Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Direct *N*-Glycosylation of Tosyl- and Nosyl Carbamates with Trichloroacetimidate Donors

Ariza Khanam,[a] Pintu Kumar Mandal[a,b,]*

[a]*Medicinal and Process Chemistry Division, CSIR-Central Drug Research Institute, BS-10/1, Sector 10, Jankipuram extension, Sitapur Road, P.O. Box 173, Lucknow, 226 031, India.*

[b]*Academy ofScientific and Innovative Research (AcSIR), Ghaziabad- 201002, India*

* Corresponding author; Email: *pintuchem06@gmail.com/ pk.mandal@cdri.res.in*

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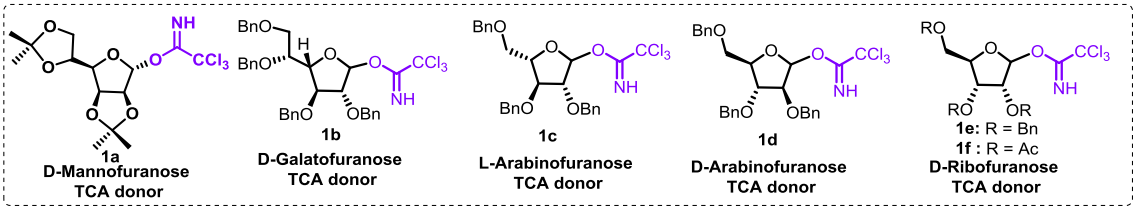
1. EXPERIMENTAL SECTION

General Information. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions in oven dried round-bottom flasks, unless otherwise noted. Reagents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as the visualizing agent also by warming ceric sulfate [2% $Ce(SO_4)_2$ in 5% H_2SO_4 in EtOH]-sprayed plates on a hot plate. Silica gel 230-400 mesh was used for column chromatography. All NMR spectra were recorded with Bruker DRX 400 MHz spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C) at ambient temperature using $CDCl_3$, CD_3OD or $(CD_3)_2CO$ as solvents. Chemical shifts δ are given in ppm relative to the residual signals of tetramethylsilane in $CDCl_3$ for ^1H and ^{13}C NMR. Coupling constants are given in hertz. High-resolution mass spectra (HRMS) were recorded as ESI-HRMS on Q-TOF mass spectrometer. Either protonated molecular ions $[M + H]^+$, sodium adducts $[M + Na]^+$, or ammonium adducts $[M + NH_4]^+$ were used for empirical formula confirmation. Commercially available grades of organic solvents are used for column chromatography for purifications.

2. Glycofuranosyl TCA donors: Glycofuranosyl TCA donors (1a, 1ea, 1eab)



Ref.

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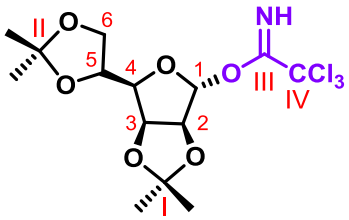
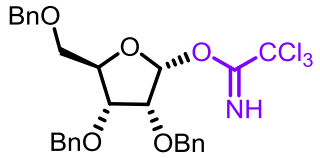
5. J.L. Pirat, D. Virieux, L. Clarion, J.N. Volle, N. Bakalara, M. Mersel, J. Montbrun, H.J. Cristau, New phosphorus containing heterocyclic compounds, sugar analogues, and compositions having anti-cancer activity containing the same. WO 2009004096 A1, **2009**.
6. L. G. Donadıo, G. Gola, R. M. D. Lederkremer, C. G. Rodriguez, *Carbohydr. Res*, **2006**, *341*, 2487–2497.
7. Y. Su, J. Xie, Y. Wang, X. Hub, X. fu, *Eur. J. Med.Chem.* **2010**, *45*, 2713–2718.
8. Y. Luo, D. L. A. Zechel, *Can. J. Chem.* **2006**, *84*, 743–747.



2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl trichloroacetamidate (1a).[5] To a solution of compound 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (1.00 g, 3.84 mmol) and trichloroacetonitrile (3.85 mL, 38.4 mmol) in CH_2Cl_2 (30 mL) was added sodium hydride (0.11 g, 4.6 mmol) and the reaction mixture was stirred for 1 h at room temperature. After that, the mixture was filtered through Celite, and the filtrate was evaporated under reduced pressure to give colored oil. This oil was triturated with hexane to give a white solid precipitate. The precipitate was removed by filtration, and the solvent was removed from the filtrate. The resulting oil crystallized spontaneously to give pure trichloroacetamidate **1a**

(1.13 g, 73 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1 H, NH), 6.26 (s, 1 H, H-1), 4.91 (dd, *J* = 3.4, 5.9 Hz, 1 H, H-3), 4.86 (d, *J* = 5.9 Hz, 1 H, H-2), 4.46-4.41 (m, 1 H, H-5), 4.14-4.10 (m, 2 H, H-4, H-6_b), 4.04 (dd, *J* = 4.2, 8.9, H-6_a), 1.51 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7 (CqNH-III), 113.5 (Cq-I), 109.5(Cq-II), 104.8 (C-1), 91.0 (Cq-IV^{CCl3}), 84.8 (C-2), 82.9 (C-4), 79.3 (C-3), 72.7 (C-5), 67.1 (C-6), 26.9 (CH_3), 26.0 (CH_3), 25.1 (CH_3), 24.8 (CH_3).

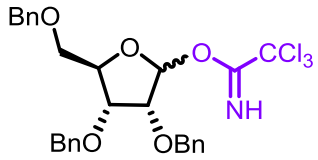
Compounds **1b—1e** were prepared according to the literature procedures.[6-8]



2,3,5-Tri-*O*-benzyl-α-D-ribofuranosyl Trichloroacetimidate (1eα)

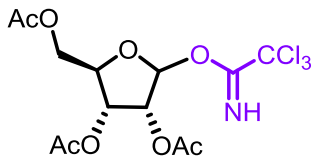
To a stirred solution of compound 2,3,5-tri-*O*-benzyl-D-ribofuranose (500 mg, 1.19 mmol) in CH_2Cl_2 (15 mL), trichloroacetonitrile (1.2 mL, 11.9 mmol) followed by 1,8-diaz abic yclo-[5.4.0]undec-7-ene (DBU; 80 µL, 0.53 mmol) were added successively at 0◦C. The resulting mixture was stirred for 1 h at room temperature. Thereafter, the mixture was evaporated under reduced pressure to give light colored oil. The resulting oil was purified by silica to give pure trichloroacetamidate **1eα** (495 mg, 88 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1 H, NH), 7.39-7.38 (m, 2 H, Ar), 7.35-7.27 (m, 13 H, Ar), 6.20 (d, *J* = 6.8 Hz, 1 H, H-1), 4.79 (dd, *J* = 11.8 Hz, 3 H, PhCH_2), 4.68 (d, *J* = 12.3 Hz, 1 H, PhCH_2), 4.58 (dd, *J* = 12.3 Hz, 2 H, PhCH_2), 4.08-4.06 (m, 1 H), 4.03 (dd, *J* = 8.2,11.3 Hz, 1 H), 3.88 (d, *J* = 4.1, 11.3 Hz, 1 H), 3.64-3.61 (m, 1 H), 3.57 (d, *J* = 2.9, 6.7 Hz, 1 H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 161.1 (Cq, C=NH), 138.6, 138.1, 138.0, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 97.0 (C-1), 91.1 (Cq^{CCl3}), 76.5, 74.7, 74.2, 73.5, 72.9, 71.6, 63.4, (C-5).



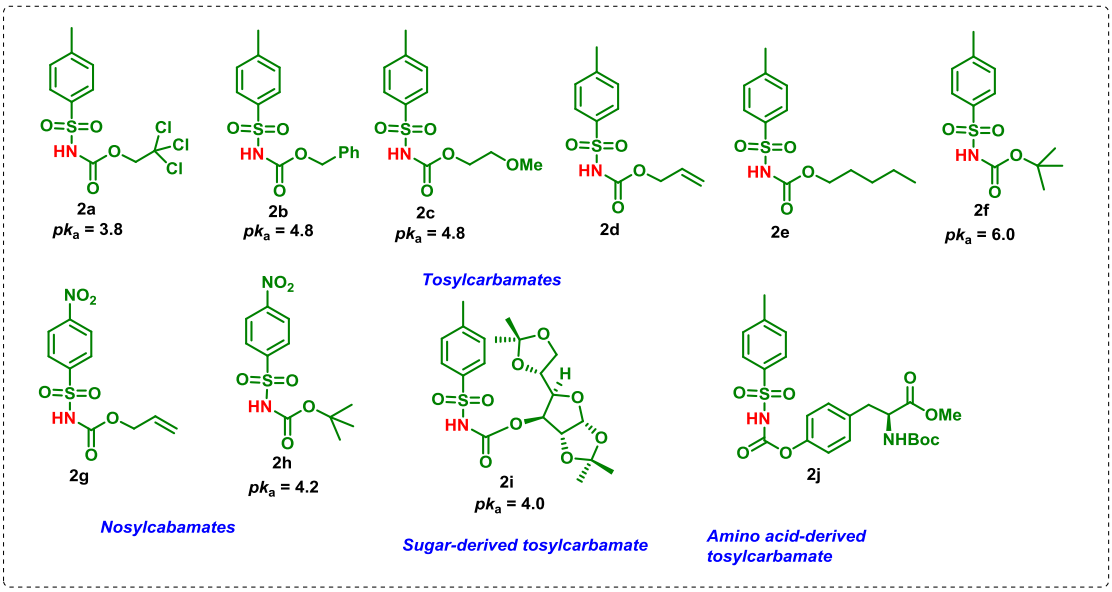
2,3,5-Tri-*O*-benzyl-α/β-D-ribofuranosyl Trichloroacetimidate (1eαβ)

To a stirred solution of compound 2,3,5-tri-*O*-benzyl-D-ribofuranose (500 mg, 1.19 mmol) in CH_2Cl_2 (15 mL), trichloroacetonitrile (1.2 mL, 11.9 mmol) followed by K_2CO_3 (328 mg, 2.38 mmol) were added successively at 0◦C. The resulting mixture was stirred for 1 h at room temperature. Thereafter, the mixture was evaporated under reduced pressure to give light colored oil. The resulting oil was purified by silica to give pure trichloroacetamidate **1eαβ** (488 mg, 84 %, α: β = 3.3:1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1 H, NH), 8.52 (s, 0.3 H), 7.39-7.27 (m, 19 H), 6.32 (s, 1 H, H-1_{β}), 6.20 (d, *J* = 6.8 Hz, 1 H, H-1_{α}), 4.82-4.75 (m, 3.3 H), 4.71-4.64 (m, 1.4 H), 4.62-4.53 (m, 3 H), 4.49-4.43 (m, 0.6 H), 4.14-4.11 (m, 0.3 H), 4.07-3.99 (m, 2.3 H), 3.88 (dd, *J* = 4.1, 11.3 Hz, 1 H), 3.70 (dd, *J* = 4.1, 11.3 Hz, 0.3 H), 3.65-3.61 (m, 1 H), 3.58 (dd, *J* = 2.9, 6.7 Hz, 1.2 H), 3.54-3.52 (m, 0.2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 160.8 (Cq, C=NH), 138.5, 138.2, 138.0, 137.8, 137.5, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 103.4 (C-1β), 97.0 (C-1α), 91.9, 91.1 (Cq^{CCl3}), 82.1, 78.5, 77.3, 76.4, 74.6, 74.2, 73.4, 73.3, 72.9, 72.6, 72.2, 71.6, 70.3, 63.4 (C-5).



2,3,5-Tri-*O*-acetyl-α/β-D-ribofuranosyl trichloroacetimidate (1f).[8] To a stirred solution of compound 2,3,5-tri-*O*-acetyl-D-ribofuranose (500 mg, 1.92 mmol) in CH_2Cl_2 (15 mL), trichloroacetonitrile (1.96 mL, 19.2 mmol) followed by 1,8-diaz abic yclo-[5.4.0]undec-7-ene (DBU; 80 µL, 0.53 mmol) were added successively at 0◦C. The resulting mixture was stirred for 1 h at room temperature. Thereafter, the mixture was evaporated under reduced pressure to give light colored oil. The resulting oil was purified by silica to give pure trichloroacetamidate **2f** (560 mg, 73 %) as a white solid.

3. Carbamate derivatives: Characterization data of Carbamates derivatives (2a-2j)



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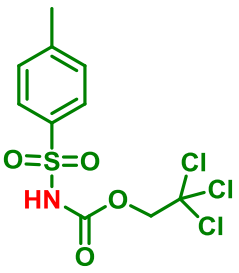
18. N. Mainolfi, , M. P. Moyer, E. Saiah, 3-Phosphoglycerate Dehydrogenase Inhibitors And Uses Thereof. WO2017/156181, **2017**.

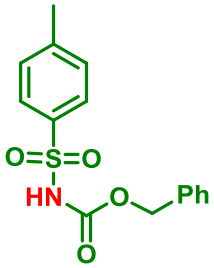
General Procedure: Synthesis of Tosyl carbamates. An alcohol derivative (5.0 mmol), dissolved in a minimum quantity of dry DCM was taken in a round bottom flask and stirred at 0◦C. Tosyl isocyanate (1.0 mmol) was added slowly to a reaction mixture and stirred for 5-6 h at rt. After completion, an excess of alcohol was removed *in vacuo*. The crude product was purified by flash column chromatography with the eluent Petroleum ether/ EtOAc (3:2) to afford the desired carbamate derivatives as a white solid.



2,2,2-Trichloroethyl *N*-(4-methylbenzenesulfonyl)carbamate (2a).[14]

Trichloroethyl alcohol (4.9 ml, 50.71 mmol) was cooled down in an ice bath. Then *p*-toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. Afforded the desired product **2a** (3.00 g, 86 %) as a white crystalline solid. (3.00 g, 8.80 mmol, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, N*H*, 1H), 7.95 (d, *J* = 8.4 Hz, 2 H, Ar), 7.35 (d, *J* = 8.1 Hz, 2 H, Ar), 4.69

(s, 2 H), 2.45 (s, 3 H, $CH_{3\ Ts}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1 (C=O), 145.5, 134.9, 129.7, 128.5, 93.9 (CCl_3), 75.2 (CH_2), 21.7 (CH_3).

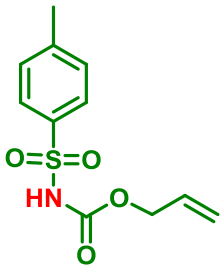


Benzyl *N*-(4-methylbenzenesulfonyl)carbamate (2b).[15]

Benzyl alcohol (1.1 ml, 10.7 mmol) was cooled down in an ice bath. Then *p*-toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. afford the desired product **2b** (2.9 g, 94 %) as a white crystalline solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 2 H, Ar_{Ts}), 7.57(s, 1 H, NH), 7.34-723 (m, 7 H), 5.09 (s, 2 H), 2.44 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2 (C=O), 145.1, 135.5, 134.4, 129.6, 128.7, 128.6, 128.5, 128.4, 68.6, 21.7 (CH_{3Ts}).

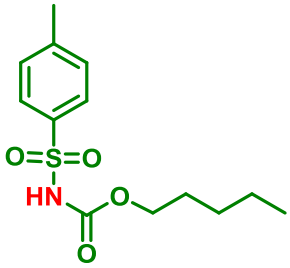
2-methoxyethyl *N*-(4-methylbenzenesulfonyl)carbamate (2c)[16]

The compound **2c, 2d** was prepared using the general procedure.



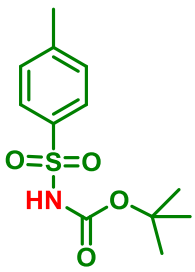
Allyl *N*-(4-methylbenzenesulfonyl)carbamate (2d).[16]

Allyl alcohol (3.4 ml, 50.71 mmol) was cooled down in an ice bath. Then *p*-toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. Afforded the desired product **2d** (2.1 g, 90 %) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.5 Hz, 2 H, Ar), 7.62 (s, N*H*, 1H), 7.34 (d, *J* = 8.3 Hz, 2 H, Ar), 5.87-5.77 (m, 1 H), 5.30-5.22 (m, 2 H), 4.57-4.55 (m, 2 H), 2.45 (s, 3 H, CH_3, Ts); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2 (C=O), 145.1, 135.5, 130.9, 129.6, 128.4, 119.4, 67.4 ($CH_{2\ Alloc}$), 21.7 (CH_3).



Pentyl *N*-(4-methylbenzenesulfonyl)carbamate (2e).

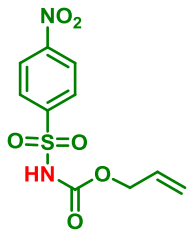
Pentyl alcohol (3.0 ml, 27.2 mmol) was cooled down in an ice bath. Then *p*-toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. Afforded the desired product **2e** (2.1 g, 90 %) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2 H, Ar), 7.66 (s, 1 H, NH), 7.34 (d, *J* = 8.4 Hz, 2 H, Ar), 4.07 (t, *J* = 6.7 Hz, 2 H, O*CH*$_2$), 2.45 (s, 3 H, CH_{3Ts}), 1.59-1.55 (m, 2 H), 1.33-1.17 (m, 4 H), 0.86 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0 (C=O), 145.0, 135.6, 129.6, 128.4, 67.2 (O*C*H$_2$), 28.1, 27.7, 22.2, 21.7 (CH_{3Ts}), 13.9 (CH_3).



***Tert*-butyl *N*-(4-methylbenzenesulfonyl)carbamate (2f)**[17]

t-BuOH (9.6 ml, 101.42 mmol) was stirred at rt. Then *p*-toluenesulfonyl isocyanate (1.5 ml, 10.14 mmol) was added. Afforded the desired product **2f** (2.1 g, 86%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2 H, Ar), 7.33(d, *J* = 8.1 Hz, 2 H, Ar), 7.30 (s, N*H*, 1H), 2.45 (s, 3 H, CH_3, Ts), 1.38 (s, 9 H, CH_3 Boc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1 (C=O), 144.7, 135.9, 129.5, 128.2, 84.1 (CH_{Boc}), 27.9 ($CH_{3\ Boc}$), 21.7 ($CH_{3\ Ts}$).

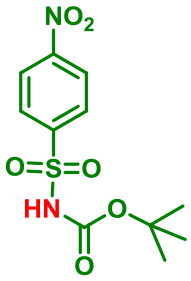
General Procedure: Synthesis of Nosyl carbamates. 4-nitrophenylsulfonamide (4.9 mmol), Boc anhydride/allyl chloroformate (7.5 mmol) in dry DCM was stirred for five min. and then added DMAP (0.4 mmol) at rt. After 20 min, triethylamine (7.5 mmol) was added dropwise to a stirring solution at 0◦C and allowed to stir overnight and extracted with 1M aq. HCl (2 x 25 mL) and dried over Na_2SO_4. The organic phase was evaporated *in a vacuum* and purified by flash column chromatography, furnishing the desired carbamate derivatives as a white solid.



Allyl *N*-(4-nitrophenyl)sulfonylcarbamate (2g).[18]

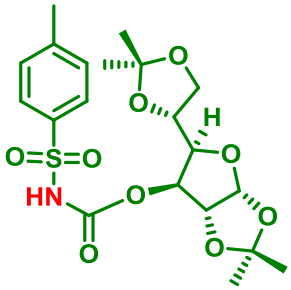
Triethylamine (1.05 mL, 7.5 mmol) was added dropwise over 15 minutes to a stirring solution of allyl chloroformate (0.8 mL, 7.5 mmol), DMAP (54 mg, 0.44 mmol) and 4-nitrophenylsulfonamide (996 mg, 4.93 mmol) in DCM (10 mL). Yielding the desired product **2g** as a white solid (900 mg, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.9 Hz, 2H,

Ar), 8.16 (d, *J* = 8.9 Hz, 2H, Ar), 5.88-5.79 (m, 1H, CH_{Allyl}), 5.25 (dq, *J* = 17.2, 1.6 Hz, 1H, $CH_{2\ Allyl}{}^{b}$), 5.19 (dq, *J* = 10.4, 1.4 Hz, 1H, $CH_{2\ Allyl}{}^{b}$), 4.51 (dt, *J* = 5.5, 1.5 Hz, 2H, OCH_2).



***Tert*-butyl *N*-(4-nitrophenyl)sulfonylcarbamate (2h).**[18]

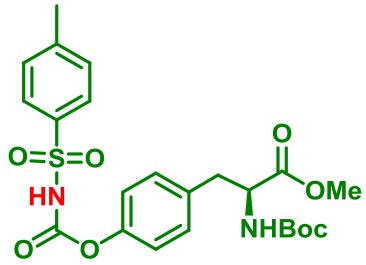
Triethylamine (0.5 mL, 3.6 mmol) was added dropwise over 15 minutes to a stirring solution of 4-nitrophenylsulfonamide (481 mg, 2.38 mmol), Boc anhydride (930 mg, 4.26 mmol) and DMAP (36 mg, 0.29 mmol) at rt. Yielding the desired product **2h**, as a white solid (600 mg, 80 %).^{1}H NMR (400 MHz, DMSO-d_6): δ 8.46 (d, *J* = 8.8 Hz, 2H, Ar), 8.24 (d, *J* = 8.8 Hz, 2H, Ar), 1.41 (s, 9 H, CH_3).



1,2:5,6-di-O-isopropylidene-α-D-glucofuranosyl tosylcarbamate (2i).

To a solution of the 2,3:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1.00 g, 3.8 mmol) in CH_2Cl_2 (2.5 mL) cooled at 0 °C was added *p*-toluenesolfonyl isocyanate (0.59 mL, 3.8 mmol) dropwise under nitrogen. The resulting reaction mixture was stirred for long time and concentrated under vacuum. The residue was purified by flash column chromatography (1:1 EtOAc/Hexane) to the desired product, 17, (1.4 g, 81 %) as a colourless oil. ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.2 Hz, 2H, Ar), 7.77 (brs, 1H, NH), 7.38 (d, *J* = 8.2 Hz, 2H, Ar), 5.76 (d, *J* = 3.7 Hz, 1 H, H-1), 5.17 (d, *J* = 2.9 Hz, 1H, H-3), 4.42 (d, *J* = 3.7 Hz, 1H, H-2), 4.11–4.08 (m, 1H, H-4), 4.02 – 3.91 (m, 3H, H-5, H-6_a, H-6_b), 2.46 (s, 3H, Tosyl-CH_3), 1.48 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1 (C-N-O), 145.3, 135.4, 129.7, 128.4, 112.5, 109.6, 104.9 (C-1), 82.9 (C-2), 79.7 (C-4), 78.5 (C-3), 71.9 (C-5), 67.3 (C-6), 26.8 (*C*H_3), 26.6 (*C*H_3), 26.2 (*C*H_3), 25.1 (*C*H_3), 21.7 (Tosyl-CH_3).



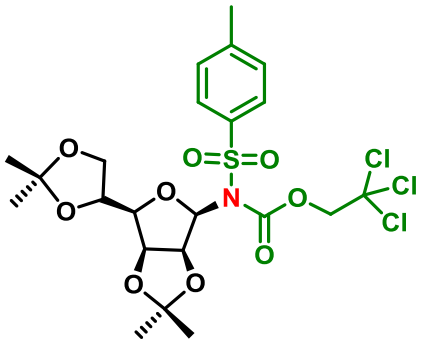
N'-Tosyl *O*-(N-Boc-tyrosine methyl ester) carbamate (2j).

To a solution of Boc-L-tyrosine methyl ester 12 (500 mg, 1.7 mmol) in dry CH_2Cl_2 (9 mL) at rt under nitrogen was added *p*-toluenesolfonyl isocyanate (0.23 mL, 1.53 mmol). The resulting mixture was stirred at rt for 6 hr and concentrated under vacuum. The crude residue was purified by flash column chromatography (hexanes/ EtOAc = 1/1) to furnish the desired product 19 (1.001 g, 2.07 mmol, 80 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H, Ar^{Ts}), 7.30 (d, *J* = 8.3 Hz, 2H, Ar^{Ts}), 6.97 (d, *J* = 8.1 Hz, 2H, Ar^{Tyr}), 6.73 (d, *J* = 8.2 Hz, 1H, Ar^{Tyr}), 5.01 (brs, 1H), 4.54 (q, *J* = 6.6 Hz, 1H, C*H*-NH,), 3.71 (s, 3H, OCH_3), 3.05 – 2.95 (m, 2H), 2.43 (s, 3H), 1.41 (s, 9H, CH_3 ^{Boc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7 ($C=O^{Boc}$), 155.3 ($C=O^{carbamate}$), 143.6, 139.2, 130.4,129.7, 126.4, 115.5, 80.2 (tert-C^{Boc}), 54.7 (*C*H-NH), 52.3 (OCH_3), 37.6 (CH_2), 28.3 (CH_3 ^{Boc}), 21.5 (CH_3 ^{Ts}).

4. Characterization data of synthesized N-glycofuranosides (3a-3z, 3v', 3aa, 4, 5, 6)

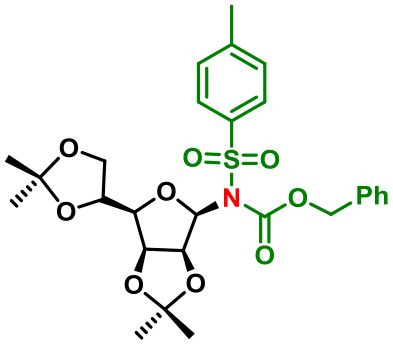
General procedure for *N*-glycosylations.

To a stirred solution of trichloroacetimidate glycosyl donor **1a-e** (1.0 mmol) in dry DCM (2 mL) under a nitrogen atmosphere, 1.2 equivalents of carbamate acceptor (**2a-g**) were added to a stirred solution. The reaction was stirred at room temperature for 24 h. After completion, the reaction mixture was diluted with CH_2Cl_2 and washed with 01M aq. NaOH to remove trichloroacetamide. The aqueous layer was then extracted with DCM (3 x 20 ml). The combined organic fractions were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product over SiO_2 using hexane-EtOAc (6:1) as the eluant furnished pure *N*-glycoside products (**5a-r)**.



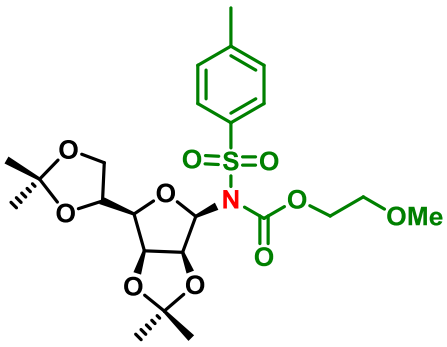
2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl 2,2,2-trichloroethyl tosylcarbamate (3a). Synthesized according to general procedure in 1 mmol scale, afforded **3a** (499 mg, yield 85%, β only); eluant, hexane-EtOAc (4:1); as a colorless

syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 7.30 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 6.29 (brs, 1 H, H-1), 5.28 (d, *J* = 6.0 Hz, 1 H, H-2), 5.02 (dd, *J* = 3.5, 6.0 Hz, 1 H, H-3), 4.74 (d, *J* = 12.2 Hz, 1 H, CH_2^{Troc}), 4.64 (d, *J* = 11.9 Hz, 1 H, (CH_2^{Troc}), 4.49 (dd, *J* = 4.1, 6.9 Hz, 1 H, H-3), 4.39-4.35 (m, 1 H, H-5), 4.11 (dd, *J* = 6.5, 8.7 Hz, 1 H, H-6_a), 4.02 (dd, *J* = 5.1, 8.7 Hz, 1 H, H-6_b), 2.43 (s, 3 H, CH_3^{Ts}), 1.55 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5 (C=O), 145.1, 136.2, 129.6, 128.2, 113.2 (Cq, *C*$(Me)_2$), 109.1 (Cq, *C*$(CH_3)_2$), 94.4 (C-1), 93.6 (*C*Cl_3), 86.3 (C-2), 85.7 (C-4), 81.4 (C-3), 76.1 (CH_2^{Troc}), 73.9 (C-5), 66.5 (C-6), 26.8(*C*H_3), 26.3(*C*H_3), 25.3(*C*H_3), 24.4 (*C*H_3), 21.6 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{22}H_{33}Cl_3N_2O_9S^+$ [M+NH_4]$^+$: 605.0889, found: 605.0886.

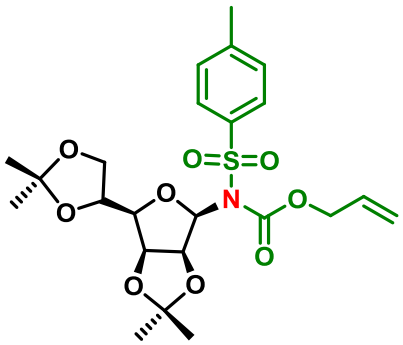


2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl benzyl tosylcarbamate (3b). Synthesized according to general procedure in 1 mmol scale, afforded **3b** (465 mg, yield 85%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.5 Hz, 2 H, Ar^{Ts}), 7.38-7.31 (m, 3 H, Ar), 7.17-7.15 (m, 2 H, Ar), 7.11 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 6.25 (brs, 1 H, H-1), 5.23 (dd, *J* = 1.0, 6.1 Hz, 1 H, H-2), 5.04 (brs, 2 H, (OCH_2Ph), 4.89 (dd, *J* = 4.0, 5.9 Hz, 1 H, H-3), 4.42 (dd, *J* = 4.2, 7.1 Hz, 1 H, H-4), 4.36-4.31 (m, 1 H, H-5), 4.10 (dd, *J* = 6.4, 8.7 Hz, 1 H, H-6_a), 4.01 (dd, *J* = 4.7, 8.9 Hz, 1 H, H-6_b), 2.38 (s, 3 H, CH_3^{Ts}), 1.53 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3 (C=O), 144.5, 136.3, 133.8, 129.3, 128.8, 128.6, 128.5, 128.2, 126.9, 112.9 (Cq, *C*$(Me)_2$), 109.1 (Cq, *C*$(Me)_2$), 93.6 (C-1),

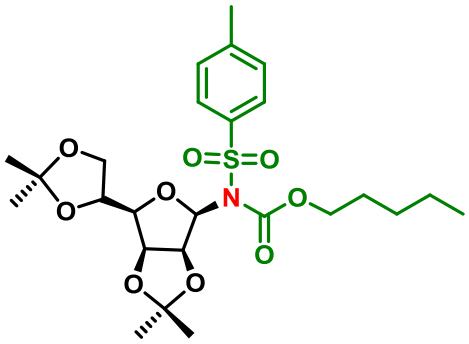
86.4 (C-2), 85.5 (C-4), 81.5 (C-3), 73.9 (C-5), 69.5 (O*C*H$_2$Ph), 66.5 (C-6), 26.9 (*C*H$_3$), 26.2 (*C*H$_3$), 25.3 (*C*H$_3$), 24.3 (*C*H$_3$), 21.6 (*C*H$_3^{Ts}$); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{27}H_{37}N_2O_9S^+$ [M+ NH_4]$^+$: 565.2214, found: 565.2209.



2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl 2-methoxyethyl tosylcarbamate (3c). Synthesized according to general procedure in 1 mmol scale, afforded **3c** (413 mg, yield 83%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 7.30 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 6.25 (brs, 1 H, H-1), 5.22 (dd, *J* = 1.0, 6.0 Hz, 1 H, H-2), 4.99 (dd, *J* = 4.1, 5.9 Hz, 1 H, H-3), 4.43(dd, *J* = 3.9, 6.8 Hz, 1 H, H-4),4.37-4.33 (m, 1 H, H-5), 4.19-4.17 (m, 2 H, OC*H*$_2$), 4.10 (dd, *J* = 6.4, 8.9 Hz, 1 H, H-6$_b$), 4.01 (dd, *J* = 5.1, 8.7 Hz, 1 H, H-6$_a$), 3.46-3.44 (m, 2 H, C*H*$_2$OMe), 3.30 (s, 3 H, OC*H*$_3$), 2.44 (s, 3 H, C*H*$_3^{Ts}$), 1.54 (s, 3 H, C*H*$_3$), 1.45 (s, 3 H, C*H*$_3$), 1.38 (s, 3 H, C*H*$_3$), 1.35 (s, 3 H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3 (C=O), 144.7, 136.5, 129.3, 128.4, 112.9 (Cq, *C*(Me)$_2$), 109.0 (Cq, *C*(Me)$_2$), 93.6 (C-1), 86.4 (C-2), 85.4 (C-4), 81.5 (C-3), 73.9 (C-5), 69.7 (*C*H$_2$OMe), 66.5 (O*C*H$_2$), 66.4 (C-6), 58.8 (O*C*H$_3$), 26.8 (*C*H$_3$), 26.2 (*C*H$_3$), 25.3 (*C*H$_3$), 24.3 (*C*H$_3$), 21.6 (*C*H$_3^{Ts}$); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{23}H_{34}NO_{10}S^+$ [M+ H]$^+$: 516.1898, found: 516.1895.

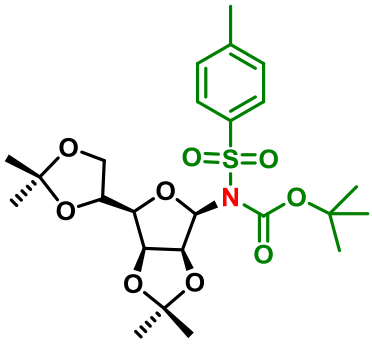


2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl allyl tosylcarbamate (3d). Synthesized according to general procedure in 1 mmol scale, afforded **3d** (422 mg, yield 85%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.4 Hz, 2 H, Ar^{Ts}), 7.29(d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 6.24 (brs, 1 H, H-1), 5.77-5.67 (m, 1 H, =C*H*), 5.26-5.21 (m, 3 H, H-2, $=CH_2$), 4.98 (dd, *J* = 4.1, 6.1 Hz, 1 H, H-3), 4.58-4.47 (m, 2 H, CH_{2Allyl}), 4.40 (dd, *J* = 3.9, 6.8 Hz, 1 H, H-4),4.38-4.33 (m, 1 H, H-5), 4.10 (dd, *J* = 6.4, 8.9 Hz, 1 H, $H\text{-}6_a$), 4.02 (dd, *J* = 5.1, 8.7 Hz, 1 H, $H\text{-}6_b$), 2.43 (s, 3 H, CH_3^{Ts}), 1.54 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3);^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1 (C=O), 144.7, 136.5, 130.4 (=*C*H), 129.4, 128.4, 119.8 (=*C*H_2), 113.0 (Cq, *C*$(Me)_2$), 109.0 (Cq, *C*$(Me)_2$), 93.7 (C-1), 86.4 (C-2), 85.5 (C-4), 81.5 (C-3), 73.9 (C-5), 68.2 (CH_{2Allyl}), 66.5 (C-6), 26.8 (*C*H_3), 26.2 (*C*H_3), 25.3 (*C*H_3), 24.4 (*C*H_3), 21.6 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m/z* Calcd for $C_{23}H_{35}N_2O_9S^+$ $[M+ NH_4]^+$: 515.2058, found: 515.2043.



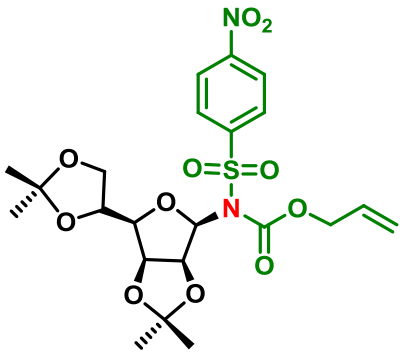
2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl *n*-pentyl tosylcarbamate (3e). Synthesized according to general procedure in 1 mmol scale,

afforded **3e** (416 mg, yield 79%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 7.29 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 6.25 (brs, 1 H, H-1), 5.25 (dd, *J* = 0.8, 6.1 Hz, 1 H, H-2), 4.99 (dd, *J* = 4.1, 5.9 Hz, 1 H, H-3), 4.46 (dd, *J* = 4.1, 6.9 Hz, 1 H, H-4), 4.38-4.34 (m, 1 H, H-5), 4.11 (dd, *J* = 6.4, 8.7 Hz, 1 H, H-6_a), 4.05-4.01 (m, 3 H, H-6_b, OCH_2), 2.44 (s, 3 H, CH_3^{Ts}), 1.54 (s, 3 H, CH_3), 1.50-1.43 (m, 2 H, CH_2), 1.45 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 128-1.21 (m, 2 H, CH_2), 1.17-1.10 (m, 2 H, CH_2), 0.86 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5 (C=O), 144.6, 136.9, 129.4, 128.1, 112.9 (Cq, $C(Me)_2$), 109.0 (Cq, $C(Me)_2$), 93.6 (C-1), 86.4 (C-2), 85.6 (C-4), 81.6 (C-3), 73.9 (C-5), 68.1 (OCH_2), 66.5 (C-6), 27.9 (CH_2), 27.6 (CH_2), 26.8 (CH_3), 26.2 (CH_3), 25.3 (CH_3), 24.4 (CH_3), 22.2 (CH_2), 21.6 (CH_3^{Ts}), 13.8 (CH_3); HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{41}N_2O_9S^+$ $[M+ NH_4]^+$: 545.2527, found: 545.2514.

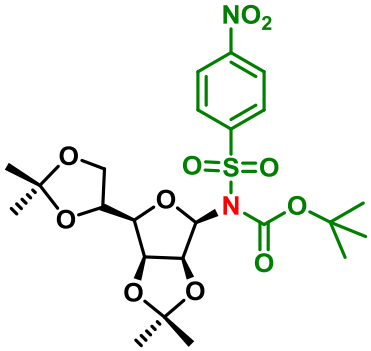


2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl *tert*-butyl tosylcarbamate (3f). Synthesized according to general procedure in 1 mmol scale, afforded **5a** (343 mg, yield 67%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 7.29 (d, *J* = 8.0 Hz, 2 H, Ar^{T}), 6.21 (brs, 1 H, H-1), 5.25 (dd, *J* = 1.1, 6.1 Hz, 1 H, H-2), 5.00 (dd, *J* = 4.1, 6.0 Hz, 1 H, H-3), 4.51 (dd, *J* = 4.1, 6.9 Hz, 1 H, H-4), 4.39-4.35 (m, 1 H, H-5), 4.12 (dd, *J* = 6.3, 8.7 Hz, 1 H, H-6_a), 4.06 (dd, *J* = 4.9, 8.8 Hz, 1 H, H-6_b), 2.44 (s, 3 H, CH_3^{Ts}), 1.53 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.26 (s, 9 H, CH_3^{Boc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0 (C=O), 144.3, 137.3, 129.3, 127.7, 112.9 (Cq, $C(Me)_2$), 108.9 (Cq, $C(Me)_2$), 93.2 (C-

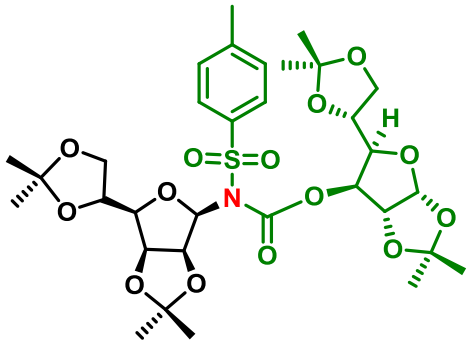
1), 86.3 (C-2), 85.5 (C-4), 85.4 (Cq $_{Boc}$), 81.7 (C-3), 74.0 (C-5), 66.5 (C-6), 27.7 (CH_3^{Boc}), 26.8 (CH_3), 26.2 (CH_3), 25.3 (CH_3), 24.4 (CH_3), 21.6 (CH_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{24}H_{35}NO_9S^+$ $[M+ 2H]^{2+}$: 515.2031, found: 515.2037.



2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl allyl *N*-(4-nitrophenyl) sulfonylcarbamate (3g). Synthesized according to general procedure in 1 mmol scale, afforded **3g** (432 mg, yield 82%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 9.0 Hz, 2 H, Ar^{Ns}), 8.16 (d, *J* = 9.0 Hz, 2 H, Ar^{Ns}), 6.24 (brs, 1 H, H-1), 5.79-5.69 (m, 1 H, =CH_{allyl}), 5.31-5.29 (m, 1H, H-2), 5.27-5.25 (m, 2 H, =C$H_{2\ allyl}$), 4.98 (dd, *J* = 4.1, 6.1 Hz, 1 H H-3), 4.61-4.46 (m, 3 H, H-4, OC$H_{2\ allyl}$), 4.39-4.34 (m, 1 H, H-5), 4.11 (dd, *J* = 6.4, 8.9 Hz, 1 H, H-6_a), 4.01 (dd, *J* = 5.1, 8.7 Hz, 1 H, H-6_b), 1.55 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3);^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5 (C=O), 150.6, 144.9, 129.8 (CH_{allyl}), 129.7, 124.0, 120.8 (CH_{2Allyl}), 113.3 (Cq, $C(Me)_2$), 108.9 (Cq, $C(Me)_2$), 94.1 (C-1), 86.3 (C-2), 85.7 (C-4), 81.3 (C-3), 73.9 (C-5), 68.8 (OC$H_{2\ allyl}$), 66.2 (C-6), 26.8 (CH_3), 26.2 (CH_3), 25.2 (CH_3), 24.3 (CH_3); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{22}H_{29}N_2O_{11}S^+$ $[M+ H]^+$: 529.1487, found: 529.1477.

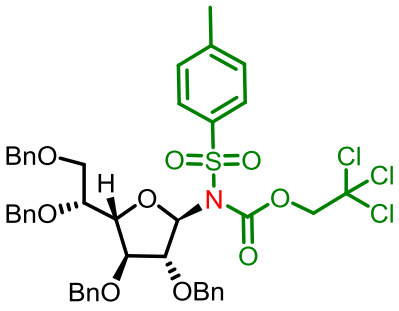


2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl *tert*-butyl *N*-(4-nitrophenyl)sulfonylcarbamate (3h). Synthesized according to general procedure in 1 mmol scale, afforded **3h** (359 mg, yield 66%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 9.0 Hz, 2 H, Ar^{Ns}), 8.17 (d, *J* = 9.0 Hz, 2 H, Ar^{Ns}), 6.20 (brs, 1 H, H-1), 5.29 (dd, *J* = 1.0, 6.1 Hz, 1 H, H-2), 5.02 (dd, *J* = 4.1, 6.0 Hz, 1 H, H-3), 4.54 (dd, *J* = 4.1, 6.0 Hz, 1 H, H-4), 4.41-4.36 (m, 1 H, H-5), 4.13 (dd, *J* = 6.5, 8.7 Hz, 1 H, H-6_a), 4.04 (dd, *J* = 5.1, 8.7 Hz, 1 H, H-6_b), 1.54 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.29 (s, 9 H, CH_3^{Boc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4 (C=O), 150.3, 145.8, 128.9, 123.9, 113.1 (Cq, *C*$(Me)_2$), 108.9 (Cq, *C*$(Me)_2$), 93.7 (C-1), 86.8 (Cq $_{Boc}$), 86.3 (C-2), 85.7 (C-4), 81.4 (C-3), 74.0 (C-5), 66.2 (C-6), 27.7 (CH_3^{Boc}), 26.8 (CH_3), 26.2 (CH_3), 25.2 (CH_3), 24.3 (CH_3); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{23}H_{36}N_3O_{11}S^+$ $[M+ NH_4]^+$: 562.2065, found: 562.2061.



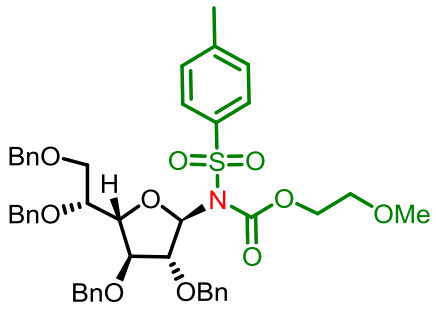
(1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranosyl) *N*-(2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl) *N*-tosyl carbamate (3i). Synthesized according to general procedure in 1 mmol scale, afforded **3i** (398 mg, yield 57%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* =

8.4 Hz, 2 H, Ar^{Ts}), 7.33 (d, *J* = 8.1 Hz, 2 H, Ar^{Ts}), 6.27 (brs, 1 H, H-1), 5.70 (d, *J* = 3.6 Hz, 1 H, H-1'), 5.31 (dd, *J* = 1.0, 6.1 Hz, 1 H, H-2), 5.28 (d, *J* = 2.8 Hz, 1 H), 5.04 (dd, *J* = 4.1, 6.1 Hz, 1 H, H-3), 4.51 (dd, *J* = 4.2, 6.2 Hz, 1 H, H-4), 4.39-4.34 (m, 1 H, H-5), 4.29 (d, *J* = 3.6 Hz, 1 H), 4.10 (dd, *J* = 6.5, 8.7 Hz, 1 H, H-6_a), 4.02 (dd, *J* = 4.8, 8.8 Hz, 1 H, H-6_b), 3.96 (dd, *J* = 2.8, 8.9 Hz, 1 H), 3.80-3.74 (m, 2 H, H-$6'_{ab}$), 3.20-3.17 (m, 1 H), 2.45 (s, 3 H, CH_3^{Ts}), 1.55 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.37 (S, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3 (C=O), 144.7, 137.0, 129.7, 127.7, 113.1 (Cq, $C(Me)_2$), 112.6 (Cq, $C(Me)_2$), 109.5 (Cq, $C(Me)_2$), 109.0 (Cq, $C(Me)_2$), 105.0 (C-1'), 94.1 (C-1), 86.5 (C-2), 85.8 (C-4), 82.9, 81.5 (C-3), 79.9, 79.1, 73.9 (C-5), 71.3, 67.5 (C-6'), 66.4 (C-6), 28.8 (CH_3), 28.7 (CH_3), 28.6 (CH_3), 26.2 (CH_3), 26.1 (CH_3), 25.2 (CH_3), 24.9 (CH_3), 24.3 (CH_3), 21.6 (CH_3^{Ts}); HRMS (ESI-TOF) *m/z* Calcd for $C_{32}H_{49}N_2O_{14}S^+$ $[M+NH_4]^+$: 717.2899, found: 717.2896.

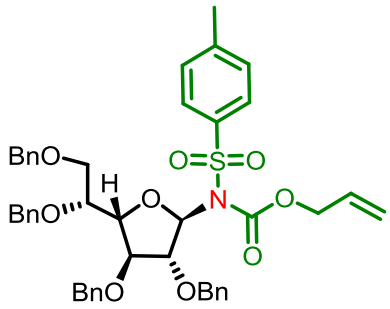


2,3,5,6-Tetra-*O*-benzyl-β-D-galactofuranosyl 2,2,2-trichloroethyl tosylcarbamate (3j). Synthesized according to general procedure in 1 mmol scale, afforded **3j** (702 mg, yield 81%, β =only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2 H, Ar^{Ts}), 7.37-7.28 (m, 17 H, Ar), 7.25-7.23 (m, 3 H, Ar), 7.01 (d, *J* = 8.2 Hz, 2 H, Ar^{Ts}), 6.57 (d, *J* = 7.2 Hz, 1 H, H-1), 4.94 (d, *J* = 11.3 Hz, 1 H, PhCH_2), 4.78-4.72 (m, 2 H, PhCH_2), 4.69-4.58 (m, 5 H), 4.49-4.41 (m, 6 H), 3.98-3.97 (m, 1 H, H-5), 3.65 (dd, *J* = 6.4, 9.5 Hz, 1 H, H-6_a), 3.50 (dd, *J* = 6.0, 9.6 Hz, 1 H, H-6_b), 2.29 (s, 3 H, CH_3^{Ts}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2 (C=O), 144.4, 138.7, 138.6, 138.1, 137.6, 136.7, 129.7, 129.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0,

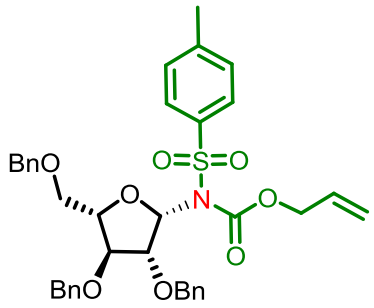
127.9, 127.7, 127.6, 127.5, 93.8 (*C*Cl_3), 83.3 (C-1), 79.5, 75.9 (CH_2^{Troc}), 75.2, 74.8, 74.6 (Ph*C*H_2), 74.4 (C-5), 74.1, 73.5, 73.4, 72.7 (Ph*C*H_2), 69.9 (C-6), 21.5 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{44}H_{48}Cl_3N_2O_9S^+$ $[M+ NH_4]^+$: 885.2141, found: 885.2142.



2,3,5,6-Tetra-*O*-benzyl-β-D-galactofuranosyl 2-methoxyethyl tosylcarbamate (3k). Synthesized according to general procedure in 1 mmol scale, afforded **3k** (660 mg, yield 83%, α: β = 1:20); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.83 (m, 2 H), 7.36-7.22 (m, 20 H), 7.05-7.03 (m, 2 H), 5.47 (d, *J* = 9.0 Hz, 1 H, H-1), 4.98-4.92 (m, 1 H), 4.86-4.67 (m, 4 H), 4.64-4.56 (m, 2 H), 4.51-4.39 (m, 3 H), 4.14-4.04 (m, 2 H), 3.98-3.96 (m, 1 H), 3.77-3.74 (m, 1 H), 3.66-3.49 (m, 3 H, H-2, H-6_{ab}), 3.35-3.26 (m, 2 H, CH_2OMe), 3.11 (s, 3 H, OCH_3), 2.33 (s, 3 H, CH_3^{Ts}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2 (C=O), 151.6, 144.1, 144.0, 138.9, 138.7, 138.4, 138.3, 138.2, 137.9, 137.8, 137.0, 136.7, 129.2, 129.1, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 86.3 (C-1), 84.7, 82.7, 79.6, 76.0, 75.9, 75.6, 74.7, 74.6, 74.2, 74.1, 73.9, 73.5, 72.8, 72.7, 69.8, 69.7 (*C*H_2OMe), 69.4, 68.6 (C-6), 66.1, 65.8 (O*C*H_2), 58.7, 58.5 (O*C*H_3), 21.6, 21.5 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{45}H_{53}N_2O_{10}S^+$ $[M+ NH_4]^+$: 813.3415, found: 813.3410.

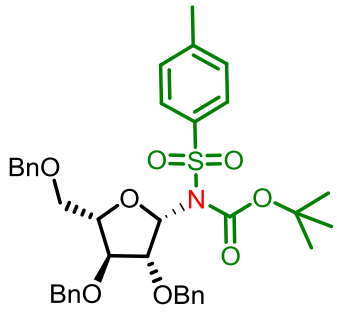


2,3,5,6-Tetra-*O*-benzyl-β-D-galactofuranosyl allyl tosylcarbamate (3l). Synthesized according to general procedure in 1 mmol scale, afforded **3l** (637 mg, yield 82%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.2 Hz, 2 H), 7.37-7.24 (m, 20 H), 7.04 (d, *J* = 8.2 Hz, 2 H), 5.64-5.54 (m, 1 H, =C*H*), 5.47 (d, *J* = 7.2 Hz, 1 H, H-1), 5.16-5.12 (m, 1 H, =CH_2), 4.96 (d, *J* = 11.5 Hz, 2 H, PhCH_2, =CH_2), 4.83-4.78 (m, 4 H), 4.67-4.65 (m, 1 H), 4.59 (d, *J* = 11.7 Hz, 1 H), 4.51-4.43 (m, 3 H), 4.35-4.30 (m, 1 H), 3.96 -3.95 (m, 1 H), 3.78-3.74 (m, 1 H), 3.67 (dd, *J* = 2.7, 9.3 Hz, 1 H), 3.64-3.61 (m, 2 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 151.4, 144.2, 138.8, 138.2, 137.9, 136.6, 130.7 (=*C*H), 129.1, 128.6, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 118.9 (=*C*H_2), 86.2 (C-1), 84.7, 76.1, 75.3, 74.8, 74.5, 73.8, 73.5, 72.9, 68.7 (C-6), 67.6 (O*C*$H_{2\ allyl}$), 21.6 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{45}H_{51}N_2O_9S^+$ [M+ NH_4]$^+$: 795.3310, found: 795.3299.

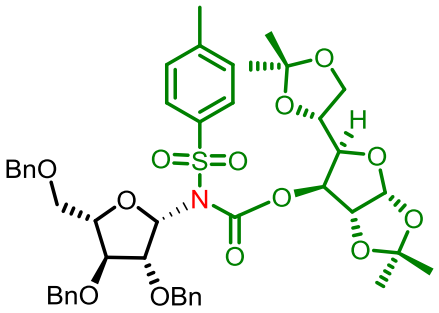


2,3,5-Tri-*O*-benzyl-β-L-arabinofuranosyl allyl tosylcarbamate (3m). Synthesized according to general procedure in 1 mmol scale, afforded **3m** (532 mg, yield 81%, α: β = 1:30); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2 H), 7.36-7.26 (m, 15 H), 7.24-7.22 (m, 2 H), 6.25 (d, *J* = 5.6 Hz, 1 H, H-1), 5.77-5.67 (m, 1 H, =C*H*), 5.23-5.15 (m, 2 H, =CH_2), 5.01-

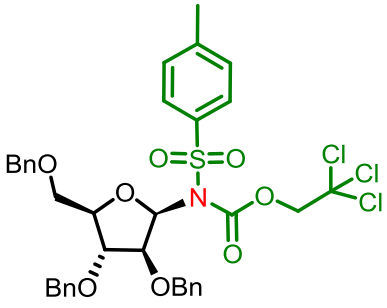
4.98 (m, 1 H, H-2), 4.76 (d, *J* = 11.5 Hz, 1 H, PhC*H*$_2$), 4.65 (d, *J* = 11.5 Hz, 1 H, PhC*H*$_2$), 4.59-4.51 (m, 6 H, PhC*H*$_2$, O*C*H$_{2allyl}$), 4.49-4.45 (m, 1 H, H-4), 4.19 (dd, *J* = 6.4, 8.6 Hz, 1 H, H-3), 3.64 (dd, *J* = 2.5, 11.1 Hz, 1 H, H-5$_a$), 3.52 (dd, *J* = 4.9, 11.1 Hz, 1 H, H-5$_b$), 2.40 (s, 3 H, C*H*$_3^{Ts}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5 (C=O), 144.6, 138.2, 138.0, 137.5, 136.5, 130.7 (=*C*H), 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 119.7(=*C*H$_2$), 92.2 (C-1), 85.5 (C-2), 82.7 (C-3), 81.9 (C-4), 73.4 (Ph*C*H$_2$), 72.5 (Ph*C*H$_2$), 72.4 (Ph*C*H$_2$), 70.0 (C-5), 67.9 (O*C*H$_{2allyl}$), 21.6 (*C*H$_3^{Ts}$); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{37}H_{43}N_2O_8S^+$ [M+ NH_4]$^+$: 675.2735, found: 675.2716.



2,3,5-Tri-*O*-benzyl-β-L-arabinofuranosyl *tert*-butyl tosylcarbamate (3n). Synthesized according to general procedure in 1 mmol scale, afforded **3n** (444 mg, yield 66%, α: β = 1:30); eluant, hexane-EtOAc (4:1); as a pale yellow syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2 H), 7.39-7.36 (m, 2 H), 7.34-7.26 (m, 13 H), 7.24-7.21 (m, 2 H), 6.21 (d, *J* = 5.6 Hz, 1 H, H-1), 5.03 (t, *J* = 5.9 Hz, 1 H, H-2), 4.78 (d, *J* = 11.6 Hz, 1 H, PhC*H*$_2$), 4.68 (d, *J* = 11.5 Hz, 1 H, PhC*H*$_2$), 4.61-4.54 (m, 4 H, PhC*H*$_2$), 4.52-4.49 (m, 1 H, H-4), 4.20 (dd, *J* = 6.4, 8.6 Hz, 1 H, H-3), 3.67 (dd, *J* = 2.6, 11.1 Hz, 1 H, H-5$_a$), 3.54 (dd, *J* = 4.8, 11.1 Hz, 1 H, H-5$_b$), 2.40 (s, 3 H, C*H*$_3^{Ts}$), 1.29 (s, 9 H, C*H*$_3^{Boc}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2 (C=O), 144.1, 138.2, 138.1, 137.5, 137.4, 129.2, 128.5, 128.3, 128.0, 127.9, 127.7, 91.5 (C-1), 85.2 (C-2), 84.7 (Cq, $_{Boc}$), 82.4 (C-3), 81.5 (C-4), 73.3 (Ph*C*H$_2$), 72.4 (Ph*C*H$_2$), 72.3 (Ph*C*H$_2$), 69.9 (C-5), 27.8 (*C*H$_3^{Boc}$), 21.5 (*C*H$_3^{Ts}$); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{38}H_{47}N_2O_8S^+$ [M+ NH_4]$^+$: 691.3048, found: 691.3043.

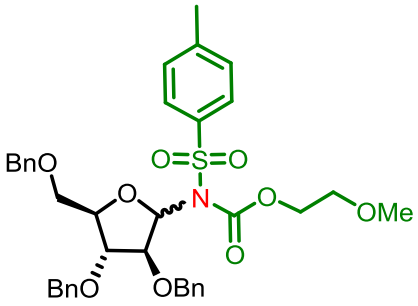


(1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranosyl) *N*-(2,3,5-tri-*O*-benzyl-β-L-arabinofuranosyl) *N*-tosyl carbamate (3o). Synthesized according to general procedure in 1 mmol scale, afforded **3o** (644 mg, yield 75%, α: β = 1:20); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.84 (m, 2 H), 7.37-7.28 (m, 13 H), 7.27-7.23 (m, 4 H), 6.24 (d, *J* = 5.6, 1 H, H-1), 5.49 (d, *J* = 3.6, 1 H, H-1'), 5.28-5.20 (m, 1 H), 4.96-4.93 (m, 0.7 H), 4.78-4.72 (m, 1 H, H-2), 4.66-4.58 (m, 3 H), 4.56-4.43 (m, 4 H), 4.21 (dd, *J* = 6.1, 8.1 Hz, 0.7 H), 4.05-3.96 (m, 2.3 H), 3.92-3.79 (m, 3 H), 3.74-3.64 (m, 1 H, H-5_a), 3.53 (dd, *J* = 4.9, 11.1 Hz, 1 H, H-5_b), 2.41 (s, 3 H, CH_3^{Ts}), 1.45 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 1.17 (s, 6 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 150.0 (C=O), 144.6, 144.4, 138.1, 138.0, 137.9, 137.6, 137.4, 136.9, 129.6, 129.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 112.3 (Cq, *C*$(Me)_2$), 109.4 (Cq, *C*$(Me)_2$), 104.9, 104.8 (C-1'), 91.9 (C-1), 86.6, 84.6, 84.2 (C-2), 83.7, 82.7, 82.3, 81.7, 80.2, 79.9, 79.7, 78.9, 78.7, 73.4, 73.3, 72.7, 72.5, 72.4, 71.6, 71.4, 71.3, 69.9 (C-5), 67.4 (C-6'), 26.9 (*C*H_3), 26.6 (*C*H_3), 26.1 (*C*H_3), 25.1 (*C*H_3), 21.6 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m/z* Calcd for $C_{46}H_{57}N_2O_{13}S^+$ $[M+ NH_4]^+$: 877.3576, found: 877.3561.



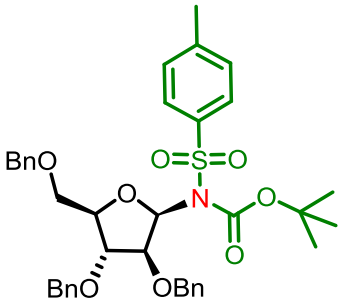
2,3,5-Tri-*O*-benzyl-β-D-arabinofuranosyl 2,2,2-trichloroethyl tosylcarbamate (3p). Synthesized according to general procedure in 1 mmol

scale, afforded **3p** (575 mg, yield 77%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.2 Hz, 2 H, Ar^{Ts}), 7.34-7.28 (m, 13 H), 7.27-7.22 (m, 4 H), 6.28 (d, *J* = 5.7 Hz, 1 H, H-1), 5.07 (t, *J* = 6.1 Hz, 1 H, H-2), 4.77 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.73-4.65 (m, 3 H, PhCH_2), 4.64-4.59 (m, 1 H, PhCH_2), 4.58-4.51 (m, 3 H, PhCH_2, OCH_2^{Troc}), 4.50-4.49 (m, 1 H, H-4), 4.22 (dd, *J* = 6.4, 8.2 Hz, 1 H, H-3), 3.65 (dd, *J* = 2.6, 11.1 Hz, 1 H, H-5$_a$), 3.52 (dd, *J* = 5.1, 11.1 Hz, 1 H, H-5$_b$), 2.39 (s, 3 H, CH_3^{T}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7 (C=O), 144.9, 138.1, 137.9, 137.4, 136.2, 129.5, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 93.1 (*C*Cl_3), 92.4 (C-1), 84.9 (C-2), 82.4 (C-3), 81.8 (C-4), 75.9 (Ph*C*H_2), 73.4 (Ph*C*H_2), 72.6 (O*C*H_2^{Troc}), 72.5 (Ph*C*H_2), 69.9 (C-5), 21.7 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{36}H_{40}Cl_3N_2O_8S^+$ [M+ NH_4]$^+$: 765.1565, found: 765.1567.

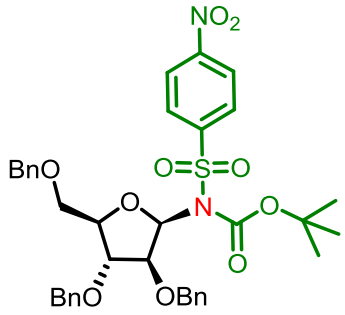


2,3,5-Tri-*O*-benzyl-α/β-D-arabinofuranosyl 2-methoxyethyl tosylcarbamate (3q). Synthesized according to general procedure in 1 mmol scale, afforded **3q** (527 mg, yield 78%, α: β = 1:2); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.89 (m, 2 H), 7.36-7.25 (m, 16 H), 7.22-7.19 (m, 1 H), 6.85 (d, *J* = 5.5 Hz, 1 H, H-1), 5.01-4.99 (m, 0.5 H), 4.78-4.69 (m, 1 H), 4.68-4.60 (m, 1 H), 4.59-4.54 (m, 3 H), 4.52-4.48 (m, 1 H), 4.46-4.39 (m, 1 H), 4.37-4.33 (m, 0.5 H), 4.20-4.16 (m, 1.5 H), 4.13-4.05 (m, 1 H), 4.02-3.97 (m, 0.5 H), 3.78-3.74 (m, 0.5 H), 3.69-3.62 (m, 1 H), 3.54-3.49 (m, 0.5 H), 3.46-3.42 (m, 1 H), 3.34-3.32 (m, 1 H), 3.22 (s, 3 H, OCH_3), 2.40 (s, 3 H, CH_3^{Ts}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 151.8, 151.7, 144.6, 144.4, 138.2, 138.1, 138.0, 137.5, 137.2, 136.9, 136.5, 129.3, 128.6, 128.5, 128.4, 128.3,

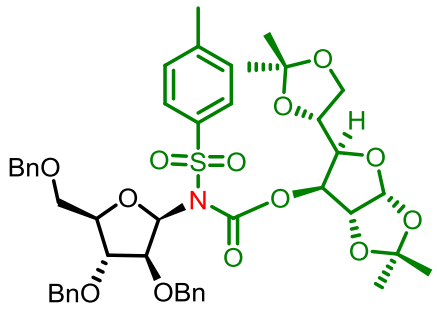
128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 92.1 (C-1), 85.5, 85.4 (C-2), 84.0, 83.1, 82.6, 81.7, 79.4, 73.4, 73.3, 73.2, 72.5, 72.4, 70.9, 70.0 (C-5), 69.7, 69.6 (CH$_2$OMe), 66.3, 65.9, 58.7, 58.5 (OCH_3), 21.7 (CH_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{37}H_{45}N_2O_9S^+$ [M+ NH_4]$^+$: 693.2840, found: 693.2820.



2,3,5-Tri-*O*-benzyl-β-D-arabinofuranosyl *tert*-butyl tosylcarbamate (3r). Synthesized according to general procedure in 1 mmol scale, afforded **3r** (457 mg, yield 68%, α: β = 1:30); eluant, hexane-EtOAc (4:1); as a pale syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2 H), 3.39-3.36 (m, 3 H), 7.35-7.32 (m, 5 H), 7.31-7.22 (m, 9 H), 6.22 (d, *J* = 5.7 Hz, 1 H, H-1), 5.04 (t, *J* = 6.1 Hz, 1 H, H-2), 4.78 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.68 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.62-4.57 (m, 3 H, PhCH_2), 4.55-4.51 (m, 2 H, PhCH_2, H-4), 4.20 (dd, *J* = 6.4, 8.2 Hz, 1 H, H-3), 3.67 (dd, *J* = 2.6, 11.1 Hz, 1 H, H-5$_a$), 3.54 (dd, *J* = 4.9, 11.1 Hz, 1 H, H-5$_a$), 2.39 (s, 3 H, CH_3^{Ts}), 1.29 (s, 9 H, CH_3^{Boc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3 (C=O), 144.1, 138.3, 138.1, 137.6, 137.4, 129.2, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 91.6 (C-1), 85.2 (Cq $_{Boc}$), 84.8 (C-2), 82.5 (C-3), 81.5 (C-4), 73.4 (PhCH_2), 72.4 (PhCH_2), 72.3 (PhCH_2), 70.0 (C-5), 27.8 (CH_3^{Boc}), 21.6 (CH_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{38}H_{47}N_2O_8S^+$ [M+ NH_4]$^+$: 691.3048, found: 691.3040.

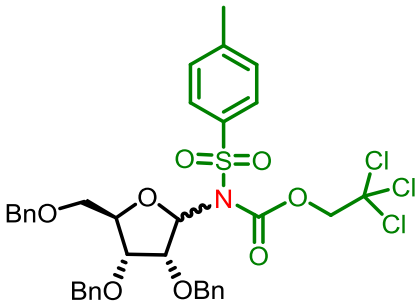


2,3,5-Tri-*O*-benzyl-β-D-arabinofuranosyl *tert*-butyl *N*-(4-nitrophenyl)sulfonylcarbamate (3s). Synthesized according to general procedure in 1 mmol scale, afforded **3s** (472 mg, yield 67%, α: β = 1:20); eluant, hexane-EtOAc (4:1); as a pale syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8.16 (m, 4 H), 7.38-7.36 (m, 4 H), 7.34-7.30 (m, 9 H), 7.27-7.25 (m, 2 H), 6.17 (d, *J* = 5.6 Hz, 1 H, H-1), 5.04 (t, *J* = 6.1 Hz, 1 H, H-2), 4.77 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.65 (dd, *J* = 11.8. Hz, 2 H, PhCH_2), 4.6.0-4.50 (m, 4 H, PhCH_2, H-4), 4.21 (dd, *J* = 6.5, 8.2 Hz, 1 H, H-3), 3.67 (dd, *J* = 2.5, 11.1 Hz, 1 H, H-5_a), 3.54 (dd, *J* = 4.9, 10.8 Hz, 1 H, H-5_b), 1.31 (s, 9 H, CH_3^{Boc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3 (C=O), 149.8, 145.8, 138.0, 137.9, 137.3, 129.4, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 123.9, 91.9 (C-1), 86.4 (Cq $_{Boc}$), 84.8 (C-2), 82.3 (C-3), 81.6 (C-4), 73.5 (PhCH$_2$), 72.5 (PhCH$_2$), 72.4 (PhCH$_2$), 69.9 (C-5), 27.8 (CH_3^{Boc}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{37}H_{44}N_3O_{10}S^+$ $[M+ NH_4]^+$: 772.2742, found: 772.2740.



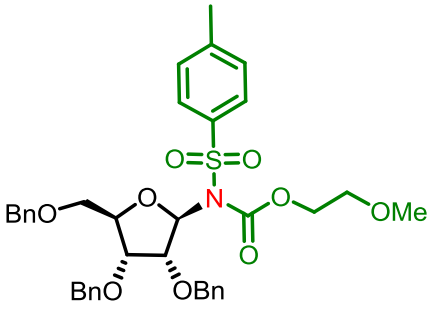
(1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranosyl) *N*-(2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl) *N*-tosyl carbamate (3t). Synthesized according to general procedure in 1 mmol scale, afforded **3t** (618 mg, yield 72%, α: β = 1:20); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.3 Hz, 2 H), 7.37-7.30 (m, 10 H), 7.29-7.25 (m, 7 H), 6.24 (d, *J* = 5.6 Hz, 1 H, H-1), 5.66 (d, *J* = 3.6

Hz, 1 H, H-1'), 5.27 (d, *J* = 2.8 Hz, 1 H), 5.09 (dd, *J* = 5.9, 6.2 Hz, 1 H, H-2), 4.75 (d, *J* = 11.7 Hz, 1 H, PhC*H*$_2$), 5.68 (d, *J* = 11.6 Hz, 1 H, PhC*H*$_2$), 4.62-4.58 (m, 2 H, PhC*H*$_2$), 4.56-4.59 (m, 3 H, PhC*H*$_2$, H-4), 4.22-4.19 (m, 2 H), 4.04 (dd, *J* = 2.8, 8.7 Hz, 1 H, H-3), 3.82-3.76 (m, 2 H, H-6'), 3.74-3.68 (m, 1 H), 3.65 (dd, *J* = 2.6, 11.1 Hz, 1 H, H-5$_a$), 3.52 (dd, *J* = 5.2, 11.1 Hz, 1 H, H-5$_b$), 2.41 (s, 3 H, C*H*$_3^{Ts}$), 1.46 (s, 3 H, C*H*$_3$), 1.31 (s, 3 H, C*H*$_3$), 1.24 (s, 3 H, C*H*$_3$), 1.14 (s, 3 H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7 (C=O), 144.6, 138.1, 137.9, 137.5, 136.9, 129.5, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 112.4 (Cq, *C*(Me)$_2$), 109.4 (Cq, *C*(Me)$_2$), 104.9 (C-1'), 92.4 (C-1), 85.6 (C-2), 82.9, 82.4, 81.7, 79.9, 79.3, 73.4 (Ph*C*H$_2$), 72.7 (Ph*C*H$_2$), 72.6 (Ph*C*H$_2$), 71.5, 70.0 (C-5), 67.5 (C-6'), 26.8 (*C*H$_3$), 26.7 (*C*H$_3$), 26.2 (*C*H$_3$), 25.0 (*C*H$_3$), 21.6 (*C*H$_3^{Ts}$); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{46}H_{57}N_2O_{13}S^+$ $[M+ NH_4]^+$: 877.3576, found: 877.3559.

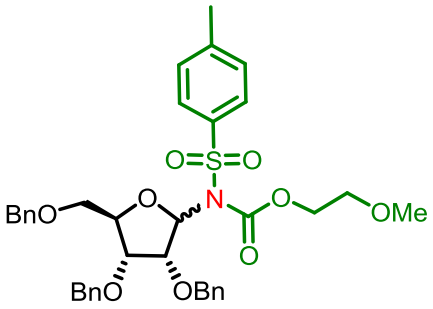


2,3,5-Tri-*O*-benzyl-α/β-D-ribofuranosyl 2,2,2-trichloroethyl tosylcarbamate (3u). Synthesized according to general procedure in 1 mmol scale, afforded **3u** (536 mg, yield 75%, α: β = 1:2.3); eluant, hexane-EtOAc (4:1); as a pale yellow syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.2 Hz, 2 H), 7.45-7.43 (m, 1 H), 7.37-7.24 (m, 14 H), 7.18-7.14 (m, 2 H), 6.25 (d, *J* = 3.2 Hz, 0.3 H), 6.07 (d, *J* = 9.1 Hz, 0.7 H, H-1), 4.91 (brs, 1 H), 4.82-4.59 (m, 2 H), 4.57-4.49 (m, 3 H), 4.47-4.40 (m, 2 H), 4.32-4.19 (m, 2 H), 4.09-4.02 (m, 1 H), 3.90-3.69 (m, 1 H), 3.64-3.56 (m, 1 H), 2.34 (s, 3 H, C*H*$_3^{Ts}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 150.2 (C=O), 144.9, 144.5, 138.9, 138.1, 137.9, 137.8, 137.2, 136.4, 136.1, 129.4, 129.2, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 127.4, 93.8 (*C*Cl_3), 92.9, 83.7, 80.8, 77.8, 75.8, 75.7, 75.6, 74.9, 74.1,

73.7, 73.3, 72.4, 72.1, 71.5, 71.1, 69.6, 64.4, 21.6 (CH$_3^{Ts}$); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{36}H_{40}Cl_3N_2O_8S^+$ [M+ NH_4]$^+$: 765.1565, found: 765.1567.

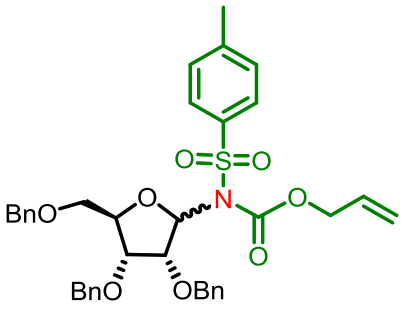


2,3,5-Tri-*O*-benzyl-β-D-ribofuranosyl 2-methoxyethyl tosylcarbamate (3v). Synthesized according to general procedure in 1 mmol scale, afforded **3v** (513 mg, yield 76%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.3 Hz, 2 H), 7.44-7.42 (m, 2 H), 7.36-7.24 (m, 11 H), 7.13 (d, *J* = 8.1 Hz, 4 H), 6.00 (d, *J* = 9.0 Hz, 1 H, H-1), 4.89 (brs, 2 H, OCH_2), 4.53 (ABq, *J* = 12.1 Hz, 2 H, PhCH_2), 4.50-4.37 (m, 2 H), 4.30-4.27 (m, 2 H), 4.12-4.08 (m, 2 H), 4.06-4.01 (m, 1 H), 3.90 (dd, *J* = 4.9, 10.4 Hz, 1 H, H-5$_a$), 3.59-3.56 (m, 1 H, H-5$_b$), 3.38-3.36 (m, 2 H, CH_2OMe), 3.18 (s, 3 H, OCH_3), 2.37 (s, 3 H, CH_3^{Ts}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 144.1, 139.1, 138.0, 137.9, 136.9, 130.9, 129.1, 128.6, 128.5, 128.3, 128.2, 127.8, 127.7, 127.5, 127.4, 127.3, 83.5 (C-1), 75.4, 75.2, 74.1, 71.4, 69.7 (*C*H$_2$OMe), 65.9, 64.5 (C-5), 58.6 (O*C*H$_3$), 21.6 (*C*H$_3^{Ts}$); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{37}H_{45}N_2O_9S^+$ [M+ NH_4]$^+$: 693.2840, found: 693.2840.



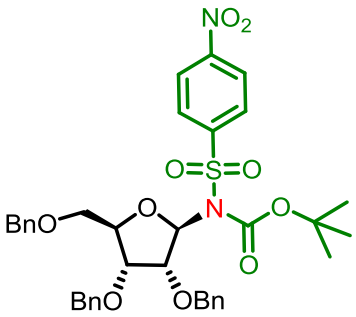
2,3,5-Tri-*O*-benzyl-α/β-D-ribofuranosyl 2-methoxyethyl tosylcarbamate (3v'). Synthesized according to general procedure in 1 mmol scale, afforded **3v** (486 mg, yield

72%, α:β 1:2.6); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.83 (m, 2 H), 7.44-7.41 (m, 2 H), 7.36-7.28 (m, 11 H), 7.26-7.24 (m, 2 H), 7.14-7.12 (m, 2 H), 6.30 (d, *J* = 5.2 Hz, 1 H, H-1α), , 6.00 (d, *J* = 9.0 Hz, 1 H, H-1$_\beta$), 4.89-4.87 (m, 1.5 H), 4.83-4.78 (m, 0.5 H), 4.69-4.58 (m, 1.6 H), 4.58-4.53 (m, 3 H), 4.51-4.46 (m, 2 H), 4.32-4.27 (m, 1.6 H), 4.18-4.04 (m, 2.4 H), 4.08-3.96 (m, 2 H), 3.94-3.88 (m, 1 H), 3.75-3.65 (m, 0.6 H), 3.61-3.47 (m, 1.5 H), 3.39-3.31 (m, 2 H, C*H*$_2$OMe), 3.18 (s, 3 H, OC*H*$_3$), 2.37 (s, 3 H, C*H*$_3^{Ts}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 151.8, 144.4, 144.1, 139.0, 138.2, 138.0, 137.9, 137.7, 137.4, 136.8, 129.3, 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 88.8, 83.5, 80.1, 77.8, 77.5, 77.2, 75.5, 75.2, 74.4, 74.1, 72.7, 72.5, 71.4, 70.3, 69.7, 69.6, (*C*H$_2$OMe), 65.9, 65.6, 64.5, 64.4 (C-5), 58.6, 58.5 (O*C*H$_3$), 21.6 (*C*H$_3^{Ts}$); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{37}H_{45}N_2O_9S^+$ $[M+ NH_4]^+$: 693.2840, found: 693.2840.

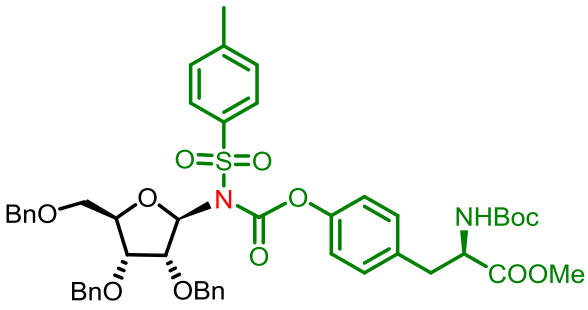


2,3,5-Tri-*O*-benzyl-α/β-D-ribofuranosyl allyl tosylcarbamate (3w). Synthesized according to general procedure in 1 mmol scale, afforded **3w** (552 mg, yield 84%, α: β = 1:3.8); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.81(m, 2 H), 7.45-7.43 (m, 1 H), 7.35-7.24 (m, 14 H), 7.15-7.13 (m, 2 H), 6.30 (d, *J* = 5.3 Hz, 0.2 H), 6.01 (d, *J* = 9.0 Hz, 0.8 H, H-1), 5.70-5.59 (m, 1 H, =C*H*), 5.17-5.05 (m, 2 H, =C*H*$_2$), 4.93-4.88 (m, 2 H), 4.61-4.53 (m, 3 H), 4.49-4.39 (m, 3 H), 4.29-4.14 (m, 2 H), 4.06-4.00 (m, 1 H), 3.93-3.88 (m, 0.7 H), 3.73-3.69 (m, 0.3 H), 3.61-3.50 (m, 1 H), 2.37 (s, 3 H, C*H*$_3^{Ts}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 144.2, 138.9,

137.9, 137.8, 137.6, 136.9, 136.8, 131.3, 130.7 (=*C*H), 129.3, 129.1, 128.8, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 119.1(=*C*$H_{2\ Allyl}$), 88.9, 83.4 (C-1), 80.3, 75.2, 74.4, 74.1, 74.0, 73.4, 72.8, 71.4, 71.3, 68.8, 67.7, 67.6, 64.5, 21.6 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m/z* Calcd for $C_{37}H_{43}N_2O_8S^+$ [M+ NH_4]$^+$: 675.2735, found: 675.2723.

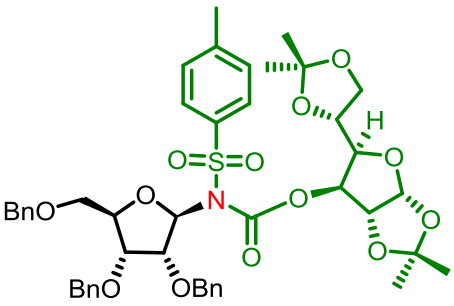


2,3,5-Tri-*O*-benzyl-β-D-ribofuranosyl *tert*-butyl *N*-(4-nitrophenyl)sulfonylcarbamate (3x). Synthesized according to general procedure in 1 mmol scale, afforded **3x** (458 mg, yield 65%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.96 (m, 4 H), 7.45-7.44 (m, 2 H), 7.39-7.26 (m, 11 H), 7.14-7.11 (m, 2 H), 5.92 (d, *J* = 9.1 Hz, 1 H, H-1), 4.98 (d, *J* = 12.1 Hz, 1 H, PhCH_2), 4.89 (d, *J* = 12.1 Hz, 1 H), 4.58 (ABq, *J* = 12.2 Hz, 2 H), 4.54-4.49 (m, 1 H), 4.37-4.31 (m, 2 H), 4.28-4.20 (m, 1 H), 4.08-3.96 (m, 2 H, H-5), 3.68-3.63 (m, 1 H), 1.31 (s, 9 H, CH_3^{Boc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 146.0, 138.9, 137.9, 137.3, 129.0, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 123.5, 85.9, 83.5 (tert-C^{Boc}), 75.4, 74.2, 73.9, 71.6, 71.5, 64.7 (C-5), 27.8 (*C*H_3^{Boc}); HRMS (ESI-TOF) *m/z* Calcd for $C_{37}H_{44}N_3O_{10}S^+$ [M+ NH_4]$^+$: 722.2742, found: 722.2742.



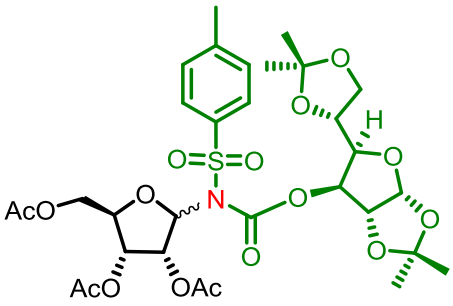
***N'*-(2,3,5-Tri-O-benzyl-β-D-ribofuranosyl) *N'*-tosyl *O*-(*N*-Boc-tyrosine methyl ester) carbamate (3y).** Synthesized according to

general procedure in 1 mmol scale, afforded **3y** (572 mg, yield 64%, α:β = 1:20); eluant, hexane-EtOAc (4:1); as a pale syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85(d, *J* = 8.1 Hz, 2 H), 7.45-7.43 (m, 2 H), 7.36-7.25 (m, 12 H), 7.15-7.13 (m, 3 H), 7.01 (d, *J* = 8.3 Hz, 2 H), 6.69 (d, *J* = 8.3 Hz, 2 H), 6.09 (d, *J* = 9.0 Hz, 1 H, H-1), 4.91 (brs, 2 H), 4.61-4.41 (m, 5 H, PhCH_2, C*H*-NH), 4.34-4.31 (m, 2 H), 4.09-4.05 (m, 1 H, H-5_a), 3.94 (dd, *J* = 4.9, 10.2 Hz, 1 H, H-5_b), 3.68 (s, 3 H, OCH_3), 3.63-3.59 (m, 1 H), 3.09-2.97(m, 2 H, CH_2), 2.39 (s, 3 H, CH_3^{Ts}), 1.41 (s, 9 H, CH_3^{Boc}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 172.1, 155.1, 148.8, 144.5, 143.5, 138.9, 137.9, 137.7, 136.7, 134.3, 130.4, 130.3, 129.9, 129.7, 129.3, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.4, 121.2, 115.5, 83.8 (C-1), 80.1 (tert-C^{Boc}), 75.3, 74.1, 73.9, 71.5, 64.6 (C-5), 54.6, 54.3 (*C*H-NH), 52.3, 52.2 (O*C*H_3), 37.5 (*C*H_2), 28.3 (*C*H_3^{Boc}), 21.7, 21.5 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{49}H_{58}N_3O_{12}S^+$ $[M+NH_4]^+$: 912.3736, found: 912.3732.

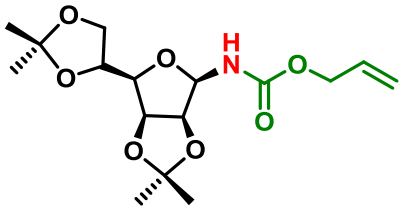


(1,2;5,6-di-*O*-isopropylidene-β-D-glucofuranosyl) *N*-(2,3,5-tri-*O*-benzyl-β-D-ribofuranosyl) *N*-tosyl carbamate (3z). Synthesized according to general procedure in 1 mmol scale, afforded **3z** (506 mg, yield 59%, β only); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.1 Hz, 2 H), 7.44-7.42 (m, 2 H), 7.34-7.25 (m, 13 H), 7.17-7.15 (m, 2 H), 5.99 (d, *J* = 9.1 Hz, 1 H, H-1), 5.63 (d, *J* = 2.7 Hz, 1 H, H-1'), 5.26 (d, *J* = 2.6 Hz, 1 H), 4.89 (brs, 2 H), 4.59-4.45 (m, 5 H), 4.20-4.18 (m, 2 H), 4.07-4.01 (m, 1 H), 3.97 (dd, *J* = 2.5, 8.7 Hz, 1 H), 3.94-3.89 (m, 1 H), 3.85-3.76 (m, 2 H), 3.59-3.56 (m, 1 H), 3.39-3.36 (m, 1 H), 2.39 (s, 3 H, CH_3^{Ts}), 1.45 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 163.6, 144.3, 138.9, 137.9, 137.6, 137.4, 129.4, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.5, 127.4, 126.9, 112.4 (Cq, *C*$(Me)_2$), 109.4 (Cq, *C*$(Me)_2$), 105.1 (C-1'), 91.9, 83.7, 82.6, 95.6, 78.7, 75.2, 74.5, 74.2 (Ph*C*H_2), 71.6 (Ph*C*H_2), 71.5 (Ph*C*H_2), 71.3, 67.3 (C-6'), 64.4 (C-5), 26.9 (*C*H_3), 26.6 (*C*H_3), 26.0 (*C*H_3), 24.9 (*C*H_3), 21.6 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m/z* Calcd for $C_{46}H_{57}N_2O_{13}S^+$ $[M+ NH_4]^+$: 877.3576, found: 877.3552.

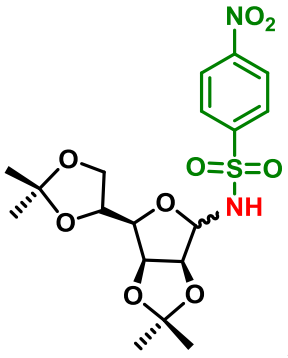


(1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranosyl) *N*-(2,3,5-tri-*O*-acetyl-α/β-D-ribofuranosyl) *N*-tosyl carbamate (3aa). Synthesized according to general procedure in 1 mmol scale, afforded **3aa** (357 mg, yield 50%, α: β = 1:1.5); eluant, hexane-EtOAc (4:1); as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 7.34 (d, *J* = 8.3 Hz, 2 H, Ar^{Ts}), 6.07 (d, *J* = 2.9, Hz, 1 H), 5.91 (d, *J* = 9.1, Hz, 0.5 H), 5.79-5.76 (m, 1 H), 5.73-5.79 (m, 1 H), 5.54-5.47 (m, 1 H), 5.28-5.17 (m, 1 H), 5.05-5.01 (m, 0.5 H), 4.50-4.45 (m, 0.5 H), 4.32-4.31 (m, 0.5 H), 4.26-4.19 (m, 1 H), 4.09-3.98 (m, 3 H), 3.95-3.81 (m, 2 H), 3.65-3.62 (m, 0.6 H), 2.45 (s, 3 H, CH_3^{Ts}), 2.14 (s, 3 H, CH_3^{Ac}), 2.07 (s, 3 H, CH_3^{Ac}), 2.03 (s, 3 H, CH_3^{Ac}), 1.45 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.24 (s, 6 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 169.9 (C=O^{Ac}), 169.5, 169.4 (C=O^{Ac}), 169.3, 169.1 (C=O^{Ac}), 149.6 (C=O), 144.9, 144.8, 136.8, 136.3, 129.6, 129.5, 128.3, 127.9, 112.4, 112.2 (Cq, *C*$(Me)_2$), 110.6, 109.3 (Cq, *C*$(Me)_2$), 105.0, 104.9 (C-1'), 91.0, 82.7, 82.4, 81.6, 79.9, 79.6, 79.2, 78.9, 73.6, 71.7, 71.5, 69.6, 68.7, 67.5, 67.4, 66.1, 63.7, 62.6, 26.8, 26.7 (*C*H_3), 26.6, 26.5 (*C*H_3), 26.1, 26.0 (*C*H_3), 25.0, 24.9 (*C*H_3), 21.6, 21.5 (*C*H_3^{Ts}), 20.8 (*C*H_3^{Ac}), 20.6 (*C*H_3^{Ac}), 20.5 (*C*H_3^{Ac}); HRMS (ESI-TOF) *m/z* Calcd for $C_{31}H_{45}N_2O_{16}S^+$ $[M+ NH_4]^+$: 733.2484, found: 733.2485.



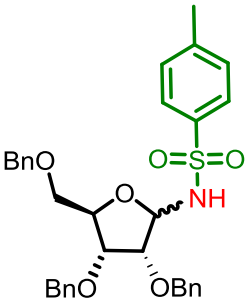
2,3;5,6-Di-*O*-isopropylidene-β-D-mannofuranosyl allyl carbamate (4).

A comp **3g** (180 mg, 0.222mmol) and K_2CO_3 (63 mg, 0.457 mmol) , dissolved in minimum quantity of DMF (5 ml) was taken in a round bottom flask and stirred at rt . PhSH (0.03 mL, 0.28 mmol) was added slowly to a reaction mixture and allowed to stirred for 5-6 h. Et_2O (10 mL) was added in the reaction mixture and was extracted with 1M aq. HCl (2 x 5 mL), washed with brine (10 mL) and dried over Na_2SO_4. The crude product was concentrated and purified by flash column chromatography (1:5 to 1:2 EtOAc/hexane) to yield the desired product **4** (119 mg, 66 %), as a clear syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96-5.86 (m, 1 H, =C*H*), 5.53 (brs, 1 H, NH), 5.34-5.22 (m, 3 H, H-1, =CH_2), 4.89 (brs, 2 H, H-2, H-3), 4.58-4.56 (m, 2 H, C$H_{2\ Allyl}$), 4.39-4.35 (m, 1 H, H-5), 4.09-4.01 (m, 3 H, H-4, H-6), 1.49 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4 (C=O), 132.2 (=*C*H), 118.2 (=*C*H_2),, 112.9 (Cq, *C*$(Me)_2$), 109.1 (Cq, *C*$(Me)_2$), 88.1 (C-1), 85.3 (C-2), 81.2 (C-4), 80.5 (C-3), 73.4 (C-5), 66.7 (C-6), 66.0 (C$H_{2\ Allyl}$), 26.9 (*C*H_3), 25.9 (*C*H_3), 25.1 (*C*H_3), 24.6 (*C*H_3); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{16}H_{25}NO_7^+$ $[M+ Na]^+$: 366.1523, found: 366.1522.



***N*-(4-nitrophenyl)sulfonyl 1-amino-1-deoxy- 2,3;5,6-Di-*O*-isopropylidene-α/β-D-mannofuranoside (5).**

A stirring solution of **3g** (116 mg, 0.144 mmol) in MeOH/THF (1:2, 9 mL).was treated with sodium p-toluenesulfinate (35 mg, 0.187 mmol mmol) and Pd(PPh3)4 (23 mg, 0.021 mmol) followed by degassing the solvent with an argon balloon for 30 minutes . After stirring the reaction for 2 hrs, EtOAc (10 mL) was added and the reaction mixture was extracted with NH4Cl (2 x 10 mL), washed with water (10 mL), dried over Na2SO4 and concentrated under vacuum. Flash column chromatography (1:8 to 1:2 EtOAc/Hexane) was performed to separate the desired product **5** (71 mg, 61 %, α:β 1:1.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37-8.32 (m, 2 H, Ar^{Ns}), 8.13-8.08 (m, 2 H, Ar^{Ns}), 6.00-5.92 (m, 1 H), 5.39-5.37 (m, 0.7 H), 5.05 (dd, *J* = 3.5, 9.8 Hz, 0.3 H), 4.74-4.66 (m, 3 H), 4.26-4.19 (m, 1 H), 3.88-3.82 (m, 1 H), 3.72-3.70 (m, 1 H), 3.48-3.31 (m, 1 H), 1.45 (s, 3 H, C*H*$_3$), 1.34 (s, 3 H, C*H*$_3$), 1.31 (s, 3 H, C*H*$_3$), 1.29 (s, 3 H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 150.1, 147.0, 146.9, 146.7, 146.5, 128.5, 128.4, 124.3, 124.1, 113.6, 113.5 (Cq, *C*$(Me)_2$), 109.3, 109.2 (Cq, *C*$(Me)_2$), 89.4, 89.3, 85.6, 85.5, 83.9, 83.8, 80.5, 79.6, 79.4, 79.2, 79.0, 78.3, 72.6, 72.5, 66.4, 66.0, 26.9, 26.8 (*C*H_3), 25.7, 25.6 (*C*H_3), 25.1, 24.9 (*C*H_3), 24.6, 24.5 (*C*H_3); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{18}H_{24}N_2NaO_9S^+$ $[M+ Na]^+$: 447.1095, found: 447.1090.



2,3,5-Tri-*O*-benzyl-α/β-D-ribofuranosyl *p*-toluenesulfonamide (6).

In a stirred solution of **3v** (50 mg, 0.07 mmol) in dry MeOH (10 ml), K_2CO_3 (46 mg, 0.33 mmol) was added to a solution. The resulting mixture was stirred under reflux for 3 h. After this time, the crude product was evaporated *in vacuo*. The residue was purified by flash column chromatography to yield two anomers (α/β 1:1.8) of the desired product 6 (23 mg 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.61 (m, 2 H, Ar), 7.38-7.28 (m, 11 H, Ar), 7.24-

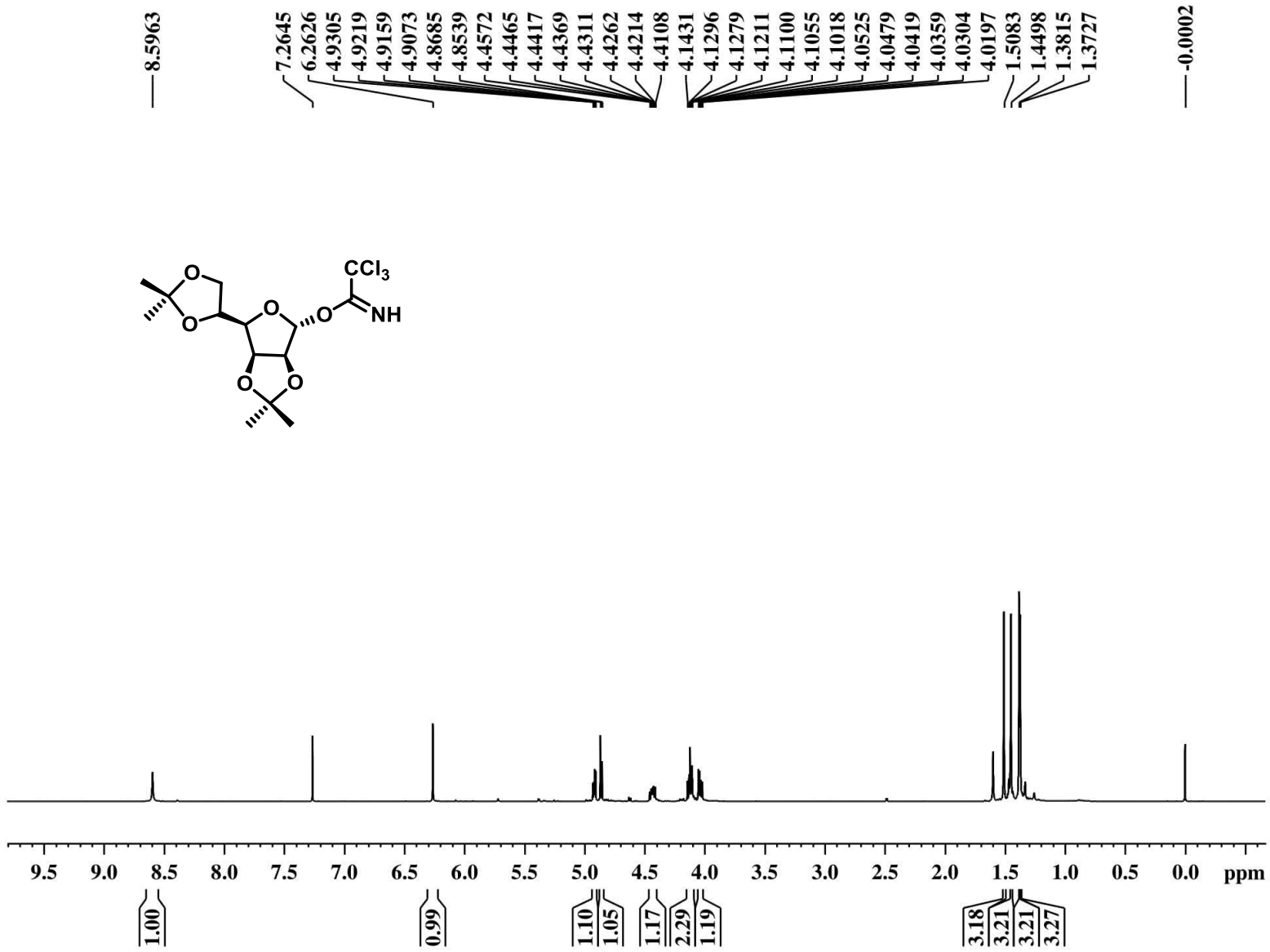
7.14 (m, 6 H), 6.23 (d, *J* = 9.0 Hz, 0.4 H), 5.51-5.27 (m, 1 H), 4.86-4.61 (m, 2 H), 4.58-4.51 (m, 2 H), 4.48-4.45 (m, 1 H), 4.42-4.31 (m, 2 H), 4.15-3.91 (m, 2 H), 3.43-3.30 (m, 2 H), 2.37 (s, 3 H, CH_3^{Ts}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 142.9, 140.9, 139.3, 138.1, 137.8, 137.6, 137.3, 137.2, 129.5, 129.3, 128.7, 128.6, 128.5, 18.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.1. 126.9, 83.2, 81.5, 81.1, 78.6, 77.7, 76.9, 74.9, 74.2, 73.4, 73.2, 72.8, 72.3, 71.2, 70.6, 69.9, 65.4, 21.6, 21.5 (*C*H_3^{Ts}); HRMS (ESI-TOF) *m*/*z* Calcd for $C_{33}H_{35}NNaO_6S^+$ $[M+ Na]^+$: 596.2077, found: 596.2080.

5. Spectral data of **1a, 1eα, 1eαβ**

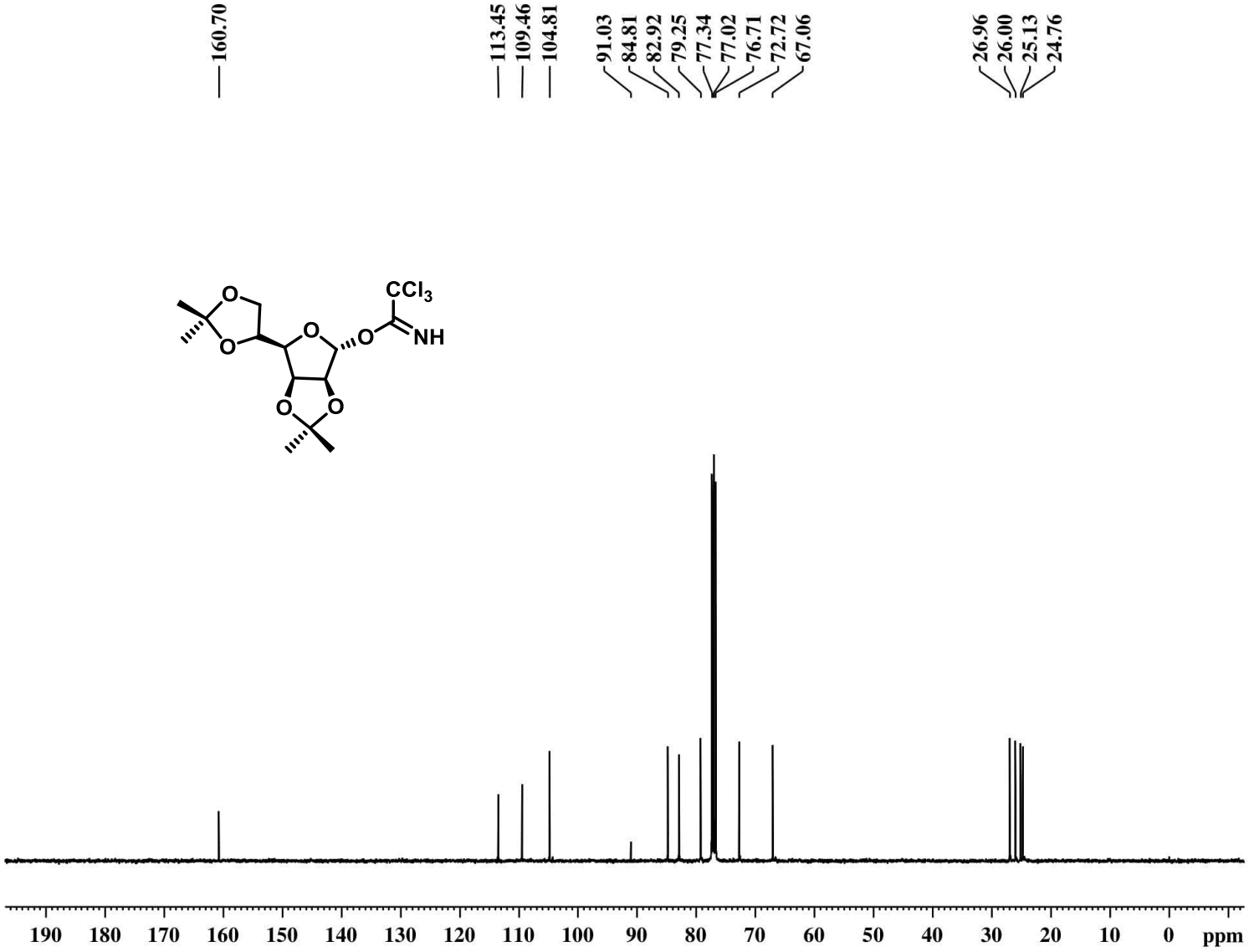
6. Spectral data of **2a, 2b, 2d, 2e, 2f. 2g, 2h, 2i, 2j**

7. Confirmation the exact structure **3a** by NMR (**NOESY correlation data**) and Spectra Data, HRMS of all the synthesized *N*-glycofuranosides (**3a-3z, 3v', 3aa**)

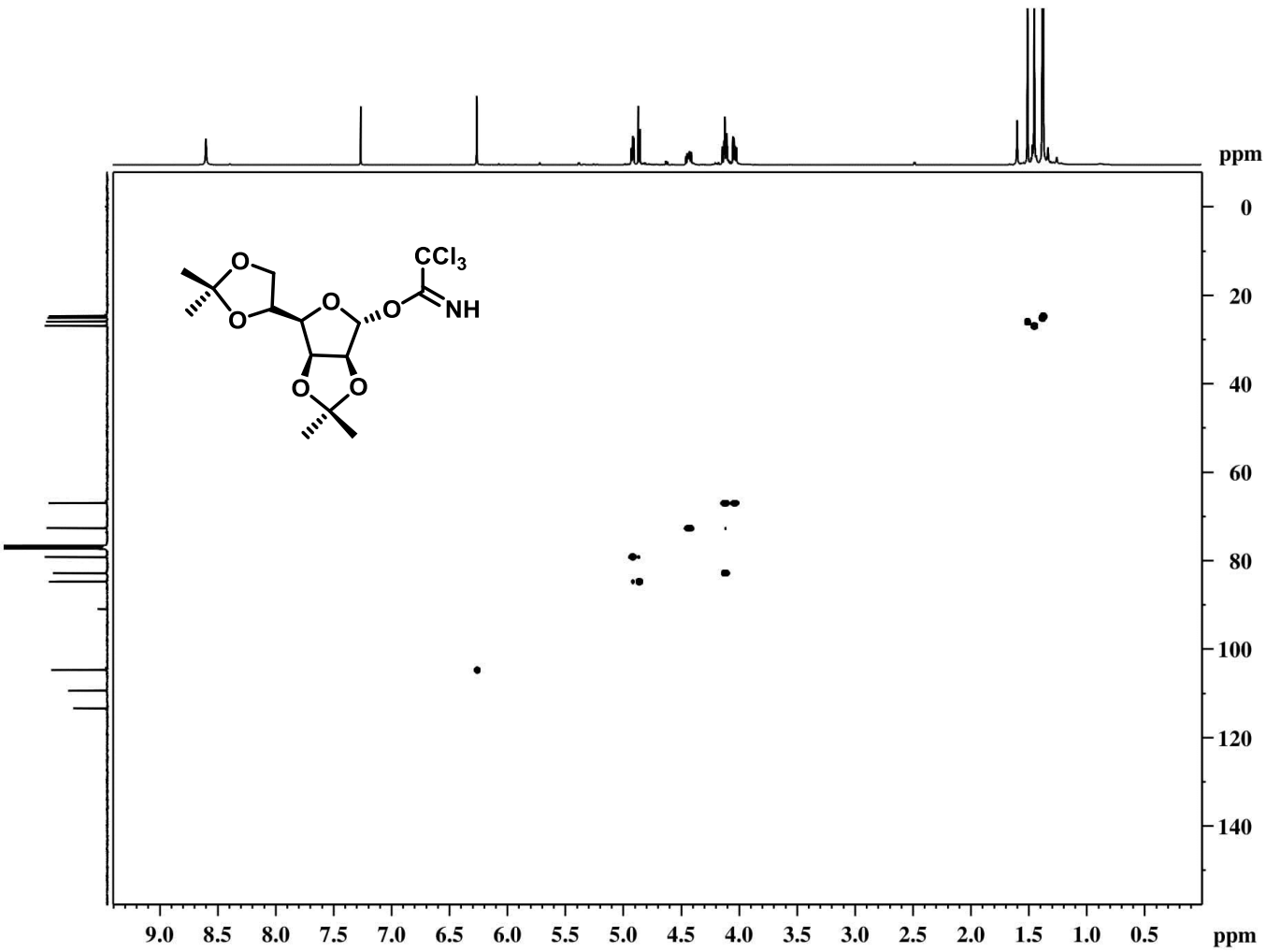
8. Spectra Data, HRMS of compounds **4, 5, 6**



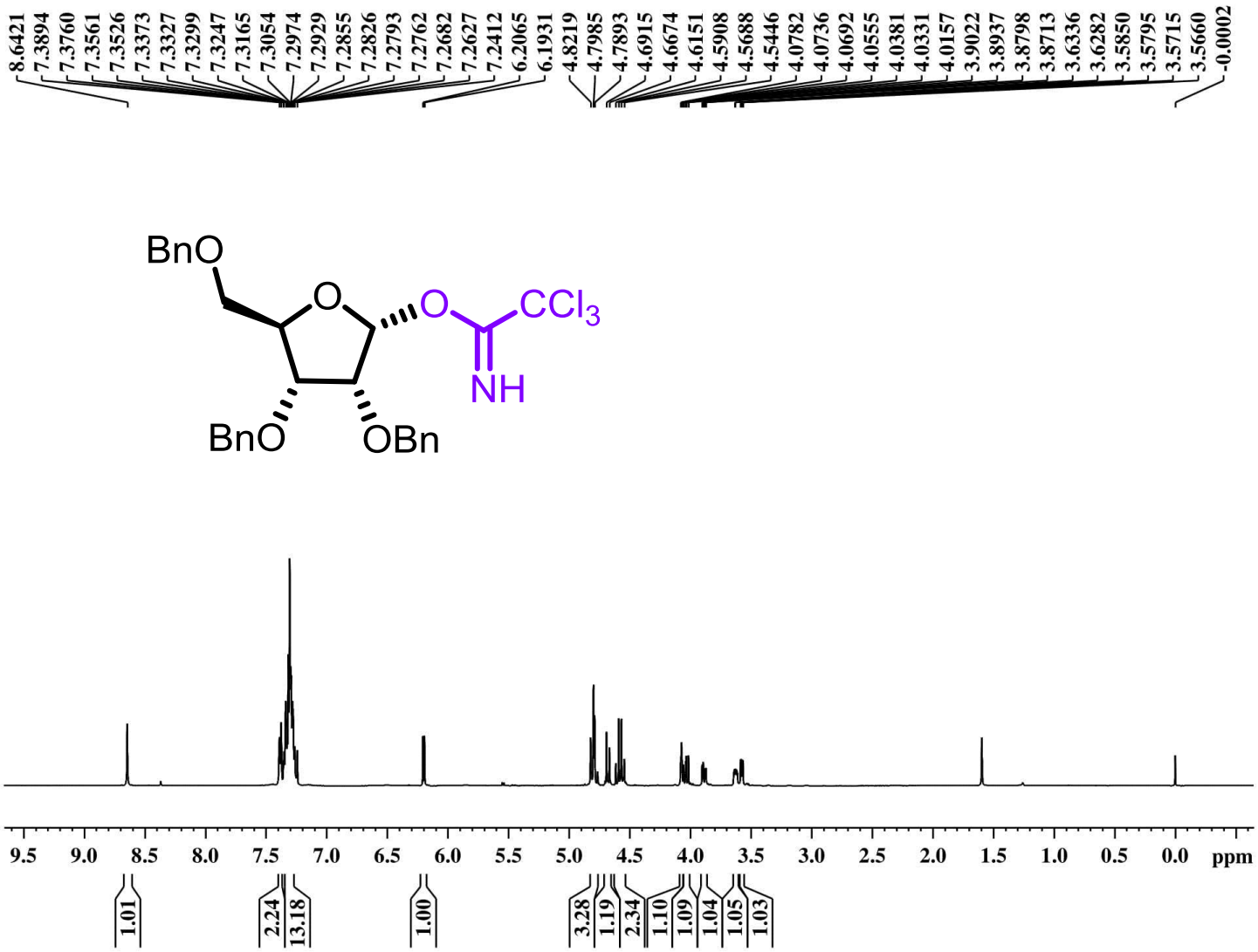
^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$)



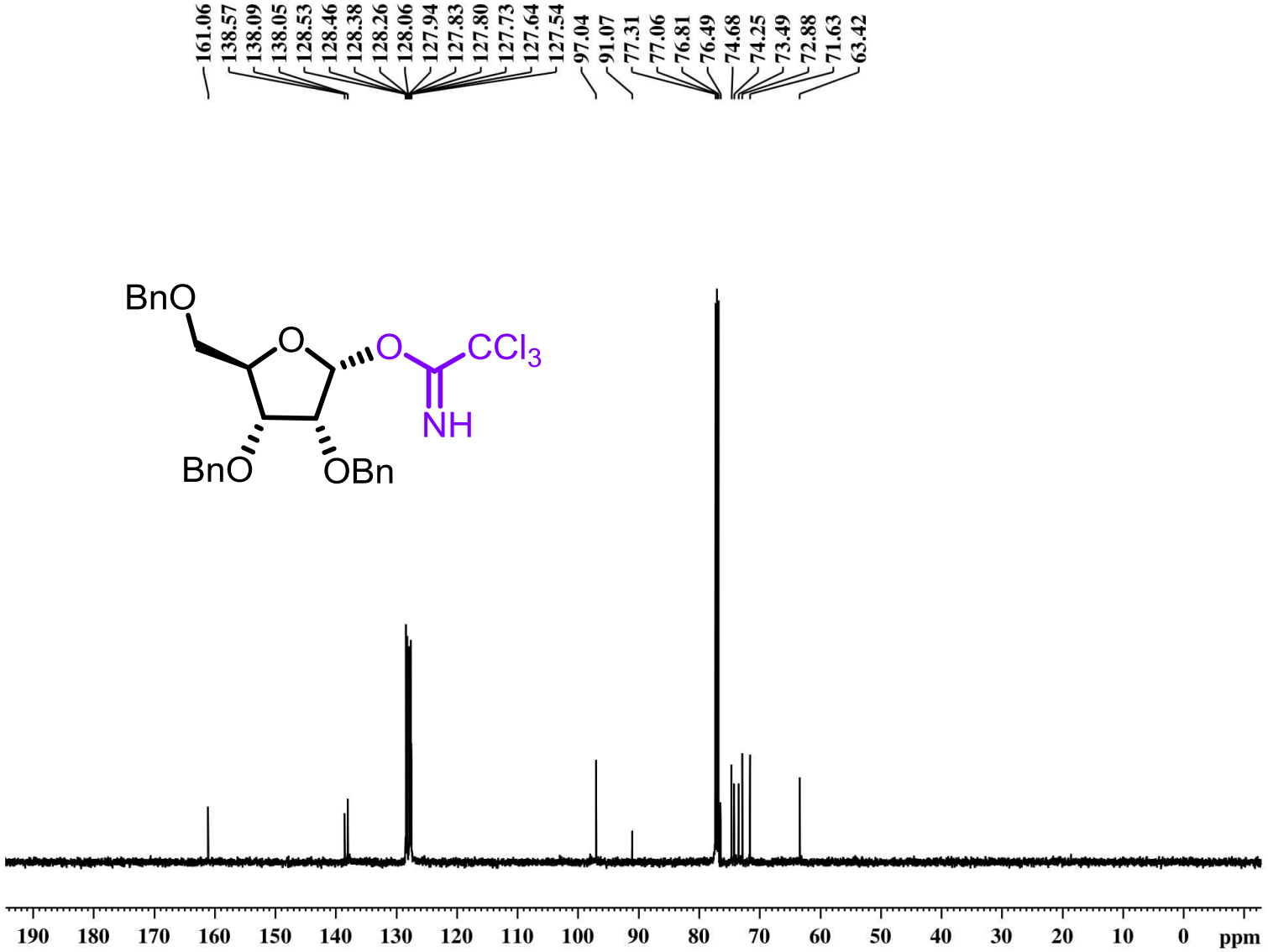
^{13}C NMR spectrum of **2a** (100 MHz, MHz, $CDCl_3$)



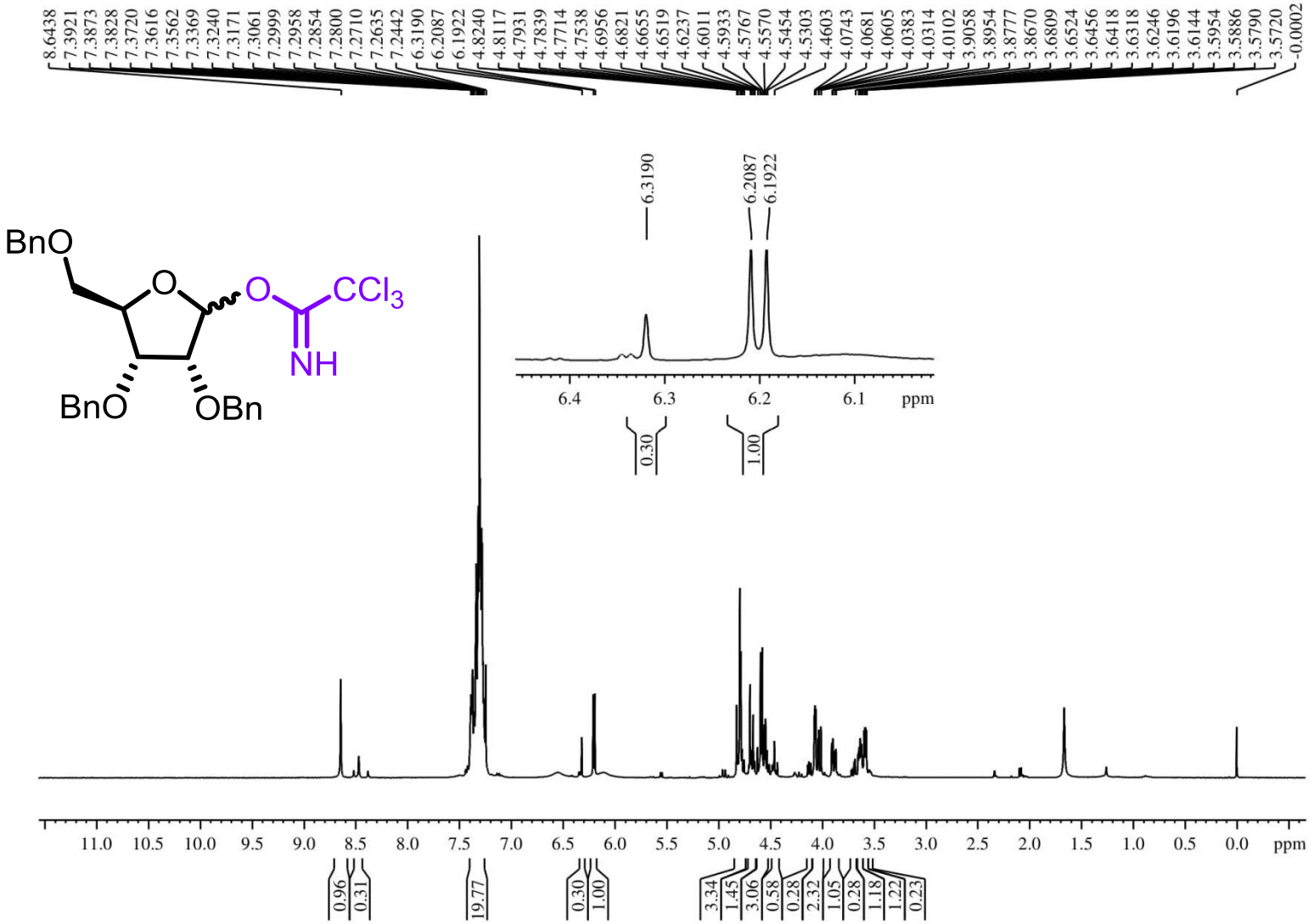
2D HSQC spectrum of **1a** ($CDCl_3$).



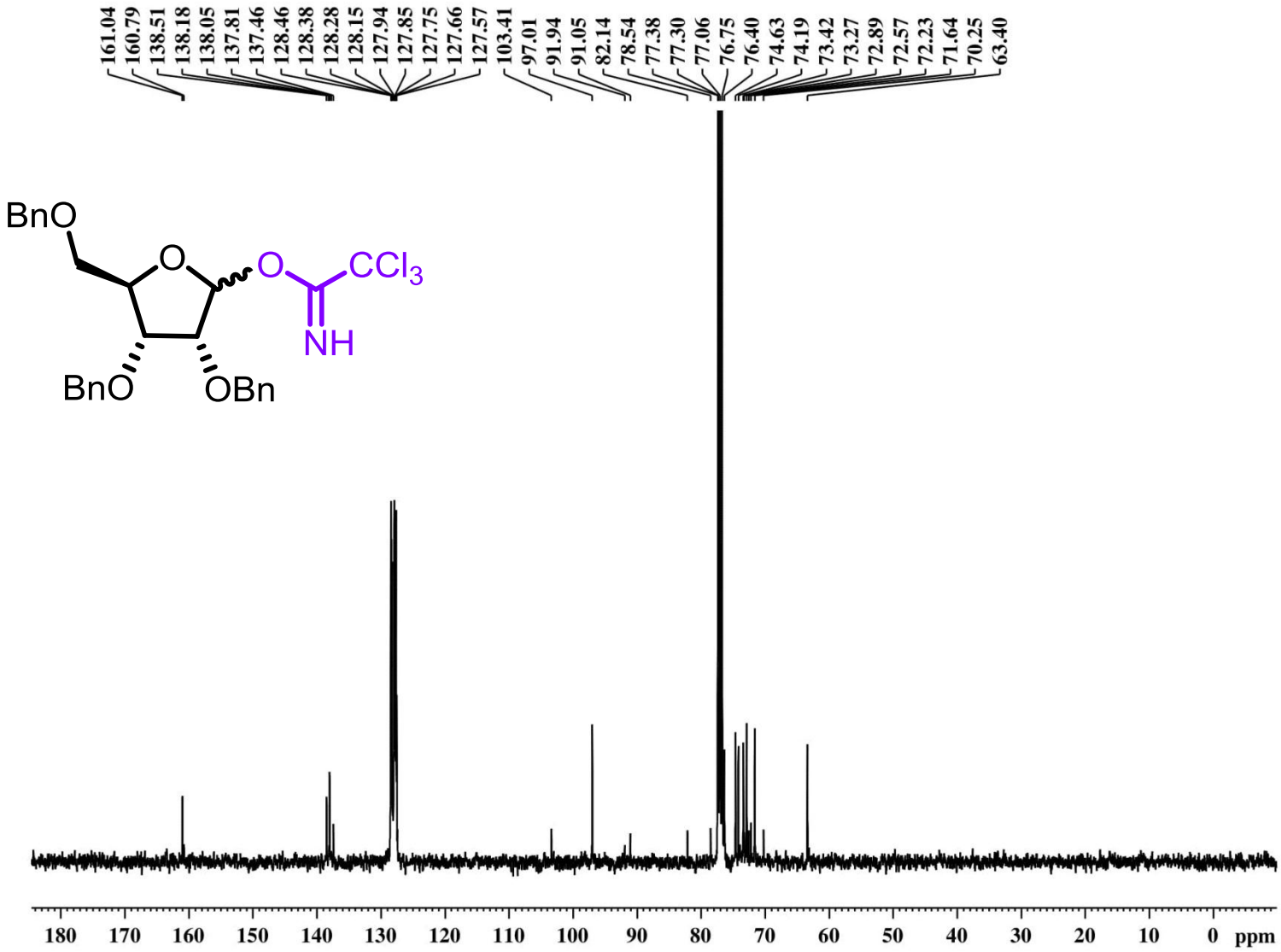
^{1}H NMR spectrum of **1eα** (400 MHz, $CDCl_3$)



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

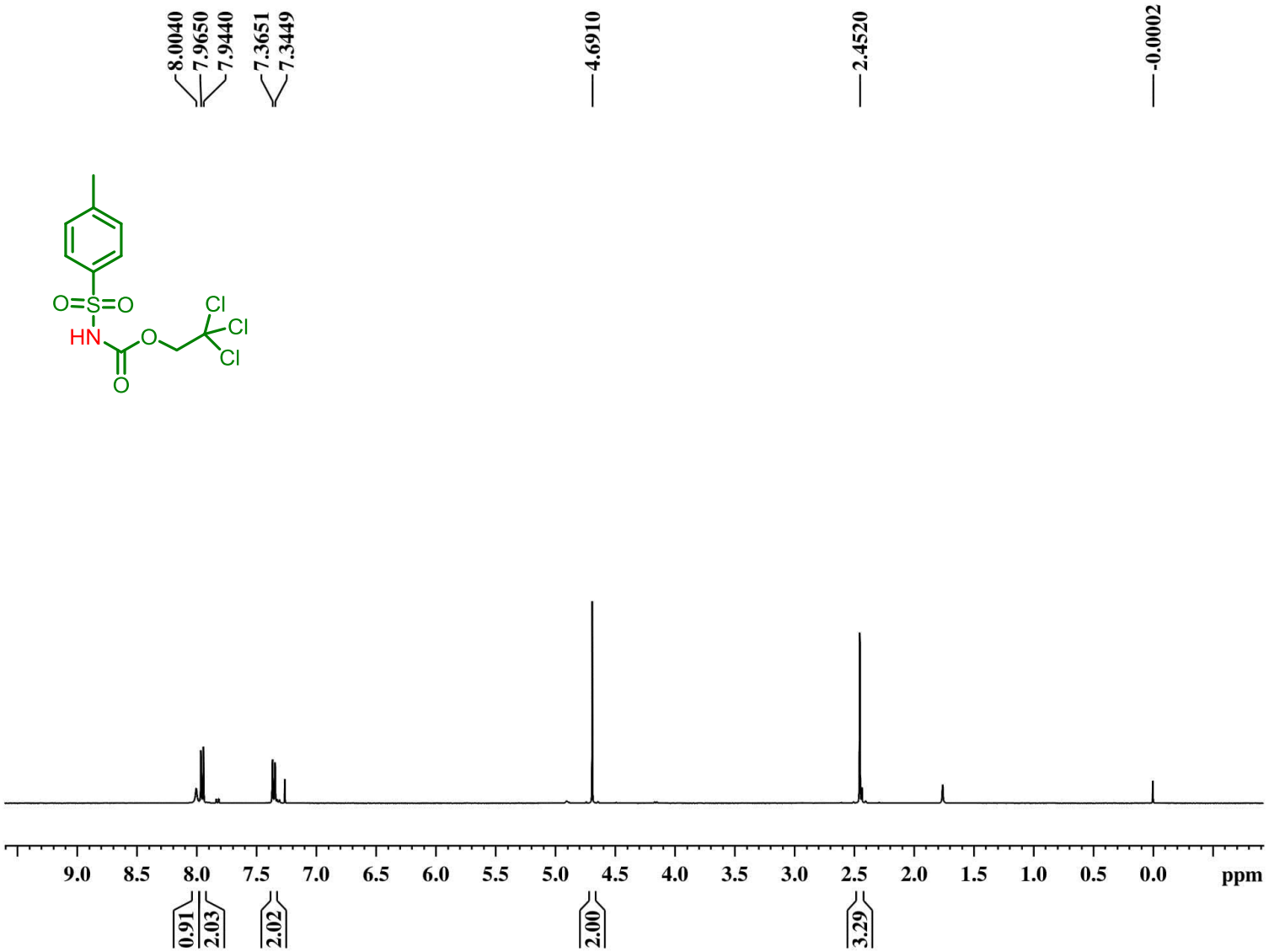


^{1}H NMR spectrum of **1eαβ** (400 MHz, $CDCl_3$)

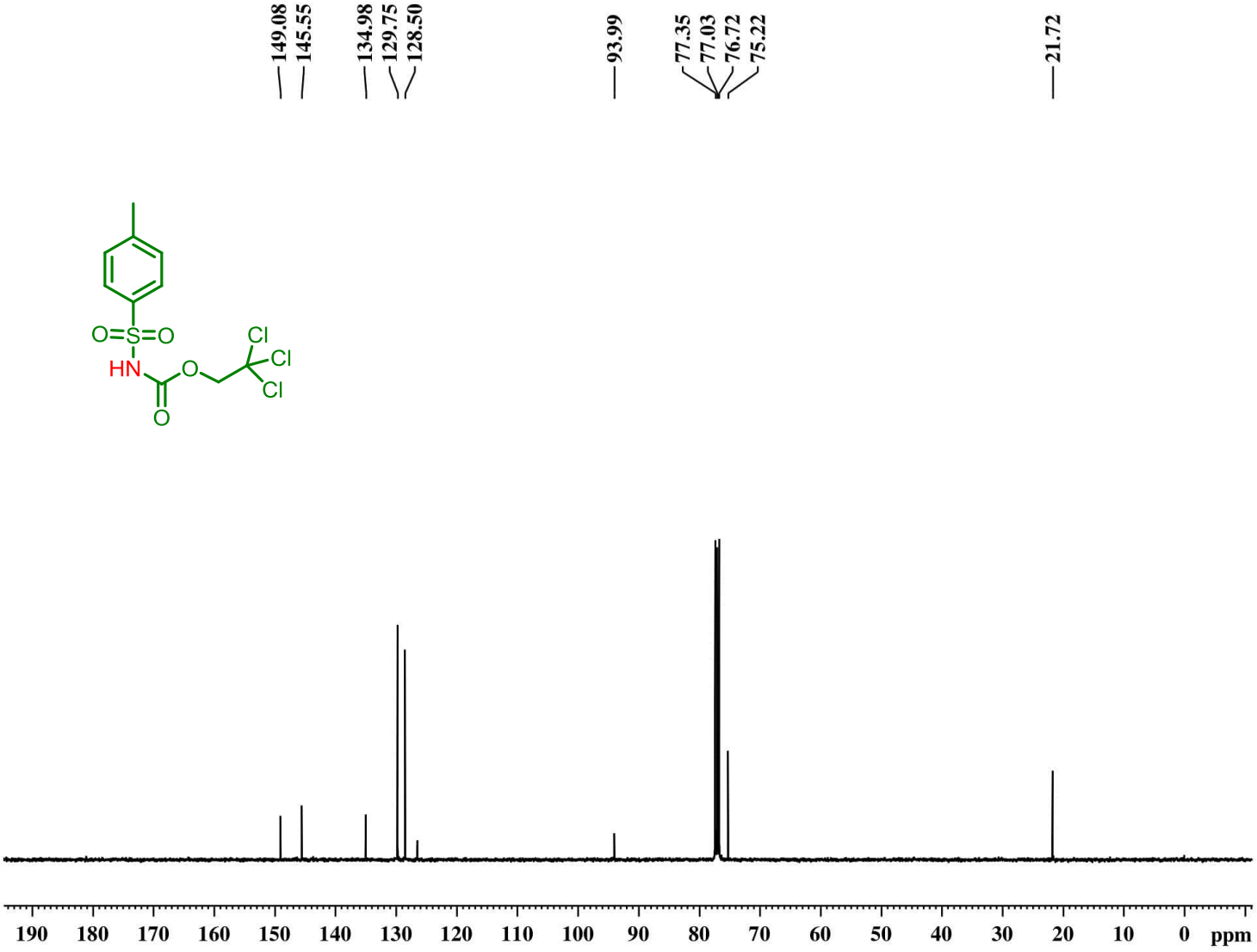


^{13}C NMR spectrum of **1eαβ** (100 MHz, MHz, $CDCl_3$)

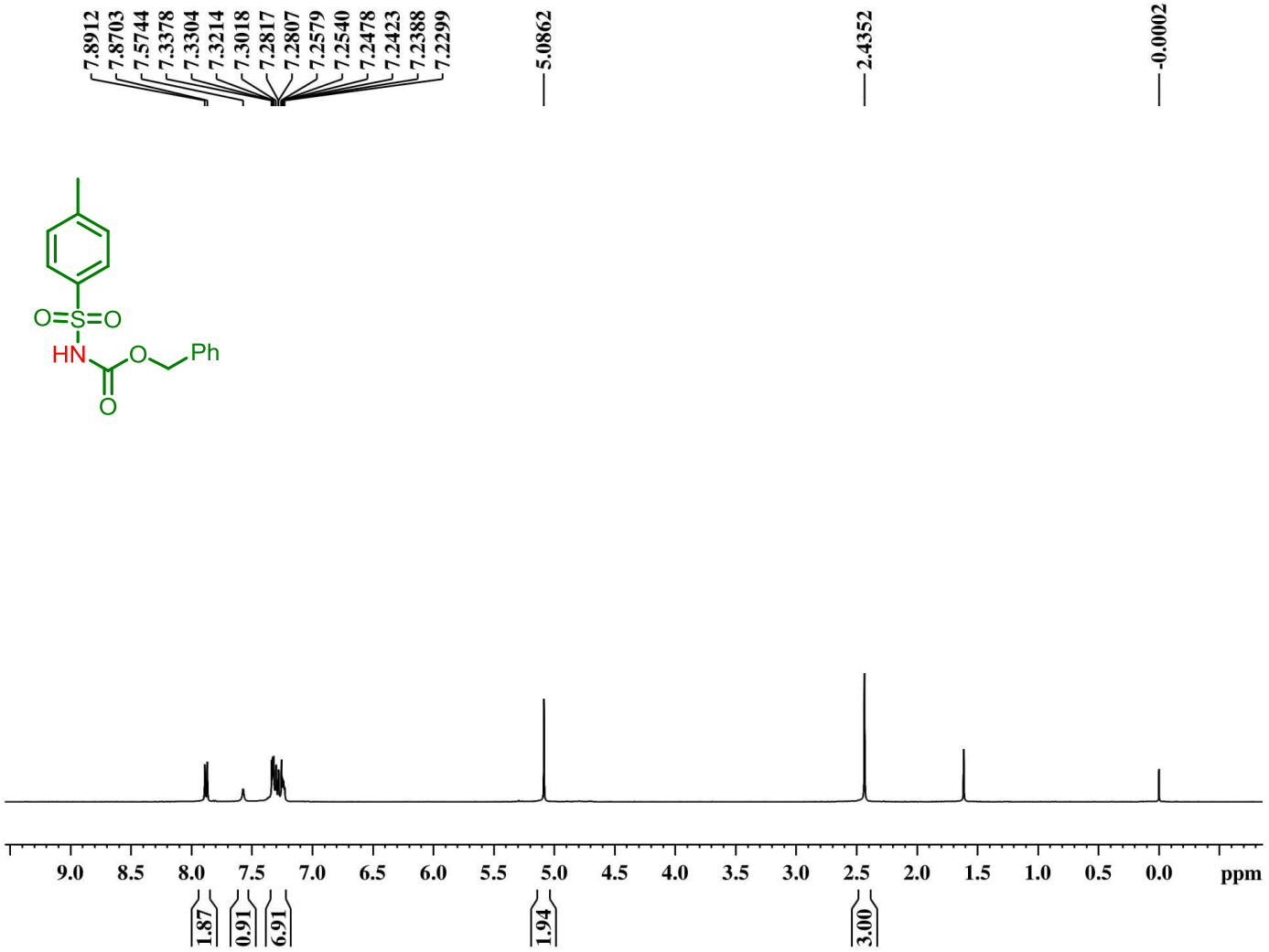
6. Spectral data of **2a, 2b, 2d, 2e, 2f. 2g, 2h, 2i, 2j**



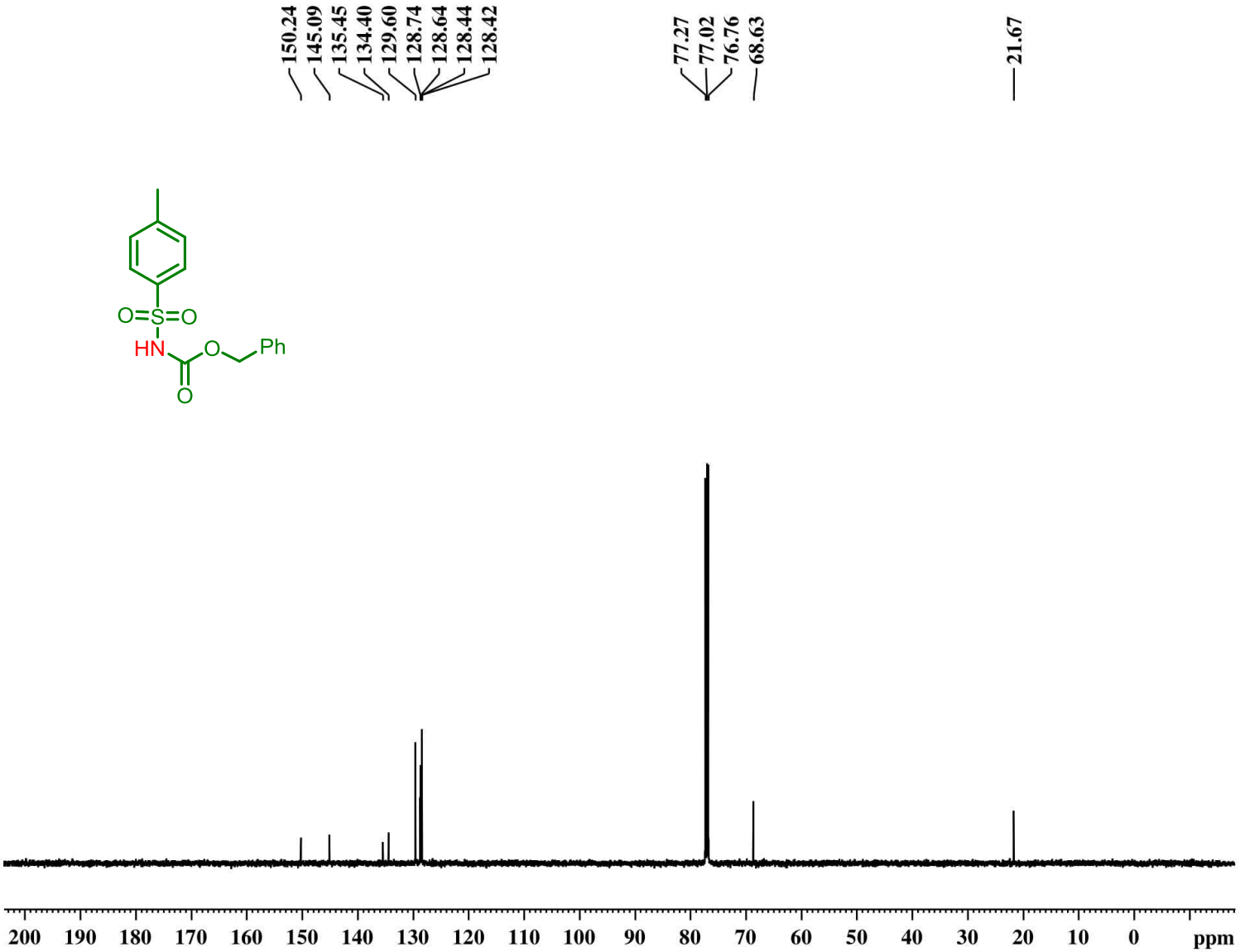
^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)



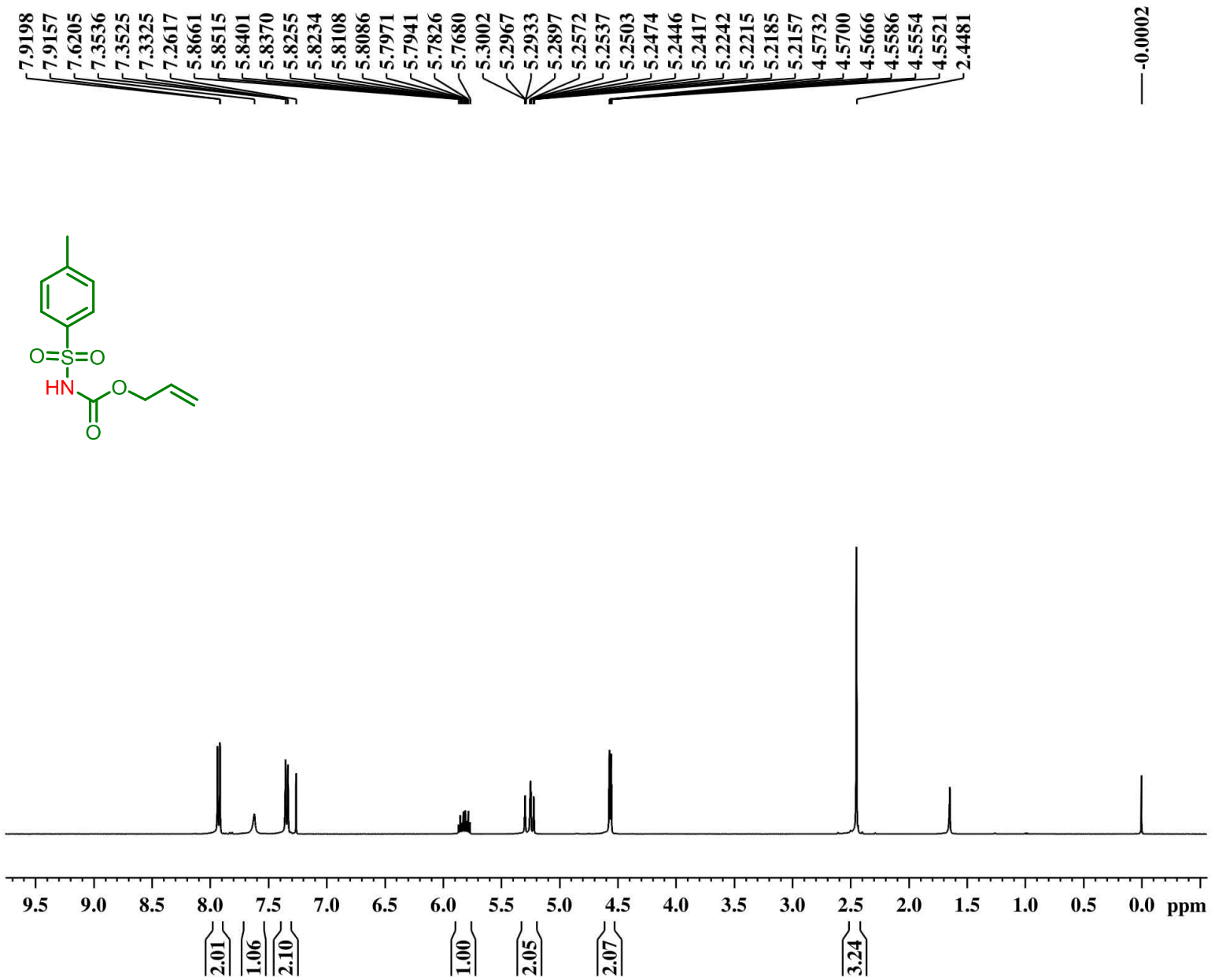
^{13}C NMR spectrum of **2a** (100 MHz, MHz, $CDCl_3$)



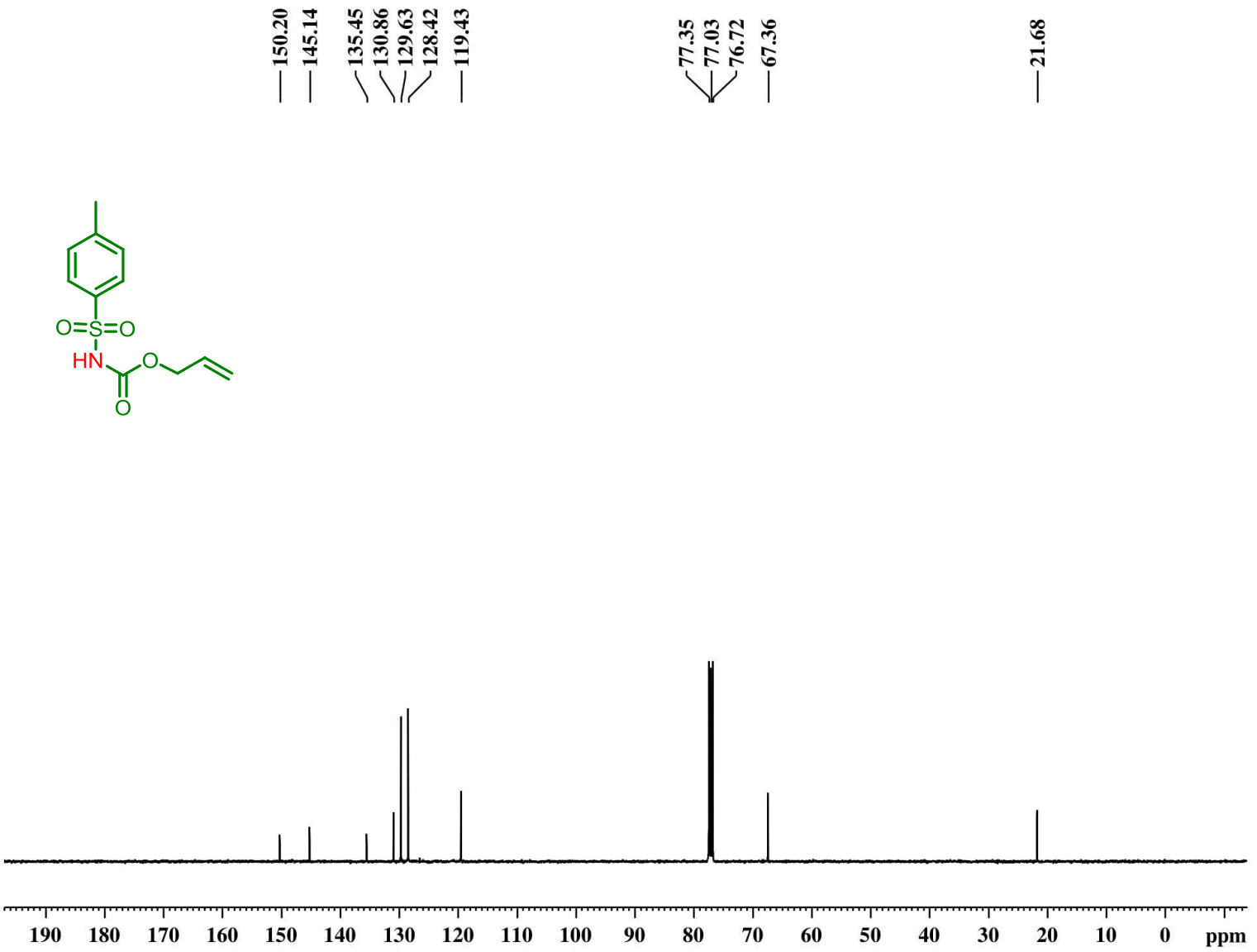
^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$)



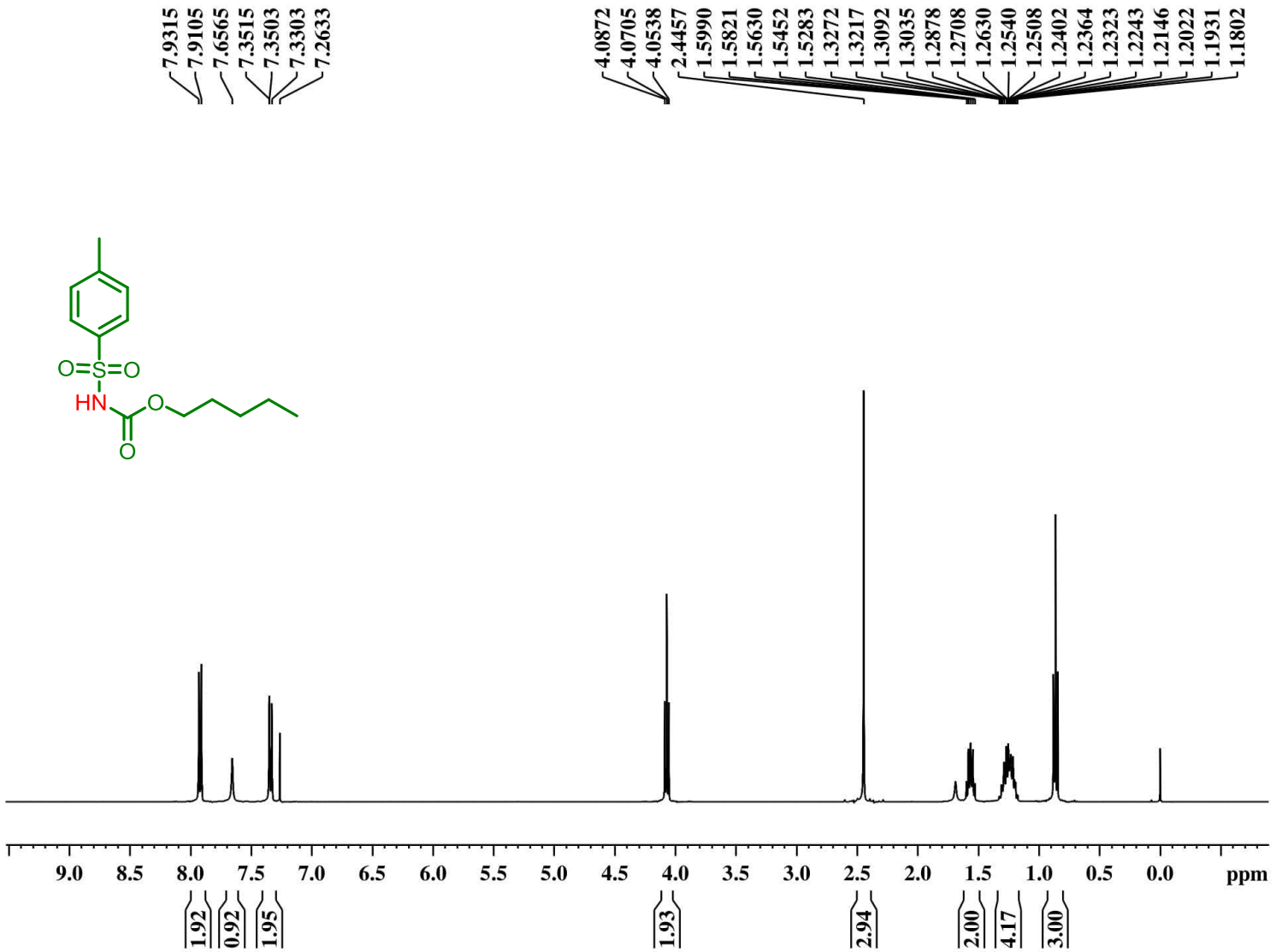
^{13}C NMR spectrum of **2b** (100 MHz, MHz, $CDCl_3$)



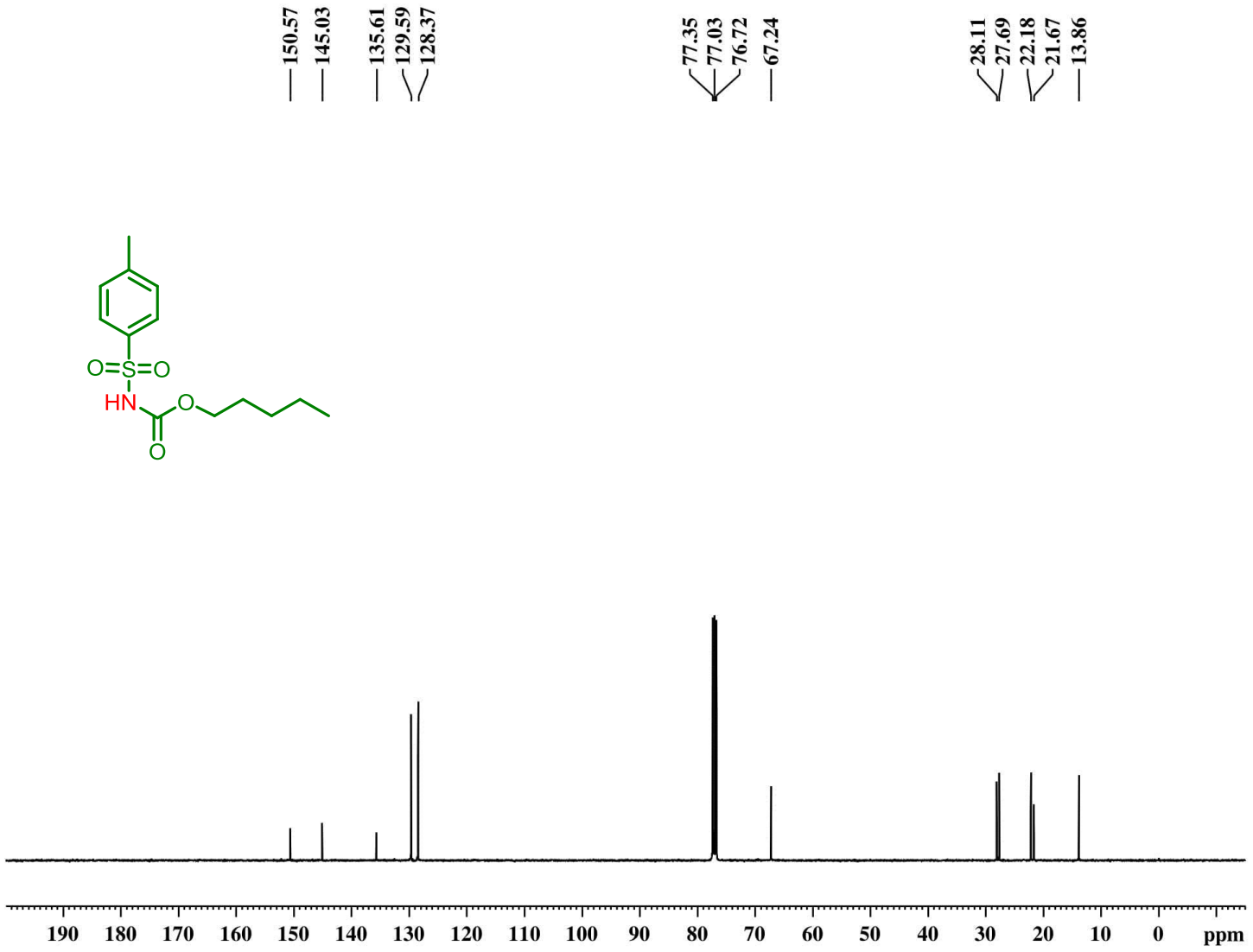
^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$)



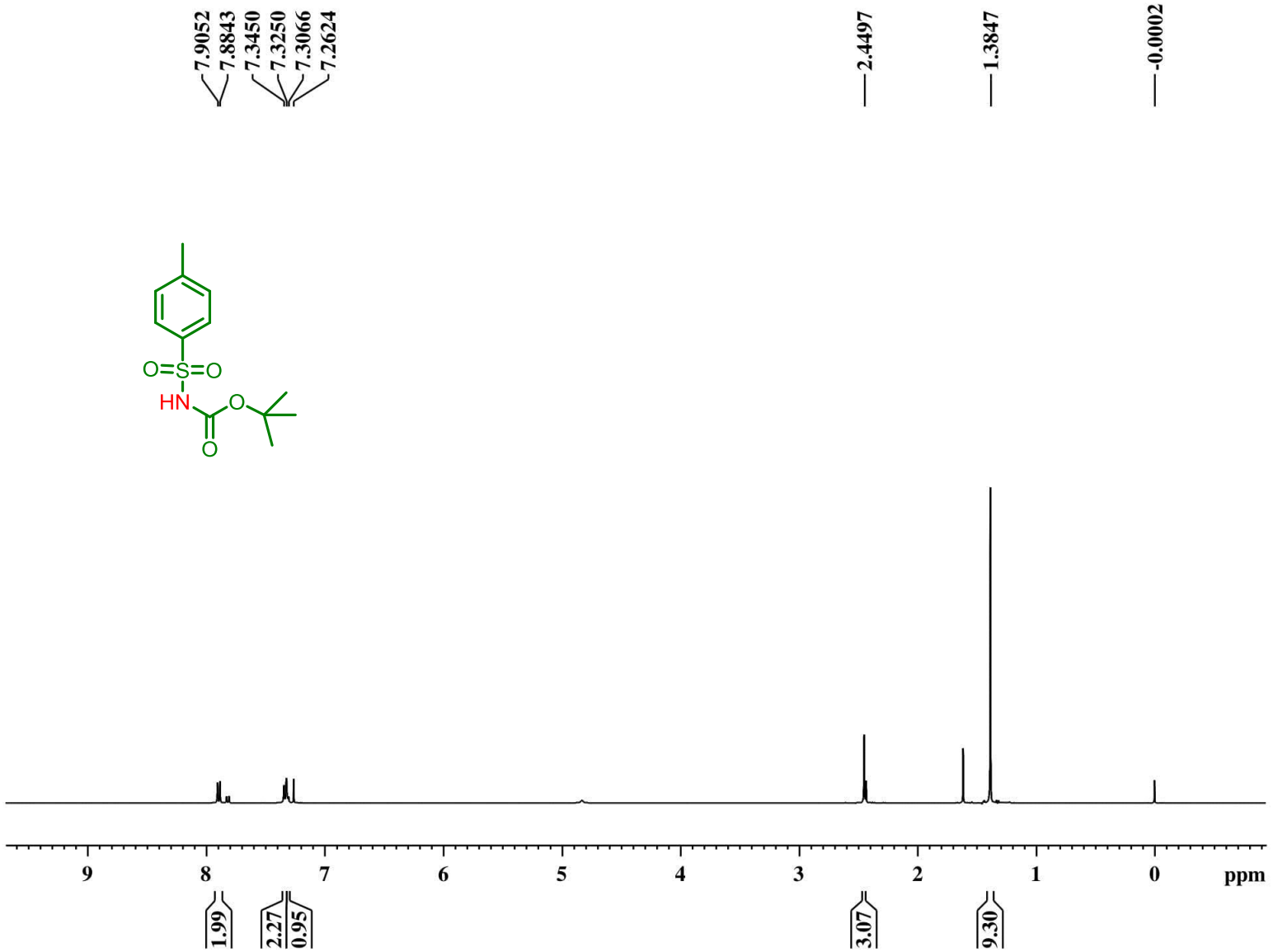
^{13}C NMR spectrum of **2d** (100 MHz, MHz, $CDCl_3$)



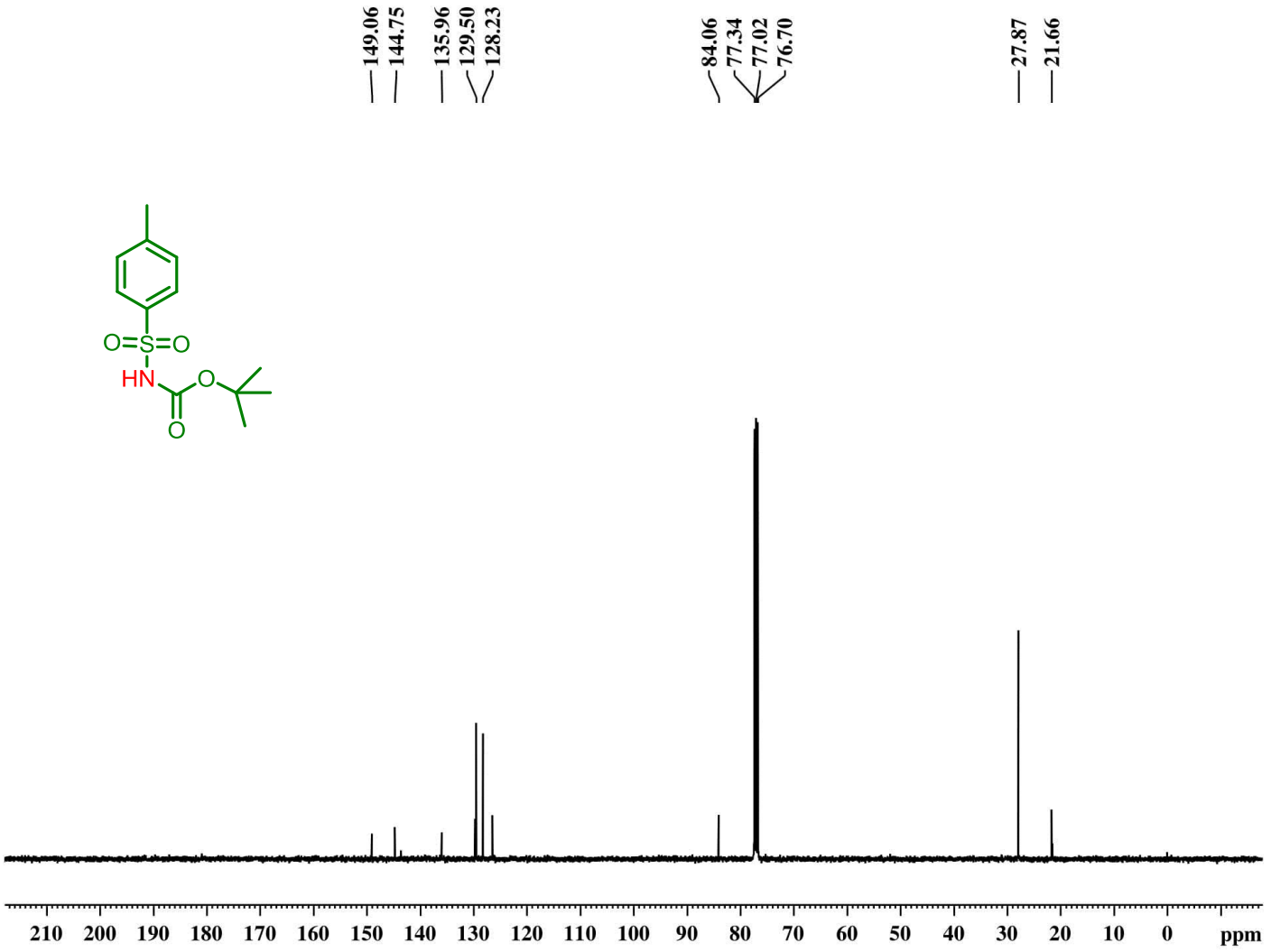
^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$)



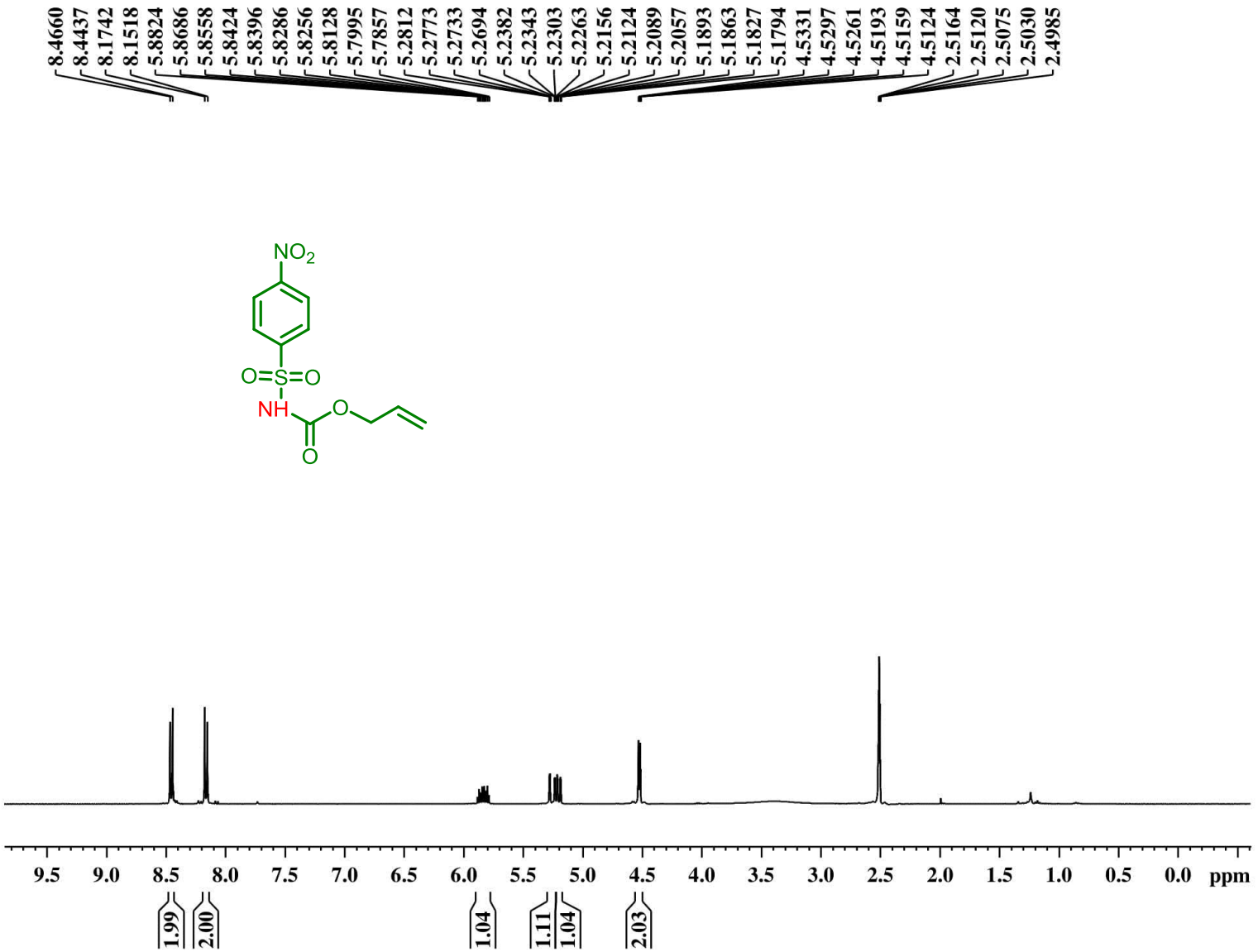
^{13}C NMR spectrum of **2e** (100 MHz, MHz, $CDCl_3$)



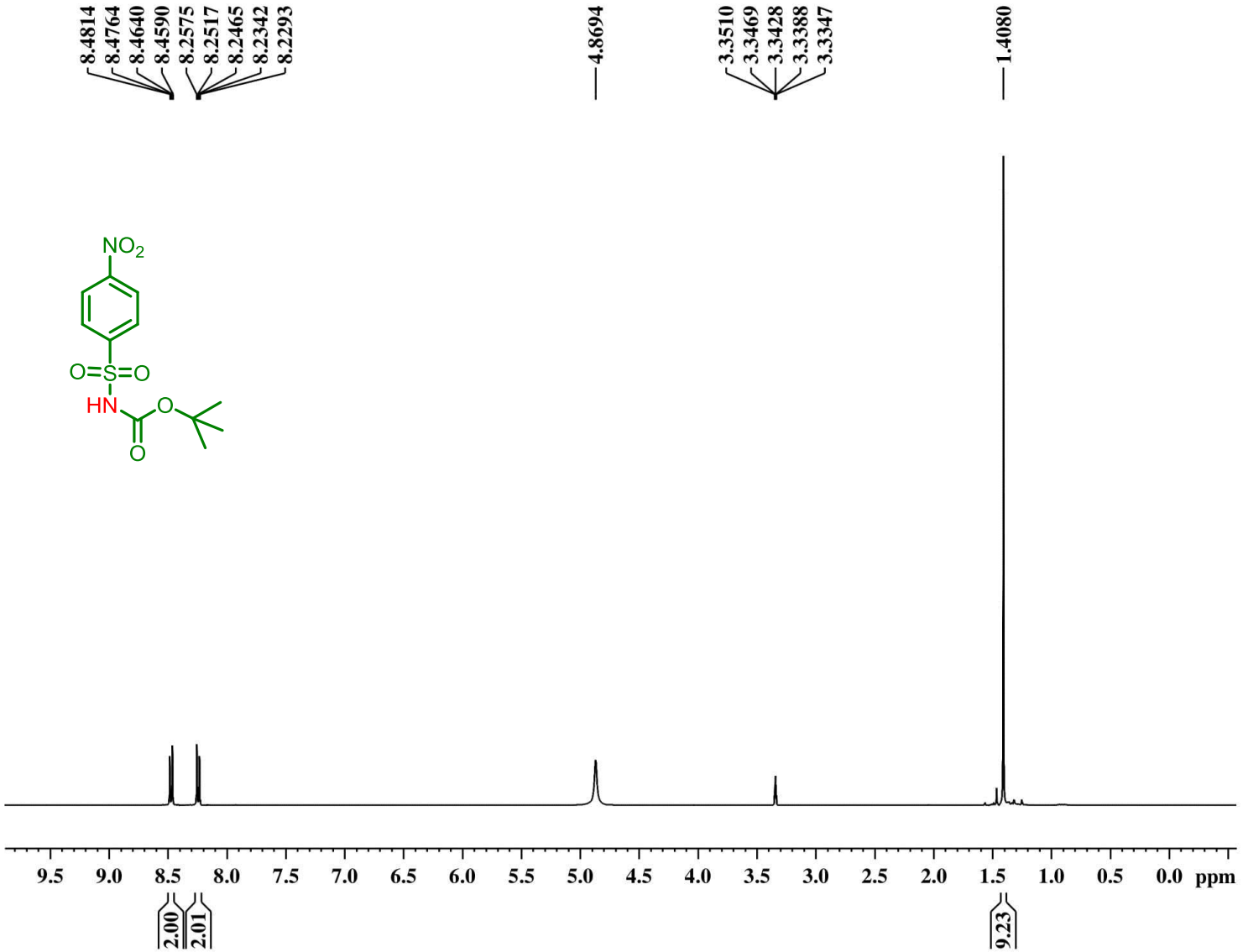
^{1}H NMR spectrum of **2f** (400 MHz, $CDCl_3$)



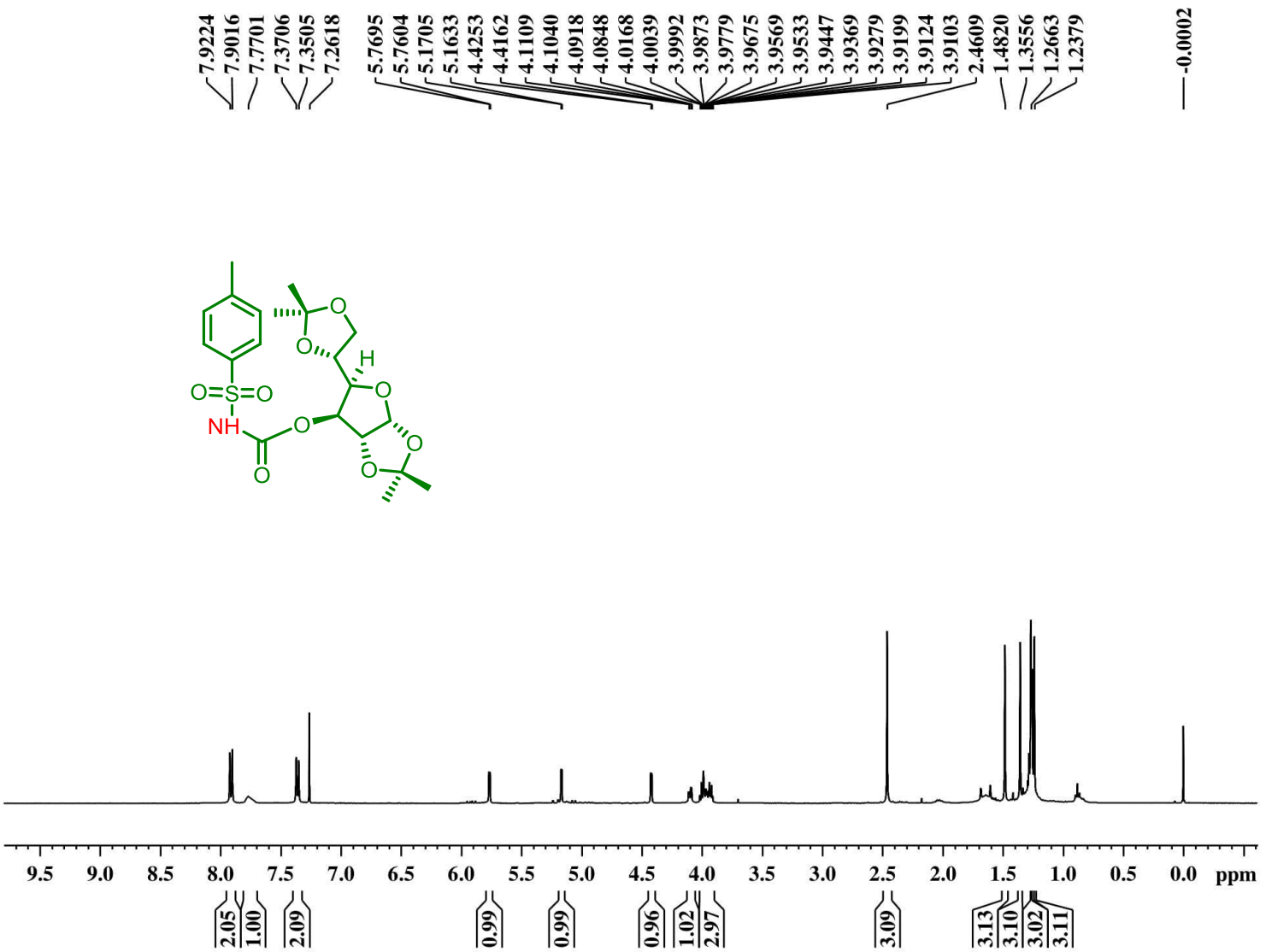
^{13}C NMR spectrum of **2f** (100 MHz, MHz, $CDCl_3$)



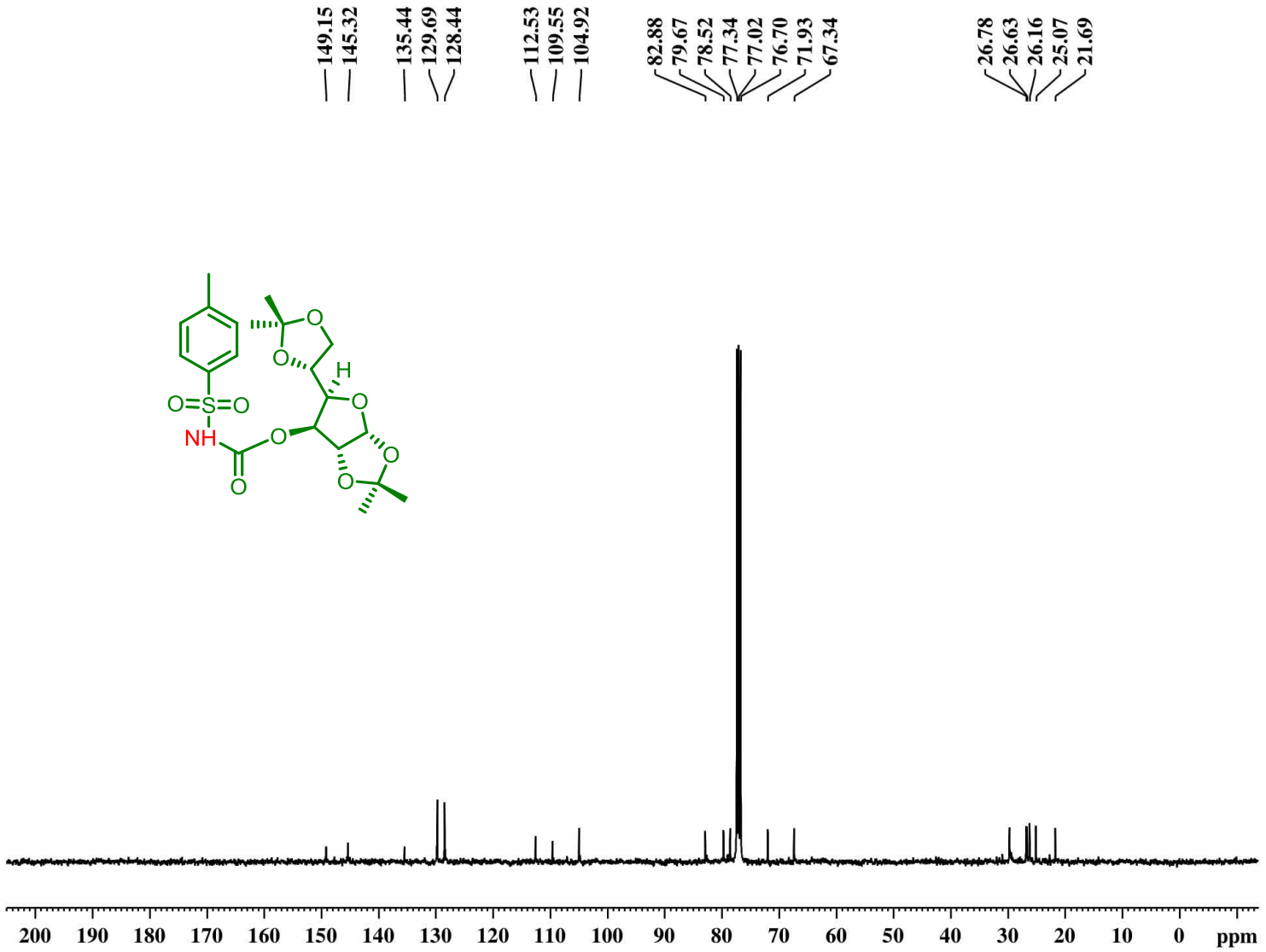
^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$)



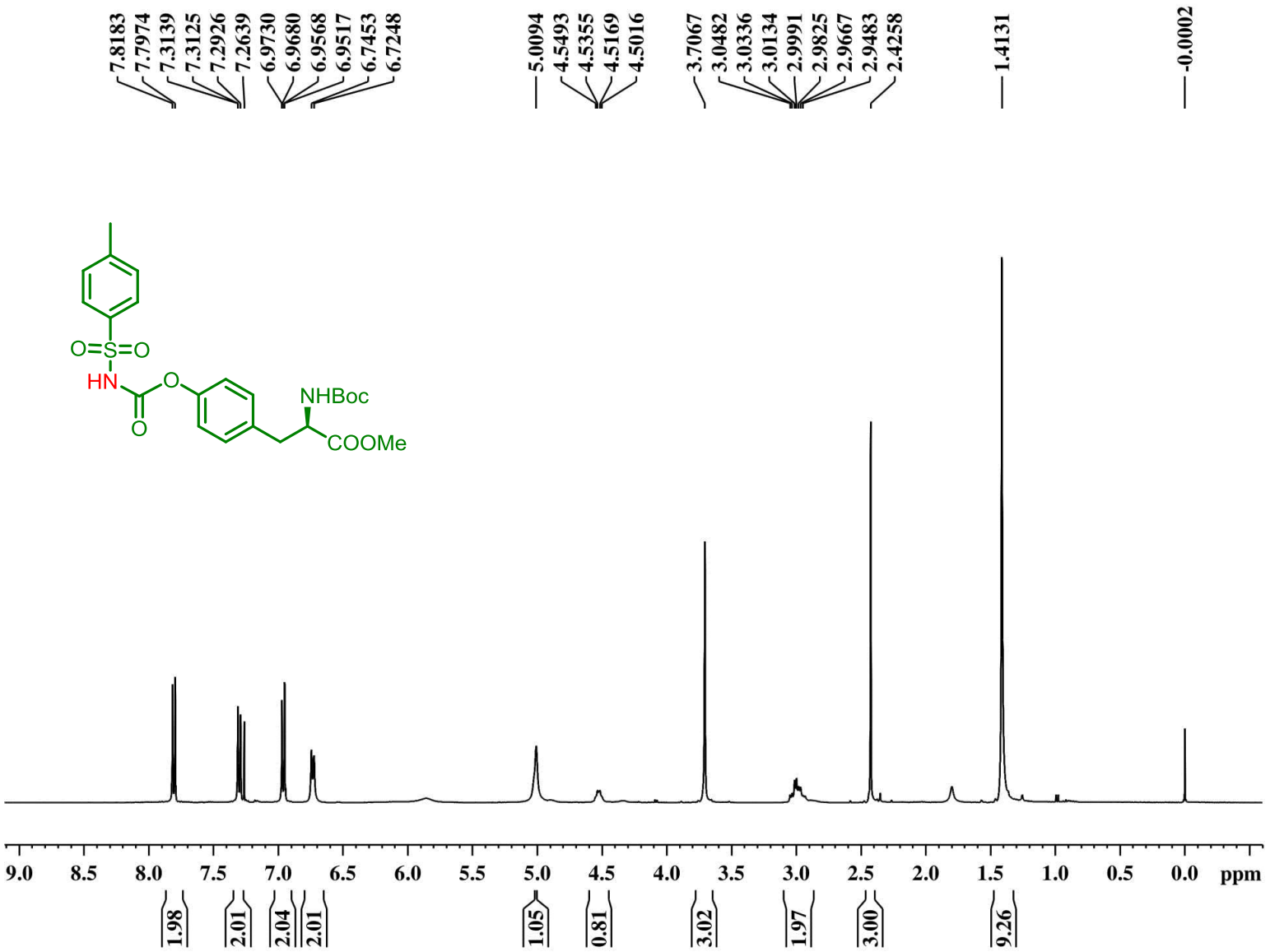
^{1}H NMR spectrum of **2h** (400 MHz, DMSO-d6)



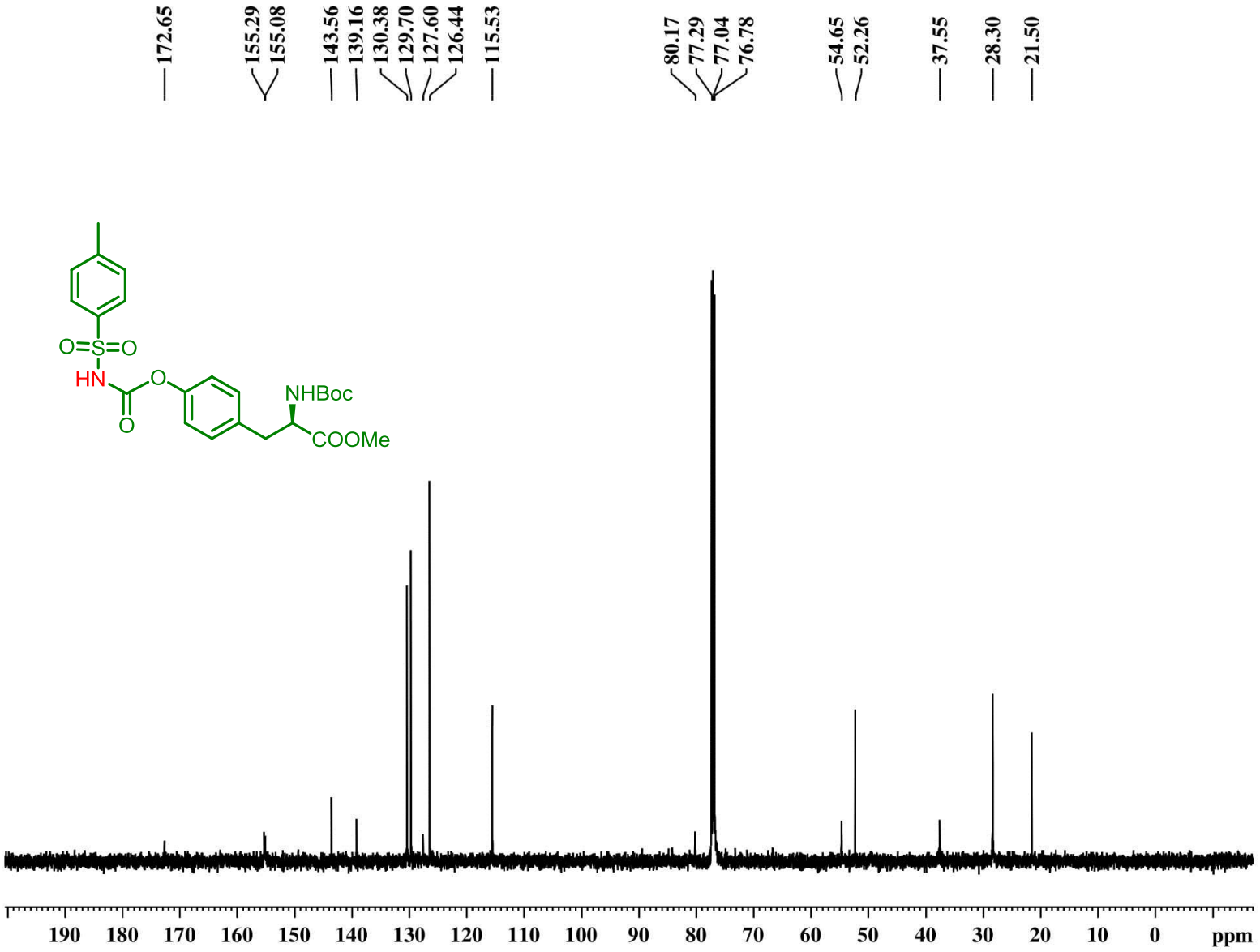
^{1}H NMR spectrum of **2i** (400 MHz, $CDCl_3$)



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

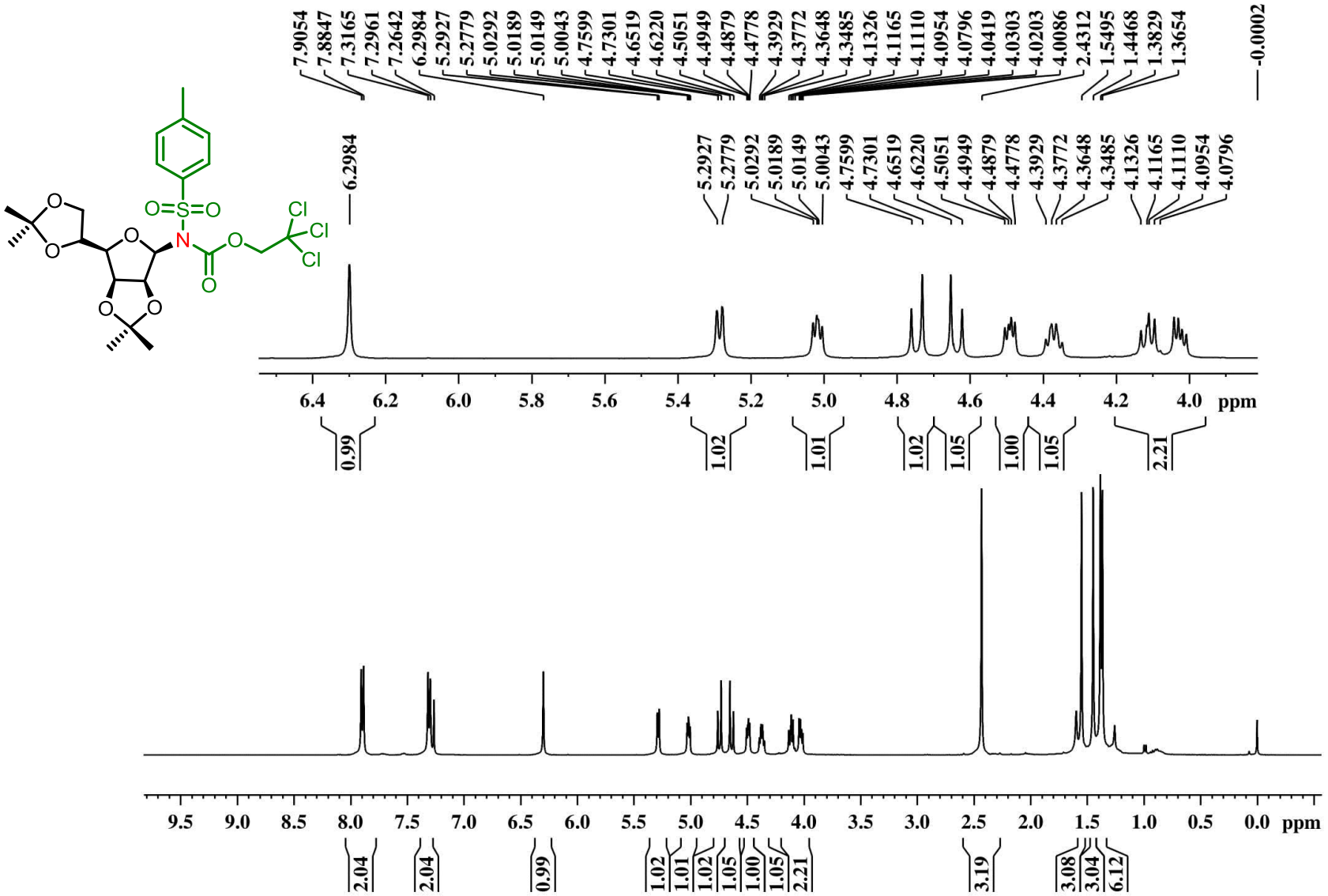


^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$)

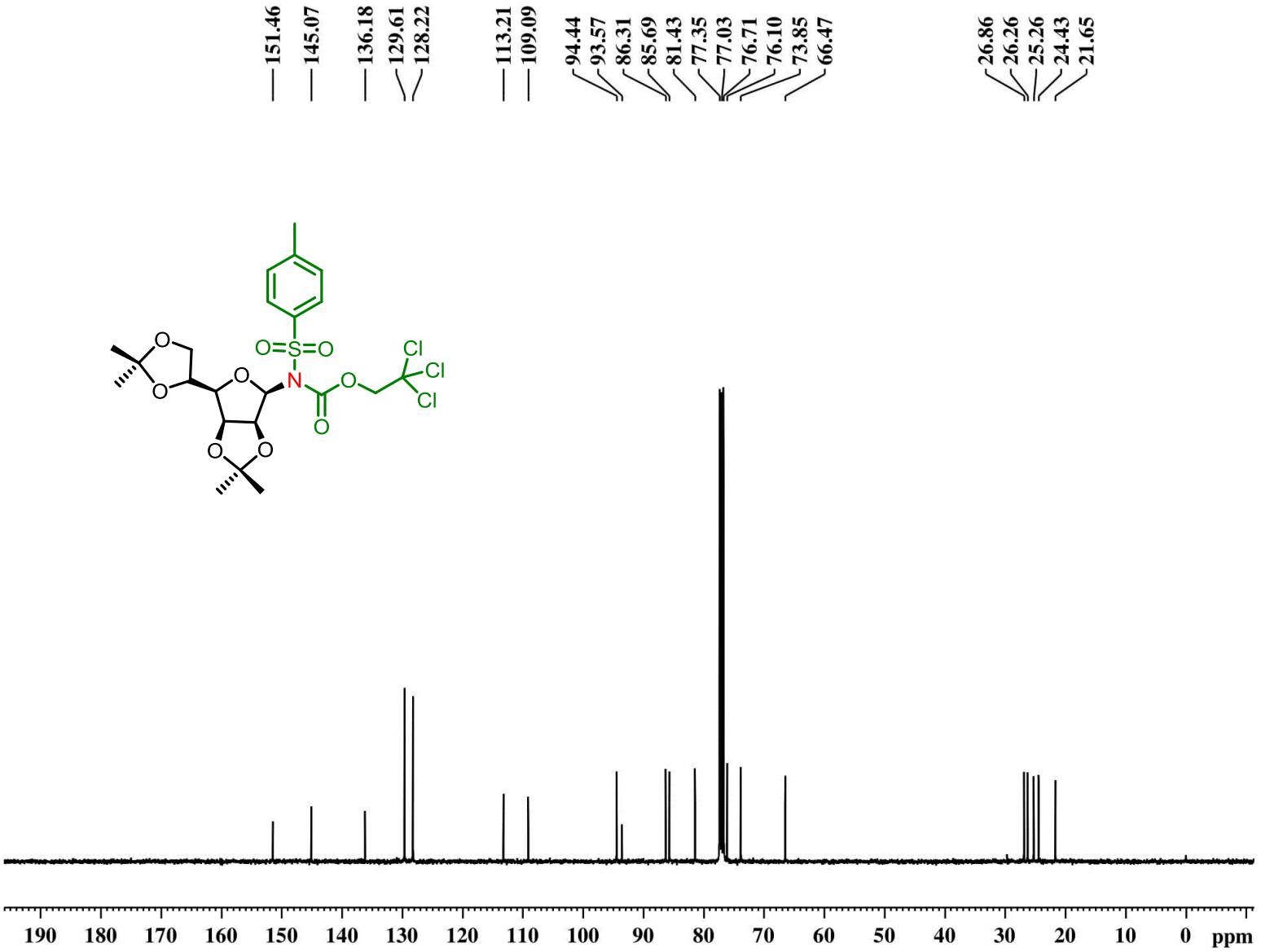


^{13}C NMR spectrum of **2j** (100 MHz, MHz, $CDCl_3$)

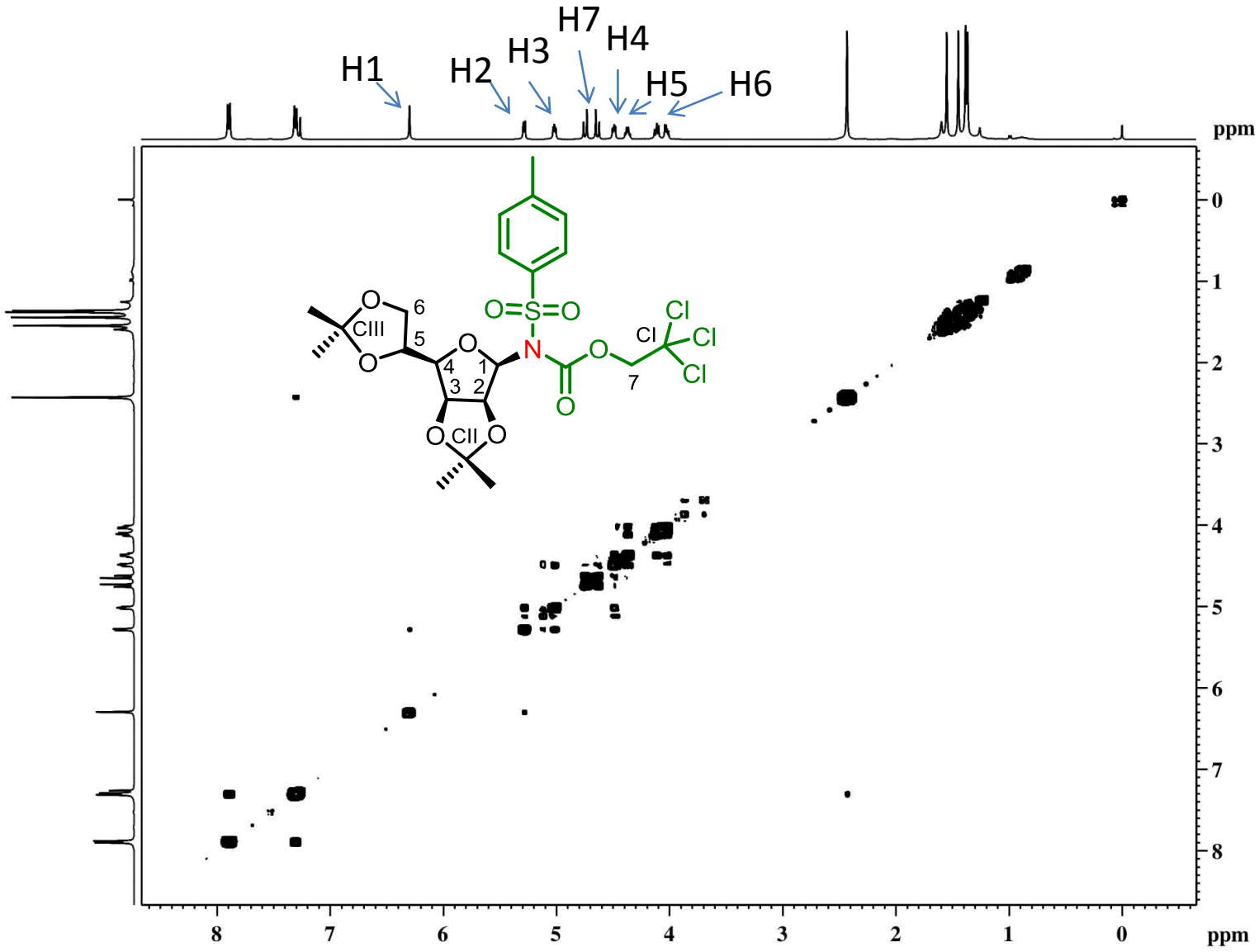
7. Confirmation the exact structure **3a** by NMR (**NOESY corelation**) and Spectra Data, HRMS of all the synthesized *N*-glycofuranosides (**3a-3z, 3v' , 3aa**)



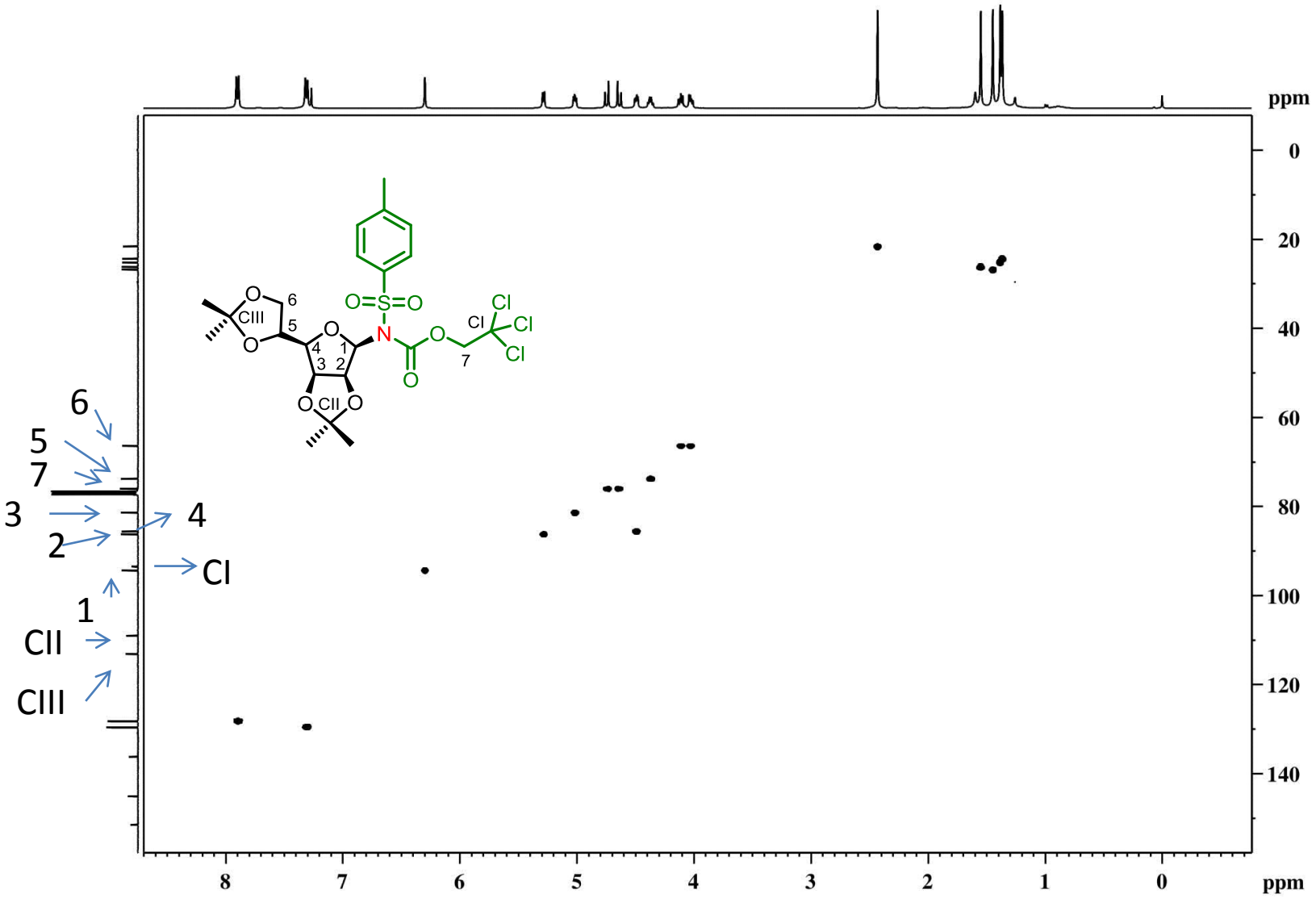
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



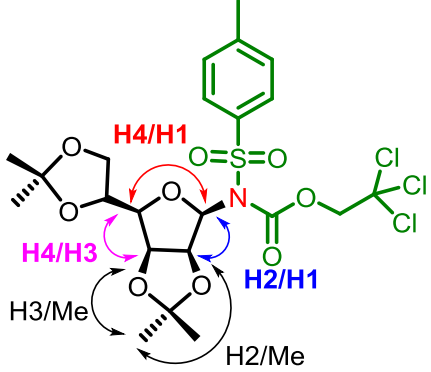
^{13}C NMR spectrum of **3a** (100 MHz, MHz, $CDCl_3$)



2D COSY spectrum of **3a** (400 MHz, MHz, $CDCl_3$)

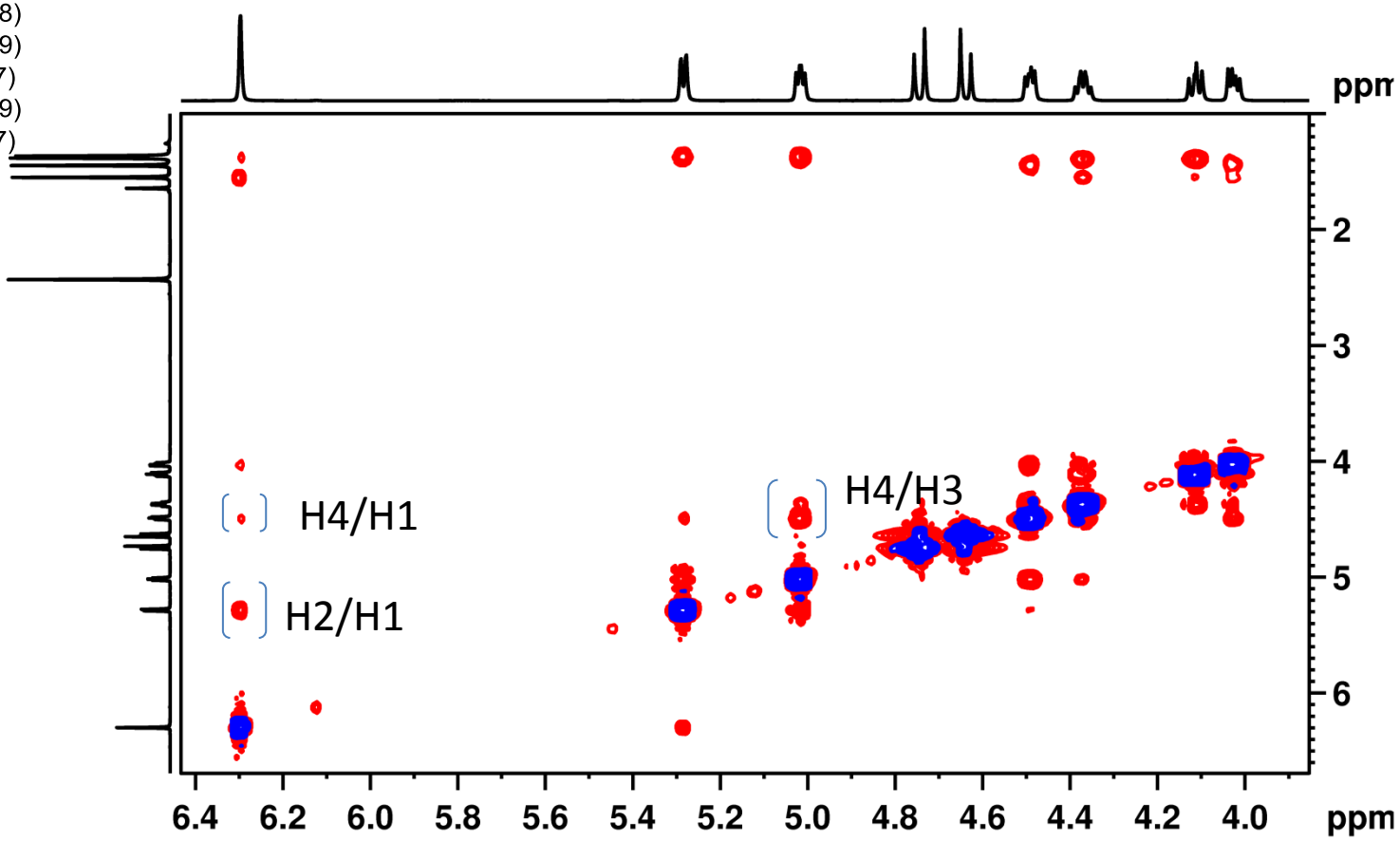


2D HSQC spectrum of **3a** ($CDCl_3$).

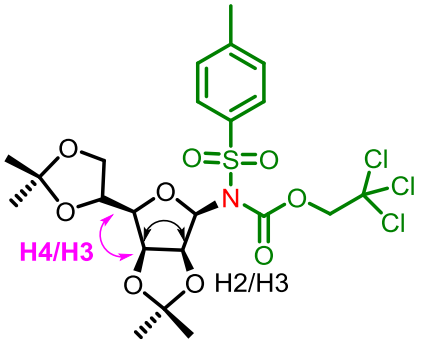


NOESY expansion of **3a**, the characteristic nOe's of H2/H1, H4/H1, and H4/H3 are labelled.

Cross peaks
(H-1, δ 6.29)-(H-2, δ 5.28)
(H-1, δ 6.29)-(H-4, δ 4.49)
(H-2, δ 5.28)-(Me, δ 1.37)
(H-3, δ 5.02)-(H-4, δ 4.49)
(H-3, δ 5.02)-(Me, δ 1.37)



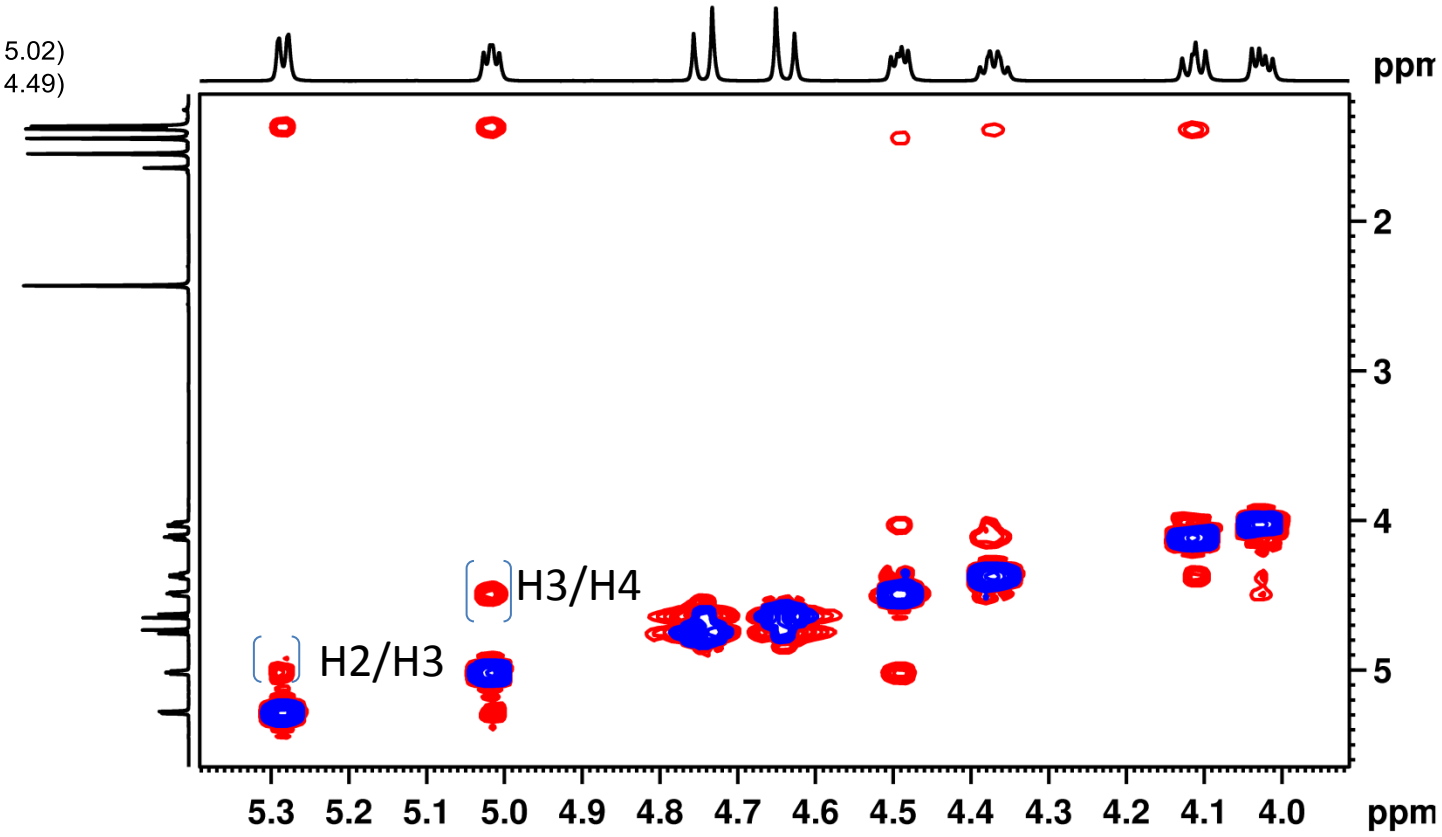
2D NOESY spectrum of **3a** ($CDCl_3$) Expansion.



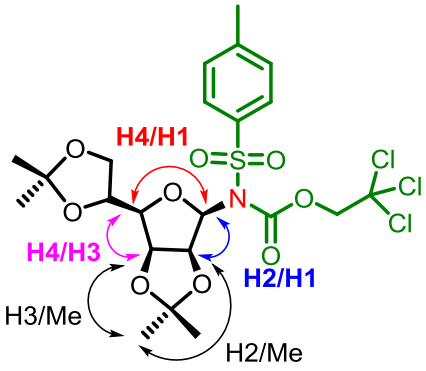
NOESY expansion of **3a**, the characteristic nOe's of H2/H3 and H3/H4 are labelled.

Cross peaks

(H-2, δ 5.28)-(H-3, δ 5.02)
(H-3, δ 5.02)-(H-4, δ 4.49)

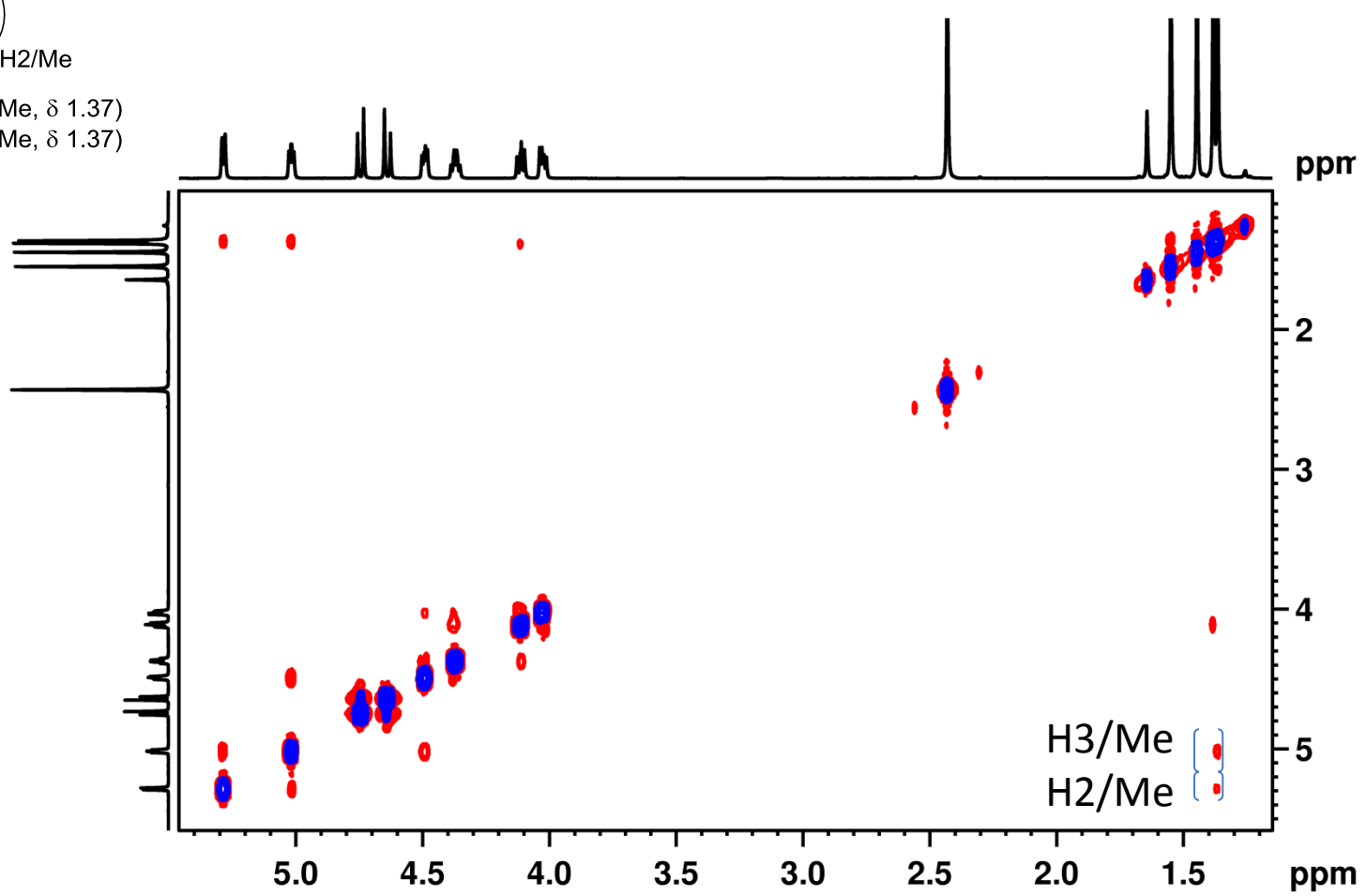


2D NOESY spectrum of **3a** ($CDCl_3$) Expansion.

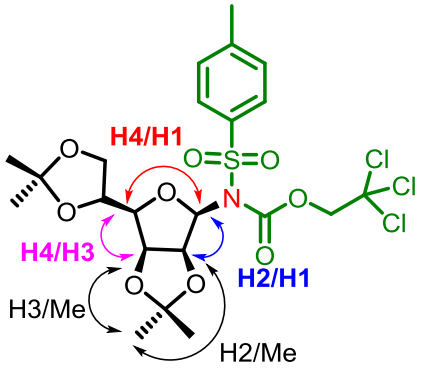


(H-2, δ 5.28)-(Me, δ 1.37)
(H-3, δ 5.02)-(Me, δ 1.37)

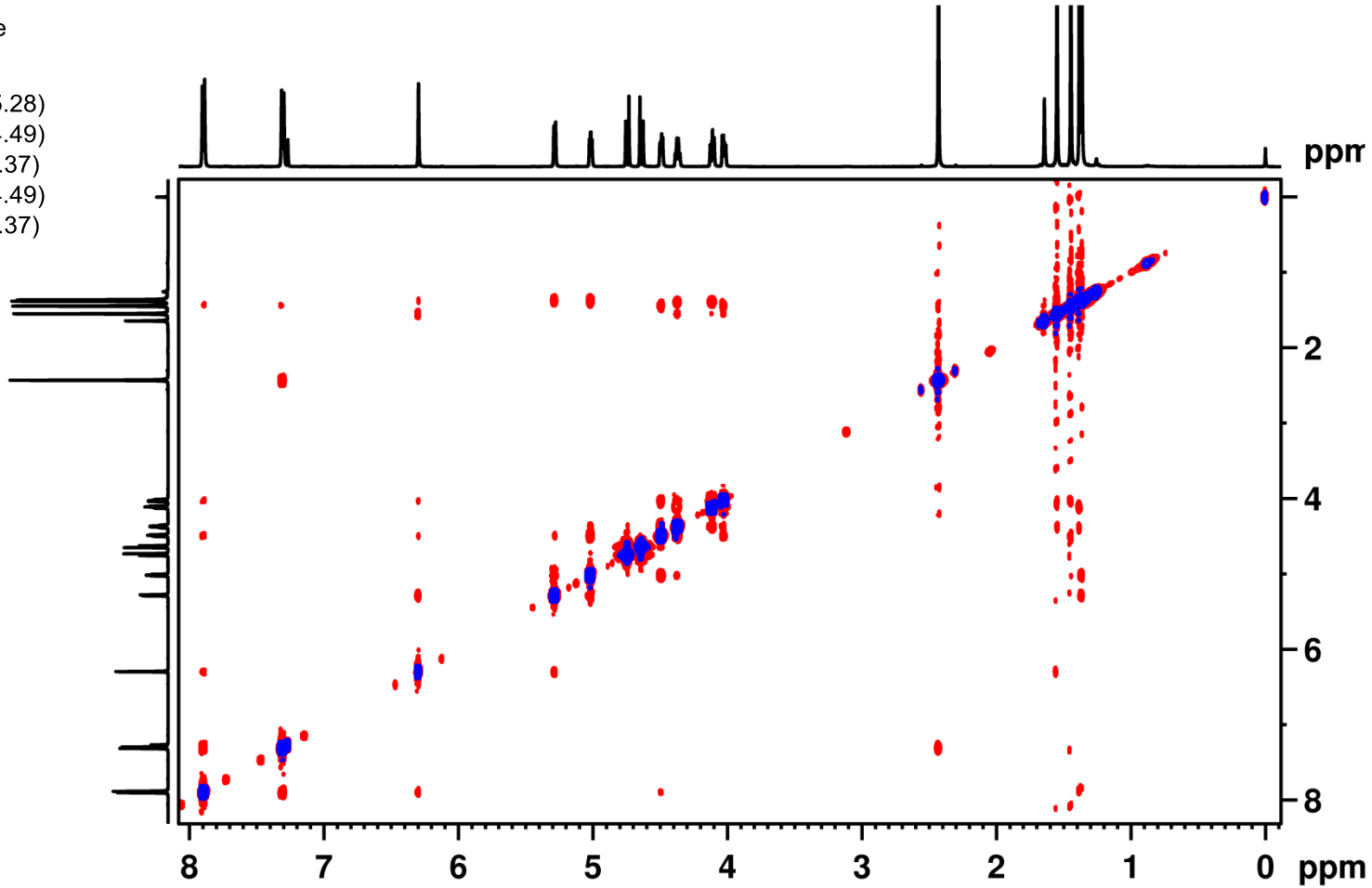
NOESY expansion of **3a**, the characteristic nOe's of H2/Me and H3/Me are labelled.



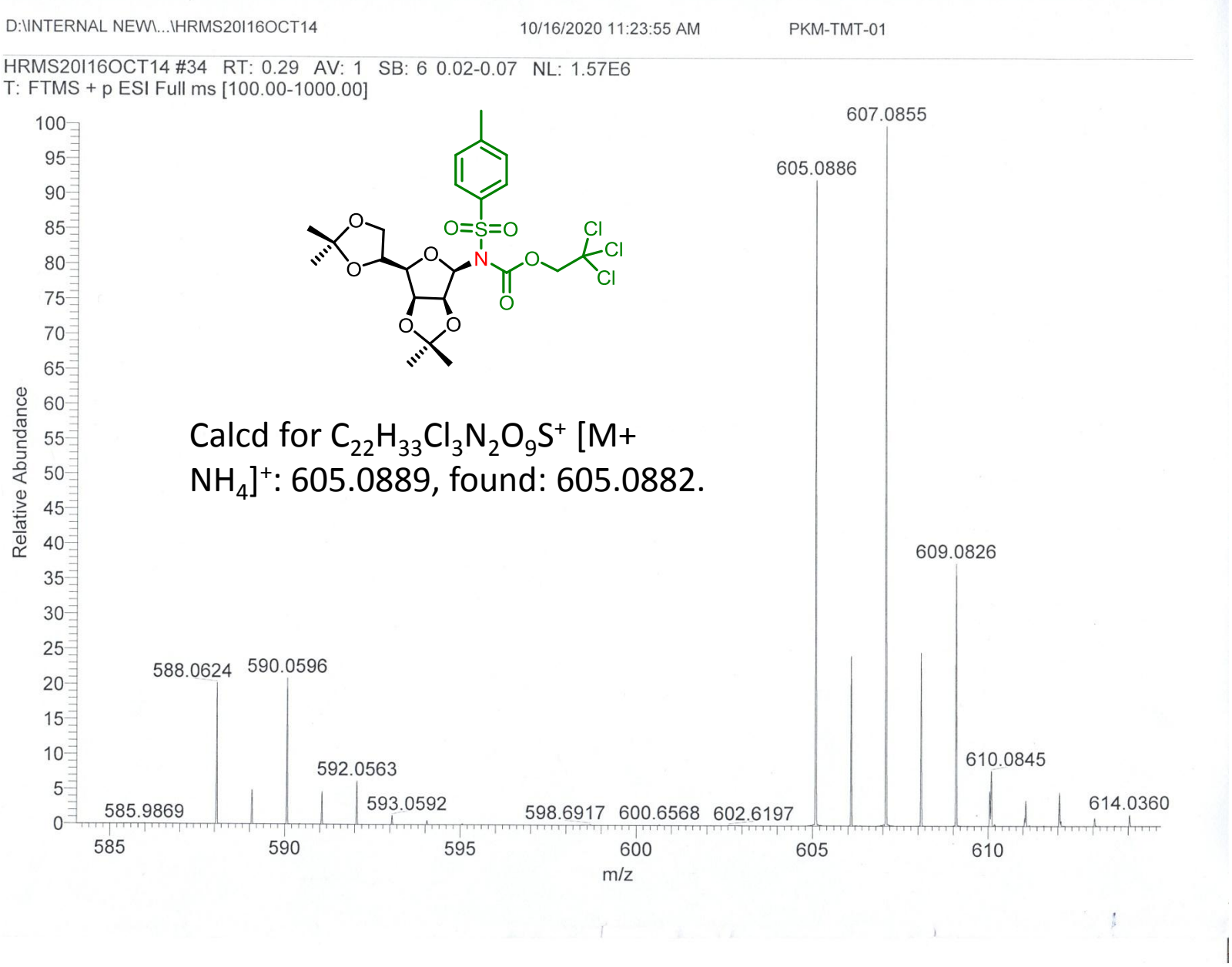
2D NOESY spectrum of **3a** ($CDCl_3$) Expansion).



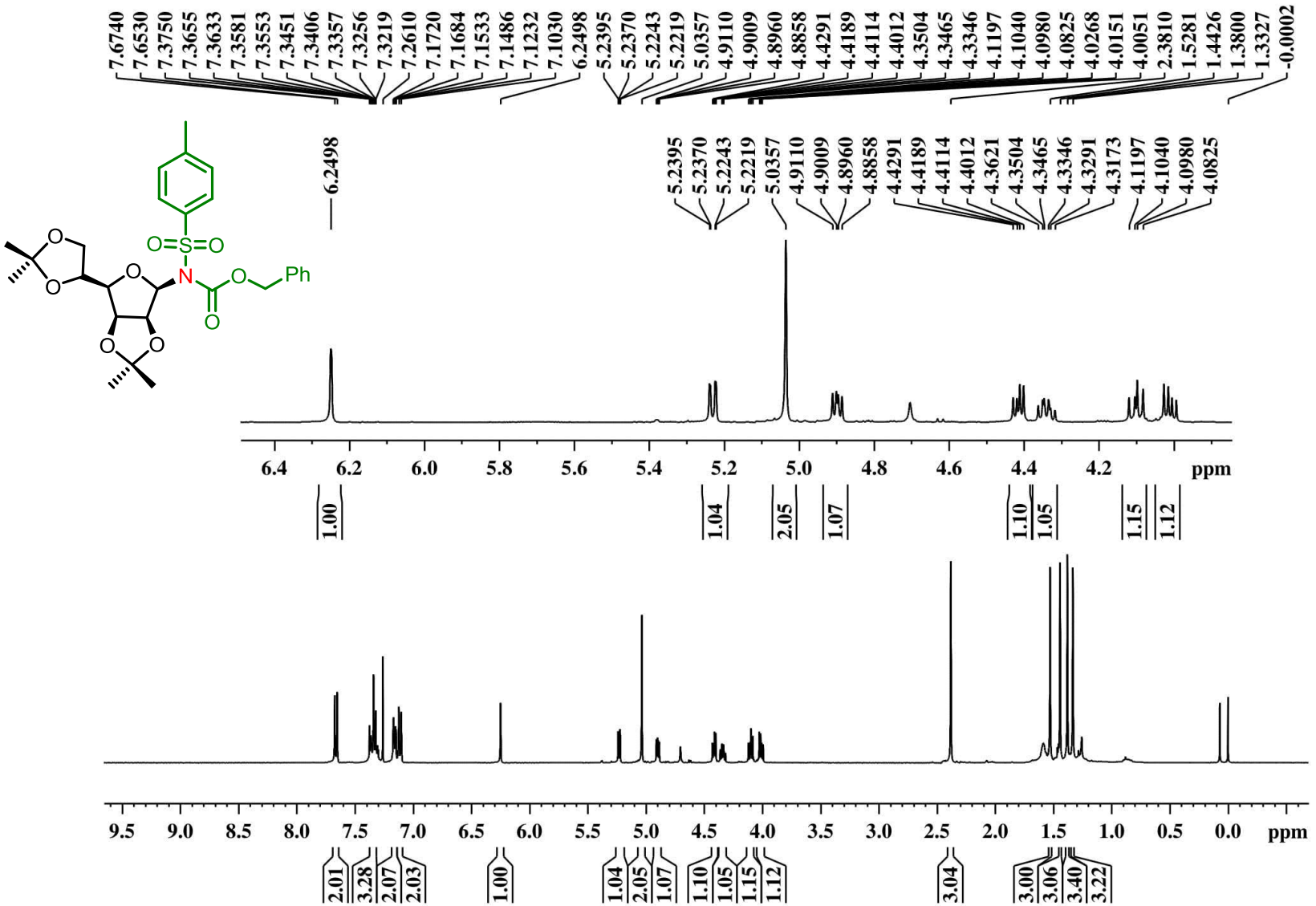
Cross peaks
(H-1, δ 6.29)-(H-2, δ 5.28)
(H-1, δ 6.29)-(H-4, δ 4.49)
(H-2, δ 5.28)-(Me, δ 1.37)
(H-3, δ 5.02)-(H-4, δ 4.49)
(H-3, δ 5.02)-(Me, δ 1.37)



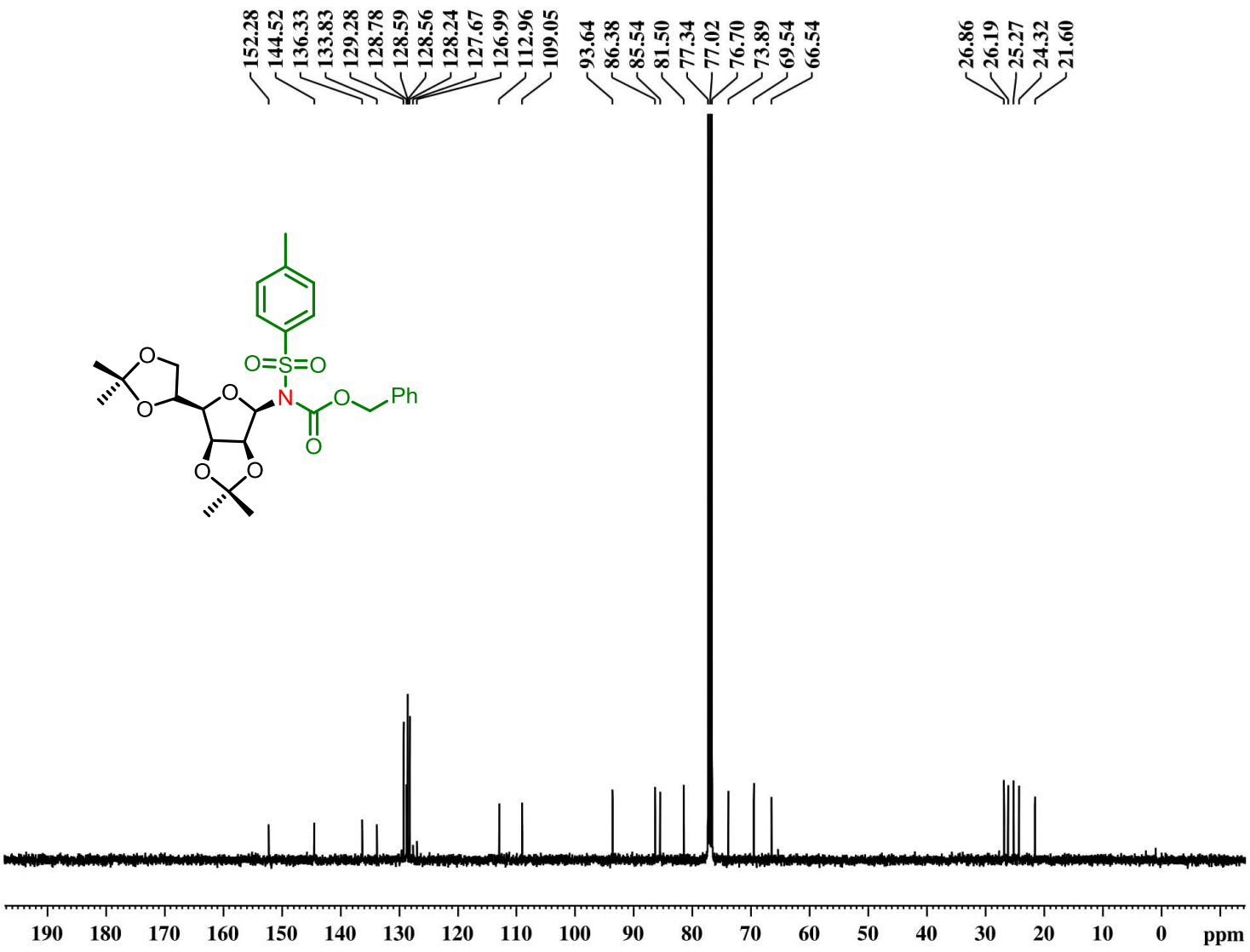
2D NOESY spectrum of **3a** ($CDCl_3$).


D:\INTERNAL NEW\...\HRMS20I16OCT14
10/16/2020 11:23:55 AM
PKM-TMT-01
HRMS20I16OCT14 #34 RT: 0.29 AV: 1 SB: 6 0.02-0.07 NL: 1.57E6
T: FTMS + p ESI Full ms [100.00-1000.00]
Calcd for $C_{22}H_{33}Cl_3N_2O_9S^+$ [M+ $NH_4]^+$: 605.0889, found: 605.0882.
Relative Abundance
m/z
607.0855
605.0886
609.0826
610.0845
614.0360
588.0624
590.0596
592.0563
593.0592
585.9869
598.6917
600.6568
602.6197

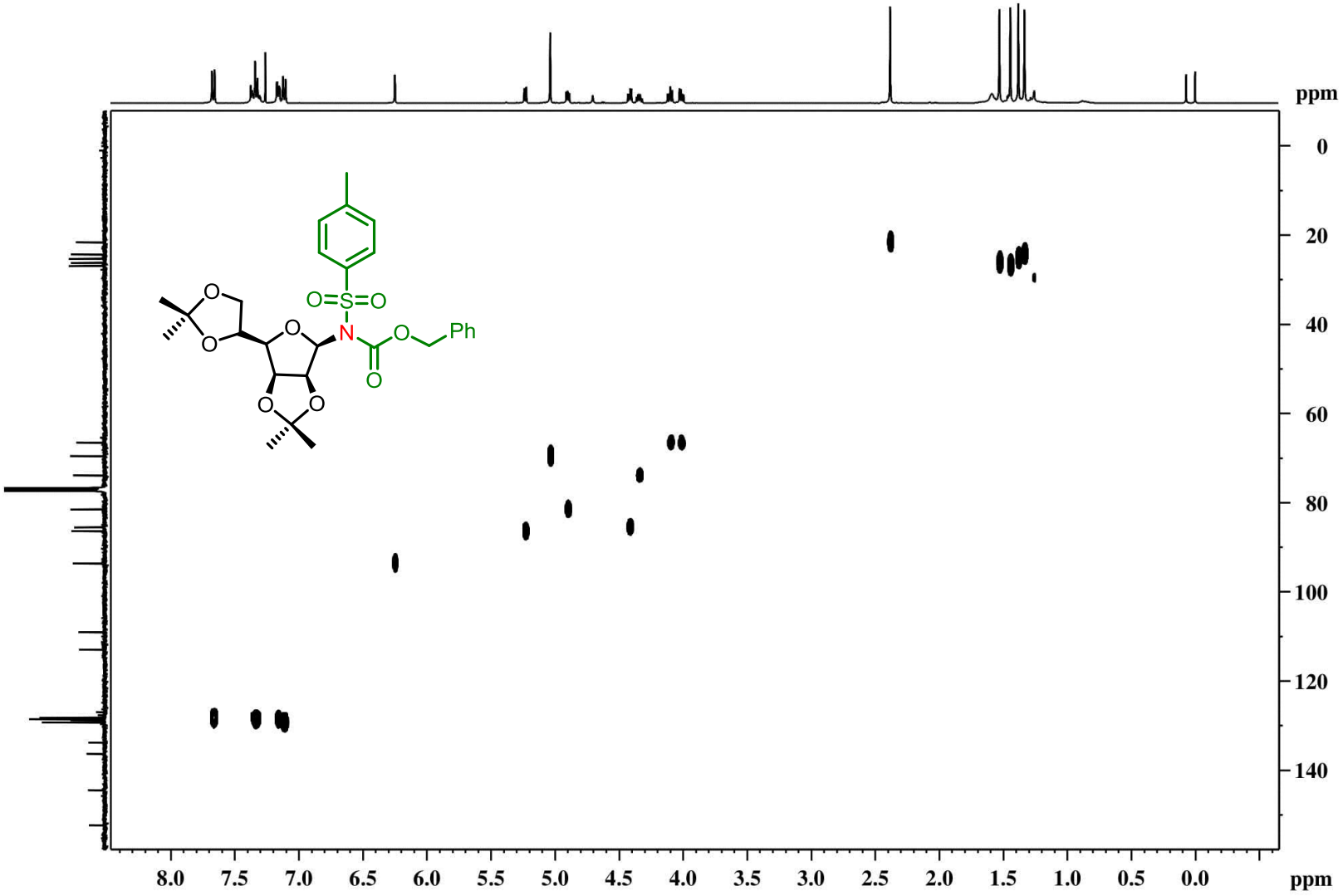
HRMS of **3a**



^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



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

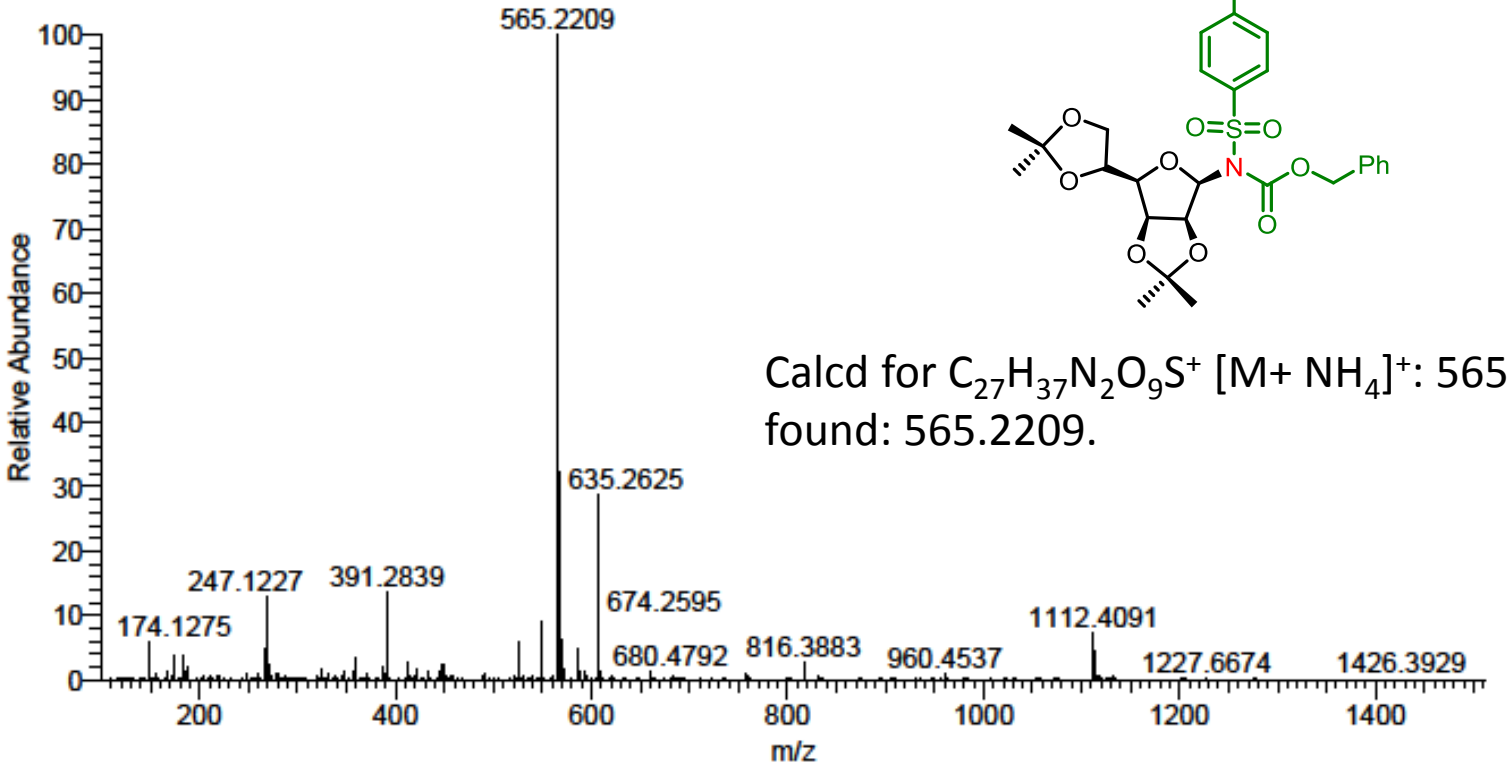


2D HSQC spectrum of **3b** ($CDCl_3$).

SAIF [HRMS Report]

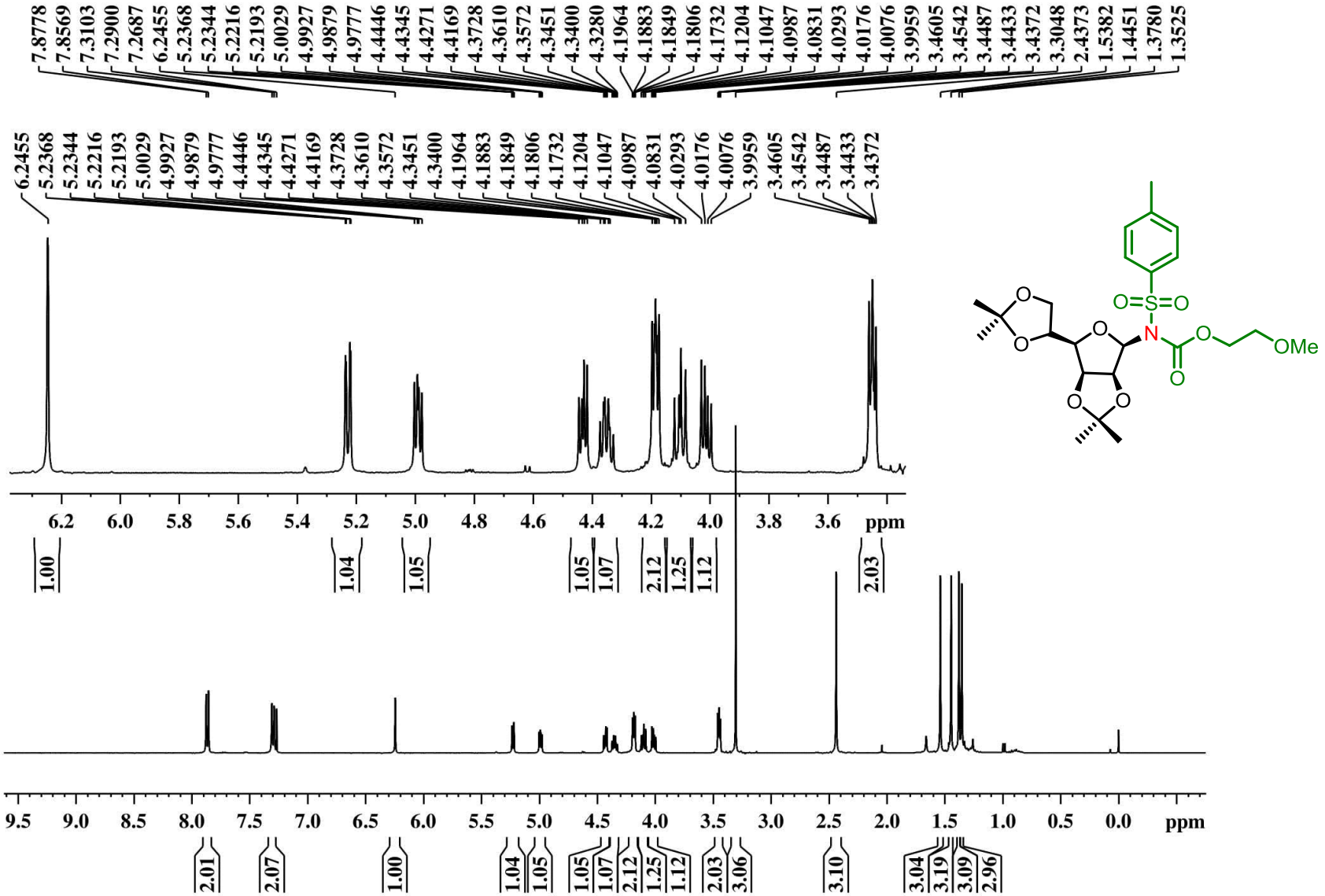
Data File:	HRMS20I01OCT01	Original Data Path:	D:\INTERNAL NEW\2020\OCT 2020
Sample ID:	PKM-TMb-02	Sample Name:	
Acquisition Date:	10/01/20 10:49:37 AM	Run Time(min):	0.00
Vial:	CStk1-01:01	Injection Volume(µl):	1.00

HRMS20I01OCT01 #12-25 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 4.11E6
T: FTMS + p ESI Full ms [100.00-1500.00]

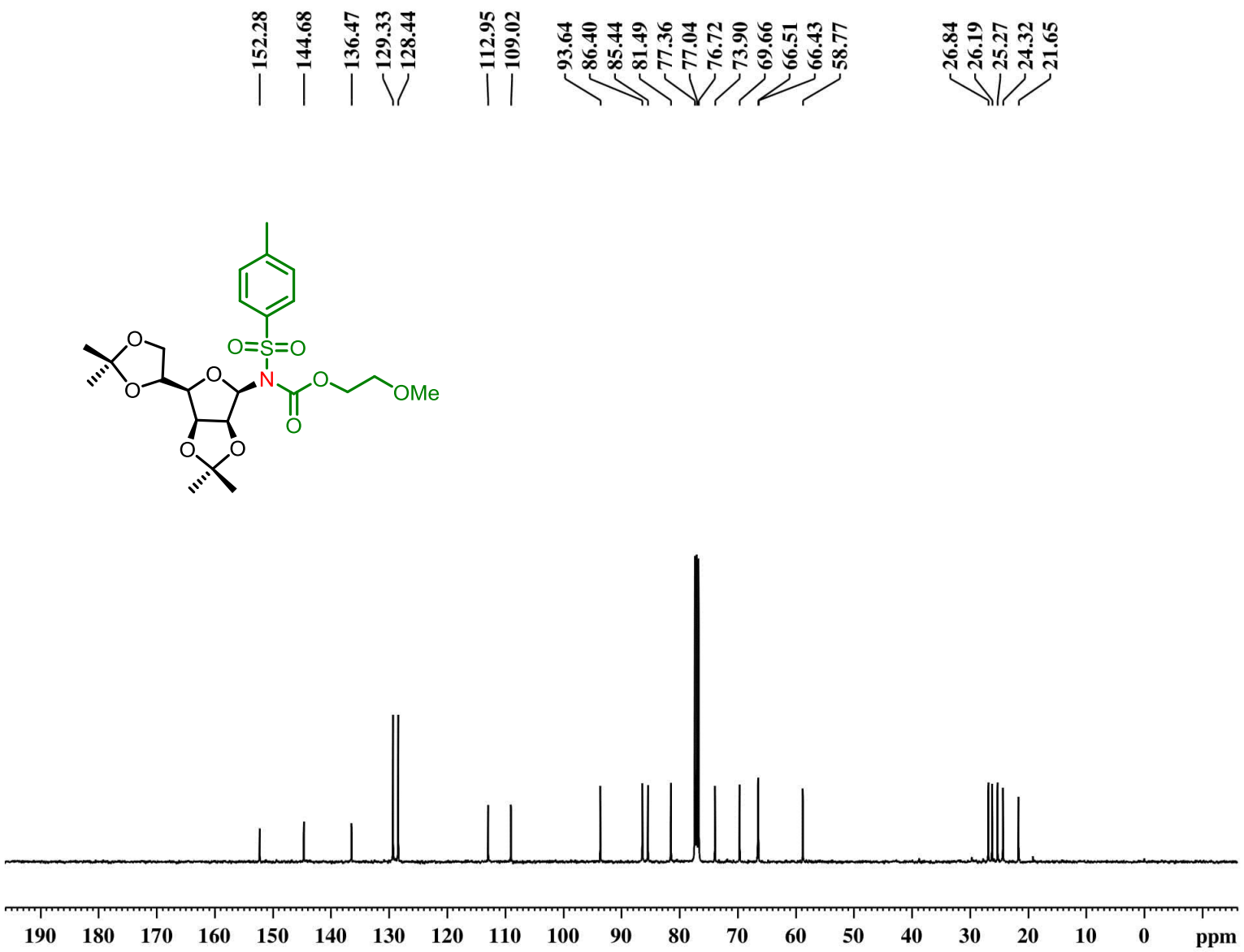


Calcd for $C_{27}H_{37}N_2O_9S^+$ $[M+ NH_4]^+$: 565.2214, found: 565.2209.

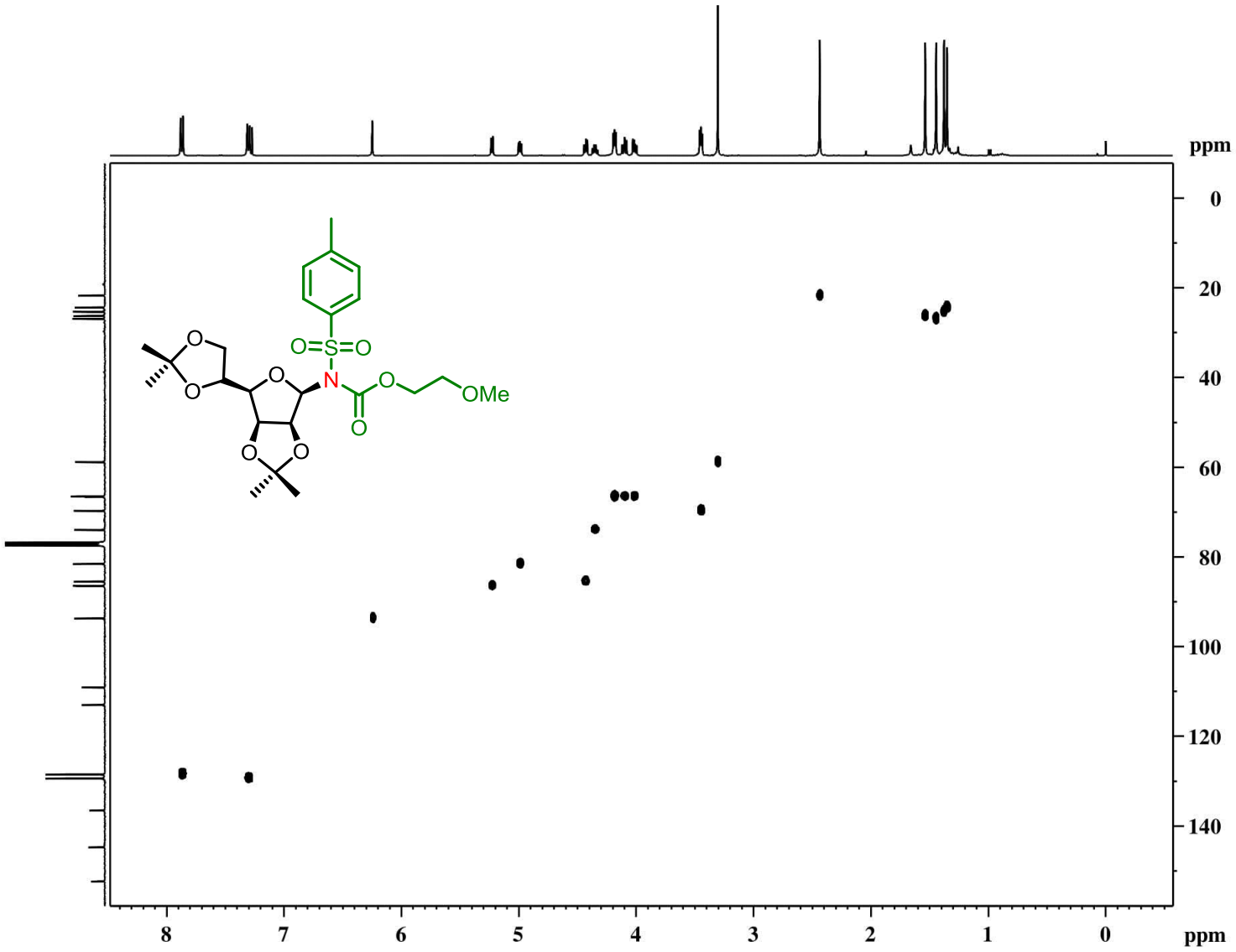
HRMS of **3b**



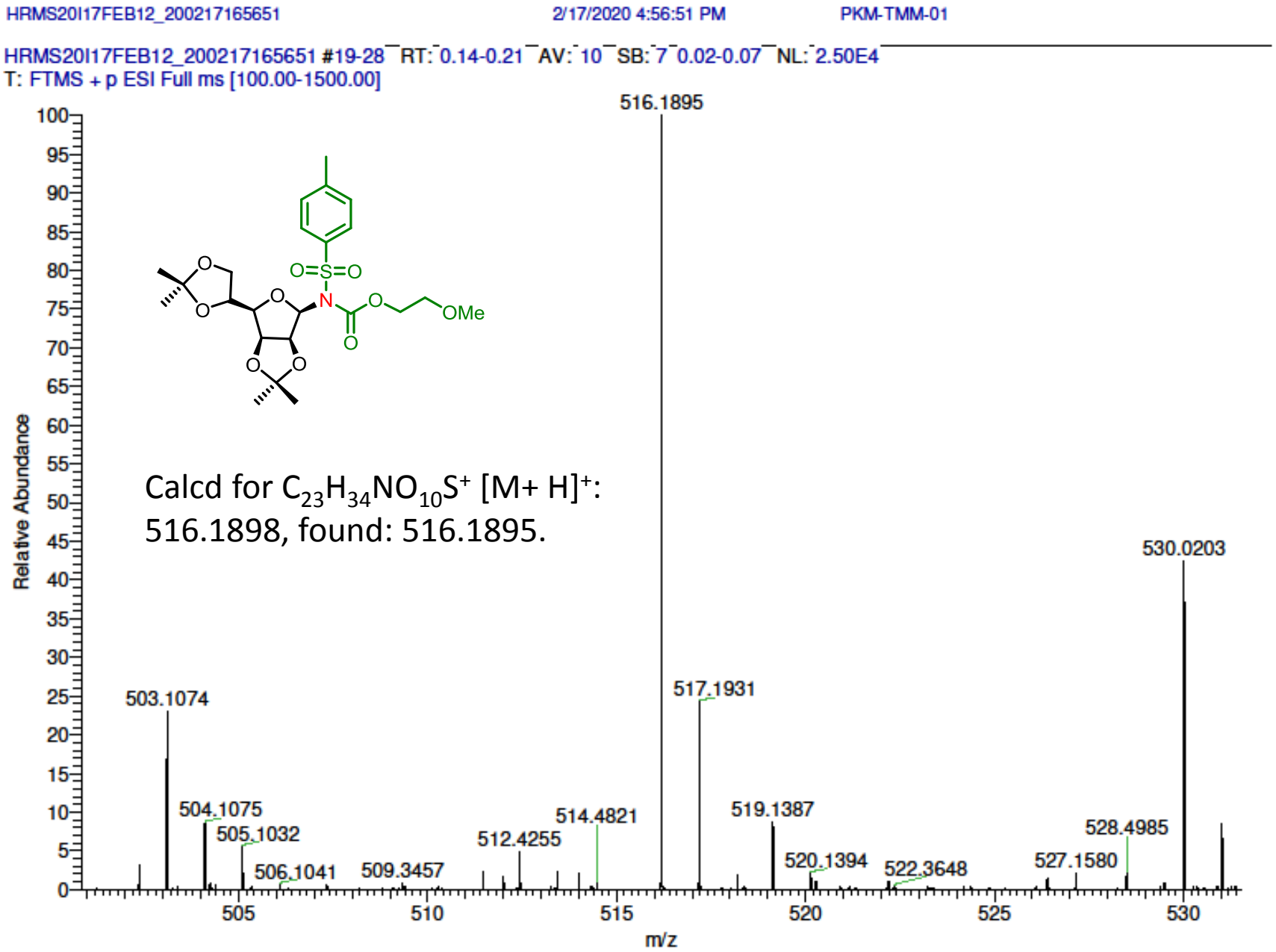
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



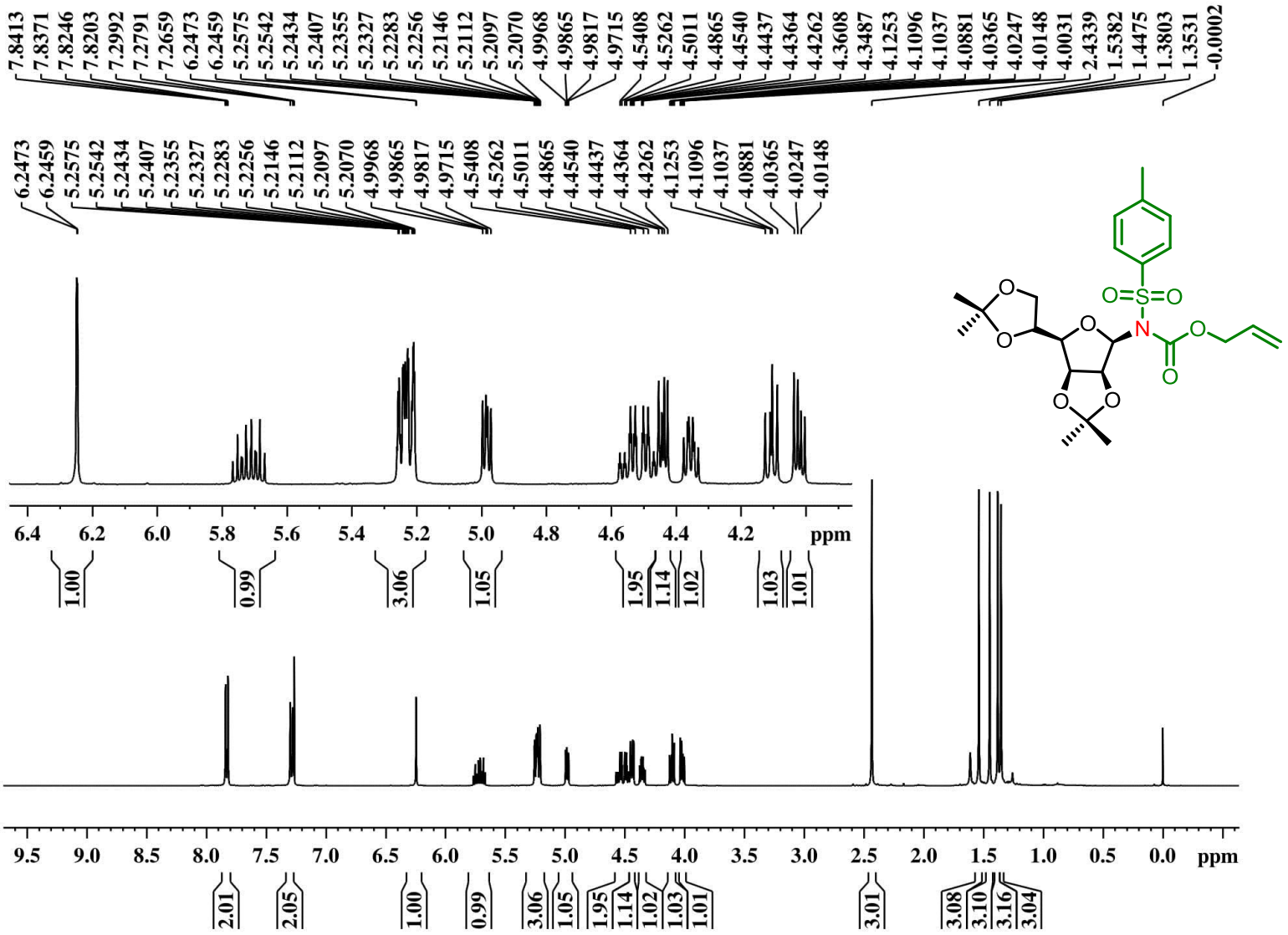
^{13}C NMR spectrum of **3c** (100 MHz, MHz, $CDCl_3$)



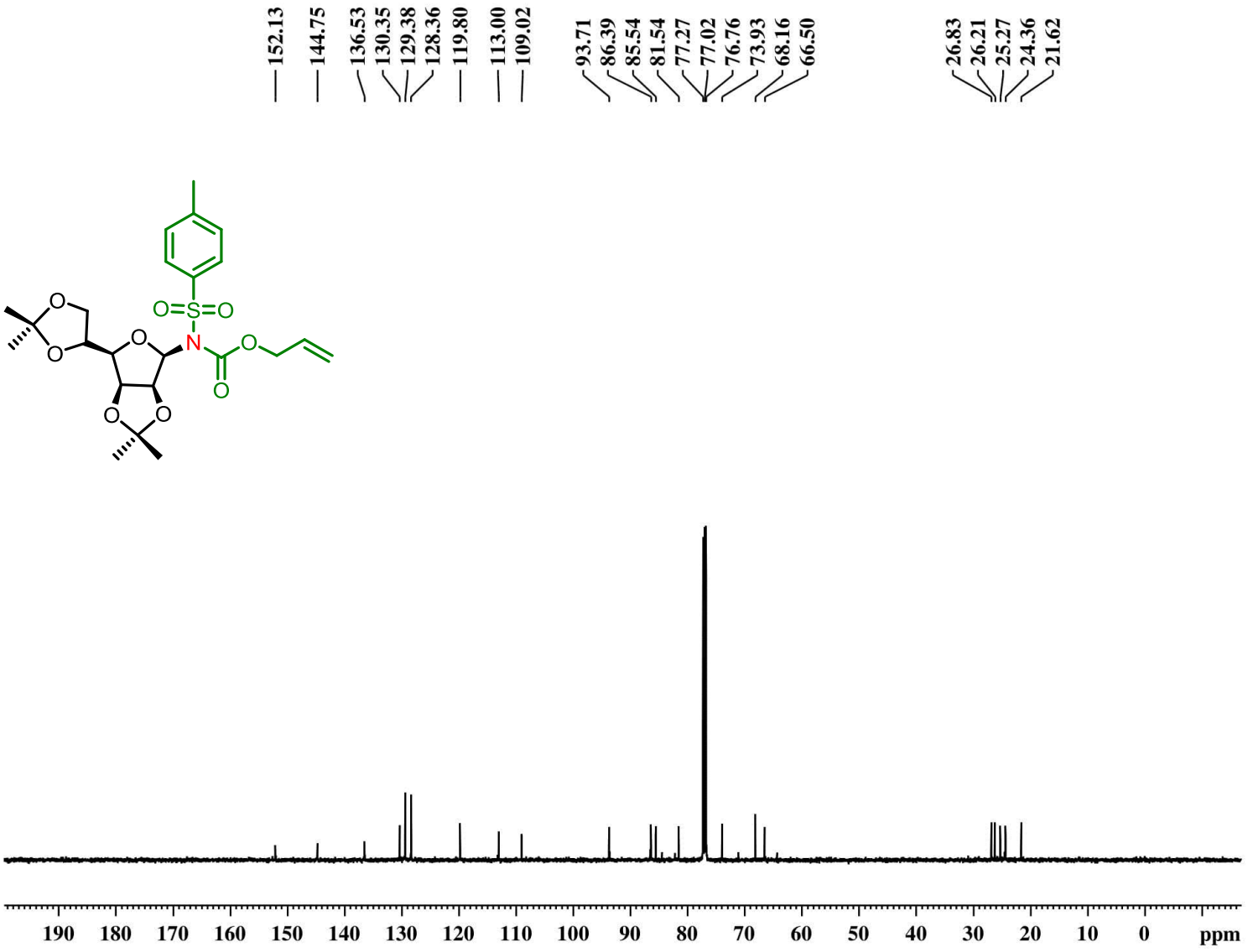
2D HSQC spectrum of **3c** ($CDCl_3$).


HRMS20I17FEB12_200217165651
2/17/2020 4:56:51 PM
PKM-TMM-01
HRMS20I17FEB12_200217165651 #19-28 RT: 0.14-0.21 AV: 10 SB: 7 0.02-0.07 NL: 2.50E4
T: FTMS + p ESI Full ms [100.00-1500.00]
Calcd for C23H34NO10S+ [M+ H]+:
516.1898, found: 516.1895.
Relative Abundance
m/z
516.1895
530.0203
517.1931
503.1074
504.1075
505.1032
506.1041
509.3457
512.4255
514.4821
519.1387
520.1394
522.3648
527.1580
528.4985

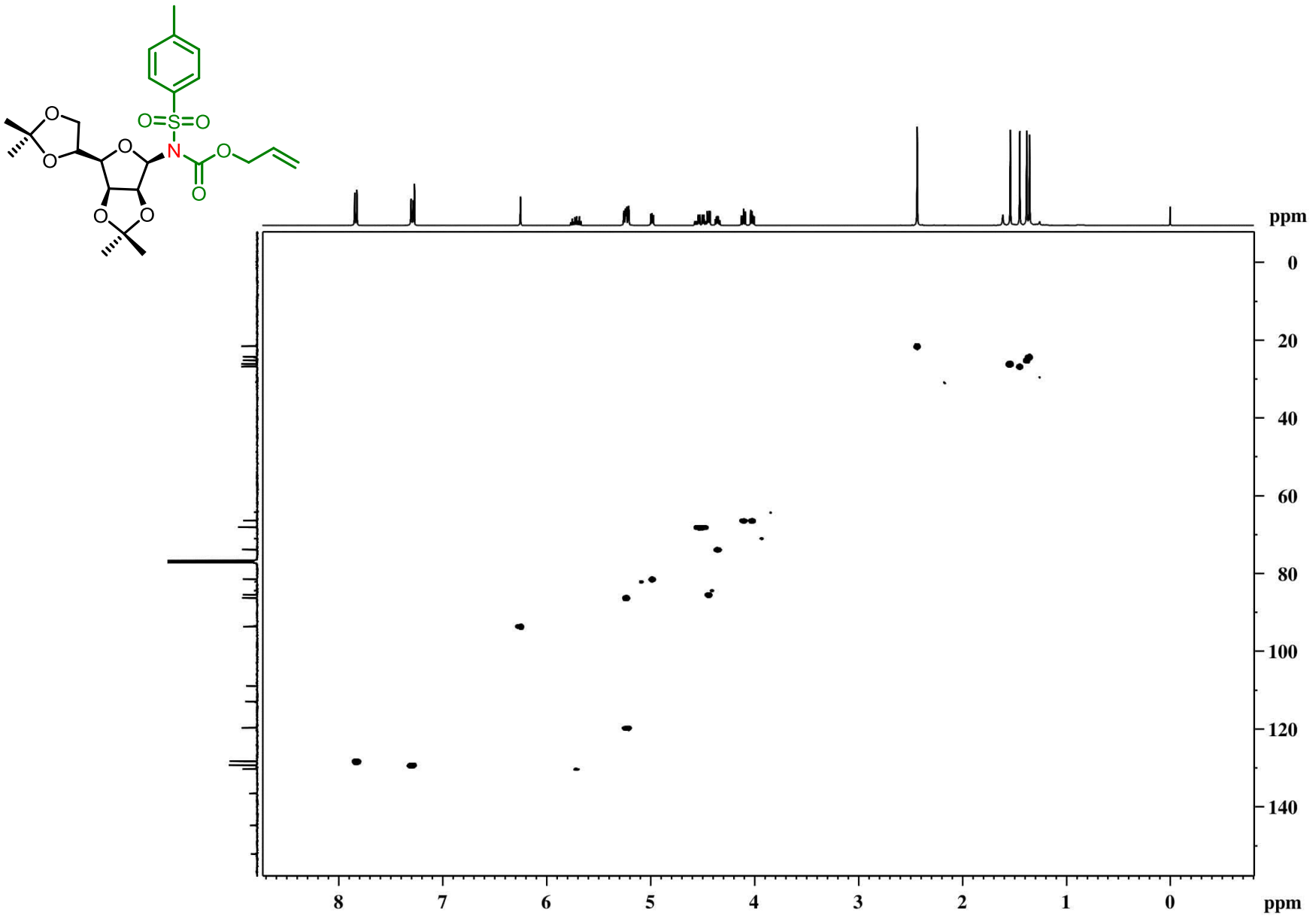
HRMS of **3c**



^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)



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

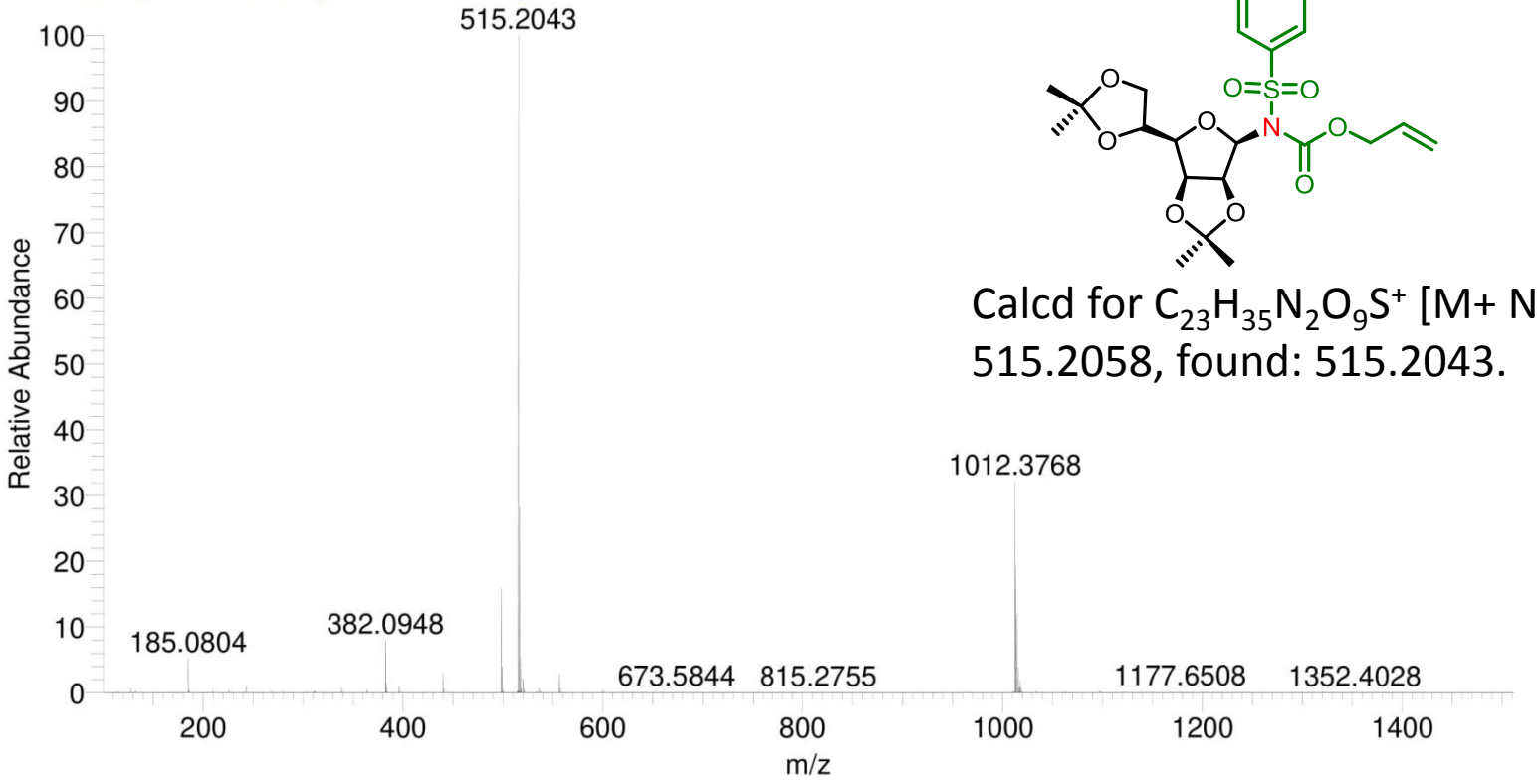


2D HSQC spectrum of **3d** ($CDCl_3$).

SAIF [HRMS Report]

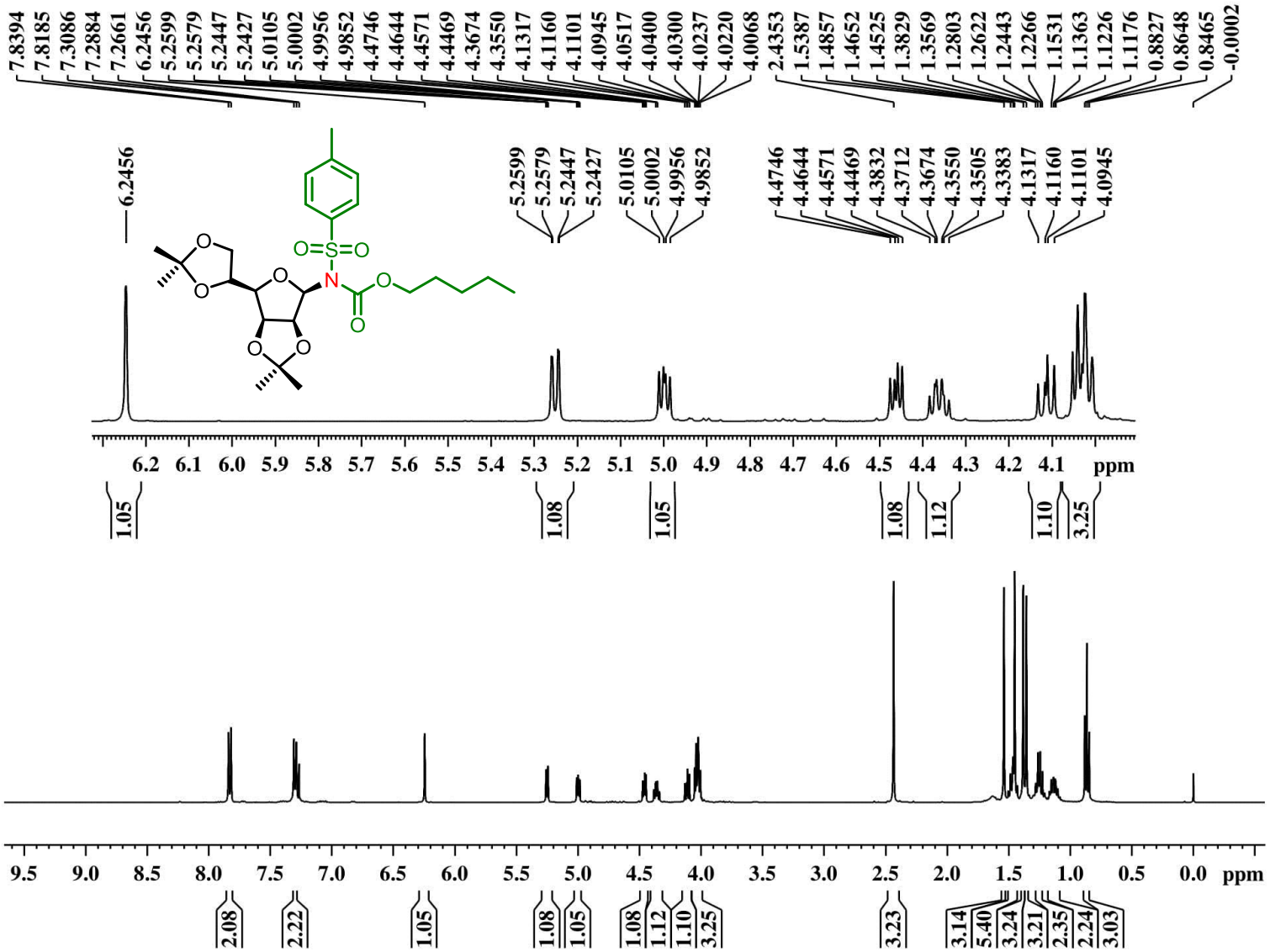
Data File:	HRMS20I01OCT04	Original Data Path:	D:\INTERNAL NEW\2020\OCT 2020
Sample ID:	PKM-TMA-01	Sample Name:	
Acquisition Date:	10/01/20 10:55:36 AM	Run Time(min):	0.00
Vial:	CStk1-01:4	Injection Volume(µl):	1.00

HRMS20I01OCT04 #12-25 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 1.05E8
T: FTMS + p ESI Full ms [100.00-1500.00]

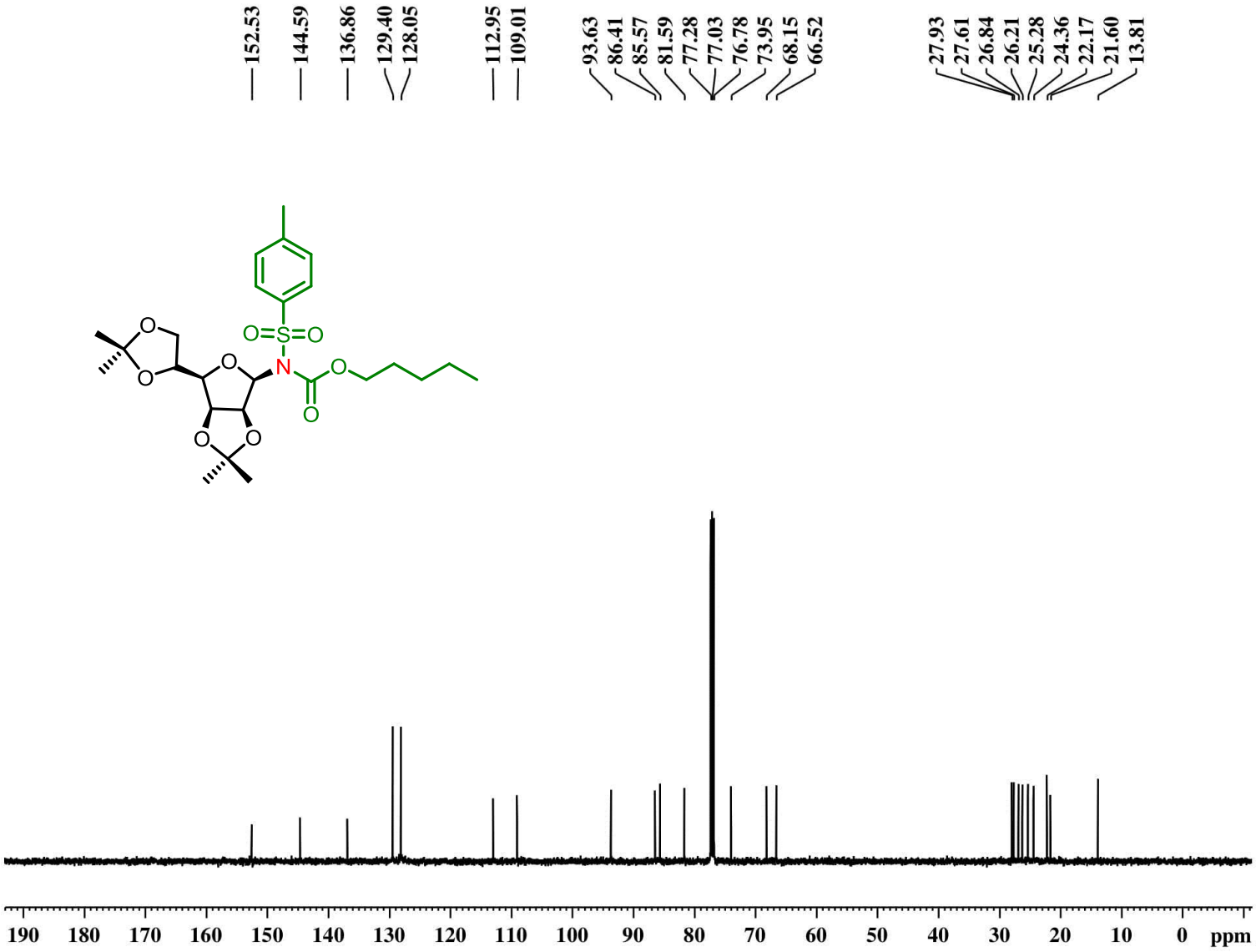


Calcd for $C_{23}H_{35}N_2O_9S^+$ $[M+ NH_4]^+$: 515.2058, found: 515.2043.

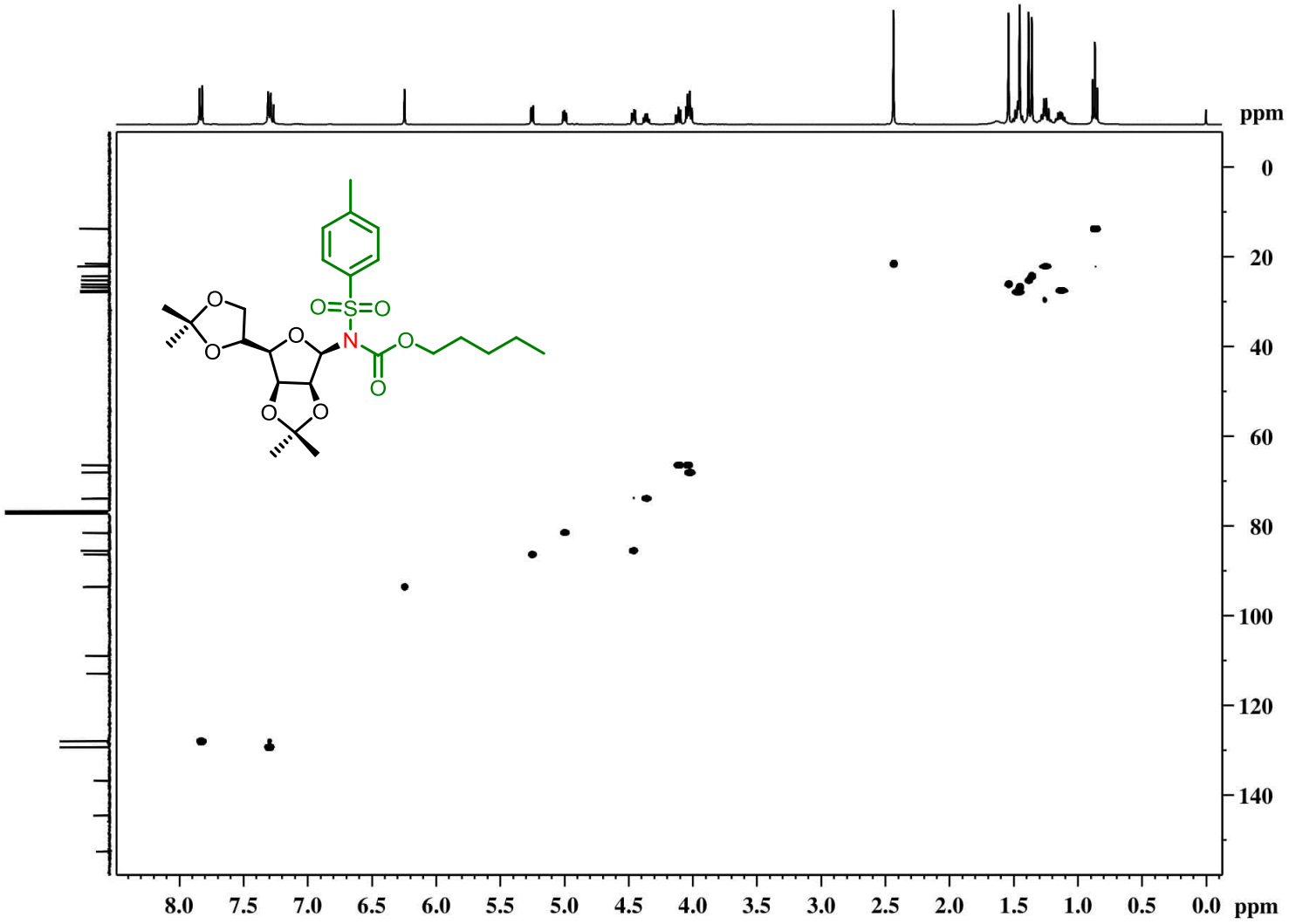
HRMS of **3d**



^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



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

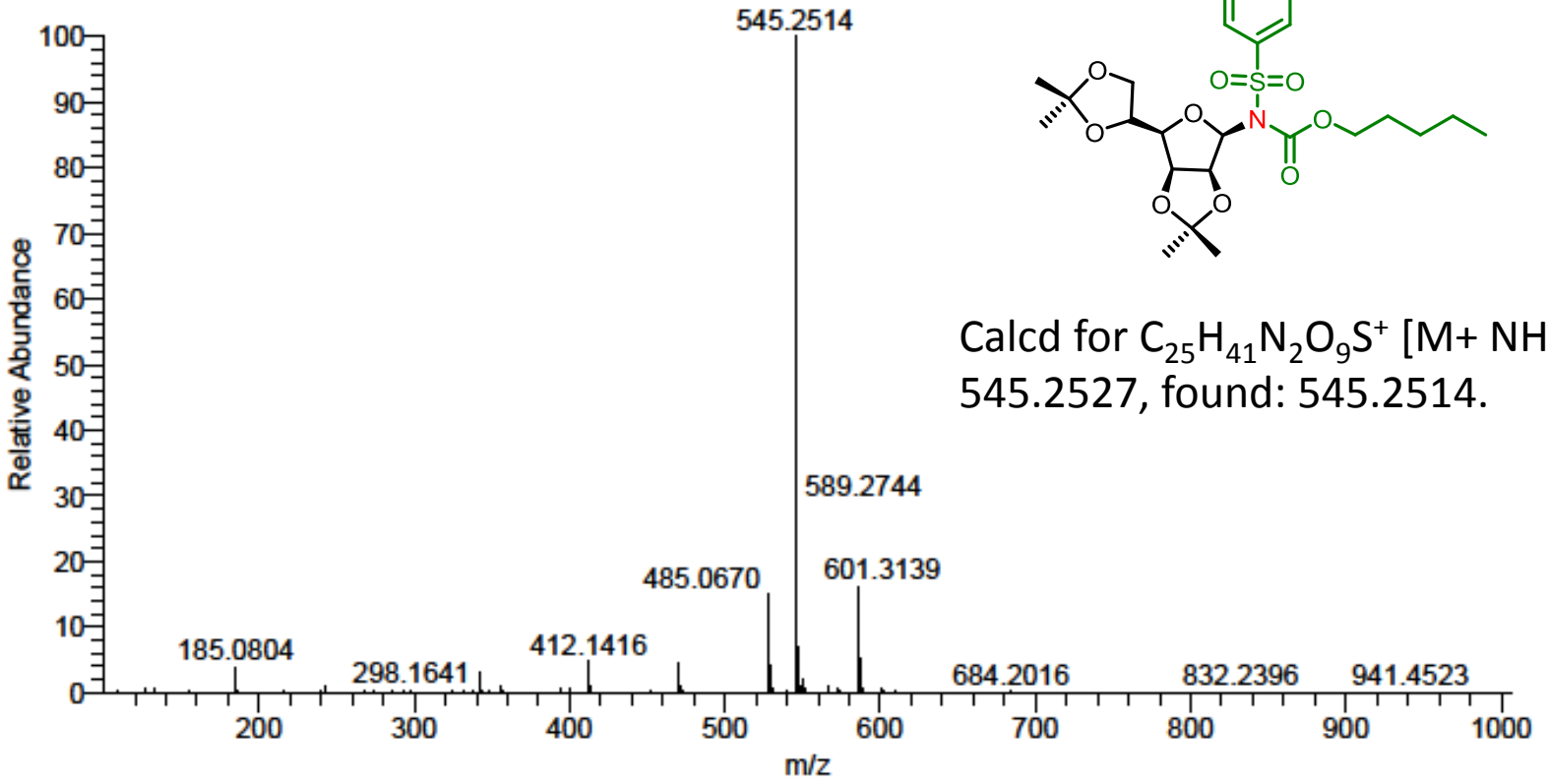


2D HSQC spectrum of **3e** ($CDCl_3$).

SAIF [HRMS Report]

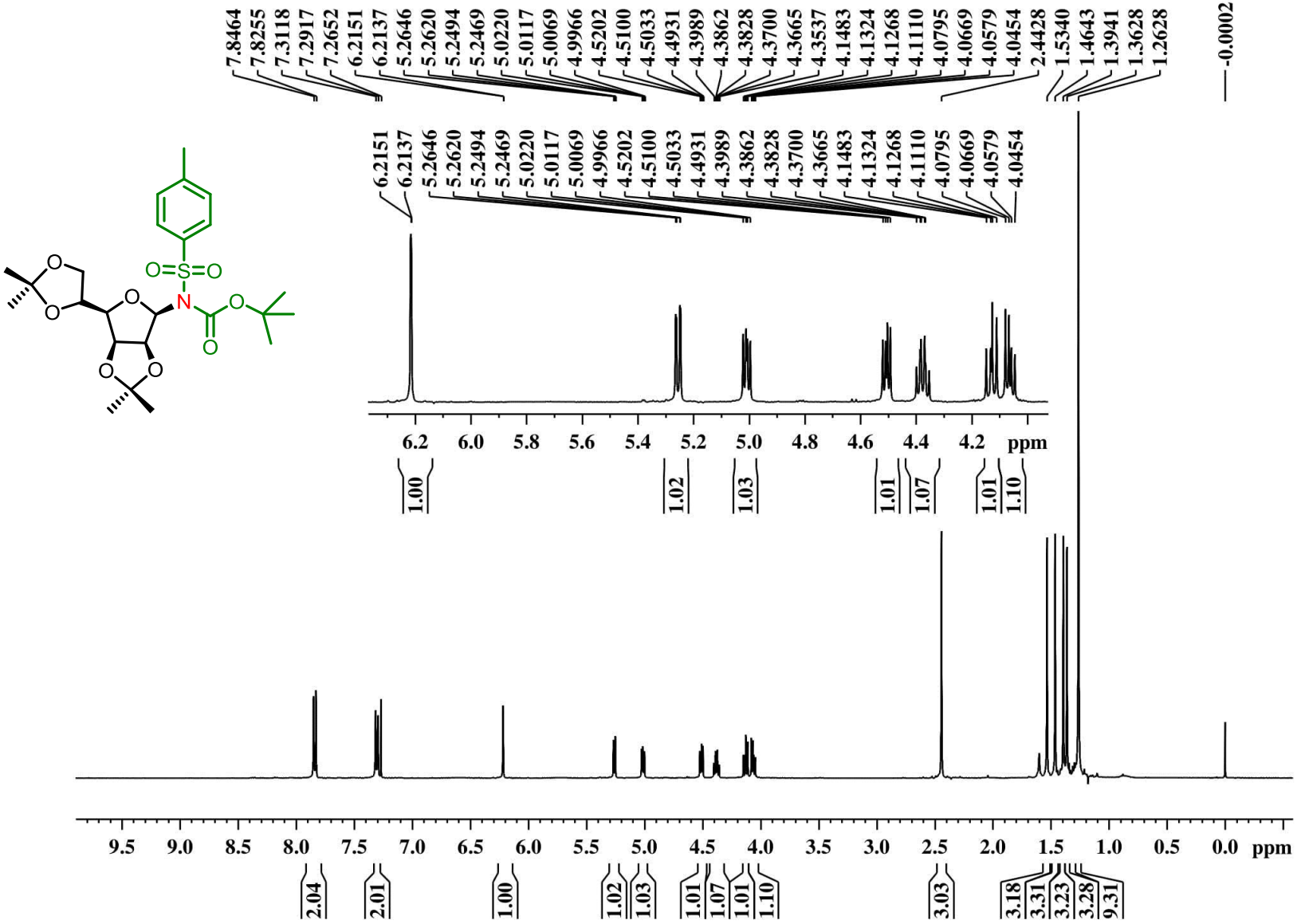
Data File:	HRMS20I01JUN08	Original Data Path:	D:\INTERNALS\2020\May 2020
Sample ID:	PKM-TMP-01	Sample Name:	
Acquisition Date:	06/01/20 12:36:07 PM	Run Time(min):	0.00
Vial:	CStk1-01:8	Injection Volume(µl):	1.00

HRMS20I01JUN08 #13-27 RT: 0.11-0.21 AV: 15 SB: 1 0.01 NL: 3.43E7
T: FTMS + p ESI Full ms [100.00-1000.00]

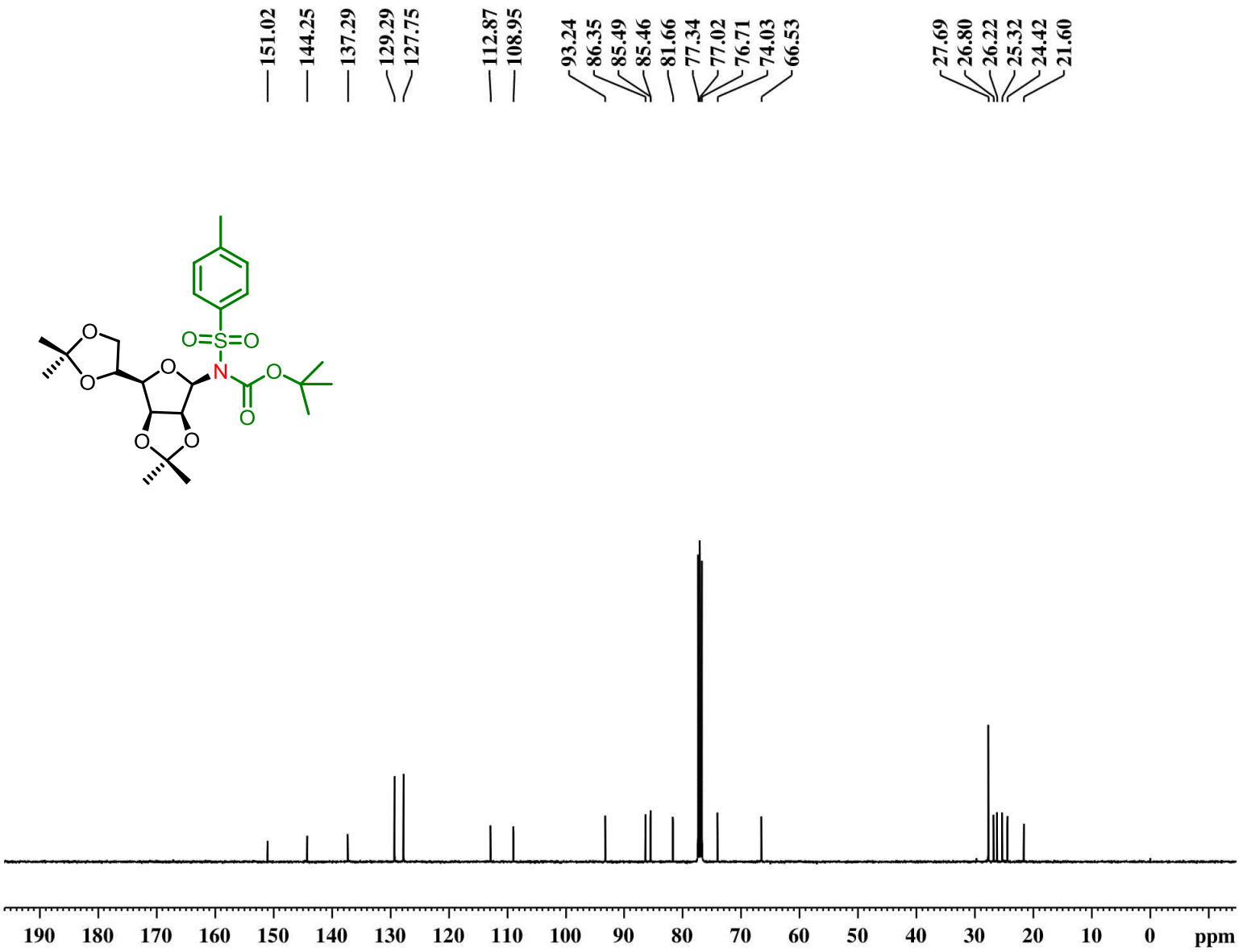


Calcd for $C_{25}H_{41}N_2O_9S^+$ $[M+NH_4]^+$: 545.2527, found: 545.2514.

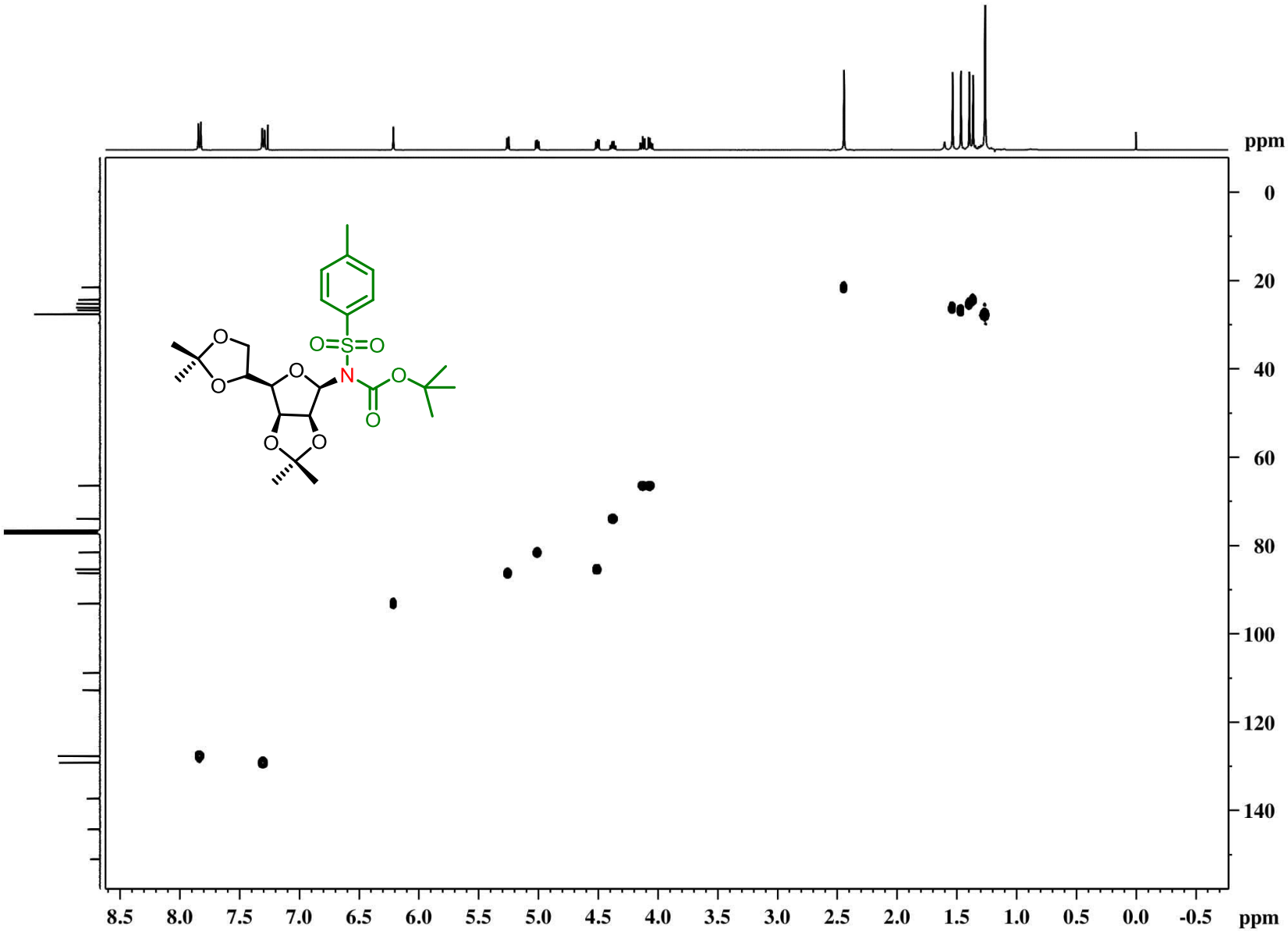
HRMS of **3e**



^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



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

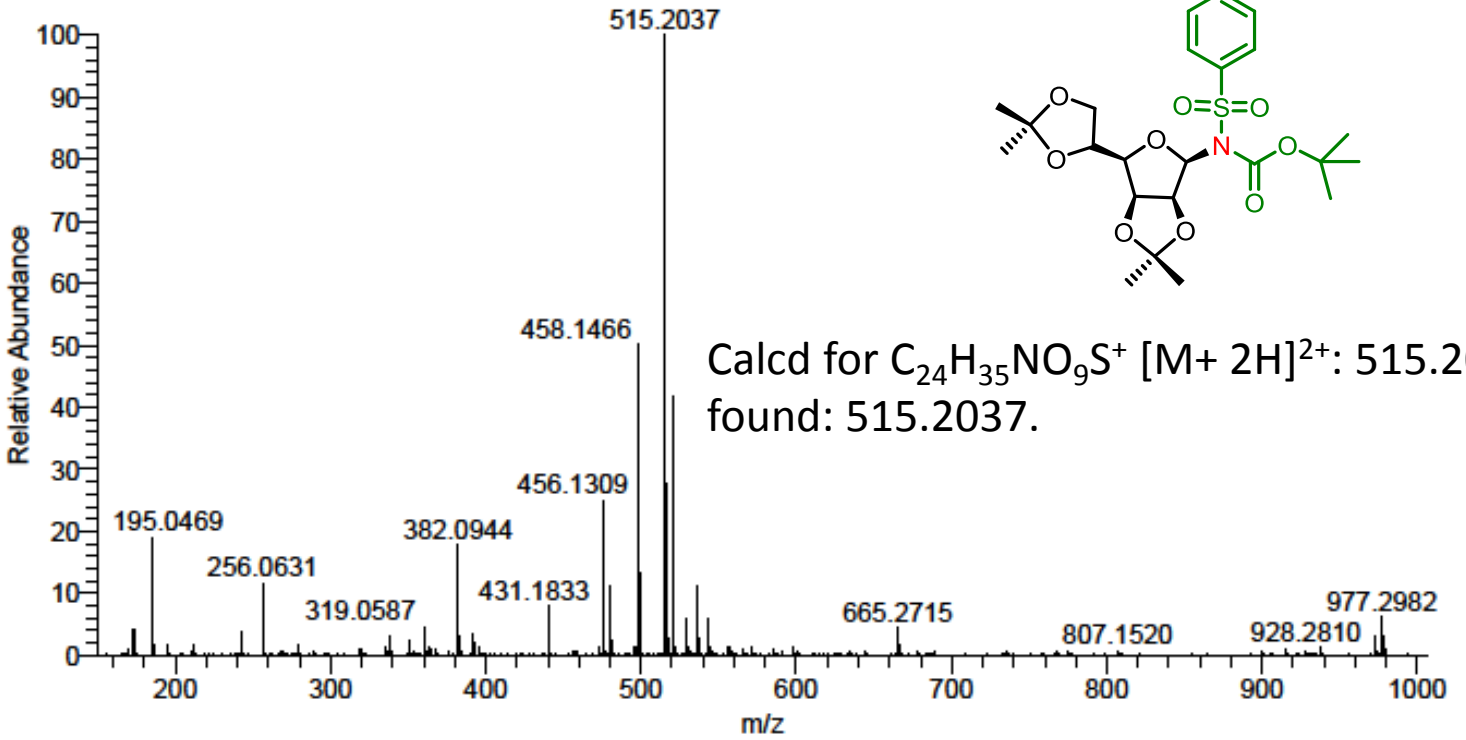


2D HSQC spectrum of **3f** ($CDCl_3$).

SAIF [HRMS Report]

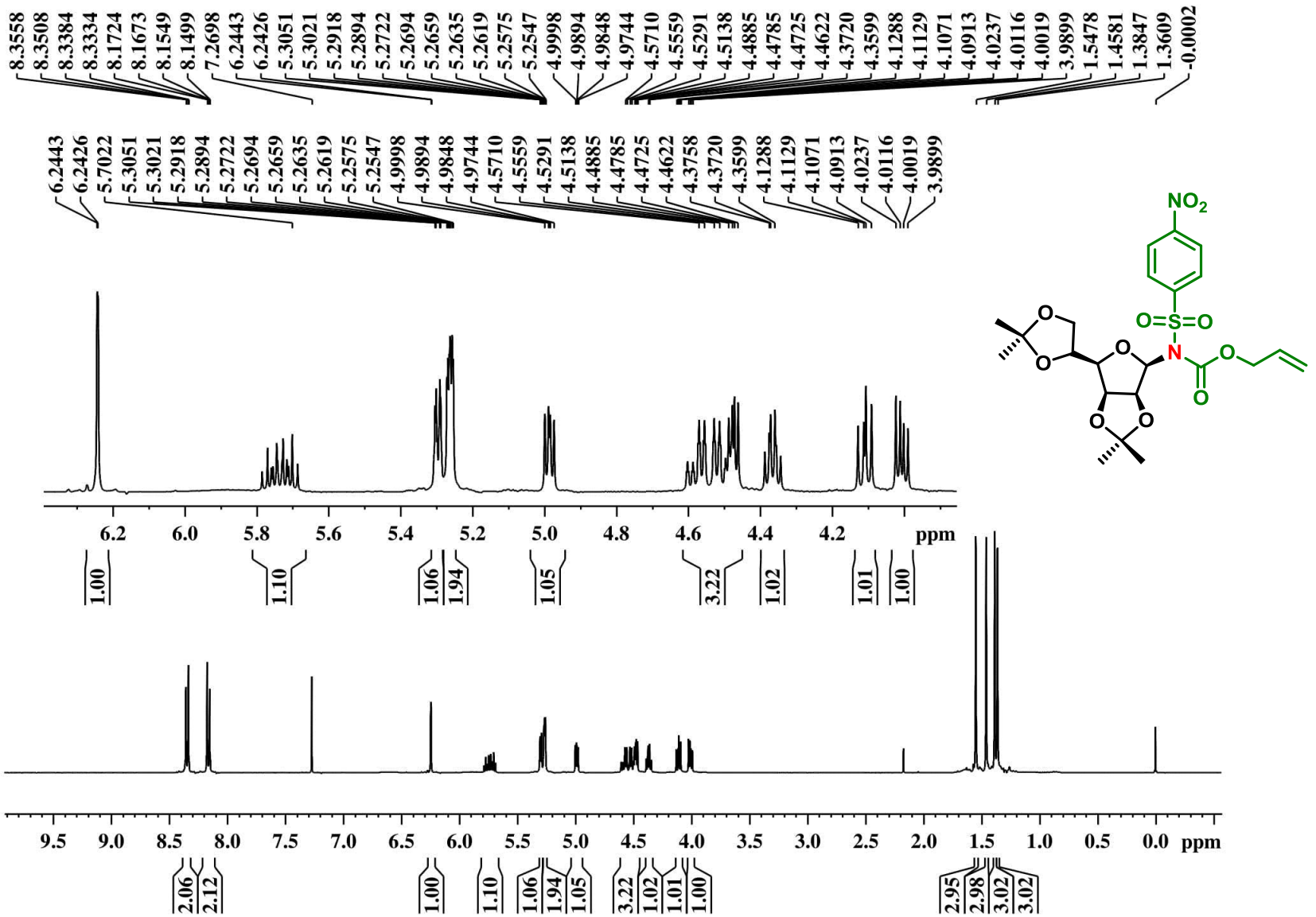
Data File:	HRMS21I06JAN06	Original Data Path:	D:\INTERNAL NEW\2021\Jan 2021
Sample ID:	PKM-TMB-01	Sample Name:	
Acquisition Date:	01/06/21 11:43:10 AM	Run Time(min):	0.00
Vial:	CStk1-01:6	Injection Volume(µl):	1.00

HRMS21I06JAN06 #29-61 RT: 0.25-0.50 AV: 33 SB: 1 0.00 NL: 1.70E6
T: FTMS + p ESI Full ms [150.00-1000.00]

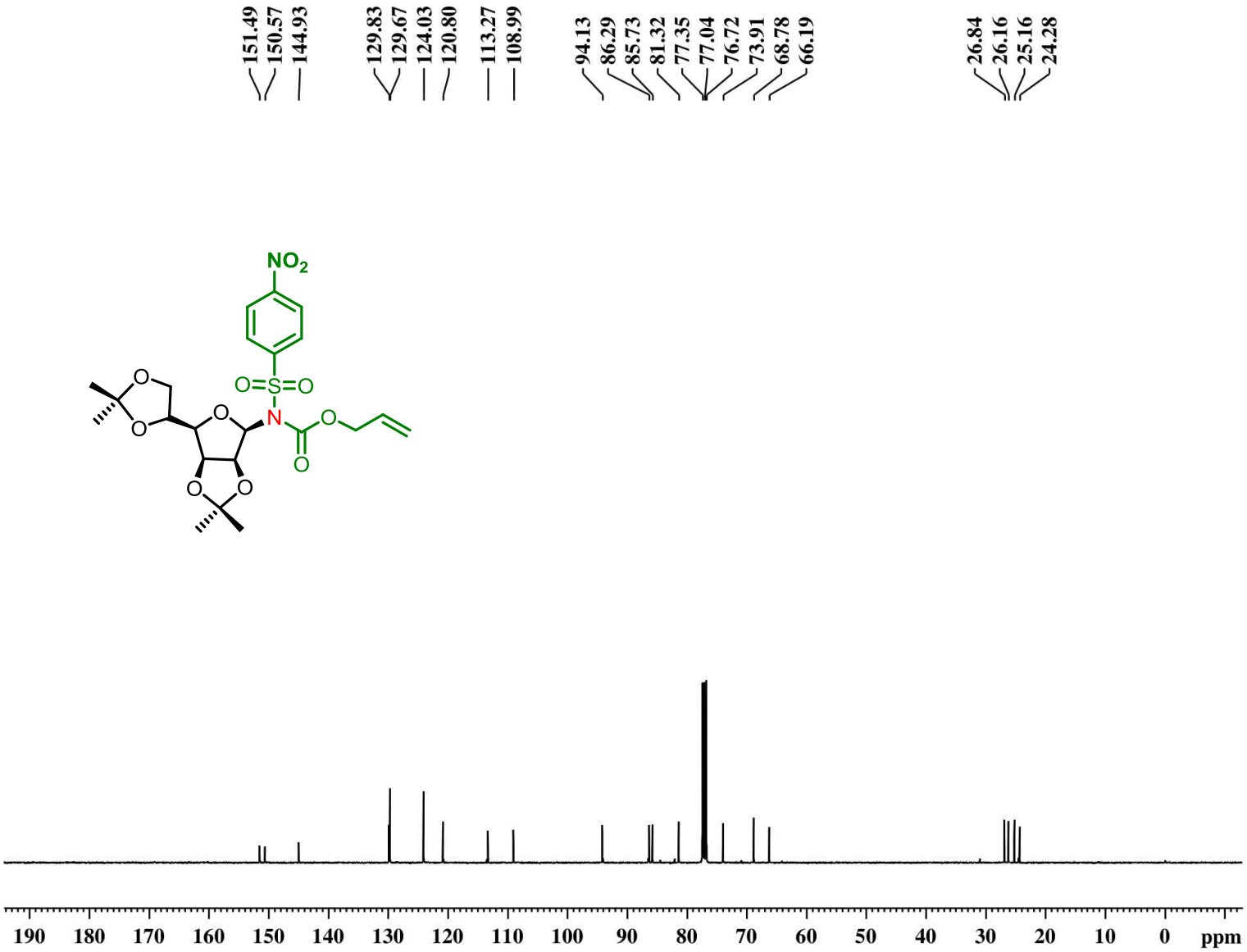


Calcd for $C_{24}H_{35}NO_9S^+$ $[M+ 2H]^{2+}$: 515.2031, found: 515.2037.

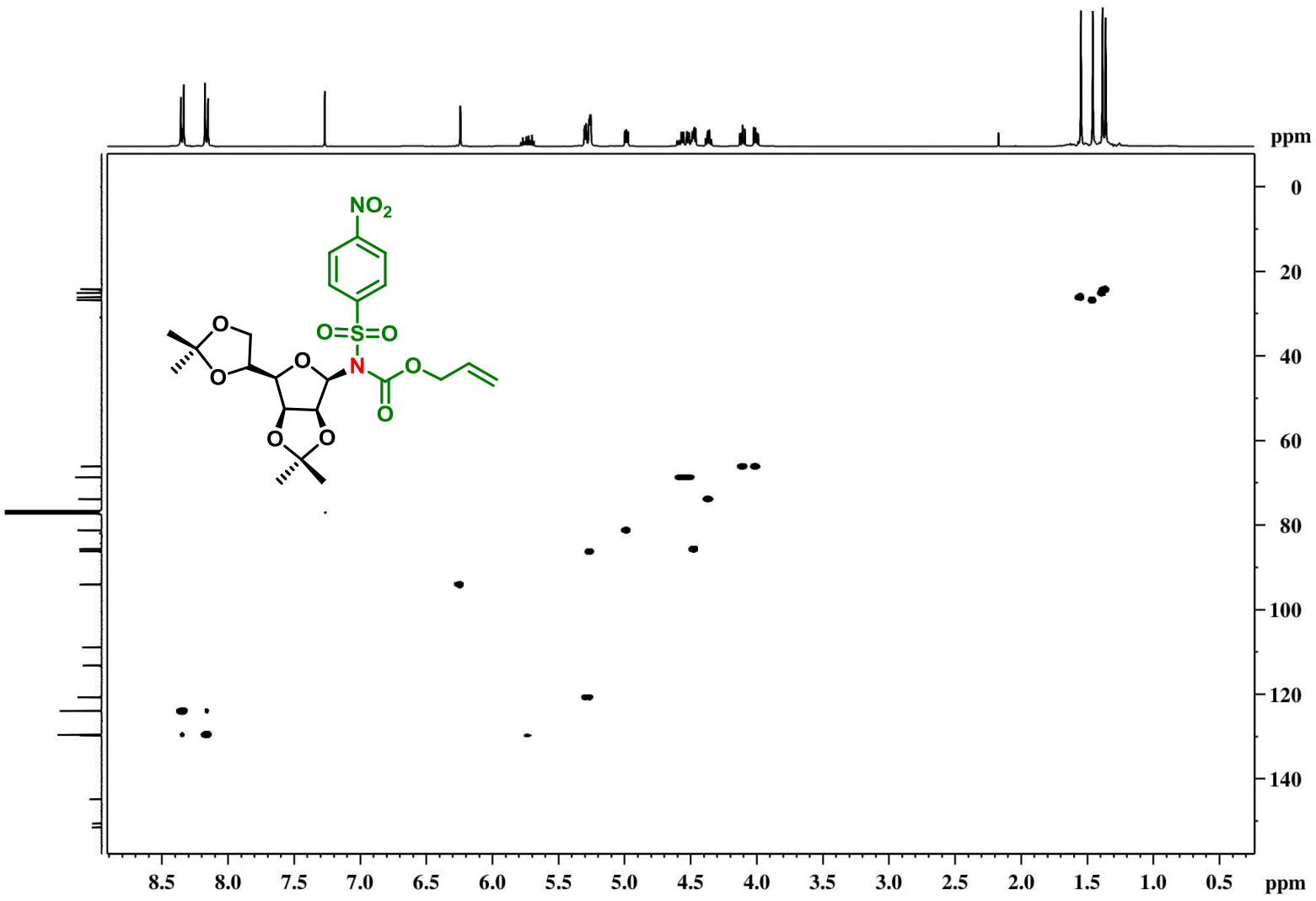
HRMS of **3f**



^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



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

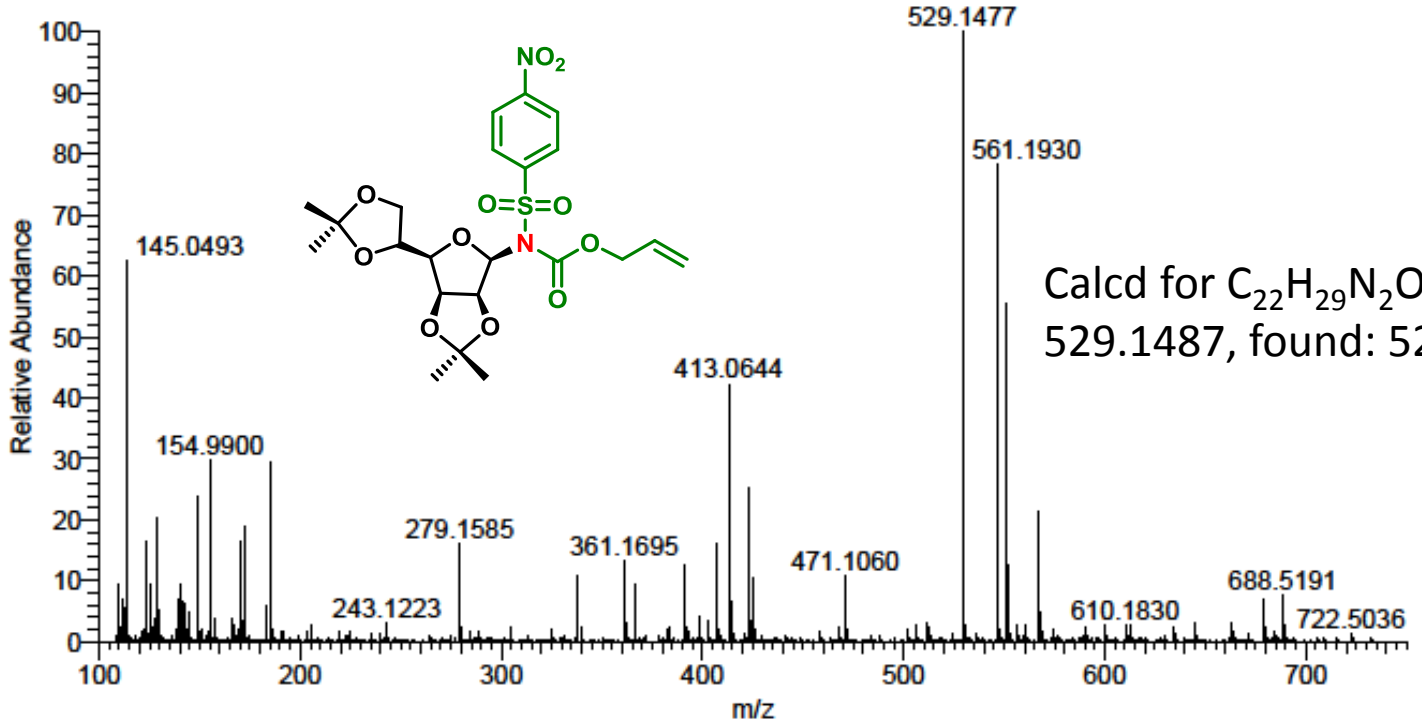


2D HSQC spectrum of **3g** ($CDCl_3$).

SAIF [HRMS Report]

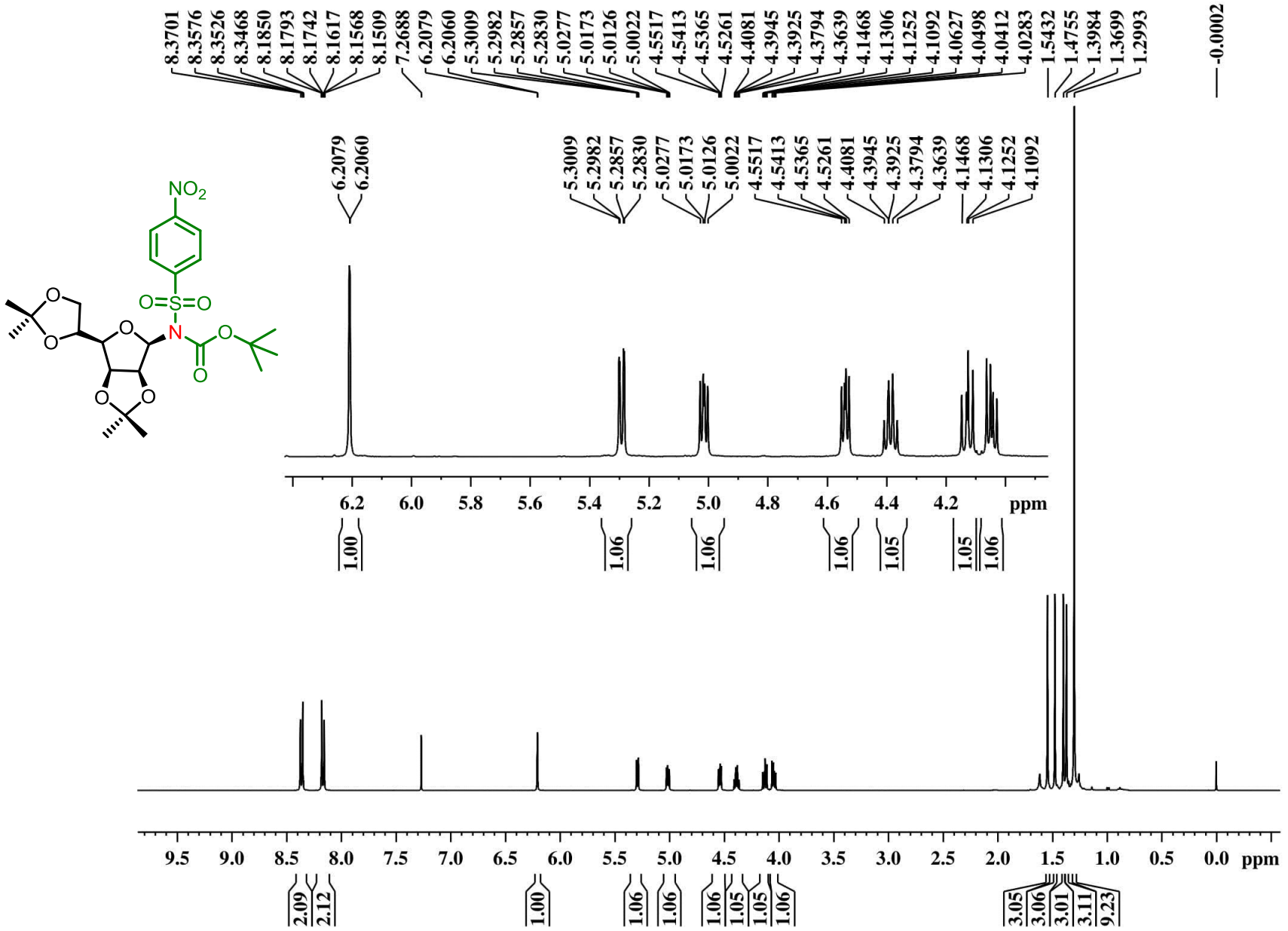
Data File:	HRMS21I05JAN19	Original Data Path:	D:\INTERNAL NEW\2021\Jan 2021
Sample ID:	PKM-NMA-01	Sample Name:	
Acquisition Date:	01/05/21 11:59:09 AM	Run Time(min):	0.00
Vial:	CStk1-01:19	Injection Volume(µl):	1.00

HRMS21I05JAN19 #30-60 RT: 0.25-0.50 AV: 31 SB: 1 0.01 NL: 2.18E5
T: FTMS + c ESI Full ms [100.00-750.00]

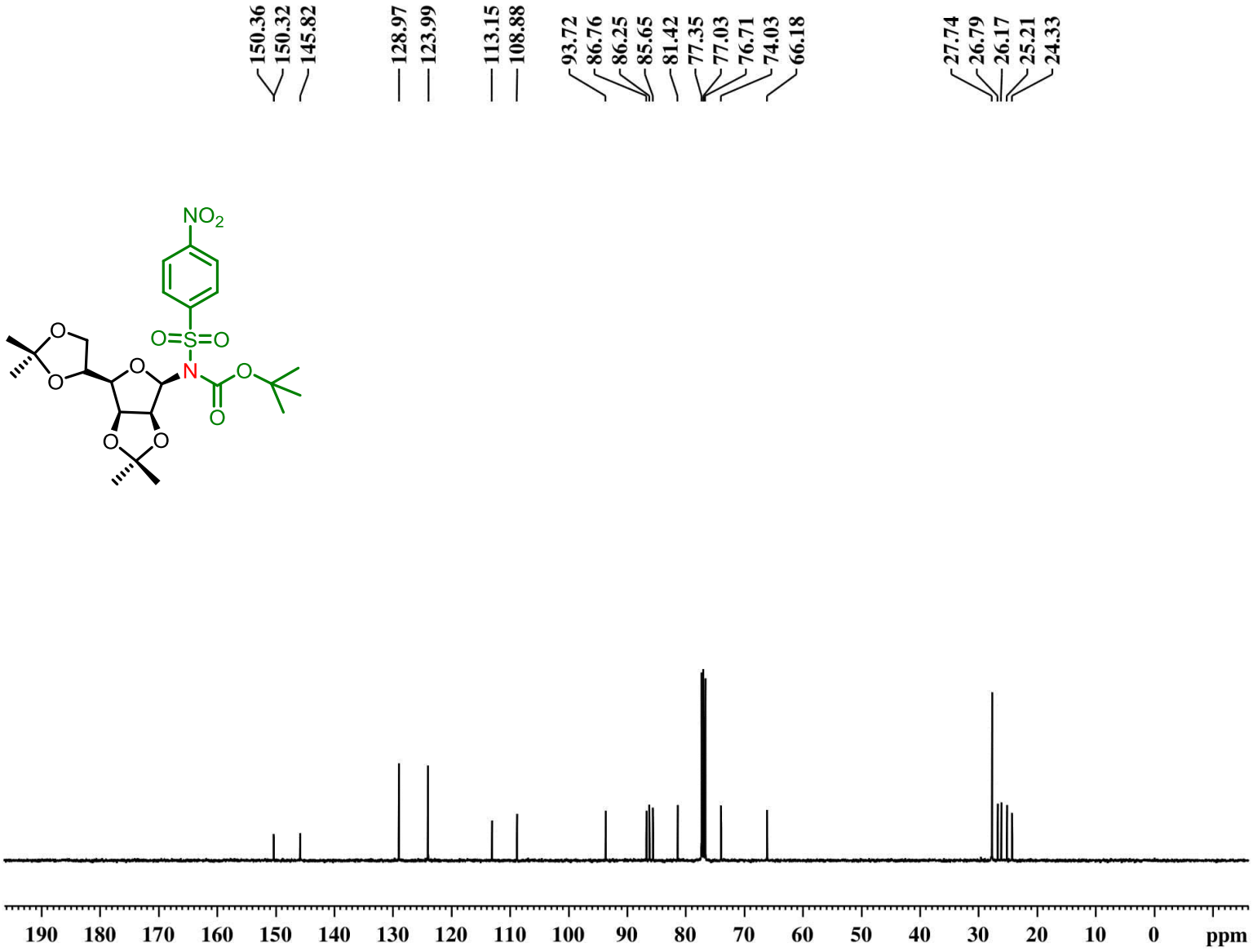


Calcd for $C_{22}H_{29}N_2O_{11}S^+$ $[M+H]^+$: 529.1487, found: 529.1477.

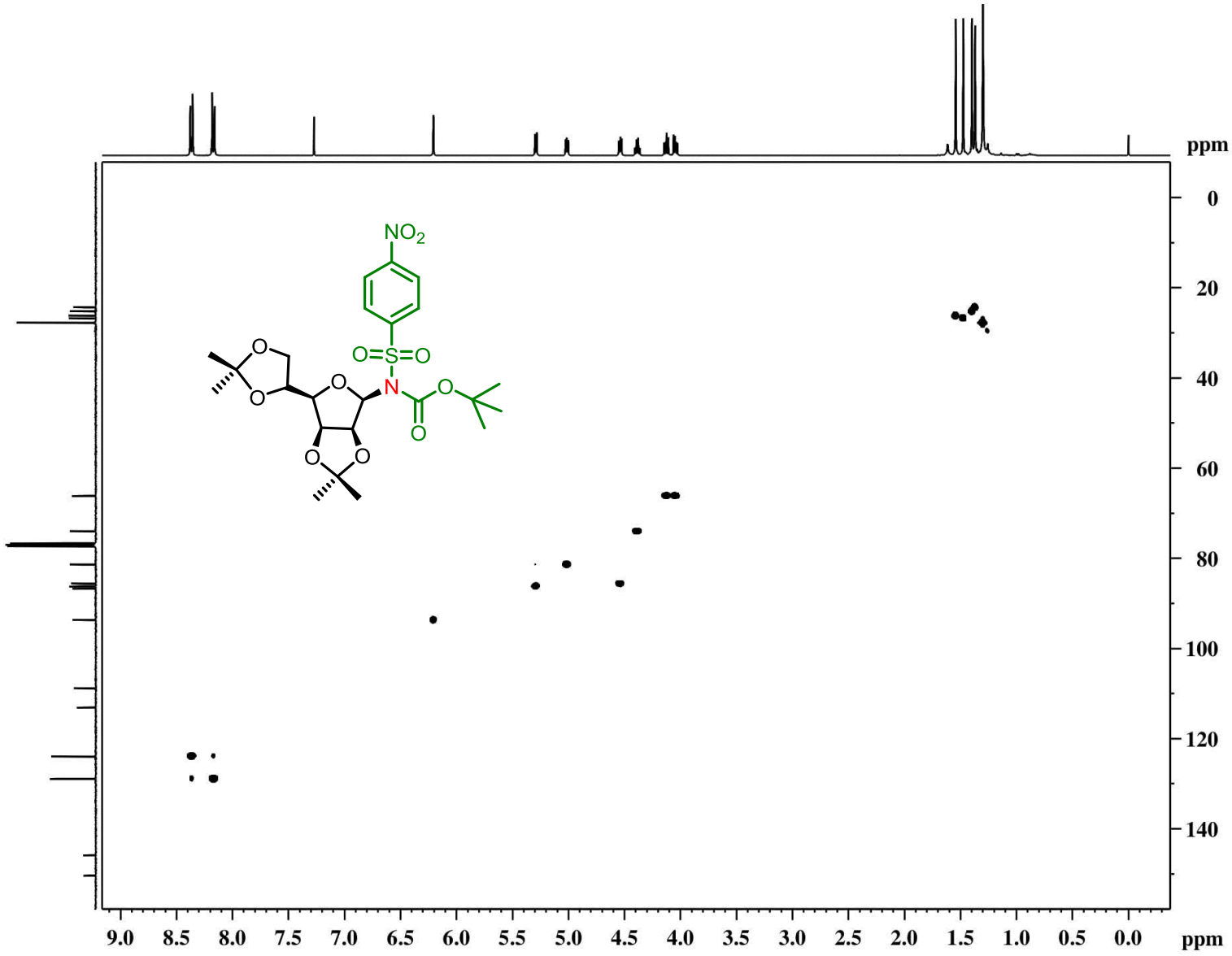
HRMS of **3g**



^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



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

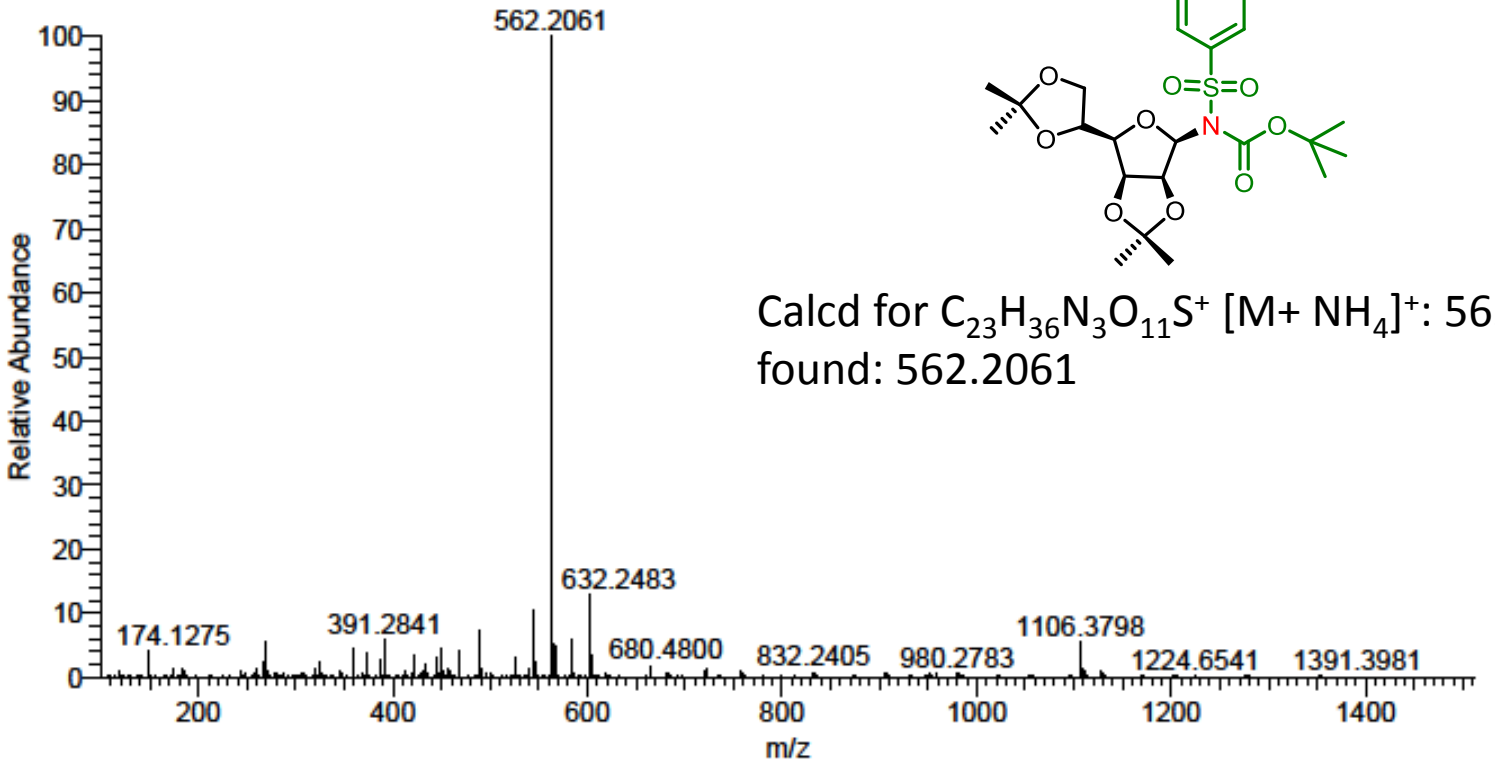


2D HSQC spectrum of **3h** ($CDCl_3$).

SAIF [HRMS Report]

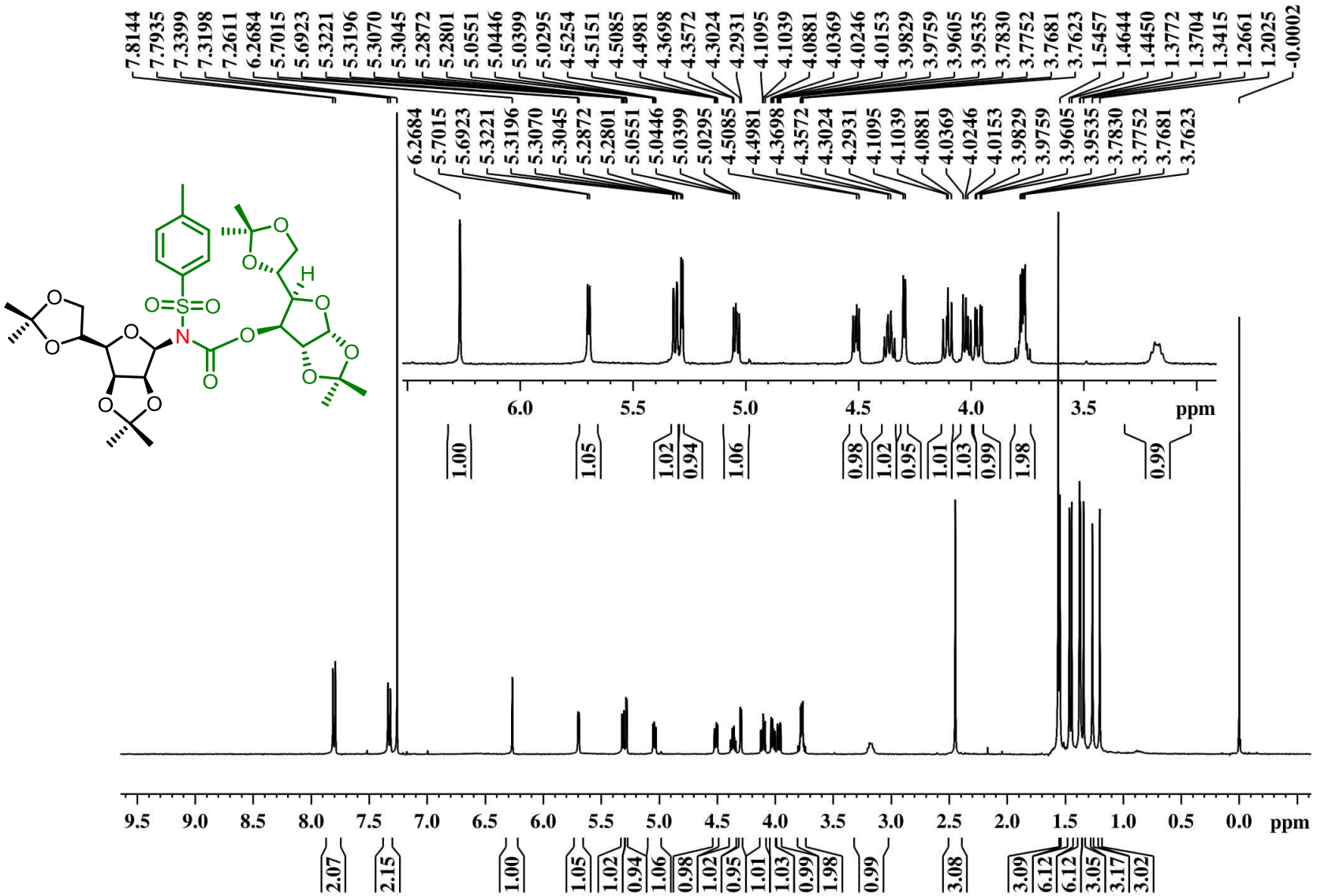
Data File:	HRMS20I01OCT03	Original Data Path:	D:\INTERNAL NEW\2020\OCT 2020
Sample ID:	PKM-NMB-01	Sample Name:	
Acquisition Date:	10/01/20 10:53:37 AM	Run Time(min):	0.00
Vial:	CStk1-01:3	Injection Volume(µl):	1.00

HRMS20I01OCT03 #12-24 RT: 0.11-0.21 AV: 13 SB: 1 0.01 NL: 3.90E6
T: FTMS + p ESI Full ms [100.00-1500.00]

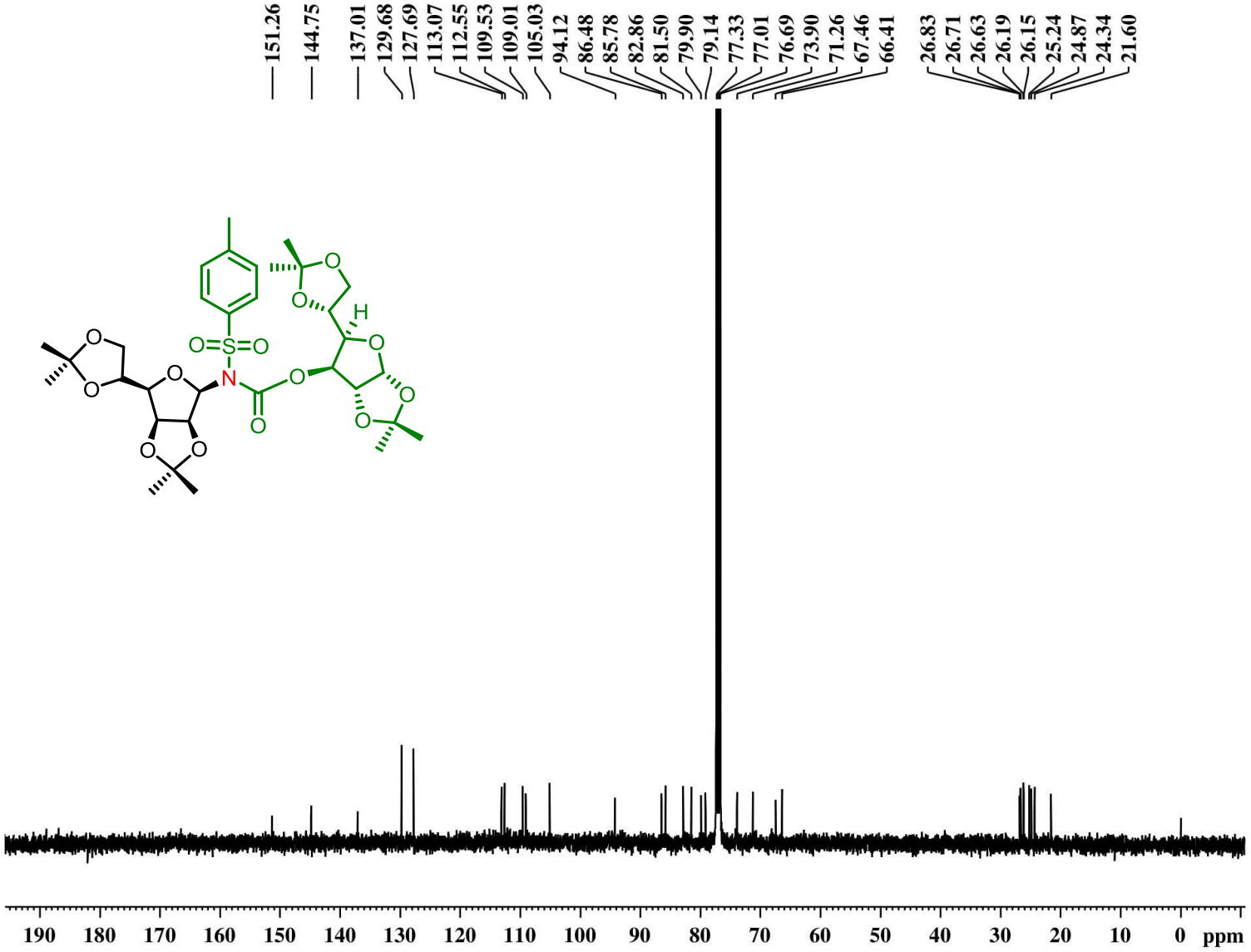


Calcd for $C_{23}H_{36}N_3O_{11}S^+$ $[M+ NH_4]^+$: 562.2065, found: 562.2061

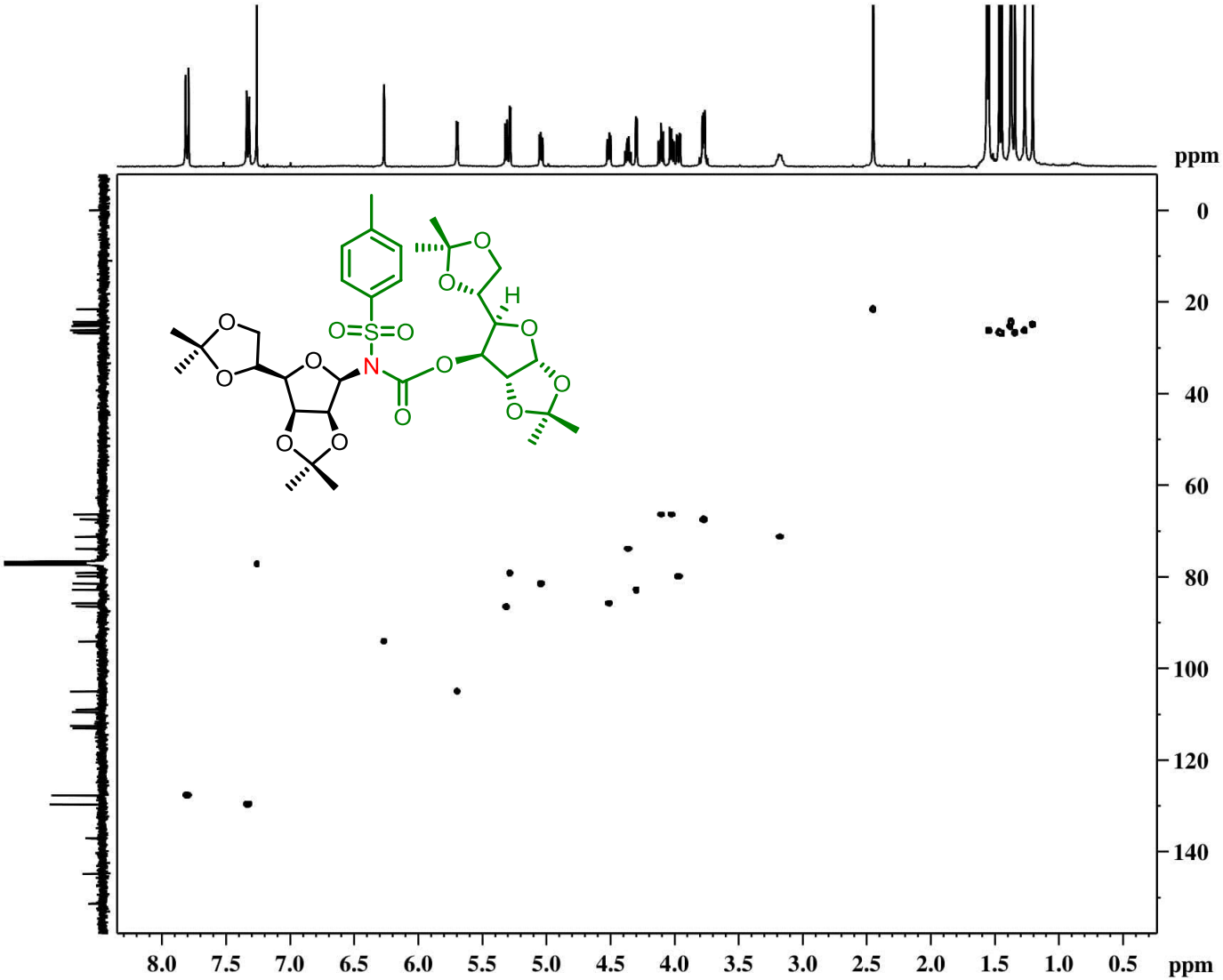
HRMS of **3h**



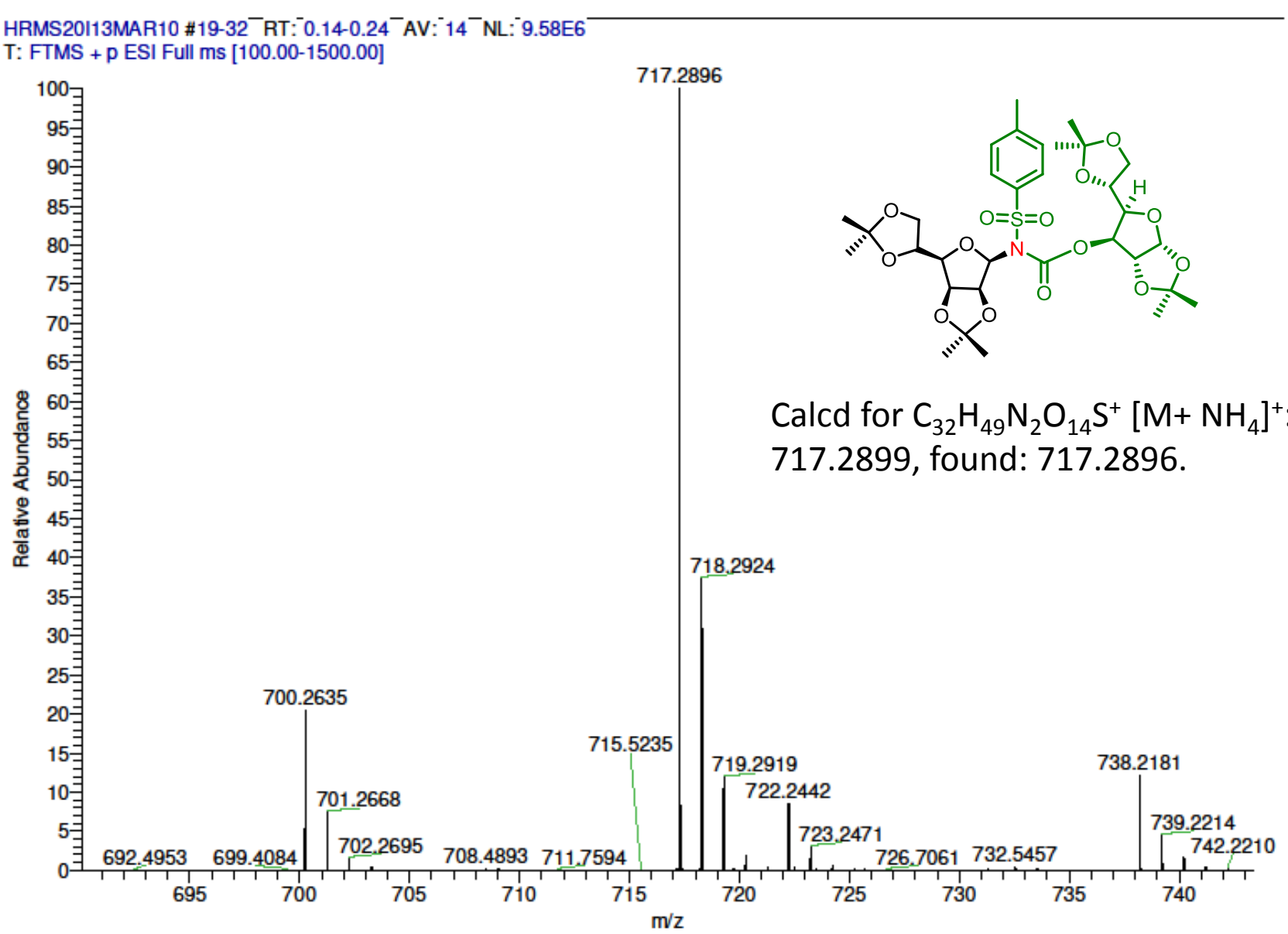
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



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

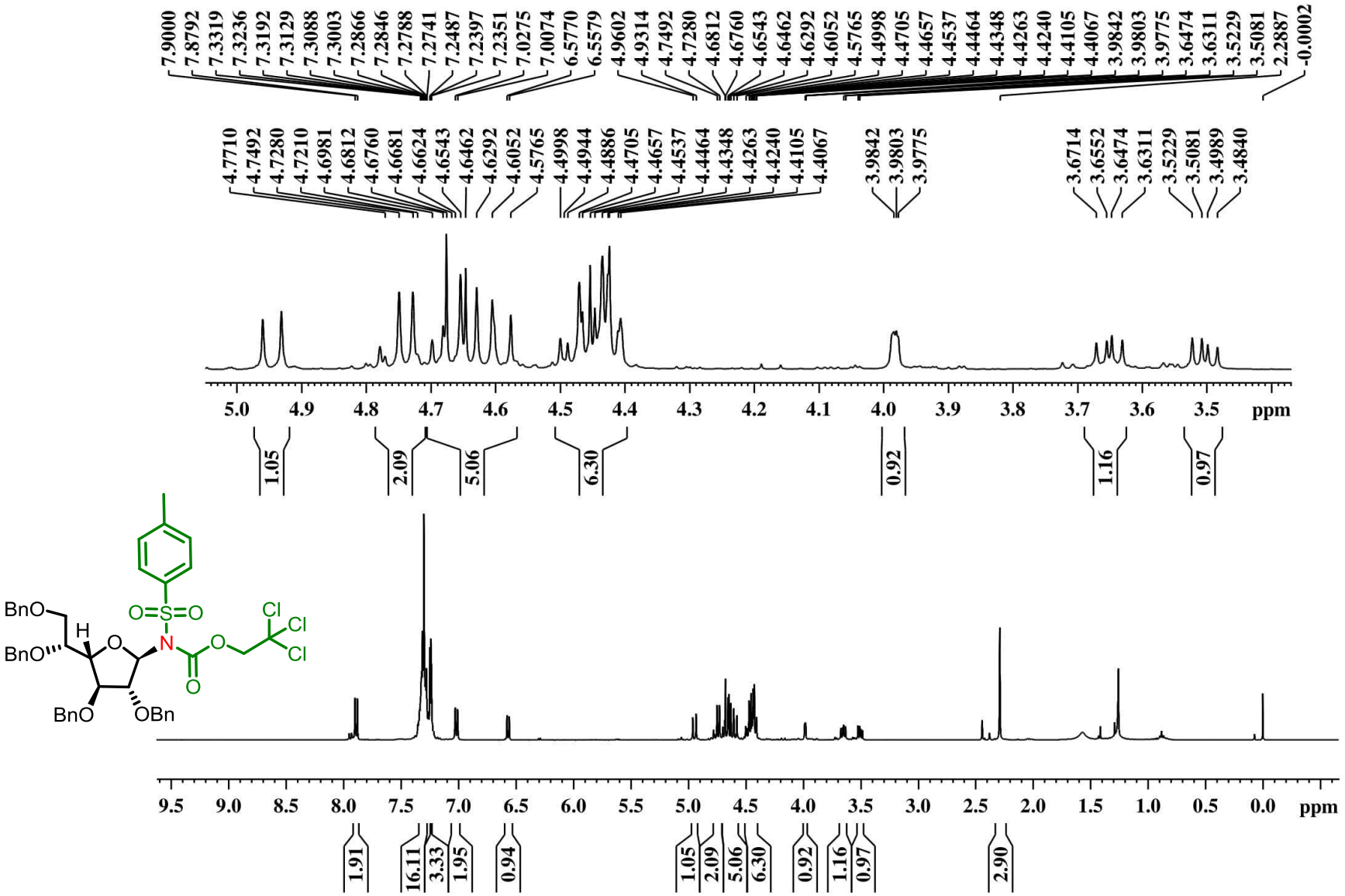


2D HSQC spectrum of **3i** ($CDCl_3$).

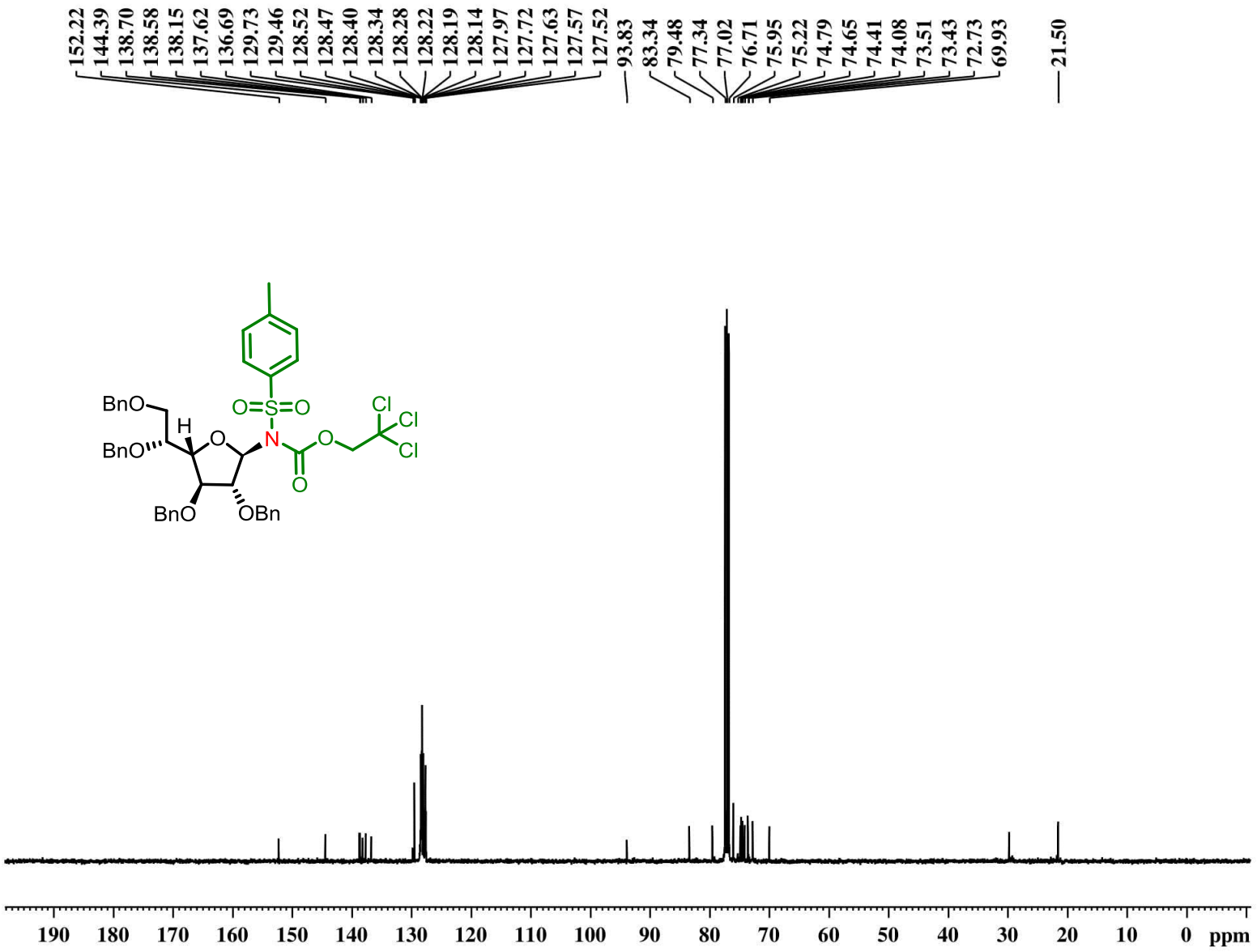


Calcd for $C_{32}H_{49}N_2O_{14}S^+$ $[M+ NH_4]^+$: 717.2899, found: 717.2896.

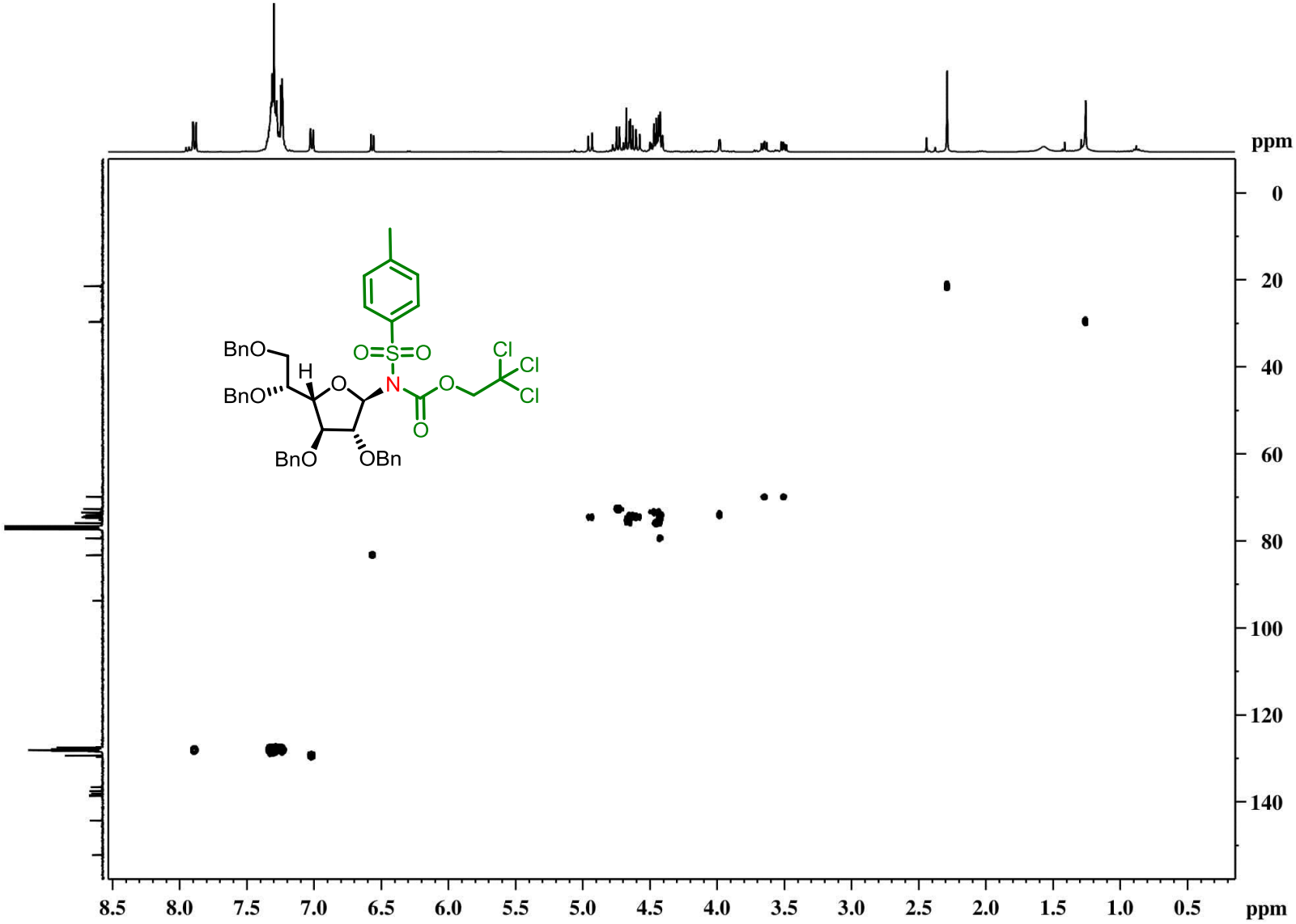
HRMS of **3i**



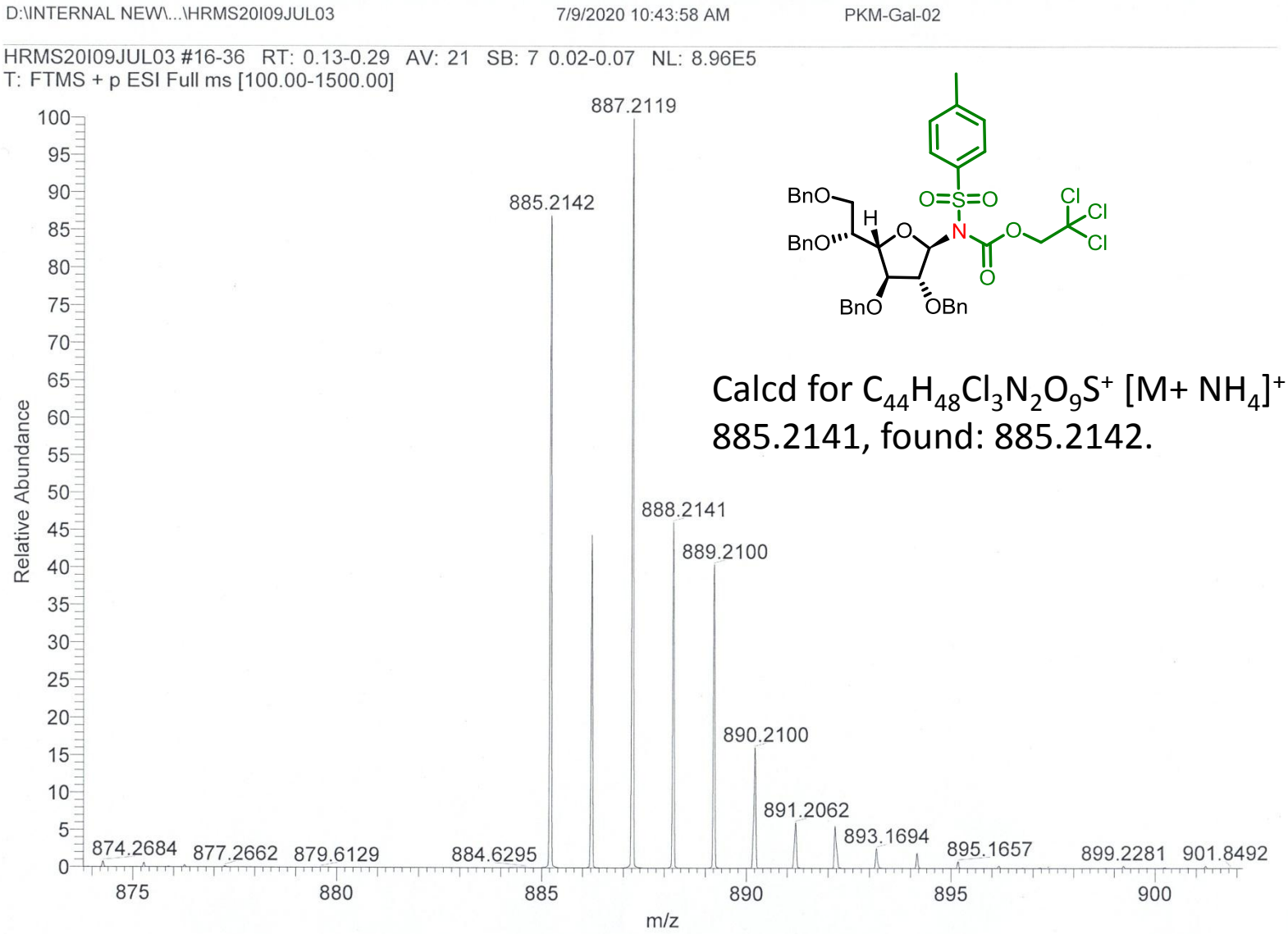
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



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

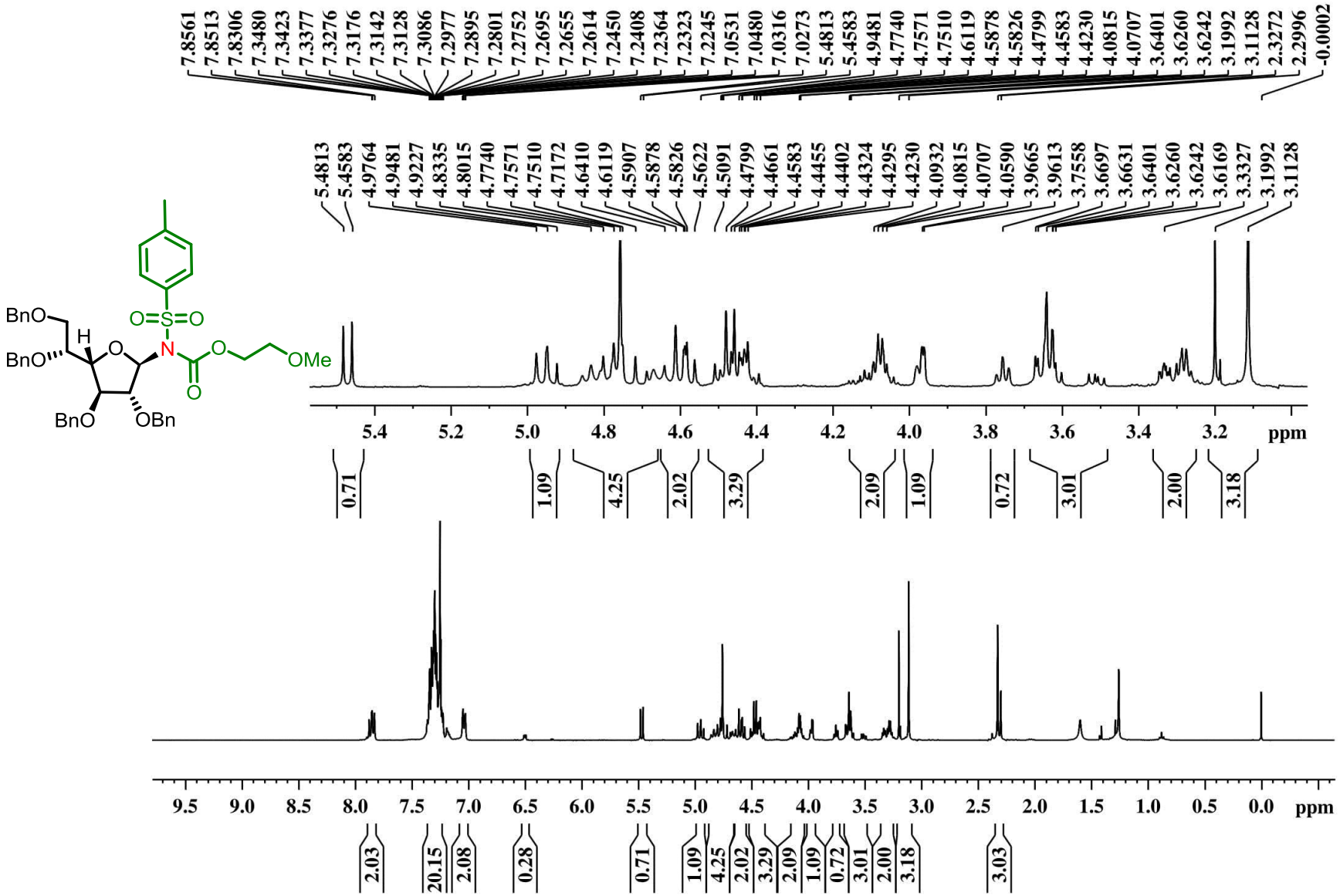


2D HSQC spectrum of **3j** ($CDCl_3$).

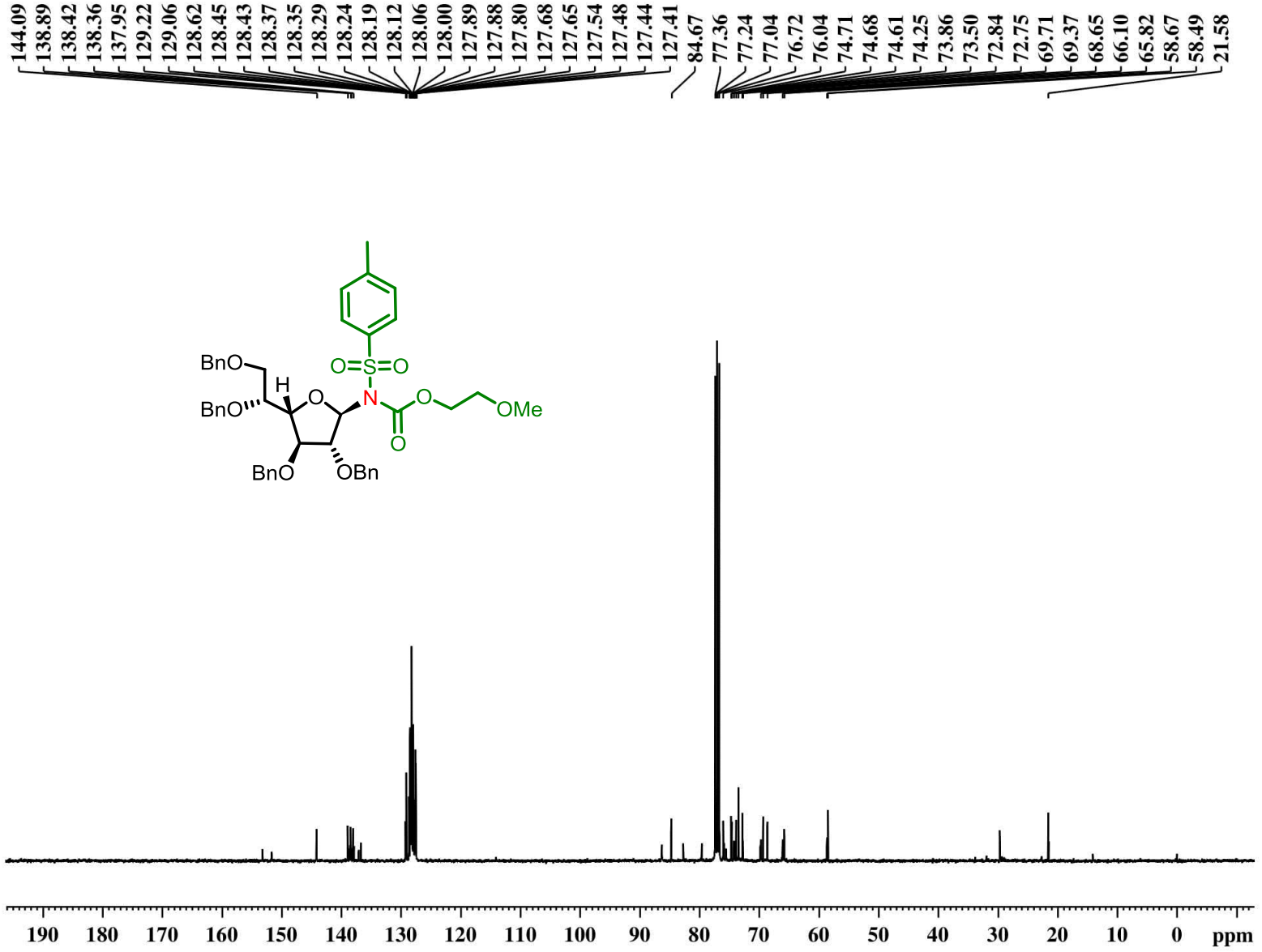


Calcd for $C_{44}H_{48}Cl_3N_2O_9S^+$ $[M+NH_4]^+$: 885.2141, found: 885.2142.

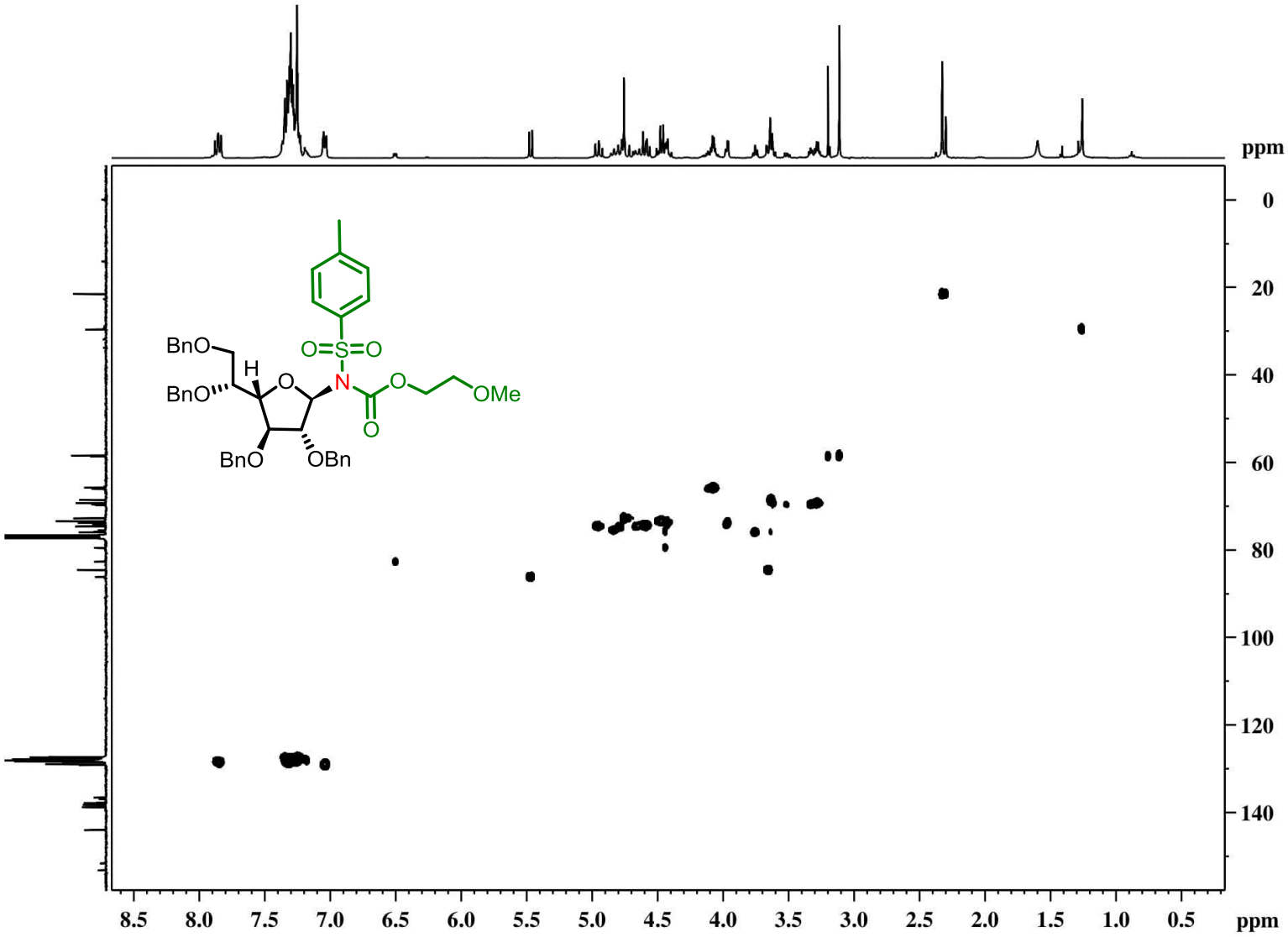
HRMS of **3j**



^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



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

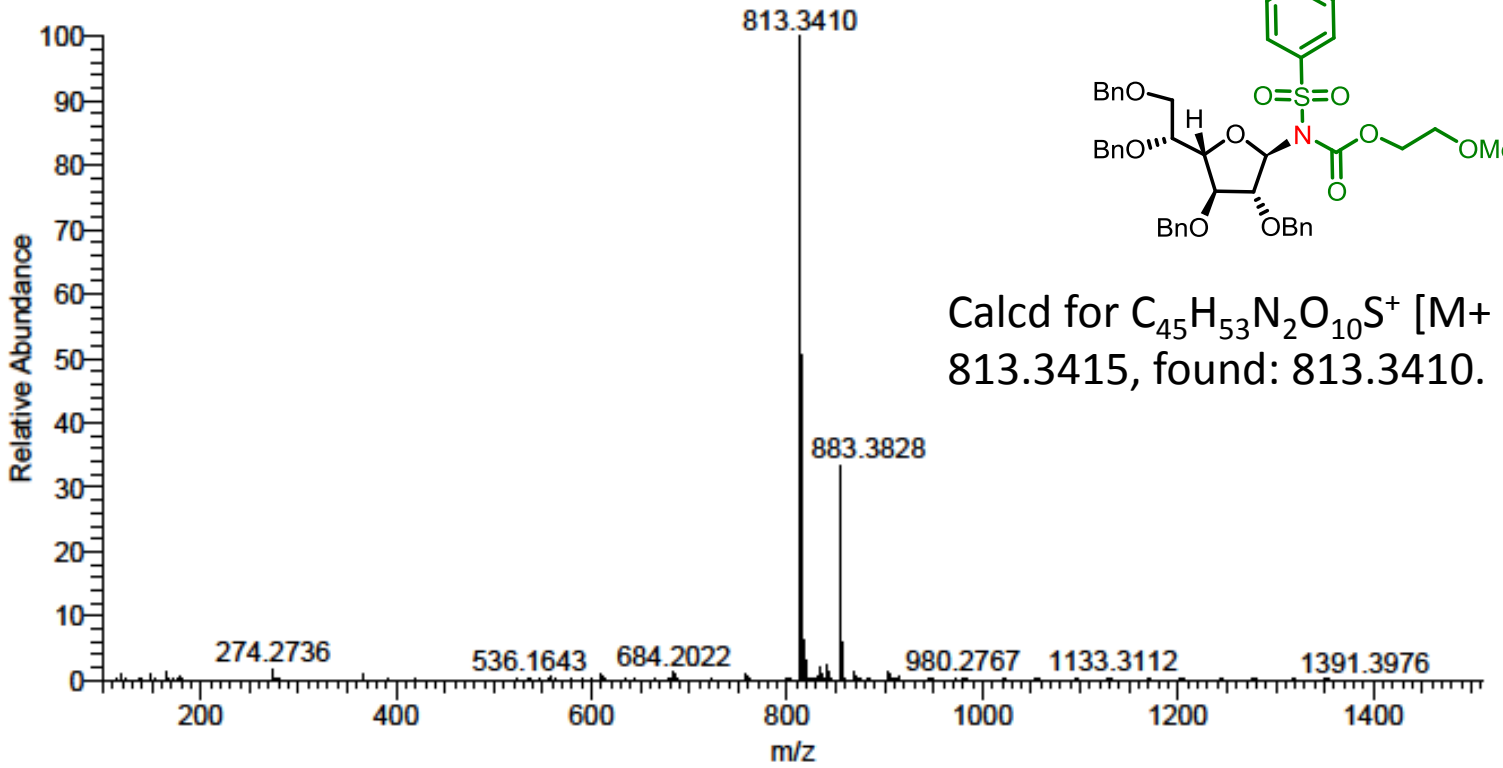


2D HSQC spectrum of **3k** ($CDCl_3$).

SAIF [HRMS Report]

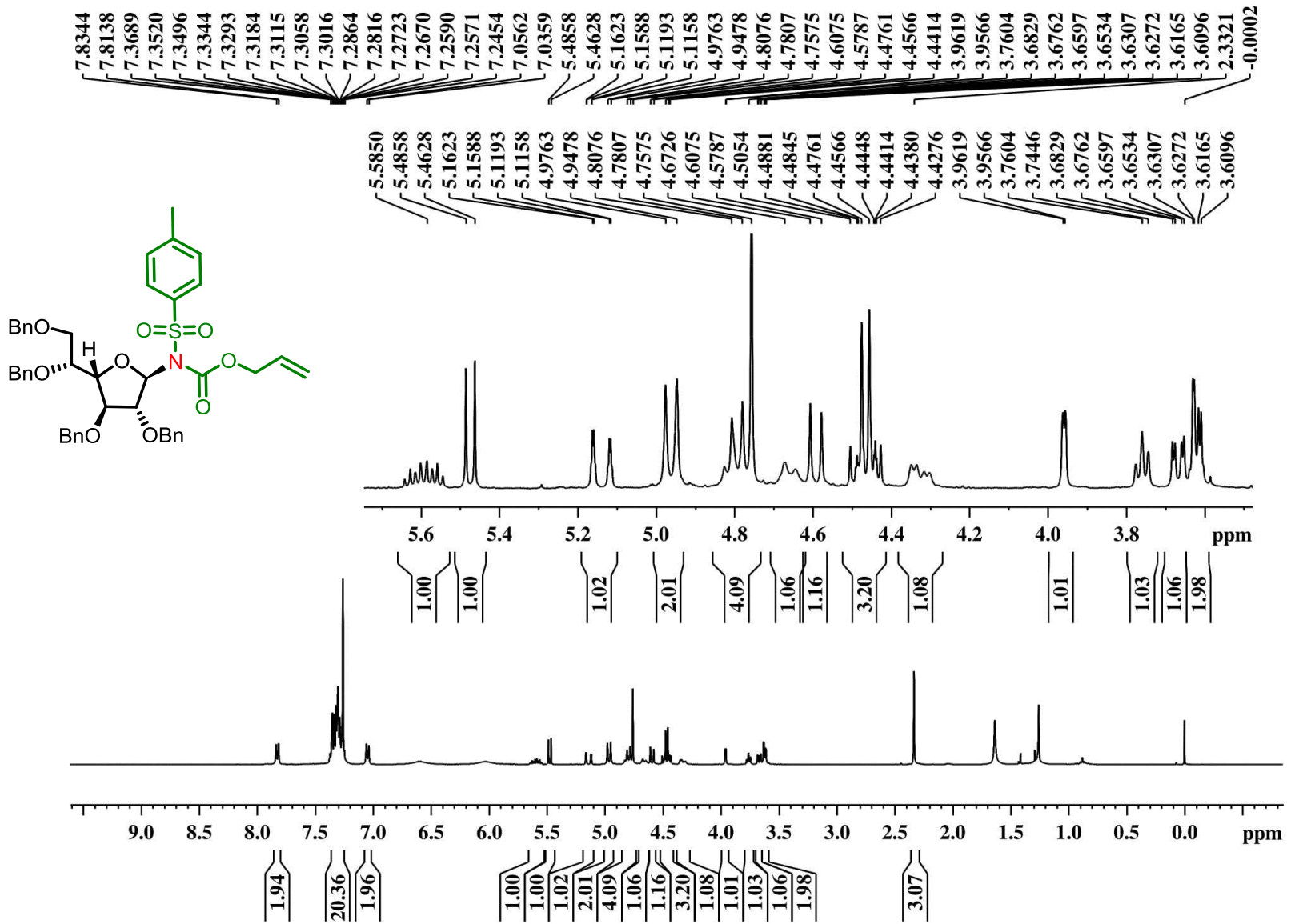
Data File:	HRMS20I09JUL05	Original Data Path:	D:\INTERNAL NEW\2020\July 2020
Sample ID:	PKM-Gal-03	Sample Name:	
Acquisition Date:	07/09/20 10:47:56 AM	Run Time(min):	0.00
Vial:	CStk1-01:5	Injection Volume(ul):	1.00

HRMS20I09JUL05 #13-25 RT: 0.11-0.21 AV: 13 SB: 1 0.01 NL: 3.07E6
T: FTMS + p ESI Full ms [100.00-1500.00]

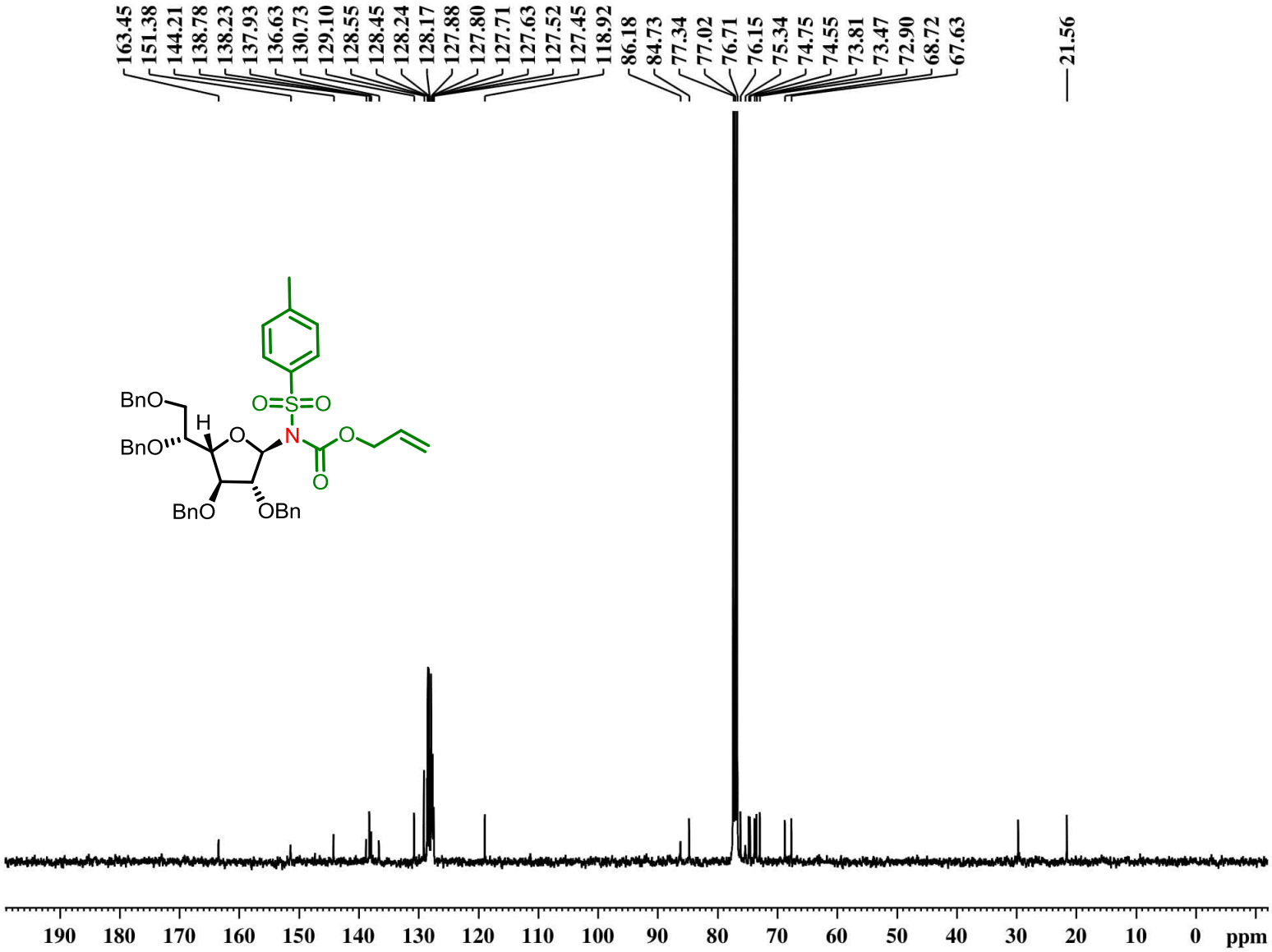


Calcd for $C_{45}H_{53}N_2O_{10}S^+$ [M+ NH_4]$^+$: 813.3415, found: 813.3410.

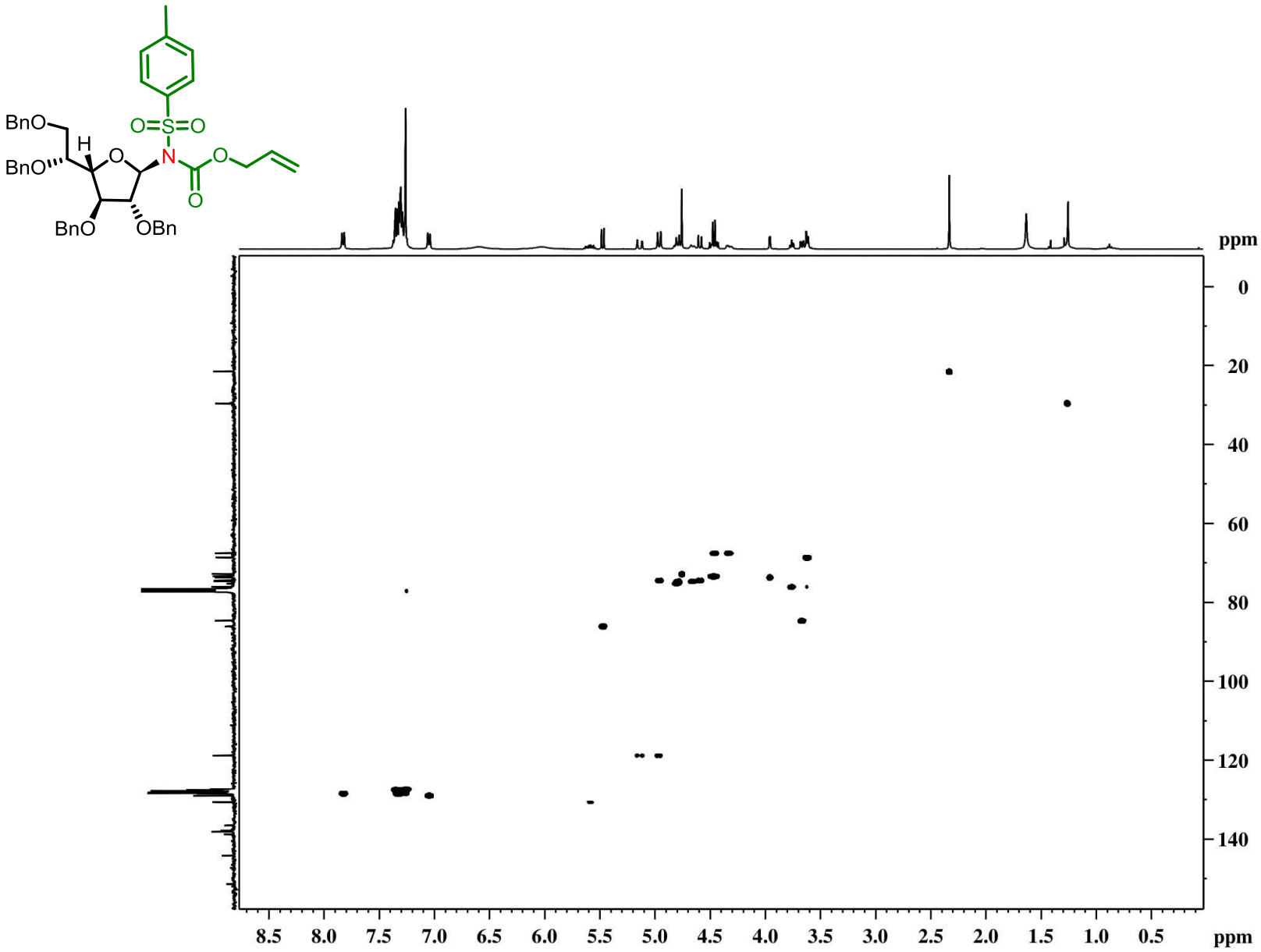
HRMS of **3k**



^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



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

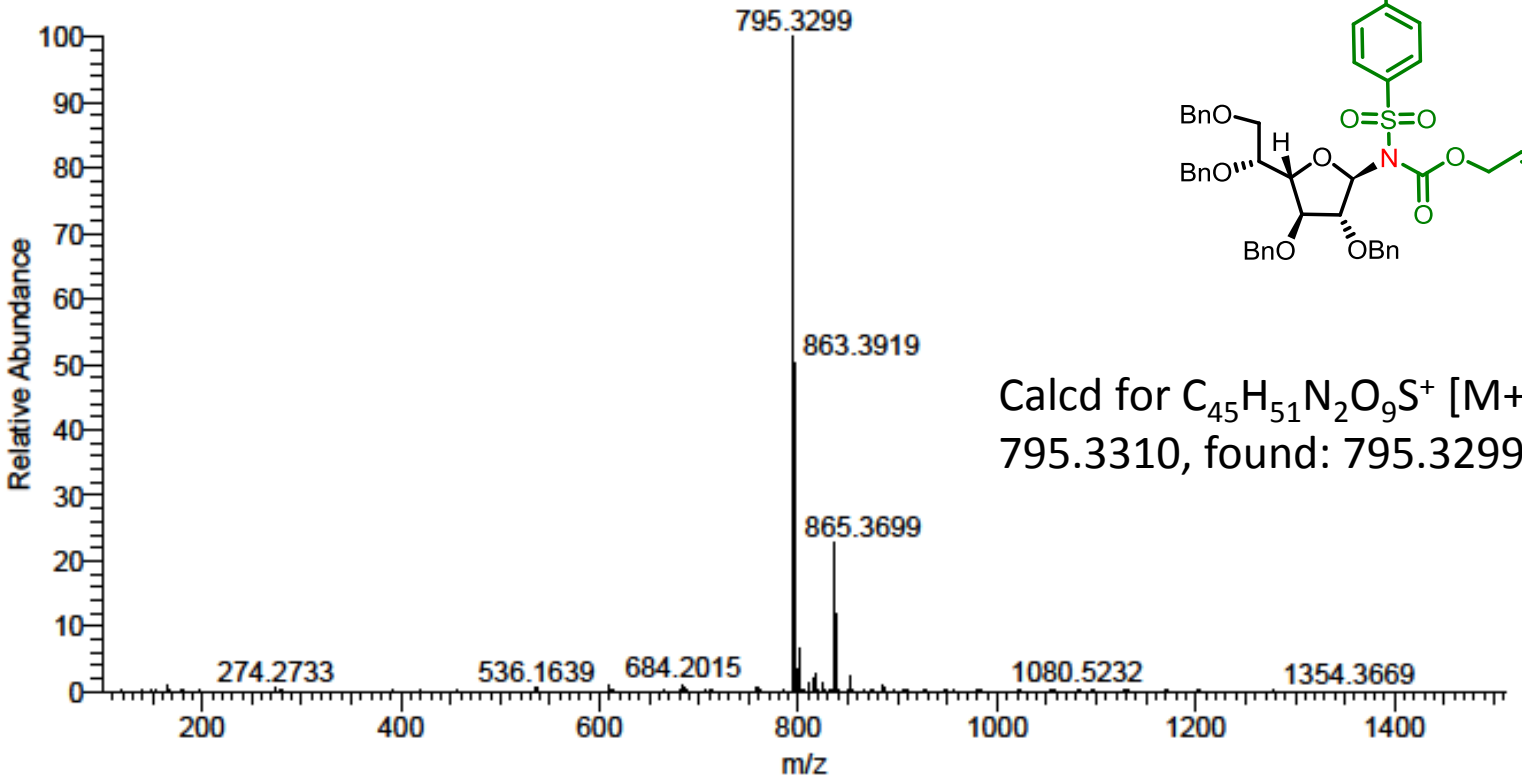


2D HSQC spectrum of **3l**($CDCl_3$).

SAIF [HRMS Report]

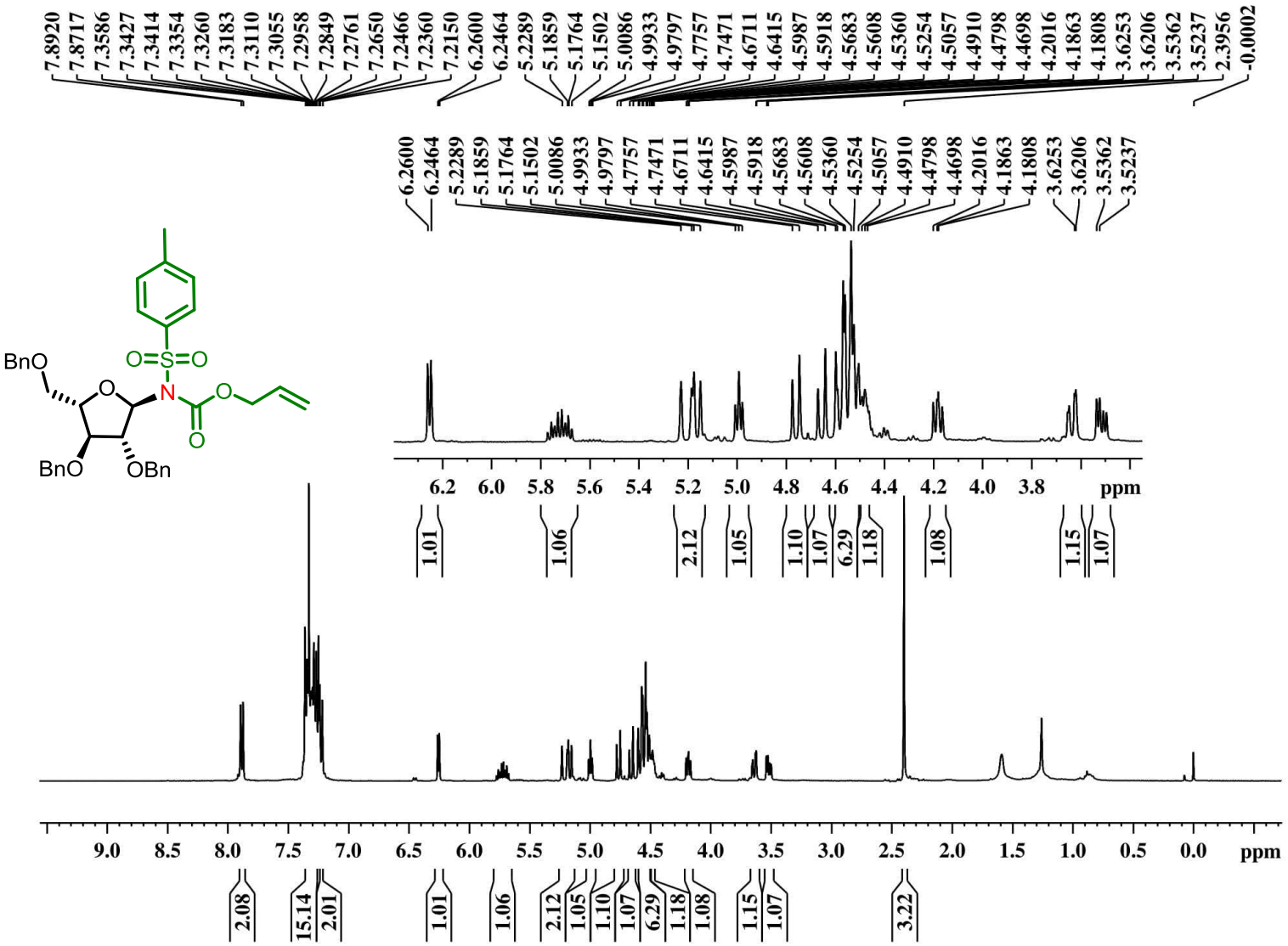
Data File:	HRMS20I30JUN08	Original Data Path:	D:\INTERNAL NEW\2020\June 2020
Sample ID:	PKM-TGA-01	Sample Name:	
Acquisition Date:	06/30/20 12:09:11 PM	Run Time(min):	0.00
Vial:	CStk1-01:8	Injection Volume(µl):	1.00

HRMS20I30JUN08 #12-25 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 5.87E6
T: FTMS + p ESI Full ms [100.00-1500.00]

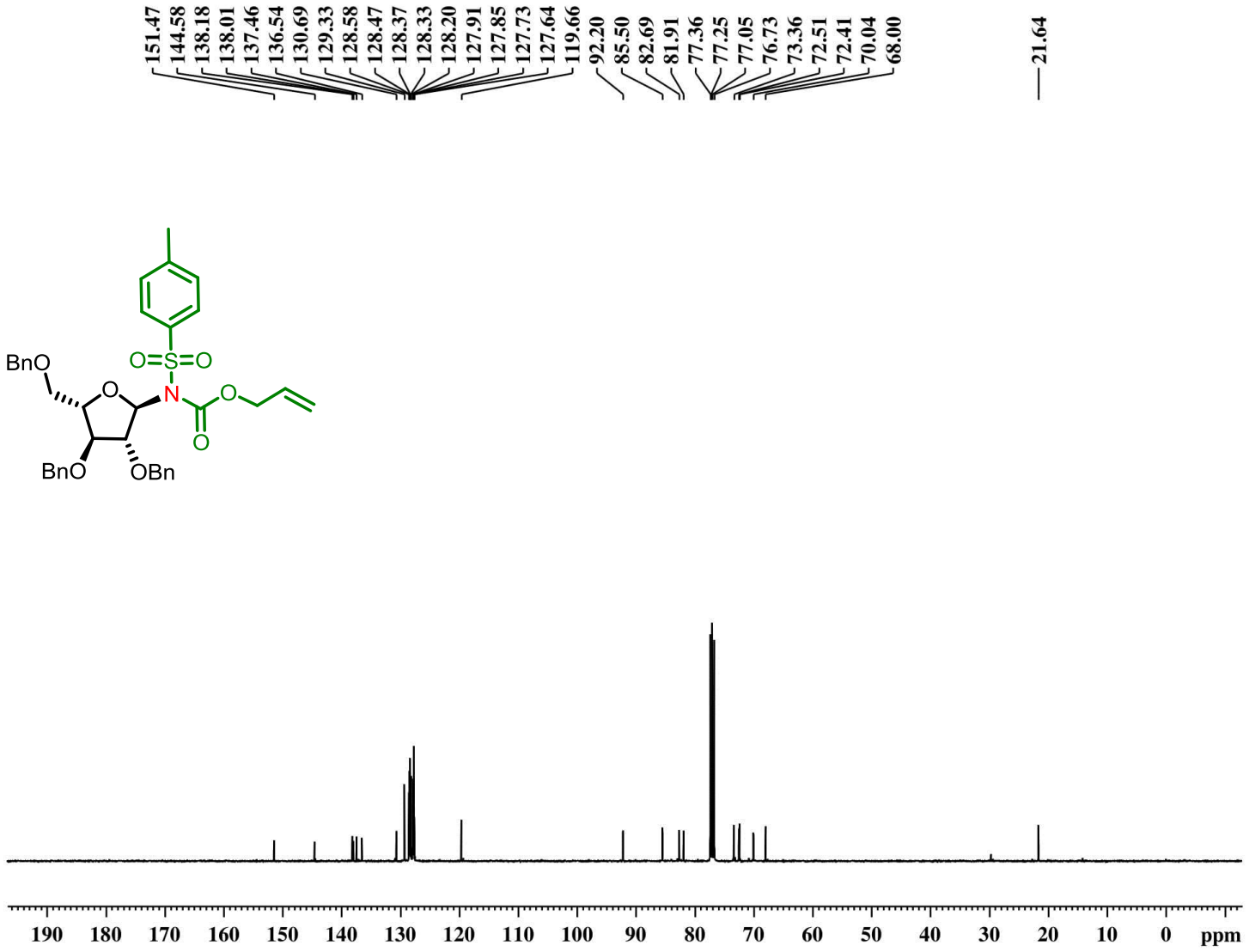


Calcd for $C_{45}H_{51}N_2O_9S^+$ $[M+ NH_4]^+$: 795.3310, found: 795.3299.

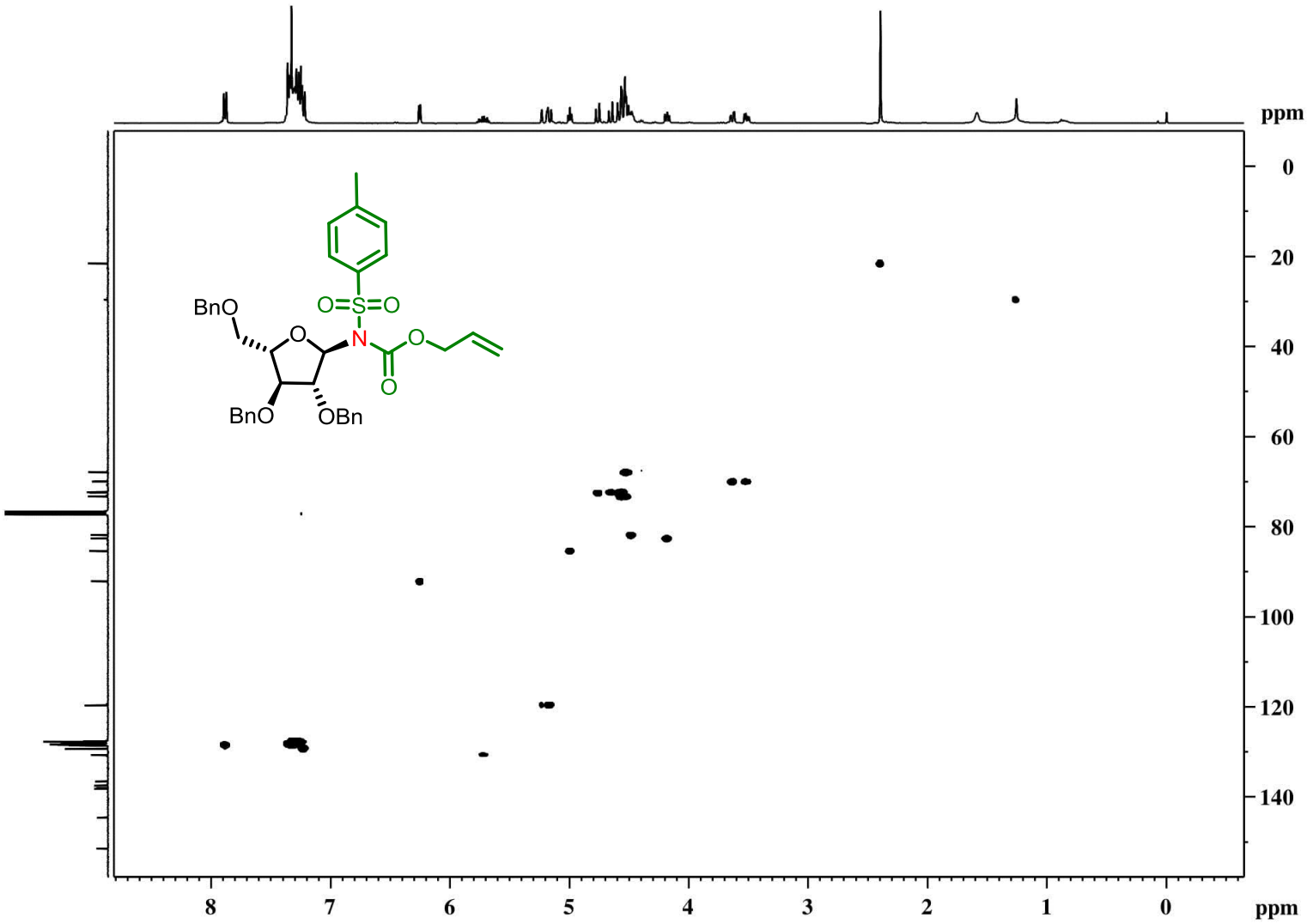
HRMS of **3l**



^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



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

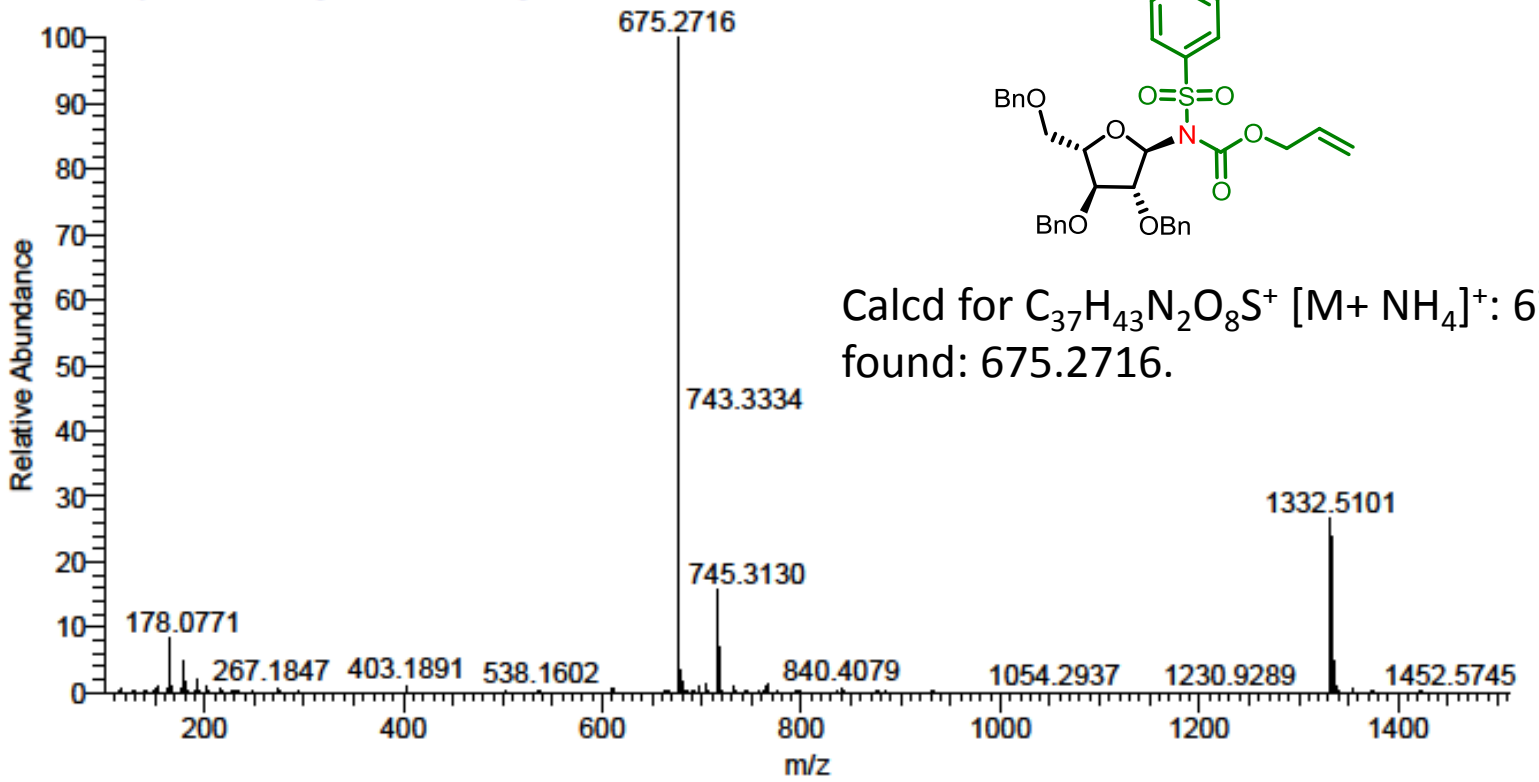


2D HSQC spectrum of **3m** ($CDCl_3$).

SAIF [HRMS Report]

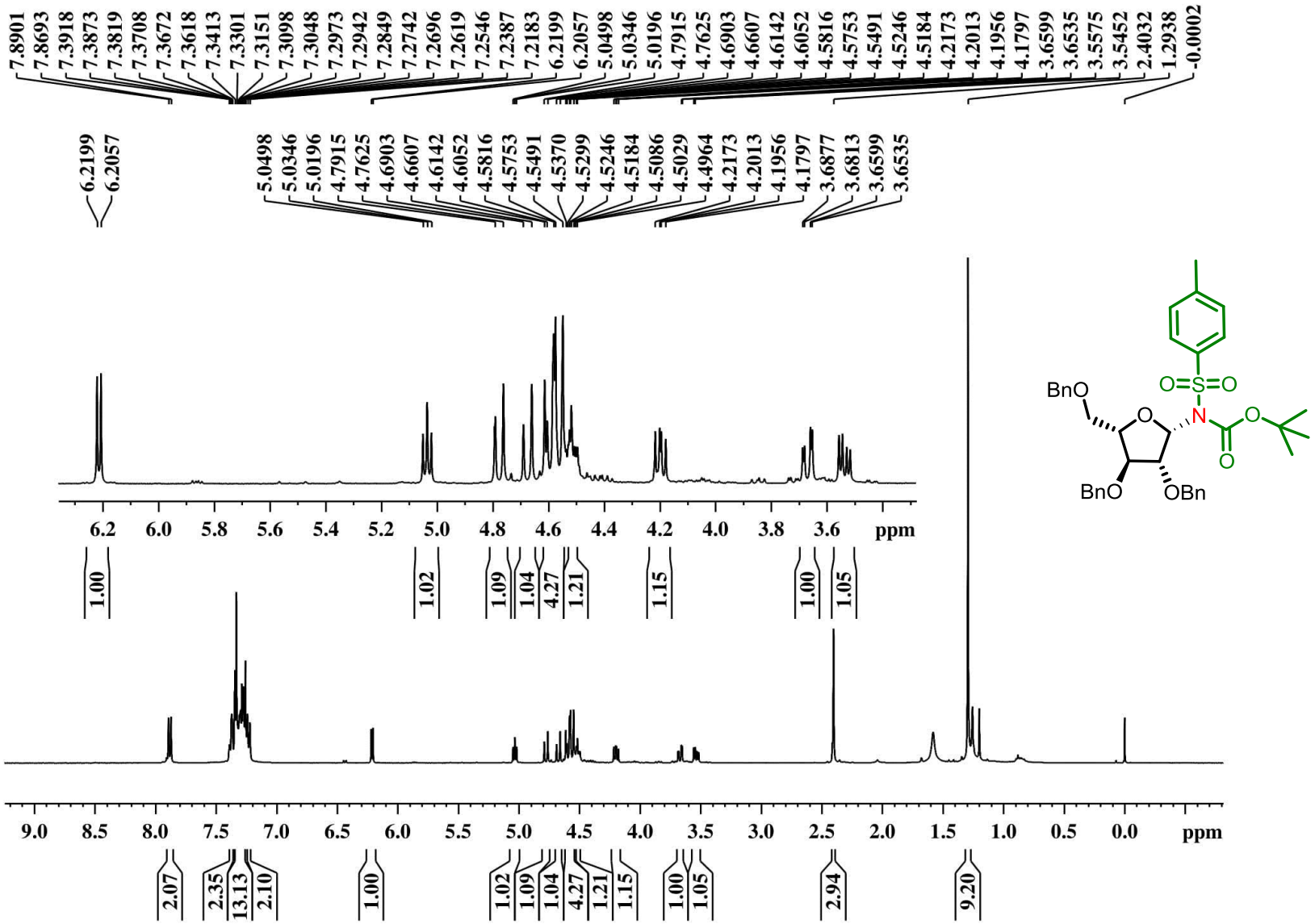
Data File:	HRMS20I06OCT15	Original Data Path:	D:\INTERNAL NEW\2020\OCT 2020
Sample ID:	PKM-LAf-03	Sample Name:	
Acquisition Date:	10/06/20 11:46:48 AM	Run Time(min):	0.00
Vial:	CStk1-01:15	Injection Volume(µl):	1.00

HRMS20I06OCT15 #12-25 RT: 0.12-0.21 AV: 14 SB: 1 0.01 NL: 2.02E7
T: FTMS + p ESI Full ms [100.00-1500.00]

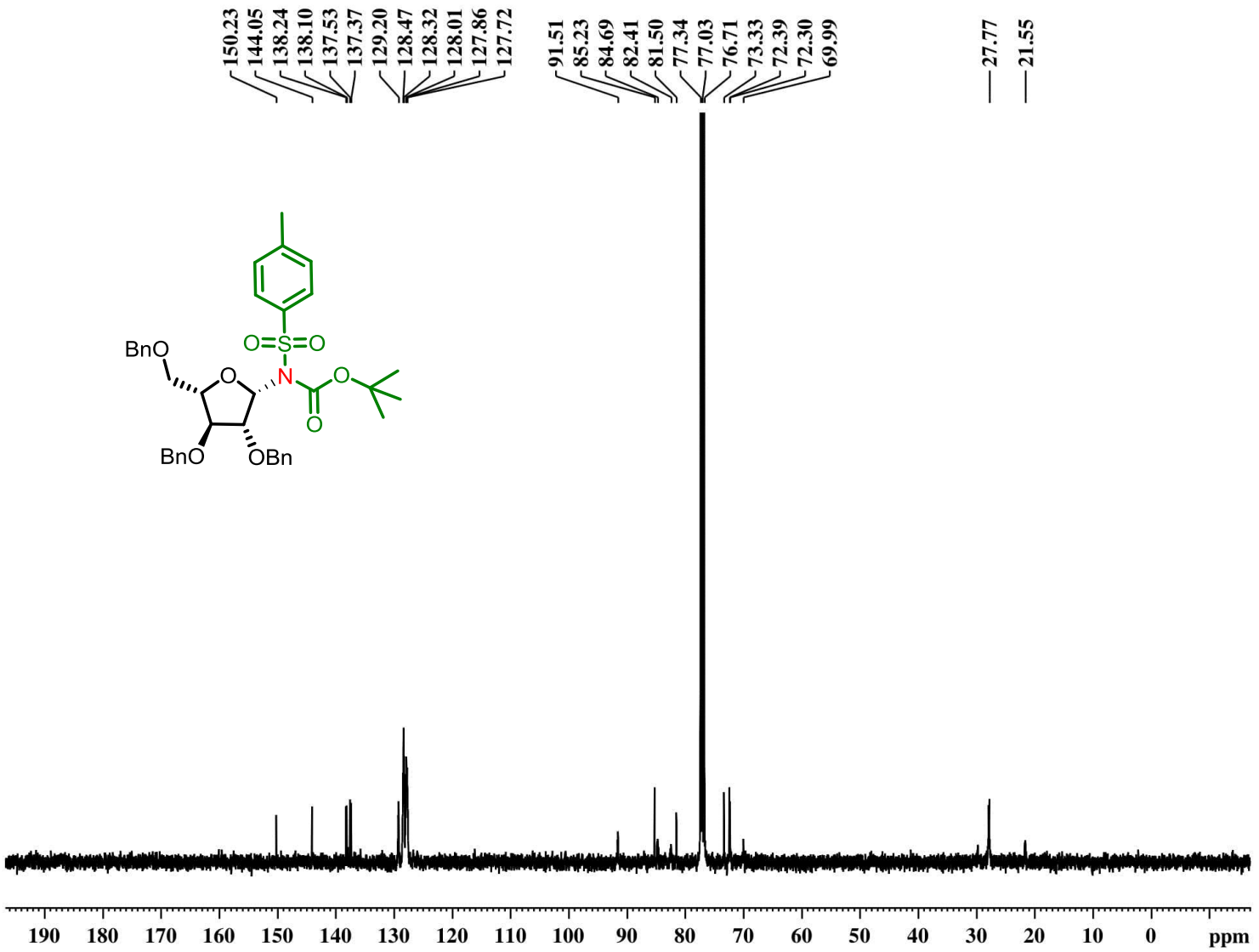


Calcd for $C_{37}H_{43}N_2O_8S^+$ [M+ NH_4]$^+$: 675.2735, found: 675.2716.

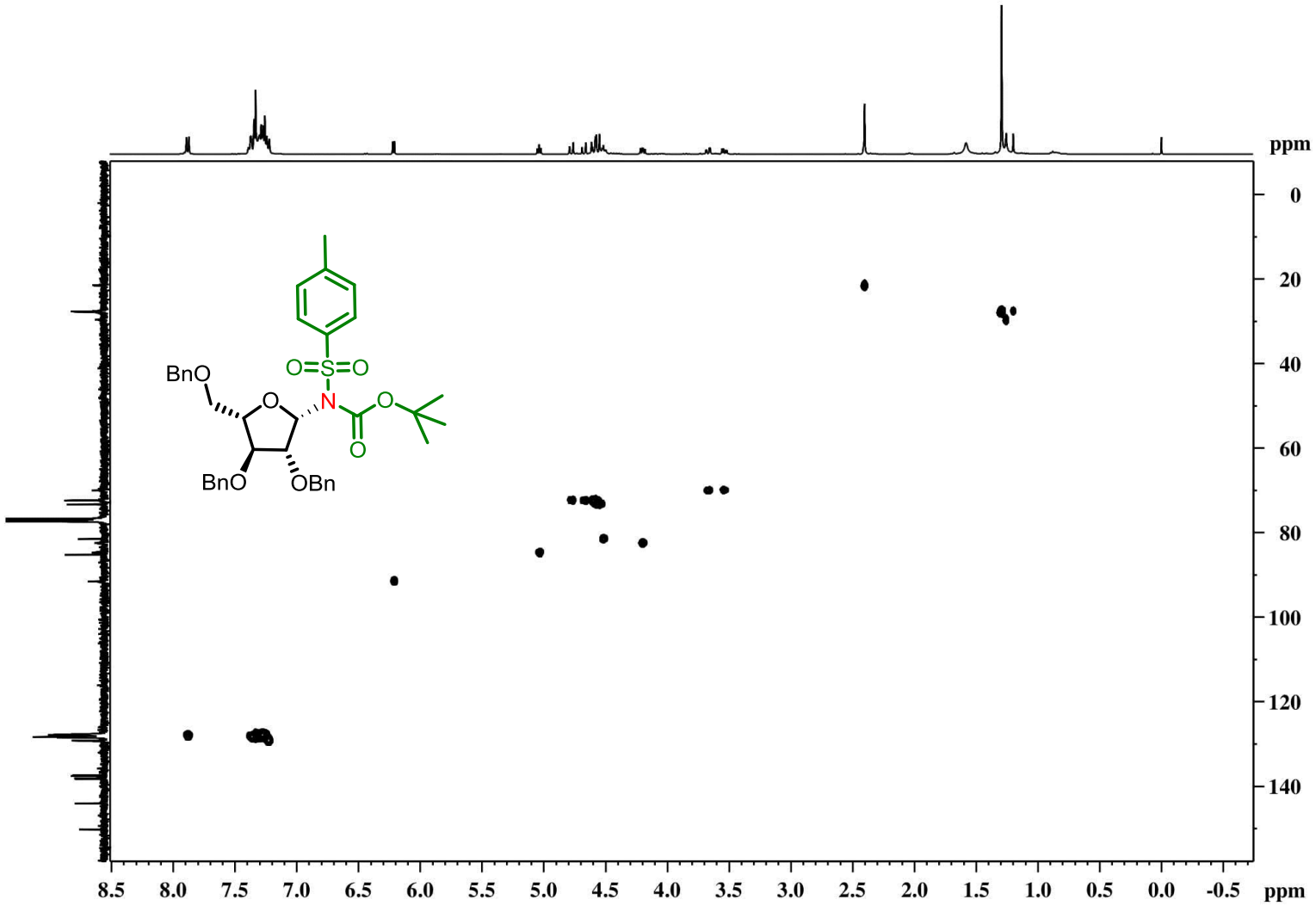
HRMS of **3m**



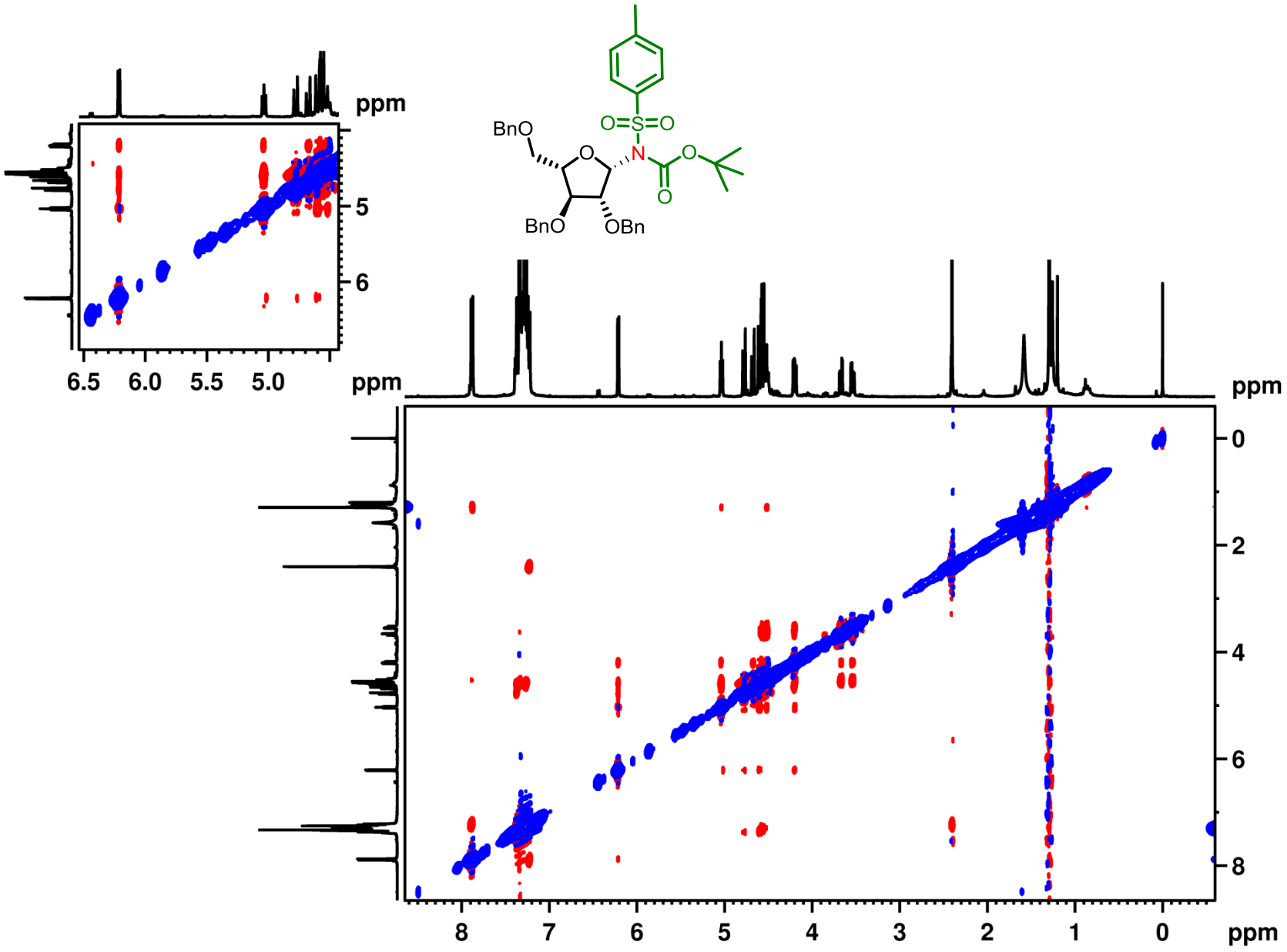
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



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



2D HSQC spectrum of **3n**($CDCl_3$).

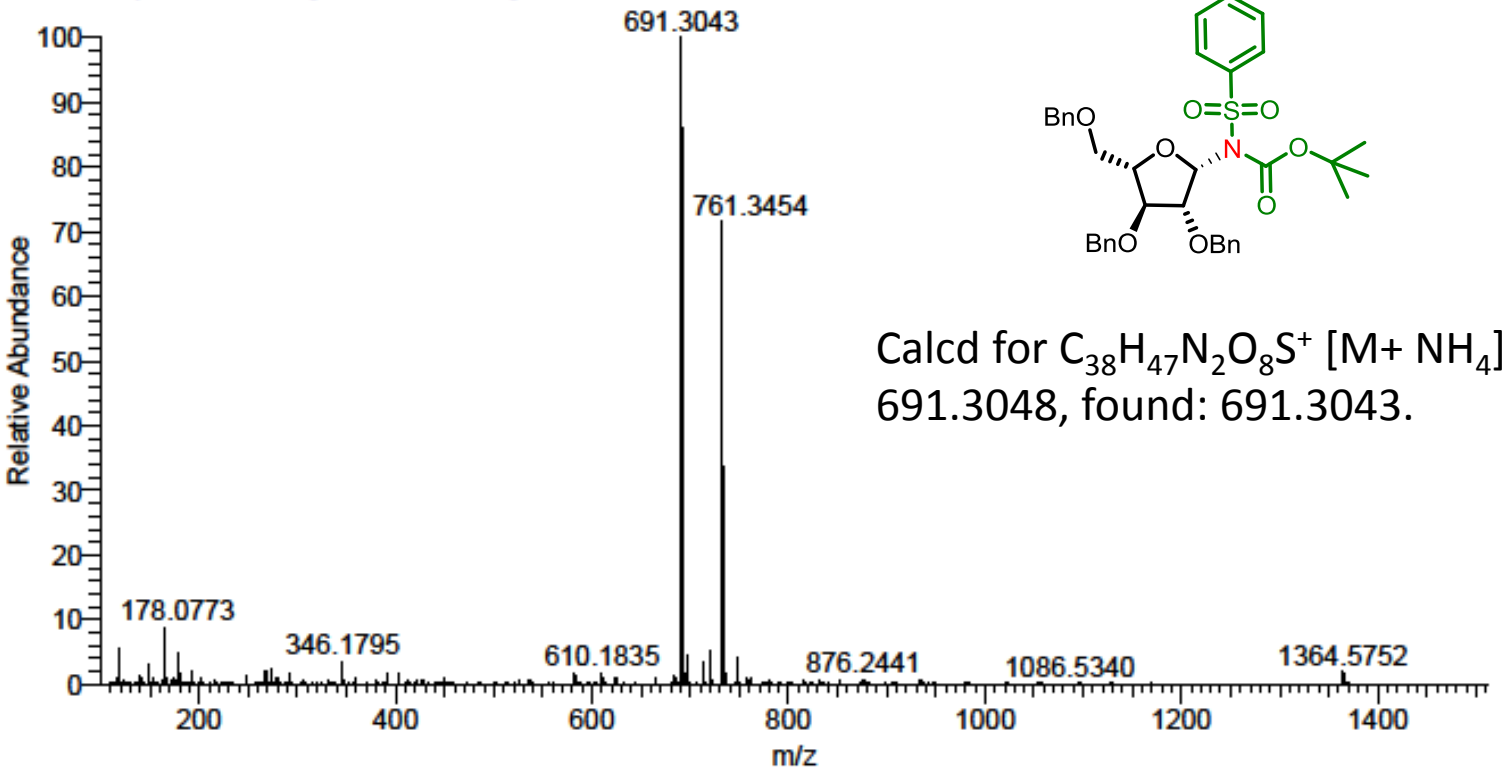


2D NOESY spectrum of **3n** ($CDCl_3$).

SAIF [HRMS Report]

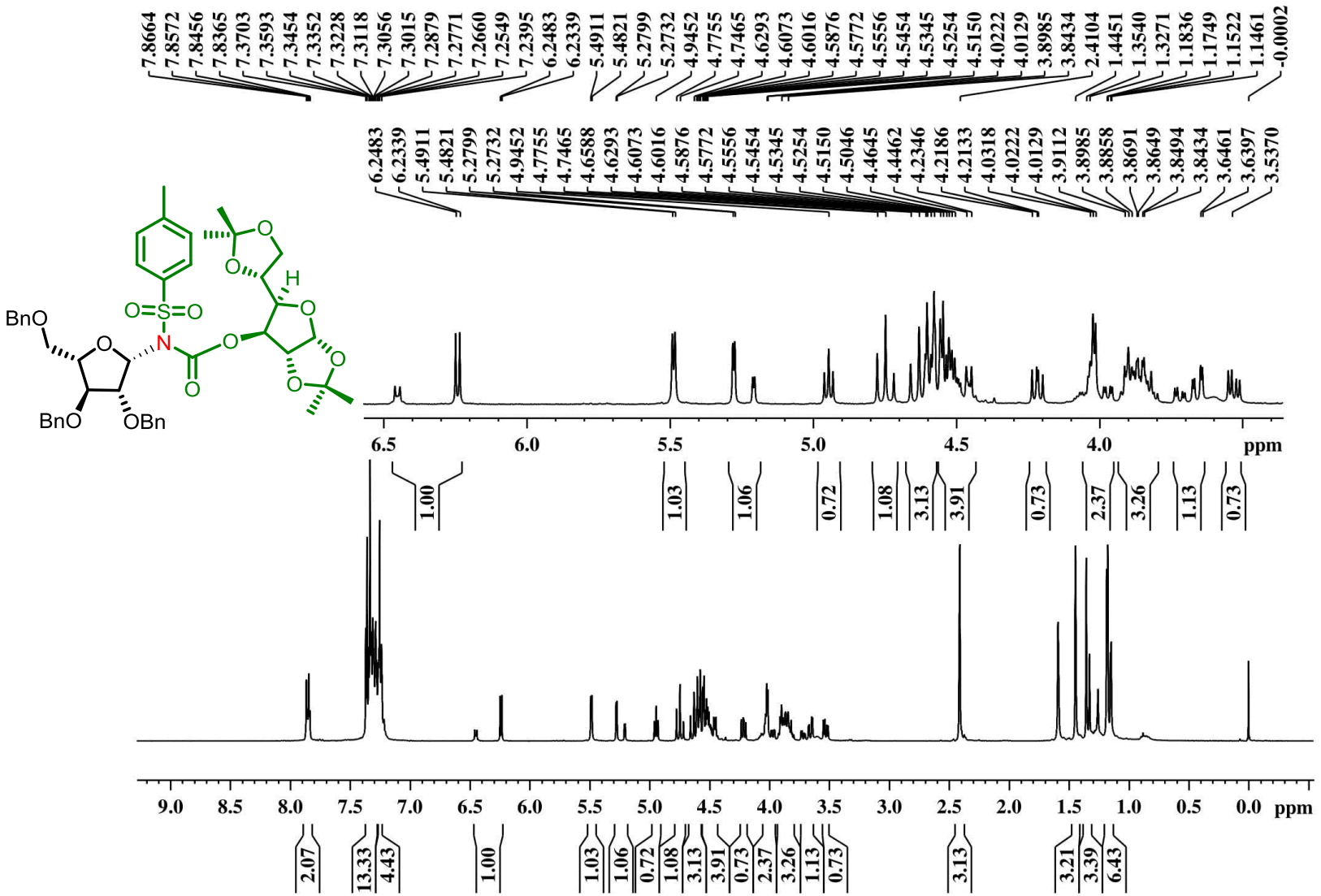
Data File:	HRMS20I05OCT36	Original Data Path:	D:\INTERNAL NEW\2020\OCT 2020
Sample ID:	PKM-LAf-02	Sample Name:	
Acquisition Date:	10/05/20 03:54:02 PM	Run Time(min):	0.00
Vial:	CStk1-01:36	Injection Volume(µl):	1.00

HRMS20I05OCT36 #12-23 RT: 0.11-0.21 AV: 12 SB: 1 0.01 NL: 1.09E6
T: FTMS + p ESI Full ms [100.00-1500.00]

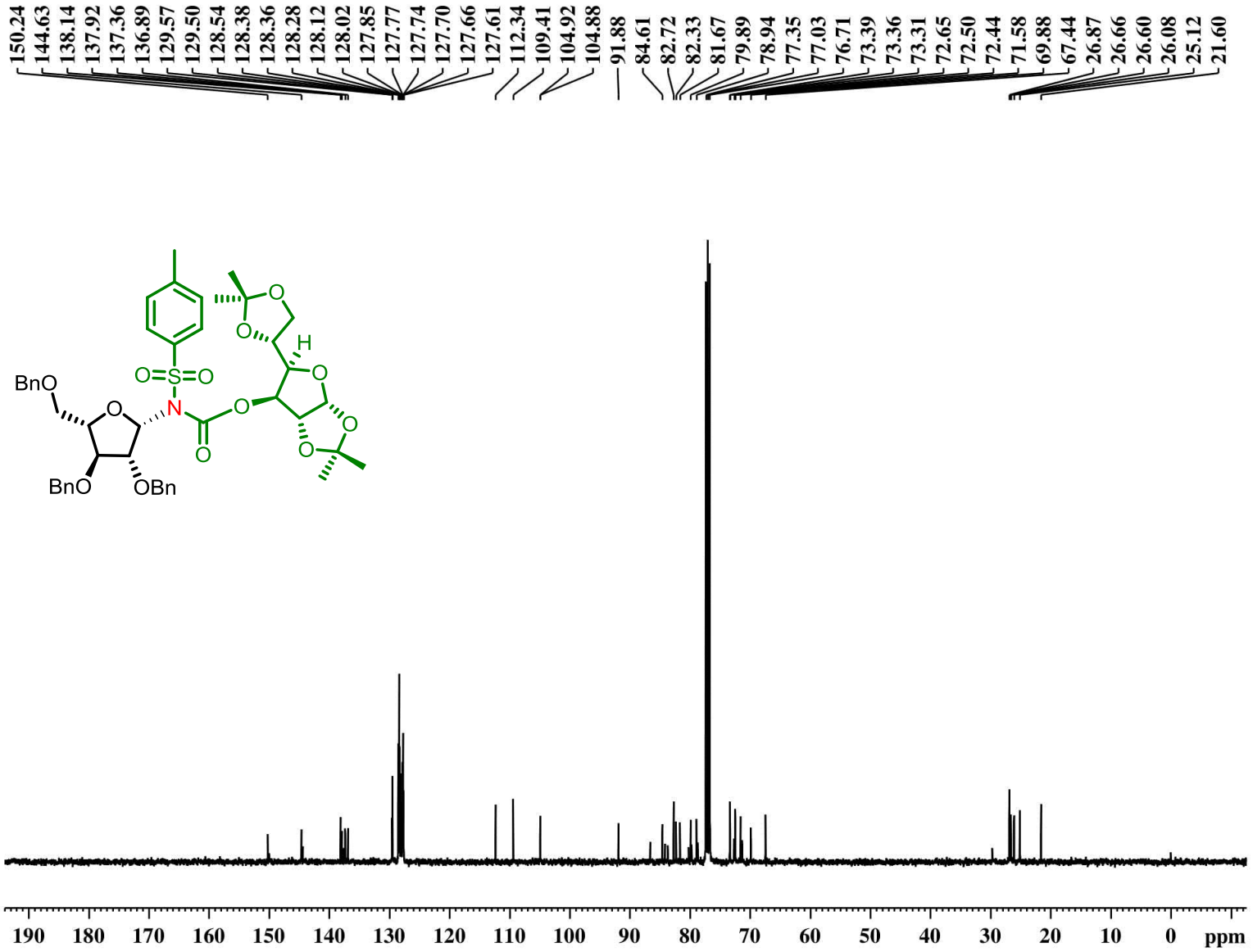


Calcd for $C_{38}H_{47}N_2O_8S^+$ $[M+ NH_4]^+$: 691.3048, found: 691.3043.

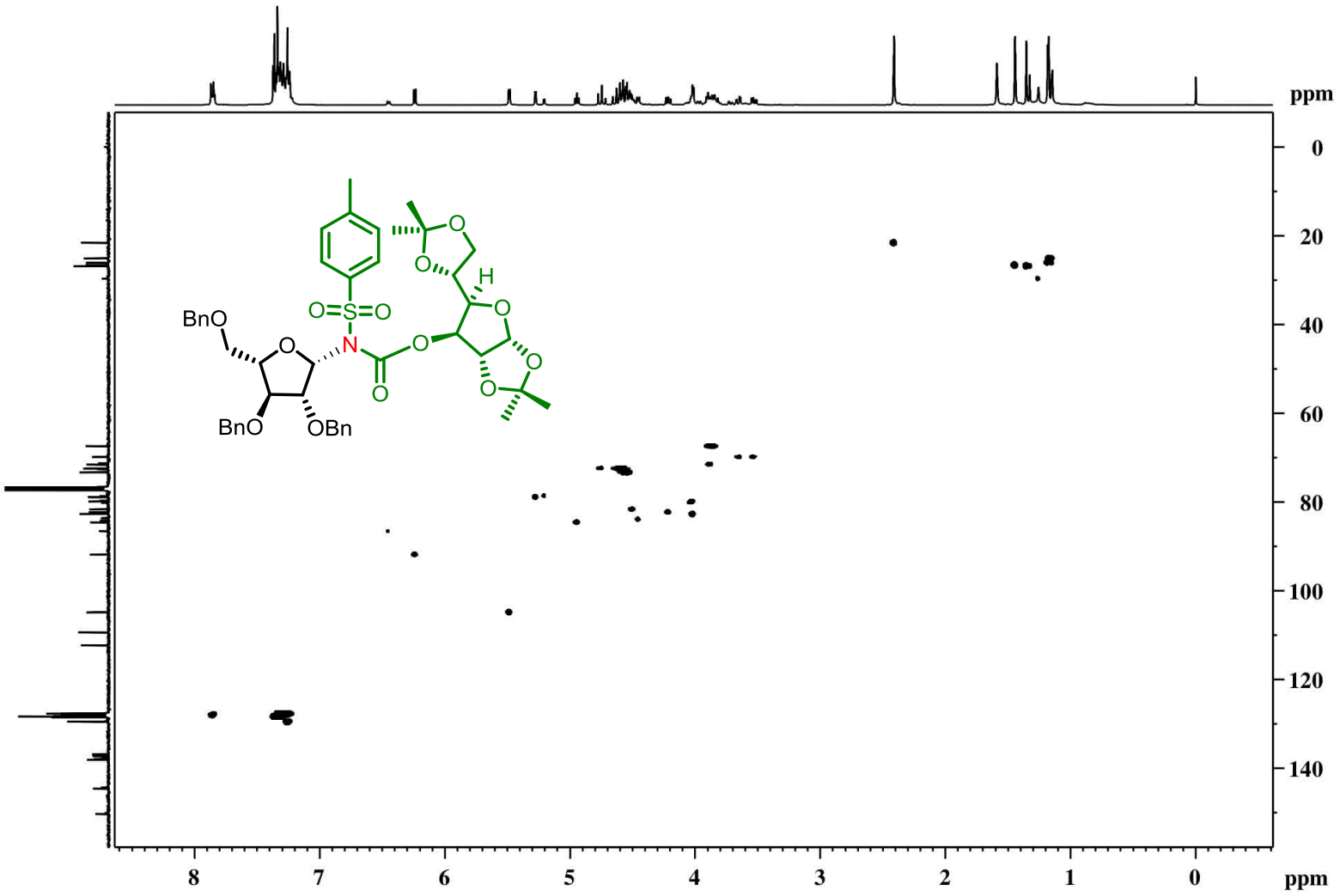
HRMS of **3n**



^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



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

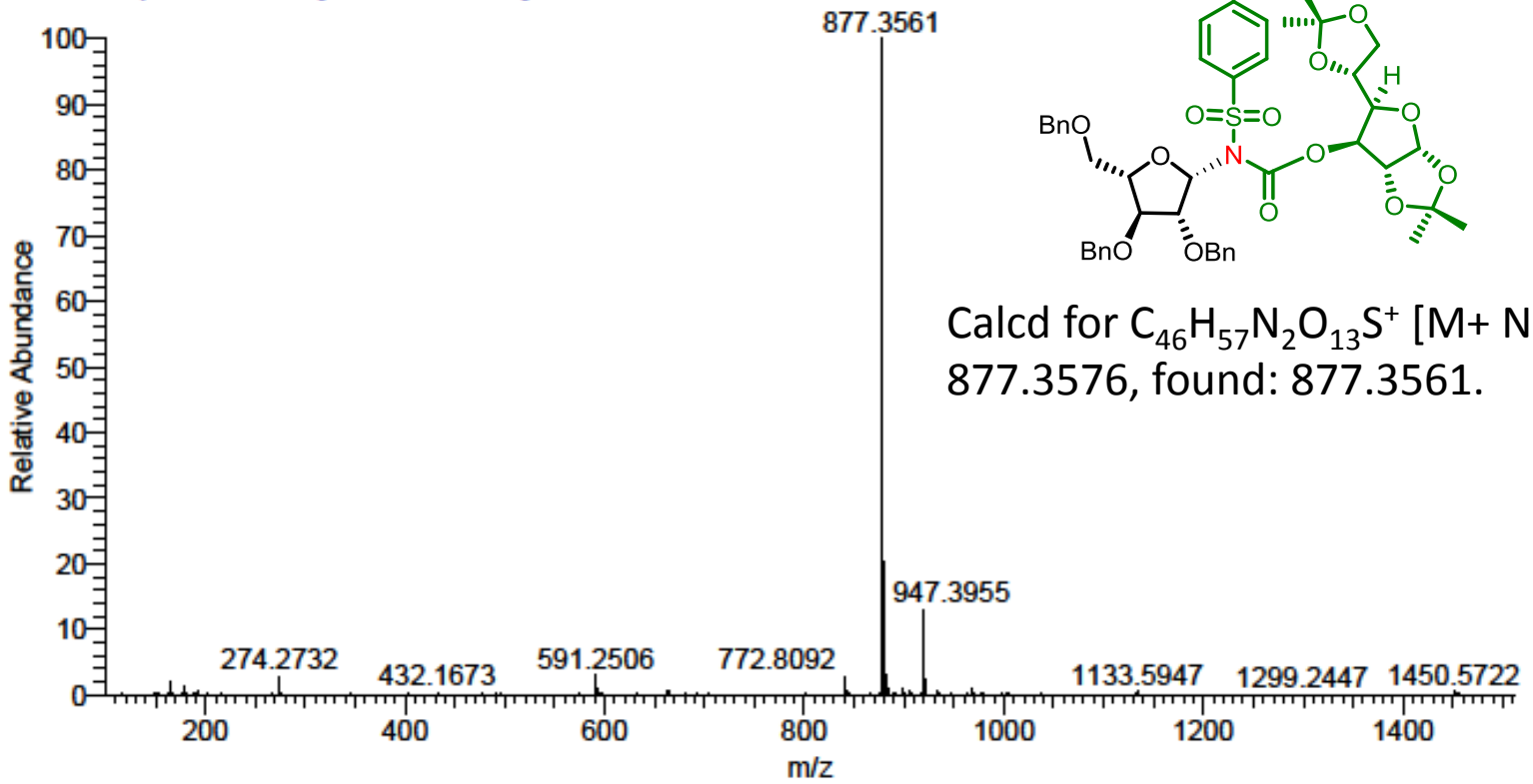


2D HSQC spectrum of **3o** ($CDCl_3$).

SAIF [HRMS Report]

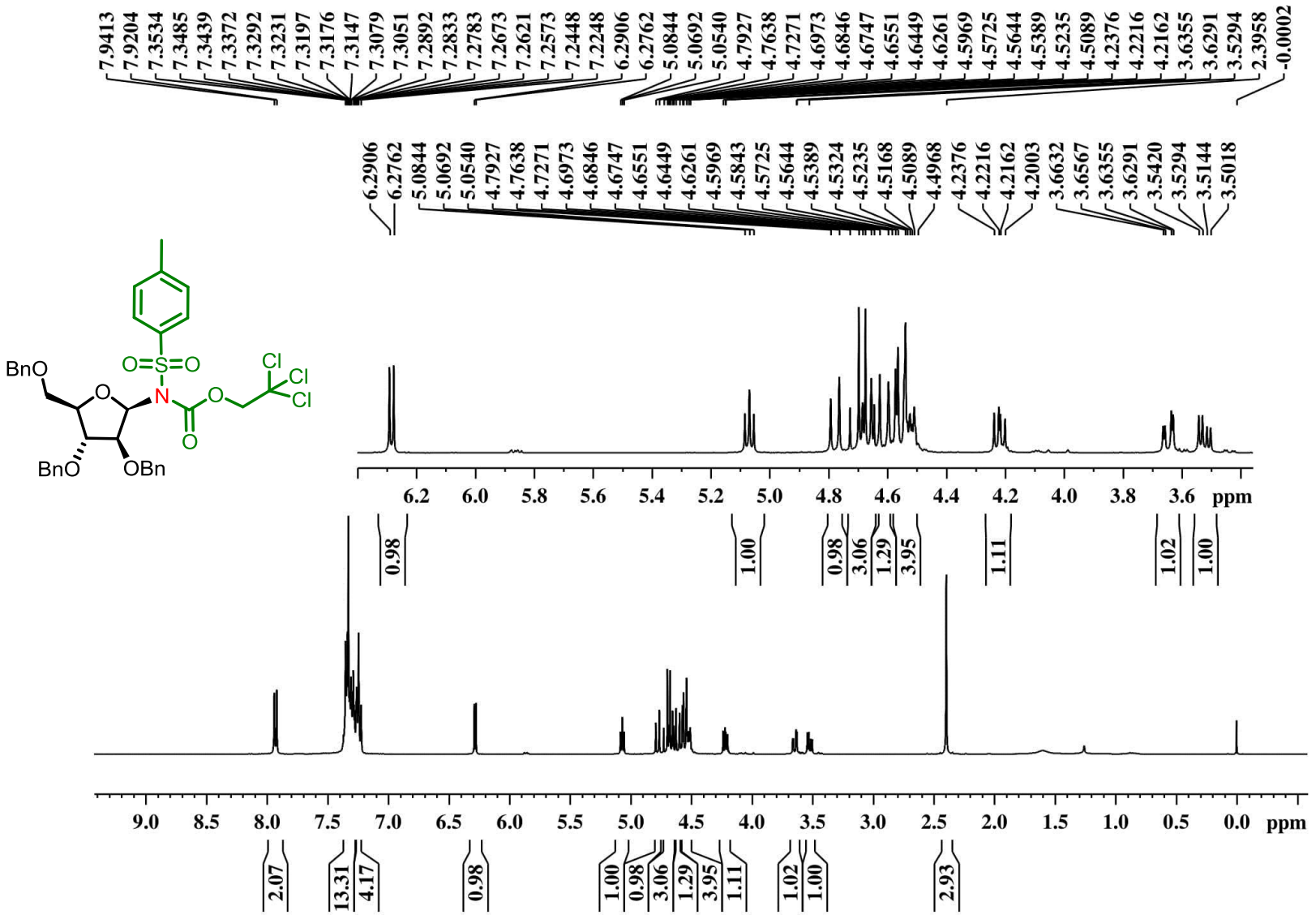
Data File:	HRMS20I06OCT14	Original Data Path:	D:\INTERNAL NEW\2020\OCT 2020
Sample ID:	PKM-LAf-04	Sample Name:	
Acquisition Date:	10/06/20 11:44:49 AM	Run Time(min):	0.00
Vial:	CStk1-01:14	Injection Volume(µl):	1.00

HRMS20I06OCT14 #11-24 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 1.63E7
T: FTMS + p ESI Full ms [100.00-1500.00]

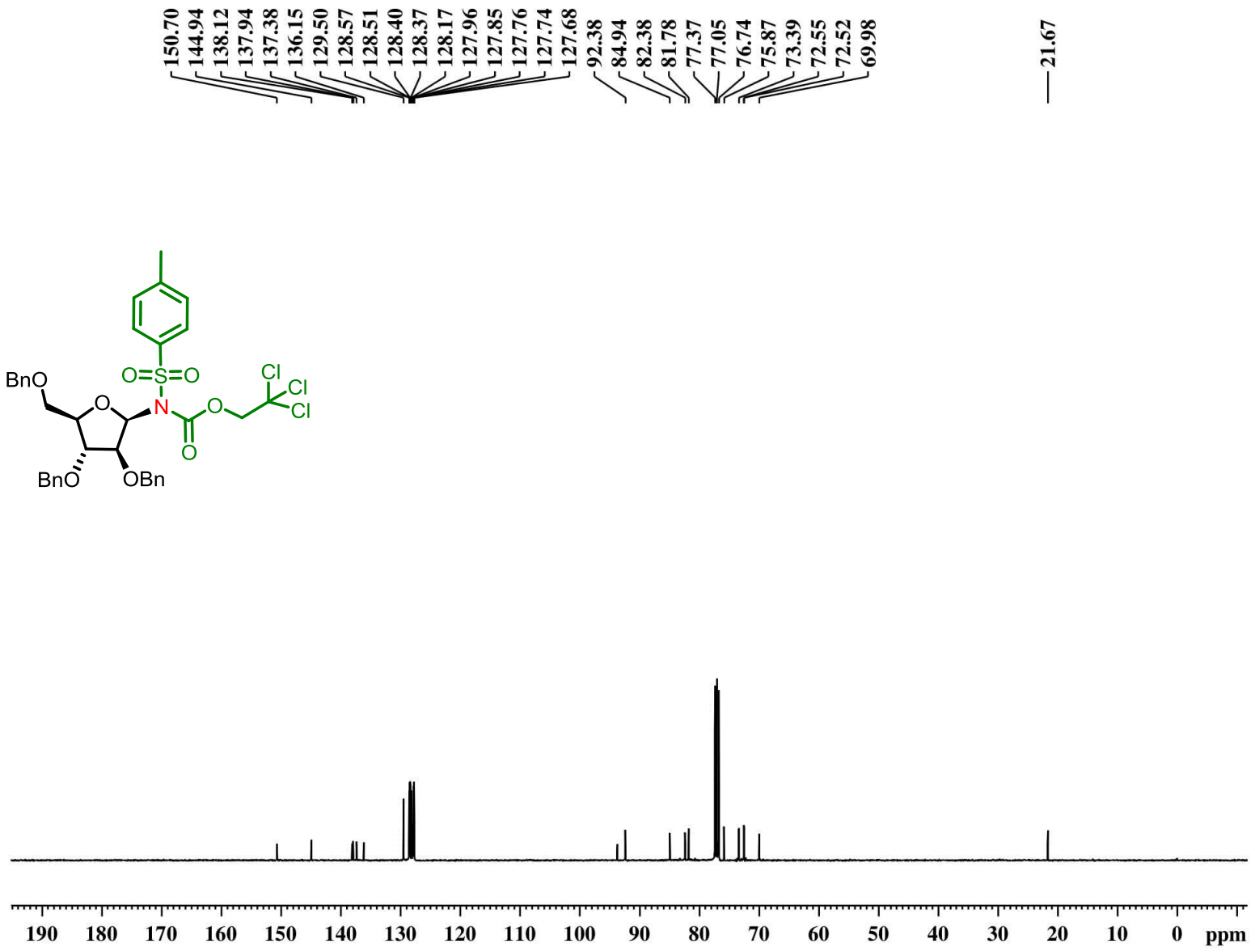


Calcd for $C_{46}H_{57}N_2O_{13}S^+$ $[M+ NH_4]^+$: 877.3576, found: 877.3561.

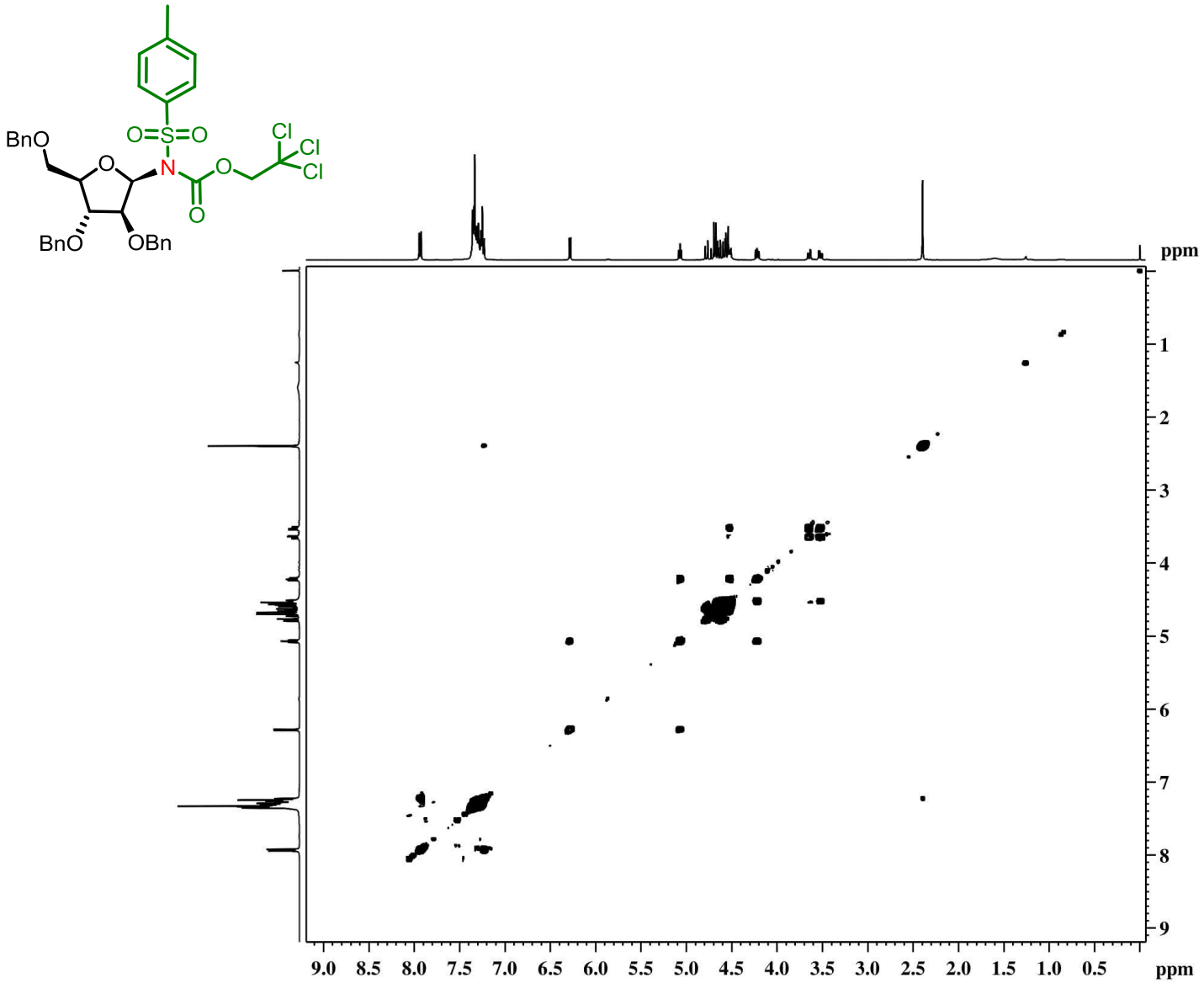
HRMS of **3o**



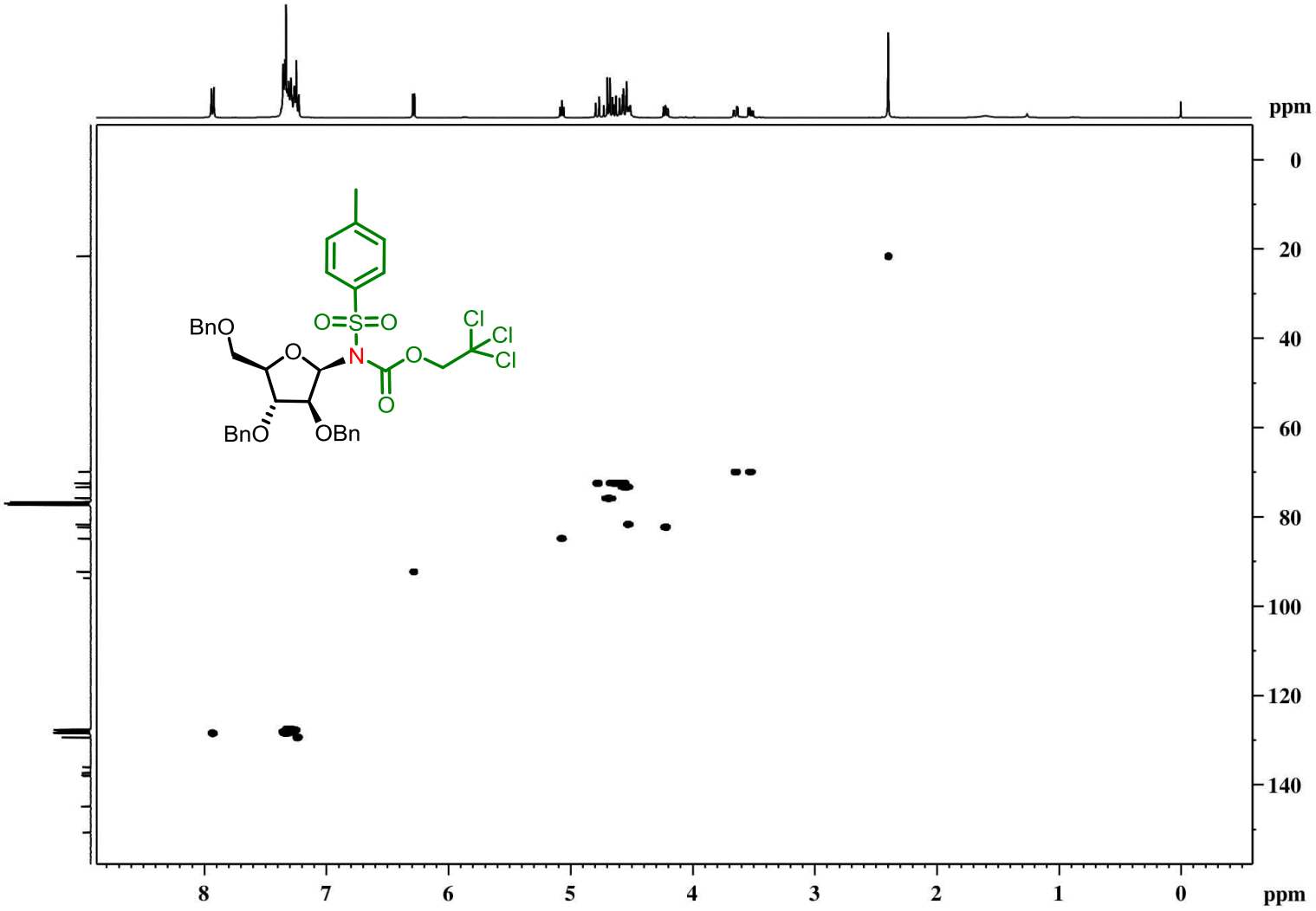
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)



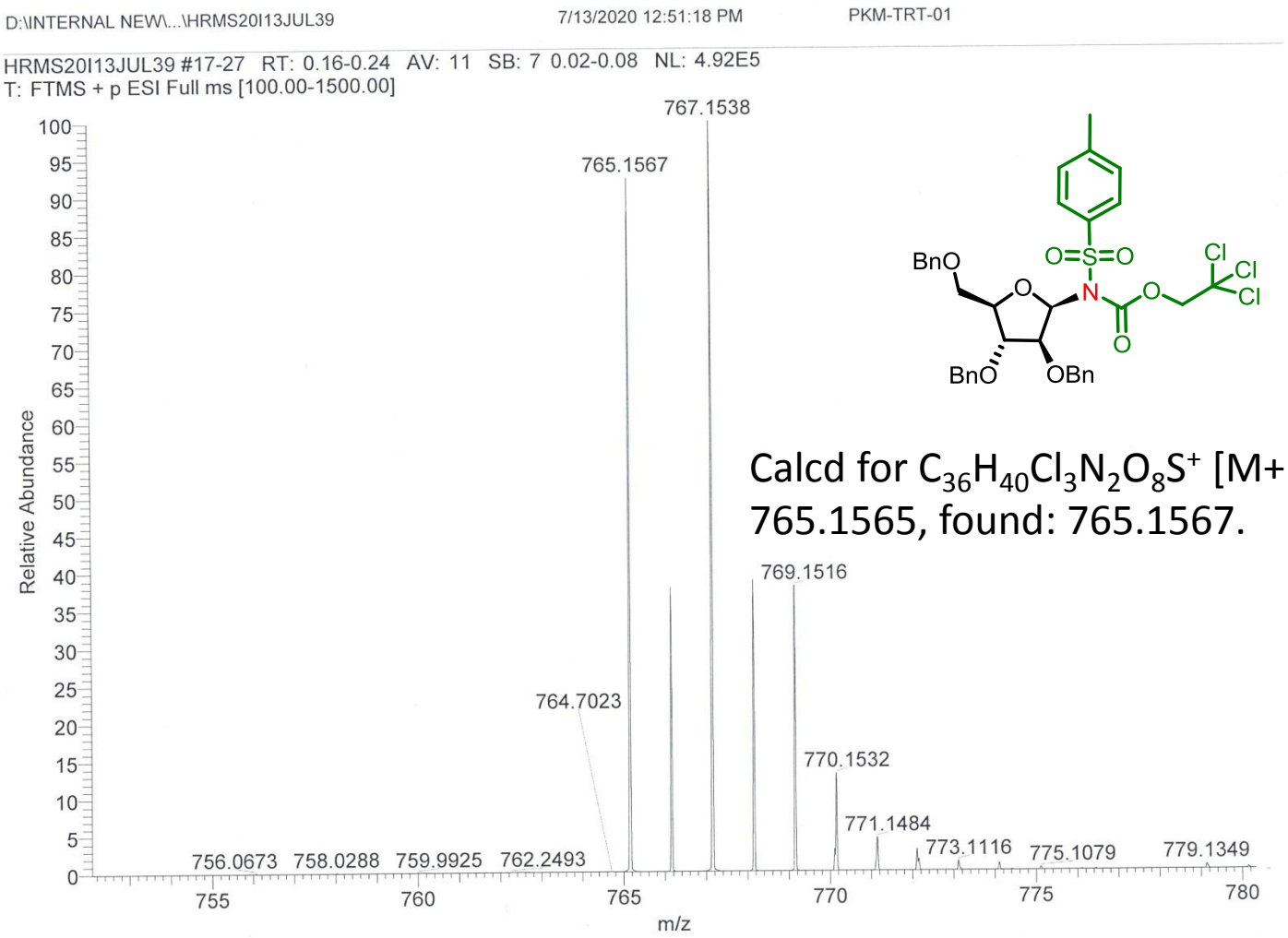
^{13}C NMR spectrum of **3p** (100 MHz, MHz, $CDCl_3$)



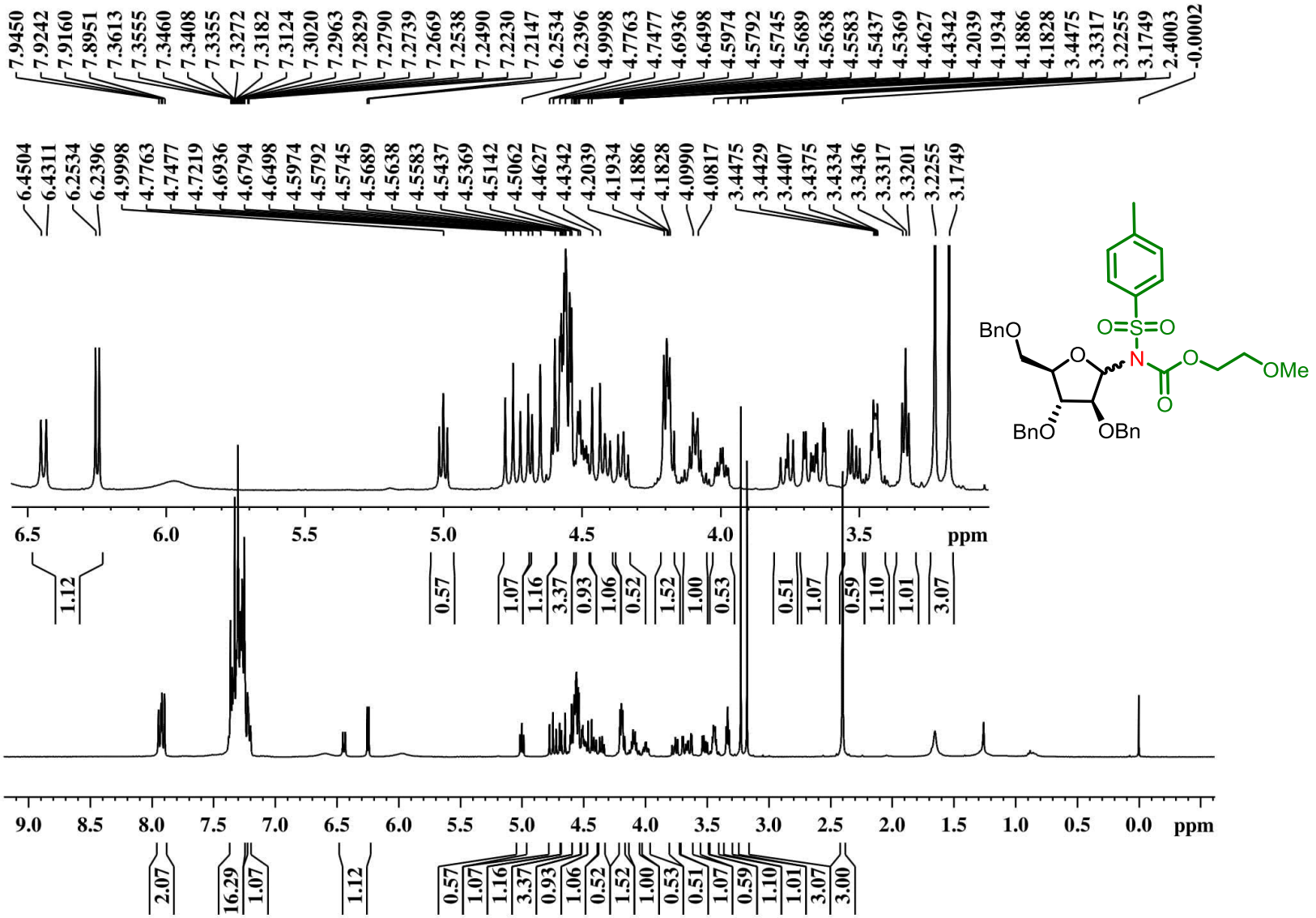
2D COSY spectrum of **3p** ($CDCl_3$).



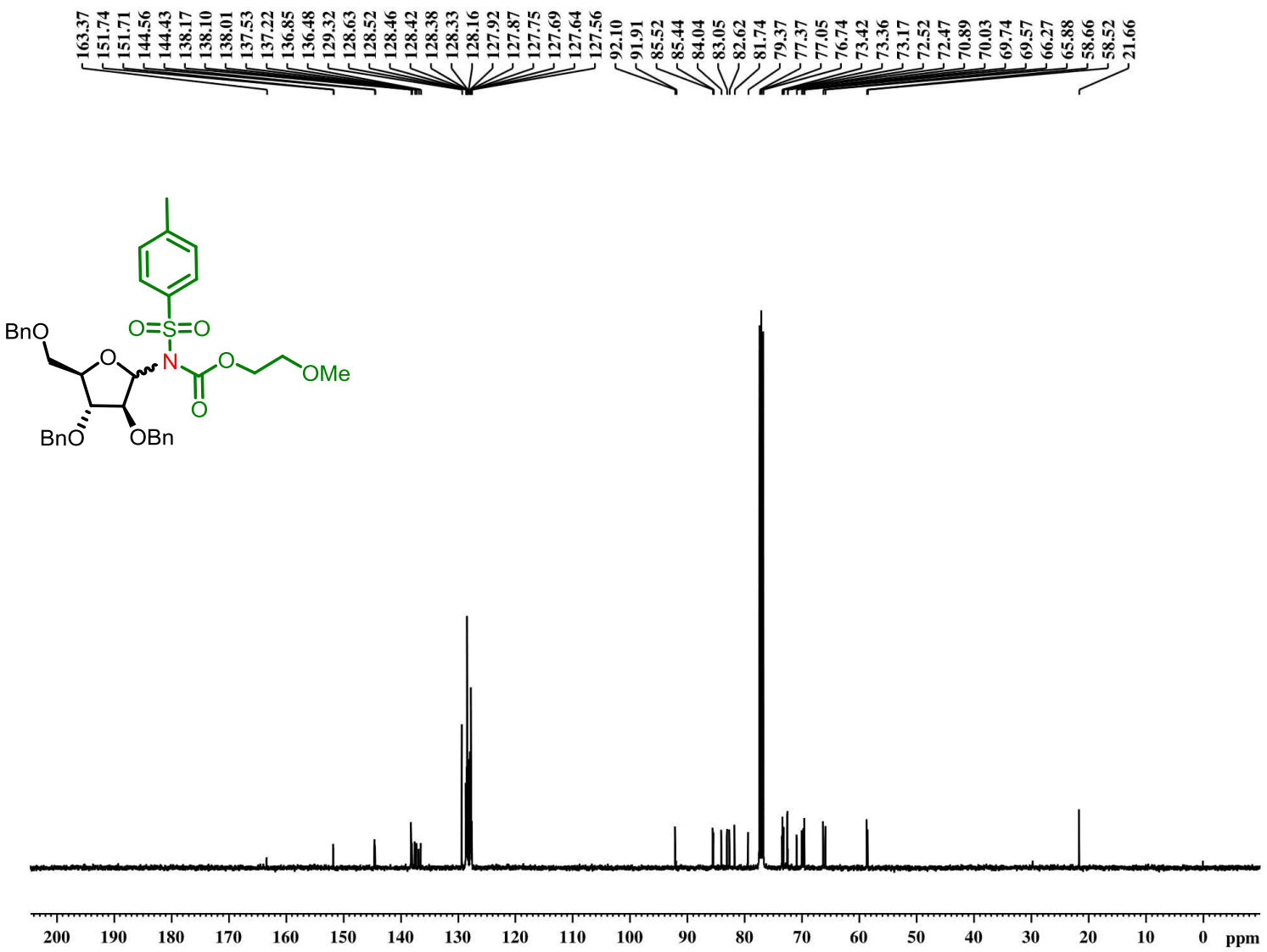
2D HSQC spectrum of **3p** ($CDCl_3$).


D:\INTERNAL NEW\...\HRMS20I13JUL39
7/13/2020 12:51:18 PM
PKM-TRT-01
HRMS20I13JUL39 #17-27 RT: 0.16-0.24 AV: 11 SB: 7 0.02-0.08 NL: 4.92E5
T: FTMS + p ESI Full ms [100.00-1500.00]
767.1538
765.1567
769.1516
764.7023
770.1532
771.1484
773.1116
775.1079
779.1349
756.0673
758.0288
759.9925
762.2493
Relative Abundance
m/z
BnO
O=S=O
Cl
Cl
Cl
N
O
O
BnO
OBn
Calcd for C36H40Cl3N2O8S+ [M+ NH4]+:
765.1565, found: 765.1567.

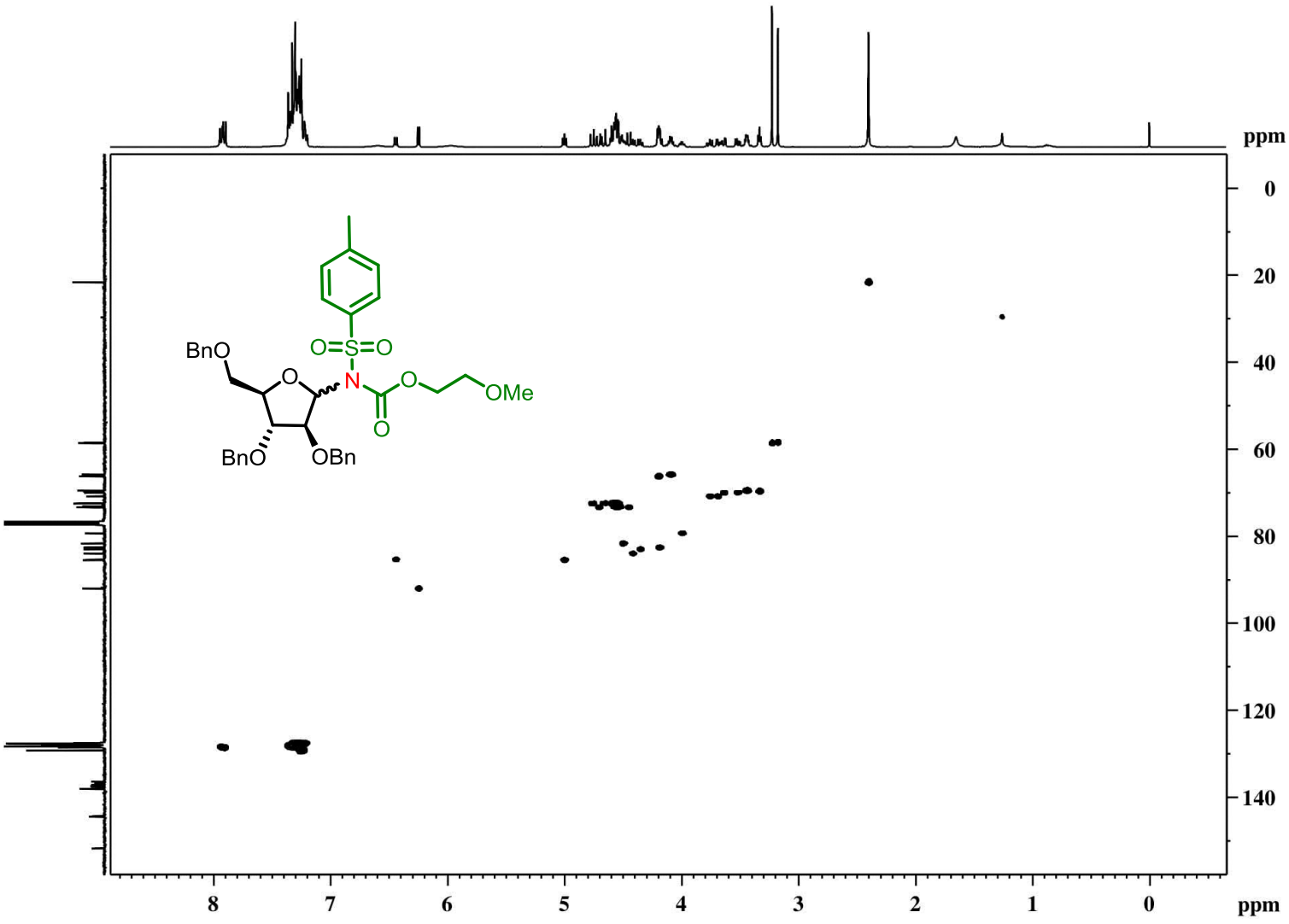
HRMS of **3p**



^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)



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

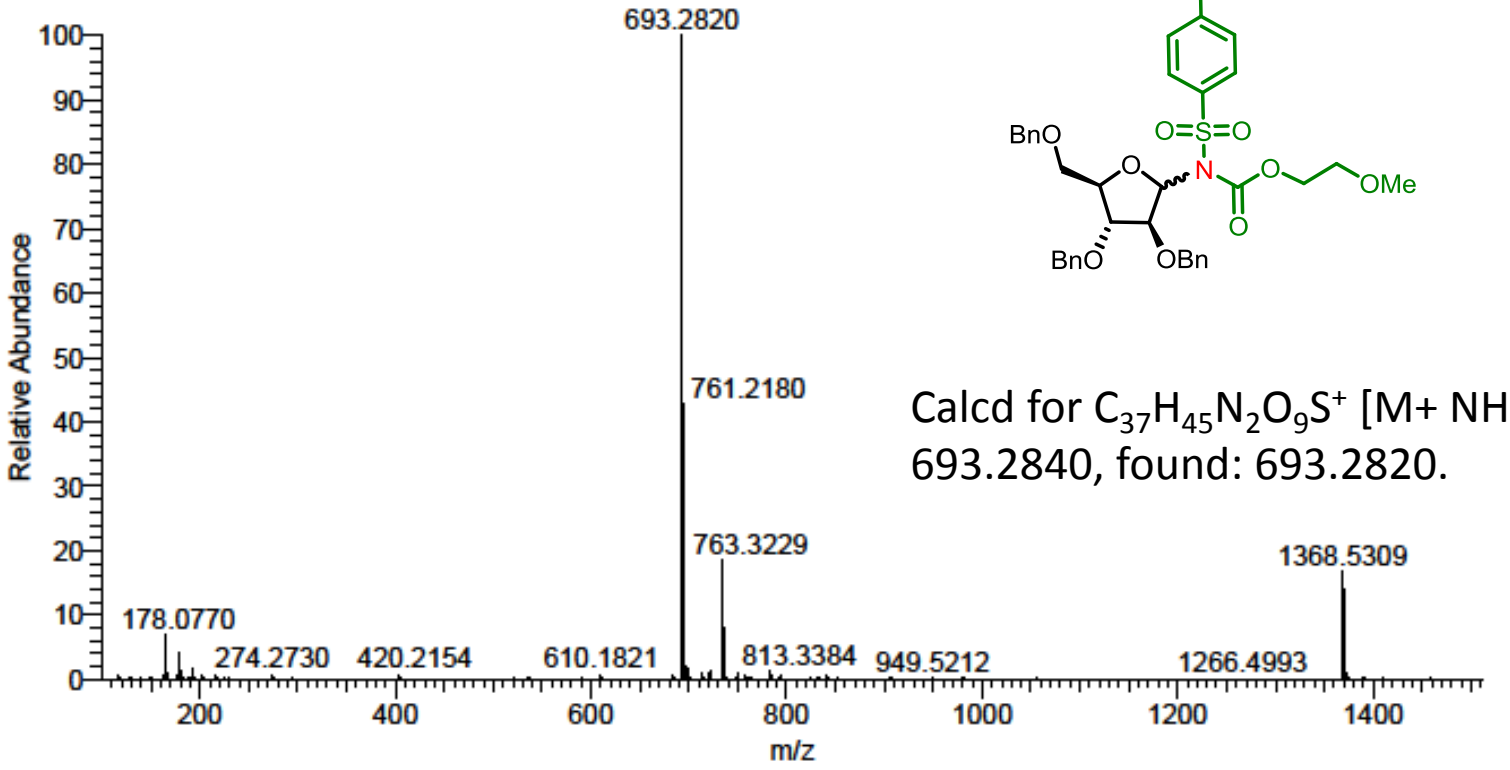


2D HSQC spectrum of **3q** ($CDCl_3$).

SAIF [HRMS Report]

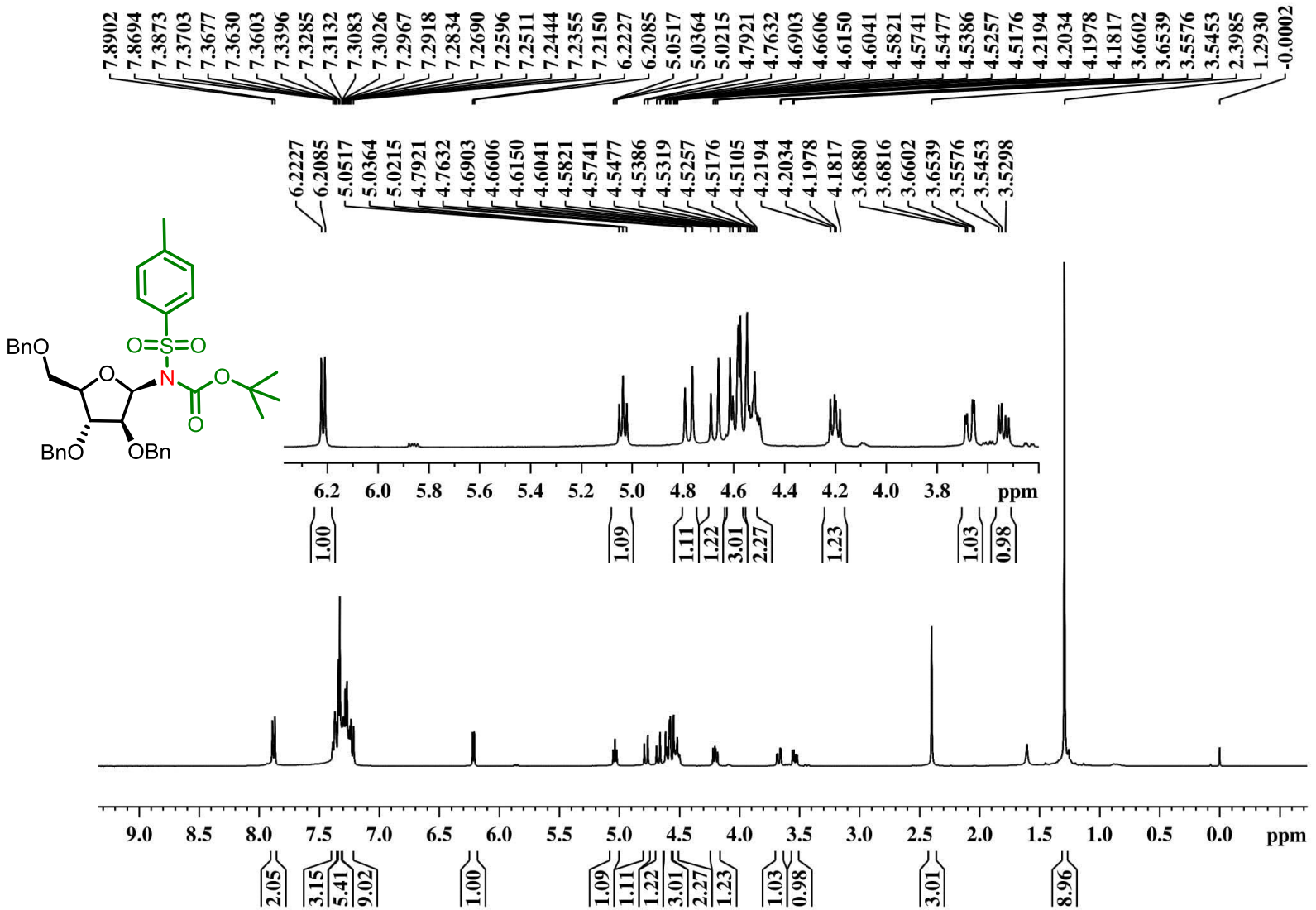
Data File:	HRMS20I14AUG21	Original Data Path:	D:\INTERNAL NEW\2020\Aug 2020
Sample ID:	PKM-Ara-02	Sample Name:	
Acquisition Date:	08/14/20 11:58:42 AM	Run Time(min):	0.00
Vial:	CStk1-01:21	Injection Volume(µl):	1.00

HRMS20I14AUG21 #11-24 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 1.27E7
T: FTMS + p ESI Full ms [100.00-1500.00]

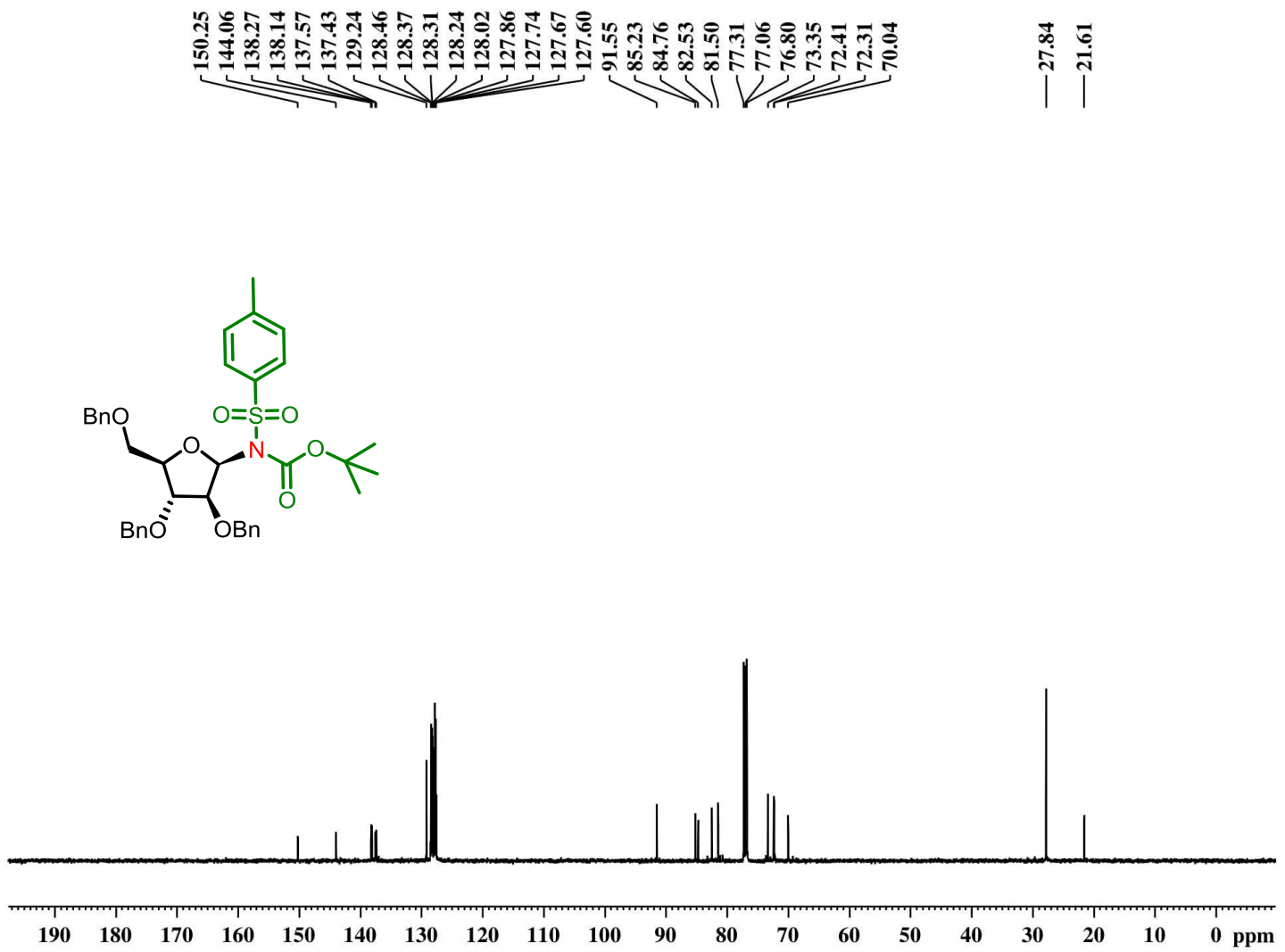


Calcd for $C_{37}H_{45}N_2O_9S^+$ $[M+ NH_4]^+$: 693.2840, found: 693.2820.

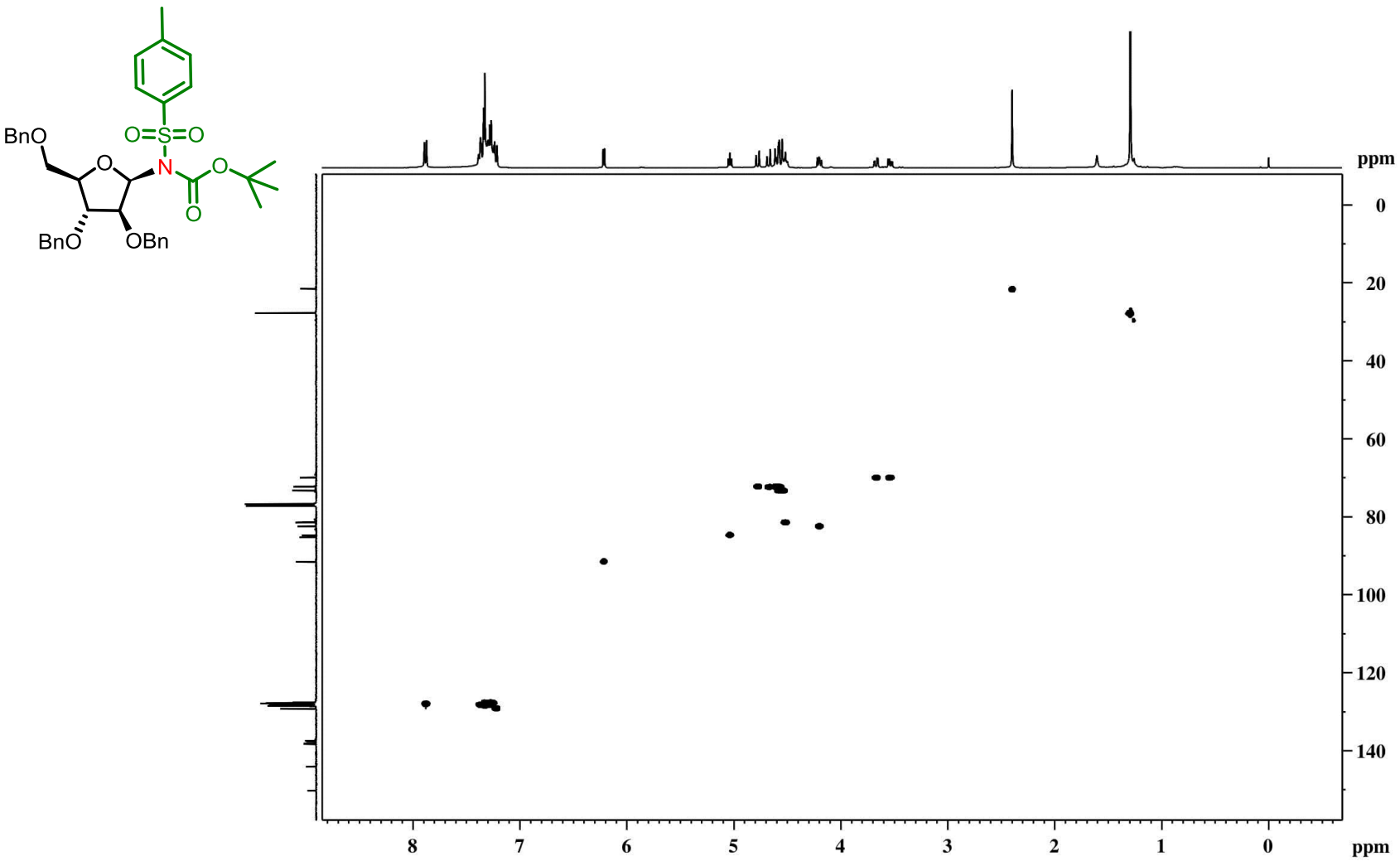
HRMS of **3q**



^{1}H NMR spectrum of **3r**(400 MHz, $CDCl_3$)



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

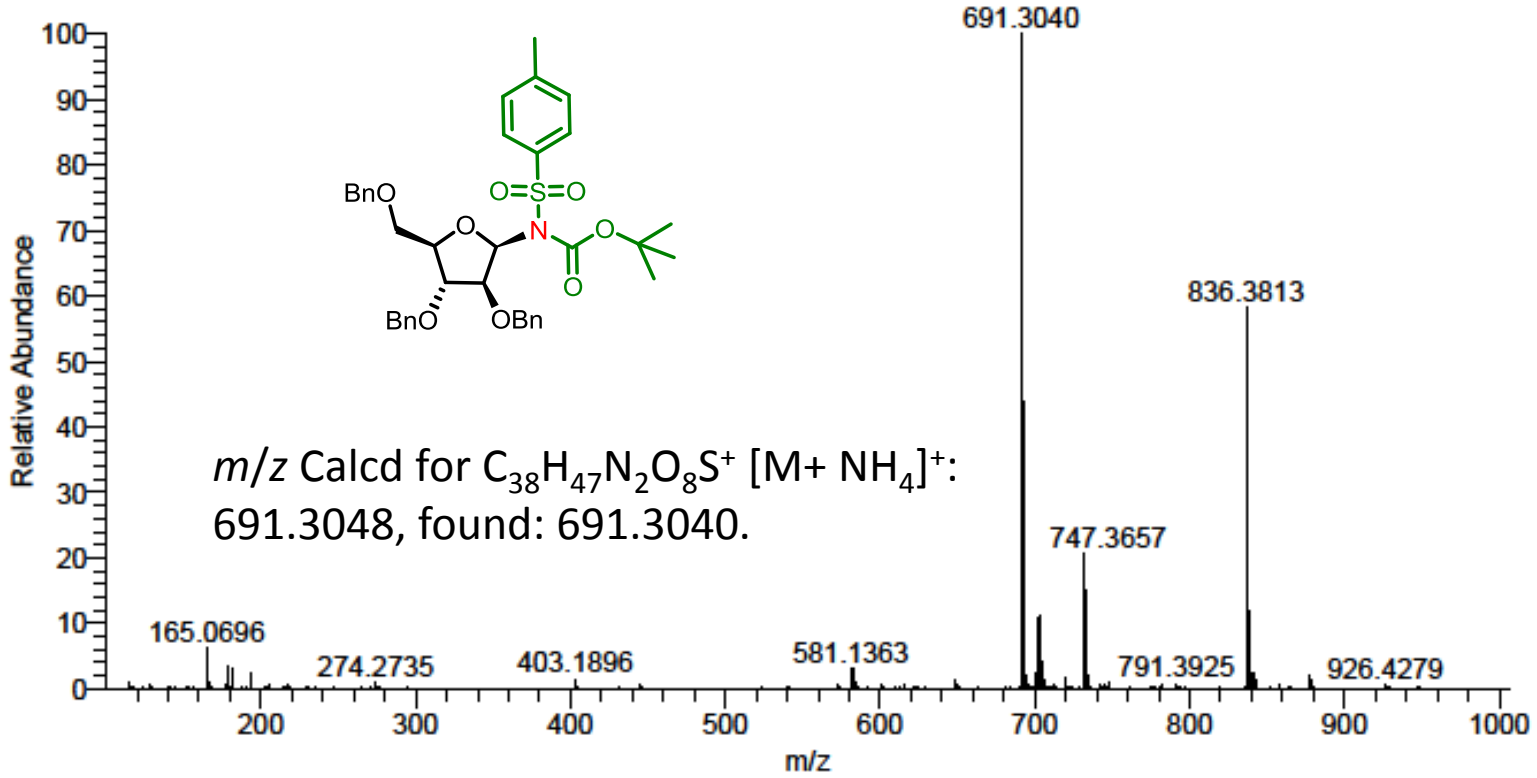


2D HSQC spectrum of **3r** ($CDCl_3$).

SAIF [HRMS Report]

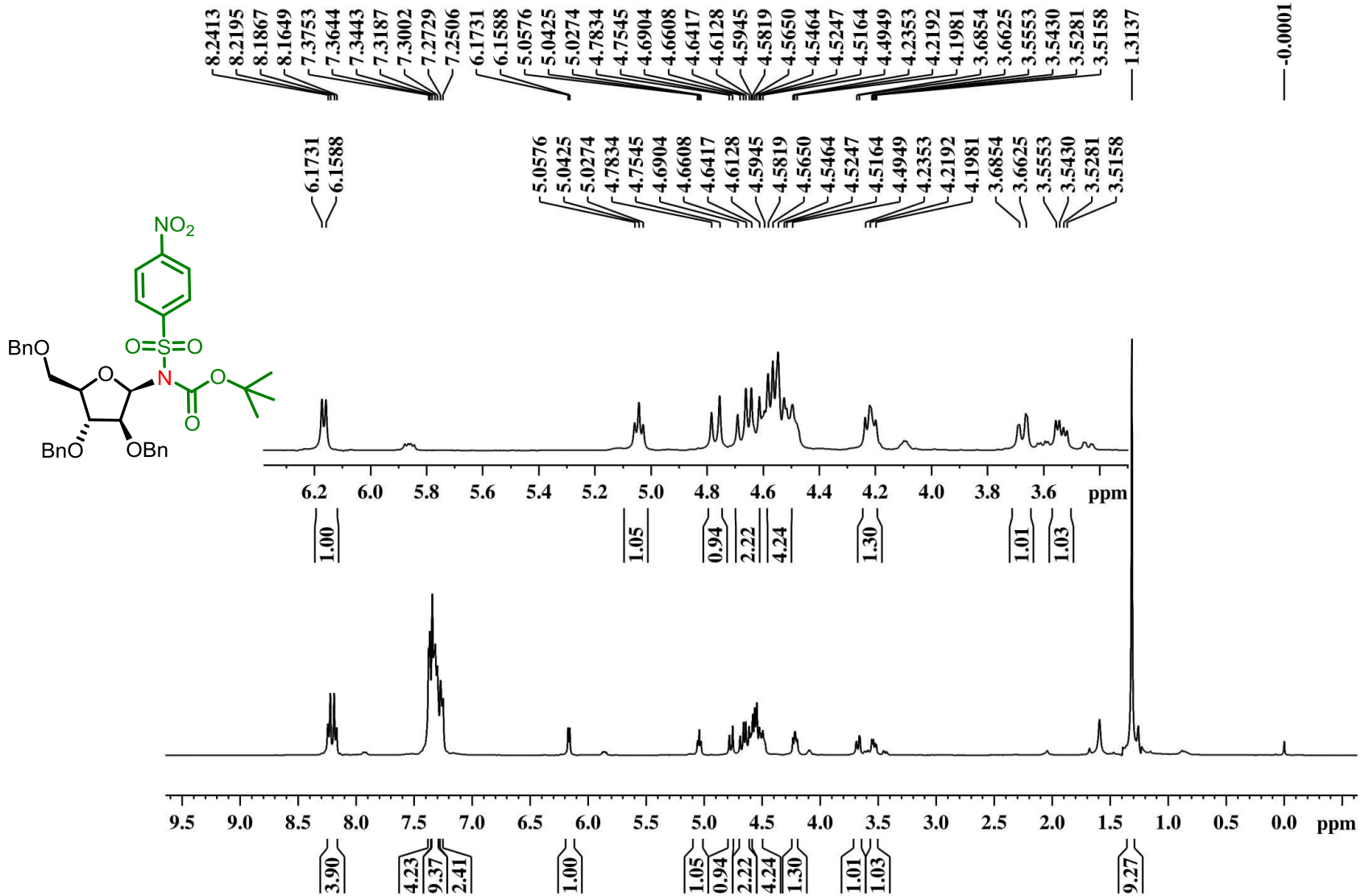
Data File:	HRMS20I16OCT13	Original Data Path:	D:\INTERNAL NEW\2020\OCT 2020
Sample ID:	PKM-ARA-06	Sample Name:	
Acquisition Date:	10/16/20 11:21:58 AM	Run Time(min):	0.00
Vial:	CStk1-01:13	Injection Volume(µl):	1.00

HRMS20I16OCT13 #12-25 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 1.36E7
T: FTMS + p ESI Full ms [100.00-1000.00]

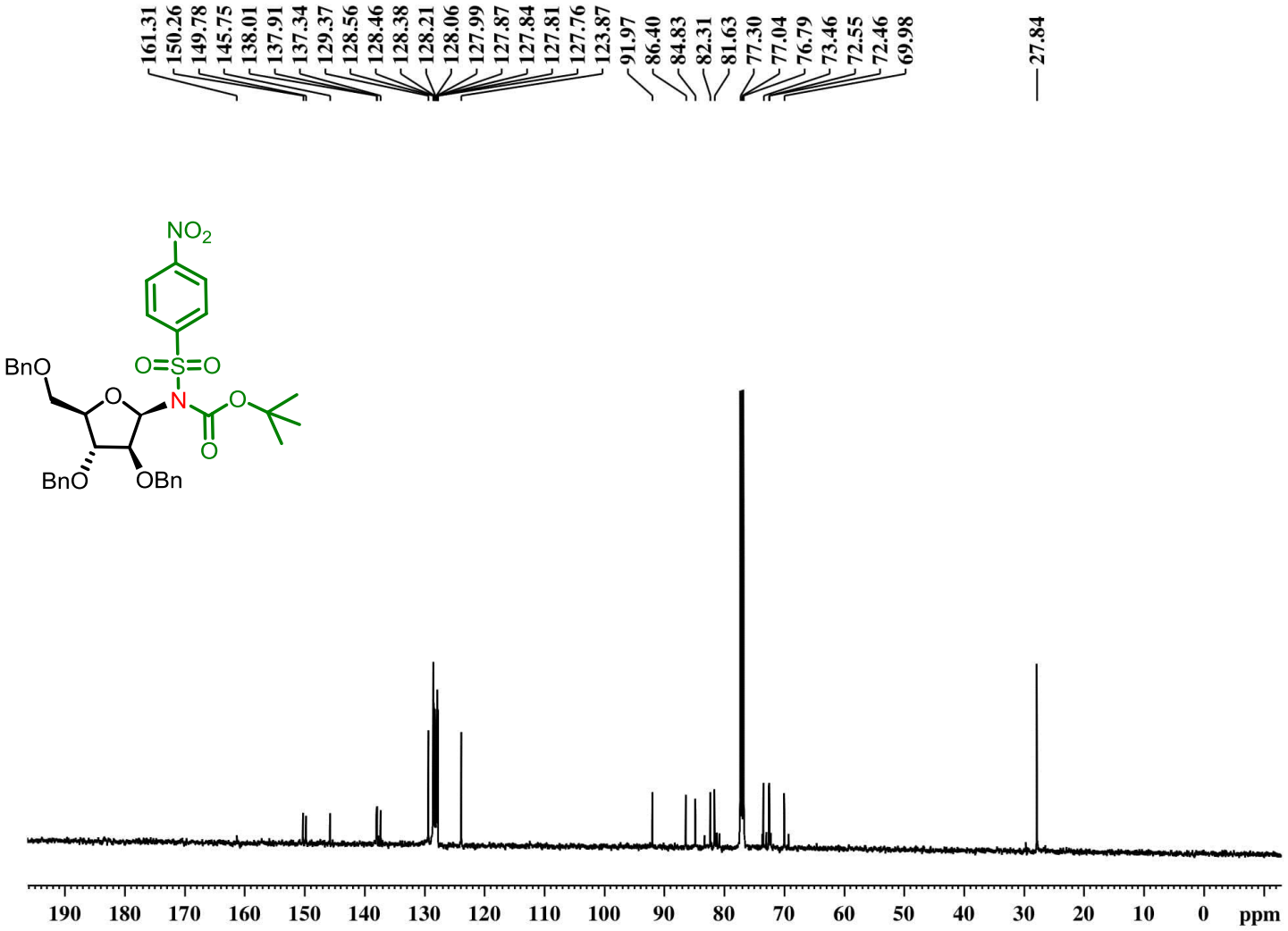


m/z Calcd for $C_{38}H_{47}N_2O_8S^+$ $[M+ NH_4]^+$: 691.3048, found: 691.3040.

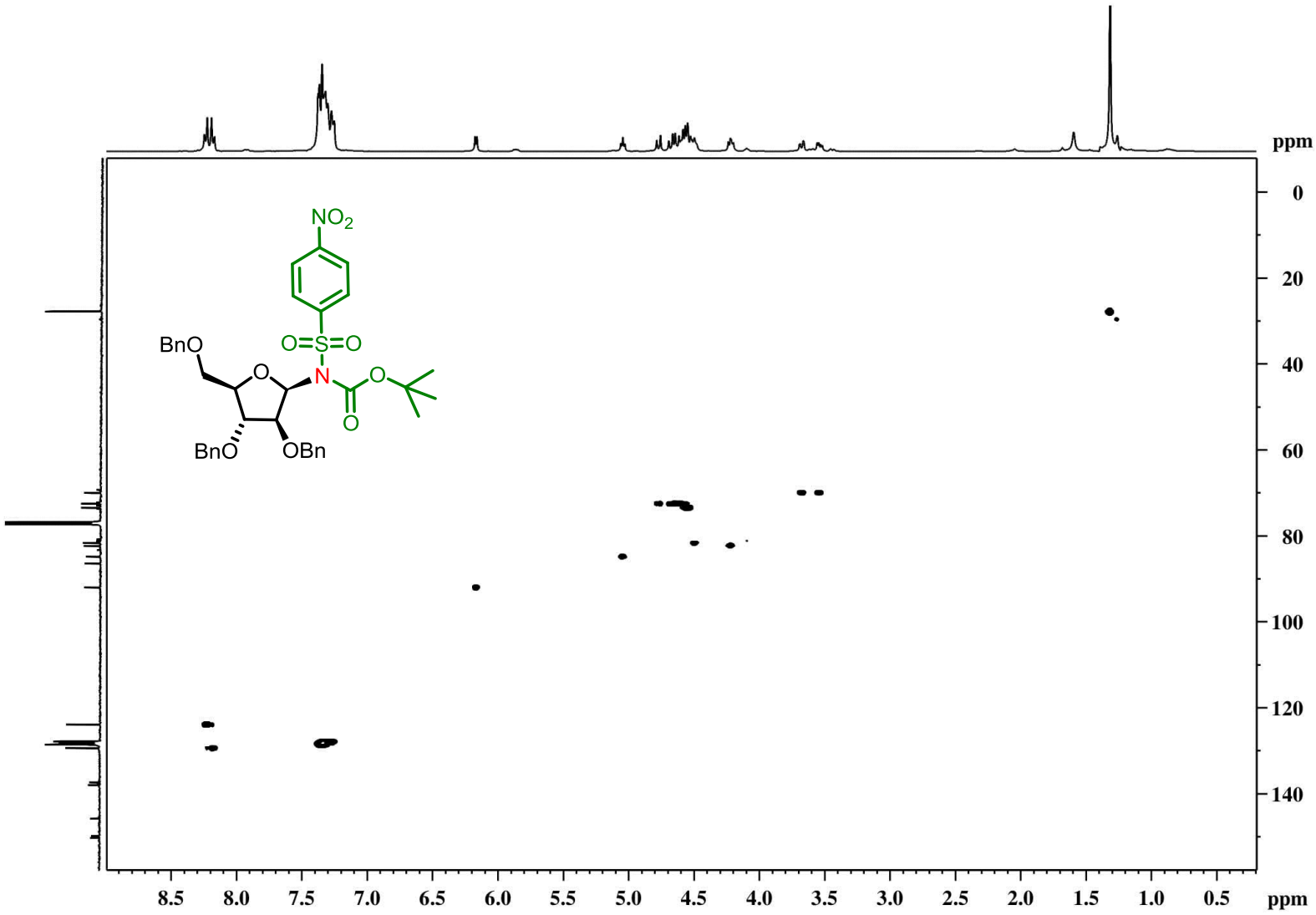
HRMS of **3r**



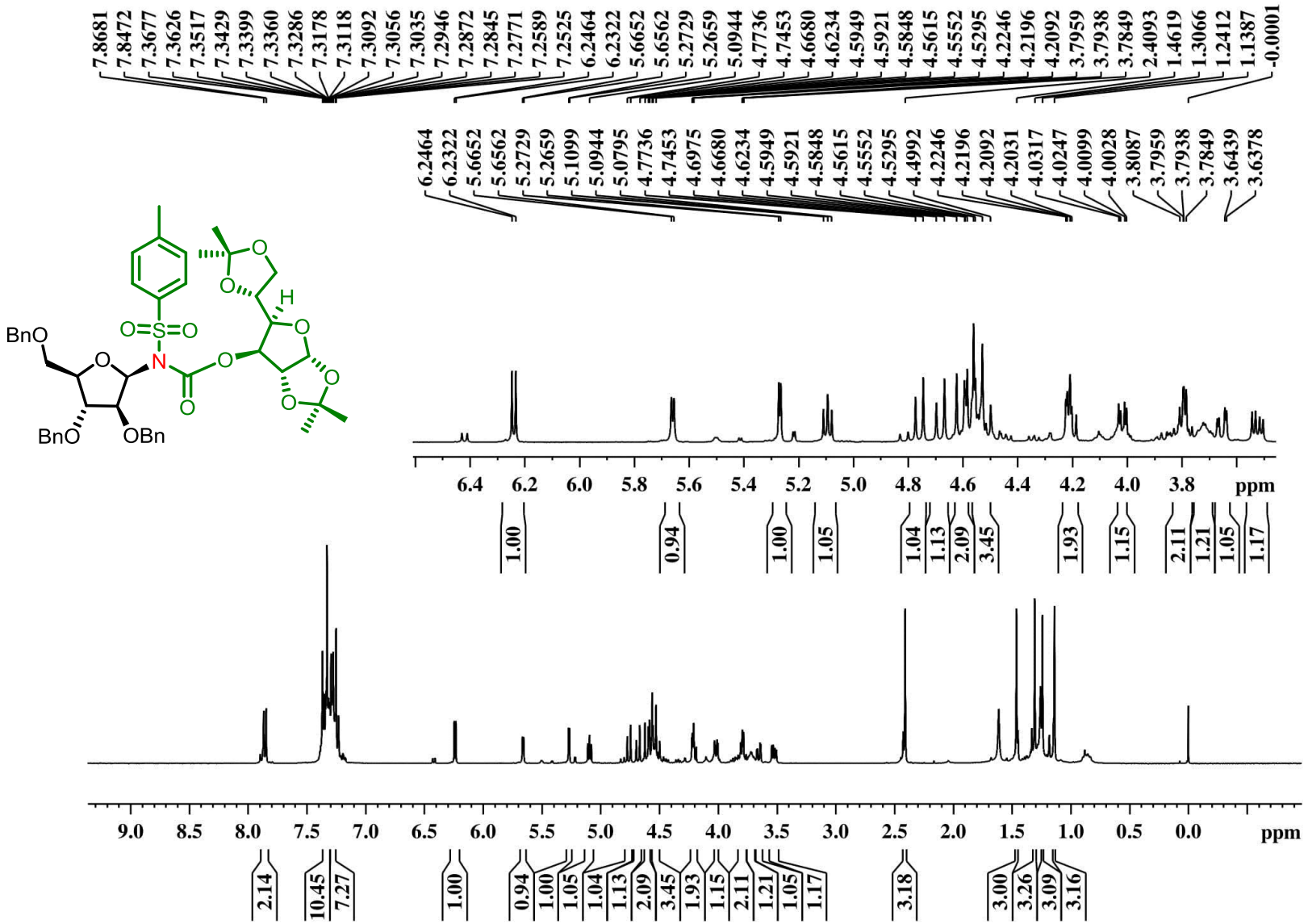
^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$)



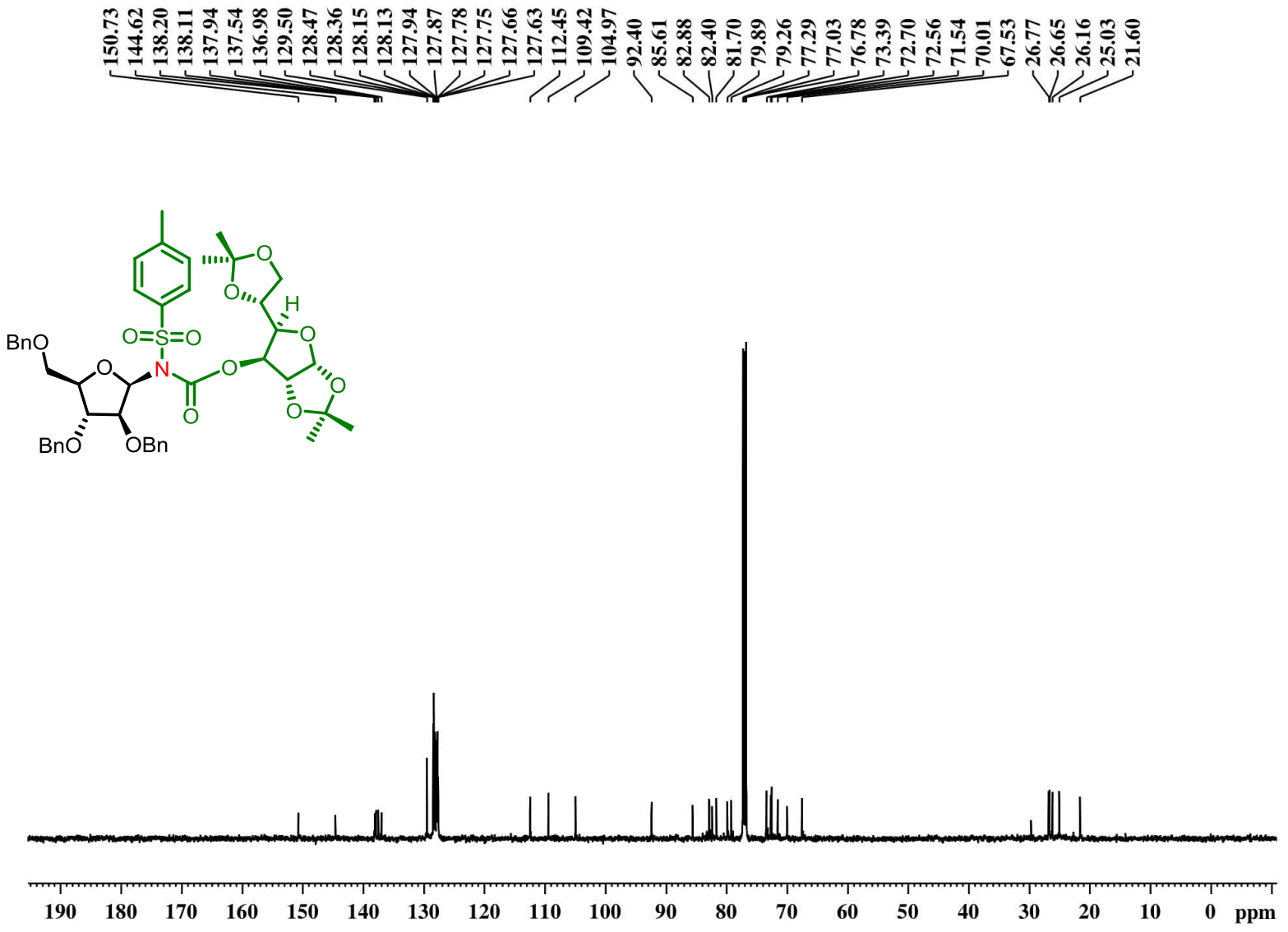
^{13}C NMR spectrum of **3s** (100 MHz, MHz, $CDCl_3$)



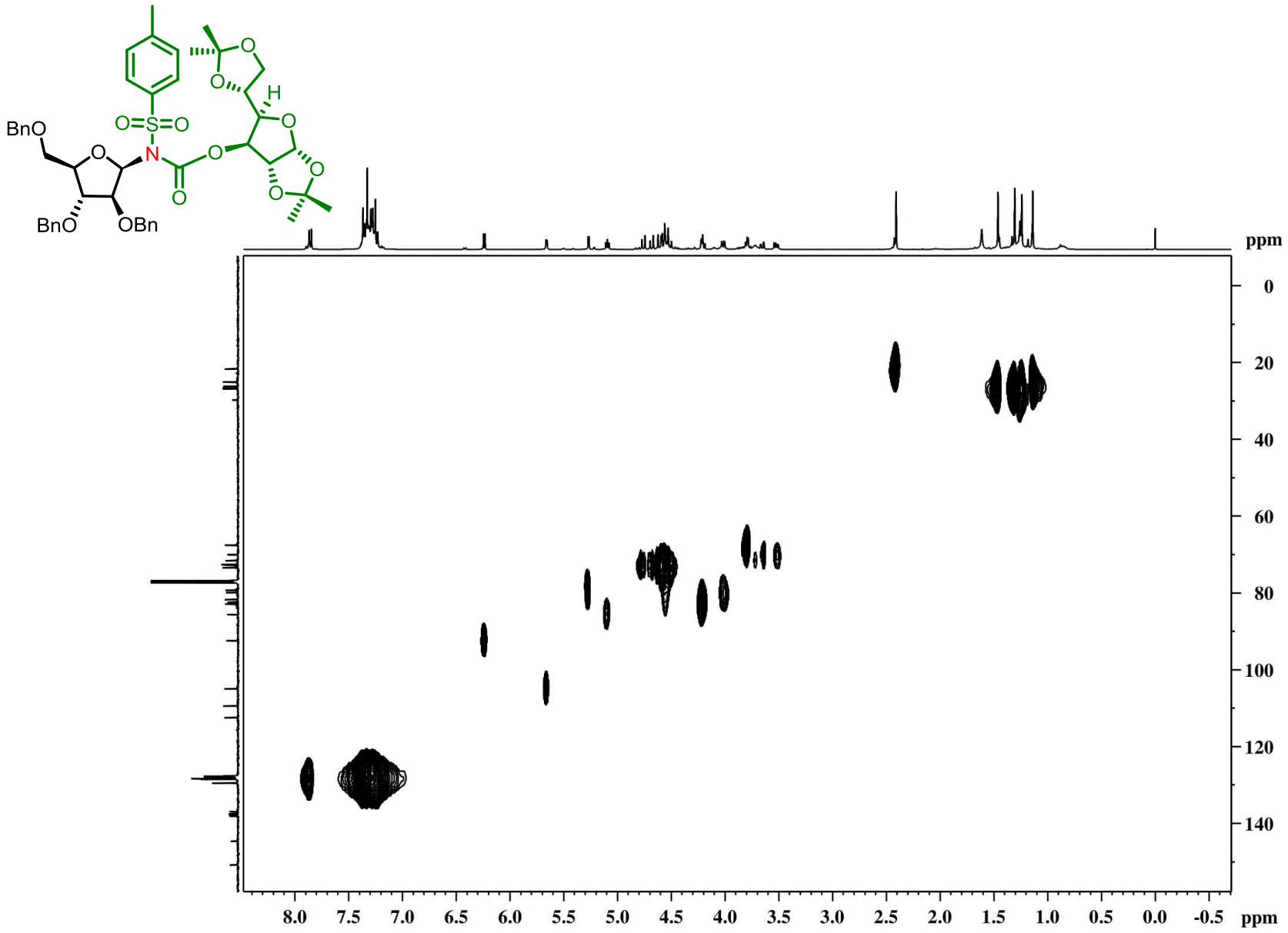
2D HSQC spectrum of **3s** ($CDCl_3$).



^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)



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

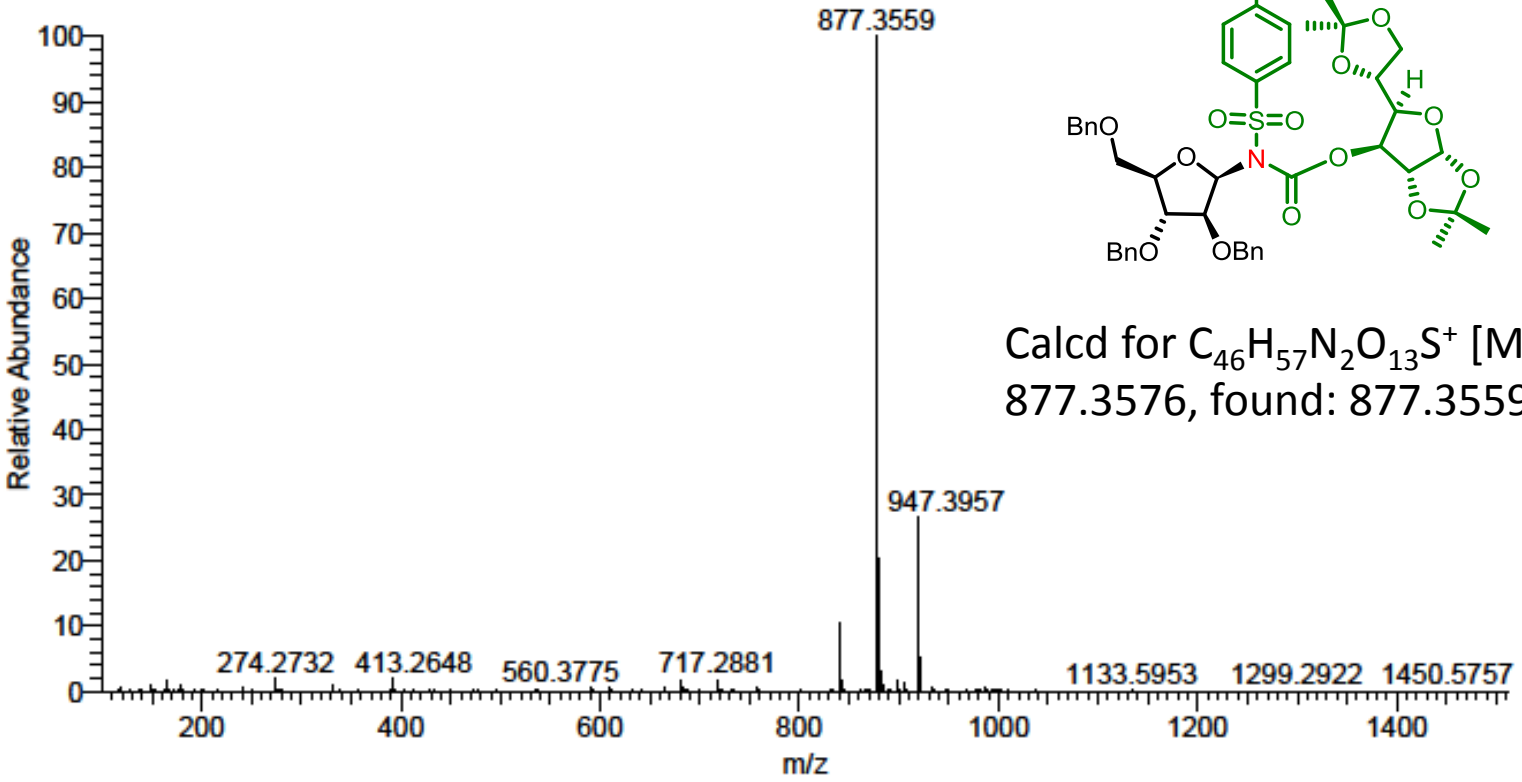


2D HSQC spectrum of **3t** ($CDCl_3$).

SAIF [HRMS Report]

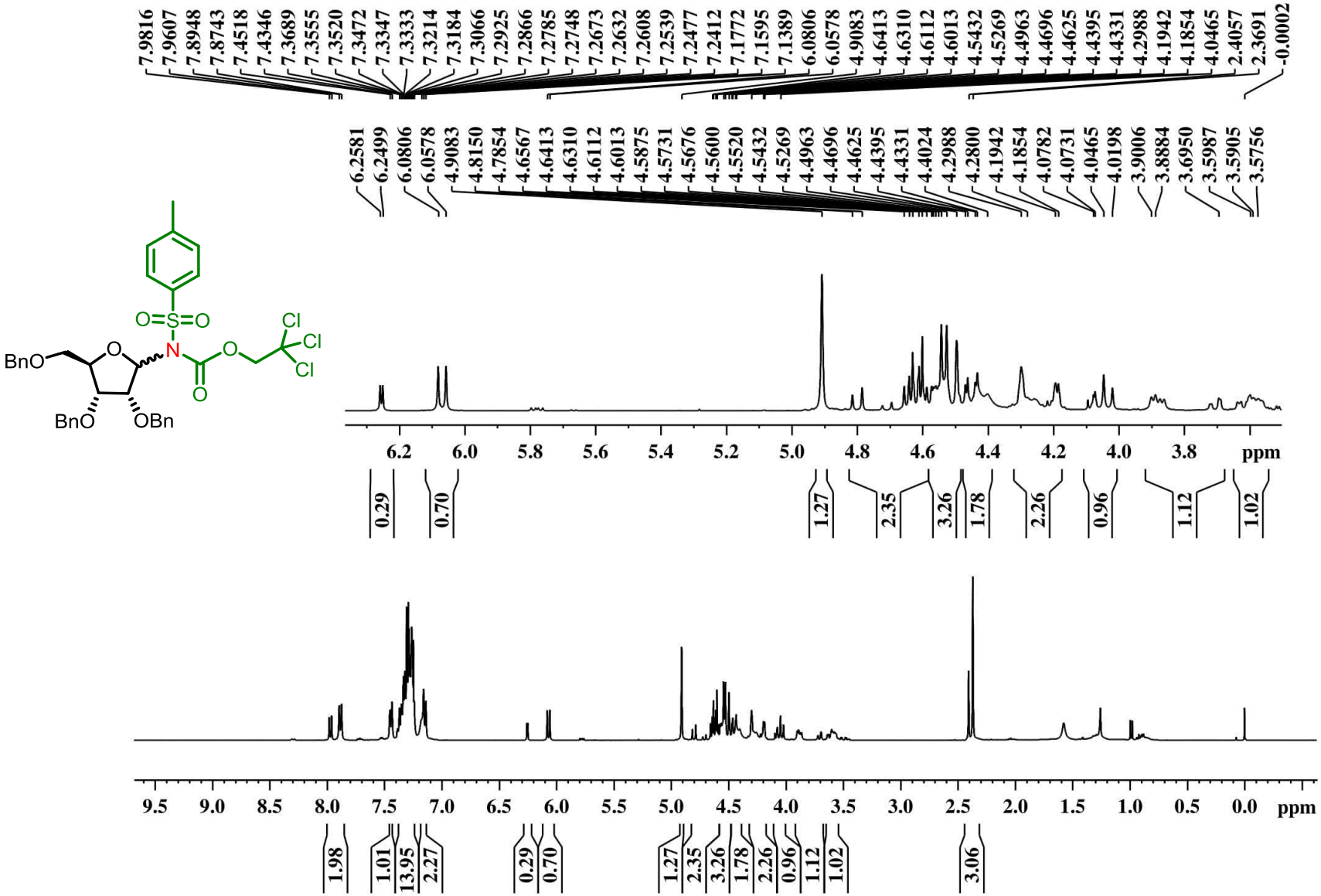
Data File:	HRMS20I13AUG12	Original Data Path:	D:\INTERNAL NEW\2020\Aug 2020
Sample ID:	PKM-Ara-04	Sample Name:	
Acquisition Date:	08/13/20 04:48:25 PM	Run Time(min):	0.00
Vial:	CStk1-01:12	Injection Volume(µl):	1.00

HRMS20I13AUG12 #11-24 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 5.37E6
T: FTMS + p ESI Full ms [100.00-1500.00]

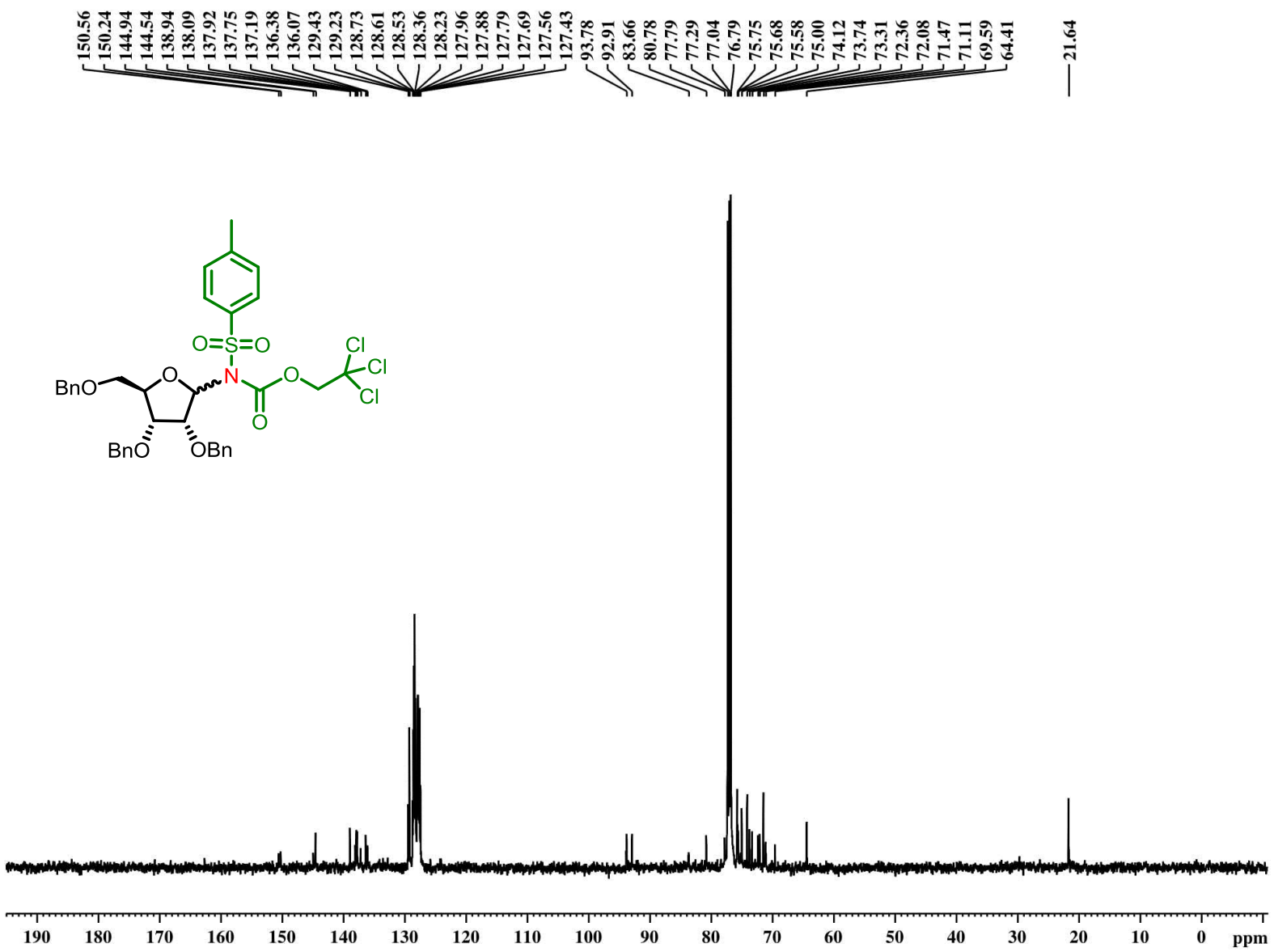


Calcd for $C_{46}H_{57}N_2O_{13}S^+$ $[M+ NH_4]^+$: 877.3576, found: 877.3559.

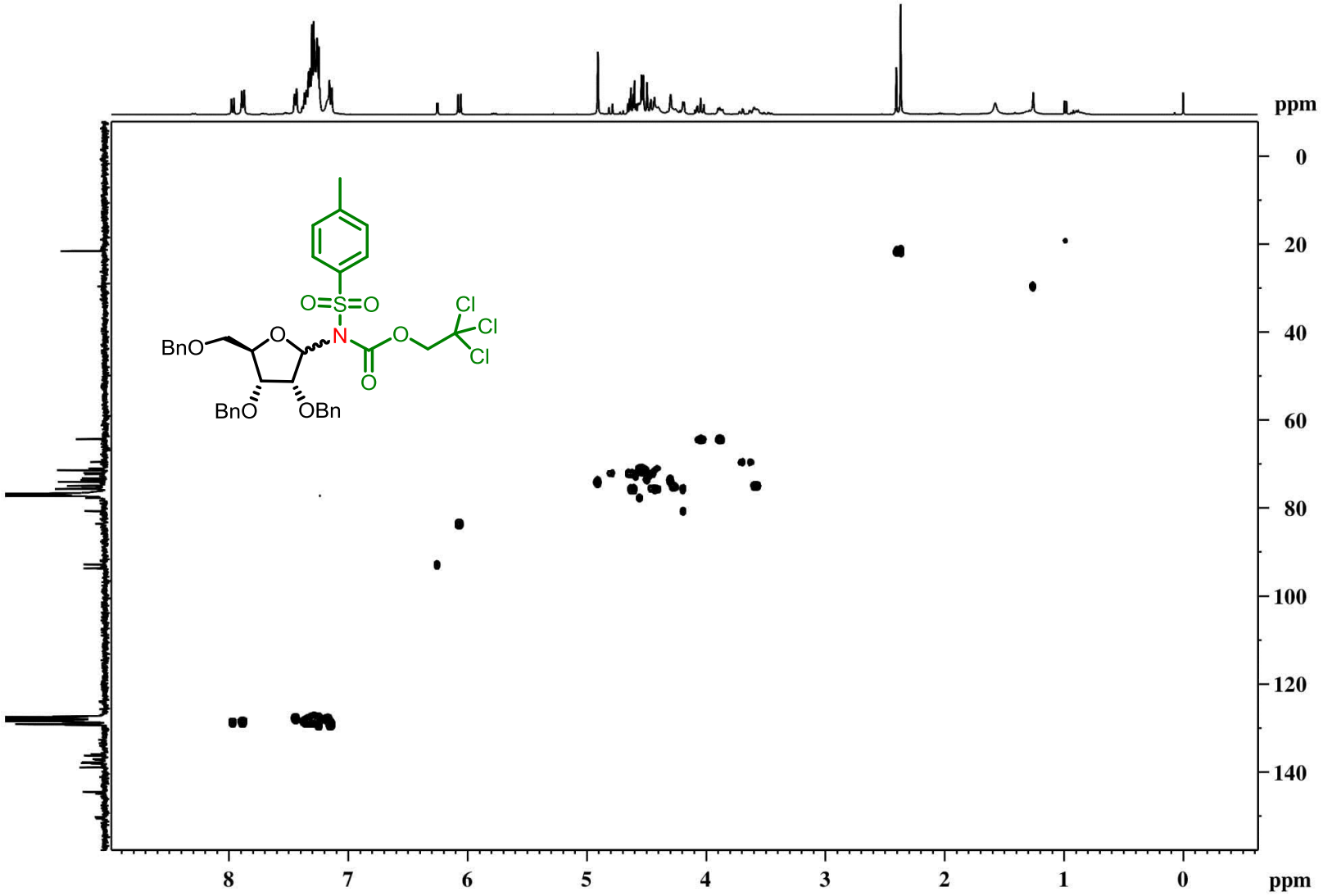
HRMS of **3t**



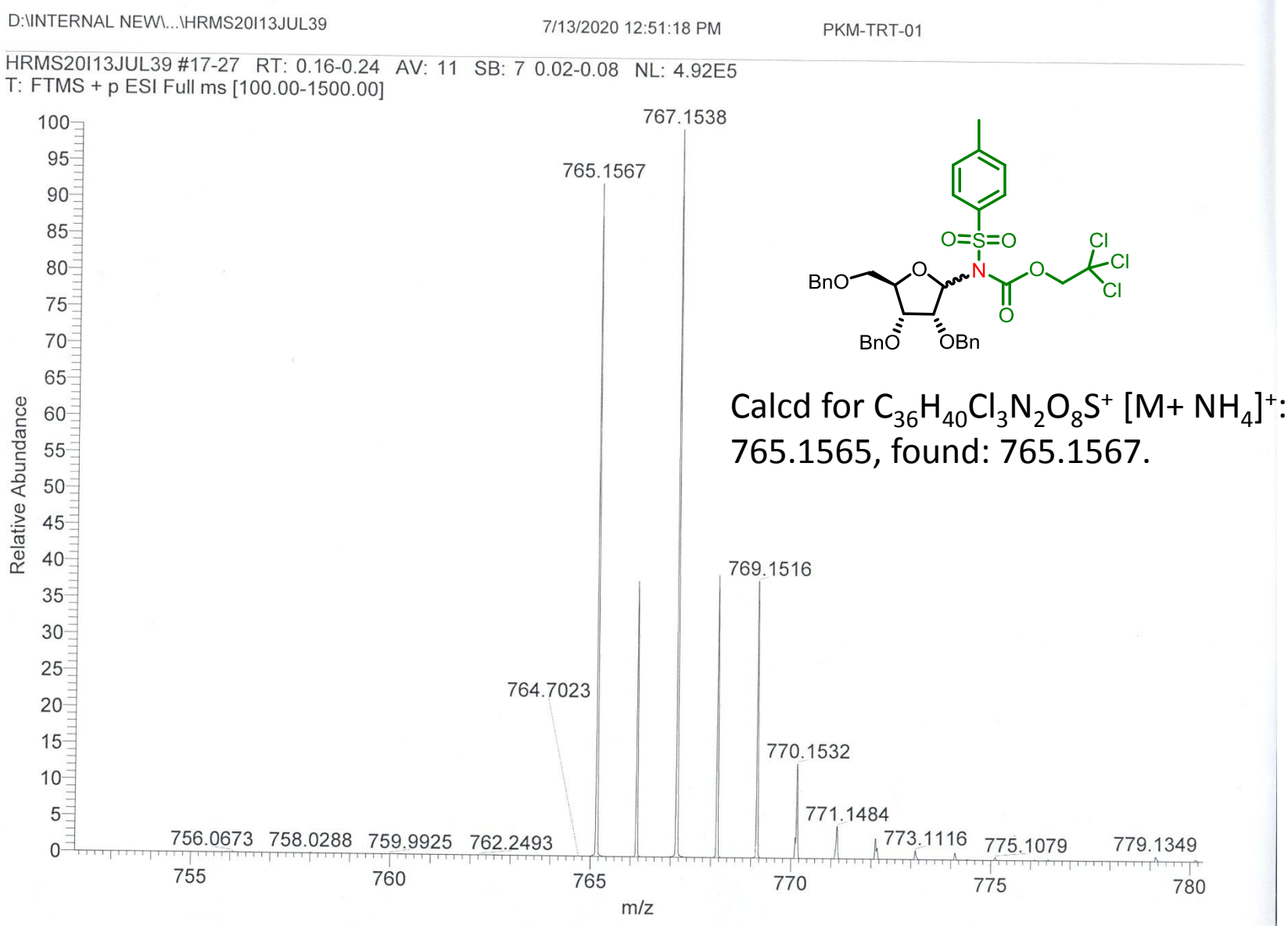
^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$)



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

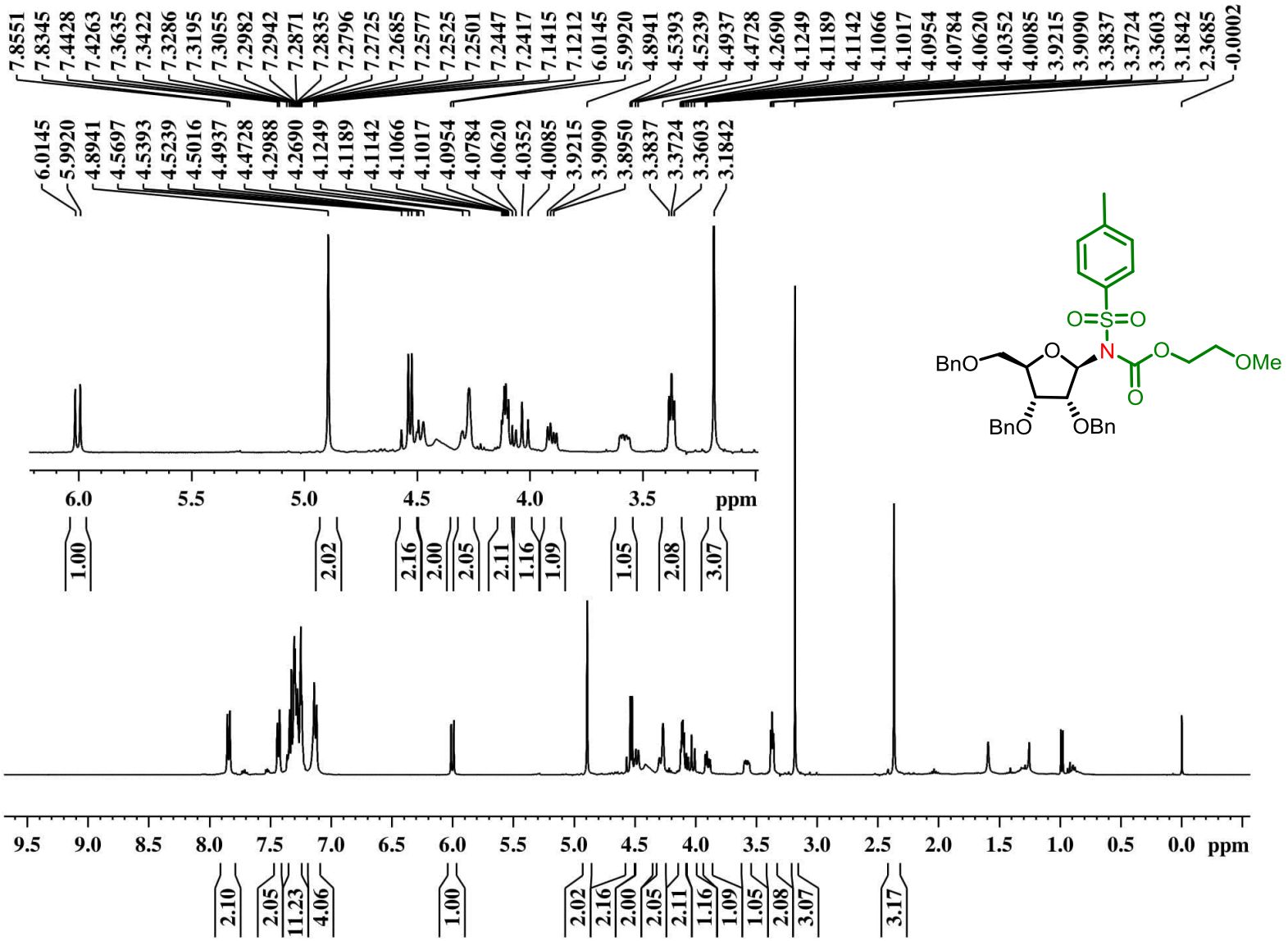


2D HSQC spectrum of **3u** ($CDCl_3$).

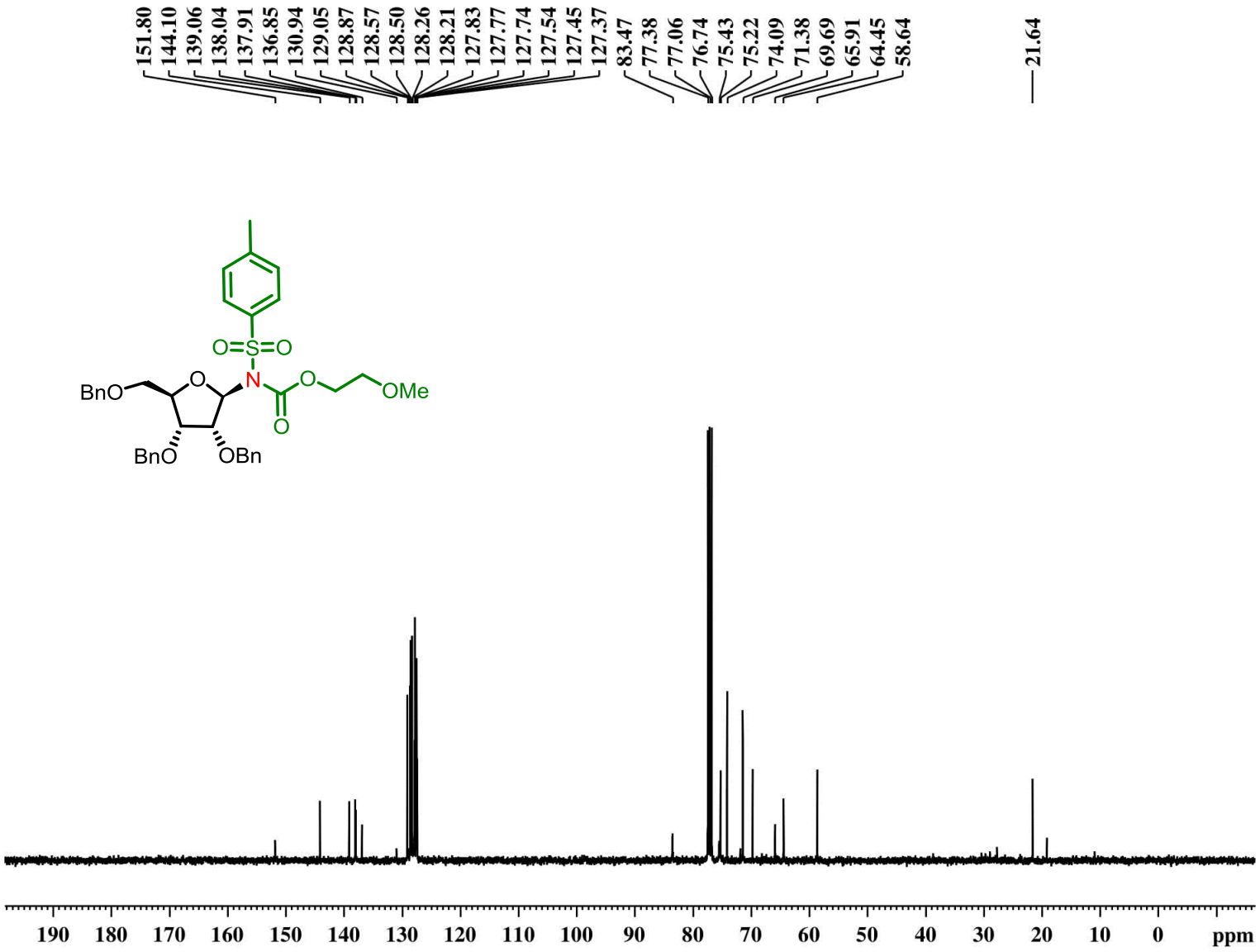


Calcd for $C_{36}H_{40}Cl_3N_2O_8S^+$ $[M+ NH_4]^+$: 765.1565, found: 765.1567.

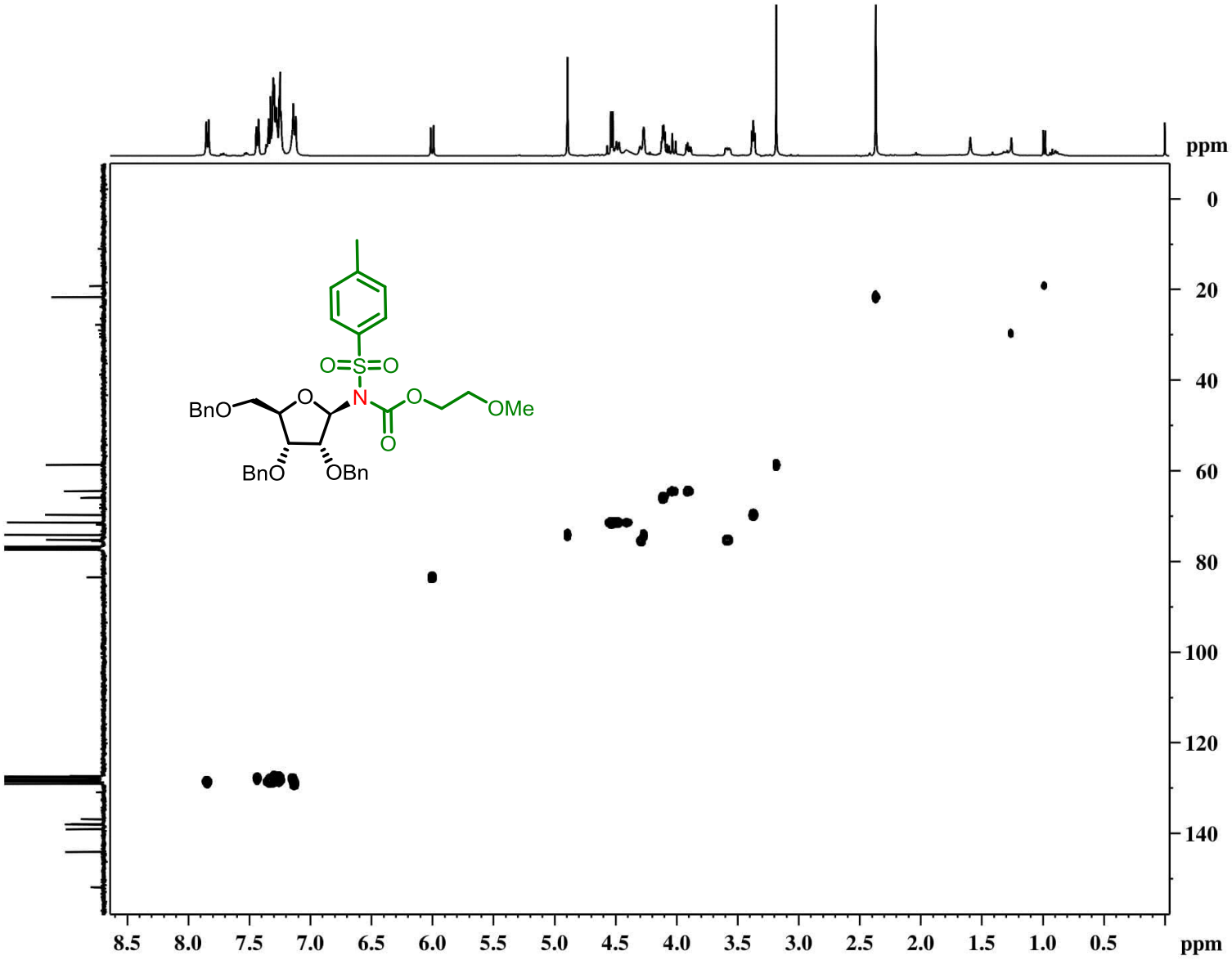
HRMS of **3u**



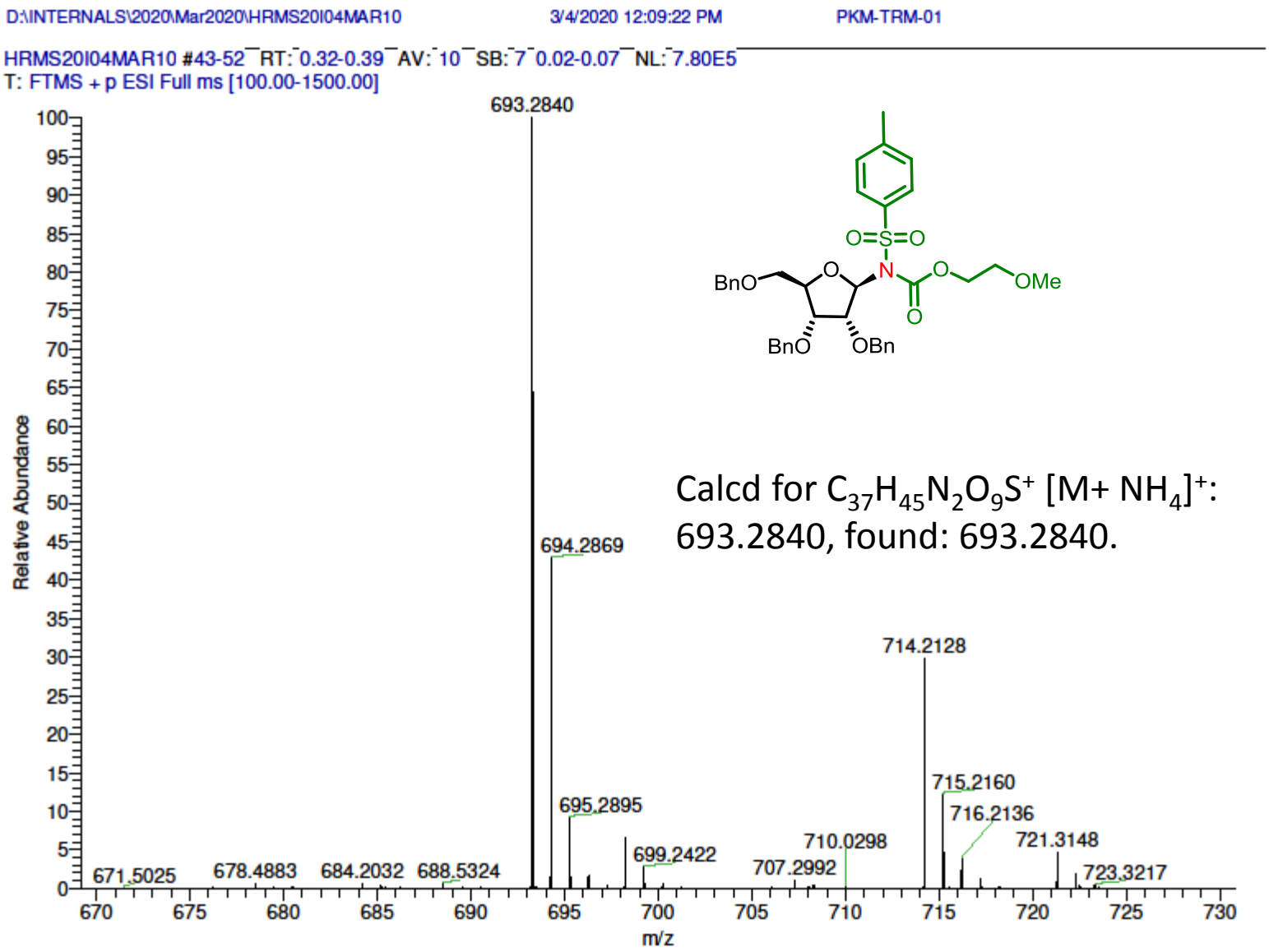
^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$)



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

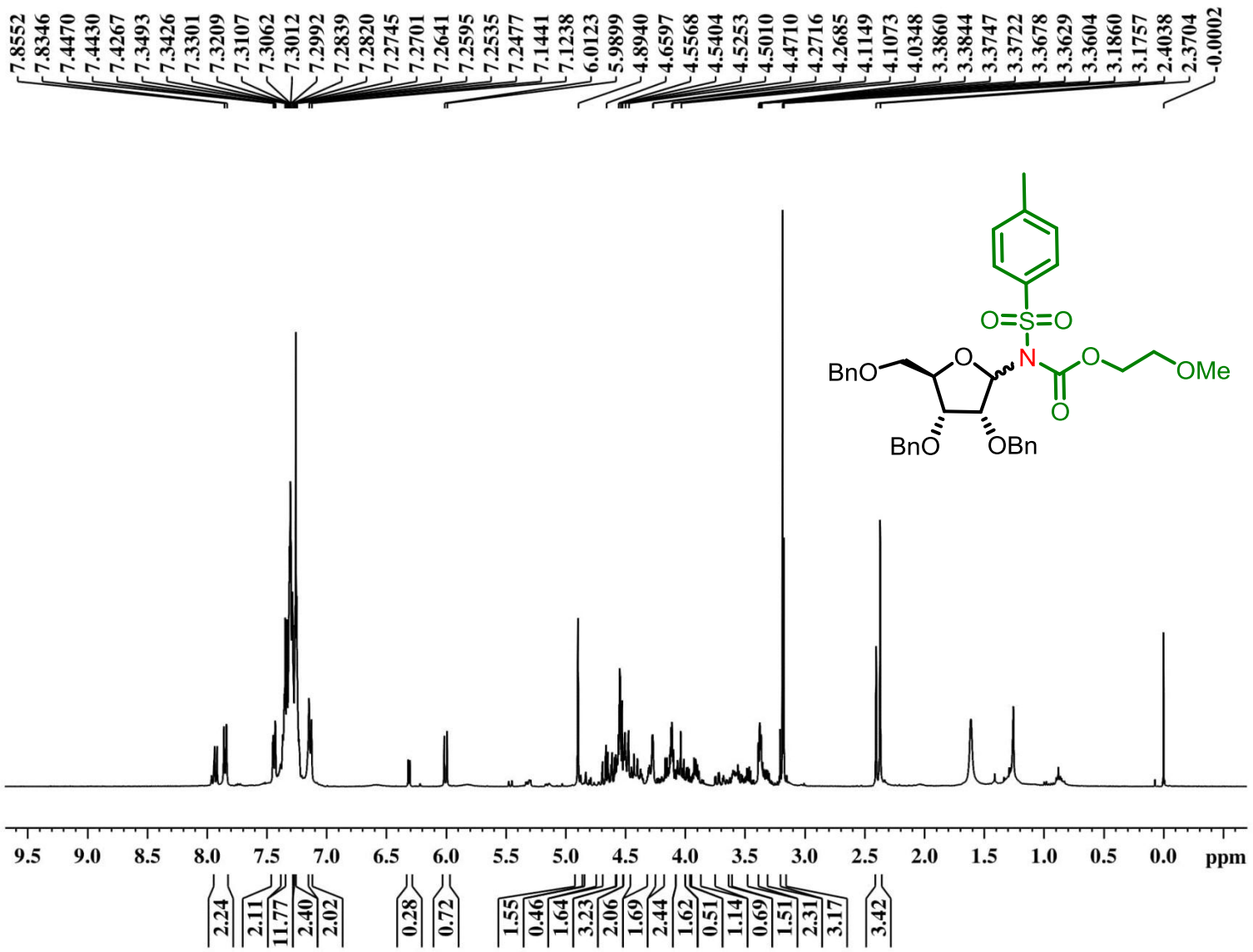


2D HSQC spectrum of **3v** ($CDCl_3$).

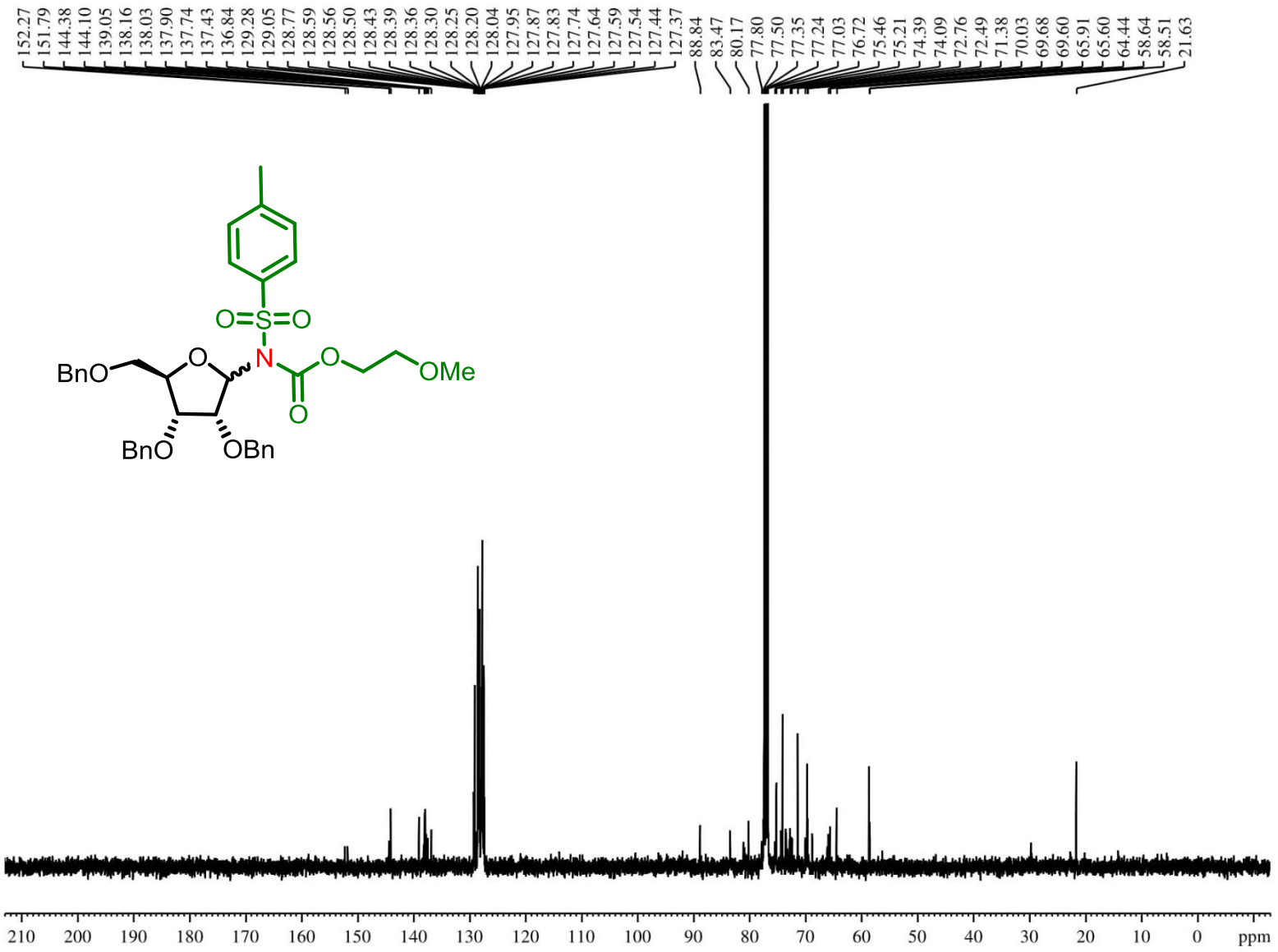


Calcd for $C_{37}H_{45}N_2O_9S^+$ $[M+ NH_4]^+$: 693.2840, found: 693.2840.

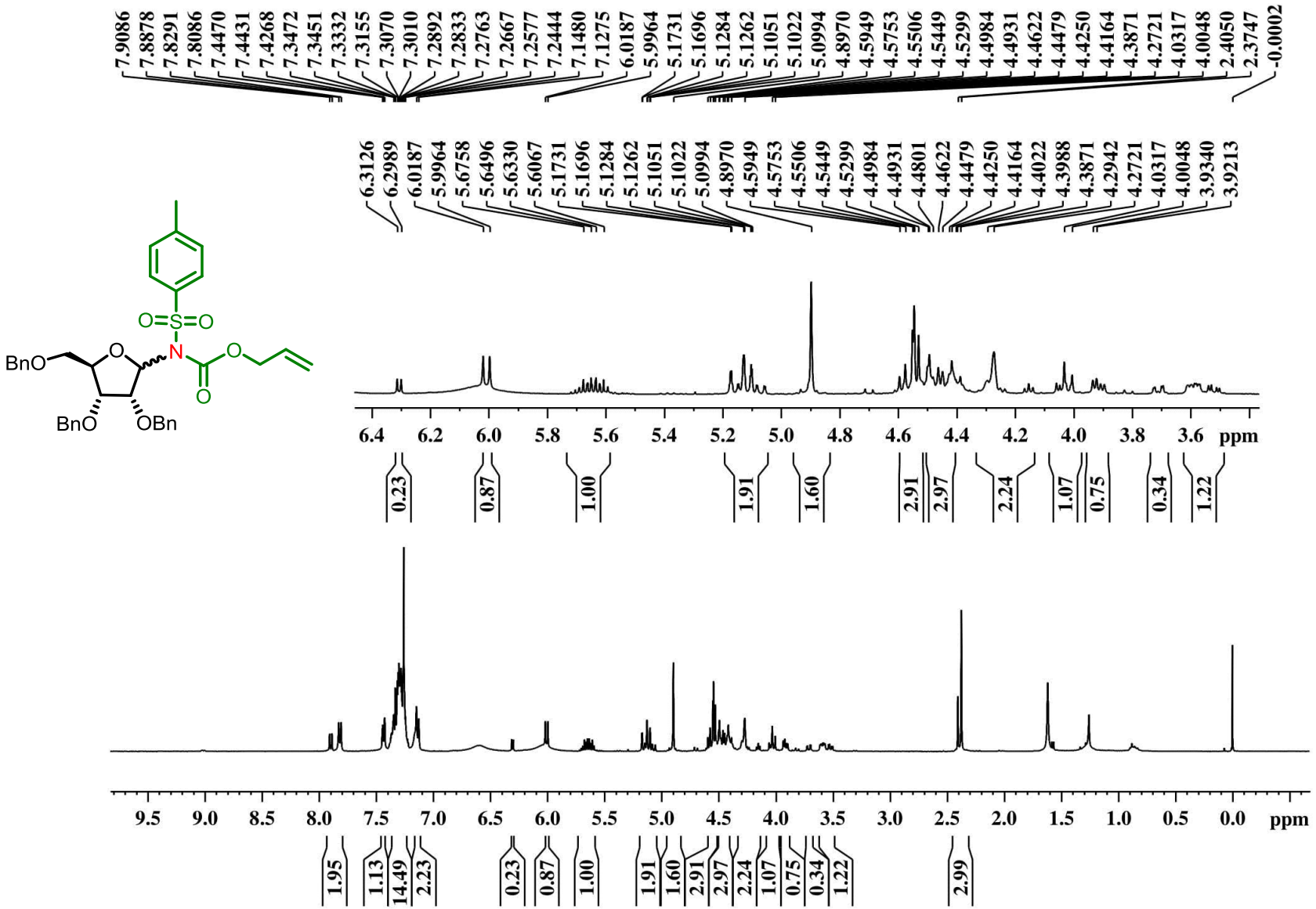
HRMS of **3v**



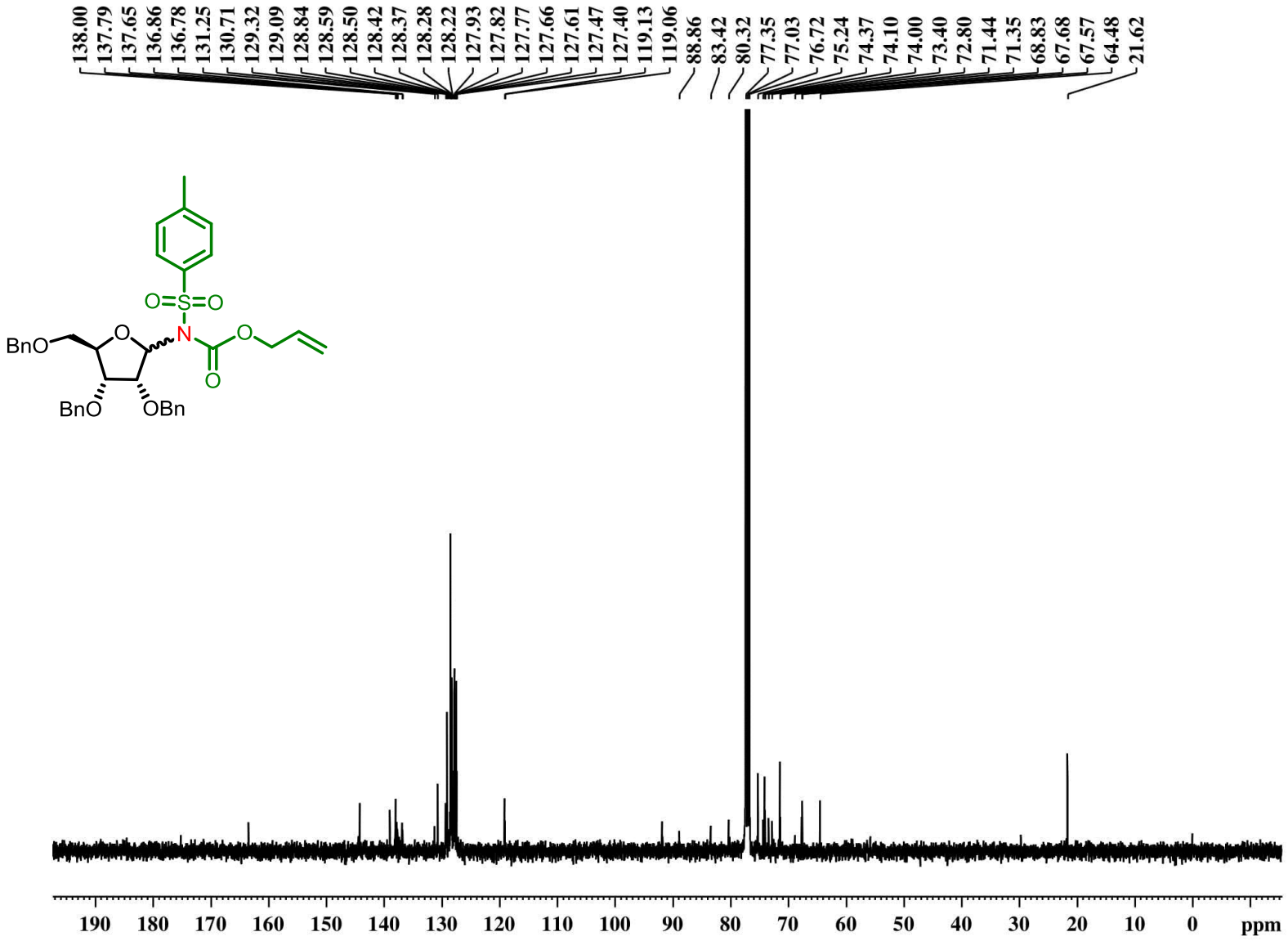
^{1}H NMR spectrum of **3v'** (400 MHz, $CDCl_3$)



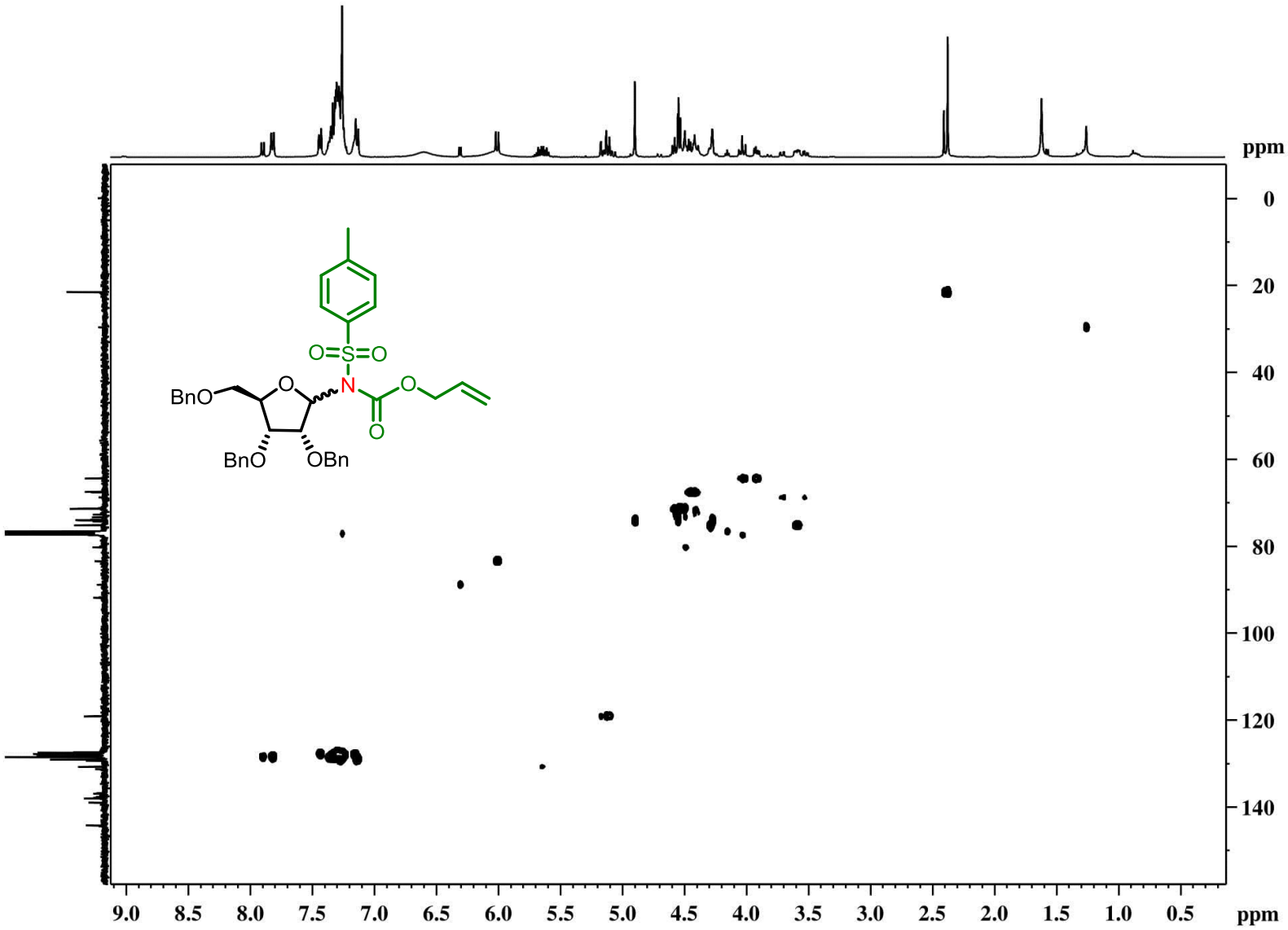
^{13}C NMR spectrum of **3v'** (100 MHz, MHz, $CDCl_3$)



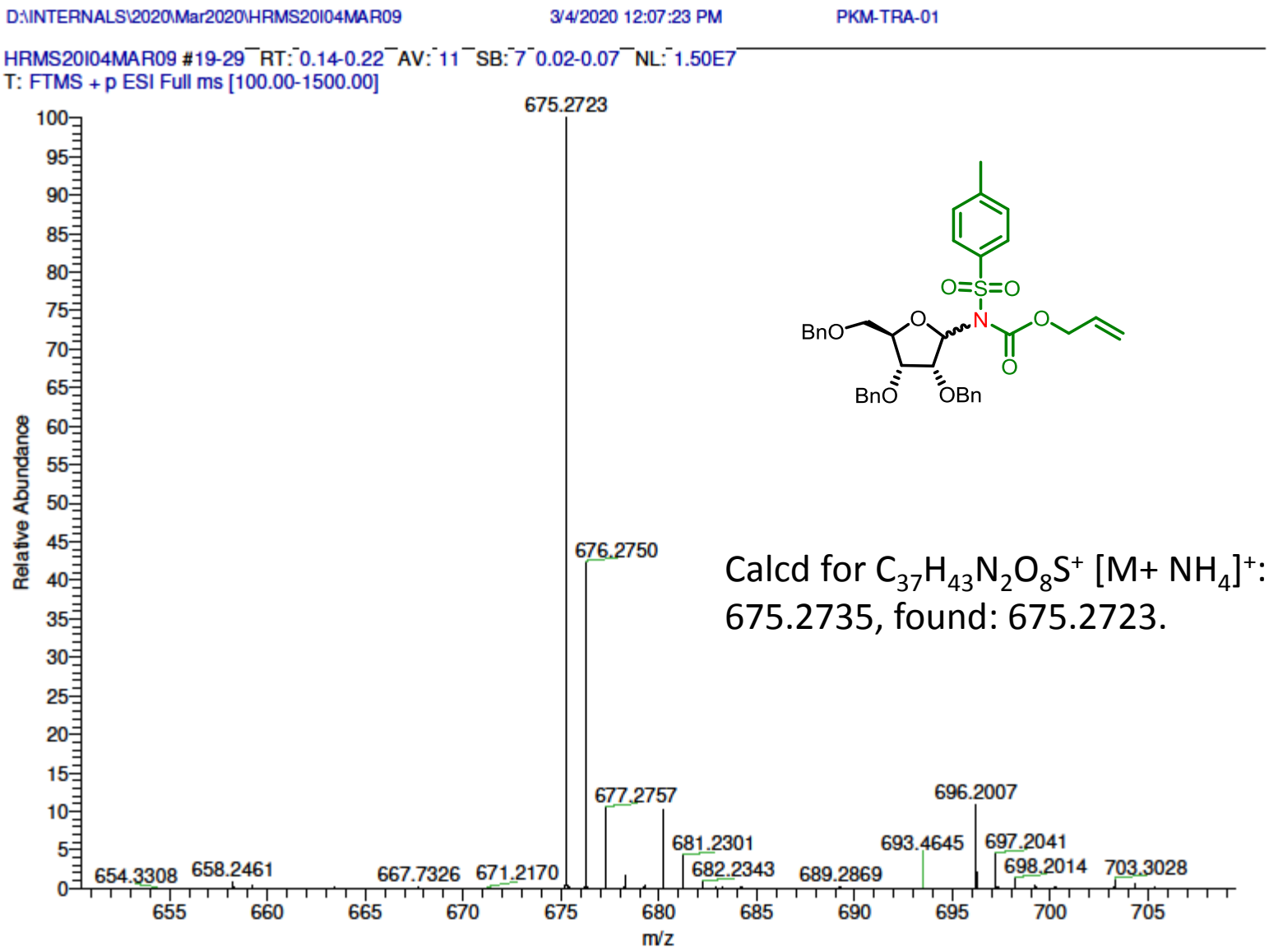
^{1}H NMR spectrum of **3w** (400 MHz, $CDCl_3$)



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

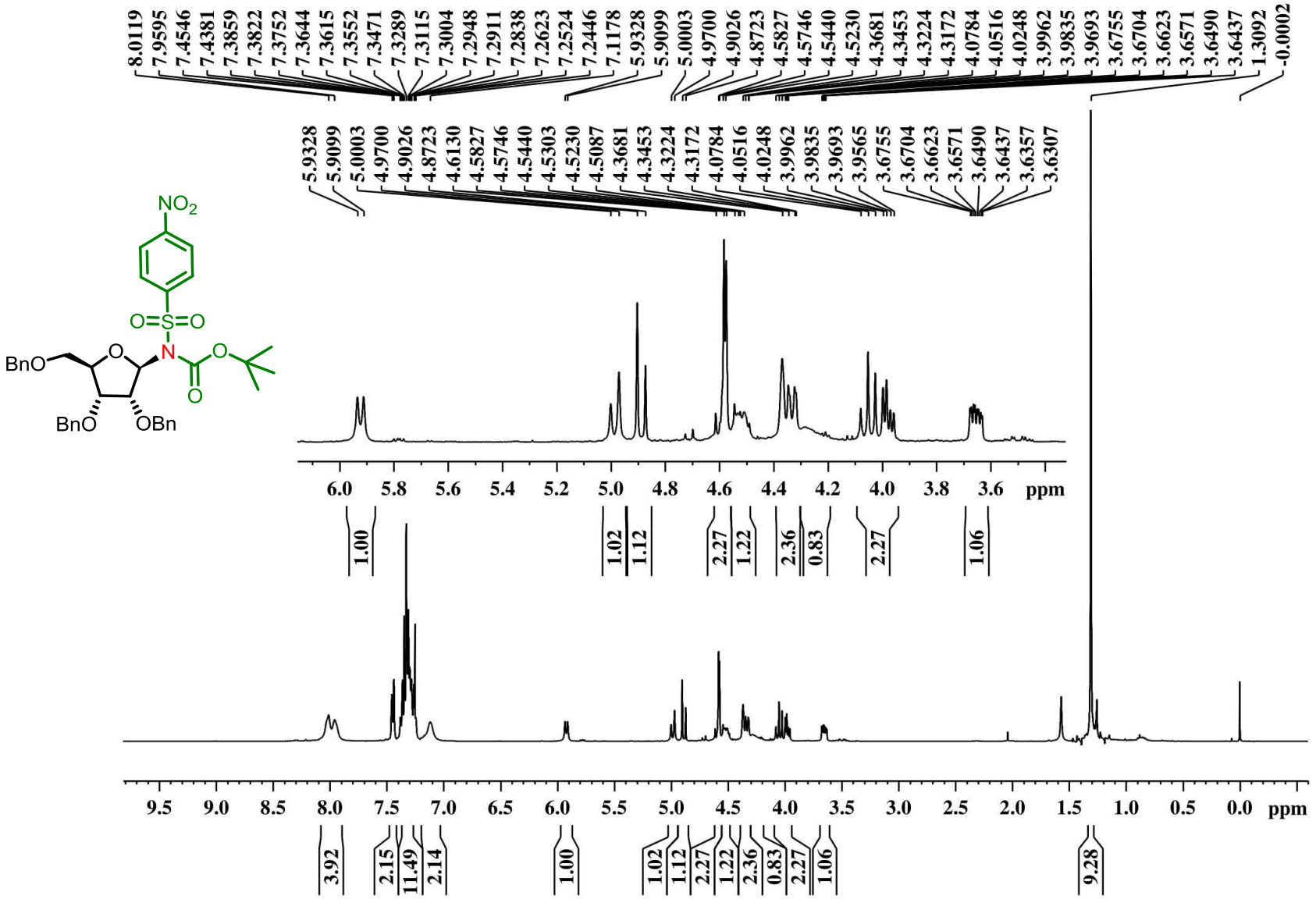


2D HSQC spectrum of **3w** ($CDCl_3$).

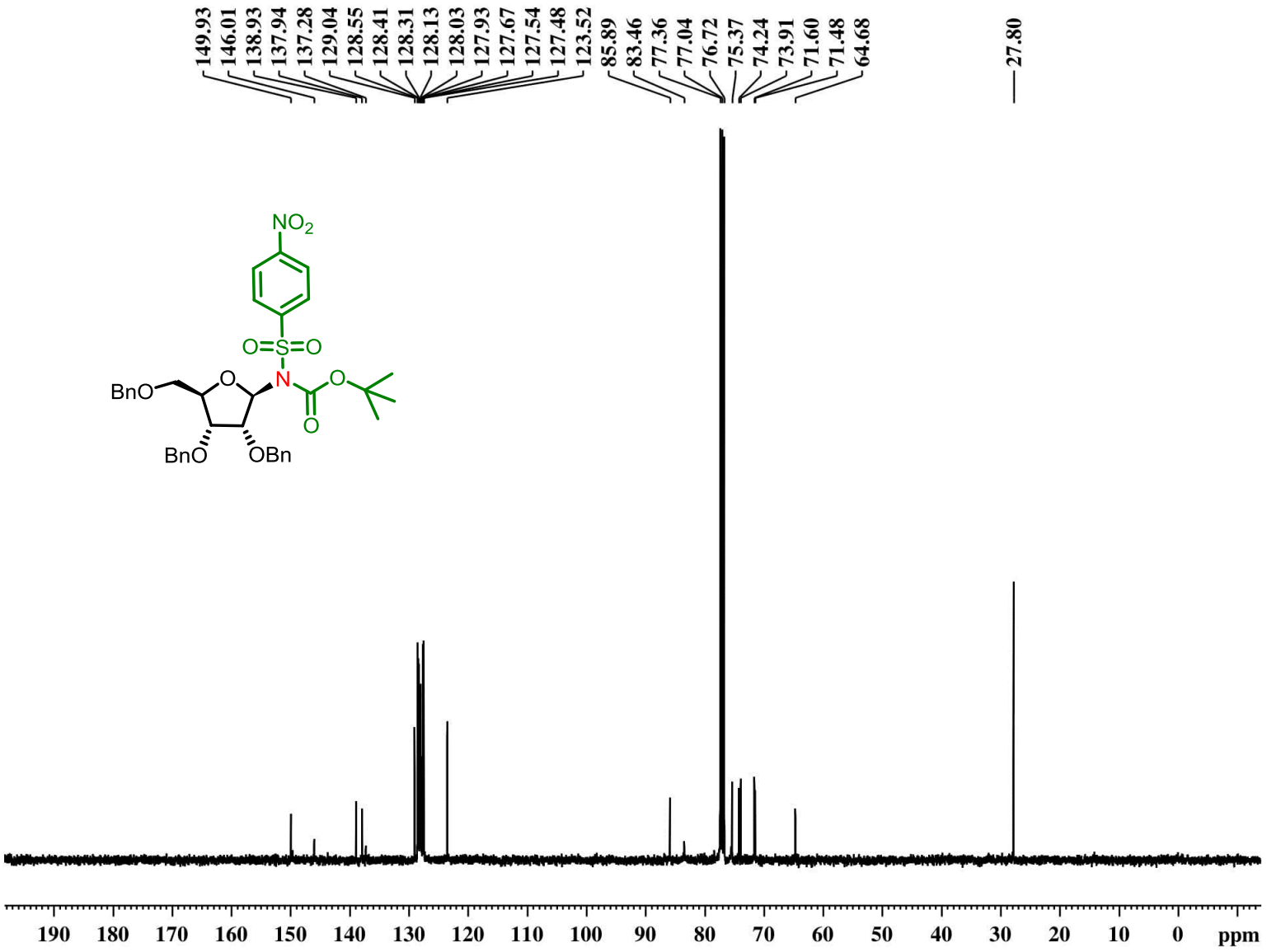


Calcd for $C_{37}H_{43}N_2O_8S^+$ $[M+ NH_4]^+$: 675.2735, found: 675.2723.

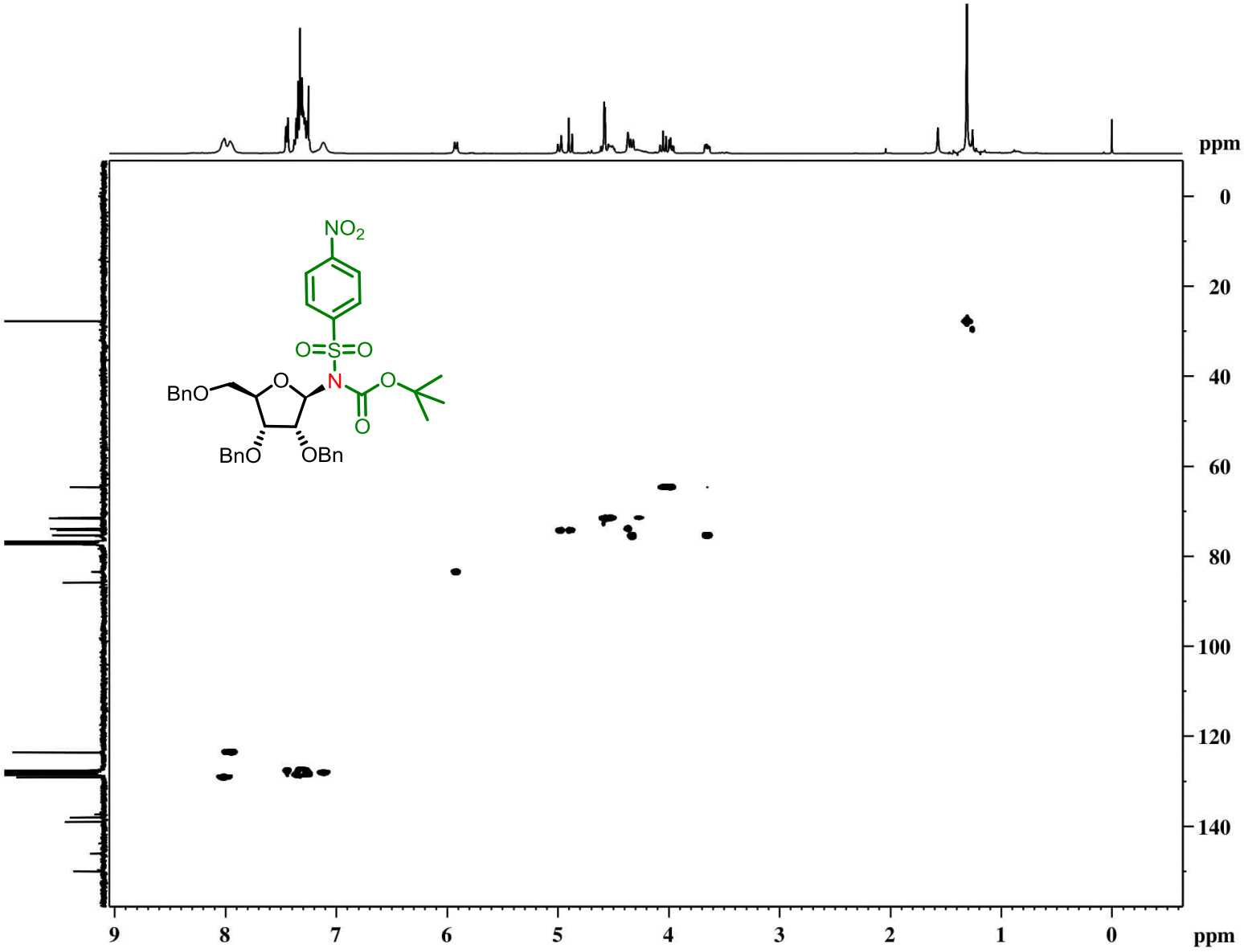
HRMS of **3w**



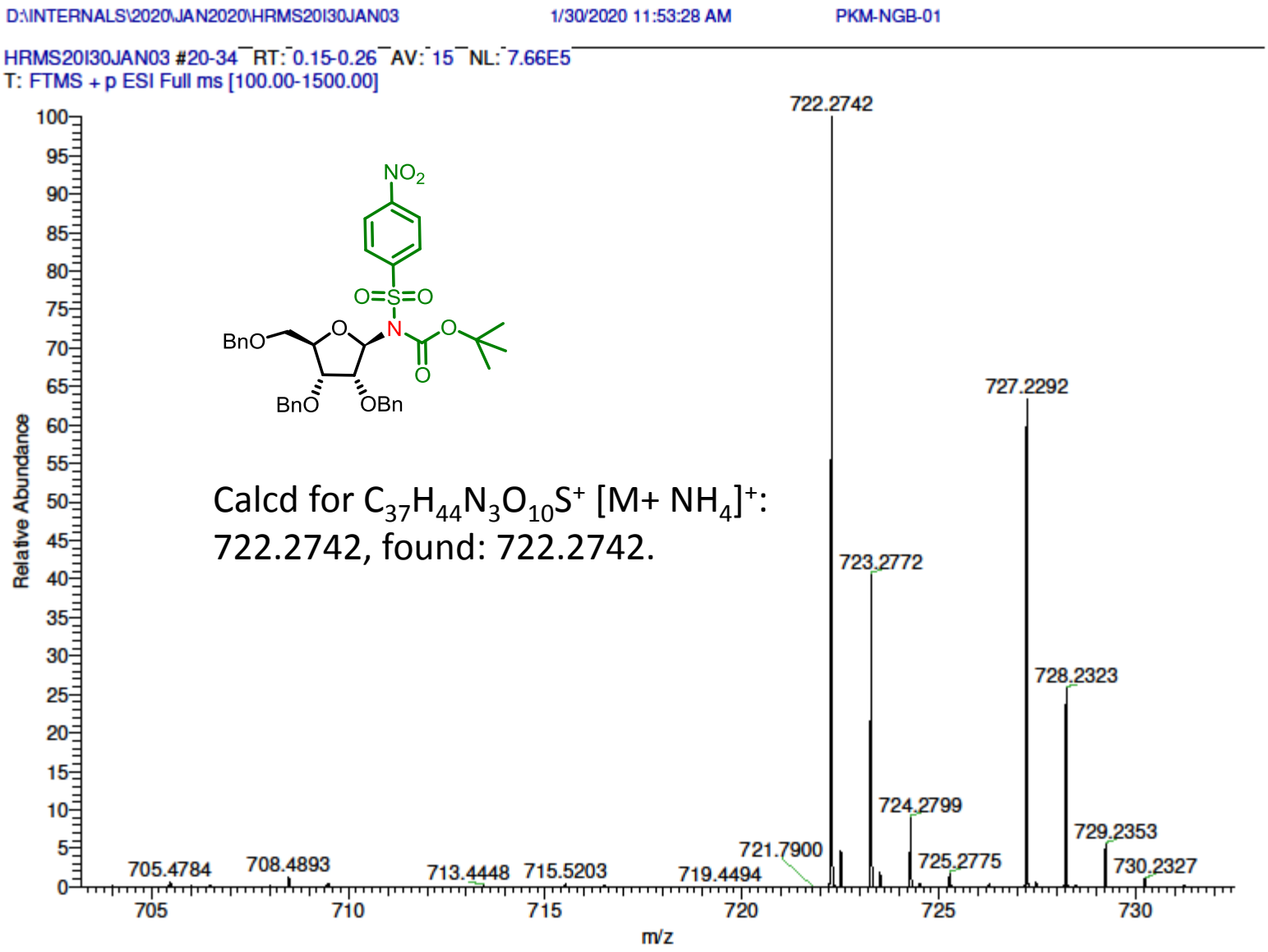
^{1}H NMR spectrum of **3x** (400 MHz, $CDCl_3$)



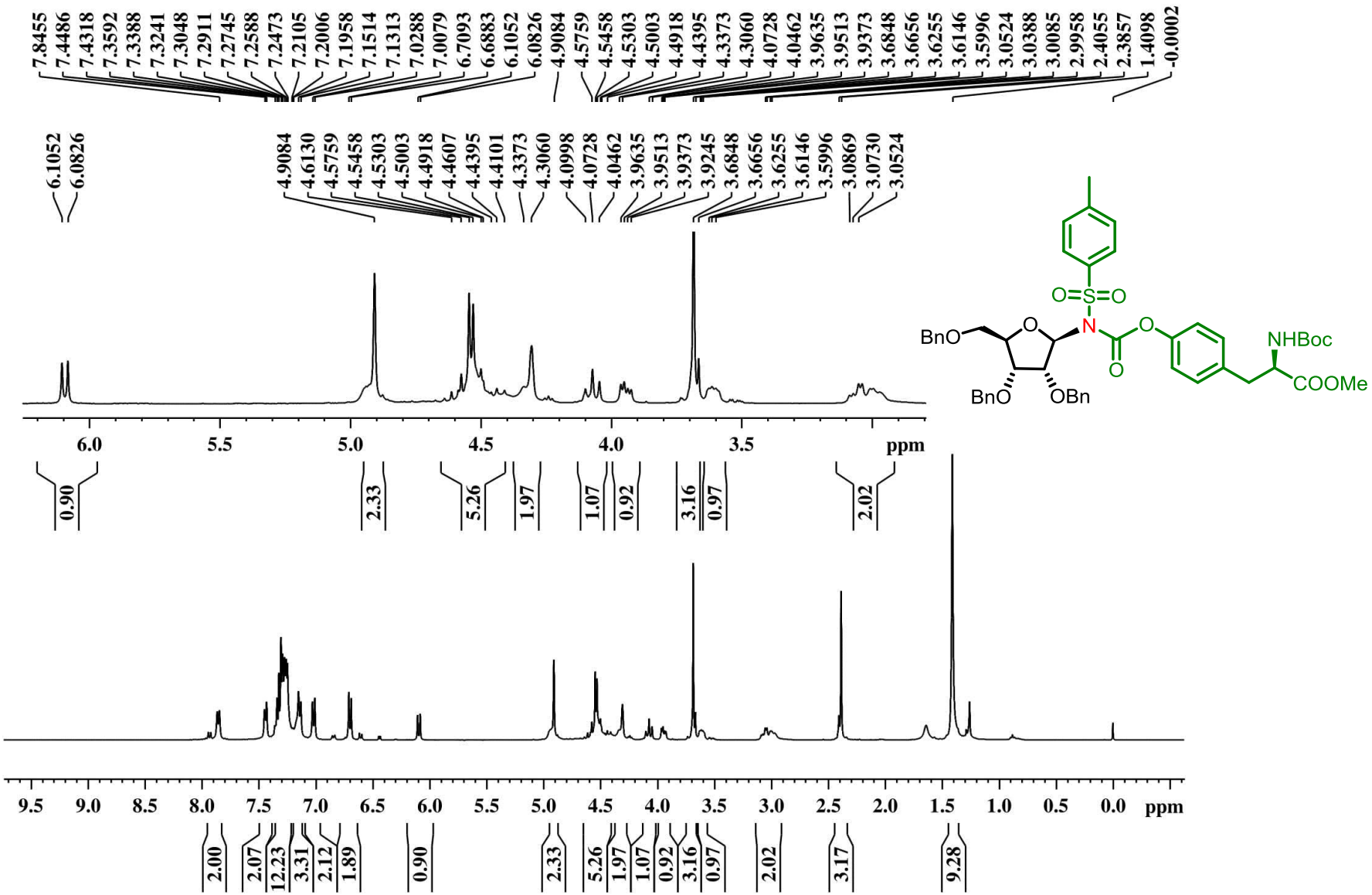
^{13}C NMR spectrum of **3x** (100 MHz, MHz, $CDCl_3$)



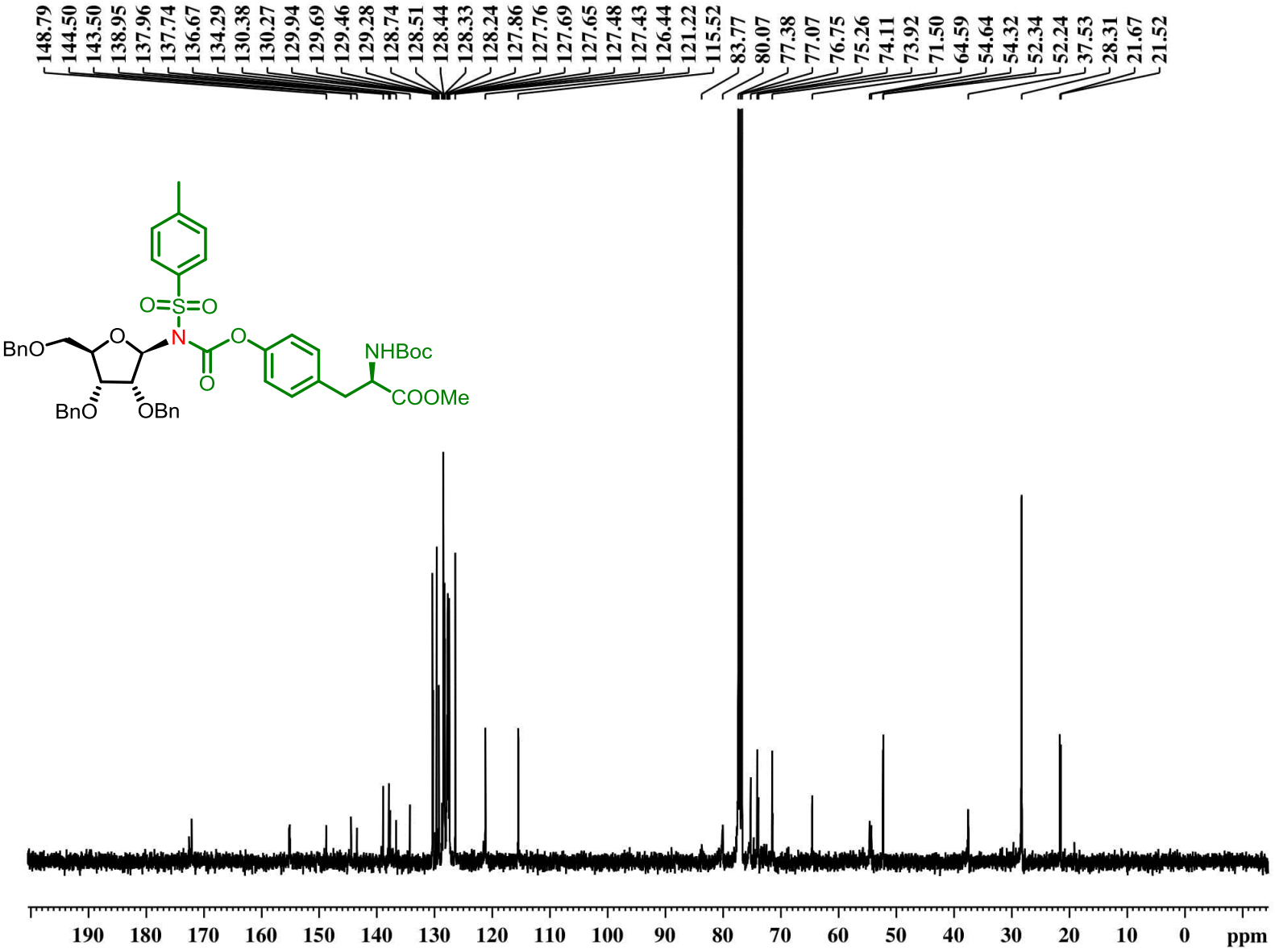
2D HSQC spectrum of **3x** ($CDCl_3$).


D:\INTERNALS\2020\JAN2020\HRMS20I30JAN03
1/30/2020 11:53:28 AM
PKM-NGB-01
HRMS20I30JAN03 #20-34 RT: 0.15-0.26 AV: 15 NL: 7.66E5
T: FTMS + p ESI Full ms [100.00-1500.00]
NO2
O=S=O
N
O
BnO
BnO
OBn
Calcd for C37H44N3O10S+ [M+ NH4]+:
722.2742, found: 722.2742.
Relative Abundance
m/z
722.2742
727.2292
723.2772
728.2323
724.2799
729.2353
725.2775
730.2327
721.7900
705.4784
708.4893
713.4448
715.5203
719.4494

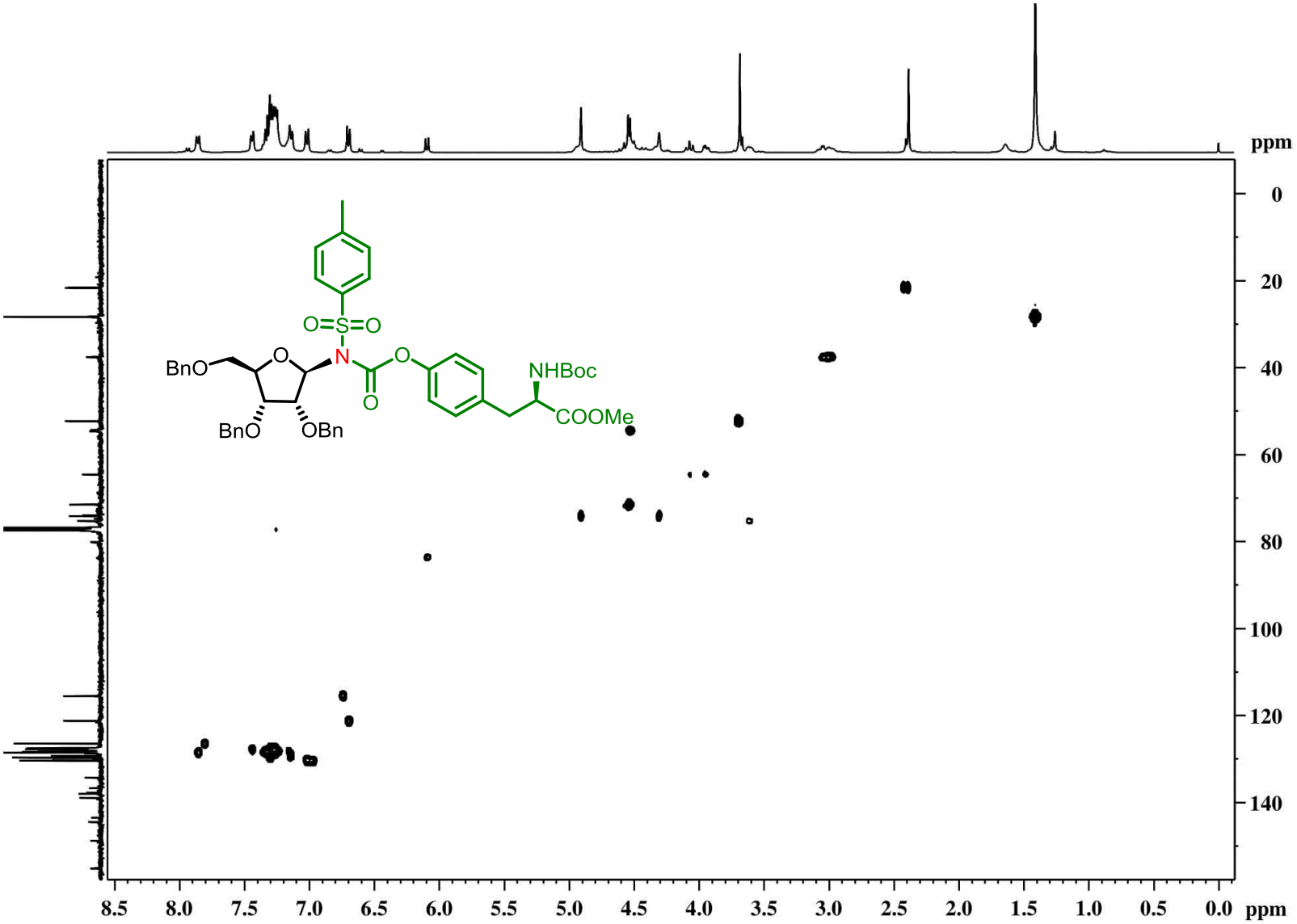
HRMS of **3x**



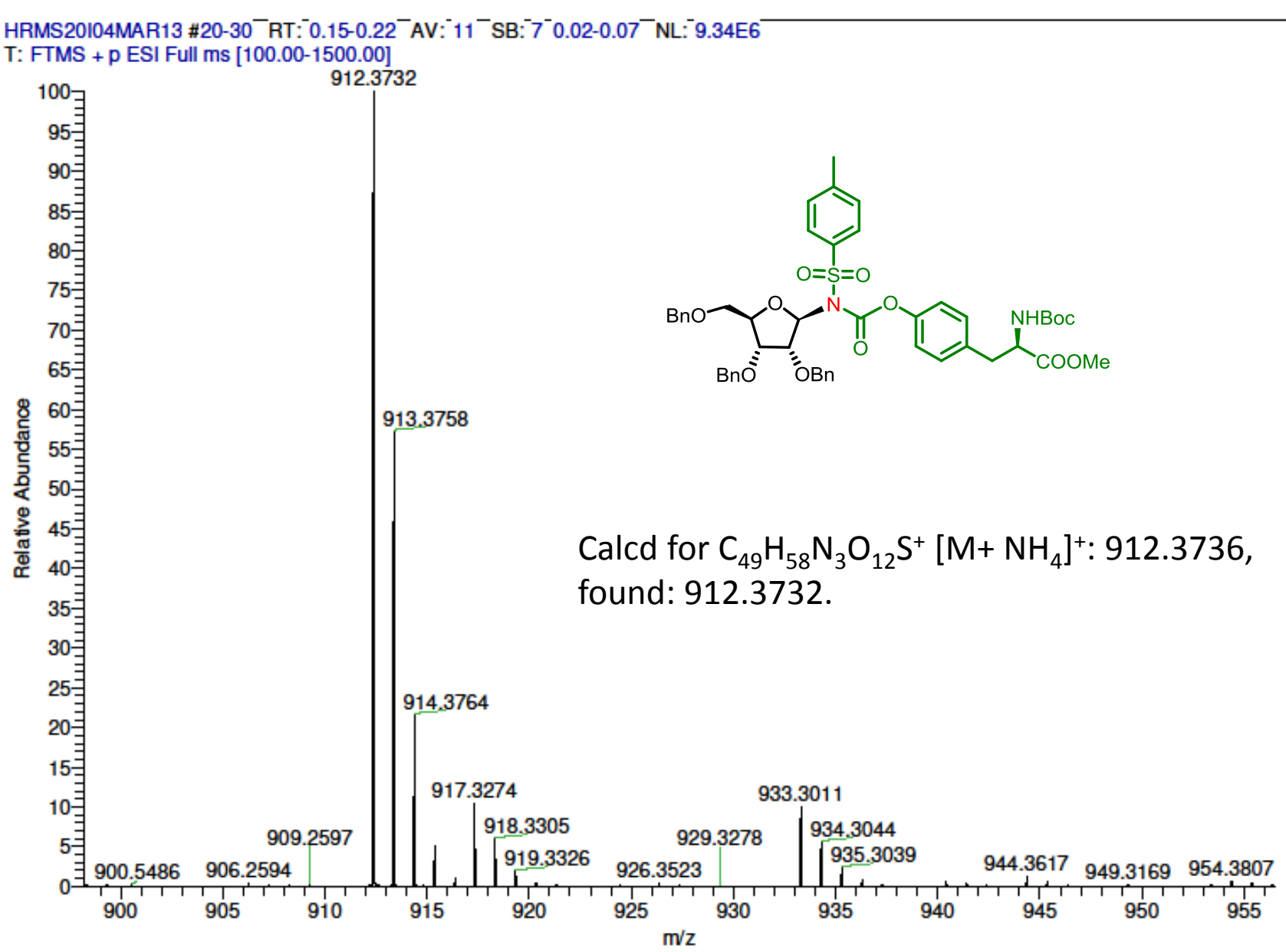
^{1}H NMR spectrum of **3y** (400 MHz, $CDCl_3$)



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

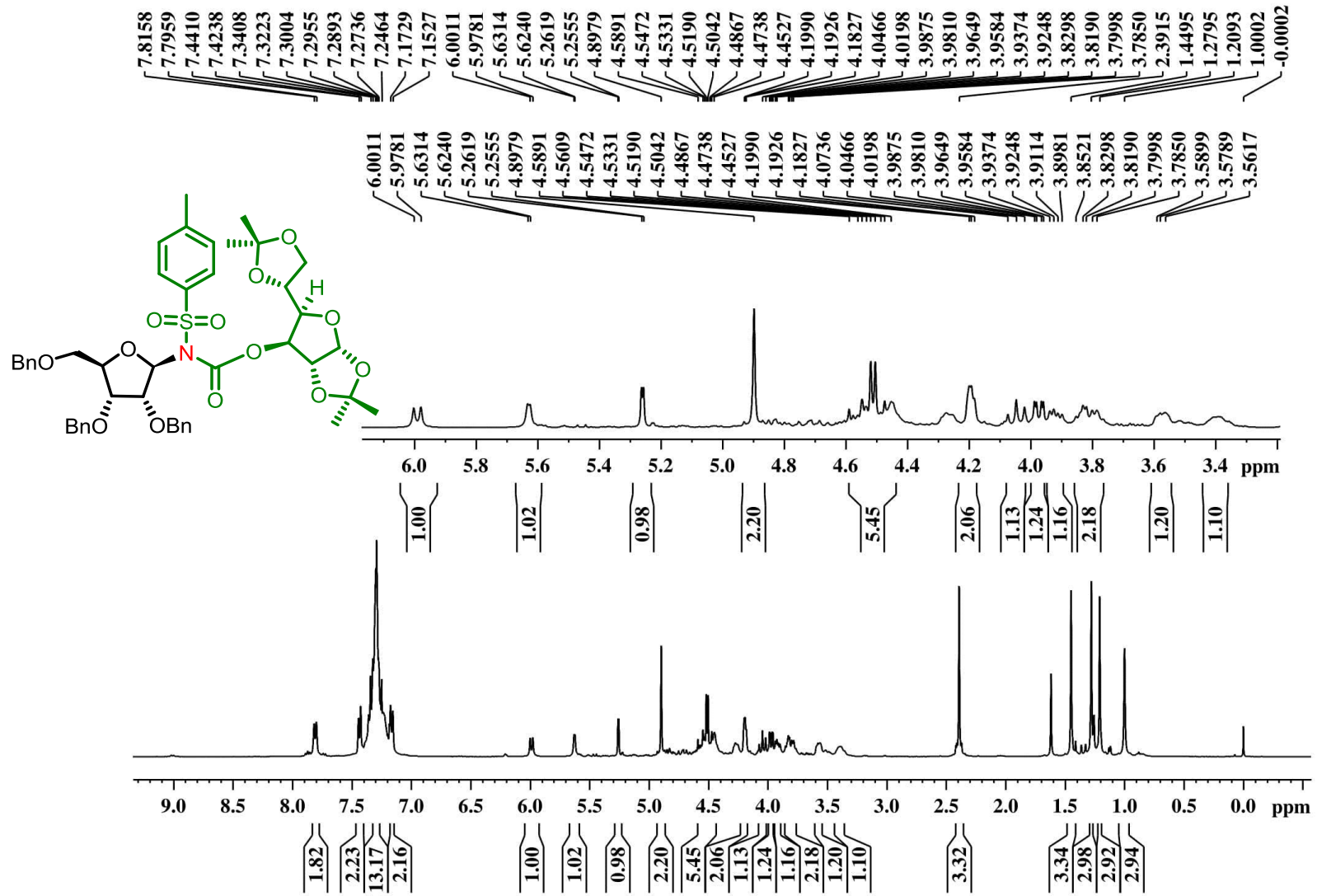


2D HSQC spectrum of **3y** ($CDCl_3$).

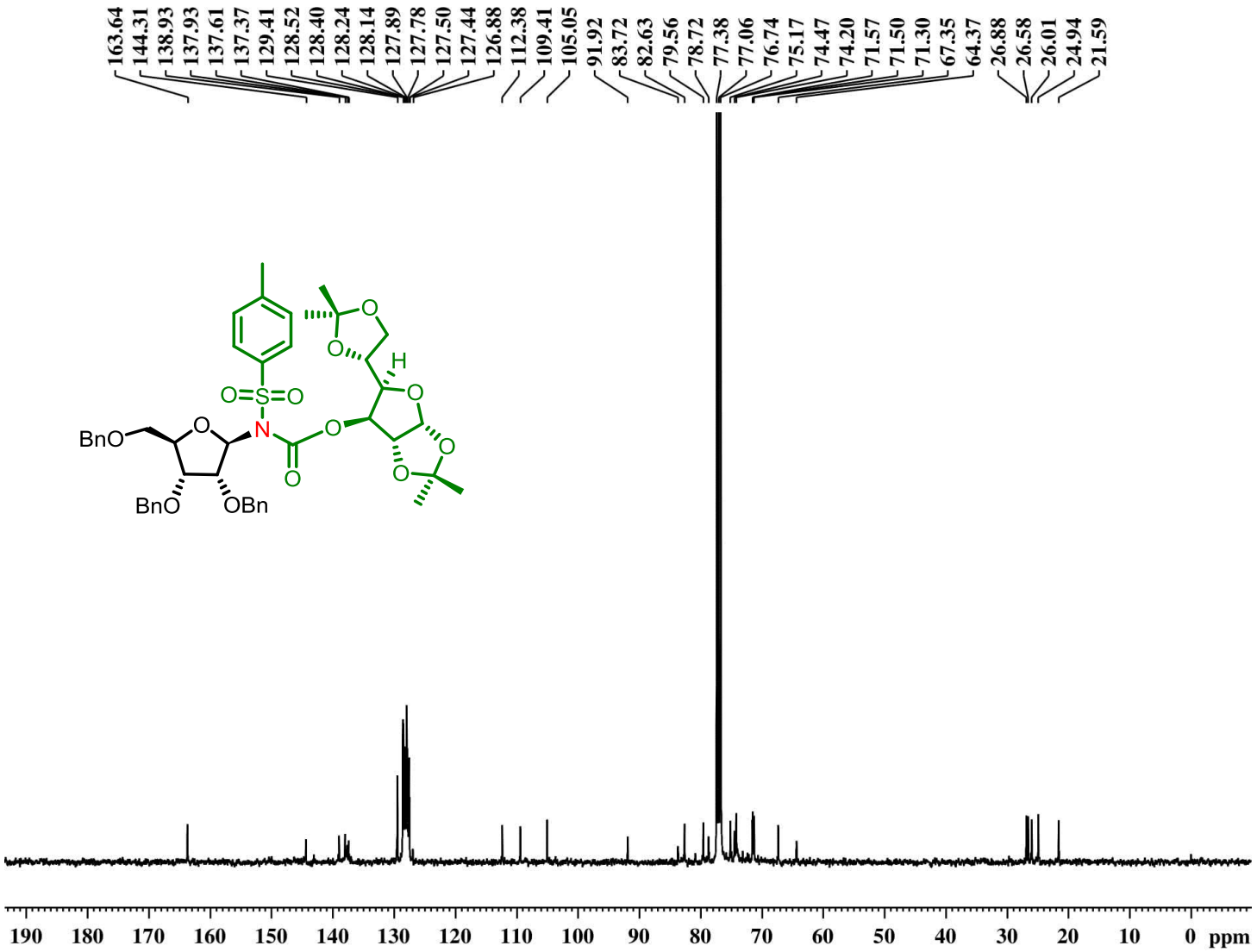


Calcd for $C_{49}H_{58}N_3O_{12}S^+$ [M+ NH_4]$^+$: 912.3736, found: 912.3732.

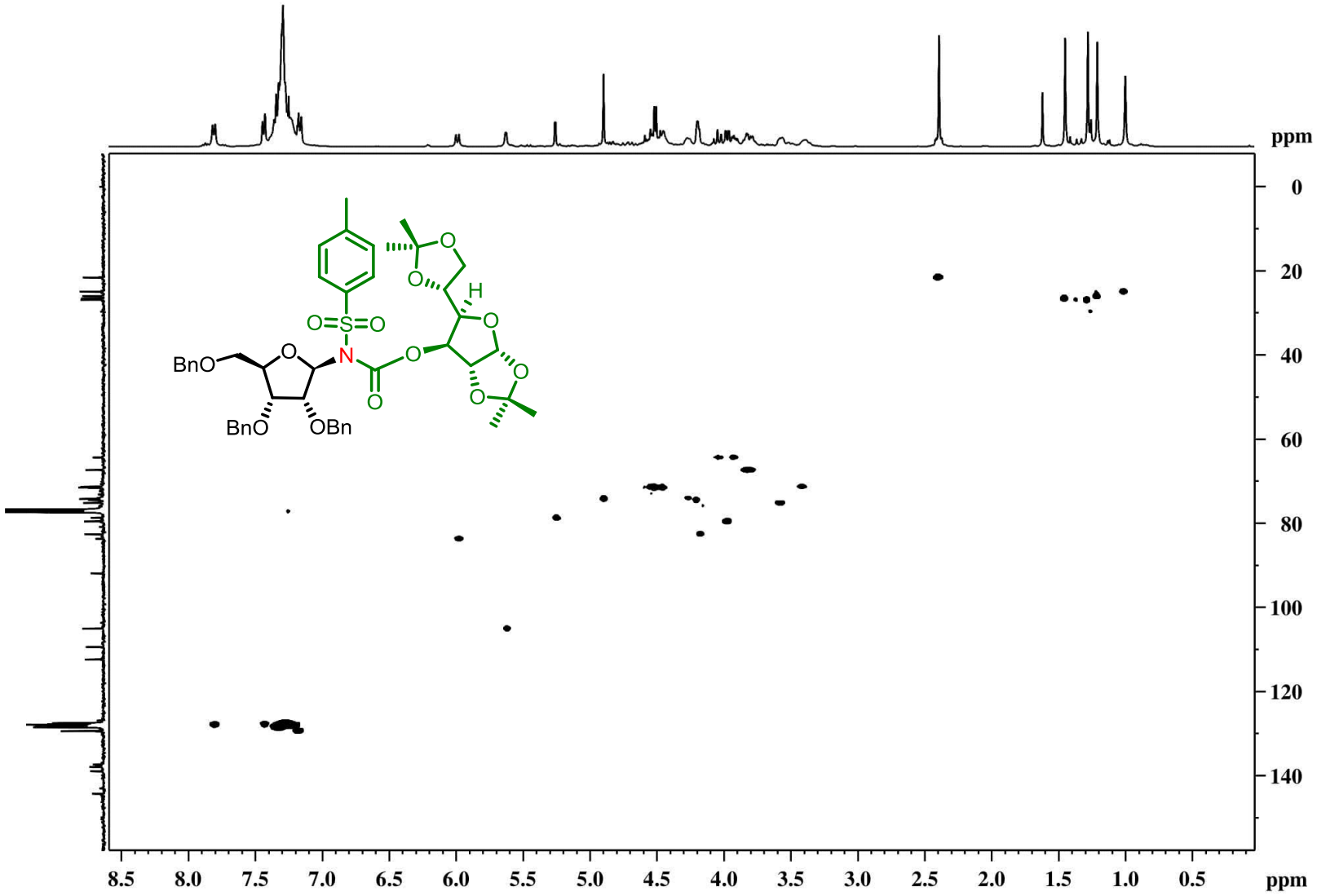
HRMS of **3y**



^{1}H NMR spectrum of **3z** (400 MHz, $CDCl_3$)



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

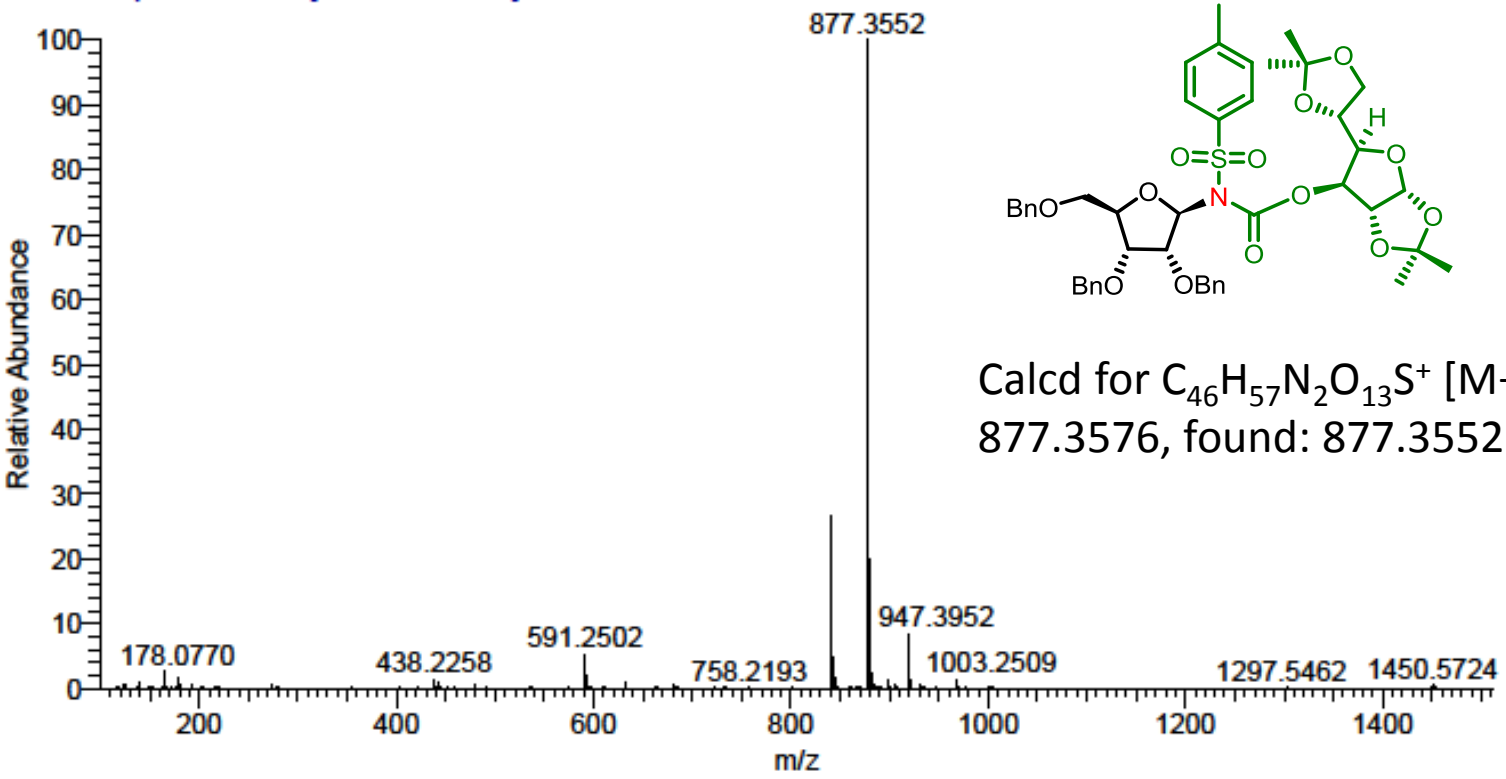


2D HSQC spectrum of **3z** ($CDCl_3$).

SAIF [HRMS Report]

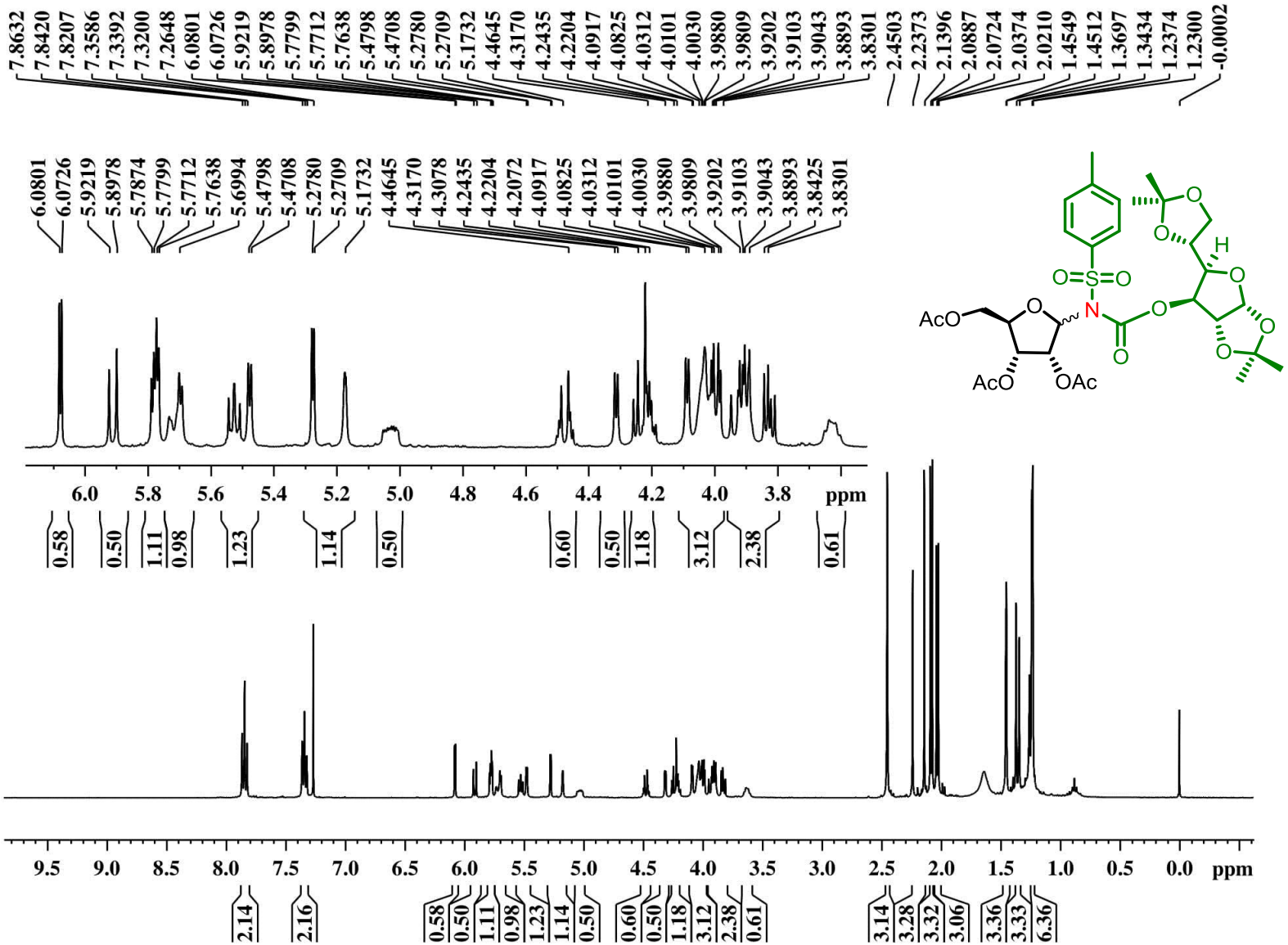
Data File:	HRMS20I19AUG01	Original Data Path:	D:\INTERNAL NEW\2020\Aug 2020
Sample ID:	PKM-TRG-01	Sample Name:	
Acquisition Date:	08/19/20 10:52:14 AM	Run Time(min):	0.00
Vial:	CStk1-01:01	Injection Volume(µl):	1.00

HRMS20I19AUG01 #13-26 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 1.12E7
T: FTMS + p ESI Full ms [100.00-1500.00]

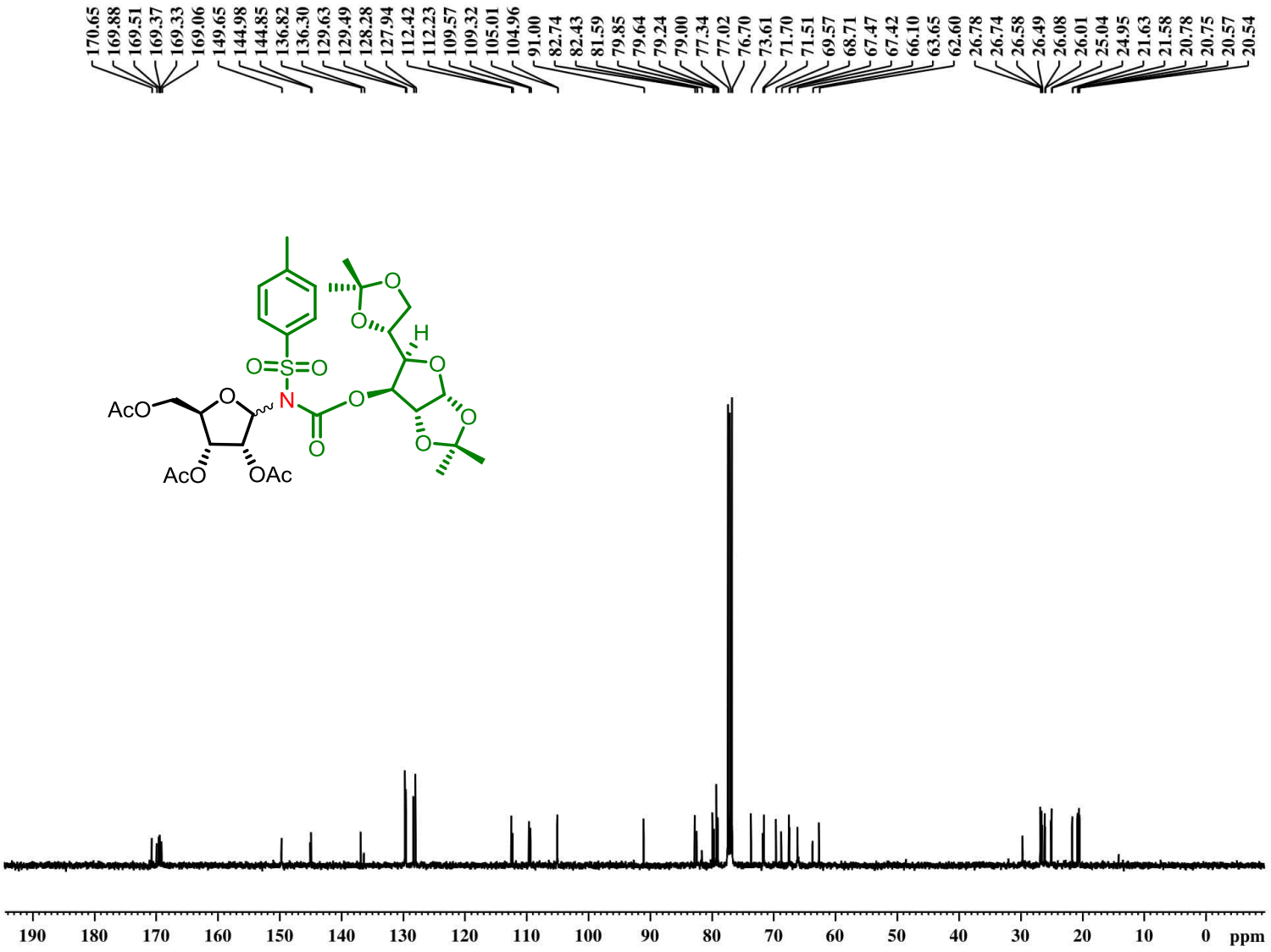


Calcd for $C_{46}H_{57}N_2O_{13}S^+$ $[M+ NH_4]^+$: 877.3576, found: 877.3552.

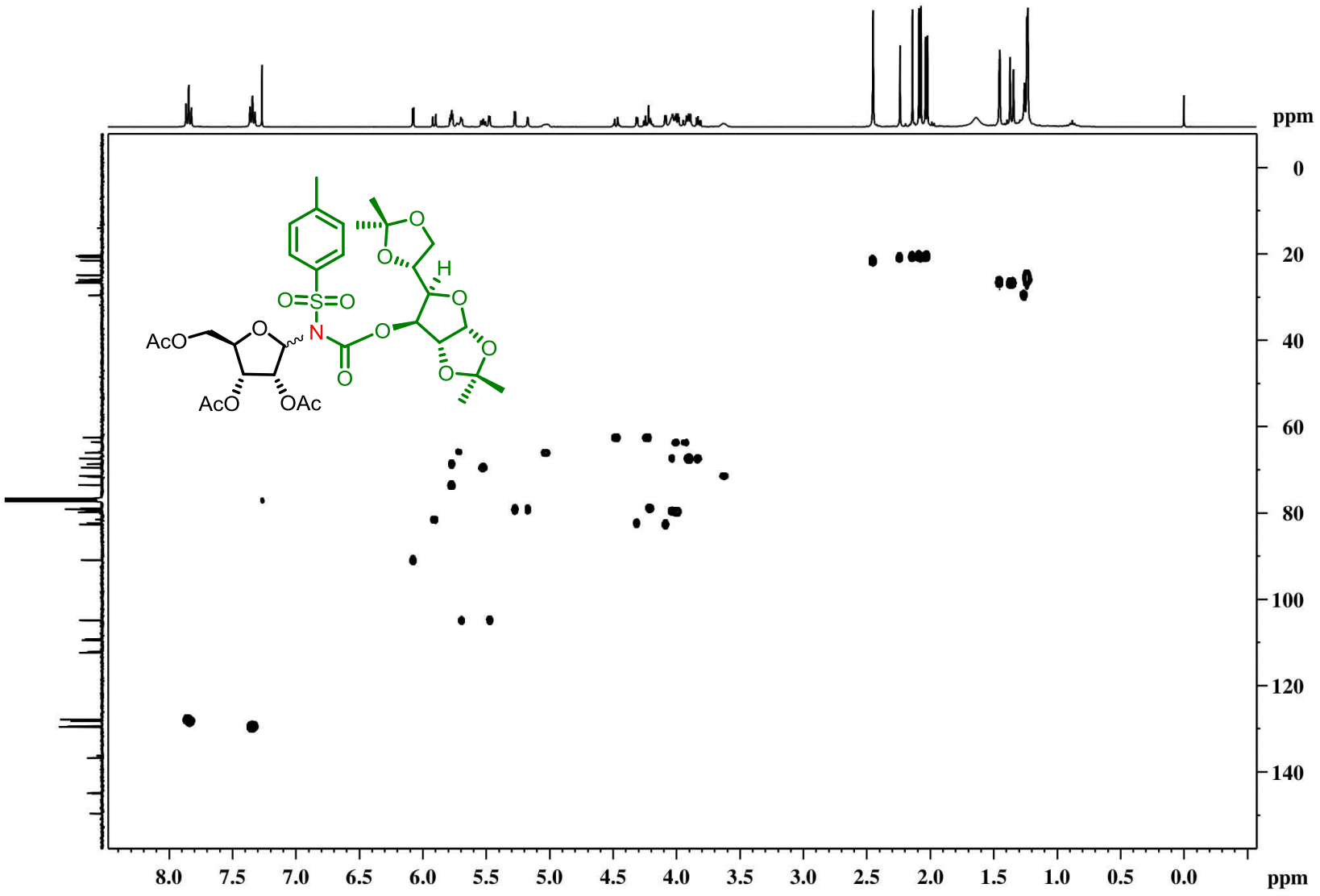
HRMS of **3z**



^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)



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

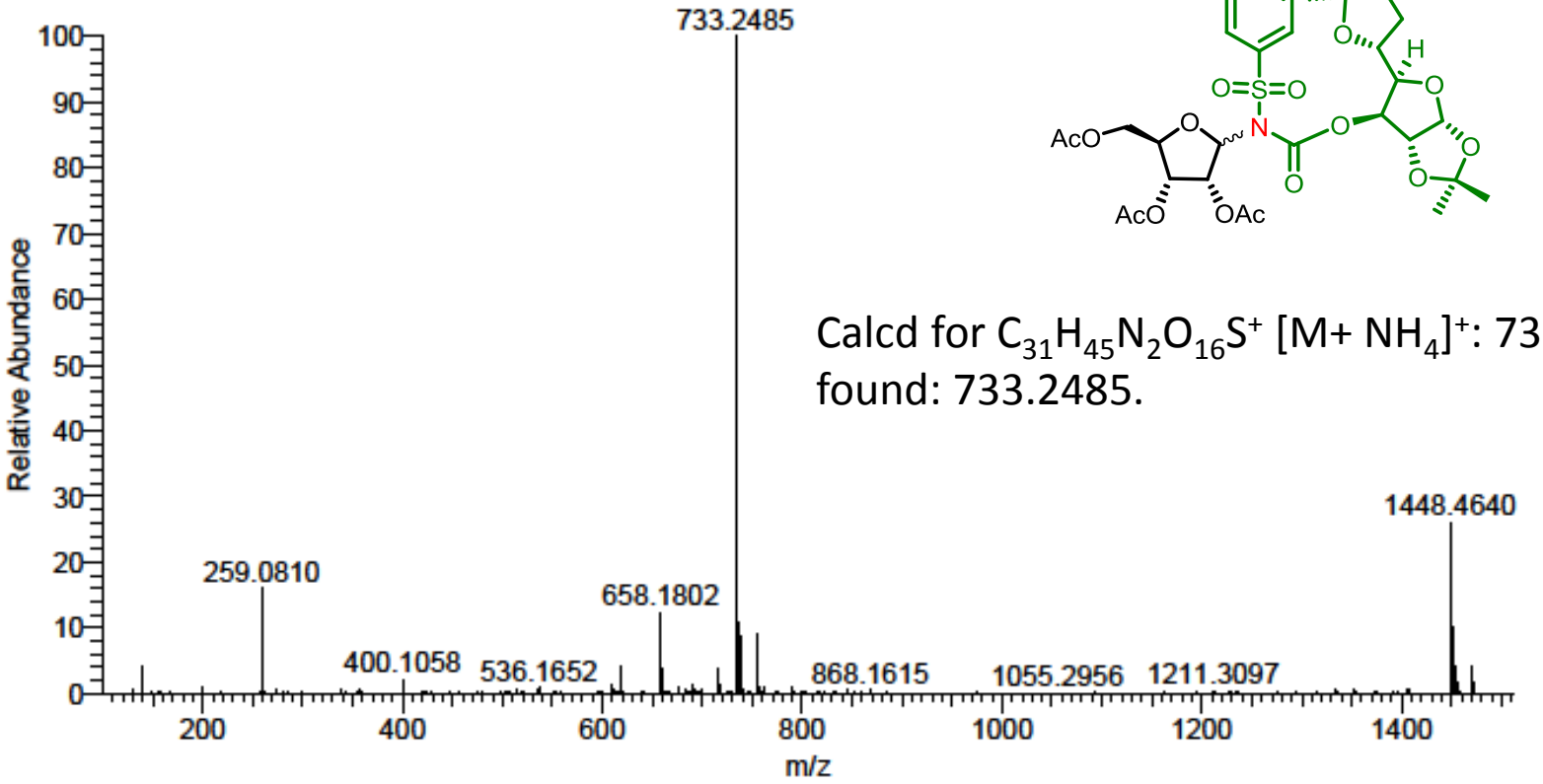


2D HSQC spectrum of **3aa**($CDCl_3$).

SAIF [HRMS Report]

Data File:	HRMS20I18MAR15	Original Data Path:	D:\INTERNALS\2020\Mar2020
Sample ID:	PKM-ARG-01	Sample Name:	
Acquisition Date:	03/18/20 12:00:57 PM	Run Time(min):	0.00
Vial:	CStk1-01:15	Injection Volume(µl):	1.00

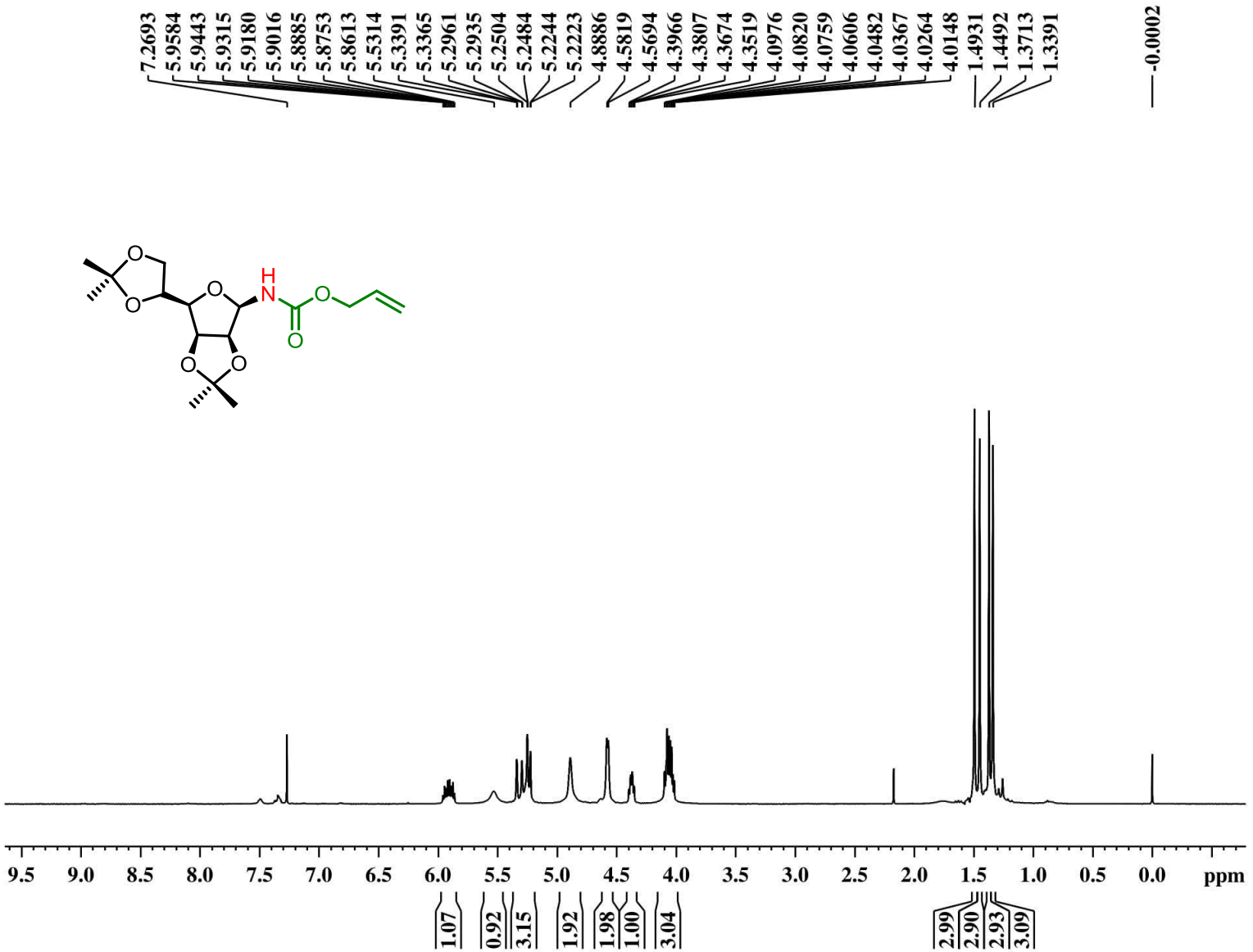
HRMS20I18MAR15 #15-28 RT: 0.11-0.21 AV: 14 SB: 1 0.01 NL: 1.28E7
T: FTMS + p ESI Full ms [100.00-1500.00]



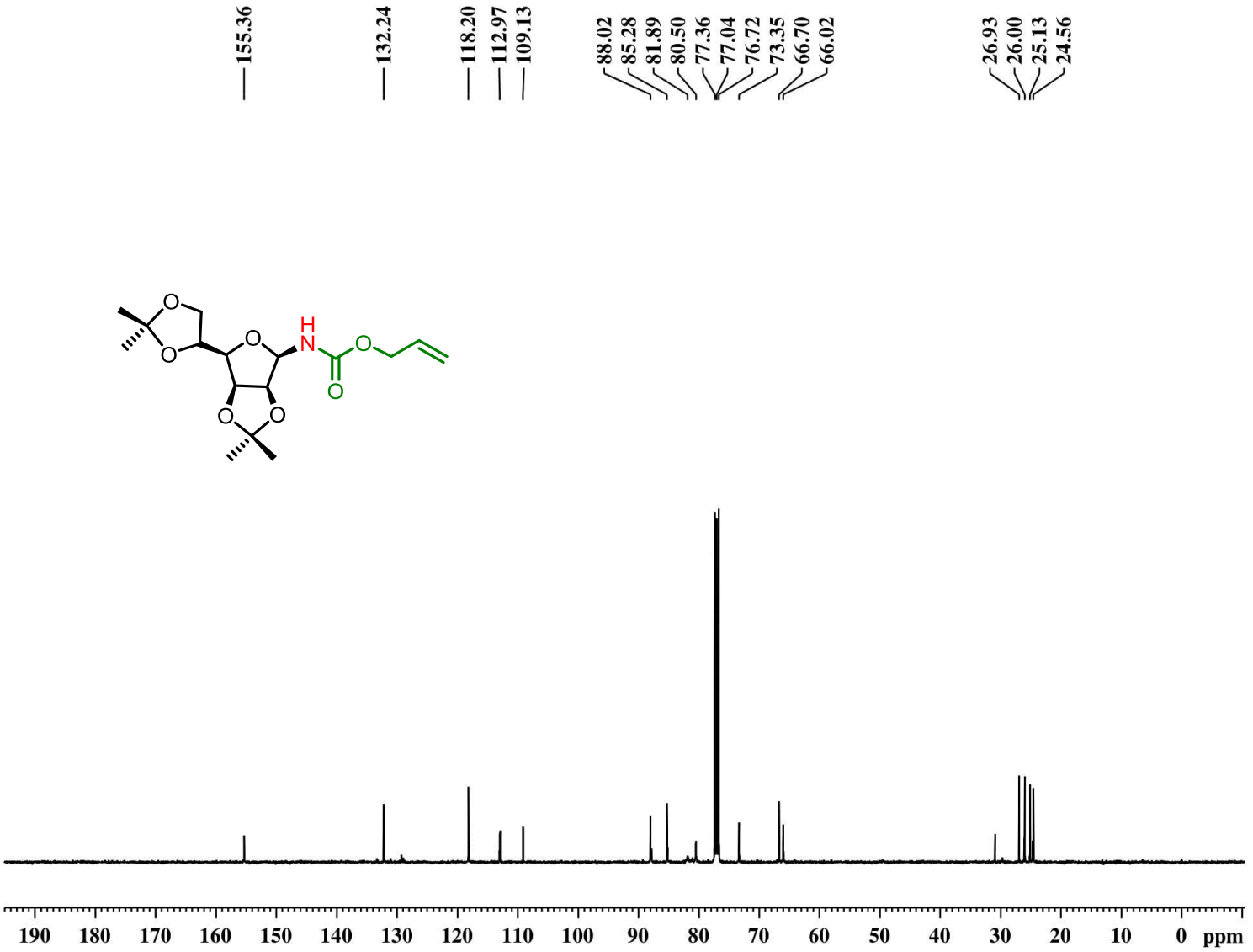
Calcd for $C_{31}H_{45}N_2O_{16}S^+$ $[M+ NH_4]^+$: 733.2484, found: 733.2485.

HRMS of **3aa**

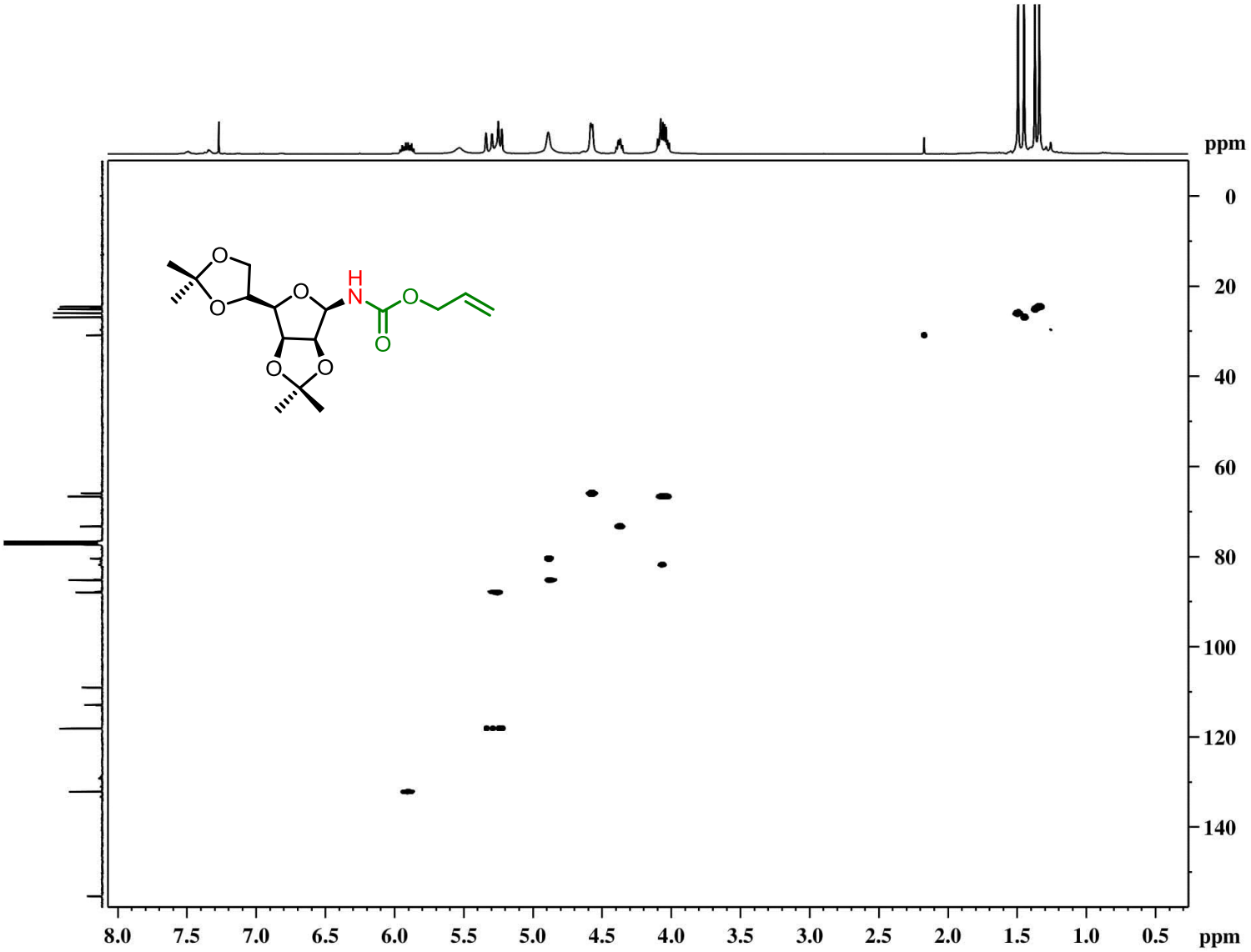
8. Spectra Data, HRMS of compounds **4, 5, 6**



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



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

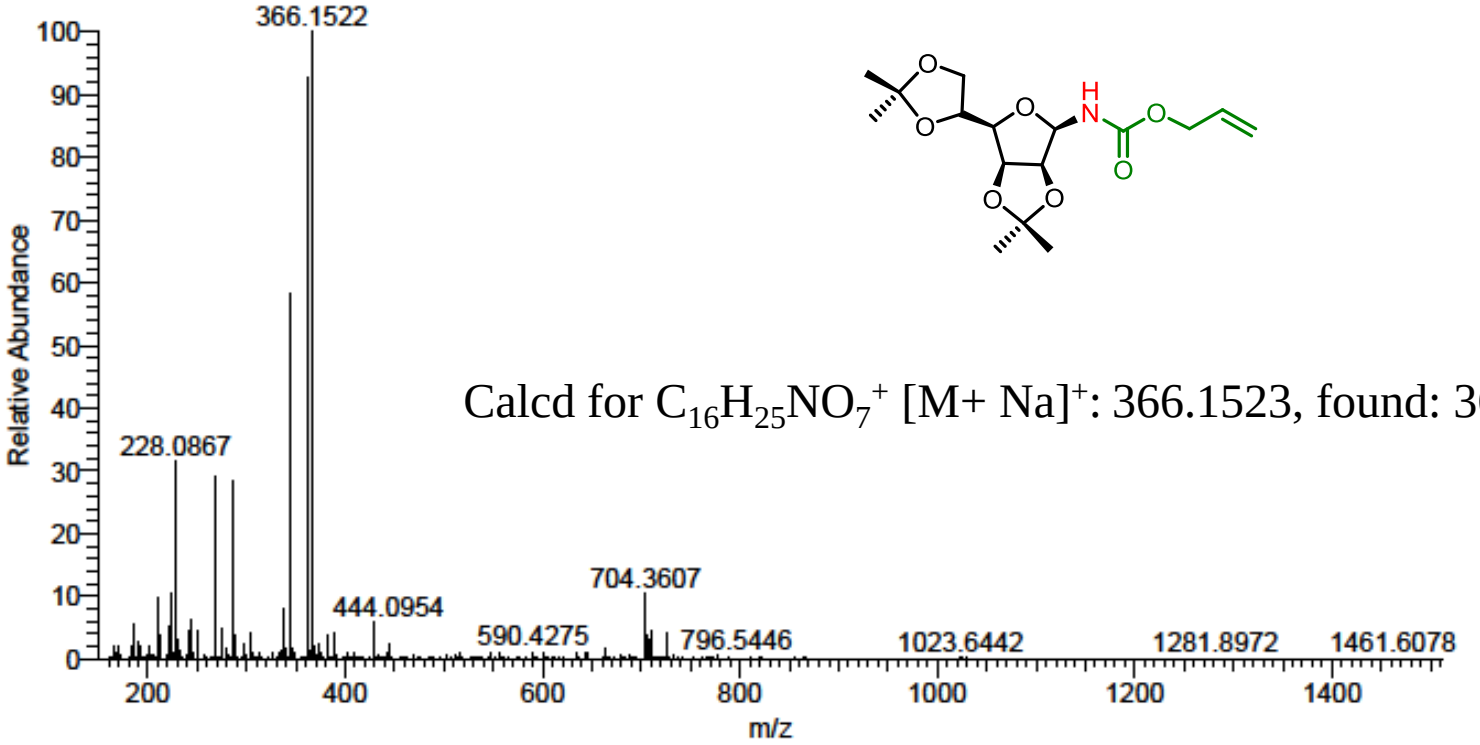


2D HSQC spectrum of **4** ($CDCl_3$).

SAIF [HRMS Report]

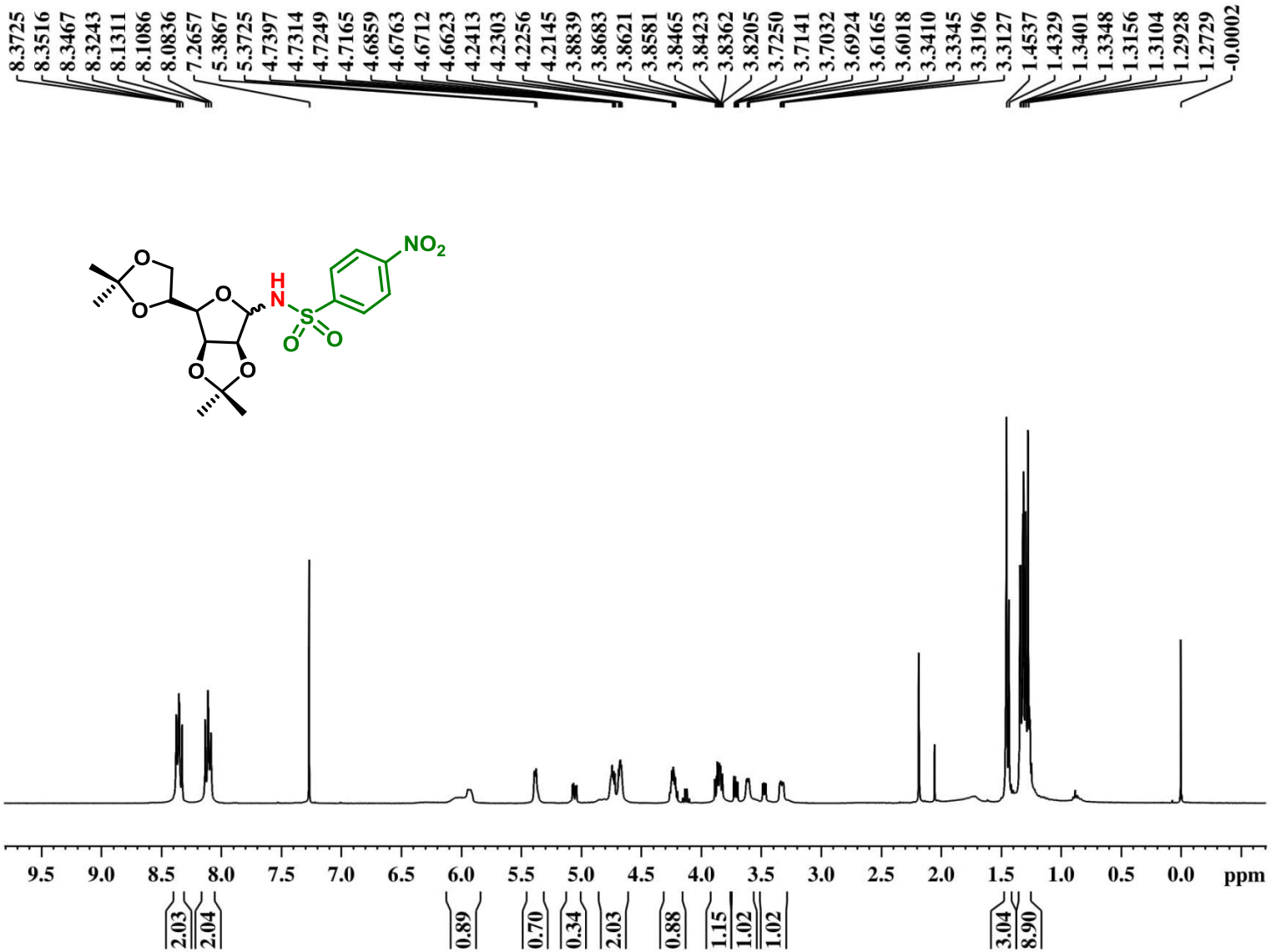
Data File:	HRMS20I01DEC09	Original Data Path:	D:\INTERNAL NEW\2020\DEC 2020
Sample ID:	PKM-DP-05	Sample Name:	
Acquisition Date:	12/01/20 01:01:22 PM	Run Time(min):	0.00
Vial:	CStk1-01:9	Injection Volume(µl):	1.00

HRMS20I01DEC09 #29-61 RT: 0.25-0.50 AV: 33 SB: 1 0.00 NL: 1.18E6
T: FTMS + p ESI Full ms [150.00-1500.00]

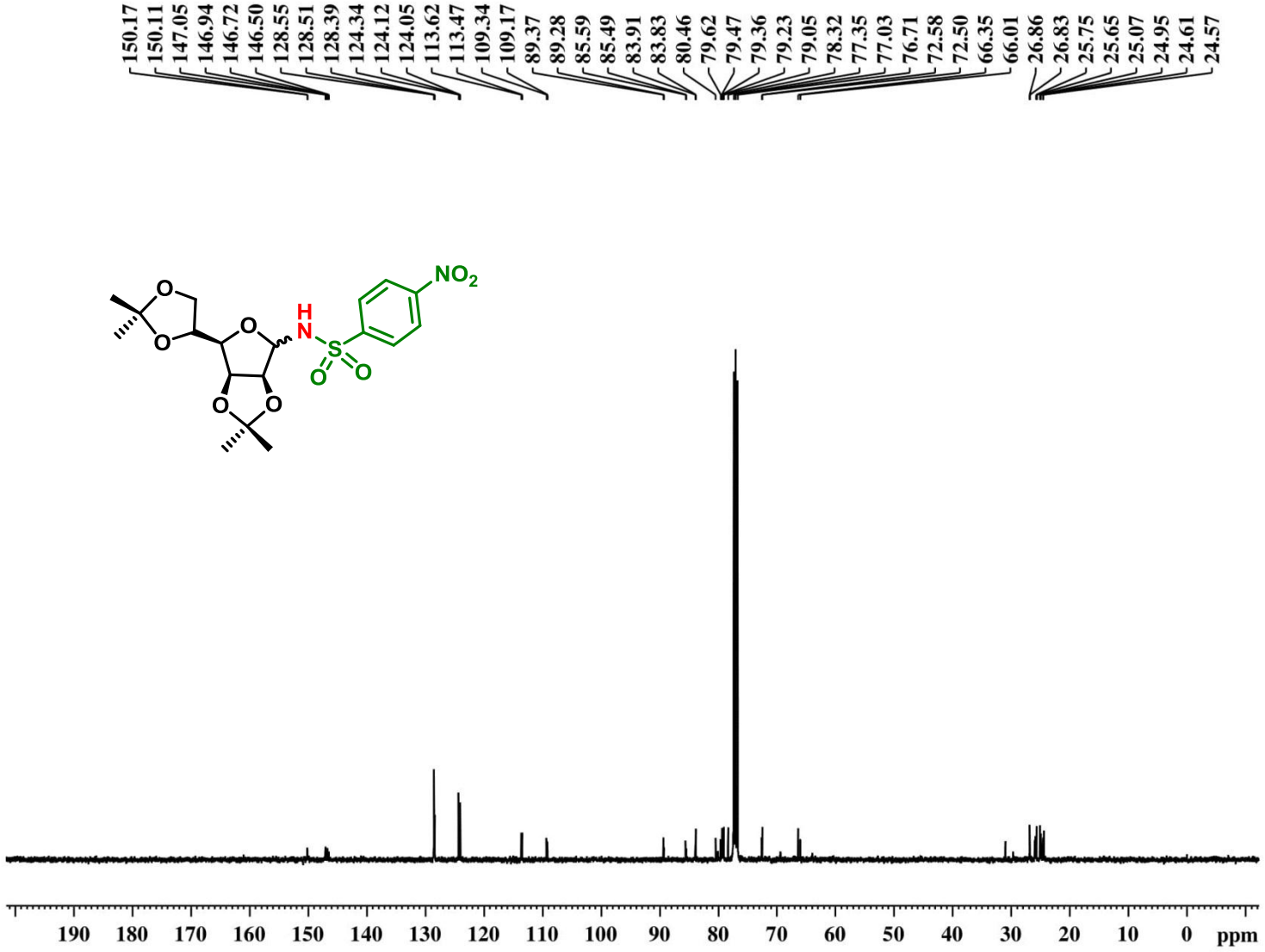


Calcd for $C_{16}H_{25}NO_7^+$ [M+ Na]$^+$: 366.1523, found: 366.1522.

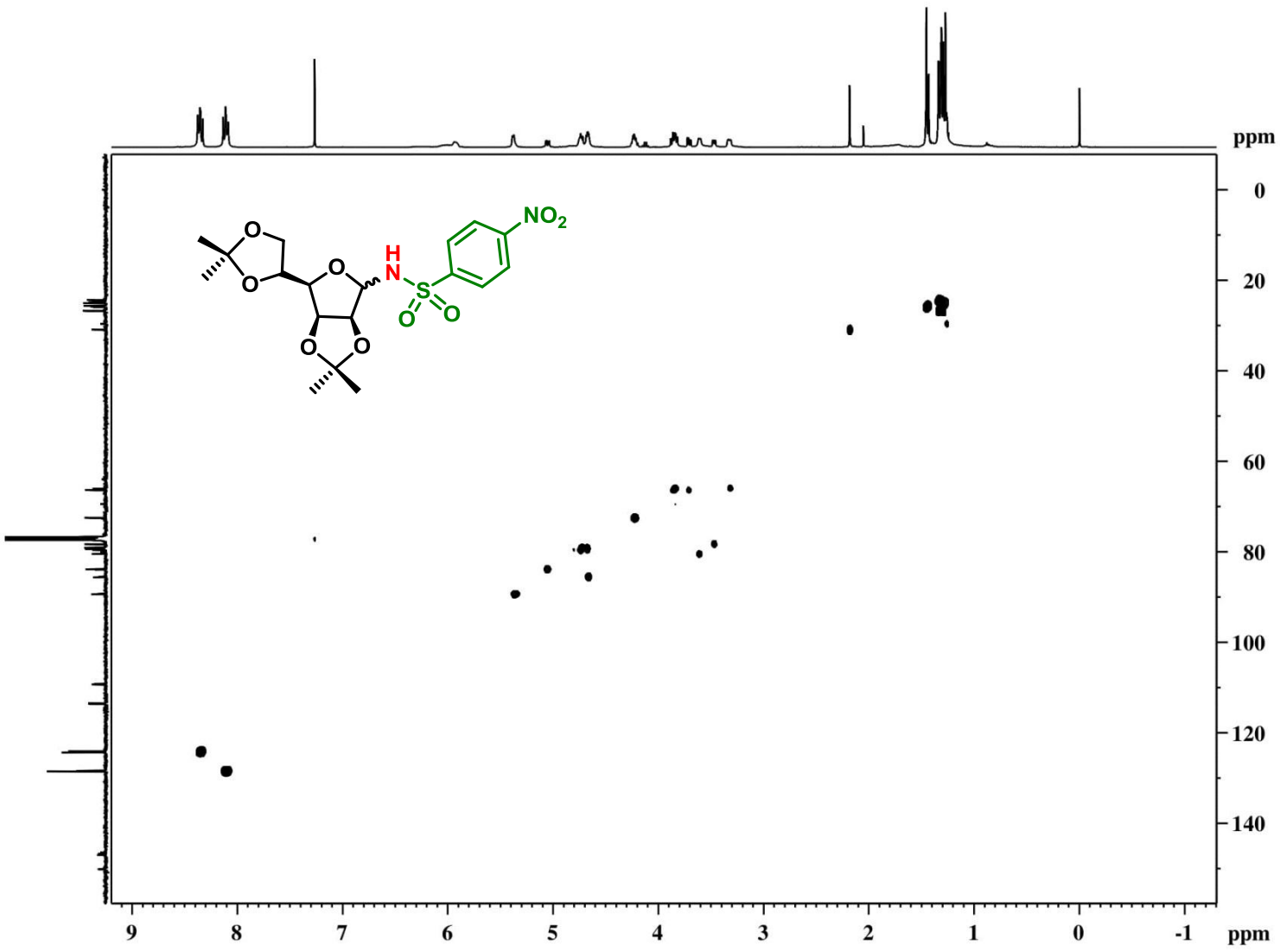
HRMS of **4**



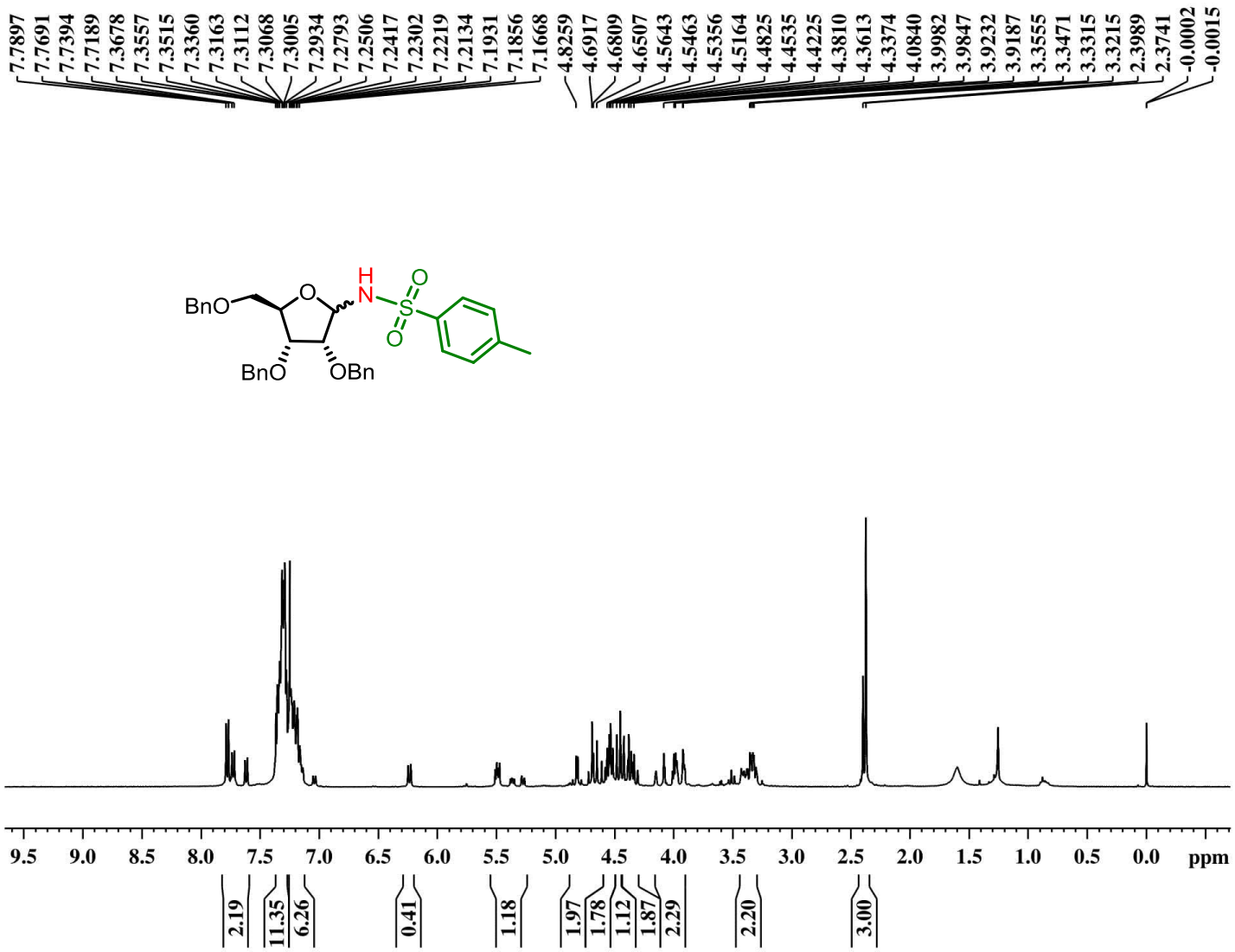
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)



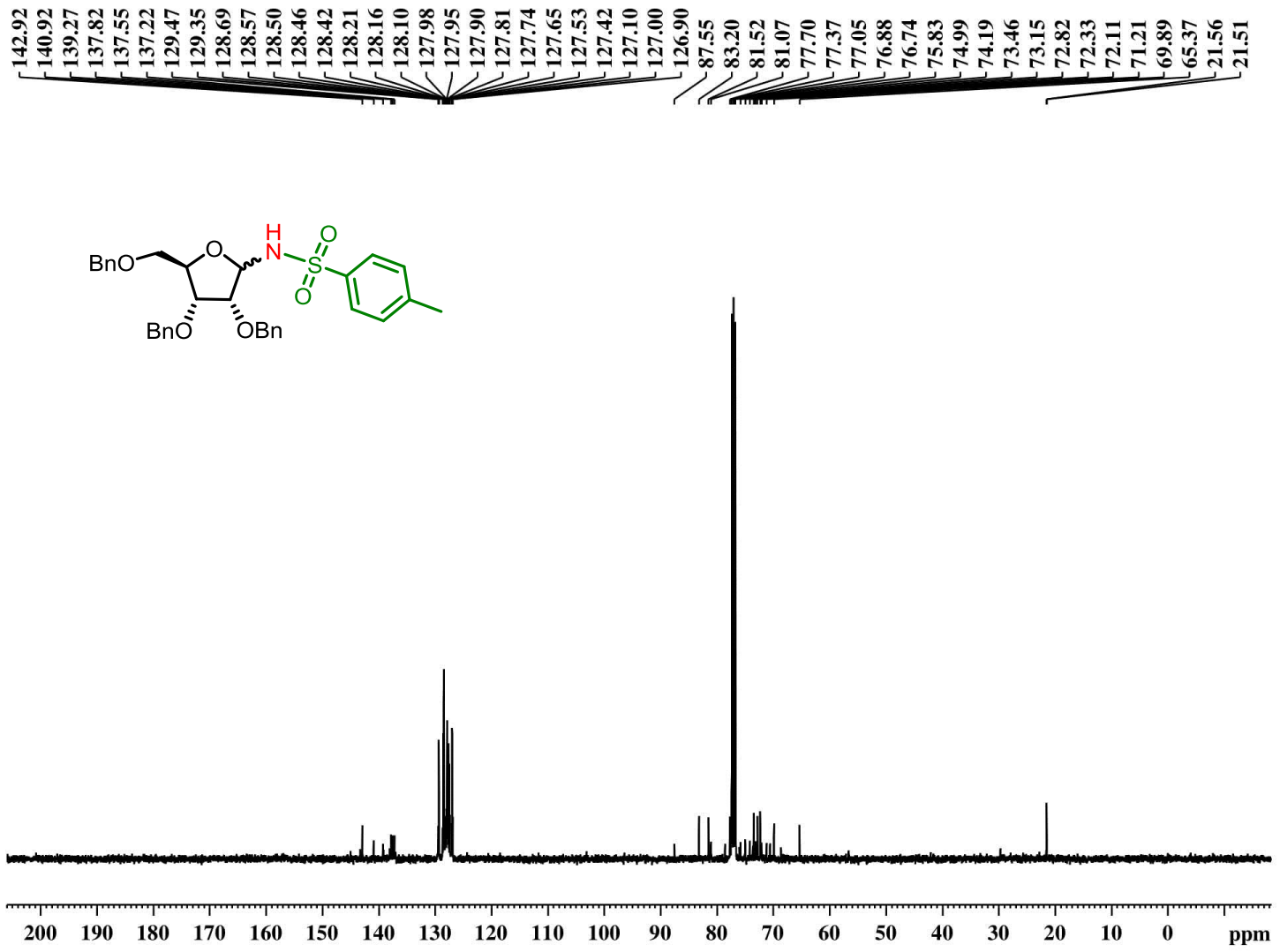
^{13}C NMR spectrum of **5** (100 MHz, MHz, $CDCl_3$)



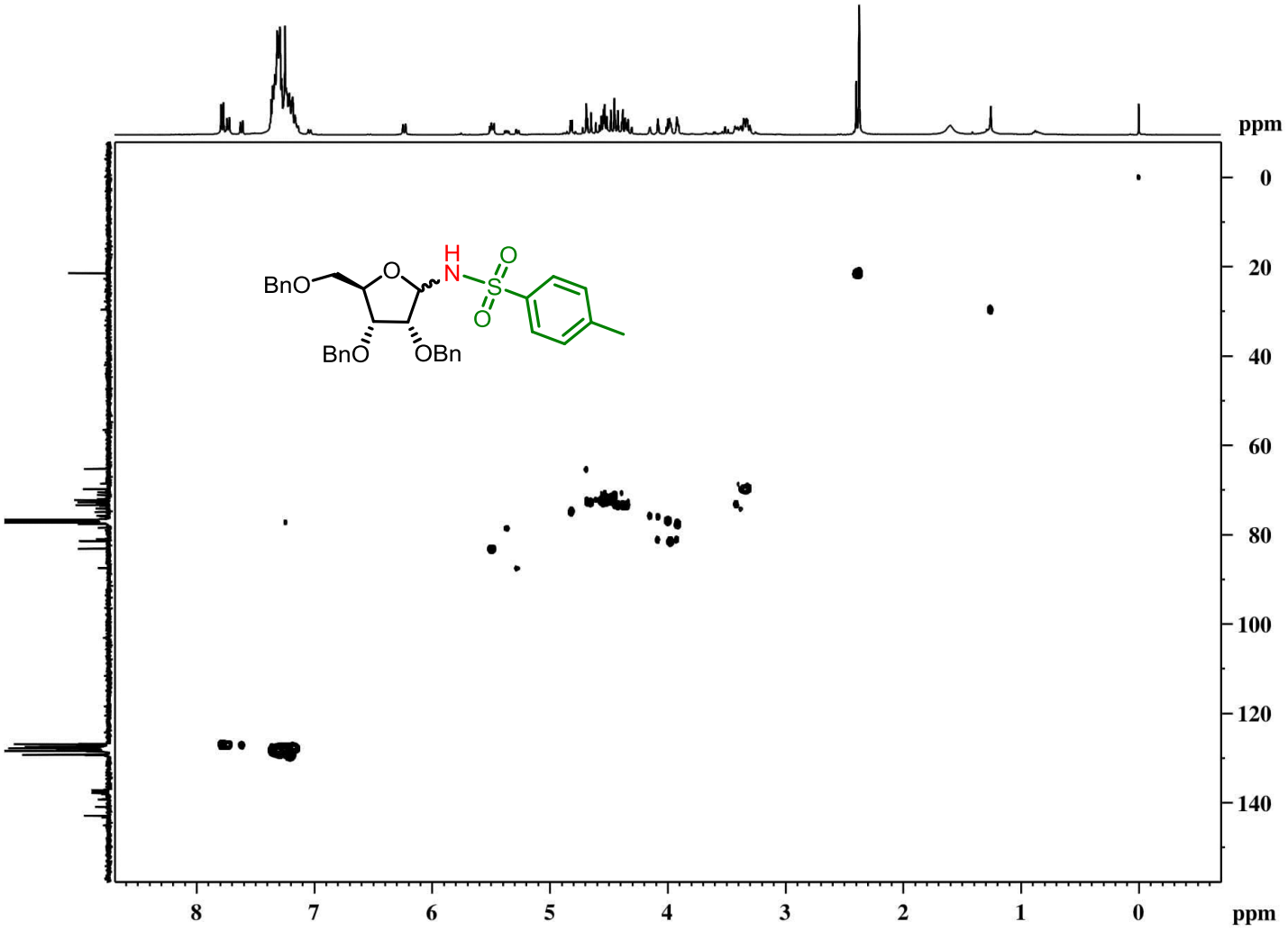
2D HSQC spectrum of **5**($CDCl_3$).



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



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

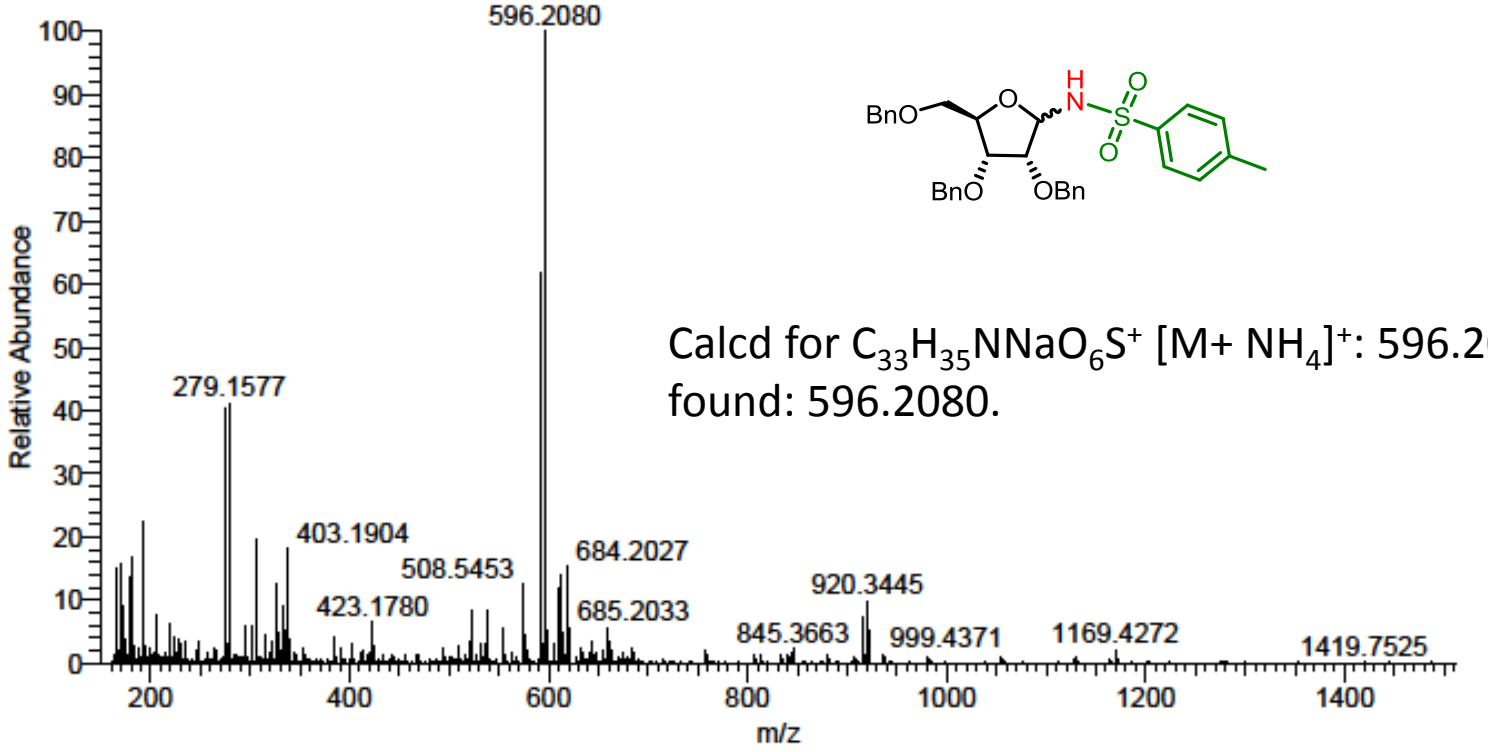


2D HSQC spectrum of **6** ($CDCl_3$).

SAIF [HRMS Report]

Data File:	HRMS20I09NOV03	Original Data Path:	D:\INTERNAL NEW\2020\NOV 2020
Sample ID:	PKM-DP-03	Sample Name:	
Acquisition Date:	11/09/20 11:00:45 AM	Run Time(min):	0.00
Vial:	CStk1-01:3	Injection Volume(µl):	1.00

HRMS20I09NOV03 #13-24 RT: 0.11-0.21 AV: 12 SB: 1 0.00 NL: 6.86E4
T: FTMS + p ESI Full ms [150.00-1500.00]



Calcd for $C_{33}H_{35}NNaO_6S^+$ $[M+ NH_4]^+$: 596.2077, found: 596.2080.

HRMS of **6**