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Solid phase synthesis of *C*-terminal glycopeptides via oxime resin aminolysis

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I. Experimental Section

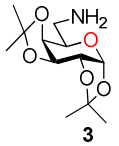
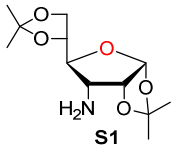
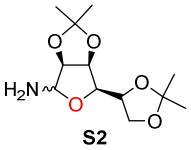
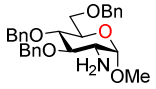
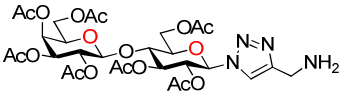
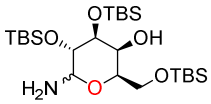
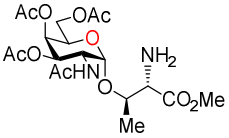
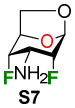
General Methods

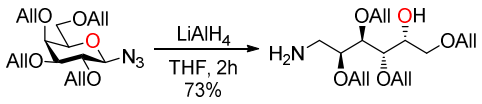
All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Methylene chloride (CH_2Cl_2) and tetrahydrofuran (THF) were purified using a Vacuum Atmospheres Inc. Solvent Purification System. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. 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 visualizing agent and charring with a solution of 3 g of PhOH and 5 mL of H_2SO_4 in 100 mL of EtOH, followed by heating with a heatgun. SiliaFlash® P60 40-63 µm (230-400 mesh) was used for flash column chromatography. NMR spectra were recorded with an Agilent DD2 500 MHz spectrometer and calibrated using residual undeuterated solvent (Chloroform-*d*: ^{1}H δ = 7.26 ppm, ^{13}C δ = 77.16 ppm) as an internal reference. Coupling constants (*J*) are reported in Hertz (Hz), and the following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q= quartet, p = quintet, m = multiplet, br = broad. Assignments of NMR signals were made by homonuclear (COSY) and heteronuclear (HSQC, HMBC, HOESY, 19F) two dimensional correlation spectroscopy. Infrared spectra were recorded using an ABB Bomem MB-Series Arid Zone FT-IR MB-155 Spectrometer. The absorptions are given in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were measured with an Agilent 6210 LC Time of Flight mass spectrometer in electrospray mode. Either protonated molecular ions $[M + nH]^{n+}$, sodium adducts $[M + Na]^+$ or ammonium adducts $[M + NH_4]^+$ were used for empirical formula confirmation. Optical rotations were measured with a JASCO DIP-360 digital polarimeter, and are reported in units of 10^{-1} (deg cm^2 g^{-1}). Oxime resin (1.1 mmol/g), coupling reagents and *N*-Boc-protected amino acids were purchased from Matrix Innovation, Bachem, Advanced Chemtech and GL Shangai.

Preparation of starting glycosylamines

The following amines were prepared according to previous known protocol (see **Table S1**).

Table S1. References used to prepared amines **3**, and **S1–S7**.

Amines	References
 **3**	1
 **S1**	2
 **S2**	3
 **S3**	4
 **S4**	5
 **S5**	6
 **S6**	7
 **S7**	8



S8 **S9**

1-amino-1-deoxy-2,3,4,6-tetra-*O*-allyl-D-galactitol (S9). To a solution of **S8**[9] (138.2 mg, 0.393 mmol, 1 equiv) in THF (4.62 mL) at 0 °C, was added $LiAlH_4$ (1 M in THF, 0.43 mL, 0.433 mmol, 1,1 equiv) and the mixture was stirred at 0 °C for 2 h. The mixture was then quenched with the addition of a saturated solution of potassium sodium tartrate tetrahydrate (5 mL) and the mixture was stirred at room temperature for 1 h. The mixture was then extracted with EtOAc (3 × 15 mL). The organic solution was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The obtained crude was purified by flash column chromatography (silica gel, MeOH/CH_2Cl_2, 1:19 → 1:9) to give **S9** as a colorless oil (98.5 mg, 0.287 mmol, 73% yield). R_f = 0.47 (silica, MeOH/CH_2Cl_2, 1:9); $[\alpha]_D^{25}$ = −18.6 (*c* 0.6, $CHCl_3$); IR (ATR, Diamond) ν 3334, 3080, 2923, 2870, 1652, 1077, 922 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 5.99 – 5.85 (m, 4H, OAll), 5.32 – 5.23 (m, 4H, OAll), 5.20 – 5.15 (m, 4H, OAll), 4.24 – 4.02 (m, 6H, OAll), 4.01 (ddt, *J* = 5.5, 2.7, 1.3 Hz, 2H, OAll), 3.96 (td, *J* = 6.3, 2.2 Hz, 1H, H5), 3.71 (t, *J* = 5.1 Hz, 1H, H3), 3.68 – 3.64 (m, 2H, H2, H4), 3.59 (s, 2H, NH_2), 3.53 – 3.51 (m, 2H, H6a, H6b), 3.10 (dd, *J* = 13.3, 5.0 Hz, 1H, H1a), 2.98 (dd, *J* = 13.3, 5.4 Hz, 1H, H1b) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.69, 134.68, 134.66, 134.63 (4C, 4 × OAll), 117.68, 117.65, 117.62, 117.3 (4C, 4 × OAll), 80.1 (1C, C3), 78.6 (1C, C2), 77.6 (1C, C4), 73.4, 73.2, 72.4, 72.2 (4C, 4 × OAll), 71.1 (1C, C6), 69.9 (1C, C5), 41.1 (1C, C1) ppm; HRMS calcd for $C_{18}H_{32}NO_5^+$ 342.2275, found 342.2264.

Preparation of linear peptides

Coupling of the first N-Boc amino acid on oxime resin

1.0 g of oxime resin (1.1 mmol/g) was added to a peptide synthesis vessel. The resin was treated three times with CH_2Cl_2. Amino acid (3.0 equiv, 3.3 mmol) and 6-Cl-HOBt (3.0 equiv, 3.3 mmol) were dissolved in DMF (10 mL) in a 50 mL flask and the mixture was stirred for 10 minutes at 0 °C. DIC (3.0 equiv, 3.3 mmol), DIPEA (6.0 equiv, 6.6 mmol) and DMAP (0.1 equiv, 0.11 mmol) were added and the mixture was introduced into the peptide synthesis vessel and stirred mechanically for 3h. The mixture was filtered under vacuum and the resin was washed [DMF (3 x 10 mL), MeOH (3 x 10 mL), DMF (3 x 10

mL), MeOH (3 x 10 mL)] and dried under reduced pressure. The first amino acid has been coupled twice to maximize the resin loading.

Acetylation of unreacted sites on oxime resin

The resin was treated three times with DMF (3 x 20 mL). A solution of 50% v/v DMF/acetic anhydride (20 mL) and DIPEA (1.0 mL) were added to the peptide synthesis vessel and shaken for 1 hour. Then, the mixture was filtered under vacuum and the resin was washed [DMF (3 x 10 mL), MeOH (3 x 10 mL), DMF (3 x 10 mL), MeOH (3 x 10 mL)].

Removal of the *N*-Boc protecting group

The resin was treated three times with CH_2Cl_2 (25 mL). A 50% v/v solution (20 mL) of trifluoroacetic acid (TFA) in CH_2Cl_2 was added to the peptide synthesis vessel and shaken for 30 minutes. Then, the mixture was filtered under vacuum and the resin was washed with [DMF (3 x 10 mL), MeOH (3 x 10 mL), DMF (3 x 10 mL), MeOH (3 x 10 mL)] and with a solution of 10% v/v DIPEA in CH_2Cl_2 (20 mL).

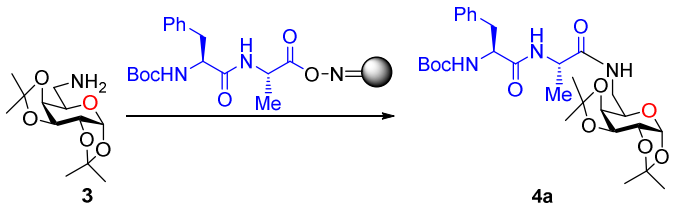
Coupling of the subsequent *N*-Boc protected α-amino acids

The amino acid (3.0 equiv, 3.3 mmol) was dissolved in DMF (10 mL) in a 50 mL flask. The solution was cooled to 0 °C, then HCTU (3.0 equiv, 3.3 mmol) and 6-Cl-HOBt (3.0 equiv, 3.3 mmol) were added. The mixture was poured into the peptide synthesis vessel, in which the resin had been previously treated with CH_2Cl_2 (3 X 20 mL). DIPEA (6.0 equiv, 6.6 mmol) was also added to the vessel and the mixture was shaken for 3 h. After filtration under vacuum, the resin was washed [DMF (3 x 10 mL), MeOH (3 x 10 mL), DMF (3 x 10 mL), MeOH (3 x 10 mL)] and dried under reduce pressure. The Kaiser ninhydrin test was performed to monitor the efficiency of the coupling, and the coupling procedure was repeated if needed.

Optimisation of the preparation of *C*-terminal glycopeptides

Initially, we used 2.5 equivalents of DIPEA and 5 equivalents of AcOH at a concentration of 0.02 M for 2 hours at room temperature (Table S1). We firstly evaluated various solvents (entries 1–4) and CH_2Cl_2 provided the best results with formation of *C*-terminal glycopeptide **4a** in 84% yield (entry 3). Then, removing the base (entry 5), increasing the concentration (entry 6) or increasing the reaction time (entry 7) gave compound **4a** in lower yields. Finally, using a Bronsted acid, LiBr, instead of acetic acid provided a much lower yield for the desired glycopeptide (entry 8).[10] The optimised conditions (entry 3) generated limited amount of by-products, thus allowing facile flash column chromatography purification after simply concentrating the crude mixture under reduced pressure.

Table S1. Optimisation of the preparation of *C*-terminal glycopeptide **4a** from galactosylamine **3**.

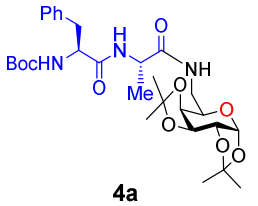


Entry	Solvent	DIPEA/AcOH (equivalent)	Concentration (M)	Time (h)	Yield (%)[a]
1	$CHCl_3$	2.5/5	0.02	2	76
2	THF	2.5/5	0.02	2	76
3	**CH_2Cl_2**	**2.5/5**	**0.02**	**2**	**84**
4	CH_2Cl_2/DMF	2.5/5	0.02	2	83
5	CH_2Cl_2	0/5	0.02	2	57
6	CH_2Cl_2	2.5/5	0.04	2	71
7	CH_2Cl_2	2.5/5	0.02	18	74
8[b]	CH_2Cl_2	2.5/5	0.02	2	16

[a]Yields refer to isolated pure products after flash column chromatography.
[b]LiBr was used instead of AcOH.

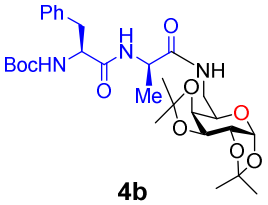
General procedure for cleavage of oxime resin

To a peptide synthesis vessel was added the oxime resin (1,1 mmol.g^{-1}, 1 equiv.) and was treated with CH_2Cl_2 (3 × 5 mL). To a solution of the oxime resin in CH_2Cl_2 (0.02 M) were added amino sugar (1 equiv.) and DIPEA (2.5 equiv.). The vessel was mechanically stirred for a few seconds and acetic acid (5 equiv.) was added to the vessel and the mixture was shaken at room temperature for the indicated time. The content of the syringe was then collected in a flask and the resin was washed with CH_2Cl_2 (3 × 5 mL) and MeOH (3 × 5 mL). The organic phase was concentrated under reduced pressure and the resulting crude was purified by flash column chromatography.



4a

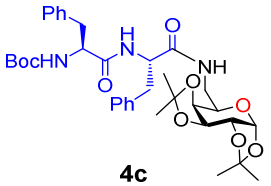
1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-L-alanylamido-α-D-glucopyranoside (4a). The mixture was stirred 2 h and the resulting crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 1:1 → 3:1) to give **4a** as an amorphous white solid (96.2 mg, 0.166 mmol, 84% yield). R_f = 0.54 (silica, EtOAc/Et_2O 3:1); $[\alpha]_D$ = -26,6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 2H, Ar), 7.26 – 7.22 (m, 1H, Ar), 7.22 – 7.18 (m, 2H, Ar), 6.51 (d, *J* = 7.2 Hz, 1H, N*H*Ala), 6.33 (s, 1H, C6-N*H*), 5.47 (d, *J* = 4.9 Hz, 1H, H1), 4.94 (d, *J* = 5.5 Hz, 1H, N*H*Phe), 4.59 (dd, *J* = 7.9, 2.4 Hz, 1H, H3), 4.40 (p, *J* = 7.1 Hz, 1H, C*H*Ala), 4.35 (q, *J* = 7.5, 6.8, 6.3 Hz, 1H, C*H*Phe), 4.29 (dd, *J* = 5.0, 2.4 Hz, 1H, H2), 4.18 (dd, *J* = 7.8, 1.8 Hz, 1H, H4), 3.88 (ddd, *J* = 8.9, 3.7, 1.6 Hz, 1H, H6a), 3.59 (ddd, *J* = 13.7, 7.2, 3.9 Hz, 1H, H5), 3.19 (ddd, *J* = 12.9, 8.7, 3.7 Hz, 1H, H6b), 3.09 (dd, *J* = 13.9, 6.4 Hz, 1H, CH_2aPhe), 3.04 (dd, *J* = 13.9, 7.3 Hz, 1H, CH_2bPhe), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.40 (s, 9H, C(CH_3)$_3$), 1.33 (s, 3H, CH_3), 1.31 (d, *J* = 7.8 Hz, 3H, CH_3Ala), 1.30 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.1, 171.2, 155.8 (3C, 3 × *C*O), 136.5, 129.4, 128.9, 127.2 (6C, Ar), 109.6, 109.0 (2C, 2 × *C*(CH_3)$_2$), 96.4 (1C, C1), 80.7 (1C, *C*(CH_3)$_3$), 71.7 (1C, C4), 71.0 (1C, C3), 70.7 (1C, C2), 66.0 (1C, C5), 55.9 (1C, *C*HPhe), 49.1 (1C, C*H*Ala), 40.1 (1C, C6), 38.1 (1C, *C*H_2Phe), 28.4 (3C, C(*C*H_3)$_3$), 26.2, 26.1, 25.1, 24.5 (4C, 4 × *C*H_3), 18.3 (1C, *C*H_3Ala) ppm; HRMS calcd for $C_{29}H_{44}N_3O_9^+$ $[M + H]^+$ 578.3078, $[M+H]^+$; found: 578.3080.



4b

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-D-alanylamido-α-D-glucopyranoside (4b). The mixture was stirred 2 h and the resulting crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 1:1 → 3:1) to give **4b** as an amorphous white solid (87.8 mg, 0.152 mmol, 80 % yield). R_f = 0.58 (silica, EtOAc/Et_2O, 3:1); $[\alpha]_D^{25}$ = -15,3 (*c* 1.0, $CHCl_3$);

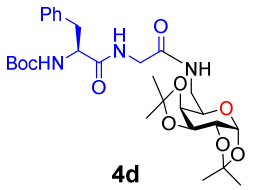
IR (ATR, Diamond) ν 3306, 3292, 2980, 1642, 1639, 1367, 1068 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H, Ar), 7.24 – 7.18 (m, 3H, Ar), 6.42 (d, *J* = 7.5 Hz, 1H, N*H*Ala), 6.35 (s, 1H, C6-N*H*), 5.51 (d, *J* = 5.0 Hz, 1H, H1), 5.33 (s, 1H, NH, N*H*Phe), 4.59 (dd, *J* = 7.9, 2.5 Hz, 1H, H3), 4.39–4.31 (m, 2H, C*H*Ala, C*H*Phe), 4.30 (dd, *J* = 5.0, 2.5 Hz, 1H, H2), 4.17 (dd, *J* = 7.9, 1.8 Hz, 1H, H4), 3.82 (ddd, *J* = 9.4, 3.4, 1.8 Hz, 1H, H5), 3.69 (ddd, *J* = 14.0, 7.9, 3.4 Hz, 1H, H6a), 3.18 (ddd, J = 14.0, 9.3, 3.8 Hz, 1H, H6b), 3.03 (qd, *J* = 13.8, 7.1 Hz, 2H, CH_2Phe), 1.48 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.40 (s, 9H, C(CH_3)$_3$), 1.33 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.22 (d, *J* = 7.1 Hz, 3H, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*): δ 172.1, 171.2, 155.8 (3C, 3 × *C*O), 136.5, 129.4, 128.9, 127.2 (6C, Ar), 109.6, 109.0 (2C, 2 × *C*(CH$_3$)$_2$), 96.4 (1C, C1), 80.7 (1C, *C*(CH$_3$)$_3$), 71.7 (1C, C4), 70.9 (1C, C3), 70.6 (1C, C2), 66.0 (1C, C5), 55.9 (1C, *C*HPhe), 49.1 (1C, C*H*Ala), 40.1 (1C, C6), 38.1 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 26.14, 26.11, 25.1, 24.5 (4C, 4 × *C*H$_3$), 18.3 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{44}N_3O_9^+$ $[M + H]^+$ 578.3078, found 578.3094.



4c

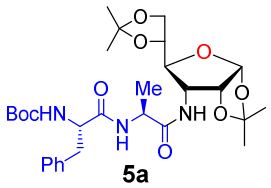
1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-alanyl)]-L-phenylalanylamido-α-D-glucopyranoside (4c). The mixture was stirred 2 h and the resulting crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 1:1 → 3:1) to give **4c** as an amorphous white solid (97.1 mg, 0.168 mmol, 79% yield). R_f = 0.61 (silica, EtOAc/Et_2O, 3:1); $[\alpha]_D^{25}$ = −38.7 (*c* 0.4, $CHCl_3$); IR (ATR, Diamond) *v* 3285, 2980, 2935, 1695, 1643, 1165, 1068 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H, Ar), 7.25 – 7.18 (m, 3H, Ar), 6.60 (d, *J* = 7.9 Hz, 1H, N*H*Phe), 6.18 (s, 1H, C6-N*H*), 5.43 (d, *J* = 5.0 Hz, 1H, H1), 4.87 (s, 1H, N*H*Ala), 4.57 (q, *J* = 7.2 Hz, 1H, C*H*Phe), 4.51 (dd, *J* = 7.9, 2.4 Hz, 1H, H3), 4.26 (dd, *J* = 4.9, 2.4 Hz, 1H, H2), 4.09 (p, *J* = 7.3, 6.8, 5.9 Hz, 1H, C*H*Ala), 3.86 – 3.74 (m, 2H, H4, H5), 3.46 – 3.38 (m, 1H, H6a), 3.32 – 3.23 (m, 1H, H6b), 3.07 (d, *J* = 7.1 Hz, 2H, CH_2Phe), 1.50 (s, 3H, CH_3), 1.43 (s, 9H, C(CH_3)$_3$), 1.39 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.28 (d, *J* = 6.0 Hz, 6H, CH_3, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.4, 170.8, 154.2 (3C, 3 × *C*O), 136.8, 129.4, 128.9, 127.0, (6C, Ar), 109.4, 108.9 (2C, 2 × *C*(CH$_3$)$_2$), 96.3 (1C, C1), 80.5 (1C, *C*(CH$_3$)$_3$), 71.2 (1C, C4), 70.8 (1C, C3), 70.6 (1C, C2), 65.5 (1C, C5), 54.7 (1C, *C*HPhe), 50.7 (1C, C*H*Ala), 39.9

(1C, C6), 38.4 (1C, *C*H_2Phe), 28.4 (3C, C(*C*H_3)$_3$), 26.2, 26.0, 25.2, 24.5 (4C, 4 × *C*H_3), 18.2 (1C, *C*H_3Ala) ppm. HRMS calcd for $C_{29}H_{44}N_3O_9^+$: 578.3078, $[M+H]^+$; found: 578.3085.



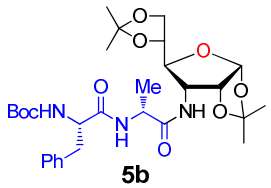
4d

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-glycylamido-α-D-glucopyranoside (4d). The mixture was stirred 2 h and the resulting crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 1:1 → 3:1) to give **4d** a white solid (42.6 mg, 0.076 mmol, 46% yield). R_f = 0.51 (silica, EtOAc/Et_2O, 3:1); $[\alpha]_D^{25}$ = 58,0 (*c* 1.0, $CHCl_3$); IR (ATR, Diamond) ν 3227, 2982, 2924, 1676, 1647, 1516, 1072 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H, Ar), 7.24 – 7.18 (m, 3H, Ar), 6.87 (s, 1H, N*H*Gly), 6.50 (s, 1H, C6-N*H*), 5.49 (d, *J* = 5.0 Hz, 1H, H1), 5.26 (d, *J* = 7.9 Hz, 1H, N*H*Phe), 4.59 (dd, *J* = 7.9, 2,4 Hz, 1H, H3), 4.37 (q, *J* = 7.4 Hz, 1H, C*H*Phe), 4.29 (dd, *J* = 5.0, 2.4 Hz, 1H, H2), 4.18 (dd, *J* = 8.0, 1.8 Hz, 1H, H4), 3.91 (dd, *J* = 16.8, 5.7 Hz 1H, C*H*aGly), 3.86 (ddd, *J* = 9.0, 3.7, 1.8 Hz, 1H, H5), 3.81 (dd, *J* = 16.8, 5.4 Hz, 1H, C*H*bGly), 3.62 (ddd, *J* = 13.6, 7.3, 3.2 Hz, 1H, H6a), 3.22 (ddd, *J* = 13.5, 9.0, 4.1 Hz, 1H, H6b), 3.12 (dd, *J* = 13.9, 6.5 Hz, 1H, CH_2aPhe), 2.98 (dd, J = 13.7, 7.4 Hz, 1H, CH_2bPhe), 1.48 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.38 (s, 9H, C(CH_3)$_3$), 1.32 (s, 3H, CH_3), 1.31 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*): δ 171.9, 168.8, 155.9 (3C, 3 × *C*O), 136.7, 129.3, 128.8, 127.1 (6C, Ar), 109.6, 109.0 (2C, 2 × *C*(CH$_3$)$_2$), 96.3 (1C, C1), 80.6 (1C, *C*(CH$_3$)$_3$), 71.6 (1C, C4), 70.8 (1C, C3), 70.6 (1C, C2), 66.4 (1C, C5), 55.9 (1C, *C*HPhe), 43.1 (1C, *C*H$_2$Gly), 40.0 (1C, C6), 38.1 (1C, CH$_2$Phe), 28.3 (3C, C(*C*H$_3$)$_3$), 26.2, 26.1, 25.1, 24.5 (4C, 4 × *C*H$_3$) ppm. HRMS calcd for $C_{28}H_{42}N_3O_9^+$ $[M + H]^+$ 564,2921, found 564,2927.



5a

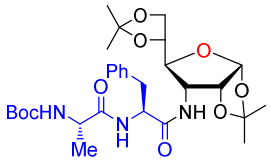
1,2:5,6-di-*O*-isopropylidene-3-deoxy-3-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-L-alanylamido-α-D-allofuranoside (5a). The mixture was stirred 2 h and the resulting crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 1:1 → 3:1) to give **5a,** a white solid (78.7 mg, 0.136 mmol, 71% yield). R_f = 0.66 (silica, EtOAc/Et_2O, 3:1); $[\alpha]_D^{25}$ = 36,9 (*c* 1.0, $CHCl_3$); IR (ATR, Diamond) ν 3287, 2982, 2934, 1656, 1647, 1160, 1014 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7,31 – 7,27 (m, 2H, Ar), 7,25 – 7,17 (m, 3H, Ar), 6.55 (d, *J* = 7.1 Hz, 1H, N*H*Ala), 6.27 (d, *J* = 7.1 Hz, 1H, C3-N*H*), 5.81 (d, *J* = 3.7 Hz, 1H, H1), 4.92 (s, 1H, N*H*Phe), 4.60 (dd, J = 4.9, 3.7 Hz, 1H, H2), 4.42 (p, *J* = 7.1 Hz, 1H, C*H*Ala), 4.36 (s, 1H, C*H*Phe), 4.23 (td, *J* = 9.1, 4.8 Hz, 1H, H3), 4.17 (td, *J* = 6.5, 5.0 Hz, 1H, H5), 4.08 (dd, *J* = 8.4, 6.6 Hz, 1H, H6a), 3.89 (dd, *J* = 8.4, 6.3 Hz, 1H, H6b), 3.85 (dd, *J* = 9.5, 5.0 Hz, 1H, H4), 3.07 (d, *J* = 6.3 Hz, 2H, CH_2Phe), 1.56 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.39 (s, 9H, C(CH_3)$_3$), 1.33 (s, 3H, CH_3), 1.324 (s, 3H, CH_3) 1.317 (d, 3H, *J* = 7.1 Hz, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*): δ 171.6, 171.2, 155.5 (3C, 3 × *C*O), 136.5, 129.5, 128.9, 127.2 (6C, Ar), 112.9, 109.9 (2C, 2 × *C*(CH$_3$)$_2$), 104.3 (1C, C1), 80.5 (1C, *C*(CH$_3$)$_3$), 79.2 (1C, C2), 79.0 (1C, C4), 75.9 (1C, C5), 65.9 (1C, C6), 55.7 (1C, *C*HPhe), 53.6 (1C, C3), 49.1 (1C, *C*HAla), 38.3 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 26.8, 26.6, 26.5, 25.4 (4C, 4 × *C*H$_3$), 18.5 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{44}N_3O_9^+$ $[M + H]^+$ 578.3078, found 578.3083.



5b

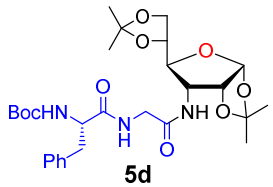
1,2:5,6-di-*O*-isopropylidene-3-deoxy-3-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-D-alanylamido-α-D-allofuranoside (5b). The mixture was stirred 2 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 1:1 → 3:1) to give **5b**, a white solid (89.0 mg, 0.154 mmol, 79% yield). R_f = 0.59 (silica, EtOAc/Et_2O, 3:1); $[\alpha]_D^{25}$ = 61.8 (*c* 0.8, $CHCl_3$); IR (ATR, Diamond) *v* 3340, 2980, 1691, 1647, 1645, 1518, 1167 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.33

– 7.28 (m, 2H, Ar), 7.25 – 7.17 (m, 3H, Ar), 6.39 (d, *J* = 8.0 Hz, 1H, C3-N*H*), 6.21 (d, *J* = 7.6 Hz, 1H, N*H*Ala), 5.83 (d, J = 3.7 Hz, 1H, H1), 5.12 (s, 1H, N*H*Phe), 4.60 (dd, *J* = 4.9, 3.7 Hz, 1H, H2), 4.37 (p, *J* = 8.5, 7.8 Hz, 1H, C*H*Ala), 4.34 – 4.27 (m, 1H, C*H*Phe), 4.26 – 4.16 (m, 2H, H3, H5), 4.02 (dd, *J* = 8.4, 6.9 Hz, 1H, H6a), 3.89 (dd, *J* = 9.6, 3.8 Hz, 1H, H4), 3.87 (dd, *J* = 8.4, 6.2 Hz, 1H, H6b), 3.09 – 3.00 (m, 2H, CH_2Phe), 1.56 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.40 (s, 9H, C(CH_3)$_3$), 1.33 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.20 (d, *J* = 6.9 Hz, 3H, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.6, 171.3, 155.5 (3C, 3 × *C*O), 136.8, 129.4, 128.9, 127.2 (6C, Ar), 112.8, 110.0 (2C, 2 × *C*(CH$_3$)$_2$), 104.2 (1C, C1), 80.5 (1C, *C*(CH$_3$)$_3$), 79.1 (1C, C2), 78.9 (1C, C4), 75.3 (1C, C5), 65.1 (1C, C6), 56.2 (1C, *C*HPhe), 52.8 (1C, C3), 48.9 (1C, C*H*Ala), 38.8 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 26.8, 26.5, 26.4, 25.3 (4C, 4 × *C*H$_3$), 17.7 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{44}N_3O_9^+$ [M + H]$^+$ 578.3078, found 578.3078.



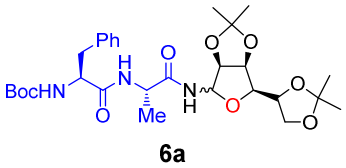
5c

1,2:5,6-di-*O*-isopropylidene-3-deoxy-3-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-alanyl)]-L-phenylalanylamido-α-D-allofuranoside (5c). The mixture was stirred 2 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Et$_2$O, 1:1 → 3:1) to give **5c**, a white solid (76.1 mg, 0.132 mmol, 69% yield). R_f = 0.60 (silica, EtOAc/Et$_2$O, 3:1); [α]$_D^{25}$ = 35,0 (*c* 1.0, CHCl$_3$); IR (ATR, Diamond) *v* 3288, 2982, 2934, 1655, 1647, 1163, 1016 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H, Ar), 7.27 – 7.21 (m, 3H, Ar), 6.87 (d, *J* = 6.3 Hz, 1H, N*H*Phe), 6.03 (d, *J* = 6.8 Hz, 1H, C3-N*H*), 5.77 (d, *J* = 3.7 Hz, 1H, H1), 4.96 (d, *J* = 5.3 Hz, 1H, N*H*Ala), 4.65 (q, *J* = 7.8 Hz, 1H, C*H*Phe), 4.52 (t, *J* = 3.9 Hz, 1H, H2), 4.16 (s, 1H, C*H*Ala), 4.13 – 4.01 (m, 3H, H3, H5, H6a), 3.86 (t, *J* = 7.8, 7.0 Hz, 1H, H6b), 3.68 (dd, *J* = 9.5, 3.6 Hz, 1H, H4), 3.11 (dd, *J* = 13.8, 6.1 Hz, 1H, C*H*aPhe), 2.99 (dd, *J* = 13.7, 8.1 Hz, 1H, C*H*bPhe), 1.42 (s, 15H, 2 × CH_3, C(CH_3)$_3$), 1.35 (s, 3H, CH_3), 1.30 (d, *J* = 7.1 Hz, 3H, CH_3Ala), 1.27 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.5, 170.5, 155.5 (3C, 3 × *C*O), 136.4, 129.4, 128.9, 127.4 (6C, Ar), 112.7, 109.8 (2C, 2 × *C*(CH$_3$)$_2$), 104.3 (1C, C1), 80.3 (1C, *C*(CH$_3$)$_3$), 78.9 (1C, C2), 78.6 (1C, C4), 75.5 (1C, C5), 65.1 (1C, C6), 54.4 (1C, *C*HPhe), 53.2 (1C, C3), 50.3 (1C, C*H*Ala), 38.6 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 26.7, 26.4, 25.5 (4C, 4 × *C*H$_3$), 18.6 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{44}N_3O_9^+$ [M + H]$^+$ 578.3078, found 578.3079.



5d

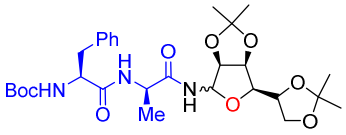
1,2:5,6-di-*O*-isopropylidene-3-deoxy-3-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-alanyl)]-glycylamido-α-D-allofuranoside (5d). The mixture was stirred 2 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 1:1 → 3:1) to give **5d**, a white solid (51.4 mg, 0.091 mmol, 47% yield). R_f = 0.42 (silica, EtOAc/Et_2O, 3:1); $[\alpha]_D$ = 46.5 (*c* 0.4 $CHCl_3$); IR (ATR, Diamond) *v* 3423, 3342, 2988, 1701, 1655, 1647, 1016 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H, Ar), 7.25 – 7.14 (m, 3H, Ar), 6.82 (s, 1H, N*H*Gly), 6.45 (s, 1H, C3-N*H*), 5.81 (d, *J* = 3.7 Hz, 1H, H1), 5.07 (s, 1H, N*H*Phe), 4.61 (dd, *J* = 4.9, 3.8 Hz, 1H, H2), 4.40 (q, *J* = 8.0, 6.1 Hz, 1H, C*H*Phe), 4.26 – 4.17 (m, 2H, H3, H5), 4.04 (ddd, *J* = 7.9, 6.8, 1.0 Hz, 1H, H6a), 3.96 – 3.83 (m, 4H, H4, H6b, CH_2Gly), 3.12 (dd, *J* = 13.9, 6.2 Hz, 1H, CH_2aPhe), 3.06 – 2.96 (m, 1H, CH_2bPhe), 1.54 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.37 (s, 9H, C(CH_3)$_3$), 1.32 (s, 6H, 2 × CH_3) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.1, 168.4, 155.6 (3C, 3 × *C*O), 136.6, 129.3, 128.8, 127.1 (6C, Ar), 112.8, 109.9 (2C, 2 × *C*(CH_3)$_2$), 104.2 (1C, C1), 80.5 (1C, *C*(CH_3)$_3$), 79.0 (1C, C2), 78.6 (1C, C4), 75.6 (1C, C5), 65.4 (1C, C6), 55.9 (1C, *C*HPhe), 53.2 (1C, C3), 43.3 (1C, *C*H_2Gly), 38.4 (1C, *C*H_2Phe), 28.4 (3C, C(*C*H_3)$_3$), 26.7, 26.4, 25.3 (4C, 4 × *C*H_3) ppm. HRMS calcd for $C_{28}H_{42}N_3O_9^+$ $[M + H]^+$ 564.2921, found 564.2919.



6a

2,3:5,6-di-*O*-isopropylidene-1-deoxy-1-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-L-alanylamido-α/β-D-mannofuranoside (6a). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, acetone/toluene, 0:1 → 1:1) to give an anomeric mixture (α/β, 1.67:1) of **6a** as an amorphous white solid (52.8 mg, 0.091 mmol, 54% yield). Pure fractions of each anomers could be isolated for characterizations. *Analytical data for* **6aα** : R_f = 0.69 (silica, acetone/toluene 3:7); $[\alpha]_D^{25}$ = -21.8 (*c* 0.5, $CHCl_3$); IR (ATR, Diamond) ν 3296, 2982, 2937, 1651, 1506, 1067 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H, Ar), 7.24 – 7.15 (m, 3H, Ar), 6.86

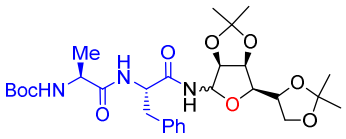
(d, *J* = 9.3 Hz, 1H, C1-N*H*), 6.66 (d, *J* = 5.2 Hz, 1H, N*H*Ala), 5.35 (dd, *J* = 9.3, 3.8 Hz, 1H, H1), 4.98 (d, *J* = 7.2 Hz, 1H, N*H*Phe), 4.77 (dd, *J* = 6.1, 3.4 Hz, 1H, H3), 4.57 (dd, *J* = 6.0, 3.8 Hz, 1H, H2), 4.46 (p, *J* = 7.1 Hz, 1H, C*H*Ala), 4.41 – 4.34 (m, 1H, C*H*Phe), 4.36 (ddd, J = 8.4, 5.8, 4.2 Hz, 1H, H5), 4.07 (dd, *J* = 8.9, 5.9 Hz, 1H, H6a) 4.04 (dd, *J* = 8.9, 4.2 Hz, 1H, H6b), 3.47 (dd, *J* = 8.4, 3.4 Hz, 1H, H4), 3.10 – 2.97 (m, 2H, C*H*$_2$Phe), 1.53 (s, 3H, C*H*$_3$), 1.42 (s, 3H, C*H*$_3$), 1.38 (s, 9H, C(C*H*$_3$)$_3$), 1.362 (s, 3H, C*H*$_3$), 1.358 (s, 3H, C*H*$_3$), 1.33 (d, *J* = 7.1 Hz, 3H, C*H*$_3$Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.7, 171.3, 155.5 (3C, 3 × *C*O), 136.6, 129.5, 128.8, 127.1 (6C, Ar), 113.3, 109.5 (2C, 2 × *C*(CH$_3$)$_2$), 80.4 (1C, *C*(CH$_3$)$_3$), 80.1 (1C, C1), 79.8 (1C, C3), 79.1 (1C, C2), 78.5 (1C, C4), 72.9 (1C, C5), 67.3 (1C, C6), 55.6 (1C, *C*HPhe), 49.0 (1C, *C*HAla), 38.4 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 27.2, 25.9, 25.3, 24.8 (4C, 4 × *C*H$_3$), 18.2 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{47}N_4O_9^+$ [M + NH4]$^+$ 595.3338, found 595.3325. *Analytical data for* **6aβ** : R_f = 0.64 (silica, acetone/toluene 3:7); $[\alpha]_D^{25}$ = -12,9 (*c* 0.3, $CHCl_3$); IR (ATR, Diamond) ν 3285, 2984, 2934, 1647, 1541, 1067 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 4H, Ar, C1-N*H*), 7.21 – 7.16 (m, 2H, Ar), 6.33 (d, *J* = 7.2 Hz, 1H, N*H*Ala), 5.34 (d, *J* = 6.8 Hz, 1H, H1), 4.95 (d, *J* = 5.1 Hz, 1H, N*H*Phe), 4.88 (dd, *J* = 5.9, 3.8 Hz, 1H, H3), 4.81 (d, *J* = 6.0 Hz, 1H, H2), 4.41 – 4.34 (m, 2H, H5, C*H*Ala), 4.26 (q, *J* = 6.2 Hz, 1H, C*H*Phe), 4.10 – 3.98 (m, 3H, H4, H6a, H6b,), 3.11 (dd, *J* = 14.0, 6.1 Hz, 1H, C*H*$_2$aPhe), 3.03 (dd, *J* = 13.9, 7.5 Hz, 1H, C*H*$_2$bPhe), 1.49 (s, 3H, C*H*$_3$), 1.42 (s, 3H, C*H*$_3$), 1.41 (s, 9H, C(C*H*$_3$)$_3$), 1.35 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.30 (d, *J* = 7.2 Hz, 3H, C*H*$_3$Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.1, 171.6, 156.1 (3C, 3 × *C*O), 136.0, 129.3, 129.1, 127.5 (6C, Ar), 113.0, 109.2 (2C, 2 × *C*(CH$_3$)$_2$), 86.9 (1C, C1), 85.5 (1C, C2), 82.3 (1C, C4), 81,2 (1C, *C*(CH$_3$)$_3$), 80.6 (1C, C3), 73.4 (1C, C5), 67.0 (1C, C6), 56.5 (1C, *C*HPhe), 49.3 (1C, *C*HAla), 37.8 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 27.0, 26.1, 25.3, 24.7 (4C, 4 × *C*H$_3$), 17.3 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{47}N_4O_9^+$ [M + NH_4]$^+$ 595.3338, found 595.3327.



6b

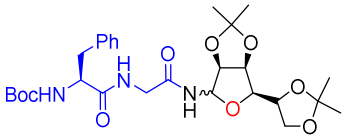
2,3:5,6-di-*O*-isopropylidene-1-deoxy-1-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-D-alanylamido-α/β-D-mannofuranoside (6b). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, acetone/toluene, 0:1 → 1:1) to give an anomeric

mixture (α/β, 1:1.58) of **6b** as an amorphous white solid (41.3 mg, 0.071 mmol, 59% yield). Pure fractions of each anomers could be isolated for characterizations. *Analytical data for* **6bα** : R_f = 0.52 (silica, acetone/toluene 3:7); $[\alpha]_D^{25}$ = -4.7 (*c* 0.6, $CHCl_3$); IR (ATR, Diamond) ν 3306, 2980, 1701, 1653, 1369, 1165, 1067 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H, Ar), 7.26 – 7.16 (m, 3H, Ar), 7.00 (d, *J* = 9.3 Hz, 1H, C1-N*H*), 6.29 (d, *J* = 7.6 Hz, 1H, N*H*Ala), 5.32 (dd, *J* = 9.3, 3.8 Hz, 1H, H1), 5.03 (s, 1H, N*H*Phe), 4.77 (dd, *J* = 6.1, 3.4 Hz, 1H, H3), 4.58 (dd, *J* = 6.0, 3.8 Hz, 1H, H2), 4.43 (p, *J* = 6.8 Hz, 1H, C*H*Ala), 4.38 – 4.31 (m, 1H, C*H*Phe) 4.34 (dt, *J* = 8.4, 5.0 Hz, 1H, H5), 4.05 – 4.01 (m, 2H, H6a, H6b), 3.48 (dd, *J* = 8.4, 3.4 Hz, 1H, H4), 3.11 – 2.97 (m, 2H, CH_2Phe), 1.52 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.40 (s, 9H, C(CH_3)$_3$), 1.36 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.20 (d, *J* = 6.9 Hz, 3H, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*): δ 171.8, 171.3, 155.3 (3C, 3 × *C*O), 136.6, 129.4, 128.9, 127.2 (6C, Ar), 113.4, 109.5 (2C, 2 × *C*(CH$_3$)$_2$), 80.4 (1C, *C*(CH$_3$)$_3$), 80.3 (1C, C1), 79.8 (1C, C3), 79.2 (1C, C2), 78.5 (1C, C4), 72.9 (1C, C5), 67.3 (1C, C6), 56.1 (1C, *C*HPhe), 48.9 (1C, *C*HAla), 39.0 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 27.2, 26.0, 25.3, 24.8 (4C, 4 × *C*H$_3$), 17.8 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{47}N_4O_9^+$ $[M + NH4]^+$ 595.3338, found 595.3319. *Analytical data for* **6bβ** : R_f = 0.54 (silica, acetone/toluene, 3:7); $[\alpha]_D^{25}$ = 16.8 (*c* 0.9, $CHCl_3$); IR (ATR, Diamond crystal); ν 3356, 3190, 2924, 1645, 1367, 1167, 1067 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 5.9 Hz, 1H, C1-N*H*), 7.32 – 7.28 (m, 2H, Ar), 7.25 – 7.22 (m, 1H, Ar), 7.19 – 7.15 (m, 2H, Ar), 6.44 (d, *J* = 7.3 Hz, 1H, N*H*Ala), 5.27 (d, J = 6.7 Hz, 1H, H1), 5.19 (d, J = 6.8 Hz, 1H, N*H*Phe), 4.90 (dd, J = 5.9, 3.7 Hz, 1H, H3), 4.84 (d, J = 5.7 Hz, 1H, H2), 4.42 – 4.32 (m, 2H, H5, C*H*Ala), 4.18 (q, J = 7.2 Hz, 1H, C*H*Phe), 4.09 – 4.03 (m, 2H, H4, H6a), 4.00 (dd, J = 8.6, 4.8 Hz, 1H, H6b), 3.07 (dd, *J* = 13.6, 7.2 Hz, 1H, CH_2aPhe), 3.02 (dd, *J* = 13.7, 7.7 Hz, 1H, CH_2bPhe), 1.47 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.41 (s, 9H, C(CH_3)$_3$), 1.35 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.18 (d, *J* = 7.1 Hz, 3H, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.4, 171.6, 155.9 (3C, 3 × *C*O), 136.5, 129.8, 128.9, 127.3 (6C, Ar), 112.9, 109.1 (2C, 2 × *C*(CH$_3$)$_2$), 86.8 (1C, C1), 85.3 (1C, C2), 82.3 (1C, C4), 80.82 (1C, C3), 80.76 (1C, *C*(CH$_3$)$_3$), 73.5 (1C, C5), 66.9 (1C, C6), 56.8 (1C, *C*HPhe), 48.9 (1C, *C*HAla), 37.9 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 27.0, 26.1, 25.2, 24.7 (4C, 4 × *C*H$_3$), 17.2 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{47}N_4O_9^+$ $[M + NH4]^+$ 595.3338, found 595.3316.



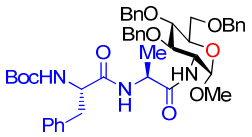
6c

2,3:5,6-di-*O*-isopropylidene-1-deoxy-1-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-alanyl)]-D-phenylalanylamido-α-D-mannofuranoside (6c). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, acetone/toluene, 0:1 → 1:1) to give an inseparable anomeric mixture (α/β, 1.52:1) as an amorphous white solid (57.1 mg, 0.099 mmol, 57% yield). R_f = 0.58 (silica, acetone/toluene 3:7); $[\alpha]_D^{25}$ = −5.6 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.15 (m, 10H, Ar), 7.14 (s, 1H, C1-N*H*β), 6.74 (s, 1H, N*H*Pheβ), 6.54 – 6.42 (m, 2H, C1-N*H*α, N*H*Pheα), 5.42 (d, *J* = 6.3 Hz, 1H, H1β), 5.33 (dd, *J* = 9.4, 3.8 Hz, 1H, H1α), 4.90 (s, 1H, N*H*Alaα), 4.75 (dd, *J* = 5.9, 3.6 Hz, 1H, H3β), 4.72 (dd, *J* = 6.0, 3.4 Hz, 1H, H3α), 4.70 (d, *J* = 5.4 Hz, 1H, H2β), 4.67 – 4.61 (m, 2H, C*H*Pheα, C*H*Pheβ), 4.51 (dd, *J* = 6.0, 3.8 Hz, 1H, H2α), 4.37 (td, *J* = 7.9, 6.4, 4.6 Hz, 1H, H5β), 4.33 (dt, *J* = 7.9, 5.9, 4.7 Hz, 1H, H5α), 4.15 (s, 1H, C*H*Alaα), 4.13 – 4.03 (m, 4H, $H6^{I}$α, $H6^{II}$α, $H6^{I}$β, $H6^{II}$β), 3.95 (qd, *J* = 7.1, 3.9 Hz, 1H, C*H*Alaβ), 3.71 (dd, *J* = 8.1, 3.6 Hz, 1H, H4β), 3.48 (dd, *J* = 7.9, 3.4 Hz, 1H, H4α), 3.38 (dd, *J* = 13.8, 3.2 Hz, 1H, CH_2aPheβ), 3.11 – 3.02 (m, 2H, CH_2Pheα), 2.95 (dd, *J* = 13.9, 6.3 Hz, 1H, CH_2bPheβ), 1.47 (s, 3H, CH_3β), 1.45 – 1.42 (m, 15H, C(CH_3)$_3$α, CH_3α, CH_3β), 1.39 – 1.33 (m, 12H, CH_3Alaβ, 2 × CH_3α, CH_3β), 1.32 – 1.28 (m, 18H, C(CH_3)$_3$β, CH_3Alaα, CH_3α, CH_3β) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.5, 172.1, 171.4, 170.6, 157.6, 156.4 (6C, 6 × *C*O), 138.0, 136.1, 135.9, 129.6, 129.5, 129.2, 128.7, 128.4, 127.6, 127.2 (12C, Ar), 113.3, 113.0, 109.4, 109.3 (4C, 4 × *C*(CH$_3$)$_2$), 86.7 (1C, C1β), 85.2 (1C, C2β), 81.6 (1C, C4β), 81.1 (2C, 2 × *C*(CH$_3$)$_3$), 80.4 (1C, *C*3β), 79.9 (1C, C1α), 79.8 (1C, C3α), 79.1 (1C, C2α), 78.4 (1C, C4α), 73.3 (1C, *C*5β), 73.0 (1C, C5α), 67.09 (1C, C6α) , 67.08 (1C, *C*6β), 54.6 (1C, *C*HPheα), 53.6 (1C, *C*HPheβ), 51.7 (1C, *C*HAlaβ), 50.3 (1C, *C*HAlaα) 38.7 (1C, *C*H$_2$Pheα), 37.1 (1C, *C*H$_2$Pheβ), 28.4 (3C, C(*C*H$_3$)$_3$α), 28.3 (3C, C(*C*H$_3$)$_3$β), 27.13 (1C, C*H*$_3$α), 27.05 (1C, C*H*$_3$β), 26.2 (1C, *C*H$_3$β), 25.8 (1C, C*H*$_3$α) , 25.4 (1C, C*H*$_3$α), 25.2 (1C, C*H*$_3$β), 24.8 (1C, C*H*$_3$β), 24.7 (1C, C*H*$_3$α), 18.5 (1C, *C*H$_3$Alaα), 17.9 (1C, *C*H$_3$Alaβ) ppm. HRMS calcd for $C_{29}H_{47}N_4O_9^+$ $[M + NH_4]^+$ 595.3338, found 595.3318.



6d

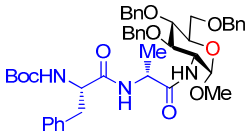
2,3:5,6-di-*O*-isopropylidene-1-deoxy-1-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-glycylamido-β-D-mannofuranoside (6d). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, acetone/toluene, 0:1 → 1:1) to give an anomeric mixture (α/β, 1.4:1) as an amorphous white solid (62.6 mg, 0.111 mmol, 64% yield). A pure fraction of the β anomer was used for characterization. $R_{f\alpha}$ = 0.39 (silica, acetone/toluene 3:7); $R_{f\beta}$ = 0.43 (silica, acetone/toluene 3:7); *Analytical data for* **6dβ** : $[\alpha]_D^{25}$ = 6.2 (c 0.7, $CHCl_3$); IR (ATR, Diamond) ν 3273, 2926, 1684, 1653, 1207, 1163, 1067 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 5.4 Hz, 1H, C1-N*H*), 7.35 – 7.24 (m, 3H, Ar), 7.20 – 7.15 (m, 2H, Ar), 6.71 (t, *J* = 5.8 Hz, 1H, N*H*Gly), 5.32 (d, *J* = 6.7 Hz, 1H, H1), 5.06 (d, *J* = 6.1 Hz, 1H, N*H*Phe), 4.89 (dd, *J* = 5.9, 3.6 Hz, 1H, H3), 4.85 (d, *J* = 5.9 Hz, 1H, H2), 4.35 (ddd, *J* = 7.4, 6.3, 4.8 Hz, 1H, H5), 4.22 (dt, *J* = 8.0, 6.0 Hz, 1H, C*H*Phe), 4.08 – 4.04 (m, 2H, H4, H6a), 4.00 (dd, *J* = 8.7, 4.8 Hz, 1H, H6b), 3.93 (dd, *J* = 16.9, 6.2 Hz, 1H, CH_2aGly), 3.81 (dd, *J* = 16.9, 5.5 Hz, 1H, CH_2bGly), 3.15 (dd, *J* = 13.9, 5.9 Hz, 1H, CH_2aPhe), 3.00 (d, *J* = 14.0, 8.1 Hz, 1H, CH_2bPhe), 1.48 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.40 (s, 9H, C(CH_3)$_3$), 1.35 (s, 3H, CH_3), 1.32 ppm (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 169.4, 156.1 (3C, 3 × *C*O), 136.3, 129.2, 129.0, 127.4 (6C, Ar), 113.0, 109.2 (2C, 2 × *C*(CH$_3$)$_2$), 86.8 (1C, C1), 85.3 (1C, C2), 82.3 (1C, C4), 81.1 (1C, *C*(CH$_3$)$_3$), 80.7 (1C, C3), 73.5 (1C, C5), 66.9 (1C, C6), 56.7 (1C, *C*HPhe), 43.5 (1C, CH_2Gly), 37.6 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 27.0, 26.1, 25.3, 24.7 (4C, 4 × *C*H$_3$) ppm; HRMS calcd for $C_{28}H_{45}N_4O_9^+$ $[M + NH_4]^+$ 581.3181, found 581.3155.



7a

Methyl-3,4,6-Tri-*O*-benzyl-2-deoxy-2-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-L-alanylamido-α-D-glucopyranoside (7a). The mixture was stirred 48 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Hexane, 1:1 → 3:1) to give **7a**, a white solid (49.3 mg, 0.063 mmol, 90% yield). R_f = 0.54 (silica, EtOAc/Hexane 3:1); $[\alpha]_D^{25}$ = 32.0 (*c* 0.5, $CHCl_3$); IR

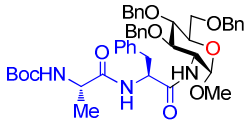
(ATR, Diamond) ν 3290, 1637, 1497, 1124, 1047, 727, 694 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.22 (m, 16H, Ar), 7.19 – 7.11 (m, 4H, Ar), 6.56 (s, 1H, N*H*Ala), 6.05 (s, 1H, C2-N*H*), 4.87 (s, 1H, N*H*Phe), 4.78 (d, *J* = 13.8 Hz, 1H, C*H*$_2$aOBn), 4.76 (d, *J* = 13.4 Hz, 1H, C*H*$_2$bOBn), 4.67 (d, *J* = 2.9 Hz, 1H, H1), 4.66 (d, *J* = 10.4 Hz, 1H, C*H*$_2$aOBn) 1H, 4.64 (d, *J* = 12.1 Hz, 1H, C*H*$_2$aOBn), 4.52 (d, *J* = 12.1 Hz, 1H, C*H*$_2$bOBn), 4.49 (d, *J* = 10.8 Hz, 1H, C*H*$_2$bOBn), 4.35 (s, 1H, C*H*Phe), 4.32 – 4.22 (m, 2H, H2, C*H*Ala), 3.80 – 3.66 (m, 5H, H3, H4, H5, H6a, H6b), 3.36 (s, 3H, OC*H*$_3$) 3.06 (d, *J* = 5.9 Hz, 2H, C*H*$_2$Phe), 1.39 (s, 9H, C(C*H*$_3$)$_3$), 1.21 (d, *J* = 6.6 Hz, 3H, C*H*$_3$Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.5, 171.1, 155.5 (3C, 3 × *C*O), 138.5, 138.2, 138.1, 136.4, 129.4, 128.9, 128.54, 128.53, 128.52, 128.02, 127.96, 127.9, 127.82, 127.80, 127.2 (24C, Ar), 98.7 (1C, C1), 80.9 (1C, C3), 80.6 (1C, *C*(CH$_3$)$_3$), 78.3 (1C, C4), 75.2, 75.1, 73.6 (3C, 3 × *C*H$_2$OBn), 70.9 (1C, C5), 68.6 (1C, C6), 55.7 (1C, *C*HPhe), 55.3 (1C, O*C*H$_3$), 53.0 (1C, C2), 49.1 (1C, *C*HAla), 38.2 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 18.5 (1C, CH$_3$Ala) ppm. HRMS calcd for $C_{45}H_{56}N_3O_9^+$ [M + H]$^+$ 782.4011, found 782.3980 .



7b

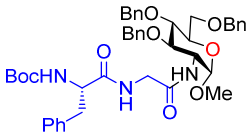
Methyl-3,4,6-Tri-*O*-benzyl-2-deoxy-2-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-D-alanylamido-α-D-glucopyranoside (7b). The mixture was stirred 48 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Hexane, 1:1 → 3:1) to give **7b**, a white solid (46.1 mg, 0.059 mmol, 63% yield). R_f = 0.56 (silica, EtOAc/Hexane 1:1); $[\alpha]_D^{25}$ = 70.9 (*c* 0.6, $CHCl_3$); IR (ATR, Diamond) ν 3300, 2916, 2868, 1691, 1636, 1047, 695 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 13H, Ar), 7.25 – 7.07 (m, 7H, Ar), 6.00 (d, *J* = 7.9 Hz, 1H, C2-N*H*), 5.80 (d, *J* = 5.5 Hz, 1H, N*H*Ala), 4.80 (d, *J* = 12.0 Hz, 1H, C*H*$_2$aOBn), 4.78 (s, 1H, N*H*Phe), 4.77 (d, *J* = 10.9 Hz, 1H, C*H*$_2$aOBn), 4.65 (d, *J* = 3.7 Hz, 1H, H1), 4.63 (d, *J* = 12.2 Hz, 1H, C*H*$_2$aOBn), 4.61 (d, *J* = 13.4 Hz, 1H, C*H*$_2$bOBn), 4.52 (d, *J* = 12.1 Hz, 1H, C*H*$_2$bOBn), 4.51 (d, *J* = 10.9 Hz, 1H, C*H*$_2$bOBn), 4.26 – 4.18 (m, 2H, H2, C*H*Ala), 4.07 (q, *J* = 7.5 Hz, 1H, C*H*Phe), 3.76 – 3.65 (m, 5H, H3, H4, H5, H6a, H6b), 3.32 (s, 3H, OC*H*$_3$), 2.98 (dd, *J* = 13.7, 7.3 Hz, 1H, C*H*$_2$aPhe), 2.78 (dd, *J* = 12.5, 7.1 Hz, 1H, C*H*$_2$bPhe), 1.40 (s, 9H, C(C*H*$_3$)$_3$), 1.08 (d, *J* = 6.7 Hz, 3H, C*H*$_3$Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.5, 171.0, 155.4 (3C, 3 × *C*O), 138.3, 138.1, 136.6, 129.3, 128.8, 128.6, 128.53, 128.51, 128.5, 128.0, 128.0, 127.9,

127.8, 127.7, 127.2 (24C, Ar), 98.7 (1C, C1), 80.9 (1C, C3), 80.4 (1C, *C*(CH_3)$_3$), 78.4 (1C, C4), 75.0, 74.8, 73.6 (3C, 3 × *C*H_2OBn), 70.9 (1C, C5), 68.7 (1C, C6), 56.4 (1C, *C*HPhe), 55.3 (1C, O*C*H_3), 52.9 (1C, C2), 48.8 (1C, *C*HAla), 38.6 (1C, *C*H_2Phe), 28.4 (3C, C(*C*H_3)$_3$), 17.8 (1C, CH_3Ala) ppm. HRMS calcd for $C_{45}H_{56}N_3O_9^+$ $[M + H]^+$ 782.4011, found 782.3992.



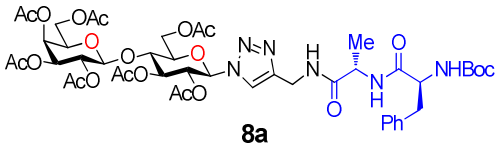
7c

Methyl-3,4,6-Tri-*O*-benzyl-2-deoxy-2-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-alanyl)]-L-phenylalanylamido-α-D-glucopyranoside (7c). The mixture was stirred 48 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Hexane, 1:1 → 3:1) to give a white solid **7c**, (36.0 mg, 0.046 mmol, 88% yield). R_f = 0.56 (silica, EtOAc/Hexane 3:1); $[\alpha]_D^{25}$ = 29.2 (*c* 0.3, $CHCl_3$); IR (ATR, Diamond) ν 3281, 2924, 2831, 1691, 1639, 1051, 692 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.26 (m, 10H, Ar), 7.26 – 7.09 (m, 10H, Ar), 6.57 (d, *J* = 8.0 Hz, 1H, N*H*Phe), 6.28 (d, *J* = 7.4 Hz, 1H, C2-N*H*), 4.77 (s, 1H, N*H*Ala), 4.75 (d, *J* = 10.9 Hz, 1H, C*H*$_2$aOBn), 4.73 (d, *J* = 11.2 Hz, 1H, C*H*$_2$bOBn), 4.69 – 4.59 (m, 4H, H1, C*H*Phe, C*H*$_2$aOBn, C*H*$_2$aOBn), 4.52 (d, *J* = 12.1 Hz, 1H, C*H*$_2$bOBn), 4.48 (d, *J* = 10.8 Hz, 1H, C*H*$_2$bOBn), 4.24 (td, *J* = 9.5, 3.6 Hz, 1H, H2), 4.03 (p, *J* = 7.2, 6.3 Hz, 1H, C*H*Ala), 3.76 – 3.65 (m, 5H, H3, H4, H5, H6a, H6b), 3.28 (s, 3H, OC*H*$_3$), 3.04 (d, *J* = 6.5 Hz, 2H, C*H*$_2$Phe), 1.42 (s, 9H, C(C*H*$_3$)$_3$), 1.24 (d, *J* = 7.1 Hz, 3H, C*H*$_3$Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.5, 170.7, 155.5 (3C, 3 × *C*O), 138.6, 138.2, 138.1, 136.5, 129.4, 128.7, 128.5, 128.483, 128.477, 128.0, 127.94, 127.90, 127.81, 127.76, 127.7, 127.1 (24C, Ar), 98.5 (1C, C1), 80.6 (1C, *C*(CH_3)$_3$), 80.5 (1C, C3), 78.4 (1C, C4), 75.02, 74.95, 73.6 (3C, 3 × *C*H_2OBn), 70.7 (1C, C5), 68.7 (1C, C6), 55.1 (1C, O*C*H_3), 53.8 (1C, *C*HPhe), 53.4 (1C, C2), 50.7 (1C, *C*HAla), 37.5 (1C, *C*H_2Phe), 28.4 (3C, C(*C*H_3)$_3$), 18.3 (1C, CH_3Ala) ppm. HRMS calcd for $C_{45}H_{54}N_3O_9^+$ $[M + H]^+$ 780.3866, found 780.3858.



7d

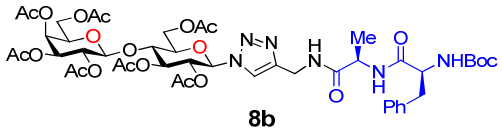
Methyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-glycylamido-α-D-glucopyranoside (7d). The mixture was stirred 48 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Hexane, 1:1 → 3:1) to give a white solid (31.7 mg, 0.041 mmol, 51% yield). R_f = 0.42 (silica, EtOAc/Hexane 3:1); $[\alpha]_D^{25}$ = 70.3 (*c* 0.1, $CHCl_3$); IR (ATR, Diamond) ν 3304, 2914, 2866, 1691, 1637, 1047, 691 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.21 (m, 16H, Ar), 7.19 – 7.13 (m, 4H, Ar), 6.21 (s, 1H, N*H*Gly), 5.84 (d, *J* = 7.8 Hz, 1H, C2-N*H*), 4.84 (s, 1H, N*H*Phe), 4.83 (d, *J* = 12.0 Hz, 1H, CH_2aOBn), 4.80 (d, *J* = 11.0 Hz, 1H, CH_2aOBn), 4.67 – 4.58 (m, 3H, H1, CH_2aOBn, CH_2bOBn), 4.52 (d, *J* = 11.7 Hz, 2H, 2 × CH_2bOBn), 4.28 – 4.19 (m, 2H, H2, C*H*Phe), 3.78 – 3.65 (m, 6H, H3, H4, H5, H6a, H6b, CH_2aGly), 3.55 (dd, *J* = 16.7, 4.7 Hz, 1H, CH_2bGly), 3.32 (s, 3H, OCH_3), 3.08 (dd, *J* = 13.8, 6.4 Hz, 1H, CH_2aPhe), 2.92 (dd, *J* = 13.1, 7.2 Hz, 1H, CH_2bPhe), 1.40 (s, 9H, C(CH_3)$_3$) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.7, 168.2, 155.6 (3C, 3 × *C*O), 139.0, 138.2, 138.1, 136.5, 129.3, 128.9, 128.6, 128.5, 128.5, 128.1, 128.0, 127.9, 127.9, 127.8, 127.2 (24C, Ar), 98.6 (1C, C1), 80.8 (1C, C3), 80.5 (1C, *C*(CH$_3$)$_3$), 78.5 (1C, C4), 75.1, 75.0, 73.6 (3C, 3 × *C*H_2OBn), 70.9 (1C, C5), 68.6 (1C, C6), 56.0 (1C, *C*HPhe), 55.2 (1C, OCH_3), 52.9 (1C, C2), 43.2 (1C, *C*H_2Gly), 38.3 (1C, *C*H_2Phe), 28.4 (3C, C(*C*H$_3$)$_3$) ppm. HRMS calcd for $C_{44}H_{54}N_3O_9^+$ $[M + H]^+$ 768.3855, found 768.3805.



8a

1-[4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4-[(*N*-(*N*-tert-butoxycarbonyl)-L-phenylalanyl)]-L-alanylamidomethyl-[1,2,3]-triazole (8a). The mixture was stirred 18h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 3:1 → 9:1) to give **8a**, a white solid (39.1 mg, 0.038 mmol, 73% yield). R_f = 0.48 (silica, MeOH/CH_2Cl_2, 1:20); $[\alpha]_D^{25}$ = -24.8 (*c* 0.5, $CHCl_3$); IR (ATR, Diamond); ν 3310, 2926, 1751, 1653, 1217, 1167, 1043 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.69 (s, 1H, Ar), 7.32 – 7.27 (m, 2H, Ar), 7.26 –

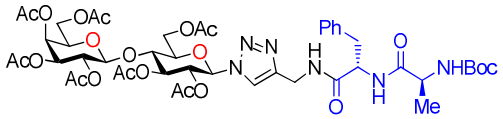
7.22 (m, 1H, Ar), 7.20 – 7.16 (m, 2H, Ar), 6.74 (s, 1H, CH_2NH), 6.35 (d, J = 7.6 Hz, 1H, NHAla), 5.80 – 5.73 (m, 1H, $H1^I$), 5.46 – 5.31 (m, 3H, $H2^I$, $H4^1$, $H4^{II}$), 5.13 (dd, J = 10.4, 7.9 Hz, 1H, $H2^{II}$), 4.97 (dd, J = 10.5, 3.5 Hz, 1H, $H3^{II}$), 4.95 (s, 1H, NHPhe), 4.52 (d, J = 7.9 Hz, 1H, $H1^{II}$), 4.50 – 4.46 (m, 2H, CH_2aNH, $H6a^I$), 4.45 – 4.38 (m, 2H, CHAla, CH_2bNH), 4.34 (s, 1H, CHPhe), 4.17 – 4.06 (m, 3H, $H6b^I$, $H6a^{II}$, $H6b^{II}$), 3.99 – 3.93 (m, 1H, $H3^I$), 3.90 (td, J = 6.8, 1.0 Hz, 1H, $H5^{II}$), 3.82 (ddd, J = 9.9, 4.8, 1.8 Hz, 1H, $H5^I$), 3.01 (dd, J = 14.1, 6.6 Hz, 1H, CH_2aPhe), 2.97 (dd, J = 14.4, 7.9 Hz, 1H, CH_2bPhe), 2.16 (s, 3H, $COCH_3$), 2.11 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.05 (s, 6H, 2 × $COCH_3$), 1.97 (s, 3H, $COCH_3$), 1.86 (s, 3H, $COCH_3$), 1.39 (s, 9H, $C(CH_3)_3$), 1.31 (d, J = 7.1 Hz, 3H, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.9, 171.5, 170.5, 170.5, 170.3, 170.2, 169.7, 169.2, 169.2 (10C, 10 × CO), 136.4, 129.3, 129.0, 127.4, 121.0 (8C, Ar), 101.3 (1C, $C1^{II}$), 85.7 (1C, $C1^I$), 80.9 (1C, $C(CH_3)_3$), 76.0 (1C, $C5^I$), 75.7 (1C, $C3^I$), 72.7 (1C, $C2^I$), 71.1 (1C, $C3^{II}$), 71.0 (1C, $C5^{II}$), 70.7 (1C, $C4^I$), 69.2 (1C, $C2^{II}$), 66.7 (1C, $C4^{II}$), 61.7 (1C, $C6^I$), 61.0 (1C, $C6^{II}$), 56.0 (1C, CHPhe), 49.0 (1C, CHAla), 38.0 (1C, CH_2Phe), 35.2 (1C, CH_2NH), 28.4 (3C, $C(CH_3)_3$), 21.0, 20.85, 20.82, 20.79, 20.77, 20.7, 20.4 (7C, 7 × $COCH_3$), 17.6 (1C, CH_3Ala) ppm. HRMS calcd for $C_{46}H_{63}N_6O_{21}^+$ $[M + H]^+$ 1035.4041, found 1035.4046.



8b

1-[4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4-[(*N*-(*N*-tert-butoxycarbonyl)-L-phenylalanyl)]-D-alanylamidomethyl-[1,2,3]-triazole (8b). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Et_2O, 3:1 → 9:1) to give **8b**, a white solid (32.6 mg, 0.031 mmol, 60% yield). R_f = 0.36 (silica, MeOH/CH_2Cl_2 1:20); IR (ATR, Diamond) ν 3321, 2980, 1744, 1647, 1217, 1167, 1043 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (s, 1H, Ar), 7.32 – 7.23 (m, 3H, Ar), 7.20 – 7.16 (m, 2H, Ar), 7.11 (s, 1H, CH_2NH), 6.11 (d, J = 7.1 Hz, 1H, NHAla), 5.76 (d, J = 8.9 Hz, 1H, $H1^I$), 5.42 – 5.31 (m, 3H, $H2^I$, $H4^I$, $H4^{II}$), 5.13 (dd, J = 10.5, 7.9 Hz, 1H, $H2^{II}$), 5.10 (d, J = 6.1 Hz, 1H, NHPhe), 4.97 (dd, J = 10.4, 3.4 Hz, 1H, $H3^{II}$), 4.51 (d, J = 7.8 Hz, 1H, $H1^{II}$), 4.50 – 4.43 (m, 3H, CH_2NH, $Hb6^I$), 4.41 (p, J = 7.5 Hz, 1H, CHAla), 4.21 – 4.07 (m, 4H, $Ha6^{II}$, $Hb6^{II}$, $Hb6^I$, CHPhe), 3.98 – 3.92 (m, 1H, $H3^I$), 3.92 – 3.86 (m, 2H, $H5^I$, $H5^{II}$), 3.03 (d, J = 7.3 Hz, 2H, CH_2Phe), 2.16 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.059 (s, 3H, $COCH_3$), 2.056 (s, 3H, $COCH_3$), 1.97 (s, 3H, $COCH_3$), 1.85 (s, 3H, $COCH_3$), 1.38

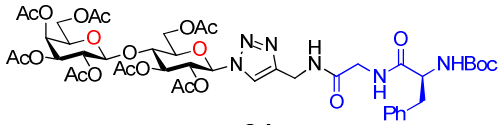
(s, 9H, C(CH_3)$_3$), 1.20 (d, J = 7.1 Hz, 3H, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.0, 171.5, 170.5, 170.4, 170.3, 170.2, 169.6, 169.3, 169.2, 155.9 (10C, 10 × *C*O), 136.5, 129.3, 128.9, 127.3, 121.0 (8C, Ar), 101.3 (1C, C1^{II}), 85.7 (1C, C1^{I}), 80.8 (1C, *C*(CH$_3$)$_3$), 76.1 (1C, C5^{I}), 75.8 (1C, C3^{I}) , 72.7 (1C, C2^{I}), 71.1 (1C, C3^{II}), 71.0 (1C, C5^{II}), 70.8 (1C, C4^{I}), 69.2 (1C, C2^{II}), 66.7 (1C, C4^{II}), 61.9 (1C, C6^{I}), 61.0 (1C, C6^{II}), 56.8 (1C, *C*HPhe), 48.9 (1C, *C*HAla), 38.2 (1C, *C*H$_2$Phe), 35.3 (1C, *C*H$_2$NH), 28.4 (3C, C(*C*H$_3$)$_3$), 21.0, 20.9, 20.8, 20.8, 20.8, 20.7, 20.4 (7C, 2 × CO*C*H$_3$), 17.5 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{46}H_{63}N_6O_{21}^+$ [M + H]$^+$ 1035.4041, found 1035.3986.



8c

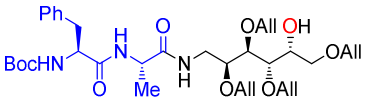
1-[4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4-[(*N*-(*N*-tert-butoxycarbonyl)-L-alanyl)]-L-phenylalanylamidomethyl-[1,2,3]-triazole (8c). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Et$_2$O, 3:1 → 9:1) to give **8c**, a white solid (38.3 mg, 0.037 mmol, 71% yield) R_f = 0.40 (silica, MeOH/CH$_2$Cl$_2$, 1:20); $[\alpha]_D^{25}$ = -32.9 (*c* 1.0, CHCl$_3$); IR (ATR, Diamond) ν 3318, 2937, 1747, 1643, 1225, 1167, 1047 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (s, 1H, Ar), 7.26 – 7.17 (m, 3H, Ar), 7.10 – 7.06 (m, 2H, Ar), 6.95 (s, 1H, CH$_2$N*H*), 6.55 (d, J = 7.4 Hz, 1H, N*H*Phe), 5.79 (d, J = 9.0 Hz, 1H, H1^{I}), 5.45 – 5.38 (m, 2H, H2^{I}, H4^{I}), 5.37 (dd, J = 3.5, 1.0 Hz, 1H, H4^{II}), 5.13 (dd, J = 10.5, 7.9 Hz, 1H, H2^{II}), 4.97 (dd, J = 10.5, 3.5 Hz, 1H, H3^{II}), 4.82 (d, J = 4.2 Hz, 1H, N*H*Ala), 4.66 (q, J = 7.8, 6.4 Hz, 1H, C*H*Phe), 4.53 (d, J = 7.9 Hz, 1H, H1^{II}), 4.49 (dd, J = 12.2, 1.9 Hz, 1H, H6a^{I}), 4.44 (t, J = 5.6 Hz, 2H, C*H*$_2$N*H*), 4.18 – 4.08 (m, 3H, H6b^{I}, H6a^{II}, H6b^{II}), 4.05 – 3.95 (m, 2H, H3^{I}, C*H*Ala), 3.93 – 3.87 (m, 2H, H5^{I}, H5^{II}), 3.22 (dd, J = 13.6, 5.4 Hz, 1H, C*H*$_2$aPhe), 3.02 (dd, J = 13.9, 6.5 Hz, 1H, C*H*$_2$bPhe), 2.16 (s, 3H, COC*H*$_3$), 2.08 (s, 3H, COC*H*$_3$), 2.06 (s, 3H, COC*H*$_3$), 2.06 (s, 3H, COC*H*$_3$), 2.05 (s, 3H, COC*H*$_3$), 1.97 (s, 3H, COC*H*$_3$), 1.84 (s, 3H, COC*H*$_3$), 1.33 (s, 9H, C(C*H*$_3$)$_3$), 1.27 (d, J = 7.2 Hz, 3H, C*H*$_3$Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.5, 171.0, 170.5, 170.4, 170.3, 170.2, 169.7, 169.2, 169.1, 145.5 (10C, 10 × *C*O), 136.3, 129.4, 128.9, 127.2, 121.3 (8C, Ar), 101.3 (1C, C1^{II}), 85.6 (1C, C1^{I}), 81.1 (1C, *C*(CH$_3$)$_3$), 76.0 (1C, C5^{I}), 75.7 (1C, C3^{I}), 72.8 (1C, C2^{I}), 71.1 (1C, C3^{II}), 71.0 (1C, C5^{II}), 70.6 (1C, C4^{I}), 69.2 (1C, C2^{II}), 66.7 (1C, C4^{II}), 61.9 (1C, C6^{I}), 61.0 (1C, C6^{II}), 53.8 (1C, *C*HPhe), 51.2 (1C, *C*HAla), 37.5 (1C, *C*H$_2$Phe), 35.2 (1C, *C*H$_2$NH), 28.3 (3C, C(*C*H$_3$)$_3$), 20.91, 20.86, 20.82, 20.79, 20.77, 20.6, 20.4 (7C,

2 × CO*C*H$_3$), 17.9 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{46}H_{63}N_6O_{21}^+$ [M + H]$^+$ 1035.4041, found 1035.4035.



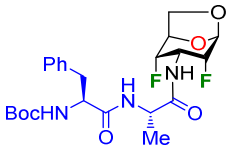
8d

1-[4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4-[(*N*-(*N*-tert-butoxycarbonyl)-L-phenylalanyl)]-glycylamidomethyl-[1,2,3]-triazole (8d). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Et$_2$O, 3:1 → 9:1) to give **8d**, a white solid (33.2 mg, 0.031 mmol, 50% yield). R_f = 0.46 (silica, MeOH/CH$_2$Cl$_2$, 1:20); $[\alpha]_D^{25}$ = - 8.9 (*c* 0.7, CHCl$_3$); IR (ATR, Diamond) ν 3337, 2928, 1747, 1670, 1213, 1167, 1043 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (s, 1H, Ar), 7.31 – 7.22 (m, 3H, Ar), 7.20 – 7.15 (m, 2H, Ar), 7.11 (s, 1H, CH$_2$N*H*), 6.77 (s, 1H, N*H*Gly), 5.79 (dt, J = 8.9, 6.5 Hz, 1H, H1^{I}), 5.40 (dt, J = 8.9, 7.0 Hz, 2H, H2^{I}, H4^{I}), 5.37 (dd, J = 3.4, 0.7 Hz, 1H, H4^{II}), 5.15 – 5.11 (m, 1H, N*H*Phe), 5.13 (dd, J = 10.3, 7.9 Hz, 1H, H2^{II}), 4.98 (dd, J = 10.4, 3.5 Hz, 1H, H3^{II}), 4.53 (d, J = 7.9 Hz, 1H, H1^{II}), 4.51 – 4.46 (m, 2H, H6a^{I}, C*H*$_2$aNH), 4.43 (dd, J = 15.4, 5.5 Hz, 1H, C*H*$_2$bNH), 4.30 (q, J = 7.0 Hz, 1H, C*H*Phe), 4.17 – 4.08 (m, 3H, H6a^{II}, H6b^{II}, H6b^{I}), 4.01 – 3.88 (m, 4H, H3^{I}, H5^{I}, H5^{II}, CH$_2$aGly), 3.84 (dd, J = 16.9, 5.6 Hz, 1H, C*H*$_2$bGly), 3.10 (dd, J = 13.7, 6.6 Hz, 1H, C*H*$_2$aPhe), 2.99 (dd, J = 13.6, 7.5 Hz, 1H, C*H*$_2$bPhe), 2.16 (s, 3H, COC*H*$_3$), 2.10 (s, 3H, COC*H*$_3$), 2.08 (s, 3H, COC*H*$_3$), 2.062 (s, 3H, COC*H*$_3$), 2.058 (s, 3H, COC*H*$_3$), 1.97 (s, 3H, COC*H*$_3$), 1.85 (s, 3H, COC*H*$_3$), 1.36 (s, 9H, C(C*H*$_3$)$_3$) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 170.52, 170.46, 170.3, 170.2, 169.9, 169.3, 169.2, 169.2, 156.0 (10C, 10 × *C*O), 136.4, 129.3, 128.9, 127.3, 121.3 (8C, Ar), 101.2 (1C, C1^{II}), 85.6 (1C, C1^{I}), 80.9 (1C, *C*(CH$_3$)$_3$), 76.0 (1C, C5^{I}), 75.7(1C, C3^{I}), 72.7 (1C, C2^{I}), 71.0 (1C, C3^{II}), 70.9 (1C, C5^{II}), 70.7 (1C, C4^{I}), 69.1 (1C, C2^{II}), 66.7 (1C, C4^{II}), 61.8 (1C, C6^{I}), 60.9 (1C, C6^{II}), 56.5 (1C, *C*HPhe), 43.1 (1C, *C*H$_2$Gly), 38.0 (1C, *C*H$_2$Phe), 35.0 (1C, *C*H$_2$NH), 28.3 (3C, C(*C*H$_3$)$_3$), 21.0, 20.84, 20.81, 20.79, 20.76, 20.6, 20.4 (7C, 2 × CO*C*H$_3$) ppm. HRMS calcd for $C_{45}H_{61}N_6O_{21}^+$ [M + H]$^+$ 1021.3884, found 1021.3895.



9

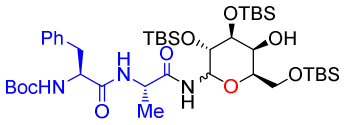
1-[(*N*-(*N*-tert-butoxycarbonyl)-L-phenylalanyl)]-L-alanylamido-1-deoxy-2,3,4,6-tetra-*O*-allyl-D-galactitol (9). The mixture was stirred 24 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Hexane, 1:1 → 1:0) to give **9** as a colorless oil (62.7 mg, 0.095 mmol, 97% yield). R_f = 0.62 (silica, EtOAc/Hexane, 4:1); $[\alpha]_D^{25}$ = −25.8 (*c* 0.6, $CHCl_3$); IR (ATR, Diamond) ν 3285, 2978, 1632, 1562, 1524, 1167, 1044 cm^{-1}; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 2H, Ar), 7.27 – 7.20 (m, 1H, Ar), 7.21 – 7.16 (m, 2H, Ar), 6.66 (dd, *J* = 6.7, 3.7 Hz, 1H, C1-N*H*), 6.54 (d, *J* = 7.2 Hz, 1H, N*H*Ala), 5.98 – 5.83 (m, 4H, OAll), 5.34 – 5.13 (m, 8H, OAll), 4.91 (d, *J* = 6.3 Hz, 1H, N*H*Phe), 4.38 – 4.29 (m, 1H, C*H*Phe) 4.34 (p, *J* = 7.0 Hz, 1H, C*H*Ala), 4.25 (ddt, *J* = 12.5, 5.3, 1.5 Hz, 1H, OAll), 4.17 (ddt, *J* = 12.3, 5.5, 1.4 Hz, 1H, OAll), 4.15 – 4.07 (m, 2H, OAll), 4.06 (tt, *J* = 6.6, 5.8, 1.3 Hz, 1H, OAll), 4.04 – 3.95 (m, 4H, OAll, H5), 3.83 (td, *J* = 12.8, 6.7, 6.2 Hz, 1H, CH_2aNH), 3.73 – 3.67 (m, 2H, H2, H4), 3.61 (dd, *J* = 6.1, 3.9 Hz, 1H, H3), 3.55 (dd, *J* = 9.4, 6.3 Hz, 1H, H6a), 3.52 (dd, *J* = 9.5, 6.4 Hz, 1H, H6b), 3.23 (dt, *J* = 14.1, 4.0 Hz, 1H, CH_2bNH), 3.07 (d, *J* = 6.1 Hz, 2H, CH_2Phe), 1.39 (s, 9H, C(CH_3)$_3$), 1.30 (d, *J* = 7.0 Hz, 3H, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.9, 171.0, 155.6 (3C, 3 × *C*O), 136.6 (1C, Ar), 134.7, 134.6, 134.5 (4C, 4 × OAll), 129.5, 128.8, 127.2 (5C, Ar), 117.8, 117.6, 117.4, 117.4 (4C, 4 × OAll), 81.2 (1C, *C*(CH$_3$)$_3$), 80.6 (1C, C3), 77.7 (1C, C4), 75.9 (1C, C2), 73.5, 73.4, 72.4 (3C, 3 × OAll), 71.3 (1C, C6), 71.2 (1C, OAll), 69.6 (1C, C5), 55.8 (1C, *C*HPhe), 49.2 (1C, *C*HAla), 39.2 (1C, C1), 38.2 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 18.7 (1C, *C*H$_3$Ala) ppm; HRMS calcd for $C_{35}H_{54}N_3O_9^+$ $[M + H]^+$ 660.3855, found 660.3848.



10

1,6-anhydro-3-[(*N*-(*N*-*tert*-butoxycarbonyl)-L-phenylalanyl)]-L-alanylamido-2,3,4-trideoxy-2,4-difluoro-β-D-glucopyranoside (10). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Hexane, 1:9 → 1:3) to give **10**, a white solid (16.0 mg, 0.033 mmol, 65% yield).R_f = 0.53 (silica, EtOAc/Hexane, 15:85); $[\alpha]_D^{25}$= −43.0 (*c* 0.7, $CHCl_3$; IR (ATR,

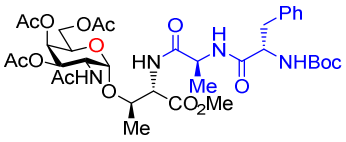
Diamond) ν 3337, 2934, 1649, 1520, 1167, 984, 669 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H, Ar), 7.25 – 7.17 (m, 3H, Ar), 6.89 (s, 1H, C3-N*H*), 6.57 (s, 1H, N*H*Ala), 5.62 (t, *J* = 1.7 Hz, 1H, H1), 5.06 (s, 1H, N*H*Phe), 4.84 – 4.78 (m, 1H, H5), 4.58 – 4.51 (m, 1H, C*H*Ala), 4.55 (dt, *J* = 47.9, 3.1 Hz, 1H, H4), 4.41 – 4.34 (m, 1H, C*H*Phe), 4.40 (m, 1H, 49.5 Hz is observed, H2), 4.39 (tdt, *J* = 30.1, 8.3, 4.1 Hz, 1H, H3), 3.87 – 3.79 (m, 2H, H6a, H6b), 3.05 (d, *J* = 6.6 Hz, 2H, CH_2Phe), 1.39 (s, 9H, C(CH_3)$_3$), 1.34 (d, *J* = 7.1 Hz, 1H, CH_3Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.0, 171.5, 155.6 (3C, 3 × *C*O), 136.6, 129.4, 128.8, 127.1 (6C, Ar), 98.5 (d, *J* = 24.4 Hz, 1C, C1), 86.7 (d, *J* = 185.9 Hz, 1C, C4), 85.4 (d, *J* = 186.8 Hz, 1C, C2), 73.8 (d, *J* = 18.9 Hz, 1C, C5), 63.9 (d, *J* = 6.6 Hz, 1C, C6), 55.7 (1C, *C*HPhe), 49.1 (1C, *C*HAla), 43.4 (t, *J* = 17.5 Hz, 1C, C3), 38.3 (1C, *C*H_2Phe), 28.4 (3C, C(*C*H_3)$_3$), 18.5 (1C, *C*H_3Ala) ppm; ^{19}F NMR (470 MHz, Chloroform-*d*) δ -199.10 (ddt, *J* = 47.5, 31.5, 11.6, 6.5 Hz, 1F, F4), -201.75 (ddd, *J* = 49.5, 28.9, 7.6 Hz, 1F, F2) ppm. HRMS calcd for $[M - H]^-$ 482.21082, found 482.21077.



11

2,3,6-Tri-*O*-tertbutyldimethylsilyl-1-deoxy-1-[(*N*-(*N*-tert-butoxycarbonyl)-L-phenylalanyl)]-D-alanylamido-α/β-D-galactopyranoside (11). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Hexane, 1:4 → 1:1) to give an anomeric mixture (1.7:1; α/β) of **11** as an amorphous white solid (28.6 mg, 0.034 mmol, 58% yield). R_f = 0.60 (silica, EtOAc/Hexane, 1:1); $[\alpha]_D^{25}$ = 6,2 (*c* 0.2, MeOH); IR (ATR, Diamond) *v* 3312, 2930, 2856, 1647, 1256, 835 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H, Ar), 7.28 – 7.17 (m, 6H, Ar), 6.87 (d, *J* = 9.2 Hz, 1H, C1-N*H*β), 6.53 (d, *J* = 8.9 Hz, 1H, C1-N*H*α), 6.44 (d, *J* = 7.3 Hz, 1H, N*H*βAla), 6.29 (d, *J* = 6.0 Hz, 1H, N*H*αAla), 5.75 (dd, *J* = 9.4, 3.9 Hz, 1H, H1α), 5.66 (d, *J* = 9.4 Hz, 1H, H1β), 5.10 (d, *J* = 6.8 Hz, 1H, N*H*αPhe), 5.03 (d, *J* = 7.5 Hz, 1H, N*H*βPhe), 4.39 – 4.27 (m, 4H, C*H*Alaα, C*H*Alaβ, C*H*Pheα, C*H*Pheβ), 4.26 (dd, *J* = 2.3, 1.3 Hz, 1H, H4β), 4.14 (t, *J* = 3.0 Hz, 1H, H3α), 4.12 (q, J = 2.2, 1.1 Hz, 1H, H2β), 3.95 (dd, J = 4.0, 2.9 Hz, 1H, H2α), 3.92 (s, 1H, H3β), 3.90 (t, J = 2.7 Hz, 1H, H4α), 3.73 – 3.65 (m, 2H, H5α, H5β), 3.65 – 3.56 (m, 4H, $H6^{I}$α, $H6^{II}$α, $H6^{I}$β, $H6^{II}$β), 3.13 – 2.99 (m, 4H, CH_2Pheα, CH_2Pheβ), 1.410 (s, 9H, C(CH_3)$_3$α), 1.406 (s, 9H, C(CH_3)$_3$β), 1.24 – 1.18 (m, 6H, CH_3Alaα, CH_3Alaβ),

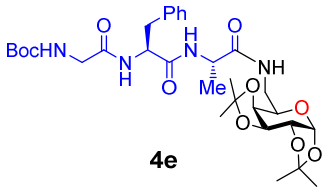
0.94 (s, 9H, (CH_3)$_3$CSiβ), 0.92 (s, 9H, (CH_3)$_3$CSiα), 0.90 (s, 9H, (CH_3)$_3$CSiβ), 0.88 (s, 18H, 2 × (CH_3)$_3$CSiα), 0.88 (s, 9H, (CH_3)$_3$CSiβ), 0.150 (s, 3H, CH_3β), 0.148 (s, 3H, CH_3β), 0.14 (s, 6H, 2 × CH_3β), 0.13 (s, 3H, CH_3α), 0.12 (s, 3H, CH_3α), 0.10 (s, 3H, CH_3α), 0.08 (s, 3H, CH_3α), 0.054 (s, 3H, CH_3α), 0.052 (s, 3H, CH_3α), 0.044 (s, 3H, CH_3β), 0.039 ppm (s, 3H, CH_3β); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 171.1, 170.7, 170.6, 155.7, 155.4 (6C, 3 × *C*Oα, 3 × *C*Oβ), 136.7, 136.6, 129.44, 129.40, 128.9, 127.19, 127.15 (10C, Ar), 87.1 (1C, C4β), 86.4 (1C, C1β), 83.7 (1C, C4β), 81.0 (1C, C3β), 80.5 (1C, C1α), 80.3 (2C, 2 × *C*(CH_3)$_3$), 80.1 (1C, C2β), 78.4 (1C, C3α), 78.0 (1C, C2α), 71.7 (1C, C5β), 71.2 (1C, C5α), 63.9 (1C, C6α), 63.8 (1C, C6β), 56.0 (2C, *C*HPheα, *C*HPheβ), 49.1 (1C, *C*HAlaα), 48.8 (1C, *C*HAlaβ), 39.2 (1C, *C*H_2Pheα), 38.9 (1C, *C*H_2Pheβ), 28.4 (6C, (*C*H_3)$_3$α, C(*C*H_3)$_3$ β), 26.1 (3C, (*C*H_3)$_3$CSiβ), 26.0 (3C, (*C*H_3)$_3$CSiα), 25.89 (3C, (*C*H_3)$_3$CSiα), 25.86 (3C, (*C*H_3)$_3$CSiβ), 25.79 (3C, (*C*H_3)$_3$CSiα), 25.7 (3C, (*C*H_3)$_3$CSiβ), 18.6 (2C, *C*H_3Alaβ, *C*H_3Alaα), 18.44 (1C, (CH_3)$_3$*C*Siβ), 18.41, 18.12 (2C, 2 × (CH_3)$_3$*C*Siα), 18.06, 18.0 (2C, 2 × (CH_3)$_3$*C*Siβ), 17.9 (1C, (CH_3)$_3$*C*Siα), -4.26, -4.31 (2C, 2 × *C*H_3α), -4.55 (1C, *C*H_3β), -4.57 (1C, *C*H_3α), -4.7 (1C, *C*H_3β), -4.8 (2C, *C*H_3α, *C*H_3β), -4.9 , -5.17, -5.22 (3C, 3 × *C*H_3β), -5.2, -5.3 (2C, 2 × *C*H_3α) ppm. HRMS calcd for $C_{41}H_{78}N_3O_9Si_3^+$ [M + H]$^+$ 840.5040, found 840.5038.



12

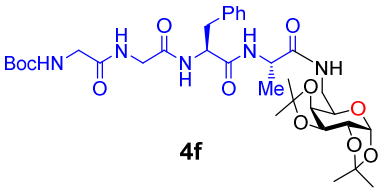
N-[((N-tert-butoxycarbonyl)-L-phenylalanyl)-L-alanyl]-*O*-[2-(acetylamino)-3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranosyl]-L-threonine methyl ester (12). The mixture was stirred 18 h and the obtained crude was purified by flash column chromatography (silica gel, MeOH/CH_2Cl_2, 1:19 → 1:9) to give **12**, a white solid (17.2 mg, 0.022 mmol, 58% yield). R_f = 0.41 (silica, MeOH/CH_2Cl_2, 1:19); $[\alpha]_D^{25}$ = 47.2 (c 0.4, $CHCl_3$); IR (ATR, Diamond) ν 3294, 2924, 1745, 1649, 1367, 1221, 1045 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 1H, N*H*Thr), 7.35 – 7.27 (m, 3H, Ar), 7.23 – 7.20 (m, 2H, Ar), 6.65 (d, *J* = 9.5 Hz, 1H, N*H*Ac), 6.42 (s, 1H, N*H*Ala), 5.38 (d, *J* = 2.2 Hz, 1H, H4), 5.30 (dd, *J* = 9.9, 2.1 Hz, 1H, H3), 5.15 (d, *J* = 5.0 Hz, 1H, N*H*Phe), 4.82 (d, *J* = 3.9 Hz, 1H, H1), 4.59 – 4.48 (m, 4H, H2, C*H*Phe, C*H*αThr, C*H*Ala), 4.39 – 4.33 (m, 2H, H5, C*H*βThr), 4.08 (d, *J* = 6.4 Hz, 2H, H6a, H6b), 3.73 (s, 3H, CO_2CH_3), 3.13 (dd, *J* = 13.9, 7.7 Hz, 1H, CH_2aPhe), 3.05 (dd, *J* = 14.1, 5.4 Hz, 1H, CH_2bPhe),

2.15 (s, 3H, COCH_3), 2.10 (s, 3H, COCH_3), 2.02 (s, 3H, COCH_3), 1.99 (s, 3H, COCH_3), 1.37 (s, 9H, C(CH_3)$_3$), 1.32 (d, J = 7.1 Hz, 3H, CH_3Ala), 1.23 (d, J = 6.5 Hz, 3H, CH_3Thr); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.8, 171.8, 171.2, 171.0, 170.9, 170.6, 170.5, 151.4 (8C, 8 × *C*O), 136.1, 129.4, 129.0, 127.5 (6C, Ar), 98.8 (1C, C1), 80.6 (1C, *C*(CH$_3$)$_3$), 75.3 (1C, *CH*βThr), 68.3 (1C, C3), 67.6 (1C, C4), 67.1 (1C, C5), 62.5 (1C, C6), 56.3 (1C, CHαThr), 56.1 (1C, C*H*Phe), 52.9 (1C, CO$_2$*C*H$_3$), 49.1 (1C, *C*HAla), 47.7 (1C, C2), 38.1 (1C, *C*H$_2$Phe), 28.3 (3C, C(*C*H$_3$)$_3$), 23.3, 21.0, 20.9, 20.8 (4C, 3 × CO*C*H$_3$), 19.3 (1C, *C*H$_3$Thr), 15.6 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{36}H_{53}N_4O_{15}^+$ [M + H]$^+$ 781.3502 found 781.3489.



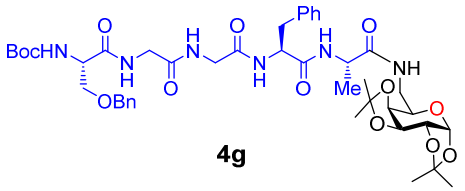
4e

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-glycyl-L-phenylalanyl)]-L-alanylamido-α-D-glucopyranoside (4e). The mixture was stirred 2 h and the obtained crude was purified by flash column chromatography (silica gel, EtOAc/Et$_2$O, 1:1 → 3:1) to give **4e**, a white solid (96.7 mg, 0.152 mmol, 79% yield). R$_f$ = 0.38 (silica, MeOH/DCM, 1:19); [α]$_D^{25}$ = −13.4 (*c* 0.5, CHCl$_3$); IR (ATR, Diamond) ν 3267, 2930, 1718, 1628, 1067, 1007, 700 cm^{-1}; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H, Ar), 7.25 – 7.22 (m, 1H, Ar), 7.21 – 7.17 (m, 2H, Ar), 6.68 (d, J = 7.3 Hz, 1H, N*H*Phe), 6.60 (d, J = 6.6 Hz, 1H, N*H*Ala), 6.46 (s, 1H, C6-N*H*), 5.48 (d, J = 5.0 Hz, 1H, H1), 5.24 (s, 1H, N*H*Gly), 4.65 (q, J = 6.8 Hz, 1H, C*H*Phe), 4.58 (dd, J = 7.9, 2.4 Hz, 1H, H3), 4.43 (p, J = 7.3 Hz, 1H, C*H*Ala), 4.28 (dd, J = 5.0, 2.4 Hz, 1H, H2), 4.20 (dd, J = 7.9, 1.8 Hz, 1H, H4), 3.87 (ddd, J = 8.8, 4.0, 1.7 Hz, 1H, H5), 3.75 (d, J = 5.1 Hz, 2H, CH$_2$Gly), 3.62 (ddd, J = 13.8, 7.3, 3.9 Hz, 1H, H6a), 3.22 – 3.10 (m, 2H, H6b, C*H*$_2$aPhe), 3.07 (dd, J = 13.9, 6.4 Hz, 1H, C*H*$_2$bPhe), 1.463 (s, 3H, C*H*$_3$), 1.458 (s, 3H, C*H*$_3$), 1.41 (s, 9H, C(C*H*$_3$)$_3$), 1.33 (s, 3H, C*H*$_3$), 1.31 – 1.28 (m, 6H, C*H*$_3$, C*H*$_3$Ala) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.0, 170.4, 170.1 (4C, 4 × *C*O), 136.1, 129.3, 129.0, 127.5 (6C, Ar), 109.6, 108.9 (2C, 2 × *C*(CH$_3$)$_2$), 96.4 (1C, C1), 80.9 (1C, *C*(CH$_3$)$_3$), 71.6 (1C, C4), 70.9 (1C, C3), 70.7 (1C, C2), 66.4 (1C, C5), 54.6 (1C, *C*HPhe), 49.1 (1C, *C*HAla), 44.8 (1C, *C*H$_2$Gly), 40.1 (1C, C6), 37.7 (1C, *C*H$_2$Phe), 28.4 (3C, C(*C*H$_3$)$_3$), 26.2, 26.1, 25.2, 24.5 (4C, 4 × *C*H$_3$), 18.1 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{31}H_{47}N_4O_{10}^+$ [M + H]$^+$ 635.3287, found 635.3300.



4f

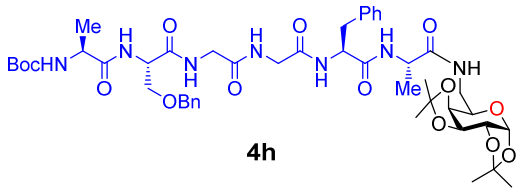
1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-α-D-glucopyranoside (4f). The mixture was stirred 2 h and the obtained crude was purified by flash column chromatography (silica gel, MeOH/CH_2Cl_2, 0:1 → 1:9) to give **4f** as an amorphous white solid (0.091 mg, 0.131 mmol, 68% yield). R_f = 0.27 (silica, MeOH/CH_2Cl_2, 1:19); $[\alpha]_D^{25}$ = −10.7 (*c* 1.0, MeOH); IR (ATR, Diamond) ν 3290, 2988, 1634, 1501, 1070, 1009, 700 cm^{-1}; ^1H NMR (500 MHz, Methanol-d_4) δ 7.31 – 7.25 (m, 4H, Ar), 7.24 – 7.19 (m, 1H, Ar), 5.46 (d, *J* = 4.9 Hz, 1H, H1), 4.62 (dd, *J* = 7.9, 2.4 Hz, 1H, H3), 4.58 (dd, *J* = 9.5, 5.1 Hz, 1H, C*H*Phe), 4.33 (dd, *J* = 5.0, 2.4 Hz, 1H, H2), 4.29 (q, *J* = 7.3 Hz, 1H, C*H*Ala), 4.22 (dd, *J* = 7.9, 1.8 Hz, 1H, H4), 3.95 (ddd, *J* = 8.4, 4.2, 1.5 Hz, 1H, H5), 3.86 – 3.67 (m, 4H, 2 × CH_2Gly), 3.40 (dd, *J* = 13.8, 4.3 Hz, 1H, H6a), 3.24 – 3.16 (m, 2H, H6b, CH_2aPhe), 2.95 (dd, *J* = 13.9, 9.5 Hz, 1H, CH_2bPhe), 1.46 (s, 12H, C(CH_3)$_3$, CH_3), 1.43 (s, 3H, CH_3), 1.36 (d, *J* = 7.2 Hz, 3H, CH_3Ala), 1.34 (s, 3H, CH_3), 1.30 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, Methanol-d_4) δ 175.3, 173.3, 172.0, 158.6 (5C, 5 × *C*O), 138.5, 130.2, 129.6, 127.9 (6C, Ar), 110.5, 110.0 (2C, 2 × *C*(CH$_3$)$_2$), 97.8 (1C, C1), 80.9 (1C, *C*(CH$_3$)$_3$), 72.7 (1C, C4), 72.2 (1C, C3), 71.9 (1C, C2), 67.3 (1C, C5), 56.5 (1C, *C*HPhe), 50.9 (1C, *C*HAla), 44.7 (1C, *C*H$_2$Gly), 43.7 (1C, *C*H$_2$Gly), 41.1 (1C, C6), 38.3 (1C, *C*H$_2$Phe), 28.7 (3C, C(*C*H$_3$)$_3$), 26.4, 26.3, 25.2, 24.6 (4C, 4 × *C*H$_3$), 18.1 (1C, *C*H$_3$Ala) ppm. HRMS calcd for $C_{33}H_{50}N_5O_{11}^+$ $[M + H]^+$ 692.3501, found 692.3508.



4g

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-((*O*-benzyl)-L-seryl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-α-D-glucopyranoside (4g). The mixture was stirred 3 h and the obtained crude was purified by flash column chromatography (silica gel, MeOH/CH_2Cl_2, 1:9 → 15:85) to give **4g** as an amorphous white solid (74.7 mg, 0.086 mmol, 71% yield). R_f = 0.31 (silica, MeOH/DCM, 1:19); $[\alpha]_D^{25}$ = −10.0 (*c* 0.4, MeOH); IR (ATR, Diamond) ν 3285, 2986, 1634, 1526, 1070, 1005, 700

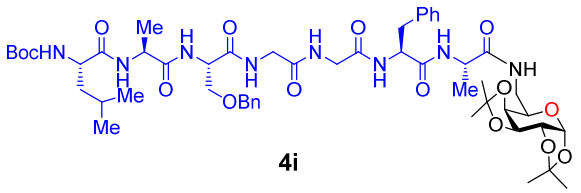
cm^{-1}; ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.37 – 7.16 (m, 10H, Ar), 5.45 (d, J = 4.9 Hz, 1H, H1), 4.62 (dd, J = 7.9, 2.5 Hz, 1H, H3), 4.58 (dd, J = 9.4, 5.3 Hz, 1H, CHPhe), 4.53 (d, J = 2.8 Hz, 2H, CH_2OBn), 4.32 (dd, J = 5.0, 2.5 Hz, 1H, H2), 4.31 – 4.26 (m, 2H, CHAla, CHSer), 4.22 (dd, J = 7.9, 1.9 Hz, 1H, H4), 3.94 (ddd, J = 8.4, 4.5, 1.8 Hz, 1H, H5), 3.88 – 3.86 (m, 2H, CH_2Gly), 3.82 (dd, J = 9.7, 5.5 Hz, 1H, CH$_2$aSer), 3.71 (dd, J = 9.7, 4.8 Hz, 1H, CH$_2$bSer), 3.65 (d, J = 16.7 Hz, 1H, CHaGly), 3.56 (d, J = 16.7 Hz, 1H, CHbGly), 3.39 (dd, J = 13.7, 4.5 Hz, 1H, H6a), 3.23 – 3.15 (m, 2H, H6b, CH_2aPhe), 2.96 (dd, J = 14.0, 9.5 Hz, 1H, CH_2bPhe), 1.44 (s, 12H, C(CH_3)$_3$, CH_3), 1.42 (s, 3H, CH_3), 1.36 – 1.31 (m, 6H, CH_3, CH_3Ala), 1.29 (s, 3H, CH_3) ppm; ^{13}C NMR (126 MHz, Methanol-d_4) δ 175.2, 173.9, 173.3, 171.7, 158.1 (6C, 6 × CO), 139.2, 138.5, 130.3, 129.6, 129.5, 128.9, 127.9 (12C, Ar), 110.5, 109.9 (2C, 2 × C(CH$_3$)$_2$), 97.7 (1C, C1), 81.2 (1C, C(CH$_3$)$_3$), 74.2 (1C, CH$_2$OBn), 72.6 (1C, C4), 72.1 (1C, C3), 71.9 (1C, C2), 71.0 (1C, CH$_2$Ser), 67.3 (1C, C5), 56.5 (1C, CHSer), 56.4 (1C, CHPhe), 50.8 (1C, CHAla), 44.0, 43.4 (2C, 2 × CH$_2$Gly), 41.1 (1C, C6), 38.4 (1C, CH$_2$Phe), 28.7 (3C, C(CH$_3$)$_3$), 26.4, 26.4, 25.2, 24.6 (4C, 4 × CH$_3$), 18.1 (1C, CH$_3$Ala) ppm. HRMS calcd for $C_{43}H_{61}N_6O_{13}^+$ [M + H]$^+$ 869.4291, found 869.4298.



4h

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-L-alanyl-((*O*-benzyl)-L-seryl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-α-D-glucopyranoside (4h). The mixture was stirred 18 h and the resulting crude was purified by trituration with diethyl ether to give **4h** as an amorphous white solid (31.3 mg, 0.033 mmol, 56% yield). [α]$_D^{25}$ = −28.2 (*c* 0.2, DMSO); IR (ATR, Diamond) ν 3288, 2982, 2934, 1701, 1630, 1514, 1167 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (t, J = 5.7 Hz, 1H, NHGly), 8.15 (d, J = 7.5 Hz, 1H, NHAla), 8.07 (d, J = 8.4 Hz, 1H, NHPhe), 7.94 (d, J = 7.5 Hz, 2H, NHGly, NHSer), 7.86 (t, J = 5.8 Hz, 1H, C6-NH), 7.34 – 7.14 (m, 10H, Ar), 7.05 (d, J = 7.5 Hz, 1H, NHAla), 5.41 (d, J = 4.9 Hz, 1H, H1), 4.58 (dd, J = 7.9, 2.4 Hz, 1H, H3), 4.57 – 4.49 (m, 2H, CHPhe, CHSer), 4.47 (s, 2H, CH_2OBn), 4.31 (dd, J = 4.9, 2.4 Hz, 1H, H2), 4.23 (p, J = 7.2 Hz, 1H, CHAla), 4.16 (dd, J = 8.0, 1.8 Hz, 1H, H4), 4.02 (p, J = 7.3 Hz, 1H, CHAla), 3.84 (ddd, J = 7.3, 5.0, 1.7 Hz, 1H, H5), 3.77 – 3.66 (m, 3H, CH_2Gly, CHaGly), 3.65 – 3.56 (m, 2H, CH$_2$Ser), 3.52 (dd, J = 16.8, 5.5 Hz, 1H, CHbGly), 3.19 (dt, J = 13.4, 5.6 Hz, 1H, H6a), 3.09 (ddd, J = 13.5, 7.9, 5.8 Hz, 1H, H6b), 3.03 (dd, J = 13.9, 4.1 Hz, 1H,

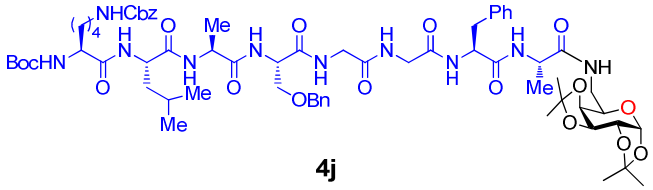
C*H*aPhe), 2.72 (dd, *J* = 13.9, 10.1 Hz, 1H, C*H*bPhe), 1.37 (s, 3H, CH_3), 1.36 (s, 9H, C(CH_3)$_3$), 1.35 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.20 (d, *J* = 7.1 Hz, 3H, CH_3Ala), 1.16 (d, *J* = 7.1 Hz, 3H, CH_3Ala); 172.8, 172.6, 170.7, 169.8, 168.7, 168.4, 155.2 (7C, 7 × *C*O), 138.1, 137.9, 129.2, 128.2, 128.0, 127.5, 127.4, 126.2 (12C, Ar), 108.4, 108.0 (2C, 2 × *C*(CH$_3$)$_2$), 95.7 (1C, C1), 78.2 (1C, *C*(CH$_3$)$_3$), 72.1 (1C, *C*H$_2$OBn), 70.6 (1C, C4), 70.1 (1C, C3), 69.9 (1C, C2), 69.7 (1C, *C*H$_2$Ser), 65.5 (1C, C5), 53.8 (1C, *C*HPhe), 52.6 (1C, *C*HSer), 49.7, 48.5 (2C, 2 × *C*HAla), 42.1, 41.7 (2C, 2 × *C*H$_2$Gly), 39.7 (1C, C6), 37.5 (1C, *C*H$_2$Phe), 28.2 (3C, C(*C*H$_3$)$_3$), 26.0, 25.8, 25.0, 24.3 (4C, 4 × *C*H$_3$), 18.5, 18.0 (2C, 2 × *C*H$_3$Ala) ppm. HRMS calcd for $C_{29}H_{44}N_3O_9^+$ [M + H]$^+$ 940.4662, found 940.4650.



4i

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-L-leucyl-L-alanyl-((*O*-benzyl)-L-seryl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-α-D-glucopyranoside (4i). The mixture was stirred 24 h and the resulting crude was purified by trituration with diethyl ether to give **4i** as an amorphous white solid (42.2 mg, 0.04 mmol, 52% yield). $[\alpha]_D^{25}$ = −8.7 (*c* 0.4, DMSO); IR (ATR, Diamond) ν 3285, 2978, 1632, 1502, 1252, 1167, 697 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.21 (t, *J* = 5.1 Hz, 1H, N*H*Gly), 8.14 (d, *J* = 7.8 Hz, 1H, N*H*Ala), 8.13 (d, *J* = 9.0 Hz, 1H, N*H*Ser), 8.06 (d, *J* = 8.3 Hz, 1H, N*H*Phe), 7.95 (t, *J* = 5.7 Hz, 1H, N*H*Gly), 7.88 (d, *J* = 7.3 Hz, 1H, N*H*Ala), 7.84 (t, *J* = 5.7 Hz, 1H, C6-N*H*), 7.35 – 7.21 (m, 10H, Ar), 6.93 (d, *J* = 8.4 Hz, 1H, N*H*Leu), 5.41 (dd, *J* = 4.9 Hz, 1H, H1), 4.58 (dd, *J* = 7.9, 2.3 Hz, 1H, H3), 4.56 – 4.48 (m, 2H, C*H*Phe, C*H*Ser), 4.47 (d, *J* = 2.1 Hz, 2H, CH_2OBn), 4.36 (p, *J* = 6.8 Hz, 1H, C*H*Ala), 4.31 (dd, *J* = 4.9, 2.3 Hz, 1H, H2), 4.23 (p, *J* = 7.0 Hz, 1H, C*H*Ala), 4.17 (dd, *J* = 8.0, 1.6 Hz, 1H, H4), 3.96 (td, *J* = 14.5, 5.8, 1.8 Hz, 1H, C*H*αLeu), 3.86 – 3.82 (m, 1H, H5), 3.78 – 3.67 (m, 3H, CH_2Gly, C*H*aGly), 3.63 – 3.55 (m, 2H, CH_2Ser), 3.52 (dd, *J* = 16.8, 5.4 Hz, 1H, C*H*bGly), 3.20 (td, *J* = 13.4, 7.8, 5.6 Hz, 1H, H6a), 3.12 – 3.06 (m, 1H, H6b), 3.03 (dd, *J* = 13.9, 4.0 Hz, 1H, CH_2aPhe), 2.73 (dd, *J* = 13.8, 10.1 Hz, 1H, CH_2bPhe), 1.63 – 1.53 (m, 1H, C*H*γLeu), 1.43 – 1.31 (m, 17H, CH_2Leu, C(C*H*$_3$)$_3$, 2 × C*H*$_3$), 1.28 (s, 3H, C*H*$_3$), 1.23 (s, 3H, C*H*$_3$), 1.20 (d, *J* = 7.1 Hz, 6H, 2 × C*H*$_3$Ala), 0.83 (t, *J* = 6.3 Hz, 6H, 2 × C*H*$_3$Leu) ppm; ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 172.6, 172.32, 172.28, 170.7, 169.7, 168.8, 168.4, 155.4 (8C, 8 × *C*O), 138.1, 137.9, 129.2, 128.2, 128.0, 127.5, 127.4, 126.2,

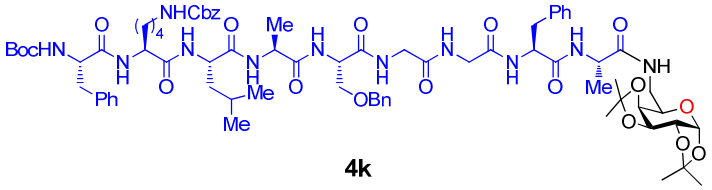
125.5 (12C, Ar), 108.4, 108.0 (2C, 2 × $C(CH_3)_2$), 95.7 (1C, C1), 78.0 (1C, $C(CH_3)_3$), 72.1 (1C, CH_2OBn), 70.6 (1C, C4), 70.1 (1C, C3), 69.9 (1C, C2), 69.6 (1C, CH_2Ser), 65.5 (1C, C5), 53.8 (1C, CHPhe), 52.7 (1C, CHSer), 52.6 (1C, CHαLeu), 48.5, 47.9 (2C, 2 × CHAla), 42.1, 41.7 (2C, 2 × CH_2Gly), 40.6 (1C, CH_2Leu), 39.7 (1C, C6), 37.5 (1C, CH_2Phe), 28.2 (3C, $C(CH_3)_3$), 26.0, 25.8, 25.0, 24.3 (4C, 4 × CH_3), 24.2 (1C, CHγLeu), 23.1, 21.4 (2C, 2 × CH_3Leu), 18.5, 18.3 (2C, 2 × CH_3Ala) ppm. HRMS calcd for $C_{52}H_{77}N_8O_{15}^+$ $[M + NH_4]^+$ 1053.5503, found 1053.5528.



4j

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-((*N*'-benzyloxycarbonyl)-L-lysyl)-L-leucyl-L-alanyl-((*O*-benzyl)-L-seryl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-α-D-glucopyranoside (4j). The mixture was stirred 32 h and the resulting crude was purified by trituration with diethyl ether to give **4j** as an amorphous white solid (32.1 mg, 0.024 mmol, 36% yield). $[\alpha]_D^{25}$ = −20.6 (*c* 0.3, DMSO); IR (ATR, Diamond) *v* 3288, 2953, 1626, 1501, 1244, 1067, 696 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.21 (t, *J* = 5.6 Hz, 1H, N*H*Gly), 8.16 (d, *J* = 7.4 Hz, 1H, N*H*Ala), 8.09 – 8.06 (m, 2H, N*H*Phe, N*H*Ala), 8.04 (d, *J* = 7.7 Hz, 1H, N*H*Ser), 7.95 (t, *J* = 5.8 Hz, 1H, N*H*Gly), 7.86 (t, *J* = 5.8 Hz, 1H, C6-N*H*), 7.76 (d, *J* = 8.3 Hz, 1H, N*H*Leu), 7.38 – 7.13 (m, 16H, Ar, N*H*Cbz), 6.89 (d, *J* = 8.2 Hz, 1H, N*H*Lys), 5.41 (d, *J* = 4.9 Hz, 1H, H1), 4.99 (s, 2H, CH_2Cbz), 4.58 (dd, *J* = 7.9, 2.4 Hz, 1H. H3), 4.57 – 4.48 (m, 2H, C*H*Phe, C*H*Ser), 4.47 (s, 2H, CH_2OBn), 4.37 – 4.29 (m, 2H, C*H*Ala, C*H*αLeu), 4.31 (dd, *J* = 4.9, 2.4 Hz, 1H, H2), 4.23 (p, *J* = 7.1 Hz, 1H, C*H*Ala), 4.16 (dd, *J* = 7.9, 1.8 Hz, 1H, H4), 3.89 – 3.82 (m, 2H, H5, C*H*Lys), 3.78 – 3.66 (m, 3H, CH_2Gly, CH_2aGly), 3.64 – 3.55 (m, 2H, CH_2Ser), 3.52 (dd, *J* = 16.7, 5.6 Hz, 1H, CH_2bGly), 3.20 (dt, *J* = 13.4, 5.6 Hz, 1H, H6a), 3.09 (ddd, *J* = 13.5, 7.8, 5.8 Hz, 1H, H6b), 3.03 (dd, *J* = 13.9, 4.0 Hz, 1H, CH_2aPhe), 3.00 – 2.89 (m, 2H, CH_2εLys), 2.72 (dd, *J* = 13.8, 10.1 Hz, 1H, CH_2bPhe), 1.65 – 1.45 (m, 3H, C*H*γLeu, CH_2βLys), 1.45 – 1.39 (m, 2H, CH_2Leu), 1.39 – 1.31 (m, 17H, CH_2δLys, 2 × CH_3, C(CH_3)$_3$), 1.30 – 1.24 (m, 2H, CH_2γLys), 1.28 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.20 (d, *J* = 7.1 Hz, 3H, CH_3Ala), 1.19 (d, *J* = 7.1 Hz, 3H, CH_3Ala), 0.83 (d, *J* = 6.4 Hz, 3H, CH_3Leu), 0.80 (d, *J* = 6.5 Hz, 3H, CH_3Leu) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.5, 172.2, 172.0, 171.8, 170.7, 169.7, 168.7, 168.4, 156.1, 155.4 (10C, 10 × *C*O), 138.1, 137.9, 137.3, 129.2, 128.4, 128.2,

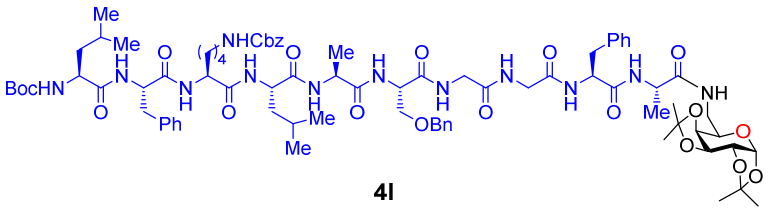
128.0, 127.8, 127.5, 127.4, 126.2 (18C, Ar), 108.4, 108.0 (2C, 2 × *C*(CH_3)$_2$), 95.6 (1C, C1), 78.1 (1C, *C*(CH_3)$_3$), 72.1 (1C, *C*H_2OBn), 70.6 (1C, C4), 70.1 (1C, C3), 69.9 (1C, C2), 69.7 (1C, *C*H_2Ser), 65.5 (1C, C5), 65.1 (1C, *C*H_2Cbz), 54.4 (1C, *C*HLys), 53.8 (1C, *C*HPhe), 52.7 (1C, *C*HSer), 50.6 (1C, *C*HαLeu), 48.5, 48.0 (2C, 2 × *C*HAla), 42.1, 41.7 (2C, 2 × *C*H_2Gly), 41.0 (1C, *C*H_2Leu), 40.1 (1C, *C*H_2εLys), 39.7 (1C, C6), 37.5 (1C, *C*H_2Phe), 31.4 (1C, *C*H_2βLys), 29.1 (1C, *C*H_2δLys), 28.2 (3C, C(*C*H_3)$_3$), 26.0, 25.8, 25.0, 24.3 (4C, 4 × *C*H_3), 24.0 (1C, *C*HγLeu), 23.2 (1C, *C*H_3Leu), 22.8 (1C, *C*H_2γLys), 21.5 (1C, *C*H_3Leu), 18.5, 18.0 (2C, 2 × *C*H_3Ala) ppm. HRMS calcd for $C_{66}H_{93}N_{10}O_{18}$ $[M - H]^-$ 1313.6675, found 1313.6650.



4k

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-L-phenylalanyl-((*N*'-benzyloxycarbonyl)-L-lysyl)-L-leucyl-L-alanyl-((*O*-benzyl)-L-seryl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-D-glucopyranoside (4k). The mixture was stirred 6 days and the resulting crude was purified by trituration with diethyl ether to give **4k** as an amorphous white solid (50.6 mg, 0.035 mmol, 49% yield). $[\alpha]_D^{25} = -5.9$ (*c* 0.3, DMSO); IR (ATR, Diamond) *v* 3281, 2934, 1626, 1514, 1244, 1067, 696 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.21 (t, *J* = 5.6 Hz, 1H, N*H*Gly), 8.16 (d, *J* = 7.5 Hz, 1H, N*H*Ala), 8.08 (d, *J* = 8.5 Hz, 1H, N*H*Phe), 8.06 – 8.03 (m, 2H, N*H*Ser, N*H*Ala), 8.00 (d, *J* = 8.2 Hz, 1H, N*H*Leu), 7.95 (t, *J* = 5.8 Hz, 1H, N*H*Gly), 7.91 (d, *J* = 8.0 Hz, 1H, N*H*Lys), 7.86 (t, *J* = 5.8 Hz, 1H, C6-N*H*), 7.38 – 7.12 (m, 21H, Ar, N*H*Cbz), 6.95 (d, *J* = 8.5 Hz, 1H, N*H*Phe), 5.41 (d, *J* = 4.9 Hz, 1H, H1), 4.99 (s, 2H, C*H*$_2$Cbz), 4.58 (dd, *J* = 7.9, 2.4 Hz, 1H, H3), 4.58 – 4.48 (m, 2H, C*H*Phe, C*H*Ser), 4.46 (s, 2H, C*H*$_2$OBn), 4.39 – 4.26 (m, 4H, H2, C*H*Ala, C*H*αLeu, C*H*Lys), 4.23 (p, *J* = 7.3 Hz, 1H, C*H*Ala), 4.16 (dd, *J* = 8.0, 1.8 Hz, 1H, H4), 4.16 – 4.12 (m, 1H, C*H*Phe), 3.84 (ddd, *J* = 7.2, 5.1, 1.8 Hz, 1H, H5), 3.78 – 3.66 (m, 3H, C*H*$_2$Gly, C*H*aGly), 3.64 – 3.56 (m, 2H, C*H*$_2$Ser), 3.52 (dd, *J* = 16.8, 5.5 Hz, 1H, C*H*bGly), 3.20 (dt, *J* = 13.3, 5.5 Hz, 1H, H6a), 3.09 (ddd, *J* = 13.6, 7.9, 5.7 Hz, 1H, H6b), 3.03 (dd, *J* = 13.8, 4.1 Hz, 1H, C*H*$_2$aPhe), 3.00 – 2.92 (m, 3H, C*H*$_2$aPhe, C*H*$_2$εLys), 2.71 (ddd, *J* = 14.2, 10.4, 4.1 Hz, 2H, C*H*$_2$bPhe, C*H*$_2$bPhe), 1.69 – 1.47 (m, 3H, C*H*γLeu, C*H*$_2$βLys), 1.46 – 1.39 (m, 4H, C*H*$_2$Leu, C*H*$_2$δLys), 1.37 (s, 3H, C*H*$_3$), 1.35 (s, 3H, C*H*$_3$) 1.31 – 1.24 (m, 14H, C(C*H*$_3$)$_3$, C*H*$_2$γLys, C*H*$_3$), 1.23 (s, 3H, C*H*$_3$), 1.199 (d, *J* = 7.2 Hz, 3H, C*H*$_3$Ala), 1.196 (d, *J* = 7.0 Hz, 3H, C*H*$_3$Ala), 0.84 (d, *J* = 6.6 Hz, 3H, C*H*$_3$Leu), 0.81 (d, *J* =

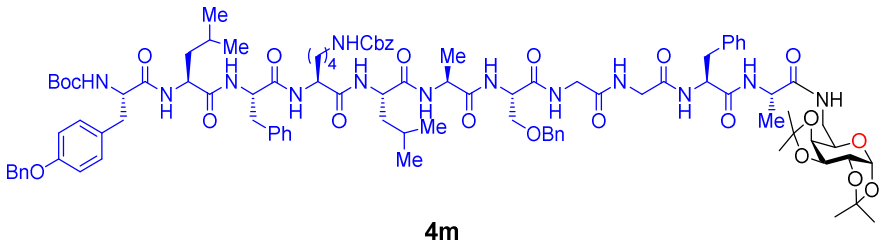
6.4 Hz, 3H, CH_3Leu) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.6, 172.2, 171.7, 171.5, 171.4, 170.7, 169.7, 168.7, 168.4, 156.0, 155.2 (11C, 11 × *C*O), 138.2, 138.1, 137.9, 137.3, 137.1, 130.7, 129.2, 128.3, 128.2, 128.02, 128.01, 127.8, 127.7, 127.5, 127.4, 126.22, 126.16 (24C, Ar), 108.4, 108.0 (2C, 2 × *C*$(CH_3)_2$), 95.6 (1C, C1), 78.1 (1C, *C*$(CH_3)_3$), 72.1 (1C, *C*H_2OBn), 70.6 (1C, C4) , 70.1 (1C, C3), 69.9 (1C, C2), 69.7 (1C, *C*H_2Ser), 65.5 (1C, C5), 65.1 (1C, *C*H_2Cbz), 55.8, 53.8 (2C, 2 × *C*HPhe), 52.6 (1C, *C*HSer), 52.2 (1C, *C*HLys), 50.7 (1C, *C*HαLeu), 48.5, 48.0 (2C, 2 × *C*HAla), 42.5, 42.1 (2C, 2 × *C*H_2Gly), 40.7 (1C, *C*H_2Leu), 40.2 (1C, *C*H_2εLys), 39.8 (1C, C6), 37.5, 37.2 (2C, 2 × *C*H_2Phe), 32.0 (1C, *C*H_2βLys), 29.2 (1C, *C*H_2δLys), 28.1 (3C, C(*C*$H_3)_3$), 26.0, 25.8, 25.0, 24.3 (4C, 4 × *C*H_3), 24.1 (1C, *C*HγLeu), 23.1 (1C, *C*H_3Leu), 22.5 (1C, *C*H_2γLys), 21.5 (1C, *C*H_3Leu), 18.6, 18.0 (2C, 2 × *C*H_3Ala) ppm. HRMS calcd for $C_{75}H_{102}N_{11}O_{19}$ $[M - H]^-$ 1460.7359, found 1460.7307.



4l

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-L-leucyl-L-phenylalanyl-((*N*'-benzyloxycarbonyl)-L-lysyl)-L-leucyl-L-alanyl-((*O*-benzyl)-L-seryl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-D-glucopyranoside (4l). The mixture was stirred 6 days and the resulting crude was purified by trituration with diethyl ether to give **4l** as an amorphous white solid (25.6 mg, 0.016 mmol, 23% yield $[\alpha]_D^{25} = -14.6$ (*c* 0.5, DMSO); IR (ATR, Diamond) ν 3283, 2934, 1626, 1514, 1250, 1067, 696 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.21 (t, *J* = 5.8 Hz, 1H, N*H*Gly), 8.16 (d, *J* = 7.5 Hz, 1H, N*H*Lys), 8.11 (d, *J* = 7.6 Hz, 1H, N*H*Ala), 8.09 – 8.02 (m, 3H, N*H*Phe, N*H*Ser, N*H*Leu), 7.97 – 7.92 (m, 2H, N*H*Gly, N*H*Ala), 7.85 (t, *J* = 5.8 Hz, 1H, C6-N*H*), 7.73 (d, *J* = 8.2 Hz, 1H, N*H*Phe), 7.37 – 7.13 (m, 21H, Ar, N*H*Cbz), 6.91 (d, *J* = 8.4 Hz, 1H, N*H*Leu), 5.40 (d, *J* = 4.9 Hz, 1H, H1), 4.99 (s, 2H, CH_2Cbz), 4.58 (dd, *J* = 7.9, 2.5 Hz, 1H, H3), 4.56 – 4.47 (m, 3H, 2 × C*H*Phe, C*H*Ser), 4.46 (s, 2H, CH_2OBn), 4.37 – 4.28 (m, 2H, C*H*Ala, C*H*αLeu), 4.31 (dd, *J* = 4.9, 2.4 Hz, 1H, H2), 4.26 – 4.19 (m, 2H, C*H*Ala, C*H*Lys), 4.16 (dd, *J* = 7.9, 1.7 Hz, 1H, H4), 3.90 – 3.81 (m, 2H, H5, C*H*αLeu), 3.77 – 3.66 (m, 3H, CH_2Gly, CH_2aGly), 3.64 – 3.49 (m, 3H, CH_2Ser, CH_2bGly), 3.23 – 3.13 (m, 1H, H6a), 3.09 (ddd, *J* = 13.6, 8.0, 5.8 Hz, 1H, H6b), 3.05 – 2.92 (m, 4H, CH_2aPhe, CH_2aPhe, CH_2εLys), 2.74 (ddd, *J* = 28.6, 13.9, 9.4 Hz, 2H, CH_2bPhe,

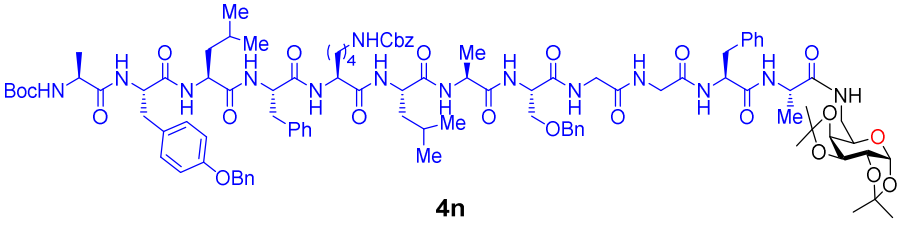
CH_2bPhe), 1.68 – 1.54 (m, 2H, CHγLeu, CH_2βaLys), 1.52 – 1.41 (m, 4H, CHγLeu, CH_2Leu, CH_2βbLys), 1.40 – 1.32 (m, 17H, C(CH_3)$_3$, CH_2δLys, 2 × CH_3), 1.27 (s, 3H, CH_3), 1.26 – 1.16 (m, 13H, CH_3, 2 × CH_3Ala, CH_2Leu, CH_2γLys), 0.85 (d, J = 6.6 Hz, 3H, CH_3Leu), 0.84 – 0.79 (m, 6H, 2 × CH_3Leu), 0.77 (d, J = 6.6 Hz, 3H, CH_3Leu) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.6, 172.3, 171.8, 171.4, 170.80, 170.76, 169.7, 168.8, 168.5, 156.1, 155.2 (12C, 12 × CO), 138.1, 137.9, 137.5, 137.3, 129.4, 129.2, 128.4, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 126.3, 126.2 (24C, Ar), 108.4, 108.0 (2C, 2 × C(CH$_3$)$_2$), 95.7 (1C, C1), 78.2 (1C, C(CH$_3$)$_3$), 72.1 (1C, CH$_2$OBn), 70.7 (1C, C4), 70.1 (1C, C3), 70.0 (1C, C2), 69.7 (1C, CH$_2$Ser), 65.5 (1C, C5), 65.2 (1C, CH$_2$Cbz), 53.8, 53.2 (2C, 2 × CHPhe), 53.1 (1C, CHαLeu), 52.7 (1C, CHSer), 52.5 (1C, CHLys), 50.8 (1C, CHαLeu), 48.5, 48.1 (2C, 2 × CHAla), 42.1, 41.7 (2C, 2 × CH$_2$Gly), 40.9, 40.7 (2C, 2 × CH$_2$Leu), 40.3 (1C, CH$_2$εLys), 38.7 (1C, C6), 37.64, 37.56 (2C, 2 × CH$_2$Phe), 31.9 (1C, CH$_2$βLys), 29.2 (1C, CH$_2$δLys), 28.2 (3C, C(CH$_3$)$_3$), 26.0, 25.8, 25.0, 24.3 (4C, 4 × CH$_3$), 24.23, 24.17 (2C, 2 × CHγLeu), 23.2, 22.9 (2C, 2 × CH$_3$Leu), 22.7 (1C, CH$_2$γLys), 21.6 (2C, 2 × CH$_3$Leu), 18.6, 18.0 (2C, 2 × CH$_3$Ala) ppm. HRMS calcd for $C_{81}H_{113}N_{12}O_{20}$ [M – H]$^-$ 1573.8200, found 1573.8142.



4m

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-(*O*-benzyl)-L-tyrosyl-L-leucyl-L-phenylalanyl-((*N*'-benzyloxycarbonyl)-L-lysyl)-L-leucyl-L-alanyl-((*O*-benzyl)-L-seryl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-D-α-glucopyranoside (4m). The mixture was stirred 7 days and the resulting crude was purified by trituration with diethyl ether to give **4m** as an amorphous white solid (15.7 mg, 8.58 μmol, 12% yield). $[\alpha]_D^{25} = -13.8$ (c 0.2, DMSO); IR (ATR, Diamond) ν 3279, 2934, 2361, 1624, 1514, 1067, 696 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.20 (t, J = 5.9 Hz, 1H, NHGly), 8.15 (d, J = 7.3 Hz, 1H, NHLys), 8.08 – 7.82 (m, 9H, NHGly, 2 × NHPhe, NHSer, 2 × NHAla, 2 × NHLeu, C6-NH), 7.45 – 7.11 (m, 28H, Ar, NHCbz), 6.91 – 6.85 (m, 3H, Ar, NHTyr), 5.40 (dd, J = 4.6, 3.7 Hz, 1H, H1), 5.04 (s, 2H, CH_2OBnTyr), 4.99 (s, 2H, CH_2Cbz), 4.58 (dd, J = 7.9, 2.5 Hz, 1H, H3), 4.55 – 4.47 (m, 3H, 2 × CHPhe, CHSer), 4.46 (s, 2H, CH_2OBnSer), 4.36 – 4.27 (m, 4H, H2, CHAla, 2 × CHαLeu), 4.27

– 4.20 (m, 2H, C*H*Ala, C*H*Lys), 4.16 (dd, *J* = 7.9, 1.6 Hz, 2H, H4), 4.07 (ddd, *J* = 10.8, 8.4, 3.9 Hz, 1H, C*H*Tyr), 3.88 – 3.79 (m, 1H, H5), 3.77 – 3.65 (m, 3H, CH_2Gly, CH_2aGly), 3.64 – 3.55 (m, 2H, CH_2Ser), 3.55 – 3.48 (m, 1H, CH_2bGly), 3.23 – 3.13 (m, 1H, H6a), 3.13 – 3.06 (m, 1H, H6b), 3.05 – 2.98 (m, 2H, CH_2aPhe, CH_2aPhe), 2.95 (dd, *J* = 6.4 Hz, 2H, CH_2εLys), 2.83 – 2.76 (m, 2H, CH_2aTyr, CH_2bPhe), 2.72 (dd, *J* = 14.1, 10.2 Hz, 1H, CH_2bPhe), 2.60 (dd, *J* = 13.3, 2.1 Hz, 1H, CH_2bTyr), 1.66 – 1.53 (m, 2H, 2 × C*H*γLeu), 1.51 – 1.32 (m, 14H, 2 × CH_2Leu, CH_2δLys, CH_2βLys, 2 × CH_3), 1.28 (s, 12H, C(CH_3)$_3$, CH_3), 1.26 – 1.15 (m, 11H, CH_2γLys, CH_3, 2 × CH_3Ala), 0.88 – 0.78 (m, 12H, 4 × CH_3Leu) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.6, 172.2, 171.6, 171.3, 170.7, 170.7, 169.8, 169.7, 168.8, 168.5, 168.4, 156.1, 155.3 (13C, 13 × CO), 137.9, 137.6, 137.3, 130.4, 130.2, 129.2, 129.2, 128.4, 128.4, 128.2, 128.0, 128.0, 127.8, 127.8, 127.6, 127.5, 127.5, 127.4, 114.3 (36C, Ar), 108.4, 108.0 (2C, 2 × *C*(CH$_3$)$_2$), 95.7 (1C, C1), 78.1 (1C, *C*(CH$_3$)$_3$), 72.1 (1C, *C*H$_2$OBnSer), 70.7 (1C, C4), 70.12 (1C, C3), 70.08 (1C, C2), 69.9 (1C, *C*H$_2$Ser), 69.2 (1C, CH_2OBnTyr), 65.1 (1C, *C*H$_2$Cbz), 55.9 (1C, *C*HTyr), 53.8, 53.4 (2C, 2 × *C*HPhe), 52.4 (1C, C*H*Lys), 51.1, 50.9 (2C, 2 × *C*HαLeu), 48.5, 48.1 (2C, 2 × *C*HAla), 42.1, 41.1 (2C, 2 × *C*H$_2$Gly), 40.8, 40.7 (2C, 2 × *C*H$_2$Leu), 40.3 (1C, *C*H$_2$εLys), 39.1 (1C, C6), 37.5, 37.3 (2C, 2 × *C*H$_2$Phe), 36.3 (1C, *C*H$_2$Tyr), 31.9 (1C, *C*H$_2$βLys), 29.2 (1C, *C*H$_2$δLys), 28.1 (3C, C(*C*H$_3$)$_3$), 26.0, 25.8, 25.0, 24.3 (4C, 4 × *C*H$_3$), 24.2, 24.1 (2C, 2 × *C*HγLeu), 23.14, 23.12 (2C, 2 × *C*H$_3$Leu), 22.6 (1C, *C*H$_2$γLys), 21.62, 21.55 (2C, 2 × *C*H$_3$Leu), 18.5, 18.0 (2C, 2 × *C*H$_3$Ala) ppm; HRMS calcd for $C_{97}H_{128}N_{13}O_{22}$ $[M - H]^-$ 1826.9302, found 1826.9222.

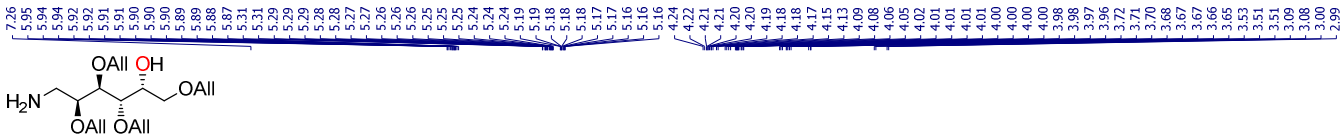


4n

1,2:3,4-di-*O*-isopropylidene-6-deoxy-6-[(*N*-(*N*-tert-butoxycarbonyl)-alanyl-((*O*-benzyl)-L-tyrosyl)-L-leucyl-L-phenylalanyl-((*N*'-benzyloxycarbonyl)-L-lysyl)-L-leucyl-L-alanyl-((*O*-benzyl)-L-seryl)-glycyl-glycyl-L-phenylalanyl)]-L-alanylamido-D-glucopyranoside (4n). The mixture was stirred 7 days and the resulting crude was purified by trituration with diethyl ether to give **4n** as an amorphous white solid (9.1 mg, 4.79 µmol, 11% yield). $[\alpha]_D^{25} = -7.5$ (*c* 0.2, DMSO); IR (ATR, Diamond) ν 3273, 2930, 1626, 1510, 1257, 1068, 696 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.14 (t, *J* = 5.2 Hz, 1H, N*H*Gly),

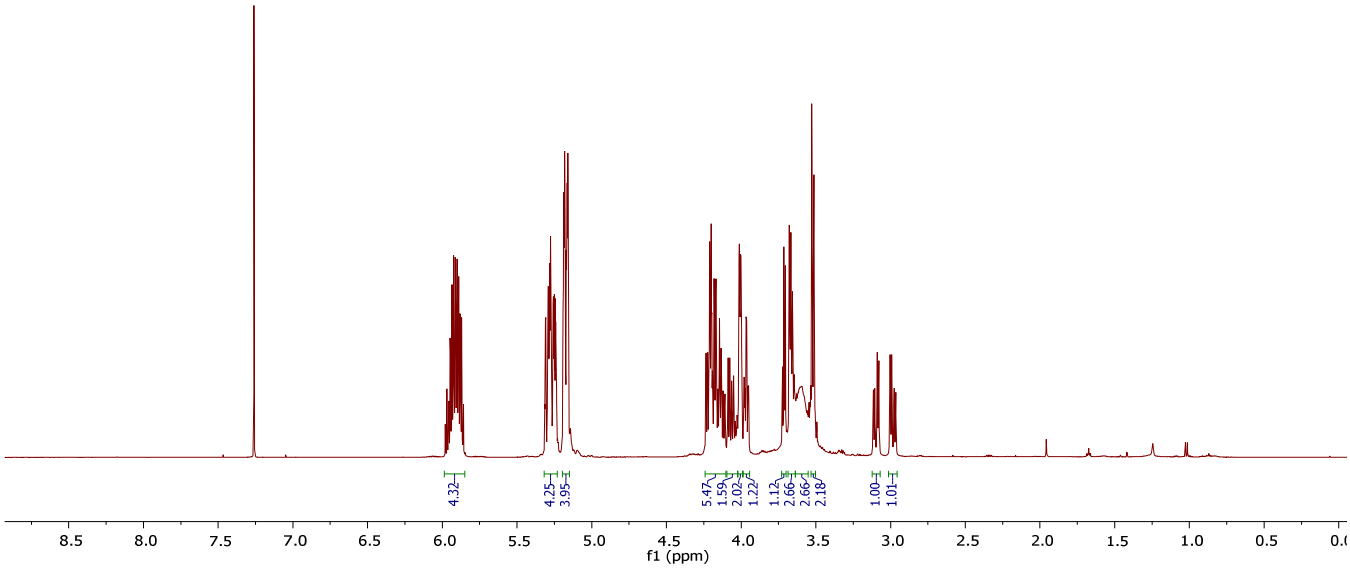
8.05 – 7.86 (m, 10H, 2 × N*H*Phe, N*H*Ser, N*H*Gly, N*H*Lys, 2 × N*H*Ala, 2 × N*H*Leu, C6-N*H*), 7.68 (d, *J* = 8.2 Hz, 1H, N*H*Tyr), 7.44 – 7.10 (m, 26H, N*H*Cbz, Ar), 7.07 (d, *J* = 8.1 Hz, 2H, Ar), 6.96 (s, 1H, N*H*Ala), 6.82 (d, *J* = 8.6 Hz, 2H, Ar), 5.40 (d, *J* = 4.8 Hz, 1H, H1), 5.01 (s, 2H, CH_2OBnTyr), 4.99 (s, 2H, CH_2Cbz), 4.61 – 4.39 (m, 7H, H3, 2 × C*H*Phe, C*H*Ser, C*H*Tyr, CH_2OBnSer), 4.35 – 4.19 (m, 6H, H2, C*H*Lys, 2 × C*H*Ala, 2 × C*H*Leu), 4.18 – 4.09 (m, 1H, H4), 3.90 – 3.78 (m, 2H, H5, C*H*Ala), 3.76 – 3.63 (m, 3H, CH_2Gly, CH_2aGly), 3.62 – 3.48 (m, 3H, CH_2bGly, CH_2Ser), 3.23 – 3.13 (m, 1H, H6a), 3.13 – 3.06 (m, 1H, H6b), 3.03 (dd, *J* = 13.6, 4.0 Hz, 2H, CH_2aPhe, CH_2aPhe), 2.95 (q, *J* = 6.5 Hz, 2H, CH_2εLys), 2.87 (dd, *J* = 13.8, 3.6 Hz, 2H, CH_2aTyr, CH_2bPhe), 2.81 (dd, *J* = 14.0, 9.1 Hz, 1H, CH_2bPhe), 2.69 (dd, *J* = 13.8, 8.5 Hz, 1H, CH_2bTyr), 1.65 – 1.54 (m, 1H, C*H*γLeu), 1.53 – 1.39 (m, 5H, CH_2βLys, C*H*γLeu, CH_2Leu), 1.39 – 1.31 (m, 19H, C(CH_3)$_3$, CH_2δLys, CH_2Leu, 2 × CH_3), 1.30 – 1.13 (m, 14H, CH_2γLys, 2 × CH_3Ala, 2 × CH_3), 1.07 (d, *J* = 7.0 Hz, 3H, CH_3Ala), 0.88 – 0.80 (m, 9H, 3 × CH_3Leu), 0.78 (d, *J* = 6.5 Hz, 3H, CH_3Leu) ppm. HRMS calcd for $C_{100}H_{134}N_{14}O_{23}^{+}$ $[M + 2H]^{2+}$ 950.4946, found 950.4938

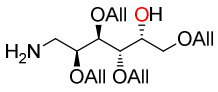
II. NMR spectra of compounds



S9

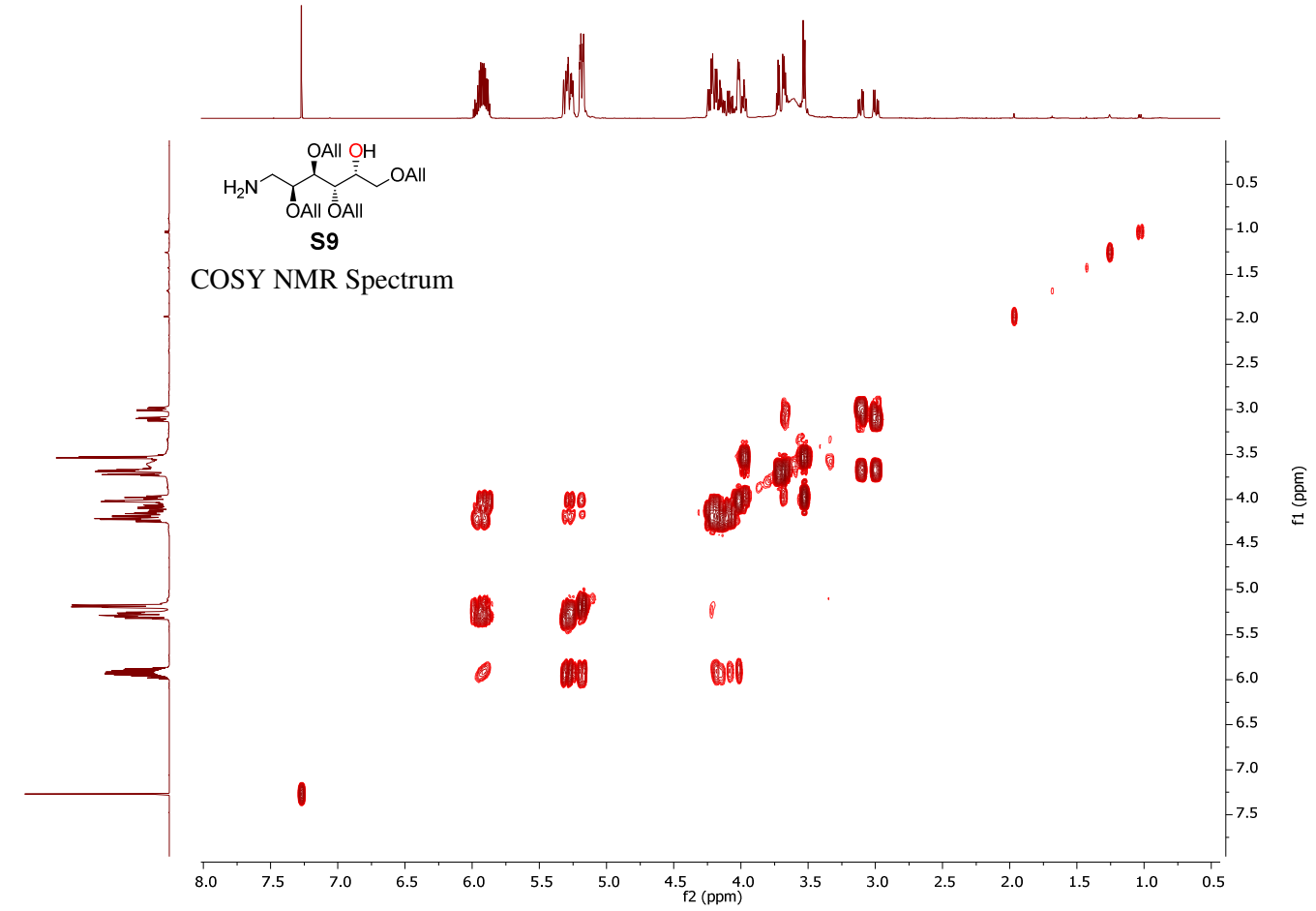
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



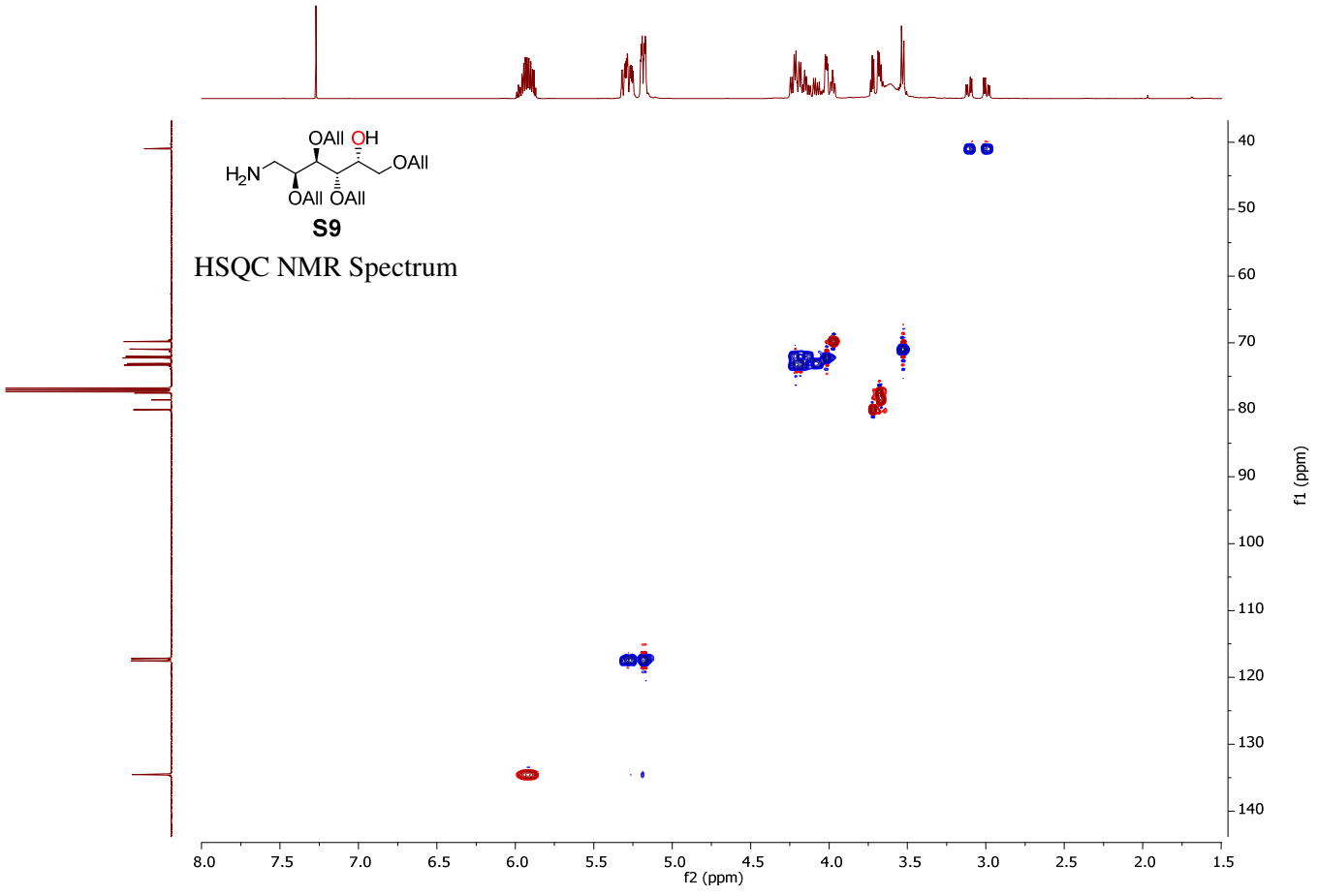


S9

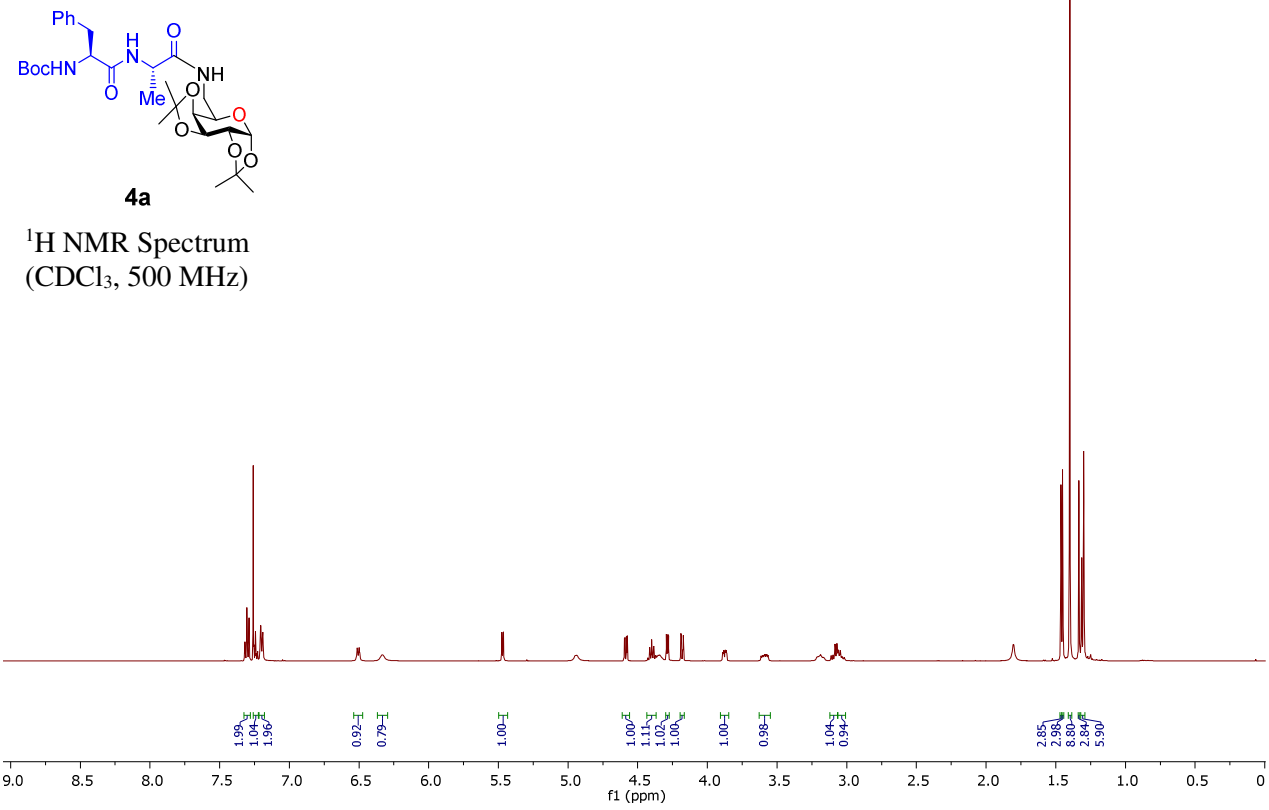
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

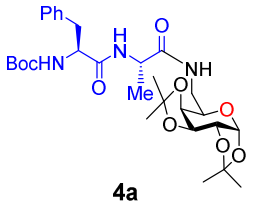


HSQC NMR Spectrum



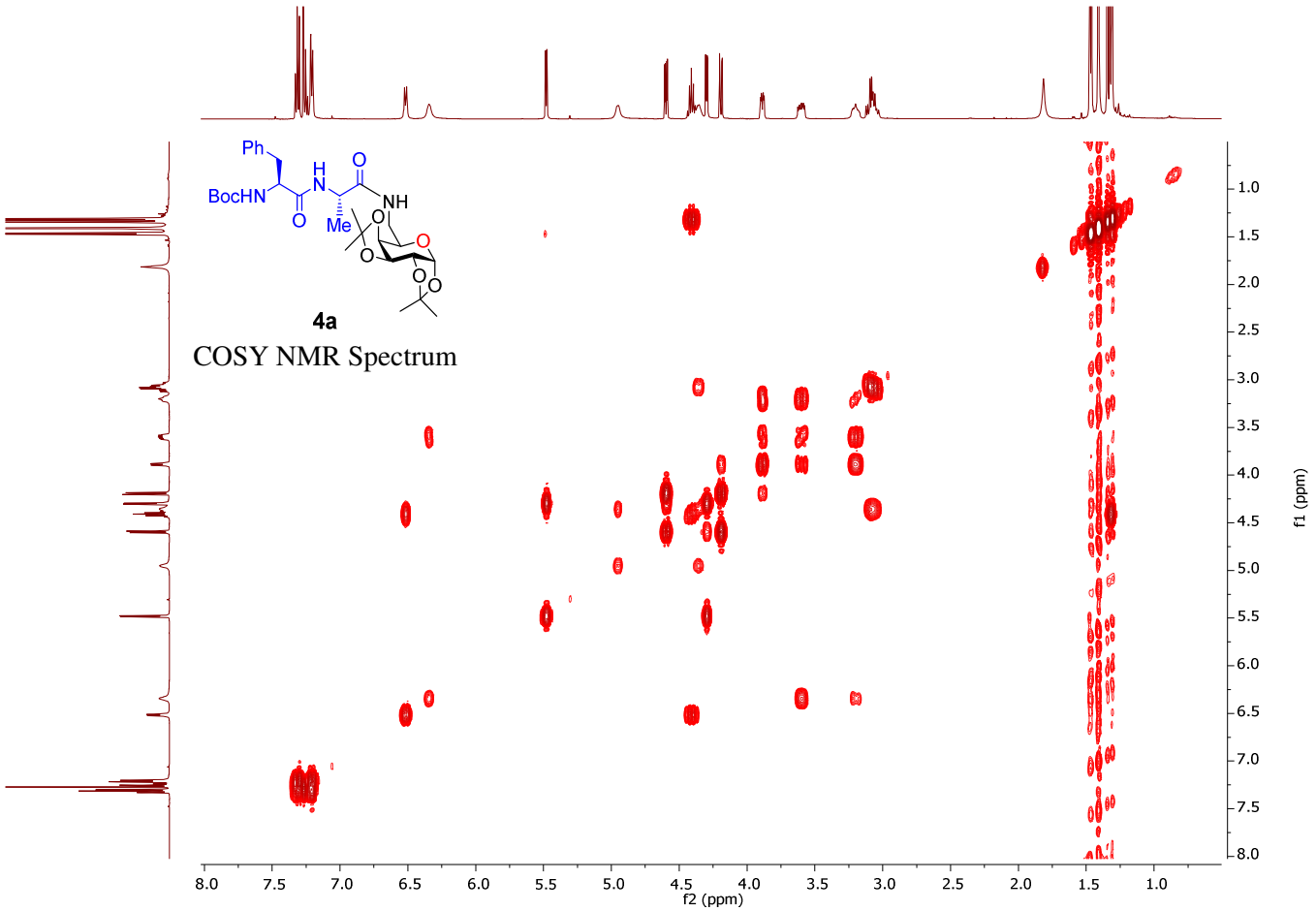
4a

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

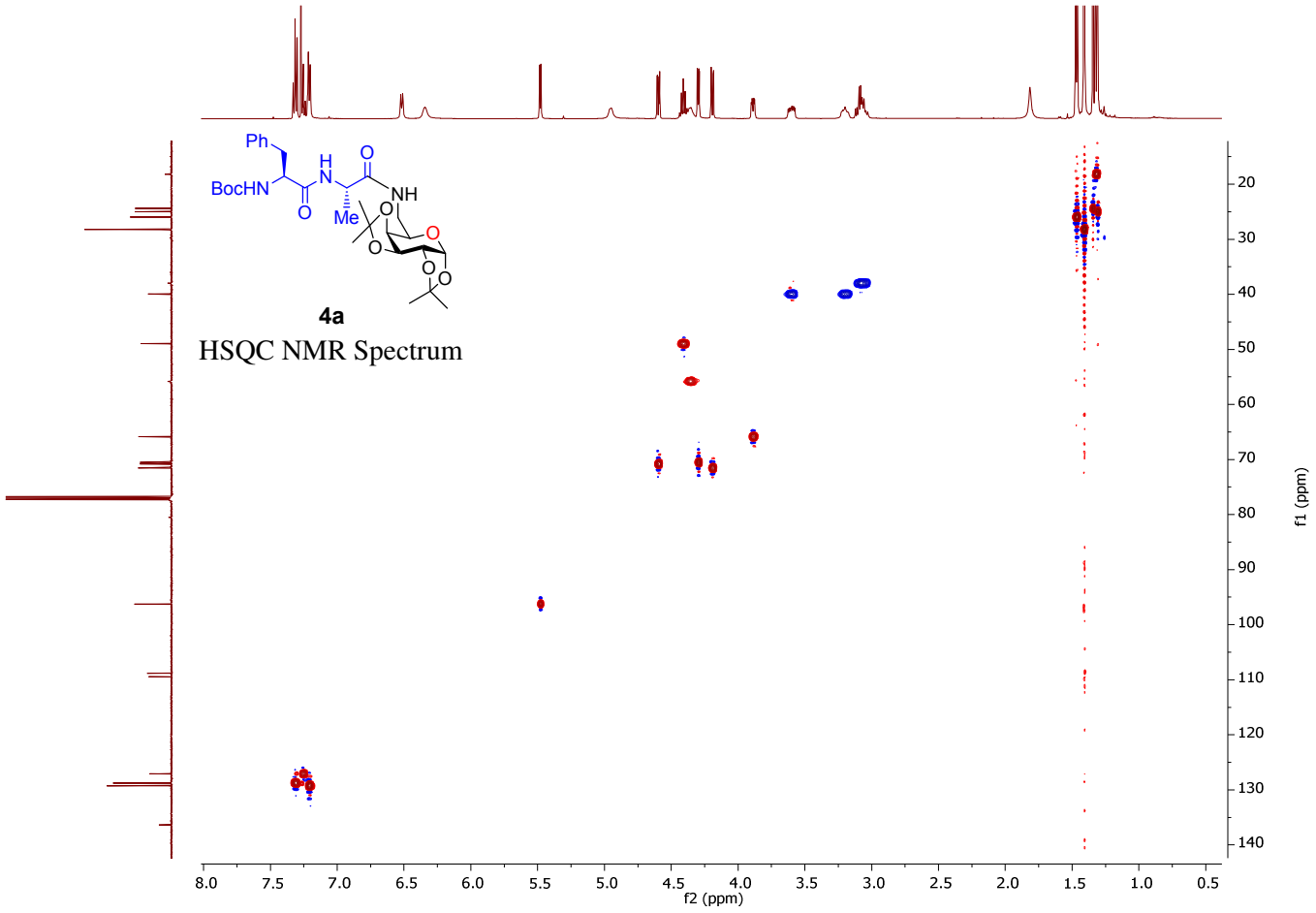


4a

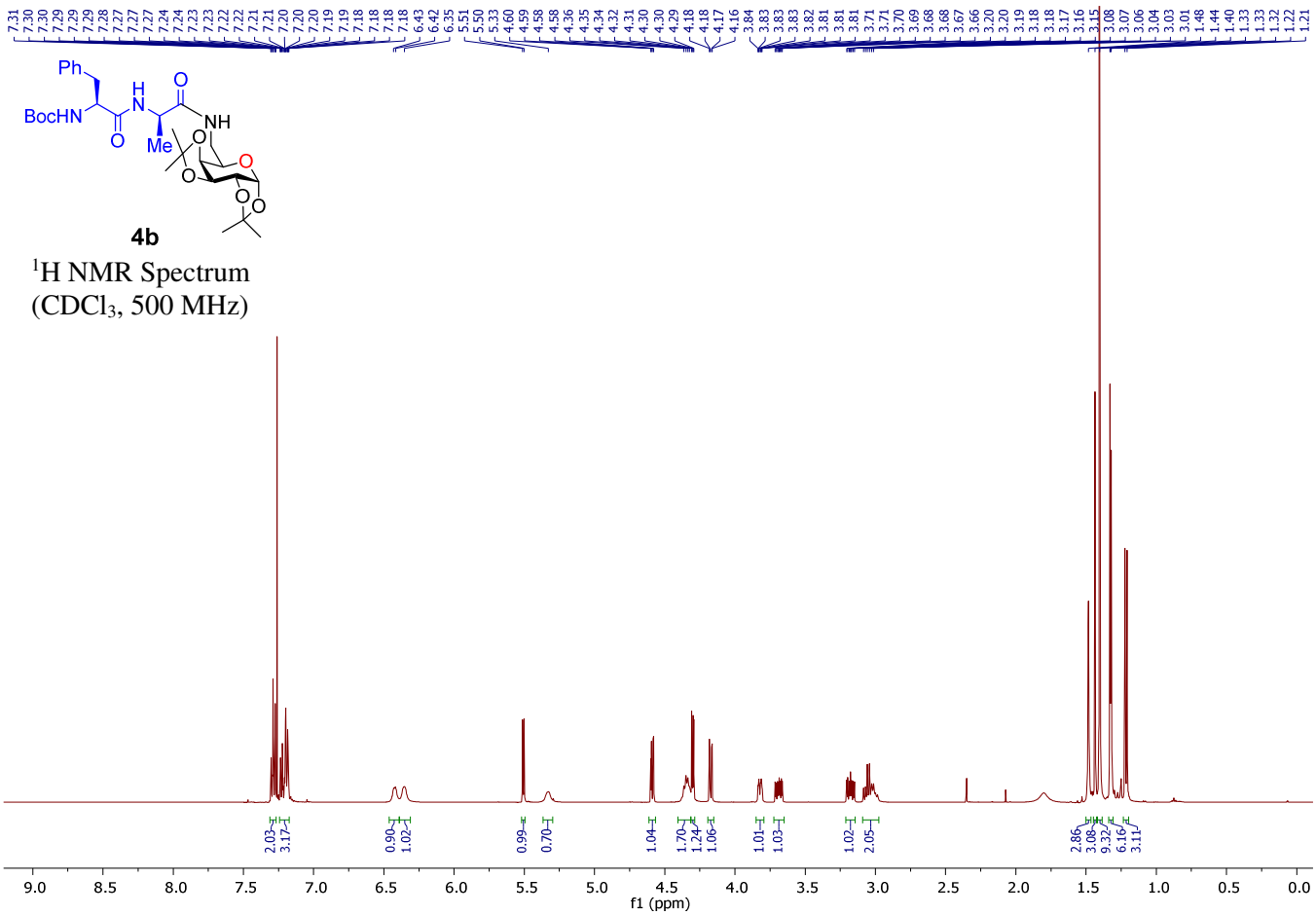
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



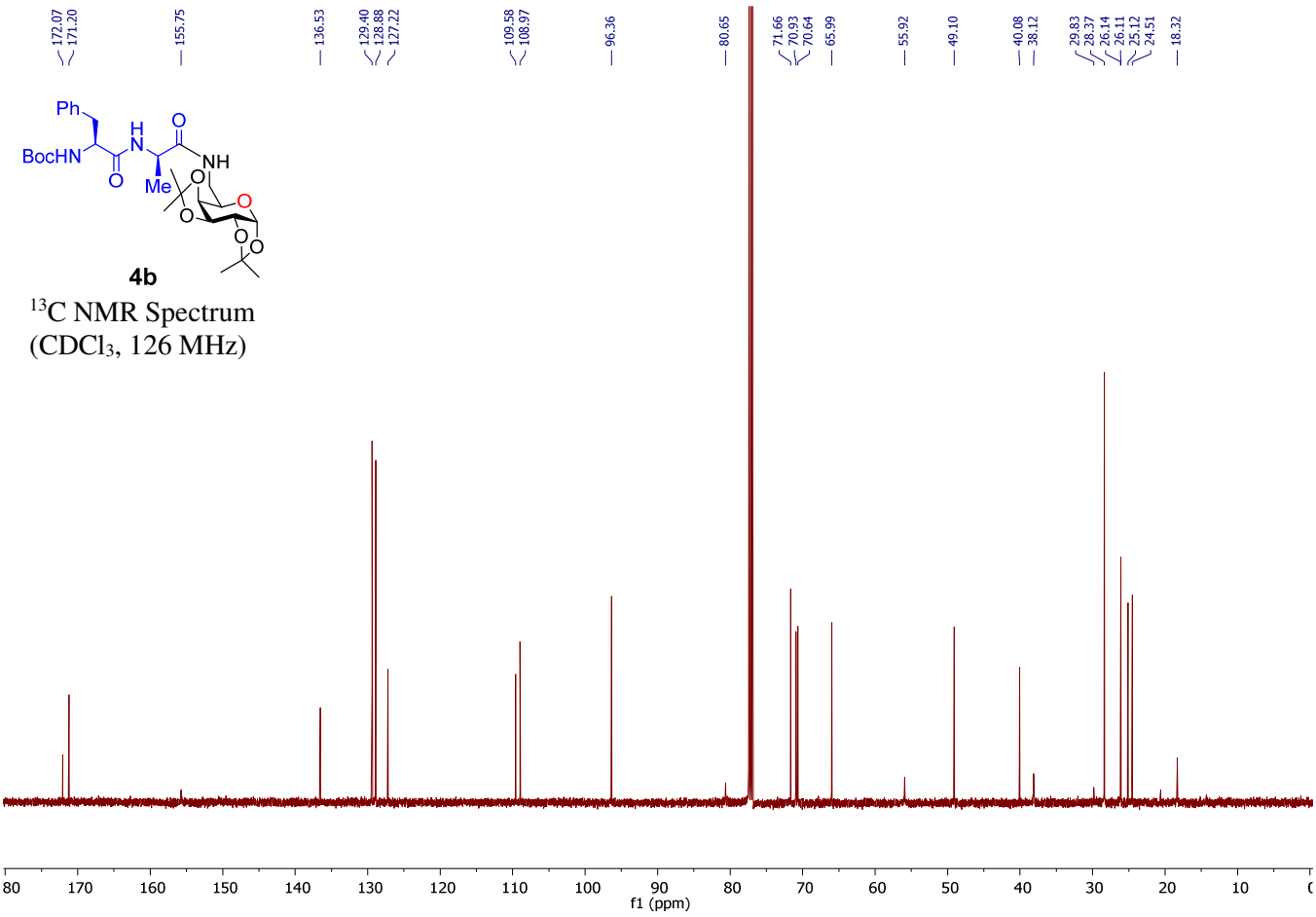
COSY NMR Spectrum



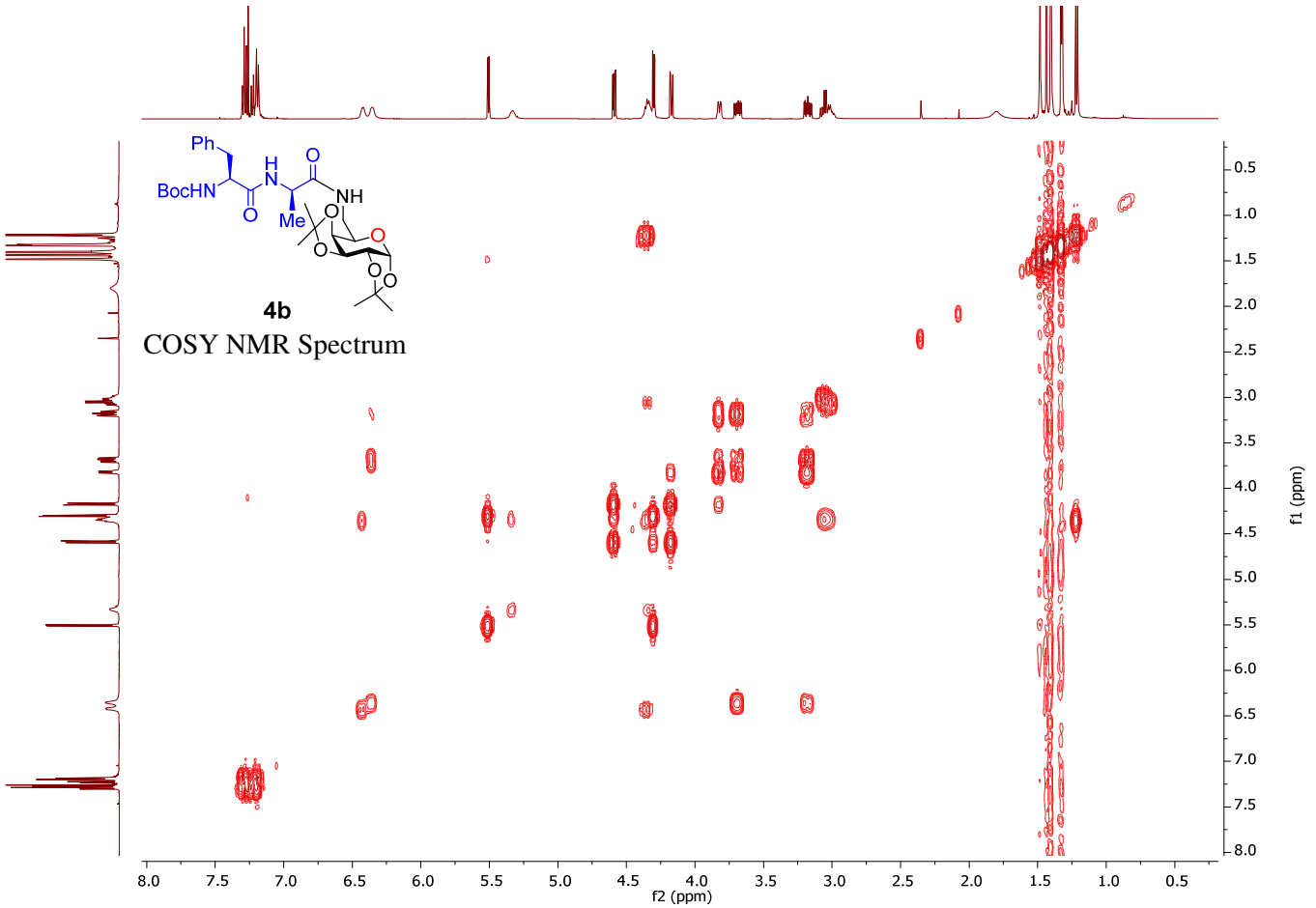
HSQC NMR Spectrum



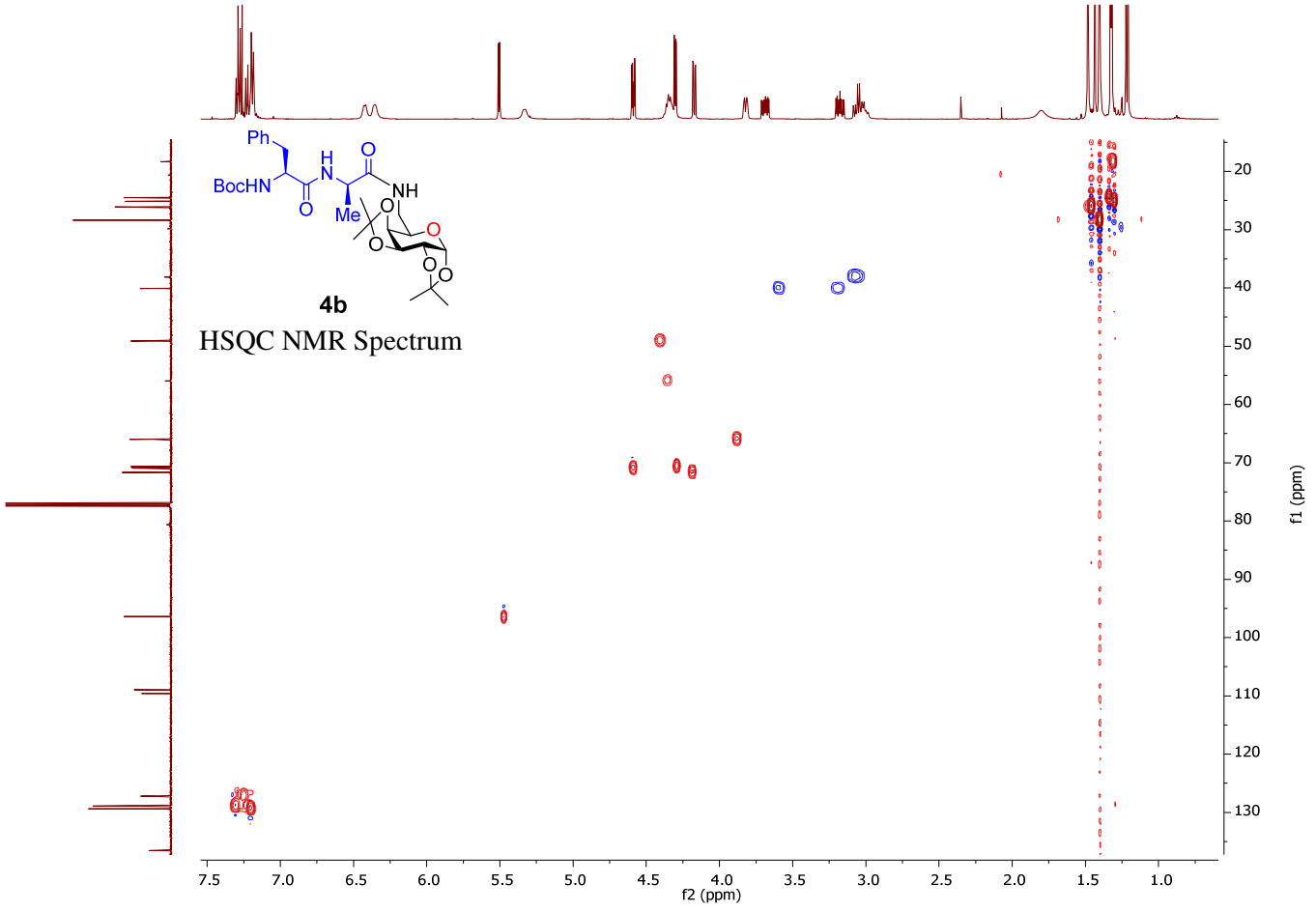
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



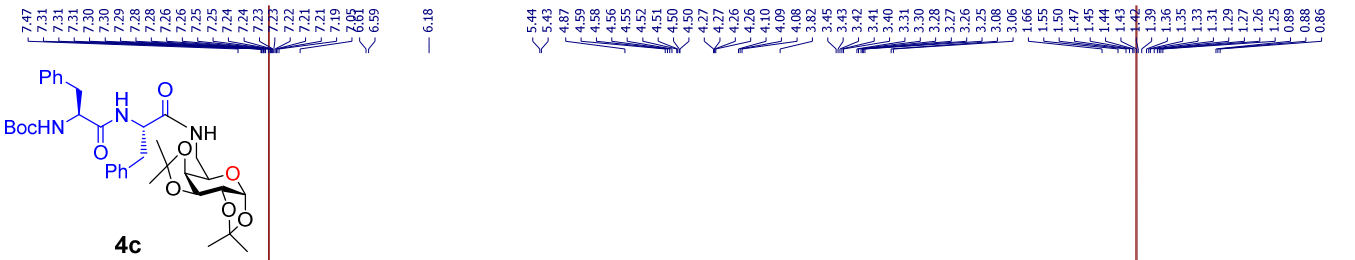
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

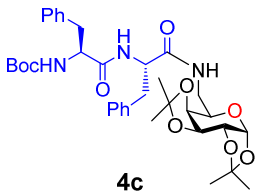


HSQC NMR Spectrum



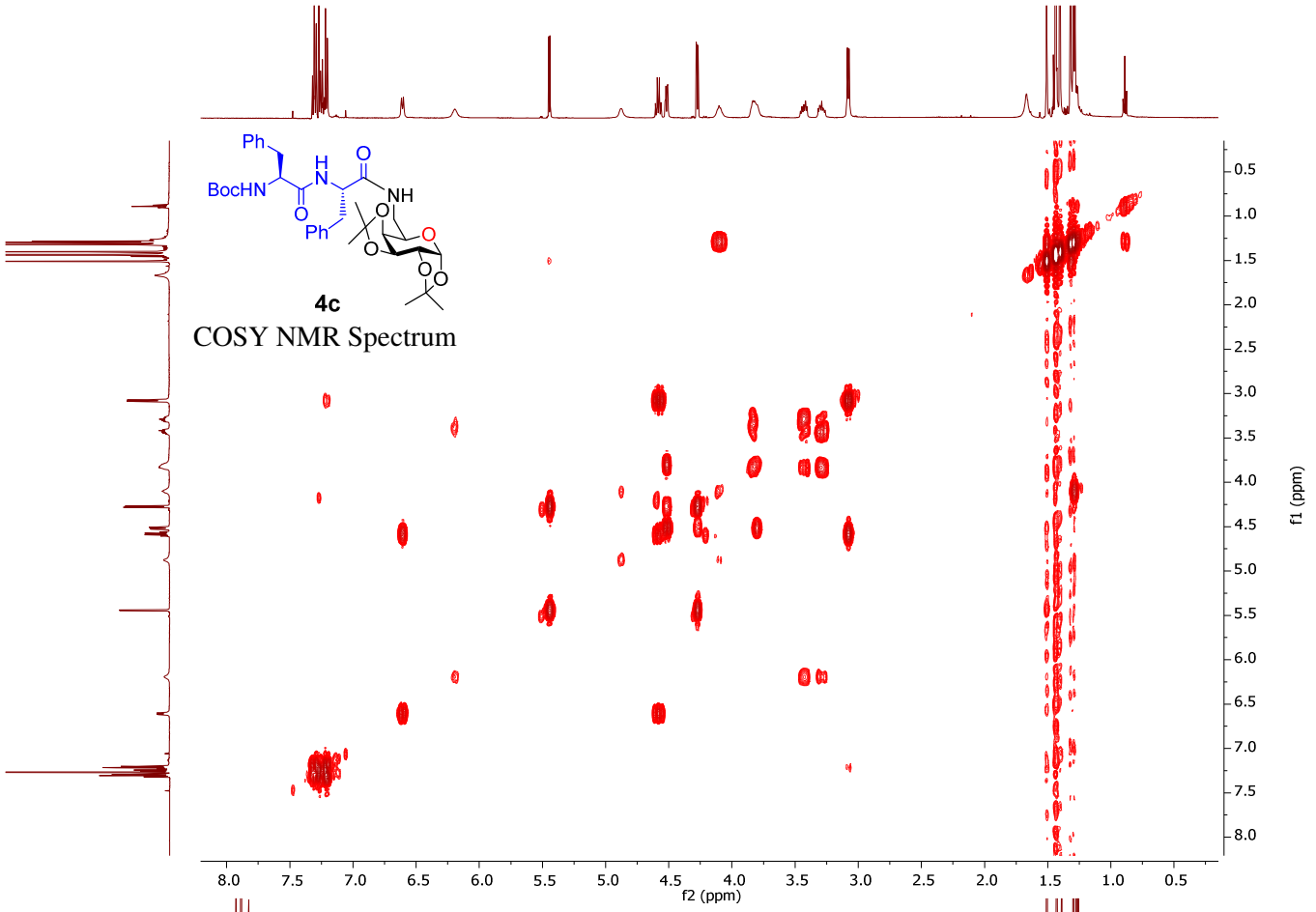
4c

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

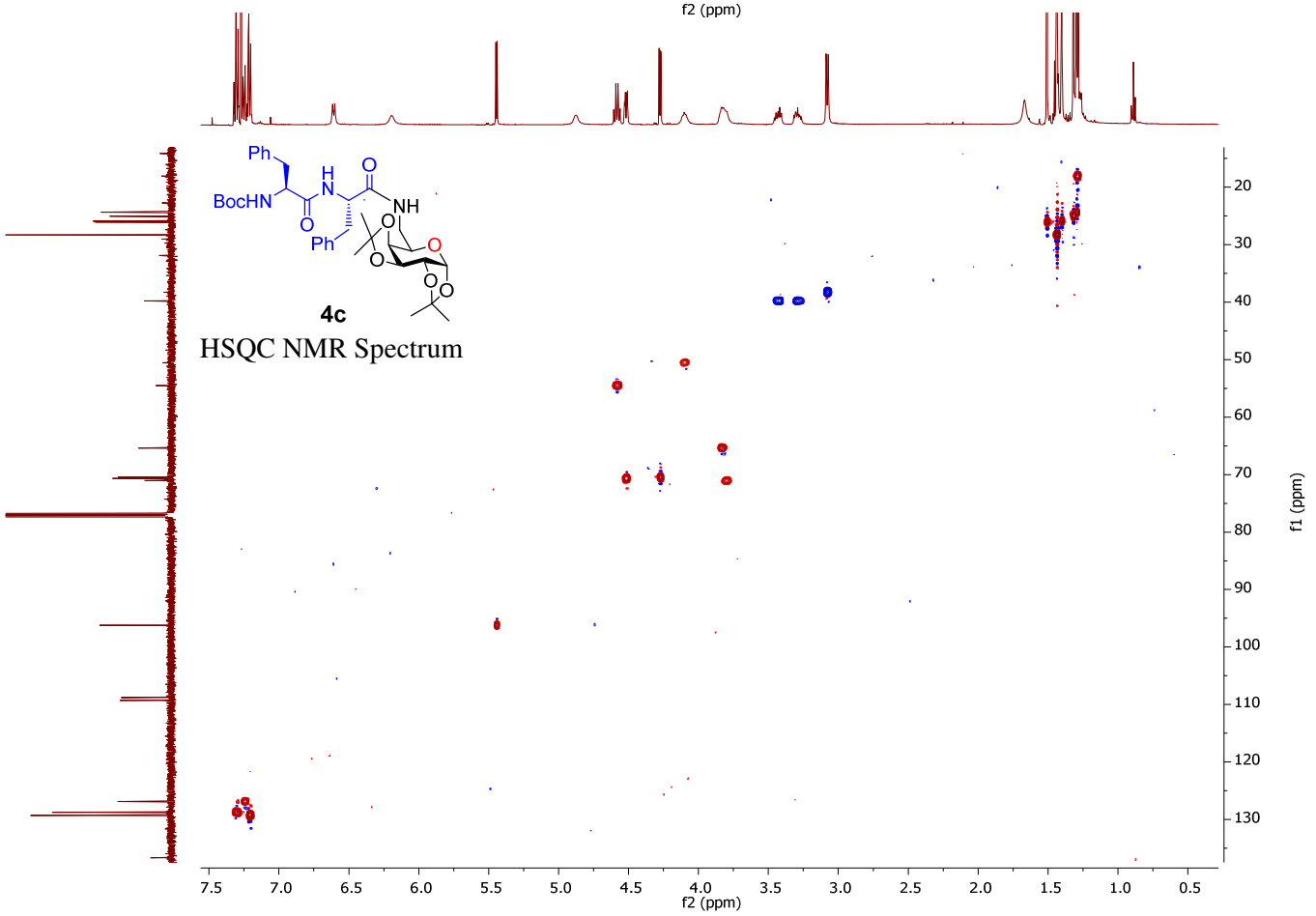


4c

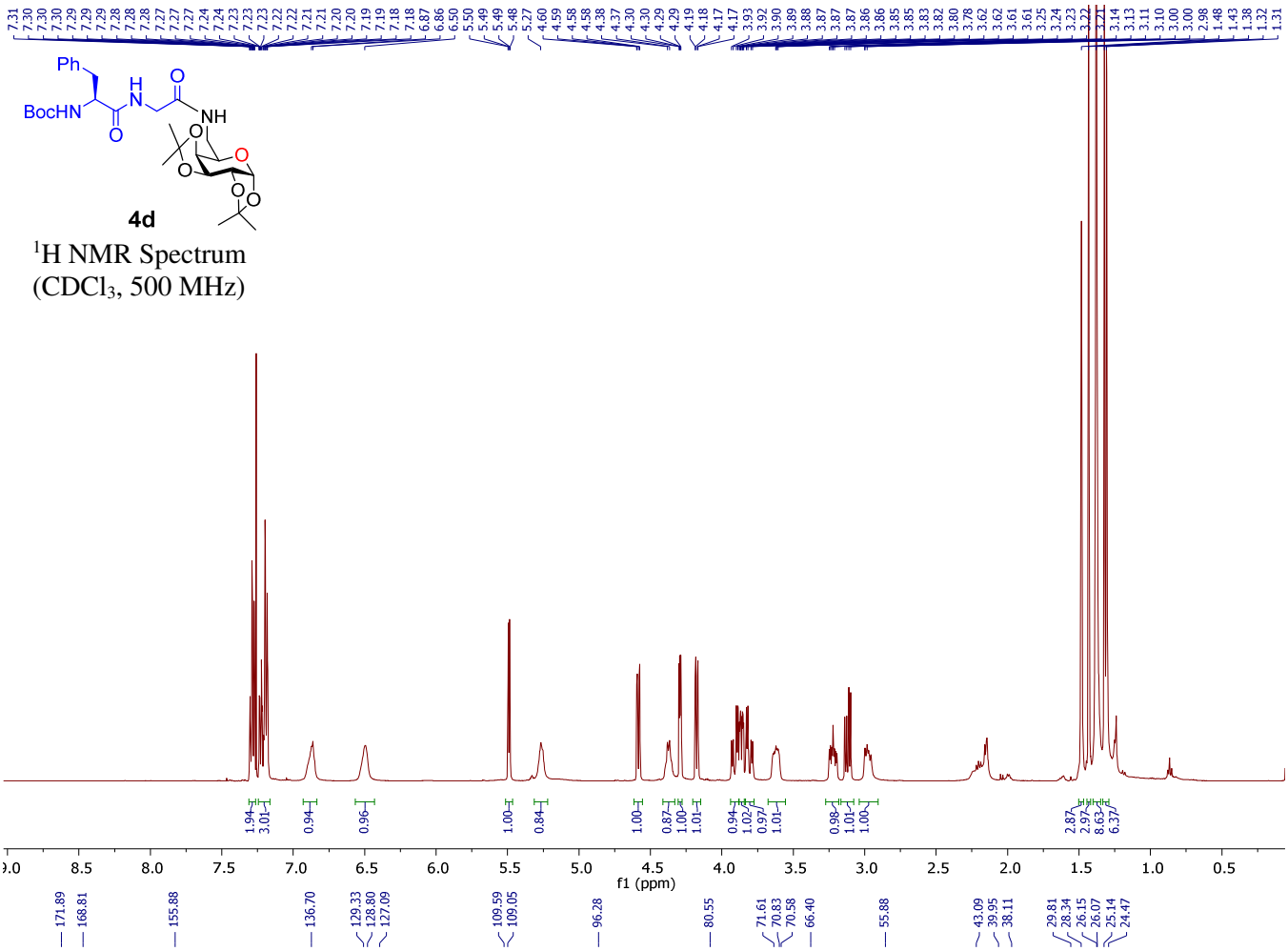
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



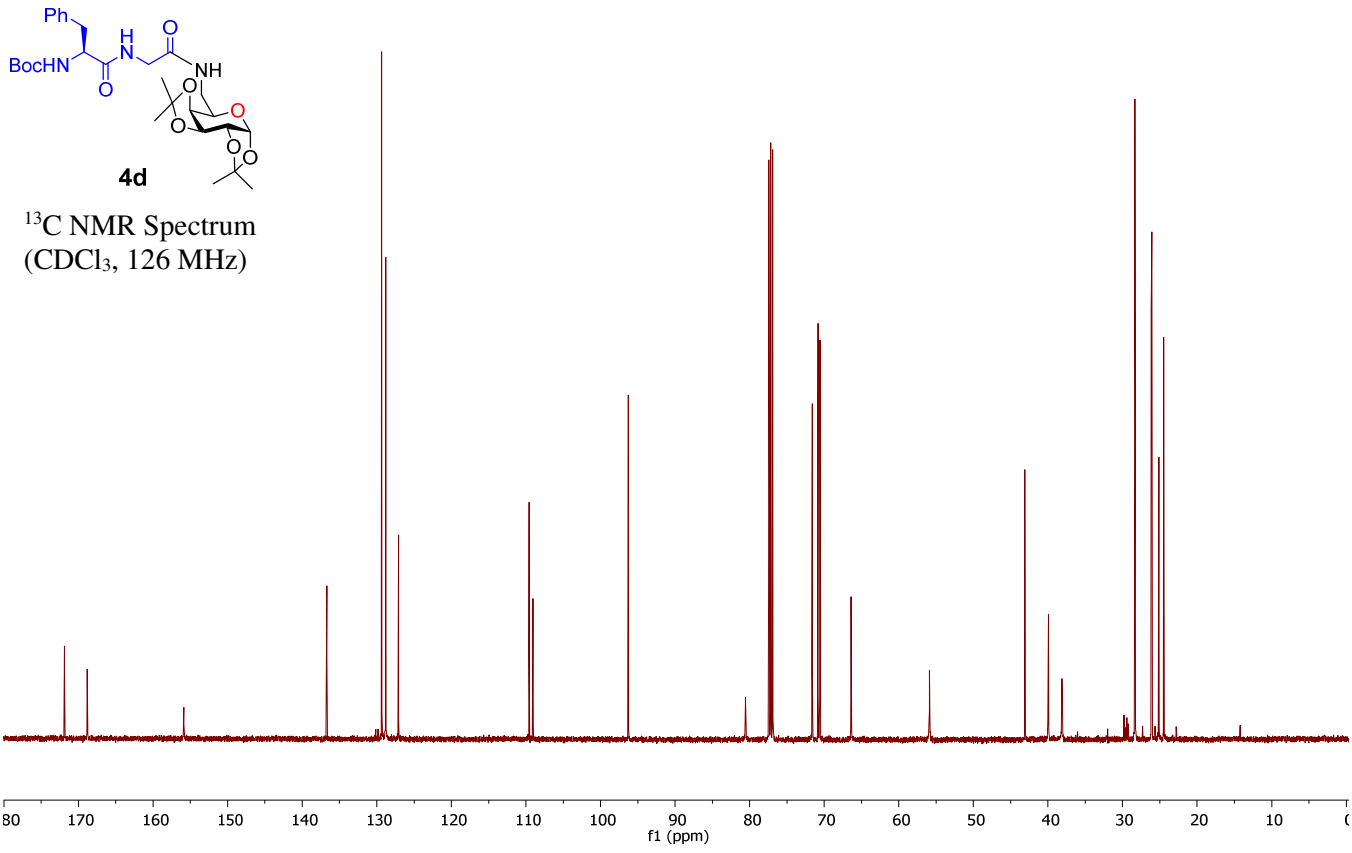
COSY NMR Spectrum



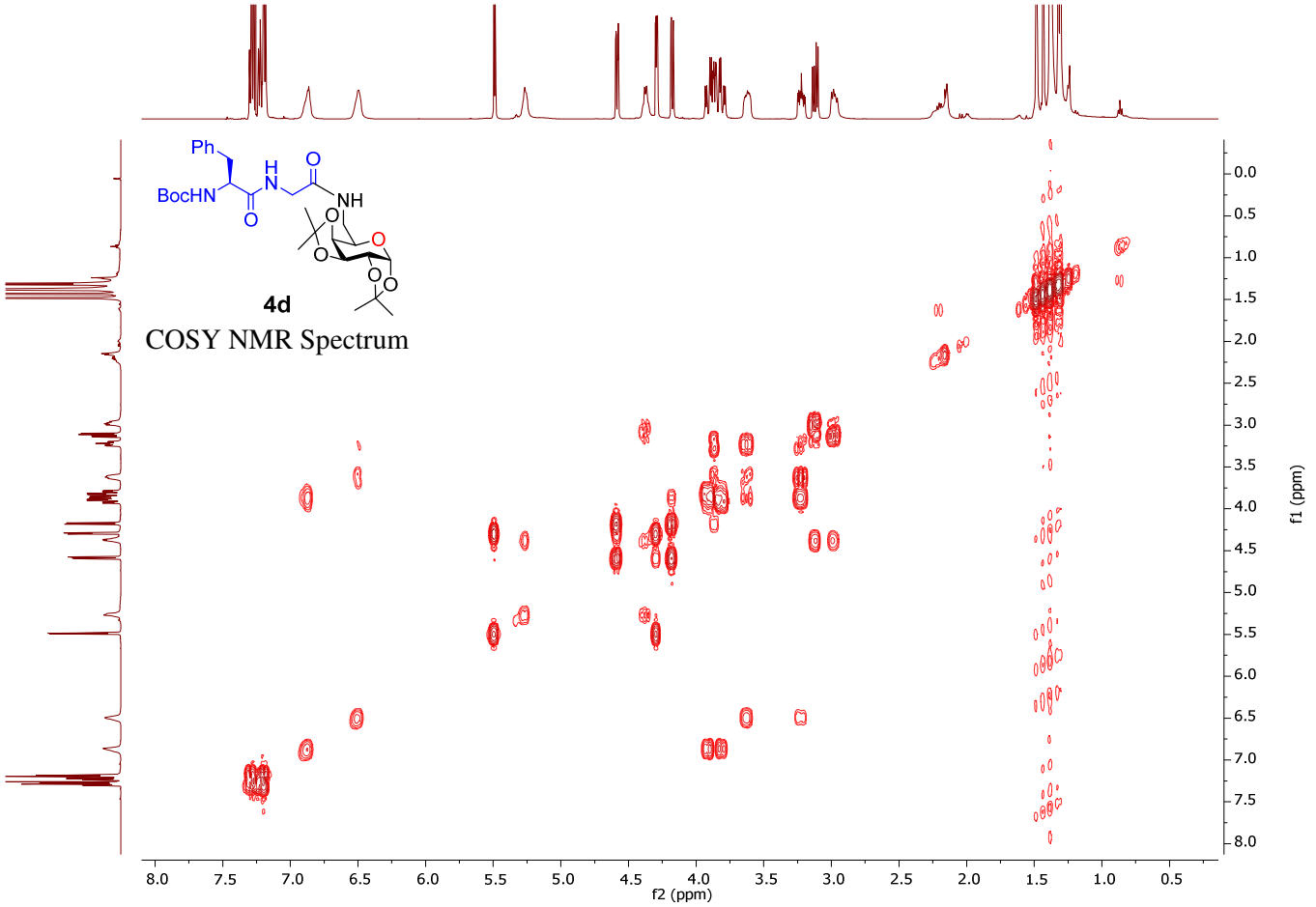
HSQC NMR Spectrum



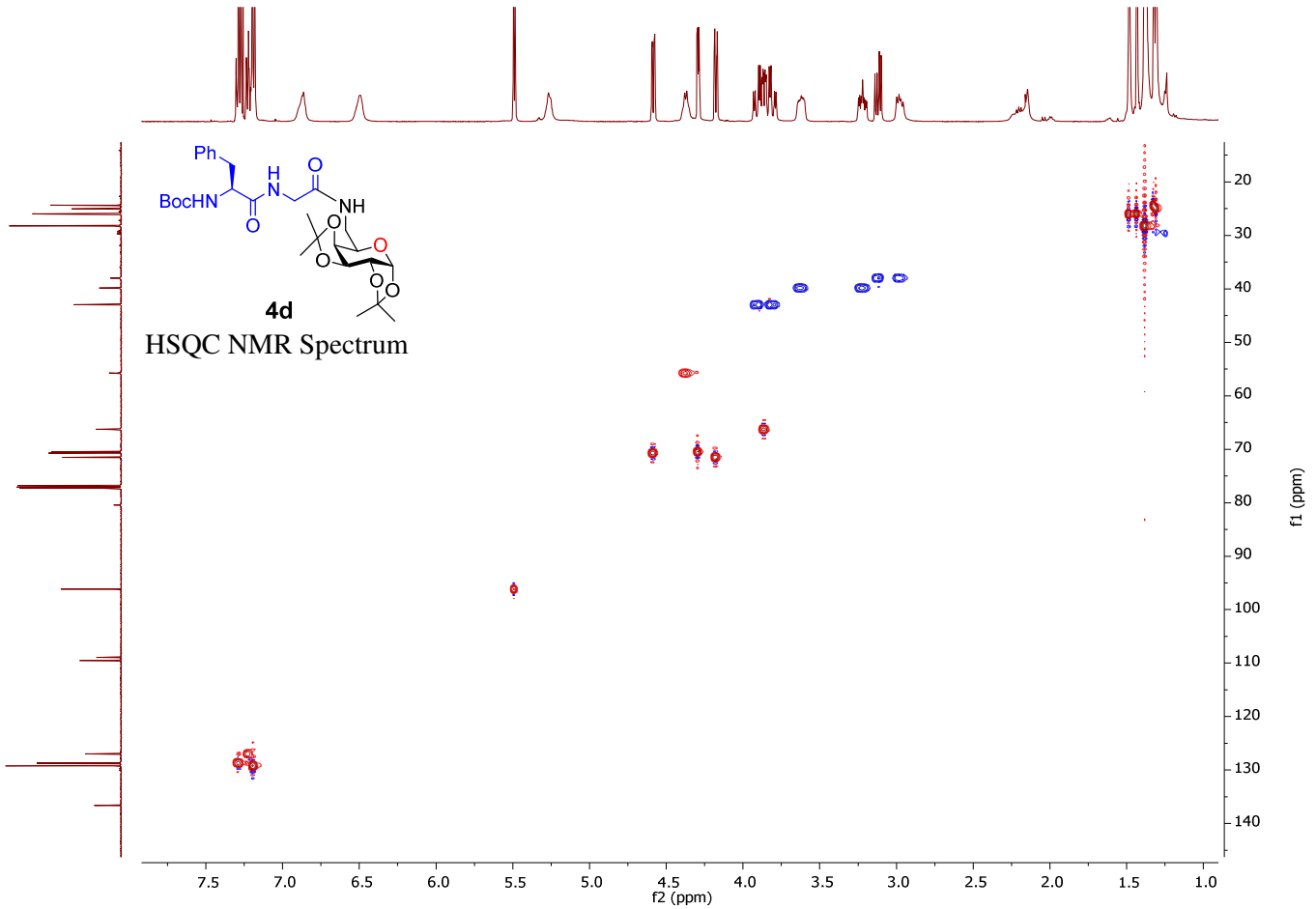
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



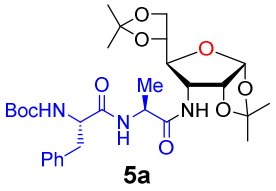
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

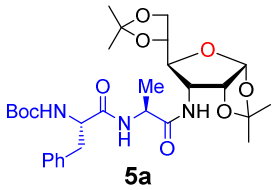


HSQC NMR Spectrum



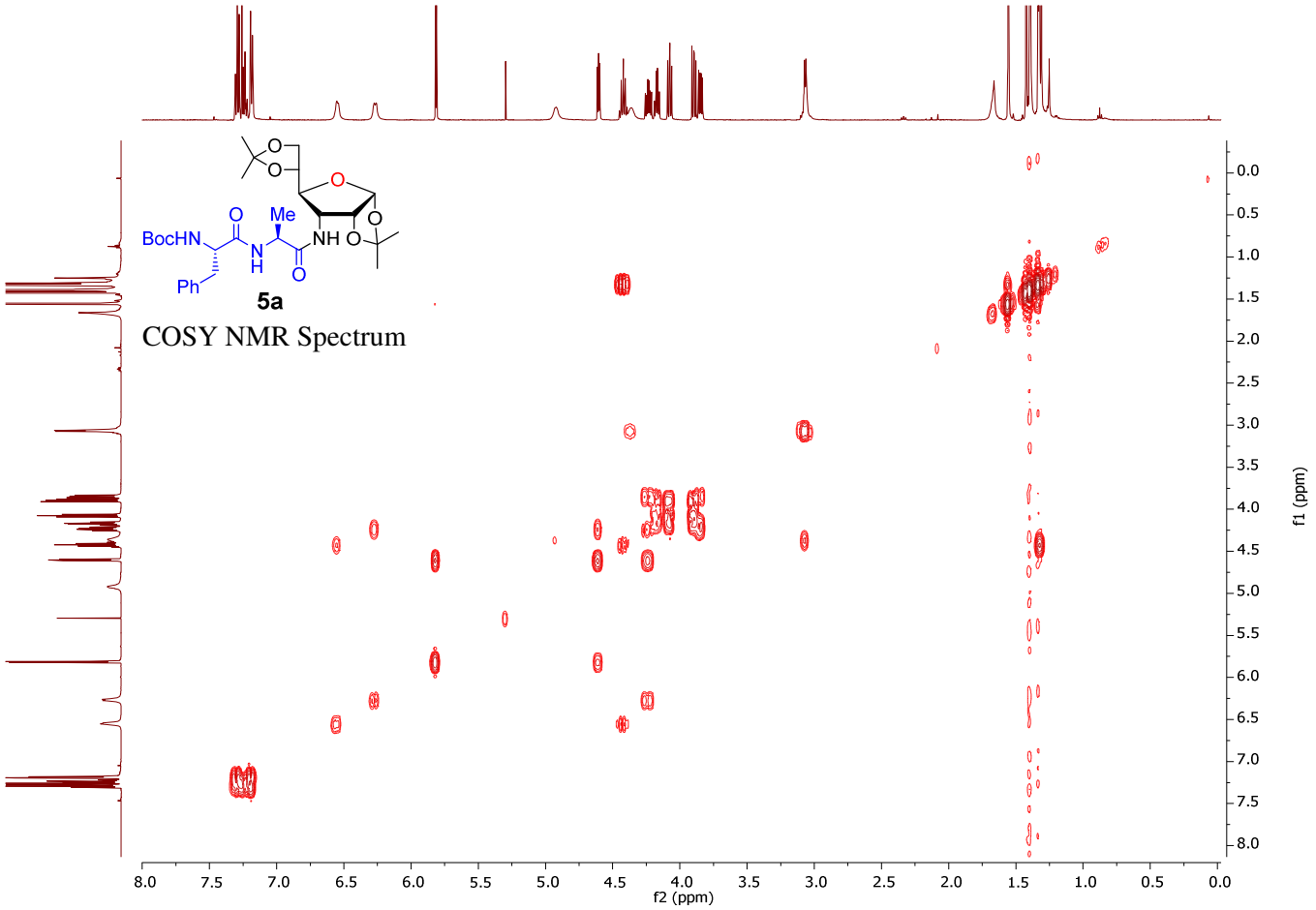
5a

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

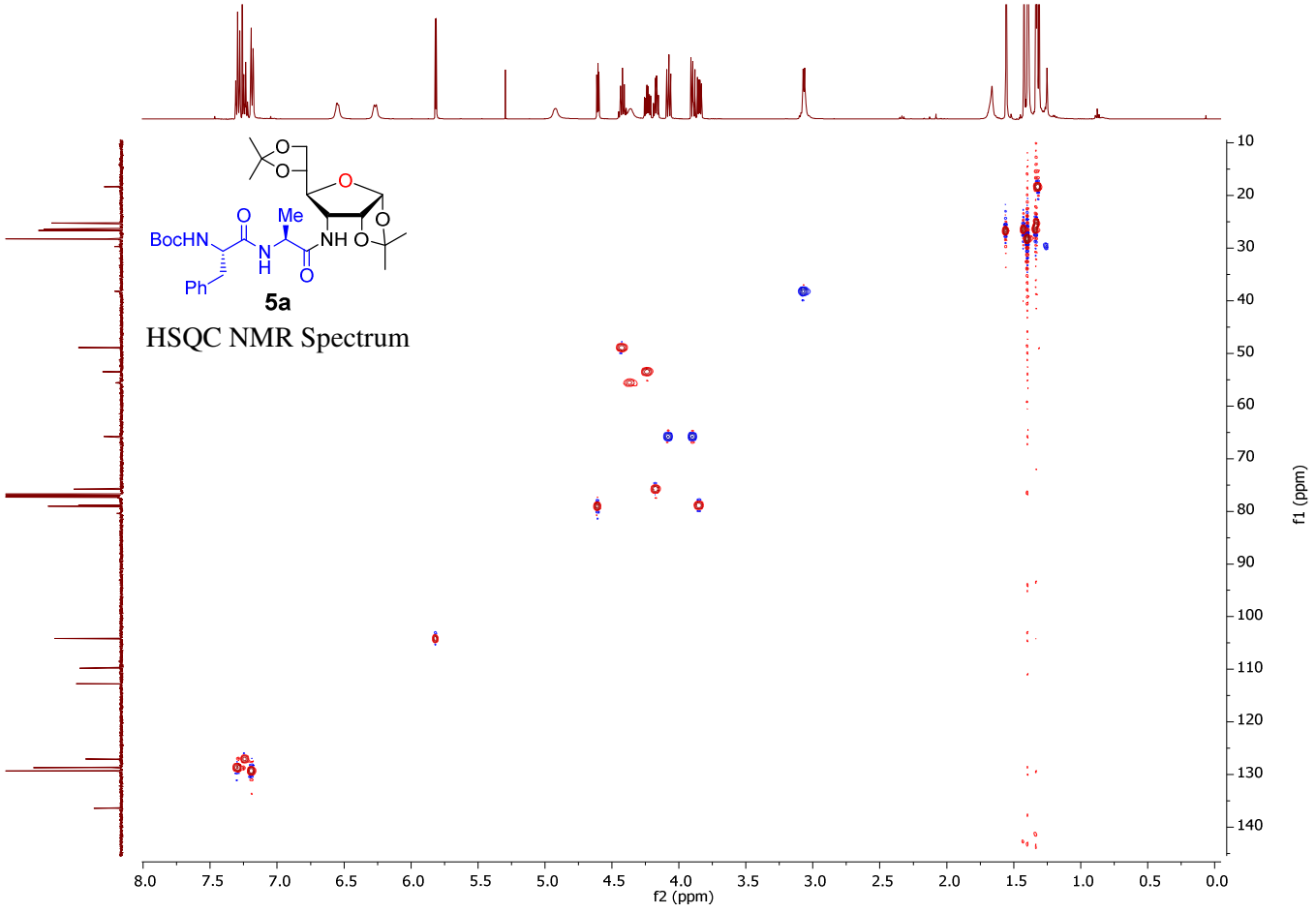


5a

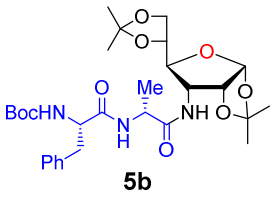
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

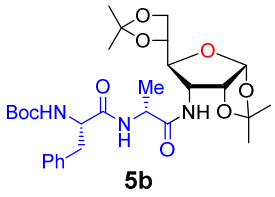


HSQC NMR Spectrum



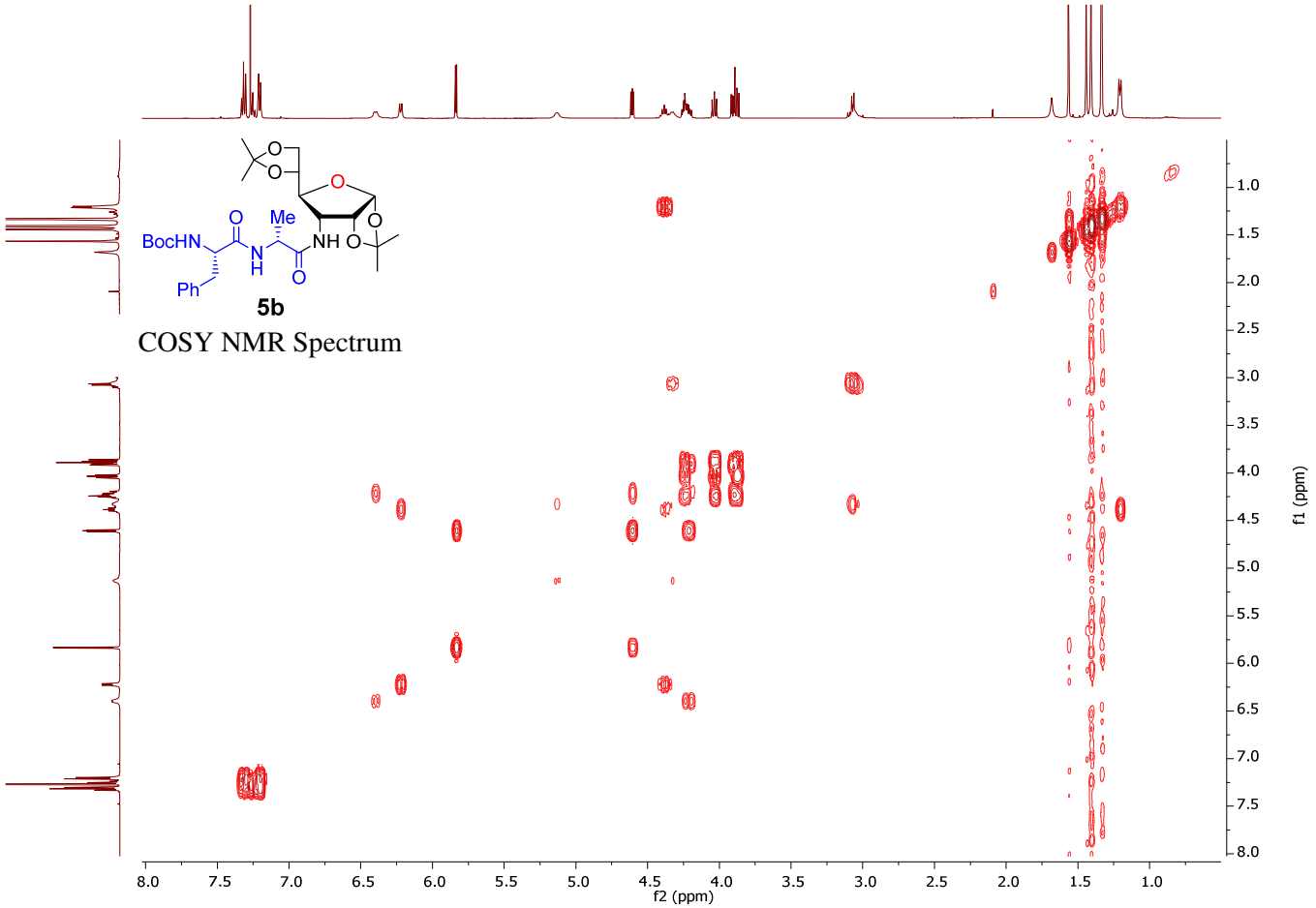
5b

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

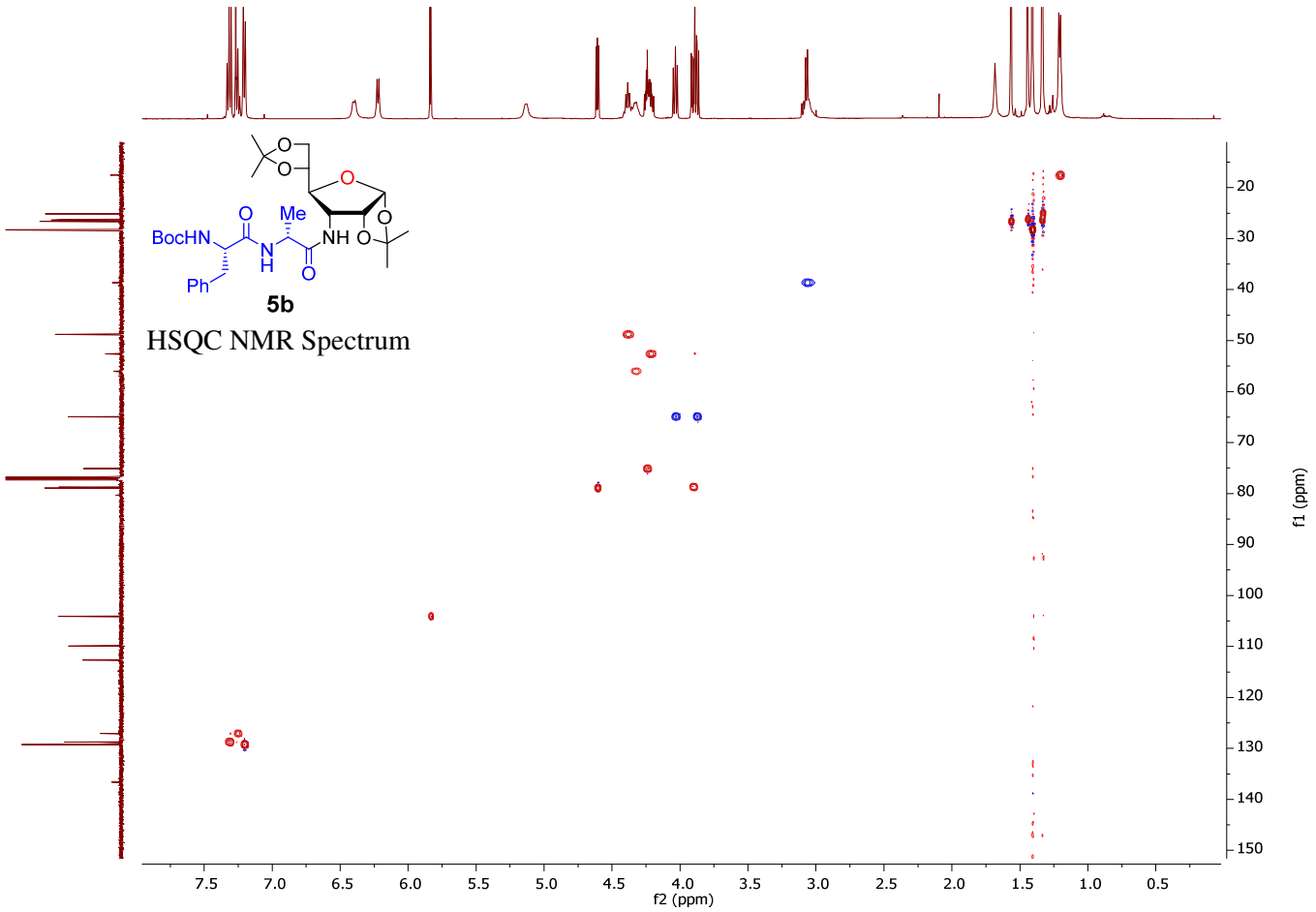


5b

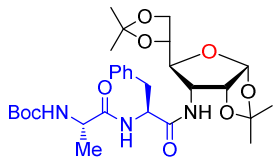
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

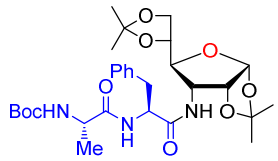


HSQC NMR Spectrum



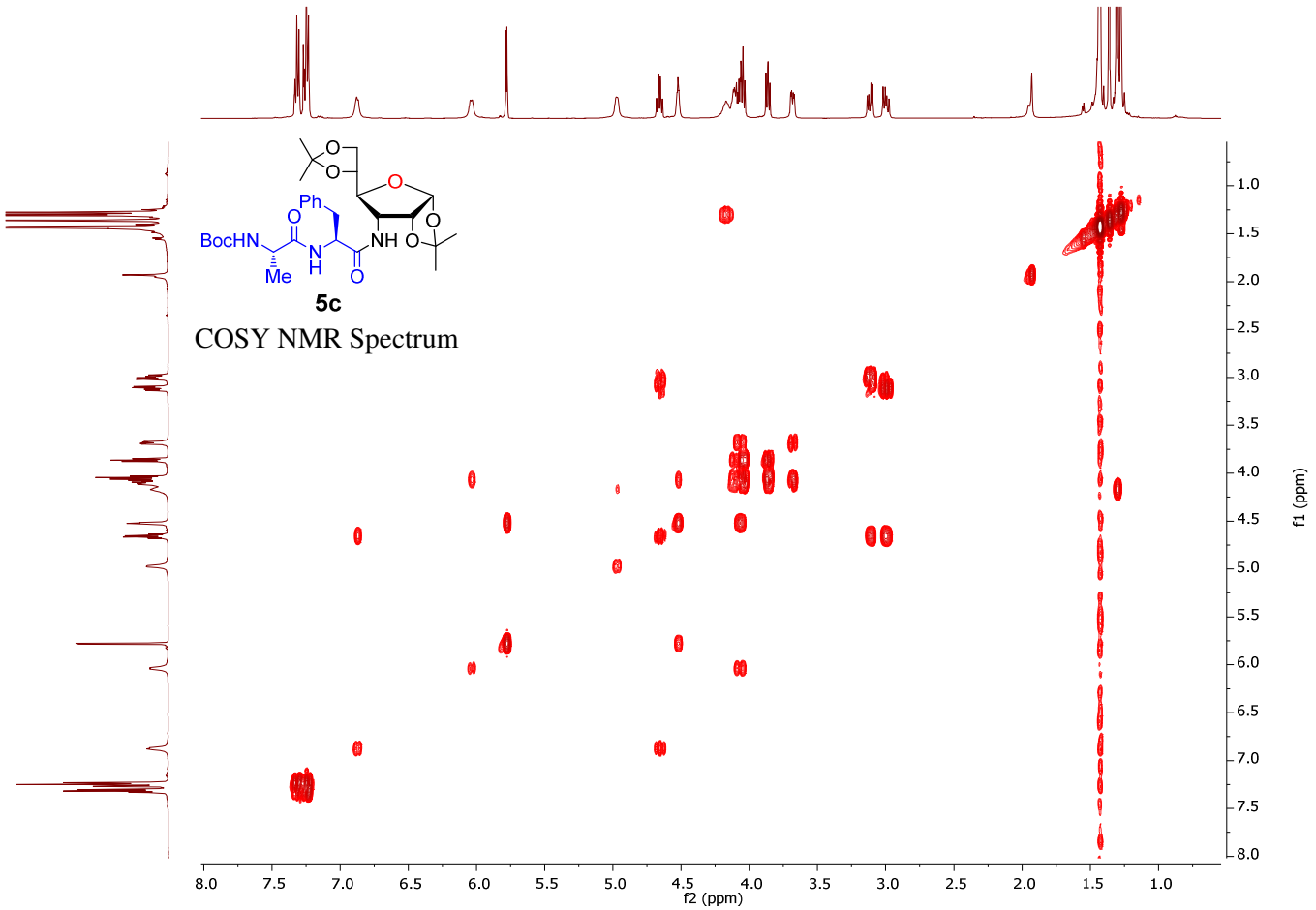
5c

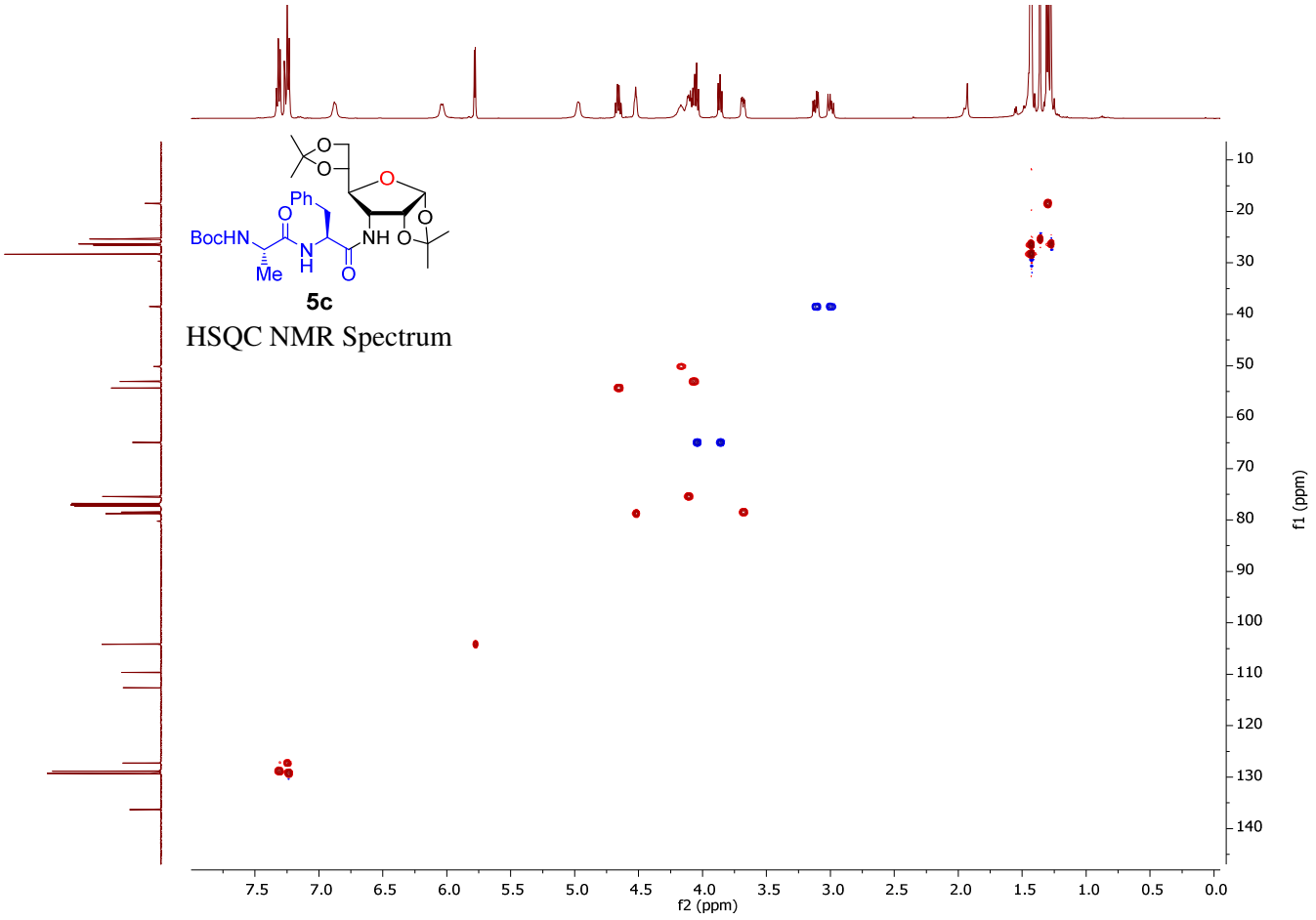
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

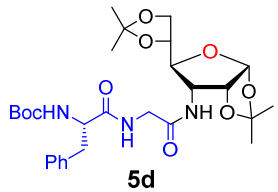


5c

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)

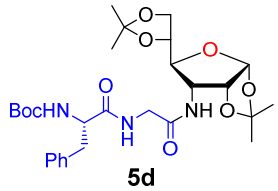

BocHN
Ph
Me
NH
O
5c
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


BocHN
Ph
Me
NH
O
5c
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



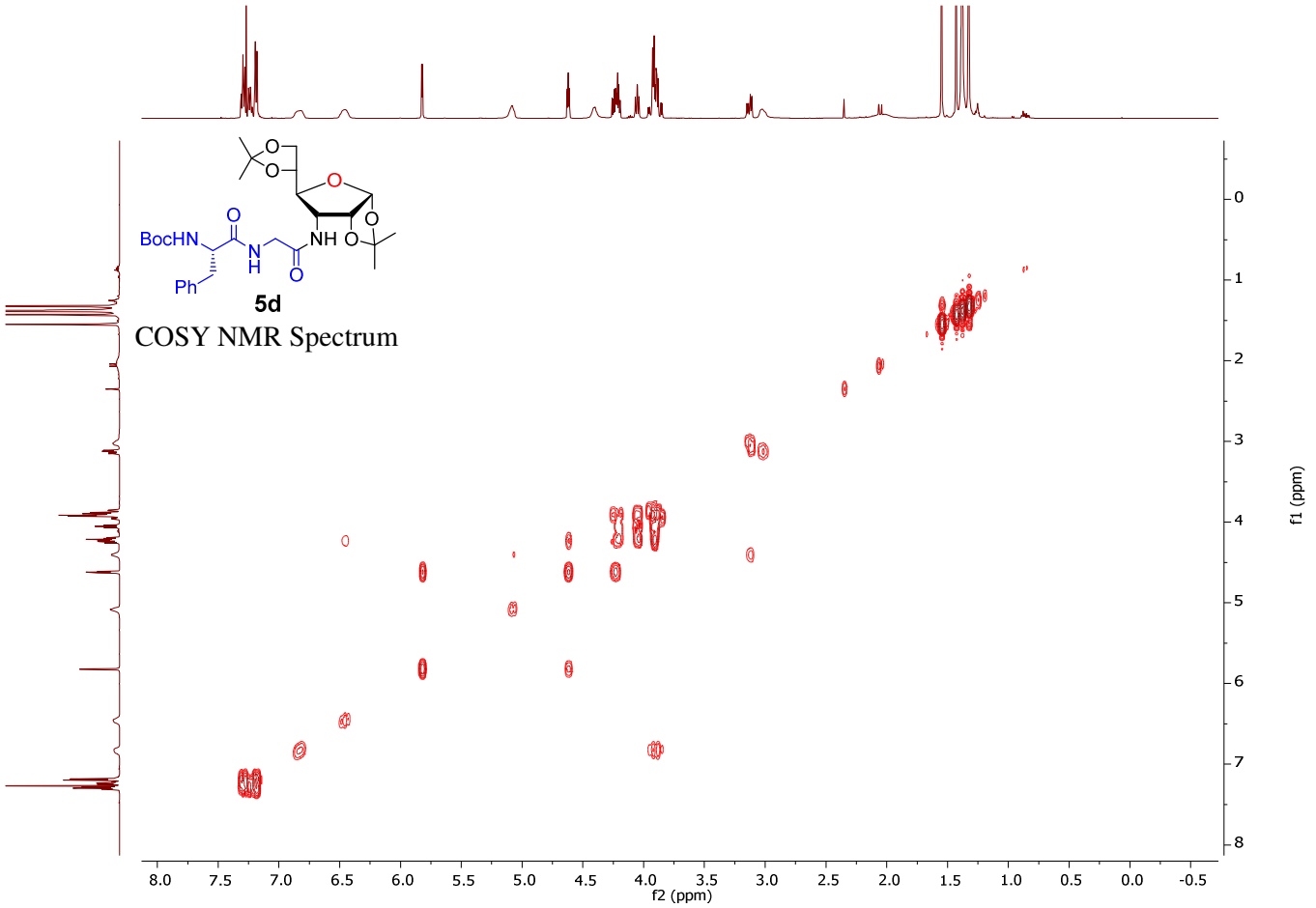
5d

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

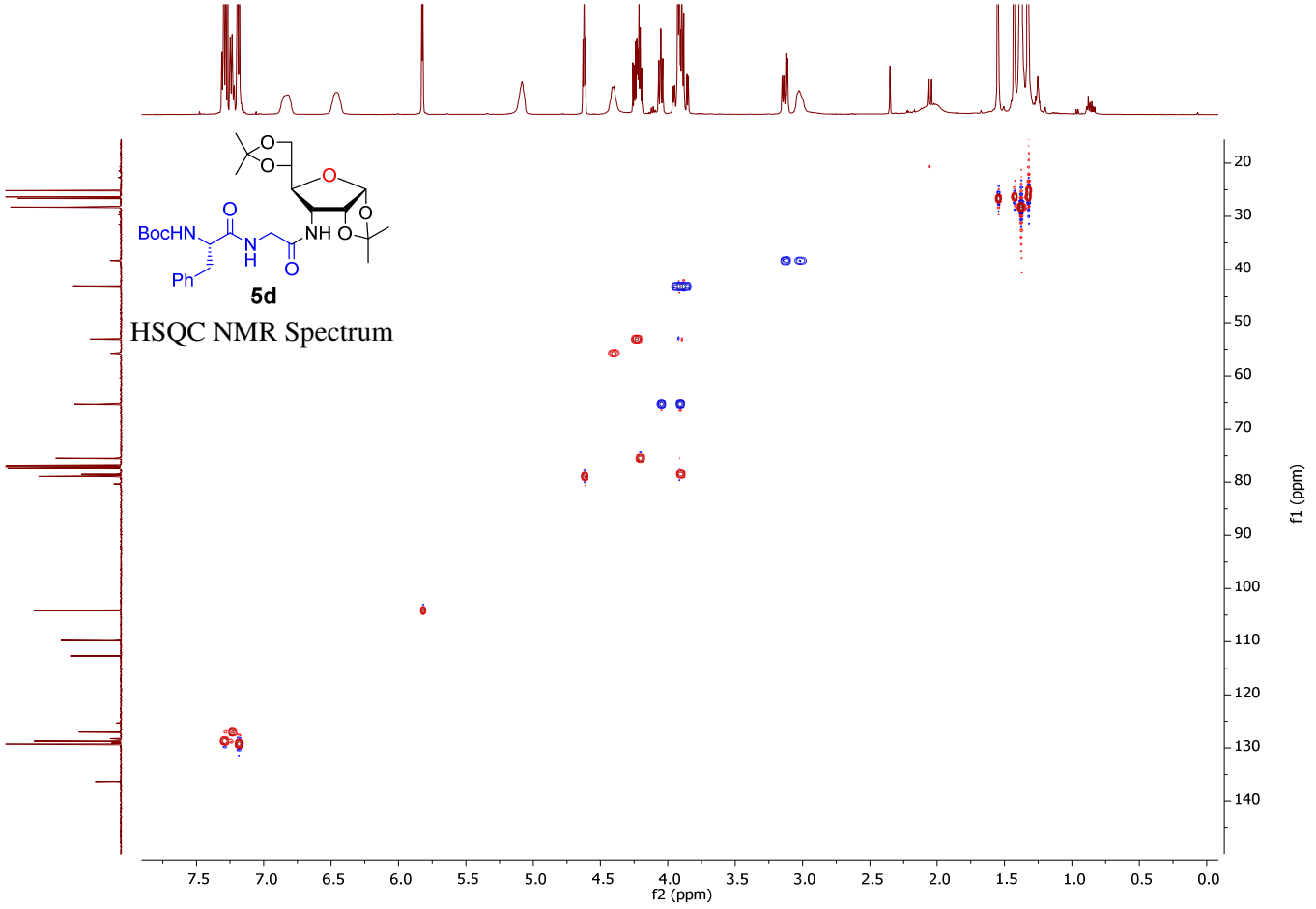


5d

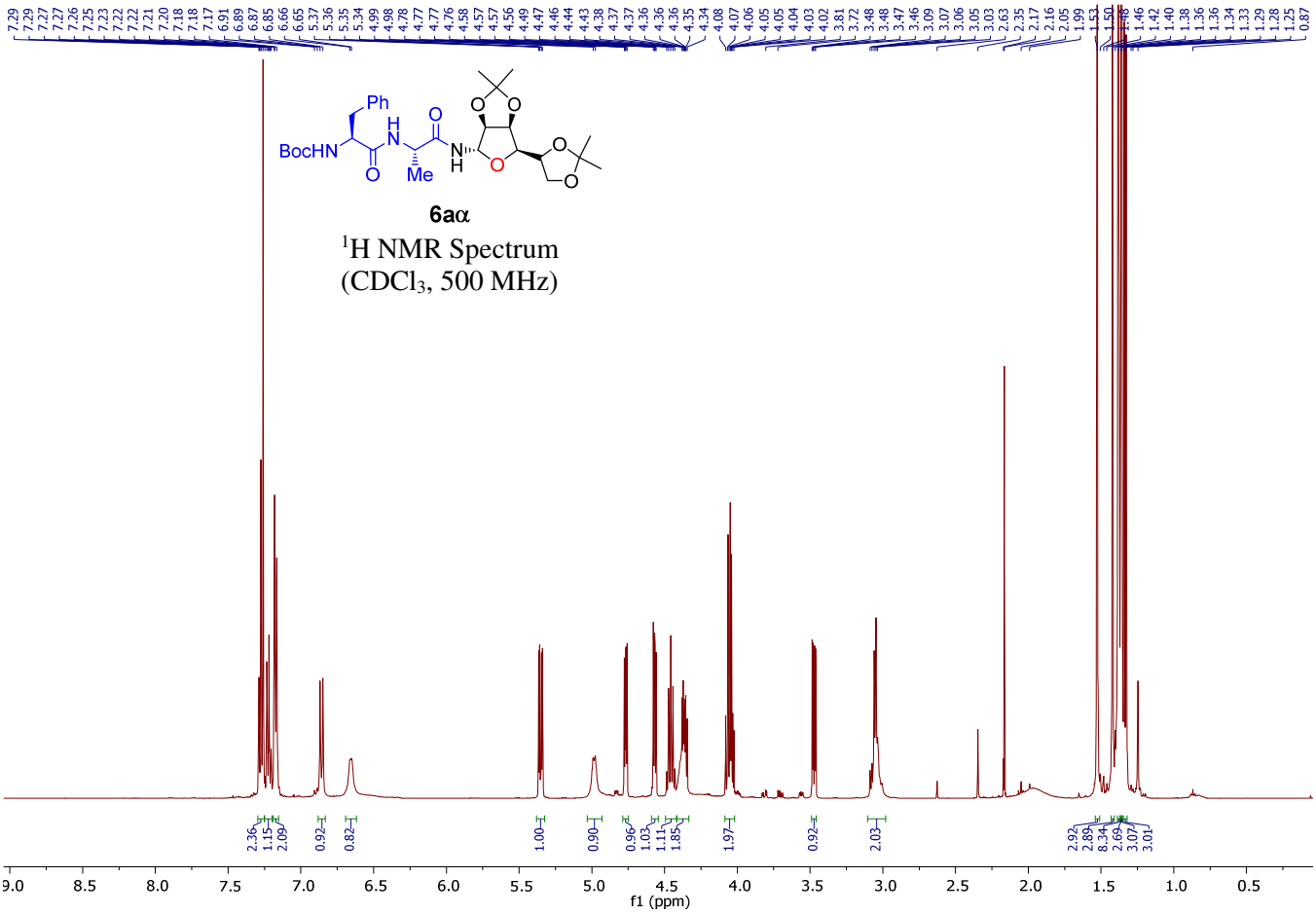
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

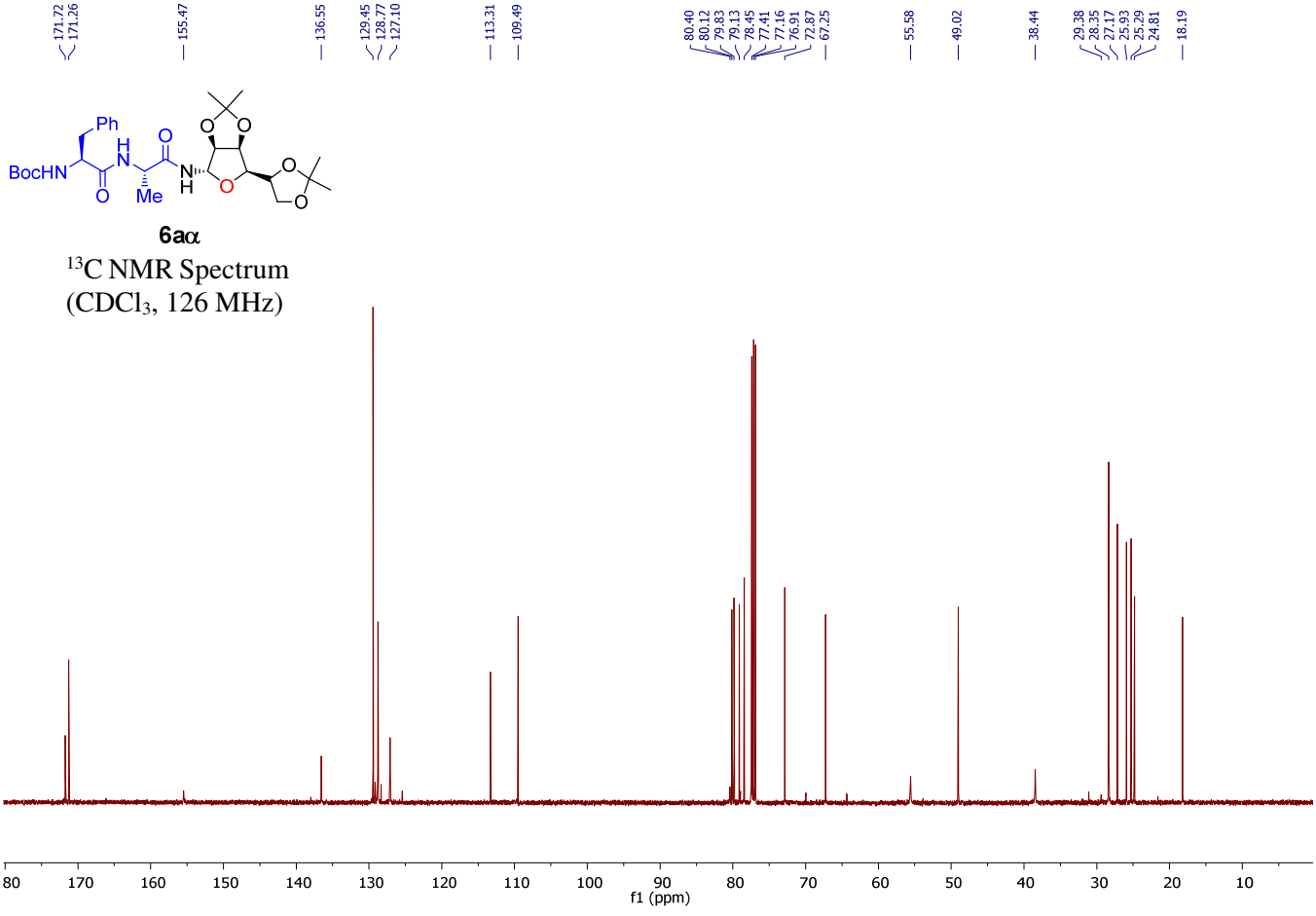


HSQC NMR Spectrum



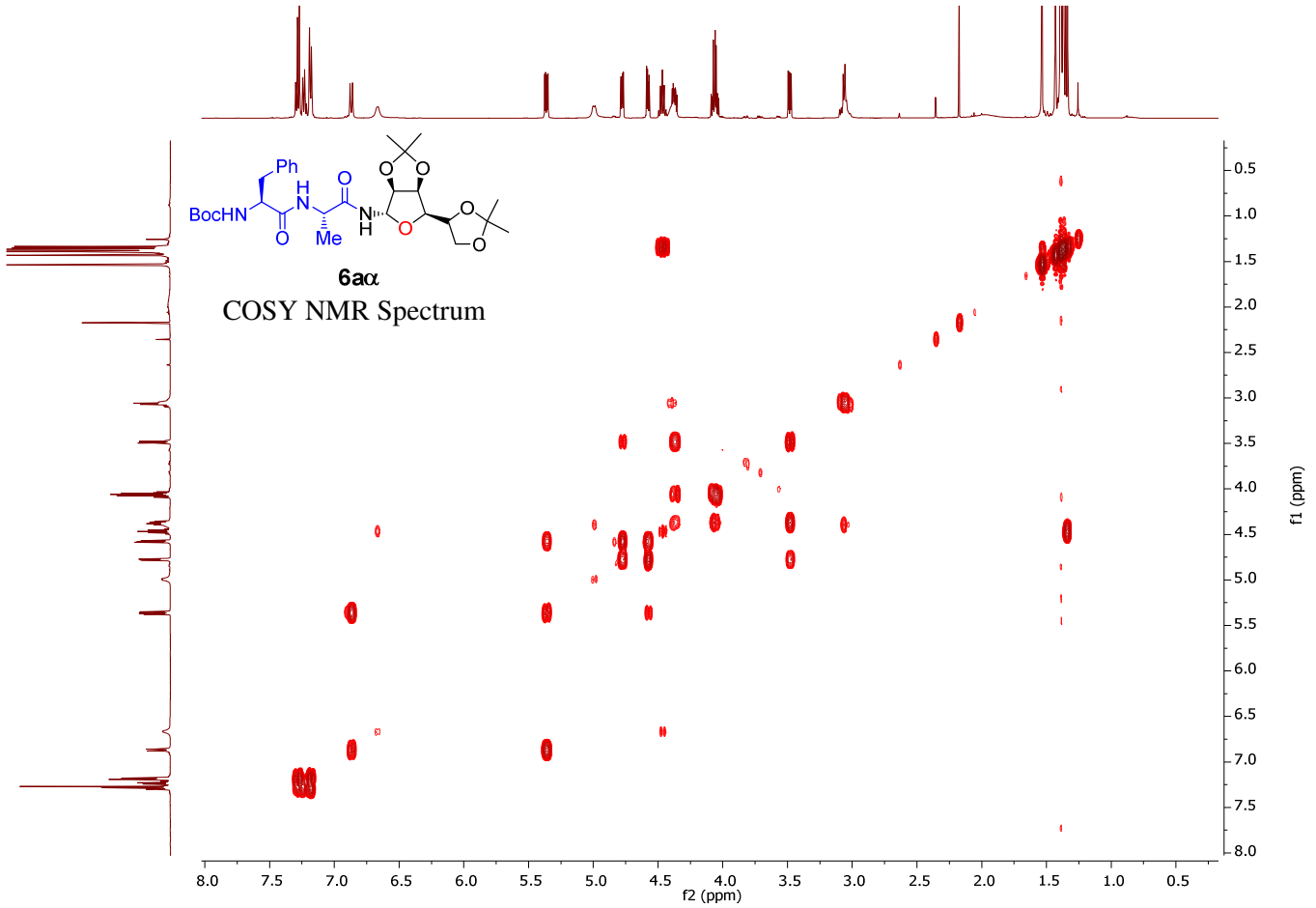
6aα

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



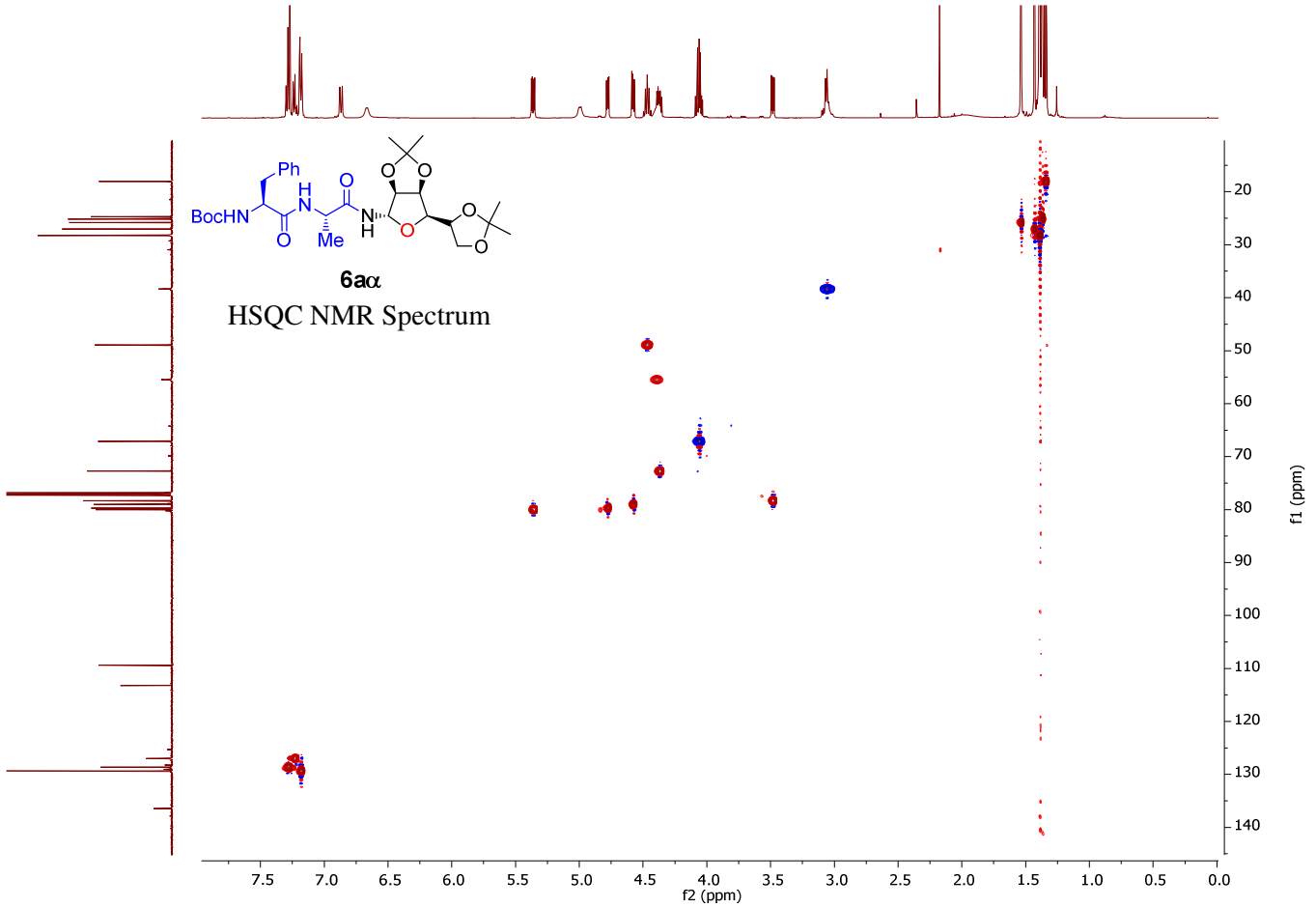
6aα

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



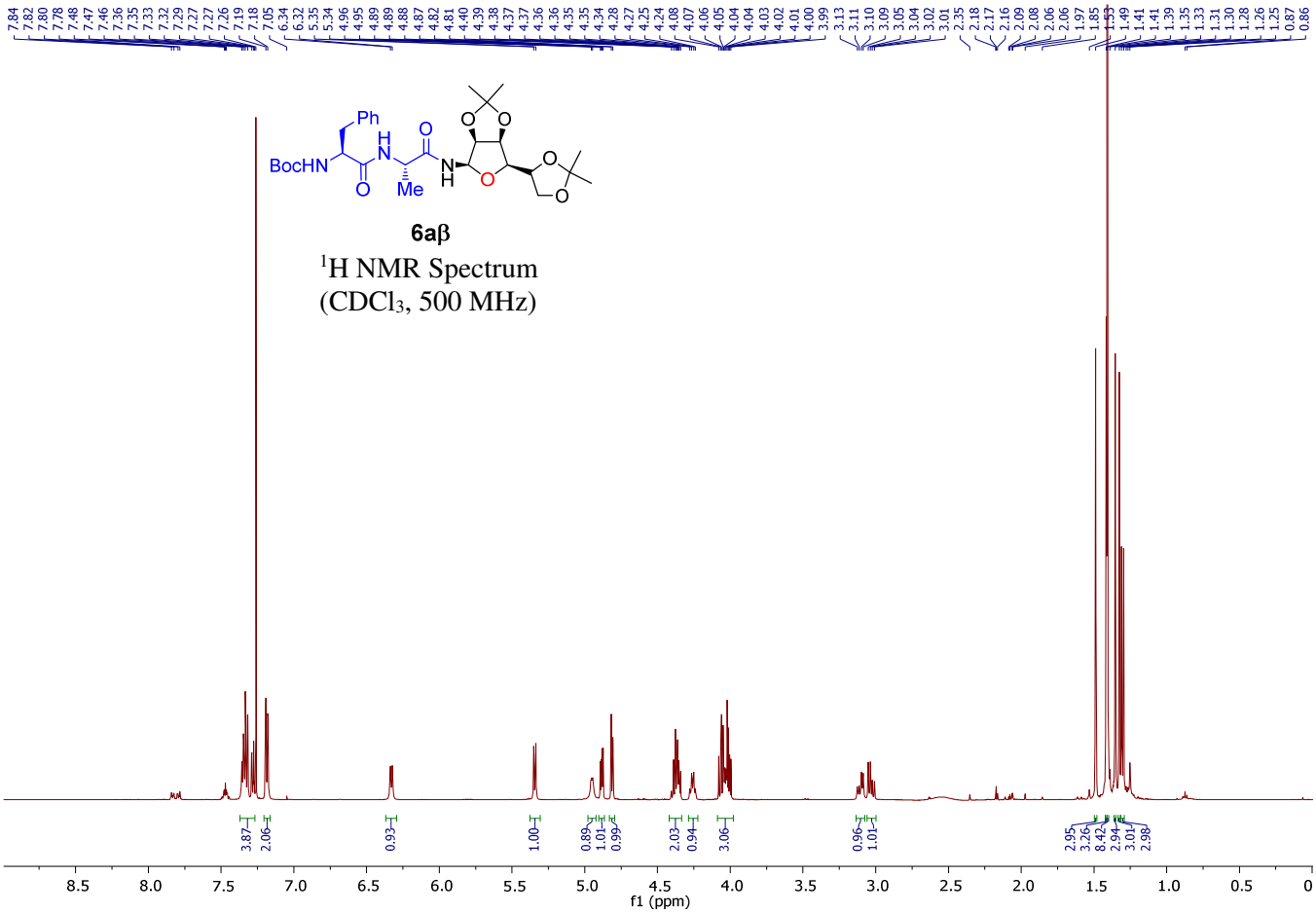
6aα

COSY NMR Spectrum



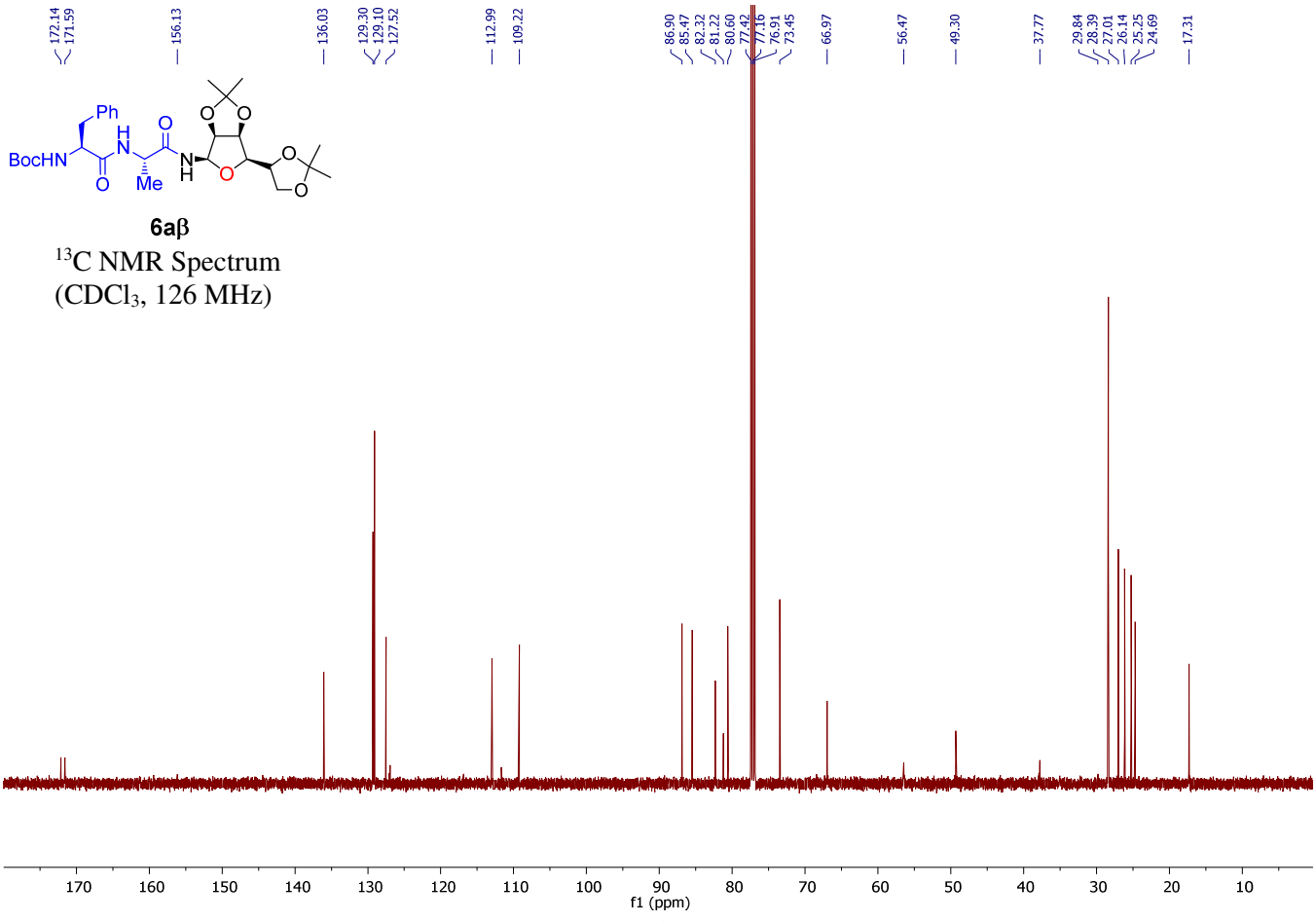
6aα

HSQC NMR Spectrum



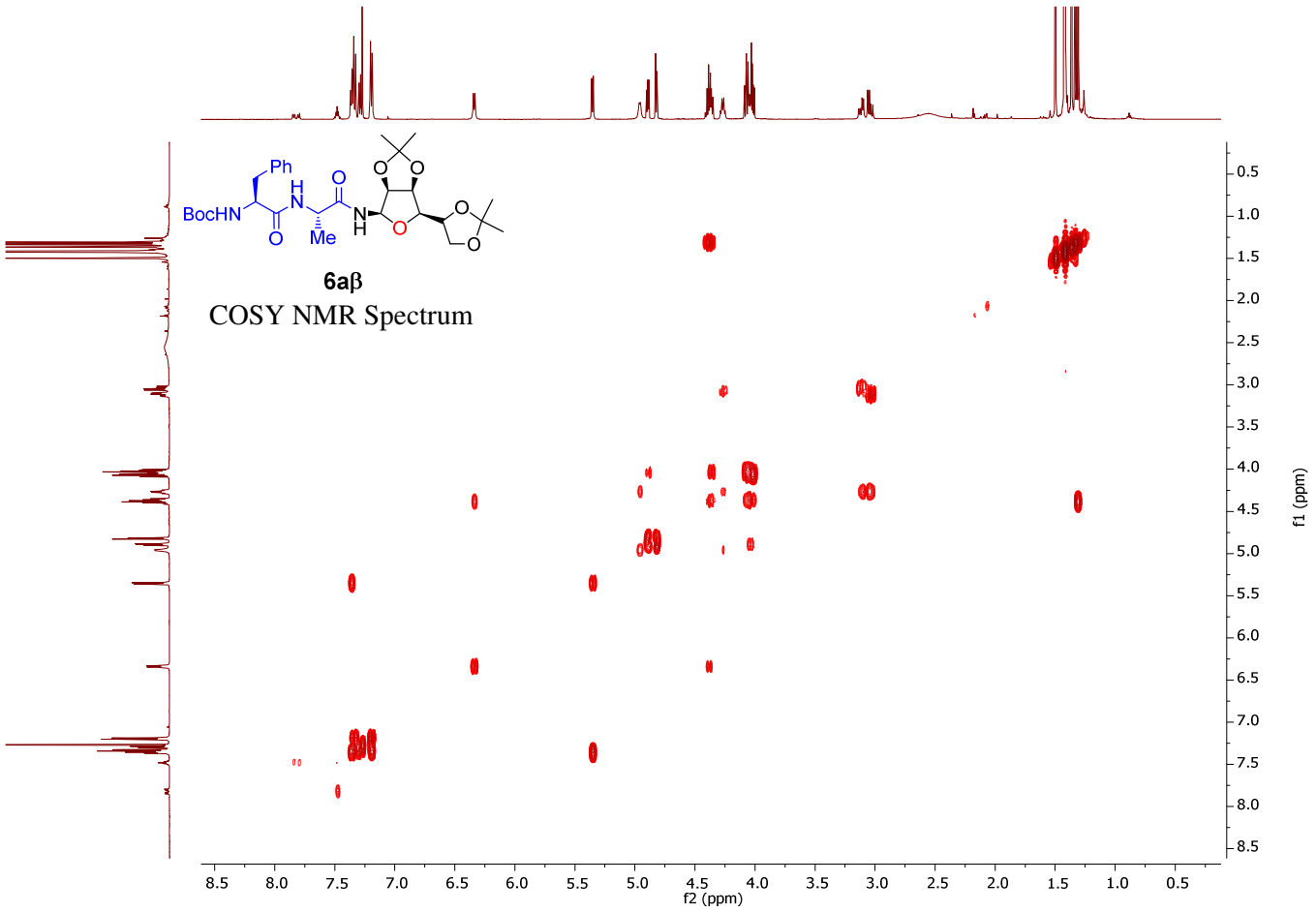
6aβ

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



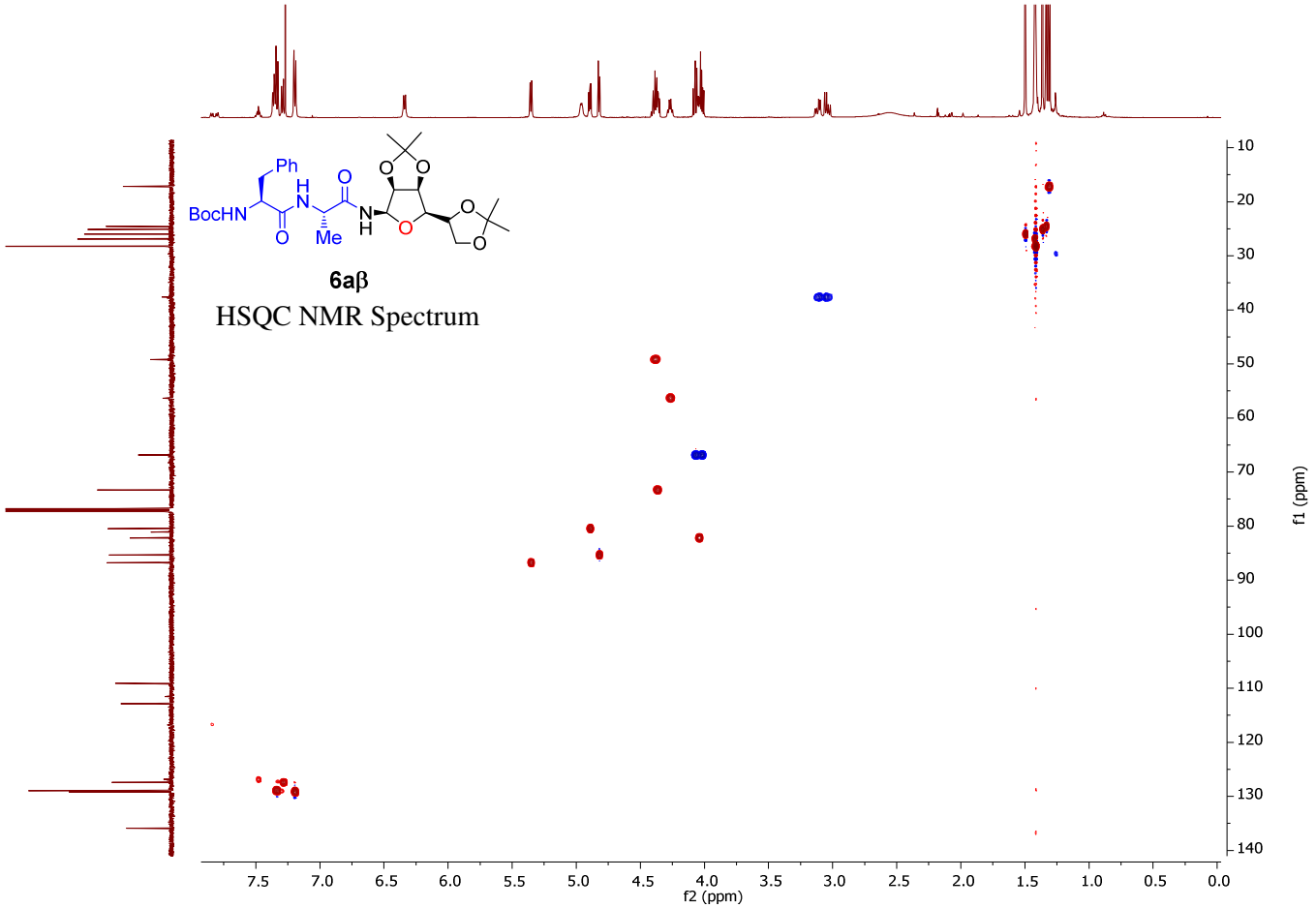
6aβ

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



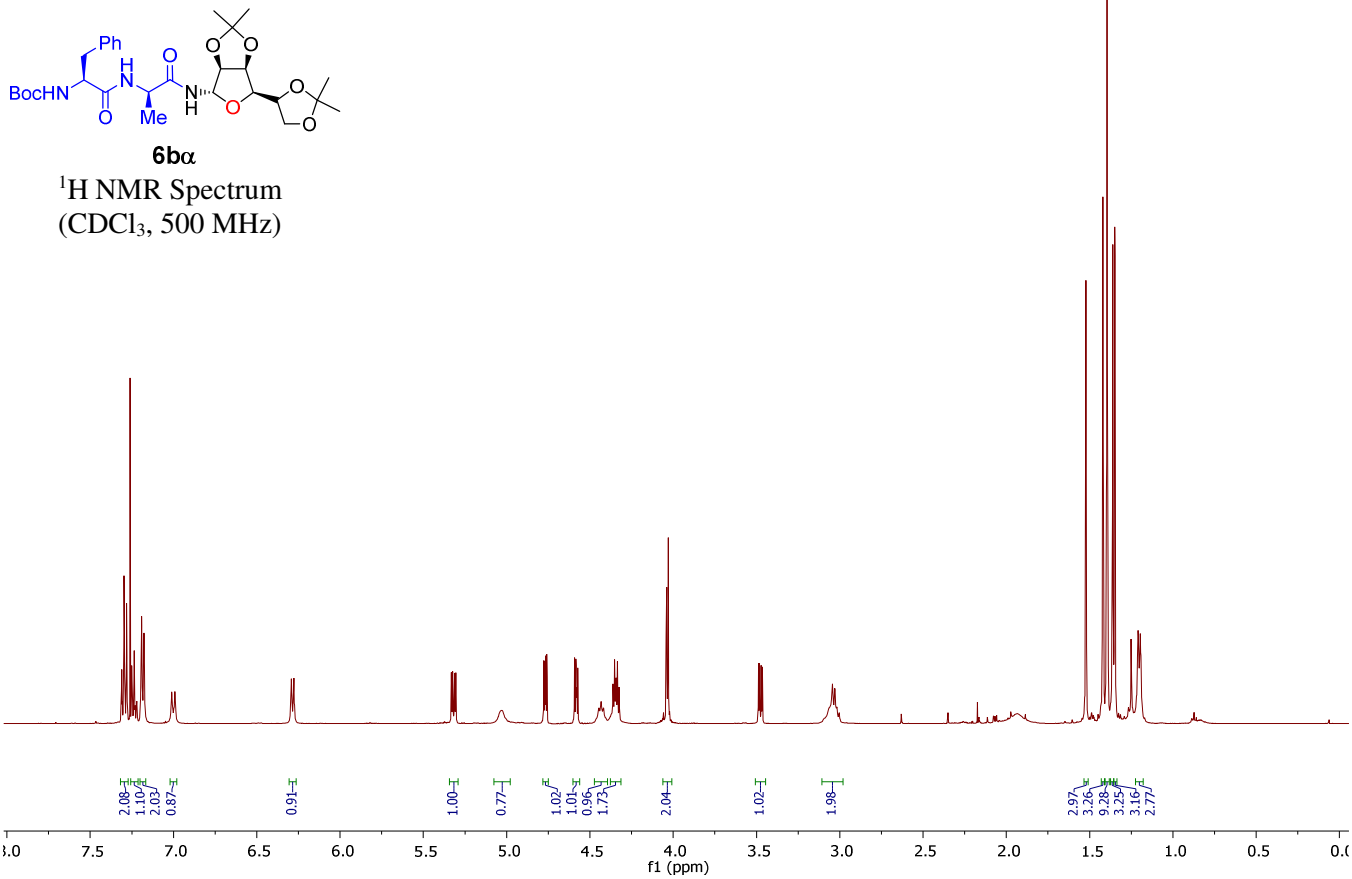
6aβ

COSY NMR Spectrum



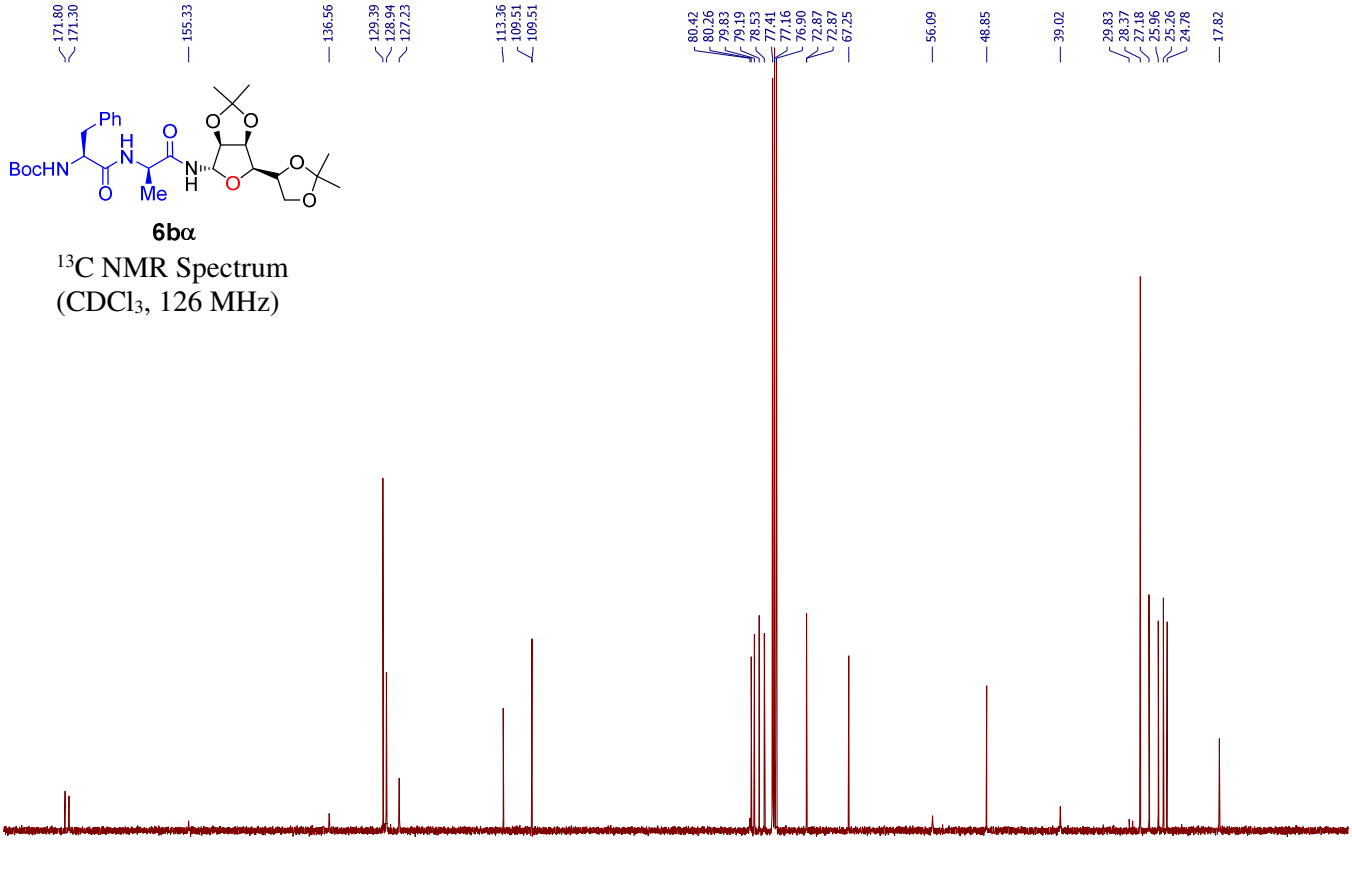
6aβ

HSQC NMR Spectrum



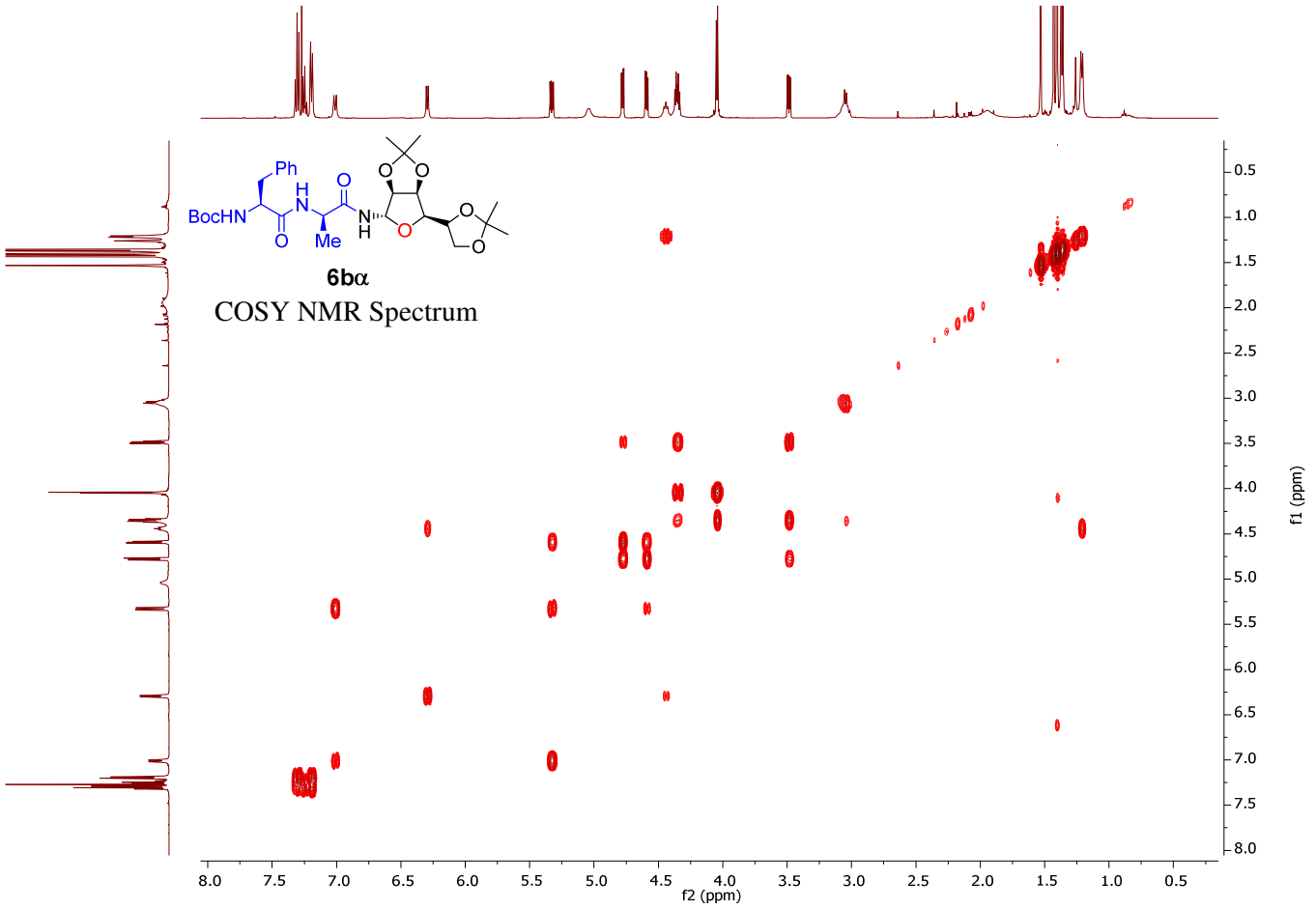
6bα

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



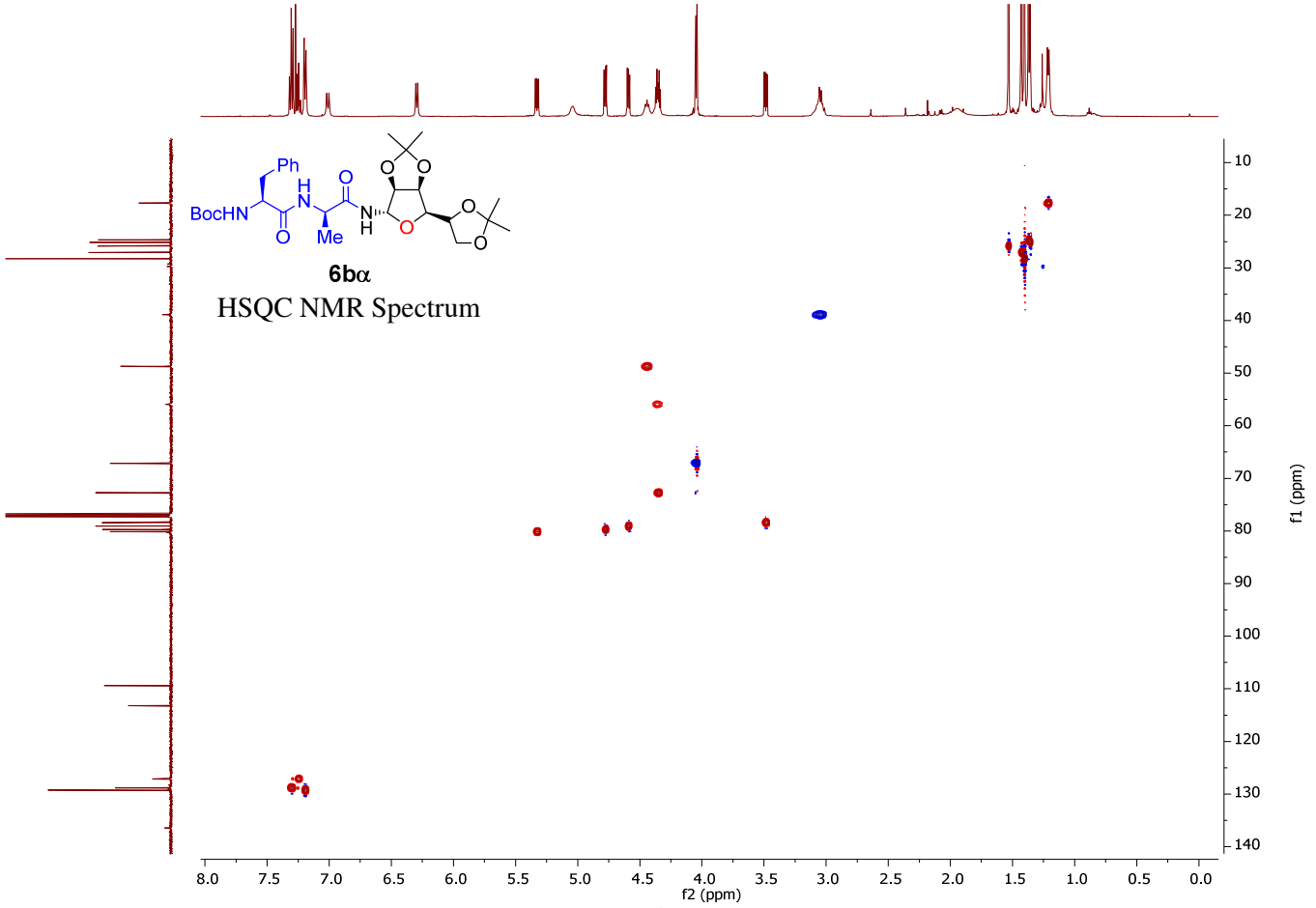
6bα

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



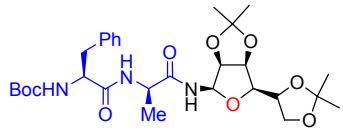
6bα

COSY NMR Spectrum



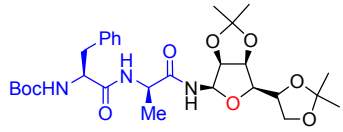
6bα

HSQC NMR Spectrum



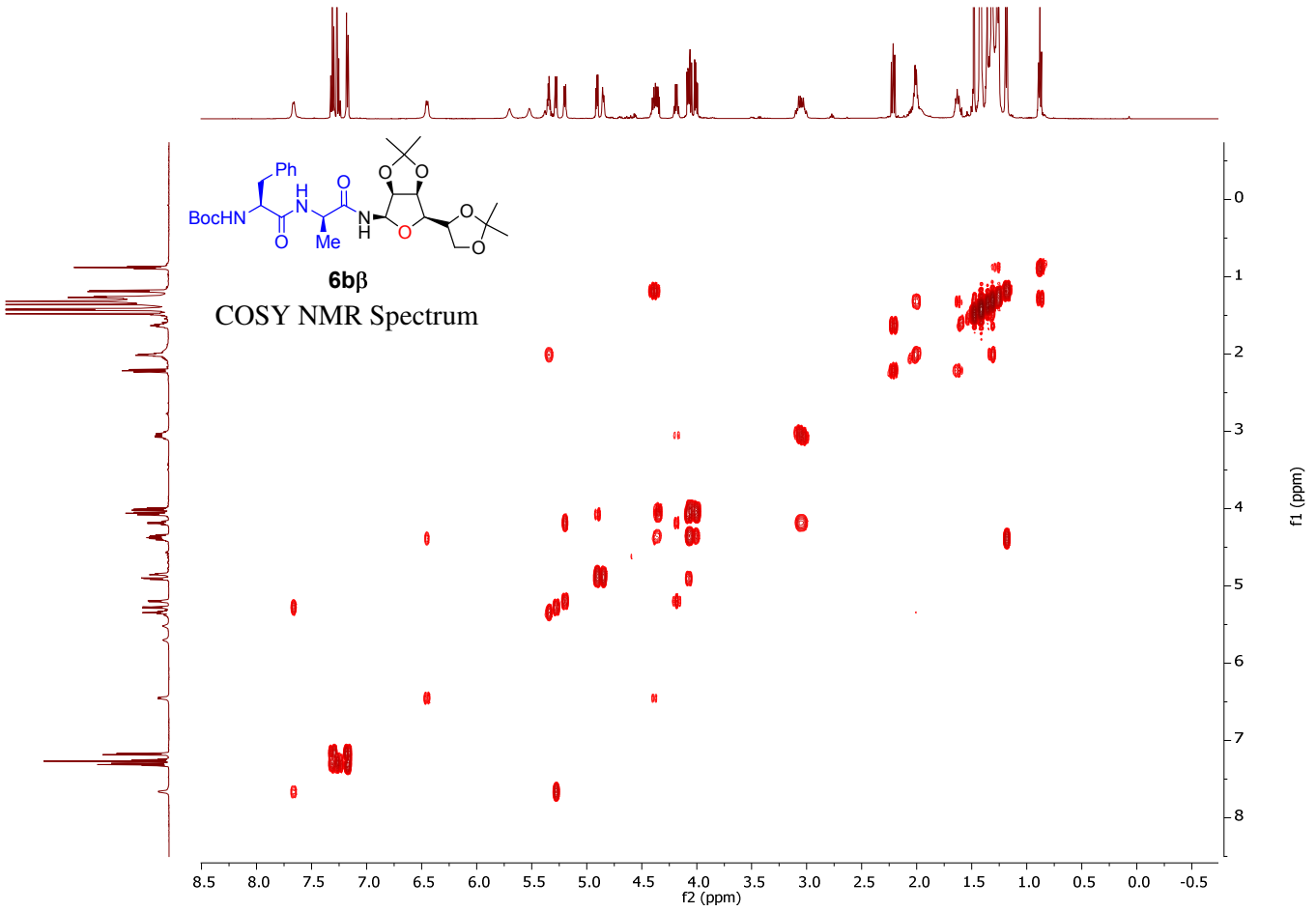
6bβ

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



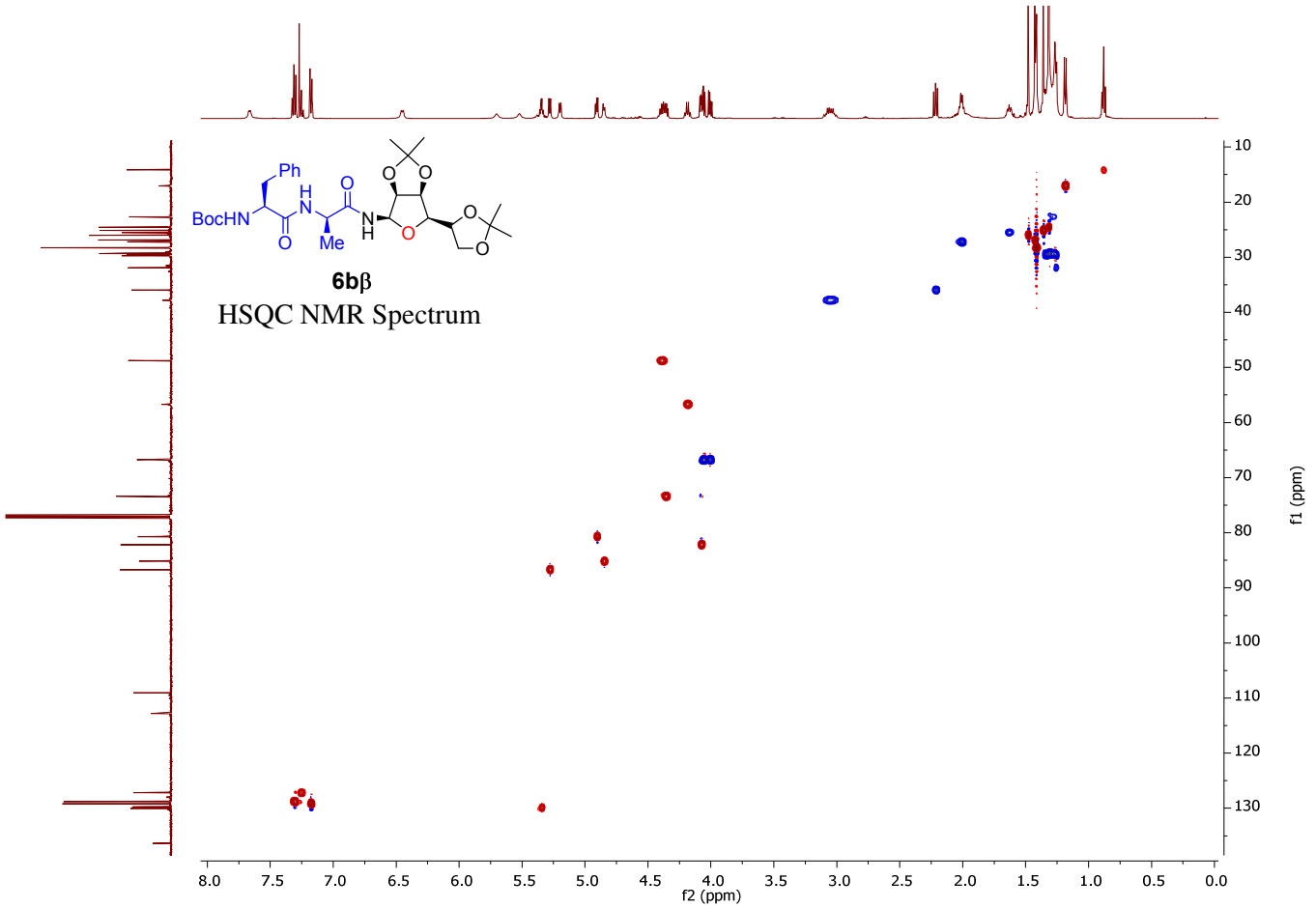
6bβ

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



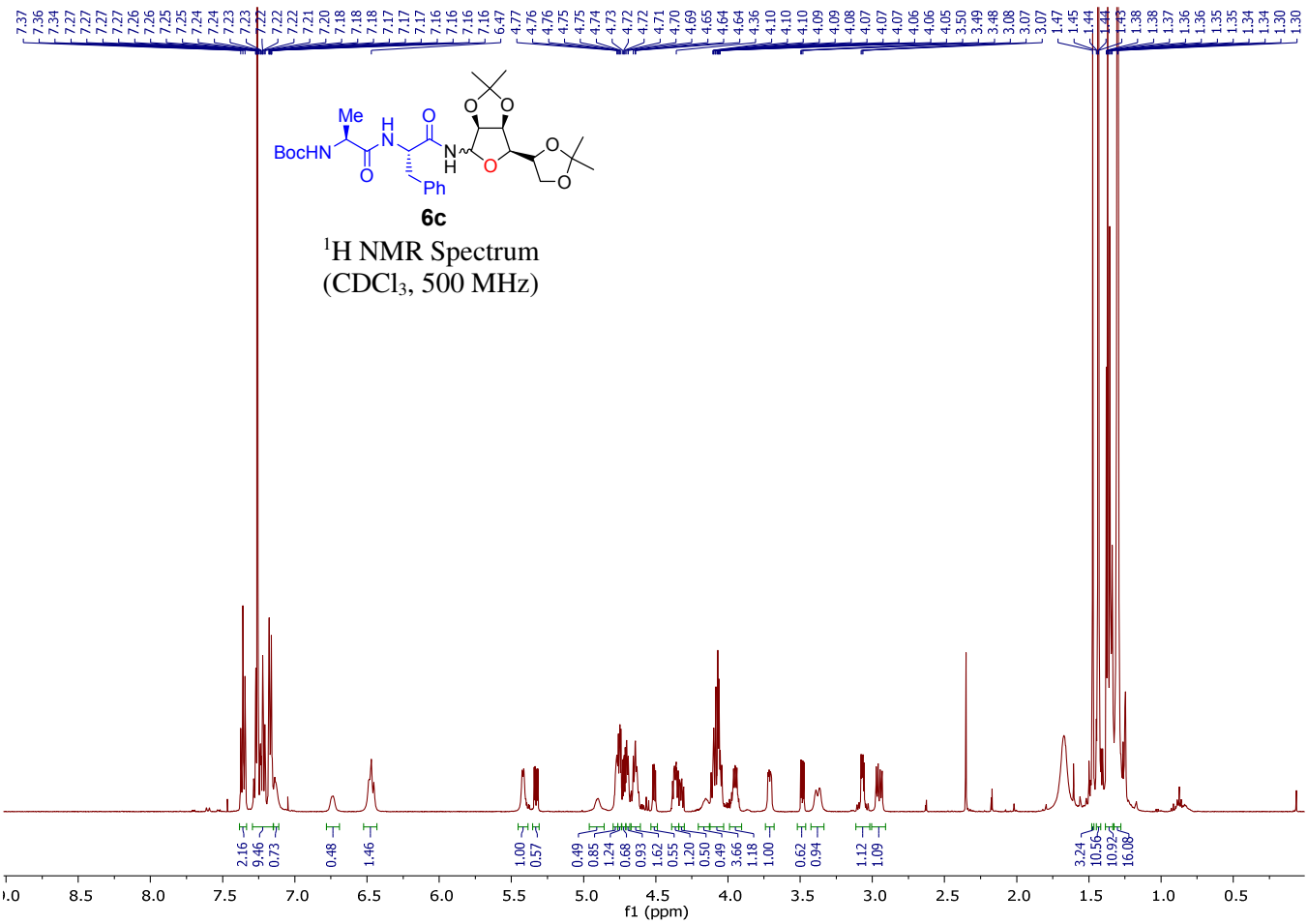
6bβ

COSY NMR Spectrum



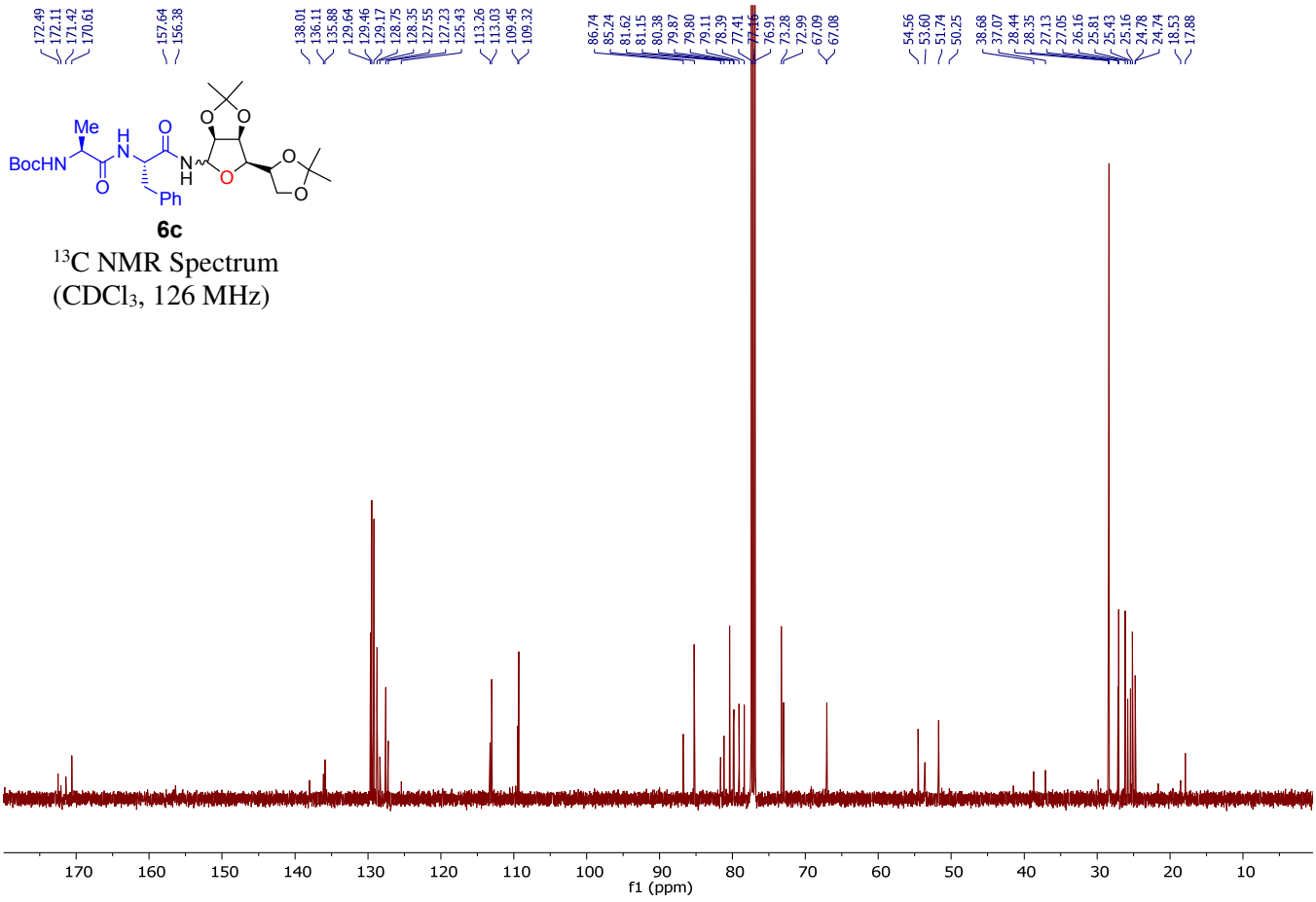
6bβ

HSQC NMR Spectrum



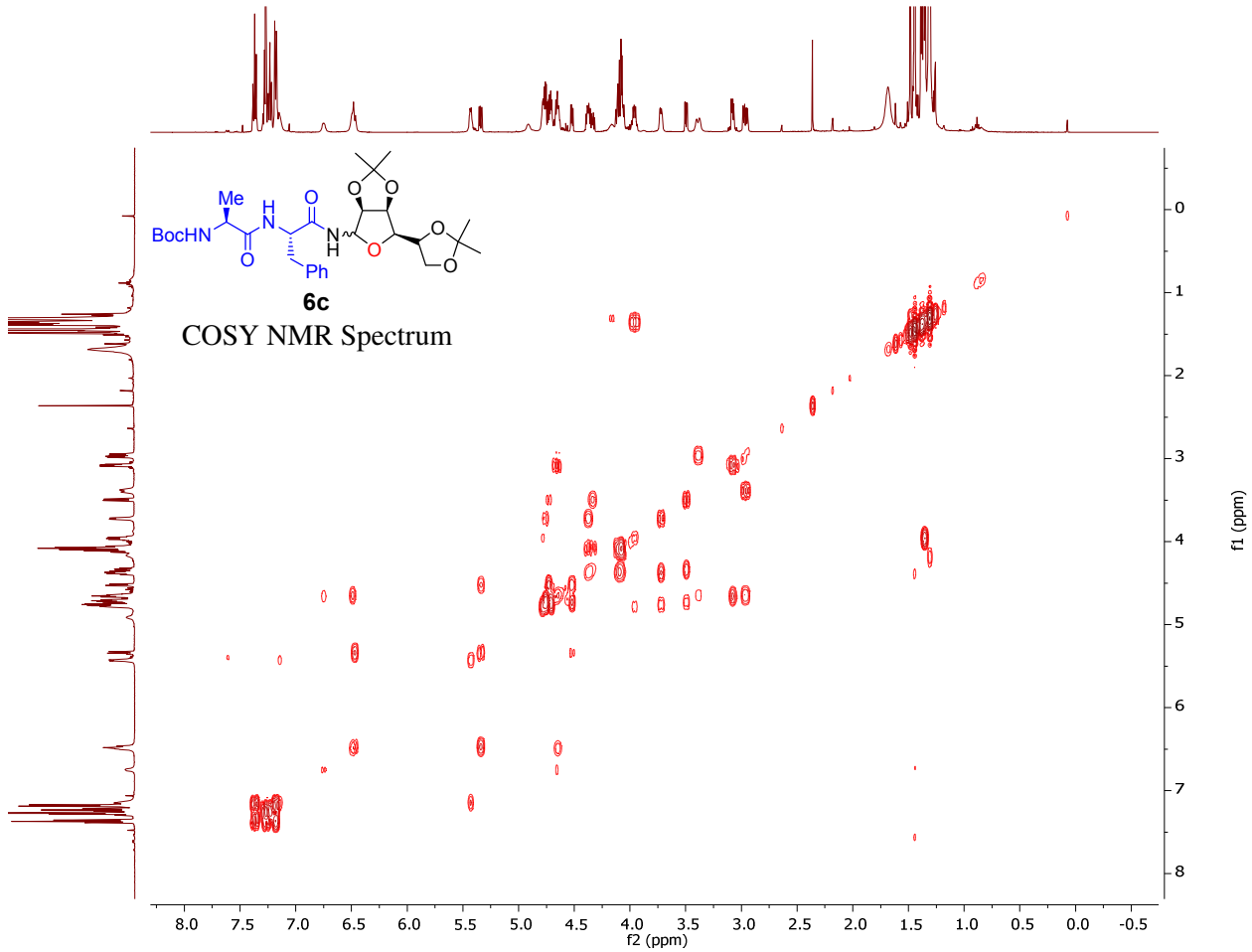
6c

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



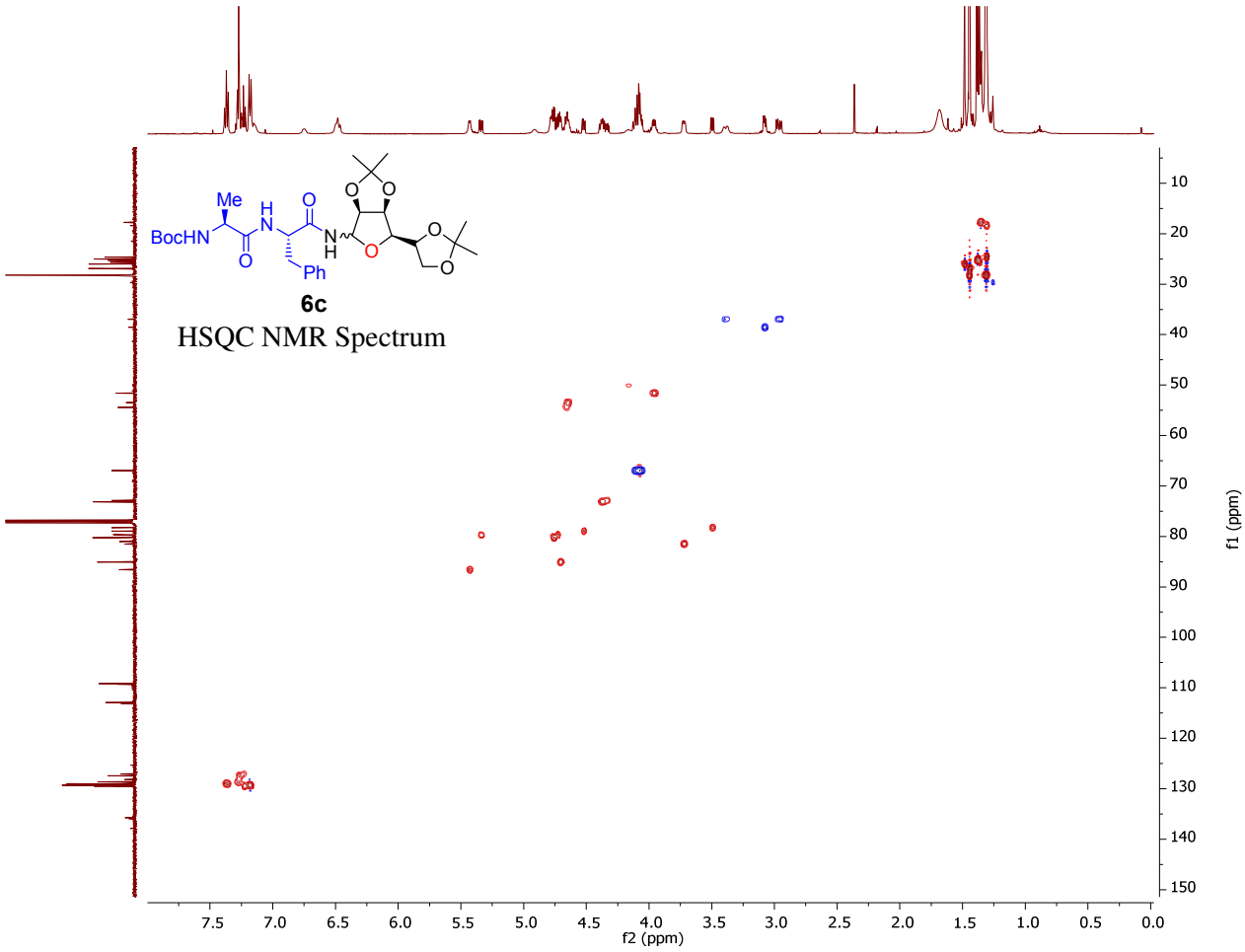
6c

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



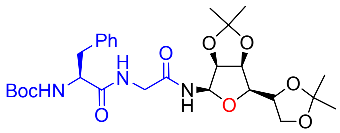
6c

COSY NMR Spectrum



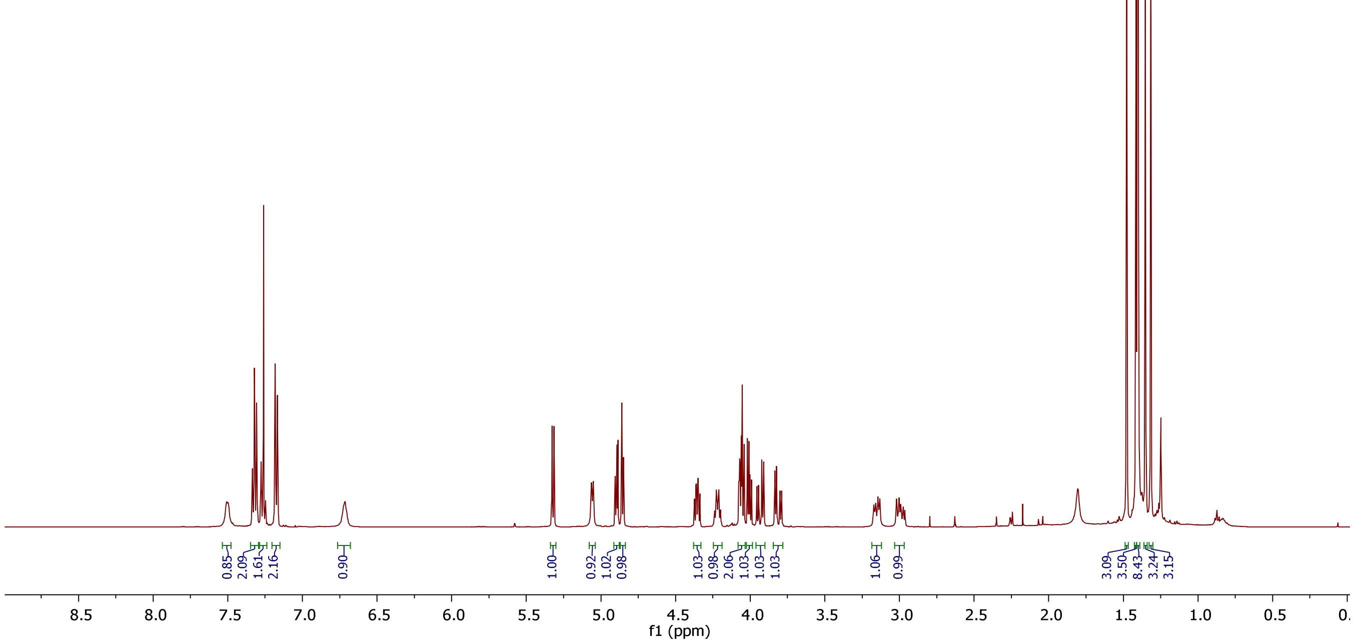
6c

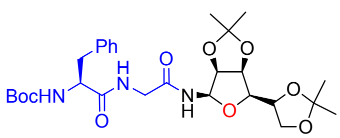
HSQC NMR Spectrum



6dβ

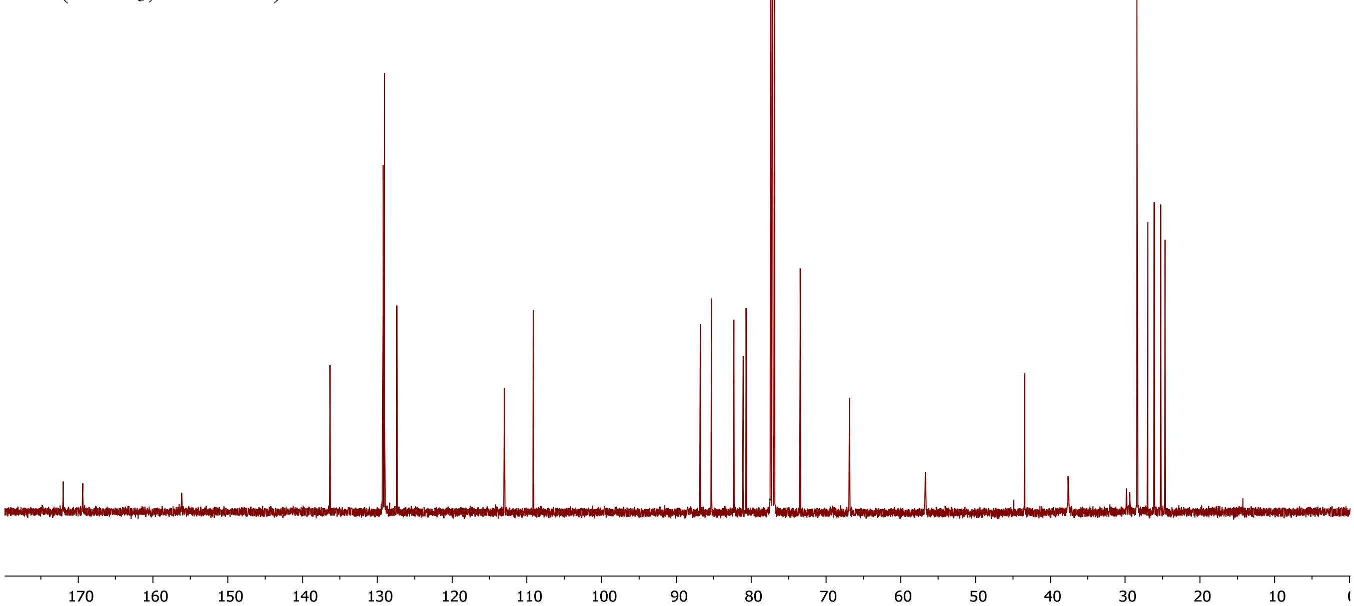
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

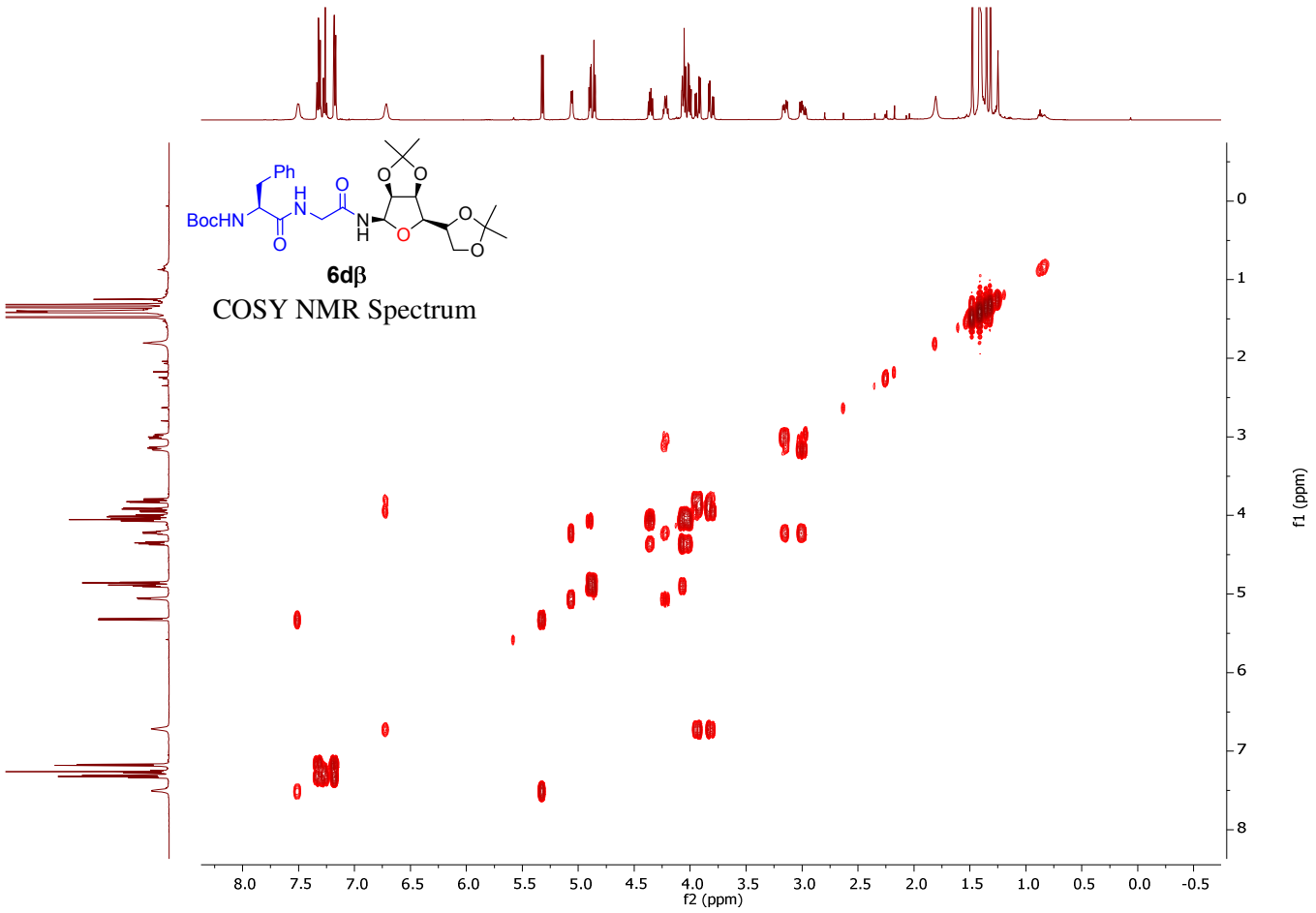


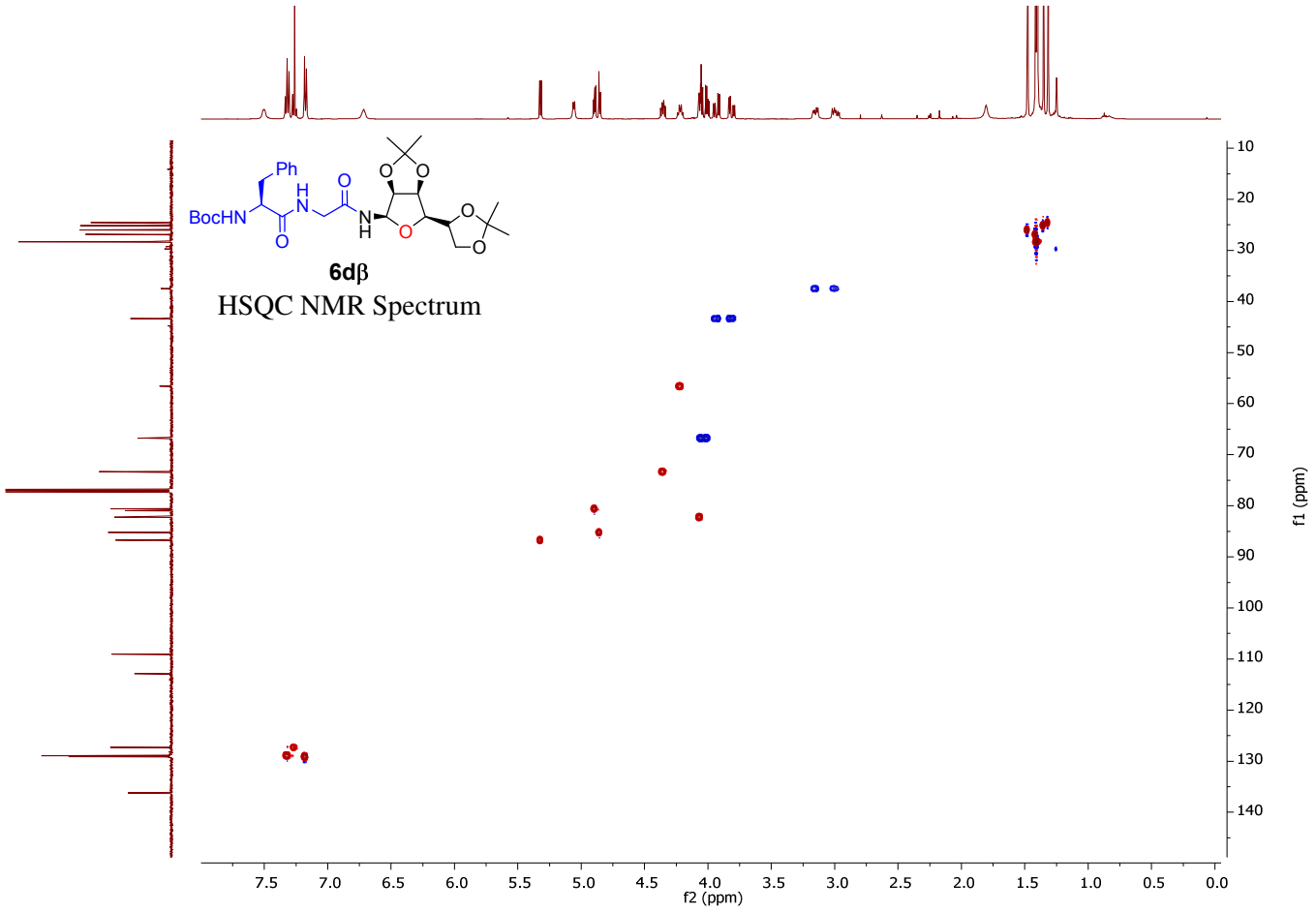


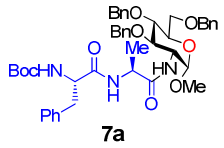
6dβ

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



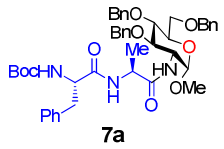

Ph
BocHN
H
N
O
O
O
O
N
H
O
O
6dβ
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


Ph
BocHN
H
N
O
O
O
O
N
H
O
O
6dβ
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



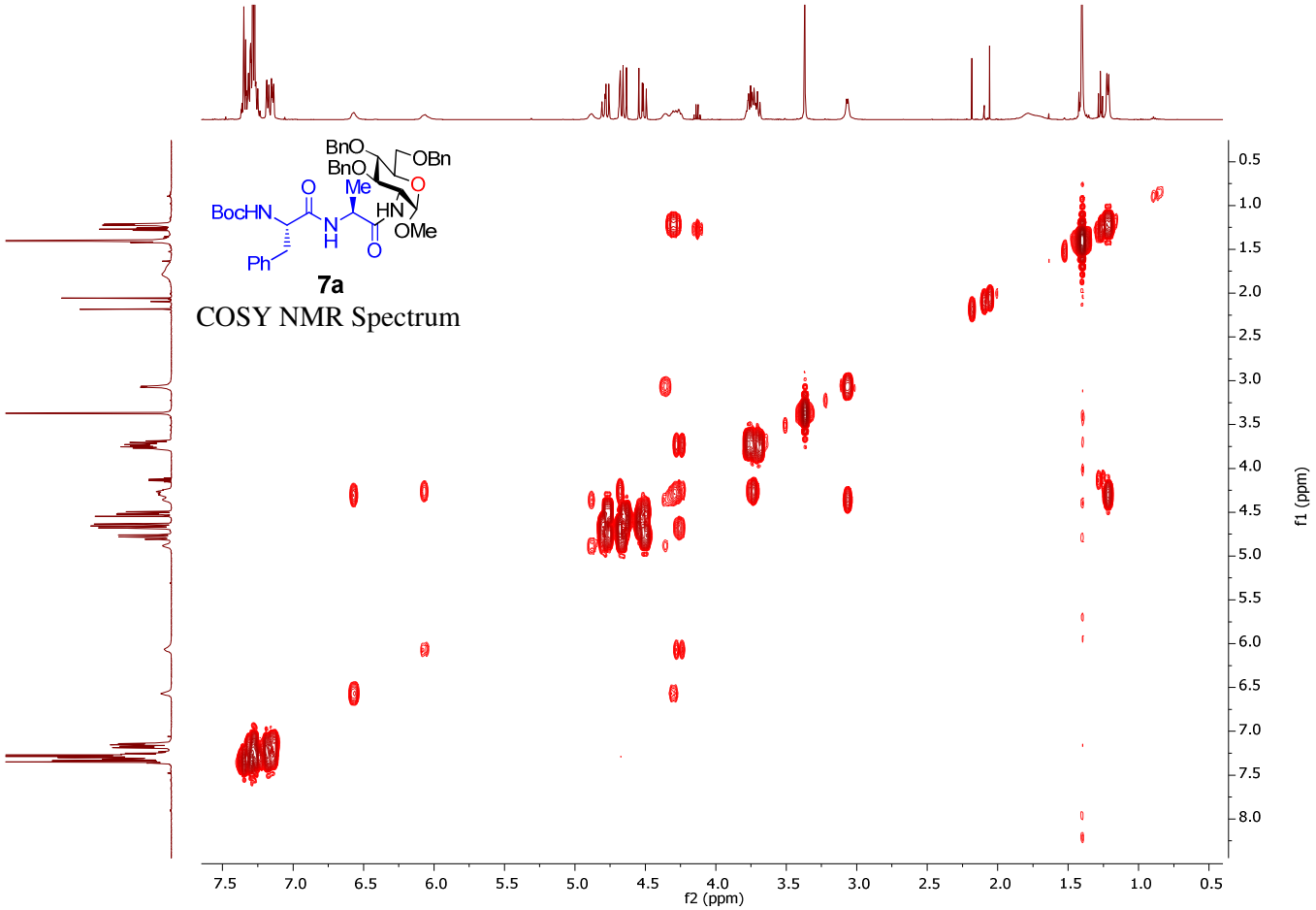
7a

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

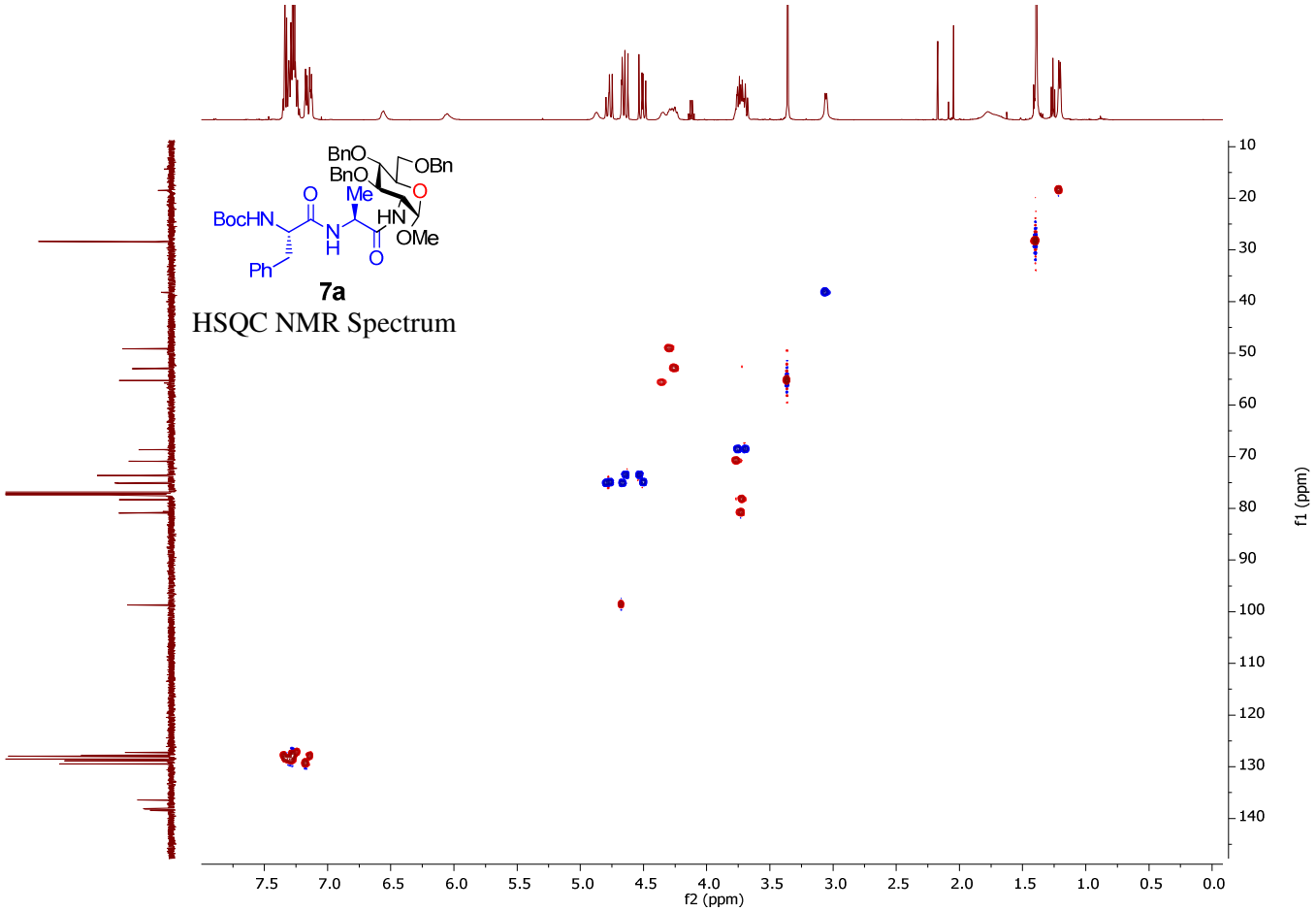


7a

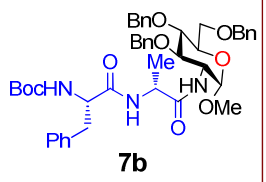
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

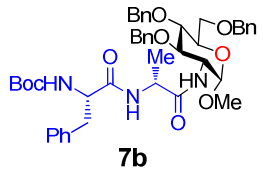


HSQC NMR Spectrum



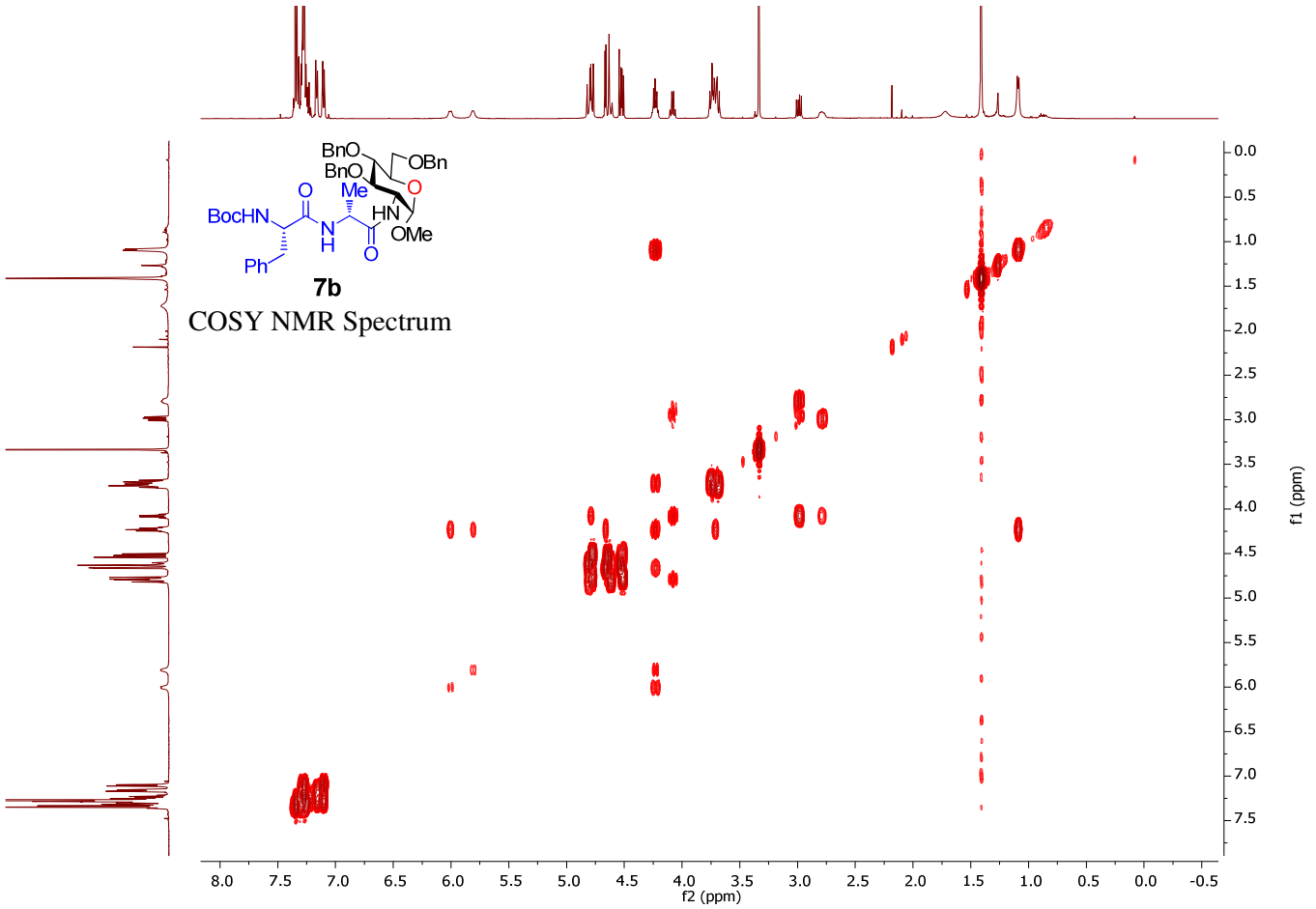
7b

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



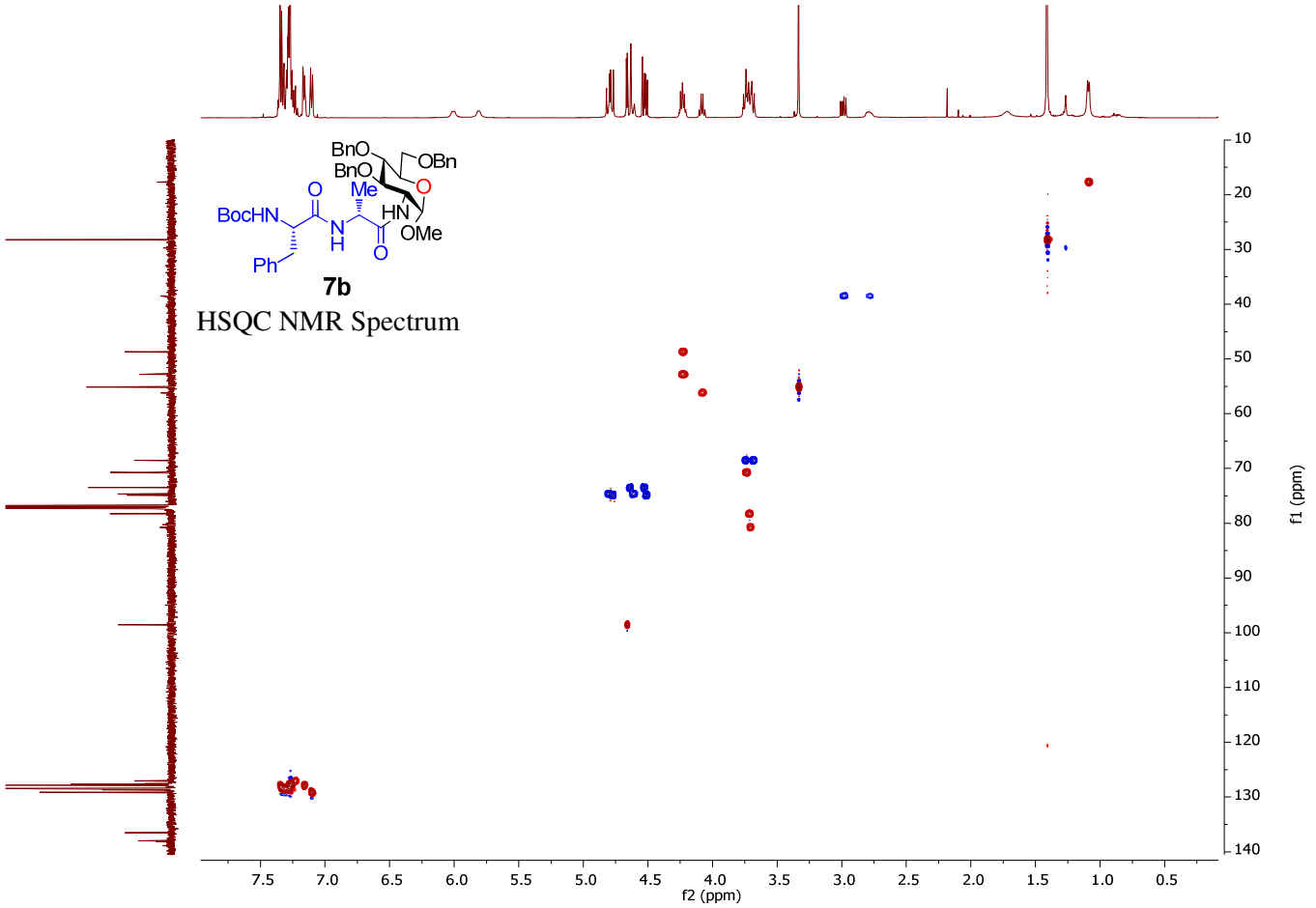
7b

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



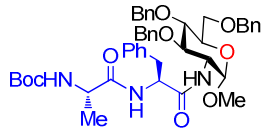
7b

COSY NMR Spectrum



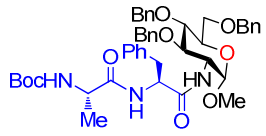
7b

HSQC NMR Spectrum



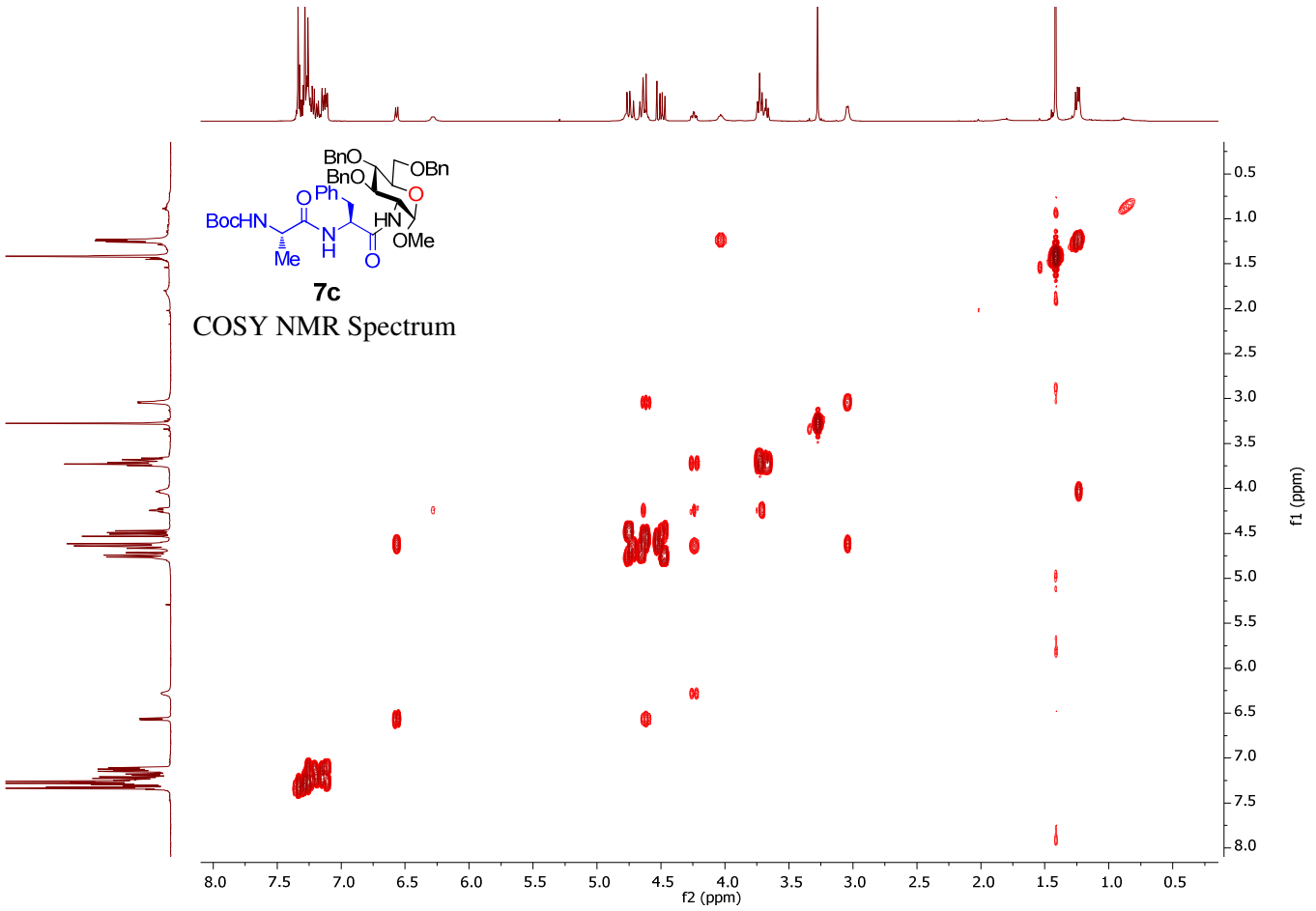
7c

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

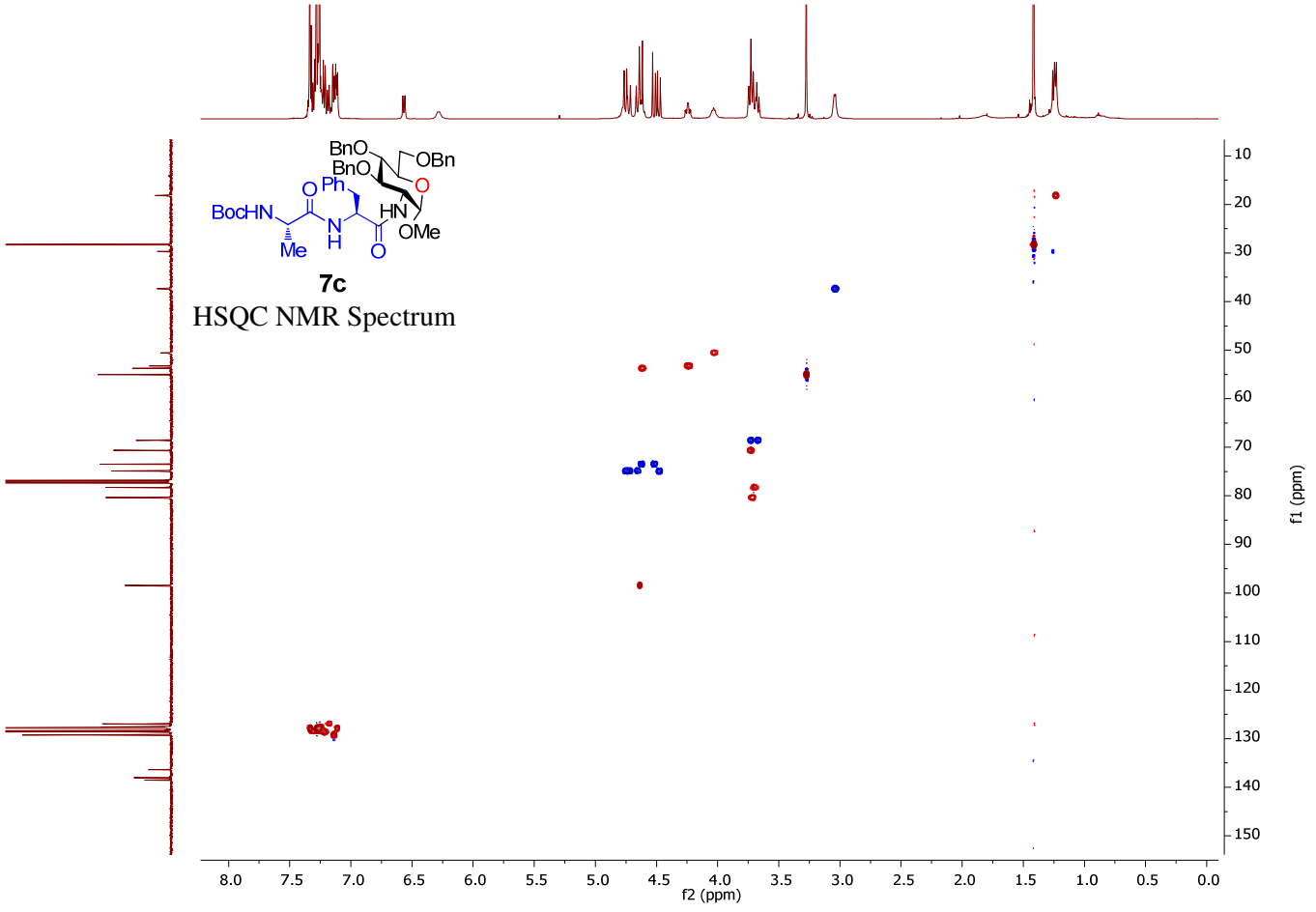


7c

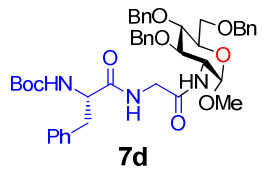
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

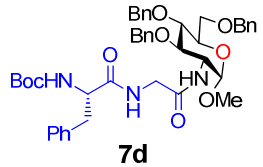


HSQC NMR Spectrum



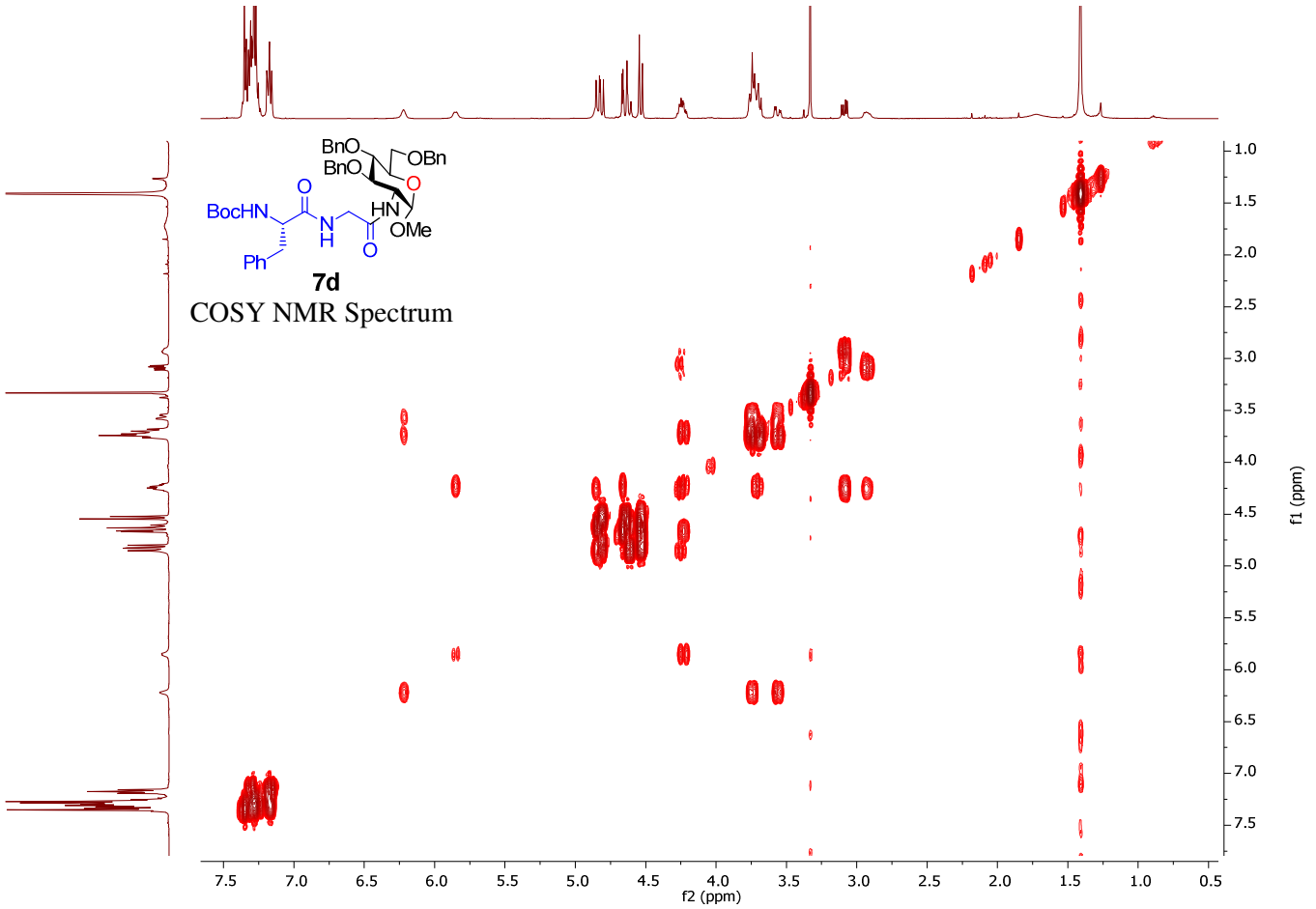
7d

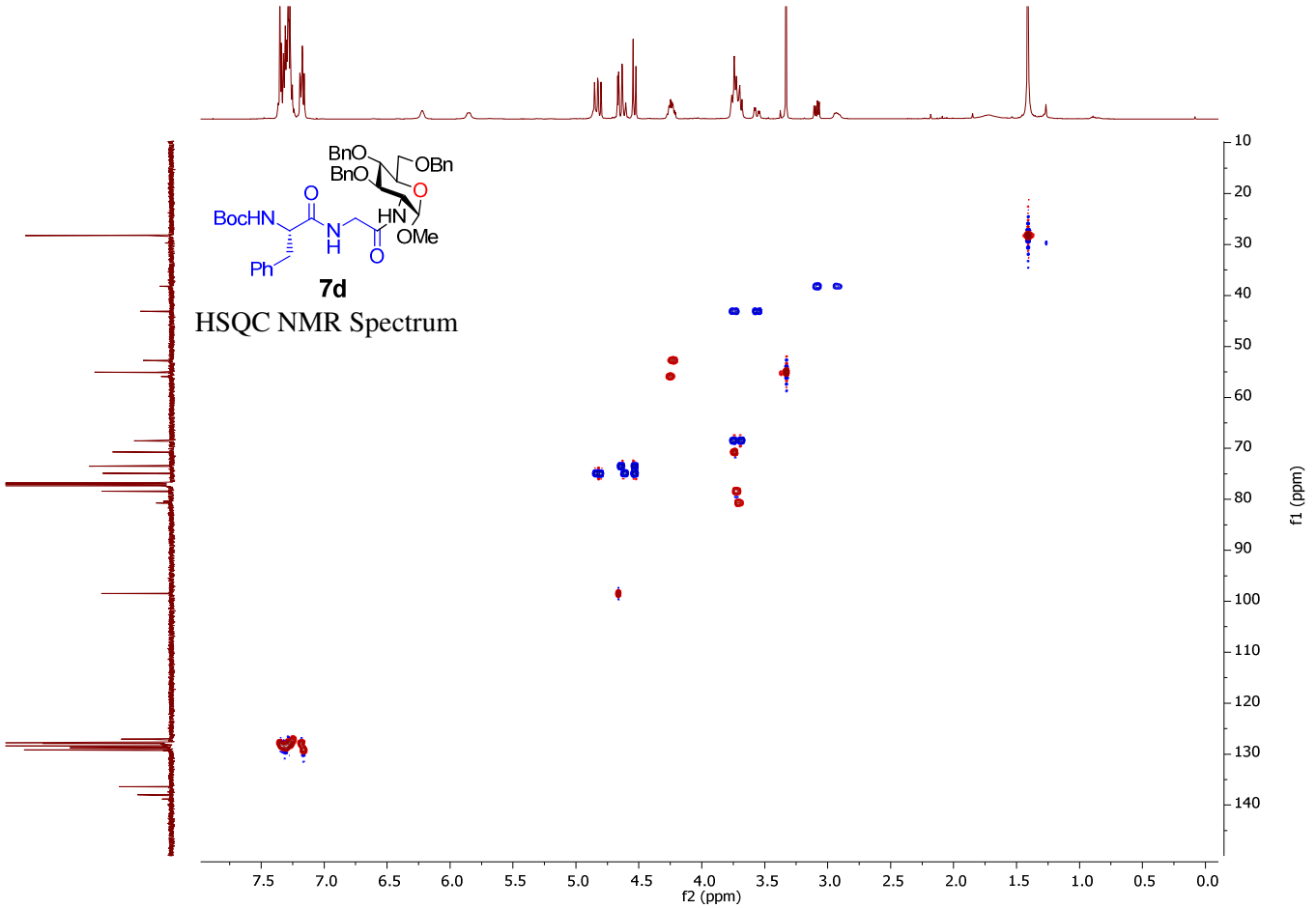
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

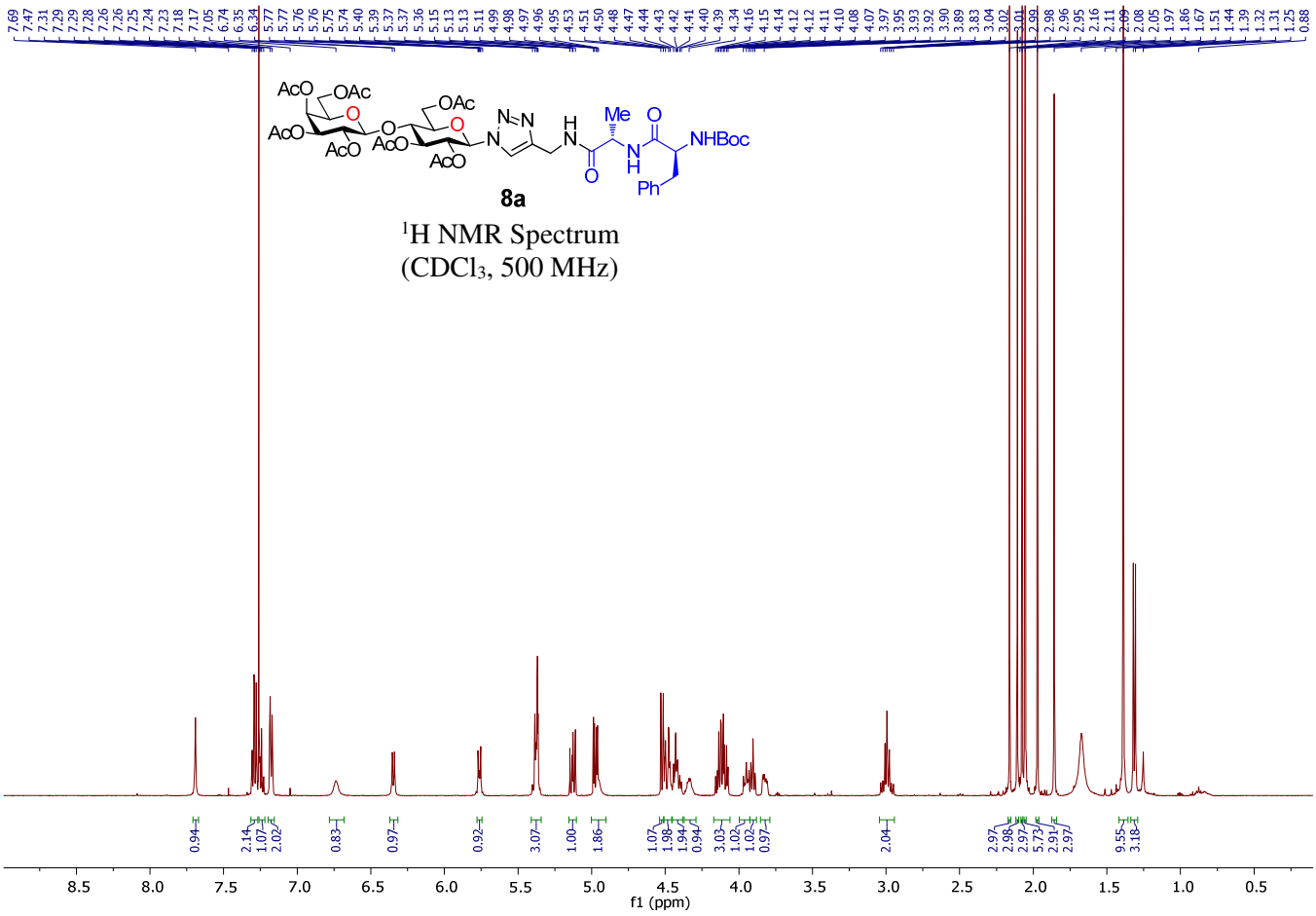


7d

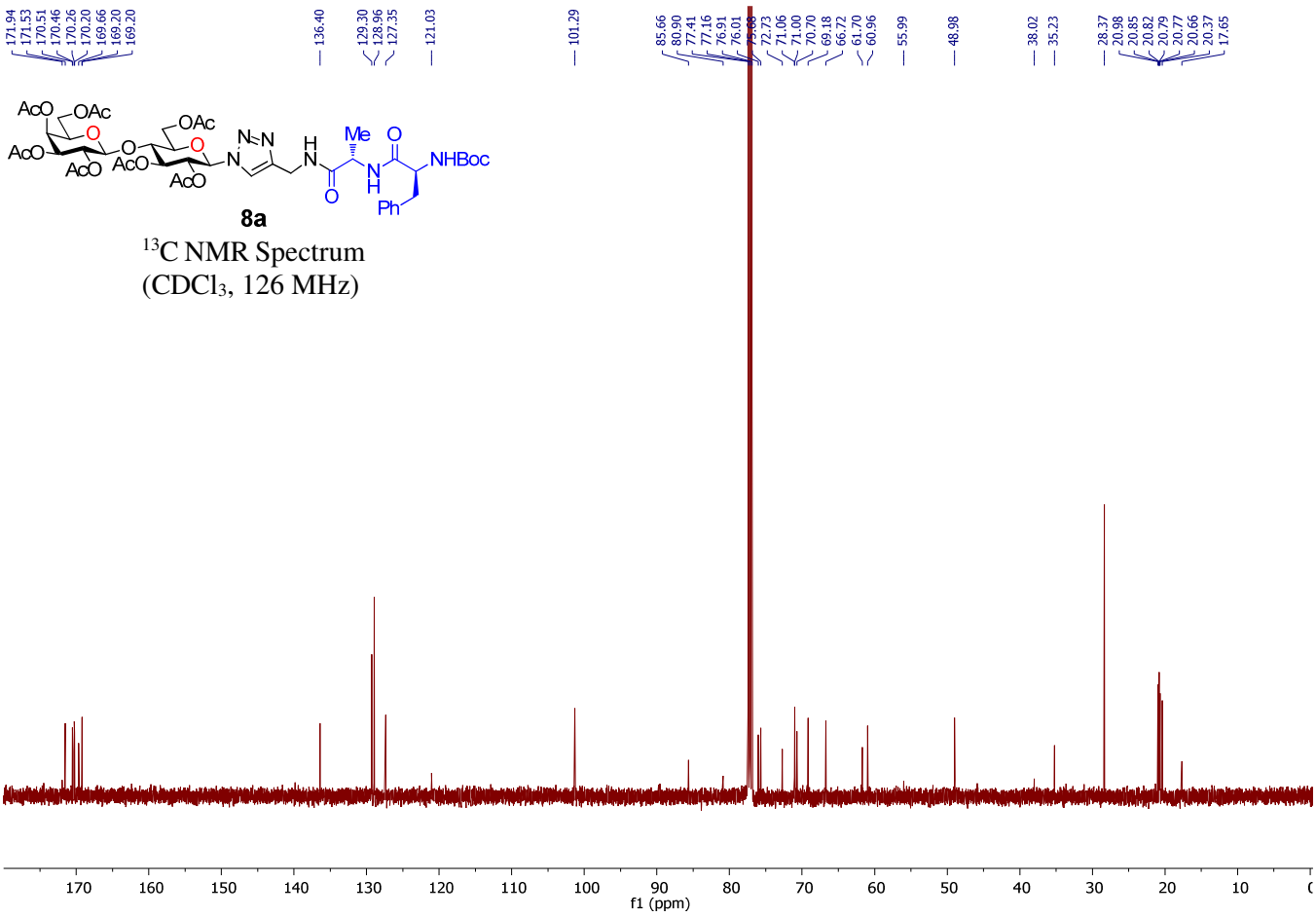
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)


BnO
BnO
OBn
O
HN
OMe
BocHN
N
H
O
O
Ph
7d
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)

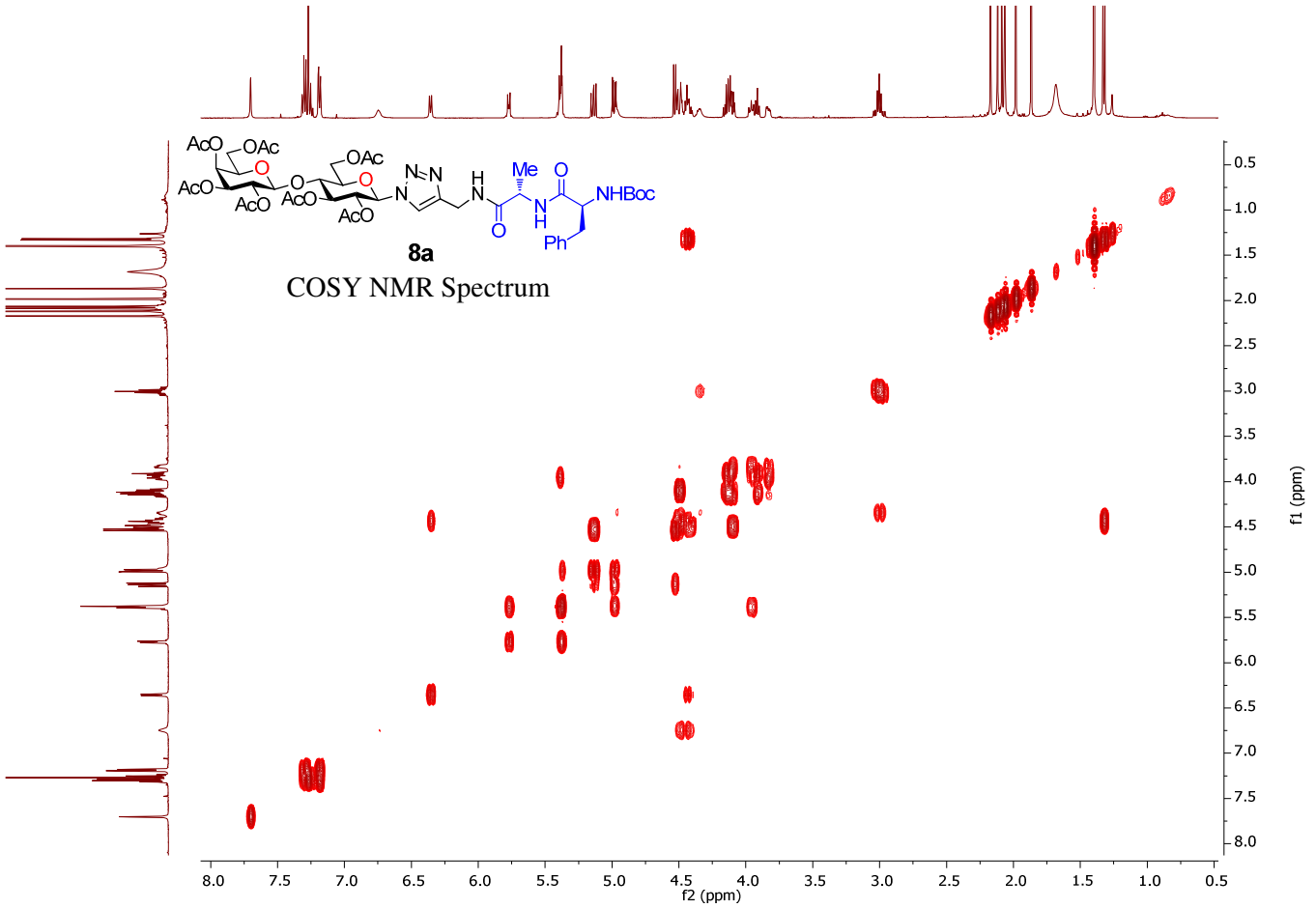

BnO
BnO
OBn
O
HN
OMe
BocHN
N
H
O
O
Ph
7d
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)

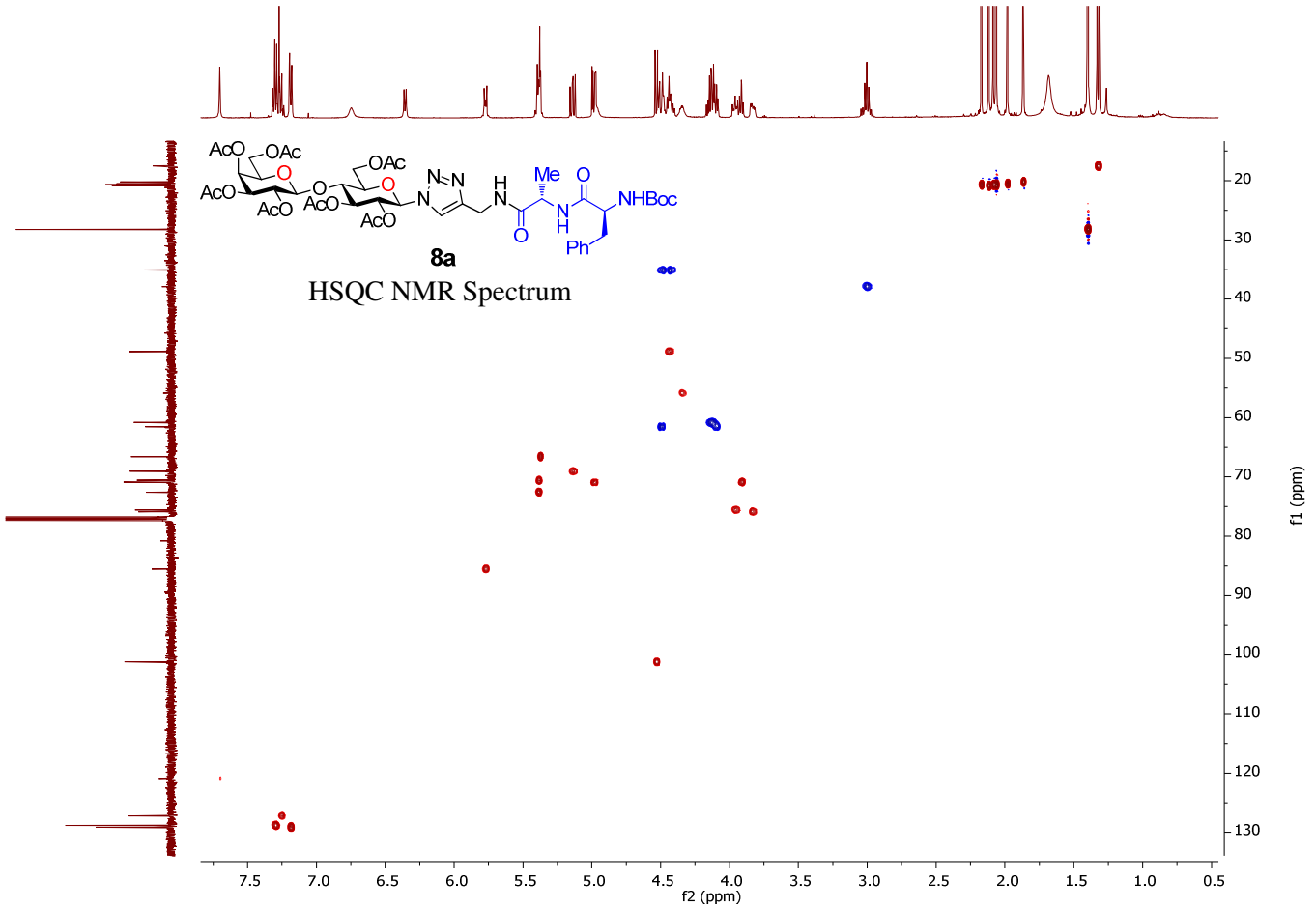


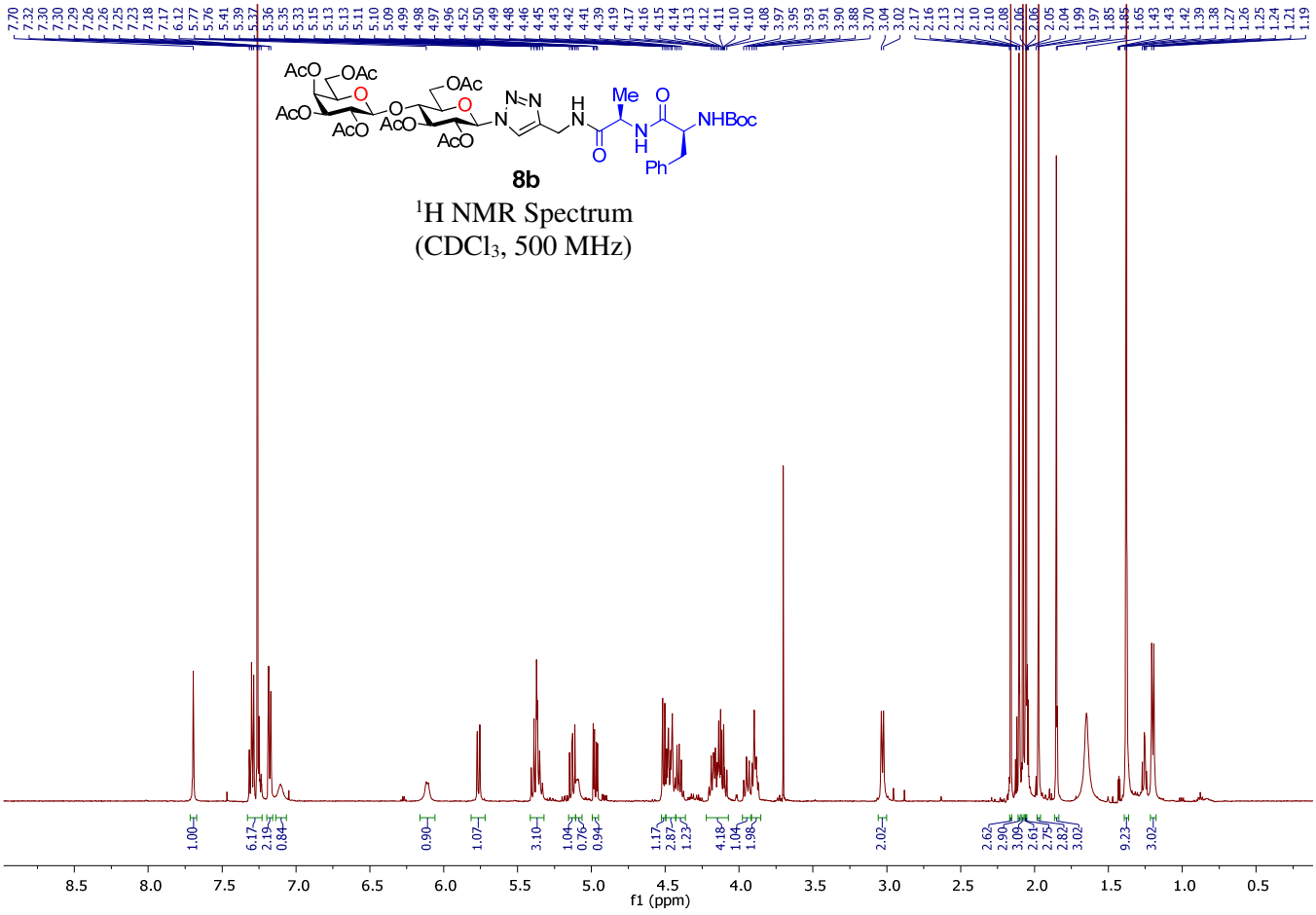
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



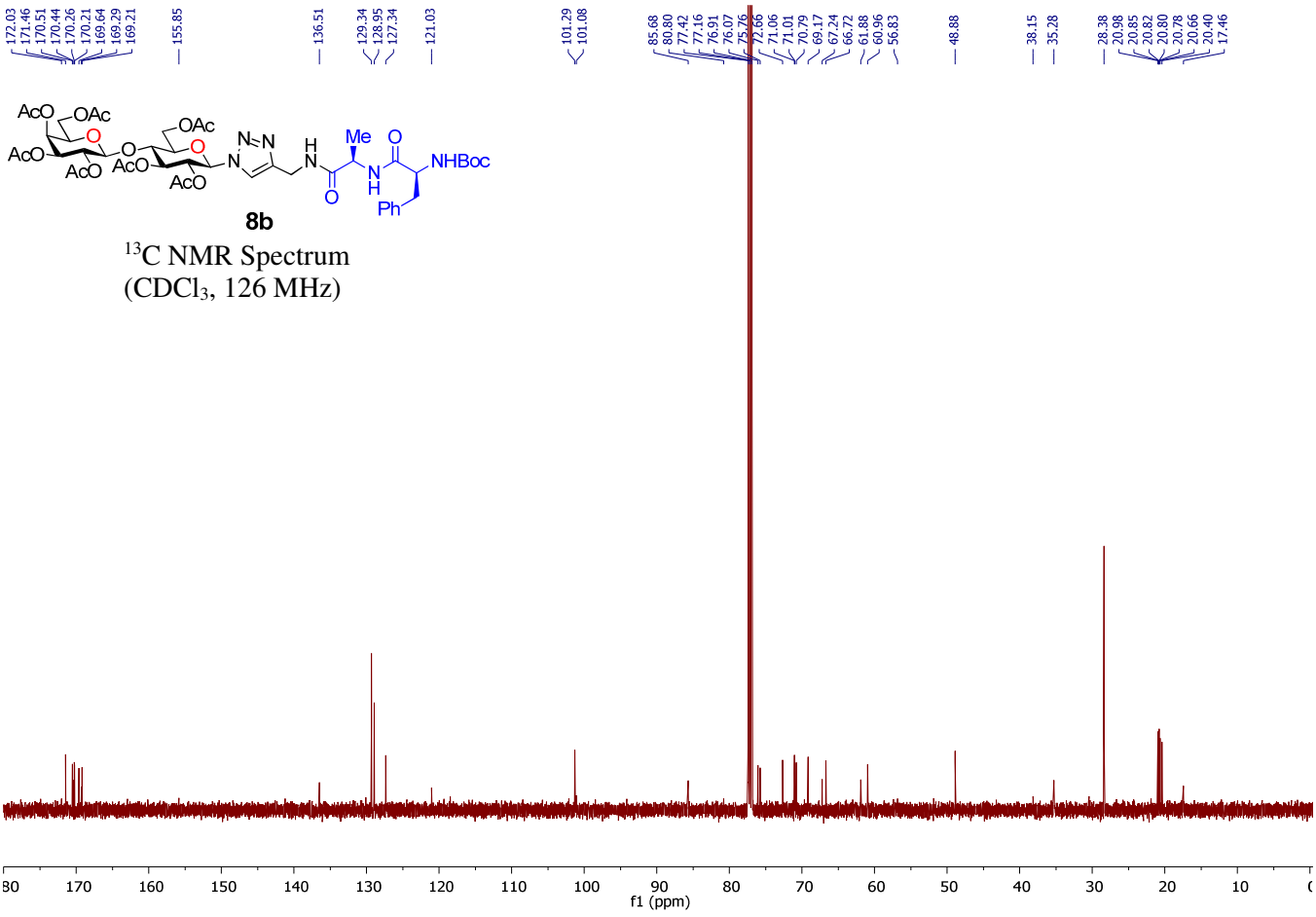
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)


8a
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)

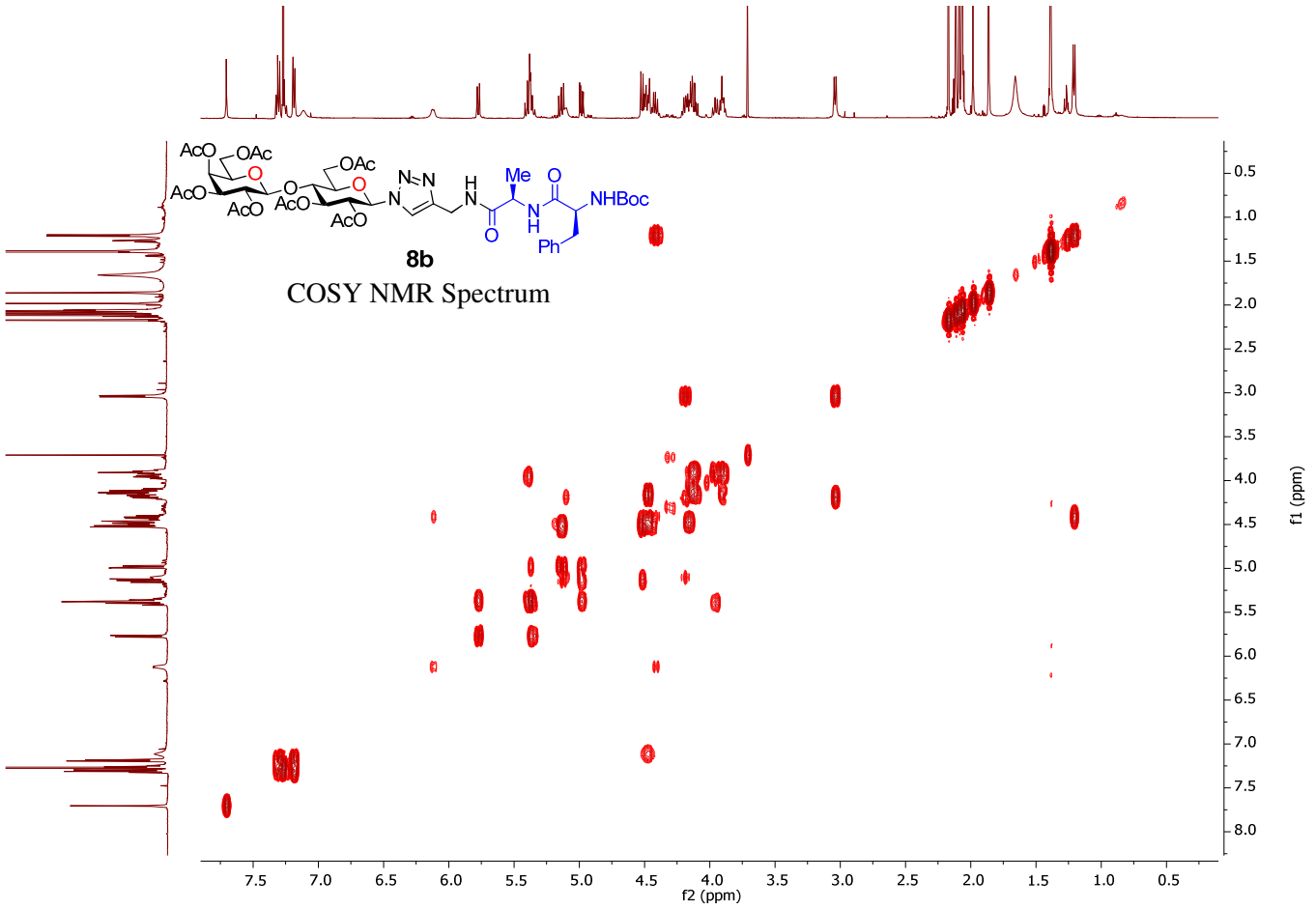

8a
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)

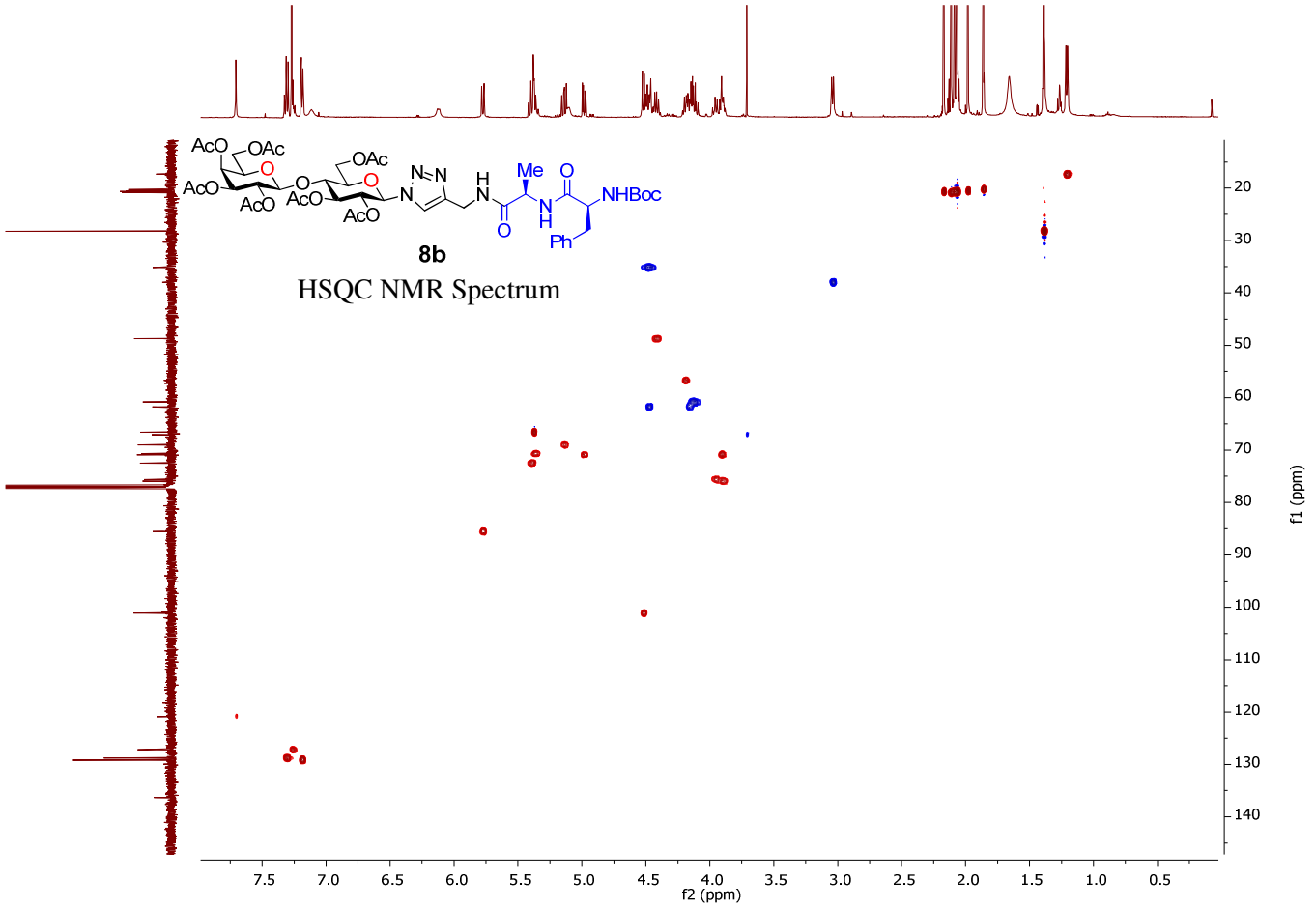


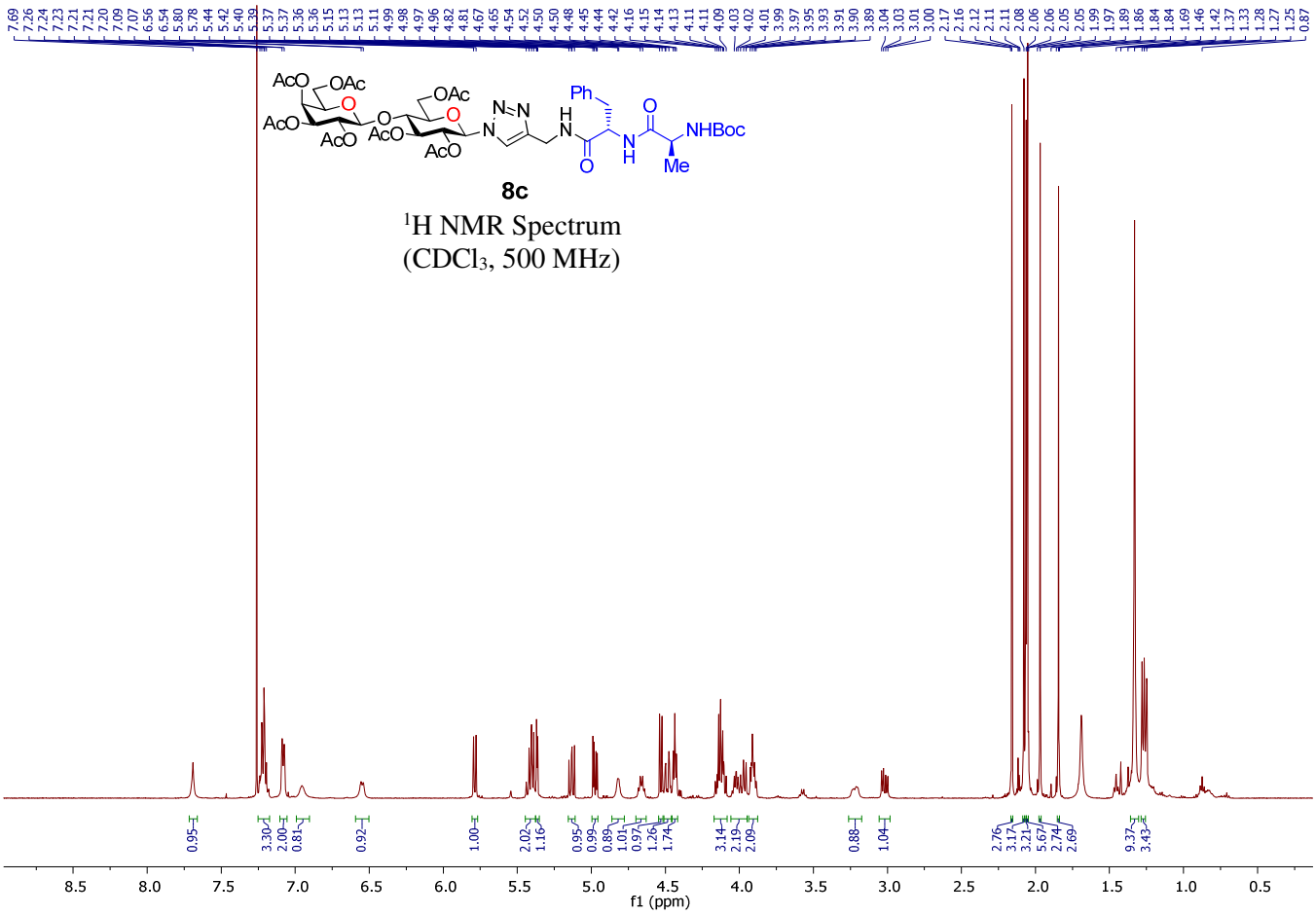
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)

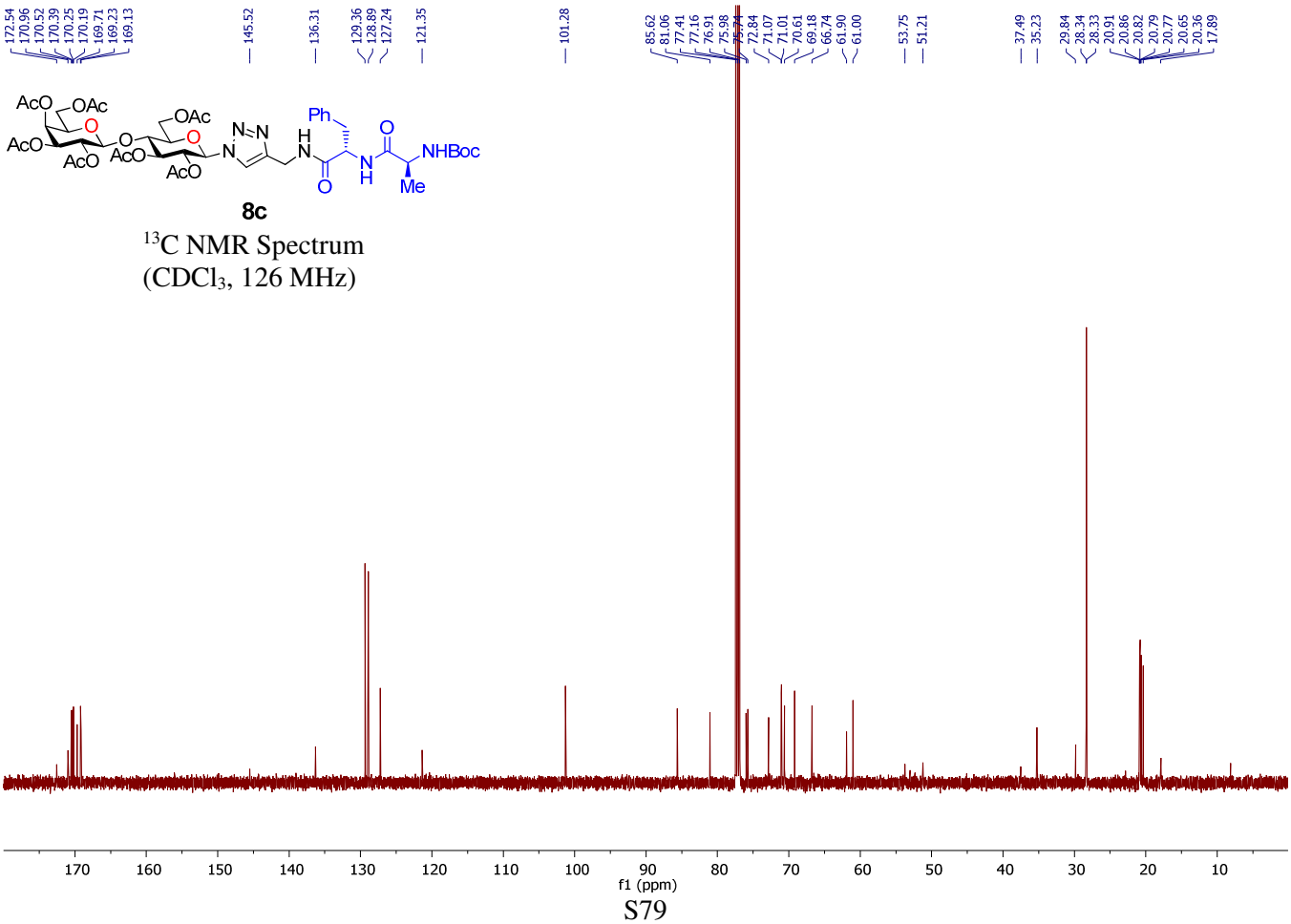

8b
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


8b
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



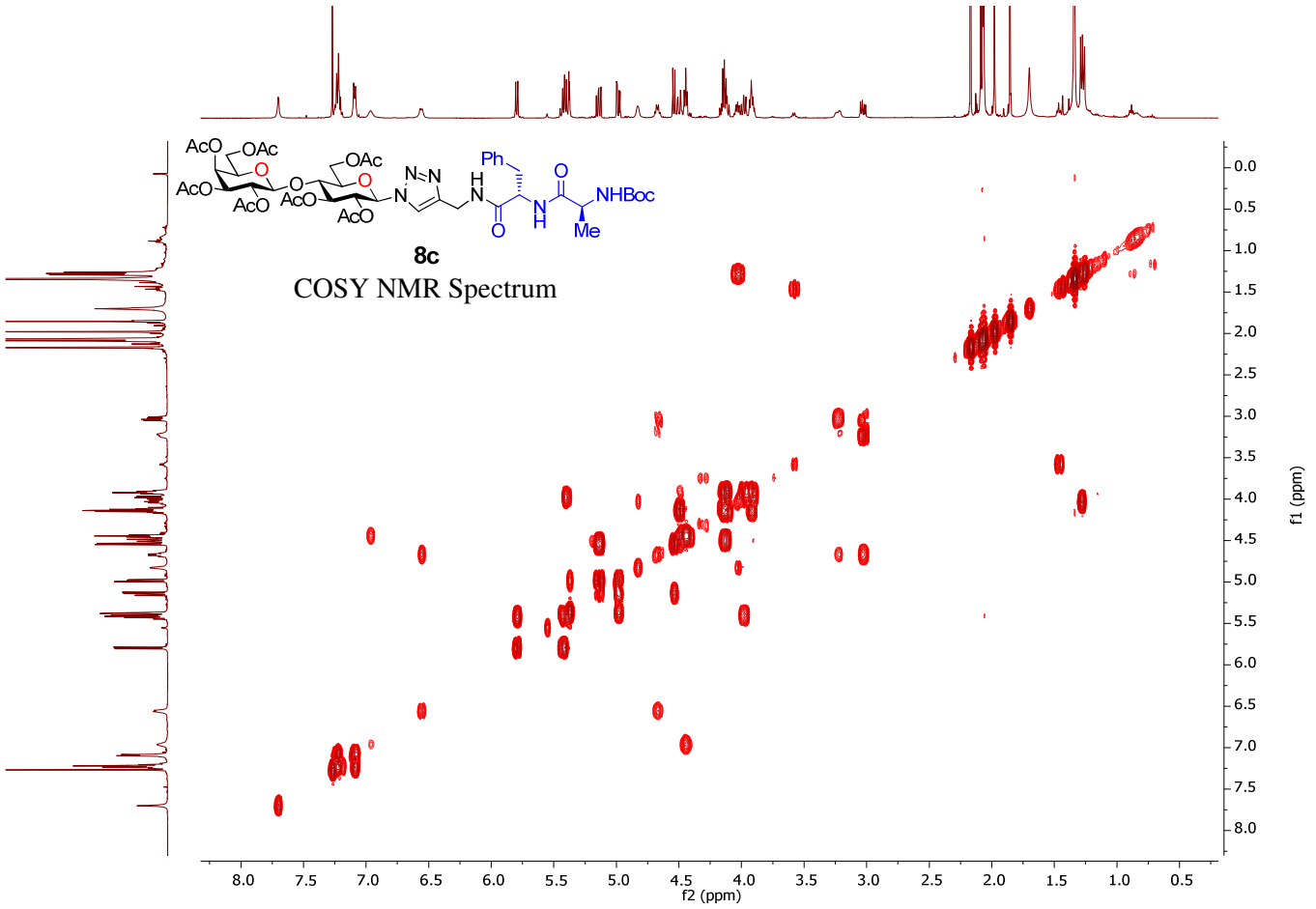
8c

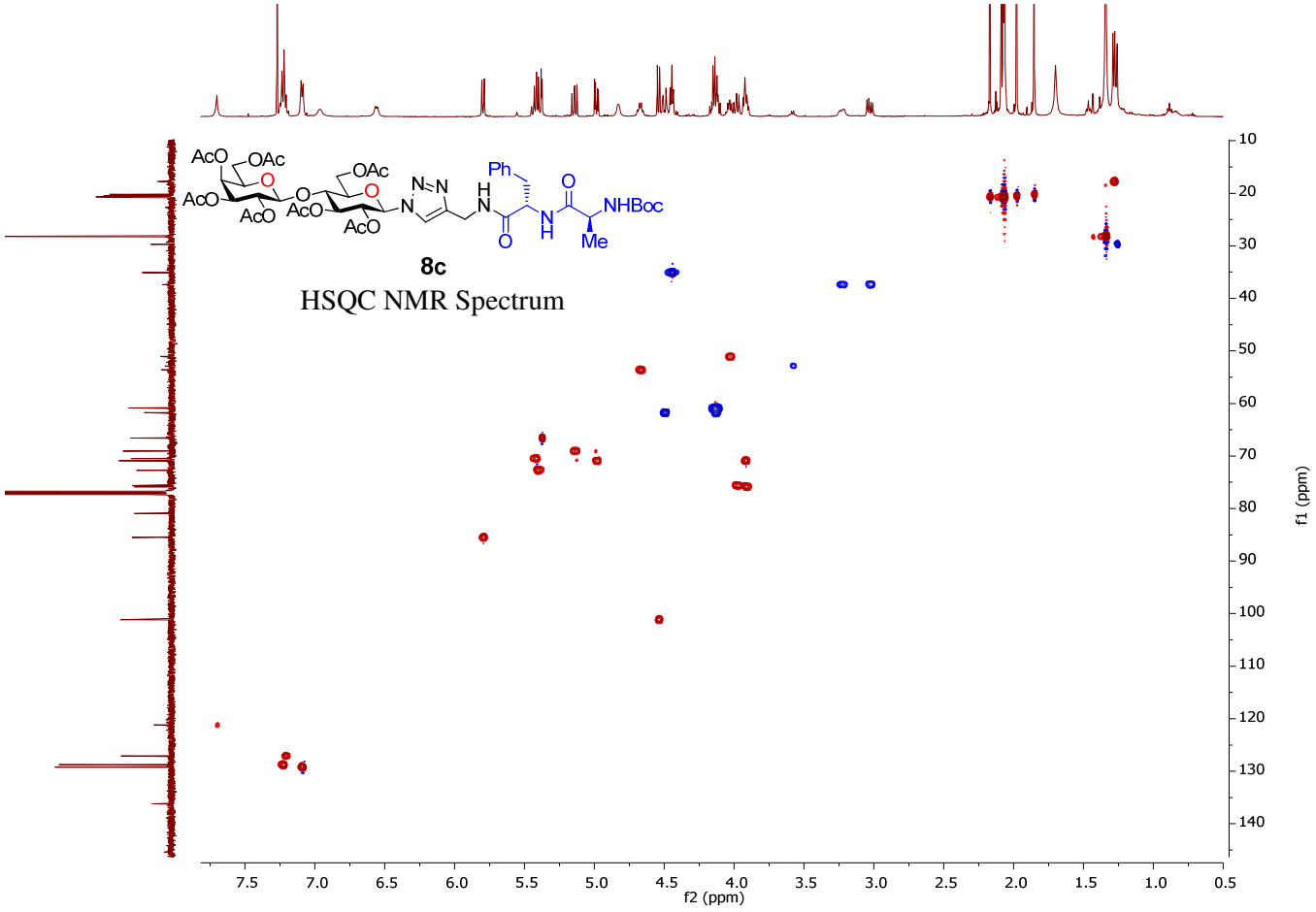
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

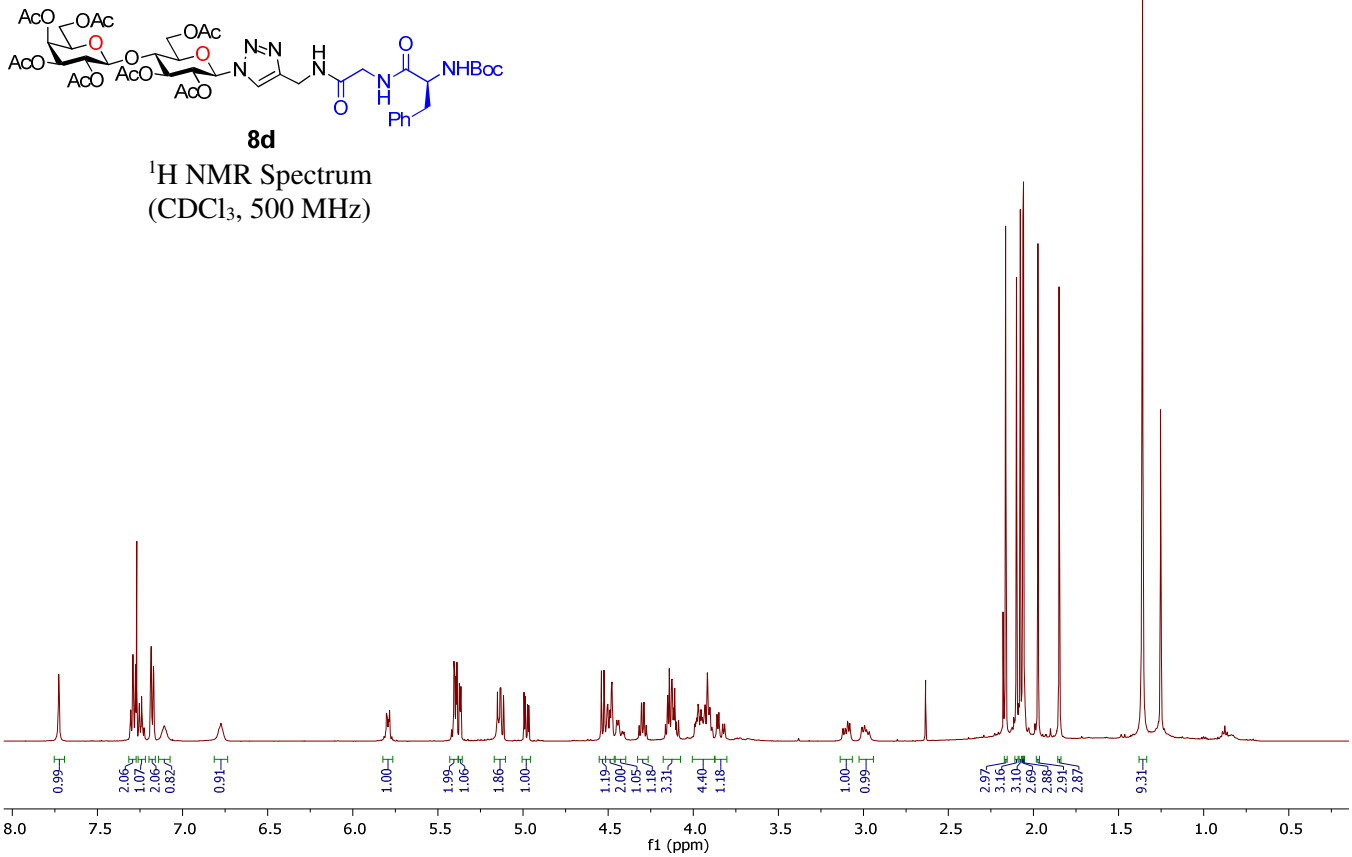


8c

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)

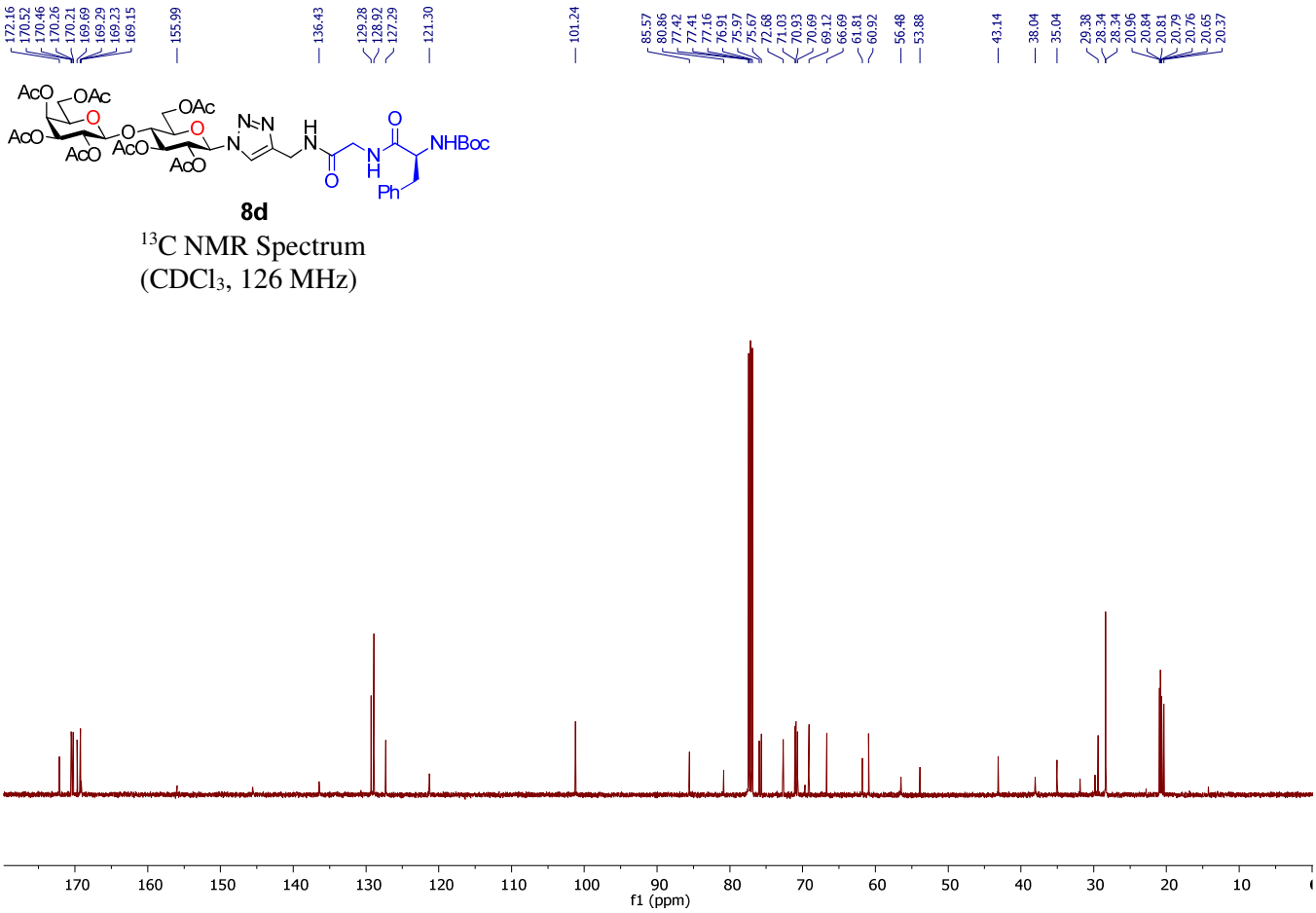

8c
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


8c
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



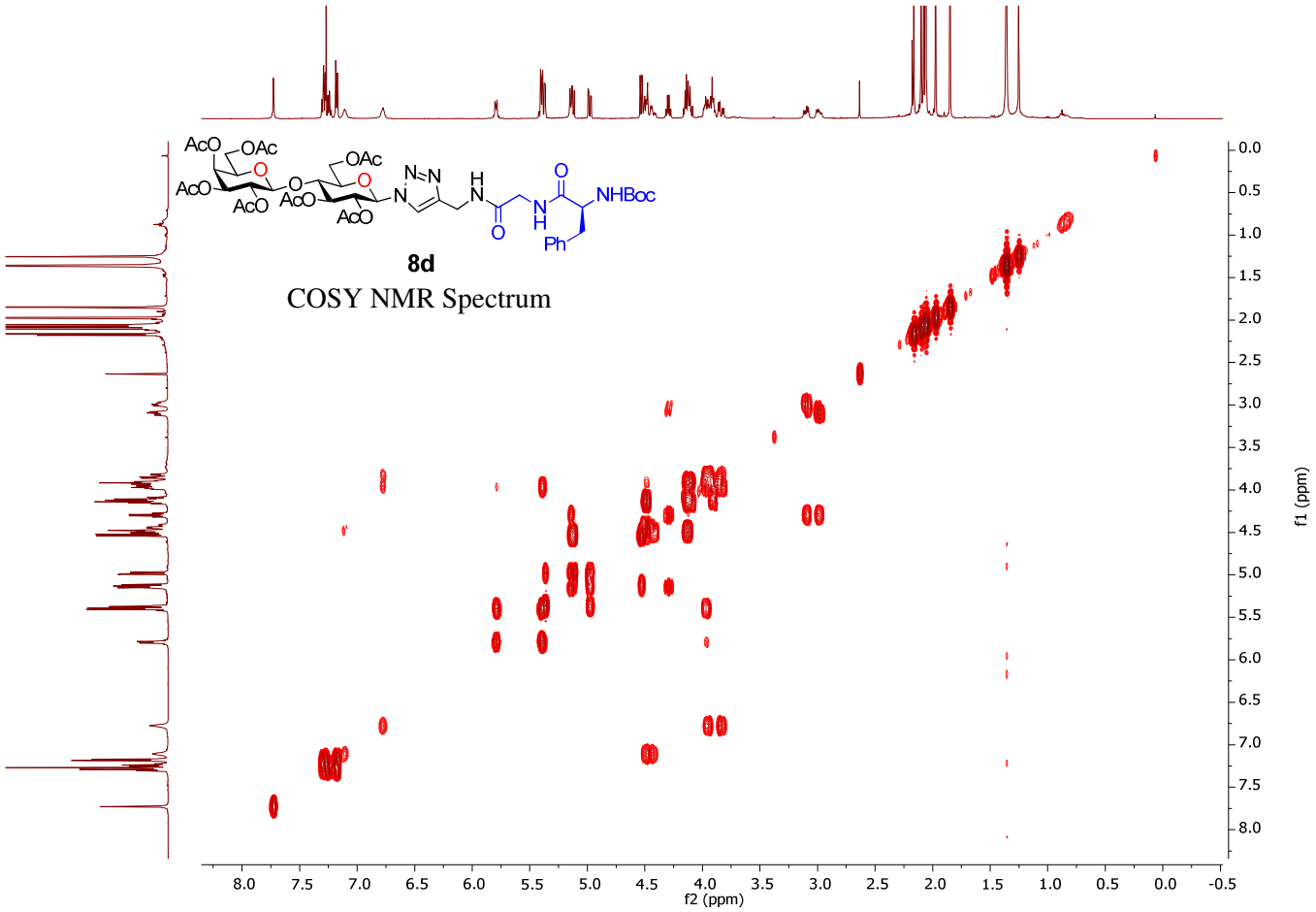
8d

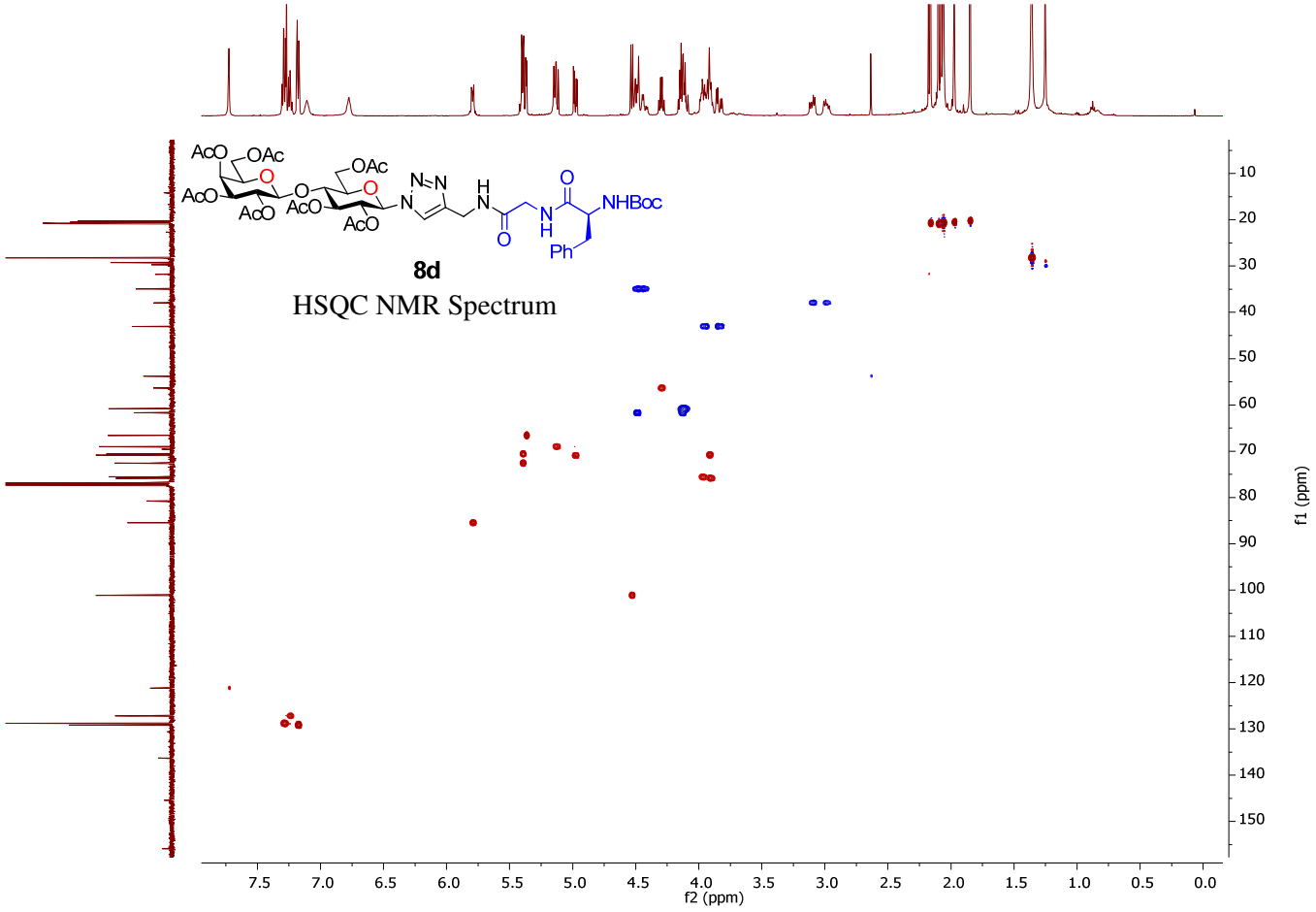
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

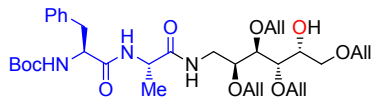


8d

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)

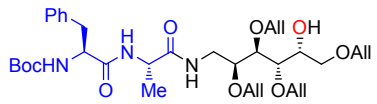

8d
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


8d
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



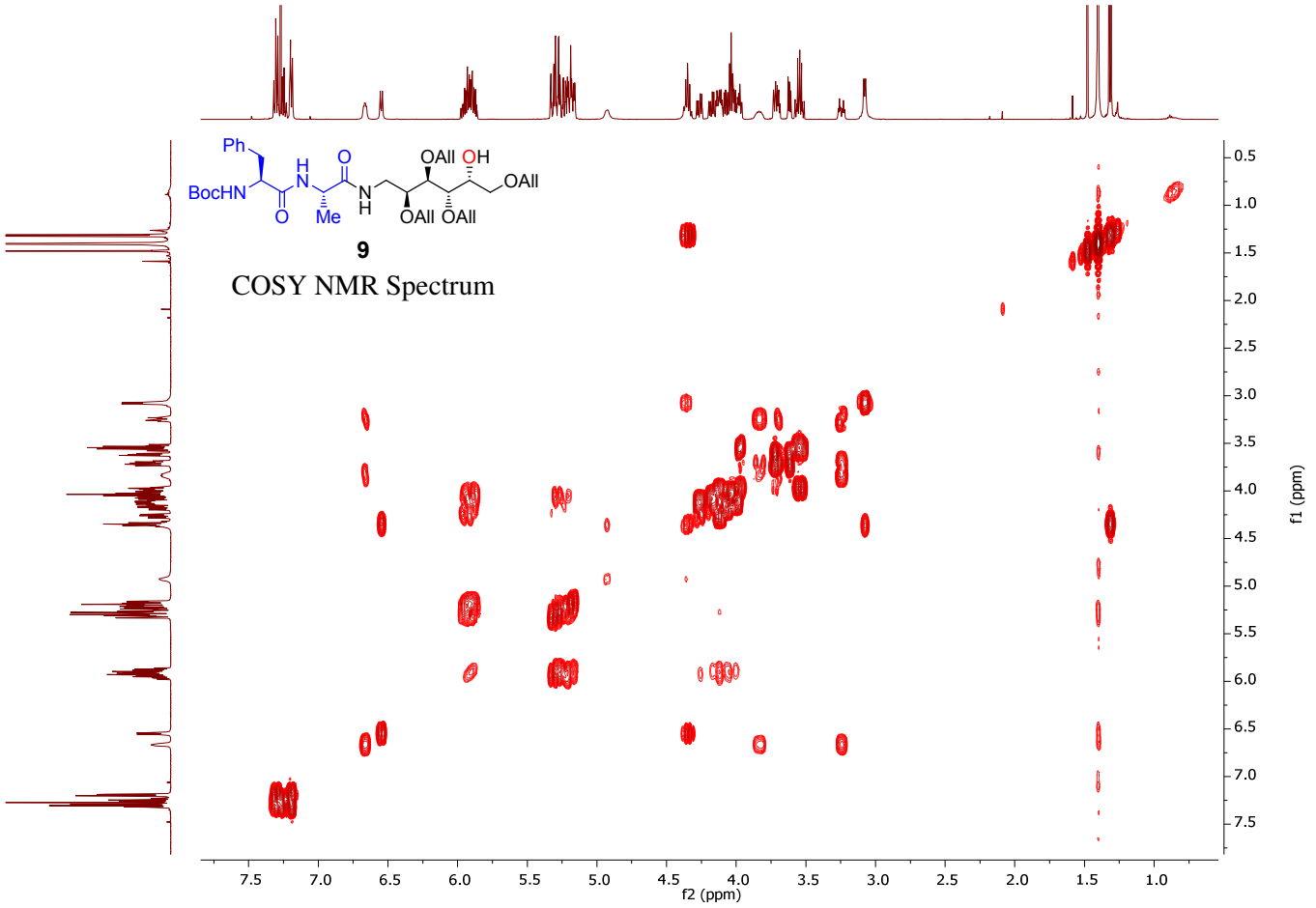
9

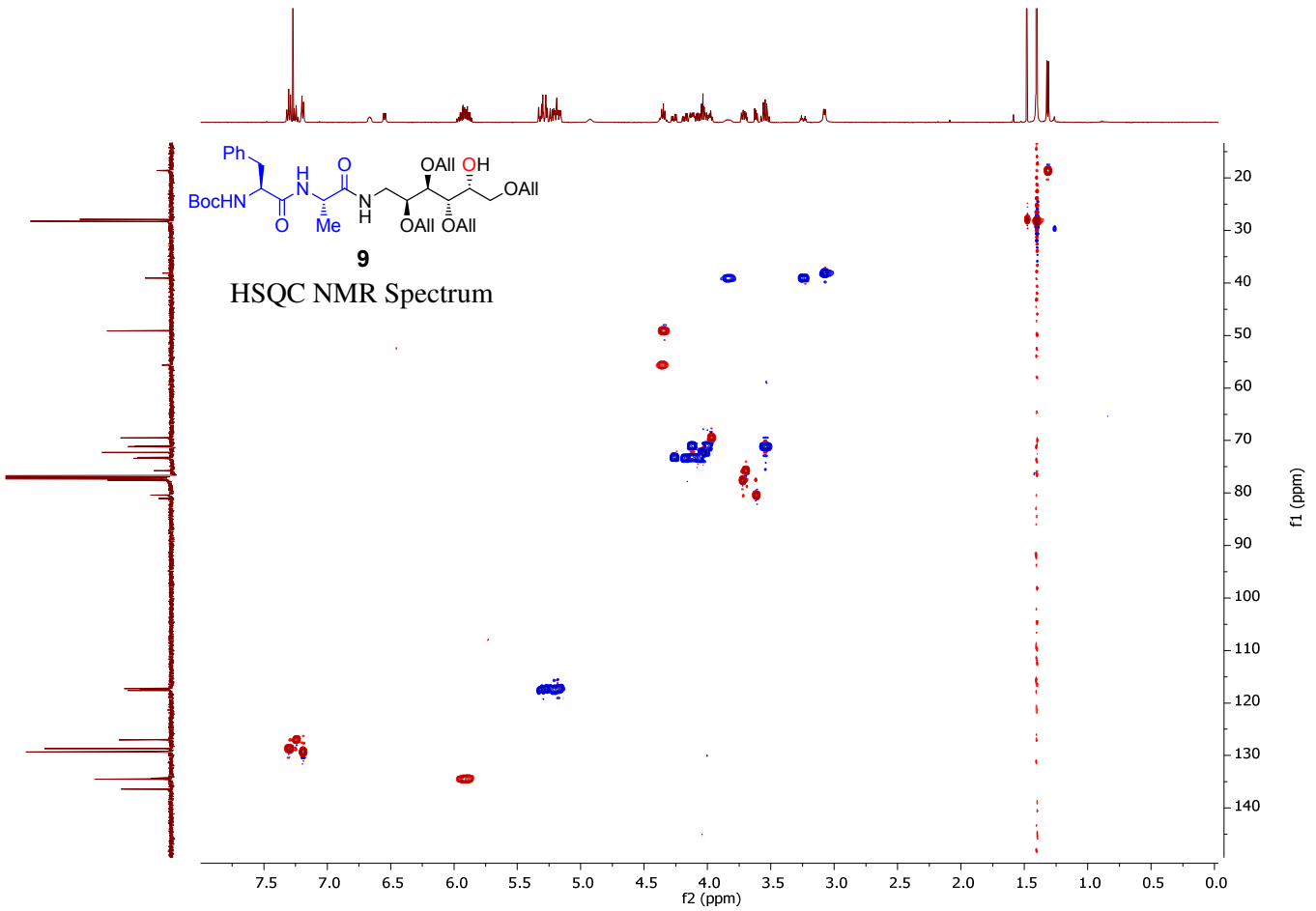
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

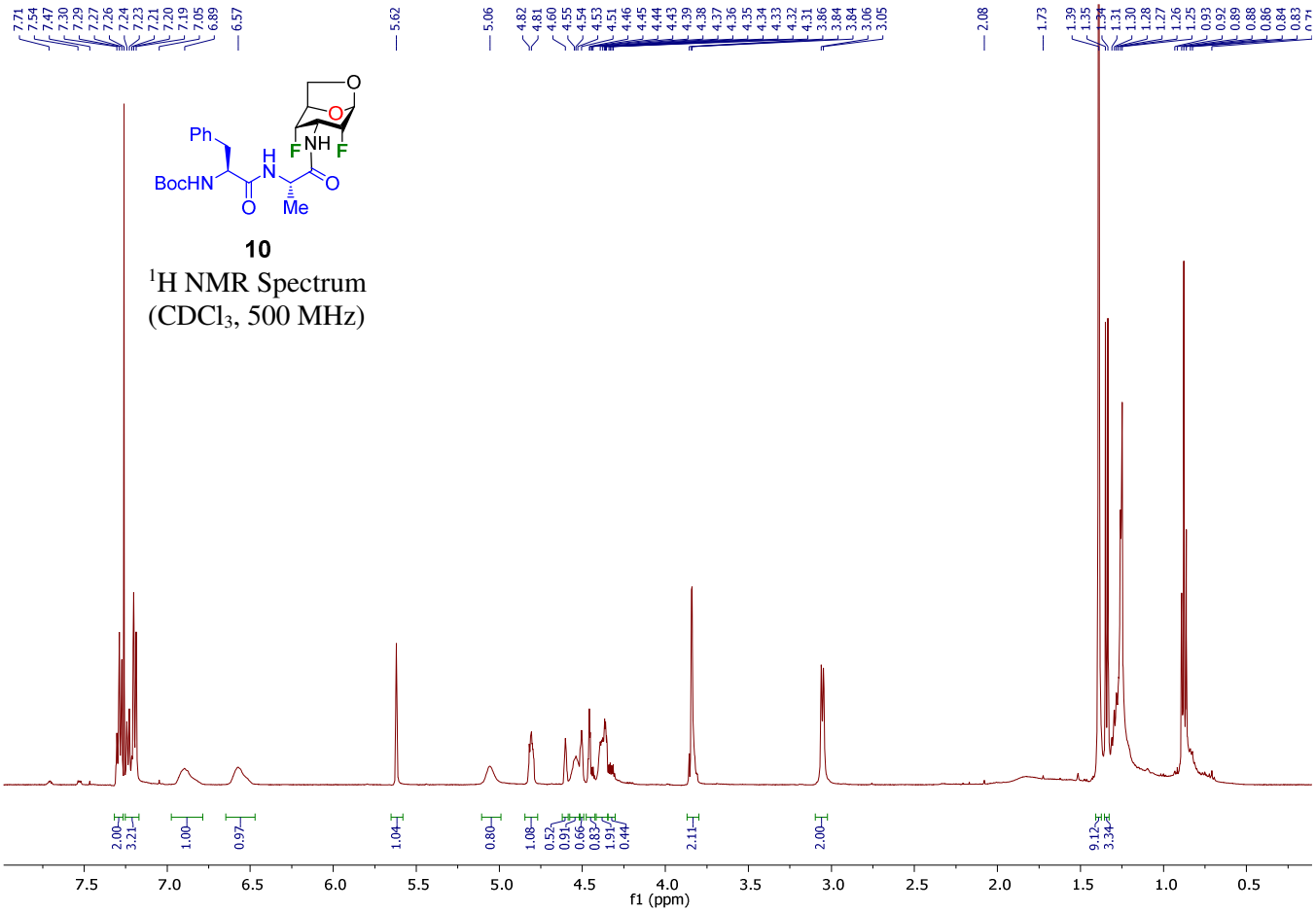


9

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)

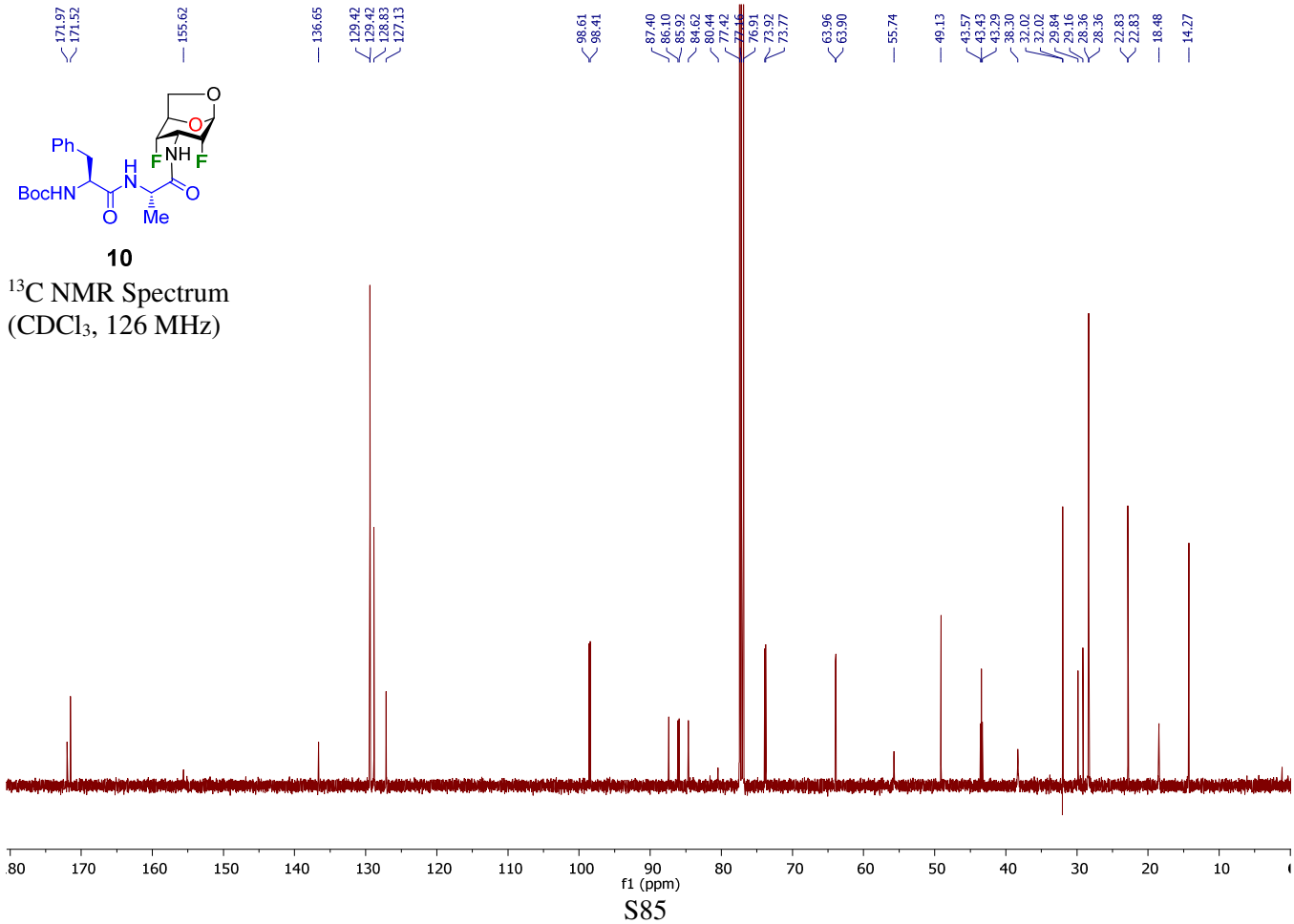

Ph
BocHN
H
N
O
Me
O
N
H
OAll OH
OAll
OAll OAll
9
COSY NMR Spectrum
f1 (ppm)
f2 (ppm)


Ph
BocHN
H
N
O
Me
O
N
H
OAll OH
OAll
OAll OAll
9
HSQC NMR Spectrum
f1 (ppm)
f2 (ppm)



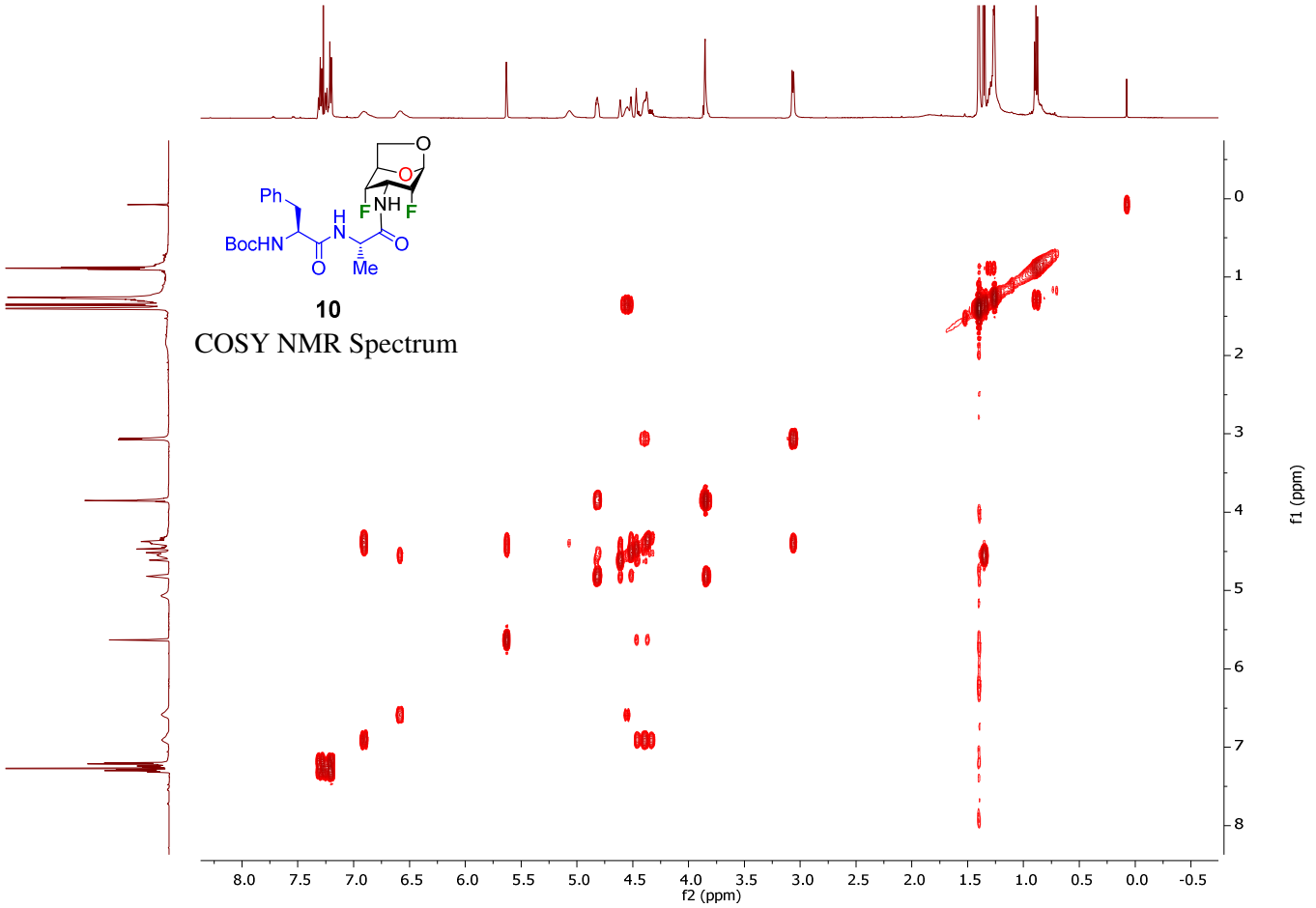
10

^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



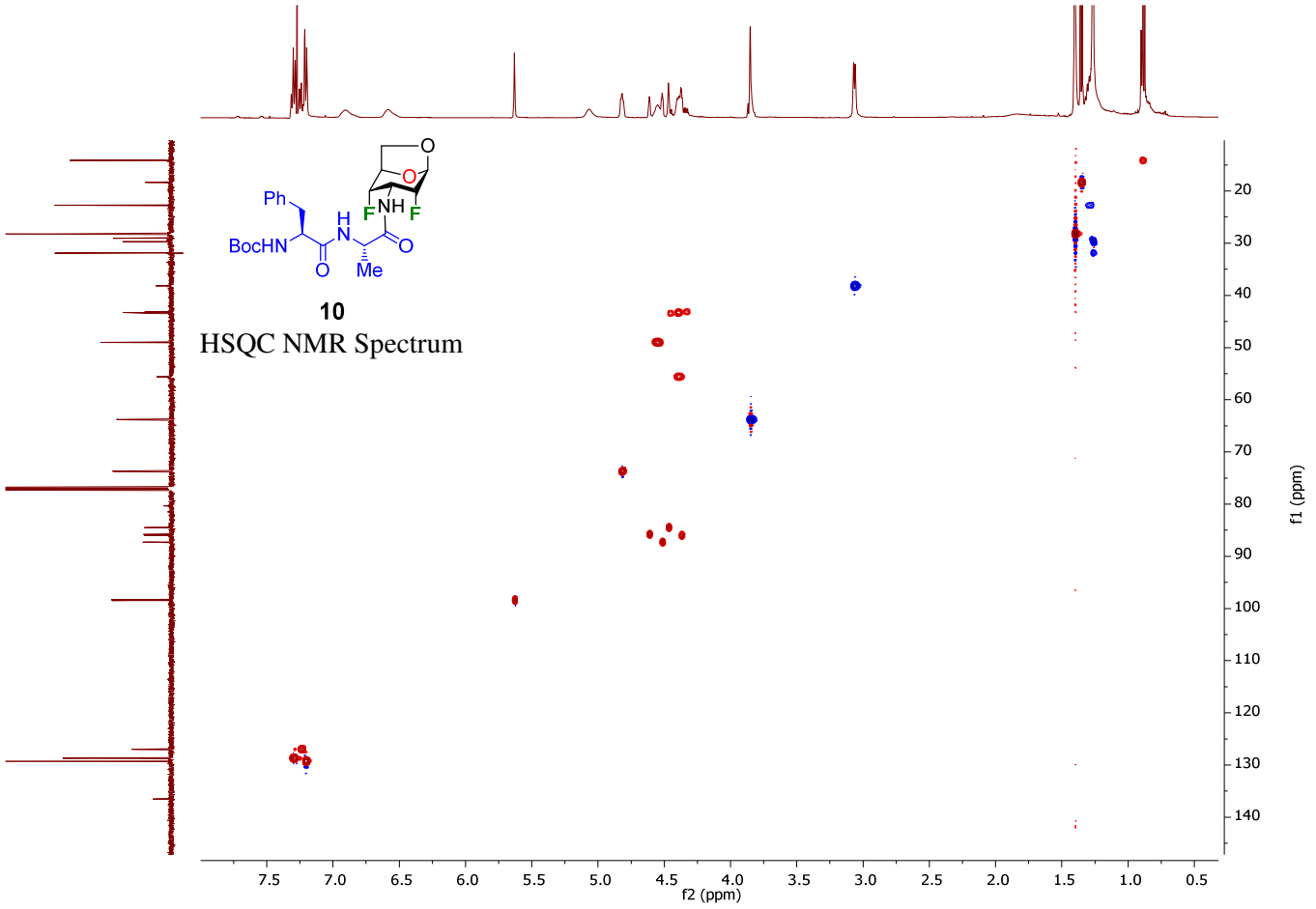
10

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



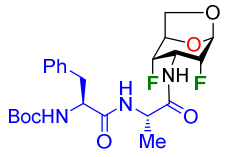
10

COSY NMR Spectrum



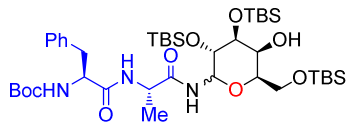
10

HSQC NMR Spectrum



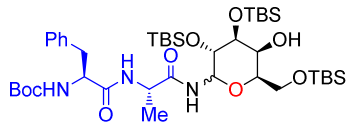
10

^{19}F NMR Spectrum
($CDCl_3$, 470 MHz)



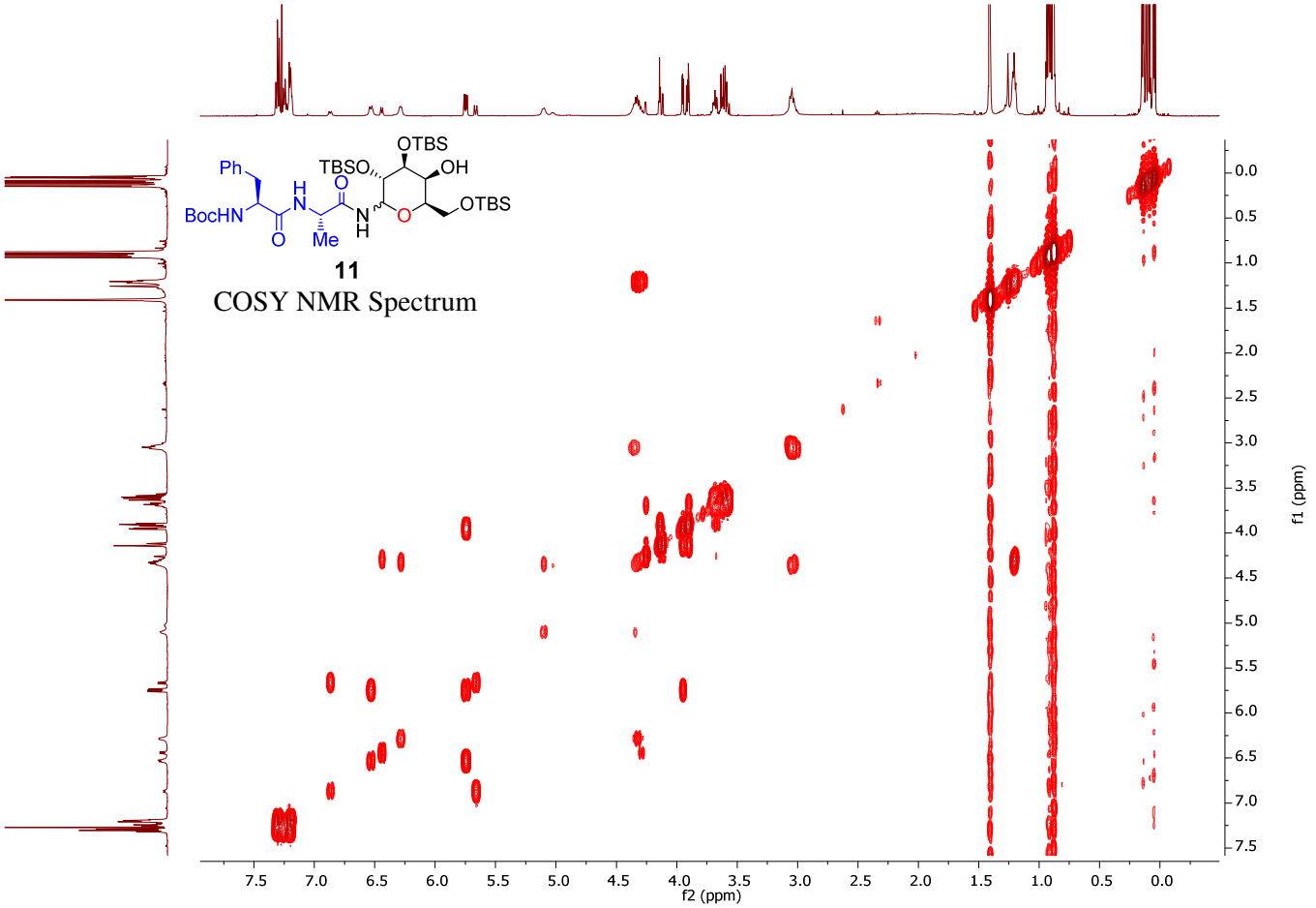
11

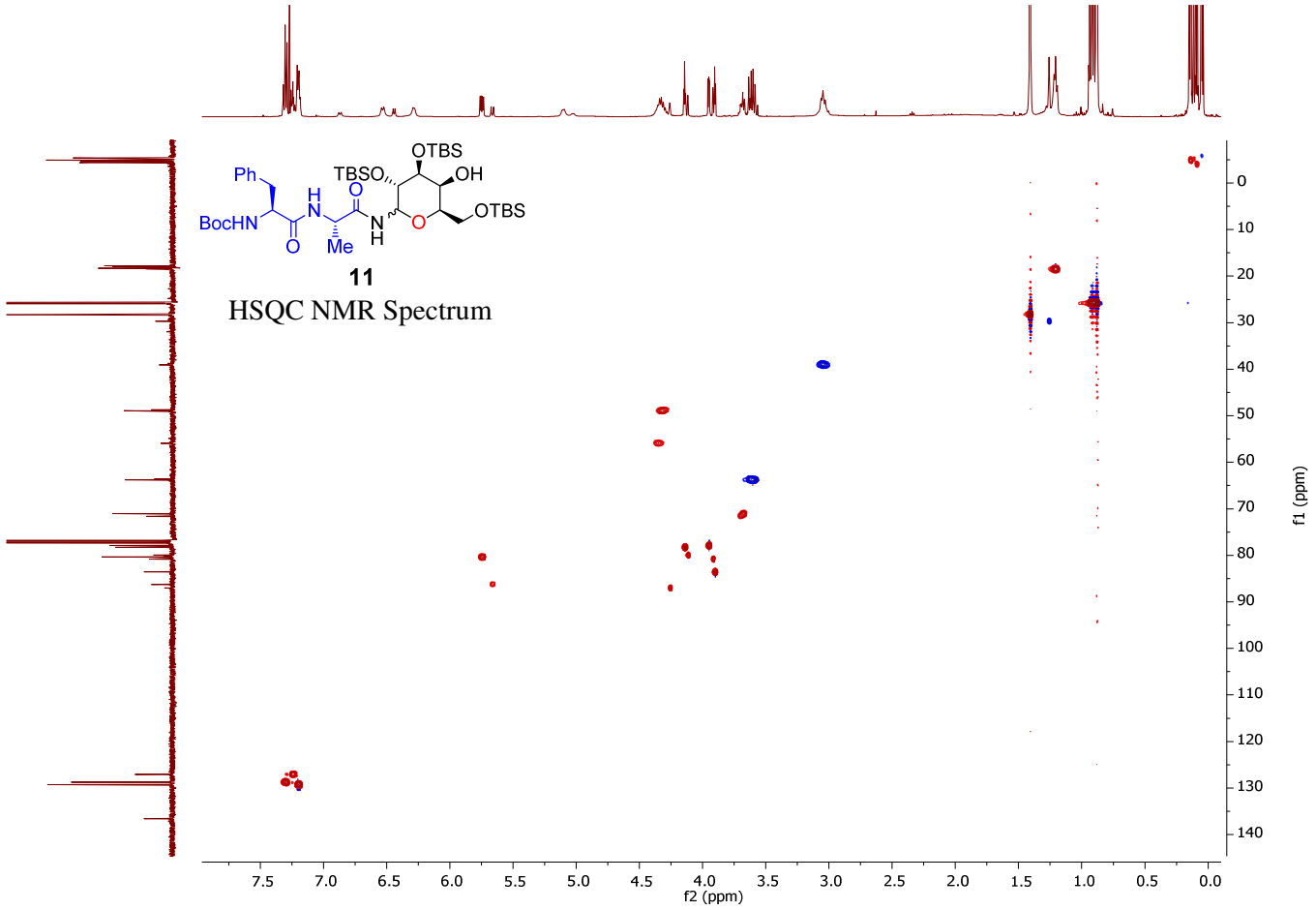
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

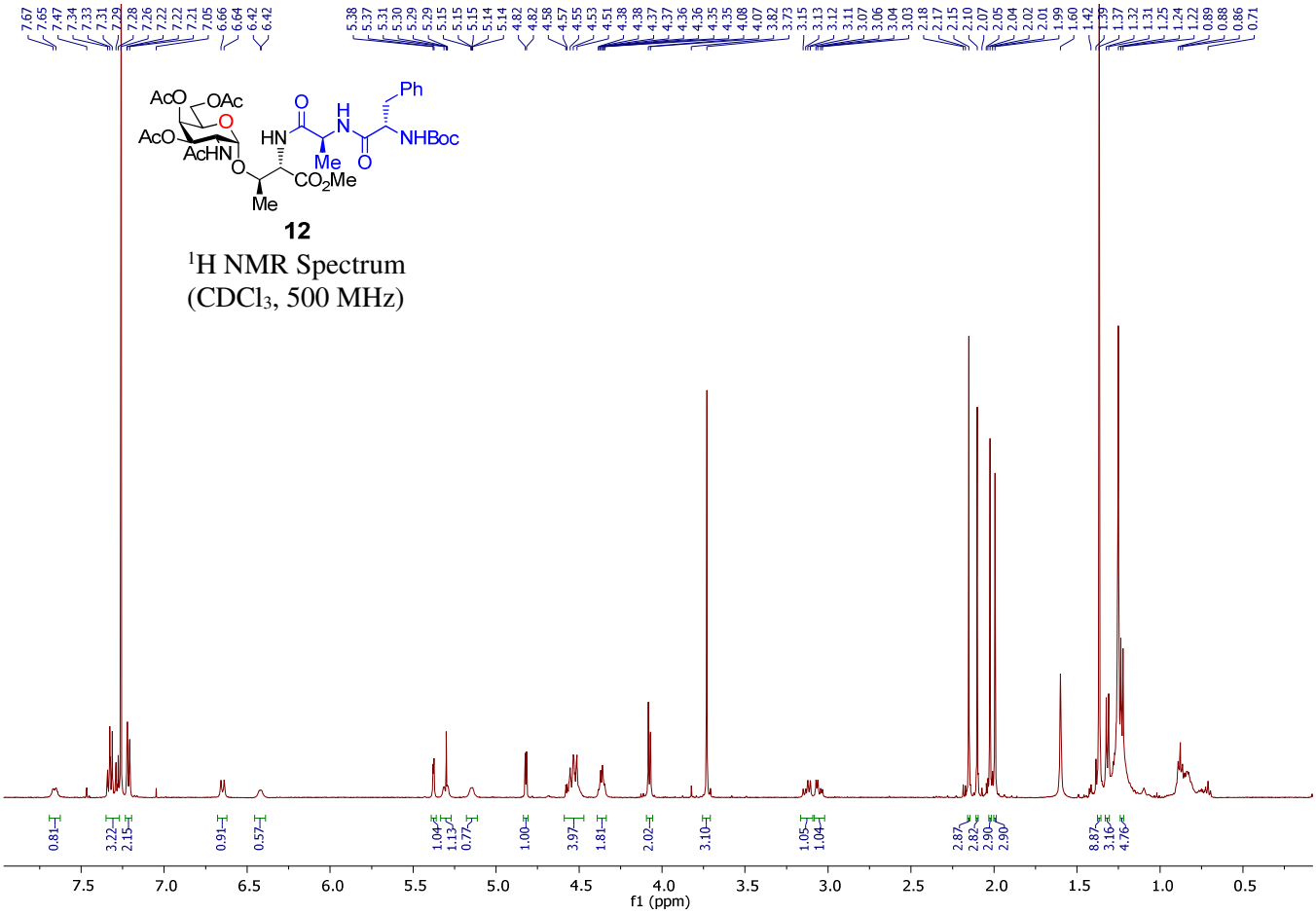


11

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)

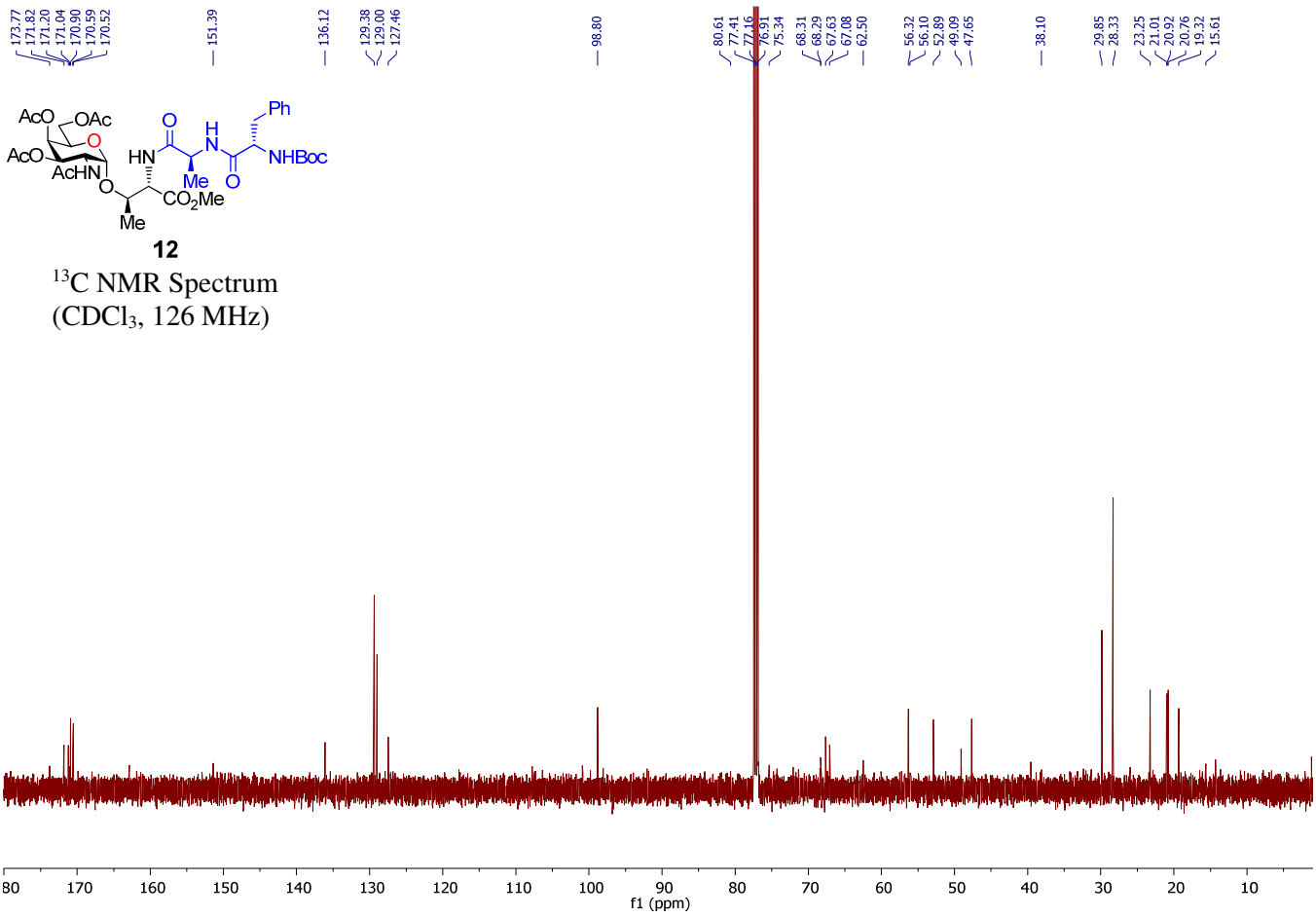

OTBS
TBSO
OH
OTBS
Ph
BocHN
H
N
O
N
H
O
Me
O
11
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


OTBS
TBSO
OH
OTBS
Ph
BocHN
H
N
O
N
H
O
Me
O
11
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



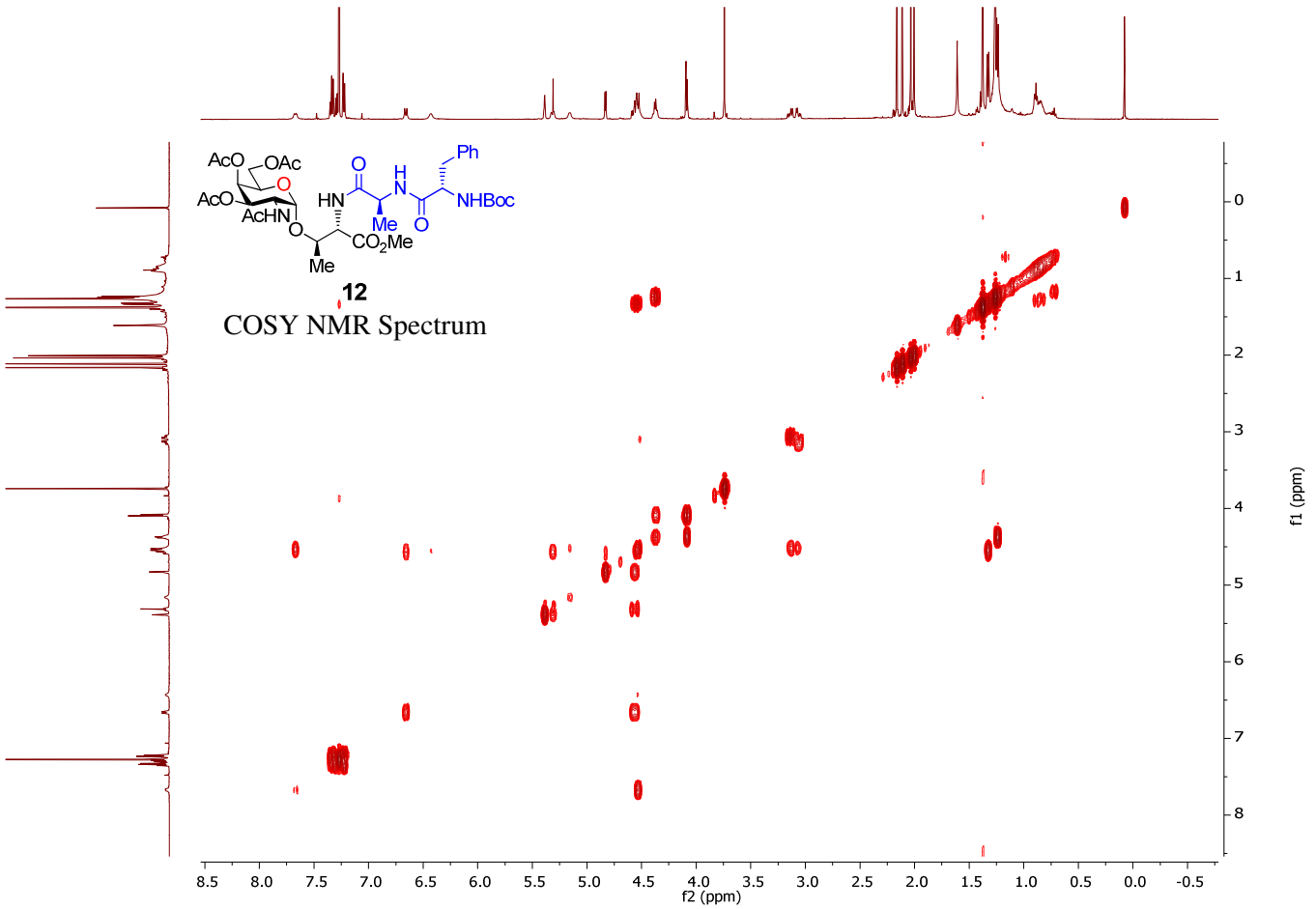
12

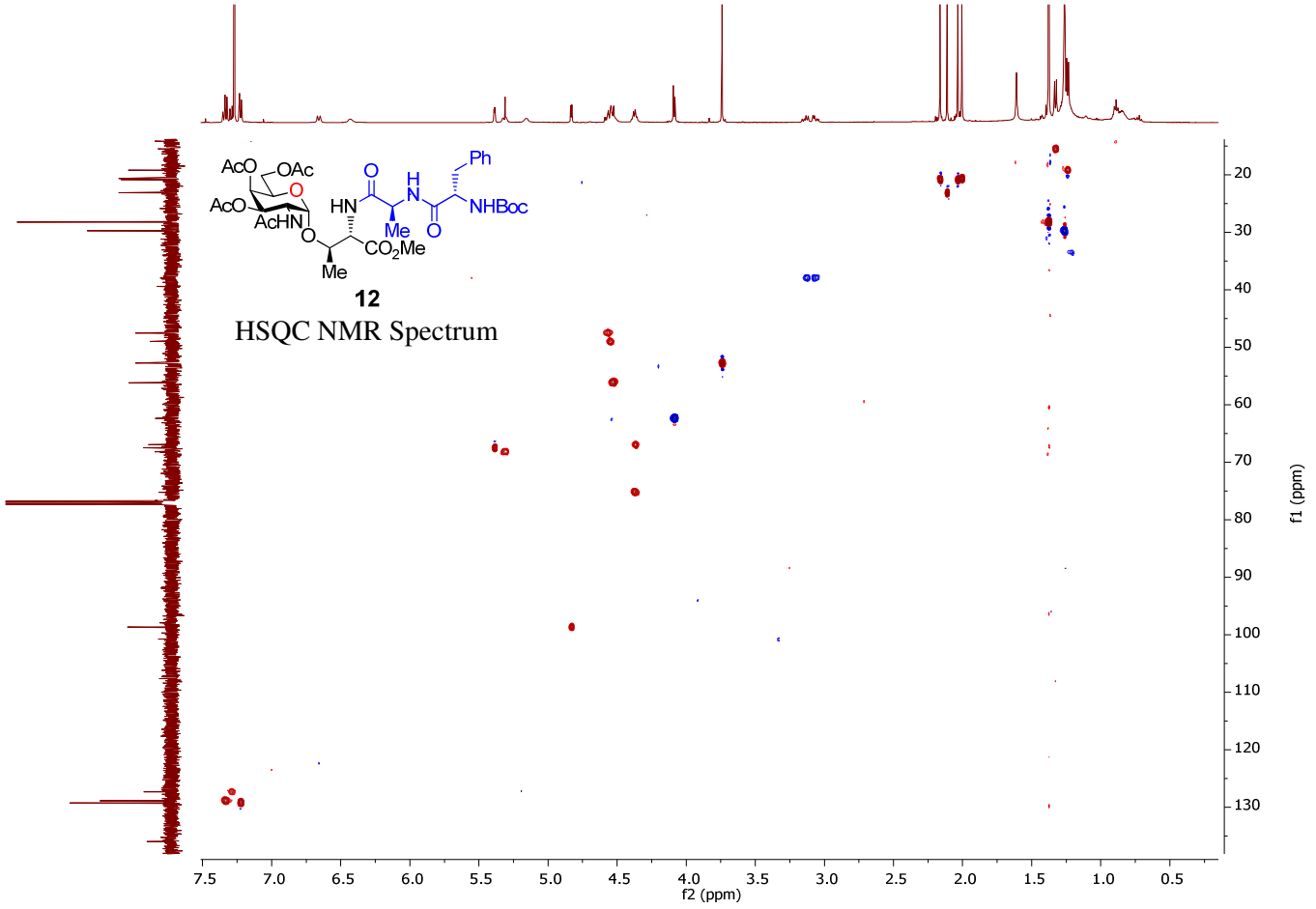
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

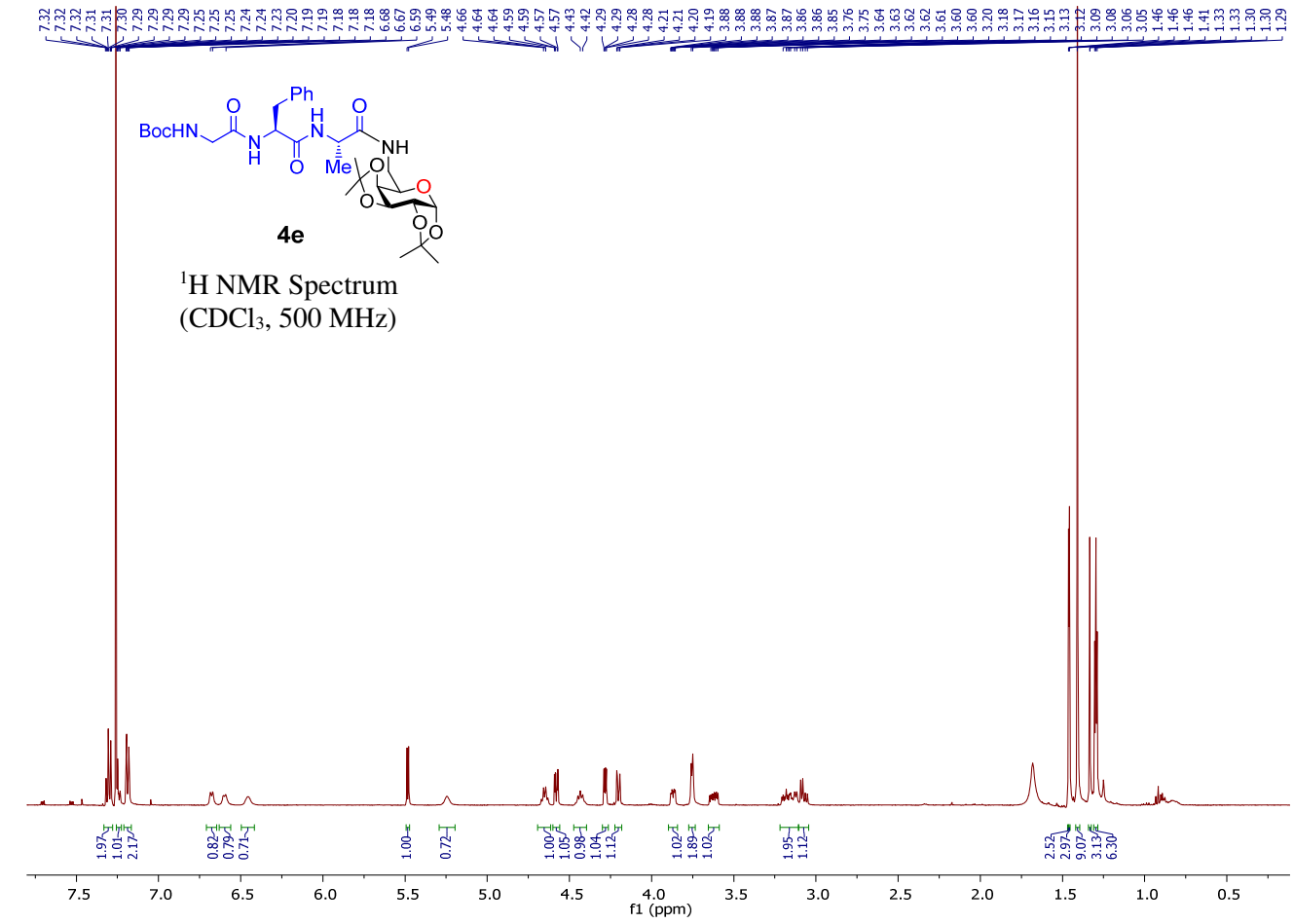


12

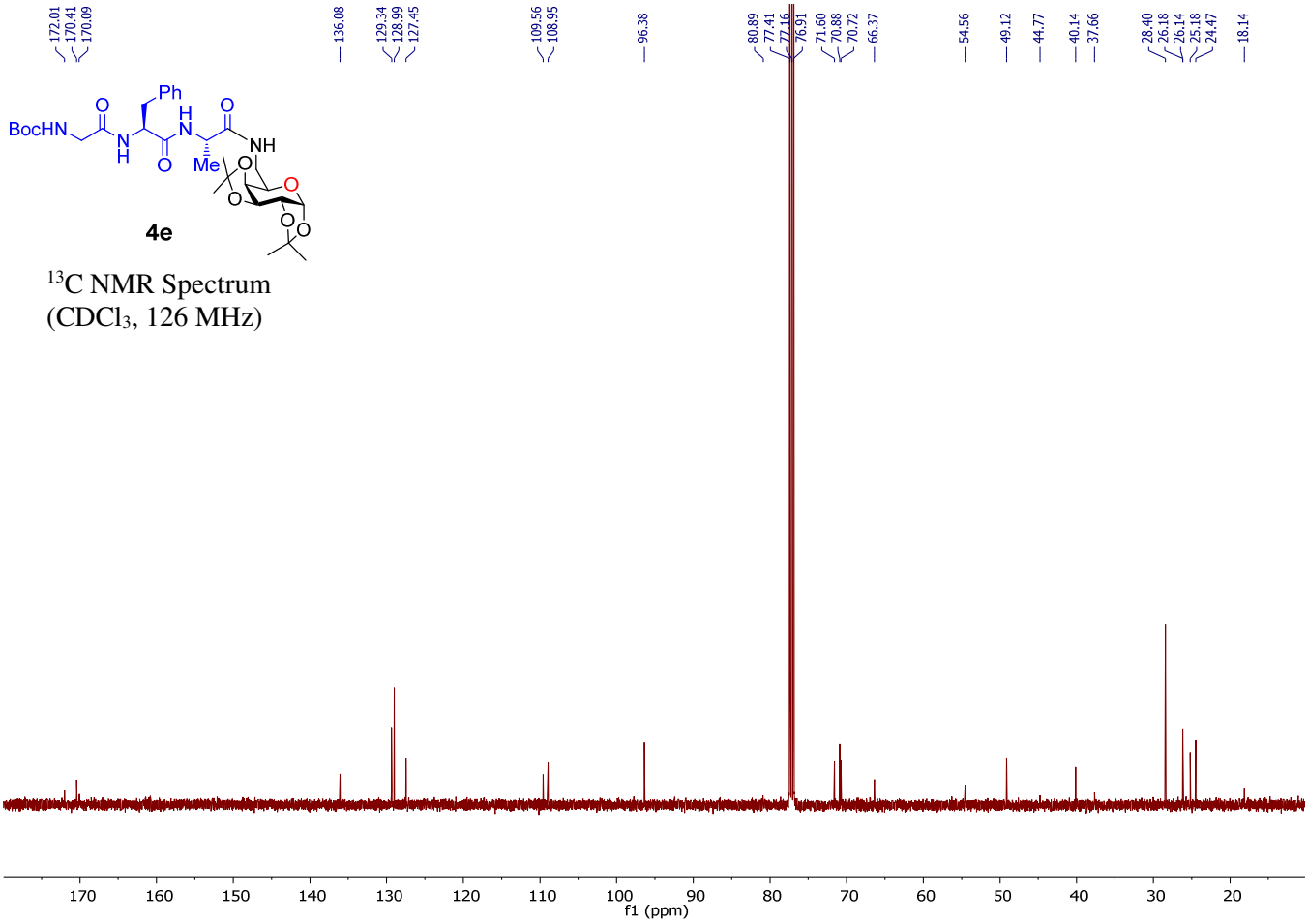
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)


AcO
OAc
AcO
AcHN
O
HN
O
H
N
Ph
NHBoc
Me
O
CO2Me
Me
12
COSY NMR Spectrum
f1 (ppm)
f2 (ppm)

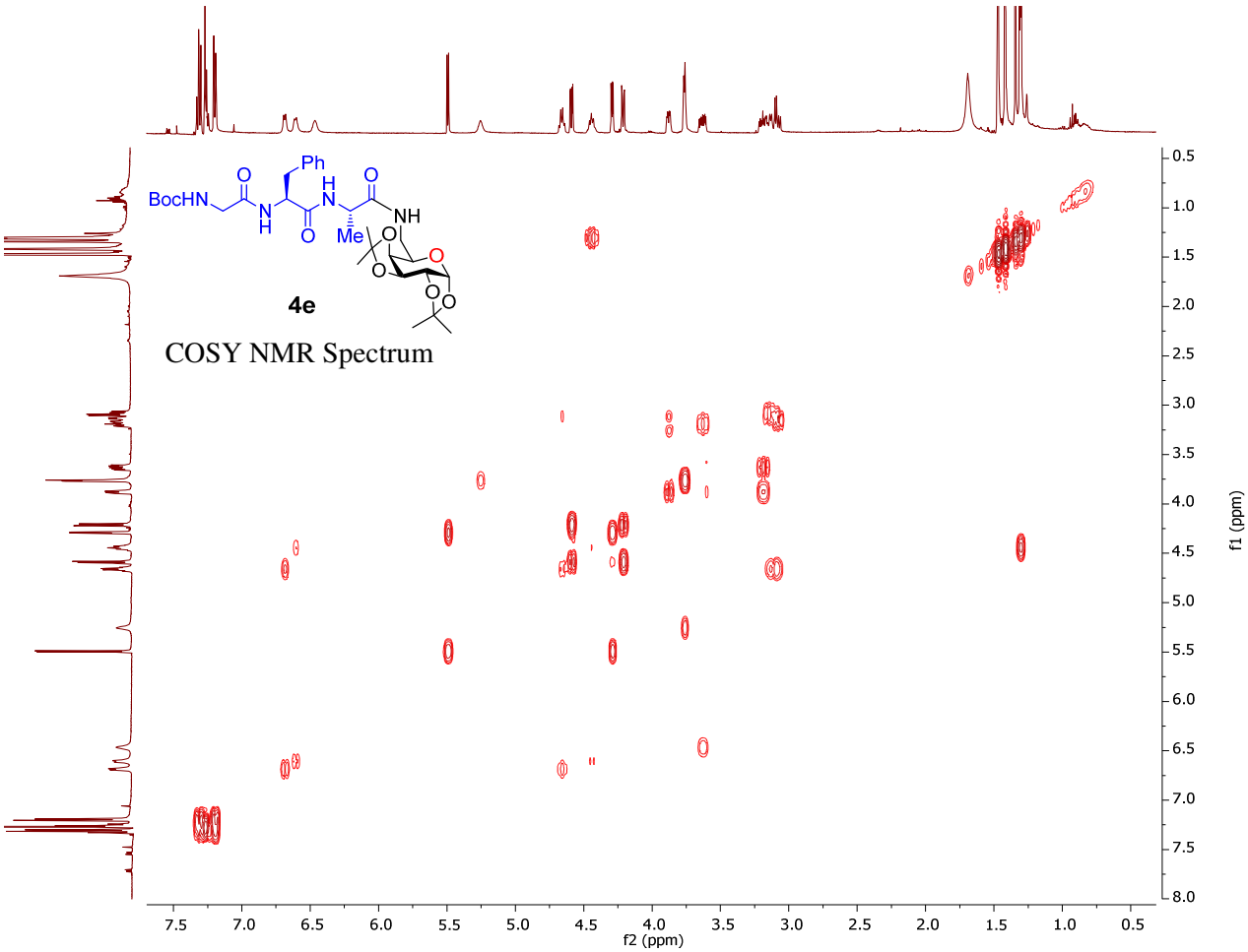

AcO
OAc
AcO
AcHN
O
HN
O
H
N
Ph
NHBoc
Me
O
CO2Me
Me
12
HSQC NMR Spectrum
f1 (ppm)
f2 (ppm)



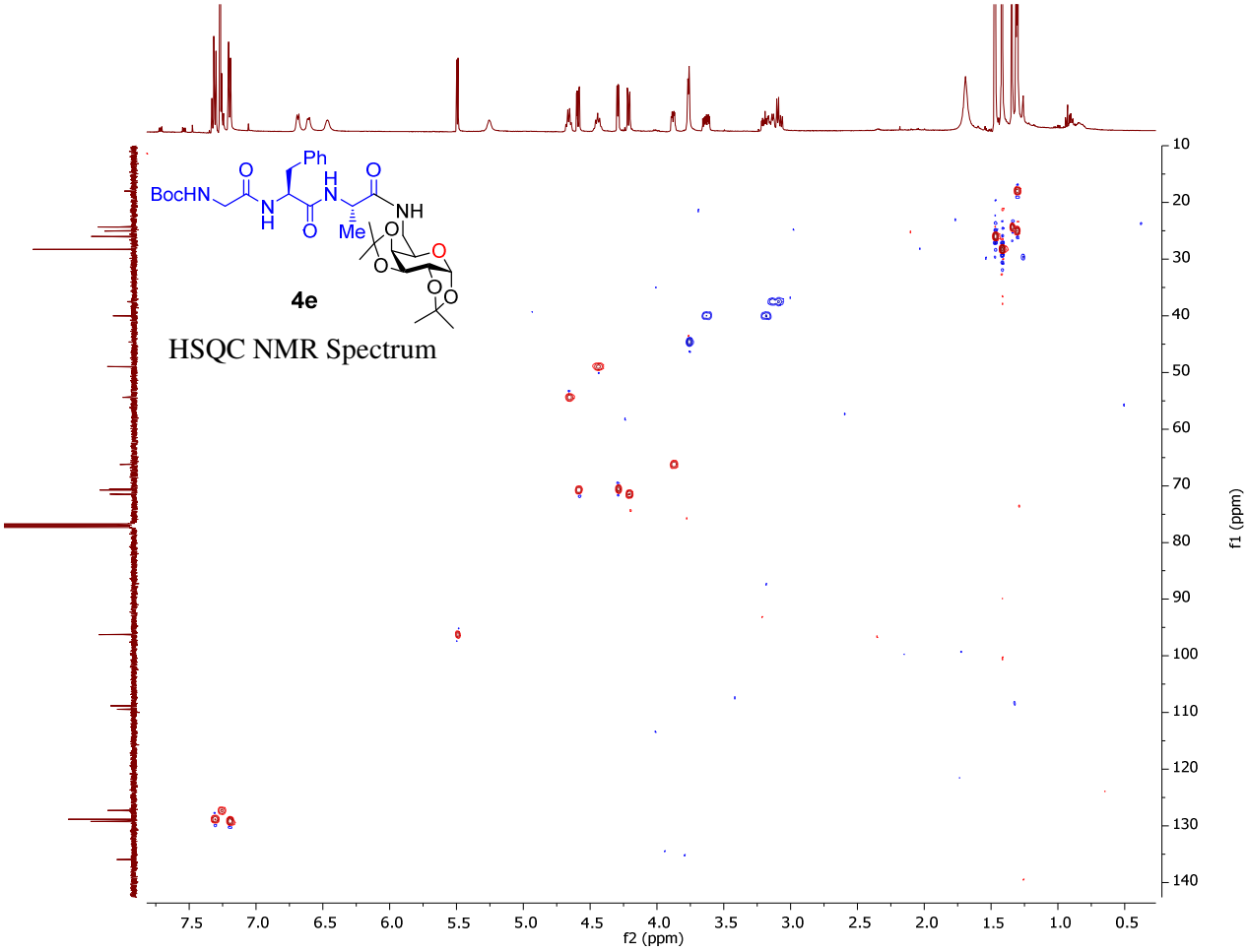
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



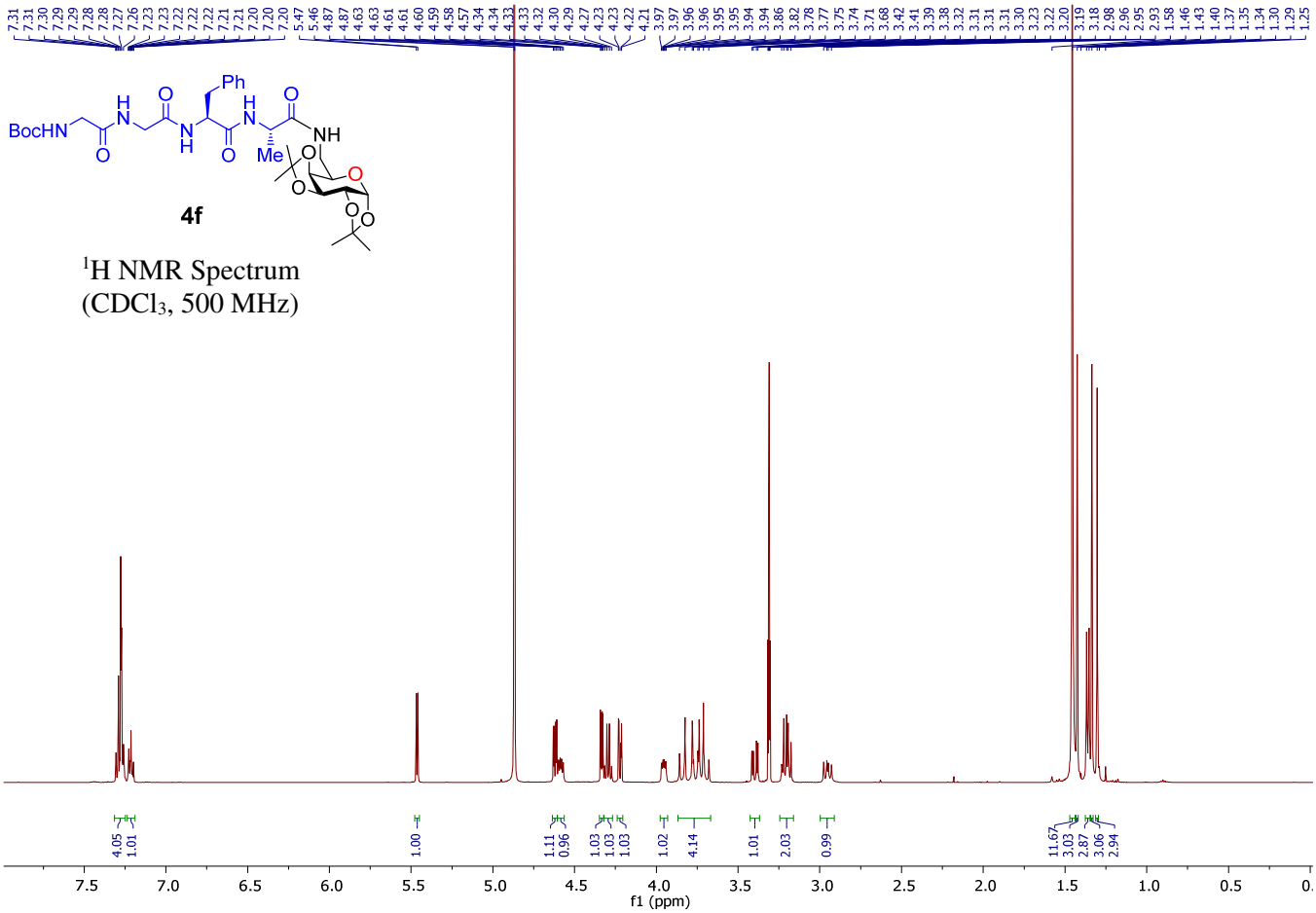
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



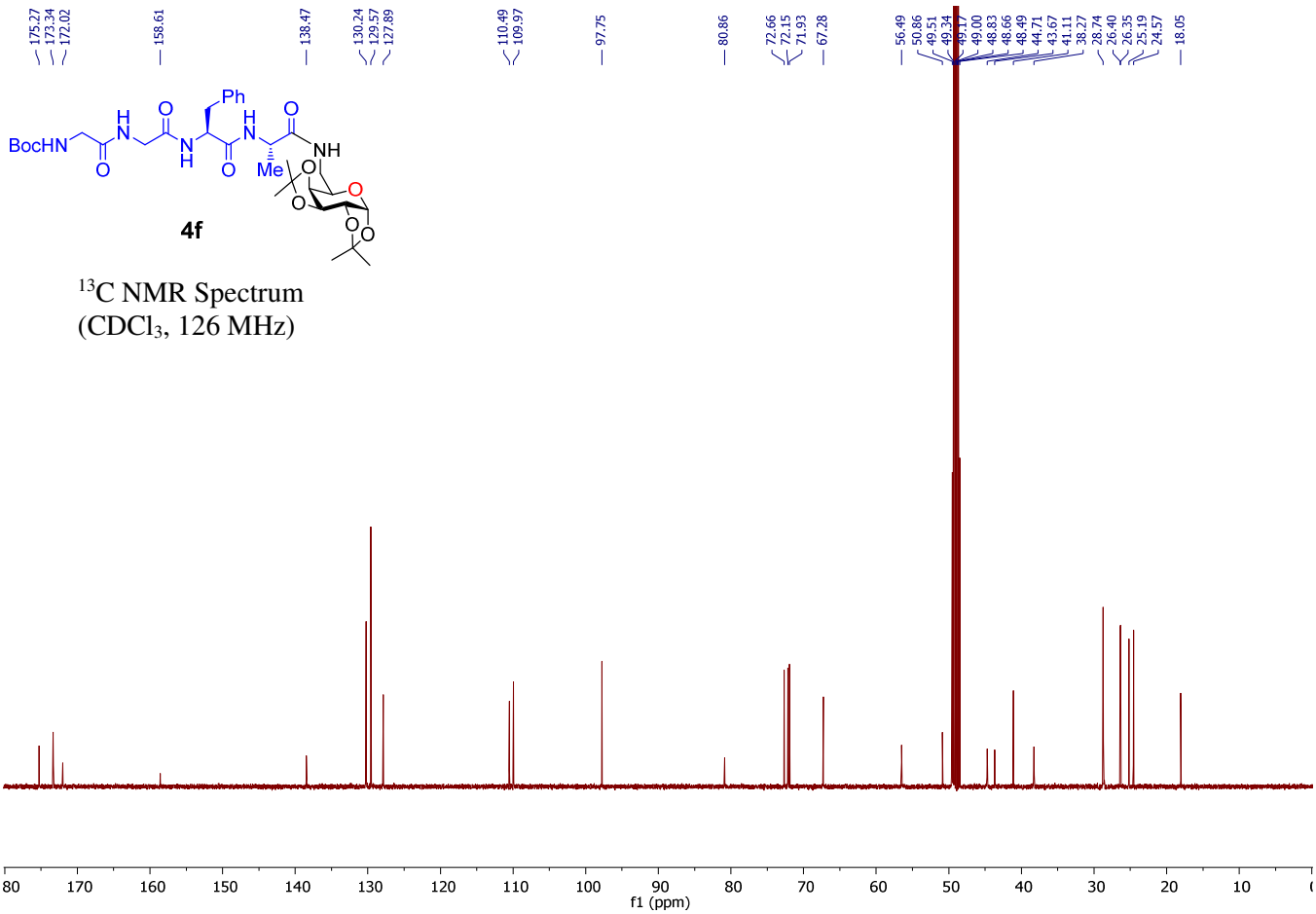
COSY NMR Spectrum



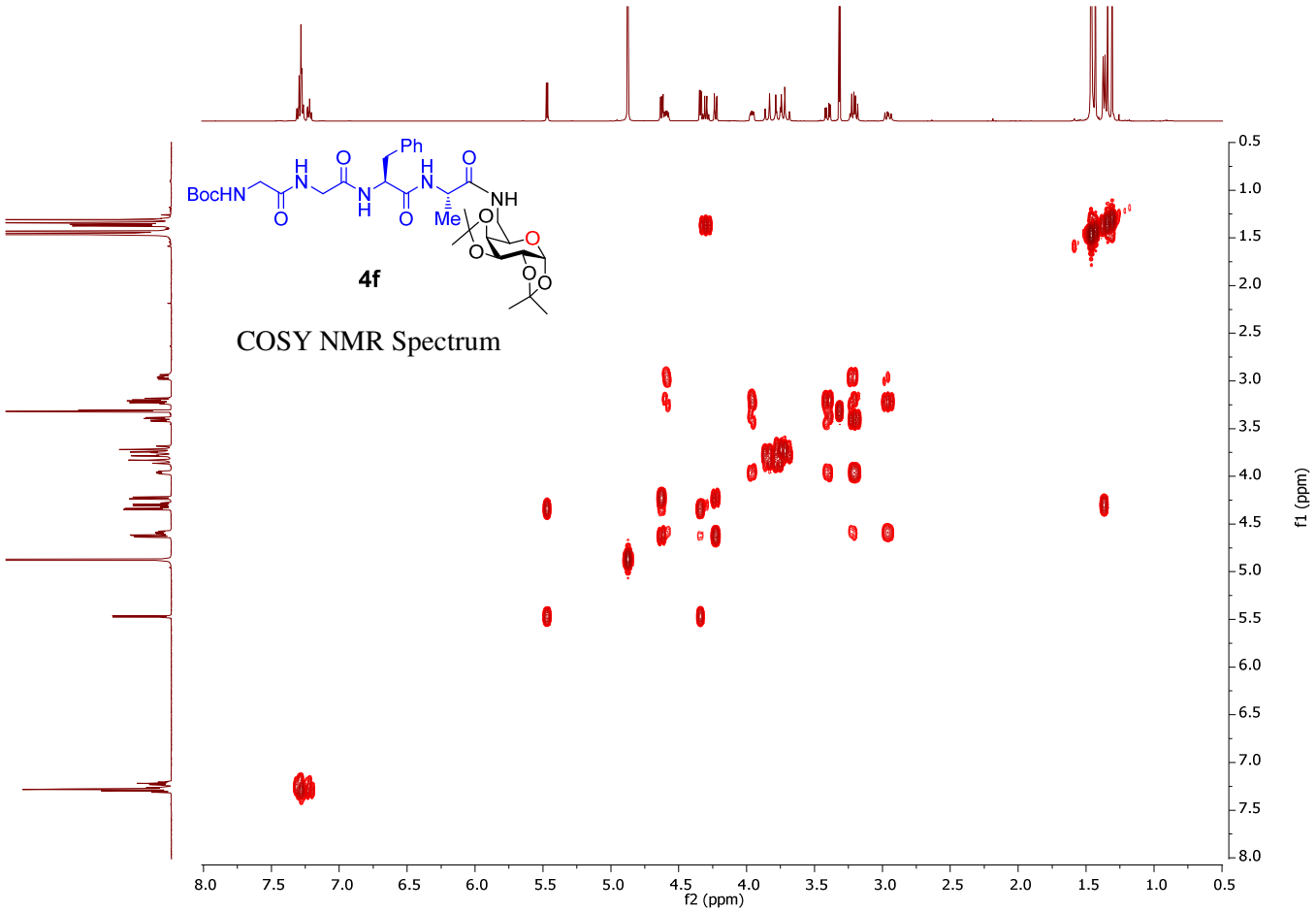
HSQC NMR Spectrum

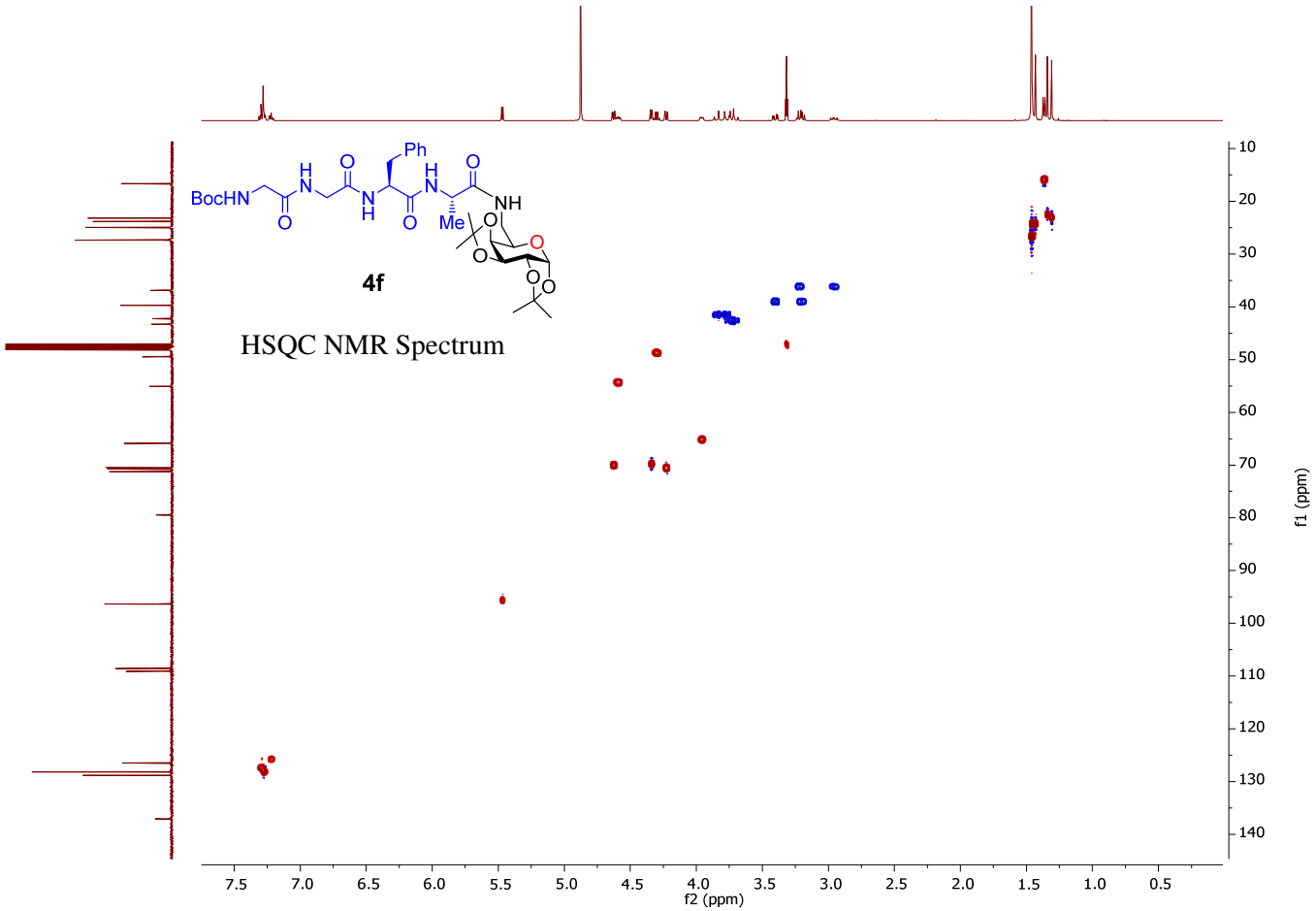


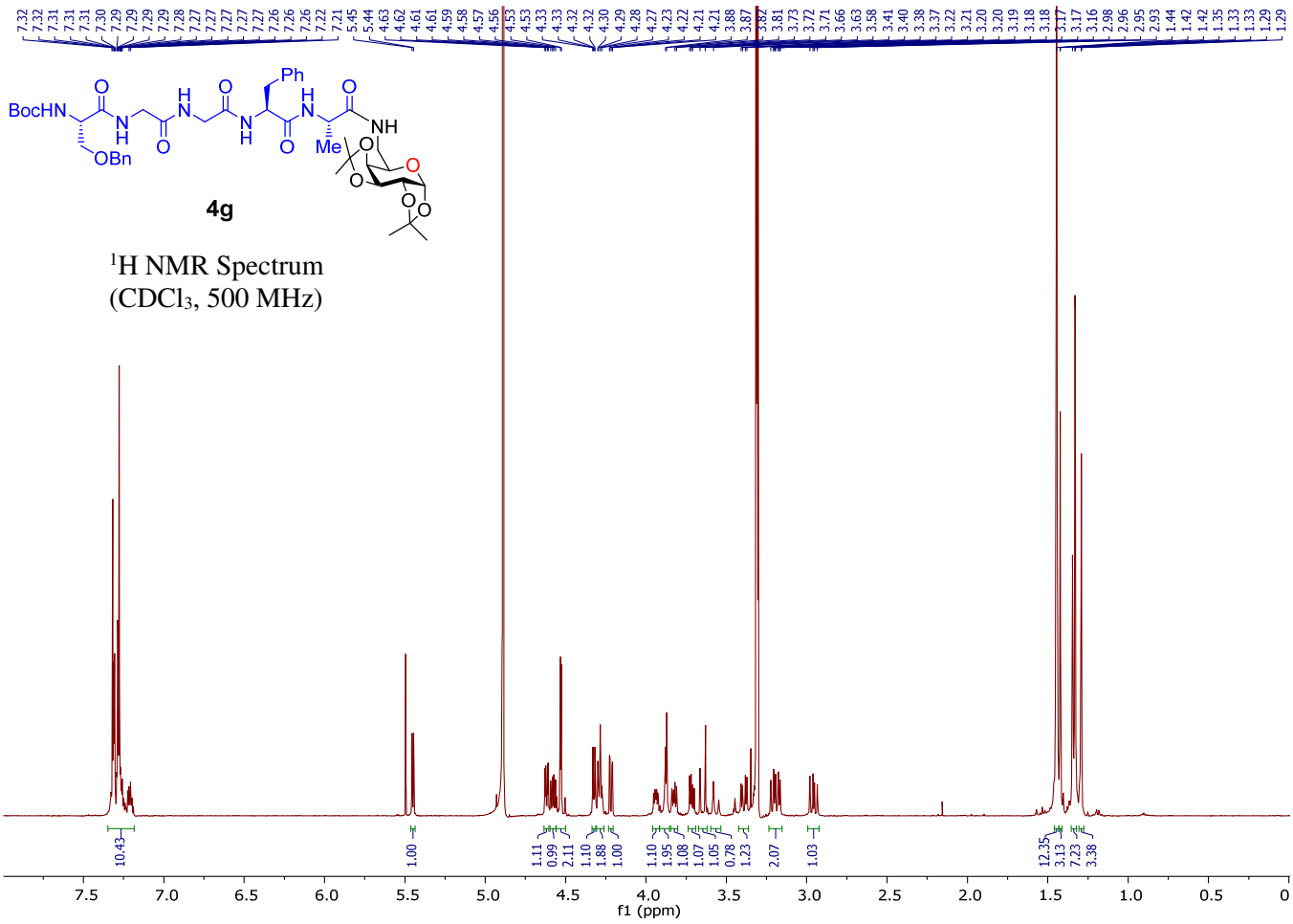
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



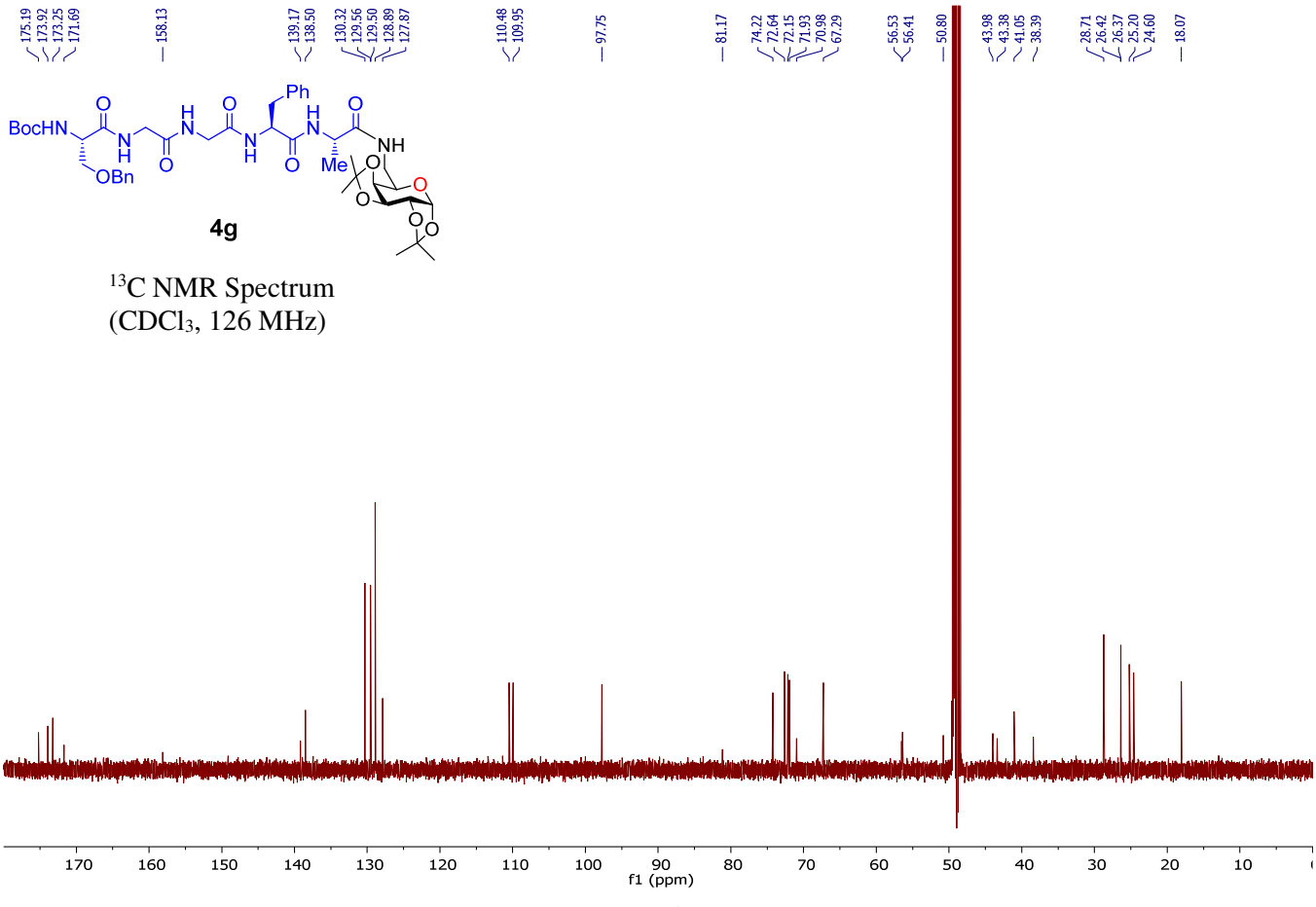
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)


BocHN
Ph
Me
NH
4f
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)

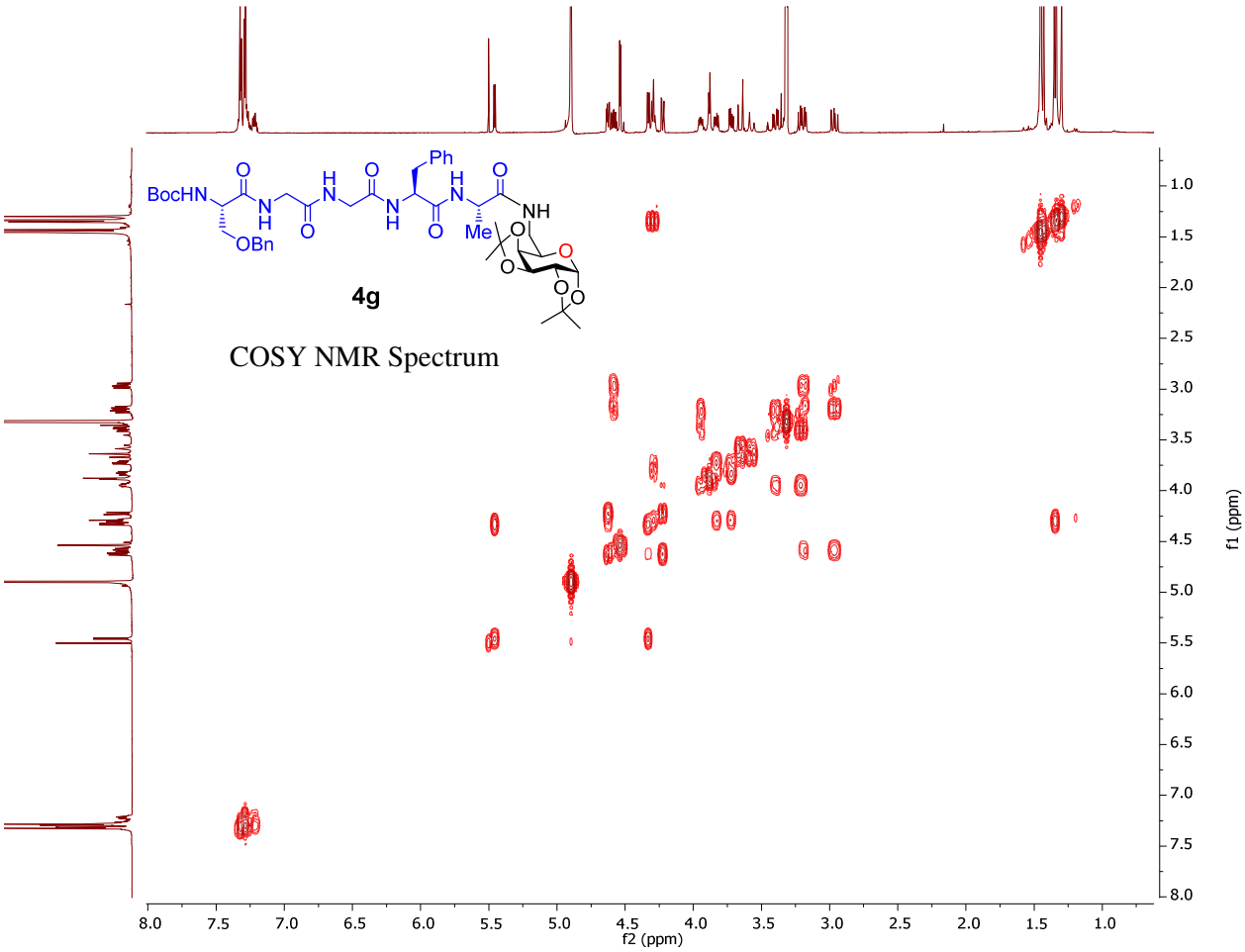

BocHN
Ph
Me
NH
4f
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



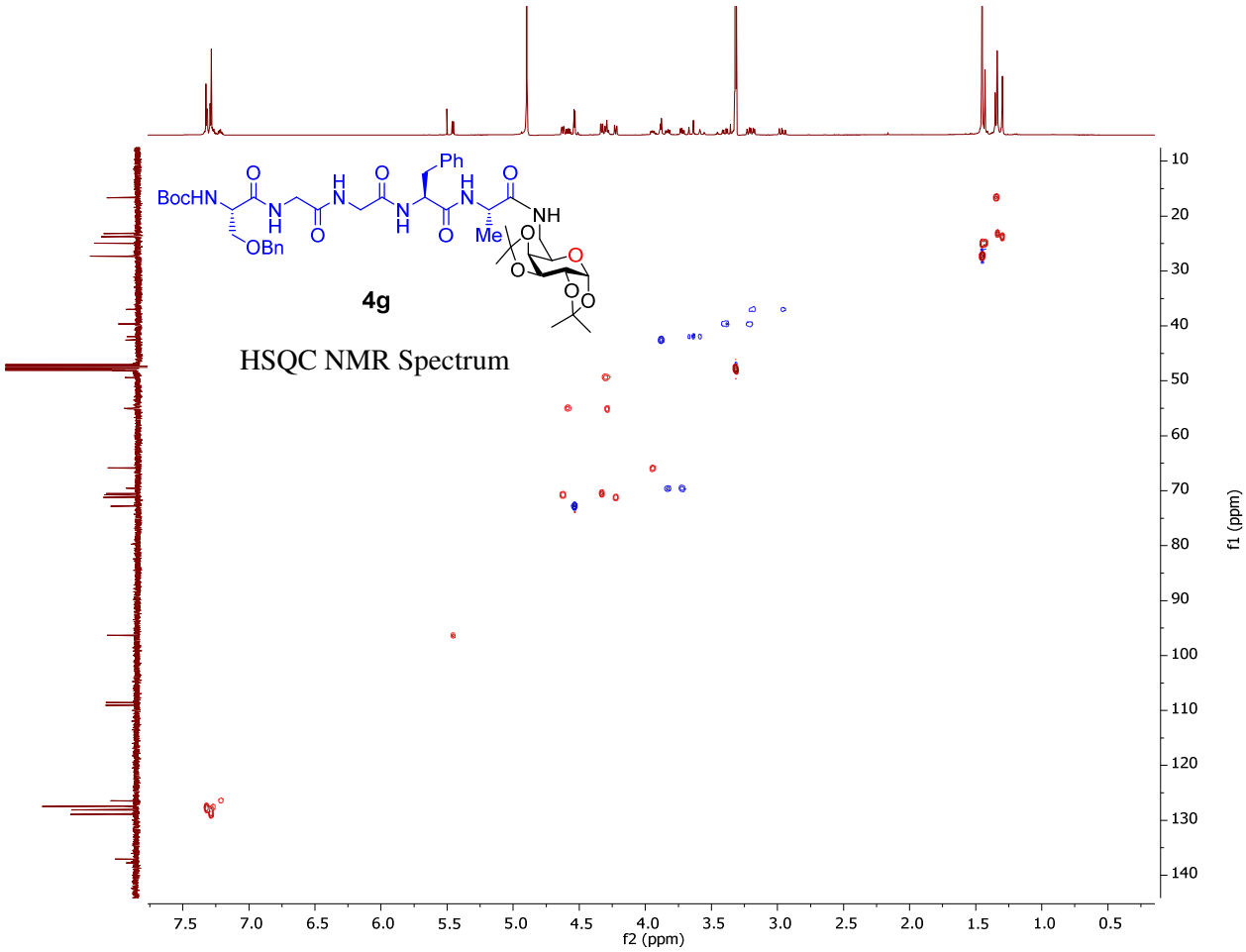
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)



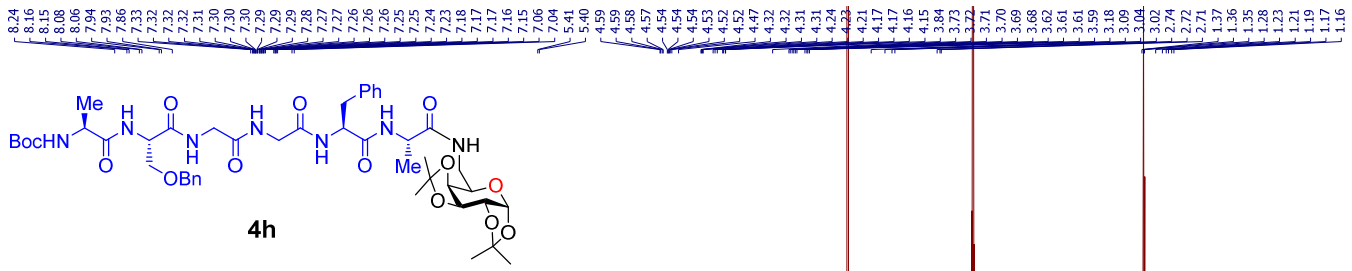
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



COSY NMR Spectrum

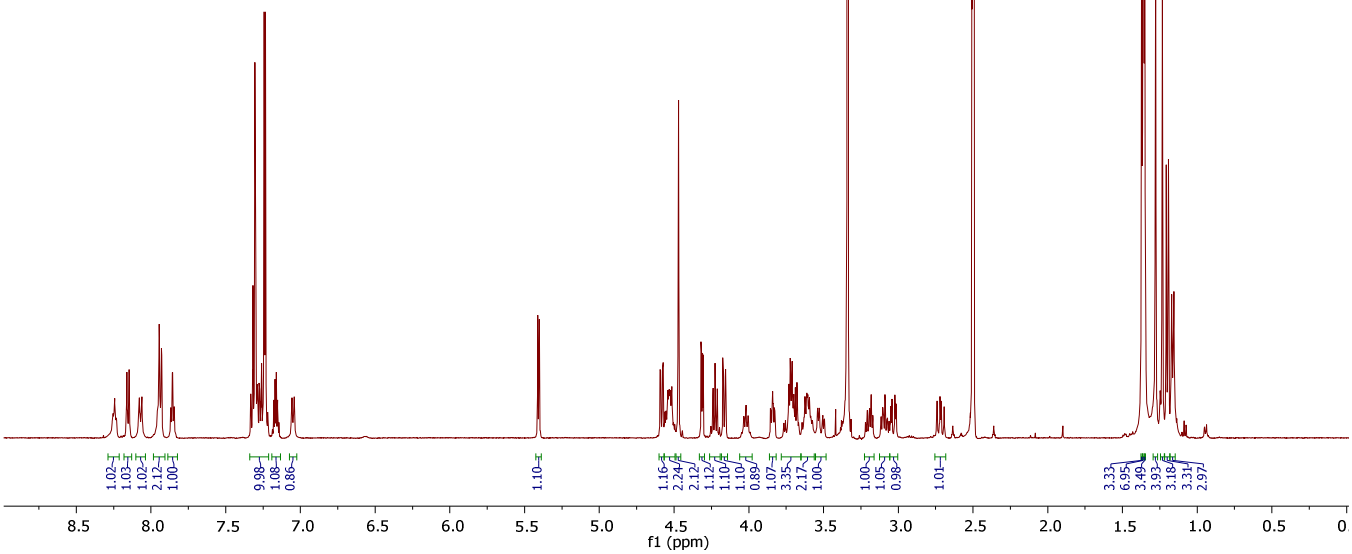


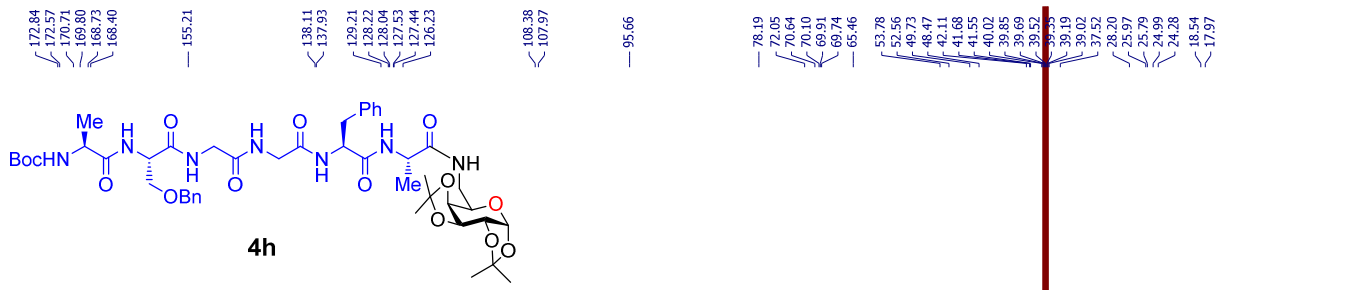
HSQC NMR Spectrum



4h

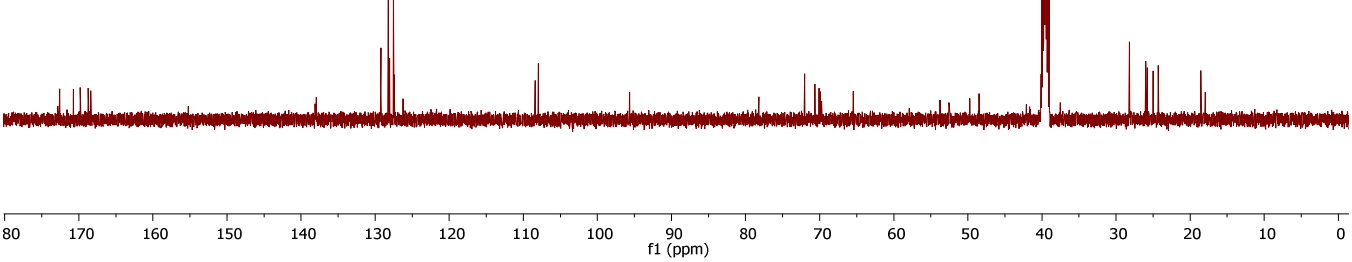
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

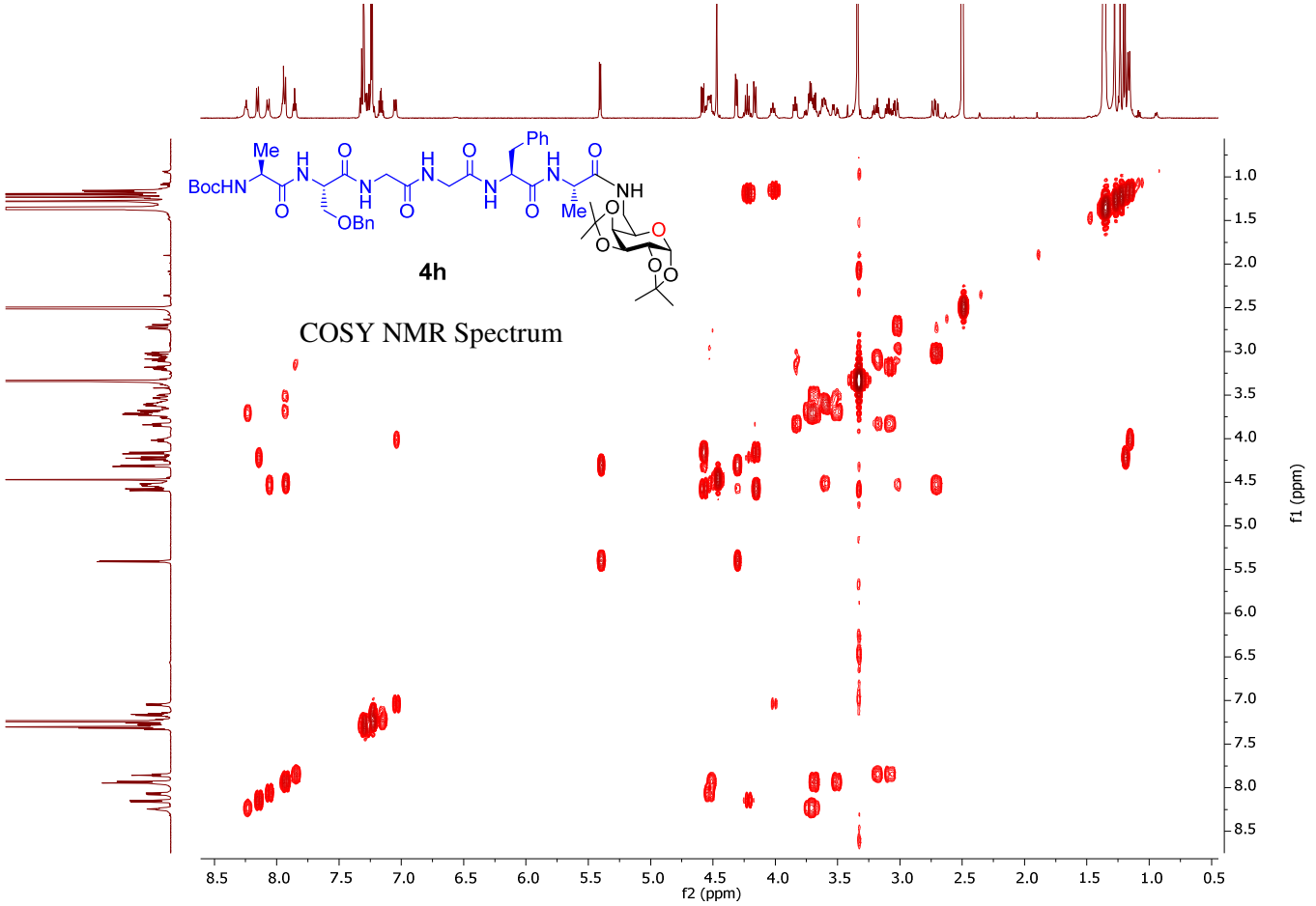


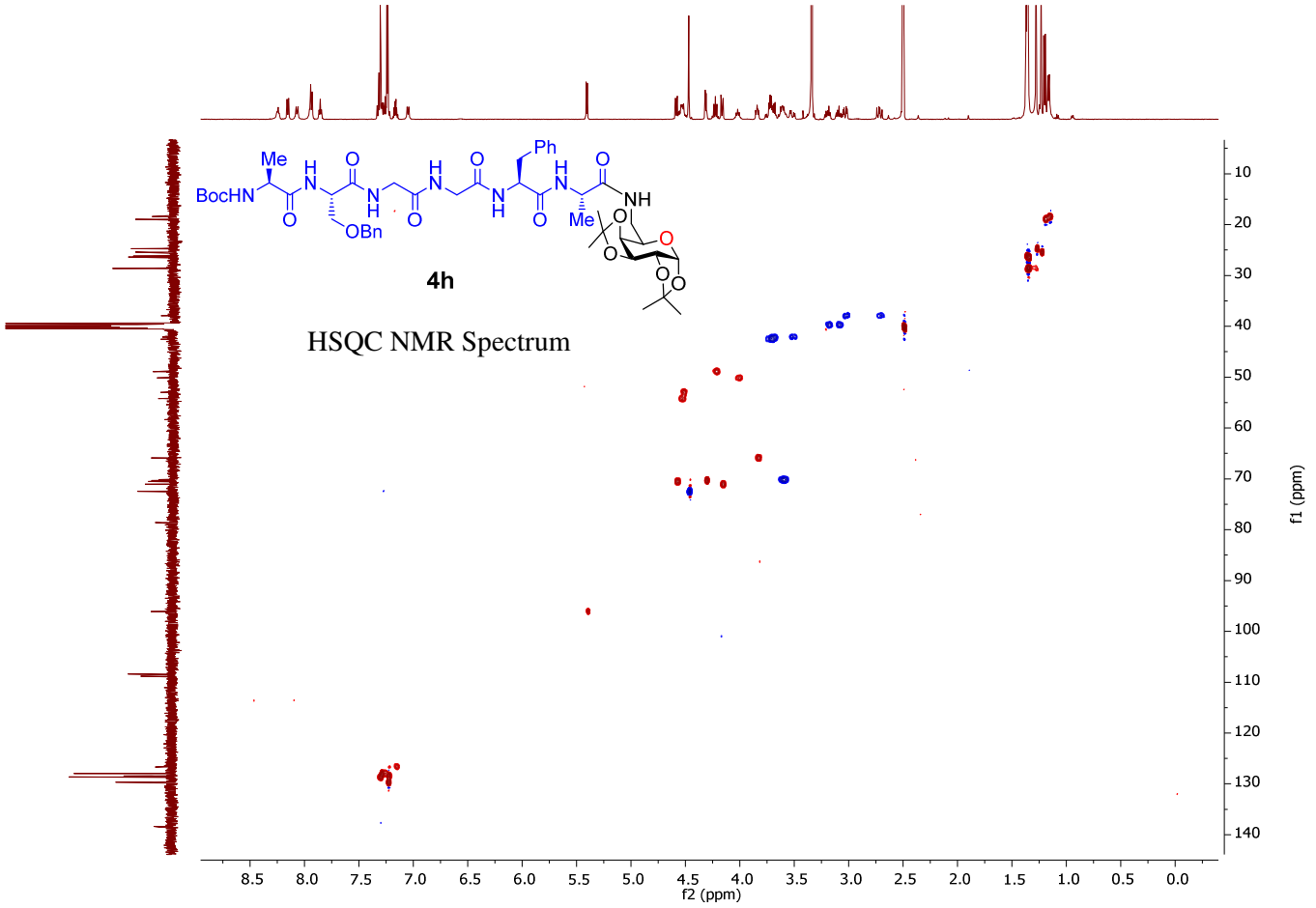


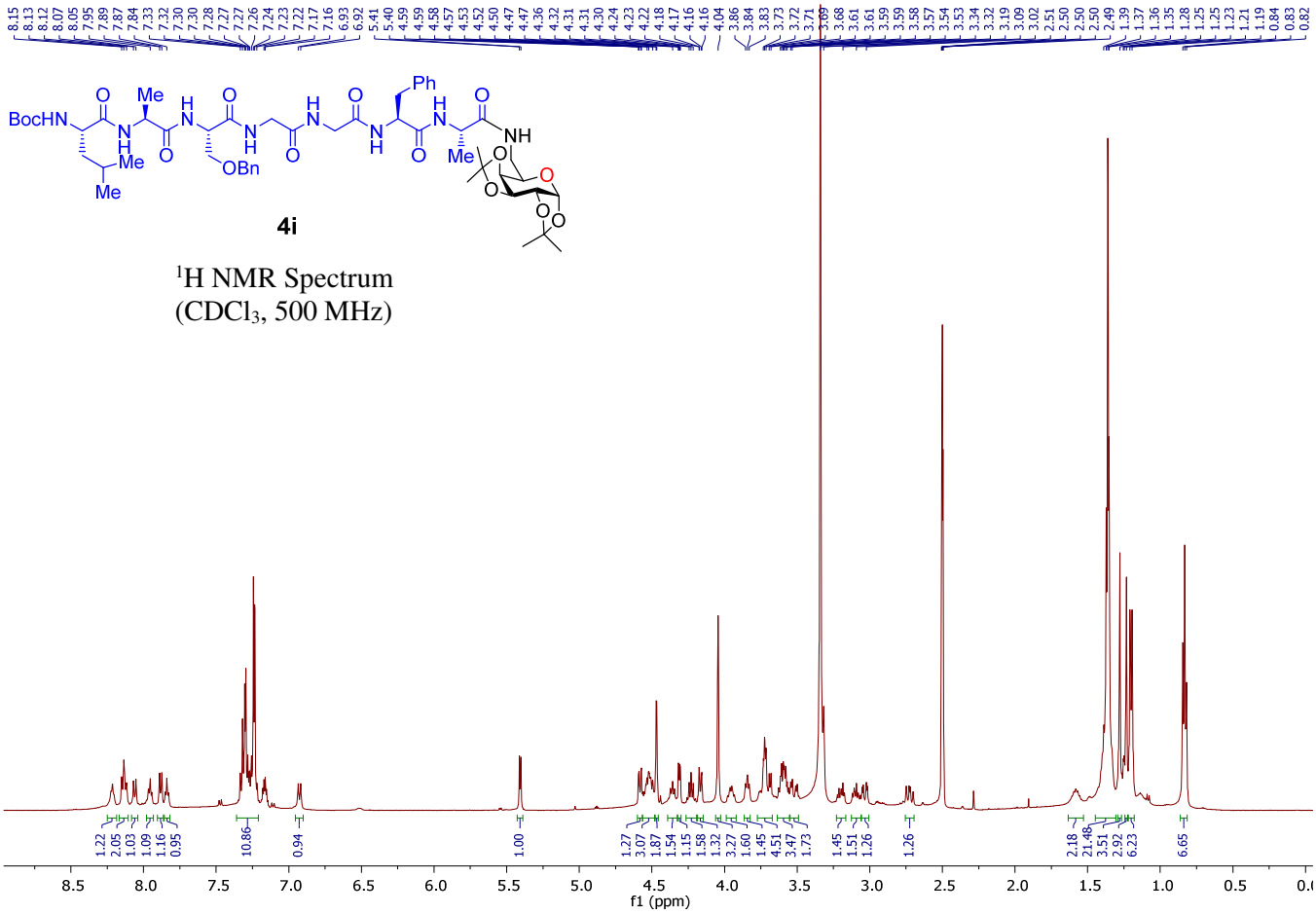
4h

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)



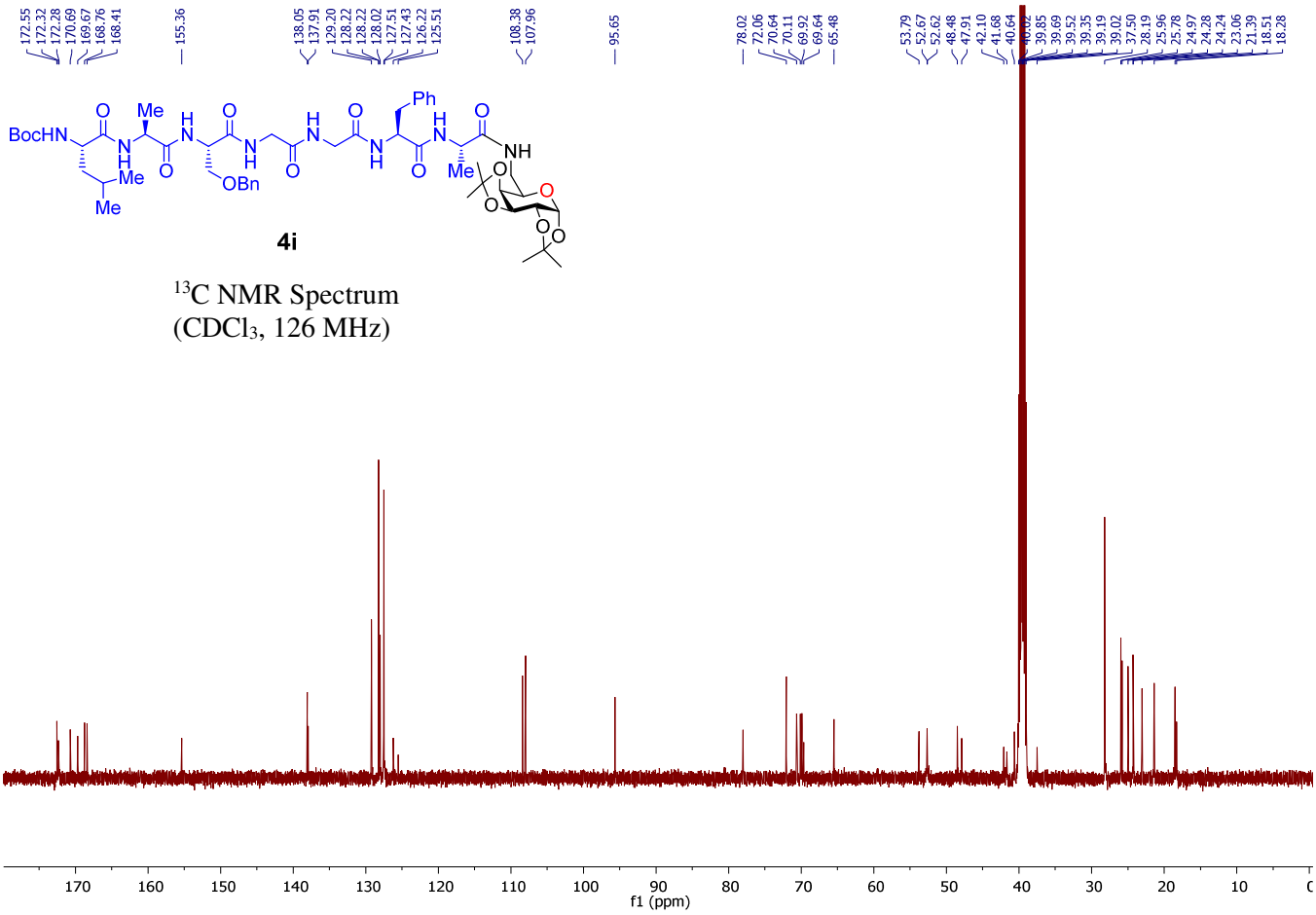

4h
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


4h
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



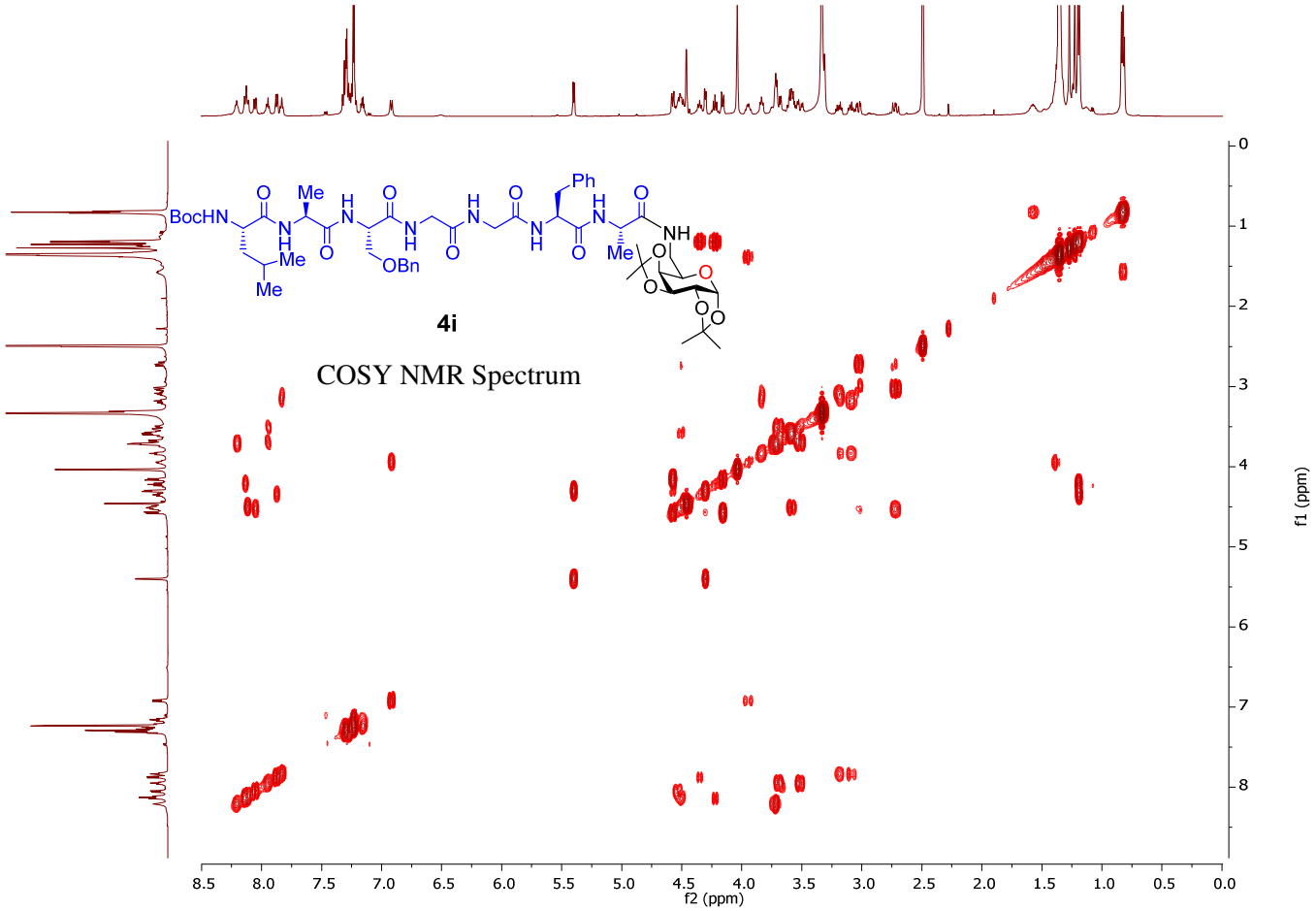
4i

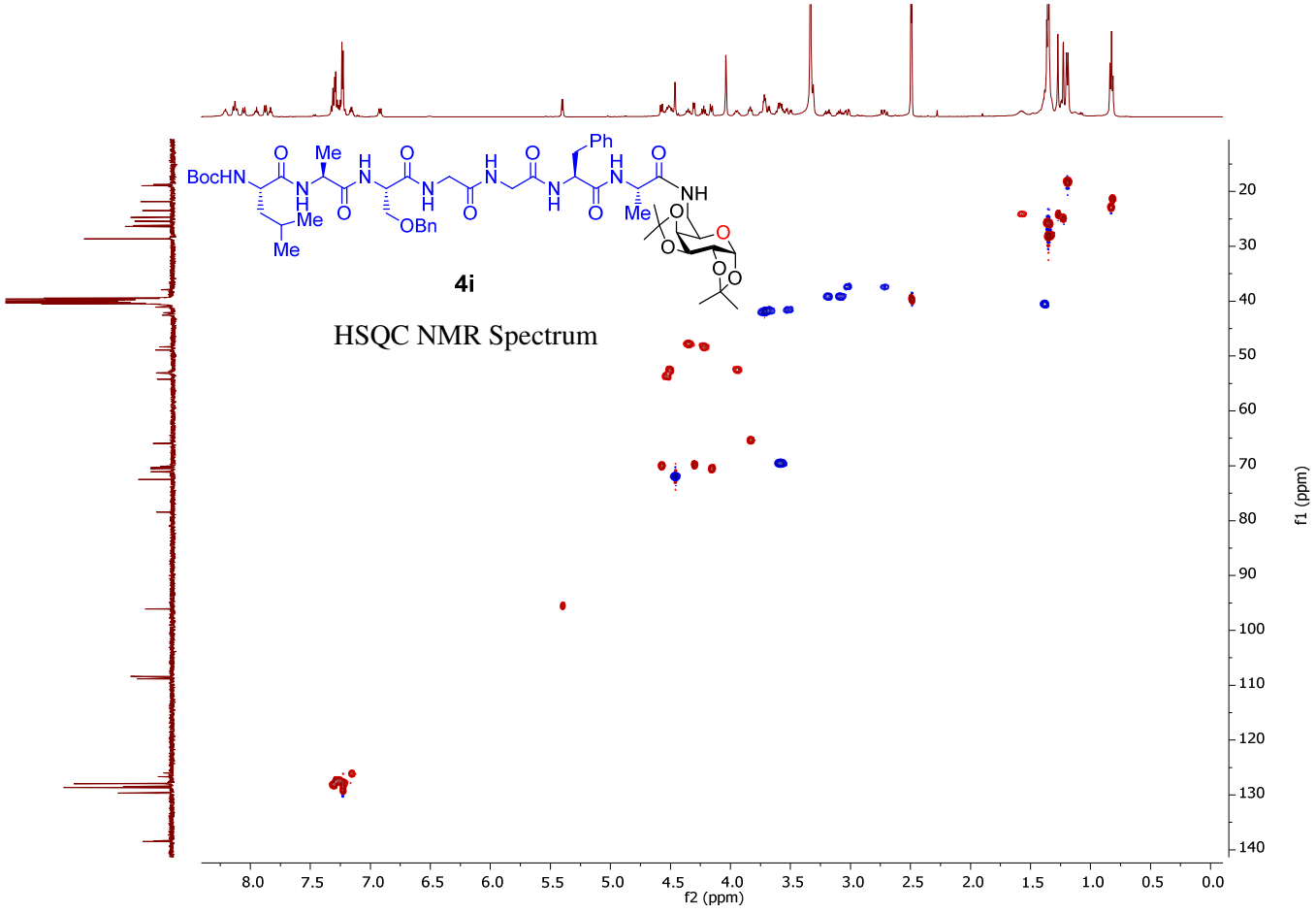
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

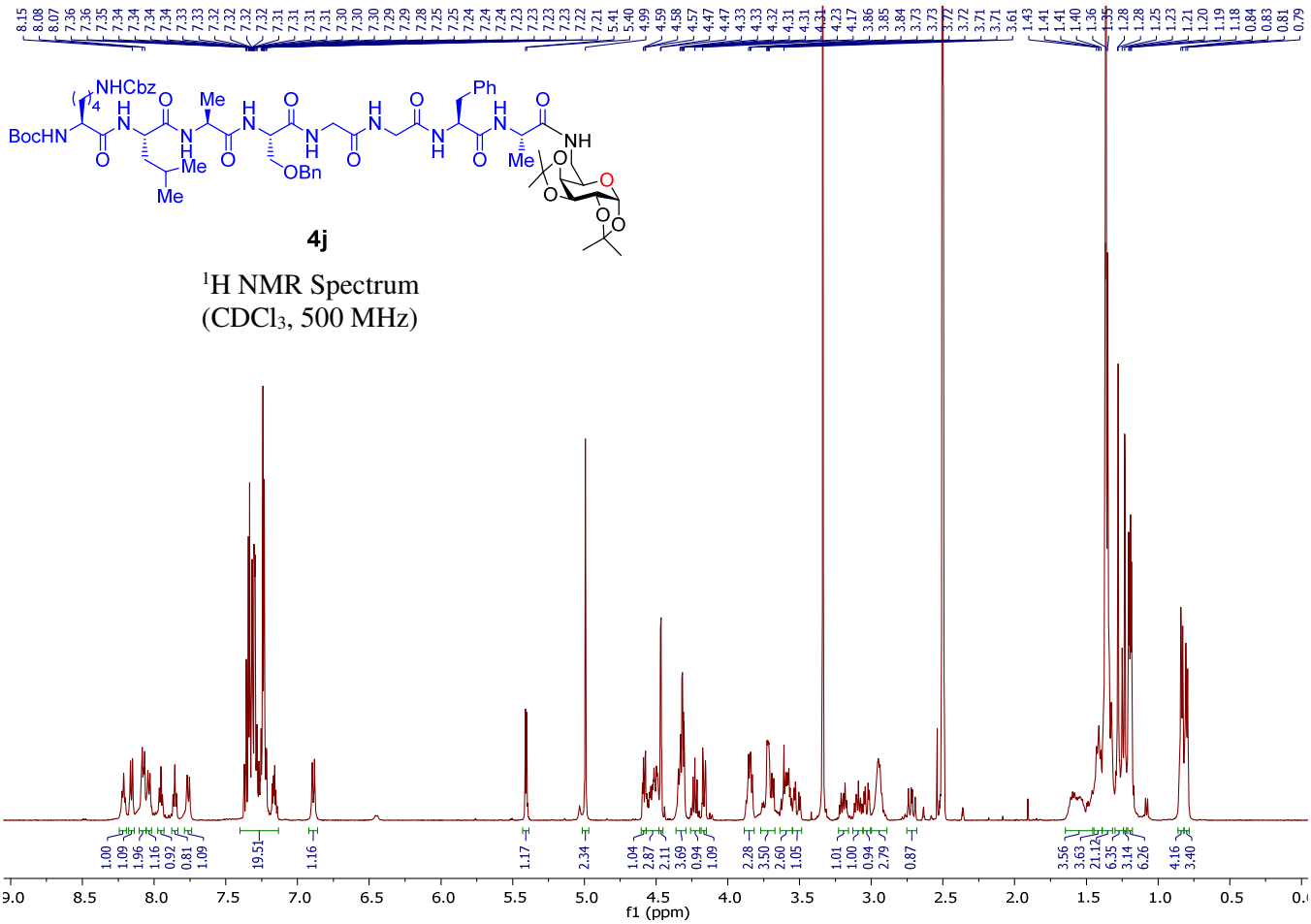


4i

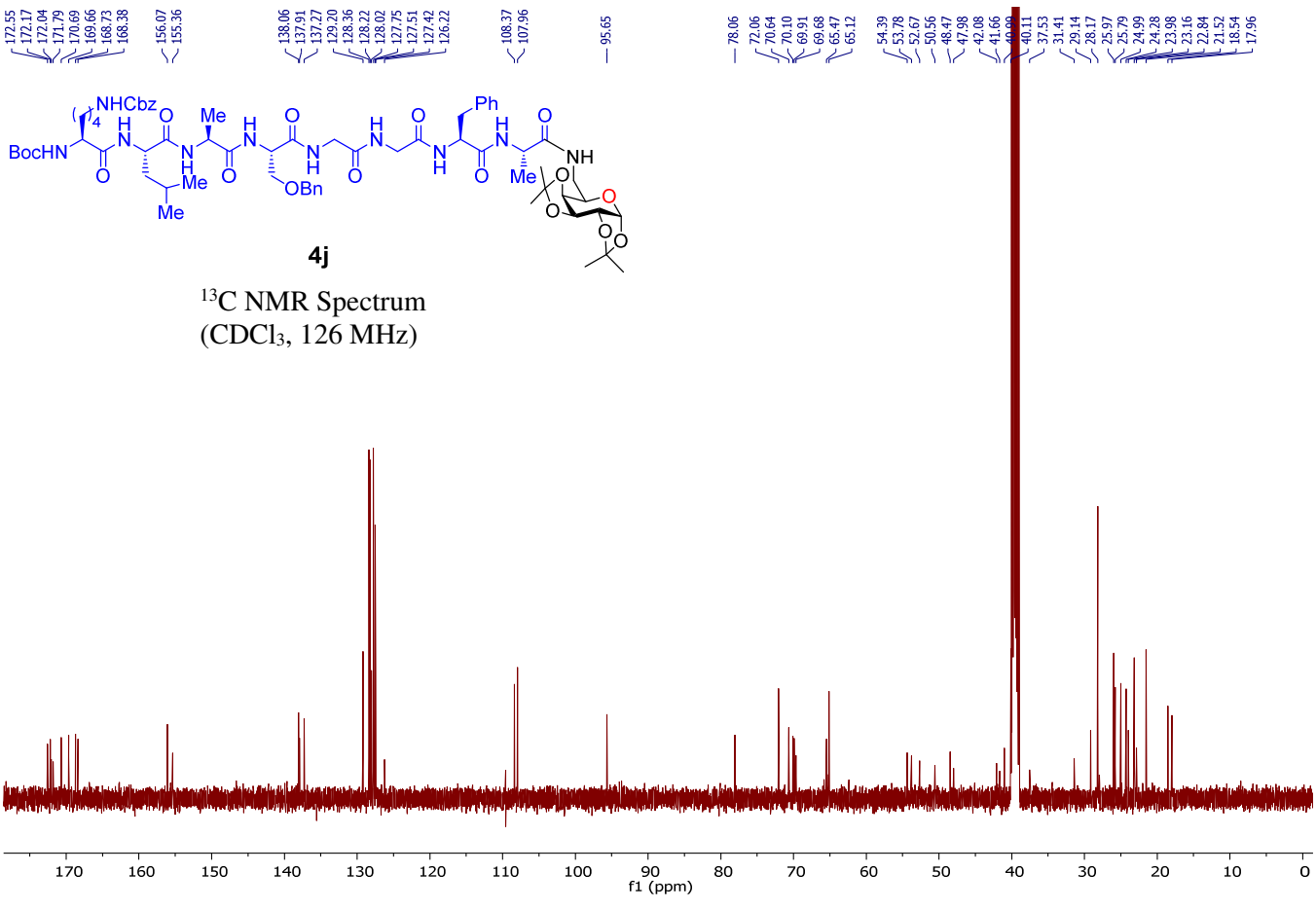
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)


4i
COSY NMR Spectrum
f2 (ppm)
f1 (ppm)

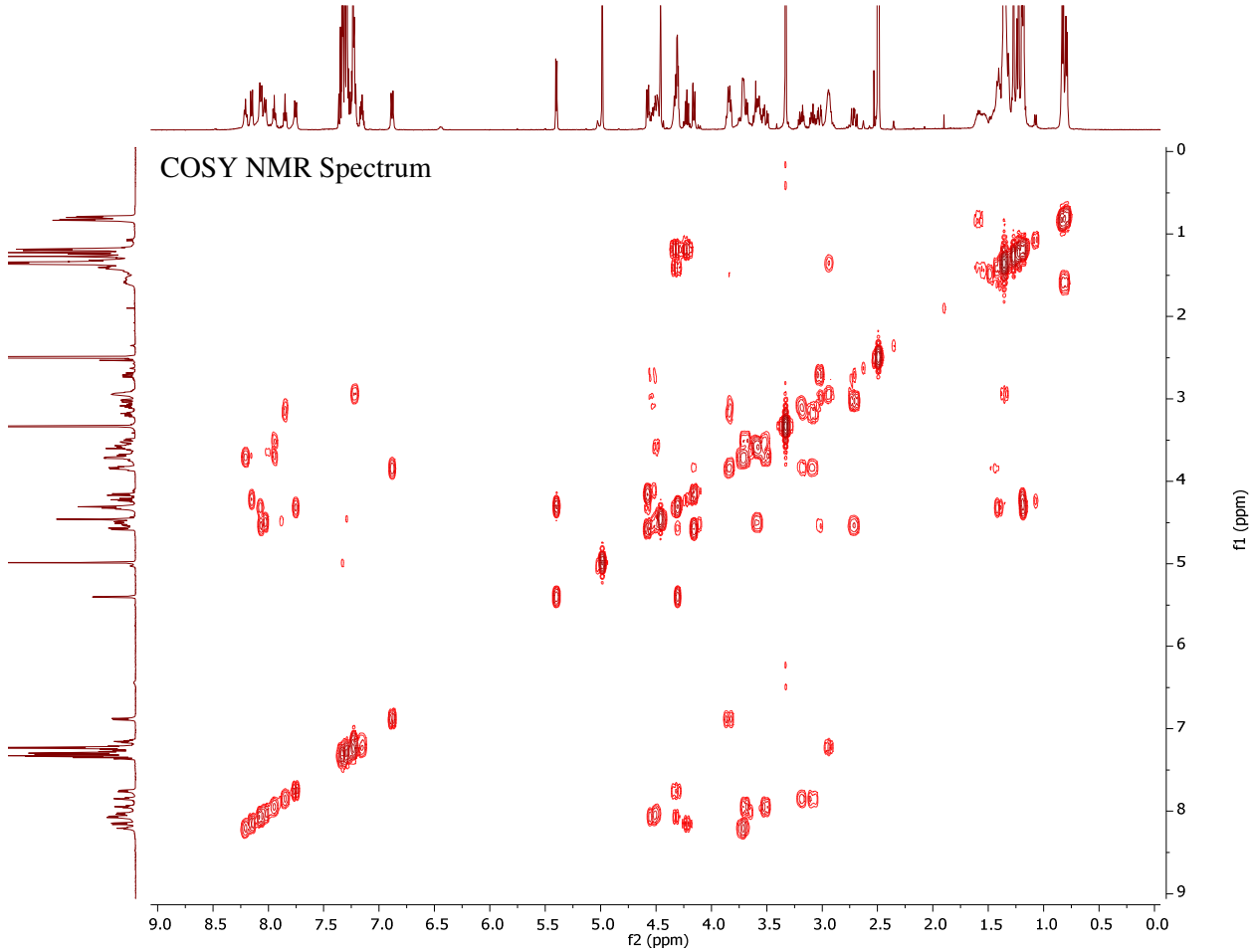

4i
HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)

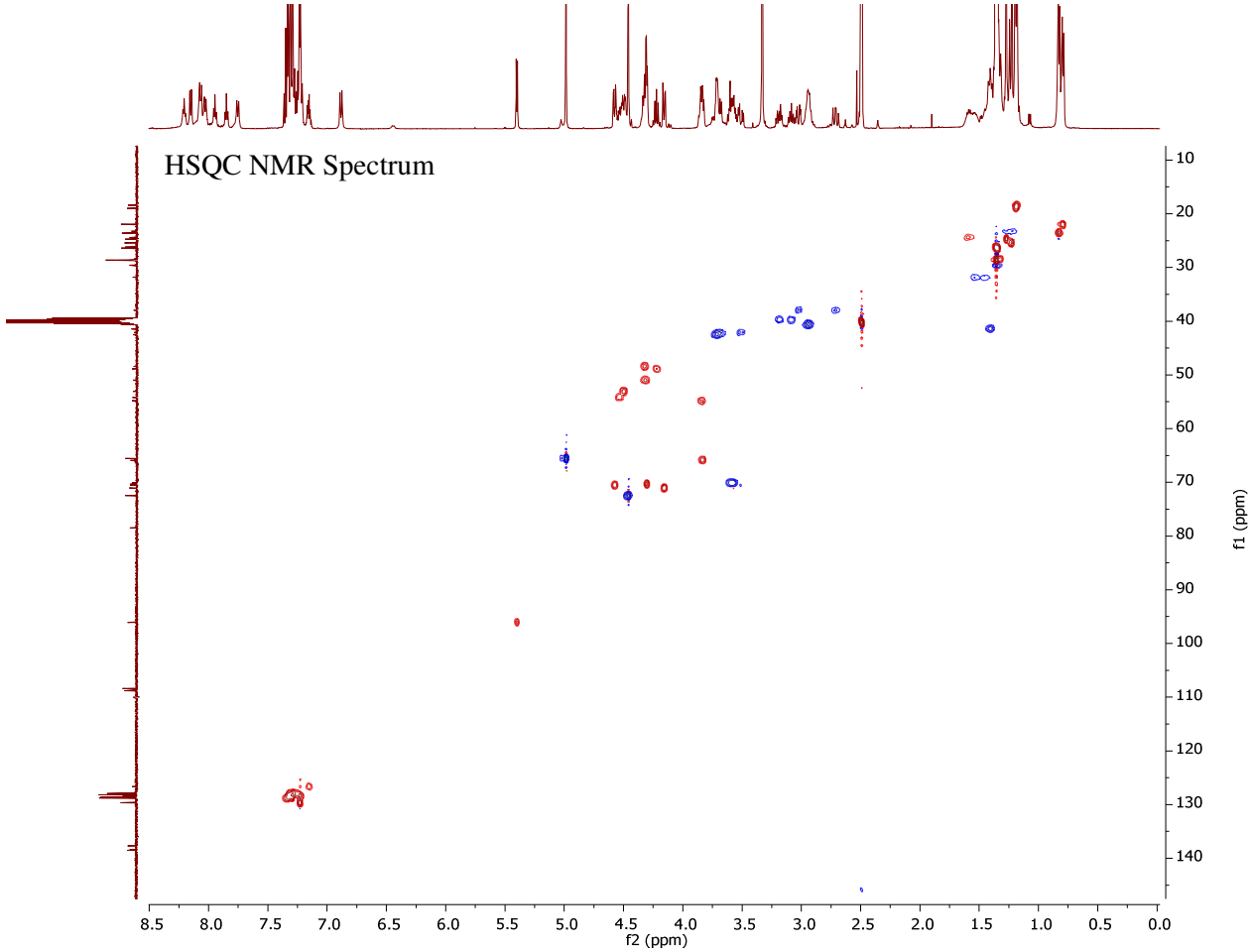


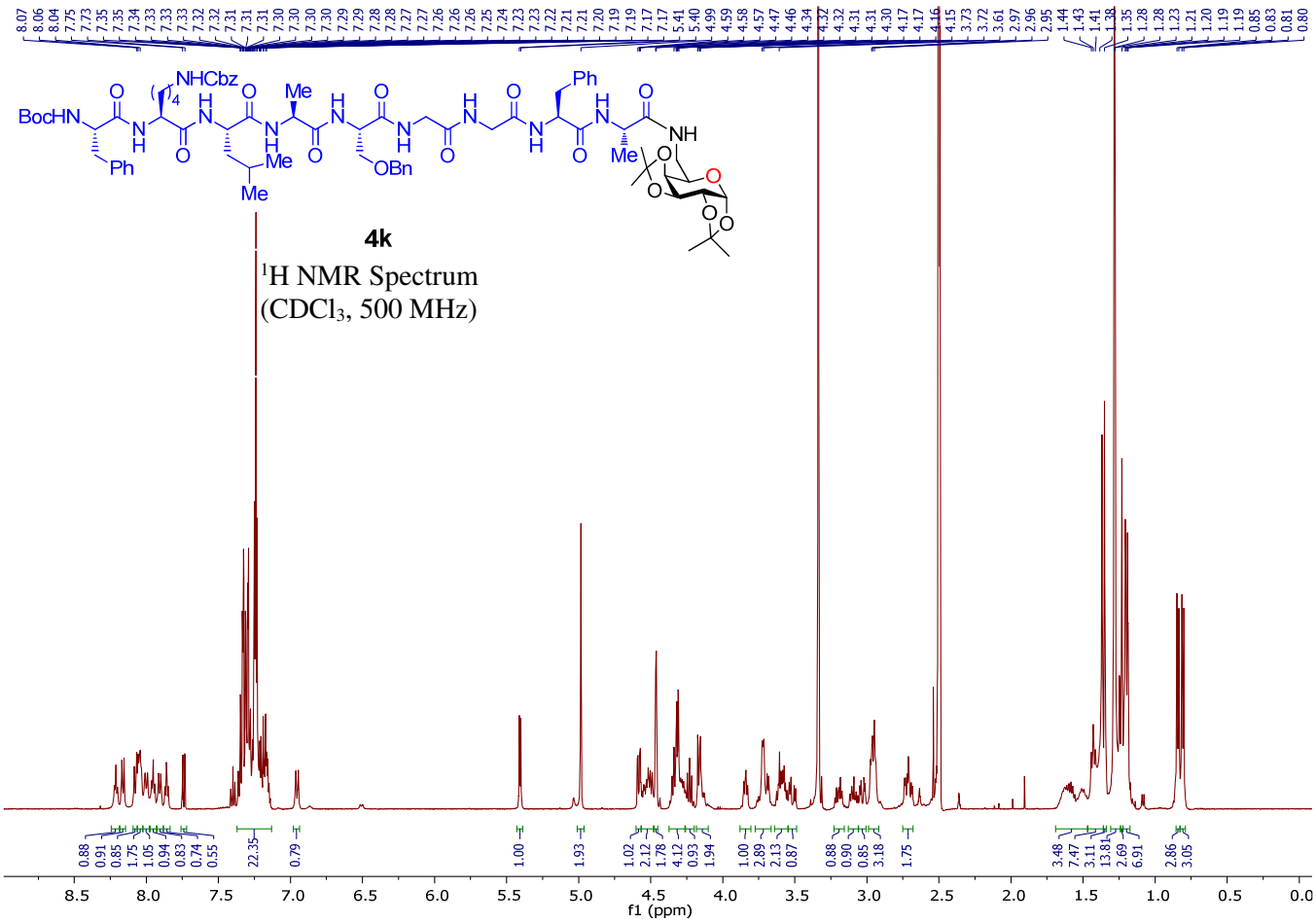
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

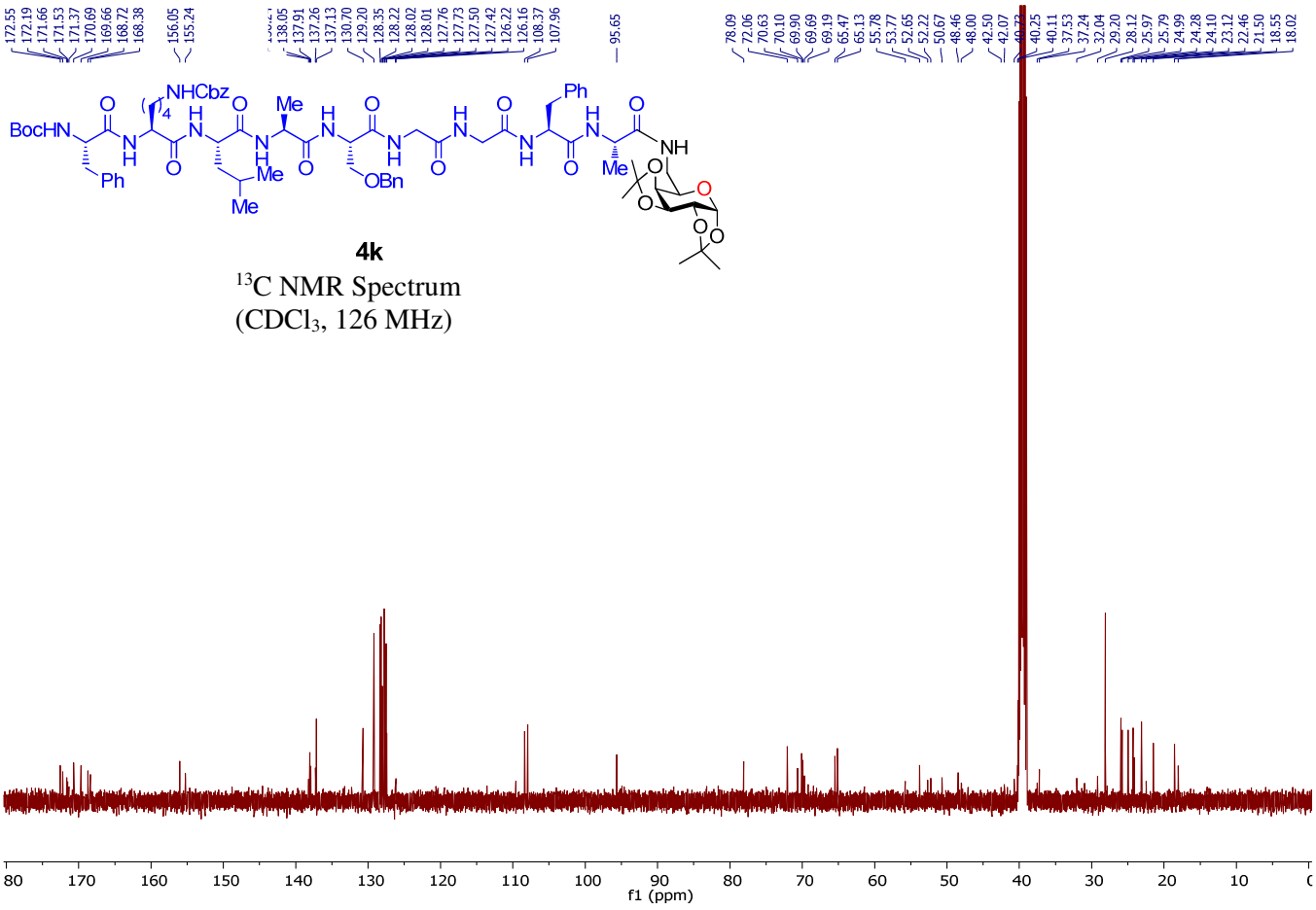


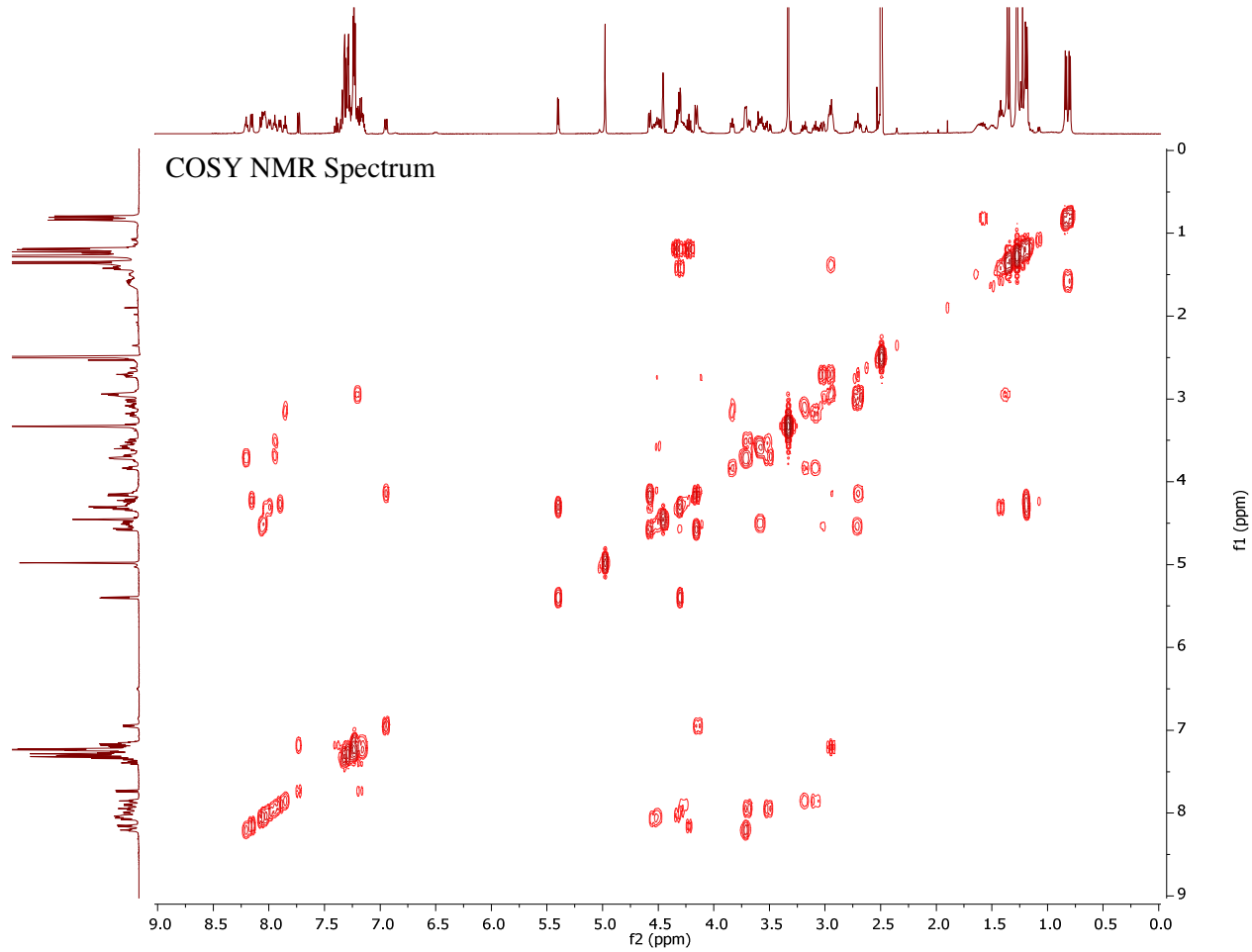
^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)

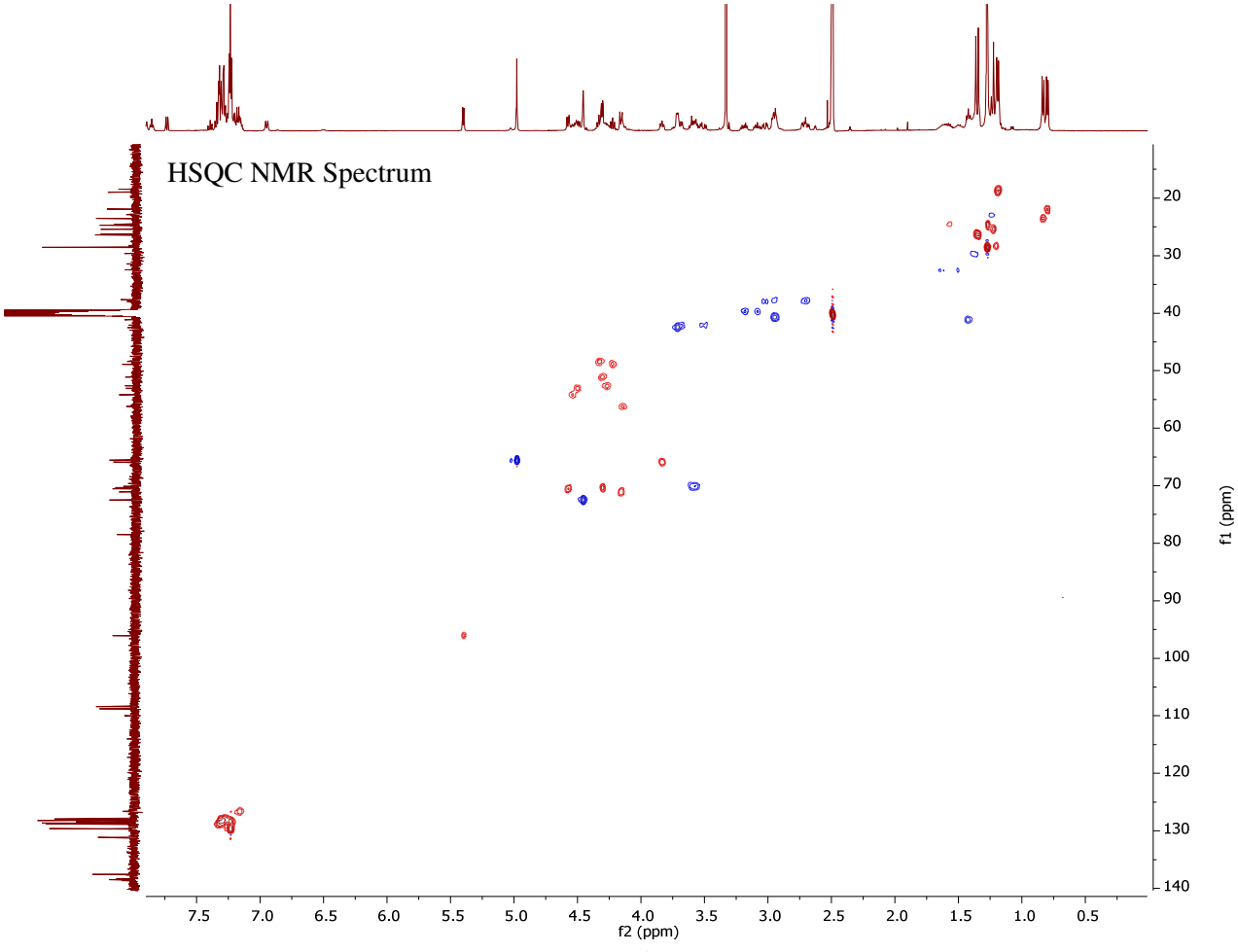

COSY NMR Spectrum
f2 (ppm)
f1 (ppm)

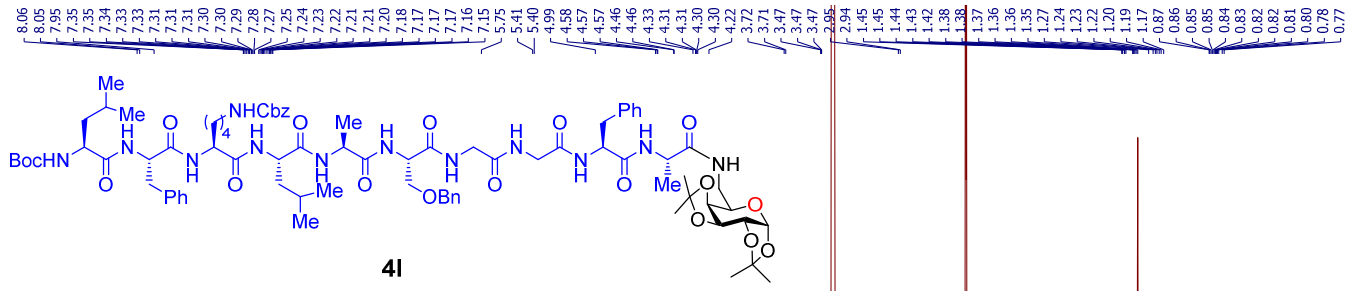

HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)


4k
1H NMR Spectrum
(CDCl3, 500 MHz)
f1 (ppm)


4k
13C NMR Spectrum
(CDCl3, 126 MHz)
f1 (ppm)

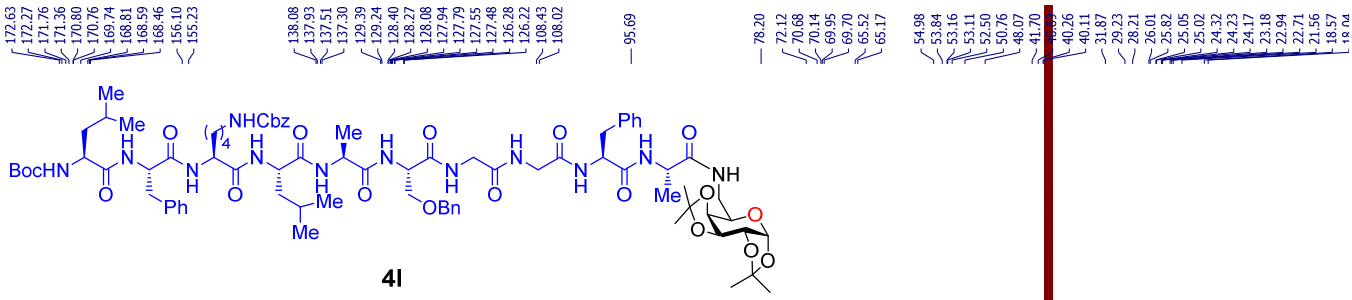

COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



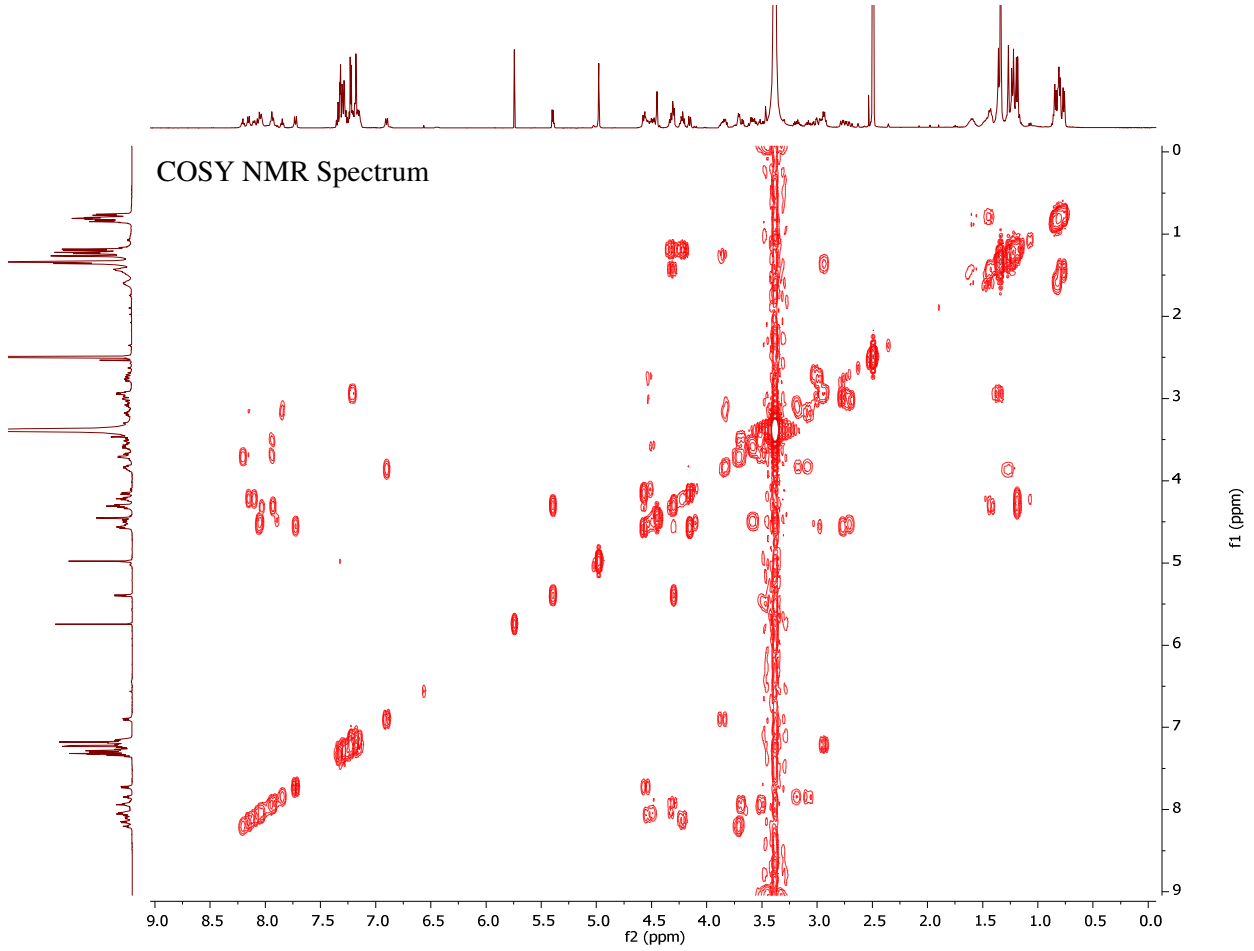
4l

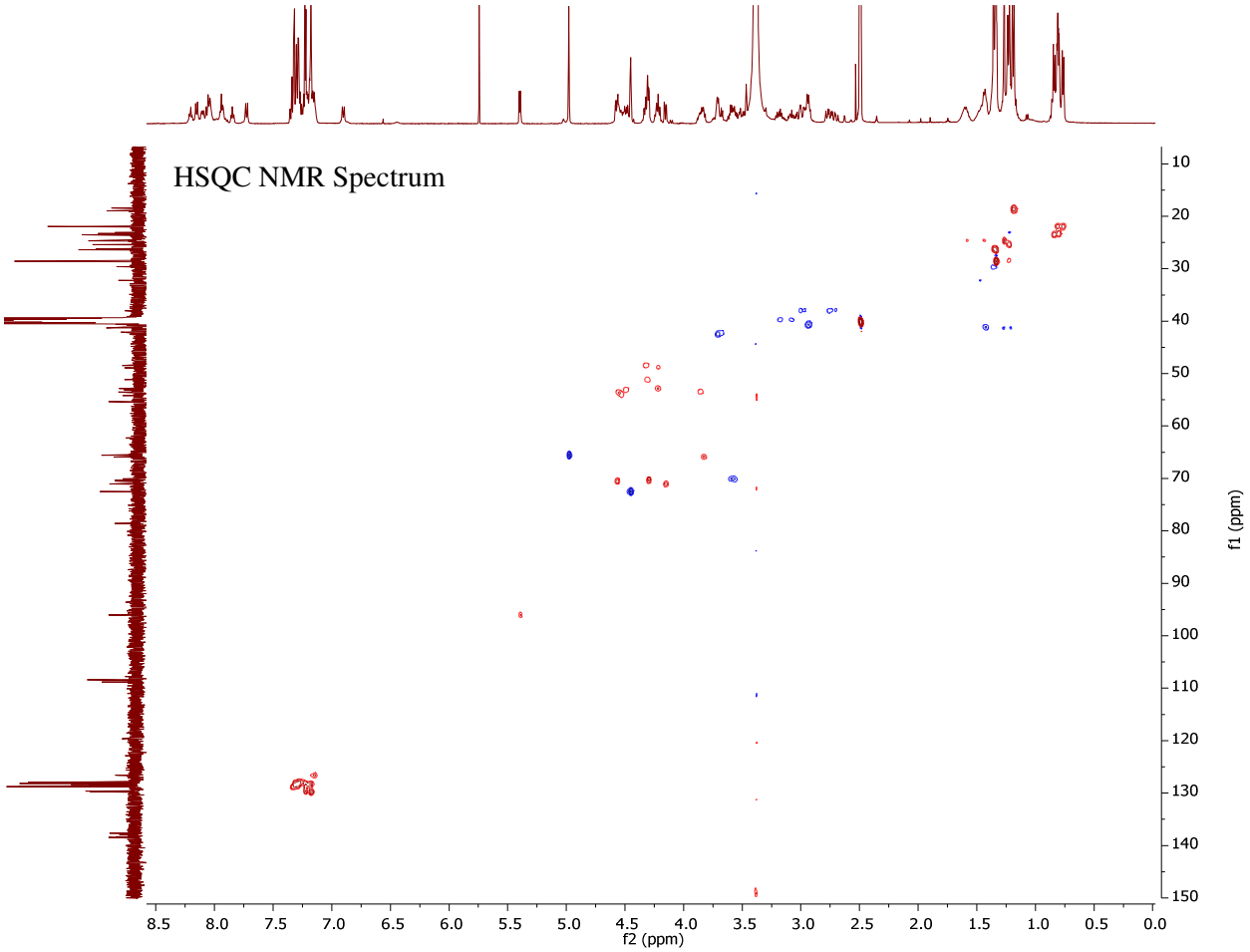
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

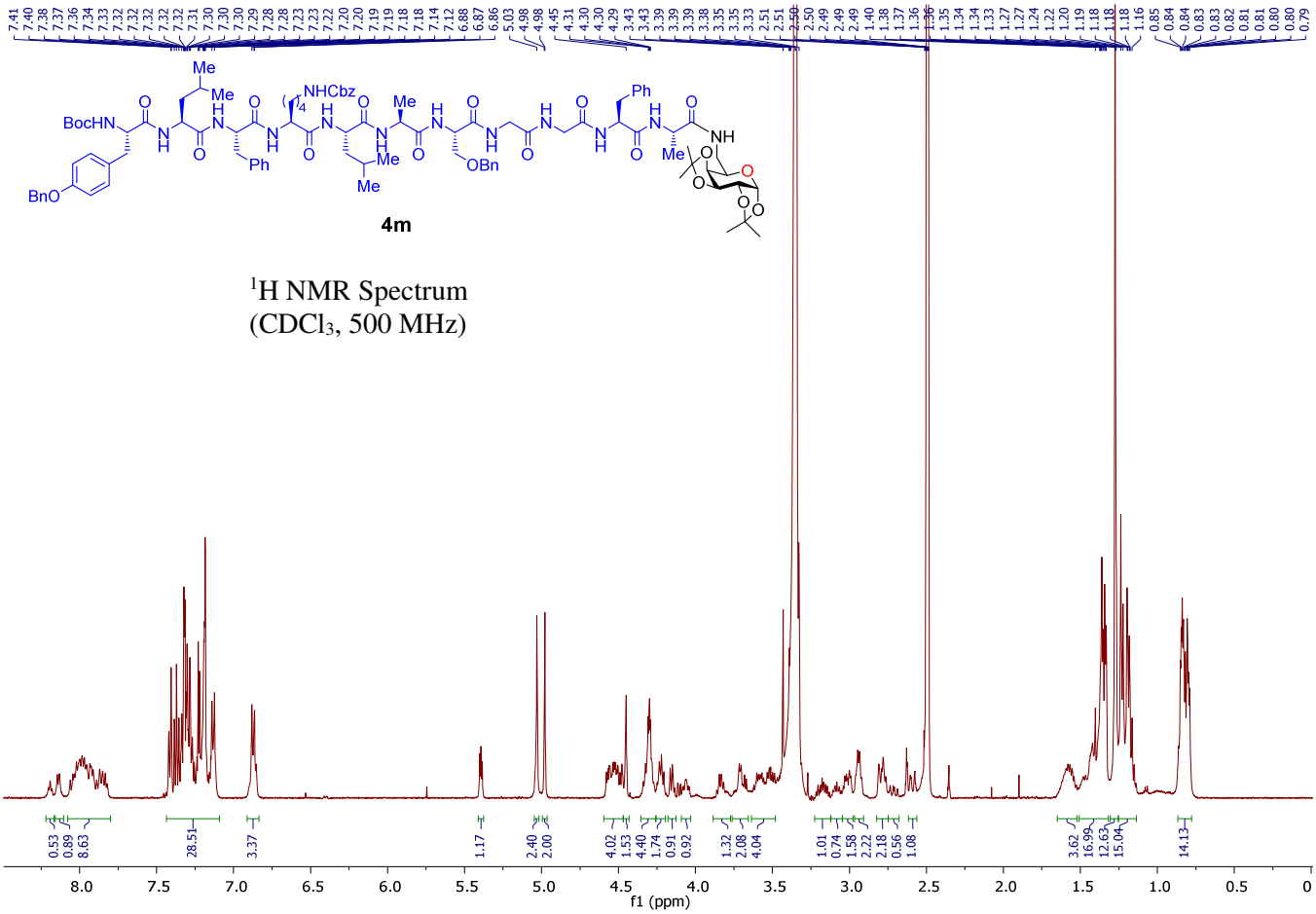


4l

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)

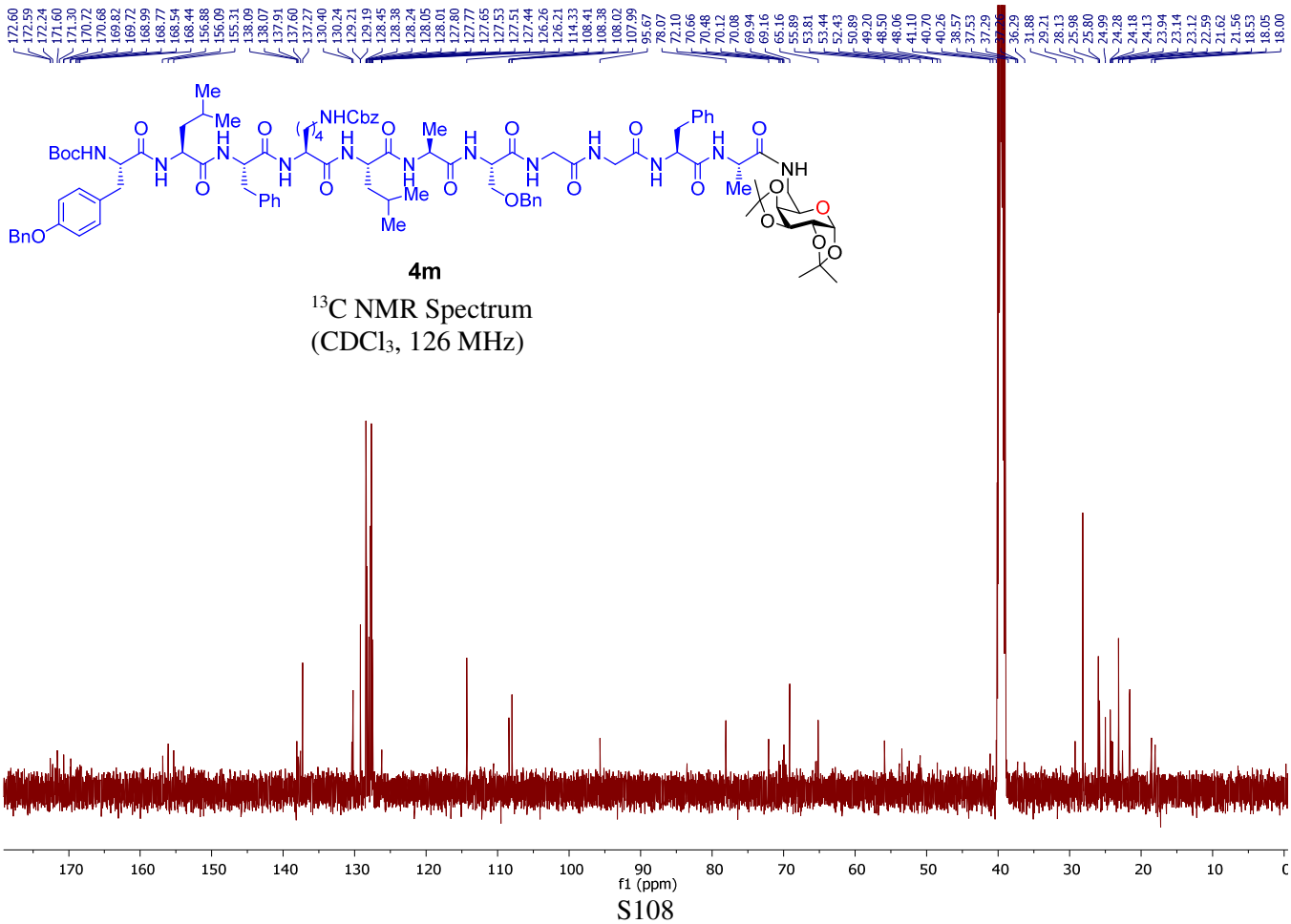

COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)



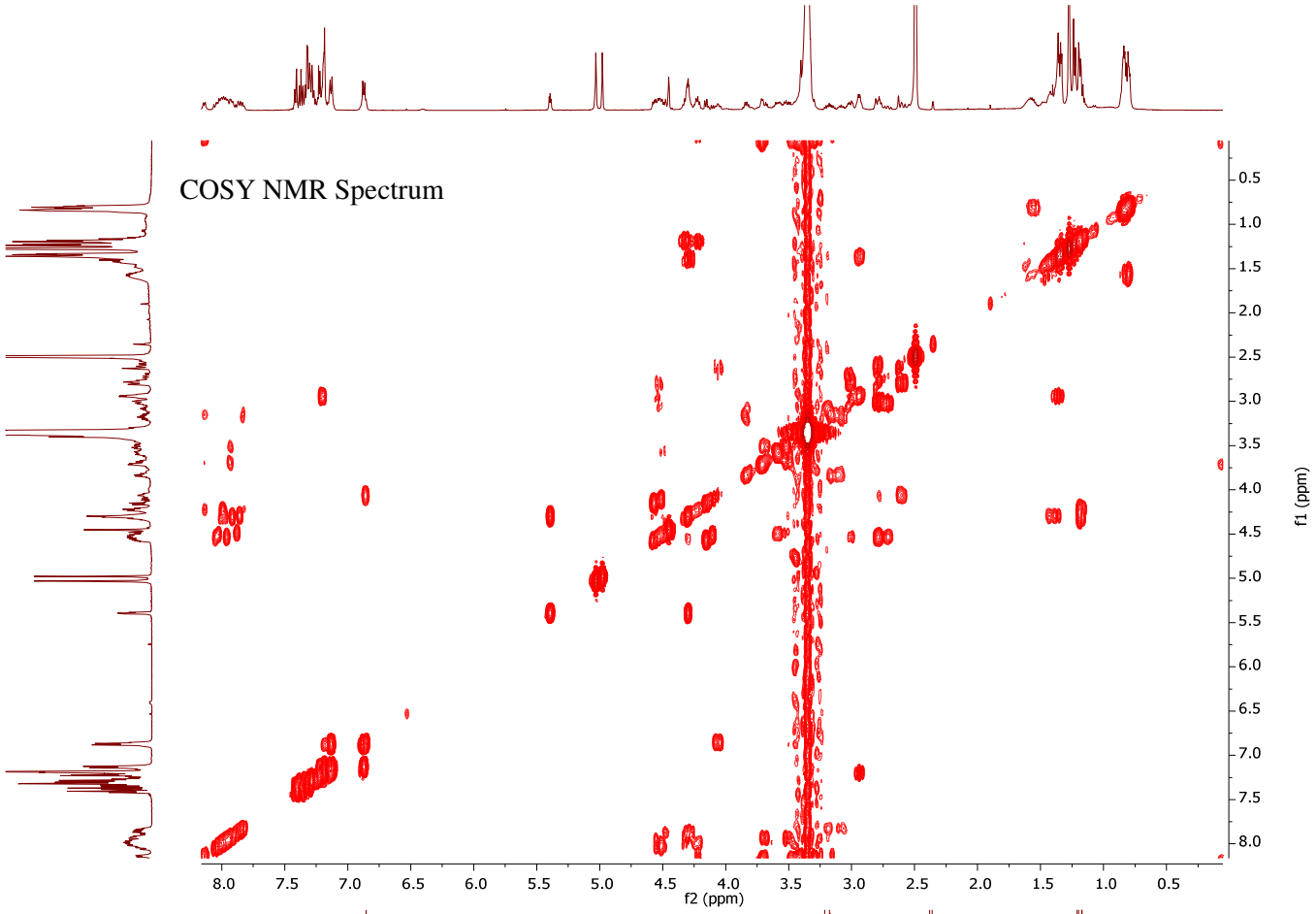
4m

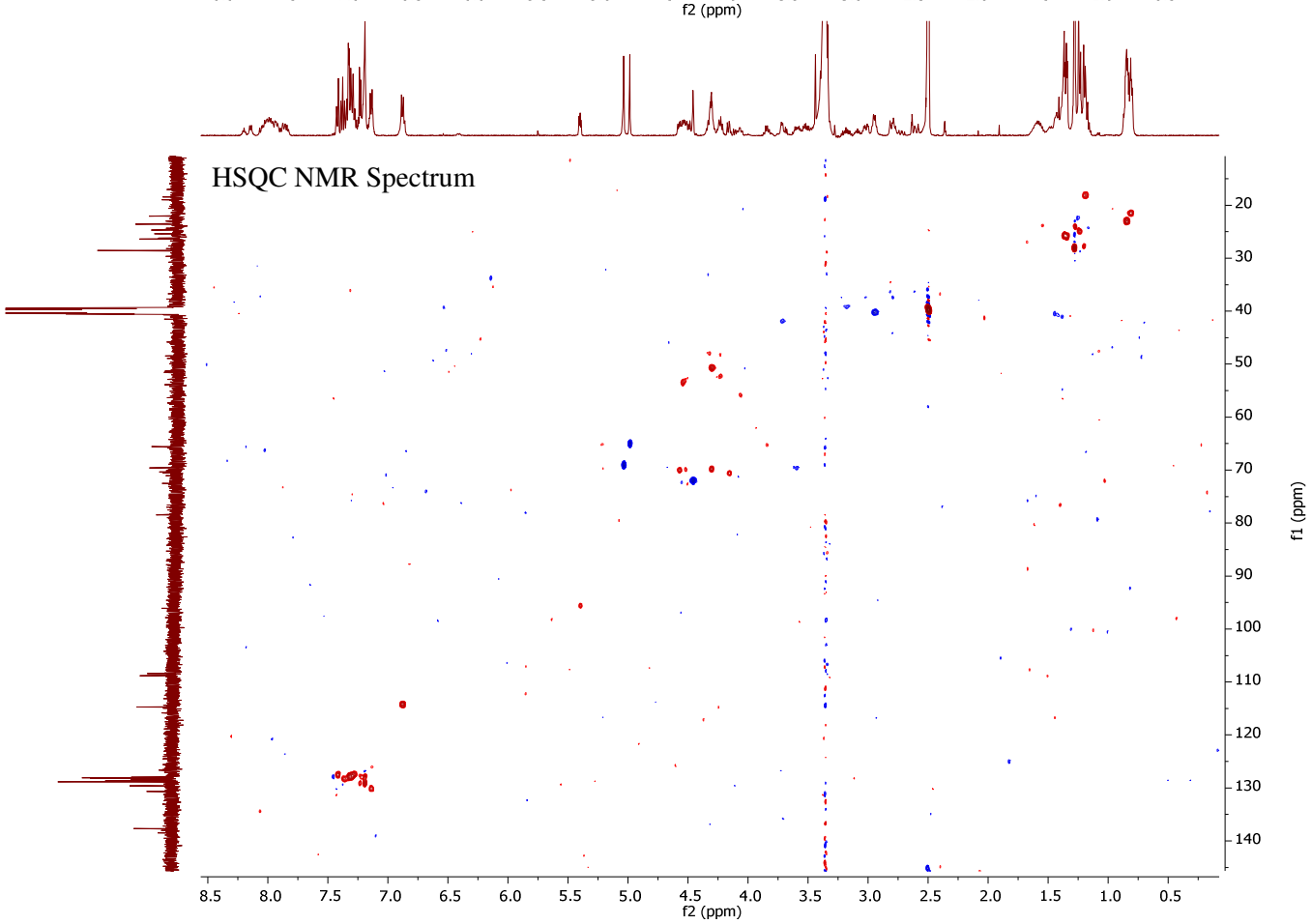
^{1}H NMR Spectrum
($CDCl_3$, 500 MHz)

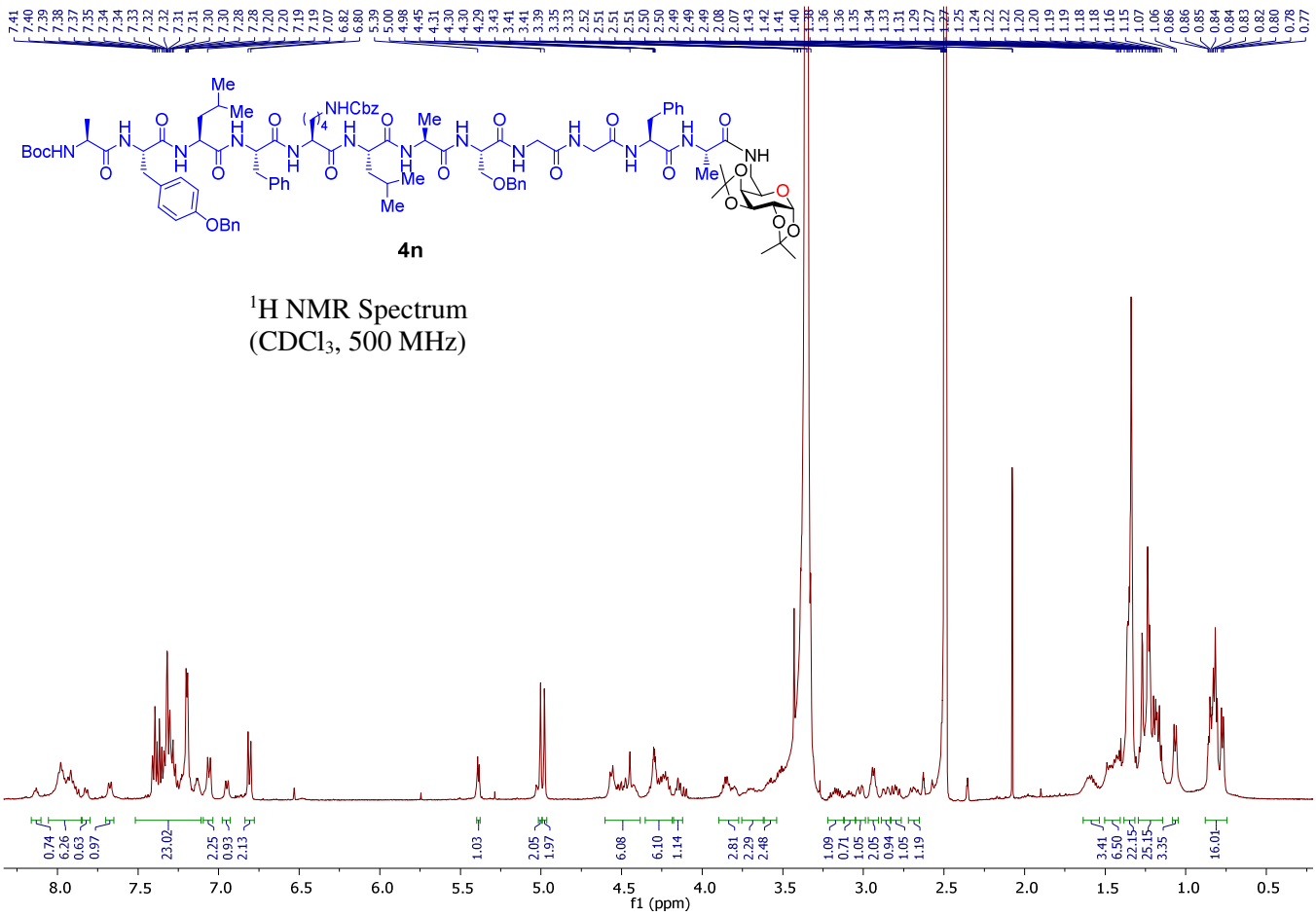


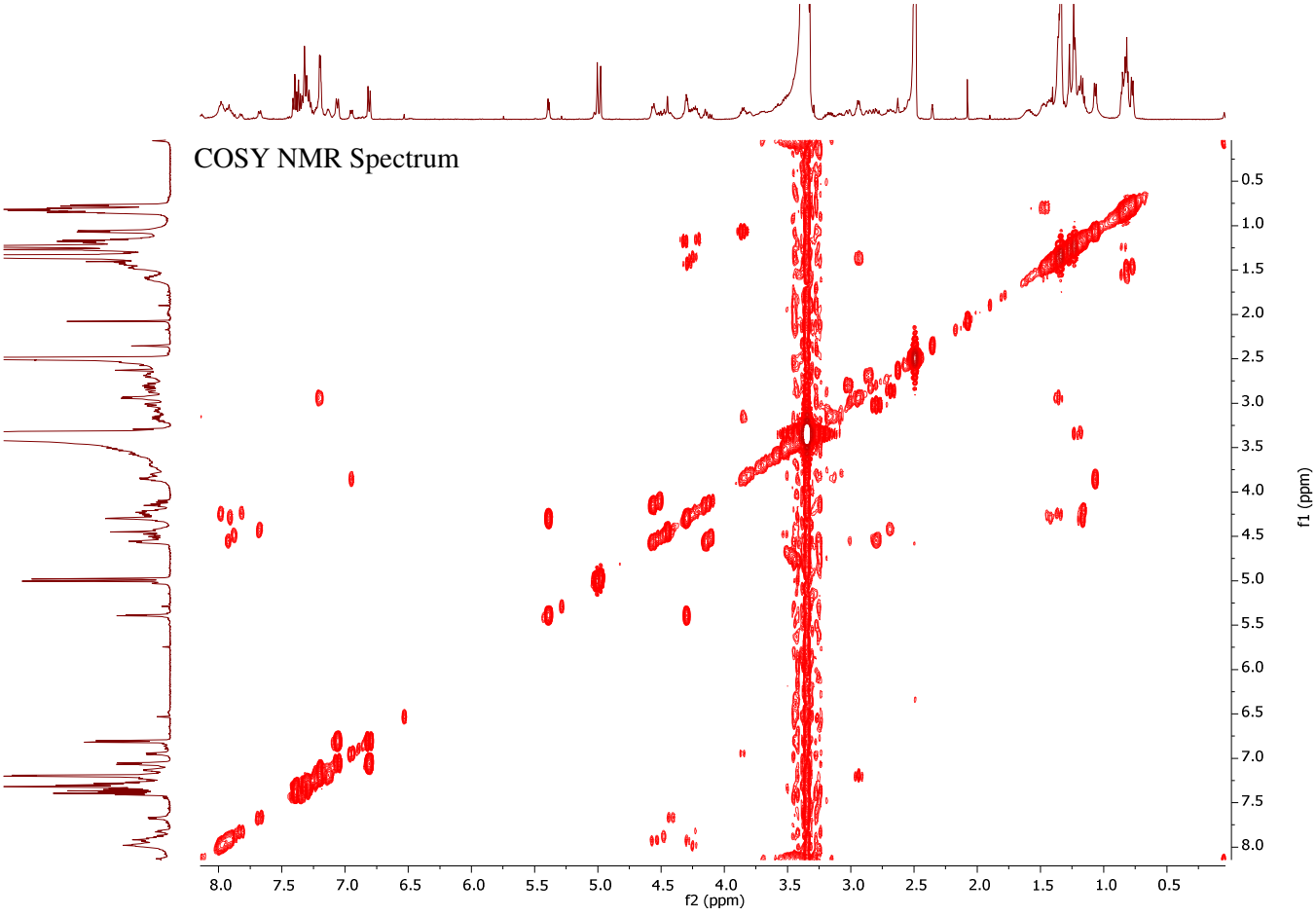
4m

^{13}C NMR Spectrum
($CDCl_3$, 126 MHz)


COSY NMR Spectrum
f2 (ppm)
f1 (ppm)


HSQC NMR Spectrum
f2 (ppm)
f1 (ppm)


4n
^{1}H NMR Spectrum
(CDCl$_3$, 500 MHz)
f1 (ppm)


COSY NMR Spectrum
f2 (ppm)
f1 (ppm)

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