Facile Triflic Acid-Catalyzed α-1,2-*Cis*-Thiol Glycosylations: Scope and Applications to the Synthesis of *S*-Linked Oligosaccharides, Glycolipids, Sublancin Glycopeptide and T_N/T_F Antigens

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1. Supporting Figure

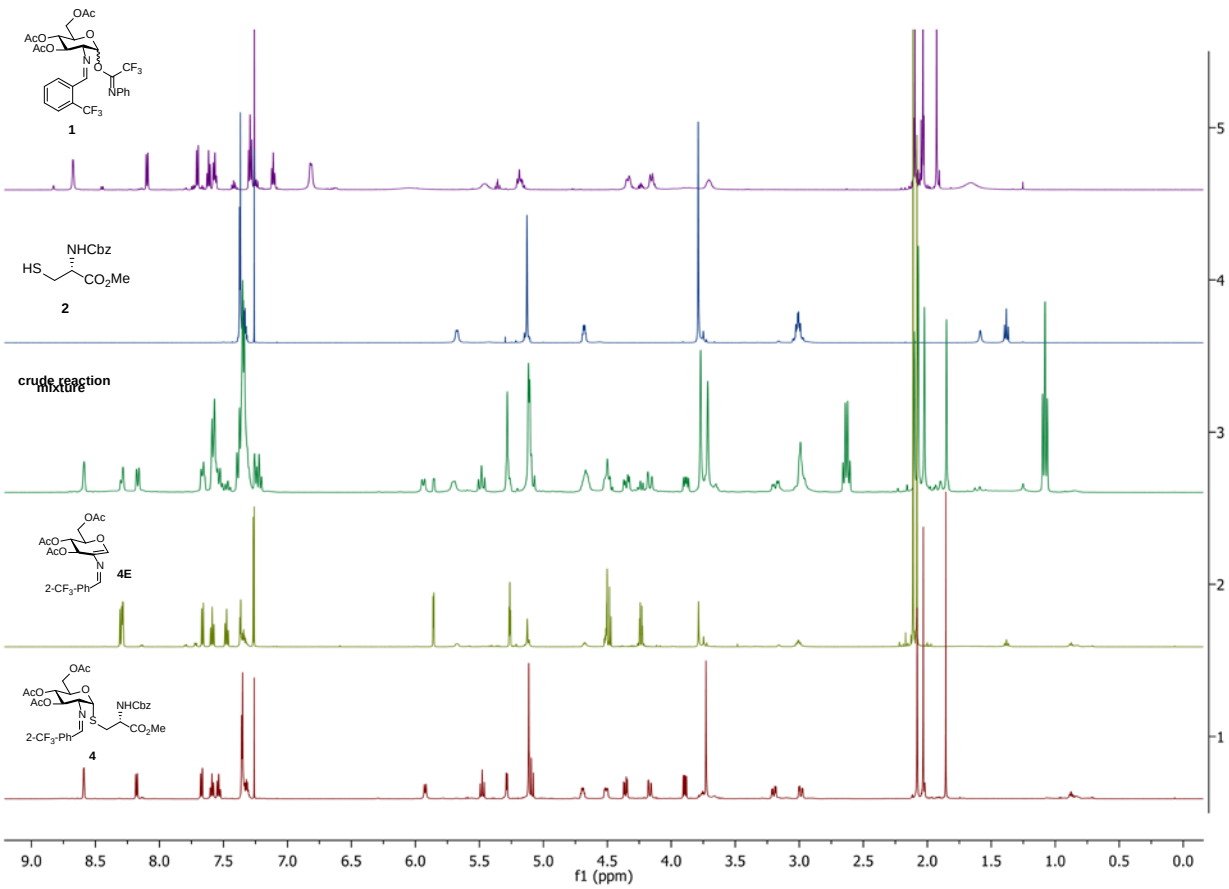


Figure S1. ^{1}H NMR Analysis of Glycosylation of Cysteine Amino acid Nucleophile 2 with *N*-Phenyl Trifluoroacetimidate Electrophile 1

The crude mixture resulted from the coupling of cysteine amino acid nucleophile **2** with *N*-phenyl trichloroacetimidate electrophile **1** was first analyzed by ^{1}H NMR spectroscopy. The crude mixture was purified by silica gel flash chromatography to separate the desired product **4** from the undesired elimination product **4E**. The result indicated the electrophile **1** was fully converted to the desired product **4** as exclusive α-isomer accompanied with the elimination product **4E**.

2. General Information

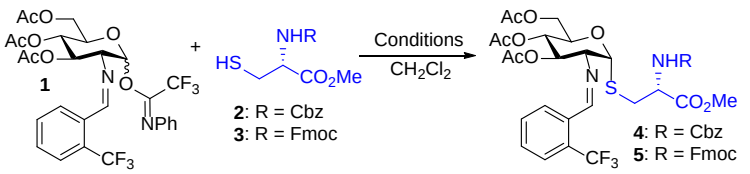
Methods and Reagents. All reactions were performed in oven-dried flasks fitted with septa under a positive pressure of nitrogen atmosphere. Organic solutions were concentrated using a Buchi rotary evaporator below 40 °C at 25 torr. Analytical thin-layer chromatography was routinely utilized to monitor the progress of the reactions and performed using pre-coated glass plates with 230-400 mesh silica gel impregnated with a fluorescent indicator (250 nm). Visualization was then achieved using UV light, iodine, or ceric ammonium molybdate. Flash column chromatography was performed using 40-63 μm silica gel (SiliaFlash F60 from Silicycle). Dry solvents were obtained from a SG Waters solvent system utilizing activated alumina columns under an argon pressure. All other commercial reagents were used as received from Sigma Aldrich, Alfa Aesar, Acros Organics, TCI, and Combi-Blocks, unless otherwise noted.

Instrumentation. All new compounds were characterized by Nuclear Magnetic Resonance (NMR) spectroscopy and High-Resolution Mass spectrometry (HRMS). All ^{1}H NMR spectra were recorded on either Agilent 400 or 600 MHz spectrometers. All ^{13}C NMR spectra were recorded on either Agilent 100 or 150 MHz spectrometer. Chemical shifts are expressed in parts per million (δ scale) referenced to the residual proton in the NMR solvent ($CDCl_3$: δ 7.26 ppm, δ 77.16 ppm). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet), integration, and coupling constant in hertz (Hz).

High resolution mass spectra (HRMS) were recorded using a Micromass LCT Premier XE instrument (Waters) and were determined by electrospray ionization (ESI).

3. Optimization Studies

Table S1. Reaction Development[a]

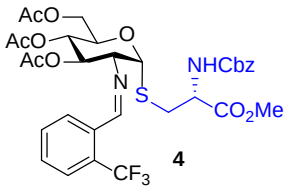


entry	**1** (equiv.)	**2** or **3** (equiv.)	catalyst	temp (^{o}C)	time (h)	**4** or **5** yield (α:β)
1	1	**2** (1.5)	15 mol% $Ni(OTf)_2$	35	16	**4**: 66% (>20:1)
2	1	**2** (1.5)	5 mol% TfOH	35	1	**4**: 64% (>20:1)
3	1	**2** (1.5)	5 mol% TfOH	25	2	**4**: 68% (>20:1)
4	1	**2** (1.5)	1 mol% TfOH	25	20	**4**: 67% (>20:1)
5	1.5	**2** (1.0)	3 mol% TfOH	25	3	**4**: 76% (>20:1)
6	2	**2** (1.0)	3 mol% TfOH	25	3	**4**: 81% (>20:1)
7	2	**2** (1.0)	5 mol% TfOH	25	1	**4**: 80% (>20:1)
8	2	**3** (1.0)	5 mol% TfOH	25	1	**5**: 78% (>20:1)

[a] The reaction was conducted with 0.1 – 0.2 mmol of 1. Yields of isolated product averaged two runs. The (α/β) ratios were determined by ^{1}H NMR analysis.

Procedure for Thiol Glycosylations Opitimization:

A 10 mL Schlenk flask was charged with *N*-phenyl trifluoroacetimidate glycosyl donor **1** (0.1 – 0.2 mmol, 1 – 2 equiv.), cysteine acceptor **2** or **3** (0.1 – 0.15 mmol, 1 – 1.5 equiv.) and dichloromethane (1 mL). The resulting solution was stirred at room temperature for 5 min under a nitrogen atmosphere before the catalyst (1 – 15 mol% with respect to donor **1**) was added. After the TLC shows completion of the reaction, it was quenched with 1 drop of Et_3N and concentrated. A crude ^{1}H NMR was taken to determine the (α/β) ratio. Further purification by silica gel column chromatography (ethyl acetate/hexane: 1/4→1/2) was performed to give the desired product.



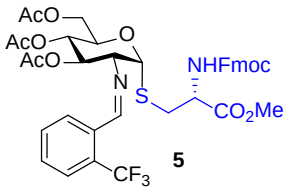
4

64 - 81%, α:β > 20:1

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.59 (d, *J* = 2.1 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.29 (m, 5H), 5.92 (d, *J* = 8.5 Hz, 1H), 5.48 (t, *J* = 9.7 Hz, 1H), 5.29 (d, *J* = 5.6 Hz, 1H), 5.10 (dd, *J* = 15.9, 6.0 Hz, 3H), 4.73 – 4.64 (m, 1H), 4.51 (dd, *J* = 10.1, 3.1 Hz, 1H), 4.36 (dd, *J* = 12.4, 4.9 Hz, 1H), 4.17 (d, *J* = 10.9 Hz, 1H), 3.89 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.73 (s, 3H), 3.20 (dd, *J* = 14.2, 5.4 Hz, 1H), 2.99 (dd, *J* = 14.2, 4.2 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ = 171.02, 170.59, 169.85, 169.59, 160.37, 155.74, 136.09, 133.03, 132.27, 130.90, 129.07, 128.50, 128.20, 128.11, 125.48, 125.45, 85.18, 71.97, 71.33, 68.56, 68.52, 67.11, 62.09, 53.93, 53.75, 52.63, 33.42, 20.66, 20.64, 20.34.

HRMS (ESI): calc. for $C_{32}H_{35}F_3N_2O_{11}SNa$ $(M+Na)^+$: 735.1806; found: 735.1818.



5

78%, α:β > 20:1

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.62 (d, *J* = 1.9 Hz, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.56 (m, 3H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.34 – 7.27 (m, 2H), 6.00 (d, *J* = 8.6 Hz, 1H), 5.49 (t, *J* = 9.7 Hz, 1H), 5.27 (d, *J* = 5.6 Hz, 1H), 5.14 – 5.06 (m, 1H), 4.74 – 4.69 (m, 1H), 4.52 (dd, *J* = 10.1, 3.0 Hz, 1H), 4.42 (qd, *J* = 10.6, 7.3 Hz, 2H), 4.28 (dd, *J* = 12.3, 5.1 Hz, 1H), 4.24 – 4.19 (m, 2H), 3.92 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.74 (s, 3H), 3.20 (dd, *J* = 14.3, 5.5 Hz, 1H), 2.99 (dd, *J* = 14.3, 4.1 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 1.87 (s, 3H).

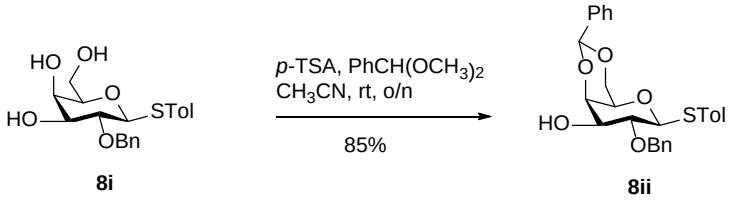
^{13}C NMR (CDCl3, 150 MHz): δ 170.96, 170.55, 169.85, 169.57, 160.36, 155.72, 143.64, 141.31, 141.28, 132.26, 130.90, 129.05, 127.71, 127.69, 127.06, 127.03, 125.49, 125.46, 125.03, 119.97, 119.94, 85.43, 72.03, 71.33, 68.64, 68.63, 67.03, 62.21, 54.05, 52.63, 47.11, 33.77, 20.65, 20.60, 20.33.

HRMS (ESI): calc. for $C_{39}H_{39}F_3N_2O_{11}SNa$ $(M+Na)^+$: 823.2119; found: 823.2116.

4. Preparation of Glycosyl Donors

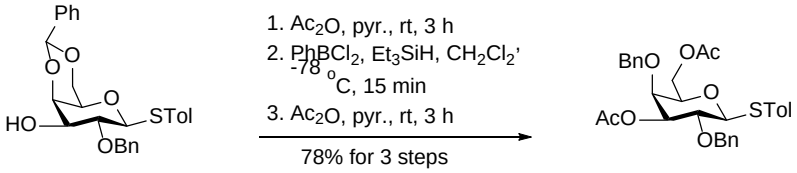
Glycosyl donors **1**, **6** and **7** were synthesis according to our former literature.[1]

4.1 Preparation of glycosyl donor 8



8i **8ii**

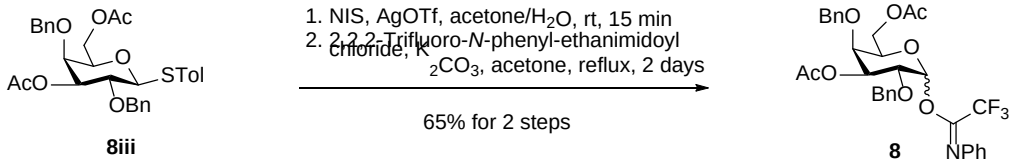
To a solution of **8i** (3.18 g, 8.46 mmol) in CH_3CN (80 mL) were added benzaldehyde dimethyl acetal (1.9 mL, 12.67 mmol) and *p*-TSA (161 mg, 0.846 mmol). After the reaction mixture was stirred at room temperature for overnight, it was quenched with Et_3N and concentrated. The residue was subjected to flush silica gel column chromatography (1:1.5, EtOAc–hexane) to give **8ii** (3.34 g, 85%) as a white foam. R_f 0.30 (1:1.5, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.62 (d, J = 8.1 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.46 – 7.39 (m, 5H), 7.36 (t, J = 7.4 Hz, 2H), 7.30 (d, J = 7.3 Hz, 1H), 7.07 (d, J = 7.9 Hz, 2H), 5.54 (s, 1H), 4.79 (d, J = 10.6 Hz, 1H), 4.70 (d, J = 10.6 Hz, 1H), 4.57 (d, J = 9.5 Hz, 1H), 4.38 (dd, J = 12.4, 1.3 Hz, 1H), 4.17 (d, J = 3.6 Hz, 1H), 4.00 (dd, J = 12.4, 1.4 Hz, 1H), 3.78 (dd, J = 9.0, 3.6 Hz, 1H), 3.62 (t, J = 9.3 Hz, 1H), 3.45 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 138.38, 137.71, 133.26, 129.65, 129.28, 128.88, 128.38, 128.20, 128.11, 127.78, 126.61, 101.37, 86.34, 77.10, 75.76, 75.23, 74.38, 69.75, 69.28, 21.19. HR ESI-TOF MS (m/z): calcd for $C_{27}H_{28}O_5SNa$ $[M + Na]^+$, 487.1550; found, 487.1555.



8ii **8iii**

A solution of **8ii** (2.0 g, 4.31 mmol) in 50 mL anhydrous pyridine was added acetic anhydride (814 µL, 8.62 mmol) and stirred at room temperature for 3 h. The reaction mixture was concentrated under reduced pressure, and the residue was subjected to flush silica gel column chromatography (1:3, EtOAc–hexane). The obtained intermediate was dissolved in 50 mL anhydrous CH_2Cl_2, $PhBCl_2$ (1.12 mL, 8.62 mmol) and Et3SiH (1.37 mL, 8.62 mmol) were added at -78 ºC under a N_2

atmosphere. 15 min later, the reaction was quenched by addition of CH_3OH and Et_3N. The mixture was concentrated and purified by silica gel column chromatograpgy (1:2, EtOAc–hexane) to afford the intermediate product as syrup. It was dissolved in pyridine (50 mL) again, followed by addition of acetic anhydride (814 μL, 2.21 mmol). After the reaction mixture was stirred at room temperature for 3 h, it was concentrated and the residue was subjected to flush silica gel column chromatography (1:4, EtOAc–hexane) to give **8iii** (1.85 g, 78% for 3 steps) as a serup. R_f 0.50 (1:3, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48 (d, J = 8.1 Hz, 2H), 7.39 – 7.28 (m, 10H), 7.06 (d, J = 7.9 Hz, 2H), 4.96 (dd, J = 9.7, 2.9 Hz, 1H), 4.87 (d, J = 11.0 Hz, 1H), 4.68 (d, J = 11.5 Hz, 1H), 4.65 – 4.52 (m, 3H), 4.30 (dd, J = 11.1, 6.7 Hz, 1H), 4.10 (dd, J = 11.2, 6.3 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.71 (t, J = 6.5 Hz, 1H), 2.33 (s, 3H), 2.02 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.40, 170.29, 138.06, 137.69, 137.63, 132.46, 129.71, 129.60, 128.38, 128.34, 127.99, 127.96, 127.88, 127.77, 88.05, 77.00, 75.59, 75.38, 75.36, 74.85, 74.13, 62.60, 21.12, 20.90, 20.78. HR ESI-TOF MS (m/z): calcd for $C_{31}H_{34}O_7SNa$ [M + Na]$^+$, 573.1917; found, 573.1911.

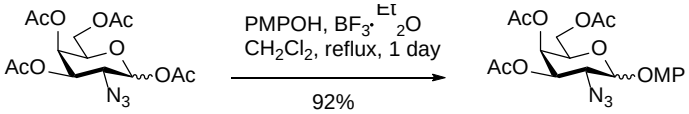


To a solution of **8iii** (1.5 g, 2.73 mmol) in acetone-H_2O (v/v, 50/1, 30 mL) were added NIS (1.23 g, 5.45 mmol) and AgOTf (140 mg, 0.545 mmol). After the reaction mixture was stirred at room temperature for 15 min, it was quenched with Et_3N, and concentrated. The residue was subjected to flush silica gel column chromatography (1:2, EtOAc–hexane) to give a hemiacetal. To a solution of this hemiacetal in anhydrous acetone (30 mL) was added 2,2,2-Trifluoro-*N*-phenyl-ethanimidoyl chloride (1.31 mL, 8.19 mmol) and K_2CO_3 (752 mg, 5.45 mmol) under N_2 protection. After 2 days of stirring under reflux, the mixture was filtered and concentrated in vacuum, and the residue was purified by Et_3N-neutralized silica gel column with EtOAc and hexanes (1:4) as the eluent to afford compound **8** (1.09 g, 65% for 2 steps) as a syrup.

For α anomer: R_f 0.55 (1:3, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.39 – 7.22 (m, 12H), 7.09 (t, J = 7.5 Hz, 1H), 6.74 (s, 2H), 6.54 (s, 1H), 5.30 (d, J = 10.0 Hz, 1H), 4.70 (dd, J = 26.1, 11.6 Hz, 3H), 4.53 (d, J = 11.3 Hz, 1H), 4.20 (d, J = 7.4 Hz, 3H), 4.10 (d, J = 8.1 Hz, 2H), 2.05 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.32, 170.30, 137.68, 137.31, 128.70, 128.51,

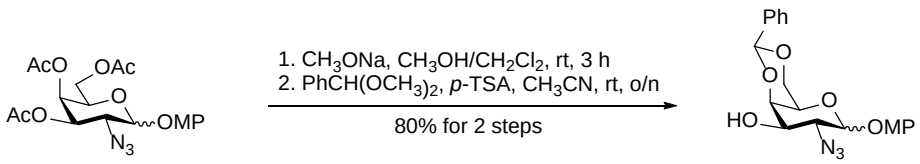
128.43, 128.11, 127.90, 127.60, 119.34, 75.29, 74.51, 73.27, 72.91, 72.11, 70.65, 62.38, 20.96, 20.72. HR ESI-TOF MS (m/z): calcd for $C_{31}H_{35}N_3O_7SNa$ $[M + Na]^+$, 616.2093; found, 616.2088. For β anomer: R_f 0.50 (1:3, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.42 – 7.27 (m, 12H), 7.11 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.6 Hz, 2H), 5.70 (s, 1H), 4.97 (s, 1H), 4.84 (d, J = 11.5 Hz, 1H), 4.69 (d, J = 11.4 Hz, 2H), 4.55 (d, J = 11.5 Hz, 1H), 4.27 (dd, J = 11.0, 6.6 Hz, 1H), 4.16 – 4.02 (m, 2H), 3.94 (s, 1H), 3.75 (s, 1H), 1.99 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.25, 170.24, 143.33, 137.67, 137.31, 128.70, 128.50, 128.42, 128.25, 128.11, 128.02, 127.96, 124.30, 119.14, 97.03, 75.48, 75.04, 75.02, 74.61, 73.47, 72.89, 61.99, 20.83, 20.68. HR ESI-TOF MS (m/z): calcd for $C_{32}H_{32}F_3NO_8Na$ $[M + Na]^+$, 638.1972; found, 638.1976.

4.2 Preparation of glycosyl donor 9



9i **9ii**

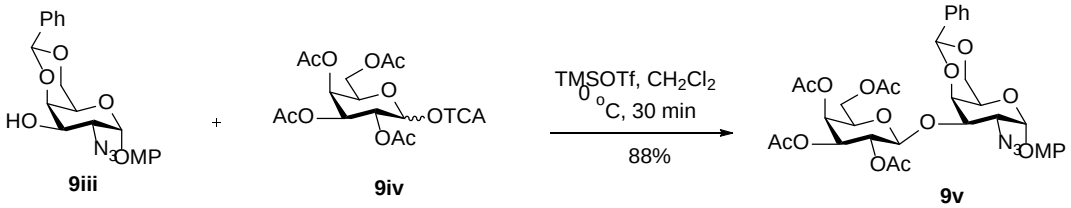
To a solution of **9i** (4.5 g, 12.03 mmol) in CH_2Cl_2 (70 mL) was added 4-Methoxyphenol (4.475 g, 36.09 mmol) and boron trifluoride diethyl etherate (2.97 mL, 24.06 mmol) at room temperature. After the reaction mixture was stirred under reflux for 1 day, it was diluted with CH_2Cl_2 and washed with 1 N NaOH and brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was subjected to flush silica gel column chromatography (1:3, EtOAc–hexane) to give **9ii** (4.85 g, 92%) as an inseparable α/β mixture. R_f 0.50 (1:2, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.04 (dd, J = 9.0, 1.4 Hz, 5H), 6.92 – 6.76 (m, 5H), 5.57 (dd, J = 11.1, 3.2 Hz, 1.7H), 5.51 (dd, J = 4.6, 2.2 Hz, 3H), 5.37 (d, J = 3.3 Hz, 1H), 4.84 (dd, J = 10.9, 3.4 Hz, 1H), 4.79 (d, J = 8.1 Hz, 1H), 4.39 (t, J = 6.6 Hz, 1.7H), 4.21 (dd, J = 11.3, 6.9 Hz, 1H), 4.17 – 4.04 (m, 5.5H), 4.00 – 3.90 (m, 1.7H), 3.84 – 3.68 (m, 8.5H), 2.17 (s, 3H), 2.16 (s, 5H), 2.08 (s, 5H), 2.07 (s, 3H), 2.04 (s, 3H), 1.98 (s, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.26, 170.01, 169.96, 169.78, 169.73, 155.91, 155.63, 150.78, 150.19, 118.71, 118.21, 114.67, 114.58, 101.89, 97.94, 70.92, 68.13, 67.48, 67.37, 66.18, 61.49, 61.25, 60.62, 60.34, 57.35, 55.62, 20.63, 20.58, 20.57. HR ESI-TOF MS (m/z): calcd for $C_{19}H_{23}N_3O_9Na$ $[M + Na]^+$, 460.1327; found, 460.1328.



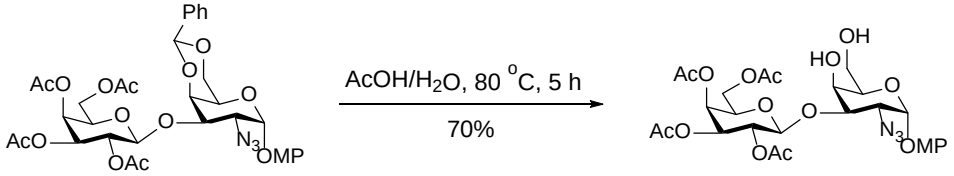
To a solution of **9ii** (4.2 g, 9.59 mmol) in CH_3OH/CH_2Cl_2 (v/v, 3/1, 80 mL) was added CH_3ONa (259 mg, 4.79 mmol). After the reaction mixture was stirred at room temperature for 3 h, it was quenched with Amberlyst 15 hydrogen resin, and concentrated. The obtained residue was dissolved in CH_3CN (80 mL), benzaldehyde dimethyl acetal (2.16 mL, 14.39 mmol) and *p*-TSA (182 mg, 0.959 mmol) were added. After the reaction mixture was stirred at room temperature for overnight, it was quenched with Et_3N and concentrated. The residue was subjected to flush silica gel column chromatography (1:2, EtOAc–hexane) to give **9iii** (3.07 g, 80% for 2 steps) as a white solid.

For α anomer: R_f 0.55 (1:2, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.55 – 7.48 (m, 2H), 7.44 – 7.35 (m, 3H), 7.12 – 7.02 (m, 2H), 6.88 – 6.81 (m, 2H), 5.60 (s, 1H), 5.58 (d, J = 3.3 Hz, 1H), 4.39 (dd, J = 10.5, 3.7 Hz, 1H), 4.37 – 4.33 (m, 1H), 4.27 (dd, J = 12.7, 1.4 Hz, 1H), 4.06 (dd, J = 12.7, 1.7 Hz, 1H), 3.88 (d, J = 0.9 Hz, 1H), 3.78 (s, 3H), 3.70 (dd, J = 10.5, 3.3 Hz, 1H), 2.60 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.28, 150.52, 137.21, 129.40, 128.35, 126.20, 117.56, 114.72, 101.27, 98.14, 75.35, 69.14, 67.39, 63.36, 60.49, 55.65. HR ESI-TOF MS (m/z): calcd for $C_{31}H_{35}N_3O_7SNa$ $[M + Na]^+$, 616.2093; found, 616.2088.

For β anomer: R_f 0.20 (1:2, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 (dd, J = 6.6, 3.0 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.11 – 7.04 (m, 2H), 6.87 – 6.79 (m, 2H), 5.57 (s, 1H), 4.74 (d, J = 8.1 Hz, 1H), 4.36 (dd, J = 12.5, 1.4 Hz, 1H), 4.22 – 4.17 (m, 1H), 4.08 (dd, J = 12.6, 1.7 Hz, 1H), 3.87 (dd, J = 10.2, 8.1 Hz, 1H), 3.78 (s, 3H), 3.61 (dd, J = 10.2, 3.8 Hz, 1H), 3.50 (d, J = 1.1 Hz, 1H), 2.66 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.68, 151.06, 137.24, 129.41, 128.31, 126.41, 118.90, 114.53, 101.79, 101.44, 74.33, 71.34, 68.92, 66.63, 63.74, 55.63. HR ESI-TOF MS (m/z): calcd for $C_{20}H_{21}N_3O_6Na$ $[M + Na]^+$, 422.1323; found, 422.1313.



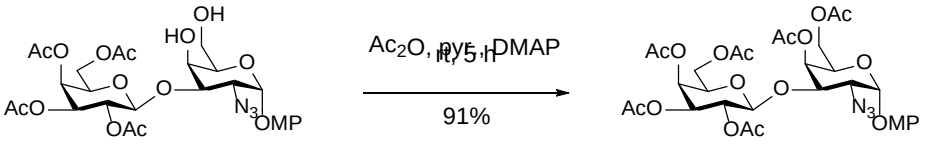
To a stirred mixture of donor **9iv** (4.06 g, 8.25 mmol), acceptor **9iii** (2.2 g, 5.5 mmol), and freshly activated MS 4Å (5 g), in anhydrous CH_2Cl_2 (100 mL) was added TMSOTf (99.4 μL, 0.55 mmol) under N_2 protection at 0 °C. After the reaction mixture was stirred for another 30 min, it was neutralized with Et_3N, filtered, and concentrated. The residue was subjected to silica gel column chromatography with EtOAc and hexanes (1:2) as the eluent to afford the **9v** (3.53 g, 88%) as a syrup. R_f 0.45 (1:1, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.59 – 7.52 (m, 2H), 7.42 – 7.31 (m, 3H), 7.10 – 7.01 (m, 2H), 6.88 – 6.80 (m, 2H), 5.60 (d, J = 3.3 Hz, 1H), 5.58 (s, 1H), 5.44 – 5.40 (m, 1H), 5.32 (dd, J = 10.4, 7.9 Hz, 1H), 5.06 (dd, J = 10.4, 3.5 Hz, 1H), 4.86 (d, J = 7.9 Hz, 1H), 4.46 (d, J = 3.1 Hz, 1H), 4.32 (dd, J = 10.8, 3.3 Hz, 1H), 4.24 (ddd, J = 17.8, 11.9, 3.9 Hz, 2H), 4.14 (dd, J = 10.0, 5.3 Hz, 1H), 4.04 (dd, J = 12.5, 1.2 Hz, 1H), 3.97 (ddd, J = 14.4, 9.1, 5.0 Hz, 2H), 3.84 (s, 1H), 3.77 (s, 3H), 2.17 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.27, 170.24, 170.12, 169.41, 155.33, 150.46, 137.54, 128.89, 128.13, 126.09, 117.61, 114.72, 102.52, 100.60, 98.32, 75.79, 75.67, 71.03, 70.91, 69.07, 68.68, 66.97, 63.67, 61.40, 58.74, 55.63, 20.71, 20.70, 20.68, 20.54. HR ESI-TOF MS (m/z): calcd for $C_{34}H_{39}N_3O_{15}Na$ $[M + Na]^+$, 752.2273; found, 752.2278.



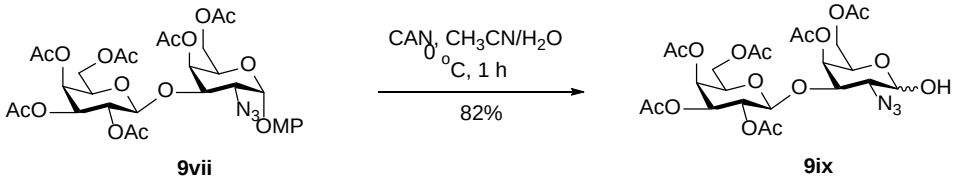
9v **9vi**

Compound **9v** (3.3 g, 4.52 mmol) was dissolved in mixed solvent of acetic acid/H_2O (4:1, 50 mL). After the reaction mixture was stirred at 80 °C for 5 h, it was concentrated and the residue was subjected to silica gel column chromatography with acetone and hexanes (1:2) as the eluent to afford the **9vi** (2.03 g, 70%) as a syrup. R_f 0.50 (1:1, acetone–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.06 – 6.98 (m, 2H), 6.85 – 6.78 (m, 2H), 5.46 (d, J = 3.5 Hz, 1H), 5.40 (d, J = 2.7 Hz, 1H), 5.29 (dd, J = 10.5, 8.0 Hz, 1H), 5.05 (dd, J = 10.5, 3.4 Hz, 1H), 4.78 (d, J = 8.0 Hz, 1H), 4.27 (d, J = 1.7 Hz, 1H), 4.22 (dd, J = 10.5, 3.1 Hz, 1H), 4.17 (dd, J = 11.5, 7.3 Hz, 1H), 4.10 (dd, J = 11.5, 5.5 Hz, 1H), 4.03 (t, J = 5.6 Hz, 1H), 3.98 (t, J = 6.6 Hz, 1H), 3.88 (dd, J = 11.7, 5.6 Hz, 1H), 3.80 (dd, J = 11.7, 5.1 Hz, 1H), 3.77 – 3.73 (m, 4H), 2.15 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.44, 170.11, 170.04, 169.63, 155.50, 150.40, 118.28, 114.72, 101.98, 98.40, 78.16, 71.29, 70.66, 69.93, 69.23, 68.39, 66.99, 62.44, 61.55, 58.42, 55.61,

20.63, 20.58, 20.56, 20.50. HR ESI-TOF MS (m/z): calcd for $C_{27}H_{35}N_3O_{15}Na$ [M + Na]$^+$, 664.1960; found, 664.1969.

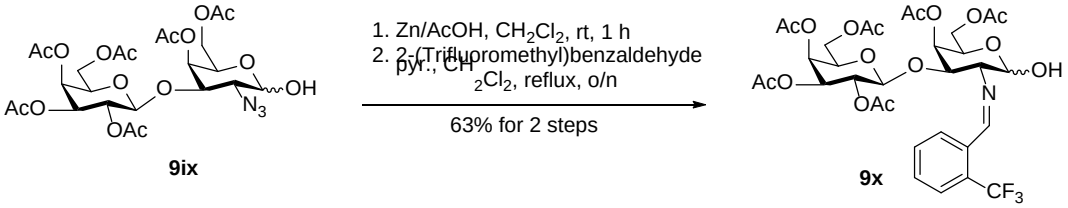


To a solution of **9vi** (1.8 g, 2.80 mmol) in pyridine (30 mL) was added acetic anhydride (1.06 mL, 11.21 mmol) and DMAP (34.2 mg, 0.28 mmol). After the reaction mixture was stirred at room temperature for 5 h, it was concentrated and the residue was subjected to flush silica gel column chromatography (1:2, EtOAc–hexane) to give **9vii** (1.85 g, 91%) as a serup. R_f 0.50 (1:1, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.04 – 6.97 (m, 2H), 6.83 – 6.78 (m, 2H), 5.51 (d, J = 3.2 Hz, 1H), 5.44 (d, J = 3.5 Hz, 1H), 5.36 – 5.34 (m, 1H), 5.19 (dd, J = 10.5, 7.8 Hz, 1H), 5.01 (dd, J = 10.5, 3.4 Hz, 1H), 4.75 (d, J = 7.8 Hz, 1H), 4.30 – 4.26 (m, 2H), 4.15 (dt, J = 11.0, 5.2 Hz, 2H), 4.08 (dd, J = 7.0, 4.2 Hz, 1H), 3.99 – 3.90 (m, 2H), 3.78 – 3.72 (m, 4H), 2.13 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.36, 170.33, 170.19, 170.02, 169.64, 169.47, 155.62, 150.20, 149.05, 136.57, 118.43, 114.61, 101.56, 98.02, 74.73, 70.84, 70.77, 69.32, 68.77, 68.13, 66.78, 62.54, 61.06, 59.40, 55.59, 20.69, 20.62, 20.60, 20.59, 20.50. HR ESI-TOF MS (m/z): calcd for $C_{31}H_{39}N_3O_{17}Na$ [M + Na]$^+$, 748.2172; found, 748.2162.

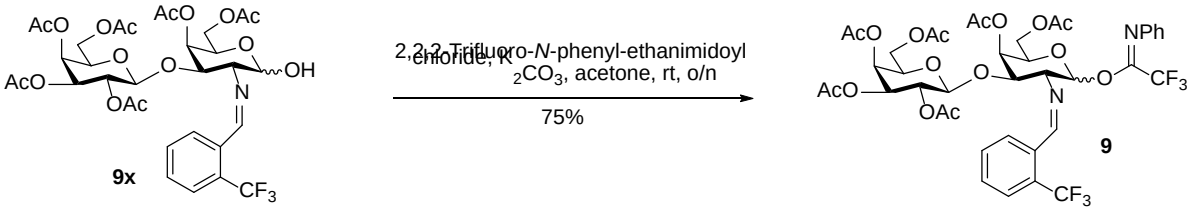


To a solution of **9vii** (2.5 g, 3.44 mmol) in acetonitrile/H_2O (1:1, 60 mL) was added cerium ammonium nitrate (5.66 g, 10.33 mmol) at 0 °C. After the reaction mixture was stirred at the same temperature for 1 h, it was diluted with ethyl acetate and washed with aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was subjected to flush silica gel column chromatography (1.5:1, EtOAc–hexane) to give **9ix** (1.75 g, 82%) as a α/β mixture. R_f 0.30 (1.5:1, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.48 (d, J = 2.9 Hz, 1.1H), 5.40 (d, J = 3.4 Hz, 1.1H), 5.37 – 5.32 (m, 2.3H), 5.16 (ddd, J = 15.2, 10.5, 7.8 Hz, 1.8H), 5.00 (dd, J = 10.4, 3.4 Hz, 1.7H), 4.71 (dd, J = 12.0, 7.8 Hz, 1.8H), 4.60 (d, J = 6.9 Hz, 1H), 4.37 – 4.32 (m, 1.1H), 4.22 – 4.05 (m, 7.4H), 3.98 (ddd, J = 20.8, 11.7, 7.4 Hz, 2.1H), 3.89 (dt, J = 16.9, 6.5 Hz, 1.9H),

3.81 – 3.76 (m, 1.3H), 3.73 (dd, *J* = 10.6, 3.5 Hz, 1.2H), 3.55 (p, *J* = 10.3 Hz, 1.7H), 3.24 (s, 1.3H), 2.15 (d, *J* = 0.4 Hz, 4.6H), 2.13 (d, *J* = 3.2 Hz, 4.4H), 2.08 (s, 2.2H), 2.06 (d, *J* = 0.4 Hz, 6.7H), 2.05 (d, *J* = 1.3 Hz, 4.4H), 2.04 (s, 1.9H), 1.97 (d, *J* = 2.3 Hz, 4.5H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 101.45, 101.42, 96.35, 92.32, 77.35, 74.40, 71.70, 70.84, 70.81, 70.77, 70.63, 69.52, 68.81, 68.77, 68.12, 67.47, 66.80, 66.75, 64.49, 62.76, 62.58, 61.06, 60.97, 60.39, 60.16, 20.77, 20.73, 20.66, 20.62, 20.60, 20.52. HR ESI-TOF MS (m/z): calcd for $C_{24}H_{33}N_3O_{16}Na$ $[M + Na]^+$, 642.1753; found, 642.1759.



To a solution of **9ix** (1.7 g, 2.74 mmol) in CH_2Cl_2 (30 mL) was added zinc powder (5.35 g, 82.25 mmol) and acetic acid (4.7 mL, 82.25 mmol). After the reaction mixture was stirred at room temperature for 1 h, it was filtered and concentrated. The obtained residue was dissolved in pyridine/CH_2Cl_2 (1:10, 30 mL), 2-(Trifluoromethyl) benzaldehyde (433 µL, 3.29 mmol) was added. After the reaction mixture was stirred under reflux for overnight, it was concentrated. The residue was subjected to flush silica gel column chromatography (2:1, EtOAc–hexane) to give **9x** (1.3 g, 63% for 2 steps) as a α/β mixture. R_f 0.30 (2:1, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 8.83 (d, *J* = 16.1 Hz, 2.2H), 8.32 (dd, *J* = 21.5, 7.4 Hz, 2.2H), 7.86 (d, *J* = 7.2 Hz, 2.3H), 7.77 (t, *J* = 7.3 Hz, 1H), 7.75 – 7.65 (m, 3.5H), 5.66 (s, 1H), 5.58 (s, 1.6H), 5.44 (s, 2.2H), 5.34 (s, 1H), 5.17 (dd, *J* = 12.3, 5.9 Hz, 2.2H), 5.05 – 4.96 (m, 3.6H), 4.73 (d, *J* = 7.4 Hz, 2.2H), 4.67 (s, 1H), 4.58 (d, *J* = 10.3 Hz, 1H), 4.44 – 4.37 (m, 2.5H), 4.34 – 4.13 (m, 11H), 4.09 (d, *J* = 3.6 Hz, 1.7H), 4.04 – 3.96 (m, 3H), 3.80 (s, 1H), 3.69 (t, *J* = 8.3 Hz, 1.6H), 2.28 (d, *J* = 13.7 Hz, 13H), 2.25 – 2.16 (m, 15H), 2.03 (d, *J* = 1.3 Hz, 5.4H), 1.62 (d, *J* = 11.0 Hz, 5.4H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 170.66, 170.39, 170.38, 170.28, 170.06, 170.02, 168.77, 161.72, 161.48, 133.49, 132.11, 131.99, 131.00, 130.75, 129.27, 128.46, 128.23, 125.84, 124.80, 122.98, 100.68, 95.41, 94.16, 77.43, 74.07, 73.72, 71.84, 70.83, 70.77, 70.63, 70.61, 70.25, 68.93, 68.85, 68.69, 67.95, 67.83, 66.72, 66.68, 63.03, 63.01, 60.98, 60.94, 60.37, 20.98, 20.81, 20.77, 20.76, 20.72, 20.64, 20.59, 20.43, 19.87. HR ESI-TOF MS (m/z): calcd for $C_{32}H_{38}F_3NO_{16}Na$ $[M + Na]^+$, 772.2035; found, 772.2041.

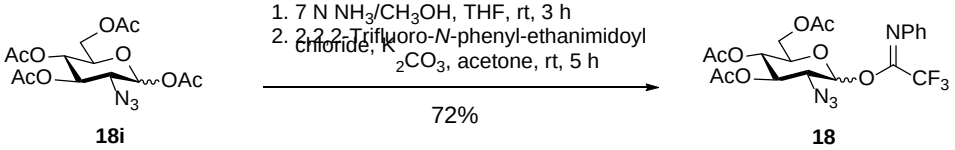


To a solution of **9x** (1.04 g, 1.39 mmol) in anhydrous acetone (12 mL) was added 2,2,2-Trifluoro-*N*-phenyl-ethanimidoyl chloride (443 μL, 2.77 mmol) and K_2CO_3 (382 mg, 2.77 mmol) under N_2 protection. After overnight stirring at room temperature, the mixture was filtered and concentrated in vacuum, and the residue was purified by Et_3N-neutralized silica gel column with EtOAc and hexanes (1:1) as the eluent to afford compound **9** (0.96 g, 75%) as a yellow solid.

For α anomer: R_f 0.65 (1.5:1, EtOAc–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (s, 1H), 8.26 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 7.7 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 6.9 Hz, 2H), 6.25 (s, 1H), 5.61 (d, J = 2.3 Hz, 1H), 5.32 (d, J = 3.3 Hz, 1H), 5.04 (dd, J = 10.4, 7.9 Hz, 1H), 4.87 (dd, J = 10.4, 3.4 Hz, 1H), 4.61 (d, J = 7.8 Hz, 1H), 4.52 – 4.40 (m, 2H), 4.28 (dd, J = 11.7, 4.7 Hz, 1H), 4.19 – 3.98 (m, 4H), 3.89 (t, J = 6.6 Hz, 1H), 2.16 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.89 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.47, 170.40, 170.23, 170.01, 169.80, 168.79, 161.70, 133.39, 132.07, 131.02, 128.96, 128.61, 128.35, 125.83, 124.23, 119.76, 119.27, 100.60, 70.88, 70.83, 70.37, 68.98, 68.51, 68.04, 66.80, 62.62, 61.14, 20.72, 20.59, 20.58, 20.45, 19.90. HR ESI-TOF MS (m/z): calcd for $C_{40}H_{42}F_6N_2O_{16}Na$ $[M + Na]^+$, 943.2331; found, 943.2338.

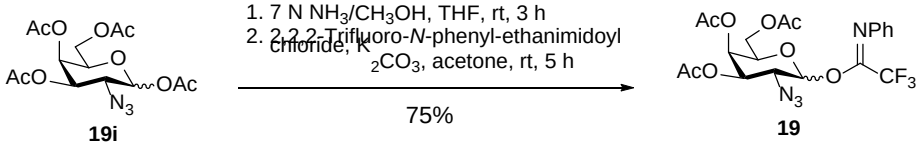
For β anomer: R_f 0.55 (1.5:1, EtOAc–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (d, J = 1.4 Hz, 1H), 8.17 (d, J = 7.7 Hz, 1H), 7.64 (ddd, J = 28.0, 21.1, 7.6 Hz, 3H), 7.23 (dd, J = 14.8, 7.0 Hz, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 7.7 Hz, 2H), 5.83 (s, 1H), 5.46 (d, J = 2.9 Hz, 1H), 5.30 (d, J = 3.2 Hz, 1H), 5.02 (dd, J = 10.4, 7.9 Hz, 1H), 4.83 (dd, J = 10.5, 3.4 Hz, 1H), 4.59 (d, J = 7.8 Hz, 1H), 4.28 – 3.93 (m, 6H), 3.85 (t, J = 6.7 Hz, 2H), 2.16 (s, 3H), 2.11 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.87 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.46, 170.32, 170.21, 169.99, 169.88, 168.73, 162.52, 143.25, 133.28, 132.06, 131.03, 129.73, 129.42, 128.65, 128.22, 125.97, 125.91, 125.19, 124.29, 122.46, 119.05, 100.78, 95.27, 77.16, 72.64, 71.48, 70.74, 70.70, 68.82, 67.65, 66.70, 62.26, 61.03, 20.67, 20.63, 20.62, 20.56, 20.40, 19.86. HR ESI-TOF MS (m/z): calcd for $C_{40}H_{42}F_6N_2O_{16}Na$ $[M + Na]^+$, 943.2331; found, 943.2336.

4.3 Preparation of glycosyl donor 18



To a solution of **18i** (1.3 g, 3.48 mmol) in THF (20 mL) was added 7 N NH_3/CH_3OH (3 mL). After the reaction mixture was stirred at room temperature for 1 h, it was diluted with ethyl acetate and washed with 1 N HCl and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The obtained residue was dissolved in anhydrous acetone (20 mL), 2,2,2-Trifluoro-*N*-phenyl-ethanimidoyl chloride (1.11 mL, 6.96 mmol) and K_2CO_3 (960 mg, 6.96 mmol) were added under N_2 protection. After 5 h stirring at room temperature, the mixture was filtered and concentrated in vacuum, and the residue was purified by Et_3N-neutralized silica gel column with EtOAc and hexanes (1:4) as the eluent to afford **18** (1.26 g, 72%) as a α/β mixture. R_f 0.50 (1:2, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.32 (td, J = 7.9, 4.2 Hz, 2.5H), 7.14 (dt, J = 11.4, 5.7 Hz, 1.3H), 6.84 (t, J = 8.2 Hz, 2.6H), 6.48 (s, 1H), 5.62 (s, 1H), 5.50 (t, J = 9.9 Hz, 0.6H), 5.14 (t, J = 9.7 Hz, 1H), 5.06 (s, 1H), 4.36 – 4.22 (m, 1H), 4.20 – 4.03 (m, 1.5H), 3.87 – 3.65 (m, 2.3H), 2.11 (s, 3H), 2.10 (s, 2H), 2.09 (s, 3H), 2.07 (s, 2H), 2.06 (s, 3H), 2.02 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.44, 170.39, 169.77, 169.56, 169.48, 142.79, 128.83, 124.70, 119.19, 119.09, 95.23, 92.95, 72.70, 72.49, 70.59, 70.03, 67.74, 62.78, 61.37, 60.44, 20.61, 20.59, 20.52, 20.50. HR ESI-TOF MS (m/z): calcd for $C_{20}H_{21}F_3N_4O_8Na$ $[M + Na]^+$, 525.1204; found, 525.1213.

4.4 Preparation of glycosyl donor 19



Compound **19** (678 mg, 75%) was prepared from **19i** (672 mg, 1.8 mmol) by the same procedure as the synthesis of **18**. R_f 0.55 (1:2, EtOAc–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) of α/β anomers δ: 7.36 – 7.27 (m, 4.2H), 7.13 (t, J = 7.5 Hz, 2H), 6.84 (d, J = 7.8 Hz, 4H), 6.47 (s, 0.5H), 5.60 (s, 0.5H), 5.53 (s, 1H), 5.41 – 5.30 (m, 2H), 4.87 (d, J = 8.9 Hz, 1H), 4.31 (d, J = 6.0 Hz, 0.8H), 4.19 – 4.05 (m, 5H), 3.96 (dd, J = 24.4, 10.4 Hz, 3H), 2.18 (s, 3.4H), 2.16 (s, 2.7H), 2.08 (s, 2.7H), 2.07 (s, 3.4H), 2.05 (s, 2.7H), 2.00 (s, 3.4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.21, 169.91, 169.58, 142.87, 128.83, 124.66, 119.23, 119.07, 95.47, 93.32, 71.75, 71.13, 69.10, 68.61, 66.83, 66.03,

61.20, 60.90, 59.86, 56.90, 20.58, 20.54, 20.52. HR ESI-TOF MS (m/z): calcd for $C_{20}H_{21}F_3N_4O_8Na$ $[M + Na]^+$, 525.1204; found, 525.1217.

5. Preparation of Thiol Nucleophiles

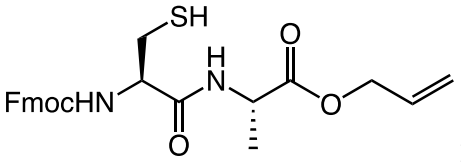
5.1 Preparation of cysteine-containing acceptors

General procedure for peptide coupling:

To a stirred solution of *N*-protected amino acid in dry DMF (0.5 M) was added HATU (1.1 eq), DIPEA (3.0 eq) followed by *C*-protected amino acid (1.05 eq) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at same temperature for 3 to 6 h (TLC control). The reaction mixture was quenched with water and extracted with EtOAc (3×). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The obtained crude product was purified by flash chromatography.

General procedure for the removal of trityl protection:

The peptide was dissolved in dry dichloromethane (0.1 M) and purged with was argon gas for few minutes, then was added TIPS (2.0 eq) followed TFA (10.0 eq) dropwise under argon atmosphere at room temperature. The reaction mixture was allowed to stir at same temperature for 1-2 hours (TLC control). The reaction mixture was evaporated, to the obtained crude gummy crude product was added diethyl ether (10 vol). The solids precipitated were filtered using sintered funnel and washed again with diethyl ether to get pure product (no column purification required).



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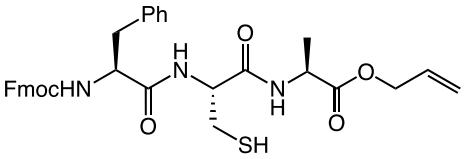
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 6.71 (d, *J* = 5.2 Hz, NH), 5.90 (ddt, *J* = 16.0, 10.6, 5.6 Hz, 1H), 5.72 (s, NH), 5.30 (dd, *J* = 26.5, 13.7 Hz, 2H), 4.70 – 4.53 (m, 3H), 4.53 – 4.32 (m, 3H), 4.23 (t, *J*

= 6.7 Hz, 1H), 3.12 – 2.98 (m, 1H), 2.74 (bs, 1H), 1.69 (t, *J* = 7.2 Hz, SH), 1.45 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 172.1, 169.1, 143.6, 141.3, 141.30, 131.3, 127.8, 127.1, 125.0, 120.0, 120.0, 119.1, 67.2, 66.2, 56.0, 48.5, 47.1, 27.1, 18.2.

HRMS (ESI): calc. for $C_{24}H_{26}N_2O_5SNa$ $[M+Na]^+$: 477.1455; found: 477.1454.

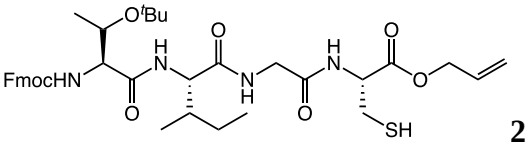


13

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.12 (m, *7*H), 6.89 (d, *J* = 26.1 Hz, NH), 5.87 (ddt, *J* = 16.4, 10.9, 5.8 Hz, 1H), 5.42 – 5.19 (m, 2H, NH), 4.68 – 4.45 (m, 5H), 4.43 – 4.27 (m, 2H), 4.17 (t, *J* = 6.9 Hz, 1H), 3.21 – 2.95 (m, 3H), 2.73 – 2.61 (m, 1H), 1.63 (t, *J* = 7.2 Hz, SH), 1.38 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 171.9, 170.9, 168.7, 143.6, 141.3, 135.9, 131.4, 129.2, 128.9, 128.8, 127.8, 127.3, 127.1, 124.9, 120.0, 118.8, 67.2, 66.1, 56.3, 54.2, 48.4, 47.0, 38.1, 26.6, 17.9.

HRMS (ESI): calc. for $C_{33}H_{35}N_3O_6SNa$ $[M+Na]^+$: 624.2139; found: 624.2134.

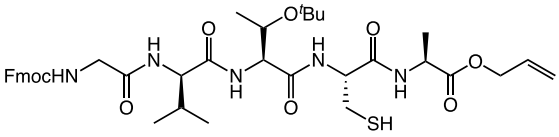


21

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 6.7 Hz, NH), 7.39 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 6.92 (bd, NH), 6.12 (m, NH), 5.94 – 5.80 (m, 1H), 5.36 – 5.18 (m, 2H), 4.87 (td, *J* = 12.5, 4.9 Hz, 1H), 4.64 (d, *J* = 4.9 Hz, 2H), 4.44 – 4.34 (m, 2H), 4.33 – 4.06 (m, 5H), 3.88 (ddd, *J* = 34.4, 16.8, 5.3 Hz, 1H), 3.08 – 2.98 (m, 2H), 2.05 – 1.93 (m, 1H), 1.84 – 1.69 (m, 1H), 1.65 – 1.50 (m, 2H), 1.33 (s, 9H), 1.21 – 1.04 (m, 4H), 1.04 – 0.86 (m, 6H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 171.7, 170.4, 170.1, 169.5, 156.1, 143.8, 143.62, 141.3, 131.3, 131.3, 127.7, 127.0, 125.1, 120.1, 119.2, 76.0, 67.2, 66.9, 66.4, 59.3, 58.4, 54.1, 47.2, 43.2, 36.3, 28.2, 26.6, 25.04, 16.8, 15.8, 11.4.

HRMS (ESI): calc. for $C_{37}H_{51}N_4O_8S$ $[M+H]^+$: 711.3432; found: 711.3435.



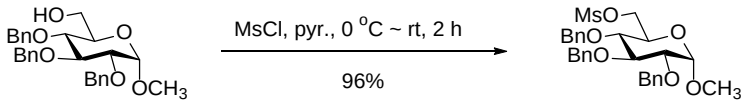
23

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (s, NH), 7.94 (s, NH), 7.74 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 9.6 Hz, 2H), 7.05 (s, NH), 6.12 (s, NH), 5.90 – 5.73 (m, 1H), 5.21 (dd, *J* = 26.3, 13.8 Hz, 2H), 5.06 (s, 1H), 4.83 – 4.73 (m, 1H), 4.65 – 4.51 (m, 3H), 4.45 – 4.15 (m, 3H), 4.08 – 3.87 (m, 3H), 3.09 – 2.98 (m, 1H), 2.87 – 2.72 (m, 1H), 2.02 (dd, *J* = 12.9, 6.6 Hz, 1H), 1.65 (t, *J* = 7.4 Hz, SH), 1.37 (d, *J* = 7.1 Hz, 3H), 1.25 (s, 9H), 1.05 (d, *J* = 5.5 Hz, 3H), 0.93 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.2, 170.8, 169.6, 169.3, 168.9, 156.7, 143.8, 141.2, 131.5, 127.7, 127.0, 125.1, 119.9, 118.7, 75.4, 67.3, 66.1, 61.5, 58.1, 57.6, 53.7, 48.2, 47.0, 44.4, 32.1, 29.3, 28.3, 19.0, 18.5, 18.1.

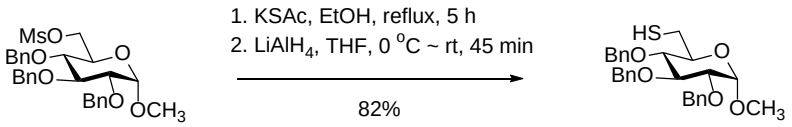
HRMS (ESI): calc. for $C_{39}H_{54}N_5O_9S$ $[M+H]^+$: 768.5.

5.2 Preparation of glucosyl acceptor 14



14i **14ii**

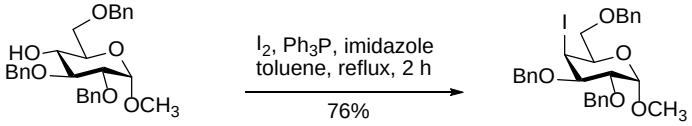
To a solution of **14i** (2.7 g, 5.82 mmol) in 30 mL of anhydrous pyridine was added MsCl (901 μL, 11.64 mmol) under N_2 protection at 0 °C. After 2 hours of stirring at the same temperature, the reaction mixture was quenched with methanol and concentrated. The residue was subjected to silica gel column chromatography with EtOAc and hexanes (1:3) as the eluent to afford compound **26** (3.03 g, 96%) as a syrup. R_f 0.45 (1:2, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.43 – 7.21 (m, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.81 (dd, *J* = 21.3, 11.5 Hz, 1H), 4.70 – 4.54 (m, 1H), 4.36 (qd, *J* = 11.0, 3.2 Hz, 1H), 4.02 (t, *J* = 9.2 Hz, 1H), 3.84 (ddd, *J* = 10.1, 4.1, 2.2 Hz, 1H), 3.56 – 3.45 (m, 1H), 3.38 (s, 1H), 2.97 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 138.48, 137.92, 137.73, 128.51, 128.50, 128.43, 128.07, 128.06, 128.00, 127.97, 127.89, 127.69, 98.16, 81.79, 79.76, 76.93, 75.75, 75.11, 73.46, 68.62, 68.39, 55.45, 37.51. HR ESI-TOF MS (m/z): calcd for $C_{29}H_{34}SO_8Na$ $[M + Na]^+$, 565.1867; found, 565.1878.



14ii **14**

To a solution of **14ii** (3.3 g, 6.09 mmol) in ethanol (60 mL) was added KSAc (2.08 g, 18.27 mmol). After it was stirred under reflux for 5 h, it was diluted with ethyl acetate and washed with aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was subjected to flush silica gel column chromatography (1:6, EtOAc–hexane) to give an intermediate. To the obtained syrup in THF (60 mL) was added $LiAlH_4$ (1.85 g, 48.7 mmol) at 0 °C. After it was stirred at rt for 45 min, it was quenched with addition of ethyl acetate. The mixture was diluted with CH_2Cl_2 and washed with 1 N HCl and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was subjected to flush silica gel column chromatography (1:8, EtOAc–hexane) to give **14** (2.4 g, 82%) as a syrup. R_f 0.65 (1:4, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.44 – 7.16 (m, 1H), 5.01 (d, J = 10.8 Hz, 1H), 4.92 (d, J = 11.1 Hz, 1H), 4.86 – 4.77 (m, 1H), 4.71 – 4.56 (m, 1H), 4.00 (t, J = 9.2 Hz, 1H), 3.73 (ddd, J = 9.7, 7.1, 2.6 Hz, 1H), 3.53 (dd, J = 9.6, 3.6 Hz, 1H), 3.45 (t, J = 9.3 Hz, 1H), 3.41 (s, 1H), 2.87 (ddd, J = 13.8, 8.7, 2.7 Hz, 1H), 2.65 – 2.57 (m, 1H), 1.52 (t, J = 8.3 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ: 138.64, 138.08, 128.47, 128.46, 128.40, 128.08, 127.96, 127.93, 127.86, 127.63, 97.93, 81.99, 80.13, 79.67, 75.72, 75.07, 73.37, 70.69, 55.21, 26.39. HR ESI-TOF MS (m/z): calcd for $C_{28}H_{32}SO_5Na$ $[M + Na]^+$, 503.1863; found, 503.1859.

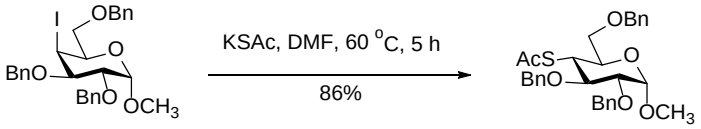
5.3 Preparation of glucosyl acceptor 15



15i **15ii**

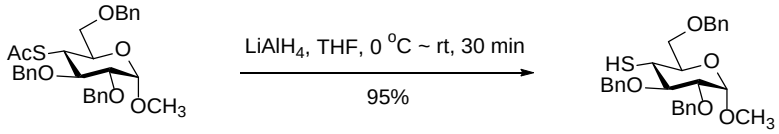
To a solution of **15i** (1.6 g, 3.45 mmol) in toluene (60 mL) were added I_2 (1.75 g, 6.9 mmol), imidazole (703 mg, 10.35 mmol) and Ph_3P (2.71 g, 10.35 mmol). After it was stirred under reflux for 2 h, it was filtered and concentrated. The residue was subjected to flush silica gel column chromatography (1:10, EtOAc–hexane) to give **15ii** (3.34 g, 76%) as a syrup. R_f 0.70 (1:3, EtOAc–hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 – 7.12 (m, 1H), 4.86 (d, J = 12.0 Hz, 1H), 4.75 (d, J = 11.6 Hz, 1H), 4.71 – 4.52 (m, 1H), 3.85 (dd, J = 9.5, 3.8 Hz, 1H), 3.64 (dd, J = 9.6, 6.0 Hz, 1H),

3.52 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.39 (s, 1H), 3.31 (t, *J* = 6.1 Hz, 1H), 3.21 (dd, *J* = 9.5, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 138.34, 137.93, 137.80, 128.43, 128.39, 128.35, 128.12, 127.81, 127.78, 127.75, 127.68, 99.04, 77.84, 75.71, 74.18, 73.96, 73.74, 71.24, 67.08, 55.34, 41.23. HR ESI-TOF MS (m/z): calcd for $C_{28}H_{31}IO_5Na$ $[M + Na]^+$, 597.1108; found, 597.1106.



15ii **15iii**

To a solution of **15ii** (1.5 g, 2.61 mmol) in DMF (30 mL) was added KSAc (1.19 g, 10.45 mmol). After it was stirred at 60 ºC for 5 h, it was diluted with ethyl acetate and washed with H_2O and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was subjected to flush silica gel column chromatography (1:6, EtOAc–hexane) to give **15iii** (1.17 g, 86%) as a syrup. R_f 0.40 (1:4, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.39 – 7.17 (m, 1H), 4.93 (d, *J* = 11.1 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.73 – 4.62 (m, 1H), 4.52 (s, 1H), 3.93 – 3.88 (m, 1H), 3.84 (dd, *J* = 10.6, 9.5 Hz, 1H), 3.68 (t, *J* = 11.1 Hz, 1H), 3.65 – 3.58 (m, 1H), 3.41 (s, 1H), 2.24 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 193.42, 138.63, 138.07, 138.03, 128.44, 128.23, 128.19, 128.10, 127.91, 127.71, 127.63, 127.50, 127.42, 98.33, 97.44, 80.93, 78.34, 75.93, 73.45, 73.35, 69.87, 69.82, 55.39, 45.80, 30.61. HR ESI-TOF MS (m/z): calcd for $C_{30}H_{34}SO_6Na$ $[M + Na]^+$, 545.1968; found, 545.1963.

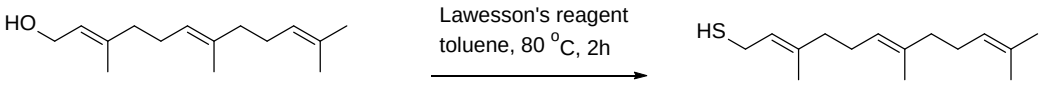


15iii **15**

To a solution of **15iii** (590 mg, 1.13 mmol) in THF (20 mL) was added $LiAlH_4$ (344 mg, 9.04 mmol) at 0 ºC. After it was stirred at rt for 30 min, it was quenched with addition of ethyl acetate. The mixture was diluted with CH_2Cl_2 and washed with 1 N HCl and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was subjected to flush silica gel column chromatography (1:7, EtOAc–hexane) to give **15** (515 mg, 95%) as a syrup. R_f 0.45 (1:4, EtOAc–hexane); ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 7.54 – 7.21 (m, 1H), 4.99 (d, *J* = 10.6 Hz, 1H), 4.82 (dd, *J* = 24.7, 11.3 Hz, 1H), 4.72 – 4.61 (m, 1H), 4.52 (d, *J* = 12.1 Hz, 1H), 3.80 (dd, *J* = 10.7, 3.9 Hz, 1H), 3.72 (ddd, *J* = 19.2, 12.0, 5.9 Hz, 1H), 3.55 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.41 (s, 1H), 3.09 (td, *J* = 10.5, 6.7 Hz, 1H), 1.67 (d, *J* = 6.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 138.41, 138.05,

137.95, 128.46, 128.40, 128.34, 128.19, 128.10, 127.94, 127.76, 127.73, 127.65, 98.53, 81.81, 80.64, 76.29, 73.56, 73.20, 72.30, 69.49, 55.39, 41.89. HR ESI-TOF MS (m/z): calcd for $C_{28}H_{32}SO_5Na$ $[M + Na]^+$, 503.1863; found, 503.1857.

5.4 Preparation of thiol-Farnesol acceptor 16



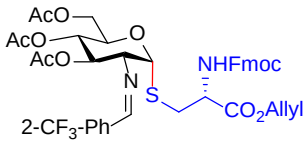
trans,trans-Farnesol **16**

To a solution of **trans,trans-Farnesol** (0.4 mL, 1.58 mmol) in dry toluene (5 mL) was added Lawesson's reagent (0.42 g, 0.95 mmol). After it was stirred at 80 ºC for 2 h, it was cooled down, filtered and concentrated. The residue was subjected to flush silica gel column chromatography (hexane) to give **16** (316 mg, 84%) as a colorless oil. R_f 0.25 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.34 (td, J = 7.8, 1.1 Hz, 1H), 5.12 – 5.06 (m, 2H), 3.16 (t, J = 7.4 Hz, 2H), 2.12 – 1.94 (m, 8H), 1.68 (s, 3H), 1.66 (s, 2H), 1.60 (s, 5H), 1.39 (t, J = 7.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 137.47, 135.27, 131.26, 124.31, 124.25, 124.09, 123.72, 123.61, 123.28, 39.67, 39.37, 26.70, 26.27, 25.67, 22.09, 17.66, 16.00, 15.75. HR ESI-TOF MS (m/z): calcd for $C_{15}H_{26}SNa$ $[M + Na]^+$, 261.1647; found, 261.1648.

6. Scope of Glycosylation

General Procedure for Triflic Acid-Catalyzed Thiol Glycosylation:

A 10 mL Schlenk flask was charged with *N*-phenyl trifluoroacetimidate glycosyl donor **1, 6 – 9, 18, 19** (0.2 mmol, 1 – 2 equiv.), thiol acceptor **10-17** (0.1 mmol, 1 equiv.) and dichloromethane (1 mL). The resulting solution was stirred at room temperature for 2 min under a nitrogen atmosphere before the TfOH (5 mol%) was added. After 1 h of stirring at room temperature, the reaction was quenched with 1 drop of Et_3N and concentrated. A crude ^1H NMR was taken to determine the (α/β) ratio. Further purification by silica gel column chromatography (ethyl acetate/hexane: 1/4→1/2) was performed to give the desired product.

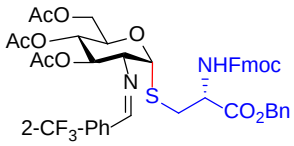


1a: 76%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.61 (d, *J* = 2.0 Hz, 1H), 8.20 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.64 – 7.51 (m, 4H), 7.40 (dd, *J* = 14.0, 7.0 Hz, 2H), 7.31 (dd, *J* = 15.2, 7.6 Hz, 2H), 6.01 (d, *J* = 8.6 Hz, 1H), 5.87 (ddd, *J* = 16.5, 11.2, 5.9 Hz, 1H), 5.49 (t, *J* = 9.7 Hz, 1H), 5.25 (ddd, *J* = 17.4, 11.5, 9.1 Hz, 3H), 5.10 (dd, *J* = 10.1, 9.6 Hz, 1H), 4.78 – 4.70 (m, 1H), 4.64 (d, *J* = 5.8 Hz, 2H), 4.52 (dd, *J* = 10.2, 3.2 Hz, 1H), 4.42 (p, *J* = 10.6 Hz, 2H), 4.25 (ddd, *J* = 12.5, 11.2, 6.2 Hz, 3H), 3.92 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.23 (dd, *J* = 14.2, 5.4 Hz, 1H), 3.01 (dd, *J* = 14.3, 4.0 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.50, 169.87, 169.73, 155.69, 143.85, 143.62, 141.31, 137.07, 131.26, 128.51, 128.14, 127.79, 127.73, 127.71, 127.04, 125.07, 124.98, 119.99, 119.97, 119.34, 85.32, 76.11, 72.50, 71.86, 68.41, 67.07, 66.43, 62.07, 54.18, 47.05, 34.58, 20.73, 20.61, 20.58.

HRMS (ESI): calc. for $C_{41}H_{41}F_3N_2O_{11}SNa$ $[M + Na]^+$, 849.2275; found: 849.2278.

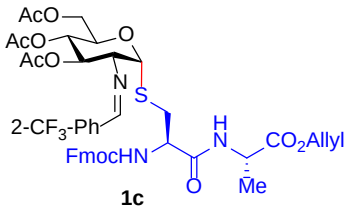


1b: 71%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.59 (d, *J* = 1.9 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.51 (m, 4H), 7.40 (dd, *J* = 13.5, 7.0 Hz, 2H), 7.36 – 7.27 (m, 8H), 6.05 (d, *J* = 8.6 Hz, 1H), 5.46 (t, *J* = 9.7 Hz, 1H), 5.16 (dd, *J* = 12.4, 3.4 Hz, 3H), 5.10 – 5.04 (m, 1H), 4.80 – 4.73 (m, 1H), 4.43 (ddt, *J* = 17.3, 13.7, 6.8 Hz, 3H), 4.28 – 4.16 (m, 3H), 3.85 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.23 (dd, *J* = 14.3, 5.2 Hz, 1H), 2.99 (dd, *J* = 14.3, 4.0 Hz, 1H), 2.04 (s, 3H), 2.01 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.55, 169.84, 169.56, 160.34, 155.73, 143.63, 141.27, 134.86, 132.28, 130.90, 129.09, 128.62, 128.59, 128.57, 127.71, 127.69, 127.06, 127.03, 125.49, 125.04, 119.97, 119.94, 85.35, 72.02, 71.29, 68.63, 67.65, 67.07, 62.18, 54.15, 53.77, 47.10, 33.77, 20.66, 20.59, 20.33.

HRMS (ESI): calc. for $C_{45}H_{43}F_3N_2O_{11}SNa$ $[M + Na]^+$, 899.2432; found: 899.2433.



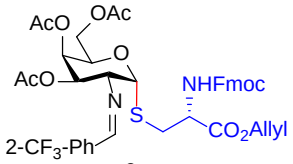
1c

75%,α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.62 (d, *J* = 1.7 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.54 (ddd, *J* = 24.2, 15.3, 7.5 Hz, 4H), 7.38 (dd, *J* = 12.8, 7.2 Hz, 2H), 7.30 (ddd, *J* = 16.4, 7.6, 1.0 Hz, 2H), 6.84 (d, *J* = 5.7 Hz, 1H), 5.88 (ddd, *J* = 16.3, 11.0, 5.7 Hz, 1H), 5.71 (s, 1H), 5.52 (t, *J* = 9.7 Hz, 1H), 5.41 (s, 1H), 5.36 – 5.29 (m, 1H), 5.24 (dd, *J* = 10.5, 1.1 Hz, 1H), 5.11 (t, *J* = 9.8 Hz, 1H), 4.67 – 4.50 (m, 4H), 4.43 (dt, *J* = 17.0, 10.2 Hz, 3H), 4.25 (ddd, *J* = 24.6, 13.0, 5.8 Hz, 3H), 3.91 (dd, *J* = 9.9, 5.6 Hz, 1H), 3.14 – 3.06 (m, 1H), 2.93 – 2.85 (m, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 1.86 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.96, 170.69, 169.87, 169.58, 160.45, 155.90, 143.69, 143.59, 141.29, 141.26, 133.05, 132.21, 131.44, 130.89, 129.09, 129.04, 127.75, 127.72, 127.10, 127.06, 125.50, 125.46, 125.00, 124.91, 119.98, 119.96, 118.81, 85.36, 71.99, 71.47, 68.82, 68.45, 67.19, 66.01, 62.16, 55.00, 48.39, 47.07, 33.38, 20.72, 20.65, 20.34, 18.00.

HRMS (ESI): calc. for $C_{44}H_{46}F_3N_3O_{12}SNa$ [M + Na]$^+$, 920.2647; found: 920.2643.



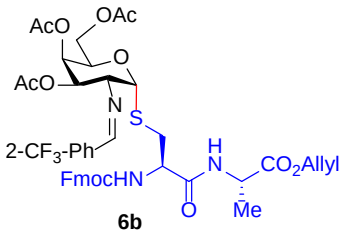
6a

73%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.63 (s, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.58 (ddd, *J* = 33.7, 14.2, 7.5 Hz, 4H), 7.40 (dd, *J* = 13.5, 7.0 Hz, 2H), 7.32 (dt, *J* = 15.0, 7.6 Hz, 2H), 5.96 (d, *J* = 8.5 Hz, 1H), 5.92 – 5.82 (m, 1H), 5.48 (s, 1H), 5.40 – 5.27 (m, 3H), 5.20 (d, *J* = 10.5 Hz, 1H), 4.72 – 4.60 (m, 3H), 4.40 (d, *J* = 7.1 Hz, 2H), 4.26 – 4.06 (m, 4H), 3.22 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.00 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.21 (s, 3H), 2.04 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.46, 170.03, 169.62, 160.33, 155.67, 143.67, 141.29, 132.22, 131.30, 130.77, 129.03, 127.69, 127.04, 125.04, 119.96, 119.11, 85.43, 69.13, 67.62, 67.12, 66.79, 66.36, 62.18, 54.10, 47.07, 32.99, 29.67, 20.75, 20.61, 20.33.

HRMS (ESI): calc. for $C_{41}H_{41}F_3N_2O_{11}SNa$ [M + Na]$^+$, 849.2275; found: 849.2273.



6b

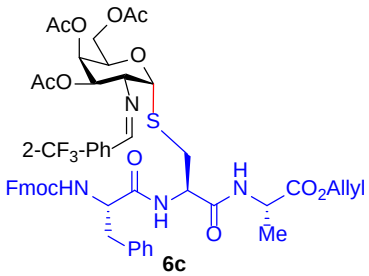
68%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.63 (d, *J* = 1.9 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.48 (m, 4H), 7.39 (dd, *J* = 15.2, 7.6 Hz, 2H), 7.36 – 7.28 (m, 2H), 6.97 (d, *J* = 6.0 Hz, 1H), 5.94 – 5.76 (m, 2H), 5.48 (d, *J* = 2.4 Hz, 2H), 5.31 (ddd, *J* = 56.3, 24.8, 6.8 Hz, 3H), 4.67 – 4.50 (m, 4H), 4.40 (dd, *J* = 31.9, 5.9 Hz, 3H), 4.21 (t, *J* = 6.9 Hz, 1H), 4.16 (d, *J* = 6.0 Hz, 2H), 4.10 (dd, *J* = 10.4, 5.5 Hz, 1H), 3.15 (dd, *J* = 13.5, 5.7 Hz, 1H), 2.93 – 2.85 (m, 1H), 2.19 (s, 3H), 2.00 (s, 3H), 1.87 (s, 3H), 1.38 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 172.00, 170.56, 170.08, 169.66, 169.60, 160.40, 155.90, 143.73, 143.61, 141.29, 141.27, 133.32, 132.18, 131.44, 130.74, 129.15, 129.04, 128.94, 127.74, 127.72, 127.09, 127.05, 125.48, 125.44, 125.01, 124.96, 123.15, 119.98, 119.97, 118.79, 85.31, 69.47,

69.24, 67.44, 67.11, 67.03, 66.84, 65.98, 62.22, 53.78, 48.35, 47.06, 32.54, 20.76, 20.63, 20.34, 18.08.

HRMS (ESI): calc. for $C_{44}H_{46}F_3N_3O_{12}SNa$ $[M + Na]^+$, 920.2647; found: 920.2641.



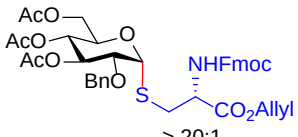
6c

78%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.63 (d, *J* = 1.7 Hz, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.74 (dd, *J* = 17.5, 5.8 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.46 (m, 4H), 7.39 (dd, *J* = 13.4, 6.9 Hz, 2H), 7.33 – 7.23 (m, 5H), 7.18 (s, 2H), 6.92 (s, 1H), 6.81 (s, 1H), 5.93 – 5.83 (m, 1H), 5.46 (dd, *J* = 9.3, 3.8 Hz, 2H), 5.32 (ddd, *J* = 9.6, 9.0, 2.2 Hz, 3H), 5.24 (dd, *J* = 10.5, 1.1 Hz, 1H), 4.66 – 4.41 (m, 7H), 4.31 – 4.12 (m, 4H), 4.05 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.07 (d, *J* = 36.9 Hz, 3H), 2.87 (d, *J* = 13.3 Hz, 1H), 2.16 (s, 3H), 2.04 (s, 3H), 1.85 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.90, 170.68, 170.09, 169.59, 169.07, 160.44, 143.72, 141.25, 133.56, 132.18, 131.49, 130.74, 129.30, 129.18, 129.03, 128.78, 127.72, 127.21, 127.05, 124.97, 119.97, 119.94, 118.76, 84.73, 69.23, 67.46, 67.15, 67.02, 66.72, 65.96, 62.11, 53.77, 48.38, 47.04, 31.47, 29.25, 20.73, 20.71, 20.32, 17.89.

HRMS (ESI): calc. for $C_{53}H_{55}F_3N_4O_{13}SNa$ $[M + Na]^+$, 1067.3331; found: 1067.3337.



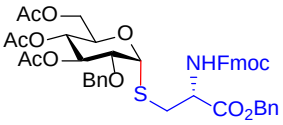
7a: 93%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.76 (dd, *J* = 7.5, 0.7 Hz, 2H), 7.59 (dd, *J* = 19.0, 7.5 Hz, 2H), 7.40 (q, *J* = 7.4 Hz, 2H), 7.35 – 7.26 (m, 5H), 6.06 (d, *J* = 8.7 Hz, 1H), 5.91 (ddd, *J* = 16.5, 11.2, 5.9 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.24 (ddd, *J* = 19.2, 9.9, 2.1 Hz, 3H), 4.98 – 4.90 (m, 1H), 4.78 – 4.70 (m, 1H), 4.64 (dd, *J* = 22.9, 9.0 Hz, 3H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.40 (dd, *J* = 7.0,

1.7 Hz, 2H), 4.35 – 4.26 (m, 1H), 4.24 – 4.12 (m, 3H), 3.80 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.25 (dd, *J* = 14.5, 5.0 Hz, 1H), 2.90 (dd, *J* = 14.5, 3.8 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.50, 169.94, 169.87, 169.73, 155.69, 143.85, 143.62, 141.31, 137.07, 131.26, 128.51, 128.14, 127.79, 127.73, 127.71, 127.04, 125.07, 124.98, 119.99, 119.97, 119.34, 85.32, 76.11, 72.50, 71.86, 68.41, 67.07, 66.43, 62.07, 54.18, 47.05, 34.58, 20.73, 20.61, 20.58.

HRMS (ESI): calc. for $C_{40}H_{43}NO_{12}SNa$ $[M + Na]^+$, 784.2398; found: 784.2392.

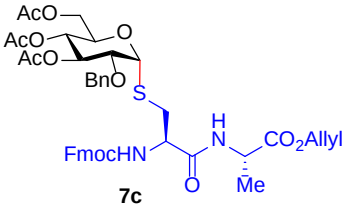


7b: 95%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.59 (dd, *J* = 18.7, 7.5 Hz, 2H), 7.46 – 7.23 (m, 14H), 6.12 (d, *J* = 8.8 Hz, 1H), 5.17 (dt, *J* = 23.4, 5.9 Hz, 4H), 4.92 (t, *J* = 9.8 Hz, 1H), 4.76 (dt, *J* = 8.6, 4.2 Hz, 1H), 4.59 (d, *J* = 12.3 Hz, 1H), 4.51 (d, *J* = 12.3 Hz, 1H), 4.40 (dd, *J* = 6.9, 4.2 Hz, 2H), 4.31 – 4.08 (m, 4H), 3.76 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.26 (dd, *J* = 14.5, 4.9 Hz, 1H), 2.88 (dd, *J* = 14.5, 3.7 Hz, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.50, 170.11, 169.86, 169.72, 155.71, 143.87, 143.62, 141.31, 141.27, 137.08, 134.84, 128.70, 128.65, 128.64, 128.51, 128.14, 127.80, 127.73, 127.71, 127.05, 125.08, 124.98, 119.99, 119.97, 85.30, 72.50, 71.82, 68.42, 68.39, 67.72, 67.08, 62.06, 54.20, 47.05, 34.68, 20.73, 20.63, 20.54.

HRMS (ESI): calc. for $C_{44}H_{45}NO_{12}SNa$ $[M + Na]^+$, 834.2555; found: 834.2565.



7c

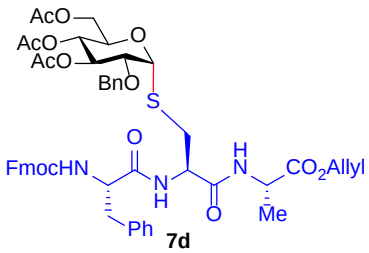
92%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.76 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 13.1, 7.3 Hz, 2H), 7.30 (qdd, *J* = 20.3, 10.7, 6.6 Hz, 7H), 6.86 (d, *J* = 6.4 Hz, 1H), 5.96 – 5.79 (m, 2H), 5.47 (d, *J* = 5.3 Hz, 1H), 5.39 – 5.20 (m, 3H), 4.95 (t, *J* = 9.8 Hz, 1H), 4.73 – 4.48 (m, 5H), 4.47 – 4.34 (m, 3H), 4.34 – 4.26 (m, 1H), 4.26 – 4.17 (m, 2H), 4.12 (dd, *J* = 14.2, 7.1 Hz,

1H), 3.83 (dd, *J* = 9.0, 5.2 Hz, 1H), 3.11 (d, *J* = 9.6 Hz, 1H), 2.81 (dd, *J* = 13.6, 4.9 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.37 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.92, 170.58, 169.85, 169.73, 169.40, 155.86, 143.69, 143.58, 141.31, 141.28, 136.96, 131.49, 128.57, 128.51, 128.26, 128.17, 128.01, 127.91, 127.77, 127.75, 127.65, 127.59, 127.11, 127.08, 125.00, 120.01, 119.99, 118.81, 85.20, 76.21, 72.70, 72.14, 68.52, 68.43, 67.16, 66.01, 62.06, 54.94, 48.42, 47.06, 33.95, 20.75, 20.68, 20.61, 17.92.

HRMS (ESI): calc. for $C_{43}H_{48}N_2O_{13}SNa$ $[M + Na]^+$, 855.2769; found: 855.2764.



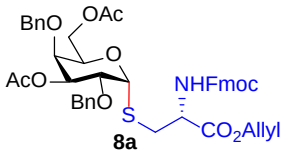
7d

87%, α:β > 20:1

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.50 (dd, *J* = 13.9, 7.5 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.22 (m, 10H), 7.18 (s, 2H), 6.85 (d, *J* = 38.5 Hz, 2H), 5.94 – 5.84 (m, 1H), 5.56 (d, *J* = 4.3 Hz, 1H), 5.27 (ddd, *J* = 13.8, 12.1, 1.3 Hz, 4H), 4.95 (t, *J* = 9.7 Hz, 1H), 4.71 – 4.38 (m, 8H), 4.36 – 4.11 (m, 5H), 3.81 (dd, *J* = 9.9, 5.5 Hz, 1H), 3.18 – 2.96 (m, 3H), 2.88 – 2.77 (m, 1H), 2.05 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.34 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.79, 170.87, 170.68, 169.88, 169.73, 168.83, 143.68, 141.26, 136.97, 135.96, 131.53, 129.22, 128.82, 128.50, 128.14, 127.87, 127.72, 127.26, 127.08, 124.96, 119.97, 118.77, 84.81, 76.25, 72.66, 72.19, 68.61, 68.45, 67.11, 65.98, 61.92, 53.43, 48.45, 47.05, 38.05, 33.11, 20.74, 20.62, 17.70.

HRMS (ESI): calc. for $C_{38}H$ $C_{52}H_{57}N_3O_{14}SNa$ $[M + Na]^+$, 1002.3453; found: 1002.3458.



8a

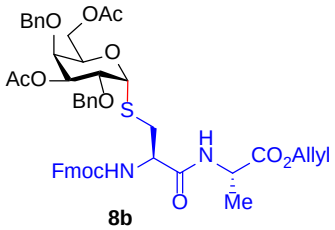
86%, α:β > 20:1

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.60 (dd, *J* = 17.0, 7.5 Hz, 2H), 7.44 – 7.21 (m, 14H), 6.16 (d, *J* = 8.8 Hz, 1H), 5.97 – 5.83 (m, 1H), 5.40 – 5.20 (m, 3H), 5.07 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.77 – 4.61 (m, 5H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 11.2 Hz, 1H), 4.39

(td, *J* = 17.9, 10.5 Hz, 2H), 4.33 – 4.16 (m, 4H), 4.12 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.98 (d, *J* = 1.6 Hz, 1H), 3.29 (dd, *J* = 14.5, 5.1 Hz, 1H), 2.88 (dd, *J* = 14.5, 3.7 Hz, 1H), 2.04 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.54, 170.20, 169.98, 155.75, 143.84, 143.71, 141.27, 141.24, 137.55, 137.41, 131.39, 128.52, 128.41, 128.18, 128.12, 127.93, 127.79, 127.65, 127.10, 127.05, 125.17, 125.08, 119.90, 119.11, 85.71, 75.29, 74.89, 73.35, 72.58, 72.49, 69.30, 67.06, 66.29, 62.88, 54.27, 47.06, 34.20, 20.95, 20.66.

HRMS (ESI): calc. for $C_{38}H$ $C_{45}H_{47}NO_{11}SNa$ $[M + Na]^+$, 832.2762; found: 832.2761.



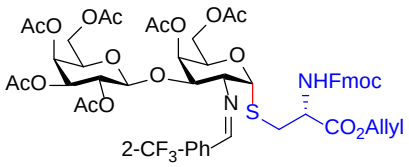
8b

86%, α:β > 4.5:1

^{1}H NMR (CDCl$_3$, 600 MHz): α/β mixture, inseparable, δ 7.79 – 7.70 (m, 2H), 7.64 – 7.54 (m, 2H), 7.44 – 7.25 (m, 14H), 7.17 (d, *J* = 20.4 Hz, 0.2H), 6.97 (d, *J* = 6.8 Hz, 1H), 6.09 (d, *J* = 5.7 Hz, 0.2H), 5.97 (d, *J* = 6.7 Hz, 1H), 5.93 – 5.82 (m, 1H), 5.45 (s, 1H), 5.31 (d, *J* = 17.3 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 5.16 – 5.05 (m, 1H), 4.97 (d, *J* = 9.0 Hz, 0.2H), 4.86 (d, *J* = 10.8 Hz, 0.2H), 4.74 – 4.48 (m, 7H), 4.44 (d, *J* = 5.8 Hz, 2H), 4.37 (d, *J* = 5.3 Hz, 1H), 4.21 (dd, *J* = 18.3, 11.6 Hz, 4H), 4.12 – 3.94 (m, 3H), 3.84 (d, *J* = 10.1 Hz, 1H), 3.19 (dd, *J* = 32.9, 11.6 Hz, 1.2H), 2.97 (d, *J* = 8.1 Hz, 0.2H), 2.80 (d, *J* = 10.3 Hz, 1H), 2.04 (s, 3H), 1.95 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.99, 170.51, 170.17, 169.61, 155.98, 146.78, 143.73, 143.66, 141.31, 141.26, 137.48, 137.43, 135.83, 131.66, 131.53, 128.51, 128.45, 128.40, 128.38, 128.14, 128.09, 128.04, 127.98, 127.96, 127.90, 127.71, 127.70, 127.14, 127.08, 125.02, 124.96, 121.19, 119.95, 119.92, 118.71, 118.57, 85.41, 75.56, 75.12, 75.04, 74.56, 74.41, 73.50, 72.76, 72.52, 69.30, 66.98, 65.93, 65.84, 63.01, 62.72, 55.23, 54.62, 48.54, 48.35, 47.09, 33.68, 29.67, 20.97, 20.87, 20.66, 18.08, 17.93.

HRMS (ESI): calc. for $C_{38}H$ $C_{48}H_{52}N_2O_{12}SNa$ $[M + Na]^+$, 903.3133; found: 903.3136.



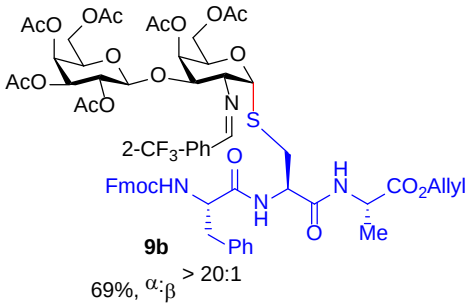
9a

63%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.61 (s, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 7.81 – 7.68 (m, 3H), 7.65 – 7.52 (m, 4H), 7.40 (dd, *J* = 13.1, 7.2 Hz, 2H), 7.31 (dd, *J* = 16.3, 7.9 Hz, 2H), 5.90 (d, *J* = 8.5 Hz, 1H), 5.87 – 5.77 (m, 1H), 5.51 – 5.48 (m, 1H), 5.23 (ddd, *J* = 21.7, 14.4, 6.8 Hz, 4H), 5.01 (dd, *J* = 10.4, 7.9 Hz, 1H), 4.83 (dd, *J* = 10.5, 3.5 Hz, 1H), 4.60 (ddd, *J* = 30.9, 23.7, 6.4 Hz, 4H), 4.42 – 4.19 (m, 5H), 4.17 – 4.01 (m, 5H), 3.84 (t, *J* = 6.6 Hz, 1H), 3.16 (dd, *J* = 14.1, 5.7 Hz, 1H), 2.95 (dd, *J* = 14.1, 4.0 Hz, 1H), 2.17 (s, 3H), 2.12 (s, 3H), 2.05 (d, *J* = 6.8 Hz, 6H), 1.89 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.10, 170.53, 170.35, 170.25, 170.15, 170.04, 169.86, 168.76, 160.10, 155.66, 143.81, 143.64, 141.28, 133.56, 133.30, 132.28, 132.14, 131.23, 130.90, 129.04, 128.72, 127.70, 127.00, 125.73, 125.07, 119.99, 119.06, 100.65, 85.64, 75.21, 70.75, 70.70, 69.08, 68.84, 68.69, 68.47, 67.16, 67.11, 66.70, 66.31, 63.02, 60.98, 60.36, 54.06, 47.06, 32.95, 21.02, 20.76, 20.69, 20.67, 20.61, 20.46, 19.92.

HRMS (ESI): calc. for $C_{53}H_{57}F_3N_2O_{19}SNa$ $[M + Na]^+$, 1137.3121; found: 1137.3125.



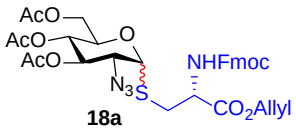
9b

69%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.61 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 7.80 – 7.66 (m, 3H), 7.52 (ddt, *J* = 30.9, 15.4, 7.6 Hz, 4H), 7.39 (dd, *J* = 14.6, 7.2 Hz, 2H), 7.34 – 7.20 (m, 6H), 7.15 (s, 2H), 6.93 (d, *J* = 6.7 Hz, 1H), 6.77 (s, 1H), 5.87 (ddd, *J* = 16.2, 11.0, 5.7 Hz, 1H), 5.46 (d, *J* = 3.0 Hz, 1H), 5.37 – 5.22 (m, 5H), 4.99 (dd, *J* = 10.4, 7.9 Hz, 2H), 4.80 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.64 – 4.41 (m, 6H), 4.34 – 4.26 (m, 2H), 4.19 – 4.02 (m, 5H), 3.76 (d, *J* = 6.9 Hz, 1H), 3.07 (s, 2H), 2.96 (d, *J* = 6.8 Hz, 1H), 2.82 (d, *J* = 10.5 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.88 (s, 3H), 1.43 (s, 3H), 1.33 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.99, 170.85, 170.82, 170.34, 170.24, 170.01, 169.96, 169.07, 168.74, 160.09, 143.65, 141.27, 141.23, 136.02, 133.34, 132.07, 131.46, 130.84, 129.26, 128.79, 128.72, 127.79, 127.75, 127.14, 127.08, 124.94, 120.02, 120.00, 118.71, 100.65, 84.97, 75.54, 70.75, 70.60, 68.92, 68.78, 68.49, 68.45, 67.11, 66.70, 65.92, 62.95, 60.93, 60.35, 55.94, 53.78, 48.33, 47.06, 30.89, 29.66, 29.24, 20.82, 20.77, 20.67, 20.63, 20.60, 20.45, 19.86, 17.86.

HRMS (ESI): calc. for $C_{65}H_{71}F_3N_4O_{21}SNa$ [M + Na]$^+$, 1355.4176; found: 1355.4182.



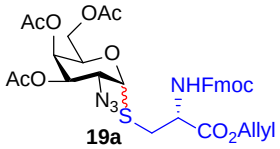
18a

75% (α:β = 1.6:1)

^{1}H NMR (CDCl$_3$, 600 MHz): α/β mixture, inseparable, δ 7.76 (d, *J* = 7.3 Hz, 4.4H), 7.60 (d, *J* = 5.5 Hz, 5H), 7.33 (dd, *J* = 33.0, 25.9 Hz, 9H), 6.04 (d, *J* = 8.4 Hz, 1.3H), 5.91 (d, *J* = 5.9 Hz, 2.6H), 5.69 – 5.50 (m, 3.6H), 5.48 – 5.09 (m, 9.2H), 5.00 (t, *J* = 9.6 Hz, 1.6H), 4.94 (t, *J* = 9.7 Hz, 1H), 4.70 (d, *J* = 41.2 Hz, 7H), 4.55 – 4.00 (m, 17H), 3.98 – 3.92 (m, 1H), 3.51 (d, *J* = 8.8 Hz, 1.6H), 3.35 – 3.21 (m, 2.6H), 3.04 (dd, *J* = 20.4, 9.2 Hz, 2.6H), 2.08 (s, 3H), 2.05 (s, 4.8H), 2.03 (s, 4.8H), 1.99 (s, 4.8H), 1.65 (s, 3H), 1.56 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.48, 170.30, 170.01, 169.69, 155.68, 143.84, 143.74, 141.26, 131.27, 131.18, 127.73, 127.69, 127.05, 125.14, 125.08, 124.91, 119.97, 119.47, 119.12, 92.28, 85.39, 71.64, 71.25, 68.80, 68.56, 67.97, 67.31, 66.75, 66.54, 66.44, 62.04, 61.95, 61.53, 61.14, 60.35, 54.22, 53.40, 47.17, 47.04, 35.49, 30.43, 29.78, 29.66, 29.24, 28.79, 20.67, 20.64, 20.60, 20.58, 20.55.

HRMS (ESI): calc. for $C_{33}H_{36}N_4O_{11}SNa$ [M + Na]$^+$, 719.1993; found: 719.1998.



19a

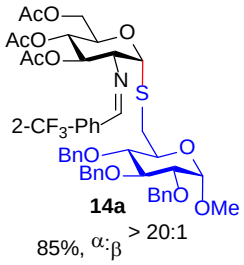
82% (α:β = 2:1)

^{1}H NMR (CDCl$_3$, 600 MHz): α/β mixture, inseparable, δ 7.75 (t, *J* = 10.1 Hz, 5.2H), 7.61 (t, *J* = 8.8 Hz, 5.2H), 7.40 (dd, *J* = 12.1, 7.2 Hz, 5.5H), 7.36 – 7.29 (m, 5.4H), 6.07 (d, *J* = 8.5 Hz, 2H), 5.90 (ddd, *J* = 16.3, 10.5, 5.8 Hz, 2.8H), 5.66 (d, *J* = 8.3 Hz, 1H), 5.59 (d, *J* = 3.2 Hz, 1H), 5.46 –

5.23 (m, 11.2H), 5.03 (dd, *J* = 11.1, 2.8 Hz, 2H), 4.76 – 4.62 (m, 8H), 4.52 – 4.32 (m, 8H), 4.31 – 4.18 (m, 7H), 4.08 (dddd, *J* = 22.7, 18.2, 11.4, 6.4 Hz, 8H), 3.87 – 3.79 (m, 1H), 3.36 – 3.25 (m, 3H), 3.04 (td, *J* = 14.0, 5.3 Hz, 3H), 2.18 (s, 6H), 2.13 (s, 3H), 2.05 (d, *J* = 9.0 Hz, 6H), 1.99 (s, 6H), 1.64 (s, 3H), 1.56 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.34, 170.29, 170.04, 169.82, 169.70, 169.46, 155.66, 143.83, 143.76, 143.63, 141.35, 141.30, 141.26, 131.31, 131.23, 127.70, 127.68, 127.03, 127.00, 125.12, 125.03, 125.00, 119.95, 119.36, 119.07, 92.75, 85.63, 69.67, 69.17, 67.83, 67.50, 67.35, 66.97, 66.88, 66.49, 66.42, 61.76, 61.73, 60.35, 57.98, 57.75, 54.15, 47.12, 47.06, 34.90, 29.85, 21.01, 20.61, 20.55, 20.49.

HRMS (ESI): calc. for $C_{33}H_{36}N_4O_{11}SNa$ $[M + Na]^+$, 719.1993; found: 719.1999.



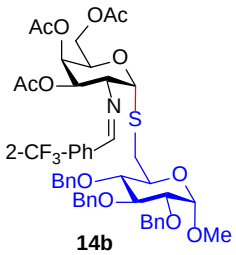
14a

85%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.60 (d, *J* = 1.9 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.53 (dd, *J* = 14.6, 7.4 Hz, 2H), 7.36 – 7.22 (m, 15H), 5.57 (t, *J* = 9.7 Hz, 1H), 5.42 (d, *J* = 5.6 Hz, 1H), 5.13 (t, *J* = 9.8 Hz, 1H), 4.93 (dd, *J* = 18.2, 10.9 Hz, 2H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 11.0 Hz, 1H), 4.59 – 4.53 (m, 2H), 4.51 (d, *J* = 3.5 Hz, 1H), 4.33 (dd, *J* = 12.3, 4.3 Hz, 1H), 4.02 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.97 – 3.88 (m, 2H), 3.85 – 3.79 (m, 1H), 3.46 – 3.40 (m, 2H), 3.31 (s, 3H), 2.99 (dd, *J* = 13.7, 2.3 Hz, 1H), 2.63 (dd, *J* = 13.1, 8.2 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.56, 169.89, 169.68, 169.63, 159.89, 138.61, 138.05, 138.01, 132.23, 130.92, 130.78, 129.09, 128.72, 128.59, 128.41, 128.40, 128.37, 127.99, 127.96, 127.88, 127.79, 127.74, 127.62, 97.76, 84.21, 81.88, 80.42, 80.17, 75.69, 75.14, 73.33, 73.22, 72.10, 71.75, 69.70, 68.70, 67.90, 62.10, 55.07, 30.53, 20.70, 20.66, 20.37.

HRMS (ESI): calc. for $C_{48}H_{52}F_3NO_{12}SNa$ $[M + Na]^+$, 946.3055; found: 946.3063.



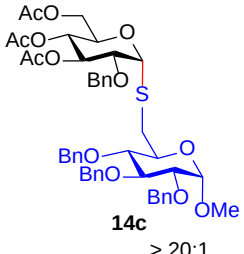
14b

87%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.62 (d, *J* = 2.0 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.54 (dt, *J* = 24.8, 7.4 Hz, 2H), 7.39 – 7.21 (m, 15H), 5.48 (dd, *J* = 8.1, 4.0 Hz, 2H), 5.42 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.93 (dd, *J* = 24.2, 10.9 Hz, 2H), 4.81 – 4.56 (m, 5H), 4.52 (d, *J* = 3.5 Hz, 1H), 4.18 – 4.05 (m, 3H), 3.94 (t, *J* = 9.2 Hz, 1H), 3.86 – 3.78 (m, 1H), 3.46 – 3.40 (m, 2H), 3.29 (s, 3H), 3.00 (dd, *J* = 13.8, 2.3 Hz, 1H), 2.64 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.18 (s, 3H), 1.98 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.30, 170.11, 169.68, 159.89, 138.61, 138.06, 138.02, 132.18, 130.65, 129.07, 128.42, 128.40, 128.37, 127.99, 127.97, 127.88, 127.81, 127.76, 127.62, 125.44, 97.72, 84.47, 81.91, 80.50, 80.18, 75.70, 75.18, 73.32, 69.74, 69.54, 67.19, 66.85, 61.97, 54.99, 30.23, 20.75, 20.66, 20.37.

HRMS (ESI): calc. for $C_{48}H_{52}F_3NO_{12}SNa$ $[M + Na]^+$, 946.3055; found: 946.3061.



14c

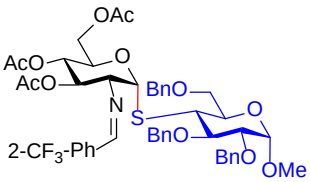
88%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.42 – 7.13 (m, 20H), 5.58 (d, *J* = 5.6 Hz, 1H), 5.30 (dd, *J* = 15.4, 5.7 Hz, 1H), 5.03 – 4.88 (m, 3H), 4.80 (dd, *J* = 30.1, 11.5 Hz, 2H), 4.68 – 4.58 (m, 3H), 4.53 (d, *J* = 3.5 Hz, 1H), 4.44 (d, *J* = 12.2 Hz, 1H), 4.39 (ddd, *J* = 10.2, 4.0, 2.1 Hz, 1H), 4.29 (dd, *J* = 12.4, 4.2 Hz, 1H), 4.00 (t, *J* = 9.2 Hz, 1H), 3.95 (dd, *J* = 12.4, 2.0 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.78 (dd, *J* = 9.9, 5.6 Hz, 1H), 3.54 (t, *J* = 9.3 Hz, 1H), 3.48 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.38 (s, 3H), 2.94 (dd, *J* = 13.9, 2.5 Hz, 1H), 2.67 (dd, *J* = 13.9, 6.7 Hz, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ ^{z}170.49, 169.90, 169.76, 138.64, 138.03, 137.97, 137.12, 128.45, 128.39, 128.08, 128.03, 127.96, 127.86, 127.83, 127.81, 127.77, 127.60, 98.05, 83.62, 81.88, 80.10,

79.94, 75.66, 75.55, 75.26, 73.41, 72.09, 71.62, 70.20, 68.40, 67.56, 61.93, 55.34, 30.39, 20.75, 20.68, 20.62.

HRMS (ESI): calc. for $C_{47}H_{54}O_{13}SNa$ $[M + Na]^+$, 881.3177; found: 881.3178.

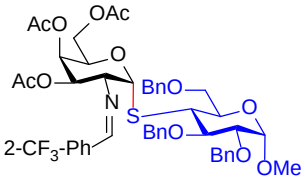


15a: 84% α:β > 20:1

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.32 (d, *J* = 1.8 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.23 (m, 10H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.3 Hz, 2H), 5.82 (d, *J* = 5.8 Hz, 1H), 5.40 (t, *J* = 9.7 Hz, 1H), 5.06 (t, *J* = 9.8 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.64 (ddd, *J* = 22.5, 16.1, 7.7 Hz, 5H), 4.40 – 4.33 (m, 1H), 4.21 (dd, *J* = 12.3, 3.9 Hz, 1H), 4.02 (t, *J* = 9.9 Hz, 1H), 3.90 – 3.76 (m, 4H), 3.71 (dd, *J* = 9.9, 5.7 Hz, 1H), 3.51 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.41 (s, 3H), 3.02 (t, *J* = 10.5 Hz, 1H), 2.02 (d, *J* = 6.2 Hz, 6H), 1.82 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.49, 169.71, 169.68, 159.57, 138.21, 137.99, 137.96, 133.19, 132.16, 130.77, 128.92, 128.42, 128.40, 128.04, 127.92, 127.88, 127.69, 127.66, 127.23, 126.94, 125.43, 98.24, 84.83, 83.43, 80.72, 75.87, 73.65, 73.12, 72.01, 71.53, 70.05, 69.84, 68.41, 68.35, 61.82, 55.36, 43.99, 20.71, 20.66, 20.27.

HRMS (ESI): calc. for $C_{48}H_{52}F_3NO_{12}SNa$ $[M + Na]^+$, 946.3055; found: 946.3052.

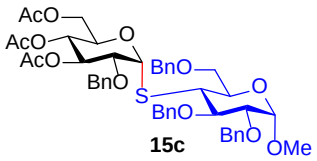


15b: 86% α:β > 20:1

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.36 (d, *J* = 1.9 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.21 (m, 10H), 7.17 – 6.91 (m, 5H), 5.81 (d, *J* = 5.7 Hz, 1H), 5.36 (d, *J* = 2.4 Hz, 1H), 5.22 (dd, *J* = 10.6, 3.3 Hz, 1H), 4.95 (d, *J* = 11.1 Hz, 1H), 4.76 – 4.54 (m, 6H), 4.36 (t, *J* = 6.6 Hz, 1H), 4.06 – 3.73 (m, 7H), 3.51 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.42 (s, 3H), 3.01 – 2.89 (m, 1H), 2.14 (s, 3H), 1.96 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.15, 170.12, 169.66, 159.60, 138.34, 138.10, 138.00, 133.46, 132.17, 130.67, 128.98, 128.41, 128.38, 128.03, 127.98, 127.88, 127.72, 127.64, 127.19, 127.00, 125.41, 98.15, 85.13, 83.56, 80.77, 75.85, 73.33, 73.07, 70.34, 69.79, 69.12, 67.14, 66.52, 61.92, 55.32, 43.94, 29.67, 20.74, 20.69, 20.29.

HRMS (ESI): calc. for $C_{48}H_{52}F_3NO_{12}SNa$ [M + Na]$^+$, 946.3055; found: 946.3058.



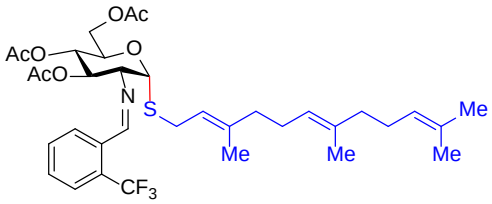
15c

89%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.40 – 7.13 (m, 18H), 6.94 (dd, *J* = 6.4, 2.7 Hz, 2H), 6.02 (d, *J* = 5.6 Hz, 1H), 5.20 (dd, *J* = 20.3, 10.8 Hz, 2H), 4.89 (dd, *J* = 10.7, 8.6 Hz, 2H), 4.75 – 4.66 (m, 2H), 4.64 – 4.55 (m, 3H), 4.40 (d, *J* = 12.3 Hz, 1H), 4.18 (ddd, *J* = 16.4, 11.2, 2.9 Hz, 2zH), 4.02 (t, *J* = 9.9 Hz, 1H), 3.97 (d, *J* = 12.3 Hz, 1H), 3.81 (ddd, *J* = 21.8, 10.2, 5.8 Hz, 4H), 3.63 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.57 (dd, *J* = 9.4, 3.4 Hz, 1H), 3.40 (s, 3H), 3.03 (t, *J* = 10.8 Hz, 1H), 2.00 (d, *J* = 5.7 Hz, 6H), 1.91 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.44, 169.92, 169.59, 139.00, 137.96, 137.87, 137.07, 128.42, 128.39, 128.33, 128.17, 128.07, 127.91, 127.69, 127.67, 127.46, 127.11, 126.26, 98.10, 83.98, 82.41, 81.00, 75.51, 75.25, 73.65, 73.07, 71.89, 71.37, 70.04, 69.93, 68.19, 68.14, 61.75, 55.40, 44.21, 20.72, 20.71, 20.63.

HRMS (ESI): calc. for $C_{47}H_{54}O_{13}SNa$ [M + Na]$^+$, 881.3177; found: 881.3173.



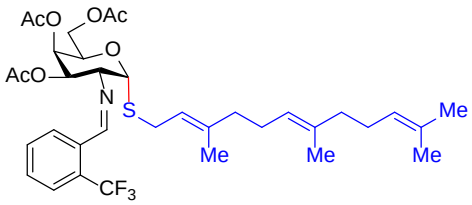
16a: 81% α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.59 (d, *J* = 2.0 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 5.58 (t, *J* = 9.6 Hz, 1H), 5.32 (d, *J* = 5.7 Hz, 1H), 5.23 (t, *J* = 7.7 Hz, 1H), 5.08 (ddd, *J* = 13.2, 8.3, 7.6 Hz, 3H), 4.63 (ddd, *J* = 10.2, 4.9, 2.0 Hz, 1H), 4.36 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.14 (dd, *J* = 12.2, 2.0 Hz, 1H), 3.93 (dd, *J* = 9.9, 5.6

Hz, 1H), 3.29 (dd, *J* = 13.2, 8.9 Hz, 1H), 3.08 (dd, *J* = 13.2, 6.6 Hz, 1H), 2.13 – 1.99 (m, 12H), 1.97 – 1.91 (m, 2H), 1.86 (s, 3H), 1.67 (d, *J* = 6.0 Hz, 6H), 1.57 (d, *J* = 10.6 Hz, 6H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.62, 169.95, 169.62, 159.82, 139.93, 135.30, 133.26, 132.22, 131.27, 130.69, 129.15, 129.00, 125.39, 125.35, 124.24, 123.72, 119.12, 82.87, 72.15, 71.95, 69.00, 67.79, 62.47, 39.66, 39.60, 29.67, 26.78, 26.67, 26.38, 25.64, 20.74, 20.69, 20.37, 17.65, 15.95.

HRMS (ESI): calc. for $C_{35}H_{46}F_3NO_7SNa$ $[M + Na]^+$, 704.2839; found: 704.2833.

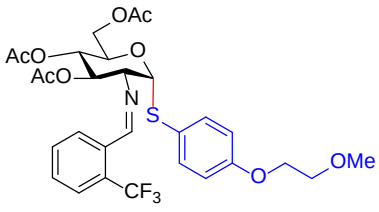


16b: 82% α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.62 (d, *J* = 2.0 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 5.50 (d, *J* = 2.4 Hz, 1H), 5.42 (dd, *J* = 10.5, 3.3 Hz, 1H), 5.36 (d, *J* = 5.7 Hz, 1H), 5.22 (t, *J* = 7.7 Hz, 1H), 5.06 (dt, *J* = 7.1, 3.8 Hz, 2H), 4.77 (t, *J* = 6.4 Hz, 1H), 4.18 (d, *J* = 6.4 Hz, 2H), 4.09 (dd, *J* = 10.4, 5.7 Hz, 1H), 3.31 (dd, *J* = 13.2, 9.1 Hz, 1H), 3.06 (dd, *J* = 13.2, 6.5 Hz, 1H), 2.19 (s, 3H), 2.12 – 1.99 (m, 9H), 1.98 – 1.91 (m, 2H), 1.86 (s, 3H), 1.67 (d, *J* = 9.1 Hz, 6H), 1.58 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.43, 170.13, 169.66, 159.83, 139.81, 135.26, 133.52, 132.18, 131.25, 130.55, 129.13, 125.39, 125.35, 124.25, 123.76, 119.24, 83.07, 69.76, 67.22, 67.05, 66.80, 62.43, 39.65, 39.61, 29.67, 26.67, 26.54, 26.42, 25.64, 20.75, 20.72, 20.36, 17.64, 15.94, 15.91.

HRMS (ESI): calc. for $C_{35}H_{46}F_3NO_7SNa$ $[M + Na]^+$, 704.2839; found: 704.2836.



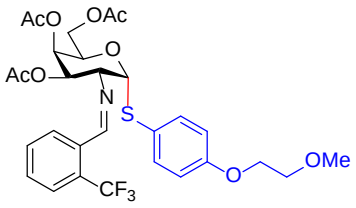
17a: 85% α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.65 (d, *J* = 1.7 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.64 (t, *J* = 9.7 Hz, 1H), 5.51 (d, *J* = 5.6 Hz, 1H), 5.13 (t, *J* = 9.8 Hz, 1H), 4.74 (ddd,

J = 10.2, 4.8, 1.8 Hz, 1H), 4.32 (dd, *J* = 12.3, 5.0 Hz, 1H), 4.14 – 4.06 (m, 2H), 4.02 – 3.93 (m, 2H), 3.79 – 3.68 (m, 2H), 3.43 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.57, 169.90, 169.65, 160.17, 158.83, 134.76, 133.23, 132.27, 130.81, 129.19, 129.05, 128.99, 128.18, 125.45, 125.41, 124.96, 123.46, 115.28, 87.38, 72.22, 71.71, 70.87, 68.87, 68.16, 67.32, 62.20, 59.18, 20.68, 20.36.

HRMS (ESI): calc. for $C_{29}H_{32}F_3NO_9SNa$ [M + Na]$^+$, 650.1642; found: 650.1637.

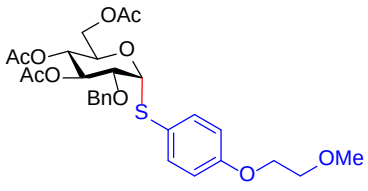


17b: 83% α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ ^{1}H NMR (600 MHz, cdcl$_3$) δ 8.67 (d, *J* = 1.9 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.51 (ddd, *J* = 13.8, 10.7, 4.5 Hz, 3H), 4.87 (t, *J* = 6.5 Hz, 1H), 4.18 – 4.00 (m, 5H), 3.79 – 3.68 (m, 2H), 3.43 (s, 3H), 2.17 (s, 3H), 1.99 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.39, 170.10, 169.69, 160.17, 158.79, 135.00, 133.49, 132.24, 130.67, 129.17, 125.45, 125.41, 123.58, 115.18, 87.91, 70.88, 69.53, 67.37, 67.30, 67.16, 66.93, 62.02, 59.18, 20.72, 20.68, 20.36.

HRMS (ESI): calc. for $C_{29}H_{32}F_3NO_9SNa$ [M + Na]$^+$, 650.1642; found: 650.1635.



17c

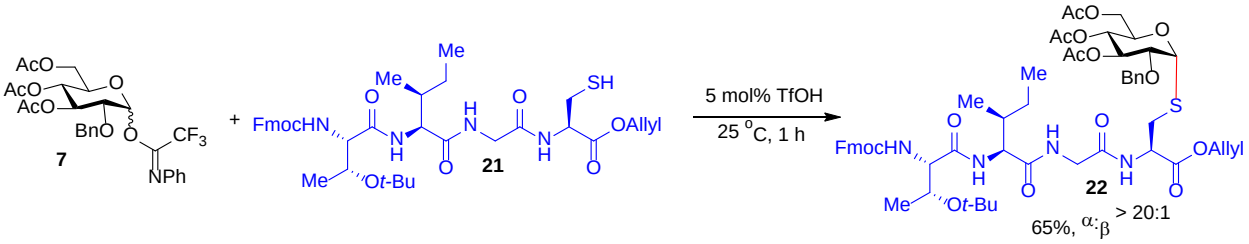
92%, α:β > 20:1

^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.42 – 7.26 (m, 7H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.45 (d, *J* = 5.5 Hz, 1H), 5.35 (t, *J* = 9.6 Hz, 1H), 4.97 (t, *J* = 9.8 Hz, 1H), 4.71 (d, *J* = 12.2 Hz, 1H), 4.63 – 4.55 (m, 2H), 4.27 (dd, *J* = 12.3, 5.2 Hz, 1H), 4.14 – 4.07 (m, 2H), 3.98 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.85 (dd, *J* = 9.9, 5.5 Hz, 1H), 3.76 – 3.70 (m, 2H), 3.44 (s, 3H), 2.04 – 2.01 (m, 9H).

^{13}C NMR (CDCl3, 150 MHz): δ 170.50, 169.92, 169.79, 158.95, 137.20, 134.67, 128.47, 128.07, 127.88, 123.60, 115.33, 87.42, 76.29, 72.39, 72.14, 70.88, 68.69, 67.91, 67.36, 62.14, 59.20, 20.75, 20.67, 20.64.

HRMS (ESI): calc. for $C_{28}H_{34}O_{10}SNa$ $[M + Na]^+$, 585.1765; found: 585.1768.

7. Synthesis of Sublancin Glycopeptide Fragment 22

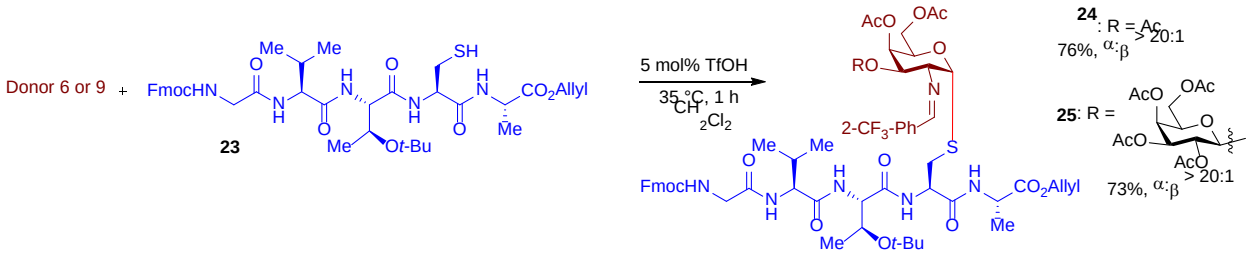


^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.81 (d, *J* = 6.6 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.26 (m, 5H), 6.46 (dd, *J* = 7.4, 4.8 Hz, 1H), 6.35 (d, *J* = 6.5 Hz, 1H), 5.81 (ddd, *J* = 25.2, 15.0, 5.5 Hz, 2H), 5.37 – 5.09 (m, 4H), 5.03 – 4.91 (m, 2H), 4.69 (d, *J* = 12.3 Hz, 1H), 4.61 (dd, *J* = 12.5, 6.6 Hz, 1H), 4.47 (d, *J* = 12.3 Hz, 1H), 4.40 – 4.16 (m, 7H), 4.13 – 4.00 (m, 2H), 3.91 (dd, *J* = 13.0, 6.3 Hz, 1H), 3.83 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.63 (dd, *J* = 17.0, 4.4 Hz, 1H), 3.14 (dd, *J* = 14.0, 4.3 Hz, 1H), 2.93 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.31 (s, 9H), 1.14 (d, *J* = 6.4 Hz, 3H), 0.99 – 0.92 (m, 5H), 0.90 – 0.84 (m, 4H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.46, 170.81, 170.62, 170.49, 170.00, 169.76, 169.49, 168.97, 156.06, 143.84, 143.64, 141.24, 137.40, 131.08, 128.39, 128.37, 127.96, 127.88, 127.72, 127.56, 126.99, 125.16, 125.12, 120.01, 119.99, 119.27, 83.12, 81.74, 81.45, 75.55, 71.96, 71.36, 68.37, 67.91, 67.39, 67.01, 66.44, 61.89, 59.92, 58.13, 55.97, 53.72, 50.85, 47.09, 42.95, 36.59, 35.97, 31.91, 30.77, 29.69, 29.65, 29.35, 29.24, 28.12, 26.67, 25.25, 22.68, 20.77, 20.68, 20.65, 16.40, 15.58, 14.12, 11.12.

HRMS (ESI): calc. for $C_{56}H_{72}N_4O_{16}SNa$ $[M + Na]^+$, 1111.4556; found: 1111.4562.

8. Synthesis of S-linked TN and TF Glycopeptide Fragments 24 and 25



24:

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.60 (d, *J* = 1.7 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 3H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.62 – 7.49 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 6.69 (s, 1H), 5.84 (ddd, *J* = 22.8, 10.8, 5.7 Hz, 1H), 5.74 (s, 1H), 5.52 – 5.17 (m, 5H), 4.81 (s, 1H), 4.65 – 4.46 (m, 5H), 4.40 (dd, *J* = 19.9, 8.3 Hz, 3H), 4.26 – 3.87 (m, 8H), 3.11 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.91 (dd, *J* = 13.6, 5.3 Hz, 1H), 2.17 (s, 3H), 2.10 – 2.00 (m, 4H), 1.84 (s, 3H), 1.31 (d, *J* = 7.2 Hz, 3H), 1.25 (s, 9H), 1.01 (d, *J* = 5.6 Hz, 3H), 0.92 (dd, *J* = 14.0, 6.8 Hz, 6H).

^{13}C NMR (CDCl3, 150 MHz): δ 171.97, 170.61, 170.10, 169.62, 169.45, 169.29, 160.13, 156.68, 143.73, 141.24, 133.57, 133.31, 132.06, 131.53, 130.72, 128.99, 127.71, 127.05, 125.44, 125.02, 123.12, 119.98, 118.60, 83.95, 75.64, 69.27, 67.27, 67.21, 67.18, 66.69, 66.22, 65.84, 61.99, 57.57, 55.95, 53.77, 52.97, 48.26, 47.04, 44.50, 29.67, 29.25, 28.07, 20.74, 20.68, 20.34, 19.14, 18.03, 18.00.

HRMS (ESI): calc. for $C_{59}H_{73}F_3N_6O_{16}SNa$ $[M + Na]^+$, 1233.4648; found: 1233.4656.

25:

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.58 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.23 (s, 1H), 6.67 (s, 1H), 5.83 (ddd, *J* = 16.2, 10.9, 5.7 Hz, 1H), 5.76 (s, 1H), 5.47 (s, 1H), 5.35 – 5.18 (m, 4H), 5.11 (s, 1H), 5.00 (dd, *J* = 10.4, 7.9 Hz, 1H), 4.81 (dd, *J* = 10.5, 3.4 Hz, 1H), 4.73 (d, *J* = 4.9 Hz, 1H), 4.60 – 4.46 (m, 5H), 4.45 – 4.34 (m, 3H), 4.34 – 4.20 (m, 3H), 4.17 – 4.01 (m, 5H), 3.93 (d, *J* = 4.7 Hz, 2H), 3.82 (t, *J* = 6.8 Hz, 1H), 3.02 (dd, *J* = 13.6, 6.7 Hz, 1H), 2.87 (dd, *J* = 13.5, 5.2 Hz, 1H), 2.18 – 2.15 (m, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.04 (d, *J* = 3.0 Hz, 6H), 1.88 (s, 3H), 1.45 (s, 3H), 1.27 (d, *J* = 7.2 Hz, 3H), 1.25 (s, 9H), 0.98 (s, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H).

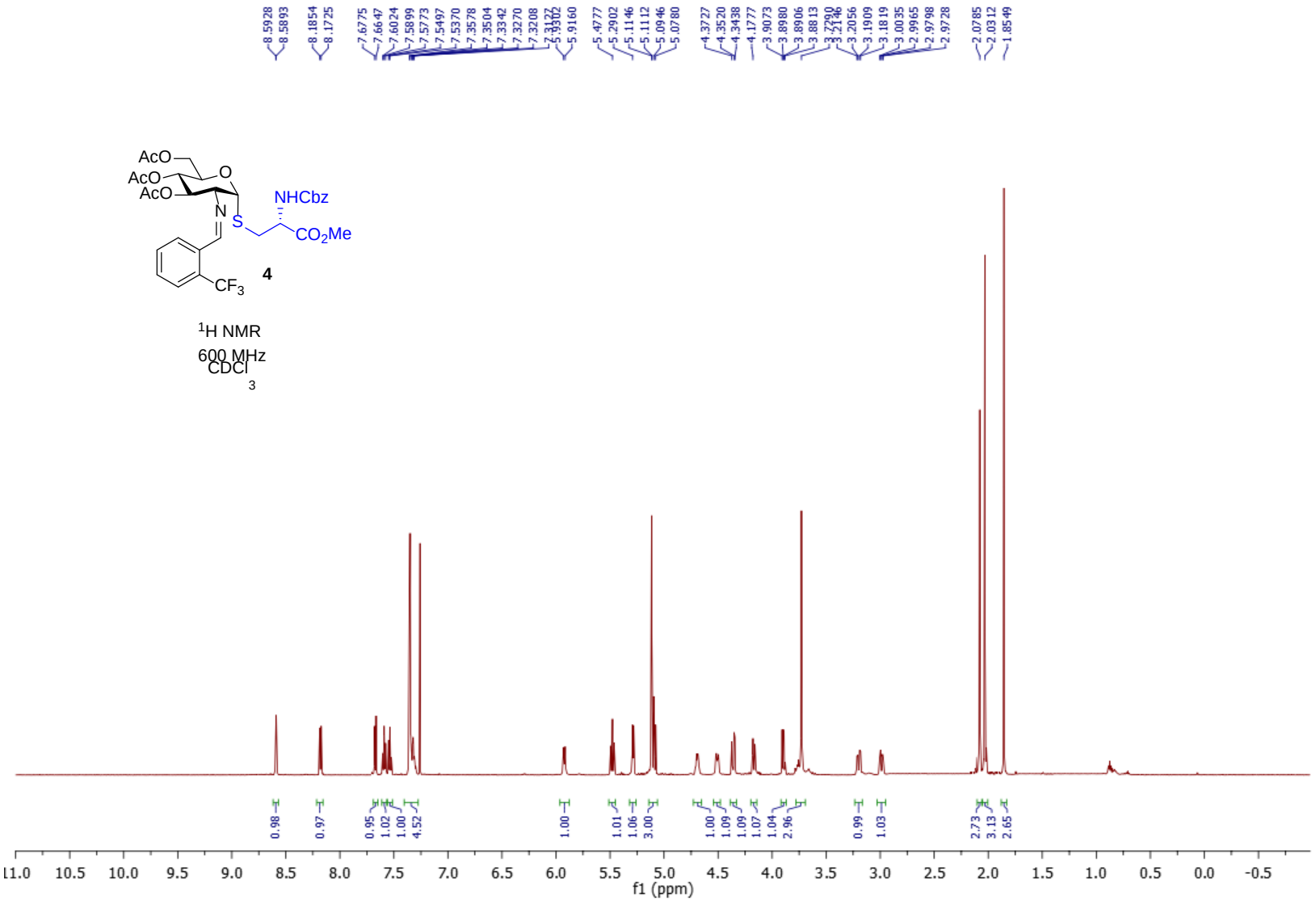
^{13}C NMR (CDCl3, 150 MHz): δ 171.99, 170.72, 170.65, 170.37, 170.25, 170.04, 169.96, 169.36, 169.21, 168.73, 159.88, 143.73, 141.24, 133.33, 132.03, 131.48, 130.83, 128.71, 127.73, 127.07, 125.03, 120.00, 118.61, 100.65, 84.10, 75.59, 75.57, 70.77, 70.58, 69.14, 68.81, 68.39, 68.31, 67.28, 66.64, 66.22, 65.82, 62.87, 60.87, 58.27, 57.41, 55.94, 53.76, 52.95, 48.23, 47.04, 44.52, 29.66, 29.24, 27.96, 20.77, 20.67, 20.61, 20.46, 19.90, 19.15, 17.99, 17.91.

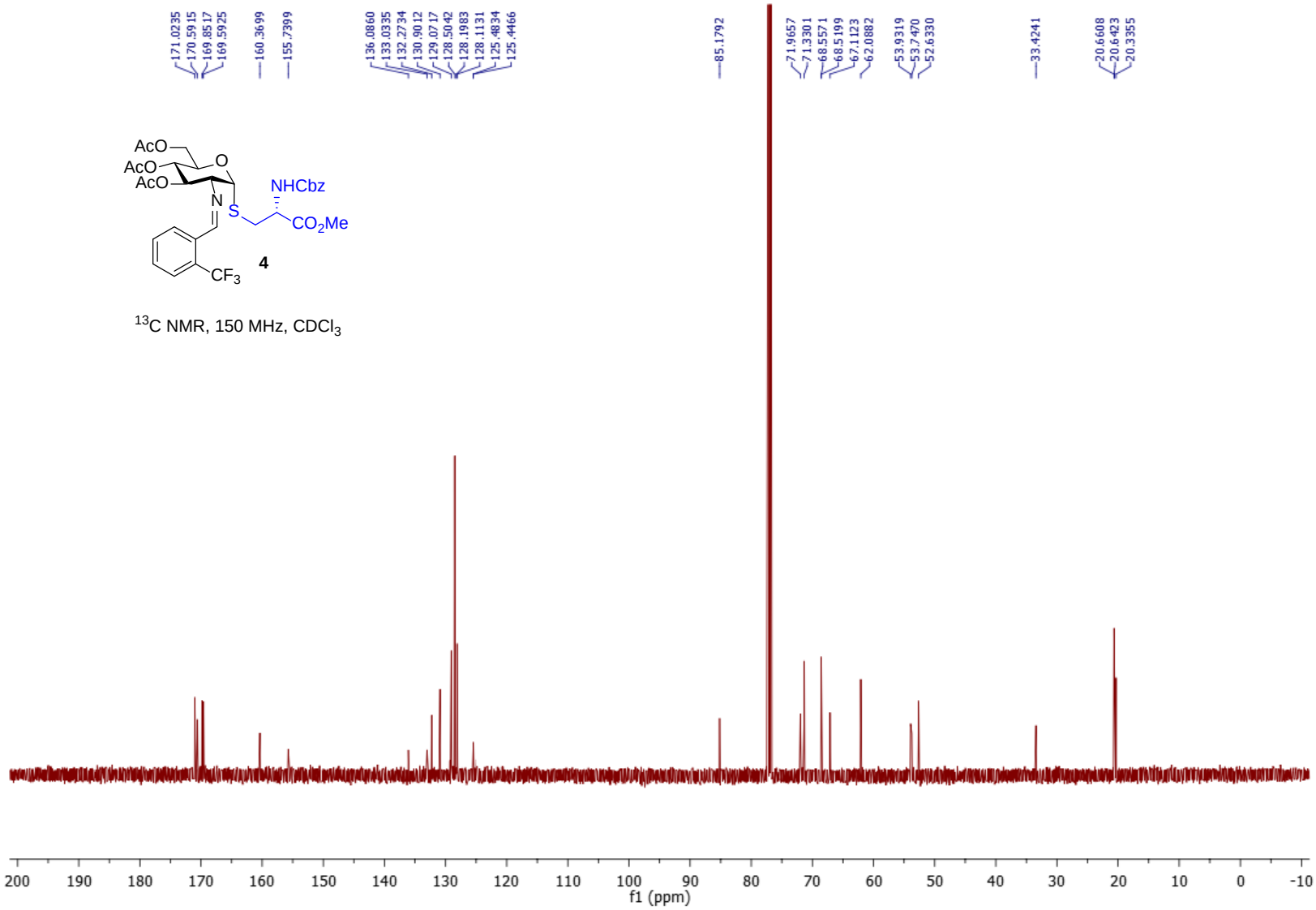
HRMS (ESI): calc. for $C_{71}H_{89}F_3N_6O_{24}SNa$ $[M + Na]^+$, 1521.5493; found: 1521.5498.

9. References

[1] E. T. Sletten, Y.-J. Tu, H. B. Schlegel, H. M. Nguyen, *ACS Catal.* **2019,** *9*, 2110.

10. Spectral Data




171.0235
170.5915
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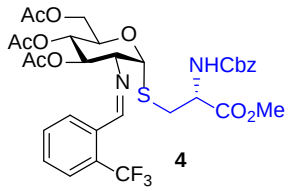
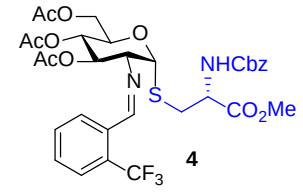
169.5925
160.3699
155.7399
136.0860
133.0335
132.2734
130.9012
129.0717
128.5042
128.1983
128.1131
125.4834
125.4466
85.1792
71.9657
71.3301
68.5571
68.5199
67.1123
62.0882
53.9319
53.7470
52.6330
33.4241
20.6608
20.6423
20.3355
AcO
AcO
AcO
O
N
S
NHCbz
CO2Me
CF3
4
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



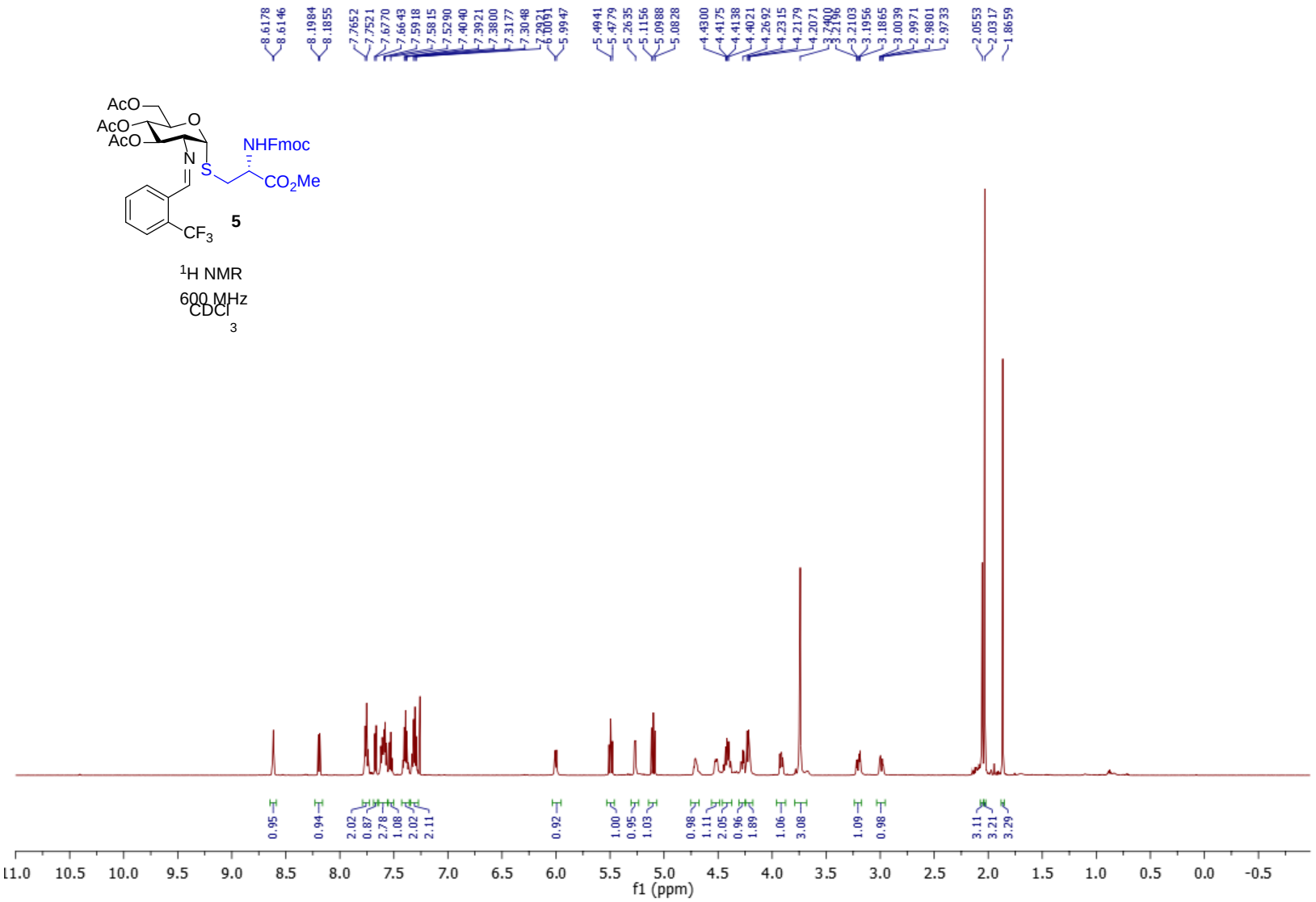
4

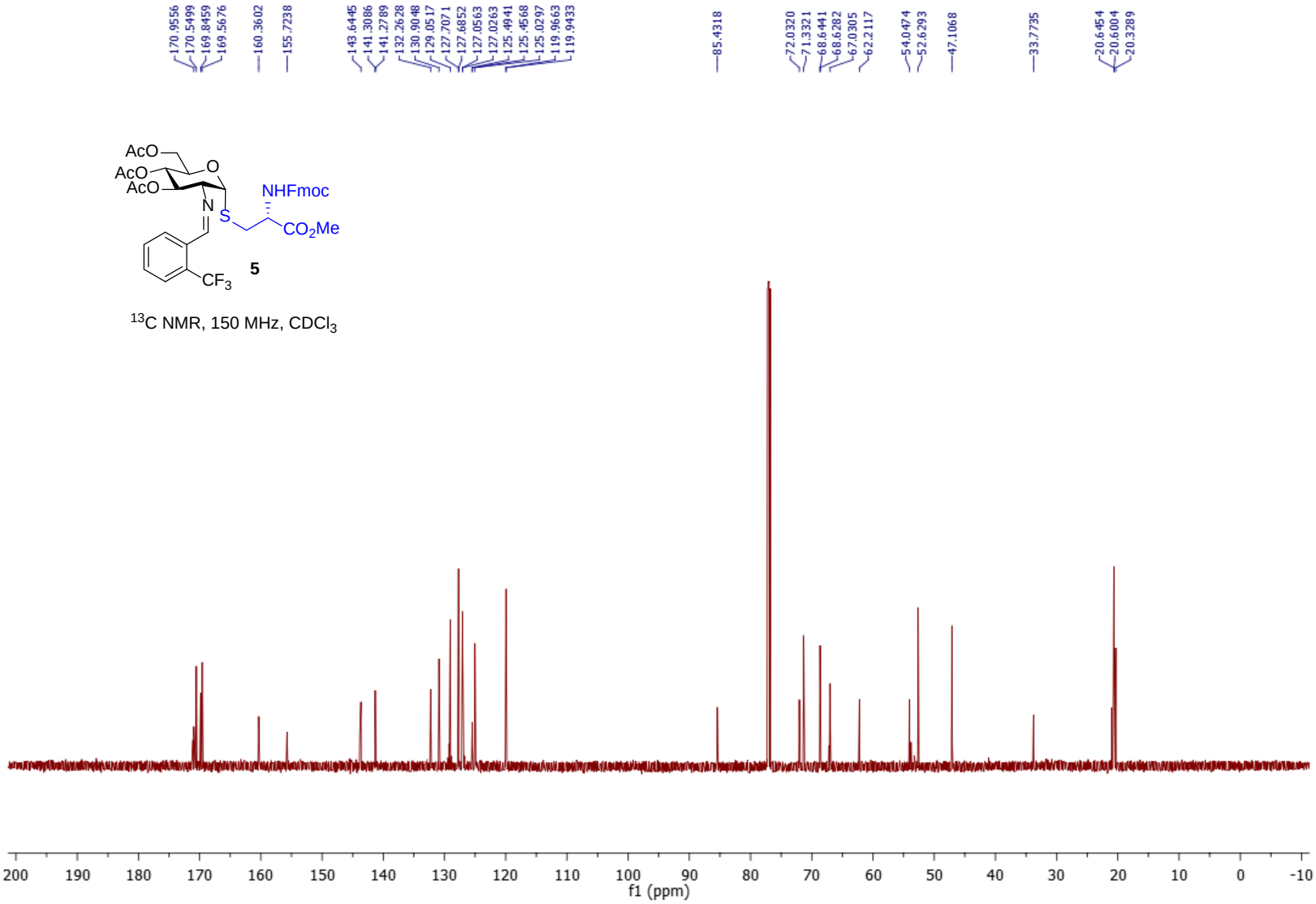
coupled ^{13}C NMR, 150 MHz, $CDCl_3$



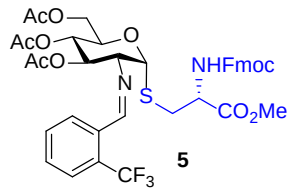
4

^{1}H-^{13}C HSQC, 600/150MHz, $CDCl_3$


AcO
AcO
AcO
O
N
S
NHFmoc
CO2Me
CF3
5
1H NMR
600 MHz
CDCl3
f1 (ppm)

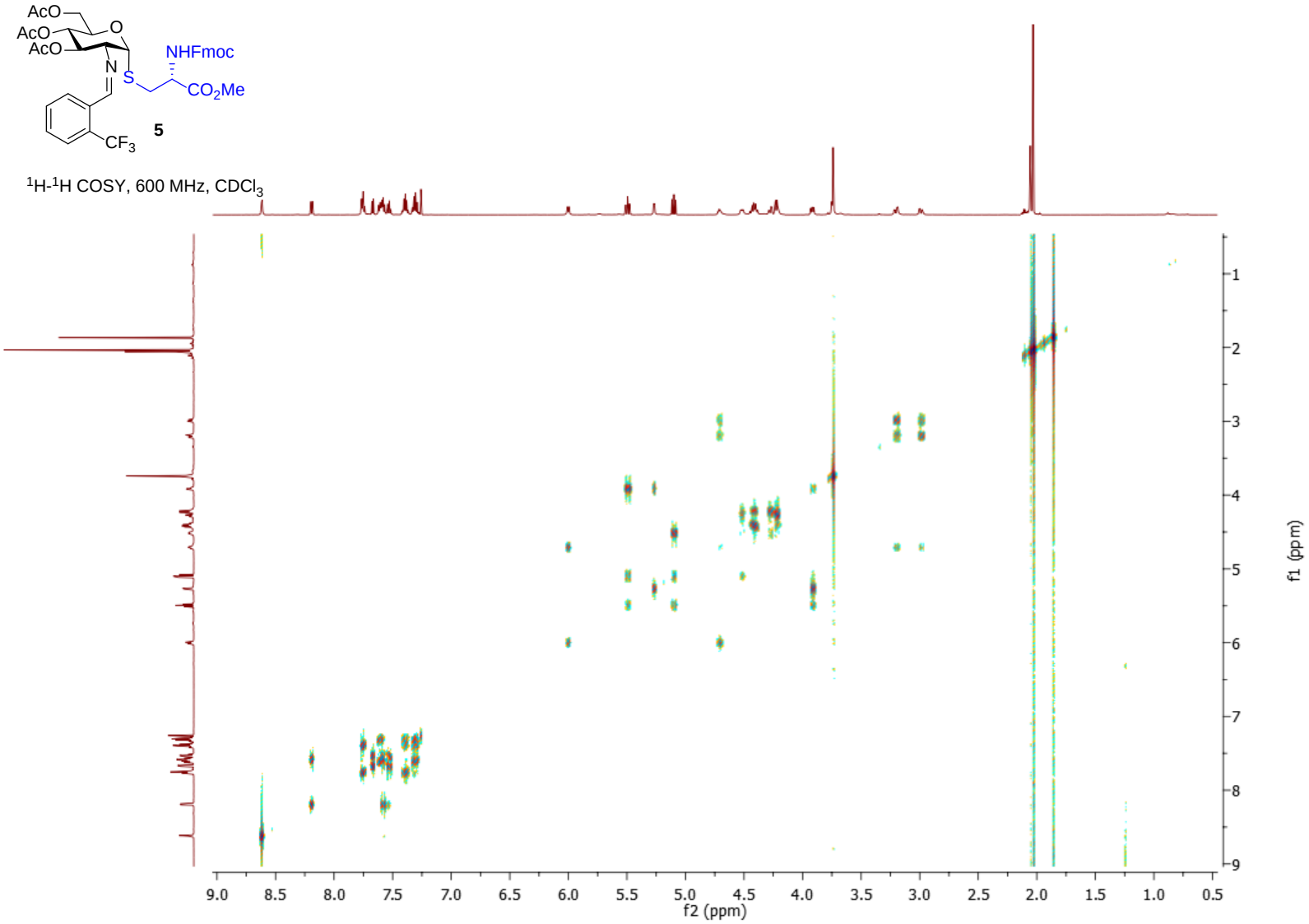


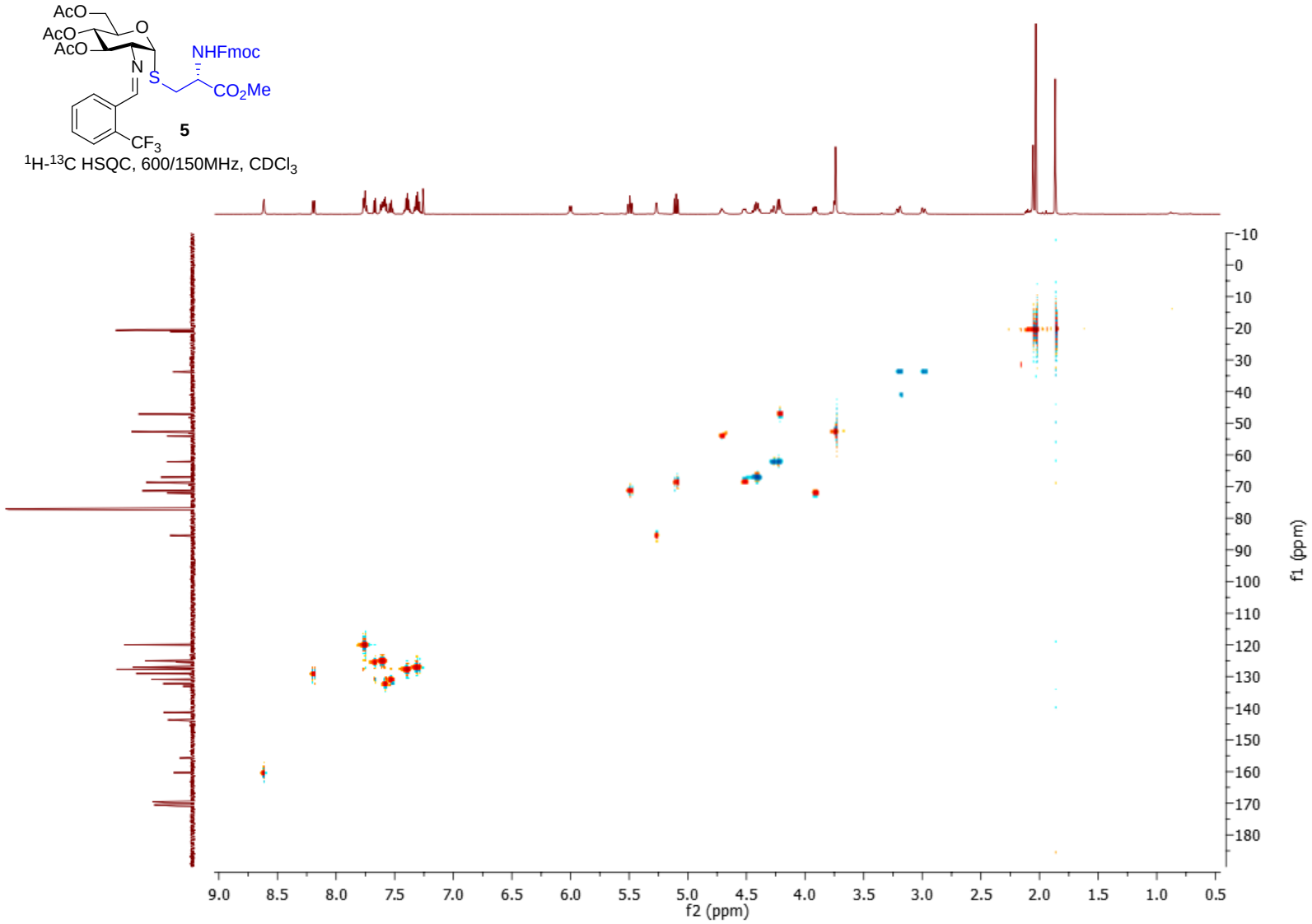
^{13}C NMR, 150 MHz, $CDCl_3$

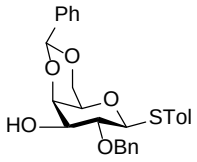


5

coupled ^{13}C NMR, 150 MHz, $CDCl_3$


AcO
AcO
AcO
O
N
S
NHFmoc
CO2Me
CF3
5
1H-1H COSY, 600 MHz, CDCl3
f2 (ppm)
f1 (ppm)


AcO
AcO
AcO
O
N
S
NHFmoc
CO2Me
CF3
5
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

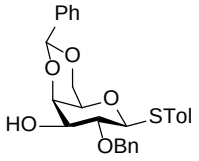


8ii

^{1}H NMR

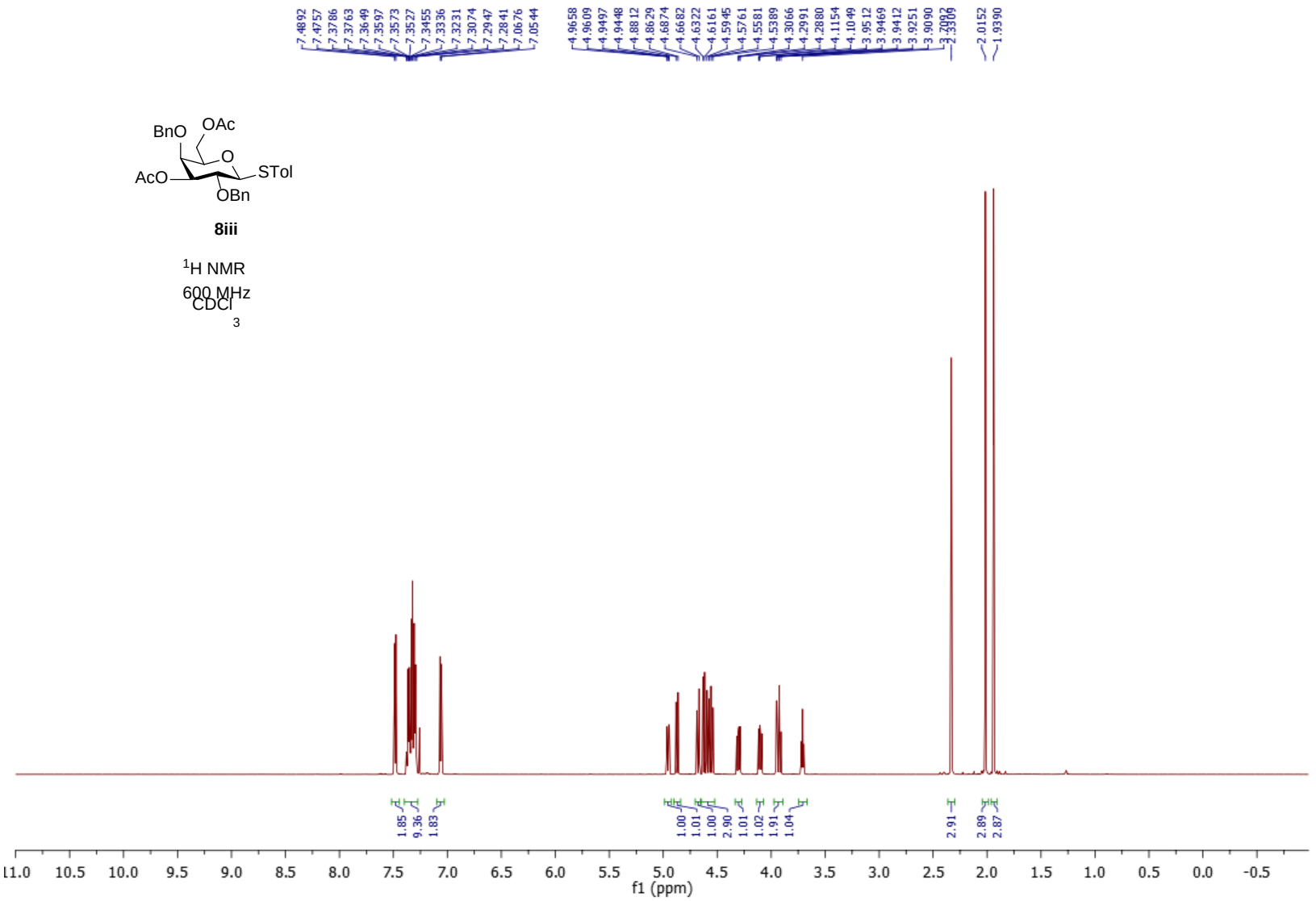
600 MHz

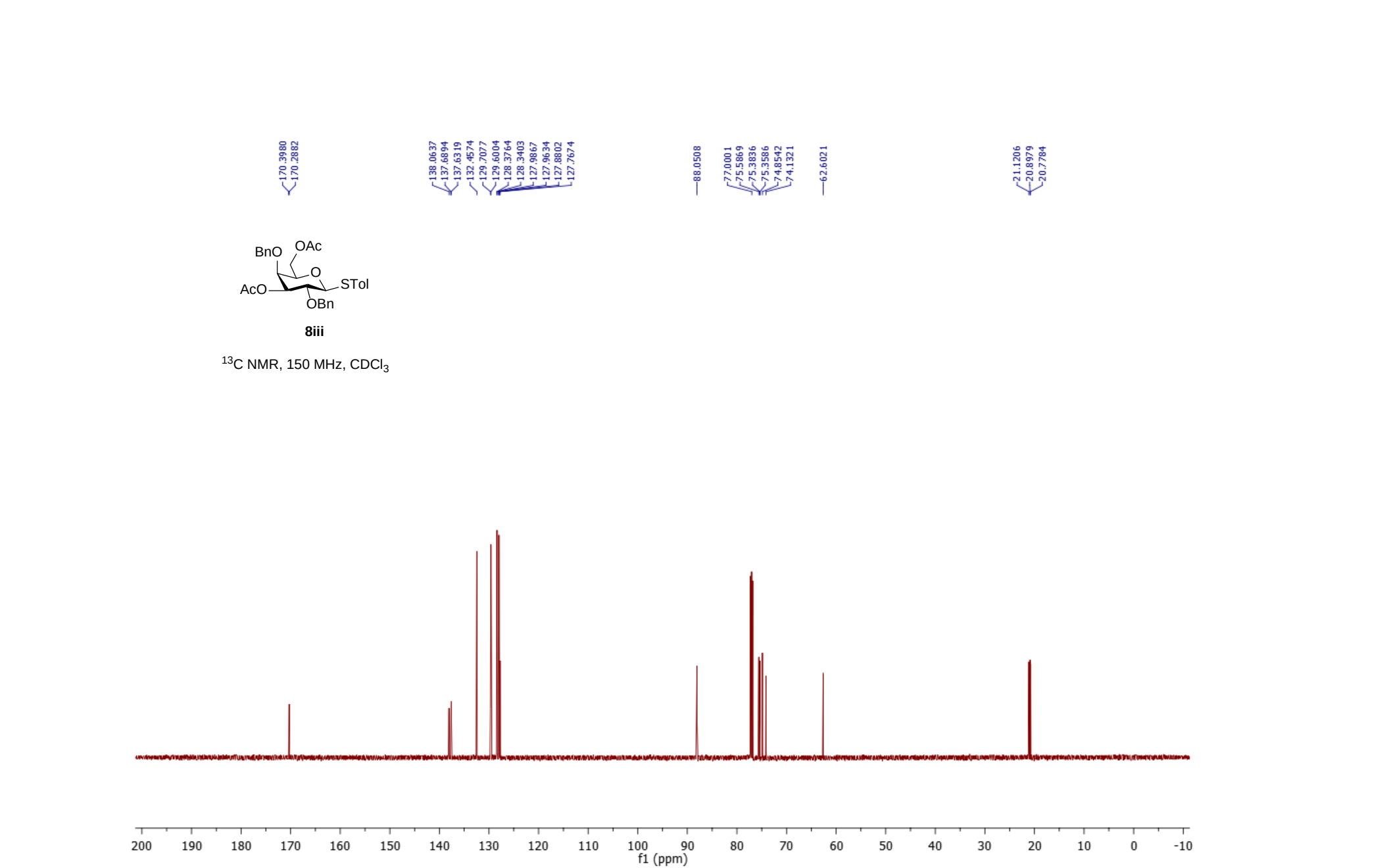
$CDCl_3$



8ii

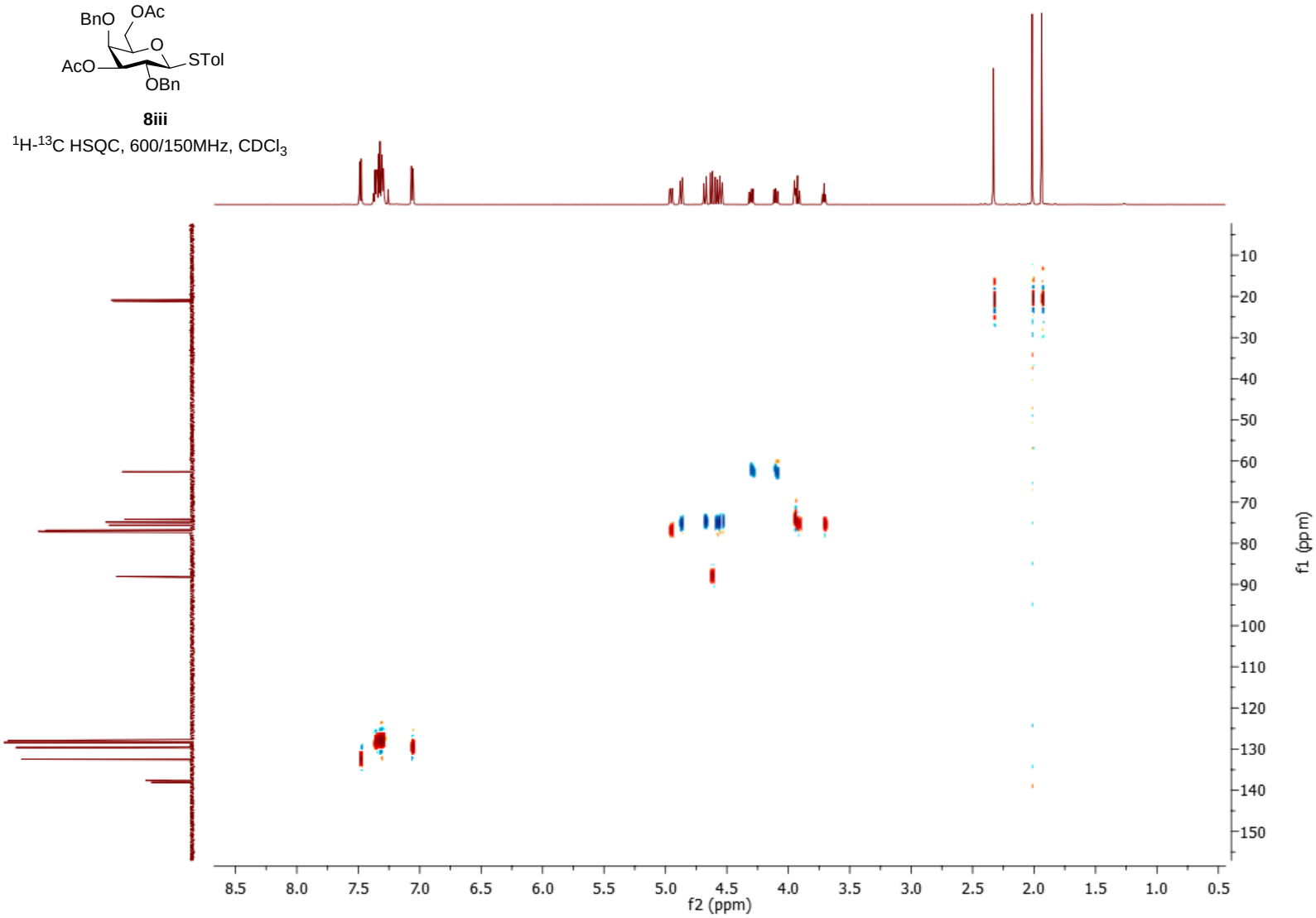
^{13}C NMR, 150 MHz, $CDCl_3$

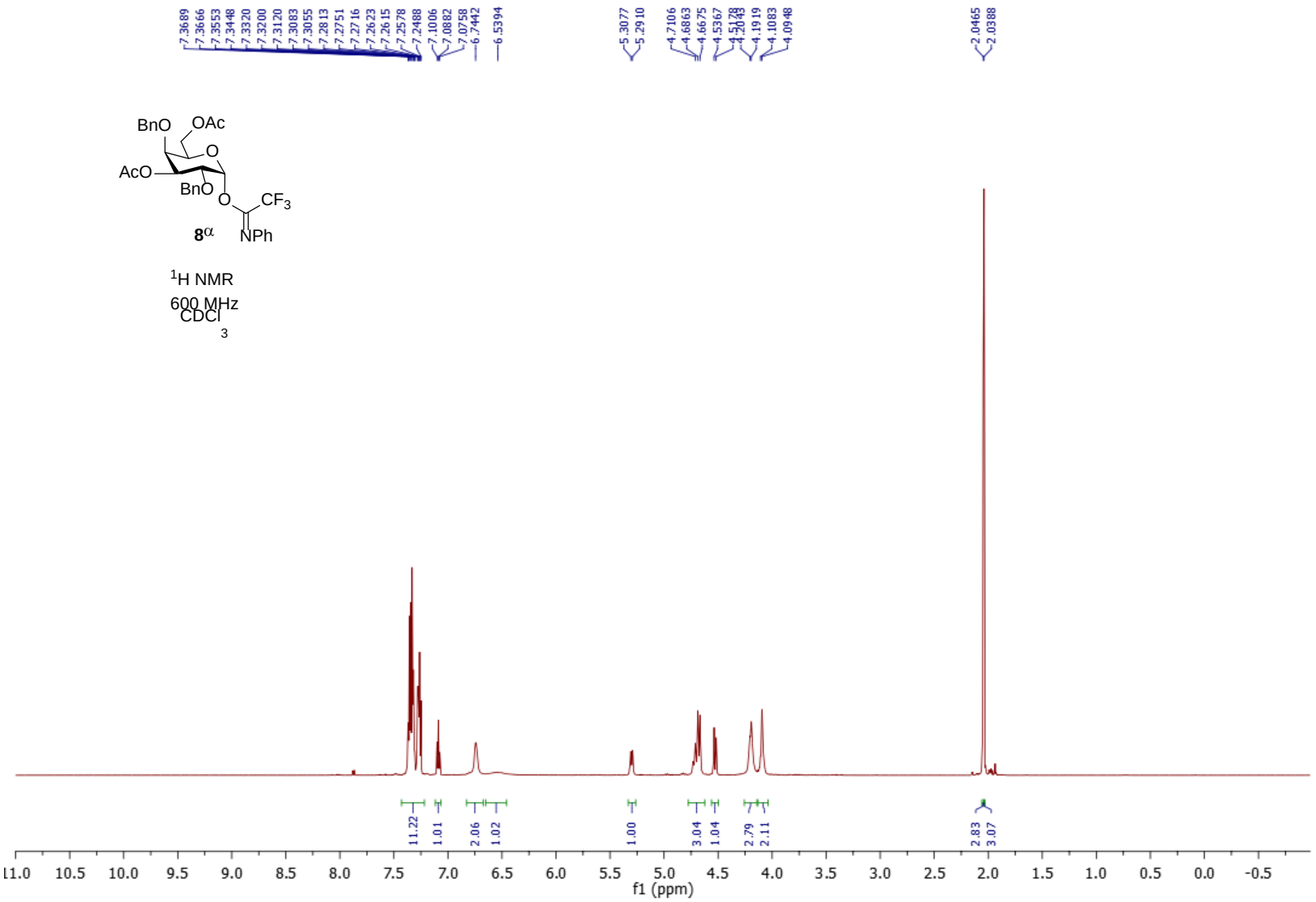

BnO
OAc
O
AcO
STol
OBn
8iii
1H NMR
600 MHz
CDCl3
7.4892
7.4757
7.3786
7.3763
7.3649
7.3597
7.3573
7.3527
7.3455
7.3336
7.3231
7.3074
7.2947
7.2841
7.0676
7.0544
4.9658
4.9609
4.9497
4.9448
4.8812
4.8629
4.6874
4.6682
4.6322
4.6161
4.5945
4.5761
4.5581
4.5389
4.3066
4.2991
4.2880
4.1154
4.1049
3.9512
3.9469
3.9412
3.9251
3.9090
2.0152
1.9990
1.85
9.36
1.83
1.00
1.01
1.00
2.90
1.01
1.02
1.91
1.04
2.91
2.89
2.87
f1 (ppm)

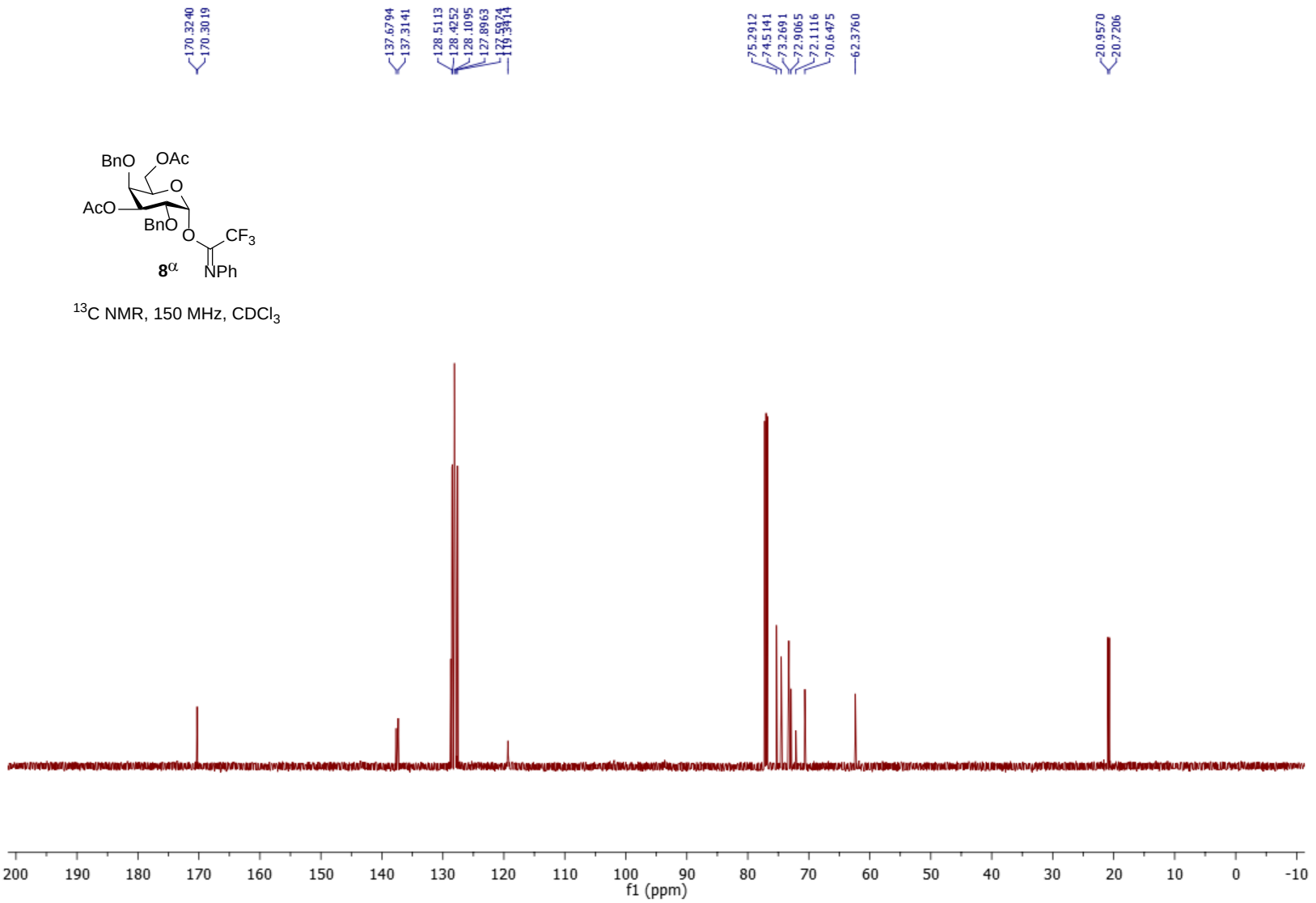


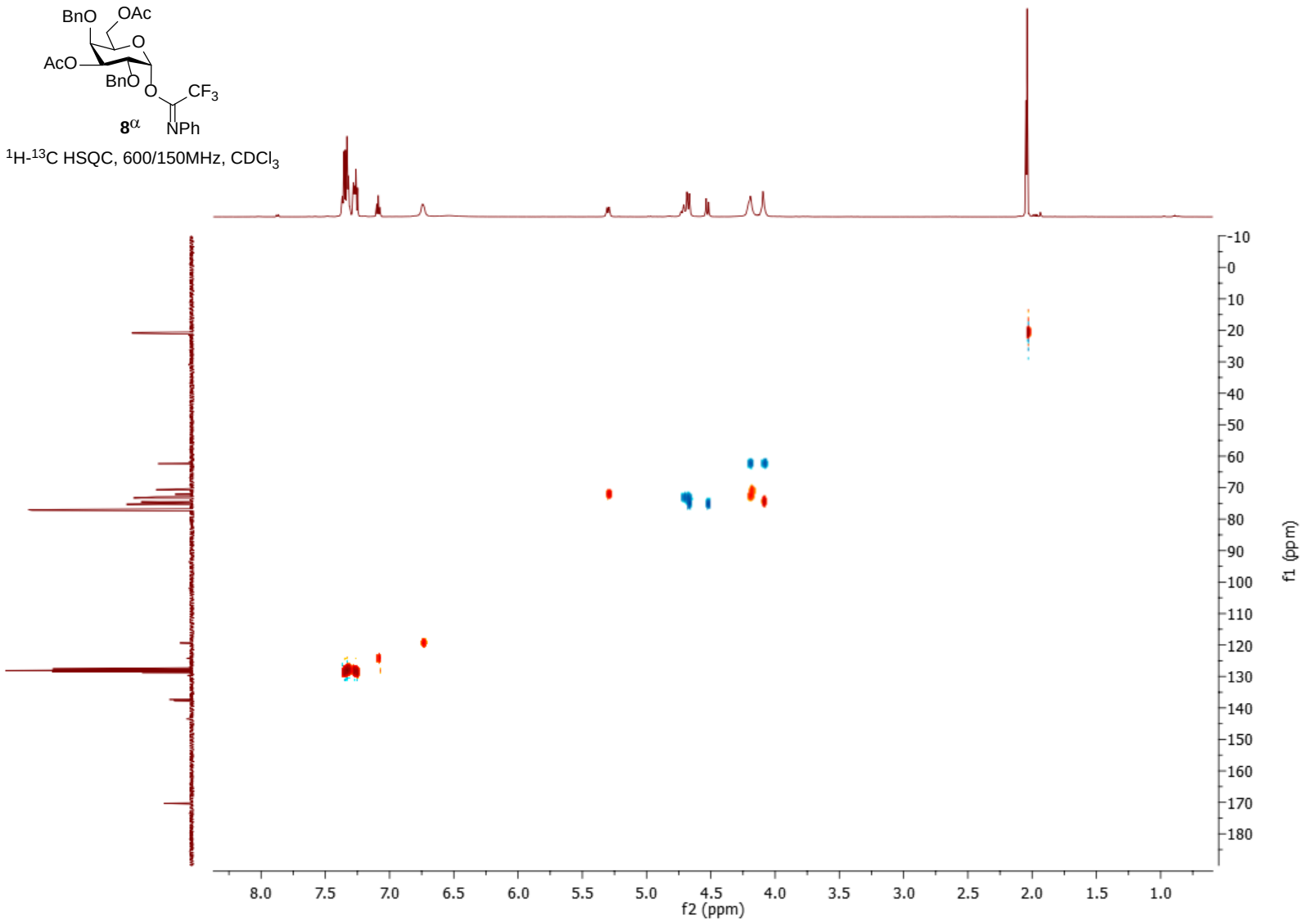
8iii

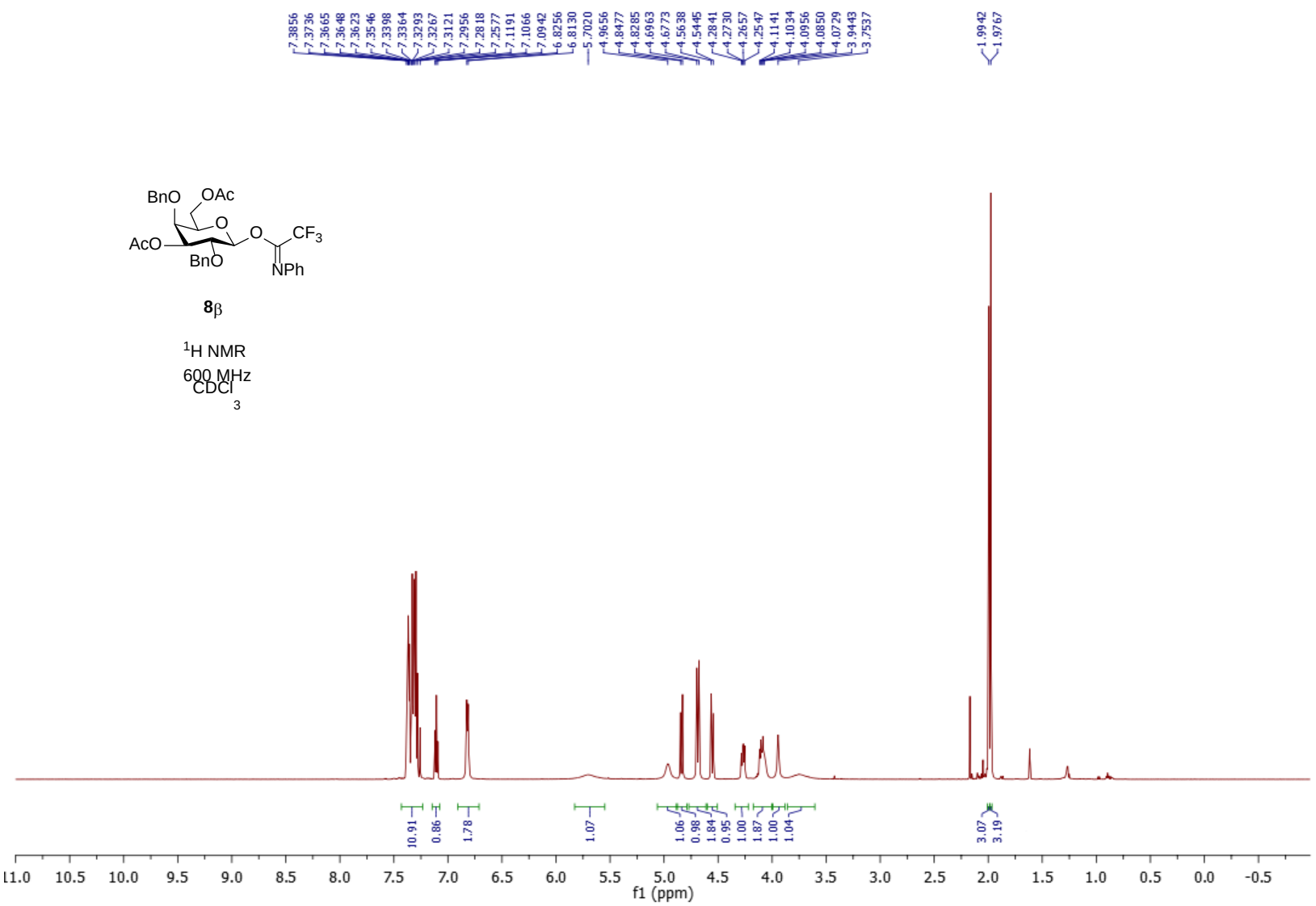
^{13}C NMR, 150 MHz, $CDCl_3$

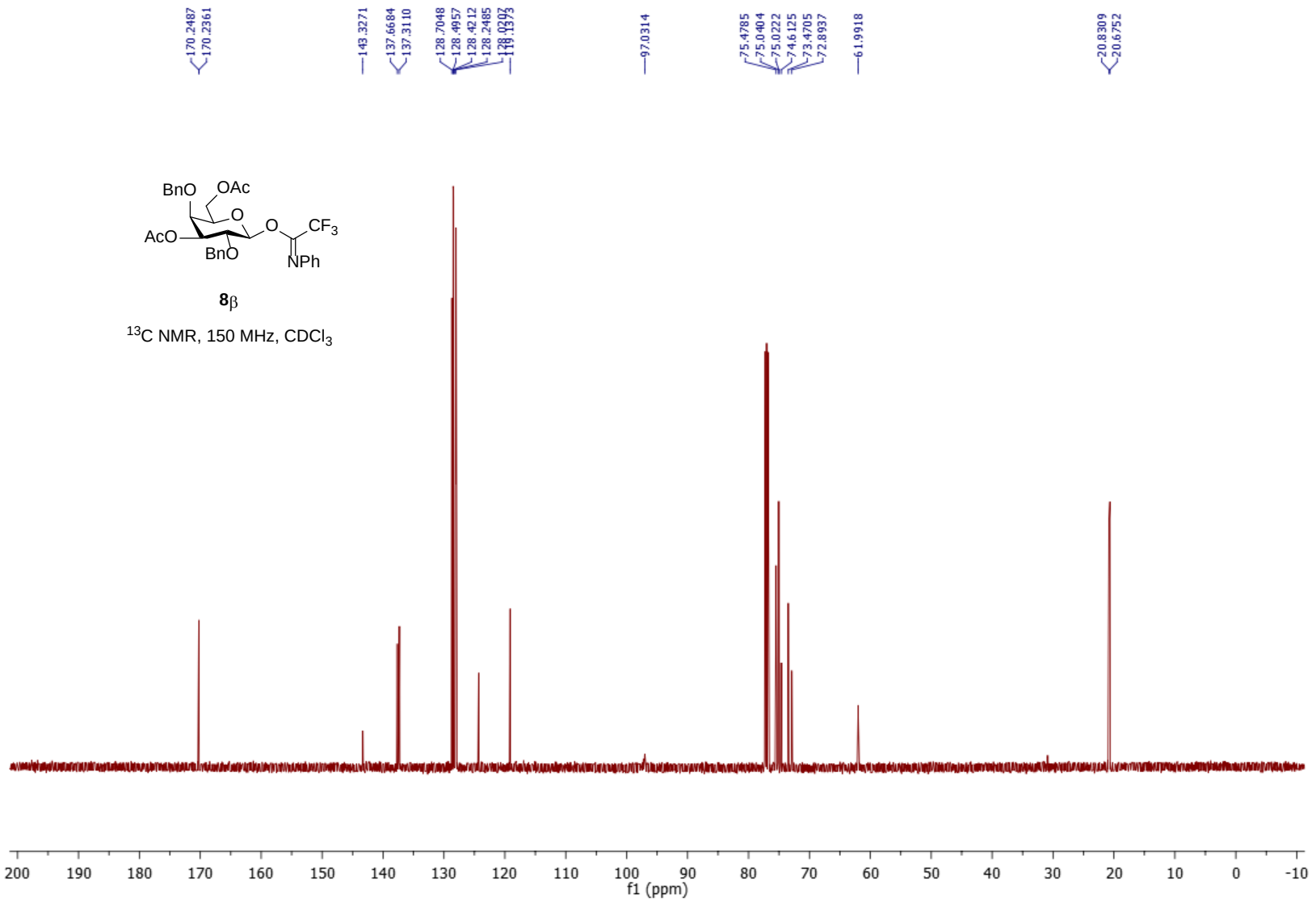

BnO
OAc
O
AcO
STol
OBn
8iii
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


7.3689
7.3666
7.3553
7.3448
7.3320
7.3200
7.3120
7.3083
7.3055
7.2813
7.2751
7.2716
7.2623
7.2615
7.2578
7.2488
7.1006
7.0882
7.0758
6.7442
6.5394
5.3077
5.2910
4.7106
4.6863
4.6675
4.5367
4.1919
4.1083
4.0948
2.0465
2.0388
BnO
OAc
O
AcO
BnO
O
CF3
NPh
8α
1H NMR
600 MHz
CDCl3
11.22
1.01
2.06
1.02
1.00
3.04
1.04
2.79
2.11
2.83
3.07
f1 (ppm)


170.3240
170.3019
137.6794
137.3141
128.5113
128.4252
128.1095
127.8963
77.5074
77.3141
75.2912
74.5141
73.2691
72.9065
72.1116
70.6475
62.3760
20.9570
20.7206
BnO
OAc
O
AcO
BnO
O
CF3
NPh
8α
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

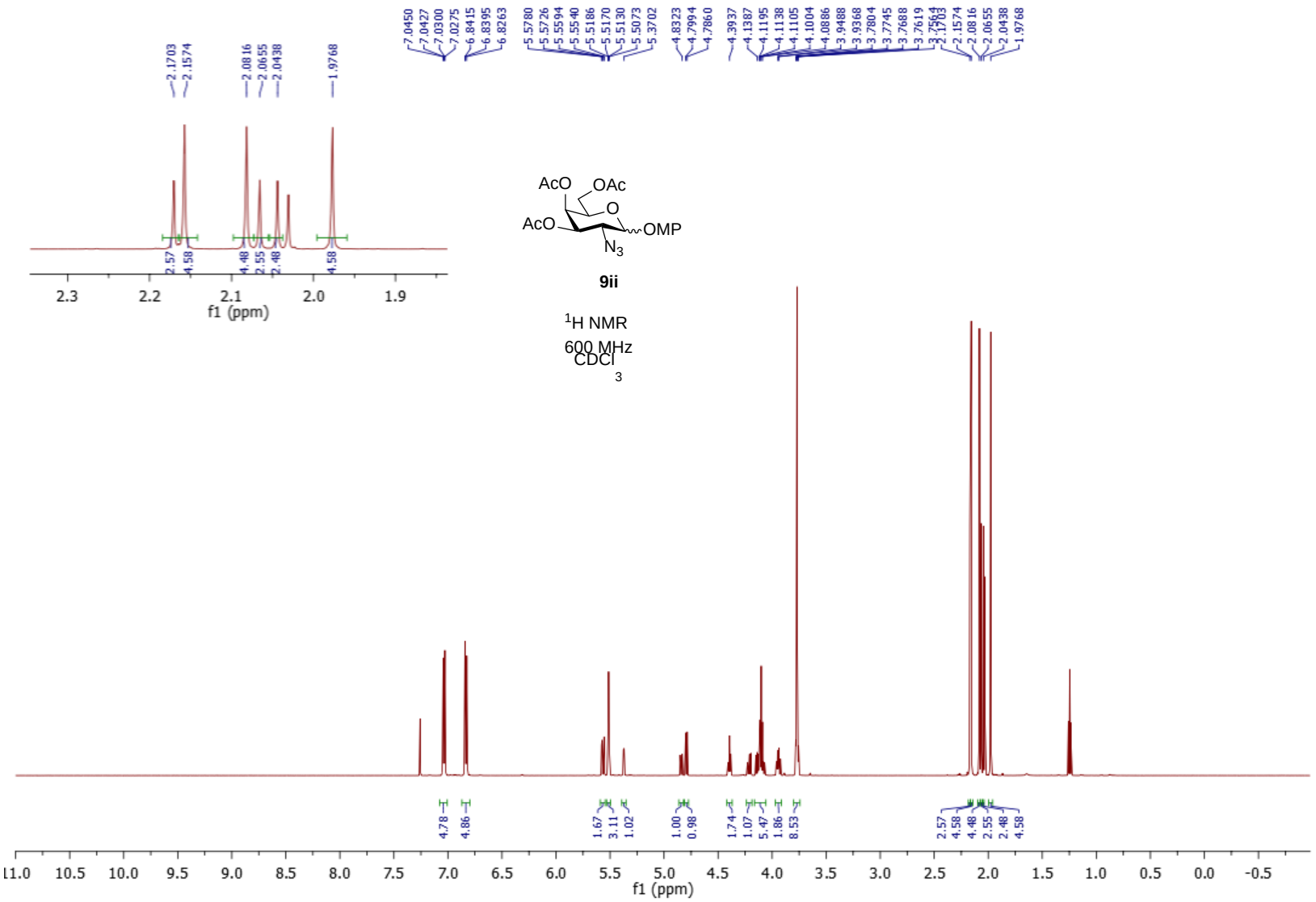

BnO
OAc
O
AcO
BnO
O
CF3
NPh
8α
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

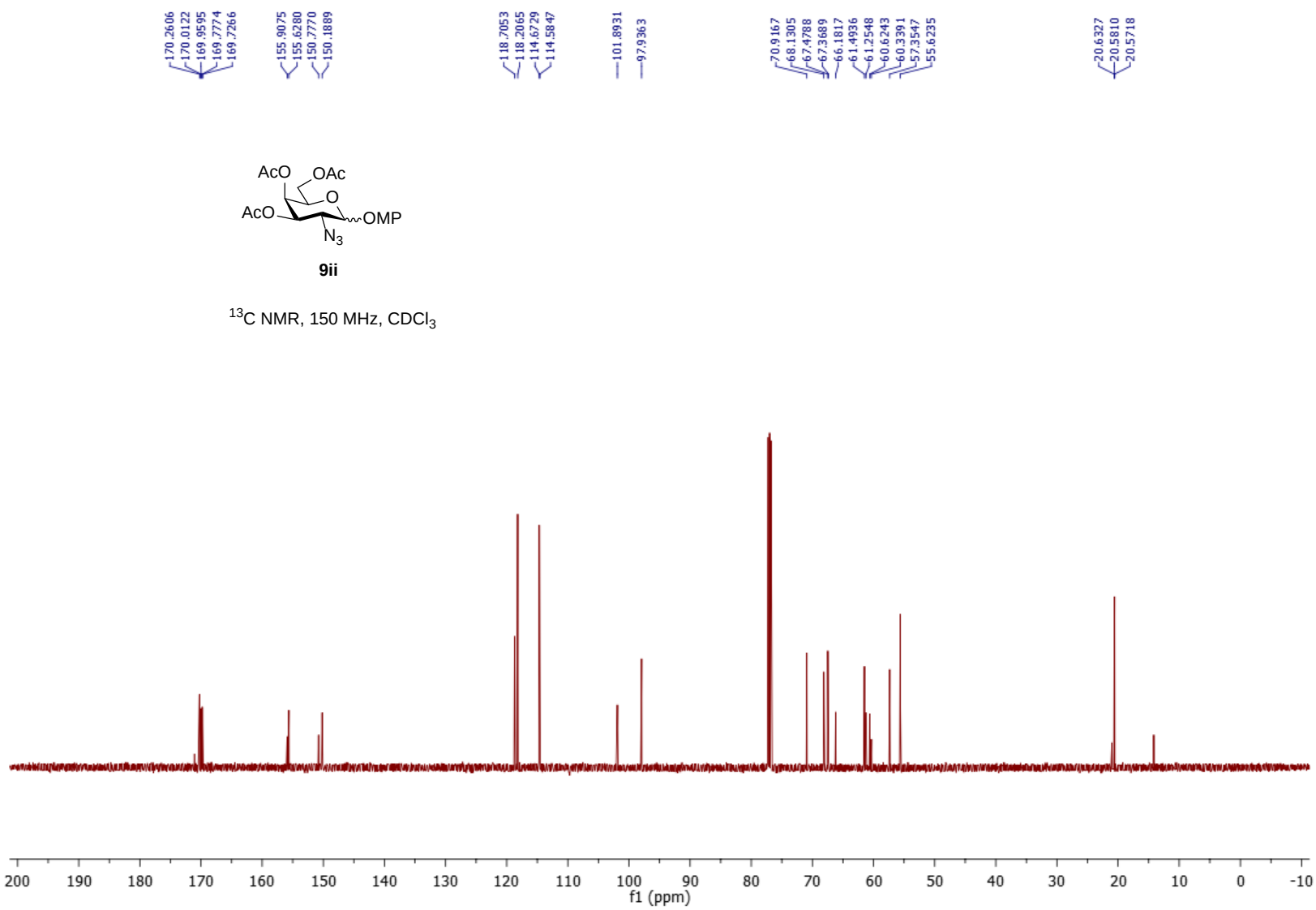

7.3856
7.3736
7.3665
7.3648
7.3623
7.3546
7.3398
7.3364
7.3293
7.3267
7.3121
7.2956
7.2818
7.2577
7.1191
7.1066
7.0942
6.8256
6.8130
5.7020
4.9656
4.8477
4.8285
4.6963
4.6773
4.5638
4.5445
4.2841
4.2730
4.2657
4.2547
4.1141
4.1034
4.0956
4.0850
4.0729
3.9443
3.7537
1.9942
1.9767
BnO
OAc
O
AcO
BnO
O
CF3
NPh
8β
1H NMR
600 MHz
CDCl3
10.91
0.86
1.78
1.07
1.06
0.98
1.84
0.95
1.00
1.87
1.00
1.04
3.07
3.19
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



8β

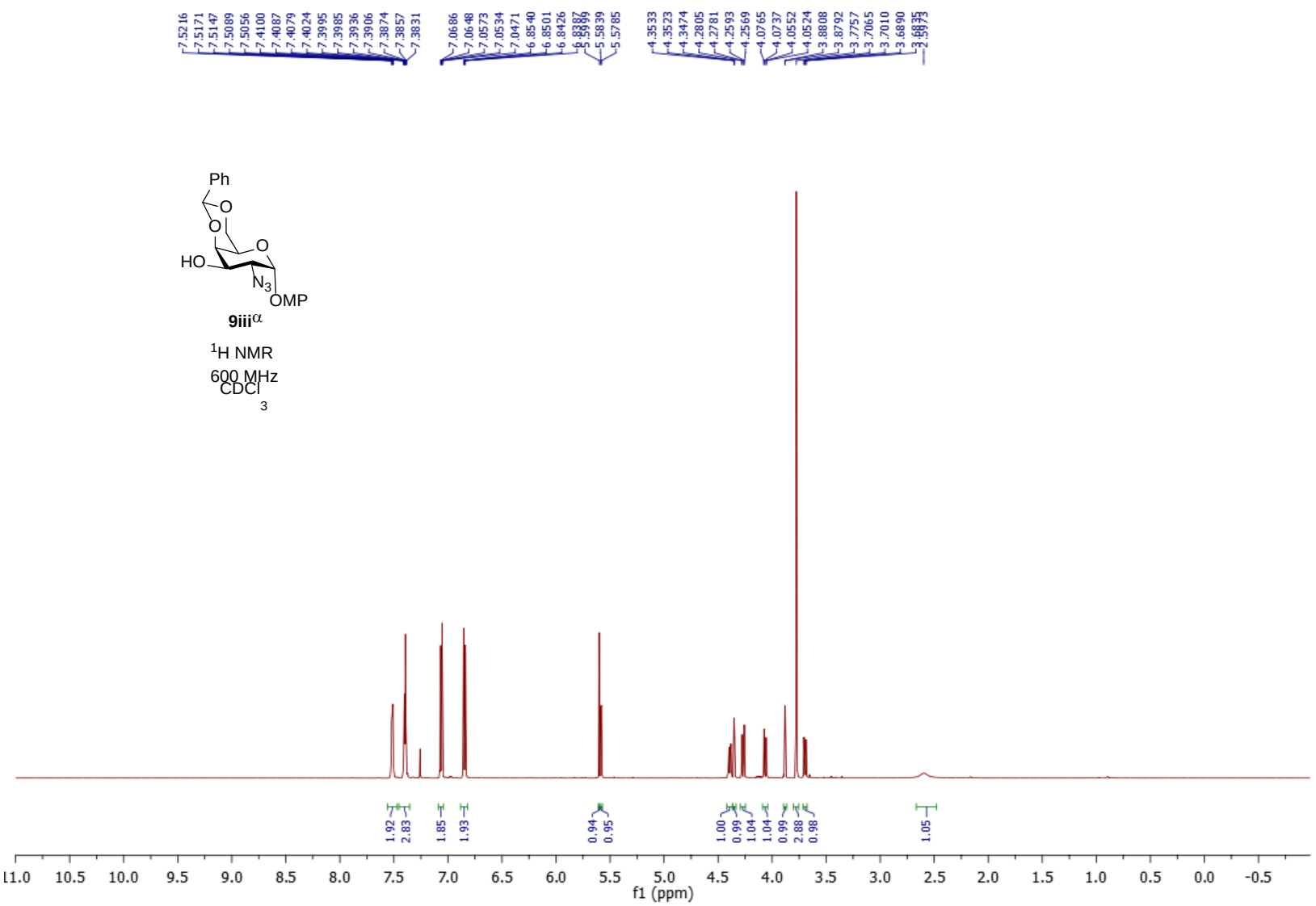
^{13}C NMR, 150 MHz, $CDCl_3$

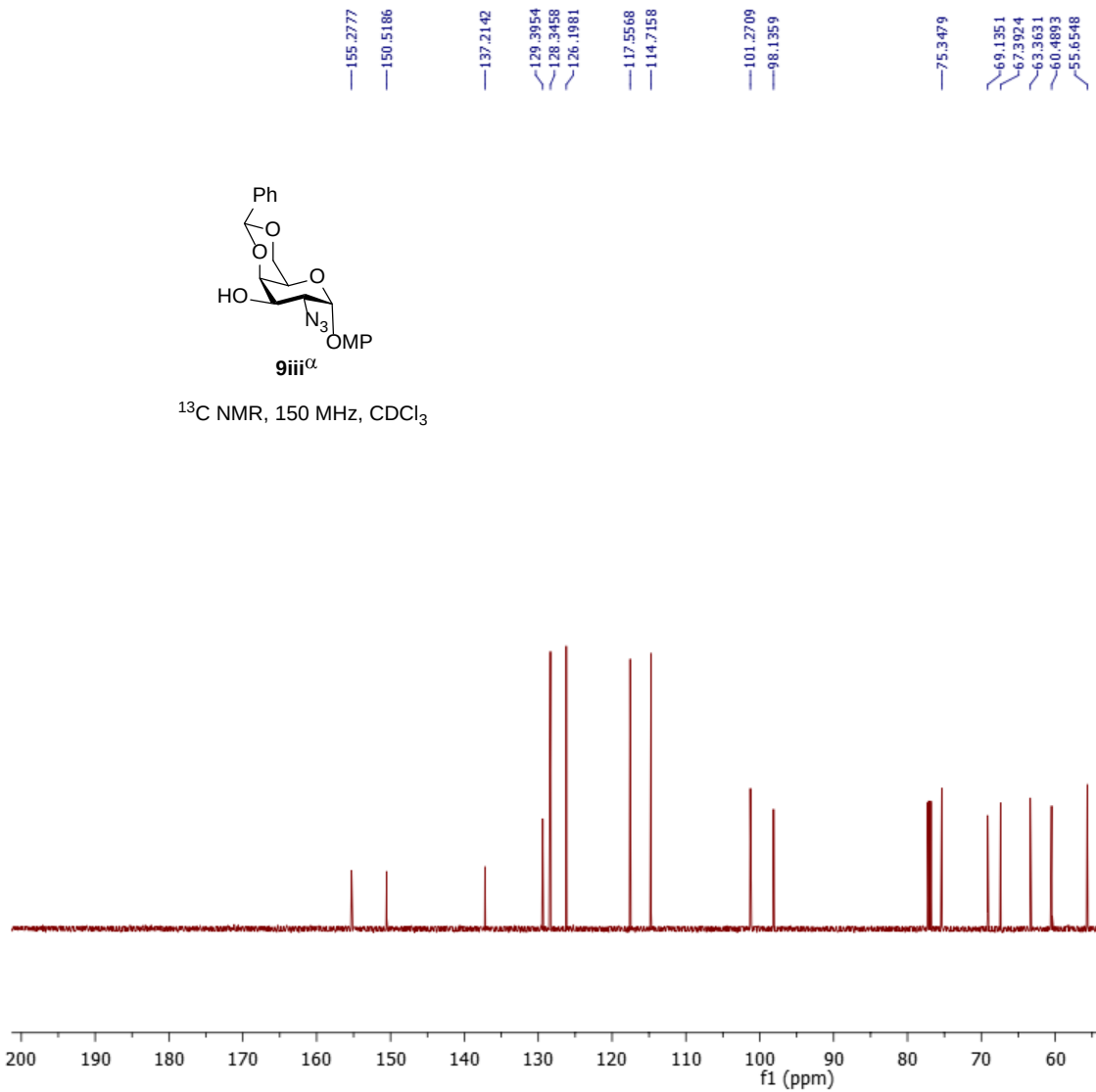

AcO
OAc
O
AcO
OMP
N3
9ii
1H NMR
600 MHz
CDCl3
f1 (ppm)



9ii

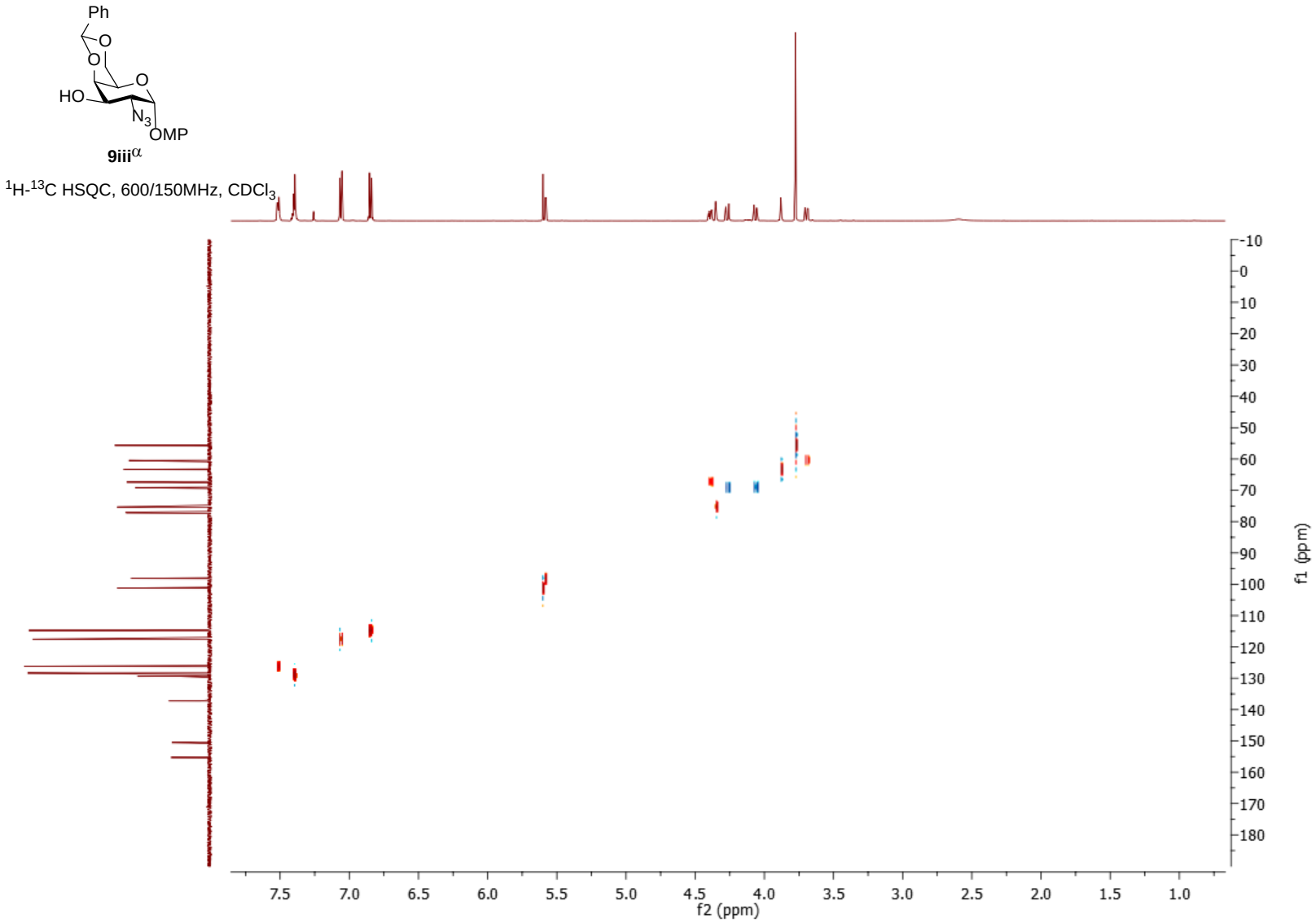
^{13}C NMR, 150 MHz, $CDCl_3$

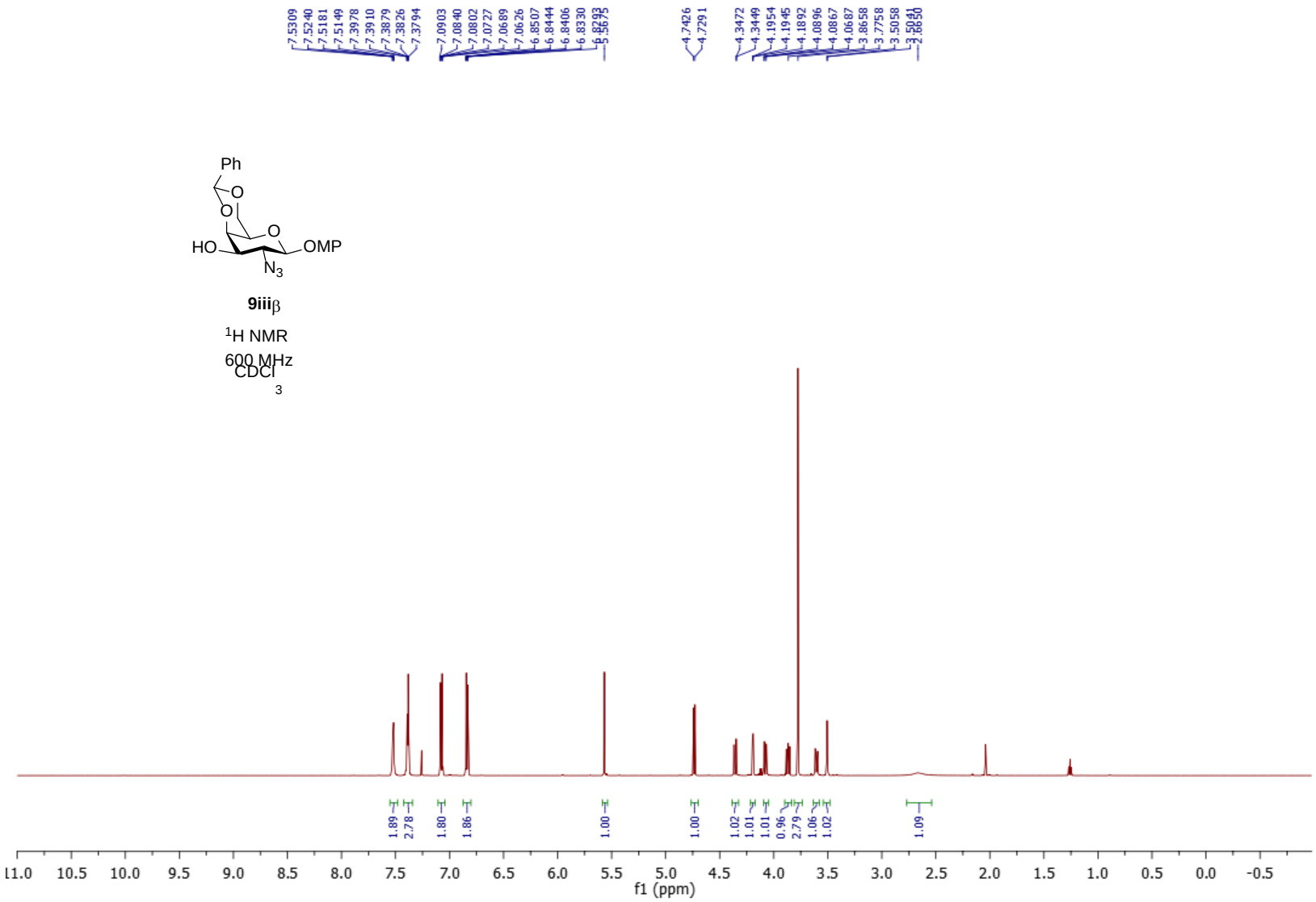

7.5216
7.5171
7.5147
7.5089
7.5056
7.4100
7.4087
7.4079
7.4024
7.3995
7.3985
7.3936
7.3906
7.3874
7.3857
7.3831
7.0686
7.0648
7.0573
7.0534
7.0471
6.8540
6.8501
6.8426
5.5999
5.5839
5.5785
4.3533
4.3523
4.3474
4.2805
4.2781
4.2593
4.2569
4.0765
4.0737
4.0552
4.0524
3.8808
3.8792
3.7757
3.7065
3.7010
3.6890
2.5973
Ph
O
O
O
HO
N3
OMP
9iiiα
1H NMR
600 MHz
CDCl3
1.92
2.83
1.85
1.93
0.94
0.95
1.00
0.99
1.04
1.04
0.99
2.88
0.98
1.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

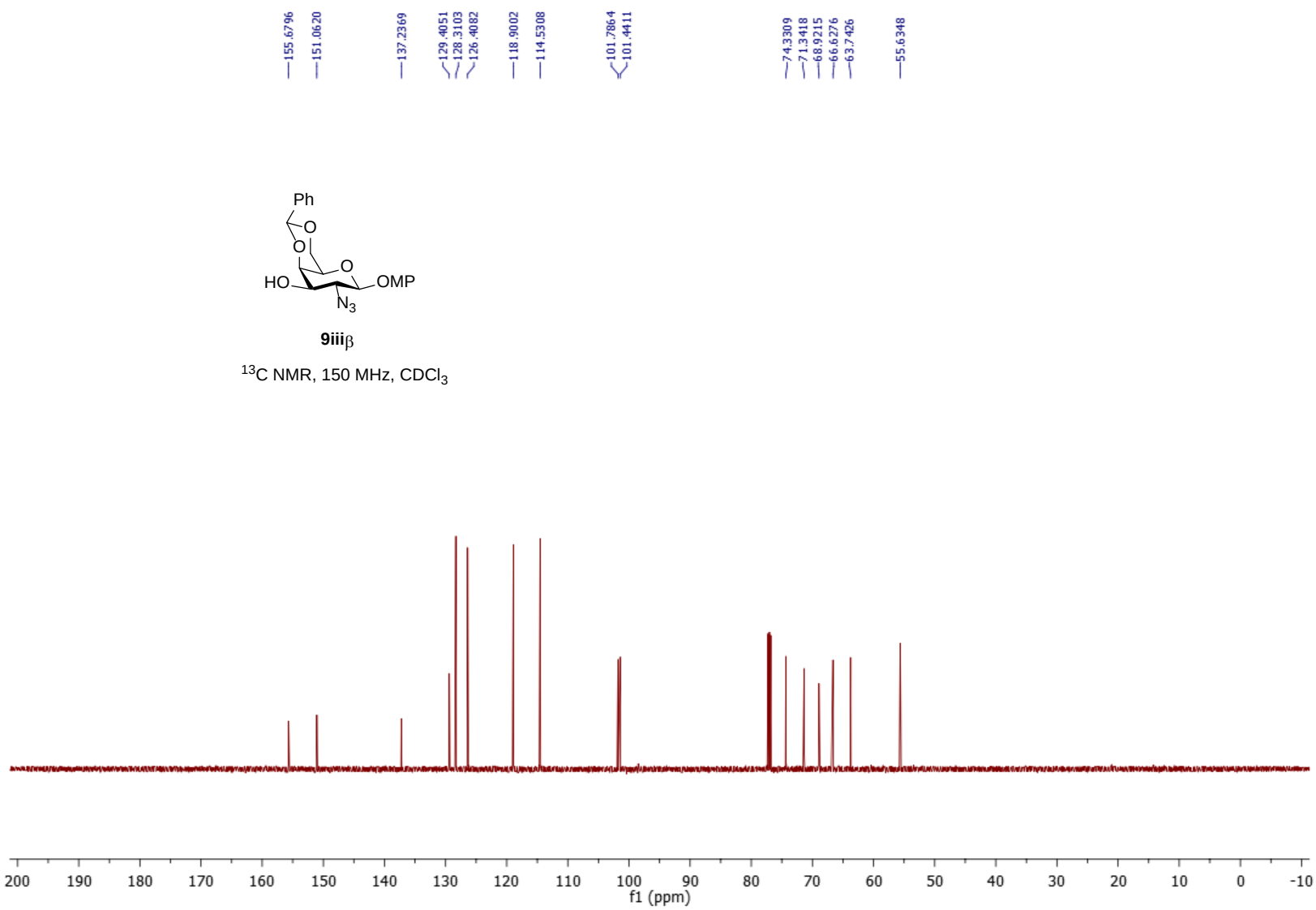


9iii$^{\alpha}$

^{13}C NMR, 150 MHz, $CDCl_3$

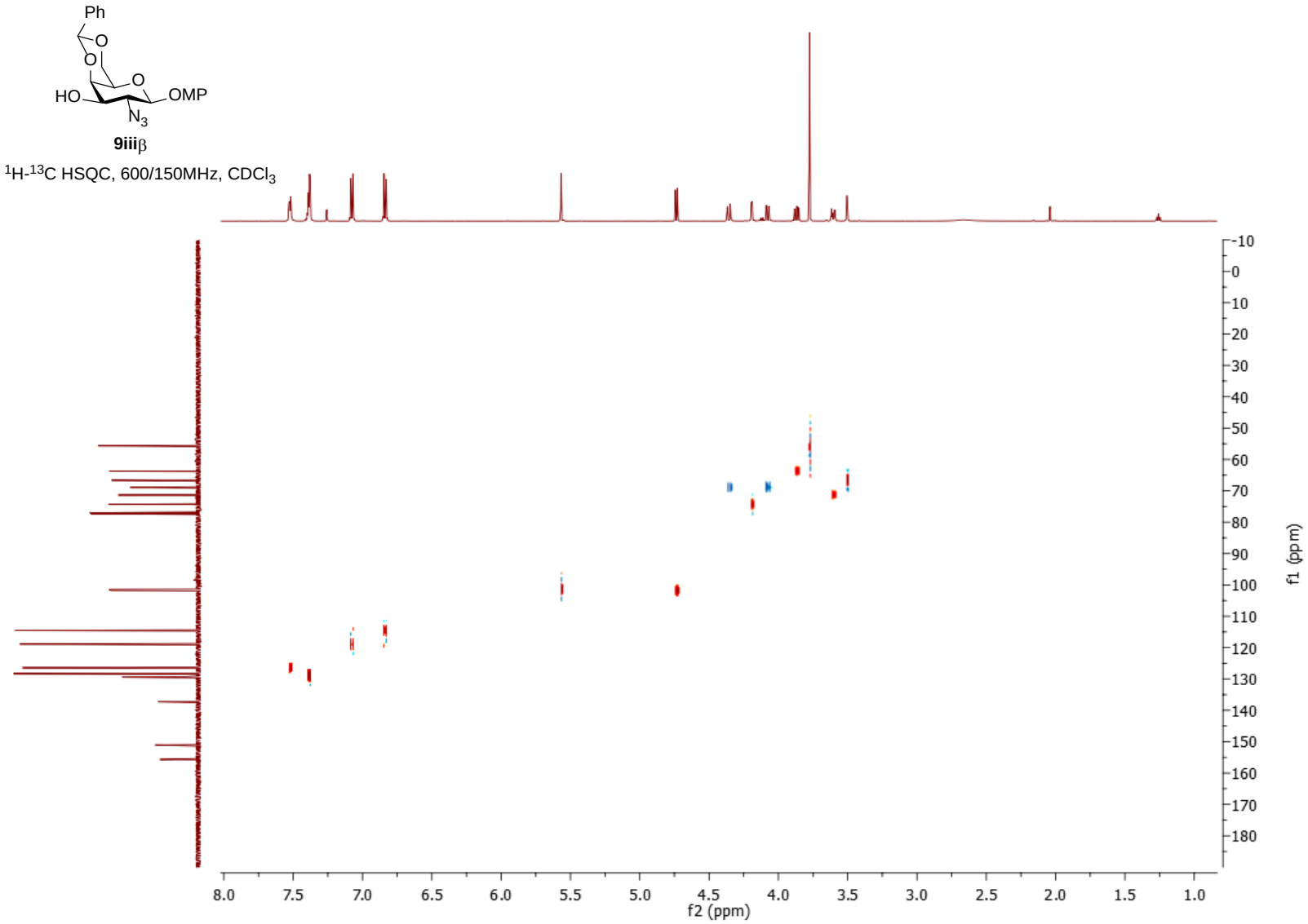

Ph
O
O
O
HO
N3
OMP
9iii$^{\alpha}$
^{1}H-^{13}C HSQC, 600/150MHz, CDCl$_3$
f2 (ppm)
f1 (ppm)

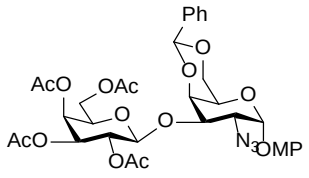

7.5309
7.5240
7.5181
7.5149
7.3978
7.3910
7.3879
7.3826
7.3794
7.0903
7.0840
7.0802
7.0727
7.0689
7.0626
6.8507
6.8444
6.8406
6.8330
6.8293
5.5675
4.7426
4.7291
4.3472
4.3449
4.1954
4.1945
4.1892
4.0896
4.0867
4.0687
3.8658
3.7758
3.5058
3.5041
2.6650
Ph
O
O
O
HO
OMP
N3
9iiiβ
1H NMR
600 MHz
CDCl3
1.89
2.78
1.80
1.86
1.00
1.00
1.02
1.01
1.01
0.96
2.79
1.06
1.02
1.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



9iiiβ

^{13}C NMR, 150 MHz, $CDCl_3$


Ph
O
O
O
HO
OMP
N3
9iiiβ
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

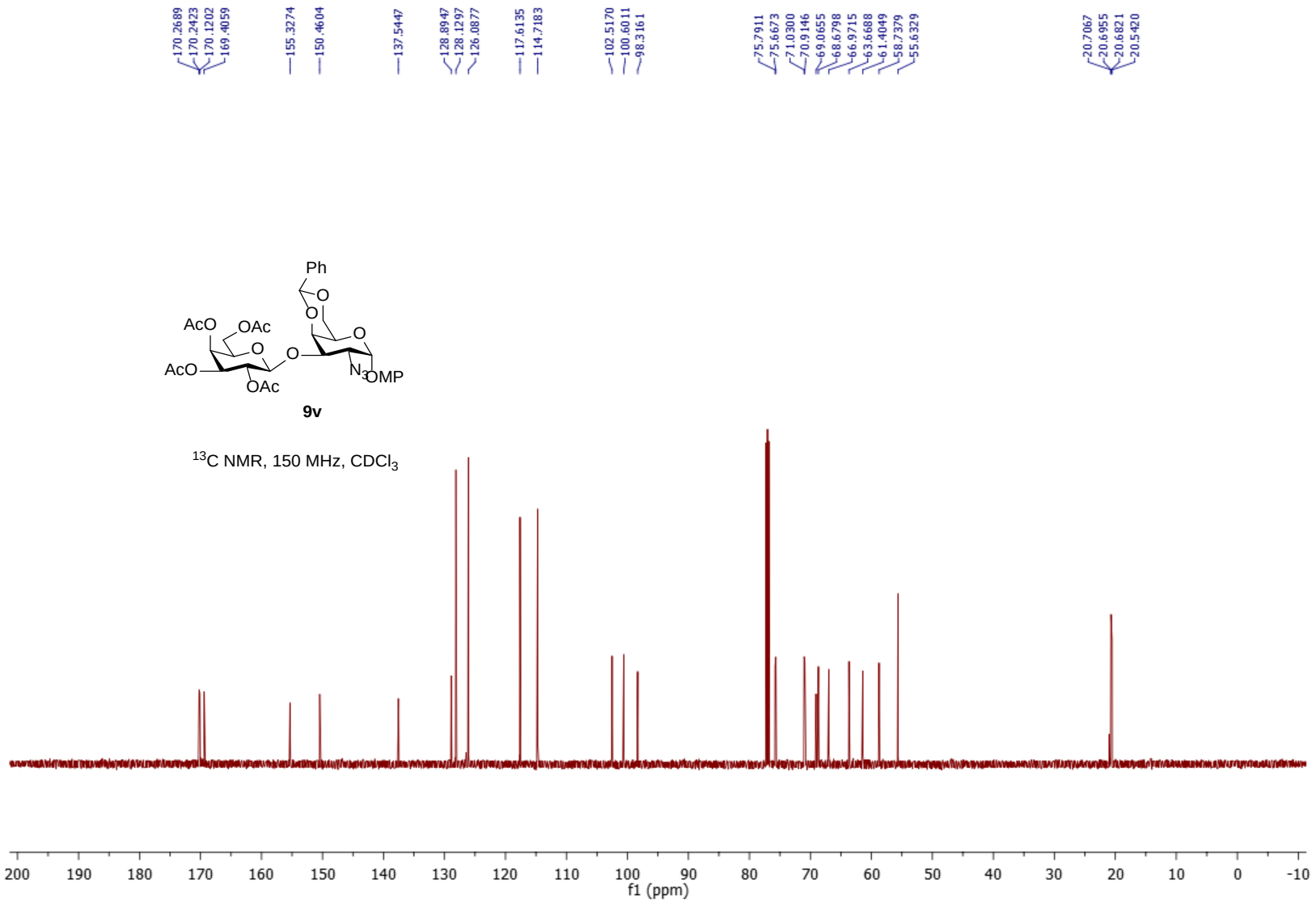


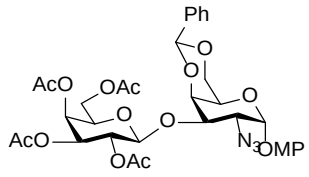
9v

^{1}H NMR

600 MHz

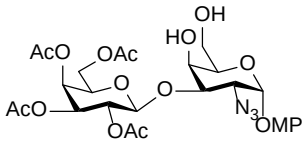
$CDCl_3$


170.2689
170.2423
170.1202
169.4059
155.3274
150.4604
137.5447
128.8947
128.1297
126.0877
117.6135
114.7183
102.5170
100.6011
98.3161
75.7911
75.6673
71.0300
70.9146
69.0655
68.6798
66.9715
63.6688
61.4049
58.7379
55.6329
20.7067
20.6955
20.6821
20.5420
Ph
AcO
OAc
AcO
OAc
N3
OMP
9v
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



9v

^{1}H-^{13}C HSQC, 600/150MHz, $CDCl_3$

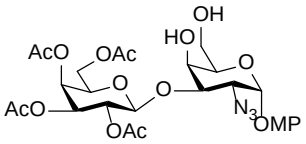


9vi

^{1}H NMR

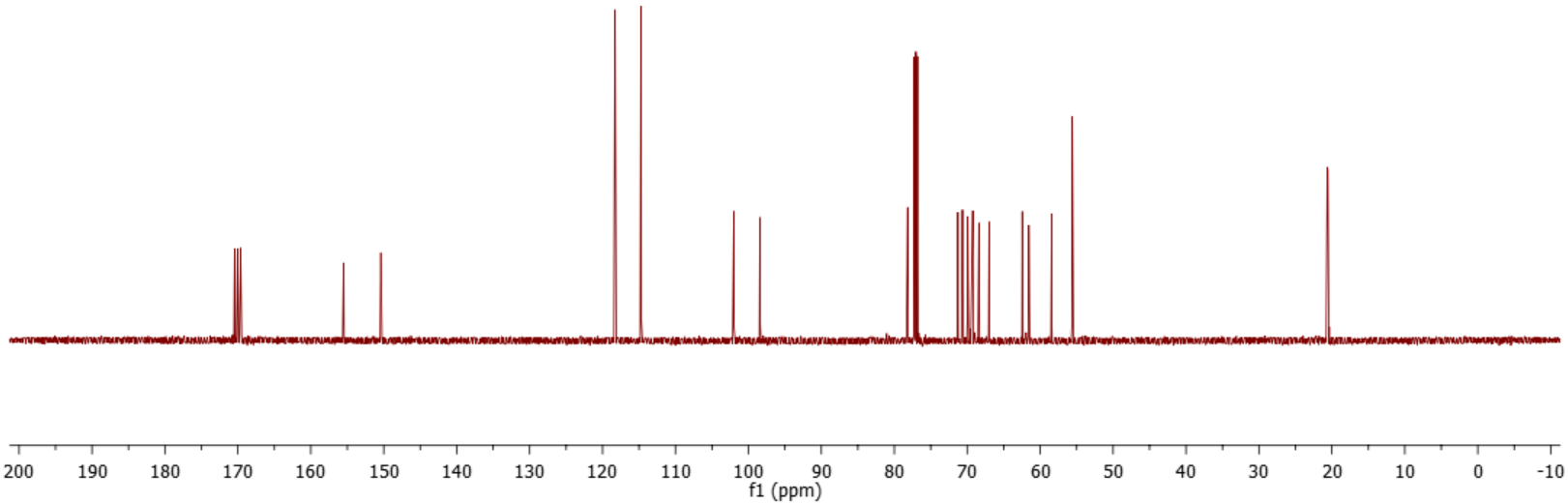
600 MHz

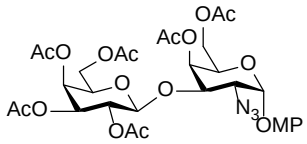
$CDCl_3$



9vi

^{13}C NMR, 150 MHz, $CDCl_3$



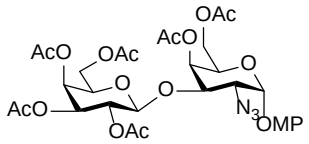


9vii

^{1}H NMR

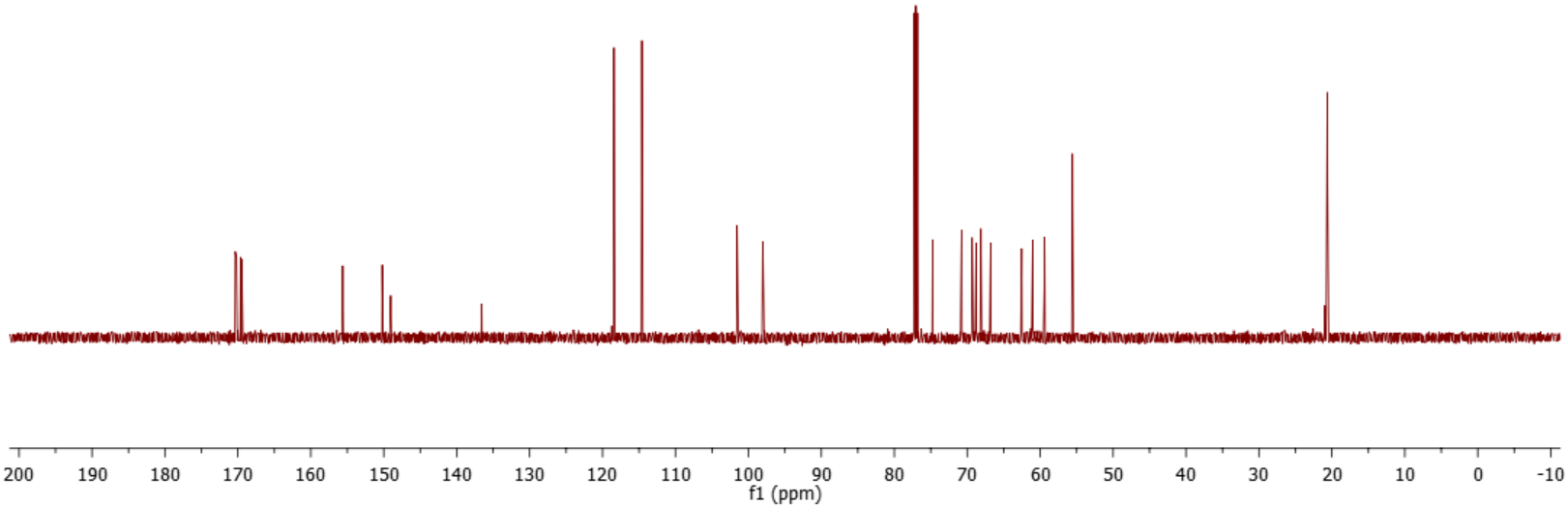
600 MHz

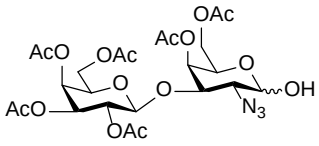
$CDCl_3$



9vii

^{13}C NMR, 150 MHz, $CDCl_3$



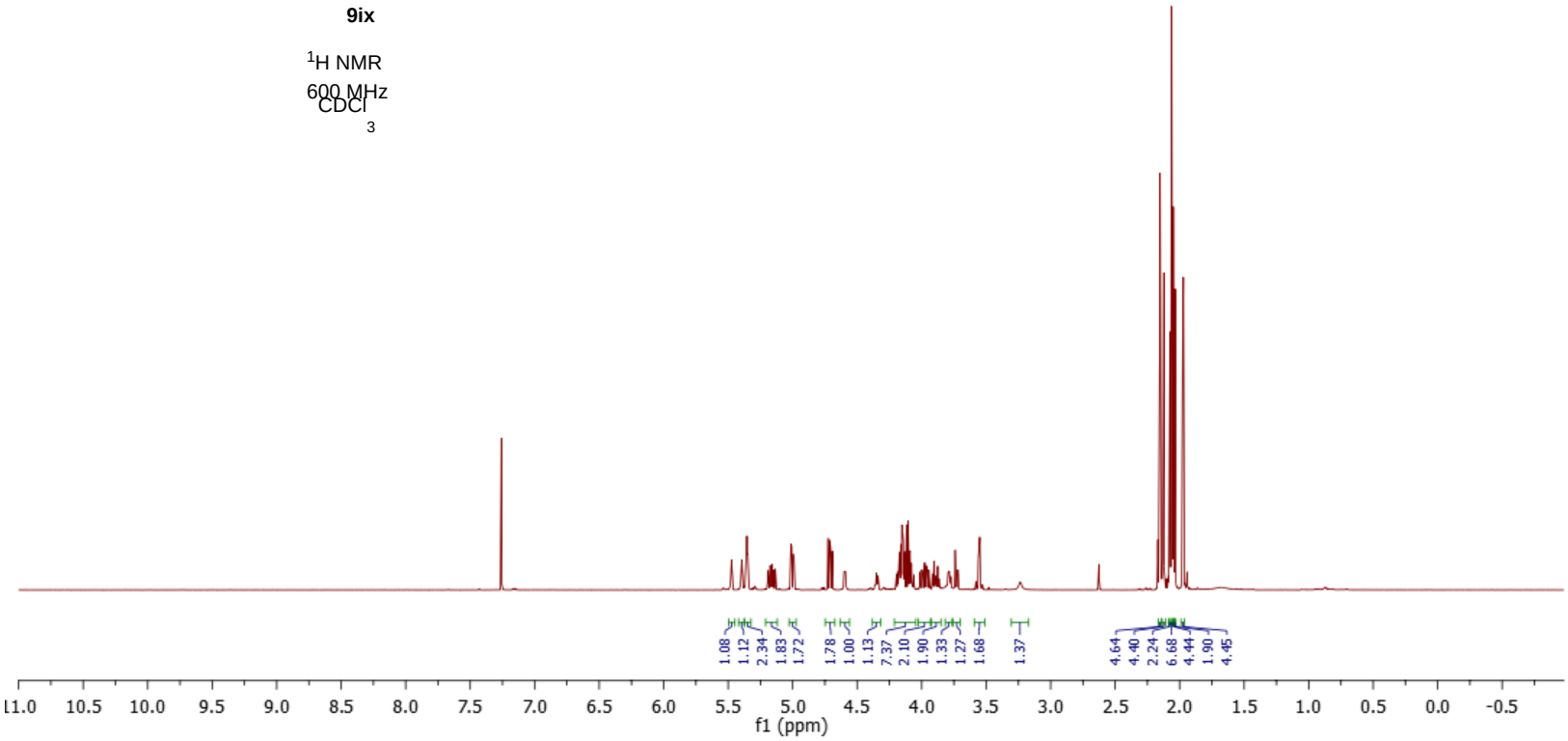


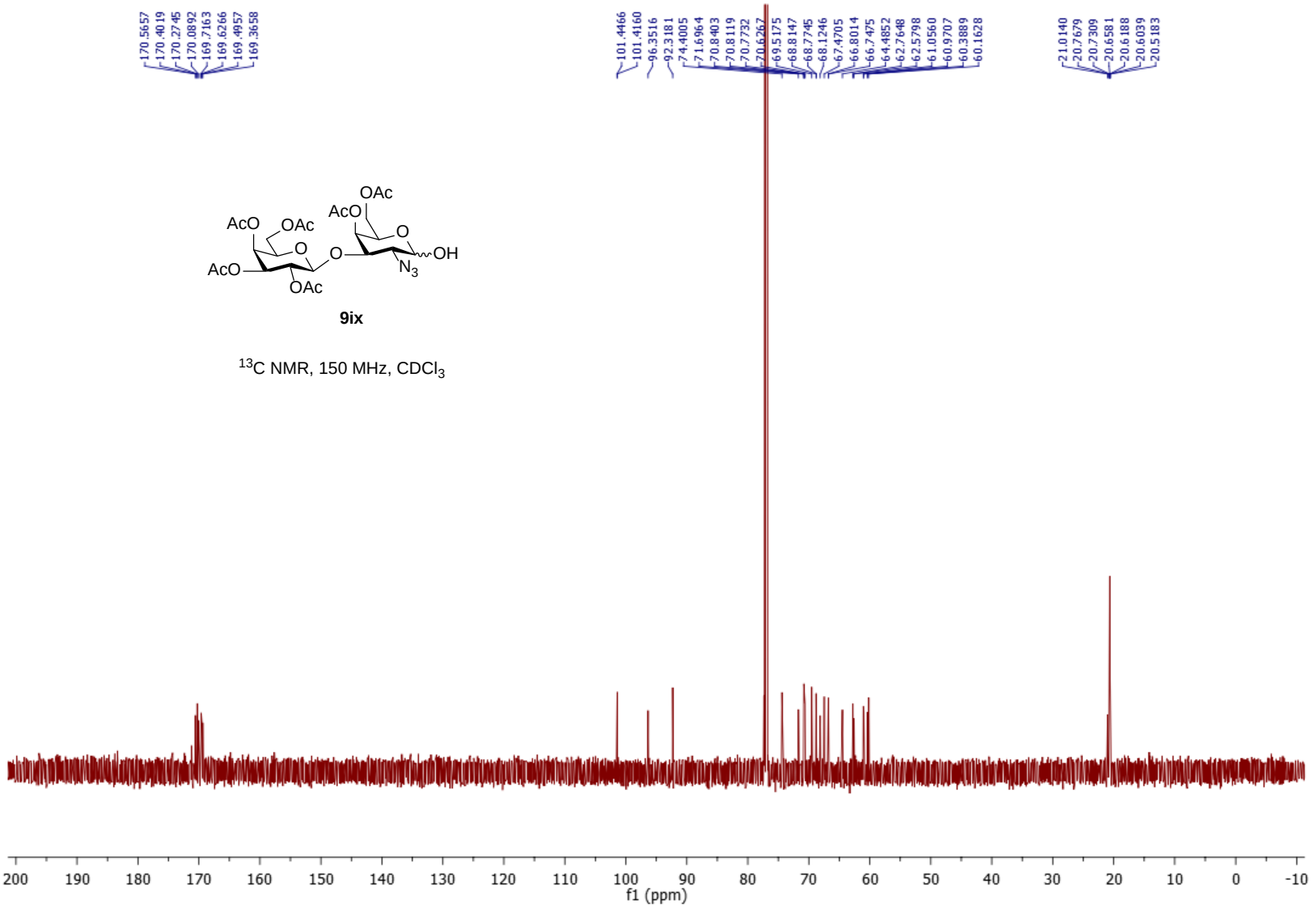
9ix

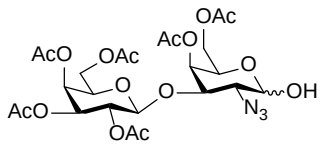
^{1}H NMR

600 MHz

$CDCl_3$

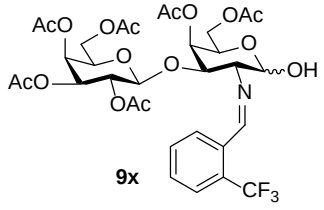



170.5657
170.4019
170.2745
170.0892
169.7163
169.6266
169.4957
169.3658
101.4466
101.4160
96.3516
92.3181
74.4005
71.6964
70.8403
70.8119
70.7732
70.6267
69.5175
68.8147
68.7745
68.1246
67.4705
66.8014
66.7475
64.4852
62.7648
62.5798
61.0560
60.9707
60.3889
60.1628
21.0140
20.7679
20.7309
20.6581
20.6188
20.6039
20.5183
OAc
AcO
AcO
OAc
O
O
AcO
OAc
O
OH
N3
9ix
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



9ix

^{1}H-^{13}C HSQC, 600/150MHz, $CDCl_3$

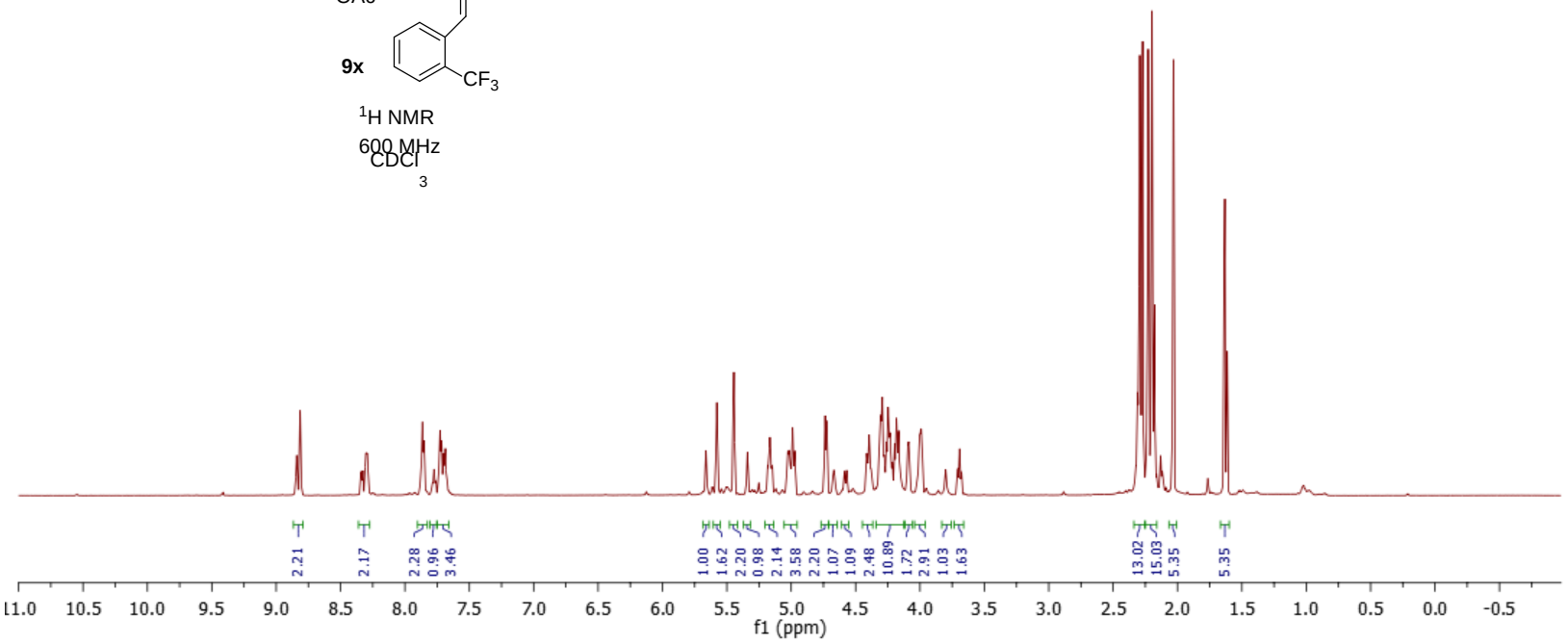


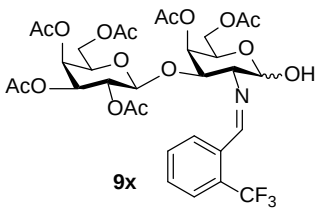
9x

^{1}H NMR

600 MHz

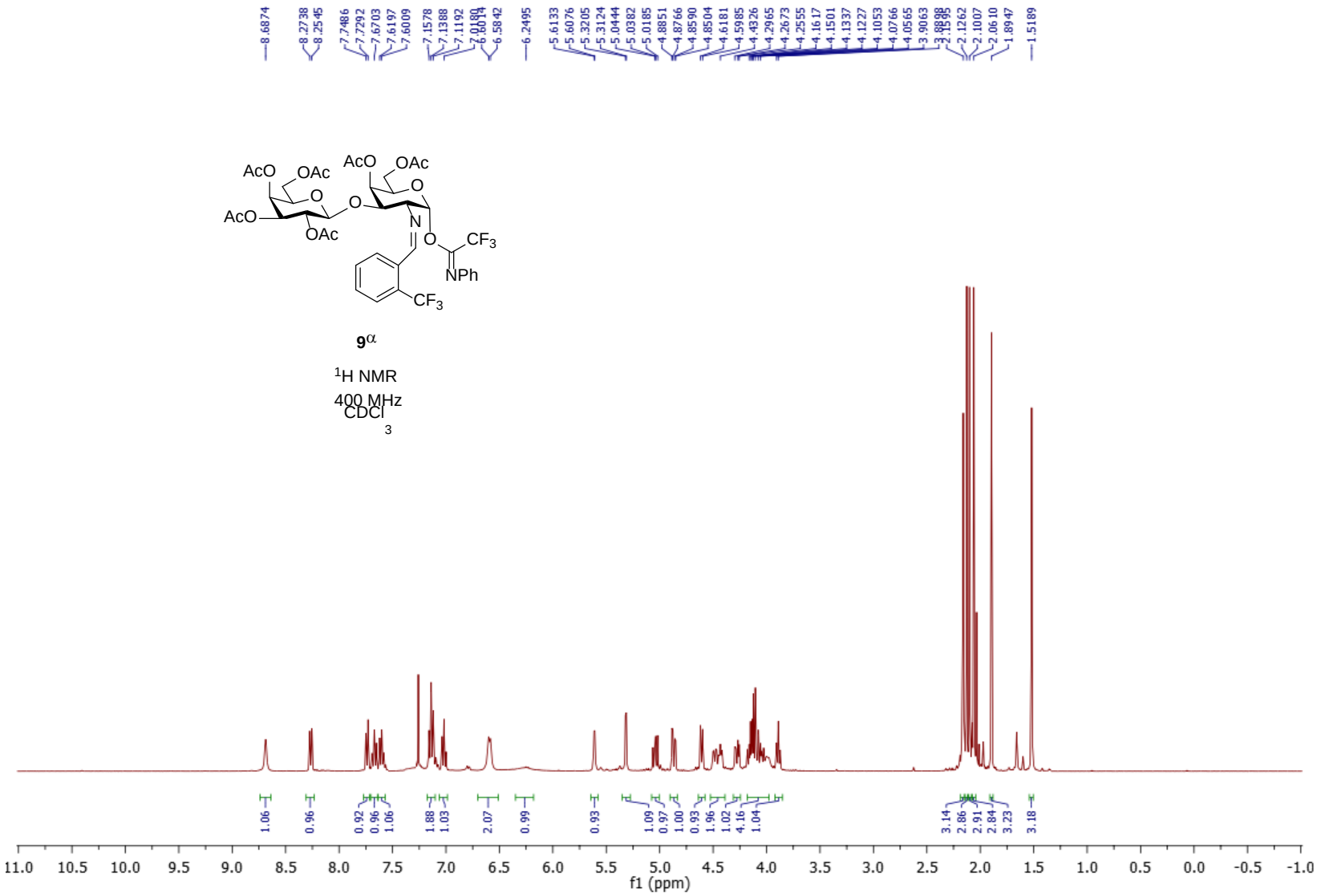
$CDCl_3$





9x

^{13}C NMR, 150 MHz, $CDCl_3$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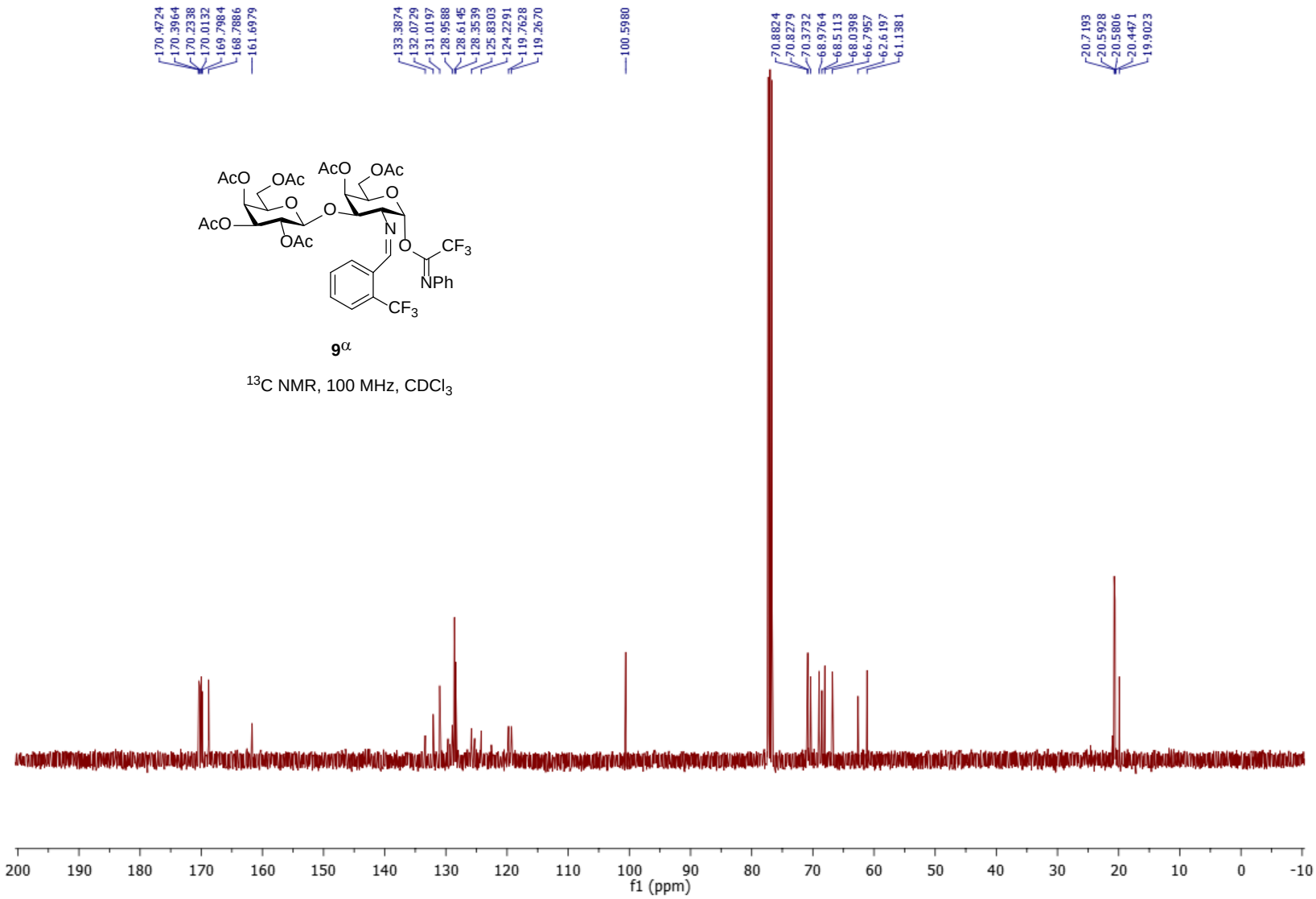
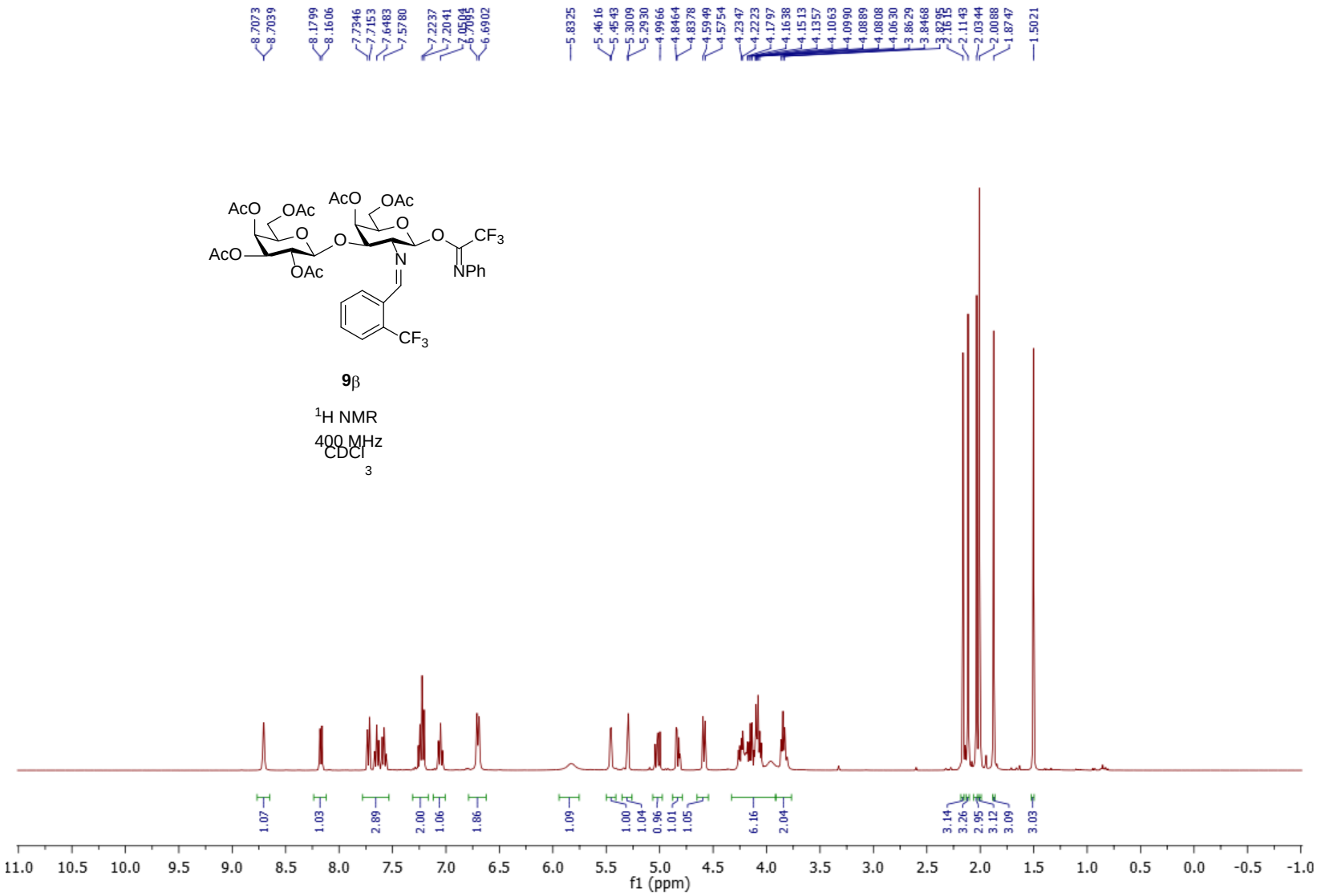
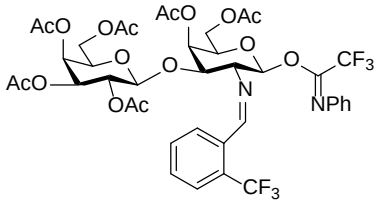
8.2738
8.2545
7.7486
7.7292
7.6703
7.6197
7.6009
7.1578
7.1388
7.1192
7.0180
6.6014
6.5842
6.2495
5.6133
5.6076
5.3205
5.3124
5.0444
5.0382
5.0185
4.8851
4.8766
4.8590
4.8504
4.6181
4.5985
4.4326
4.2965
4.2673
4.2555
4.1617
4.1501
4.1337
4.1227
4.1053
4.0766
4.0565
3.9063
2.1262
2.1007
2.0610
1.8947
1.5189
AcO
OAc
AcO
OAc
O
O
AcO
OAc
O
N
O
CF3
NPh
CF3
9α
1H NMR
400 MHz
CDCl3
1.06
0.96
0.92
0.96
1.06
1.88
1.03
2.07
0.99
0.93
1.09
0.97
1.00
0.93
1.96
1.02
4.16
1.04
3.14
2.86
2.91
2.84
3.23
3.18
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



9$^{\alpha}$

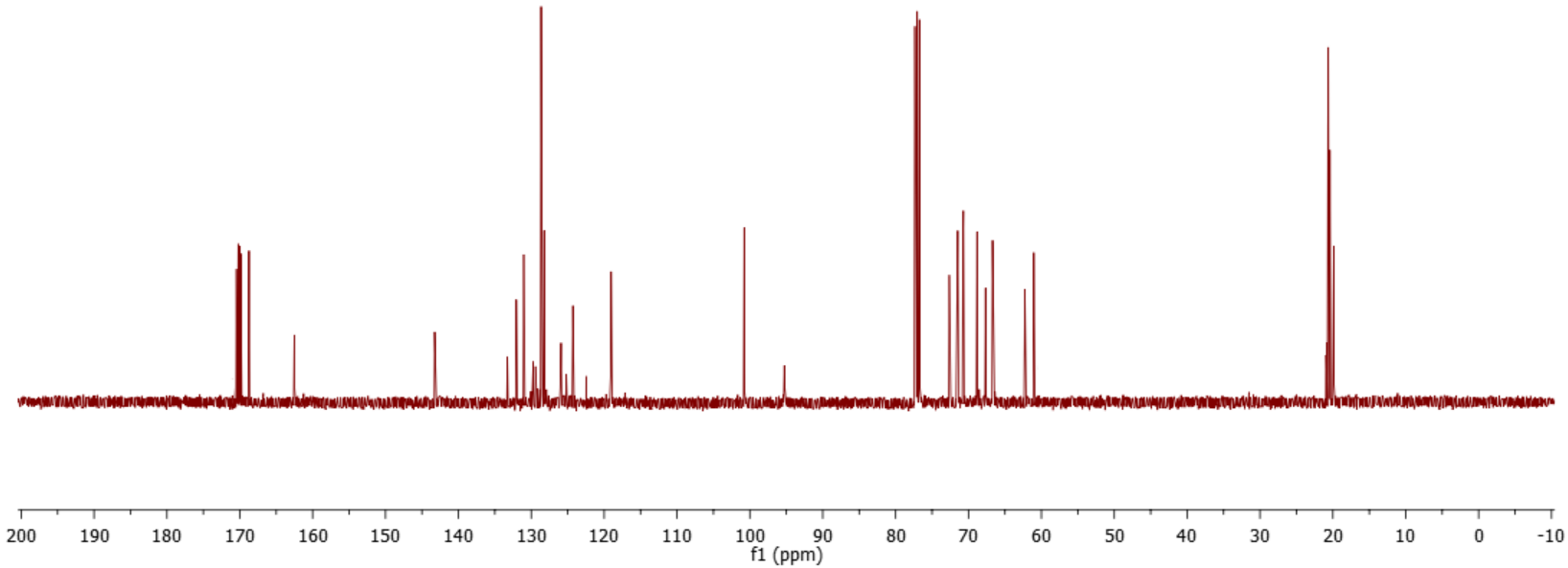
^{13}C NMR, 100 MHz, $CDCl_3$

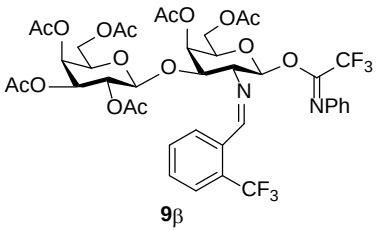

8.7073
8.7039
8.1799
8.1606
7.7346
7.7153
7.6483
7.5780
7.2237
7.2041
7.0504
6.7095
6.6902
5.8325
5.4616
5.4543
5.3009
5.2930
4.9966
4.8464
4.8378
4.5949
4.5754
4.2347
4.2223
4.1797
4.1638
4.1513
4.1357
4.1063
4.0990
4.0889
4.0808
4.0630
3.8629
3.8468
3.8295
3.7615
2.1143
2.0344
2.0088
1.8747
1.5021
AcO
OAc
AcO
OAc
O
O
AcO
OAc
O
O
N
O
CF3
NPh
CF3
9β
1H NMR
400 MHz
CDCl3
1.07
1.03
2.89
2.00
1.06
1.86
1.09
1.00
1.04
0.96
1.01
1.05
6.16
2.04
3.14
3.26
2.95
3.12
3.09
3.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



9β

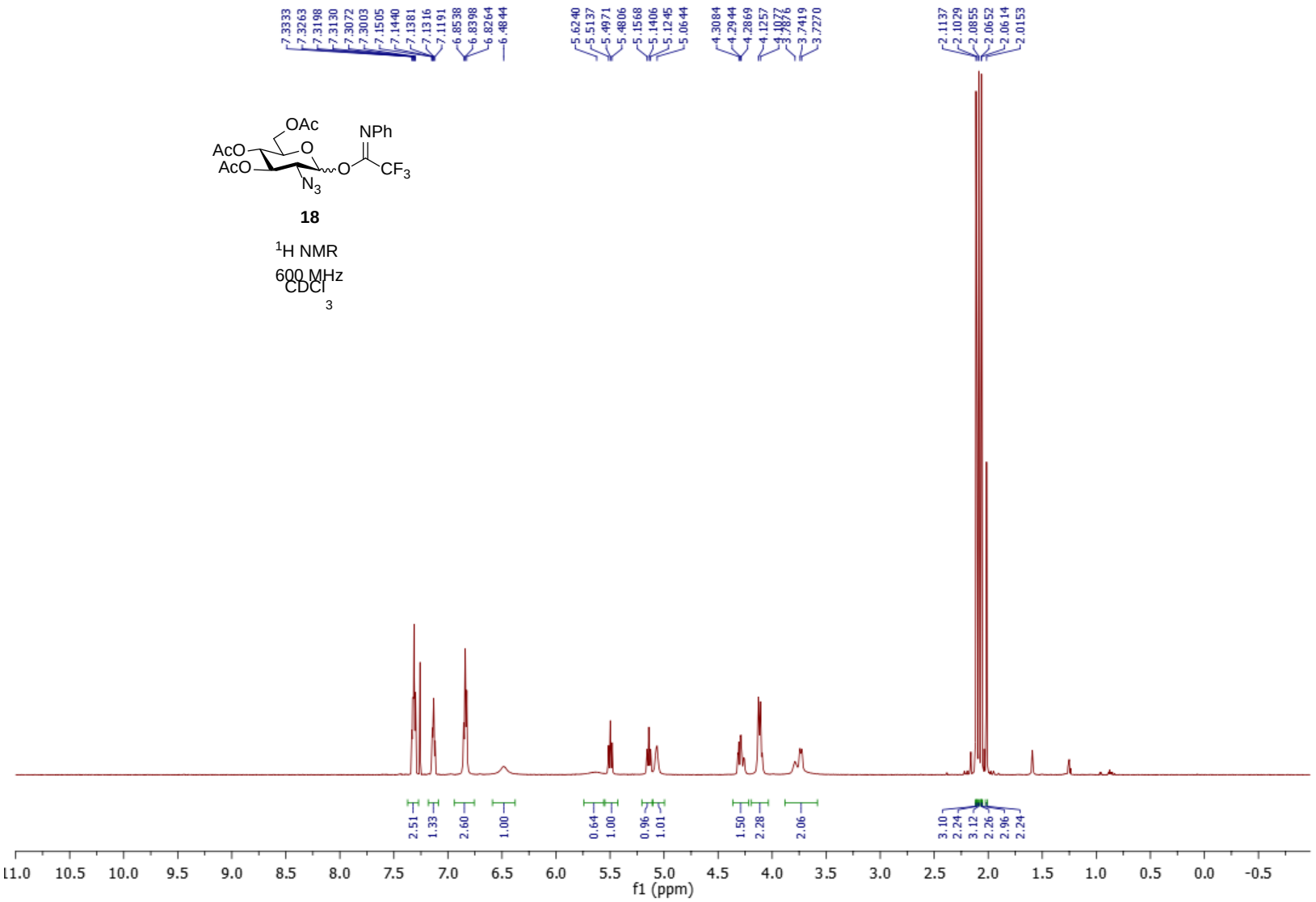
^{13}C NMR, 100 MHz, $CDCl_3$

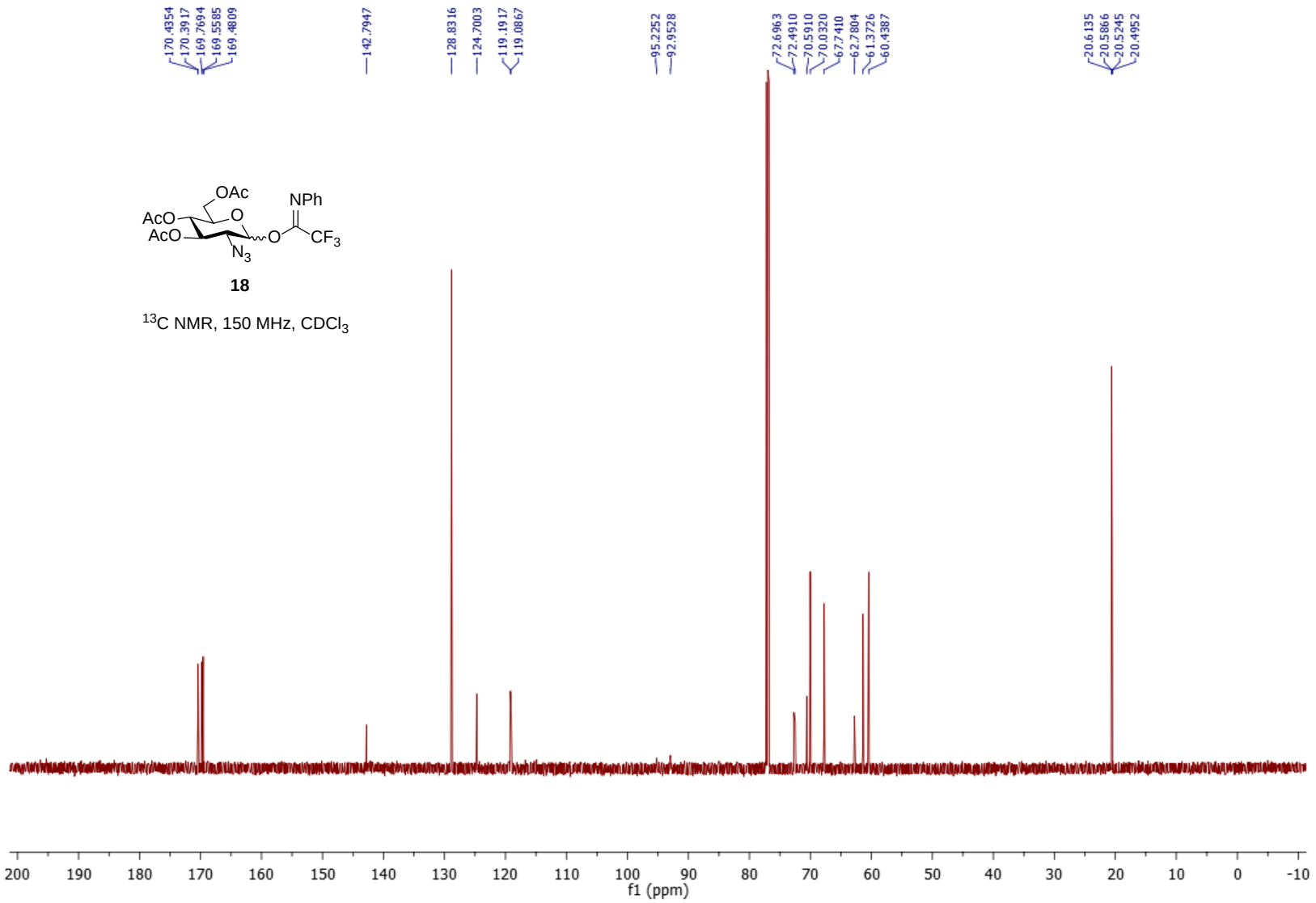


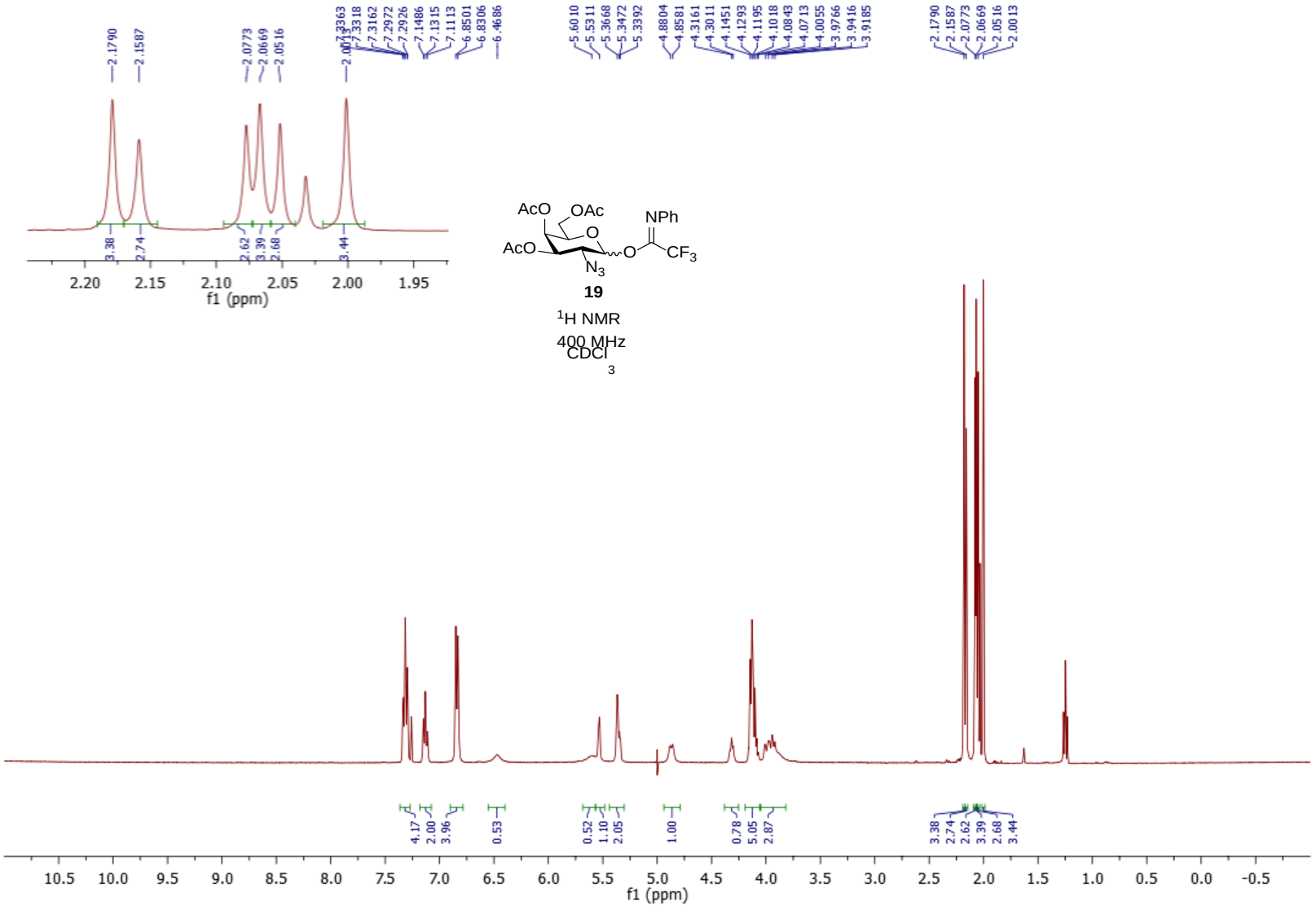


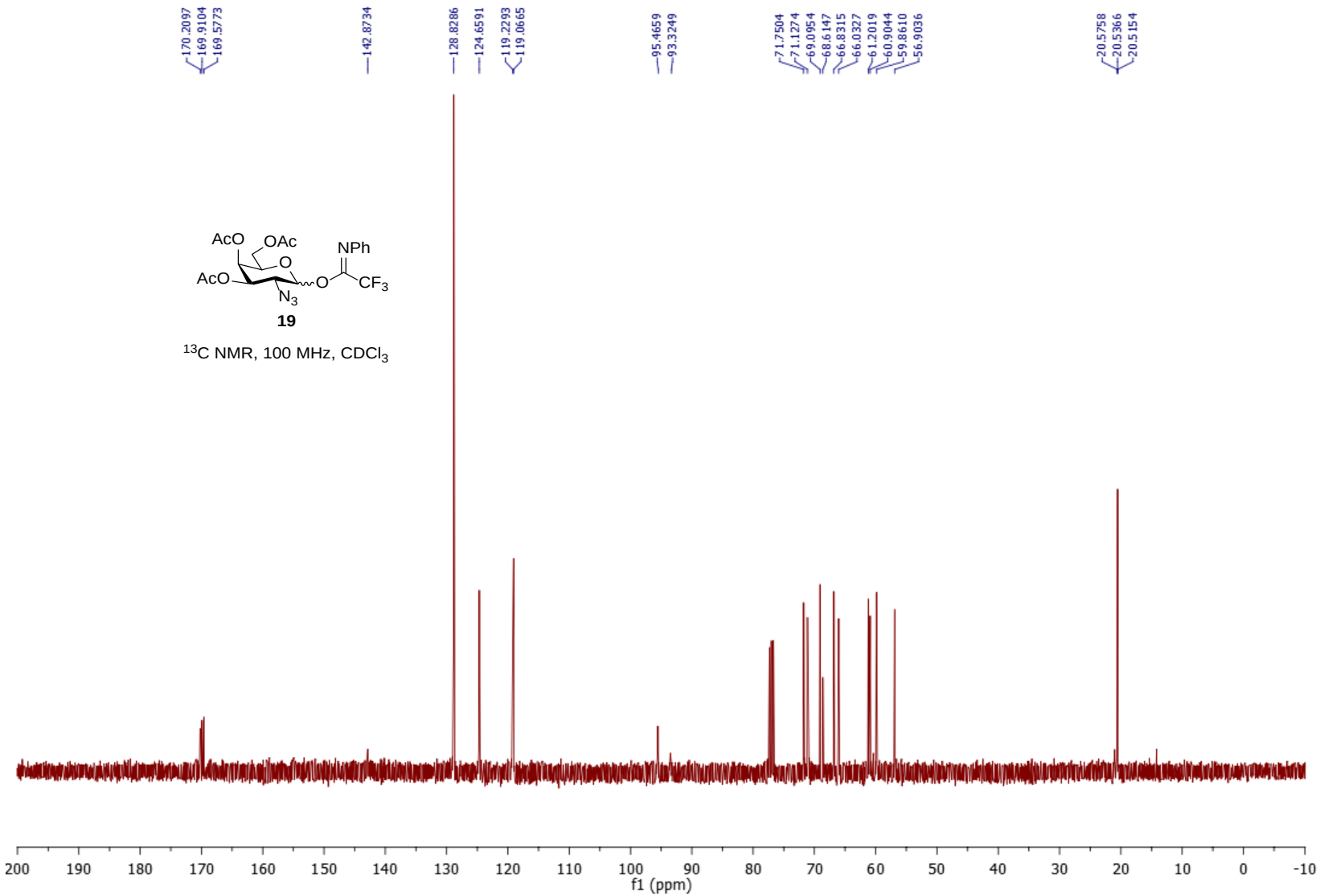
9β

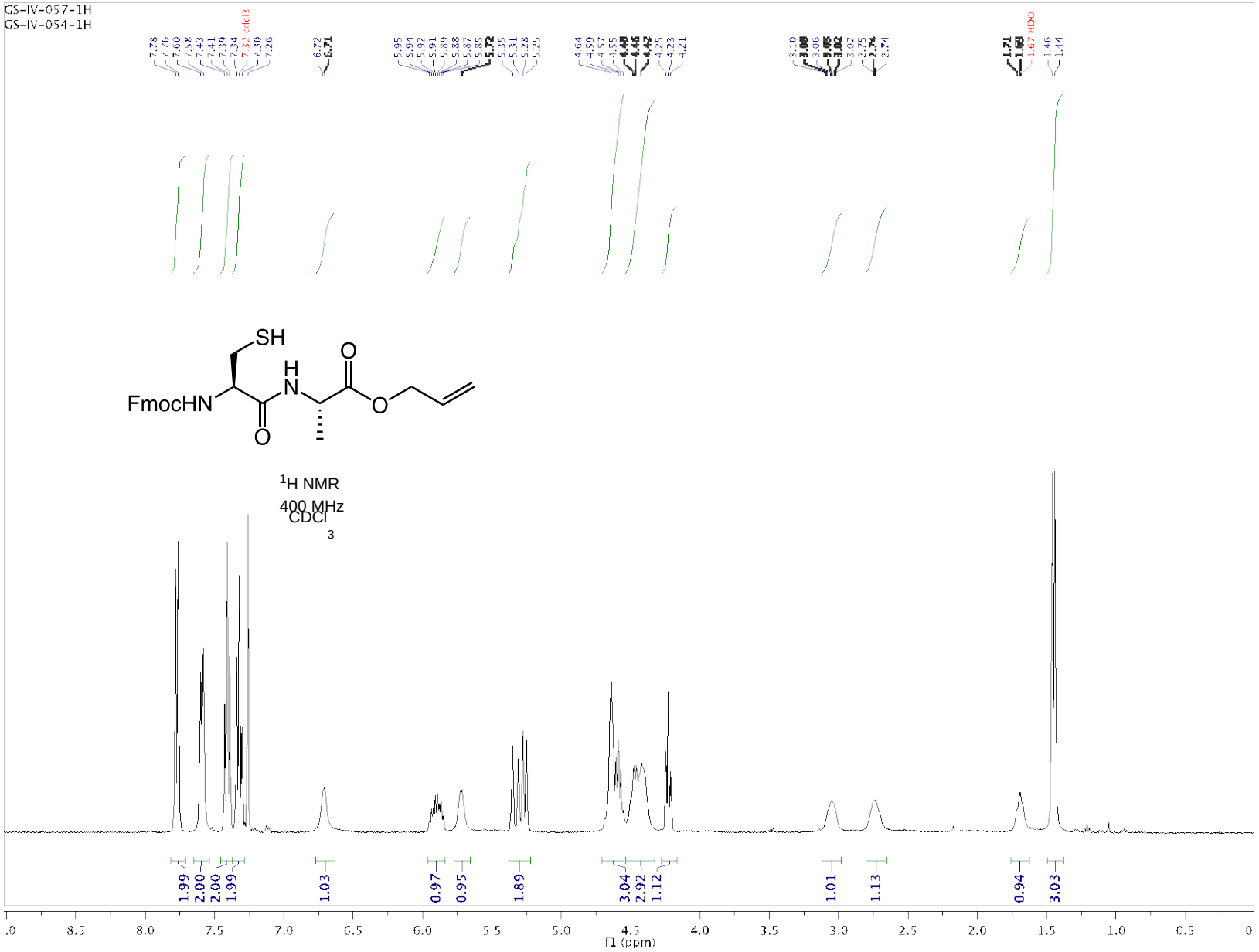
^{1}H-^{13}C HSQC, 400/100MHz, $CDCl_3$

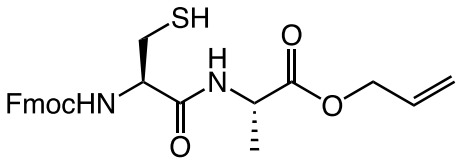

OAc
AcO
AcO
O
N3
O
NPh
CF3
18
1H NMR
600 MHz
CDCl3
f1 (ppm)


170.4354
170.3917
169.7694
169.5585
169.4809
142.7947
128.8316
124.7003
119.1917
119.0867
95.2252
92.9528
72.6963
72.4910
70.5910
70.0320
67.7410
62.7804
61.3726
60.4387
20.6135
20.5866
20.5245
20.4952
OAc
NPh
AcO
O
AcO
O
CF3
N3
18
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

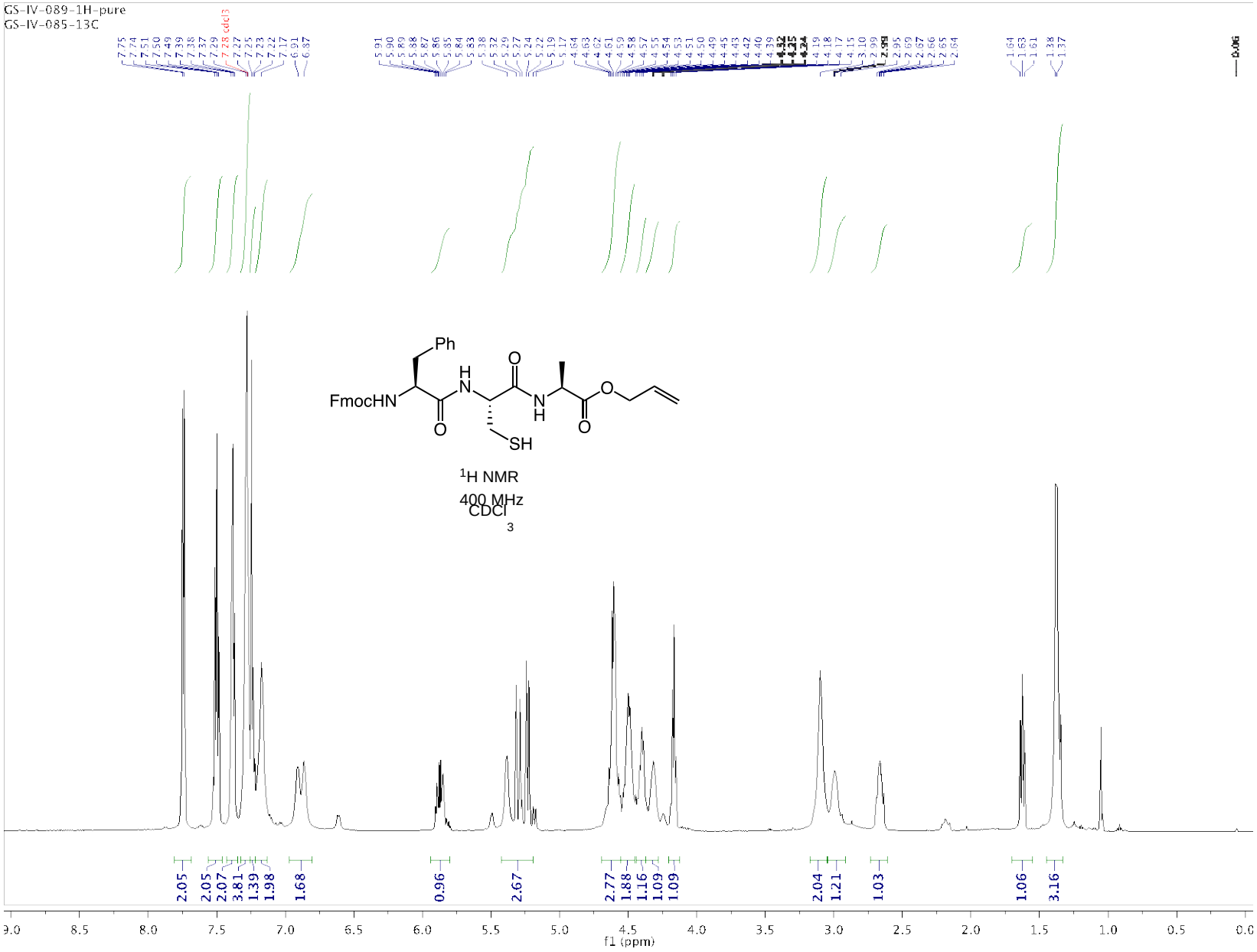

AcO
OAc
NPh
O
AcO
O
CF3
N3
19
1H NMR
400 MHz
CDCl3
f1 (ppm)

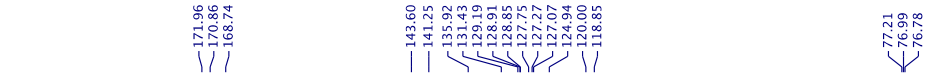

170.2097
169.9104
169.5773
142.8734
128.8286
124.6591
119.2293
119.0665
95.4659
93.3249
71.7504
71.1274
69.0954
68.6147
66.8315
66.0327
61.2019
60.9044
59.8610
56.9036
20.5758
20.5366
20.5154
AcO
OAc
O
AcO
O
NPh
CF3
N3
19
13C NMR, 100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

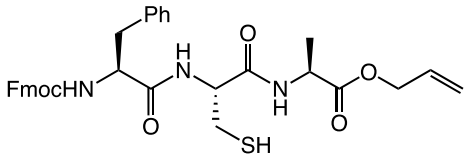

GS-IV-057-1H
GS-IV-054-1H
7.78
7.76
7.60
7.58
7.43
7.41
7.39
7.34
7.32 cdcl3
7.30
7.26
6.72
6.71
5.95
5.94
5.92
5.91
5.89
5.88
5.87
5.85
5.72
5.35
5.31
5.28
5.25
4.64
4.59
4.57
4.55
4.48
4.46
4.42
4.25
4.23
4.21
3.10
3.08
3.06
3.05
3.02
3.02
2.75
2.74
2.74
1.71
1.69
1.67 HDO
1.46
1.44
SH
H
N
O
O
FmocHN
O
1H NMR
400 MHz
CDCl3
1.99
2.00
2.00
1.99
1.03
0.97
0.95
1.89
3.04
2.92
1.12
1.01
1.13
0.94
3.03
f1 (ppm)



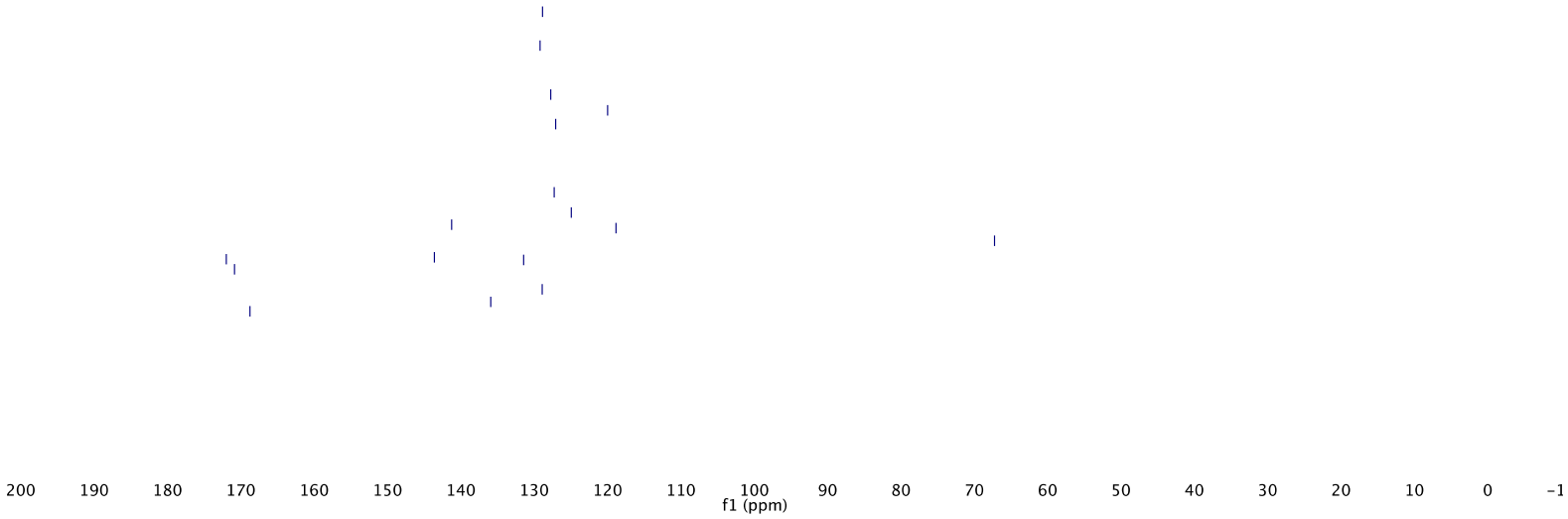
^{13}C NMR, 100 MHz, $CDCl_3$

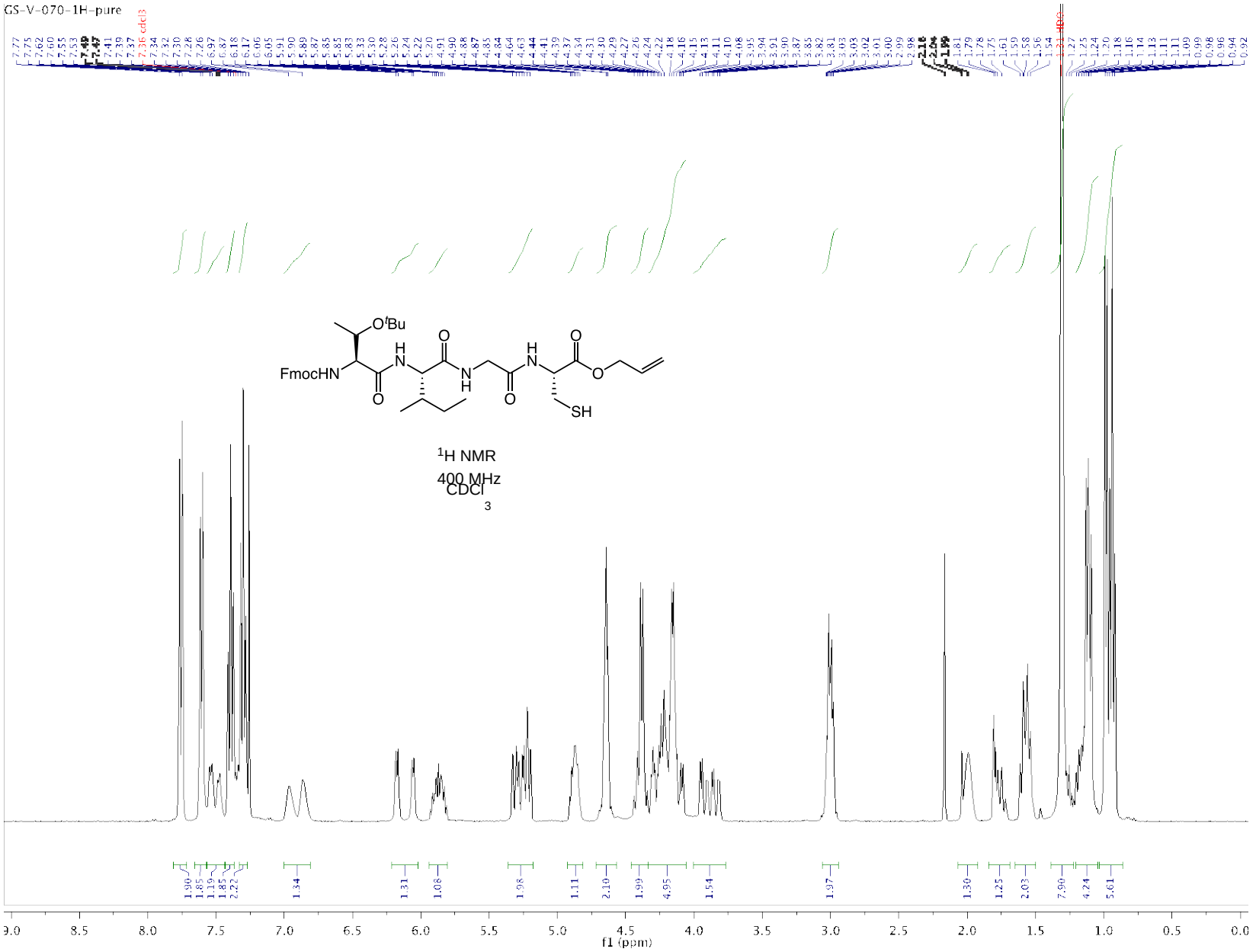

GS-IV-089-1H-pure
GS-IV-085-13C
FmocHN
Ph
H
N
O
N
H
O
O
O
SH
1H NMR
400 MHz
CDCl3
2.05
2.05
2.07
3.81
1.39
1.98
1.68
0.96
2.67
2.77
1.88
1.16
1.09
1.09
2.04
1.21
1.03
1.06
3.16
f1 (ppm)

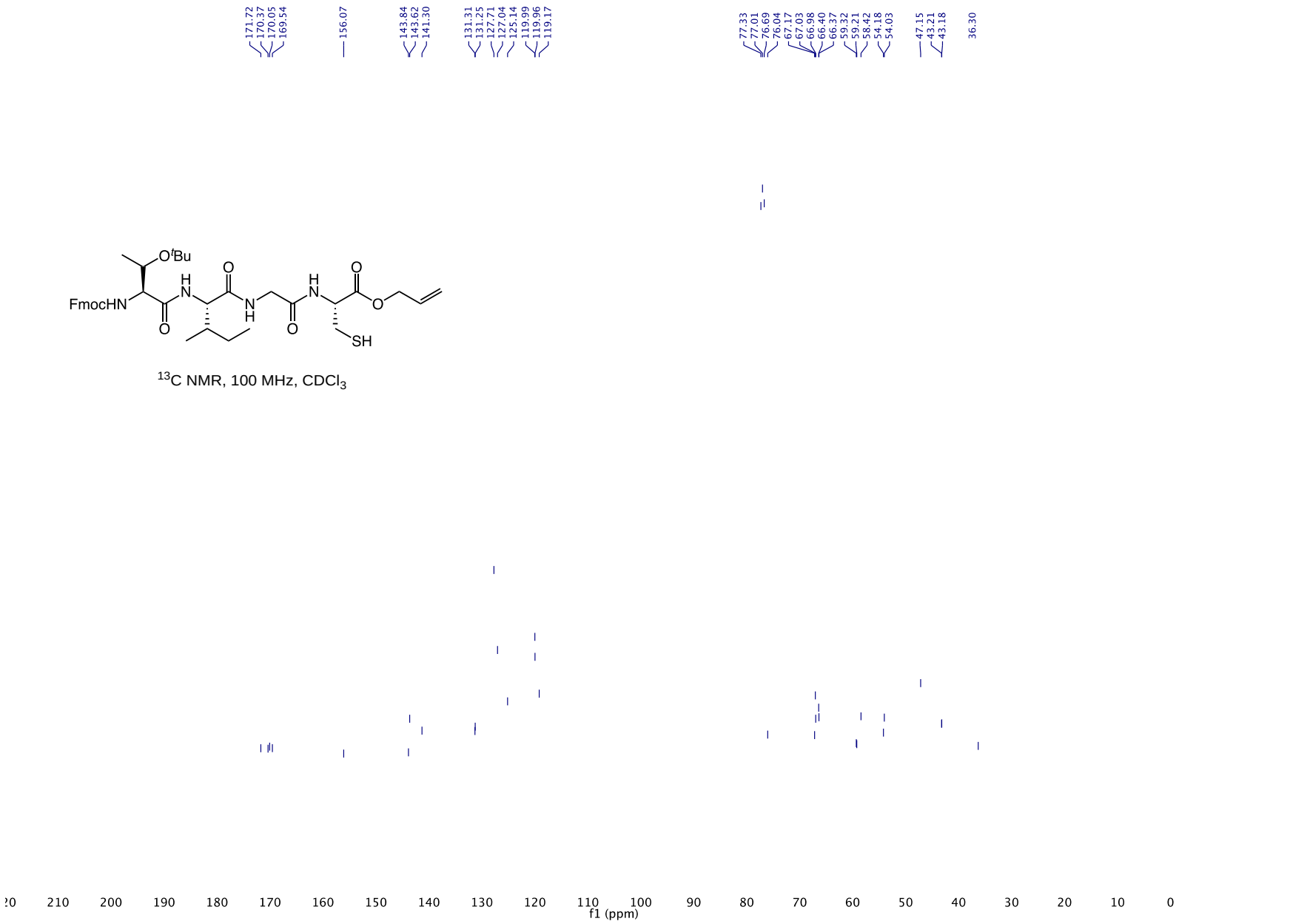




^{13}C NMR, 100 MHz, $CDCl_3$

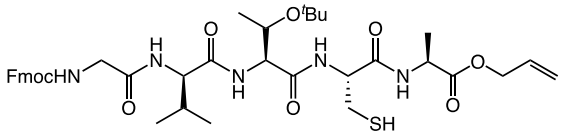



GS-V-070-1H-pure
FmocHN
O^{t}Bu
SH
^{1}H NMR
400 MHz
CDCl$_3$
f1 (ppm)



^{13}C NMR, 100 MHz, $CDCl_3$

8.22



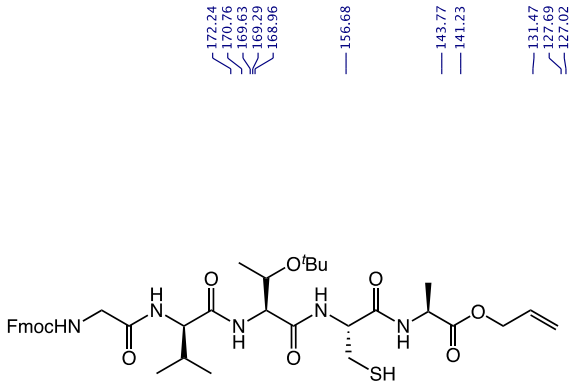
^{1}H NMR

400 MHz

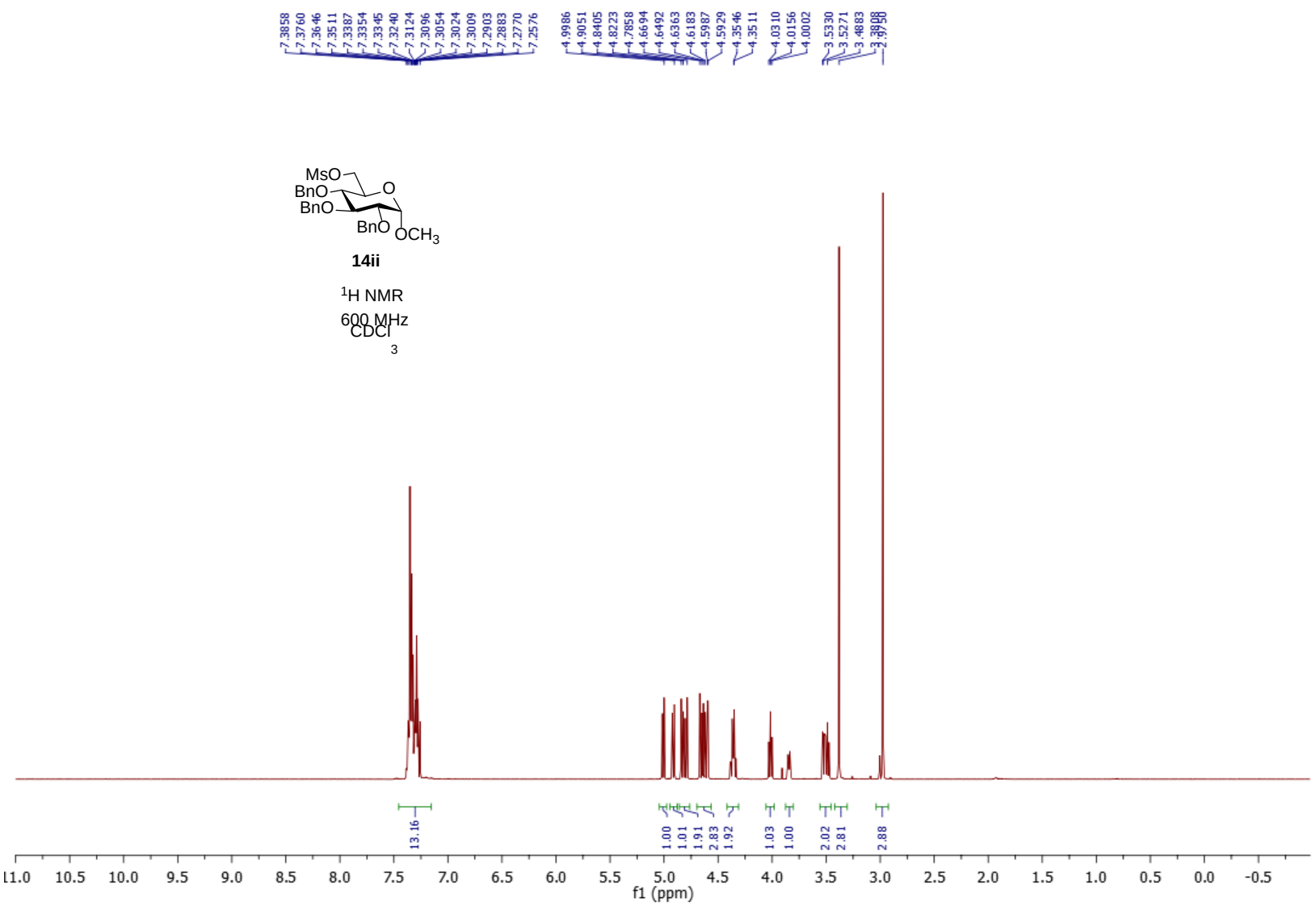
$CDCl_3$

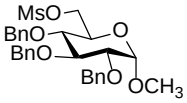
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)



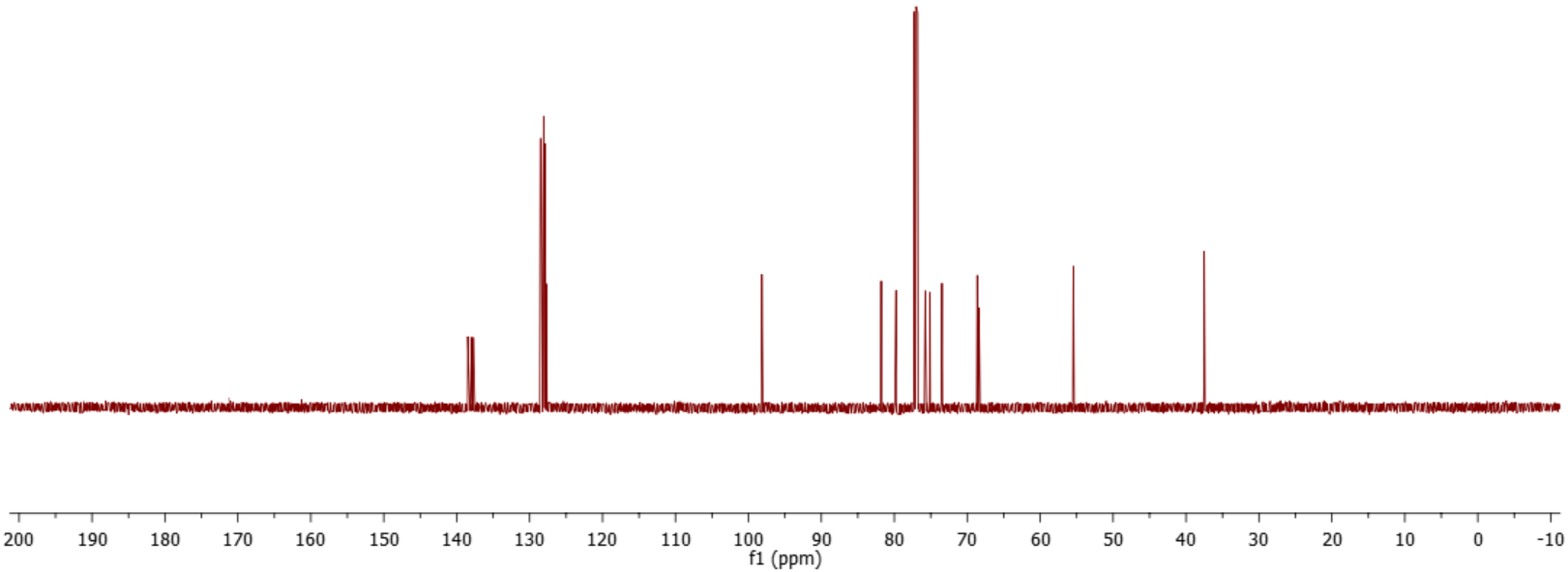
^{13}C NMR, 100 MHz, $CDCl_3$

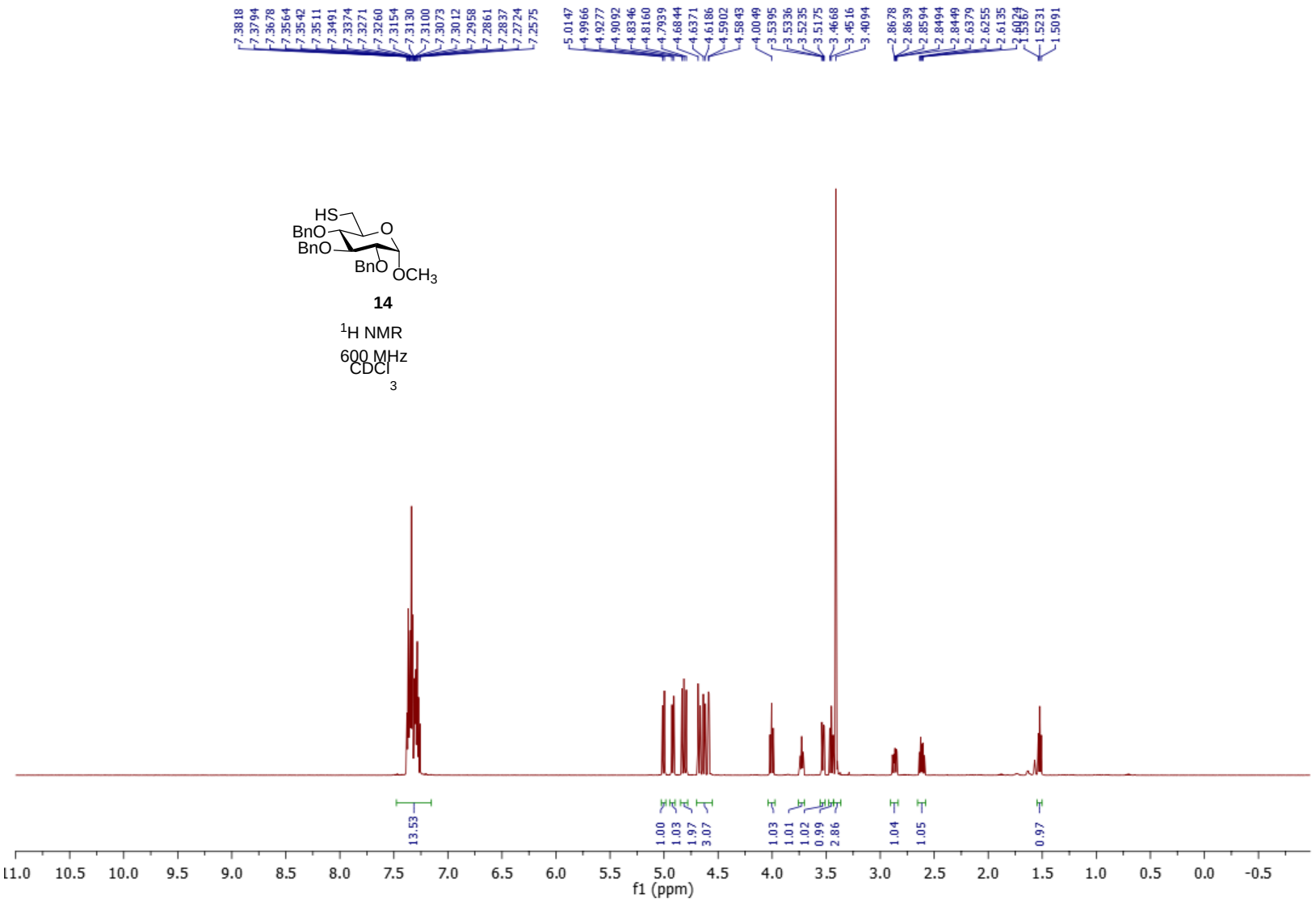

7.3858
7.3760
7.3646
7.3511
7.3387
7.3354
7.3345
7.3240
7.3124
7.3096
7.3054
7.3024
7.3009
7.2903
7.2883
7.2770
7.2576
4.9986
4.9051
4.8405
4.8223
4.7858
4.6694
4.6492
4.6363
4.6183
4.5987
4.5929
4.3546
4.3511
4.0310
4.0156
4.0002
3.5330
3.5271
3.4883
3.3808
2.9750
MsO
BnO
BnO
O
BnO
OCH3
14ii
1H NMR
600 MHz
CDCl3
13.16
1.00
1.01
1.91
2.83
1.92
1.03
1.00
2.02
2.81
2.88
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

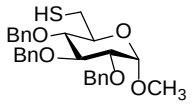


14ii

^{13}C NMR, 150 MHz, $CDCl_3$

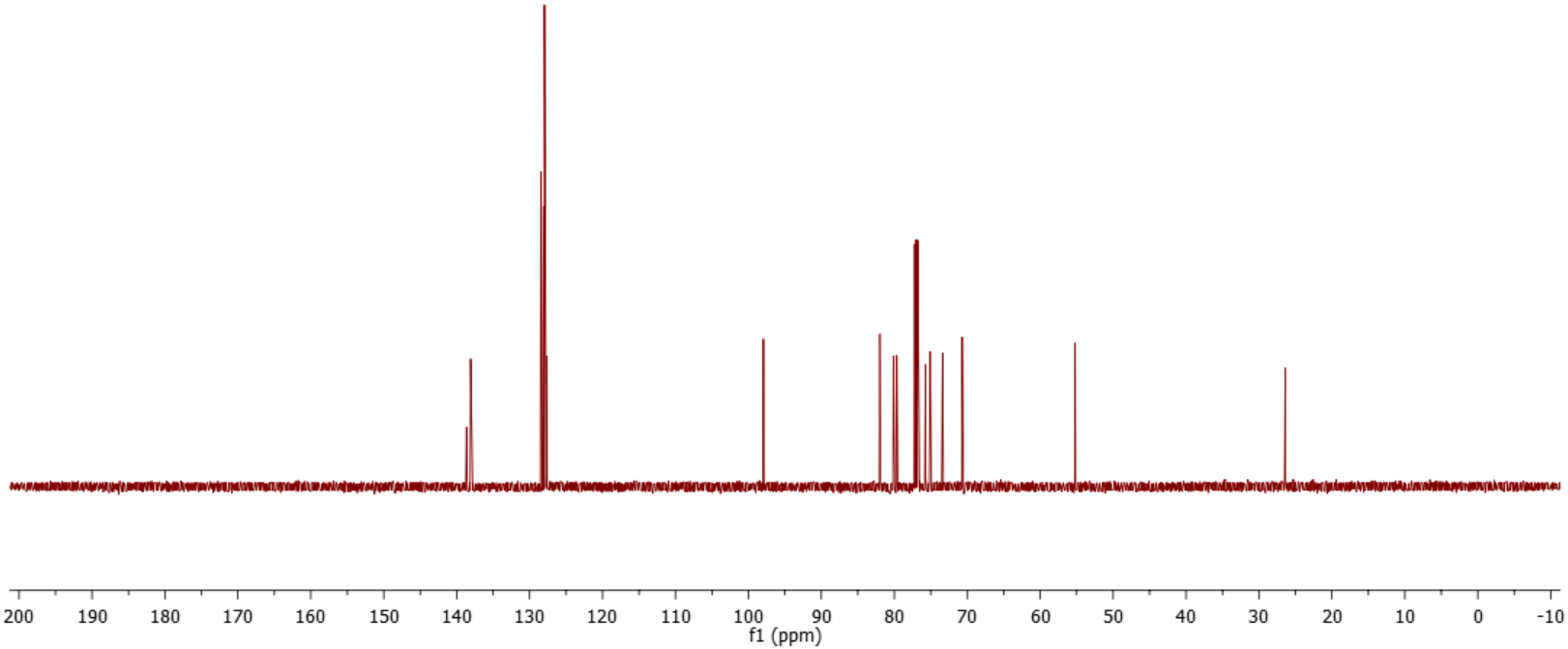


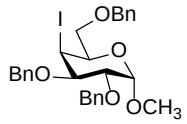

7.3818
7.3794
7.3678
7.3564
7.3542
7.3511
7.3491
7.3374
7.3271
7.3260
7.3154
7.3130
7.3100
7.3073
7.3012
7.2958
7.2861
7.2837
7.2724
7.2575
5.0147
4.9966
4.9277
4.9092
4.8346
4.8160
4.7939
4.6844
4.6371
4.6186
4.5902
4.5843
4.0049
3.5395
3.5336
3.5235
3.5175
3.4668
3.4516
3.4094
2.8678
2.8639
2.8594
2.8494
2.8449
2.6379
2.6255
2.6135
1.5231
1.5091
HS
BnO
BnO
O
BnO
OCH3
14
1H NMR
600 MHz
CDCl3
13.53
1.00
1.03
1.97
3.07
1.03
1.01
1.02
0.99
2.86
1.04
1.05
0.97
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



14

^{13}C NMR, 150 MHz, $CDCl_3$



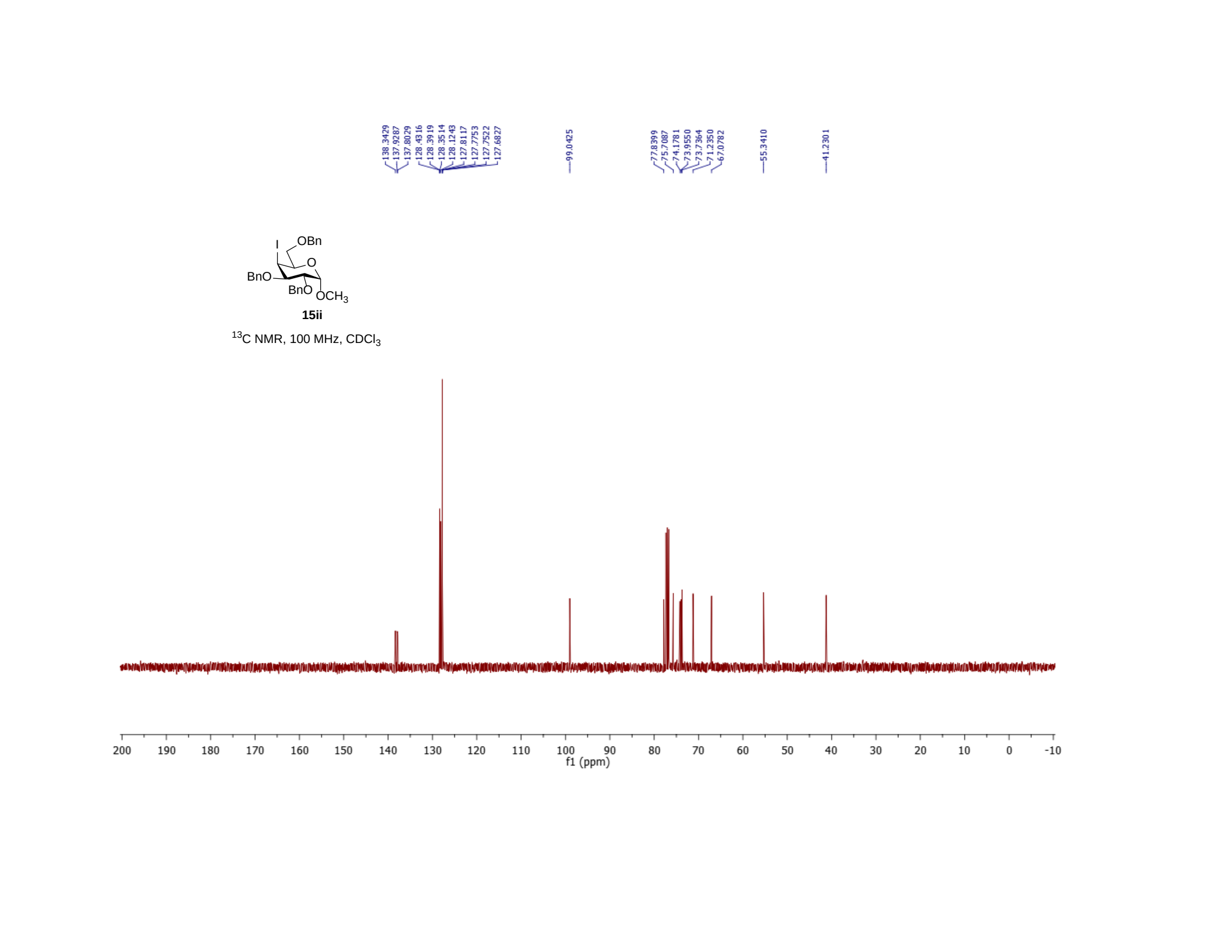


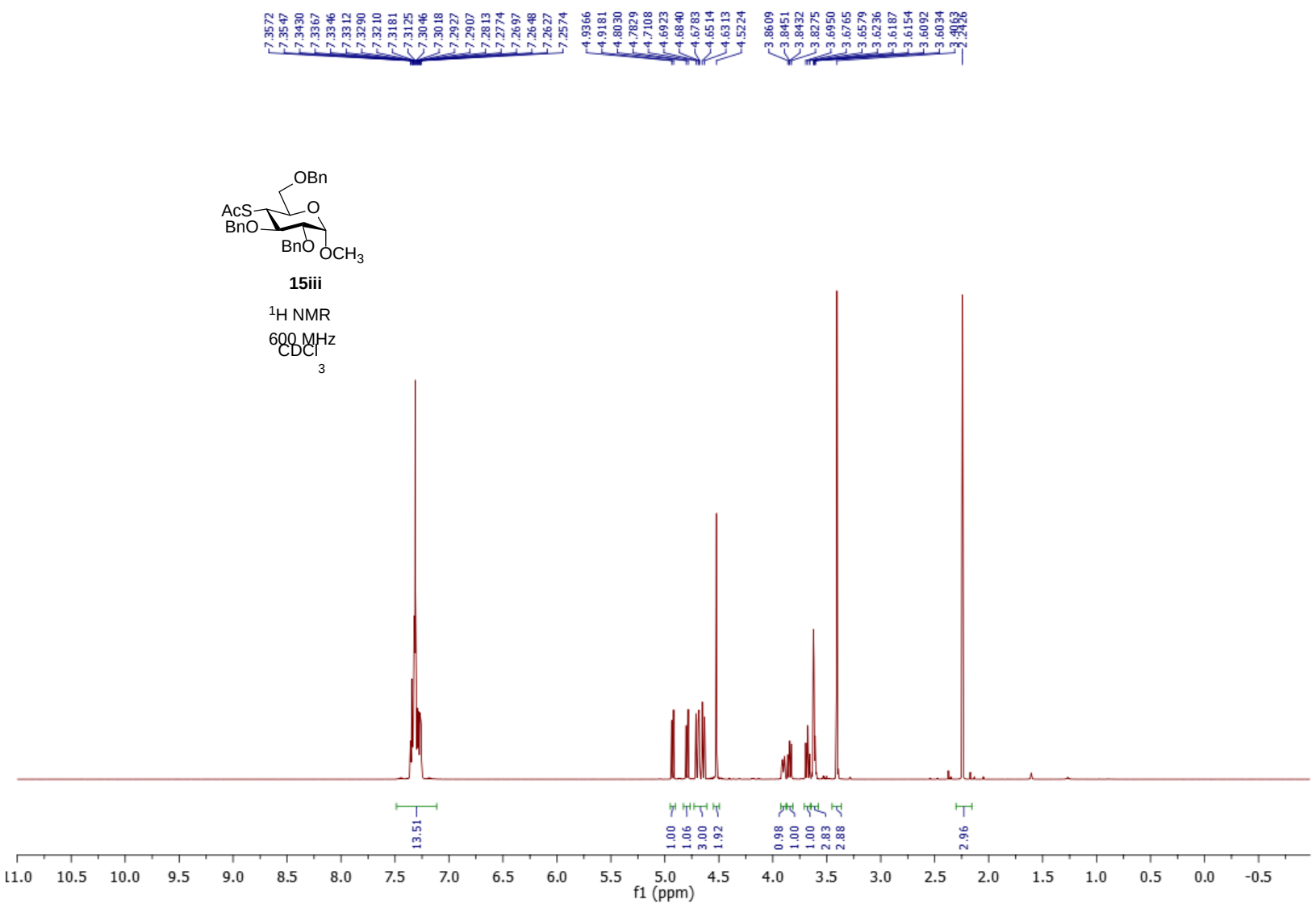
15ii

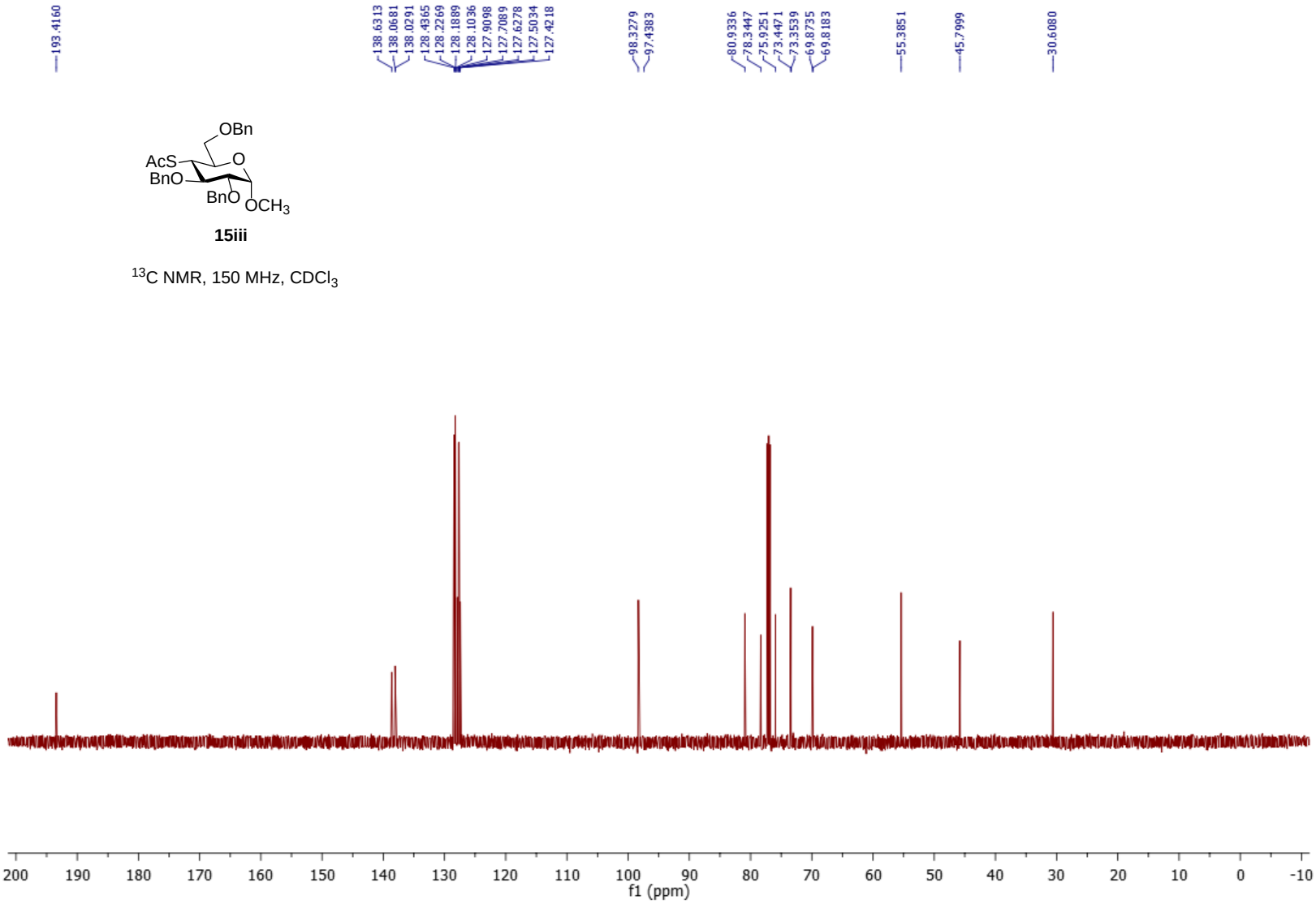
^{1}H NMR

400 MHz

$CDCl_3$

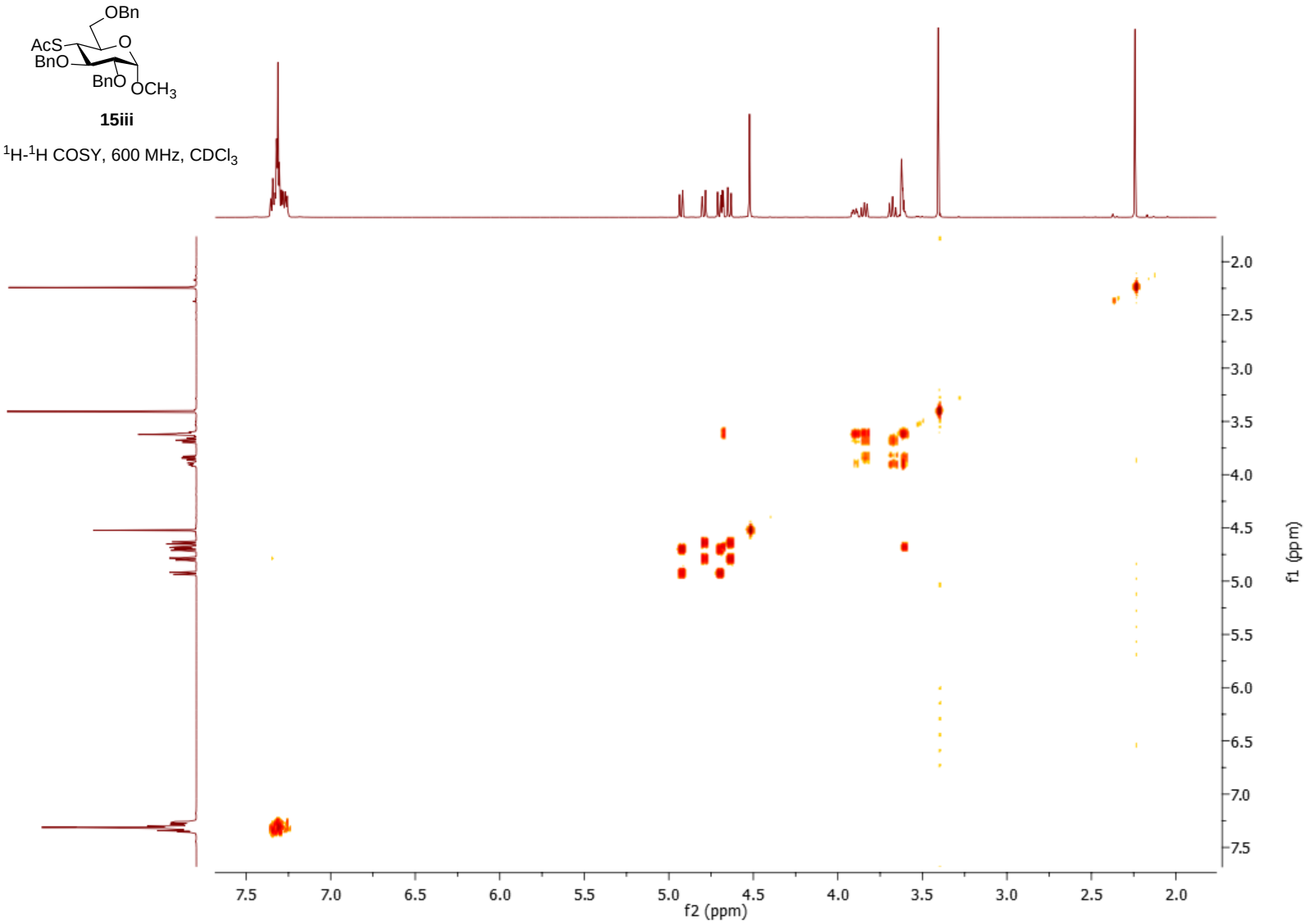

138.3429
137.9287
137.8029
128.4316
128.3919
128.3514
128.1243
127.8117
127.7753
127.7522
127.6827
99.0425
77.8399
75.7087
74.1781
73.9550
73.7364
71.2350
67.0782
55.3410
41.2301
I
OBn
O
BnO
BnO
OCH3
15ii
13C NMR, 100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

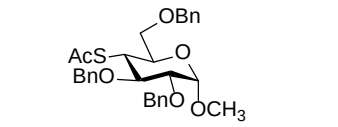

7.3572
7.3547
7.3430
7.3367
7.3346
7.3312
7.3290
7.3210
7.3181
7.3125
7.3046
7.3018
7.2927
7.2907
7.2813
7.2774
7.2697
7.2648
7.2627
7.2574
4.9366
4.9181
4.8030
4.7829
4.7108
4.6923
4.6840
4.6783
4.6514
4.6313
4.5224
3.8609
3.8451
3.8432
3.8275
3.6950
3.6765
3.6579
3.6236
3.6187
3.6154
3.6092
3.6034
3.4063
2.2426
OBn
AcS
O
BnO
BnO
OCH3
15iii
1H NMR
600 MHz
CDCl3
13.51
1.00
1.06
3.00
1.92
0.98
1.00
1.00
2.83
2.88
2.96
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



15iii

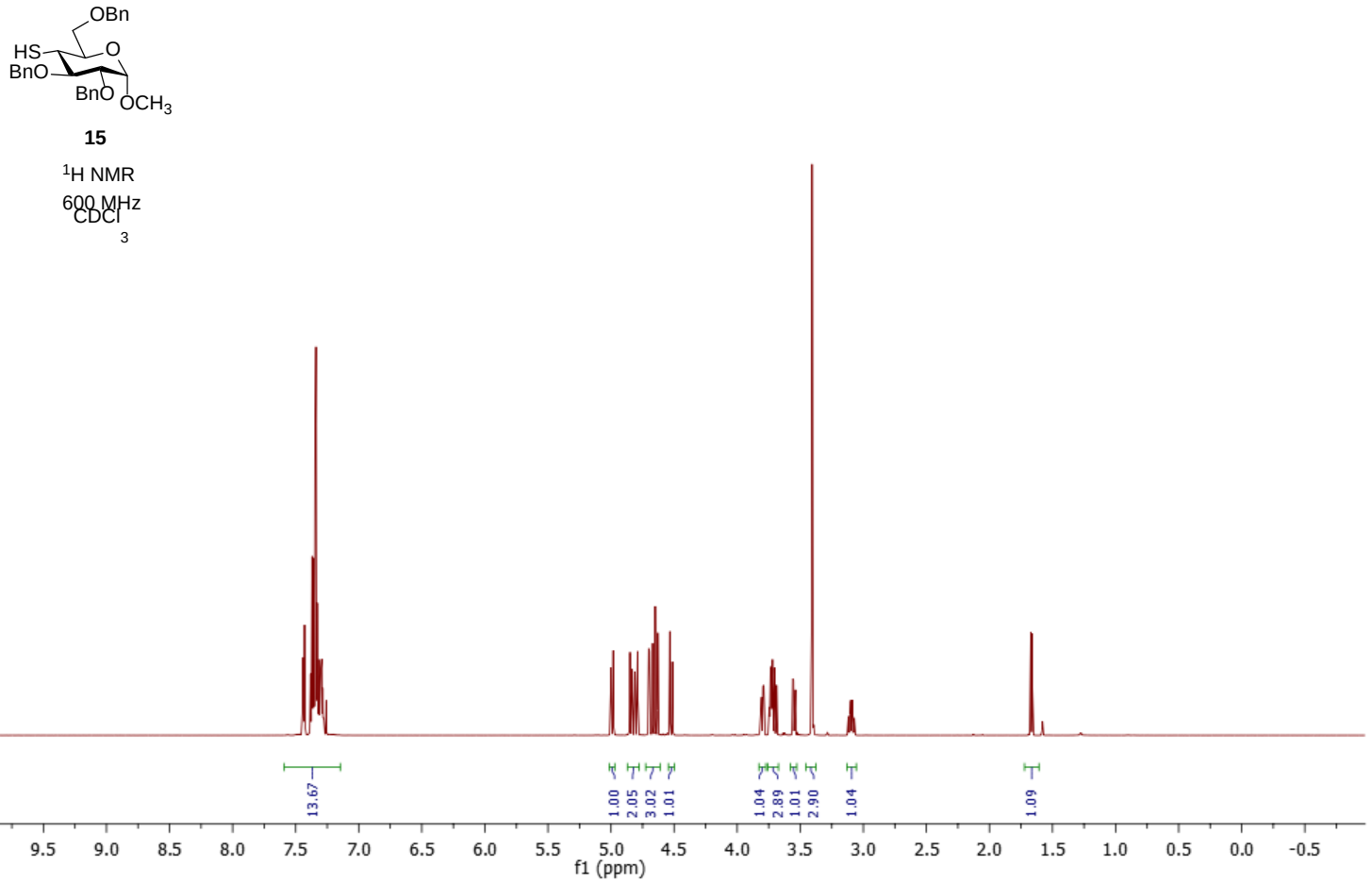
^{13}C NMR, 150 MHz, $CDCl_3$

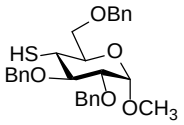

OBn
AcS
O
BnO
BnO
OCH3
15iii
1H-1H COSY, 600 MHz, CDCl3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
f1 (ppm)



15iii

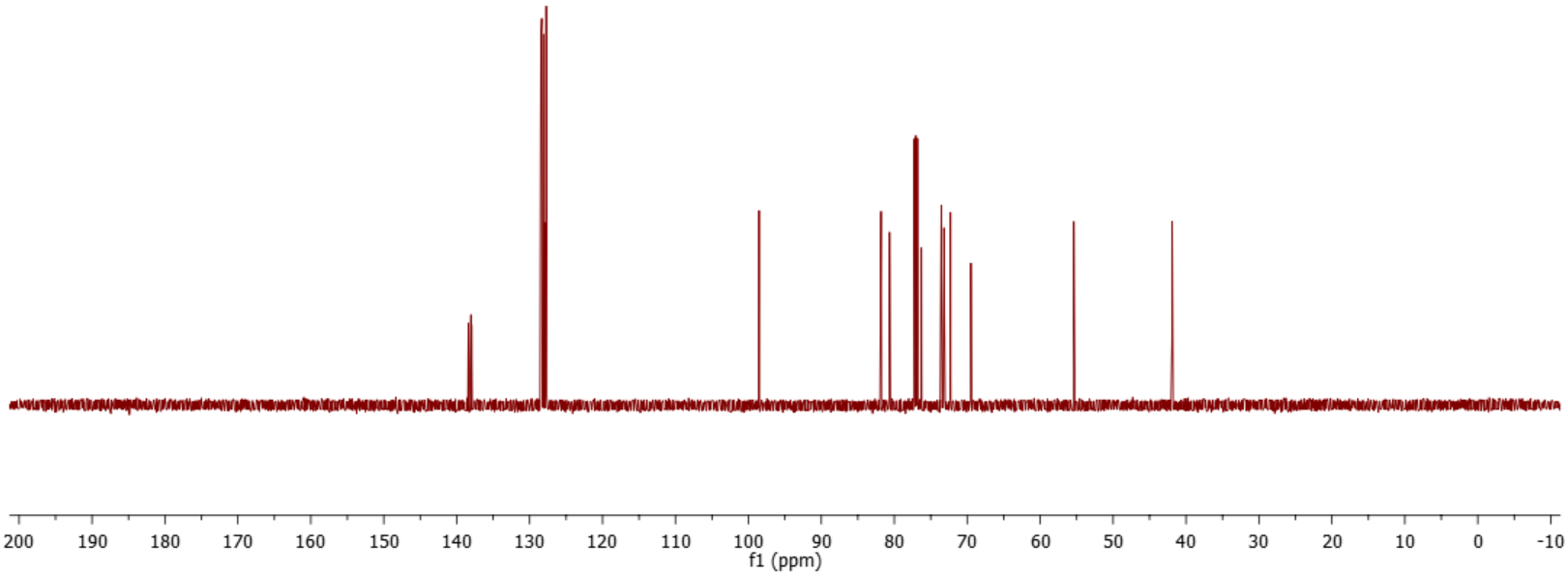
^{1}H-^{13}C HSQC, 600/150MHz, $CDCl_3$

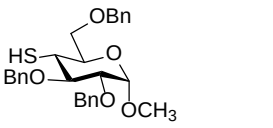

7.4413
7.4293
7.3818
7.3791
7.3697
7.3573
7.3467
7.3394
7.3293
7.3265
7.3168
7.3133
7.3062
7.3036
7.3010
7.2926
7.2864
7.2803
7.2786
7.2575
5.0001
4.9824
4.8497
4.8321
4.8099
4.7897
4.7016
4.6958
4.6703
4.6495
4.6288
4.5332
4.5130
3.7354
3.7195
3.7041
3.5592
3.5534
3.1178
3.1066
3.1003
3.0890
3.0827
3.0714
1.6717
1.6605
OBn
HS
O
BnO
BnO
OCH3
15
1H NMR
600 MHz
CDCl3
13.67
1.00
2.05
3.02
1.01
1.04
2.89
1.01
2.90
1.04
1.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



15

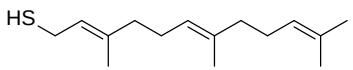
^{13}C NMR, 150 MHz, $CDCl_3$





15

^{1}H-^{13}C HSQC, 600/150MHz, $CDCl_3$

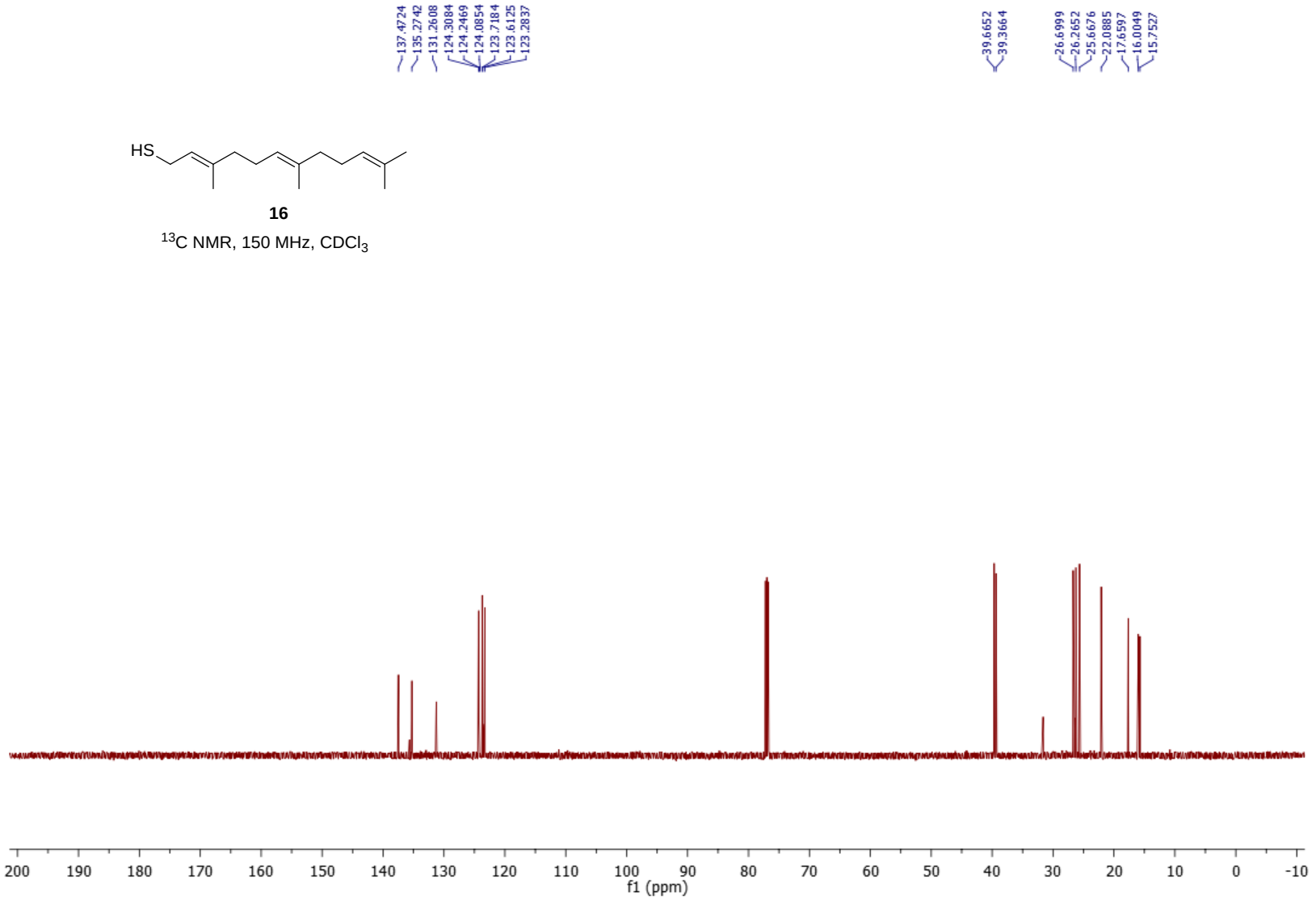


16

^{1}H NMR

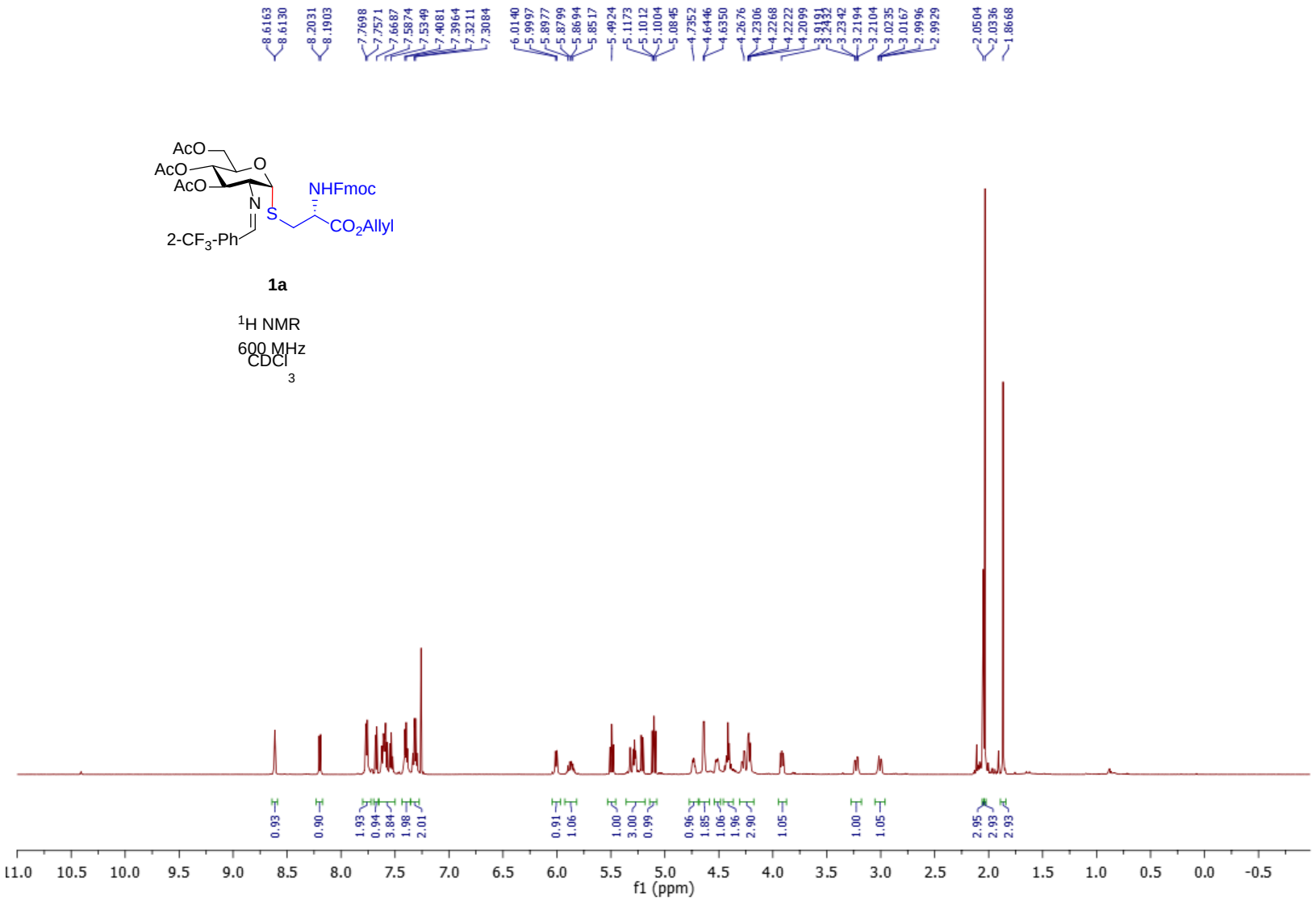
600 MHz

$CDCl_3$



16

^{13}C NMR, 150 MHz, $CDCl_3$

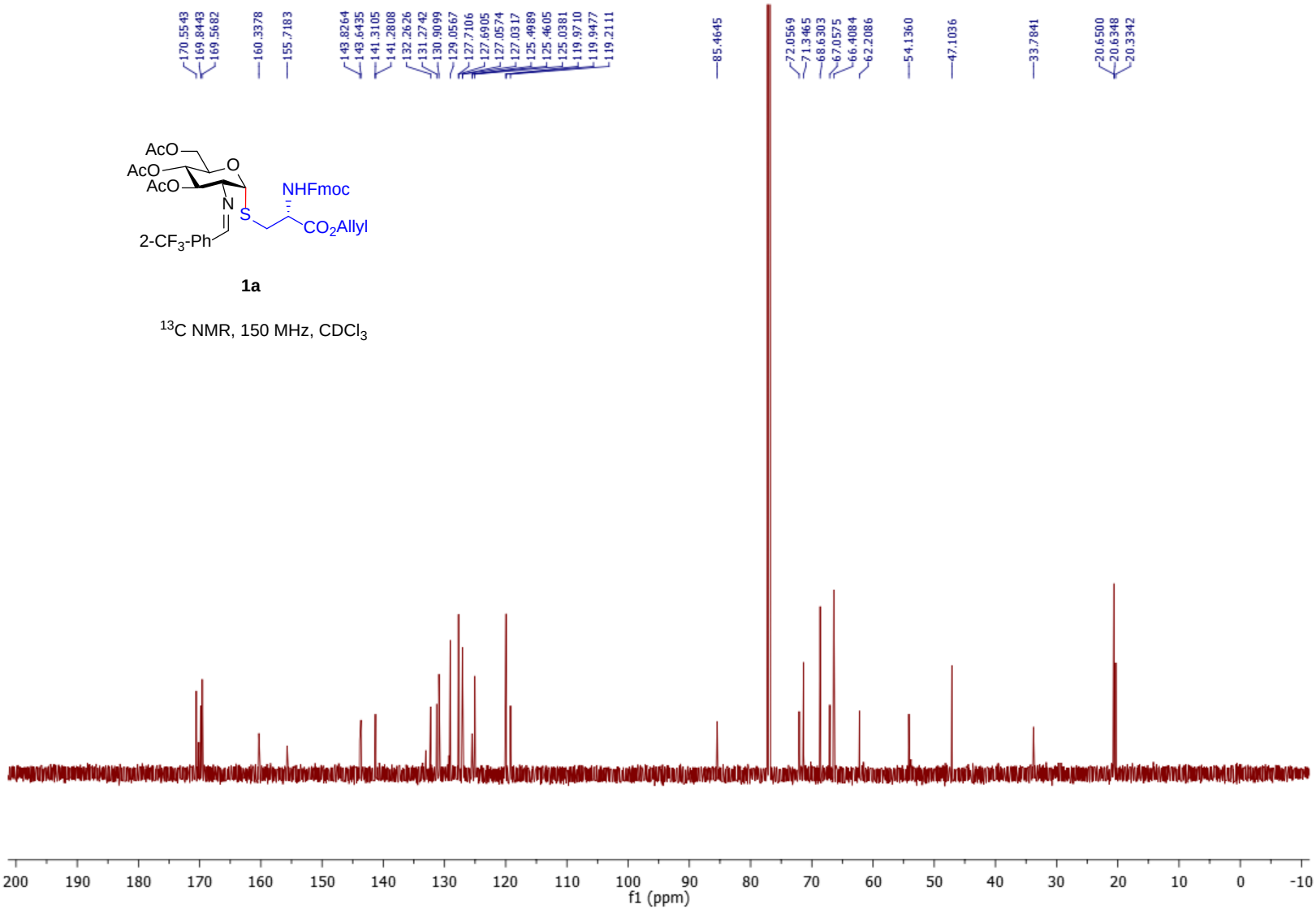


1a

^{1}H NMR

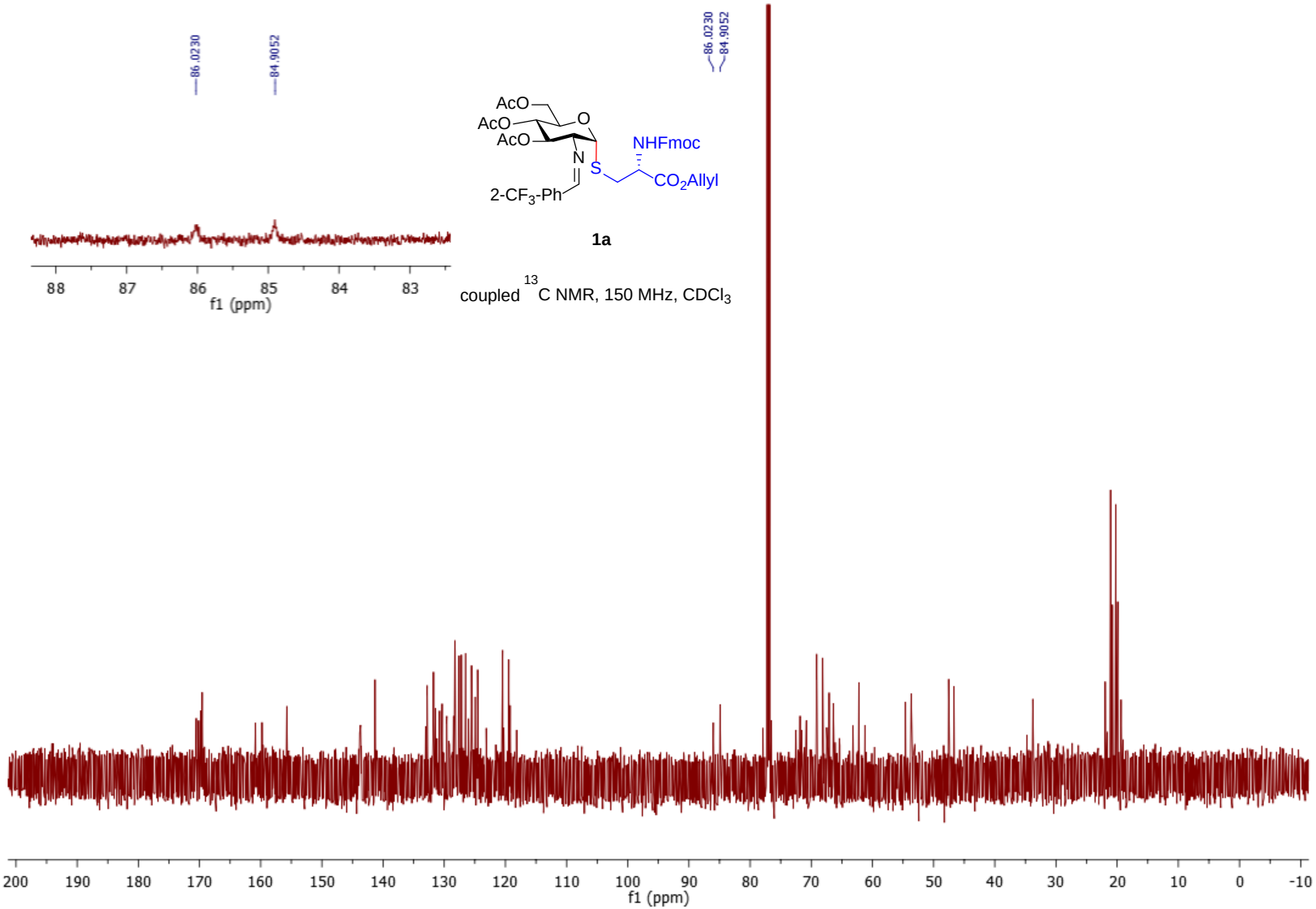
600 MHz

$CDCl_3$



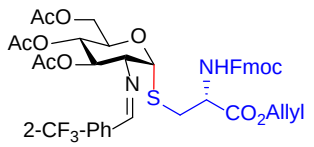
1a

^{13}C NMR, 150 MHz, $CDCl_3$



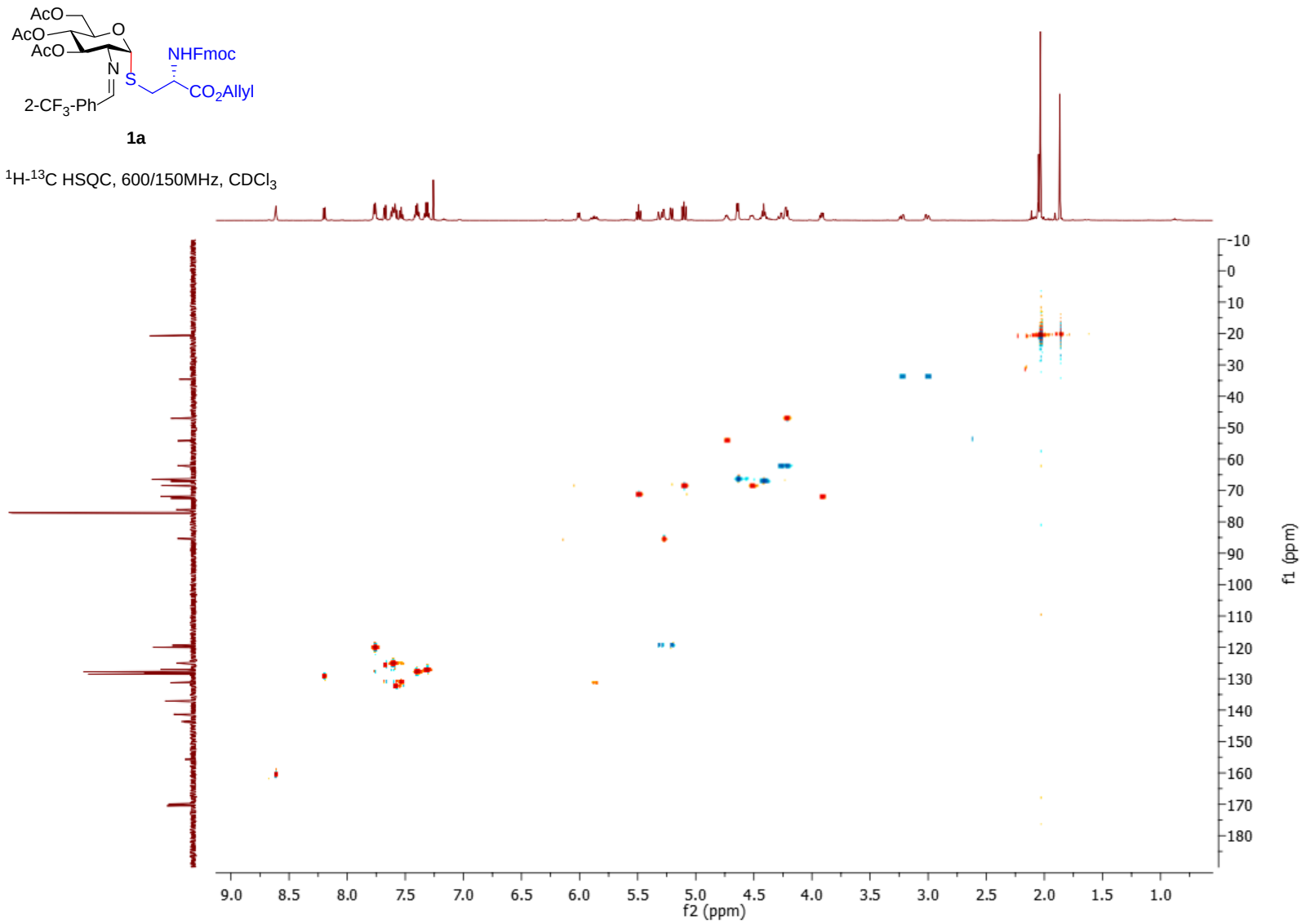
1a

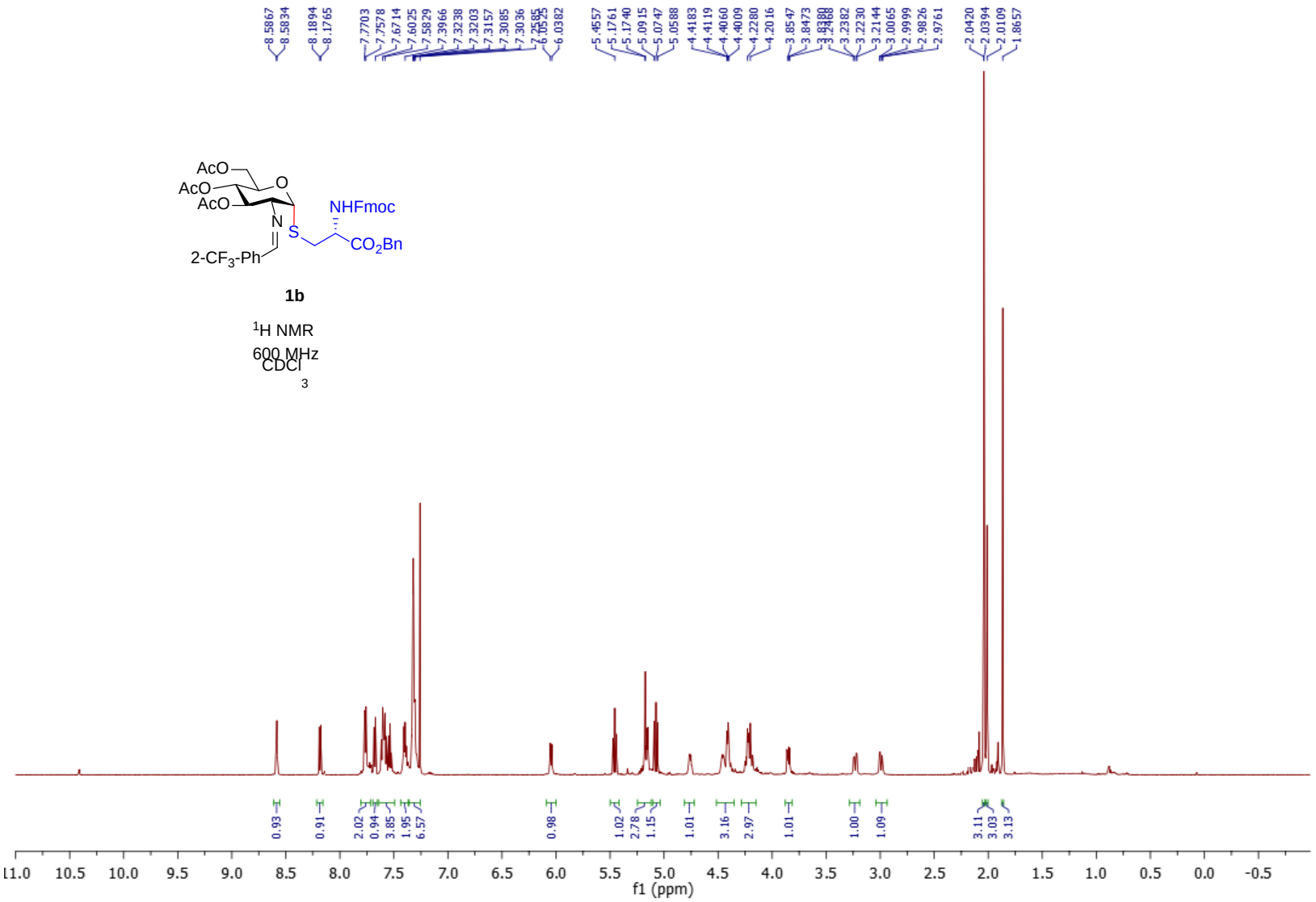
coupled ^{13}C NMR, 150 MHz, $CDCl_3$

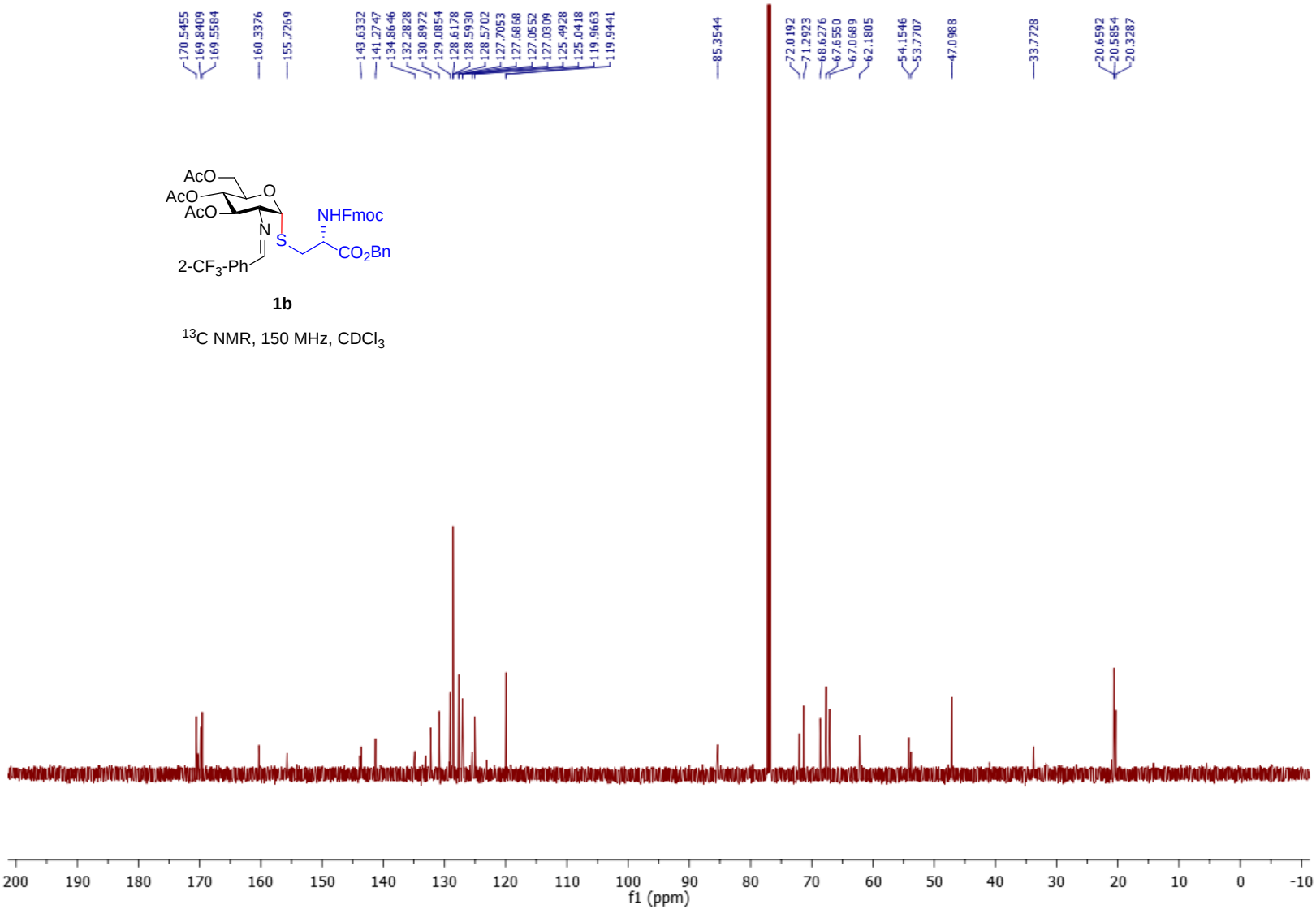


1a

^{1}H-^{1}H COSY, 600 MHz, $CDCl_3$

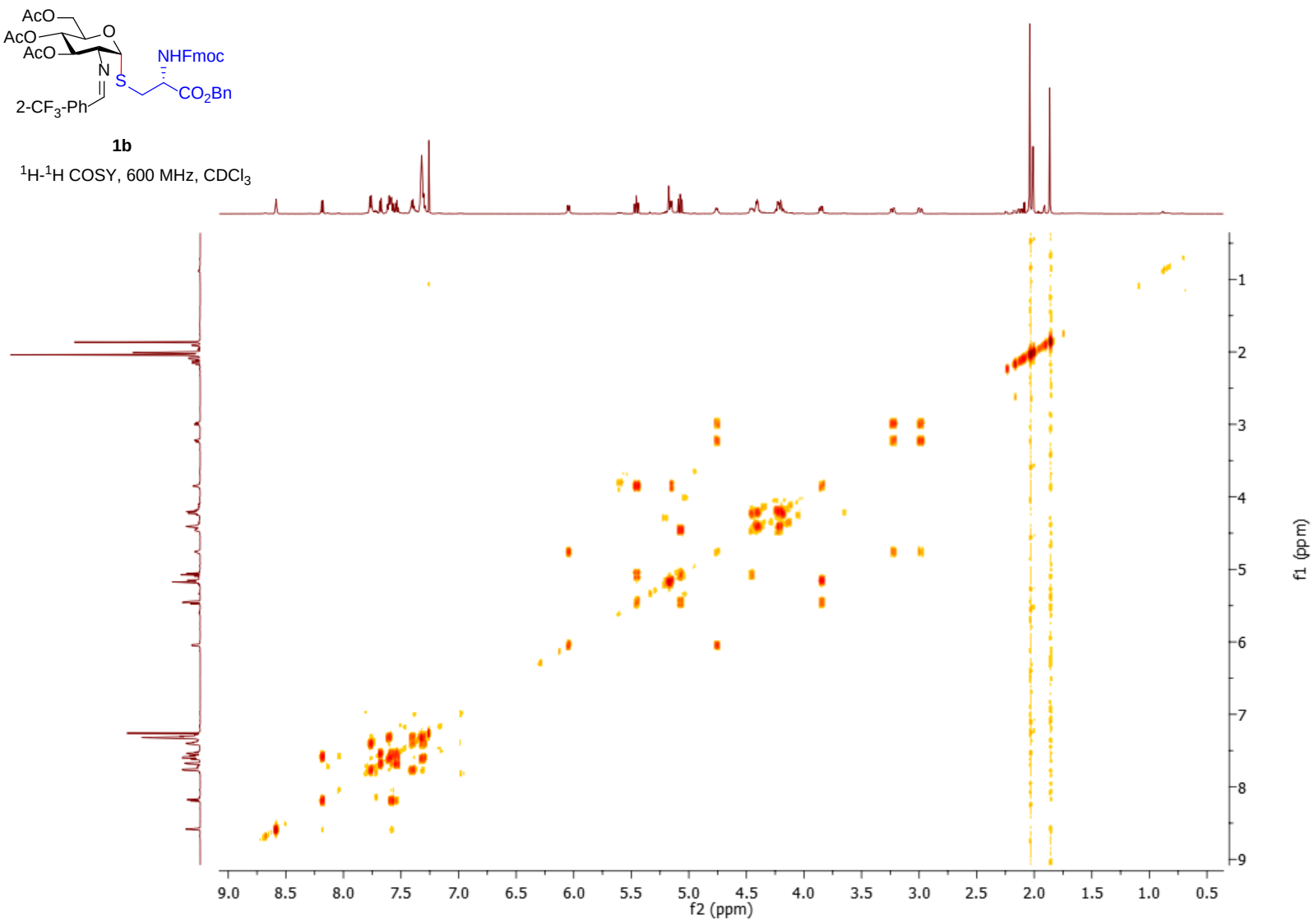

AcO
AcO
AcO
O
N
S
NHFmoc
CO2Allyl
2-CF3-Ph
1a
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


AcO
AcO
AcO
O
N
S
NHFmoc
CO2Bn
2-CF3-Ph
1b
1H NMR
600 MHz
CDCl3
f1 (ppm)



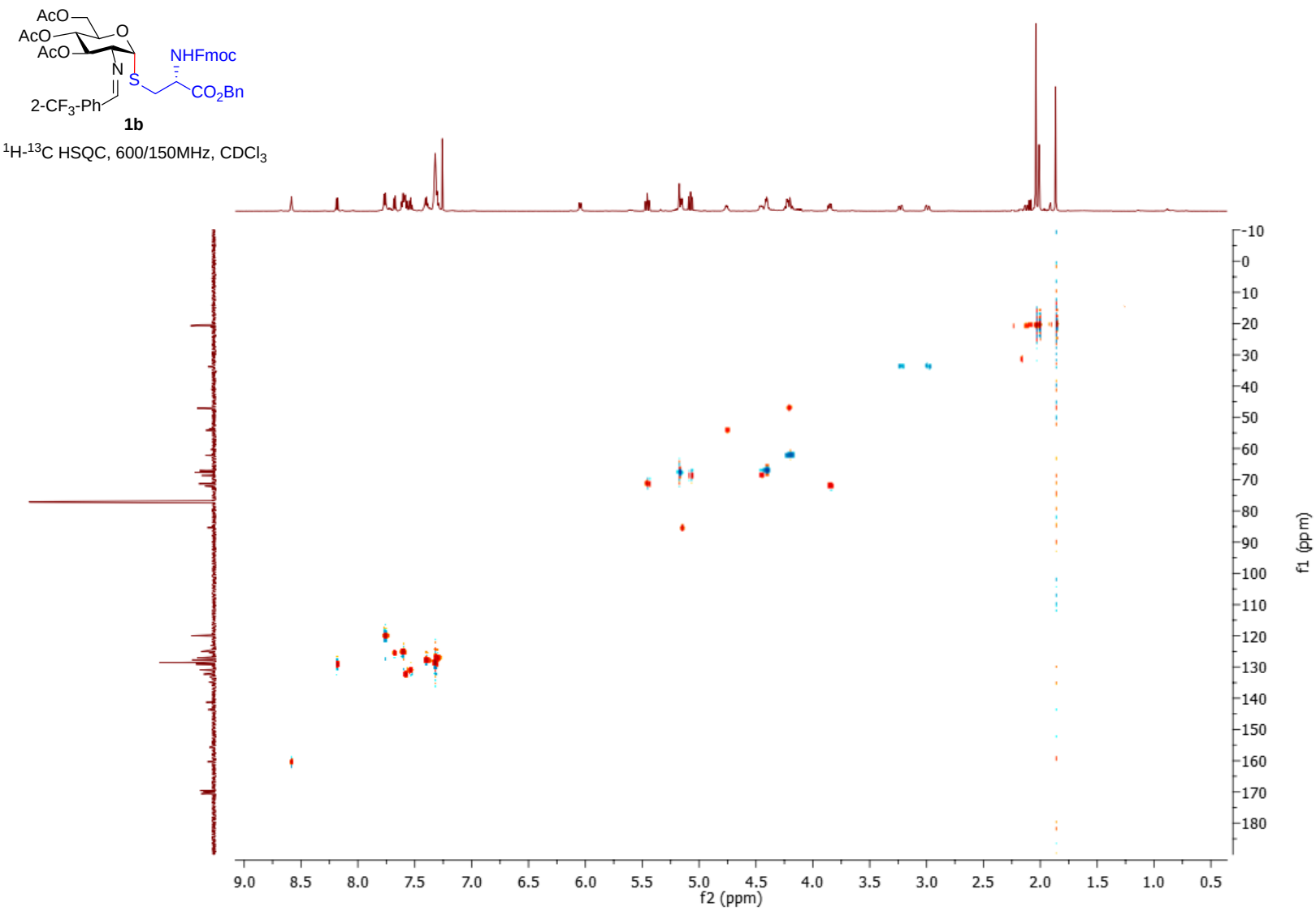
1b

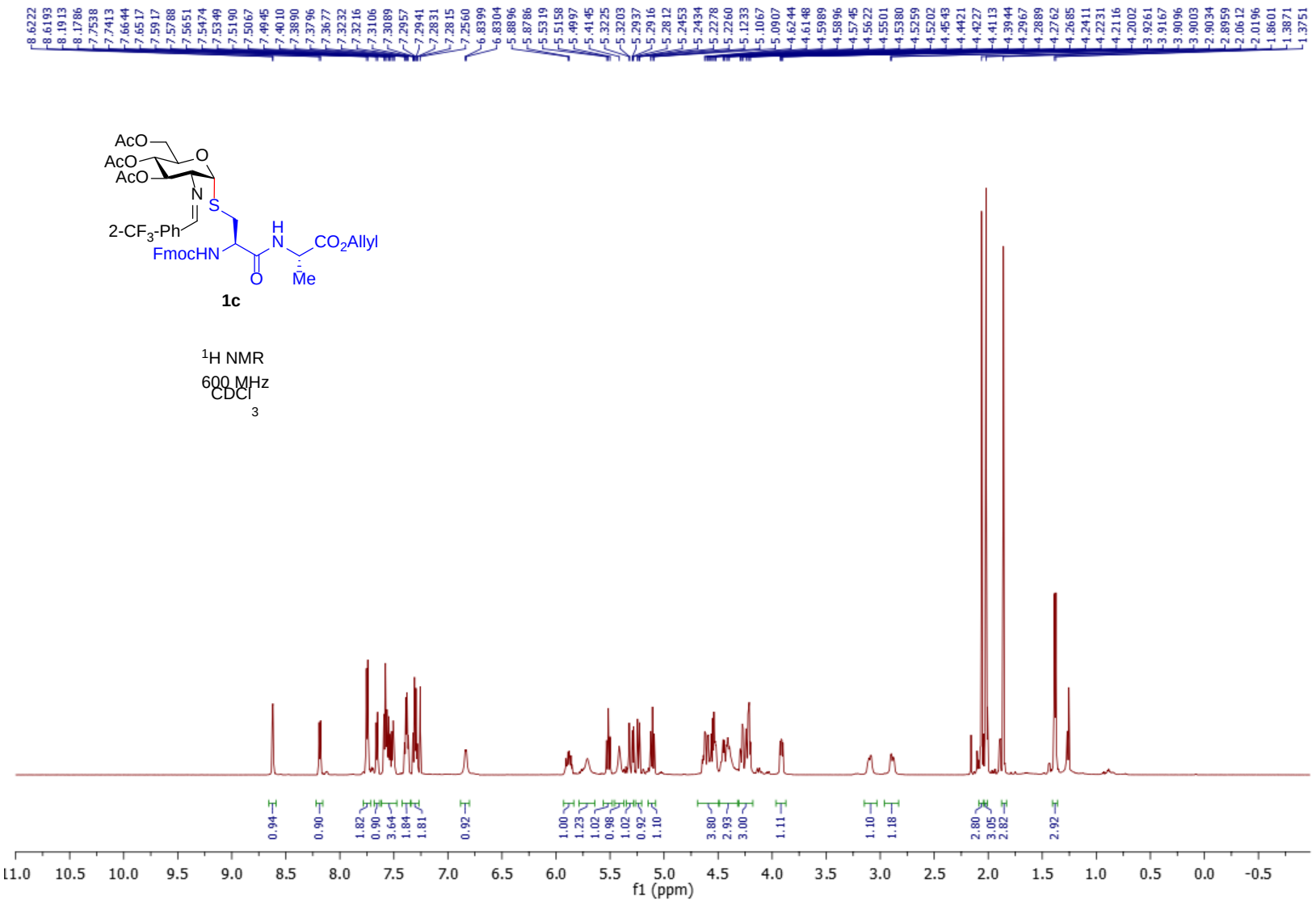
^{13}C NMR, 150 MHz, $CDCl_3$

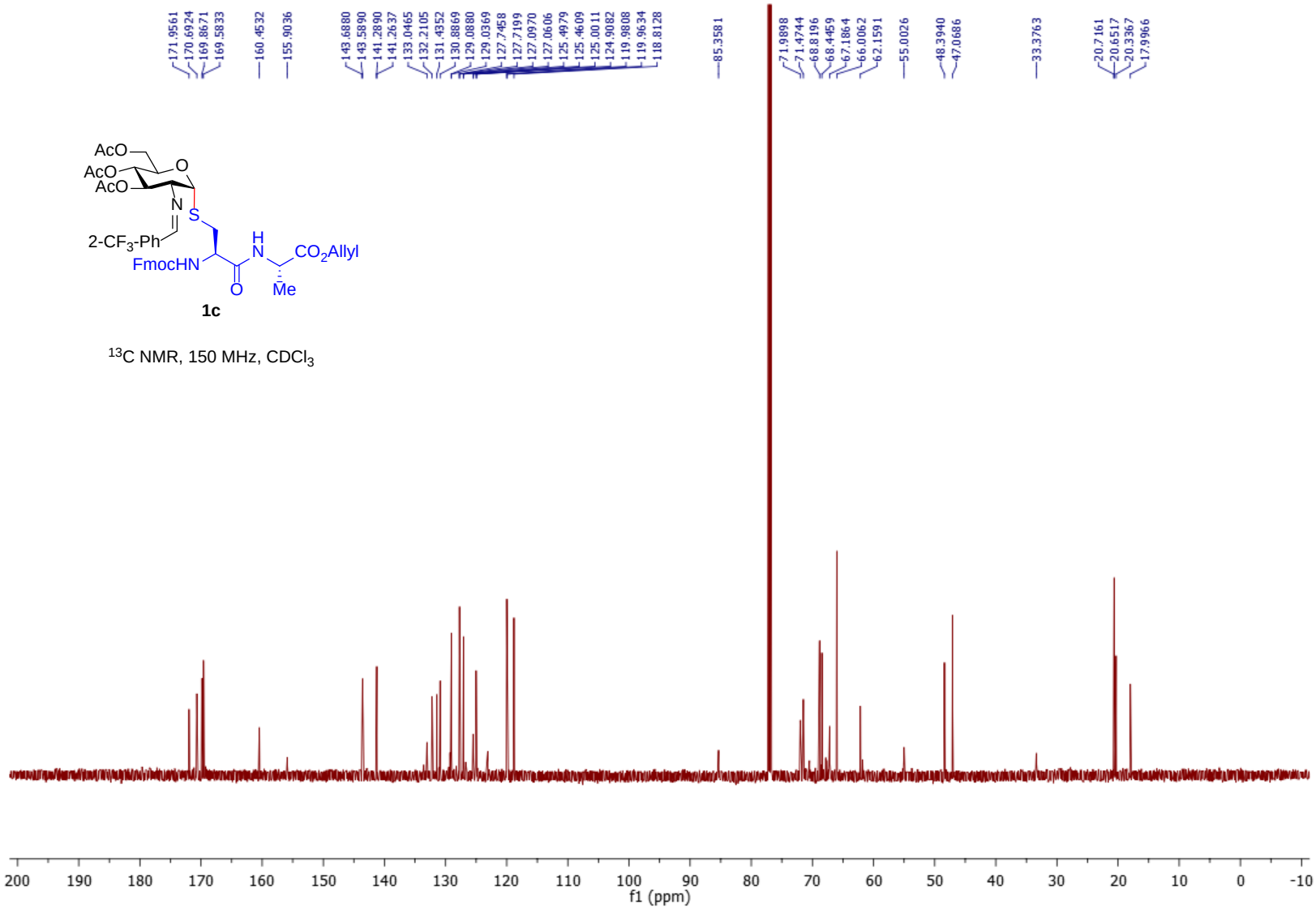


1b

^{1}H-^{1}H COSY, 600 MHz, $CDCl_3$


AcO
AcO
AcO
O
N
S
NHFmoc
CO2Bn
2-CF3-Ph
1b
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


AcO
AcO
AcO
O
N
S
2-CF3-Ph
FmocHN
H
N
CO2Allyl
O
Me
1c
1H NMR
600 MHz
CDCl3
f1 (ppm)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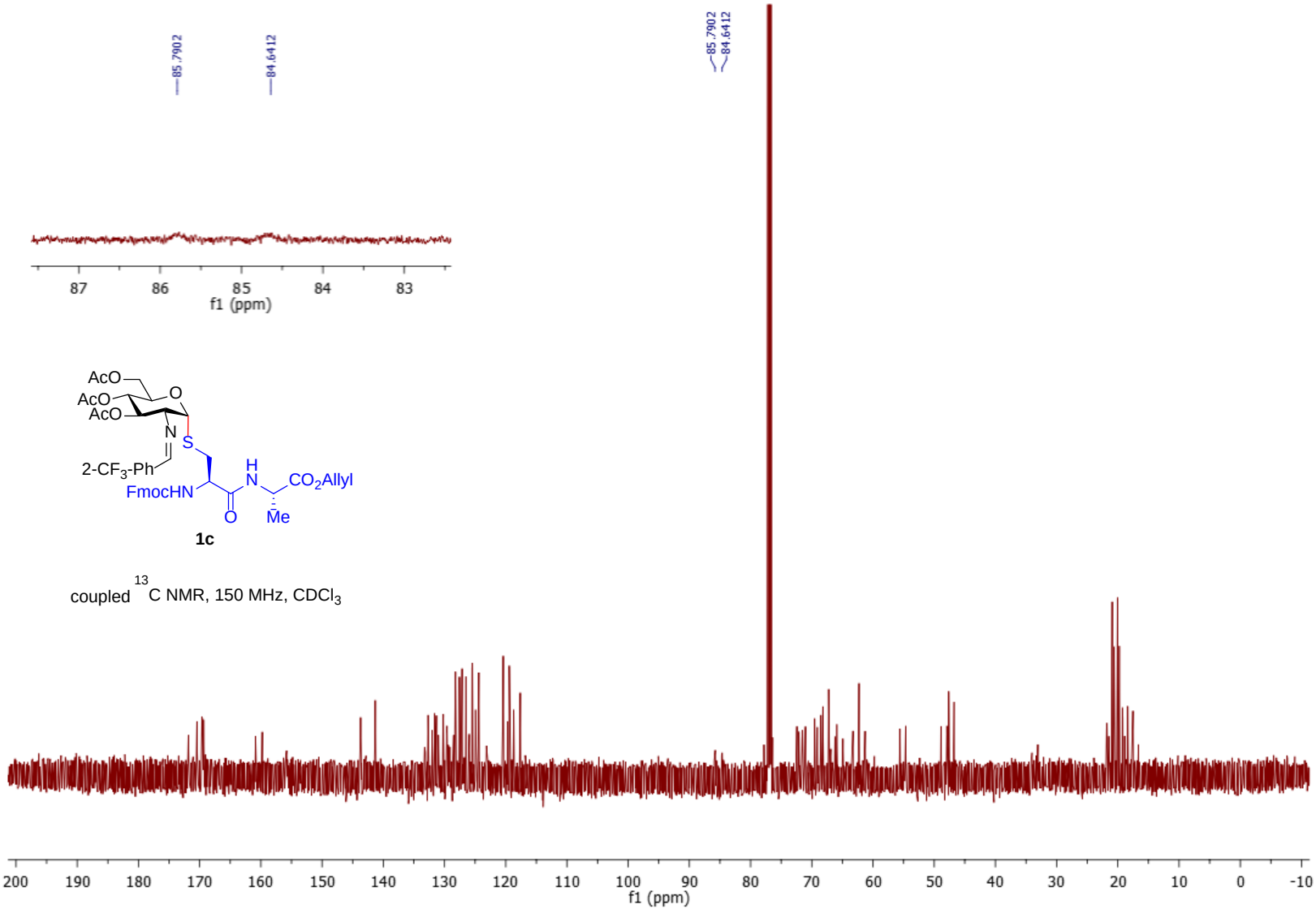
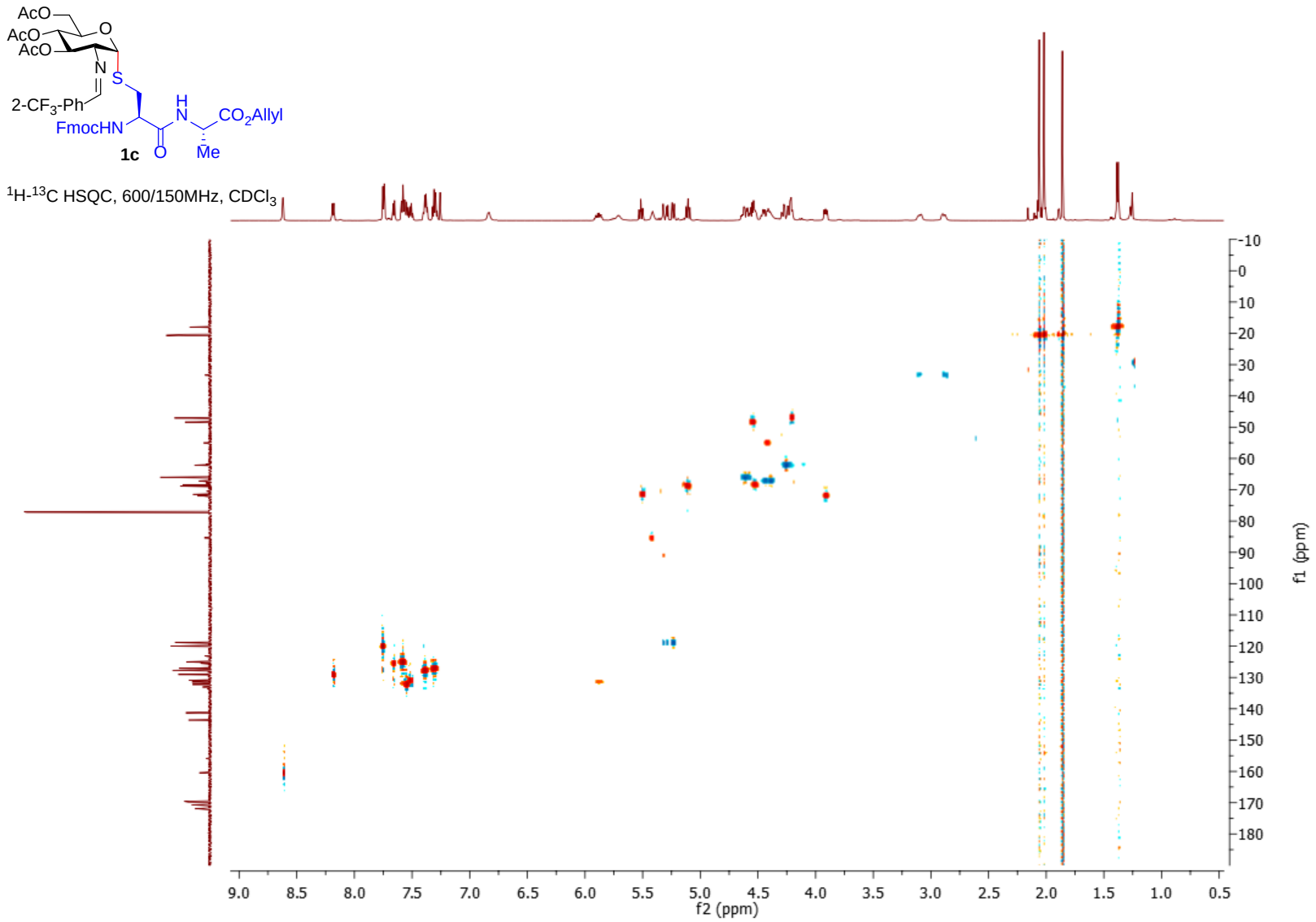
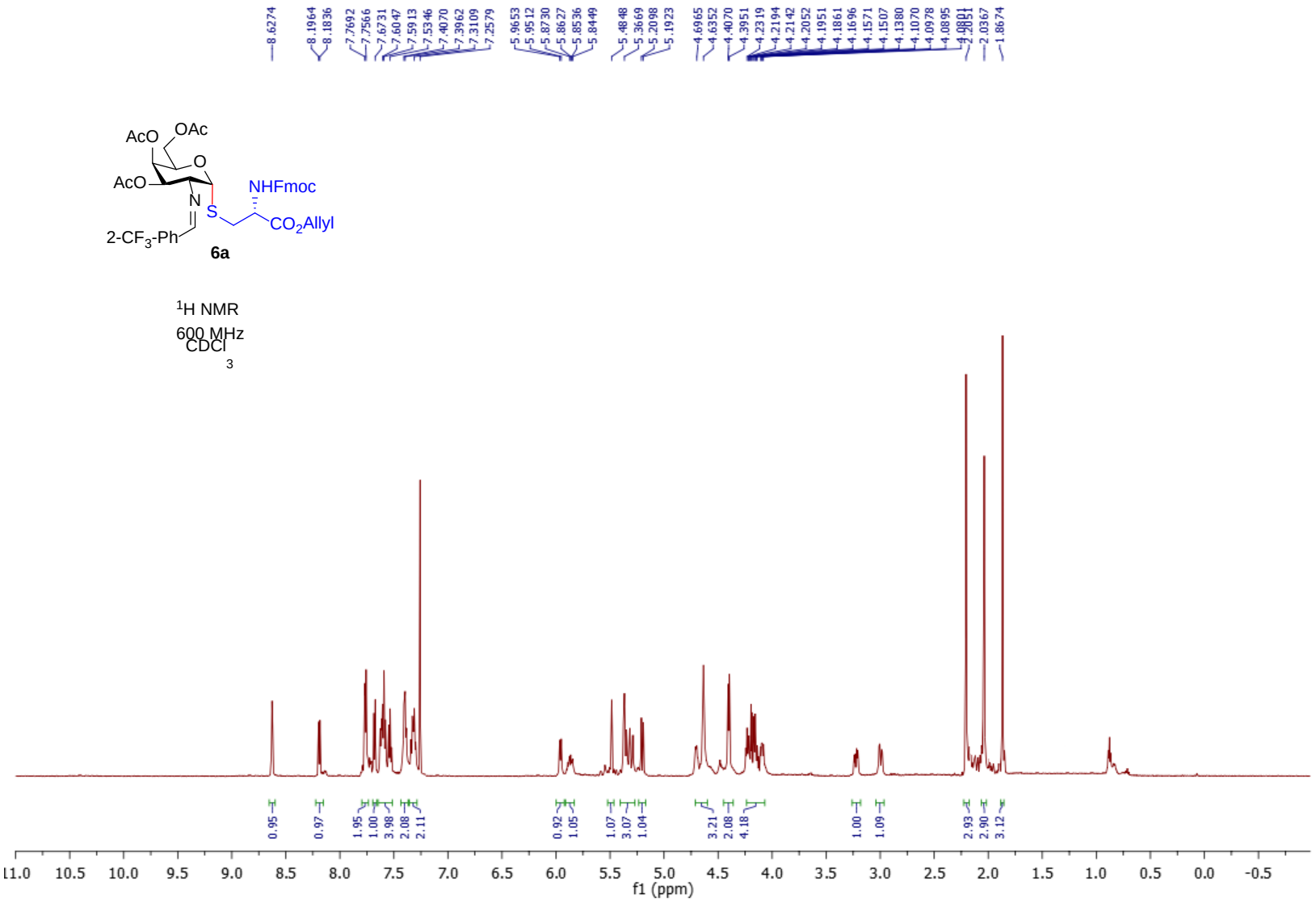
170.6924
169.8671
169.5833
160.4532
155.9036
143.6880
143.5890
141.2890
141.2637
133.0465
132.2105
131.4352
130.8869
129.0880
129.0369
127.7458
127.7199
127.0970
127.0606
125.4979
125.4609
125.0011
124.9082
119.9808
119.9634
118.8128
85.3581
71.9898
71.4744
68.8196
68.4459
67.1864
66.0062
62.1591
55.0026
48.3940
47.0686
33.3763
20.7161
20.6517
20.3367
17.9966
AcO
AcO
AcO
O
N
S
2-CF3-Ph
FmocHN
H
N
CO2Allyl
O
Me
1c
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


85.7902
84.6412
87
86
85
84
83
f1 (ppm)
AcO
AcO
AcO
O
N
S
2-CF3-Ph
FmocHN
H
N
CO2Allyl
O
Me
1c
coupled 13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AcO
AcO
AcO
O
N
S
2-CF3-Ph
H
N
CO2Allyl
FmocHN
O
Me
1c
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)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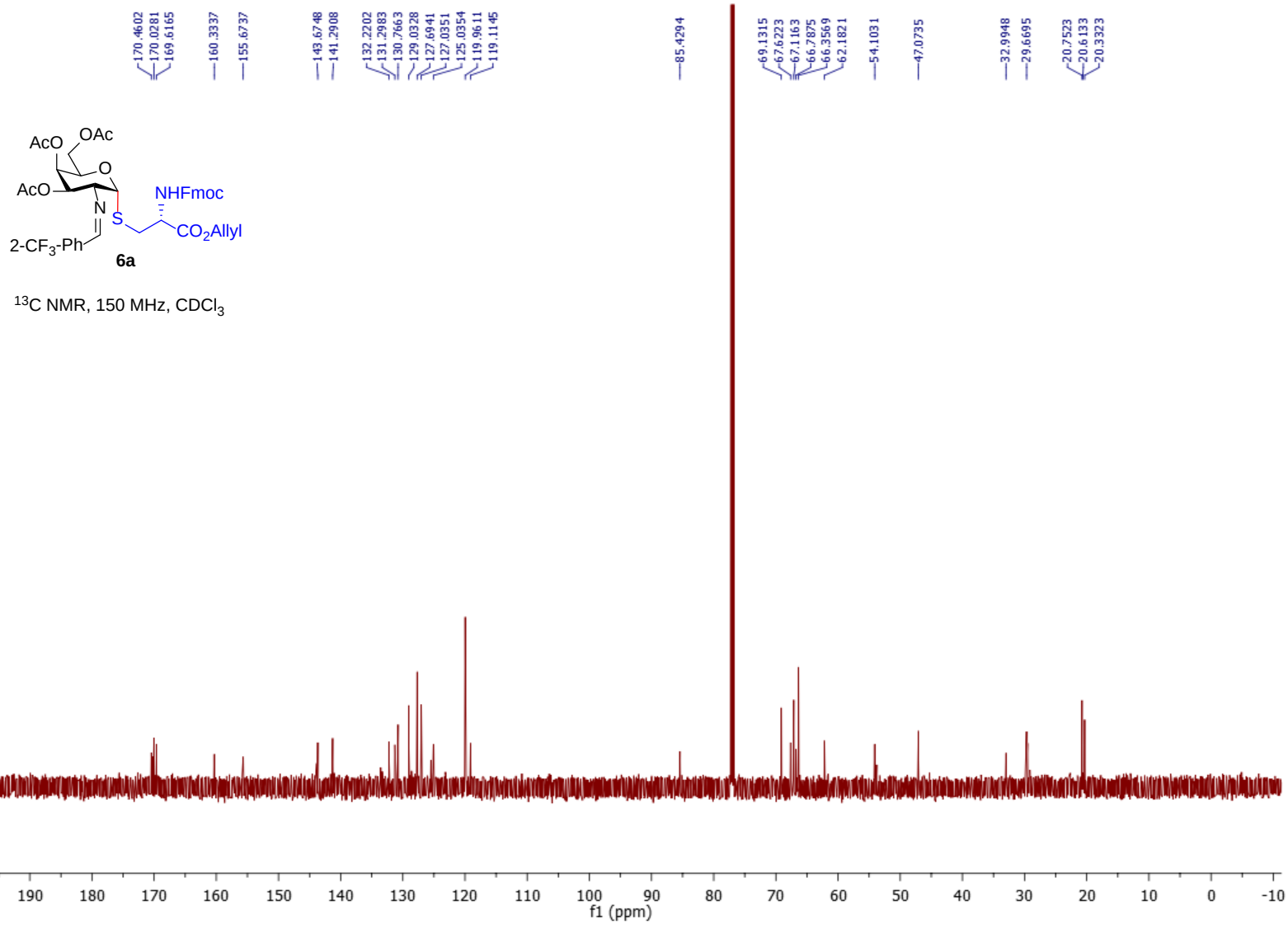
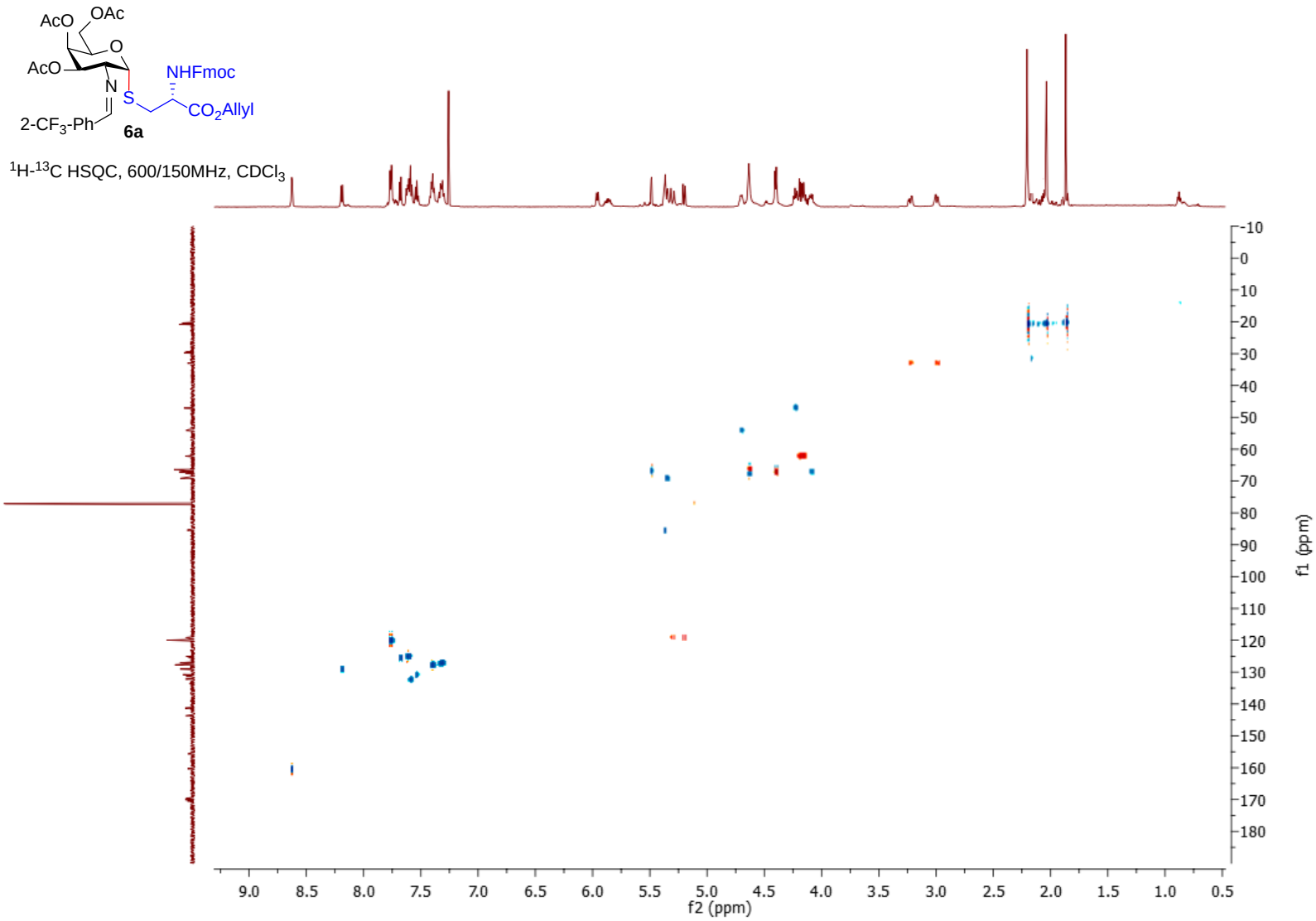
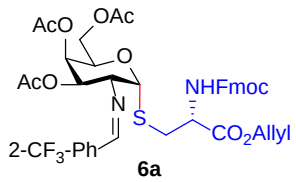
8.1964
8.1836
7.7692
7.7566
7.6731
7.6047
7.5913
7.5346
7.4070
7.3962
7.3109
7.2579
5.9653
5.9512
5.8730
5.8627
5.8536
5.8449
5.4848
5.3669
5.2098
5.1923
4.6965
4.6352
4.4070
4.3951
4.2319
4.2194
4.2142
4.2052
4.1951
4.1861
4.1696
4.1571
4.1507
4.1380
4.1070
4.0978
4.0895
2.0851
2.0367
1.8674
AcO
OAc
O
AcO
N
S
NHFmoc
CO2Allyl
2-CF3-Ph
6a
1H NMR
600 MHz
CDCl3
0.95
0.97
1.95
1.00
3.98
2.08
2.11
0.92
1.05
1.07
3.07
1.04
3.21
2.08
4.18
1.00
1.09
2.93
2.90
3.12
f1 (ppm)

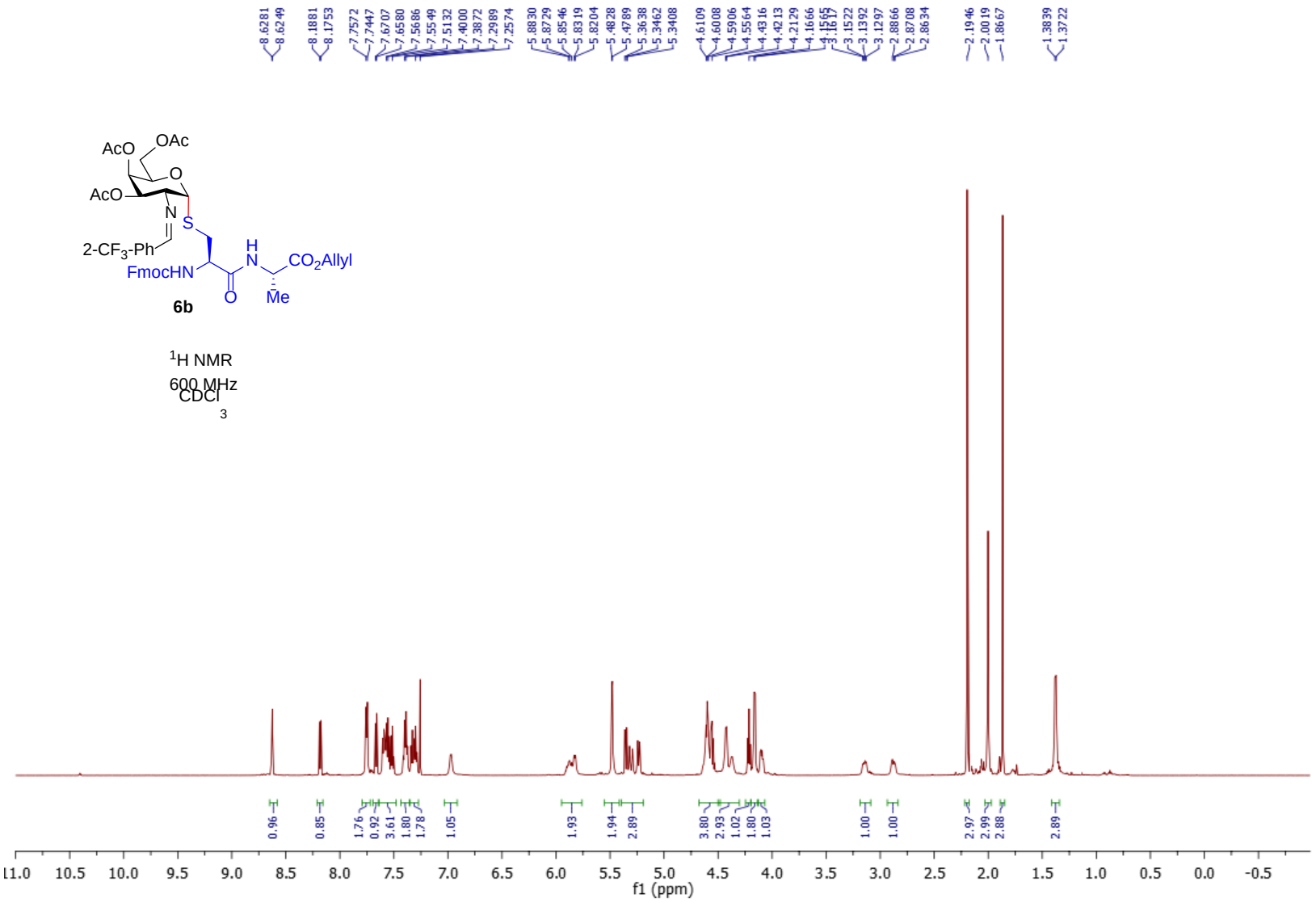

170.4602
170.0281
169.6165
160.3337
155.6737
143.6748
141.2908
132.2202
131.2983
130.7663
129.0328
127.6941
127.0351
125.0354
119.9611
119.1145
85.4294
69.1315
67.6223
67.1163
66.7875
66.3569
62.1821
54.1031
47.0735
32.9948
29.6695
20.7523
20.6133
20.3323
AcO
OAc
O
AcO
N
S
NHFmoc
CO2Allyl
2-CF3-Ph
6a
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

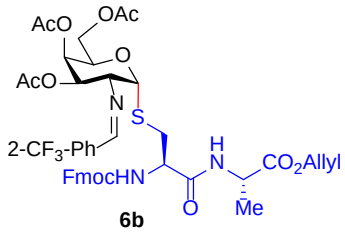

AcO
OAc
O
AcO
N
S
NHFmoc
CO2Allyl
2-CF3-Ph
6a
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)



6a

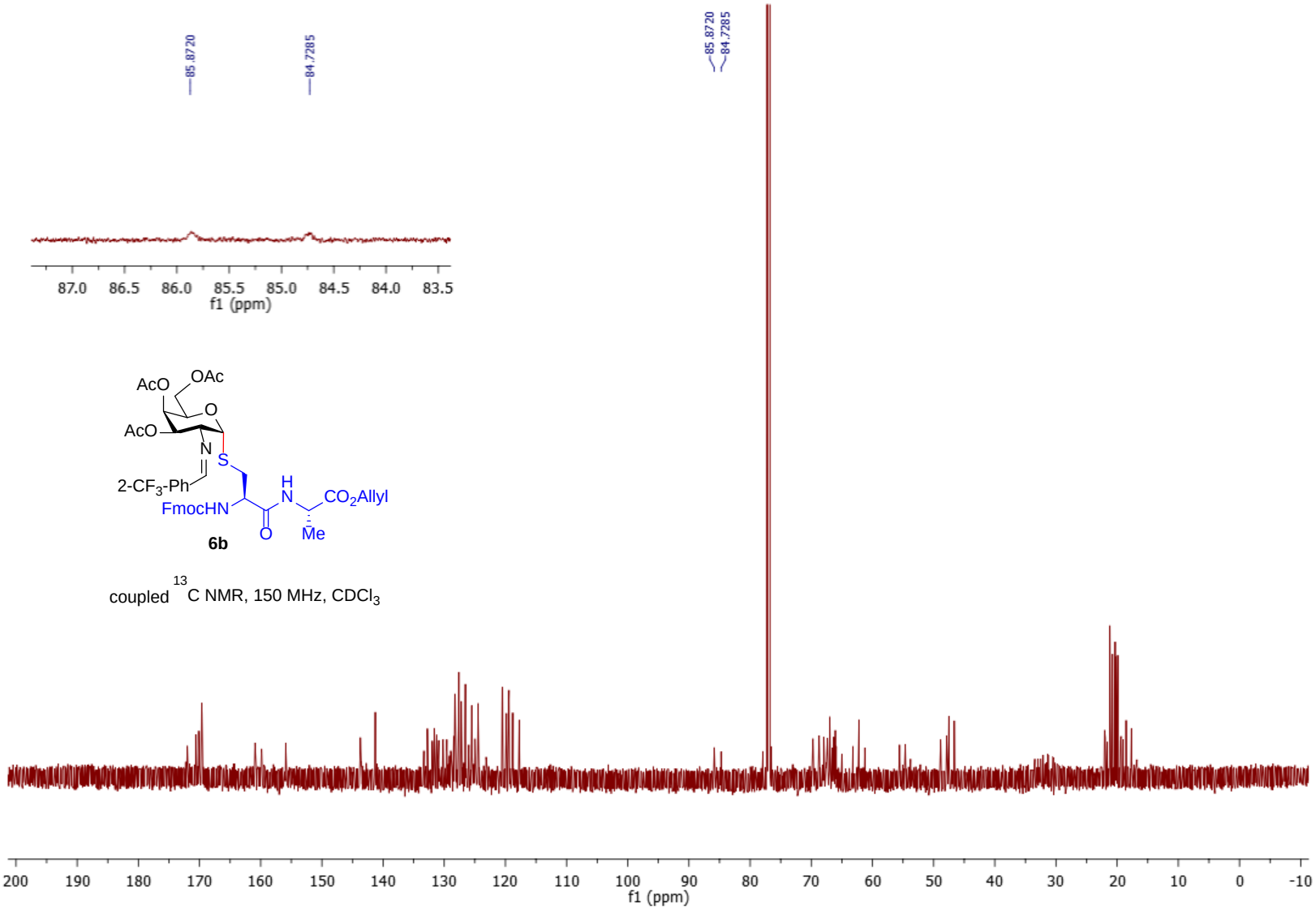
^{1}H-^{13}C Coupled HSQC, 600/150MHz, $CDCl_3$

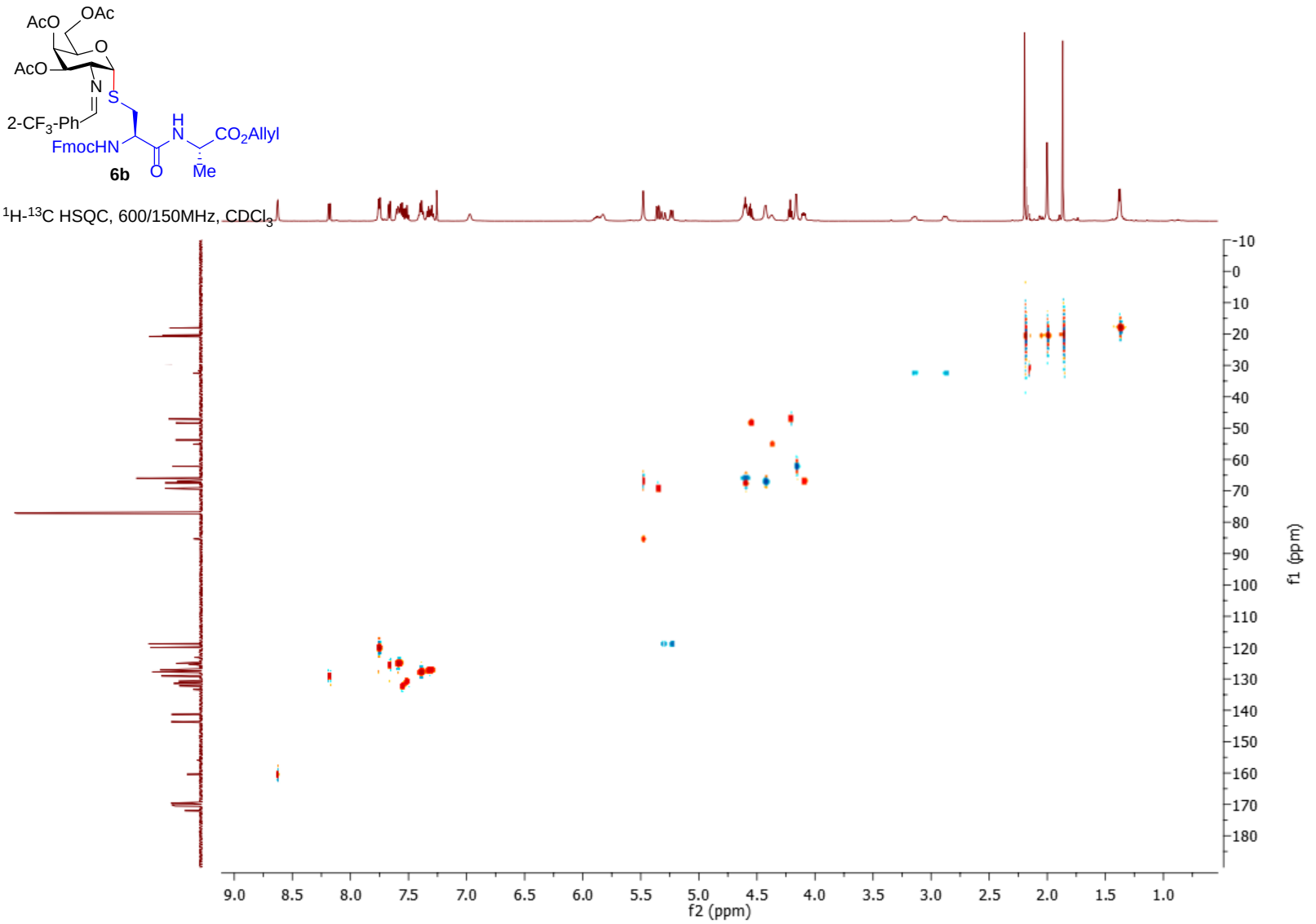

8.6281
8.6249
8.1881
8.1753
7.7572
7.7447
7.6707
7.6580
7.5686
7.5549
7.5132
7.4000
7.3872
7.2989
7.2574
5.8830
5.8729
5.8546
5.8319
5.8204
5.4828
5.4789
5.3638
5.3462
5.3408
4.6109
4.6008
4.5906
4.5564
4.4316
4.4213
4.2129
4.1666
3.1617
3.1522
3.1392
3.1297
2.8866
2.8708
2.8634
2.1946
2.0019
1.8667
1.3839
1.3722
AcO
OAc
O
AcO
N
S
2-CF3-Ph
FmocHN
H
N
CO2Allyl
O
Me
6b
1H NMR
600 MHz
CDCl3
0.96
0.85
1.76
0.92
3.61
1.80
1.78
1.05
1.93
1.94
2.89
3.80
2.93
1.02
1.80
1.03
1.00
1.00
2.97
2.99
2.88
2.89
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

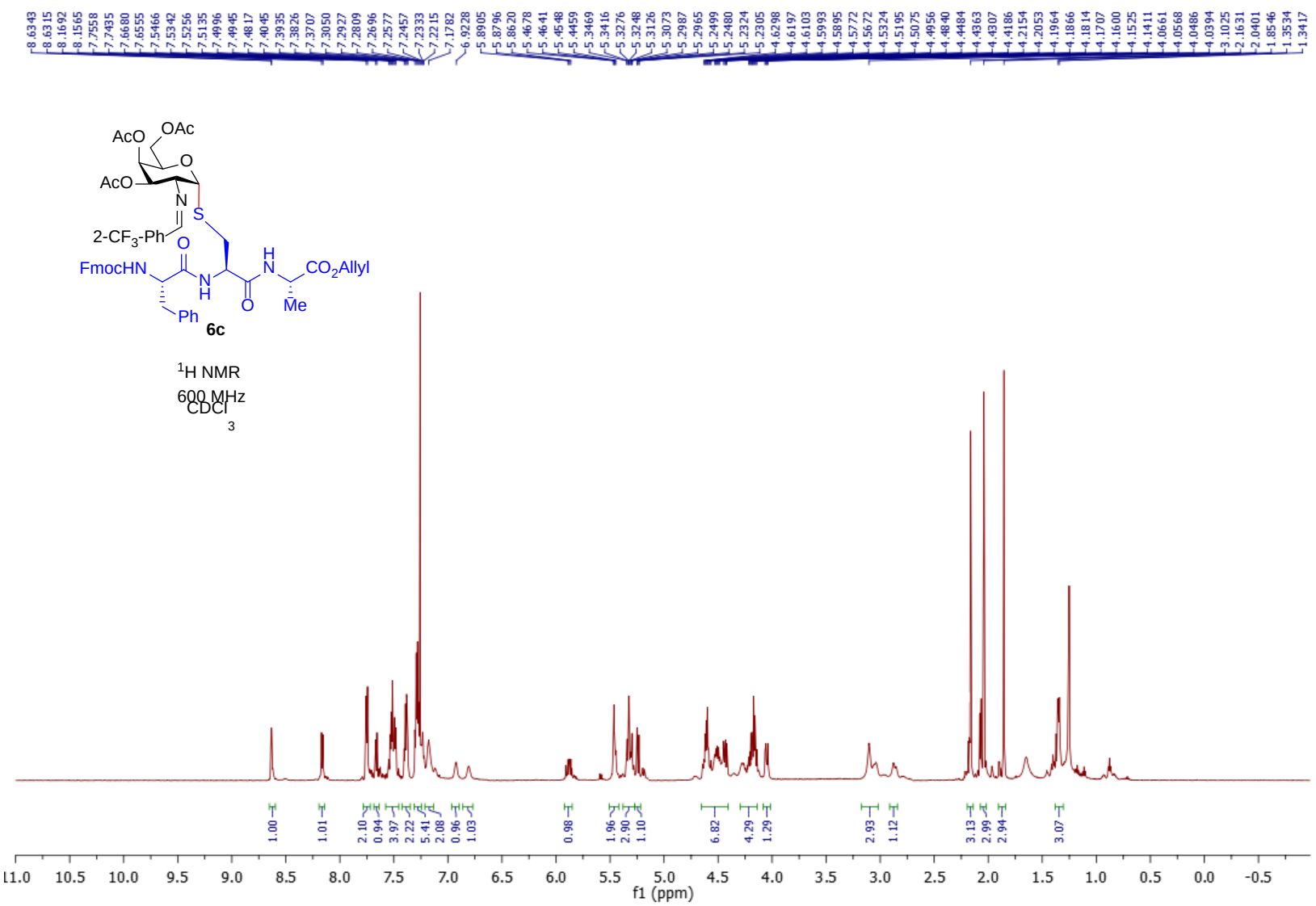


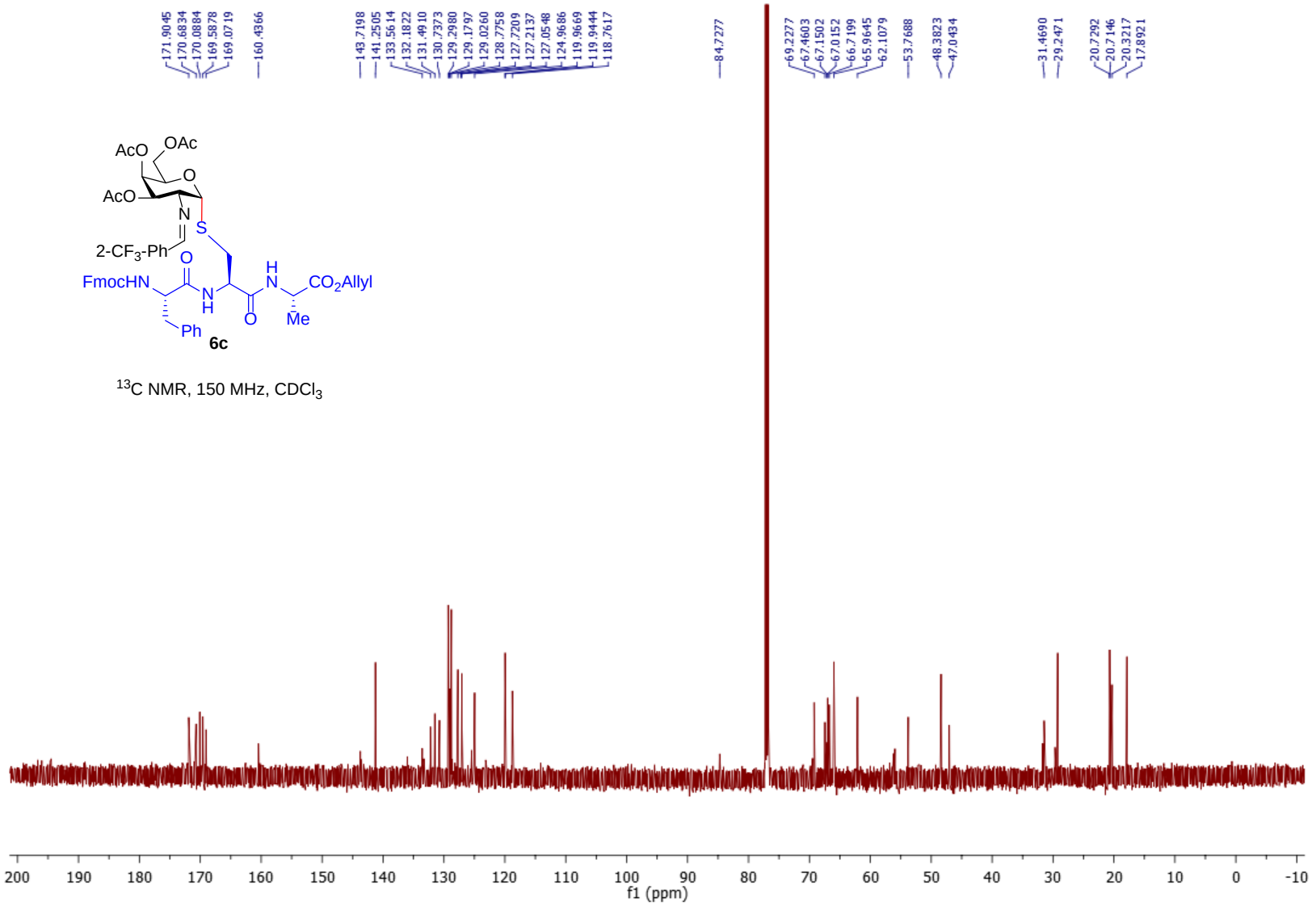
6b

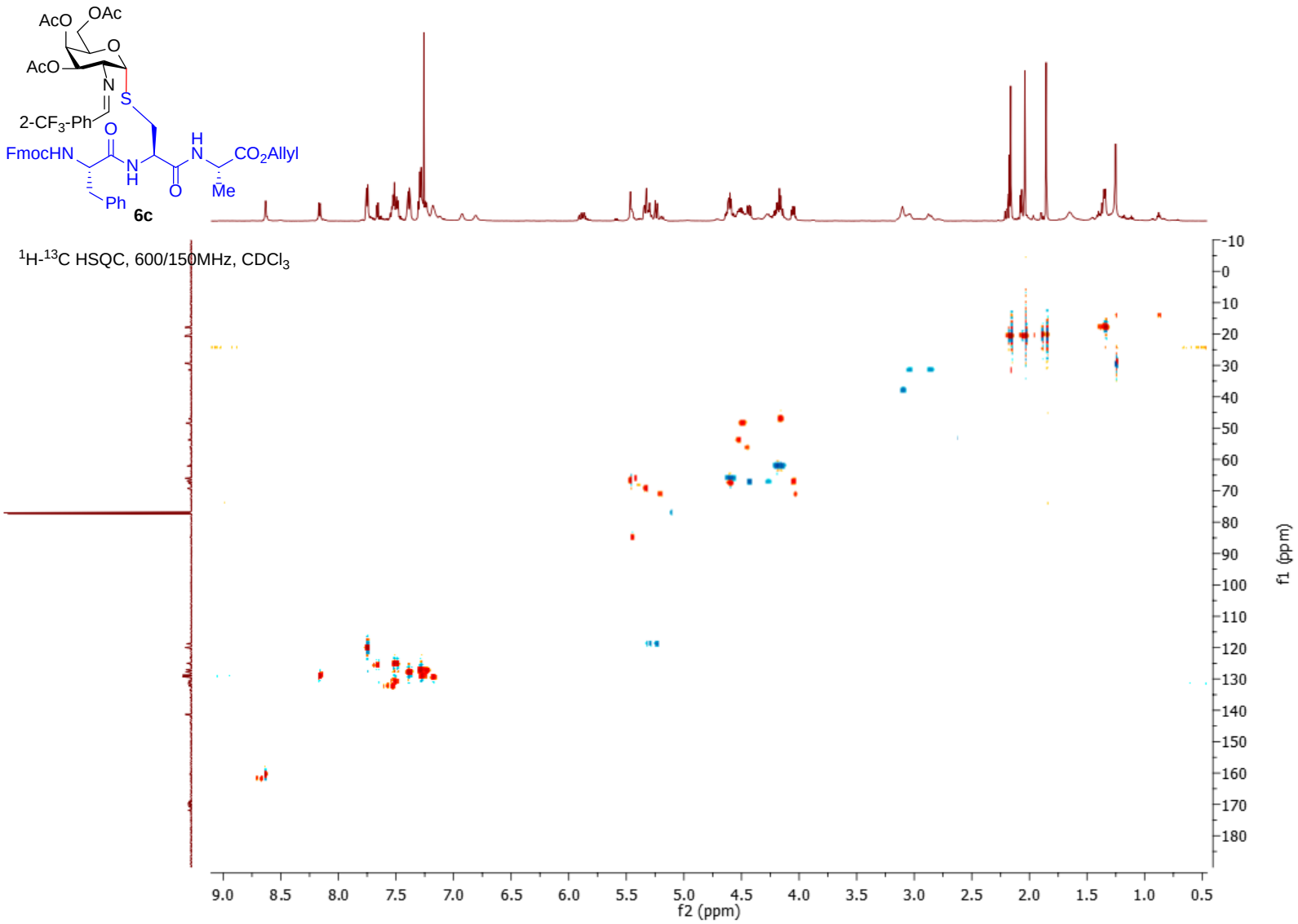
^{13}C NMR, 150 MHz, $CDCl_3$

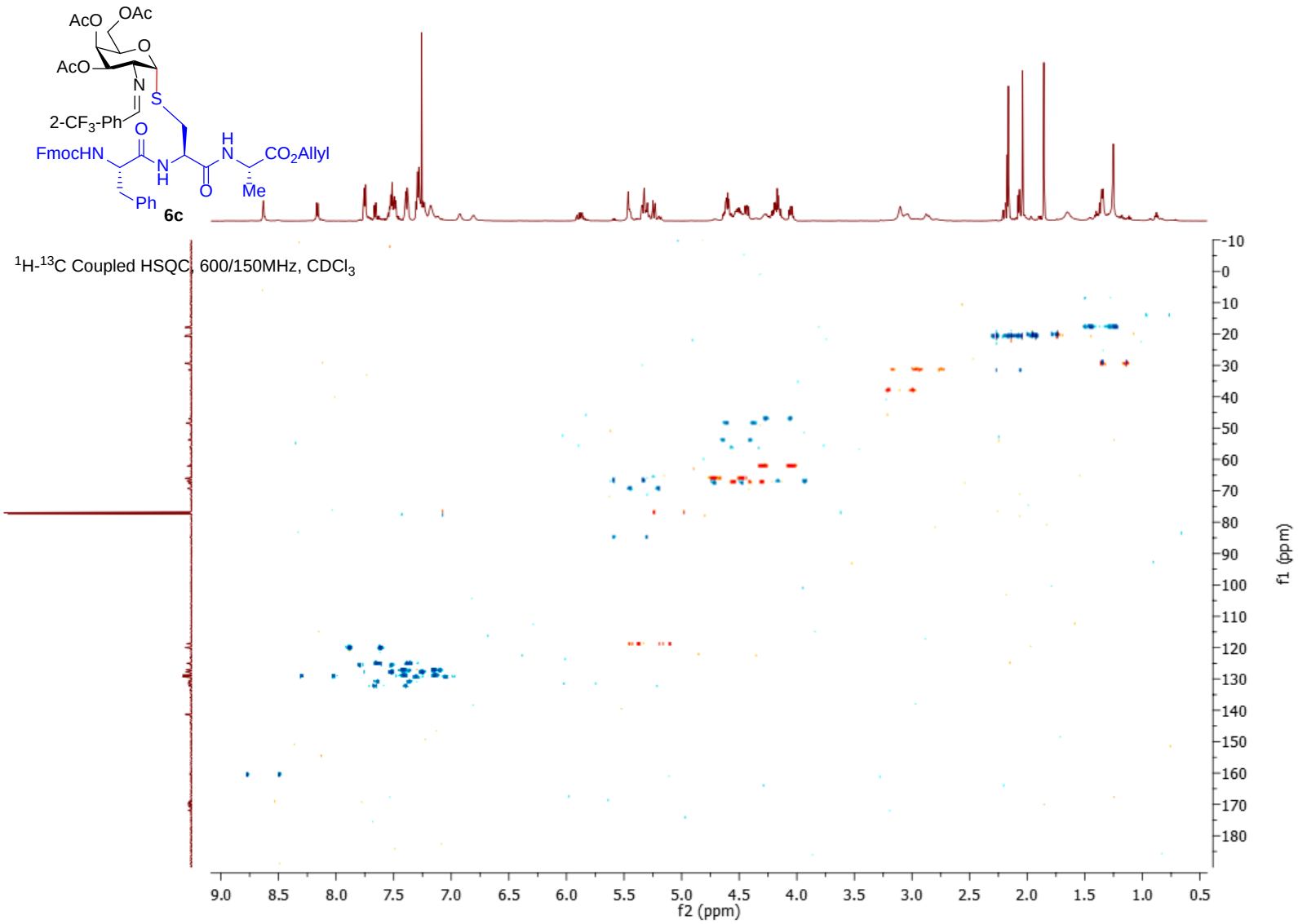

85.8720
84.7285
87.0
86.5
86.0
85.5
85.0
84.5
84.0
83.5
f1 (ppm)
AcO
OAc
O
AcO
N
S
2-CF3-Ph
H
N
FmocHN
CO2Allyl
O
Me
6b
coupled 13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

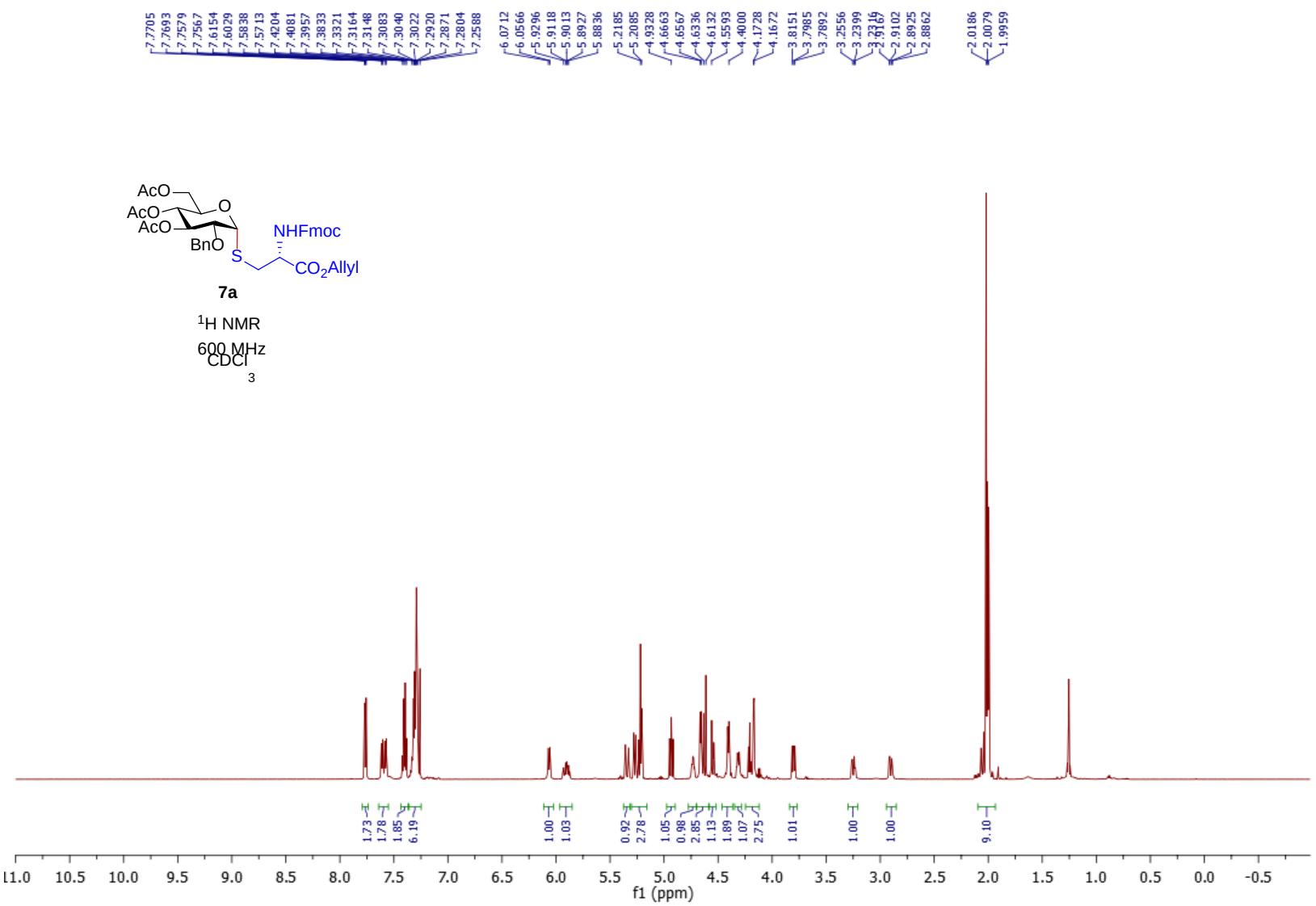

AcO
OAc
O
AcO
N
S
2-CF3-Ph
FmocHN
H
N
CO2Allyl
O
Me
6b
1H-13C HSQC, 600/150MHz, CDCl3
f1 (ppm)
f2 (ppm)

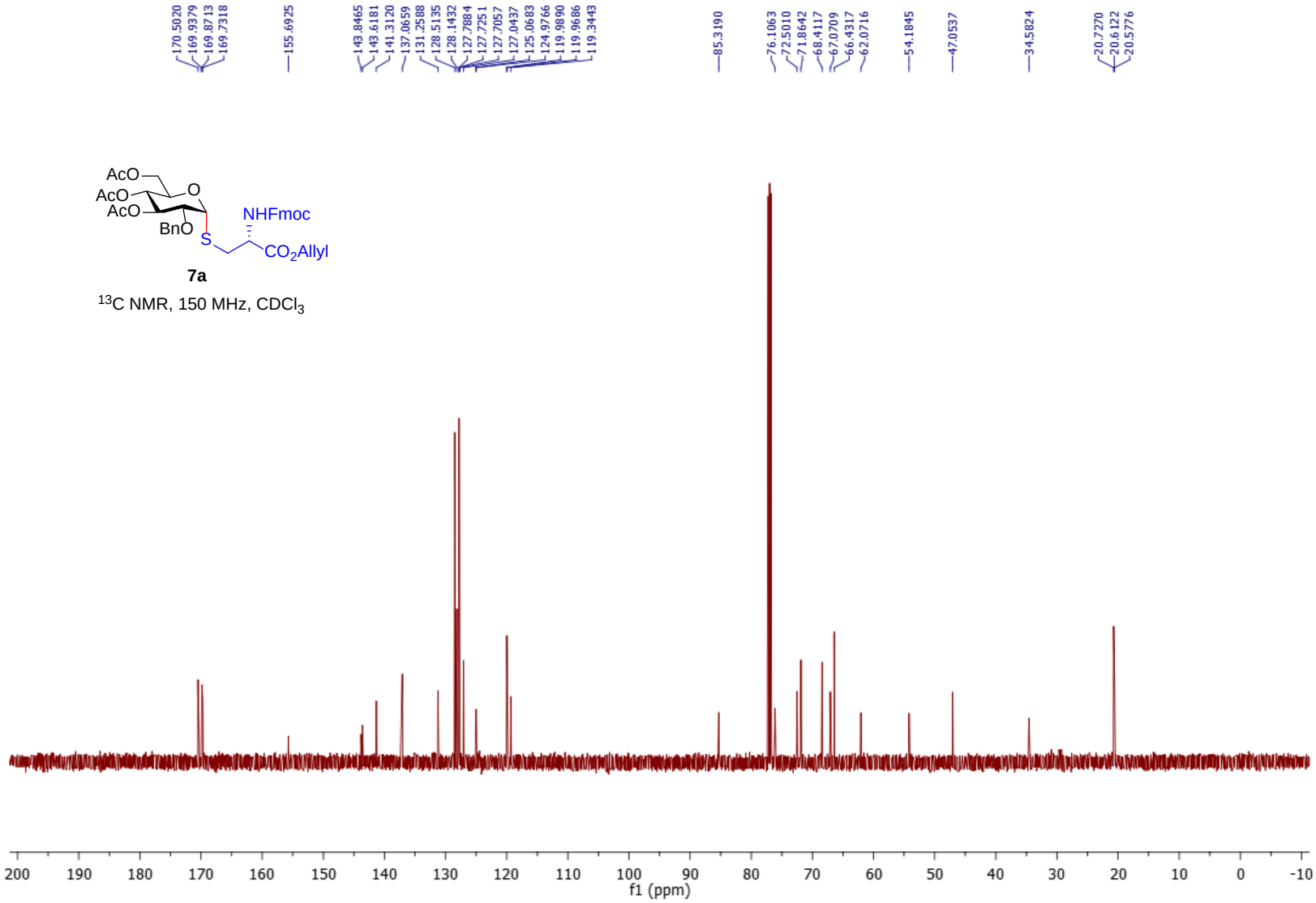

AcO
OAc
O
AcO
N
S
2-CF3-Ph
O
FmocHN
N
H
H
N
CO2Allyl
O
Me
Ph
6c
1H NMR
600 MHz
CDCl3
f1 (ppm)

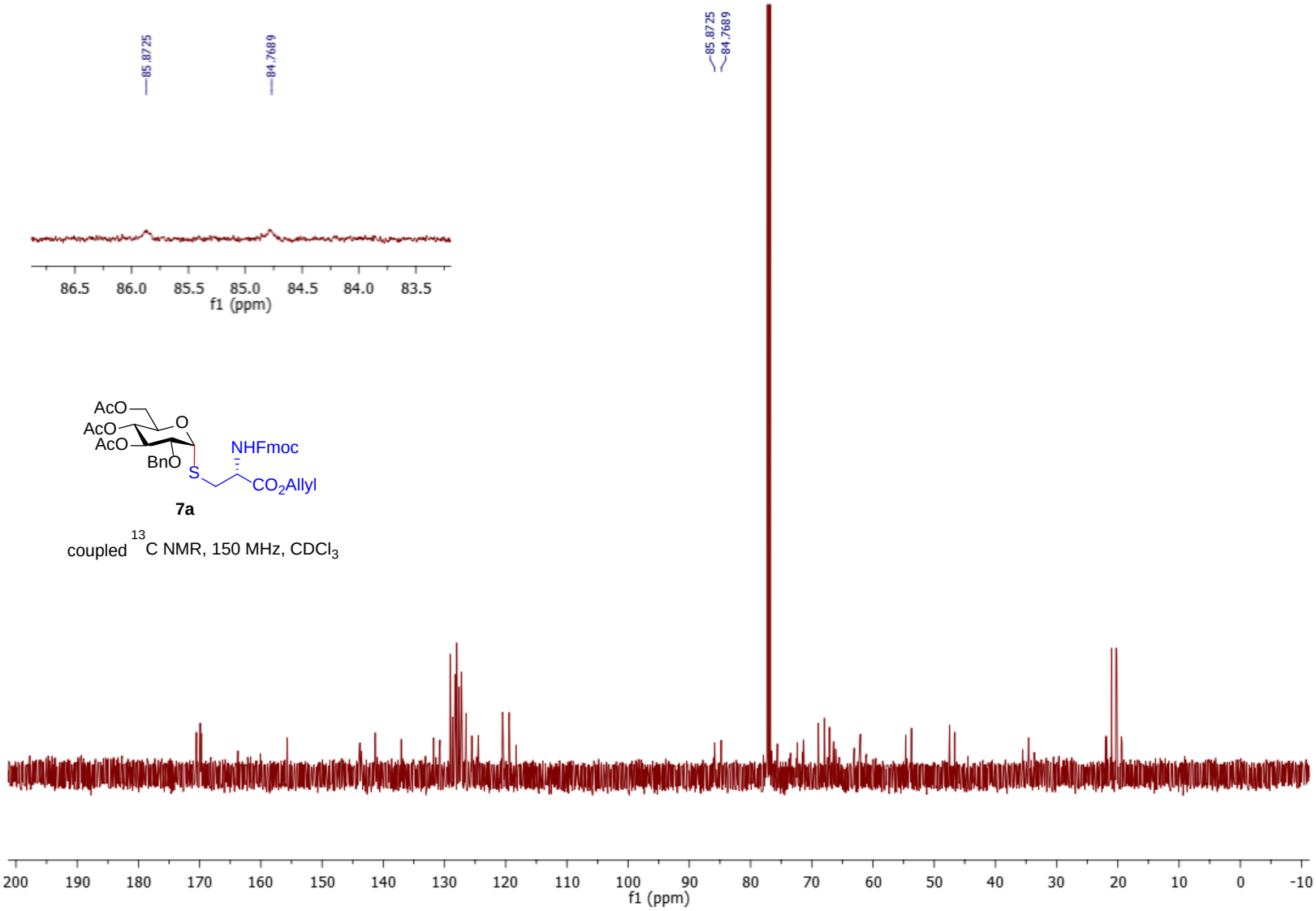

171.9045
170.6834
170.0884
169.5878
169.0719
160.4366
143.7198
141.2505
133.5614
132.1822
131.4910
130.7373
129.2980
129.1797
129.0260
128.7758
127.7209
127.2137
127.0548
124.9686
119.9669
119.9444
118.7617
84.7277
69.2277
67.4603
67.1502
67.0152
66.7199
65.9645
62.1079
53.7688
48.3823
47.0434
31.4690
29.2471
20.7292
20.7146
20.3217
17.8921
AcO
OAc
O
AcO
N
S
2-CF3-Ph
O
FmocHN
N
H
H
N
CO2Allyl
O
Me
Ph
6c
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

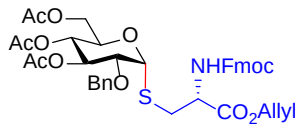

AcO
OAc
AcO
O
N
S
2-CF3-Ph
O
FmocHN
N
H
H
N
CO2Allyl
O
Me
Ph
6c
1H-13C HSQC, 600/150MHz, CDCl3
f1 (ppm)
f2 (ppm)


AcO
OAc
O
AcO
N
S
2-CF3-Ph
O
FmocHN
N
H
H
N
CO2Allyl
O
Me
Ph
6c
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f1 (ppm)
f2 (ppm)


7.7705
7.7693
7.7579
7.7567
7.6154
7.6029
7.5838
7.5713
7.4204
7.4081
7.3957
7.3833
7.3321
7.3164
7.3148
7.3083
7.3040
7.3022
7.2920
7.2871
7.2804
7.2588
6.0712
6.0566
5.9296
5.9118
5.9013
5.8927
5.8836
5.2185
5.2085
4.9328
4.6663
4.6567
4.6336
4.6132
4.5593
4.4000
4.1728
4.1672
3.8151
3.7985
3.7892
3.2556
3.2399
2.9167
2.9102
2.8925
2.8862
2.0186
2.00079
1.9959
AcO
AcO
AcO
O
BnO
S
NHFmoc
CO2Allyl
7a
1H NMR
600 MHz
CDCl3
1.73
1.78
1.85
6.19
1.00
1.03
0.92
2.78
1.05
0.98
2.85
1.13
1.89
1.07
2.75
1.01
1.00
1.00
9.10
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

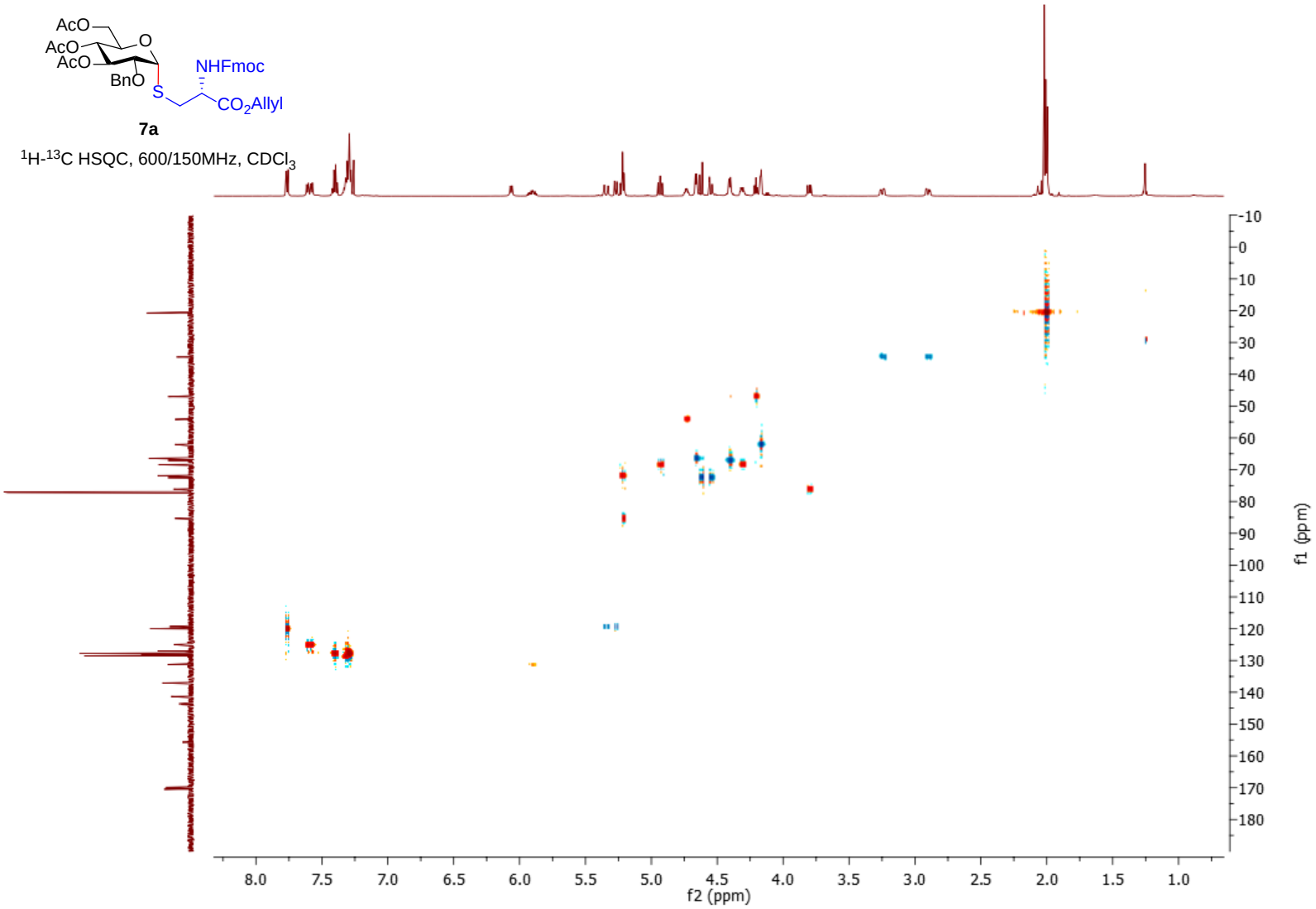

170.5020
169.9379
169.8713
169.7318
155.6925
143.8465
143.6181
141.3120
137.0659
131.2588
128.5135
128.1432
127.7884
127.7251
127.7057
127.0437
125.0683
124.9766
119.9890
119.9686
119.3443
85.3190
76.1063
72.5010
71.8642
68.4117
67.0709
66.4317
62.0716
54.1845
47.0537
34.5824
20.7270
20.6122
20.5776
AcO
AcO
AcO
O
BnO
S
NHFmoc
CO2Allyl
7a
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

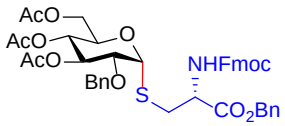

85.8725
84.7689
86.5
86.0
85.5
85.0
84.5
84.0
83.5
f1 (ppm)
AcO
AcO
AcO
O
BnO
S
NHFmoc
CO2Allyl
7a
coupled 13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



7a

^{1}H-^{1}H COSY, 600 MHz, $CDCl_3$


AcO
AcO
AcO
O
BnO
S
NHFmoc
CO2Allyl
7a
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

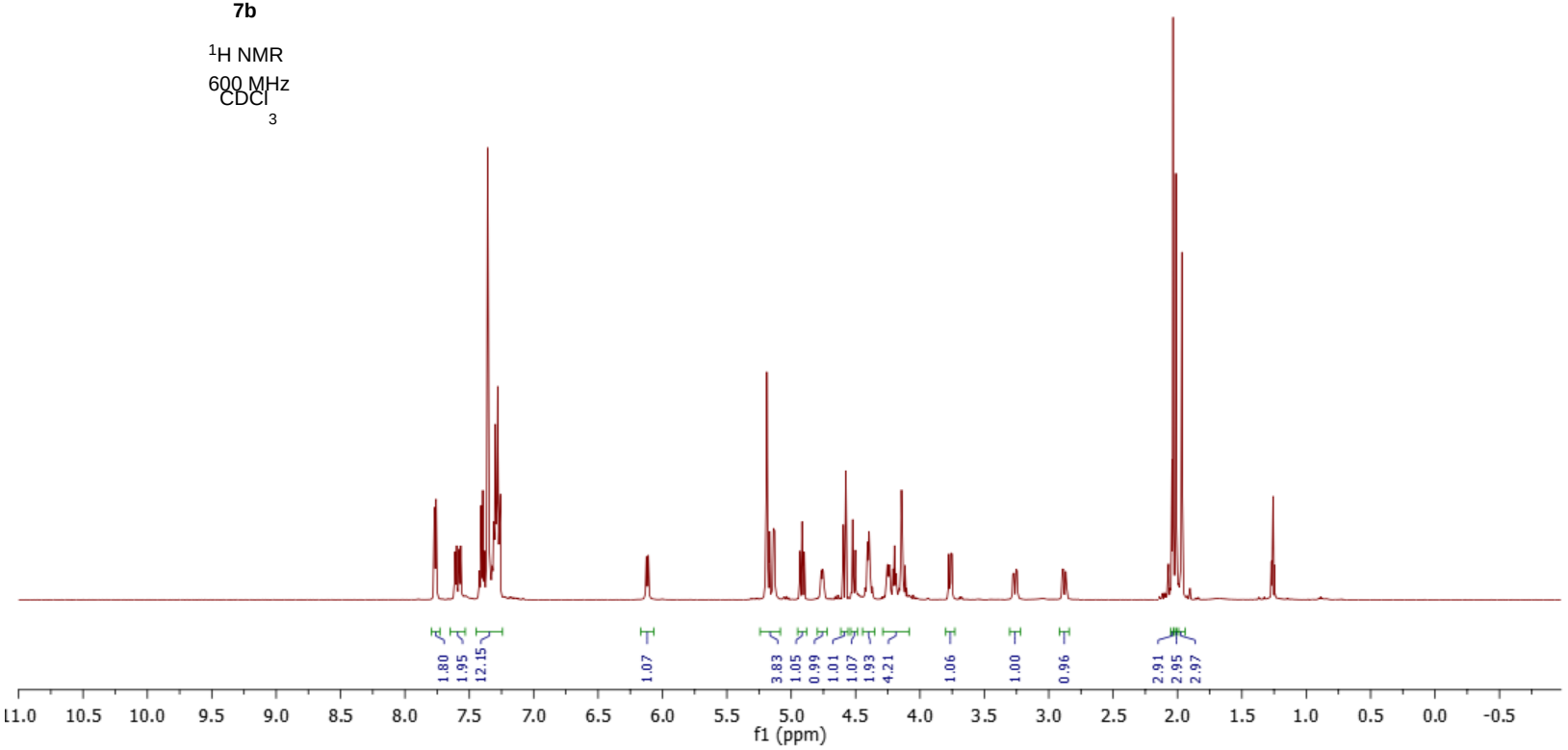


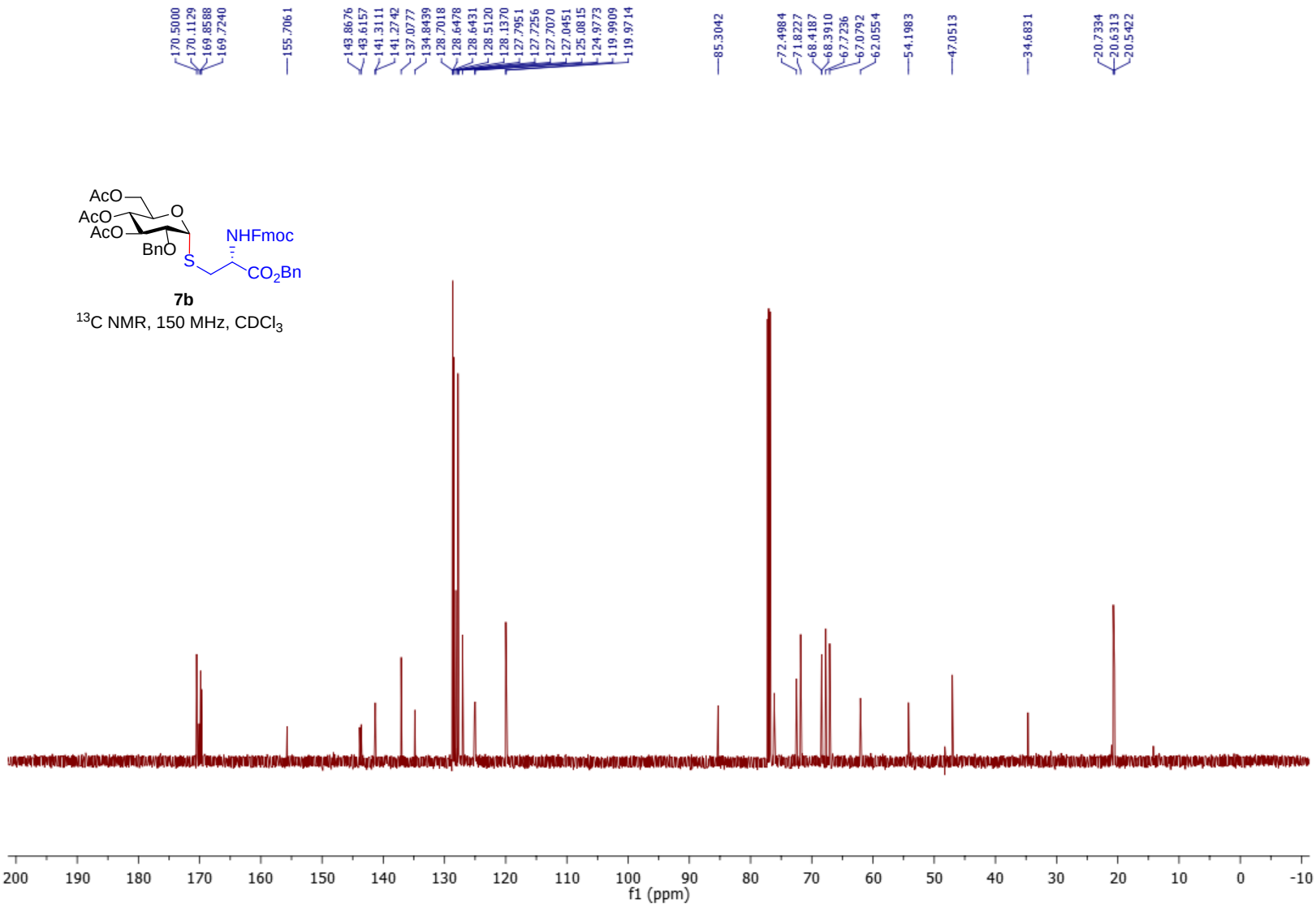
7b

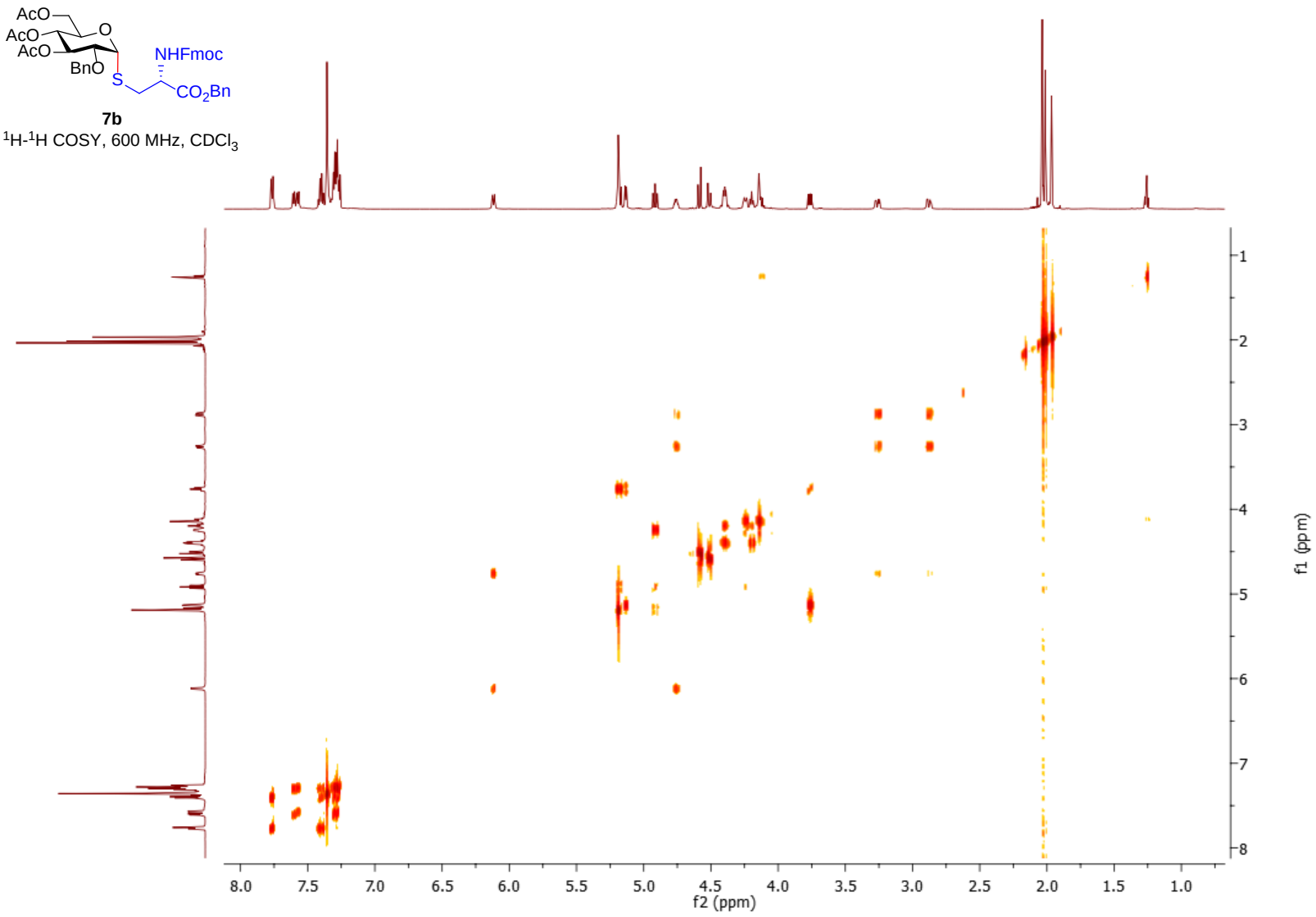
^{1}H NMR

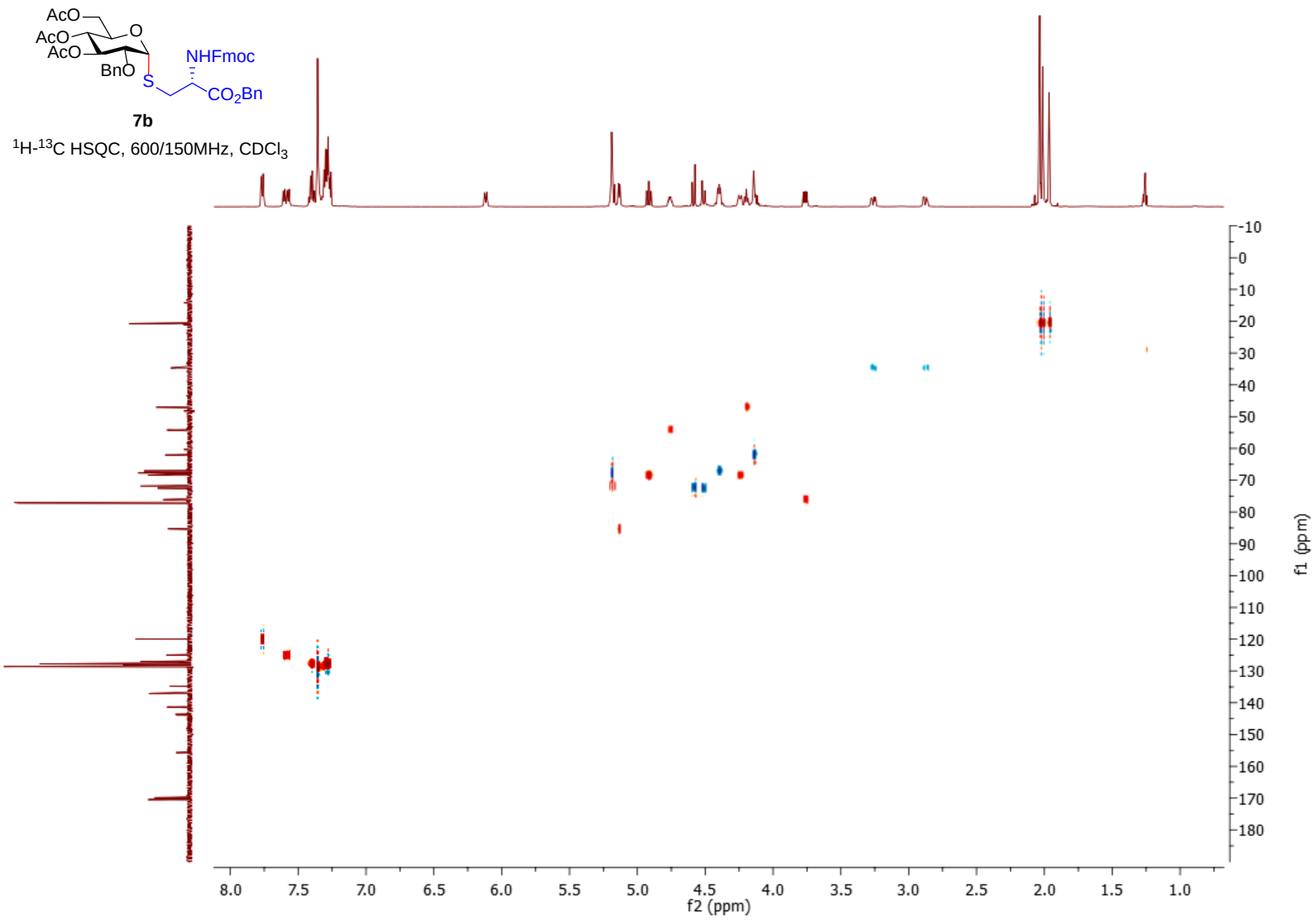
600 MHz

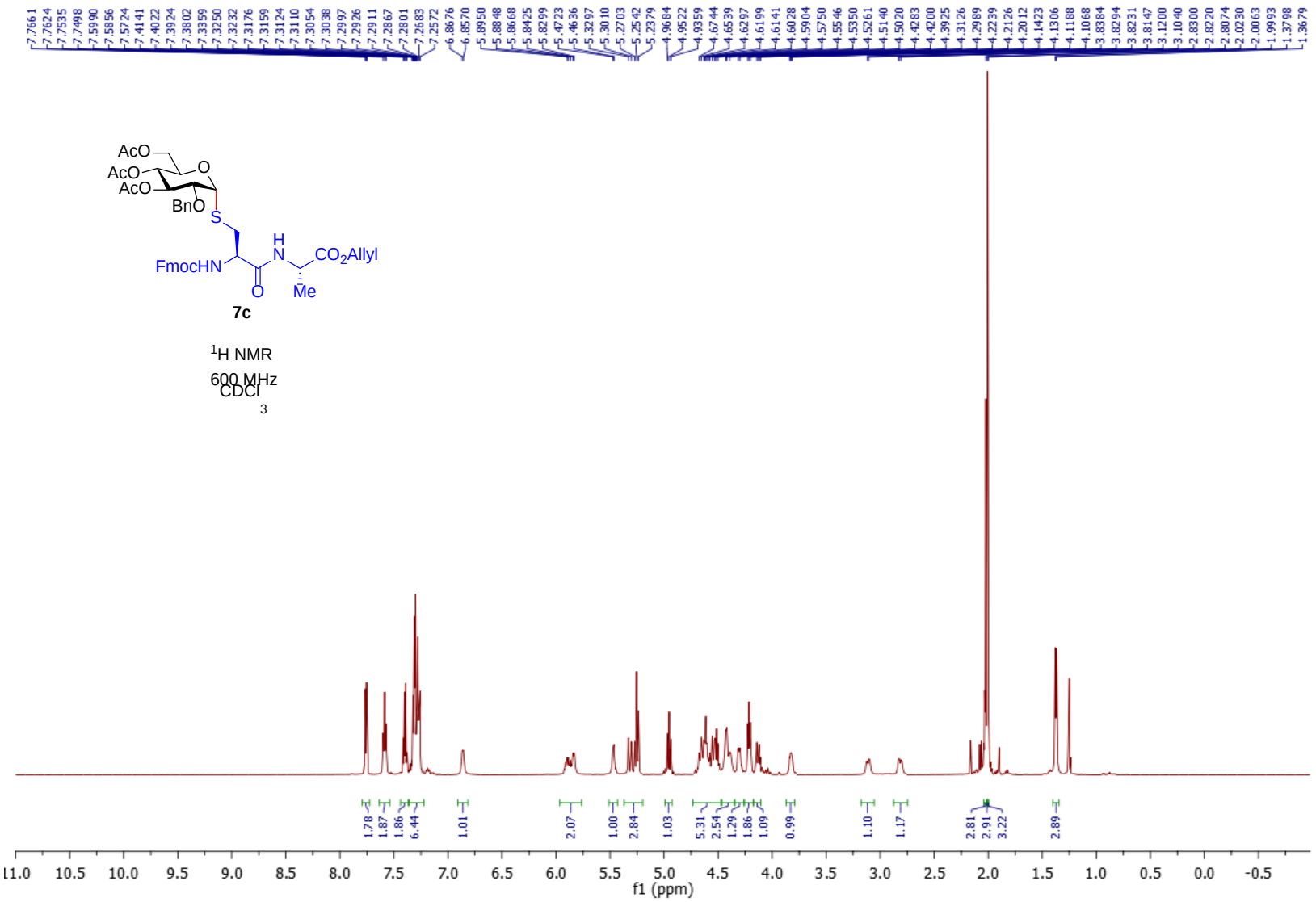
$CDCl_3$

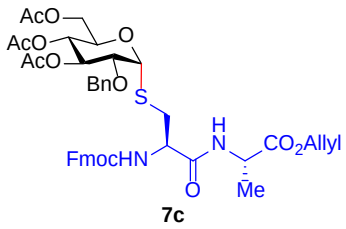



170.5000
170.1129
169.8588
169.7240
155.7061
143.8676
143.6157
141.3111
141.2742
137.0777
134.8439
128.7018
128.6478
128.6431
128.5120
128.1370
127.7951
127.7256
127.7070
127.0451
125.0815
124.9773
119.9909
119.9714
85.3042
72.4984
71.8227
68.4187
68.3910
67.7236
67.0792
62.0554
54.1983
47.0513
34.6831
20.7334
20.6313
20.5422
AcO
AcO
AcO
O
BnO
S
NHFmoc
CO2Bn
7b
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AcO
AcO
AcO
O
BnO
S
NHFmoc
CO2Bn
7b
1H-1H COSY, 600 MHz, CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

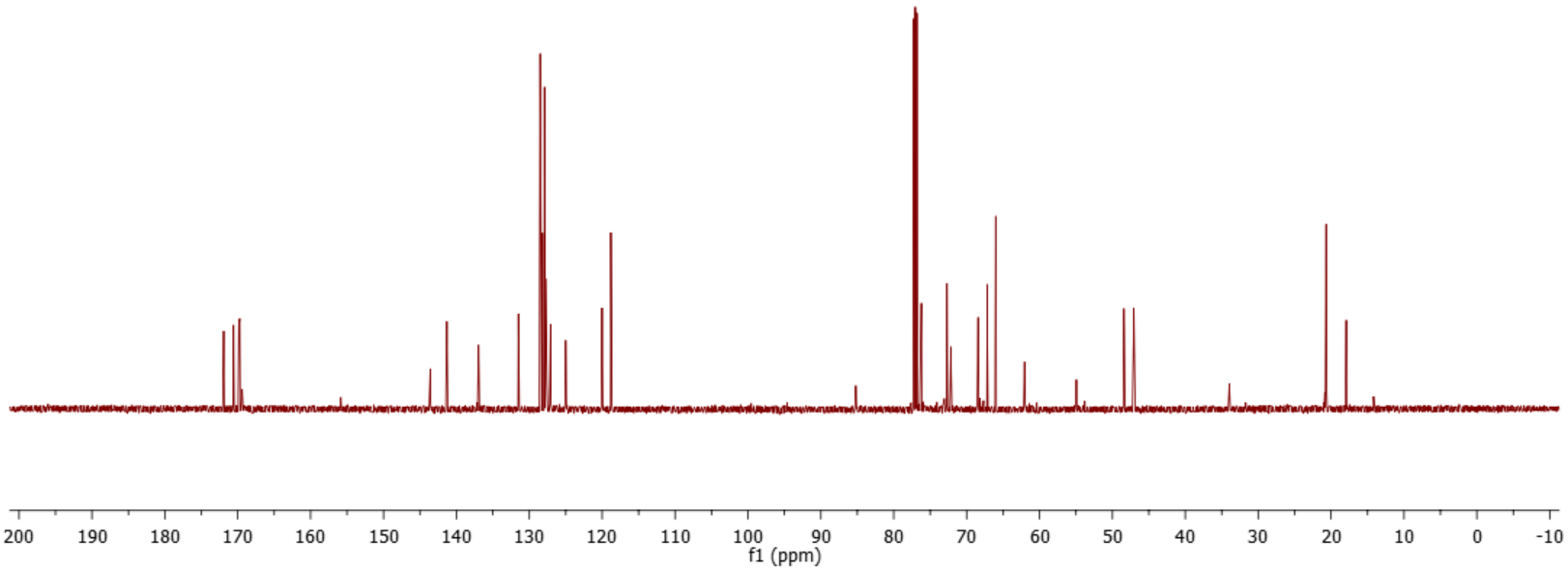

AcO
AcO
AcO
BnO
O
S
NHFmoc
CO2Bn
7b
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

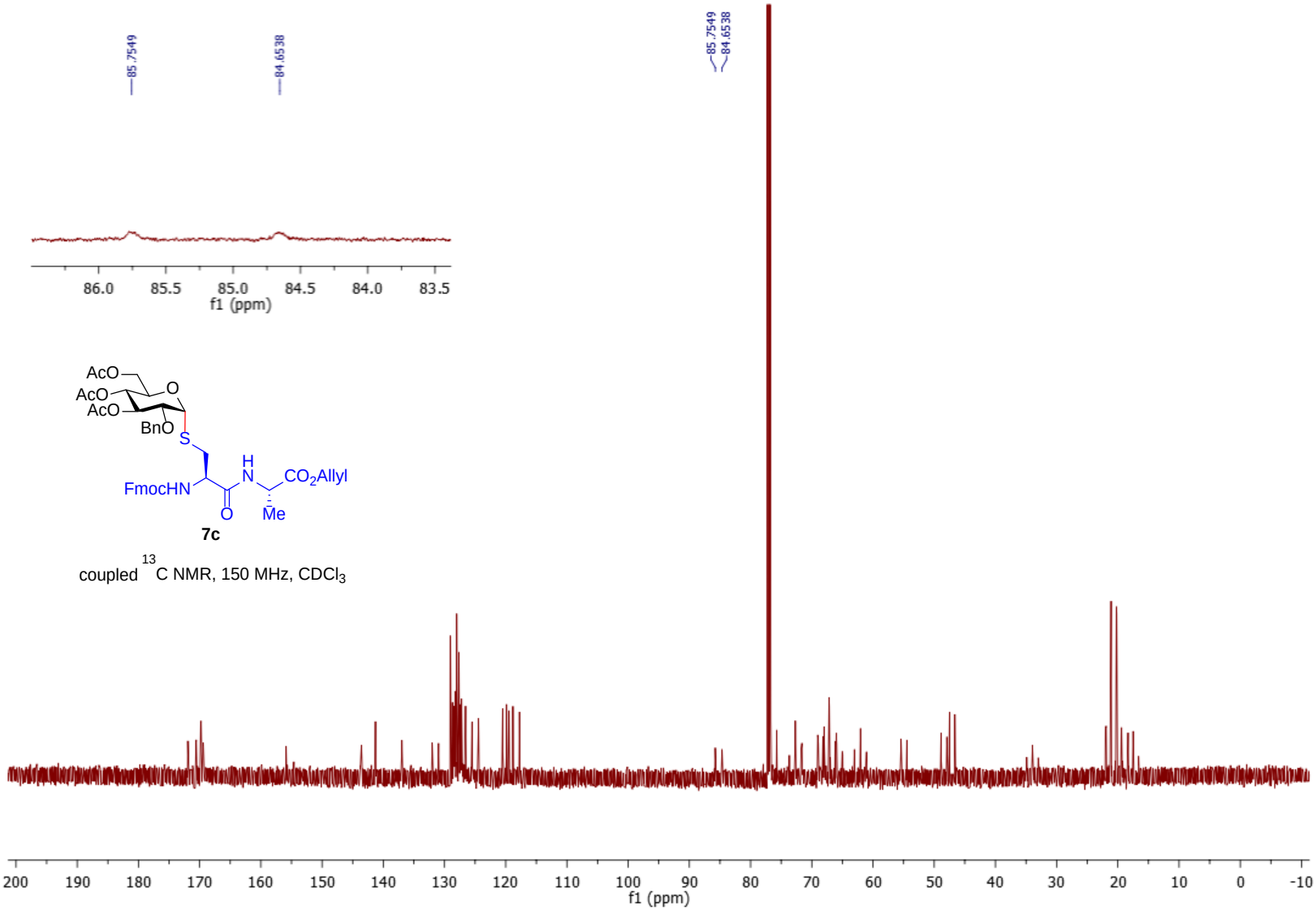

AcO
AcO
AcO
O
BnO
S
FmocHN
H
N
CO2Allyl
O
Me
7c
1H NMR
600 MHz
CDCl3
f1 (ppm)

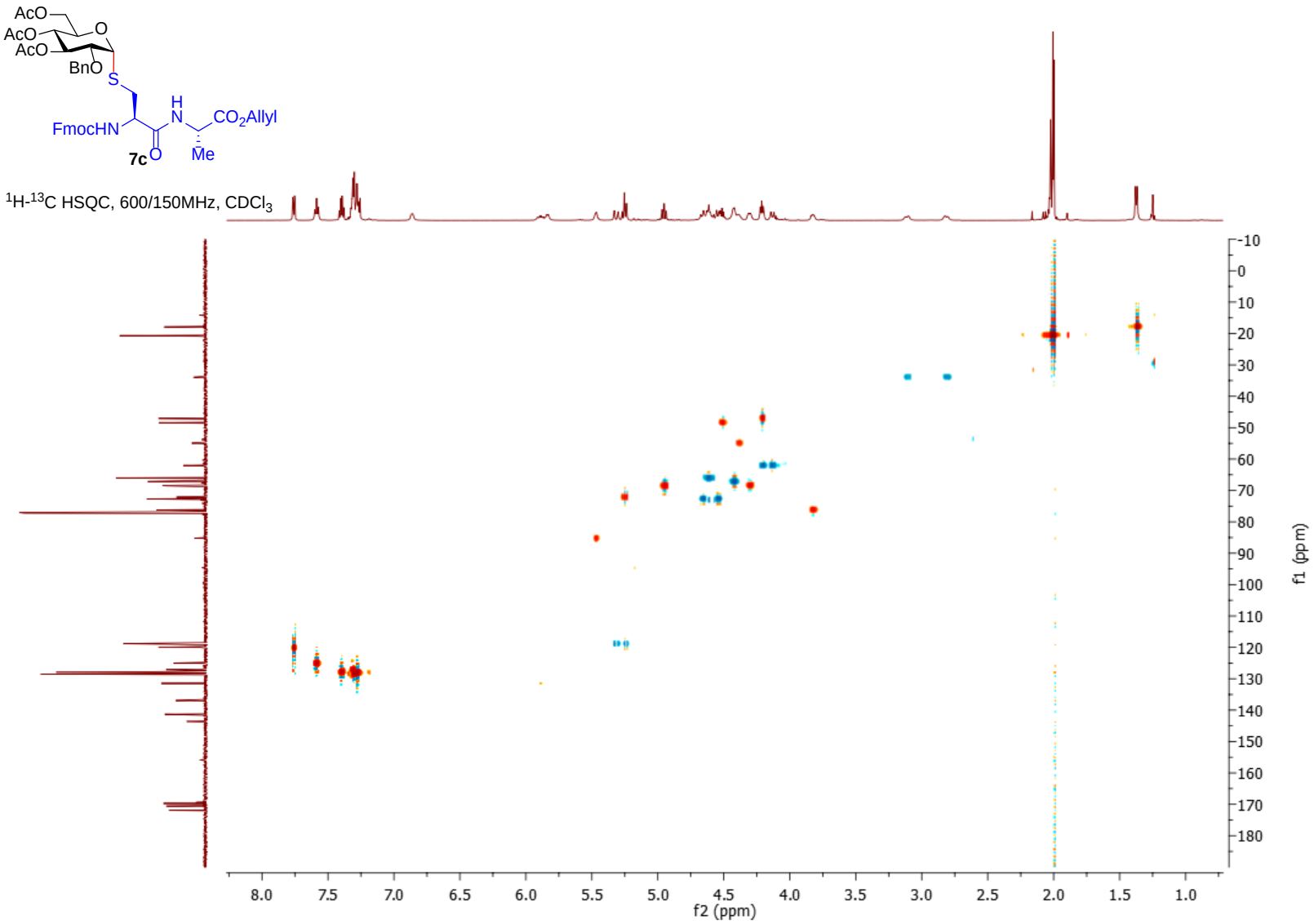


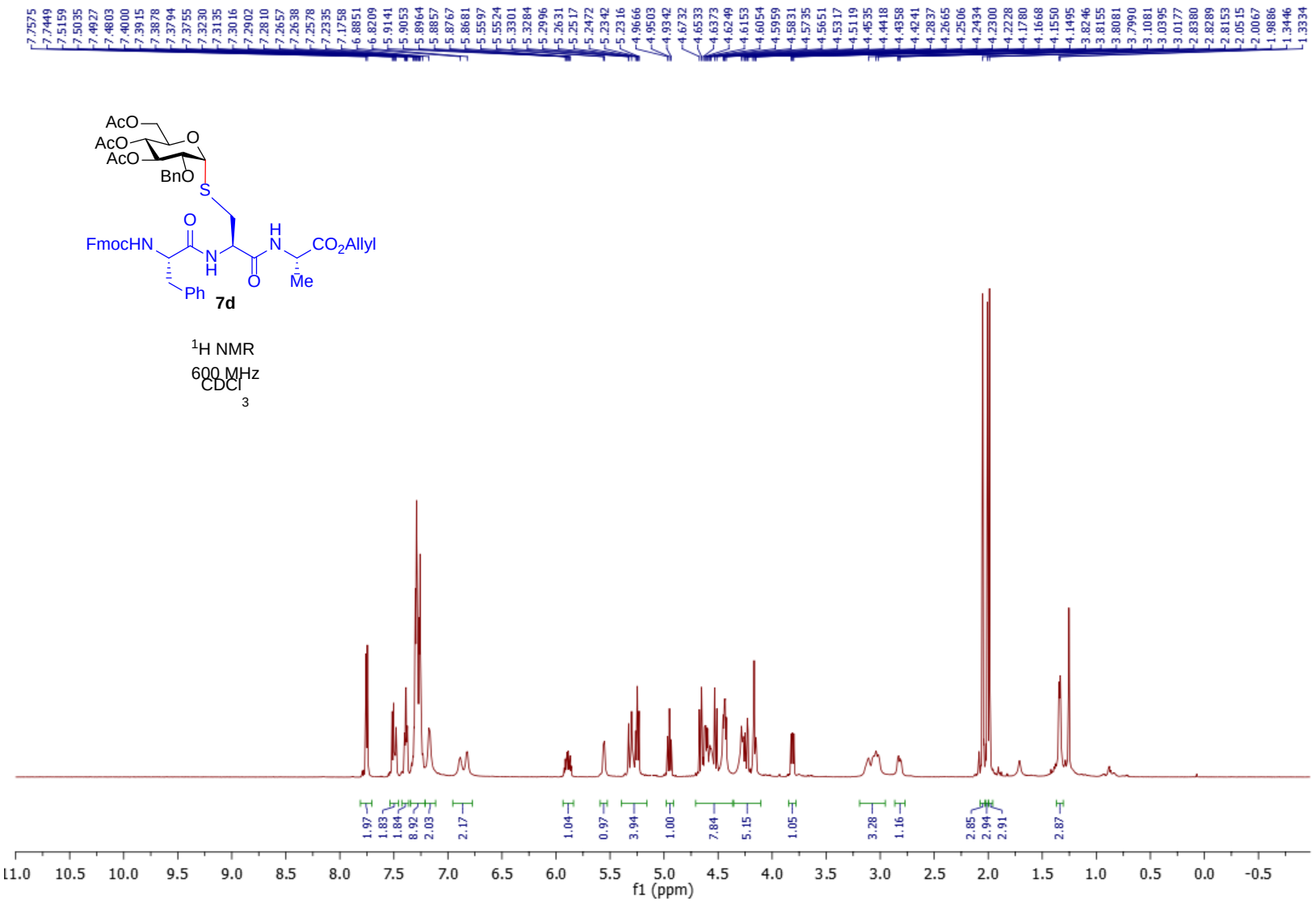
7c

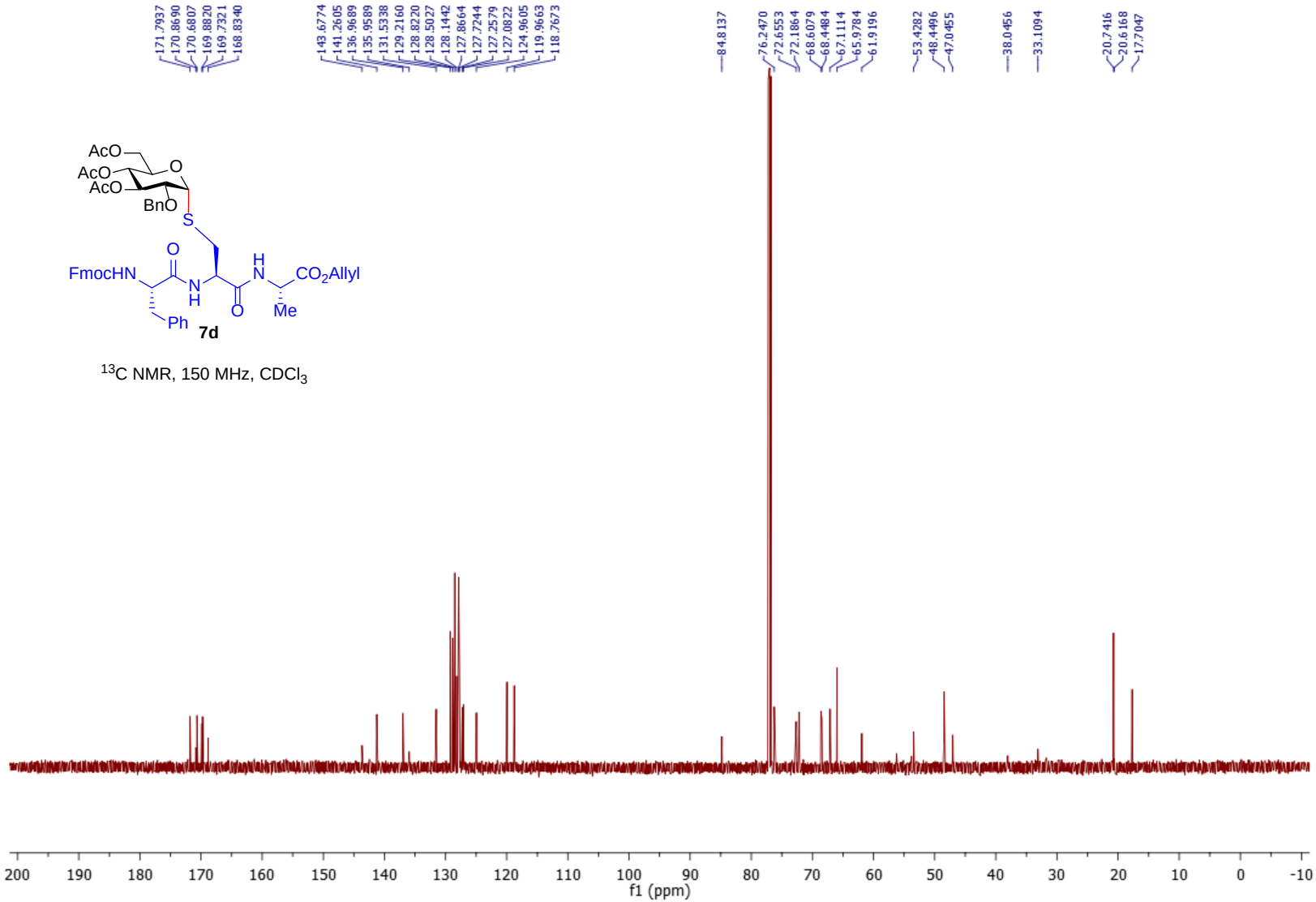
^{13}C NMR, 150 MHz, $CDCl_3$




85.7549
84.6538
86.0
85.5
85.0
84.5
84.0
83.5
f1 (ppm)
AcO
AcO
AcO
O
BnO
S
FmocHN
H
N
CO2Allyl
O
Me
7c
coupled 13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

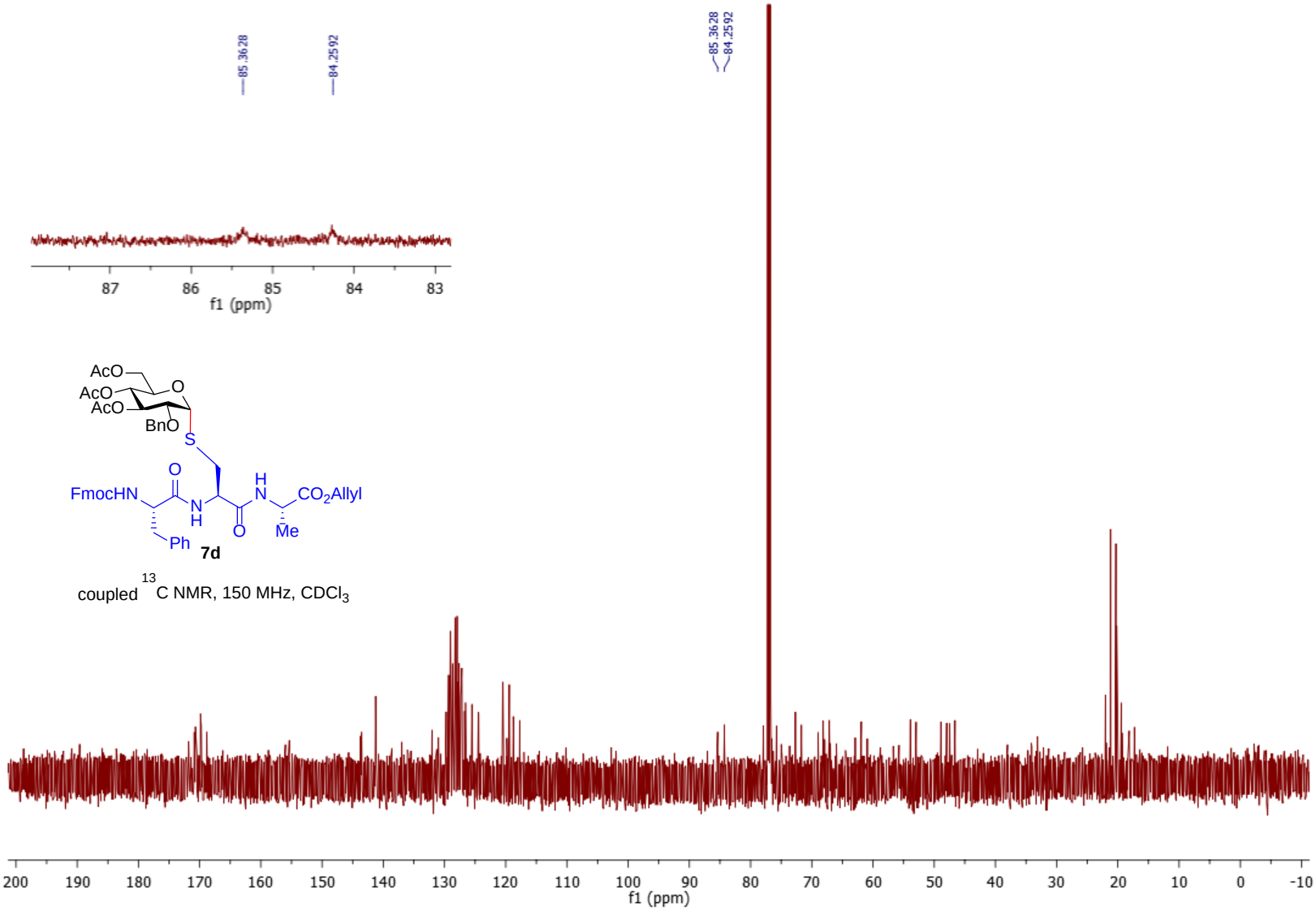

AcO
AcO
AcO
O
BnO
S
FmocHN
H
N
CO2Allyl
O
Me
7c
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

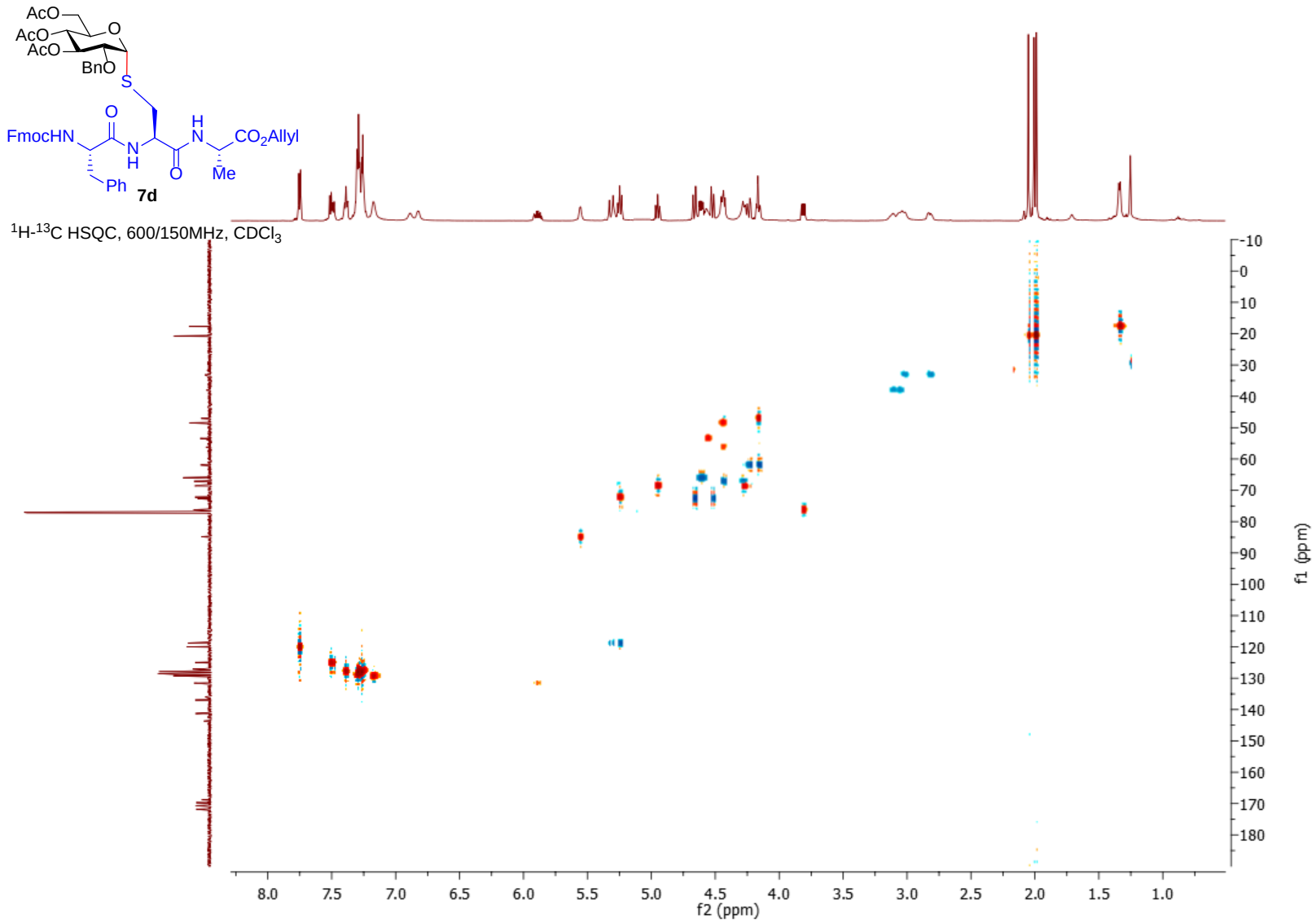

AcO
AcO
AcO
O
BnO
S
FmocHN
O
N
H
H
N
O
CO2Allyl
Me
Ph
7d
1H NMR
600 MHz
CDCl3
f1 (ppm)

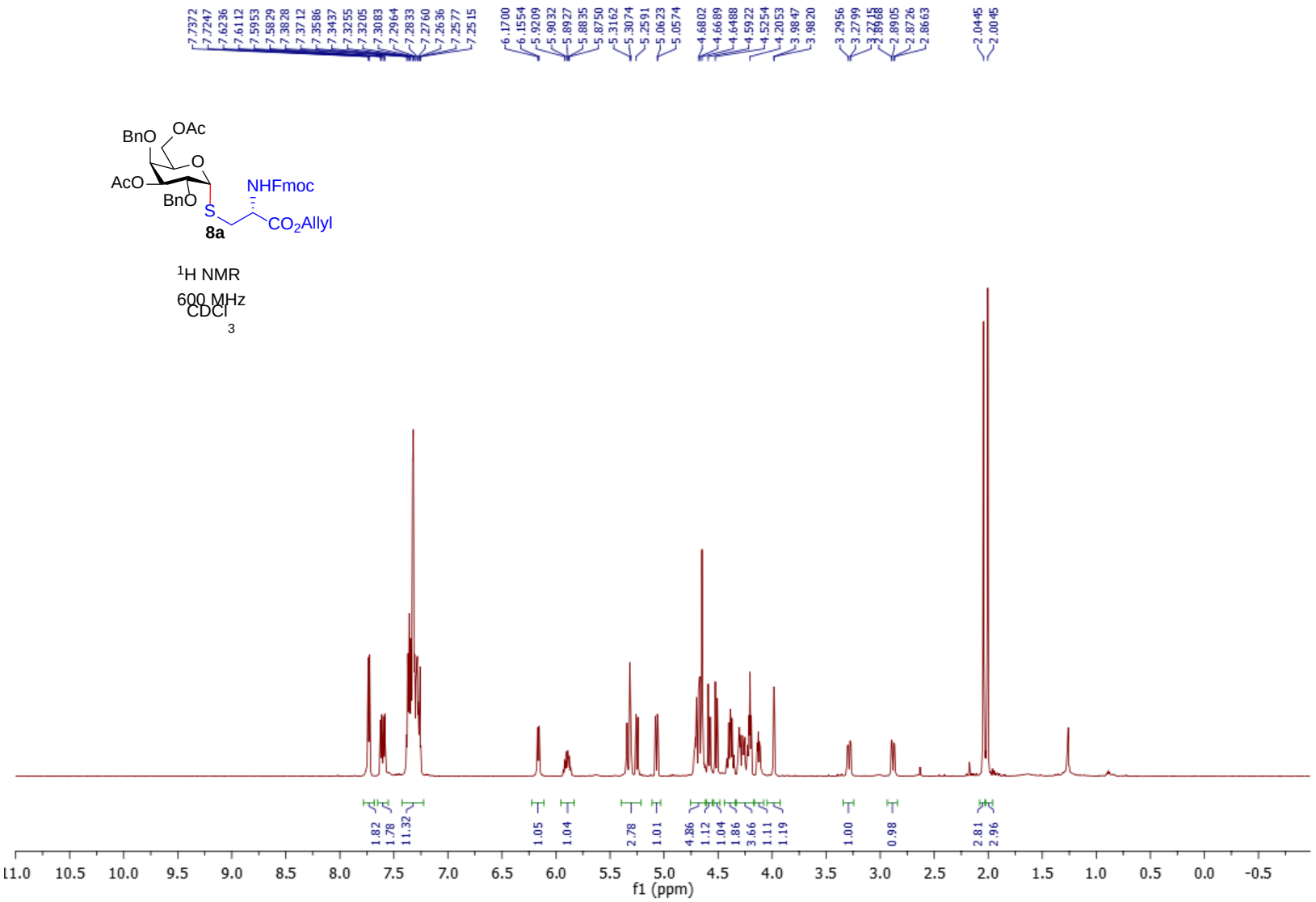


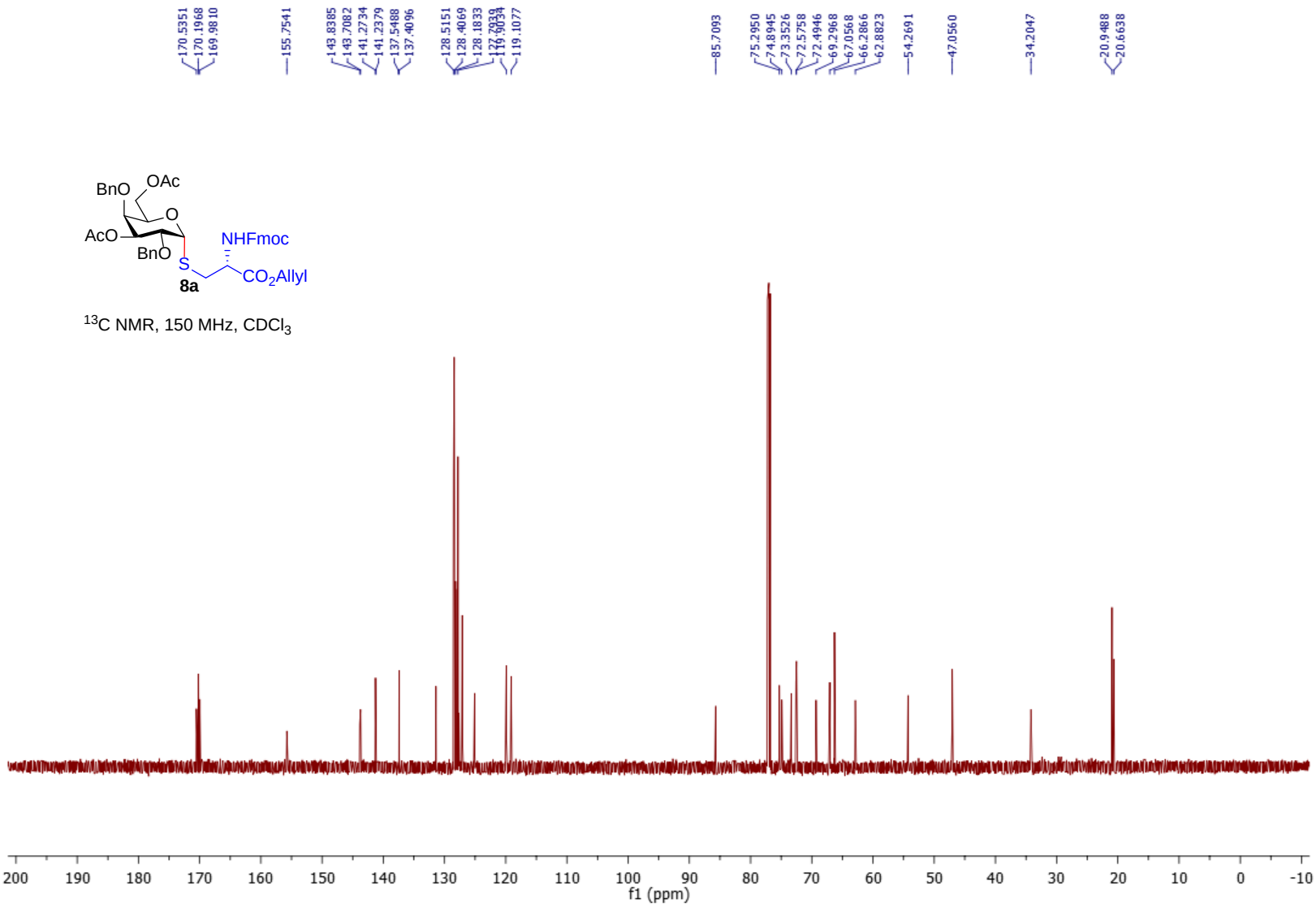
7d

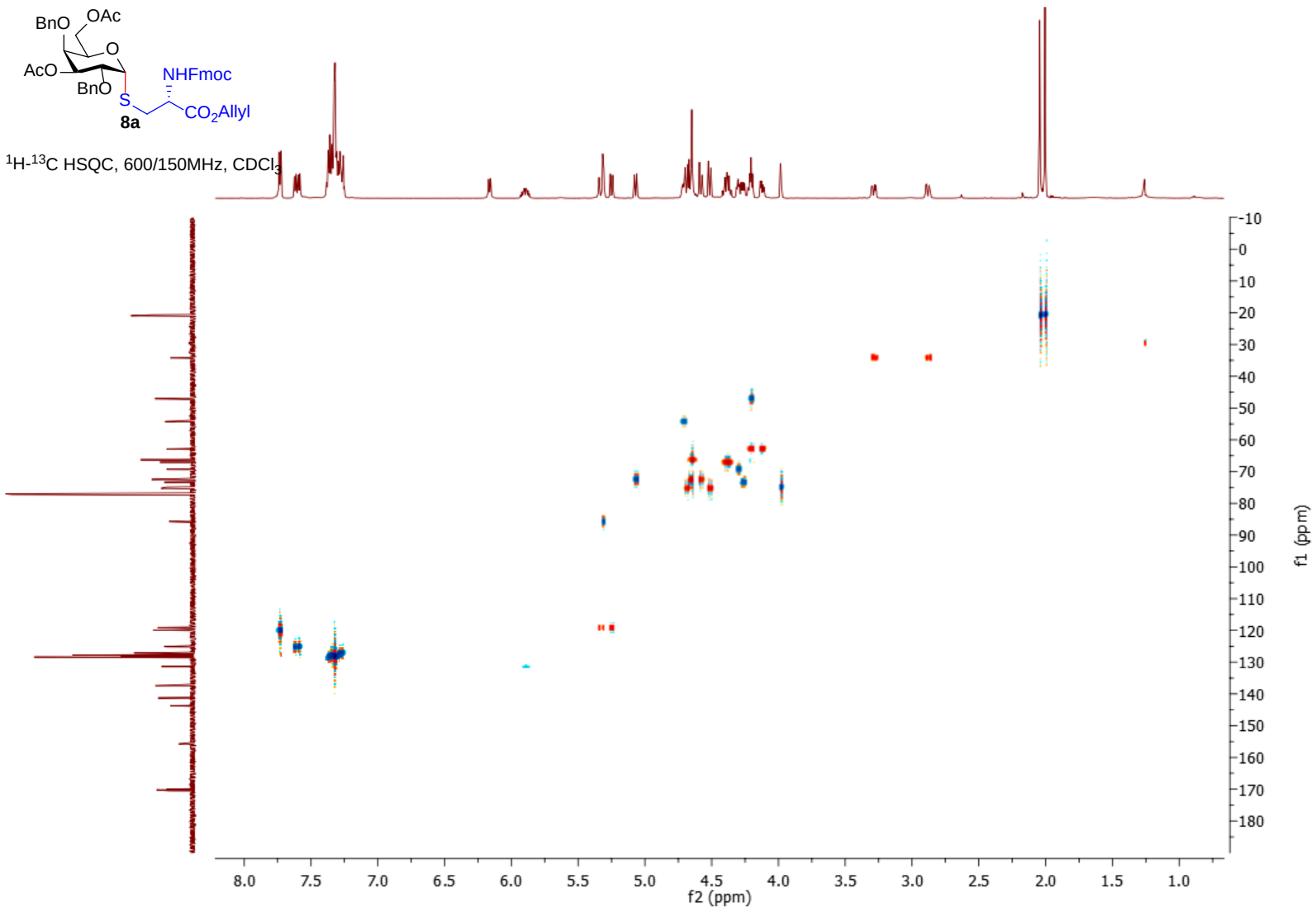
^{13}C NMR, 150 MHz, $CDCl_3$

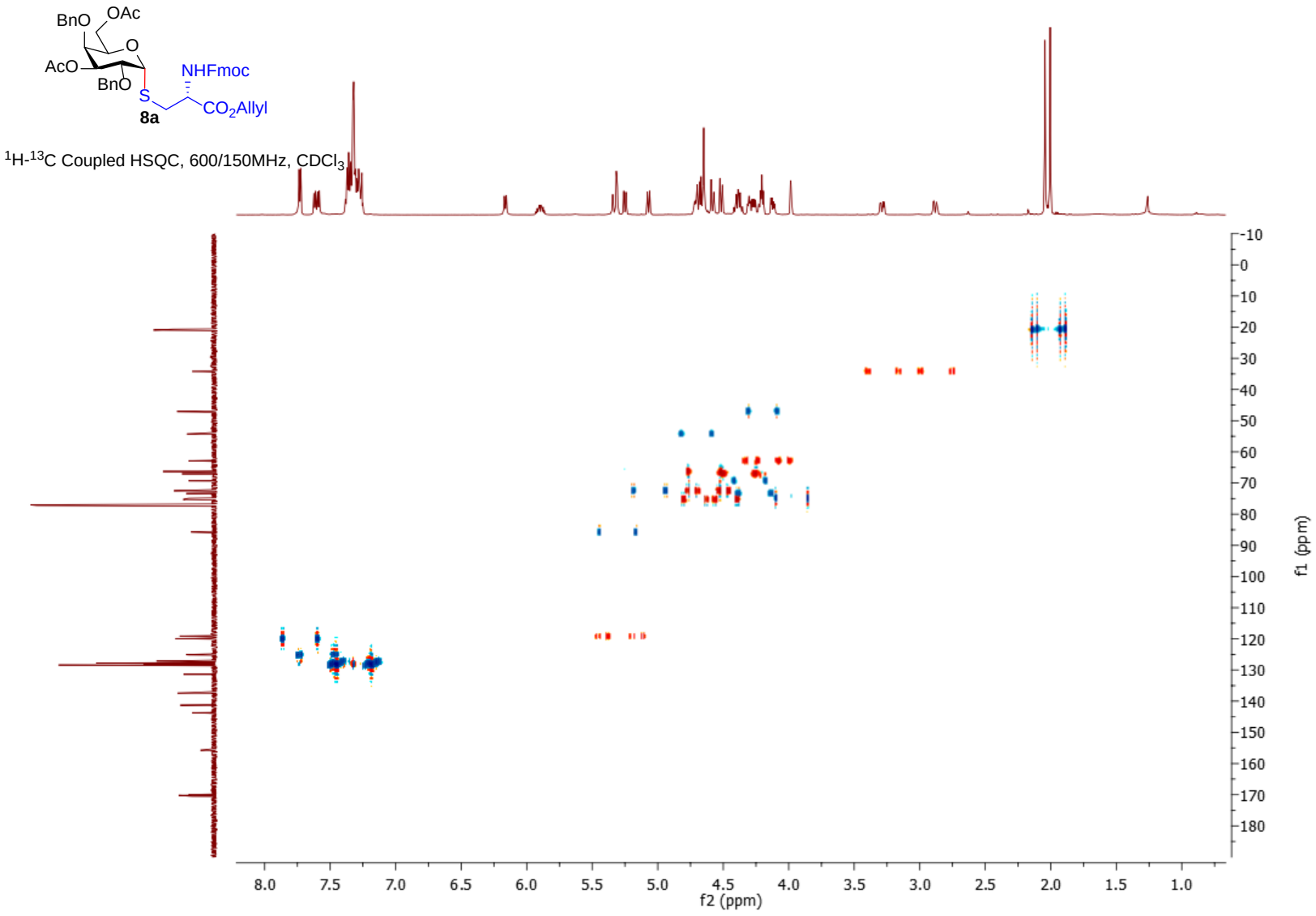

85.3628
84.2592
87
86
85
84
83
f1 (ppm)
AcO
AcO
AcO
BnO
O
S
FmocHN
O
N
H
H
N
O
CO2Allyl
Me
Ph
7d
coupled 13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

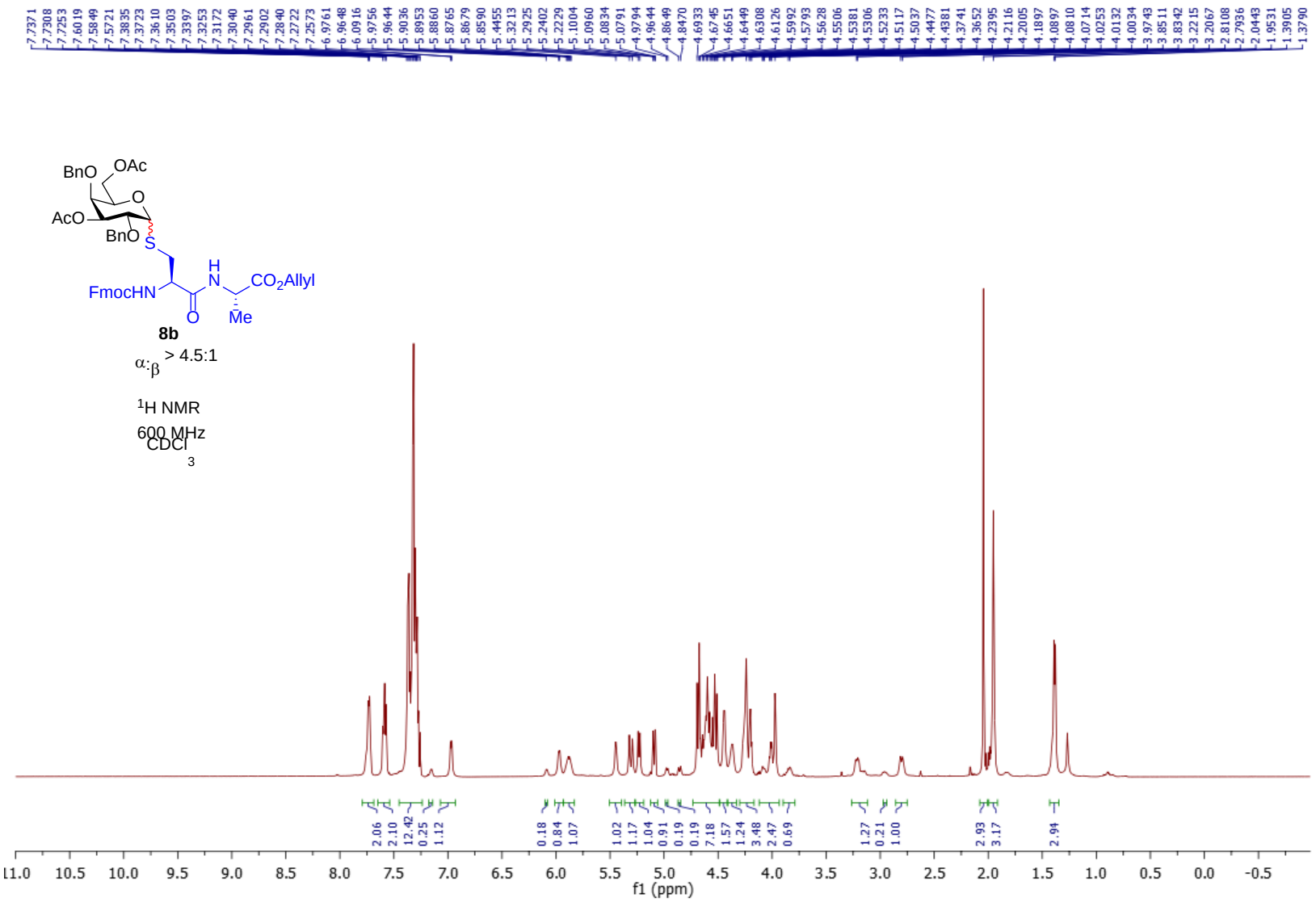

AcO
AcO
AcO
BnO
O
S
FmocHN
O
N
H
H
N
O
CO2Allyl
Ph
Me
7d
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

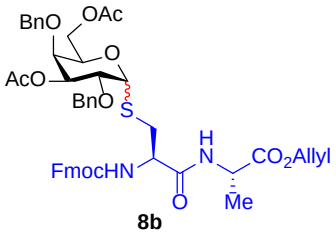

7.7372
7.7247
7.6236
7.6112
7.5953
7.5829
7.3828
7.3712
7.3586
7.3437
7.3255
7.3205
7.3083
7.2964
7.2833
7.2760
7.2636
7.2577
7.2515
6.1700
6.1554
5.9209
5.9032
5.8927
5.8835
5.8750
5.3162
5.3074
5.2591
5.0623
5.0574
4.6802
4.6689
4.6488
4.5922
4.5254
4.2053
3.9847
3.9820
3.2956
3.2799
3.2715
3.2668
2.8905
2.8726
2.8663
2.0445
2.0045
BnO
OAc
O
AcO
BnO
S
NHFmoc
CO2Allyl
8a
1H NMR
600 MHz
CDCl3
1.82
1.78
11.32
1.05
1.04
2.78
1.01
4.86
1.12
1.04
1.86
3.66
1.11
1.19
1.00
0.98
2.81
2.96
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


170.5351
170.1968
169.9810
155.7541
143.8385
143.7082
141.2734
141.2379
137.5488
137.4096
128.5151
128.4069
128.1833
119.1077
85.7093
75.2950
74.8945
73.3526
72.5758
72.4946
69.2968
67.0568
66.2866
62.8823
54.2691
47.0560
34.2047
20.9488
20.6638
BnO
OAc
O
AcO
BnO
S
NHFmoc
CO2Allyl
8a
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


BnO
OAc
O
AcO
BnO
S
NHFmoc
CO2Allyl
8a
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


BnO
OAc
O
AcO
BnO
S
NHFmoc
CO2Allyl
8a
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

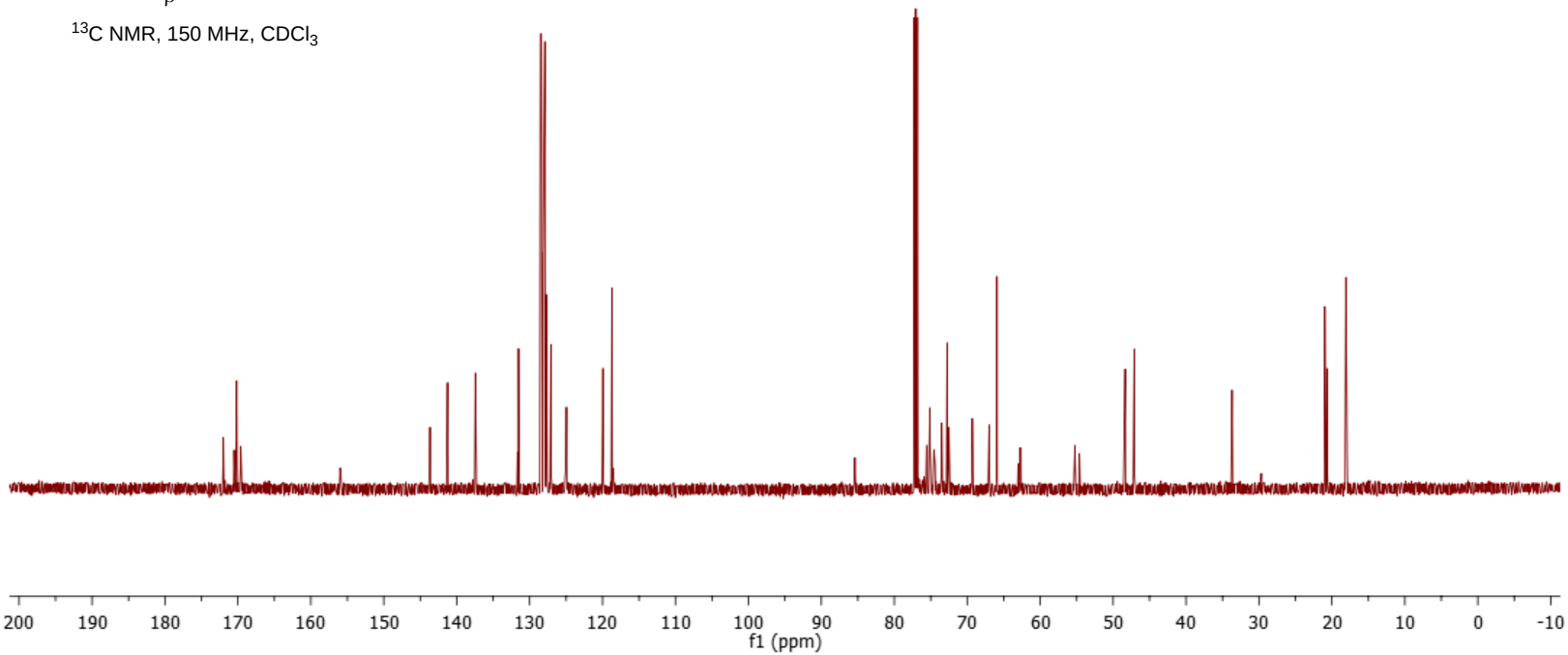

BnO
OAc
O
AcO
BnO
S
H
N
FmocHN
CO2Allyl
O
Me
8b
α:β > 4.5:1
1H NMR
600 MHz
CDCl3
f1 (ppm)

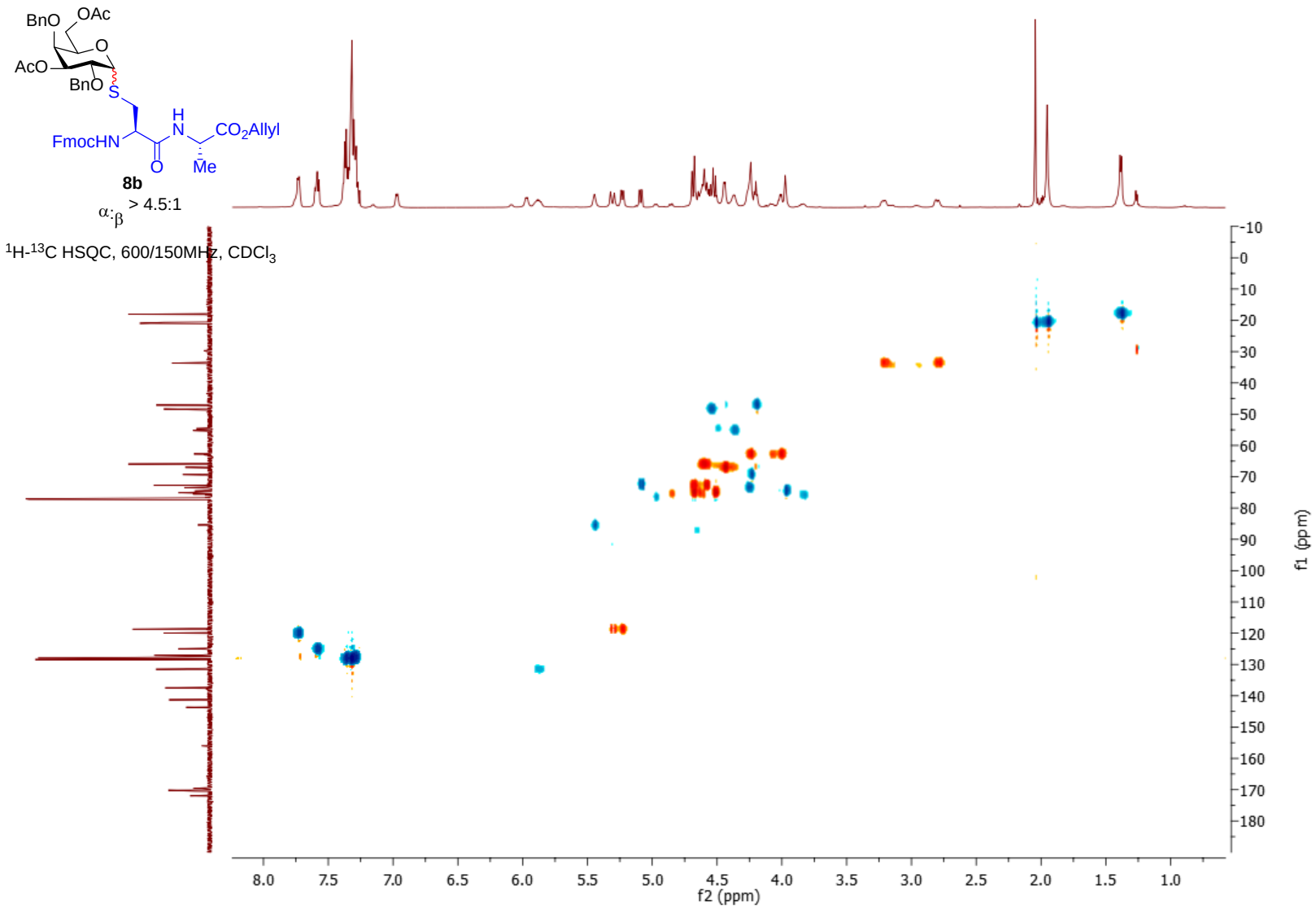


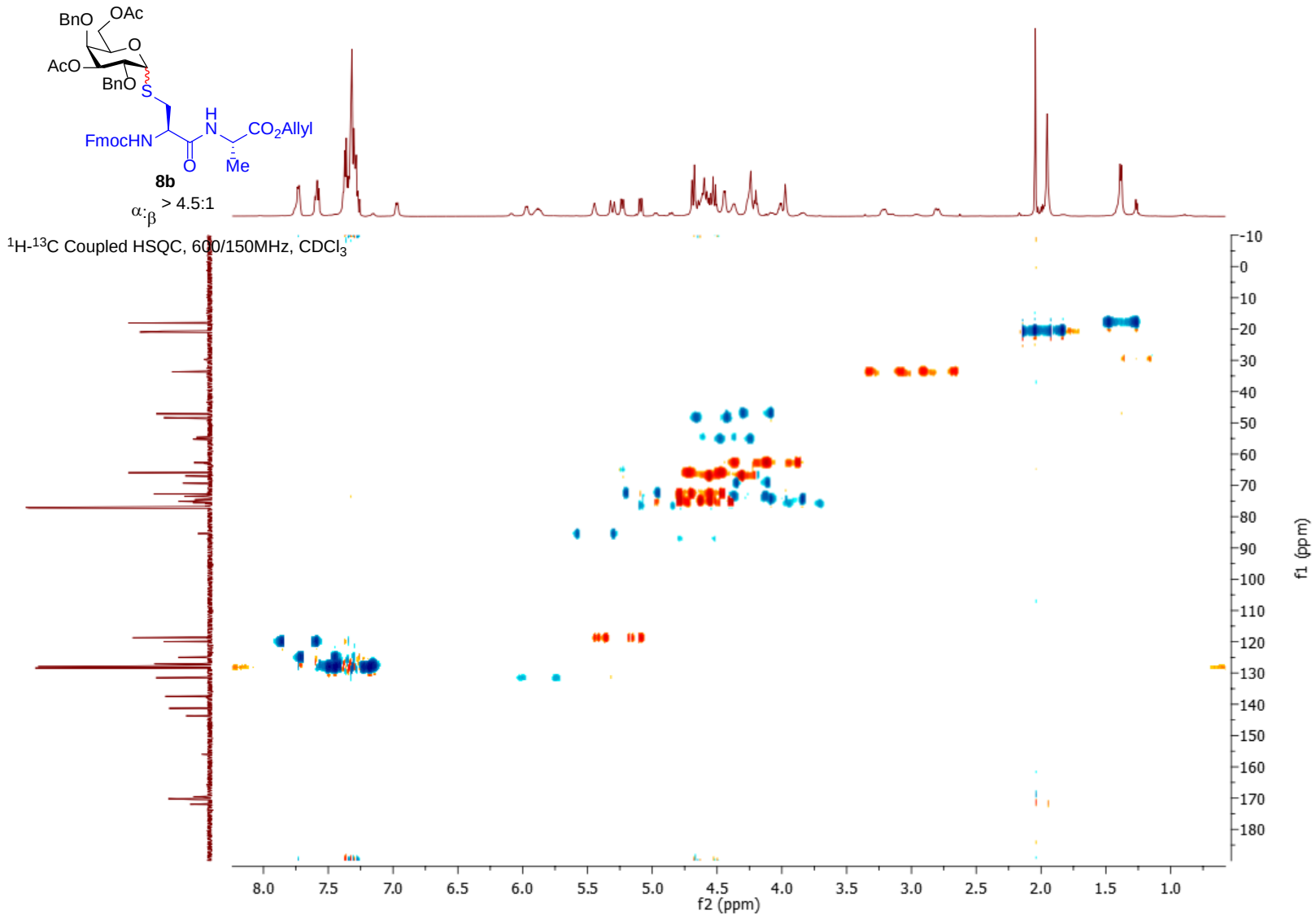
8b

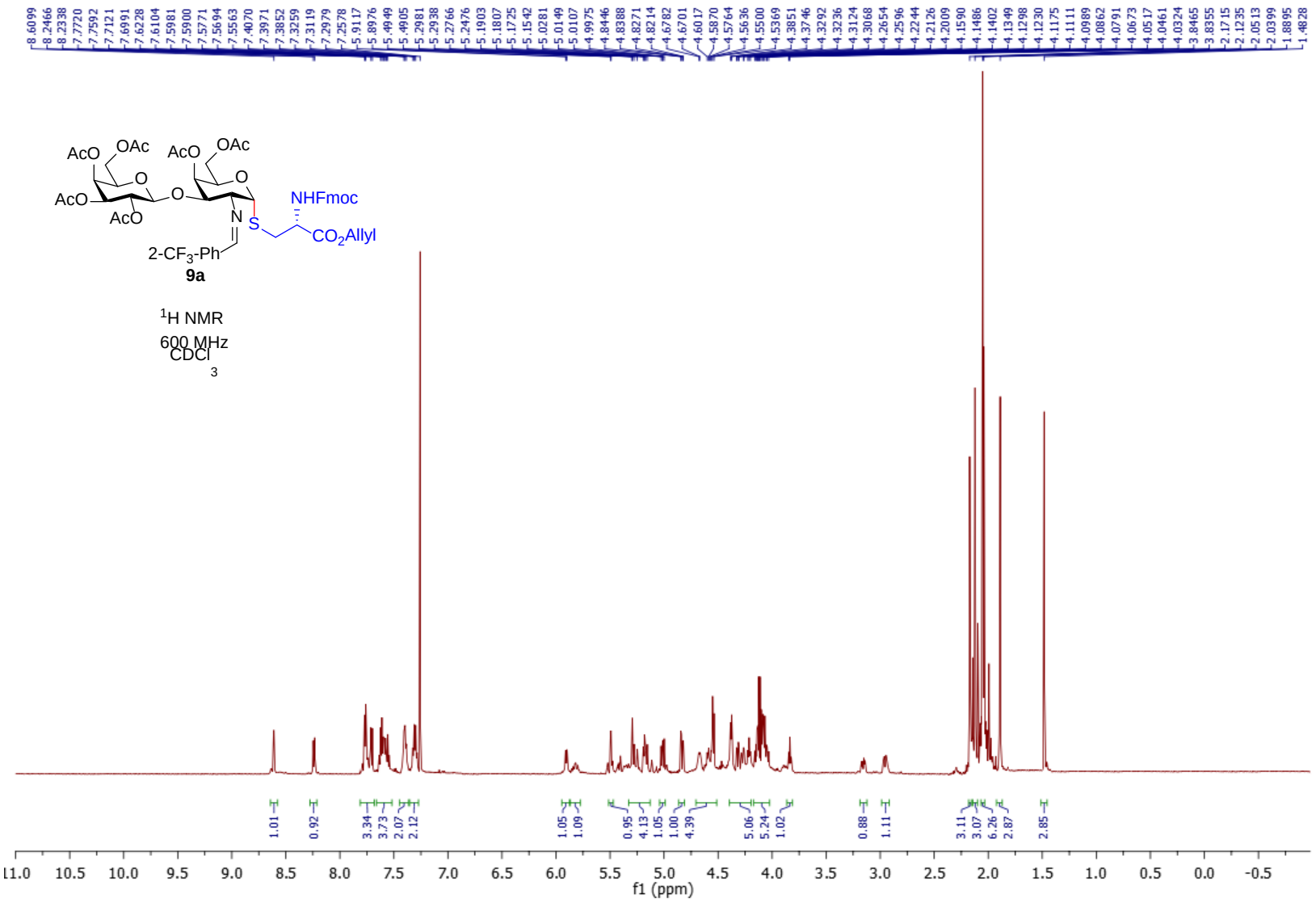
α:β > 4.5:1

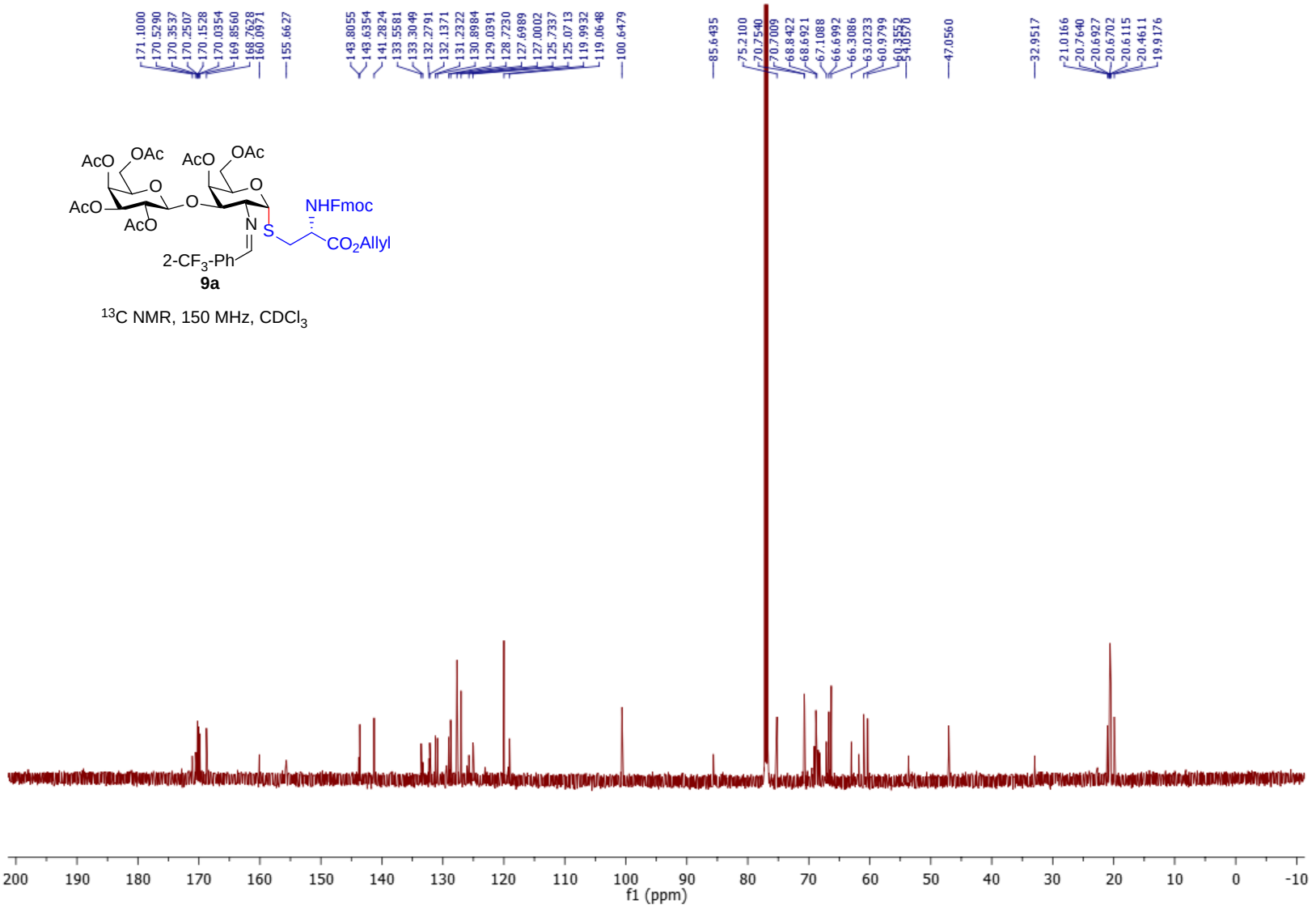
^{13}C NMR, 150 MHz, $CDCl_3$



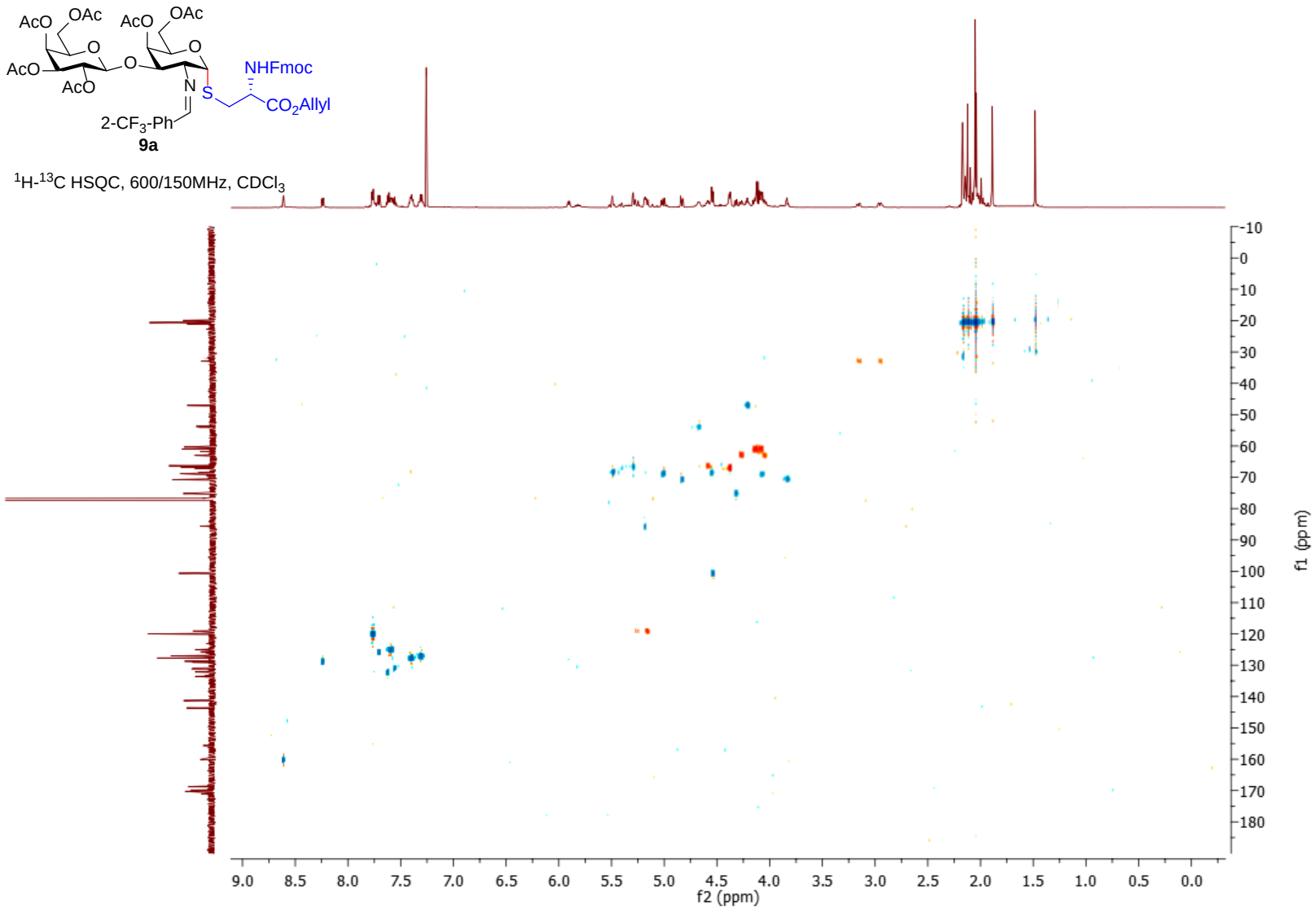

BnO
OAc
O
AcO
BnO
S
H
N
FmocHN
CO2Allyl
O
Me
8b
α:β > 4.5:1
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

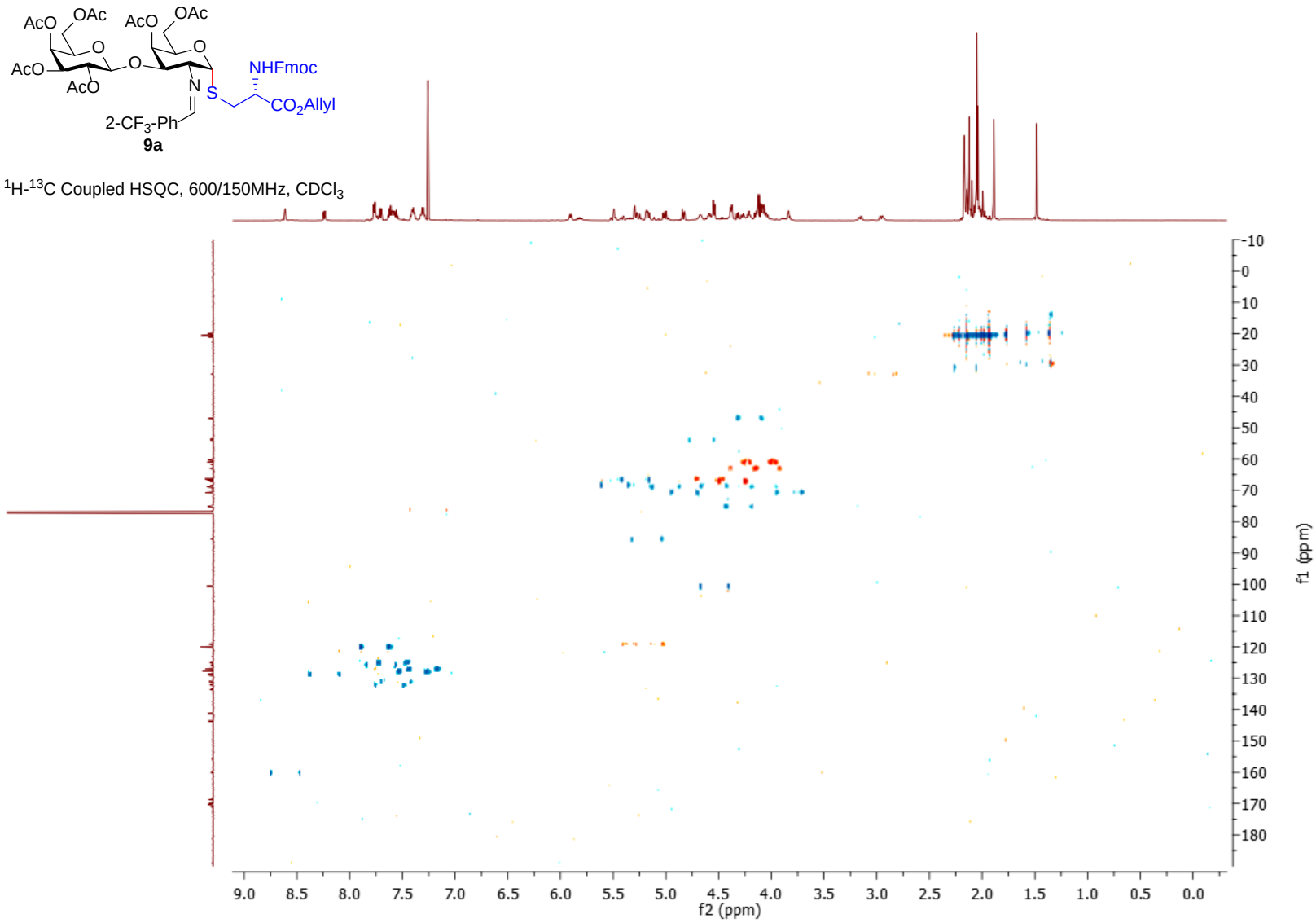

BnO
OAc
O
AcO
BnO
S
FmocHN
H
N
CO2Allyl
O
Me
8b
α:β > 4.5:1
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

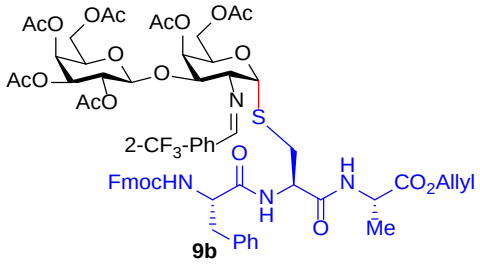

AcO
OAc
AcO
OAc
AcO
O
O
O
AcO
AcO
N
S
NHFmoc
CO2Allyl
2-CF3-Ph
9a
1H NMR
600 MHz
CDCl3
f1 (ppm)



^{13}C NMR, 150 MHz, $CDCl_3$

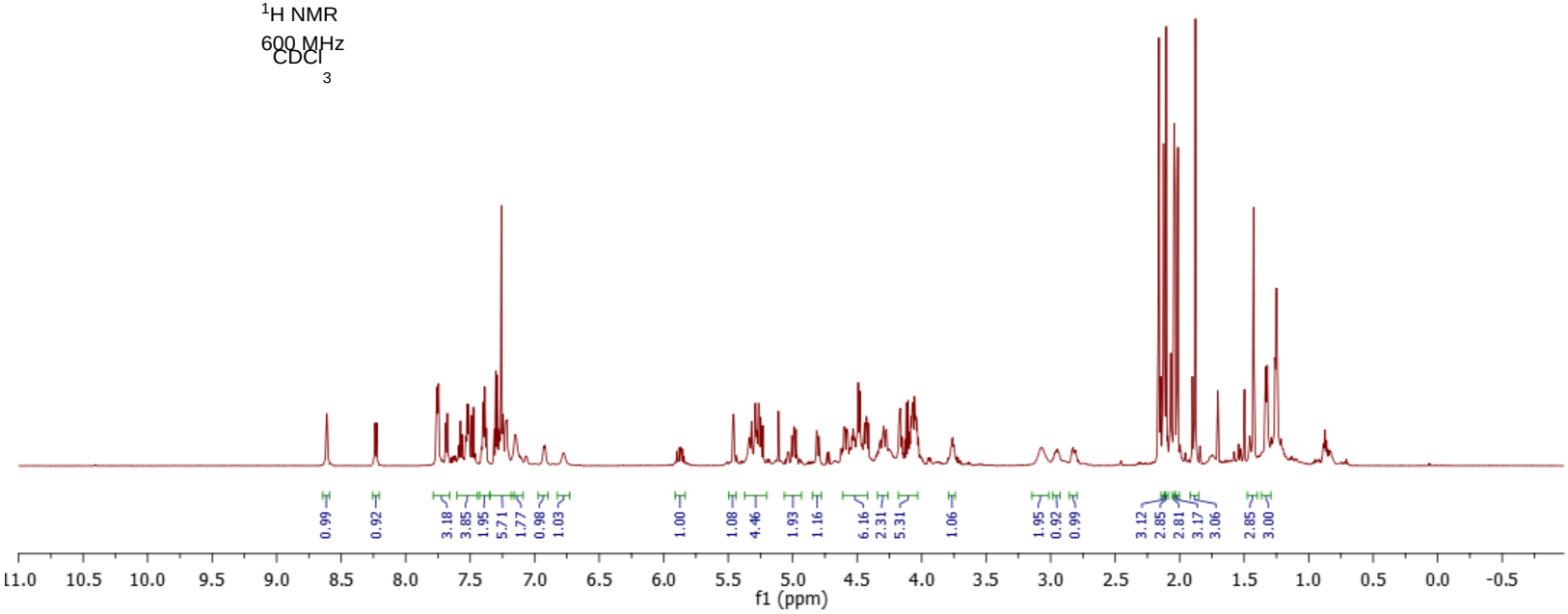

AcO
OAc
AcO
OAc
AcO
O
O
O
AcO
AcO
N
S
NHFmoc
CO2Allyl
2-CF3-Ph
9a
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

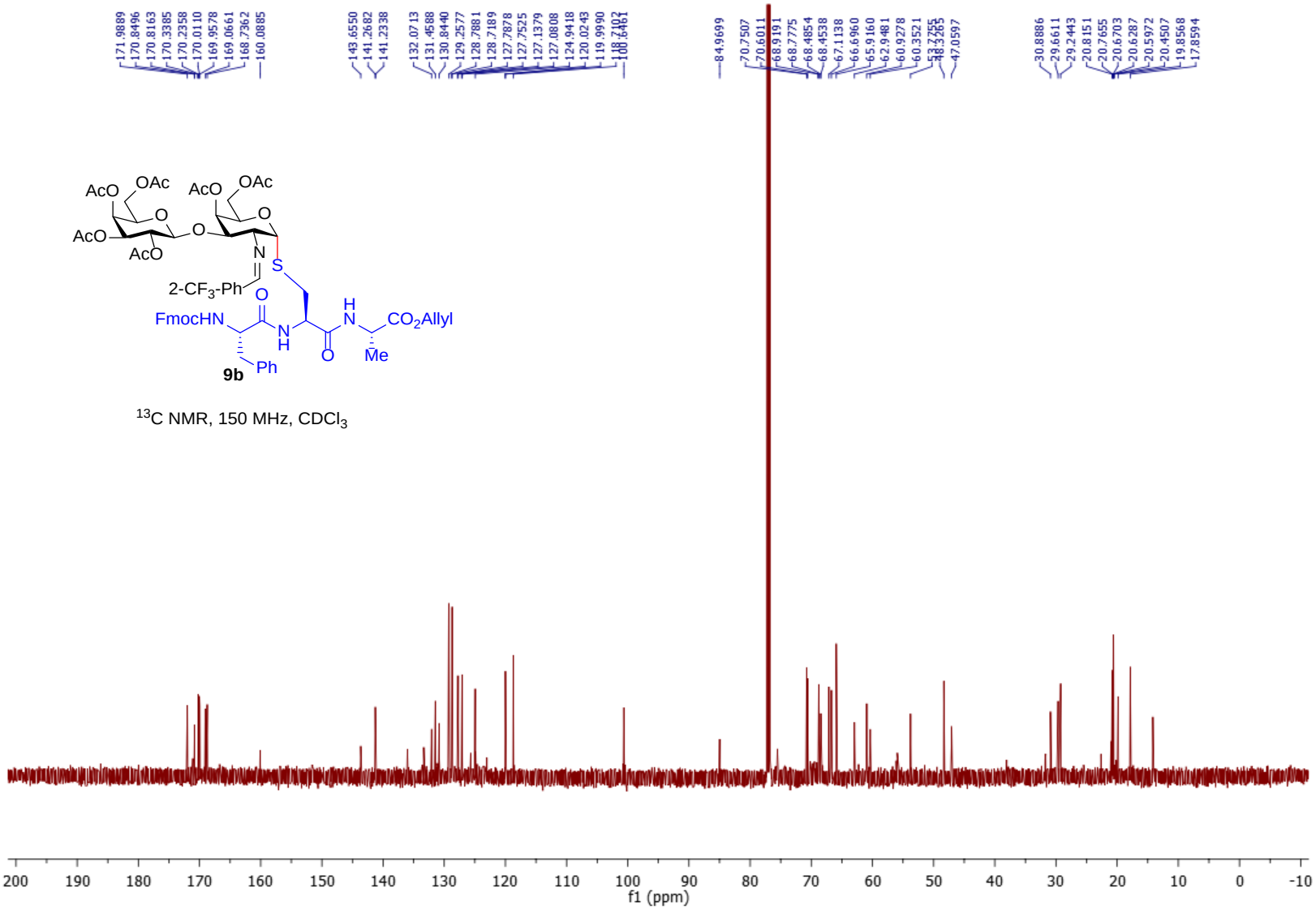

AcO
OAc
AcO
OAc
AcO
O
O
AcO
O
N
S
NHFmoc
CO2Allyl
2-CF3-Ph
9a
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f1 (ppm)
f2 (ppm)



9b

^{1}H NMR
600 MHz
$CDCl_3$

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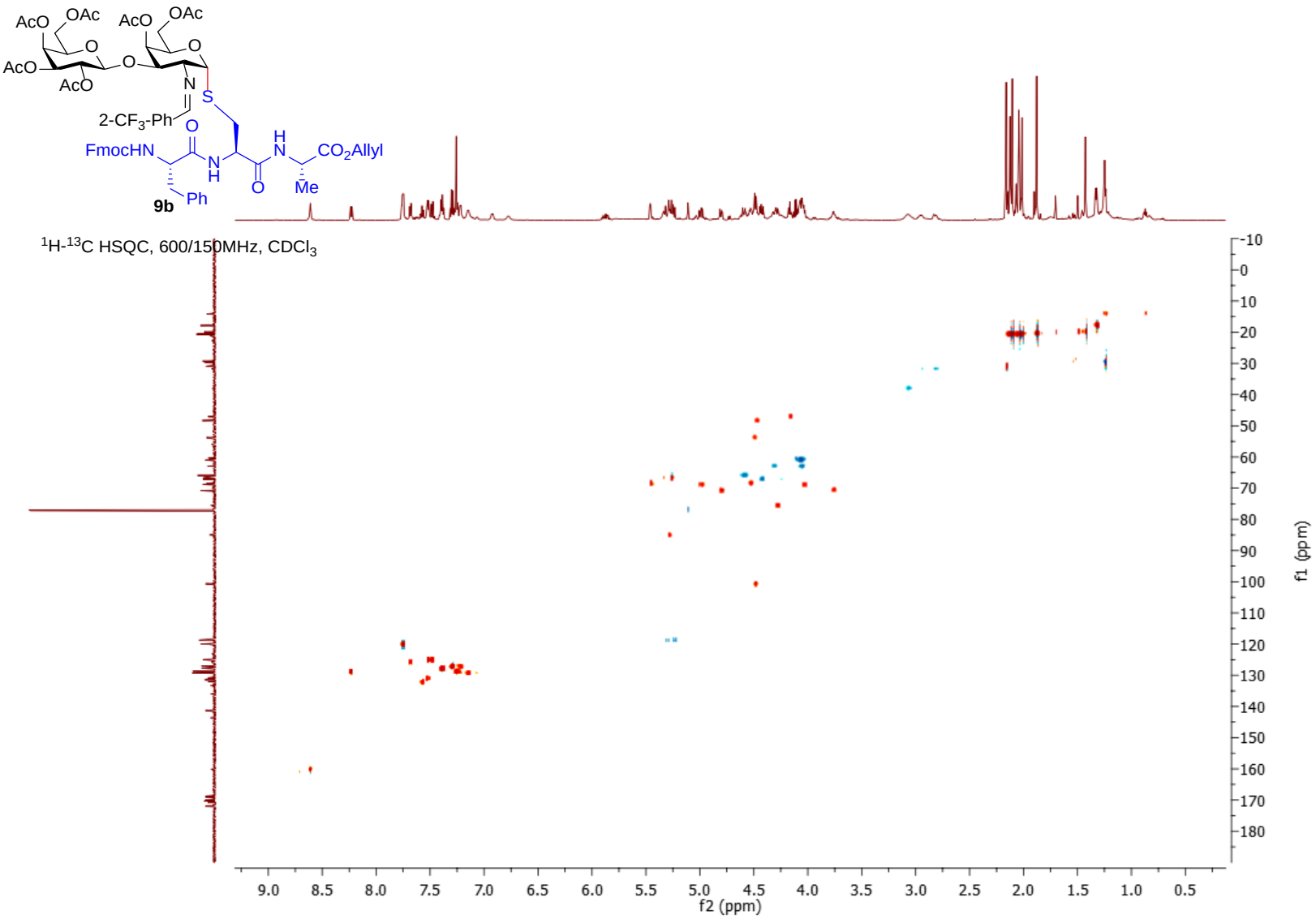
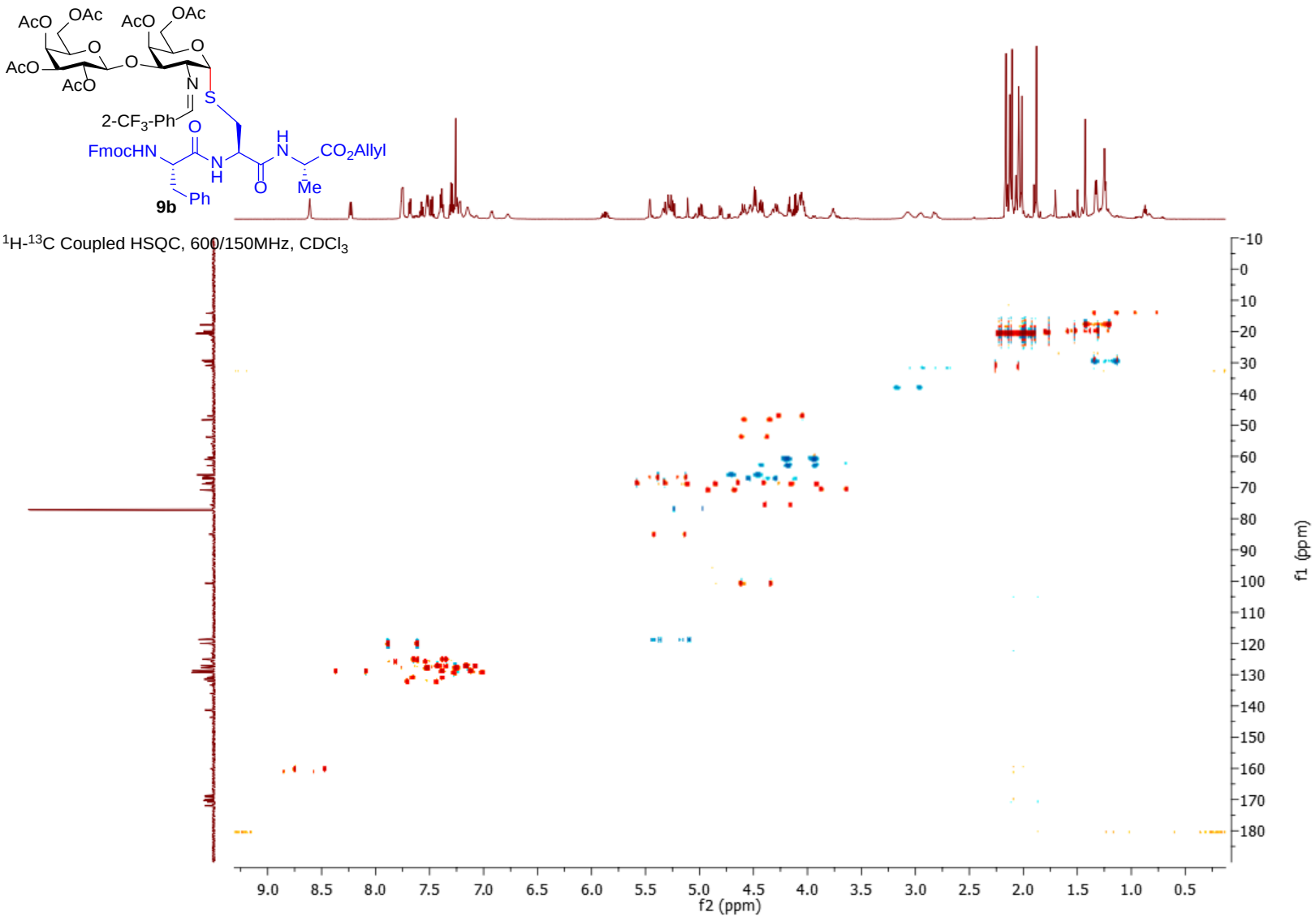
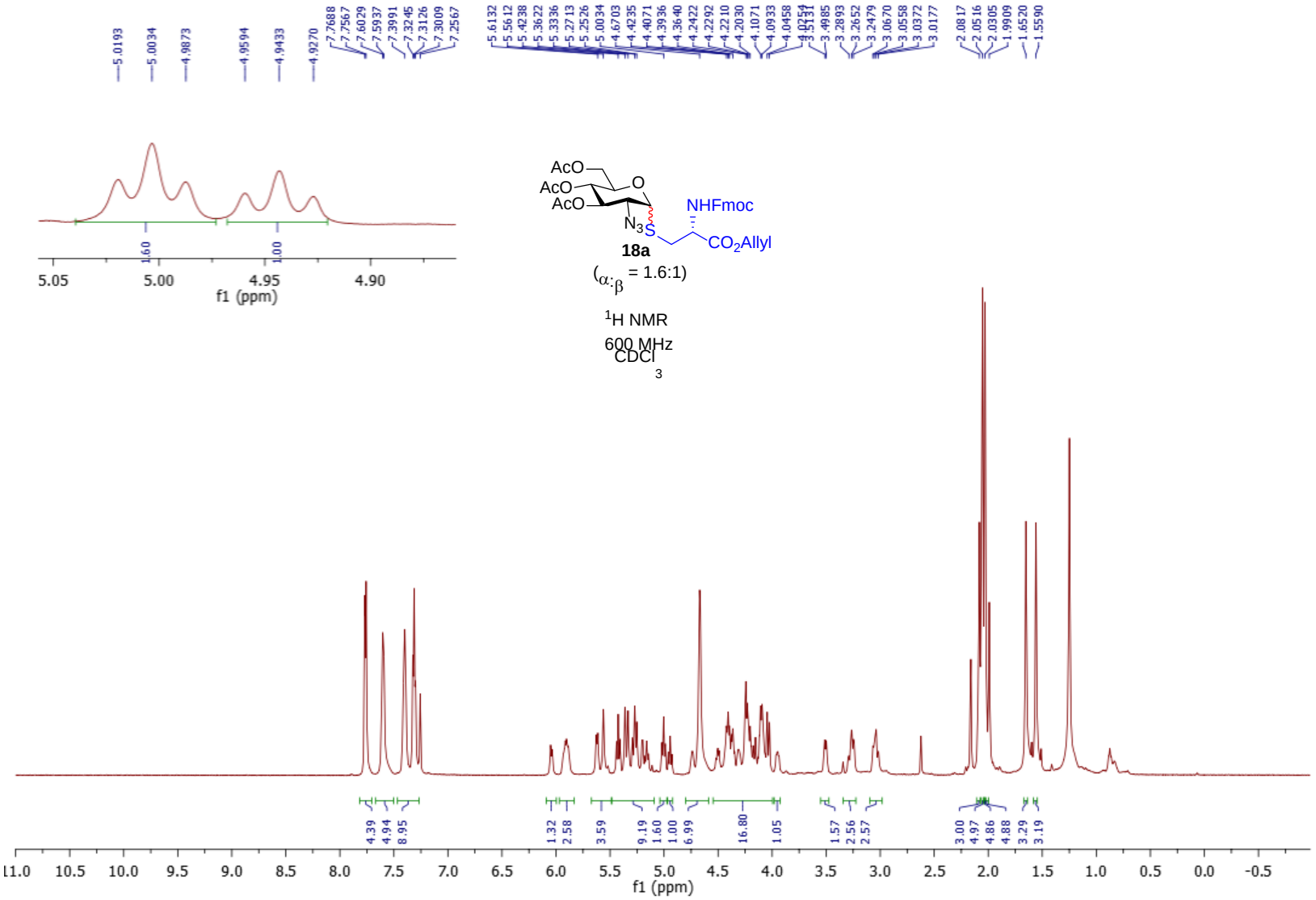
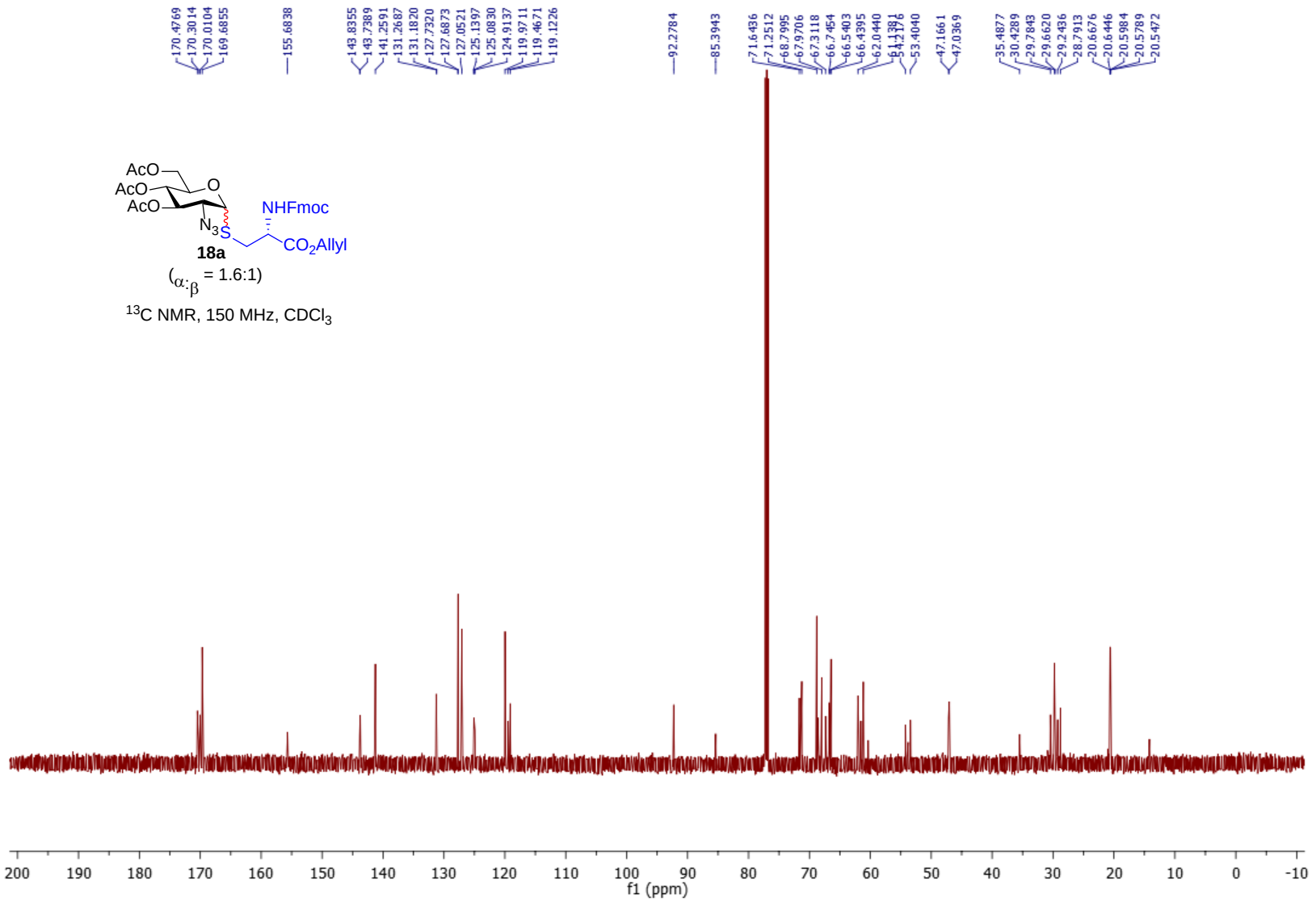
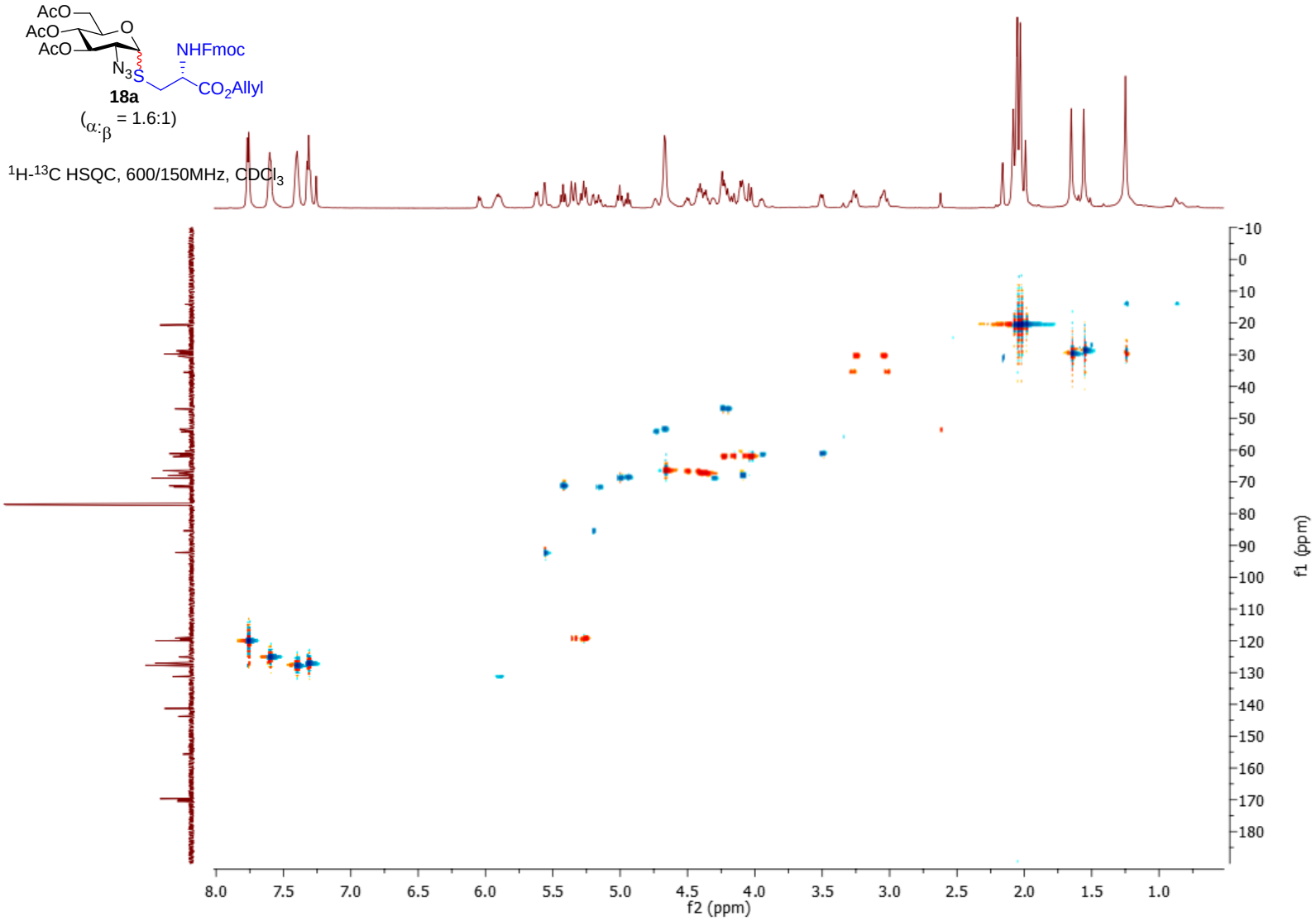
170.8496
170.8163
170.3385
170.2358
170.0110
169.9578
169.0661
168.7362
160.0885
143.6550
141.2682
141.2338
132.0713
131.4588
130.8440
129.2577
128.7881
128.7189
127.7878
127.7525
127.1379
127.0808
124.9418
120.0243
119.9990
84.9699
70.7507
70.6011
68.9191
68.7775
68.4854
68.4538
67.1138
66.6960
65.9160
62.9481
60.9278
60.3521
53.3255
47.0597
30.8886
29.6611
29.2443
20.8151
20.7655
20.6703
20.6287
20.5972
20.4507
19.8568
17.8594
AcO
OAc
AcO
OAc
AcO
AcO
O
O
O
N
S
2-CF3-Ph
O
FmocHN
N
H
H
N
CO2Allyl
O
Me
Ph
9b
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

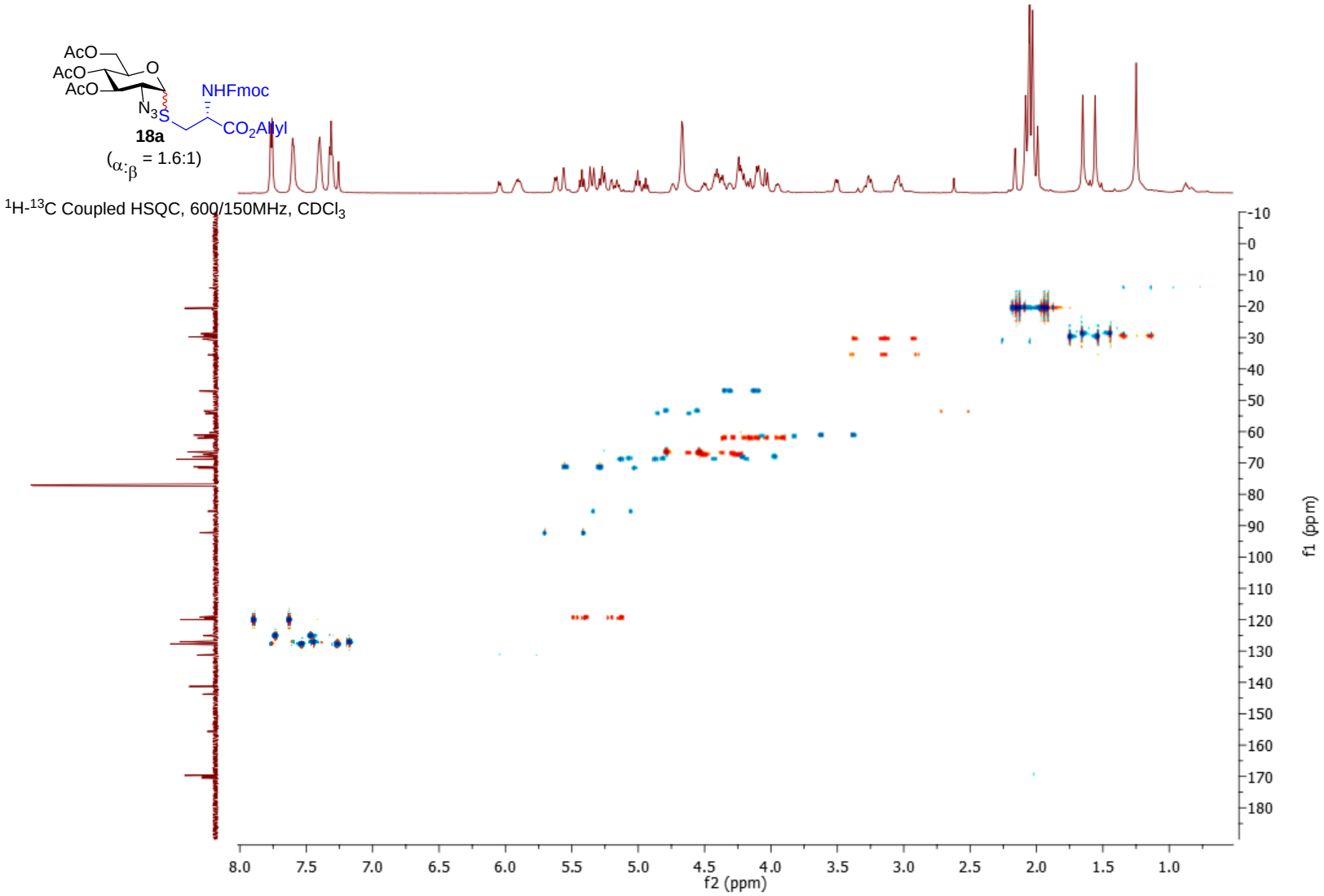

AcO
OAc
AcO
OAc
AcO
O
O
AcO
O
N
S
2-CF3-Ph
O
FmocHN
N
H
H
N
CO2Allyl
O
Me
Ph
9b
1H-13C HSQC, 600/150MHz, CDCl3
f1 (ppm)
f2 (ppm)

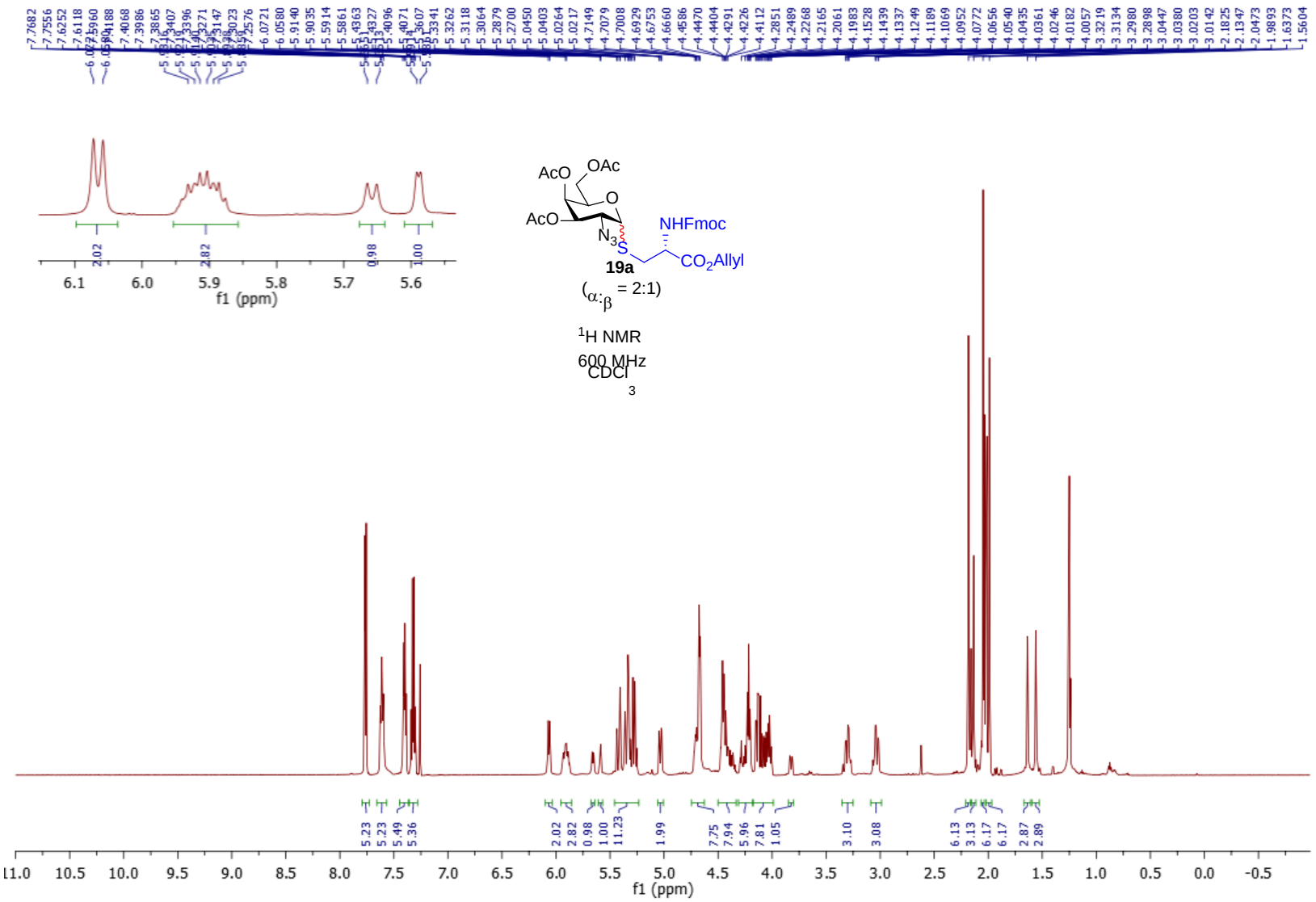

AcO
OAc
AcO
OAc
AcO
O
O
AcO
O
N
S
2-CF3-Ph
O
FmocHN
N
H
H
N
CO2Allyl
O
Me
Ph
9b
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

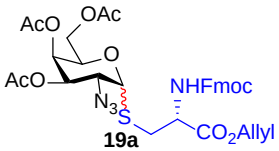

AcO
AcO
AcO
O
N3
S
NHFmoc
CO2Allyl
18a
(α:β = 1.6:1)
1H NMR
600 MHz
CDCl3
f1 (ppm)


170.4769
170.3014
170.0104
169.6855
155.6838
143.8355
143.7389
141.2591
131.2687
131.1820
127.7320
127.6873
127.0521
125.1397
125.0830
124.9137
119.9711
119.4671
119.1226
92.2784
85.3943
71.6436
71.2512
68.7995
67.9706
67.3118
66.7454
66.5403
66.4395
62.0440
61.1381
54.2176
53.4040
47.1661
47.0369
35.4877
30.4289
29.7843
29.6620
29.2436
28.7913
20.6676
20.6446
20.5984
20.5789
20.5472
AcO
AcO
AcO
O
N3
S
NHFmoc
CO2Allyl
18a
(α:β = 1.6:1)
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AcO
AcO
AcO
O
N3
S
NHFmoc
CO2Allyl
18a
(α:β = 1.6:1)
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


AcO
AcO
AcO
O
N3
S
NHFmoc
CO2Allyl
18a
(α:β = 1.6:1)
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f1 (ppm)
f2 (ppm)

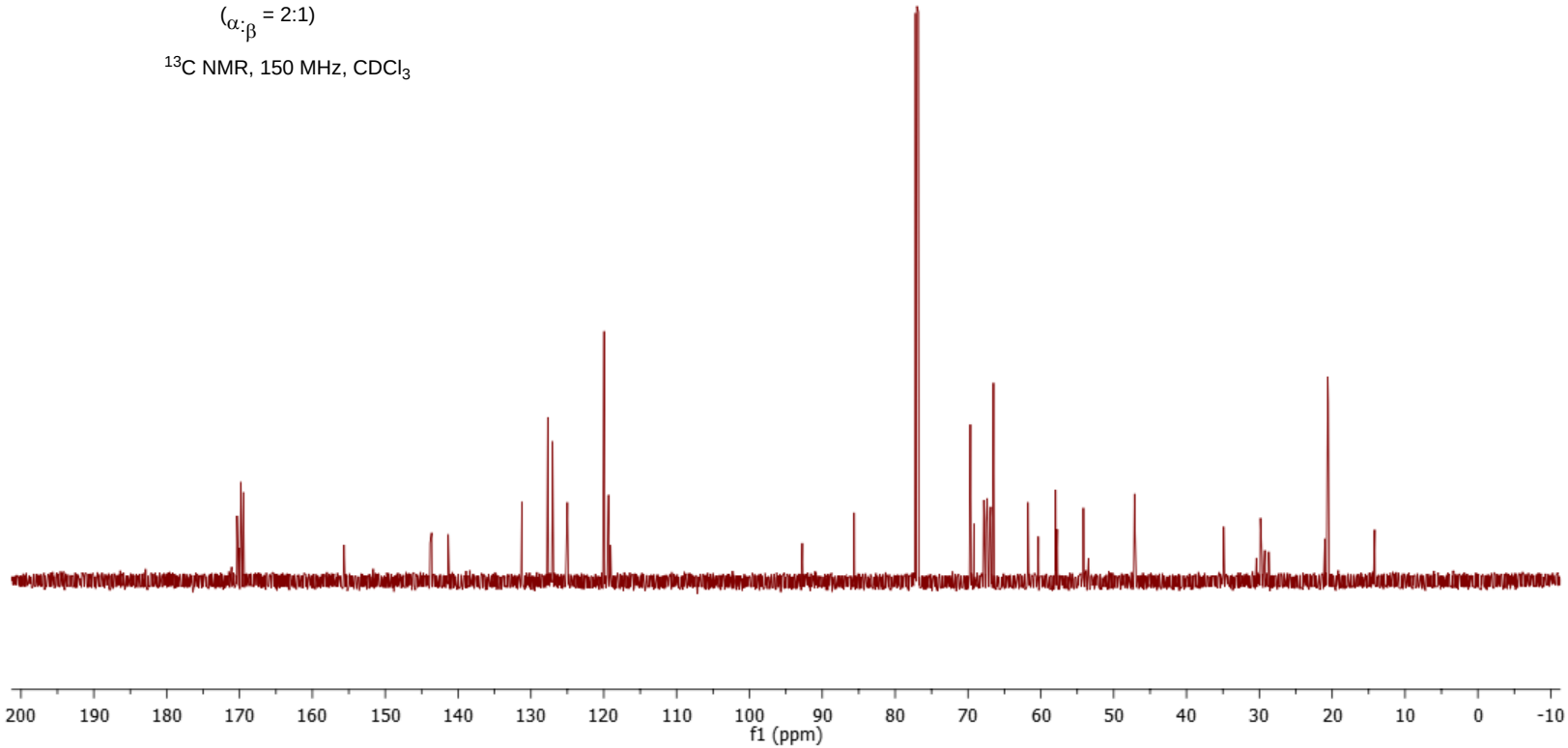

AcO
OAc
O
AcO
N3
S
NHFmoc
CO2Allyl
19a
(α:β = 2:1)
1H NMR
600 MHz
CDCl3
f1 (ppm)

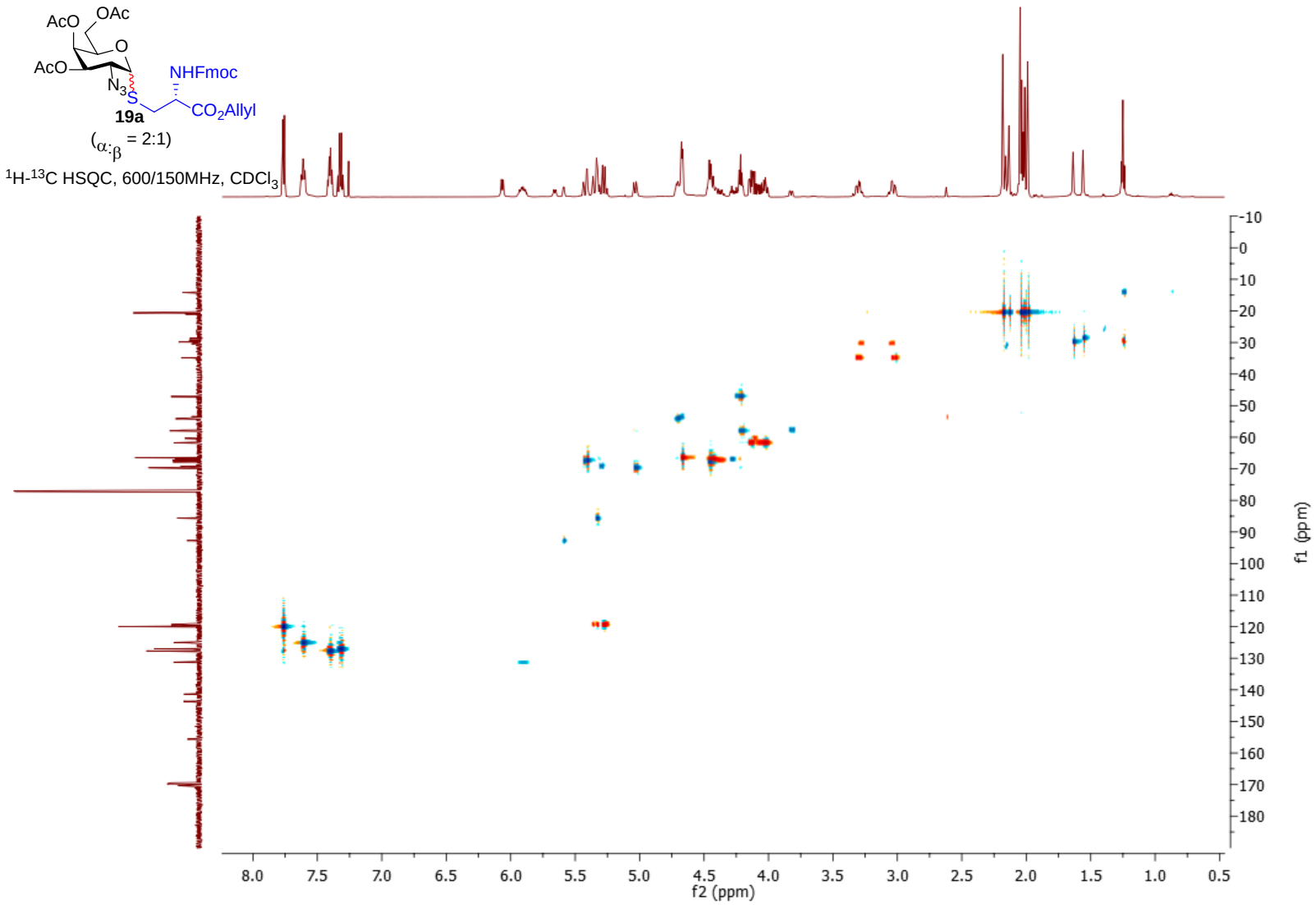


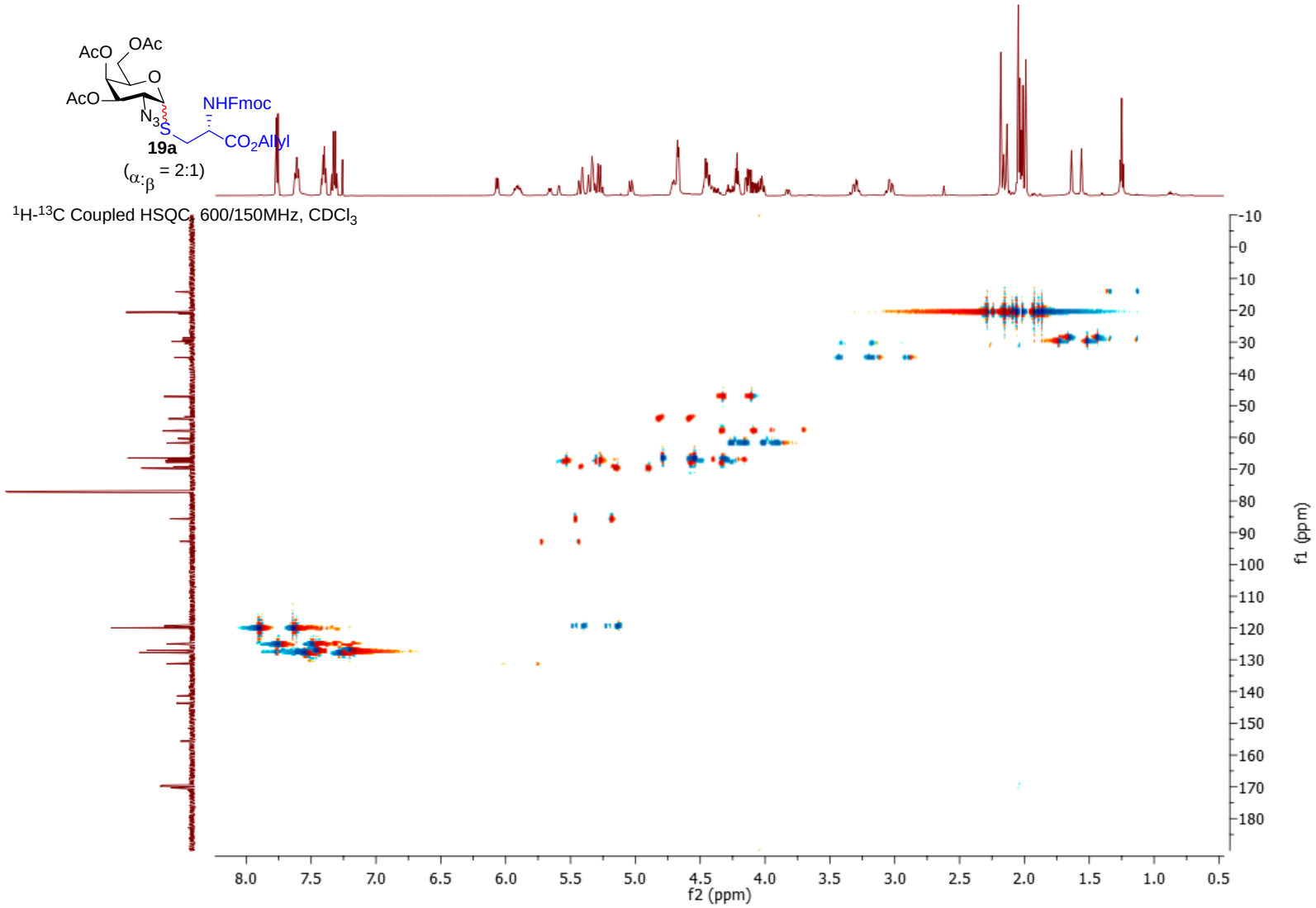
19a

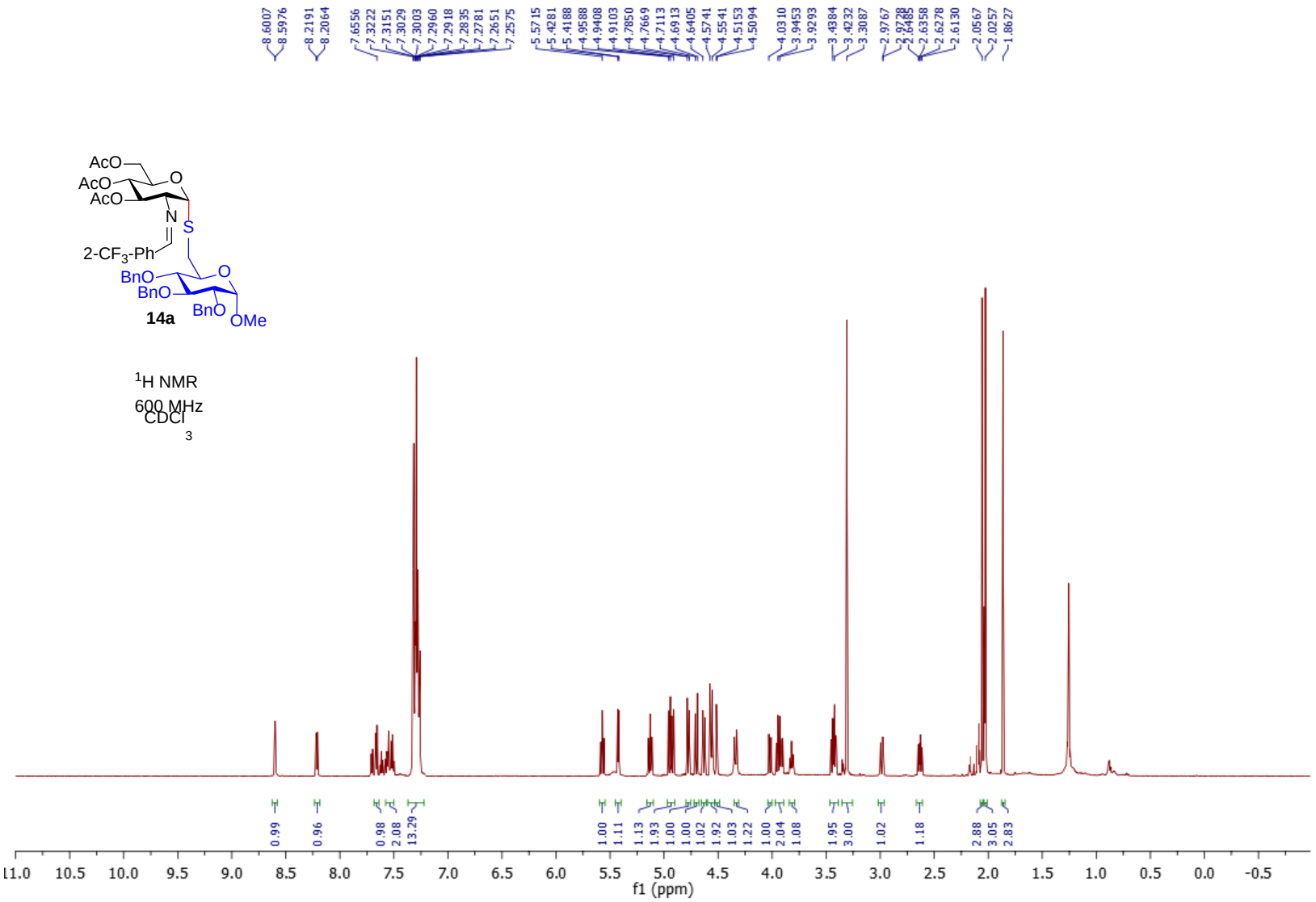
(α:β = 2:1)

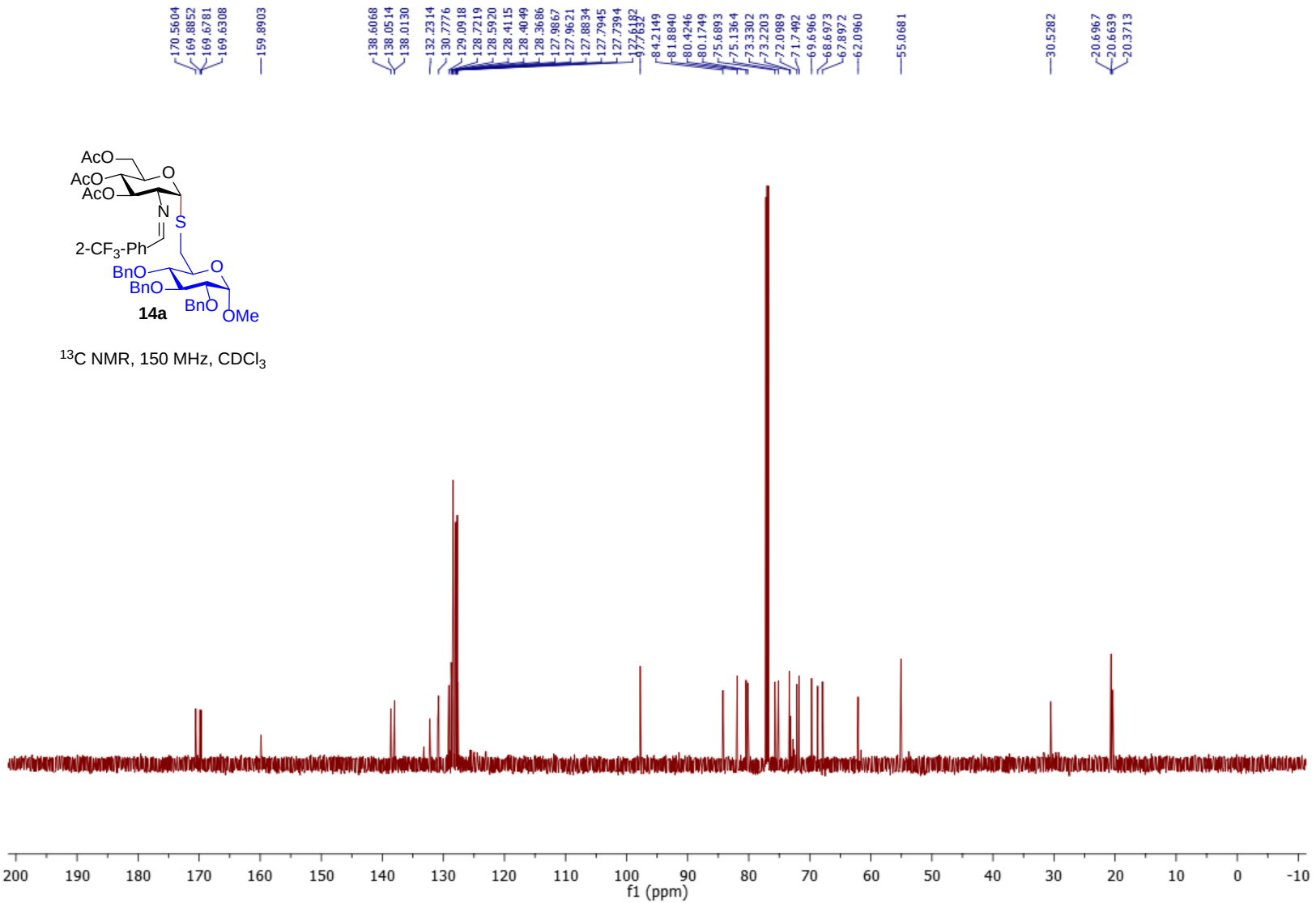
^{13}C NMR, 150 MHz, $CDCl_3$




AcO
OAc
O
AcO
N3
S
NHFmoc
CO2Allyl
19a
(α:β = 2:1)
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


AcO
OAc
O
AcO
N3
S
NHFmoc
CO2Allyl
19a
(α:β = 2:1)
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


8.6007
8.5976
8.2191
8.2064
7.6556
7.3222
7.3151
7.3029
7.3003
7.2960
7.2918
7.2835
7.2781
7.2651
7.2575
5.5715
5.4281
5.4188
4.9588
4.9408
4.9103
4.7850
4.7669
4.7113
4.6913
4.6405
4.5741
4.5541
4.5153
4.5094
4.0310
3.9453
3.9293
3.4384
3.4232
3.3087
2.9767
2.9728
2.6488
2.6358
2.6278
2.6130
2.0567
2.0257
1.8627
AcO
AcO
AcO
O
N
S
2-CF3-Ph
BnO
BnO
BnO
O
OMe
14a
1H NMR
600 MHz
CDCl3
0.99
0.96
0.98
2.08
13.29
1.00
1.11
1.13
1.93
1.00
1.02
1.92
1.03
1.22
1.00
2.04
1.08
1.95
3.00
1.02
1.18
2.88
3.05
2.83
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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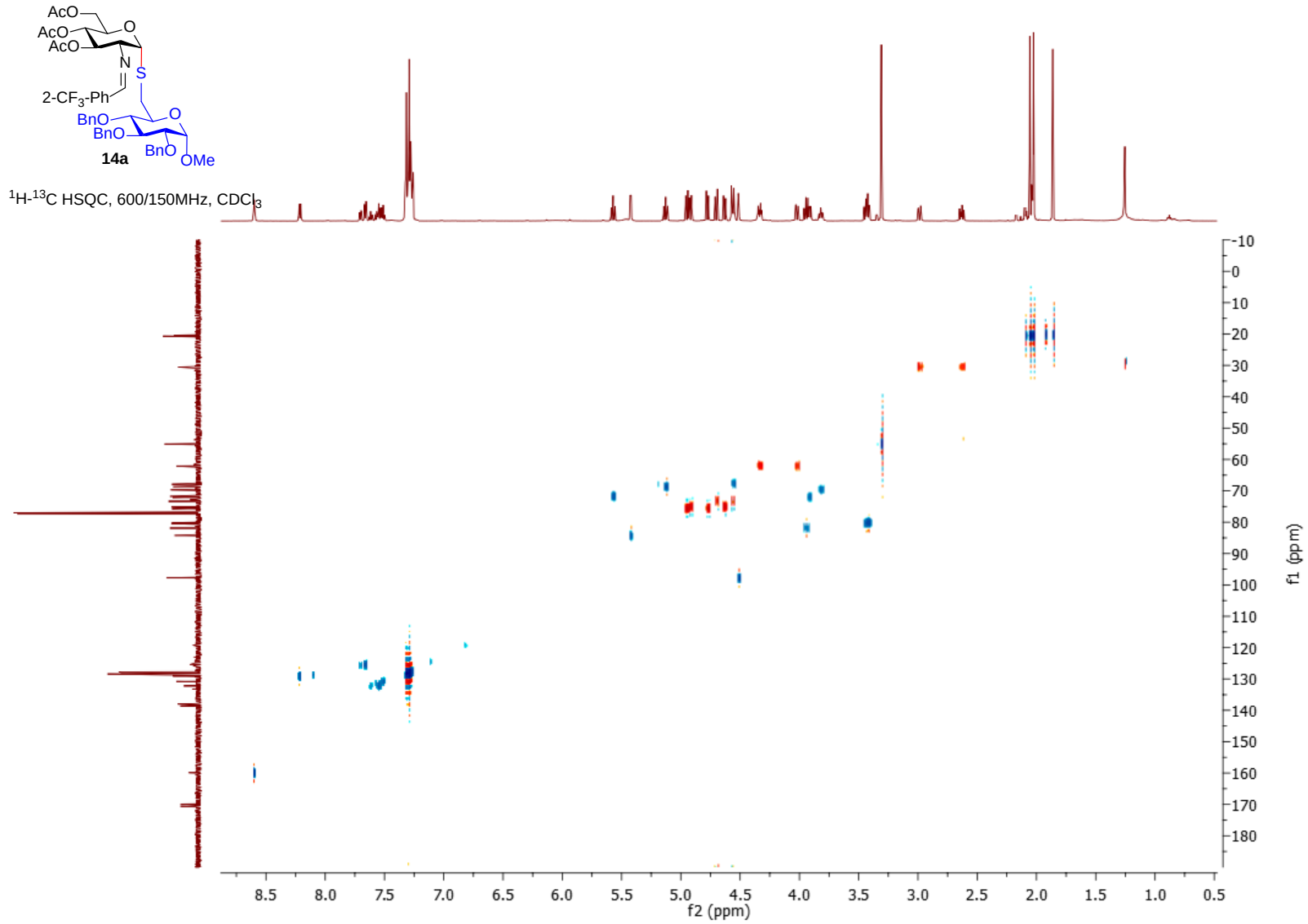
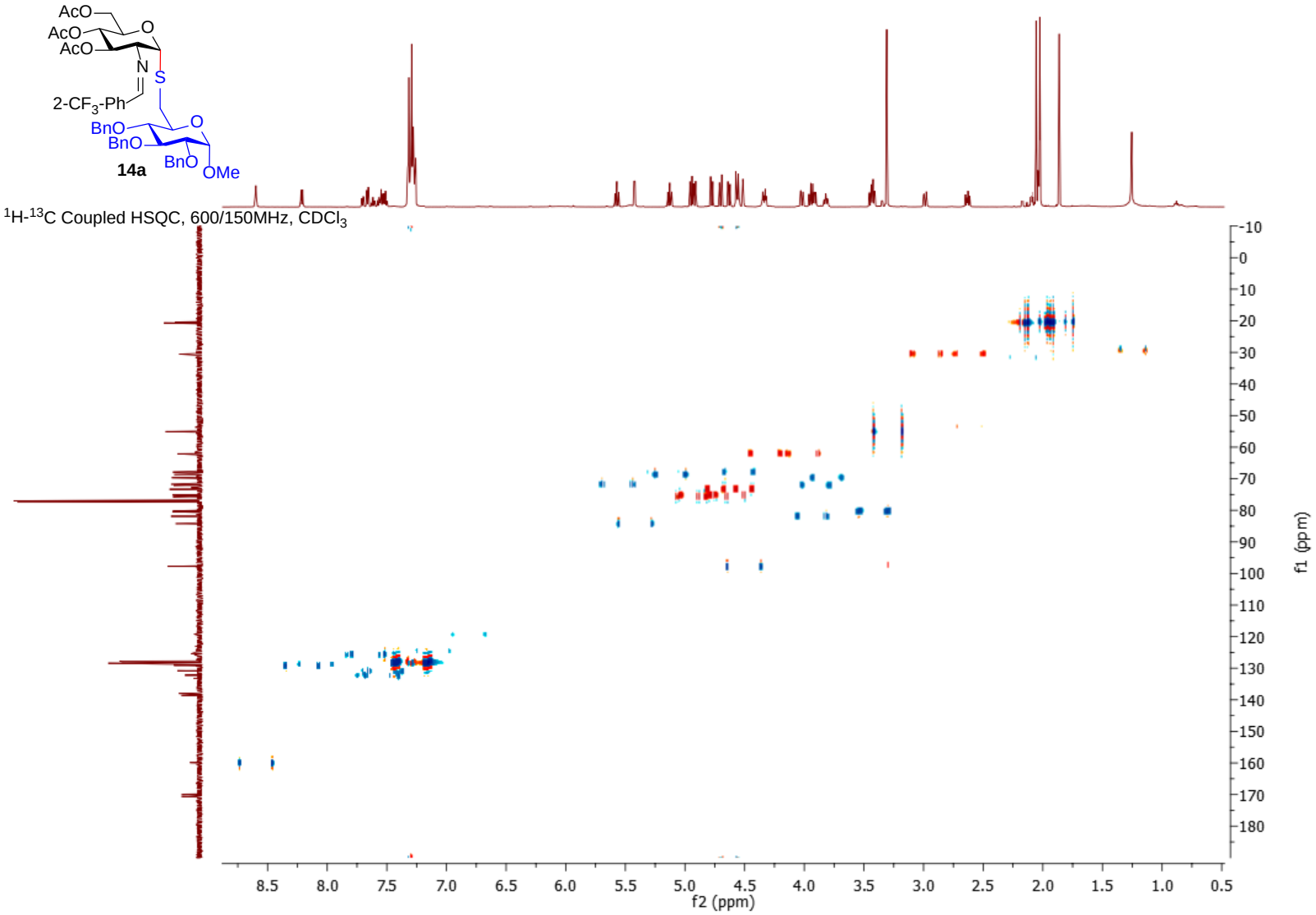
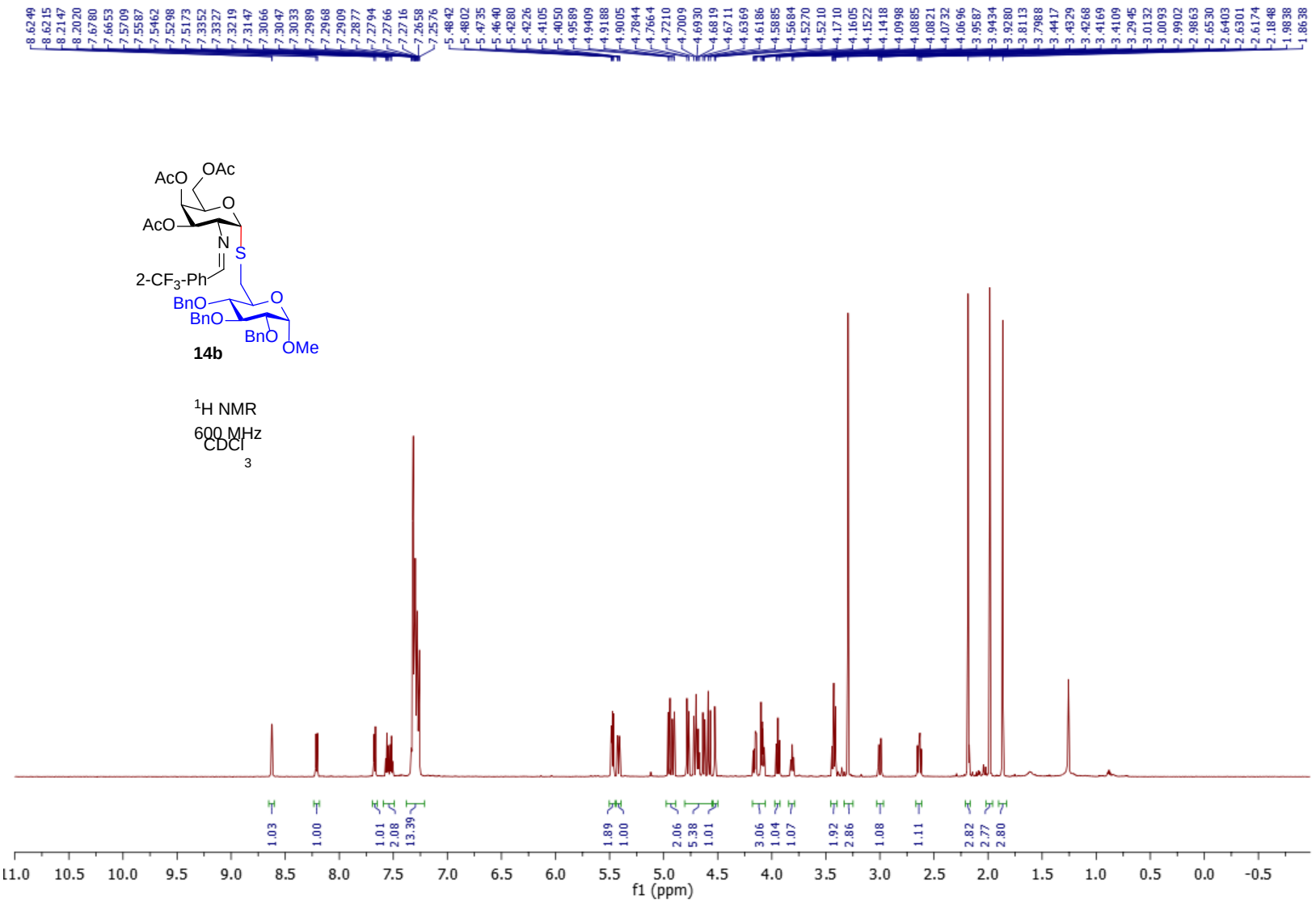
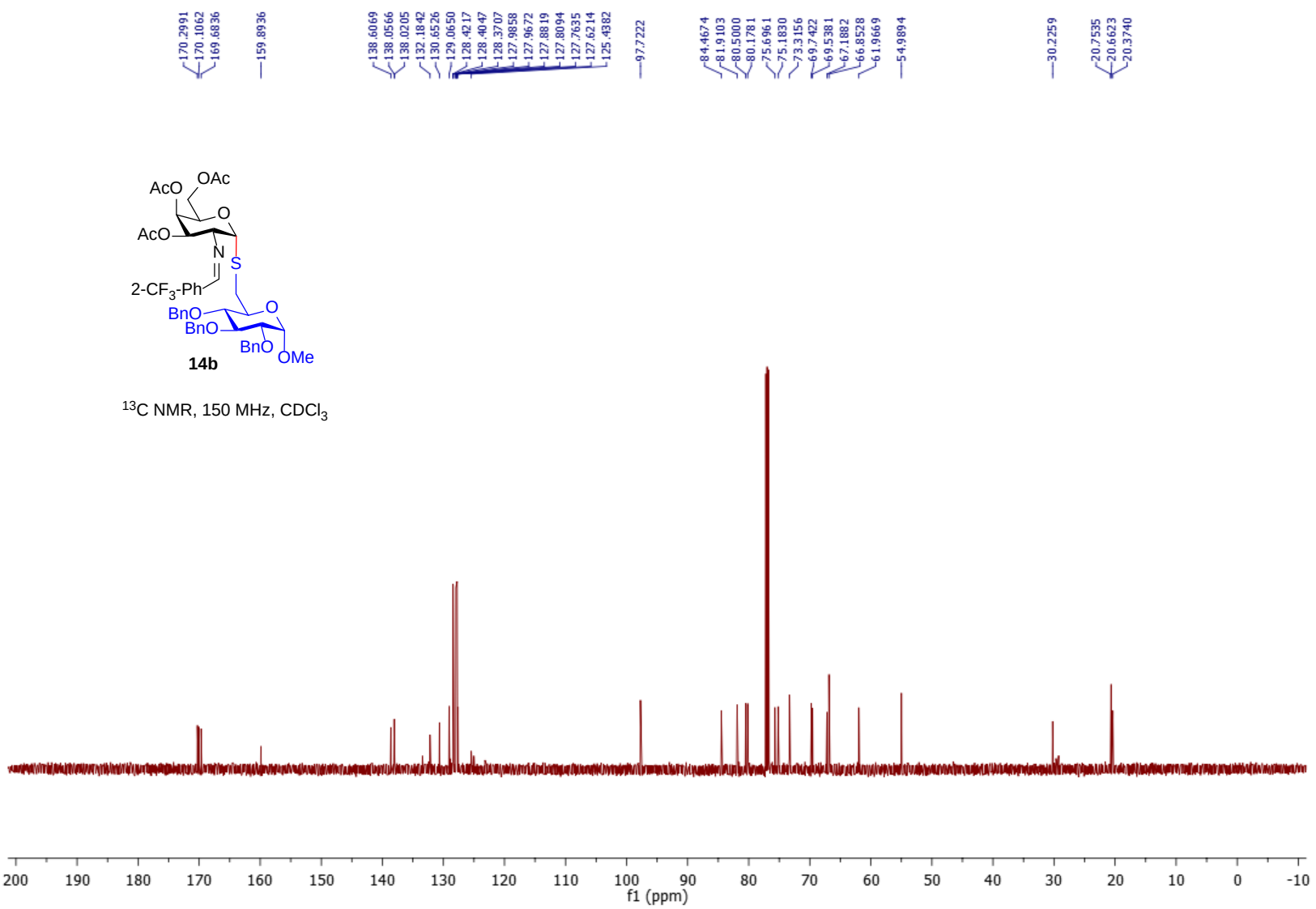
169.8852
169.6781
169.6308
159.8903
138.6068
138.0514
138.0130
132.2314
130.7776
129.0918
128.7219
128.5920
128.4115
128.4049
128.3686
127.9867
127.9621
127.8834
127.7945
127.7394
84.2149
81.8840
80.4246
80.1749
75.6893
75.1364
73.3302
73.2203
72.0989
71.7492
69.6966
68.6973
67.8972
62.0960
55.0681
30.5282
20.6967
20.6639
20.3713
AcO
AcO
AcO
O
N
S
2-CF3-Ph
BnO
BnO
BnO
O
OMe
14a
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AcO
AcO
AcO
O
N
S
2-CF3-Ph
BnO
BnO
BnO
O
BnO
OMe
14a
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


AcO
AcO
AcO
O
N
S
2-CF3-Ph
BnO
BnO
BnO
O
OMe
14a
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


AcO
OAc
O
AcO
N
S
2-CF3-Ph
BnO
O
BnO
BnO
OMe
14b
1H NMR
600 MHz
CDCl3
f1 (ppm)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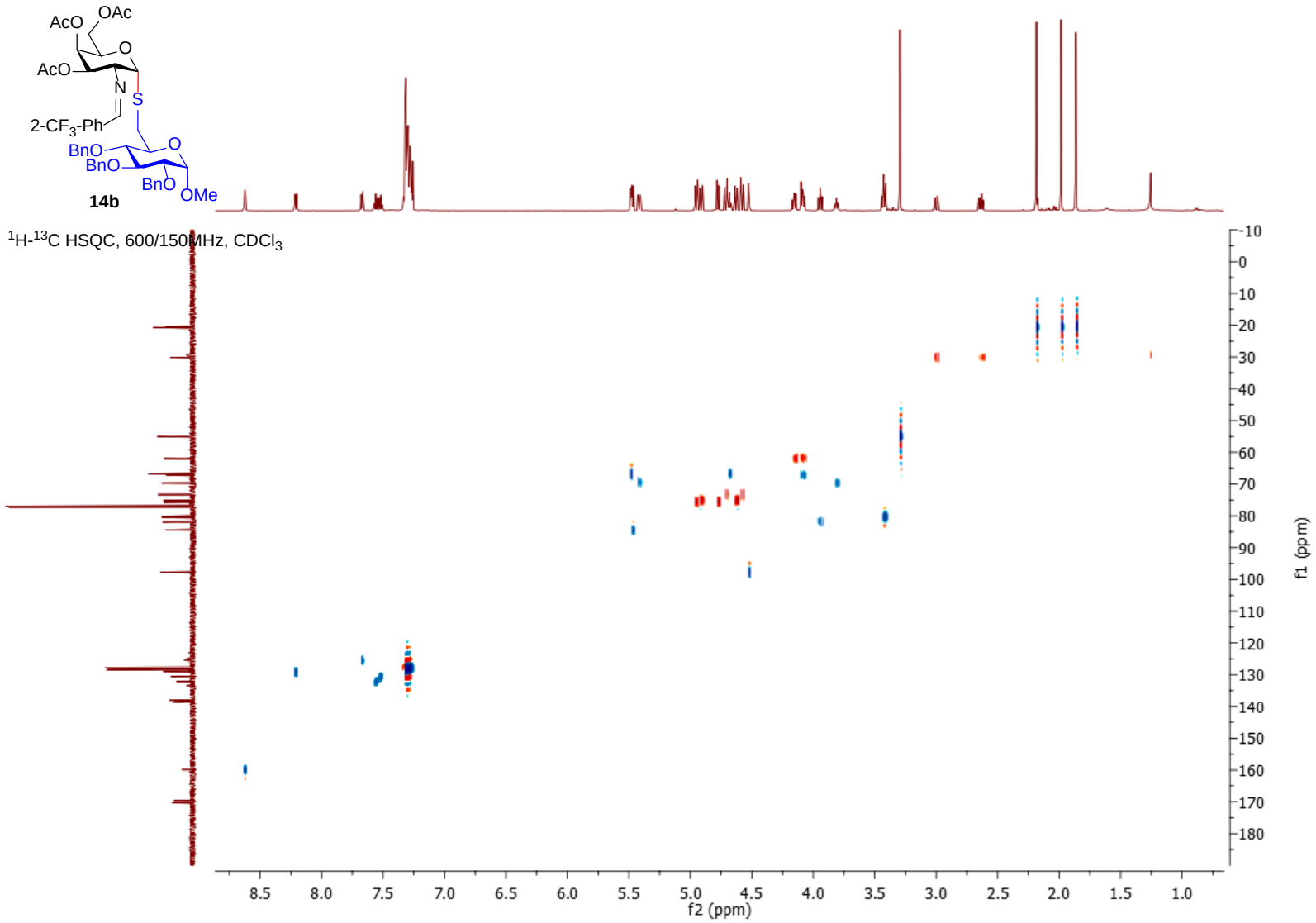
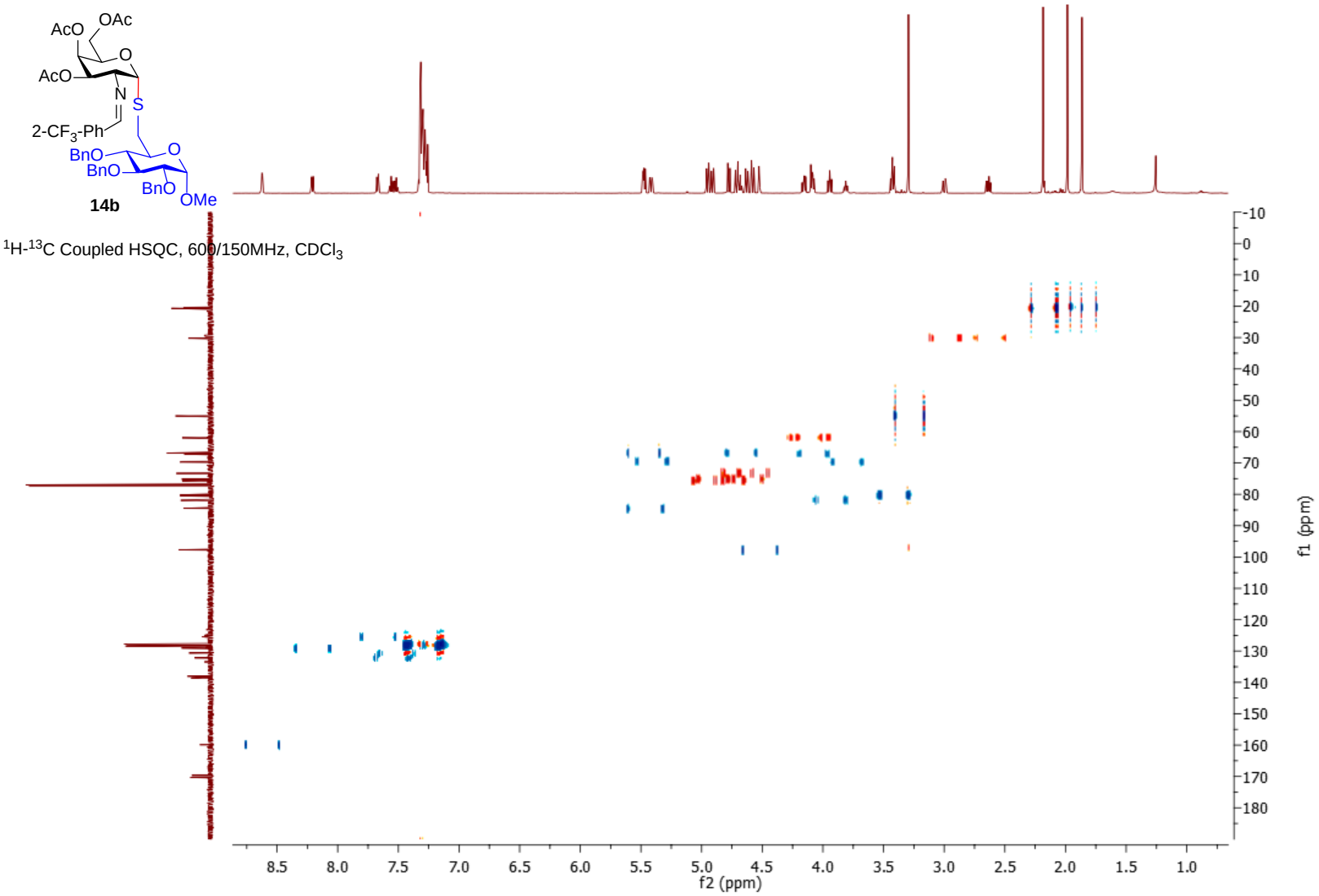
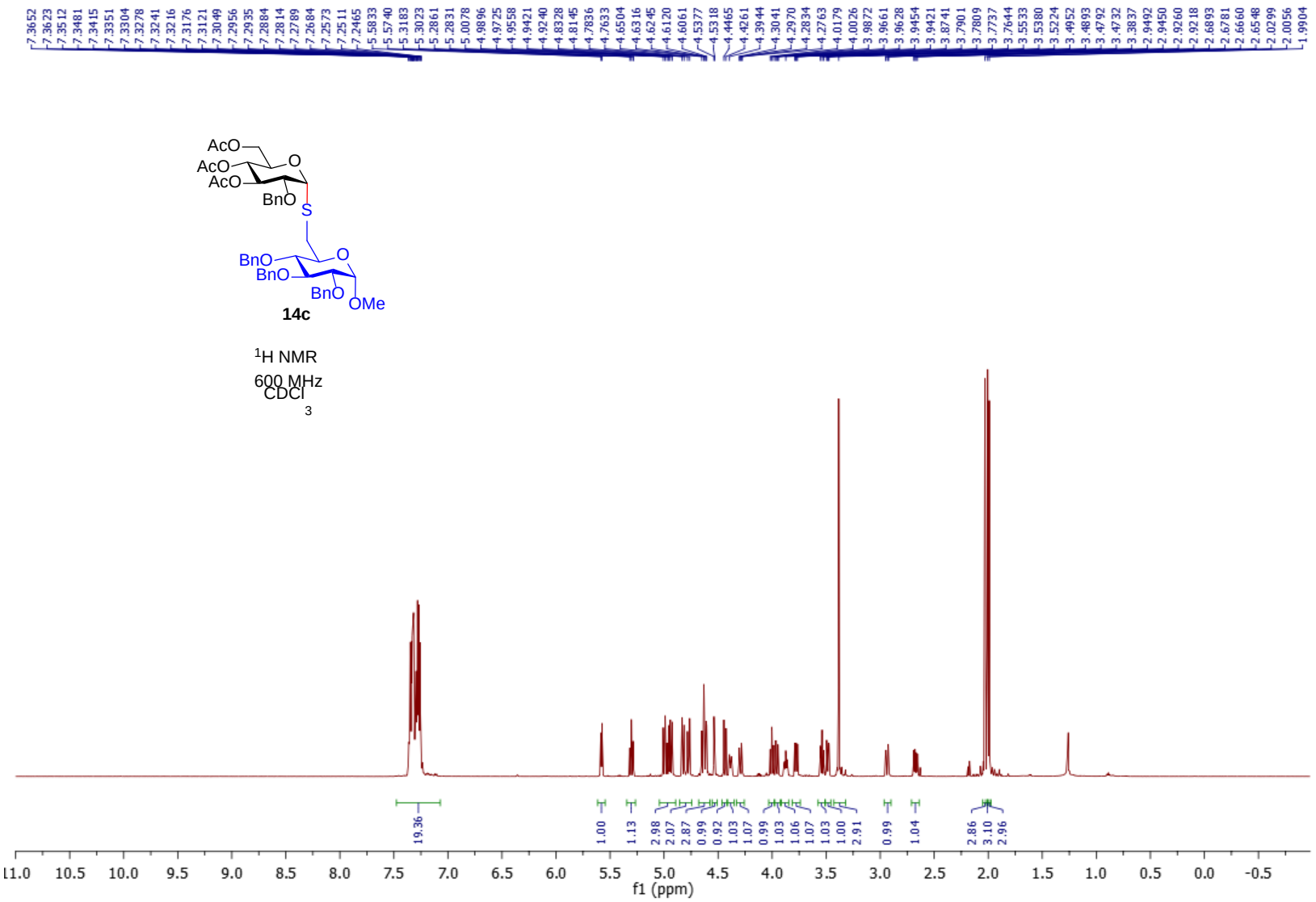
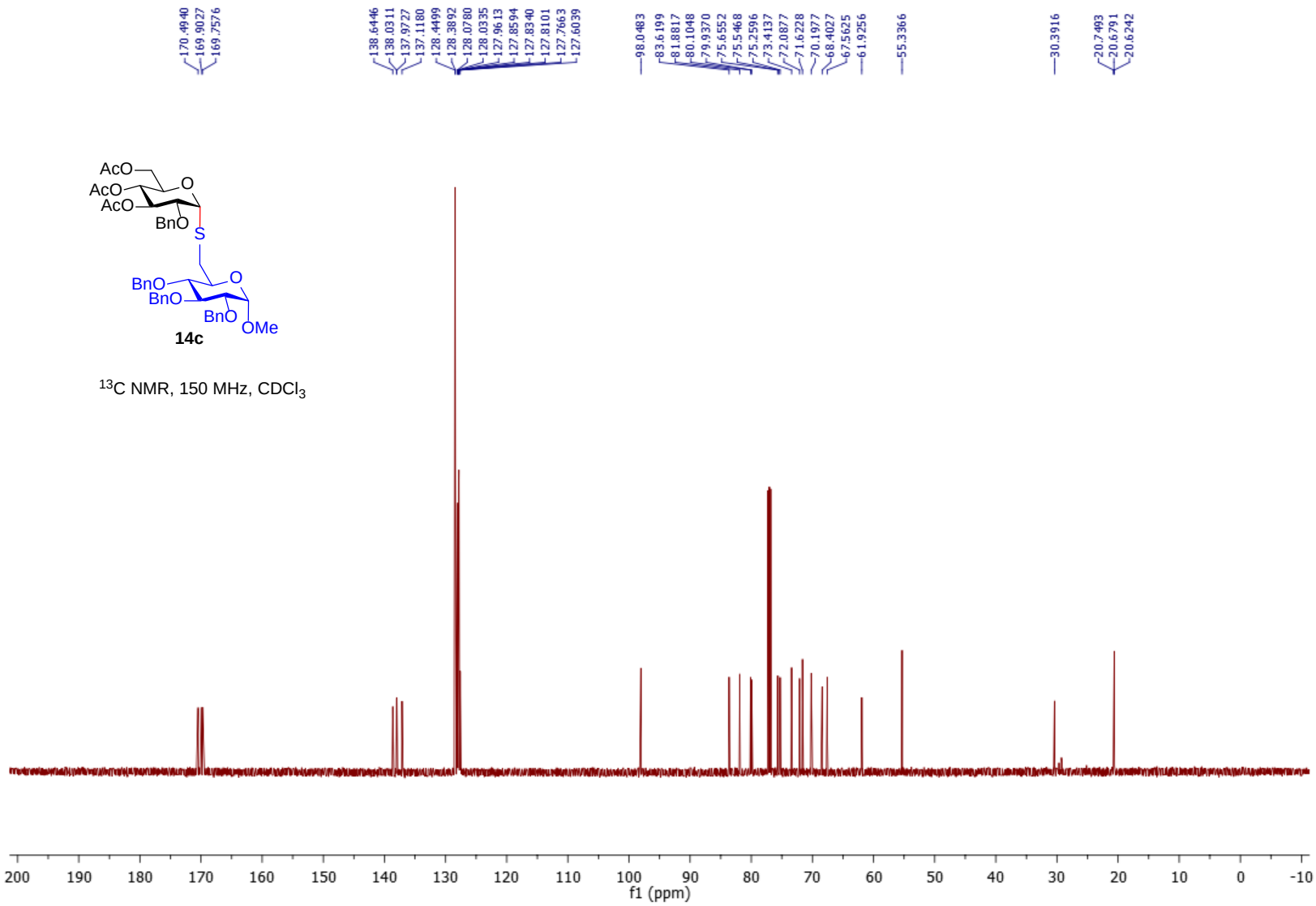
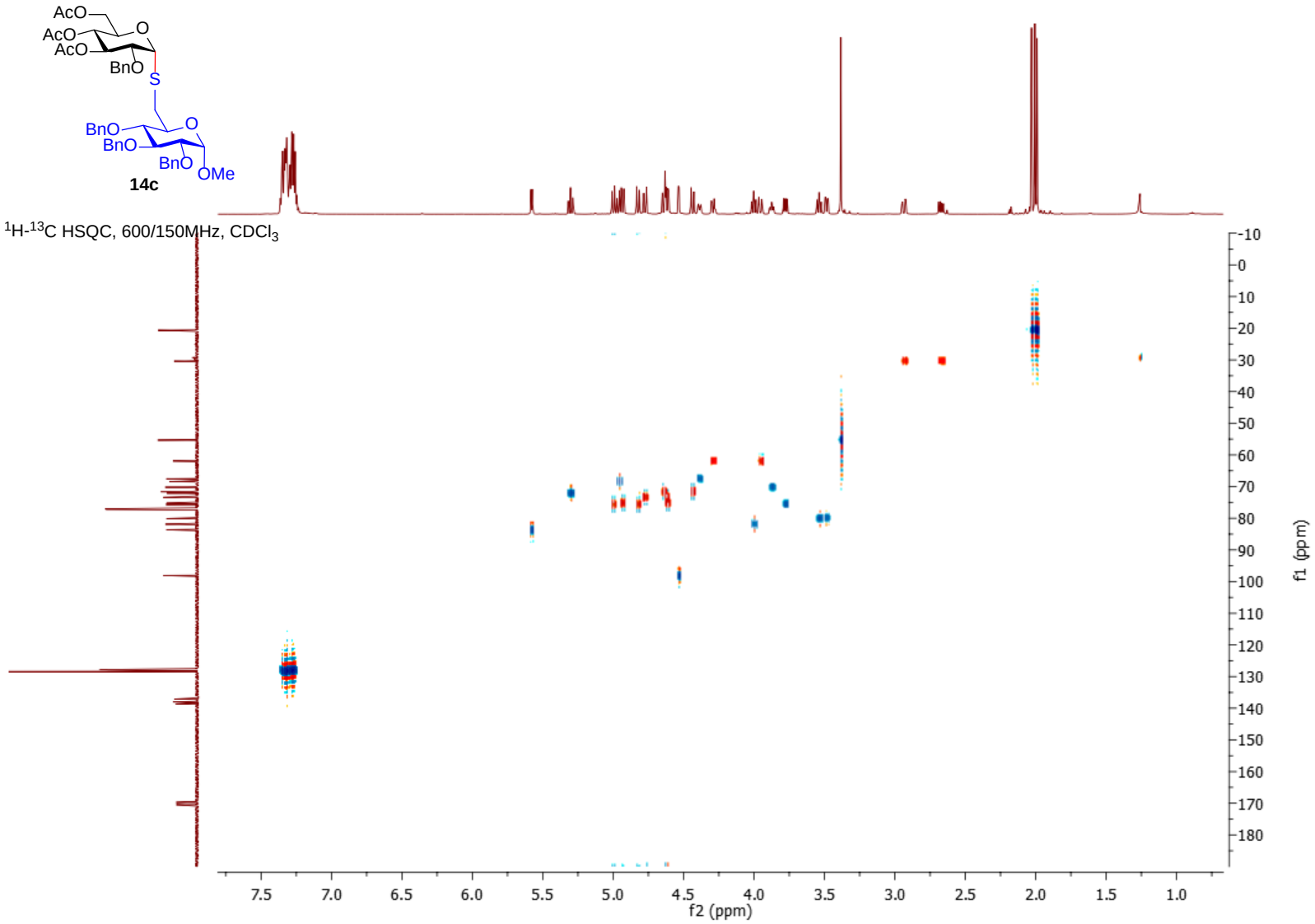
170.1062
169.6836
159.8936
138.6069
138.0566
138.0205
132.1842
130.6526
129.0650
128.4217
128.4047
128.3707
127.9858
127.9672
127.8819
127.8094
127.7635
127.6214
125.4382
97.7222
84.4674
81.9103
80.5000
80.1781
75.6961
75.1830
73.3156
69.7422
69.5381
67.1882
66.8528
61.9669
54.9894
30.2259
20.7535
20.6623
20.3740
AcO
OAc
O
AcO
N
S
2-CF3-Ph
BnO
BnO
O
BnO
OMe
14b
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

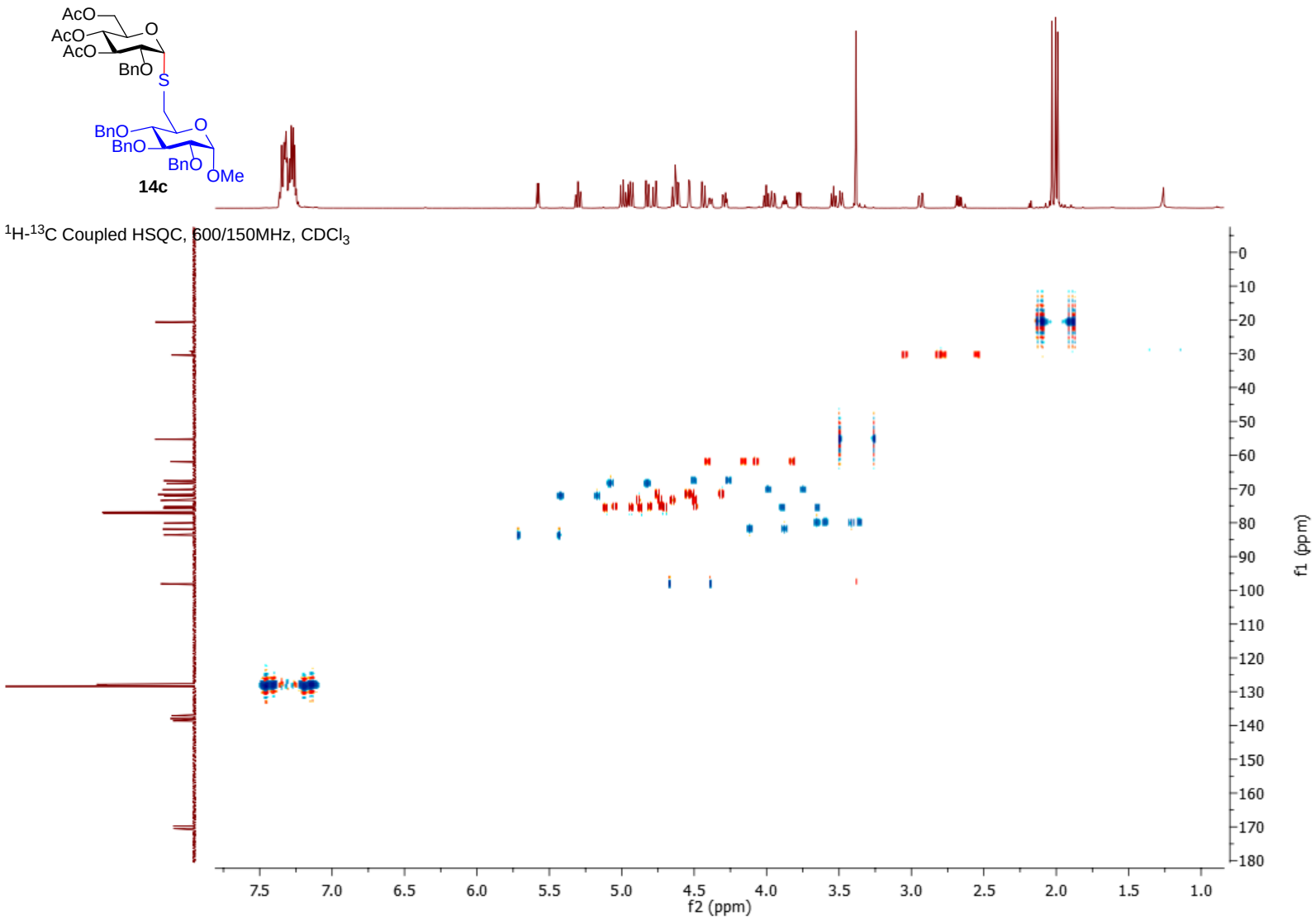

AcO
OAc
O
AcO
N
S
2-CF3-Ph
BnO
O
BnO
BnO
OMe
14b
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

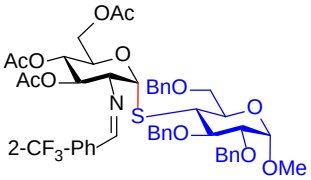

AcO
OAc
AcO
O
N
S
2-CF3-Ph
BnO
BnO
BnO
O
OMe
14b
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)


AcO
AcO
AcO
O
BnO
S
BnO
BnO
BnO
O
OMe
14c
1H NMR
600 MHz
CDCl3
f1 (ppm)


170.4940
169.9027
169.7576
138.6446
138.0311
137.9727
137.1180
128.4499
128.3892
128.0780
128.0335
127.9613
127.8594
127.8340
127.8101
127.7663
127.6039
98.0483
83.6199
81.8817
80.1048
79.9370
75.6552
75.5468
75.2596
73.4137
72.0877
71.6228
70.1977
68.4027
67.5625
61.9256
55.3366
30.3916
20.7493
20.6791
20.6242
AcO
AcO
AcO
O
BnO
S
BnO
BnO
BnO
O
OMe
14c
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


AcO
AcO
AcO
O
BnO
S
BnO
BnO
O
BnO
OMe
14c
1H-13C HSQC, 600/150MHz, CDCl3
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)


AcO
AcO
AcO
O
BnO
S
BnO
BnO
O
BnO
OMe
14c
^{1}H-^{13}C Coupled HSQC, 600/150MHz, $CDCl_3$
f2 (ppm)
f1 (ppm)

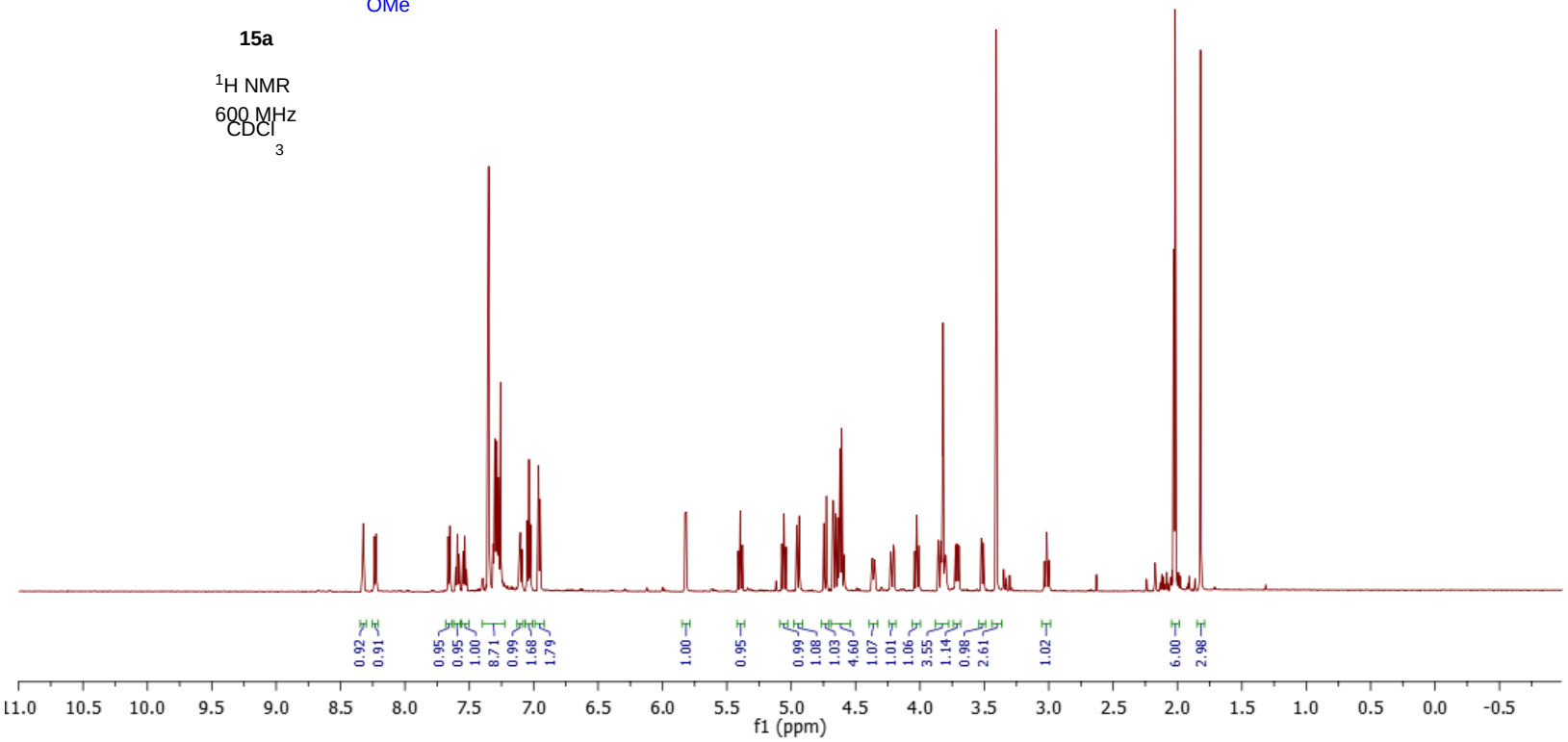


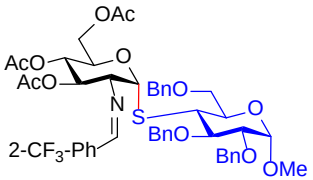
15a

^{1}H NMR

600 MHz

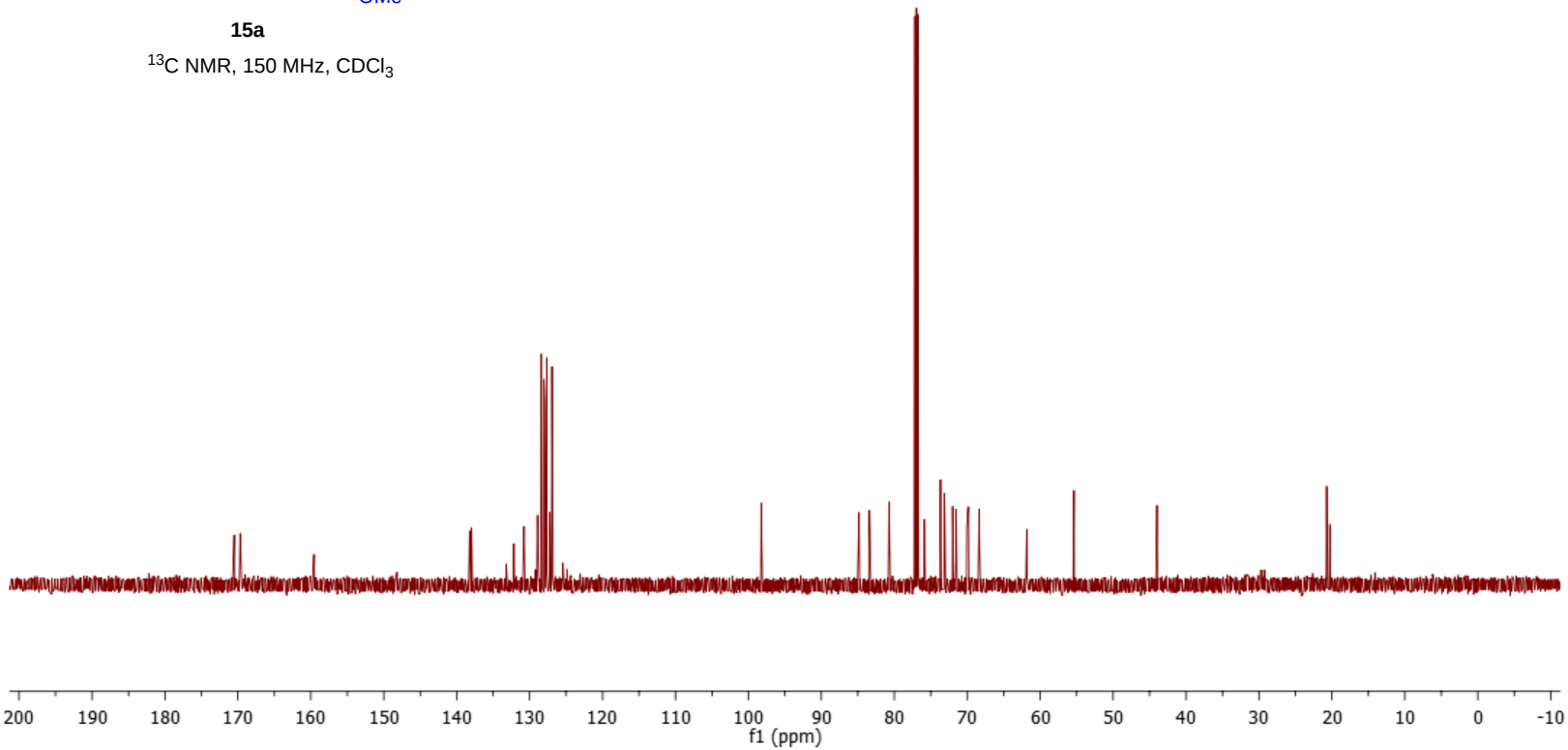
$CDCl_3$

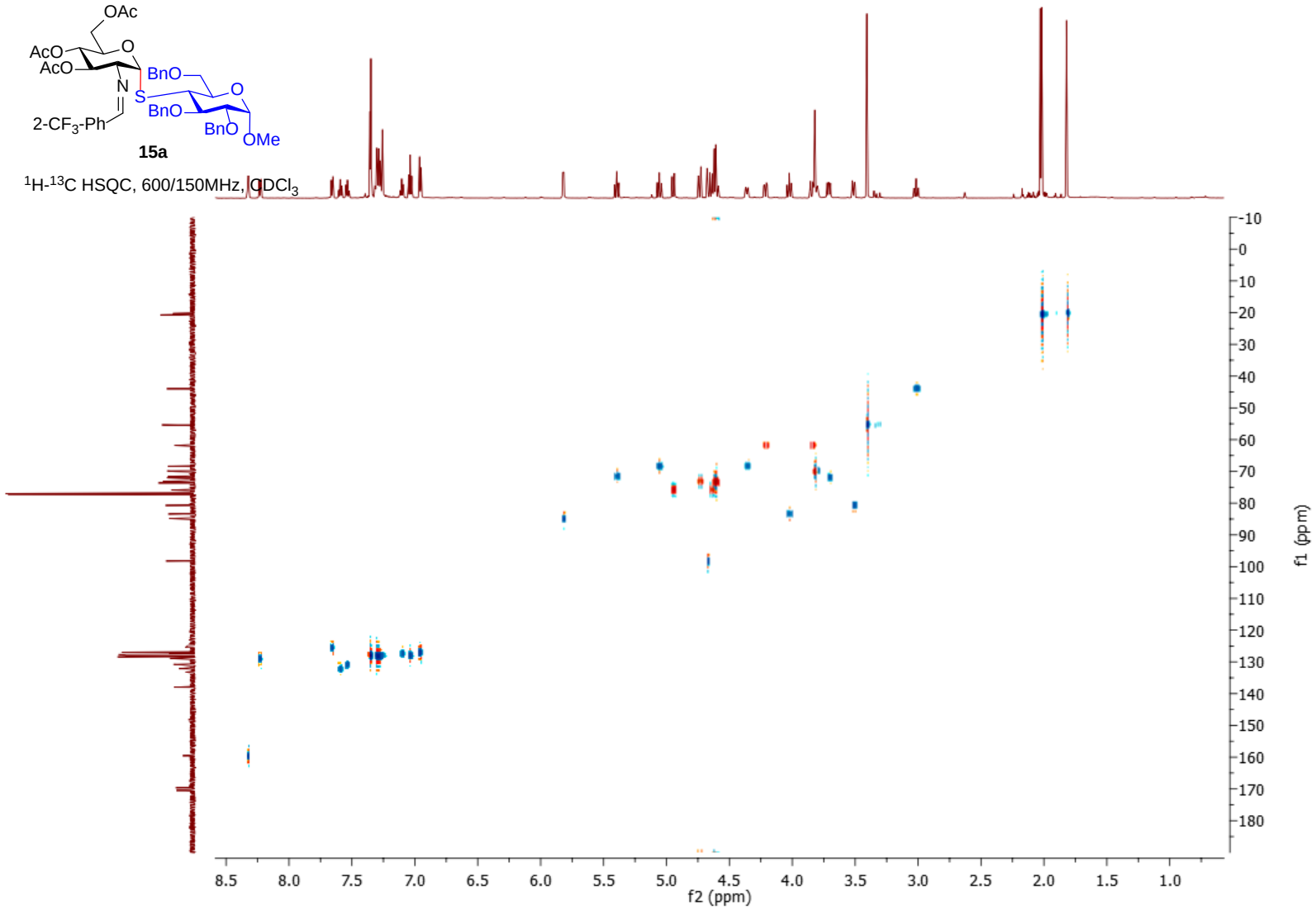


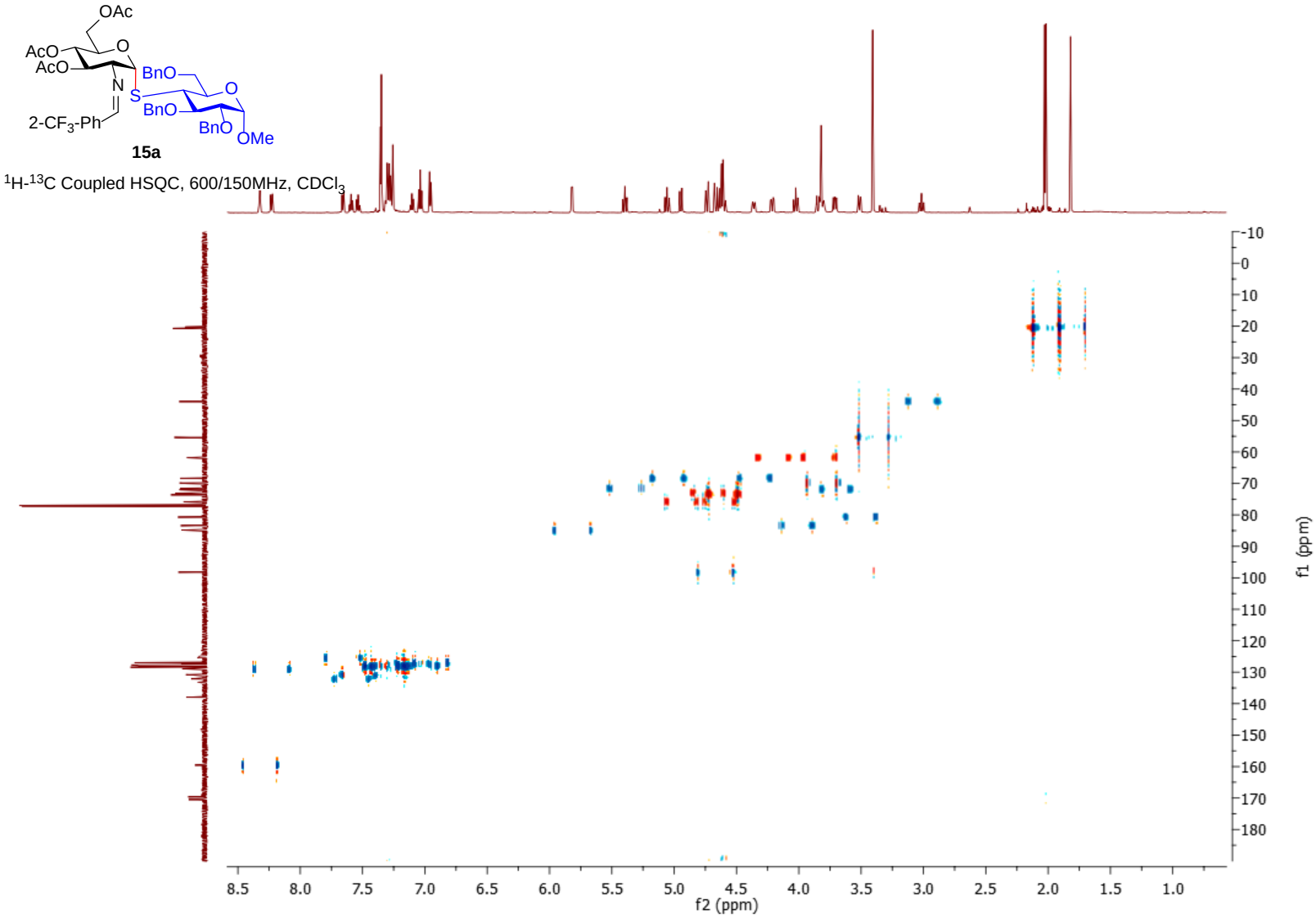


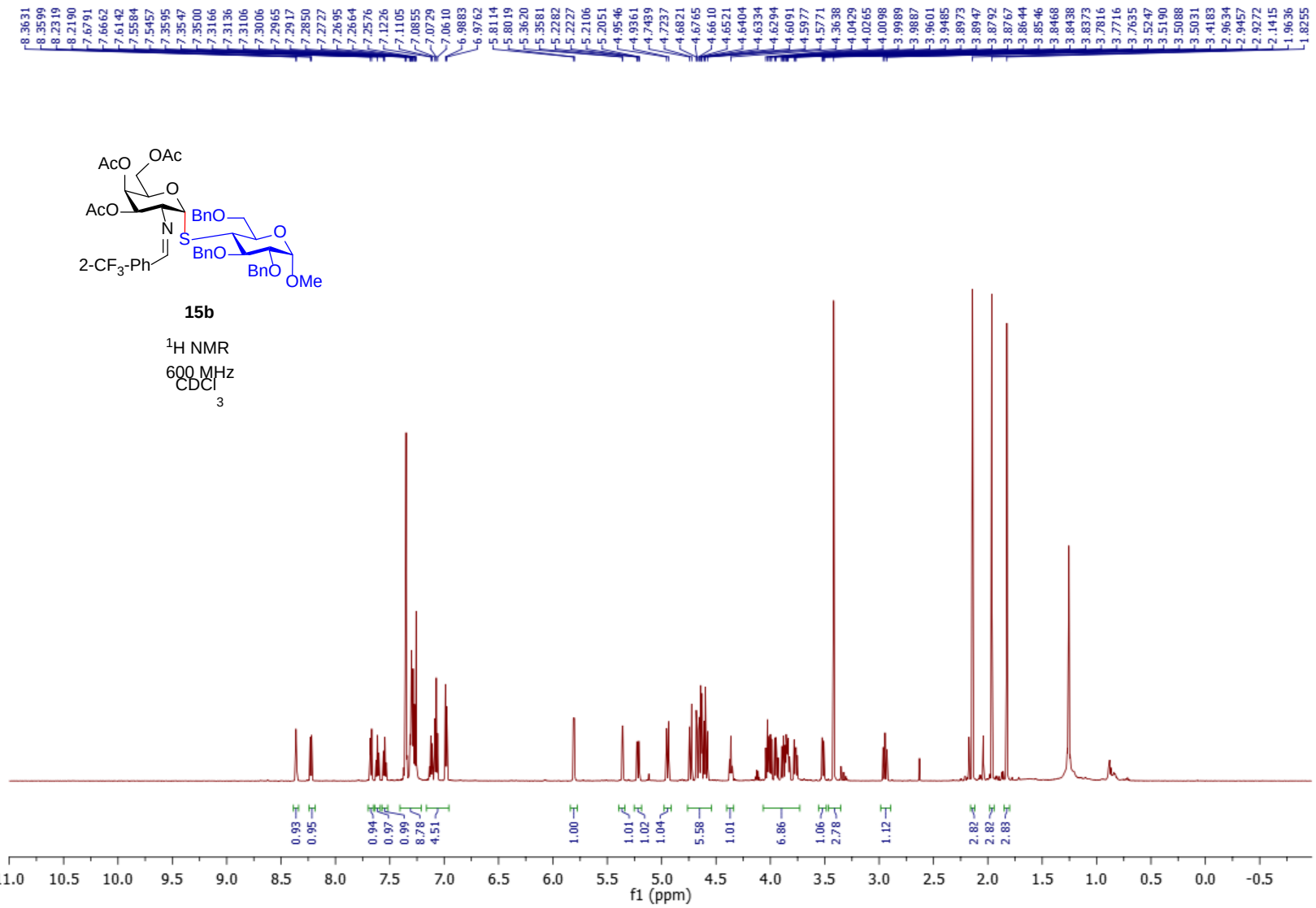
15a

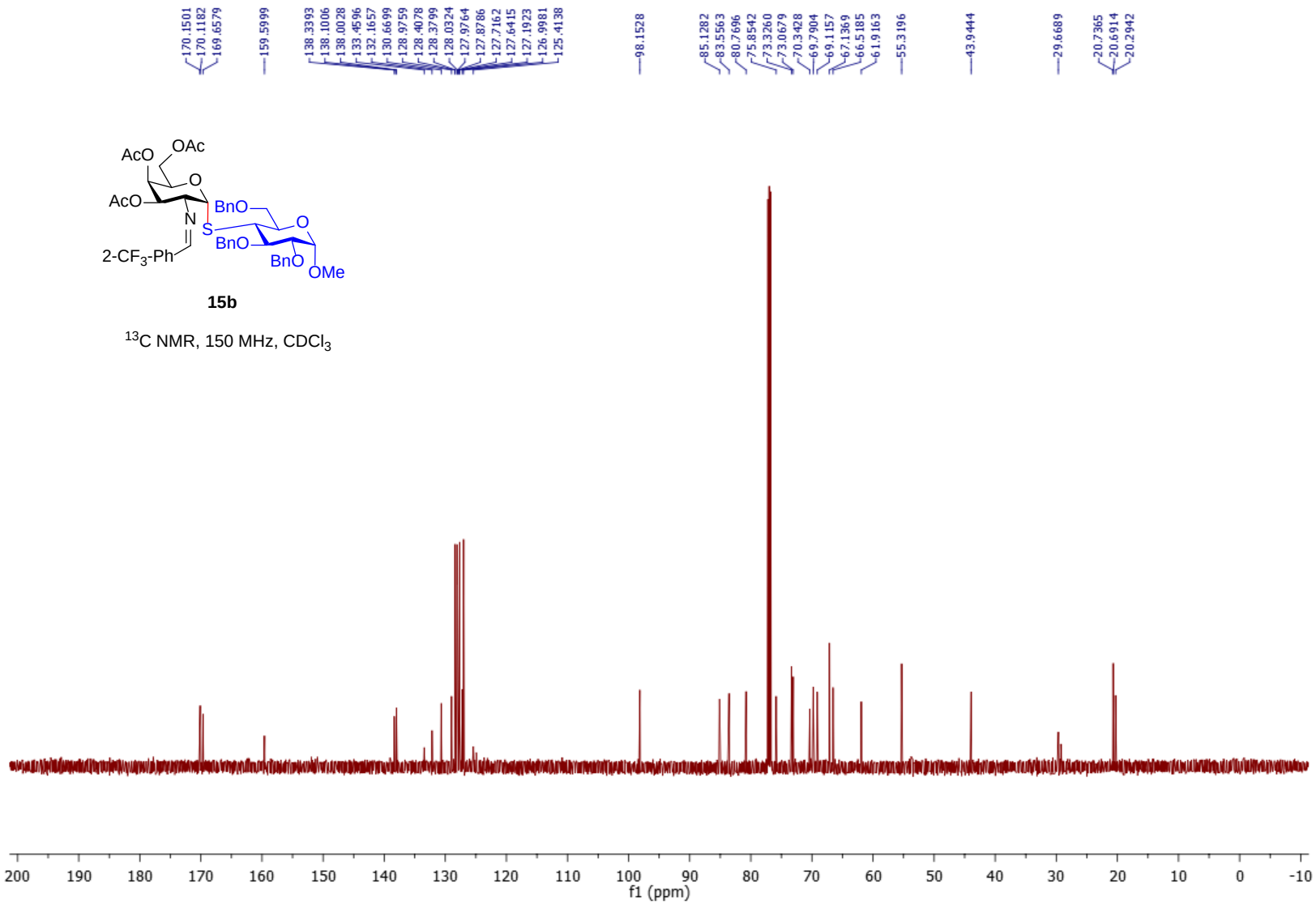
^{13}C NMR, 150 MHz, $CDCl_3$




OAc
AcO
AcO
O
N
S
BnO
BnO
BnO
O
OMe
2-CF3-Ph
15a
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

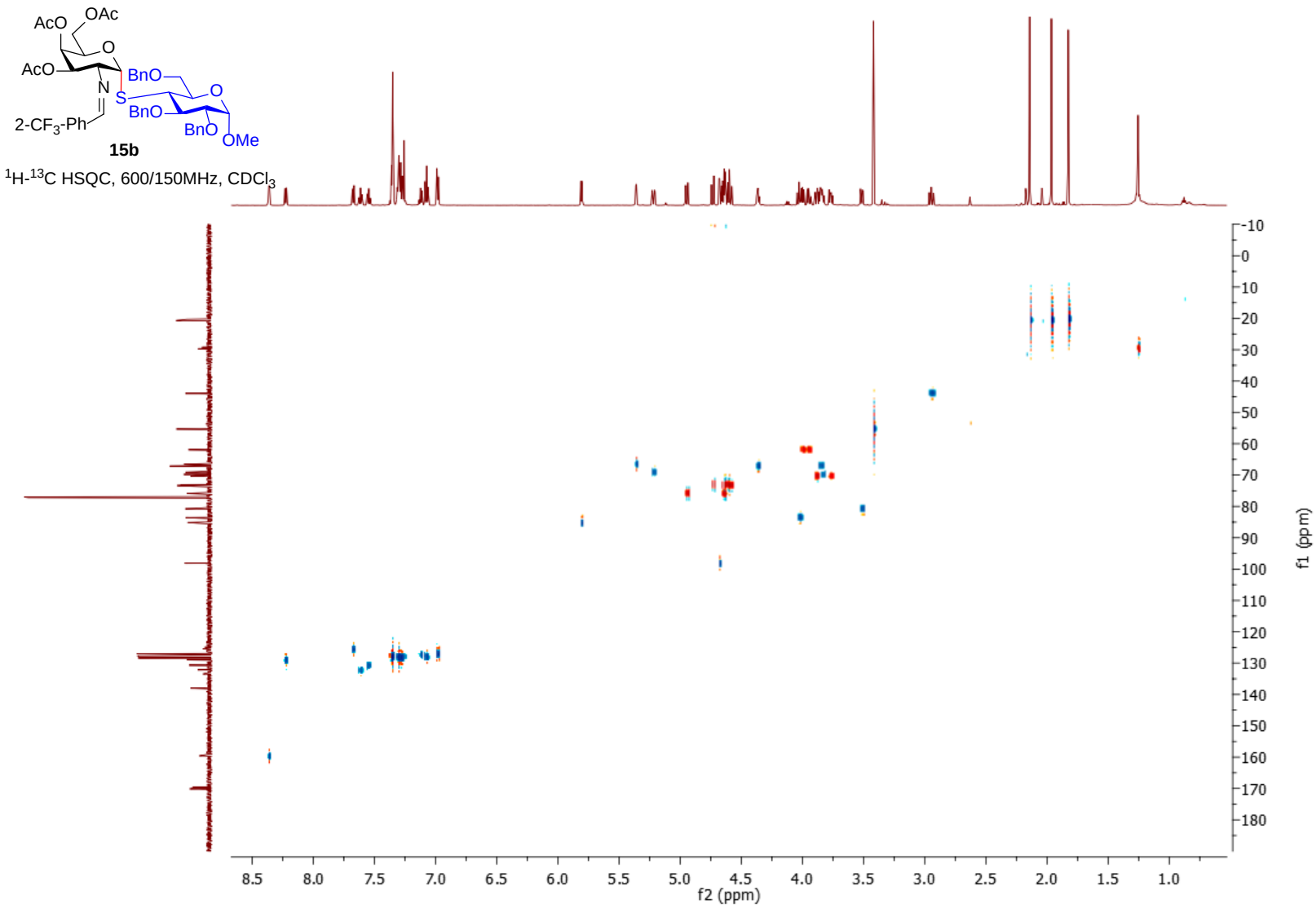

OAc
AcO
AcO
O
N
S
BnO
BnO
BnO
O
BnO
OMe
2-CF3-Ph
15a
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

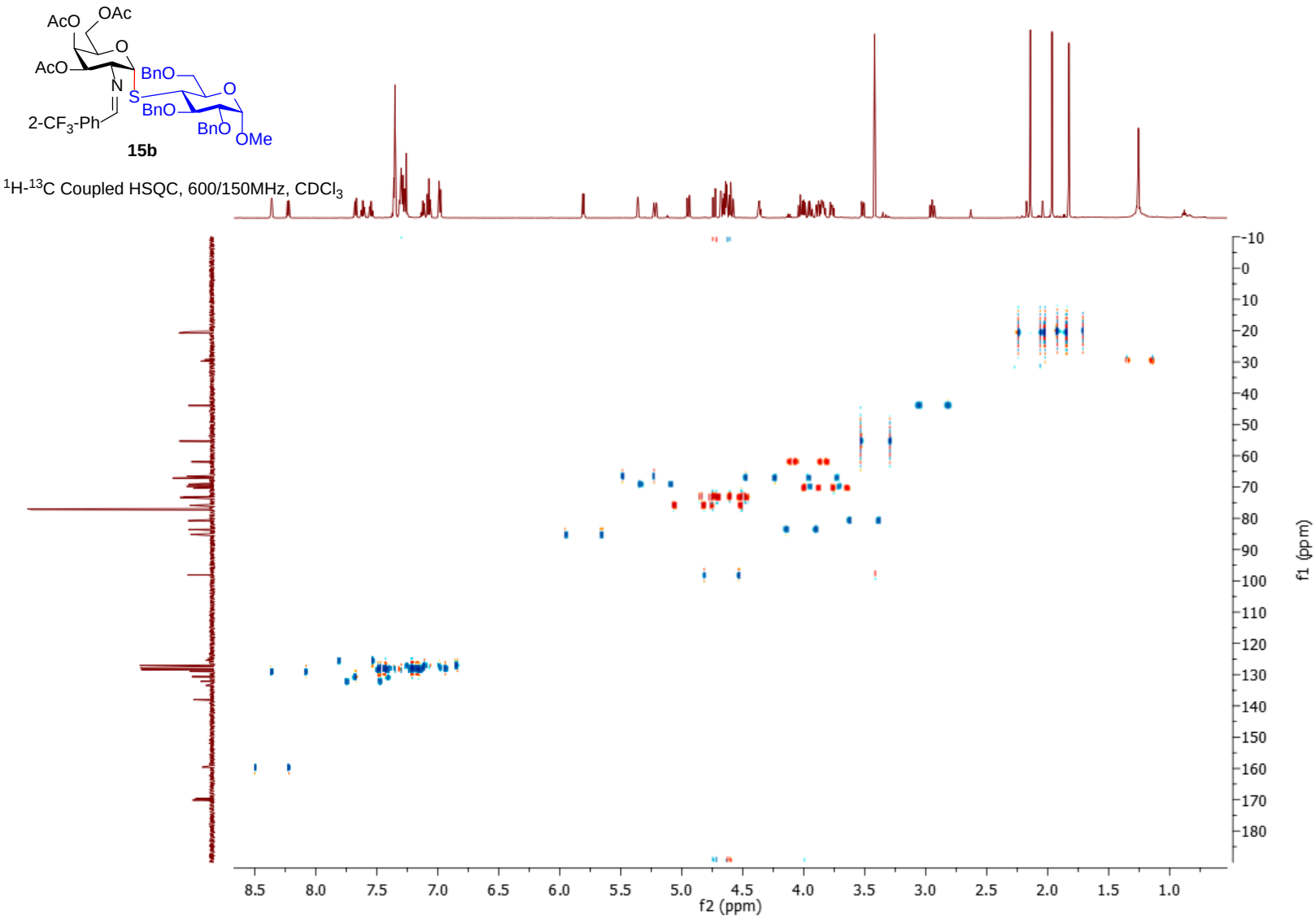

8.3631
8.3599
8.2319
8.2190
7.6791
7.6662
7.6142
7.5584
7.5457
7.3595
7.3547
7.3500
7.3166
7.3136
7.3106
7.3006
7.2965
7.2917
7.2850
7.2727
7.2695
7.2664
7.2576
7.1226
7.1105
7.0855
7.0729
7.0610
6.9883
6.9762
5.8114
5.8019
5.3620
5.3581
5.2282
5.2227
5.2106
5.2051
4.9546
4.9361
4.7439
4.7237
4.6821
4.6765
4.6610
4.6521
4.6404
4.6334
4.6294
4.6091
4.5977
4.5771
4.3638
4.0429
4.0265
4.0098
3.9989
3.9887
3.9601
3.9485
3.8973
3.8947
3.8792
3.8767
3.8644
3.8546
3.8468
3.8438
3.8373
3.7816
3.7716
3.7635
3.5247
3.5190
3.5088
3.5031
3.4183
2.9634
2.9457
2.9272
2.1415
1.9636
1.8255
AcO
OAc
O
AcO
BnO
N
S
O
BnO
BnO
OMe
2-CF3-Ph
15b
1H NMR
600 MHz
CDCl3
0.93
0.95
0.94
0.97
0.99
8.78
4.51
1.00
1.01
1.02
1.04
5.58
1.01
6.86
1.06
2.78
1.12
2.82
2.83
2.83
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

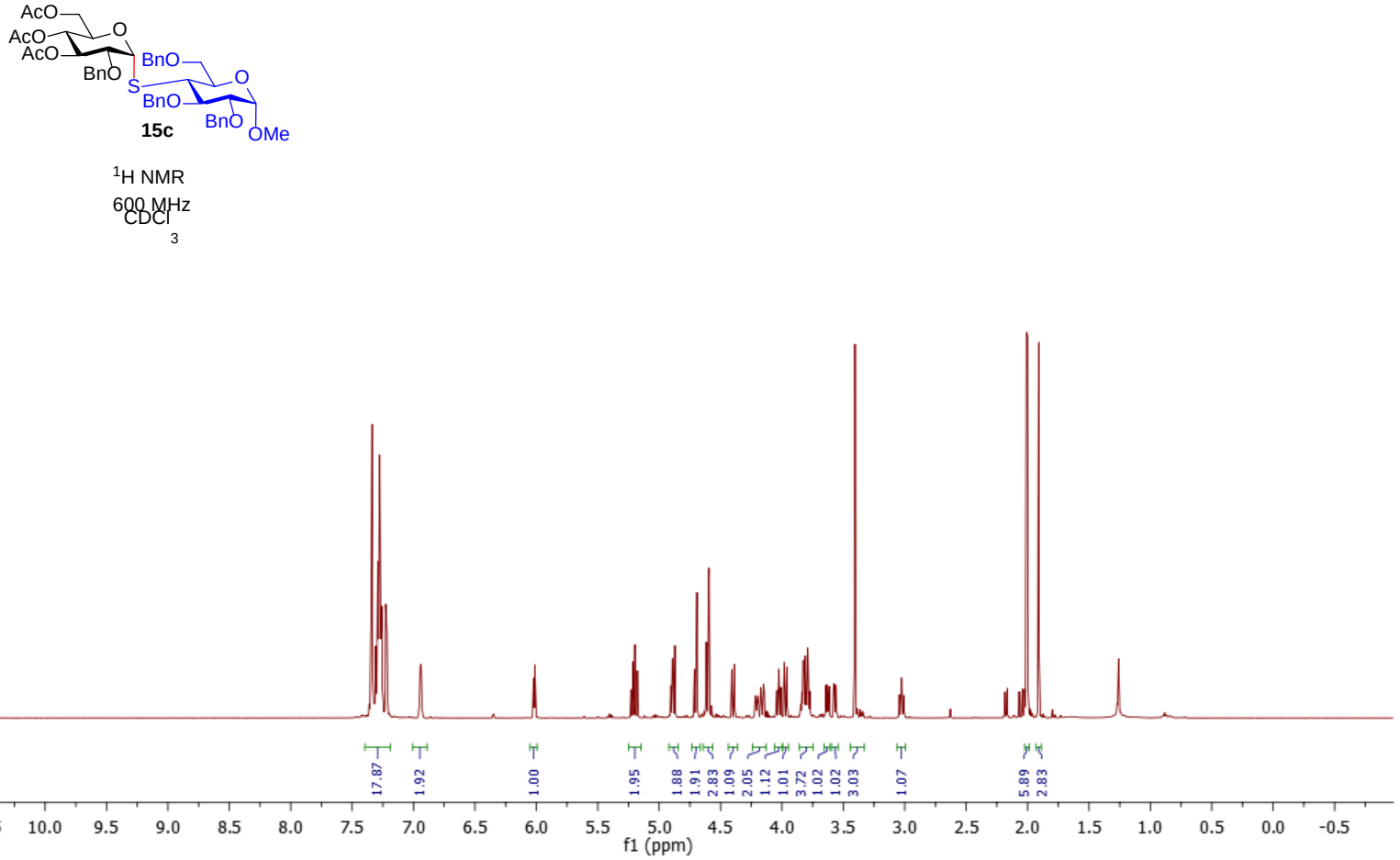


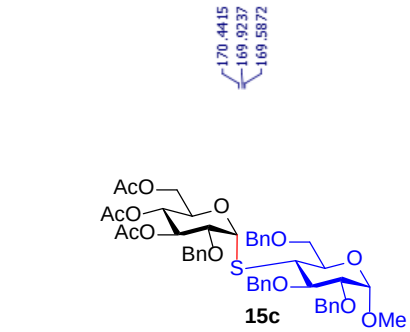
15b

^{13}C NMR, 150 MHz, $CDCl_3$


AcO
OAc
O
AcO
BnO
N
S
O
BnO
2-CF3-Ph
BnO
OMe
15b
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

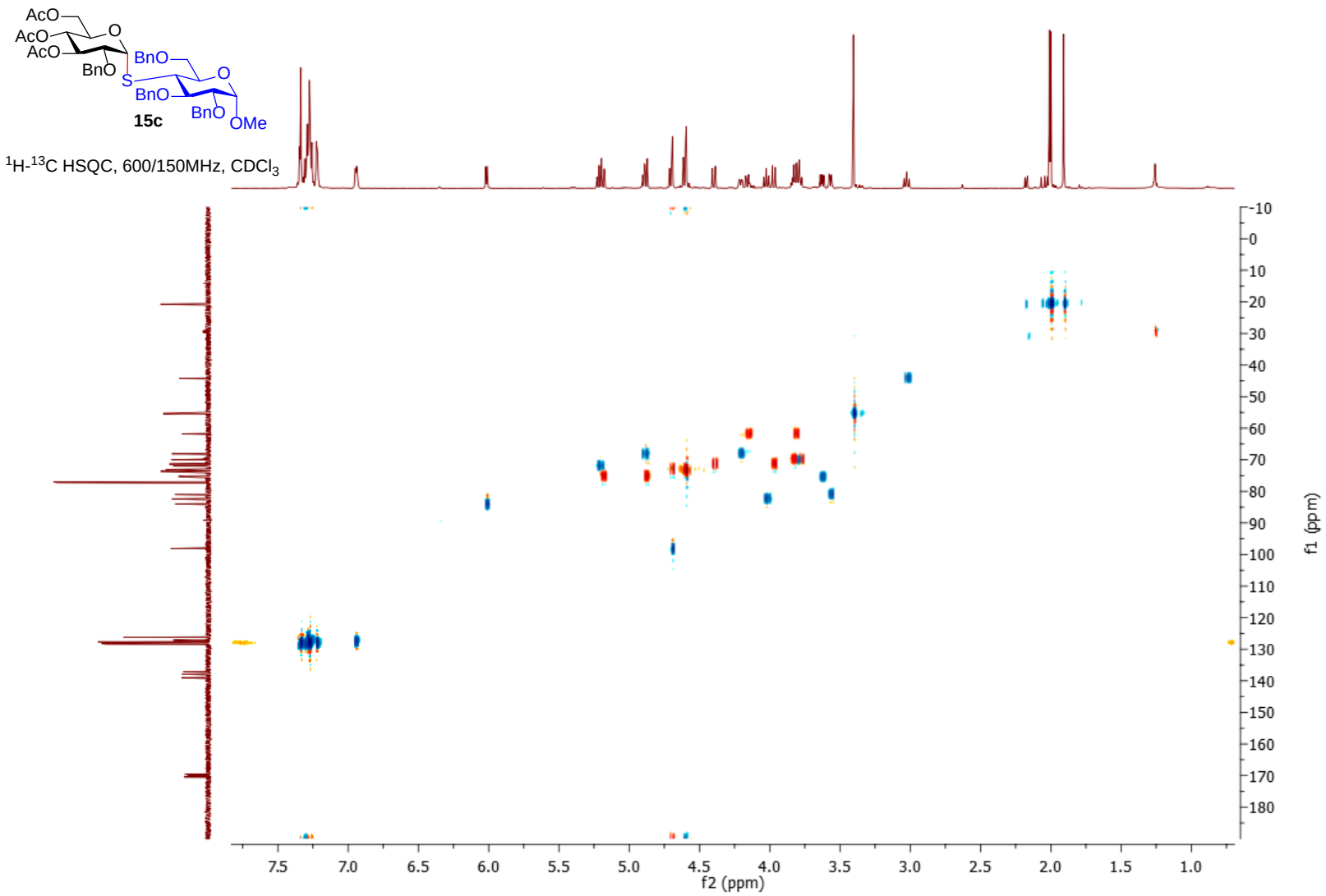

AcO
OAc
O
AcO
BnO
N
S
O
BnO
2-CF3-Ph
BnO
OMe
15b
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

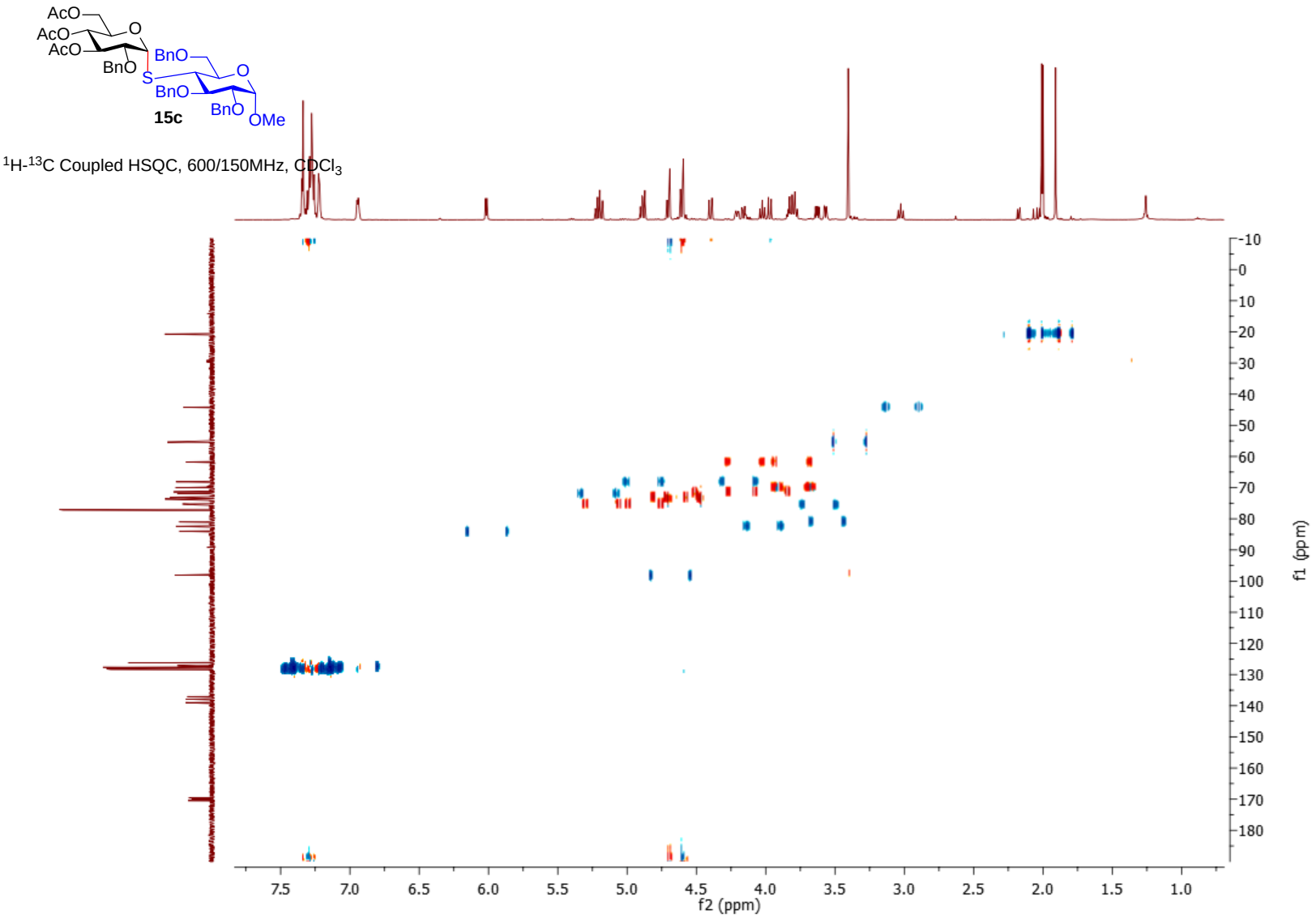

7.3465
7.3414
7.3369
7.3279
7.3196
7.3073
7.2950
7.2898
7.2761
7.2746
7.2680
7.2573
7.2463
7.2271
7.2227
7.2165
6.9488
6.9454
6.9393
6.9336
6.0206
6.0112
5.2130
5.1971
4.8919
4.8885
4.8719
4.7122
4.6982
4.6923
4.6151
4.5979
4.5943
4.3875
3.9812
3.9606
3.8280
3.8099
3.7898
3.0259
3.0079
2.0094
1.9999
1.9087
AcO
AcO
AcO
O
BnO
S
BnO
BnO
O
BnO
OMe
15c
1H NMR
600 MHz
CDCl3
17.87
1.92
1.00
1.95
1.88
1.91
2.83
1.09
2.05
1.12
1.01
3.72
1.02
1.02
3.03
1.07
5.89
2.83
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

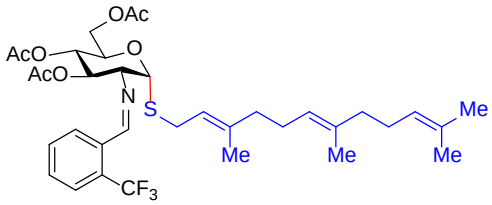


15c

^{13}C NMR, 150 MHz, $CDCl_3$


AcO
AcO
AcO
O
BnO
S
BnO
O
BnO
BnO
OMe
15c
^{1}H-^{13}C HSQC, 600/150MHz, CDCl$_3$
f2 (ppm)
f1 (ppm)


AcO
AcO
AcO
BnO
O
BnO
S
BnO
O
BnO
OMe
15c
^{1}H-^{13}C Coupled HSQC, 600/150MHz, CDCl$_3$
f2 (ppm)
f1 (ppm)

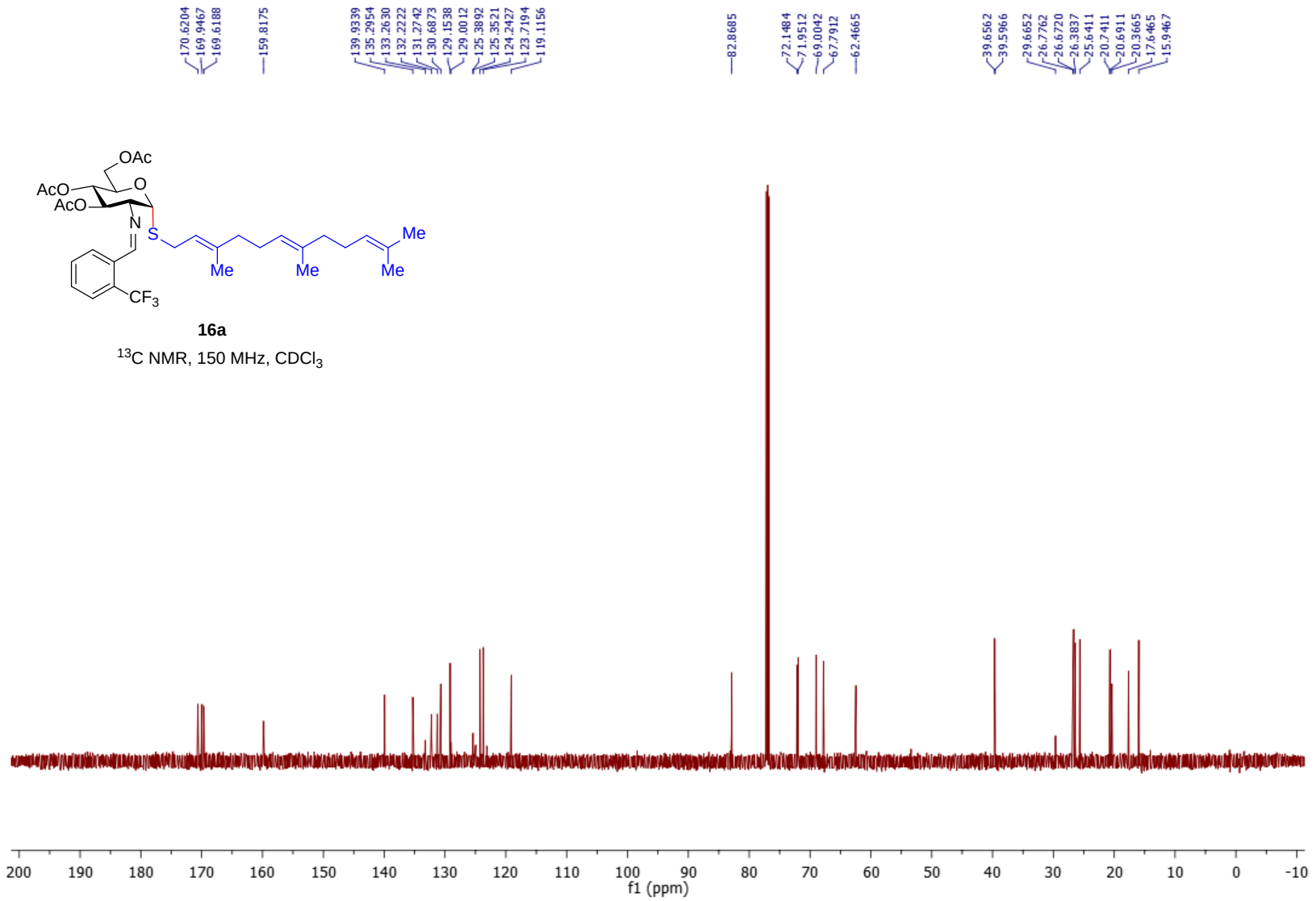


16a

^{1}H NMR

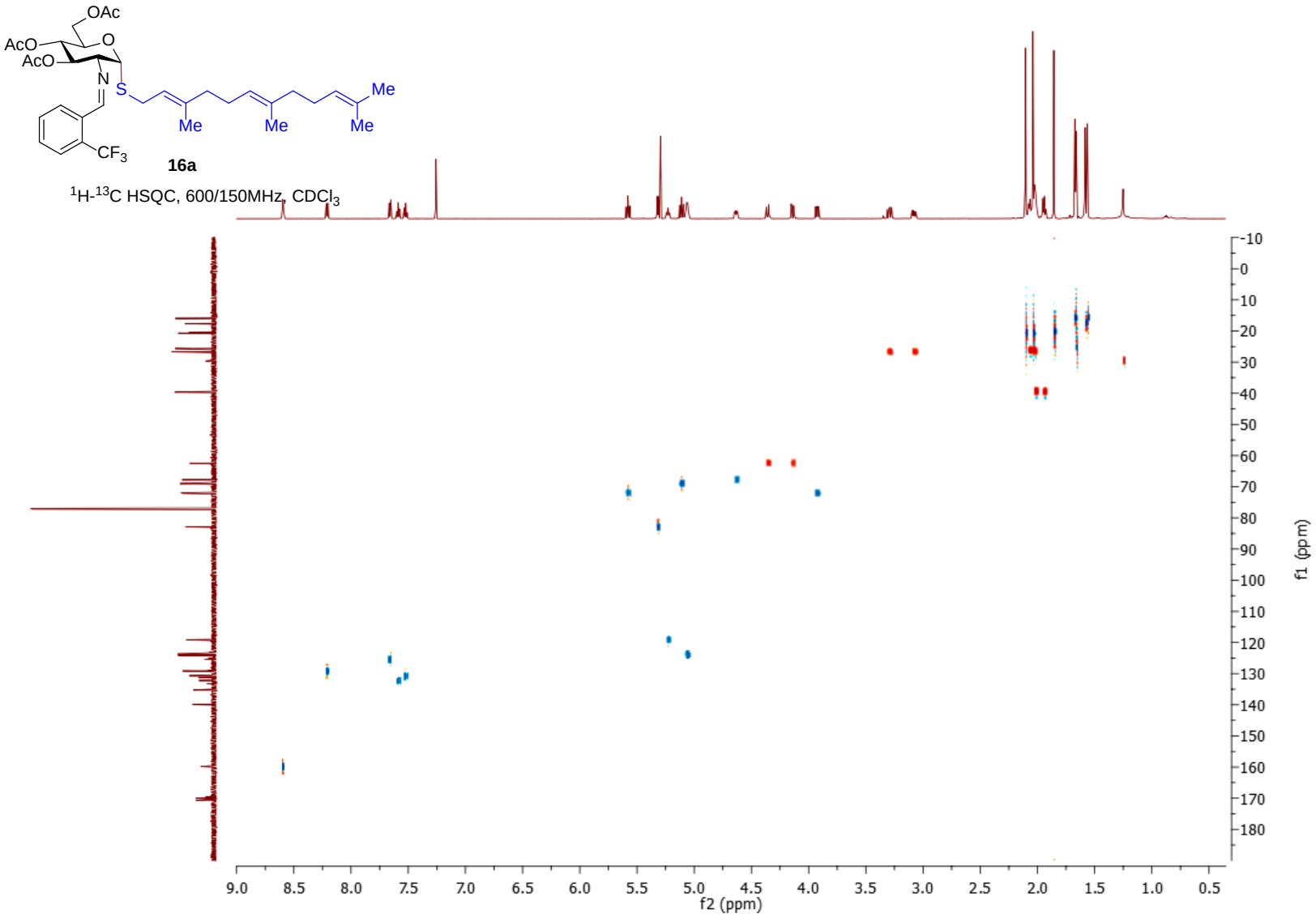
600 MHz

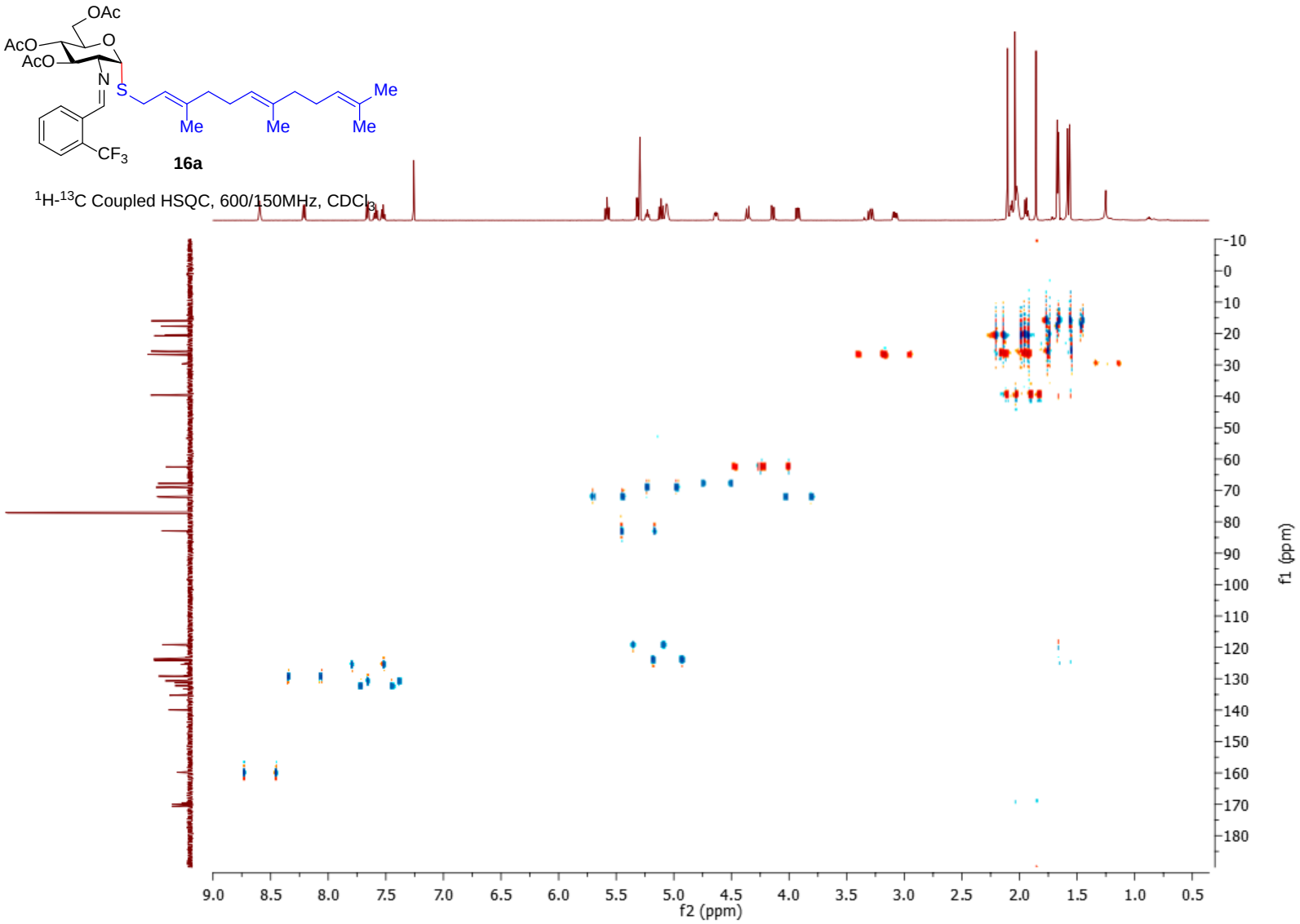
$CDCl_3$

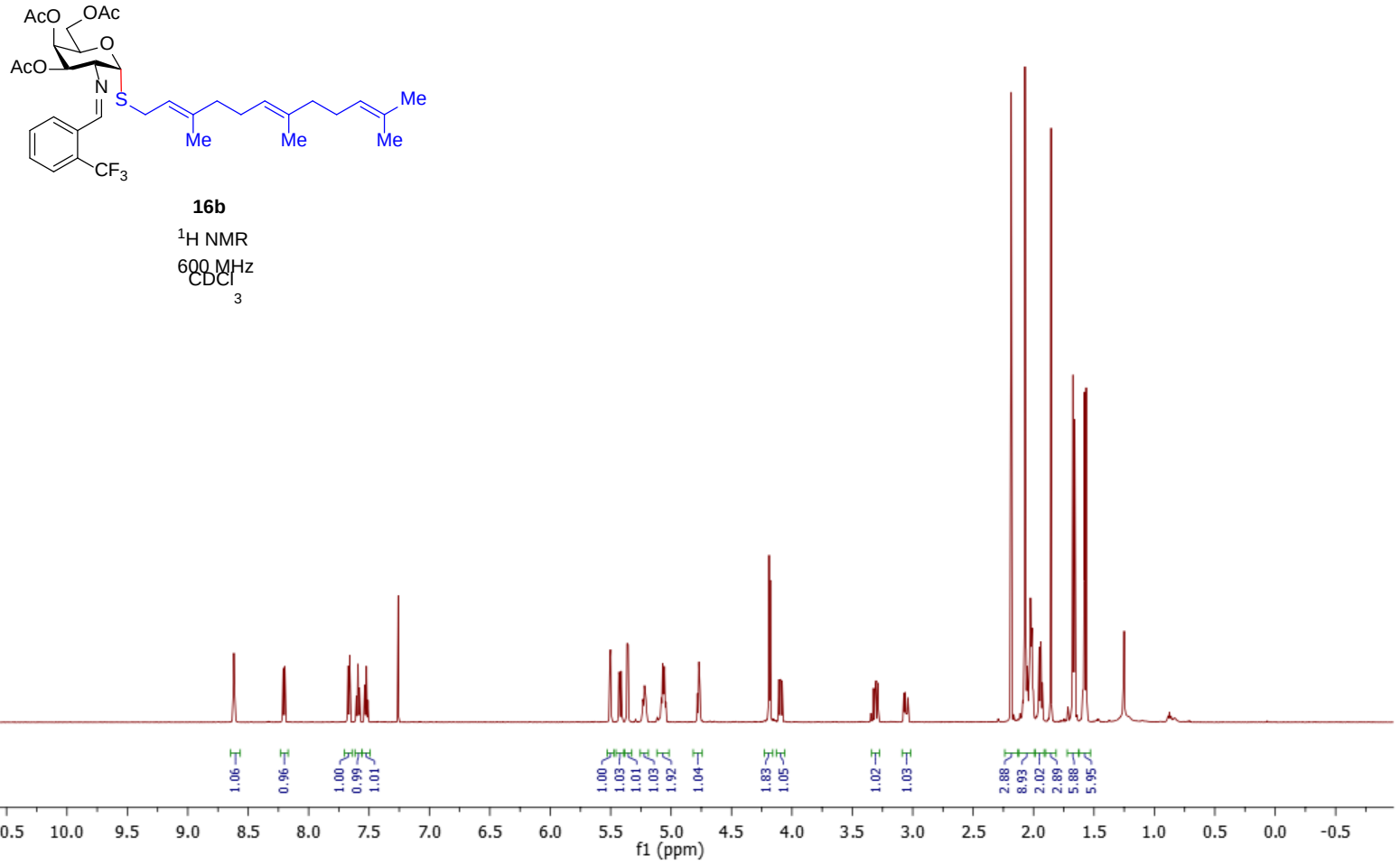


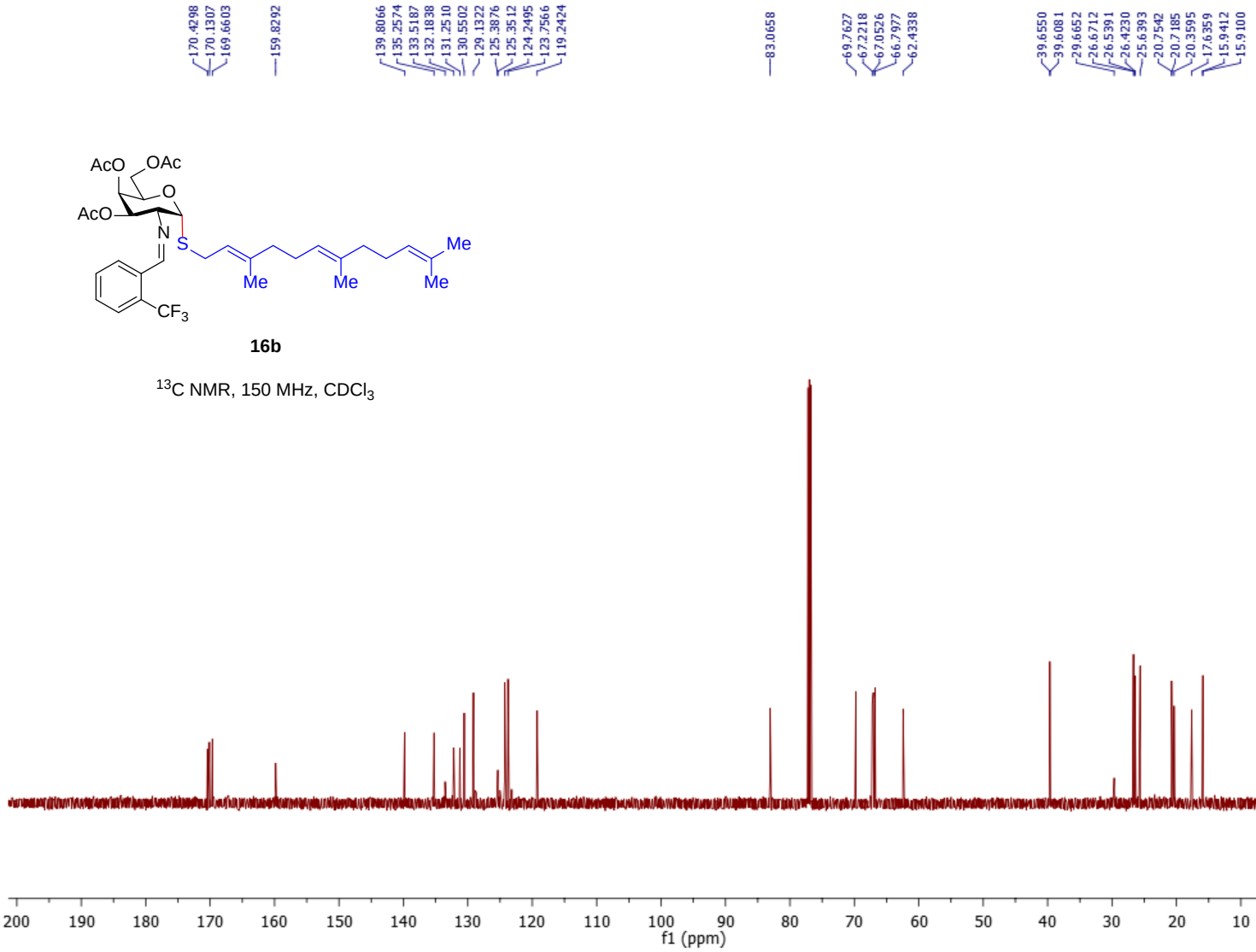
16a

^{13}C NMR, 150 MHz, $CDCl_3$


OAc
AcO
AcO
O
N
S
Me
Me
Me
Me
CF3
16a
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

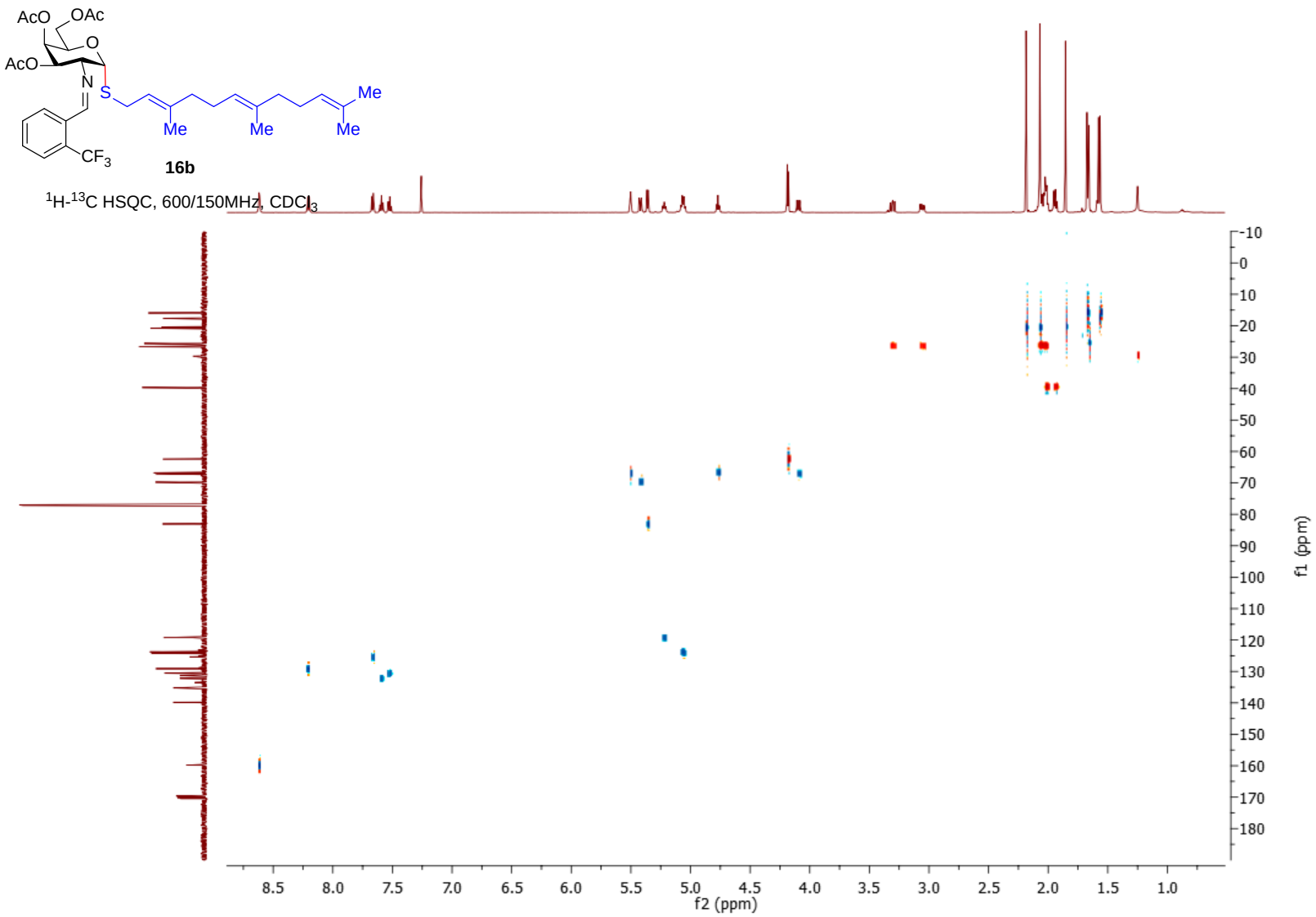

OAc
AcO
AcO
O
N
S
Me
Me
Me
Me
CF3
16a
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

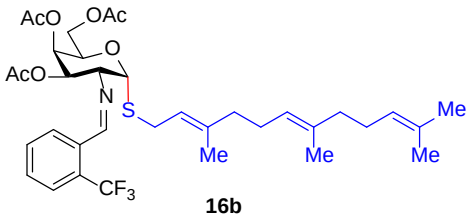

AcO
OAc
O
AcO
N
S
Me
Me
Me
Me
CF3
16b
1H NMR
600 MHz
CDCl3
f1 (ppm)



16b

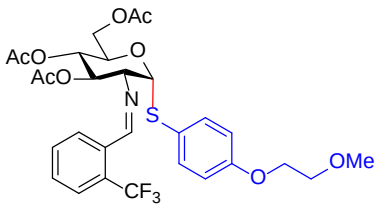
^{13}C NMR, 150 MHz, $CDCl_3$


AcO
OAc
O
AcO
N
S
Me
Me
Me
Me
CF3
16b
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)



16b

^{1}H-^{13}C Coupled HSQC, 600/150MHz, $CDCl_3$

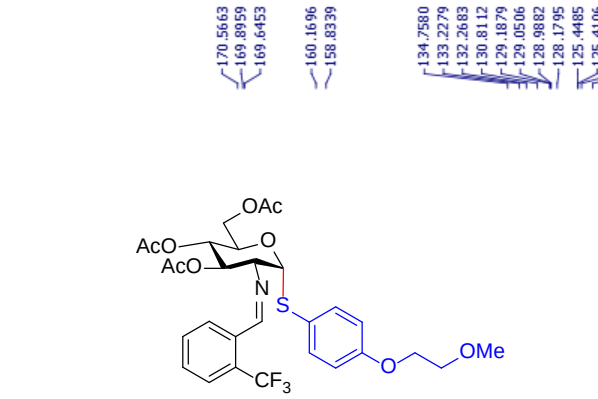


17a

^{1}H NMR

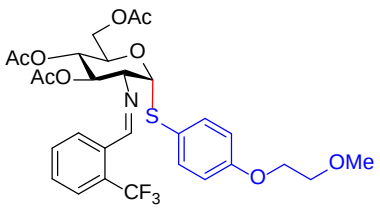
600 MHz

$CDCl_3$



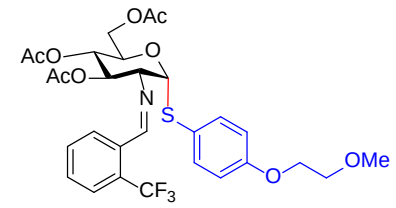
17a

^{13}C NMR, 150 MHz, $CDCl_3$



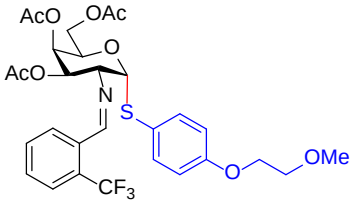
17a

^{1}H-^{13}C HSQC, 600/150MHz, $CDCl_3$



17a

^{1}H-^{13}C Coupled HSQC, 600/150MHz, $CDCl_3$

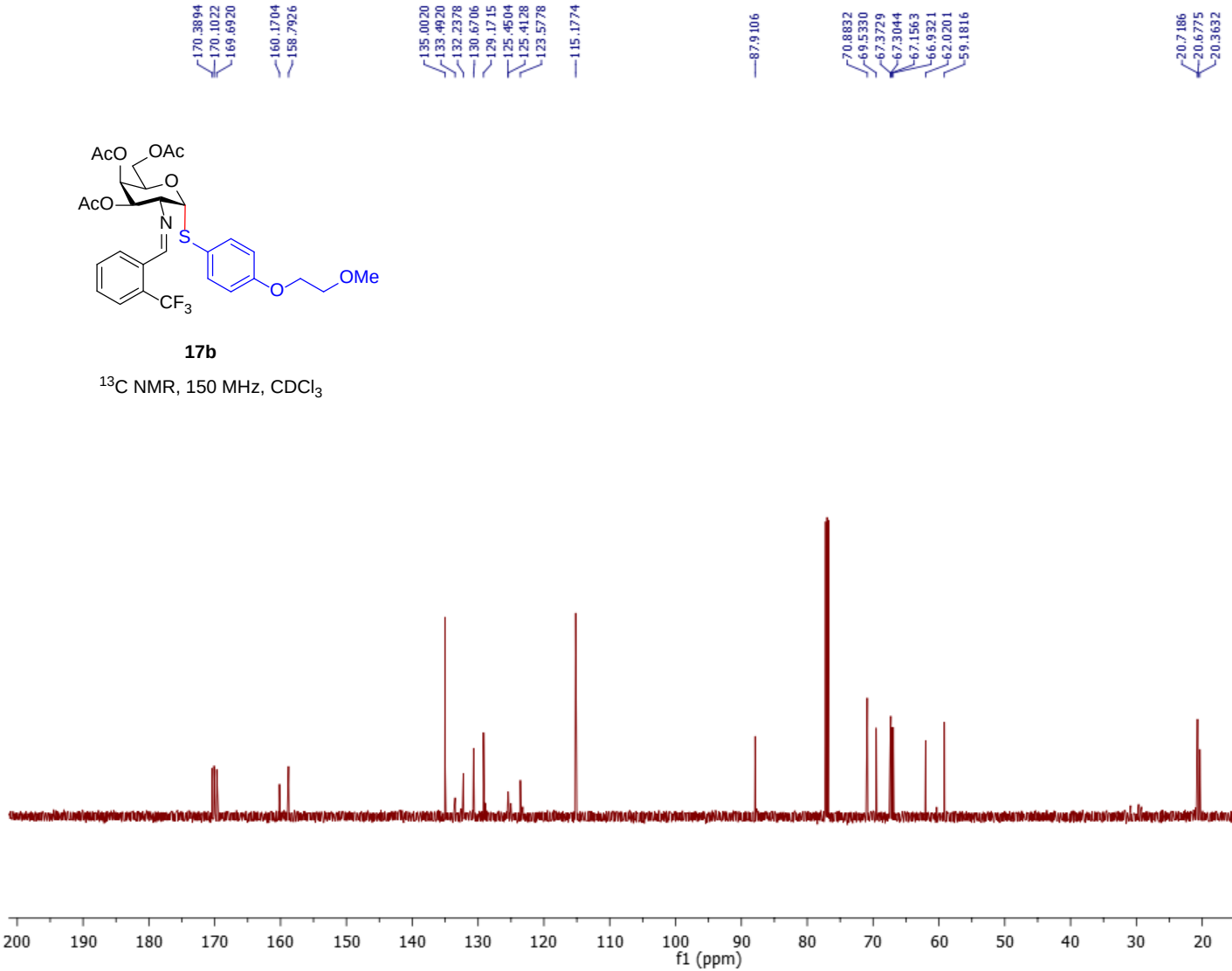


17b

^{1}H NMR

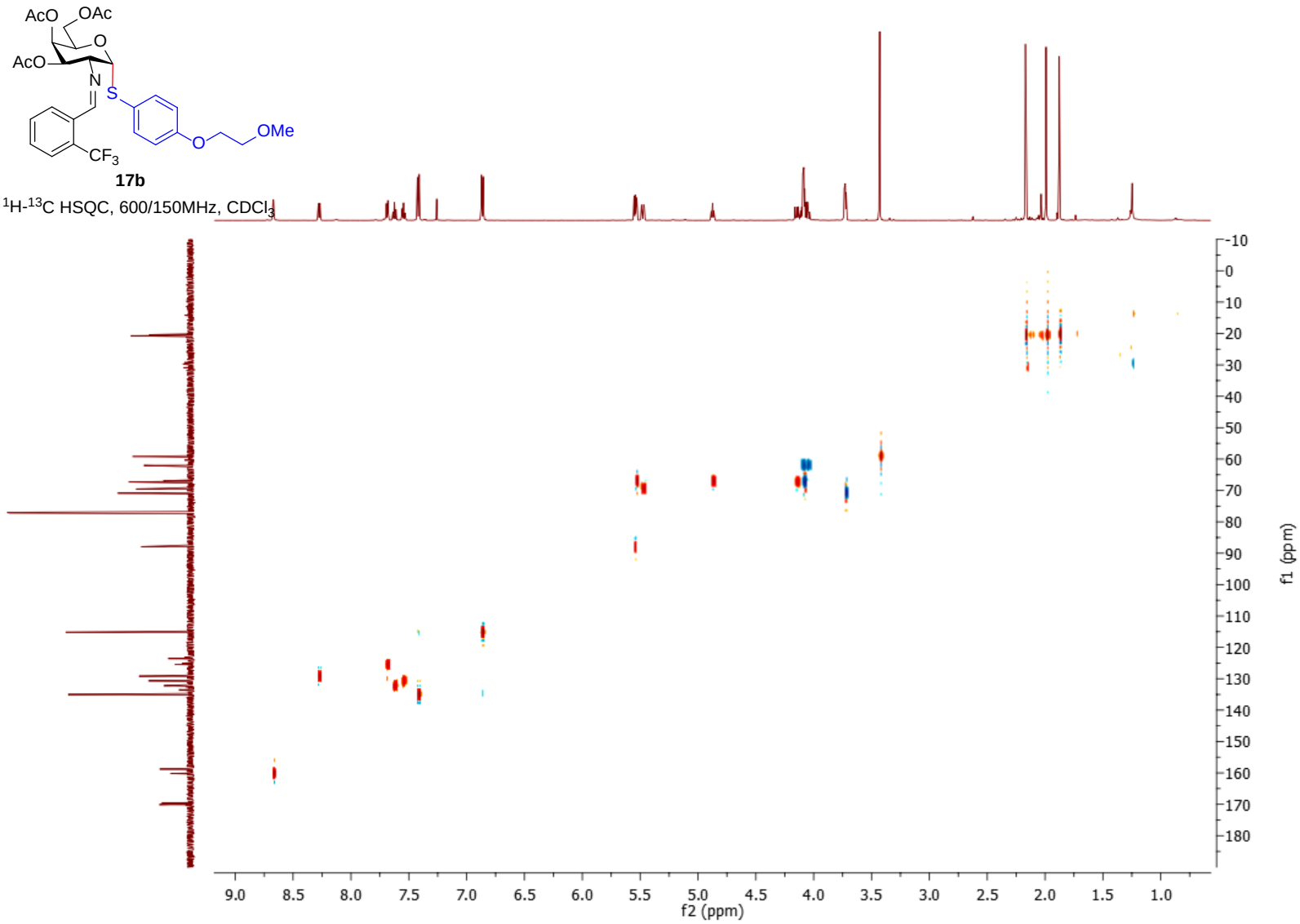
600 MHz

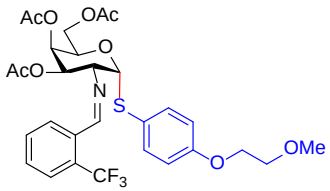
$CDCl_3$



17b

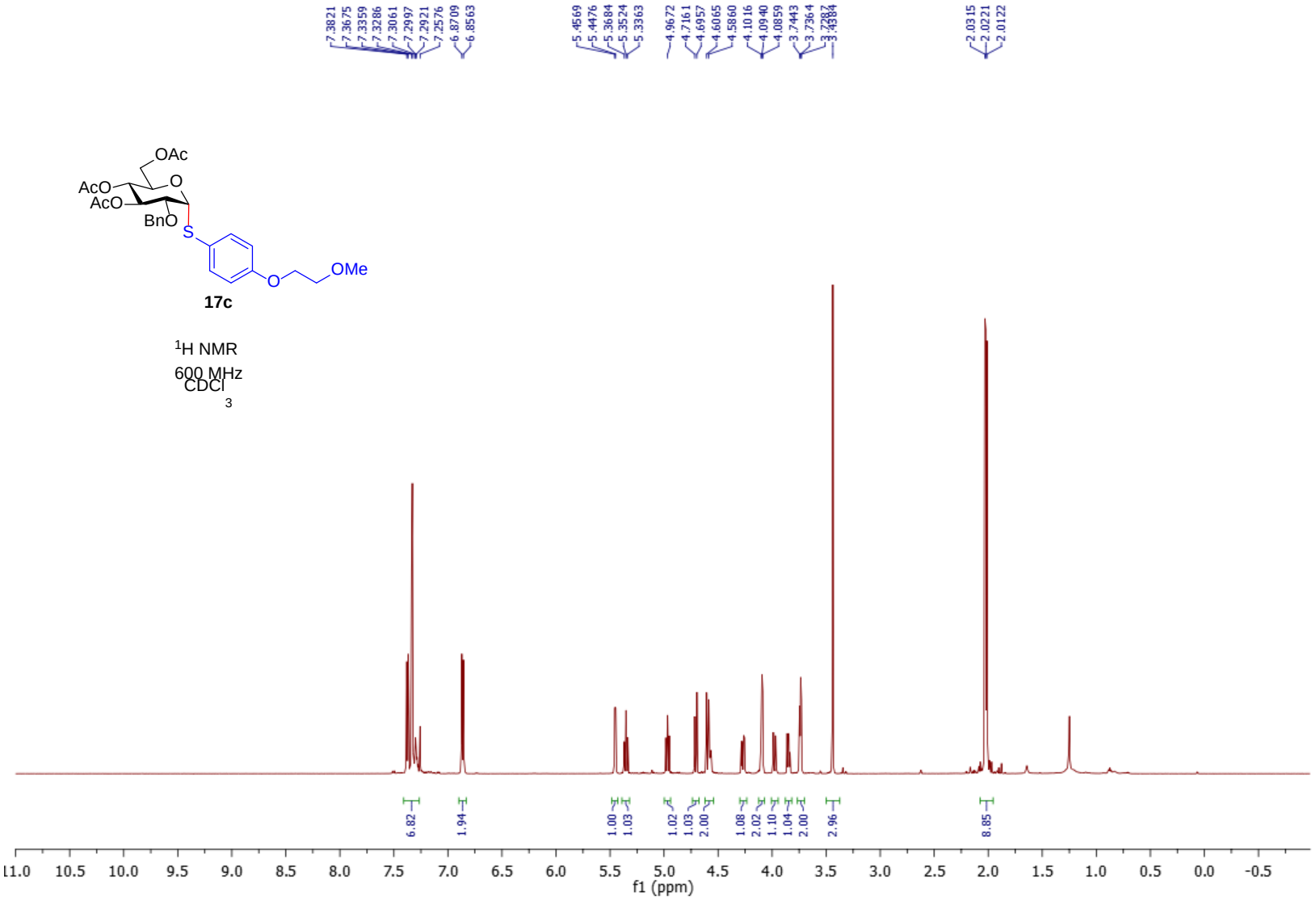
^{13}C NMR, 150 MHz, $CDCl_3$

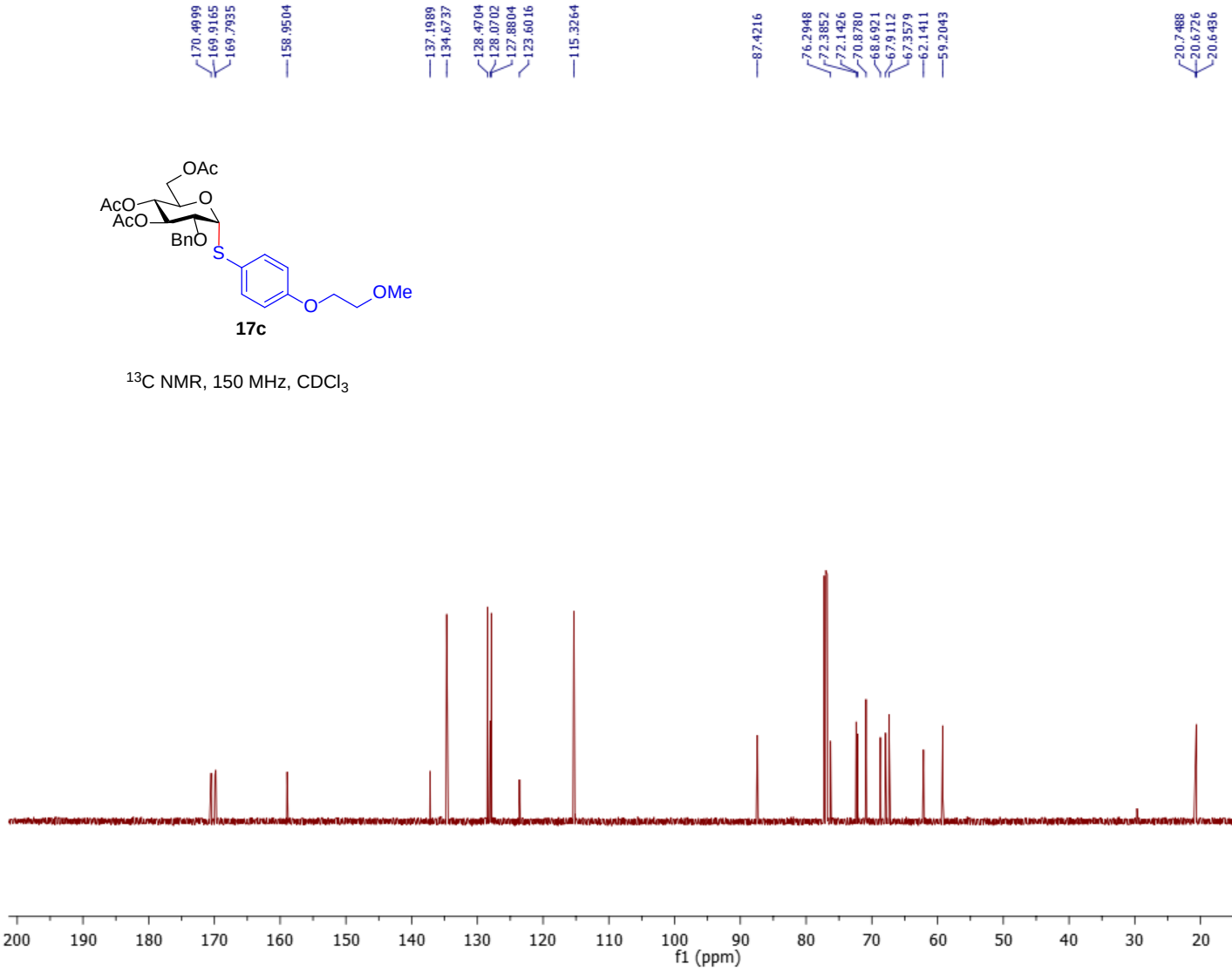

AcO
OAc
O
AcO
N
S
O
OMe
CF3
17b
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)



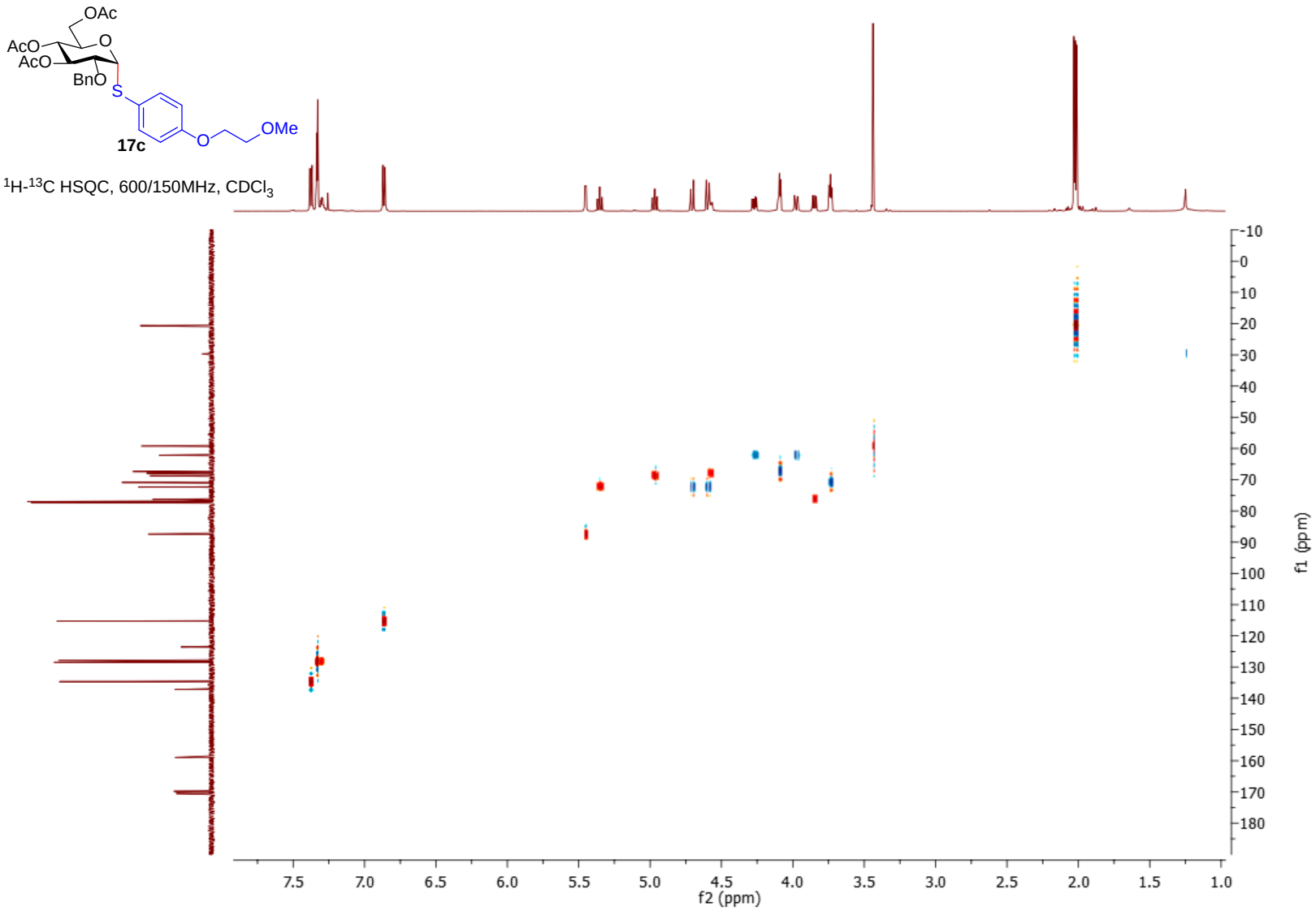
17b

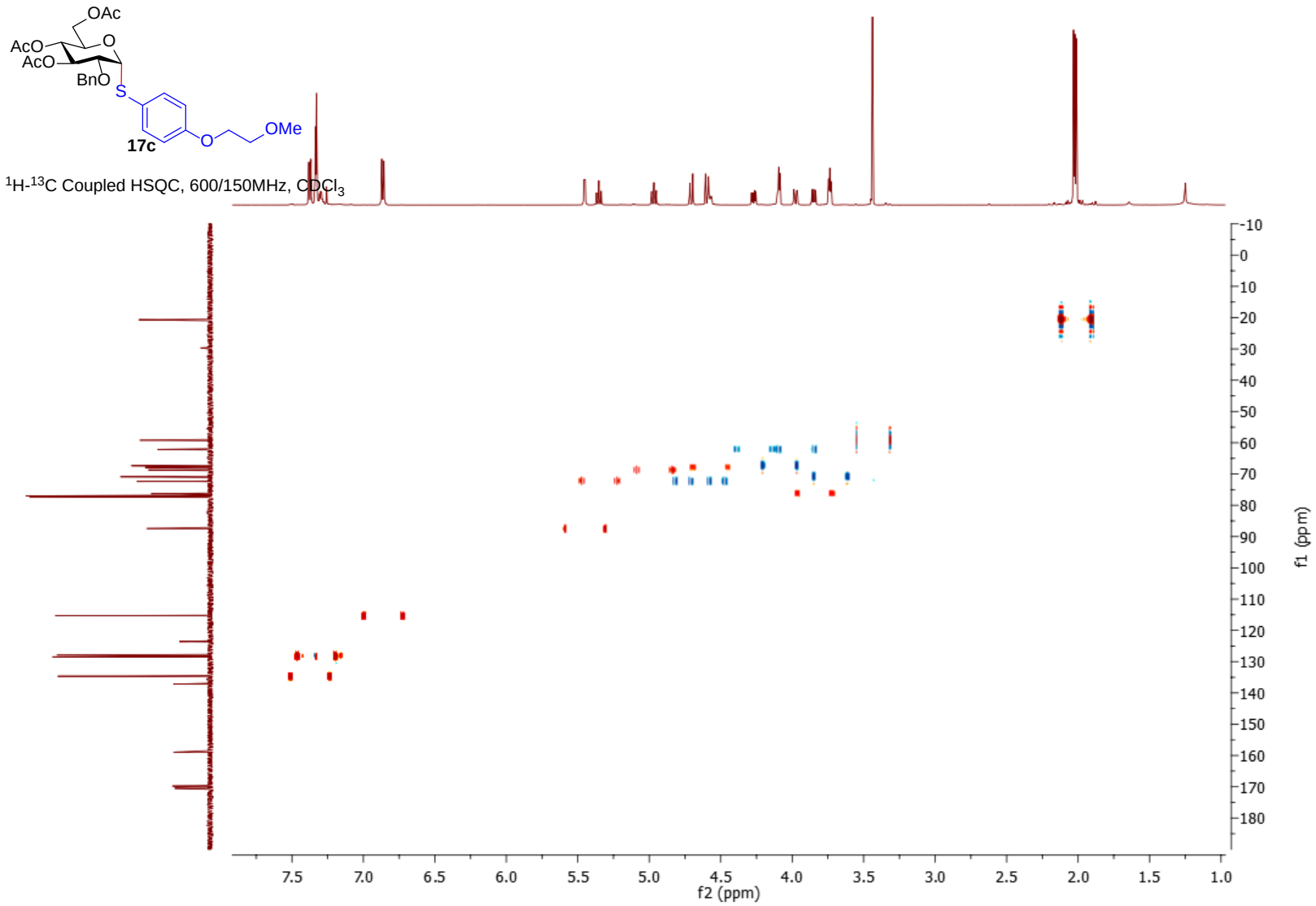
^{1}H-^{13}C Coupled HSQC, 600/150MHz, $CDCl_3$

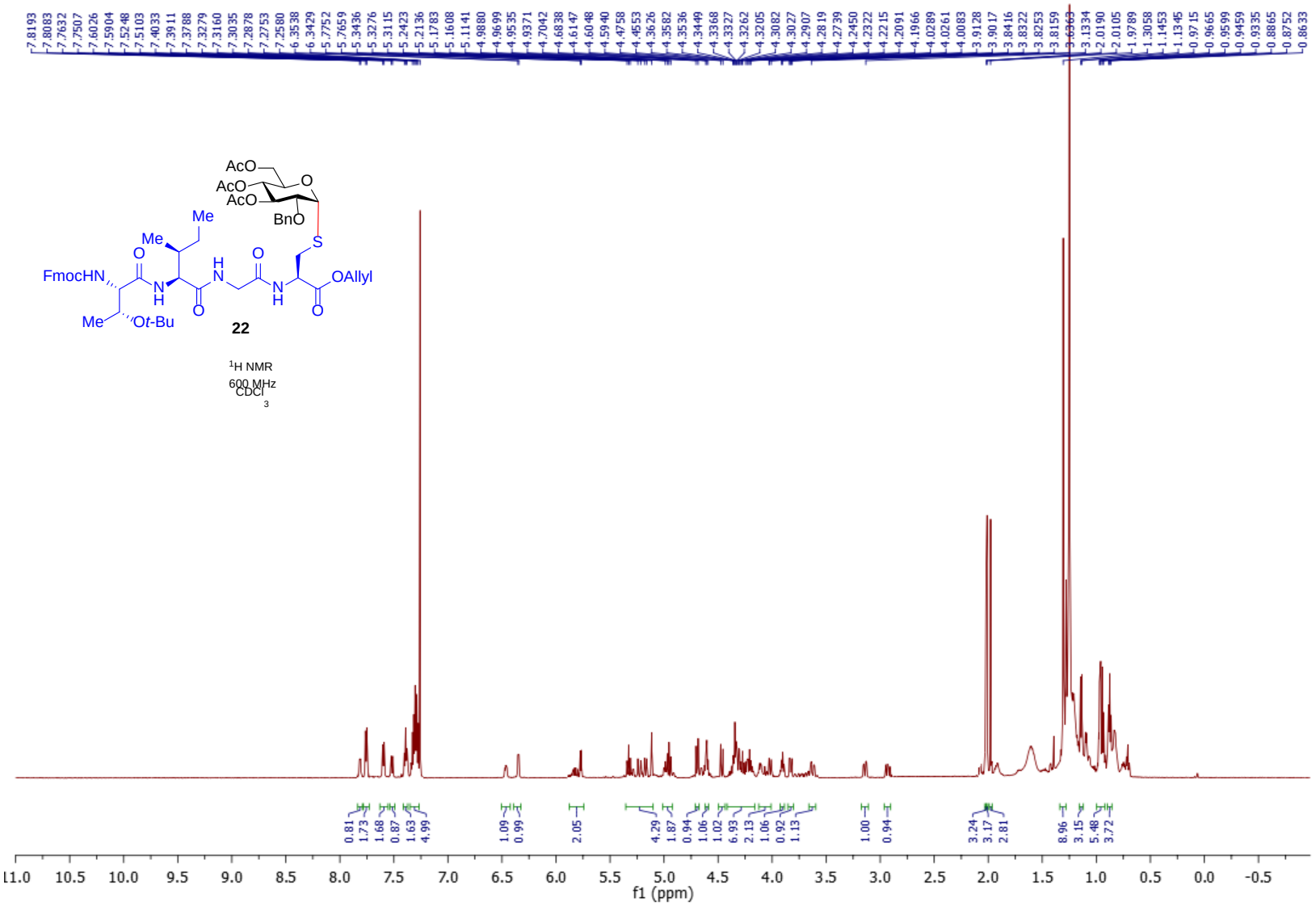

7.3821
7.3675
7.3359
7.3286
7.3061
7.2997
7.2921
7.2576
6.8709
6.8563
5.4569
5.4476
5.3684
5.3524
5.3363
4.9672
4.7161
4.6957
4.6065
4.5860
4.1016
4.0940
4.0859
3.7443
3.7364
2.0315
2.0221
2.0122
OAc
AcO
AcO
O
BnO
S
O
OMe
17c
1H NMR
600 MHz
CDCl3
6.82
1.94
1.00
1.03
1.02
1.03
2.00
1.08
2.02
1.10
1.04
2.00
2.96
8.85
f1 (ppm)

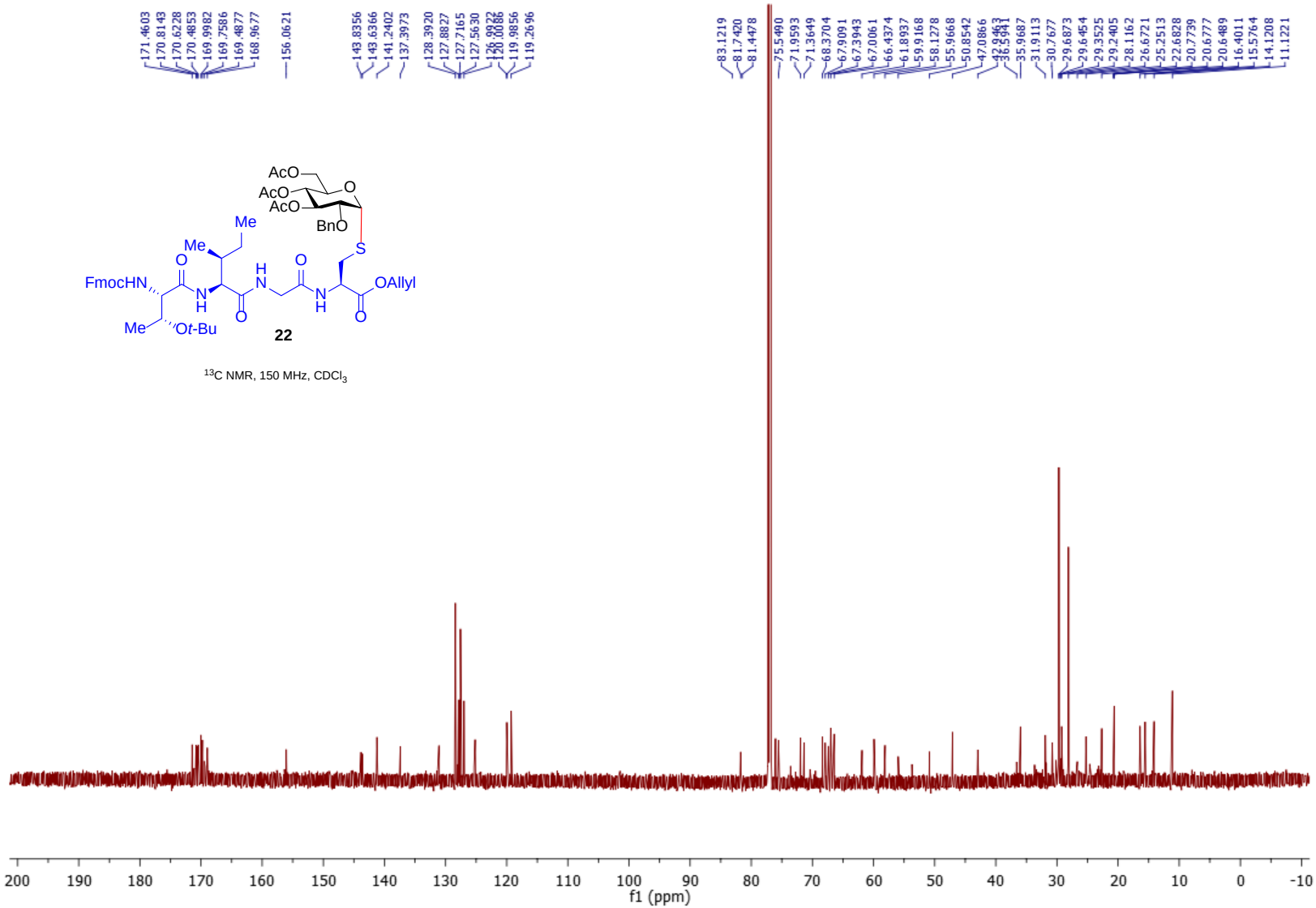


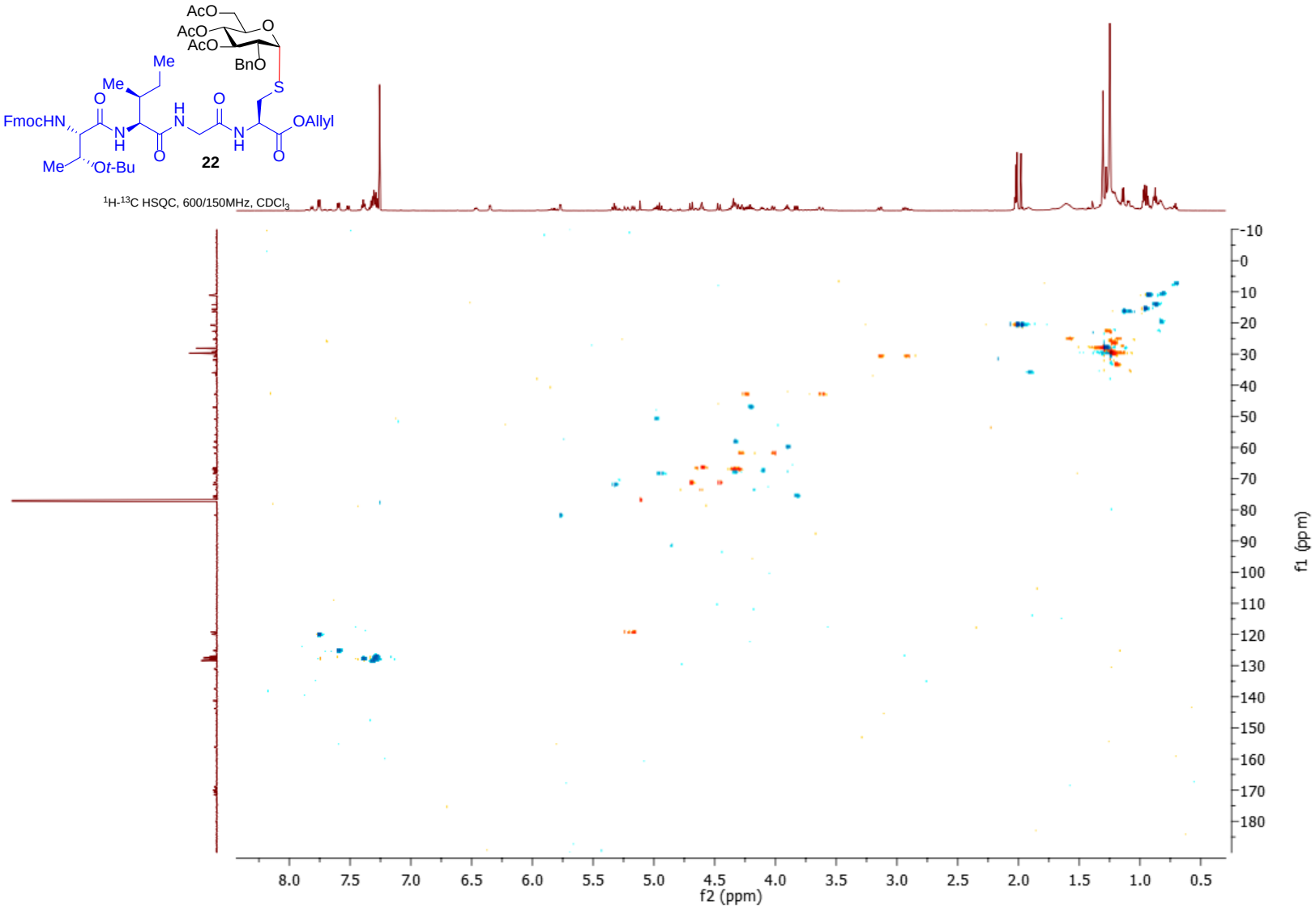
^{13}C NMR, 150 MHz, $CDCl_3$

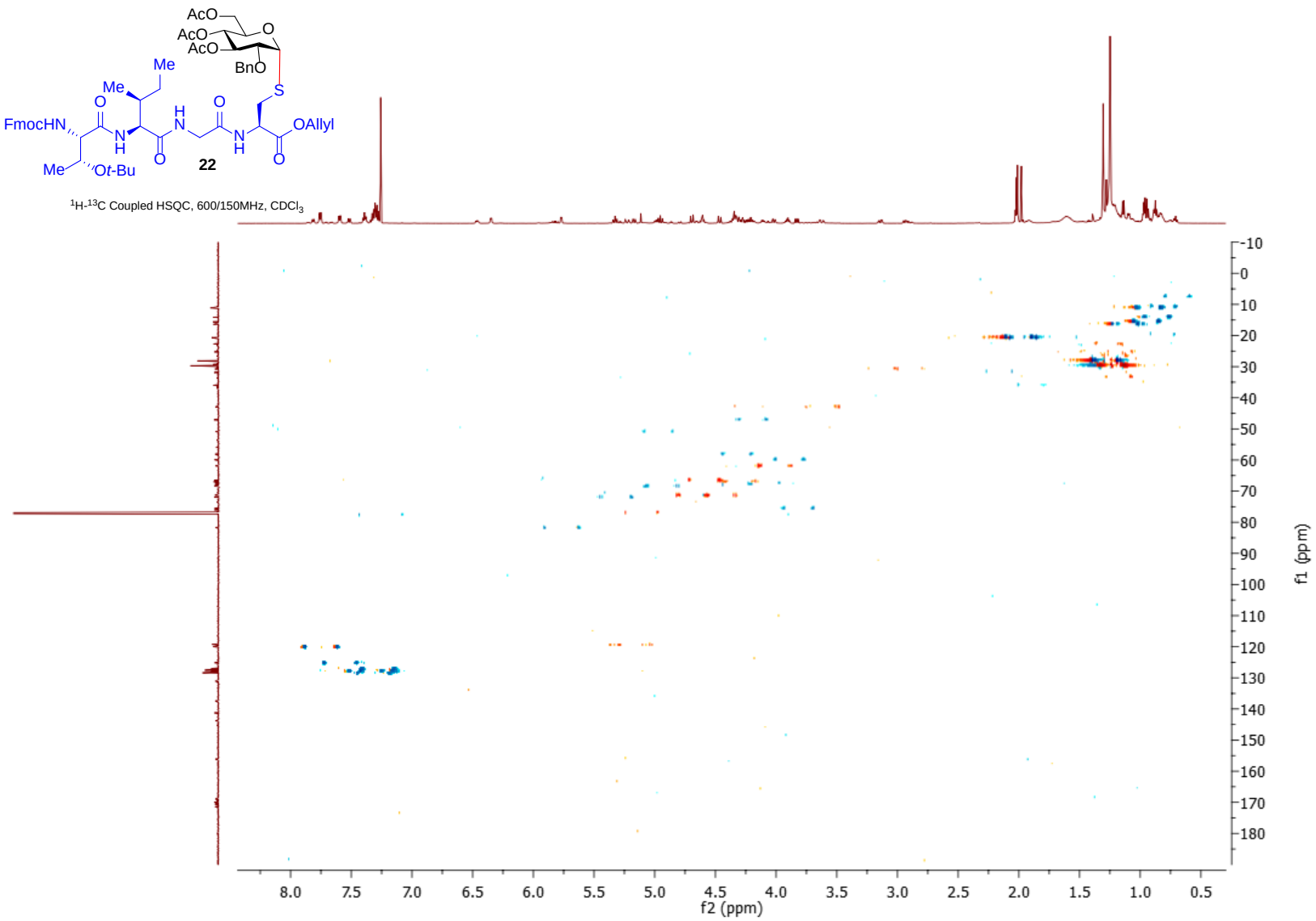

OAc
AcO
AcO
O
BnO
S
O
OMe
17c
^{1}H-^{13}C HSQC, 600/150MHz, $CDCl_3$
f2 (ppm)
f1 (ppm)


OAc
AcO
AcO
BnO
O
S
O
OMe
17c
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

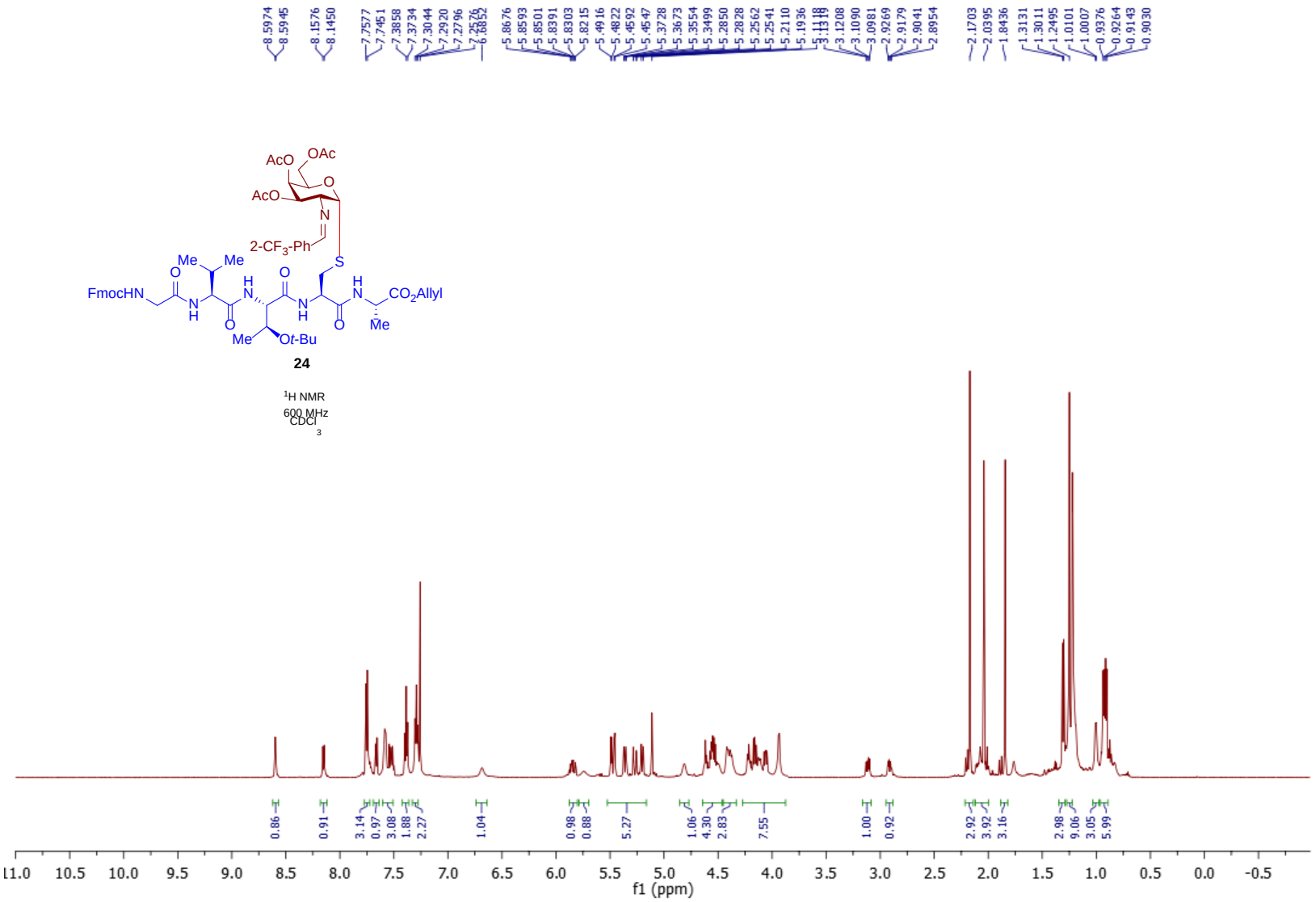

AcO
AcO
AcO
O
BnO
S
Me
Me
FmocHN
O
N
H
H
N
O
N
H
O
O
OAllyl
Me
Ot-Bu
22
1H NMR
600 MHz
CDCl3
f1 (ppm)

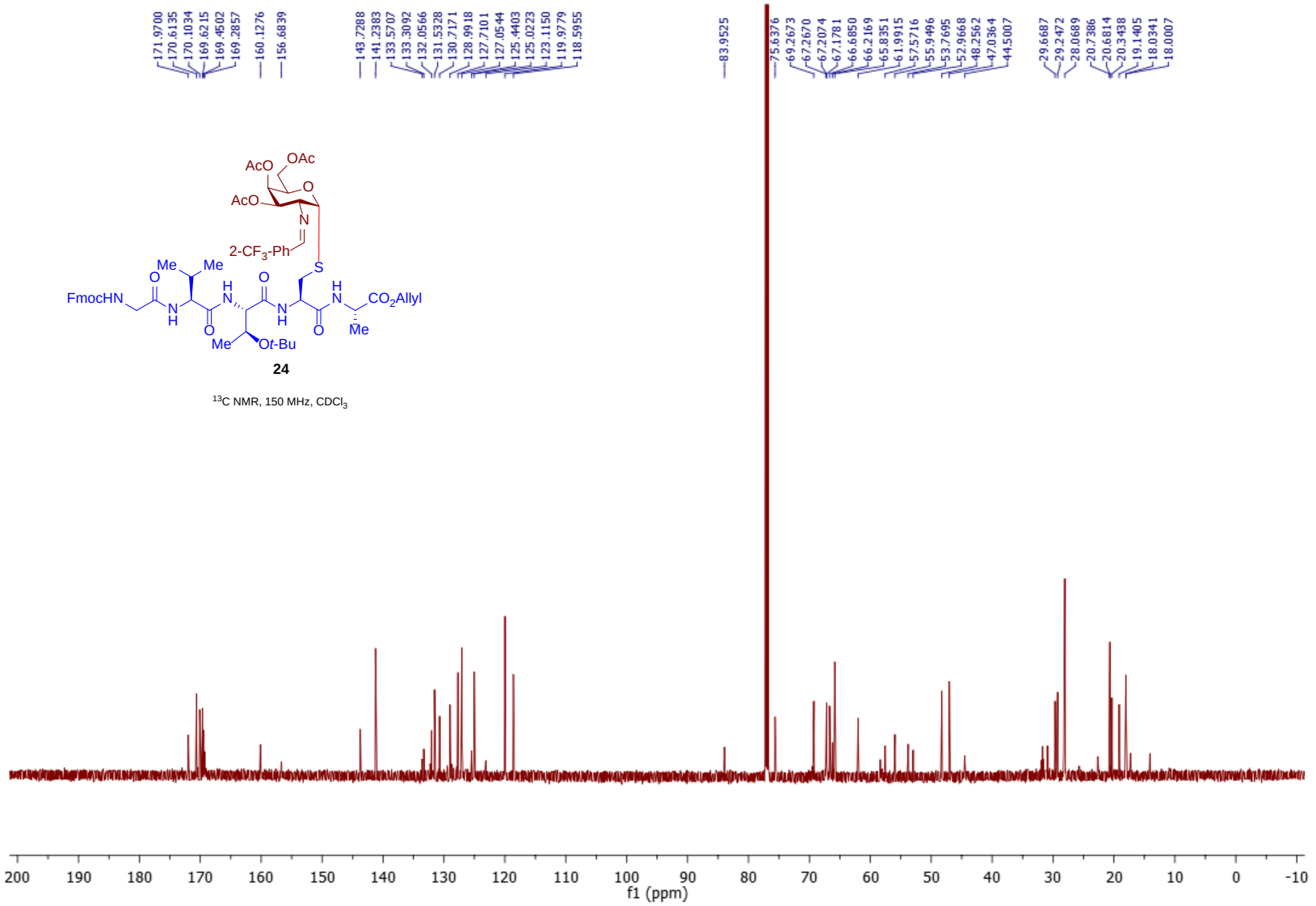

171.4603
170.8143
170.6228
170.4853
169.9982
169.7586
169.4877
168.9677
156.0621
143.8356
143.6366
141.2402
137.3973
128.3920
127.8827
127.7165
127.5630
119.9856
119.2696
83.1219
81.7420
81.4478
75.5490
71.9593
71.3649
68.3704
67.9091
67.3943
67.0061
66.4374
61.8937
59.9168
58.1278
55.9668
50.8542
47.0866
42.9463
38.5941
35.9687
31.9113
30.7677
29.6873
29.6454
29.3525
29.2405
28.1162
26.6721
25.2513
22.6828
20.7739
20.6777
20.6489
16.4011
15.5764
14.1208
11.1221
AcO
AcO
AcO
O
BnO
S
Me
Me
O
H
N
O
FmocHN
N
H
O
N
H
O
OAllyl
Me
Ot-Bu
22
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

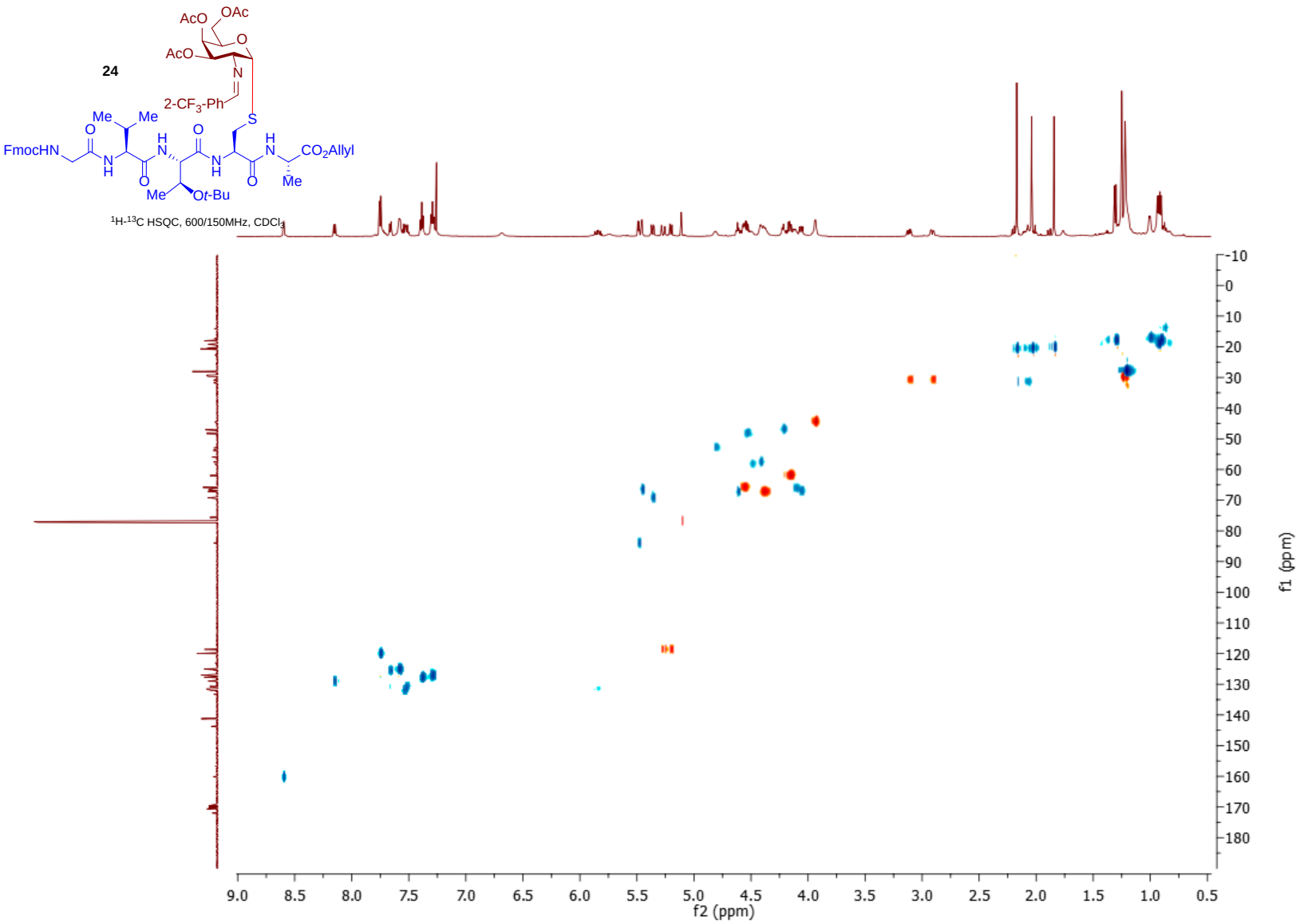

AcO
AcO
AcO
O
BnO
S
Me
Me
O
FmocHN
N
H
H
N
O
N
H
O
OAllyl
O
Me
Ot-Bu
22
1H-13C HSQC, 600/150MHz, CDCl3
f1 (ppm)
f2 (ppm)

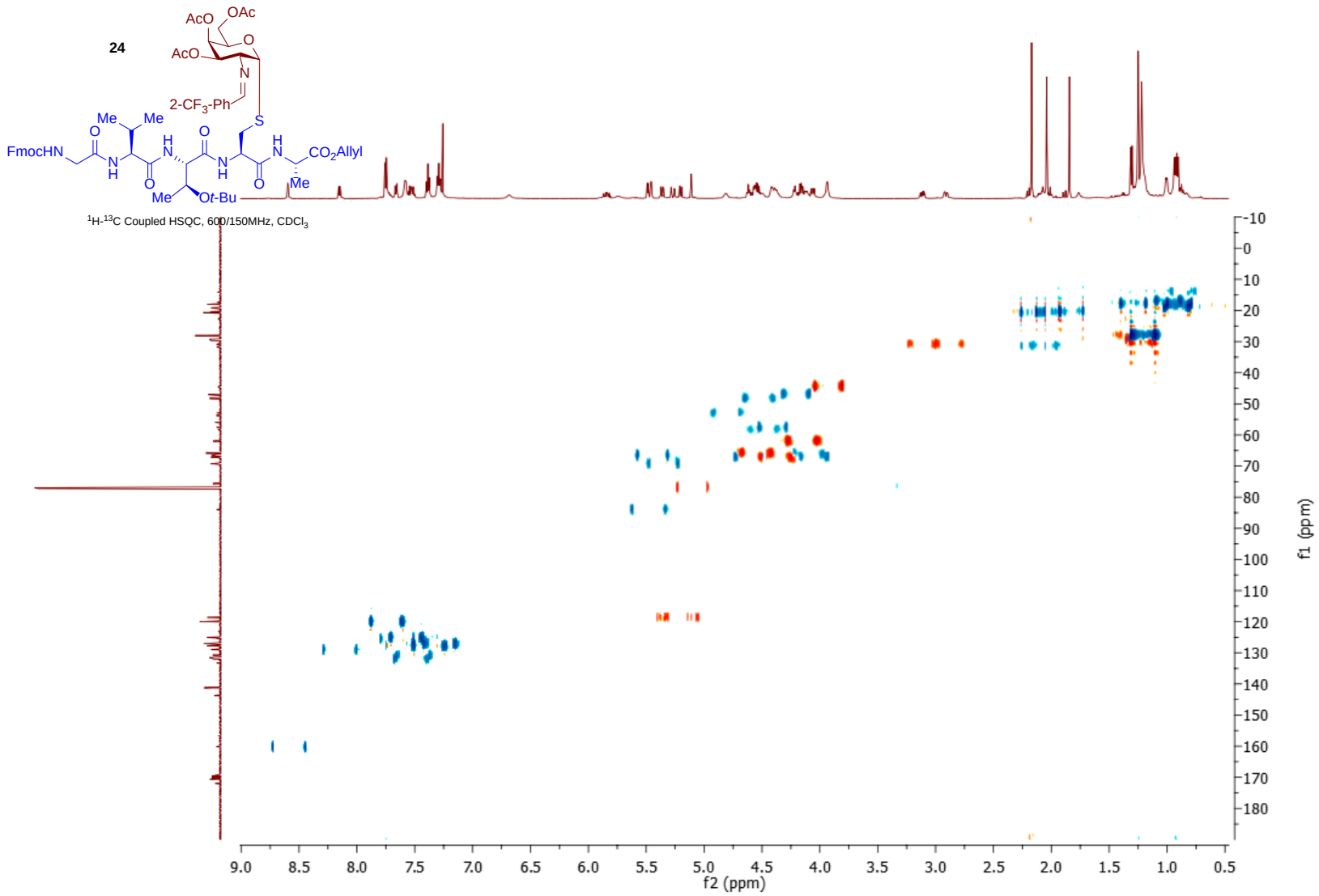


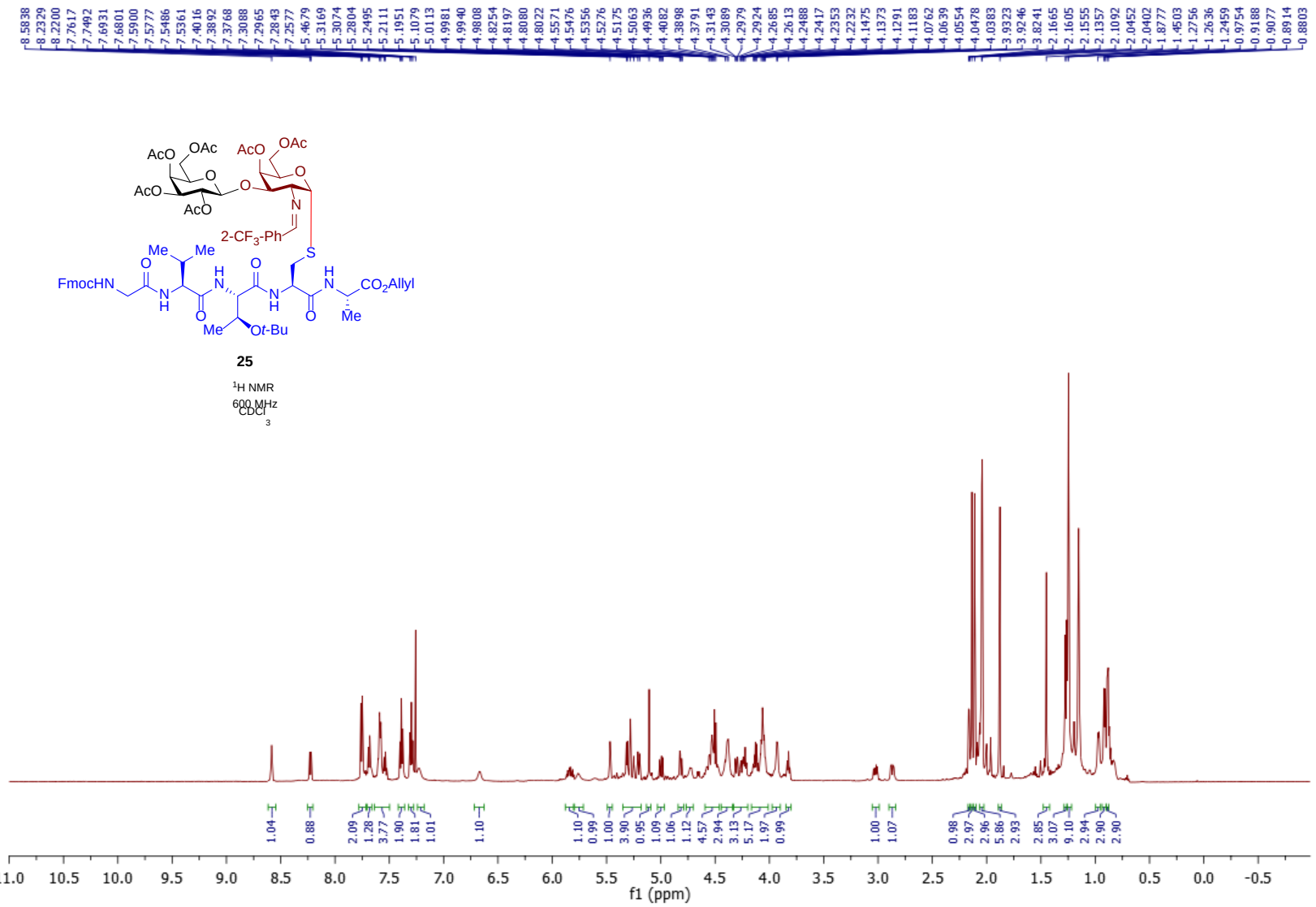
^{1}H-^{13}C Coupled HSQC, 600/150MHz, $CDCl_3$

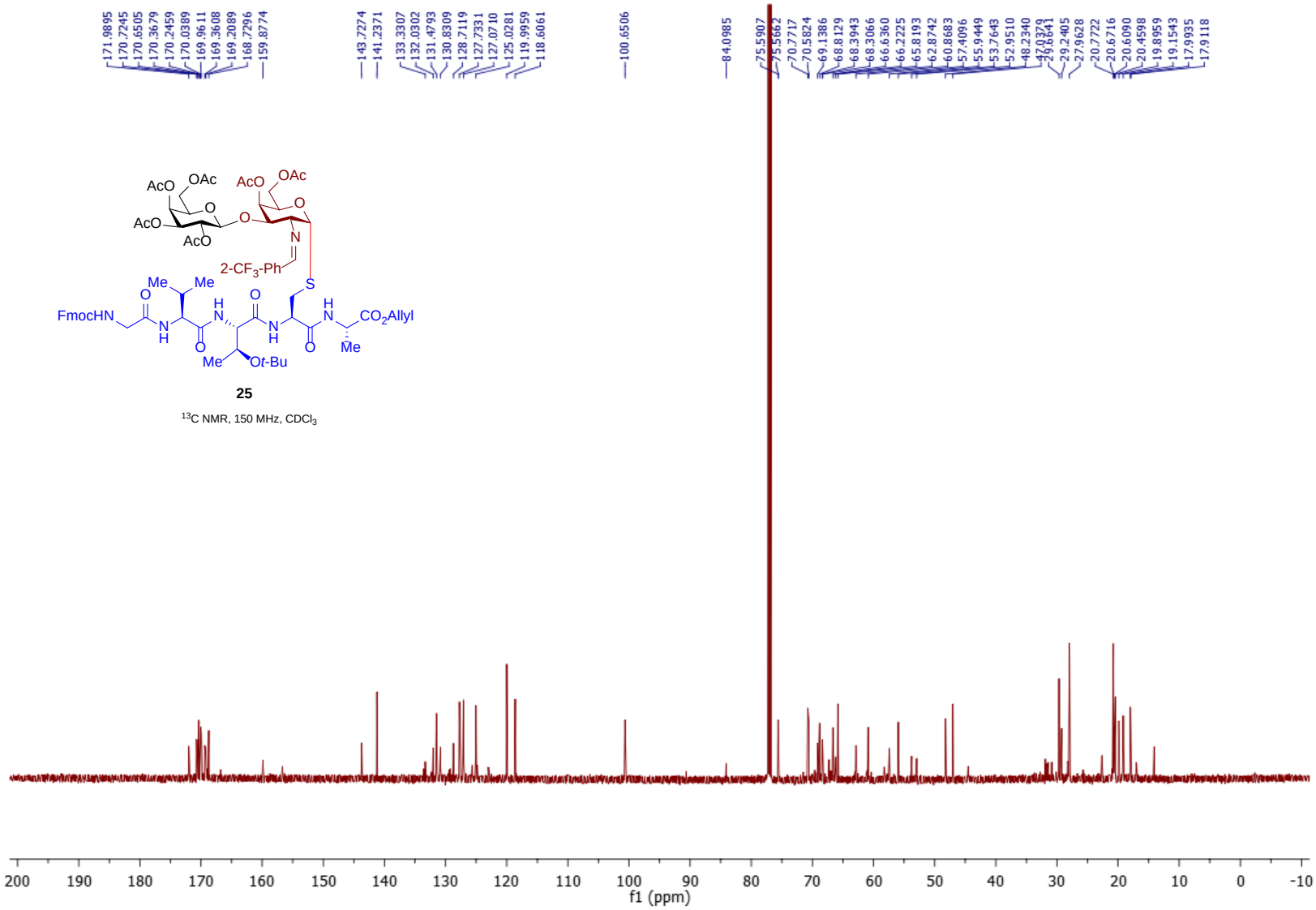

8.5974
8.5945
8.1576
8.1450
7.7577
7.7451
7.3858
7.3734
7.3044
7.2920
7.2796
6.8852
5.8676
5.8593
5.8501
5.8391
5.8303
5.8215
5.4916
5.4822
5.4592
5.4547
5.3728
5.3673
5.3554
5.3499
5.2850
5.2828
5.2562
5.2541
5.2110
5.1936
3.1208
3.1090
3.0981
2.9269
2.9179
2.9041
2.8954
2.1703
2.0395
1.8436
1.3131
1.3011
1.2495
1.0101
1.0007
0.9376
0.9264
0.9143
0.9030
AcO
OAc
AcO
O
N
2-CF3-Ph
S
Me
Me
FmocHN
O
N
H
H
N
O
O
N
H
H
N
O
CO2Allyl
Me
Me
Ot-Bu
24
1H NMR
600 MHz
CDCl3
0.86
0.91
3.14
0.97
3.08
1.88
2.27
1.04
0.98
0.88
5.27
1.06
4.30
2.83
7.55
1.00
0.92
2.92
3.92
3.16
2.98
9.06
3.05
5.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


171.9700
170.6135
170.1034
169.6215
169.4502
169.2857
160.1276
156.6839
143.7288
141.2383
133.5707
133.3092
132.0566
131.5328
130.7171
128.9918
127.7101
127.0544
125.4403
125.0223
123.1150
119.9779
118.5955
83.9525
75.6376
69.2673
67.2670
67.2074
67.1781
66.6850
66.2169
65.8351
61.9915
57.5716
55.9496
53.7695
52.9668
48.2562
47.0364
44.5007
29.6687
29.2472
28.0689
20.7386
20.6814
20.3438
19.1405
18.0341
18.0007
AcO
OAc
AcO
O
N
2-CF3-Ph
S
Me
Me
FmocHN
O
N
H
H
N
O
O
N
H
H
N
CO2Allyl
O
Me
Me
Ot-Bu
24
13C NMR, 150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


24
AcO
OAc
AcO
O
N
2-CF3-Ph
S
Me
Me
FmocHN
O
N
H
H
N
O
N
H
O
H
N
CO2Allyl
Me
Me
Ot-Bu
Me
1H-13C HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

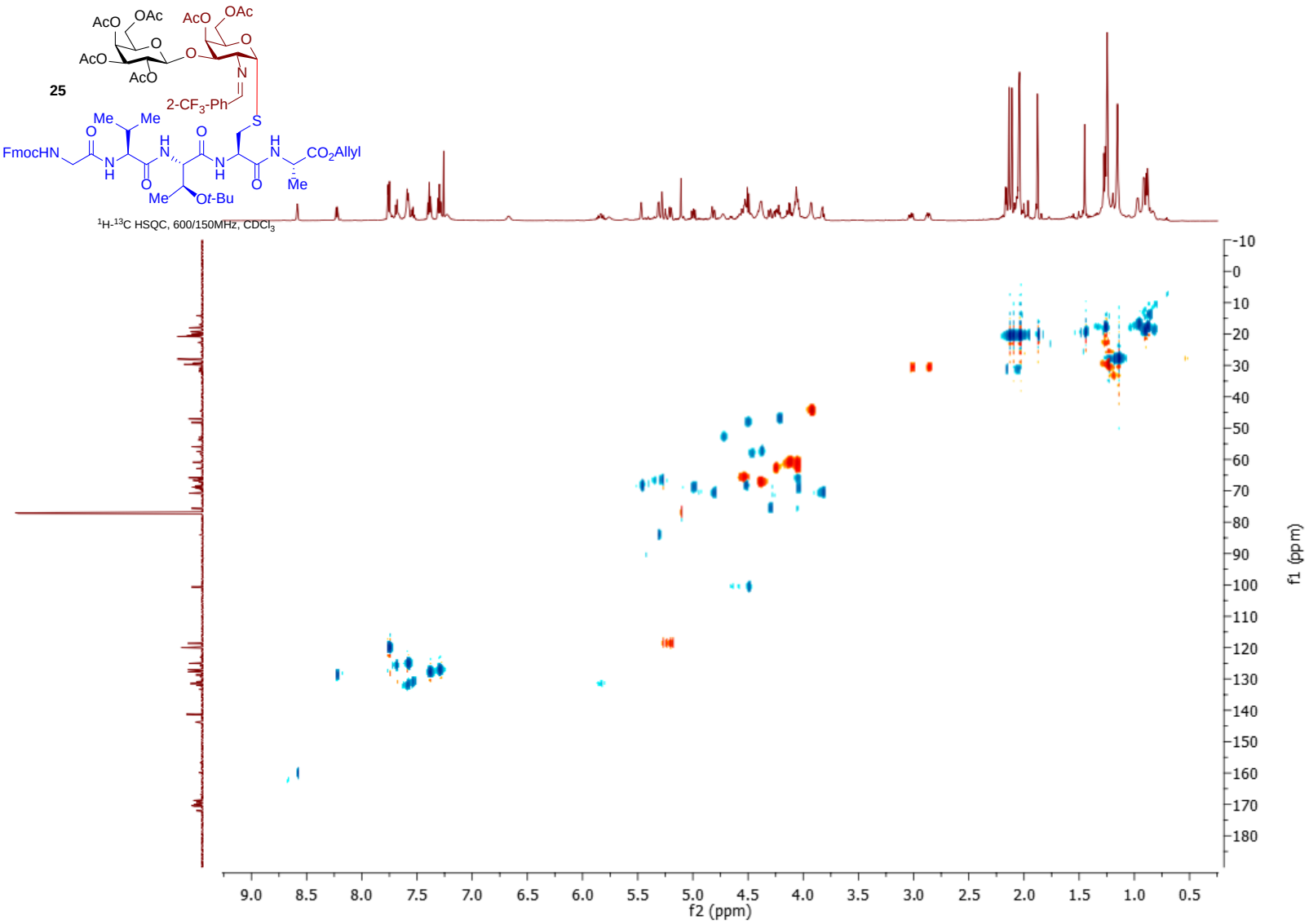

24
AcO
OAc
AcO
O
N
2-CF3-Ph
S
Me
Me
FmocHN
O
N
H
H
N
O
N
H
H
N
O
CO2Allyl
Me
Me
Ot-Bu
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)

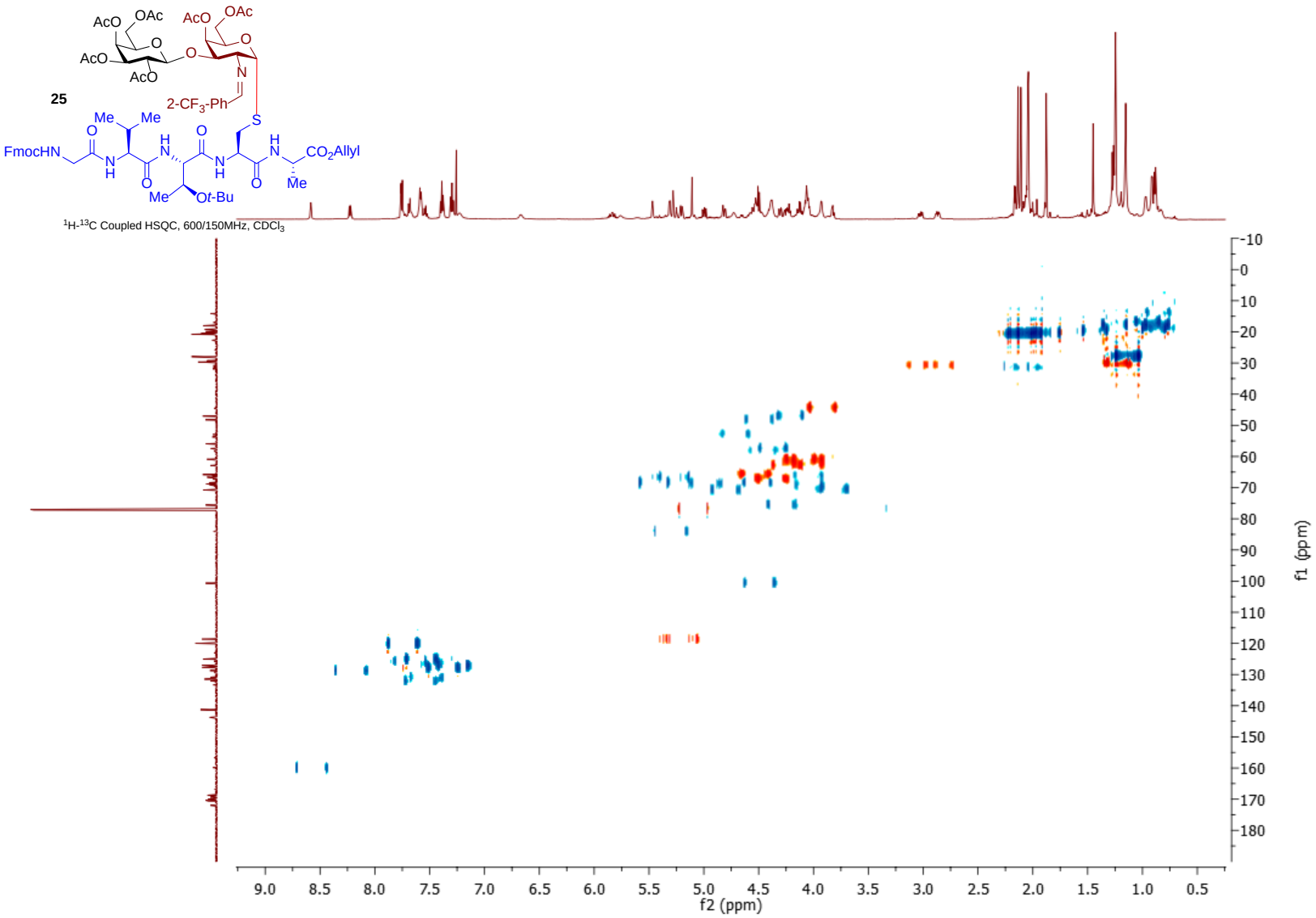

AcO
OAc
AcO
OAc
AcO
O
O
O
AcO
N
2-CF3-Ph
S
Me
Me
FmocHN
O
N
H
O
H
N
O
N
H
O
H
N
CO2Allyl
O
Me
Me
Ot-Bu
25
1H NMR
600 MHz
CDCl3
f1 (ppm)



25

^{13}C NMR, 150 MHz, $CDCl_3$


25
AcO
OAc
AcO
OAc
AcO
AcO
O
O
O
N
2-CF3-Ph
S
FmocHN
Me
Me
O
H
N
O
H
N
O
H
N
CO2Allyl
Me
Me
Ot-Bu
1H-13C HSQC, 600/150MHz, CDCl3
f1 (ppm)
f2 (ppm)


25
2-CF3-Ph
FmocHN
CO2Allyl
Ot-Bu
1H-13C Coupled HSQC, 600/150MHz, CDCl3
f2 (ppm)
f1 (ppm)