Facile and Stereospecific Synthesis of Diverse β-*N*-Glycosyl Sulfonamide Scaffolds via Palladium Catalysis

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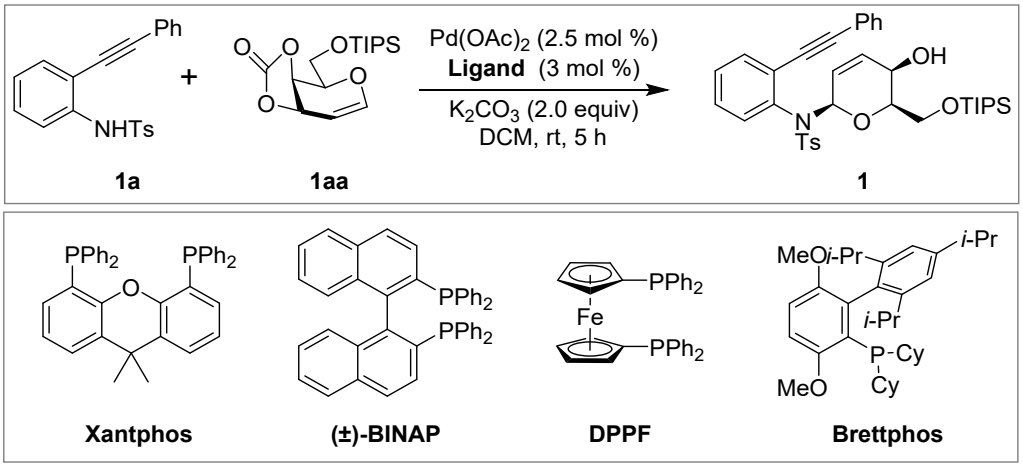
1. General information and materials

^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) or 600MR DD2 (600 MHz) spectrometer at ambient temperature. ^{1}H-NMR chemical shifts were recorded relative to the solvent residual peak ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). ^{13}C NMR chemical shifts are reported relative to the solvent residual peak ($CDCl_3$ at 77.0 ppm, DMSO-d_6 at 39.5 ppm). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet. NMR yield was determined by ^{1}H NMR using CH_2Br_2 as an internal standard before working up the reaction. Structural assignments were made with additional information from gCOSY, gHSQC, gHMBC, NOESY experiments. High resolution mass spectra (HR-MS) were acquired on a 7 Tesla SolariX FT-ICR MS (Bruker Daltonics, Bremen, Germany) or Agilent 6546 LC/Q-TOF (Agilent, United States) with an ESI source. X-ray crystallography analysis of single crystals was performed on an Agilent SuperNova-CCD X-Ray diffractometer. All air and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under nitrogen atmosphere.

All reagents from commercial sources were used as received, unless otherwise specified. $Pd(OAc)_2$ and Xantphos were purchased from Bide Pharmatech. Other reagents were purchased from suppliers such as Bide Pharmatech, Energy Chemical, Tokyo Chemical Industry, Meryer and Alfa Aesar. All deuterated solvents were purchased from Cambridge Isotope Laboratories. All solvents were refluxed with sodium/benzophenone or calcium hydride and distilled before use.

2. Optimization of reaction conditions (Table S1-S5):

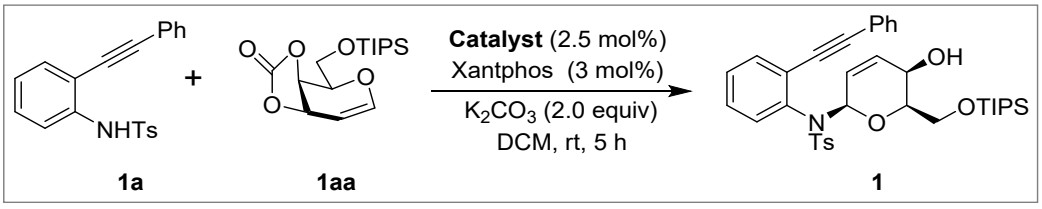
Table S1. Evaluation of ligands.[a]



Entry	Ligand	Yield (%)[b]	*β*/*α*[c]
1[d]	Brettphos	trace	N.D.
2	dppf	18	*β* only
3	(±)-BINAP	36	*β* only
4[d]	Ph_3P	44	*β* only
5	**Xantphos**	**85**	***β* only**

[a] Reaction conditions (unless otherwise specified): **1a** (0.1 mmol), **1aa** (0.15 mmol), $Pd(OAc)_2$ (2.5 mol%), ligand (3 mol%), K_2CO_3 (0.2 mmol), DCM (2.0 mL), room temperature, 5 h, under nitrogen atmosphere. [b] Determined by ^1H NMR using CH_2Br_2 as an internal standard. [c] *β*/*α* ratio was determined by ^1H NMR analysis. [d] 6 mol% of ligands were used. N.D. : not determined.

Table S2. Evaluation of Palladium catalysts. [a]

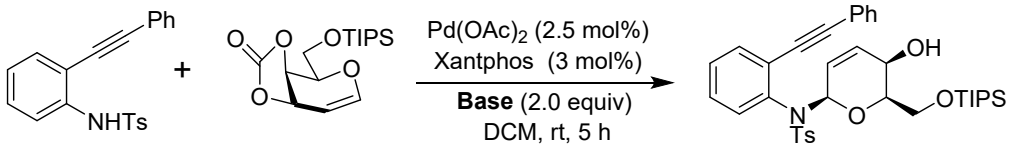


Entry	Catalyst	Yield (%)[b]	*β*/*α*[d]
1	**$Pd(OAc)_2$**	**85**	***β* only**
2[c]	$Pd_2(dba)_3$	36	*β* only
3	$Pd(PPh_3)_4$	15	*β* only

Entry	Catalyst	Yield (%)[b]	*β*/*α*[d]
4	$PdCl_2$	trace	N.D.
5	$PdCl_2(PPh_3)_2$	trace	N.D.

[a]Reaction conditions (unless otherwise specified): **1a** (0.1 mmol), **1aa** (0.15 mmol), catalyst (2.5 mol%), Xantphos (3 mol%), K_2CO_3 (0.2 mmol), DCM (2.0 mL), room temperature, 5 h, under nitrogen atmosphere. [b] Determined by ^1H NMR using CH_2Br_2 as an internal standard. [c]$Pd_2(dba)_3$ (1.25 mol%) was used. [d]*β*/*α* ratio was determined by ^1H NMR analysis. N.D. : not determined.

Table S3. Evaluation of bases. [a]

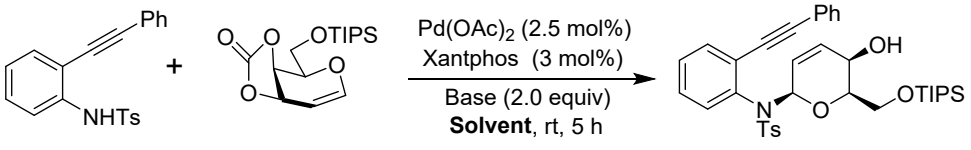


1a **1aa** **1**

Entry	Base	Yield (%)[b]	*β*/*α*[c]
1	**K_2CO_3**	**85**	***β* only**
2	K_3PO_4	75	*β* only
3	Cs_2CO_3	56	*β* only
4	Et_3N	38	*β* only
5	DBU	0	N.D.
6	DABCO	30	*β* only
7	DIPEA	28	*β* only

[a] Reaction conditions (unless otherwise specified): **1a** (0.1 mmol), **1aa** (0.15 mmol), catalyst (2.5 mol%), Xantphos (3 mol%), base (0.2 mmol), DCM (2.0 mL), room temperature, 5 h, under nitrogen atmosphere. [b] Determined by ^1H NMR using CH_2Br_2 as an internal standard. [c]*β*/*α* ratio was determined by ^1H NMR analysis. N.D. : not determined.

Table S4. Evaluation of solvents. [a]



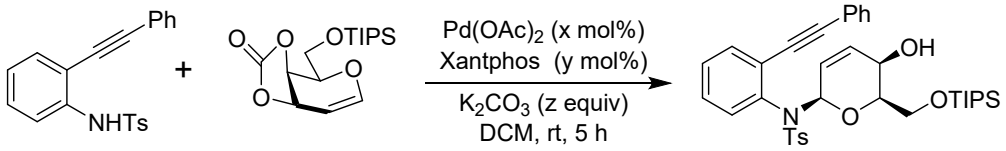
1a **1aa** **1**

Entry	Solvent	Yield (%)[b]	*β*/*α*[c]

1	DCE	64	*β* only
2	**DCM**	**85**	***β* only**
3	DMF	trace	N.D.
4	Tol	18	*β* only
5	THF	20	*β* only
6	CH_3CN	trace	*β* only

[a] Reaction conditions (unless otherwise specified): **1a** (0.1 mmol), **1aa** (0.15 mmol), $Pd(OAc)_2$ (2.5 mol%), Xantphos (3 mol%), K_2CO_3 (0.2 mmol), solvent (2.0 mL), room temperature, 5 h, under nitrogen atmosphere. [b] Determined by ^1H NMR using CH_2Br_2 as an internal standard. [c] *β/α* ratio was determined by ^1H NMR analysis. N.D. : not determined.

Table S5. Control experiments and evaluation of catalyst loading. [a]



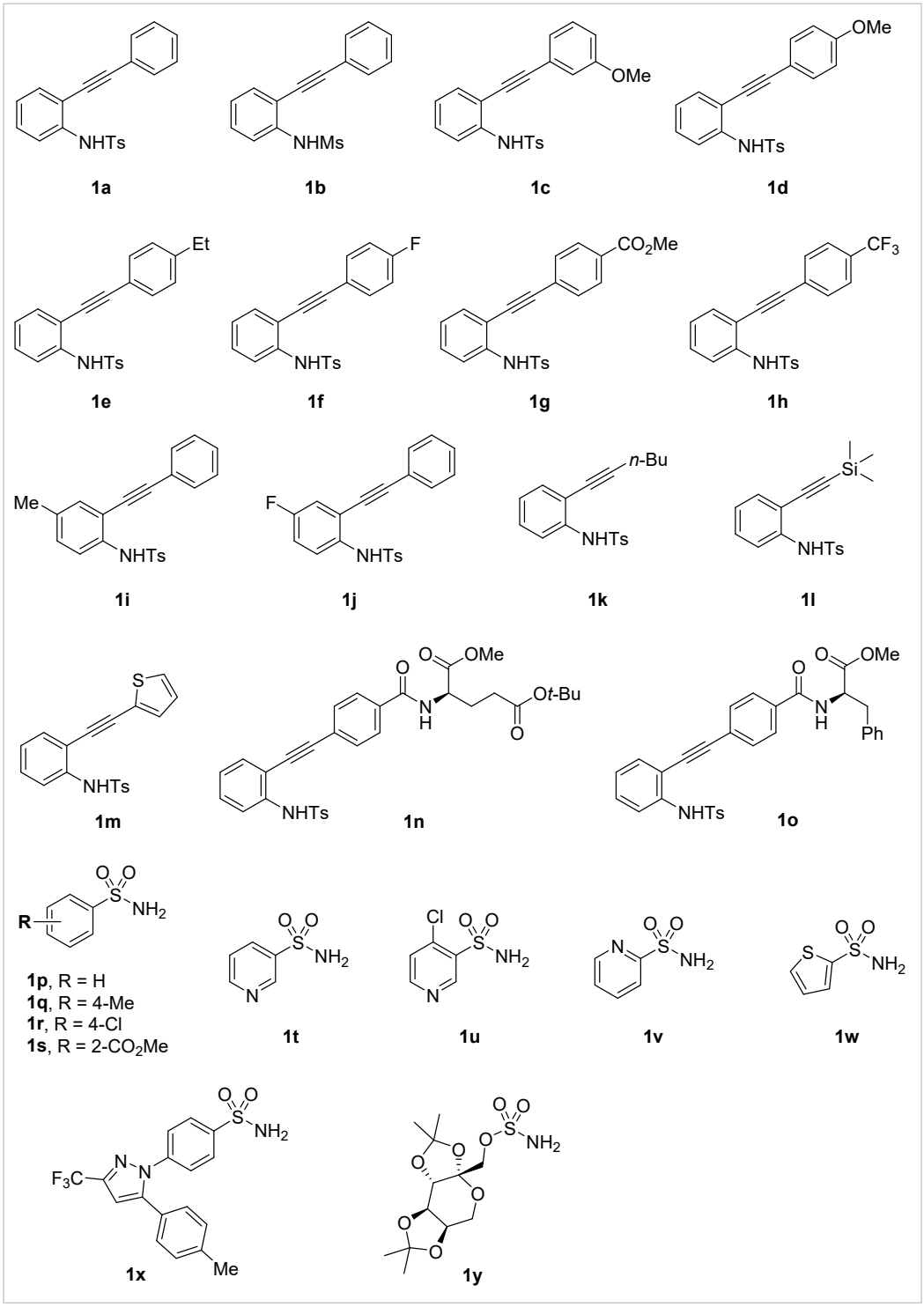
1a **1aa** **1**

Entry	Catalyst	Ligand	Base	Yield[b]	*β/α*[c]
1	**$Pd(OAc)_2$**	**Xantphos**	**K_2CO_3**	**85**	***β* only**
2	--	Xantphos	K_2CO_3	0	N.D.
3	$Pd(OAc)_2$	--	K_2CO_3	0	N.D.
4	$Pd(OAc)_2$	Xantphos	--	56	*β* only
5[d]	$Pd(OAc)_2$	Xantphos	K_2CO_3	49	*β* only

[a] Reaction conditions (unless otherwise specified): **1a** (0.1 mmol), **1aa** (0.15 mmol), $Pd(OAc)_2$ (2.5 mol%), Xantphos (3 mol%), K_2CO_3 (0.2 mmol), DCM (2.0 mL), room temperature, 5 h, under nitrogen atmosphere. [b] Determined by ^1H NMR using CH_2Br_2 as an internal standard. [c] *β/α* ratio was determined by ^1H NMR analysis. [d] $Pd(OAc)_2$ (1 mol%), Xantphos (1.2 mol%) was used. N.D. : not determined.

3. Procedures for substrates preparation

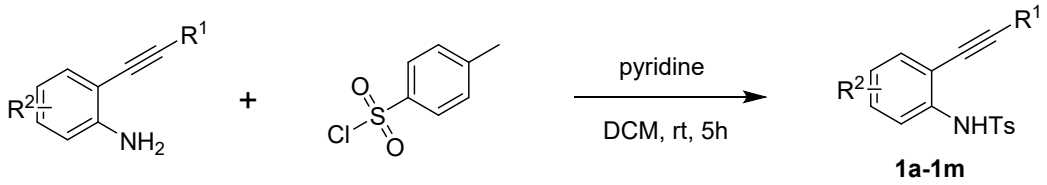
Table S6. Sulfonamide substrates were used in this study.



Compounds **1a-1m** were prepared according to the previously reported procedure.[1-5]

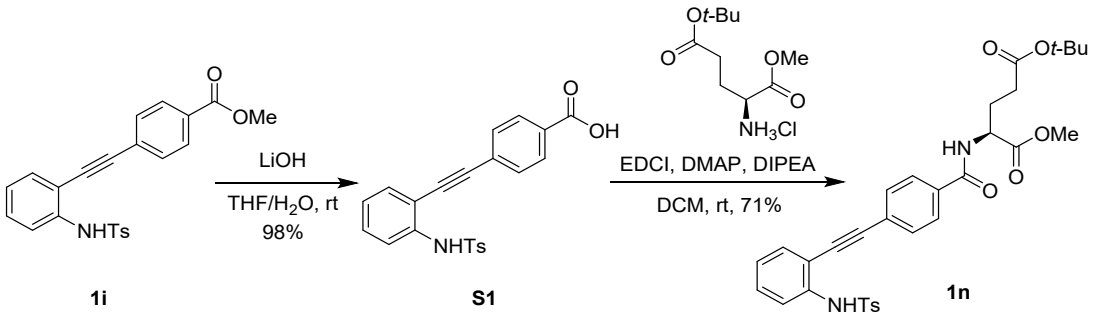
Compounds **1p-1y** are commercially available.

General procedure A: synthesis of sulfonamide substrates



To a solution of substituted *ortho*-alkynyl aniline compounds (4 mmol) and 4-methylbenzenesulfonyl chloride (4.8 mmol, 1.2 equiv.) in anhydrous CH_2Cl_2 (15 mL) was added pyridine (12 mmol, 3.0 equiv.) slowly at room temperature. The reaction was stirred at room temperature and monitored by TLC. After full conversion, the mixture was quenched with water (15 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel flash chromatography (eluting with petroleum ether/EtOAc = 25:1) to give the target compounds **1a-1m**.

4-(*tert*-Butyl) 1,2-dimethyl (1S)-1-(4-((2-((4-methylphenyl)sulfonamido)phenyl) ethynyl)benzamido)butane-1,2,4-tricarboxylate (1n)

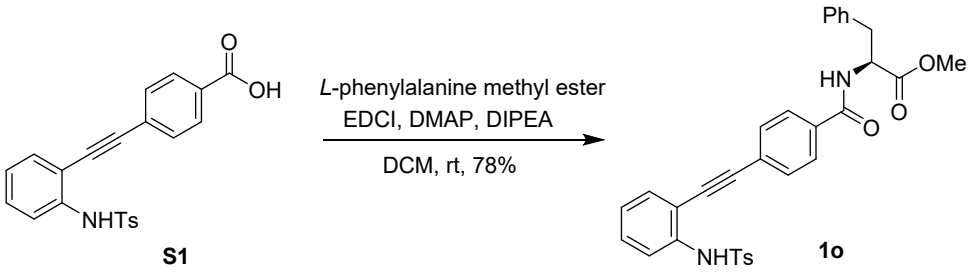


To a solution of **1i** (90 mg, 0.22 mmol) in THF/H_2O (5 mL, 1:1) was added LiOH (15.8 mg, 0.66 mmol) at 0 °C. After stirring at room temperature for 1 h, the mixture was diluted in EtOAc (10 mL) and washed with brine (20 mL). The combined organic extracts was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (eluting with petroleum ether/EtOAc = 1/1) to afford the **S1** (84 mg, 98%).

To a solution of **S1** (60 mg, 0.15 mmol), EDCI (46 mg, 0.24 mmol), DMAP (2 mg, 0.015 mmol) and *L*-glutamic acid 5-*tert*-butyl 1-methyl ester hydrochloride (50 mg, 0.2 mmol) in DCM (5 mL). After stirring at room temperature for 6 h, the mixture was

diluted in DCM (10 mL) and washed with brine (2 ×10 mL). The solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (eluting with petroleum ether/EtOAc = 2/1) to afford **1n** (62.8 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.70 – 7.63 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 5.9 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.78 (dd, *J* = 12.3, 7.7 Hz, 1H), 3.79 (s, 3H), 2.45 (qd, *J* = 17.2, 8.4 Hz, 2H), 2.33 (s, 3H), 2.20 (ddd, *J* = 13.9, 11.9, 6.0 Hz, 2H), 1.44 (d, *J* = 11.9 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9, 172.4, 166.2, 144.1, 137.5, 136.0, 133.5, 132.2, 131.6, 130.0, 129.6, 127.4, 127.1, 125.5, 124.9, 121.1, 114.6, 94.91, 86.1, 81.2, 52.7, 52.6, 31.7, 28.0, 26.6, 21.5. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{32}H_{34}N_2O_7SNa$ $[M+Na]^+$ 613.1984 found 613.1967.

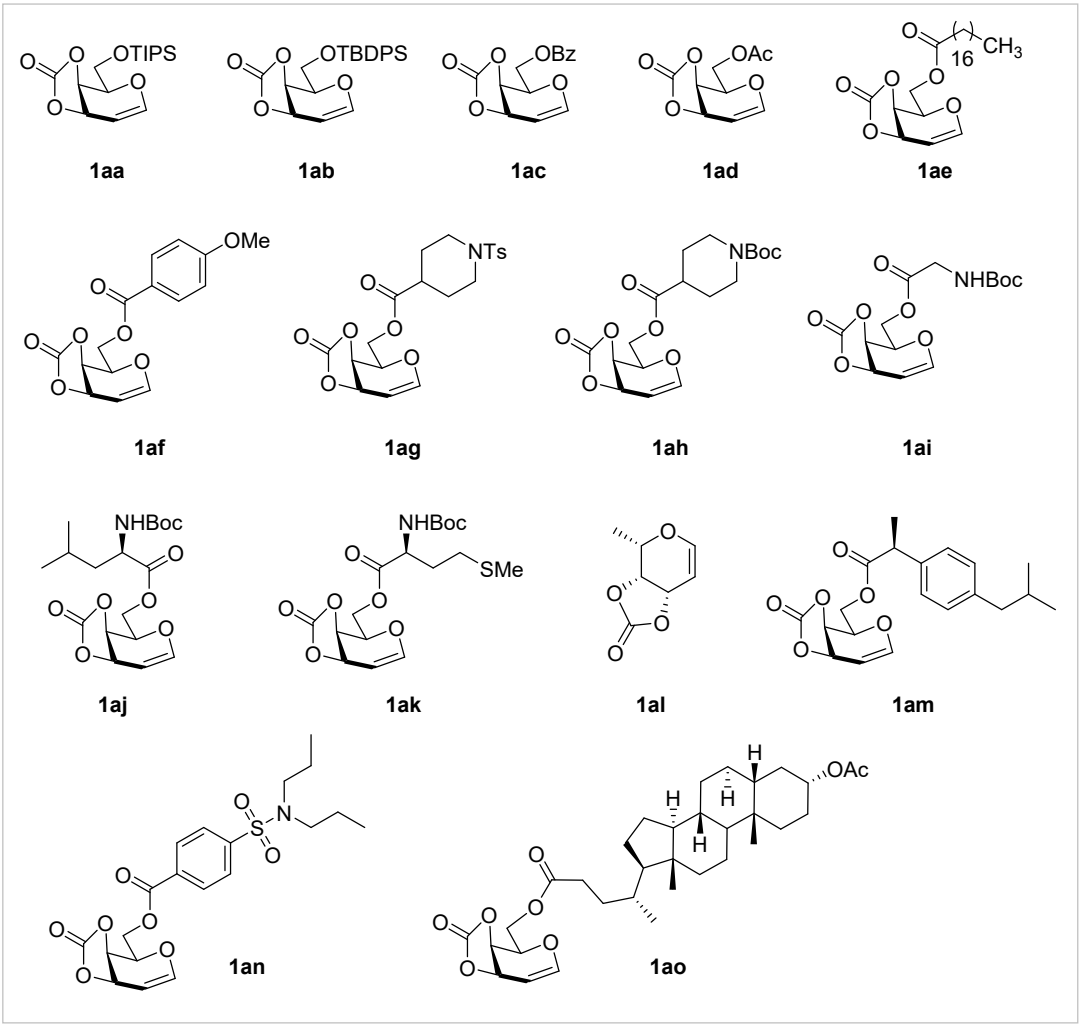
Methyl (4-((2-((4-methylphenyl)sulfonamido)phenyl)ethynyl)benzoyl)-*L*-phenylalaninate (1o)



To a solution of **S1** (60 mg, 0.15 mmol), EDCI (46 mg, 0.24 mmol), DMAP (2 mg, 0.015 mmol) and *L*-phenylalanine methyl ester hydrochloride (43 mg, 0.2 mmol) in DCM (5 mL). After stirring at room temperature for 6 h, the mixture was diluted in DCM (10 mL) and washed with brine (2 ×10 mL). The solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (eluting with petroleum ether/EtOAc = 2/1) to afford the **1o** (64 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.63 (dd, *J* = 15.8, 8.2 Hz, 3H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.30 (dd, *J* = 13.4, 6.0 Hz, 4H), 7.15 (d, *J* = 7.4 Hz, 4H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 5.10 (dd, *J* = 13.1, 5.8 Hz, 1H), 3.77 (s, 3H), 3.27 (ddd, *J* = 31.3, 13.9, 5.8 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 166.0, 144.2, 137.7, 136.1, 135.9, 133.9, 132.3, 131.8,

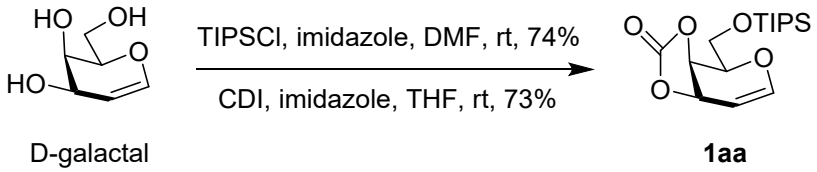
130.1, 129.7, 129.4, 128.8, 127.3, 127.3, 127.3, 125.6, 124.9, 120.9, 114.5, 95.0, 86.3, 53.7, 52.6, 37.9, 21.6. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{32}H_{28}N_2O_5SNa$ $[M+Na]^+$ 575.1617 found 575.1602.

Table S7. **3,4-*O*-carbonate glycal substrates were used in this study.**



The following substrates were known compounds: **1aa-1ah**, **1al** and **1an**.[6-7]

1,5-Anhydro-6-*O*-triisopropylsilyl-3,4-*O*-carbonate-2-deoxy-*D*-lyxo-hex-1-enopyranose (1aa)

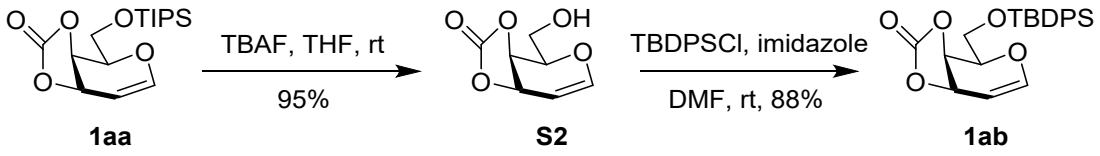


Known compound.[6] To a solution of *D*-galactal (1.5 g, 10.3 mmol) and imidazole (1.4

g, 20.6 mmol) in anhydrous DMF (25 mL) in a 50 mL round-bottomed flask was added TIPSCl (2.6 mL, 12.4 mmol) dropwise at 0 °C. After addition, the mixture was warmed up to room temperature and stirred for 10 h. The mixture was diluted with EtOAc (80 mL), washed with water (2 × 60 mL). Remove the solvents *in vacuo*, the residue was purified by silica gel column chromatography (eluting with petroleum ether/EtOAc = 3/1) to afford 6-*O*-triisopropylsilyl-*D*-galactal (2.3 g, 74%).

To a solution of 6-*O*-triisopropylsilyl-*D*-galactal (2.3 g, 7.6 mmol) in anhydrous THF (25 mL) in a 50 mL round-bottomed flask was added 1,1'- carbonyldiimidazole (1.6 g, 9.9 mmol) and imidazole (52 mg, 0.76 mmol) in the ice bath, and then the mixture was warmed up to room temperature and stirred for 10 h. The reaction mixtures were concentrated. Purification of the residue by silica gel column chromatography (eluting with petroleum ether/EtOAc = 10/1) afforded **1aa** as a colorless syrup (1.82 g, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 6.2 Hz, 1H), 5.18 (dd, *J* = 7.6, 3.0 Hz, 1H), 4.99 (d, *J* = 7.6 Hz, 1H), 4.96 – 4.86 (m, 1H), 3.97 (dd, *J* = 9.0, 4.2 Hz, 3H), 1.16 – 1.00 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1, 149.0, 98.1, 74.0, 72.7, 68.8, 61.3, 17.8, 17.8, 11.7.

1,5-Anhydro-6-*O*-(tert-butyldiphenylsilyl)-3,4-*O*-carbonate-2-deoxy-*D*-lyxo-hex-1-enopyranose (1ab)



Known compound.[6] To a solution of **1aa** (0.88 g, 2.69 mmol) in dry THF (8 mL) was added TBAF (2.96 mL, 2.96 mmol, 1 M in THF) dropwise at 0 °C. The mixture was stirred at room temperature for 1 h. After adding H_2O (20 mL), the mixture was diluted in DCM (30 mL) and washed with brine (20 mL). The solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (eluting with petroleum ether/EtOAc = 1/1) to afford the desired product **S2** (440 mg, 95%).

To a solution of **S2** (440 mg, 2.56 mmol) and imidazole (348 mg, 5.12 mmol) in

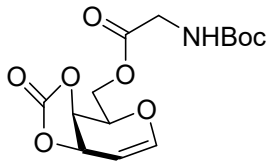
anhydrous DMF (7 mL) in a 25 mL round-bottomed flask was added TBDPSCl (0.68 mL, 2.6 mmol) dropwise at 0 °C. After addition, the mixture was warmed up to room temperature and stirred for 10 h. The mixture was diluted with EtOAc (15 mL), washed with water (2 × 15 mL). Remove the solvents in vacuo, the residue was purified by silica gel column chromatography (eluting with petroleum ether/EtOAc = 3/1) to afford **1ab** (924 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 9.5, 3.7 Hz, 4H), 7.56 – 7.32 (m, 6H), 6.63 (d, *J* = 6.3 Hz, 1H), 5.19 (dd, *J* = 7.7, 3.1 Hz, 1H), 5.04 (d, *J* = 7.7 Hz, 1H), 4.98 – 4.89 (m, 1H), 4.04 – 3.95 (m, 3H), 1.10 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.0, 149.1, 135.4, 135.4, 132.8, 132.6, 130.0, 129.9, 127.8, 127.8, 98.0, 73.8, 72.8, 68.8, 61.8, 26.8, 19.2.

General procedure B: synthesis of 3,4-*O*-carbonate galactals 1ae-1ao

S2 **1ae-1ao**

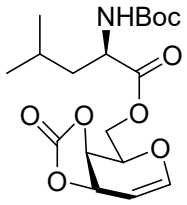
In an oven dried 25 mL round-bottom flask, **S2** (100 mg, 0.58 mmol, 1.0 equiv.) and the corresponding acid (1.5 equiv.) were dissolved in 5 mL of DCM. Then EDCI (167 mg, 0.87 mmol, 1.5 equiv.), DMAP (8 mg, 0.06 mmol, 0.1 equiv.) and DIPEA (223 μL, 1.28 mmol, 2.2 equiv.) were added. The resulting solution was stirred at room temperature for 10 h. After adding H_2O (10 mL), the mixture was diluted with CH_2Cl_2 (20 mL) and washed with brine (20 mL). Remove the solvents *in vacuo*, the residue was purified by silica gel column chromatography eluting with petroleum ether/ethyl acetate to afford the desired product.[6-7]

((3aR,4R)-2-oxo-3a,7a-dihydro-4H-[1,3]dioxolo[4,5-c]pyran-4-yl)methyl (tert-butoxycarbonyl)glycinate (1ai)



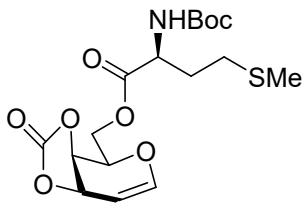
Compound **1ai** was obtained as colorless syrup (185 mg, 97% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 6.2 Hz, 1H), 5.25 (d, *J* = 10.0 Hz, 1H), 5.18 (dd, *J* = 7.7, 3.0 Hz, 1H), 4.95 (dd, *J* = 5.9, 3.0 Hz, 1H), 4.89 (d, *J* = 7.7 Hz, 1H), 4.40 (ddd, *J* = 17.0, 11.7, 6.4 Hz, 2H), 4.12 (t, *J* = 6.2 Hz, 1H), 3.87 (t, *J* = 9.0 Hz, 2H), 1.39 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 155.9, 153.8, 148.9, 98.3, 80.1, 77.4, 73.0, 71.3, 68.8, 62.9, 42.3, 28.3. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{14}H_{19}NO_8Na$ $[M+Na]^+$ 352.1008 found 352.0985.

((3aR,4R)-2-oxo-3a,7a-dihydro-4H-[1,3]dioxolo[4,5-c]pyran-4-yl)methyl (tert-butoxycarbonyl)-L-leucinate (1aj)



Compound **1aj** was obtained as colorless syrup (209 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 6.1 Hz, 1H), 5.17 (d, *J* = 5.8 Hz, 1H), 5.04 – 4.92 (m, 2H), 4.88 (d, *J* = 7.7 Hz, 1H), 4.46 – 4.33 (m, 2H), 4.23 (d, *J* = 5.1 Hz, 1H), 4.12 (t, *J* = 6.0 Hz, 1H), 1.65 (dd, *J* = 12.5, 6.2 Hz, 1H), 1.58 – 1.44 (m, 2H), 1.38 (s, 9H), 0.89 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 155.6, 153.8, 149.0, 98.3, 80.0, 73.0, 71.4, 68.8, 62.9, 52.2, 41.1, 28.3, 24.8, 22.8, 21.7. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{18}H_{27}NO_8Na$ $[M+Na]^+$ 408.1634 found 409.1617.

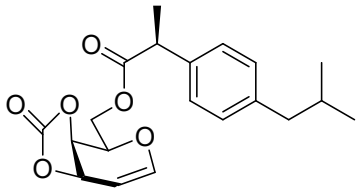
((3aR,4R)-2-oxo-3a,7a-dihydro-4H-[1,3]dioxolo[4,5-c]pyran-4-yl)methyl (tert-butoxycarbonyl)-L-methioninate (1ak)



Compound **1ak** was obtained as colorless syrup (201 mg, 86% yield). **^{1}H NMR** (400

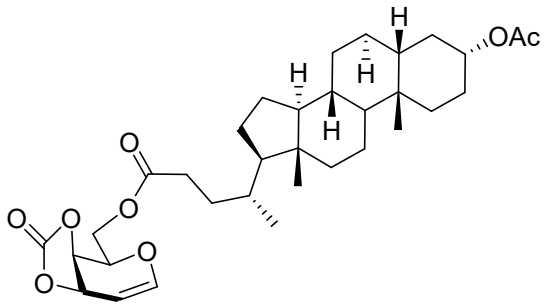
MHz, $CDCl_3$) δ 6.63 (d, *J* = 6.2 Hz, 1H), 5.28 (d, *J* = 8.2 Hz, 1H), 5.17 (dd, *J* = 7.5, 2.9 Hz, 1H), 4.94 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.88 (d, *J* = 7.7 Hz, 1H), 4.45 (dd, *J* = 11.7, 7.5 Hz, 1H), 4.35 (dd, *J* = 11.6, 5.0 Hz, 2H), 4.12 (t, *J* = 6.0 Hz, 1H), 2.49 (t, *J* = 6.1 Hz, 2H), 2.14 – 1.98 (m, 4H), 1.90 (td, *J* = 14.3, 7.4 Hz, 1H), 1.37 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 155.4, 153.7, 148.9, 98.3, 80.1, 73.0, 71.3, 68.8, 63.1, 52.7, 31.4, 29.9, 28.2, 15.3. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{17}H_{25}NO_8SNa$ $[M+Na]^+$ 426.1199 found 426.1178.

((3aR,4R)-2-oxo-3a,7a-dihydro-4H-[1,3]dioxolo[4,5-c]pyran-4-yl)methyl (2S)-2-(4-isobutylphenyl)propanoate (1am)



Compound **1am** was obtained as a colorless syrup (203 mg, 97% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 6.2 Hz, 1H), 5.03 (dd, *J* = 7.7, 3.2 Hz, 1H), 4.96 – 4.91 (m, 1H), 4.54 (d, *J* = 7.7 Hz, 1H), 4.46 (dd, *J* = 11.5, 6.8 Hz, 1H), 4.28 (dd, *J* = 11.5, 6.6 Hz, 1H), 3.99 (t, *J* = 6.3 Hz, 1H), 3.74 (q, *J* = 7.1 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.82 (td, *J* = 13.5, 6.7 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 153.6, 148.9, 140.8, 137.2, 129.4, 127.1, 98.0, 72.6, 71.0, 68.5, 61.9, 44.9, 44.8, 30.1, 22.3, 18.1. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{20}H_{24}O_6Na$ $[M+Na]^+$ 383.1471 found 383.1451.

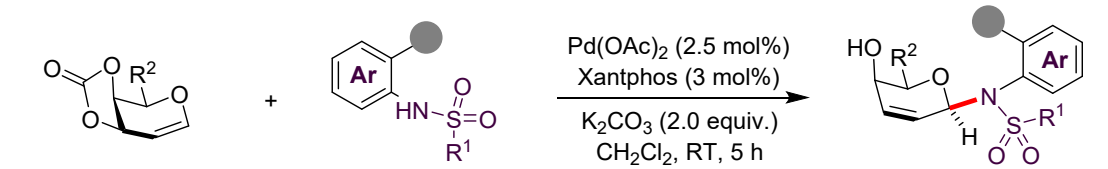
((3aR,4R)-2-oxo-3a,7a-dihydro-4H-[1,3]dioxolo[4,5-c]pyran-4-yl)methyl (4R)-4-((3R,5R,8S,9S,10R,13R,17R)-3-acetoxy-5,10,13-trimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (1ao)



Compound **1ao** was obtained as a colorless syrup (251 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.70 (d, *J* = 6.2 Hz, 1H), 5.19 (dd, *J* = 7.6, 3.0 Hz, 1H), 4.99 (dd, *J* = 5.8, 2.9 Hz, 1H), 4.88 (d, *J* = 7.7 Hz, 1H), 4.70 (dt, *J* = 11.2, 6.4 Hz, 1H), 4.45 – 4.31 (m, 2H), 4.12 (t, *J* = 6.1 Hz, 1H), 2.47 – 2.35 (m, 1H), 2.34 – 2.22 (m, 1H), 2.02 (s, 3H), 1.95 (d, *J* = 11.6 Hz, 1H), 1.87 – 1.76 (m, 5H), 1.72 – 1.63 (m, 2H), 1.61 – 1.49 (m, 2H), 1.44 – 1.35 (m, 7H), 1.31 – 1.19 (m, 4H), 1.04 (dt, *J* = 13.4, 6.2 Hz, 5H), 0.93 – 0.88 (m, 6H), 0.63 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.7, 170.6, 153.6, 149.0, 98.1, 74.3, 73.0, 71.6, 68.7, 62.2, 56.4, 55.9, 42.7, 41.8, 40.3, 40.1, 35.7, 35.3, 35.0, 34.5, 32.2, 30.9, 30.8, 28.2, 26.9, 26.6, 26.3, 24.1, 23.3, 21.5, 20.8, 18.2, 12.0. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{33}H_{48}O_8Na$ $[M+Na]^+$ 595.3247 found 595.3232.

4. General procedure C: Pd-catalyzed stereospecific *N*-glycosylation of sulfonamides with 3,4-carbonate glycals

0.1 mmol scale for substrate scopes



3,4-carbonate glycal **(1.5 equiv.)** + ***sulfonamides*** **(1.0 equiv.)** → ***glycosyl sulfonamides***

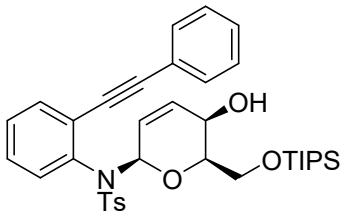
In an oven dried Schlenk tube equipped with a magnetic stirring bar was charged with sulfonamide acceptors (0.1 mmol, 1.0 equiv.), $Pd(OAc)_2$ (0.6 mg, 0.0025 mmol, 2.5 mol%), Xantphos (1.8 mg, 0.003 mmol, 3 mol%) and K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv.) under nitrogen atmosphere. Then anhydrous CH_2Cl_2 (1 mL) was added. To the

reaction mixture was added a solution of 3,4-*O*-carbonate glycals (0.15 mmol, 1.5 equiv.) in CH_2Cl_2 (1 mL) dropwisely over 10 minutes. The resulting solution was stirred at room temperature. After stirring for 5 hours, the reaction mixture was diluted with DCM (10 mL), washed with brine (2 × 5 mL). After removing the solvents *in vacuo*, the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate) to give the desired glycoside products. Removal of K_2CO_3 in the general protocol provided better yields for sulfonamide substrates **1p-1w**.

Gram-scale preparation

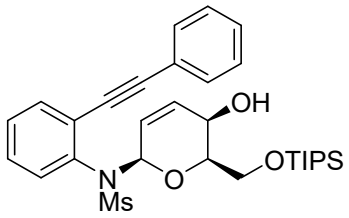
An oven-dried 100 mL round-bottomed flask equipped with a magnetic stirring bar was charged with *N*-(2-(phenylethynyl)phenyl)methanesulfonamide **1b** (678 mg, 2.5 mmol, 1.0 equiv.), $Pd(OAc)_2$ (14 mg, 0.0625 mmol, 2.5 mol%), Xantphos (43.4 mg, 0.075 mmol, 3 mol%) and K_2CO_3 (691 mg, 5.0 mmol, 2.0 equiv.) under nitrogen atmosphere, followed by the addition of anhydrous CH_2Cl_2 (20 mL). To the reaction mixture was added a solution of 3,4-*O*-carbonate galactal **1aa** (1.23 g, 3.75 mmol, 1.5 equiv.) in anhydrous CH_2Cl_2 (20 mL) slowly over 30 minutes. The resulting solution was stirred at room temperature for 5 h until TLC analysis showed complete conversion. Then, the reaction mixture was washed with brine (2 × 25 mL). The solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25/1) to afford the desired product **2** (1.13 g, 81% yield) as a white solid.

***N*-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide (1)**



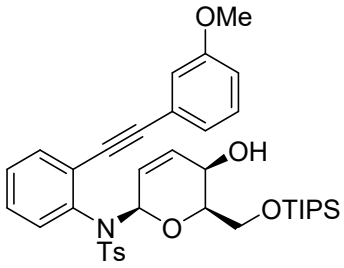
Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (52.4 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.57 (m, 3H), 7.38 – 7.32 (m, 4H), 7.19 – 7.15 (m, 3H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.35 (s, 1H), 5.97 (d, *J* = 2.6 Hz, 2H), 3.83 – 3.78 (m, 2H), 3.74 – 3.70 (m, 2H), 2.39 (s, 3H), 1.14 – 1.04 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 137.3, 137.2, 133.2, 131.9, 131.8, 129.5, 129.2, 129.1, 128.8, 128.6, 128.4, 128.2, 127.5, 123.2, 94.2, 87.1, 84.7, 76.7, 62.4, 61.0, 21.7, 18.1, 18.1, 12.0. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{36}H_{45}NO_5SSiNa$ $[M+Na]^+$ 654.2685 found 654.2662.

_N_-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-_N_-(2-(phenylethynyl)phenyl)methanesulfonamide (2)



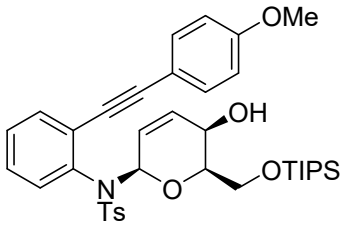
Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); White solid (46.7 mg, 84% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.39 – 7.35 (m, 5H), 6.19 (s, 1H), 6.01 – 5.96 (m 1H), 5.90 (d, *J* = 10.0 Hz, 1H), 4.02 – 3.88 (m, 3H), 3.79 – 3.76 (m, 1H), 3.18 (s, 3H), 1.15 – 1.03 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.5, 133.2, 131.8, 131.7, 130.7, 129.3, 129.0, 128.6, 128.4, 127.3, 122.9, 94.5, 86.9, 84.5, 76.6, 63.0, 61.4, 41.4, 18.0, 11.9. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{30}H_{41}NO_5SSiNa$ $[M+Na]^+$ 578.2372 found 578.2351.

_N_-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-_N_-(2-((4-methoxyphenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (3)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (53.6 mg, 81% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 3.8 Hz, 1H), 7.22 – 7.10 (m, 5H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.33 (s, 1H), 5.96 (s, 2H), 3.84 (s, 3H), 3.83 – 3.76 (m, 2H), 3.74 – 3.68 (m, 2H), 2.39 (s, 3H), 1.12 – 1.03 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 143.6, 137.4, 137.3, 133.2, 131.9, 131.8, 129.5, 129.2, 129.1, 128.8, 128.3, 127.5, 124.5, 124.2, 116.7, 115.4, 94.3, 87.0, 84.7, 76.7, 62.4, 61.0, 55.5, 21.7, 18.1, 18.1, 12.0. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{37}H_{47}NO_6SSiNa$ $[M+Na]^+$ 684.2791 found 684.2782.

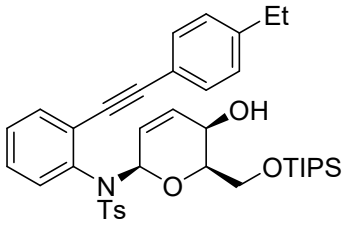
_N_-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-_N_-(2-((4-methoxyphenyl)ethynyl)phenyl)-4-methylbenzenesulfonamide (4)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (56.2 mg, 85% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.34 (s, 1H), 5.97 (s, 2H), 3.85 – 3.77 (m, 5H), 3.75 – 3.68 (m, 2H), 2.39 (s, 3H), 1.16 – 1.04 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.9, 143.5, 137.4, 136.9, 133.4, 133.0, 131.8, 131.7, 129.5, 129.1, 129.0, 128.8, 127.8, 115.3, 114.1, 94.4,

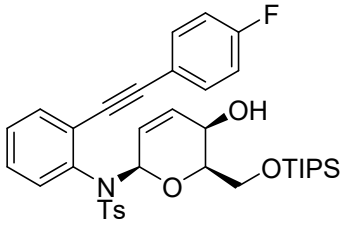
85.9, 84.7, 76.7, 62.4, 61.0, 55.4, 21.6, 18.1, 18.0, 12.0. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{37}H_{47}NO_6SSiNa$ $[M+Na]^+$ 684.2791 found 684.2781.

_N_-(2-((4-Ethylphenyl)ethynyl)phenyl)-_N_-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methylbenzenesulfonamide (5)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (54.7 mg, 83% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.21 – 7.11 (m, 5H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.33 (s, 1H), 5.97 (s, 2H), 3.82 – 3.78 (m, 2H), 3.73 – 3.69 (m, 2H), 2.67 (q, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.13 – 1.04 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 143.4, 137.2, 137.0, 133.0, 131.8, 131.7, 129.4, 129.0, 128.9, 128.7, 127.9, 127.6, 120.3, 94.4, 86.4, 84.6, 62.3, 60.9, 28.9, 21.5, 18.0, 17.9, 15.4, 11.9. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{38}H_{49}NO_5SSiNa$ $[M+Na]^+$ 682.2998 found 682.2970.

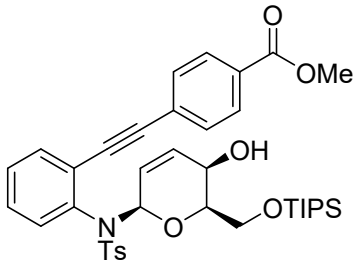
_N_-(2-((4-Fluorophenyl)ethynyl)phenyl)-_N_-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methyl benzenesulfonamide (6)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1);

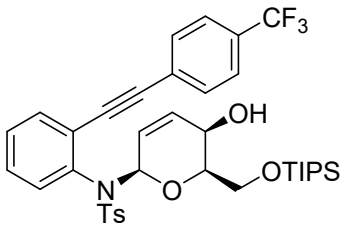
Colorless syrup (52 mg, 80% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 6.8 Hz, 3H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.17 (dd, *J* = 17.0, 7.8 Hz, 3H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.33 (s, 1H), 5.99 – 5.90 (m, 2H), 3.84 – 3.76 (m, 2H), 3.72 – 3.67 (m, 2H), 2.40 (s, 3H), 1.11 – 1.03 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 248.0 Hz), 143.5, 137.1(d, *J* = 3.0 Hz), 133.7 (d, *J* = 9.0 Hz), 133.0, 131.8, 131.5, 129.3, 129.1, 128.9, 128.7, 128.2, 127.2, 119.2, 115.6 (d, *J* = 22.0 Hz), 93.1, 86.7, 84.6, 77.2, 62.2, 60.8, 21.6, 18.0, 17.9, 11.8. ^{19}F NMR (564 MHz, $CDCl_3$) δ -110.5. **HRMS** (ESI/TOF) m/z: calculated for $C_{36}H_{44}FNO_5SSiNa$ $[M+Na]^+$ 672.2591 found 672.2585.

Methyl 4-((2-((*N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methylphenyl)sulfonamido)phenyl)ethynyl)benzoate(7)



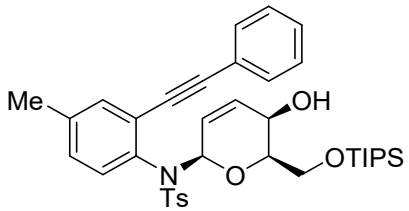
Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (53.1 mg, 77% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.70 – 7.58 (m, 5H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 3H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.33 (s, 1H), 5.99 – 5.90 (m, 2H), 3.93 (s, 3H), 3.85 – 3.77 (m, 2H), 3.73 – 3.68 (m, 2H), 2.39 (s, 3H), 1.15 – 1.01 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 143.7, 137.5, 137.3, 133.4, 132.0, 131.9, 129.8, 129.6, 129.4, 129.3, 129.1, 128.8, 127.9, 127.0, 93.3, 90.1, 84.7, 76.7, 62.4, 61.1, 52.4, 21.7, 18.1, 18.1, 12.0. **HRMS** (ESI/TOF) m/z: calculated for $C_{38}H_{47}NO_7SSiNa$ $[M+Na]^+$ 712.2740 found 712.2735.

(2R,3R,6R)-2-(Hydroxymethyl)-6-((2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)amino)-3,6-dihydro-2H-pyran-3-ol (8)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (53.2 mg, 76% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 4H), 7.62 (d, *J* = 7.3 Hz, 3H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 3H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.32 (s, 1H), 5.99 – 5.88 (m, 2H), 3.84 – 3.76 (m, 2H), 3.72 – 3.67 (m, 2H), 2.40 (s, 3H), 1.15 – 1.08 (m, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.5, 137.5, 137.2, 133.2, 132.0, 131.9, 131.6, 130.1 (q, *J* = 33.0 Hz), 129.2, 129.1, 129.0, 128.7, 128.6, 126.9, 126.7, 125.3 (q, *J* = 3.0 Hz), 123.9 (q, *J* = 270.0 Hz), 92.5, 89.4, 84.6, 76.5, 62.28, 60.9, 21.5, 17.9, 17.9, 11.9. ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.8. **HRMS** (ESI/TOF) m/z: calculated for $C_{37}H_{44}NF_3O_5SSiNa$ $[M+Na]^+$ 722.2559 found 722.2531.

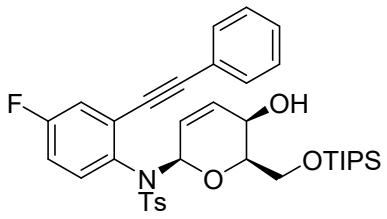
***N*-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methyl-*N*-(4-methyl-2-(phenylethynyl)phenyl)benzenesulfonamide (9)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (52.9 mg, 82% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 3.8 Hz, 2H), 7.40 (s, 1H), 7.35 (d, *J* = 3.5 Hz, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.33 (s, 1H), 5.97 (s, 2H), 3.84 – 3.76 (m, 2H), 3.73 – 3.69 (m, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 1.14 – 1.03 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 139.3, 137.4, 134.5, 133.8, 131.9, 131.9, 131.5, 129.6, 129.2, 129.0, 128.8, 128.6, 128.4, 127.0, 123.3, 93.8, 87.3, 84.7,

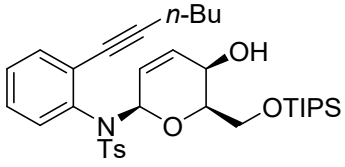
76.7, 62.4, 61.0, 21.7, 21.1, 18.1, 18.0, 12.0. **HRMS** (ESI/TOF) m/z: calculated for $C_{37}H_{47}NO_5SSiNa$ $[M+Na]^+$ 668.2842 found 668.2836.

***N*-(4-Fluoro-2-(phenylethynyl)phenyl)-*N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methylbenzenesulfonamide (10)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (49.4 mg, 76% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.62 – 7.51 (m, 2H), 7.37 (d, *J* = 2.8 Hz, 3H), 7.29 – 7.26 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.97 (dd, *J* = 8.7, 5.5 Hz, 1H), 6.85 (td, *J* = 8.6, 2.7 Hz, 1H), 6.31 (s, 1H), 6.06 – 5.87 (m, 2H), 3.86 (d, *J* = 4.2 Hz, 1H), 3.78 (dd, *J* = 11.1, 7.4 Hz, 1H), 3.73 (d, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.14 – 1.03 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 249 Hz), 143.6, 136.9, 133.4 (d, *J* = 9.0 Hz), 133.1, 131.9, 129.3, 129.0, 128.9, 128.7, 128.4, 122.6, 119.6 (d, *J* = 24 Hz), 115.3 (d, *J* = 22 Hz), 95.1, 86.0, 84.5, 76.4, 62.4, 61.0, 21.5, 18.0, 17.9, 11.9. ^{19}F NMR (564 MHz, $CDCl_3$) δ -111.3. **HRMS** (ESI/TOF) m/z: calculated for $C_{36}H_{44}FNO_5SSiNa$ $[M+Na]^+$ 672.2591 found 672.2589.

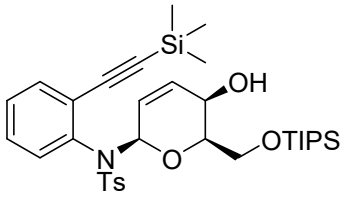
***N*-(2-(Hept-1-yn-1-yl)phenyl)-*N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methyl benzenesulfonamide (11)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (42.8 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1

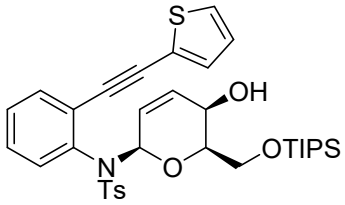
Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 13.0, 7.8 Hz, 3H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 6.00 – 5.89 (m, 2H), 3.85 – 3.75 (m, 2H), 3.75 – 3.67 (m, 2H), 2.49 – 2.43 (m, 2H), 2.41 (s, 3H), 1.65 (s, 1H), 1.61 (d, *J* = 7.1 Hz, 1H), 1.58 – 1.48 (m, 2H), 1.13 – 1.05 (m, 21H), 0.96 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 137.3, 136.9, 133.6, 131.8, 131.5, 129.5, 129.1, 128.9, 128.3, 127.4, 95.7, 84.7, 78.2, 77.5, 76.7, 62.3, 61.0, 30.8, 22.2, 21.7, 19.5, 18.1, 18.1, 13.8, 12.0. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{34}H_{49}NO_5SSiNa$ $[M+Na]^+$ 634.2998 found 634.2990.

***N*-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methyl-*N*-(2-(trimethylsilyl)ethynyl)phenyl)benzenesulfonamide(12)**



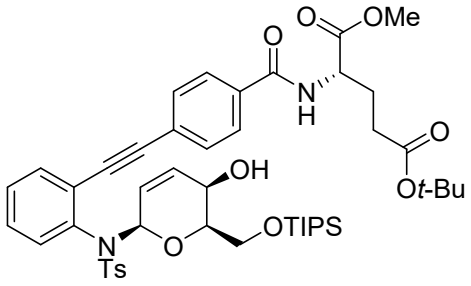
Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 40/1); Colorless syrup (42.1 mg, 67% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 6.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.30 (s, 1H), 5.96 (s, 2H), 3.81 (s, 1H), 3.77 (d, *J* = 10.4 Hz, 1H), 3.70 (s, 2H), 2.41 (s, 3H), 1.13 – 1.05 (m, 21H), 0.28 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.5, 137.7, 137.4, 133.5, 131.9, 131.6, 129.5, 129.0, 128.9, 128.4, 127.4, 102.6, 100.0, 84.7, 76.7, 62.4, 61.0, 21.7, 18.1, 18.1, 12.0, -0.1. **HRMS** (ESI/TOF) m/z: calculated for $C_{33}H_{49}NO_5SSi_2Na$ $[M+Na]^+$ 650.2768 found 650.2753.

***N*-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methyl-*N*-(2-(thiophen-2-ylethynyl)phenyl)benzenesulfonamide (13)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (50.4 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.29 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 3H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.33 (s, 1H), 6.02 – 5.88 (m, 2H), 3.81 (t, *J* = 9.5 Hz, 2H), 3.73 (d, *J* = 5.8 Hz, 2H), 2.39 (s, 3H), 1.18 – 1.05 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 137.2, 136.9, 132.9, 132.6, 132.1, 131.9, 129.4, 129.2, 129.1, 128.8, 128.4, 127.9, 127.3, 127.1, 123.1, 90.9, 87.4, 84.6, 76.7, 62.4, 61.0, 21.7, 18.1, 18.1, 12.0. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{34}H_{43}NO_5S_2SiNa$ $[M+Na]^+$ 660.2250 found 660.2237.

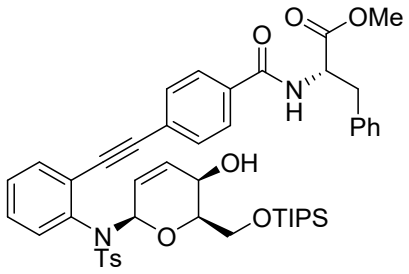
5-(tert-Butyl) 1-methyl (4-((2-((N-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl) oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methylphenyl)sulfonamido)phenyl) ethynyl)benzoyl)-L-glutamate (14)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (65.6 mg, 75% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.70 – 7.57 (m, 5H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 3H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.33 (s, 1H), 6.00 – 5.86 (m, 2H), 4.75 (dd, *J* = 12.2, 7.3 Hz, 1H), 3.82 (s, 1H), 3.77 (s, 3H), 3.71 (s, 2H), 2.46 (dd, *J* = 17.0, 7.1 Hz, 1H), 2.38 (s, 3H), 2.35 – 2.08 (m, 4H), 1.43 (s, 9H), 1.13 – 1.03 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9, 172.5, 166.5, 143.6, 137.4, 137.2, 133.3, 133.2, 132.0, 131.8, 129.4, 129.2,

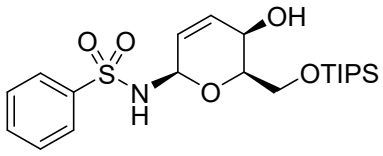
129.1, 128.8, 128.7, 127.3, 127.0, 126.8, 93.2, 89.5, 84.7, 81.3, 76.7, 62.4, 61.0, 52.8, 52.7, 31.8, 28.2, 26.9, 21.7, 18.1, 18.0, 12.0. **HRMS** (ESI/TOF) m/z: calculated for $C_{47}H_{62}N_2O_{10}SSiNa$ $[M+Na]^+$ 897.3792 found 897.3776.

Methyl (4-((2-((*N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methylphenyl)sulfonamido)phenyl)ethynyl)benzoyl)-*L*-phenylalaninate (15)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (66.1 mg, 79% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.59 (m, 7H), 7.38 – 7.28 (m, 4H), 7.19 (d, *J* = 7.5 Hz, 3H), 7.13 (d, *J* = 6.9 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 7.4 Hz, 1H), 6.33 (s, 1H), 5.99 – 5.89 (m, 2H), 5.10 (q, *J* = 5.7 Hz, 1H), 3.87 – 3.81 (m, 1H), 3.81 – 3.76 (m, 4H), 3.75 – 3.68 (m, 2H), 3.27 (qd, *J* = 13.8, 5.3 Hz, 2H), 2.40 (s, 3H), 1.13 – 1.03 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 166.2, 143.7, 137.5, 137.3, 135.9, 133.5, 133.4, 132.1, 132.1, 131.8, 129.5, 129.3, 129.1, 128.8, 128.7, 127.4, 127.2, 127.1, 126.9, 93.3, 89.7, 84.7, 62.5, 61.1, 53.7, 52.6, 38.0, 21.7, 18.1, 18.1, 12.1. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{47}H_{56}N_2O_8SSiNa$ $[M+Na]^+$ 859.3424 found 859.3400.

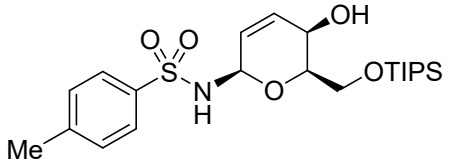
***N*-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)benzenesulfonamide (16)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1);

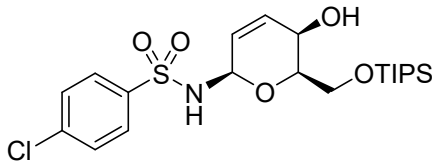
Colorless syrup (33.0 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.50 (dt, *J* = 14.9, 7.1 Hz, 3H), 6.05 (s, 1H), 5.97 (d, *J* = 5.9 Hz, 1H), 5.86 (d, *J* = 5.9 Hz, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 4.60 (s, 1H), 3.55 – 3.47 (m, 1H), 3.38 – 3.29 (m, 1H), 3.14 (d, *J* = 9.0 Hz, 1H), 2.44 (s, 1H), 1.06 – 1.01 (m, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.7, 132.4, 131.2, 128.8, 128.8, 127.3, 127.1, 90.2, 84.2, 70.9, 64.5, 17.9, 17.9, 11.7. **HRMS** (ESI/TOF) m/z: calculated for $C_{21}H_{35}NO_5SSiNa$ $[M+Na]^+$ 464.1903 found 464.1892.

_N_-((2R,5R,6R)-5-Hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methylbenzenesulfonamide (17)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1); Colorless syrup (35.1 mg, 77%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.09 – 6.01 (m, 1H), 5.97 (dt, *J* = 5.9, 1.6 Hz, 1H), 5.87 (dt, *J* = 5.9, 1.8 Hz, 1H), 5.79 (d, *J* = 10.1 Hz, 1H), 4.61 (s, 1H), 3.53 (dd, *J* = 8.6, 4.8 Hz, 1H), 3.38 (dd, *J* = 9.7, 4.8 Hz, 1H), 3.24 – 3.13 (m, 1H), 2.46 (s, 1H), 2.40 (s, 3H), 1.05 – 1.00 (m, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.0, 138.8, 131.0, 129.4, 127.5, 127.2, 90.2, 84.2, 71.0, 64.6, 21.5, 17.9, 17.9, 11.7. **HRMS** (ESI/TOF) m/z: calculated for $C_{22}H_{37}NO_5SSiNa$ $[M+Na]^+$ 478.2059 found 478.2052.

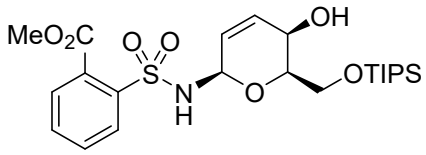
4-Chloro-_N_-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)benzenesulfonamide (18)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1); Colorless syrup (38.0 mg, 80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz,

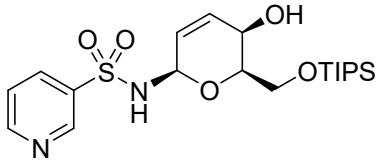
2H), 7.45 (d, *J* = 8.6 Hz, 2H), 6.05 (dt, *J* = 10.1, 1.5 Hz, 1H), 5.98 (dt, *J* = 6.0, 1.6 Hz, 1H), 5.89 (d, *J* = 9.9 Hz, 1H), 5.87 (dt, *J* = 5.9, 2.0 Hz, 1H), 4.63 (s, 1H), 3.54 (dd, *J* = 8.6, 5.1 Hz, 1H), 3.37 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.17 (t, *J* = 9.1 Hz, 1H), 2.53 (bs, 1H), 1.06 – 1.01 (m, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.3, 138.9, 131.3, 129.0, 128.7, 127.3, 90.2, 84.2, 70.8, 64.6, 17.9, 17.8, 11.8. **HRMS** (ESI/TOF) m/z: calculated for $C_{21}H_{34}ClNO_5SSiNa$ $[M+Na]^+$ 498.1513 found 498.1408.

Methyl 2-(*N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)sulfamoyl)benzoate (19)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 7/1); Colorless syrup (42.9 mg, 86%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.15 – 8.05 (m, 1H), 7.87 – 7.78 (m, 1H), 7.58 (dd, *J* = 5.4, 3.6 Hz, 2H), 6.95 (d, *J* = 10.6 Hz, 1H), 6.24 – 6.13 (m, 1H), 5.83 (d, *J* = 10.1 Hz, 1H), 5.40 (d, *J* = 10.5 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 1H), 3.52 (t, *J* = 5.5 Hz, 1H), 3.45 (t, *J* = 8.9 Hz, 1H), 3.30 (dd, *J* = 9.7, 5.1 Hz, 1H), 2.07 (d, *J* = 7.8 Hz, 1H), 1.02 – 0.95 (m, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.8, 141.9, 132.0, 131.5, 131.3, 130.5, 129.7, 129.6, 129.1, 80.5, 75.8, 61.8, 61.2, 53.3, 17.8, 17.8, 11.6. **HRMS** (ESI/TOF) m/z: calculated for $C_{23}H_{37}NO_7SSiNa$ $[M+Na]^+$ 522.1958 found 522.1949.

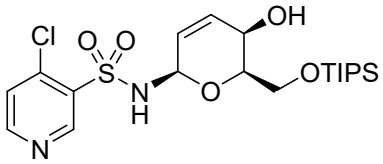
***N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)pyridine-3-sulfonamide (20)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 4/1); Colorless syrup (30.2 mg, 68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.75 (d, *J* = 4.9 Hz, 1H), 8.20 (dt, *J* = 8.1, 1.9 Hz, 1H), 7.42 (dd, *J* = 8.1, 4.8 Hz, 1H), 6.10 –

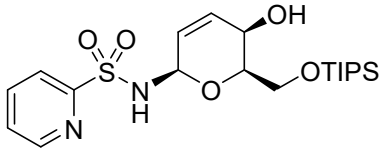
5.97 (m, 3H), 5.88 (dt, *J* = 6.0, 1.6 Hz, 1H), 4.64 (s, 1H), 3.63 – 3.49 (m, 2H), 3.30 (dd, *J* = 9.8, 5.1 Hz, 1H), 3.11 (dd, *J* = 9.7, 8.4 Hz, 1H), 1.13 – 0.93 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 148.5, 135.1, 131.7, 127.2, 90.4, 84.5, 70.9, 64.7, 18.1, 18.0, 12.0, 11.9. **HRMS** (ESI/TOF) m/z: calculated for $C_{20}H_{34}N_2O_5SSiNa$ $[M+Na]^+$465.1856 found 465.1848.

4-Chloro-*N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)pyridine-3-sulfonamide (21)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 4/1); Colorless syrup (35.8 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.66 (d, *J* = 5.2 Hz, 1H), 7.43 (d, *J* = 5.3 Hz, 1H), 6.30 (d, *J* = 10.0 Hz, 1H), 6.10 – 5.98 (m, 2H), 5.91 – 5.83 (m, 1H), 4.60 (s, 1H), 3.59 (dd, *J* = 9.0, 4.8 Hz, 1H), 3.54 – 3.43 (m, 2H), 3.33 (t, *J* = 9.3 Hz, 1H), 1.17 – 0.95 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.8, 151.0, 131.7, 127.0, 125.9, 90.6, 84.8, 71.2, 64.6, 18.1, 12.0. **HRMS** (ESI/TOF) m/z: calculated for $C_{20}H_{33}ClN_2O_5SSiNa$ $[M+Na]^+$ 499.1466 found 499.1461.

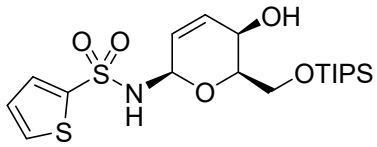
***N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)pyridine-2-sulfonamide (22)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 4/1); White solid (42.4 mg, 96% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.94 (t, *J* = 7.7 Hz, 1H), 7.48 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.10 (d, *J* = 5.3 Hz, 2H), 6.04 (d, *J* = 5.8 Hz, 1H), 5.89 (dd, *J* = 5.9, 2.4 Hz, 1H), 4.75 (s, 1H), 3.53 (t, *J* = 7.1 Hz, 1H), 3.40 (dd, *J* = 9.3, 7.0 Hz, 1H), 3.17 (ddd, *J* = 9.7, 7.2, 3.0 Hz, 1H), 1.07 – 0.99 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 149.5, 138.4,

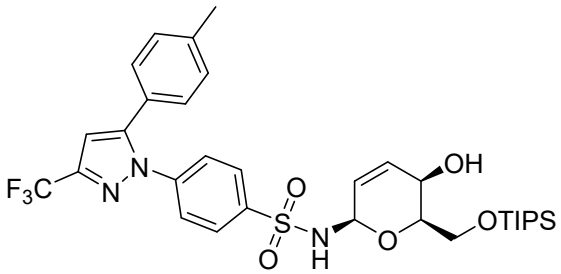
132.6, 126.6, 126.4, 121.8, 90.4, 84.9, 71.0, 64.0, 17.9, 17.8, 11.8. **HRMS** (ESI/TOF) m/z: calculated for $C_{20}H_{34}N_2O_5SSiNa$ $[M+Na]^+$ 465.1855 found 465.1849.

***N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)thiophene-2-sulfonamide (23)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1); Yellow syrup (39.3 mg, 88% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 4.1 Hz, 1H), 7.53 (d, *J* = 5.0 Hz, 1H), 7.06 – 7.04 (m, 1H), 6.08 – 5.95 (m, 3H), 5.89 – 5.81 (m, 1H), 4.65 (s, 1H), 3.56 (dd, *J* = 8.7, 5.0 Hz, 1H), 3.44 (dd, *J* = 9.7, 5.0 Hz, 1H), 3.29 (t, *J* = 9.1 Hz, 1H), 2.65 (s, 1H), 1.08 – 1.01 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.9, 132.1, 131.7, 131.5, 127.4, 127.3, 90.4, 84.5, 71.1, 64.7, 18.0, 11.9. **HRMS** (ESI/TOF) m/z: calculated for $C_{19}H_{33}NO_5S_2SiNa$ $[M+Na]^+$ 470.1467 found 470.1461.

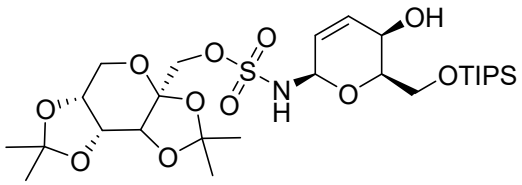
***N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl) benzenesulfonamide (24)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1); Colorless syrup (47.3 mg, 71% yield); **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.72 (s, 1H), 6.02 – 5.93 (m, 3H), 5.84 (d, *J* = 5.9 Hz, 1H), 4.62 (s, 1H), 3.56 – 3.53 (m, 1H), 3.41 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.26 (t, *J* = 9.2 Hz, 1H), 2.60 (s, 1H), 2.38 (s, 3H), 1.03 – 0.92 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.1, 143.9 (q, *J* = 38.0 Hz),

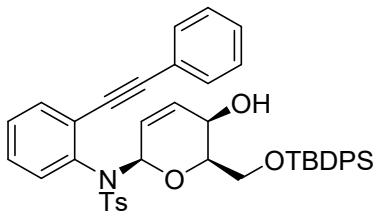
142.2, 141.0, 139.7, 131.4, 129.7, 128.7, 128.1, 127.2, 125.8, 124.8, 124.1 (q, J = 266.0 Hz), 106.3, 90.1, 84.3, 71.0, 64.7, 21.3, 17.8, 11.7. ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.5. **HRMS** (ESI/TOF) m/z: calculated for $C_{32}H_{42}F_3N_3O_5SSiNa$ $[M+Na]^+$ 688.2464 found 688.2466.

((3aS,5aR,8aR)-2,2,7,7-Tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl ((2S,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)sulfamate (25)



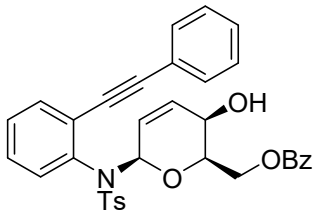
Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 6/1); Colorless syrup (42.4 mg, 68% yield); two inseparable rotamers (2.9 : 1) were obtained. NMR of major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.08 (d, J = 6.0 Hz, 1H), 6.03 (d, J = 9.9 Hz, 1H), 5.87 (d, J = 5.8 Hz, 1H), 5.57 (d, J = 9.9 Hz, 1H), 4.88 (s, 1H), 4.61 (d, J = 7.9 Hz, 1H), 4.46 (d, J = 10.6 Hz, 1H), 4.42 – 4.37 (m, 1H), 4.33 – 4.17 (m, 3H), 4.13 (d, J = 10.6 Hz, 1H), 3.90 (d, J = 12.9 Hz, 1H), 3.78 (d, J = 6.8 Hz, 1H), 3.76 – 3.70 (m, 1H), 3.66 – 3.58 (m, 1H), 1.53 (s, 3H), 1.47 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.14 – 1.05 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.6, 126.6, 109.5, 101.2, 90.9, 85.2, 71.8, 70.8, 70.1, 70.1, 69.0, 64.6, 61.6, 26.6, 26.0, 25.4, 24.2, 18.1, 18.1, 12.0. **HRMS** (ESI/TOF) m/z: calculated for $C_{27}H_{49}NO_{11}SSiNa$ $[M+Na]^+$ 646.2693 found 646.2708.

***N*-((2R,5R,6R)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-5-hydroxy-5,6-dihydro-2H-pyran-2-yl)-4-methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide (26)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (60.7 mg, 85% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 7.4 Hz, 4H), 7.65 – 7.59 (m, 4H), 7.55 – 7.28 (m, 11H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.37 (s, 1H), 6.00 (s, 2H), 3.86 – 3.75 (m, 3H), 3.66 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.26 (s, 3H), 1.11 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 137.0, 135.6, 133.4, 133.2, 131.9, 131.8, 131.6, 129.9, 129.8, 129.6, 129.1, 129.0, 128.6, 128.6, 128.4, 128.1, 127.8, 127.8, 127.5, 123.1, 94.2, 87.1, 84.6, 62.8, 61.0, 26.9, 21.5, 19.2. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{43}H_{43}NO_5SSiNa$ $[M+Na]^+$ 736.2529 found 736.2525.

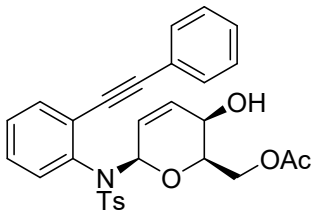
((2R,3R,6R)-3-Hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl benzoate (27)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 15/1); Colorless syrup (43.5 mg, 75% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.5 Hz, 2H), 7.69 – 7.59 (m, 6H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.36 (dd, *J* = 7.1, 6.0 Hz, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.47 (s, 1H), 6.10 – 5.95 (m, 2H), 4.40 (d, *J* = 5.1 Hz, 2H), 4.09 (t, *J* = 5.2 Hz, 1H), 3.79 (d, *J* = 4.4 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 143.8, 137.0, 136.9, 133.5, 132.0, 131.6, 131.3, 130.1, 130.0, 129.8, 129.4, 129.1, 128.8, 128.5, 128.2, 127.8,

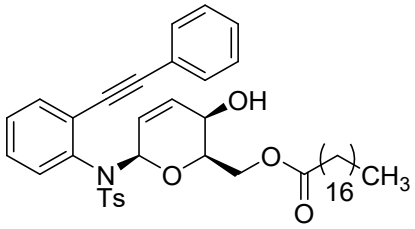
123.2, 94.6, 87.1, 84.7, 74.6, 64.6, 61.5, 21.7. **HRMS** (ESI/TOF) m/z: calculated for $C_{34}H_{29}NO_6SNa$ $[M+Na]^+$ 602.1613 found 602.1607.

((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl acetate (28)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 12/1); Colorless syrup (37.2 mg, 72% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.54 (m, 3H), 7.40 – 7.29 (m, 4H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.40 (s, 1H), 6.02 (d, *J* = 10.2 Hz, 1H), 5.99 – 5.90 (m, 1H), 4.22 (dd, *J* = 11.4, 5.0 Hz, 1H), 4.11 (dd, *J* = 11.6, 7.1 Hz, 1H), 3.90 (t, *J* = 5.4 Hz, 1H), 3.70 (dd, *J* = 9.8, 5.4 Hz, 1H), 2.41 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 143.8, 136.9, 133.4, 132.0, 131.6, 131.8, 130.0, 129.4, 129.1, 128.9, 128.7, 128.5, 128.2, 127.6, 123.1, 94.5, 87.0, 84.6, 74.4, 63.8, 61.3, 21.7, 21.1. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{29}H_{27}NO_6SNa$ $[M+Na]^+$ 540.1457 found 540.1468.

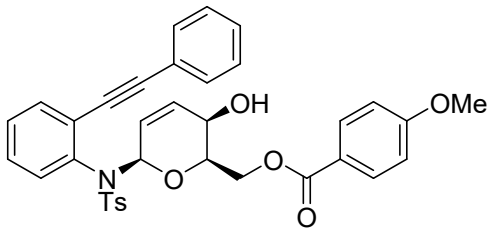
((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl stearate (29)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 25/1); Colorless syrup (54.1 mg, 73% yield); **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.71 (d, *J* = 8.2

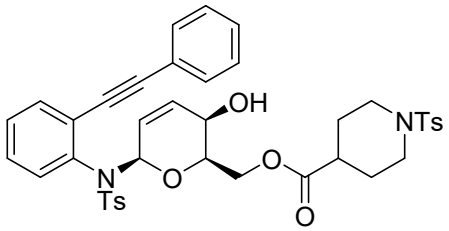
Hz, 2H), 7.63 – 7.54 (m, 3H), 7.40 – 7.29 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.40 (s, 1H), 6.02 (d, *J* = 10.2 Hz, 1H), 5.97 – 5.91 (m, 1H), 4.24 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.09 (dd, *J* = 11.4, 6.9 Hz, 1H), 3.89 (t, *J* = 5.4 Hz, 1H), 3.74 – 3.66 (m, 1H), 2.44 – 2.37 (m, 5H), 1.73 – 1.65 (m, 2H), 1.30 – 1.21 (m, 28H), 0.89 (t, *J* = 6.4 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 143.7, 136.9, 133.4, 131.9, 131.6, 131.3, 129.9, 129.3, 129.1, 128.9, 128.7, 128.5, 128.2, 127.6, 123.1, 94.5, 87.0, 84.6, 74.5, 63.4, 61.2, 34.4, 32.0, 29.8, 29.8, 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 21.7, 14.2. **HRMS** (ESI/TOF) m/z: calculated for $C_{45}H_{59}NO_6SNa$ $[M+Na]^+$ 764.3961 found 764.3952.

((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl 4-methoxybenzoate (30)



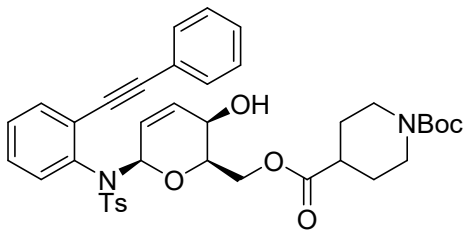
Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 15/1); Colorless syrup (44 mg, 72% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 3H), 7.35 (t, *J* = 8.2 Hz, 4H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.03 – 6.94 (m, 4H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.47 (s, 1H), 6.05 (d, *J* = 10.2 Hz, 1H), 6.00 – 5.93 (m, 1H), 4.37 (d, *J* = 5.4 Hz, 2H), 4.07 (t, *J* = 5.5 Hz, 1H), 3.88 (s, 3H), 3.78 (dd, *J* = 9.6, 5.6 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 163.7, 143.6, 136.9, 136.8, 133.3, 131.9, 131.7, 131.4, 131.2, 129.9, 129.2, 129.0, 128.7, 128.6, 128.4, 128.1, 127.6, 123.0, 122.2, 113.8, 94.4, 87.0, 84.5, 74.5, 64.2, 61.4, 55.5, 21.6. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{35}H_{31}NNaO_7S$ $[M+Na]^+$ 632.1719 found 632.1692.

((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl 1-tosylpiperidine-4-carboxylate (31)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 15/1); Colorless syrup (60.7 mg, 82% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 7.8 Hz, 4H), 7.59 (s, 1H), 7.58 – 7.53 (m, 2H), 7.39 – 7.28 (m, 6H), 7.15 (d, *J* = 7.9 Hz, 3H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.34 (s, 1H), 6.00 (d, *J* = 10.1 Hz, 1H), 5.97 – 5.89 (m, 1H), 4.21 (dd, *J* = 11.2, 5.4 Hz, 1H), 4.13 (dd, *J* = 13.2, 4.8 Hz, 1H), 3.85 (t, *J* = 6.2 Hz, 1H), 3.71 – 3.60 (m, 3H), 2.52 – 2.43 (m, 2H), 2.41 (s, 3H), 2.38 (s, 3H), 2.35 – 2.26 (m, 1H), 2.08 – 1.99 (m, 2H), 1.93 – 1.81 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 143.9, 143.7, 136.8, 133.4, 133.1, 131.9, 131.8, 131.2, 129.9, 129.8, 129.4, 129.1, 128.8, 128.5, 128.2, 127.8, 127.5, 123.0, 94.4, 86.9, 84.5, 74.4, 63.7, 61.2, 45.5, 40.2, 27.6, 27.6, 21.7, 21.6. **HRMS** (ESI/TOF) m/z: calculated for $C_{40}H_{40}N_2O_8S_2Na$ $[M+Na]^+$ 763.2124 found 763.2116.

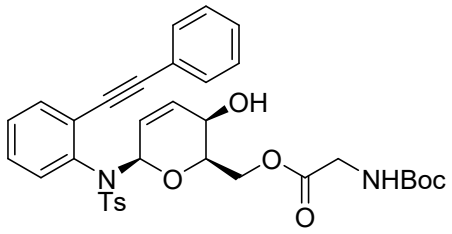
1-(tert-Butyl) 4-(((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl) phenyl)phenyl)sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl) piperidine-1,4-dicarboxylate (32)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 15/1); Colorless syrup (52.2 mg, 76% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1

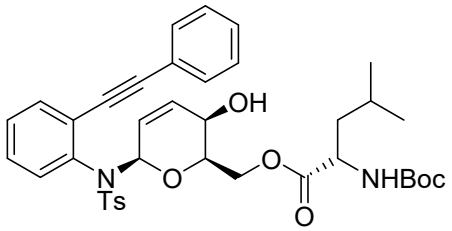
Hz, 2H), 7.58 (t, *J* = 7.1 Hz, 3H), 7.35 – 7.30 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.38 (s, 1H), 6.01 (d, *J* = 10.1 Hz, 1H), 5.97 – 5.91 (m, 1H), 4.24 (dd, *J* = 11.0, 5.4 Hz, 1H), 4.18 – 4.12 (m, 1H), 4.07 (d, *J* = 17.5 Hz, 2H), 3.88 (s, 1H), 3.69 (dd, *J* = 9.7, 5.2 Hz, 1H), 2.83 (d, *J* = 10.7 Hz, 2H), 2.52 (t, *J* = 10.8 Hz, 1H), 2.39 (s, 3H), 1.93 (d, *J* = 12.2 Hz, 2H), 1.65 (dd, *J* = 22.6, 11.5 Hz, 2H), 1.45 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 154.7, 143.8, 136.8, 133.4, 131.9, 131.7, 131.3, 129.9, 129.4, 129.1, 128.8, 128.7, 128.4, 128.2, 127.6, 123.1, 94.4, 87.0, 84.6, 79.8, 74.3, 63.5, 61.2, 41.2, 28.5, 28.1, 21.7. **HRMS** (ESI/TOF) m/z: calculated for $C_{38}H_{42}N_2O_8SNa$ $[M+Na]^+$ 709.2560 found 709.2556.

((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl (*tert*-butoxycarbonyl)glycinate (33)



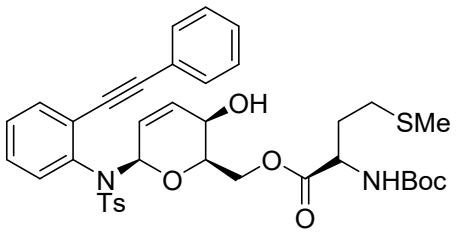
Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1); Colorless syrup (47.5 mg, 75% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 5.9 Hz, 3H), 7.37 – 7.29 (m, 4H), 7.22 – 7.12 (m, 3H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.36 (s, 1H), 6.01 (d, *J* = 10.1 Hz, 1H), 5.95 – 5.88 (m, 1H), 5.12 (s, 1H), 4.30 – 4.16 (m, 2H), 3.99 (dd, *J* = 17.1, 5.2 Hz, 1H), 3.91 (d, *J* = 5.7 Hz, 2H), 3.69 (s, 1H), 2.39 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 155.8, 143.9, 136.9, 133.3, 131.9, 131.7, 131.2, 129.9, 129.3, 129.2, 128.8, 128.5, 128.2, 127.5, 123.1, 94.4, 87.0, 84.5, 80.2, 74.1, 64.3, 61.1, 42.5, 28.4, 21.7. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{34}H_{36}N_2O_8SNa$ $[M+Na]^+$ 655.2090 found 655.2075.

((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl (*tert*-butoxycarbonyl)-*L*-leucinate (34)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1); Colorless syrup (48.2 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 5.2 Hz, 3H), 7.33 (d, *J* = 14.9 Hz, 4H), 7.22 – 7.11 (m, 3H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.37 (s, 1H), 5.97 (dd, *J* = 20.7, 7.3 Hz, 2H), 4.95 (d, *J* = 7.8 Hz, 1H), 4.37 – 4.26 (m, 2H), 4.19 – 4.07 (m, 1H), 3.91 (s, 1H), 3.74 (s, 1H), 2.39 (s, 3H), 1.76 – 1.61 (m, 2H), 1.55 (dd, *J* = 11.3, 6.1 Hz, 1H), 1.43 (s, 9H), 0.97 (d, *J* = 3.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5, 155.7, 143.8, 137.0, 133.4, 132.0, 131.3, 129.8, 129.4, 129.2, 128.9, 128.8, 128.5, 128.3, 127.5, 123.2, 94.4, 87.1, 84.6, 80.3, 74.2, 63.7, 60.9, 52.5, 41.7, 28.5, 25.0, 23.0, 22.0, 21.8. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{38}H_{44}N_2NaO_8S$ $[M+Na]^+$ 711.2716 found 711.2736.

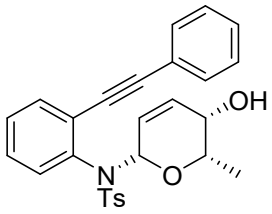
((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl (tert-butoxycarbonyl)-*L*-methioninate (35)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 10/1); Colorless syrup (50.9 mg, 72% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 3H), 7.37 – 7.30 (m, 4H), 7.18 (dd, *J* = 18.3, 7.6 Hz, 2H),

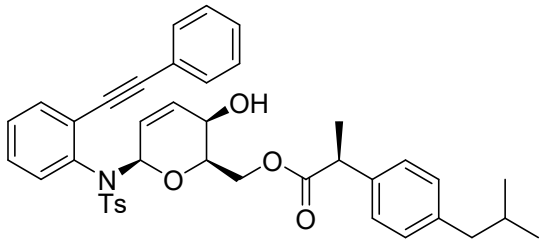
7.15 (d, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.38 (s, 1H), 6.05 – 5.90 (m, 2H), 5.18 (d, *J* = 6.9 Hz, 1H), 4.45 (s, 1H), 4.35 – 4.14 (m, 2H), 3.92 (t, *J* = 5.7 Hz, 1H), 3.74 – 3.70 (m, 1H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 2.18 (dd, *J* = 11.4, 5.8 Hz, 1H), 2.11 (s, 3H), 1.98 (dd, *J* = 12.9, 6.0 Hz, 1H), 1.45 (d, *J* = 8.1 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 155.3, 143.7, 136.8, 133.2, 131.8, 131.0, 129.8, 129.2, 129.1, 128.7, 128.6, 128.3, 128.1, 127.4, 123.0, 94.2, 86.9, 84.3, 80.2, 74.0, 63.9, 60.8, 52.9, 32.0, 30.1, 28.3, 21.5, 15.5. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{37}H_{42}N_2NaO_8S_2$ $[M+Na]^+$ 729.2280 found 729.2271.

_N_-((2S,5S,6S)-5-hydroxy-6-methyl-5,6-dihydro-2H-pyran-2-yl)-4-methyl-_N_-(2-(phenylethynyl)phenyl)benzenesulfonamide (36)



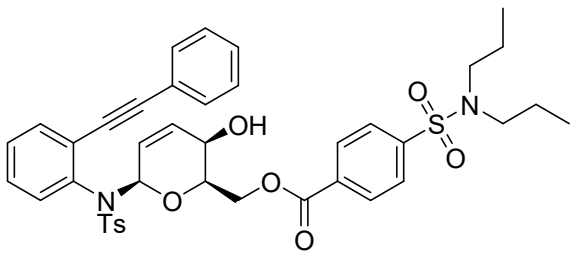
Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1); Colorless syrup (37.2 mg, 81% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 3H), 7.37 – 7.30 (m, 4H), 7.17 (dd, *J* = 21.4, 7.7 Hz, 3H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.32 (s, 1H), 5.97 (s, 2H), 3.80 (d, *J* = 6.1 Hz, 1H), 3.47 (d, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 1.19 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.6, 137.3, 137.3, 133.4, 132.3, 132.0, 131.7, 129.6, 129.2, 129.1, 128.9, 128.7, 128.5, 128.2, 127.7, 123.3, 94.4, 87.1, 87.1, 84.8, 84.8, 72.5, 63.8, 21.7, 16.8. **HRMS** (ESI/TOF) m/z: calculated for $C_{27}H_{25}NO_4SNa$ $[M+Na]^+$ 482.1402 found 482.1398.

((2R,3R,6R)-3-hydroxy-6-((4-methyl-_N_-(2-(phenylethynyl)phenyl)phenyl) sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl (S)-3-(4-isobutylphenyl)-2-methylpropanoate (37)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 12/1); Colorless syrup (51.1 mg, 77% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 5.4 Hz, 3H), 7.36 (s, 3H), 7.31 – 7.26 (m, 3H), 7.17 – 7.05 (m, 5H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.38 (s, 1H), 5.98 (d, *J* = 10.0 Hz, 1H), 5.89 (s, 1H), 4.28 (dd, *J* = 11.3, 5.1 Hz, 1H), 4.11 – 4.03 (m, 1H), 3.85 – 3.76 (m, 2H), 3.56 (s, 1H), 2.45 (d, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 1.84 (dd, *J* = 12.9, 6.4 Hz, 1H), 1.55 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 143.6, 140.8, 137.6, 136.9, 136.7, 133.3, 131.9, 131.4, 131.2, 129.7, 129.5, 129.2, 129.0, 128.8, 128.6, 128.4, 128.0, 127.5, 127.2, 123.0, 94.4, 86.9, 84.5, 74.2, 63.5, 61.0, 45.1, 45.0, 30.2, 22.4, 21.5, 18.8. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{40}H_{41}NNaO_6S$ $[M+Na]^+$ 686.2552 found 686.2548.

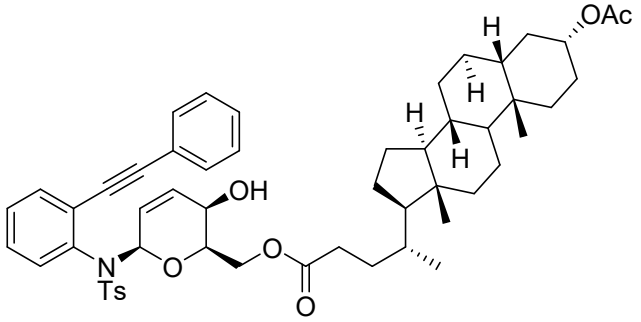
((2R,3R,6R)-3-Hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl)sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl 4-(*N,N*-dipropylsulfamoyl)benzoate (38)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 8/1); Colorless syrup (49 mg, 66% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.70 – 7.54 (m, 5H), 7.40 – 7.32 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.46 (s, 1H), 6.12 – 5.96 (m, 2H), 4.45 (d, *J* = 5.6 Hz, 2H), 4.09 (s, 1H), 3.80 (s, 1H), 3.15 – 3.08 (m, 4H), 2.32

(s, 3H), 1.58 – 1.52 (m, 5H), 0.87 (t, J = 7.4 Hz, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2, 144.9, 143.8, 136.9, 133.5, 133.3, 132.0, 131.7, 131.3, 130.4, 130.2, 129.5, 129.1, 128.8, 128.5, 128.2, 127.7, 127.3, 123.1, 94.6, 87.0, 84.7, 74.5, 65.1, 61.5, 50.1, 22.1, 21.7, 11.3. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{40}H_{42}N_2NaO_8S_2$ $[M+Na]^+$ 765.2280 found 765.2265.

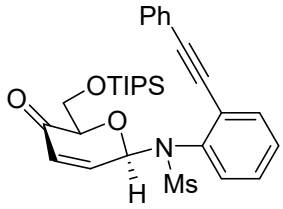
((2R,3R,6R)-3-hydroxy-6-((4-methyl-*N*-(2-(phenylethynyl)phenyl)phenyl)sulfonamido)-3,6-dihydro-2H-pyran-2-yl)methyl (4R)-4-((3R,5R,8S,9S,10R,13R,17R)-3-acetoxy-5,10,13-trimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (39)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 15/1); Colorless syrup (64.8 mg, 74% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.60 (t, J = 5.6 Hz, 3H), 7.34 (dd, J = 19.2, 5.5 Hz, 5H), 7.20 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.9 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 6.40 (s, 1H), 6.02 (d, J = 10.2 Hz, 1H), 5.98 – 5.91 (m, 1H), 4.74 – 4.68 (m, 1H), 4.24 (dd, J = 11.5, 5.3 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.90 (t, J = 5.6 Hz, 1H), 3.70 (dd, J = 10.1, 5.4 Hz, 1H), 2.50 – 2.31 (m, 5H), 2.02 – 1.96 (m, 5H), 1.90 – 1.78 (m, 6H), 1.68 (s, 2H), 1.59 – 1.52 (m, 2H), 1.46 – 1.34 (m, 10H), 1.16 – 1.01 (m, 7H), 0.92 (s, 3H), 0.65 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 170.7, 143.7, 136.8, 133.3, 131.9, 131.4, 131.2, 129.9, 129.2, 129.0, 128.8, 128.6, 128.4, 128.1, 127.5, 123.0, 94.4, 86.9, 84.5, 74.4, 63.4, 61.1, 56.5, 55.9, 42.7, 41.9, 40.4, 40.1, 35.8, 35.4, 35.0, 34.6, 32.2, 31.2, 31.0, 28.3, 27.0, 26.6, 26.3, 24.2, 23.3, 21.6, 21.5, 20.8, 18.3, 12.1. **HRMS** (ESI/TOF) m/z: calculated for $C_{53}H_{65}NO_8SNa$ $[M+Na]^+$ 898.4329 found 898.4321.

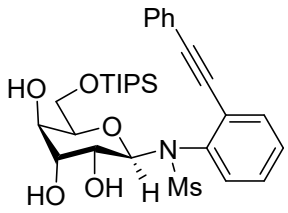
5. Synthetic Transformations of Glycoside Products

_N_-((2R,6R)-5-oxo-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-_N_-(2-(phenylethynyl)phenyl)methanesulfonamide (40)



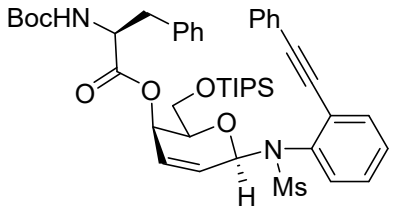
To a solution of **2** (20 mg, 0.036 mmol), sodium bicarbonate (15.1 mg, 0.18 mmol) and *tert*-butyl alcohol (17.2 μL, 0.18 mmol) in anhydrous CH_2Cl_2 (2 mL) at 0 ℃ was added Dess-Martin periodinane (76.3 mg, 0.18 mmol) in one portion. After addition, the mixture was stirred at 37 °C overnight. After completion, the reaction mixture was diluted by CH_2Cl_2 (10 mL), washed with water and brine (8 mL). Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford **40** as colorless syrup (19.6 mg, 98% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 9.1 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.44 – 7.27 (m, 5H), 6.90 (d, *J* = 10.4 Hz, 1H), 6.52 (s, 1H), 5.98 (d, *J* = 10.4 Hz, 1H), 4.31 (s, 1H), 4.19 (d, *J* = 4.0 Hz, 2H), 3.20 (s, 3H), 1.18 – 1.04 (m, 21H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 192.6, 146.1, 137.1, 133.2, 131.9, 130.7, 129.5, 128.9, 128.7, 128.4, 127.2, 122.8, 94.8, 86.5, 83.2, 80.7, 62.2, 41.1, 18.0, 17.9, 11.9. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{30}H_{39}NNaO_5SSi$ $[M+Na]^+$ 576.2216 found 576.2205.

_N_-(2-(phenylethynyl)phenyl)-_N_-((2R,3R,4R,5R,6R)-3,4,5-trihydroxy-6-(((triisopropylsilyl)oxy)methyl)tetrahydro-2H-pyran-2-yl)methanesulfonamide (41)



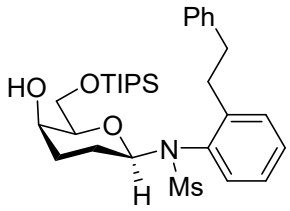
To a solution of **2** (28 mg, 0.05 mmol) in a mixture of *tert*-butyl alcohol (0.4 mL) and water (40 μL) was added NMO (35.4 mg, 0.3 mmol). The resulting solution was cooled to 0 °C and treated with 2.2% (w/v) OsO_4 in water (86 μL). After stirring overnight at 37 °C, the reaction was quenched with saturated aqueous Na_2SO_3 solution, and the resulting mixture was stirred for 0.5 h and extracted with ethyl acetate (10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography (eluting with petroleum ether/ethyl acetate = 2/1) gave the desired triol **41** (27.8 mg, 94%) as a single distereomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.58 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.29 (m, 4H), 5.65 (d, *J* = 9.2 Hz, 1H), 4.21 (dd, *J* = 11.0, 3.0 Hz, 1H), 4.11 (dd, *J* = 11.1, 2.7 Hz, 1H), 4.03 (s, 3H), 3.99 (s, 1H), 3.55 (s, 1H), 3.45 (d, *J* = 9.2 Hz, 1H), 3.13 (s, 3H), 2.73 (s, 1H), 1.19 – 1.07 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.7, 133.5, 132.0, 131.3, 129.6, 129.5, 129.3, 128.7, 126.4, 121.9, 95.7, 86.9, 86.6, 72.4, 71.4, 70.4, 66.3, 65.6, 40.7, 18.0, 11.8. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{30}H_{43}NO_7SSiNa$ $[M+Na]^+$ 612.2427 found 612.2433. The structure and stereochemistry of **41** was confirmed based on the following information: 1) the H_1 of compound **2** is at axial position from X-ray crystallographic analysis; 2) the coupling constant of H_1 and H_2 is 9.2 Hz which confirms 1,2-trans configuration, so the C2 hydroxyl group of **41** is at equatorial position; 3) dihydroxylation by OsO_4/NMO occurs at syn-face of the alkene, therefore, the C3 hydroxyl group of **41** is at axial position. Moreover, gCOSY and gHSQC experiments were also conducted to confirm the structure of **41**.

(2R,3R,6R)-6-(*N*-(2-(phenylethynyl)phenyl)methylsulfonamido)-2-(((triisopropylsilyl)oxy)methyl)-3,6-dihydro-2H-pyran-3-yl (tert-butoxycarbonyl)-*L*-phenylalaninate (42)



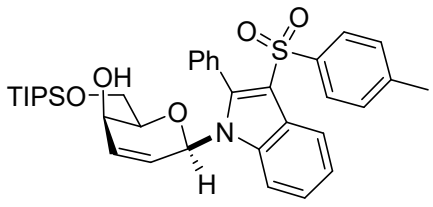
To a solution of **2** (20 mg, 0.036 mmol), DMAP (2 mg, 0.018 mmol) and Boc-L-phenylalanine (14.4 mg, 0.054 mmol) in anhydrous dichloromethane (2 mL) was added EDCI (14 mg, 0.072 mmol), followed by the addition of Et_3N (11.1 μL, 0.08 mmol). After addition, the mixture was stirred at 25 °C for 12 h. The reaction was diluted by ethyl acetate (10 mL), washed with water and brine (10 mL). The solvents were removed *in vacuo*, the residue was purified by chromatography (eluting with petroleum ether/ethyl acetate = 15/1) to afford **42** as a colorless syrup (26.5 mg, 92%).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.58 (dd, *J* = 18.0, 5.6 Hz, 3H), 7.36 (d, *J* = 3.5 Hz, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.09 (m, 4H), 6.70 (d, *J* = 6.8 Hz, 2H), 6.26 (s, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 5.88 (d, *J* = 4.6 Hz, 1H), 5.06 (d, *J* = 5.2 Hz, 1H), 4.91 (d, *J* = 7.9 Hz, 1H), 4.57 (d, *J* = 7.2 Hz, 1H), 3.91 (ddd, *J* = 27.9, 14.4, 7.7 Hz, 3H), 3.19 (s, 3H), 2.99 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.71 (dd, *J* = 13.7, 4.9 Hz, 1H), 1.42 (s, 9H), 1.12 – 1.04 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 154.9, 137.4, 135.3, 133.1, 132.0, 131.4, 129.7, 129.5, 128.8, 128.5, 128.3, 127.2, 127.0, 123.1, 94.6, 87.0, 84.3, 79.9, 75.4, 63.9, 62.0, 53.7, 41.4, 37.9, 28.4, 18.1, 12.0. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{44}H_{58}N_2NaO_8SSi$ $[M+Na]^+$ 825.3581 found 825.3560.

***N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)tetrahydro-2H-pyran-2-yl)-*N*-(2-phenethylphenyl)methanesulfonamide (43)**



A Schlenk tube was charged with **2** (20 mg, 0.036 mmol) and Pd/C (10 mg, 10% on carbon) in EtOAc (1 mL) under nitrogen atmosphere. The tube was subsequently filled with hydrogen. After stirring at 25 ℃ for 8 h, the mixture was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate = 20/1) to provide **43** (19.8 mg, 98% yield) as a colorless syrup. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.22 (m, 4H), 7.21 – 7.17 (m, 2H), 5.45 (d, *J* = 8.9 Hz, 1H), 4.06 (t, *J* = 4.4 Hz, 2H), 3.86 (s, 1H), 3.55 (t, *J* = 3.8 Hz, 1H), 3.45 (s, 1H), 3.19 – 2.84 (m, 7H), 1.86 – 1.77 (m, 1H), 1.71 – 1.54 (m, 2H), 1.46 – 1.38 (m, 1H), 1.18 – 1.04 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.2, 142.2, 134.8, 130.0, 130.0, 129.2, 128.7, 128.5, 126.7, 126.0, 87.5, 77.8, 66.1, 65.5, 40.5, 36.3, 32.9, 30.2, 22.6, 18.1, 11.9. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{30}H_{47}NNaO_5SSi$ $[M+Na]^+$ 584.2842 found 584.2830.

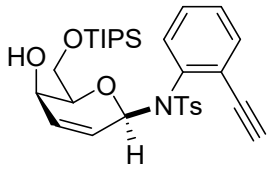
(2R,3R,6R)-6-(2-phenyl-3-tosyl-1H-indol-1-yl)-2-(((triisopropylsilyl)oxy)methyl)-3,6-dihydro-2H-pyran-3-ol (44)



A Schlenk tube was charged with **1** (20 mg, 0.0317 mmol) and $PdCl_2(CH_3CN)_2$ (0.93 mg, 0.0036 mmol) in toluene (2.0 mL). Then the reaction tube was evacuated and backfilled with nitrogen, and the process was repeated three times. After that, the reaction tube was kept heated to 90 °C and stirred for 5 h. The reaction mixture was diluted by ethyl acetate (10 mL), washed with water and brine (10 mL). Remove the

solvent *in vacuo*, the residue was purified by chromatography (eluting with petroleum ether/ethyl acetate = 20/1) to give **44** (10.8 mg, 54% yield) as a colorless syrup. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.36 – 8.26 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.51 – 7.41 (m, 4H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.22 (dd, *J* = 10.7, 5.8 Hz, 1H), 5.87 (d, *J* = 10.1 Hz, 1H), 5.76 (s, 1H), 4.11 (t, *J* = 5.9 Hz, 1H), 3.99 – 3.86 (m, 2H), 3.69 (ddd, *J* = 7.3, 5.6, 2.2 Hz, 1H), 2.42 (s, 1H), 2.32 (s, 3H), 1.09 – 1.05 (m, 3H), 1.00 (d, *J* = 7.1 Hz, 18H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.4, 143.0, 140.8, 134.8, 131.7, 130.9, 130.3, 129.9, 129.7, 129.1, 128.8, 127.9, 127.8, 126.6, 125.4, 123.9, 122.9, 120.6, 115.7, 113.3, 80.6, 62.9, 61.7, 21.4, 17.9, 17.8, 11.8. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{36}H_{45}NNaO_5SSi$ $[M+Na]^+$ 654.2685 found 654.2671.

_N_-(2-ethynylphenyl)-_N_-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methylbenzenesulfonamide (45)



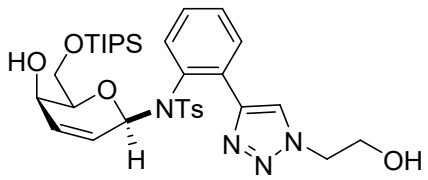
To a solution of **12** (81 mg, 0.13 mmol) in MeOH (7 mL) was added K_2CO_3 (21 mg, 0.15 mmol). The reaction was stirred at room temperature for 20 min, then the reaction was quenched with water (1 mL) and MeOH was evaporated under reduced pressure. The mixture was diluted by ethyl acetate (10 mL), washed with water and brine (2× 3 mL). Remove the solvents *in vacuo*, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford the desired product **45** (59 mg, 81% yield) as colorless syrup. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.99 – 5.89 (m, 2H), 3.86 – 3.74 (m, 2H), 3.71 (s, 2H), 3.28 (s, 1H), 2.41 (s, 3H), 1.12 – 1.07 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 137.7, 137.1, 134.2, 131.9, 131.6, 129.3, 129.1,

129.0, 128.7, 126.5, 84.7, 82.1, 81.1, 77.5, 77.2, 76.8, 76.6, 62.4, 61.0, 21.6, 18.1, 18.0, 12.0. **HRMS** (ESI/FT-ICR) m/z: calculated for $C_{30}H_{41}NO_5SSiNa$ 578.2372 found 578.2357.

General procedure for Cu-catalysed azide-alkyne cycloaddition (Click chemistry):

To a solution of **45** (16.7 mg, 0.03 mmol, 1.0 equiv.) and azido compounds (1.5 equiv.) in THF/H_2O (1:1, 0.6 mL) was sequentially added $CuSO_4$ (0.15 equiv.) and sodium ascorbate (0.3 equiv.) in one portion. The reaction mixture was stirred at RT for 2 h under nitrogen atmosphere. The reaction was diluted by ethyl acetate (3 mL), washed with water and brine (1 mL). Remove the solvents *in vacuo*, the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate) to afford the desired product.

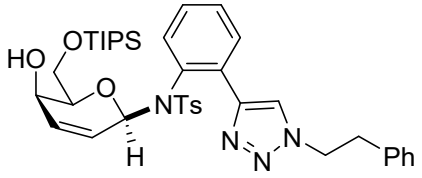
***N*-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-*N*-(2-(1-(2-hydroxyethyl)-1H-1,2,3-triazol-4-yl)phenyl)-4-methyl benzenesulfonamide (46)**



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 1/1), **46** was obtained as colorless syrup (18.1 mg, 94% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.20 (s, 1H), 5.79 (dt, *J* = 7.5, 3.8 Hz, 1H), 5.21 (d, *J* = 10.1 Hz, 1H), 4.58 (q, *J* = 4.9 Hz, 2H), 4.10 (t, *J* = 5.1 Hz, 2H), 3.76 – 3.68 (m, 2H), 3.63 (q, *J* = 7.0, 6.0 Hz, 2H), 2.44 (s, 3H), 1.12 – 1.03 (m, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.2, 136.7, 133.6, 133.0, 132.2, 131.2, 129.9, 129.9, 129.5, 129.0, 128.2, 128.0, 125.0, 84.9, 76.8, 62.2, 61.4, 60.7, 52.8, 21.7, 18.1, 18.1, 12.0. **HRMS** (ESI/TOF) m/z: calculated for $C_{32}H_{46}N_4O_6SSiNa$

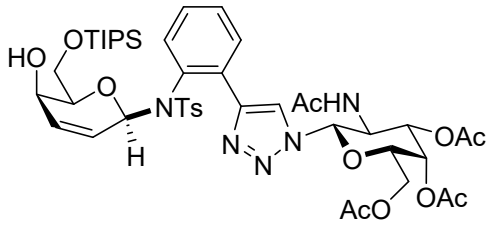
665.2805 found 665.2801.

_N_-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methyl-_N_-(2-(1-phenethyl-1H-1,2,3-triazol-4-yl)phenyl) benzenesulfonamide (47)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 3/1), compound **47** was obtained as colorless syrup (19 mg, 90% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 10.7 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 3H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 1H), 5.81 – 5.75 (m, 1H), 4.90 (d, *J* = 10.2 Hz, 1H), 4.77 (dt, *J* = 13.9, 6.9 Hz, 1H), 4.66 (dt, *J* = 14.5, 7.7 Hz, 1H), 3.75 – 3.69 (m, 2H), 3.65 – 3.60 (m, 2H), 3.31 (td, *J* = 7.2, 3.3 Hz, 2H), 2.45 (s, 3H), 1.13 – 1.08 (m, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.2, 137.1, 136.7, 133.7, 132.8, 132.0, 131.0, 130.0, 129.9, 129.6, 129.0, 128.8, 128.3, 127.8, 127.2, 124.2, 84.8, 76.9, 62.1, 60.6, 51.6, 36.7, 21.7, 18.1, 18.1, 12.0. **HRMS** (ESI/TOF) m/z: calculated for $C_{38}H_{50}N_4O_5SSiNa$ 725.3169 found 725.3162.

(2S,3S,4S,5S,6S)-5-acetamido-2-(acetoxymethyl)-6-(4-(2-((_N_-((2R,5R,6R)-5-hydroxy-6-(((triisopropylsilyl)oxy)methyl)-5,6-dihydro-2H-pyran-2-yl)-4-methyl phenyl)sulfonamido)phenyl)-1H-1,2,3-triazol-1-yl)tetrahydro-2H-pyran-3,4-diyl diacetate (48)



Purified by silica-gel column chromatography (petroleum ether/ethyl acetate = 1/2), compound **48** was obtained as colorless syrup (23.7 mg, 85% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 8.9 Hz, 1H), 6.30 (s, 1H), 6.17 (d, *J* = 9.8 Hz, 1H), 5.82 (dd, *J* = 10.3, 5.7 Hz, 1H), 5.59 (d, *J* = 10.0 Hz, 1H), 5.54 (s, 1H), 5.38 (d, *J* = 10.2 Hz, 1H), 4.74 (q, *J* = 9.9 Hz, 1H), 4.34 (t, *J* = 6.5 Hz, 1H), 4.23 (dd, *J* = 11.6, 6.1 Hz, 1H), 4.16 (dd, *J* = 11.5, 6.6 Hz, 1H), 3.75 (d, *J* = 5.7 Hz, 1H), 3.73 – 3.65 (m, 2H), 3.60 (dd, *J* = 8.1, 3.3 Hz, 1H), 2.44 (s, 3H), 2.25 (s, 3H), 2.04 (s, 6H), 1.75 (s, 3H), 1.13 – 1.07 (m, 21H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.8, 170.6, 170.6, 170.5, 144.6, 144.1, 137.0, 133.7, 133.3, 131.5, 131.2, 130.0, 129.8, 129.5, 129.0, 128.3, 123.5, 86.3, 85.0, 76.7, 73.8, 70.1, 66.9, 62.2, 61.8, 60.8, 50.8, 23.0, 21.7, 20.9, 20.8, 18.1, 18.1, 12.0. **HRMS** (ESI/TOF) m/z: calculated for $C_{44}H_{61}N_5O_{13}SSiNa$ 950.3654 found 950.3641.

6. X-Ray Crystal Structure and Data of Compound 2.

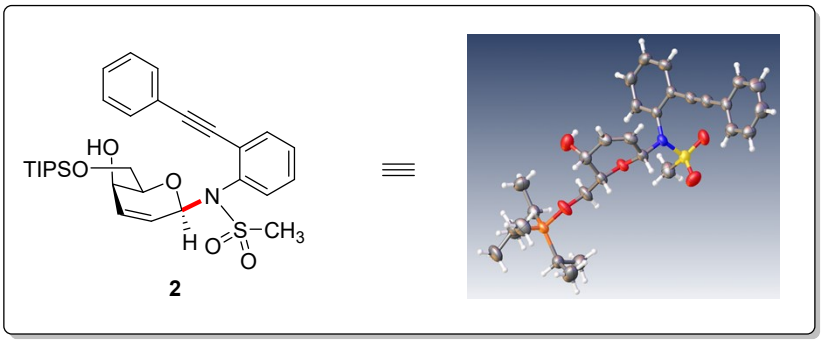


Figure S1. X-ray structure of **2** (ellipsoids are drawn at the 50% probability level)

Table 1. Crystallographic data and structure refinement for 2.

Compound **2**	Data
Empirical formula	$C_{30}H_{41}NO_5SSi$
Formula weight	555.79
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.5387(3)
b/Å	13.4947(6)
c/Å	30.0141(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3053.4(2)
Z	4
ρ_{calc}g/cm^3	1.209
μ/mm^{-1}	0.183

Compound **2**	Data
F(000)	1192.0
Crystal size/mm^3	0.36 × 0.34 × 0.3
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.31 to 58.32
Index ranges	-10 ≤ h ≤ 5, -17 ≤ k ≤ 17, -39 ≤ l ≤ 38
Reflections collected	11984
Independent reflections	6909 [R_{int} = 0.0302, R_{sigma} = 0.0660]
Data/restraints/parameters	6909/0/351
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1090
Final R indexes [all data]	R_1 = 0.0799, wR_2 = 0.1242
Largest diff. peak/hole / e Å^{-3}	0.19/-0.23
Flack parameter	0.03(6)

7. References

[1] Liu, J.; Xie, X.; Liu, Y. H. *Chem. Commun.* **2013,** *49*, 11794-11796.

[2] Yie, Y. B.; Cheung, K. P. S. C.; He, L. S.; Tsui, G. C. *Org. Chem. Front*. **2018**, *5*, 1511-1515.

[3] He, Y. P.; Cao J.; Wu, H.; Wang, Q.; Zhu. J. *Angew. Chem. Int. Ed.* **2021**, *60*, 7093-7097.

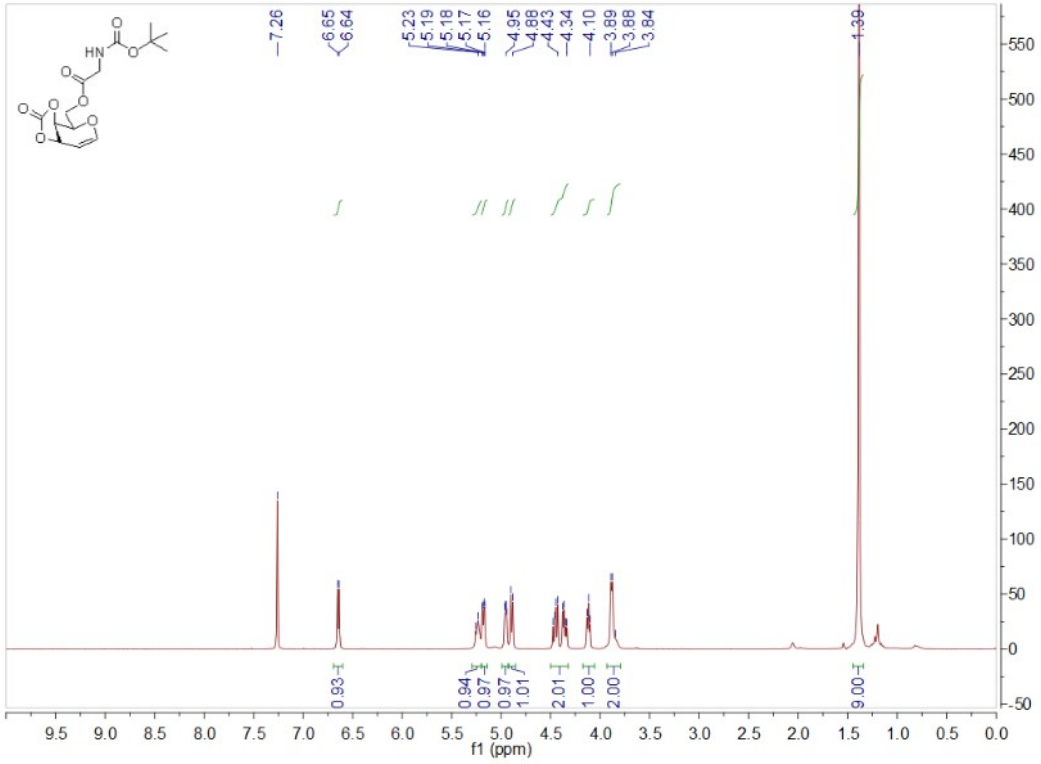
[4] L, X. M.; Zhang, B. B.; Zhang, J. G.; Wang, X.; Zhang, D. K.; Du, Y. F.; Zhao, K., *Chin. J. Chem.* **2021**, *39*, 1211-1224.

[5] Li, Y. L.; Li, J.; Yu, S. N.; Wang, J.; Yu, Y. M.; Deng, J. *Tetrahedron.* **2015,** *71*, 8271-8277.

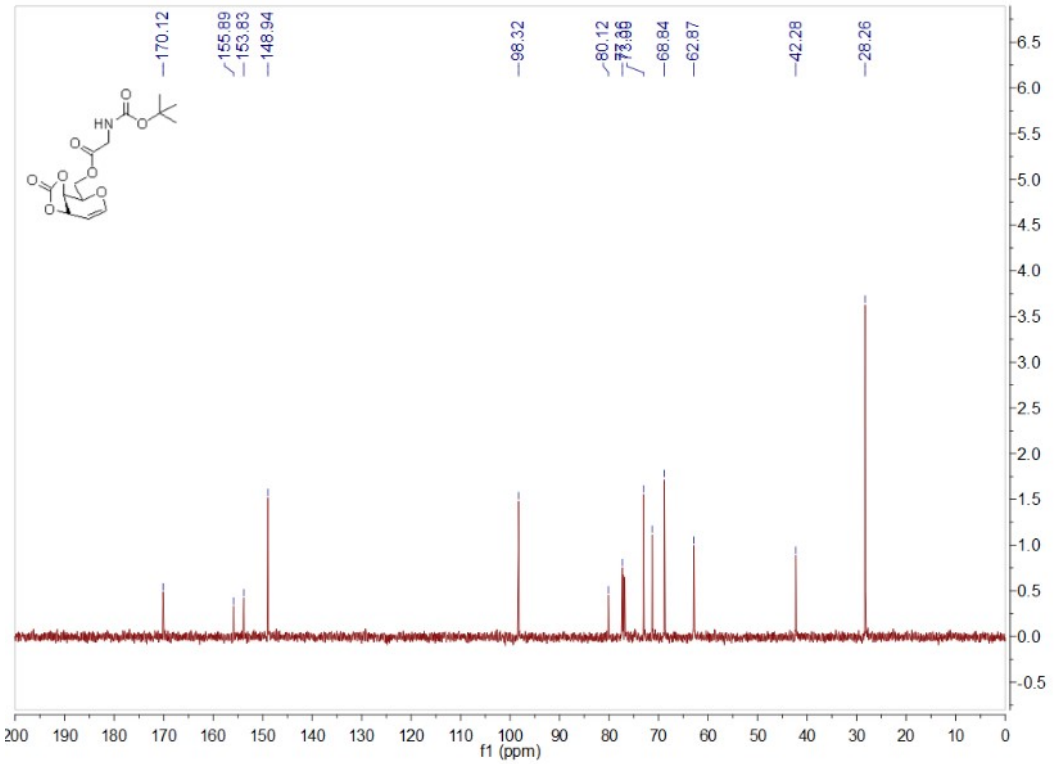
[6] Dai, Y. W.; Zheng, J. F.; Zhang, Q. *Org. Lett*. **2018**, *20*, 3923-3927.

[7] Meng, S.; Zhong, W. H.; Yao, W.; Li, Z. J. *Org. Lett*. **2020,** *22***,** 2981-2986.

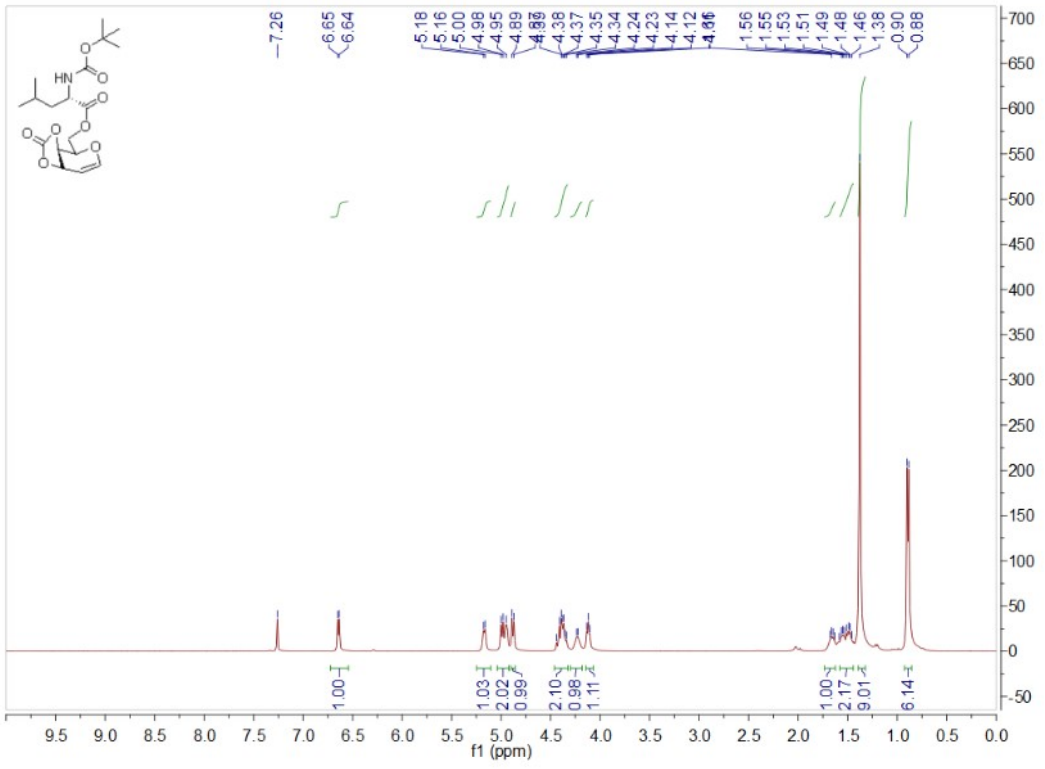
8. Copies of NMR Spectra of New Compounds



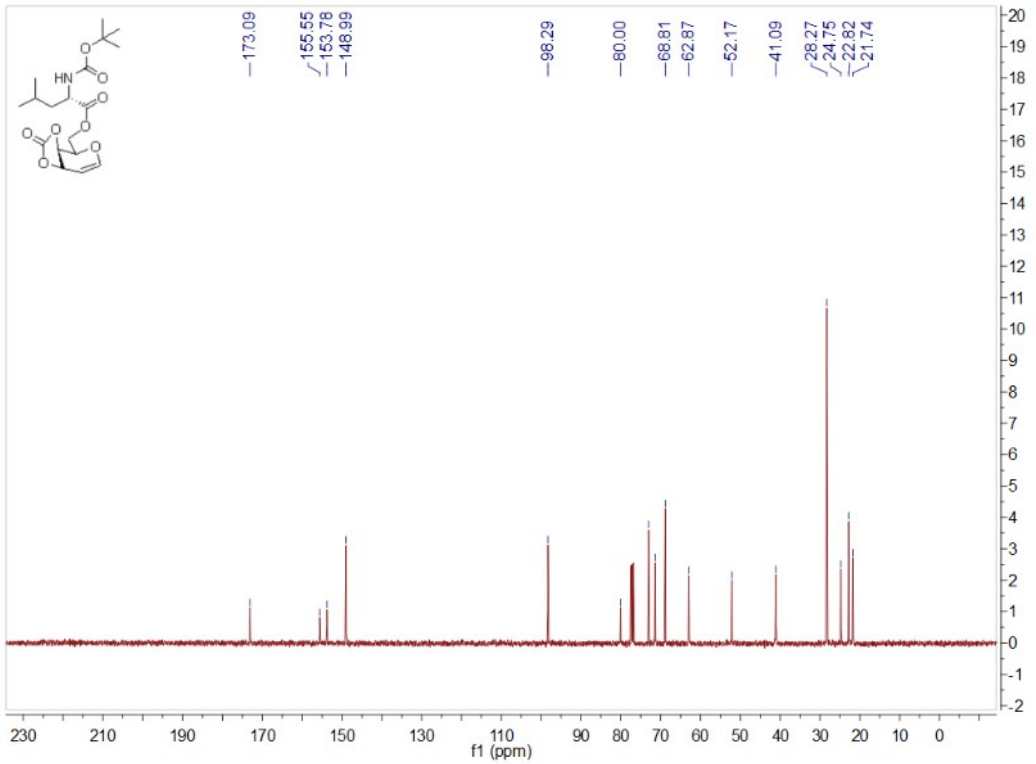
^{1}H NMR spectrum of **1ai** in $CDCl_3$ (400 MHz).



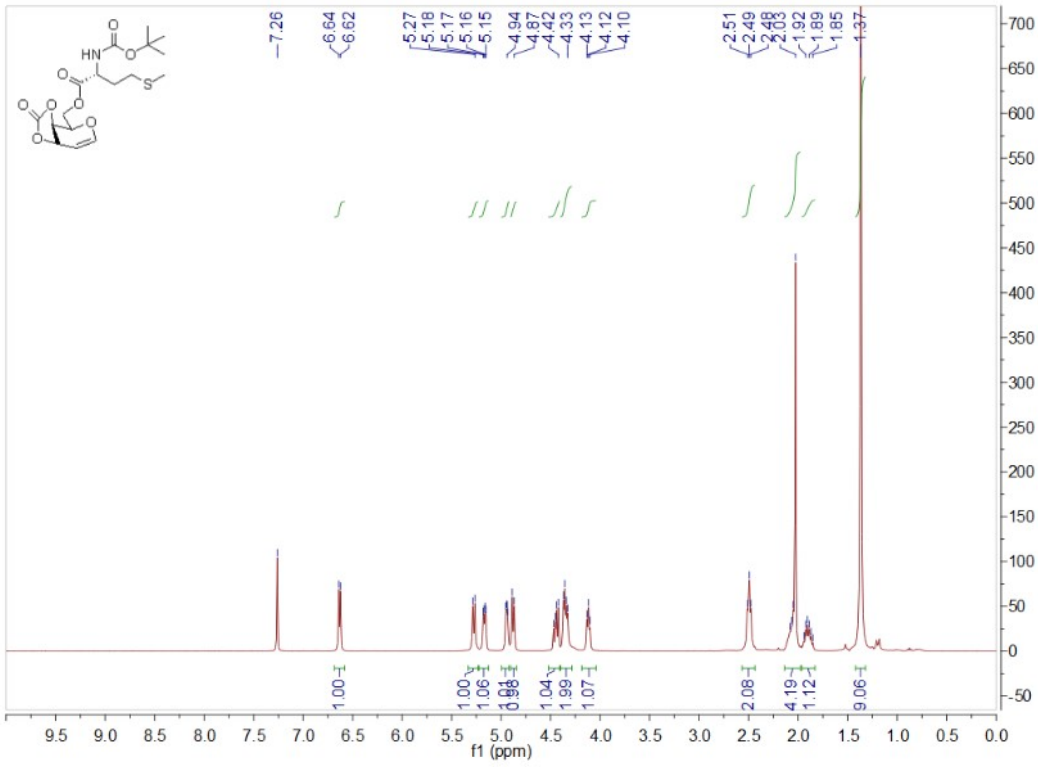
^{13}C NMR spectrum of **1ai** in $CDCl_3$ (100 MHz).



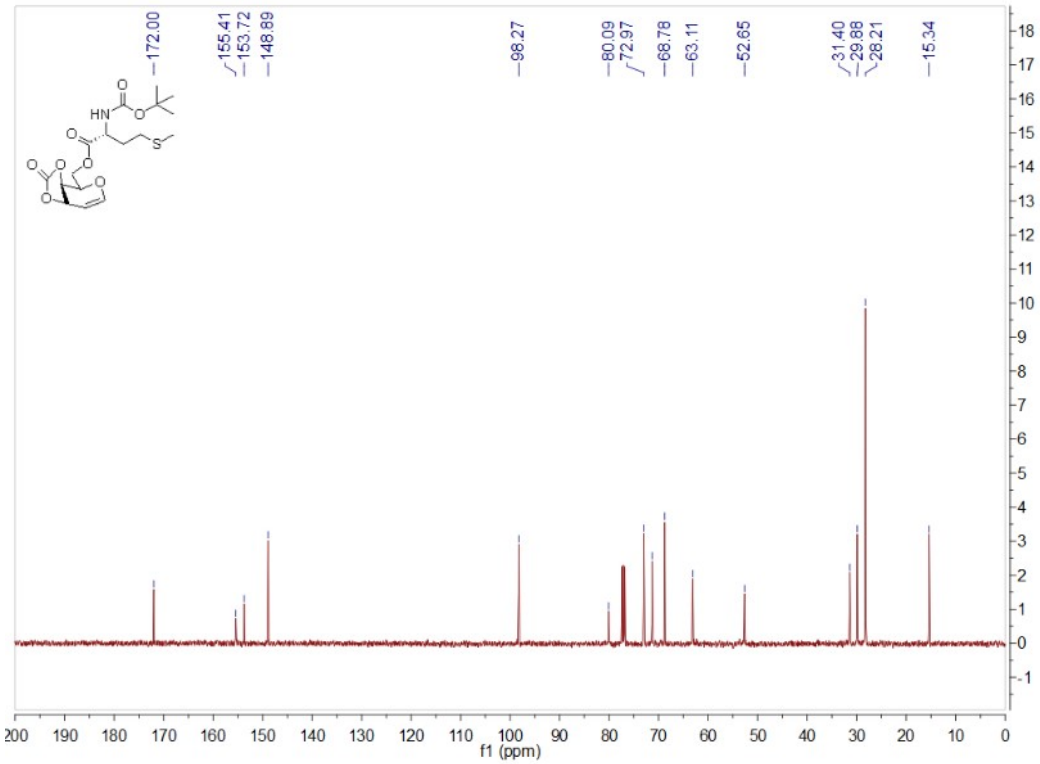
^{1}H NMR spectrum of **1aj** in $CDCl_3$ (400 MHz).



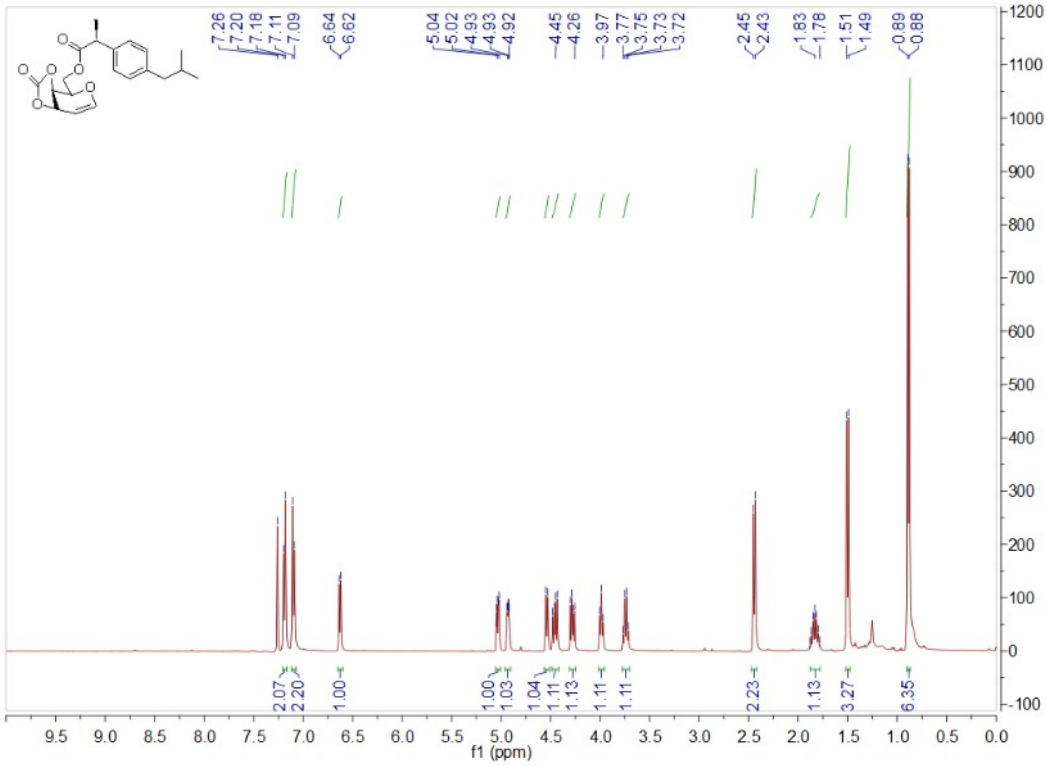
^{13}C NMR spectrum of **1aj** in $CDCl_3$ (100 MHz).



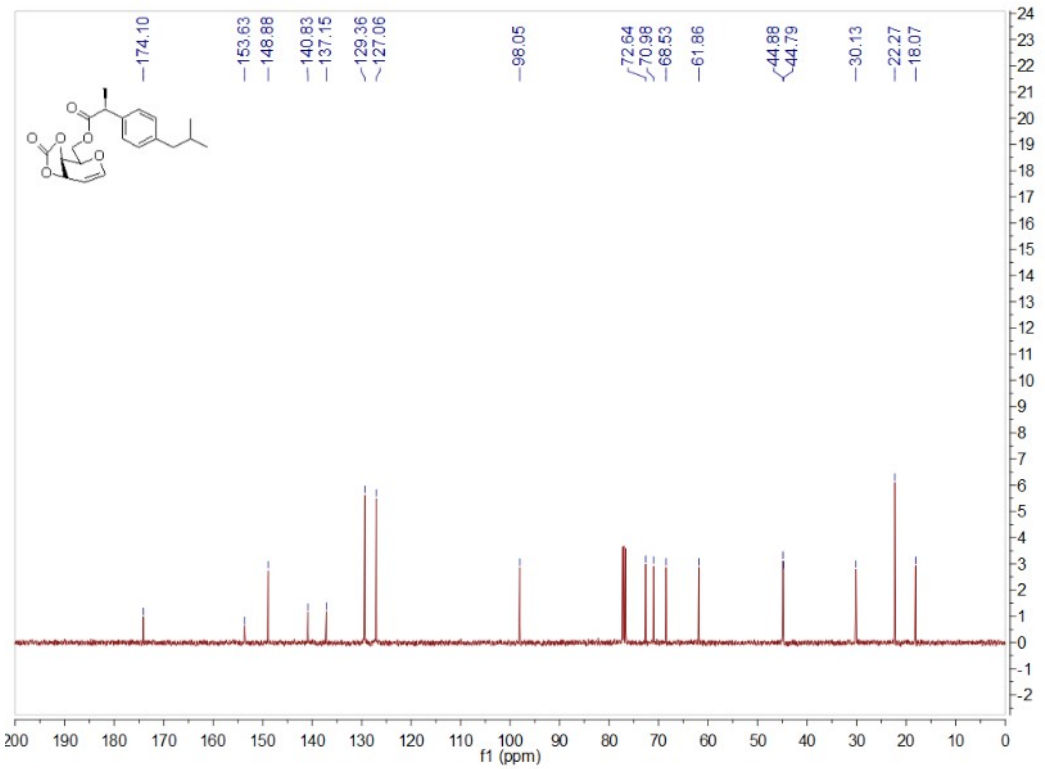
^{1}H NMR spectrum of **1ak** in $CDCl_3$ (400 MHz).



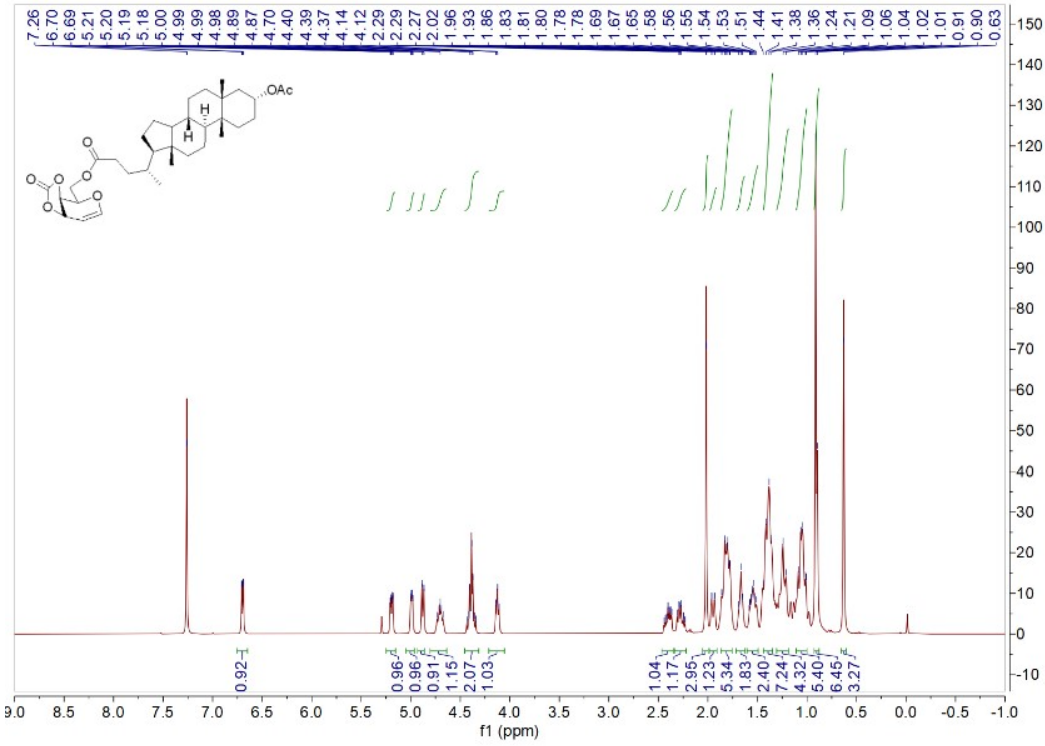
^{13}C NMR spectrum of **1ak** in $CDCl_3$ (100 MHz).



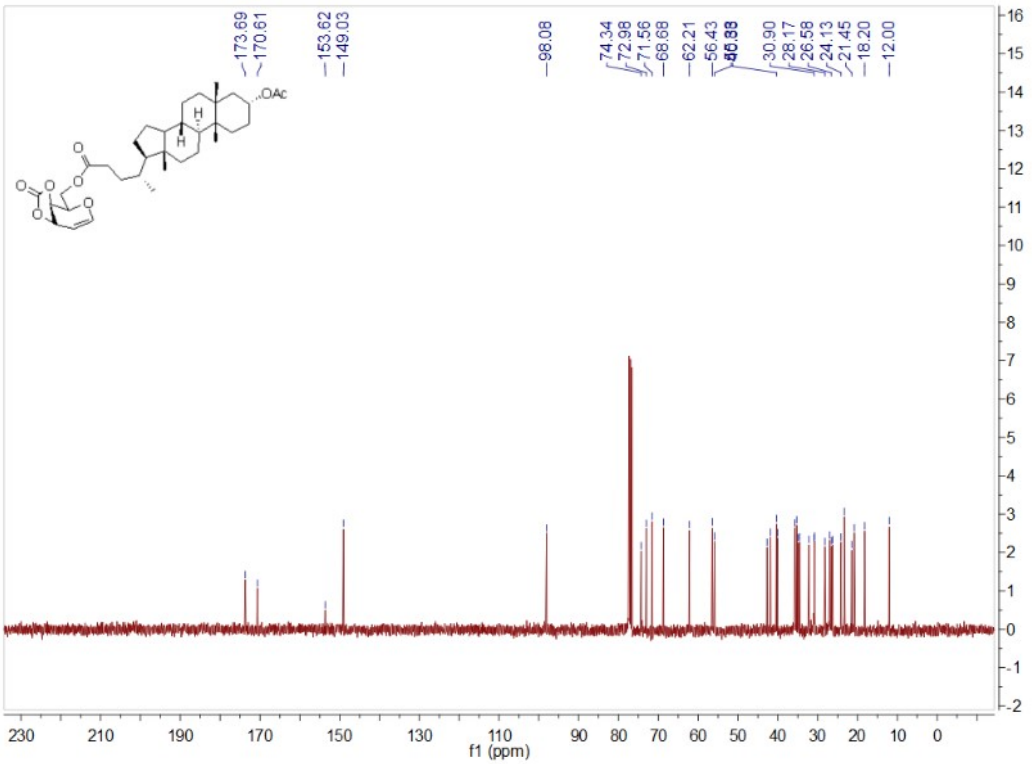
^{1}H NMR spectrum of **1am** in $CDCl_3$ (400 MHz).



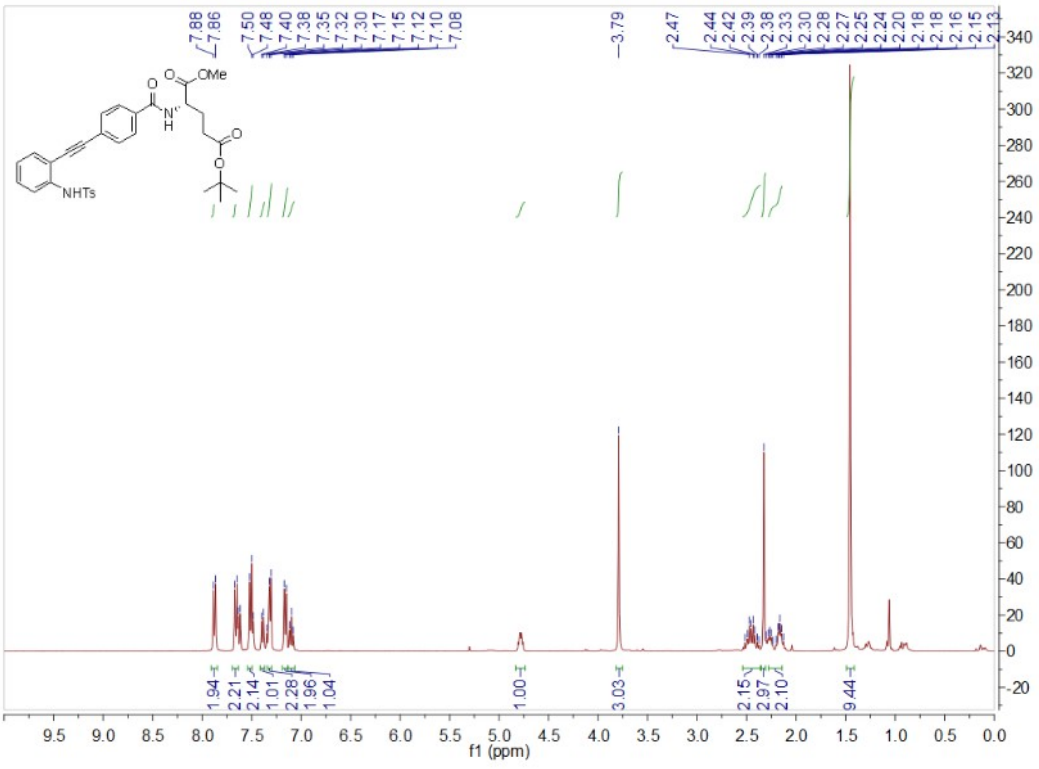
^{13}C NMR spectrum of **1am** in $CDCl_3$ (100 MHz).



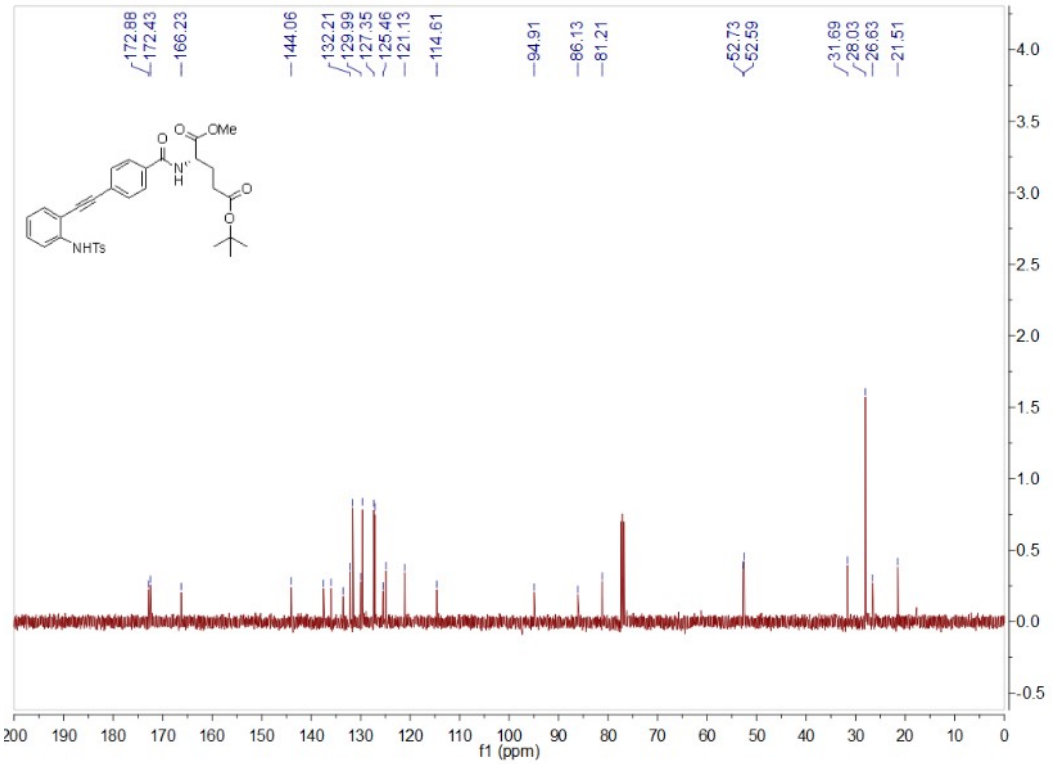
^{1}H NMR spectrum of **1ao** in $CDCl_3$ (400 MHz).



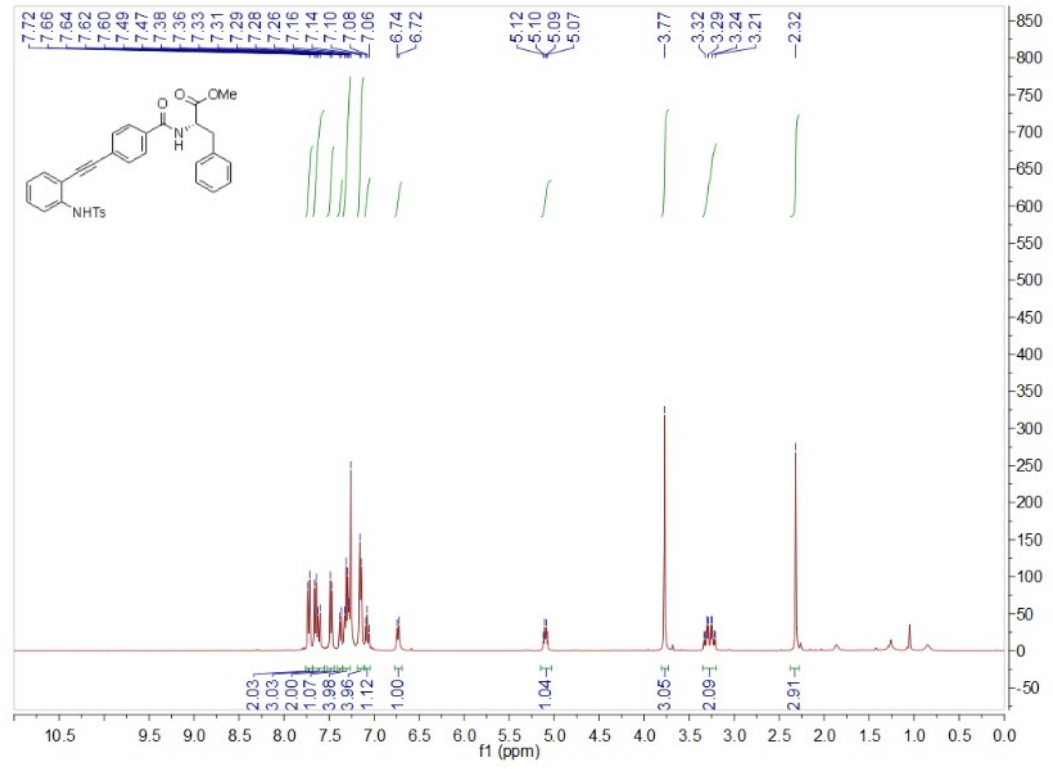
^{13}C NMR spectrum of **1ao** in $CDCl_3$ (100 MHz).



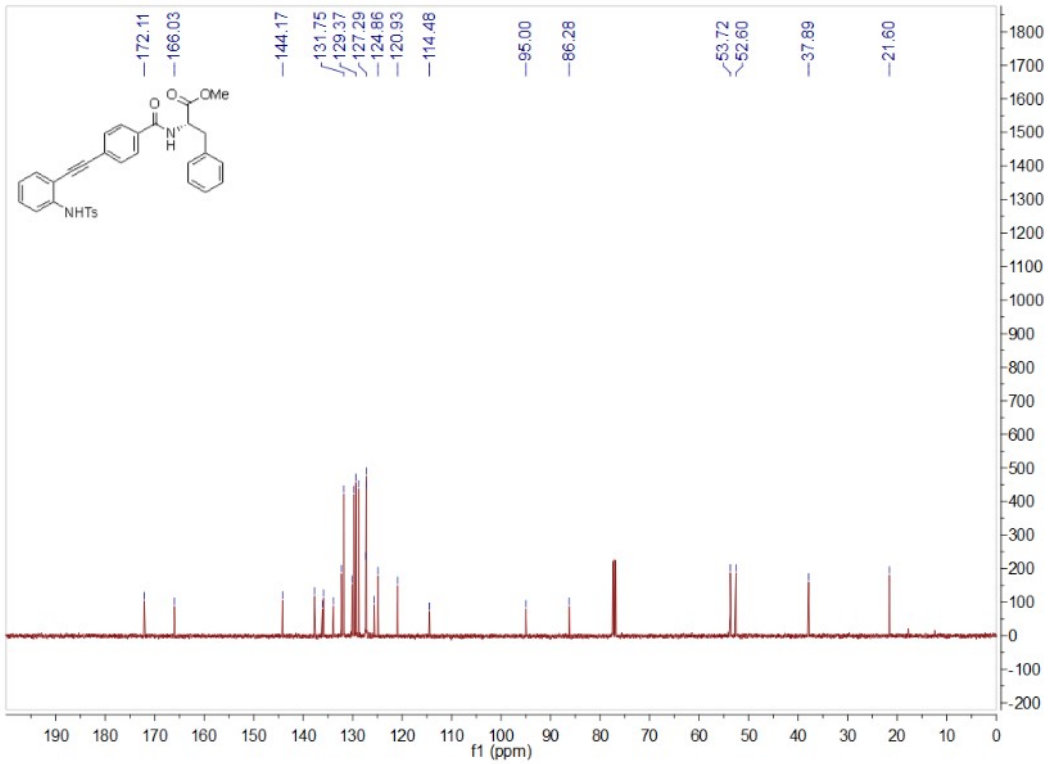
^{1}H NMR spectrum of **1n** in $CDCl_3$ (400 MHz).



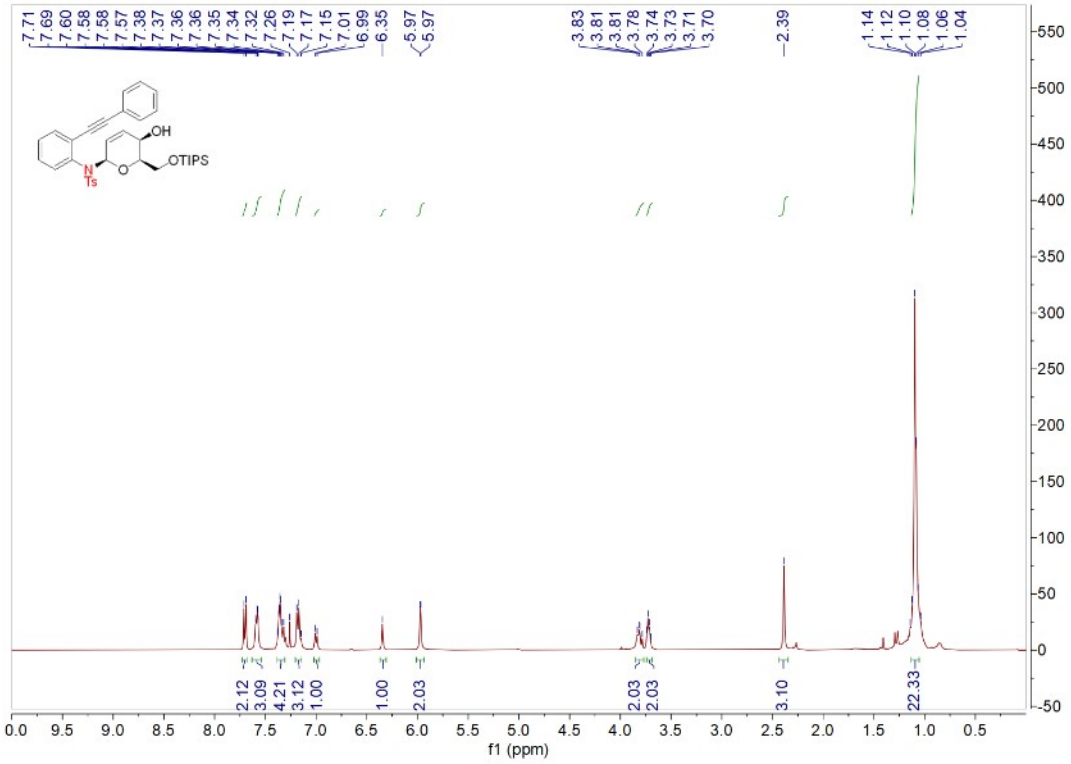
^{13}C NMR spectrum of **1n** in $CDCl_3$ (100 MHz).



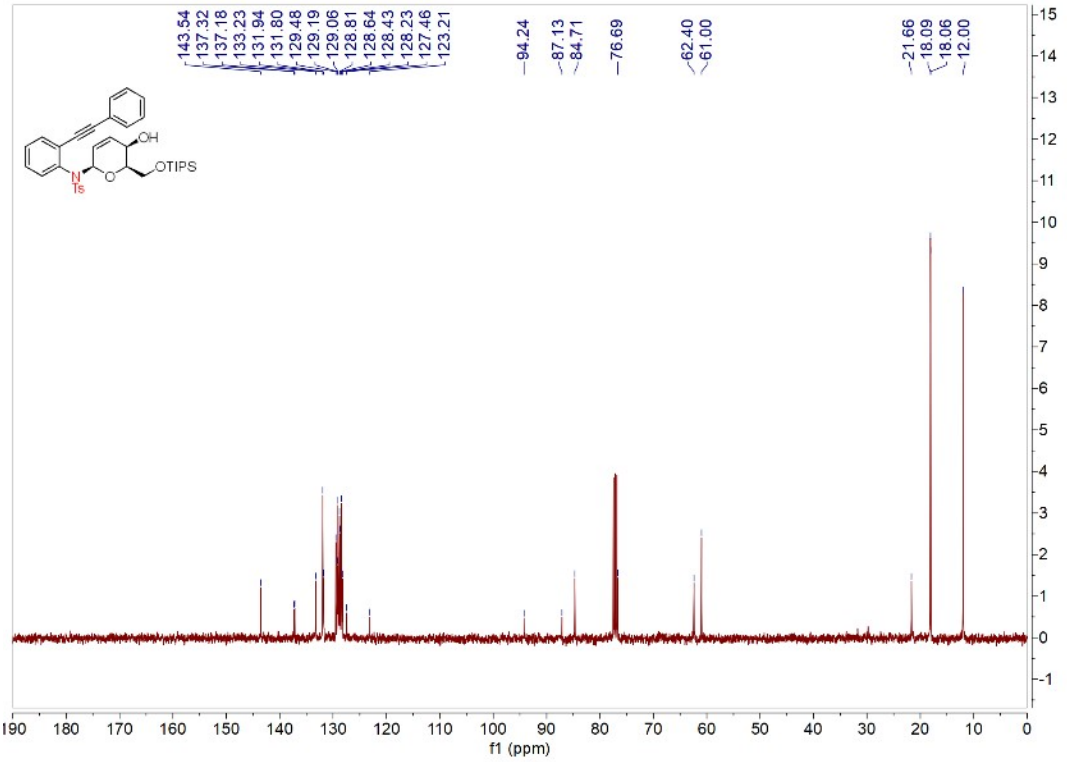
^{1}H NMR spectrum of **1o** in $CDCl_3$ (400 MHz).



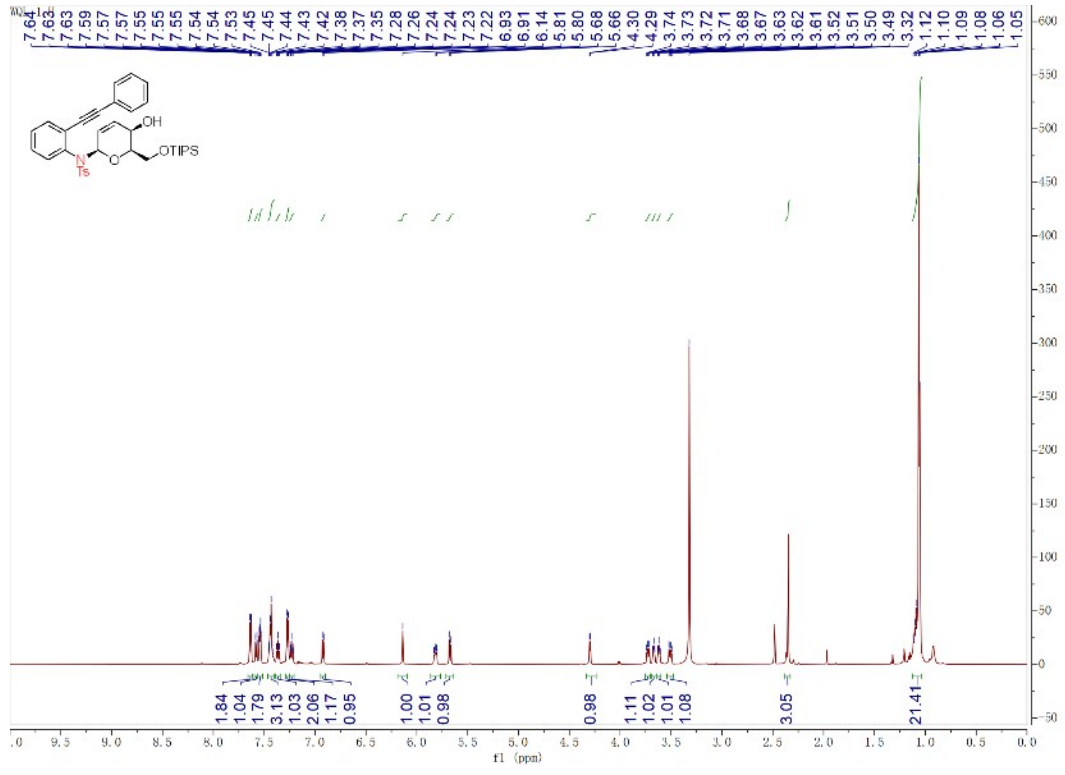
^{13}C NMR spectrum of **1o** in $CDCl_3$ (100 MHz).



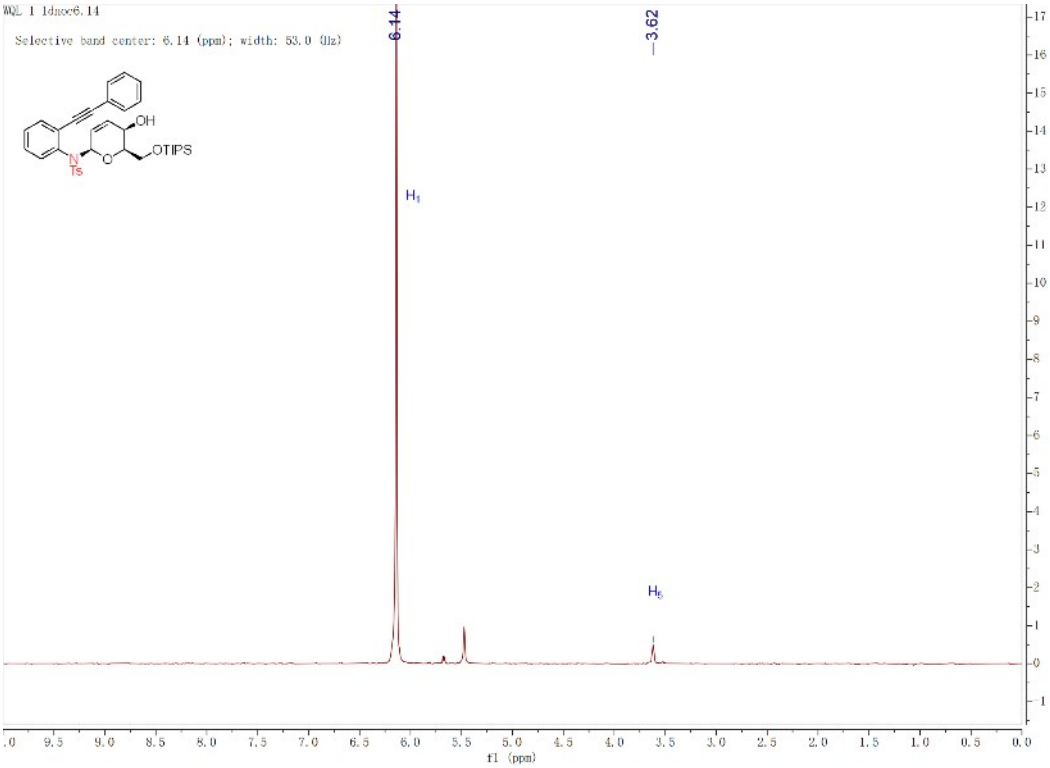
^{1}H NMR spectrum of **1** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **1** in $CDCl_3$ (100 MHz).

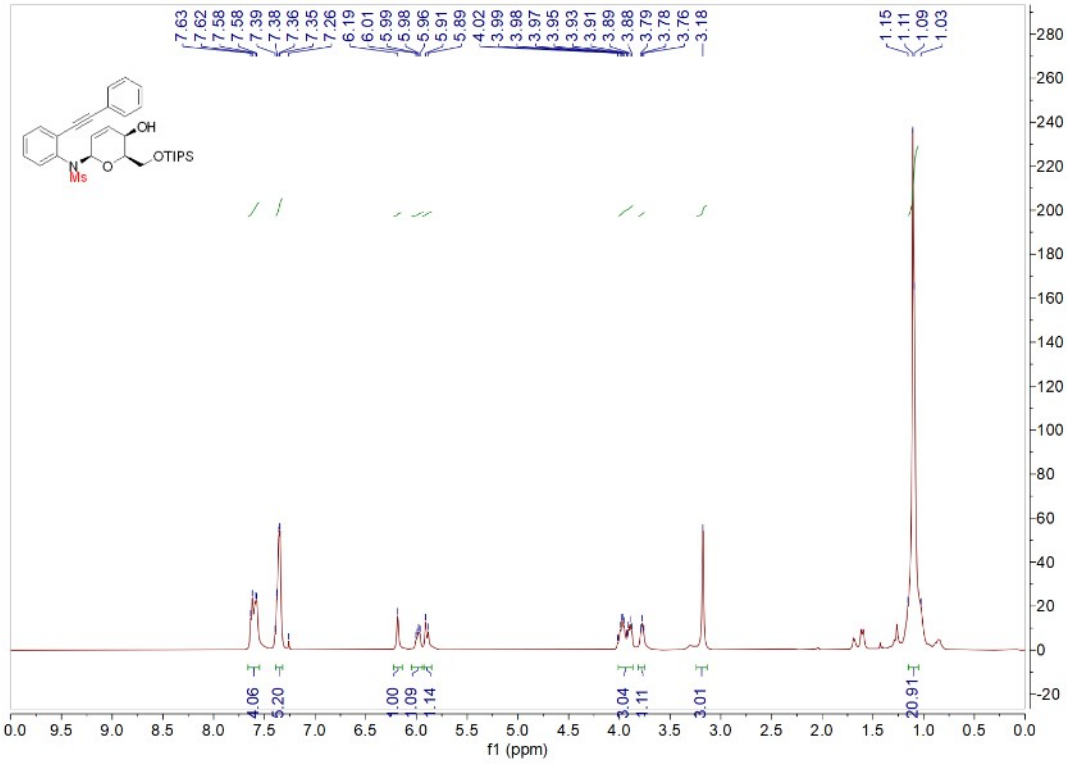


^{1}H NMR spectrum of **1** in DMSO-d_6 (600 MHz).

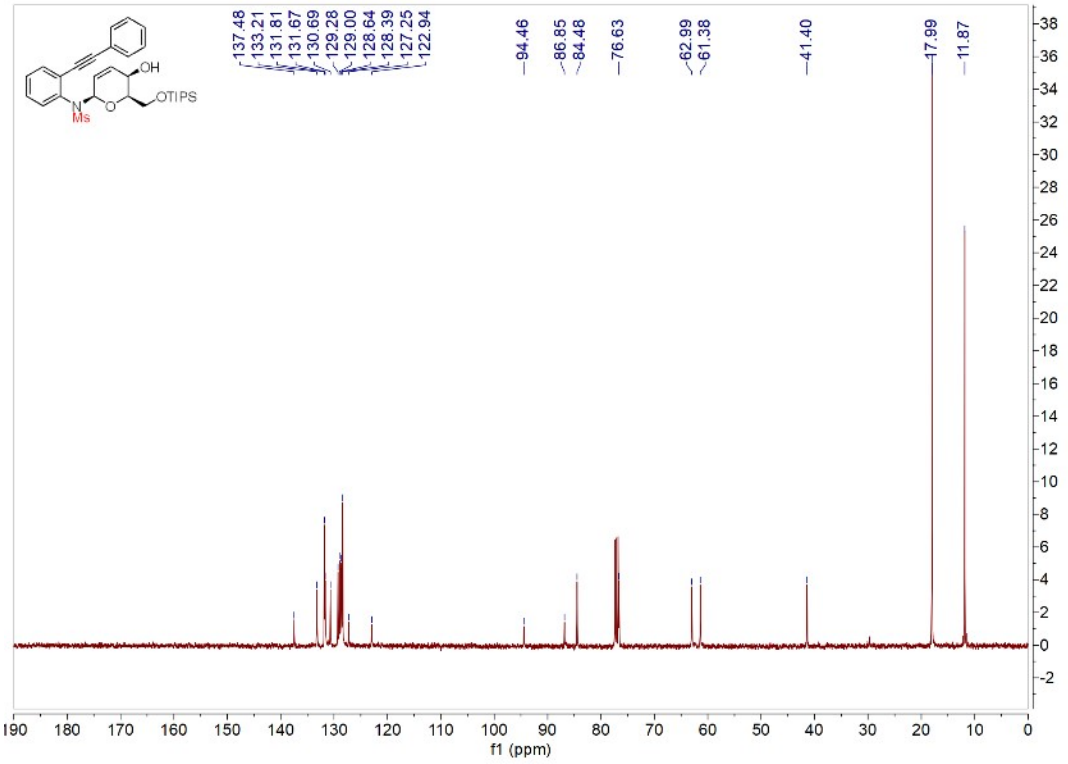


1D NOESY experiment of **1** in DMSO-d_6 (600 MHz).

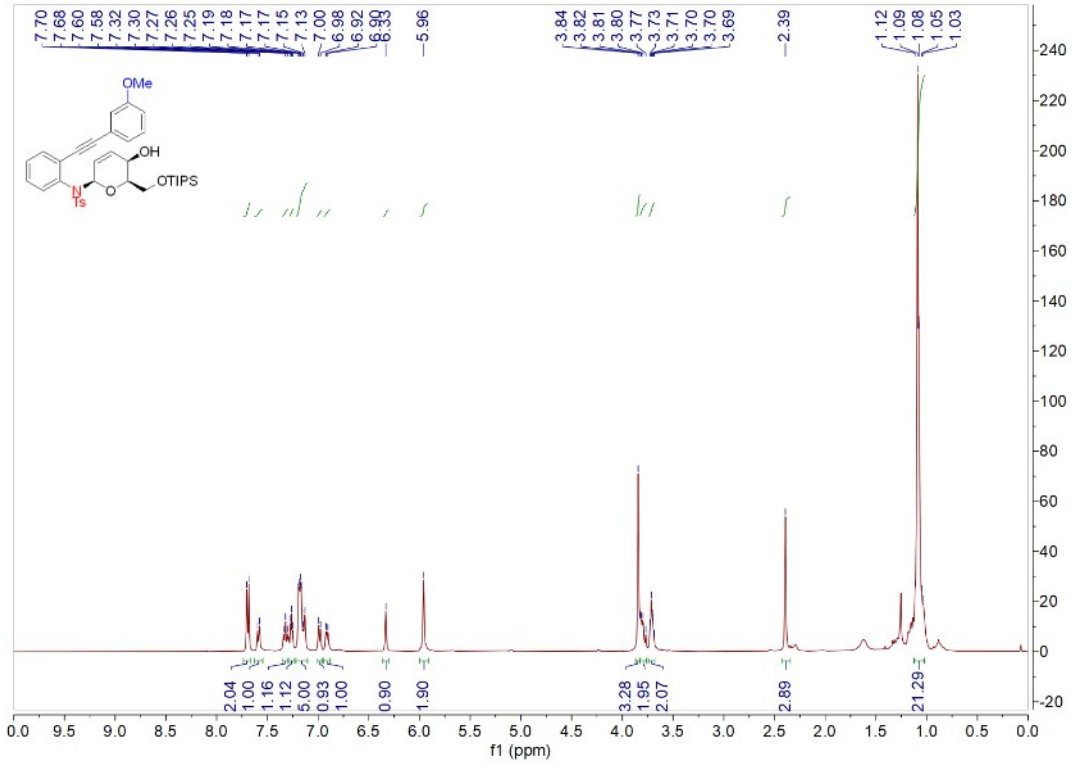
Note: The assignment of β-configuration of compound **1** comes from the observation of nuclear Overhauser effect (NOE) between H_1 and H_5. Upon irradiation of H_1 (6.14 ppm) significant enhancement of the H_5 (3.62 ppm) signal is observed.



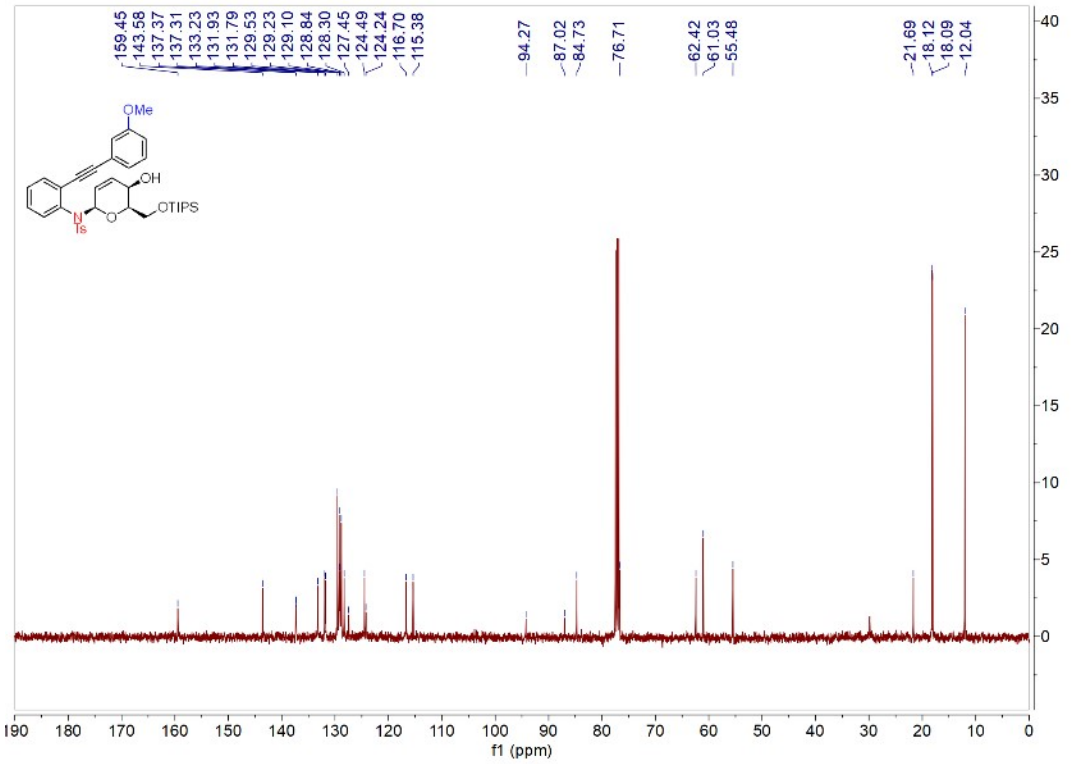
^{1}H NMR spectrum of **2** in $CDCl_3$ (400 MHz).



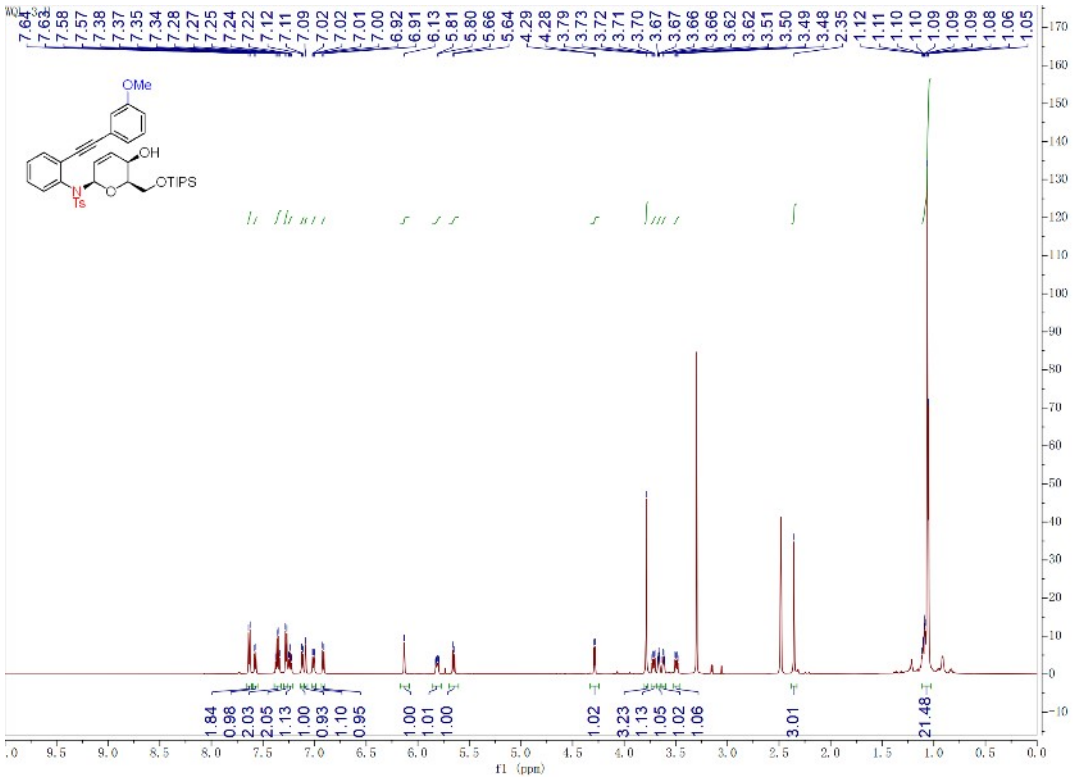
^{13}C NMR spectrum of **2** in $CDCl_3$ (100 MHz).



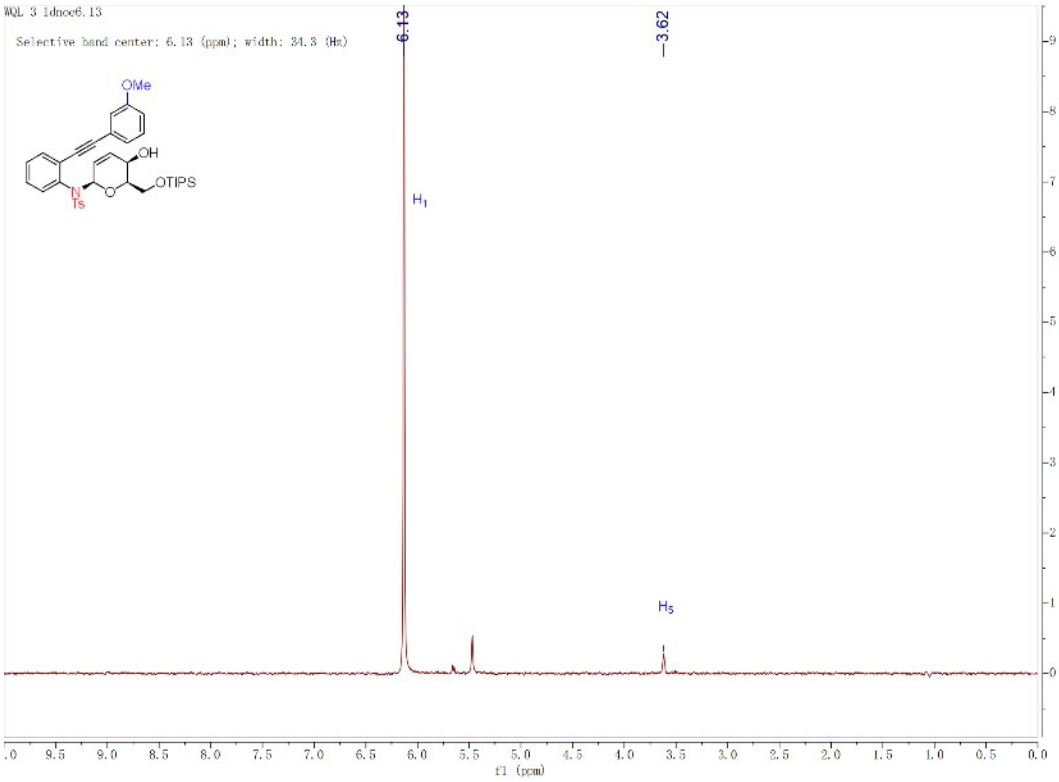
^{1}H NMR spectrum of **3** in $CDCl_3$ (100 MHz).



^{13}C NMR spectrum of **3** in $CDCl_3$ (100 MHz).

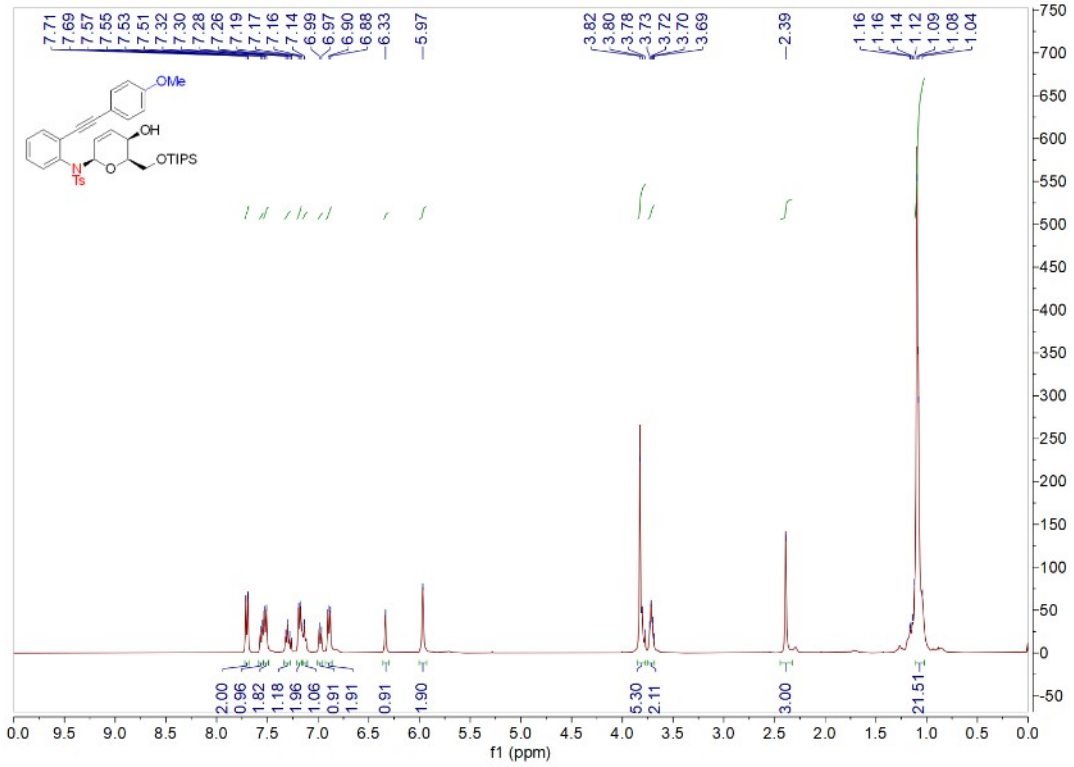


^{1}H NMR spectrum of **3** in DMSO-d_6 (600 MHz).

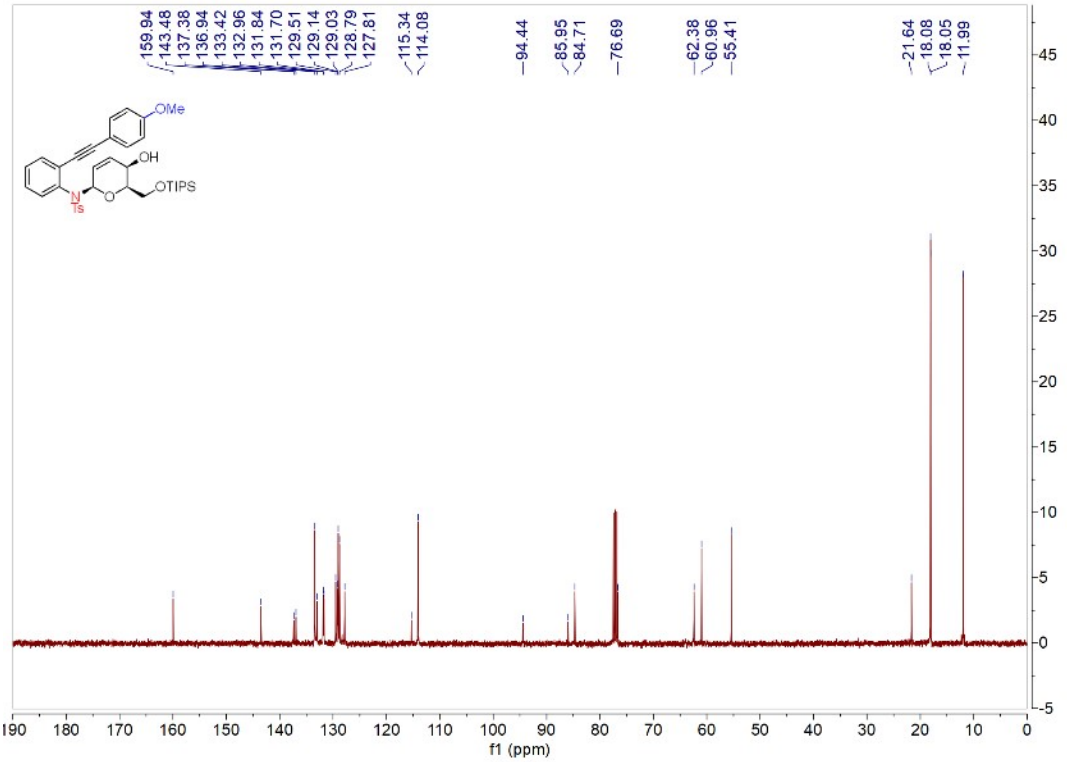


1D NOESY experiment of **3** in DMSO-d_6 (600 MHz).

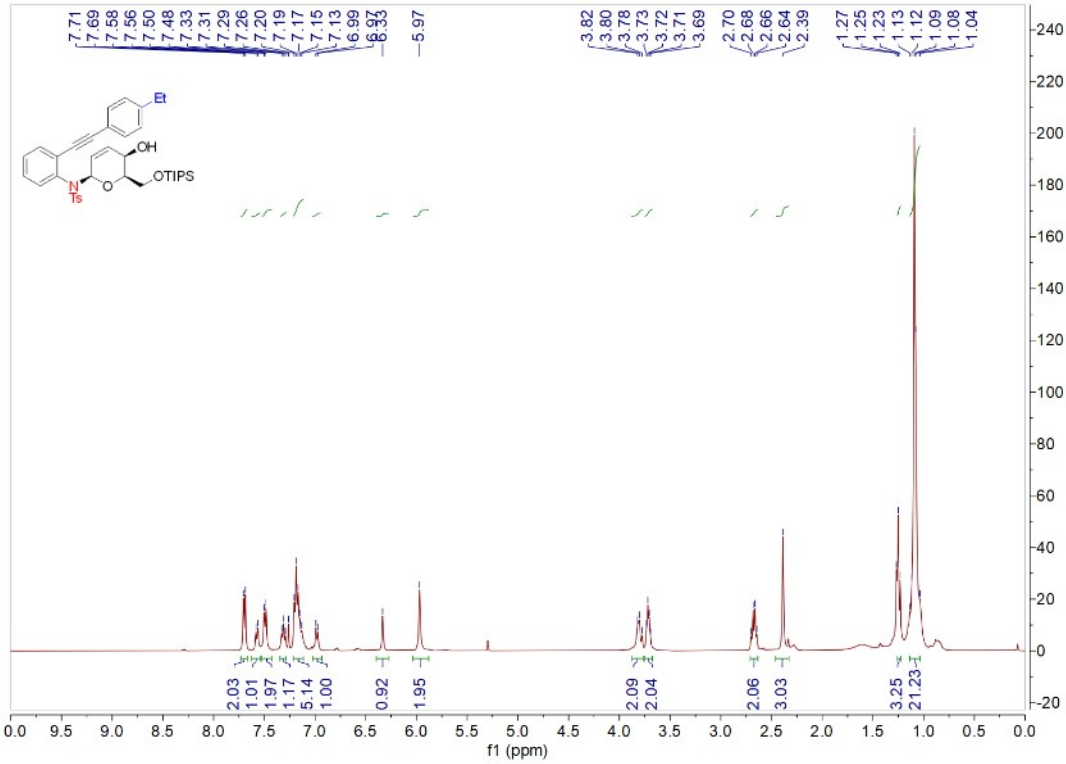
Note: The assignment of β-configuration of compound **3** comes from the observation of NOE between H_1 and H_5. Upon irradiation of H_1 (6.13 ppm) significant enhancement of the H_5 (3.62 ppm) signal is observed.



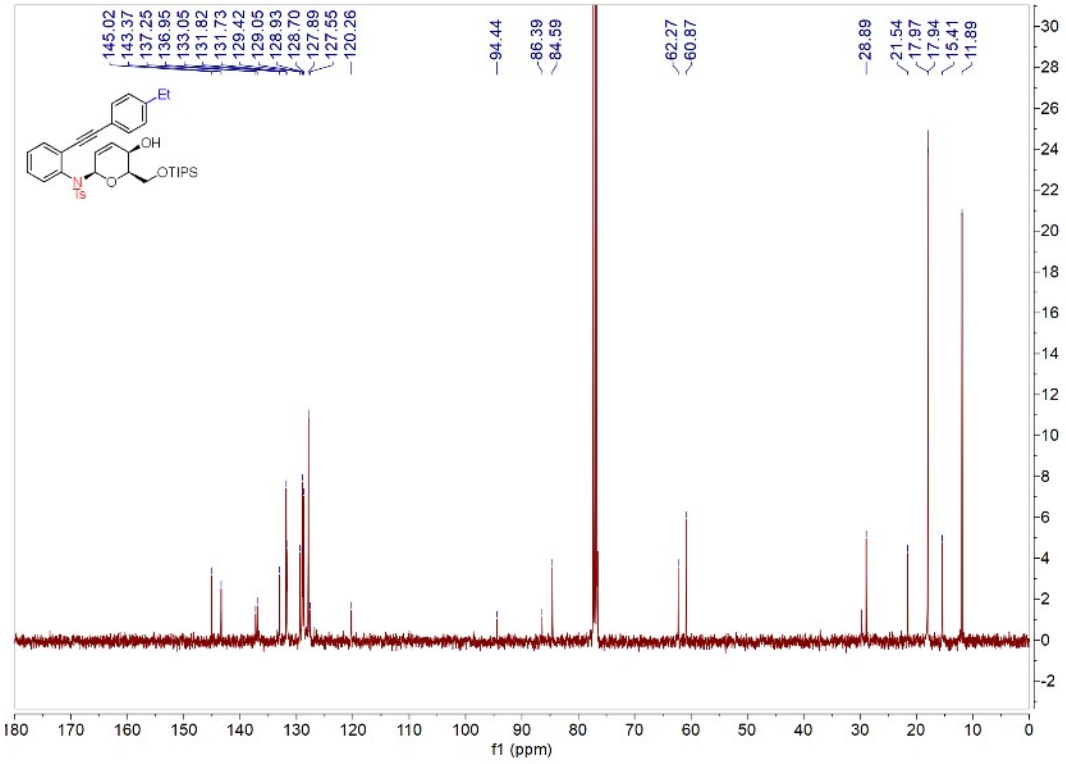
^{1}H NMR spectrum of **4** in $CDCl_3$ (400 MHz).



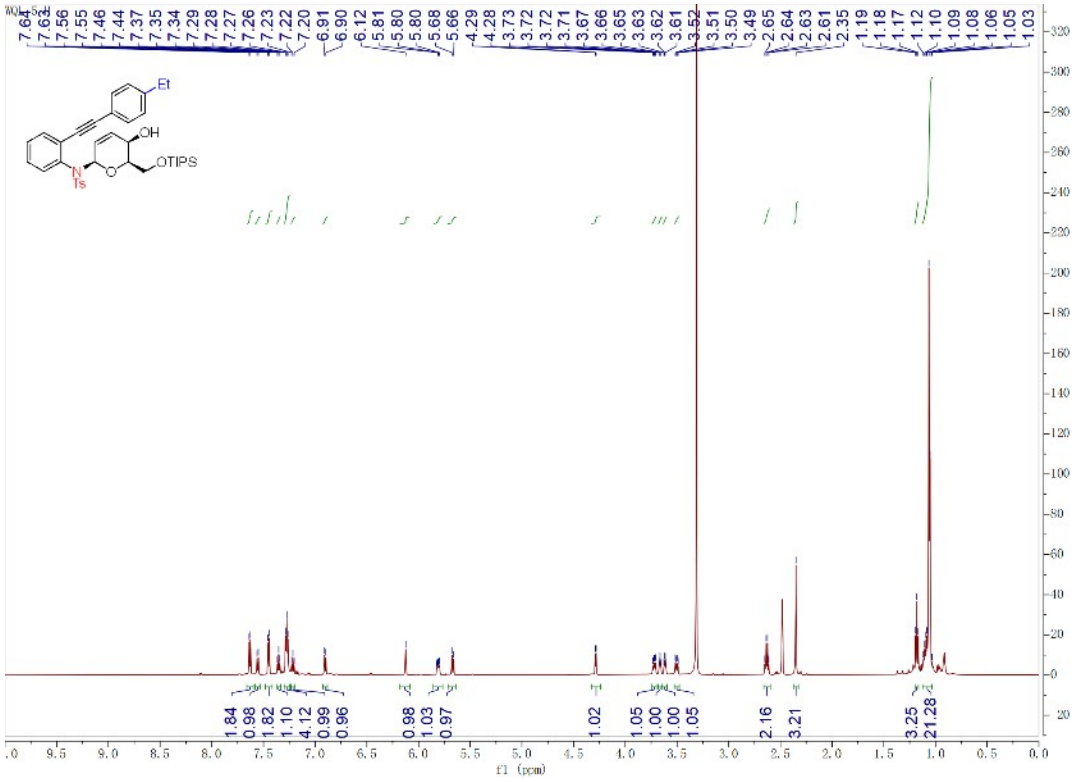
^{13}C NMR spectrum of **4** in $CDCl_3$ (100 MHz).



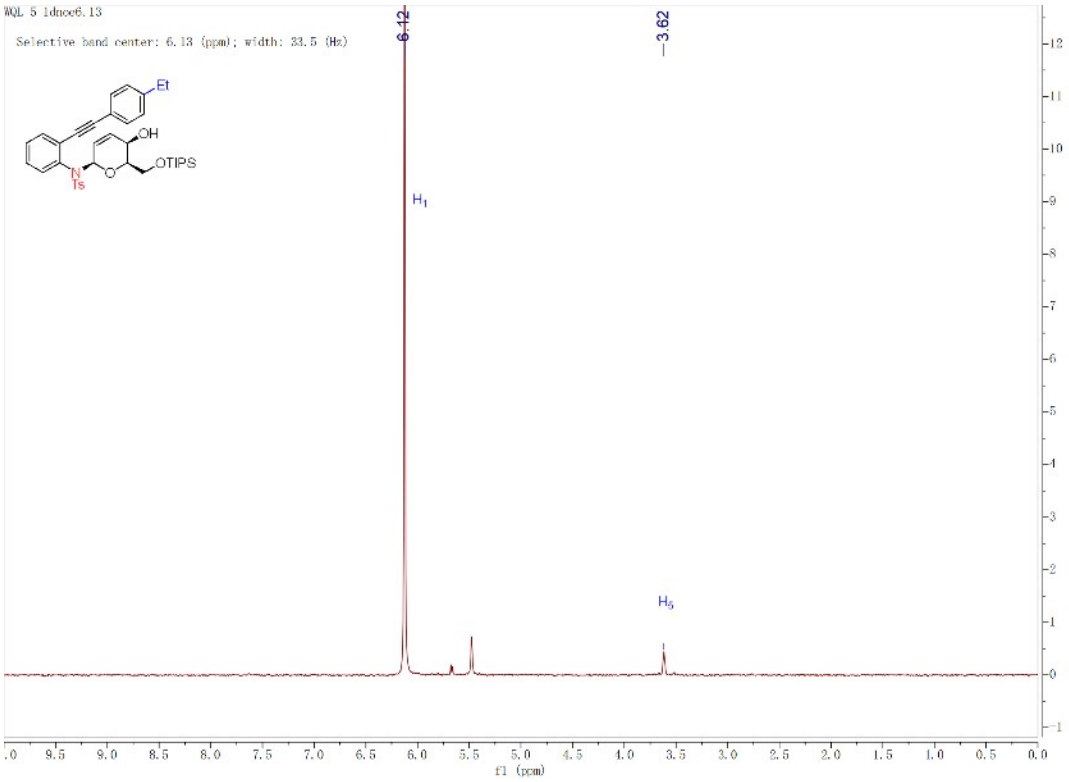
^{1}H NMR spectrum of **5** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **5** in $CDCl_3$ (100 MHz).

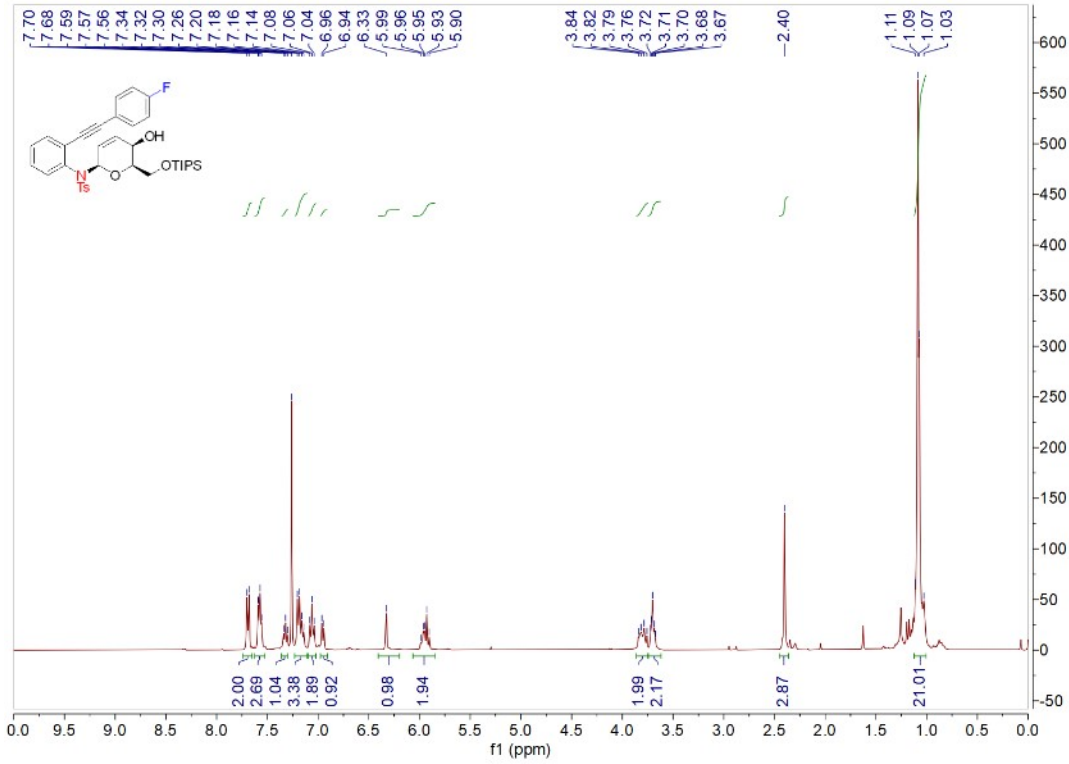


^{1}H NMR spectrum of **5** in DMSO-d_6 (600 MHz).

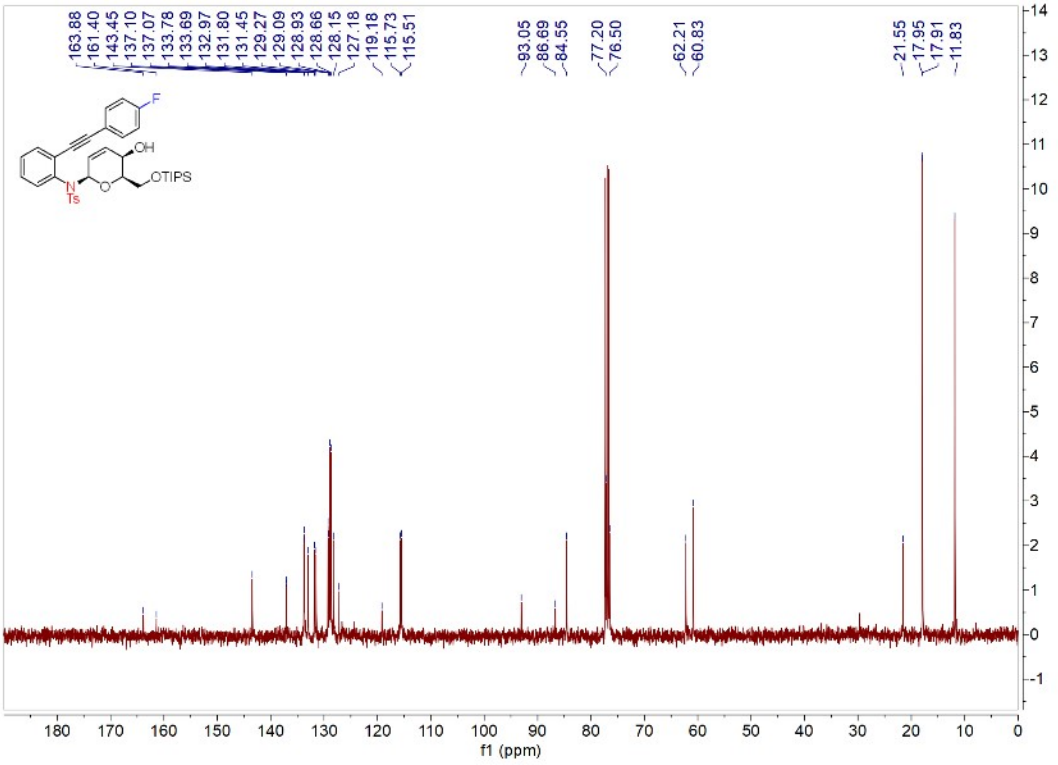


1D NOESY experiment of **5** in DMSO-d_6 (600 MHz).

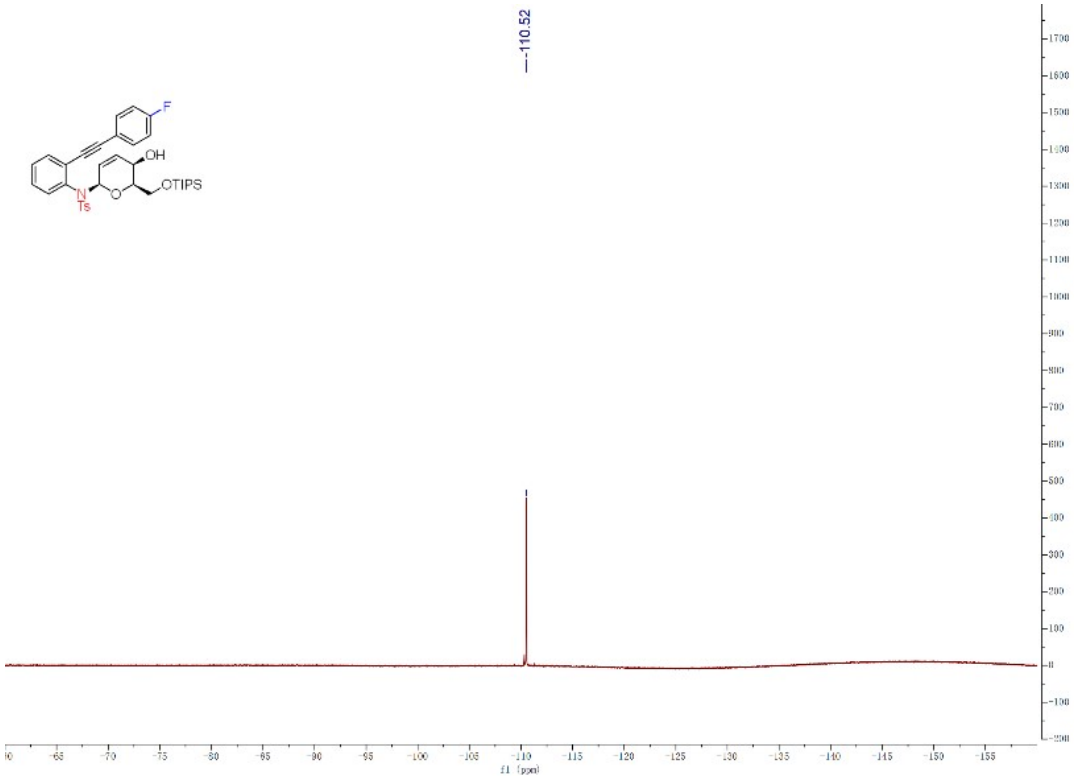
Note: The assignment of β-configuration of compound **5** comes from the observation of NOE between H_1 and H_5. Upon irradiation of H_1 (6.12 ppm) significant enhancement of the H_5 (3.62 ppm) signal is observed.



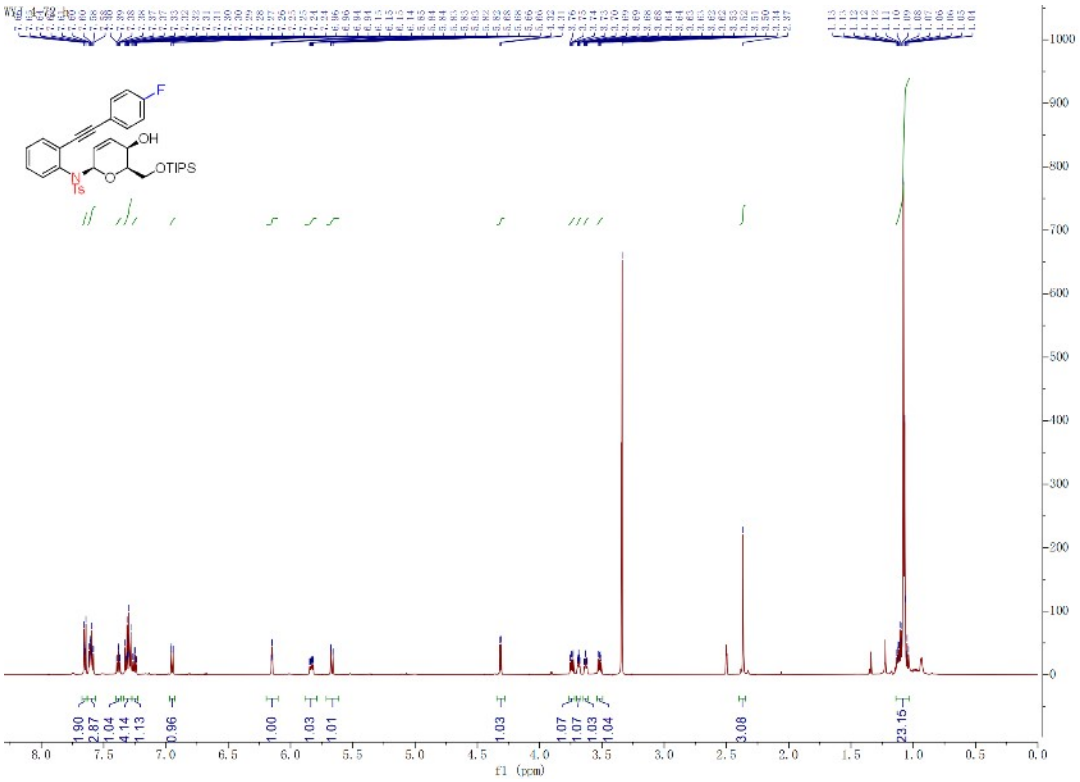
^{1}H NMR spectrum of **6** in $CDCl_3$ (400 MHz).



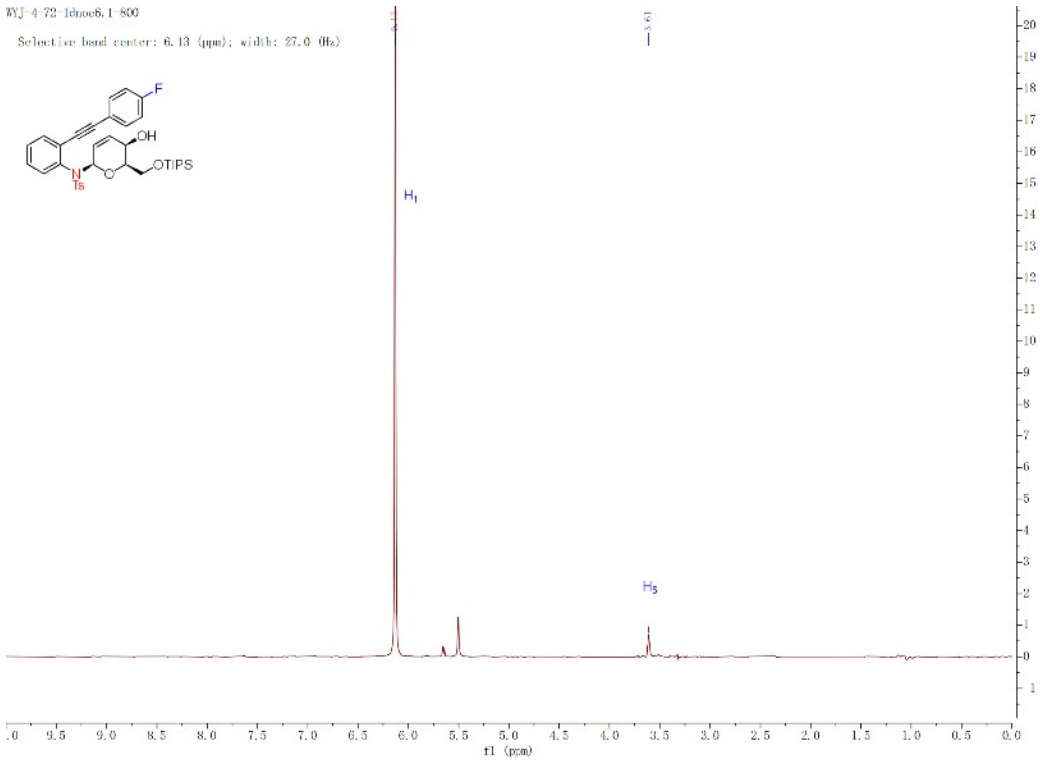
^{13}C NMR spectrum of **6** in $CDCl_3$ (100 MHz).



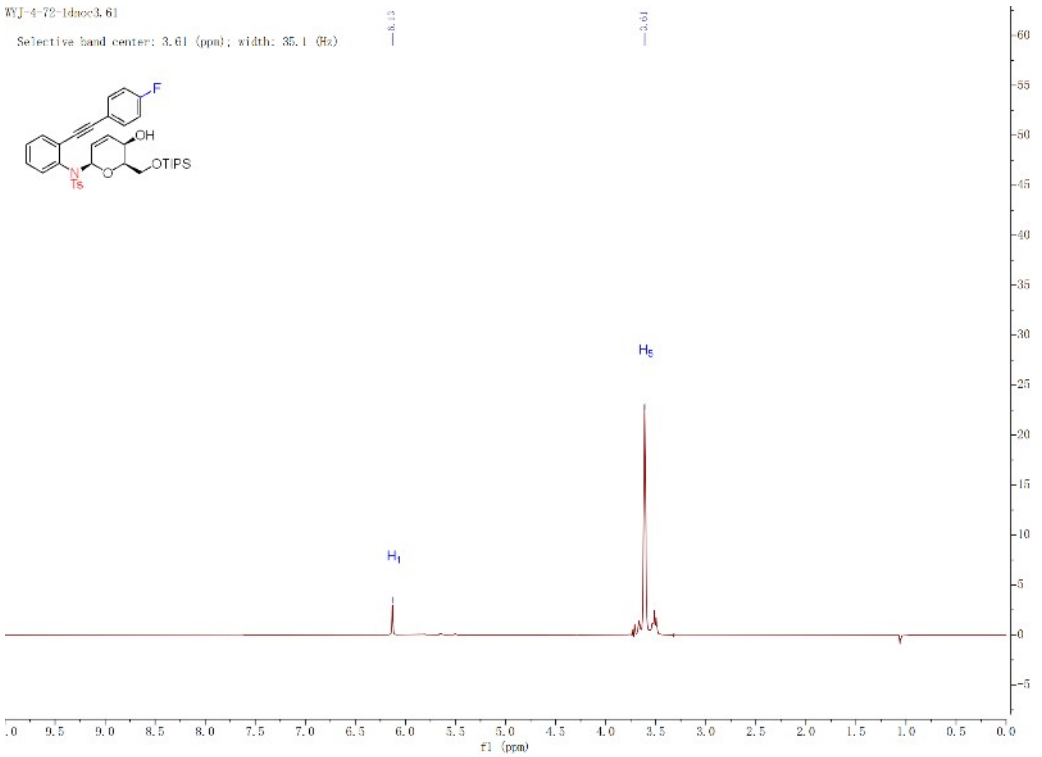
^{19}F NMR spectrum of **6** in $CDCl_3$ (564 MHz).



^{1}H NMR spectrum of **6** in DMSO-d_6 (600 MHz).

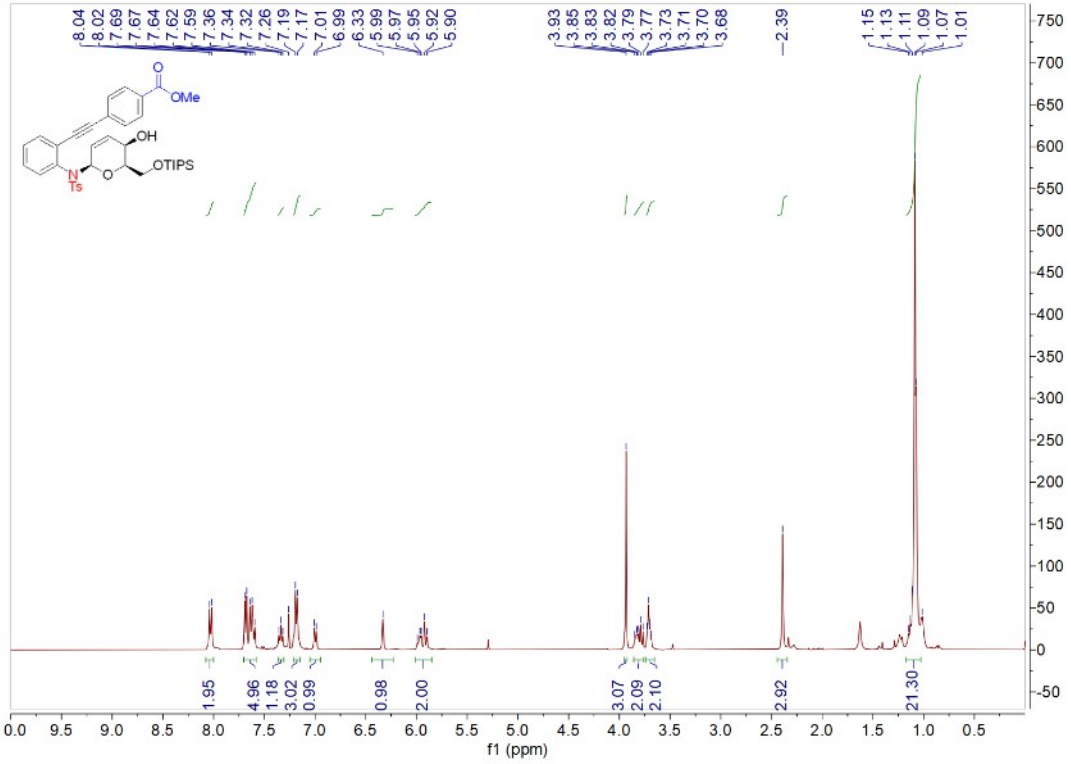


1D NOESY experiment of **6** in DMSO-d_6 (600 MHz).

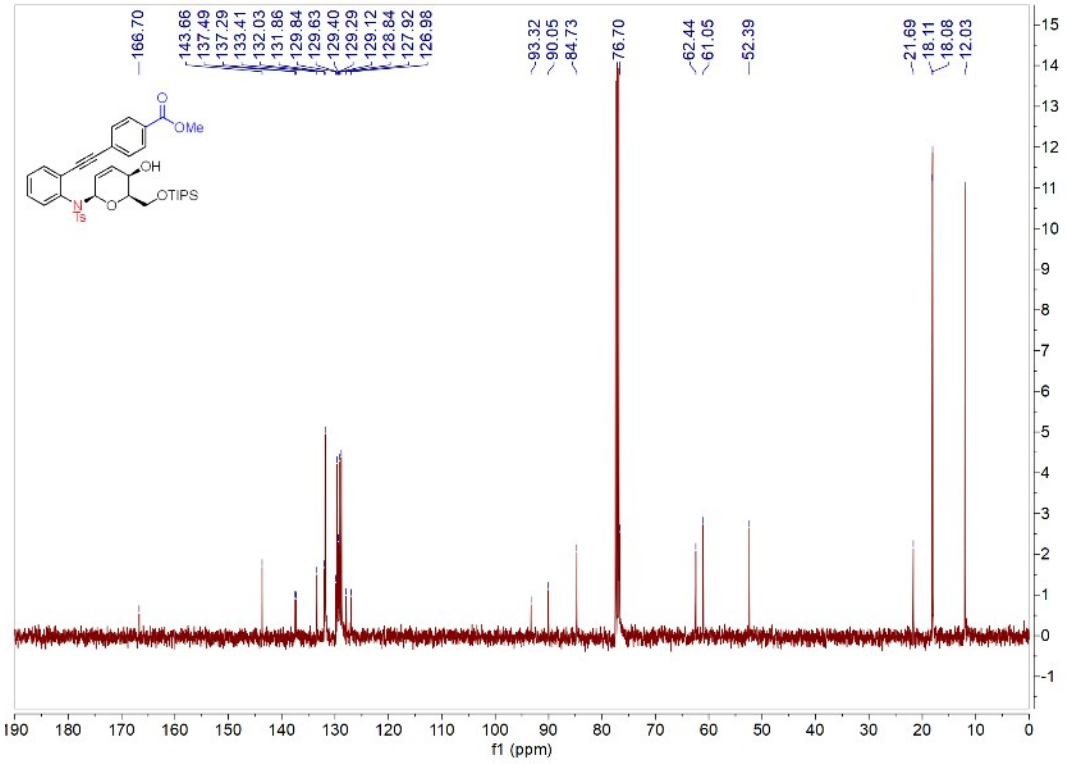


1D NOESY experiment of **6** in DMSO-d_6 (600 MHz).

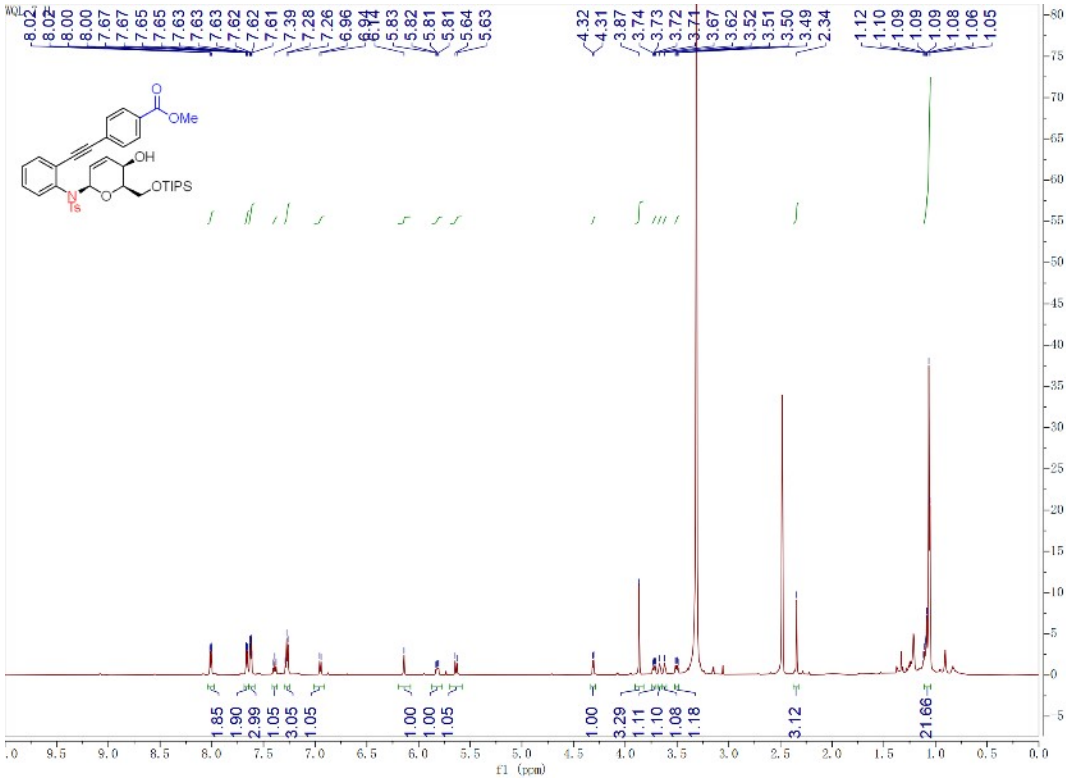
Note: The assignment of β-configuration of compound **6** comes from the observation of NOE between H_1 and H_5. Upon irradiation of H_1 (6.13 ppm) significant enhancement of the H_5 (3.61 ppm) signal is observed in **6**. An amplitude enhancement of similar magnitude is observed for the H_1 signal upon irradiation of H_5.



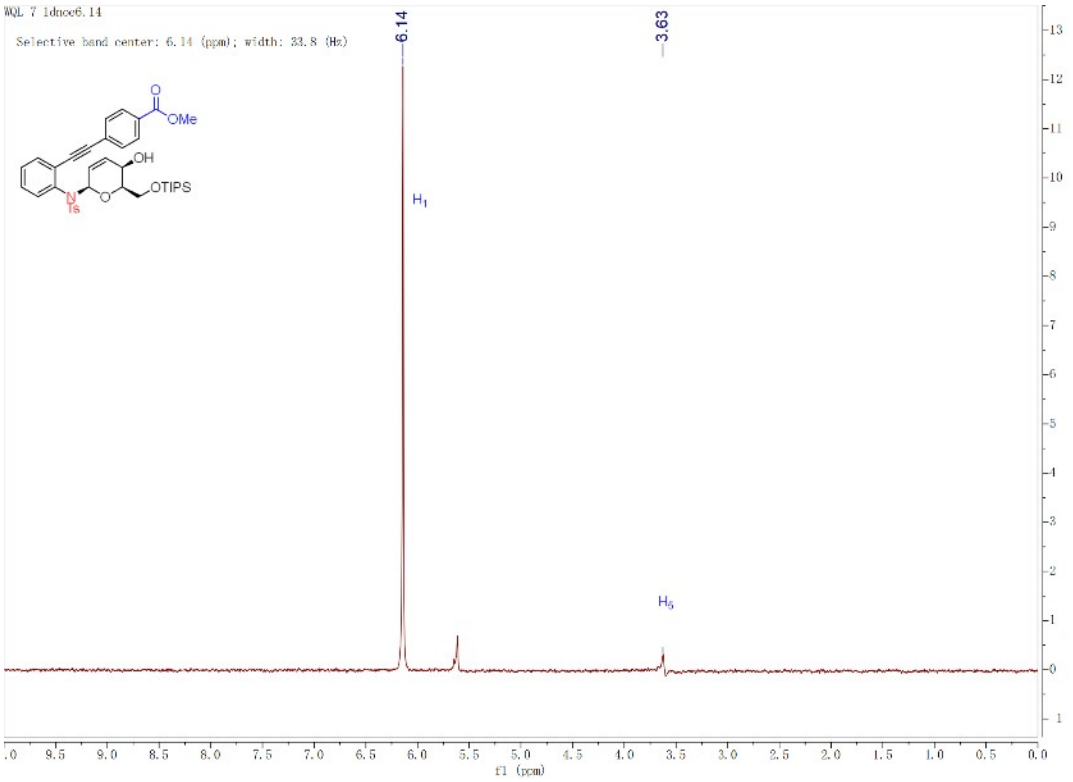
^{1}H NMR spectrum of **7** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **7** in $CDCl_3$ (100 MHz).

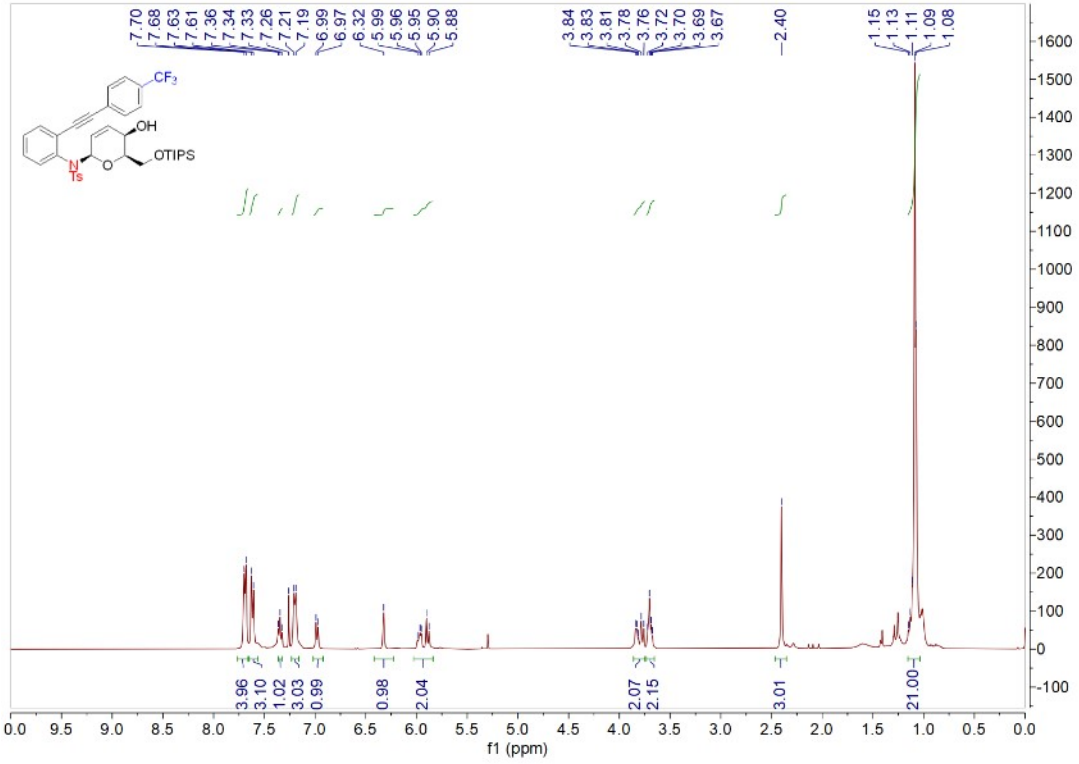


^{1}H NMR spectrum of **7** in DMSO-d_6 (600 MHz).

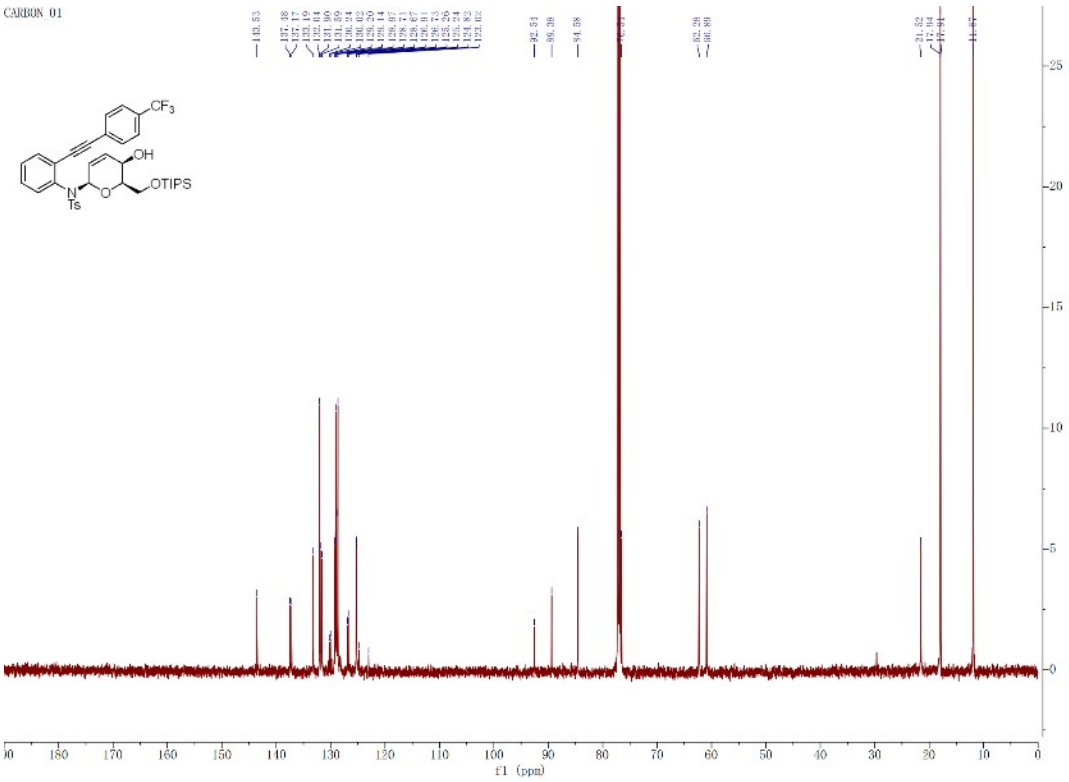


1D NOESY experiment of **7** in DMSO-d_6 (600 MHz).

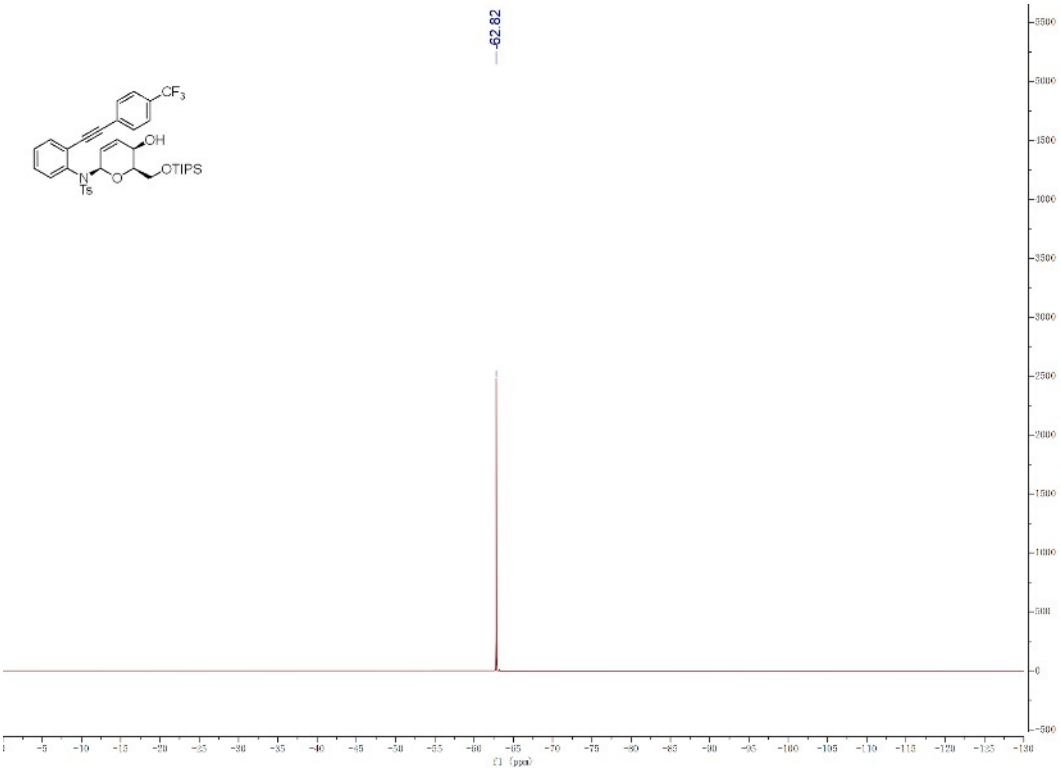
Note: The assignment of β-configuration of compound **7** comes from the observation of NOE between H_1 and H_5. Upon irradiation of H_1 (6.14 ppm) significant enhancement of the H_5 (3.63 ppm) signal is observed.



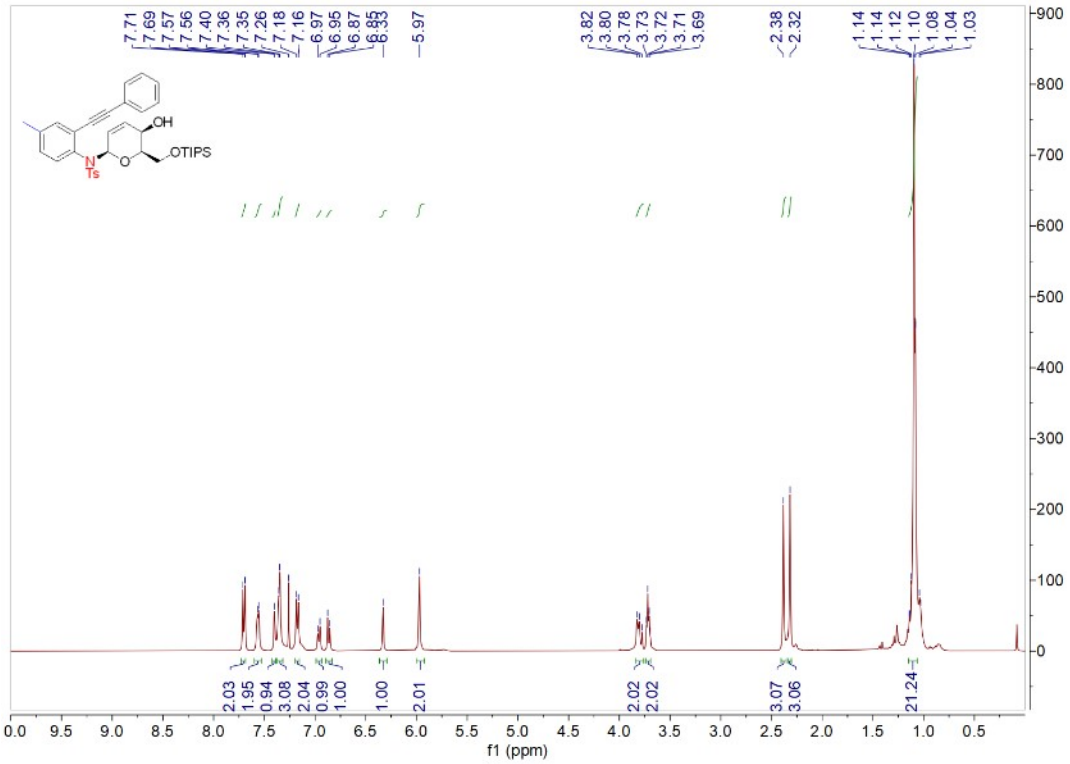
^{1}H NMR spectrum of **8** in $CDCl_3$ (600 MHz).



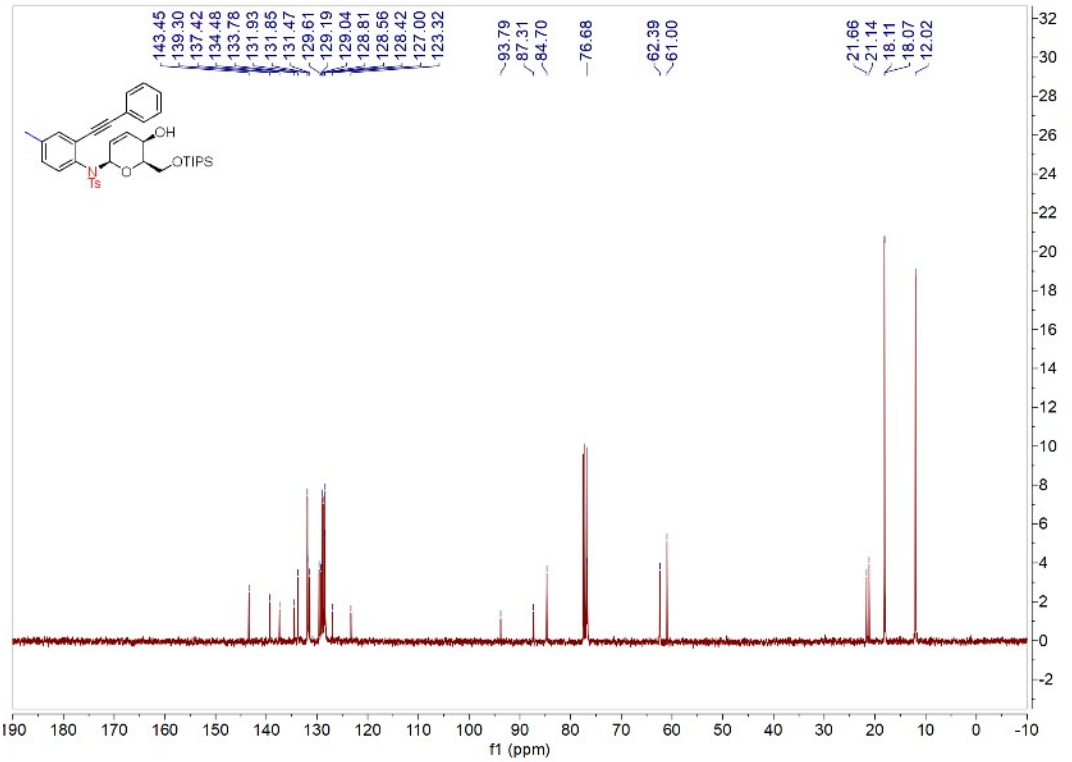
^{13}C NMR spectrum of **8** in $CDCl_3$ (150 MHz).



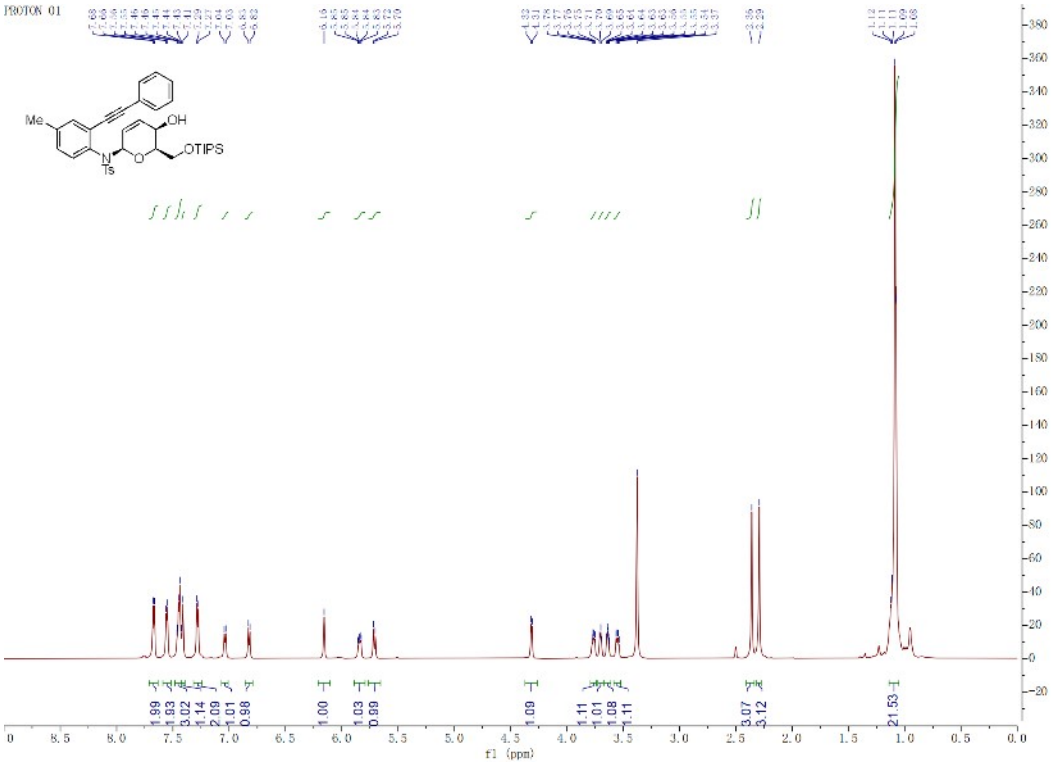
^{19}F NMR spectrum of **8** in $CDCl_3$ (564 MHz).



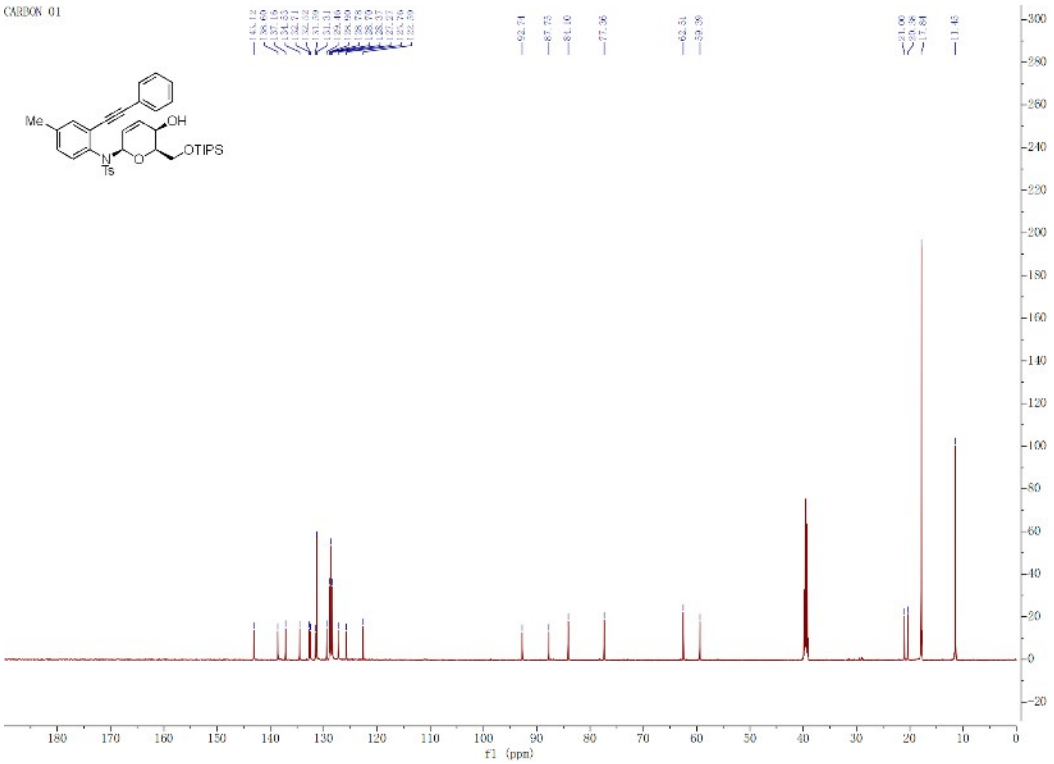
^{1}H NMR spectrum of **9** in $CDCl_3$ (400 MHz).



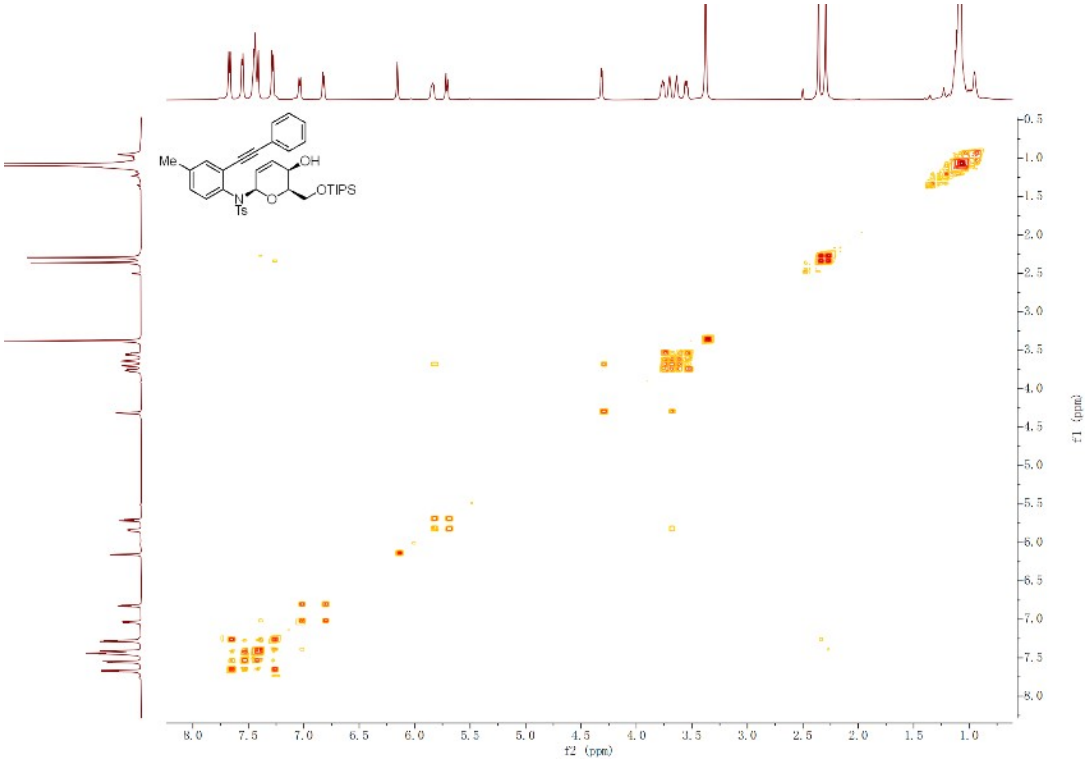
^{13}C NMR spectrum of **9** in $CDCl_3$ (100 MHz).



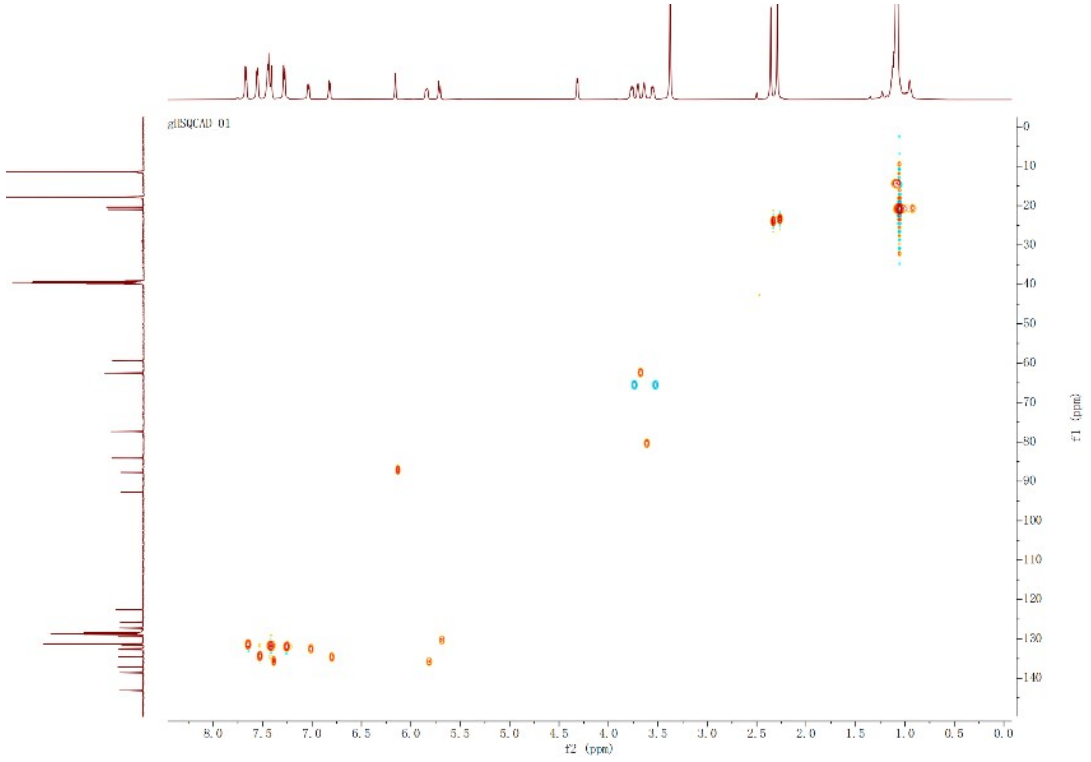
^{1}H NMR spectrum of **9** in DMSO-d_6 (600 MHz).



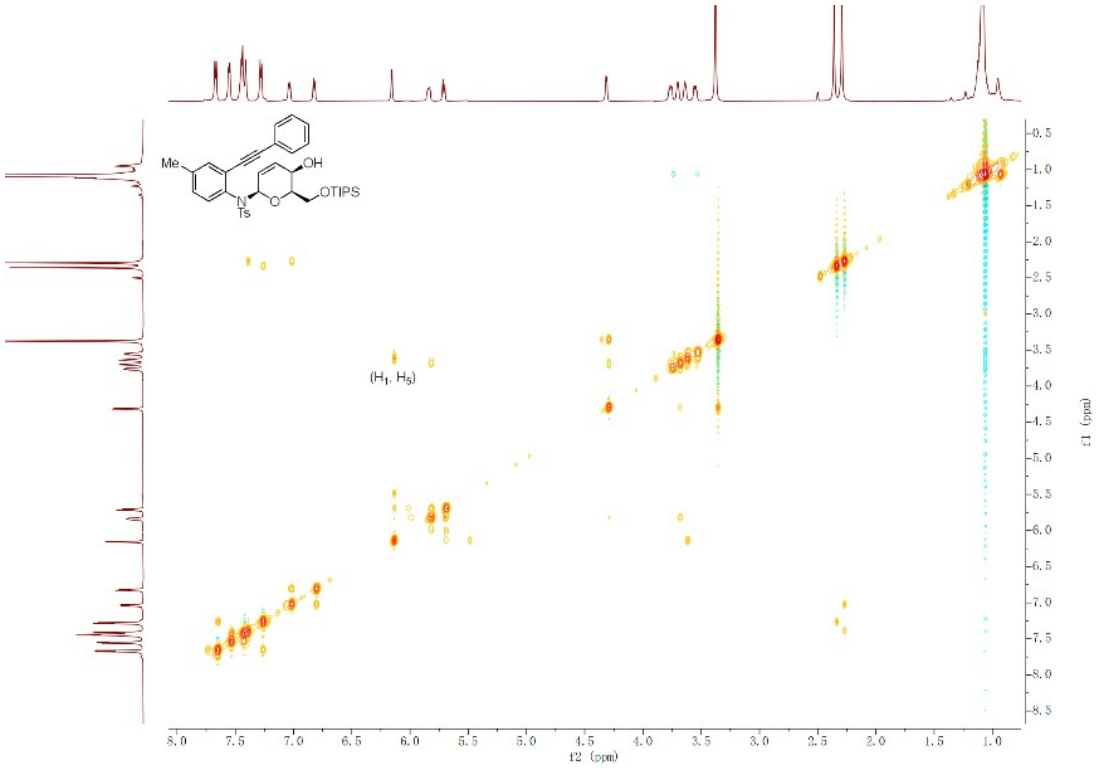
^{13}C NMR spectrum of **9** in DMSO-d_6 (150 MHz).



COSY of **9** in DMSO-d_6 (600 MHz).

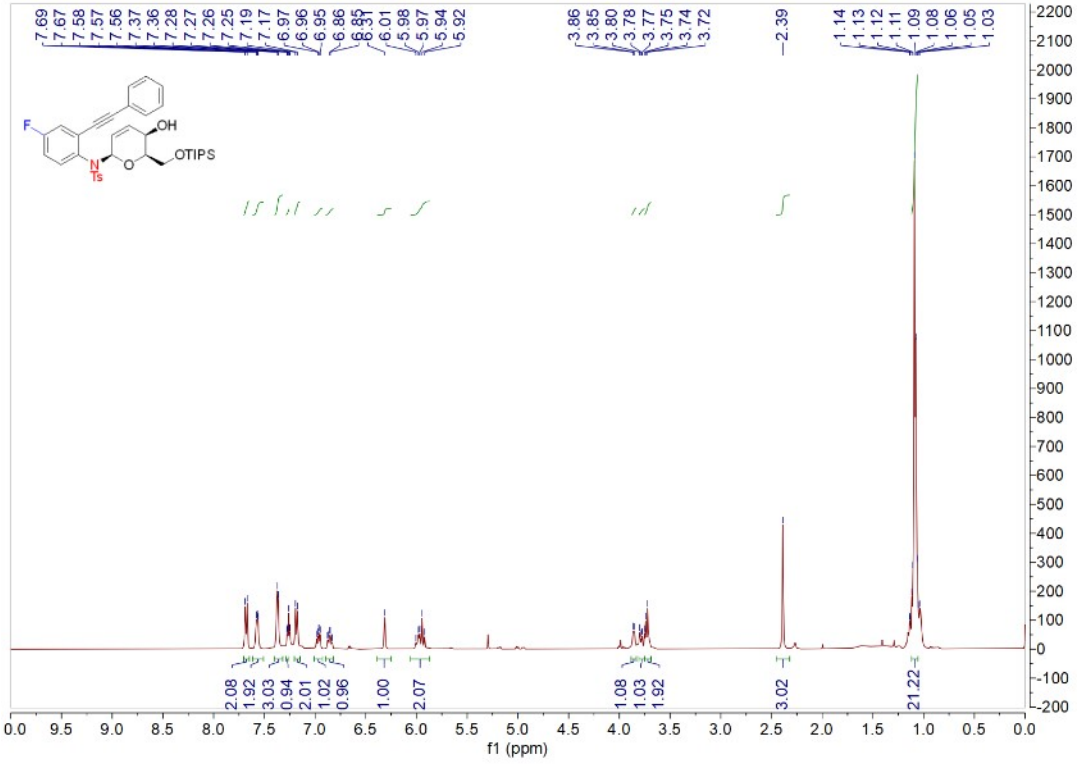


HSQC of **9** in DMSO-d_6 (600 MHz).

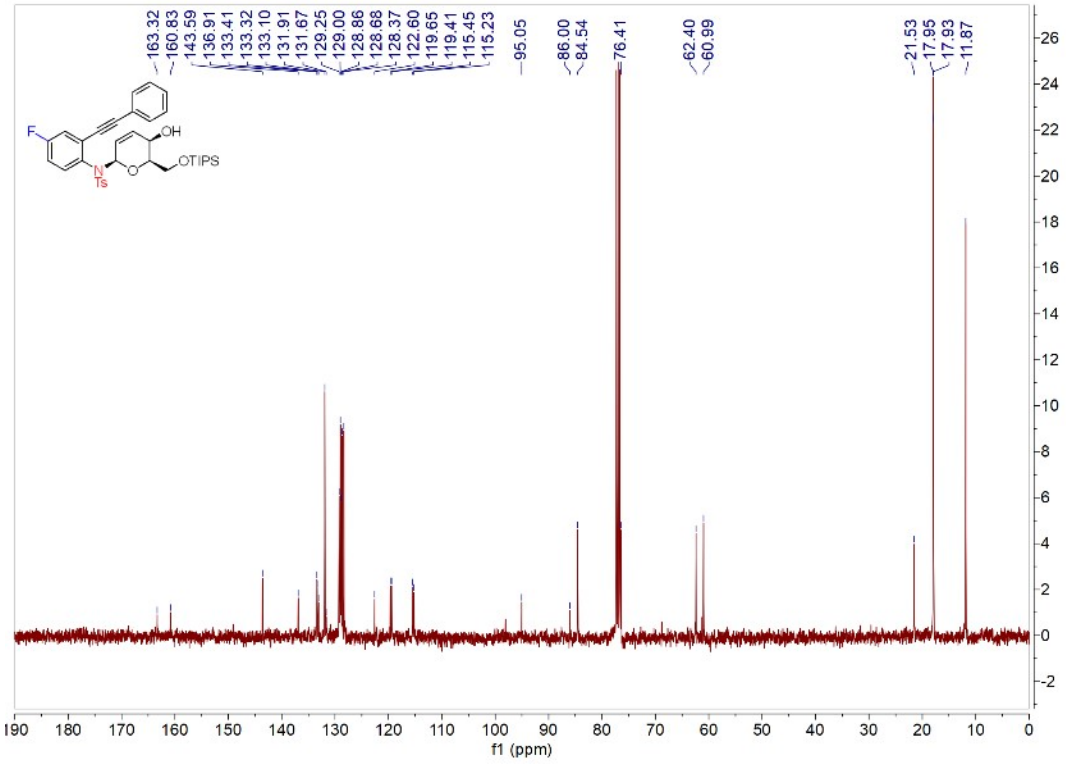


NOESY of **9** in DMSO-d_6 (600 MHz).

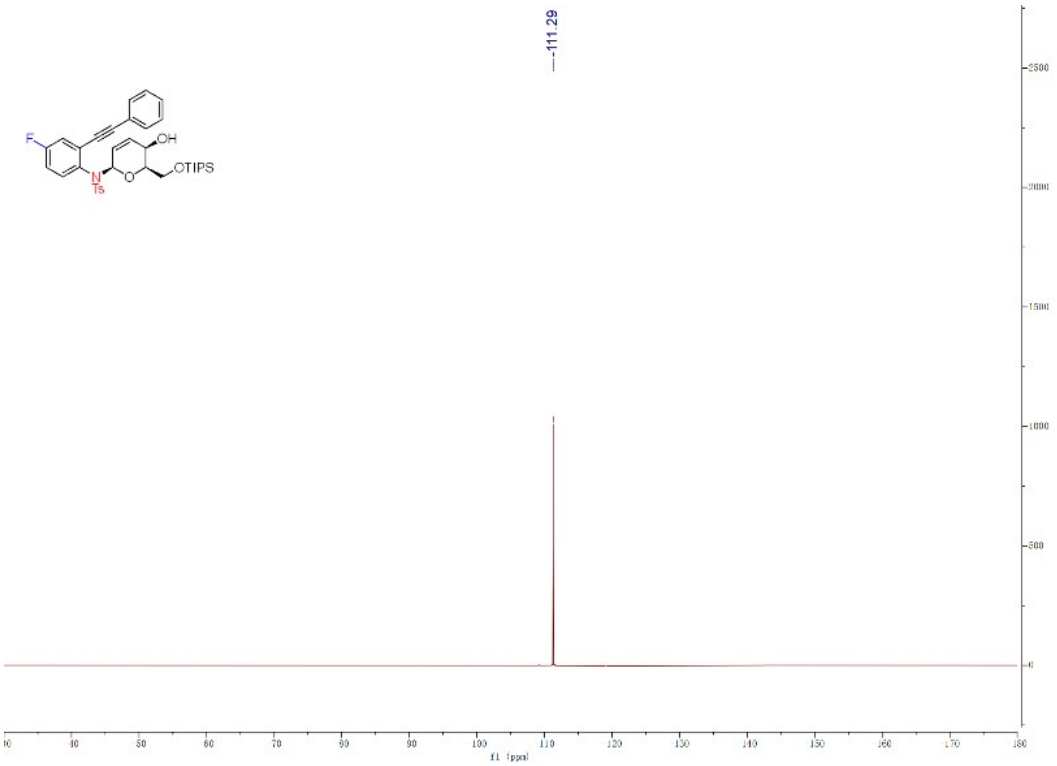
Note: As the proton peaks of the sugar ring overlapped in $CDCl_3$, deuterium DMSO gave a much better separation of these peaks. Therefore, 2D NMR experiments were conducted in DMSO-d_6. A strong correlation peak of H_1 (6.16 ppm) and H_5 (3.64 ppm) is observed in NOESY spectrum, confirming the β-glycosidic linkage of compound **9**.



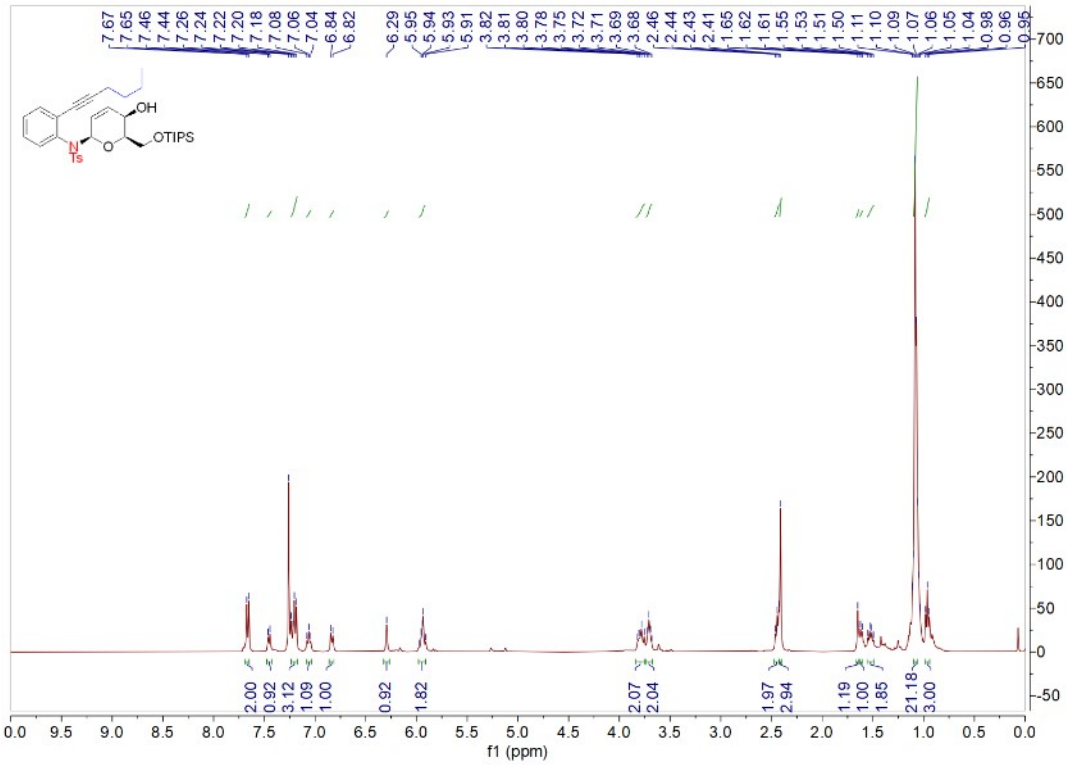
^{1}H NMR spectrum of **10** in $CDCl_3$ (400 MHz).



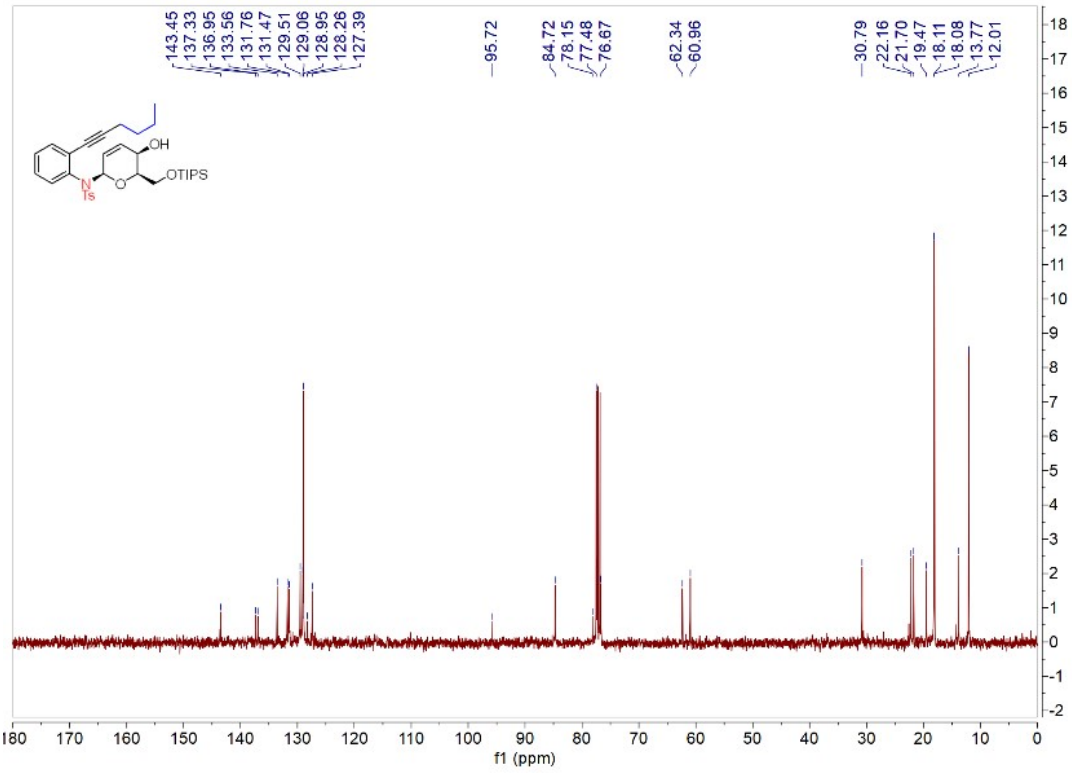
^{13}C NMR spectrum of **10** in $CDCl_3$ (100 MHz).



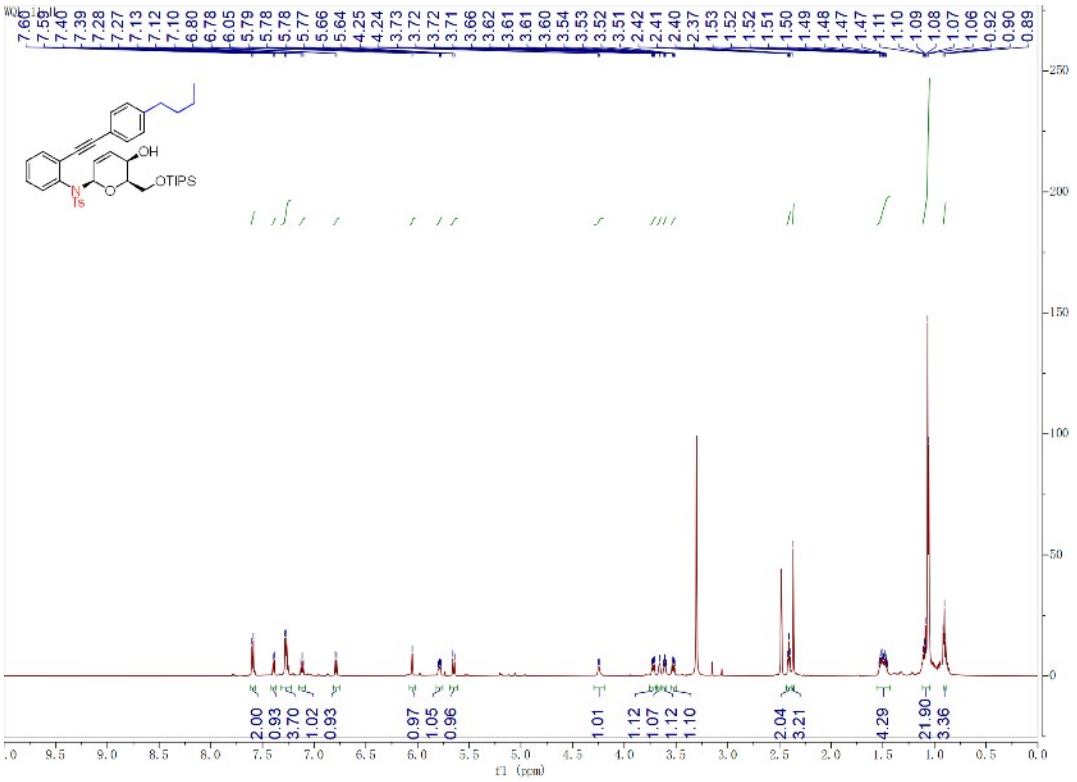
^{19}F NMR spectrum of **10** in $CDCl_3$ (564 MHz).



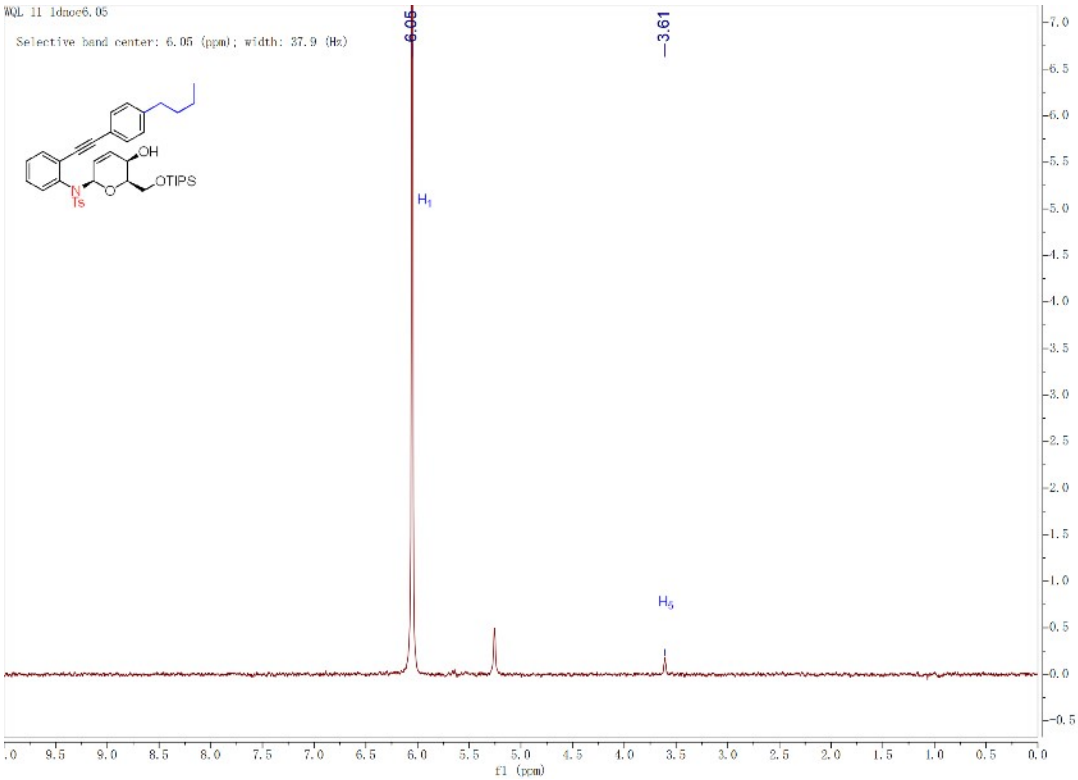
^{1}H NMR spectrum of **11** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **11** in $CDCl_3$ (100 MHz).

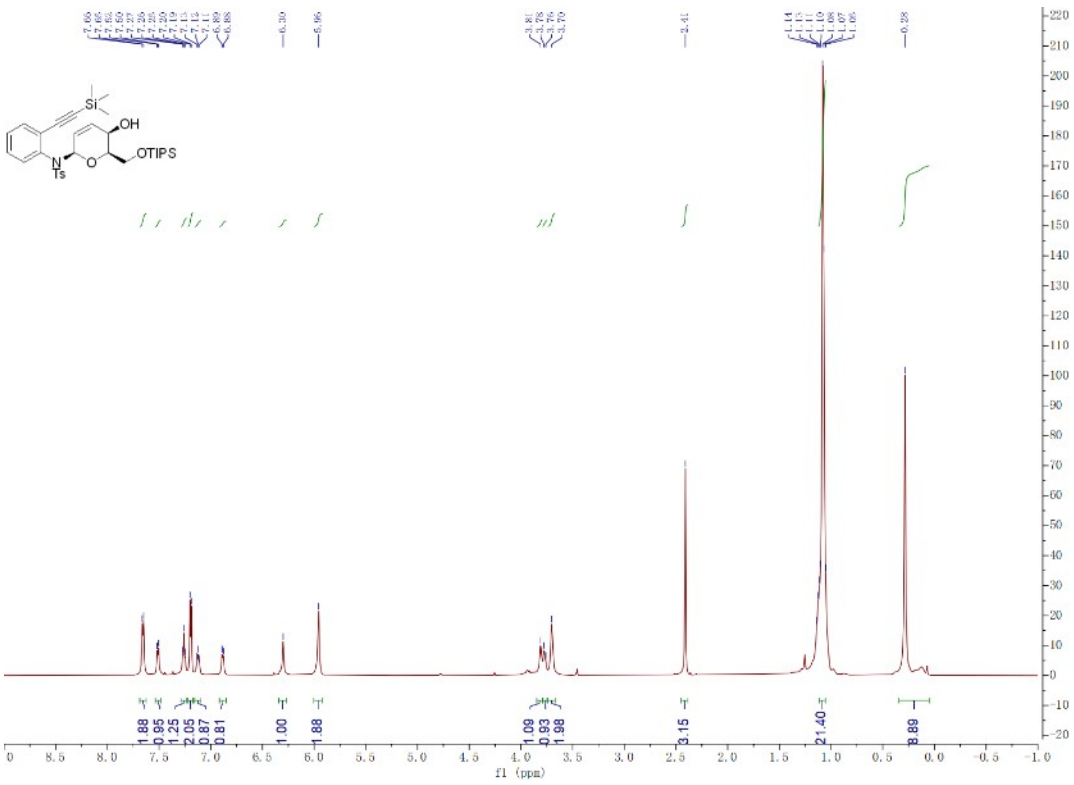


^{1}H NMR spectrum of **11** in DMSO-d_6 (600 MHz).

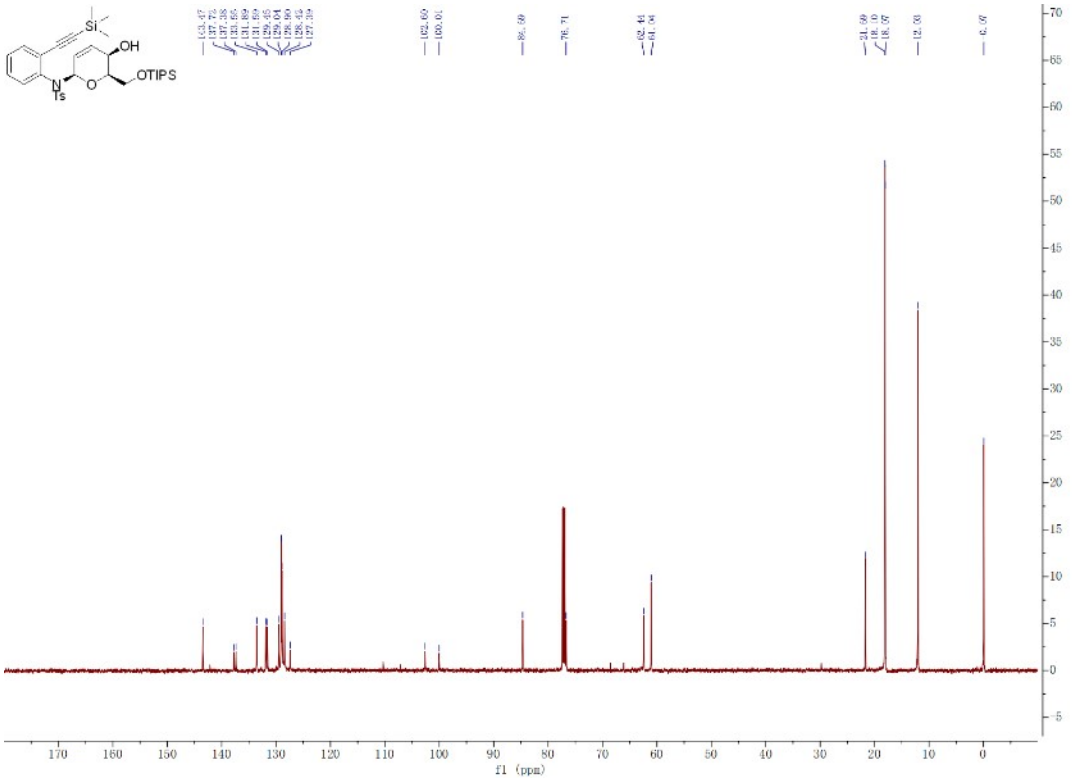


1D NOESY experiment of **11** in DMSO-d_6 (600 MHz).

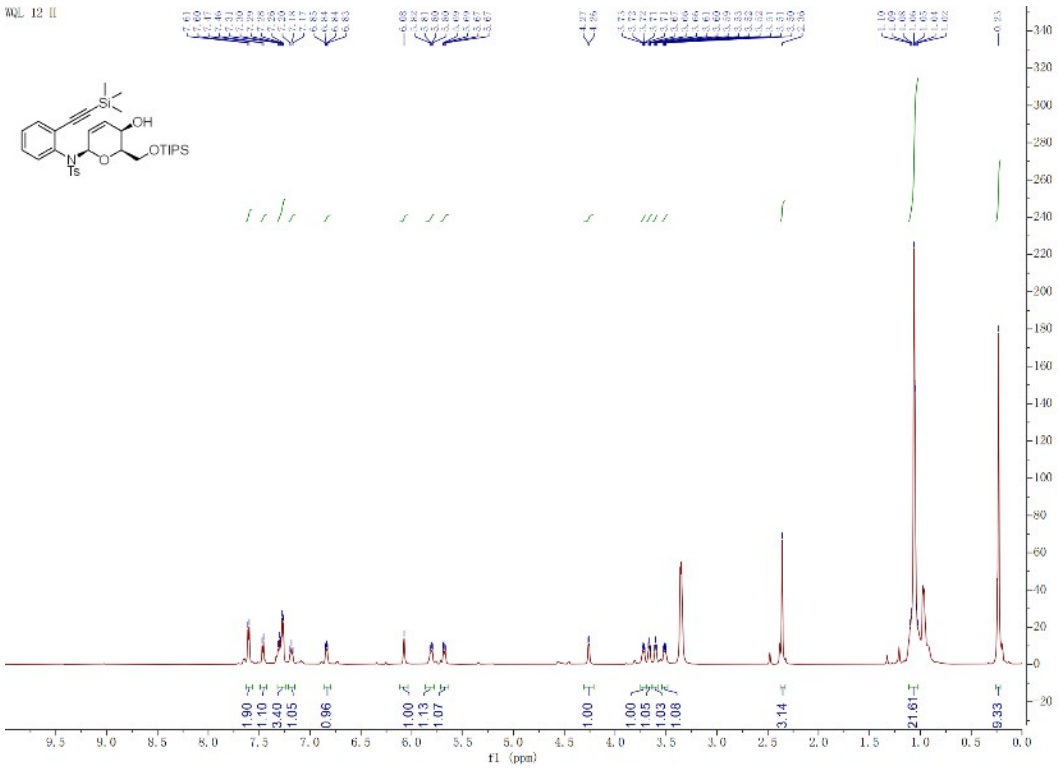
Note: The assignment of β-configuration of compound **11** comes from the observation of nuclear Overhauser effect between H_1 and H_5. Upon irradiation of H_1 (6.05 ppm) significant enhancement of the H_5 (3.61 ppm) signal is observed.



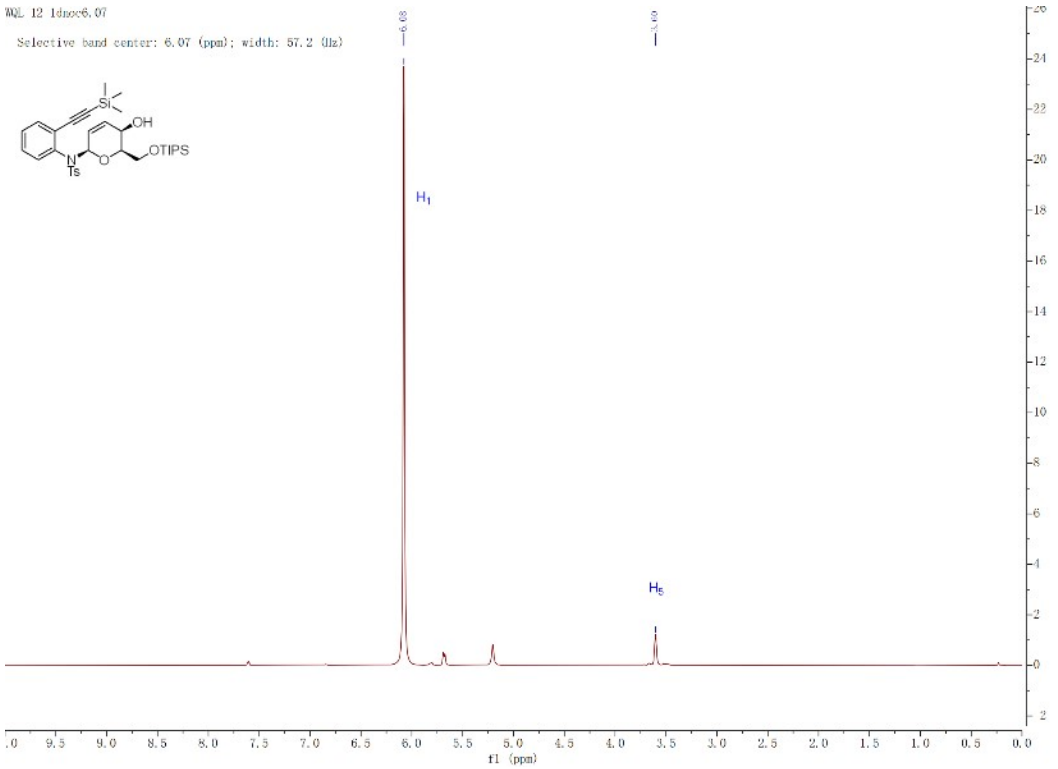
^{1}H NMR spectrum of **12** in $CDCl_3$ (600 MHz).



^{13}C NMR spectrum of **12** in $CDCl_3$ (150 MHz).



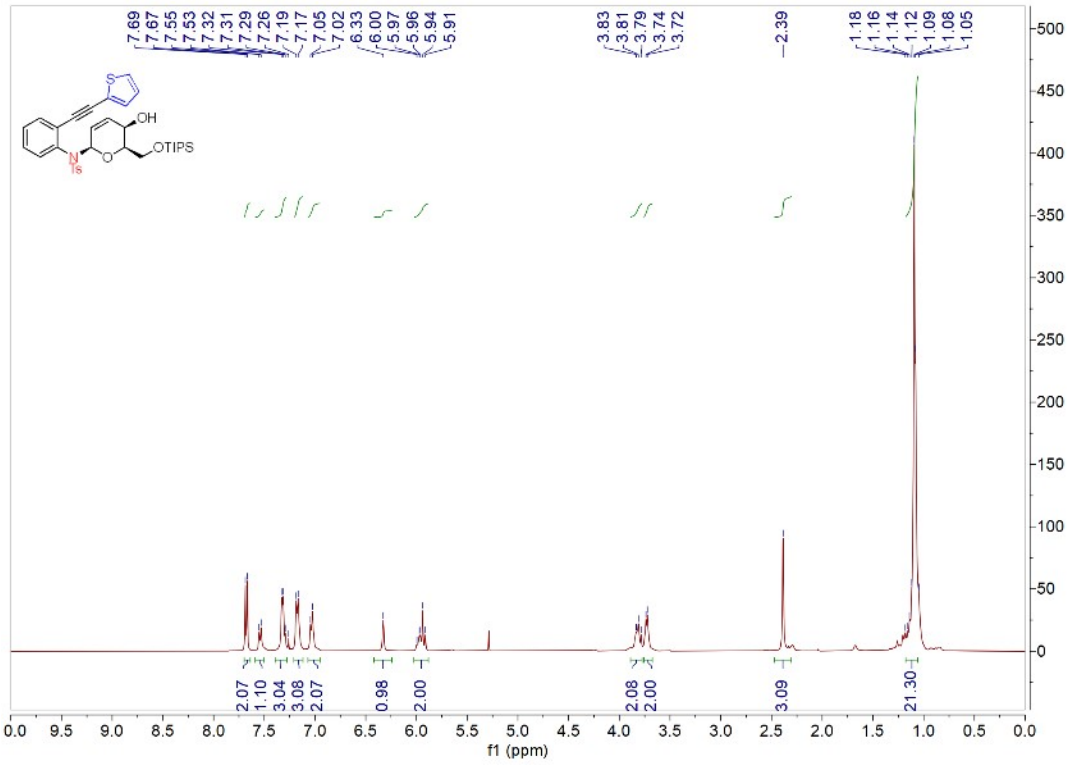
^{1}H NMR spectrum of **12** in DMSO-d_6 (600 MHz).



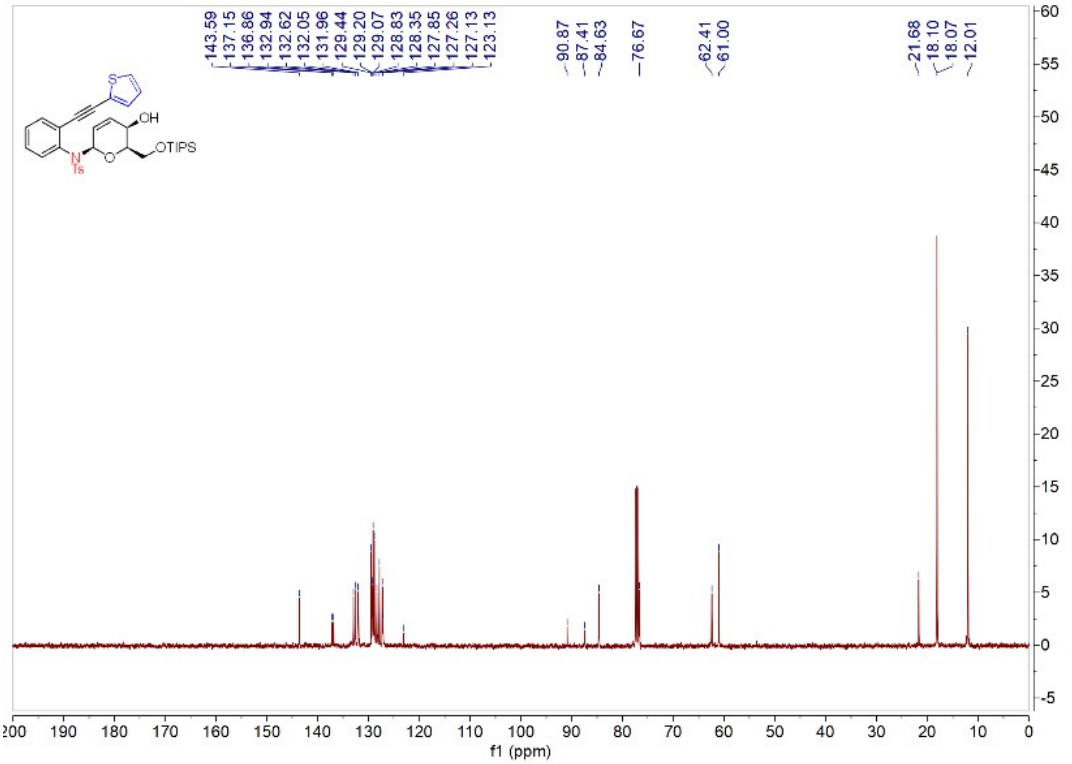
1D NOESY experiment of **12** in DMSO-d_6 (600 MHz).

Note: The assignment of β-configuration of compound **12** comes from the observation

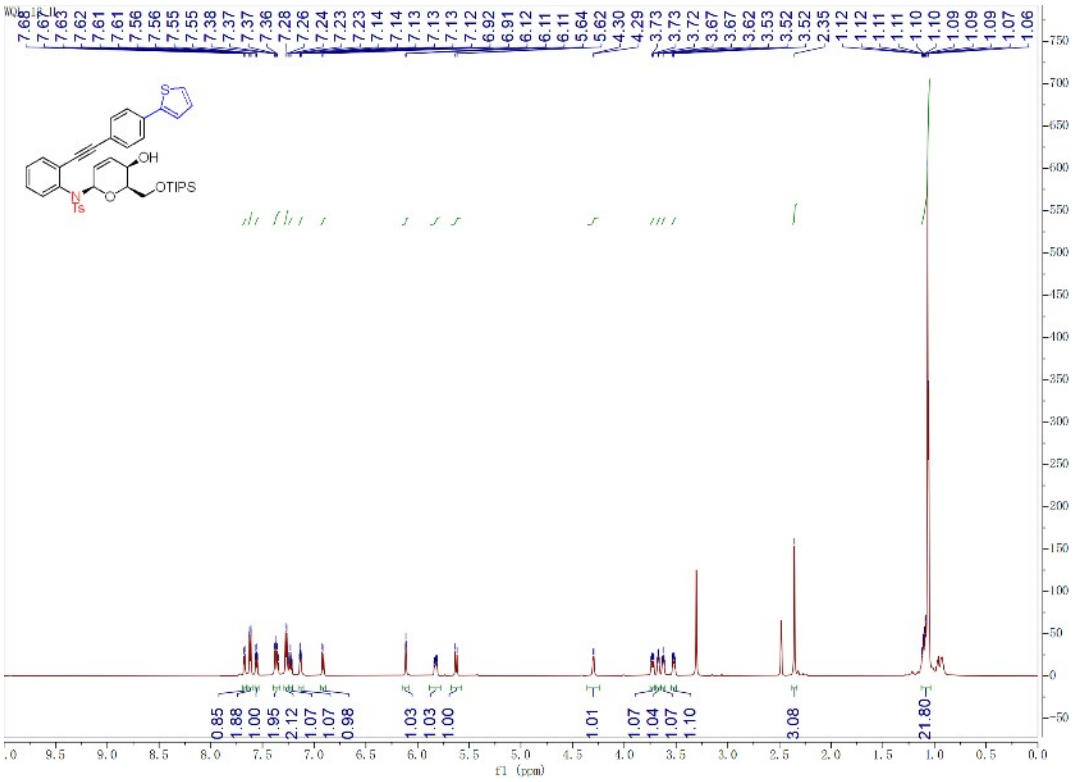
of NOE between H_1 and H_5. Upon irradiation of H_1 (6.08 ppm) significant enhancement of the H_5 (3.60 ppm) signal is observed.



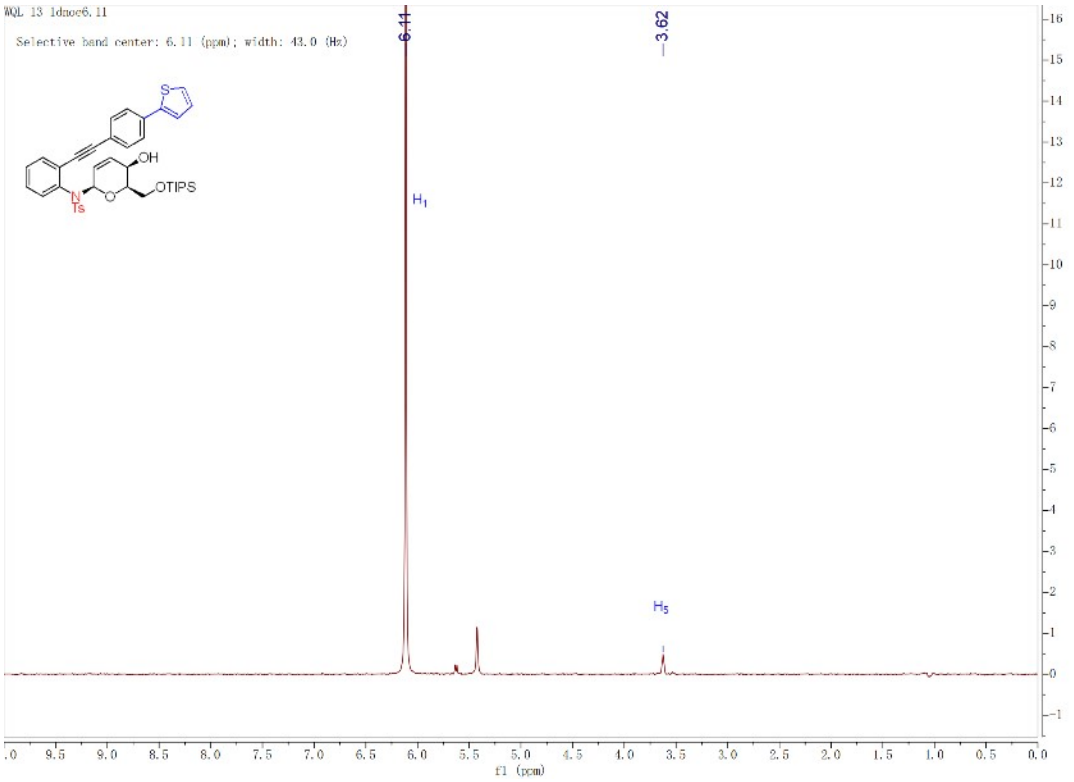
^{1}H NMR spectrum of **13** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **13** in $CDCl_3$ (100 MHz).

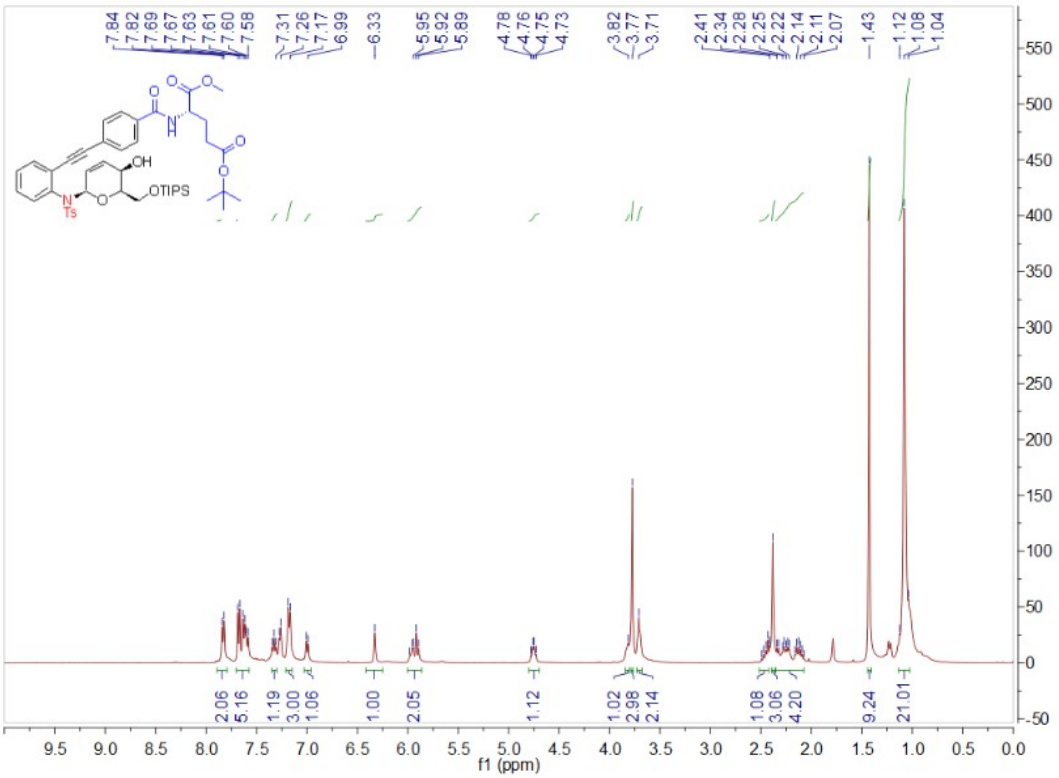


^{1}H NMR spectrum of **13** in DMSO-d_6 (600 MHz).

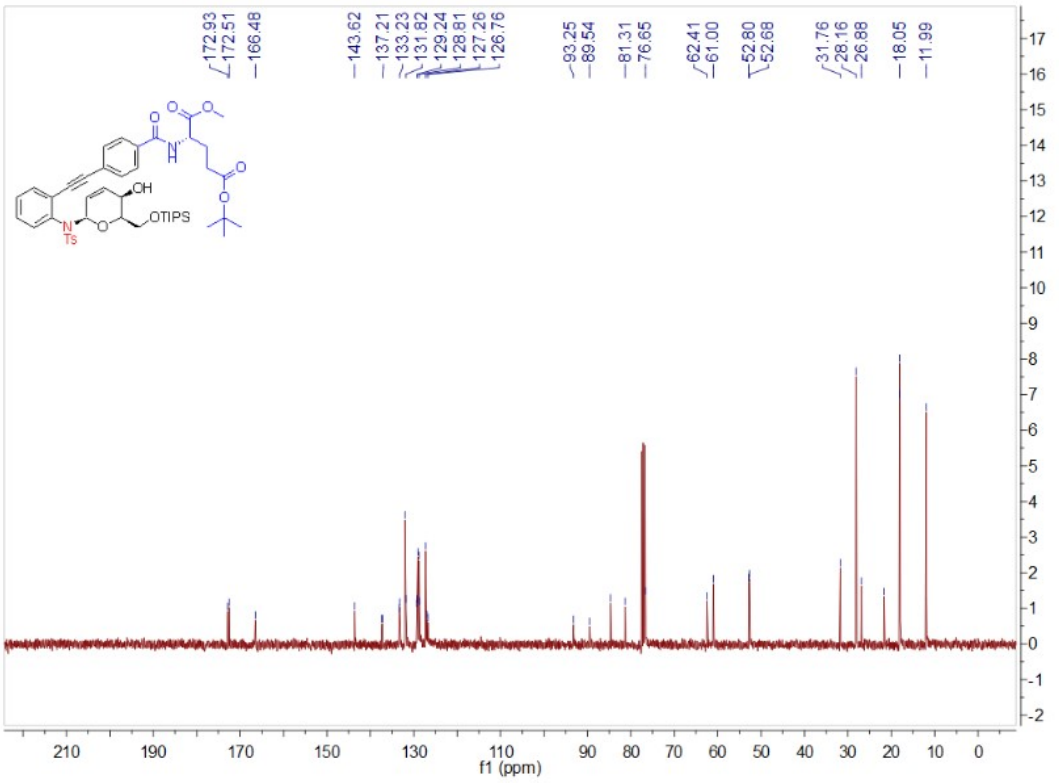


1D NOESY experiment of **13** in DMSO-d_6 (600 MHz).

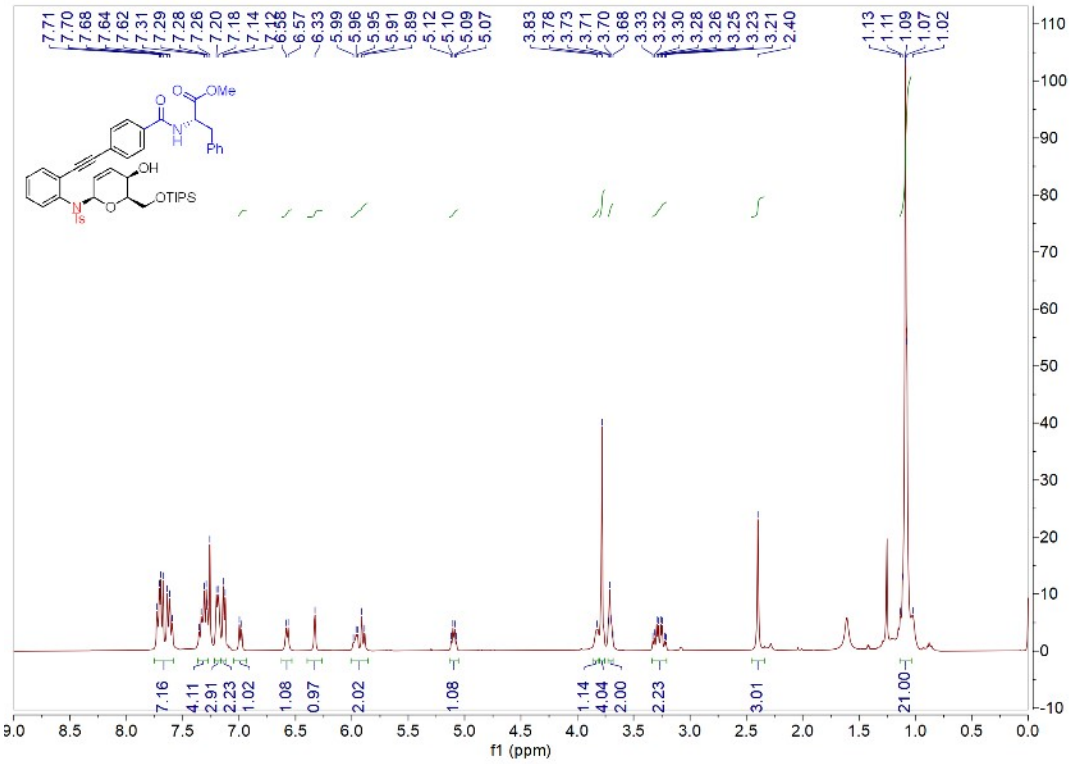
Note: The assignment of β-configuration of compound **13** comes from the observation of NOE between H_1 and H_5. Upon irradiation of H_1 (6.11 ppm) significant enhancement of the H_5 (3.62 ppm) signal is observed.



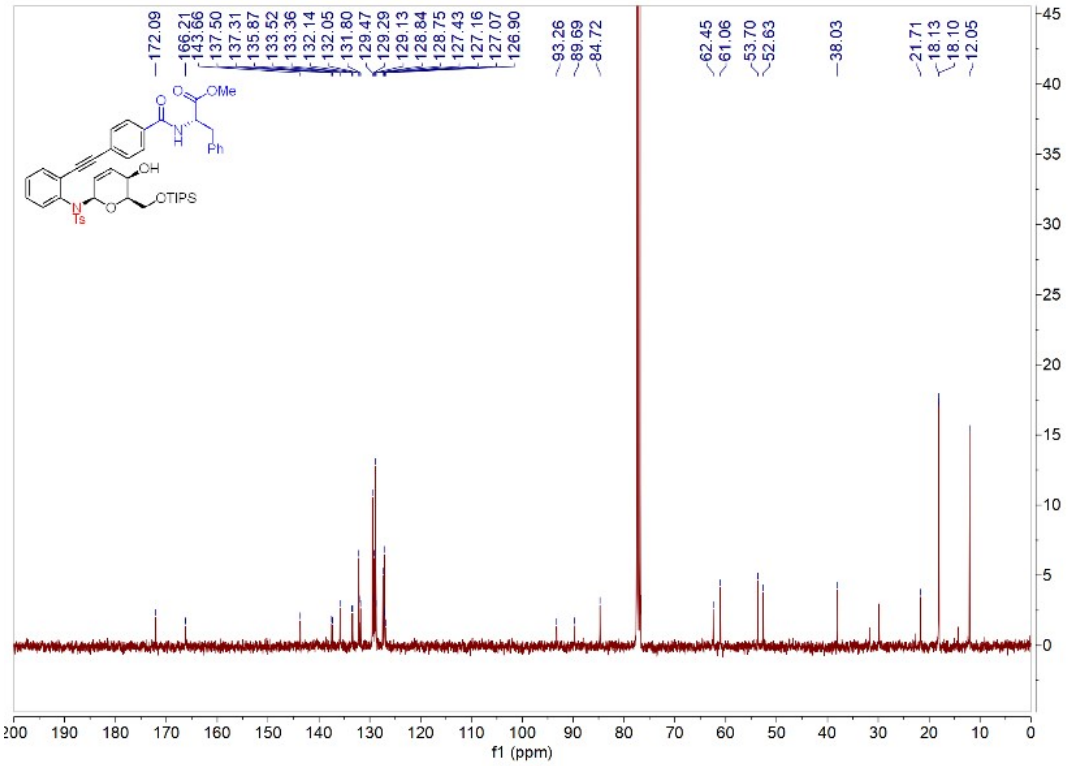
^{1}H NMR spectrum of **14** in $CDCl_3$ (400 MHz).



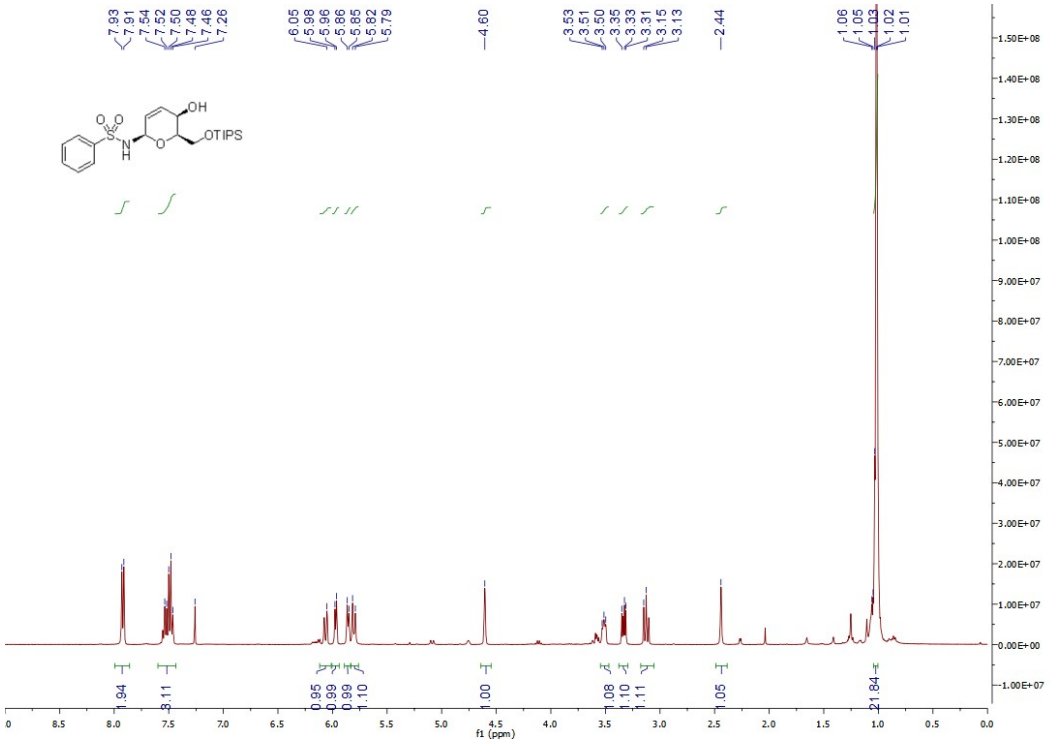
^{13}C NMR spectrum of **14** in $CDCl_3$ (100 MHz).



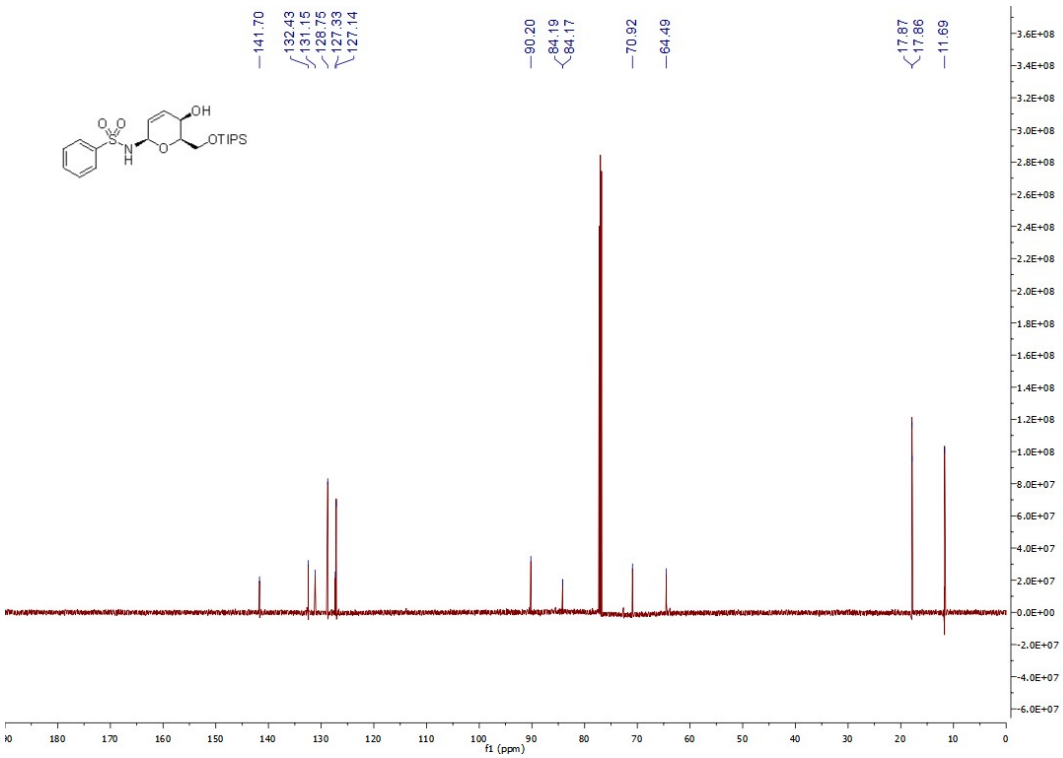
^{1}H NMR spectrum of **15** in $CDCl_3$ (400 MHz).



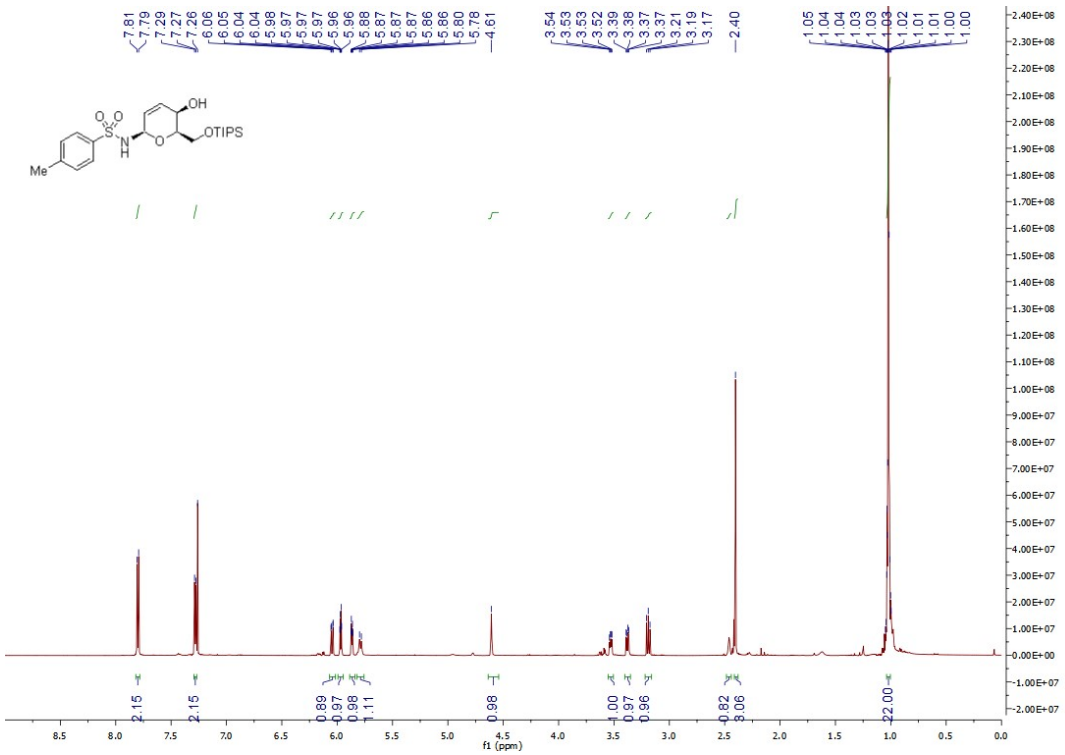
^{13}C NMR spectrum of **15** in $CDCl_3$ (100 MHz).



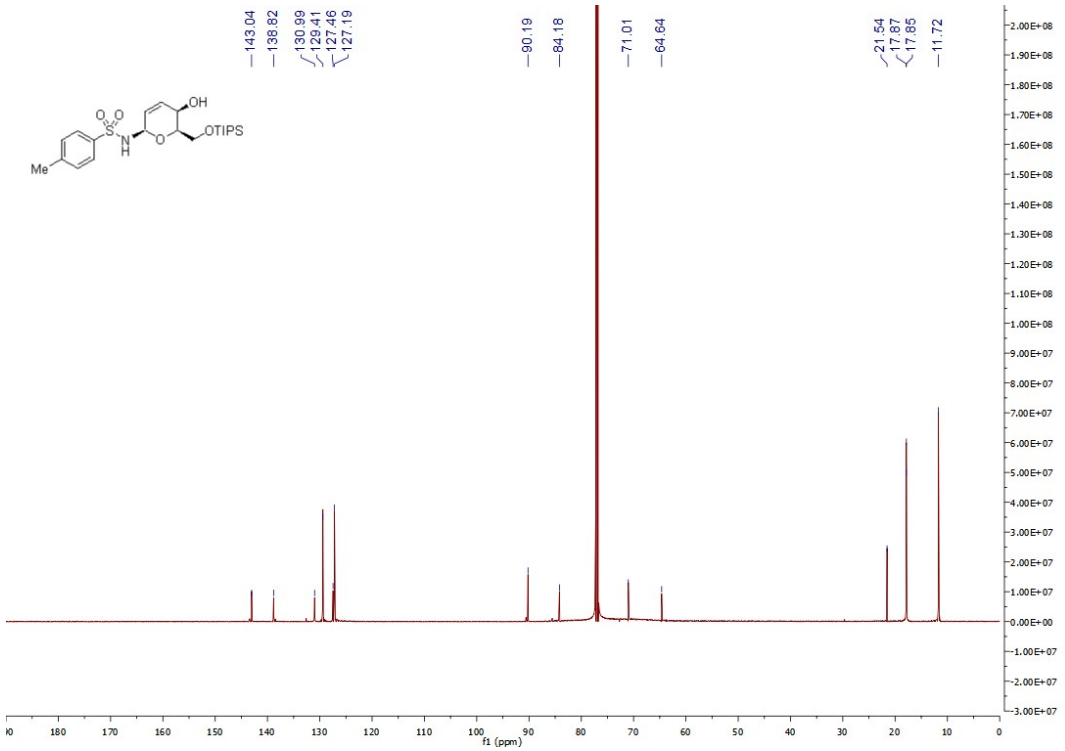
^{1}H NMR spectrum of **16** in $CDCl_3$ (400 MHz).



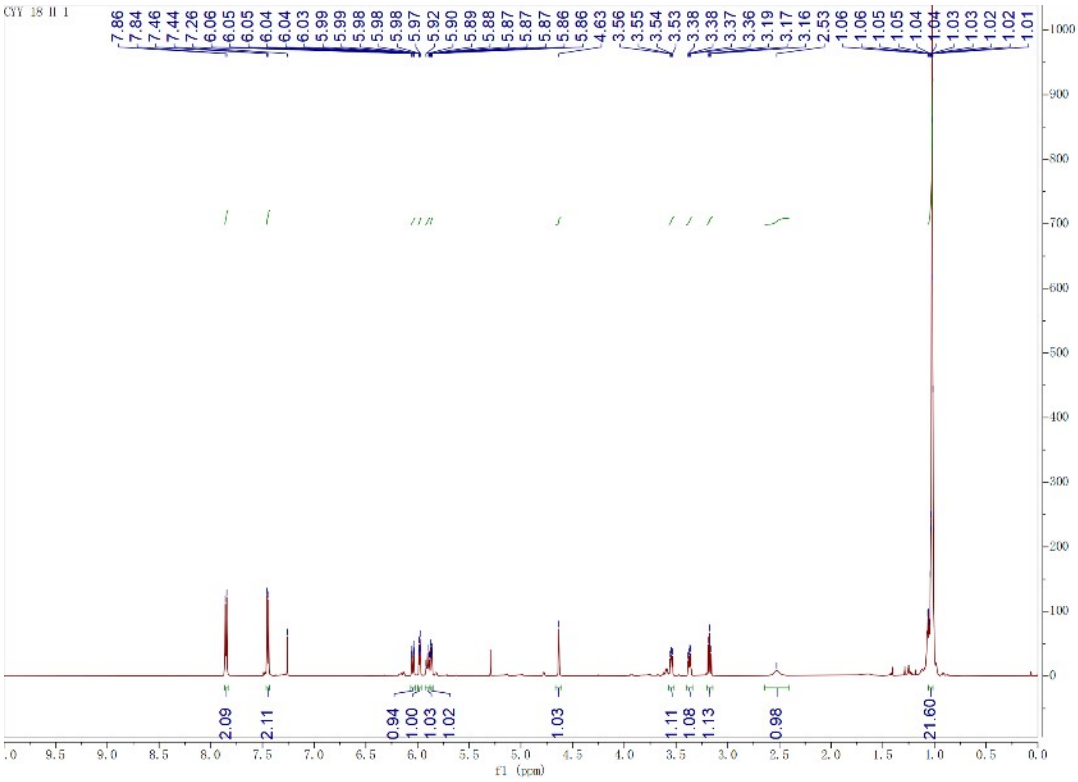
^{13}C NMR spectrum of **16** in $CDCl_3$ (150 MHz).



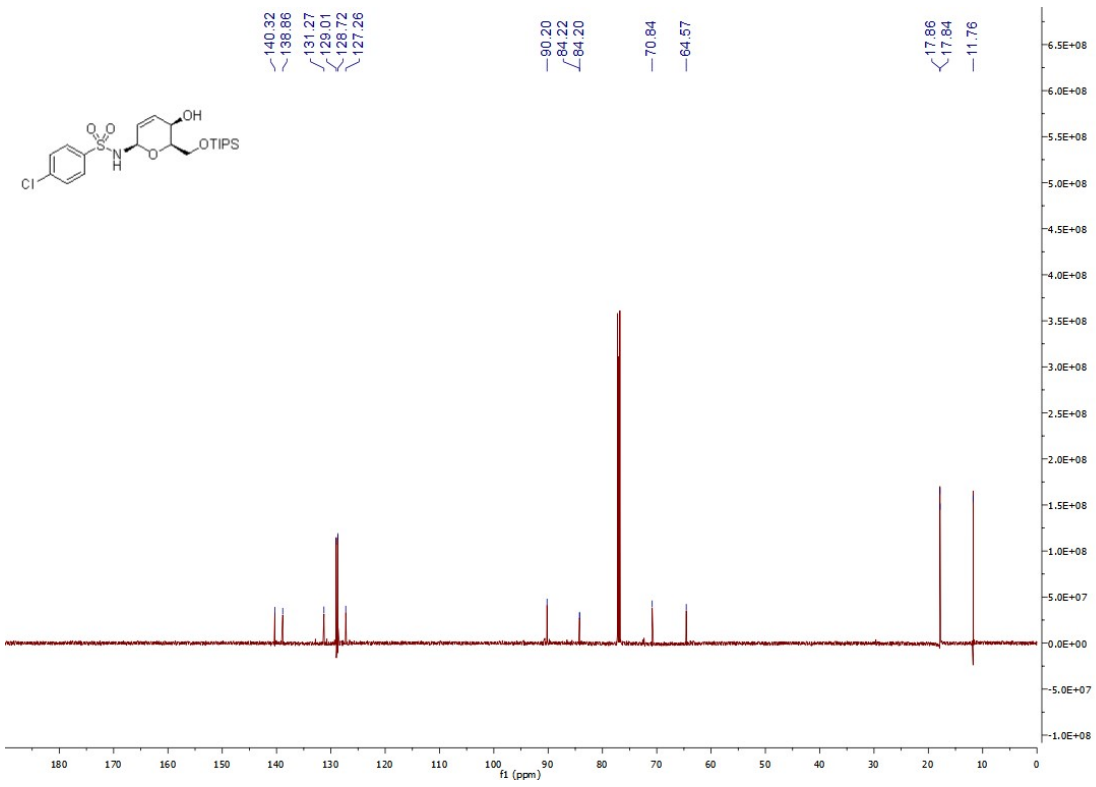
^{1}H NMR spectrum of **17** in $CDCl_3$ (600 MHz).



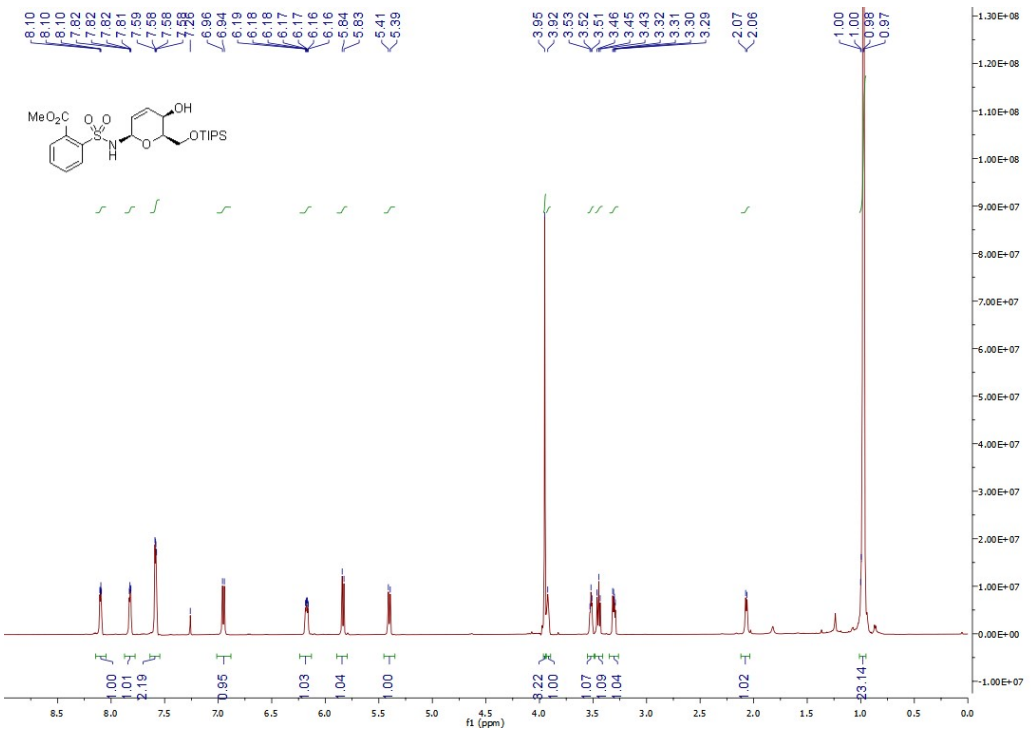
^{13}C NMR spectrum of **17** in $CDCl_3$ (150 MHz).



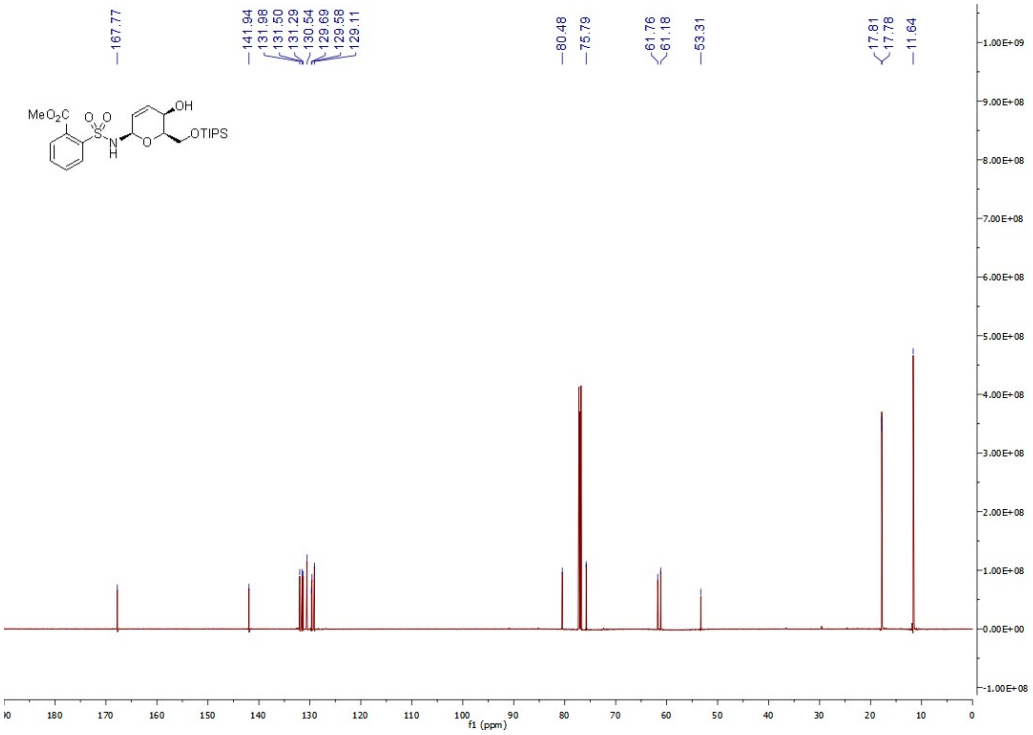
^{1}H NMR spectrum of **18** in $CDCl_3$ (600 MHz).



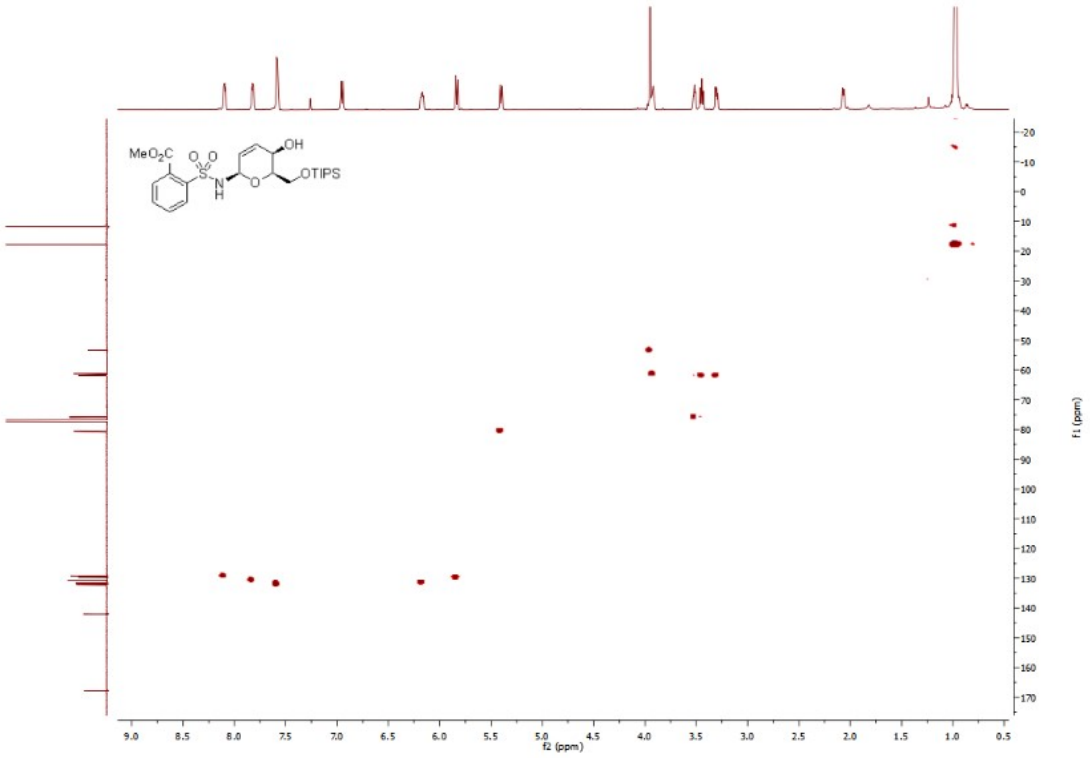
^{13}C NMR spectrum of **18** in $CDCl_3$ (150 MHz).



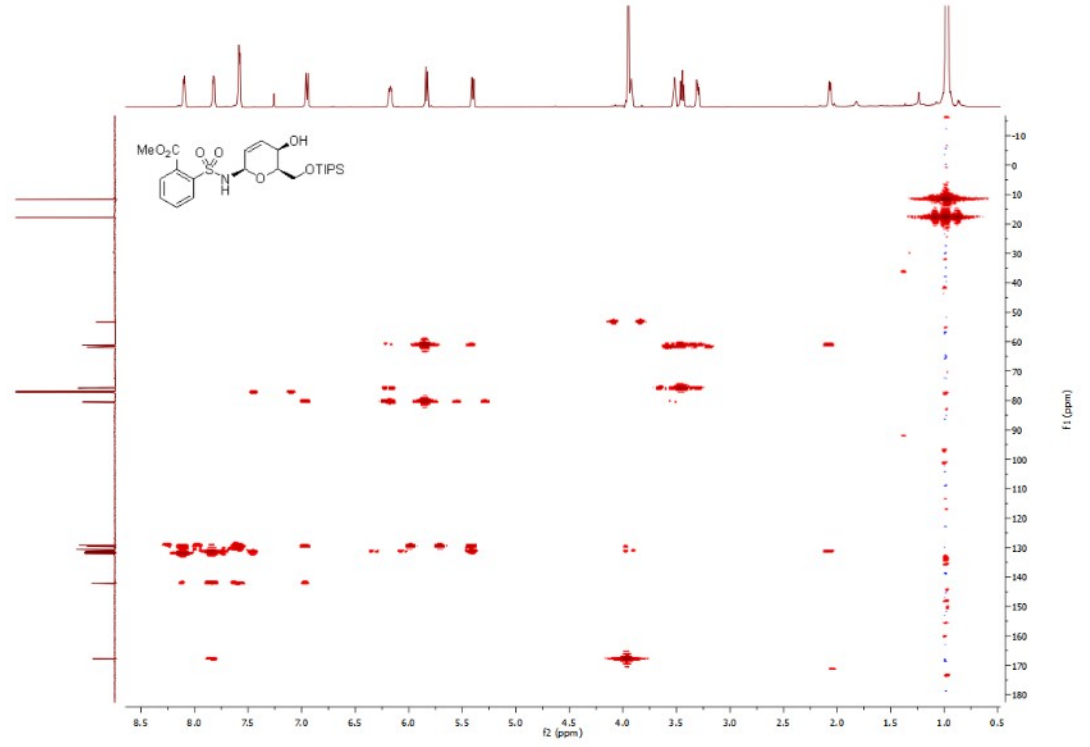
^{1}H NMR spectrum of **19** in $CDCl_3$ (600 MHz).



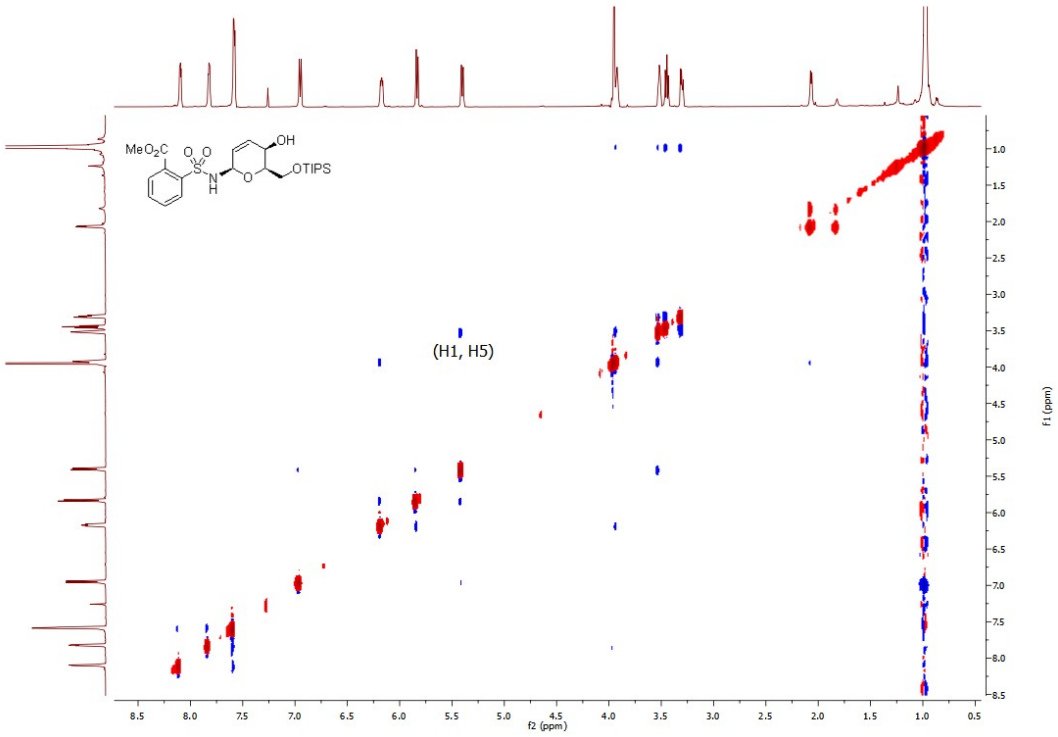
^{13}C NMR spectrum of **19** in $CDCl_3$ (150 MHz).



HSQC spectrum of **19** in $CDCl_3$ (600 MHz).

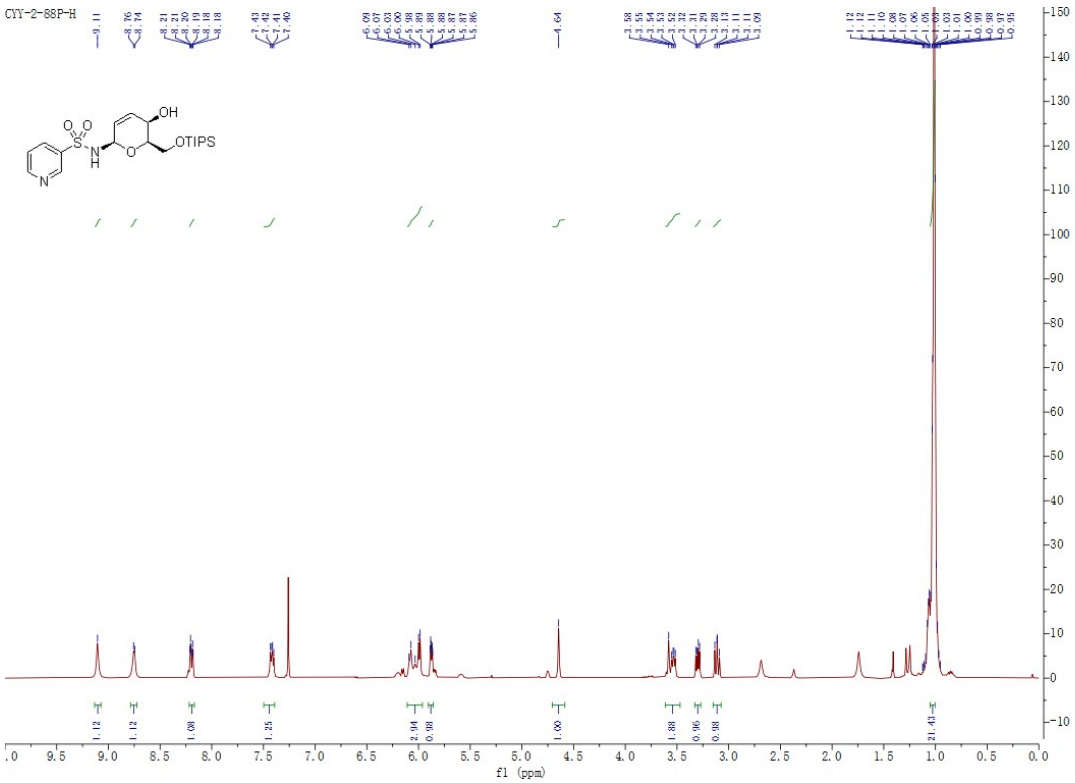


HMBC spectrum of **19** in $CDCl_3$ (600 MHz).

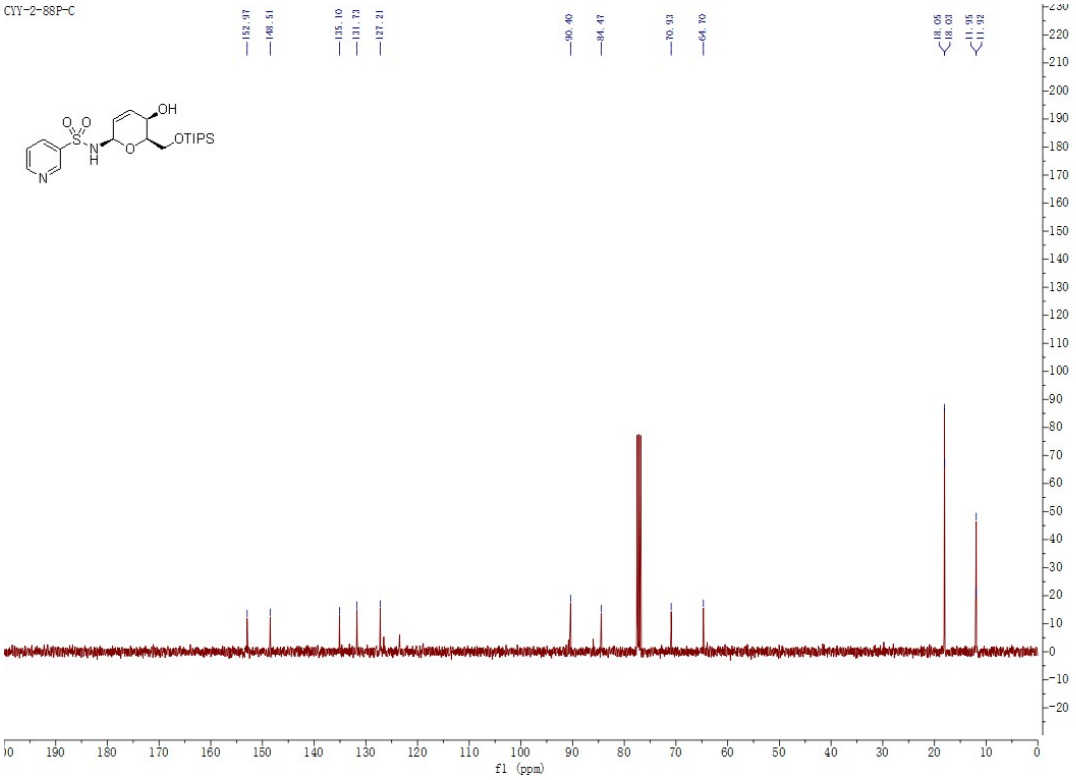


NOESY spectrum of **19** in $CDCl_3$ (600 MHz).

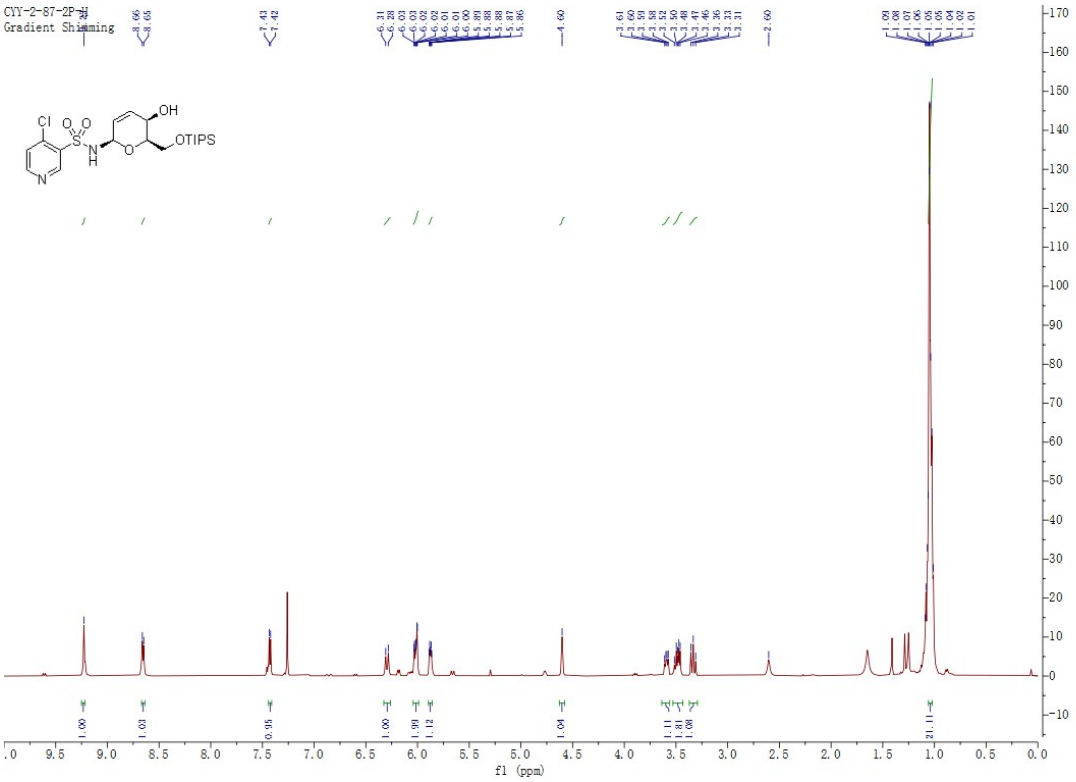
Note: A strong correlation peak of H_1 (5.40 ppm) and H_5 (3.52 ppm) is observed in NOESY spectrum, confirming the β-glycosidic linkage of glycoside product **19**.



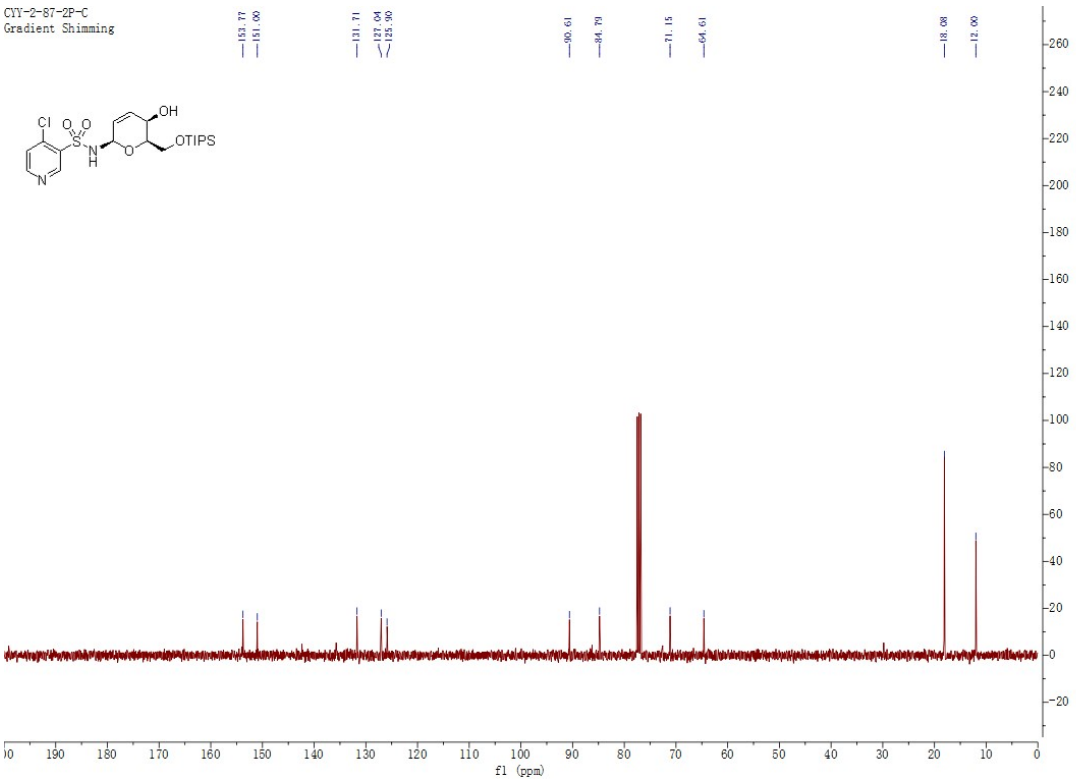
^{1}H NMR spectrum of **20** in $CDCl_3$ (400 MHz).



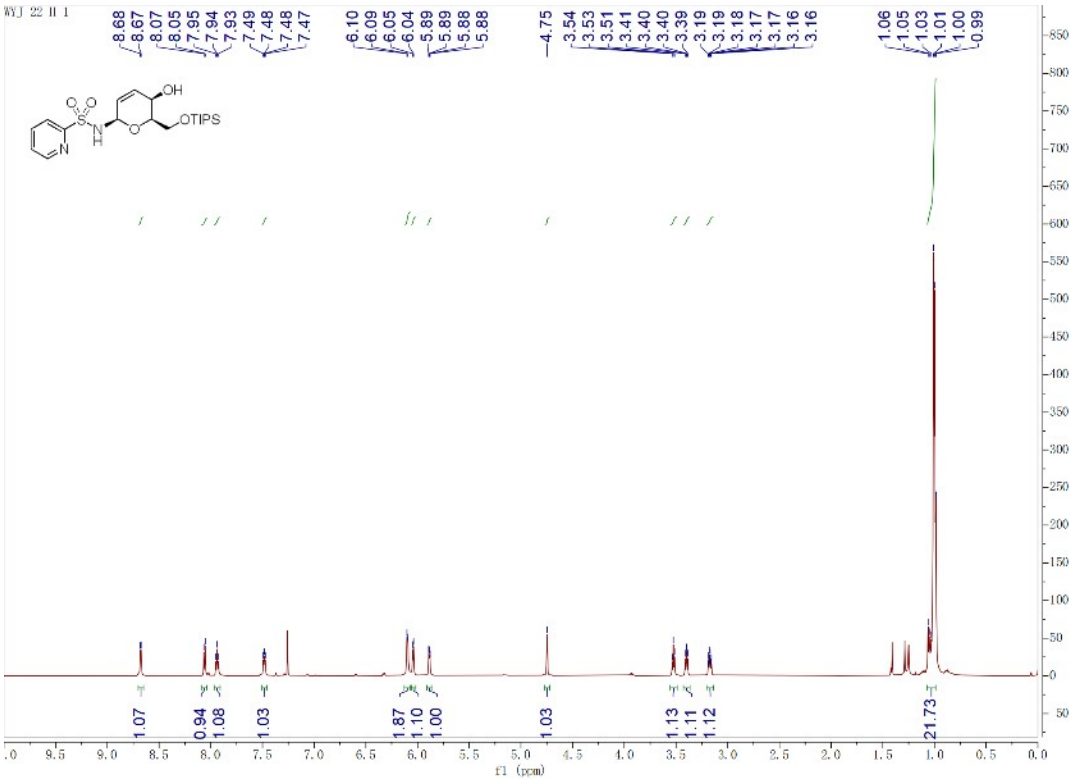
^{13}C NMR spectrum of **20** in $CDCl_3$ (100 MHz).



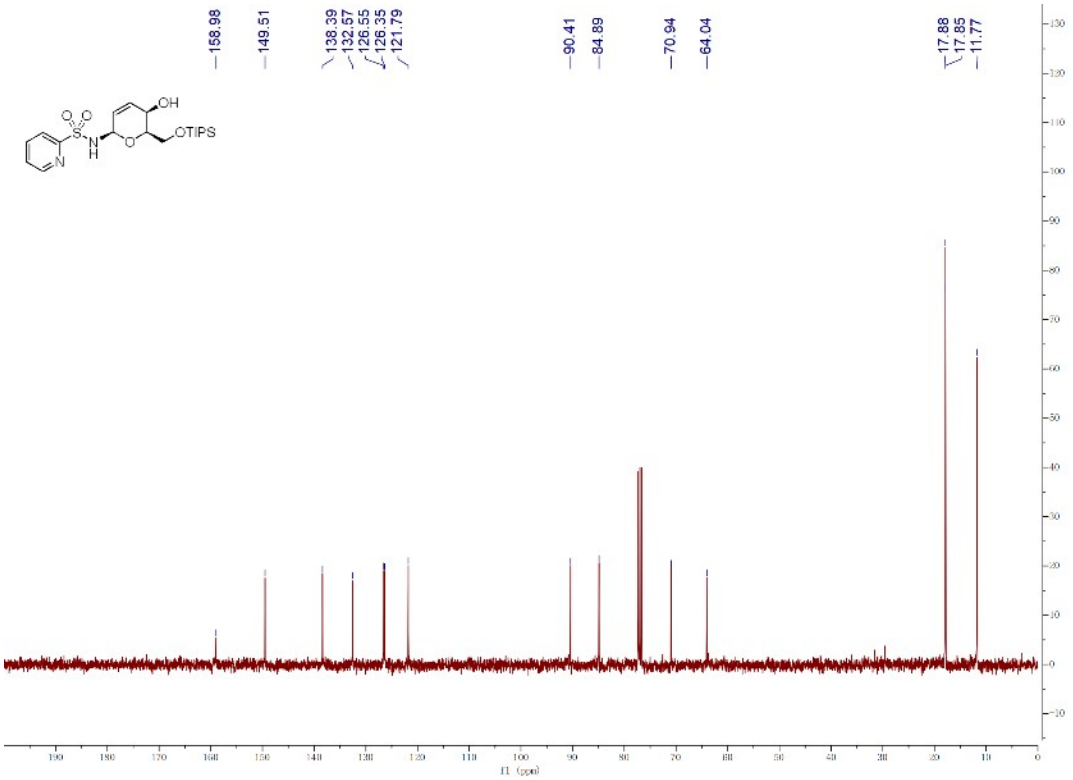
^{1}H NMR spectrum of **21** in $CDCl_3$ (400 MHz).



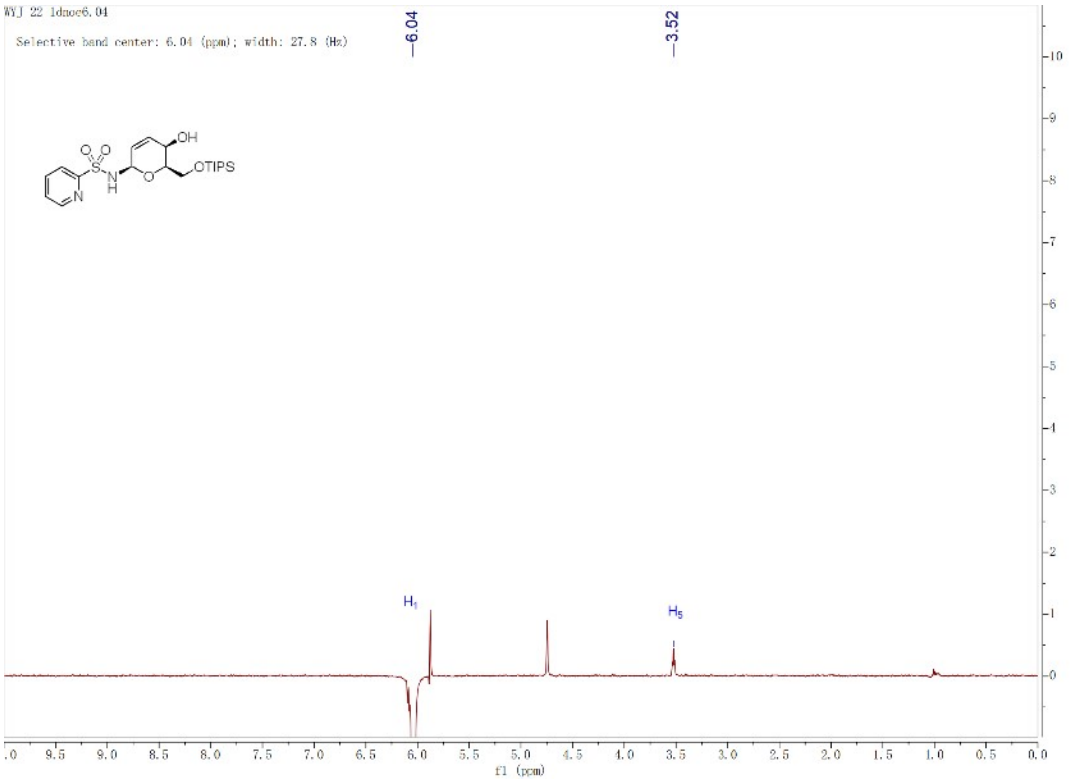
^{13}C NMR spectrum of **21** in $CDCl_3$ (100 MHz).



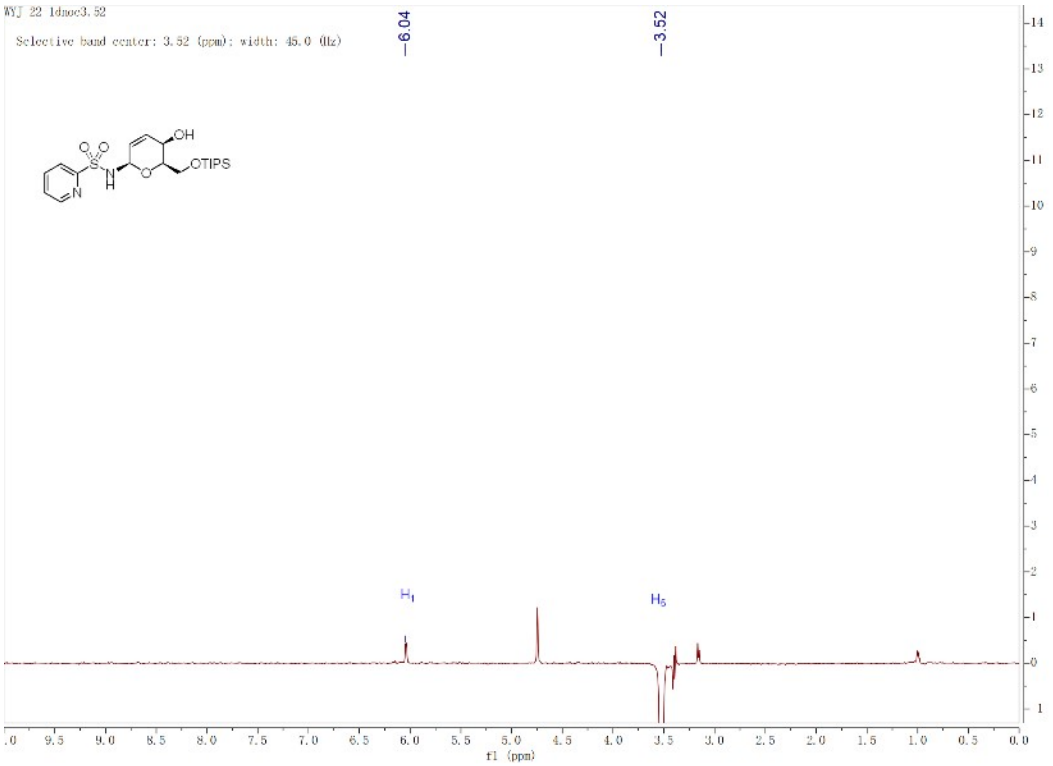
^{1}H NMR spectrum of **22** in $CDCl_3$ (600 MHz).



^{13}C NMR spectrum of **22** in $CDCl_3$ (100 MHz).

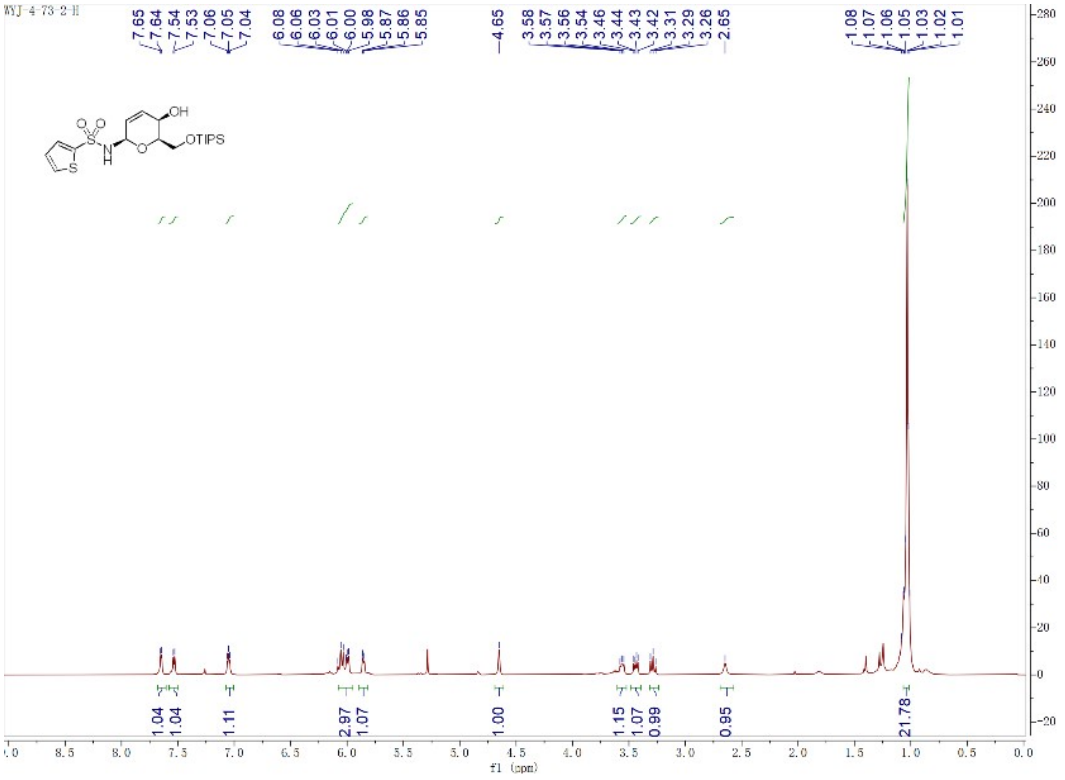


1D NOESY experiment of **22** in $CDCl_3$ (600 MHz).

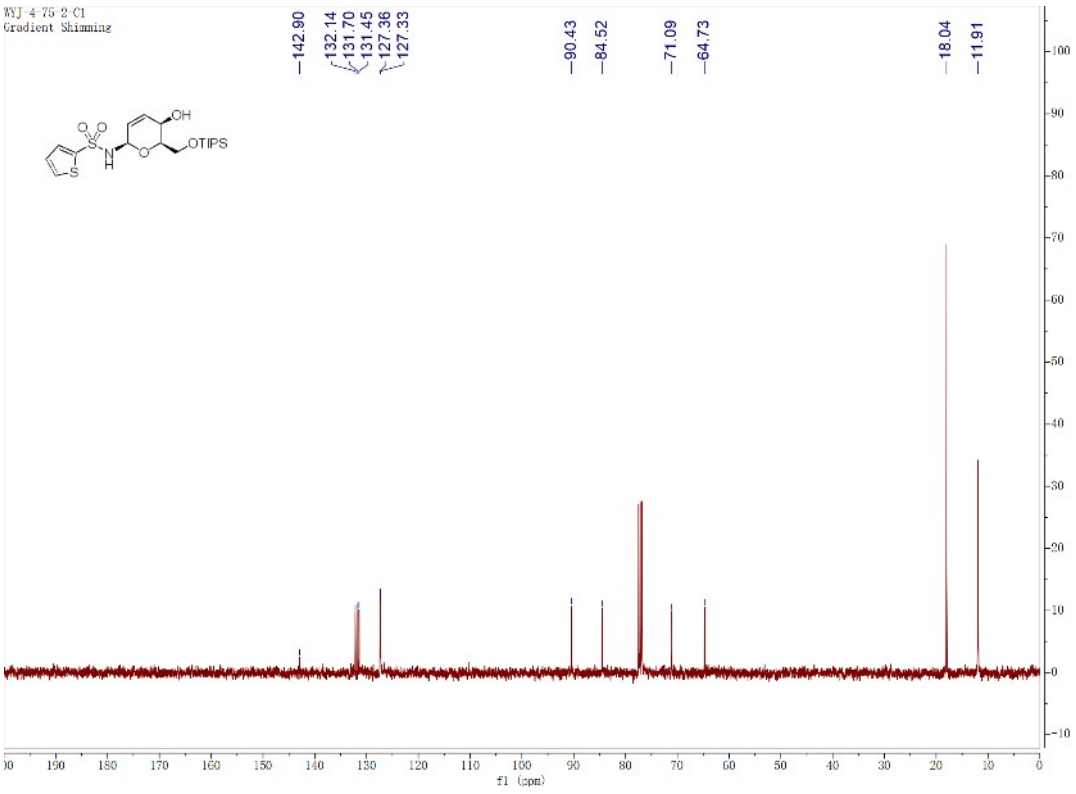


1D NOESY experiment of **22** in $CDCl_3$ (600 MHz).

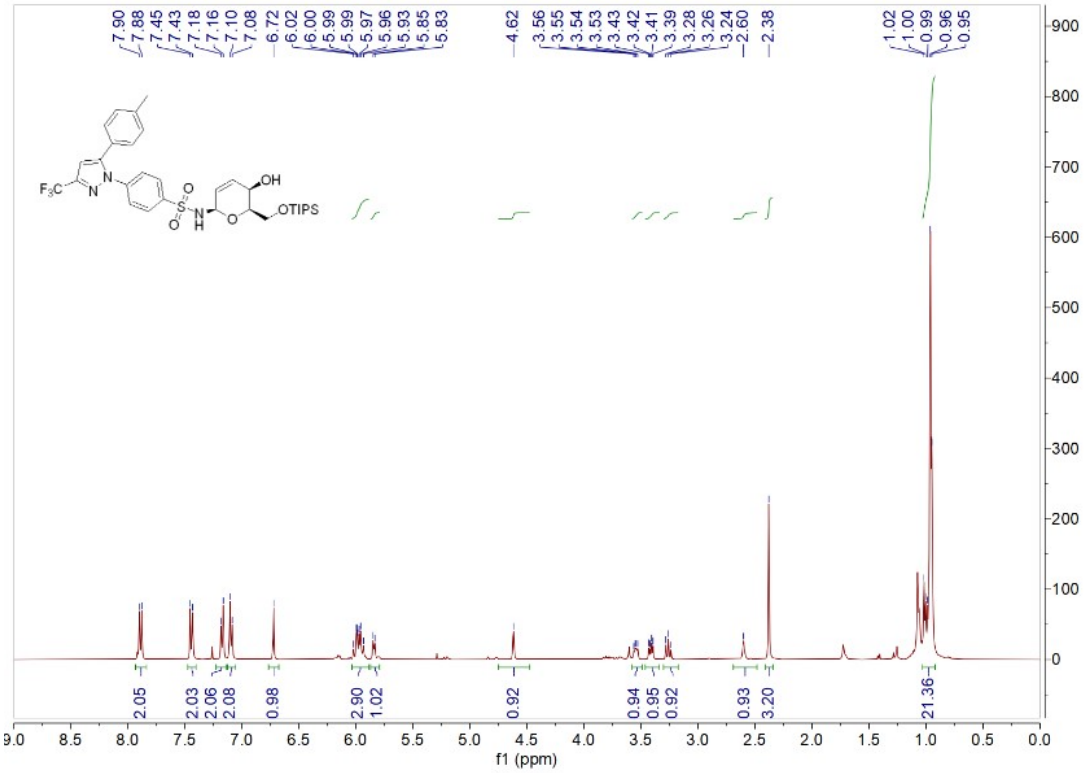
Note: The assignment of β-configuration of compound **22** comes from the observation of NOE between H_1 and H_5. Upon irradiation of H_1 (6.04 ppm) significant enhancement of the H_5 (3.52 ppm) signal is observed.



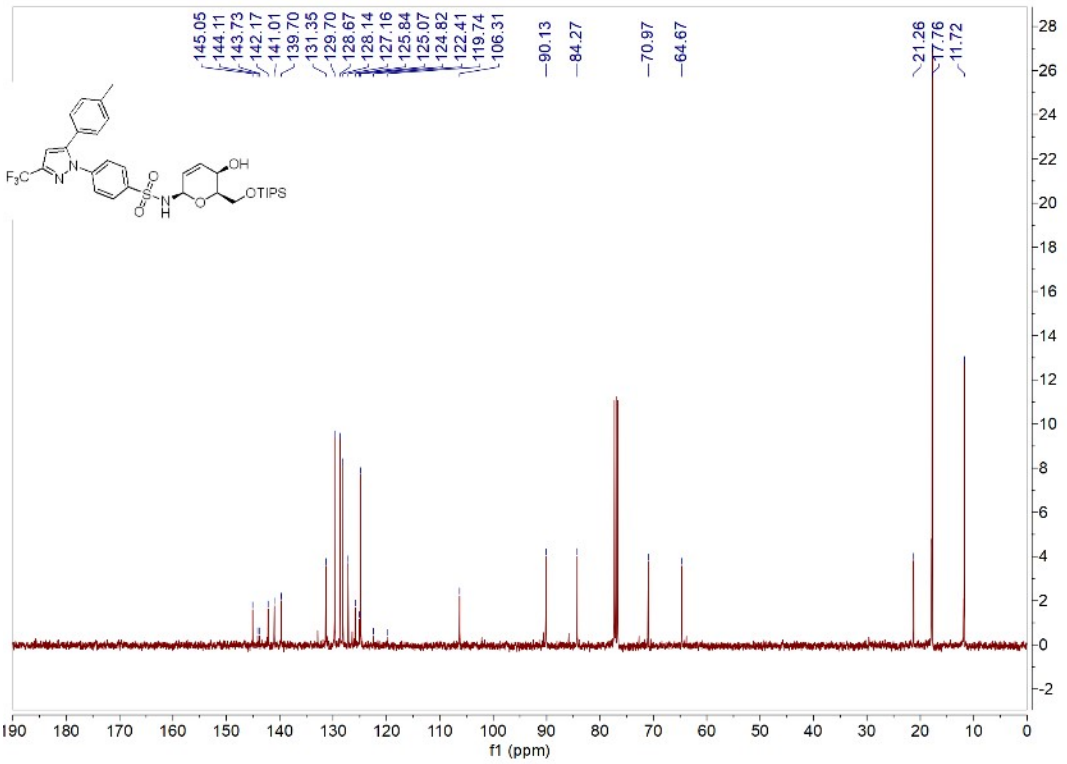
^1H NMR spectrum of **23** in $CDCl_3$ (400 MHz).



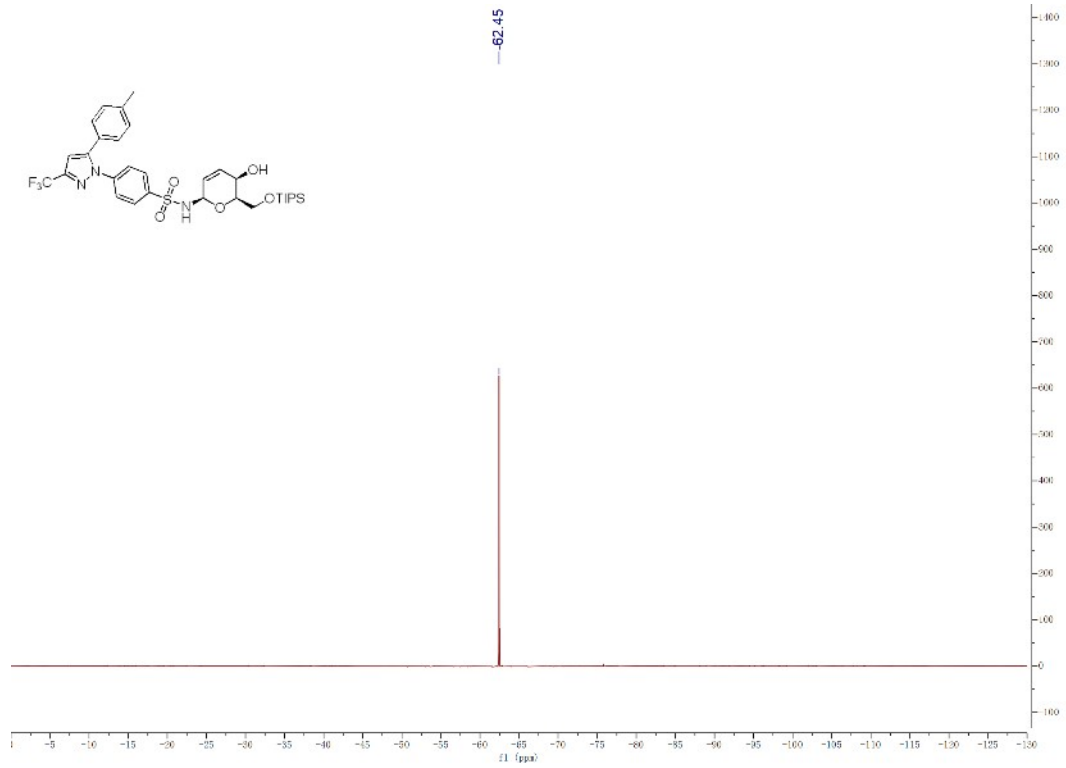
^{13}C NMR spectrum of **23** in $CDCl_3$ (100 MHz).



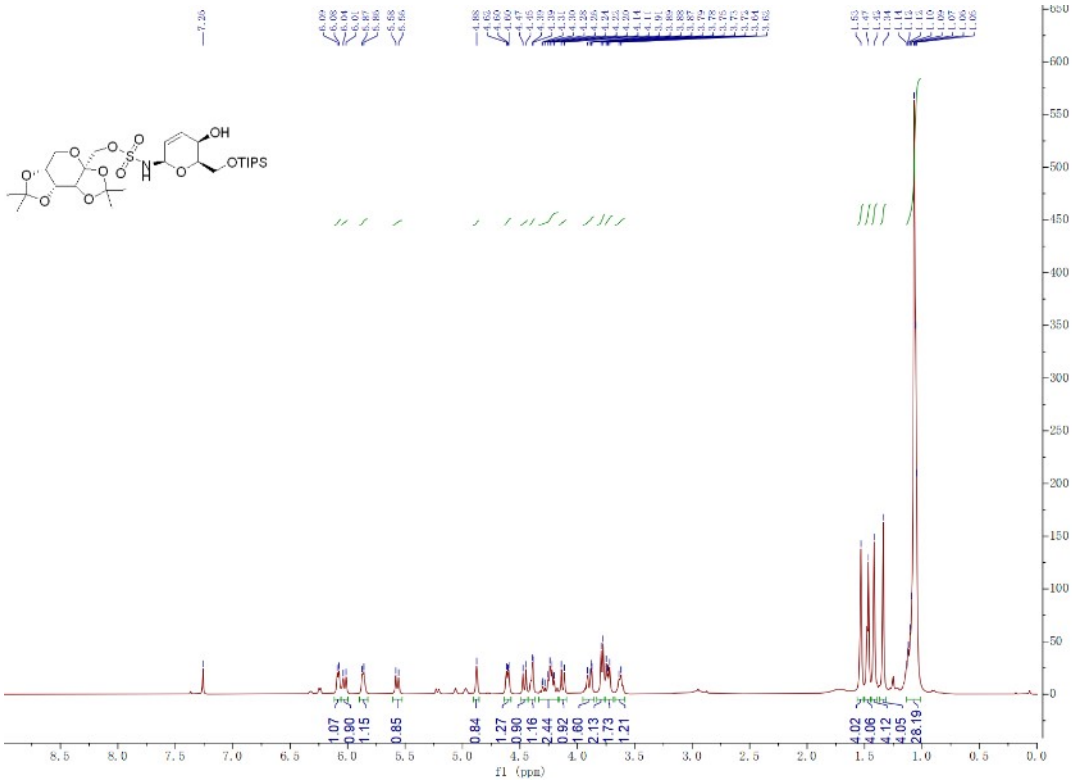
^{1}H NMR spectrum of **24** in $CDCl_3$ (400 MHz).



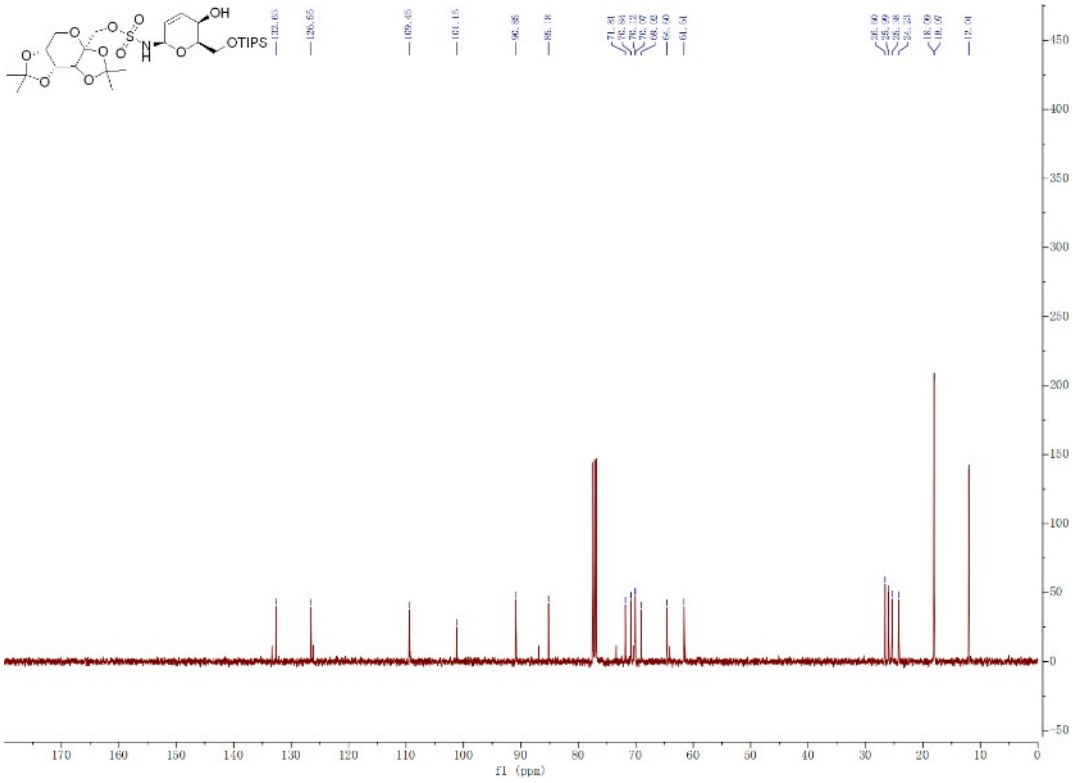
^{13}C NMR spectrum of **24** in $CDCl_3$ (100 MHz).



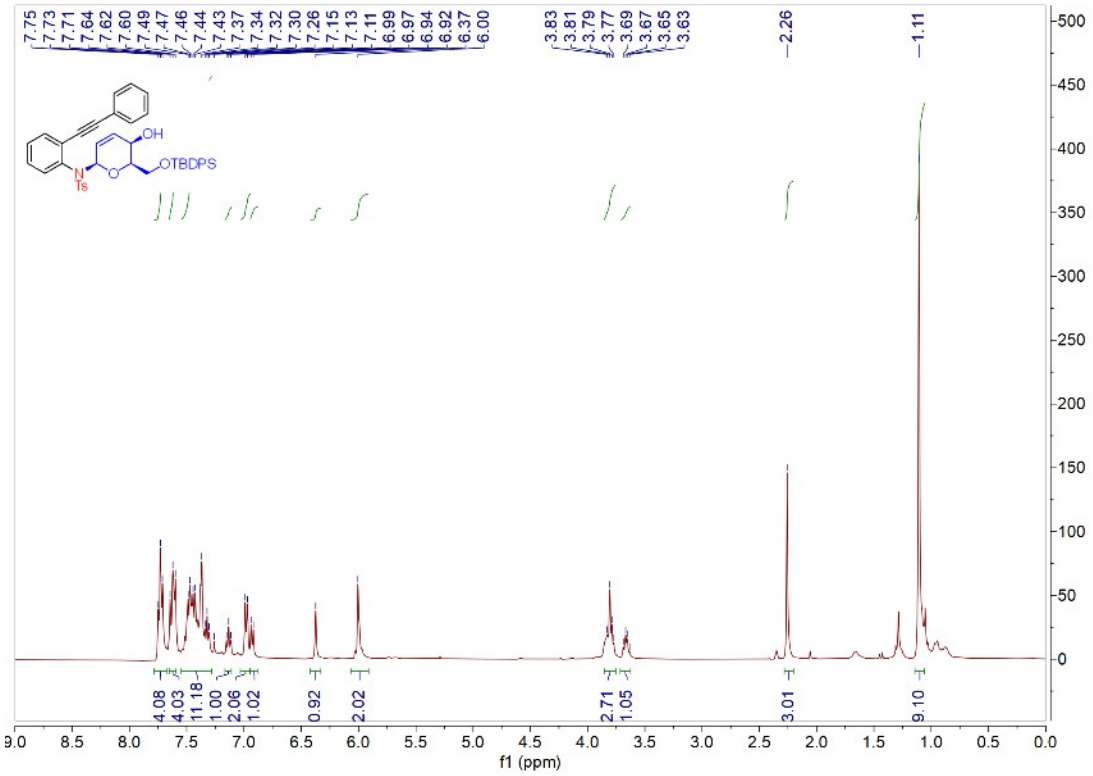
^{19}F NMR spectrum of **24** in $CDCl_3$ (564 MHz).



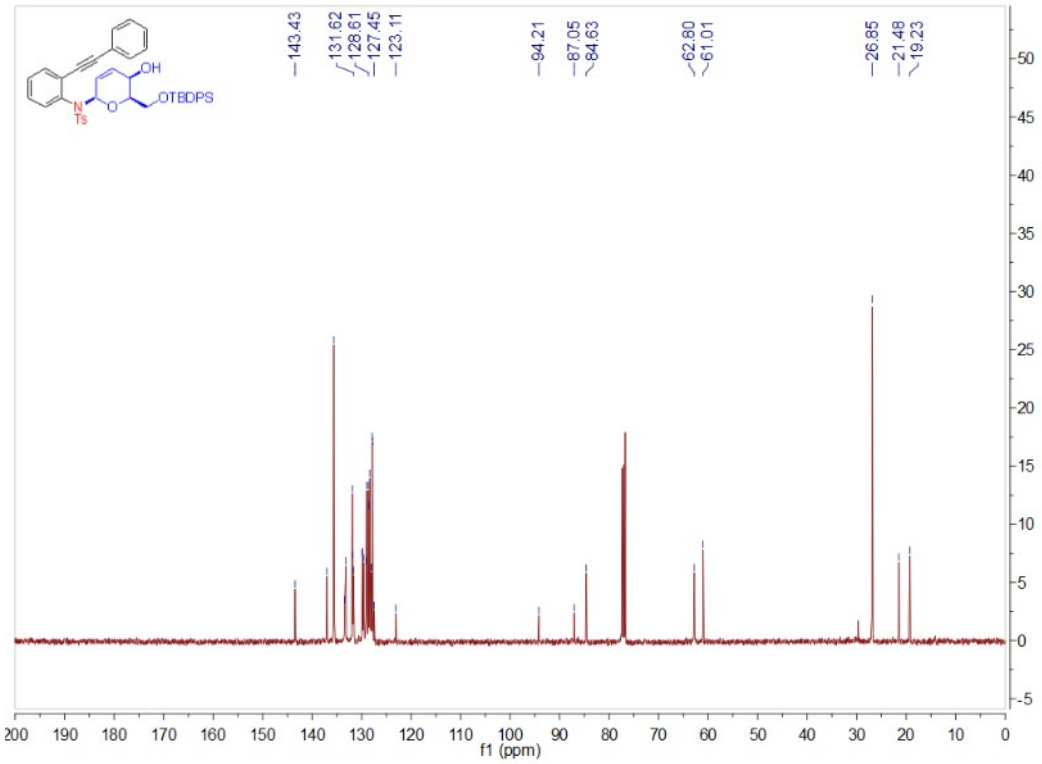
^{1}H NMR spectrum of **25** in $CDCl_3$ (400 MHz).



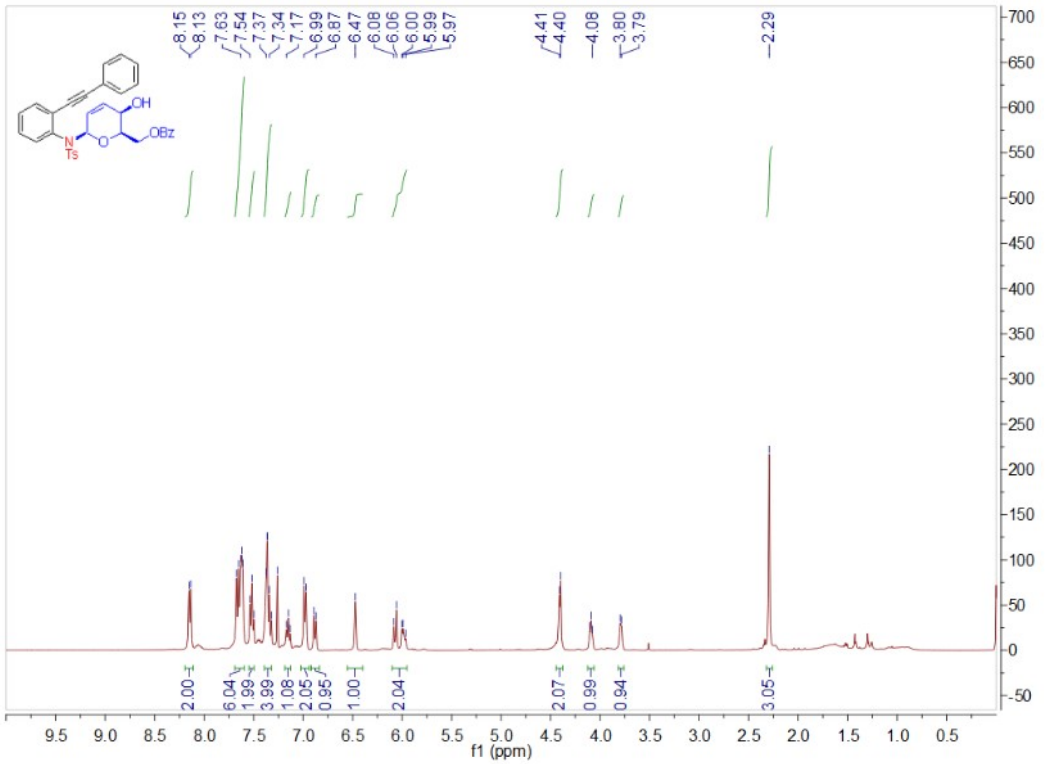
^{13}C NMR spectrum of **25** in $CDCl_3$ (100 MHz).



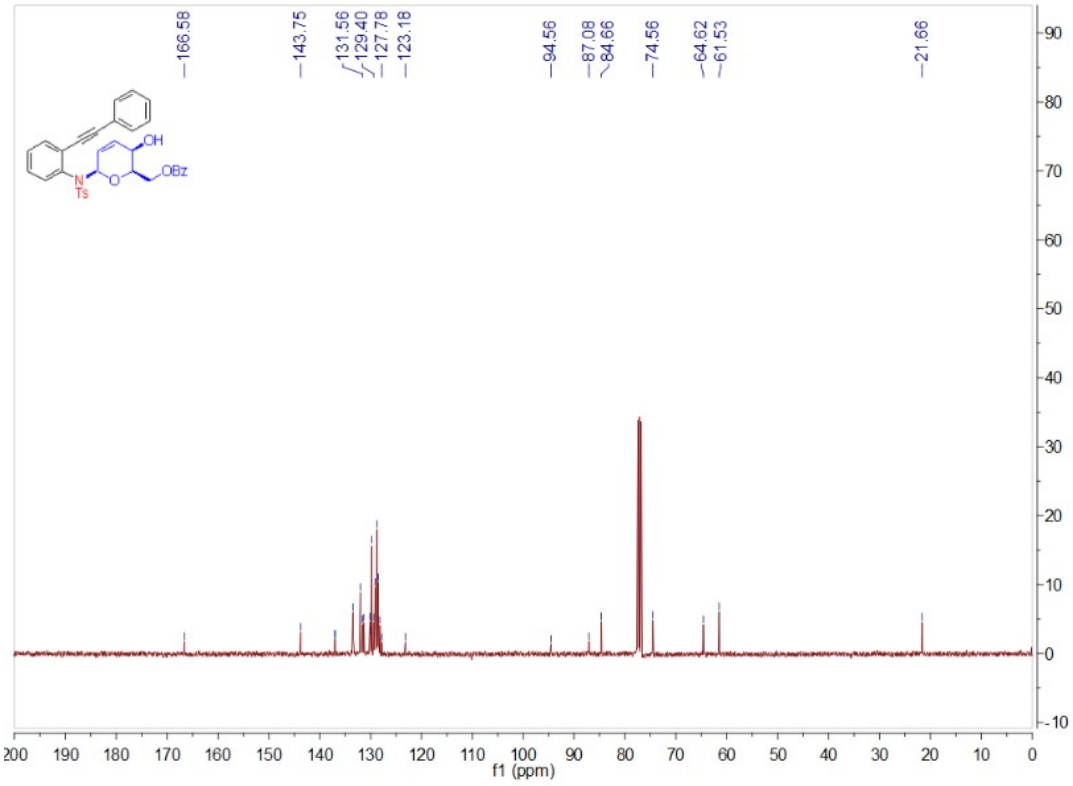
^{1}H NMR spectrum of **26** in $CDCl_3$ (400 MHz).



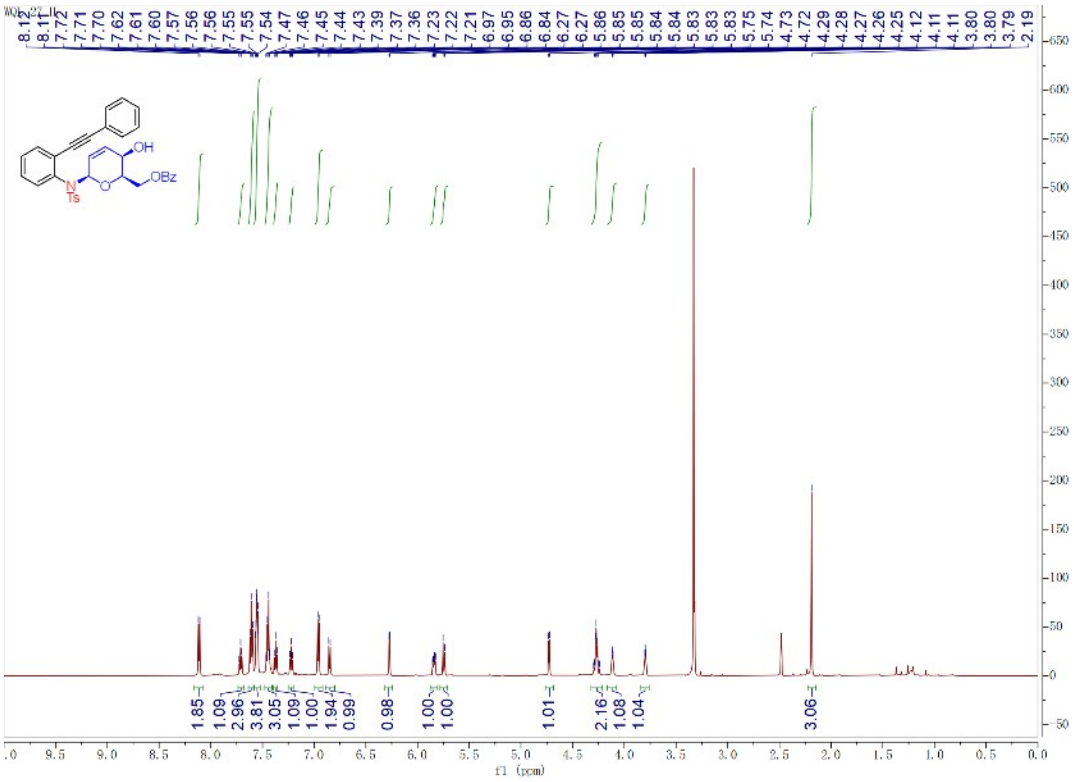
^{13}C NMR spectrum of **26** in $CDCl_3$ (100 MHz).



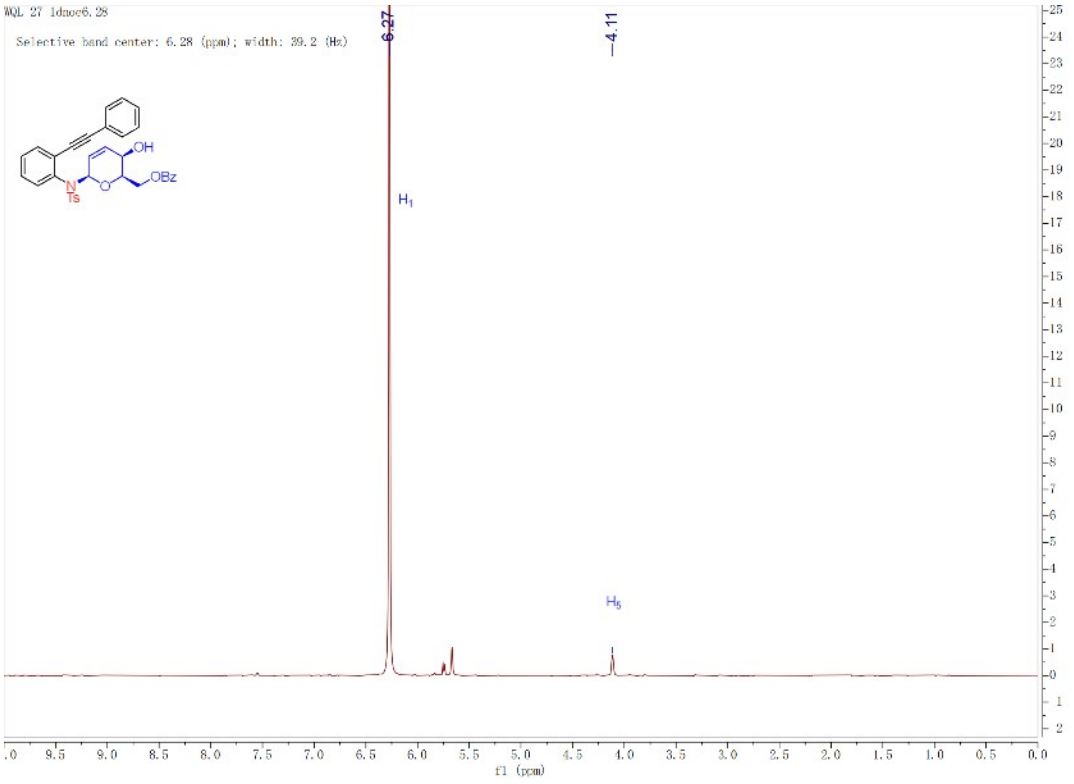
^{1}H NMR spectrum of **27** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **27** in $CDCl_3$ (100 MHz).

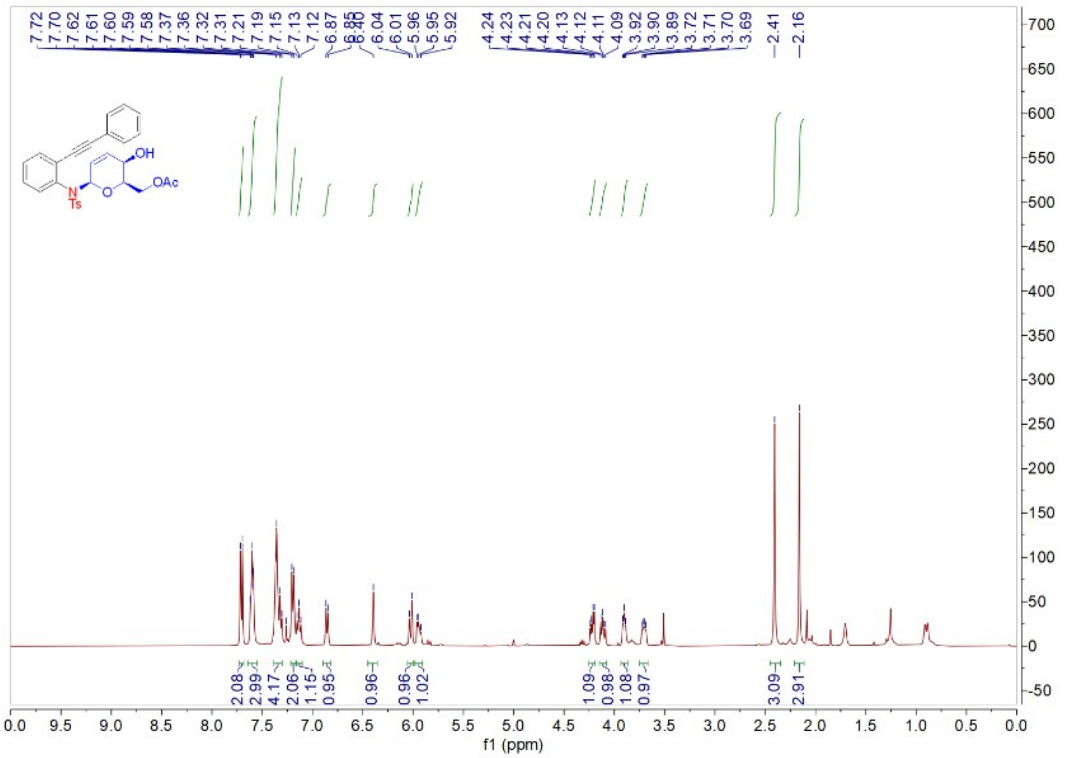


^{1}H NMR spectrum of **27** in DMSO-d_6 (600 MHz).

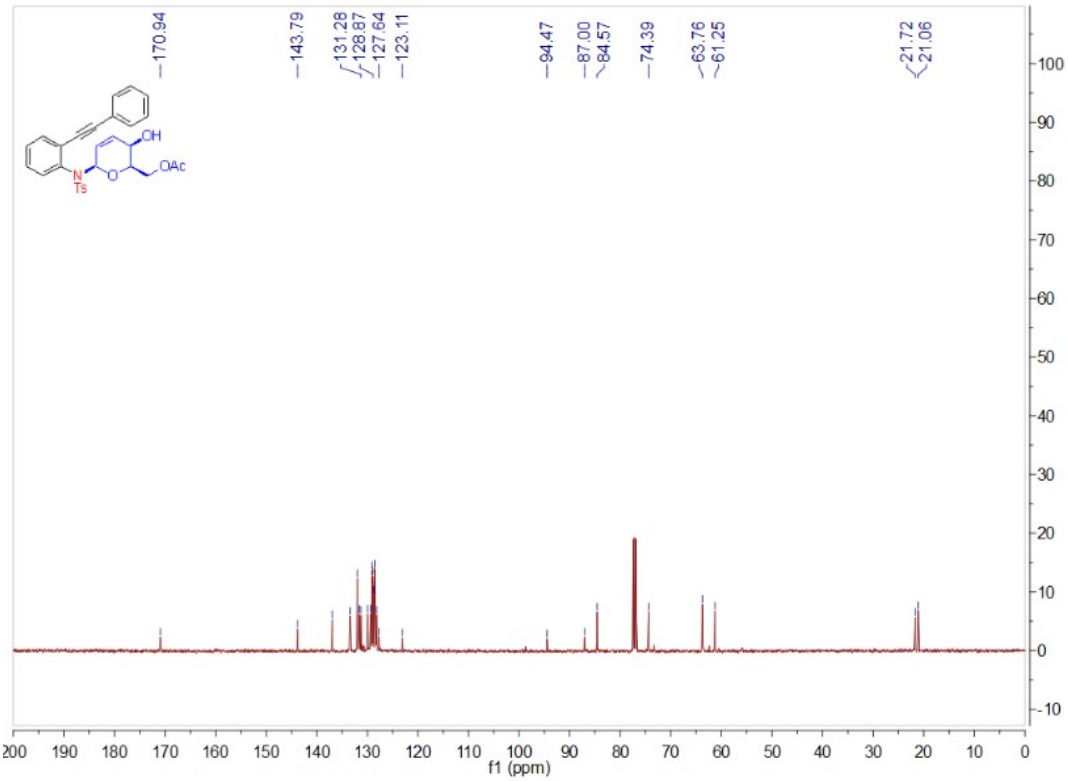


1D NOESY experiment of **27** in DMSO-d_6 (600 MHz).

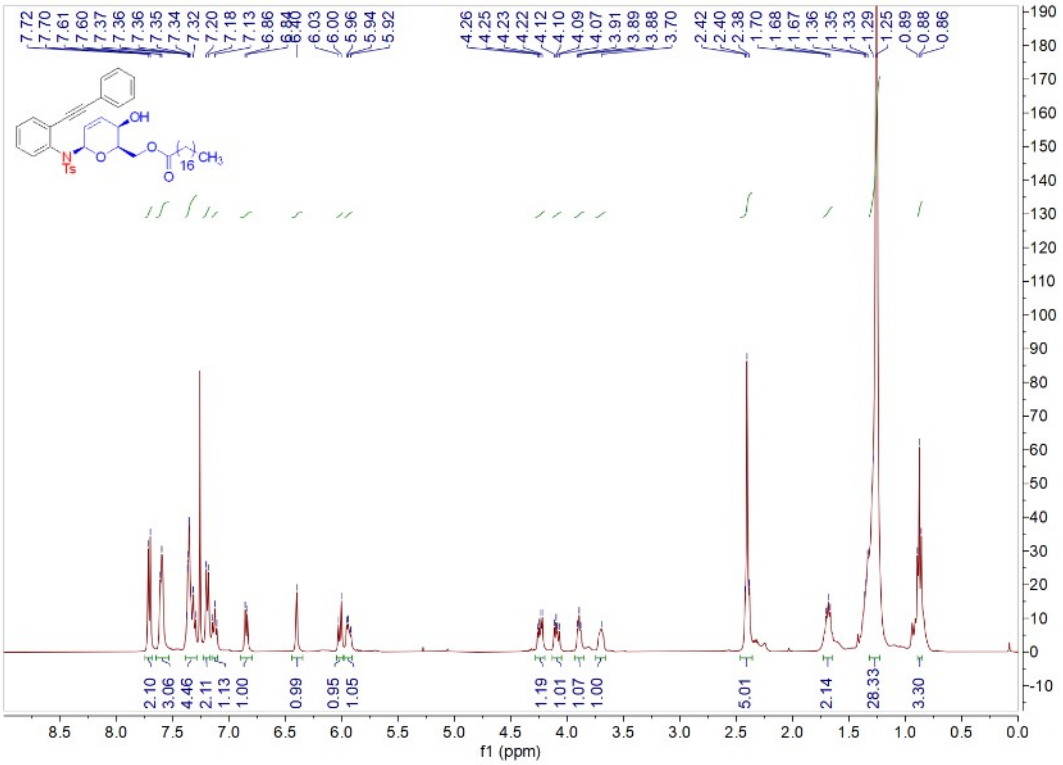
Note: The assignment of β-configuration of compound **27** comes from the observation of nuclear Overhauser effect between H_1 and H_5. Upon irradiation of H_1 (6.27 ppm) significant enhancement of the H_5 (4.11 ppm) signal is observed.



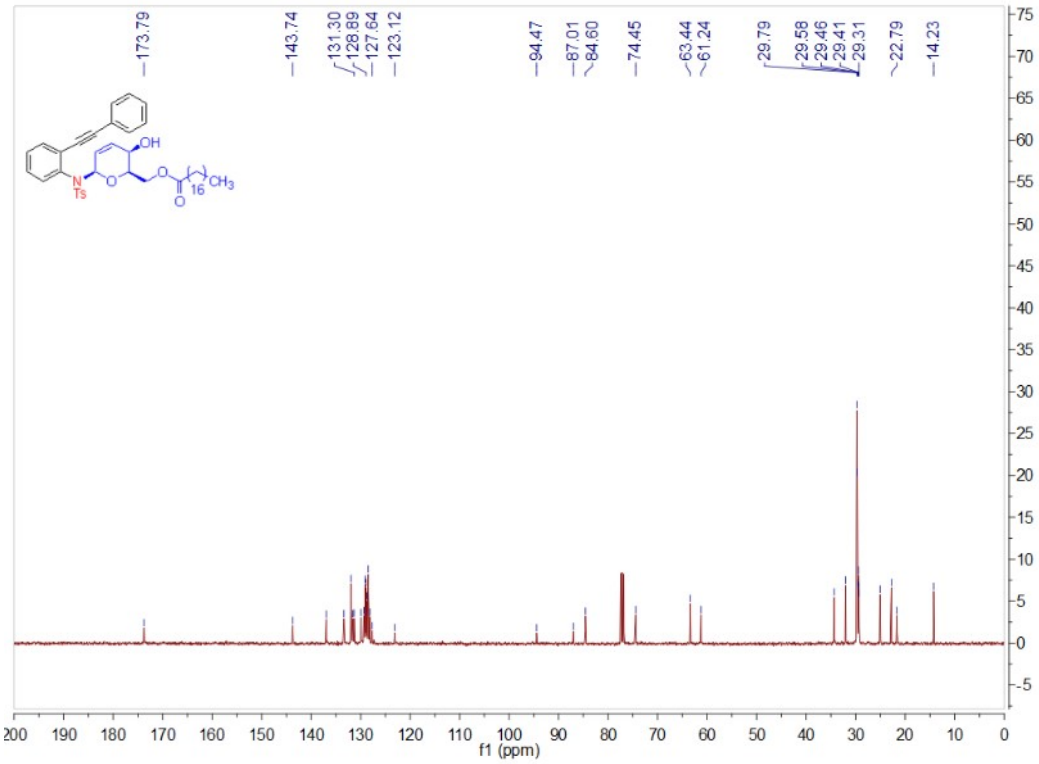
^{1}H NMR spectrum of **28** in $CDCl_3$ (400 MHz).



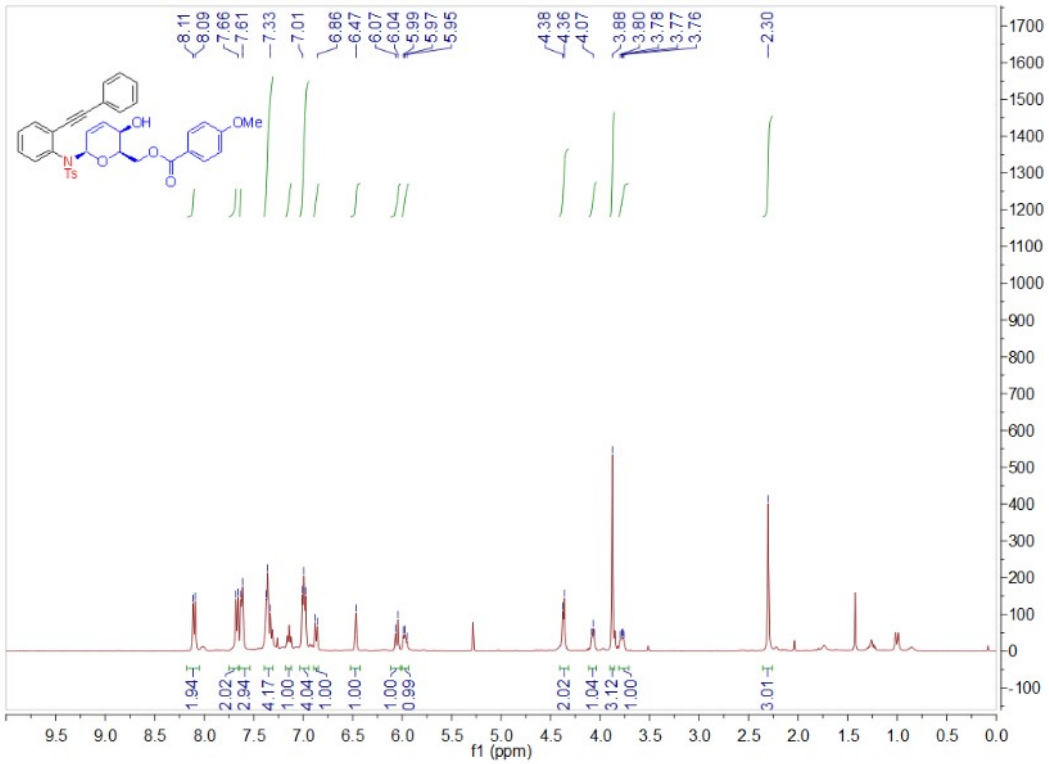
^{13}C NMR spectrum of **28** in $CDCl_3$ (100 MHz).



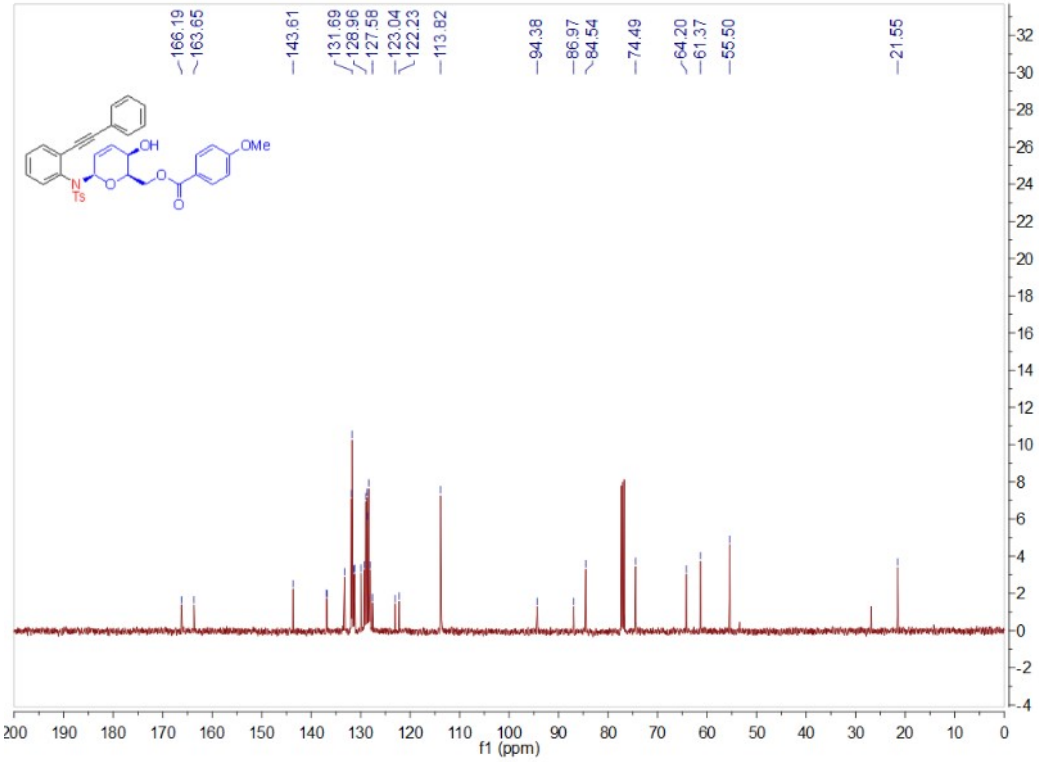
^{1}H NMR spectrum of **29** in $CDCl_3$ (400 MHz).



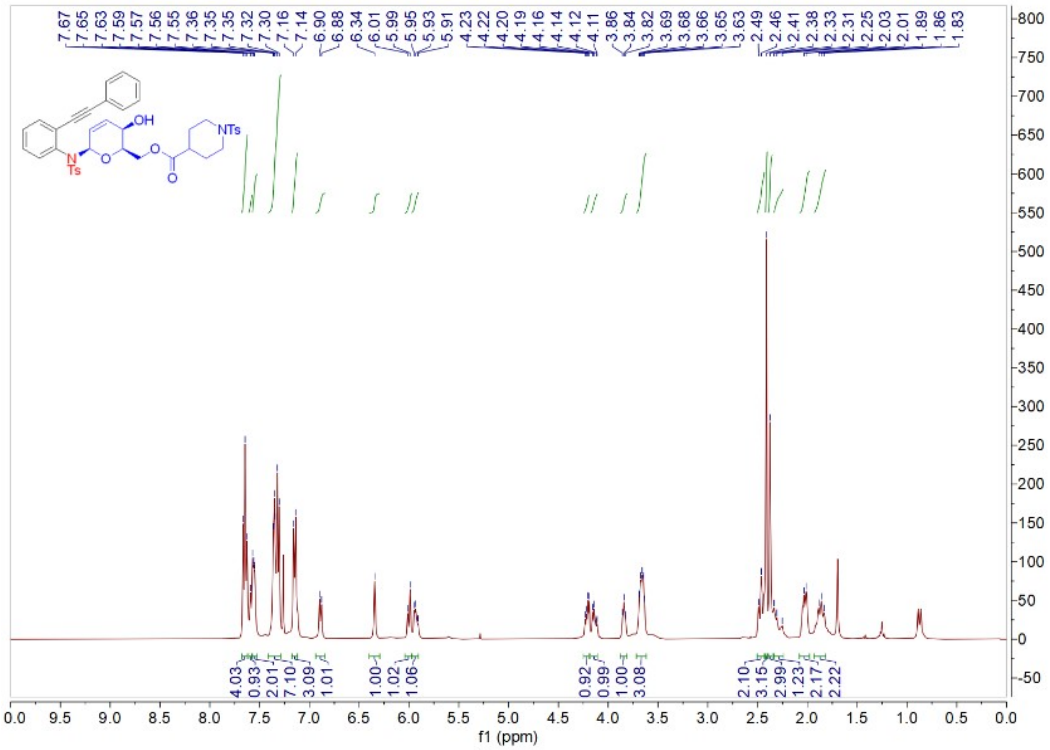
^{13}C NMR spectrum of **29** in $CDCl_3$ (100 MHz).



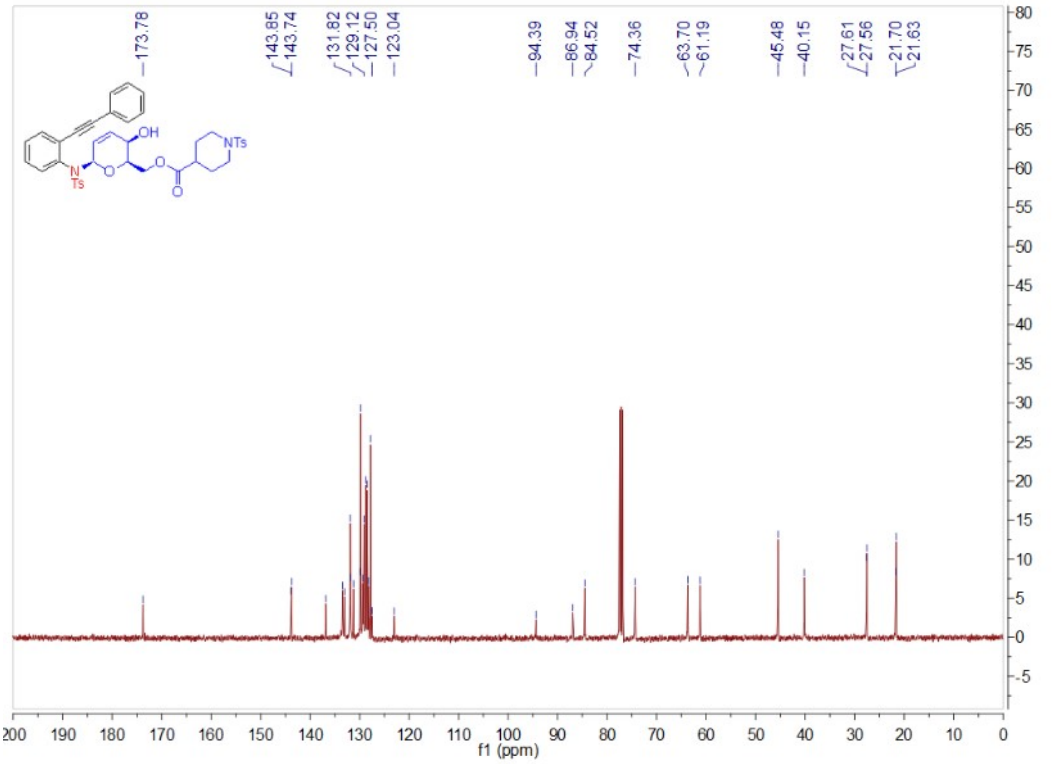
^{1}H NMR spectrum of **30** in $CDCl_3$ (400 MHz).



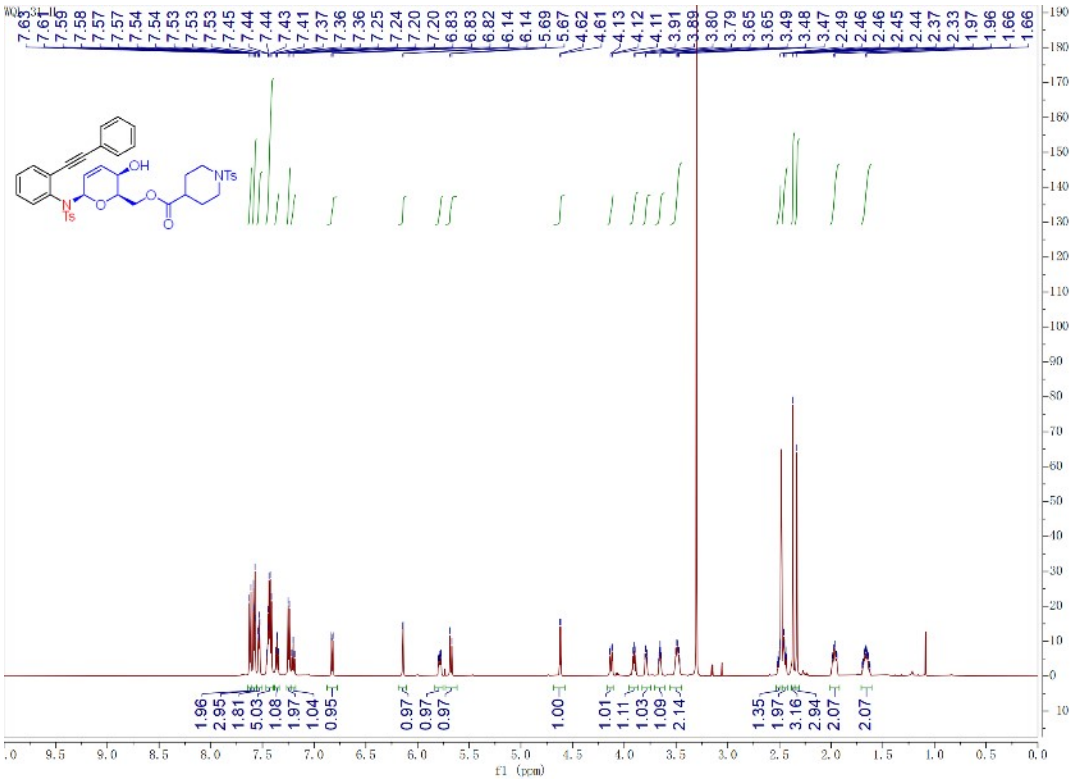
^{13}C NMR spectrum of **30** in $CDCl_3$ (100 MHz).



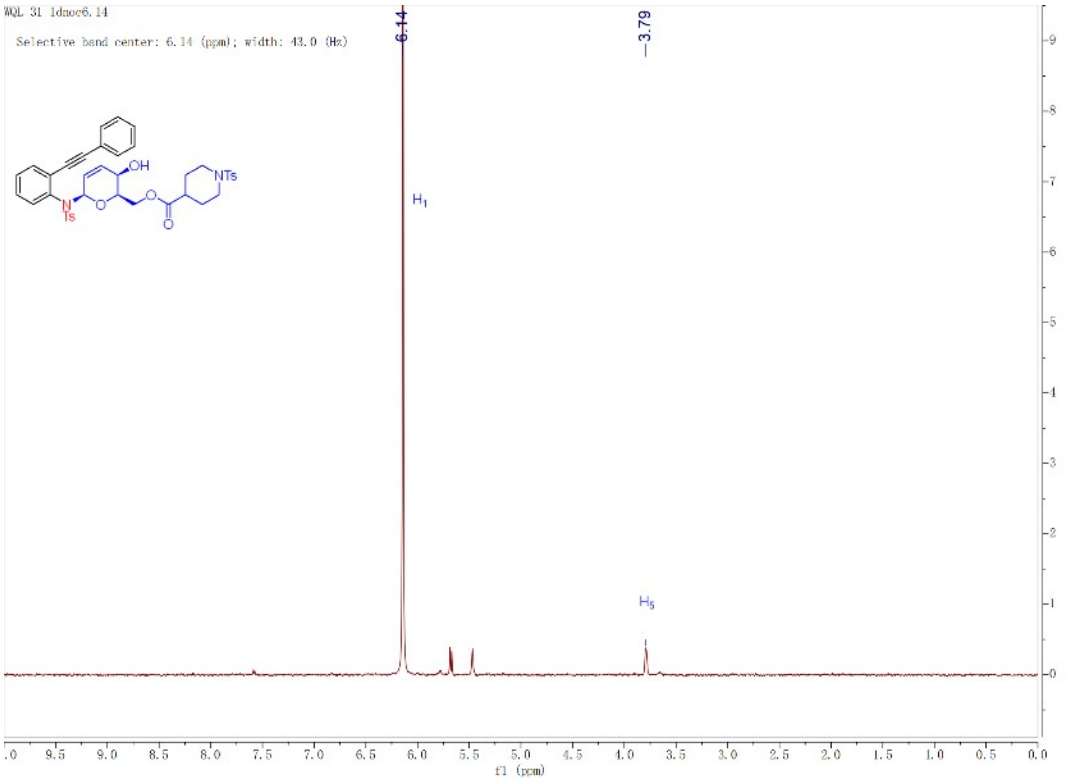
^{1}H NMR spectrum of **31** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **31** in $CDCl_3$ (100 MHz).

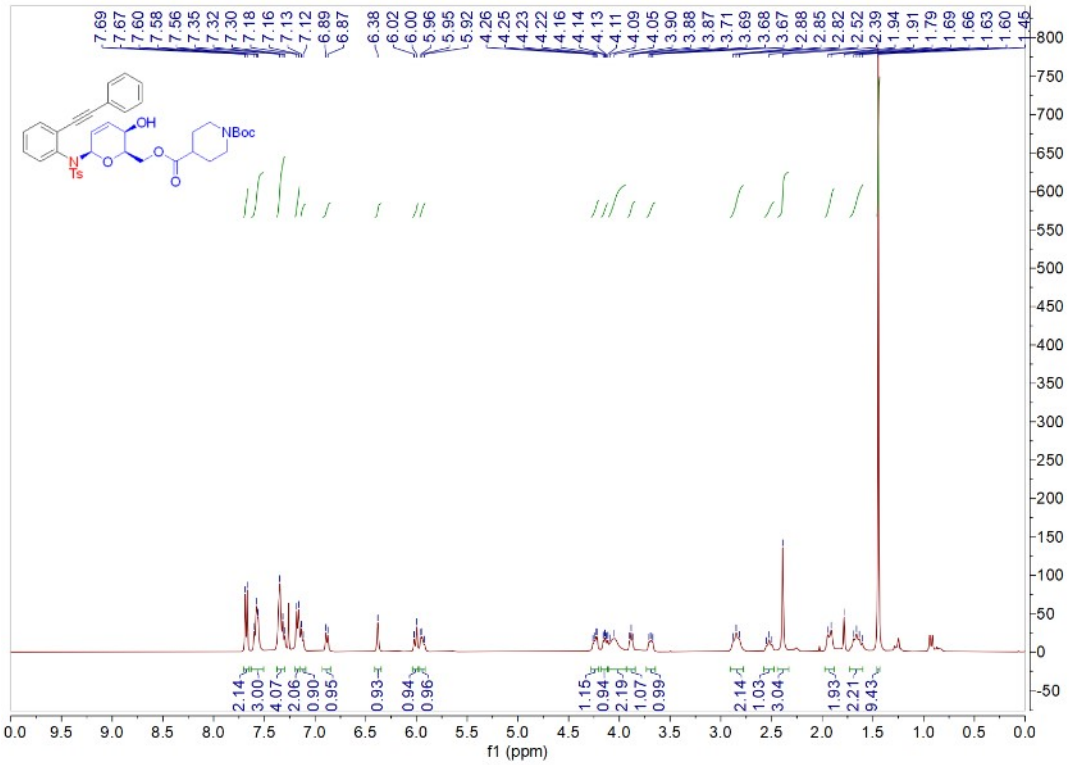


^{1}H NMR spectrum of **31** in DMSO-d_6 (600 MHz).

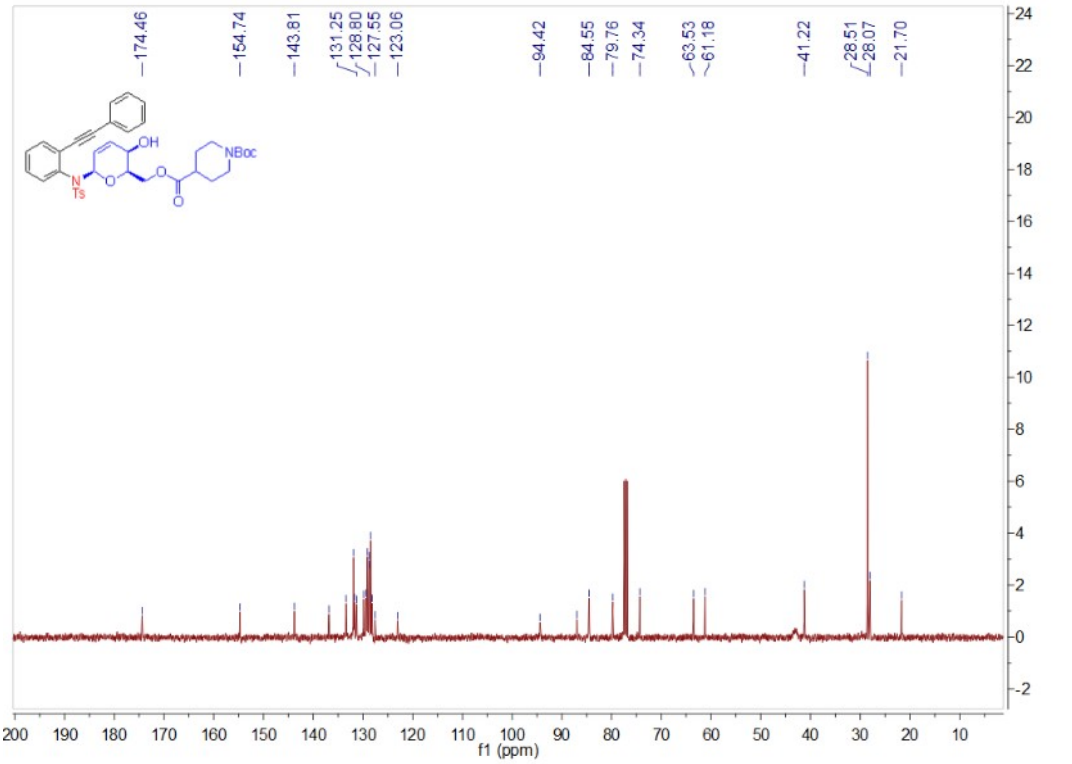


1D NOESY experiment of **31** in DMSO-d_6 (600 MHz).

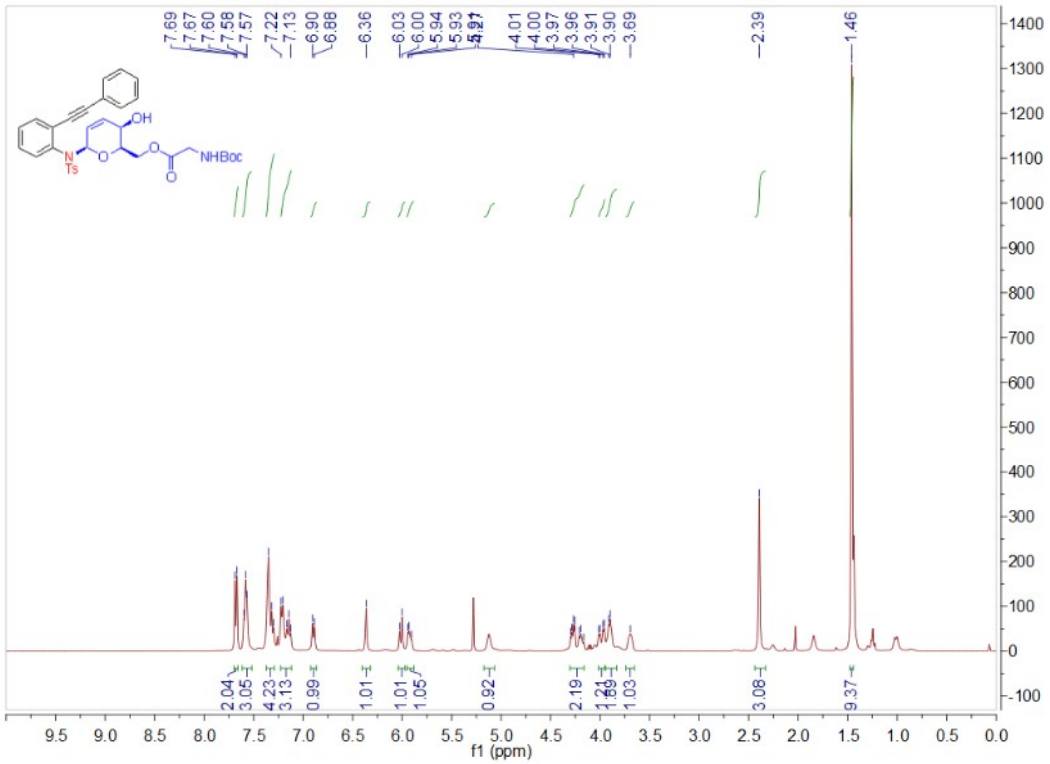
Note: The assignment of β-configuration of compound **31** comes from the observation of nuclear Overhauser effect between H_1 and H_5. Upon irradiation of H_1 (6.14 ppm) significant enhancement of the H_5 (3.79 ppm) signal is observed.



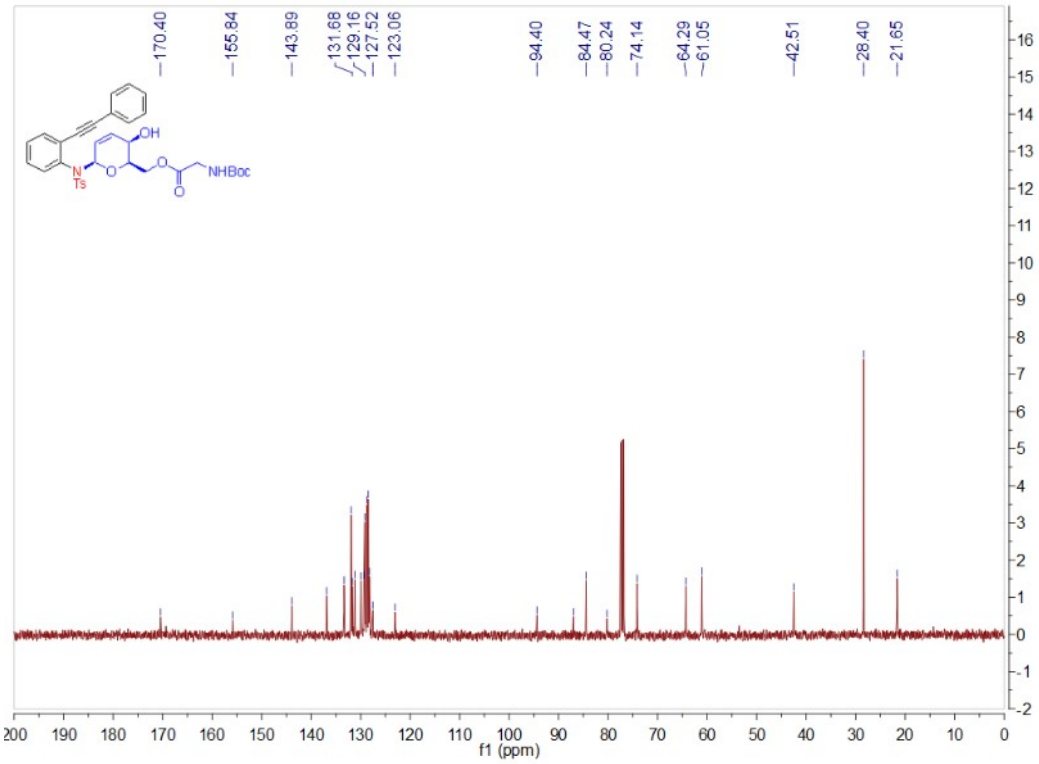
^{1}H NMR spectrum of **32** in $CDCl_3$ (400 MHz).



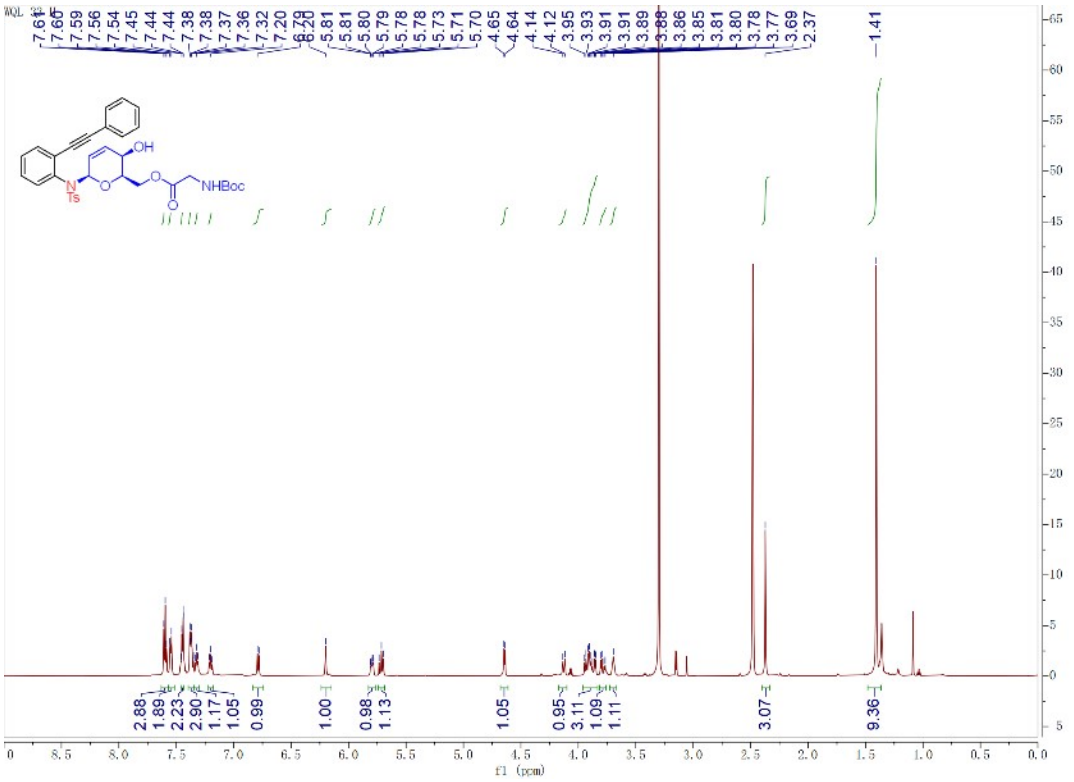
^{13}C NMR spectrum of **32** in $CDCl_3$ (100 MHz).



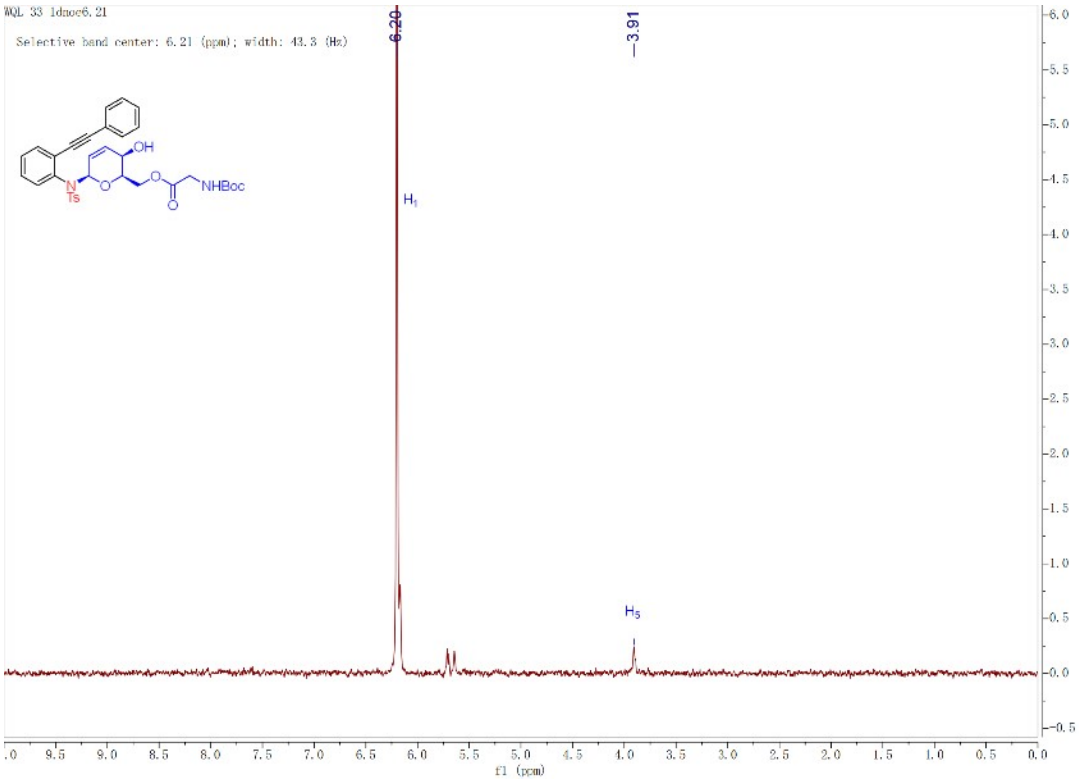
^{1}H NMR spectrum of **33** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **33** in $CDCl_3$ (100 MHz).

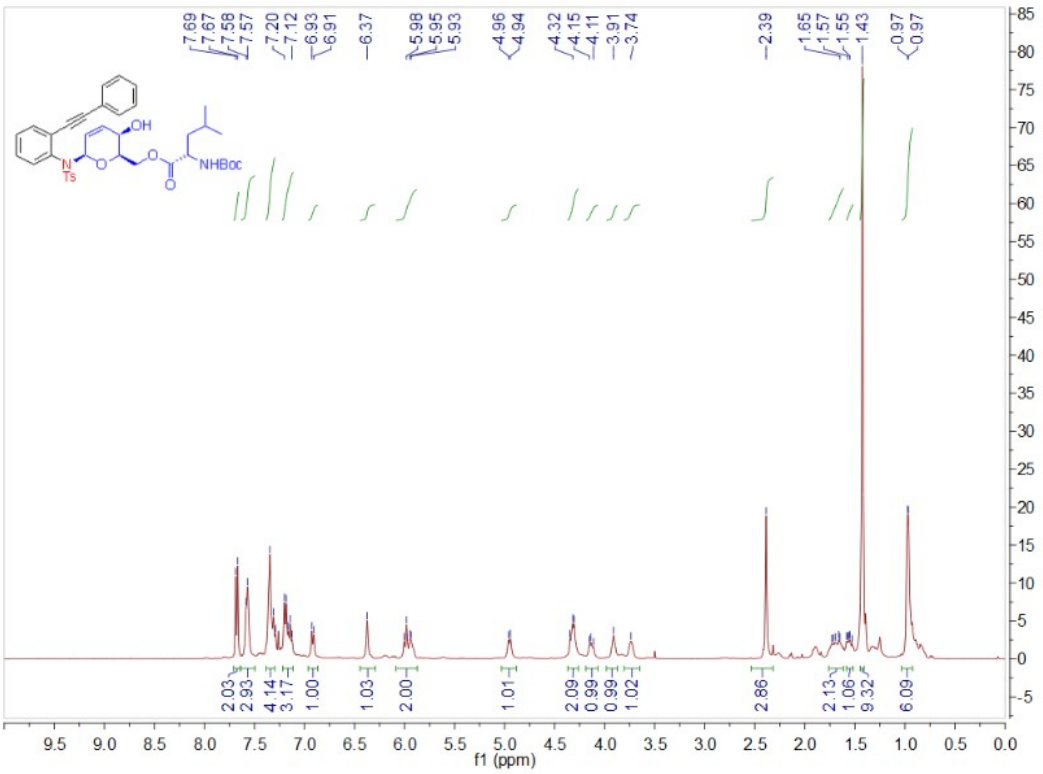


^{1}H NMR spectrum of **33** in DMSO-d_6 (600 MHz).

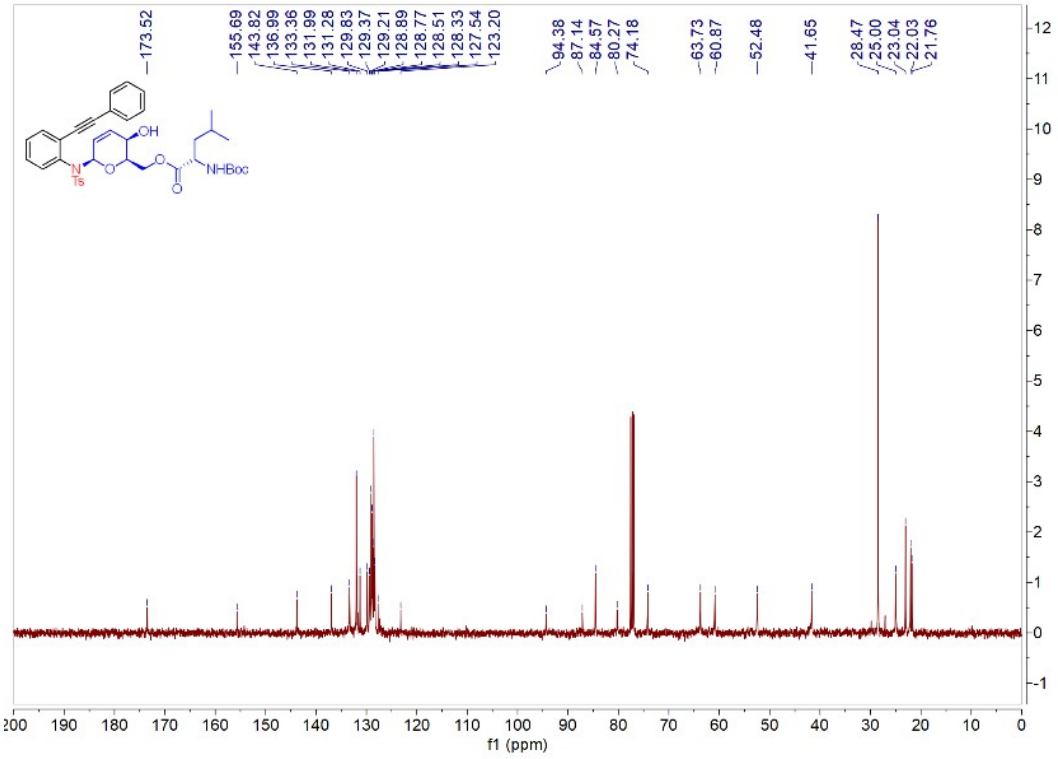


1D NOESY experiment of **33** in DMSO-d_6 (600 MHz).

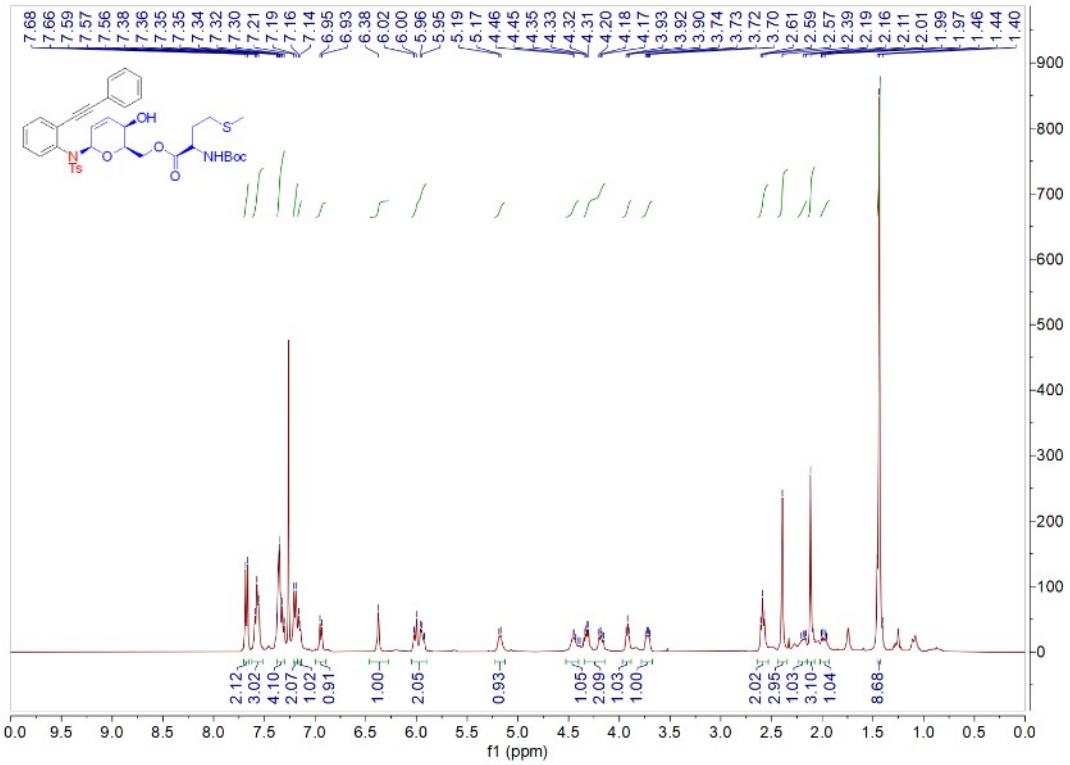
Note: The assignment of β-configuration of compound **33** comes from the observation of nuclear Overhauser effect between H_1 and H_5. Upon irradiation of H_1 (6.20 ppm) significant enhancement of the H_5 (3.91 ppm) signal is observed.



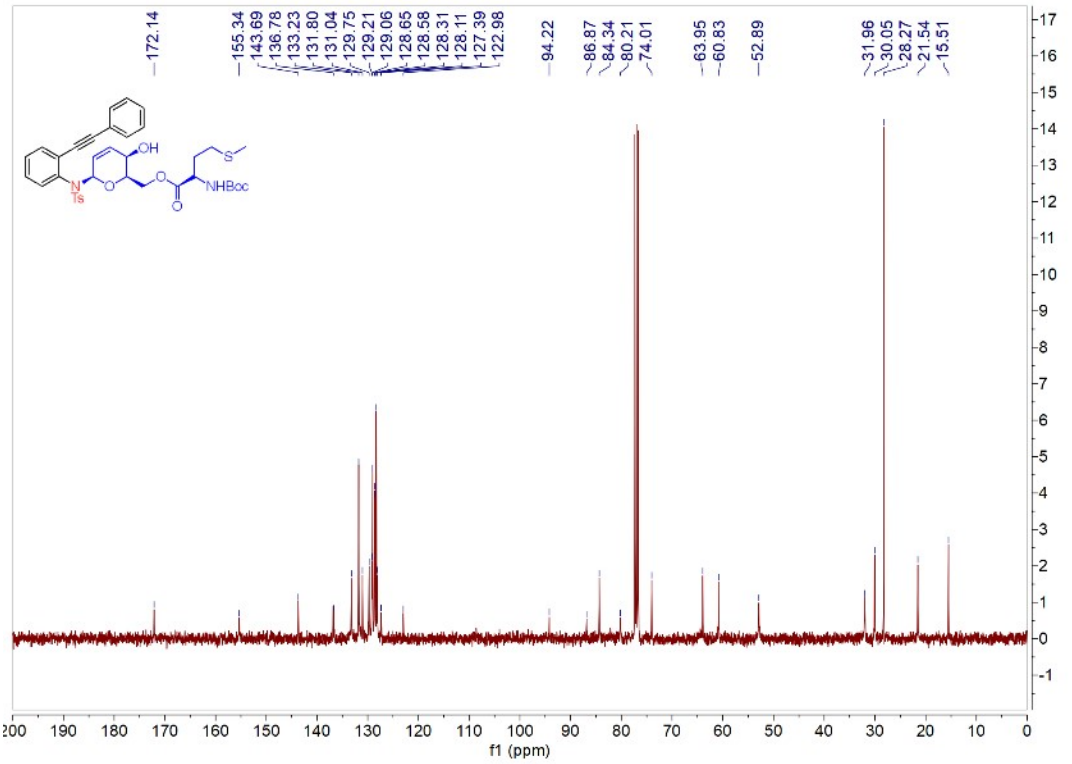
^{1}H NMR spectrum of **34** in $CDCl_3$ (400 MHz).



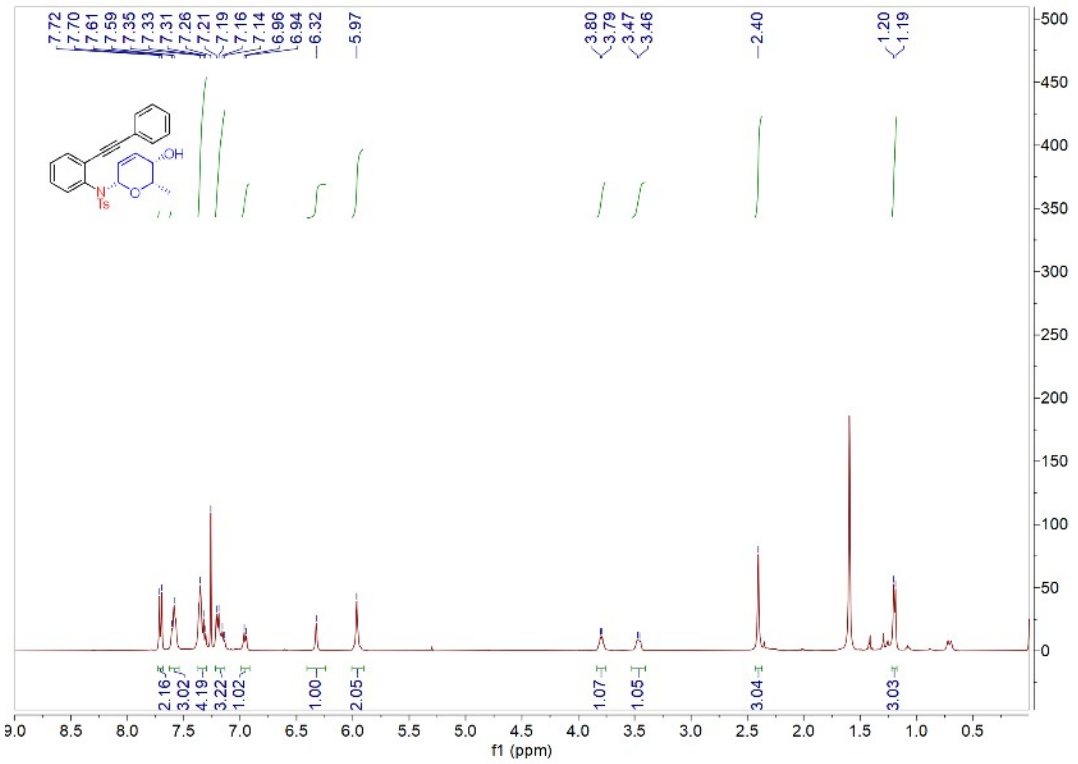
^{13}C NMR spectrum of **34** in $CDCl_3$ (100 MHz).



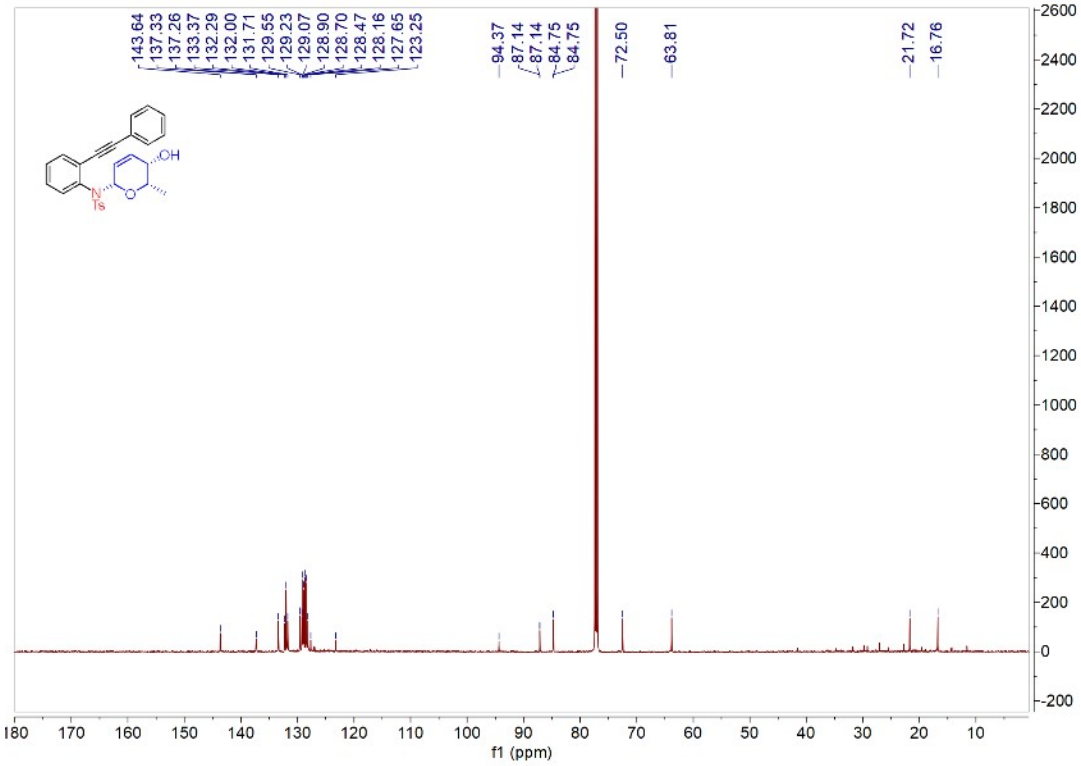
^{1}H NMR spectrum of **35** in $CDCl_3$ (400 MHz).



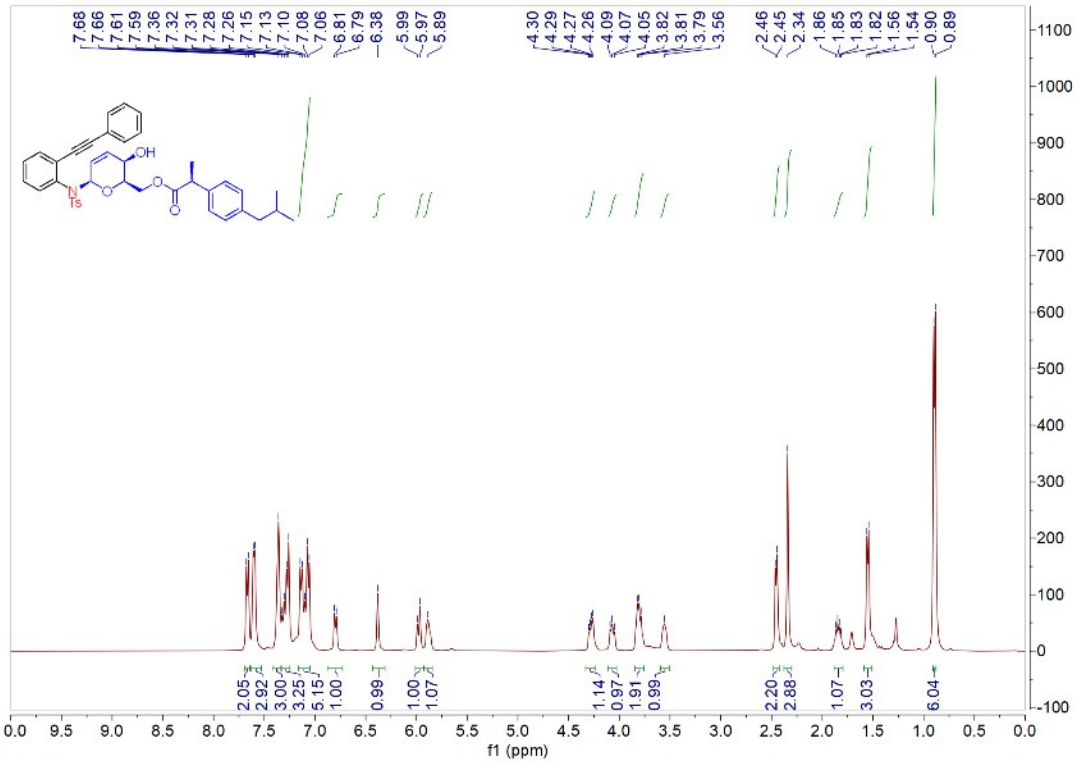
^{13}C NMR spectrum of **35** $CDCl_3$ (100 MHz).



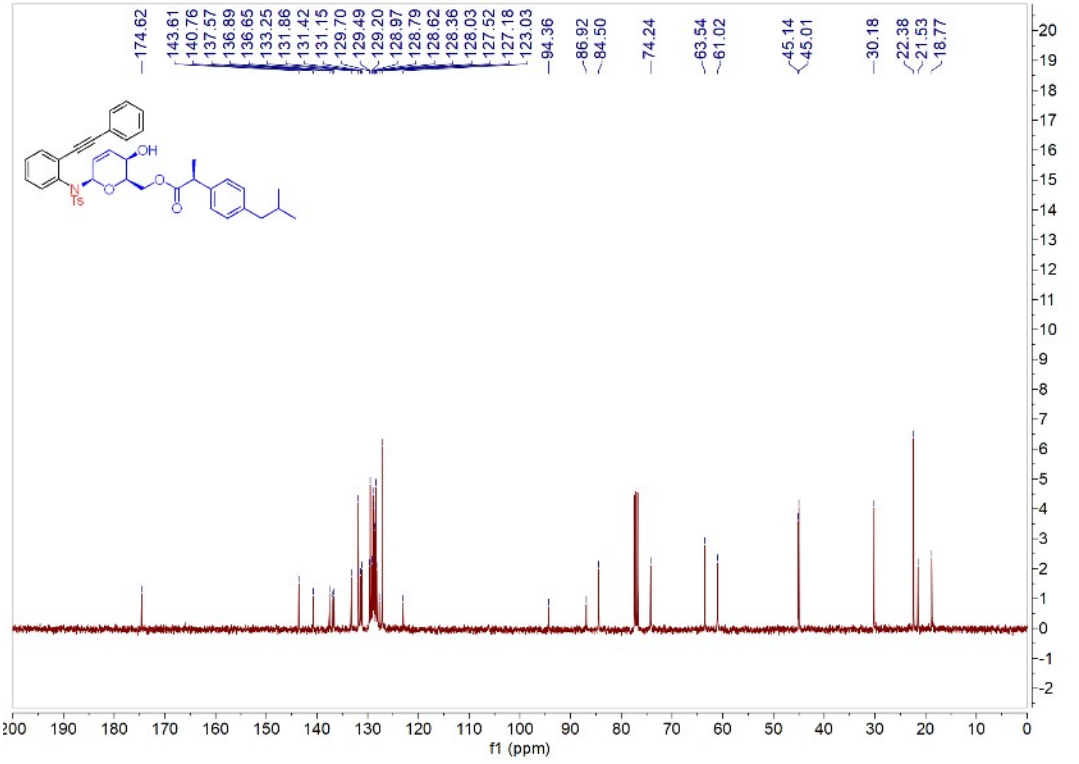
^{1}H NMR spectrum of **36** in $CDCl_3$ (400 MHz).



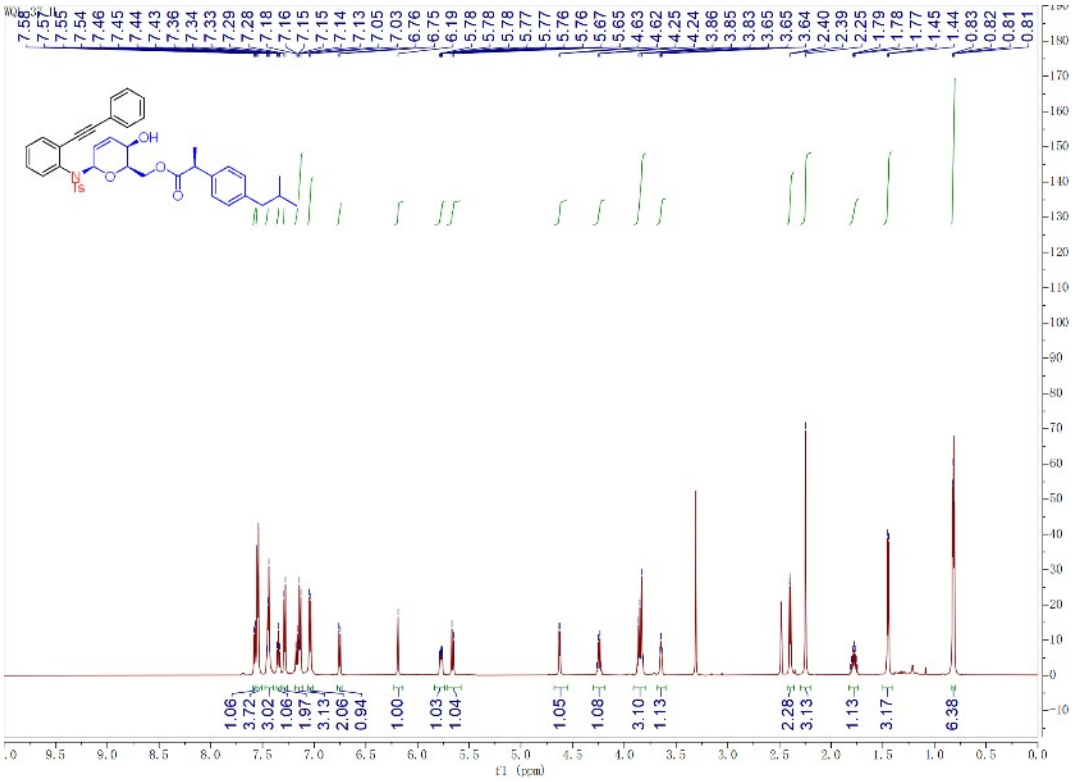
^{13}C NMR spectrum of **36** in $CDCl_3$ (150 MHz).



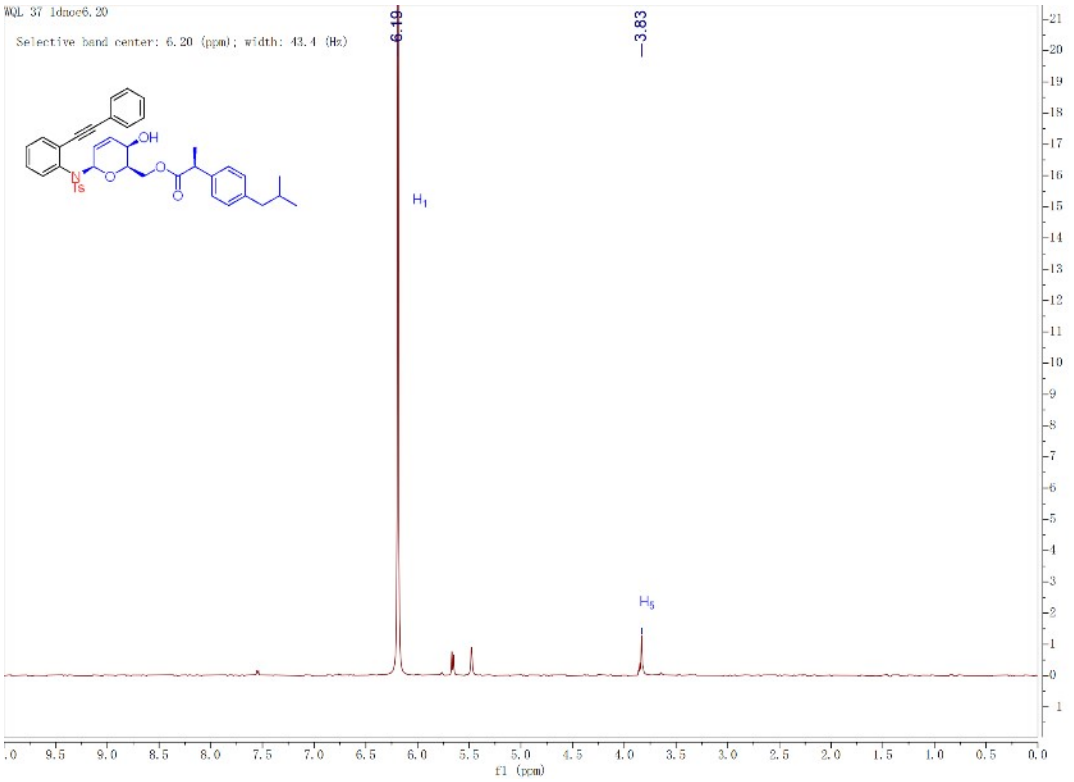
^{1}H NMR spectrum of **37** in $CDCl_3$ (400 MHz).



^{13}C NMR spectrum of **37** in $CDCl_3$ (100 MHz).

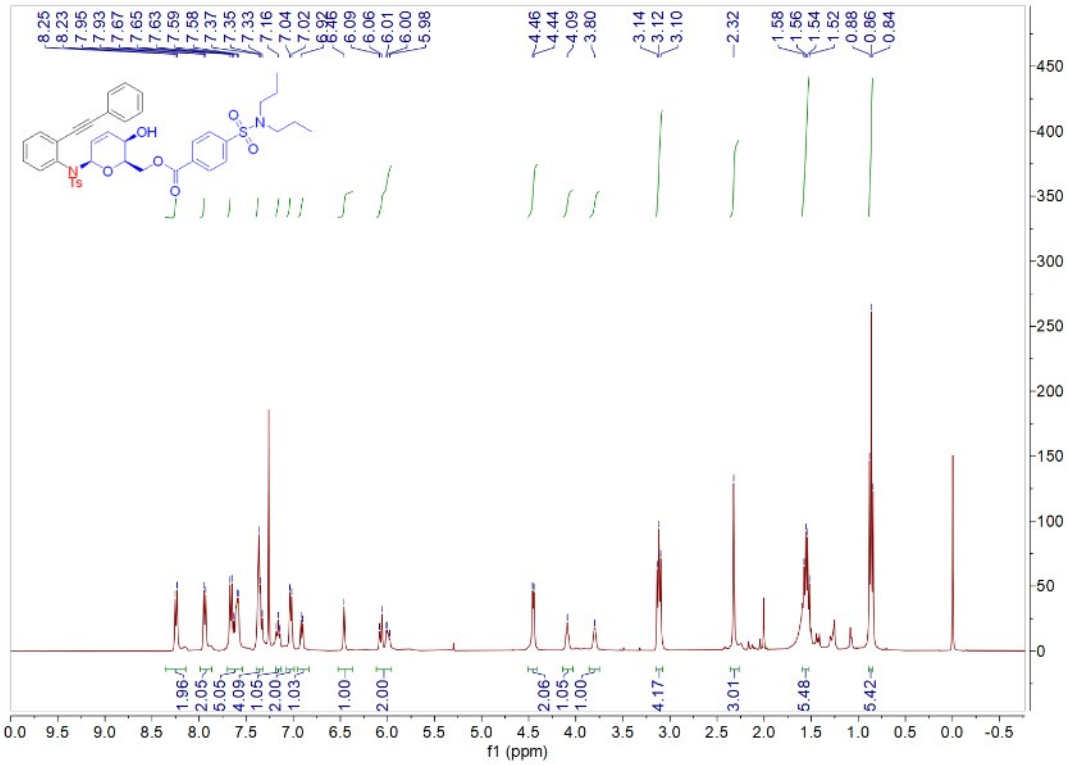


^{1}H NMR spectrum of **37** in DMSO-d_6 (600 MHz).

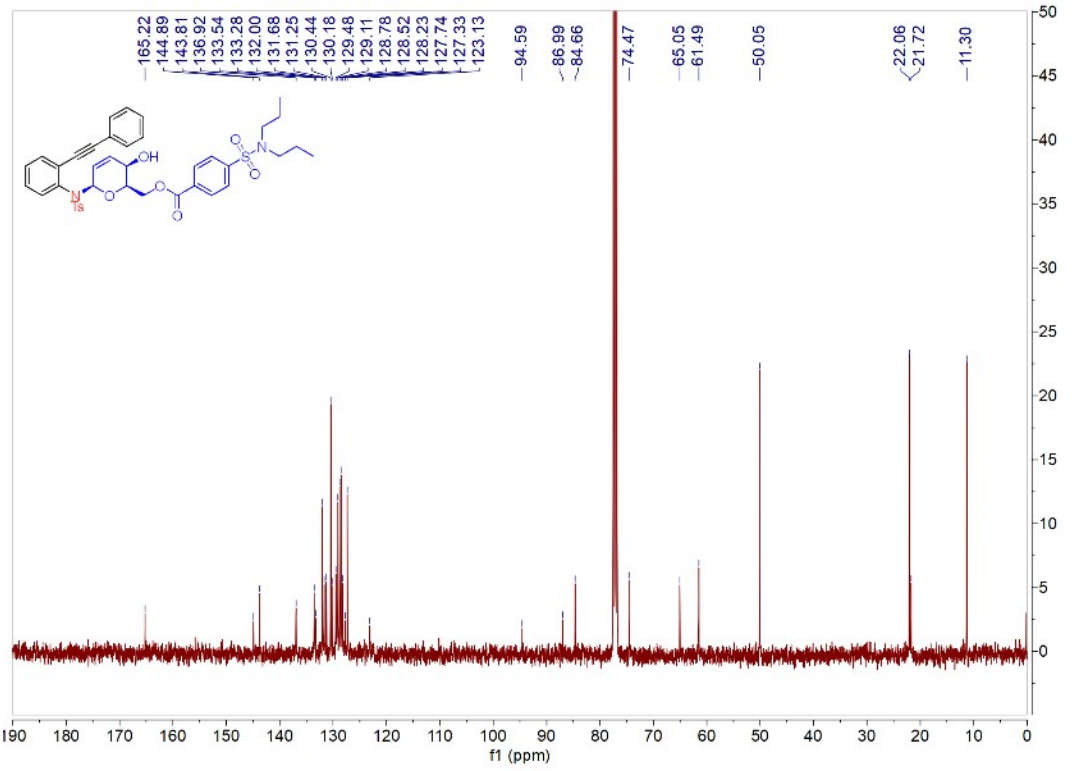


1D NOESY experiment of **37** in DMSO-d_6 (600 MHz).

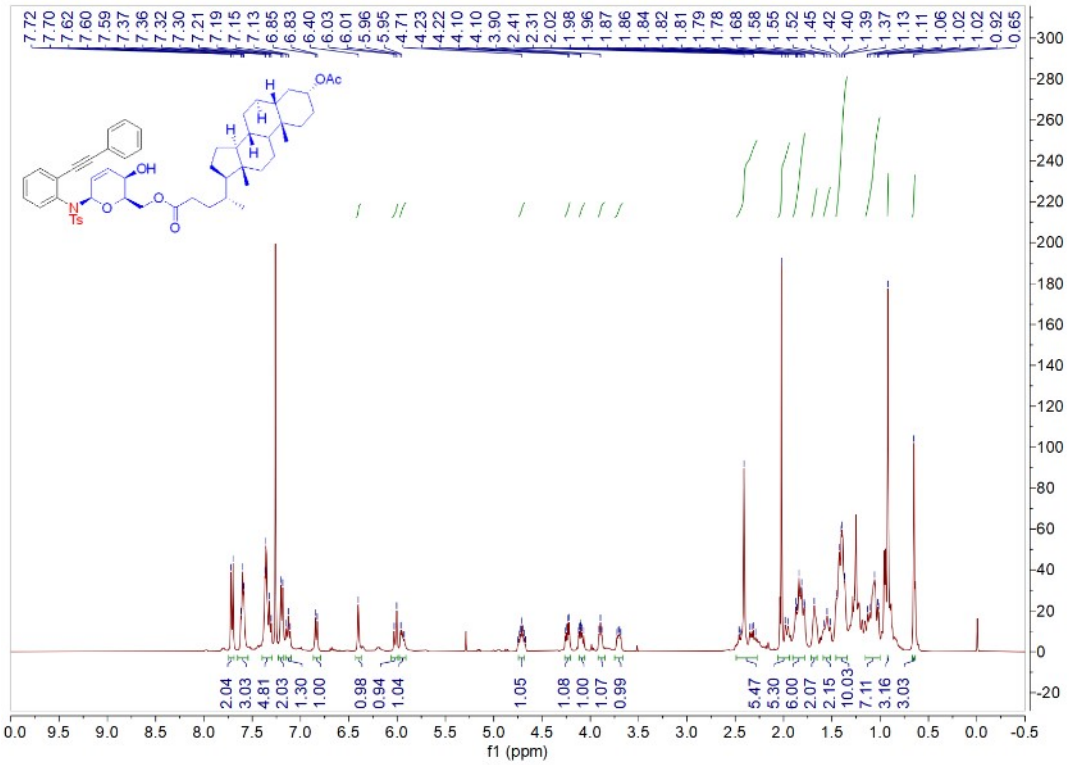
Note: The assignment of β-configuration of compound **37** comes from the observation of nuclear Overhauser effect between H_1 and H_5. Upon irradiation of H_1 (6.19 ppm) significant enhancement of the H_5 (3.83 ppm) signal is observed.



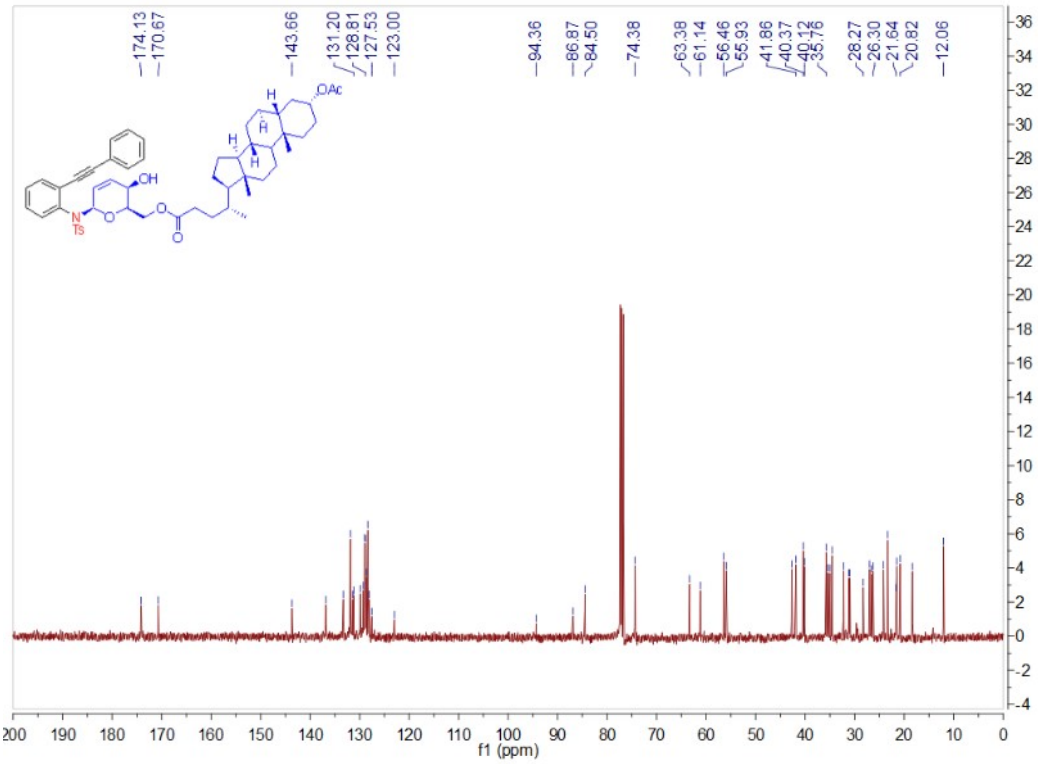
^{1}H NMR spectrum of **38** in $CDCl_3$ (400 MHz).



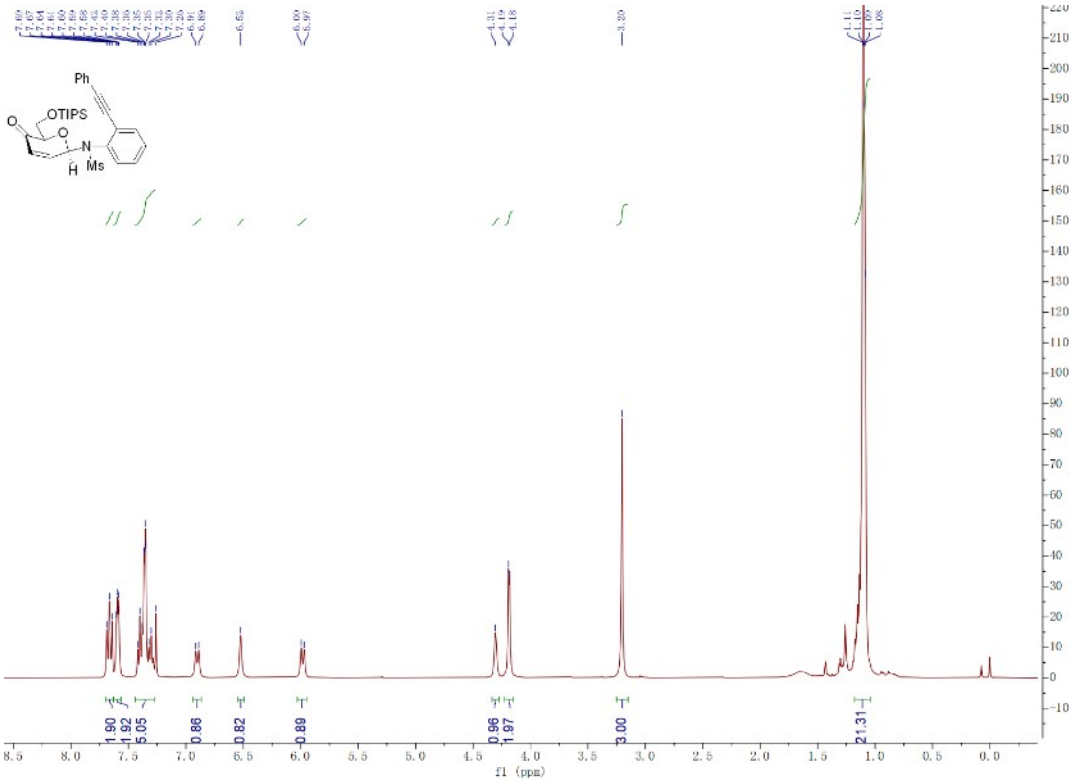
^{13}C NMR spectrum of **38** in $CDCl_3$ (100 MHz).



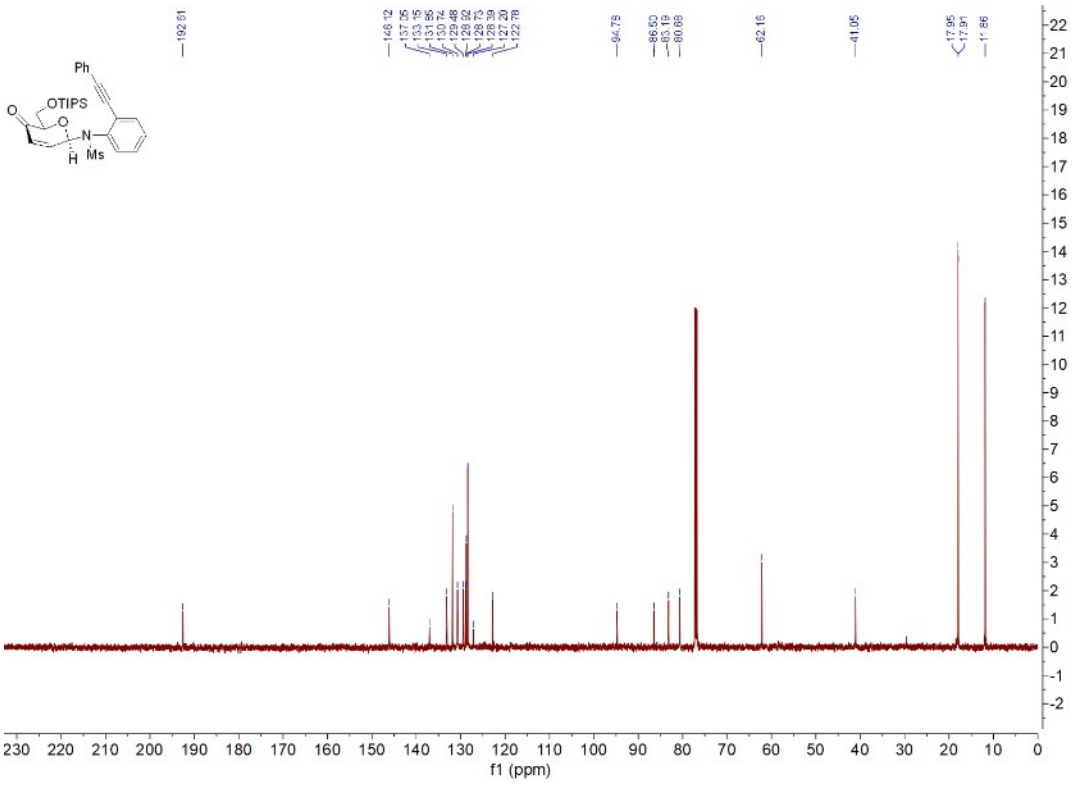
^{1}H NMR spectrum of **39** in $CDCl_3$ (400 MHz).



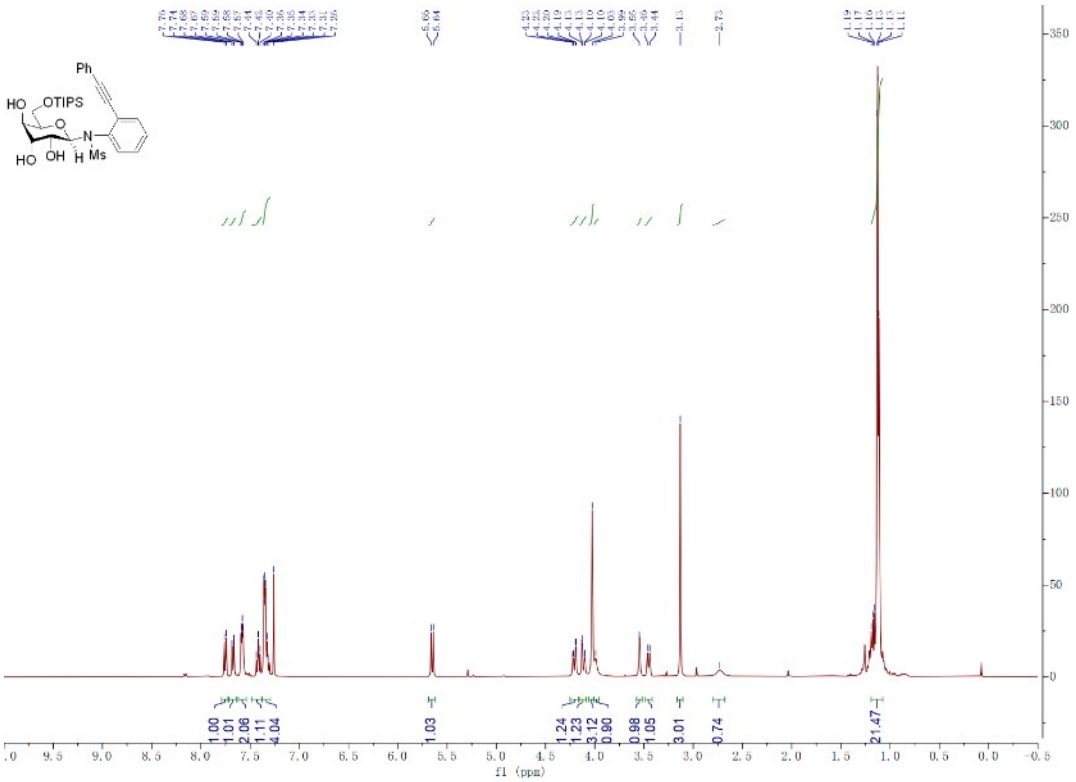
^{13}C NMR spectrum of **39** in $CDCl_3$ (100 MHz).



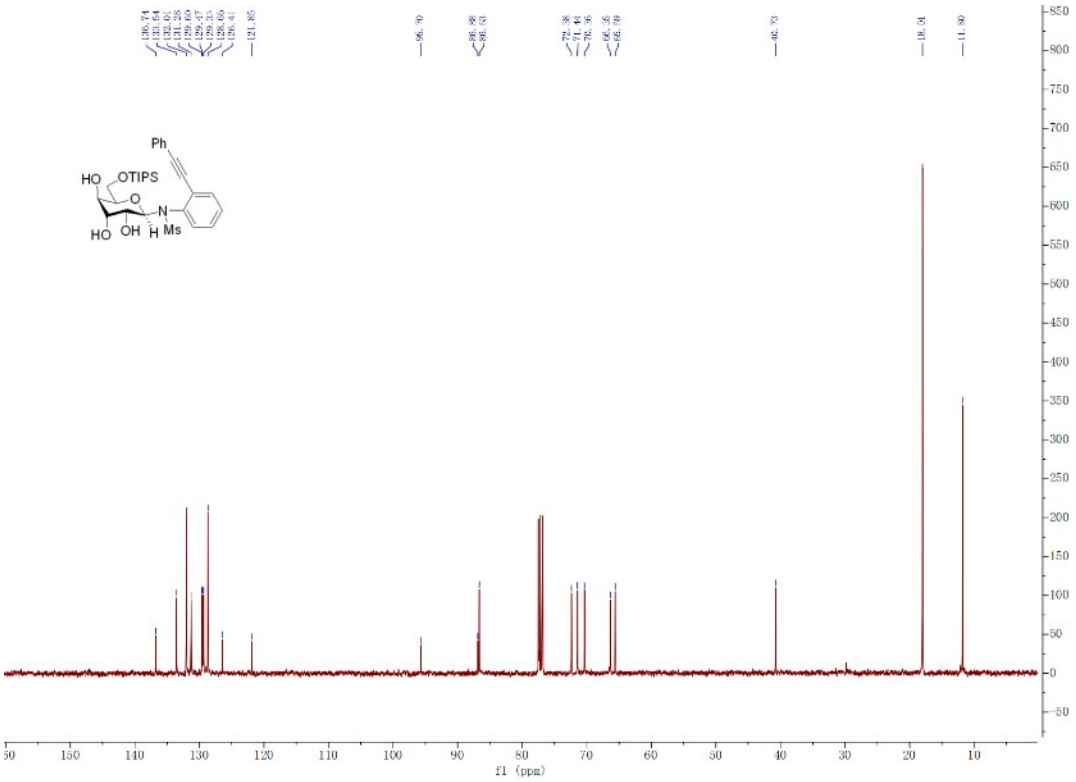
^{1}H NMR spectrum of **40** in $CDCl_3$ (400 MHz).



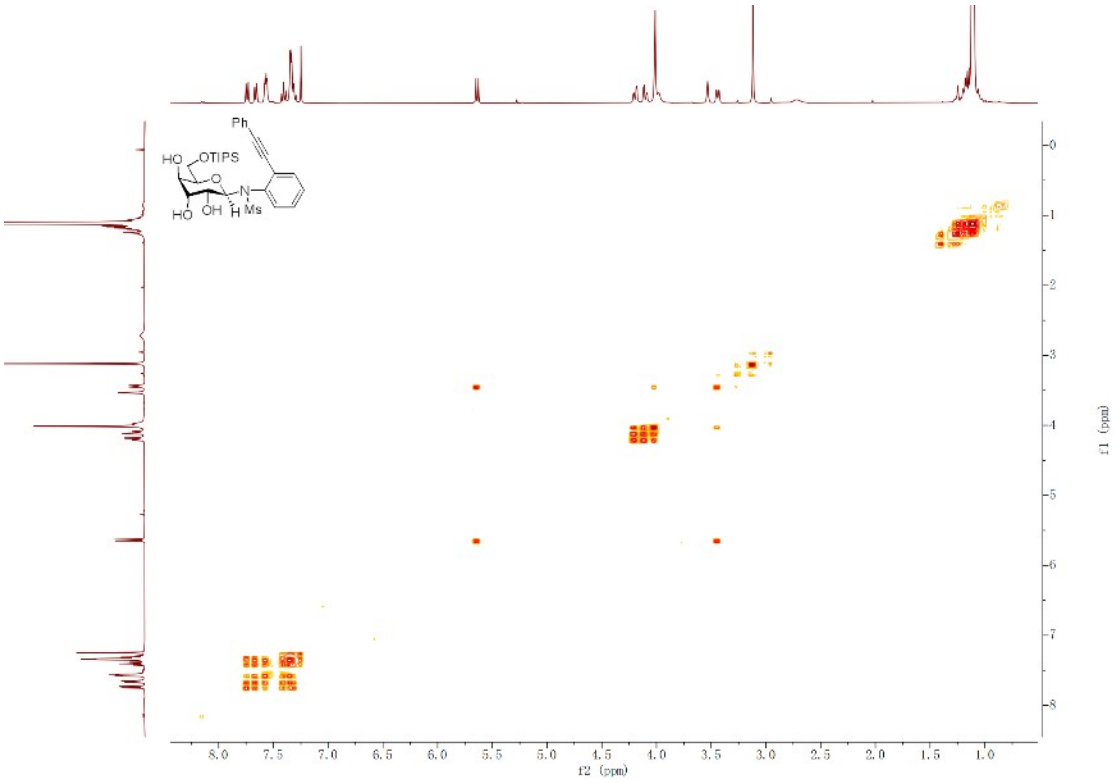
^{13}C NMR spectrum of **40** in $CDCl_3$ (150 MHz).



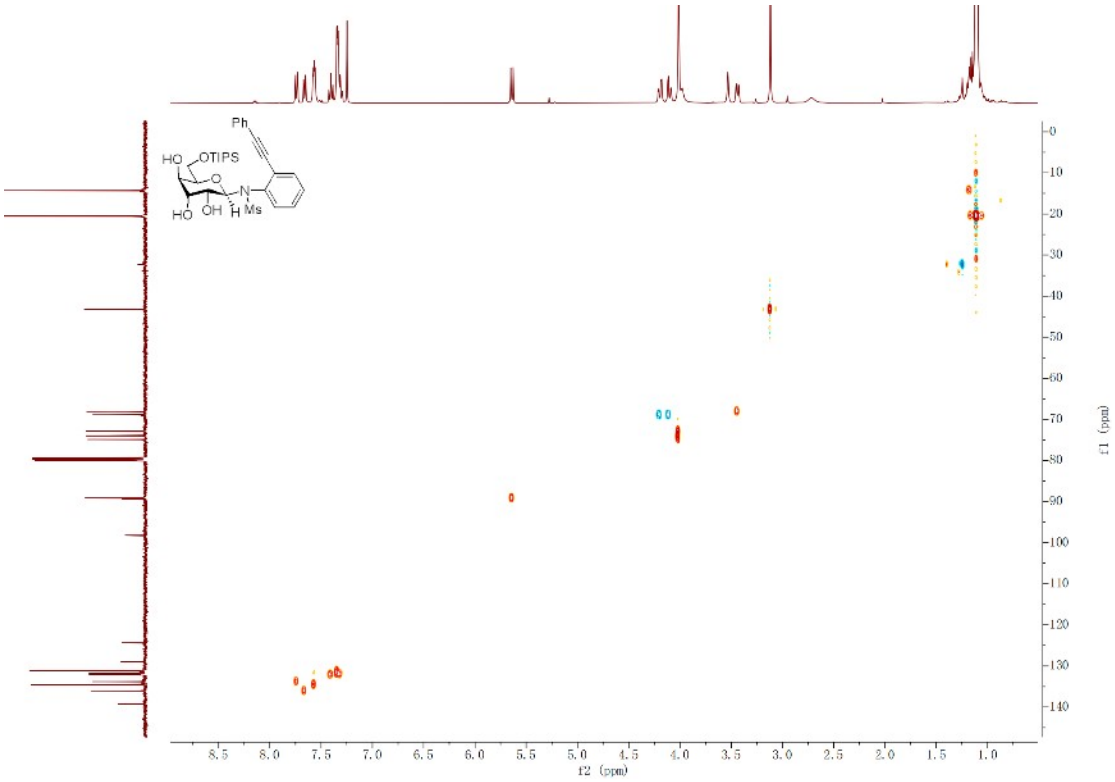
^{1}H NMR spectrum of **41** in $CDCl_3$ (400 MHz).



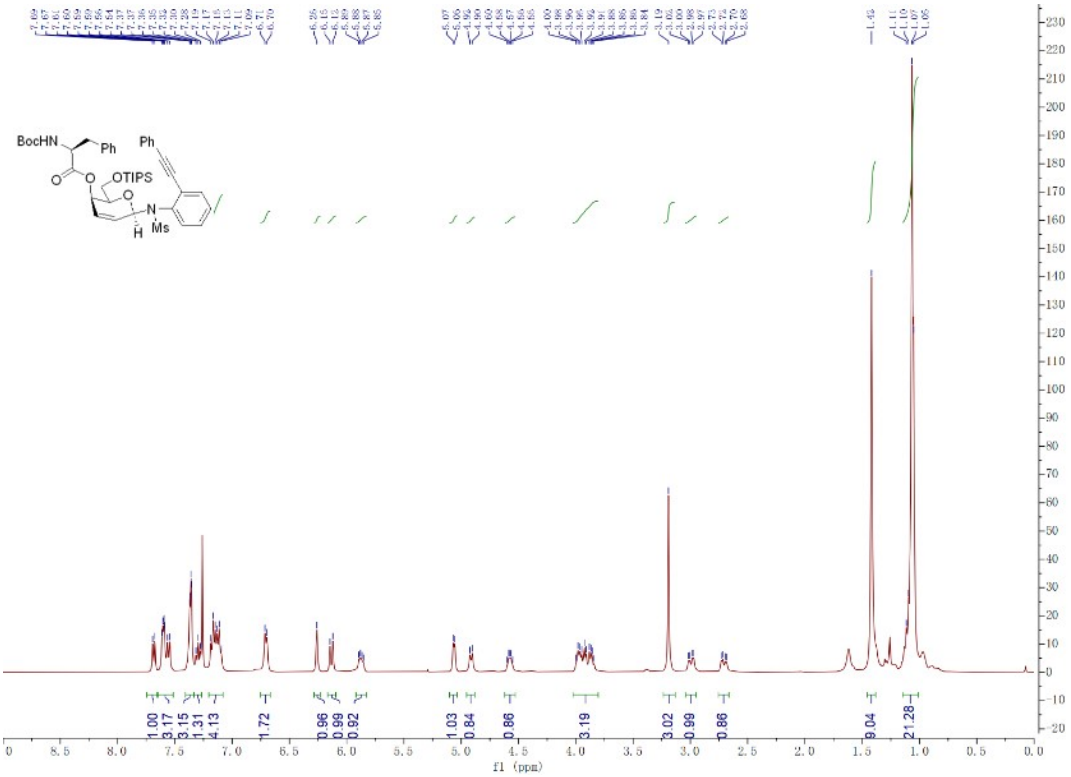
^{13}C NMR spectrum of **41** in $CDCl_3$ (100 MHz).



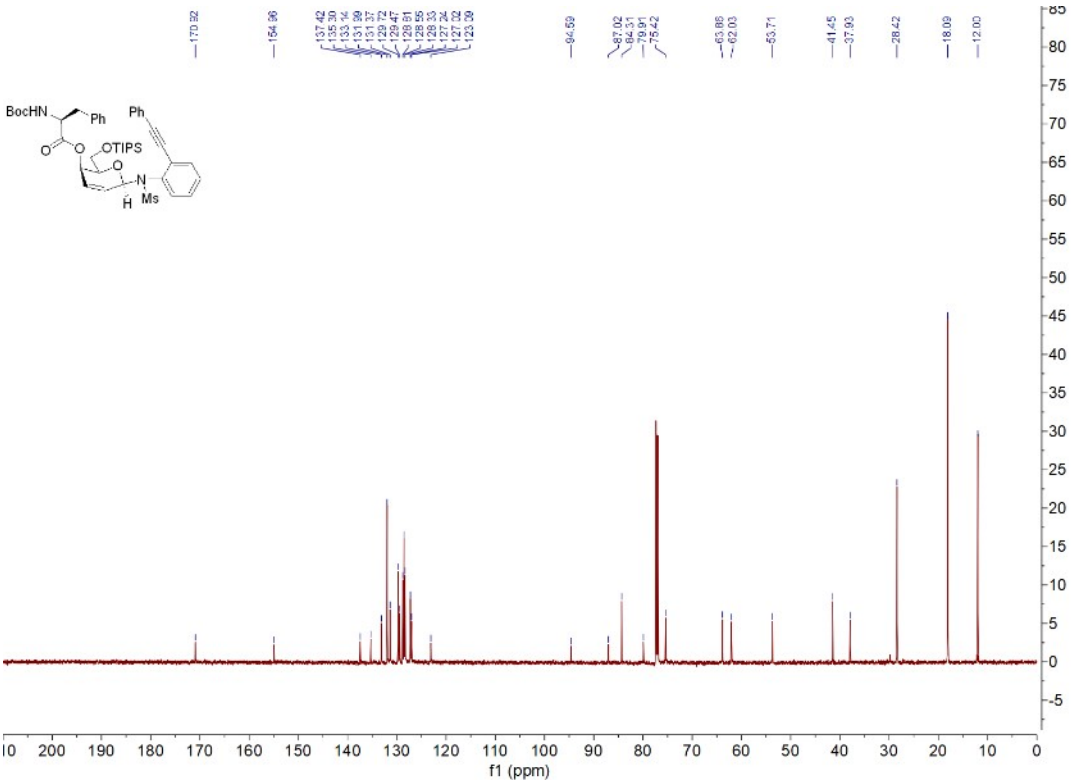
COSY spectrum of **41** in $CDCl_3$ (600 MHz).



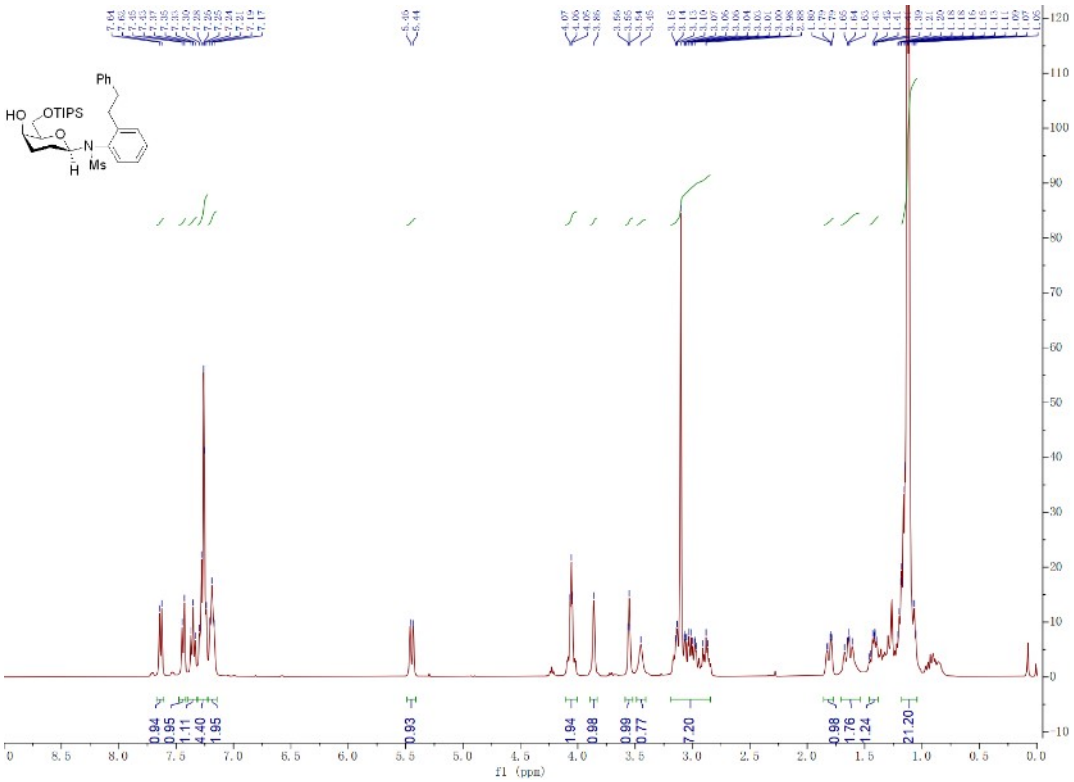
HSQC spectrum of **41** in $CDCl_3$ (600 MHz).



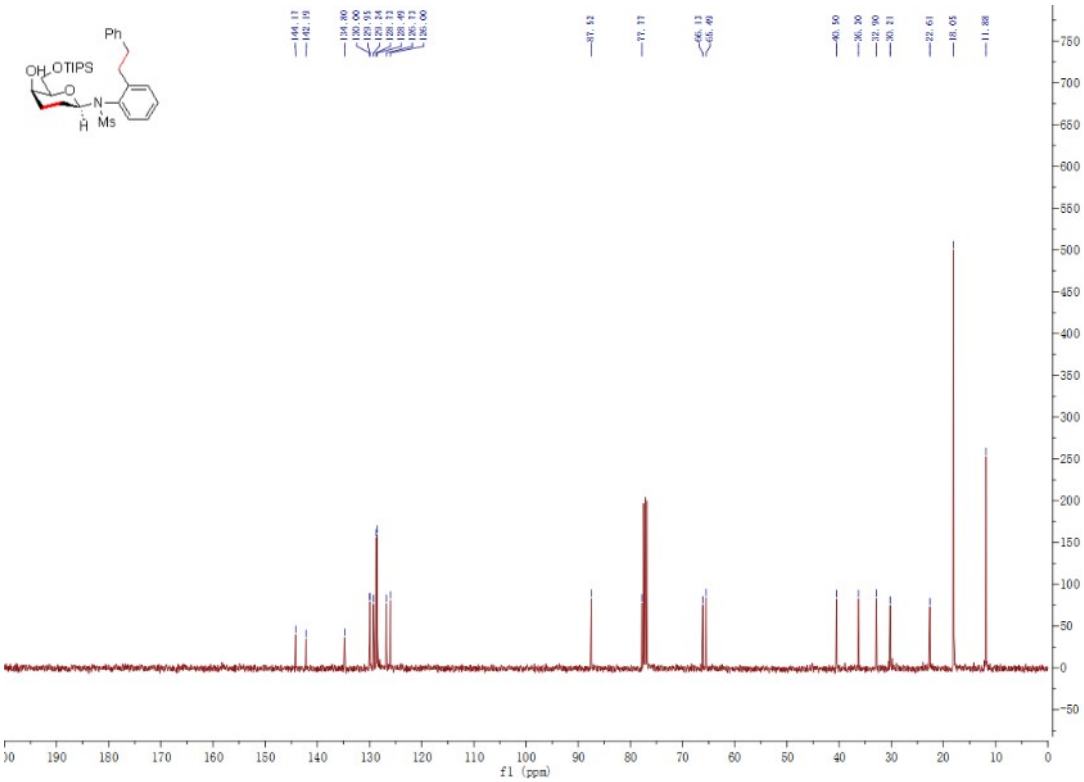
^{1}H NMR spectrum of **42** in $CDCl_3$ (400 MHz).



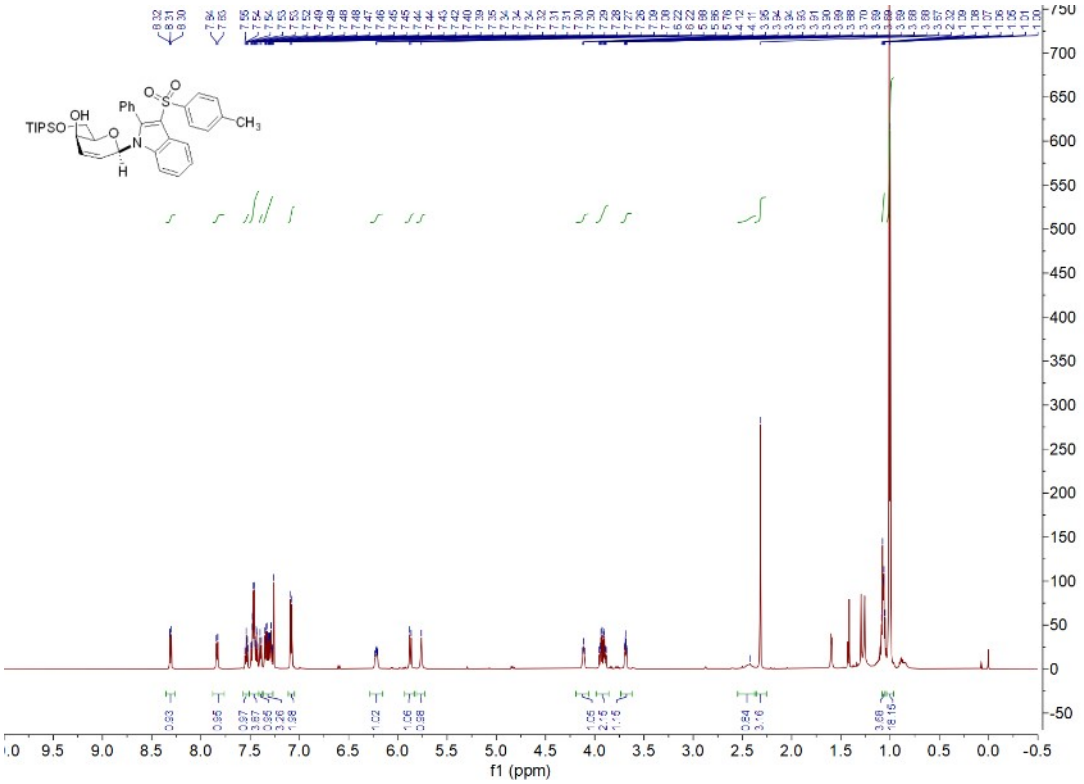
^{13}C NMR spectrum of **42** in $CDCl_3$ (100 MHz).



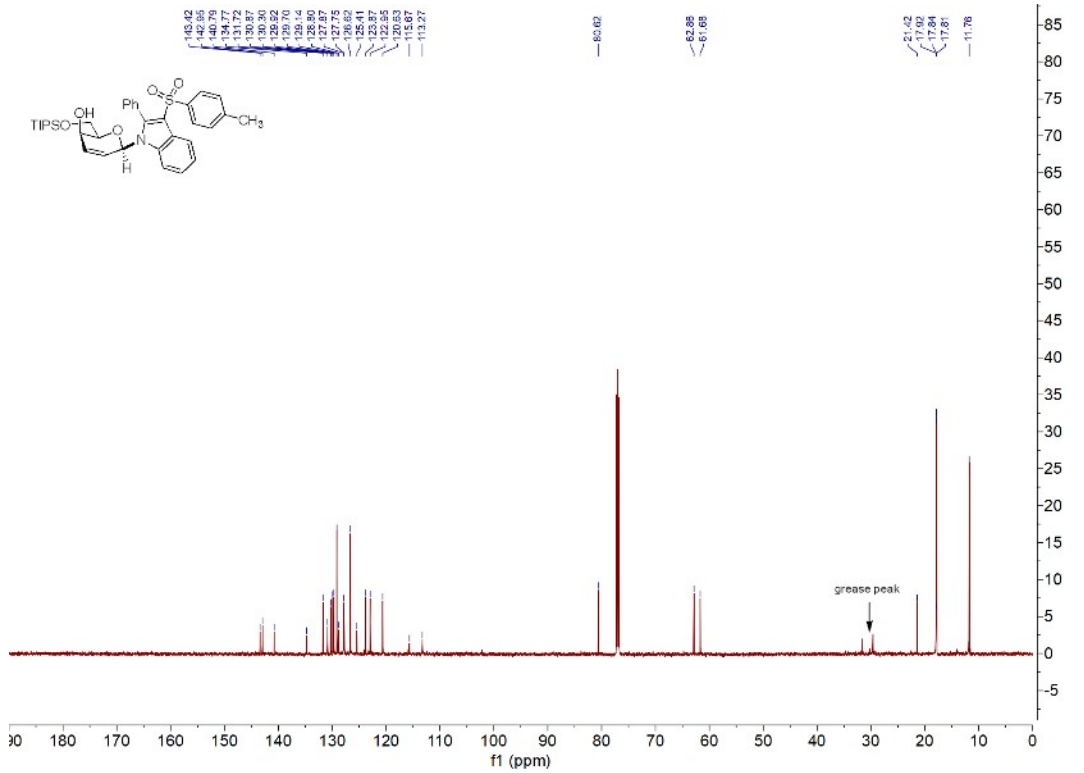
^{1}H NMR spectrum of **43** in $CDCl_3$ (400 MHz).



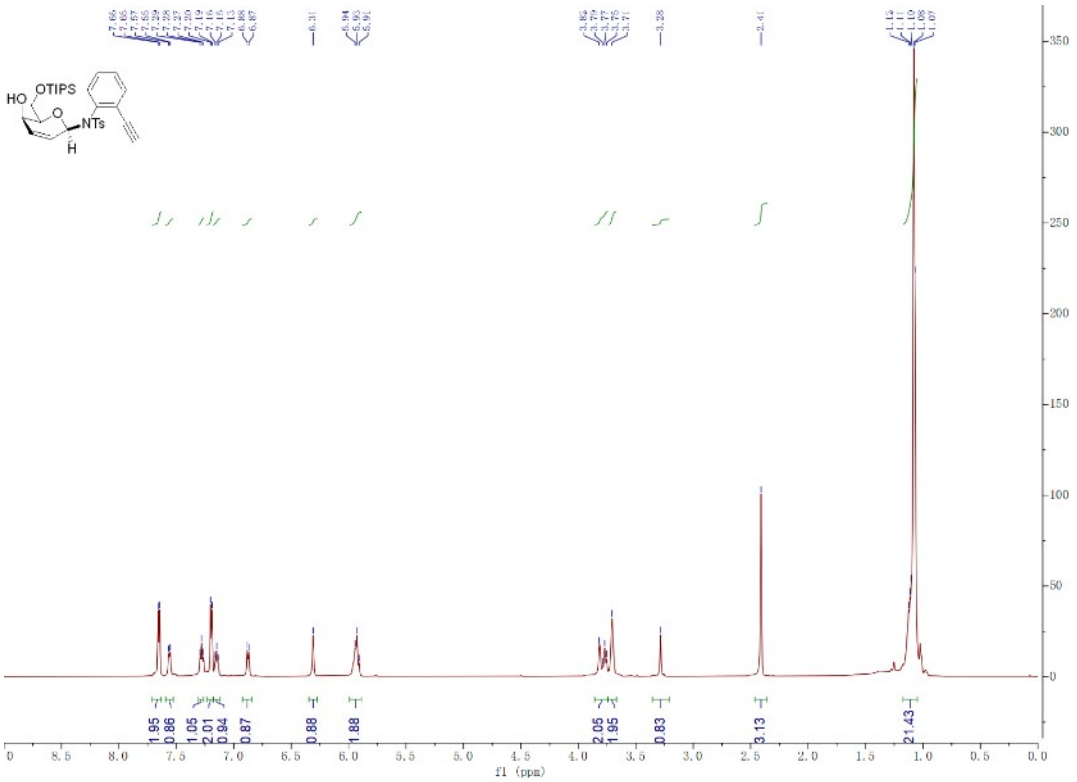
^{13}C NMR spectrum of **43** in $CDCl_3$ (100 MHz).



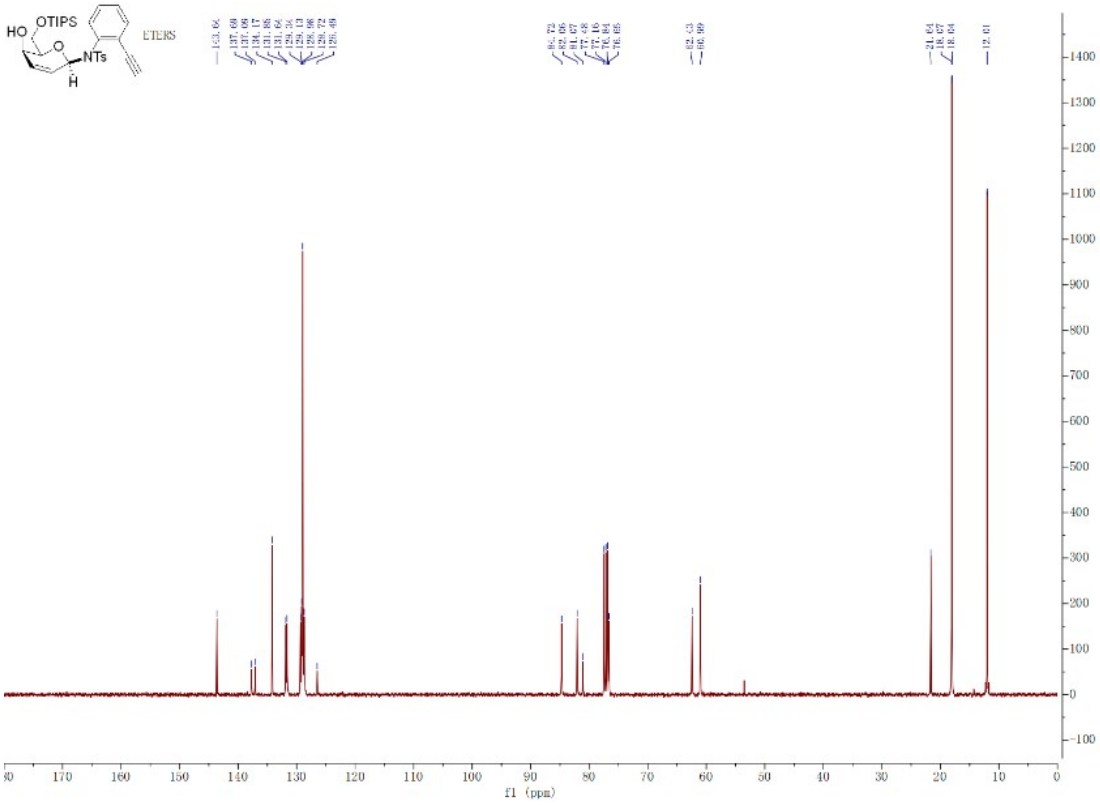
^{1}H NMR spectrum of **44** in $CDCl_3$ (600 MHz).



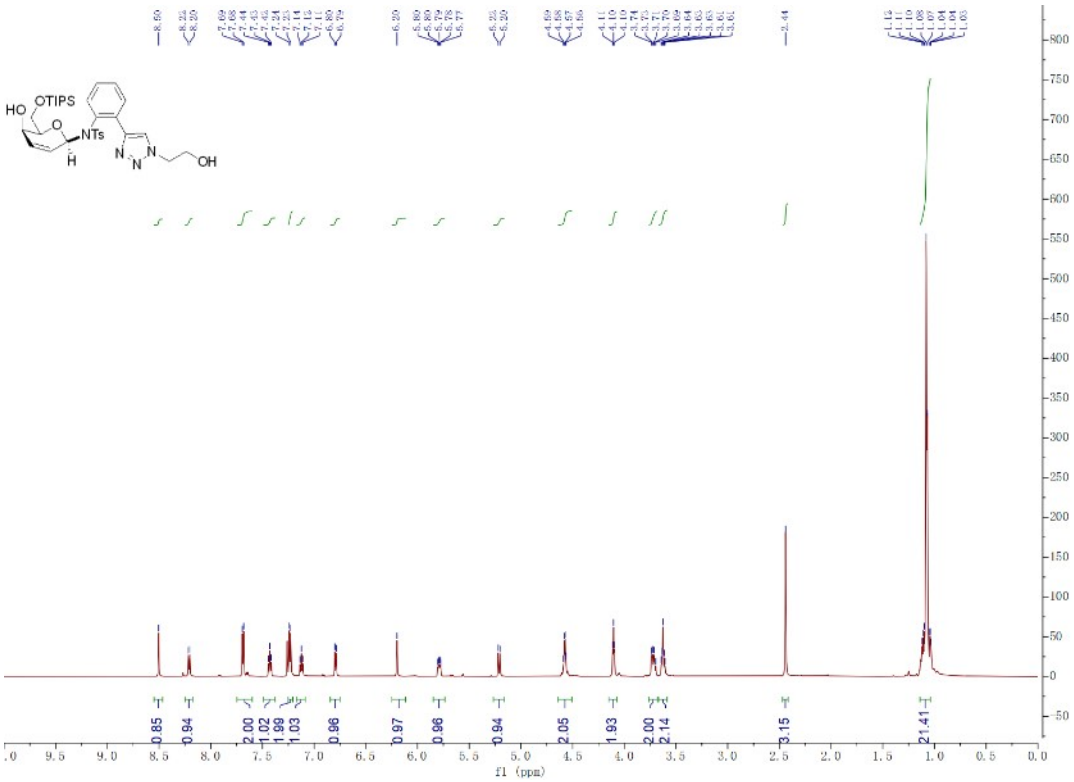
^{13}C NMR spectrum of **44** in $CDCl_3$ (150 MHz).



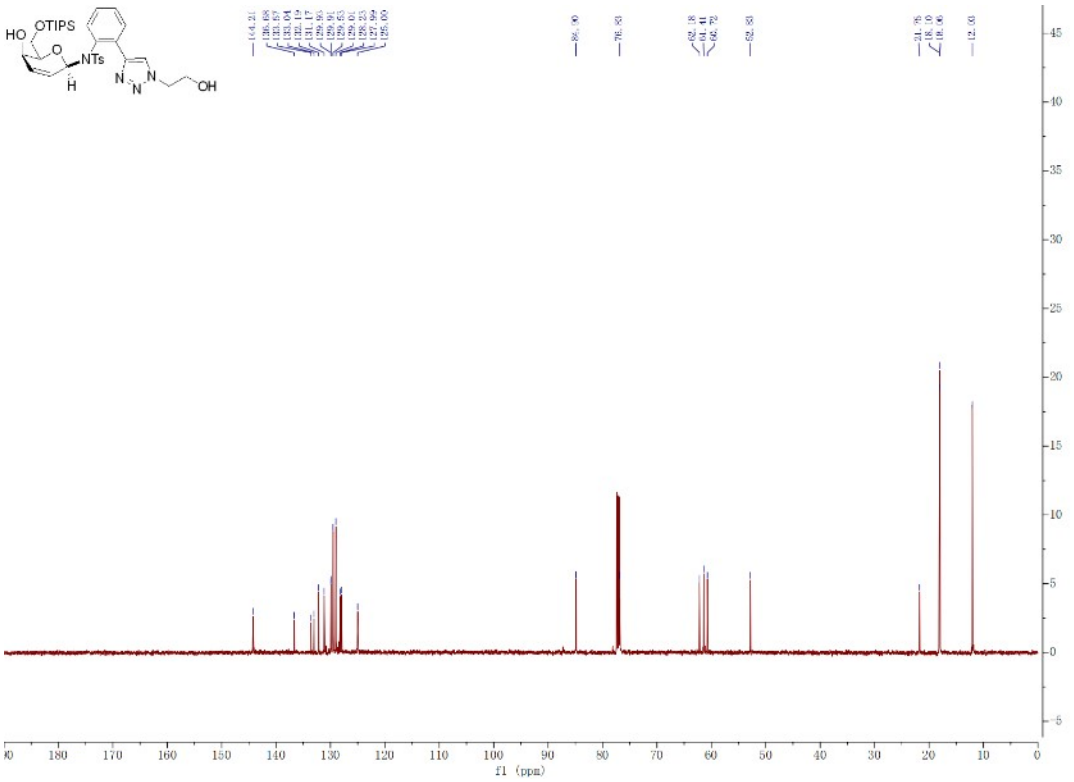
^{1}H NMR spectrum of **45** in $CDCl_3$ (600 MHz).



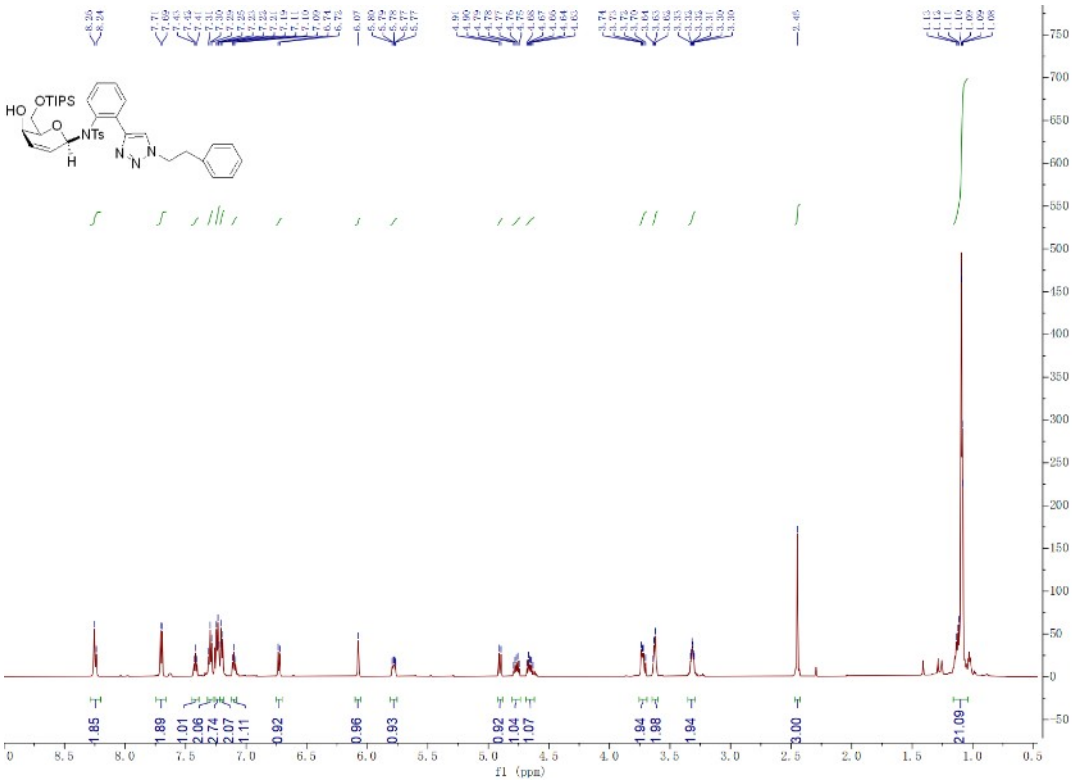
^{13}C NMR spectrum of **45** in $CDCl_3$ (100 MHz).



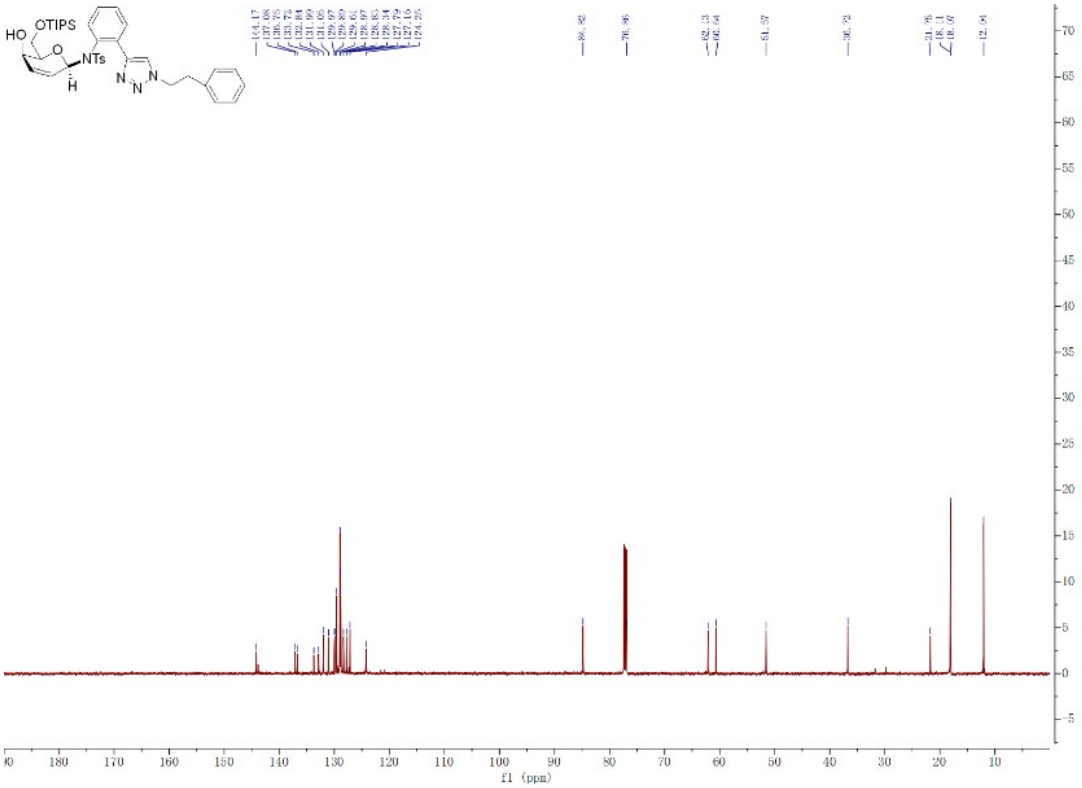
^{1}H NMR spectrum of **46** in $CDCl_3$ (600 MHz).



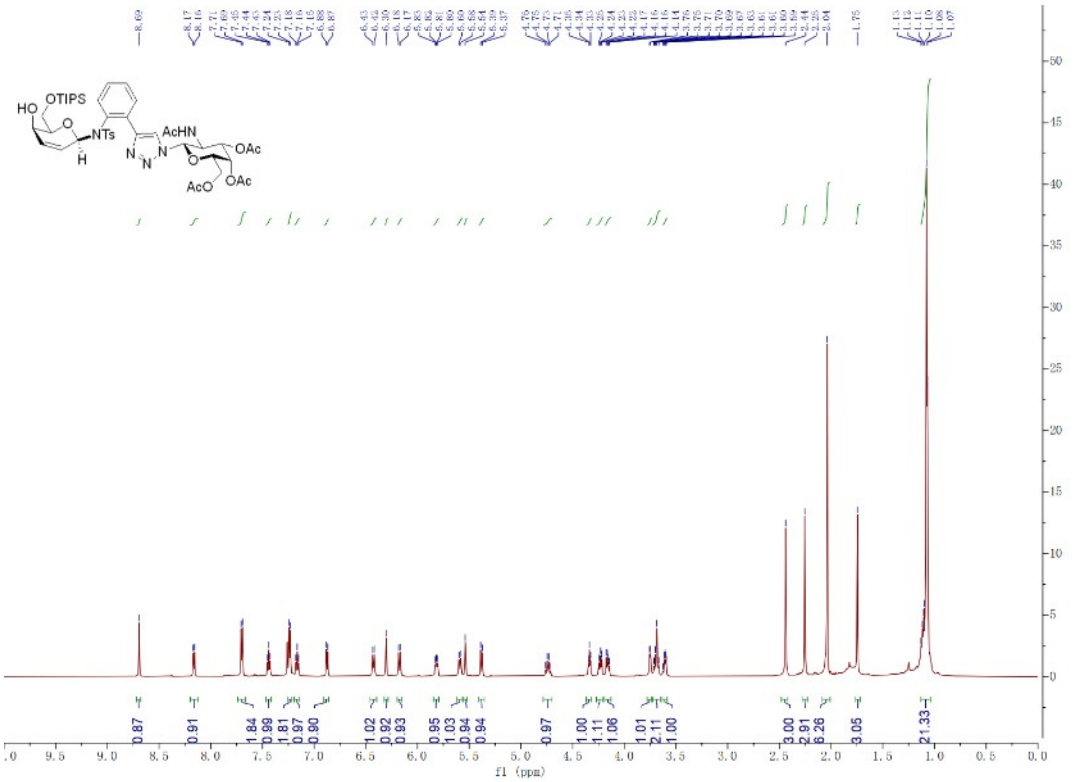
^{13}C NMR spectrum of **46** in $CDCl_3$ (150 MHz).



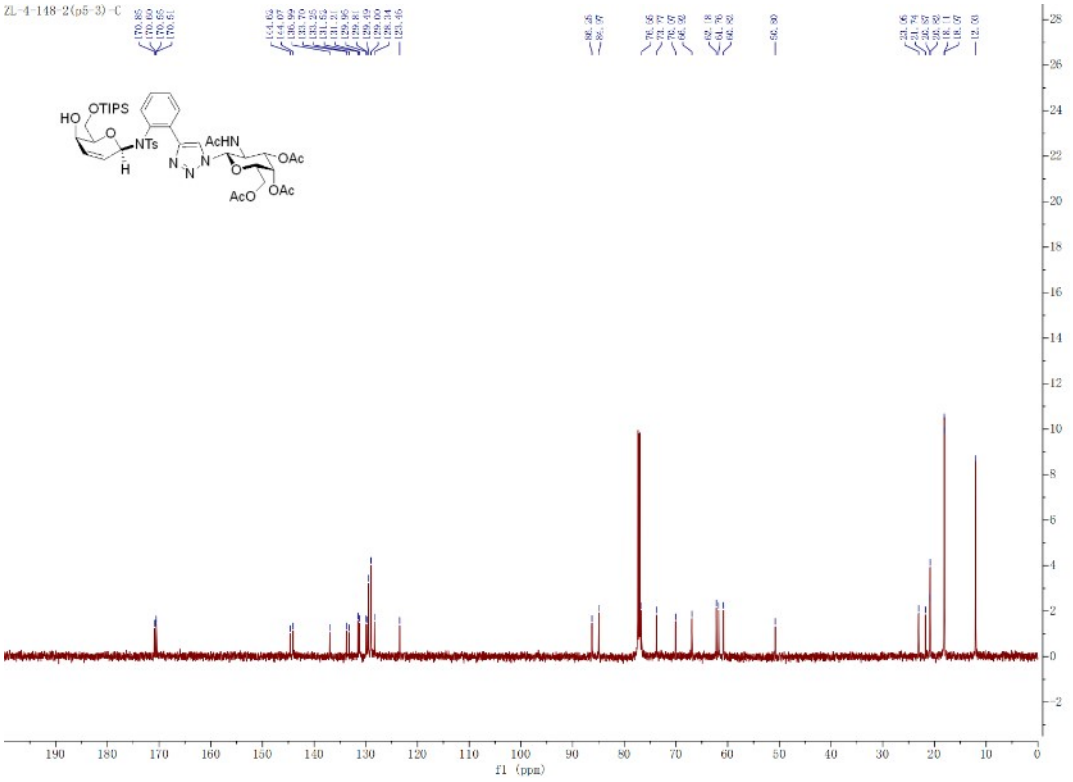
^{1}H NMR spectrum of **47** in $CDCl_3$ (600 MHz).



^{13}C NMR spectrum of **47** in $CDCl_3$ (150 MHz).



^{1}H NMR spectrum of **48** in $CDCl_3$ (600 MHz).



^{13}C NMR spectrum of **48** in $CDCl_3$ (150 MHz).