.4, 57.4, 20.8, 7.04, 6.97, 6.87, 5.4, 5.3, 5.0; HR-ESI calcd for $C_{45}H_{71}NO_{11}Si_3Na$ $[M + Na]^+$ 908.4227, found 908.4231.

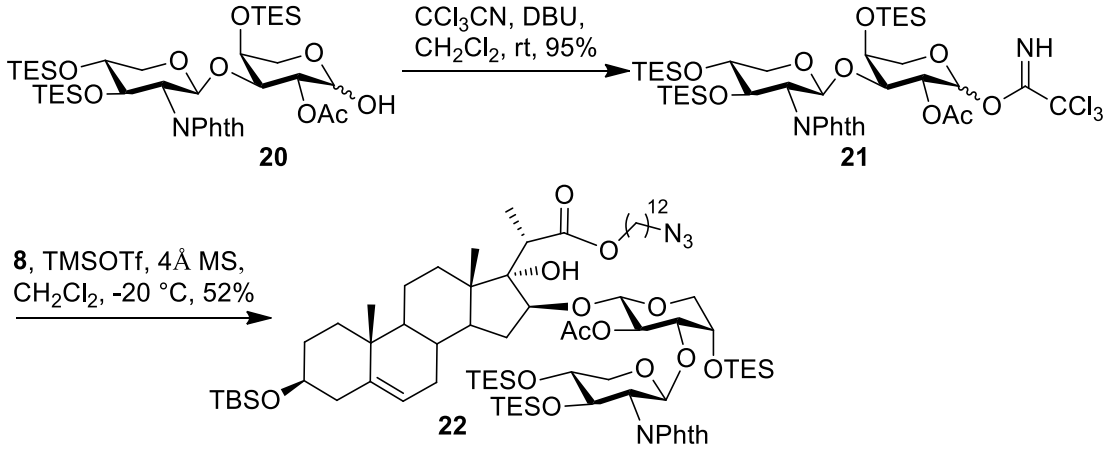
Compound **19:** a pale yellow syrup; $[\alpha]_D^{25}$ = 65.7 (*c* = 0.81 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (br s, 2H), 7.68–7.67 (m, 2H), 7.29–7.27 (m, 2H), 7.25–7.23 (m, 3H), 5.22 (d, *J* = 8.4 Hz, 1H), 4.96 (dd, *J* = 11.9, 3.4 Hz, 1H), 4.65 (d, *J* = 12.5 Hz, 1H), 4.52–4.50 (m, 1H), 4.42–4.40 (m, 2H), 4.14 (dd, *J* = 10.2, 8.6 Hz, 1H), 3.98–3.96 (m, 1H), 3.91 (dd, *J* = 11.6, 5.1Hz, 1H), 3.78–3.79 (m, 1H), 3.75 (br s, 2H), 3.71 (ddd, *J* = 10.3, 8.1, 5.1 Hz, 1H), 3.29–3.26 (m, 1H), 1.82 (s, 3H), 0.99–0.95 (m, 9H), 0.78–0.71 (m, 18H), 0.66–0.62 (m, 6H), 0.45–0.38 (m, 9H), 0.35–0.28 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 168.7, 167.8, 137.9, 133.8, 132.1, 128.4, 127.7, 127.5, 123.8, 122.9, 100.1, 95.8, 73.3, 73.0, 71.6, 69.4, 68.1, 66.1, 63.0, 57.6, 20.8, 7.0, 6.9, 5.4, 5.3, 4.6; HR-ESI calcd for $C_{45}H_{71}NO_{11}Si_3Na$ $[M + Na]^+$ 908.4227, found 908.4225.



18 **20**

Compound **20**. A suspension of **18** (5.00 g, 5.64 mmol) and 10% Pd/C (10 g) in EtOAc (130 mL) was stirred at room temperature under H_2 atmosphere (1 atm) for 48 h and then filtered. The filtrates were concentrated in vacuo. The residue was purified by a flash column chromatography (petroleum ether-EtOAc, 8:1 to 5:1) to afford hemiacetal **20** (2.56 g, 57%) as a white foam. Meanwhile, disaccharide **18** (1.12 g, 22%) was recovered. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (br s, 2H), 7.74–7.70 (m, 2H), 5.29 (br s, 0.68H), 5.28–5.25 (m, 1H), 4.87 (dd, *J* = 9.9, 3.5 Hz, 0.68H), 4.76 (dd, *J* = 8.8, 6.4 Hz, 0.32H), 4.39–4.36 (m, 0.32H), 4.28–4.24 (m, 1H), 4.06–4.04 (m, 1.7H), 4.03 (dd, *J* = 6.8, 3.1 Hz, 0.67H), 4.00 (br s, 0.35H), 3.97 (br s, 0.33H), 3.95 (br s, 0.36H), 3.94–

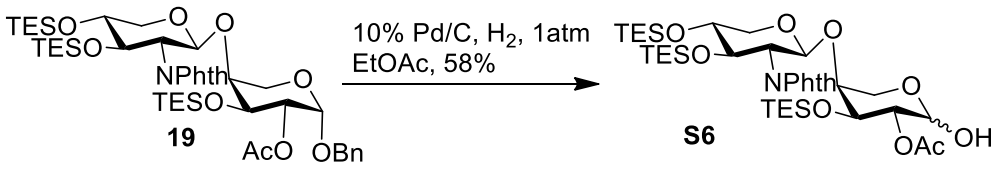
3.90 (m, 1H), 3.77 (dd, *J* = 12.4, 3.0 Hz, 0.34H), 3.73 (dd, *J* = 8.9, 2.8 Hz, 0.33H), 3.70–3.66 (m, 1H), 3.51–3.49 (m, 0.59H), 3.46 (dd, *J* = 12.0, 2.6 Hz, 0.68H), 3.33–3.29 (m, 1H), 1.97 (s, 1H), 1.91 (s, 2H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.73 (t, *J* = 8.0 Hz, 9H), 0.67–0.63 (m, 6H), 0.62–0.57 (m, 6H), 0.44–0.38 (m, 3H), 0.33–0.27(m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 170.5, 134.2, 131.9, 123.3, 99.6, 99.5, 96.3, 91.1, 73.6, 73.5, 73.1, 71.0, 70.8, 66.5, 66.4, 64.4, 57.4, 57.3, 21.1, 20.9, 7.1, 7.0, 6.91, 6.88, 5.4, 5.3, 4.92, 4.87; HR-ESI calcd for $C_{38}H_{69}N_2O_{11}Si_3$ $[M + NH_4]^+$ 813.4204, found 813.4199.



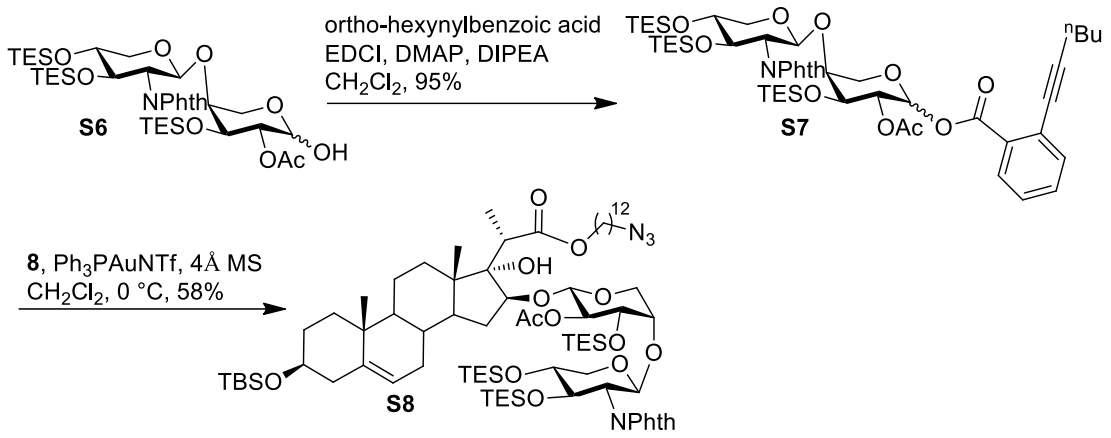
Compound **22.** A solution of hemiacetal **20** (2.24 g, 3.06 mmol), CCl_3CN (0.77 mL, 7.65 mmol), and DBU (0.091 mL, 0.61 mmol) in dry CH_2Cl_2 (60 mL) was stirred at room temperature for 14 h, the solution was concentrated in vacuo, and the resulting residue was purified by flash column chromatography (petroleum ether-EtOAc with 2% of triethylamine, 7:1) to give the instable imidates **21** (2.74 g, 95%) as pale yellow foams.

A solution of imidates **21** (1.45 g, 1.54 mmol), aglycone **8** (1.08 g, 1.54 mmol), and 4 Å MS (1.5 g) in dry CH_2Cl_2 (50 mL) was stirred at room temperature for 15 min and then cooled to –20 °C. A solution of TMSOTf (2.31 mL, 0.1 M) in dry CH_2Cl_2 was slowly added to the reaction. After being stirred for another 1 h, the reaction was quenched with triethylamine and filtered. The filtrates were concentrated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 12:1) to afford **22** (1.18 g, 52%) as a white foam: $[\alpha]_D^{25}$ = –24.5 (*c* = 0.66 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (br s, 2H), 7.71–7.70 (m, 2H), 5.27 (d, *J* = 5.1 Hz, 1H), 5.14 (d, *J* = 8.3 Hz, 1H), 4.75 (br s, 1H), 4.22 (dd, *J* = 10.3, 8.2 Hz, 1H), 4.19–4.16 (m, 1H), 4.02 (dd, *J* = 10.3, 8.4 Hz, 1H), 3.95 (d, *J* = 6.3 Hz, 1H), 3.93–3.90 (m, 2H),

3.87 (br s, 1H), 3.72–3.71 (m, 2H), 3.69–3.68 (m, 1H), 3.67–3.64 (m, 1H), 3.53 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.45 (ddd, *J* = 15.6, 10.8, 4.6 Hz, 1H), 3.29 (d, *J* = 11.3 Hz, 1H), 3.27–3.26 (m, 2H), 3.25–3.22 (m, 1H), 2.76 (q, *J* = 7.4 Hz, 1H), 2.26–2.22 (m, 1H), 2.18–2.12 (m, 2H), 1.92 (s, 3H), 0.99–0.95 (m, 12H), 0.92–0.91 (m, 9H), 0.88–0.87 (m, 9H), 0.73–0.71 (m, 12H), 0.66–0.62 (m, 6H), 0.61–0.56 (m, 6H), 0.42–0.36 (m, 3H), 0.32–0.25 (m, 3H), 0.06–0.04 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.0, 168.7, 167.4, 169.4, 141.5, 134.0, 132.1, 123.5, 121.3, 101.4, 100.1, 87.5, 84.8, 73.53, 73.48, 72.7, 71.9, 66.4, 64.6, 57.4, 51.6, 49.8, 48.6, 46.1, 42.9, 40.6, 37.4, 36.6, 35.4, 32.4, 32.2, 31.9, 31.8, 29.72, 29.70, 29.6, 29.5, 29.3, 29.0, 28.7, 26.9, 26.1, 26.0, 21.1, 20.6, 19.5, 18.4, 13.2, 13.1, 7.04, 6.95, 6.88, 5.4, 5.3, 5.0, -4.5; HR-MALDI calcd for $C_{78}H_{134}N_4O_{15}Si_4Na$ $[M + Na]^+$ 1501.8815, found 1501.8824.



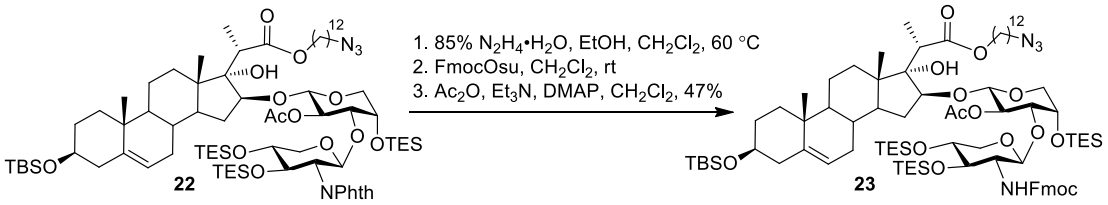
Compound **S6.** A suspension of **19** (5.60 g, 6.32 mmol) and 10% Pd/C (10 g) in EtOAc (130 mL) was stirred at room temperature under H_2 atmosphere (1 atm) for 48 h and then filtered. The filtrates were concentrated in vacuo. The residue was purified by a flash column chromatography (petroleum ether-EtOAc, 8:1 to 5:1) to afford hemiacetal **S6** (2.79 g, 55%) as white foams. Meanwhile, disaccharide **19** (1.45 g, 26%) was recovered. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (br s, 2H), 7.76–7.70 (m, 2H), 5.28–5.21 (m, 2H), 4.67 (br s, 0.33H), 4.56 (dd, *J* = 7.9, 2.3 Hz, 0.75H), 4.33–4.19 (m, 0.8H), 4.12–4.06 (m, 1H), 4.00 (dd, *J* = 11.4, 9.1 Hz, 0.2H), 3.96–3.90 (m, 3H), 3.80–3.75 (m, 2H), 3.72–3.68 (m, 1H), 3.32–3.27 (m, 1H), 2.04–1.96 (m, 3H), 0.99–0.96 (m, 9H), 0.76–0.71 (m, 18H), 0.66–0.62 (m, 6H), 0.44–0.36 (m, 9H), 0.34–0.27 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 134.3, 134.0, 132.1, 123.3, 100.5, 100.3, 91.0, 74.0, 73.3, 73.2, 72.3, 70.2, 67.9, 66.4, 66.2, 63.0, 57.5, 57.4, 21.1, 21.0, 7.0, 6.87, 6.85, 6.82, 6.6, 5.4, 5.34, 5.31, 4.7, 4.5; HR-ESI calcd for $C_{38}H_{69}N_2O_{11}Si_3$ $[M + NH_4]^+$ 813.4204, found 813.4204.



Compound **S8.** To a solution of hemiacetal **S6** (2.32 g, 2.91 mmol), ortho-hexynylbenzoic acid (0.88 g, 4.36 mmol), DMAP (0.36 g, 2.91 mmol) and DIPEA (2.40 mL, 2.91 mmol) in dry CH_2Cl_2 (60 mL) was added EDCI (2.23 g, 11.6 mmol) at room temperature. After stirring for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was diluted with EtOAc and washed with brine. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether-EtOAc, 6:1) to afford a mixture of the α/β **S7** (2.72 g, 95%) as white foams, which were immediately used in the next glycosylation.

A solution of donor **S7** (0.98 g, 1.0 mmol), aglycone **8** (0.7 g, 1.0 mmol), and 4 Å MS (1.0 g) in dry CH_2Cl_2 (30 mL) was stirred at room temperature for 15 min and then cooled to 0 °C, and $Ph_3PAuNTf_2$ (0.15 g, 0.2 mmol) was added to the reaction. After being stirred for another 1 h, the reaction was quenched with triethylamine and filtered. The filtrates were concentrated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether-EtOAc, 12:1) to afford **S8** (0.87 g, 59%) as a white foam: $[\alpha]_D^{25} = -26.7$ (*c* = 1.4 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (br s, 2H), 7.74–7.72 (m, 2H), 5.31–5.28 (m, 2H), 4.48 (d, *J* = 3.2 Hz, 1H), 4.22 (br s, 1H), 4.16–4.12 (m, 2H), 4.04 (dd, *J* = 19.1, 9.0 Hz, 1H), 3.97–3.92 (m, 3H), 3.74–3.70 (m, 1H), 3.69–3.67 (m, 1H), 3.66–3.60 (m, 4H), 3.47 (ddd, *J* = 15.6, 10.8, 4.6 Hz, 1H), 3.30–3.27 (m, 1H), 3.24 (t, *J* = 7.0 Hz, 2H), 2.93–2.90 (m, 1H), 2.29–2.20 (m, 2H), 2.17 (dd, *J* = 13.5, 3.0 Hz, 1H), 2.01 (s, 3H), 0.99 (s, 3H), 0.98–0.95 (m, 9H), 0.88 (s, 9H), 0.80 (s, 3H), 0.75–0.69 (m, 18H), 0.60–0.58 (m, 6H), 0.39–0.25 (m, 12H), 0.05 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.4, 169.4, 168.9, 167.6, 141.5, 134.2, 132.4, 131.9, 131.1, 129.0, 123.5, 123.10, 121.14, 100.6, 100.3, 90.4, 84.9, 75.4, 74.2, 73.2, 73.0, 72.7, 66.4, 65.7, 64.8, 57.4, 51.6, 49.7, 48.4, 45.8, 42.9, 40.8, 37.4,

36.6, 34.9, 32.3, 32.2, 32.0, 31.9, 29.8, 29.6, 29.59, 29.57, 29.4, 29.3, 29.0 28.4, 26.8, 26.1, 25.9, 22.8, 21.2, 20.7, 19.6, 18.4, 14.3, 13.6, 12.9, 7.0, 6.84, 6.77, 5.4, 5.3, 4.6, -4.5; HR-MALDI calcd for $C_{78}H_{134}N_4O_{15}Si_4Na$ $[M + Na]^+$ 1501.8815, found 1501.8832.

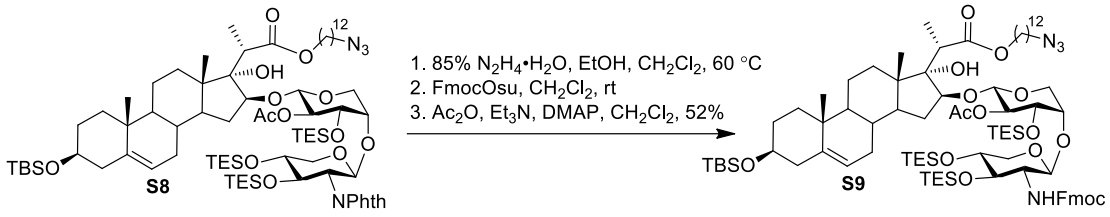


Compound **23.** To a solution of **22** (2.26 g, 1.53 mmol) in EtOH and CH_2Cl_2 (60 mL, v/v, 5:1) was added 85% $N_2H_4 \cdot H_2O$ (11.3 mL) at room temperature. The reaction mixture was heated at 60 °C for 3 h. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with H_2O and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 6:1) to afford an amine mixture.

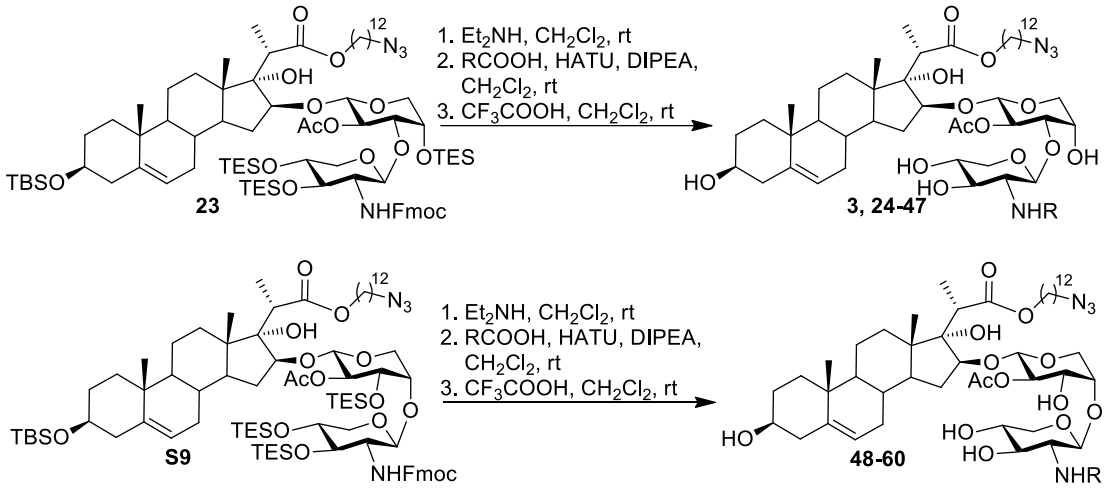
To a solution of the mixture above (1.17 g, 0.89 mmol) in CH_2Cl_2 (30 mL) was added FmocOSu (0.45 g, 1.34 mmol) at room temperature. After the mixture was stirred for 16 h, the reaction mixture was concentrated in vacuo to give a residue, which was purified by a flash column chromatography (petroleum ether-EtOAc, 10:1) to afford a white foam crude product (1.19 g).

To a solution of the crude product above (1.09 g, 0.71mmol) in dry CH_2Cl_2 (30 mL) was added Et_3N (0.30 mL, 2.14 mmol), Ac_2O (0.13 mL, 1.42 mmol), DMAP (0.087 g, 0.71 mmol) sequentially at room temperature. After stirring for 16 h, the reaction mixture was quenched with methanol. The reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with H_2O, saturated aqueous $NaHCO_3$ and brine, respectively, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by a flash column chromatography (petroleum ether-EtOAc, 12:1) to afford **23** (1.04 g, 47% over three steps) as a white foam: $[\alpha]_D^{25}$ = –45.6 (*c* = 1.3 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 6.9 Hz, 2H), 7.39 (t, *J* = 6.8 Hz, 2H), 7.30 (t, *J* = 6.9 Hz, 2H), 6.03 (d, *J* = 10.4 Hz, 1H), 5.31 (br s, 1H), 4.96 (br s, 1H), 4.83 (br s, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.43–4.40 (m, 1H), 4.34 (br s, 1H), 4.28 (dd, *J* = 17.4, 9.3 Hz, 1H), 4.23–4.21 (m, 1H),

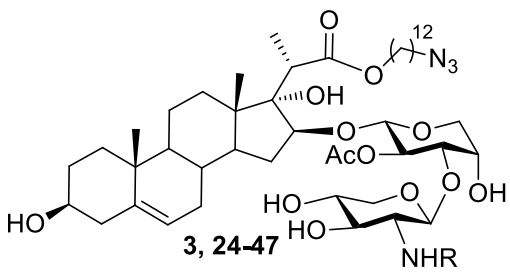
4.13–4.11 (m, 1H), 4.03–3.99 (m, 3H), 3.89 (br s, 1H), 3.80–3.76 (m, 2H), 3.71–3.68 (m, 2H), 3.49 (br s, 2H), 3.29–3.28 (m, 1H), 3.25–3.23 (m, 3H), 3.15–3.14 (m, 1H), 2.28–2.26 (m, 2H), 2.16–2.15 (m, 1H), 2.04 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.0, 169.2, 155.2, 144.4, 144.0, 141.5, 141.43, 141.36, 131.1, 129.0, 127.8, 127.7, 127.1, 125.4, 125.2, 121.3, 120.1, 120.0, 100.6, 96.7, 91.7, 85.1, 72.7, 70.1, 69.8, 68.0, 66.8, 65.5, 64.8, 60.3, 59.4, 52.1, 51.6, 49.7, 48.5, 47.4, 45.9, 43.0, 40.9, 37.4, 36.7, 35.0, 32.2, 32.1, 29.7, 29.62, 29.59, 29.3, 29.2, 29.0, 28.5, 26.8, 26.1, 25.7, 21.0, 20.6, 19.3, 18.4, 14.1, 13.5, 7.1, 7.0, 4.9, 4.8, -4.5; HR-MALDI calcd for $C_{85}H_{142}N_4O_{15}Si_4Na$ $[M + Na]^+$ 1593.9441, found 1593.9425.



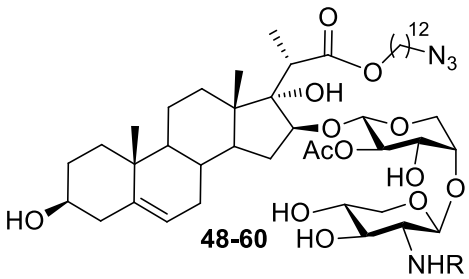
Compound **S9.** Similar procedures were conducted on glycoside **S8**, and **S9** (52%, over three steps) was obtained as a white foam: $[\alpha]_D^{25}$ = –40.9 (*c* = 0.24 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.60–7.57 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 6.08 (d, *J* = 9.9 Hz, 1H), 5.31 (d, *J* = 4.6 Hz, 1H), 4.78–4.75 (m, 2H), 4.38 (dd, *J* = 10.5, 7.3 Hz, 1H), 4.32 (dd, *J* = 10.4, 7.2 Hz, 1H), 4.27–4.21 (m, 2H), 4.17 (t, *J* = 7.1 Hz, 1H), 4.01 (dd, *J* = 10.9, 8.4 Hz, 1H), 3.98 (br s, 1H), 3.89–3.87 (m, 1H), 3.82–3.79 (m, 2H), 3.78–3.75 (m, 1H), 3.72–3.70 (m, 2H), 3.53 (br s, 1H), 3.48 (ddd, *J* = 15.6, 10.8, 4.7 Hz, 1H), 3.39–3.35 (m, 2H), 3.25 (t, *J* = 7.0 Hz, 1H), 2.96–2.95 (m, 1H), 2.29–2.23 (m, 1H), 2.17 (dd, *J* = 13.4, 2.6 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.4, 169.4, 155.4, 144.18, 144.16, 141.6, 141.4, 127.7, 127.1, 125.3, 121.2, 120.1, 101.0, 84.9, 72.8, 72.7, 70.4, 69.5, 66.8, 64.8, 60.4, 52.2, 51.6, 49.8, 48.5, 47.4, 45.9, 43.0, 40.8, 37.4, 36.7, 32.4, 32.2, 32.0, 29.9, 29.7, 29.6, 29.6, 29.4, 29.3, 29.0, 28.6, 26.9, 26.1, 26.0, 21.2, 20.7, 19.6, 18.4, 13.5, 13.1, 7.1, 7.0, 6.9, 4.9, 4.8, 4.8, -4.4; HR-MALDI calcd for $C_{85}H_{142}N_4O_{15}Si_4Na$ $[M + Na]^+$ 1593.9441, found 1593.9437.



OSW-1 analogues (**3**, **24**−**47, 48**−**60**). To a solution of **23** (1.04 g, 0.66 mmol) in CH_2Cl_2 (10 mL) was added ethylenediamine (10 mL), at room temperature. After the mixture was stirred for 16 h, the reaction mixture was concentrated in vacuo to give a residue, which was purified by a flash column chromatography (petroleum ether-EtOAc, 12:1) to afford an amine crude product (0.91 g). To a solution of the corresponding carboxylic acid (2.0 equiv) and HATU (4.0 equiv) in CH_2Cl_2, was added the free amino group crude product (1.0 equiv) in CH_2Cl_2. After stirring for 10 min at room temperature, *N*,*N*-diisopropylethylamine (10.0 equiv) was added. The stirring continued for 1 h at room temperature and the reaction was then poured into water, and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After a flash column chromatography, the residue in CH_2Cl_2 and CF_3COOH (v/v, 2:1) was stirred at room temperature for 30 min and then the reaction mixture was concentrated in vacuo to give a residue, which was diluted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated. After a crude purification with flash column chromatography, the residue was further purified by HPLC to afford 25 (1→3)-linked OSW-1 analogues (**3**, **24**−**47**). Similar procedures were conducted on **S9** and another 13 (1→4)-linked OSW-1 analogues (**48**−**60**) were obtained accordingly.



3, 24-47



48-60

OSW-1 analogue **3** was obtained as a white solid (14.8 mg, 36%): $[\alpha]_D^{25}$ = –34.5 (*c* = 0.52 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.95–7.94 (m, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.34 (d, *J* = 4.9 Hz, 1H), 4.94 (dd, *J* = 7.7, 5.7 Hz, 1H), 4.79 (d, *J* = 5.7 Hz, 1H), 4.62 (br s, 1H), 4.22 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.17 (d, *J* = 5.6 Hz, 1H), 4.06 (dd, *J* = 11.9, 4.0 Hz, 1H), 4.01–3.99 (m, 1H), 3.98 (dd, *J* = 4.9, 2.5 Hz, 1H), 3.86 (dd, *J* = 7.9, 4.3 Hz, 1H), 3.85–3.82 (m, 1H), 3.78–3.76 (m, 2H), 3.70–3.68 (m, 1H), 3.64–3.61 (m, 1H), 3.48 (dd, *J* = 12.1, 2.5 Hz, 1H), 3.42–3.36 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.88 (q, *J* = 7.3 Hz, 1H), 2.26–2.19 (m, 3H), 1.76 (s, 3H), 1.03 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 171.3, 168.2, 142.2, 137.2, 133.2, 129.4, 127.6, 126.2, 124.4, 122.5, 122.3, 120.7, 102.5, 102.2, 89.9, 85.9, 77.5, 73.0, 72.4, 71.2, 70.9, 68.3, 65.6, 64.9, 55.5, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.6, 36.4, 33.4, 33.2, 33.1, 32.3, 30.64, 30.61, 30.56, 30.3, 29.9, 29.6, 29.3, 27.8, 26.9, 21.7, 20.9, 19.9, 13.8, 13.6; HR-ESI calcd for $C_{55}H_{79}F_3N_6O_{14}Na$ $[M + Na]^+$ 1127.5499, found 1127.5499.

OSW-1 analogue **24** was obtained as a white solid (9.4 mg, 30%): $[\alpha]_D^{25}$ = –17.4 (*c* = 0.29 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 5.34 (d, *J* = 4.9 Hz, 1H), 5.00 (dd, *J* = 8.8, 6.7 Hz, 1H), 4.61 (br s, 1H), 4.50 (d, *J* = 6.9 Hz, 1H), 4.32 (dt, *J* = 10.9, 7.1 Hz, 1H), 4.17 (d, *J* = 6.7 Hz, 1H), 4.00–3.97 (m, 1H), 3.96–3.92 (m, 2H), 3.87–3.82 (m, 2H), 3.71 (dd, *J* = 8.5, 2.9 Hz, 1H), 3.69 (dd, *J* = 8.3, 6.6 Hz, 1H), 3.53 (td, *J* = 8.2, 4.7 Hz, 1H), 3.50–3.45 (m, 2H), 3.39 (ddd, *J* = 16.0, 10.9, 4.9 Hz, 1H), 3.28 (t, *J* = 6.9 Hz, 2H), 3.24 (dd, *J* = 11.7, 8.7 Hz, 1H), 2.89 (q, *J* = 7.4 Hz, 1H), 2.25–2.20 (m, 3H), 2.14 (s, 3H), 1.98 (s, 3H), 1.03 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.5, 173.6, 171.4, 142.2, 122.3, 103.5, 102.7, 89.2, 85.9, 78.6, 74.0, 72.4, 72.0, 71.2, 69.4, 65.9, 65.8, 55.9, 52.5, 51.4, 49.8, 49.6, 47.3, 43.0, 42.0, 38.5, 37.6, 36.6, 33.5, 33.2, 33.1, 32.3, 30.66, 30.64, 30.4, 30.3, 29.9, 29.8, 27.8, 27.0, 23.1, 21.7, 21.3, 19.8, 13.7, 13.6; HR-ESI calcd for $C_{48}H_{78}N_4O_{14}Na$ $[M + Na]^+$ 957.5407, found 957.5417.

OSW-1 analogue **25** was obtained as a white solid (8.6 mg, 30%): $[\alpha]_D^{25}$ = –24.3 (*c* = 0.15 in

CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 5.34 (d, *J* = 5.0 Hz, 1H), 4.98 (dd, *J* = 8.2, 6.1 Hz, 1H), 4.60–4.59 (m, 2H), 4.30 (dt, *J* = 10.9, 7.1 Hz, 1H), 4.18 (d, *J* = 6.1 Hz, 1H), 4.01 (dd, *J* = 11.8, 4.0 Hz, 1H), 3.99–3.96 (m, 1H), 3.93 (dd, *J* = 6.2, 3.7 Hz, 1H), 3.85 (dd, *J* = 12.2, 4.4 Hz, 1H), 3.81 (dd, *J* = 8.1, 4.9 Hz, 1H), 3.78 (d, *J* = 6.3 Hz, 1H), 3.75 (dd, *J* = 8.3, 3.3 Hz, 1H), 3.55 (td, *J* = 7.3, 4.2 Hz, 1H), 3.49–3.46 (m, 2H), 3.39 (ddd, J=16.0, 11.0, 5.0Hz, 1H), 3.29–3.27 (m, 3H), 2.90 (q, *J* = 7.4 Hz, 1H), 2.25–2.16 (m, 5H), 2.13 (s, 3H), 1.03 (s, 3H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.88 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.6, 176.0, 171.3, 142.2, 122.3, 102.6, 89.6, 86.0, 77.3, 73.3, 72.4, 71.6, 71.0, 68.8, 65.8, 65.4, 65.0, 54.7, 52.5, 51.4, 49.8, 49.6, 47.3, 43.0, 42.1, 39.4, 38.5, 37.7, 36.5, 33.5, 33.2, 33.1, 32.3, 30.7, 30.6, 30.4, 30.3, 29.9, 29.7, 27.8, 27.0, 21.7, 21.3, 20.2, 19.8, 14.2, 13.8, 13.6; HR-ESI calcd for $C_{50}H_{82}N_4O_{14}Na$ $[M + Na]^+$ 985.5720, found 985.5724.

OSW-1 analogue **26** was obtained as a white solid (11 mg, 35%): $[\alpha]_D^{25}$ = –25.6 (*c* = 0.28 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 5.34 (d, *J* = 4.9 Hz, 1H), 4.97 (dd, *J* = 7.9, 5.9 Hz, 1H), 4.62–4.61 (m, 2H), 4.29 (dt, *J* = 10.9, 7.1 Hz, 1H), 4.19 (d, *J* = 5.8 Hz, 1H), 4.02 (dd, *J* = 12.0, 4.1 Hz, 1H), 3.98 (dt, *J* = 10.9, 6.6 Hz, 1H), 3.93 (dd, *J* = 6.5, 3.8 Hz, 1H), 3.85 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.80 (dt, *J* = 13.5, 6.6 Hz, 2H), 3.76 (dd, *J* = 8.0, 3.3 Hz, 1H), 3.55 (td, *J* = 7.0, 4.2 Hz, 1H), 3.49–3.47 (m, 2H), 3.40 (ddd, *J* = 16.0, 10.9, 4.9 Hz, 1H), 3.28 (t, *J* = 8.9Hz, 2H), 2.91 (q, *J* = 7.4 Hz, 1H), 2.26–2.18 (m, 5H), 2.13 (s, 3H), 1.03 (s, 3H), 0.95–0.89 (m, 6H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 176.1, 171.3, 142.2, 122.3, 102.5, 102.3, 89.7, 86.0, 77.0, 73.1, 72.4, 71.6, 71.5, 70.9, 68.5, 65.8, 65.2, 64.8, 54.6, 52.5, 51.4, 49.8, 49.6, 47.3, 43.0, 42.0, 38.5, 37.7, 37.5, 36.4, 33.5, 33.2, 33.11, 33.08, 32.3, 30.70, 30.67, 30.60, 30.5, 30.4, 30.3, 30.0, 29.8, 27.9, 27.0, 26.8, 23.8, 21.7, 21.3, 19.8, 14.5, 13.8, 13.6; HR-ESI calcd for $C_{56}H_{94}N_4O_{14}Na$ $[M + Na]^+$ 1069.6659, found 1069.6661.

OSW-1 analogue **27**[S5] was obtained as a white solid (11.7 mg, 33%): $[\alpha]_D^{25}$ = –22.2 (*c* = 0.35 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.09 (t, *J* = 8.0 Hz, 1H), 5.34 (d, *J* = 4.9 Hz, 1H), 4.98 (dd, *J* = 8.0, 5.9 Hz, 1H), 4.61 (br s, 2H), 4.29 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.19 (d, *J* = 5.9 Hz, 1H), 4.02 (dd, *J* = 12.2, 4.3 Hz, 1H), 3.99–3.96 (m, 1H), 3.92 (dd, *J* = 6.3, 3.7 Hz, 1H), 3.85 (dd, *J* = 12.1, 4.6 Hz, 1H), 3.82–3.76 (m, 3H), 3.64 (s, 1H), 3.55 (td, *J* = 7.1, 4.2 Hz, 1H), 3.49–3.46 (m, 2H), 3.39 (ddd, *J* = 16.0, 10.9, 4.9 Hz, 1H), 3.29–3.27 (m, 3H), 2.91 (q, *J* = 7.4 Hz, 1H), 2.65–2.58 (m, 2H), 2.28 (dt, *J* = 15.2, 7.5 Hz, 2H), 2.25–2.18 (m, 5H), 2.13 (s, 3H), 1.03 (s, 3H), 0.88 (s,

3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 176.0, 171.3, 153.2, 152.9, 142.2, 137.5, 132.3, 130.9, 130.8, 122.3, 102.6, 102.4, 89.7, 86.0, 77.0, 73.2, 72.4, 71.6, 70.9, 68.6, 65.8, 65.3, 64.9, 54.7, 52.5, 51.4, 49.8, 49.6, 47.3, 43.0, 42.0, 38.5, 37.7, 37.4, 36.5, 33.5, 33.2, 33.1, 33.0, 32.3, 30.71, 30.67, 30.42, 30.39, 30.34, 30.31, 30.26, 30.0, 29.8, 29.6, 29.1, 29.0, 27.9, 27.2, 27.0, 26.6, 23.8, 21.7, 21.3, 19.9, 14.5, 13.8, 13.7; HR-ESI calcd for $C_{64}H_{107}N_5O_{16}Na$ $[M + Na]^+$ 1224.7605, found 1224.7607.

OSW-1 analogue **28** was obtained as a white solid (17.5 mg, 30%): $[\alpha]_D^{25}$ = –26.4 (*c* = 0.48 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.10 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 5.34 (d, *J* = 4.8 Hz, 1H), 4.97 (dd, *J* = 8.1, 6.1 Hz, 1H), 4.61 (br s, 1H), 4.59 (d, *J* = 5.5 Hz, 1H), 4.27 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.18 (d, *J* = 6.0 Hz, 1H), 4.00 (dd, *J* = 11.9, 4.0 Hz, 1H), 3.95 (dt, *J* = 6.5, 4.4 Hz, 1H), 3.93–3.92 (m, 1H), 3.85 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.82–3.78 (m, 2H), 3.75–3.72 (m, 5H), 3.67–3.64 (m, 4H), 3.56–3.53 (m, 1H), 3.48–3.46 (m, 2H), 3.39 (ddd, *J* = 16.0, 10.7, 4.8 Hz, 1H), 3.29–3.26 (m, 3H), 2.90 (q, *J* = 7.4 Hz, 1H), 2.57 (t, *J* = 7.3 Hz, 2H), 2.24–2.19 (m, 5H), 2.06 (s, 3H), 1.03 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 175.9, 171.3, 145.9, 142.2, 131.8, 130.8, 122.3, 113.5, 102.5, 89.7, 85.9, 77.3, 73.2, 72.4, 71.5, 70.9, 68.7, 65.8, 65.3, 65.0, 54.7, 54.6, 52.5, 51.4, 49.8, 49.6, 47.3, 43.0, 42.0, 41.7, 38.5, 37.7, 36.8, 36.4, 35.3, 33.5, 33.2, 33.1, 32.3, 30.77, 30.69, 30.66, 30.4, 30.3, 29.9, 29.7, 28.7, 27.9, 27.0, 21.7, 21.2, 19.9, 13.8, 13.7; HR-ESI calcd for $C_{60}H_{93}Cl_2N_5O_{14}Na$ $[M + Na]^+$ 1200.5988, found 1200.5995.

OSW-1 analogue **29** was obtained as a white solid (12.7 mg, 33%): $[\alpha]_D^{25}$ = –31.2 (*c* = 0.15 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.83–7.81 (m, 2H), 7.01–6.99 (m, 2H), 5.34 (d, *J* = 5.0 Hz, 1H), 4.96 (dd, *J* = 7.7, 5.6 Hz, 1H), 4.83 (d, *J* = 5.0 Hz, 1H), 4.22 (dt, *J* = 10.9, 6.9 Hz, 1H), 4.17 (d, *J* = 5.5 Hz, 1H), 4.08 (dd, *J* = 12.0, 3.7 Hz, 1H), 4.02–4.01 (m, 1H), 3.99 (dd, *J* = 5.3, 2.6 Hz, 1H), 3.87 (dd, *J* = 6.2, 3.3 Hz, 1H), 3.86 (s, 3H), 3.85–3.84 (m, 1H), 3.79–3.76 (m, 2H), 3.71–3.69 (m, 1H), 3.64–3.61 (m, 1H), 3.48 (dd, *J* = 12.1, 2.5 Hz, 1H), 3.41–3.38 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.88 (q, *J* = 7.3 Hz, 1H), 2.26–2.19 (m, 3H), 1.81 (s, 3H), 1.03 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.8, 171.4, 169.1, 164.0, 142.2, 130.4, 127.8, 122.3, 114.7, 102.6, 102.0, 90.0, 86.0, 77.4, 72.8, 72.4, 70.9, 70.8, 68.2, 65.6, 64.9, 64.5, 56.0, 54.9, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.6, 36.5, 33.4, 33.2, 33.1, 32.3, 30.7, 30.63, 30.58, 30.3, 29.9, 29.6, 27.9, 26.9, 21.7, 20.9, 19.8, 13.8, 13.6; HR-ESI calcd for $C_{54}H_{82}N_4O_{15}Na$ $[M + Na]^+$ 1049.5669, found 1049.5672.

OSW-1 analogue **30** was obtained as a white solid (5.0 mg, 16%): $[\alpha]_D^{25}$ = –32.1 (*c* = 0.21 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.70 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.40 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 6.94–6.88 (m, 2H), 5.34 (d, *J* = 4.1 Hz, 1H), 4.95–4.94 (m, 1H), 4.84–4.81 (m, 1H), 4.61 (br s, 1H), 4.22 (d, *J* = 4.7 Hz, 1H), 4.19–4.13 (m, 2H), 4.09–4.08 (m, 1H), 3.99 (dt, *J* = 6.3, 3.2 Hz, 1H), 3.88–3.85 (m, 2H), 3.84–3.83 (m, 1H), 3.77–3.75(m, 2H), 3.65 (dd, *J* = 9.4, 5.8 Hz, 1H), 3.49–3.43 (m, 2H), 3.39 (dt, *J* = 11.0, 5.7 Hz, 1H), 3.28 (t, *J* = 6.9 Hz, 2H), 3.06–3.00 (m, 1H), 2.24–2.18 (m, 3H), 1.88 (s, 3H), 1.03 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 180.0, 173.4, 171.3, 170.4, 161.9, 142.3, 135.0, 130.9, 128.6, 122.3, 120.0, 118.8, 116.7, 102.4, 100.9, 90.5, 86.0, 72.4, 71.9, 70.5, 65.7, 63.8, 52.5, 51.4, 49.8, 49.6, 47.2, 43.6, 43.0, 41.9, 38.5, 37.7, 36.5, 36.3, 33.5, 33.2, 33.1, 32.3, 30.64, 30.61, 30.5, 30.29, 30.26, 30.0, 29.6, 27.9, 26.9, 23.7, 21.7, 20.8, 20.5, 19.8, 14.5, 14.0, 13.7; HR-ESI calcd for $C_{55}H_{82}N_4O_{16}Na$ $[M + Na]^+$ 1077.5618, found 1077.5617.

OSW-1 analogue **31** was obtained as a white solid (6.2 mg, 20%): $[\alpha]_D^{25}$ = –24.7 (*c* = 0.22 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.68–7.67 (m, 1H), 7.62 (dd, *J* = 12.0, 2.2 Hz, 1H), 7.20–7.17 (m, 1H), 5.34 (d, *J* = 5.1 Hz, 1H), 4.95 (dd, *J* = 7.8, 5.7 Hz, 1H), 4.80 (d, *J* = 5.6 Hz, 1H), 4.62 (br s, 2H), 4.22 (dt, *J* = 10.9, 6.9 Hz, 1H), 4.17 (d, *J* = 5.6 Hz, 1H), 4.07 (dd, *J* = 11.9, 3.9 Hz, 1H), 3.99–3.97 (m, 2H), 3.94 (s, 3H), 3.86 (dd, *J* = 8.5, 3.7 Hz, 1H), 3.85–3.83 (m, 1H), 3.78–3.76 (m, 2H), 3.70–3.67 (m, 1H), 3.64–3.61 (m, 1H), 3.48 (dd, *J* = 12.1, 2.5 Hz, 1H), 3.41–3.36 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.88 (q, *J* = 7.3 Hz, 1H), 2.26–2.19 (m, 3H), 1.82 (s, 3H), 1.03 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.8, 171.3, 168.0, 153.9, 152.2, 152.1, 142.2, 130.9, 128.2, 125.5, 122.3, 116.3, 113.9, 102.5, 102.2, 89.9, 86.0, 77.6, 73.0, 72.4, 71.0, 70.8, 68.2, 65.6, 64.8, 56.8, 55.3, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.6, 36.4, 33.4, 33.2, 33.1, 32.3, 30.6, 30.3, 29.9, 29.6, 27.8, 26.9, 21.7, 20.9, 19.8, 13.8, 13.6; HR-ESI calcd for $C_{54}H_{81}FN_4O_{15}Na$ $[M + Na]^+$ 1067.5575, found 1067.5579.

OSW-1 analogue **32** was obtained as a white solid (4.1 mg, 13%): $[\alpha]_D^{25}$ = –24.8 (*c* = 0.13 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.54–7.50 (m, 2H), 5.34 (d, *J* = 5.0 Hz, 1H), 4.95–4.94 (m, 1H), 4.75 (d, *J* = 6.1 Hz, 1H), 4.23 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.17 (d, *J* = 5.7 Hz, 1H), 4.06 (s, 3H), 4.05–4.03 (m, 1H), 3.97 (dd, *J* = 6.6, 4.0 Hz, 1H), 3.95–3.92 (m, 1H), 3.87 (dd, *J* = 7.5, 3.3 Hz, 1H), 3.84 (dd, *J* = 5.6, 3.5 Hz, 1H), 3.80–3.76 (m, 2H), 3.68–3.66 (m, 1H), 3.63–3.60 (m, 1H), 3.48 (dd, *J* = 12.1, 2.4 Hz, 1H), 3.41–3.37 (m, 1H), 3.36–3.34 (m, 1H), 3.28 (t, *J* = 6.9 Hz, 2H),

2.88 (q, *J* = 7.4 Hz, 1H), 2.26–2.19 (m, 3H), 1.84 (s, 3H), 1.03 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 180.3, 179.7, 171.2, 166.6, 157.2, 155.5, 142.2, 140.5, 130.3, 122.3, 113.1, 112.9, 102.5, 102.4, 89.8, 86.1, 86.0, 77.9, 73.2, 72.4, 71.3, 71.1, 70.9, 68.4, 65.6, 65.1, 62.4, 55.8, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.6, 36.4, 33.5, 33.2, 33.1, 32.3, 30.6, 30.3, 29.9, 29.6, 27.8, 26.9, 21.7, 20.9, 19.8, 13.8, 13.6; HR-ESI calcd for $C_{54}H_{80}F_2N_4O_{15}Na$ $[M + Na]^+$ 1085.5480, found 1085.5483.

OSW-1 analogue **33** was obtained as a white solid (3.8 mg, 12%): $[\alpha]_D^{25}$ = –25.4 (*c* = 0.14 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.00–6.97 (m, 2H), 5.35 (d, *J* = 4.9 Hz, 1H), 5.00 (dd, *J* = 7.0, 5.1 Hz, 1H), 4.62 (br s, 2H), 4.28–4.25 (m, 1H), 4.24 (d, *J* = 4.9 Hz, 1H), 4.14 (dd, *J* = 12.2, 3.1 Hz, 1H), 4.11–4.10 (m, 1H), 3.99–3.95 (m, 2H), 3.89–3.86 (m, 2H), 3.78 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.67–3.65 (m, 1H), 3.61 (dd, *J* = 8.7, 5.4 Hz, 1H), 3.50 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.43–3.37 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.95 (q, *J* = 7.4 Hz, 1H), 2.26–2.19 (m, 3H), 2.03 (s, 3H), 1.04 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 180.0, 171.5, 164.3, 162.7, 161.3, 161.0, 142.3, 122.3, 112.5, 102.4, 102.0, 90.4, 86.1, 72.4, 71.7, 70.7, 70.2, 67.3, 65.9, 64.5, 63.4, 53.9, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.1, 38.5, 37.7, 36.4, 33.4, 33.2, 33.1, 32.3, 30.7, 30.6, 30.4, 30.3, 29.9, 29.7, 27.8, 27.0, 21.7, 21.0, 19.8, 13.9, 13.6; HR-ESI calcd for $C_{53}H_{77}F_3N_4O_{14}Na$ $[M + Na]^+$ 1073.5281, found 1073.5283.

OSW-1 analogue **34** was obtained as a white solid (10 mg, 29%): $[\alpha]_D^{25}$ = –40.1 (*c* = 0.45 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 8.03–8.02 (m, 2H), 7.93–7.91 (m, 2H), 5.34 (d, *J* = 4.9 Hz, 1H), 4.96 (dd, *J* = 8.0, 5.9 Hz, 1H), 4.78 (d, *J* = 6.0 Hz, 1H), 4.23 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.17 (d, *J* = 5.9 Hz, 1H), 4.06 (dd, *J* = 11.9, 4.1 Hz, 1H), 4.00–3.97 (m, 2H), 3.89–3.85 (m, 2H), 3.80–3.77 (m, 1H), 3.72–3.69 (m, 1H), 3.64–3.61 (m, 1H), 3.49 (dd, *J* = 12.1, 2.3 Hz, 1H), 3.41–3.35 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 3.15–3.12 (m, 4H), 2.87 (q, *J* = 7.3 Hz, 1H), 2.26–2.19 (m, 3H), 1.77 (s, 3H), 1.03 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.6, 171.1, 168.1, 144.3, 142.2, 139.4, 129.5, 128.2, 122.3, 102.5, 102.4, 89.7, 85.9, 77.9, 73.2, 72.4, 71.3, 71.0, 68.6, 65.7, 65.1, 55.8, 52.5, 51.4, 51.2, 49.8, 49.6, 47.3, 43.0, 42.0, 38.5, 37.6, 36.5, 33.5, 33.2, 33.1, 32.3, 30.65, 30.63, 30.61, 30.31, 30.28, 29.9, 29.7, 27.9, 26.9, 23.1, 21.7, 21.0, 19.8, 13.8, 13.6, 11.5; HR-ESI calcd for $C_{59}H_{93}N_5O_{16}SNa$ $[M + Na]^+$ 1182.6230, found 1182.6230.

OSW-1 analogue **35** was obtained as a white solid (8.4 mg, 26%): $[\alpha]_D^{25}$ = –32.1 (*c* = 0.32 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 5.34

(d, *J* = 4.9 Hz, 1H), 4.93 (dd, *J* = 6.5, 4.6 Hz, 1H), 4.84 (d, *J* = 2.5 Hz, 1H), 4.61 (br s, 2H), 4.23 (d, *J* = 4.4 Hz, 1H), 4.19 (dt, *J* = 10.8, 7.2 Hz, 1H), 4.12 (dd, *J* = 12.3, 2.6 Hz, 1H), 3.97 (dt, *J* = 10.9, 6.8 Hz, 1H), 3.92–3.91 (m, 1H), 3.90 (dd, *J* = 6.5, 3.2 Hz, 1H), 3.83–3.82 (m, 1H), 3.82–3.80 (m, 1H), 3.75 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.61–3.63 (m, 2H), 3.55 (dd, *J* = 7.3, 4.1 Hz, 1H), 3.45 (dd, *J* = 11.5, 3.1 Hz, 1H), 3.42–3.41 (m, 1H), 3.38 (dd, *J* = 11.8, 4.5 Hz, 1H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.88 (q, *J* = 7.4 Hz, 1H), 2.45 (dd, *J* = 7.1, 2.6 Hz, 1H), 2.26–2.19 (m, 3H), 2.05 (s, 3H), 1.17 (d, *J* = 7.4 Hz, 3H), 1.04 (s, 3H), 0.95–0.89 (m, 12H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.9, 176.5, 171.3, 142.3, 141.5, 139.8, 130.4, 128.6, 122.3, 102.1, 99.5, 90.6, 86.0, 72.4, 70.8, 70.5, 69.9, 67.0, 65.9, 64.1, 62.5, 52.5, 51.4, 49.8, 49.6, 47.7, 47.2, 46.2, 43.0, 42.0, 38.5, 37.7, 36.2, 33.4, 33.2, 33.1, 32.3, 31.5, 30.7, 30.4, 30.3, 29.9, 29.7, 27.9, 26.9, 22.82, 22.80, 21.7, 21.1, 19.9, 19.3, 14.0, 13.6; HR-ESI calcd for $C_{59}H_{92}N_4O_{14}Na$ $[M + Na]^+$ 1103.6502, found 1103.6496.

OSW-1 analogue **36** was obtained as a white solid (11.3 mg, 36%): $[\alpha]_D^{25}$ = –39.6 (*c* = 0.34 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.41–7.39 (m, 2H), 7.38–7.36 (m, 2H), 5.35 (d, *J* = 4.9 Hz, 1H), 4.92–4.91 (m, 1H), 4.85 (br s, 1H), 4.62 (br s, 1H), 4.27 (d, *J* = 3.7 Hz, 1H), 4.22 (dt, *J* = 10.8, 7.1 Hz, 1H), 4.08–4.06 (m, 1H), 4.05–4.02 (m, 1H), 3.99 (br s, 1H), 3.92–3.90 (m, 1H), 3.84–3.80 (m, 2H), 3.75 (dd, *J* = 7.9, 5.0 Hz, 1H), 3.48–3.44 (m, 3H), 3.40 (ddd, *J* = 16.0, 10.9, 4.9 Hz, 1H), 3.34 (dd, *J* = 11.4, 2.9 Hz, 1H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.99 (q, *J* = 7.3 Hz, 1H), 2.26–2.19 (m, 2H), 2.11 (s, 3H), 1.04 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 180.2, 174.5, 171.3, 142.3, 139.3, 134.8, 133.7, 130.1, 122.3, 102.0, 98.7, 91.2, 86.1, 72.4, 69.8, 69.6, 69.3, 66.3, 66.0, 63.5, 61.4, 52.5, 51.8, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.7, 36.1, 33.4, 33.2, 33.1, 32.3, 30.9, 30.71, 30.68, 30.67, 30.5, 30.3, 29.9, 29.7, 27.9, 26.9, 21.7, 21.1, 19.8, 16.4, 16.2, 14.0, 13.9; HR-ESI calcd for $C_{56}H_{83}ClN_4O_{14}Na$ $[M + Na]^+$ 1093.5487, found 1093.5488.

OSW-1 analogue **37** was obtained as a white solid (8.4 mg, 25%): ^{1}H NMR (600 MHz, CD_3OD) δ 7.53–7.51 (m, 2H), 7.44–7.41 (m, 3H), 7.37–7.34 (m, 1H), 7.27–7.21 (m, 2H), 5.34 (d, *J* = 4.6 Hz, 1H), 5.00 (dd, *J* = 7.5, 5.7 Hz, 0.41H), 4.93 (dd, *J* = 6.4, 4.9 Hz, 0.8H), 4.83 (br s, 0.62H), 4.68 (d, *J* = 4.0 Hz, 0.39H), 4.62 (br s, 0.38H), 4.27 (dt, *J* = 10.8, 7.1 Hz, 0.43H), 4.22 (d, *J* = 4.3 Hz, 1H), 4.16 (dt, *J* = 10.9, 7.3 Hz, 0.41H), 4.13 (dd, *J* = 12.3, 2.6 Hz, 0.61H), 4.04 (dd, *J* = 12.0, 3.5 Hz, 0.37H), 4.01 (dt, *J* = 11.0, 6.7 Hz, 0.41H), 3.95–3.90 (m, 2.54H), 3.87–3.80 (m, 2.41H), 3.75 (dd, *J* = 7.9, 5.0 Hz, 0.57H), 3.71 (dd, *J* = 14.3, 7.2 Hz, 0.63H), 3.67 (dd, *J* = 14.2, 7.2 Hz, 0.36H), 3.61 (t, *J* = 5.0 Hz, 0.57H), 3.58 (dd, *J* = 7.6, 4.4 Hz, 0.57H), 3.54–3.52 (m, 0.43H), 3.49 (dd, *J* =

11.9, 2.4 Hz, 0.43H), 3.46 (dd, *J* = 11.6, 3.0 Hz, 0.60H), 3.43–3.37 (m, 2H), 3.34–3.33 (m, 0.47H), 3.27–3.25 (m, 2H), 2.94 (q, *J* = 7.4 Hz, 0.42H), 2.89 (q, *J* = 7.3 Hz, 0.57H), 2.26–2.18 (m, 3H), 2.15–2.06 (m, 3H), 1.04 (s, 3H), 0.92–0.90 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.9, 179.8, 175.9, 175.6, 171.4, 171.3, 161.8, 160.2, 144.7, 144.5, 142.2, 136.9, 131.89, 131.86, 131.83, 129.97, 129.95, 129.93, 129.51, 129.50, 128.9, 128.8, 128.73, 128.71, 125.16, 125.14, 124.94, 124.92, 122.3, 116.4, 116.3, 116.1, 102.4, 102.1, 99.7, 90.5, 90.0, 86.0, 86.0, 72.4, 71.1, 70.6, 70.1, 68.2, 67.1, 65.91, 65.86, 64.2, 62.8, 53.9, 52.5, 51.4, 49.8, 49.6, 47.4, 47.3, 47.2, 43.0, 42.07, 42.02, 38.5, 37.7, 36.3, 36.2, 33.5, 33.4, 33.2, 33.1, 32.3, 30.68, 30.65, 30.63, 30.4, 30.3, 29.9, 29.7, 29.6, 27.8, 27.0, 26.9, 21.7, 21.2, 21.1, 19.9, 19.3, 19.1, 14.0, 13.9, 13.7, 13.6; HR-ESI calcd for $C_{61}H_{87}FN_4O_{14}Na$ $[M + Na]^+$ 1141.6095, found 1141.6099.

OSW-1 analogue **38** was obtained as a white solid (8.5 mg, 26%): $[\alpha]_D^{25}$ = –29.8 (*c* = 0.31 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.73 (d, *J* = 2.6 Hz, 2H), 7.72 (d, *J* = 3.6 Hz, 1H), 7.45 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.11 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.34 (d, *J* = 4.8 Hz, 1H), 4.99 (dd, *J* = 7.3, 5.5 Hz, 1H), 4.70 (d, *J* = 3.4 Hz, 1H), 4.63 (br s, 1H), 4.26–4.22 (m, 2H), 4.04 (dd, *J* = 12.1, 3.4 Hz, 1H), 4.00 (dt, *J* = 10.9, 6.7 Hz, 1H), 3.94–3.92 (m, 2H), 3.90 (s, 3H), 3.85 (dd, *J* = 11.9, 5.3 Hz, 1H), 3.81–3.77 (m, 2H), 3.75 (q, *J* = 7.1 Hz, 1H), 3.50 (dd, *J* = 7.8, 4.1 Hz, 1H), 3.48 (dd, *J* = 11.7, 2.4 Hz, 1H), 3.42–3.37 (m, 2H), 3.24 (t, *J* = 6.9 Hz, 2H), 2.94 (q, *J* = 7.4 Hz, 1H), 2.25–2.19 (m, 3H), 2.14 (s, 3H), 1.03 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.8, 176.7, 171.4, 159.1, 142.2, 137.9, 135.2, 130.5, 130.3, 128.3, 127.4, 127.0, 122.3, 119.9, 106.6, 102.4, 101.4, 90.2, 86.0, 72.4, 72.2, 70.4, 68.1, 65.9, 64.8, 63.8, 55.7, 53.5, 52.4, 51.4, 49.8, 49.6, 48.0, 47.3, 43.0, 42.1, 38.5, 37.7, 36.3, 34.4, 33.4, 33.2, 33.1, 32.3, 30.7, 30.4, 30.3, 29.9, 29.7, 27.8, 27.0, 24.4, 23.8, 21.7, 21.2, 19.8, 19.2, 14.5, 13.9, 13.7; HR-ESI calcd for $C_{60}H_{88}N_4O_{15}Na$ $[M + Na]^+$ 1127.6138, found 1127.6144.

OSW-1 analogue **39** was obtained as a white solid (7.0 mg, 22%): $[\alpha]_D^{25}$ = –38.5 (*c* = 0.15 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.60 (dd, *J* = 9.0, 3.9 Hz, 1H), 7.51 (d, *J* = 0.8 Hz, 1H), 7.47 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.25 (td, *J* = 9.1, 2.7 Hz, 1H), 5.33 (d, *J* = 5.0 Hz, 1H), 4.94 (dd, *J* = 7.6, 5.8 Hz, 1H), 4.83 (d, *J* = 5.5 Hz, 1H), 4.62 (br s, 2H), 4.20–4.16 (m, 2H), 4.07 (dd, *J* = 12.0, 3.9 Hz, 1H), 4.04–4.02 (m, 1H), 3.99–3.97 (m, 1H), 3.86 (dd, *J* = 12.1, 5.0 Hz, 1H), 3.80–3.75 (m, 3H), 3.73–3.71 (m, 1H), 3.65–3.62 (m, 1H), 3.48 (dd, *J* = 12.1, 2.5 Hz, 1H), 3.43–3.36 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.86 (q, *J* = 7.4 Hz, 1H), 2.25–2.18 (m, 3H), 1.88 (s, 3H), 1.02 (s, 3H),

0.85 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 171.3, 161.8, 160.3, 160.2, 152.6, 151.9, 142.2, 129.9, 122.3, 116.3, 116.1, 114.0, 111.8, 109.1, 108.9, 102.5, 102.0, 90.0, 86.0, 72.9, 72.4, 71.0, 70.8, 68.2, 65.6, 64.8, 54.8, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.6, 36.4, 33.4, 33.2, 32.3, 30.63, 30.58, 30.53, 30.3, 30.2, 29.9, 29.6, 27.8, 26.8, 21.7, 20.9, 19.8, 13.8, 13.6; HR-ESI calcd for $C_{55}H_{79}FN_4O_{15}Na$ $[M + Na]^+$ 1077.5418, found 1077.5427.

OSW-1 analogue **40** was obtained as a white solid (3.4 mg, 10%): $[\alpha]_D^{25}$ = –56.9 (*c* = 0.14 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 8.55 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 6.6 Hz, 1H), 7.51–7.46 (m, 3H), 5.32 (d, *J* = 5.0 Hz, 1H), 4.99–4.95 (m, 3H), 4.62 (br s, 3H), 4.28 (d, *J* = 4.0 Hz, 1H), 4.26–4.23 (m, 2H), 4.08 (br s, 1H), 4.07–4.04 (m, 1H), 3.97–3.95 (m, 1H), 3.93–3.90 (m, 1H), 3.84 (dd, *J* = 11.5, 7.1 Hz, 1H), 3.79–3.77 (m, 1H), 3.75 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.71 (br s, 1H), 3.56 (dd, *J* = 12.1, 3.2 Hz, 1H), 3.48 (dd, *J* = 11.4, 3.4 Hz, 1H), 3.38 (dt, *J* = 9.7, 4.8 Hz, 1H), 3.35 (s, 2H), 3.27 (t, *J* = 6.9 Hz, 2H), 3.04 (s, 3H), 2.91 (q, *J* = 7.3 Hz, 1H), 2.24–2.16 (m, 3H), 2.13 (s, 3H), 1.97 (s, 3H), 0.98 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 180.1, 176.5, 171.4, 142.3, 135.7, 133.0, 130.8, 129.8, 128.7, 127.3, 126.9, 126.7, 125.8, 122.3, 102.1, 91.1, 86.1, 83.6, 72.4, 70.4, 69.8, 66.0, 62.4, 54.8, 52.5, 51.3, 51.0, 49.9, 49.8, 49.6, 47.2, 43.0, 42.1, 38.5, 37.6, 36.1, 34.4, 33.2, 33.1, 32.3, 30.71, 30.68, 30.67, 30.5, 30.3, 29.9, 29.8, 27.9, 27.1, 24.4, 23.8, 23.3, 21.6, 21.1, 19.8, 19.3, 14.5, 13.9, 13.8; HR-ESI calcd for $C_{60}H_{88}N_4O_{15}Na$ $[M + Na]^+$ 1127.6138, found 1127.6142.

OSW-1 analogue **41** was obtained as a white solid (14.3 mg, 42%): $[\alpha]_D^{25}$ = –82.2 (*c* = 0.63 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 8.86 (s, 1H), 8.21–8.16 (m, 2H), 5.32 (d, *J* = 5.1 Hz, 1H), 4.92–4.91 (m, 1H), 4.65 (d, *J* = 5.9 Hz, 1H), 4.62 (br s, 1H), 4.23 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.11 (d, *J* = 6.4 Hz, 1H), 4.04–4.00 (m, 2H), 3.96 (dd, *J* = 5.6, 3.4 Hz, 1H), 3.89–3.87 (m, 1H), 3.86–3.85 (m, 1H), 3.77 (dd, *J* = 8.0, 4.7 Hz, 1H), 3.75–3.71 (m, 2H), 3.63–3.58 (m, 2H), 3.48 (dd, *J* = 12.3, 1.9 Hz, 1H), 3.41–3.33 (m, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.79 (q, *J* = 7.3 Hz, 1H), 2.25–2.16 (m, 3H), 1.83 (s, 3H), 0.99 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.5, 176.6, 171.4, 167.0, 155.8, 154.1, 151.0, 149.9, 149.4, 142.2, 139.8, 139.7, 125.7, 122.3, 114.8, 112.1, 108.1, 104.0, 102.7, 89.0, 85.9, 78.2, 74.5, 72.4, 71.8, 71.1, 69.3, 65.7, 55.5, 52.5, 51.3, 49.8, 49.6, 47.2, 43.0, 41.9, 38.5, 37.6, 36.8, 36.7, 33.4, 33.2, 33.0, 32.3, 30.64, 30.61, 30.31, 30.28, 29.9, 29.7, 27.8, 26.9, 21.6, 21.2, 19.8, 13.64, 13.55, 8.64, 8.60; HR-ESI calcd for $C_{59}H_{83}F_2N_5O_{15}Na$ $[M + Na]^+$ 1162.5746, found 1162.5750.

OSW-1 analogue **42** was obtained as a white solid (15.2 mg, 44%): $[\alpha]_D^{25}$ = –101.2 (*c* = 0.36 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 8.54 (s, 1H), 7.15 (s, 1H), 5.33 (d, *J* = 4.9 Hz, 1H), 4.22–4.18 (m, 2H), 4.07 (dd, *J* = 12.0, 3.7 Hz, 1H), 4.05–4.03 (m, 1H), 3.96–3.94 (m, 1H), 3.85 (dd, *J* = 11.7, 5.5 Hz, 1H), 3.83–3.81 (m, 2H), 3.76 (dd, *J* = 7.9, 5.0 Hz, 1H), 3.67–3.64 (m, 1H), 3.63–3.60 (m, 1H), 3.48 (dd, *J* = 11.9, 2.7 Hz, 1H), 3.43–3.39 (m, 5H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.91–2.85 (m, 3H), 2.81–2.79 (m, 2H), 2.24–2.17 (m, 3H), 2.02 (s, 3H), 1.01 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.9, 171.4, 165.6, 164.4, 154.1, 150.2, 149.6, 142.2, 128.6, 122.3, 121.7, 109.5, 108.7, 106.5, 102.3, 90.1, 86.0, 73.1, 72.4, 71.0, 70.6, 67.8, 65.7, 64.4, 54.7, 52.5, 51.3, 50.8, 49.7, 49.6, 47.2, 43.0, 42.0, 38.5, 37.6, 36.2, 33.4, 33.2, 33.0, 32.2, 30.7, 30.64, 30.59, 30.3, 30.2, 29.9, 29.5, 28.5, 27.9, 26.9, 23.7, 22.2, 21.7, 21.2, 21.1, 19.8, 14.5, 13.9, 13.7; HR-ESI calcd for $C_{62}H_{89}N_5O_{16}Na$ $[M + Na]^+$ 1182.6197, found 1182.6197.

OSW-1 analogue **43** was obtained as a white solid (11.3 mg, 35%): $[\alpha]_D^{25}$ = –36.8 (*c* = 0.45 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.58–7.55 (m, 2H), 7.07–7.04 (m, 2H), 5.34 (d, *J* = 5.0 Hz, 1H), 4.96 (dd, *J* = 7.4, 5.4 Hz, 1H), 4.73 (d, *J* = 5.3 Hz, 1H), 4.25 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.21 (d, *J* = 5.3 Hz, 1H), 4.06 (dd, *J* = 12.0, 3.1 Hz, 1H), 3.96–3.92 (m, 2H), 3.88–3.87 (m, 1H), 3.85 (dd, *J* = 12.0, 5.3 Hz, 1H), 3.81–3.79 (m, 2H), 3.61–3.57 (m, 2H), 3.48 (dd, *J* = 11.9, 2.6 Hz, 1H), 3.40 (ddd, *J* = 16.0, 11.2, 5.2 Hz, 1H), 3.36–3.33 (m, 1H), 3.27 (t, *J* = 6.9 Hz, 1H), 2.97 (q, *J* = 7.3 Hz, 1H), 2.26–2.18 (m, 3H), 2.10 (s, 3H), 1.03 (s, 3H), 0.90 (s, 2H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.8, 173.1, 171.4, 170.7, 161.7, 160.0, 142.2, 135.64, 135.62, 123.9, 123.8, 122.3, 116.3, 116.2, 102.3, 101.5, 89.9, 86.0, 76.6, 72.6, 72.4, 71.3, 70.7, 68.1, 65.8, 64.8, 64.5, 57.5, 54.7, 52.5, 51.4, 49.8, 49.6, 47.3, 43.0, 42.0, 38.5, 37.6, 36.3, 33.5, 33.2, 33.1, 32.3, 30.63, 30.62, 30.3, 29.9, 29.7, 27.8, 26.9, 21.7, 21.2, 19.8, 18.3, 17.5, 13.9, 13.8; HR-ESI calcd for $C_{57}H_{84}FN_5O_{15}Na$ $[M + Na]^+$ 1120.5840, found 1120.5844.

OSW-1 analogue **44** was obtained as a yellow solid (7.5 mg, 22%): $[\alpha]_D^{25}$ = –35.7 (*c* = 0.28 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 5.35 (d, *J* = 4.9 Hz, 1H), 4.99 (dd, *J* = 6.3, 4.6 Hz, 1H), 4.91 (d, *J* = 4.4 Hz, 1H), 4.62 (br s, 1H), 4.28–4.27 (m, 1H), 4.25–4.22 (m, 1H), 4.15 (dd, *J* = 12.3, 2.2 Hz, 1H), 4.04–4.00 (m, 2H), 3.96–3.94 (m, 1H), 3.88–3.85 (m, 2H), 3.78 (dd, *J* = 7.8, 5.0 Hz, 1H), 3.62–3.60 (m, 2H), 3.50–3.48 (m, 1H), 3.45 (dd, *J* = 12.4, 3.8 Hz, 1H), 3.40 (ddd, *J* = 16.0, 7.9, 3.3 Hz, 1H), 3.27 (t, *J* = 6.9 Hz, 2H), 3.00 (q, *J* = 7.3 Hz, 1H), 2.97–2.93 (m, 1H), 2.27–2.19 (m, 3H), 2.13 (s, 3H), 1.52 (s, 3H), 1.46 (s, 3H),

1.05 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 180.0, 176.4, 171.4, 155.2, 142.3, 131.4, 130.8, 123.22, 123.21, 122.3, 102.3, 99.7, 90.8, 86.1, 82.7, 72.4, 70.9, 70.4, 70.0, 67.0, 66.0, 64.0, 62.6, 62.3, 52.5, 52.1, 51.4, 49.8, 49.6, 47.3, 43.0, 42.1, 38.5, 37.7, 36.2, 36.0, 33.4, 33.3, 33.1, 32.3, 30.64, 30.62, 30.60, 30.4, 30.3, 29.9, 29.7, 27.9, 27.0, 26.3, 25.8, 25.3, 21.7, 21.2, 19.8, 14.0, 13.8; HR-ESI calcd for $C_{59}H_{88}Cl_2N_4O_{15}Na$ $[M + Na]^+$ 1185.5515, found 1185.5519.

OSW-1 analogue **45** was obtained as a white solid (11.4 mg, 31%): $[\alpha]_D^{25}$ = –25.2 (*c* = 0.28 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.34 (d, *J* = 4.7 Hz, 1H), 5.03–5.00 (m, 1H), 4.69 (br s, 1H), 4.62 (br s, 2H), 4.25–4.21 (m, 2H), 4.05–4.03 (m, 1H), 3.98 (dt, *J* = 10.9, 6.8 Hz, 1H), 3.92–3.91 (m, 1H), 3.87–3.82 (m, 5H), 3.82–3.79 (m, 2H), 3.74 (d, *J* = 16.6 Hz, 1H), 3.62 (d, *J* = 16.7 Hz, 1H), 3.53–3.47 (m, 3H), 3.40 (ddd, *J* = 15.8, 10.7, 4.7 Hz, 1H), 3.35–3.33 (m, 1H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.94 (q, *J* = 7.4 Hz, 1H), 2.30 (s, 3H), 2.26–2.21 (m, 3H), 2.16 (s, 3H), 1.03 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 172.8, 171.5, 169.9, 157.7, 142.3, 140.2, 137.0, 135.7, 132.5, 132.4, 130.2, 129.9, 122.3, 116.0, 114.7, 113.1, 111.3, 102.5, 102.3, 90.0, 86.0, 72.4, 72.1, 71.4, 70.5, 68.2, 65.9, 65.1, 64.0, 56.3, 54.8, 54.0, 52.5, 51.4, 49.8, 49.6, 47.3, 43.0, 42.1, 38.5, 37.7, 36.3, 33.5, 33.2, 33.1, 32.4, 30.8, 30.7, 30.6, 30.4, 30.3, 29.9, 29.7, 27.8, 26.9, 21.7, 21.3, 19.9, 13.9, 13.8, 13.7, 11.8; HR-ESI calcd for $C_{65}H_{90}ClN_5O_{16}Na$ $[M + Na]^+$ 1254.5963, found 1254.5969.

OSW-1 analogue **46** was obtained as a yellow solid (7.4 mg, 20%): $[\alpha]_D^{25}$ = –36.2 (*c* = 0.25 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 8.70 (d, *J* = 1.8 Hz, 1H), 8.26 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.00 (d, *J* = 1.8 Hz, 1H), 7.93–7.90 (m, 1H), 7.57 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.33 (d, *J* = 5.1 Hz, 1H), 4.79 (d, *J* = 6.5 Hz, 1H), 4.20–4.16 (m, 2H), 4.05 (dd, *J* = 12.0, 4.2 Hz, 1H), 4.02–3.98 (m, 2H), 3.87 (dd, *J* = 12.2, 4.9 Hz, 1H), 3.81–3.76 (m, 3H), 3.73 (dd, *J* = 15.6, 8.0 Hz, 2H), 3.66–3.63 (m, 1H), 3.49 (dd, *J* = 12.1, 2.3 Hz, 1H), 3.40–3.36 (m, 2H), 3.26 (t, *J* = 6.9 Hz, 2H), 2.87 (q, *J* = 7.2 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H), 2.24–2.18 (m, 3H), 1.84 (s, 3H), 1.00 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 182.5, 181.8, 179.8, 171.4, 171.0, 170.9, 166.4, 151.8, 151.7, 142.2, 141.5, 136.5, 136.0, 135.7, 131.9, 130.9, 130.4, 128.6, 126.9, 126.5, 124.9, 122.3, 102.6, 102.4, 89.8, 86.0, 73.5, 72.4, 71.4, 71.0, 68.3, 65.6, 65.4, 56.3, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 40.4, 38.5, 37.6, 36.5, 36.3, 33.4, 33.2, 33.1, 32.3, 30.6, 30.5, 30.2, 29.9, 29.6, 28.1, 27.8, 26.9, 23.7, 21.7, 21.1, 19.8, 14.5, 13.8, 13.6; HR-ESI calcd for $C_{65}H_{86}N_4O_{20}Na$ $[M + Na]^+$

1265.5728, found 1265.5735.

OSW-1 analogue **47** was obtained as a yellow solid (7.2 mg, 20%): $[\alpha]_D^{25}$ = –20.5 (*c* = 0.19 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (s, 1H), 7.16 (dd, *J* = 8.4, 5.1 Hz, 1H), 7.04 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.57 (td, *J* = 9.0, 2.3 Hz, 1H), 5.34 (d, *J* = 4.8 Hz, 1H), 5.03–5.01 (m, 1H), 4.68 (d, *J* = 4.2 Hz, 1H), 4.62 (br s, 1H), 4.27–4.23 (m, 2H), 4.04 (dd, *J* = 12.2, 3.2 Hz, 1H), 4.01–3.99 (m, 1H), 3.93–3.91 (m, 1H), 3.86–3.82 (m, 3H), 3.79 (dd, *J* = 7.7, 3.2 Hz, 1H), 3.66 (d, *J* = 15.8 Hz, 1H), 3.55–3.50 (m, 3H), 3.49–3.48 (m, 1H), 3.39 (ddd, *J* = 16.0, 10.9, 5.0 Hz, 1H), 3.34 (dd, *J* = 10.4, 4.1 Hz, 1H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.95 (q, *J* = 7.4 Hz, 1H), 2.88 (s, 3H), 2.26 (s, 3H), 2.24–2.20 (m, 3H), 2.17 (s, 3H), 1.03 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.8, 172.0, 171.5, 165.6, 164.0, 148.7, 148.6, 145.8, 143.1, 142.3, 141.6, 140.0, 134.1, 131.6, 131.1, 129.5, 125.2, 124.7, 124.6, 122.3, 111.5, 107.4, 102.3, 101.7, 90.0, 86.0, 72.4, 72.3, 71.3, 70.6, 68.3, 65.9, 65.0, 64.1, 54.1, 52.4, 51.4, 49.8, 49.6, 47.3, 43.5, 43.0, 42.0, 38.5, 37.7, 36.2, 34.0, 33.5, 33.2, 32.3, 30.68, 30.67, 30.65, 30.4, 30.3, 29.9, 29.7, 27.8, 27.0, 21.7, 21.3, 19.8, 13.8, 13.7, 10.8; HR-ESI calcd for $C_{66}H_{91}FN_4O_{15}SNa$ $[M + Na]^+$ 1253.6078, found 1253.6078.

OSW-1 analogue **48** was obtained as a white solid (12.7 mg, 36%): $[\alpha]_D^{25}$ = –20.7 (*c* = 0.54 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.09 (t, *J* = 7.9 Hz, 1H), 5.35–5.34 (m, 1H), 4.83 (dd, *J* = 8.2, 6.0 Hz, 1H), 4.65 (d, *J* = 7.8 Hz, 1H), 4.62 (br s, 1H), 4.32 (dt, *J* = 10.8, 7.0 Hz, 1H), 4.15 (d, *J* = 6.0 Hz, 1H), 3.97–3.91 (m, 3H), 3.89 (dd, *J* = 5.9, 3.8 Hz, 1H), 3.81 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.74 (dd, *J* = 8.3, 3.4 Hz, 1H), 3.63 (dd, *J* = 9.5, 7.9 Hz, 1H), 3.55–3.50 (m, 2H), 3.43 (dd, *J* = 9.4, 8.5 Hz, 1H), 3.40–3.37 (m, 1H), 3.28 (t, *J* = 6.9 Hz, 2H), 3.22 (dd, *J* = 11.5, 9.9 Hz, 1H), 2.93 (q, *J* = 7.4 Hz, 1H), 2.63–2.61 (m, 2H), 2.31–2.26 (m, 3H), 2.25–2.18 (m, 4H), 2.11 (s, 3H), 1.03 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.6, 177.5, 171.5, 153.2, 142.2, 137.5, 132.4, 130.9, 122.3, 103.9, 102.5, 89.3, 85.9, 77.3, 76.0, 74.0, 72.4, 71.5, 71.1, 66.6, 65.8, 65.0, 57.4, 52.5, 51.4, 49.8, 49.6, 47.3, 43.0, 42.0, 38.5, 37.7, 37.3, 36.6, 33.5, 33.2, 33.1, 33.0, 32.3, 30.65, 30.62, 30.39, 30.35, 30.32, 30.31, 30.29, 30.26, 30.17, 29.9, 29.7, 29.1, 28.9, 27.9, 27.2, 27.0, 26.7, 23.8, 21.7, 21.2, 19.9, 14.5, 13.8, 13.5; HR-ESI calcd for $C_{64}H_{107}N_5O_{16}Na$ $[M + Na]^+$ 1224.7605, found 1224.7610.

OSW-1 analogue **49** was obtained as a white solid (7.6 mg, 22%): $[\alpha]_D^{25}$ = –12.1 (*c* = 0.15 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.34

(d, *J* = 5.1 Hz, 1H), 4.86 (dd, *J* = 8.2, 6.0 Hz, 1H), 4.65 (d, *J* = 7.8 Hz, 1H), 4.62 (br s, 2H), 4.31 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.16 (d, *J* = 5.9 Hz, 1H), 3.98–3.89 (m, 4H), 3.81 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.76–3.71 (m, 5H), 3.67–3.65 (m, 4H), 3.60 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.55–3.50 (m, 2H), 3.42 (dd, J=8.0, 7.0 Hz, 1H), 3.41–3.37 (m, 1H), 3.27 (t, *J* = 6.9 Hz, 2H), 3.22 (dd, *J* = 11.6, 9.8 Hz, 1H), 2.93 (q, *J* = 7.5 Hz, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.31–2.18 (m, 5H), 2.08 (s, 3H), 1.01 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.6, 177.3, 171.6, 145.8, 142.2, 132.0, 130.8, 122.4, 113.5, 103.8, 102.5, 89.4, 86.0, 76.9, 75.9, 74.0, 72.4, 71.5, 71.1, 66.6, 65.8, 64.9, 57.4, 54.6, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 41.7, 38.5, 37.6, 36.7, 36.5, 35.2 33.5, 33.2, 33.1, 32.3, 30.64, 30.62, 30.61, 30.31, 30.28, 29.9, 29.7, 28.7, 27.8, 27.0, 21.7, 21.2, 19.9, 13.8, 13.5; HR-ESI calcd for $C_{60}H_{93}Cl_2N_5O_{14}Na$ $[M + Na]^+$ 1200.5988, found 1200.5991.

OSW-1 analogue **50** was obtained as a white solid (5.2 mg, 17%): $[\alpha]_D^{25}$ = –30.1 (*c* = 0.34 in CH_3OH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.82–7.79 (m, 2H), 6.97–6.95 (m, 2H), 5.34 (d, *J* = 4.5 Hz, 1H), 4.82–4.78 (m, 2H), 4.29 (dt, *J* = 10.8, 7.0 Hz, 1H), 4.15 (d, *J* = 5.7 Hz, 1H), 4.03–4.02 (m, 1H), 4.00–3.99 (m, 1H), 3.93–3.87 (m, 3H), 3.85 (s, 3H), 3.79 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.73 (dd, *J* = 8.1, 3.4 Hz, 1H), 3.66–3.58 (m, 2H), 3.52–3.50 (m, 1H), 3.42–3.37 (m, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.91 (q, *J* = 7.4 Hz, 1H), 2.23–2.16 (m, 3H), 2.06 (s, 3H), 1.03 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (101 MHz, CD_3OD) δ 179.6, 171.5, 170.8, 163.9, 142.2, 130.5, 127.7, 122.3, 114.7, 103.7, 102.5, 89.4, 85.9, 77.4, 75.2, 74.1, 72.4, 71.4, 70.8, 66.1, 65.7, 64.6, 57.4, 55.9, 52.5, 51.4, 49.8, 47.2, 43.0, 42.0, 38.5, 37.6, 36.5, 33.5, 33.2, 33.1, 32.3, 30.64, 30.61, 30.60, 30.3, 29.9, 29.6, 27.8, 26.9, 21.7, 21.1, 19.9, 13.8, 13.5; HR- ESI calcd for $C_{54}H_{82}N_4O_{15}Na$ $[M + Na]^+$ 1049.5669, found 1049.5670.

OSW-1 analogue **51** was obtained as a white solid (3.6 mg, 11%): $[\alpha]_D^{25}$ = –30.6 (*c* = 0.27 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.94–7.92 (m, 2H), 7.31–7.30 (m, 2H), 5.34 (d, *J* = 5.1 Hz, 1H), 4.81–4.78 (m, 2H), 4.30 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.12 (d, *J* = 6.2 Hz, 1H), 3.99–3.98 (m, 1H), 3.96 (d, *J* = 4.5 Hz, 1H), 3.92–3.88 (m, 2H), 3.84 (dd, *J* = 9.3, 7.8 Hz, 1H), 3.79 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.71 (dd, *J* = 8.5, 3.4 Hz, 1H), 3.66–3.63 (m, 2H), 3.62–3.58 (m, 1H), 3.50 (dd, *J* = 12.2, 1.9 Hz, 1H), 3.39 (ddd, *J* = 16.0, 10.8, 4.8 Hz, 1H), 3.29–3.26 (m, 3H), 2.88 (q, *J* = 7.4 Hz, 1H), 2.26–2.17 (m, 3H), 2.04 (s, 3H), 1.03 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.6, 171.5, 170.1, 142.2, 137.6, 132.9, 129.5, 127.5, 124.4, 122.6, 122.3, 103.8, 102.6, 89.2, 85.9, 77.4, 75.4, 74.1, 72.4, 71.6, 71.1, 66.6, 65.7, 65.3, 58.1, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0,

42.0, 38.5, 37.6, 36.5, 33.5, 33.2, 33.1, 32.3, 30.63, 30.61, 30.59, 30.3, 29.9, 29.6, 27.8, 26.9, 21.7, 21.1, 19.9, 13.7, 13.5; HR-ESI calcd for $C_{55}H_{79}F_3N_6O_{14}Na$ $[M + Na]^+$ 1127.5499, found 1127.5499.

OSW-1 analogue **52** was obtained as a white solid (3.3 mg, 11%): $[\alpha]_D^{25}$ = –26.1 (*c* = 0.21 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.74 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.52–7.49 (m, 1H), 7.34–7.31 (m, 1H), 7.15 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.35 (d, *J* = 4.7 Hz, 1H), 4.74 (d, *J* = 6.5 Hz, 1H), 4.30 (dt, *J* = 10.8, 7.0 Hz, 1H), 4.19 (d, *J* = 5.3 Hz, 1H), 4.06 (dd, *J* = 4.7, 2.8 Hz, 1H), 4.03 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.94–3.91 (m, 1H), 3.90–3.87 (m, 2H), 3.81–3.77 (m, 2H), 3.63–3.58 (m, 2H), 3.52 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.40 (ddd, *J* = 15.9, 10.8, 4.9 Hz, 1H), 3.34–3.32 (m, 1H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.95 (q, *J* = 7.4 Hz, 1H), 2.32 (s, 3H), 2.25–2.18 (m, 3H), 2.08 (s, 3H), 1.03 (s, 2H), 0.85 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 171.6, 171.3, 169.1, 149.5, 142.2, 134.8, 132.8, 130.6, 130.2, 129.3, 127.2, 124.2, 122.3, 103.2, 102.5, 89.6, 86.0, 77.1, 74.2, 74.0, 72.4, 71.1, 70.4, 65.8, 65.6, 64.1, 56.3, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.7, 36.5, 33.5, 33.2, 33.1, 32.3, 30.6, 30.29, 30.27, 29.9, 29.6, 27.8, 26.9, 21.7, 21.12, 21.10, 19.8, 13.8, 13.5; HR-ESI calcd for $C_{55}H_{82}N_4O_{16}Na$ $[M + Na]^+$ 1077.5618, found 1077.5628.

OSW-1 analogue **53** was obtained as a white solid (2.5 mg, 8%): $[\alpha]_D^{25}$ = –26.8 (*c* = 0.11 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.53–7.49 (m, 2H), 5.34 (d, *J* = 4.8 Hz, 1H), 4.77 (d, *J* = 7.8 Hz, 1H), 4.75 (dd, *J* = 8.5, 6.3 Hz, 1H), 4.59 (br s, 1H), 4.30 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.11 (d, *J* = 6.3 Hz, 1H), 4.04 (s, 3H), 3.98–3.96 (m, 1H), 3.96–3.95 (m, 1H), 3.92–3.88 (m, 2H), 3.82 (dd, *J* = 9.3, 7.9 Hz, 1H), 3.78 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.70 (dd, *J* = 8.6, 3.4 Hz, 1H), 3.62–3.57 (m, 2H), 3.50 (dd, *J* = 12.2, 1.7 Hz, 1H), 3.42–3.36 (m, 1H), 3.29–3.26 (m, 3H), 2.87 (q, *J* = 7.4 Hz, 1H), 2.26–2.16 (m, 3H), 2.05 (s, 3H), 1.03 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.6, 171.5, 168.3, 157.2, 155.6, 142.2, 140.4, 130.7, 122.3, 113.2, 113.0, 104.0, 102.7, 89.2, 85.9, 77.7, 75.6, 74.0, 72.4, 71.6, 71.1, 66.7, 65.7, 65.4, 62.3, 58.0, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.6, 36.5, 33.5, 33.2, 33.1, 32.3, 30.61, 30.59, 30.57, 30.3, 29.9, 29.6, 27.8, 26.9, 21.7, 21.1, 19.8, 13.7, 13.4; HR-MALDI calcd for $C_{54}H_{80}F_2N_4O_{15}Na$ $[M + Na]^+$ 1085.5480, found 1085.5478.

OSW-1 analogue **54** was obtained as a white solid (9.1 mg, 29%): $[\alpha]_D^{25}$ = –24.2 (*c* = 0.17 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 6.95–6.92 (m, 2H), 5.35 (d, *J* = 5.1 Hz, 1H), 4.80 (dd, *J* = 7.0, 4.7 Hz, 1H), 4.70 (d, *J* = 7.5 Hz, 1H), 4.28 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.21 (d, *J* = 4.6 Hz,

1H), 4.02 (dd, *J* = 11.9, 6.1 Hz, 1H), 3.98 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.93–3.89 (m, 2H), 3.86–3.83 (m, 1H), 3.80–3.77 (m, 2H), 3.59–3.53 (m, 3H), 3.40 (ddd, *J* = 16.0, 10.9, 4.8 Hz, 1H), 3.29–3.26 (m, 3H), 2.97 (q, *J* = 7.4 Hz, 1H), 2.26–2.17 (m, 3H), 2.07 (s, 3H), 1.04 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.8, 171.4, 162.8, 142.3, 122.3, 103.7, 102.2, 101.8, 89.9, 86.0, 76.9, 75.0, 73.8, 72.4, 71.5, 70.2, 66.4, 65.8, 63.3, 57.6, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.7, 36.3, 34.5, 33.5, 33.2, 33.1, 32.3, 30.8, 30.7, 30.6, 30.5, 30.3, 29.9, 29.6, 27.8, 26.9, 24.2, 23.7, 21.7, 21.0, 19.8, 16.7, 14.5, 13.8, 13.5; HR-MALDI calcd for $C_{53}H_{77}F_3N_4O_{14}Na$ [M + Na]$^+$ 1073.5281, found 1073.5299.

OSW-1 analogue **55** was obtained as a white solid (14.6 mg, 42%): $[\alpha]_D^{25}$ = –31.7 (*c* = 0.28 in CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 8.01–8.00 (m, 2H), 7.87–7.86 (m, 2H), 5.34 (d, *J* = 5.0 Hz, 1H), 4.82 (d, *J* = 7.8 Hz, 1H), 4.80 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.30 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.12 (d, *J* = 6.3 Hz, 1H), 3.99–3.98 (m, 1H), 3.97 (dd, *J* = 4.2, 2.7 Hz, 1H), 3.93–3.88 (m, 2H), 3.84 (dd, *J* = 9.4, 7.9 Hz, 1H), 3.80 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.72 (dd, *J* = 8.6, 3.4 Hz, 1H), 3.67–3.64 (m, 1H), 3.64 (s, 1H), 3.63–3.59 (m, 1H), 3.51 (dd, *J* = 12.1, 1.7 Hz, 1H), 3.39 (ddd, *J* = 15.9, 10.9, 4.8 Hz, 1H), 3.29–3.28 (m, 3H), 3.13–3.11 (m, 4H), 2.88 (q, *J* = 7.4 Hz, 1H), 2.26–2.18 (m, 3H), 2.05 (s, 3H), 1.02 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.6, 171.4, 170.0, 143.7, 142.2, 139.9, 129.6, 128.2, 122.3, 103.8, 102.6, 89.1, 85.9, 77.4, 75.5, 74.1, 72.4, 71.59, 71.56, 71.2, 66.7, 65.7, 65.5, 58.2, 52.5, 51.4, 49.8, 47.2, 43.0, 42.0, 38.5, 37.6, 36.6, 33.5, 33.2, 33.1, 32.3, 30.64, 30.62, 30.60, 30.3, 29.9, 29.6, 27.8, 26.9, 23.2, 21.7, 21.2, 19.9, 13.8, 13.5, 11.5; HR-ESI calcd for $C_{59}H_{93}N_5O_{16}SNa$ [M + Na]$^+$ 1182.6230, found 1182.6243.

OSW-1 analogue **56** was obtained as a white solid (3.3 mg, 10%): ^{1}H NMR (600 MHz, CD_3OD) δ 7.27–7.23 (m, 2H), 7.10–7.07 (m, 2H), 5.35 (d, *J* = 4.3 Hz, 1H), 4.79 (dd, *J* = 6.8, 4.5 Hz, 0.6H), 4.63 (d, *J* = 7.4 Hz, 0.5H), 4.62 (br s, 0.5H), 4.58 (d, *J* = 7.2 Hz, 0.6H), 4.34–4.27 (m, 1H), 4.19–4.18 (m, 1H), 3.98–3.93 (m, 2H), 3.93–3.90 (m, 1H), 3.88–3.87 (m, 0.4H), 3.83 (dd, *J* = 8.0, 4.8 Hz, 0.4H), 3.78–3.75 (m, 1H), 3.74 (dd, *J* = 8.2, 3.4 Hz, 0.5H), 3.70–3.64 (m, 1.4H), 3.61 (dd, *J* = 9.2, 7.3 Hz, 0.5H), 3.58 (dd, *J* = 6.8, 3.3 Hz, 0.6H), 3.52–3.46 (m, 2.5H), 3.42–3.35 (m, 1.5H), 3.27 (t, *J* = 6.9 Hz, 2H), 3.25–3.19 (m, 1H), 3.01–2.94 (m, 1H), 2.44–2.43 (m, 2H), 2.26–2.18 (m, 3H), 2.13 (s, 1.3H), 2.09 (s, 1.7H), 1.04–1.03 (m, 3H), 0.93–0.89 (m, 13H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.8, 179.6, 178.6, 178.2, 171.7, 171.3, 142.2, 141.5, 141.4, 140.4, 140.2, 130.9, 130.33, 130.27, 128.4, 128.3, 122.4, 122.3, 103.8, 103.5, 102.5, 102.1, 90.0, 89.4, 86.00, 85.95,

77.2, 76.6, 75.7, 74.9, 74.0, 73.7, 72.4, 71.44, 71.36, 71.1, 70.0, 66.3, 66.1, 65.9, 65.8, 64.8, 63.1, 57.2, 56.8, 52.5, 51.4, 49.8, 49.6, 47.5, 47.30, 47.26, 46.13, 46.08, 43.0, 42.0, 38.5, 37.7, 36.54, 36.46, 36.3, 34.5, 33.5, 33.2, 33.1, 32.3, 31.5, 30.84, 30.80, 30.76, 30.74, 30.64, 30.62, 30.5, 30.43, 30.35, 30.32, 30.28, 29.9, 29.7, 28.1, 27.8, 26.98, 26.96, 26.94, 24.4, 23.8, 22.85, 22.83, 21.7, 21.2, 21.1, 19.9, 19.8, 19.3, 19.1, 14.5, 13.9, 13.8, 13.5; HR-ESI calcd for $C_{59}H_{92}N_4O_{14}Na$ $[M + Na]^+$ 1103.6502, found 1103.6510.

OSW-1 analogue **57** was obtained as a yellow solid (6.0 mg, 17%): $[\alpha]_D^{25}$ = –88.1 (*c* = 0.23 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 8.51 (s, 1H), 7.13 (s, 1H), 5.33 (d, *J* = 4.7 Hz, 1H), 4.80 (d, *J* = 6.8 Hz, 1H), 4.76 (dd, *J* = 7.9, 5.6 Hz, 1H), 4.25 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.14 (d, *J* = 5.6 Hz, 1H), 4.04–3.96 (m, 3H), 3.90–3.86 (m, 2H), 3.78 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.69 (dd, *J* = 8.0, 3.3 Hz, 1H), 3.62–3.57 (m, 2H), 3.50 (dd, *J* = 12.1, 2.3 Hz, 1H), 3.40–3.37 (m, 6H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.89 (q, *J* = 7.4 Hz, 1H), 2.86–2.84 (m, 2H), 2.80–2.78 (m, 2H), 2.01 (s, 3H), 1.02 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 171.5, 166.6, 164.4, 154.1, 150.1, 149.7, 142.2, 128.6, 122.4, 121.6, 109.6, 108.7, 106.5, 103.9, 102.5, 89.5, 86.0, 77.2, 75.0, 73.8, 72.4, 71.1, 65.8, 65.7, 56.4, 52.5, 51.4, 50.8, 49.8, 49.6, 47.2, 43.0, 41.9, 38.5, 37.6, 36.3, 34.5, 33.5, 33.2, 33.1, 32.3, 30.8, 30.6, 30.5, 30.3, 29.9, 29.6, 28.5, 27.8, 26.9, 24.2, 23.8, 22.2, 21.7, 21.3, 21.1, 19.9, 16.7, 14.5, 13.8, 13.5; HR-ESI calcd for $C_{62}H_{89}N_5O_{16}Na$ $[M + Na]^+$ 1182.6197, found 1182.6199.

OSW-1 analogue **58** was obtained as a white solid (7.0 mg, 19%): $[\alpha]_D^{25}$ = –10.0 (*c* = 0.17 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.75–7.73 (m, 2H), 7.57–7.55 (m, 2H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.97 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.31 (d, *J* = 5.0 Hz, 1H), 4.82 (dd, *J* = 7.8, 5.6 Hz, 1H), 4.68 (d, *J* = 7.3 Hz, 1H), 4.62 (br s, 1H), 4.30 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.15 (d, *J* = 5.6 Hz, 1H), 3.96–3.94 (m, 1H), 3.93–3.90 (m, 2H), 3.84–3.83 (m, 1H), 3.83 (s, 3H), 3.79 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.76–3.73 (m, 1H), 3.71–3.68 (m, 1H), 3.66–3.64 (m, 1H), 3.57 (dd, *J* = 7.9, 3.3 Hz, 1H), 3.54–3.50 (m, 2H), 3.49–3.48 (m, 1H), 3.39 (ddd, *J* = 16.1, 10.9, 4.9Hz, 1H), 3.27–3.22 (m, 3H), 2.92 (q, *J* = 7.5 Hz, 1H), 2.30 (s, 3H), 2.25–2.16 (m, 3H), 2.09 (s, 3H), 1.01 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 174.2, 171.6, 170.0, 157.6, 142.2, 140.1, 137.2, 135.8, 132.6, 132.3, 130.2, 122.3, 115.9, 114.8, 112.9, 103.8, 102.4, 102.3, 89.6, 85.9, 76.9, 75.0, 73.8, 72.4, 71.4, 70.9, 66.2, 65.8, 64.4, 57.0, 56.2, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 42.0, 38.5, 37.6, 36.4, 34.4, 33.5, 33.2, 33.1, 32.4, 32.3, 30.8, 30.6, 30.3, 29.9, 29.6, 27.8, 26.9, 24.4,

23.8, 21.7, 21.2, 19.9, 19.3, 14.5, 14.0, 13.8, 13.5; HR-ESI calcd for $C_{65}H_{90}ClN_5O_{16}Na$ $[M + Na]^+$ 1254.5963, found 1254.5965.

OSW-1 analogue **59** was obtained as a yellow solid (4.8 mg, 13%): $[\alpha]_D^{25}$ = –44.9 (*c* = 0.11 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 8.64 (d, *J* = 1.8 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.95 (d, *J* = 1.8 Hz, 1H), 7.90–7.87 (m, 1H), 7.54 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.31 (d, *J* = 5.0 Hz, 1H), 4.84 (d, *J* = 8.0 Hz, 2H), 4.76 (dd, *J* = 8.5, 6.2 Hz, 1H), 4.26 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.11 (d, *J* = 6.2 Hz, 1H), 3.98–3.97 (m, 1H), 3.96–3.95 (m, 1H), 3.94–3.89 (m, 2H), 3.88–3.85 (m, 1H), 3.77 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.71 (dd, *J* = 8.5, 3.3 Hz, 1H), 3.69–3.66 (m, 1H), 3.64–3.59 (m, 2H), 3.50 (dd, *J* = 12.1, 1.9 Hz, 1H), 3.38 (ddd, *J* = 16.1, 11.0, 4.9 Hz, 1H), 3.29–3.25 (m, 3H), 2.84 (q, *J* = 7.4 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.23–2.14 (m, 3H), 1.97 (s, 3H), 0.99 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 182.6, 182.0, 179.6, 171.5, 171.0, 170.9, 168.0, 151.6, 151.5, 142.2, 142.1, 136.3, 135.9, 135.8, 131.7, 130.4, 128.4, 126.9, 126.4, 125.3, 122.4, 103.9, 102.6, 89.2, 85.9, 77.4, 75.4, 73.9, 72.4, 71.61, 71.58, 71.0, 66.8, 65.7, 58.2, 52.5, 51.4, 49.8, 49.6, 47.2, 43.0, 41.9, 38.5, 37.6, 36.4, 33.5, 33.2, 33.0, 32.3, 30.62, 30.59, 30.57, 30.3, 29.9, 29.6, 27.8, 26.9, 23.8, 21.6, 21.2, 21.1, 19.9, 14.5, 13.7, 13.5; HR-ESI calcd for $C_{65}H_{86}N_4O_{20}Na$ $[M + Na]^+$ 1265.5728, found 1265.5730.

OSW-1 analogue **60** was obtained as a yellow solid (12 mg, 33%): $[\alpha]_D^{25}$ = –26.7 (*c* = 0.21 in CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.27 (br s, 1H), 7.13 (dd, *J* = 8.2, 5.1 Hz, 1H), 7.03 (dd, *J* = 9.1, 2.4 Hz, 1H), 6.53 (td, *J* = 9.0, 2.3 Hz, 1H), 5.32 (d, *J* = 4.9 Hz, 1H), 4.92–4.91 (m, 1H), 4.73 (d, *J* = 7.4 Hz, 1H), 4.62 (br s, 1H), 4.31 (dt, *J* = 10.9, 7.0 Hz, 1H), 4.19 (d, *J* = 5.8 Hz, 1H), 3.97–3.93 (m, 3H), 3.91–3.90 (m, 1H), 3.83 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.74 (dd, *J* = 8.1, 3.3 Hz, 1H), 3.68–3.67 (m, 1H), 3.65–3.64 (m, 1H), 3.59–3.58 (m, 1H), 3.56–3.53 (m, 1H), 3.51–3.50 (m, 2H), 3.38 (ddd, *J* = 16.0, 11.0, 4.8 Hz, 1H), 3.26 (t, *J* = 6.9 Hz, 2H), 3.23 (dd, *J* = 7.6, 4.1 Hz, 1H), 2.96 (q, *J* = 7.4 Hz, 1H), 2.88 (s, 3H), 2.24 (d, *J* = 4.0 Hz, 1H), 2.23 (s, 3H), 2.22–2.17 (m, 3H), 2.13 (s, 3H), 0.99 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 179.7, 173.4, 171.7, 165.6, 163.9, 148.9, 145.7, 143.2, 142.2, 141.9, 139.9, 134.4, 131.6, 131.1, 129.2, 125.2, 124.6, 122.3, 111.3, 107.5, 103.5, 102.4, 89.5, 85.9, 76.8, 75.2, 73.9, 72.4, 71.5, 71.0, 66.3, 65.8, 64.7, 57.2, 52.5, 51.3, 49.8, 49.6, 47.3, 43.6, 43.0, 42.0, 38.5, 37.6, 36.4, 33.8, 33.5, 33.2, 33.1, 32.3, 30.8, 30.6, 30.3, 29.9, 29.7, 27.8, 27.0, 24.4, 23.8, 21.7, 21.2, 19.9, 14.5, 13.8, 13.5, 10.9; HR-ESI calcd for $C_{66}H_{91}FN_4O_{15}SNa$ $[M + Na]^+$ 1253.6078,

found 1253.6080.

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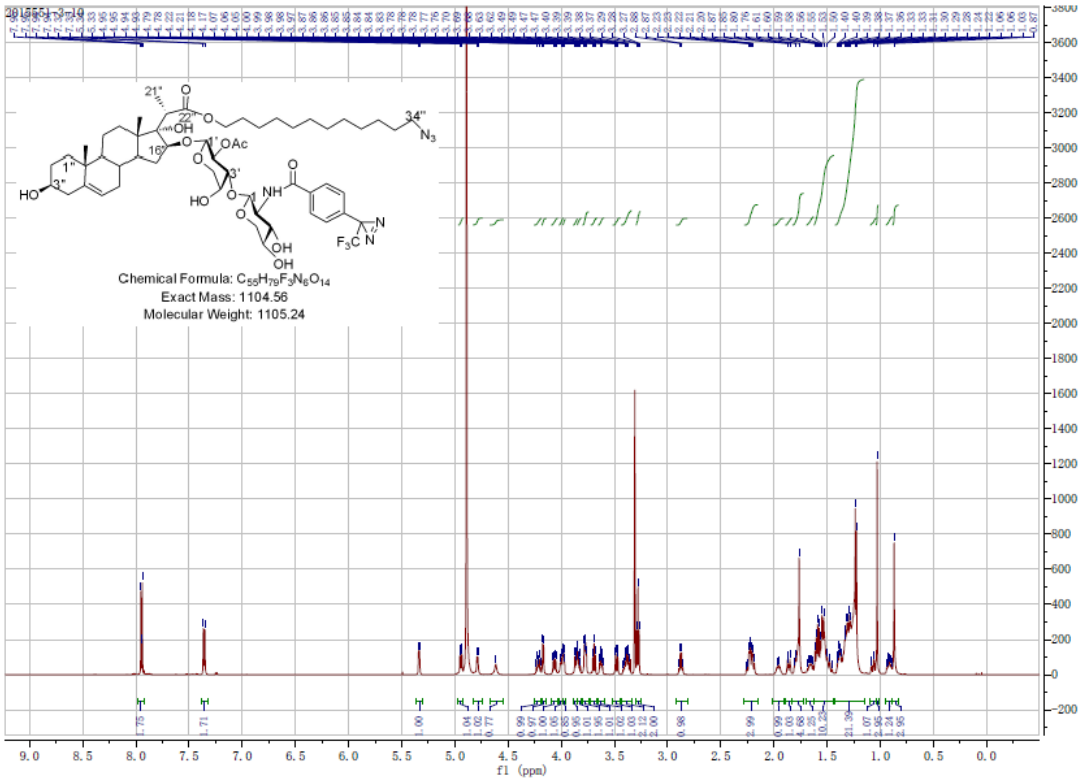
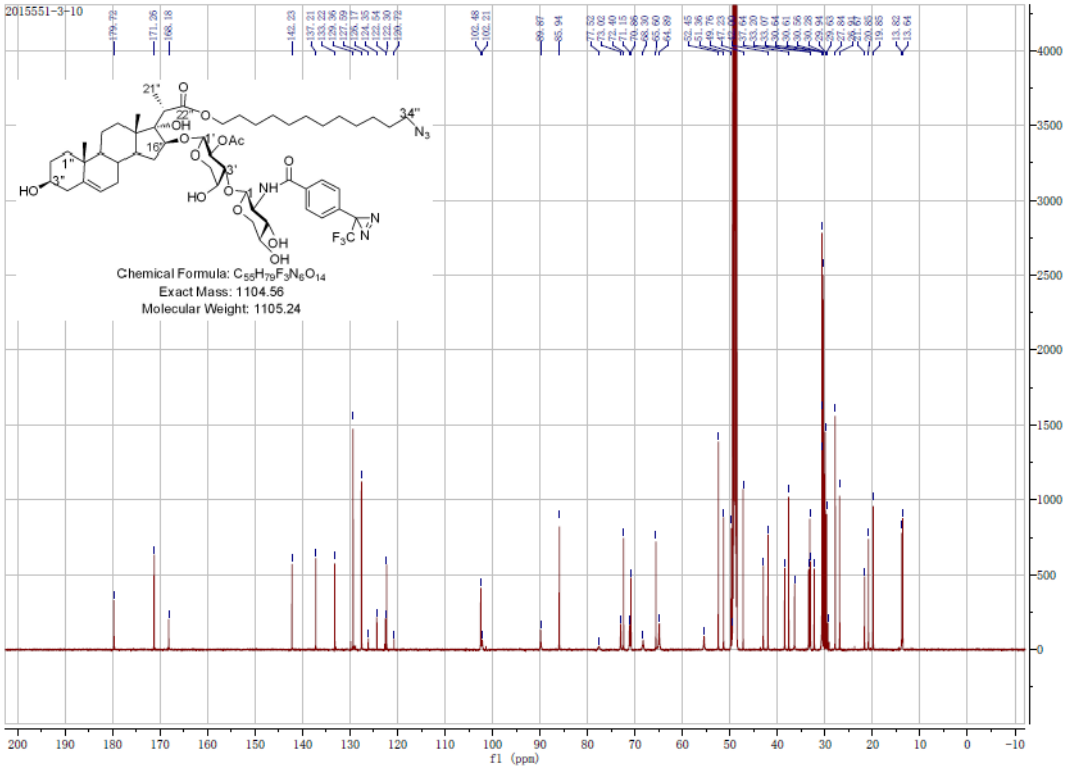
[1]H, [13]C, and 2D NMR spectra

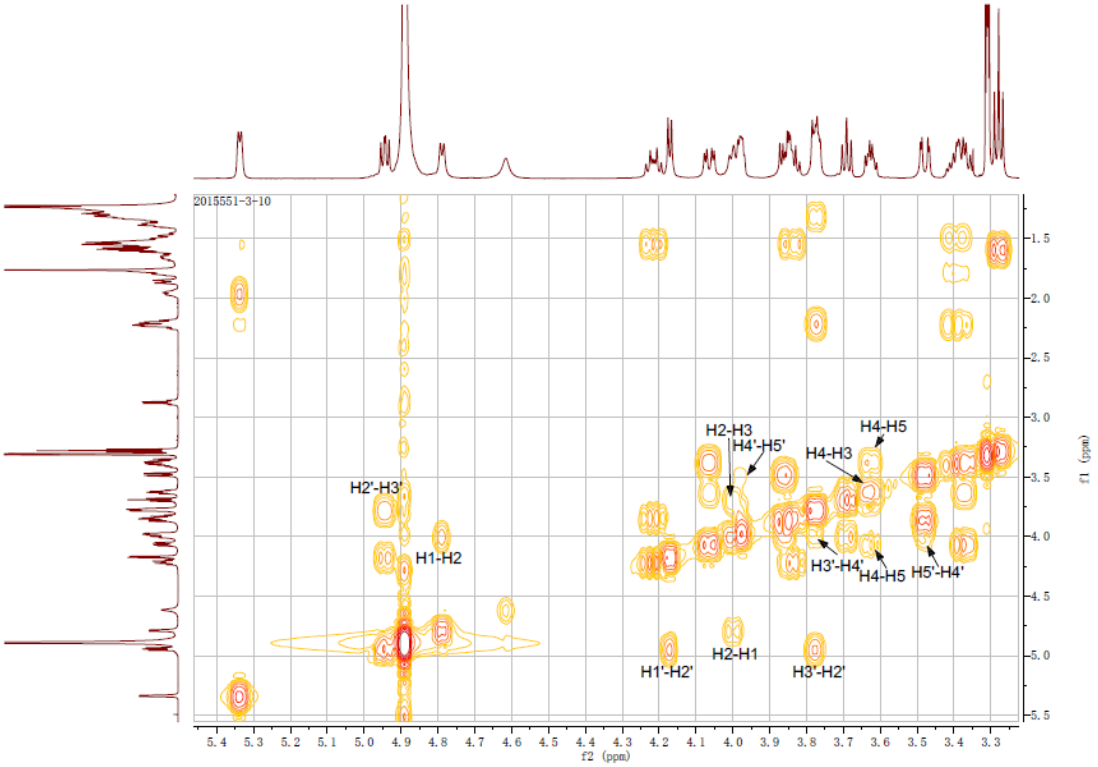
Compound **3**: [1]H NMR



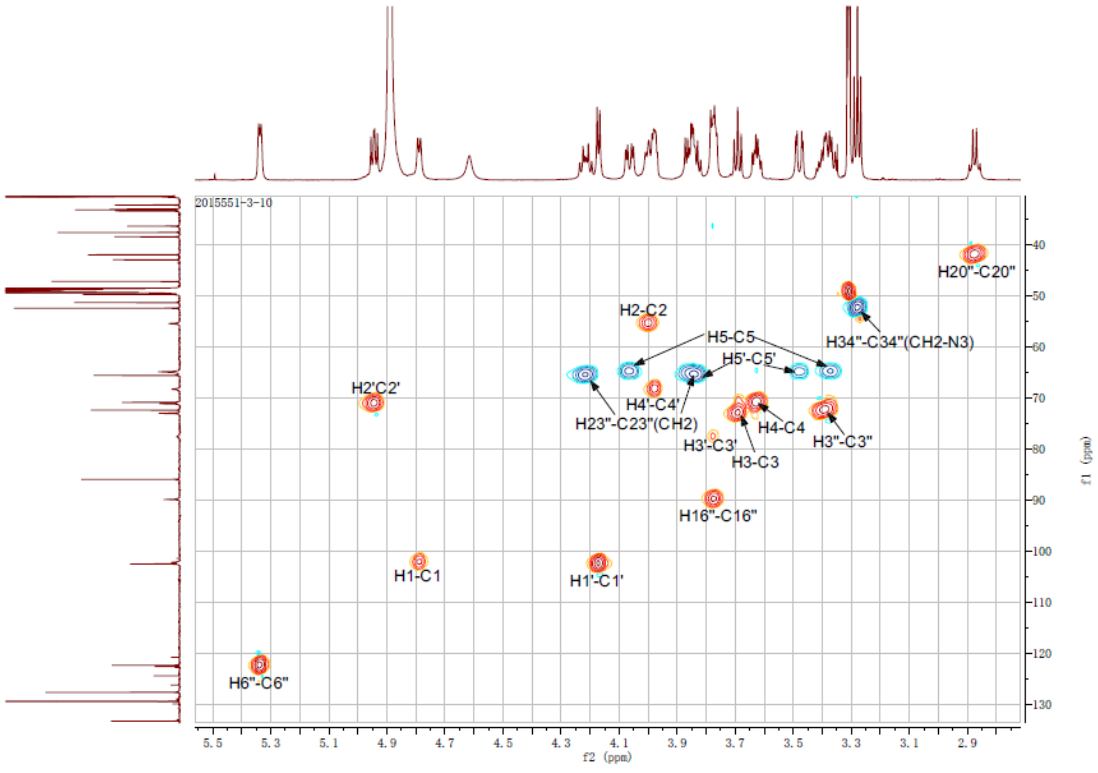
Compound **3**: [13]C NMR



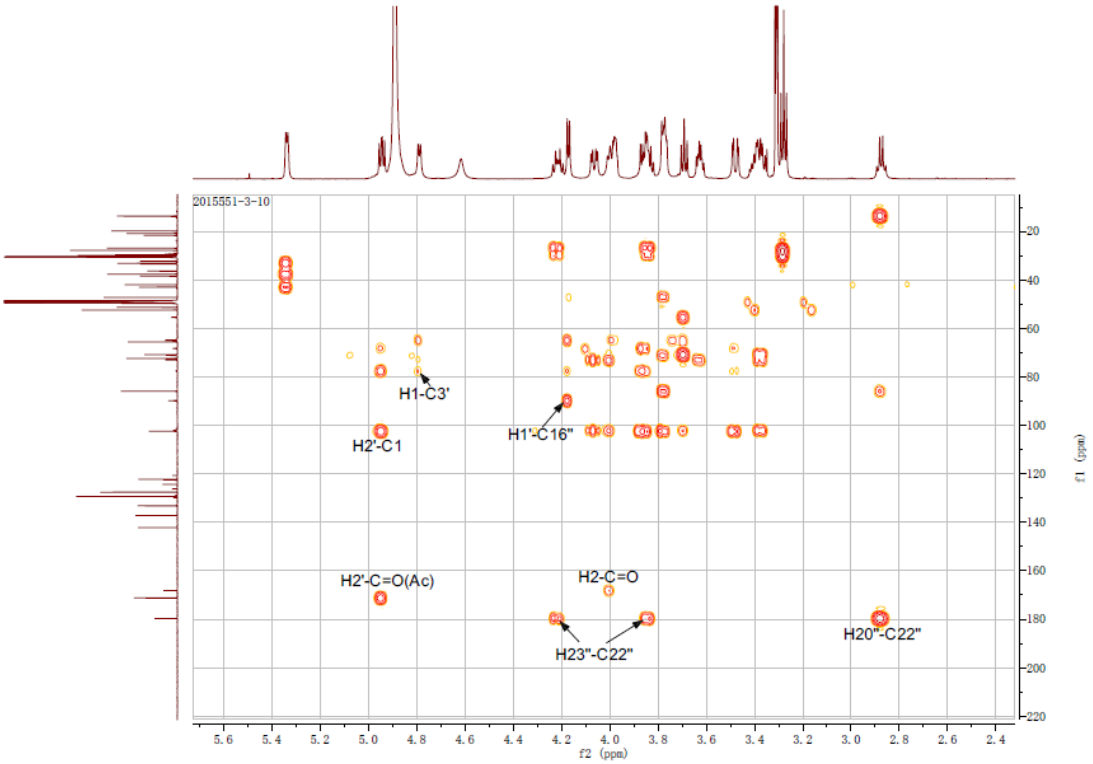
Compound **3**: COSY NMR



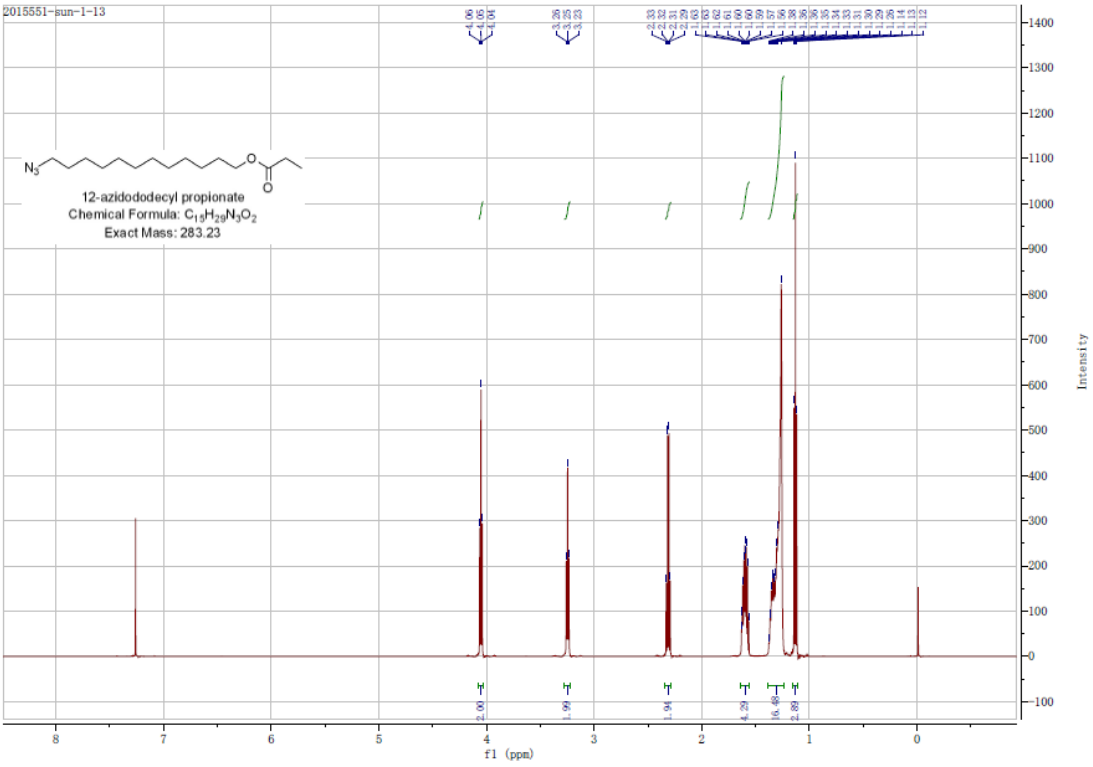
Compound **3**: HSQC NMR



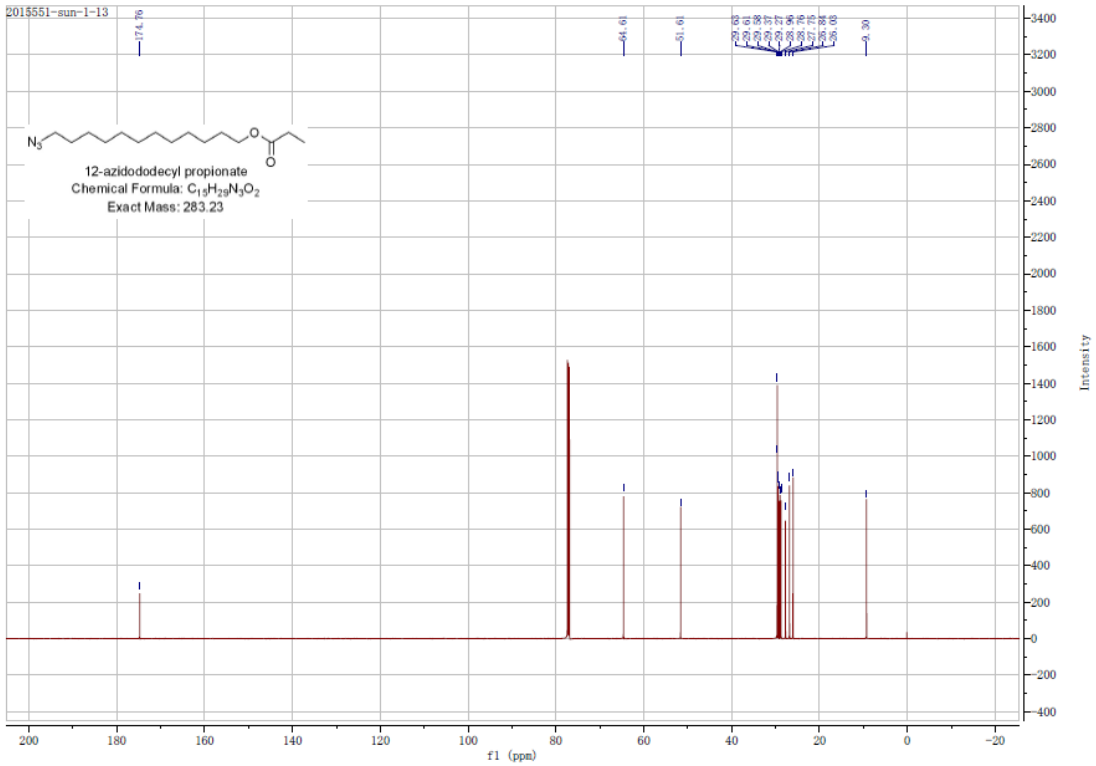
Compound **3**: HMBC NMR



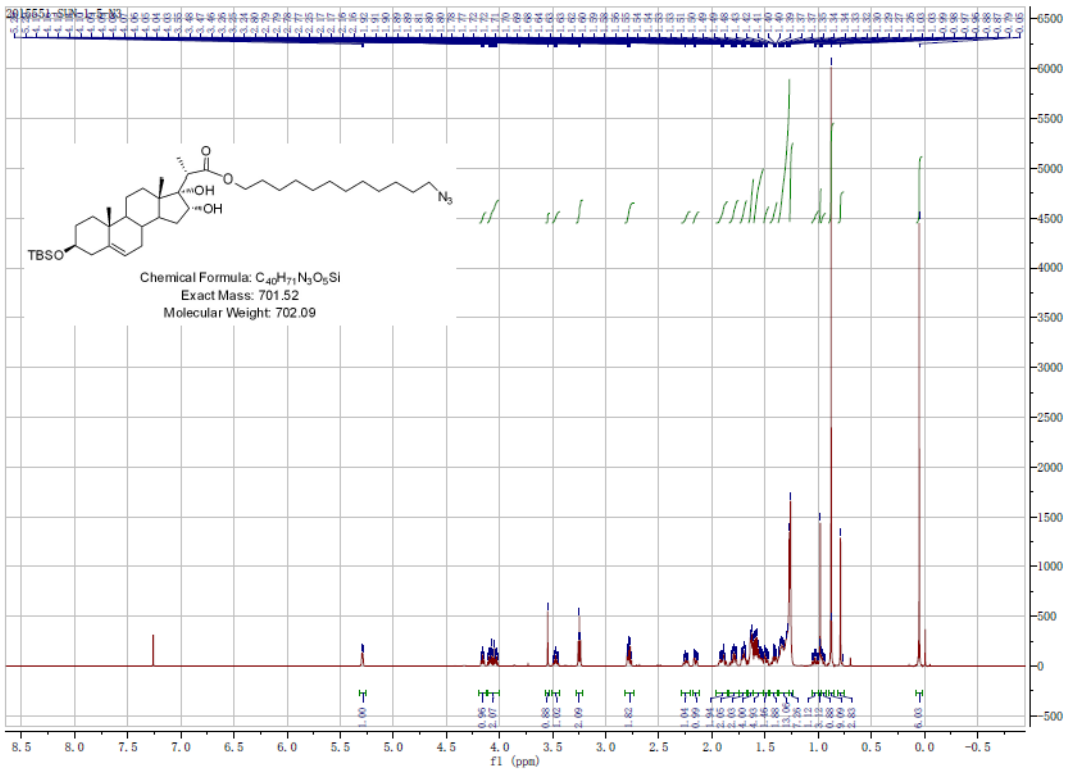
Compound **5**: ^{1}H NMR



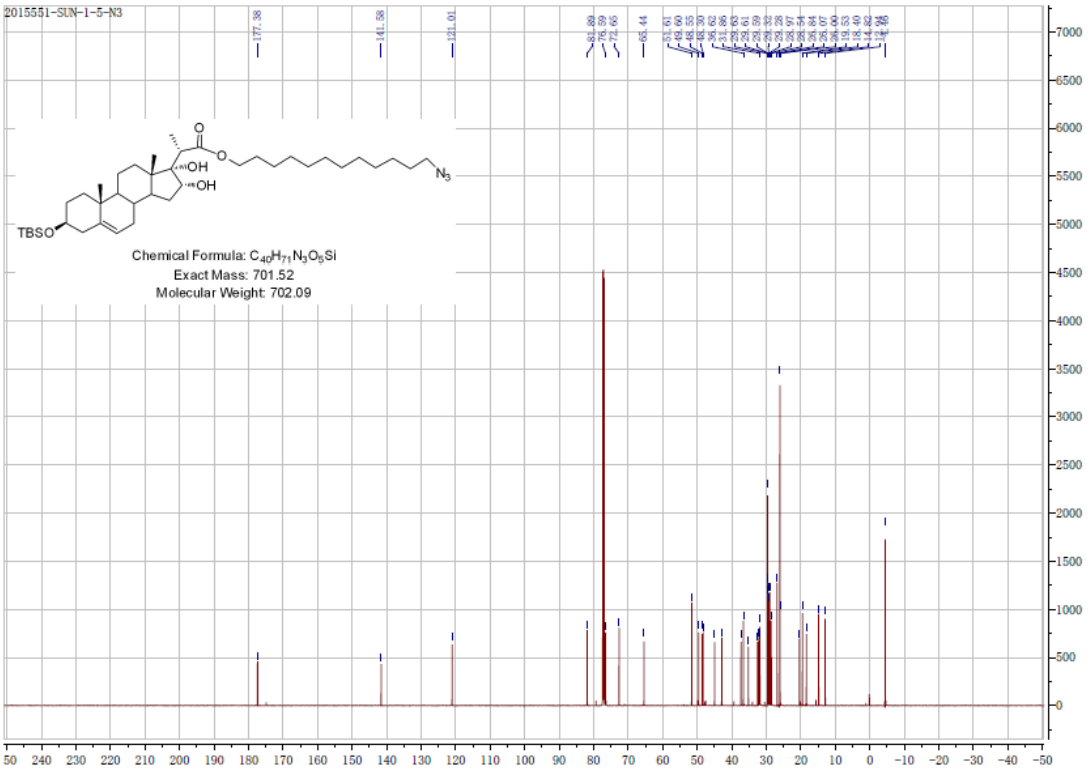
Compound **5**: ^{13}C NMR



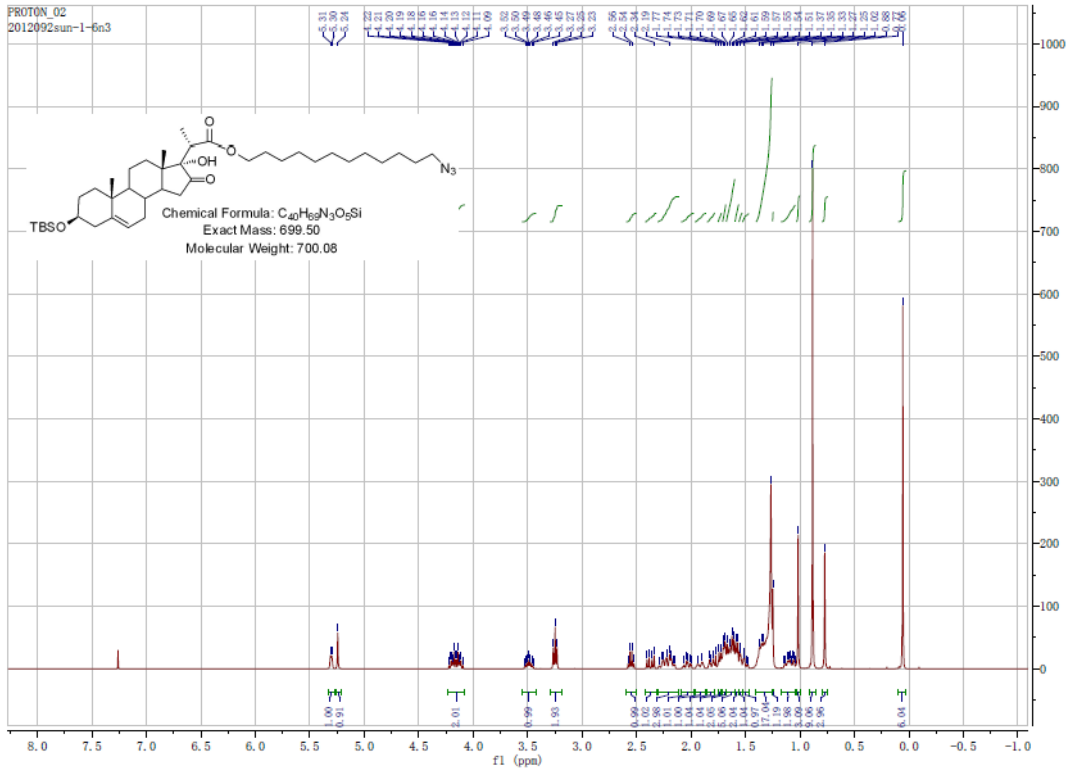
Compound **6**: ^{1}H NMR



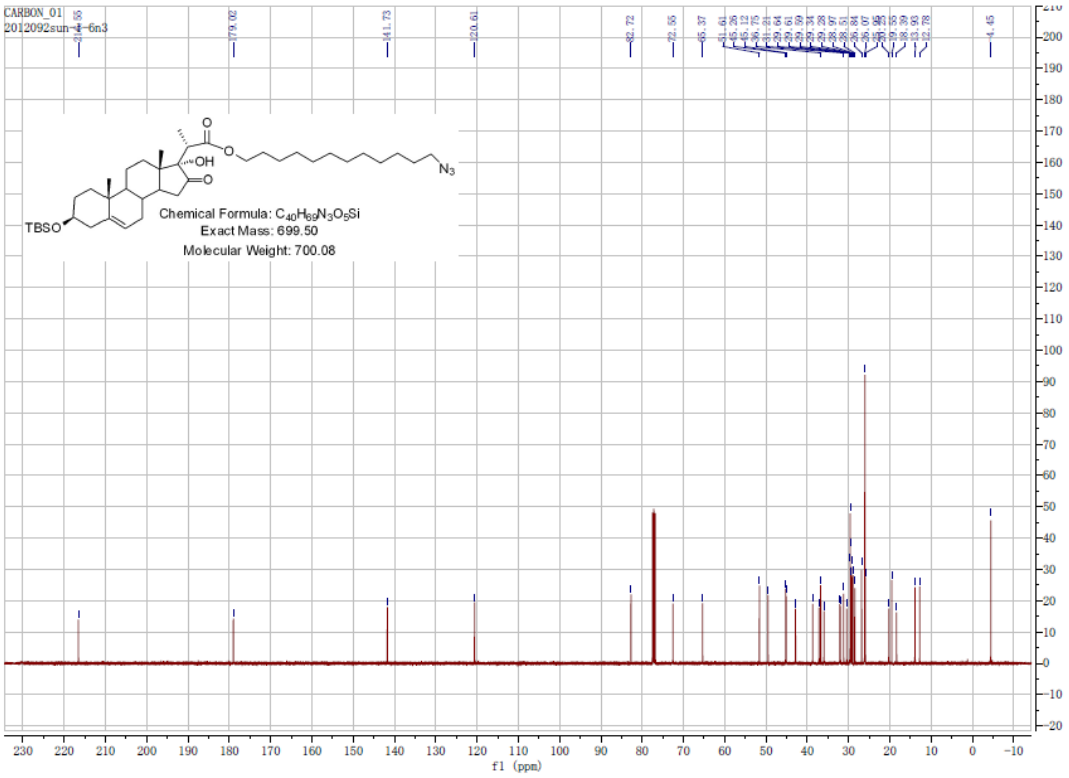
Compound **6**: ^{13}C NMR



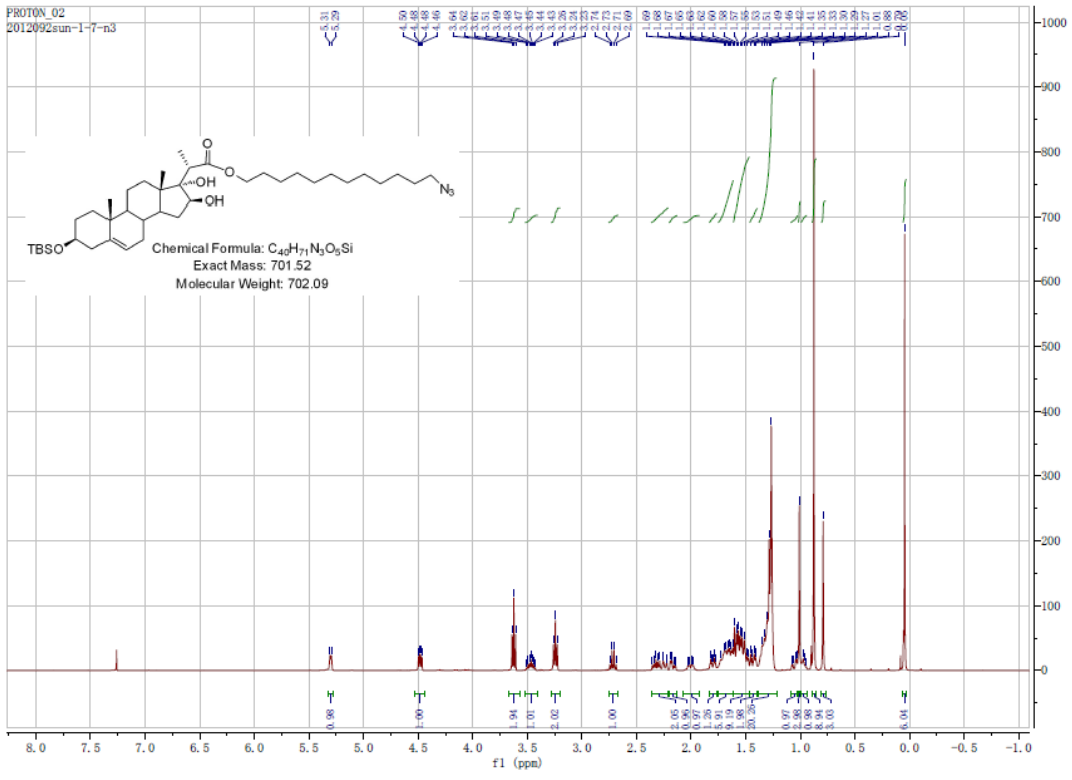
Compound **7**: ^{1}H NMR



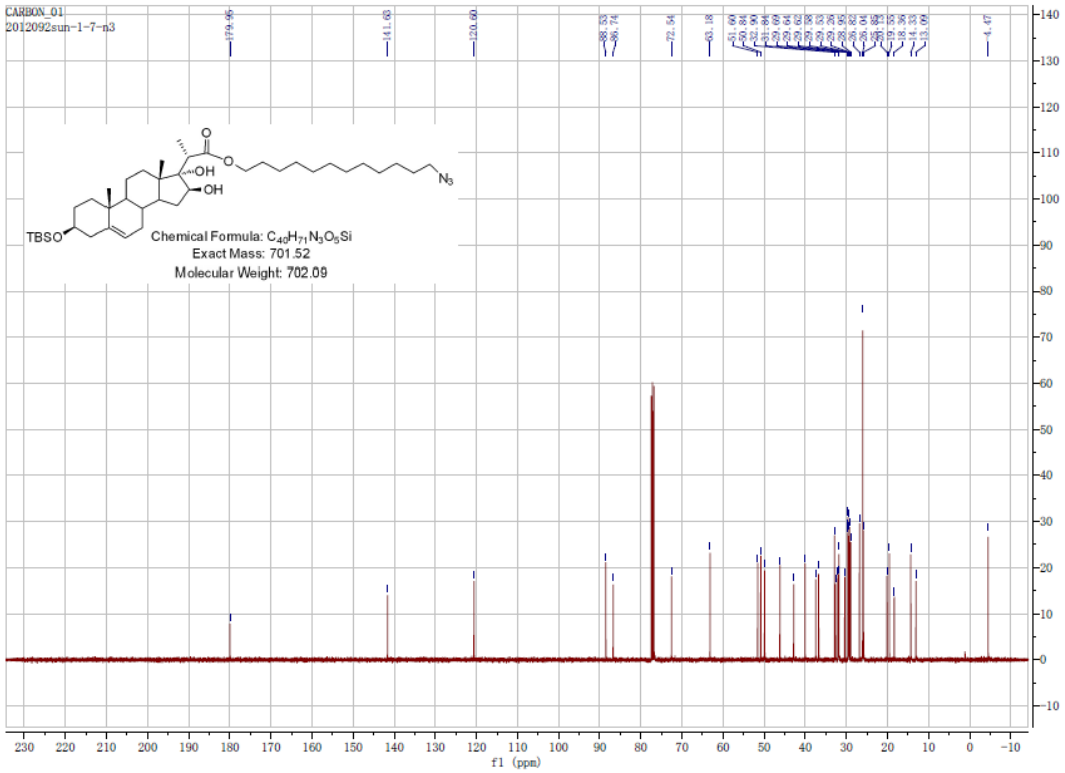
Compound **7**: ^{13}C NMR



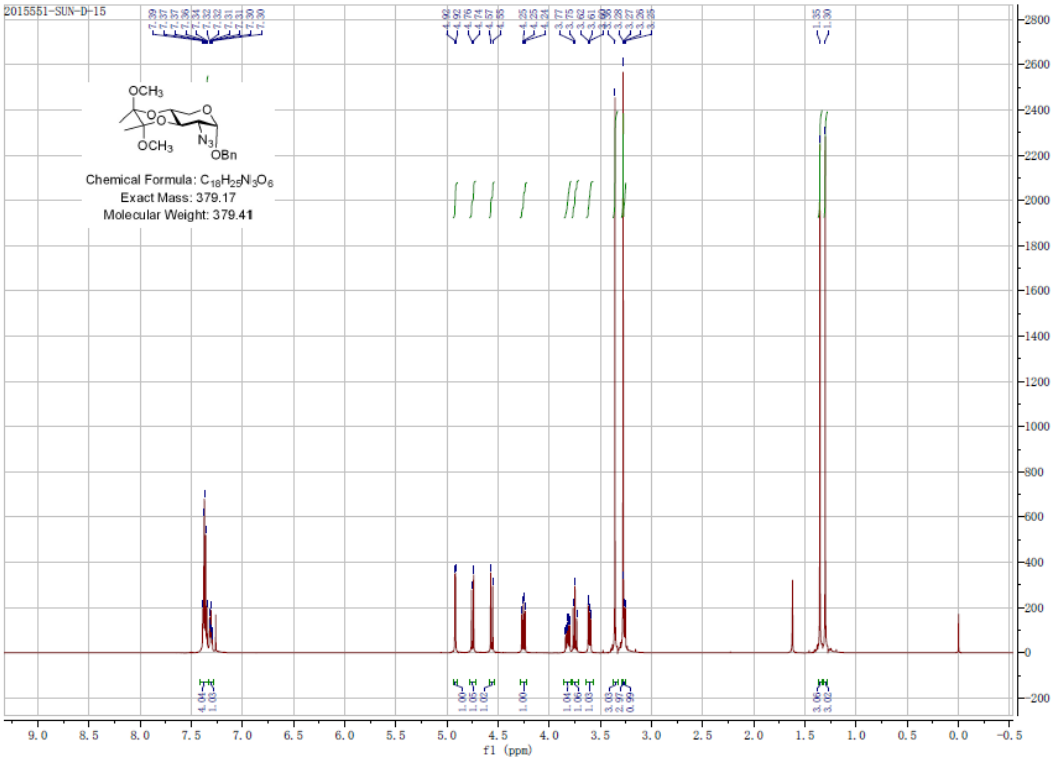
Compound **8**: ^{1}H NMR



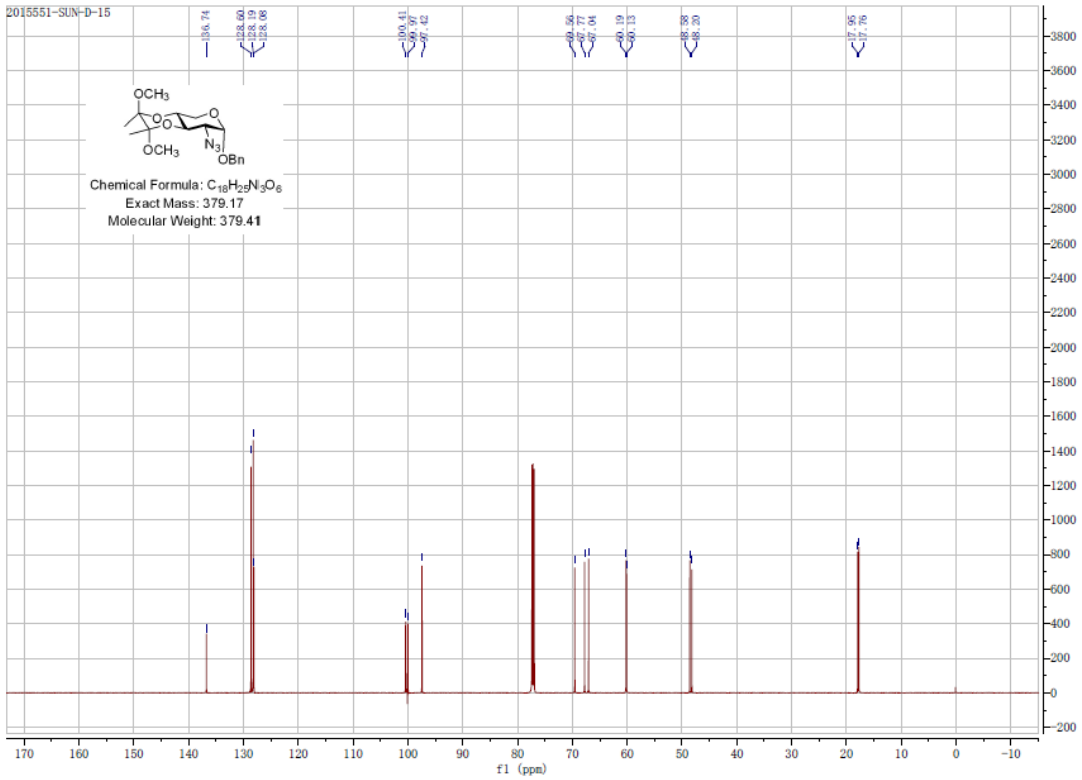
Compound **8**: ^{13}C NMR



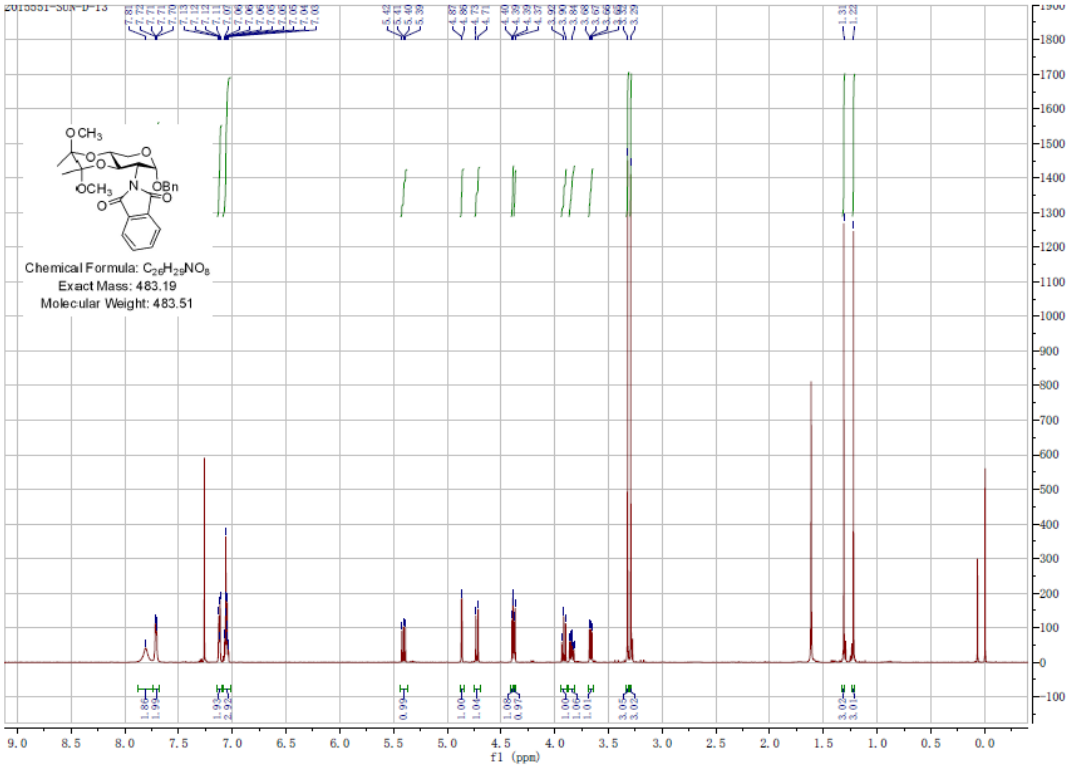
Compound **S2**: ^{1}H NMR



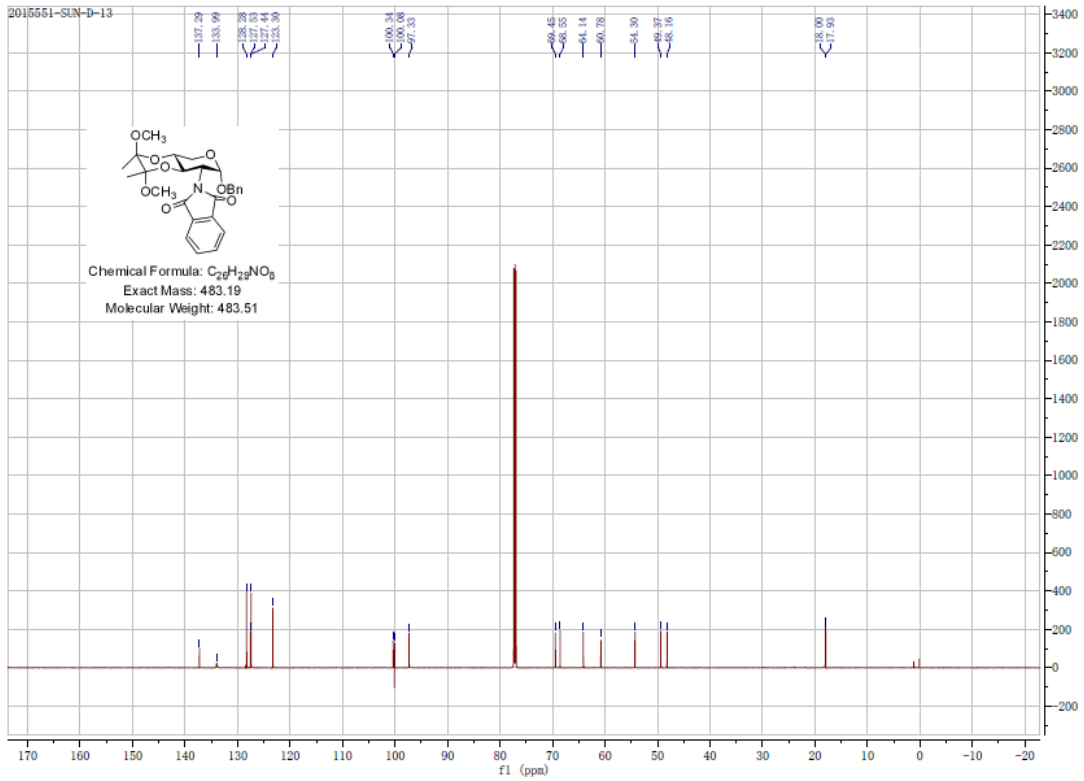
Compound **S2**: ^{13}C NMR



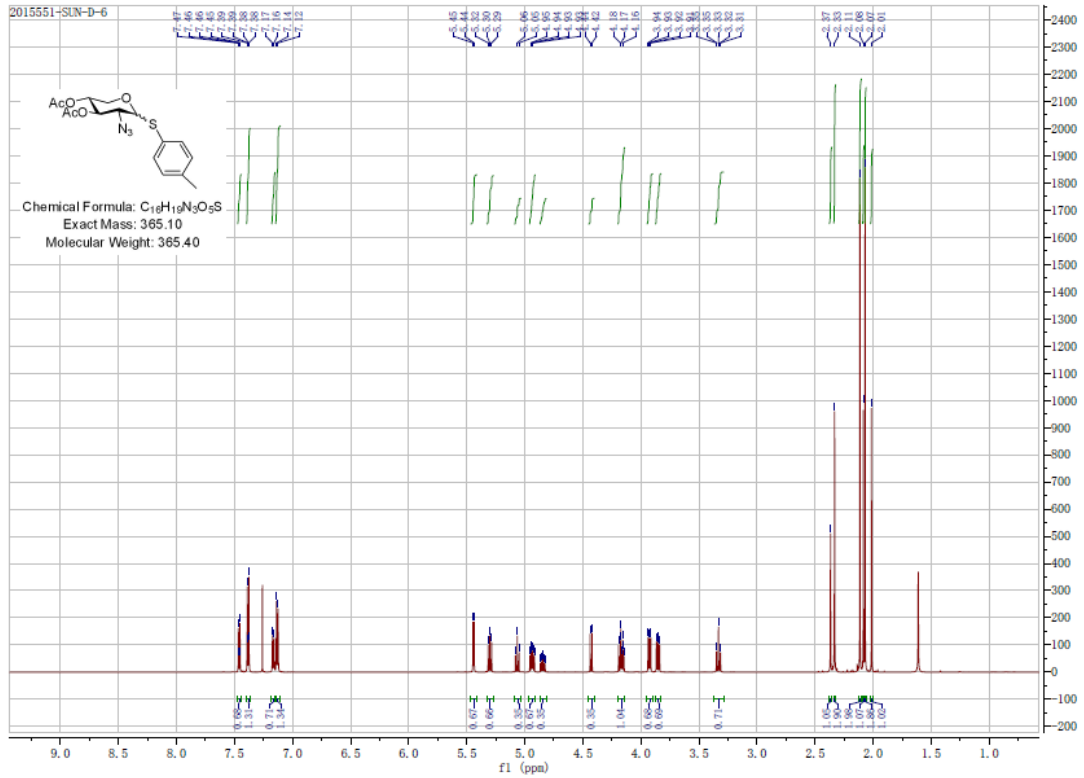
Compound **S3**: ^{1}H NMR



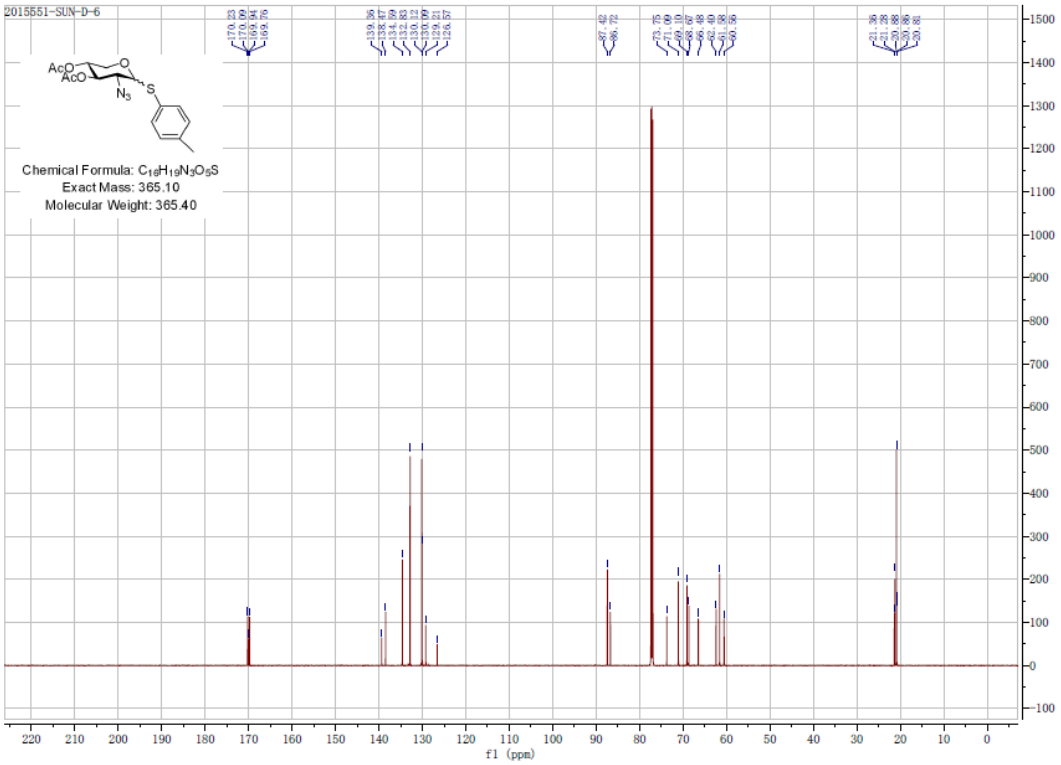
Compound **S3**: ^{13}C NMR



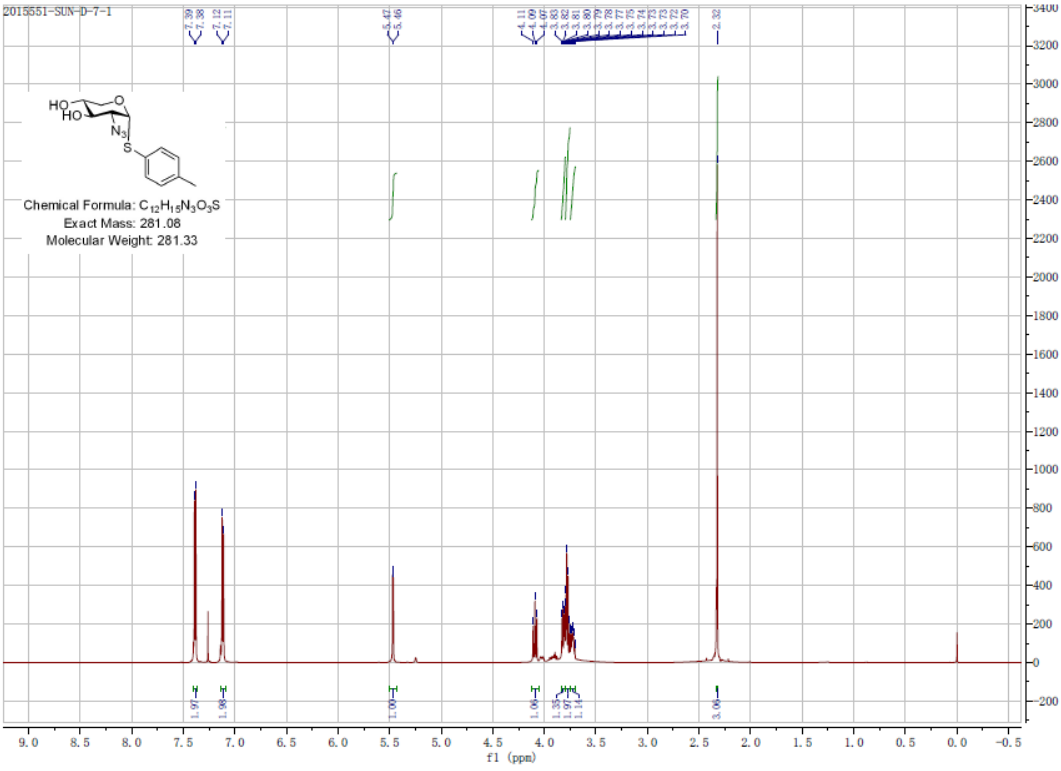
Compound **12 (α/β)**: ^{1}H NMR



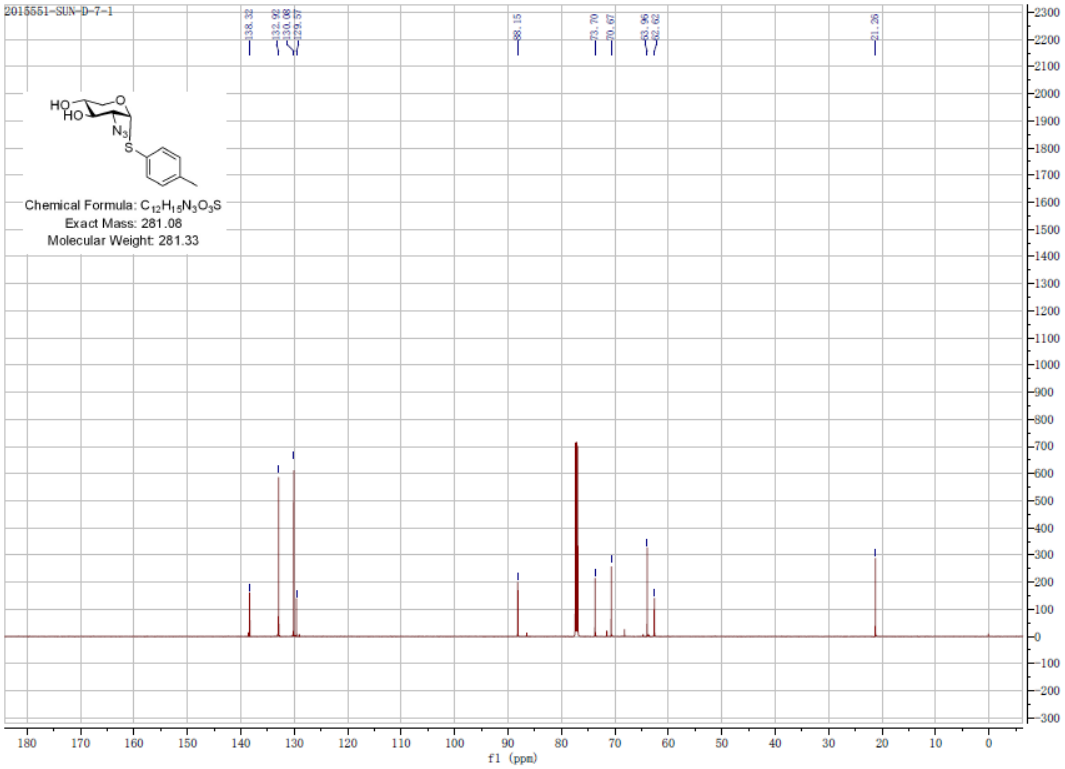
Compound **12 (α/β)**: ^{13}C NMR



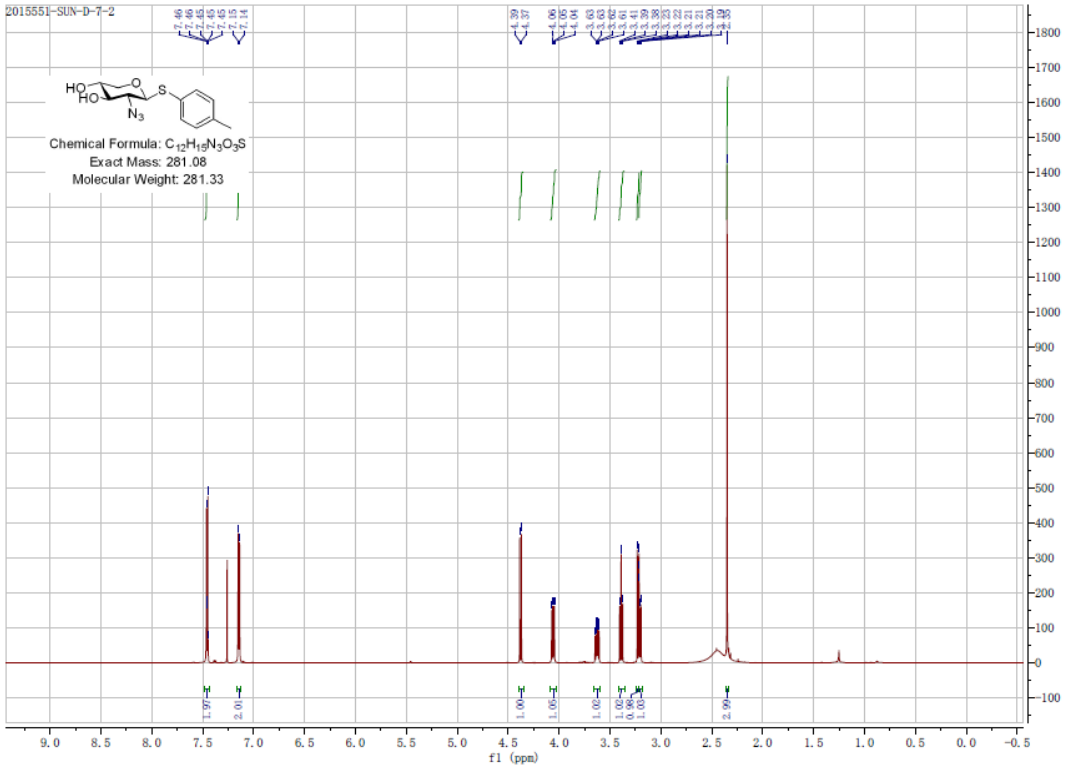
Compound **13 α**: ^{1}H NMR



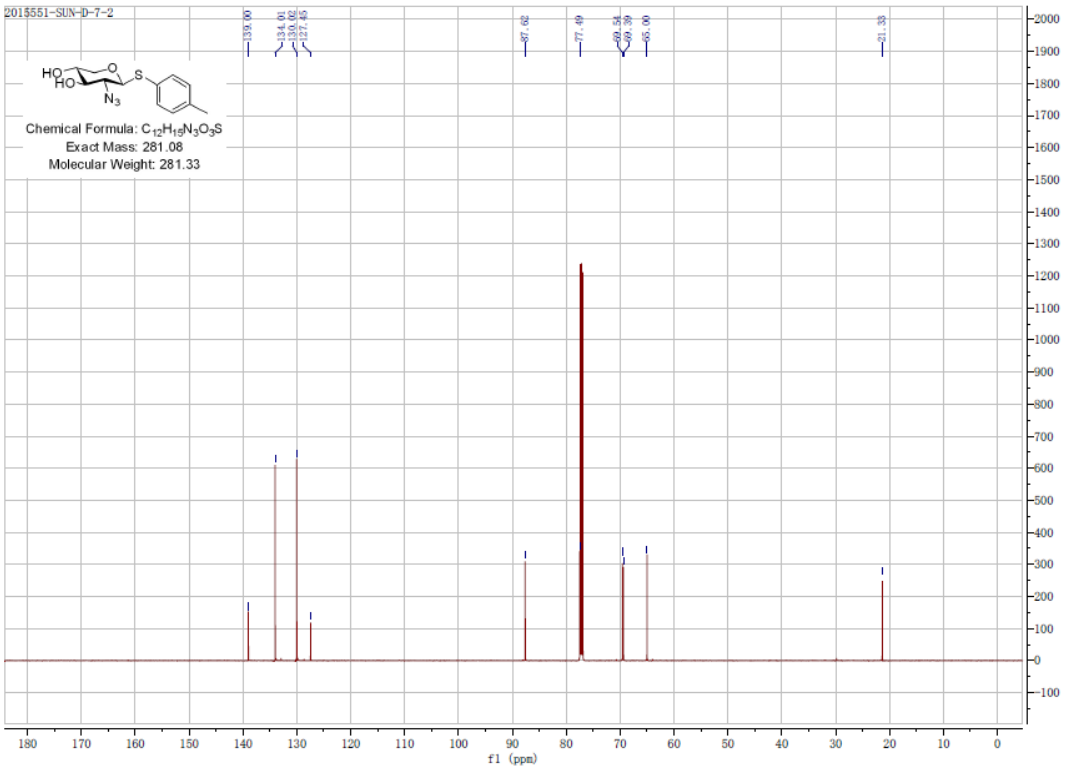
Compound **13 α**: ^{13}C NMR



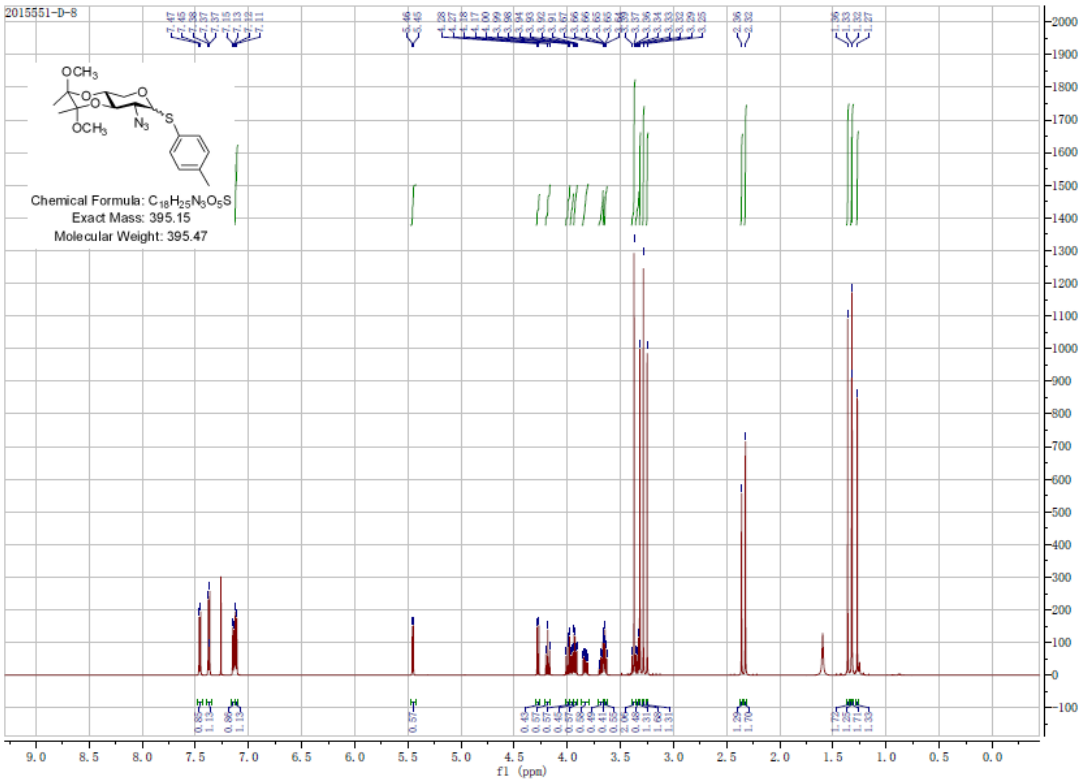
Compound **13 β**: ^{1}H NMR



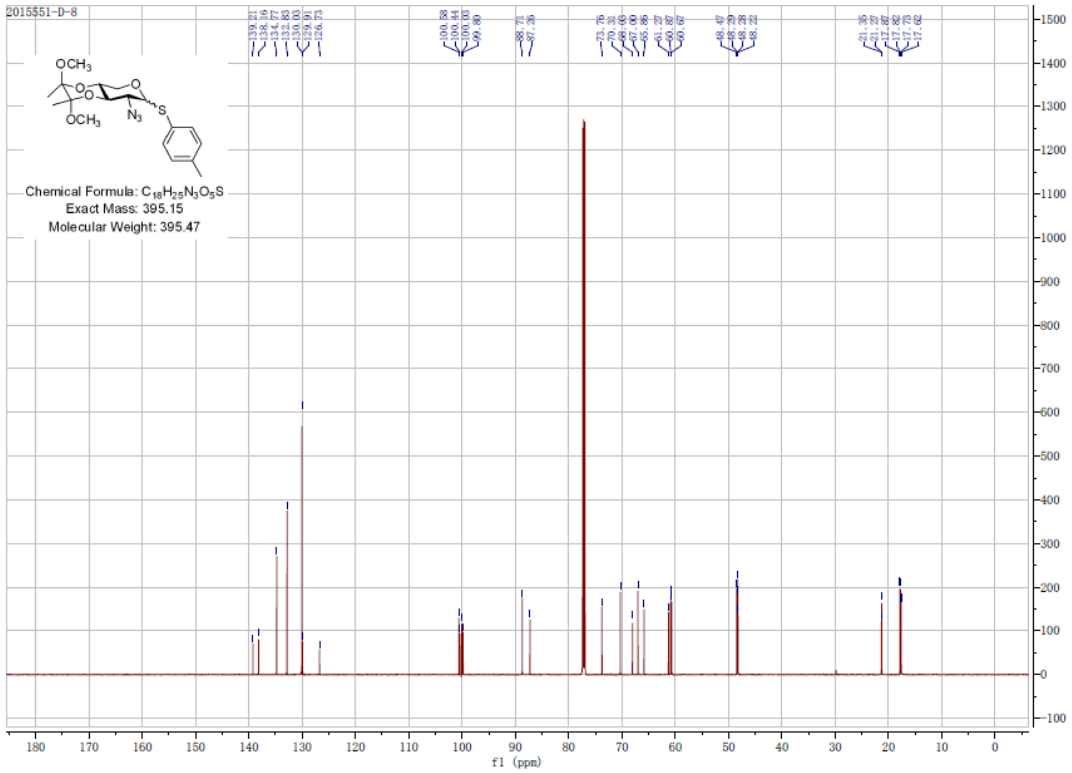
Compound **13 β**: ^{13}C NMR



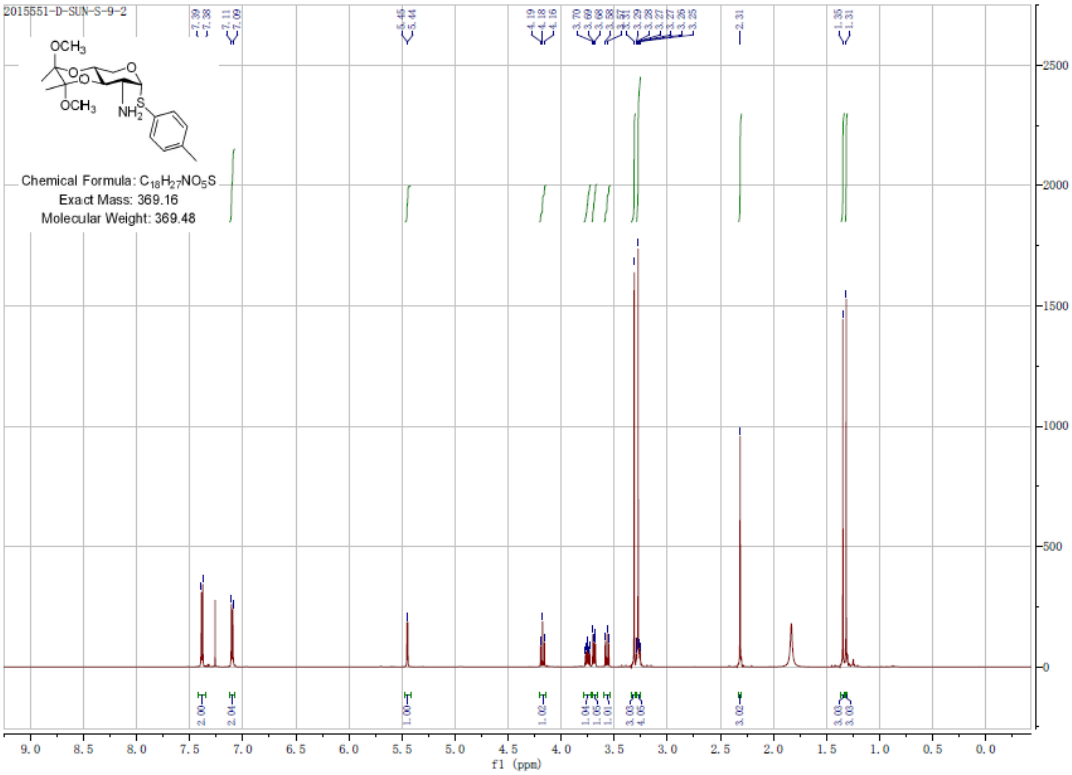
Compound **14 (α/β)**: ^{1}H NMR



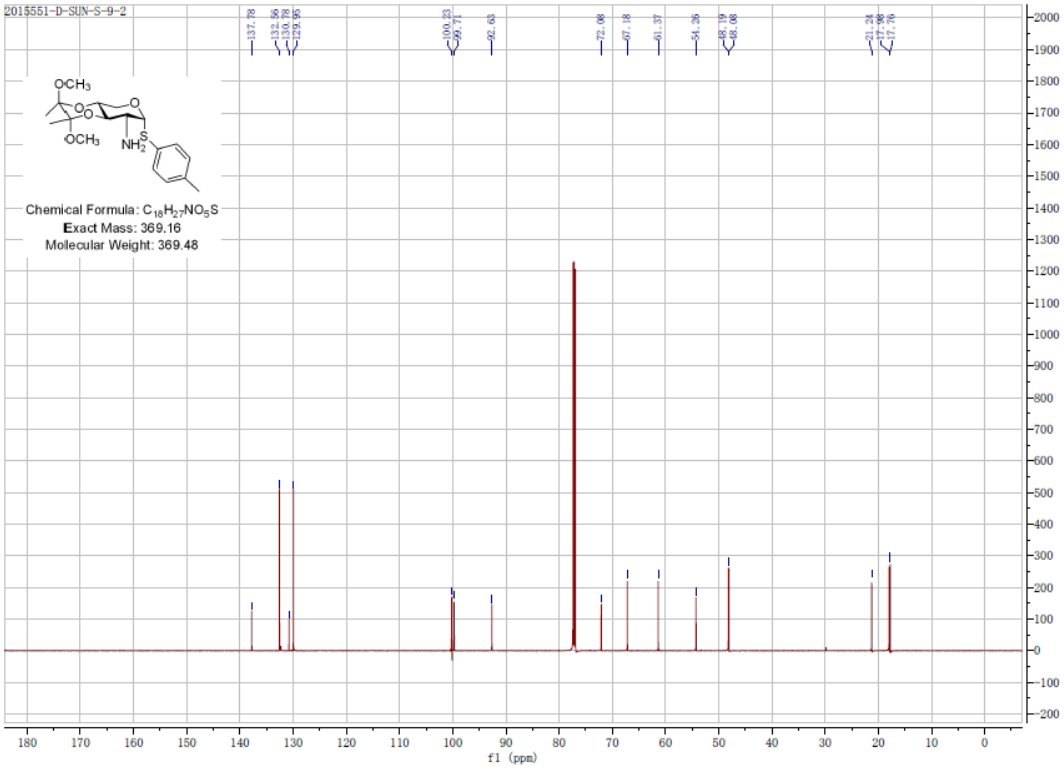
Compound **14 (α/β)**: ^{13}C NMR



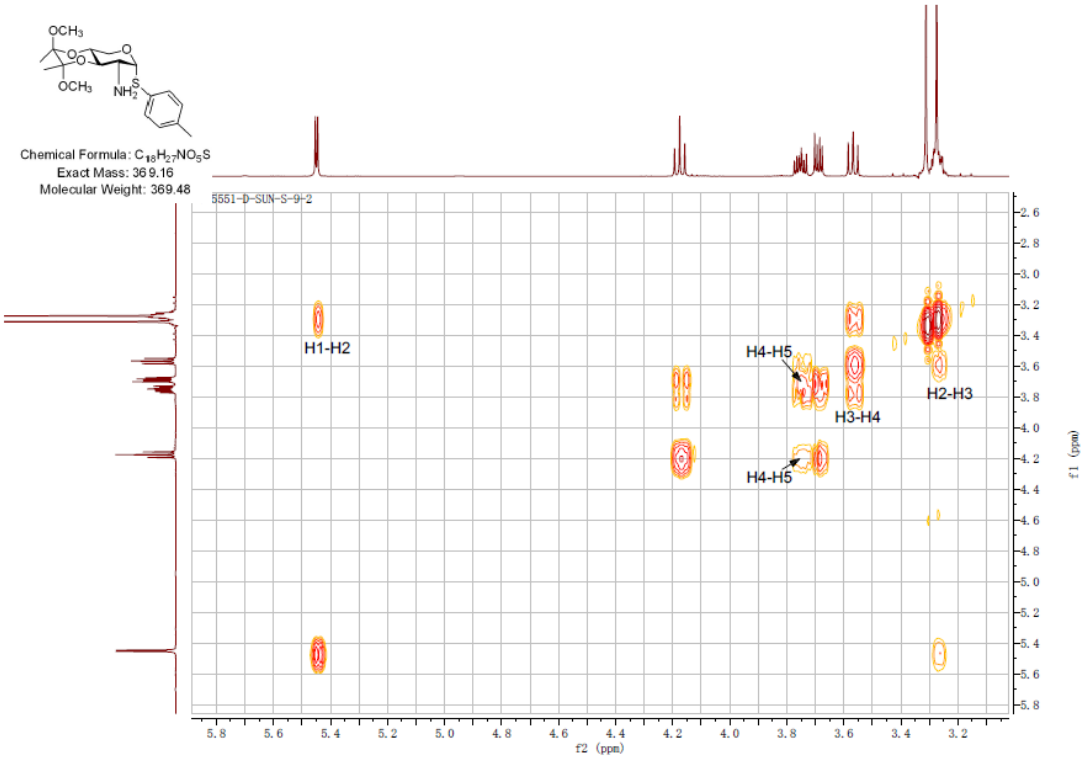
Compound **15 α**: ^{1}H NMR



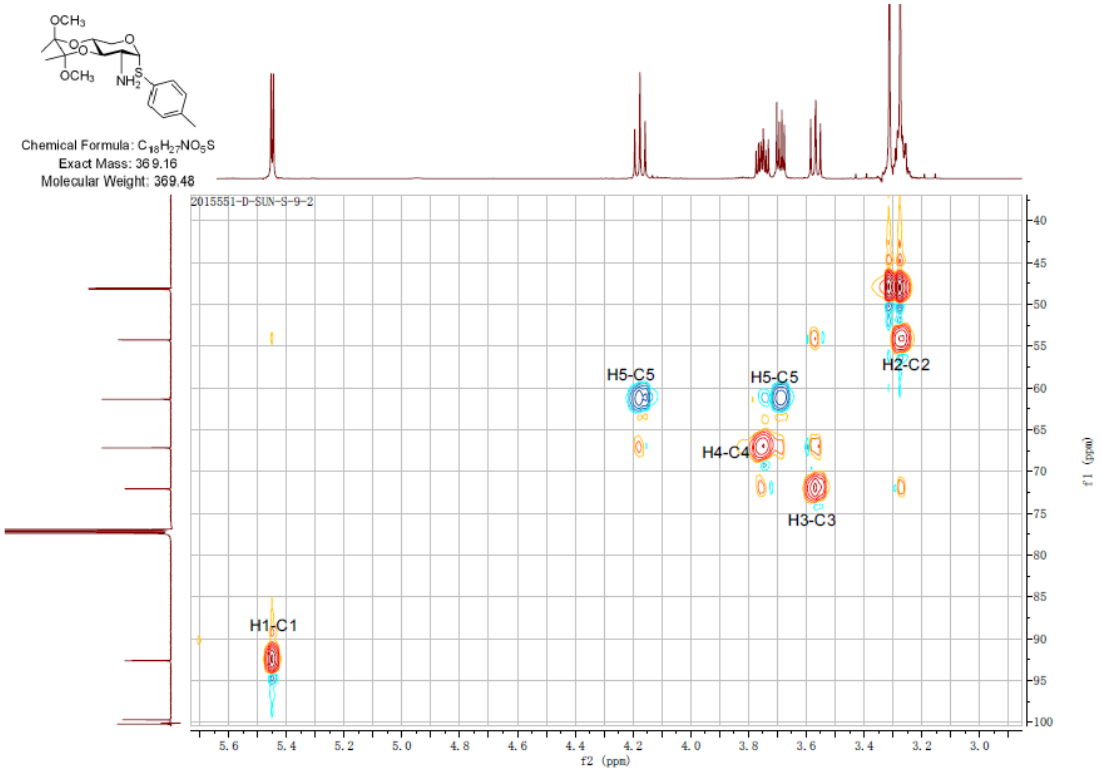
Compound **15 α**: ^{13}C NMR



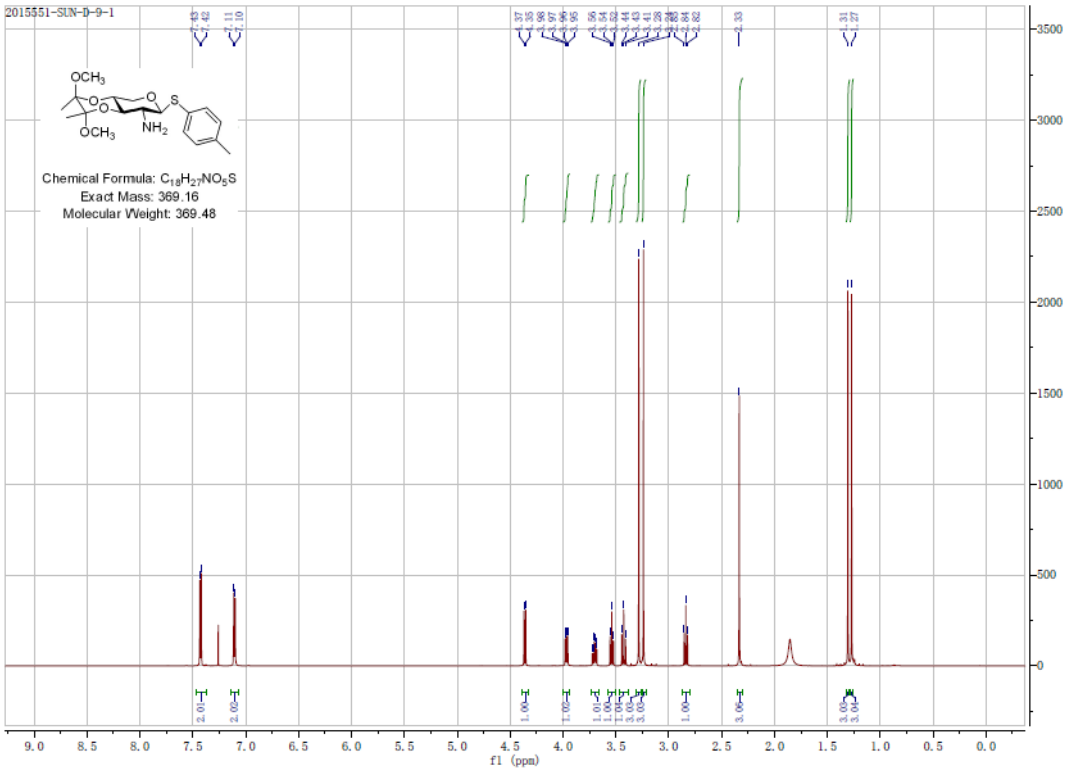
Compound **15 α**: COSY NMR



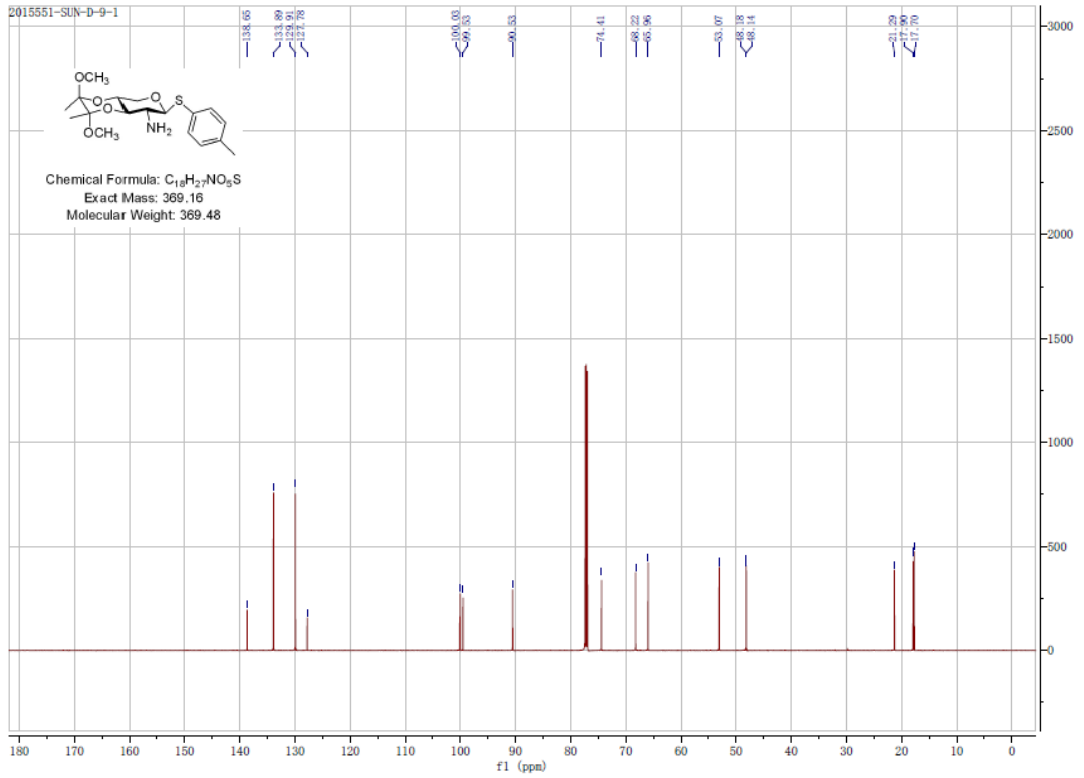
Compound **15 α**: HSQC NMR



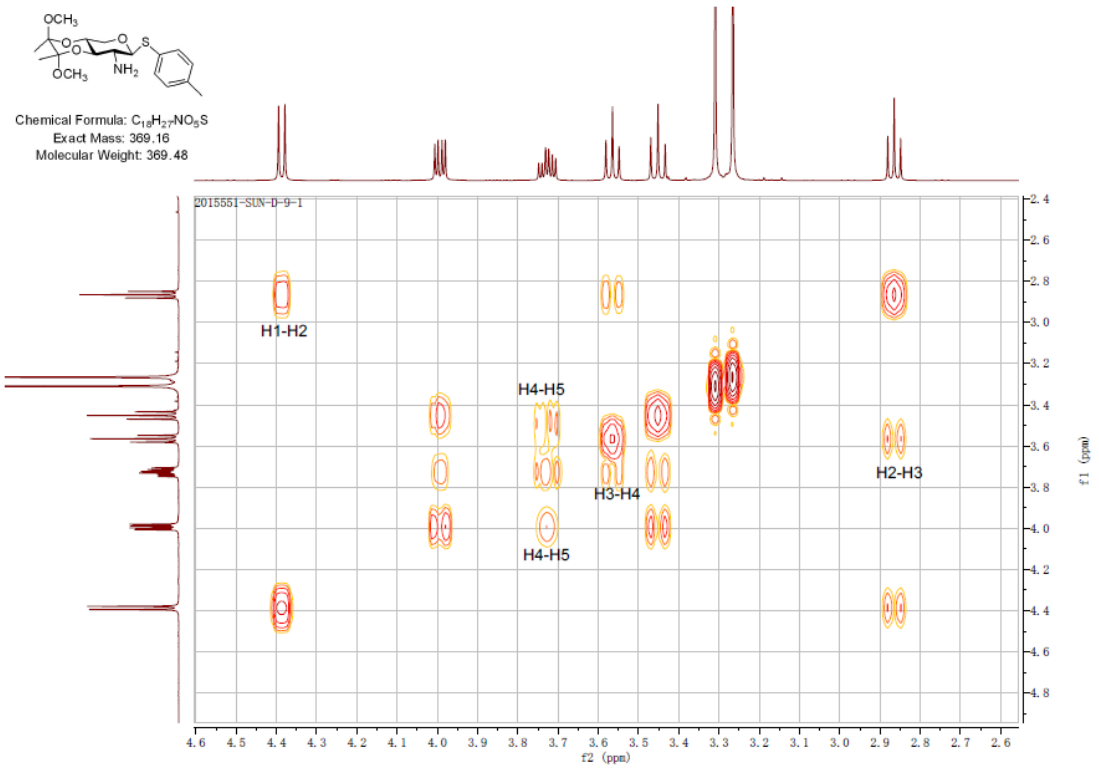
Compound **15 β**: ^{1}H NMR



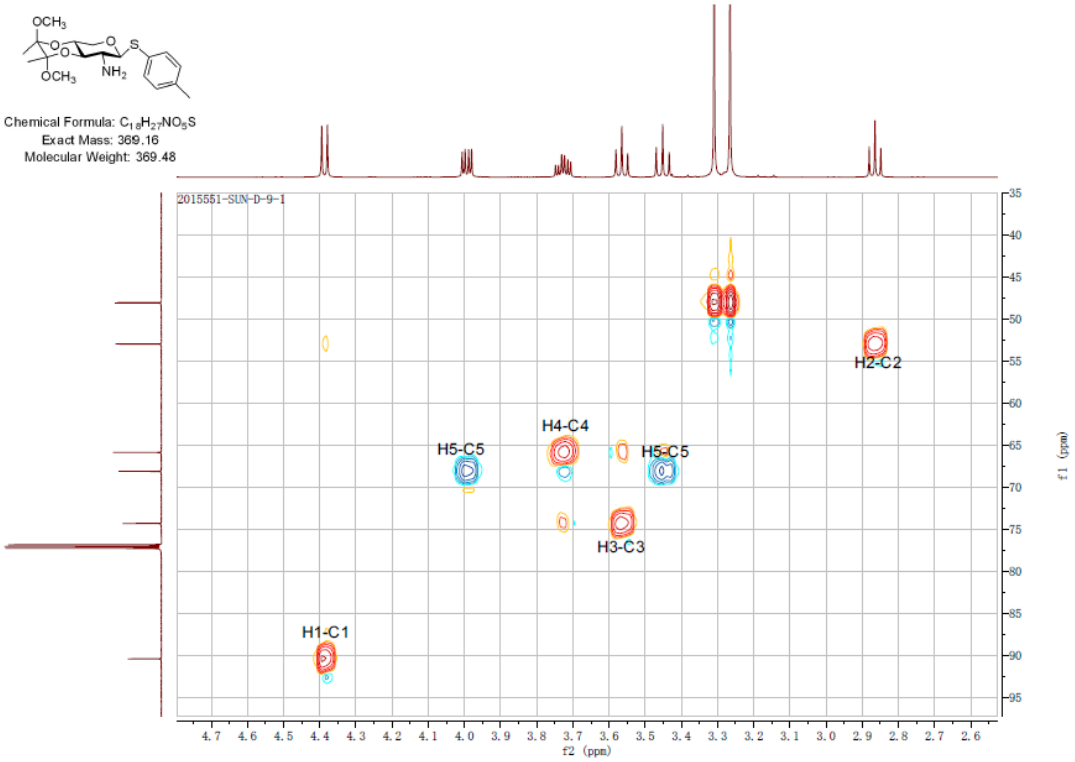
Compound **15 β**: ^{13}C NMR



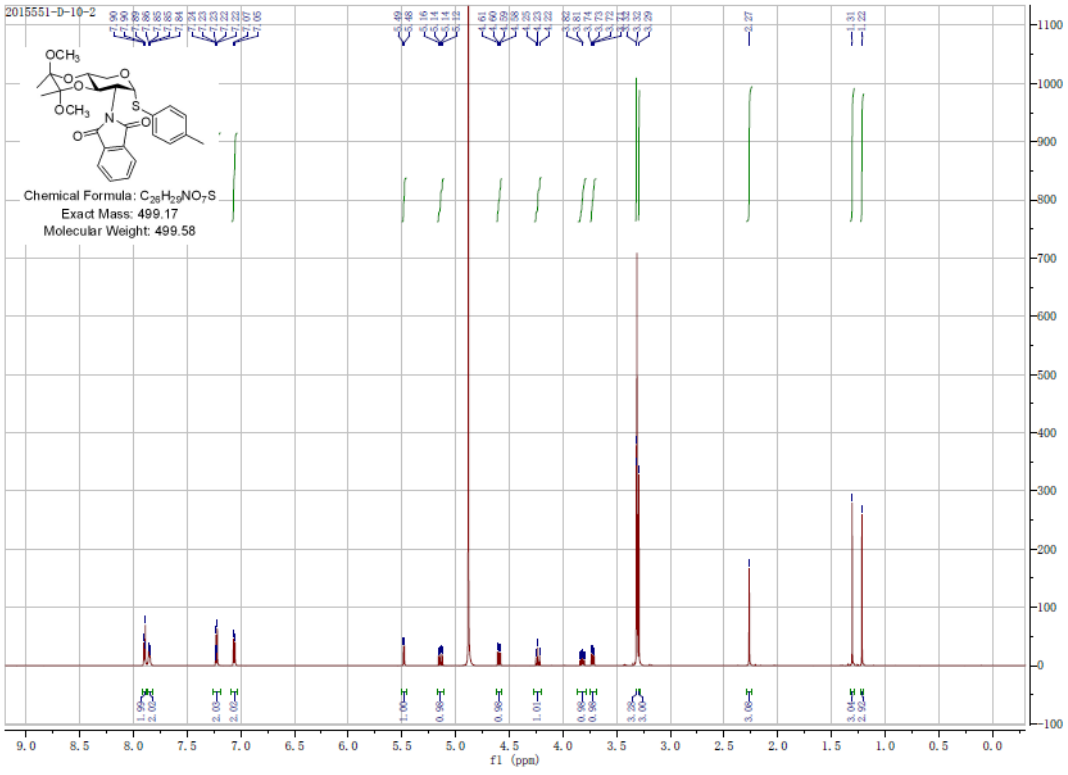
Compound **15 β**: COSY NMR



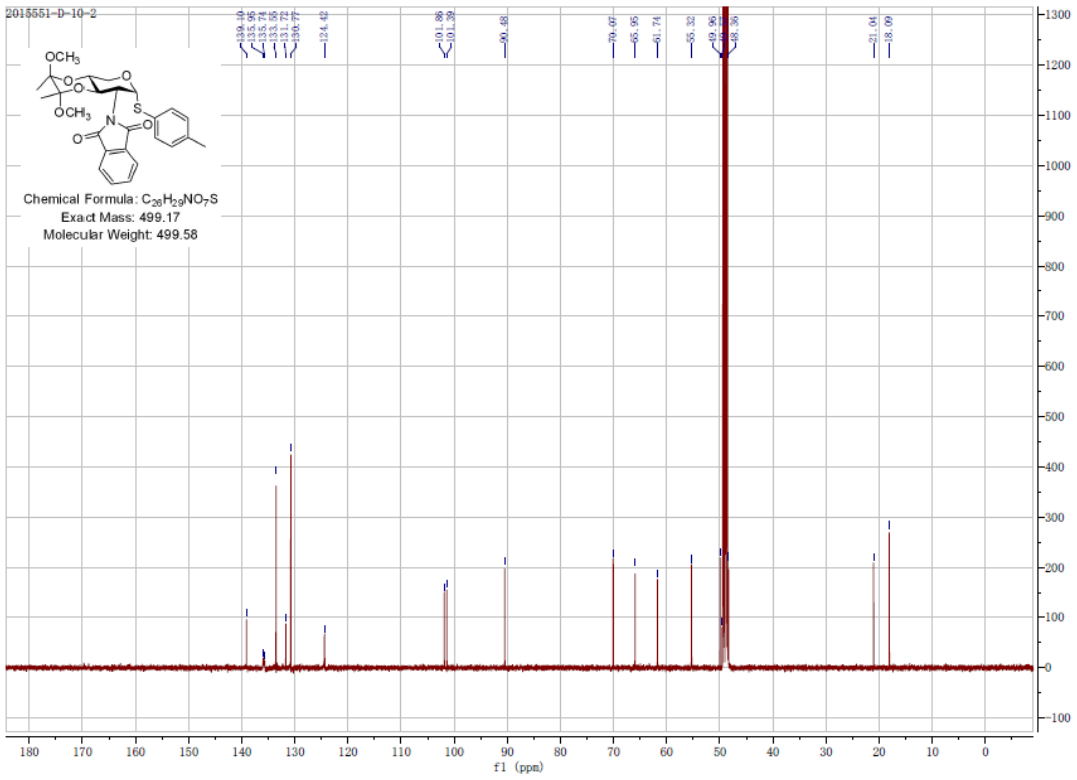
Compound **15 β**: HSQC NMR



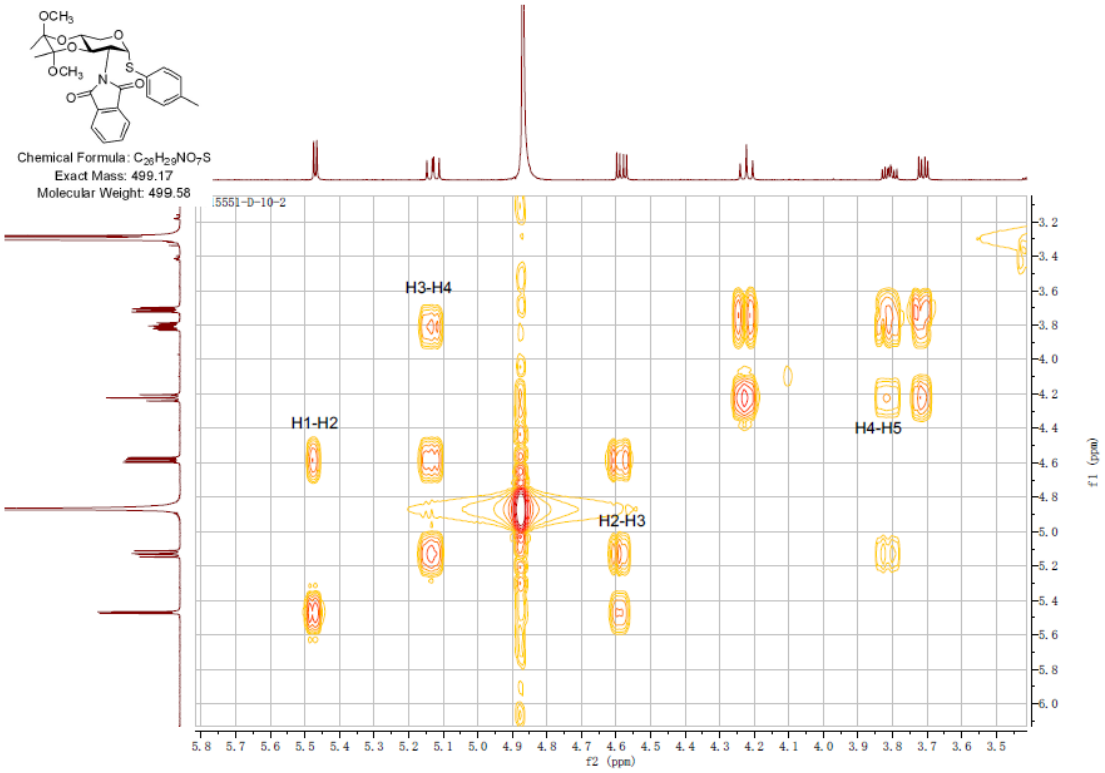
Compound **16 α**: ^{1}H NMR



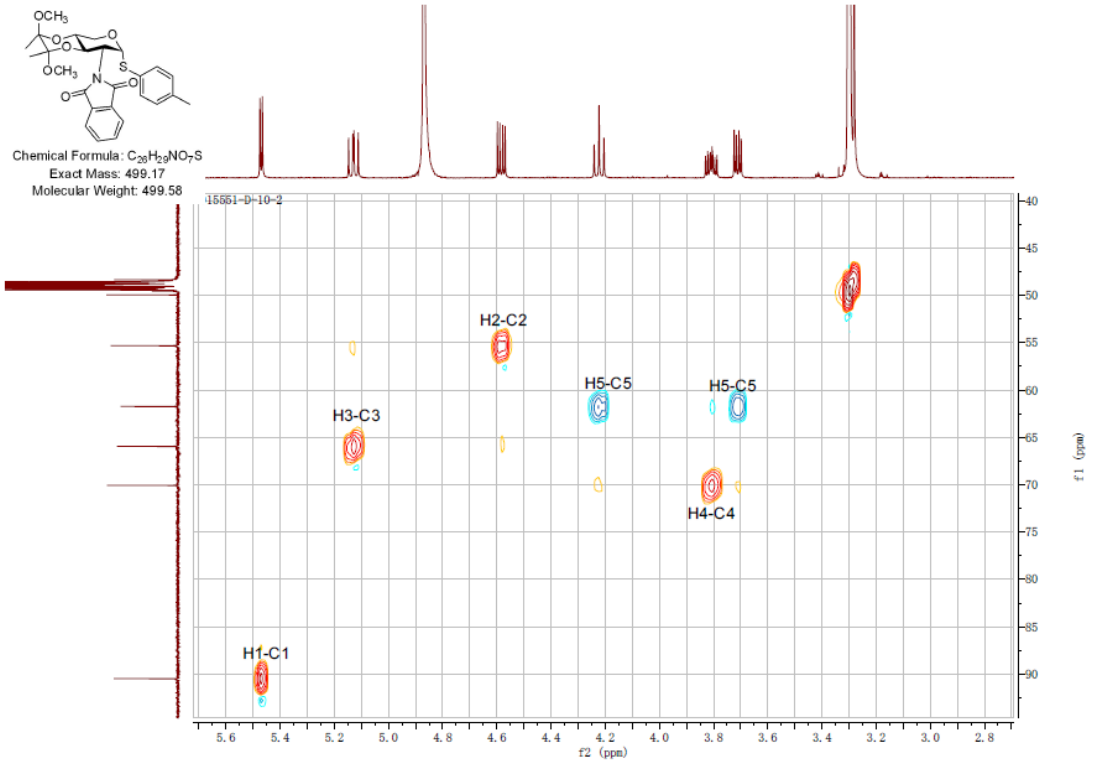
Compound **16 α**: ^{13}C NMR



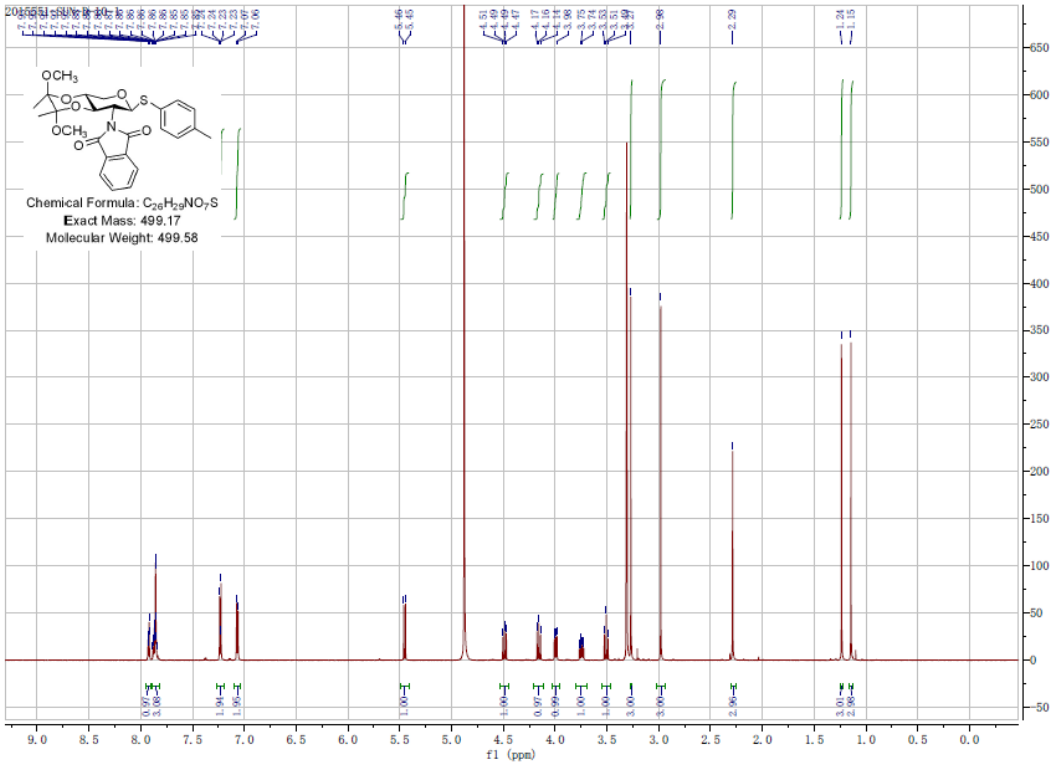
Compound **16 α**: COSY NMR



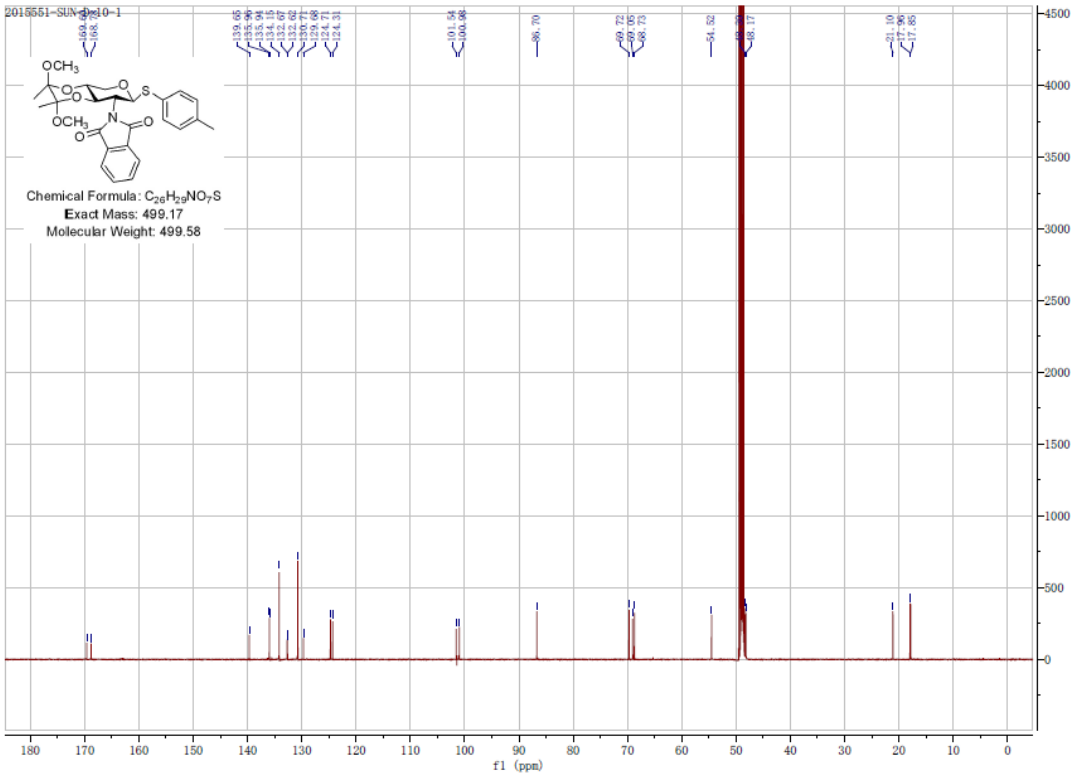
Compound **16 α**: HSQC NMR



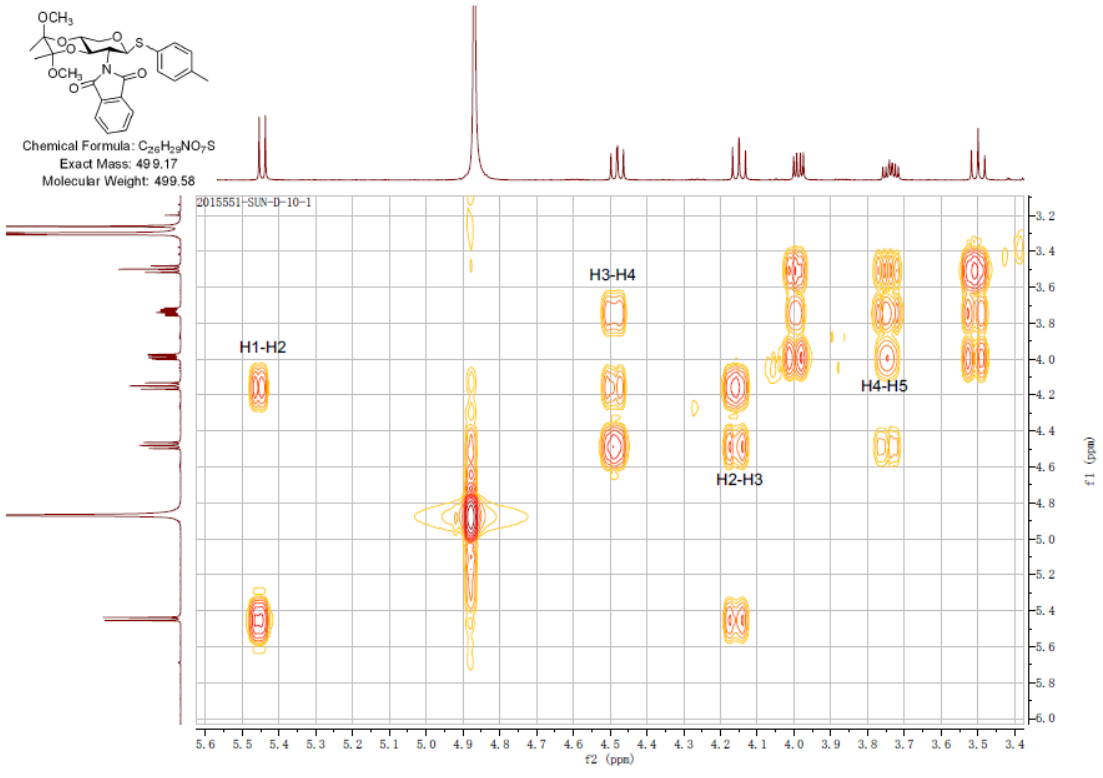
Compound **16 β**: ^{1}H NMR



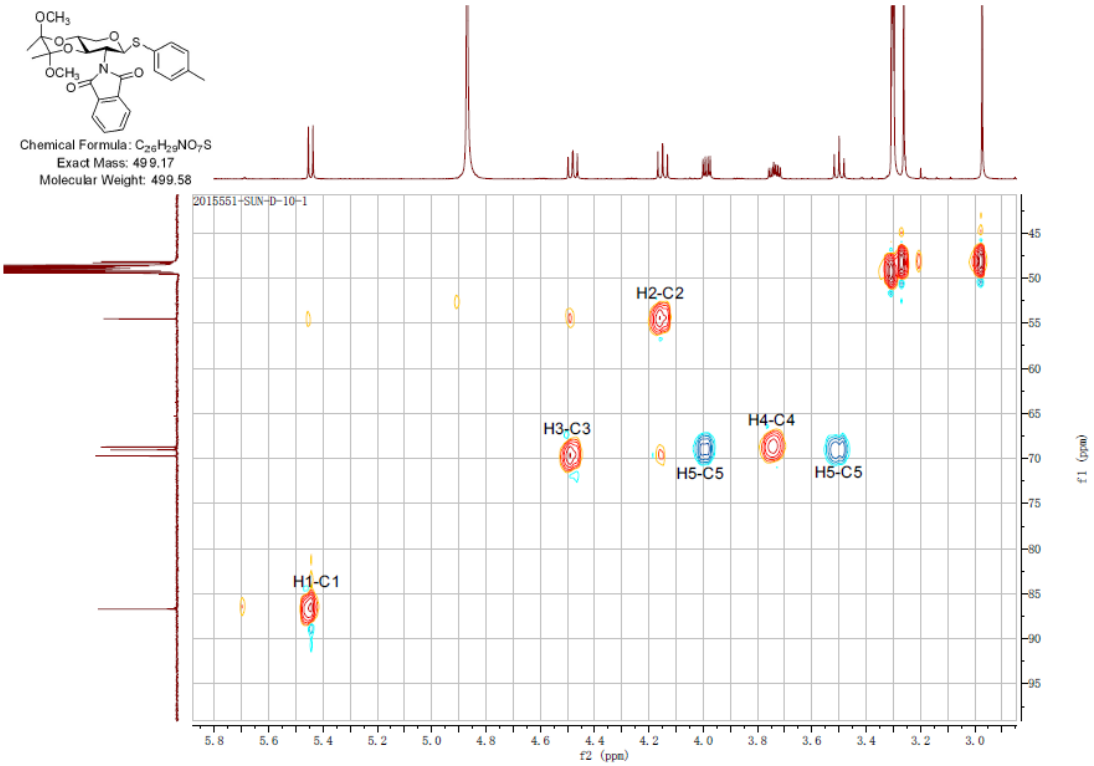
Compound **16 β**: ^{13}C NMR



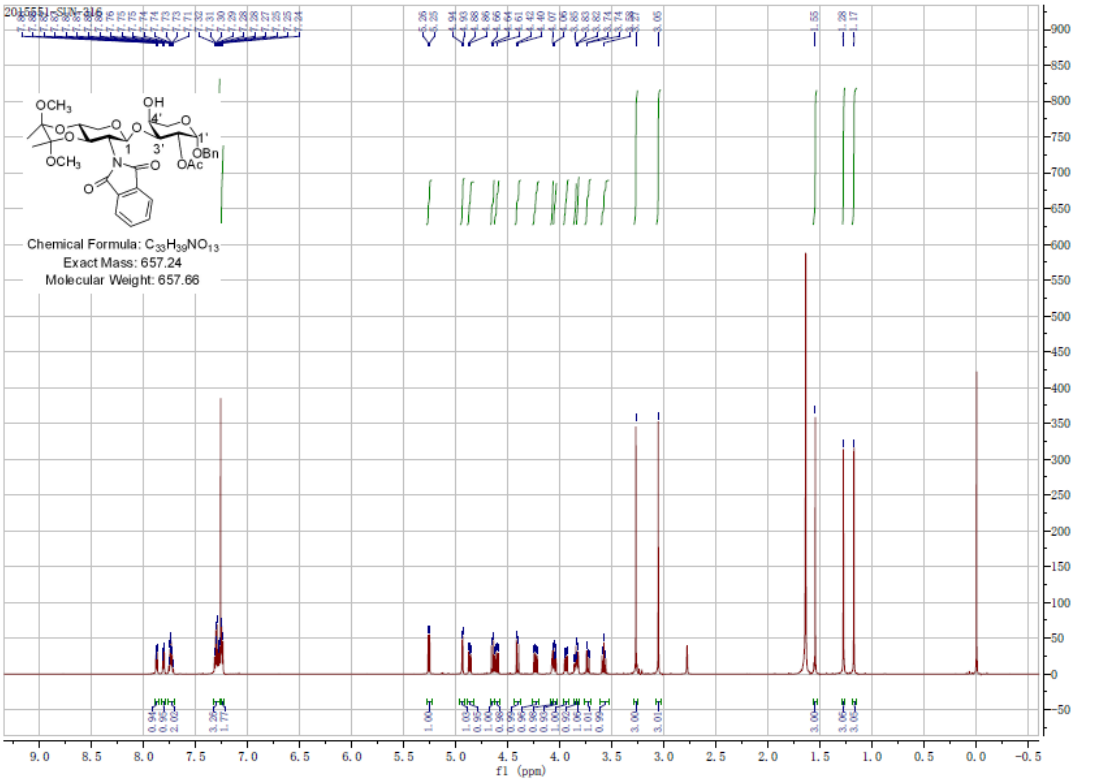
Compound **16 β**: COSY NMR



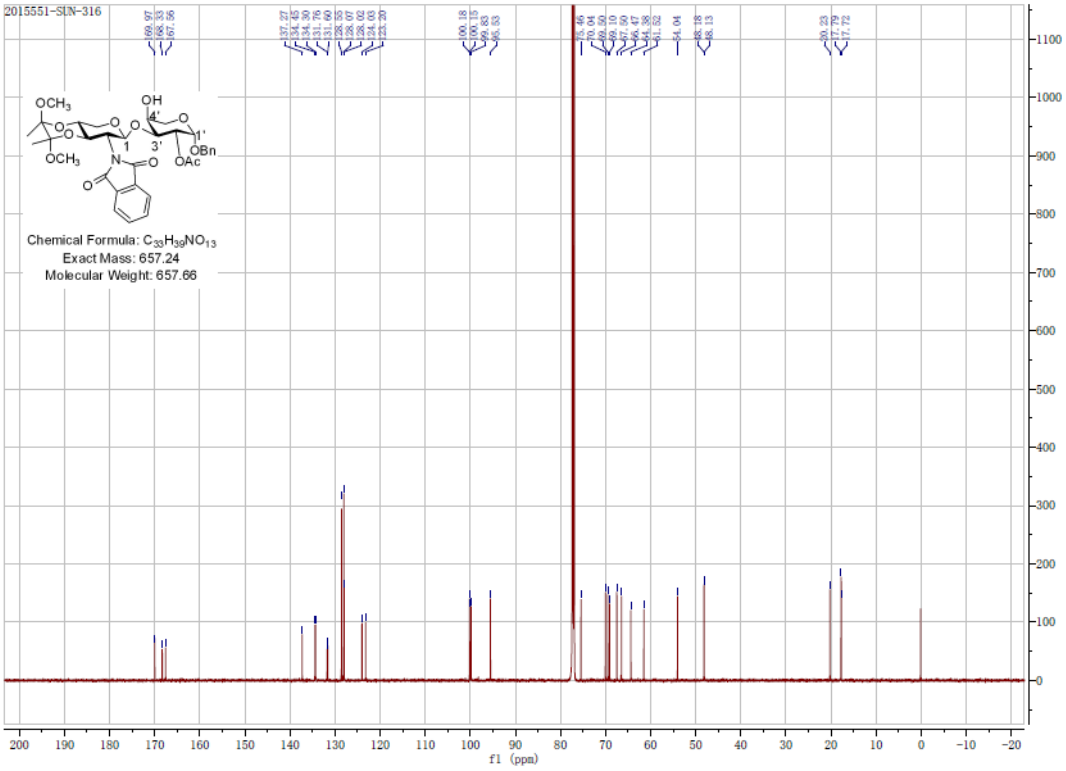
Compound **16 β**: HSQC NMR



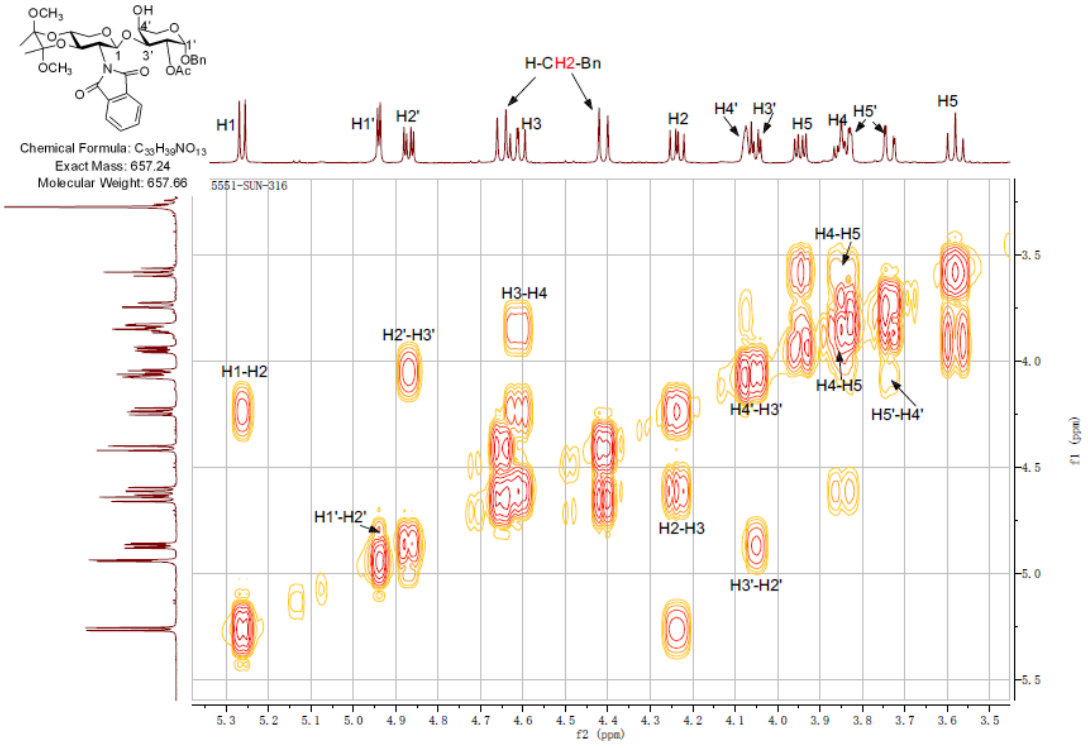
Compound **S4**: ^{1}H NMR



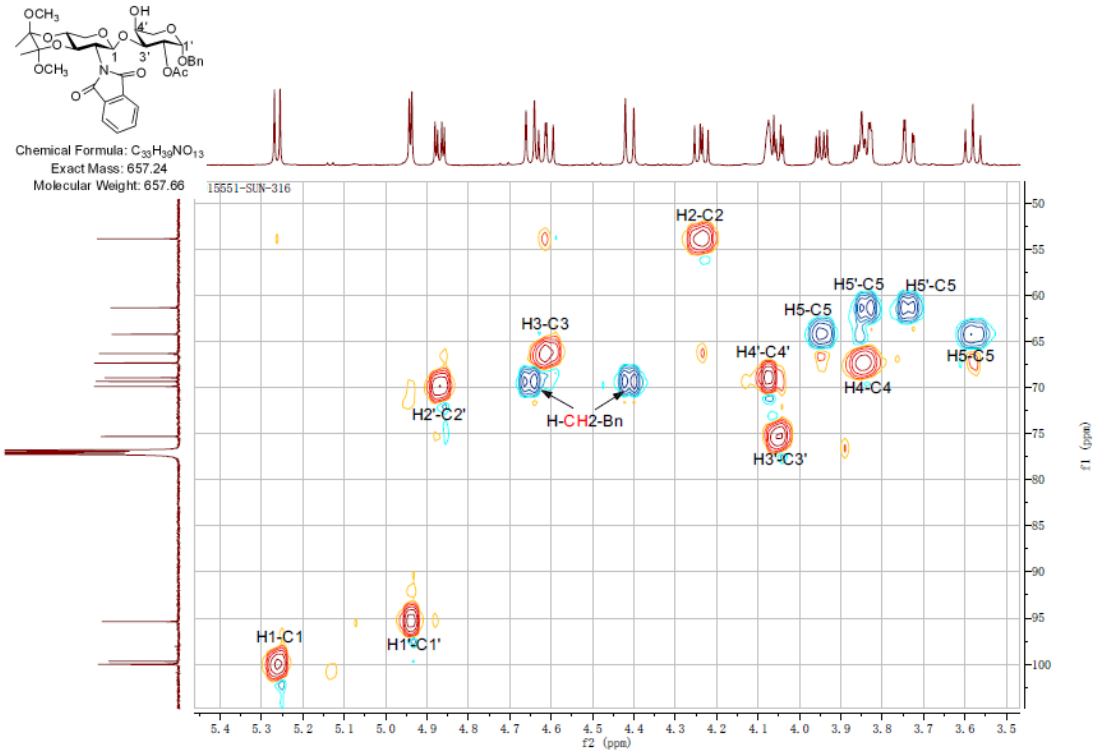
Compound **S4**: ^{13}C NMR



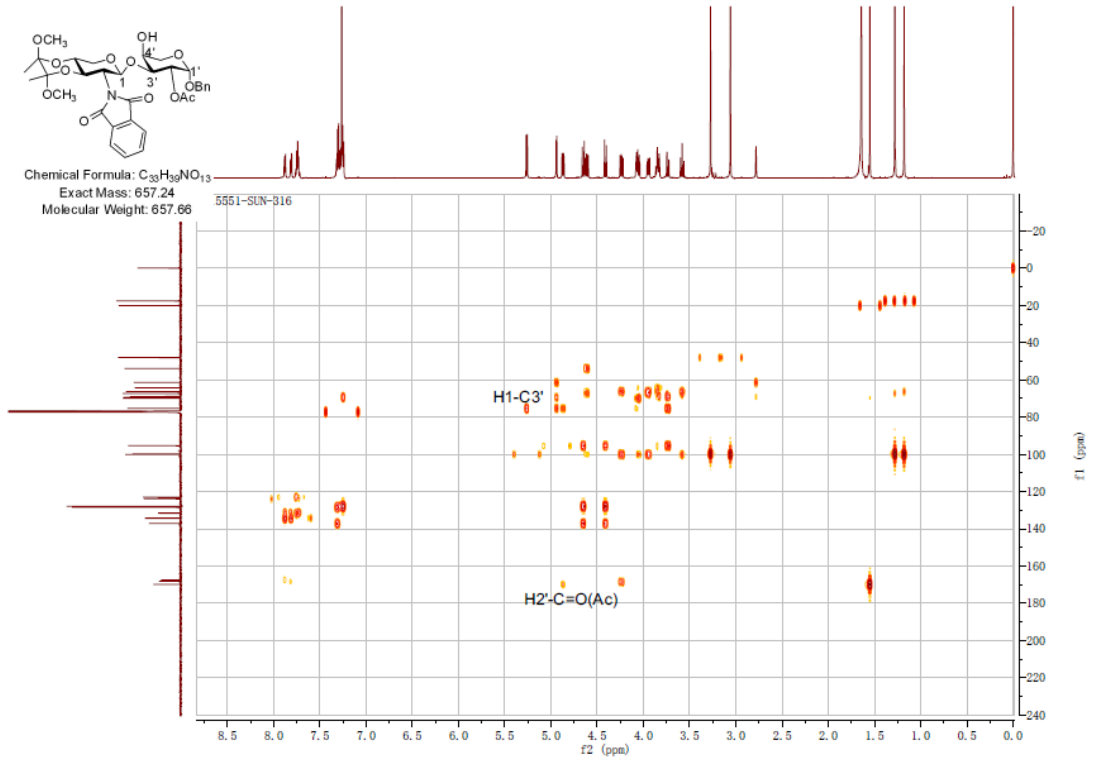
Compound **S4**: COSY NMR



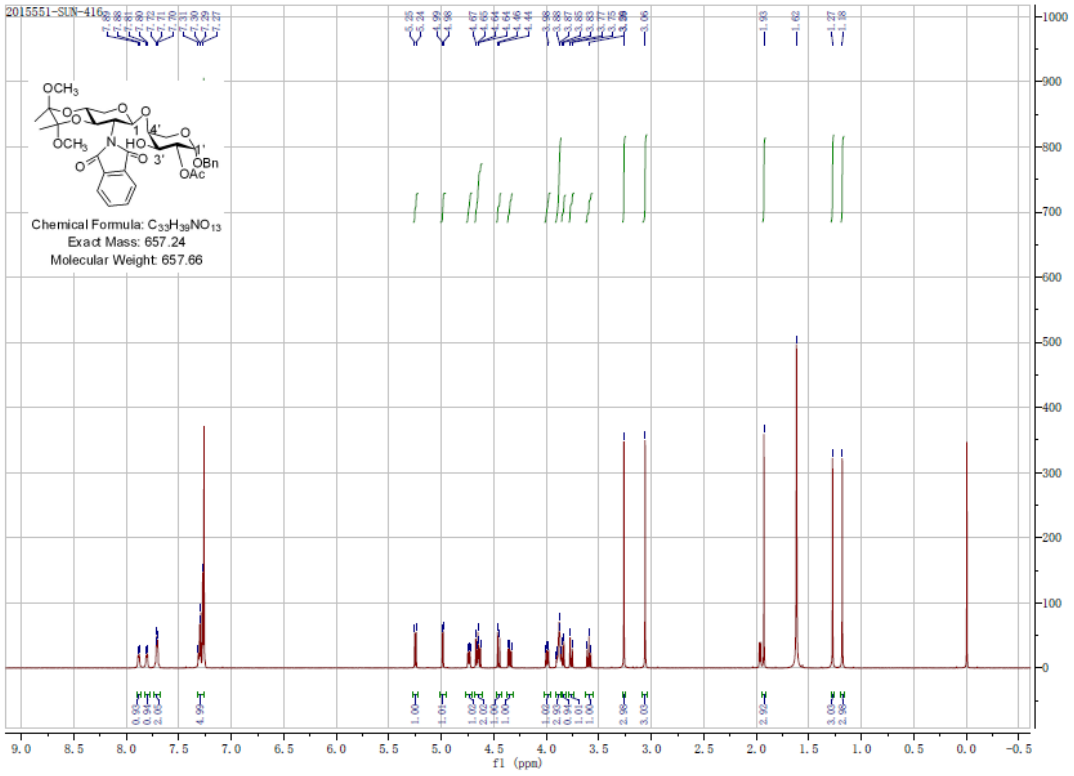
Compound **S4**: HSQC NMR



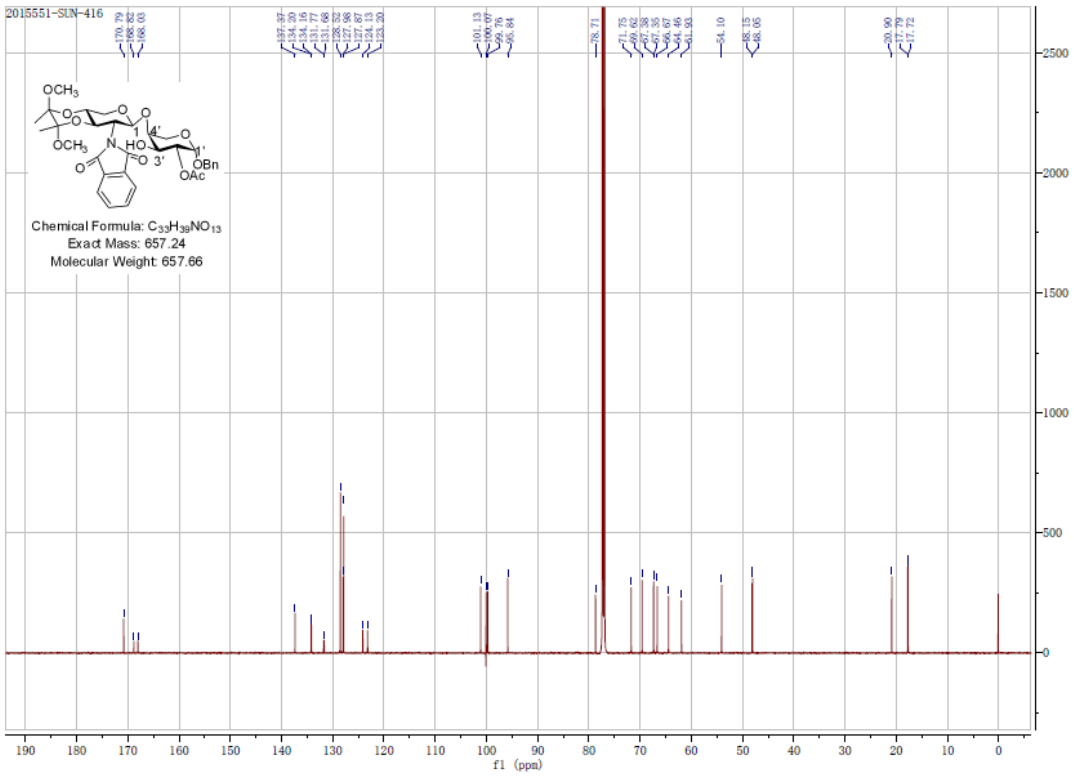
Compound **S4**: HMBC NMR



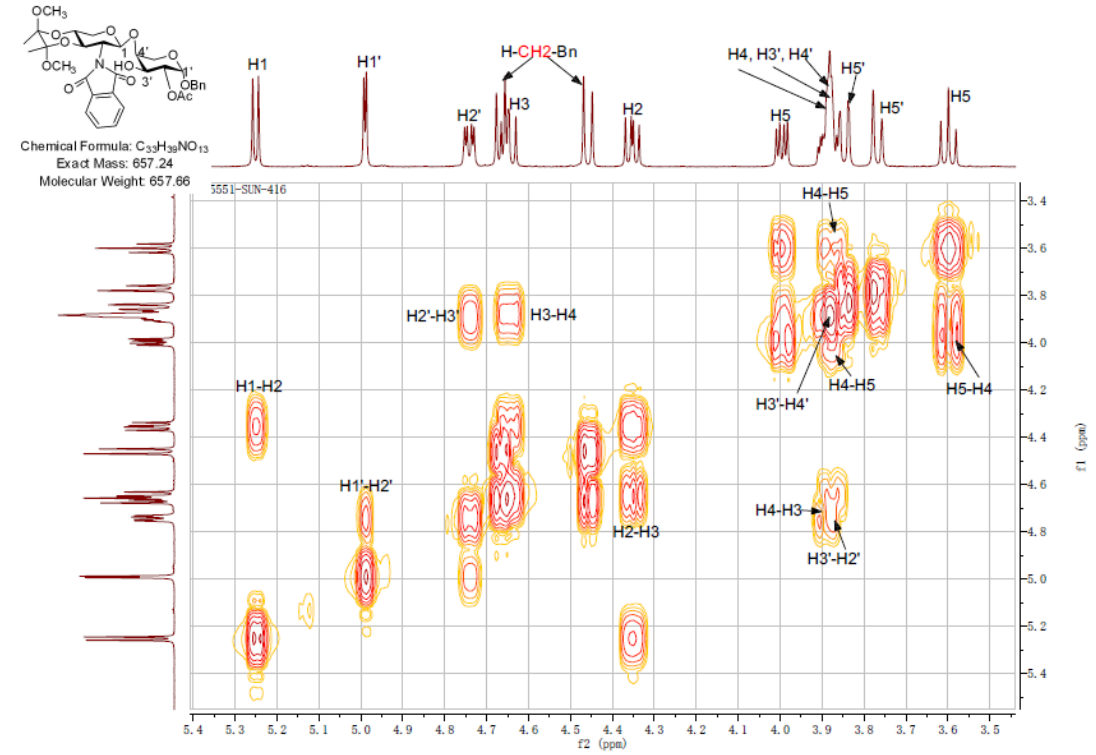
Compound **S5**: ^{1}H NMR



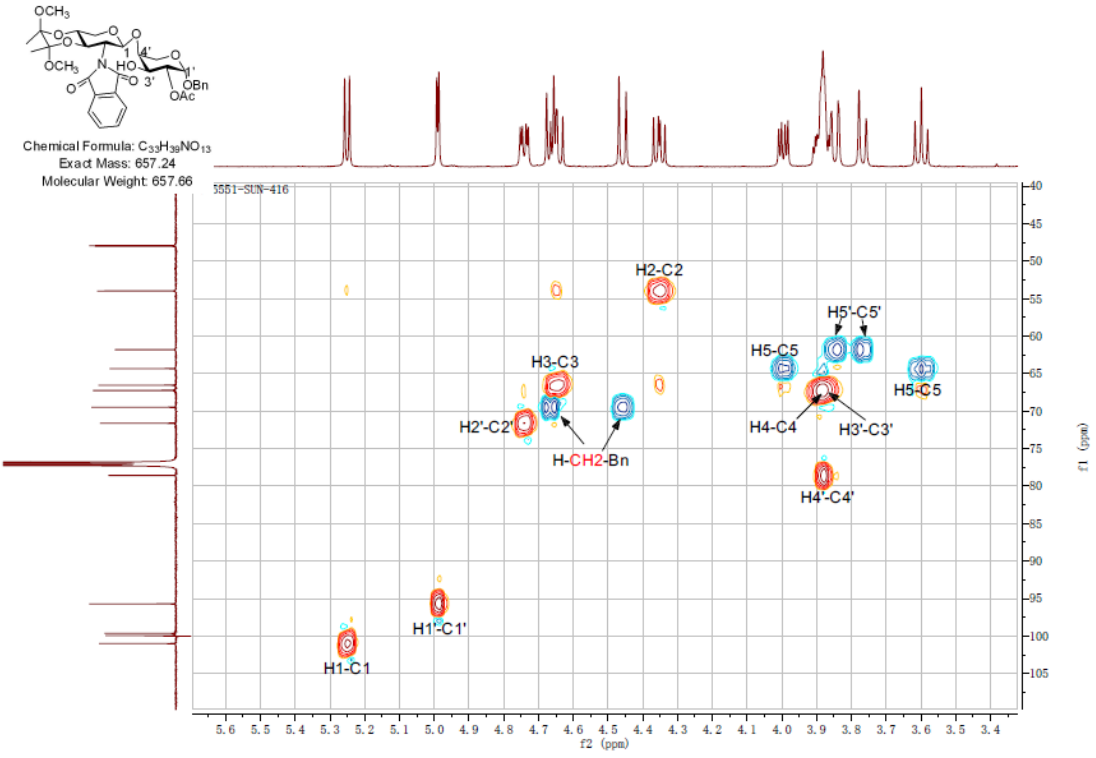
Compound **S5**: ^{13}C NMR



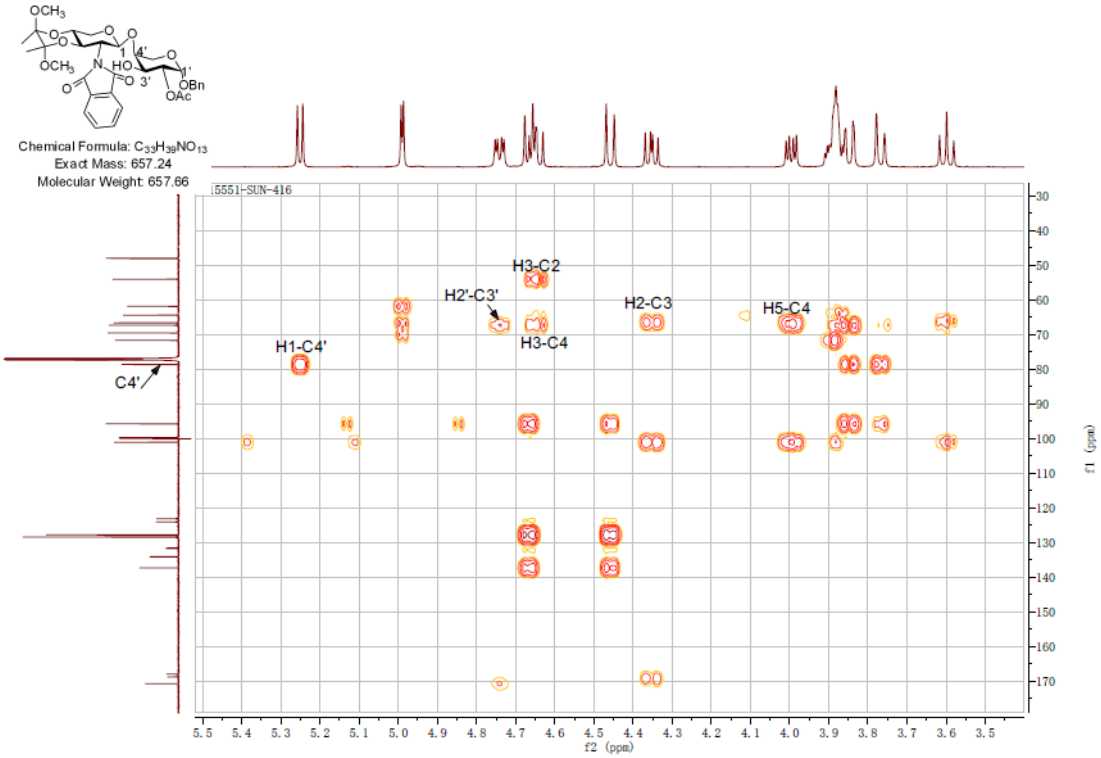
Compound **S5**: COSY NMR



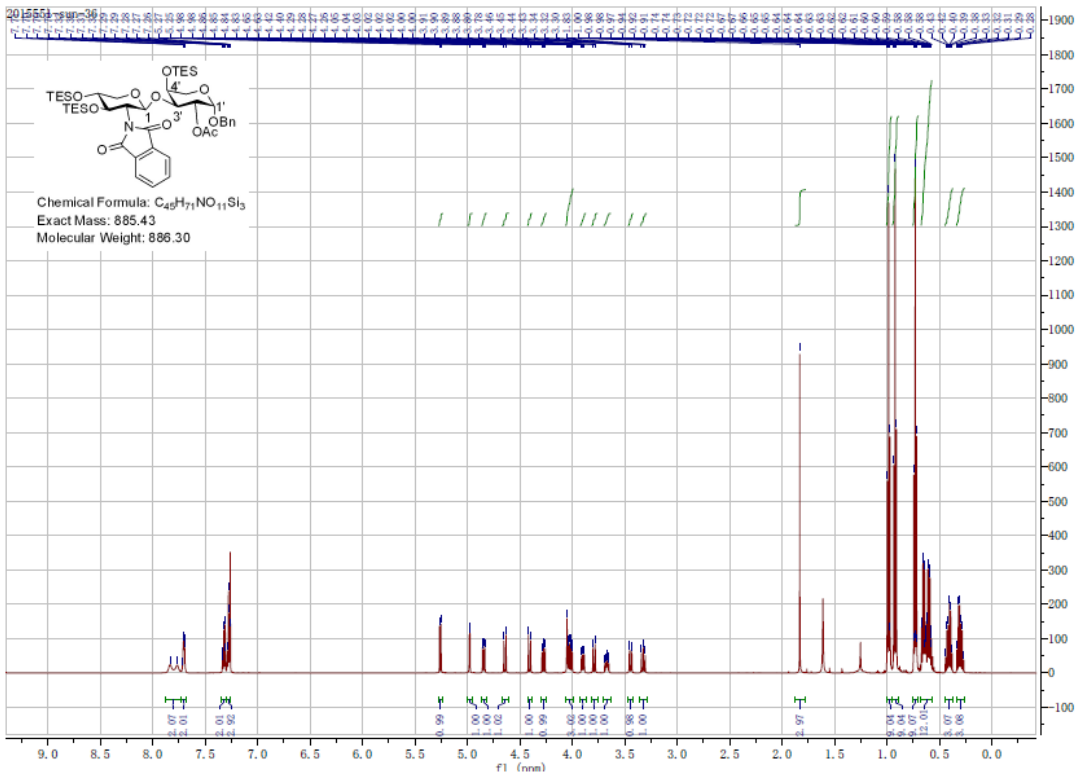
Compound **S5**: HSQC NMR



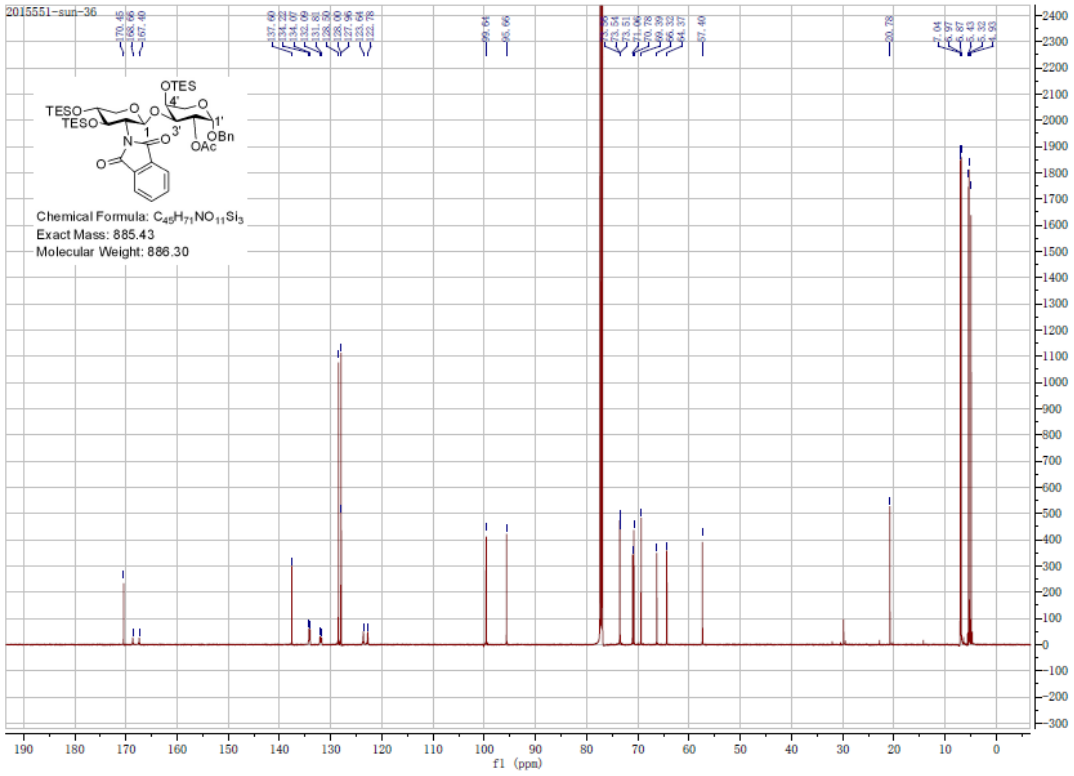
Compound **S5**: HMBC NMR



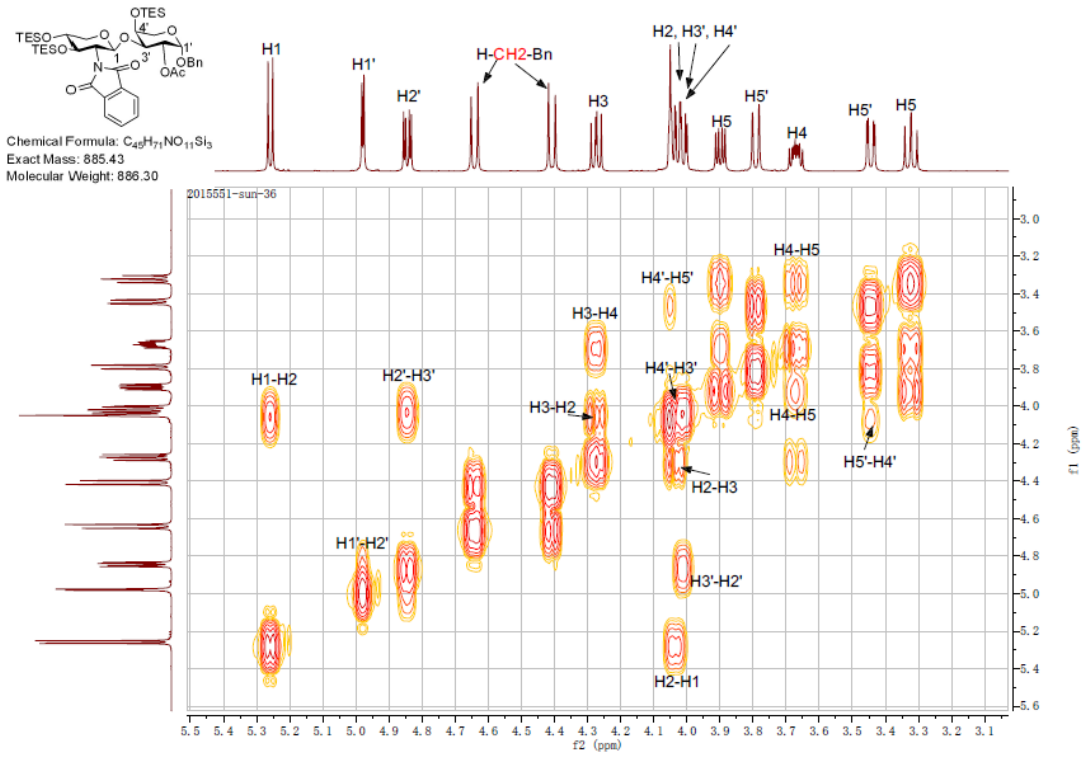
Compound **18**: ^{1}H NMR



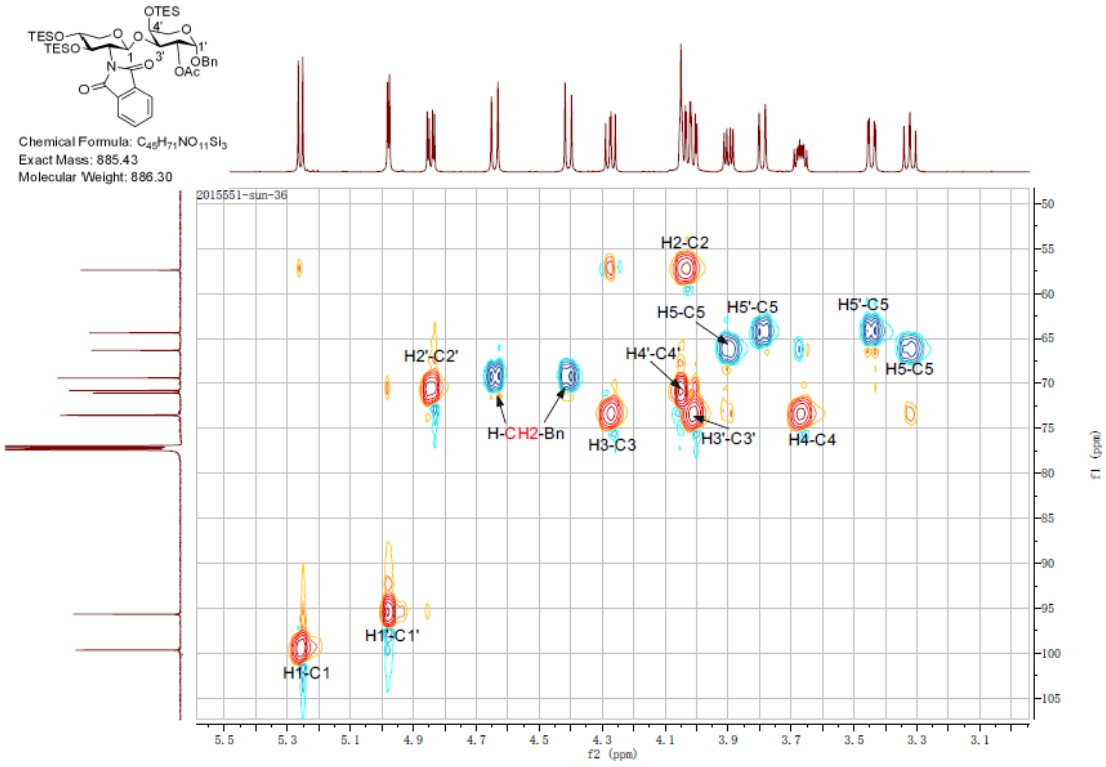
Compound **18**: ^{13}C NMR



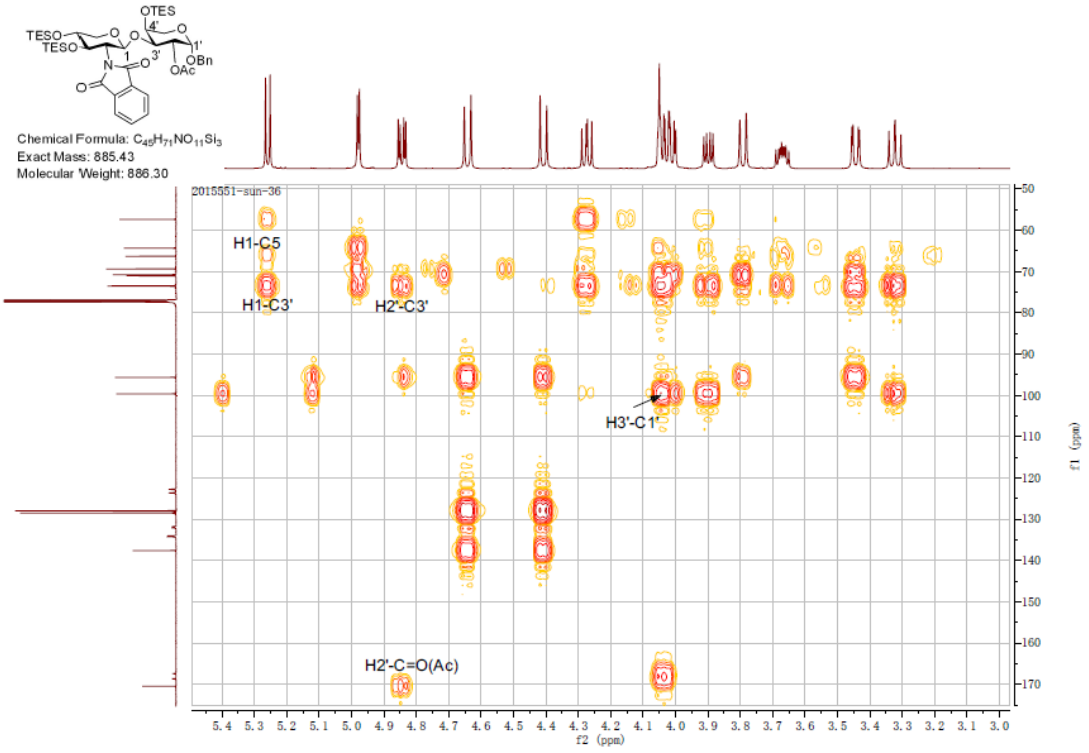
Compound **18**: COSY NMR



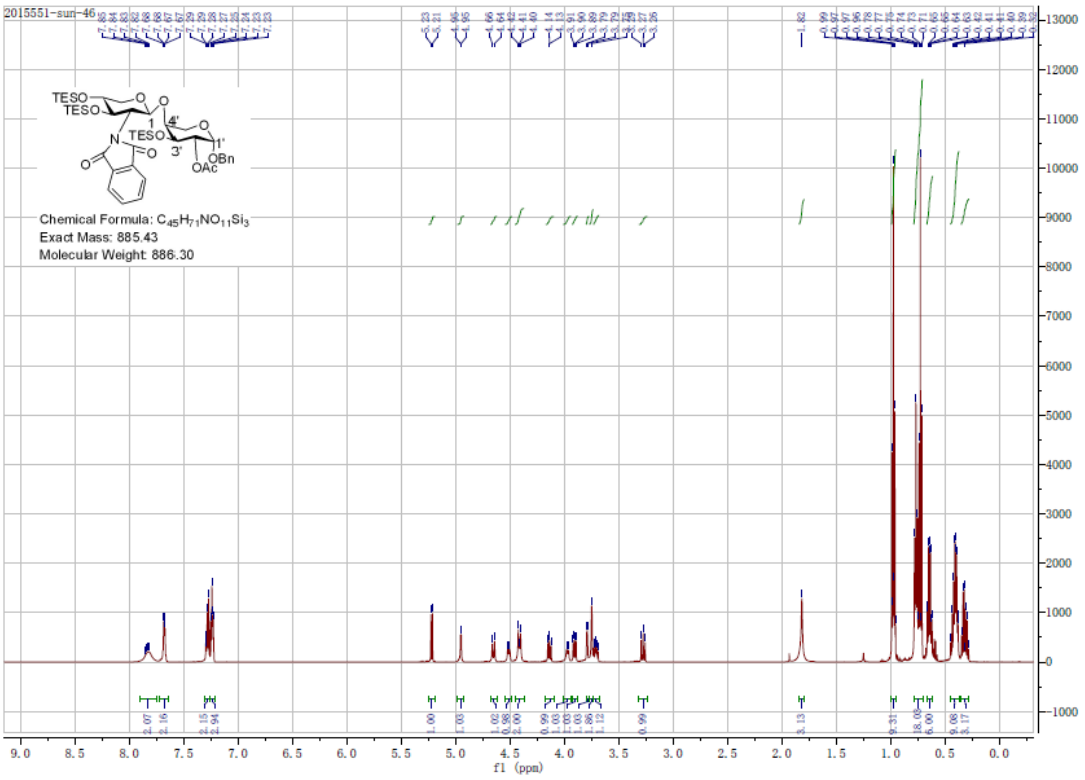
Compound **18**: HSQC NMR



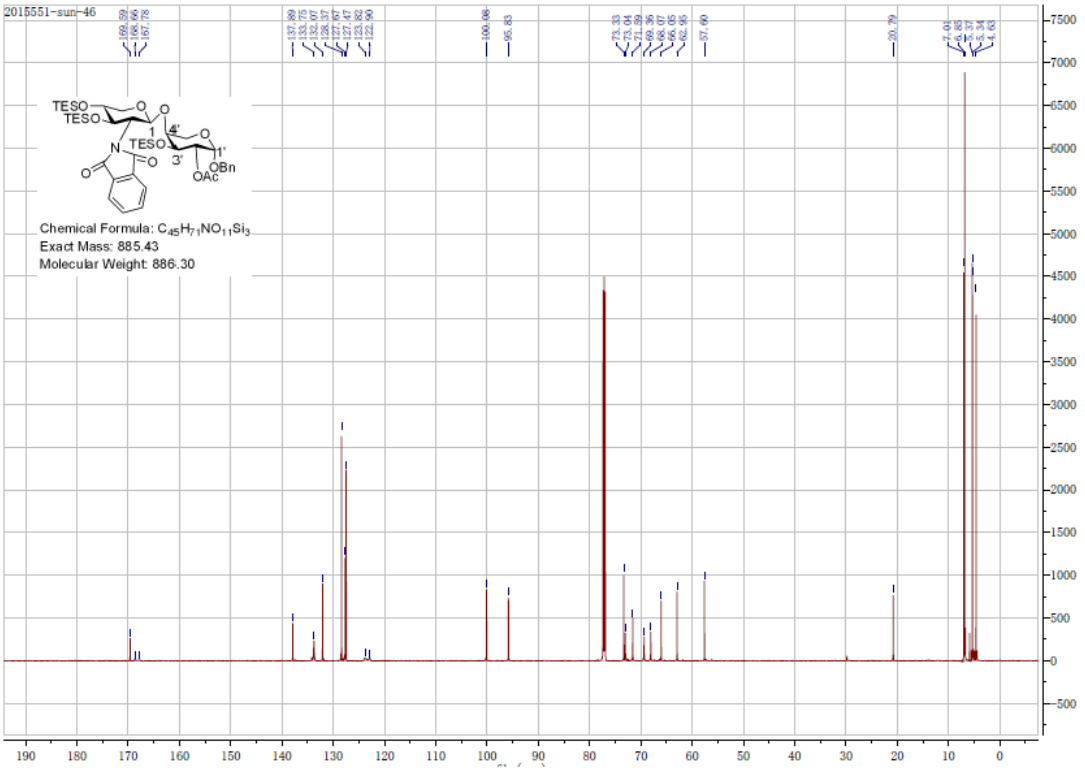
Compound **18**: HMBC NMR



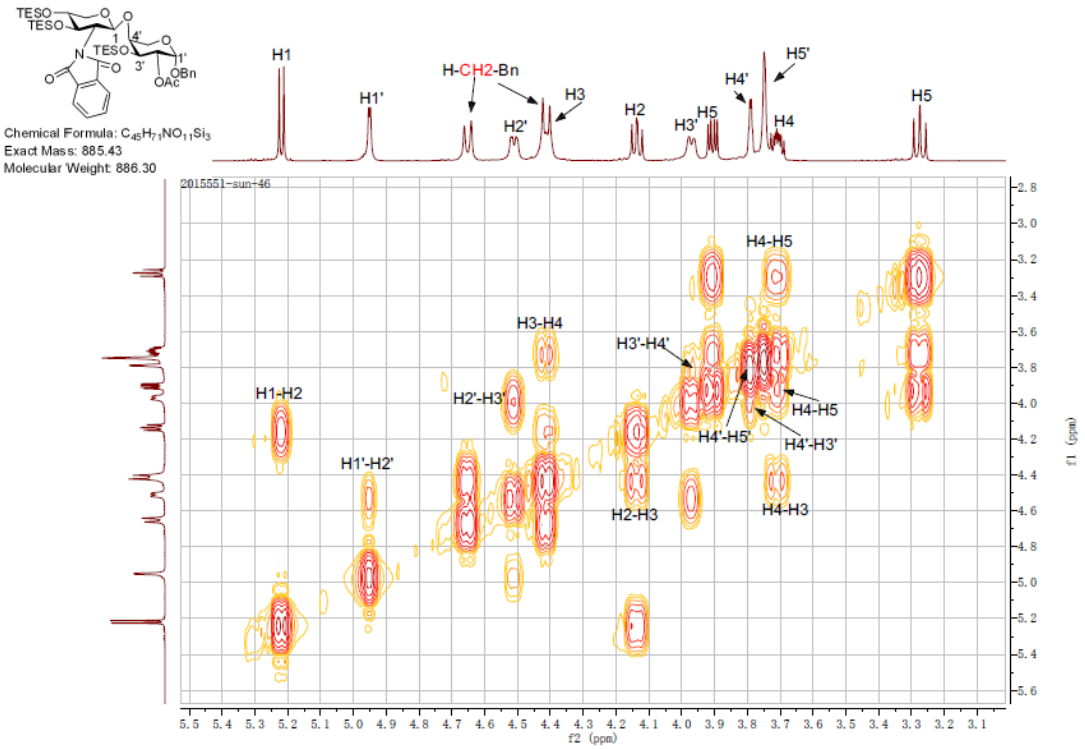
Compound **19**: ^{1}H NMR



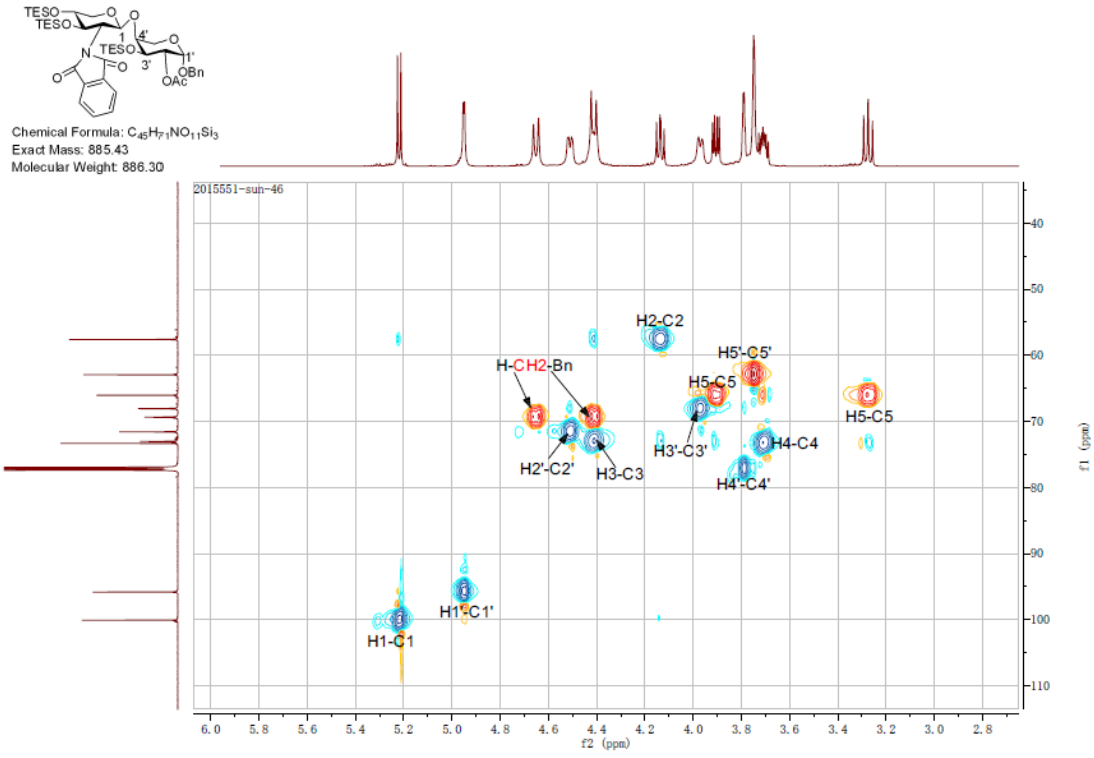
Compound **19**: ^{13}C NMR



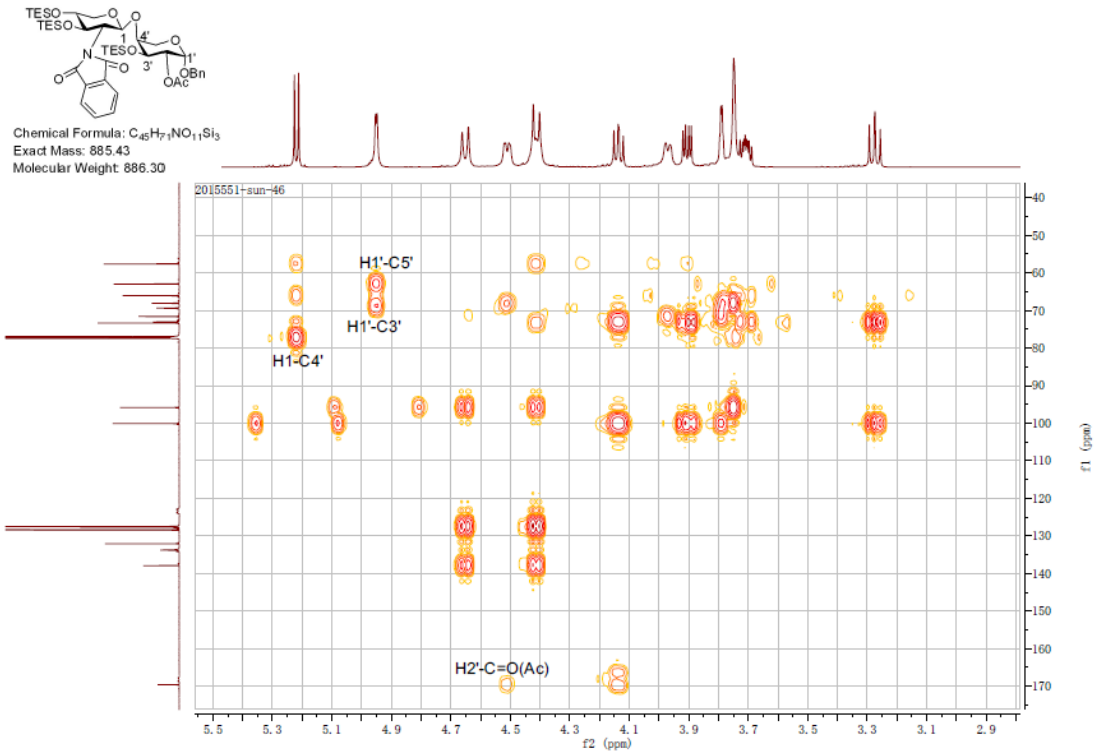
Compound **19**: COSY NMR



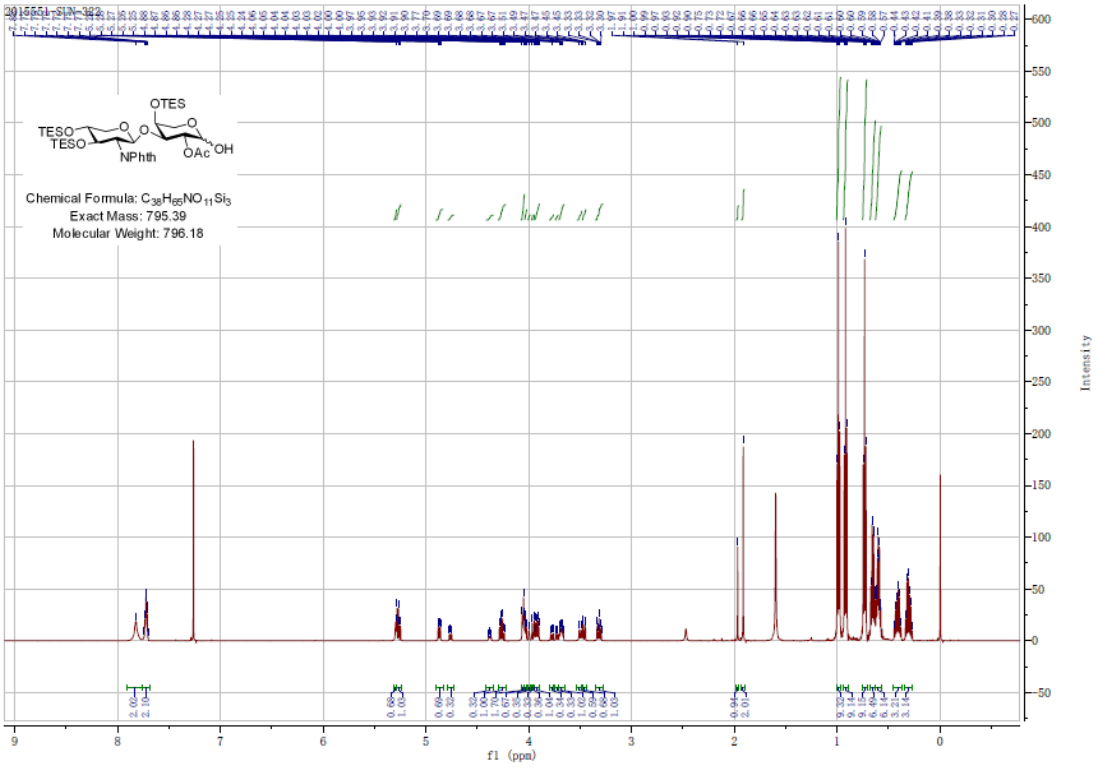
Compound **19**: HSQC NMR



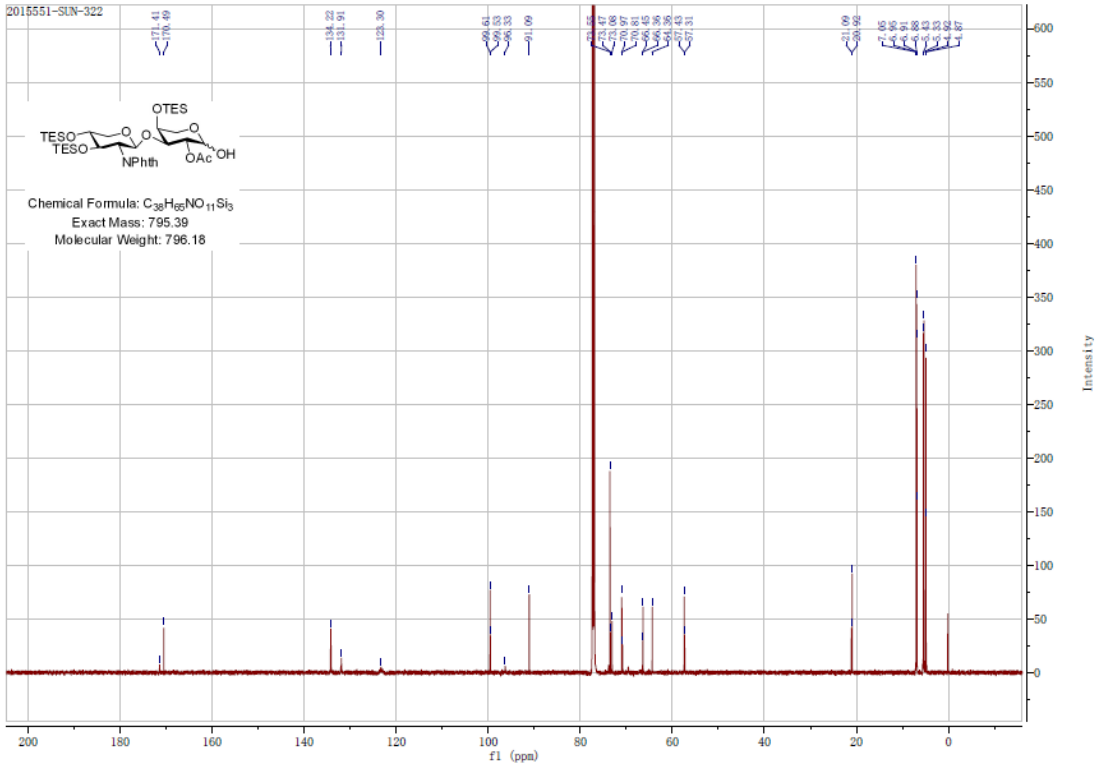
Compound **19**: HMBC NMR



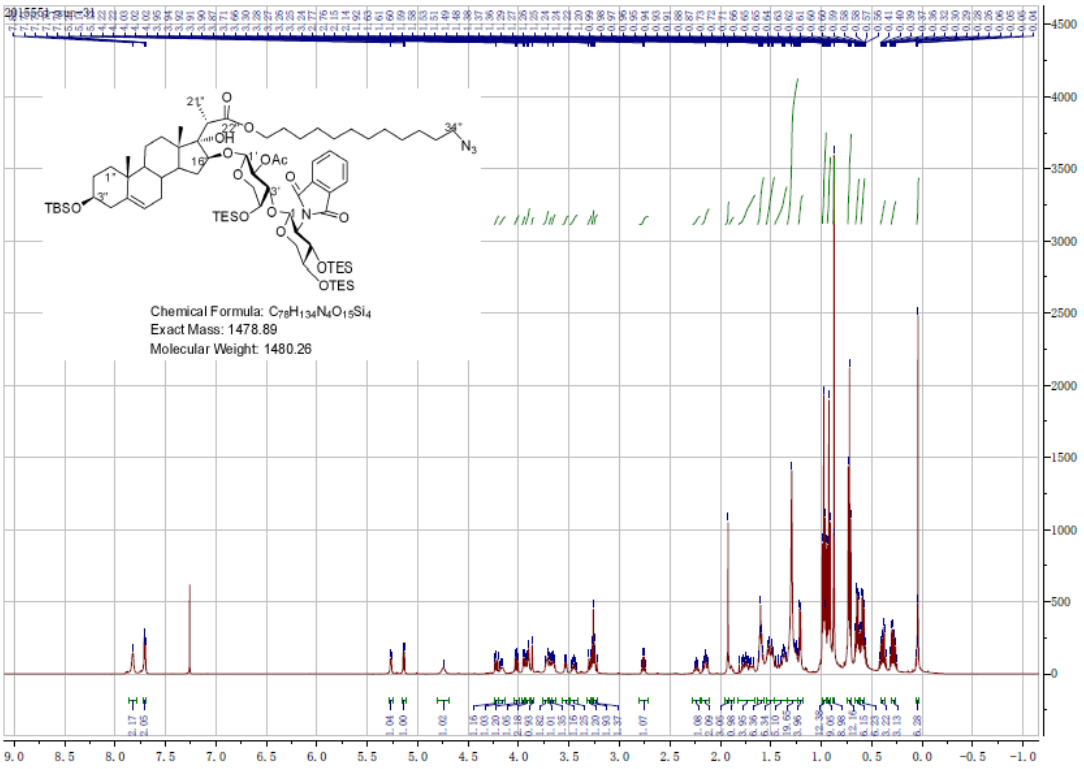
Compound **20**: ^{1}H NMR



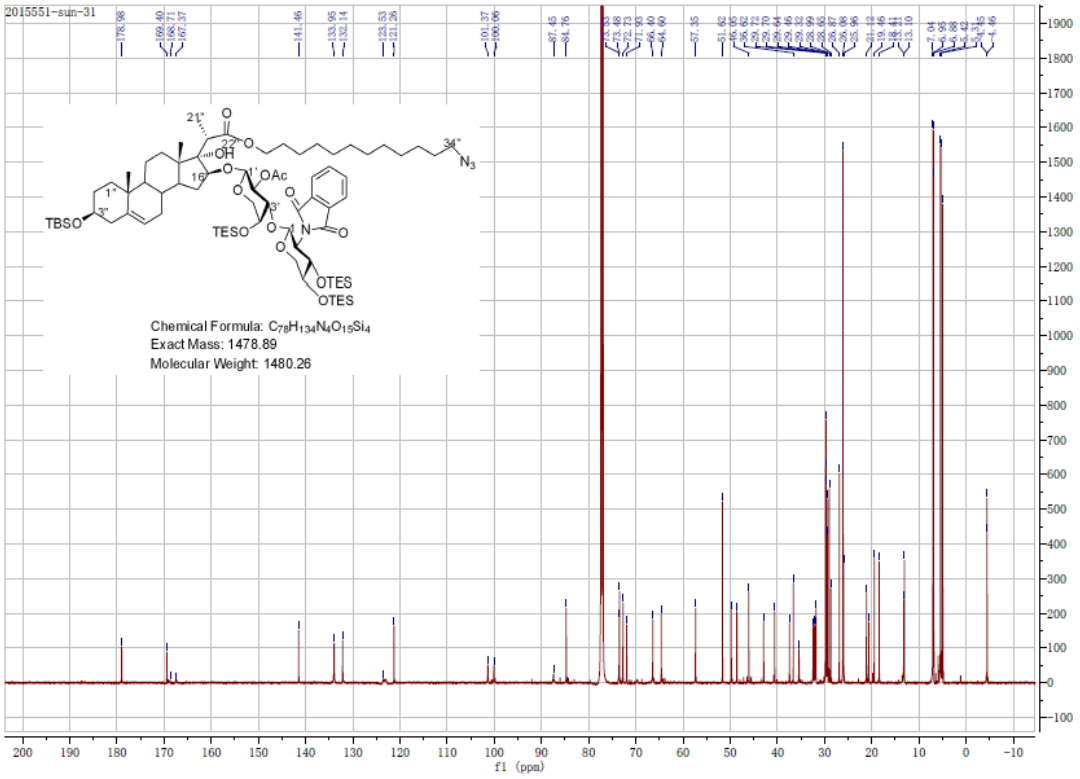
Compound **20**: ^{13}C NMR



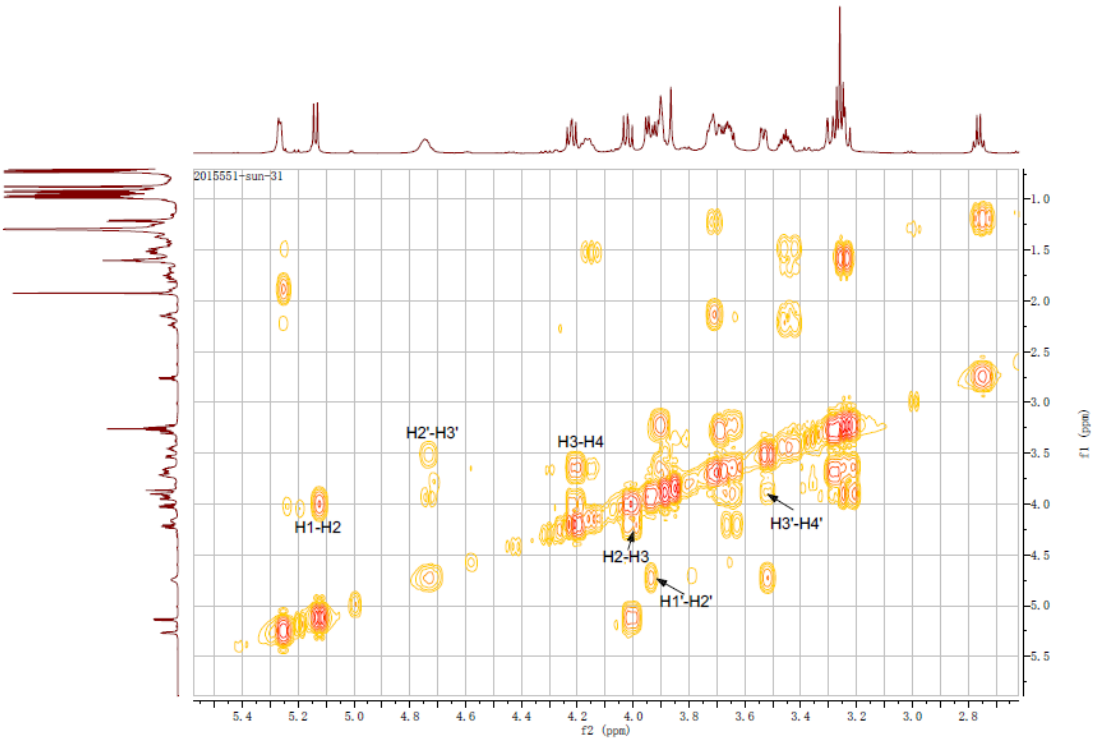
Compound **22**: ^{1}H NMR



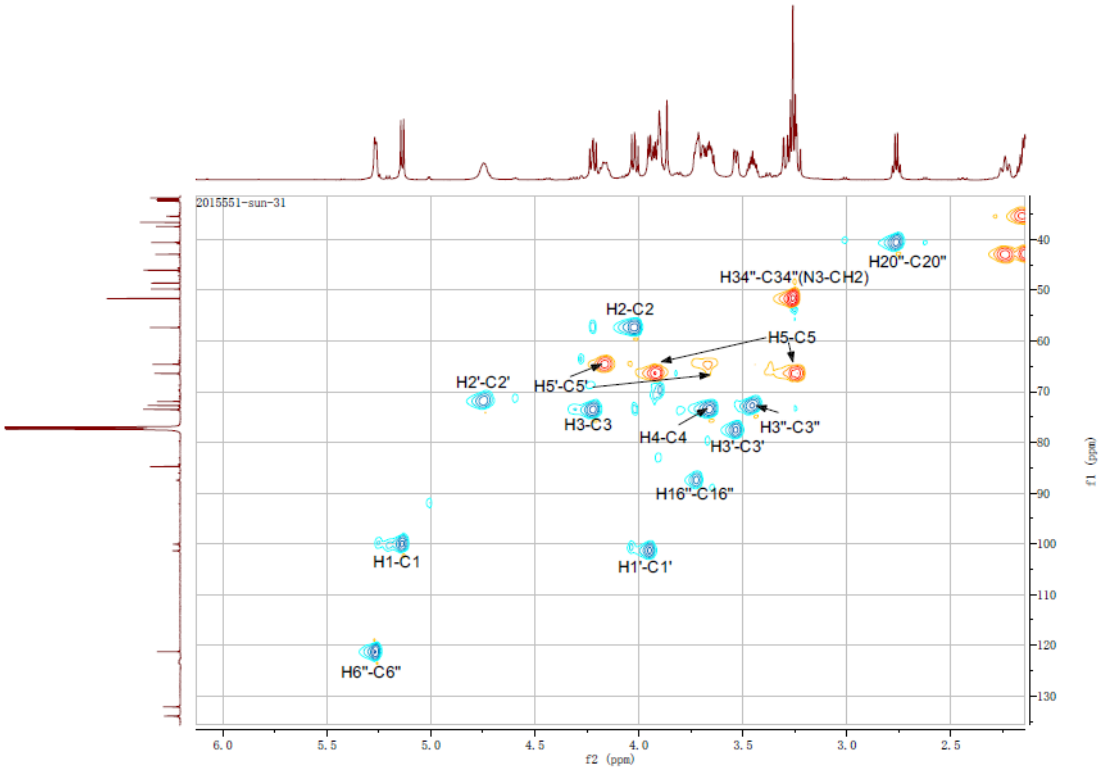
Compound **22**: ^{13}C NMR



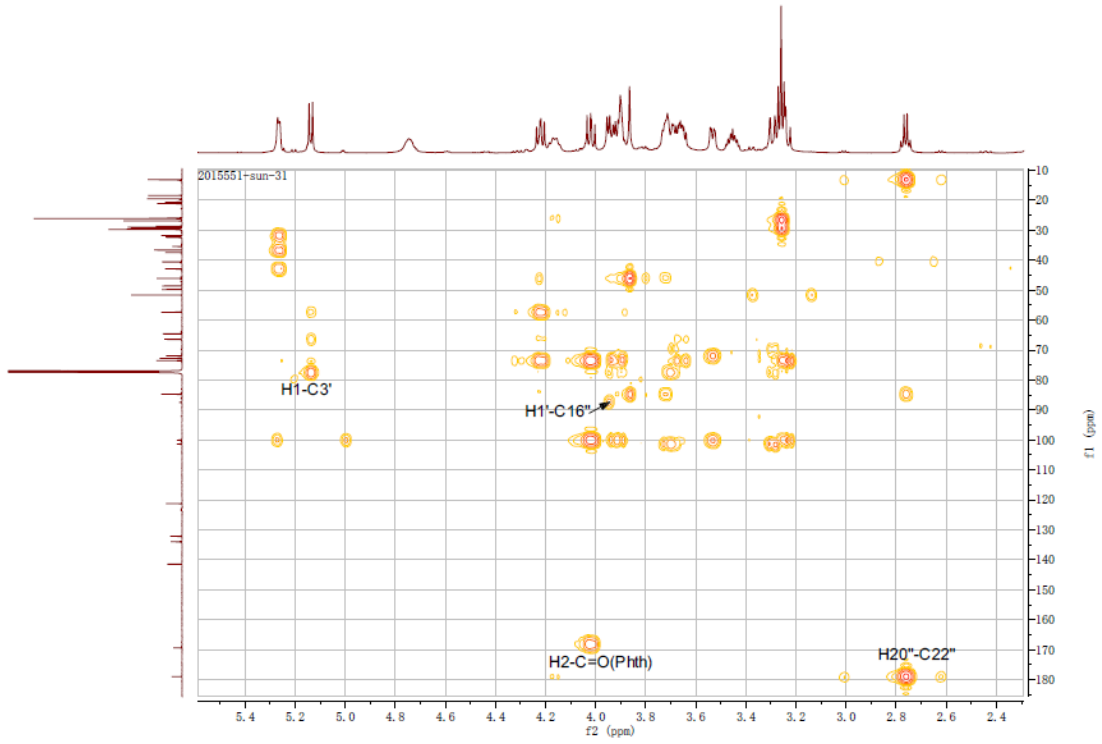
Compound **22**: COSY NMR



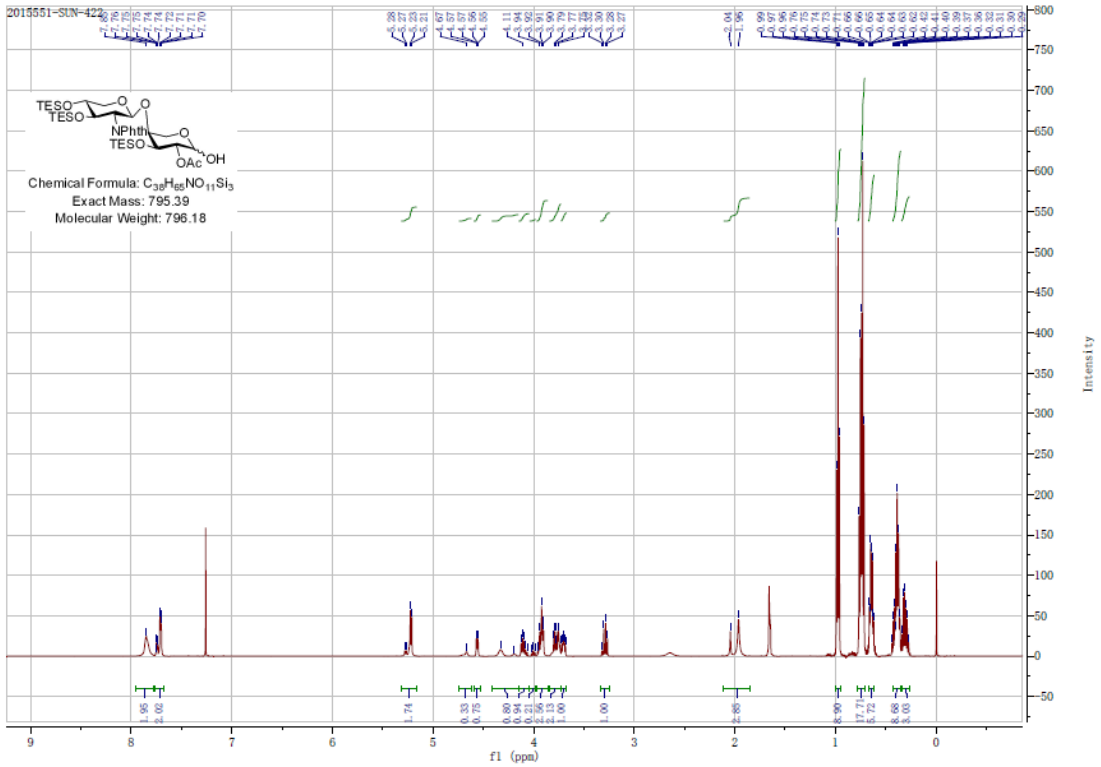
Compound **22**: HSQC NMR



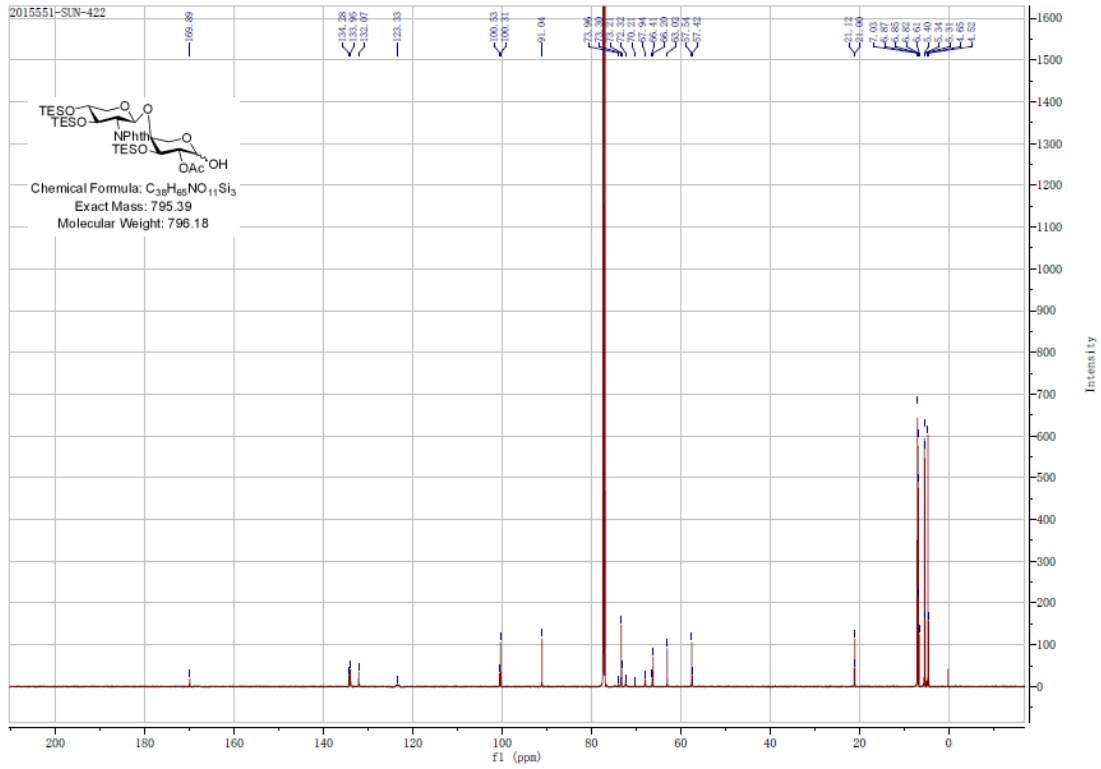
Compound **22**: HMBC NMR



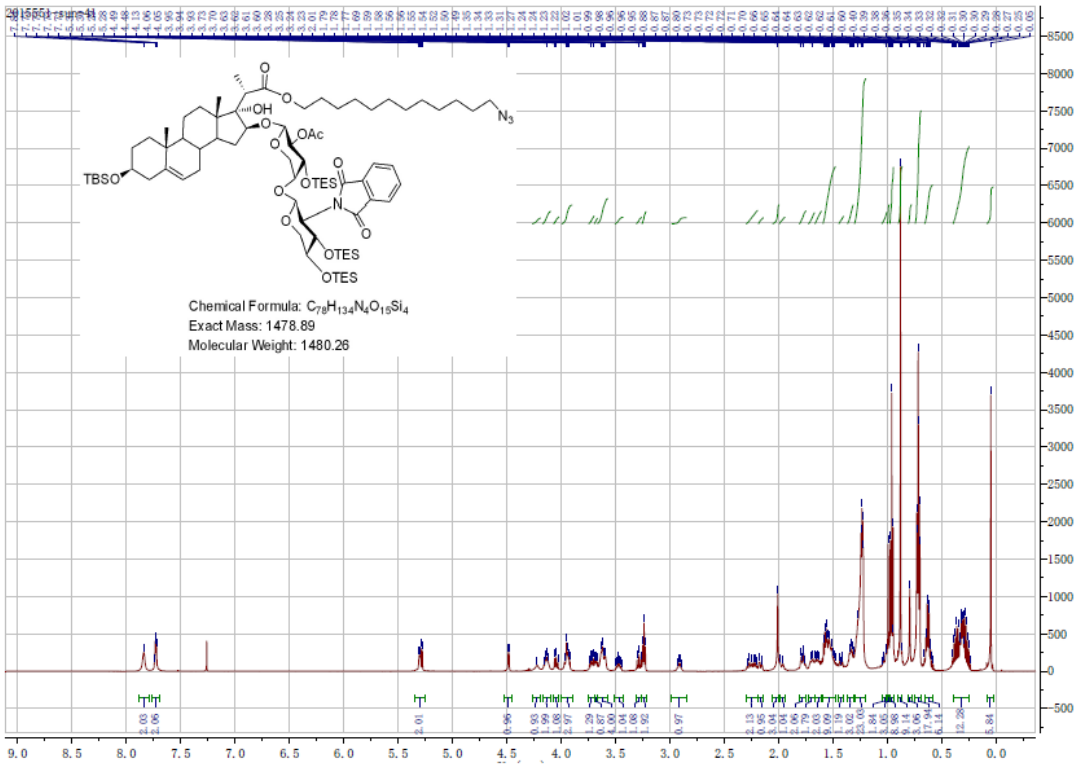
Compound **S6**: ^{1}H NMR



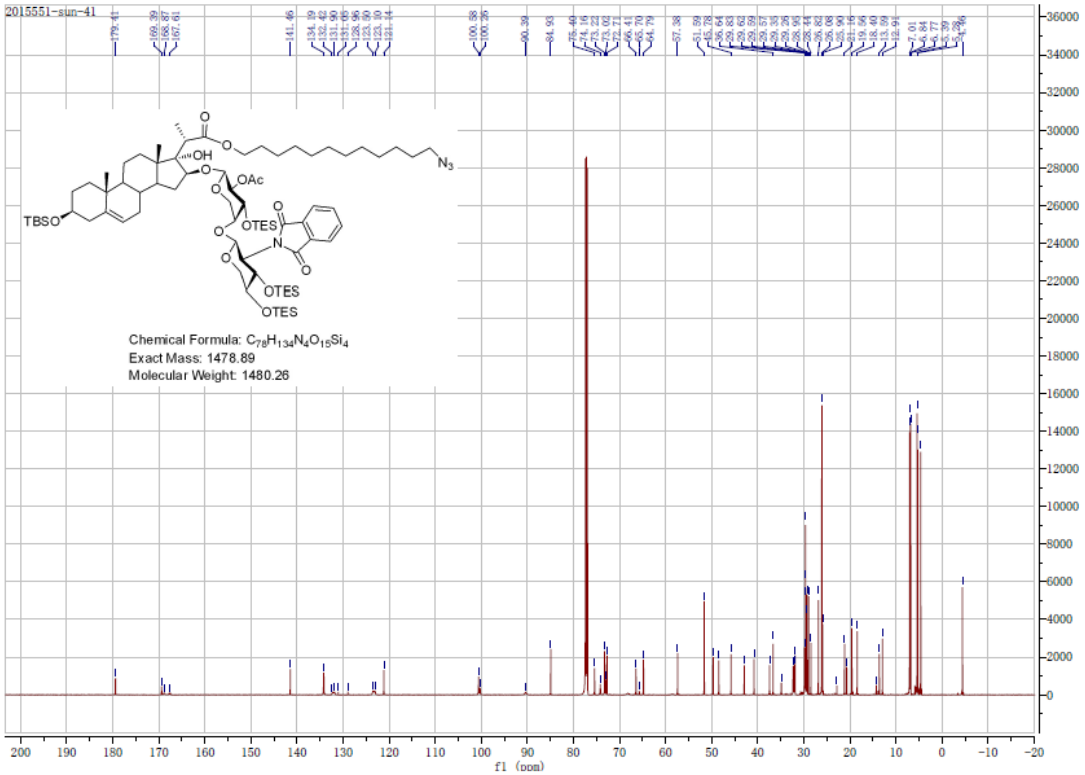
Compound **S6**: ^{13}C NMR



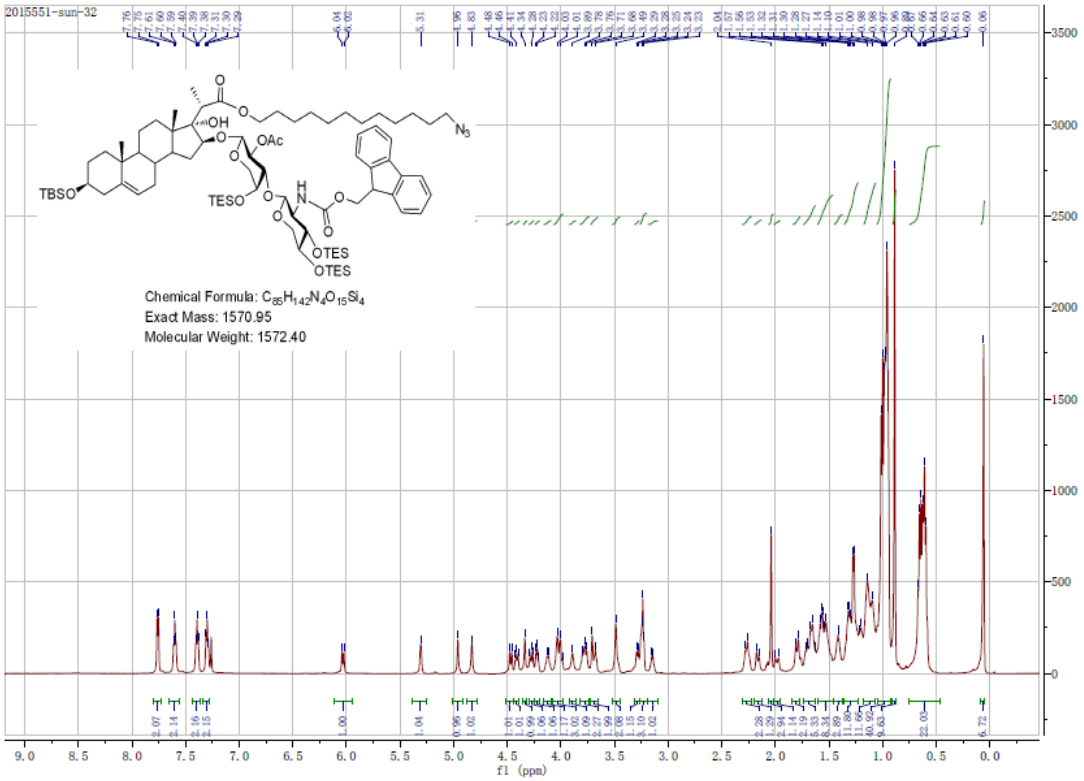
Compound **S8**: ^{1}H NMR



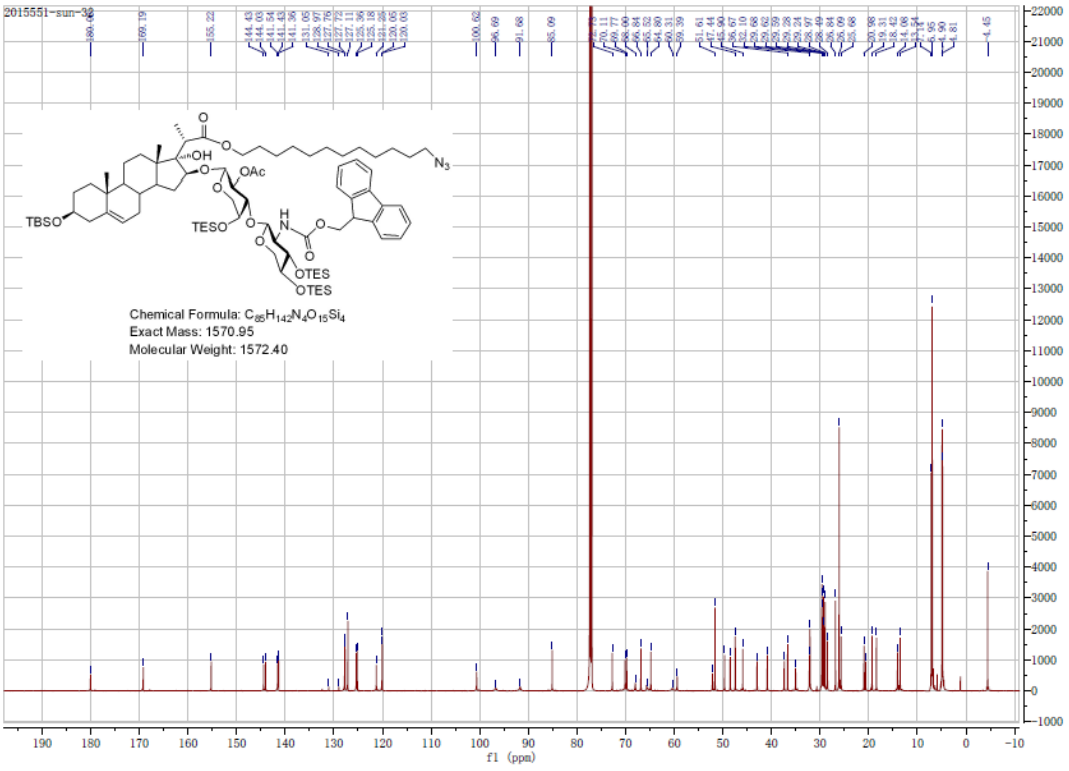
Compound **S8**: ^{13}C NMR



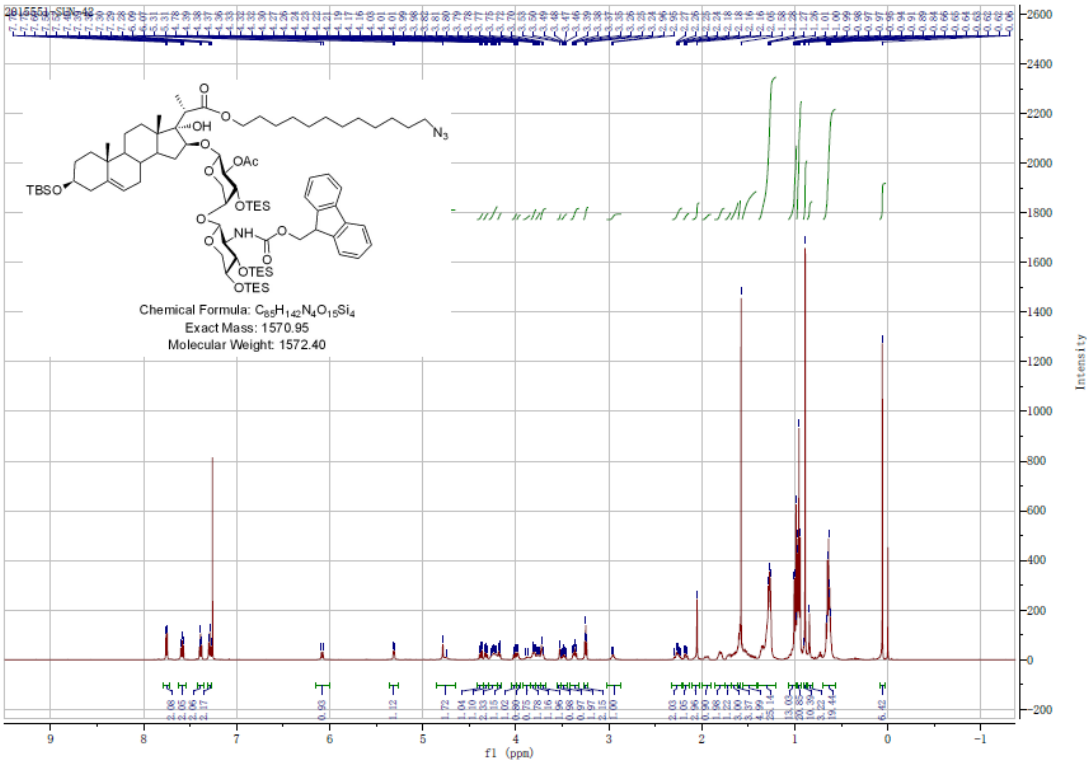
Compound **23**: ^{1}H NMR



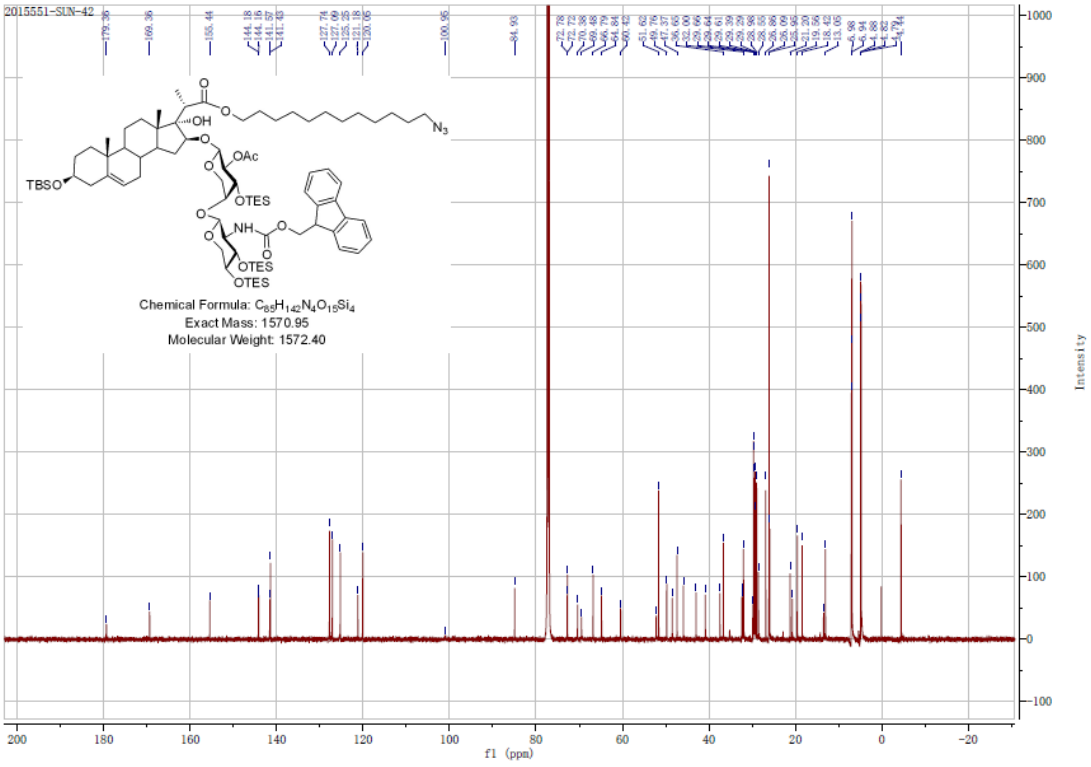
Compound **23**: ^{13}C NMR



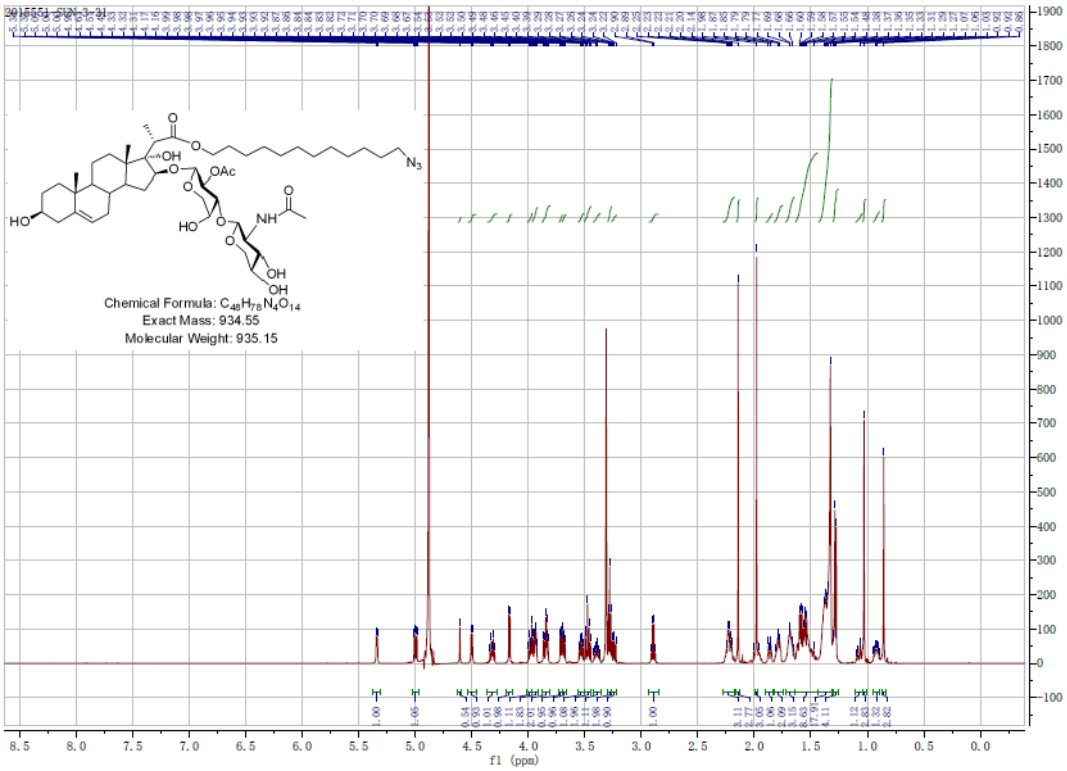
Compound **S9**: ^{1}H NMR



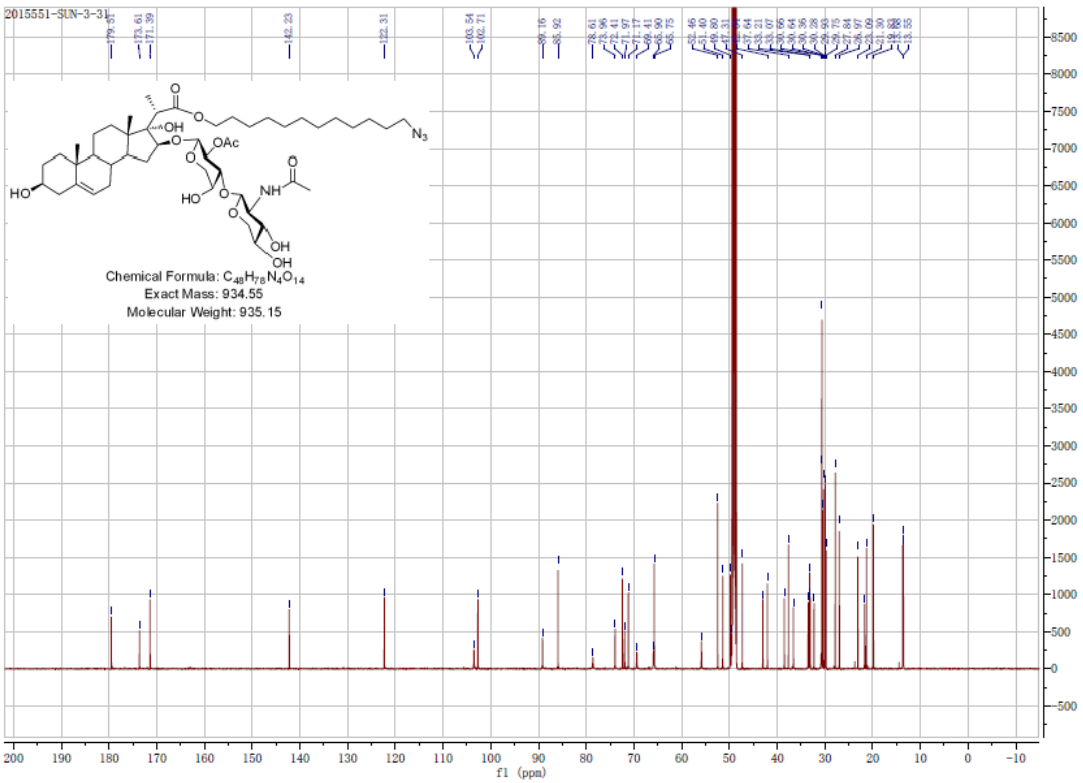
Compound **S9**: ^{13}C NMR



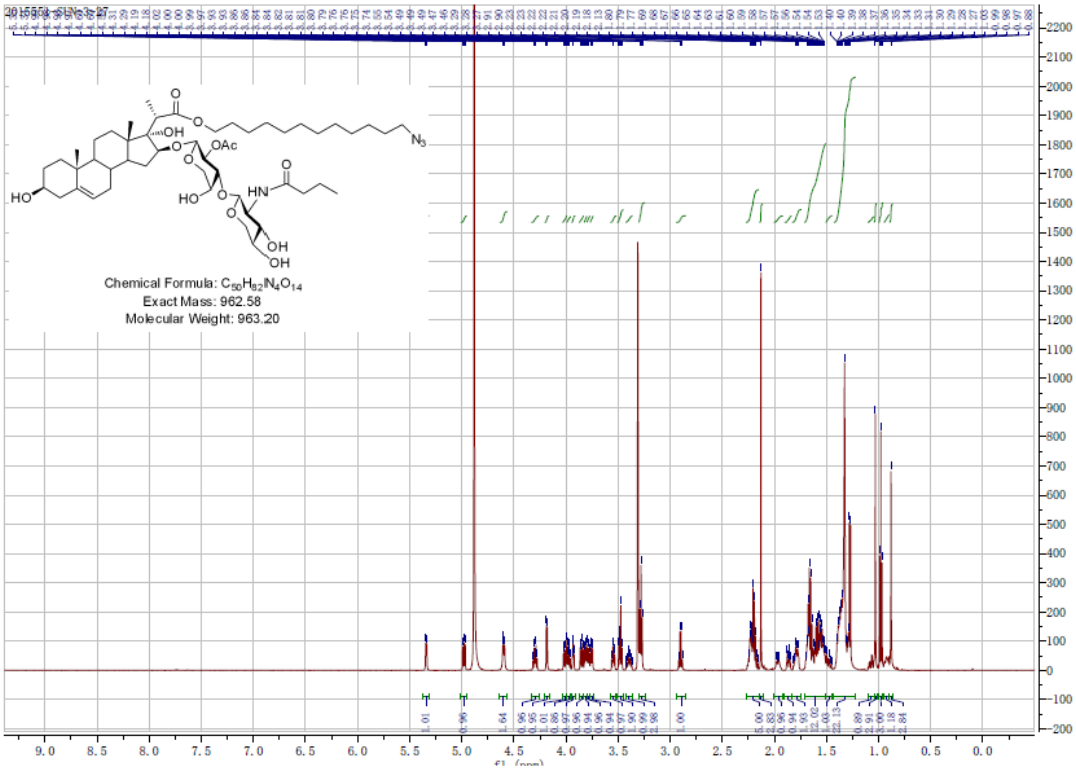
Compound **24**: ^{1}H NMR



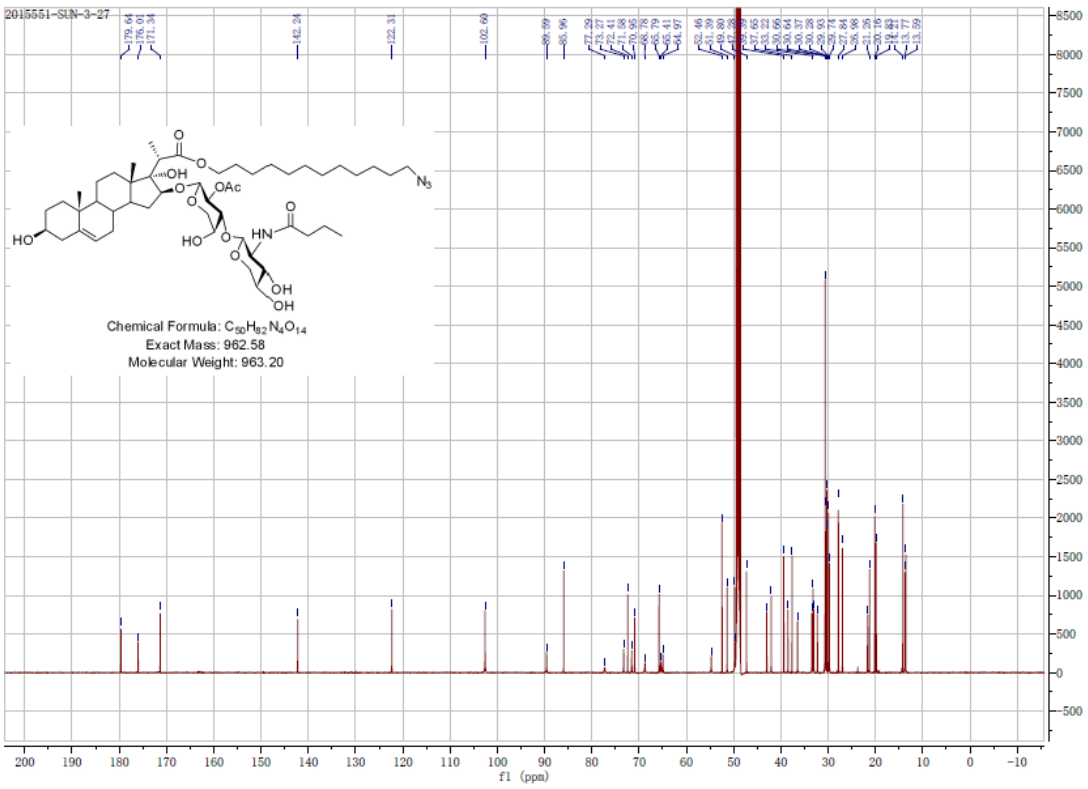
Compound **24**: ^{13}C NMR



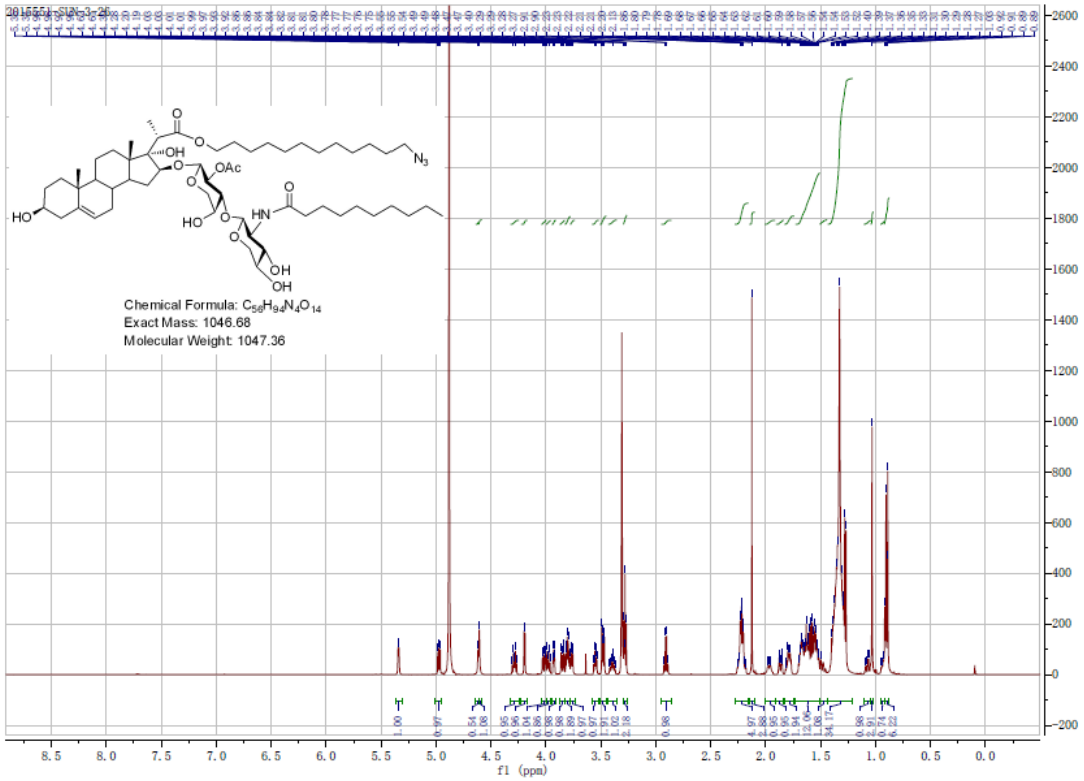
Compound **25**: ^{1}H NMR



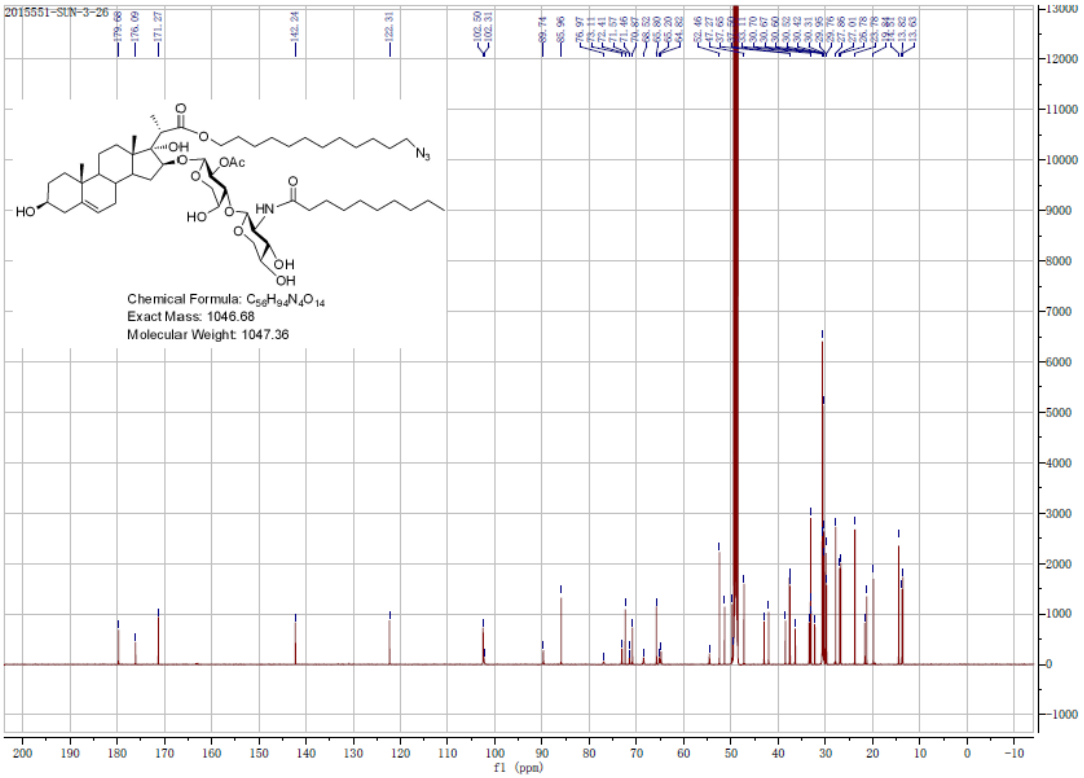
Compound **25**: ^{13}C NMR



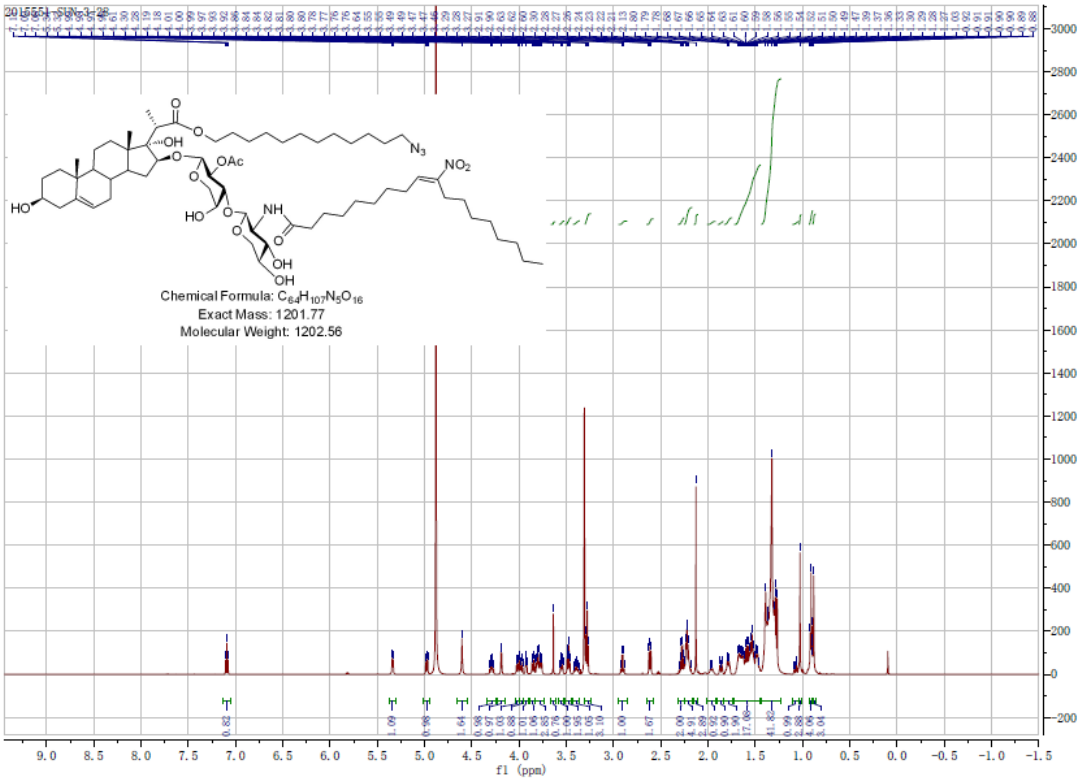
Compound **26**: ^{1}H NMR



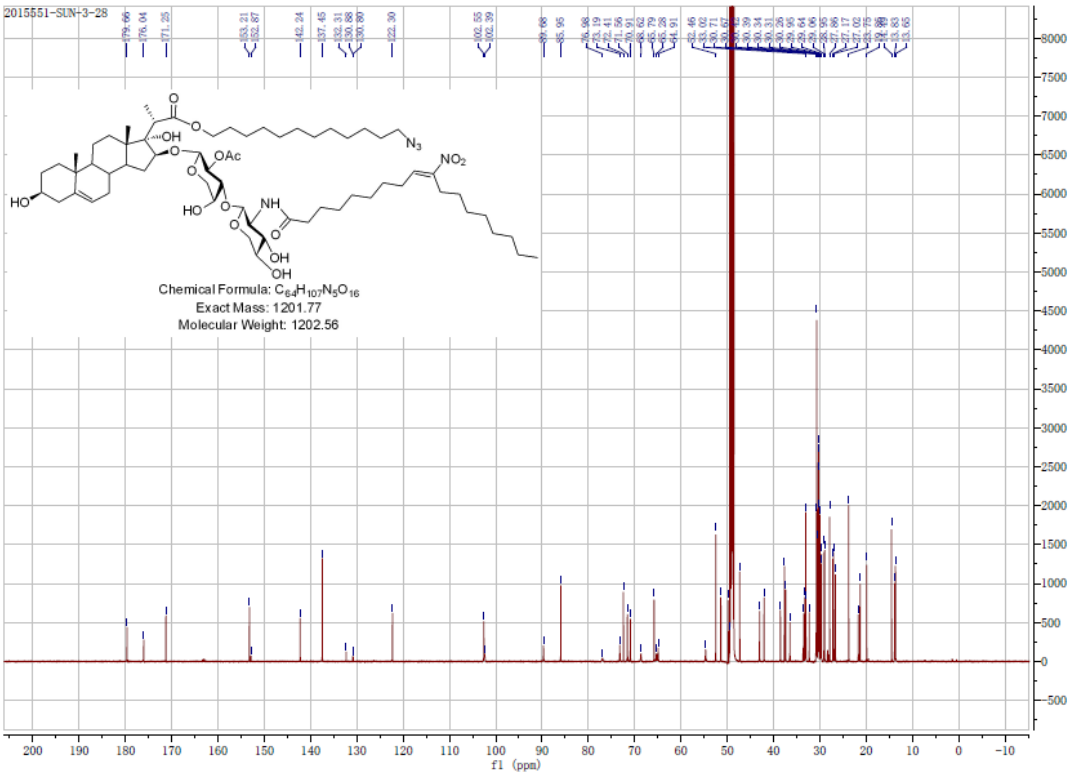
Compound **26**: ^{13}C NMR



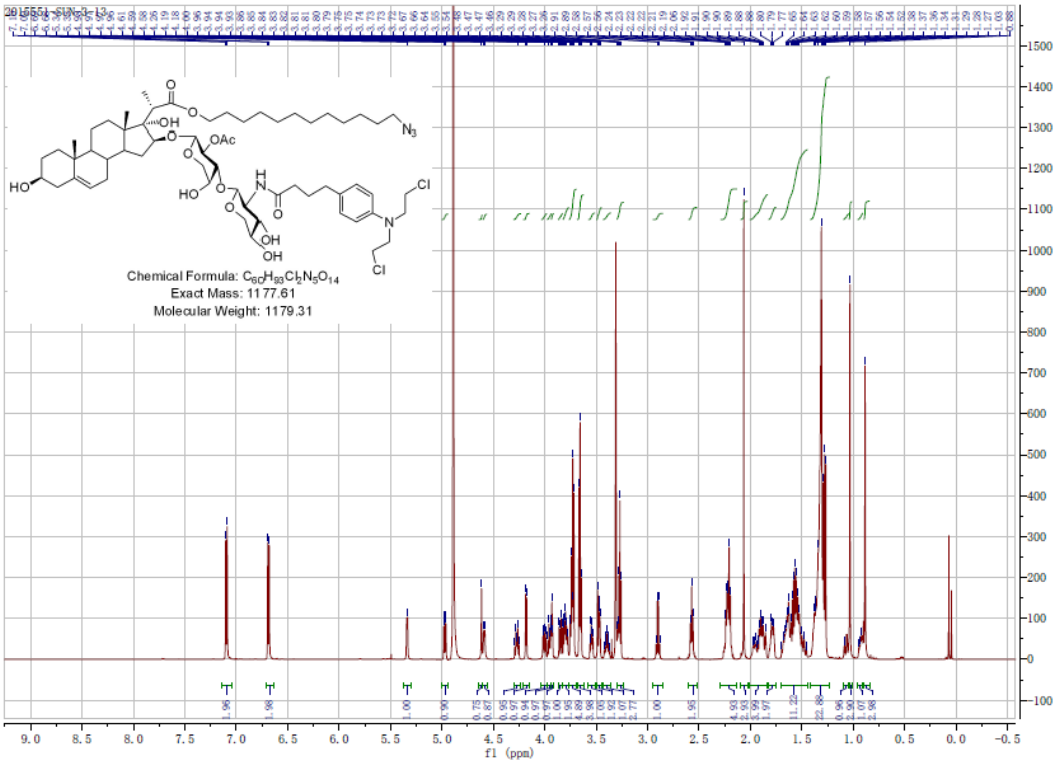
Compound **27**: ^{1}H NMR



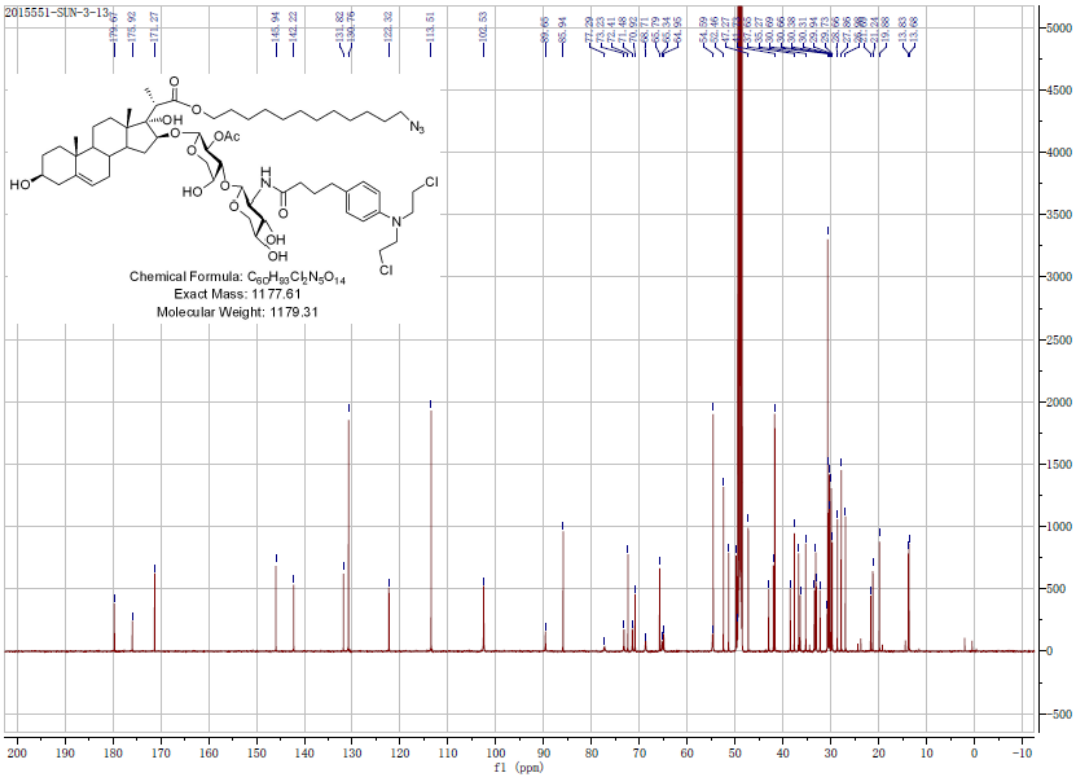
Compound **27**: ^{13}C NMR



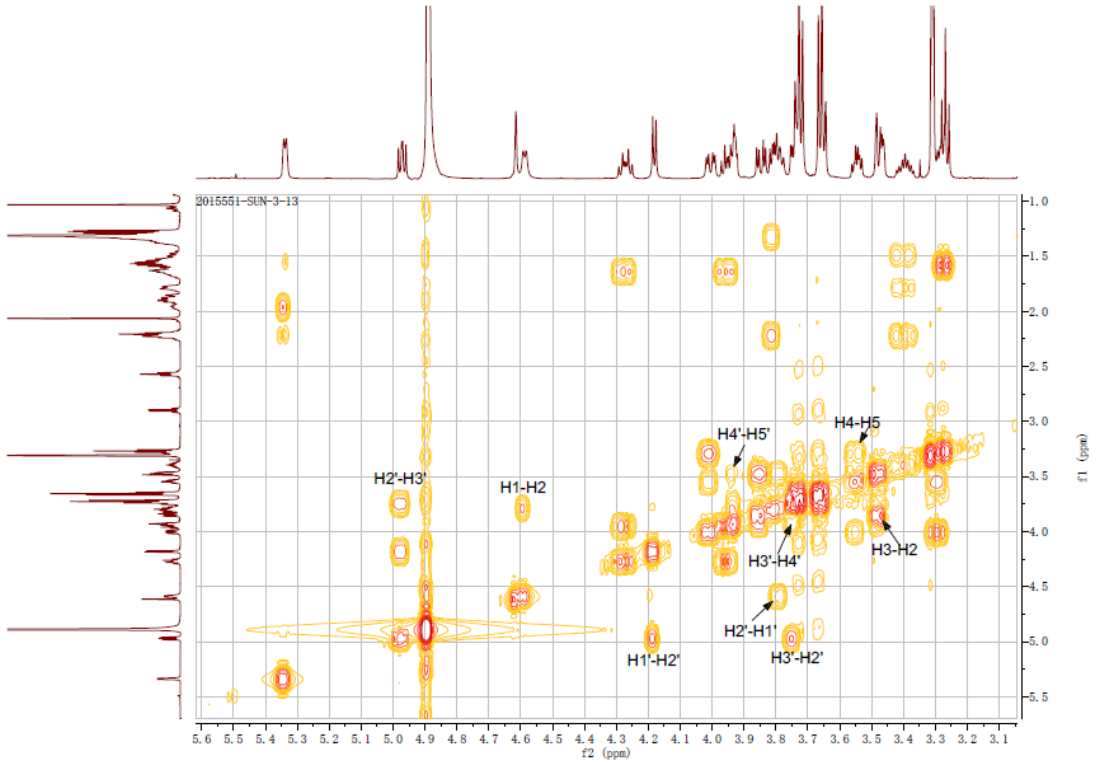
Compound **28**: ^{1}H NMR



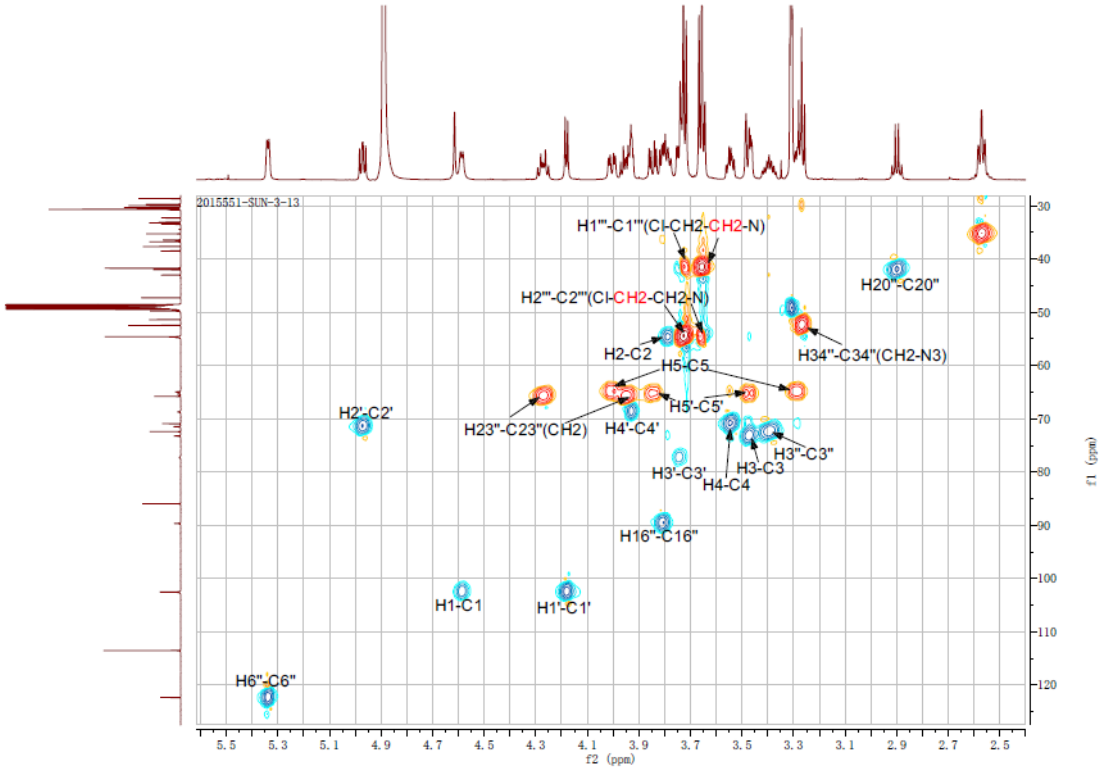
Compound **28**: ^{13}C NMR



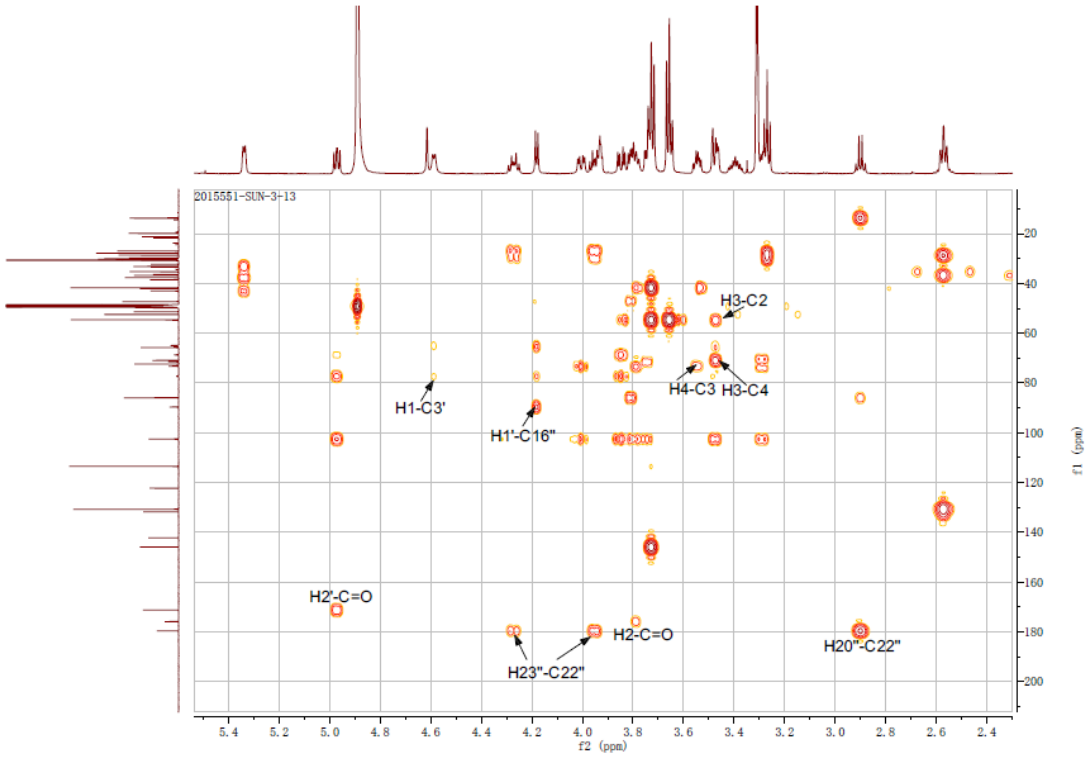
Compound **28**: COSY NMR



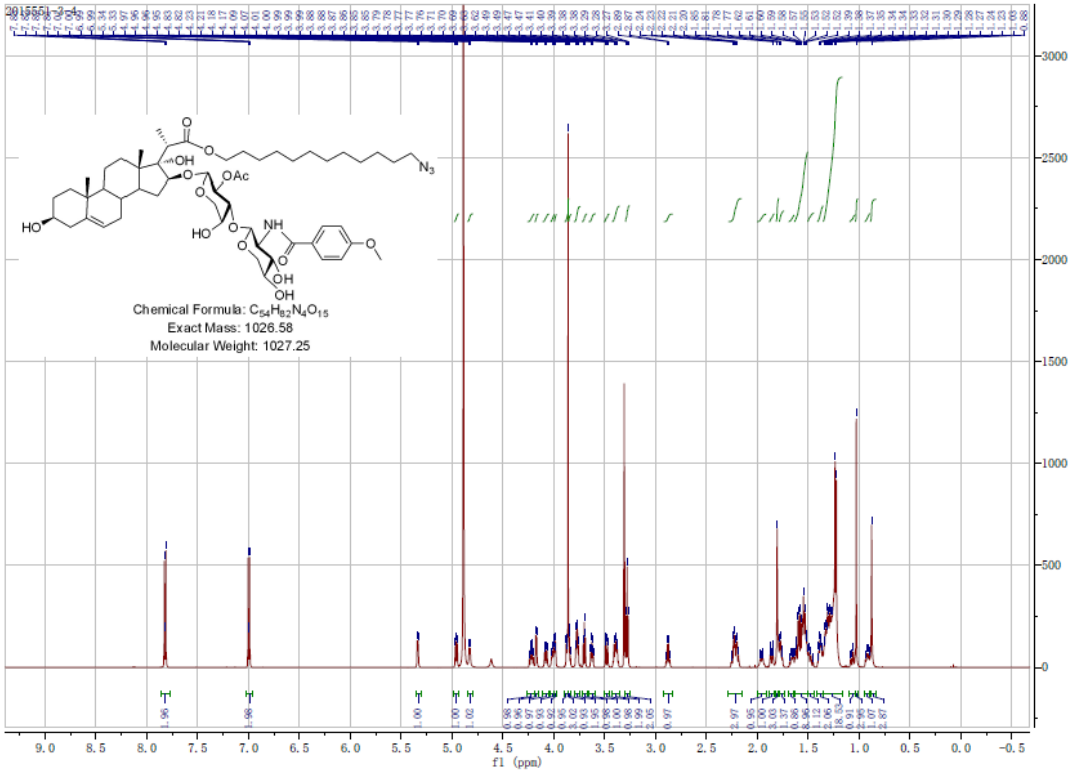
Compound **28**: HSQC NMR



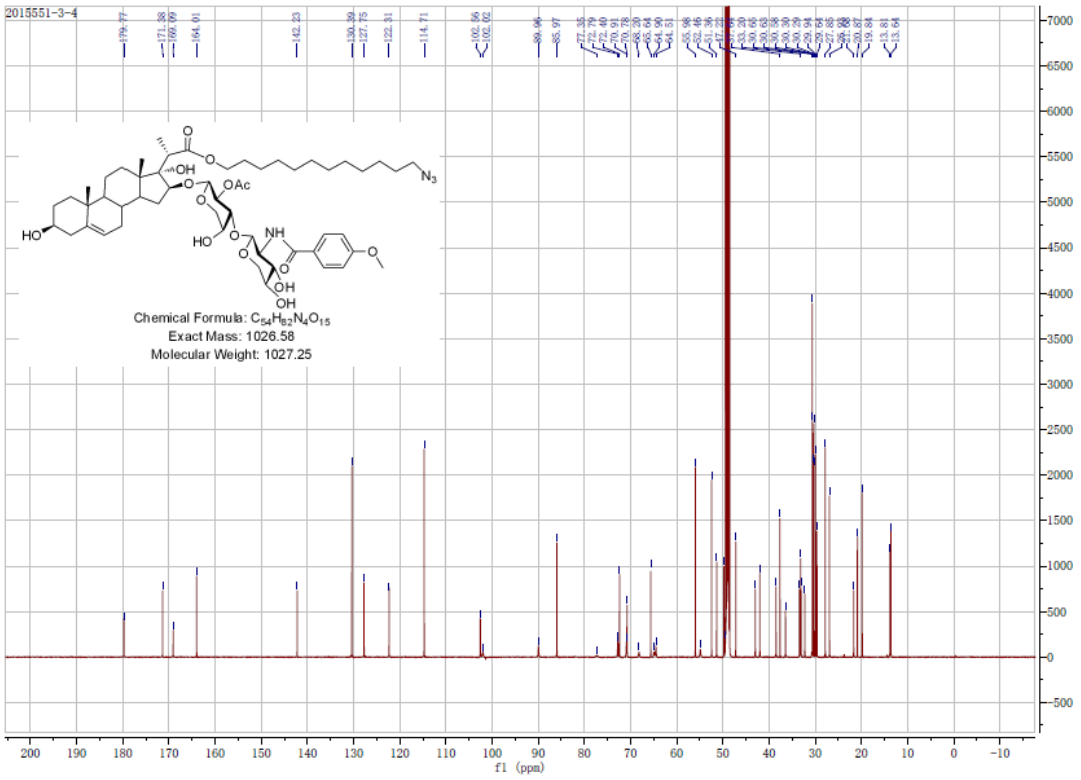
Compound **28**: HMBC NMR



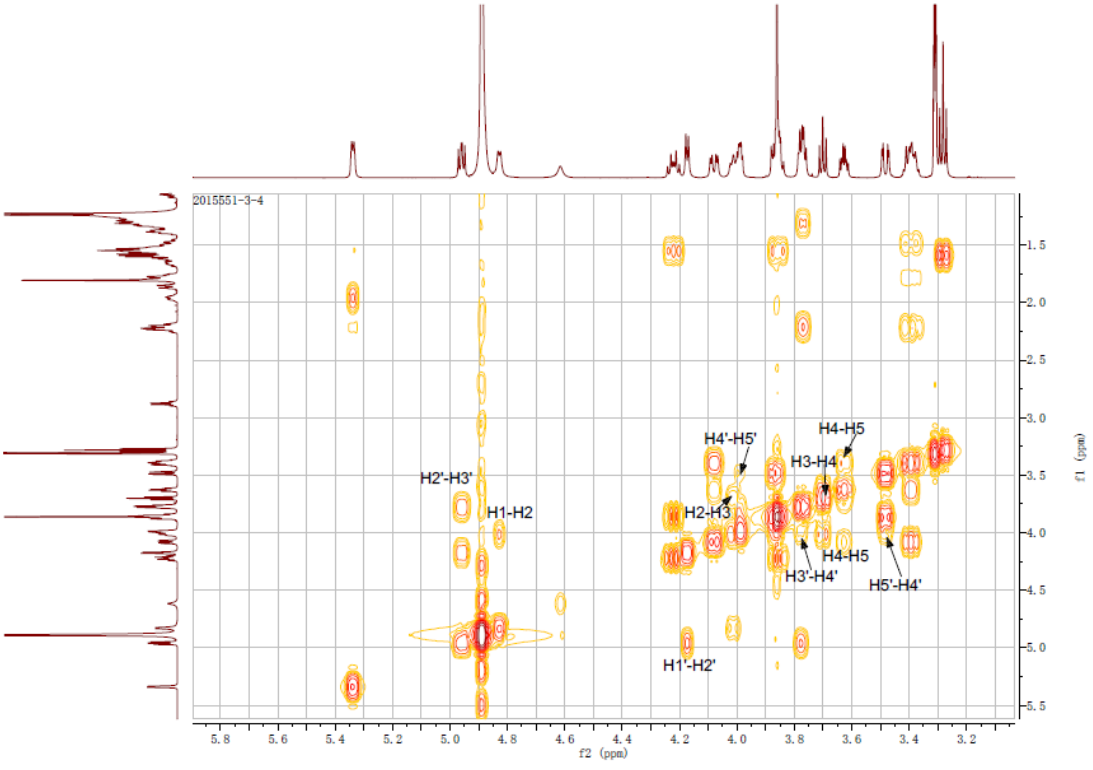
Compound **29**: ^{1}H NMR



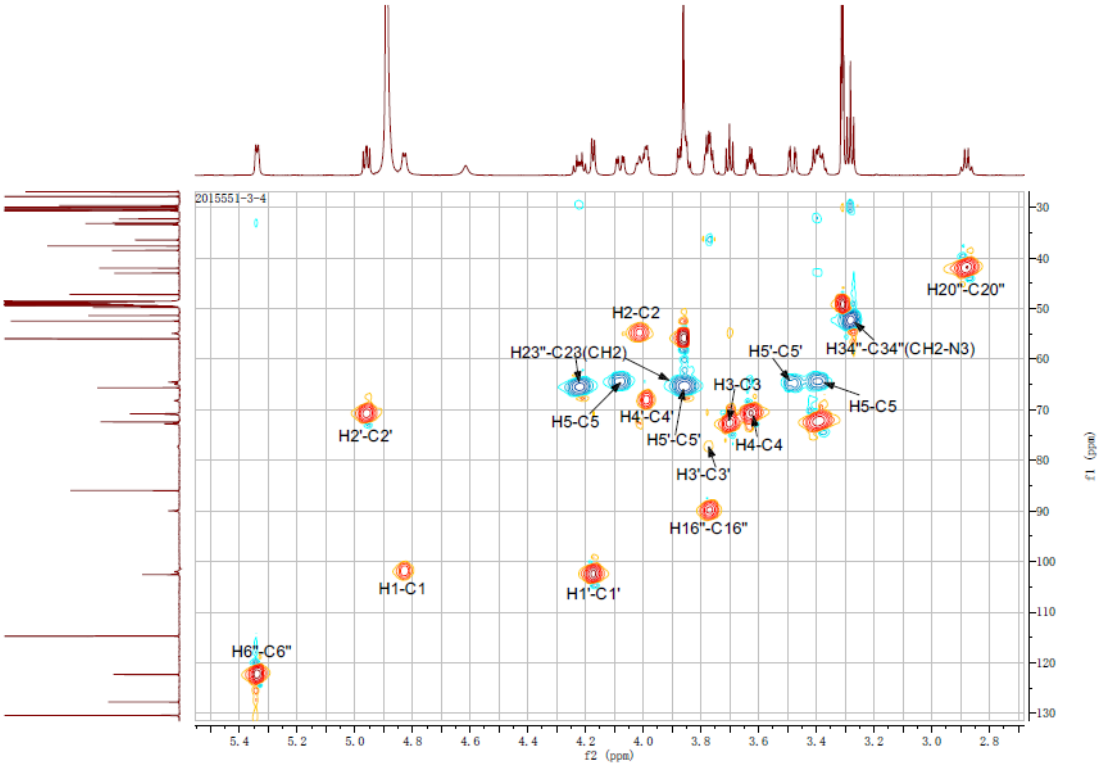
Compound **29**: ^{13}C NMR



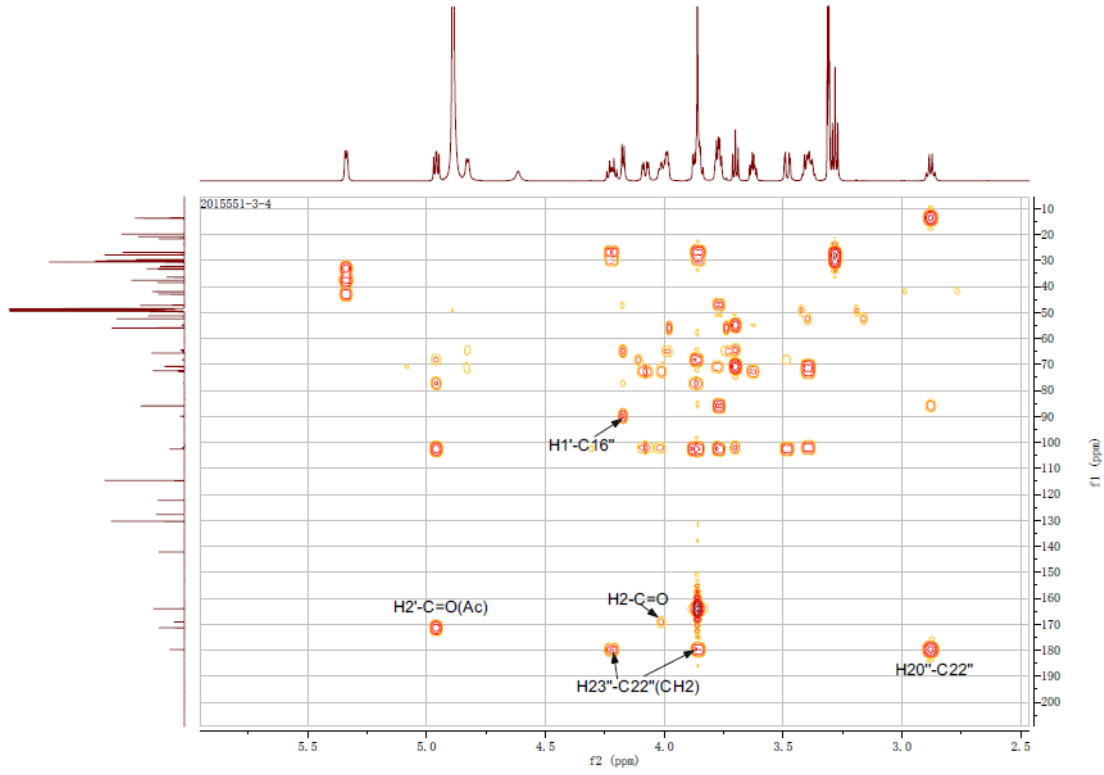
Compound **29**: COSY NMR



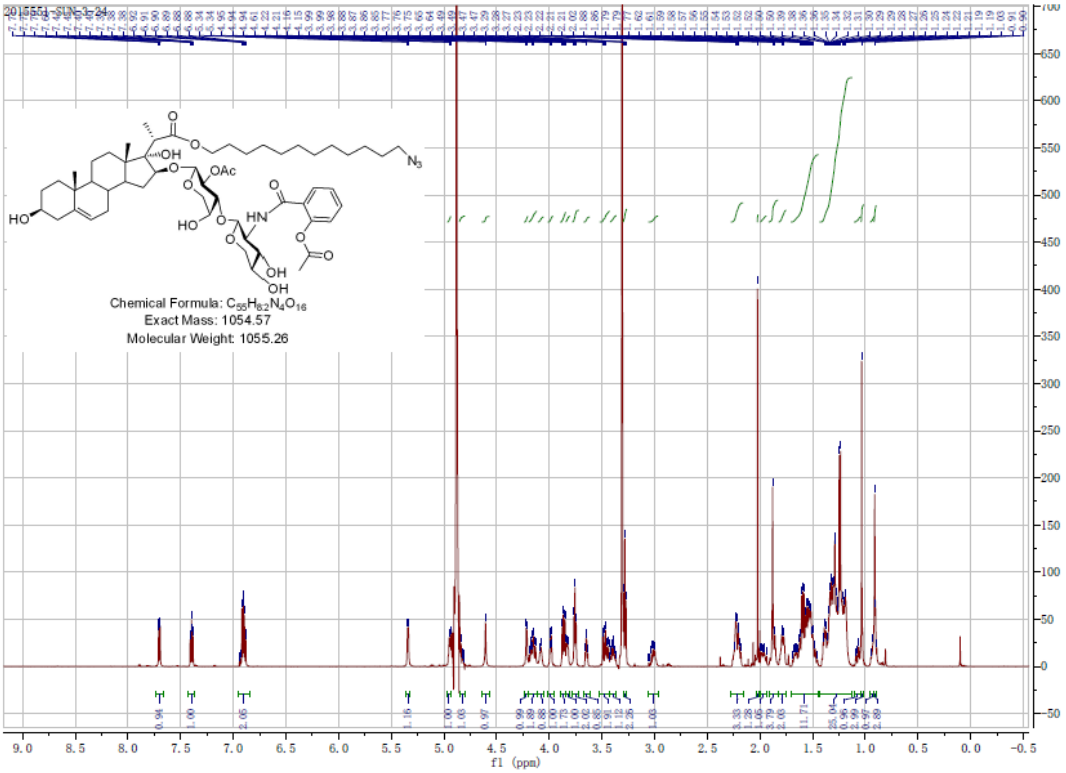
Compound **29**: HSQC NMR



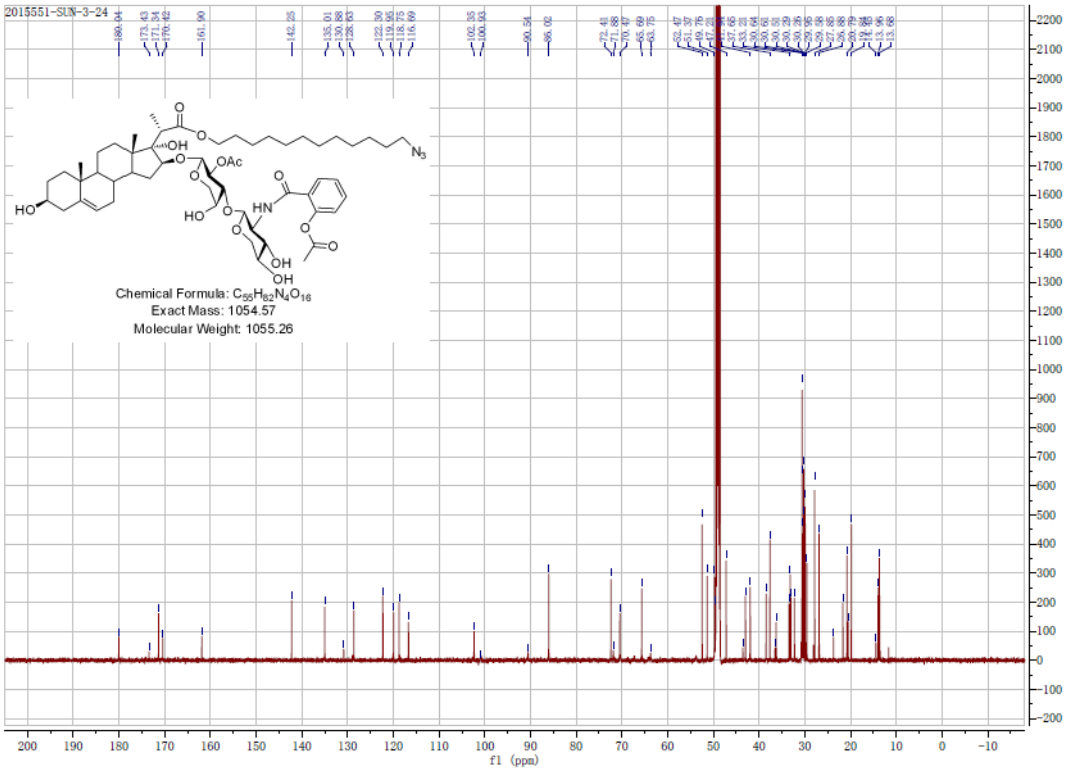
Compound **29**: HMBC NMR



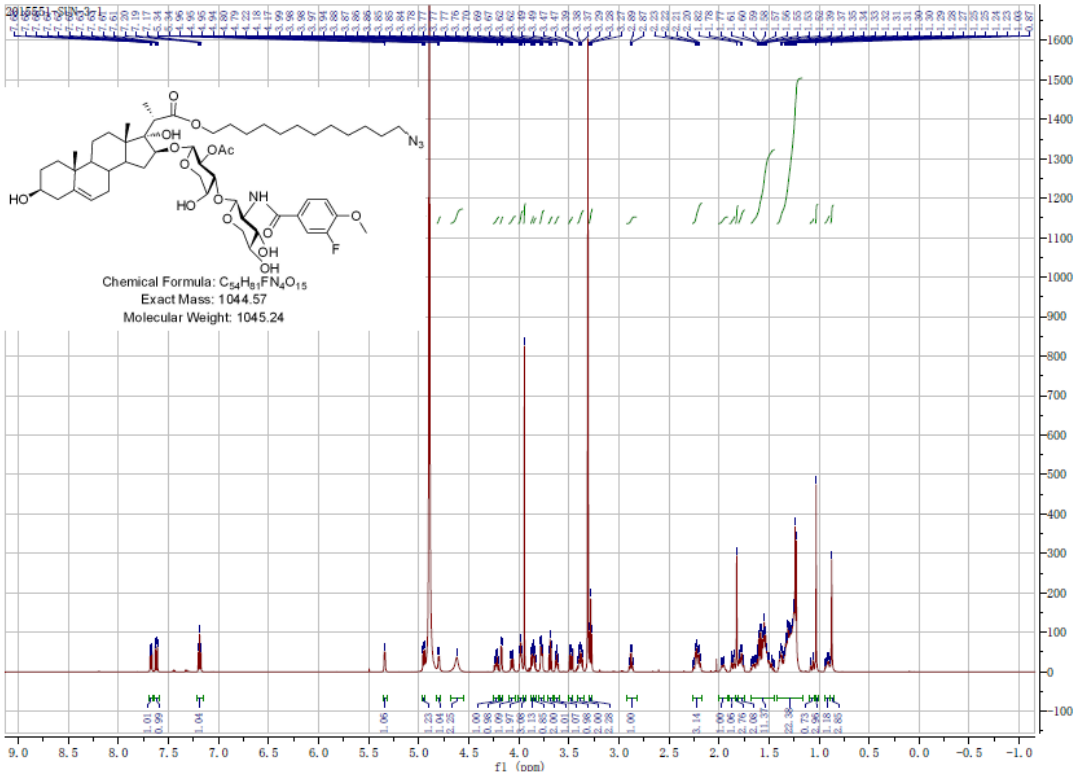
Compound **30**: ^{1}H NMR



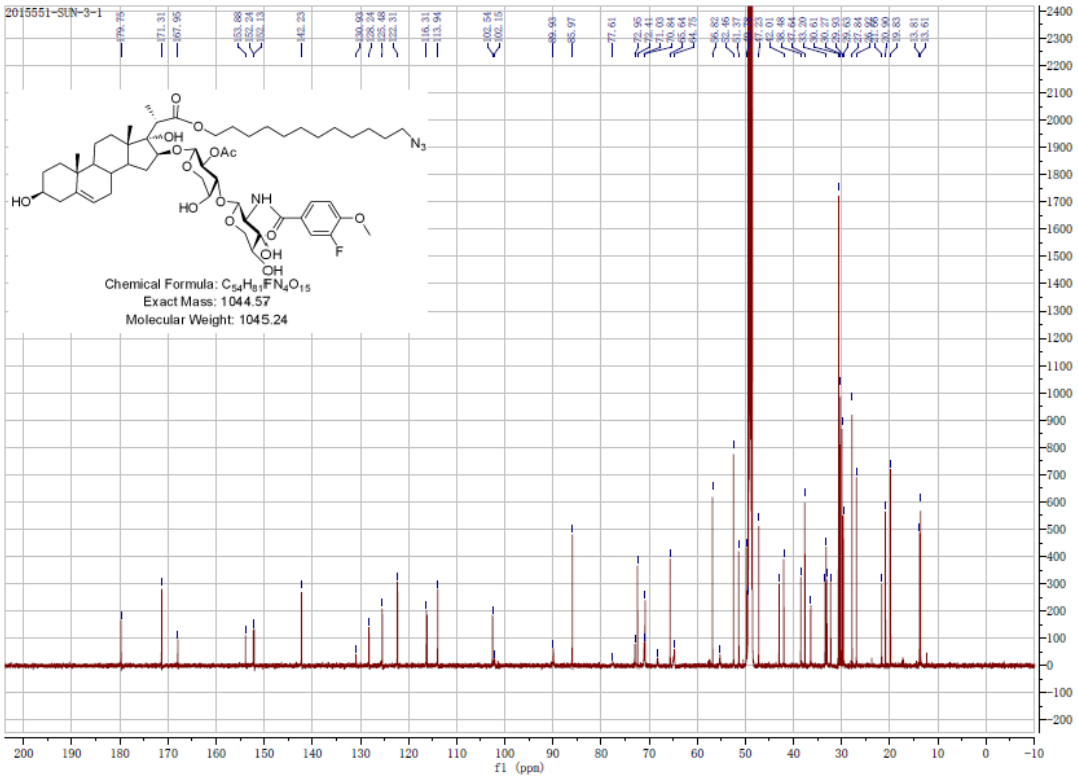
Compound **30**: ^{13}C NMR



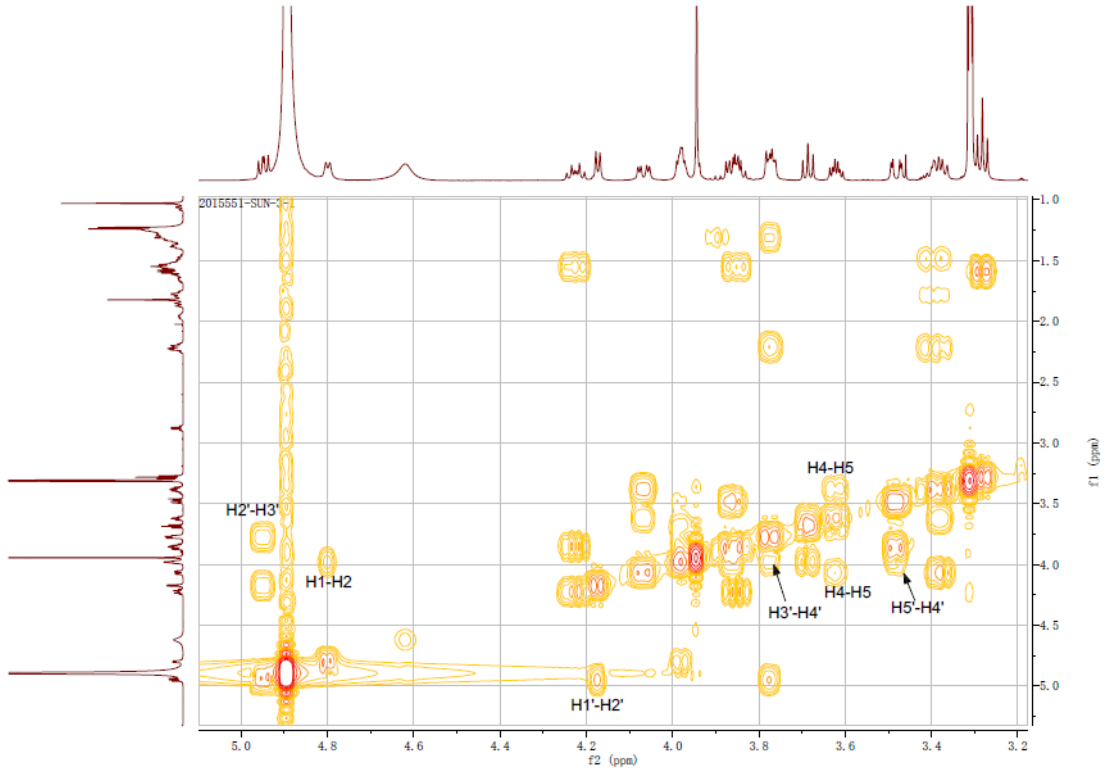
Compound **31**: ^{1}H NMR



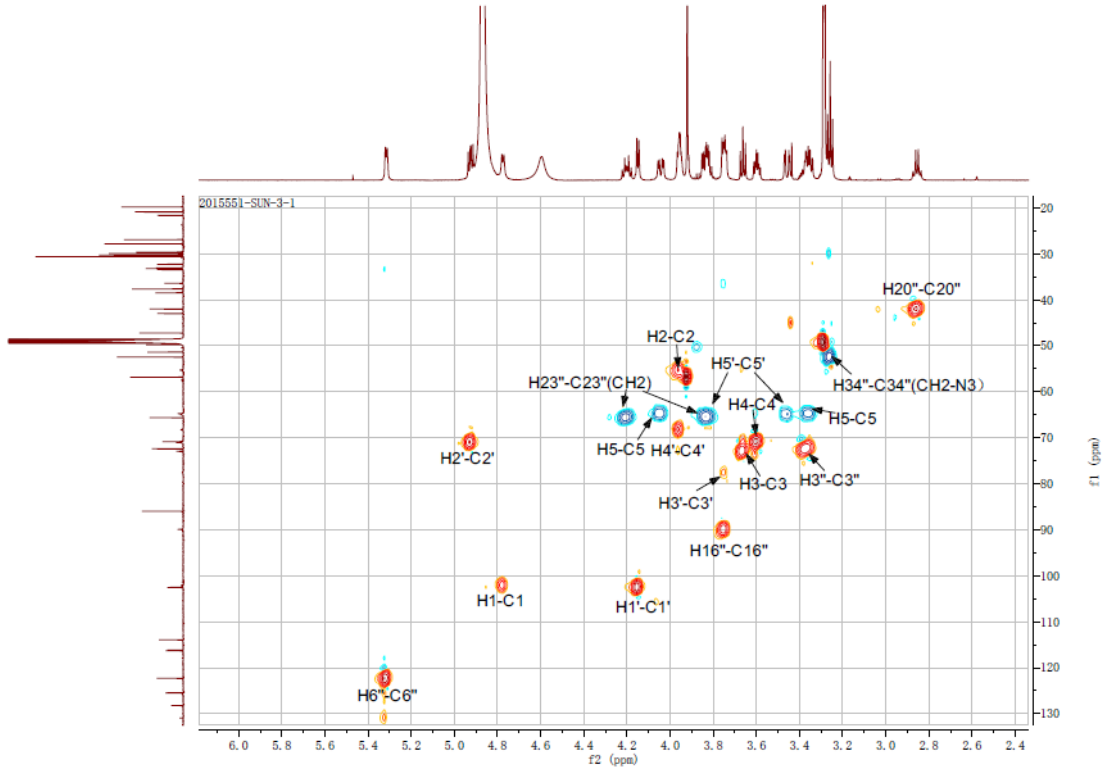
Compound **31**: ^{13}C NMR



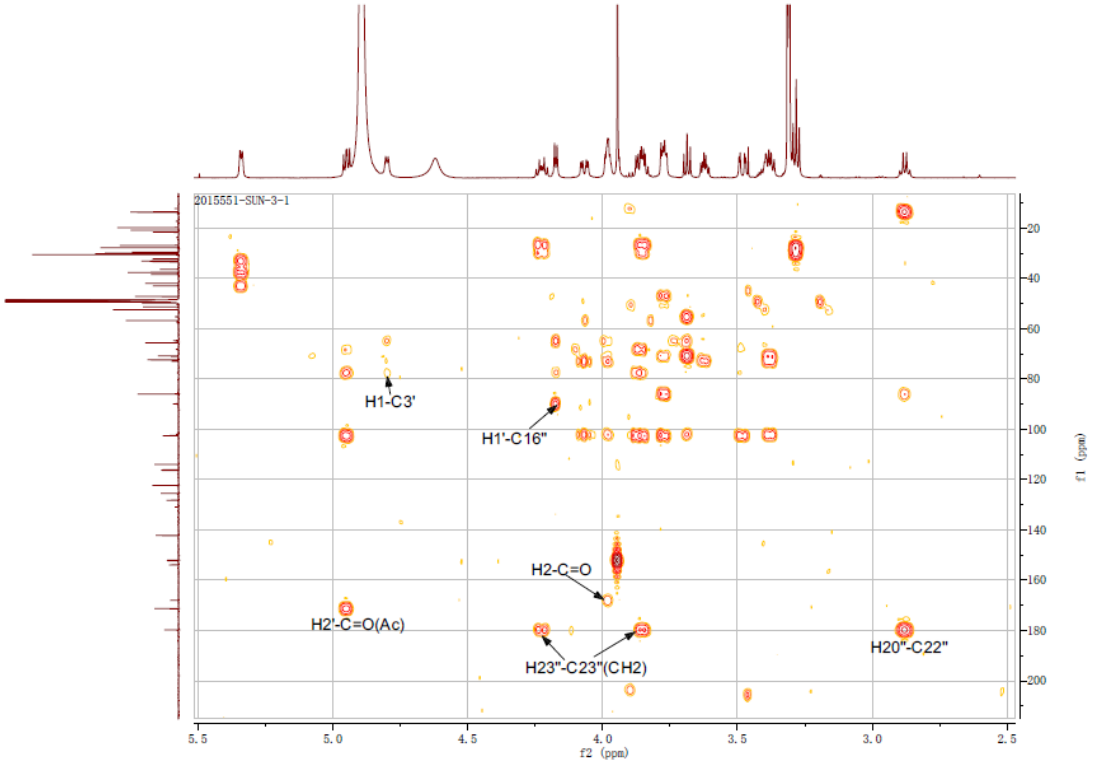
Compound **31**: COSY NMR



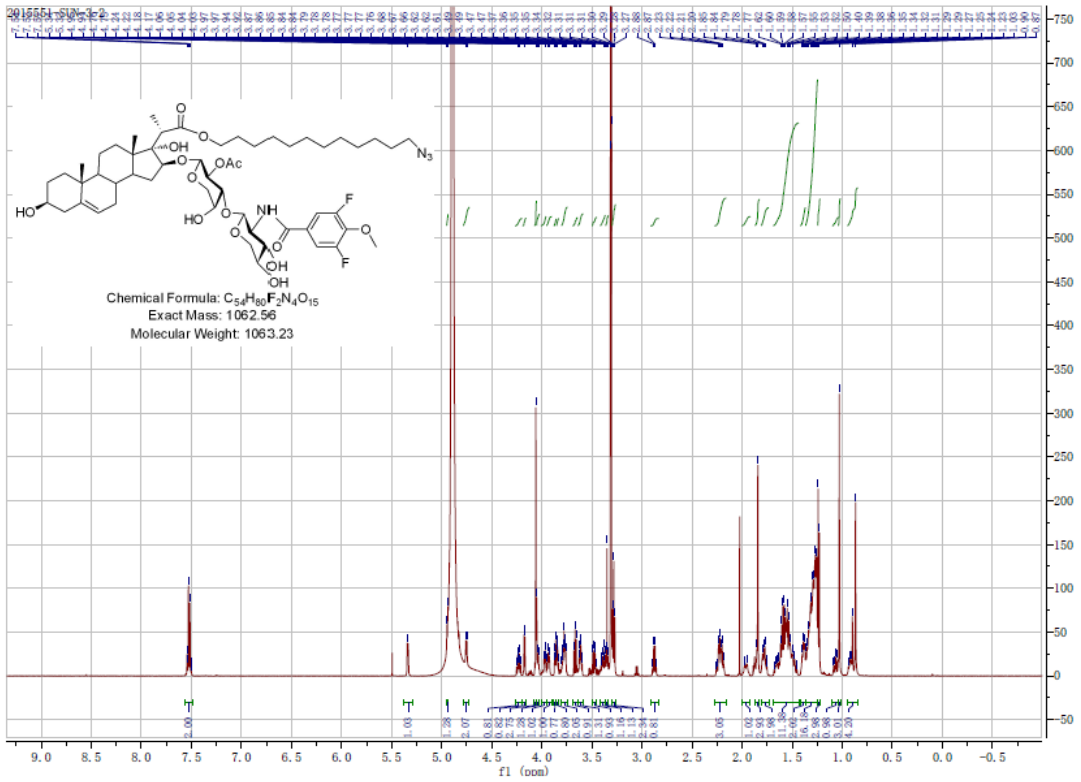
Compound **31**: HSQC NMR



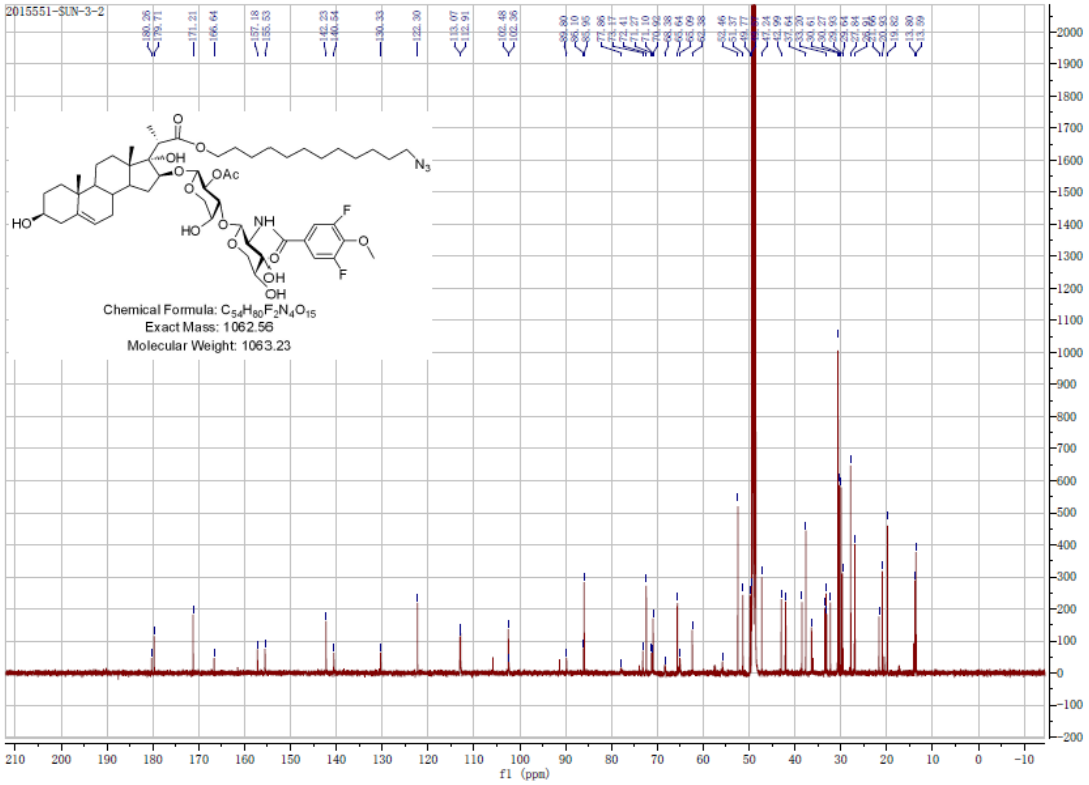
Compound **31**: HMBC NMR



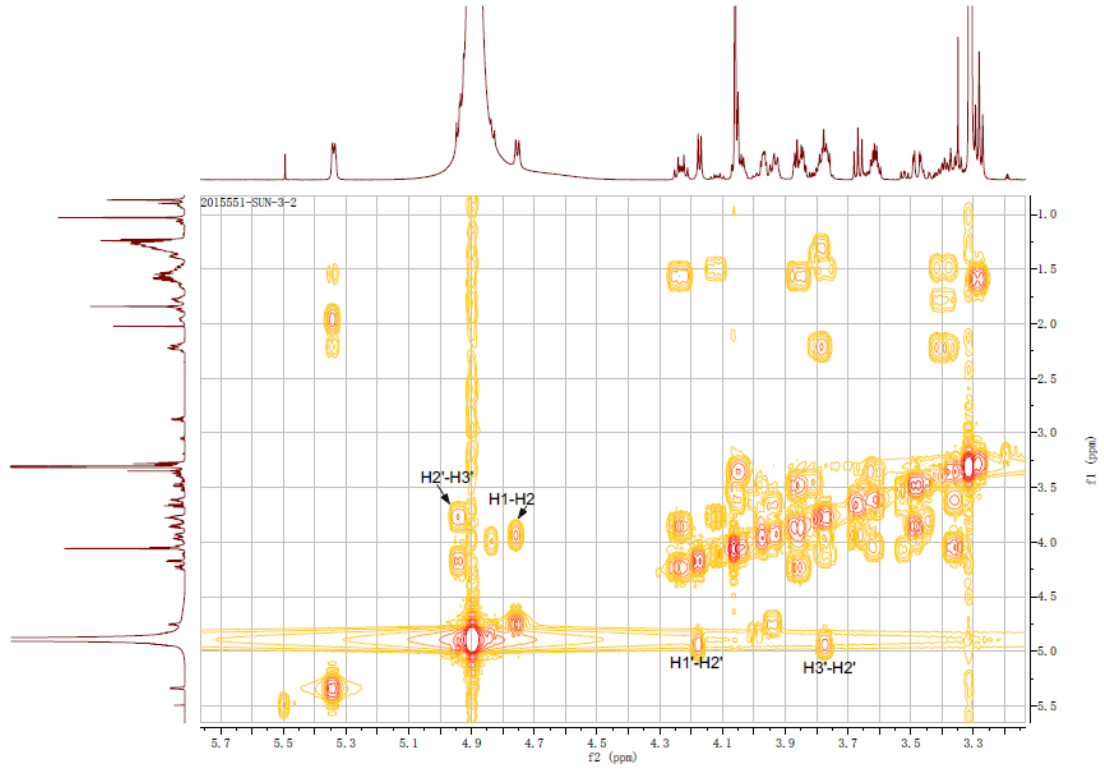
Compound **32**: ^{1}H NMR



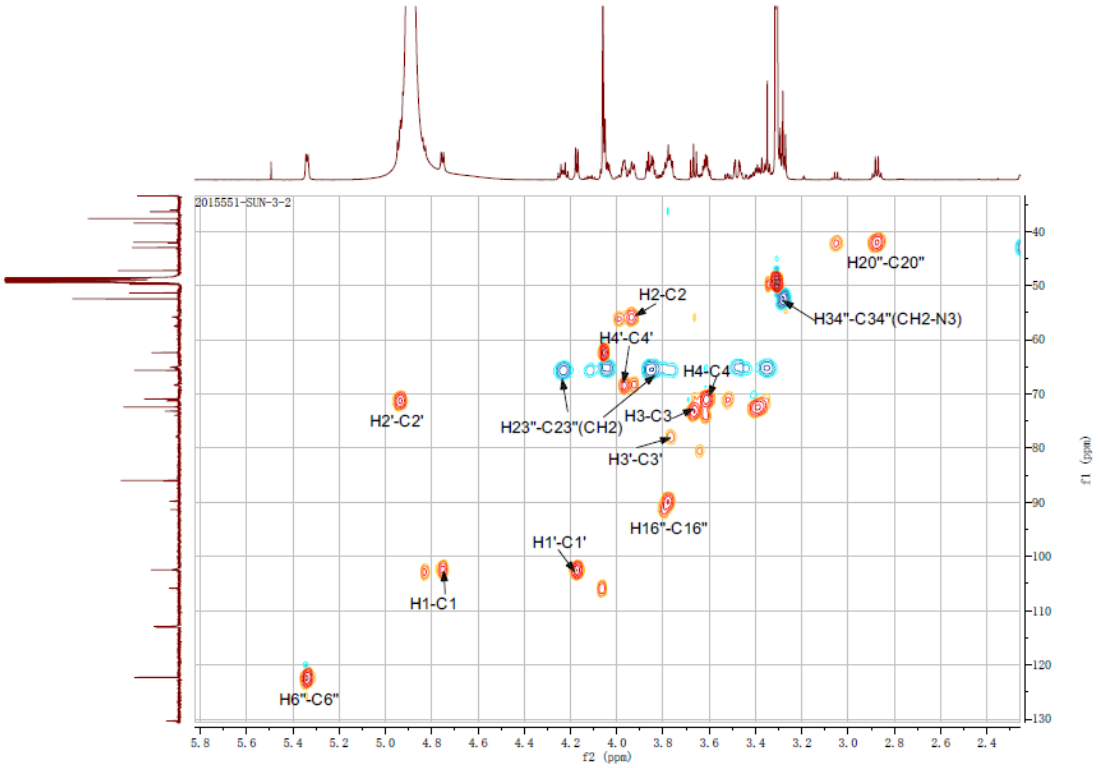
Compound **32**: ^{13}C NMR



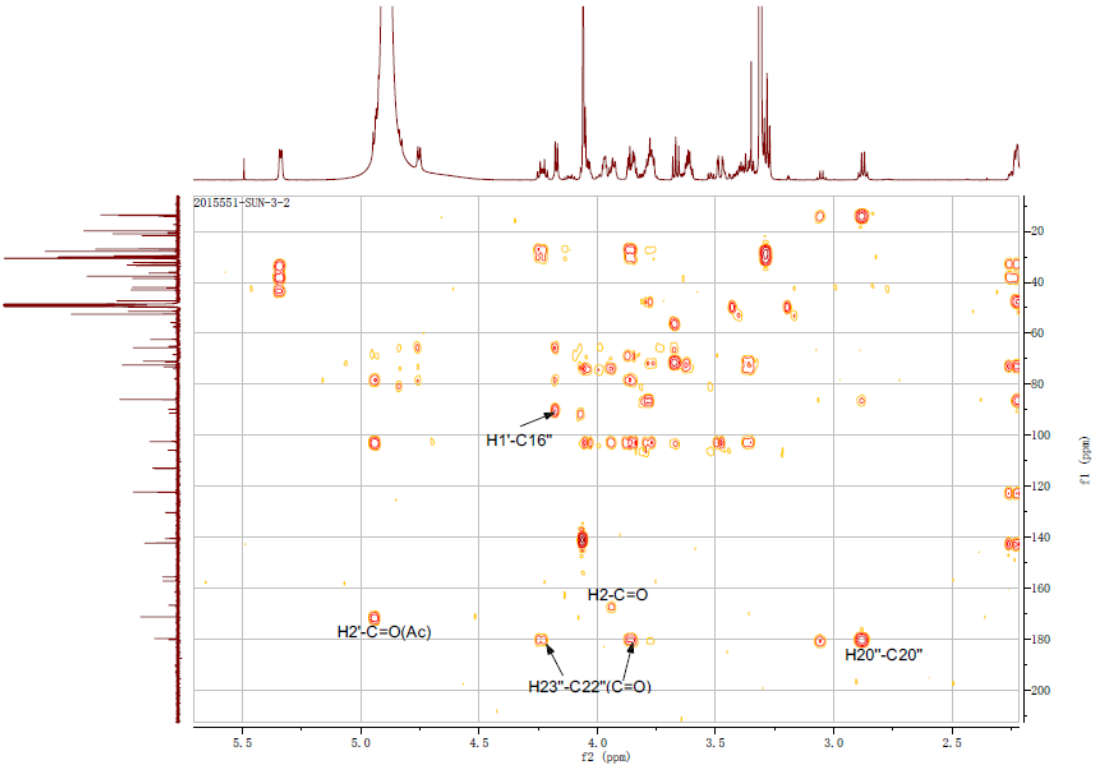
Compound **32**: COSY NMR



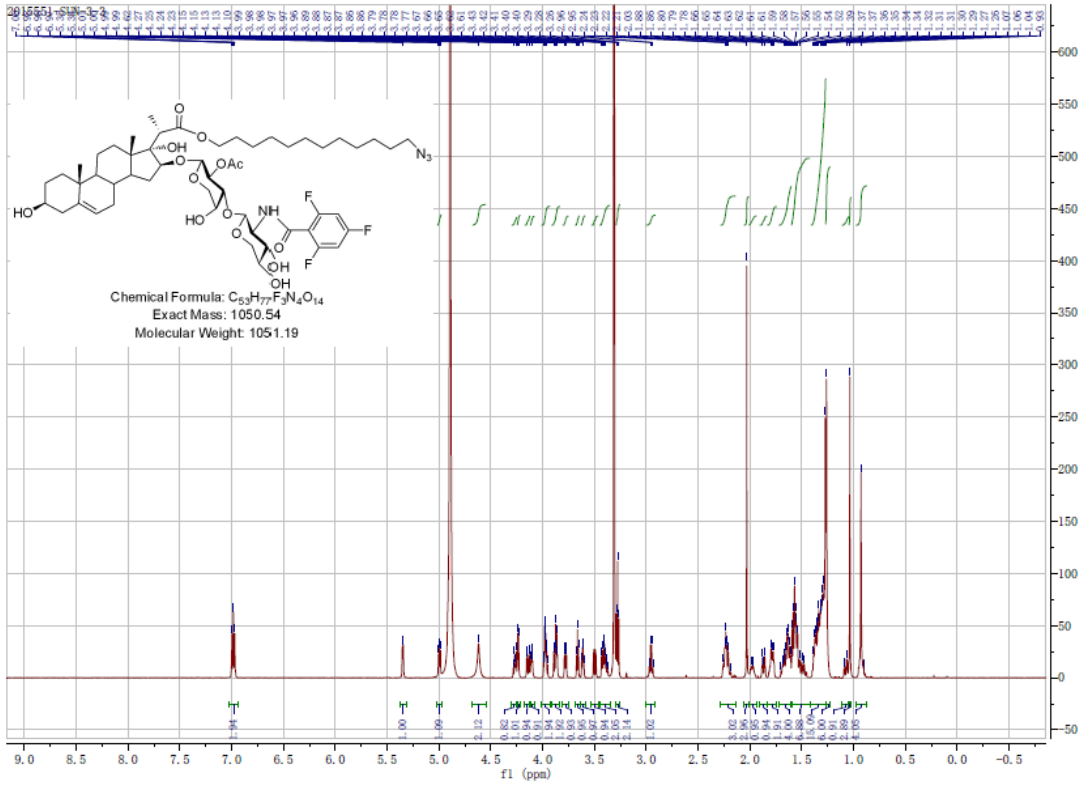
Compound **32**: HSQC NMR



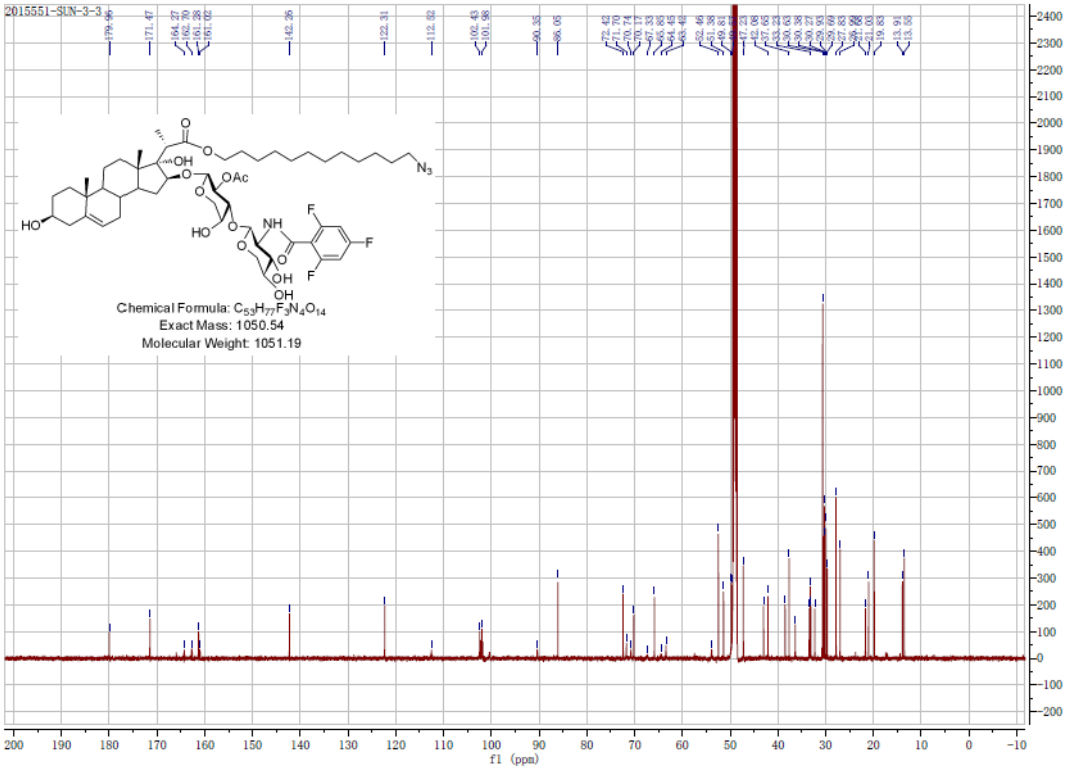
Compound **32**: HMBC NMR



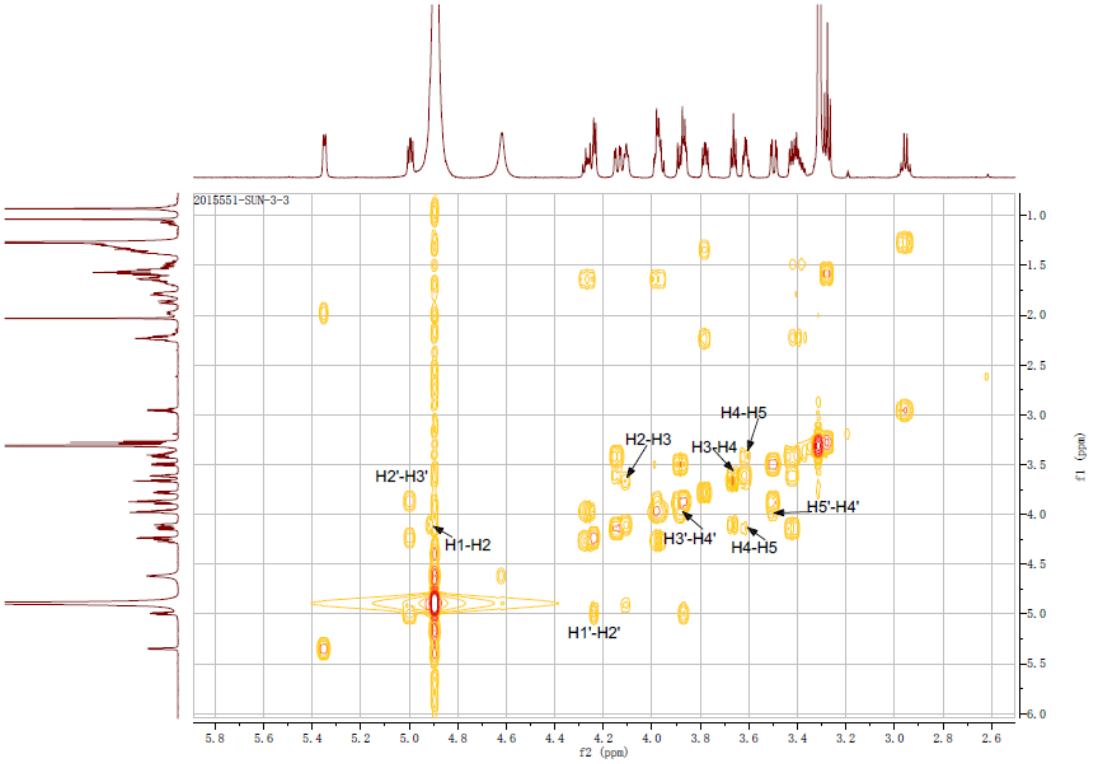
Compound **33**: ^{1}H NMR



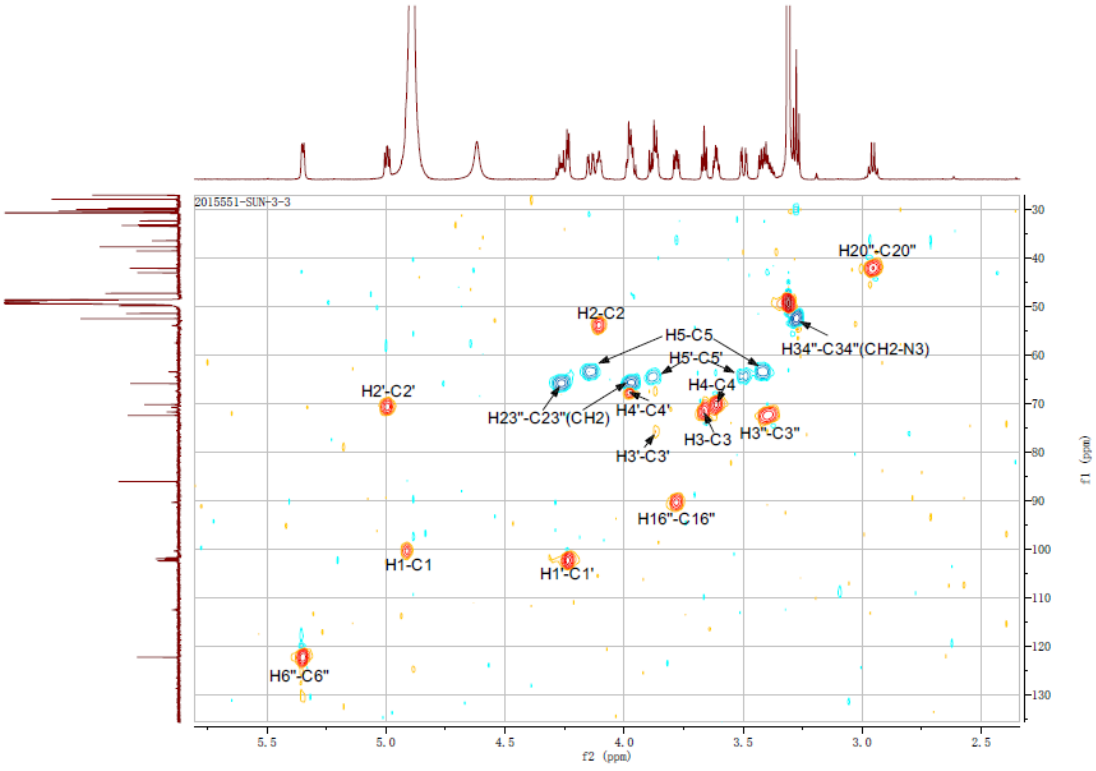
Compound **33**: ^{13}C NMR



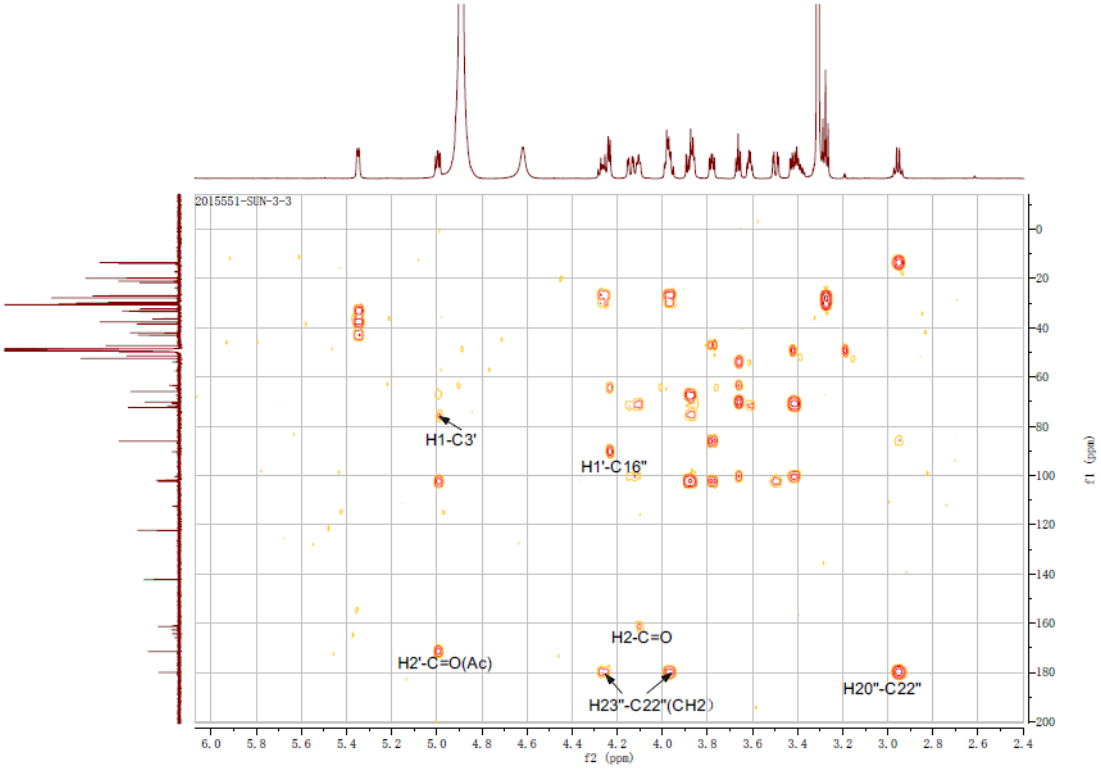
Compound **33**: COSY NMR



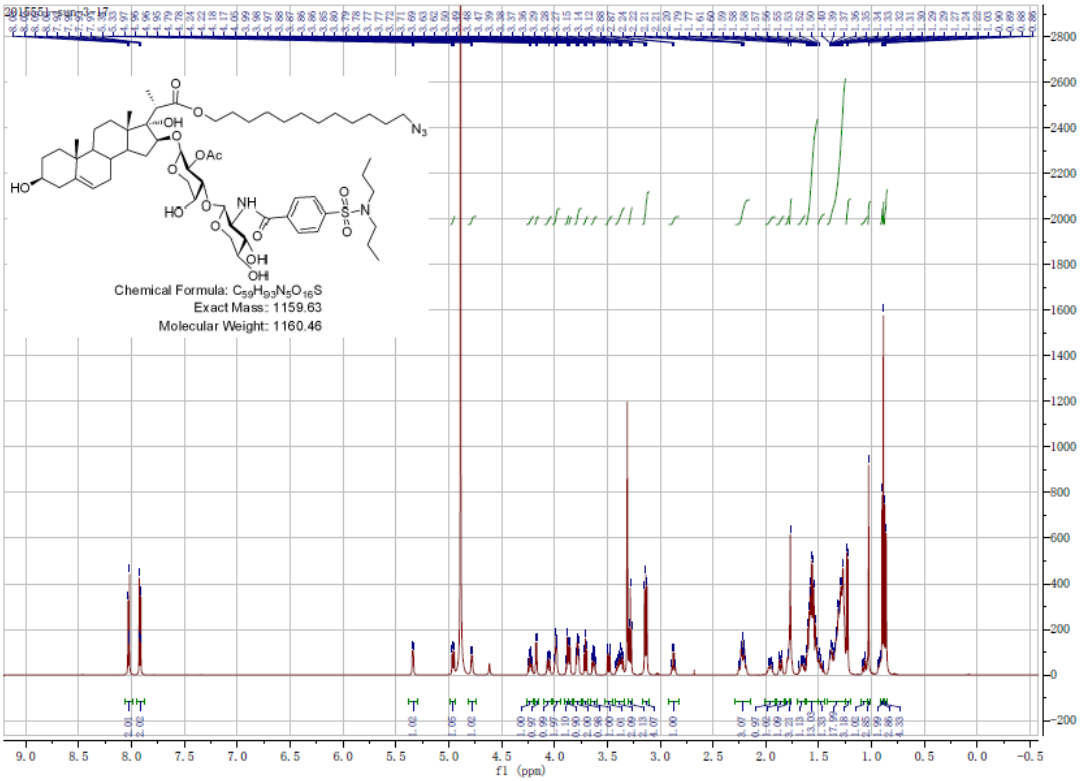
Compound **33**: HSQC NMR



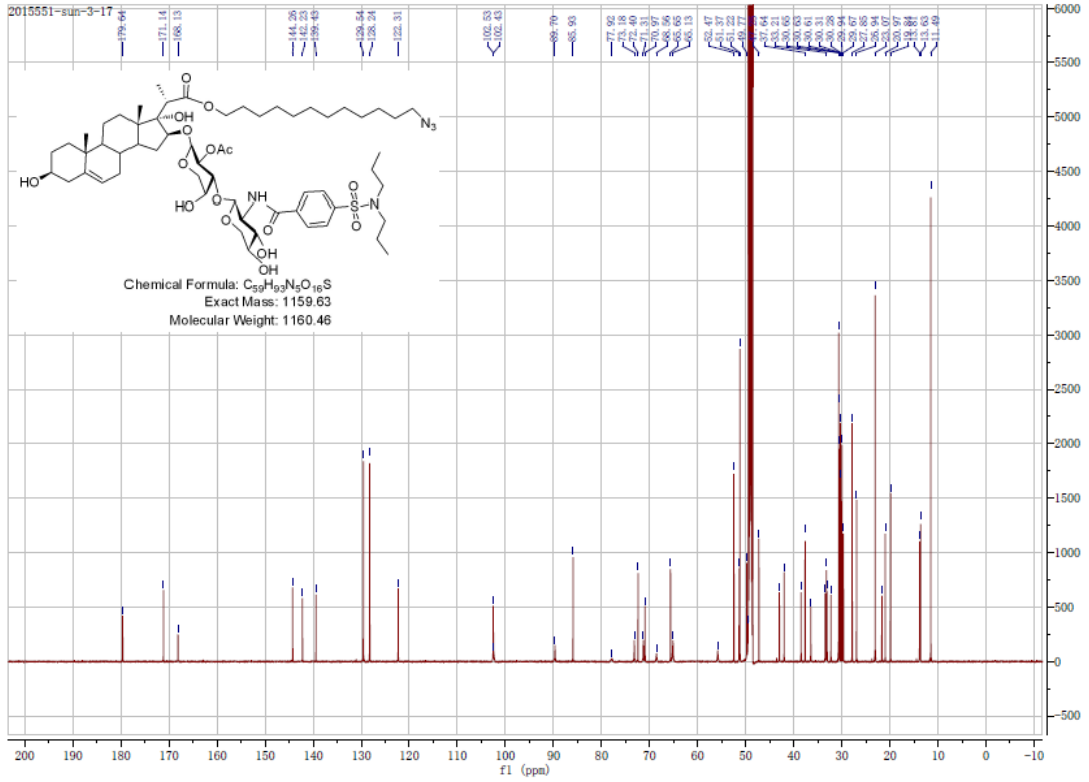
Compound **33**: HMBC NMR



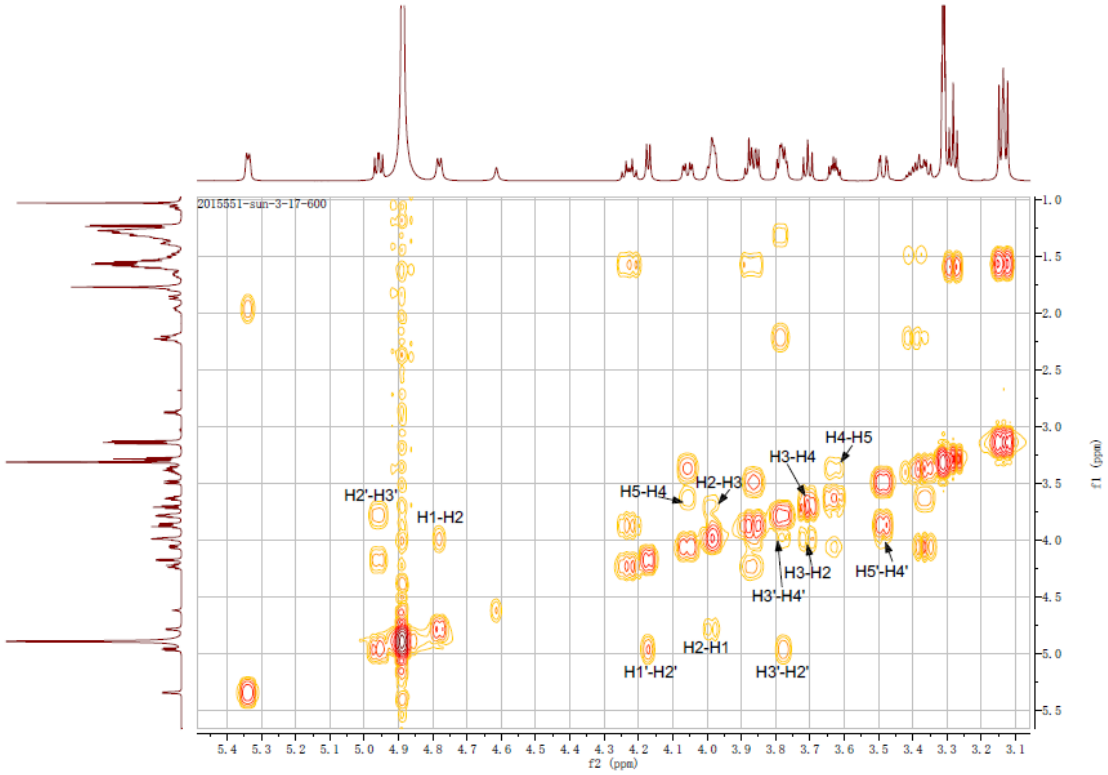
Compound **34**: ^{1}H NMR



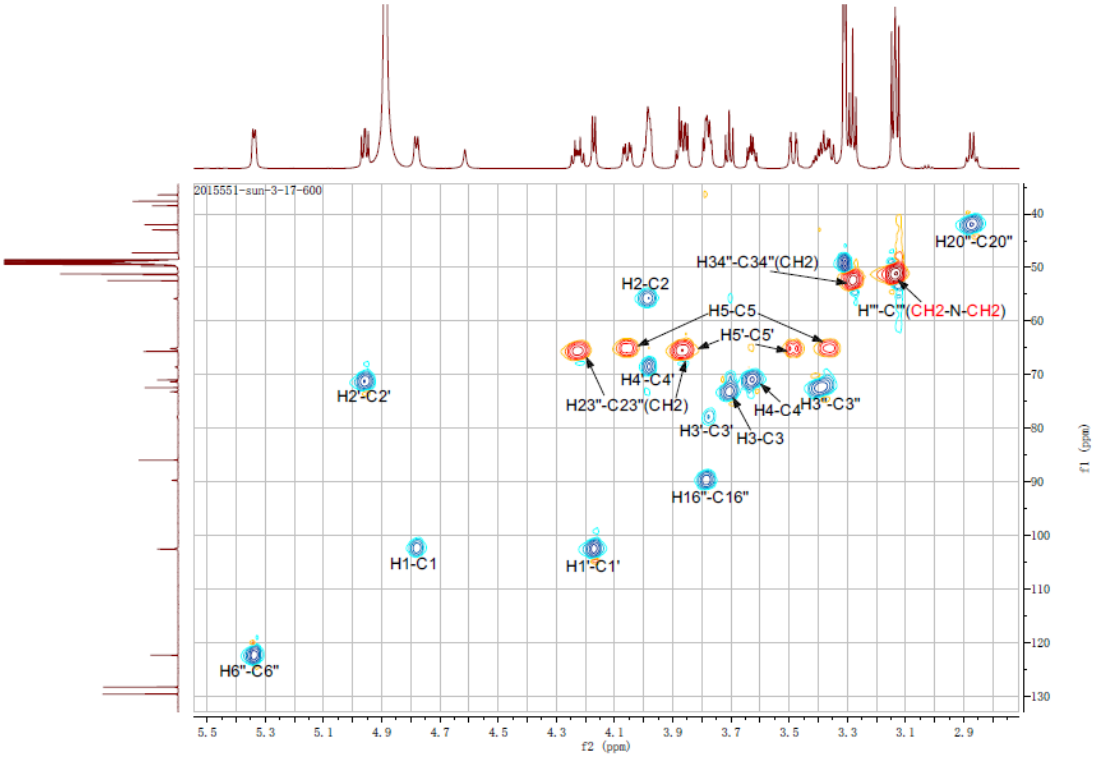
Compound **34**: ^{13}C NMR



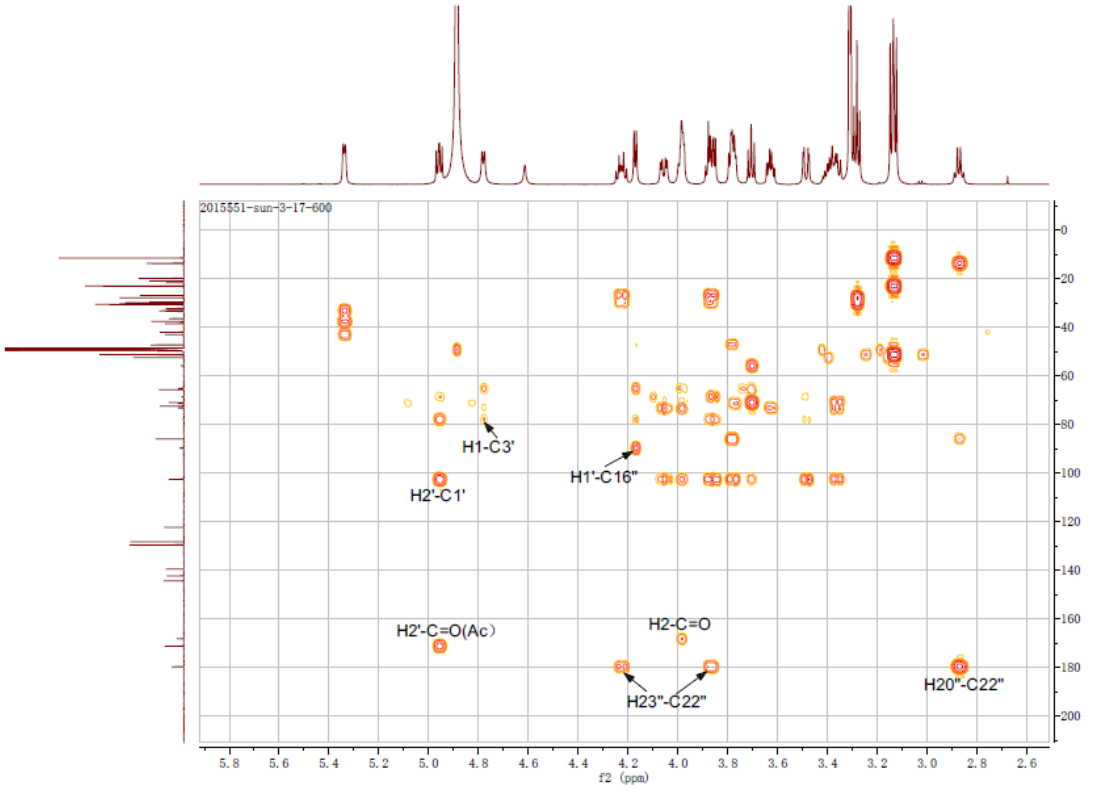
Compound **34**: COSY NMR



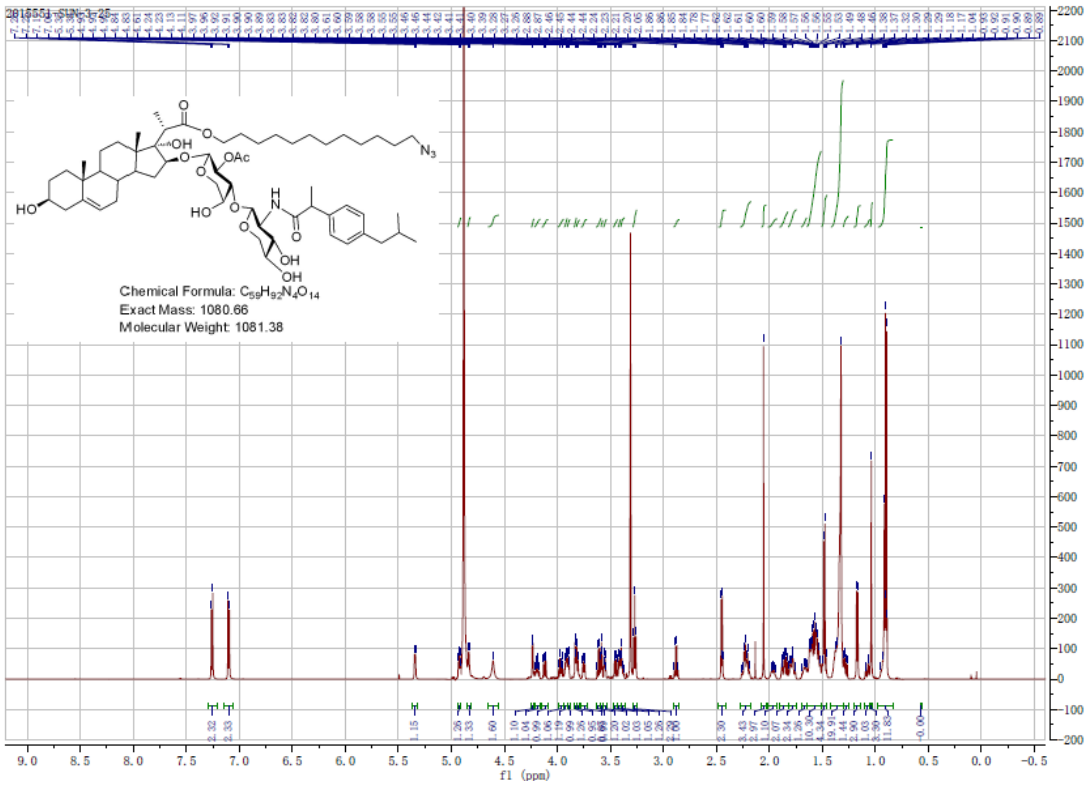
Compound **34**: HSQC NMR



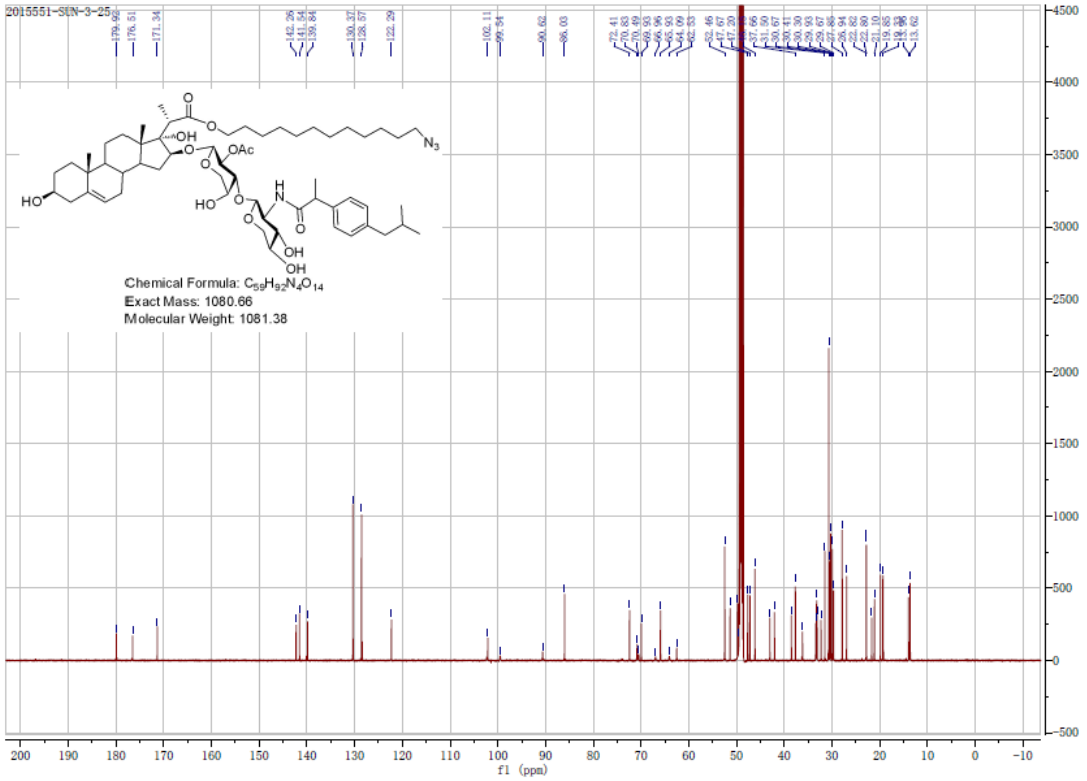
Compound **34**: HMBC NMR



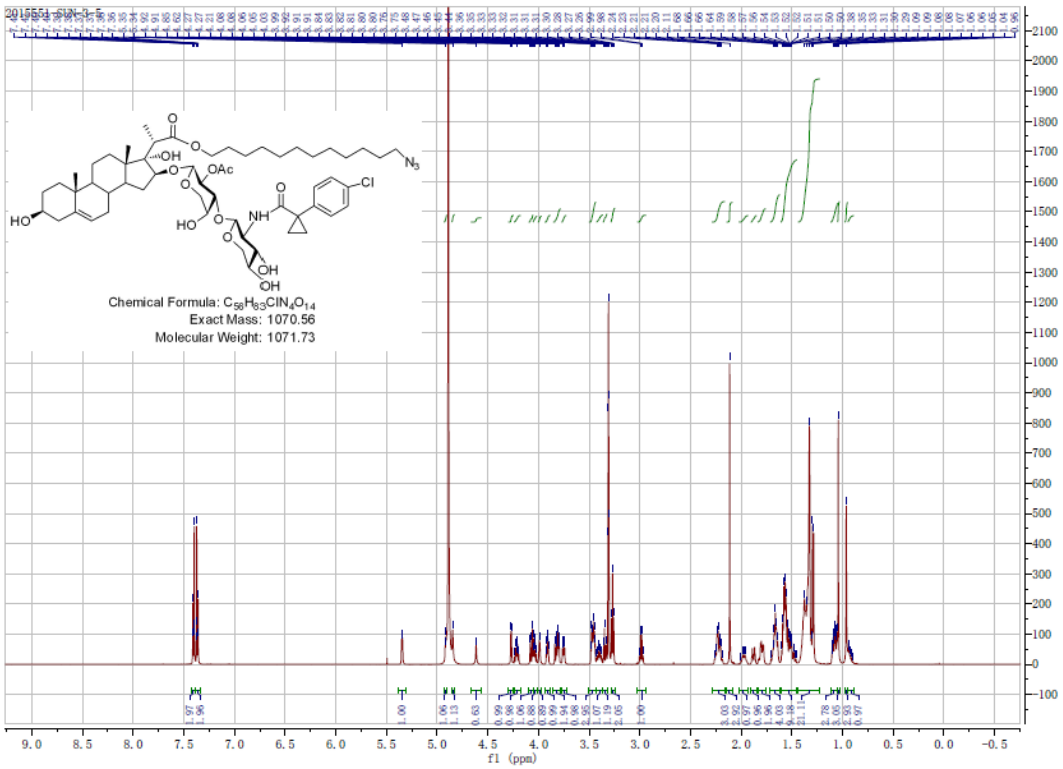
Compound **35**: ^{1}H NMR



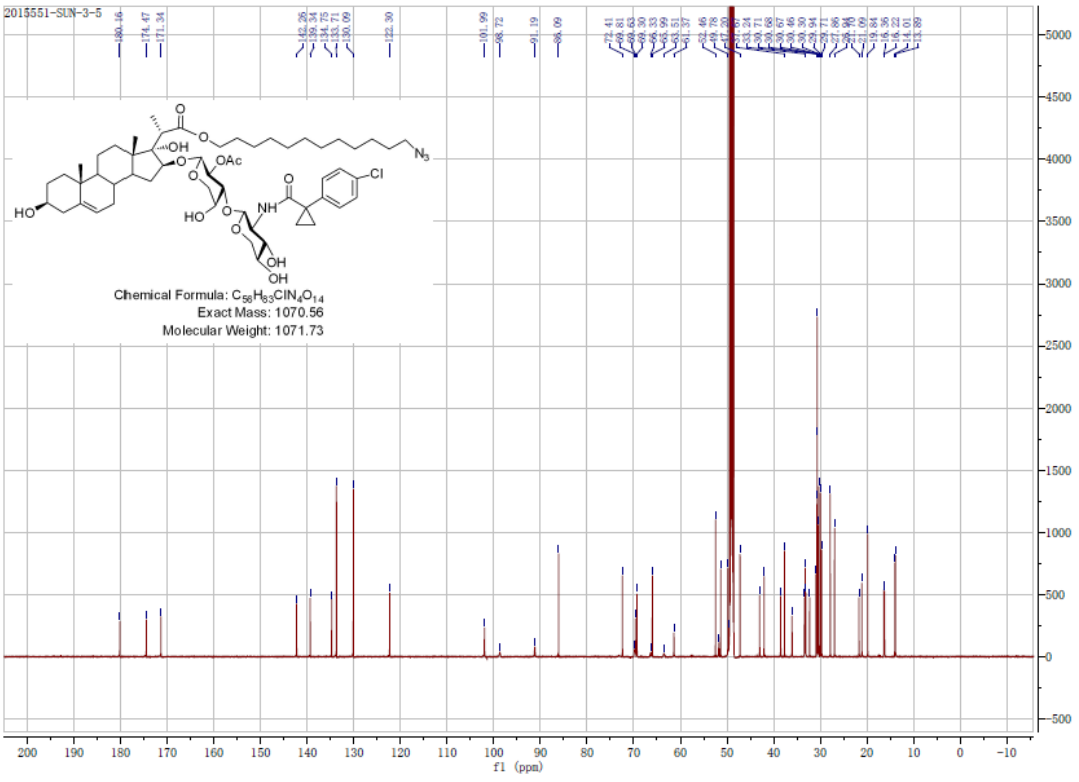
Compound **35**: ^{13}C NMR



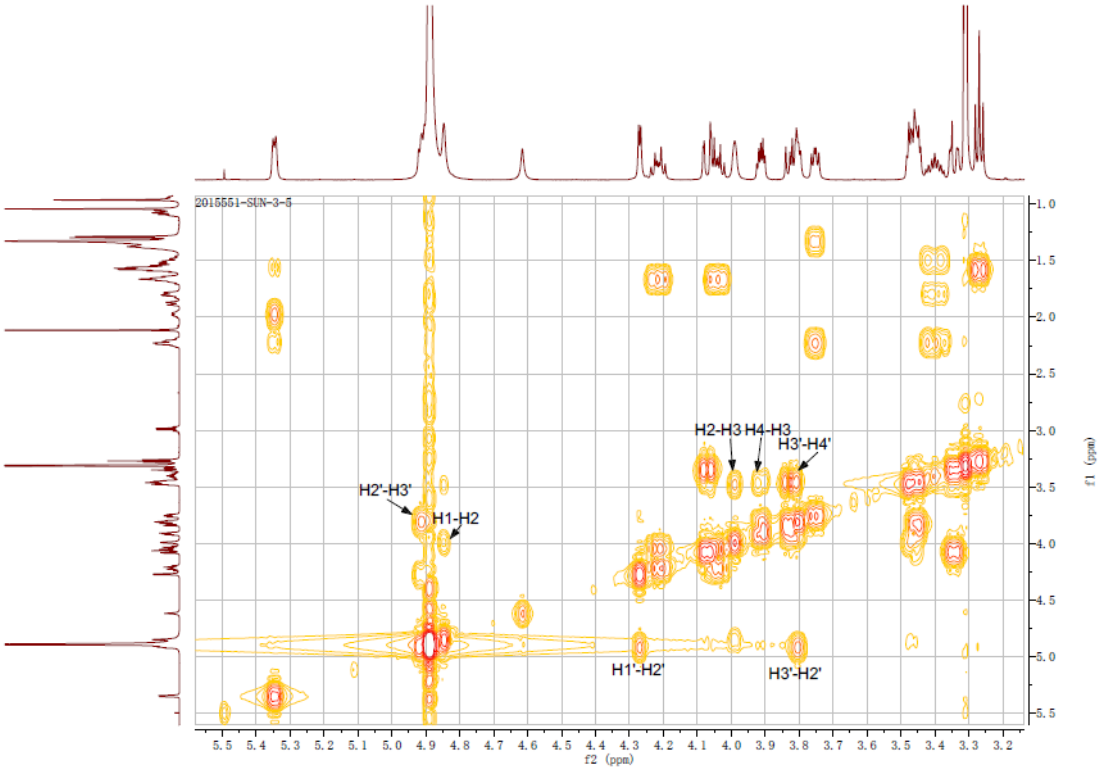
Compound **36**: ^{1}H NMR



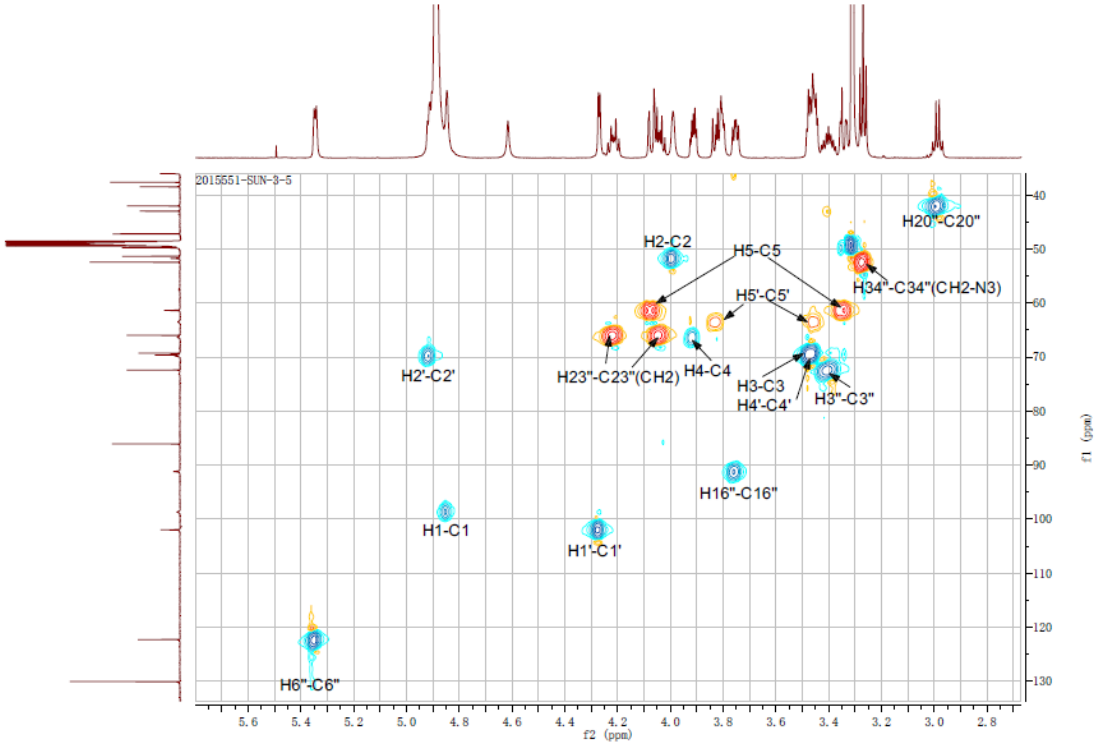
Compound **36**: ^{13}C NMR



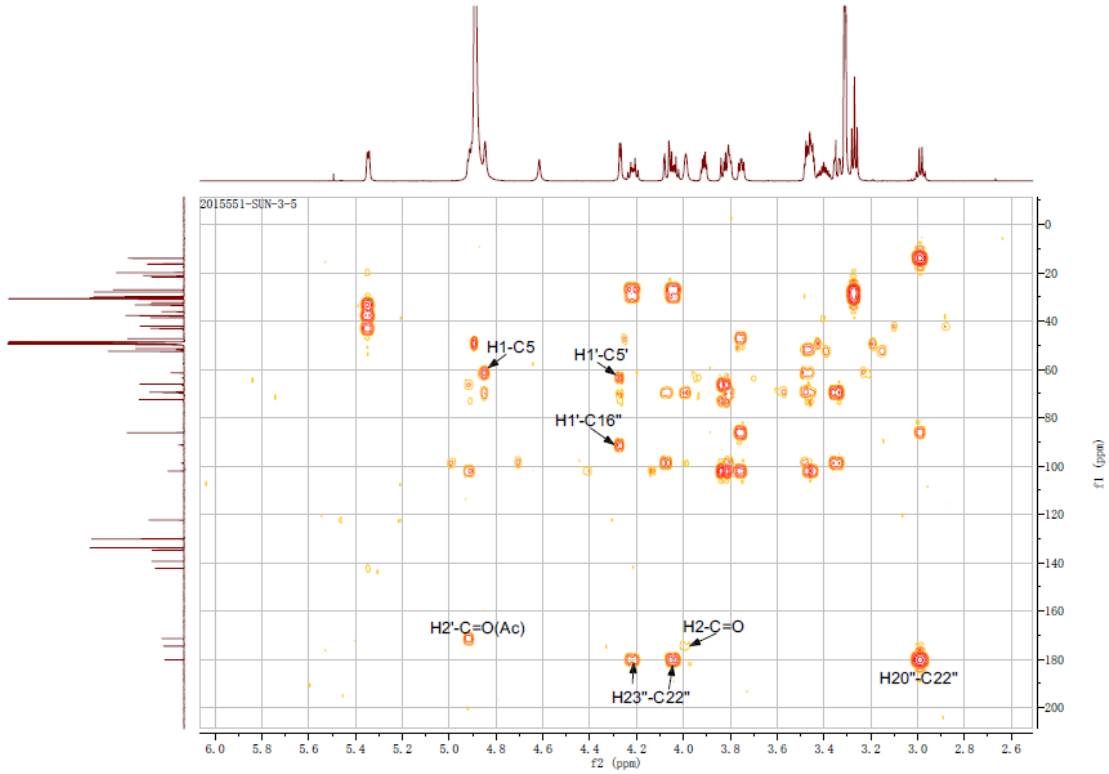
Compound **36**: COSY NMR



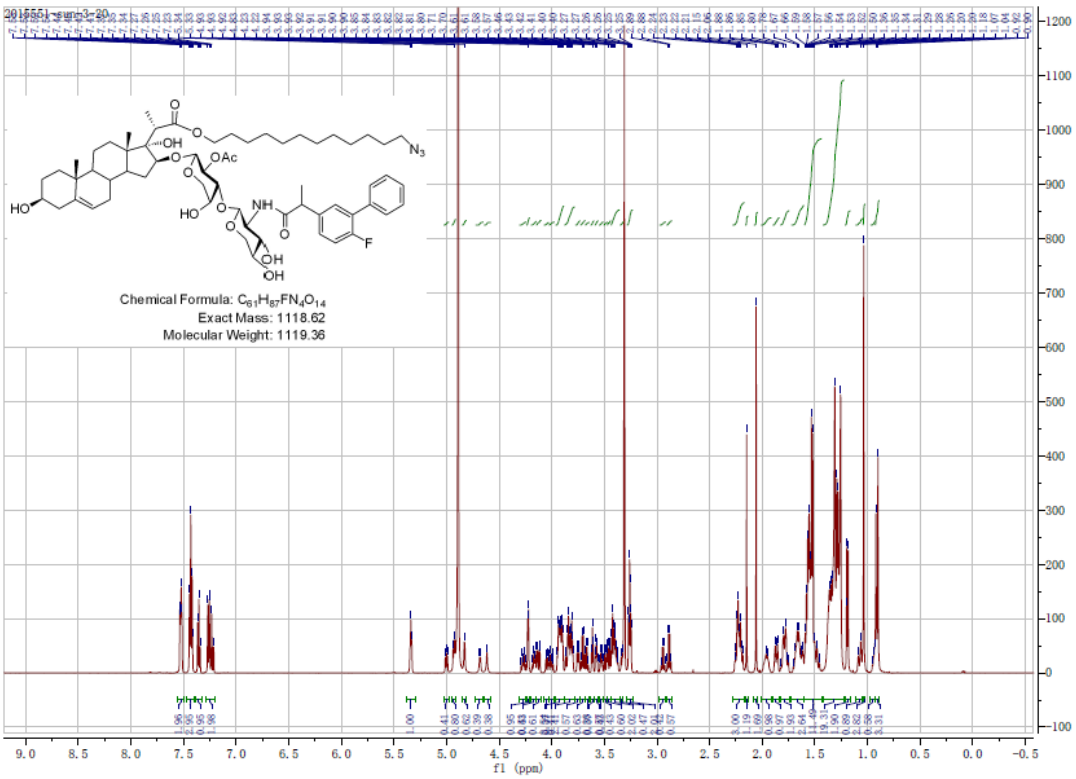
Compound **36**: HSQC NMR



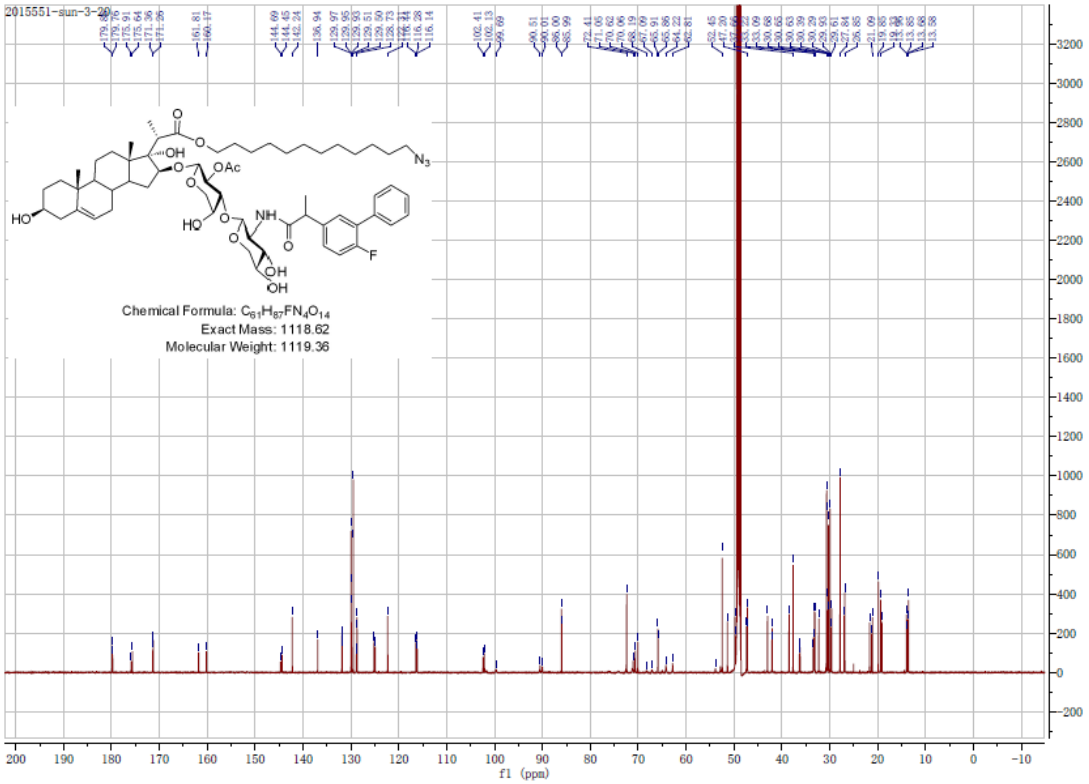
Compound **36**: HMBC NMR



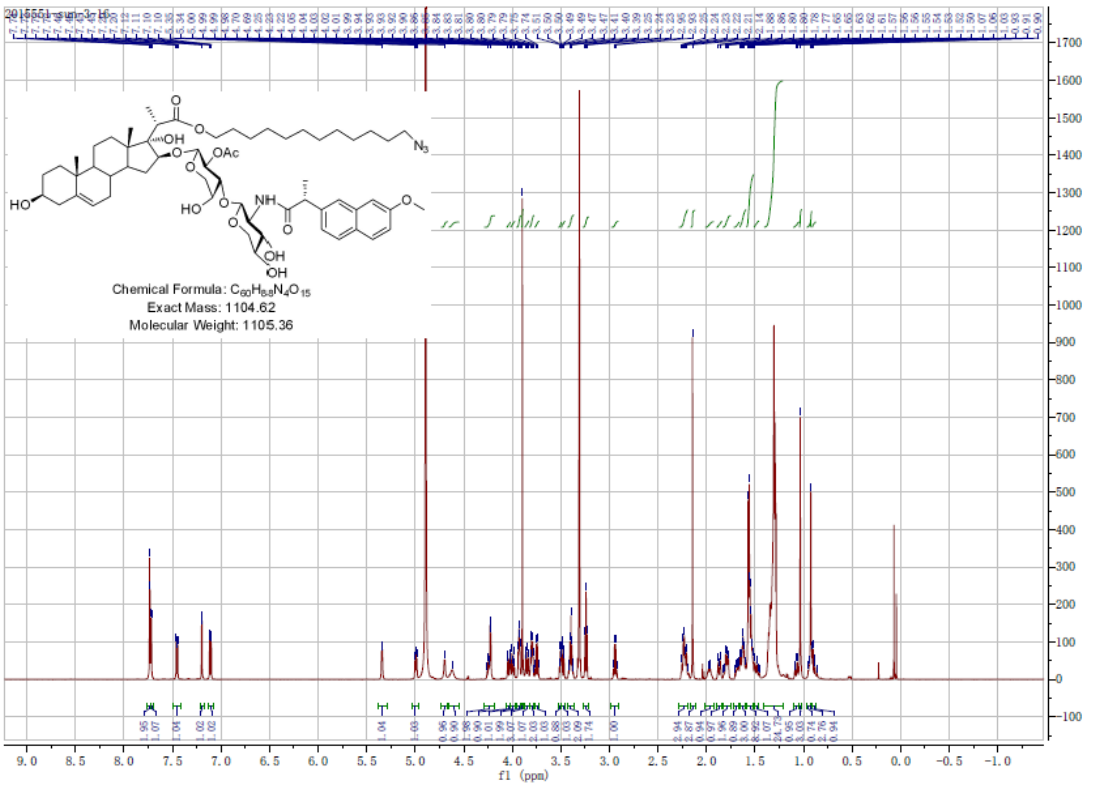
Compound **37**: ^{1}H NMR



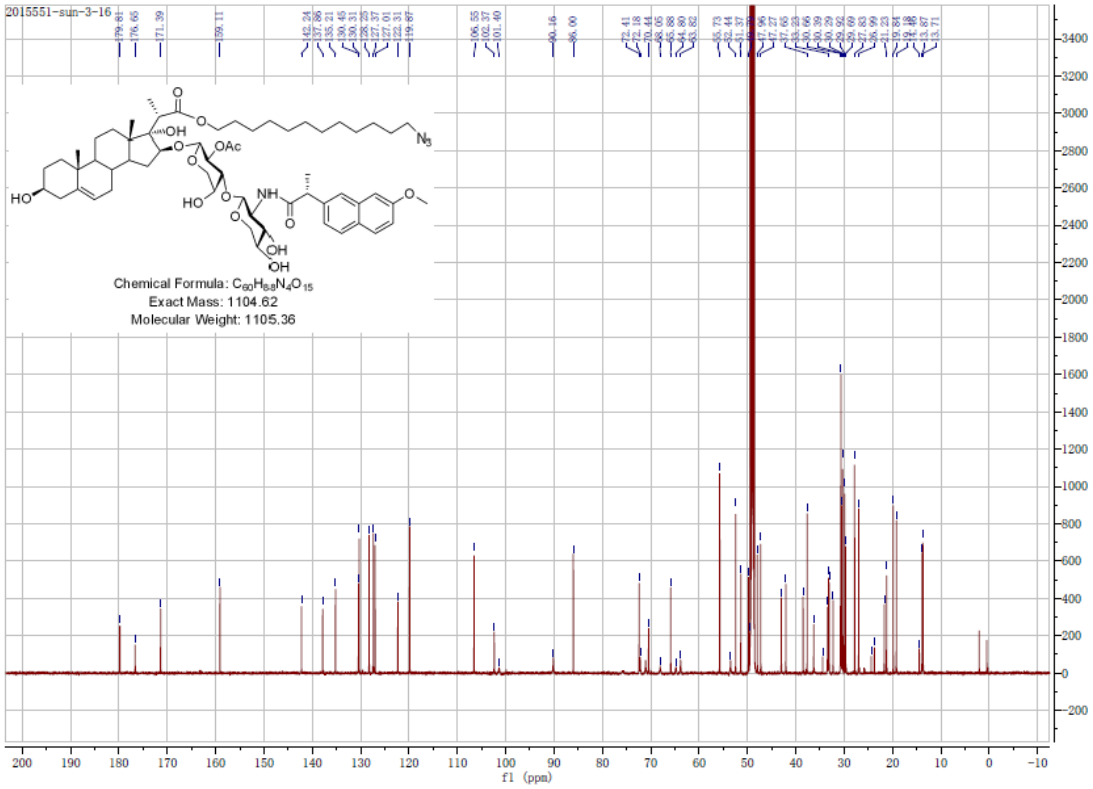
Compound **37**: ^{13}C NMR



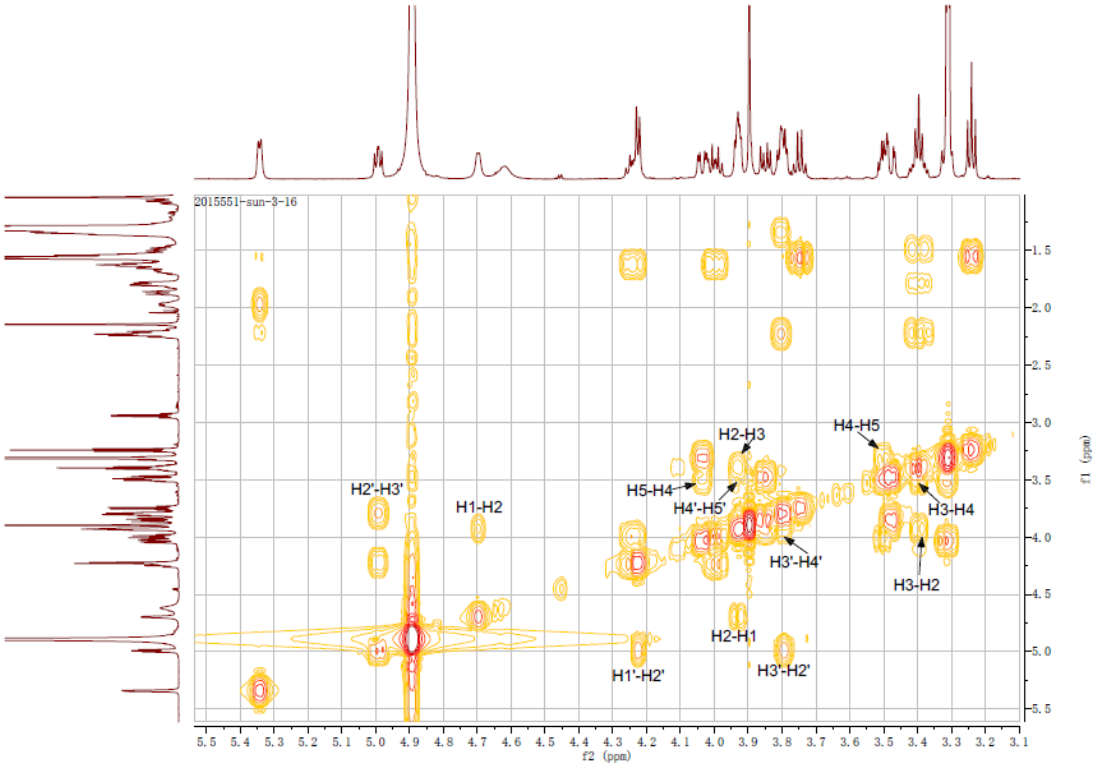
Compound **38**: ^{1}H NMR



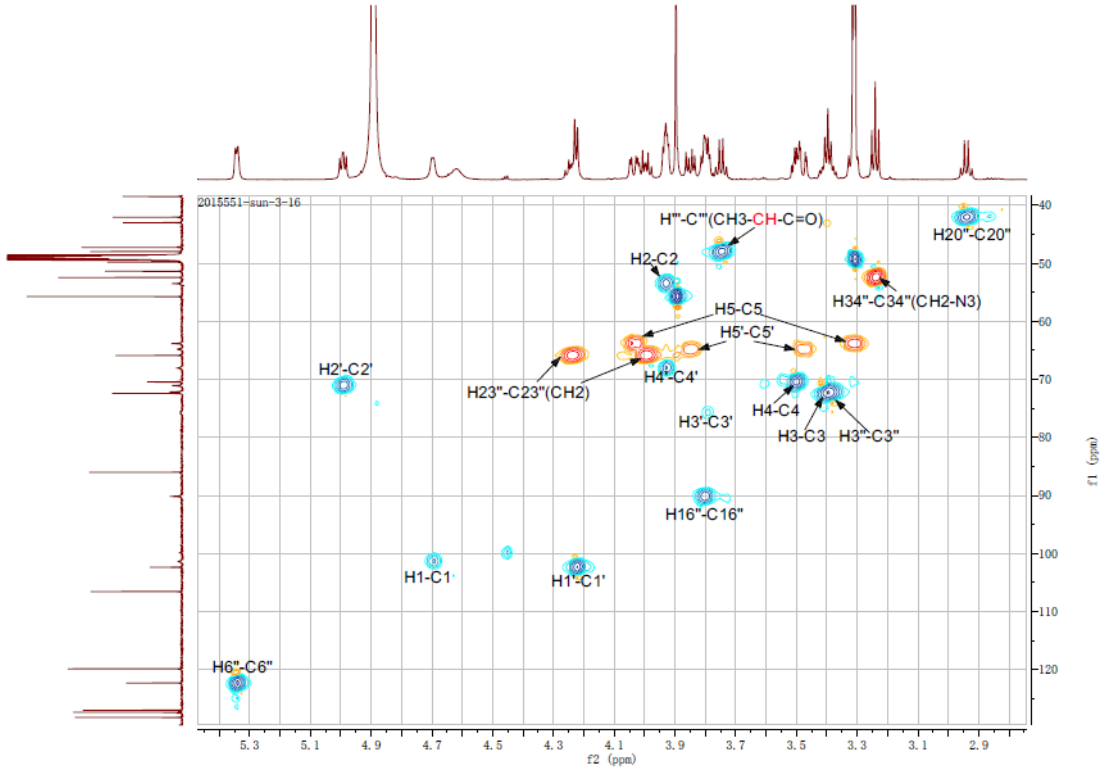
Compound **38**: ^{13}C NMR



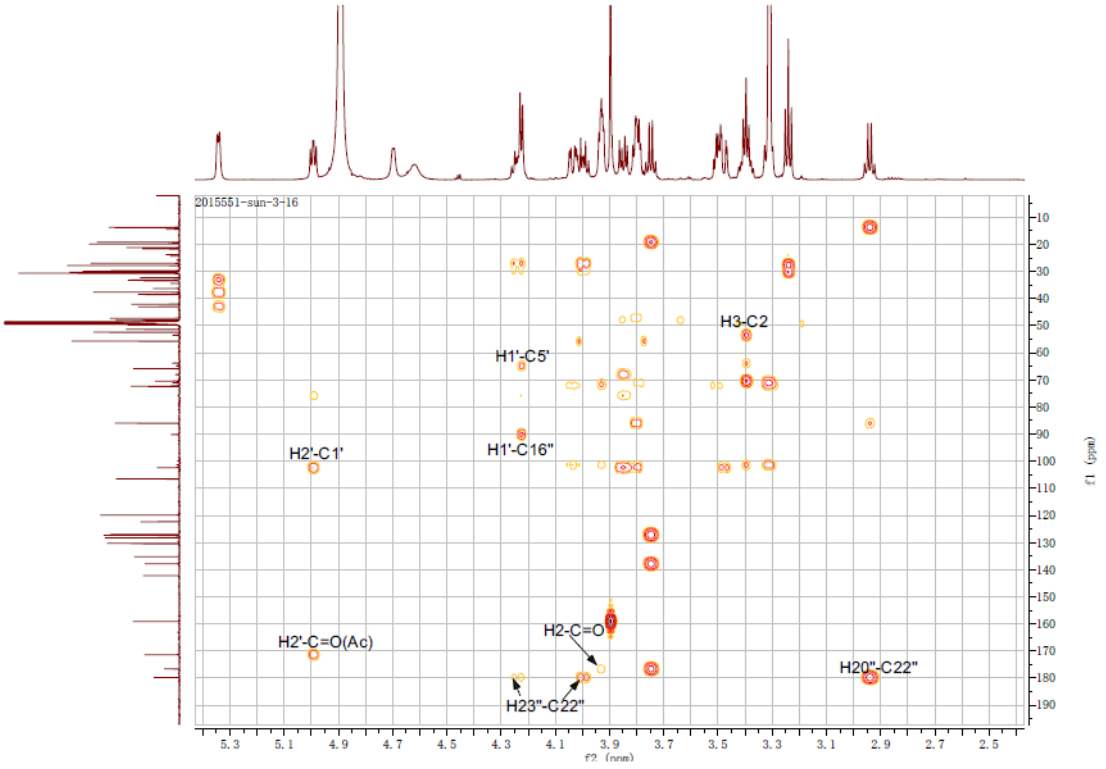
Compound **38**: COSY NMR



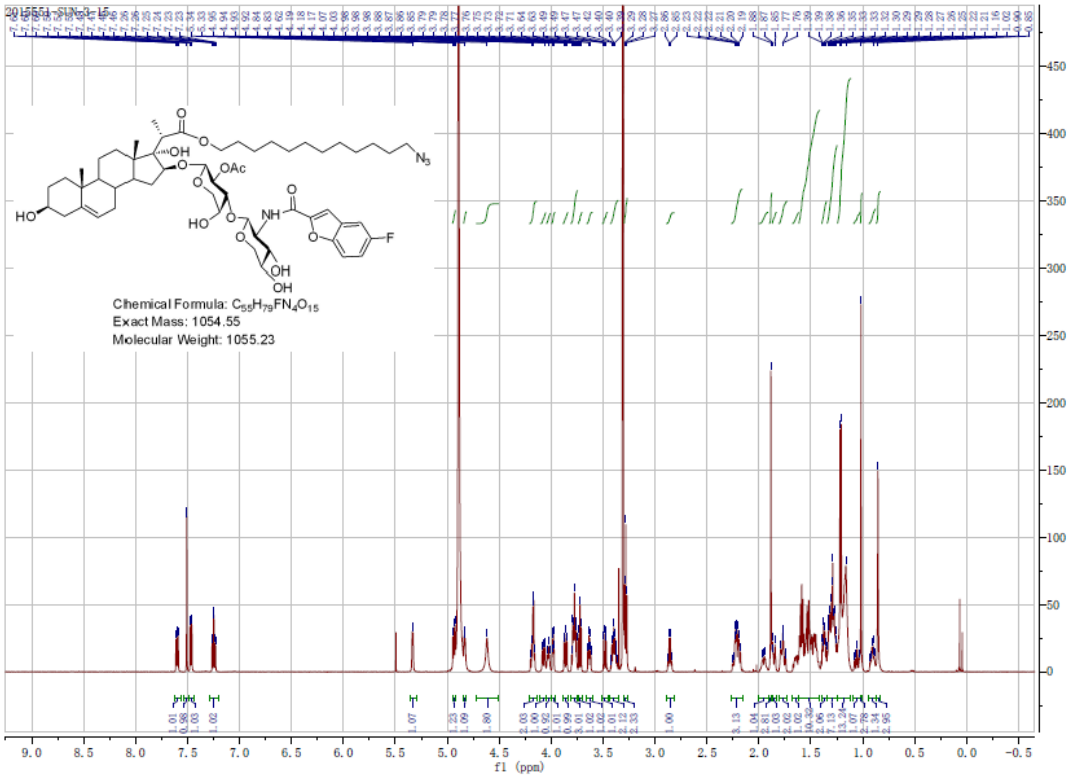
Compound **38**: HSQC NMR



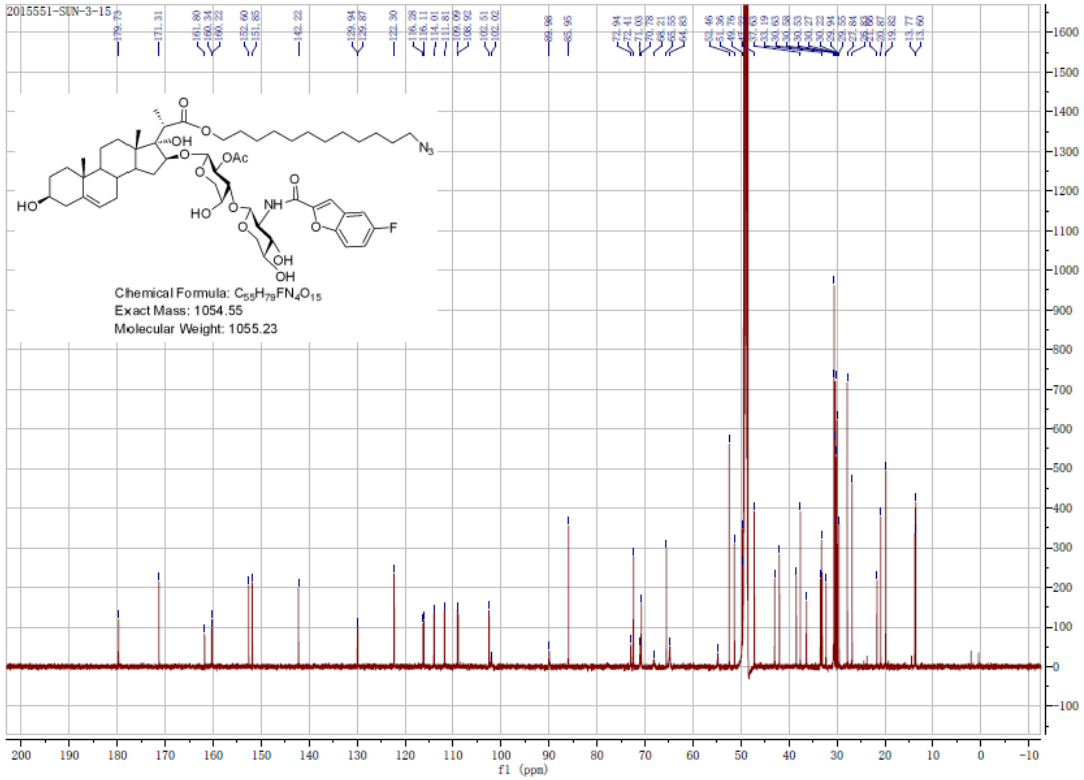
Compound **38**: HMBC NMR



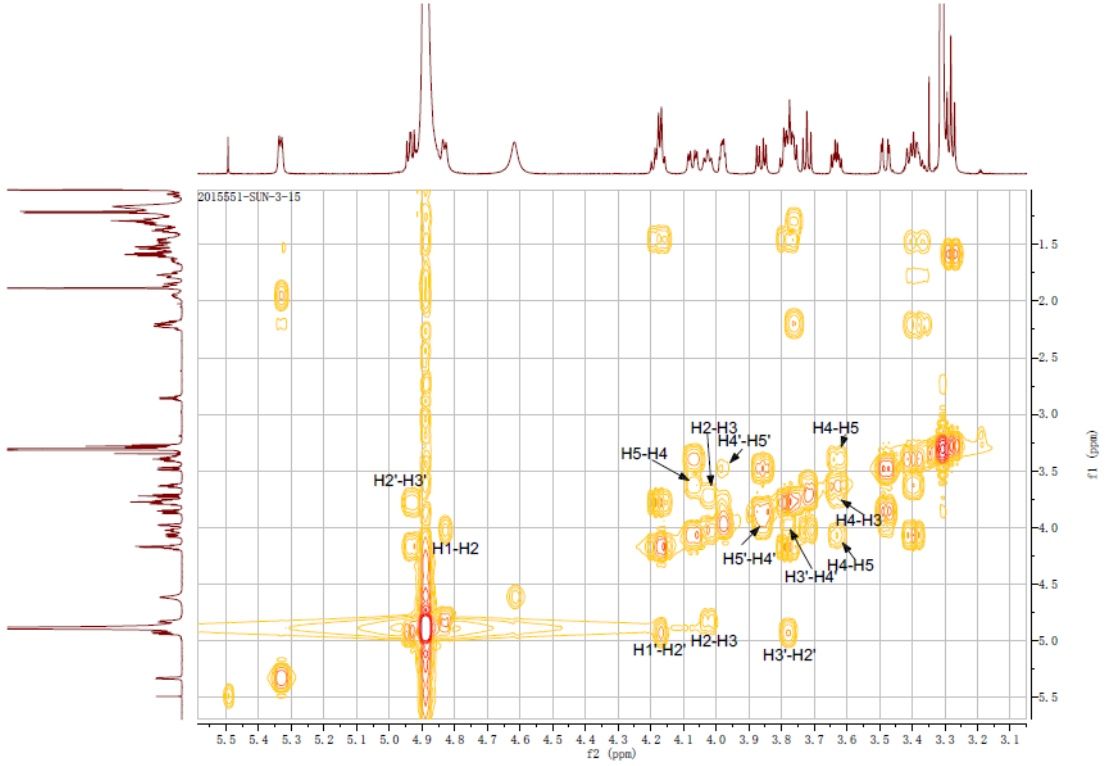
Compound **39**: ^{1}H NMR



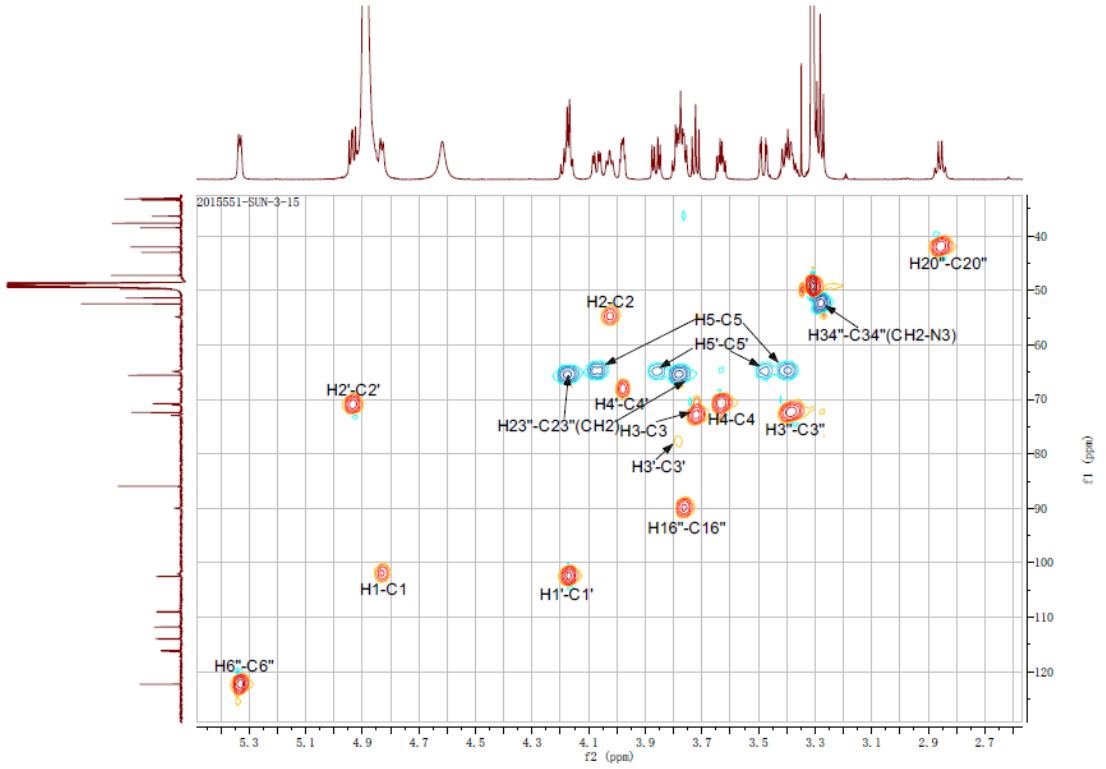
Compound **39**: ^{13}C NMR



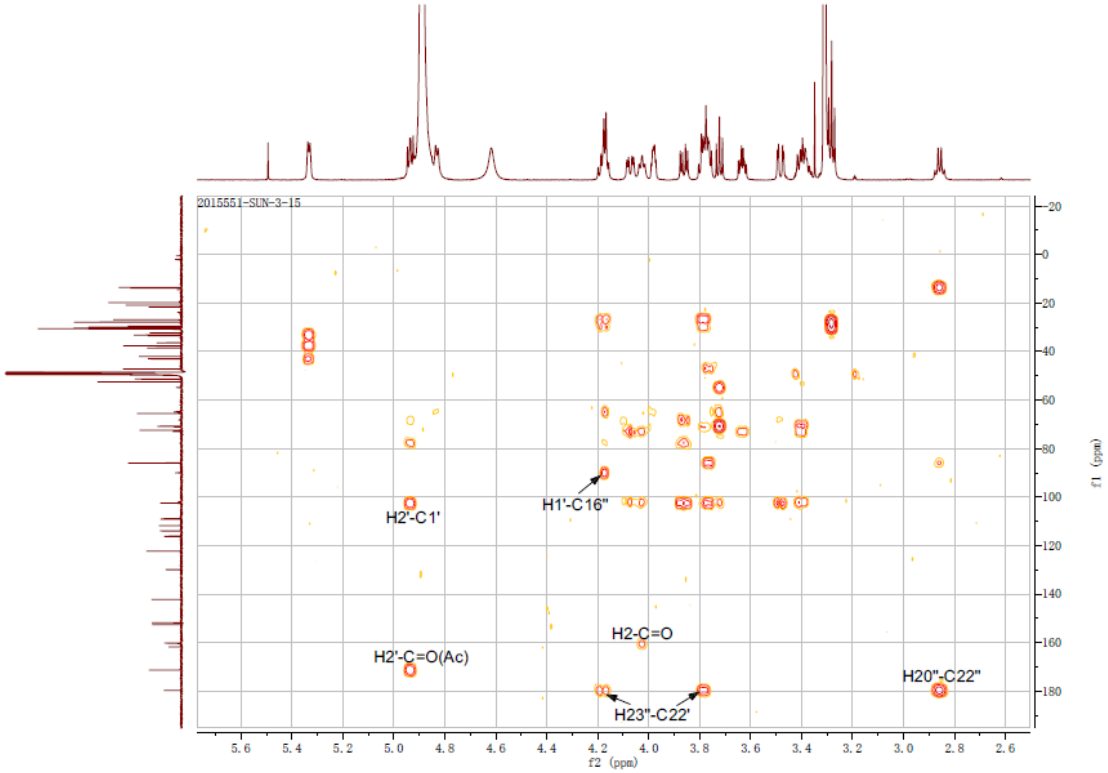
Compound **39**: COSY NMR



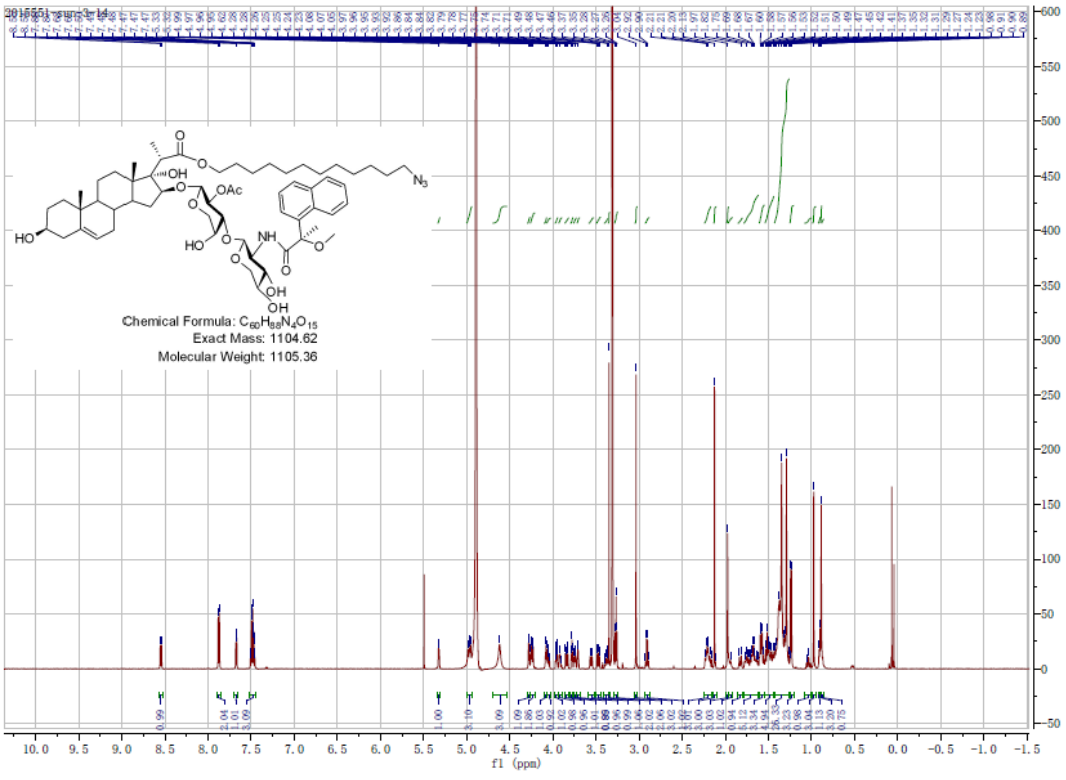
Compound **39**: HSQC NMR



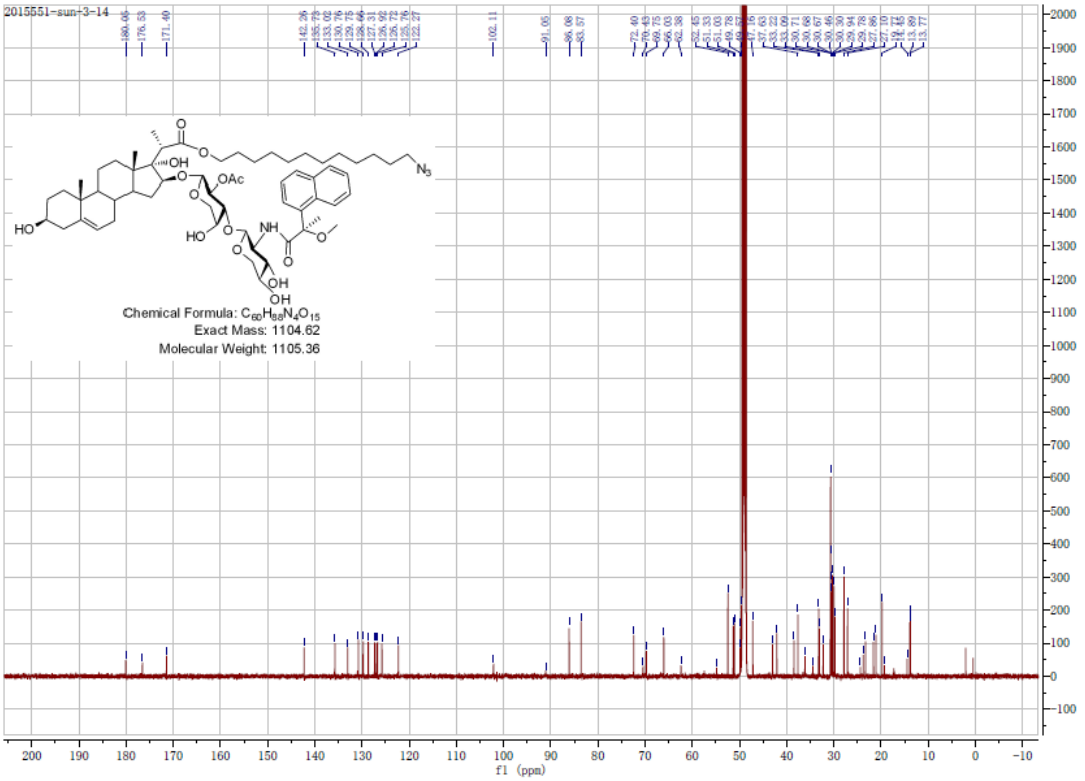
Compound **39**: HMBC NMR



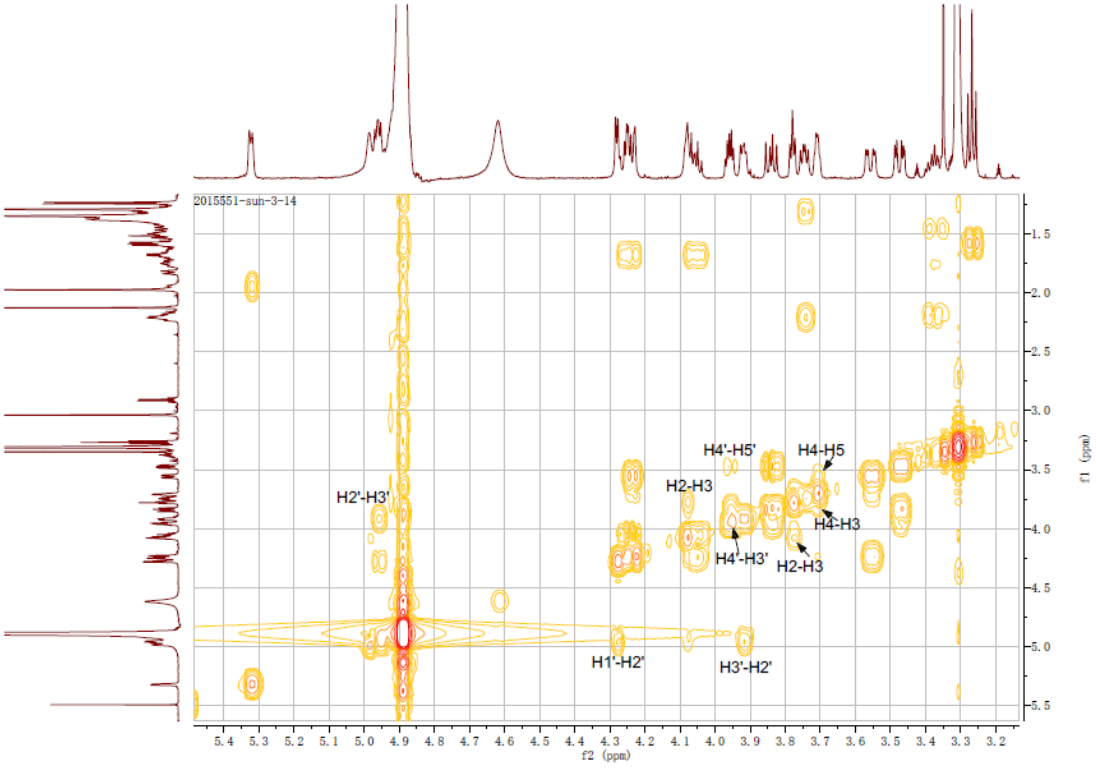
Compound **40**: ^{1}H NMR



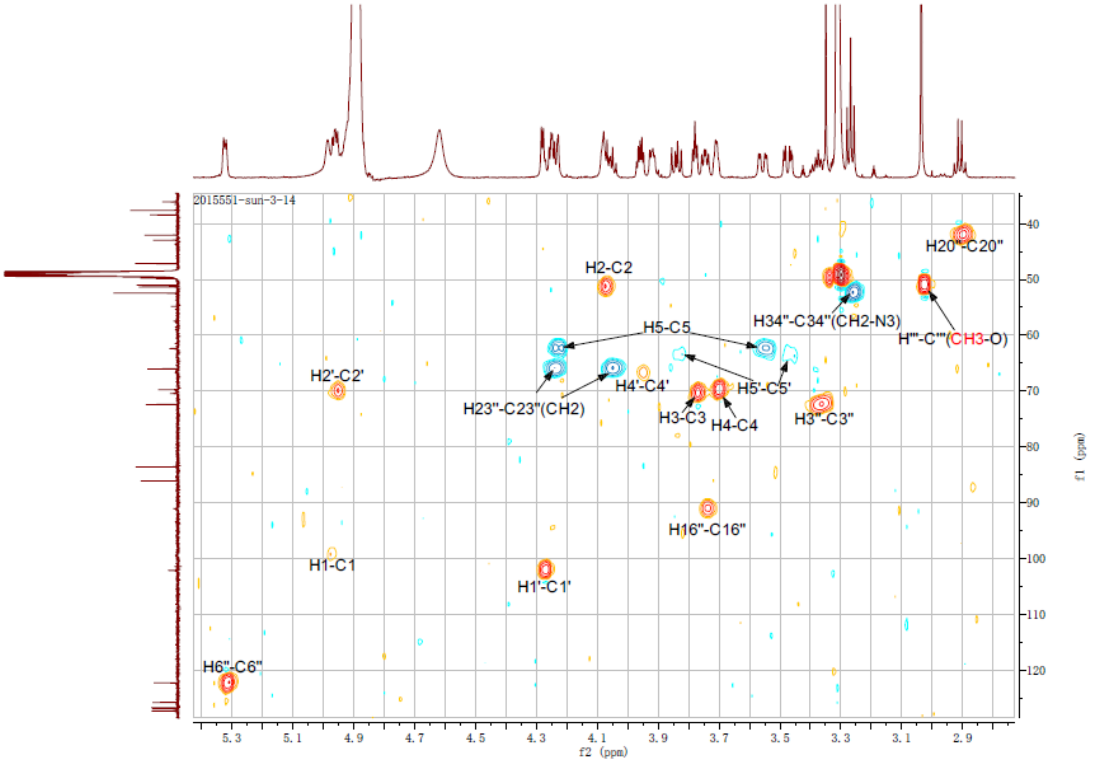
Compound **40**: ^{13}C NMR



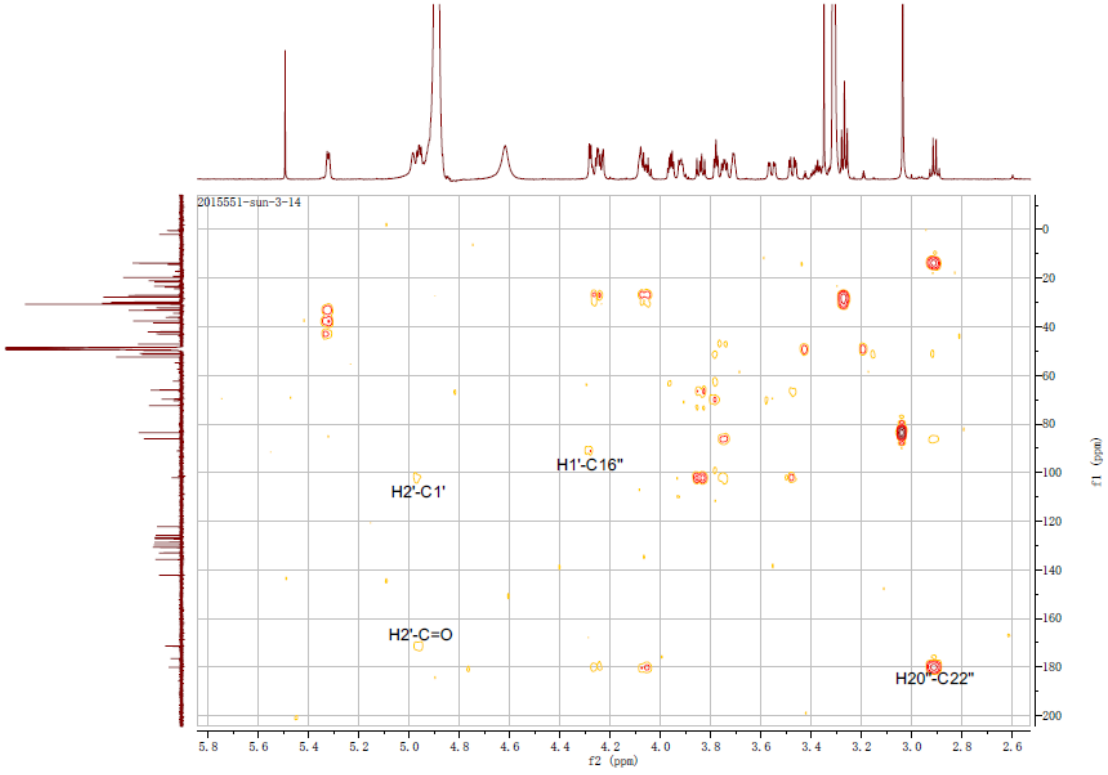
Compound **40**: COSY NMR



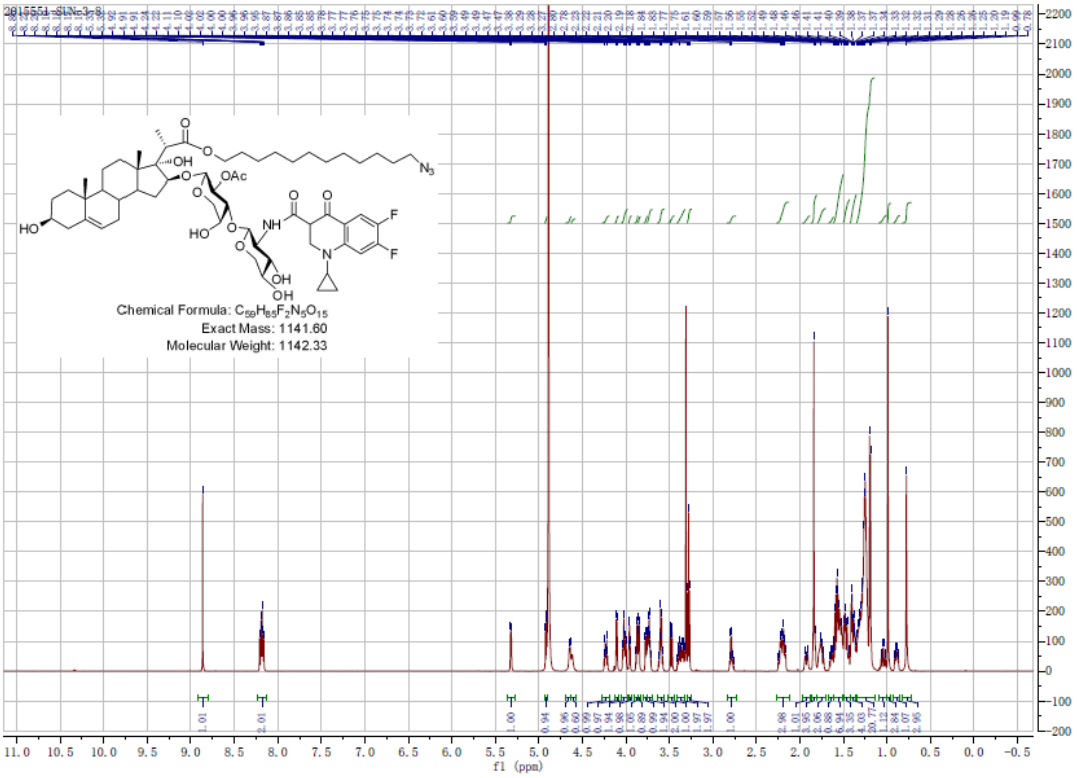
Compound **40**: HSQC NMR



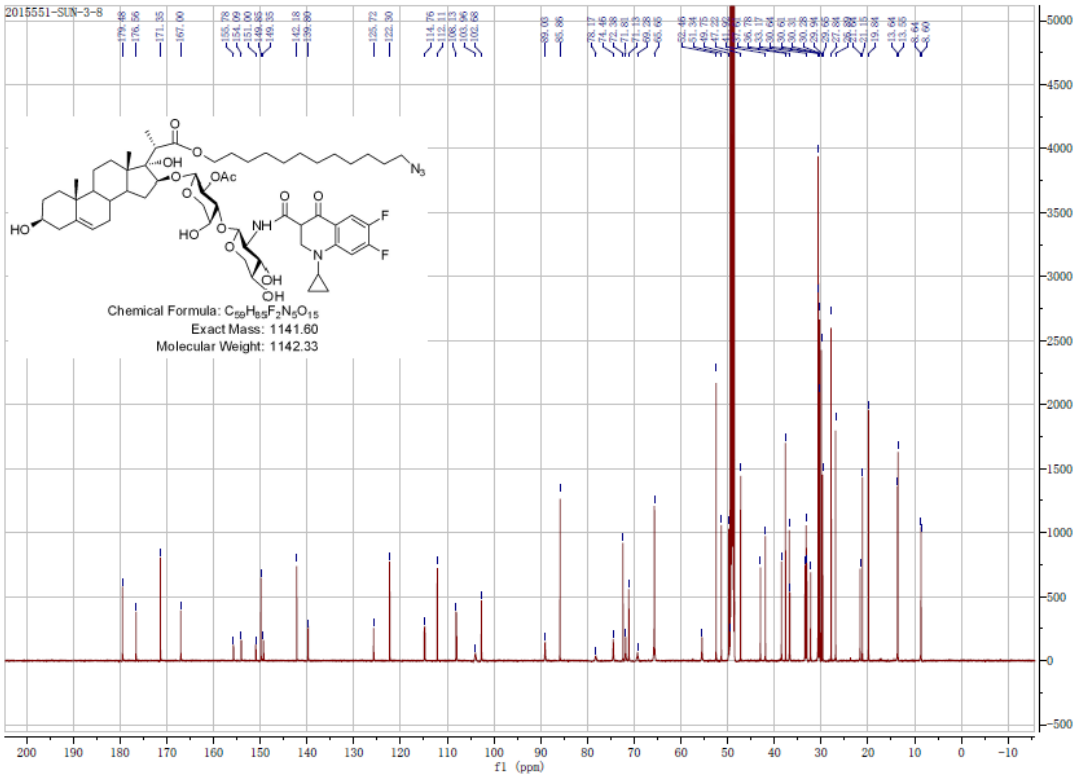
Compound **40**: HMBC NMR



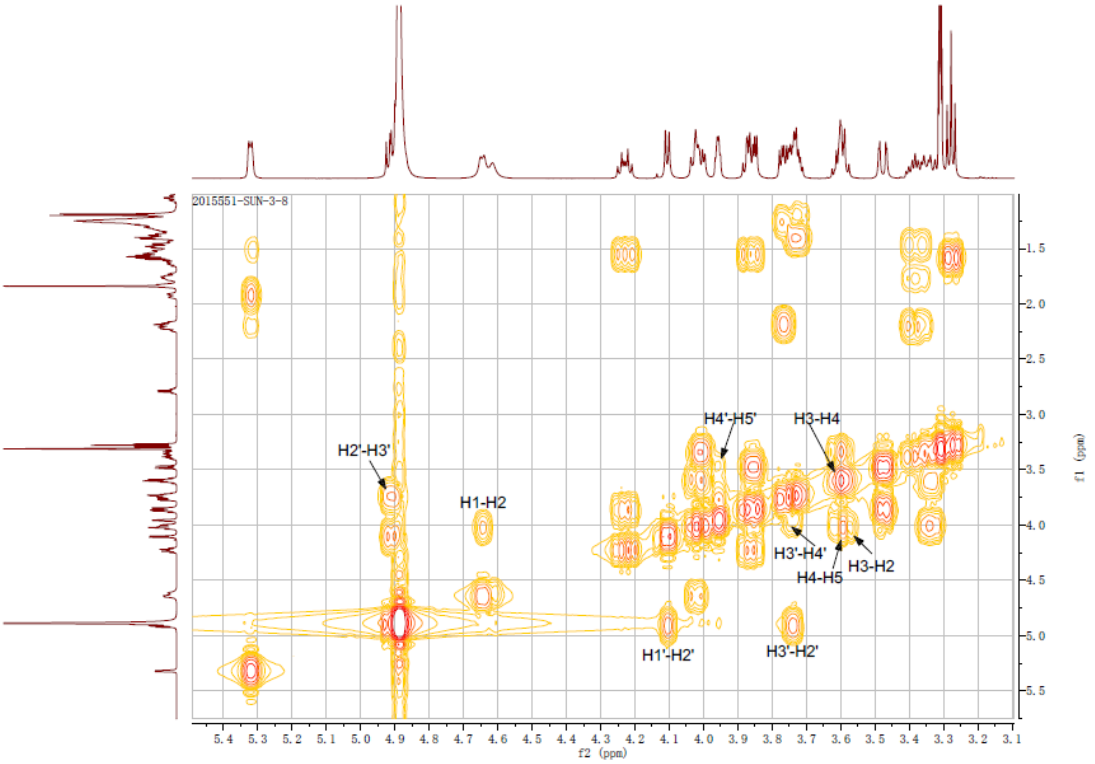
Compound **41**: ^{1}H NMR



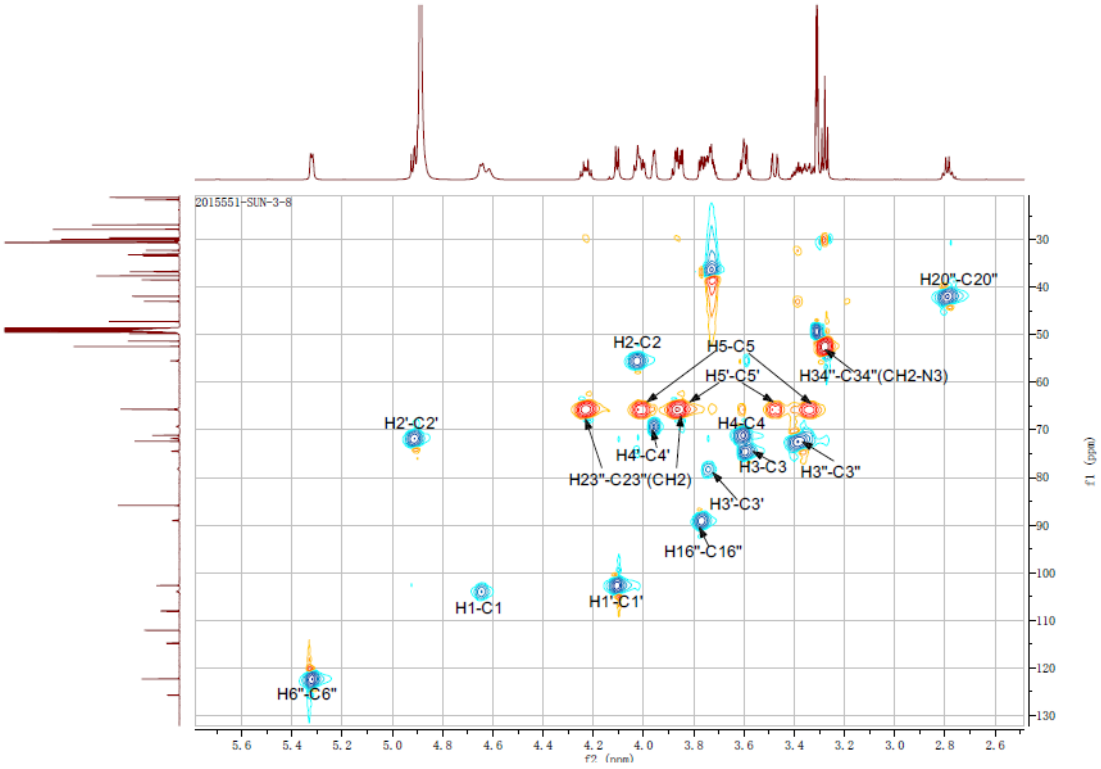
Compound **41**: ^{13}C NMR



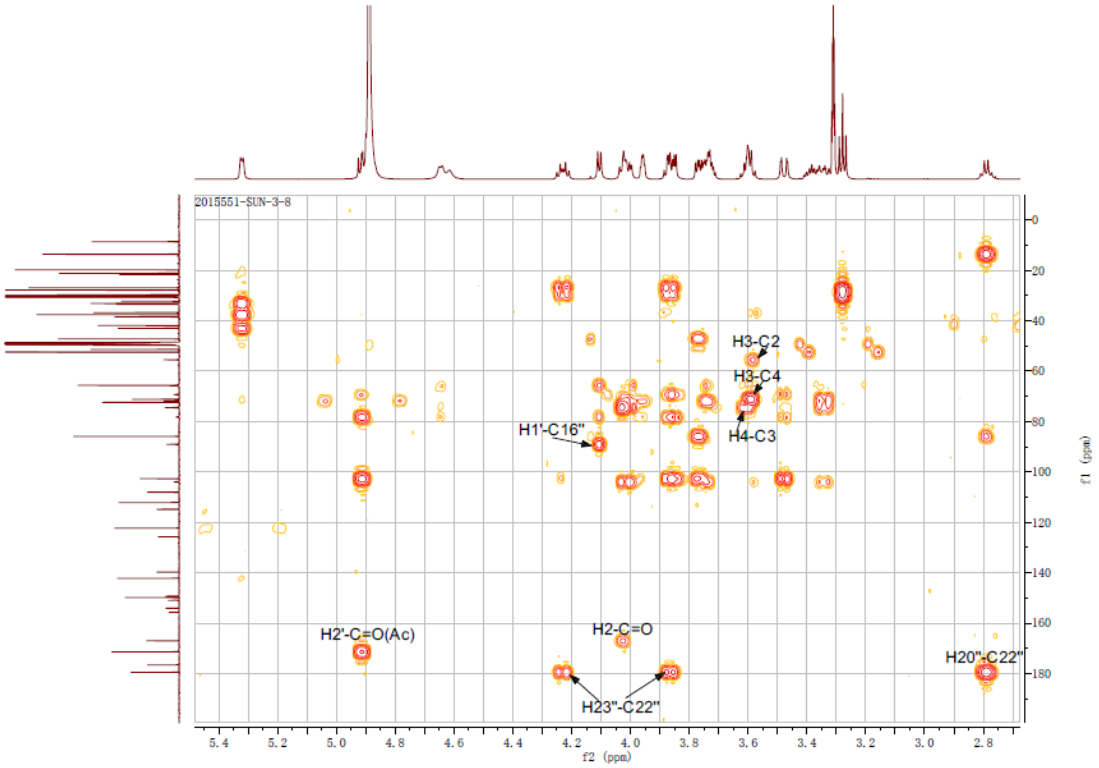
Compound **41**: COSY NMR



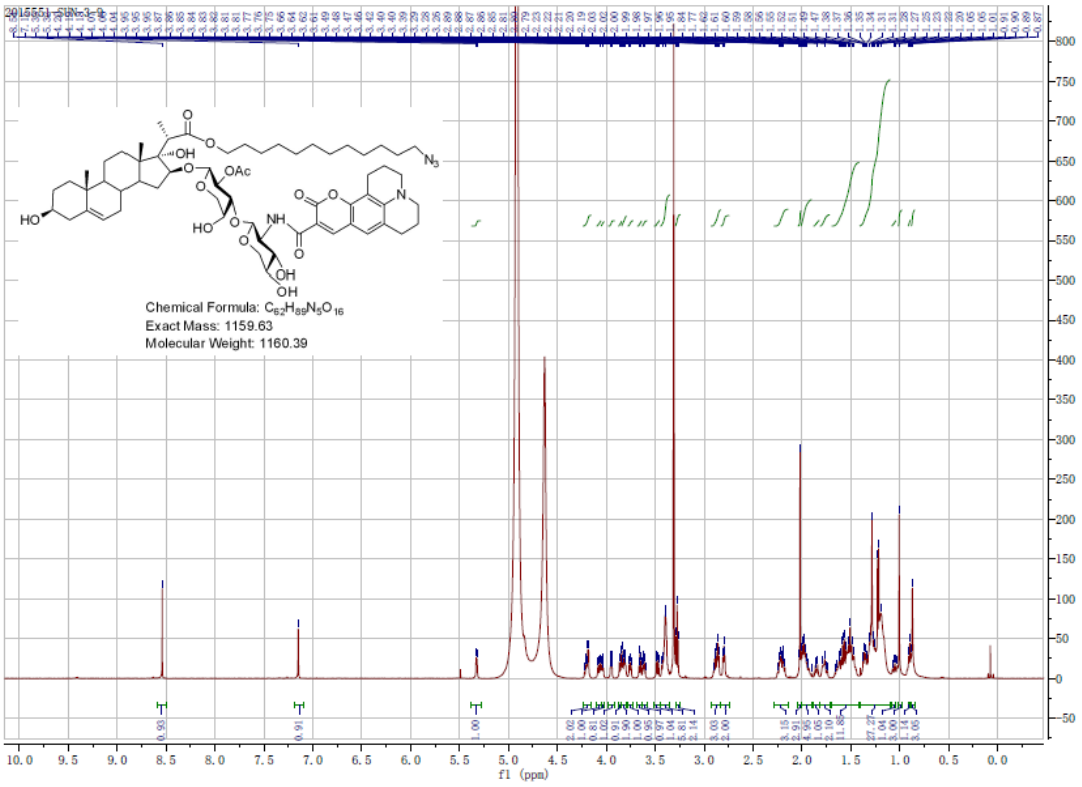
Compound **41**: HSQC NMR



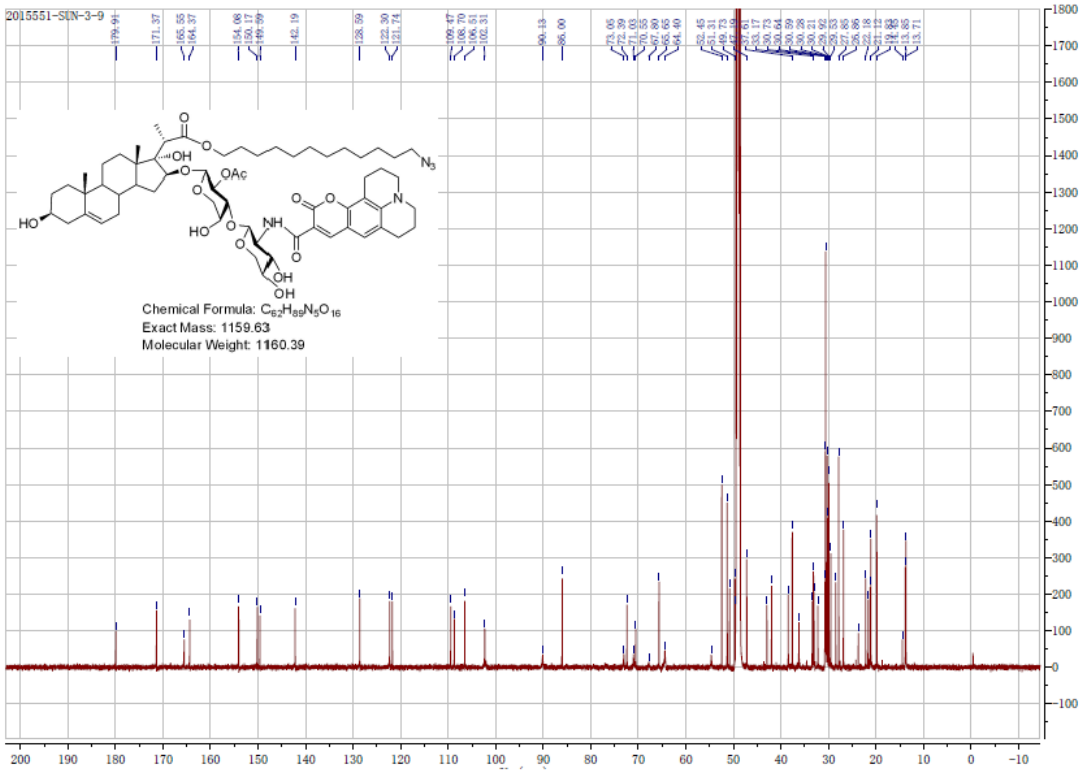
Compound **41**: HMBC NMR



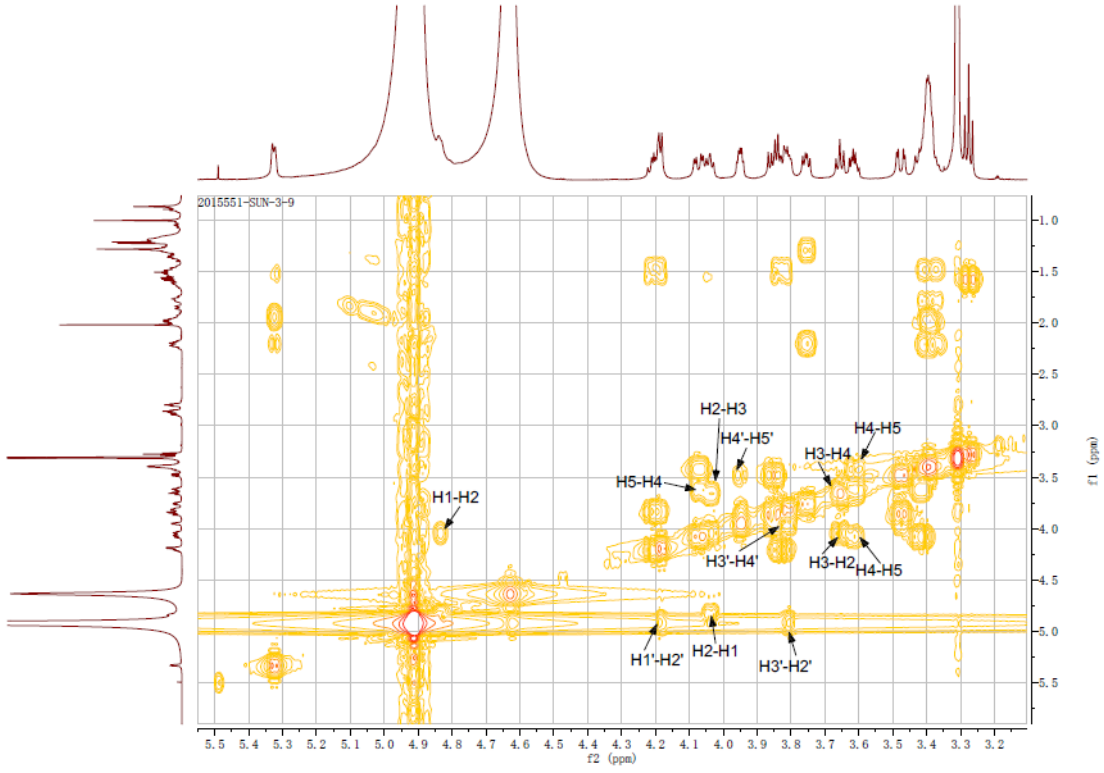
Compound **42**: ^{1}H NMR



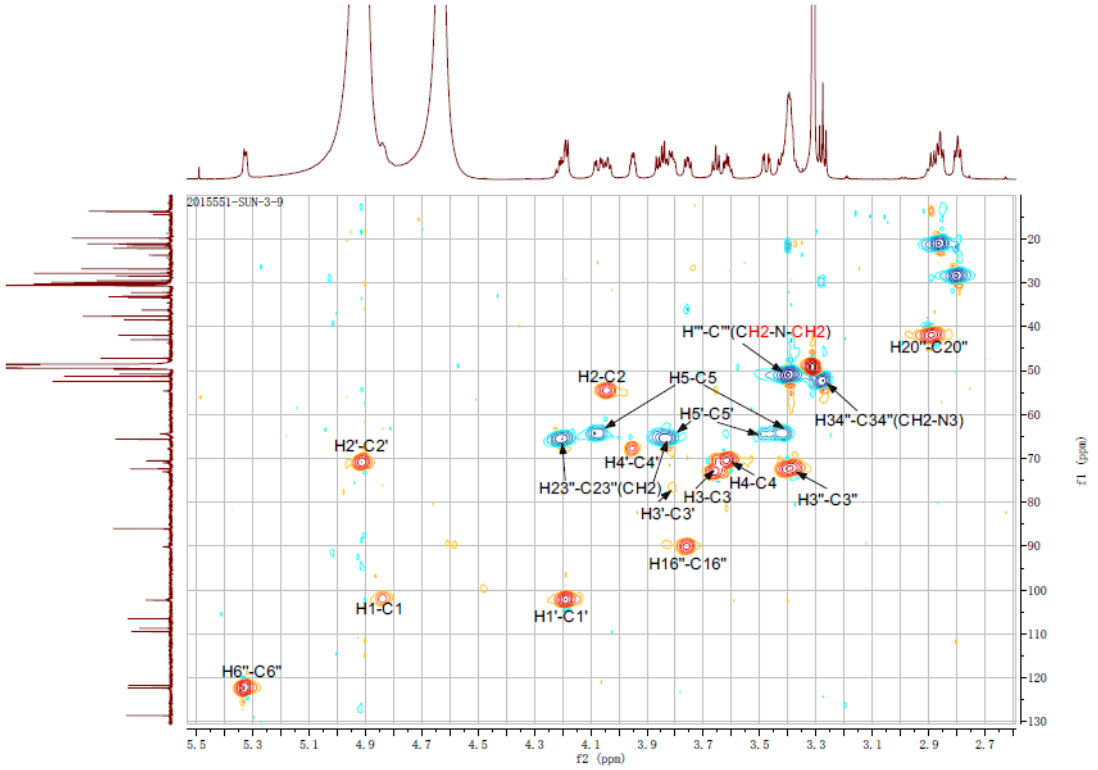
Compound **42**: ^{13}C NMR



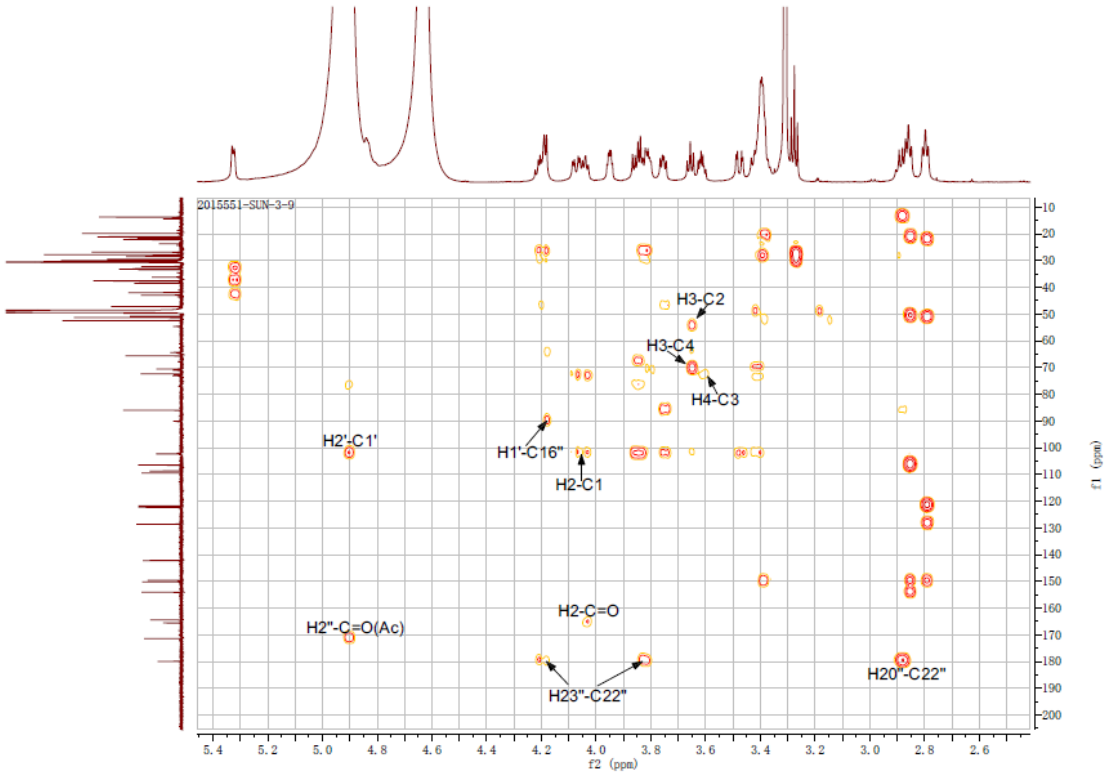
Compound **42**: COSY NMR



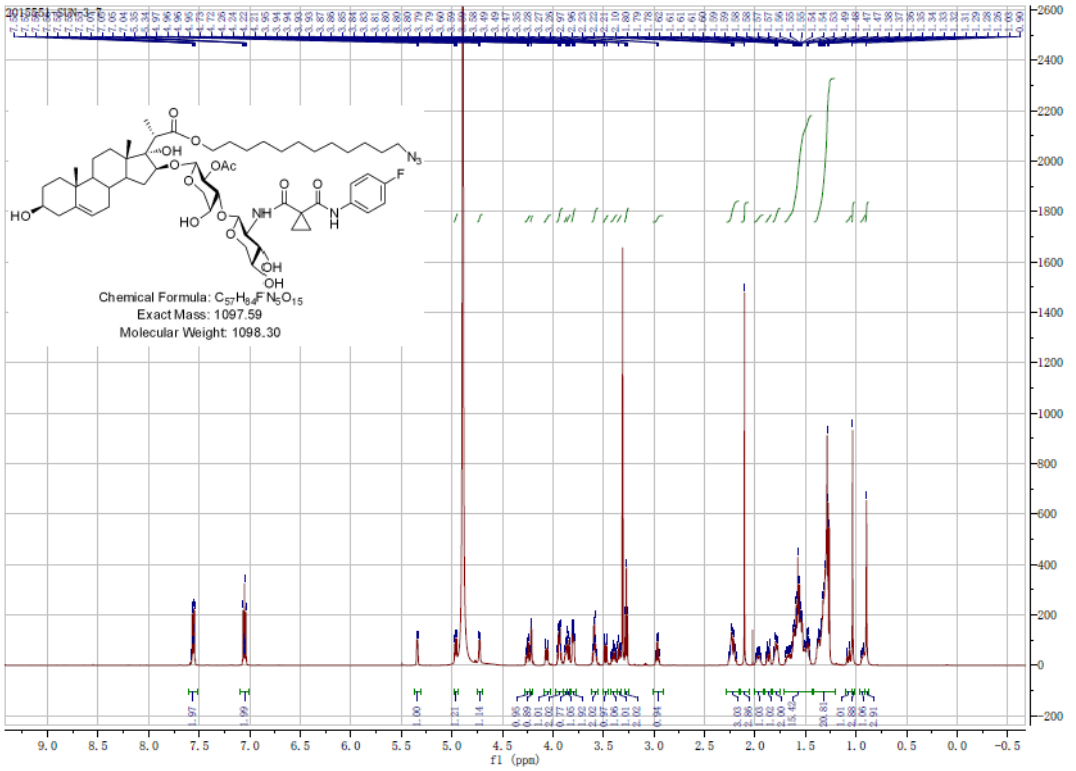
Compound **42**: HSQC NMR



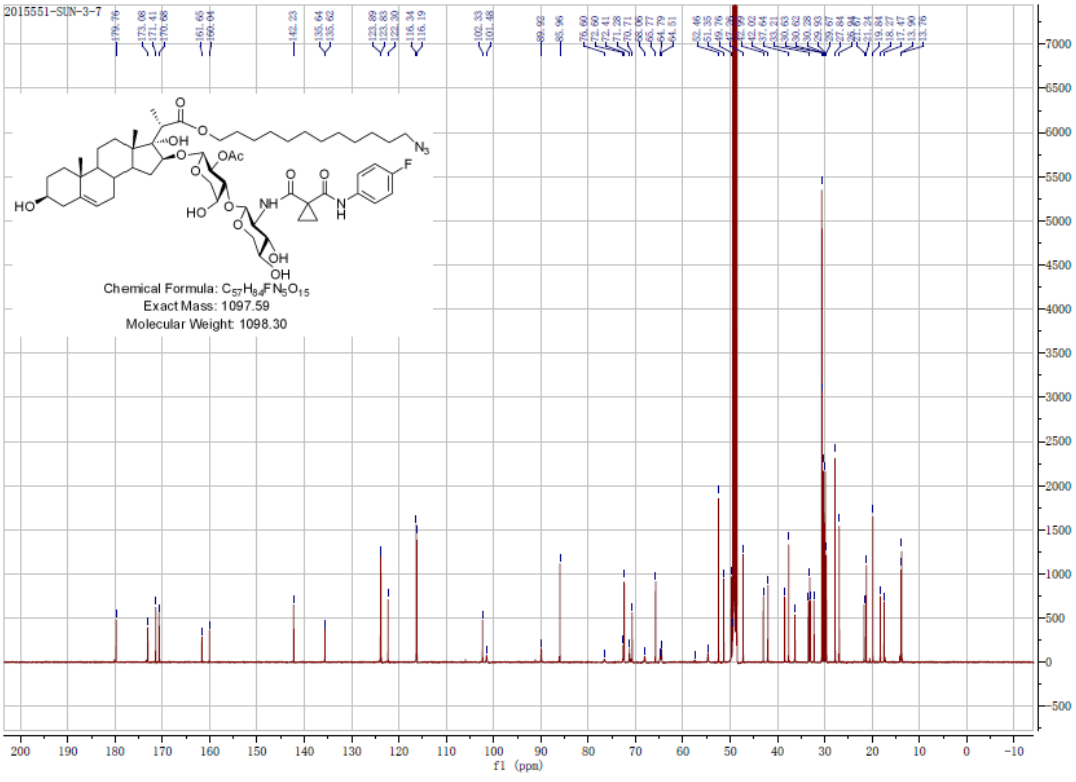
Compound **42**: HMBC NMR



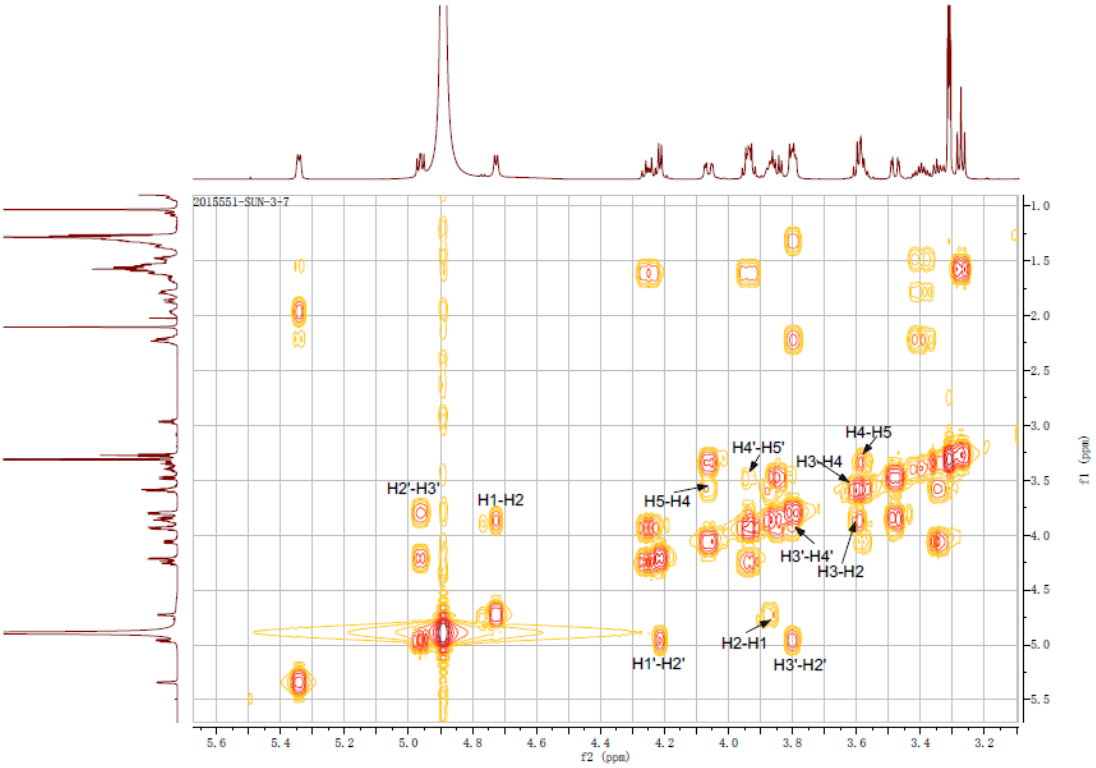
Compound **43**: ^{1}H NMR



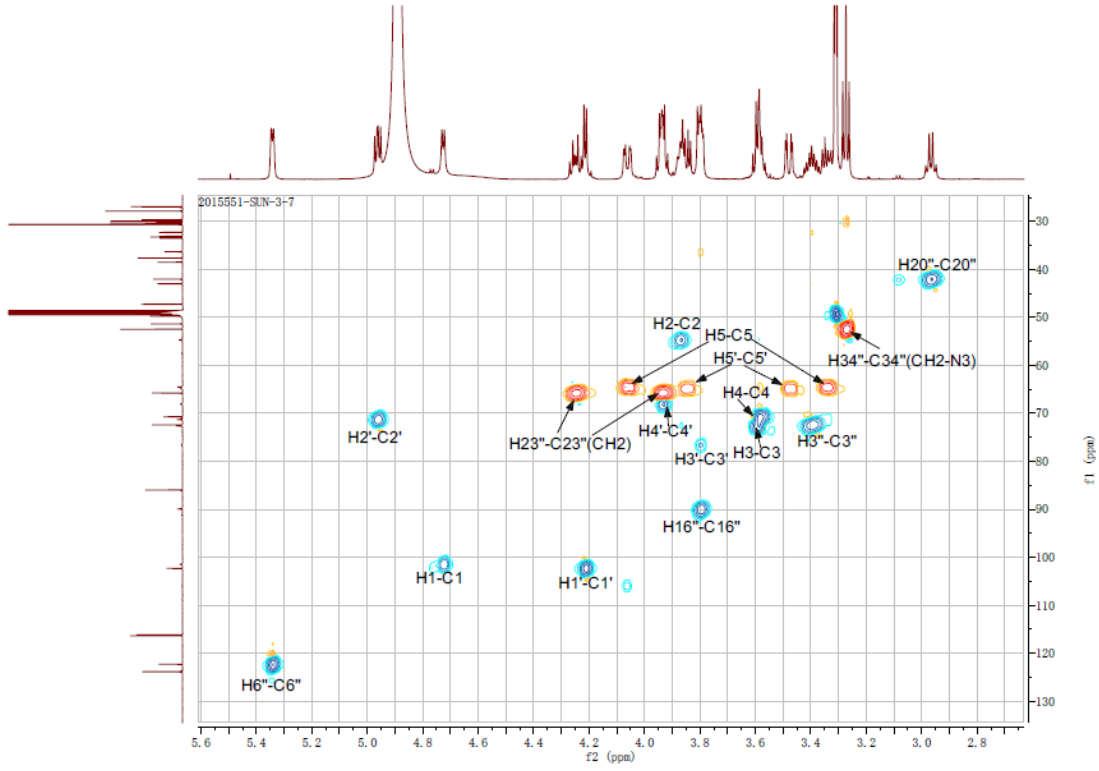
Compound **43**: ^{13}C NMR



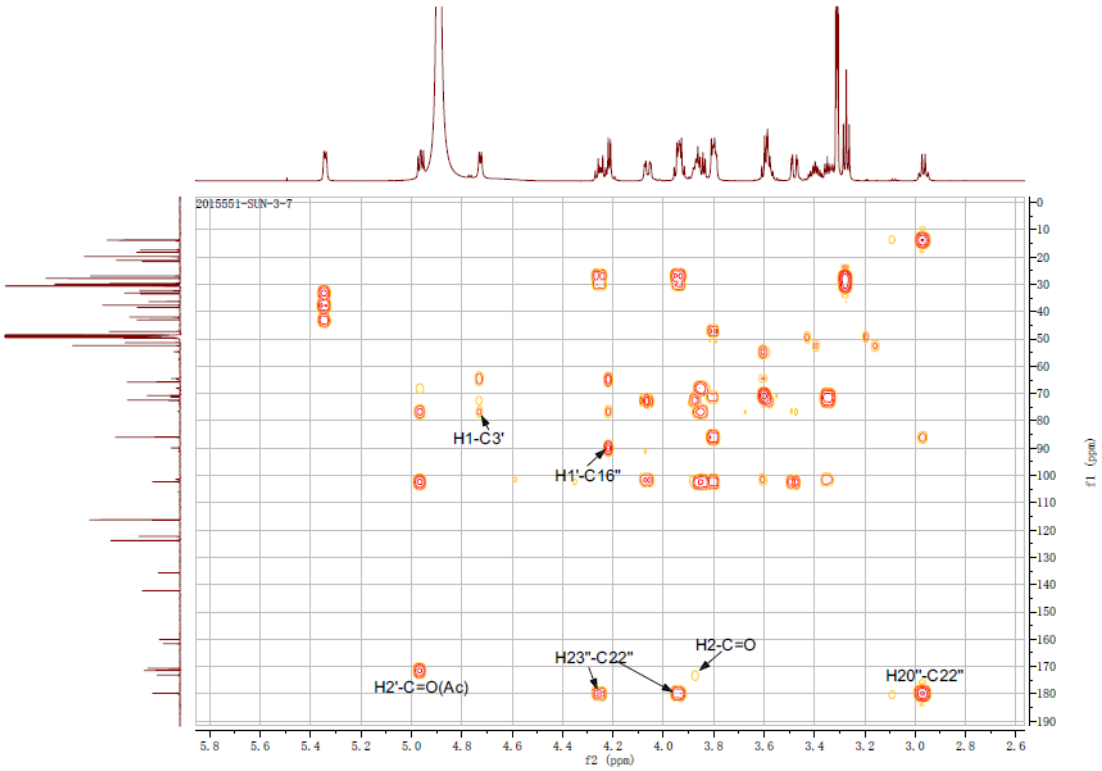
Compound **43**: COSY NMR



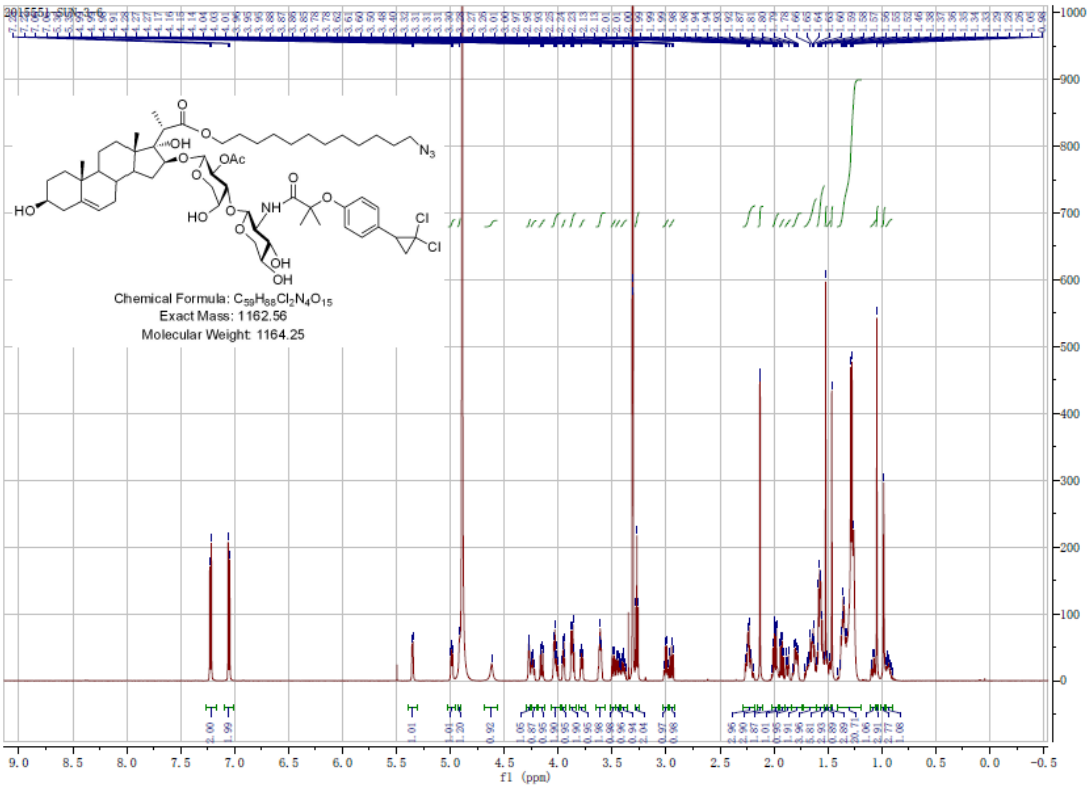
Compound **43**: HSQC NMR



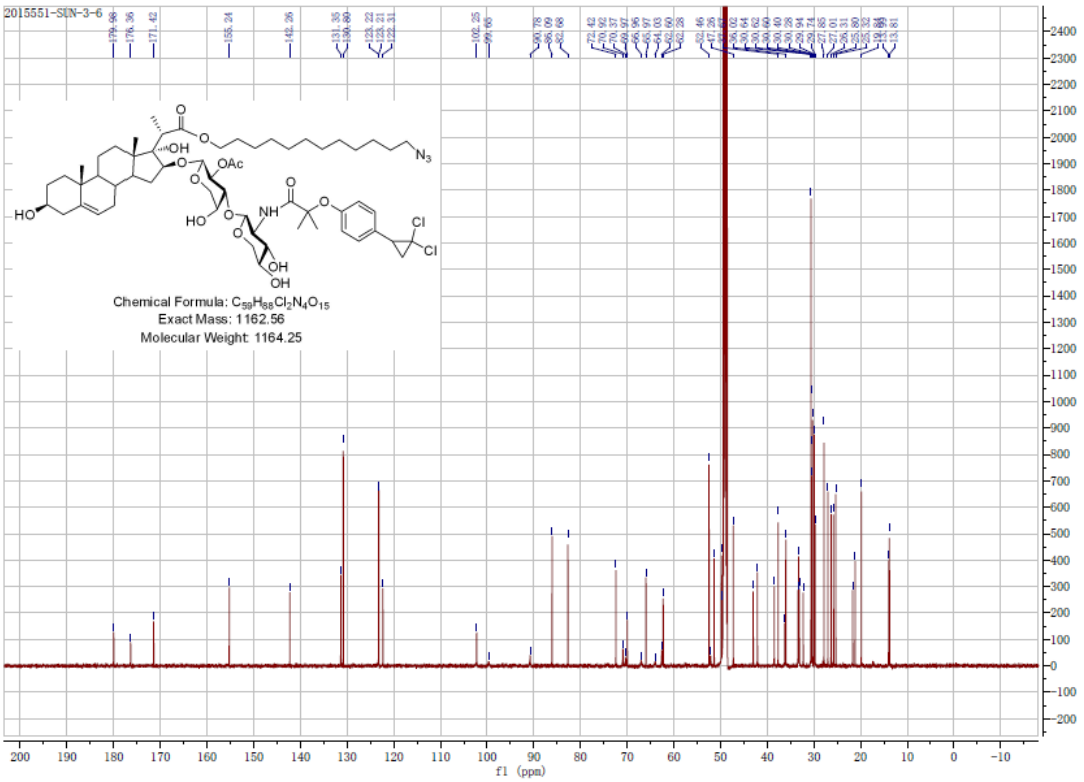
Compound **43**: HMBC NMR



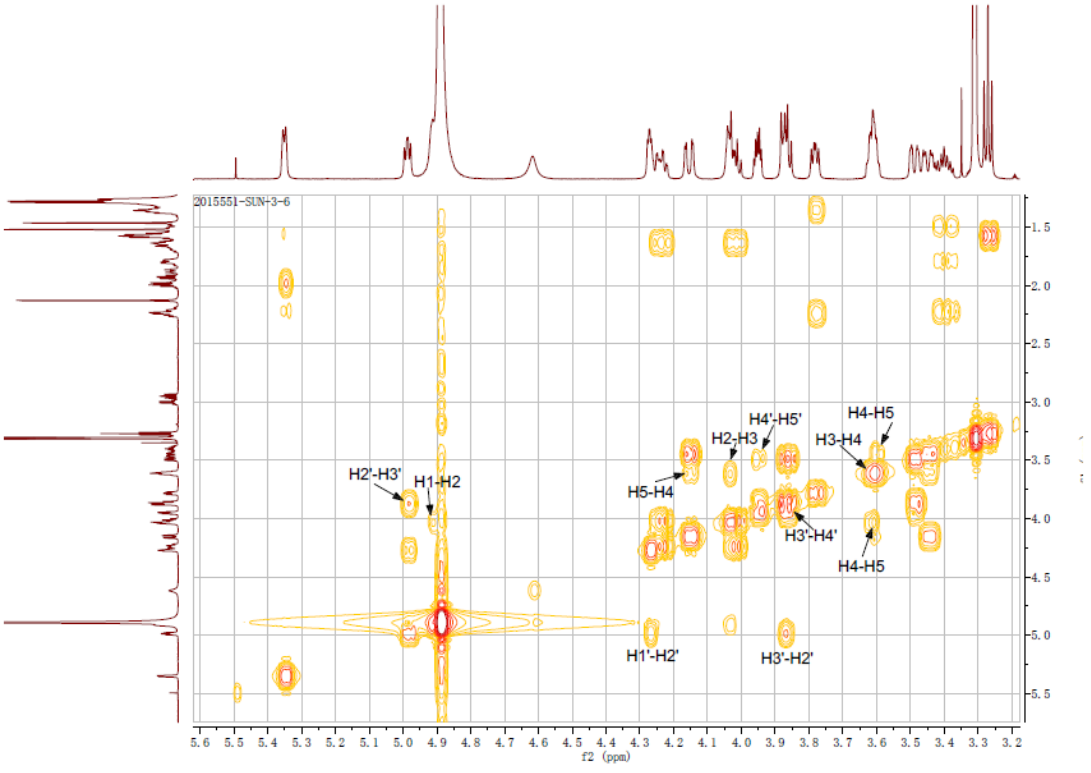
Compound **44**: ^{1}H NMR



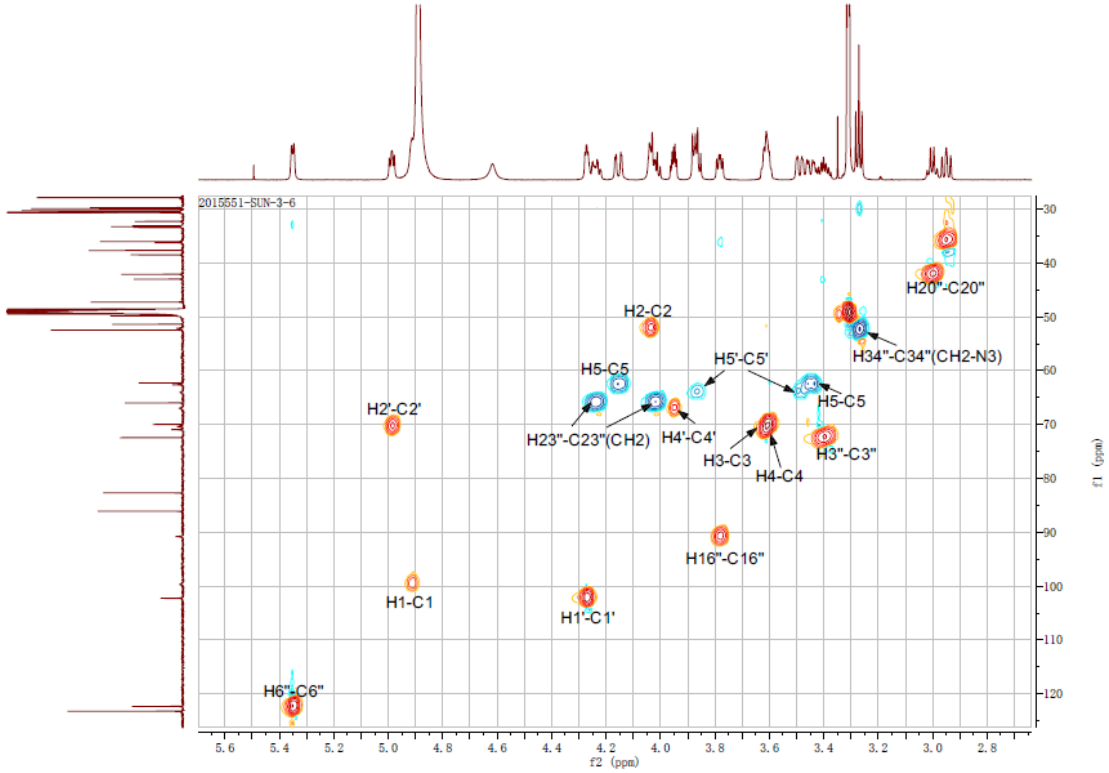
Compound **44**: ^{13}C NMR



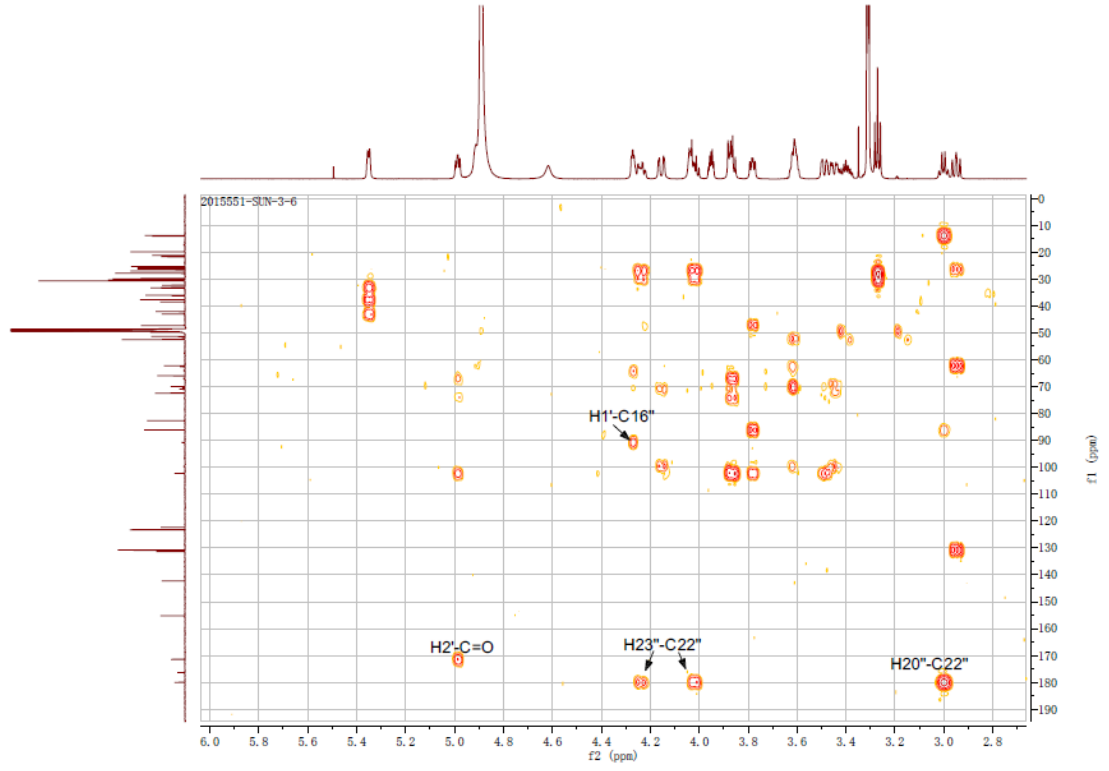
Compound **44**: COSY NMR



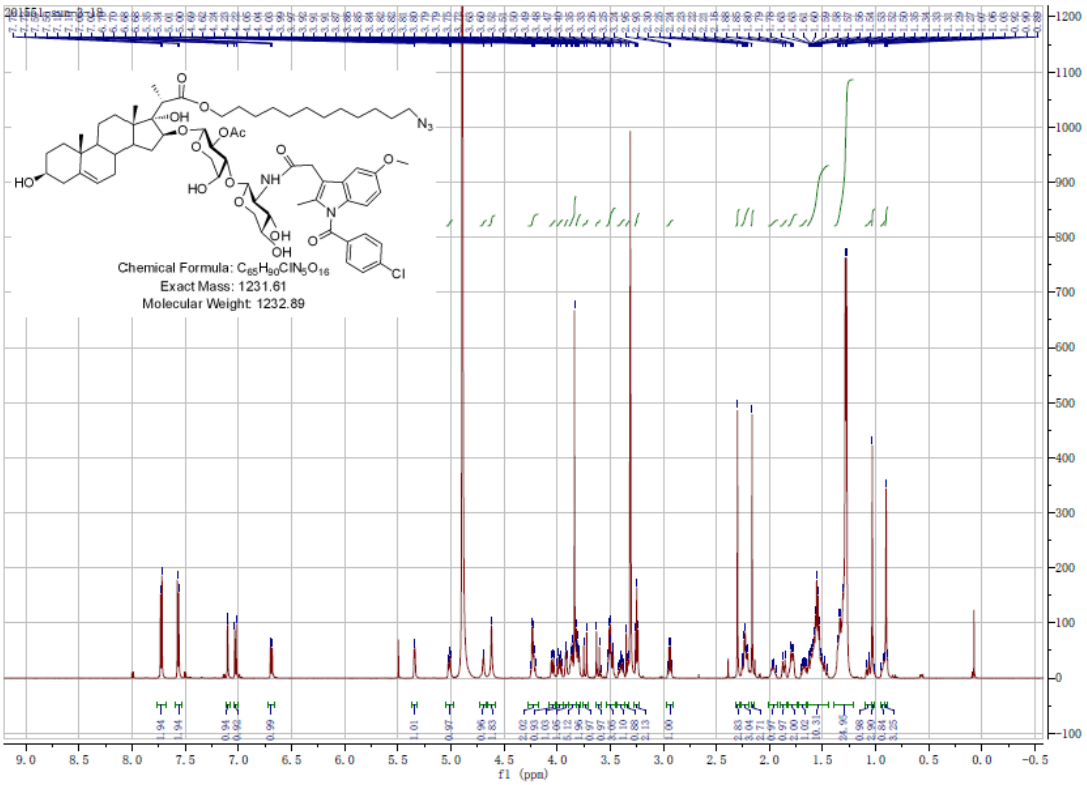
Compound **44**: HSQC NMR



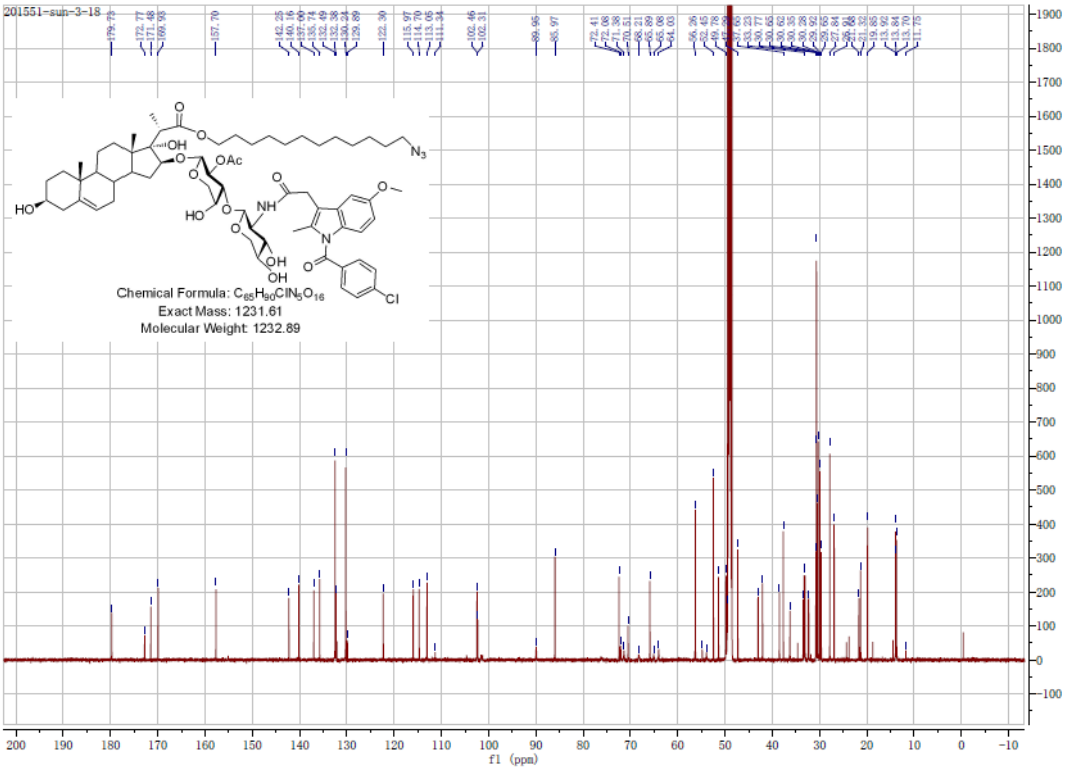
Compound **44**: HMBC NMR



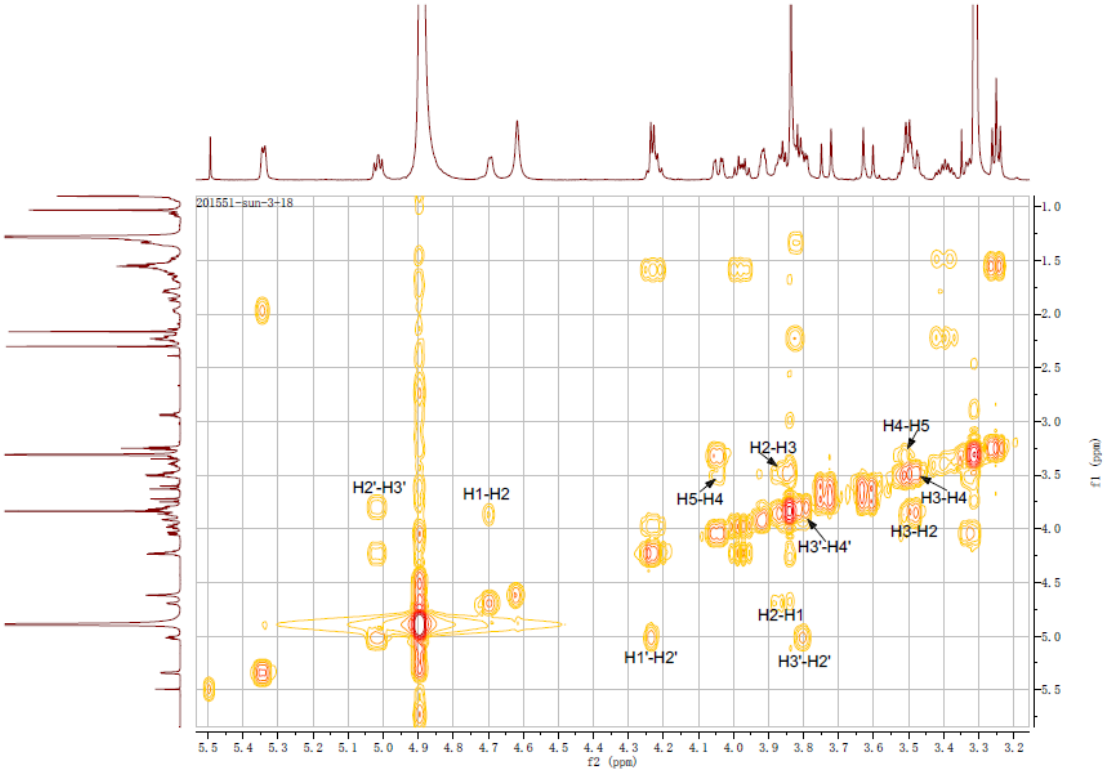
Compound **45**: ^{1}H NMR



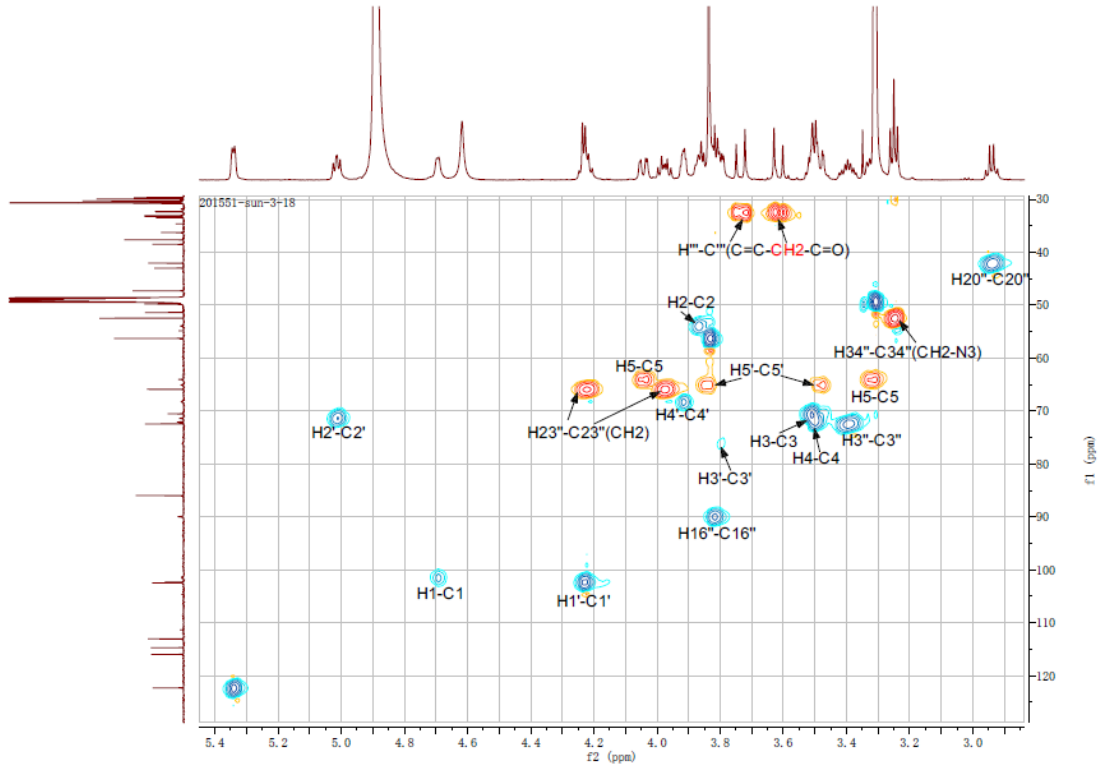
Compound **45**: ^{13}C NMR



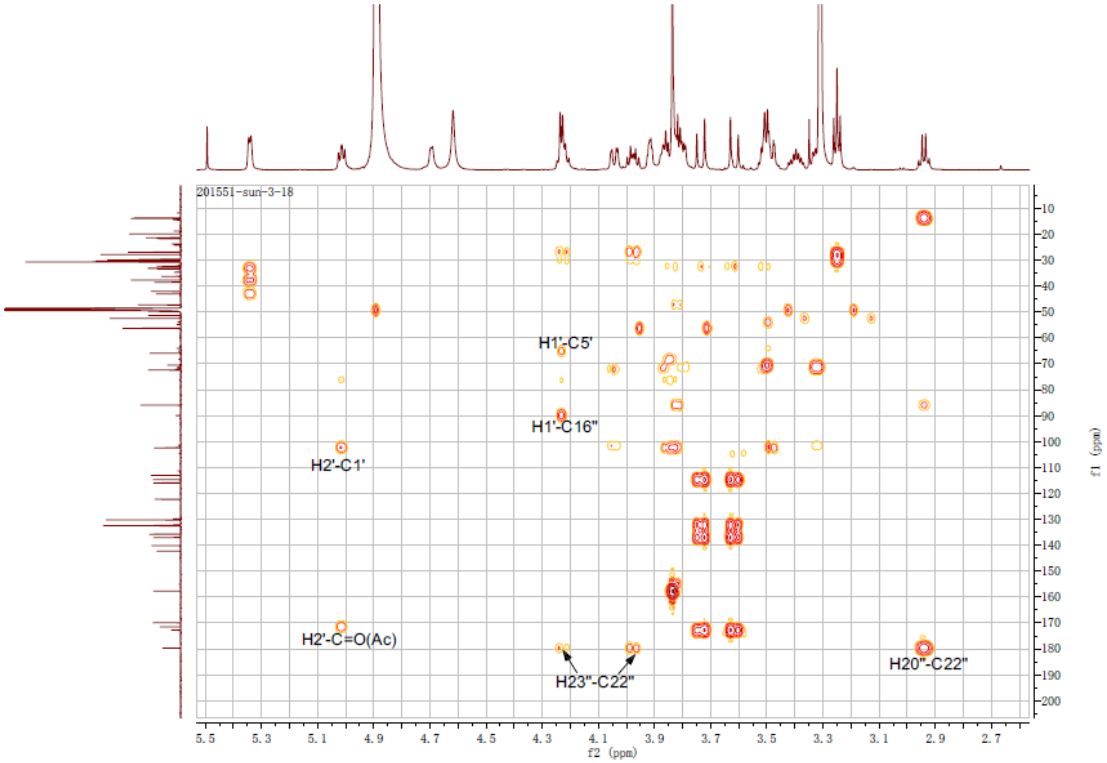
Compound **45**: COSY NMR



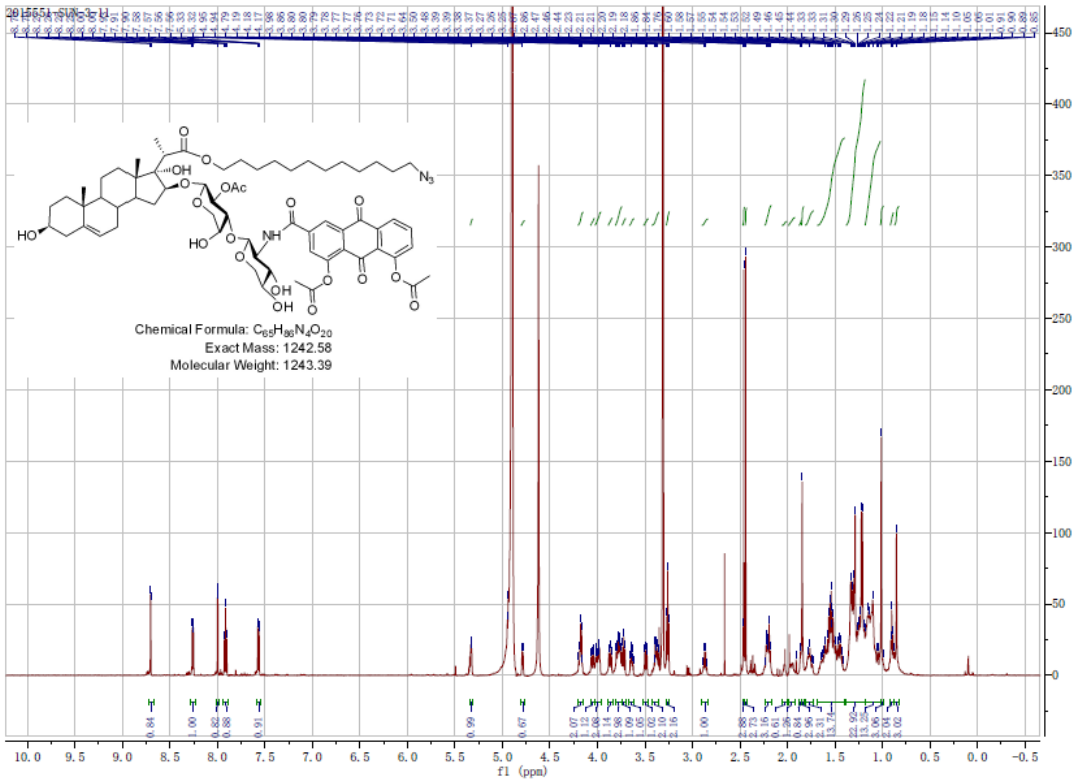
Compound **45**: HSQC NMR



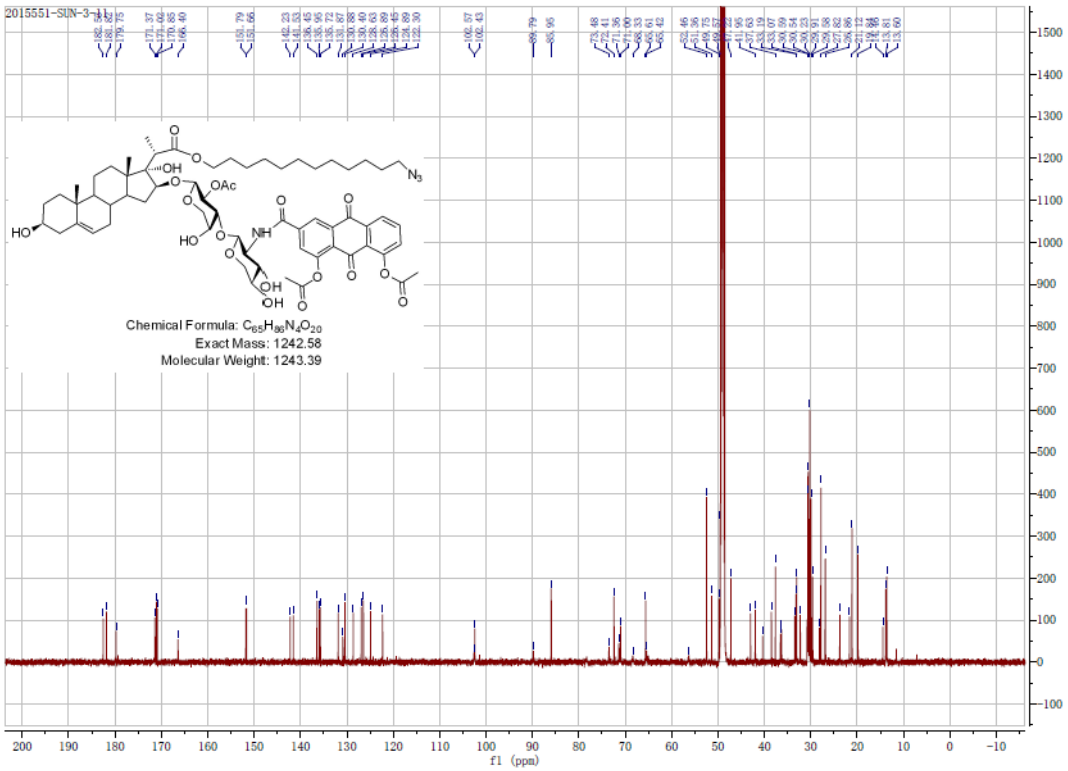
Compound **45**: HMBC NMR



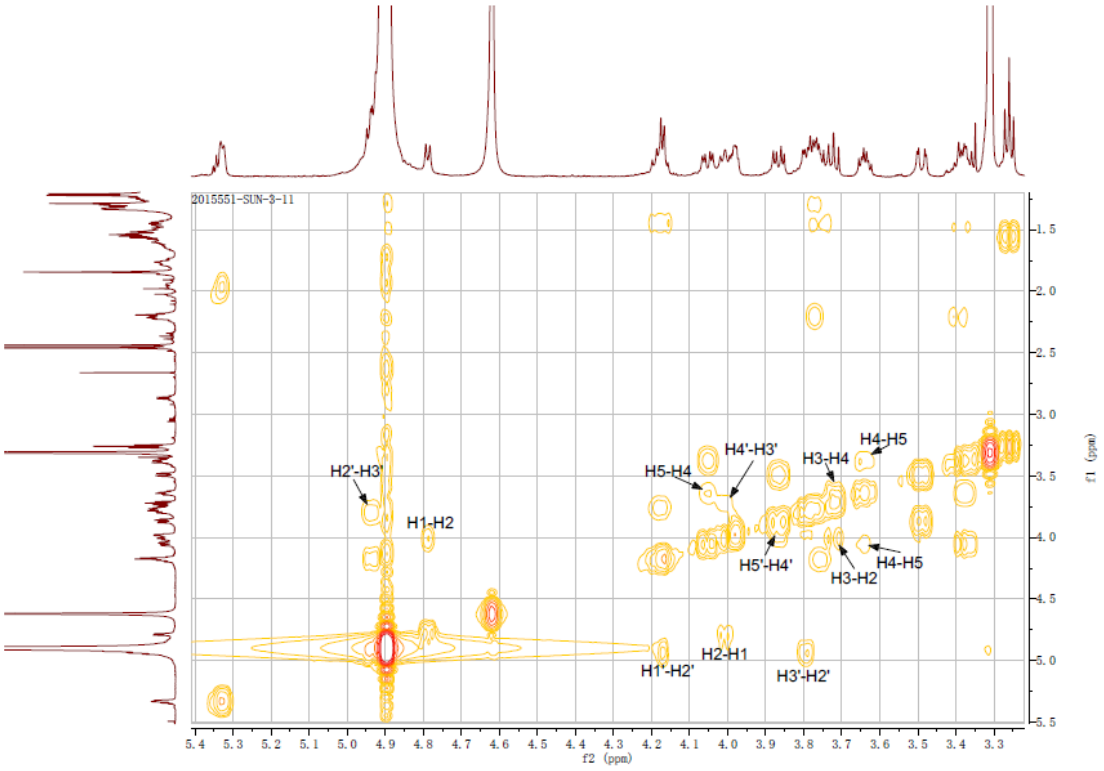
Compound **46**: ^{1}H NMR



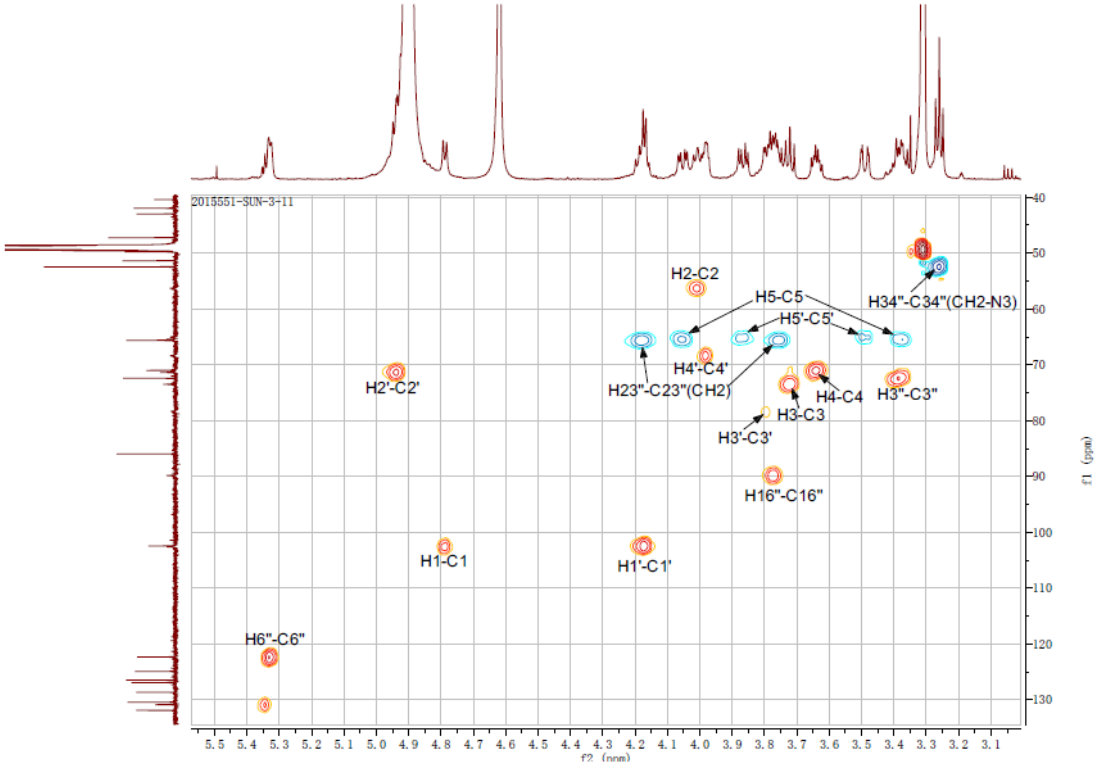
Compound **46**: ^{13}C NMR



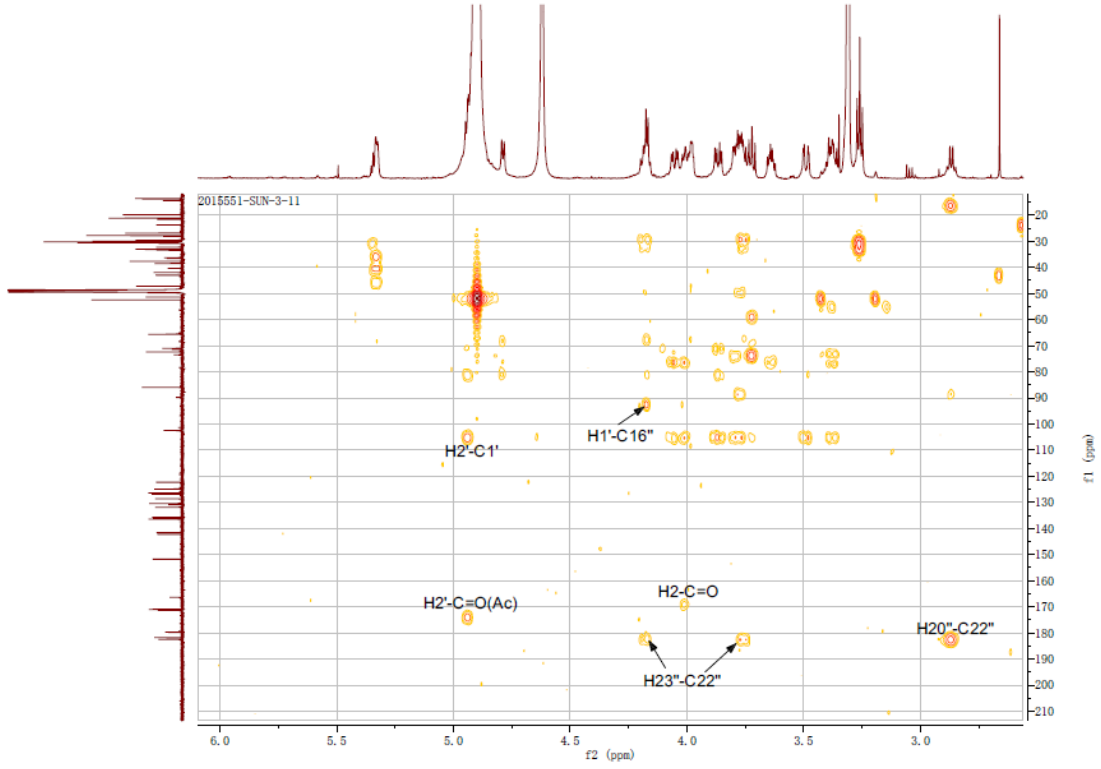
Compound **46**: COSY NMR



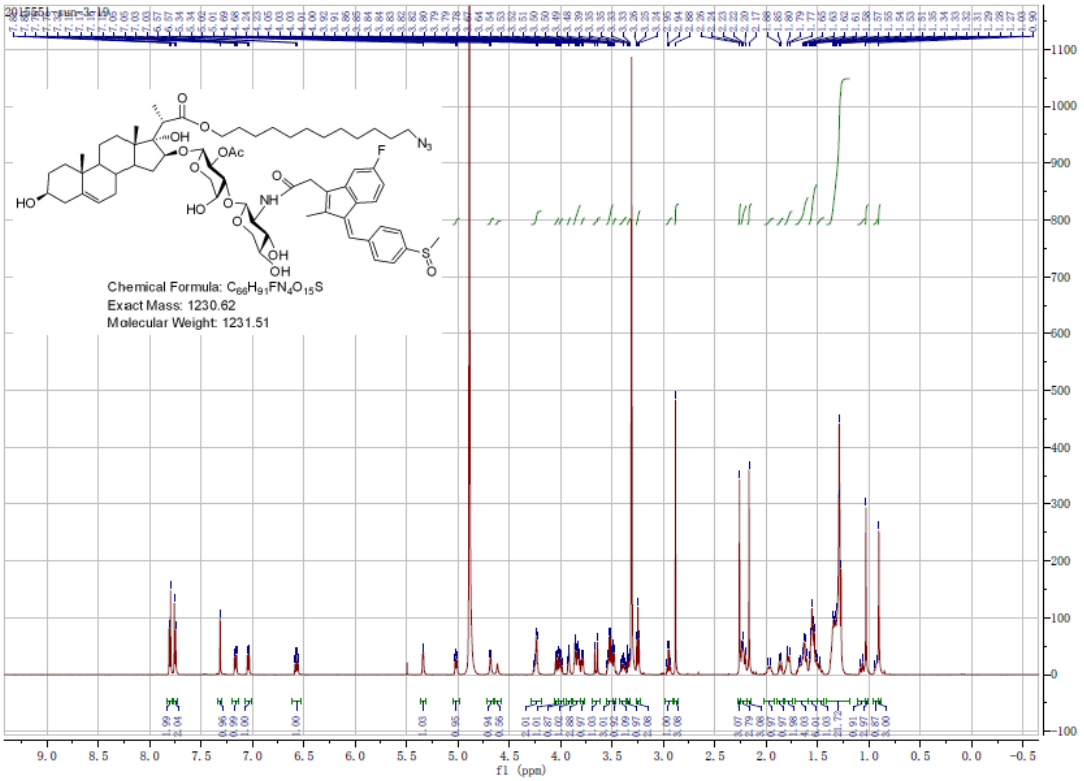
Compound **46**: HSQC NMR



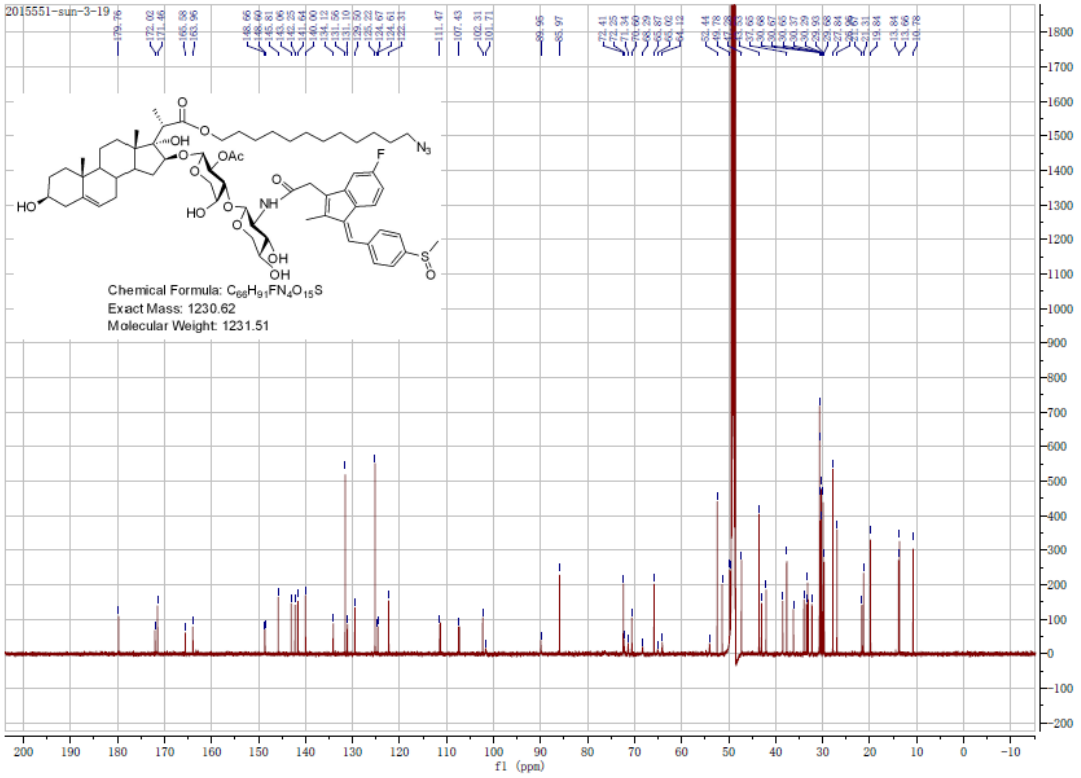
Compound **46**: HMBC NMR



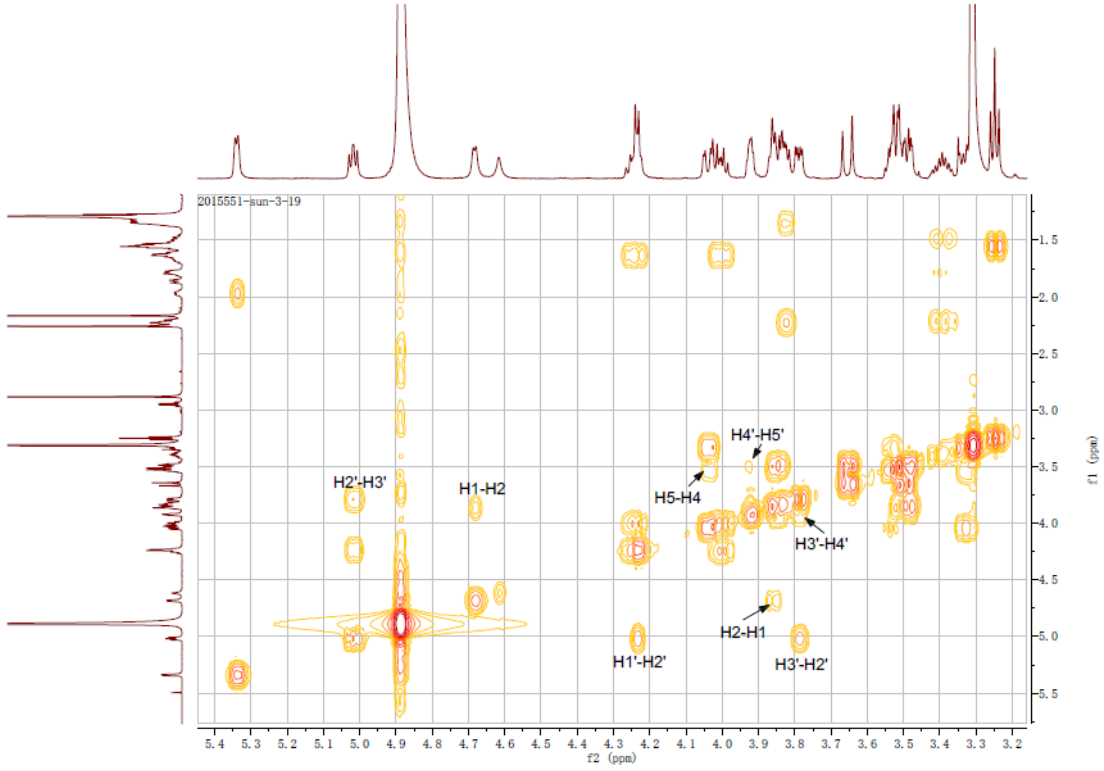
Compound **47**: ^{1}H NMR



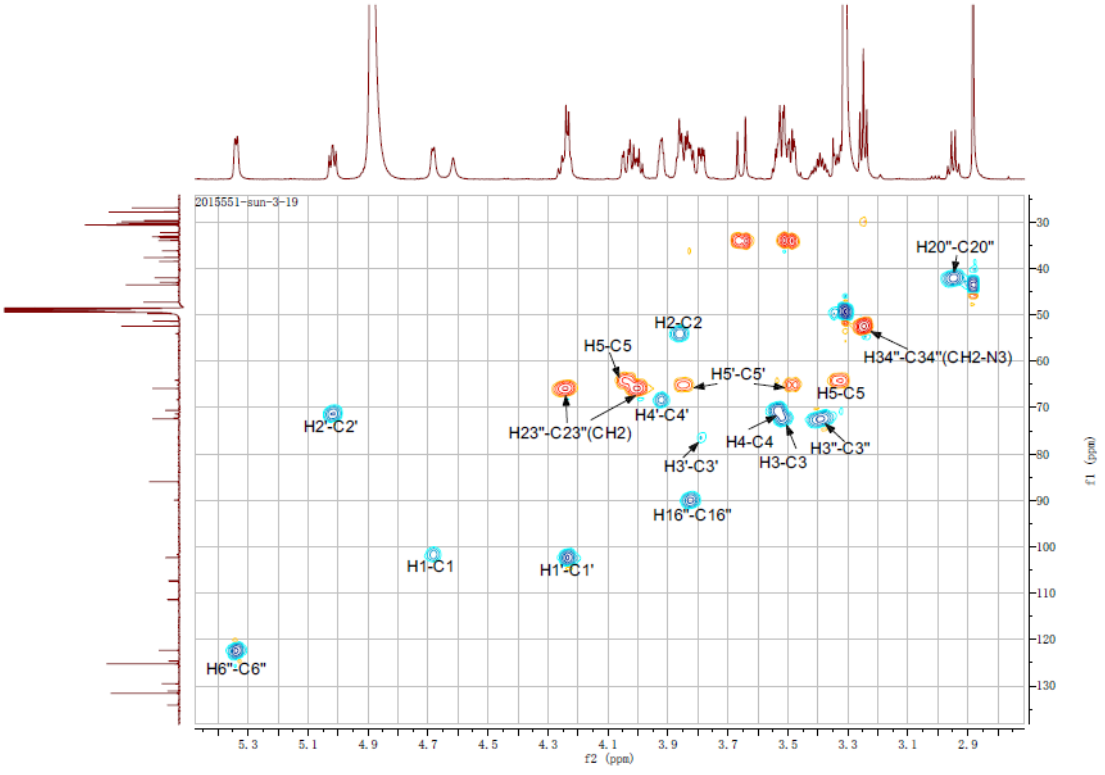
Compound **47**: ^{13}C NMR



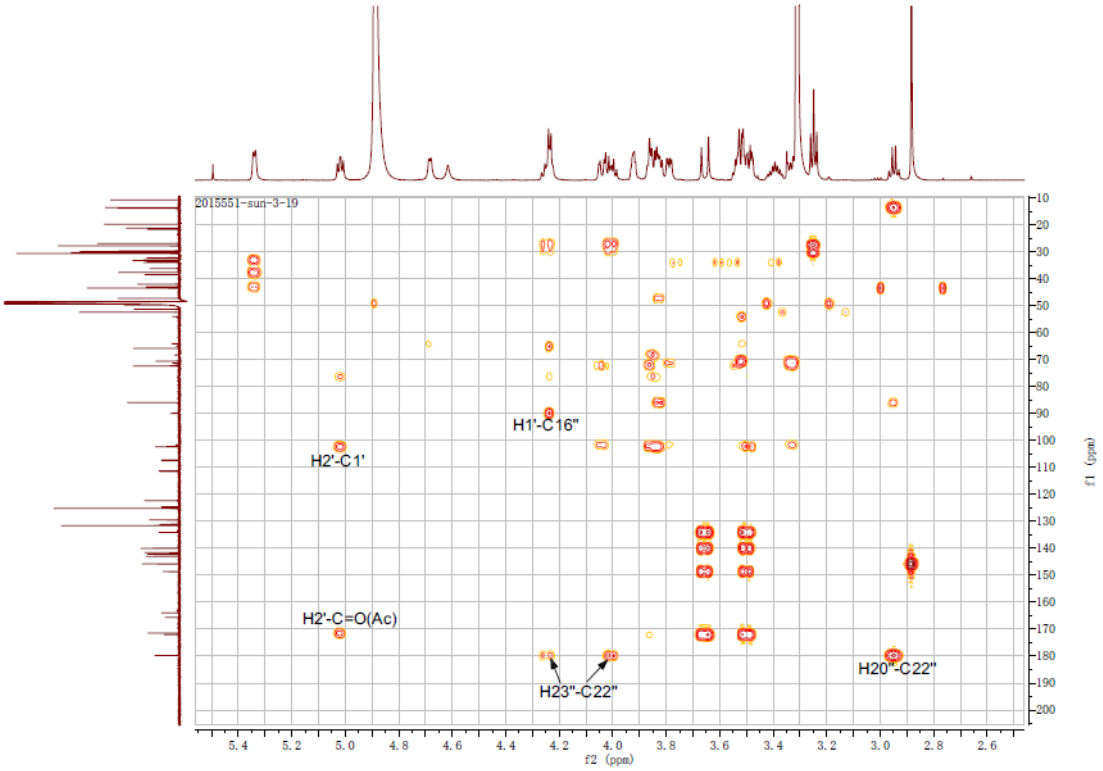
Compound **47**: COSY NMR



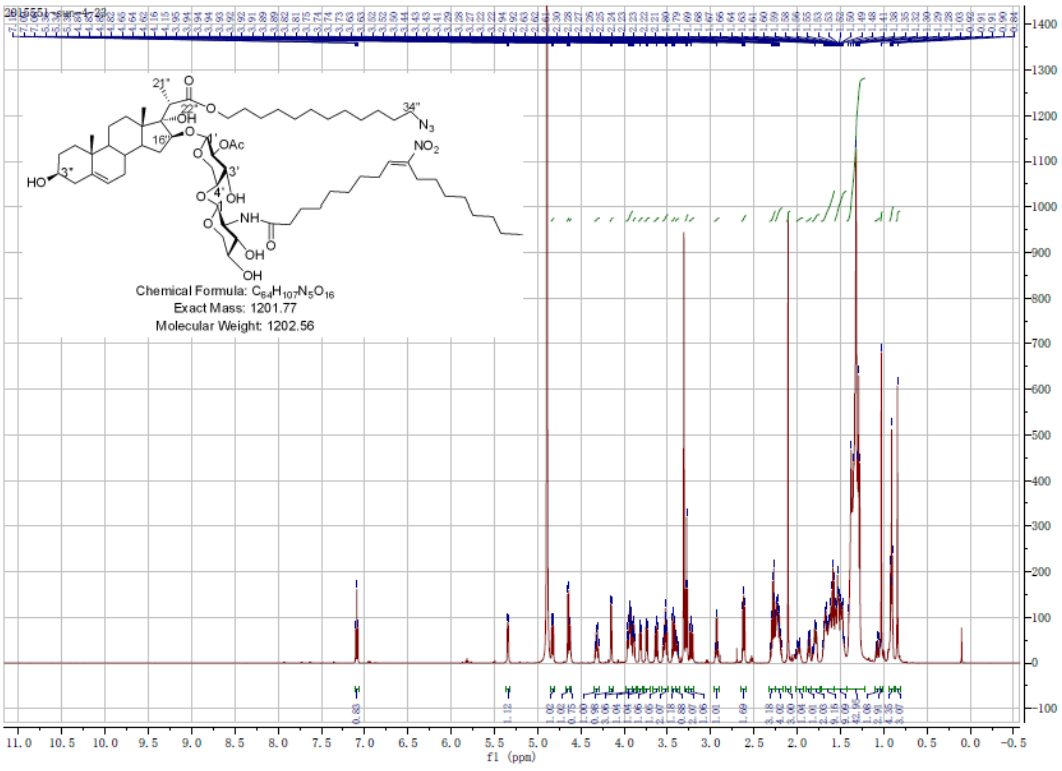
Compound **47**: HSQC NMR



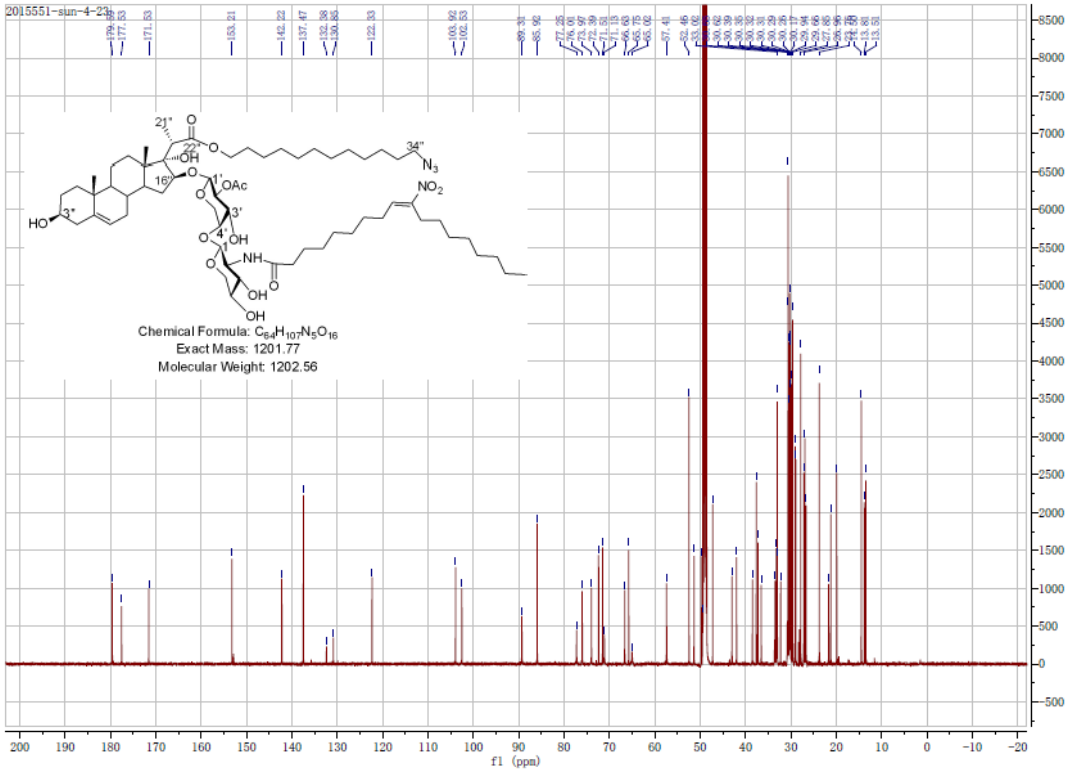
Compound **47**: HMBC NMR



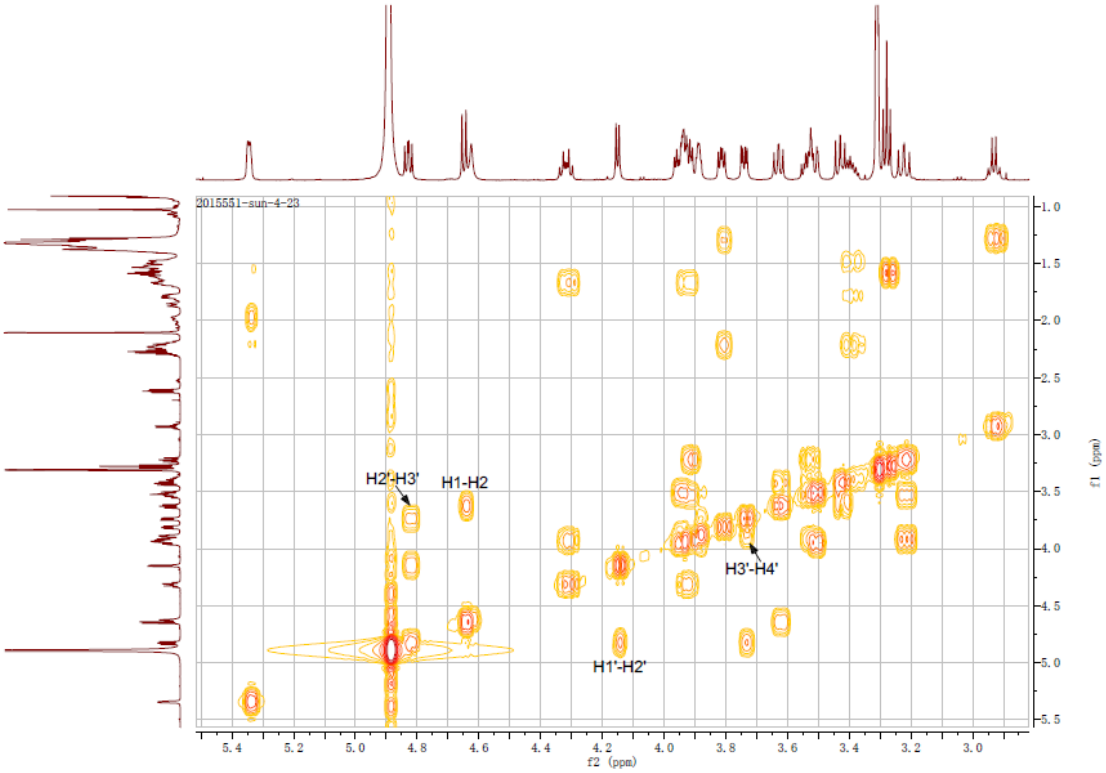
Compound **48**: ^{1}H NMR



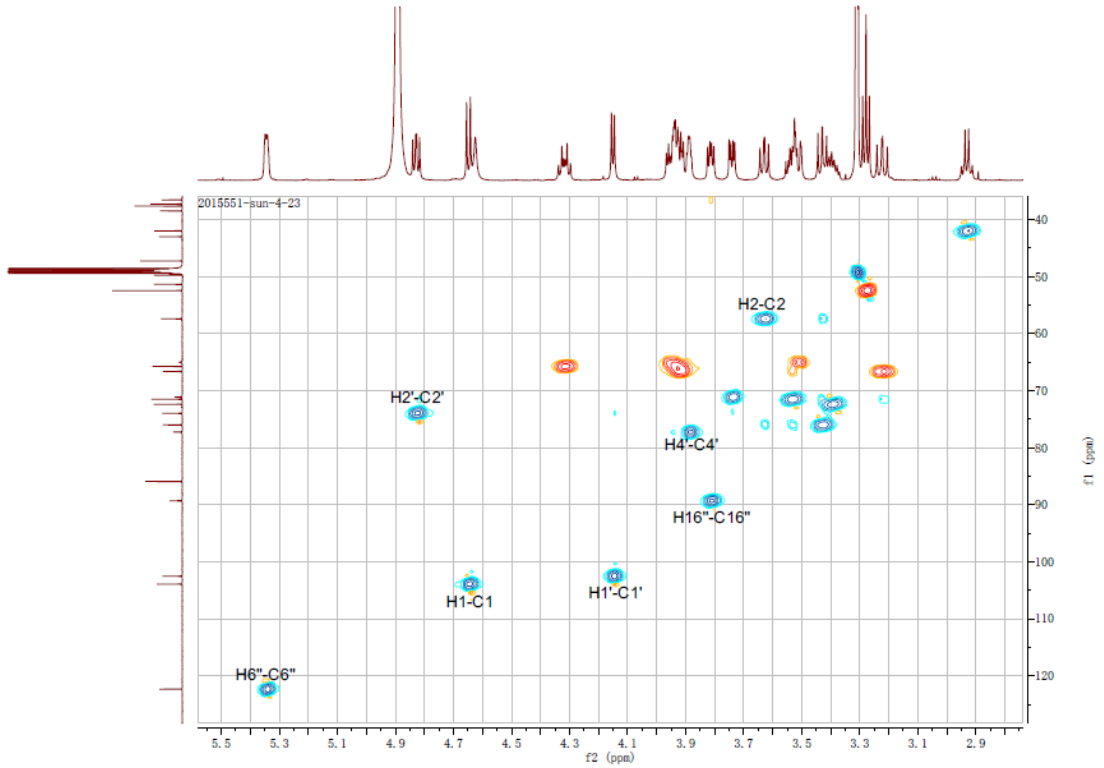
Compound **48**: ^{13}C NMR



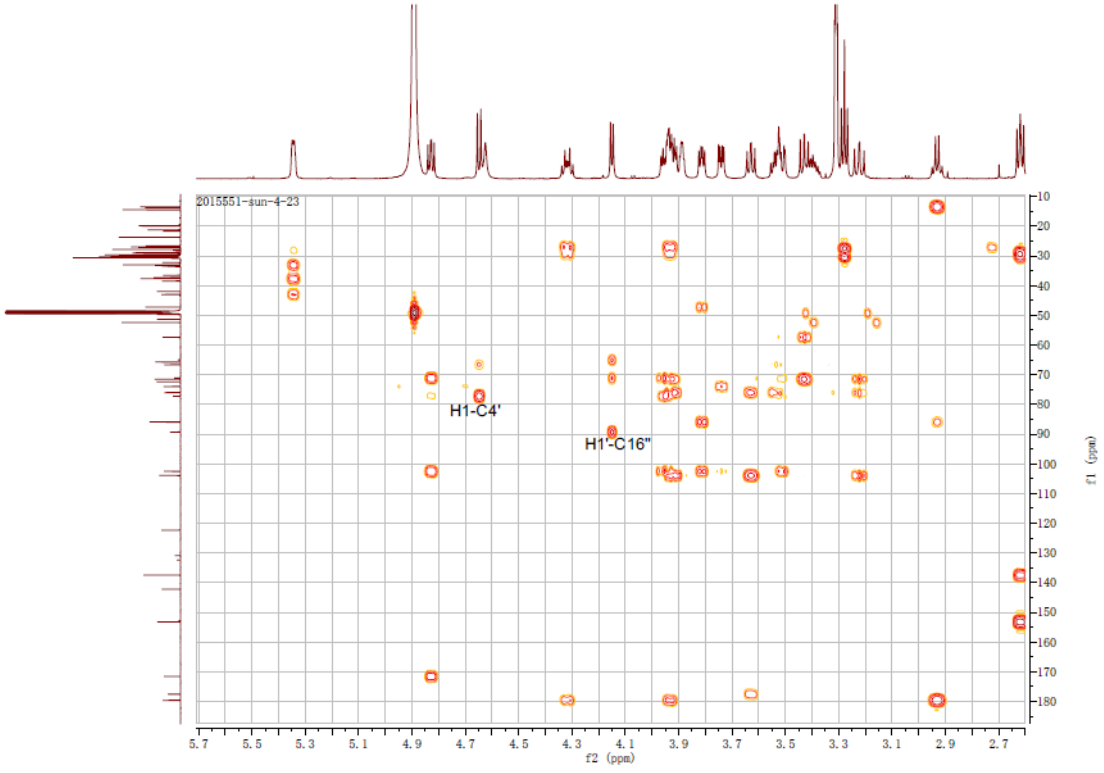
Compound **48**: COSY NMR



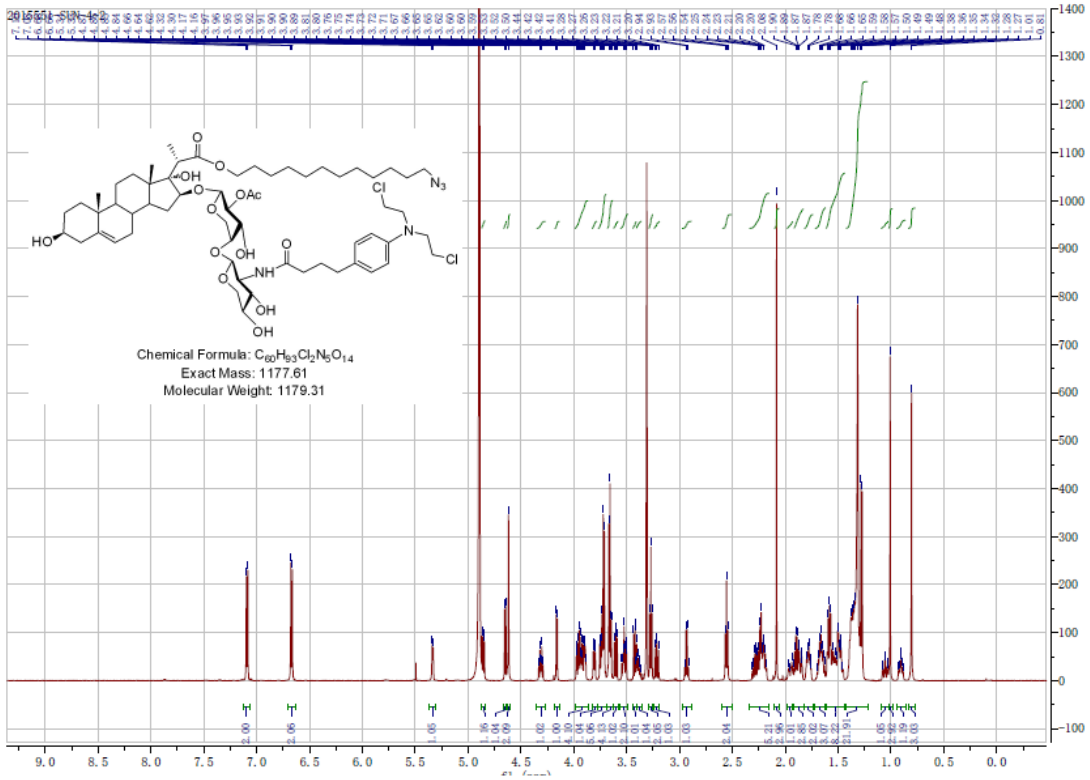
Compound **48**: HSQC NMR



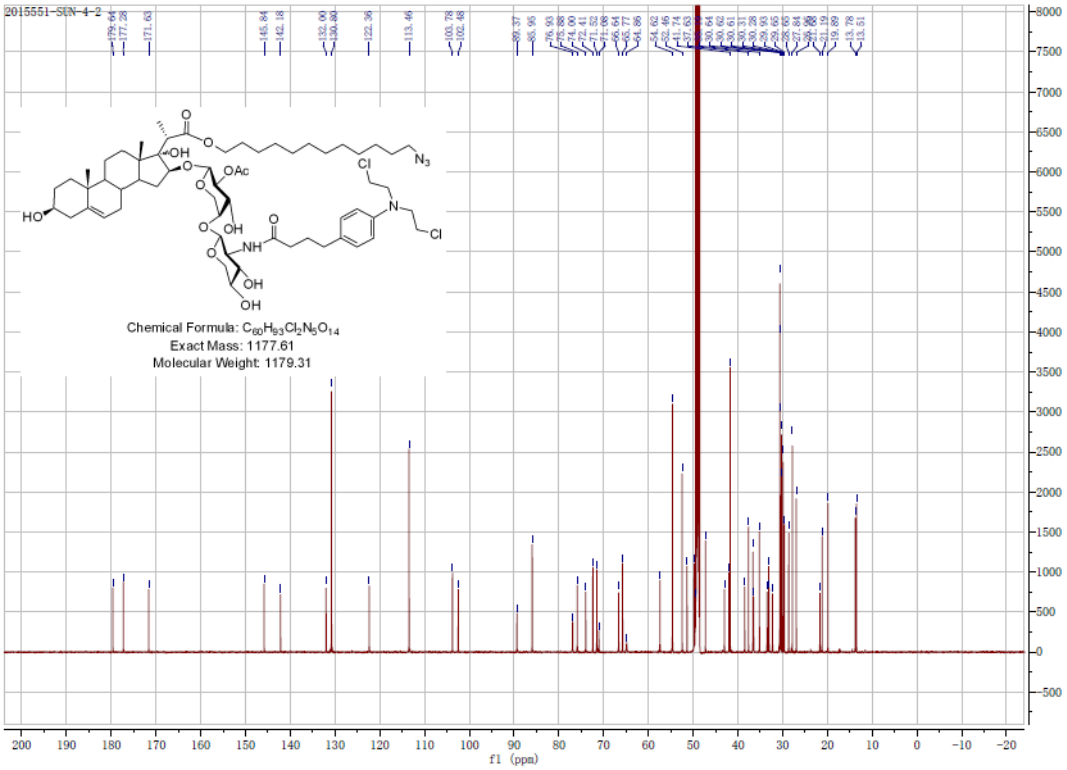
Compound **48**: HMBC NMR



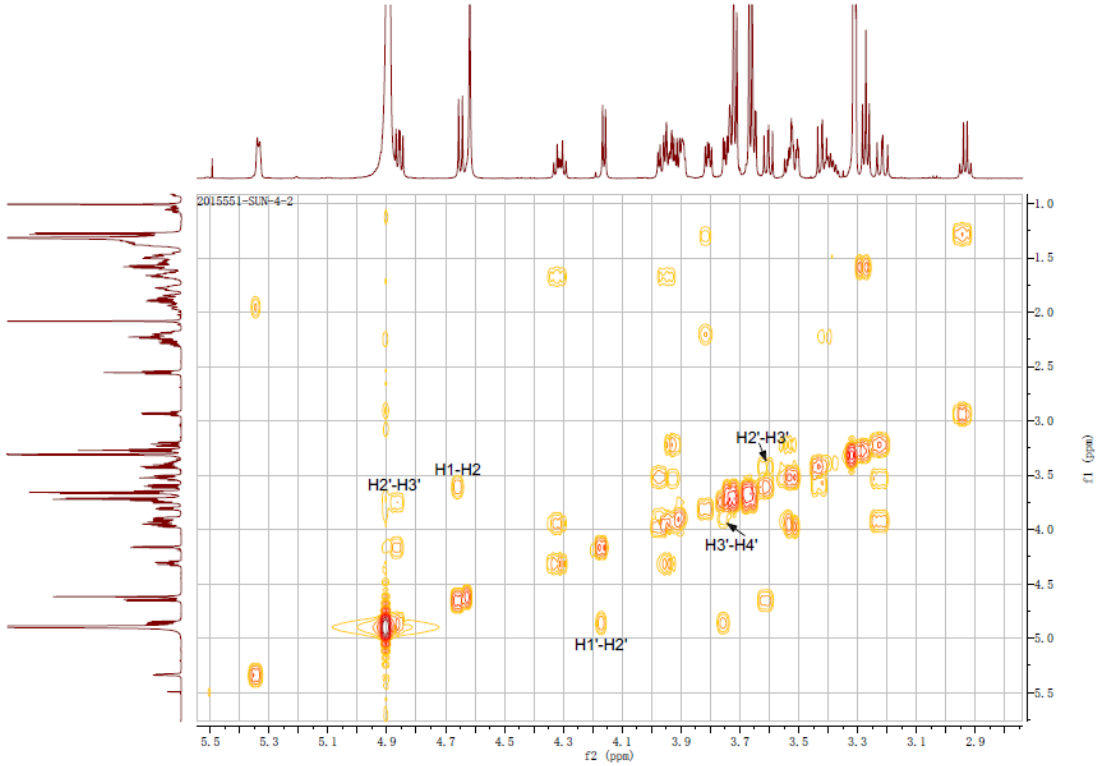
Compound **49**: ^{1}H NMR



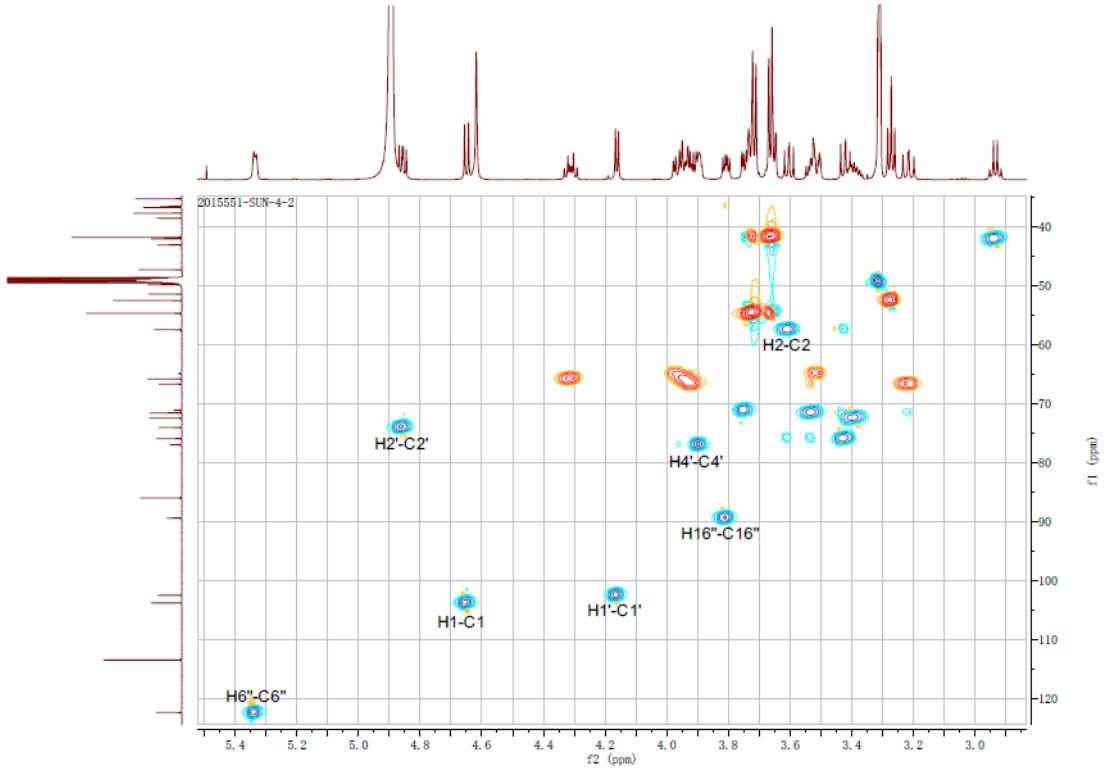
Compound **49**: ^{13}C NMR



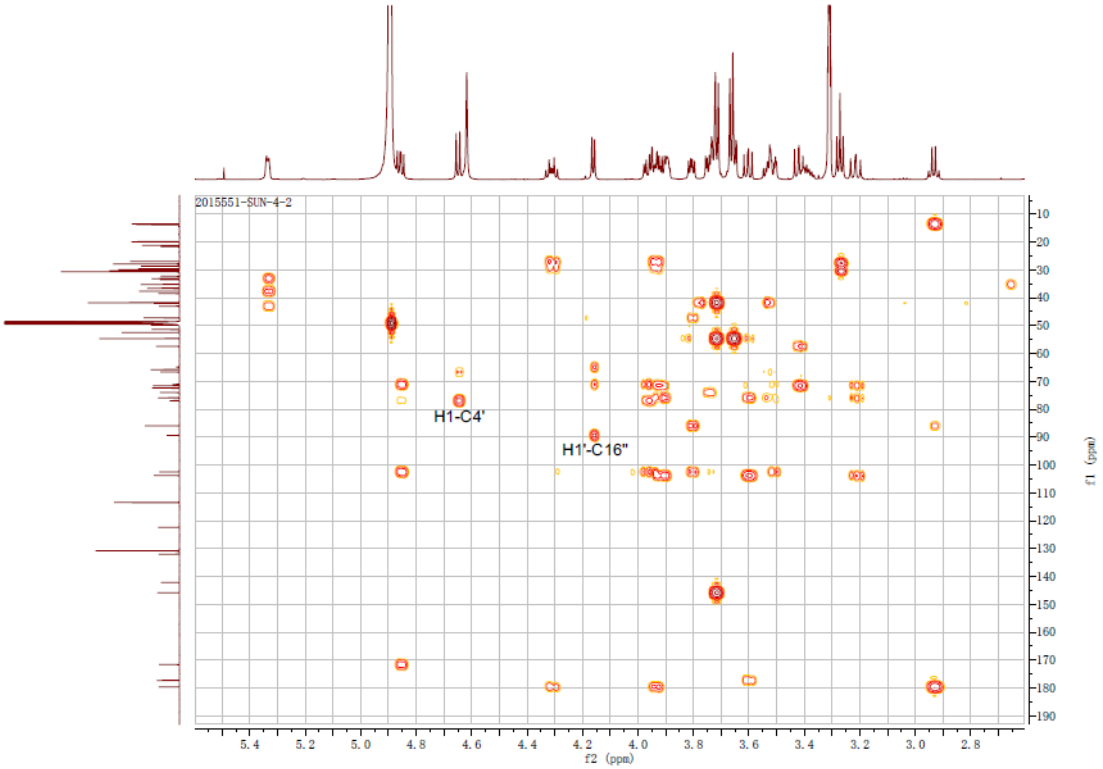
Compound **49**: COSY NMR



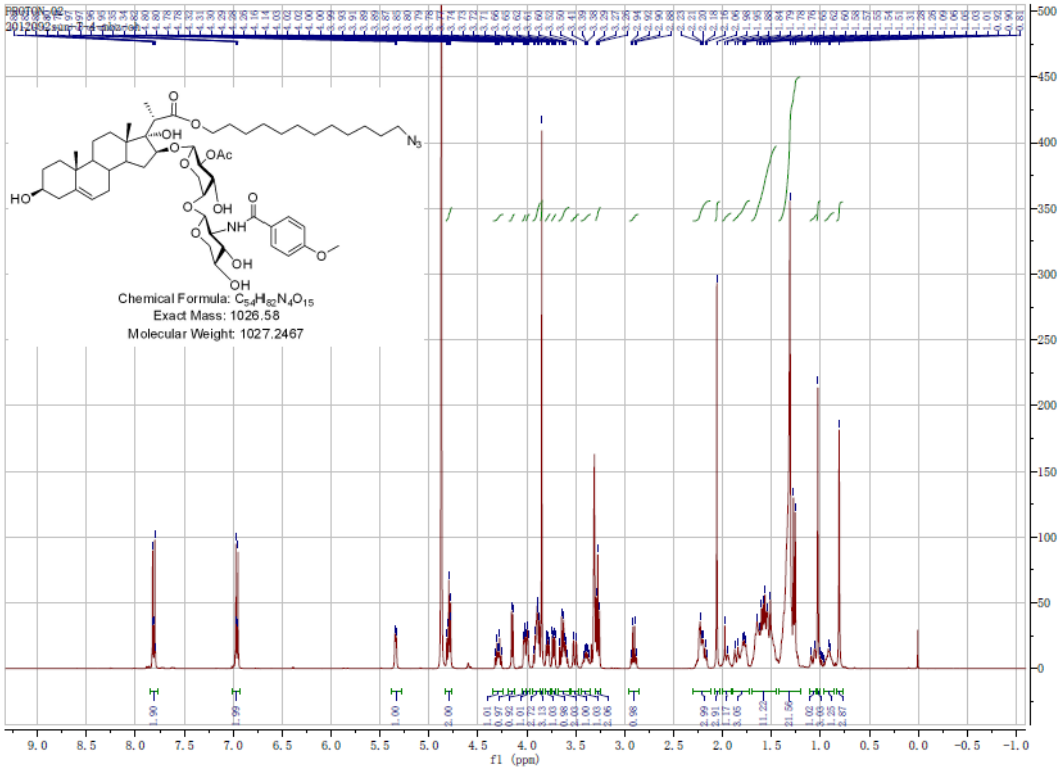
Compound **49**: HSQC NMR



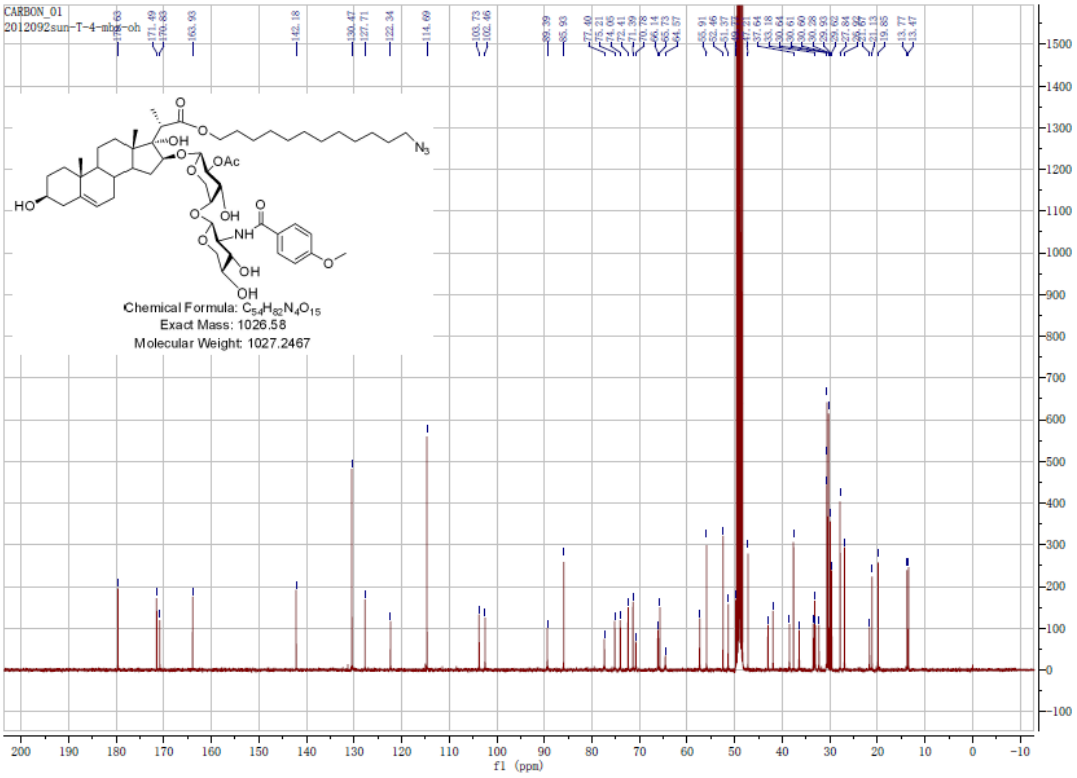
Compound **49**: HMBC NMR



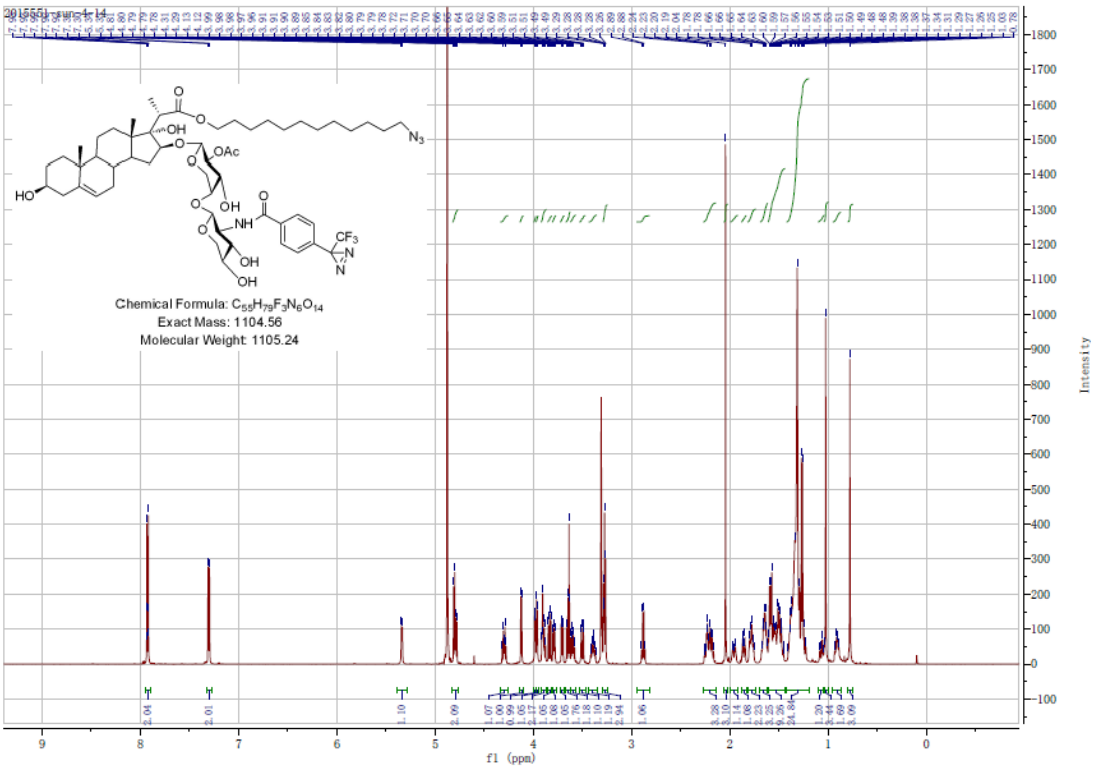
Compound **50**: ^{1}H NMR



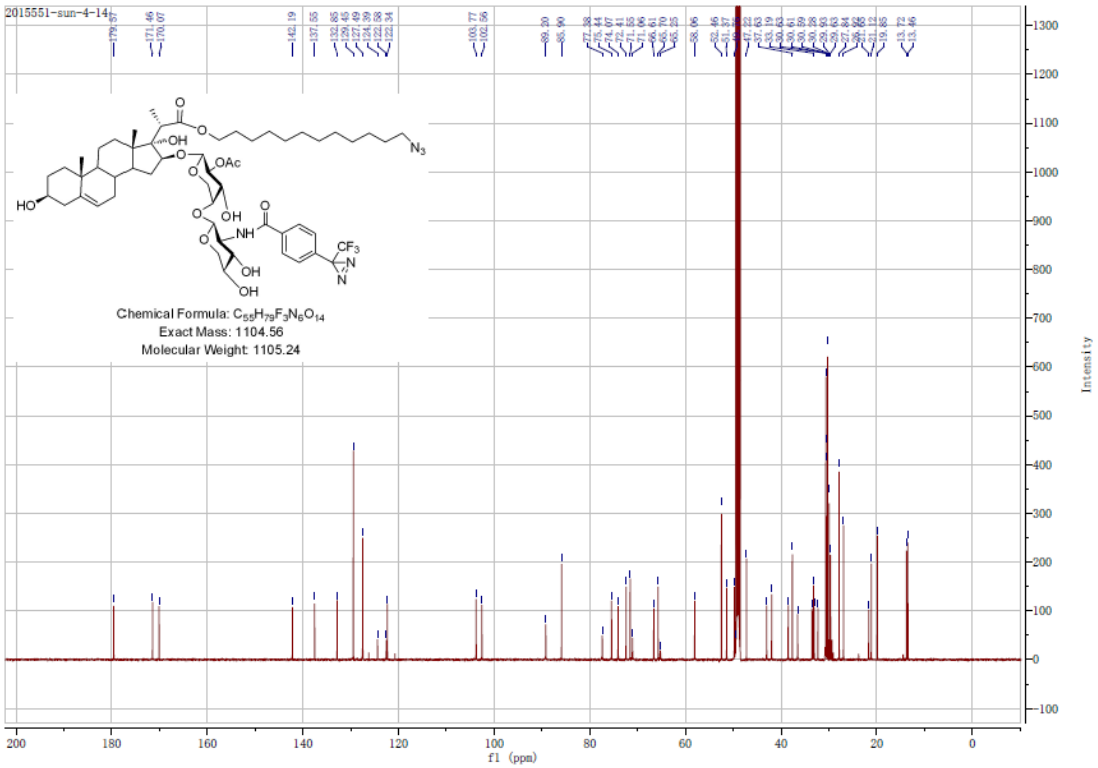
Compound **50**: ^{13}C NMR



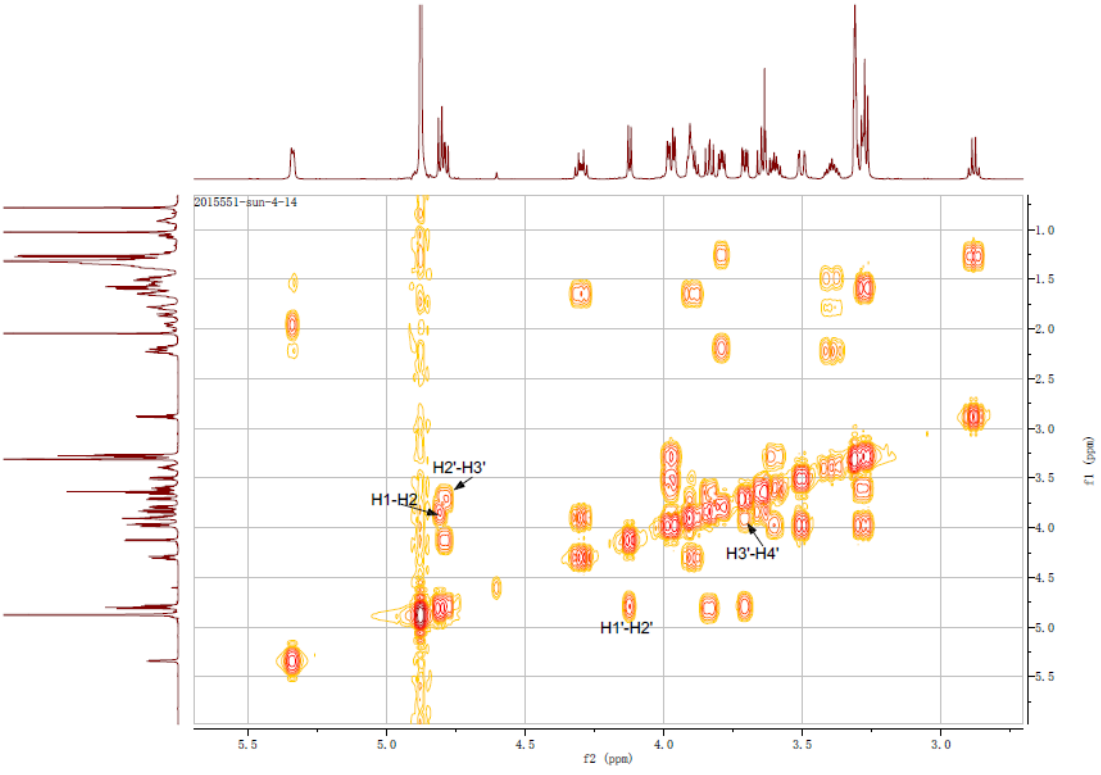
Compound **51**: ^{1}H NMR



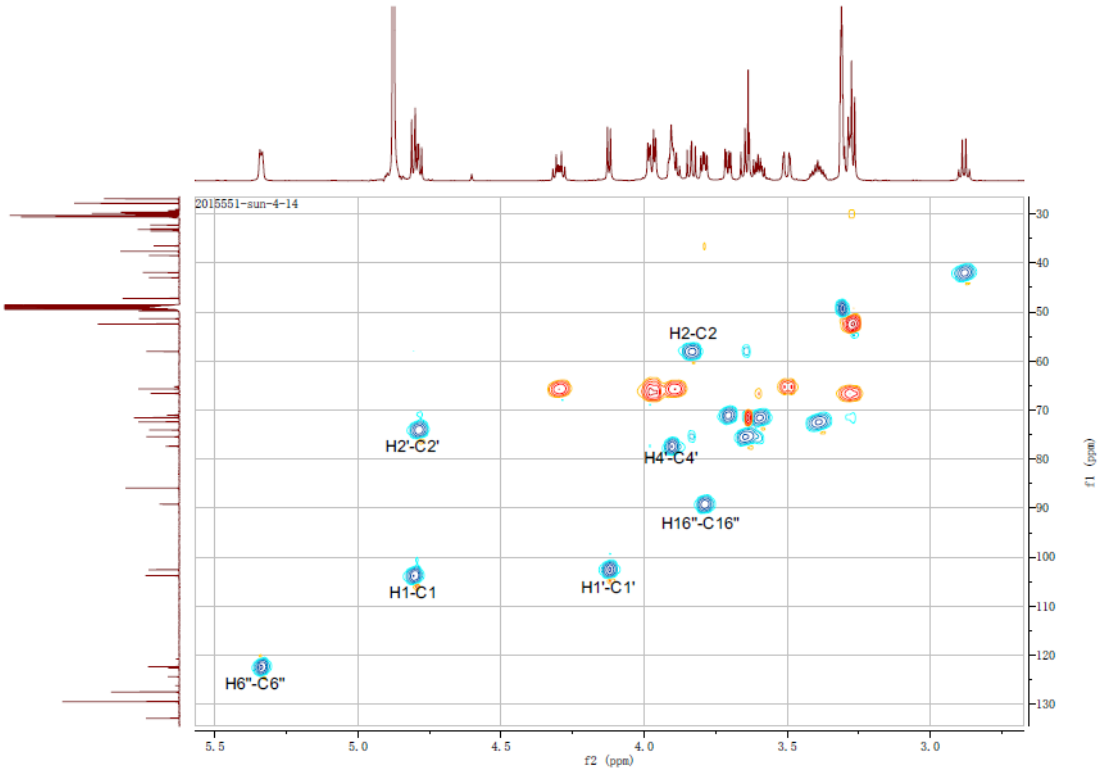
Compound **51**: ^{13}C NMR



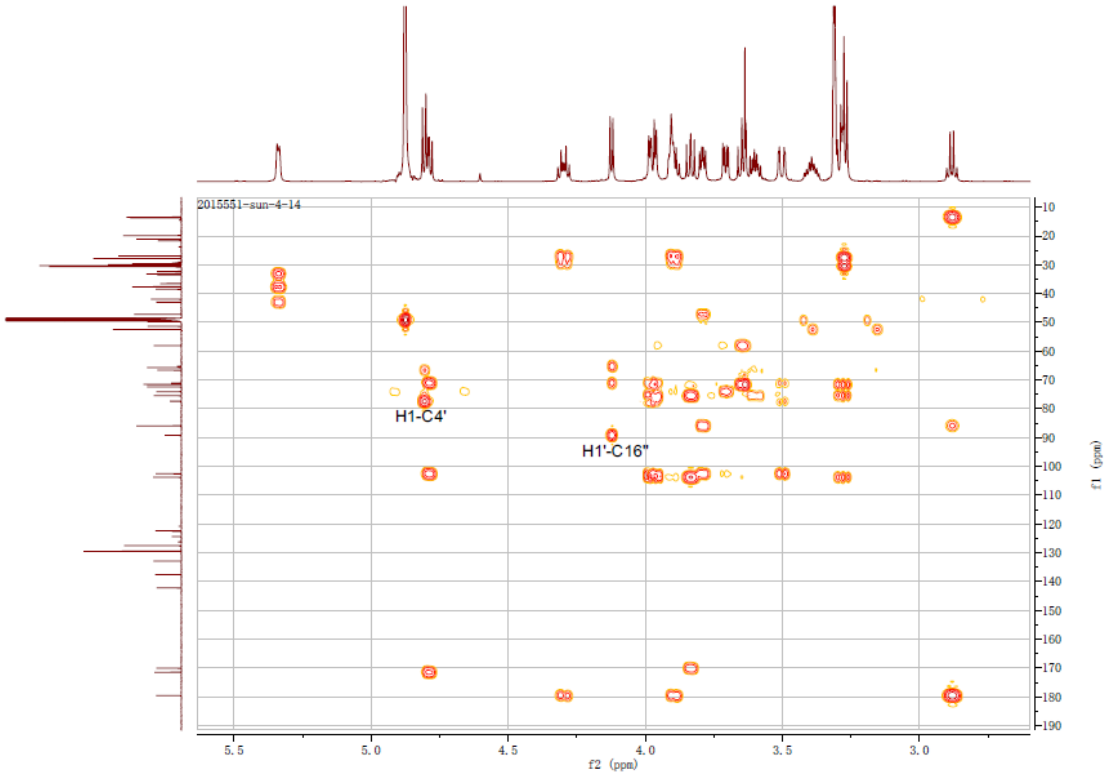
Compound **51**: COSY NMR



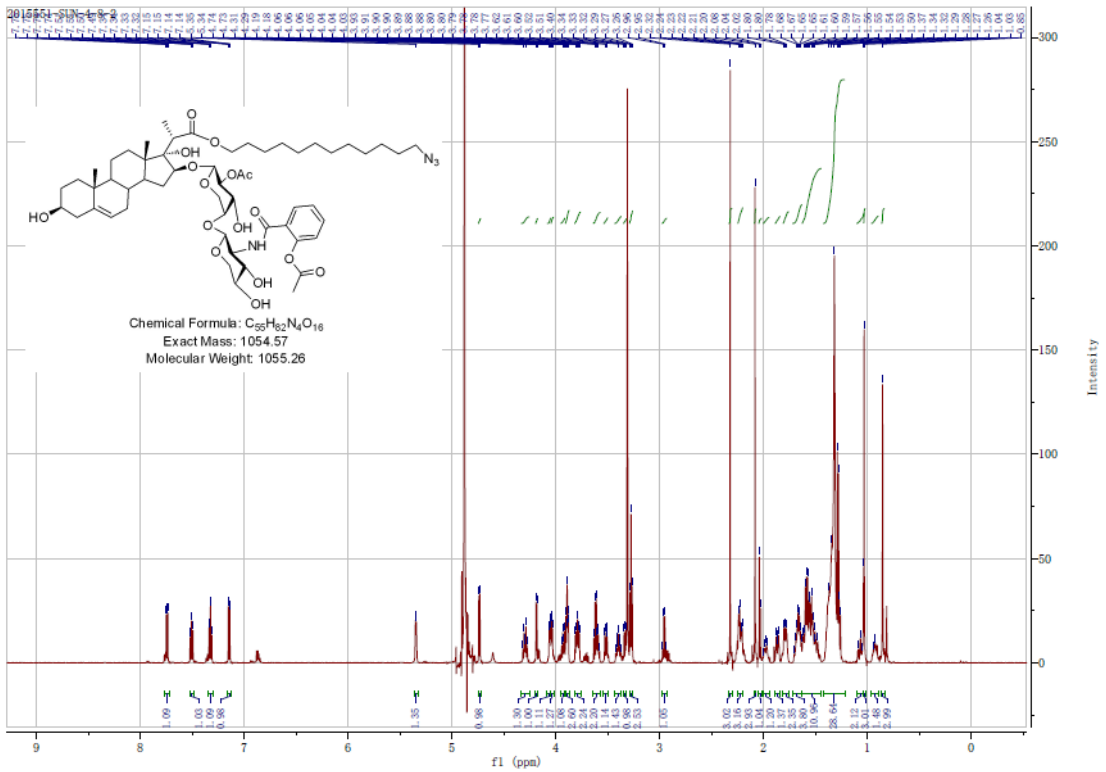
Compound **51**: HSQC NMR



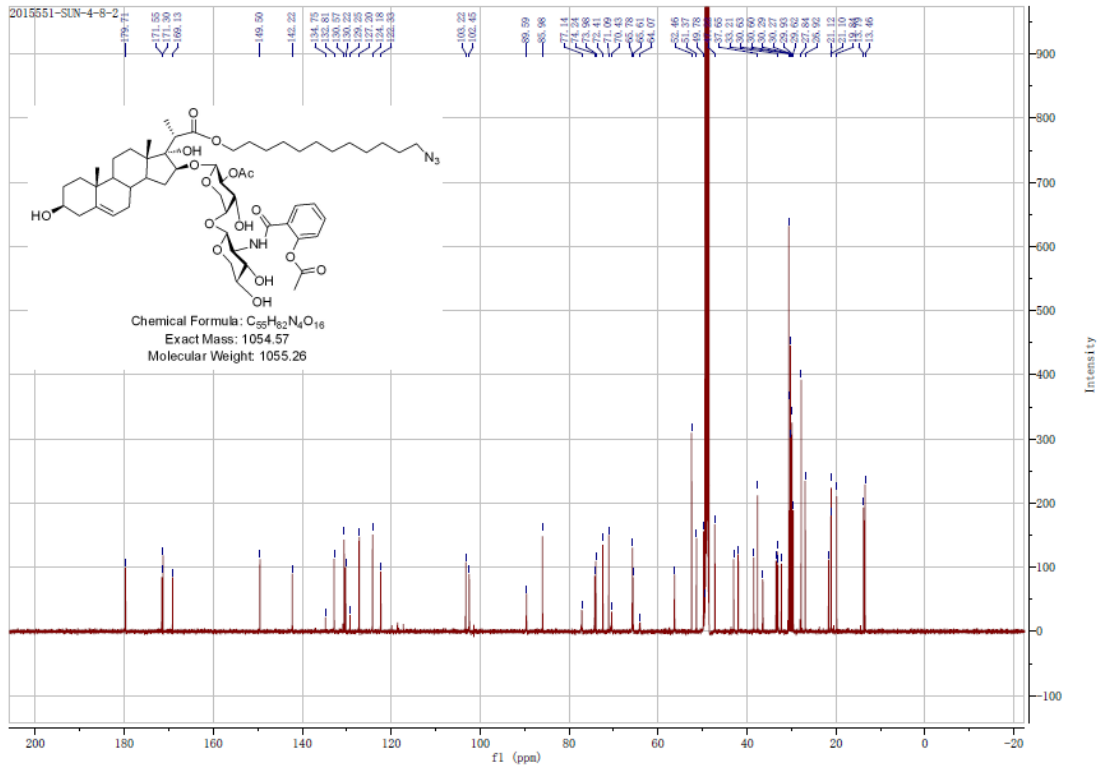
Compound **51**: HMBC NMR



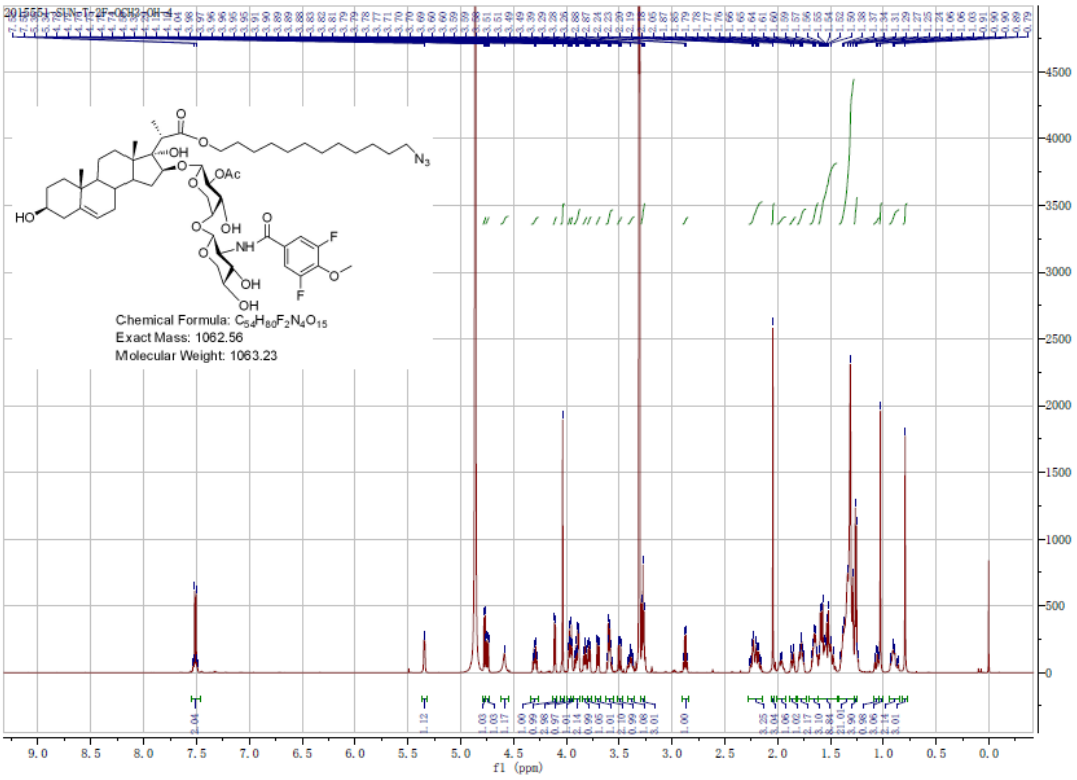
Compound **52**: ^{1}H NMR



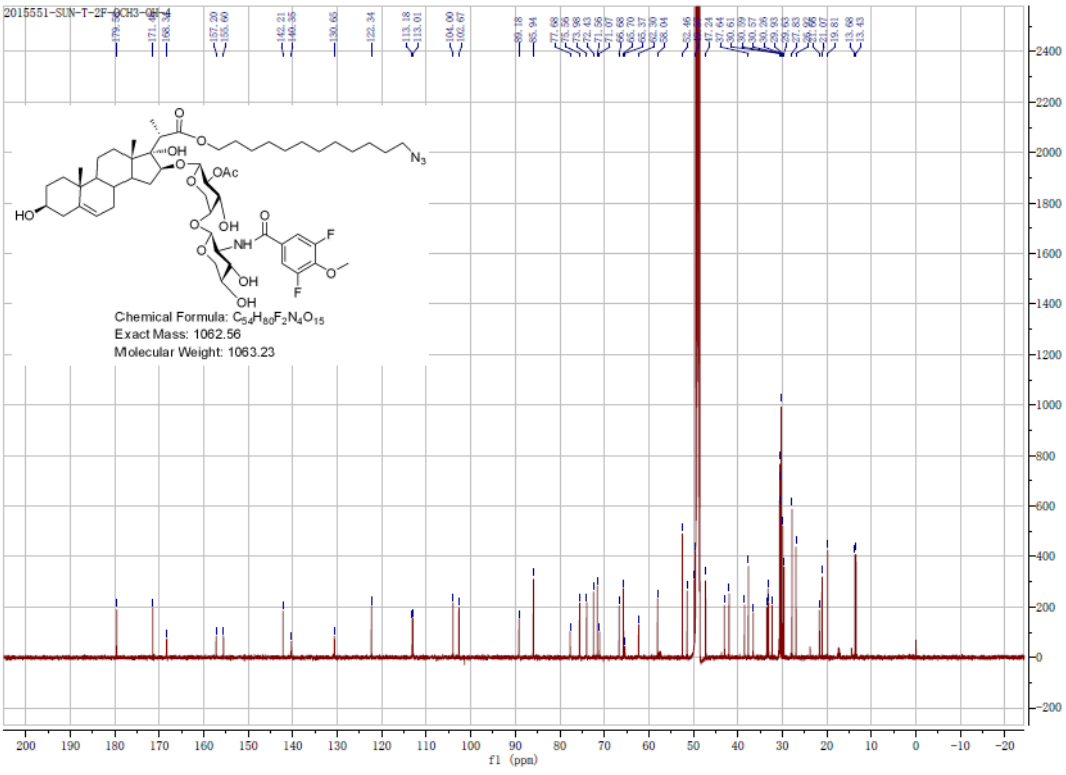
Compound **52**: ^{13}C NMR



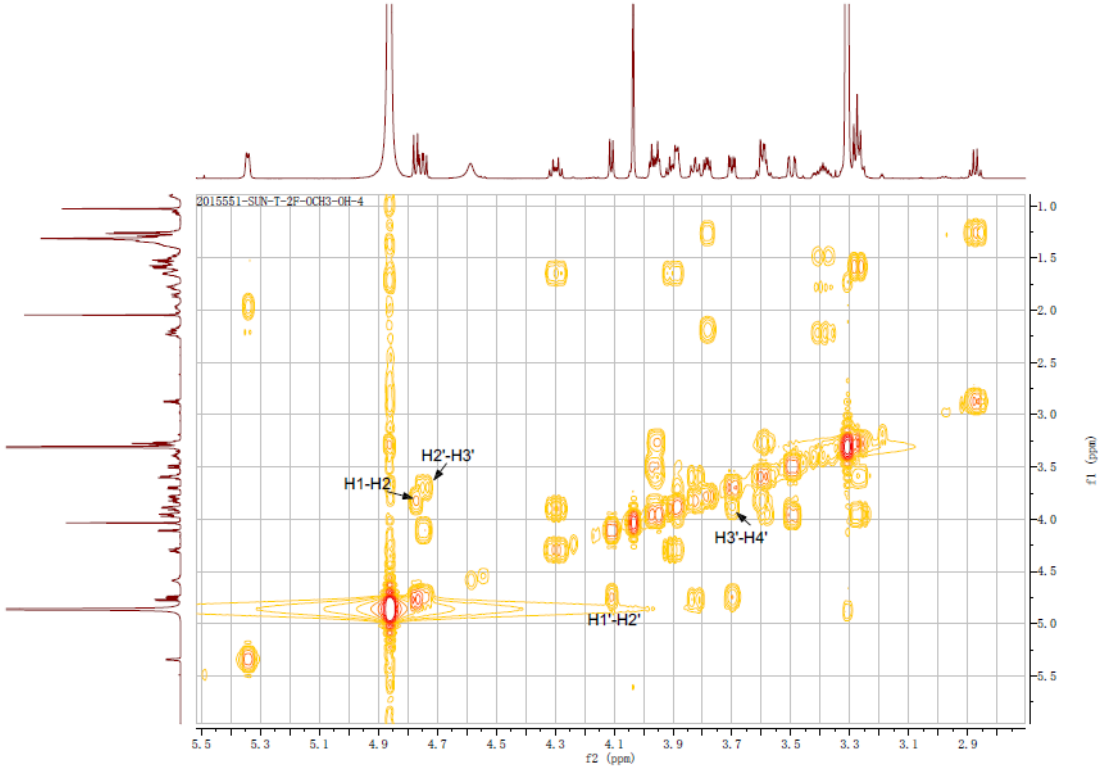
Compound **53**: ^{1}H NMR



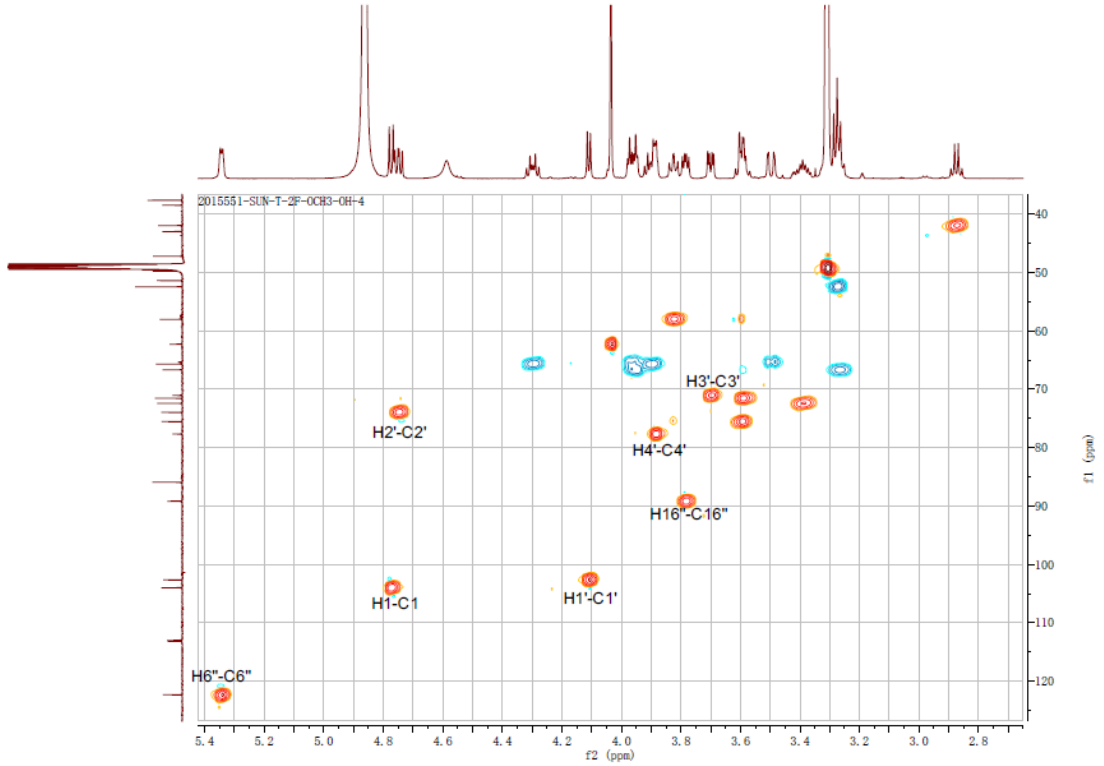
Compound **53**: ^{13}C NMR



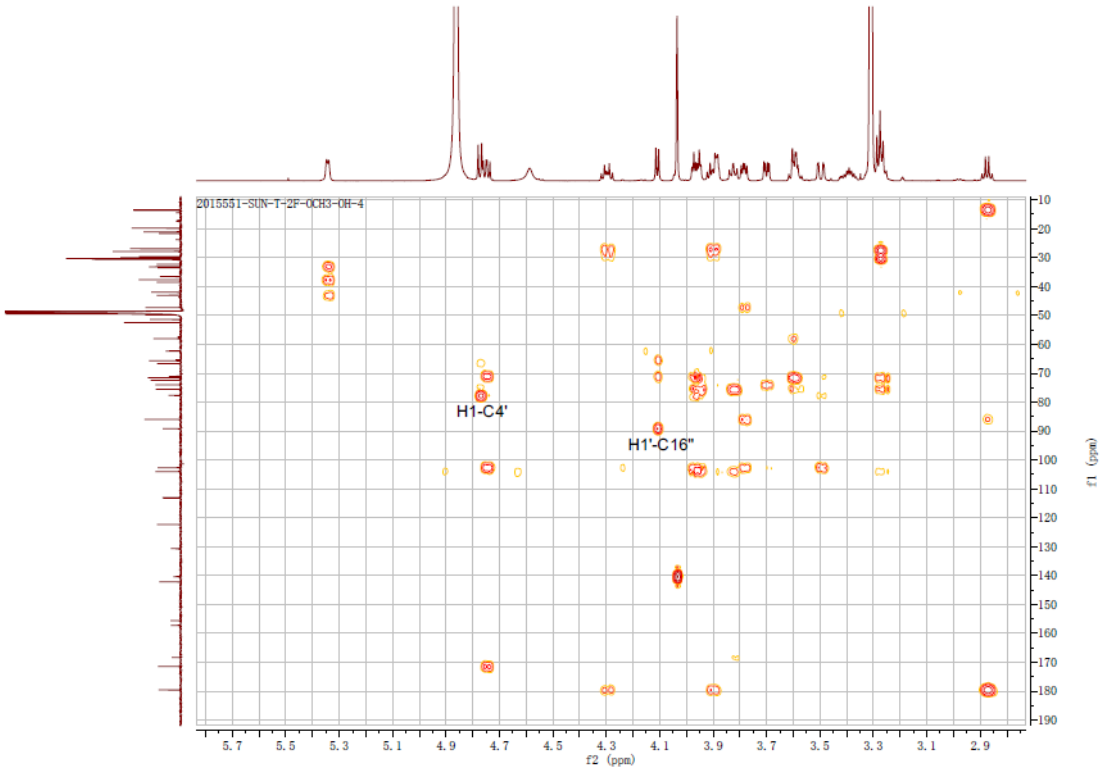
Compound **53**: COSY NMR



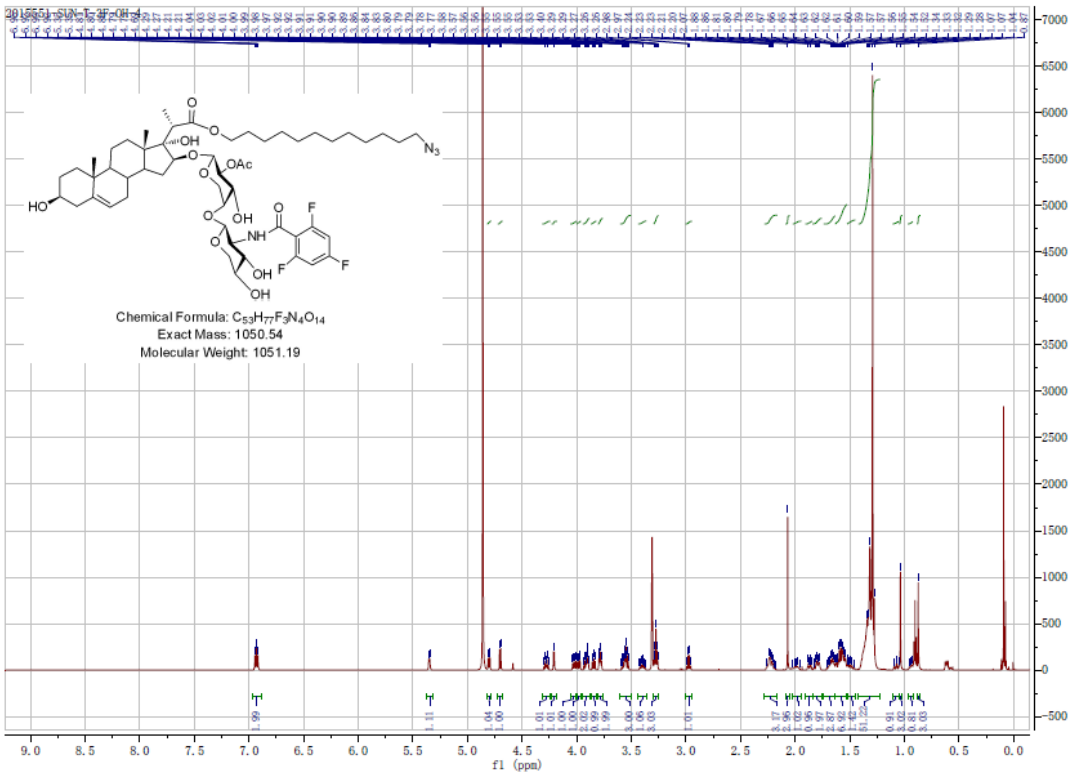
Compound **53**: HSQC NMR



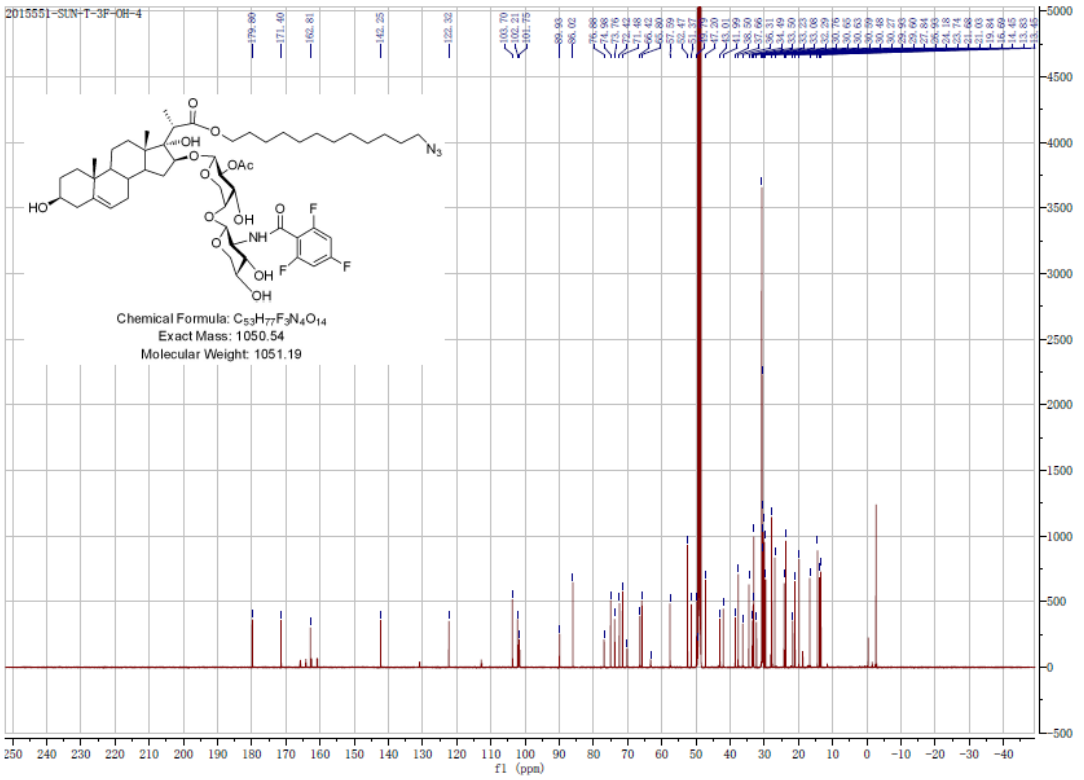
Compound **53**: HMBC NMR



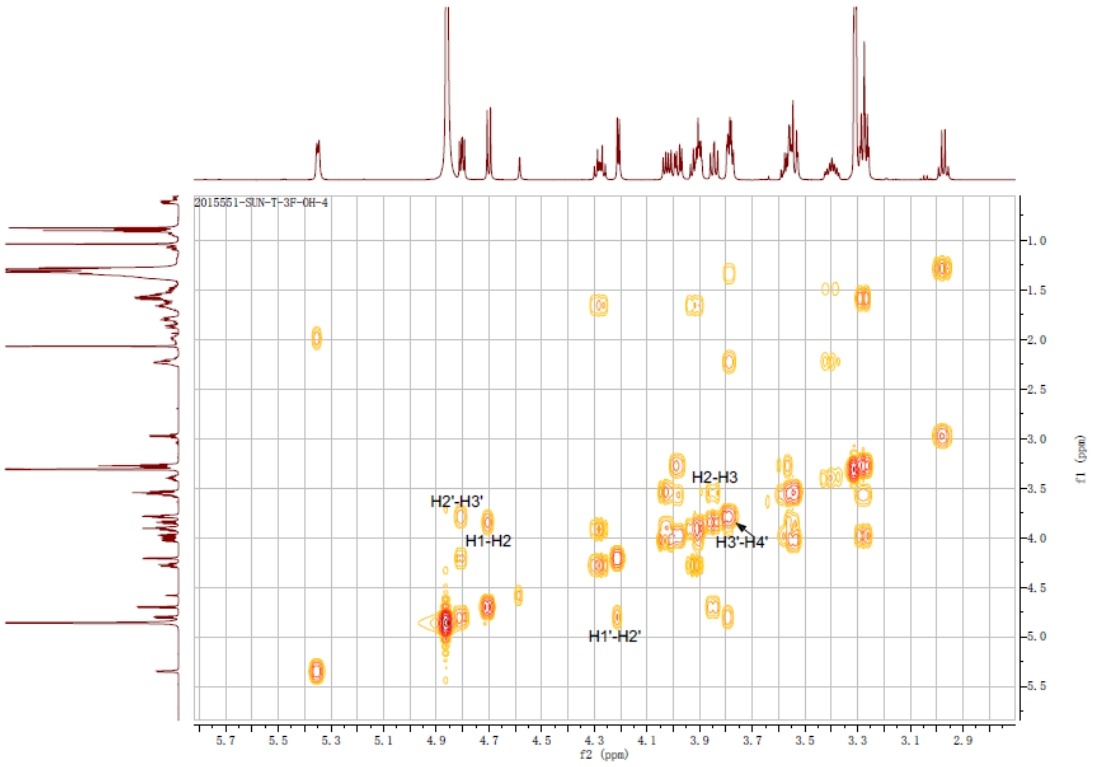
Compound **54**: ^{1}H NMR



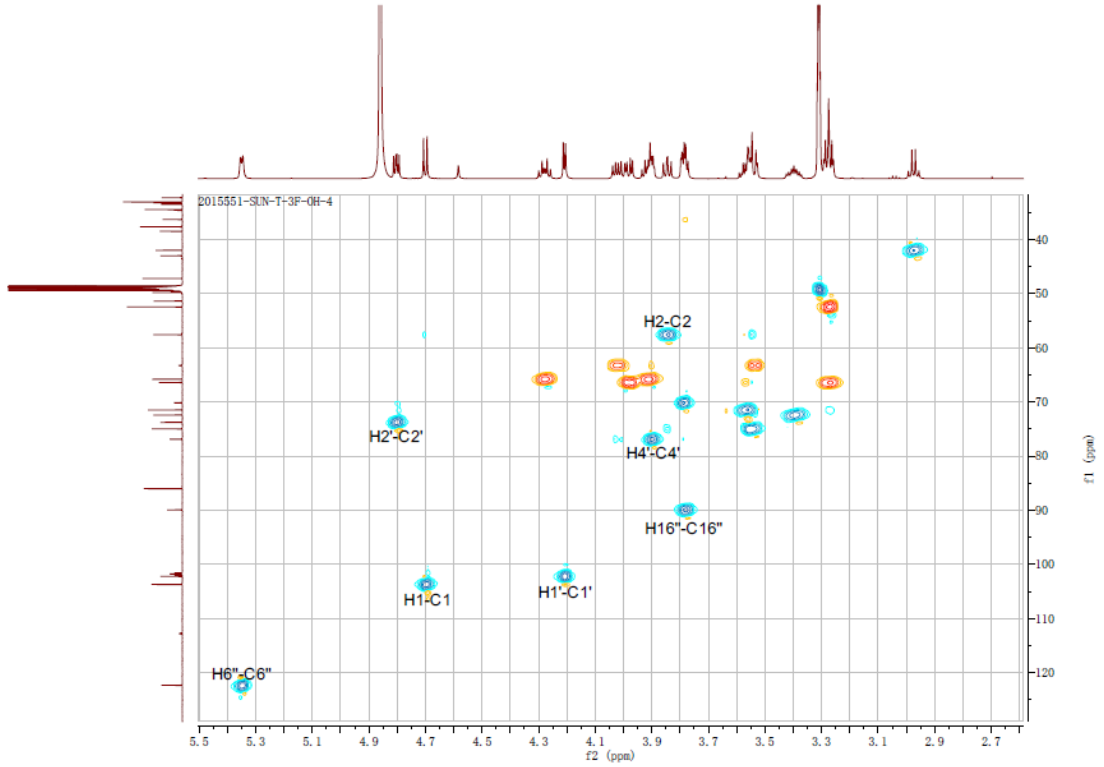
Compound **54**: ^{13}C NMR



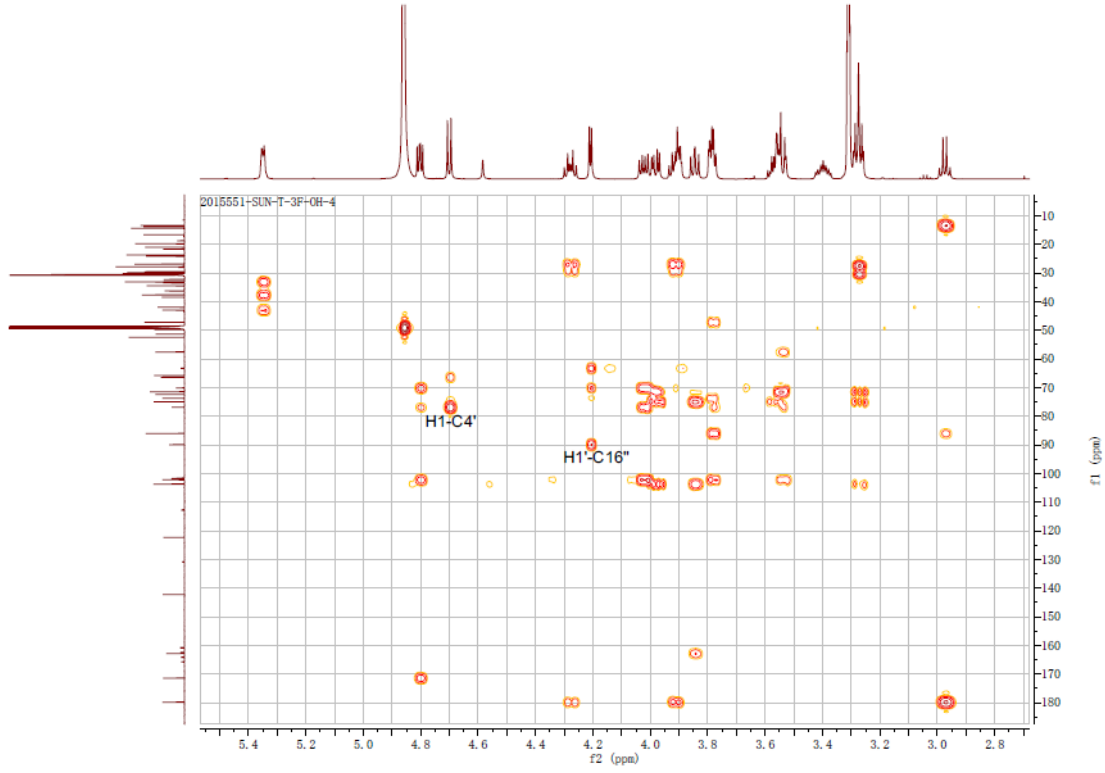
Compound **54**: COSY NMR



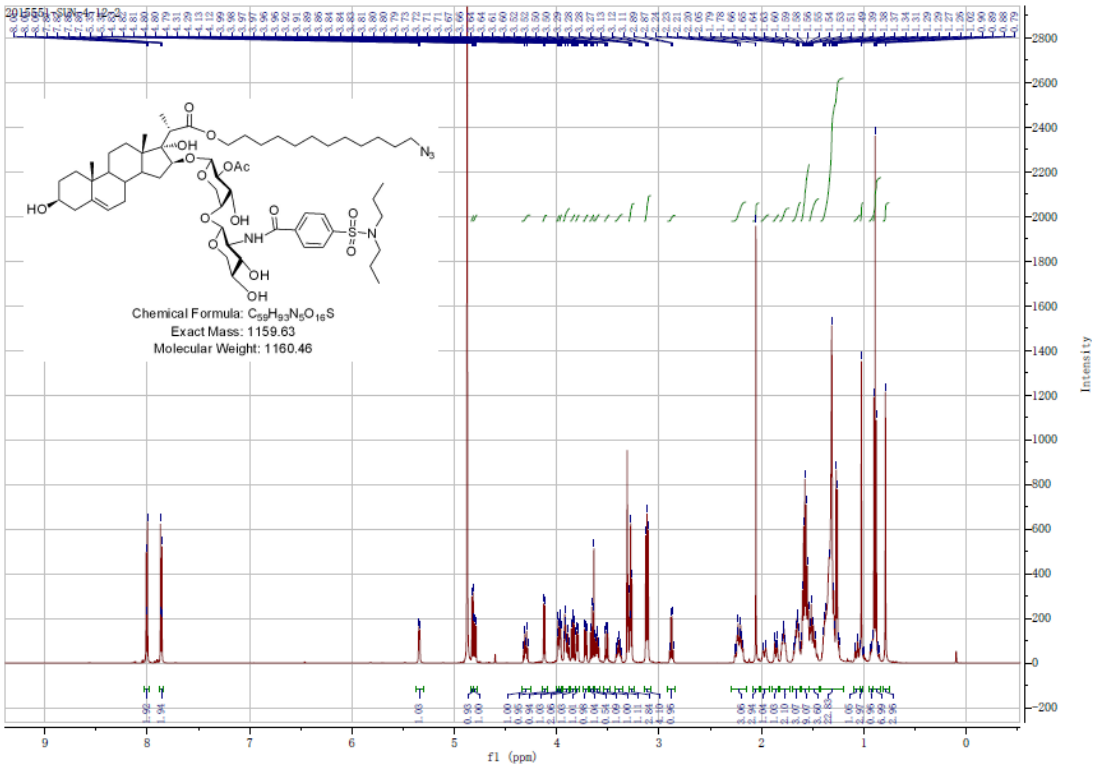
Compound **54**: HSQC NMR



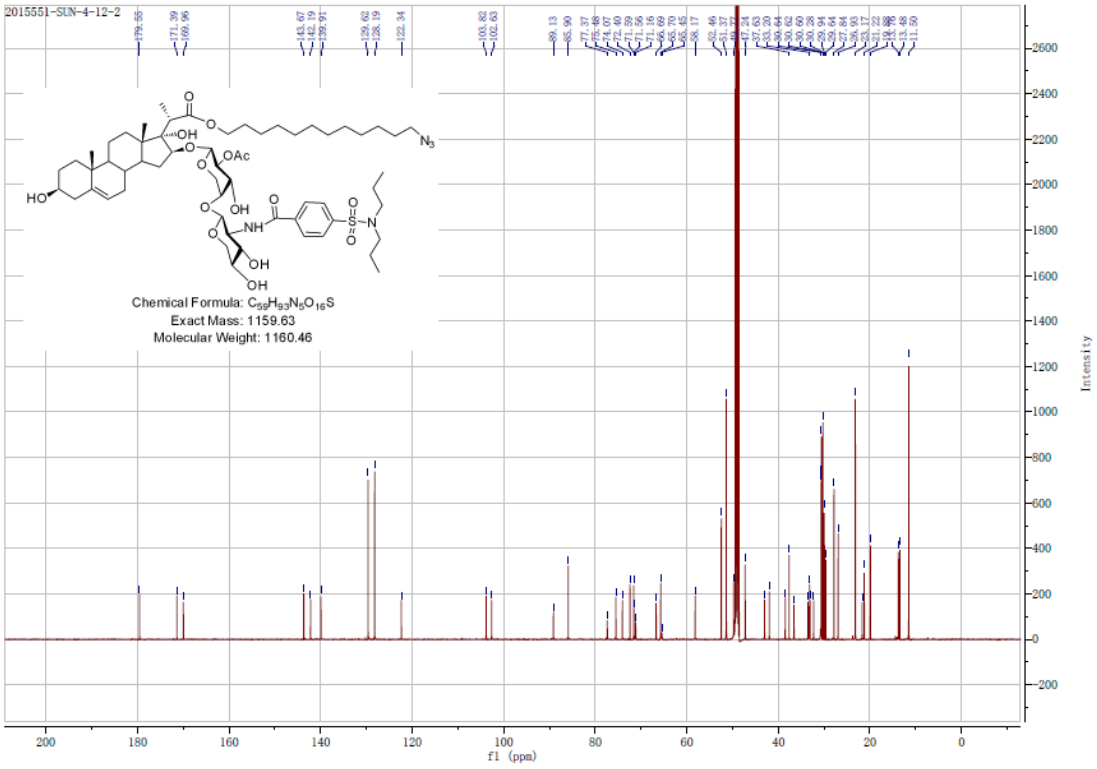
Compound **54**: HMBC NMR



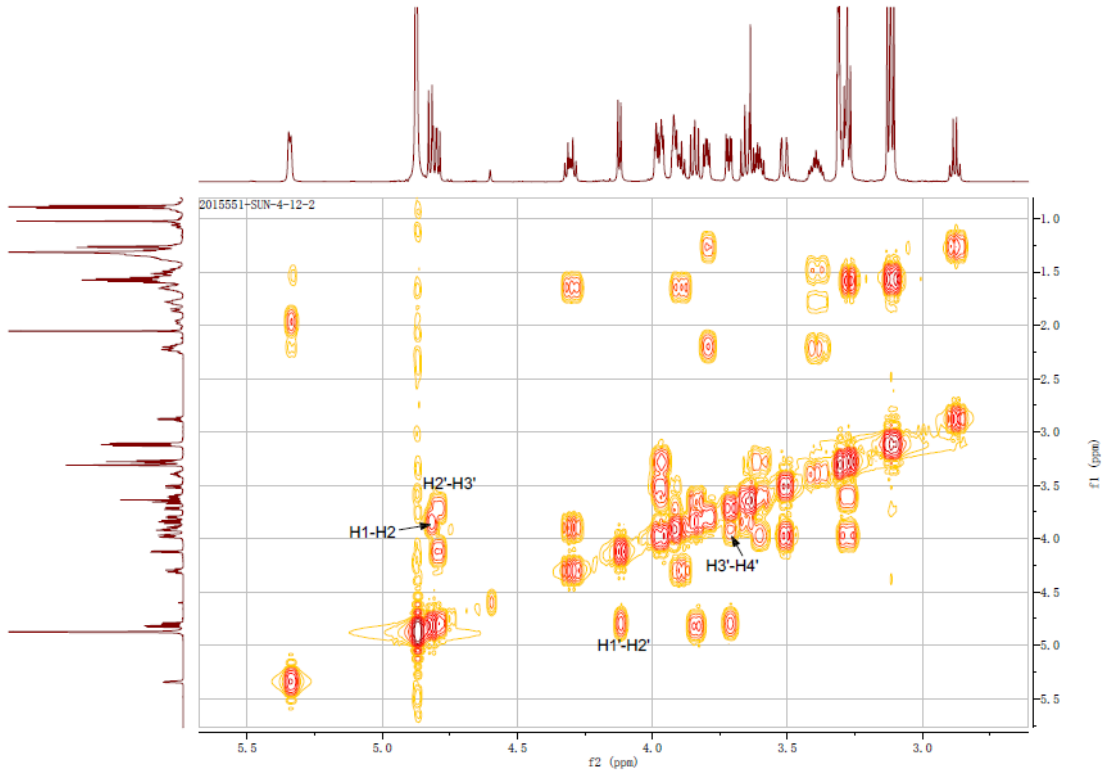
Compound **55**: ^{1}H NMR



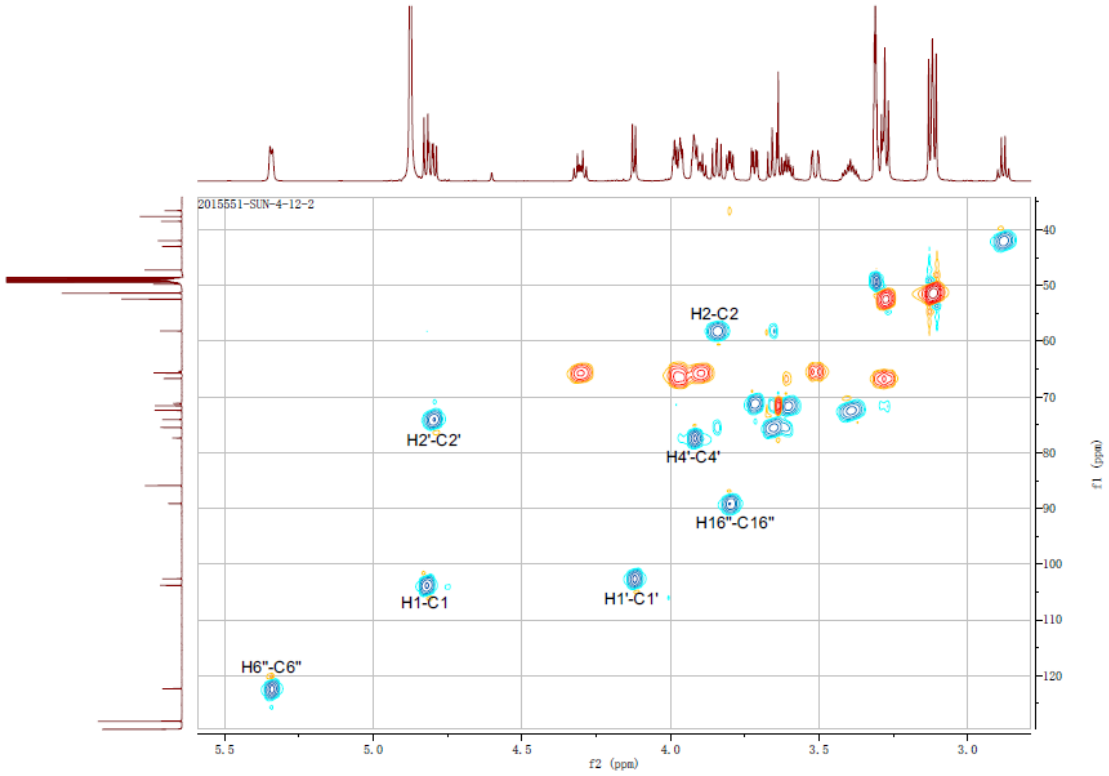
Compound **55**: ^{13}C NMR



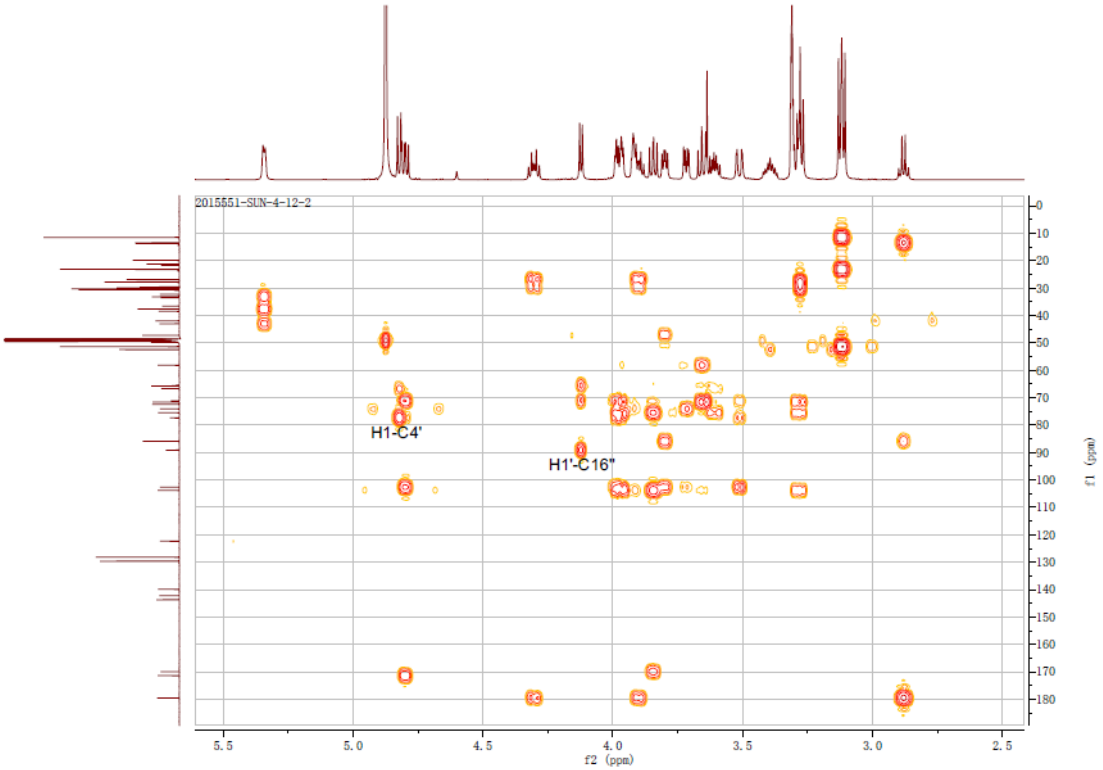
Compound **55**: COSY NMR



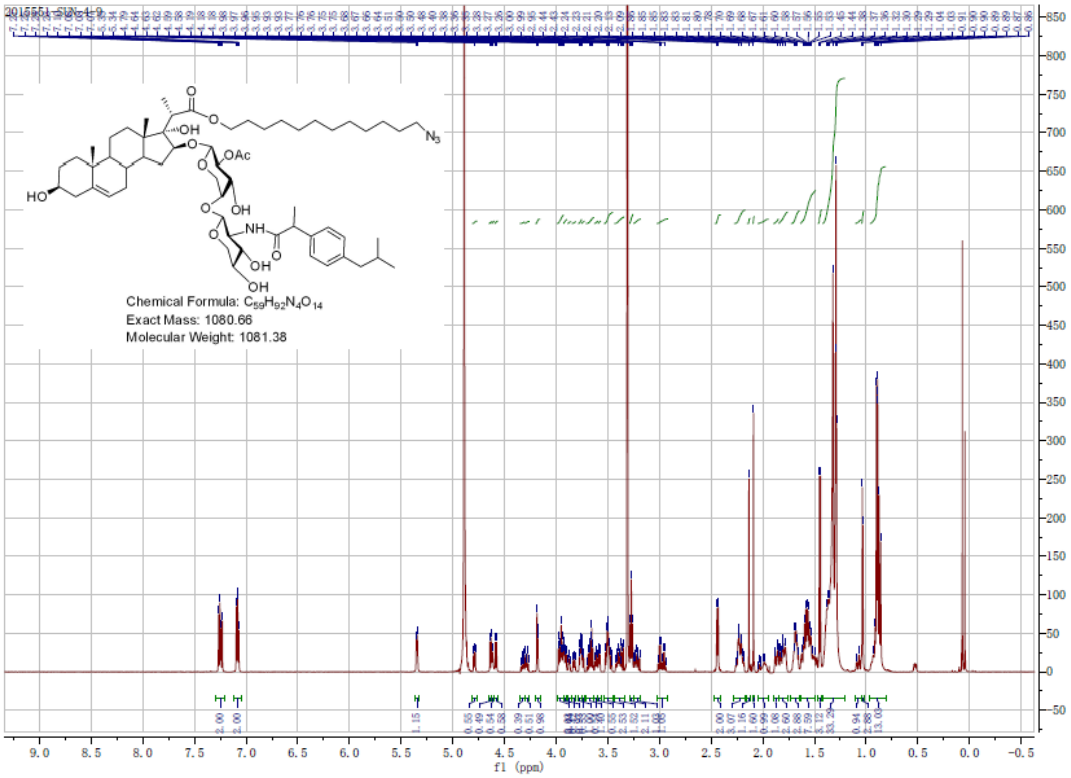
Compound **55**: HSQC NMR



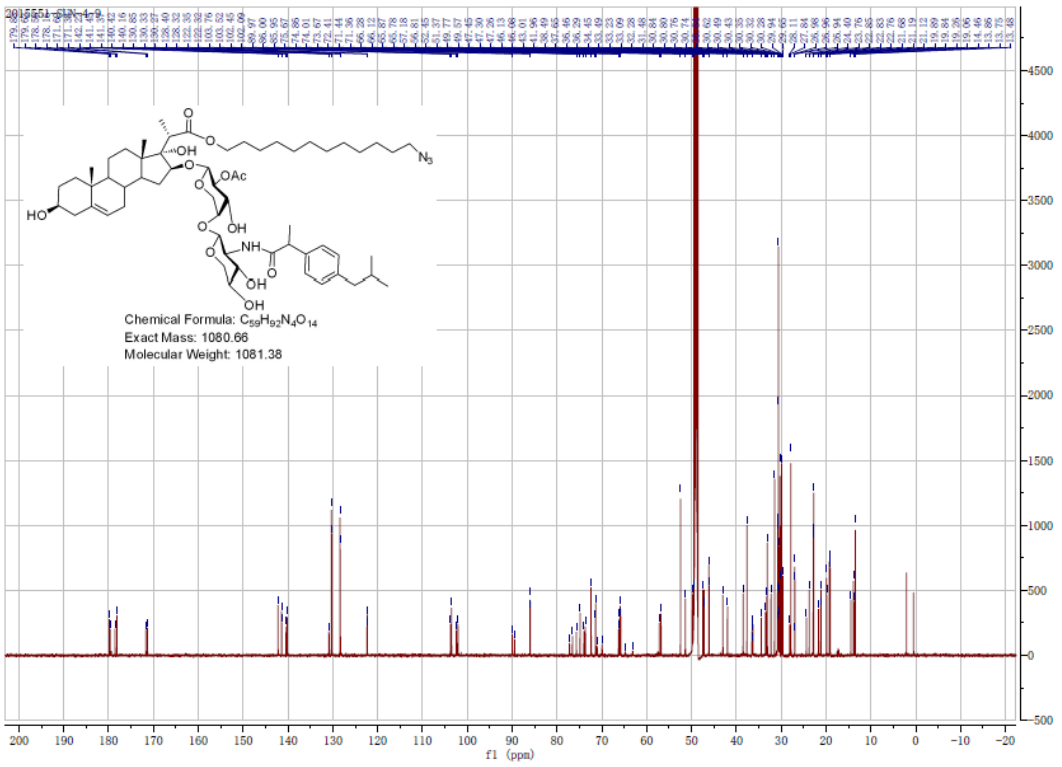
Compound **55**: HMBC NMR



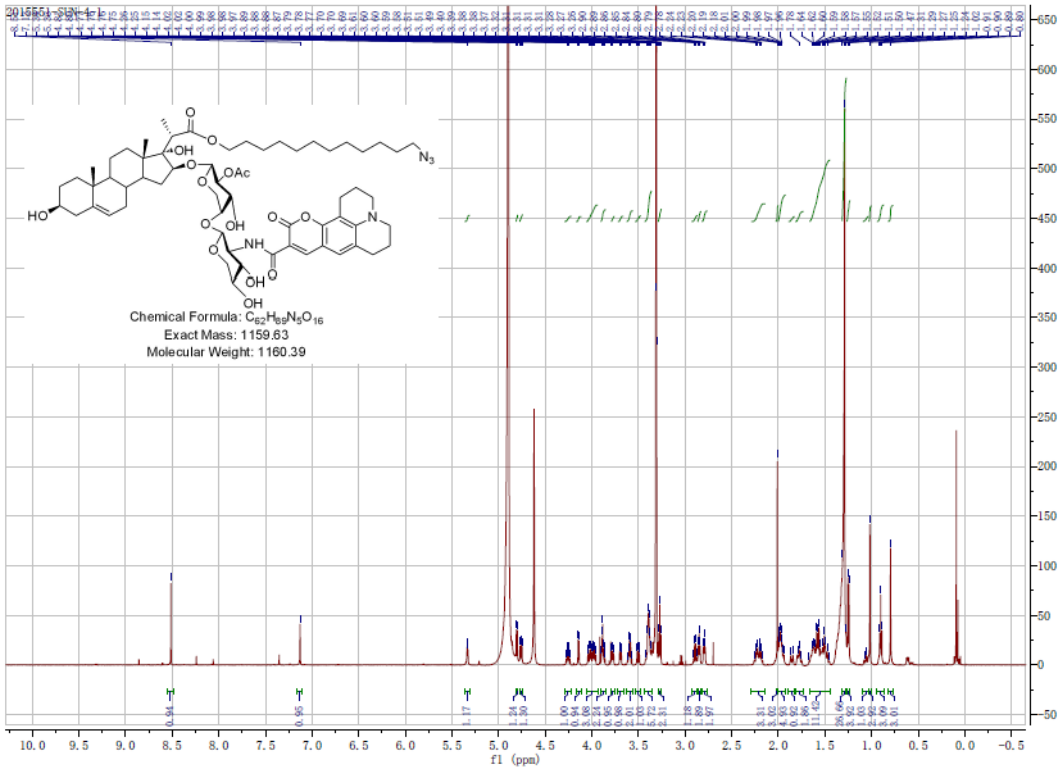
Compound **56**: ^{1}H NMR



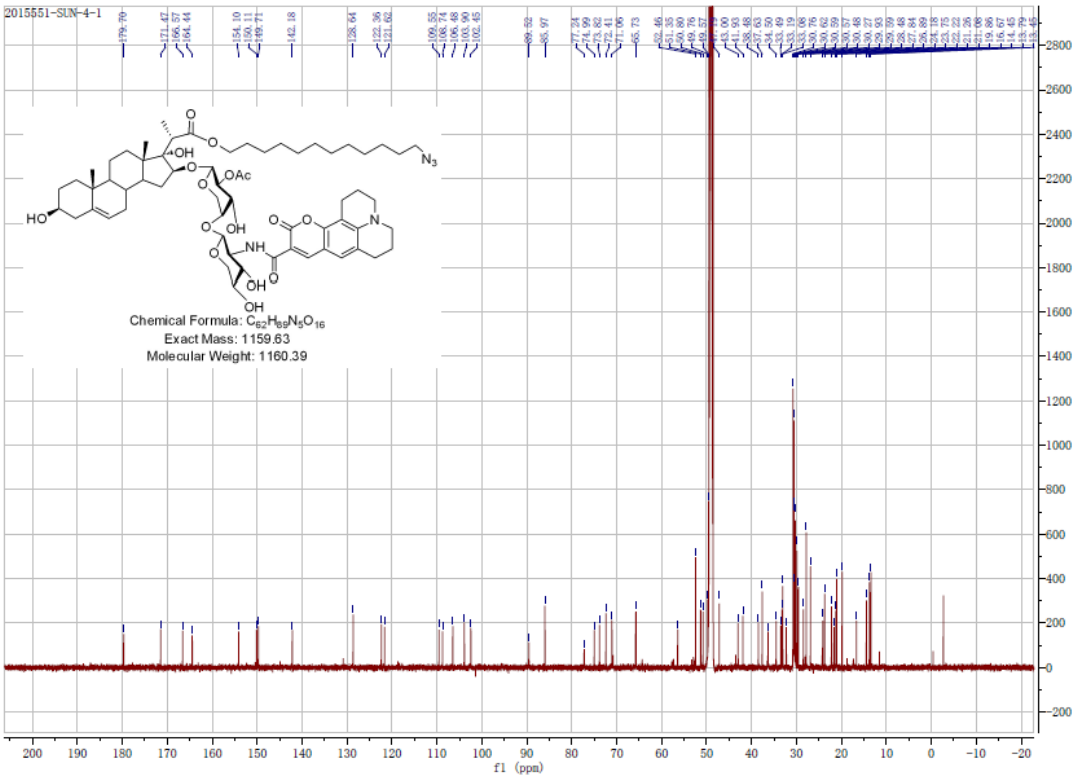
Compound **56**: ^{13}C NMR



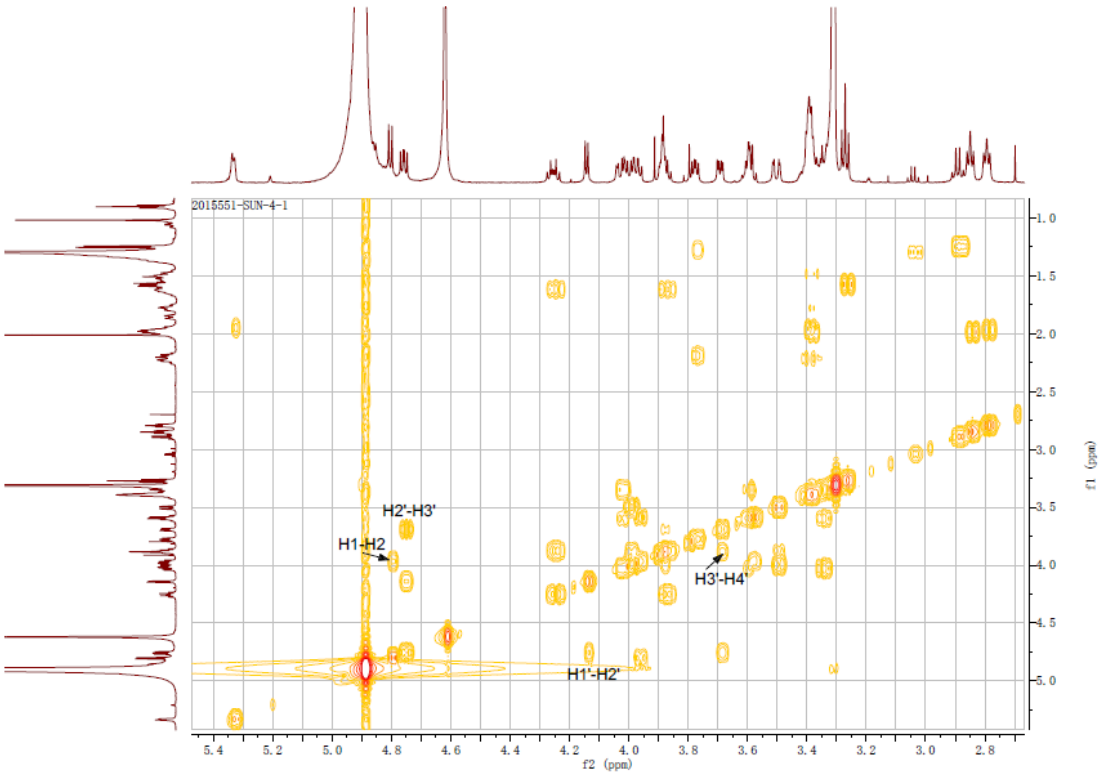
Compound **57**: ^{1}H NMR



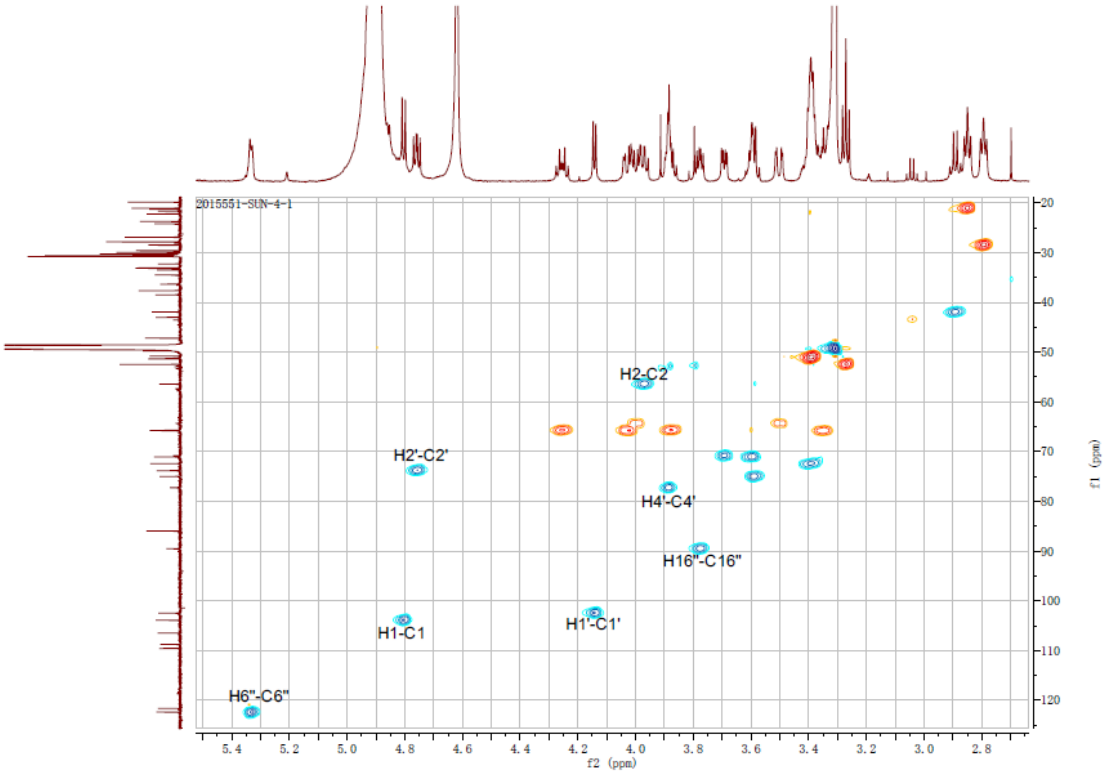
Compound **57**: ^{13}C NMR



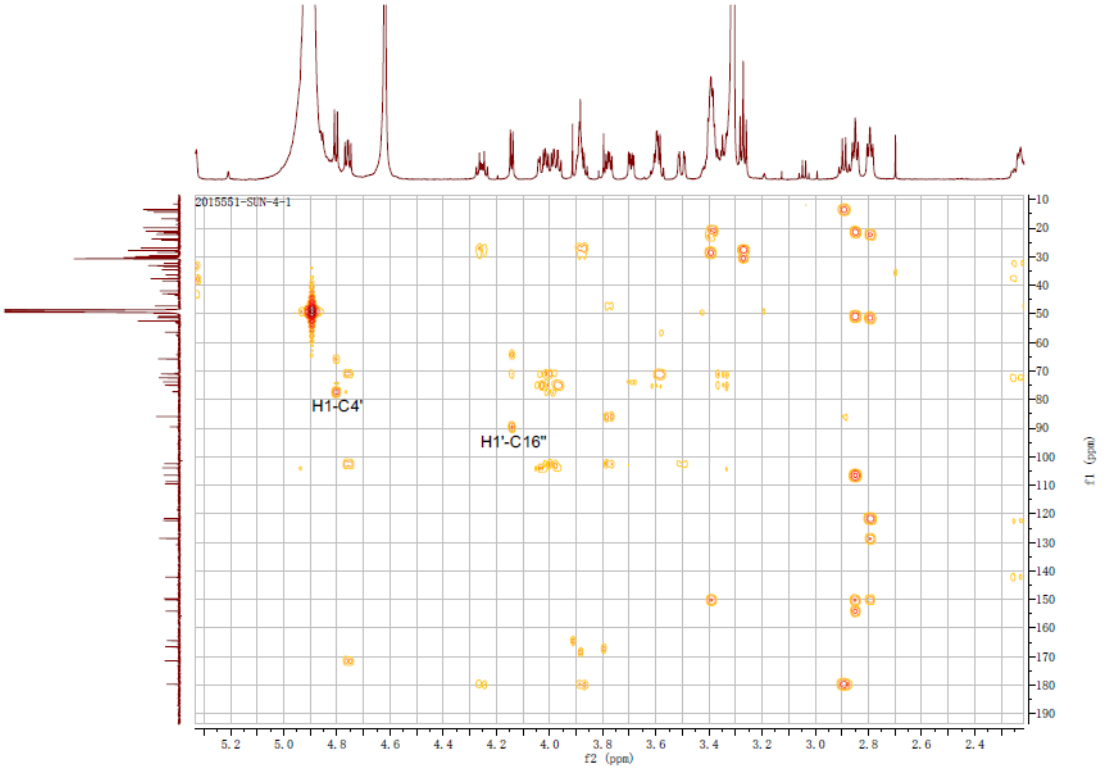
Compound **57**: COSY NMR



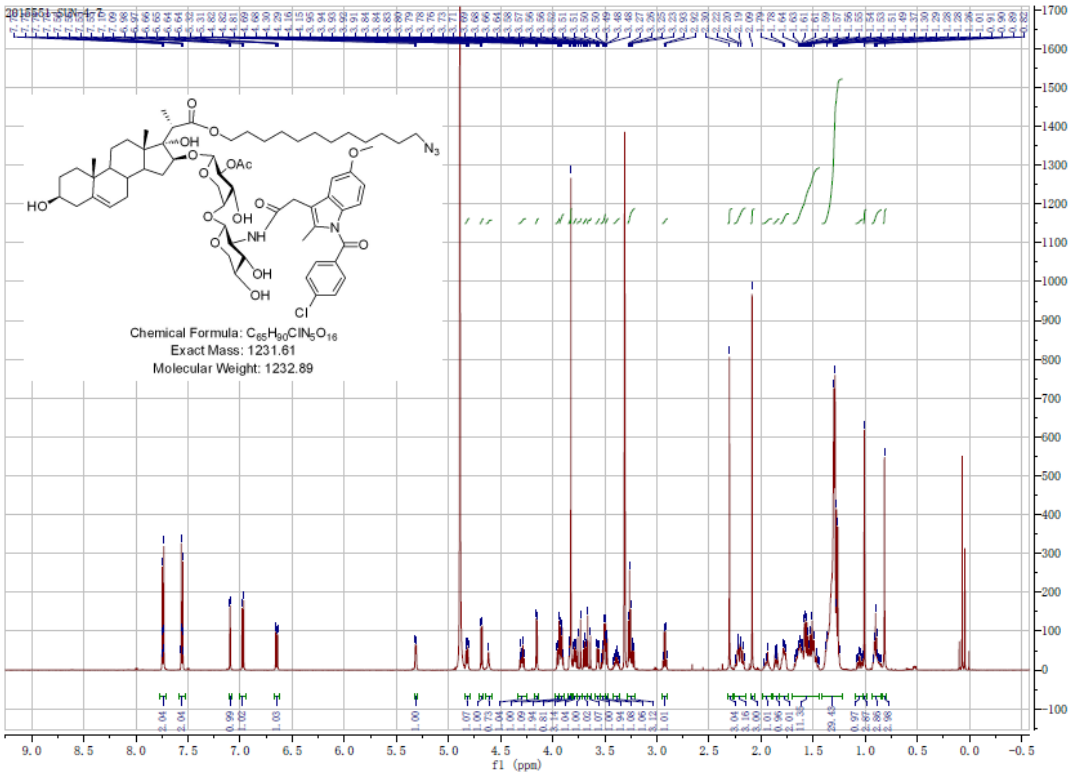
Compound **57**: HSQC NMR



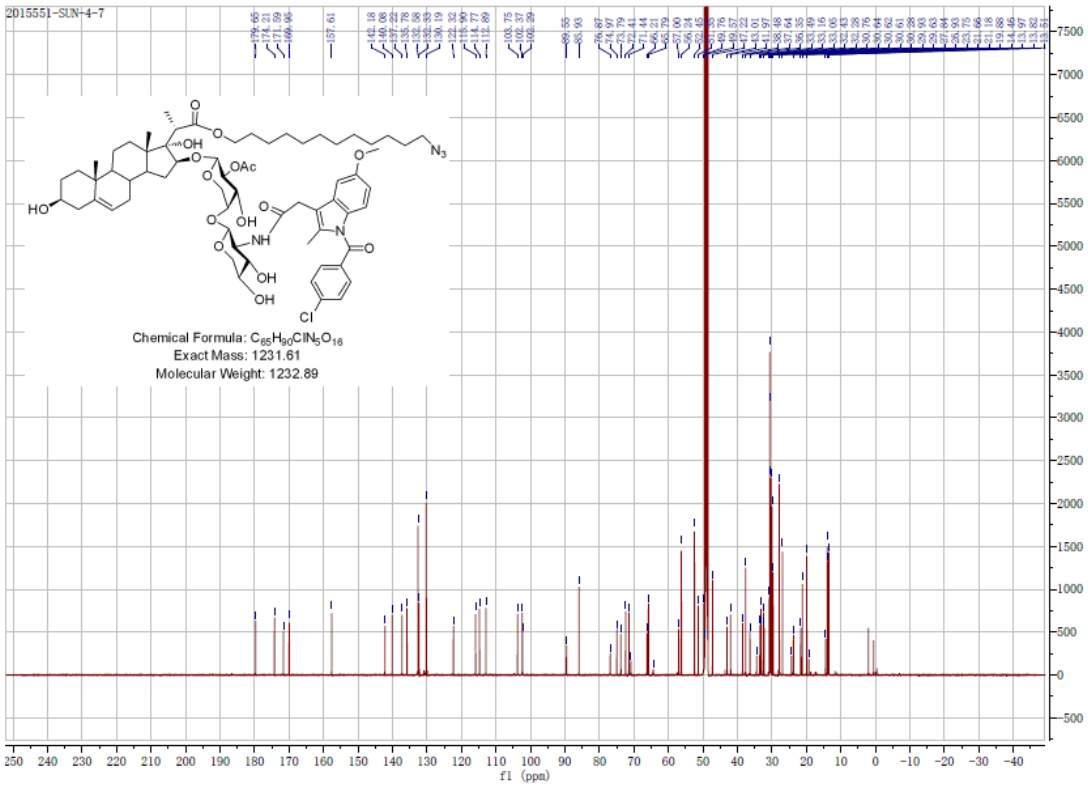
Compound **57**: HMBC NMR



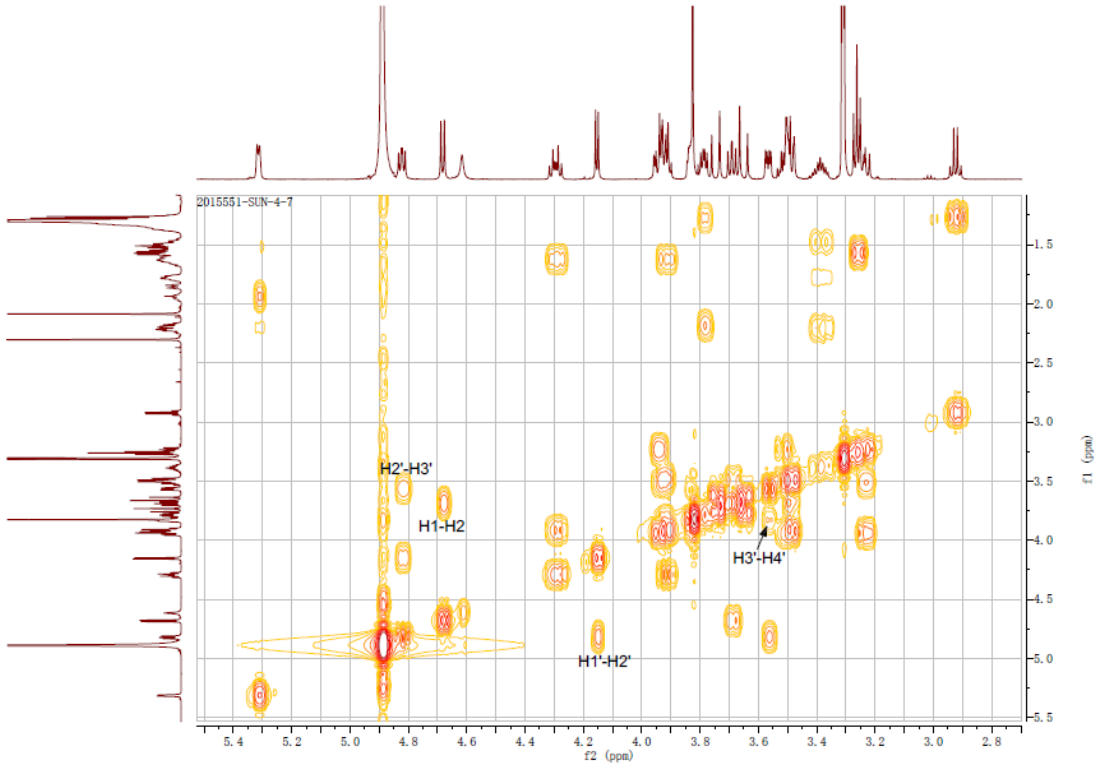
Compound **58**: ^{1}H NMR



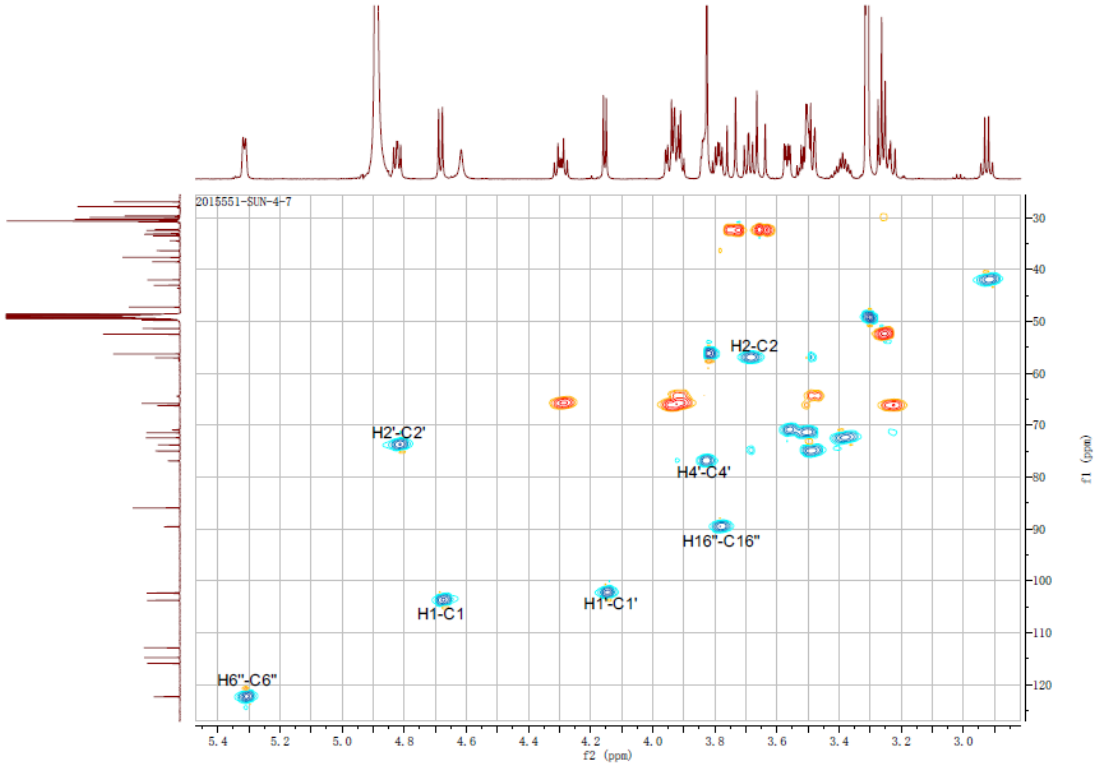
Compound **58**: ^{13}C NMR



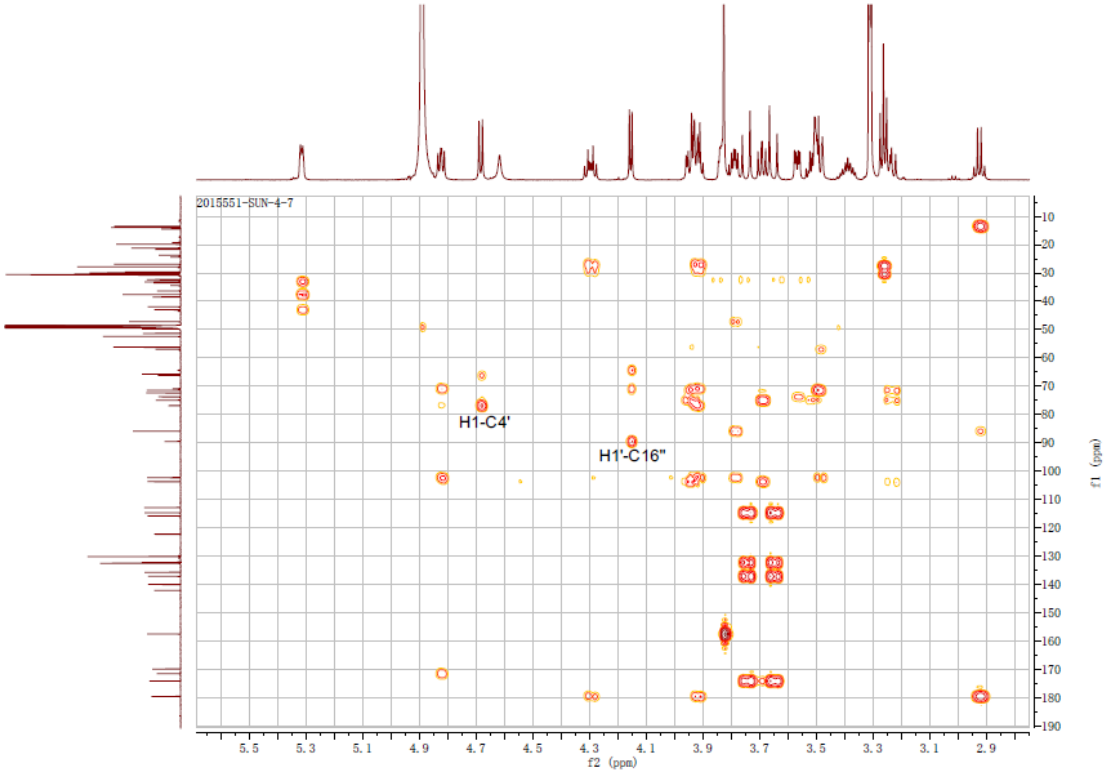
Compound **58**: COSY NMR



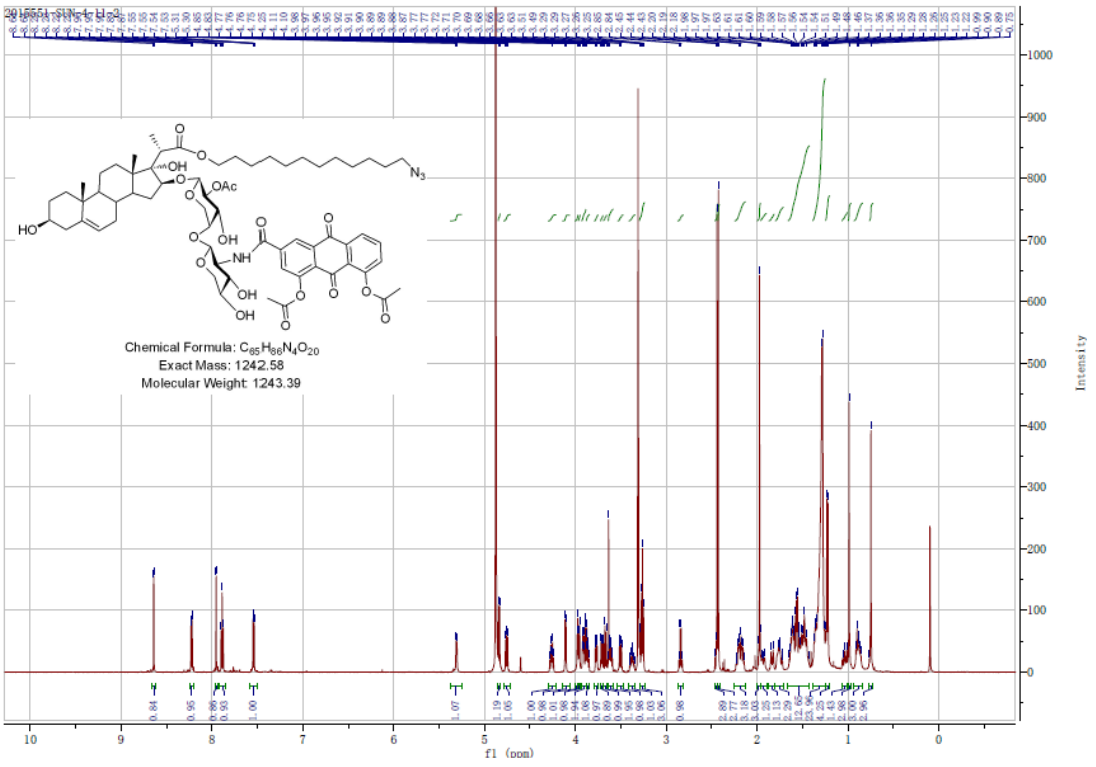
Compound **58**: HSQC NMR



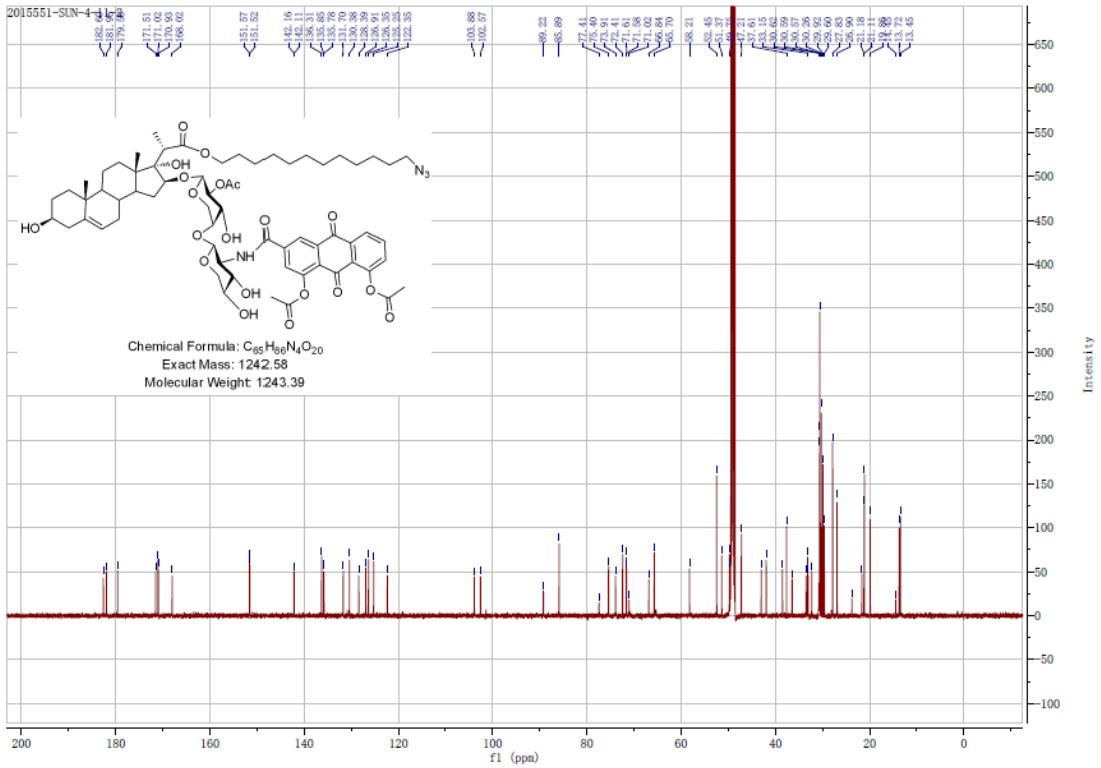
Compound **58**: HMBC NMR



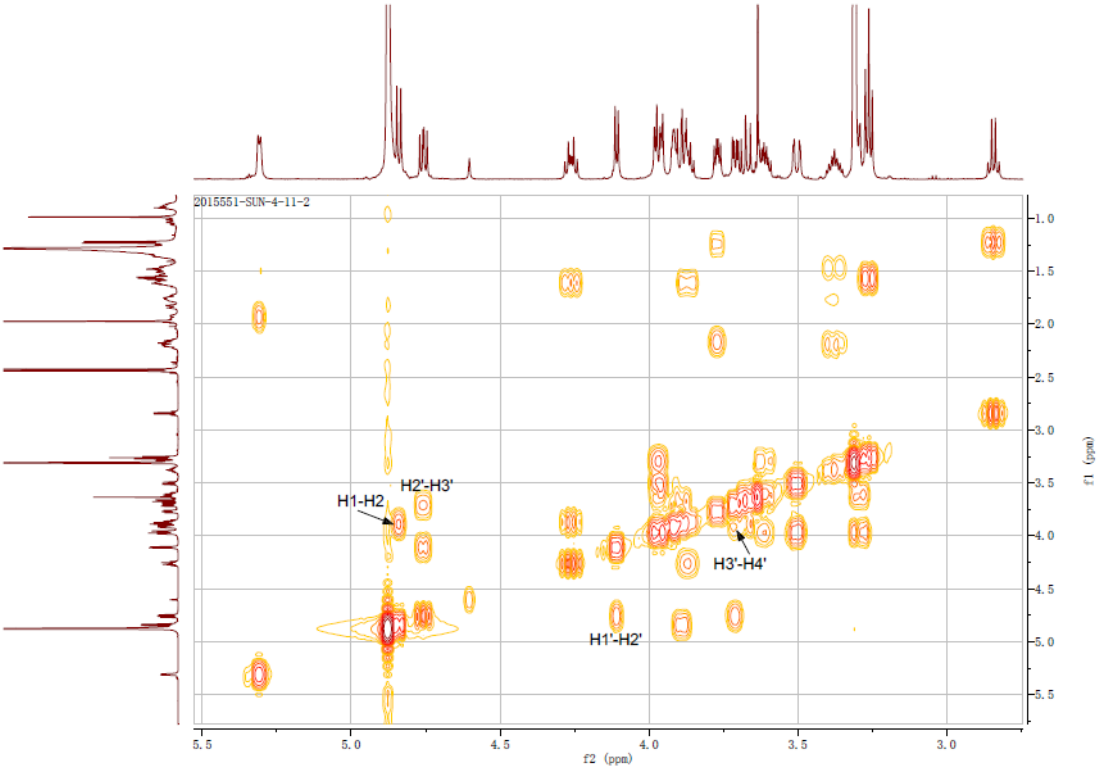
Compound **59**: ^{1}H NMR



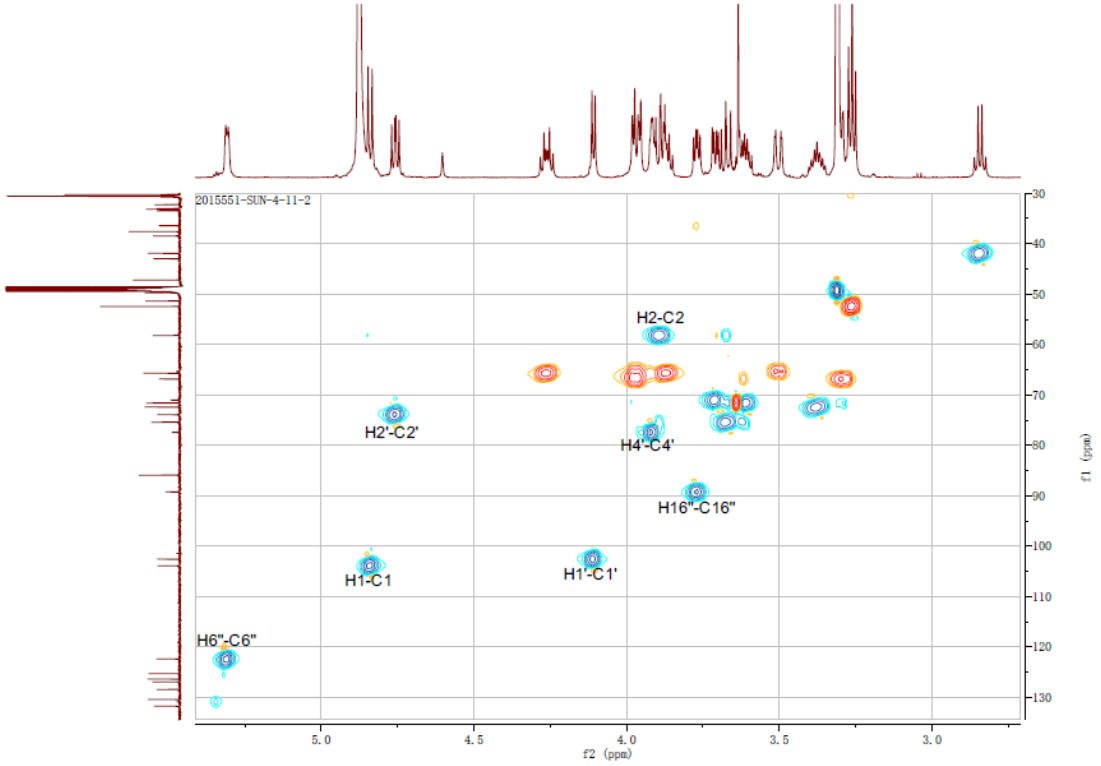
Compound **59**: ^{13}C NMR



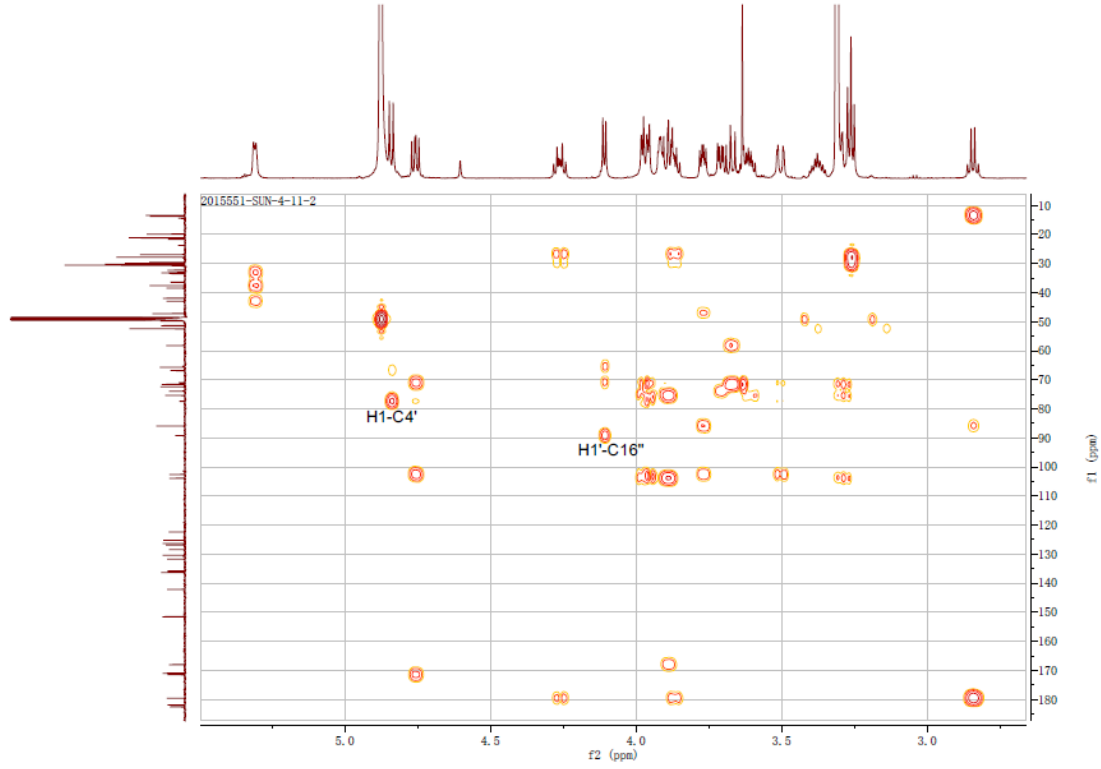
Compound **59**: COSY NMR



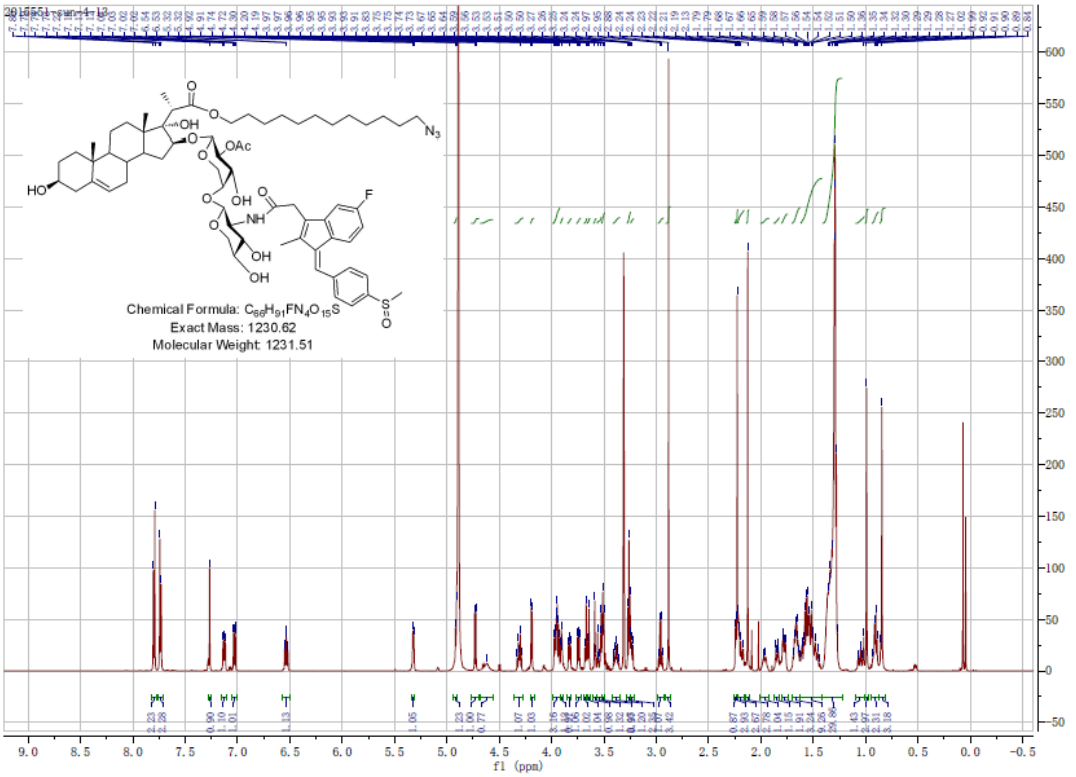
Compound **59**: HSQC NMR



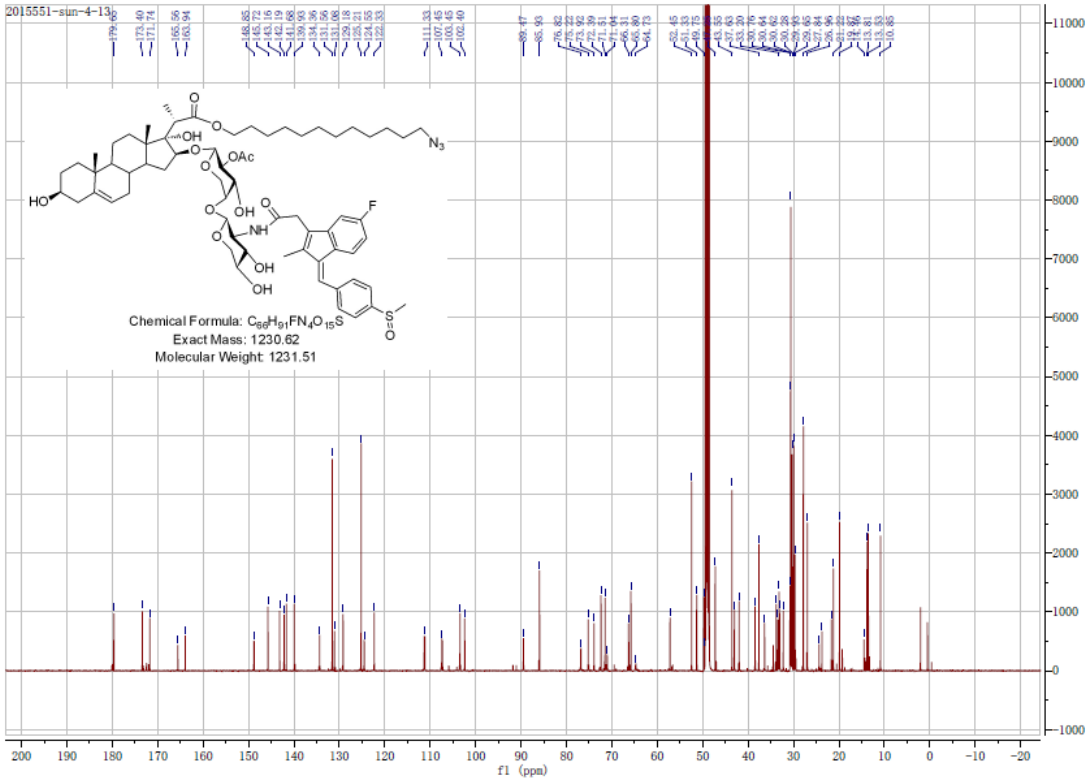
Compound **59**: HMBC NMR



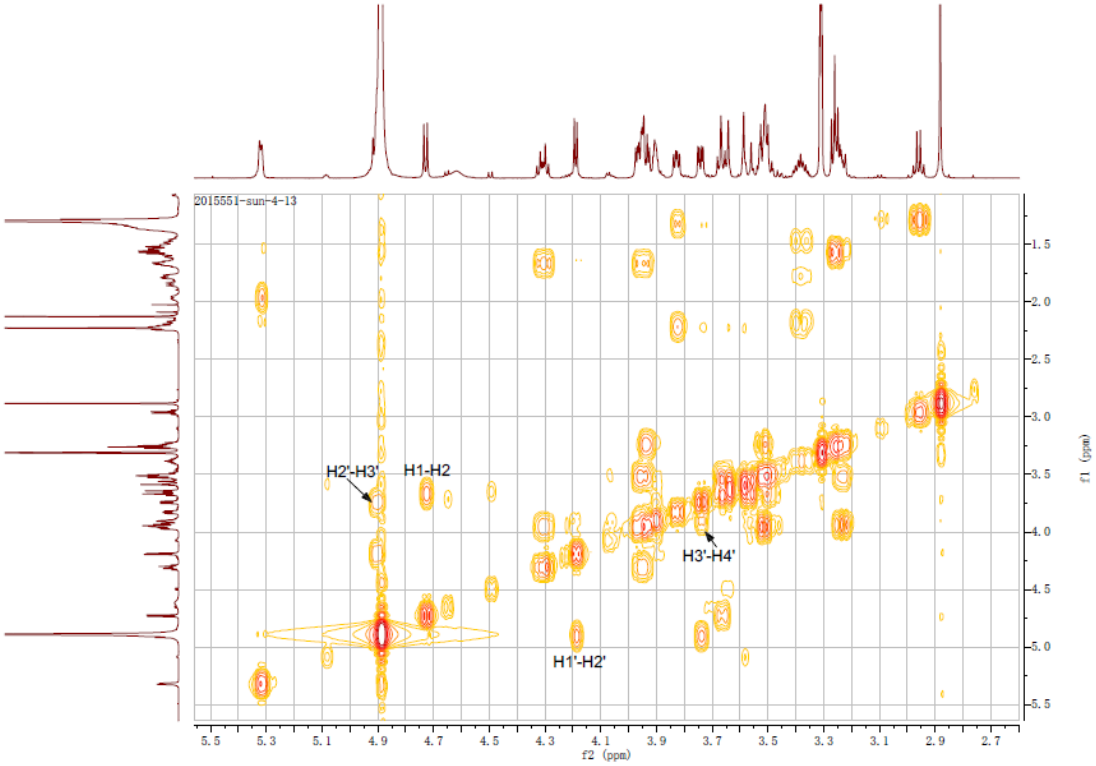
Compound **60**: ^{1}H NMR



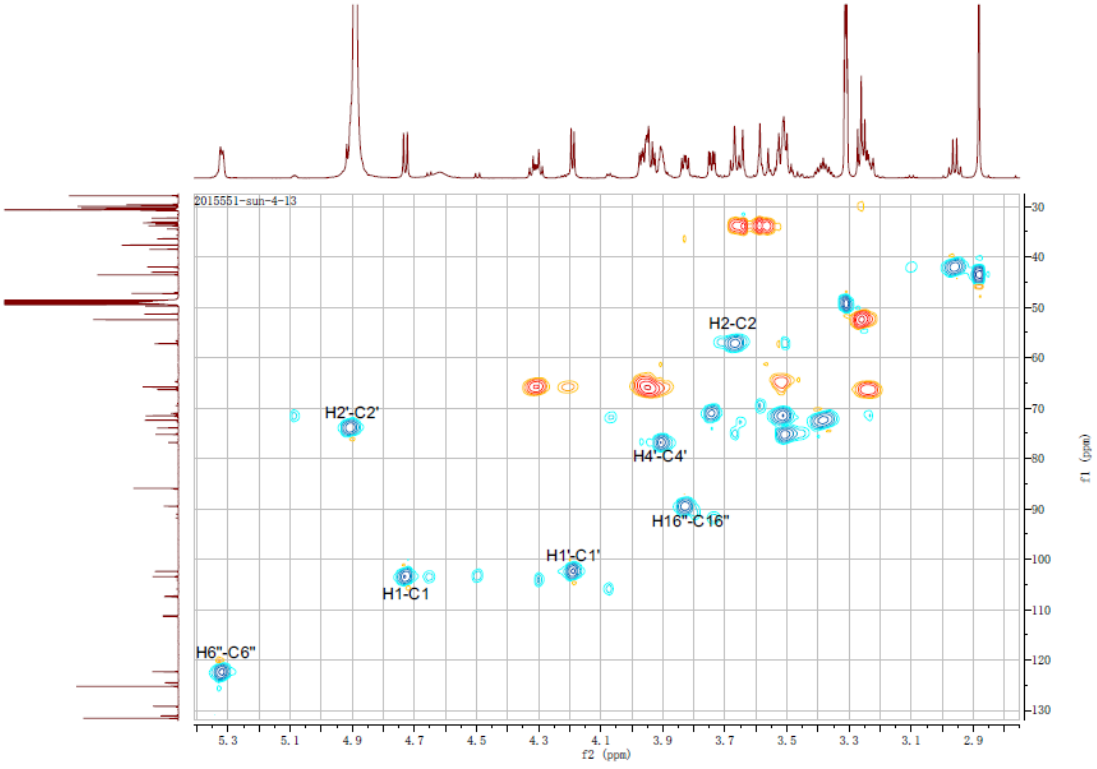
Compound **60**: ^{13}C NMR



Compound **60**: COSY NMR



Compound **60**: HSQC NMR



Compound **60**: HMBC NMR