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C6 Picoloyl Protection: a Remote Stereodirecting Group for 2-Deoxy-β-Glycosidic Formation

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1. General Materials and Methods

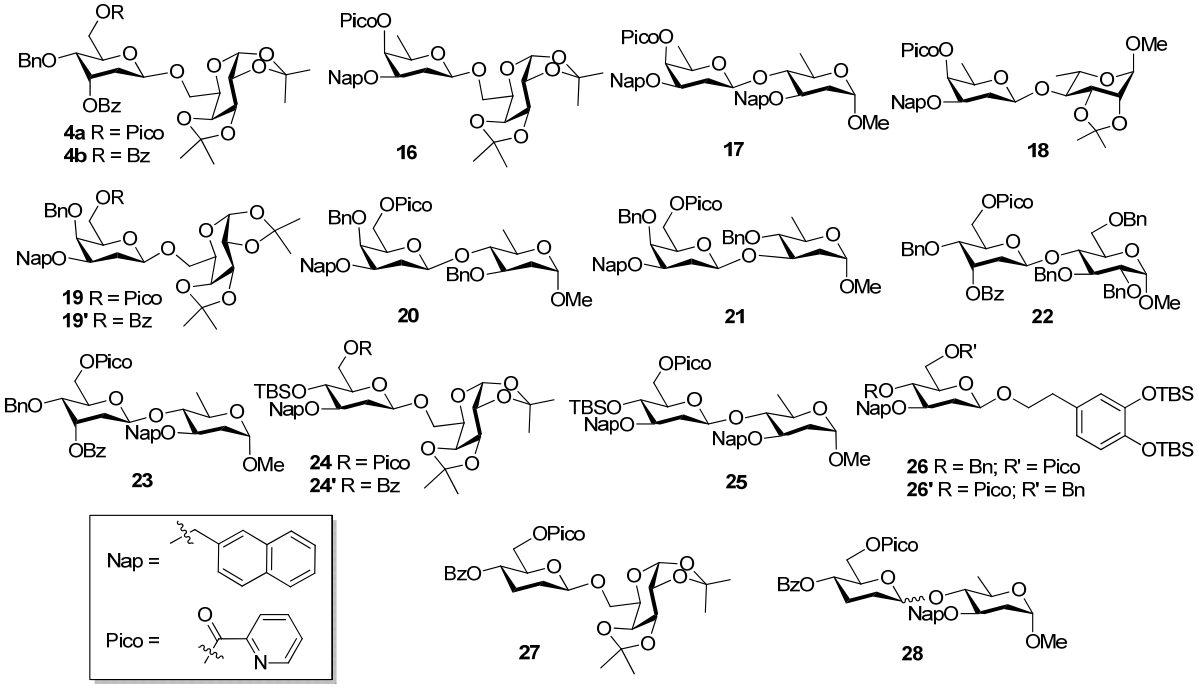
All the chemicals were purchased from Acros,® Alpha Aesar,® and Sigma Aldrich® chemical companies through local agents. Anhydrous solvents were used for the reactions unless otherwise stated. AW300 molecular sieve (MS) (from Aldrich) in powder form was activated before used (Activation protocol: heating at ~300-400 ^{o}C with hot gun under high *vacuo* followed by cooling to RT × 3-4 cycles). Exact amount of activated MS used was based on ca. 1.0 g of MS per 100 mg of glycosyl donor). All the reactions were carried out under N_2 or Ar conditions and monitored by thin layer chromatography (TLC) using silica-gel on aluminum plates (60 F-254) and by charring with *p*-anisaldehyde stain or by phosphomolybdic acid (PMA) stain or by ultraviolet (UV) detection. Silica-gel (100-200 mesh) was used for column chromatography to purify all the compounds. HPLC analysis was performed over Mightysil column (Si-60 250-4.6) and eluted with EtOAc/hexane/CH_2Cl_2 or EtOAc/hexane mixture at a 0.8 or 1 mL min-1 flow rate. Gradient pump (L-2130) and UV detector (L-2400) from Hitachi were employed for solvent elution and detection respectively. 0.063-0.200 mm Silica gel for column chromatography was obtained from Merck (Geduran Si-60). NMR spectra were recorded by 300 (Büchi console), 400 (Varian console), 500 (Varian console), or 600 (Varian console) MHz NMR spectrometers. The ^{1}H, ^{13}C NMR chemical shifts were reported in parts per million (ppm) and tetramethylsilane (TMS) signal was used as a internal standard (δ 0.00) for ^{1}H NMR whereas deuterated chloroform ($CDCl_3$) signal (δ 77.0) was used as reference for ^{13}C NMR. Coupling constants were calculated from ^{1}H NMR in Hertz (Hz). Optical rotations were measured with AA-65 automatic polarimeter. Acceptor **3** is commercially available and **10**, **12**, **13**, **14**, and **15** are known compounds and corresponding references are given in following procedure.

2. Experimental Procedures and Spectral Data

2.1 General glycosylation procedure for 2-deoxydisaccharide derivatives:

A mixture of glycosyl donor (0.24 mmol, 1.2 equiv), glycosyl acceptor (0.2 mmol, 1 equiv.) and freshly activated AW300 molecular sieve (MS) (240 mg) in CH_2Cl_2 (24.0 mL, 10 mM) was stirred under N_2 for 1 h. The mixture was cooled to −50 ^oC, *N*-iodosuccinimide (NIS) (54 mg, 0.24 mmol, 1.2 equiv.) and trifluoromethanesulfonic acid (TfOH) (4 μL, 0.048 mmol, 0.24 equiv.) were added. The resulting mixture was stirred for 24 h at same temperature. After completion of reaction (TLC), saturated sodium bicarbonate ($NaHCO_3$) solution (5.0 mL) was added slowly to the reaction mixture. Then, the mixture was warmed to room temperature, diluted with CH_2Cl_2 (50 mL) and filtered. The filtrate was washed with satd $NaHCO_3$ solution (30 mL), 5.0% sodium thiosulfate ($Na_2S_2O_3$) solution (30 mL), water (30 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to give crude product which was purified by silica-gel column chromatography. Structures of the products and exact amounts of reagents used are given in Table S-1.

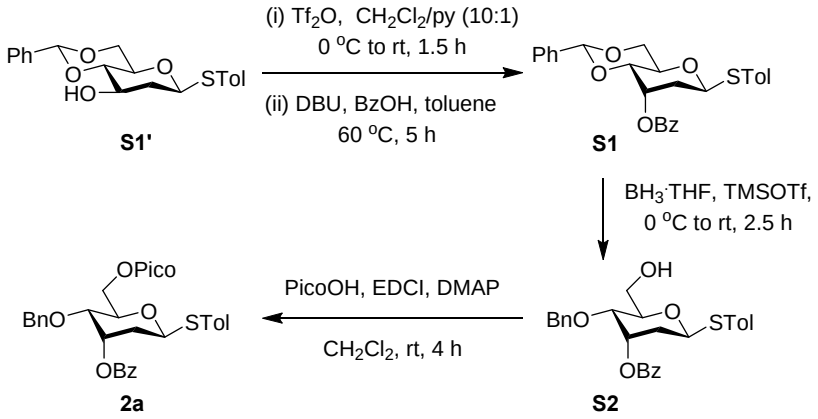
Table S-1: Exact amounts of donors, acceptors, promoters used in glycosylations



Entry	Donor (mg, mmol)	Acceptor (mg, mmol)	NIS (mg, mmol)	TfOH (µL, mmol)	Product (mg, %)
1	**2a** (137, 0.24)	**3** (52.0, 0.19)	(54.0, 0.24)	(4.2, 0.048)	**4a** (127, 95%)
2	**2b** (70, 0.12)	**3**(24.6, 0.09)	(33.2, 0.14)	(2.1, 0.024)	**4b** (47, 70%)
3	**5** (120, 0.24)	**3** (52.0, 0.19)	(54.0, 0.24)	(4.2, 0.048)	**16** (96, 80%)
4	**5** (120, 0.24)	**11** (58.0, 0.2)	(54.0, 0.24)	(4.2, 0.048)	**17** (72, 83%)
5	**5** (137, 0.27)	**13** (50, 0.22)	(61.0, 0.27)	(4.8, 0.055)	**18** (110, 84%)
6	**6** (133, 0.21)	**3** (44, 0.16)	(59.2, 0.26)	(3.9, 0.043)	**19** (80, 79%)
7	**6'** (73, 0.12)	**3** (24.2, 0.09)	(32.5, 0.14)	(2.1, 0.024)	**19'** (54, 79%)
8	**6** (135, 0.22)	**12** (43, 0.17)	(60.3, 0.26)	(3.9, 0.044)	**20** (73, 63%)
7	**6** (142, 0.23)	**14** (45, 0.18)	(63.2, 0.28)	(4.1, 0.046)	**21** (79, 60%)
9	**2a** (137, 0.24)	**10** (93, 0.2)	(54, 0.24)	(4.2, 0.048)	**22** (90, 50%)
10	**2a** (137, 0.24)	**11** (58, 0.2)	(54, 0.24)	(4.2, 0.048)	**23** (80, 54%)
11	**7** (148, 0.24)	**3** (52, 0.2)	(54, 0.24)	(4.2, 0.048)	**24** (108, 70%)
12	**7'**(63, 0.10)	**3**(20, 0.07)	(27, 0.12)	(1.7, 0.02)	**24'**(52, 90%)
13	**7** (148, 0.24)	**11** (58, 0.2)	(54, 0.24)	(4.2, 0.048)	**25** (96, 64%)
14	**8** (101, 0.17)	**15** (59, 0.15)	(37, 0.17)	(3, 0.033)	**26** (105, 79%)
15	**8'**(80, 0.13)	**15**(38.9, 0.10)	(35, 0.15)	(2.3, 0.026)	**26'**(82, 94%)
16	**9** (60, 0.12)	**3** (26, 0.10)	(27, 0.12)	(1.7, 0.02)	**27** (36, 60%)
17	**9** (120, 0.25)	**11** (54, 0.18)	(56, 0.25)	(4.4, 0.05)	**28** (63, 55%)

2.2 Preparation of 2-deoxyglycosyl donors 2 and 5-9

2.2.1 *p*-Tolyl 3-*O*-Benzoyl-4-*O*-benzyl-6-*O*-picoloyl-2-deoxy-1-thio-*β*-D-allopyranoside (2a)

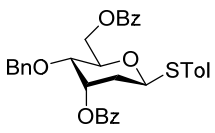


Compound S1: To the solution of **S1'**[1] (2 g, 5.59 mmol) in CH_2Cl_2/pyridine (10/1, v/v) (20 mL), triflic anhydride (1.37 mL, 8.38 mmol) was added in a dropwise fashion at 0 °C for 30 min. After completion of addition, the mixture was warmed to room temperature and stirred for 1 hour. Then, the solution was diluted with CH_2Cl_2 (150 mL), washed with water (100 mL), saturated ammonium chloride (NH_4Cl) solution (100 mL) and brine solution (100 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. To the solution of crude triflate in toluene (20 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.51 mL, 16.76 mmol) and benzoic acid (4.09 g, 33.51 mmol) and stirred at room temperature for 0.5 hour. The solution was heated to 60 °C and stirred for 5 hours. After completion of the reaction, the solution was cooled to room temperature and diluted with EtOAc (150 mL), washed with saturated $NaHCO_3$ solution (100 mL), saturated NH_4Cl solution (100 mL), water (100 mL) brine and dried ($MgSO_4$). The crude product **S1** was used for further step without purification. **Compounds S2** and **2a:** To the solution of **S1** (1.3 g, 2.81 mmol) in BH_3·THF (16.86 mL, 1 M BH_3 in THF) was added trimethylsilyl trifluoromethanesulfonate (TMSOTf) (101 μL, 0.56 mmol) at 0 °C. The solution was stirred at room temperature for 2.5 hours, quenched with triethylamine (Et_3N) (3

mL) followed by careful addition of methanol (MeOH) until the evolution of H_2 ceased. The reaction mixture was concentrated and purified by flash chromatography with 1:3 of EtOAc in hexane. To the solution of obtained compound **S2** (0.3 g, 0.64 mmol) in CH_2Cl_2 (4 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDCI) (0.18 g, 0.96 mmol), dimethylaminopyridine (DMAP) (0.02 g, 0.13 mmol) and picolinic acid (0.12 g, 0.96 mmol) at room temperature. The resulting mixture was stirred for 4 hours at room temperature. After completion of the reaction, the thick solution was diluted with CH_2Cl_2 (50 mL), washed with brine (25.0 mL × 2), dried over Na_2SO_4. The crude product was purified by silica-gel column chromatography (2:1 to 1:1 EtOAc in hexane) to provide **2a** as yellow syrup (0.36 g, 98%).

Analytical data for **2a**: R_f = 0.4 (EtOAc/hexane, 1/1, v/v); $[\alpha]_D^{35}$ +38.1 (*c* 1.5, $CHCl_3$); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 8.82–8.81 (m, 1H), 8.07 (dd, *J* = 1.5, *J* = 8.5 Hz, 2H), 8.02 – 8.01 (m, 1H), 7.84 – 7.80 (m, 1H), 7.60–7.56 (m, 1H), 7.52 – 7.50 (m, 1H), 7.47 – 7.44 (m, 2H), 7.40 (d, *J* = 8 Hz, 2H), 7.24 – 7.19 (m, 4H), 7.17 – 7.14 (m, 1H), 6.92 (d, *J* = 7.5 Hz, 2H), 5.88 (ddd, *J* = 2.5, *J* = 3, *J* = 3.5 Hz, 1H), 5.15 (dd, *J* = 2, *J* = 12 Hz, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 4.69 (dd, *J* = 2.5, *J* = 11.5 Hz, 1H), 4.63 (dd, *J* = 6.5, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 11 Hz, 1H), 4.33 (ddd, *J* = 2.5, *J* = 6.5, *J* = 9.5 Hz, 1H), 3.63 (dd, *J* = 3, *J* = 9.5 Hz, 1H), 2.36 (ddd, *J* = 2, *J* = 3.5, *J* = 14.5, 1H), 2.25 (s, 1H), 2.06 (ddd, *J* = 2.5, *J* = 12, *J* = 14.5, 1H); **δ_C (125 MHz,$CDCl_3$):** 165.8, 164.9, 150.1, 148.2, 137.9, 137.2, 137.0, 133.5, 131.0, 130.0, 129.7, 128.7, 128.6, 128.4, 128.1, 127.0, 125.5, 80.5, 74.2, 73.2, 71.1, 66.5, 65.4, 36.1, 21.3; **HRMS (ESI)**: calcd for $C_{33}H_{31}NNaO_6S^+$ $[M + Na]^+$ 592.1764, found *m*/*z* 592.1752.

2.2.2 *p*-Tolyl 3,6-di-*O*-Benzoyl-4-*O*-benzyl-2-deoxy-1-thio-*β*-D-allopyranoside (2b)

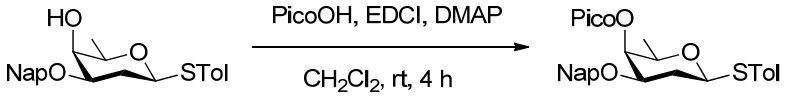


2b

2b was prepared by using standard procedures. Analytical data for **2b**: R_f = 0.4 (EtOAc/hexane, 1/4, v/v); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.07–8.05 (m, 2H), 8.02 – 7.99 (m, 2H), 7.62 – 7.55 (m, 2H), 7.49 – 7.40 (m, 6H),

7.24 – 7.14 (m, 5H), 6.94 – 6.92 (m, 2H), 5.89 – 5.87 (dd, *J* = 6 Hz, *J* = 2.8 Hz, 1H), 5.16 – 5.13 (dd, *J* = 12 Hz, *J* = 2 Hz, 1H), 4.71 – 4.67 (dd, *J* = 11.6 Hz, *J* = 2.4 Hz, 2H), 4.50 – 4.45 (dd, *J* = 11.6 Hz, *J* = 6 Hz, 1H), 4.43 – 4.40 (d, *J* = 11.6 Hz, 1H), 4.27 – 4.23 (ddd, *J* = 9.6 Hz, *J* = 6 Hz, *J* = 2.4 Hz, 1H), 3.63 – 3.59 (dd, *J* = 10 Hz, *J* = 3.2 Hz, 1H), 2.38 – 2.33 (ddd, *J* = 14.8 Hz, *J* = 3.6 Hz, *J* = 2.4 Hz, 1H), 2.27 (s, 3H), 2.06 – 1.99 (m, 1H); **δ_C (100 MHz,$CDCl_3$):** 166.2, 165.6, 137.8, 136.9, 133.2, 132.9, 129.8, 129.7, 129.5, 129.1, 128.5, 128.4, 128.3, 128.2, 127.9, 80.1, 74.1, 72.5, 70.9, 66.3, 64.2, 35.9, 21.1.

2.2.3 *p*-Tolyl 3-*O*-(2-Naphthylmethyl)-4-*O*-picoloyl-2,6-dideoxy-1-thio-*β*-D-galacto-pyranoside (5)



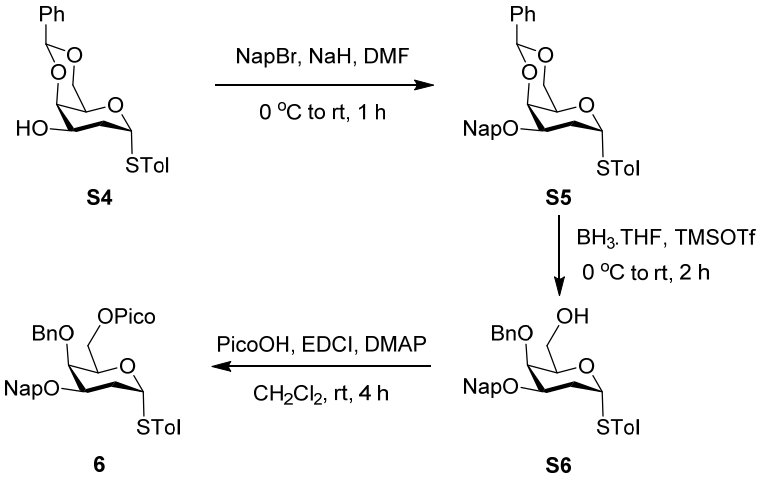
S3 **5**

To the solution of **S3**[1] (0.82 g, 2.16 mmol) in CH_2Cl_2 (15 mL) were added 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDCI) (0.83 g, 4.32 mmol), dimethylaminopyridine (DMAP) (0.05 g, 0.43 mmol) and picolinic acid (0.53 g, 4.32 mmol) respectively at room temperature. The reaction mixture was stirred for 4 hours at room temperature, diluted with CH_2Cl_2 (150 mL). The organic layer was washed with the water (50 mL), brine (50 mL) and concentrated under reduced pressure. The obtained crude product was purified by silica-gel column chromatography (elution: EtOAc/Hexane, 1/1) to give **5** (0.90 g, 83%) as white slimy amorphous.

Analytical data for **5**: R_f = 0.2 (EtOAc/hexane, 1/1, v/v); $[\alpha]_D^{35}$ +40.0 (c 3.3, $CHCl_3$); **δ_H (600 MHz, $CDCl_3$, Me_4Si):** 8.79 – 8.79 (m, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.74 (m, 4H), 7.71 (s, 1H), 7.47-7.38 (m, 6H), 7.11 (d, *J* = 7.8 Hz, 2H), 5.59 (d, *J* = 2.4 Hz, 1H), 4.85 (d, *J* = 12 Hz, 1H), 4.68 (dd, *J* = 3, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 12 Hz, 1H), 3.73 (ddd, *J* = 3,

J = 5.4, *J* = 11.4 Hz, 1H), 3.68 (q, *J* = 6.6 Hz, 1H), 2.33 (s, 3H), 2.15 – 2.07 (m, 2H), 1.30 (d, *J* = 6.6 Hz, 3H); **δ_C (150 MHz,$CDCl_3$):** 164.4, 150.3, 147.7, 137.8, 137.0, 135.2, 133.2, 133.2, 133.1, 129.6, 129.4, 128.4, 127.9, 127.7, 127.0, 126.7, 126.2, 126.0, 125.8, 125.6, 82.4, 75.0, 73.5, 70.4, 69.3, 33.2, 21.3, 17.4; **HRMS (ESI):** calcd for $C_{30}H_{29}NNaO_4S^+$ $[M + Na]^+$ 522.1710, found *m*/*z* 522.1715.

2.2.4 *p*-Tolyl 4-*O*-Benzyl-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-1-thio-α-D-galactopyranoside (6)

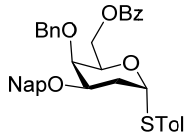


Compound S5: To the stirred solution of **S4** (1.29 g, 3.59 mmol) in *N*,*N*-dimethylformamide (DMF) (10 mL), were added 2-bromonaphthalene (1.49 g, 7.19 mmol) followed by sodium hydride (NaH) (0.17 mg, 7.19 mmol) in portion wise at 0 °C and warmed to room temperature. After completion of the reaction (10 h), quenched with saturated NH_4Cl solution (20 mL) and extracted with EtOAc (75 mL × 2) and dried (Na_2SO_4). The crude product was purified by silica-gel column chromatography (2:3 to 1:1 EtOAc/hexane) to give **S5** (1.67 g, 93.3%) as a white solid. **Compound S6**: The compound **S5** (1.0 g, 2.00 mmol) was dissolved in BH_3·THF (12.0 mL, 1.0 M BH_3 in THF) at 0 °C and added TMSOTf (72 μL, 0.40 mmol) at same temperature. The resulting mixture was warmed to room temperature and stirred for 1 hour. The reaction was slowly quenched with Et_3N (2.0

mL) and MeOH (10.0 mL). Concentrated the solution under reduced pressure and purified by silica-gel column chromatography (2:3 to 1:1 EtOAc/hexane) to give **S6** (0.78 g, 78.3%) as white solid. **Compound 6a:** To the solution of **S6** (0.65 g, 1.29 mmol) in CH_2Cl_2 (15 mL), were added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) (0.40 g, 2.58 mmol), dimethylaminopyridine (DMAP) (0.03 g, 0.25 mmol) and picolinic acid (0.31 g, 2.58 mmol) respectively at room temperature. The reaction mixture was stirred for 4 hours at room temperature, diluted with CH_2Cl_2 (100 mL). The organic layer was washed with the water (50 mL), brine (50 mL) and concentrated. The obtained crude product was purified by silica-gel column chromatography (2:3 to 1:1 EtOAc/hexane) to give **6** (0.65 g, 83%) as thick gum.

Analytical data for **6**: R_f = 0.6 (EtOAc/hexane, 2/3, v/v); $[\alpha]_D^{20}$ +188.5 (c 2.1, $CHCl_3$); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.78 – 8.76 (dt, *J* = 4.8 Hz, *J* = 0.8 Hz, 1H), 7.94 – 7.92 (d, *J* = 6.8 Hz, 1H), 7.88 – 7.83 (m, 4H), 7.76 – 7.72 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.53 – 7.21 (m, 10H), 6.96 – 6.88 (d, *J* = 8.0 Hz, 2H), 5.74 – 5.73 (d, *J* = 5.6 Hz, 1H), 5.05 – 5.02 (d, *J* = 11.6 Hz, 1H), 4.85 – 4.78 (dd, *J* = 17.2 Hz, *J* = 12.0 Hz, 2H), 4.76 – 4.73 (d, *J* = 15.6 Hz, 1H), 4.69 – 4.66 (dd, *J* = 6.4 Hz, *J* = 5.6 Hz, 1H), 4.62 – 4.57 (m, 1H), 4.51 – 4.47 (m, 1H), 4.07 (ddd, *J* = 12.0 Hz, *J* = 4.0 Hz, *J* = 2.4 Hz, 1H), 4.06 (s, 1H), 2.73 – 2.66 (td, *J* = 12.8 Hz, *J* = 5.6 Hz, 1H), 2.27 – 2.24 (dd, *J* = 13.2 Hz, *J* = 4.0 Hz, 1H), 2.20 (s, 3H); **δ_C (100 MHz,$CDCl_3$):** 164.5, 149.7, 147.6, 138.2, 136.8, 136.6, 135.5, 133.1, 132.8, 131.7, 130.6, 129.4, 128.2, 128.1, 127.7, 127.6, 127.5, 126.6, 126.1, 126.0, 125.8, 125.3, 125.1, 84.2, 75.3, 74.1, 72.9, 70.7, 69.6, 64.9, 31.5, 20.9.

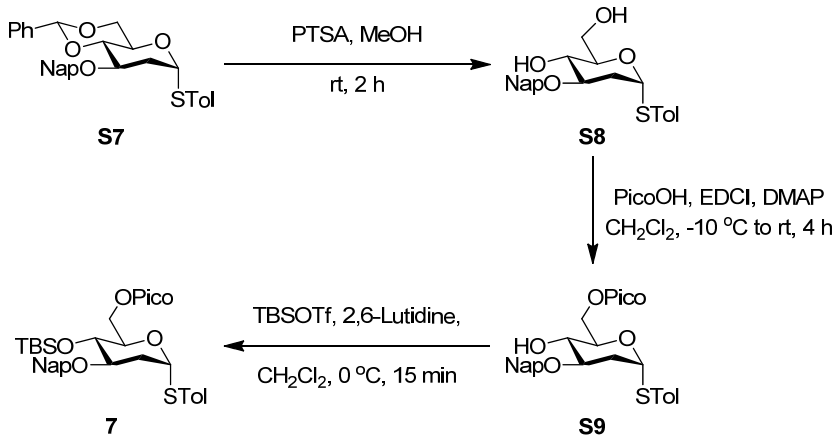
2.2.5 *p*-Tolyl 4-*O*-Benzyl-6-*O*-benzoyl-3-*O*-(2-naphthylmethyl)-2-deoxy-1-thio-α-D-galactopyranoside (6')



6'

6' was prepared by using standard procedures. Analytical data for **6'**: R_f = 0.5 (EtOAc/hexane, 1/4, v/v); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.16 – 8.13 (m, 1H), 7.92 – 7.90 (m, 2H), 7.86 – 7.81 (m, 4H), 7.56 – 7.44 (m, 5H), 7.40 – 7.36 (m, 4H), 7.31 – 7.27 (m, 3H), 6.89 – 6.87 (d, *J* = 7.6 Hz, 2H), 5.73 – 5.71 (d, *J* = 5.2 Hz, 1H), 5.03 – 5.00 (d, *J* = 11.6 Hz, 1H), 4.84 – 4.71 (dd, *J* = 20.4 Hz, *J* = 12.0 Hz, 2H), 4.74 – 4.71 (d, *J* = 11.6 Hz, 1H), 4.59 – 4.56 (dd, *J* = 7.6 Hz, *J* = 2.8 Hz, 1H), 4.51 – 4.46 (dd, *J* = 11.2 Hz, *J* = 7.6 Hz, 1H), 4.39 – 4.35 (dd, *J* = 11.2 Hz, *J* = 4.4 Hz, 1H), 4.04 – 3.96 (ddd, *J* = 12.4 Hz, *J* = 4.4 Hz, *J* = 2.4 Hz, 1H), 3.96 (s, 1H), 2.71 – 2.63 (td, *J* = 12.0 Hz, *J* = 6 Hz, 1H), 2.26 – 2.22 (dd, *J* = 13.2 Hz, *J* = 4.4 Hz, 1H), 2.21 (s, 3H); **δ_C (100 MHz,$CDCl_3$):** 166.1, 138.2, 137.0, 135.5, 134.4, 132.8, 131.6, 130.5, 129.6, 129.5, 128.8, 128.3, 128.1, 127.8, 127.6, 126.2, 126.1, 125.9, 125.3, 84.4, 75.4, 74.1, 73.2, 70.7, 69.8, 64.4, 31.5, 21.0.

2.2.6 *p*-Tolyl 4-*O*-(*tert*-Butyldimethylsilyl)-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-1-thio-α-D-glucopyranoside (7)



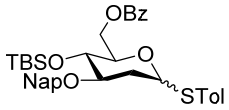
Compound S8: The compound **S7**[1] (1.39 g, 2.80 mmol) was dissolved in MeOH (20 mL) and *p*-toluenesulfonic acid (PTSA) (0.96 g, 0.56 mmol) was added at room temperature. The mixture was stirred for 2 hours, and then neutralized with Et_3N. The crude product was purified by silica-gel column chromatography (1:1 EtOAc/hexane) to give **S8** (0.94 g, 81.7 %) as white amorphous solid. **Compound S9:** To the solution of **S8** (0.40 g, 1.09 mmol) in

CH_2Cl_2 (20 mL), were added 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI) (0.42 g, 2.18 mmol), dimethylaminopyridine (DMAP) (0.01 g, 0.11 mmol) and picolinic acid (0.14 g, 1.14mmol) respectively at -10 ^oC. The reaction mixture was stirred for 4 hours at room temperature, diluted with CH_2Cl_2 (100 mL). The organic layer was washed with brine (50 mL) and concentrated. The crude product was purified by silica-gel column chromatography (2:3 to 2:1 EtOAc/hexane) to give **S9** (0.31 g, 62%) as a white powder. **Compound 7:** To the solution of **S9** (0.30, 0.58 mmol) in CH_2Cl_2 (10 mL), was added 2,6-lutidine (0.16 mL, 1.36 mmol) and TBSOTf (0.25 mL, 1.09 mmol) at 0 ^oC. The stirring was continued for another 30 min, quenched with saturated NH_4Cl solution (5.0 mL). The aqueous layer was extracted with CH_2Cl_2 (25.0 mL × 2), combined organic layers were washed with 20% aqueous $CuSO_4$ solution (25.0 mL × 2) and brine solution (25.0 mL). The organic layer was concentrated and purified by silica-gel column chromatography (1:3 EtOAc/Hexane) to obtain **7** (0.31 g, 87%) as colorless syrup.

Analytical data for **7:** R_f = 0.3 (EtOAc/hexane, 1/2, v/v); $[\alpha]_D^{35}$ +120.3 (c 3.6, $CHCl_3$); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 8.71 – 8.70 (m, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.77 – 7.68 (m, 5H), 7.44 – 7.36 (m, 4H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.50 (d, *J* = 5 Hz, 1H), 4.68 – 4.64 (m, 3H), 4.56 (dd, *J* = 6.5 Hz, *J* = 11.5 Hz, 1H), 4.49 (ddd, *J* = 2 Hz, *J* = 6.5 Hz, *J* = 9 Hz, 1H), 3.78 (ddd, *J* = 5 Hz, *J* = 8.5 Hz, *J* = 13 Hz, 1H), 3.68 (d, *J* = 9 Hz, 1H), 2.41 (ddd, *J* = 1 Hz, *J* = 5 Hz, *J* = 13 Hz, 1H), 2.15 (s, 3H), 2.01 (ddd, *J* = 5.5 Hz, *J* = 11.5 Hz, *J* = 13.5 Hz, 1H), 0.08 (s, 9H), 0.017 (s, 3H), 0.015 (s, 3H); **δ_C (125 MHz,$CDCl_3$):** 164.9, 150.0, 148.1, 137.2, 136.8, 135.9, 133.4, 133.0, 132.0, 130.9, 129.7, 128.2, 128.0, 127.8, 126.8, 126.5, 126.2, 126.0, 125.2, 84.2, 78.1, 72.2, 71.7, 71.5, 65.2, 35.7, 26.1, 21.2, 18.3, -3.6, -4.9; **HRMS (ESI):** calcd for $C_{36}H_{43}NNaO_5SSi^+$ $[M + Na]^+$ 652.2523, found *m*/*z* 652.2506.

2.2.7 *p*-Tolyl 6-*O*-Benzoyl-4-*O*-(*tert*-butyldimethylsilyl)-3-*O*-(2-naphthylmethyl)-

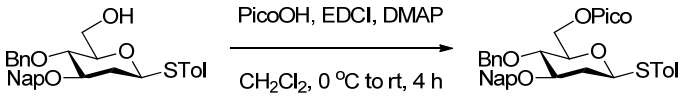
2-deoxy-1-thio-D-glucopyranoside (7')



7'

7' was prepared from **S8** using similar procedures as for **7**. Crude NMR ^{1}H and ^{13}C NMR spectra of **7'** were given in pp 69-70.

2.2.8 *p*-Tolyl 4-*O*-Benzyl-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-1-thio-*β*-D-glucopyranoside (8)



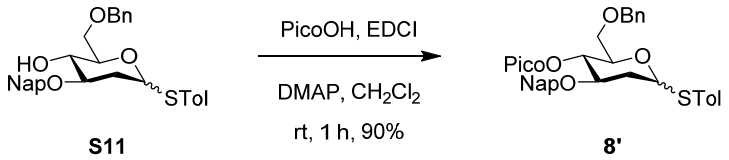
S10 **8**

To the solution of **S10**[1] (0.50 g, 0.99 mmol) in CH_2Cl_2 (10 mL), 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDCI) (0.30 g, 1.98 mmol), dimethylaminopyridine (DMAP) (23.2 mg, 0.19 mmol) and picolinic acid (0.24 g, 1.98 mmol) were added at 0 ^{o}C. The resulting mixture was stirred for 4 h at room temperature and diluted CH_2Cl_2 (100 mL). The solution was washed with water (50 mL), brine (50 mL), and concentrated. The residue was purified by silica-gel column chromatography (1:1 EtOAc/Hexane) to give **8** (0.43 g, 72%) as a gummy substance.

Analytical data for **8**: R_f = 0.3 (EtOAc/hexane, 1/1, v/v); $[\alpha]_D^{35}$ -14.3 (c 0.3, $CHCl_3$); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 8.80 – 8.79 (m, 1H, ArH), 8.03 (d, *J* = 8 Hz, 1H), 7.84 – 7.76 (m, 5H), 7.51 – 7.45 (m, 4H), 7.36 (d, *J* = 8 Hz, 2H), 7.31 – 7.23 (m, 5H), 6.92 (d, *J* = 8 Hz, 2H), 4.98 (d, *J* = 11 Hz, 1H), 4.87 (d, *J* = 11.5 Hz, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.69 (dd, *J* = 2 Hz, *J* = 12 Hz, 1H), 4.68 (d, *J* = 11 Hz, 1H), 4.67 (dd, *J* = 2.5 Hz, *J* = 12 Hz, 1H), 4.60, (dd, *J* = 6 Hz, *J* = 12 Hz, 1H), 3.80 (ddd, *J* = 5 Hz, *J* = 8.5 Hz, *J* = 11 Hz, 1H), 3.69 (ddd, *J* = 2.5 Hz, *J* = 6 Hz, *J* = 8.5 Hz, 1H), 3.53 (d, *J* = 8.5 Hz, 1H), 2.51 (ddd, *J* = 1.5 Hz, *J* = 5 Hz, *J* = 12.5

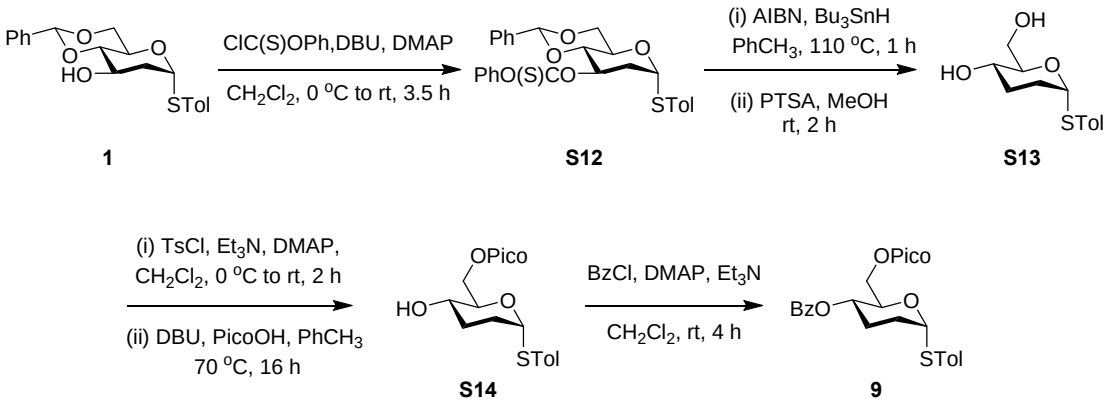
Hz, 1H), 2.25 (s, 1H), 1.83 (d, J = 12 Hz, 1H); **δ_C (125 MHz,$CDCl_3$):** 164.8, 150.2, 148.2, 138.1, 137.8, 137.0, 135.6, 133.5, 133.3, 132.8, 129.8, 129.7, 128.7, 128.5, 128.3, 128.1, 128.1, 127.9, 127.0, 126.8, 126.4, 126.2, 126.0, 125.5, 82.6, 80.9, 77.9, 77.3, 75.3, 72.0, 65.1, 37.0, 21.3; **HRMS (ESI):** calcd for $C_{37}H_{35}NNaO_5S^+$ $[M + Na]^+$ 628.2128, found *m/z* 628.2149.

2.2.9 *p*-Tolyl 6-*O*-Benzyl-3-*O*-(2-naphthylmethyl)-4-*O*-picoloyl-2-deoxy-1-thio-D-glucopyranoside (8')



To the solution of **S11**[1] (0.3 g, 0.59 mmol) in CH_2Cl_2 (12 mL), 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDCI) (0.23 g, 1.19 mmol), dimethylaminopyridine (DMAP) (14.6 mg, 0.12 mmol) and picolinic acid (88.5 mg, 0.72 mmol) were added at 0 ^oC. The resulting mixture was stirred for 1 h at room temperature and diluted CH_2Cl_2 (100 mL). The solution was washed with brine (50 mL × 2) and concentrated. The residue was purified by silica-gel column chromatography (2:3 EtOAc/Hexane) to give **8'** (0.32 g, 90%) as a gum. Crude ^1H and ^{13}C NMR spectra of **8'** were given in pp 75-76.

2.2.10 *p*-Tolyl 4-*O*-Benzoyl-6-*O*-picoloyl-2,3-dideoxy-1-thio-α-D-glucopyranoside (9)



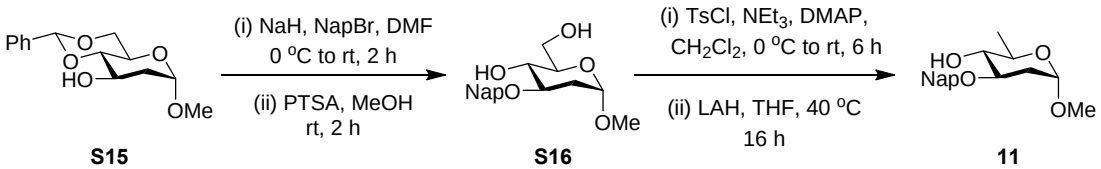
Compound S12: To the solution of **1**[1] (1.0 g, 2.79 mmol) in CH_2Cl_2 (15 mL), DBU (1.25 mL, 8.37 mmol), DMAP (1.02 g, 8.37 mmol) and *O*-phenyl chlorothionoformate (0.77 mL, 5.58 mmol) were added at 0 ^oC. The reaction mixture was gradually warmed to room temperature and stirred for 3.5 h. The solution was diluted with EtOAc (100 mL), washed with saturated NH_4Cl solution (50 mL), water (50 mL), brine (50 mL), and dried over $MgSO_4$. The crude residue was purified by silica-gel column chromatography (1:5 EtOAc/Hexane) to give **S12** (1.01 g, 70 %) as white glassy solid. **Compound S13:** To the solution of **S12** (1.01g, 1.99 mmol) in toluene (20 mL), was added tributyltin hydride (Bu_3SnH) (1.07 mL, 3.98 mmol) and azobisisobutyronitrile (AIBN) (0.16 g, 1.00 mmol) at room temperature. The solution was degassed for three times under *vacuo* and N_2. The resulting solution was refluxed for 1 hour at 110 ^oC. After completion of the reaction, the solution was concentrated under reduced pressure. The obtained crude product was dissolved in MeOH (15 mL) and added *p*-toluenesulfonic acid (0.76 g, 3.98 mmol) at room temperature. The mixture was stirred for 1 hour, then neutralized with Et_3N and concentrated under *vacuo*. The silica-gel purification (2:1 EtOAc/hexane) of crude residue provided **S13** (0.36 g, 71%) as light yellow solid. **Compound S14:** To the solution of **S13** (0.10 g, 0.4 mmol), Et_3N (0.17 mL, 1.20 mmol) and DMAP (0.01 g, 0.08 mmol) in CH_2Cl_2 (15 mL), was added tosyl chloride (TsCl) (0.10 g, 0.52 mmol) at 0 °C. The reaction mixture was stirred for 2 hours at room temperature. After completion of the reaction, the solution was washed with saturated NH_4Cl solution (10 mL), brine (10 mL) and dried (over $MgSO_4$). The crude tosylated derivative was dissolved in toluene (10 mL) and added 1,8-diazabicycloundec-7-ene (DBU) (0.18 mL, 1.20 mmol) and picolinic acid (0.20 g, 1.60 mmol) at room temperature. The resulting solution was stirred for overnight at 70 ^oC. After being cooled down to room temperature, the reaction mixture was diluted with EtOAc, washed with saturated $NaHCO_3$ solution (10 mL), water (10 mL), brine (10 mL) and dried (over $MgSO_4$). The solution of crude product **S14** in CH_2Cl_2 (5 mL), was added DMAP (0.01 g, 0.08 mmol), Et_3N (0.17 mL, 1.2 mmol) followed by BzCl (0.07 mL,

0.60 mmol) under nitrogen at 0 °C. The solution was stirred at room temperature for 4 hours. After completion of the reaction, the solution was diluted with EtOAc (25 mL), washed with saturated NH_4Cl solution (10 mL), brine (10 mL) and dried over $MgSO_4$. The crude residue was purified by silica-gel column chromatography (2:1 EtOAc/hexane) to give **9** (0.062 g, 34%) as white solid.

Analytical data for **9**: R_f = 0.5 (EtOAc hexane, 1/1, v/v); $[\alpha]_D^{35}$ +302.0 (c 1.0, $CHCl_3$);); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 8.76 – 8.74 (m, 1H), 8.06 (d, *J* = 7 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.73 – 7.75 (m, 1H), 7.58 – 7.55 (m, 1H), 7.47 – 7.42 (m, 3H), 7.38 (d, *J* = 8 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.56 (d, *J* = 5 Hz, 1H), 5.08 (dd, *J* = 5 Hz, *J* = 10.5 Hz, 1H), 4.90 (ddd, *J* = 3.5 Hz, *J* = 5.5 Hz, *J* = 10 Hz, 1H), 4.60 – 4.59 (m, 2H), 2.36 – 2.27 (m, 2H), 2.23 (s, 1H), 2.16 (dd, *J* = 3.5 Hz, 14.5 Hz, 1H), 2.02 (dd, *J* = 3.5 Hz, *J* = 14 Hz, 1H); **δ_C (125 MHz,$CDCl_3$):** 165.8, 164.9, 150.1, 147.9, 137.3, 137.0, 133.5, 132.3, 130.7, 129.9, 129.9, 129.8, 128.6, 127.0, 125.5, 84.7, 69.4, 65.0, 29.9, 25.8, 21.3; **HRMS (ESI):** calcd for $C_{26}H_{25}NNaO_5S^+$ $[M + Na]^+$ 486.1346, found *m*/*z* 486.1329.

2.3 Preparation of glycosyl acceptor 11

2.3.1 Methyl 3-*O*-(2-Naphthylmethyl)-2,6-dideoxy-α-D-glucopyranoside (11)



S15 **S16** **11**

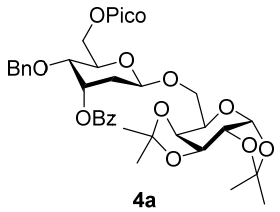
Compound S16: To the solution of **S15**[2] (2 g, 7.51 mmol) in DMF (30 mL), NaH (0.27 g, 11.26 mmol) and 2-bromonaphthalene (2.33 g, 11.26 mmol) were added slowly at 0 °C. The resulting solution was stirred for 2 hours at room temperature and quenched by slow addition of water (5 mL). Then, the suspension was diluted with CH_2Cl_2 (150 mL), washed with water (75 mL), brine (75 mL) and dried (over $MgSO_4$). The crude product was purified

by silica-gel column chromatography (2:3 EtOAc/hexane) to give Nap-protected acetal derivative (2.93 g, 7.21 mmol) which was dissolved in MeOH (30 mL) and added *p*-toluenesulfonic acid (0.25 mg, 1.44 mmol). The mixture was stirred for 2 hours at room temperature, diluted with EtOAc (100 mL) and washed with saturated $NaHCO_3$ solution (50 mL), brine (50 mL). The crude residue was purified by silica-gel column chromatography (1:2 EtOAc/hexane) to give **S16** (2.15 g, 89.9%) as light yellow solid. **Compound 11**: To the solution of **S16** (2 g, 6.28 mmol) in CH_2Cl_2 (50 mL), NEt_3 (2.63 mL, 18.88 mmol) and DMAP (74.5 mg, 0.61 mmol) in dried CH_2Cl_2 (10 mL) was added tosylchloride (TsCl) (1.55 g, 8.16 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 6 hours, diluted with EtOAc (150 mL). The organic layer was washed with saturated NH_4Cl solution (75 mL), brine (75 mL) and dried (over $MgSO_4$). The crude tosylated product was dissolved in THF (40 mL) and added lithium aluminum hydride ($LiAlH_4$) (0.71 g, 18.84 mmol) at 0 ^oC. The resulting solution was stirred at 40 °C for overnight. After completion of the reaction, the reaction mixture was slowly quenched with ice, filtered through celite and washed the celite pad with EtOAc (100 mL). The organic layer washed with water (50 mL), brine (50 mL) and dried (Na_2SO_4). The crude product was purified by column chromatography using silica-gel with 1:2 ethyl acetate in hexane to afford **11** (1.0 g, 70%) as white solid.

Analytical data for **11:** R_f = 0.4 (EtOAc/hexane, 1/2, v/v); $[\alpha]_D^{35}$ +41.1 (c 1.80, $CHCl_3$); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 7.80 – 7.78 (m, 3H), 7.74 (s, 1H), 7.45 – 7.41 (m, 3H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 3 Hz, 1H), 4.61 (d, *J* = 12 Hz, 1H), 3.76 (ddd, *J* = 5 Hz, *J* = 9 Hz, *J* = 12 Hz, 1H, H-3), 3.64 (dt, *J* = 6.5 Hz, *J* = 15.5 Hz, 1H), 3.28 (s, 3H), 3.24 (d, *J* = 9 Hz, 1H), 2.75 (bs, 1H), 2.26 (dd, *J* = 5 Hz, *J* = 13 Hz, 1H), 1.62 (dd, *J* = 3.5 Hz, *J* = 12.5 Hz, 1H), 1.29 (d, *J* = 6.5 Hz, 3H); **δ_C (125 MHz,$CDCl_3$):** 136.0, 133.4, 133.1, 128.4, 128.0, 127.8, 126.5, 126.3, 126.1, 125.8, 98.6, 77.3, 76.3, 71.3, 67.6, 54.7, 35.0, 18.0; **HRMS (ESI):** calcd for $C_{18}H_{22}NaO_4^+$ $[M + Na]^+$ 325.1410, found *m*/*z* 325.1406.

2.3 Preparation of 2-deoxydisaccharides

2.3.1 3-*O*-Benzoyl-4-*O*-benzyl-6-*O*-picoloyl-2-deoxy-β-D-allopyranosyl-(1→6) -1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (4a)



4a

The compound **4a** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **2a** (137 mg, 0.24 mmol), di-acetonide-α-D-galactopyranose **3** (52 mg, 0.19 mmol), NIS (54.0 mg, 0.24 mmol), TfOH (4.2 μL, 0.048 mmol) and activated AW300 MS (1.40 g) in CH_2Cl_2 (24 mL). The reaction mixture was stirred for 24 hours at -50 ^oC. The silica-gel column chromatography of crude product with mixture of EtOAc, hexane and CH_2Cl_2 (1:1:1) provided **4a** (125 mg) as a colorless oil (95% yield for α/β (1:16)).

Analytical data for **4a**: R_f = 0.25 (hexane/EtOAc/CH_2Cl_2, 1/1/1, v/v); $[\alpha]_D^{35}$ -6.0 (c 12.7, $CHCl_3$); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 8.76 – 8.75 (m ,1H), 8.09 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.78 – 7.75 (m, 1H), 7.58 – 7.55 (m, 1H), 7.46 – 7.43 (m, 3H), 7.25 – 7.10 (m, 5H), 5.93 (d, *J* = 2 Hz, 1H), 5.49 (d, *J* = 4.5 Hz, 1H), 5.13 (d, *J* = 9.5 Hz, 1H), 4.73 (d, *J* = 11 Hz, 1H), 4.66 (s, 2H), 4.52 (d, *J* = 8 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 4.35 – 4.33 (m, 1H), 4.26 – 4.25 (m, 1H), 4.16 (d, *J* = 7.5 Hz, 1H), 4.05 (dd, *J* = 3 Hz, *J* = 11 Hz, 1H), 3.98 (d, *J* = 7 Hz, 1H), 3.77 – 3.70 (m, 2H), 2.34 (dd, *J* = 1.5 Hz, *J* = 12.5 Hz, 1H), 1.95 (ddd, *J* = 1.5 Hz, *J* = 11 Hz, *J* = 12.5 Hz, 1H), 1.46 (s, 3H), 1.41 (s, 3H), 1.28, (s, 3H), 1.26 (s, 3H); **δ_C (125 MHz,$CDCl_3$):** 165.4, 164.6, 149.7, 147.7, 137.0, 136.7, 133.0, 129.9, 129.6, 128.3, 128.2, 128.1, 127.7, 126.7, 125.1, 109.0, 108.3, 98.8, 96.1, 73.0, 71.4, 71.2, 70.9, 70.5, 70.2, 68.7, 67.6, 66.2, 65.0, 35.4, 25.8, 24.8, 24.2; **HRMS (ESI):** calcd for $C_{38}H_{43}NNaO_{12}^+$ [M + Na]$^+$ 728.2677, found *m*/*z* 728.2664. The α/β ratios of **4a** obtained at 0.2 and 0.6 equiv. of TfOH and at 1.2 equiv of Me_2S_2-Tf_2O were determined by high-performance liquid

chromatography (HPLC) analysis, after deprotection of C6 picoloyl group in **4a**. Eluent: Hexane/EtOAc = 1/1; Retention time: α anomer = ~16.0 min; β anomer = ~10.3 min (Figure S1-S3).

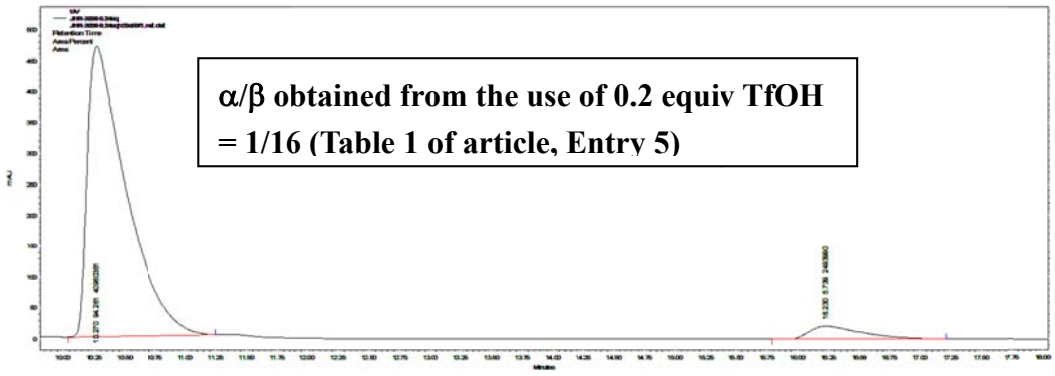


Figure S1. HPLC chromatogram of **4a** after Pico deprotection

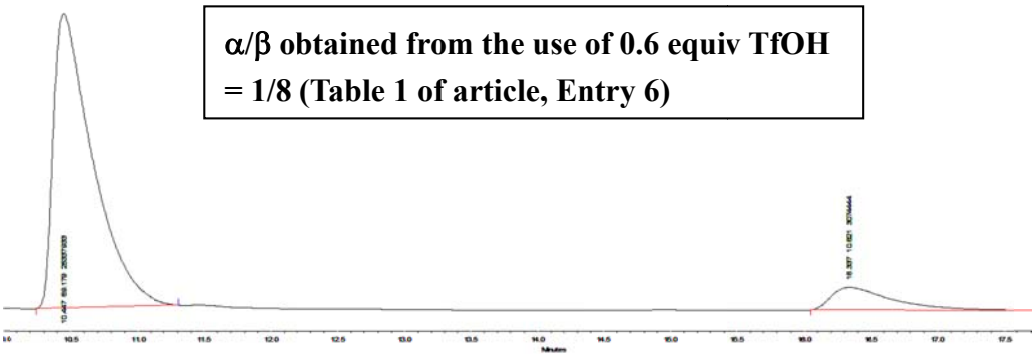


Figure S2. HPLC chromatogram of **4a** after Pico deprotection

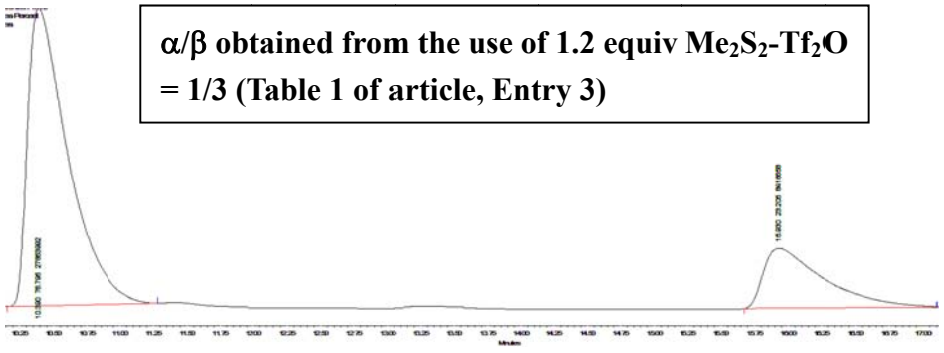
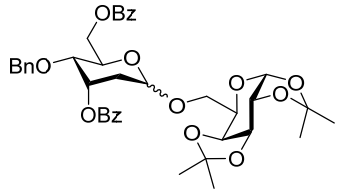


Figure S3. HPLC chromatogram of **4a** after Pico deprotection

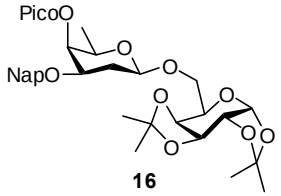
2.3.2 3,6-di-*O*-Benzoyl-4-*O*-benzyl-2-deoxy-D-allopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (4b)



4b

The compound **4b** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **2b** (70 mg, 0.12 mmol), di-acetonide-α-D-galactopyranose **3** (24.6 mg, 0.09 mmol), NIS (33.2 mg, 0.14 mmol), TfOH (2.1 μL, 0.024 mmol) and activated AW300 MS (700 mg) in CH_2Cl_2 (12 mL). The reaction mixture was stirred for 1 hour at -50 ^oC. The silica-gel column chromatography of crude product with mixture of EtOAc and hexane (1:4) gave **4b** (47 mg) as a thick oil (70% yield for α/β 1:1). α:β Ratio was determined by ^1H NMR spectrum (see pp 55-56).

2.3.3 3-*O*-(2-Naphthylmethyl)-4-*O*-picoloyl-2,6-dideoxy-β-D-galactopyranosyl-(1→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside (16)



16

The compound **16** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **5** (120 mg, 0.24 mmol), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **3** (52 mg, 0.19 mmol), NIS (54.0 mg, 0.24 mmol), TfOH (4.2 μL, 0.048 mmol) and activated AW300 MS (1.2 g) in CH_2Cl_2 (24 mL). The reaction mixture was stirred for 24 hours at -50 ^oC. The crude residue was purified by silica-gel column chromatography with mixture of ethyl acetate, hexane and DCM (1:1:2) to afford **16** (88 mg) as a white slimy amorphous (80% yield for α/β 1:7).

Analytical data for **16**: R_f = 0.5 (hexane/EtOAc/CH_2Cl_2, 1/2/1, v/v); $[\alpha]_D^{35}$ +22.1 (c 3.2, $CHCl_3$); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 8.79 (d, *J* = 4 Hz, 1H), 8.21 (d, *J* = 7.5 Hz, 1H), 7.81 – 7.76 (m, 4H), 7.73 (s, 1H), 7.46 – 7.40 (m, 4H), 5.57 (s, 1H), 5.55 (d, *J* = 4.5 Hz, 1H), 4.85 (d, *J* = 12.5 Hz, 1H), 4.69 (d, *J* = 12 Hz, 1H), 4.60 (dd, *J* = 2.5 Hz, *J* = 8 Hz, 1H), 4.57 (dd, *J* = 1.5 Hz, *J* = 10 Hz, 1H), 4.32 – 4.30 (m, 1H), 4.22 (dd, *J* = 1.5 Hz, *J* = 8 Hz, 1H), 4.09 (dd, *J* = 3 Hz, *J* = 11 Hz, 1H), 4.04 (d, *J* = 7.5 Hz, 1H), 3.74 – 3.69 (m, 2H), 3.65 (q, *J* = 6 Hz, 1H), 2.23 (dd, *J* = 3.5 Hz, *J* = 12 Hz, 1H), 2.02 (dd, *J* = 10 Hz, *J* = 12.5 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.29 (d, *J* = 6.5 Hz, 3H); **δ_C (125 MHz,$CDCl_3$):** 164.7, 150.2, 147.8, 137.1, 135.4, 133.3, 133.1, 128.3, 128.0, 127.7, 127.0, 126.5, 126.2, 126.0, 125.7, 109.5, 108.8, 101.1 (C-1'), 96.4 (C-1), 73.9 (C-3'), 71.6, 70.8, 70.5, 70.4, 69.6 (C-5'), 69.5 (C-4'), 69.1, 68.1, 33.4, 26.2, 26.1, 25.1, 24.5, 16.9; **HRMS (ESI):** calcd for $C_{35}H_{41}NNaO_{10}^+$ $[M + Na]^+$ 658.2623, found *m*/*z* 658.2605. The α/β ratio was determined by HPLC after deprotection of picoloyl protecting group in **16** and observed as 1/7 (α/β). Eluent: Hexane/EtOAc = 7/3; Retention time: α anomer = 32.8 min; β anomer = 35.3 min (Figure S4).

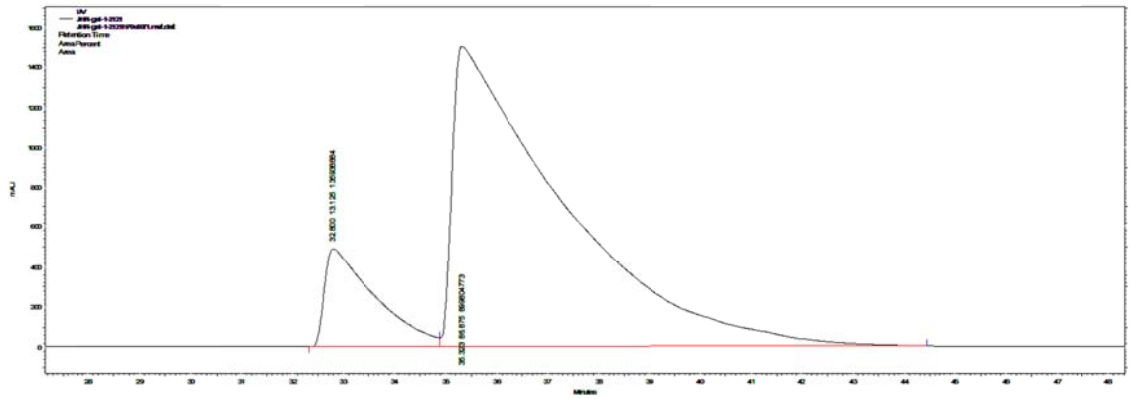
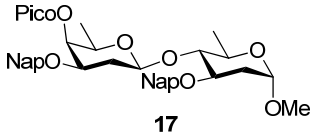


Figure S4. HPLC chromatogram of **16** after Pico deprotection

2.3.4 Methyl 3-*O*-(2-Naphthylmethyl)-4-*O*-picoloyl-2,6-dideoxy-β-D-galactopyranosyl-(1→4)-3-*O*-(2-naphthylmethyl)-2,6-dideoxy-α-D-glucopyranoside (17)



17

The compound **17** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **5** (120 mg, 0.24 mmol), methyl 3-*O*-(2-naphthylmethyl)-2,6-dideoxy-α-D-glucopyranoside **11** (58 mg, 0.19 mmol), NIS (54.0 mg, 0.24 mmol), TfOH (4.2 μL, 0.048 mmol) and activated AW300 MS (1.2 g) in CH_2Cl_2 (24 mL). The reaction mixture was stirred for 24 hours at -50 ^oC. The crude product was purified by silica-gel column chromatography (EtOAc/hexane, 1/1) to get **17** (98 mg) as a white slimy amorphous (83% yield for α/β 1:11).

Analytical data for **17**: R_f = 0.2 (EtOAc/hexane, 1/1, v/v); $[\alpha]_D^{35}$ +98.9 (c 3.1, $CHCl_3$); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 8.75 – 8.74 (m, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.68 (m, 8H), 7.58 – 7.56 (m, 1H), 7.52 (dd, *J* = 0.6 Hz, *J* = 8.4 Hz, 1H), 7.45 – 7.38 (m, 5H), 7.35 – 7.33 (m, 1H), 5.53 (s, 1H), 4.99 (d, *J* = 12 Hz, 1H), 4.87 (d, *J* = 12 Hz, 1H), 4.81 (d, *J* = 12 Hz, 1H), 4.79 (dd, *J* = 1.8 Hz, *J* = 10.2 Hz, 1H), 4.73 (d, *J* = 2.4 Hz, 1H), 4.62 (d, *J* = 12 Hz, 1H), 3.98 (ddd, *J* = 5.4 Hz, *J* = 9, *J* = 11.4 Hz,1H), 3.76 (dq, *J* = 6.6 Hz, *J* = 9 Hz, 1H), 3.65 (ddd, *J* = 3 Hz, *J* = 4.2 Hz, *J* = 12 Hz, 1H), 3.52 (q, *J* = 6 Hz, 1H), 3.42 – 3.39 (m, 1H), 3.29 (s, 3H), 2.27, (dd, *J* = 4.8 Hz, *J* = 13.2 Hz, 1H), 2.14 (ddd, *J* = 1.2 Hz, *J* = 3.6 Hz, *J* = 12 Hz, 1H), 2.02 (ddd, *J* = 1.8 Hz, *J* = 12 Hz, 1H), 1.73 (ddd, *J* = 3.6 Hz, *J* = 12 Hz, *J* = 13.2 Hz, 1H), 1.31 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6 Hz, 3H); **δ_C (125 MHz,$CDCl_3$):** 164.6, 150.2, 147.7, 137.0, 136.7, 135.3, 133.32, 133.30, 133.1, 132.9, 128.4, 128.01, 127.98, 127.79, 127.75, 127.7, 127.0, 126.8, 126.2, 126.1, 126.0, 125.94, 125.91, 125.9, 125.8, 125.5, 100.8, 98.3, 83.3, 75.9, 74.1, 72.3, 70.6, 69.8, 69.2, 66.8, 54.6, 36.0, 34.0, 18.4, 17.1; **HRMS (ESI):** calcd for $C_{41}H_{43}NNaO_8^+$ $[M + Na]^+$ 700.2881, found *m/z* 700.2894. The α/β ratio was determined by HPLC after deprotection of Picoloyl protecting group in **17** and observed as

1/11 (α/β). Eluent: Hexane/EtOAc = 7/3; Retention time: α anomer = 14.5 min; β anomer = 21.8 min (Figure S5).

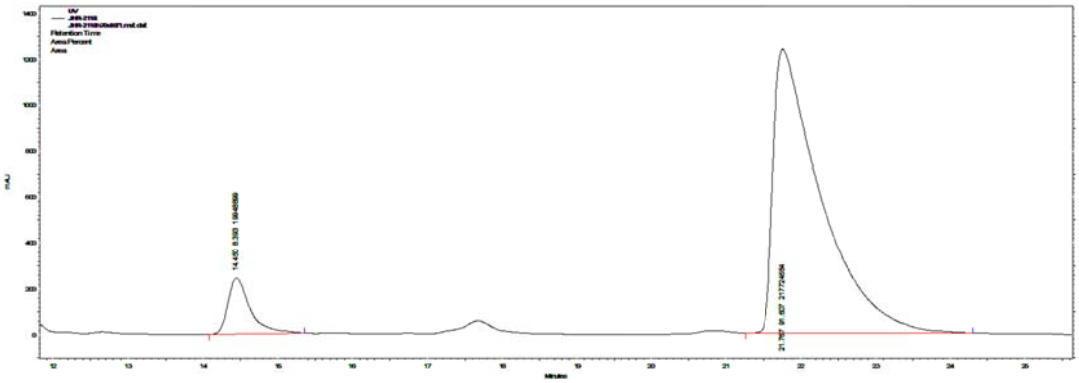
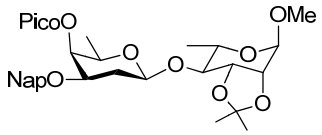


Figure S5. HPLC chromatogram of **17** after Pico deprotection.

2.3.5 Methyl 3-*O*-(2-Naphthylmethyl)-4-*O*-picoloyl-2,6-dideoxy-β-D-galactopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (18)



18

The compound **18** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **5** (137 mg, 0.27 mmol), methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside **13**[3] (50 mg, 0.22 mmol), NIS (61.0 mg, 0.27 mmol), TfOH (4.8 μL, 0.055 mmol) and activated AW300 MS (1.40 g) in CH_2Cl_2 (28 mL). The reaction mixture was stirred for 24 hours at –50 °C. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane, 2/3) to obtain **18** (110 mg, 84%) as a single anomer.

Analytical data for **18**: R_f = 0.4 (EtOAc/hexane, 2/3, v/v); $[\alpha]_D^{35}$ +45.0 (c 2.1, $CHCl_3$); **δ_H (300 MHz, $CDCl_3$, Me_4Si):** 8.85 – 8.76 (m, 1H), 8.19 (td, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.70 – 7.70 (m, 5H), 7.54 – 7.38 (m, 4H), 5.58 (d, *J* = 3.0 Hz, 1H), 4.98 – 4.82 (m, 3H), 4.69 (d, *J* = 12.1, Hz, 1H), 4.17 (t, *J* = 6.1 Hz, 1H), 4.08 (dd, *J* = 5.4 Hz, *J* = 1.8 Hz, 1H), 3.80 –

3.57 (m, 4H), 3.37 (s, 3H), 2.20 – 2.08 (m, 1H), 2.05 – 1.85 (m, 1H), 1.50 (s, 3H), 1.40 (d, *J* = 5.4 Hz, 3H), 1.32 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H); **δ_C (75 MHz,$CDCl_3$):** 164.5, 150.0, 147.6, 137.1, 135.3, 133.1, 133.0, 128.3, 127.8, 127.6, 127.0, 126.5, 126.0, 125.9, 125.6, 125.5, 109.1, 98.6, 97.8, 78.4, 77.7, 76.0, 73.9, 70.3, 69.4, 64.2, 54.7, 33.6, 27.8, 26.4, 17.6, 16.7. **HRMS (ESI):** calcd for $C_{30}H_{40}NO_9^+$ $[M + H]^+$ 594.2698, found *m*/*z* 594.2708. The α/β ratio was determined to be 1:6.2 by HPLC; Eluent: Hexane/EtOAc/CH_2Cl_2 = 60/10/30; Retention time: α anomer = 12.9 min, β anomer = 19.2 min (Figure S6).

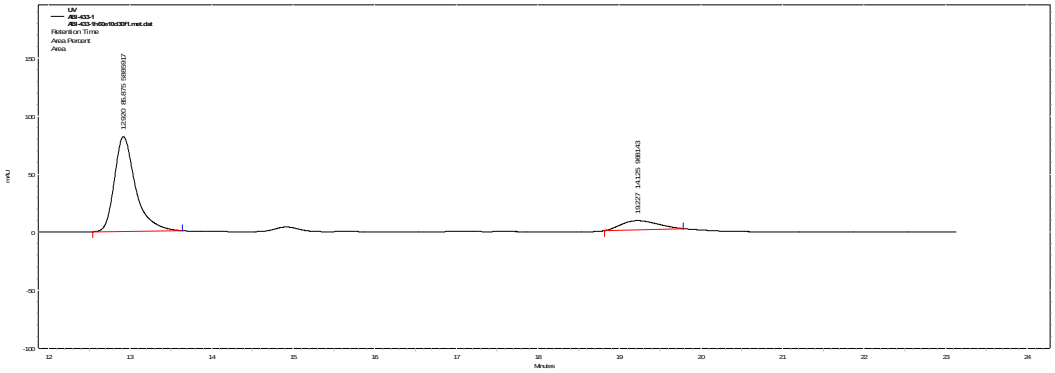
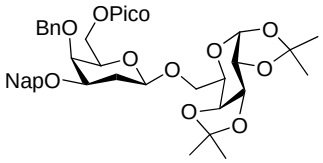


Figure S6. HPLC chromatogram of **18** after Pico deprotection.

2.3.6 4-*O*-Benzyl-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-β-D-galactopyranosyl-(1→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside (19)

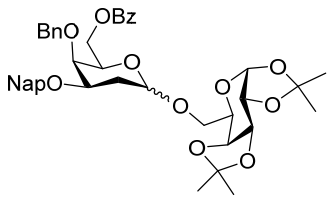


19

The compound **19** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **6** (133 mg, 0.21 mmol), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **3** (44 mg, 0.16 mmol), NIS (59.2 mg, 0.26 mmol), TfOH (3.9 μL, 0.043 mmol) and activated AW300 MS (1.3 g) in CH_2Cl_2 (21 mL). The reaction mixture was stirred for 24 hours at −50 ^oC. The silica-gel column chromatography of crude product with ethyl acetate in hexane (2:3 to 1:1) provided **19** (80 mg, 79%) as a single anomer.

Analytical data for **19**: R_f = 0.2 (EtOAc/hexane, 2/3, v/v); $[\alpha]_D^{20}$ = +2.0 (c 0.98, $CHCl_3$); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.75 – 8.73 (dq, *J* = 4.4 Hz, *J* = 0.8 Hz, 1H), 8.02 – 8.00 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.77 (m, 5H), 7.49 – 7.43 (m, 4H), 7.37 – 7.35 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 5.49 – 5.48 (d, *J* = 4.8 Hz, 1H), 5.09 – 5.08 (d, *J* = 2.8 Hz, 1H), 5.01 – 4.98 (d, *J* = 11.6 Hz, 1H), 4.81 – 4.75 (dd, *J* = 14.4 Hz, *J* = 12 Hz, 2H), 4.73 – 4.71 (d, *J* = 11.6 Hz, 1H), 4.57 – 4.54 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H), 4.51 – 4.43 (ddd, *J* = 17.6 Hz, *J* = 10.8 Hz, *J* = 6.4 Hz, 2H), 4.28 – 4.26 (dd, *J* = 5.2 Hz, *J* = 2.4 Hz, 1H), 4.21 – 4.17 (t, *J* = 6.4 Hz, 1H), 4.17 – 4.14 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 4.09 – 4.04 (ddd, *J* = 11.6 Hz, *J* = 4.4 Hz, *J* = 2.4 Hz, 1H), 4.00 (s, 1H), 3.95 – 3.91 (td, *J* = 6.4 Hz, *J* = 1.6 Hz, 1H), 3.77 – 3.73 (dd, *J* = 10.8 Hz, *J* = 6.8 Hz, 1H), 3.68 – 3.64 (dd, *J* = 10.8 Hz, *J* = 6.0 Hz, 1H), 2.33 – 2.26 (td, *J* = 12.4 Hz, *J* = 3.6 Hz, 1H), 2.12 – 2.08 (dd, *J* = 12.8 Hz, *J* = 4.8 Hz, 1H), 1.45 (s, 3H), 1.35 (s, 3H), 1.30 (s, 3H), 1.28 (s, 3H); **δ_C (100 MHz,$CDCl_3$):** 164.54, 149.8, 147.8, 138.4, 136.8, 135.9 133.2, 132.8, 128.3, 128.2, 128.0, 127.8, 127.6, 127.5, 126.7, 126.0, 125.9, 125.7, 125.4, 125.2, 109.2, 108.4, 97.3, 96.2, 74.7, 74.1, 72.5, 71.0, 70.6, 70.5, 68.9, 65.8, 65.6, 64.8, 30.9, 26.0, 25.8, 24.8, 24.4; **HRMS (ESI):** calcd for $C_{42}H_{47}NNaO_{11}^+$ $[M + Na]^+$ 764.3047, found *m*/*z* 764.3041.

2.3.7 6-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-2-deoxy-D-galactopyranosyl-(1→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside (19')

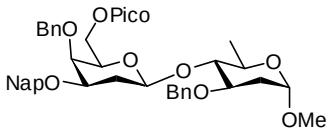


19'

The compound **19'** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **6'** (73 mg, 0.12 mmol), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **3** (24 mg, 0.09 mmol), NIS (32.5 mg, 0.14 mmol), TfOH (2.1 μL, 0.024

mmol) and activated AW300 MS (730 mg) in CH_2Cl_2 (12 mL). The reaction mixture was stirred for 1 hour at −50 °C. The silica-gel column chromatography of crude product with ethyl acetate in hexane (1:4) provided **19'** (54 mg, 79%) as anomeric mixture (α/β, 6:1). α:β Ratio was determined by NMR spectra (see pp 99-100).

2.3.8 Methyl 4-*O*-Benzyl-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-β-D-galact-opyranosyl-(1→4)-3-*O*-benzyl-2,6-dideoxy-α-D-glucopyranoside (20)



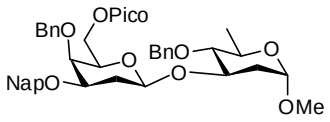
20

The compound **20** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **6** (135 mg, 0.22 mmol), methyl 3-*O*-benzyl-2,6-dideoxy-α-D-glucopyranoside **12**[2] (43 mg, 0.17 mmol), NIS (60.3 mg, 0.26 mmol), TfOH (3.9 μL, 0.044 mmol) and activated AW300 MS (1.4 g) in CH_2Cl_2 (22 mL). The reaction mixture was stirred for 48 hours at -50 °C. The silica-gel column chromatography of crude product with ethyl acetate in hexane (2:3 to 1:1) afforded **20** (73 mg, 63%) as a single anomer.

Analytical data for **20**: R_f = 0.3 (EtOAc/hexane, 2/3, v/v); $[\alpha]_D^{20}$ = +42.1 (c 0.95, $CHCl_3$); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.74 – 8.73 (dt, *J* = 4.8 Hz, *J* = 0.8 Hz, 1H), 8.00 – 7.98 (d, *J* = 7.6 Hz, 1H), 7.84 – 7.76 (m, 5H), 7.48 – 7.42 (m, 4H), 7.36 – 7.16 (m, 9H), 5.59 – 5.58 (d, *J* = 3.2 Hz, 1H), 5.00 – 4.97 (d, *J* = 11.6 Hz, 1H), 4.74 – 4.69 (m, 4H), 4.58 – 4.55 (d, *J* = 11.2 Hz, 1H), 4.52 – 4.43 (ddd, *J* = 24.8 Hz, *J* = 11.2 Hz, *J* = 7.2 Hz, 2H), 4.42 – 4.39 (d, *J* = 11.2 Hz, 1H), 4.23 – 4.20 (t, *J* = 6.0 Hz, 1H), 3.99 (s, 1H), 3.98 – 3.95 (m, 1H), 3.82 – 3.79 (ddd, *J* = 11.2 Hz, *J* = 6.4 Hz, *J* = 3.6 Hz, 1H), 3.61 – 3.54 (td, *J* = 6.4 Hz, *J* = 1.6 Hz, 1H), 3.35 – 3.30 (t, *J* = 8.8 Hz, 1H), 3.26 (s, 3H), 2.27 – 2.20 (td, *J* = 12.8 Hz, *J* = 3.6 Hz, 2H), 2.00 – 1.96 (dd, *J* = 12.4 Hz, *J* = 4.4 Hz, 1H), 1.62 – 1.55 (td, *J* = 12.2 Hz, *J* = 3.6 Hz, 1H),

1.17 – 1.15 (d, *J* = 6.0 Hz, 3H); **δ_C (100 MHz,$CDCl_3$):** 164.7, 149.8, 147.7, 138.4, 138.2, 136.8, 135.9, 133.2, 132.9, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 126.8, 126.1, 125.9, 125.8, 125.4, 125.1, 99.4, 98.1, 81.3, 77.6, 74.8, 74.0, 72.8, 70.9, 70.6, 69.5, 66.3, 65.5, 54.5, 34.9, 31.2, 18.5; **HRMS (ESI):** calcd for $C_{44}H_{47}NNaO_9^+$ $[M + Na]^+$ 756.3149, found *m*/*z* 756.3143.

2.3.9 Methyl 4-*O*-Benzyl-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-β-D-galact-opyranosyl-(1→3)-4-*O*-benzyl-2,6-dideoxy-α-D-glucopyranoside (21)



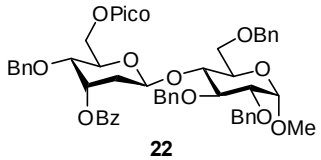
21

The compound **21** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **6** (142 mg, 0.23 mmol), methyl 4-*O*-benzyl-2,6-dideoxy-α-D-glucopyranoside **14**[4] (45 mg, 0.18 mmol), NIS (63.2 mg, 0.28 mmol), TfOH (4.1 μL, 0.046 mmol) and activated AW300 MS (1.4 g) in CH_2Cl_2 (23 mL). The reaction mixture was stirred for 24 hours at −50 °C. The silica-gel column chromatography of crude residue with ethyl acetate in hexane (2:3 to 1:1) gave **21** (79 mg, 60%) as a single anomer.

Analytical data for **21**: R_f = 0.2 (2:3 EtOAc/hexane); $[\alpha]_D^{20}$ = +61.3 (c 1.99, $CHCl_3$); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.75 – 8.73 (dt, *J* = 4.8 Hz, *J* = 0.8 Hz, 1H), 8.05 – 8.03 (d, *J* = 8 Hz, 1H), 7.82 – 7.76 (m, 5H), 7.47 – 7.44 (m, 4H), 7.39 – 7.19 (m, 9H), 5.27 – 5.26 (d, *J* = 3.2 Hz, 1H), 5.02 – 4.99 (d, *J* = 11.6 Hz, 1H), 4.76 – 4.68 (m, 4H), 4.55 – 4.49 (m, 2H), 4.44 – 4.40 (d, *J* = 11.2 Hz, *J* = 5.2 Hz, 1H), 4.36 – 4.35 (d, *J* = 3.2 Hz, 1H), 4.19 – 4.16 (t, *J* = 6.0 Hz, 1H), 4.03 – 3.94 (m, 3H), 3.65 – 3.58 (m, 1H), 3.10 (s, 3H), 2.98 – 2.93 (t, *J* = 9.2 Hz, 1H), 2.30 – 2.24 (td, *J* = 12.4 Hz, *J* = 4.0 Hz, 1H), 2.23 – 2.19 (dd, *J* = 12.8 Hz, *J* = 6.0 Hz, 1H), 1.98 – 1.93 (dd, *J* = 12.4 Hz, *J* = 4.4 Hz, 1H), 1.61 – 1.54 (td, *J* = 12.4 Hz, *J* = 4.0 Hz, 1H), 1.22 – 1.20 (d, *J* = 6.4 Hz, 3H); **δ_C (100 MHz,$CDCl_3$):** 164.7, 149.8, 147.8, 138.4, 138.3,

136.7, 135.7, 133.2, 132.9, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 126.7, 126.1, 125.9, 125.8, 125.3, 125.2, 99.9, 97.9, 84.1, 77.3, 75.0, 74.5, 74.1, 72.6, 70.5, 69.0, 66.7, 65.5, 54.2, 37.2, 31.6, 18.0; **HRMS (ESI):** calcd for $C_{44}H_{47}NNaO_9^+$ $[M + Na]^+$ 756.3149, found *m*/*z* 756.3143.

2.3.10 Methyl 3-*O*-Benzoyl-4-*O*-benzyl-6-*O*-picoloyl-2-deoxy-β-D-allopyranosyl-(1→3)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (22)



22

The compound **22** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **2a** (137 mg, 0.24 mmol), methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **10**[5] (93 mg, 0.2 mmol), NIS (54 mg, 0.24 mmol), TfOH (4.2 μL, 0.048 mmol) and activated AW300 MS (1.4 g) in CH_2Cl_2 (24 mL). The reaction mixture was stirred for 24 hours at −50 °C. The silica-gel column chromatography of crude residue with mixture of ethyl acetate, hexane and CH_2Cl_2 (2:1:1) gave **22** (90 mg) as a colorless oil (50% yield for α/β 1:8).

Analytical data for **22**: R_f = 0.2 (hexane/EtOAc/CH_2Cl_2, 2/1/1, v/v); $[\alpha]_D^{35}$ +57.8 (c 3.3, $CHCl_3$); **δ_H (500 MHz, $CDCl_3$, Me_4Si):** 8.71 (d, *J* = 4.5 Hz, 1H), 7.98 – 7.96 (m, 2H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.53 – 7.50 (m, 1H), 7.39-7.37 (m, 1H), 7.32 – 7.10 (m, 21H), 7.06 – 7.03 (m, 1H), 5.86 (d, *J* = 2.5 Hz, 1H), 5.25 (d, *J* = 9.5 Hz, 1H), 5.03 (d, *J* = 11 Hz, 1H), 4.82 (d, *J* = 11 Hz, 1H), 4.71 (d, *J* = 12.5 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.58 (s, 1H), 4.57 (d, *J* = 7.5 Hz, 1H), 4.53 (dd, *J* = 4.5 Hz, *J* = 12 Hz, 1H), 4.47 (dd, *J* = 1.5 Hz, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 5 Hz, 2H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.18 – 4.17 (m, 1H), 3.97 – 3.91 (m, 2H), 3.73 – 3.67 (m, 2H), 3.61 (d, *J* = 2 Hz, 2H), 3.50 – 3.47 (m, 1H), 3.33 (s, 3H), 2.17 (ddd, *J* = 1.5 Hz, *J* = 2.5 Hz, *J* = 14.5 Hz, 1H), 1.84 (ddd, *J* = 2 Hz, *J* = 12 Hz, *J* = 14 Hz,

1H); **δ_C (125 MHz,$CDCl_3$):** 165.7, 164.6, 149.9, 147.8, 139.3, 138.3, 137.8, 137.1, 136.8, 133.3, 129.9, 129.8, 128.6, 128.4, 128.4, 128.2, 128.1, 127.9, 127.9, 127.7, 127.4, 127.4, 127.3, 126.8, 125.3, 98.9 (C-1'), 98.3 (C-1), 80.6, 79.4, 76.9, 75.3, 73.6, 73.4, 72.6, 71.9, 71.2, 69.7, 68.5, 66.6, 64.9, 55.3, 36.0; **HRMS (ESI):** calcd for $C_{54}H_{55}NNaO_{12}^+$ $[M + Na]^+$ 932.3616, found *m/z* 932.3595. The α/β ratio was determined by HPLC after deprotection of Picoloyl protecting group in **22** and observed as 1/8 (α/β). Eluent: Hexane/EtOAc = 4/1; retention time: α anomer = 22.7 min; β anomer = 16.0 min (Figure S7).

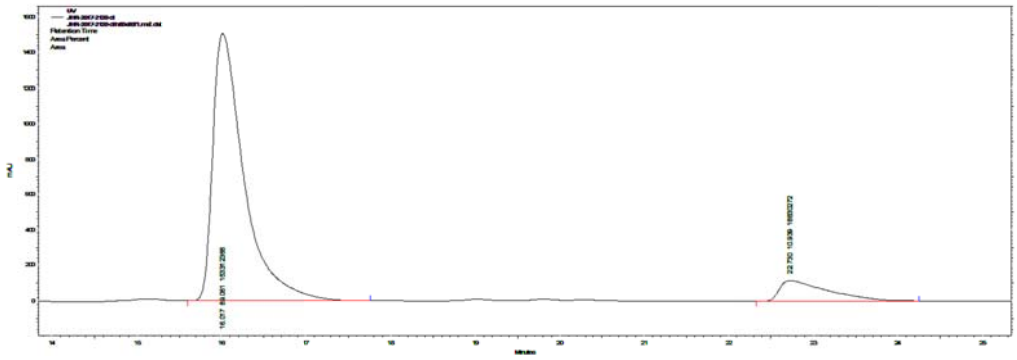
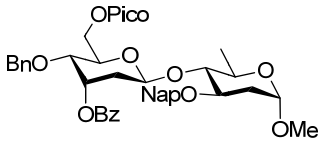


Figure S7. HPLC chromatogram of **22** after Pico deprotection.

2.3.11 Methyl 3-*O*-Benzoyl-4-*O*-benzyl-6-*O*-picoloyl-2-deoxy-β-D-allopyranosyl-(1→3)-3-*O*-(2-naphthylmethyl)-2,6-dideoxy-α-D-glucopyranoside (23)



23

The compound **23** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **2a** (137 mg, 0.24 mmol), methyl 3-*O*-(2-naphthlmethyl)-2,6-dideoxy -α-D-glucopyranoside **11** (58 mg, 0.2 mmol), NIS (54 mg, 0.24 mmol), TfOH (4.2 μL, 0.048 mmol) and activated AW300 MS (1.40 g) in CH_2Cl_2 (24 mL). The reaction mixture was stirred for 24 hours at −50℃. The crude product was purified by silica-gel column chromatography with (1:1) EtOAc in hexane to provide **23** (80 mg) as a white powder (54% yield for α/β 1:7.5).

Analytical data for **23**: R_f = 0.25 (EtOAc/hexane, 1/1, v/v); $[\alpha]_D^{35}$ +103.4 (c 0.4, $CHCl_3$); **δ_H (600 MHz, $CDCl_3$, Me_4Si):** 8.62 – 8.61 (m, 1H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.74 – 7.66 (m, 4H), 7.57 – 7.53 (m, 2H), 7.43 – 7.36 (m, 5H), 7.31 – 7.29 (m, 1H), 7.21 – 7.07 (m, 5H), 5.92 – 5.91 (m, 1H), 5.31 (d, *J* = 9.6 Hz, 1H), 4.94 (d, *J* = 12 Hz, 1H), 4.72 – 4.67 (m, 3H), 4.68 (s, 1H), 4.57 (d, *J* = 3 Hz, 2H), 4.41 (d, *J* = 11.4 Hz, 1H), 4.29 – 4.27 (m, 1H), 3.93 – 9.89 (m, 1H), 3.71 – 3.69 (m, 1H), 3.41 – 3.38 (m, 1H), 3.25 (s, 3H), 2.31 (ddd, *J* = 1.8 Hz, *J* = 3.6 Hz, *J* = 14.4 Hz, 1H), 2.17 (dd, *J* = 4.8 Hz, *J* = 13.2 Hz, 1H), 1.97 (ddd, *J* = 2.4 Hz, *J* = 9.6 Hz, *J* = 13.8 Hz, 1H), 1.67 (ddd, *J* = 3.6 Hz, *J* = 11.4 Hz, *J* = 14.4 Hz, 1H), 1.25 (d, *J* = 6.6 Hz, 3H); **δ_C (150 MHz,$CDCl_3$):** 165.9, 164.84, 149.83, 147.9, 137.3, 136.9, 136.8, 133.4, 133.39, 133.0, 130.2, 129.9, 128.7, 128.54, 128.49, 128.1, 128.02, 127.95, 127.9, 126.8, 126.1, 125.9, 125.80, 125.76, 125.3, 99.3, 98.3, 83.9, 75.6, 72.9, 72.3, 72.0, 71.3, 66.9, 66.8 (C-3'), 65.2, 54.7, 36.2, 36.0, 18.4; **HRMS (ESI):** calcd for $C_{44}H_{45}NNaO_{10}^+$ $[M + Na]^+$ 770.2936, found *m/z* 770.2952. The α/β ratio was determined by HPLC after deprotection of Picoloyl protecting group in **23** and observed as 1/7.6 (α/β). Eluent: Hexane/EtOAc = 1/1; retention time: α anomer = 12.7 min; β anomer = 11.6 min (Figure S8).

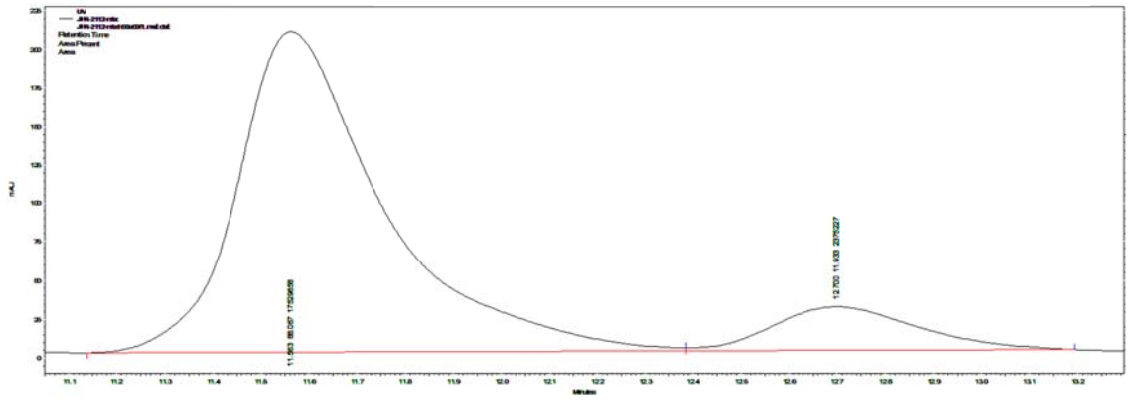
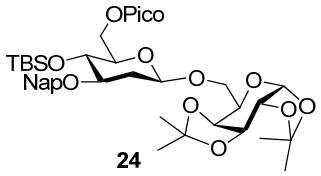


Figure S8. HPLC chromatogram of **23** after Pico deprotection.

2.3.12 4-*O*-(*tert*-Butyldimethylsilyl)-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-β-D-glucopyranosyl-(1→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside (24)



24

The compound **24** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **7** (148 mg, 0.24 mmol), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **3** (52 mg, 0.2 mmol), NIS (54 mg, 0.24 mmol), TfOH (4.2 μL, 0.048 mmol) and activated AW300 MS (1.5 g) in CH_2Cl_2 (24 mL). The reaction mixture was stirred for 24 hours at -50 ^oC. The crude residue was purified by silica-gel column chromatography with mixture of ethyl acetate, hexane and CH_2Cl_2 (1:1:1) to provide **24** (108 mg) as a thick gum (70% yield for α/β 1:12).

Analytical data for **24**: R_f = 0.4 (hexane/EtOAc/CH_2Cl_2, 1/1/1, v/v); $[\alpha]_D^{35}$ −39.7 (*c* 3.1, $CHCl_3$); **δ_H (600 MHz, $CDCl_3$, Me_4Si)**: 8.73 – 8.73 (m, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.75 (m, 5H), 7.44 – 7.40 (m, 4H), 5.49 (d, *J* = 3.6 Hz, 1H), 4.74 (d, *J* = 12 Hz, 1H), 4.70 (d, *J* = 12 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H), 4.57 (d, *J* = 12 Hz, 1H), 4.53 – 4.48 (m, 2H), 4.24 – 4.24 (m, 1H), 4.10 (d, *J* = 7.8 Hz, 1H), 3.96 – 3.93 (m, 2H), 3.70 – 3.68 (m, 1H), 3.65 – 3.62 (m, 1H), 3.59 – 3.56 (m, 1H), 3.49 (ddd, *J* = 4.2 Hz, *J* = 7.2 Hz, *J* = 10.8 Hz, 1H), 2.49 (dd, *J* = 3 Hz, *J* = 11.4 Hz, 1H), 1.63 (dd, *J* = 1.2 Hz, *J* = 11.4 Hz, 1H), 1.46 (s, 3H), 1.36 (s, 3H), 1.27 (s, 3H), 1.24 (s, 3H), 0.83 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); **δ_C (150 MHz,$CDCl_3$)**: 164.9, 150.0, 148.1, 137.0, 135.7, 133.3, 133.0, 128.1, 128.0, 127.8, 126.9, 126.6, 126.2, 126.1, 125.9, 125.2, 109.4, 108.7, 100.6, 96.4, 79.3, 74.7, 71.6, 71.5, 70.9, 70.8, 70.5, 68.9, 68.0, 65.2, 36.1, 26.1, 26.0, 25.1, 24.5, 18.3, -3.6, -4.9; **HRMS (ESI):** calcd for $C_{41}H_{55}NNaO_{11}Si^+$ $[M + Na]^+$ 788.3437, found *m/z* 788.3449. The α/β ratio was determined by HPLC after deprotection of picoloyl protecting group in **24** and observed as 1/12 (α/β). Eluent: Hexane/EtOAc = 1/1; retention time: α anomer = 12.0 min; β anomer = 9.2 min (Figure S9).

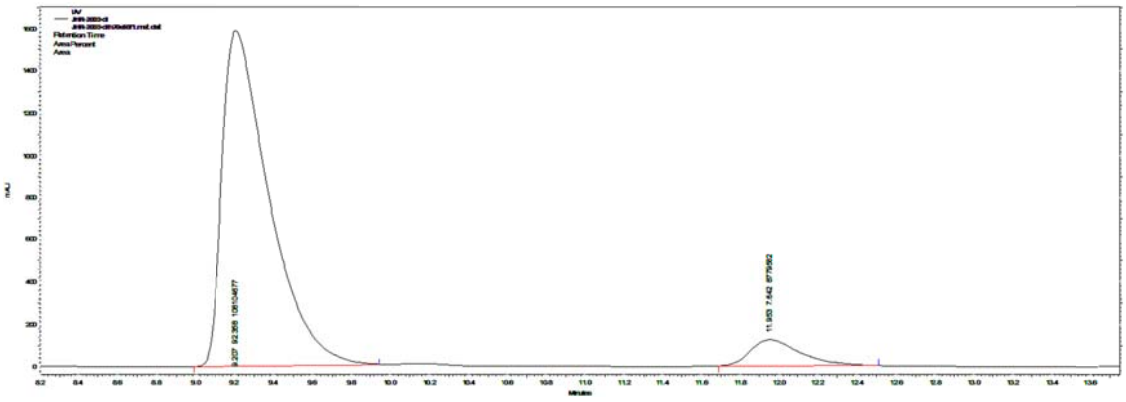
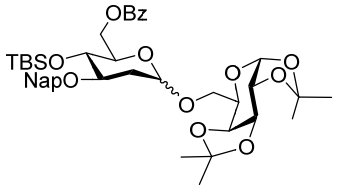


Figure S9. HPLC chromatogram of **24** after Pico deprotection.

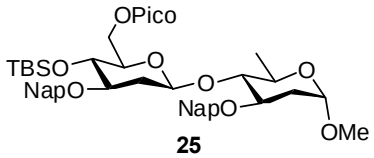
2.3.13 6-*O*-Benzoyl-4-*O*-(*tert*-butyldimethylsilyl)-3-*O*-(2-naphthylmethyl)-2-deoxy-D-glucopyranosyl-(1→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside (24')



24'

The compound **24'** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **7'** (63 mg, 0.10 mmol), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **3** (20 mg, 0.07 mmol), NIS (27 mg, 0.12 mmol), TfOH (1.7 μL, 0.02 mmol) and activated AW300 MS (600 mg) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 hour at -50 ^oC. The crude residue was purified by silica-gel column chromatography with mixture of ethyl acetate and hexane (1:4) to provide **24'** (52 mg) as a thick gum (90% yield for α/β 2:1). α/β Ratio was determined by NMR spectrum (see pp 121-122).

2.3.14 Methyl 4-*O*-(*tert*-Butyldimethylsilyl)-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-β-D-glucopyranosyl-(1→4)-3-*O*-(2-naphthylmethyl)-2,6-di-deoxy-α-D-glucopyranoside (25)



25

The compound **25** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **7** (148 mg, 0.24 mmol), methyl 3-*O*-(2-naphthlmethyl)-2,6-dideoxy -α-D-glucopyranoside **11** (58 mg, 0.2 mmol), NIS (54 mg, 0.24 mmol), TfOH (4.2 μL, 0.048 mmol) and activated AW300 MS (1.5 g) in CH_2Cl_2 (24 mL). The reaction mixture was stirred for 24 hours at -50 ^oC. The silica-gel column chromatography of crude residue with ethyl acetate and hexane (2:1) afforded **25** (96 mg) as a colorless gum (64% yield for α/β 1:9).

Analytical data for **25**: R_f = 0.25 (hexane/EtOAc, 2/1, v/v); $[\alpha]_D^{35}$ +43.8 (c 3.1, $CHCl_3$); **δ_H (600 MHz, $CDCl_3$, Me_4Si)**: 8.61-8.60 (m, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.80 (m, 3H), 7.76 – 7.67 (m, 5H), 7.58 – 7.56 (m, 1H), 7.48 – 7.40 (m, 6H), 7.26 – 7.24 (m, 1H), 4.87 (d, *J* = 12.6 Hz, 1H), 4.76 (d, *J* = 9.6 Hz, 1H), 4.73 – 4.69 (m, 3H), 4.66 (s, H-1), 4.60 (d, *J* = 11.4 Hz, 1H), 4.46 – 4.43 (m, 1H), 3.90 – 3.86 (m, 1H), 3.72 – 3.66 (m, 2H), 3.52 – 3.50 (m, 1H), 3.46 – 3.44 (m, 1H), 3.36 – 3.33 (m, 1H), 3.22 (s, 3H), 2.38 (ddd, *J* = 1.8 Hz, *J* = 3.6 Hz, *J* = 12 Hz, 1H), 2.16 (ddd, *J* = 1.2 Hz, *J* = 3.6 Hz, *J* = 12.6 Hz, 1H), 1.67 – 1.62 (m, 2H), 1.20 (d, *J* = 6 Hz, 3H), 0.85 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); **δ_C (150 MHz,$CDCl_3$):** 165.1, 150.1, 148.1, 137.00, 136.96, 136.1, 133.6, 133.5, 133.3, 133.1, 128.4, 128.3, 128.2, 128.1, 128.06, 128.01, 126.9, 126.7, 126.5, 126.34, 126.30, 126.23, 126.21, 126.1, 126.0, 125.3, 100.3, 98.4, 83.4, 79.8, 75.3, 75.1, 72.4, 71.7, 71.4, 67.1, 65.3, 54.8, 36.9, 36.2, 26.3, 18.5 (, -3.3, -4.7; **HRMS (ESI):** calcd for $C_{47}H_{57}NNaO_9Si^+$ $[M + Na]^+$ 830.3695, found *m*/*z* 830.3704. The α/β ratio was determined by HPLC after deprotection of picoloyl protecting group in **25** and observed as 1/9 (α/β). Eluent: Hexane/EtOAc = 7/3; retention time: α-anomer = 10.4 min; β-anomer = 13.5 min (Figure S10).

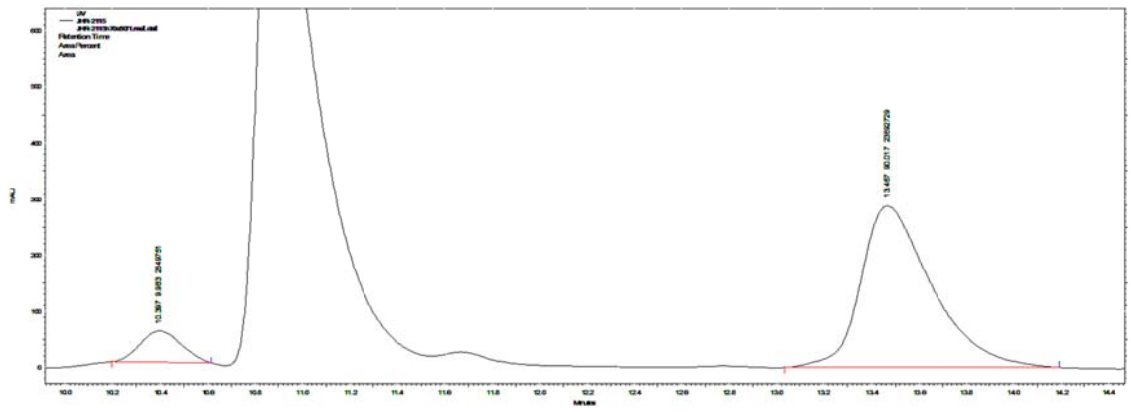
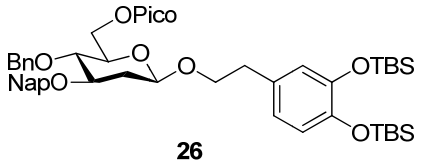


Figure S10. HPLC chromatogram of **25** after Pico deprotection.

2.3.15 2´-[(3,4-Bis(*tert*-butyldimethylsilyloxy)phenyl]ethyl 4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-β-D-glucopyranoside (26)



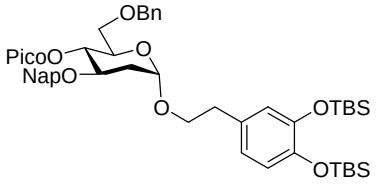
26

The compound **26** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **8** (101 mg, 0.17 mmol), 2´-(3,4-bis(*tert*-butyldimethyl silyloxy)phenyl) ethanol **15**[6] (59 mg, 0.15 mmol), NIS (37 mg, 0.17 mmol), TfOH (2.9 µL, 0.033 mmol) and activated AW300 MS (1.0 g) in CH_2Cl_2 (17 mL). The reaction mixture was stirred for 24 hours at -50 ^oC. The silica-gel column chromatography of crude residue with ethyl acetate and hexane (2:1) afforded **26** (105 mg, 79%) as a single anomer.

Analytical data for **26**: R_f = 0.2 (hexane/EtOAc, 2/1, v/v); $[\alpha]_D^{35}$ -1.5 (c 4.0, $CHCl_3$); **δ_H (600 MHz, $CDCl_3$, Me_4Si)**: 8.73 – 8.72 (m, 1H), 8.03 (d, *J* = 8 Hz, 1H), 7.82 – 7.72 (m, 5H), 7.48 – 7.45 (m, 3H), 7.42 – 7.39 (m, 1H), 7.31 – 7.21 (m, 5H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.67 (d, *J* = 2 Hz, 1H), 6.59 (dd, *J* = 2 Hz, *J* = 8 Hz, 1H), 5.00 (d, *J* = 11 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.75 (d, *J* = 11.5 Hz, 1H), 4.70 (d, *J* = 10.5 Hz, 1H), 4.65 – 4.63 (m, 2H), 4.47 (dd, *J* = 1.5 Hz, *J* = 9.5 Hz, 1H), 4.03 – 3.99 (m, 1H), 3.76 (ddd, *J* = 5.5 Hz, *J* = 8.5 Hz, *J* = 11.5 Hz, 1H), 3.66 – 3.55 (m, 3H), 2.78 – 2.75 (m, 2H), 2.40 (dd, *J* = 5 Hz, *J* = 12.5 Hz, 1H), 1.73 (d,

J = 11.5 Hz, 1H), 0.98 (s, 9H), 0.97 (s, 9H), 0.18 (s, 6H), 0.17 (s, 6H); **δ_C (150 MHz,$CDCl_3$)**: 164.9, 150.1, 148.0, 146.6, 145.3, 138.1, 137.0, 135.7, 133.4, 133.1, 131.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 126.9, 126.6, 126.3, 126.1, 125.9, 125.3, 122.0, 121.8, 120.9, 100.1, 79.6, 78.1, 75.1, 73.3, 71.7, 70.7, 65.0, 36.8, 35.7, 26.1, 18.6, 18.5, -3.93, -3.94; **HRMS (ESI):** calcd for $C_{50}H_{65}NNaO_8Si_2^+$[M + Na]$^+$ 886.4141, found *m*/*z* 886.4155.

2.3.16 2´-[(3,4-Bis(*tert*-butyldimethylsilyloxy)phenyl]ethyl 6-*O*-benzyl-3-*O*-(2-naphthylmethyl)-4-*O*-picoloyl-2-deoxy-α-D-glucopyranoside (26')

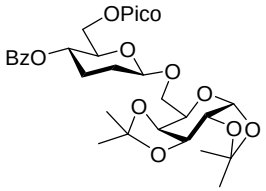


26'

The compound **26'** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **8'** (80 mg, 0.13 mmol), 2'-(3,4-bis(*tert*-butyldimethyl silyloxy)phenyl) ethanol **15**[6] (39 mg, 0.10 mmol), NIS (35 mg, 0.15 mmol), TfOH (2.3 µL, 0.026 mmol) and activated AW300 MS (800 mg) in CH_2Cl_2 (13 mL). The reaction mixture was stirred for 20 hours at -50 ^oC. The silica-gel column chromatography of crude residue with ethyl acetate and hexane (2:3 to 1:1) afforded **26'** (74 mg) as a thick gum (94% yield for α/β 10:1). Analytical data for **26'**: R_f = 0.5 (hexane/EtOAc, 3/2, v/v); **δ_H (400 MHz, $CDCl_3$, Me_4Si)**: 8.74 – 8.73 (dq, *J* = 4.8 Hz, *J* = 0.8 Hz, 1H), 8.04 – 8.02 (dd, *J* = 6.8 Hz, *J* = 0.8 Hz, 1H), 7.82 – 7.74 (m, 5H), 7.48 – 7.41 (m, 4H), 7.28 – 7.20 (m, 5H), 6.69 – 6.67 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 2 Hz, 1H), 6.58 – 6.56 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 5.01 – 4.98 (d, *J* = 11.2 Hz, 1H), 4.87 – 4.84 (d, *J* = 11.6 Hz, 1H), 4.77 – 4.74 (d, *J* = 11.6 Hz, 1H), 4.70 – 4.67 (d, *J* = 10.8 Hz, 1H), 4.66 – 4.59 (m, 2H), 4.48 – 4.45 (dd, *J* = 9.6 Hz, *J* = 1.6 Hz, 1H), 4.02 – 3.96 (m, 1H), 3.76 – 3.73 (m, 1H), 3.65 – 3.52 (m, 3H), 2.76 – 2.73 (dd, *J* = 7.6 Hz, *J* = 7.2 Hz, 2H), 2.40 (ddd, *J* = 2 Hz, *J* = 4.8 Hz, *J* = 12.4 Hz, 1H), 1.75 – 1.67 (m, 1H), 0.97 (s, 9H), 0.96 (s, 9H), 0.17 (s, 6H), 0.15 (s, 6H); **δ_C (100 MHz,$CDCl_3$)**: 164.7, 149.9, 147.8, 146.4,

145.1, 137.9, 136.8, 135.5, 133.2, 133.0, 128.0, 127.8, 127.7, 127.6, 126.5, 126.1, 125.9, 125.7, 125.1, 121.8, 121.6, 120.7, 99.9, 79.4, 77.9, 75.0, 73.1, 71.5, 70.5, 64.8, 36.6, 35.5, 25.9, 18.4, 18.4, -4.0. α/β Ratio of 26' was determined by isolation.

2.3.17 4-*O*-Benzoyl-6-*O*-picoloyl-2,3-dideoxy-β-D-glucopyranosyl-(1→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside (27)



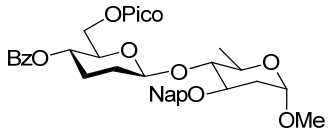
27

The compound **27** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **9** (60 mg, 0.12 mmol), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **3** (26 mg, 0.10 mmol), NIS (27 mg, 0.12 mmol), TfOH (1.7 μL, 0.02 mmol) and activated AW300 MS (600 mg) in CH_2Cl_2 (12 mL). The reaction mixture was stirred for 3 hours at −50℃. The silica-gel column chromatography of crude residue with mixture of EtOAc, CH_2Cl_2, and hexane (2:1:1) afforded **27** (36 mg, 60%) as a single anomer.

Analytical data for **27**: R_f = 0.3 (hexane/EtOAc/CH_2Cl_2, 1/1/1, v/v); $[\alpha]_D^{35}$ -20.1 (c 1.3, $CHCl_3$); **δ_H (600 MHz, $CDCl_3$, Me_4Si):** 8.72 – 8.72 (m, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.80 – 7.77 (m, 1H), 7.55 – 7.52 (m, 1H), 7.45 – 7.43 (m, 1H), 7.41 – 7.38 (m, 2H), 5.54 (d, *J* = 5.4 Hz, 1H), 5.06 (dd, *J* = 4.8 Hz, *J* = 9 Hz, 1H), 4.74 (dd, *J* = 1.8 Hz, *J* = 8.4 Hz, 1H), 4.64 (dd, *J* = 4.2 Hz, *J* = 12 Hz, 1H), 4.58 (dd, *J* = 6 Hz, *J* = 12 Hz, 1H), 4.56 (dd, *J* = 1.2 Hz, *J* = 7.8 Hz, 1H), 4.30 (dd, *J* = 2.4 Hz, *J* = 4.8 Hz, 1H), 4.19 (dd, *J* = 1.2 Hz, *J* = 7.8 Hz, 1H), 4.09 (ddd, *J* = 4.2 Hz, *J* = 6 Hz, *J* = 9 Hz, 1H), 4.04 – 4.00 (m, 2H), 3.74 – 3.71 (m, 1H), 2.38 (dd, *J* = 4.2 Hz, *J* = 12.6 Hz, 1H), 2.07 – 2.05 (m, 1H, H-$2'_{eq}$), 1.82 – 1.69 (m, 2H), 1.54 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H); **δ_C (150 MHz,$CDCl_3$):** 165.7, 164.9, 150.0, 147.9, 137.1, 133.3, 130.0, 129.8, 128.5, 127.0, 125.5, 109.5, 108.8,

102.1, 96.5, 74.9, 71.6, 70.9, 70.6, 69.0, 68.7, 68.1, 65.4, 29.5, 26.8, 26.2, 26.1, 25.1, 24.6; **HRMS (ESI):** calcd for $C_{31}H_{37}NNaO_{11}^{+}[M + Na]^{+}$ 622.2259, found *m*/*z* 622.2262.

2.3.18 4-*O*-Benzoyl-6-*O*-picoloyl-2,3-dideoxy-β-D-glucopyranosyl-(1→4)-3-*O*-(2-naph thyl methyl)-2,6-di-deoxy-α-D-glucopyranoside (28)



28

The compound **28** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **9** (120 mg, 0.25 mmol), methyl 3-*O*-(2-naphthlmethyl)-2,6-dideoxy -α-D-glucopyranoside **11** (54 mg, 0.18 mmol), NIS (56 mg, 0.25 mmol), TfOH (4.42 μL, 0.05 mmol) and activated AW300 MS (1.2 g) in CH_2Cl_2 (25 mL). The reaction mixture was stirred for 22 hours at −50 ˚C. The silica-gel column chromatography of crude residue with mixture of ethyl acetate and hexane (1:2) afforded **28** (63 mg, 55%) as anomeric mixture with 1:2 (α:β).

Analytical data for **28**: R_f = 0.2 (hexane/EtOAc, 3/2, v/v); $[\alpha]_D^{35}$ 79.0 (c 0.41, $CHCl_3$); **δ_H (600 MHz, $CDCl_3$, Me_4Si):** 8.59 - 8.58 (m, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.78 - 7.73 (m, 4H), 7.58 - 7.52 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.43 - 7.37 (m, 4H), 7.29-7.27 (m, 1H), 5.01 (dd, *J* = 4.8 Hz, *J* = 10.2 Hz, 1H), 4.95 (d, *J* = 12 Hz, 1H), 4.88 (d, *J* = 8.4 Hz, 1H), 4.77 (d, *J* = 12.6 Hz, 1H), 4.70 (d, *J* = 2.4 Hz, 1H), 4.57 (dd, *J* = 3 Hz, *J* = 12 Hz, 1H), 4.45 (dd, *J* = 5.4 Hz, *J* = 11.4 Hz, 1H), 3.97 - 3.91 (m, 2H), 3.72 (dd, *J* = 6.6 Hz, *J* = 9 Hz, 1H), 3.40 (d, *J* = 9 Hz, 1H), 3.26 (s, 3H), 2.39 (dd, *J* = 4.8 Hz, *J* = 12.6 Hz, 1H), 2.19 (dd, *J* = 4.8 Hz, *J* = 13.2 Hz, 1H), 2.02 (d, *J* = 13.8 Hz, 1H), 1.79 (ddd, *J* = 4.2 Hz, *J* = 9.6 Hz, *J* = 13.8 Hz, 1H), 1.72 - 1.60 (m, 2H), 1.30 (d, *J* = 6 Hz, 3H); **δ_C (150 MHz,$CDCl_3$):** 165.7, 164.8, 149.9, 147.7, 136.89, 136.86, 133.42, 133.37, 133.0, 129.93, 129.89, 128.6, 128.1, 128.0, 127.9, 126.8, 126.2, 126.1, 126.0, 125.8, 125.4, 102.3, 98.3, 83.7, 75.4, 72.3,

68.8, 67.0, 65.3, 54.7, 36.1, 30.3, 27.7, 18.4; **HRMS (ESI):** calcd for $C_{37}H_{39}NNaO_9^+$ [M + Na]$^+$ 664.2517, found *m*/*z* 664.2525.

The α/β ratio of **28** was determined to be 1/2 by HPLC after deprotection of Picolinoyl-group; Eluent: Hexane/EtOAc = 13/7; retention time: α anomer = 20.2 min; β anomer = 16 min (Figure S11).

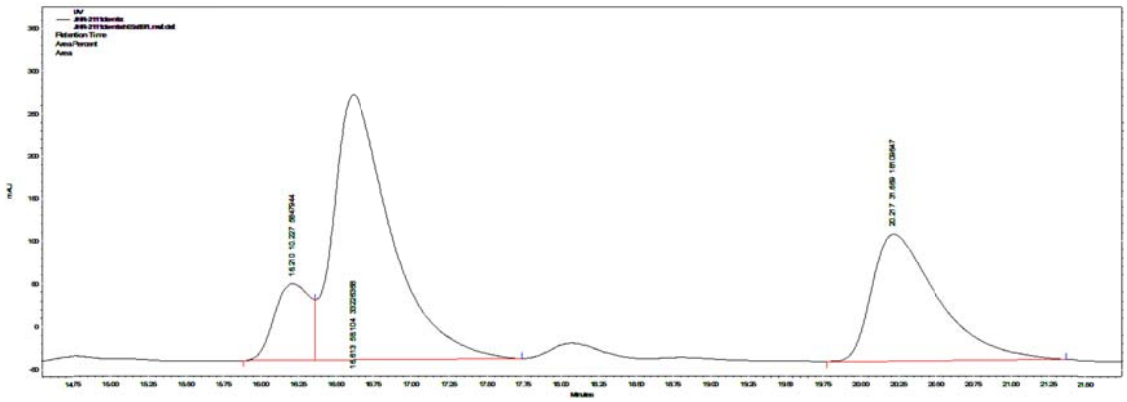
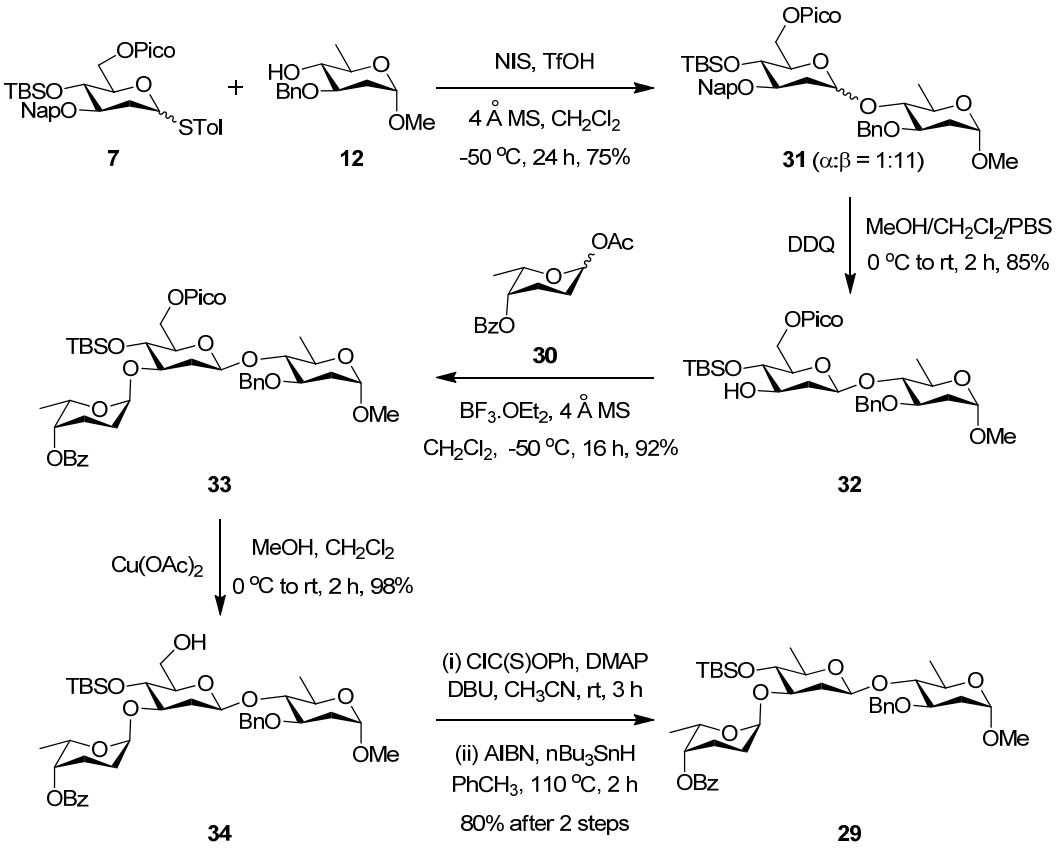


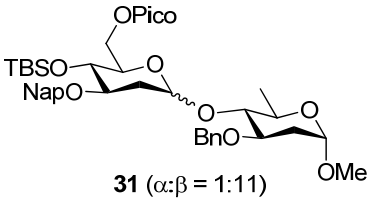
Figure S11. HPLC chromatogram of **28** after Pico deprotection.

2.4 Synthesis of deoxytrisaccharide 29



Scheme S1: Synthesis of trisaccharide derivative

2.4.1 Methyl 4-*O*-(*tert*-Butyldimethylsilyl)-3-*O*-(2-naphthylmethyl)-6-*O*-picoloyl-2-deoxy-D-glucopyranosyl-(1→4)-3-*O*-benzyl-2,6-dideoxy-α-D-glucopyranoside (31)



The compound **31** was synthesized by following the general glycosylation procedure **(2.1)** with glycosyl donor **7** (810 mg, 1.28 mmol), methyl 3-*O*-benzyl-2,6-dideoxy-α-D-glucopyranoside **12** (250 mg, 0.99 mmol), NIS (347 mg, 1.54 mmol), TfOH (22.7 µL, 0.257 mmol) and activated AW300 MS (8.0 g) in CH_2Cl_2 (128 mL). The reaction mixture was stirred for 48 hours at -50 °C. The silica-gel column chromatography of crude product with

ethyl acetate in hexane (2:3 to 1:1) gave **31** (562 mg, 75%) as a inseparable mixture with 1:11 (α:β). The α/β ratio was determined by HPLC after deprotection of Picoloyl protecting group in **31** and observed as 1/11 (α/β). Eluent: Hexane/EtOAc = 7/3; retention time: α-anomer = 14.5 min; β-anomer = 21.8 min (Figure S12).

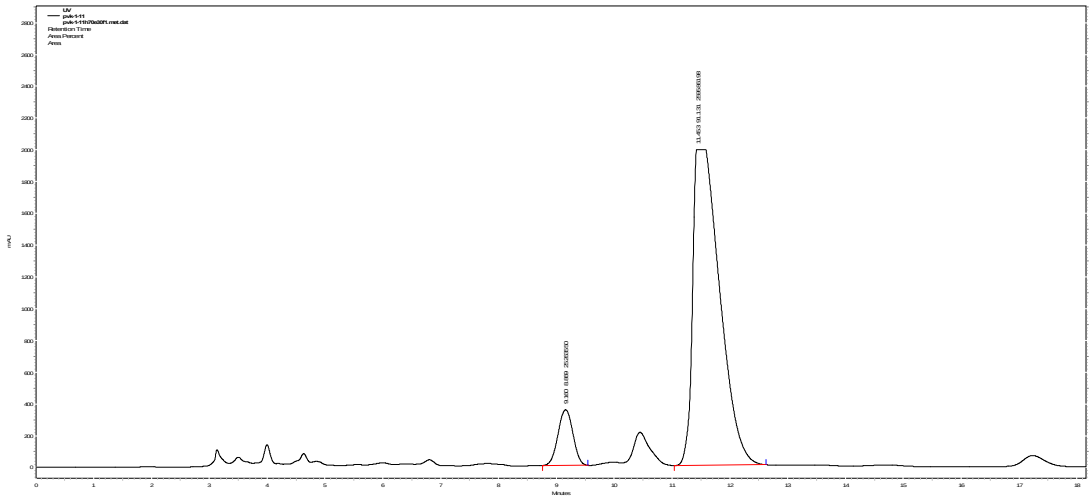
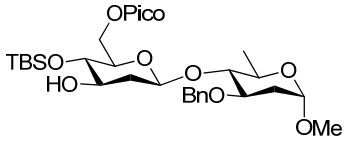


Figure S12. HPLC chromatogram of **31** after Pico deprotection.

2.4.2 Methyl 4-*O*-(*tert*-Butyldimethylsilyl)-6-*O*-picoloyl-2-deoxy-β-D-glucopyranosyl-(1→4)-3-*O*-benzyl-2,6-dideoxy-α-D-glucopyranoside (32)

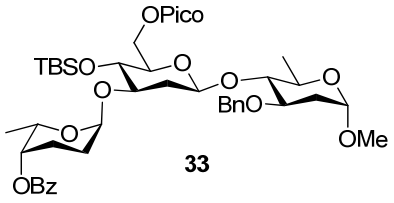


32

To the stirred solution of **31** (530 mg, 0.69 mmol) in 30 mL of mixture of (8:1:1) CH_2Cl_2:MeOH:PBS (phosphate buffered saline), was added 2,3-dichloro-5,6-dicyano -1,4-benzoquinone (317 mg, 1.39 mmol) at 0 ^oC. Then the reaction was warmed to room temperature and stirred for 2 hours. After completion of the reaction, the mixture was diluted with CH_2Cl_2 (150 mL), washed with satd. $NaHCO_3$ (100 mL), 10% $Na_2S_2O_{3(aq)}$ (100 mL), brine (100 mL) and dried (Na_2SO_4). The crude product was purified by silica-gel column chromatography with (3:2) ethyl acetate in hexane to get **32** (β, 336 mg) along with other anomer (α, 30 mg) as separate products.

Analytical data for **32:** R_f = 0.5 (EtOAc/hexane, 1/1, v/v); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.69 – 8.67 (dq, *J* = 4.8 Hz, *J* = 0.8 Hz, 1H), 8.03 – 8.00 (dt, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.73 – 7.68 (td, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.40 – 7.37 (ddd, *J* = 7.6 Hz, *J* = 4.8 Hz, *J* = 1.2 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.22 – 7.13 (m, 3H), 4.82 – 4.79 (dd, *J* = 9.6 Hz, *J* = 2.0 Hz, 1H), 4.75 – 4.72 (d, *J* = 12.0 Hz, 1H), 4.67 – 4.66 (d, *J* = 2.4 Hz, 1H), 4.65 – 4.61 (dd, *J* = 11.6 Hz, *J* = 2.0 Hz, 1H), 4.57 – 4.54 (d, *J* = 12.0 Hz, 1H), 4.42 – 4.37 (dd, *J* = 12.0 Hz, *J* = 5.6 Hz, 1H), 3.86 – 3.80 (ddd, *J* = 13.6 Hz, *J* = 8.4 Hz, *J* = 5.2 Hz, 1H), 3.71 – 3.66 (m, 2H), 3.56 – 3.52 (t, *J* = 8.8 Hz, 1H), 3.49 – 3.45 (ddd, *J* = 9.2 Hz, *J* = 5.2 Hz, *J* = 2.0 Hz, 1H), 3.33 – 3.29 (t, *J* = 18.0 Hz, 1H), 3.24 (s, 3H), 2.33 (bs, 1H), 2.28 – 2.23 (ddd, *J* = 12.4 Hz, *J* = 4.8 Hz, *J* = 1.6 Hz, 1H), 2.16 – 2.11 (ddd, *J* = 13.2 Hz, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H), 1.72 – 1.57 (m, 2H), 1.26 – 1.24 (d, *J* = 6.4 Hz, 3H), 0.88 (s, 9H), 0.14 (s, 3H), 0.06 (s, 3H); **δ_C (100 MHz,$CDCl_3$):** 164.5, 149.6, 147.6, 138.9, 136.6, 127.9, 127.2, 127.0, 126.6, 125.0, 100.0, 97.8, 83.2, 74.8, 74.2, 73.1, 71.9, 71.7, 66.5, 64.7, 54.3, 38.9, 35.6, 25.7, 18.1, 18.0, -3.8, -4.9; **HRMS (ESI):** calcd for $C_{32}H_{47}NNaO_9Si^+$ $[M + Na]^+$ 640.2918, found *m*/*z* 640.2910.

2.4.3 Compound 33



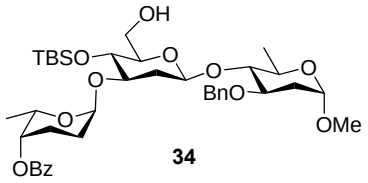
33

To the stirred solution of 4-*O*-benzoyl-L-rhodinosyl acetate **30**[7] (270 mg, 0.97 mmol), glycosyl acceptor **32** (300 mg, 0.48 mmol) and activated AW300 MS (2.7 g) in CH_2Cl_2 (45 mL), boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) (150 μL, 1.20 mmol) was added at -50 ^oC. The resulting mixture was stirred for 16 hours at same temperature. Then, the reaction was quenched with Et_3N (2 mL) and warmed to room temperature. Filtered the solution through the celite pad which was washed thoroughly with CH_2Cl_2 (150 mL). The organic layer was

washed with saturated $NaHCO_3$solution (75 mL), water (75 mL), brine (50 mL) and dried over Na_2SO_4. The flash silica-gel chromatography with 2:3 ethyl acetate in hexane provided **33** (373 mg, 92%) as a colorless oil.

Analytical data for **33:** R_f = 0.2 (EtOAc/hexane, 3/7, v/v); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.69 – 8.68 (dq, *J* = 4.4 Hz, *J* = 0.4 Hz, 1H), 8.13 – 8.11 (m, 2H), 8.05 – 8.03 (d, *J* = 7.6 Hz, 1H), 7.74 – 7.70 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.48 – 7.44 (m, 2H), 7.41 – 7.38 (ddd, *J* = 7.6 Hz, *J* = 4.8 Hz, *J* = 1.2 Hz, 1H), 7.28 – 7.15 (m, 5H), 5.14 – 5.13 (d, *J* = 3.2 Hz, 1H), 5.04 (s, 1H), 4.85 – 4.82 (dd, *J* = 9.6 Hz, *J* = 2.0 Hz, 1H), 4.74 – 4.67 (m, 3H), 4.57 – 4.54 (d, *J* = 12.0 Hz, 1H), 4.37 – 4.32 (dd, *J* = 11.6 Hz, *J* = 6.0 Hz, 1H), 4.23 – 4.18 (ddd, *J* = 12.8 Hz, *J* = 6.4 Hz, *J* = 0.8 Hz, 1H), 3.86 – 3.80 (ddd, *J* = 13.6 Hz, *J* = 8.4 Hz, *J* = 5.2 Hz, 1H), 3.76 – 3.64 (m, 3H), 3.56 – 3.52 (ddd, *J* = 8.8 Hz, *J* = 6.0 Hz, *J* = 2.4 Hz, 1H), 3.35 – 3.31 (t, *J* = 8.8 Hz, 1H), 3.24 (s, 3H), 2.55 – 2.50 (ddd, *J* = 12.8 Hz, *J* = 4.4 Hz, *J* = 2.4 Hz, 1H), 2.30 – 2.23 (m, 2H), 2.16 – 2.11 (ddd, *J* = 15.2 Hz, *J* = 4.8 Hz, *J* = 1.2 Hz, 1H), 2.09 – 2.00 (m, 1H), 1.95 – 1.89 (m, 1H), 1.63 – 1.47 (m, 2H), 1.26 – 1.24 (d, *J* = 6.4 Hz, 3H), 1.19 – 1.18 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.18 (s, 3H), 0.08 (s, 3H); **δ_C (100 MHz,$CDCl_3$):** 166.0, 164.7, 149.7, 147.8, 139.0, 136.6, 132.9, 136.6, 132.9, 130.2, 129.6, 128.3, 128.0, 127.3, 127.1, 126.6, 125.0, 99.9, 97.9, 91.3, 82.9, 74.9, 74.8, 73.2, 71.8, 70.9, 69.7, 66.6, 65.2, 64.8, 54.3, 35.7, 34.6, 25.7, 23.8, 22.9 18.1, 17.9, 17.1, -3.3, -4.4; **HRMS (ESI):** calcd for $C_{45}H_{61}NNaO_{12}Si^+$ $[M + Na]^+$ 858.3861, found *m*/*z* 858.3855.

2.4.4 Compound 34



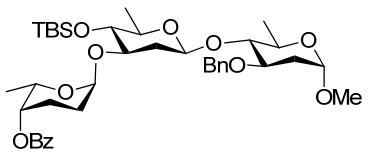
34

Copper(II) acetate monohydrate ($Cu(OAc)_2.H_2O$) (163 mg, 0.82 mmol) was added to the stirred solution of **33** (350 mg, 0.41 mmol) in CH_2Cl_2/MeOH (20:1, 21 mL) at 0 ^oC. The

resulted solution was stirred for 2 hours at ambient temperature, quenched with saturated NH_4Cl solution (5 mL), filtered through the celite pad and washed the pad with CH_2Cl_2 (150 mL). The filtrate was washed with saturated $NaHCO_3$ solution (75 mL), water (75 mL), brine (75 mL) and dried over Na_2SO_4. The crude residue was purified by silica-gel column chromatography with ethyl acetate in hexane (2:3) to afford **34** (299 mg, 98%) as a thick gum.

Analytical data for **34:** R_f = 0.4 (EtOAc/hexane, 3/7, v/v); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.12 – 8.10 (m, 2H), 7.59 – 7.55 (tt, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.38 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 5.15 – 5.14 (d, *J* = 3.2 Hz, 1H), 5.04 (s, 1H), 4.74 – 4.67 (m, 3H), 4.63 – 4.60 (d, *J* = 11.6 Hz, 1H), 4.23 – 4.18 (ddd, *J* = 12.8 Hz, *J* = 6.0 Hz, *J* = 1.2 Hz, 1H), 3.85 – 3.78 (m, 1H), 3.74 – 3.65 (m, 3H), 3.48 – 3.44 (t, *J* = 8.8 Hz, 1H), 3.43 – 3.39 (dd, *J* = 11.6 Hz, *J* = 7.2 Hz, 1H), 3.34 – 3.30 (t, *J* = 9.2 Hz, 1H), 3.29 (s, 3H), 3.22 – 3.17 (ddd, *J* = 9.2 Hz, *J* = 6.8 Hz, *J* = 2.8 Hz, 1H), 2.54 – 2.49 (ddd, *J* = 12.4 Hz, *J* = 4.4 Hz, *J* = 2.0 Hz, 1H), 2.30 – 2.21 (m, 2H), 2.09 – 2.00 (tt, *J* = 14.0 Hz, *J* = 4.4 Hz, 1H), 1.95 – 1.89 (dq, *J* = 14.0 Hz, *J* = 2.8 Hz, 1H), 1.70 – 1.63 (ddd, *J* = 13.2 Hz, *J* = 11.2 Hz, *J* = 3.6 Hz, 1H), 1.58 – 1.55 (m, 1H), 1.48 – 1.40 (m, 1H), 1.27 – 1.25 (d, *J* = 6.0 Hz, 3H), 1.18 – 1.17 (d, *J* = 6.4 Hz, 3H), 0.89 (s, 9H), 0.16 (s, 3H), 0.10 (s, 3H); **δ_C (100 MHz,$CDCl_3$):** 166.0, 138.8, 133.0, 130.2, 129.6, 128.3, 128.2, 127.5, 127.4, 100.1, 98.1, 91.3, 83.6, 76.6, 74.8, 73.2, 72.1, 71.2, 69.7, 66.8, 65.1 62.4, 54.5, 35.9, 34.8, 25.8, 23.8, 22.9, 18.0, 17.9, 17.1, -3.3, -4.3; **HRMS (ESI):** calcd for $C_{39}H_{58}NaO_{11}Si^+$ $[M + Na]^+$ 753.3646, found *m*/*z* 753.3648.

2.4.5 Compound 29



29

To the stirred solution of **34** (200 mg, 0.27 mmol) in acetonitrile (CH_3CN) (8 mL), was

added DBU (80 μL, 0.54 mmol) and DMAP (66 mg, 0.54 mmol) at 0 ^{o}C. After 5 min, *O*-phenyl chlorothionoformate (74 μL, 0.54 mmol) was also added to the reaction mixture in a dropwise fashion at 0 ^{o}C and stirred for 2 hours at room temperature. After completion of the reaction, the mixture was quenched with saturated NH_4Cl solution (5 mL), extracted with EtOAc (75 mL × 2), washed with water (75 mL), brine (75 mL) and dried over Na_2SO_4. The crude product was purified by flash column chromatography to get trisaccharide derived thionocarbonate (201 mg, 0.23 mmol) which was dissolved in toluene (10 mL). To the resulting mixture, tributyltin hydride (132 μL, 0.46 mmol) and azobisisobutyronitrile AIBN (37 mg, 0.23 mmol) was added. The solution was degassed for three times under *vacuo* and refluxed for 2 hours at 110 ^{o}C under nitrogen condition. After completion of the reaction, the solution was cooled to room temperature, concentrated and purified by column chromatography using silica-gel (2:3 ethyl acetate in hexane) to afford **29** (156 mg, 80% after two steps) as a thick gum.

Analytical data for **29:** R_f = 0.5 (EtOAc/hexane, 1/4, v/v); $[\alpha]_D^{20}$ = +12.2 (c 0.98, $CHCl_3$); **δ_H (400 MHz, $CDCl_3$, Me_4Si):** 8.13 – 8.10 (m, 2H), 7.59 – 7.55 (m, 1H), 7.47 – 7.43 (m, 2H), 7.38 – 7.23 (m, 5H), 5.12 (d, *J* = 2.8 Hz, 1H), 5.03 (s, 1H), 4.78 – 4.71 (m, 3H), 4.61 – 4.58 (d, *J* = 11.2 Hz, 1H), 4.22 – 4.17 (dd, *J* = 12.4 Hz, *J* = 6.0 Hz, 1H), 3.88 – 3.82 (m, 1H), 3.72 – 3.59 (m, 2H), 3.34 – 3.19 (m, 5H), 2.50 – 2.47 (ddd, *J* = 12.0 Hz, *J* = 4.4 Hz, *J* = 2.0 Hz, 1H), 2.31 – 2.18 (m, 2H), 2.09 – 2.00 (tt, *J* = 14.0 Hz, *J* = 4.4 Hz, 1H), 1.95 – 1.89 (dq, *J* = 14.0 Hz, *J* = 2.8 Hz, 1H), 1.72 – 1.65 (ddd, *J* = 13.2 Hz, *J* = 11.2 Hz, *J* = 3.6 Hz, 1H), 1.57 – 1.54 (m, 1H), 1.44 – 1.36 (m, 1H), 1.28 – 1.26 (d, *J* = 6.4 Hz, 3H), 1.24 – 1.22 (d, *J* = 6.0 Hz, 3H), 1.17 – 1.15 (d, *J* = 6.4 Hz, 3H), 0.91 (s, 9H), 0.16 (s, 3H), 0.11 (s, 3H); **δ_C (100 MHz,$CDCl_3$):** 166.1, 139.0, 133.0, 130.3, 129.6, 128.3, 128.1, 127.5, 127.3, 100.1, 98.1, 91.2, 83.0, 75.9, 75.7, 73.0, 73.0, 72.1, 69.9, 66.7, 65.0, 54.4, 35.7, 35.2, 25.9, 23.9, 22.9, 18.8, 18.2, 18.0, 17.1, -3.1, -3.5; **HRMS (ESI):** calcd for $C_{39}H_{58}NaO_{10}Si^+$ $[M + Na]^+$ 737.3697, found *m*/*z* 737.3698.

References:

1. J-H. Chen, J-H. Ruei and K-K. T. Mong, *Eur. J. Org. Chem.*, 2014, 1827–1831.
2. C-W T. Chang, T. Clark and M. Ngaara, *Tetrahedron Lett.*, 2001, **42**, 6797–6801.
3. S. C. Timmons and D. L. Jakeman, *Carbohydr. Res.*, 2007, **342**, 2695–2704.
4. O. Kjolberg and K. Neumann, *Acta Chem. Scand.*, 1993, **47**, 721–727
5. S. D. Debenham and E. J. Toone, *Tetrahedron: Asymmetry*, 2000, **11**, 385–387.
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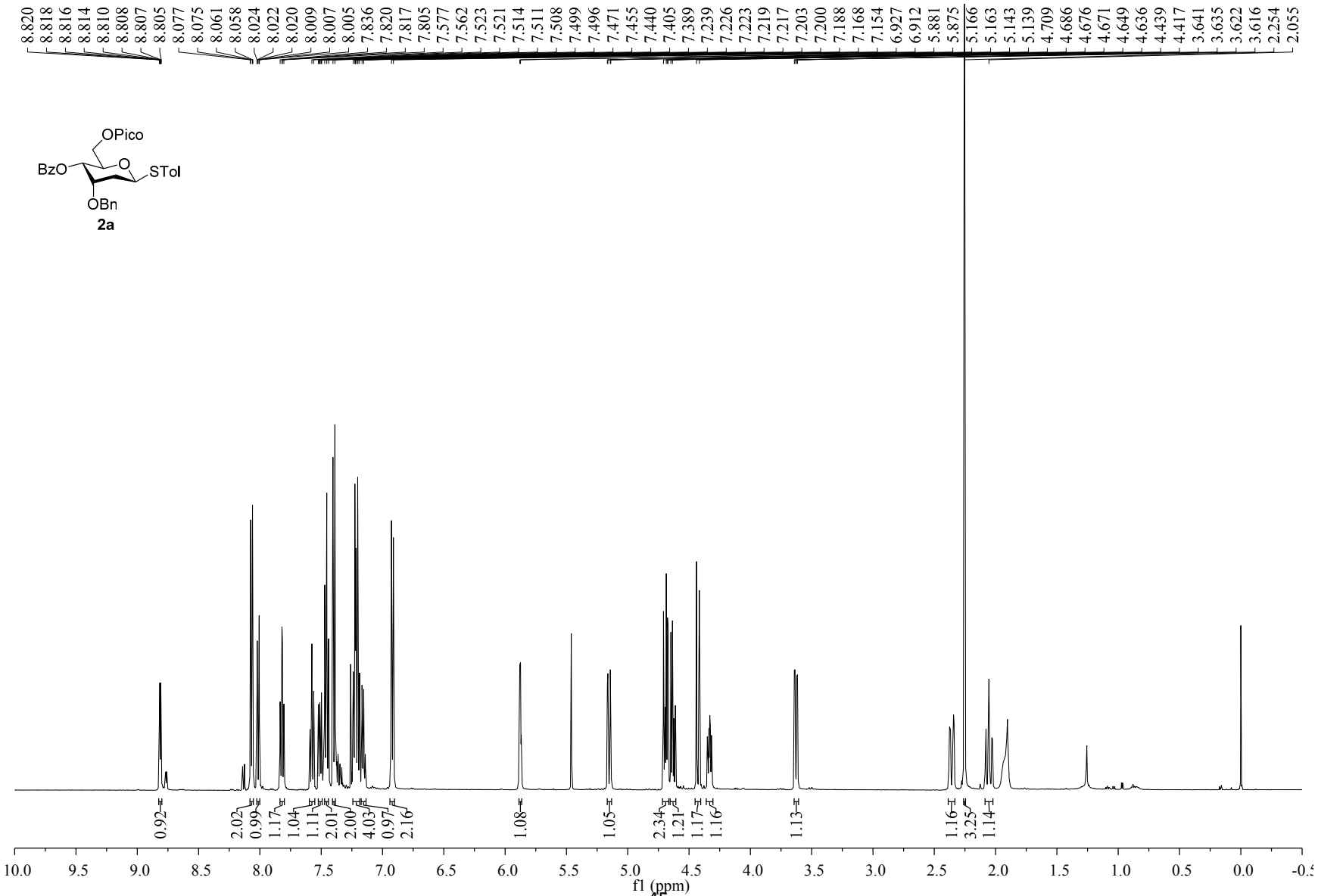
7. X. Yang, B. Fu and B. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 12433–12435.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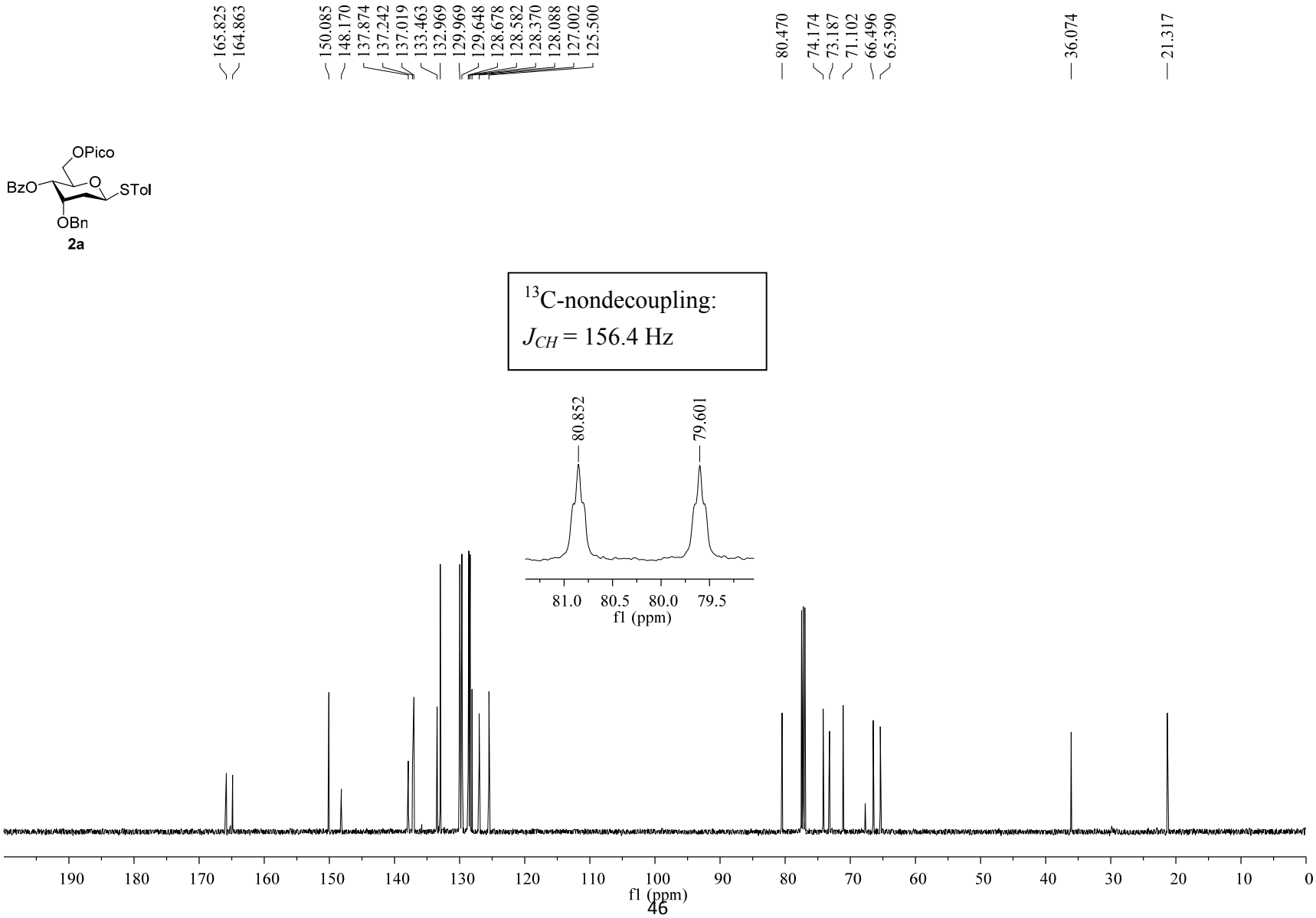
8.816
8.814
8.810
8.808
8.807
8.805
8.077
8.075
8.061
8.058
8.024
8.022
8.020
8.009
8.007
8.005
7.836
7.820
7.817
7.805
7.577
7.562
7.523
7.521
7.514
7.511
7.508
7.499
7.496
7.471
7.455
7.440
7.405
7.389
7.239
7.226
7.223
7.219
7.217
7.203
7.200
7.188
7.168
7.154
6.927
6.912
5.881
5.875
5.166
5.163
5.143
5.139
4.709
4.686
4.676
4.671
4.649
4.636
4.439
4.417
3.641
3.635
3.622
3.616
2.254
2.055
OPico
BzO
O
STol
OBn
2a
0.92
2.02
0.99
1.17
1.04
1.11
2.01
2.00
4.03
0.97
2.16
1.08
1.05
2.34
1.21
1.17
1.16
1.13
1.16
3.25
1.14
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
f1 (ppm)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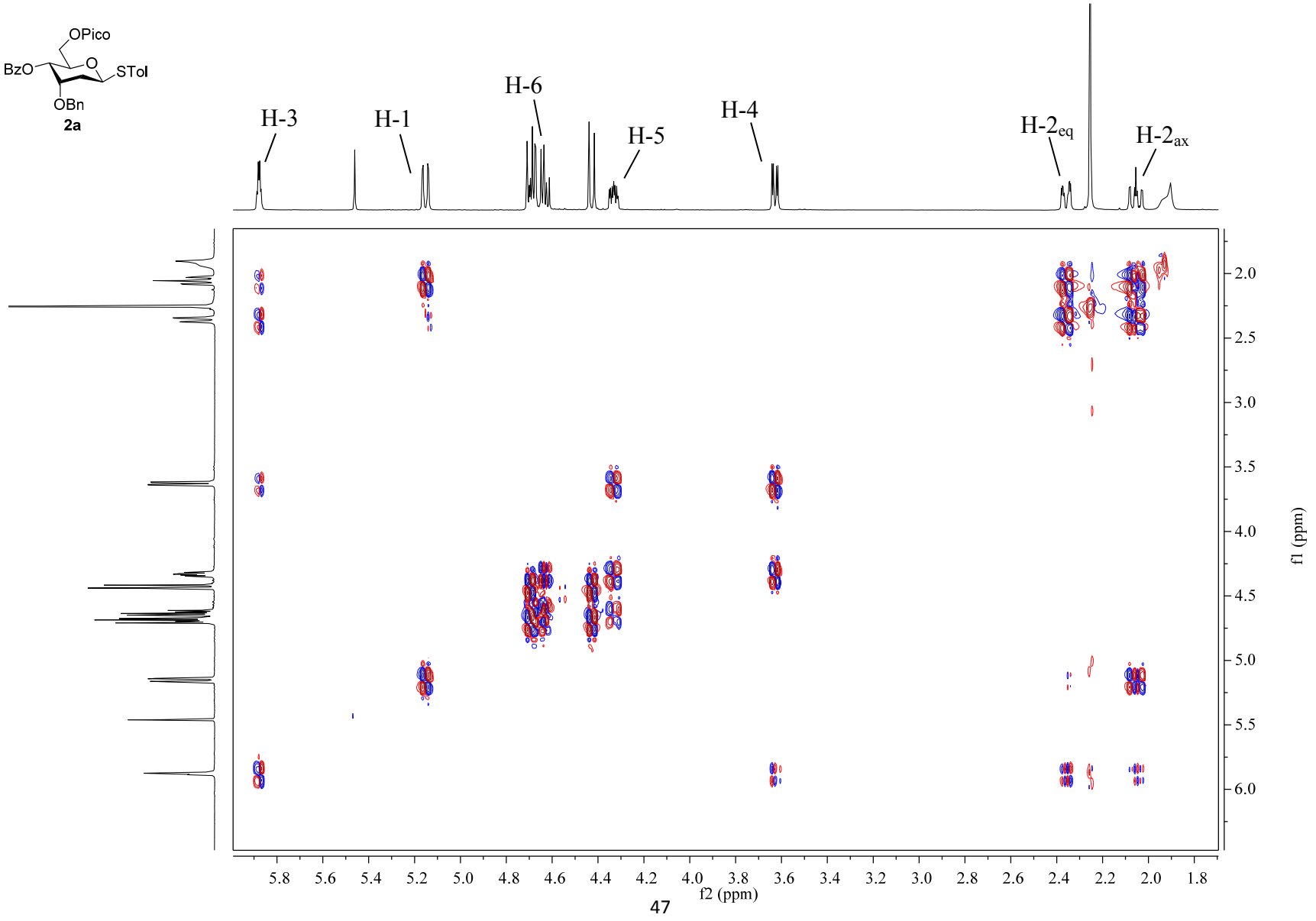
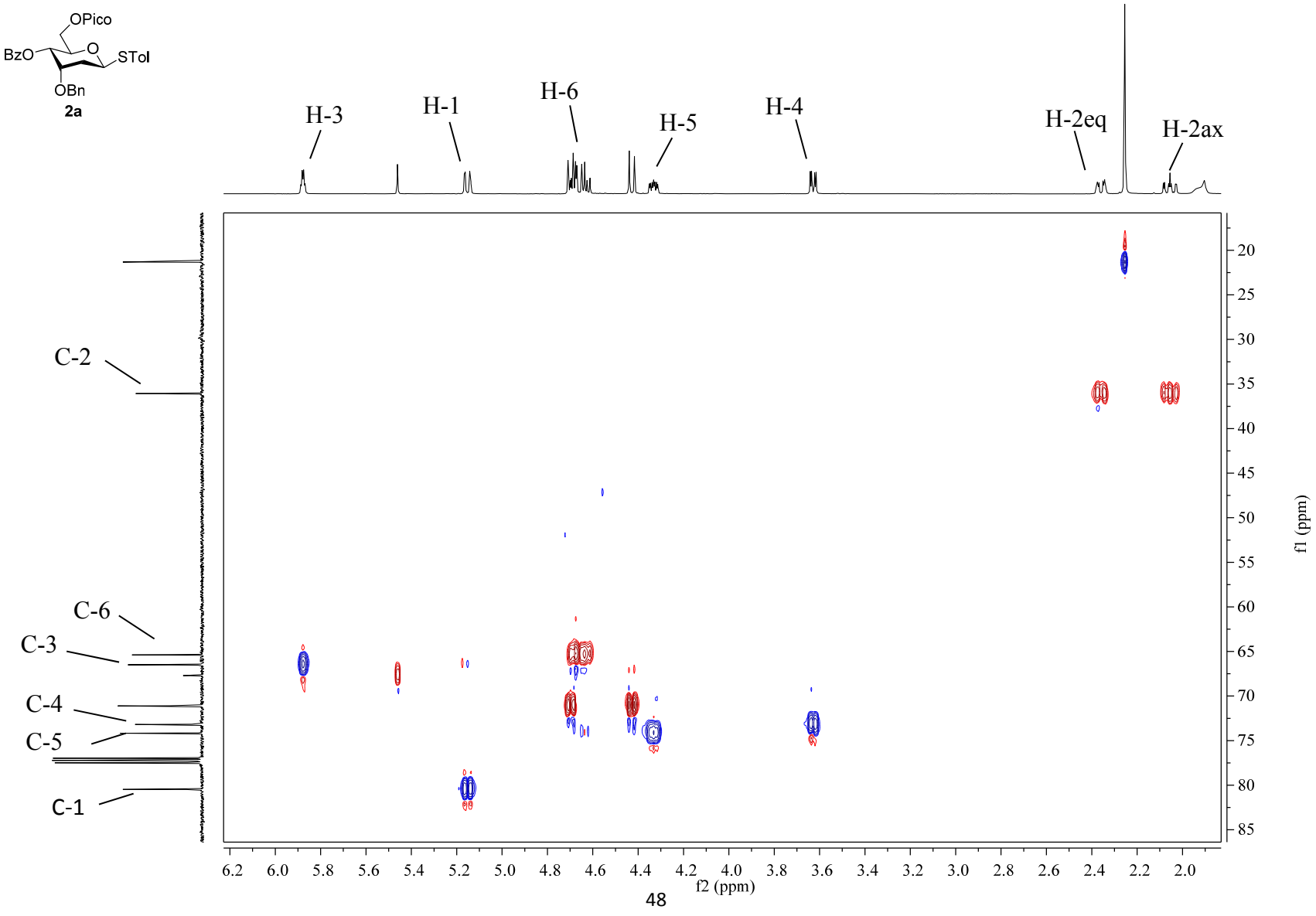
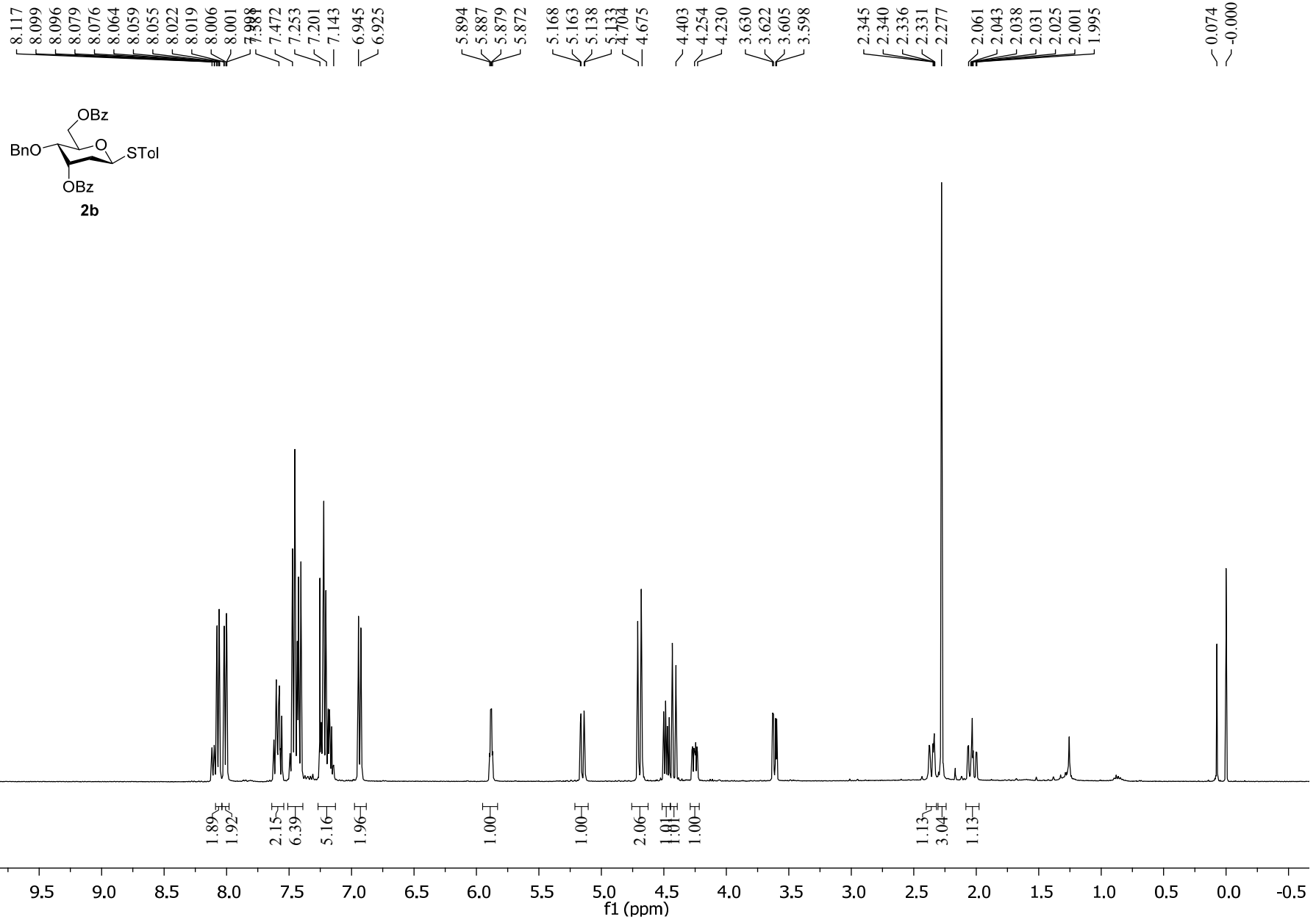
164.863
150.085
148.170
137.874
137.242
137.019
133.463
132.969
129.969
129.648
128.678
128.582
128.370
128.088
127.002
125.500
80.470
74.174
73.187
71.102
66.496
65.390
36.074
21.317
OPico
BzO
O
STol
OBn
2a
^{13}C-nondecoupling:
J_{CH} = 156.4 Hz
80.852
79.601
81.0
80.5
80.0
79.5
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OPico
BzO
O
STol
OBn
2a
H-3
H-1
H-6
H-5
H-4
H-2eq
H-2ax
f2 (ppm)
f1 (ppm)


OPico
BzO
O
STol
OBn
2a
H-3
H-1
H-6
H-5
H-4
H-2eq
H-2ax
C-2
C-6
C-3
C-4
C-5
C-1
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
f2 (ppm)
20
25
30
35
40
45
50
55
60
65
70
75
80
85
f1 (ppm)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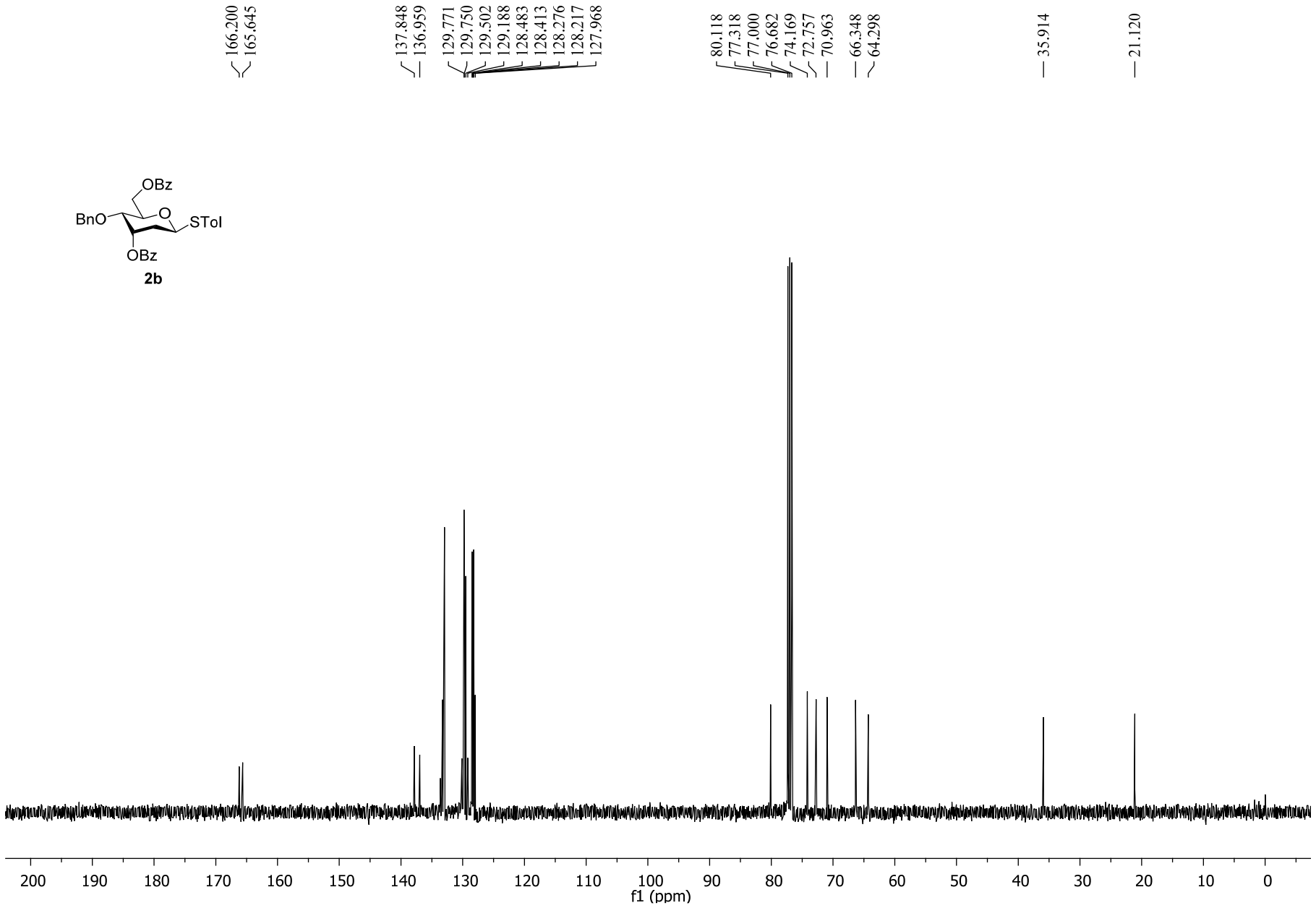
8.096
8.079
8.076
8.064
8.059
8.055
8.022
8.019
8.006
8.001
7.472
7.253
7.201
7.143
6.945
6.925
5.894
5.887
5.879
5.872
5.168
5.163
5.138
4.704
4.675
4.403
4.254
4.230
3.630
3.622
3.605
3.598
2.345
2.340
2.336
2.331
2.277
2.061
2.043
2.038
2.031
2.025
2.001
1.995
0.074
-0.000
OBz
BnO
O
STol
OBz
2b
1.89
1.92
2.15
6.39
5.16
1.96
1.00
1.00
2.06
1.01
1.00
1.13
3.04
1.13
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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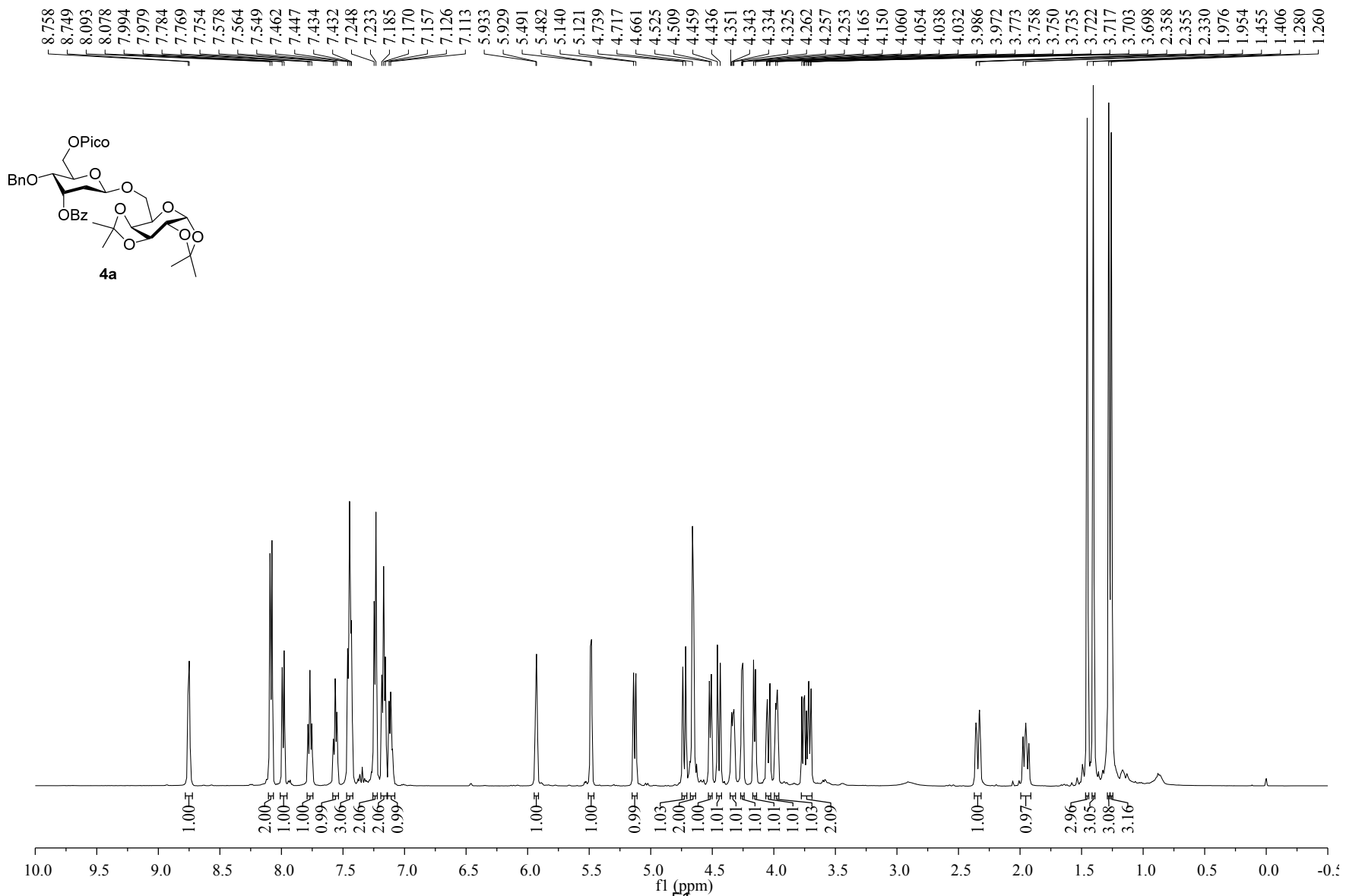
137.848
136.959
129.771
129.750
129.502
129.188
128.483
128.413
128.276
128.217
127.968
80.118
77.318
77.000
76.682
74.169
72.757
70.963
66.348
64.298
35.914
21.120
OBz
BnO
O
STol
OBz
2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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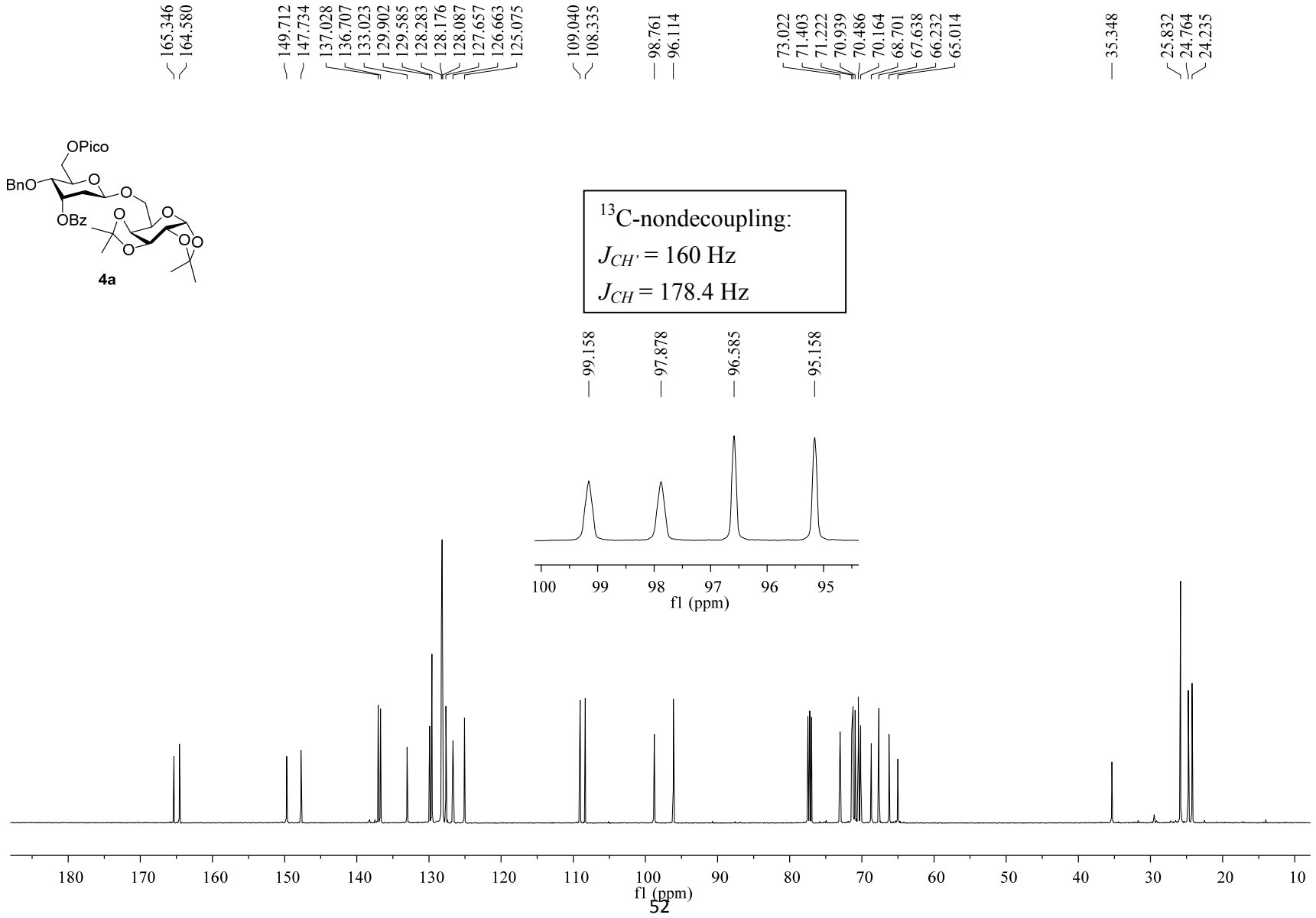
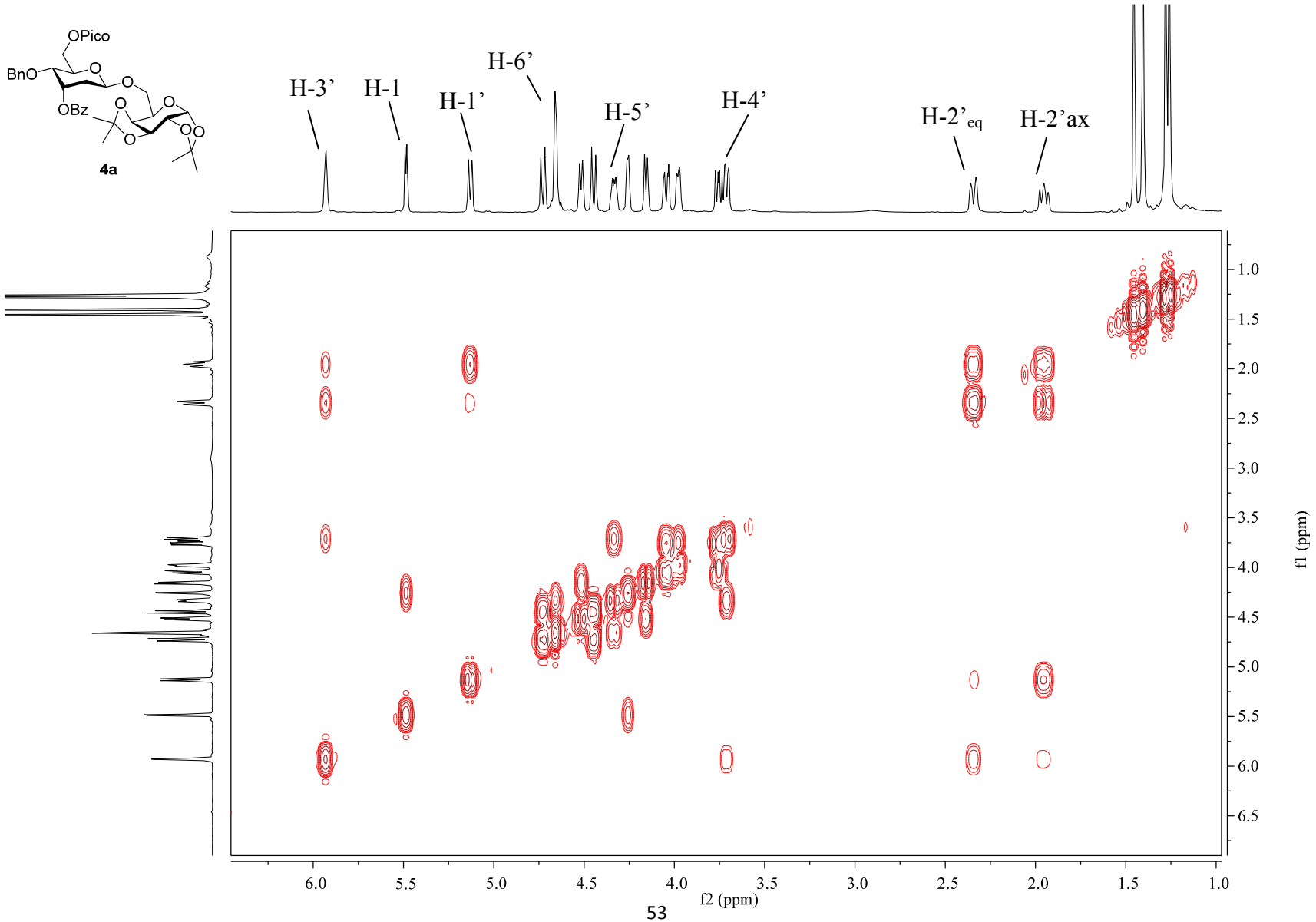
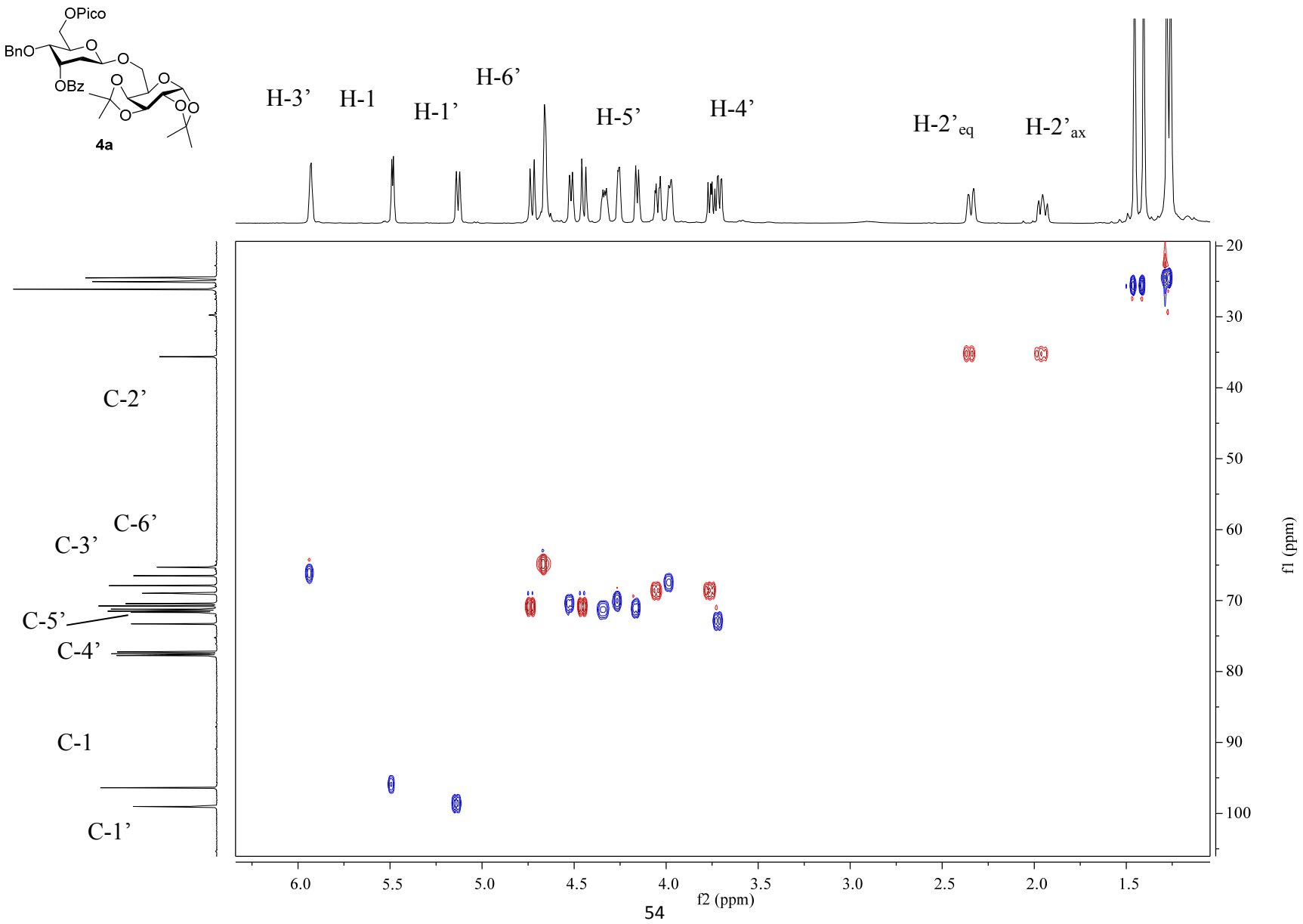
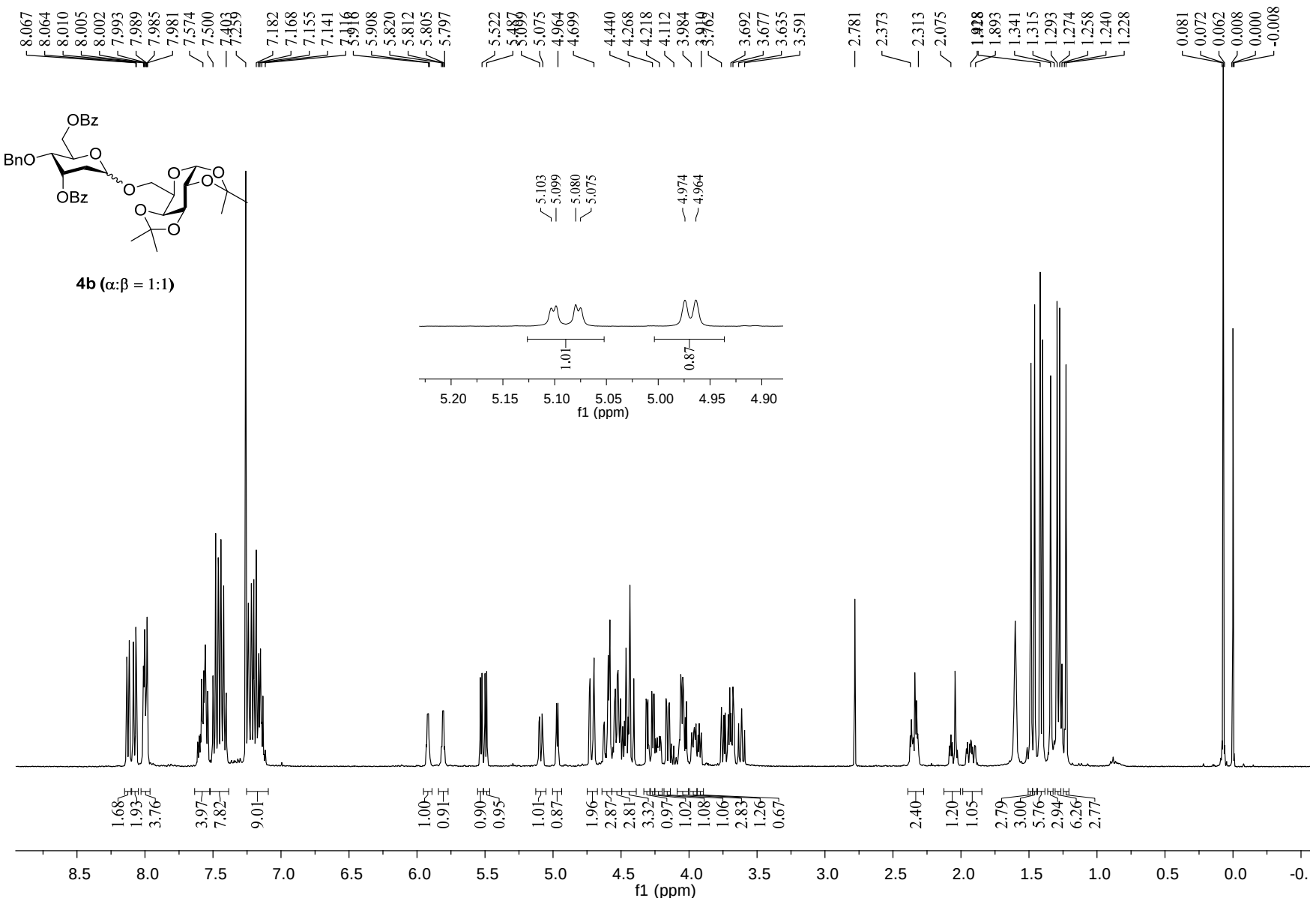
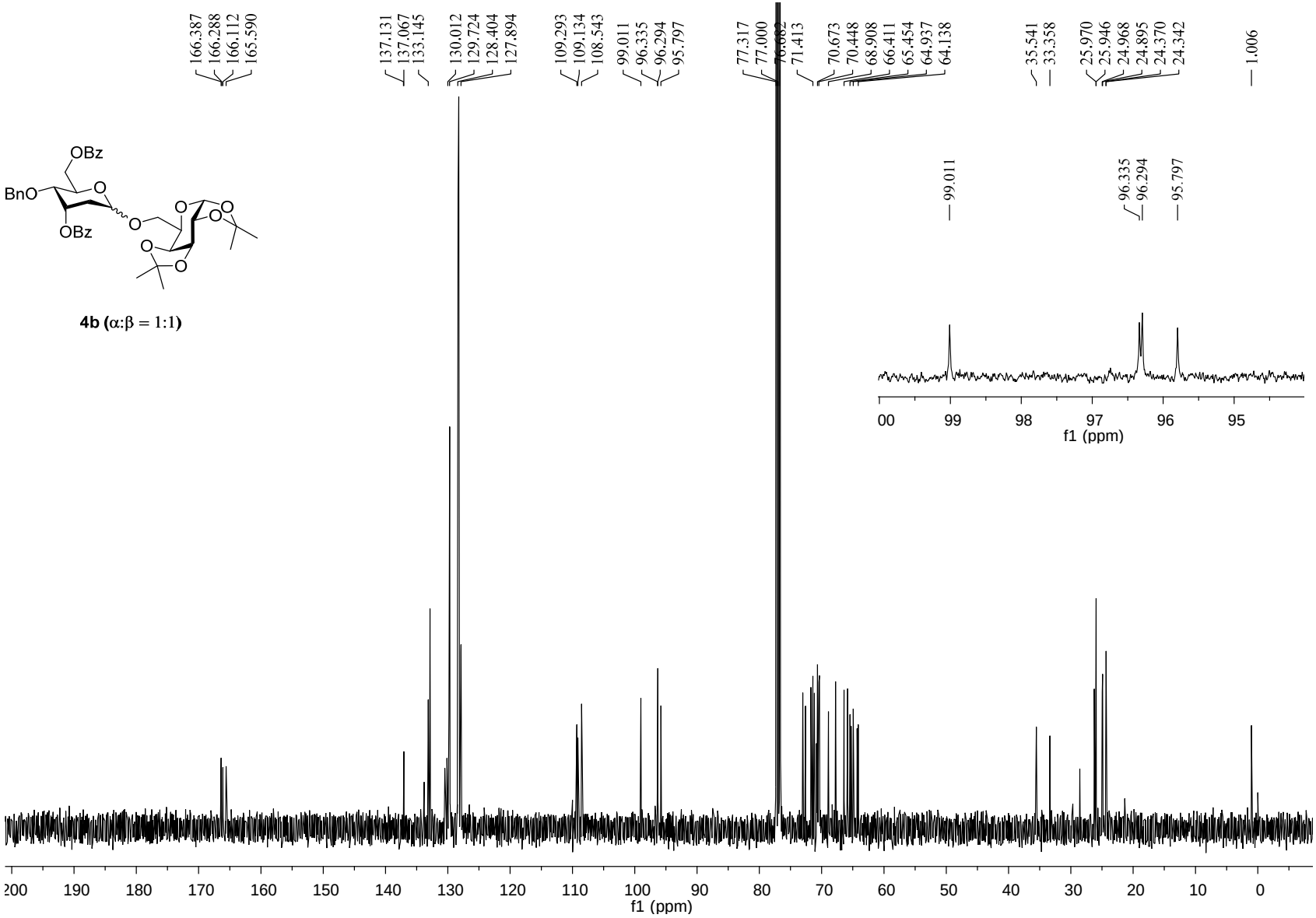
8.078
7.994
7.979
7.784
7.769
7.754
7.578
7.564
7.549
7.462
7.447
7.434
7.432
7.248
7.233
7.185
7.170
7.157
7.126
7.113
5.933
5.929
5.491
5.482
5.140
5.121
4.739
4.717
4.661
4.525
4.509
4.459
4.436
4.351
4.343
4.334
4.325
4.262
4.257
4.253
4.165
4.150
4.060
4.054
4.038
4.032
3.986
3.972
3.773
3.758
3.750
3.735
3.722
3.717
3.703
3.698
2.358
2.355
2.330
1.976
1.954
1.455
1.406
1.280
1.260
OPico
BnO
OBz
O
4a
1.00
2.00
1.00
1.00
0.99
3.06
2.06
2.06
0.99
1.00
1.00
0.99
1.03
2.00
1.00
1.01
1.01
1.01
1.01
1.03
2.09
1.00
0.97
2.96
3.05
3.08
3.16
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
f1 (ppm)


165.346
164.580
149.712
147.734
137.028
136.707
133.023
129.902
129.585
128.283
128.176
128.087
127.657
126.663
125.075
109.040
108.335
98.761
96.114
73.022
71.403
71.222
70.939
70.486
70.164
68.701
67.638
66.232
65.014
35.348
25.832
24.764
24.235
OPico
BnO
OBz
O
4a
13C-nondecoupling:
JCH' = 160 Hz
JCH = 178.4 Hz
99.158
97.878
96.585
95.158
100
99
98
97
96
95
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

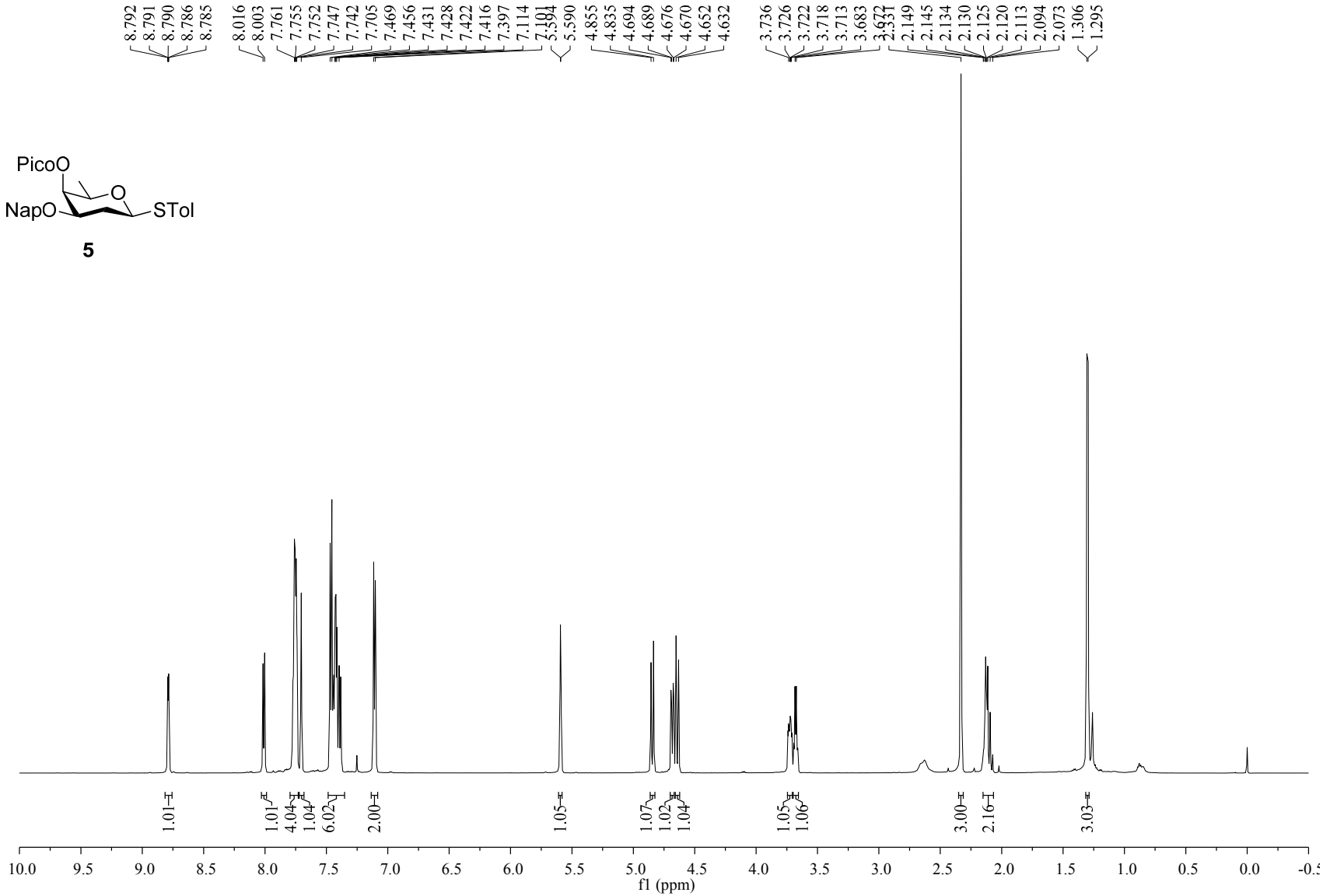

OPico
BnO
OBz
4a
H-3'
H-1
H-1'
H-6'
H-5'
H-4'
H-2'eq
H-2'ax
f2 (ppm)
f1 (ppm)

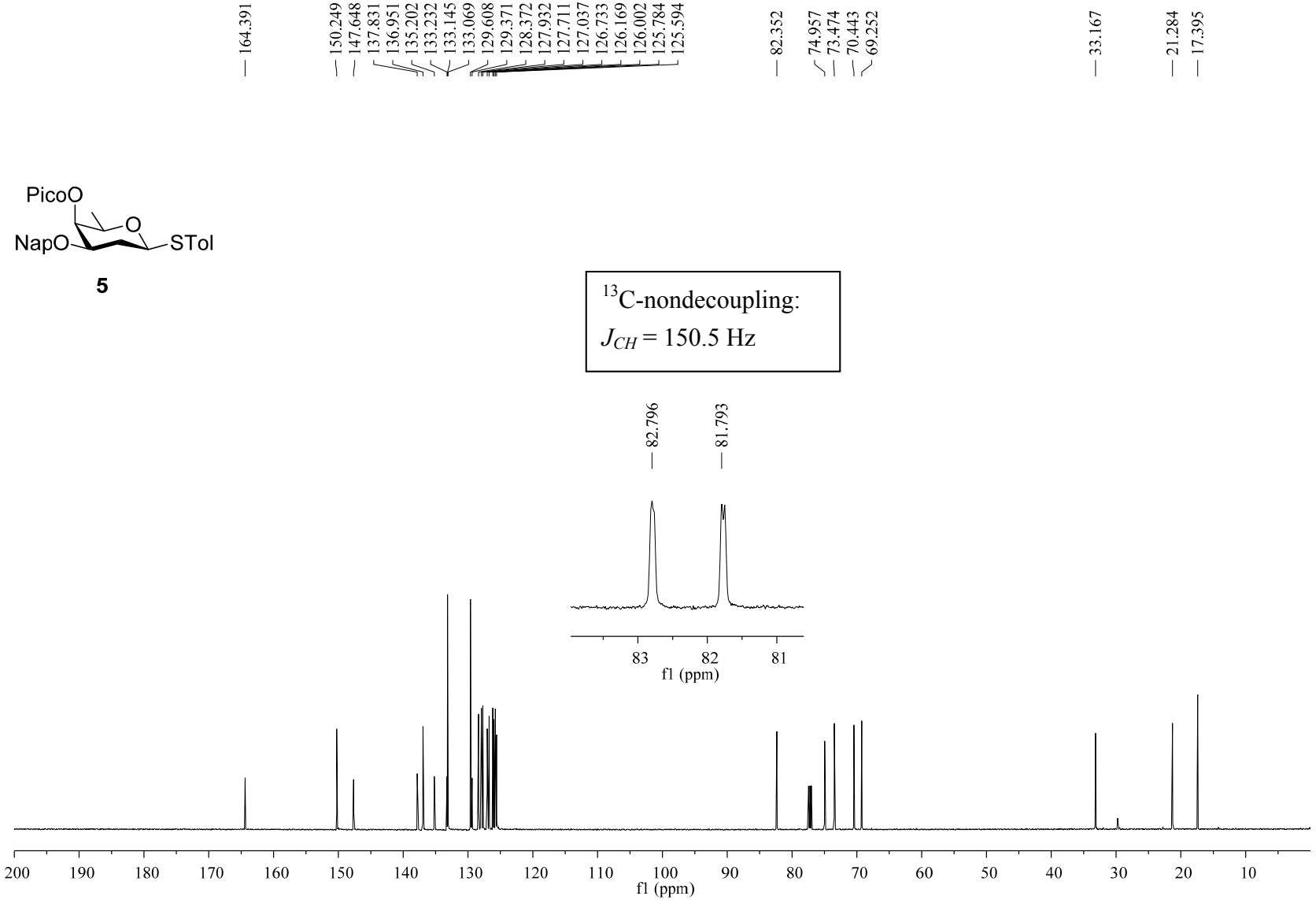

OPico
BnO
OBz
O
4a
H-3’
H-1
H-1’
H-6’
H-5’
H-4’
H-2’eq
H-2’ax
C-2’
C-6’
C-3’
C-5’
C-4’
C-1
C-1’
20
30
40
50
60
70
80
90
100
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)


OBz
BnO
OBz
O
O
O
O
O
O
O
4b (α:β = 1:1)
5.103
5.099
5.080
5.075
4.974
4.964
1.01
0.87
5.20
5.15
5.10
5.05
5.00
4.95
4.90
f1 (ppm)
8.067
8.064
8.010
8.005
8.002
7.993
7.989
7.985
7.981
7.574
7.500
7.403
7.259
7.182
7.168
7.155
7.141
5.908
5.820
5.812
5.805
5.797
5.522
5.075
4.964
4.699
4.440
4.268
4.218
4.112
3.984
3.692
3.677
3.635
3.591
2.781
2.373
2.313
2.075
1.893
1.341
1.315
1.293
1.274
1.258
1.240
1.228
0.081
0.072
0.062
0.008
0.000
-0.008
1.68
1.93
3.76
3.97
7.82
9.01
1.00
0.91
0.90
0.95
1.01
0.87
1.96
2.87
2.81
3.32
0.97
1.02
1.08
1.06
2.83
1.26
0.67
2.40
1.20
1.05
2.79
3.00
5.76
2.94
6.26
2.77
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)


166.387
166.288
166.112
165.590
137.131
137.067
133.145
130.012
129.724
128.404
127.894
109.293
109.134
108.543
99.011
96.335
96.294
95.797
77.317
77.000
71.413
70.673
70.448
68.908
66.411
65.454
64.937
64.138
35.541
33.358
25.970
25.946
24.968
24.895
24.370
24.342
1.006
OBz
BnO
OBz
O
O
O
O
O
O
O
f1 (ppm)

4b (α:β = 1:1)


PicoO
NapO
O
STol
5
8.792
8.791
8.790
8.786
8.785
8.016
8.003
7.761
7.755
7.752
7.747
7.742
7.705
7.469
7.456
7.431
7.428
7.422
7.416
7.397
7.114
5.594
5.590
4.855
4.835
4.694
4.689
4.676
4.670
4.652
4.632
3.736
3.726
3.722
3.718
3.713
3.683
2.331
2.149
2.145
2.134
2.130
2.125
2.120
2.113
2.094
2.073
1.306
1.295
1.01
1.01
4.04
1.04
6.02
2.00
1.05
1.07
1.02
1.04
1.05
1.06
3.00
2.16
3.03
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
f1 (ppm)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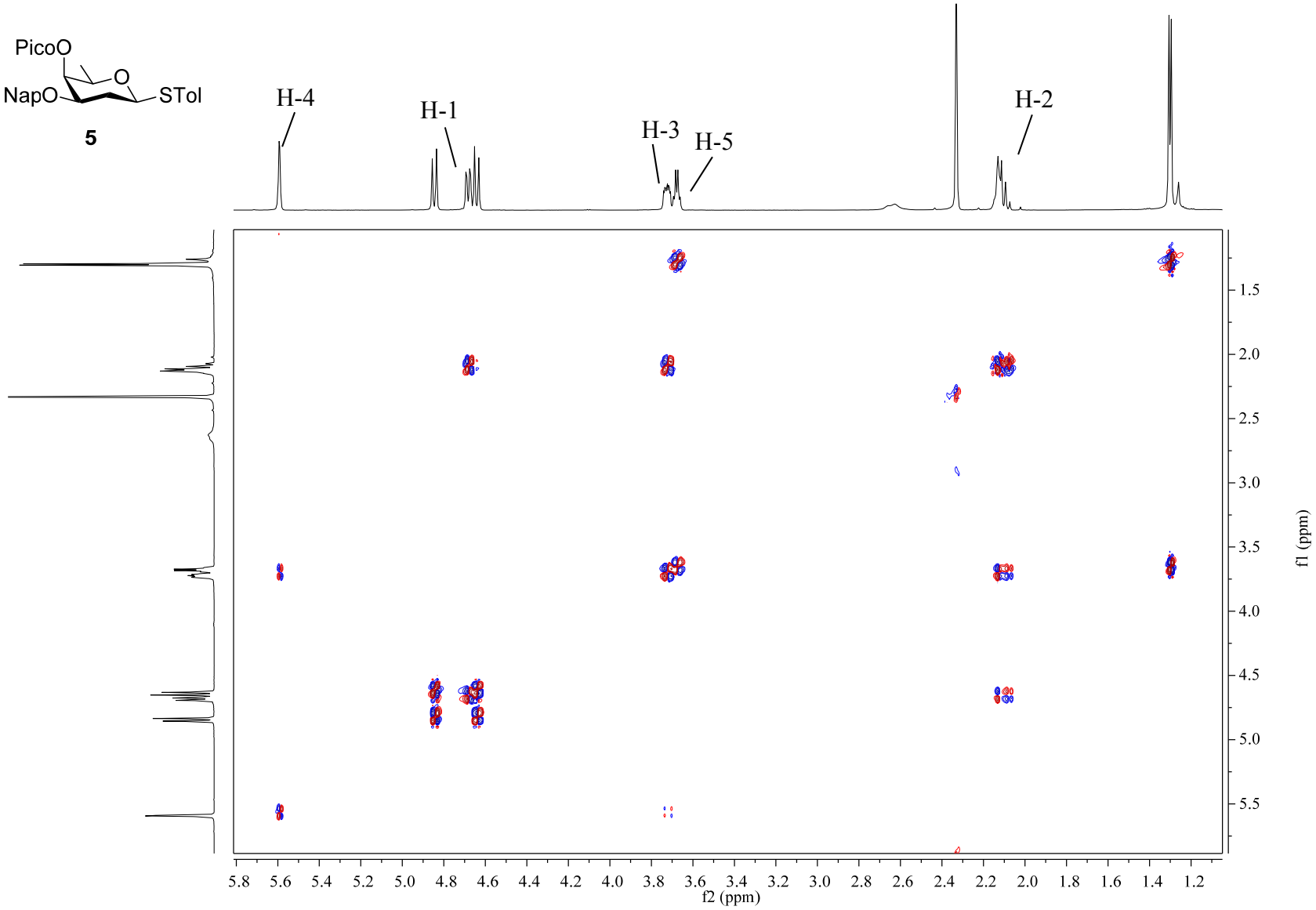
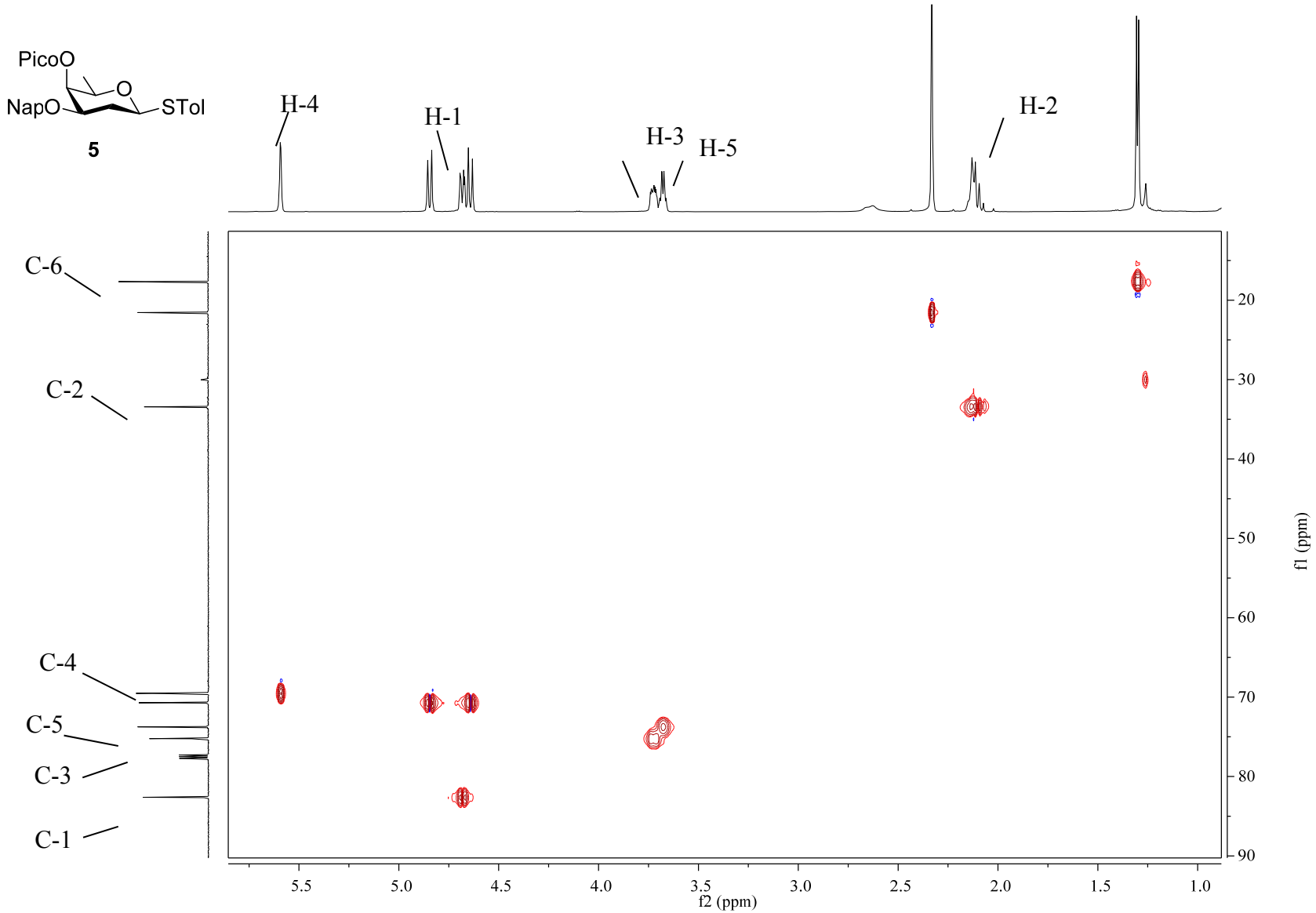
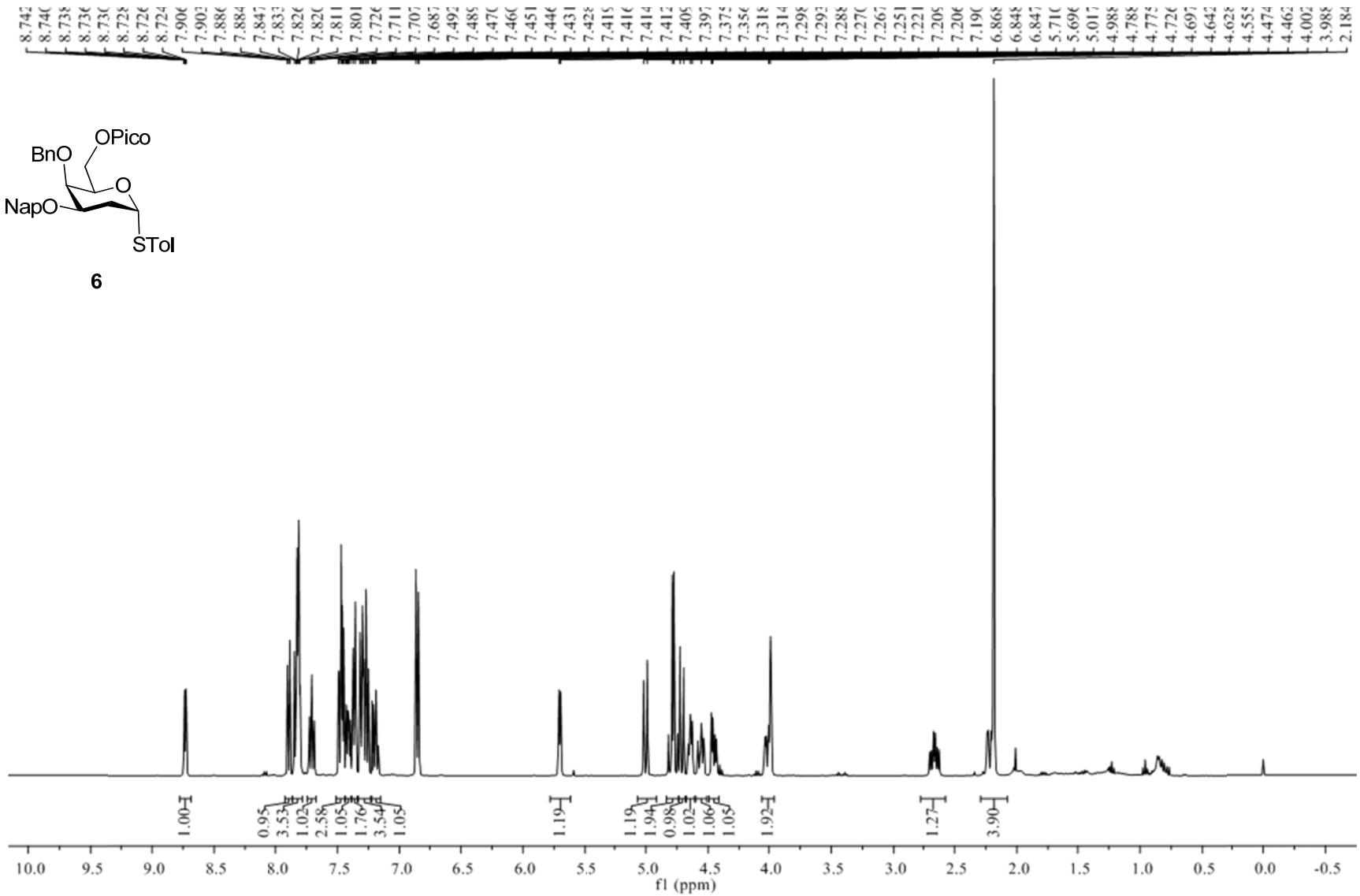
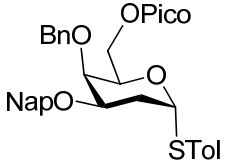
150.249
147.648
137.831
136.951
135.202
133.232
133.145
133.069
129.608
129.371
128.372
127.932
127.711
127.037
126.733
126.169
126.002
125.784
125.594
82.352
74.957
73.474
70.443
69.252
33.167
21.284
17.395
PicoO
NapO
O
STol
5
13C-nondecoupling:
JCH = 150.5 Hz
82.796
81.793
83
82
81
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


PicoO
NapO
O
STol
5
H-4
H-1
H-3
H-5
H-2
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)

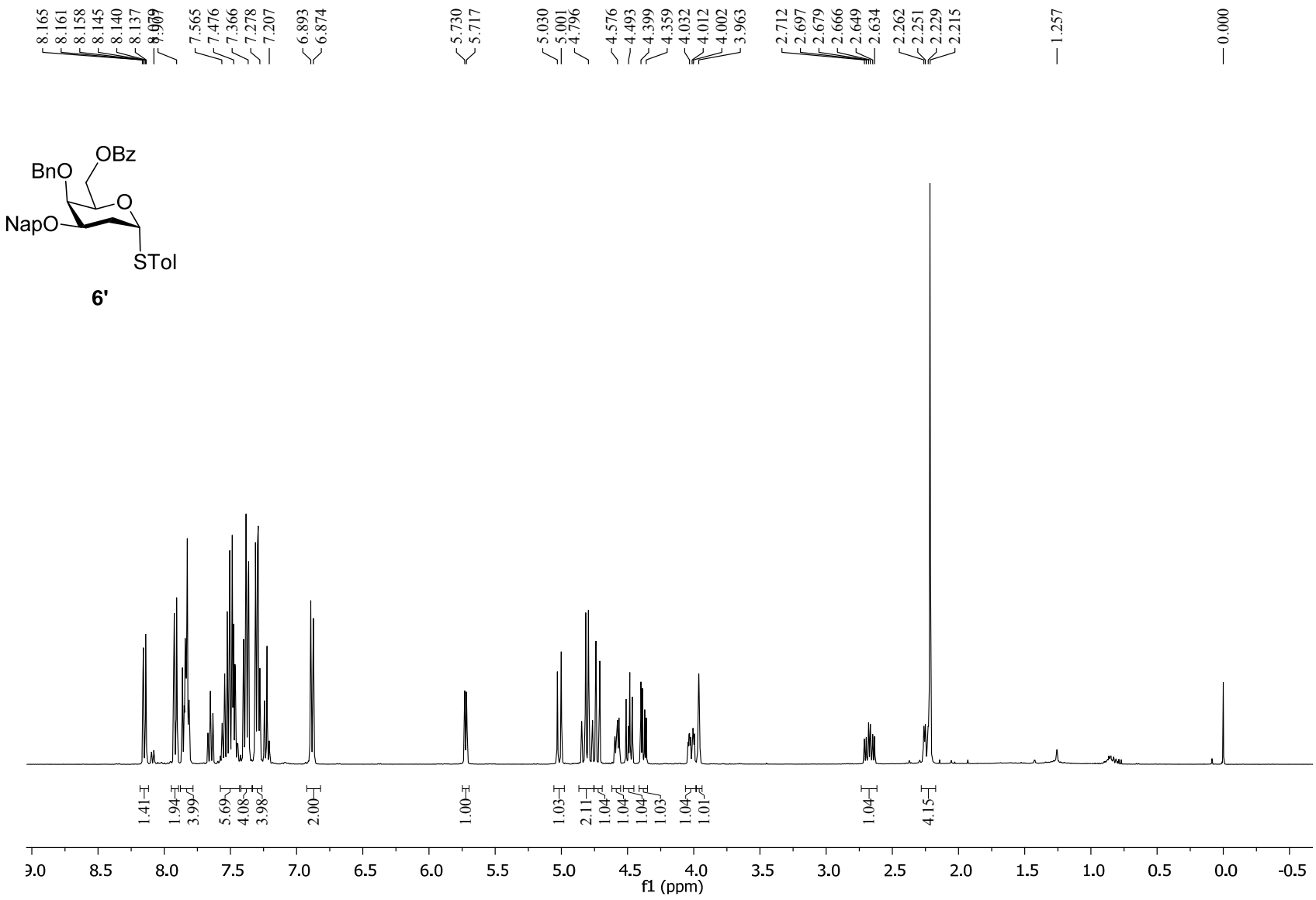

PicoO
NapO
O
STol
5
H-4
H-1
H-3
H-5
H-2
C-6
C-2
C-4
C-5
C-3
C-1
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
20
30
40
50
60
70
80
90
f1 (ppm)

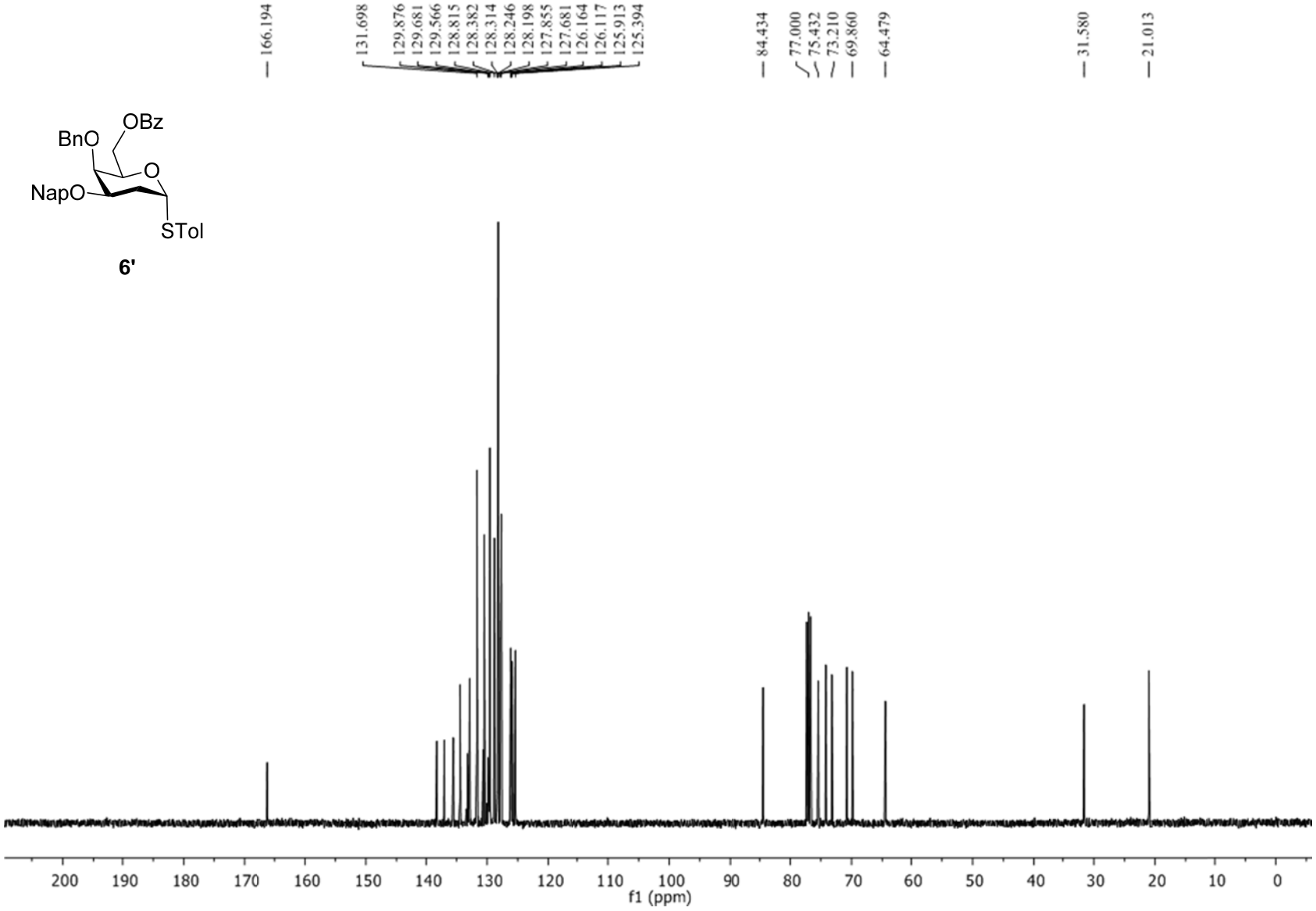

OPico
BnO
O
NapO
STol
6
1.00
0.95
3.53
1.02
2.58
1.05
1.76
3.54
1.05
1.19
1.19
1.94
0.98
1.02
1.06
1.05
1.92
1.27
3.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

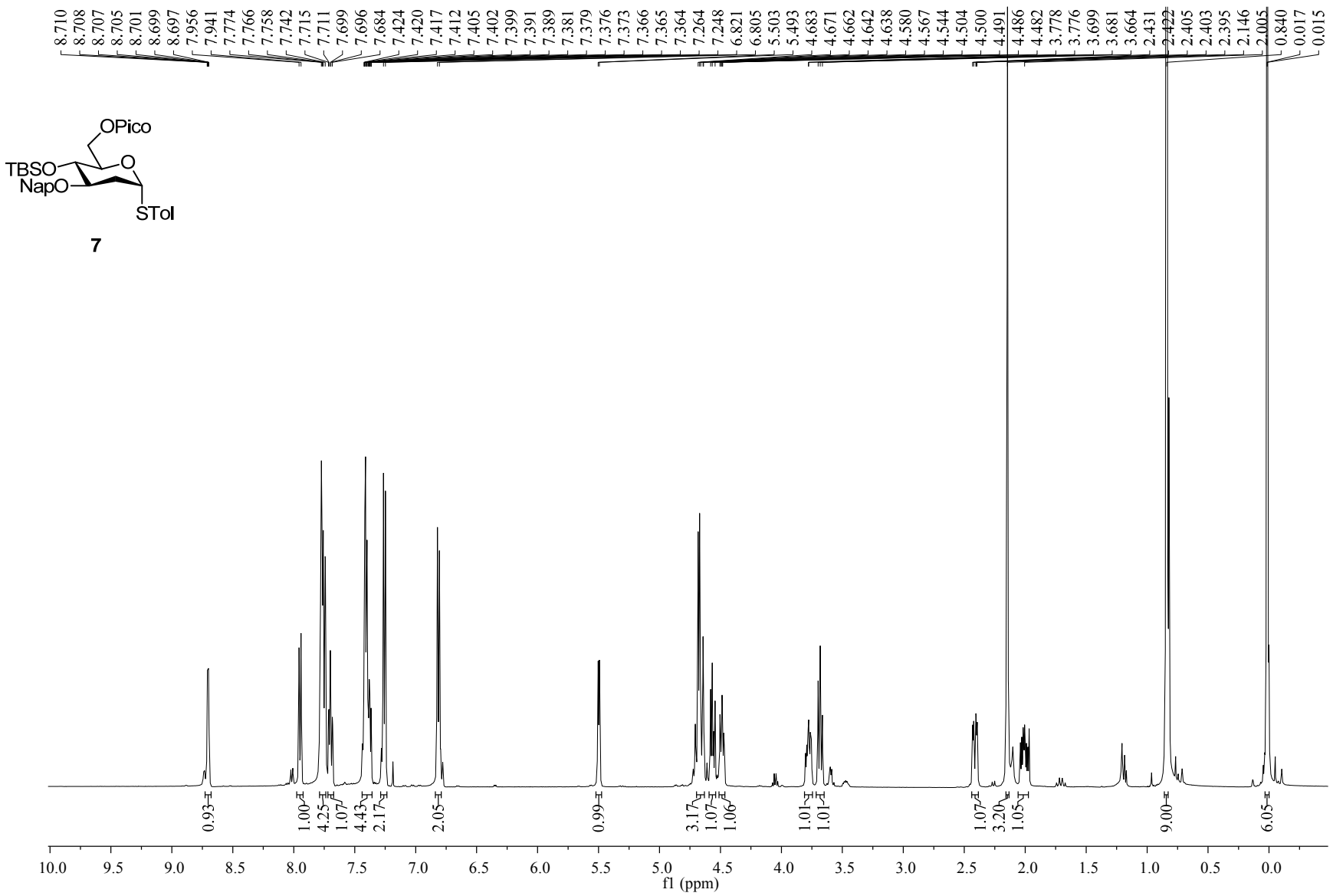

OPico
BnO
O
NapO
STol

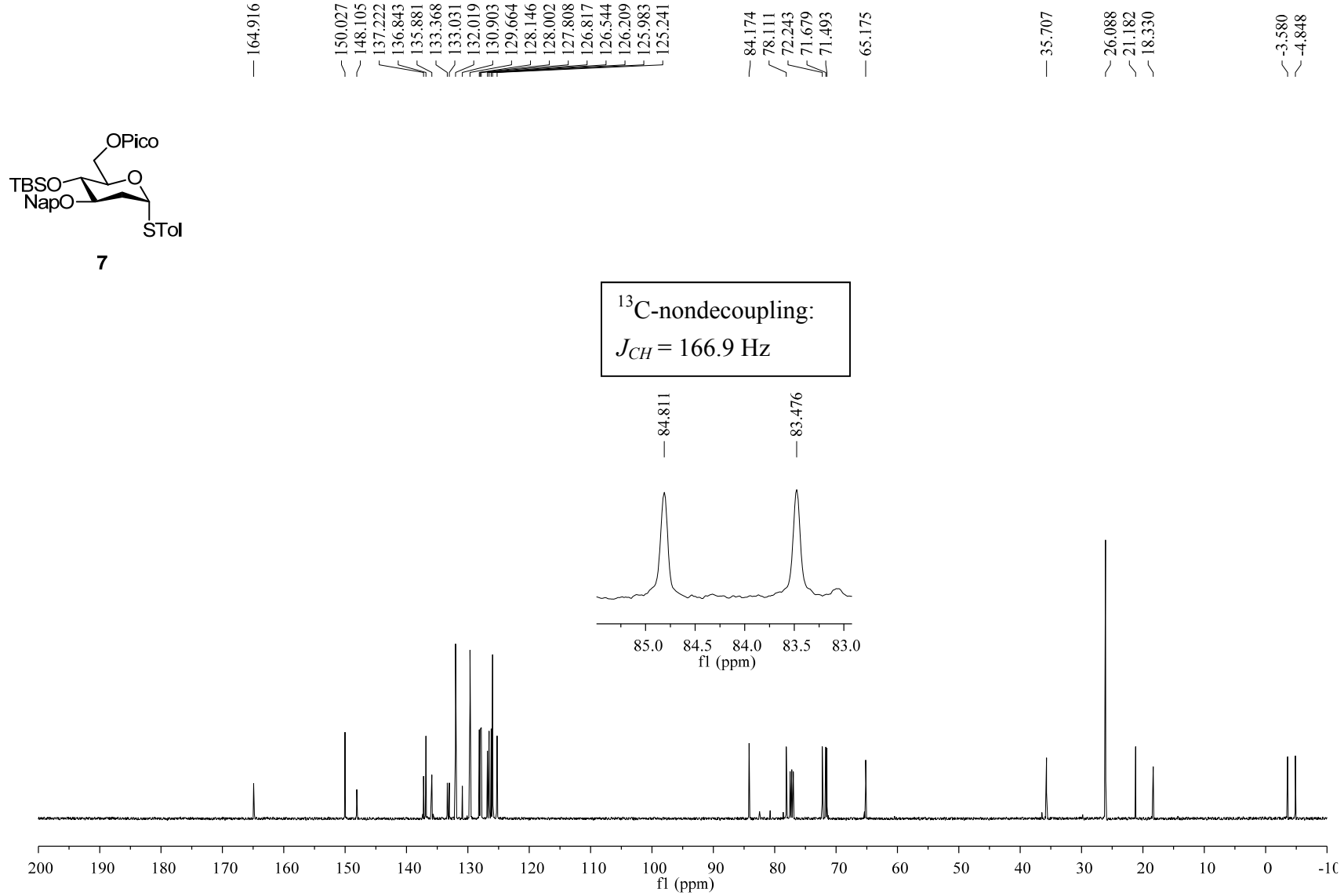
6

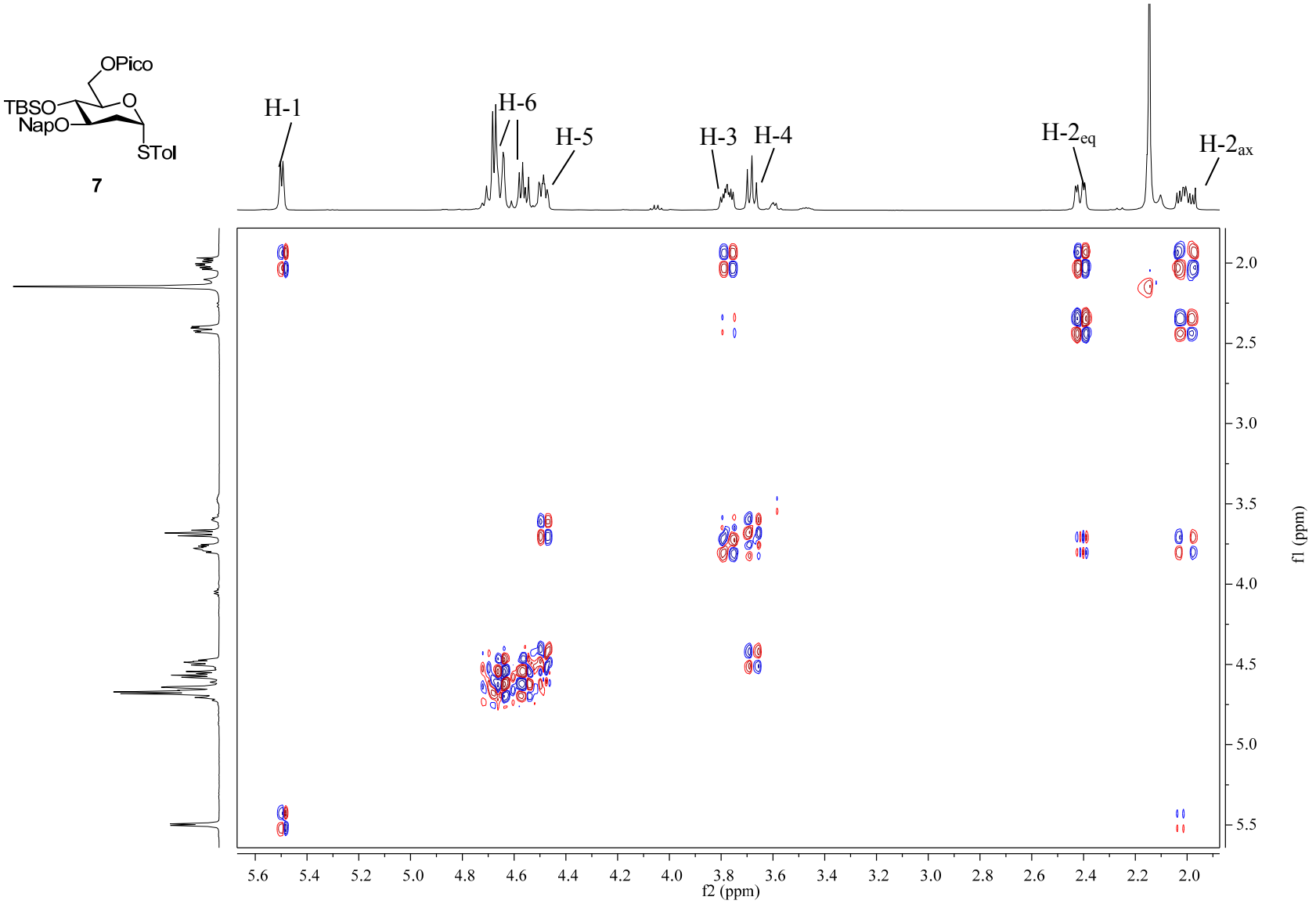
164.52
149.75
147.69
138.23
136.88
136.66
135.51
132.88
131.78
130.62
129.41
128.23
128.15
127.80
127.61
127.57
126.69
126.09
126.04
125.84
125.34
84.27
77.32
77.00
76.68
75.34
74.11
72.99
70.73
69.69
64.97
31.51
20.97
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

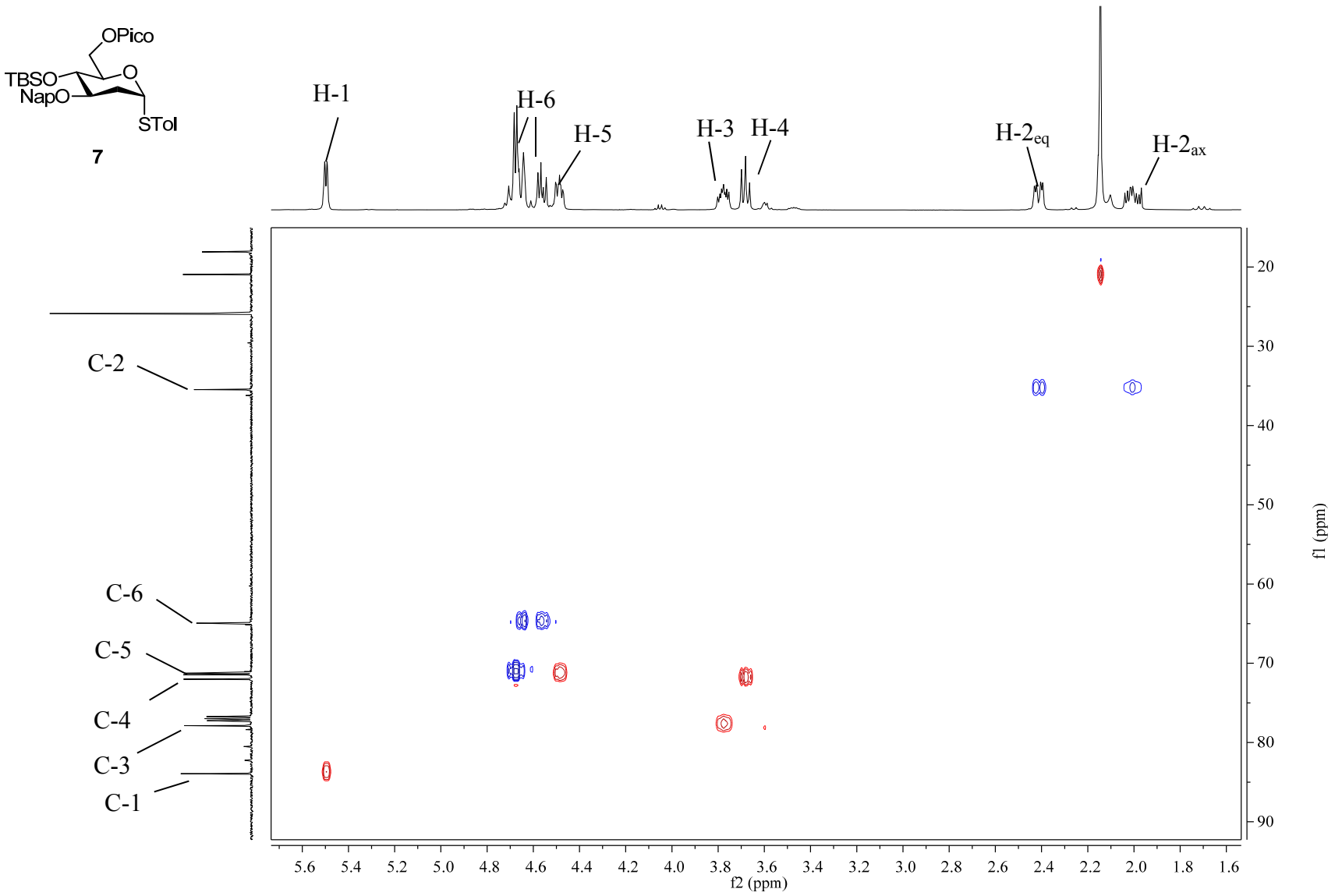

8.165
8.161
8.158
8.145
8.140
8.137
7.565
7.476
7.366
7.278
7.207
6.893
6.874
5.730
5.717
5.030
5.001
4.796
4.576
4.493
4.399
4.359
4.032
4.012
4.002
3.963
2.712
2.697
2.679
2.666
2.649
2.634
2.262
2.251
2.229
2.215
1.257
0.000
OBz
BnO
O
NapO
STol
6'
1.41
1.94
3.99
5.69
4.08
3.98
2.00
1.00
1.03
2.11
1.04
1.04
1.04
1.03
1.04
1.01
1.04
4.15
f1 (ppm)

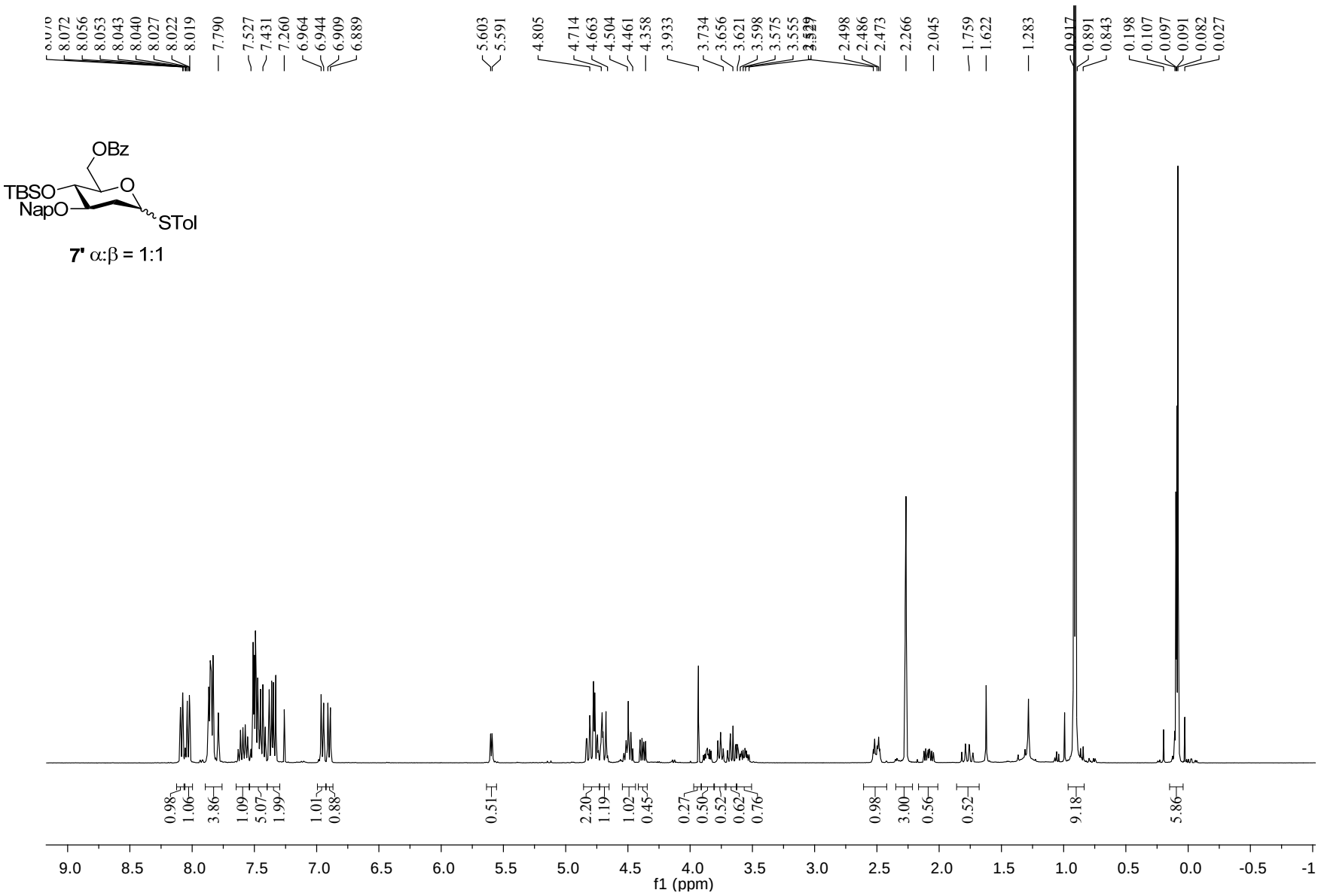

166.194
131.698
129.876
129.681
129.566
128.815
128.382
128.314
128.246
128.198
127.855
127.681
126.164
126.117
125.913
125.394
84.434
77.000
75.432
73.210
69.860
64.479
31.580
21.013
OBz
BnO
O
NapO
STol
6'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

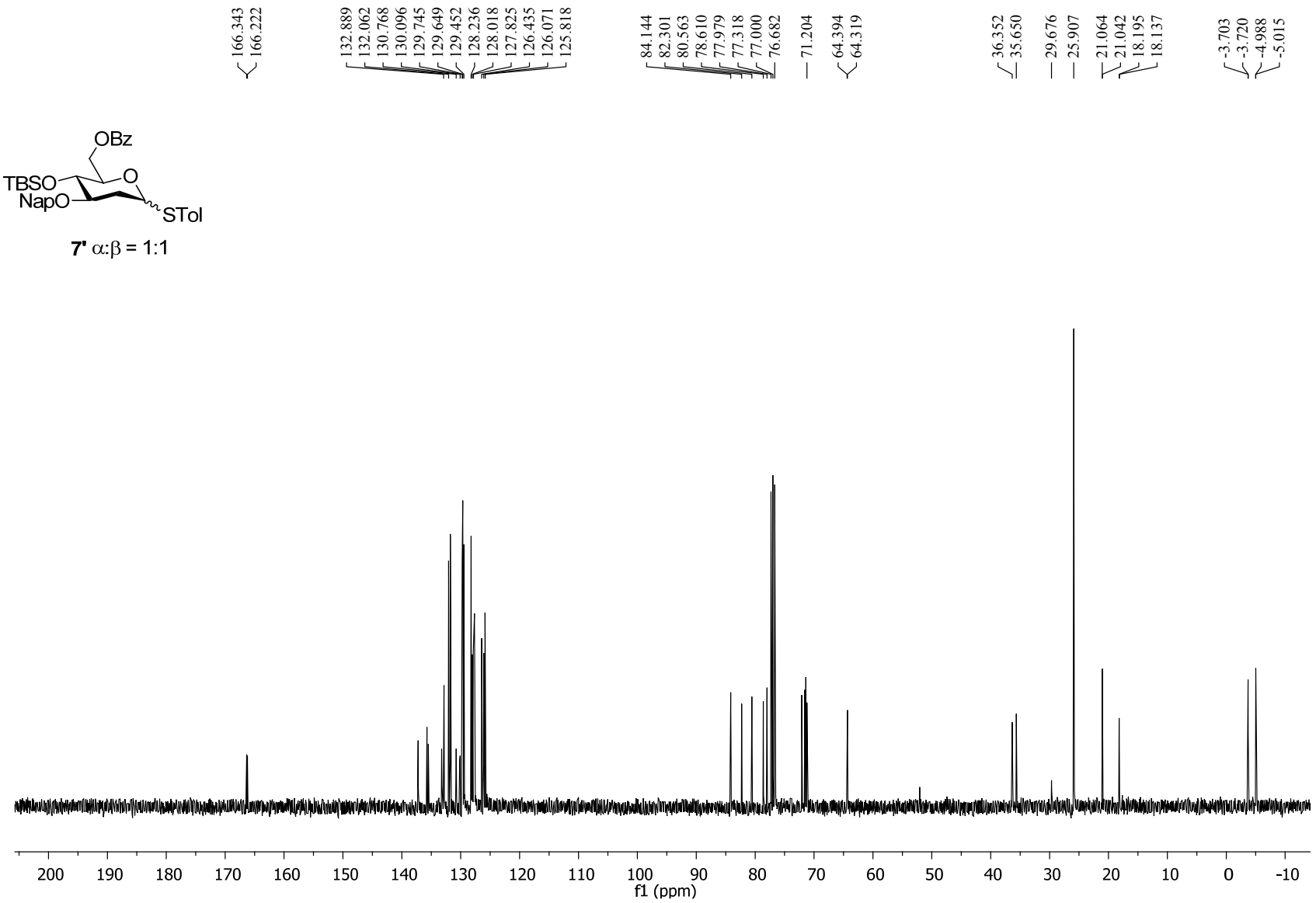

OPico
TBSO
NapO
O
STol
7
8.710
8.708
8.707
8.705
8.701
8.699
8.697
7.956
7.941
7.774
7.766
7.758
7.742
7.715
7.711
7.699
7.696
7.684
7.424
7.420
7.417
7.412
7.405
7.402
7.399
7.391
7.389
7.381
7.379
7.376
7.373
7.366
7.365
7.364
7.264
7.248
6.821
6.805
5.503
5.493
4.683
4.671
4.662
4.642
4.638
4.580
4.567
4.544
4.504
4.500
4.491
4.486
4.482
3.778
3.776
3.699
3.681
3.664
2.431
2.422
2.405
2.403
2.395
2.146
2.005
0.840
0.017
0.015
0.93
1.00
4.25
1.07
4.43
2.17
2.05
0.99
3.17
1.07
1.06
1.01
1.01
1.07
3.20
1.05
9.00
6.05
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
f1 (ppm)

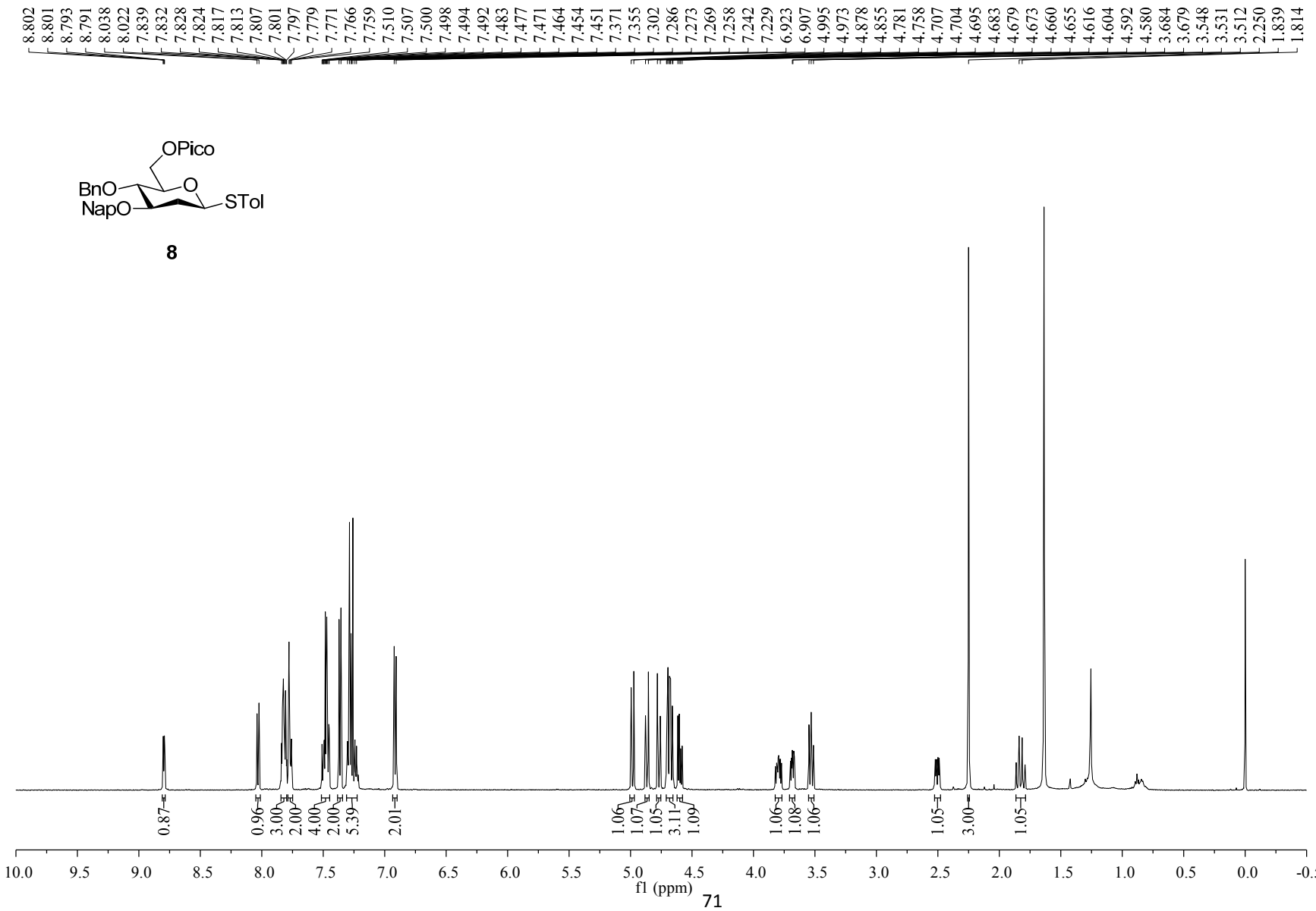

164.916
150.027
148.105
137.222
136.843
135.881
133.368
133.031
132.019
130.903
129.664
128.146
128.002
127.808
126.817
126.544
126.209
125.983
125.241
84.174
78.111
72.243
71.679
71.493
65.175
35.707
26.088
21.182
18.330
-3.580
-4.848
OPico
TBSO
NapO
O
STol
7
13C-nondecoupling:
JCH = 166.9 Hz
84.811
83.476
85.0 84.5 84.0 83.5 83.0
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

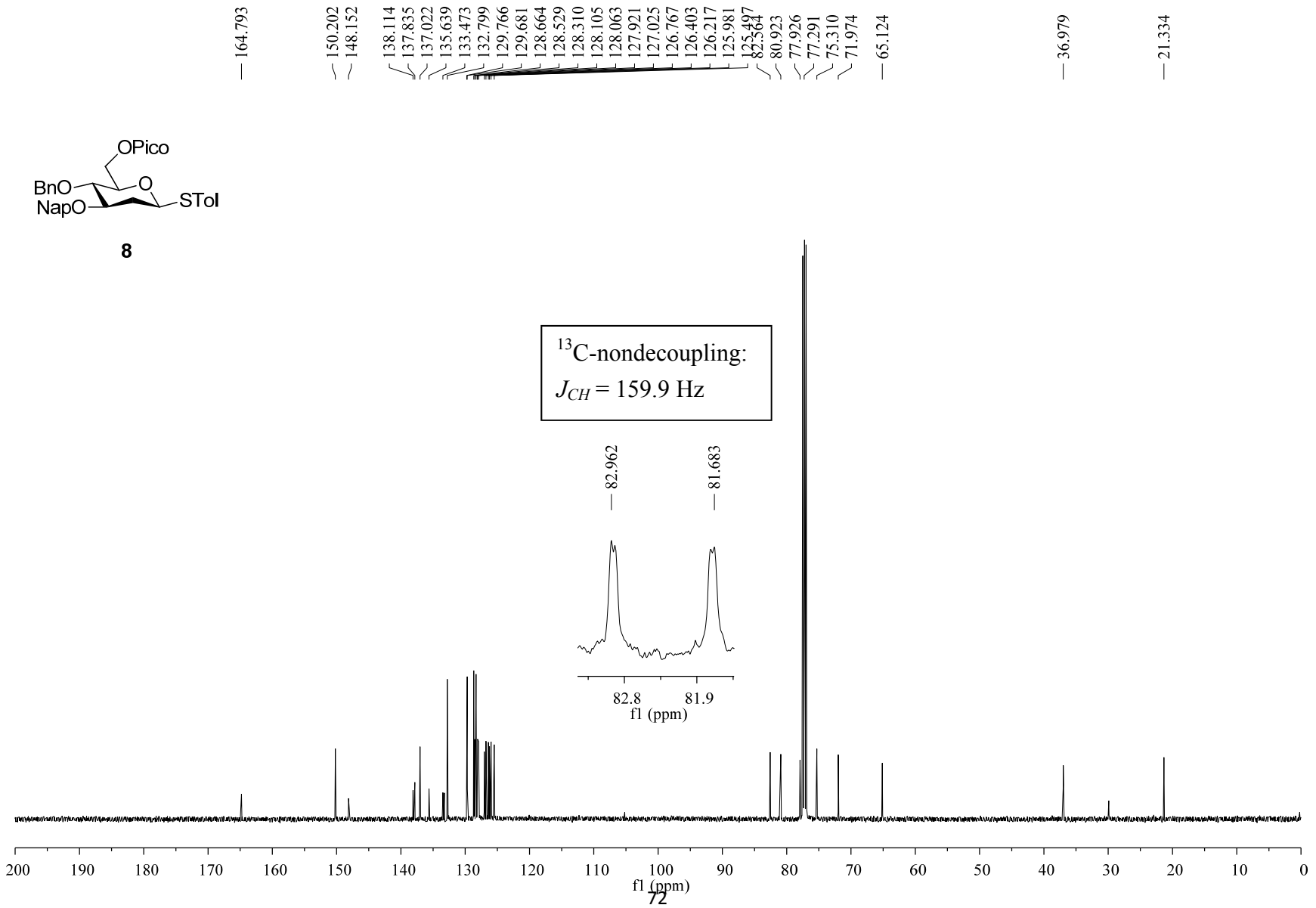

OPico
TBSO
NapO
O
STol
7
H-1
H-6
H-5
H-3
H-4
H-2eq
H-2ax
f2 (ppm)
f1 (ppm)

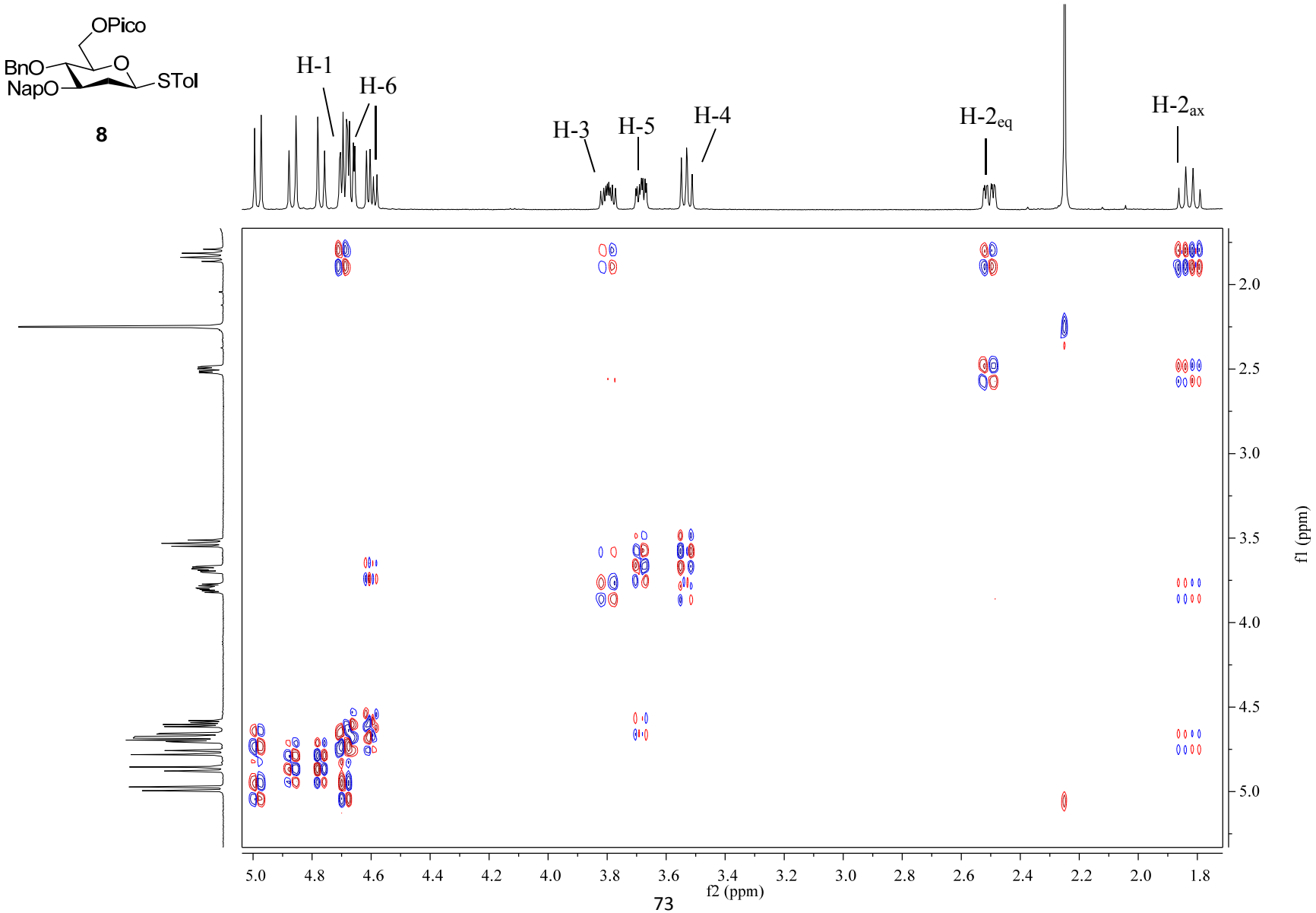

OPico
TBSO
NapO
O
STol
7
H-1
H-6
H-5
H-3
H-4
H-2eq
H-2ax
C-2
C-6
C-5
C-4
C-3
C-1
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
20
30
40
50
60
70
80
90
f1 (ppm)

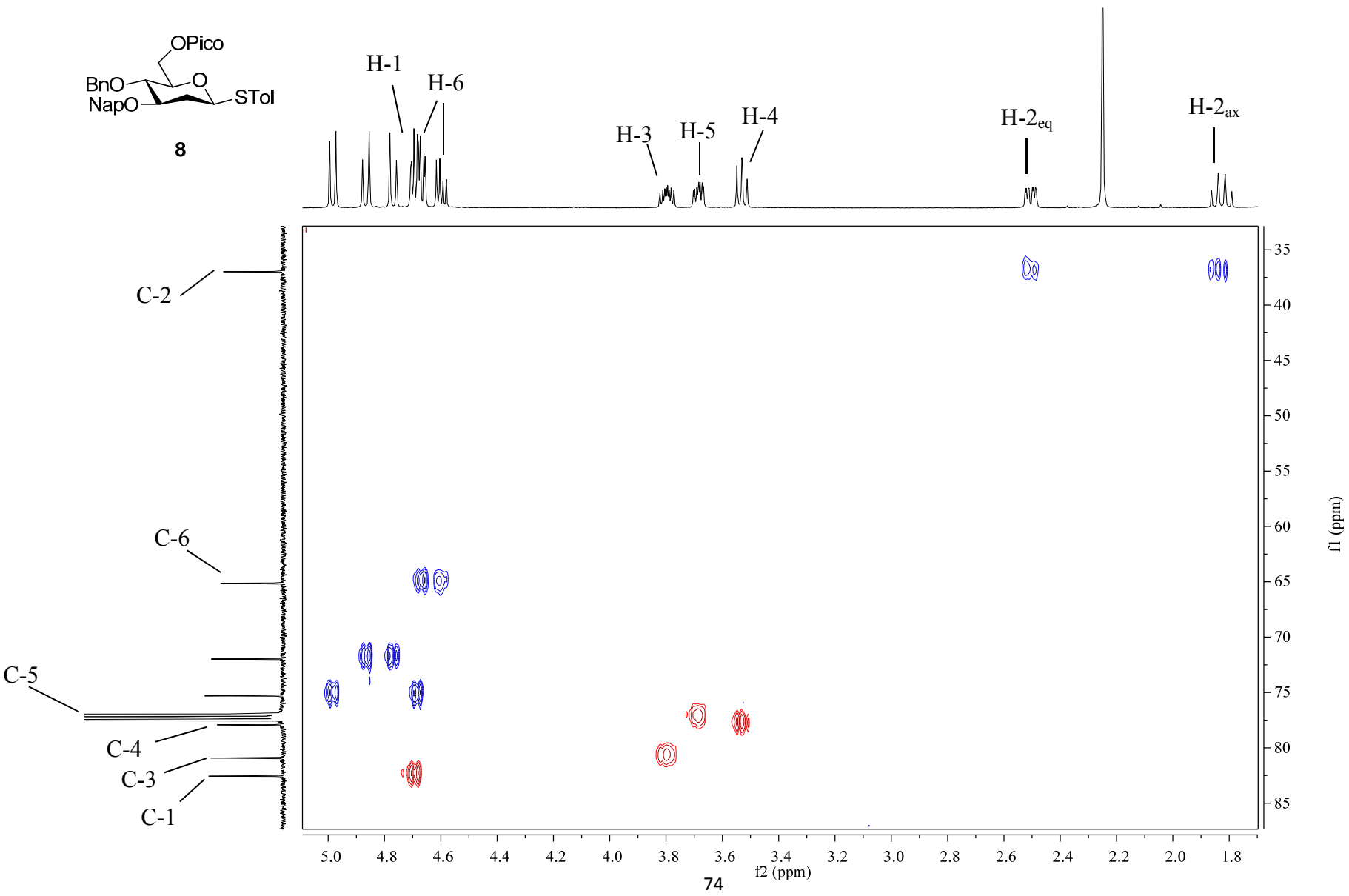

OBz
TBSO
O
NapO
STol
7' α:β = 1:1
f1 (ppm)

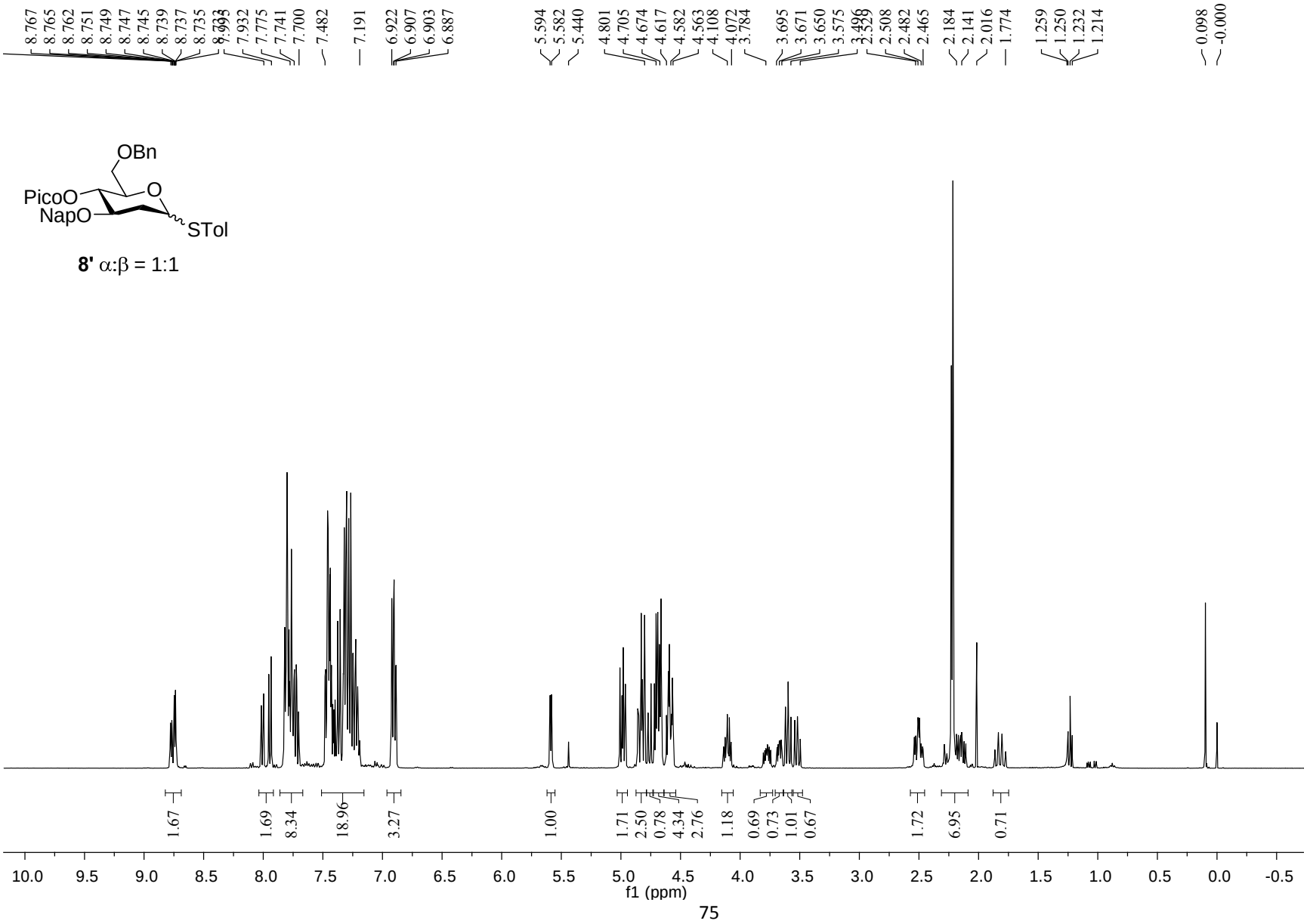

166.343
166.222
132.889
132.062
130.768
130.096
129.745
129.649
129.452
128.236
128.018
127.825
126.435
126.071
125.818
84.144
82.301
80.563
78.610
77.979
77.318
77.000
76.682
71.204
64.394
64.319
36.352
35.650
29.676
25.907
21.064
21.042
18.195
18.137
-3.703
-3.720
-4.988
-5.015
OBz
TBSO
O
NapO
STol
7' α:β = 1:1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

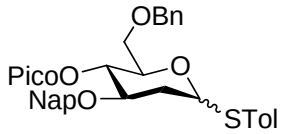

8.802
8.801
8.793
8.791
8.038
8.022
7.839
7.832
7.828
7.824
7.817
7.813
7.807
7.801
7.797
7.779
7.771
7.766
7.759
7.510
7.507
7.500
7.498
7.494
7.492
7.483
7.477
7.471
7.464
7.454
7.451
7.371
7.355
7.302
7.286
7.273
7.269
7.258
7.242
7.229
6.923
6.907
4.995
4.973
4.878
4.855
4.781
4.758
4.707
4.704
4.695
4.683
4.679
4.673
4.660
4.655
4.616
4.604
4.592
4.580
3.684
3.679
3.548
3.531
3.512
2.250
1.839
1.814
OPico
BnO
NapO
O
STol
8
0.87
0.96
3.00
2.00
4.00
2.00
5.39
2.01
1.06
1.07
1.05
3.11
1.09
1.06
1.08
1.06
1.05
3.00
1.05
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
f1 (ppm)


164.793
150.202
148.152
138.114
137.835
137.022
135.639
133.473
132.799
129.766
129.681
128.664
128.529
128.310
128.105
128.063
127.921
127.025
126.767
126.403
126.217
125.981
125.497
82.564
80.923
77.926
77.291
75.310
71.974
65.124
36.979
21.334
OPico
BnO
O
NapO
STol
8
13C-nondecoupling:
JCH = 159.9 Hz
82.962
81.683
82.8
81.9
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OPico
BnO
NapO
O
STol
8
H-1
H-6
H-3
H-5
H-4
H-2eq
H-2ax
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

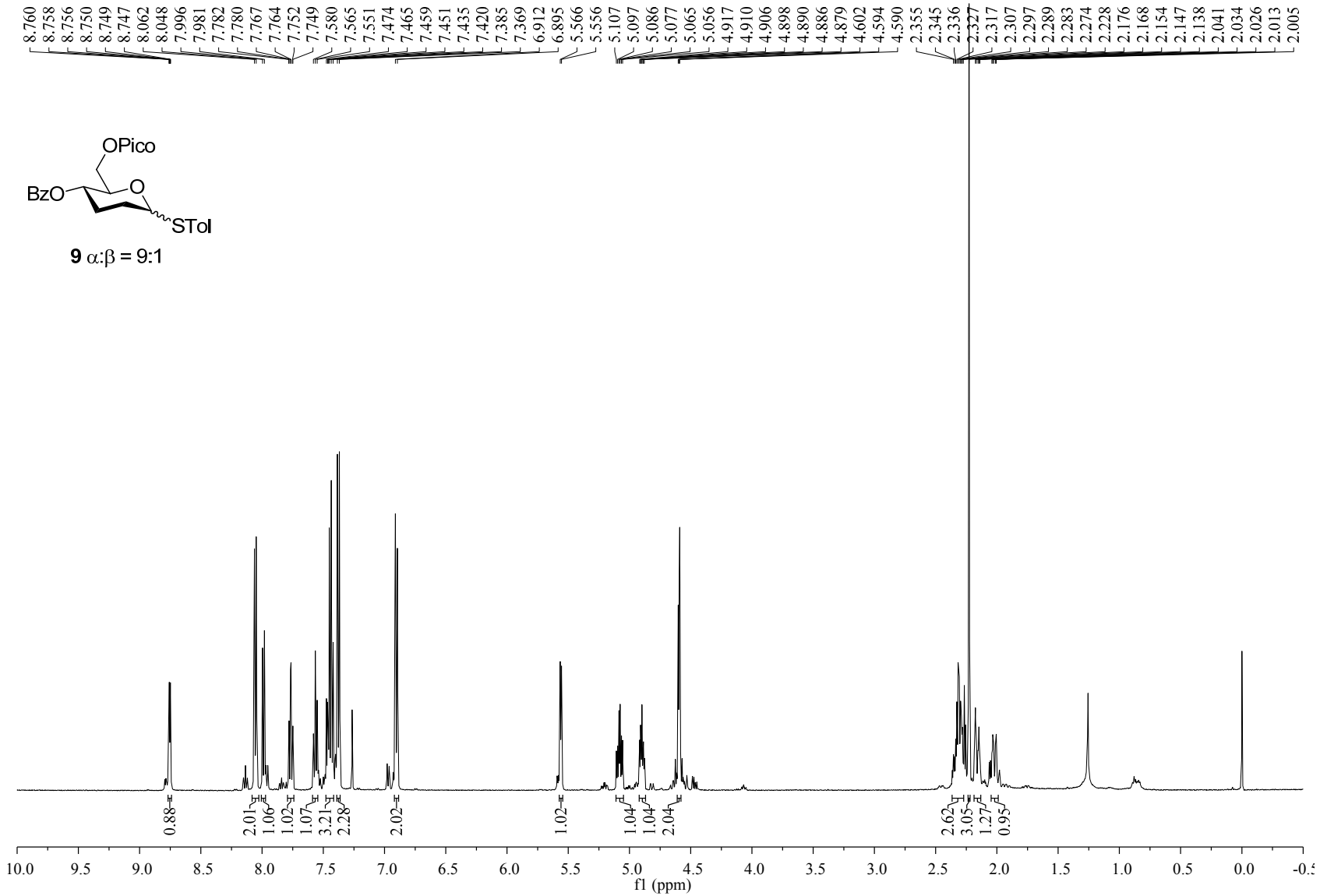

OPico
BnO
NapO
O
STol
8
H-1
H-6
H-3
H-5
H-4
H-2eq
H-2ax
C-2
C-6
C-5
C-4
C-3
C-1
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)
35
40
45
50
55
60
65
70
75
80
85
f1 (ppm)

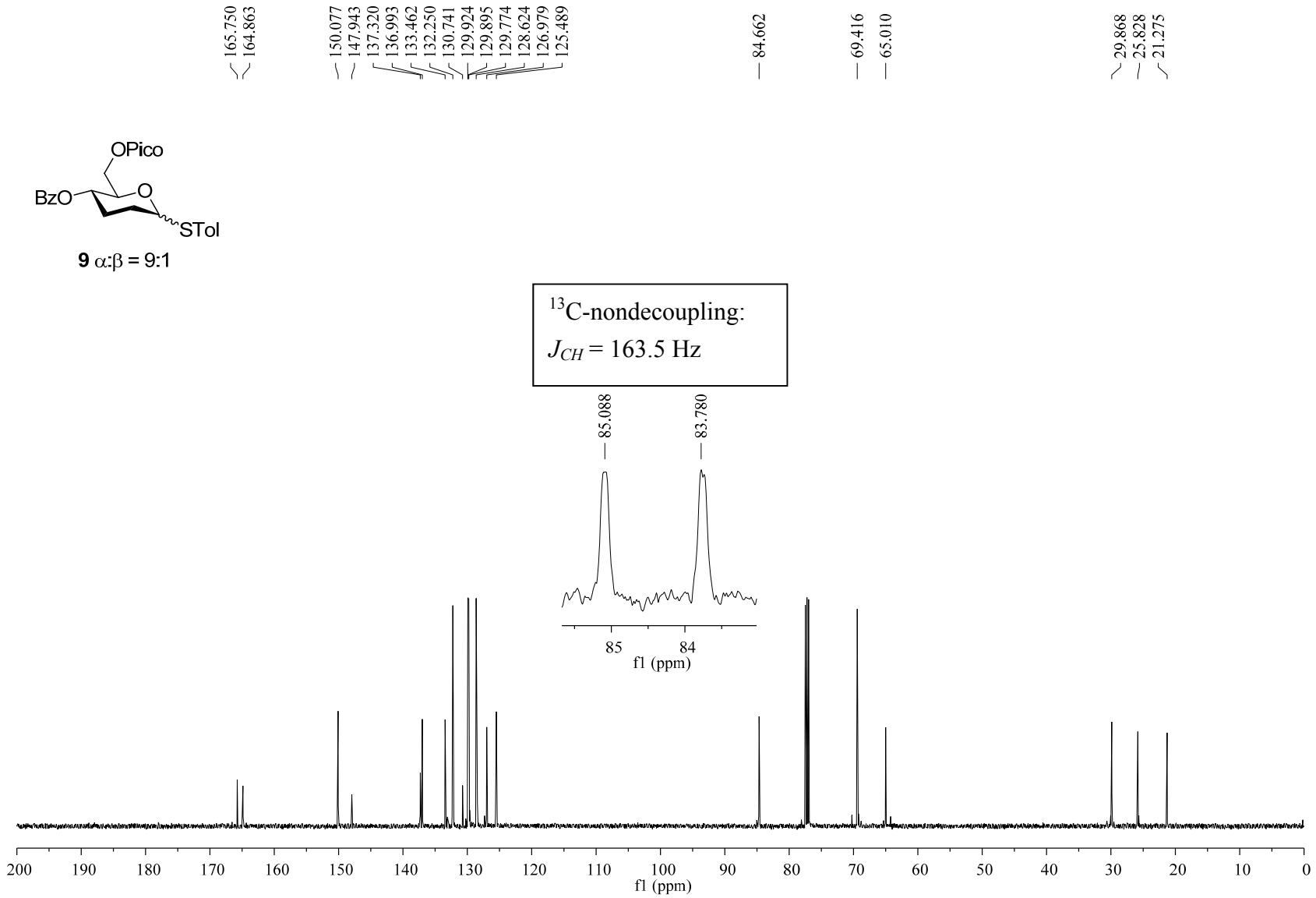

8.767
8.765
8.762
8.751
8.749
8.747
8.745
8.739
8.737
8.735
7.932
7.775
7.741
7.700
7.482
7.191
6.922
6.907
6.903
6.887
5.594
5.582
5.440
4.801
4.705
4.674
4.617
4.582
4.563
4.108
4.072
3.784
3.695
3.671
3.650
3.575
2.529
2.508
2.482
2.465
2.184
2.141
2.016
1.774
1.259
1.250
1.232
1.214
0.098
-0.000
OBn
PicoO
NapO
O
STol
8' α:β = 1:1
1.67
1.69
8.34
18.96
3.27
1.00
1.71
2.50
0.78
4.34
2.76
1.18
0.69
0.73
1.01
0.67
1.72
6.95
0.71
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)

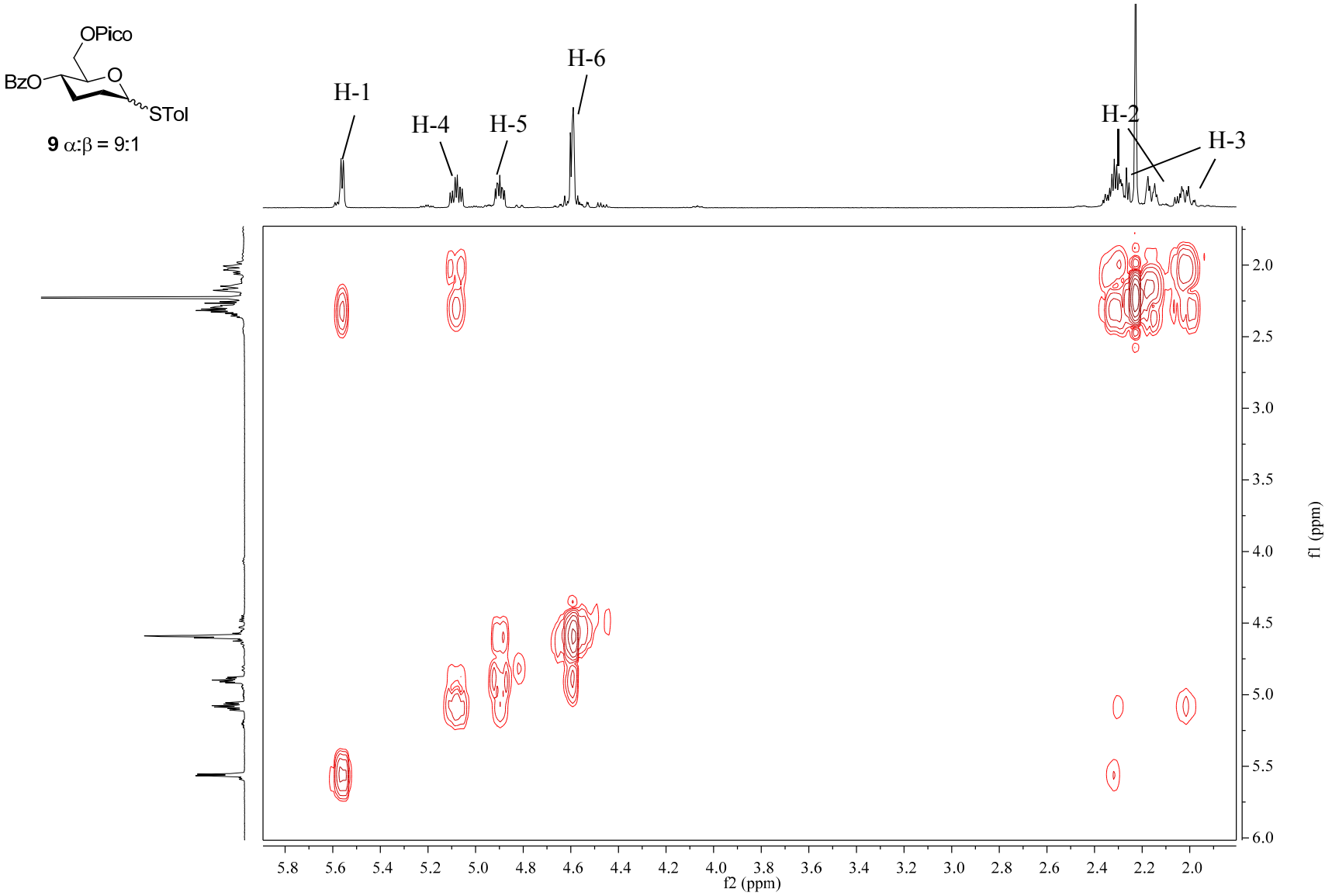

OBn
O
PicoO
NapO
STol

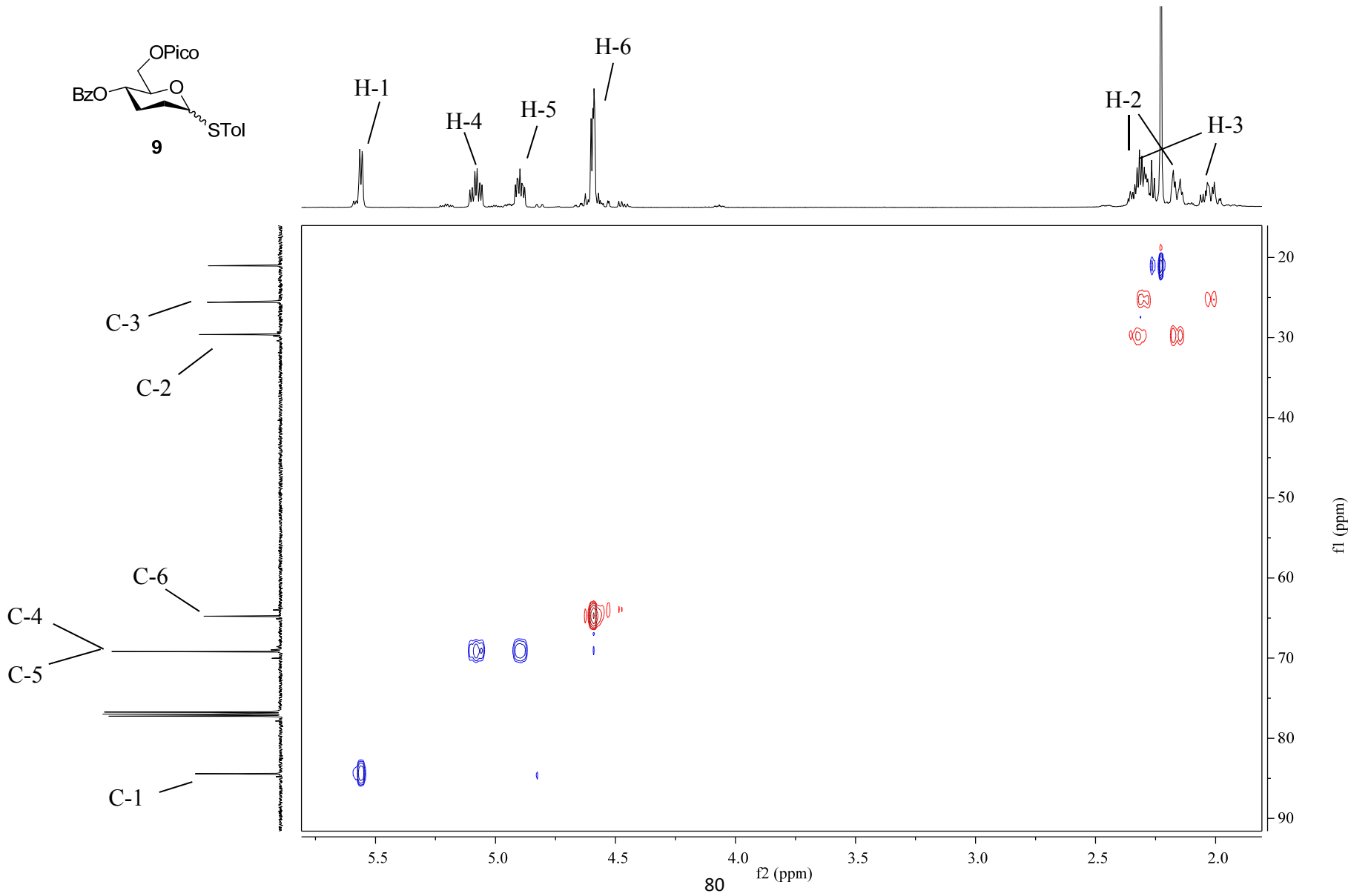
8' α:β = 1:1

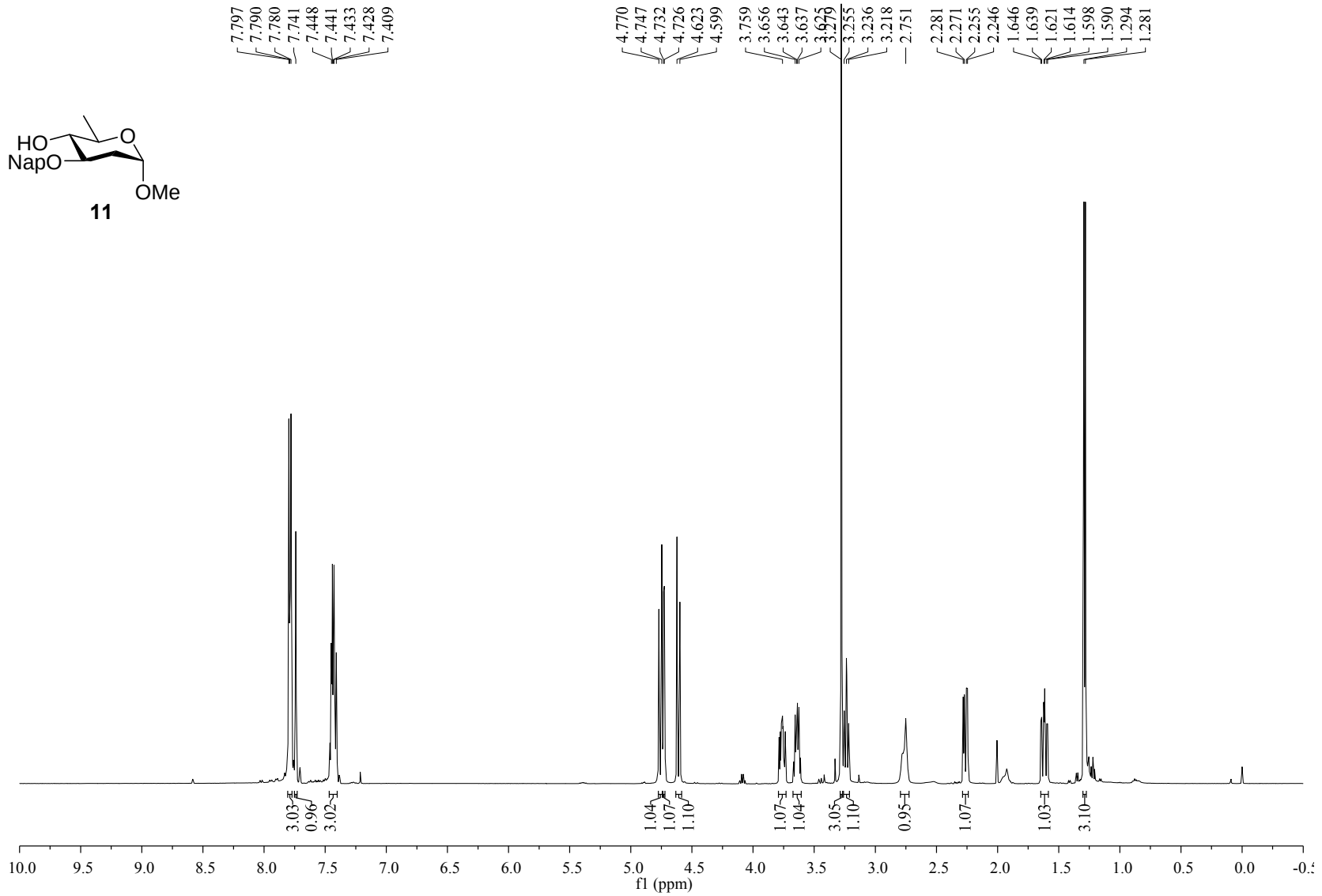
164.540
164.416
149.807
149.791
147.744
147.587
147.696
130.529
129.318
128.119
127.731
127.551
126.381
126.005
125.672
125.034
83.881
80.535
78.156
77.875
77.531
77.318
77.000
76.904
76.681
74.896
74.826
70.012
64.735
64.571
36.584
35.839
20.974
20.935
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

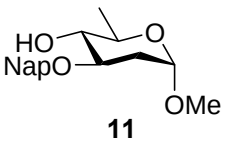

8.760
8.758
8.756
8.750
8.749
8.747
8.062
8.048
7.996
7.981
7.782
7.780
7.767
7.764
7.752
7.749
7.580
7.565
7.551
7.474
7.465
7.459
7.451
7.435
7.420
7.385
7.369
6.912
6.895
5.566
5.556
5.107
5.097
5.086
5.077
5.065
5.056
4.917
4.910
4.906
4.898
4.890
4.886
4.879
4.602
4.594
4.590
2.355
2.345
2.336
2.327
2.317
2.307
2.297
2.289
2.283
2.274
2.228
2.176
2.168
2.154
2.147
2.138
2.041
2.034
2.026
2.013
2.005
OPico
BzO
O
STol
9 α:β = 9:1
0.88
2.01
1.06
1.02
1.07
3.21
2.28
2.02
1.02
1.04
1.04
2.04
2.62
3.05
1.27
0.95
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
f1 (ppm)


165.750
164.863
150.077
147.943
137.320
136.993
133.462
132.250
130.741
129.924
129.895
129.774
128.624
126.979
125.489
84.662
69.416
65.010
29.868
25.828
21.275
OPico
BzO
O
STol
9 α:β = 9:1
13C-nondecoupling:
JCH = 163.5 Hz
85.088
83.780
85
84
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OPico
BzO
O
STol
9 α:β = 9:1
H-1
H-4
H-5
H-6
H-2
H-3
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
f2 (ppm)


OPico
BzO
O
STol
9
H-1
H-4
H-5
H-6
H-2
H-3
C-3
C-2
C-6
C-4
C-5
C-1
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
20
30
40
50
60
70
80
90
f1 (ppm)

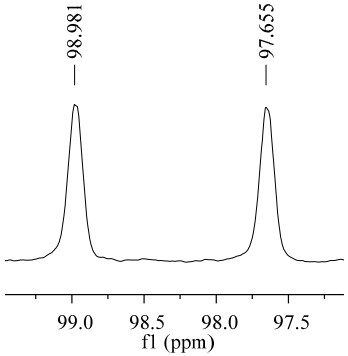

HO
NapO
O
OMe
11
7.797
7.790
7.780
7.741
7.448
7.441
7.433
7.428
7.409
4.770
4.747
4.732
4.726
4.623
4.599
3.759
3.656
3.643
3.637
3.625
3.255
3.236
3.218
2.751
2.281
2.271
2.255
2.246
1.646
1.639
1.621
1.614
1.598
1.590
1.294
1.281
3.03
0.96
3.02
1.04
1.07
1.10
1.07
1.04
3.05
1.10
0.95
1.07
1.03
3.10
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
f1 (ppm)

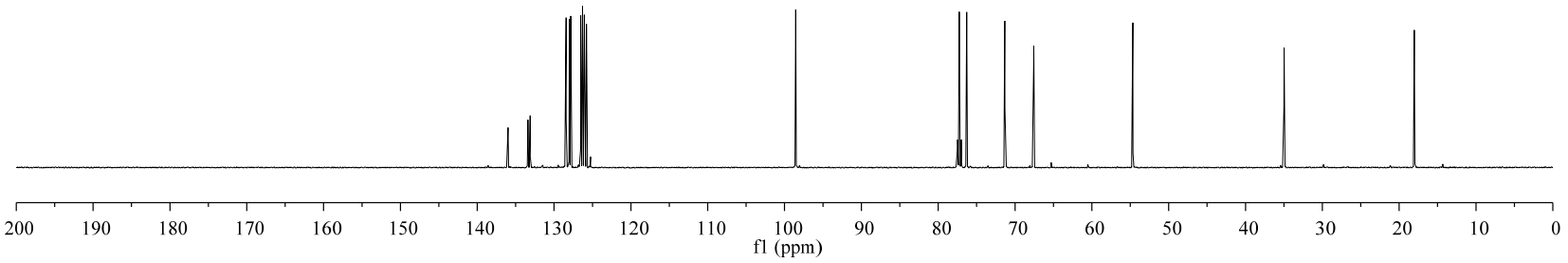


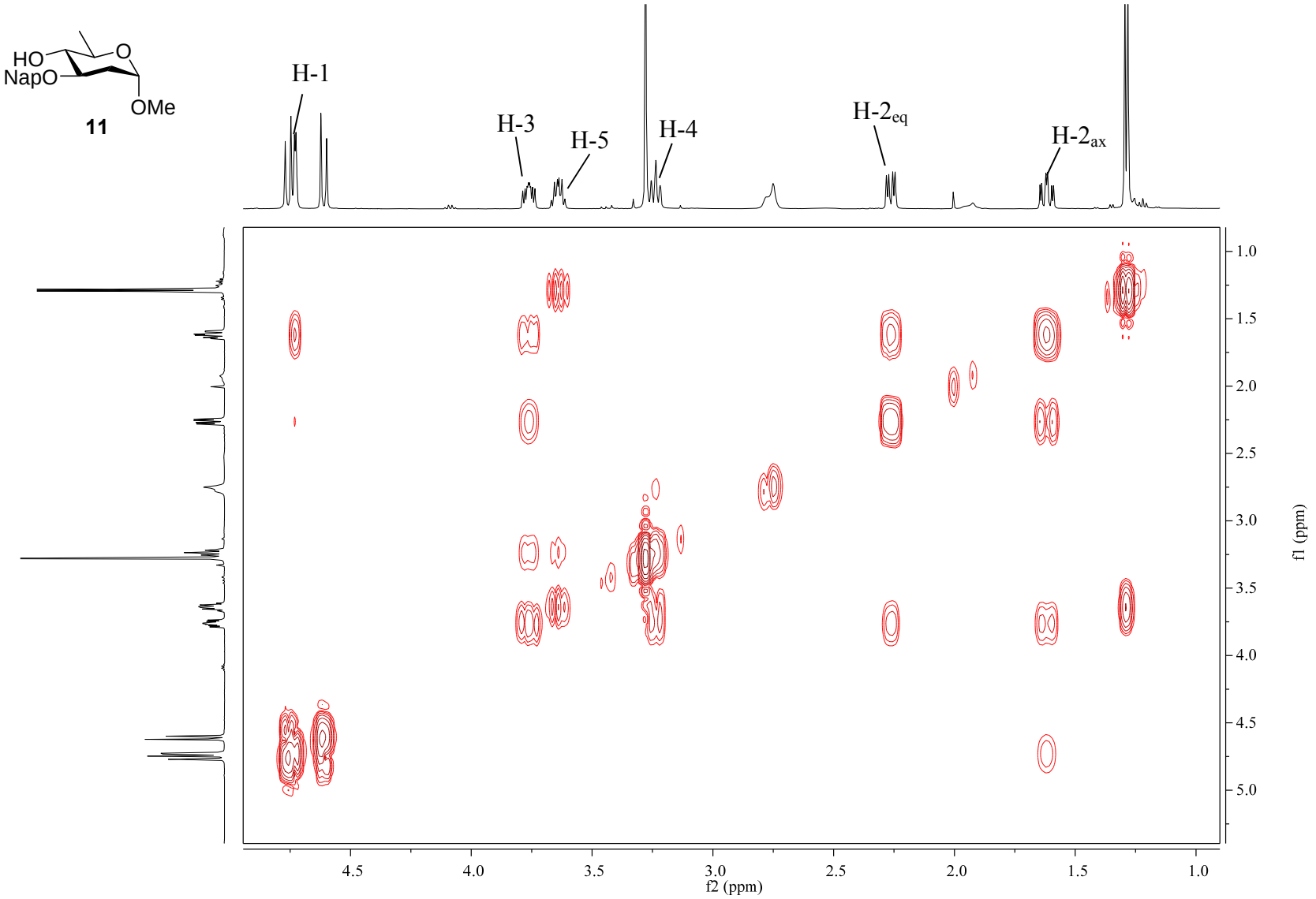
11

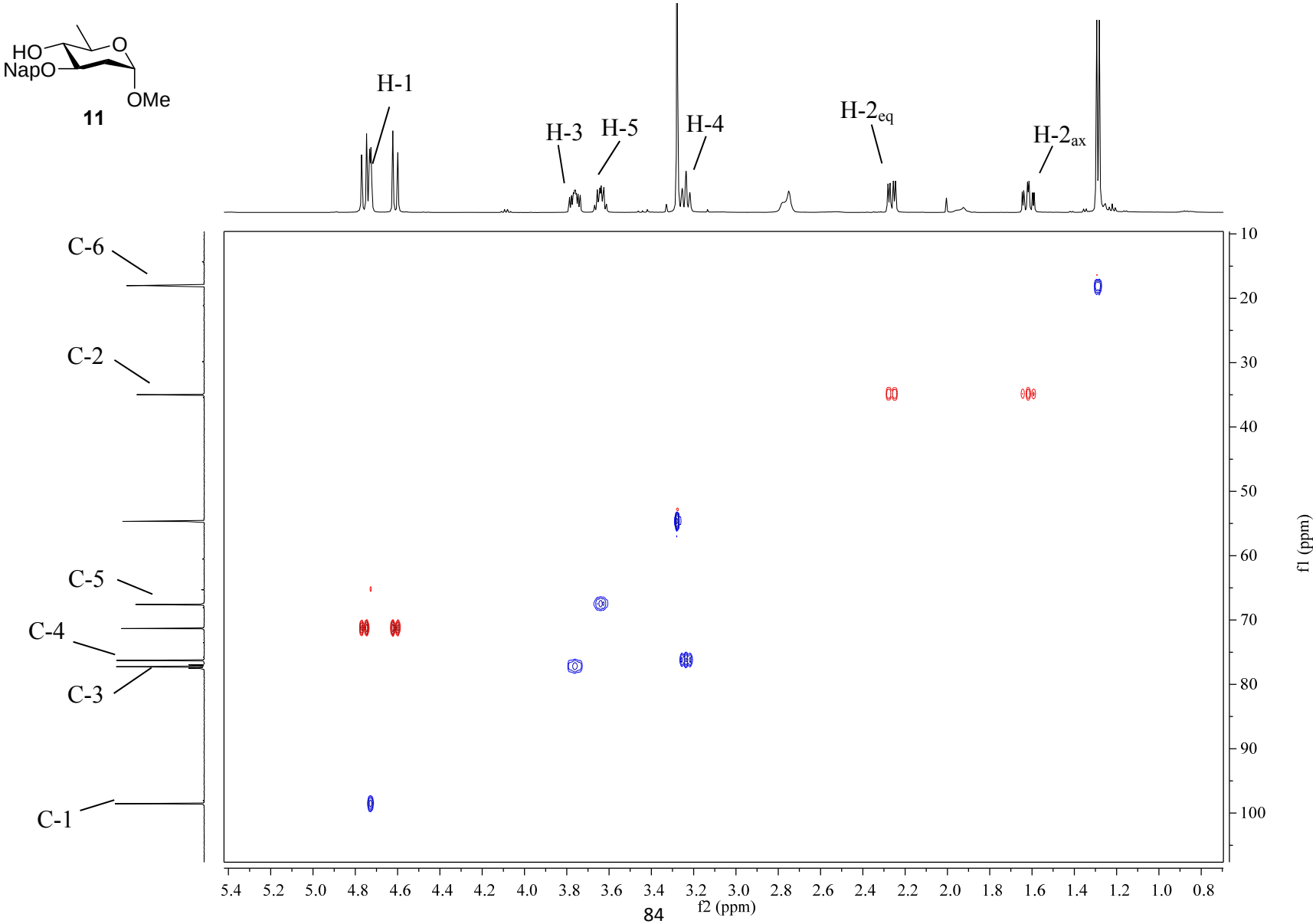
135.983
133.405
133.116
128.433
128.010
127.830
126.534
126.288
126.064
125.776
98.549
77.255
76.290
71.325
67.567
54.671
34.982
18.035

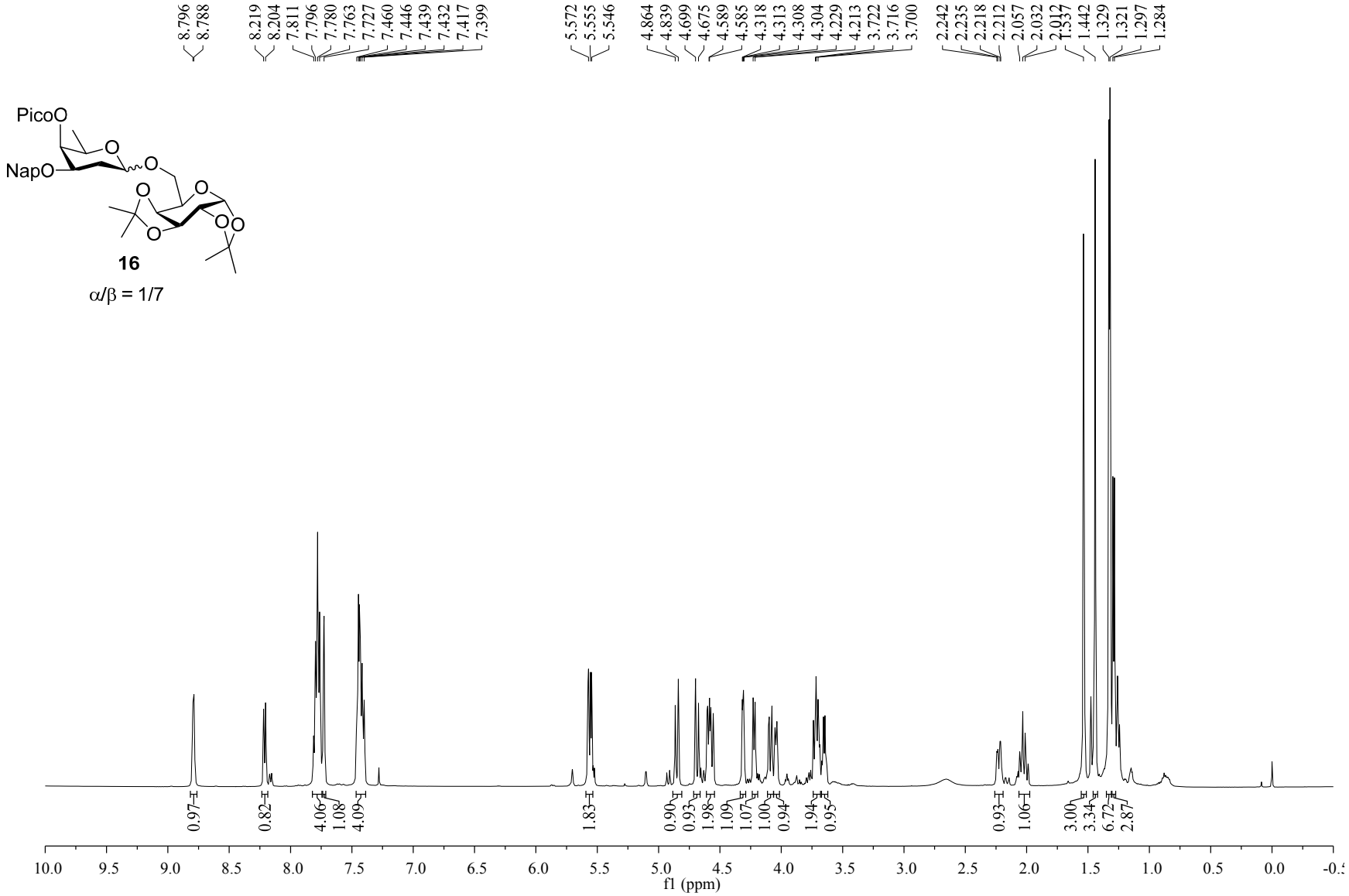
^{13}C-nondecoupling:
J_{CH} = 165.8

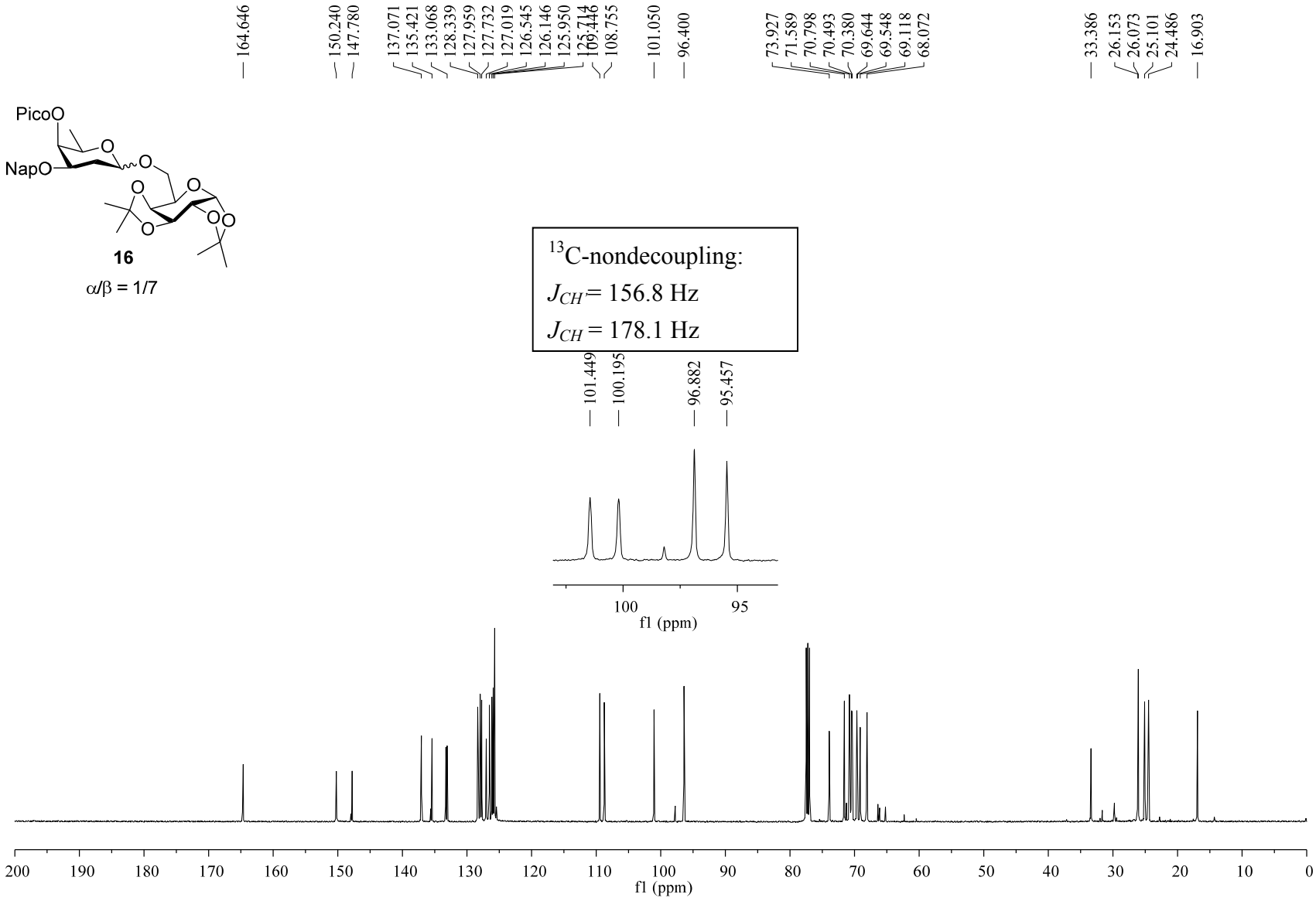


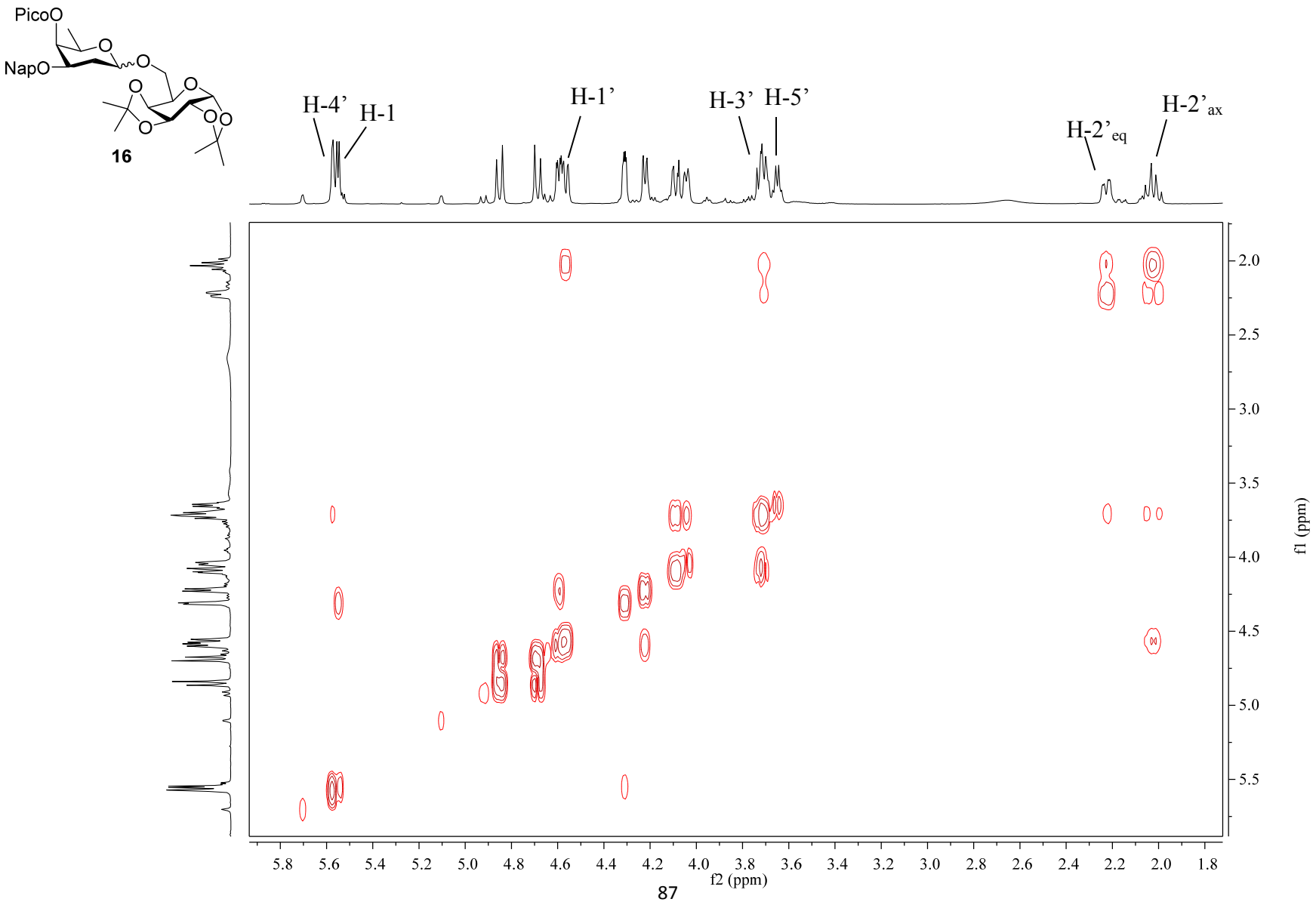


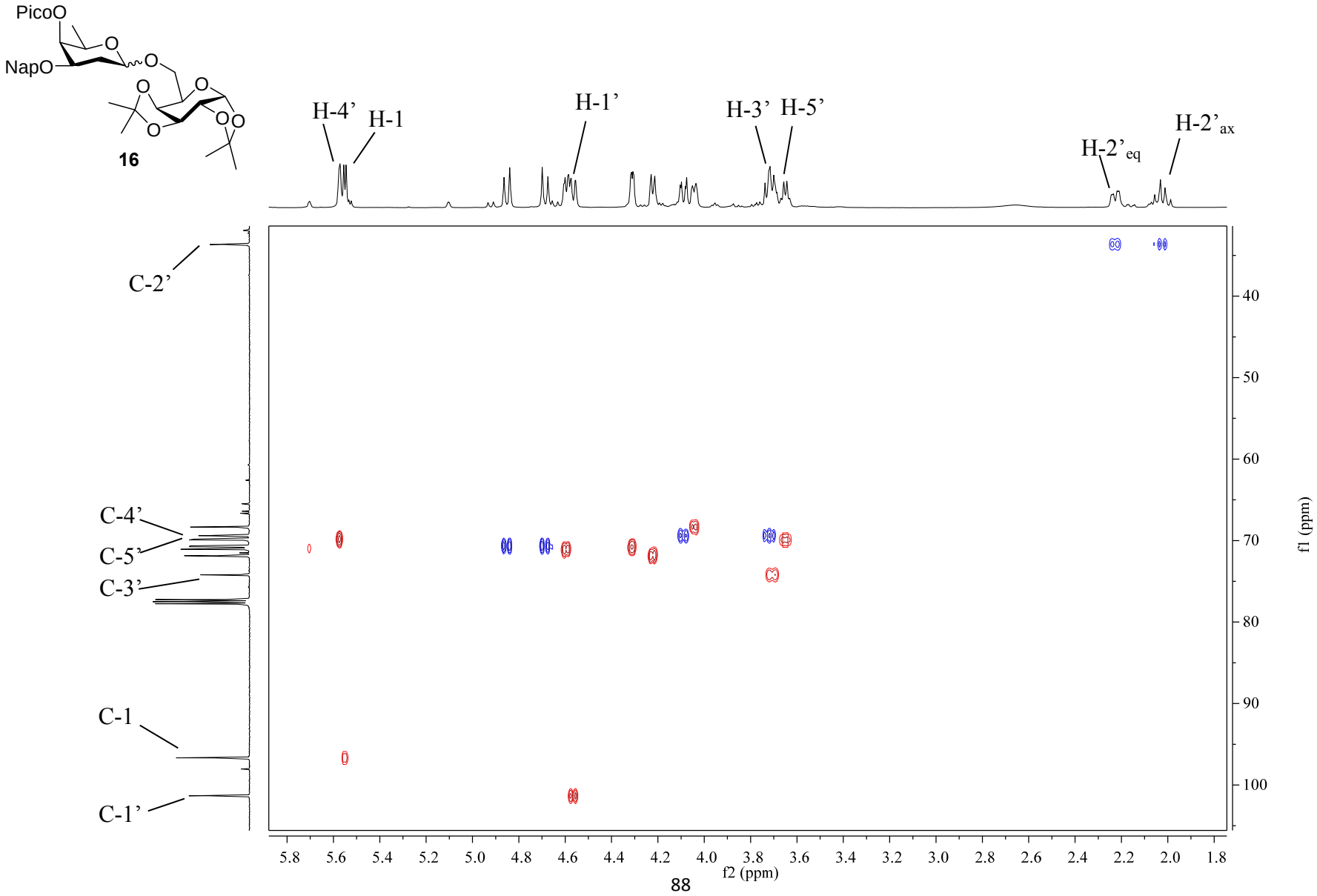

HO
NapO
O
OMe
11
H-1
H-3
H-5
H-4
H-2eq
H-2ax
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

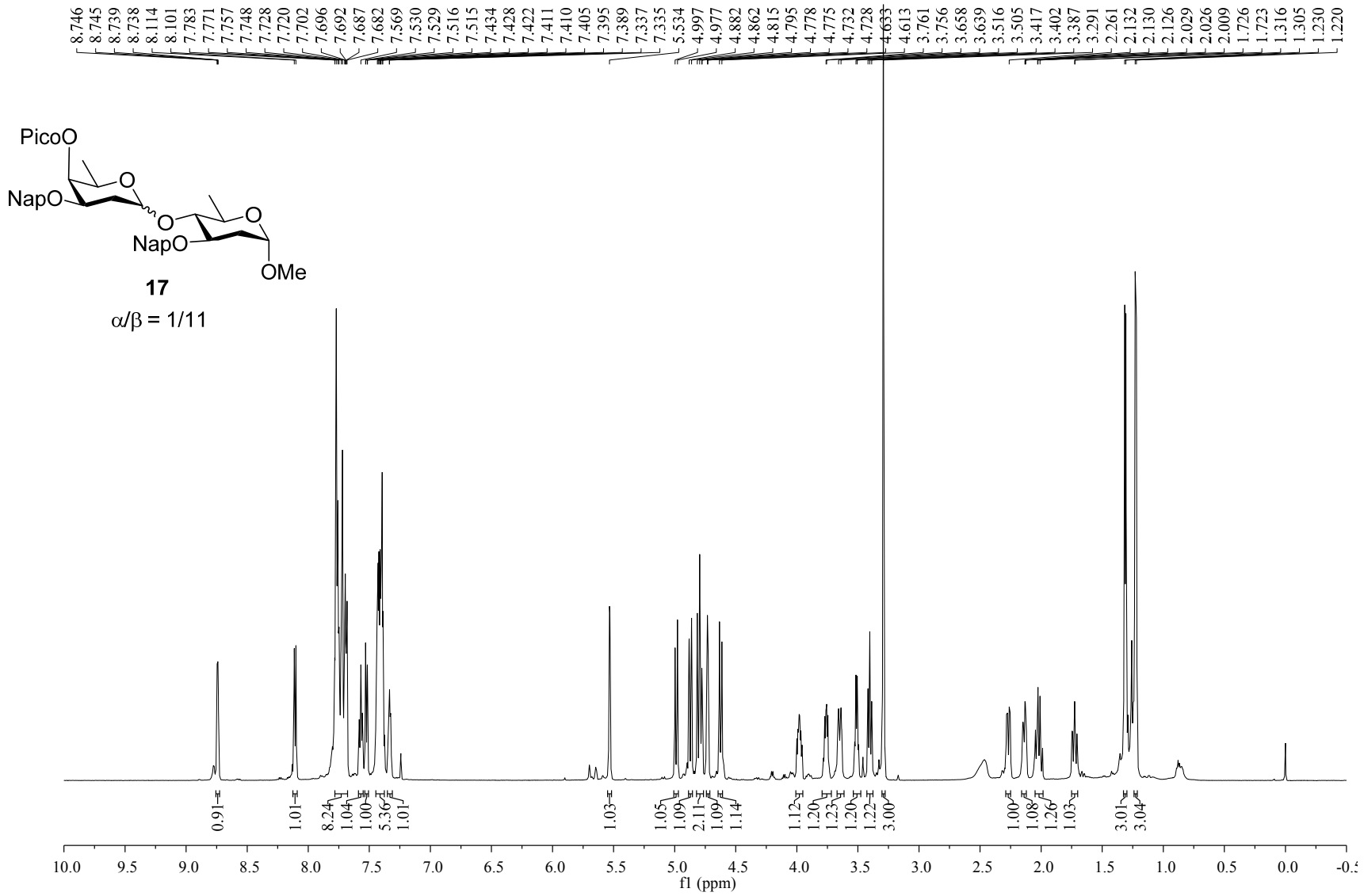

HO
NapO
O
OMe
11
H-1
H-3
H-5
H-4
H-2eq
H-2ax
C-6
C-2
C-5
C-4
C-3
C-1
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f2 (ppm)
10 20 30 40 50 60 70 80 90 100
f1 (ppm)

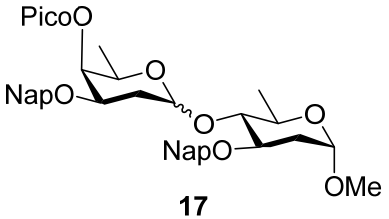

PicoO
NapO
16
α/β = 1/7
8.796
8.788
8.219
8.204
7.811
7.796
7.780
7.763
7.727
7.460
7.446
7.439
7.432
7.417
7.399
5.572
5.555
5.546
4.864
4.839
4.699
4.675
4.589
4.585
4.318
4.313
4.308
4.304
4.229
4.213
3.722
3.716
3.700
2.242
2.235
2.218
2.212
2.057
2.032
2.012
1.537
1.442
1.329
1.321
1.297
1.284
0.97
0.82
4.06
1.08
4.09
1.83
0.90
0.93
1.98
1.09
1.07
1.00
0.94
1.94
0.95
0.93
1.06
3.00
3.34
6.72
2.87
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
f1 (ppm)


164.646
150.240
147.780
137.071
135.421
133.068
128.339
127.959
127.732
127.019
126.545
126.146
125.950
125.714
109.446
108.755
101.050
96.400
73.927
71.589
70.798
70.493
70.380
69.644
69.548
69.118
68.072
33.386
26.153
26.073
25.101
24.486
16.903
PicoO
NapO
16
α/β = 1/7
13C-nondecoupling:
JCH = 156.8 Hz
JCH = 178.1 Hz
101.449
100.195
96.882
95.457
100
95
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


PicoO
NapO
O
O
O
O
O
O
O
16
H-4’
H-1
H-1’
H-3’
H-5’
H-2’eq
H-2’ax
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)


PicoO
NapO
O
16
H-4’
H-1
H-1’
H-3’
H-5’
H-2’eq
H-2’ax
C-2’
C-4’
C-5’
C-3’
C-1
C-1’
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f2 (ppm)
40
50
60
70
80
90
100
f1 (ppm)


PicoO
NapO
O
O
O
NapO
OMe
17
α/β = 1/11
8.746
8.745
8.739
8.738
8.114
8.101
7.783
7.771
7.757
7.748
7.728
7.720
7.702
7.696
7.692
7.687
7.682
7.569
7.530
7.529
7.516
7.515
7.434
7.428
7.422
7.411
7.410
7.405
7.395
7.389
7.337
7.335
5.534
4.997
4.977
4.882
4.862
4.815
4.795
4.778
4.775
4.732
4.728
4.633
4.613
3.761
3.756
3.658
3.639
3.516
3.505
3.417
3.402
3.387
3.291
2.261
2.132
2.130
2.126
2.029
2.026
2.009
1.726
1.723
1.316
1.305
1.230
1.220
0.91
1.01
8.24
1.04
1.00
5.36
1.01
1.03
1.05
1.09
2.11
1.09
1.14
1.12
1.20
1.23
1.20
1.22
3.00
1.00
1.08
1.26
1.03
3.01
3.04
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
f1 (ppm)



17

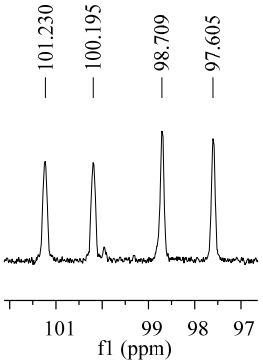
α/β = 1/11

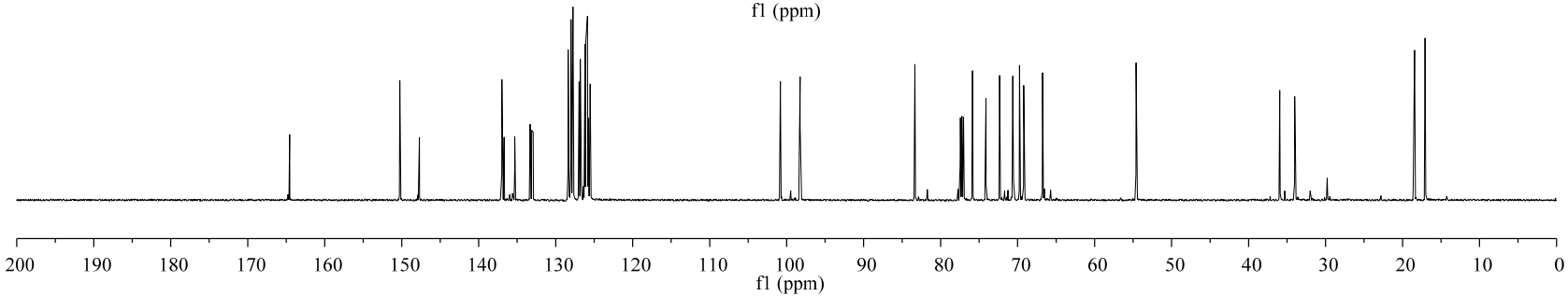
164.559
150.237
147.703
128.379
128.007
127.980
127.791
127.747
127.737
126.799
126.179
126.090
126.010
125.944
125.913
125.880
125.775
125.820
98.254
83.336
75.857
74.119
72.336
70.621
69.760
69.207
66.760
54.613
35.949
34.005
18.441
17.069

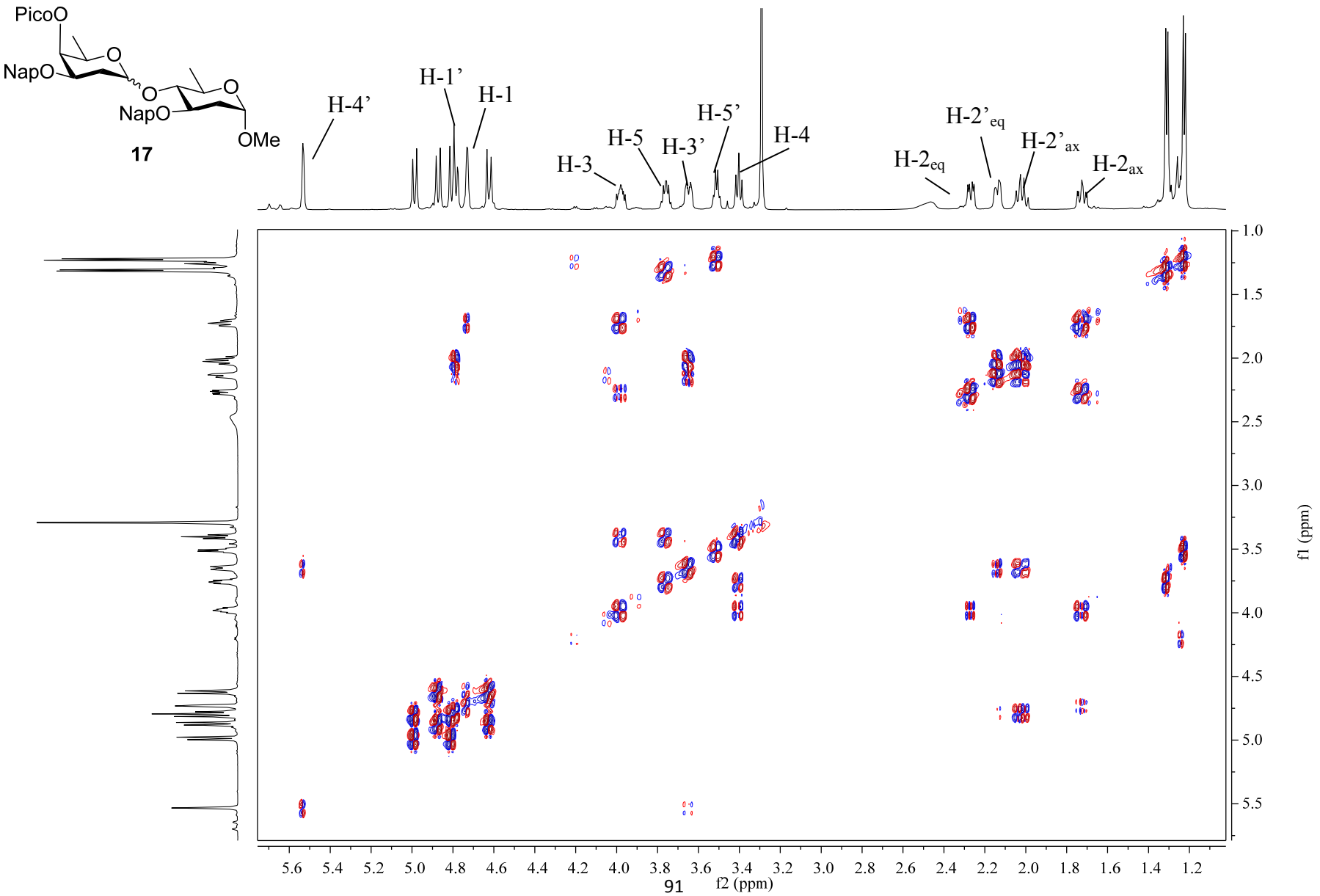
^{13}C-nondecoupling:

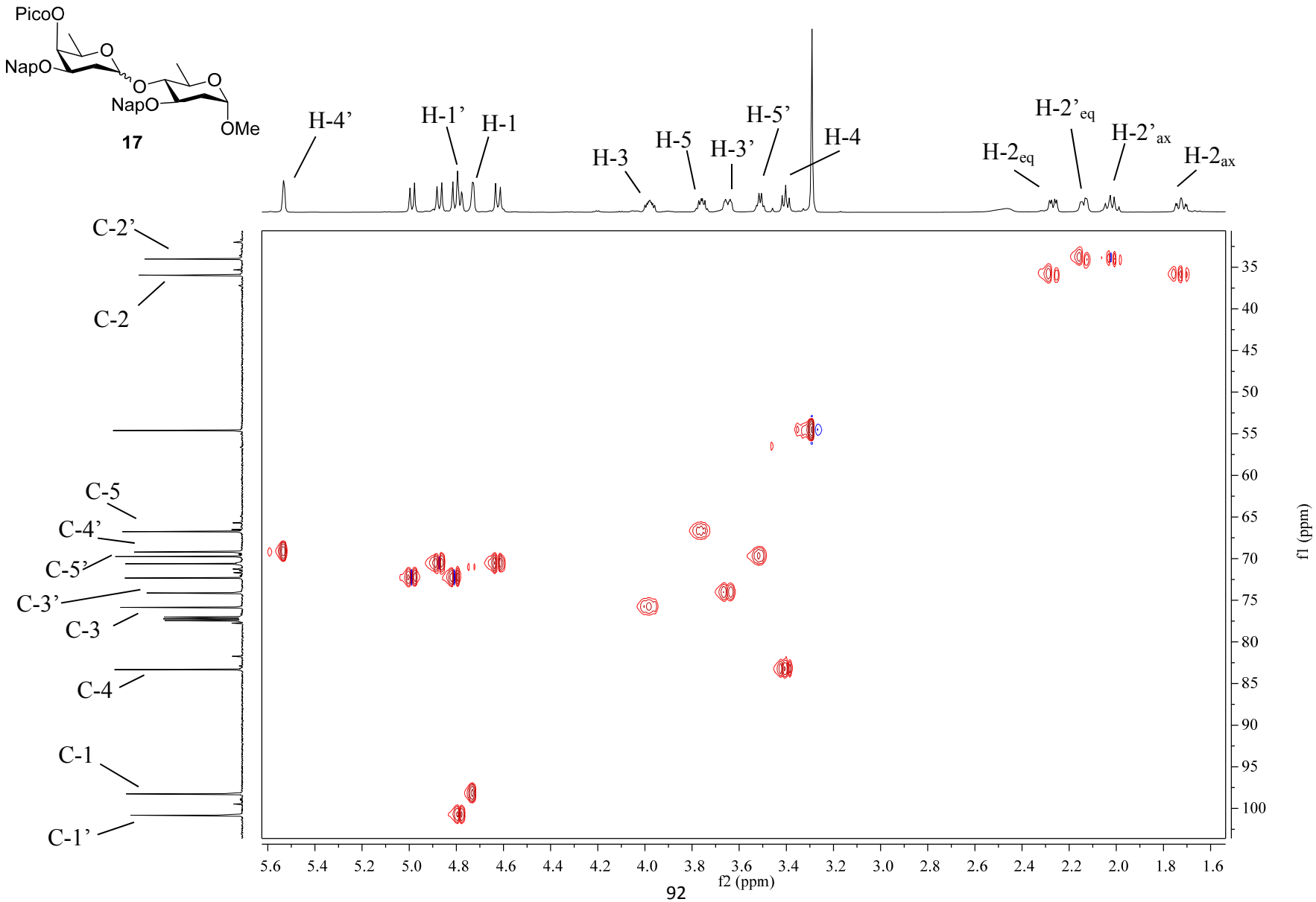
$J_{CH'}$ = 155.3 Hz

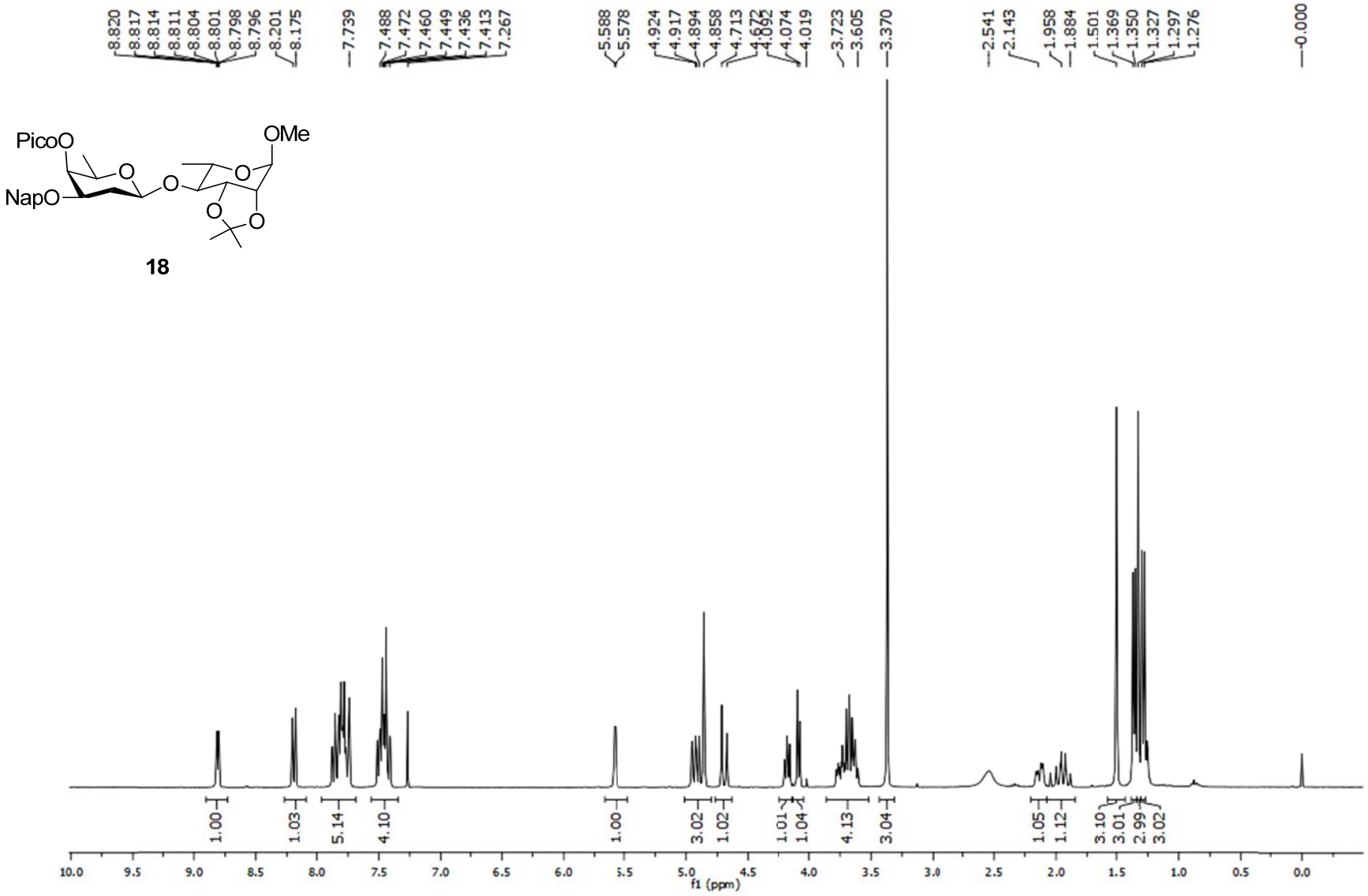
J_{CH} = 165.6 Hz

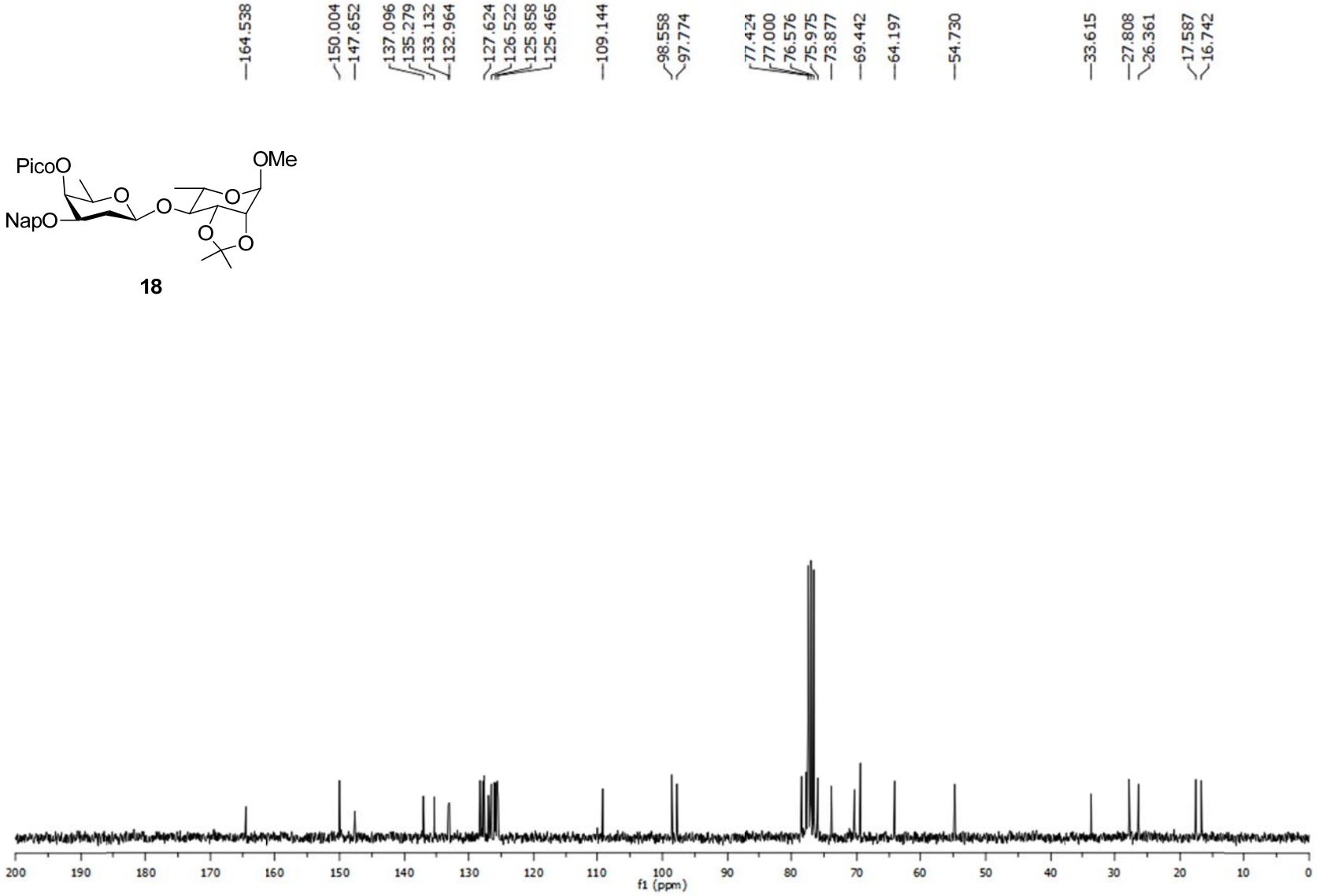


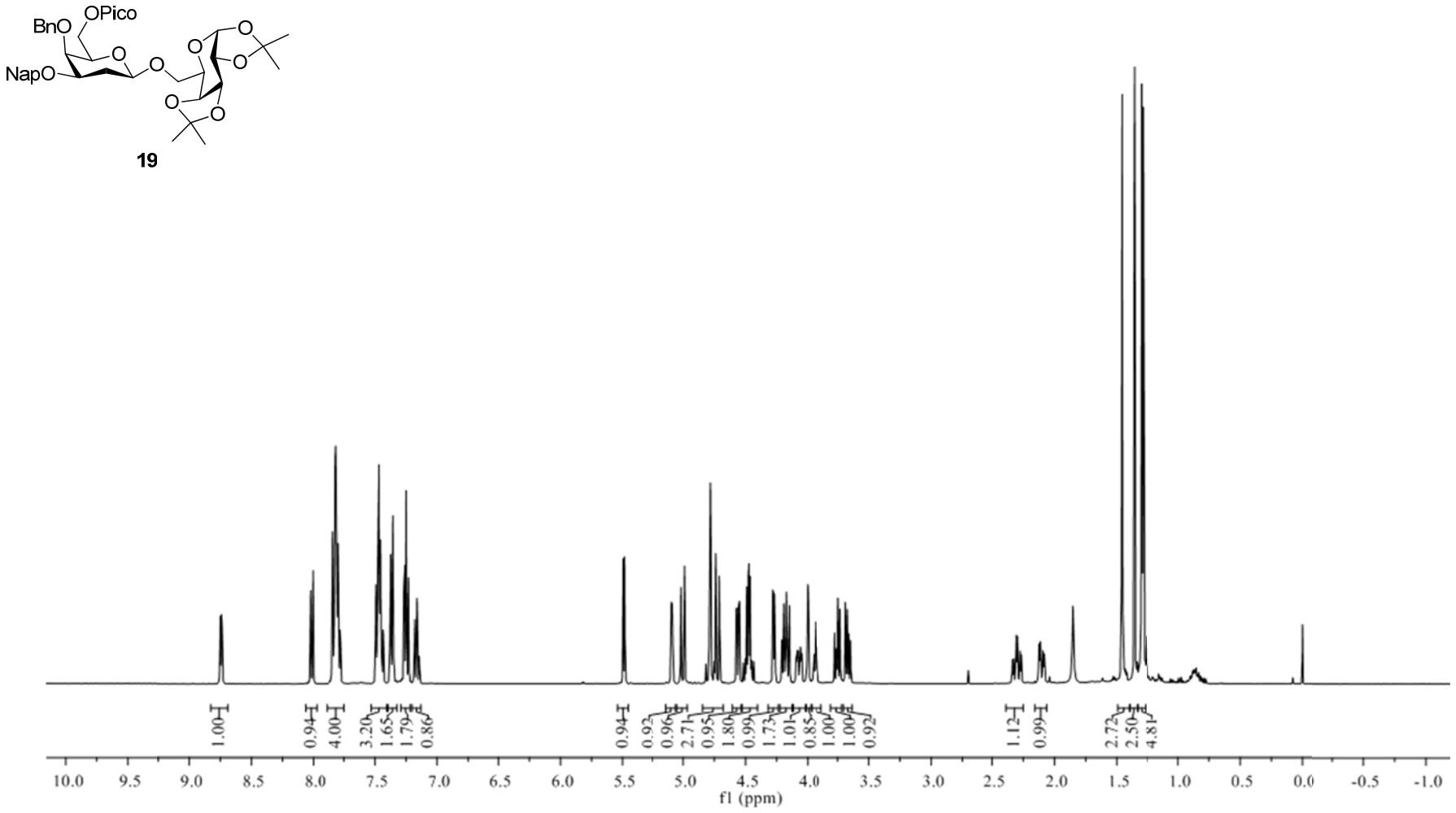


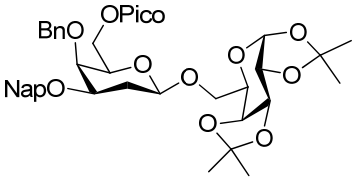

PicoO
NapO
O
O
O
NapO
OMe
17
H-4'
H-1'
H-1
H-3
H-5
H-3'
H-5'
H-4
H-2eq
H-2'eq
H-2'ax
H-2ax
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)


PicoO
NapO
O
O
NapO
OMe
17
H-4’
H-1’
H-1
H-3
H-5
H-3’
H-5’
H-4
H-2’eq
H-2’ax
H-2eq
H-2ax
C-2’
C-2
C-5
C-4’
C-5’
C-3’
C-3
C-4
C-1
C-1’
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
35
40
45
50
55
60
65
70
75
80
85
90
95
100
f1 (ppm)


8.820
8.817
8.814
8.811
8.804
8.801
8.798
8.796
8.201
8.175
7.739
7.488
7.472
7.460
7.449
7.436
7.413
7.267
5.588
5.578
4.924
4.917
4.894
4.858
4.713
4.672
4.652
4.074
4.019
3.723
3.605
3.370
2.541
2.143
1.958
1.884
1.501
1.369
1.350
1.327
1.297
1.276
0.000
PicoO
NapO
OMe
O
18
1.00
1.03
5.14
4.10
1.00
3.02
1.02
1.01
1.04
4.13
3.04
1.05
1.12
3.10
3.01
2.99
3.02
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
f1 (ppm)

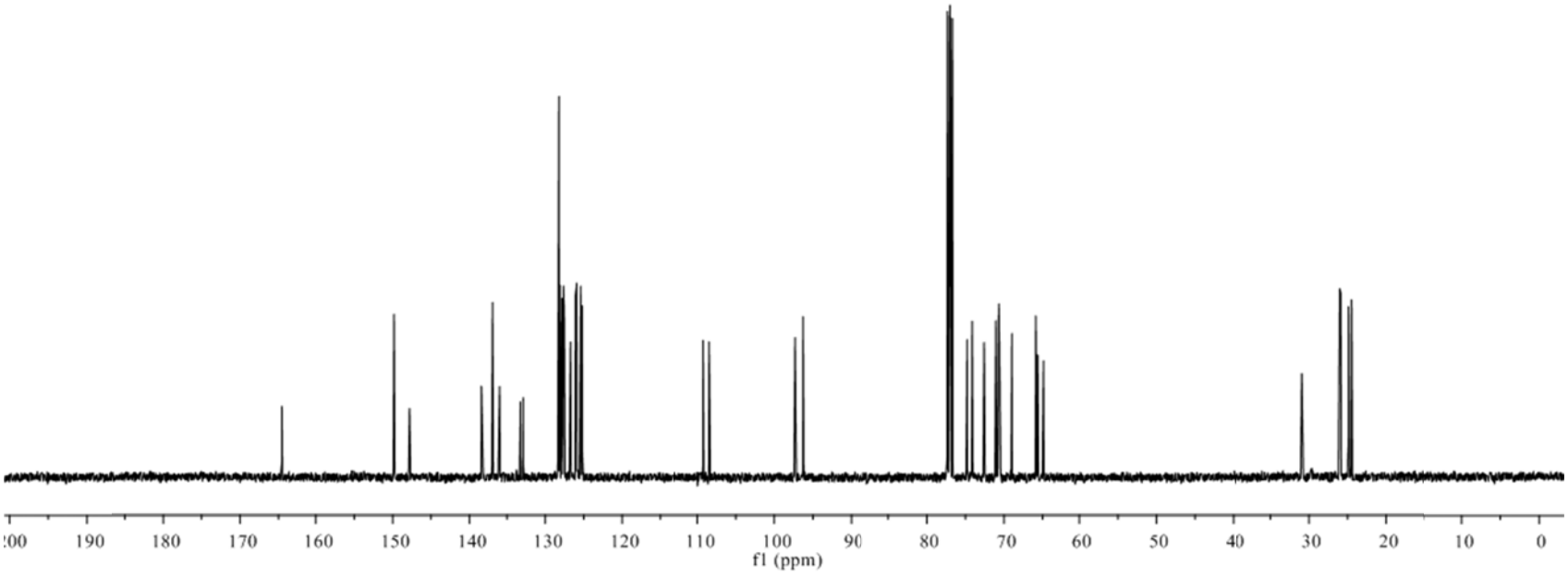

164.538
150.004
147.652
137.096
135.279
133.132
132.964
127.624
126.522
125.858
125.465
109.144
98.558
97.774
77.424
77.000
76.576
75.975
73.877
69.442
64.197
54.730
33.615
27.808
26.361
17.587
16.742
PicoO
NapO
OMe
O
O
O
O
O
18
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

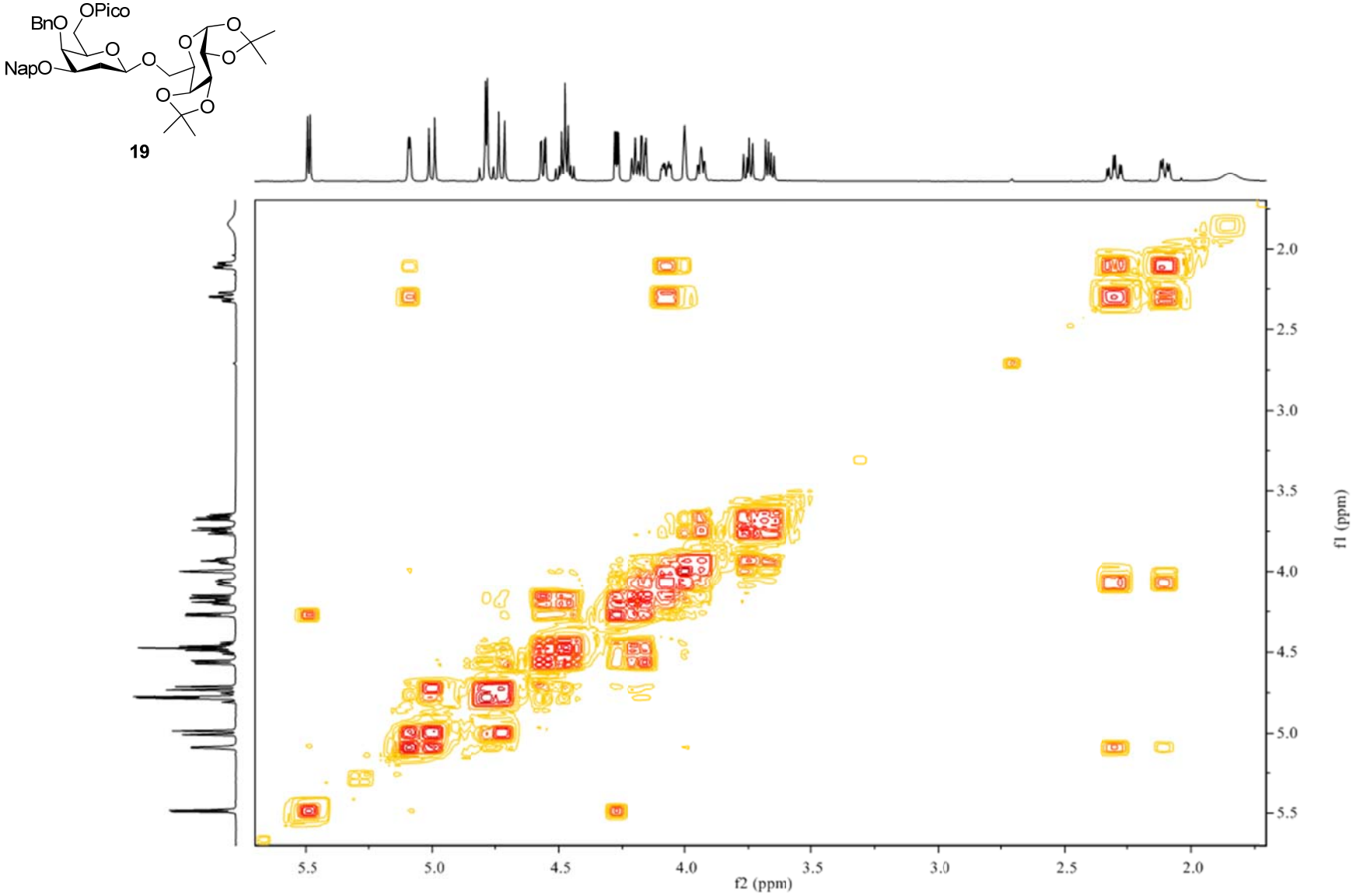

BnO
OPico
NapO
O
19
f1 (ppm)

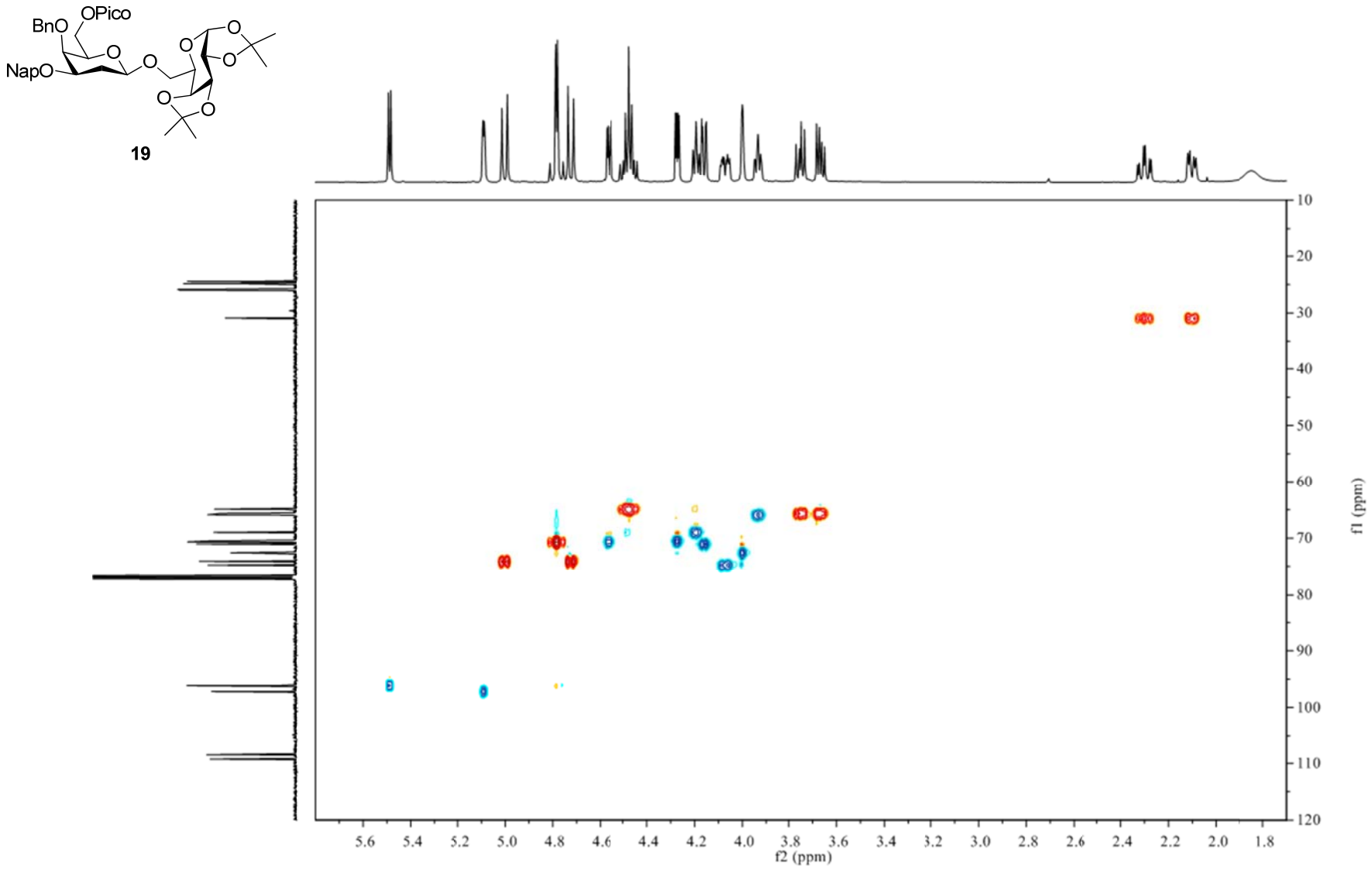


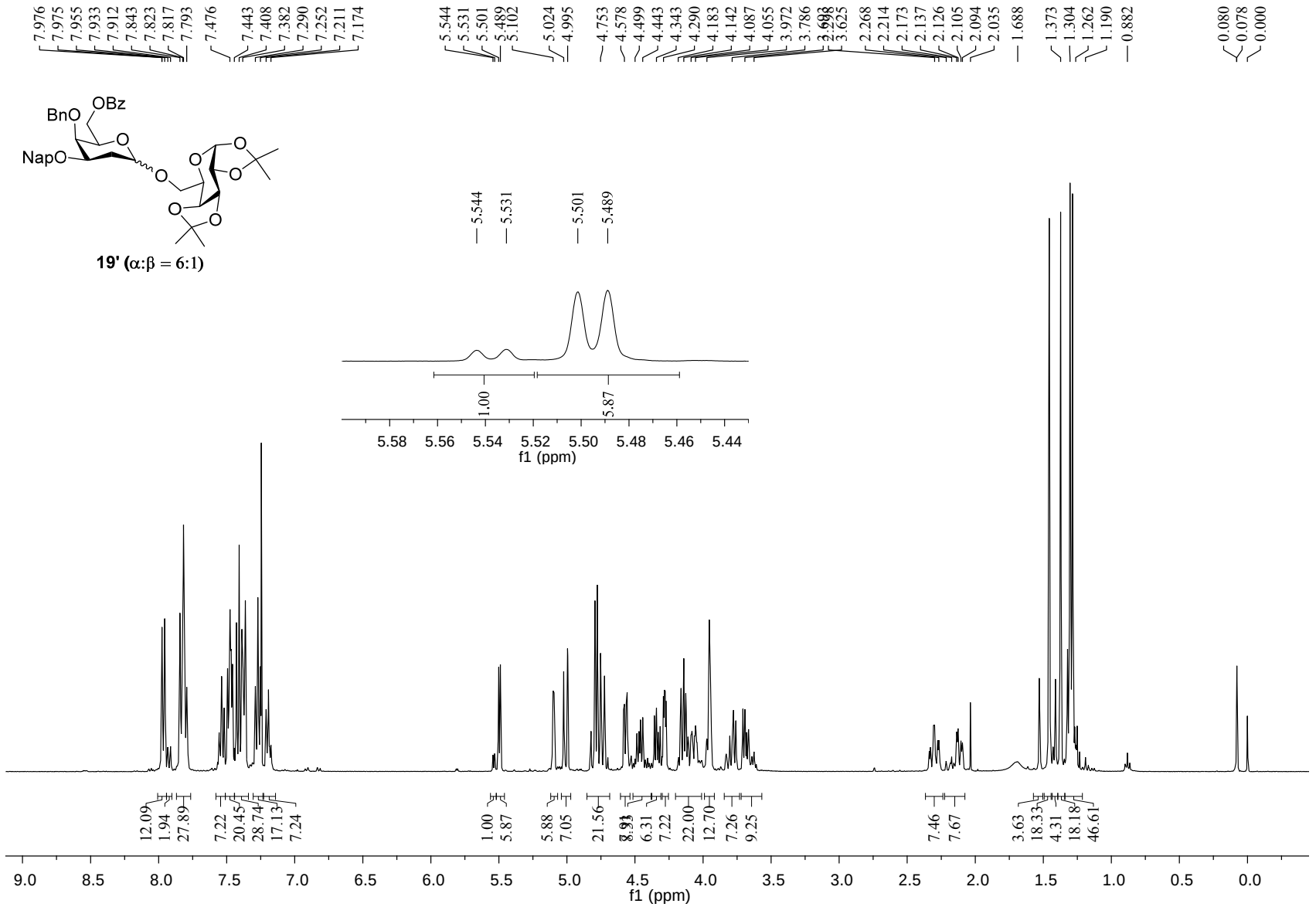
19

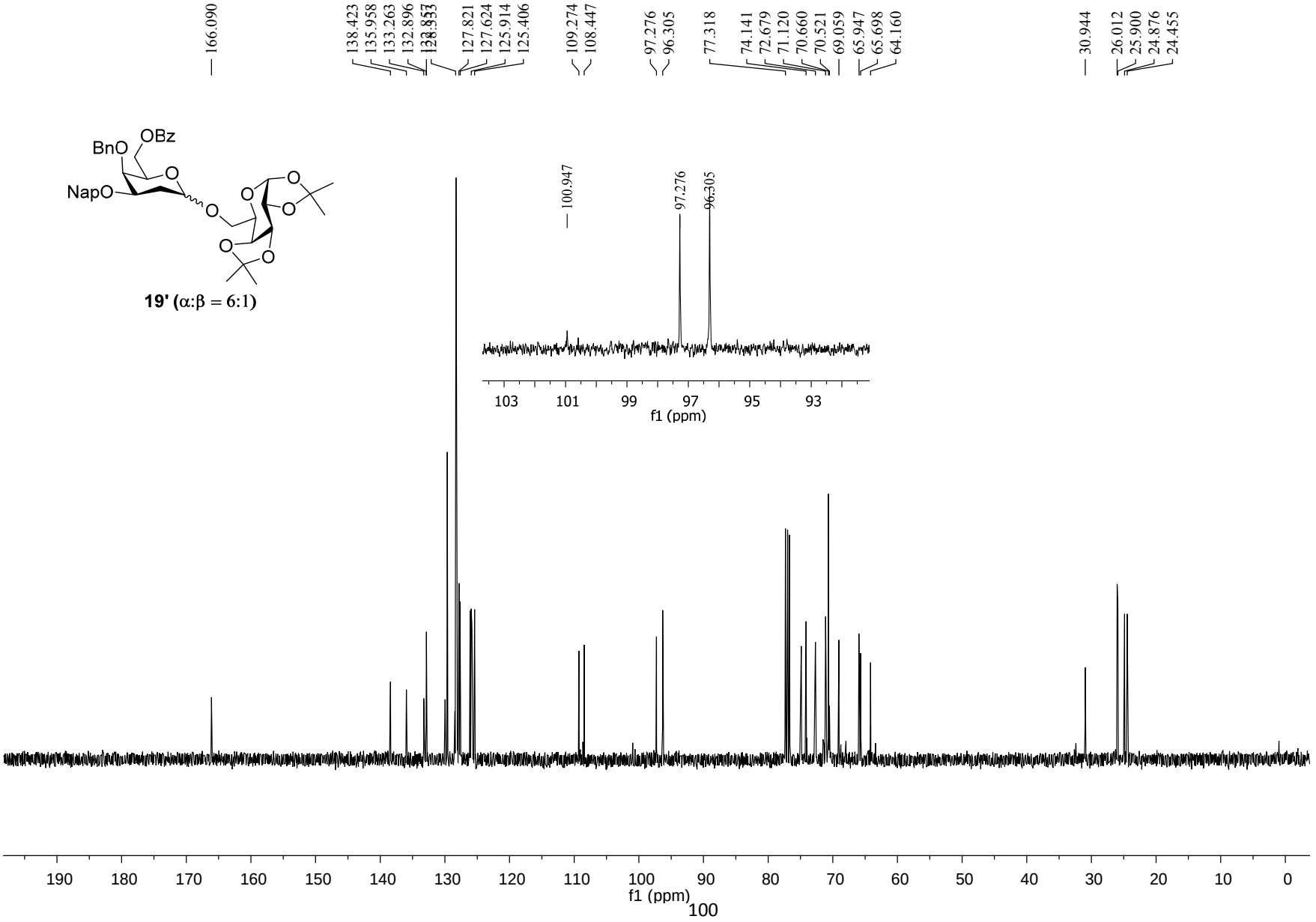
164.54
149.83
147.80
136.87
128.34
128.23
128.08
127.82
127.64
127.54
126.07
125.91
125.41
108.45
97.32
96.27
77.32
77.00
76.68
74.78
74.12
72.59
71.06
70.67
70.63
70.51
68.99
65.88
65.64
64.89
30.95
26.02
25.89
24.87
24.47

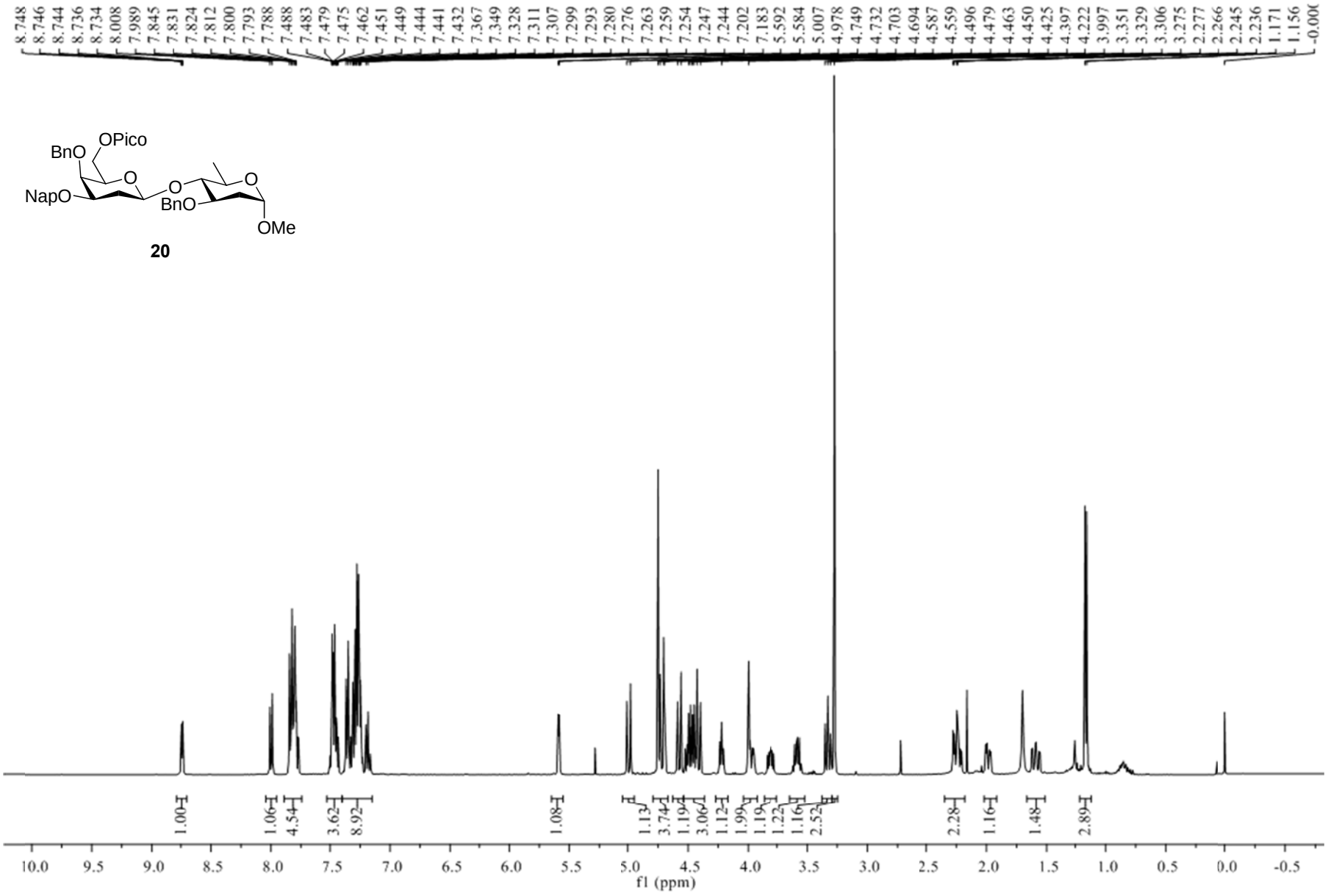


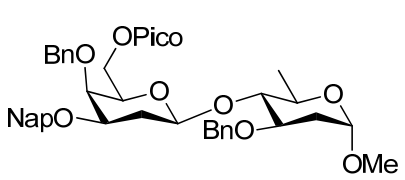

BnO
OPico
NapO
O
19
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
f1 (ppm)


BnO
OPico
NapO
O
19
f2 (ppm)
f1 (ppm)


BnO
OBz
NapO
O
19' (α:β = 6:1)
f1 (ppm)

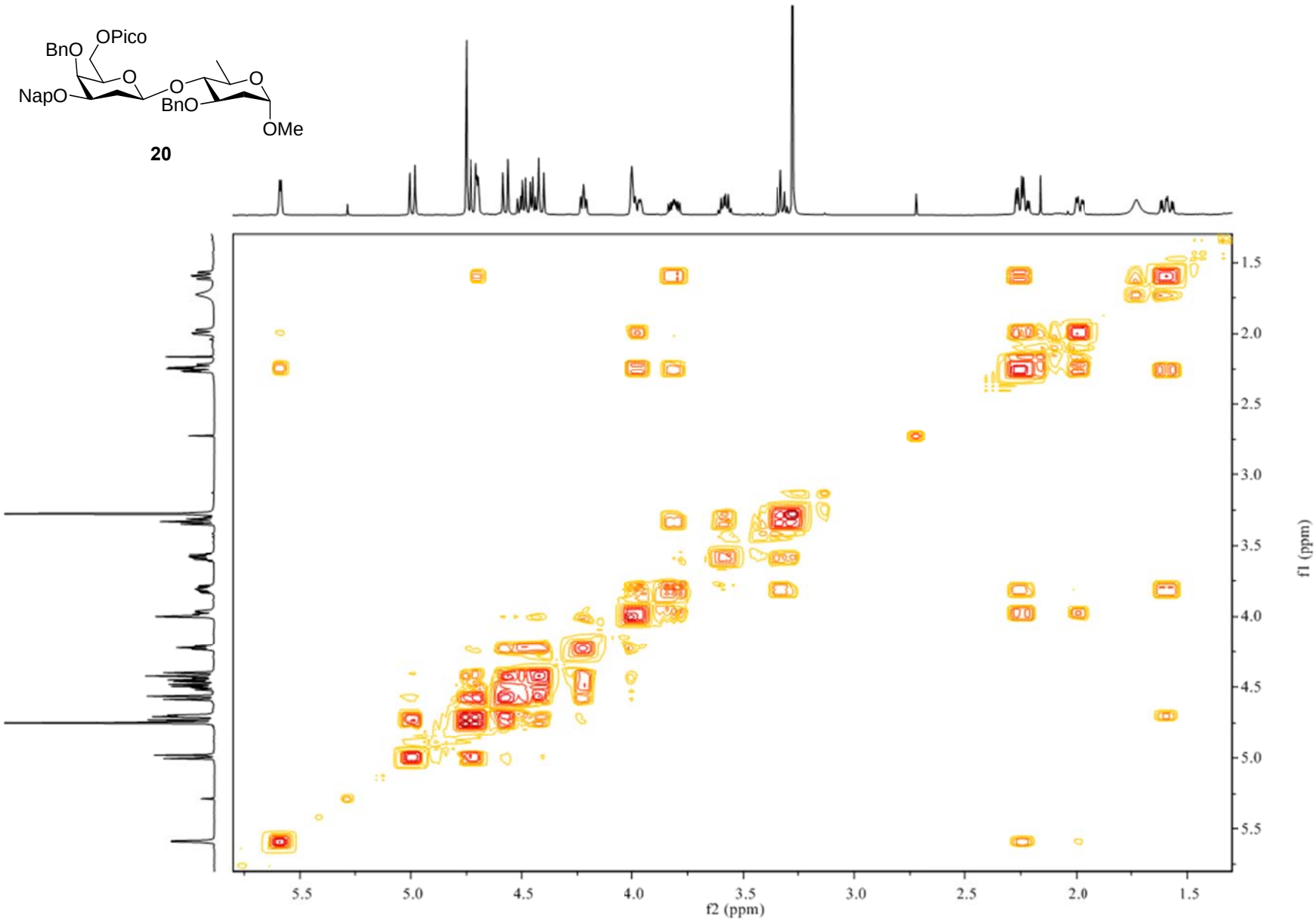

166.090
138.423
135.958
133.263
132.896
127.821
127.624
125.914
125.406
109.274
108.447
97.276
96.305
77.318
74.141
72.679
71.120
70.660
70.521
69.059
65.947
65.698
64.160
30.944
26.012
25.900
24.876
24.455
BnO
OBz
NapO
O
19' (α:β = 6:1)
100.947
97.276
96.305
103
101
99
97
95
93
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

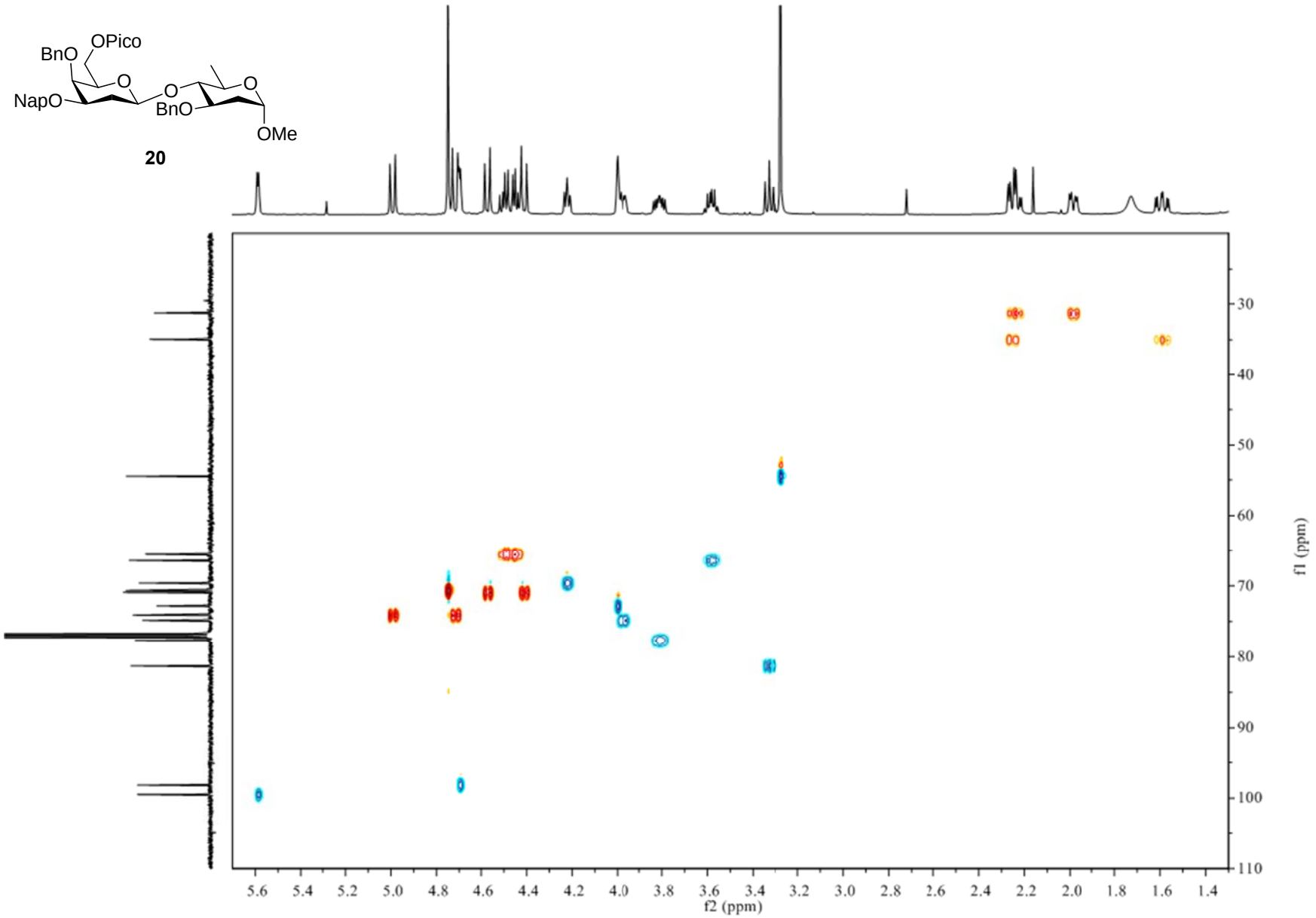

8.748
8.746
8.744
8.736
8.734
8.008
7.989
7.845
7.831
7.824
7.812
7.800
7.793
7.788
7.488
7.483
7.479
7.475
7.462
7.451
7.449
7.444
7.441
7.432
7.367
7.349
7.328
7.311
7.307
7.299
7.293
7.280
7.276
7.263
7.259
7.254
7.247
7.244
7.202
7.183
5.592
5.584
5.007
4.978
4.749
4.732
4.703
4.694
4.587
4.559
4.496
4.479
4.463
4.450
4.425
4.397
4.222
3.997
3.351
3.329
3.306
3.275
2.277
2.266
2.245
2.236
1.171
1.156
BnO
OPico
O
O
O
NapO
BnO
OMe
20
1.00
1.06
4.54
3.62
8.92
1.08
1.13
3.74
1.19
3.06
1.12
1.99
1.19
1.22
1.16
2.52
2.28
1.16
1.48
2.89
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)


BnO
OPico
O
NapO
O
BnO
O
OMe

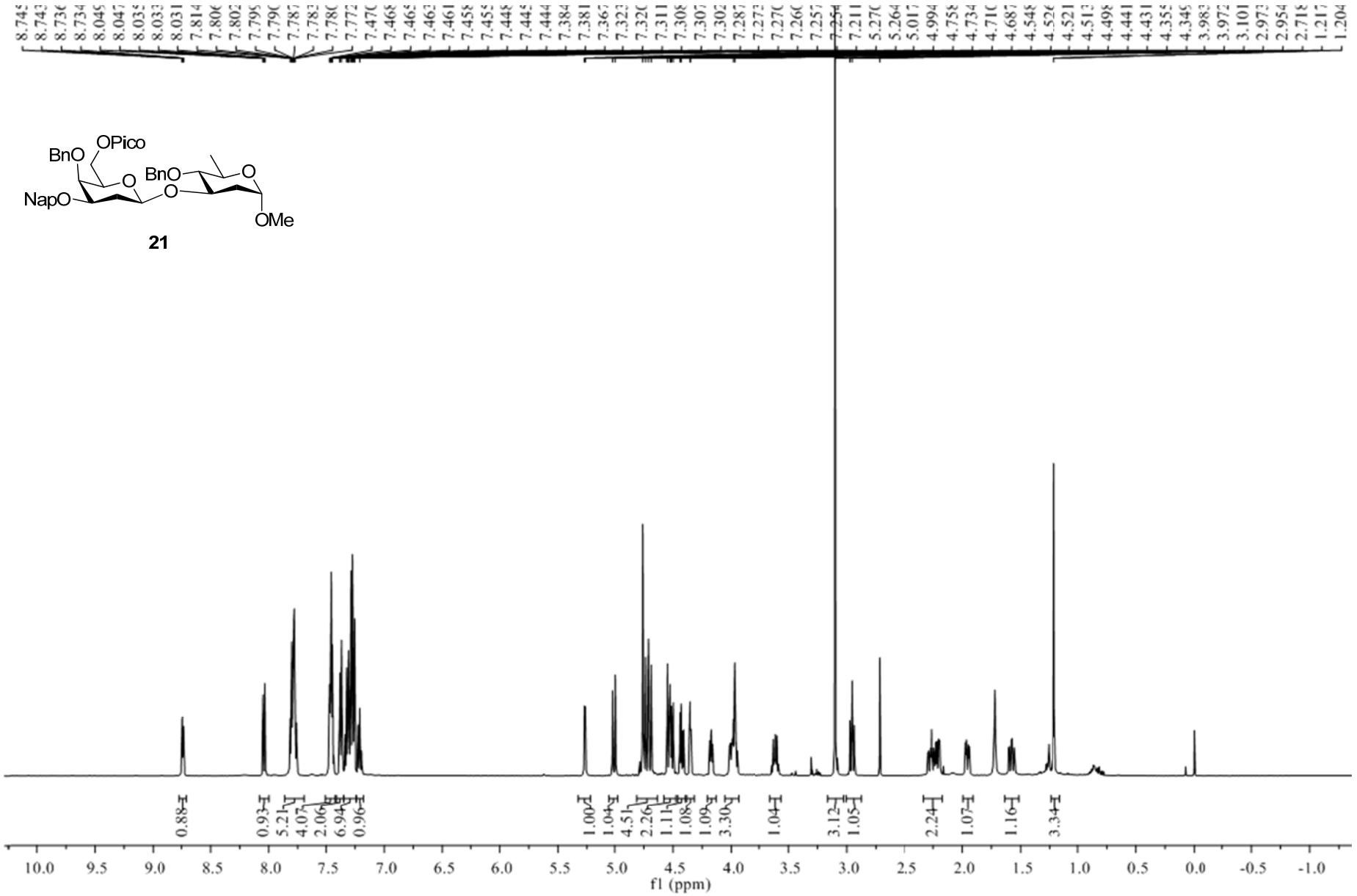
20

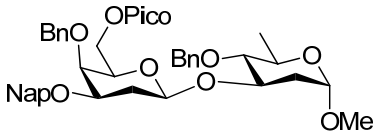
164.761
149.881
147.785
128.391
128.338
128.275
128.140
127.834
127.675
127.606
127.555
127.463
126.120
125.944
125.410
125.111
99.468
98.138
81.330
77.695
77.318
77.000
76.682
74.842
74.090
72.800
70.951
70.661
69.594
66.397
54.503
34.958
31.290
18.575
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


BnO
OPico
O
NapO
O
BnO
O
OMe
20
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
f1 (ppm)



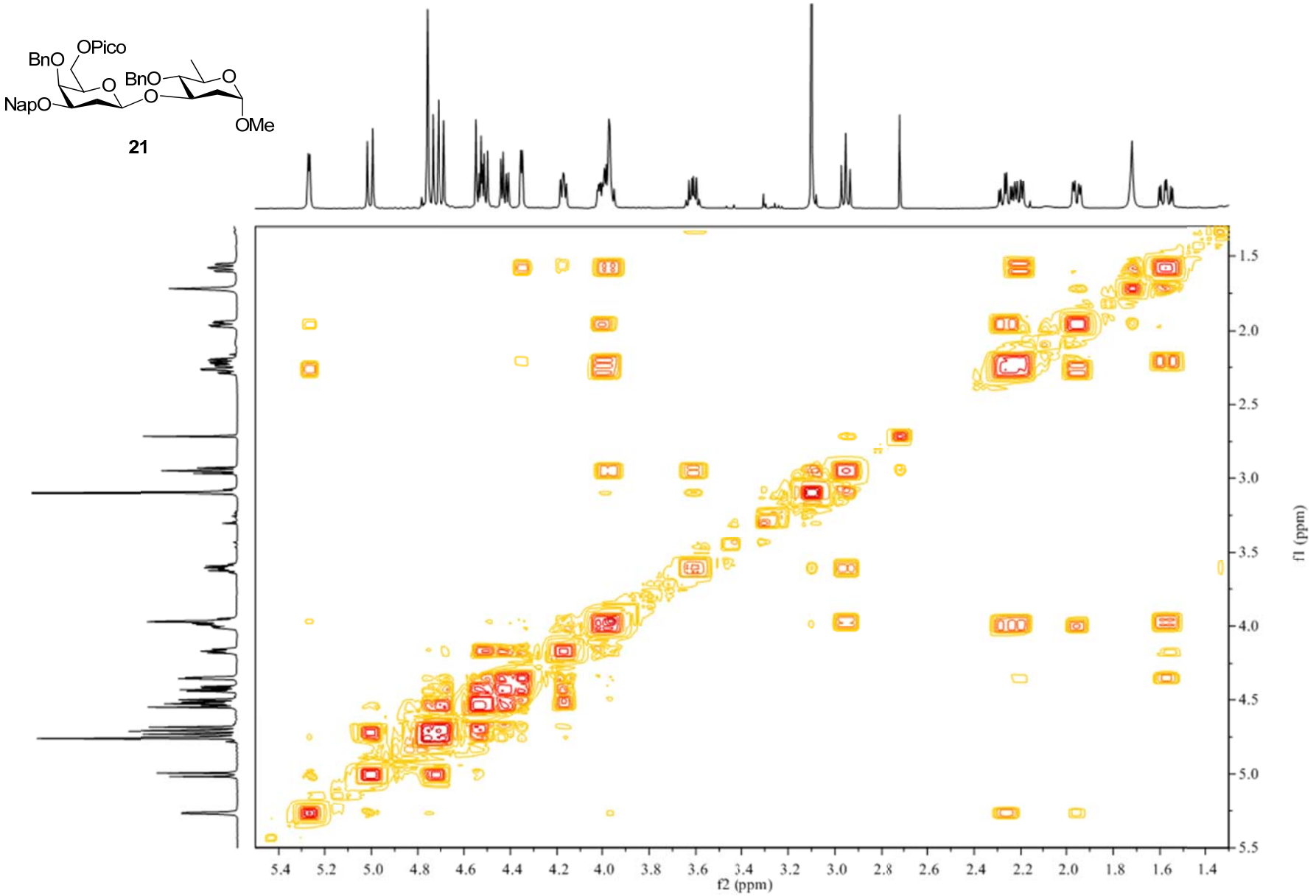
20

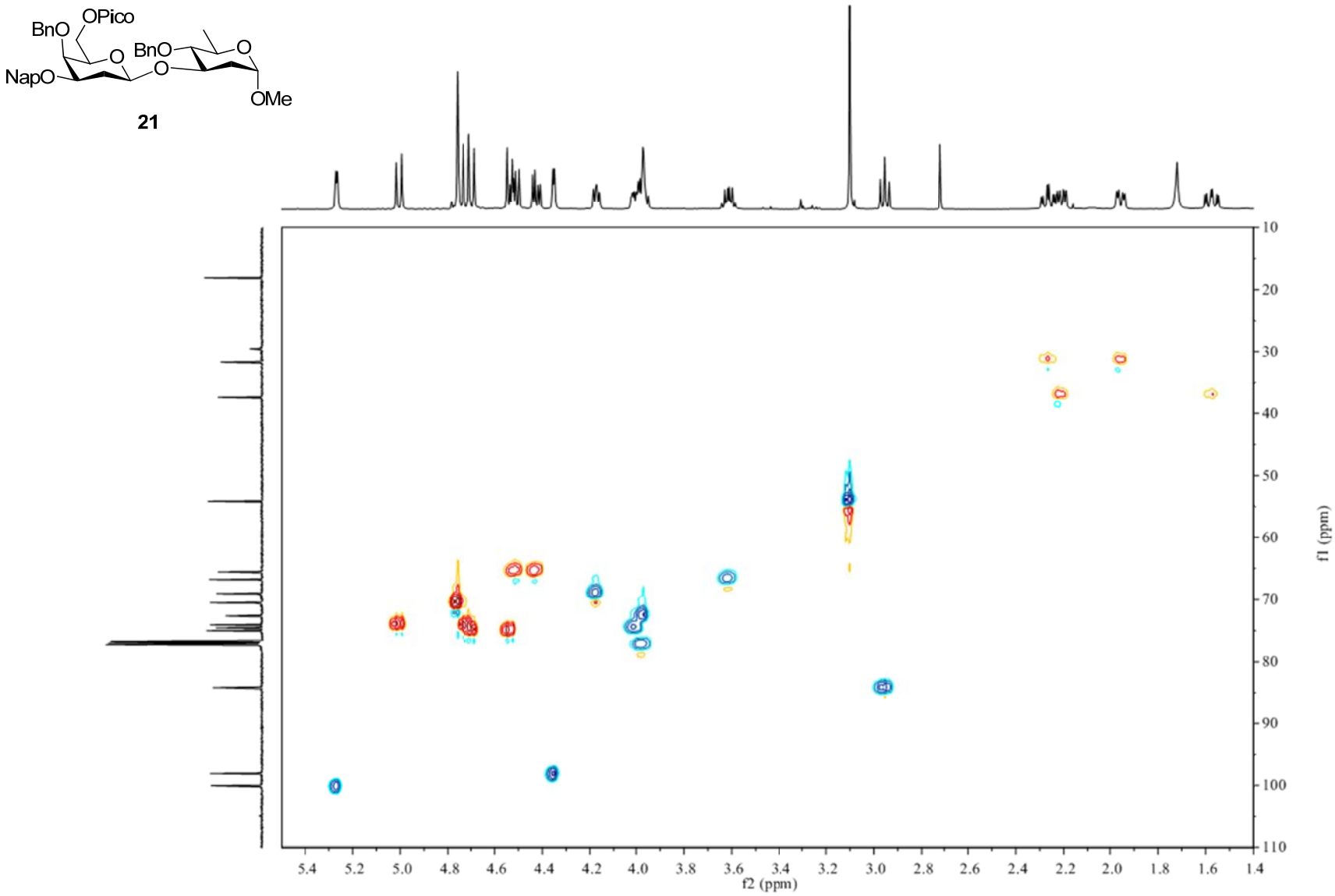

BnO
OPico
BnO
O
NapO
O
OMe
21
fl (ppm)

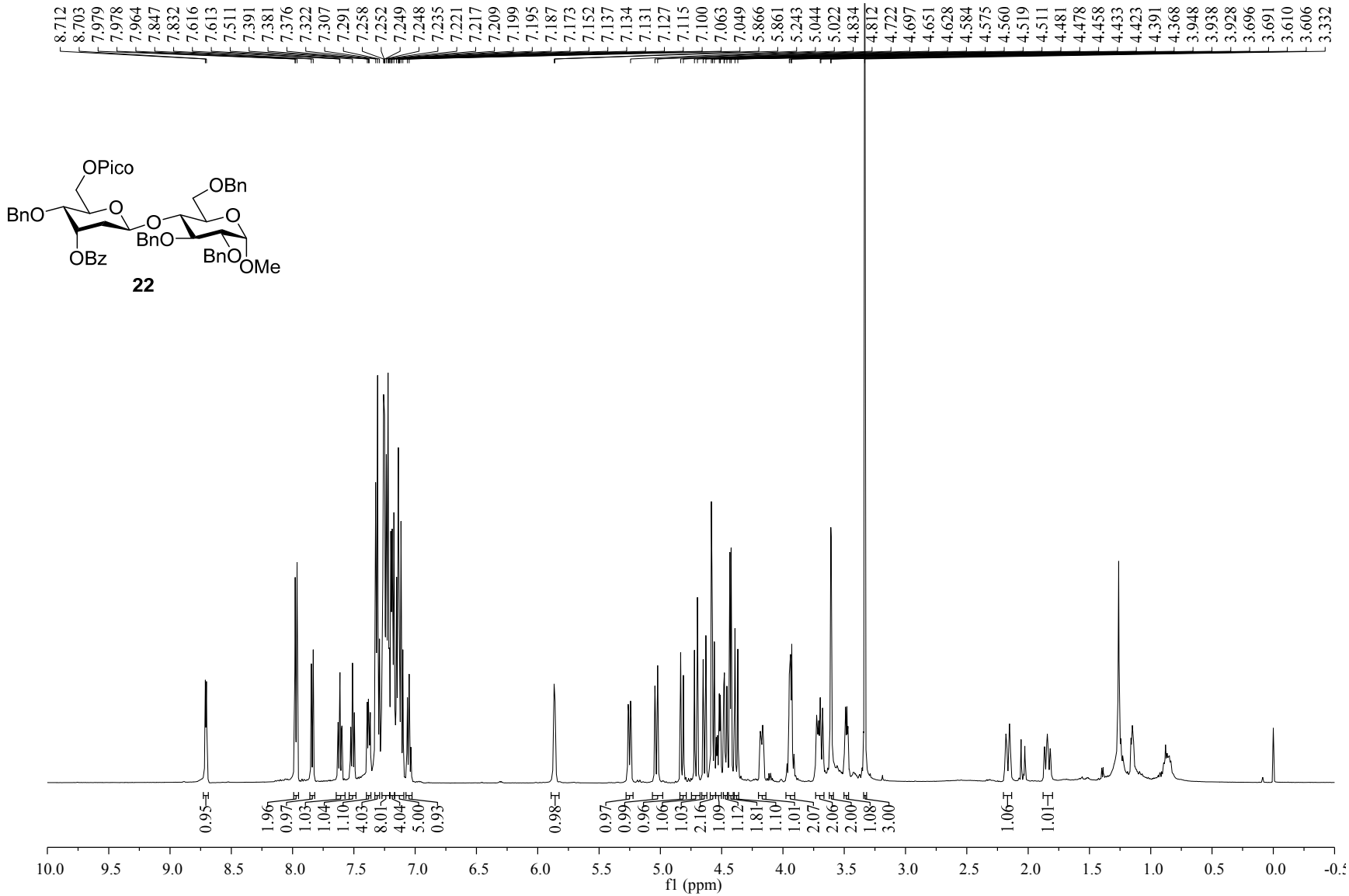

BnO
OPico
BnO
O
O
NapO
O
OMe

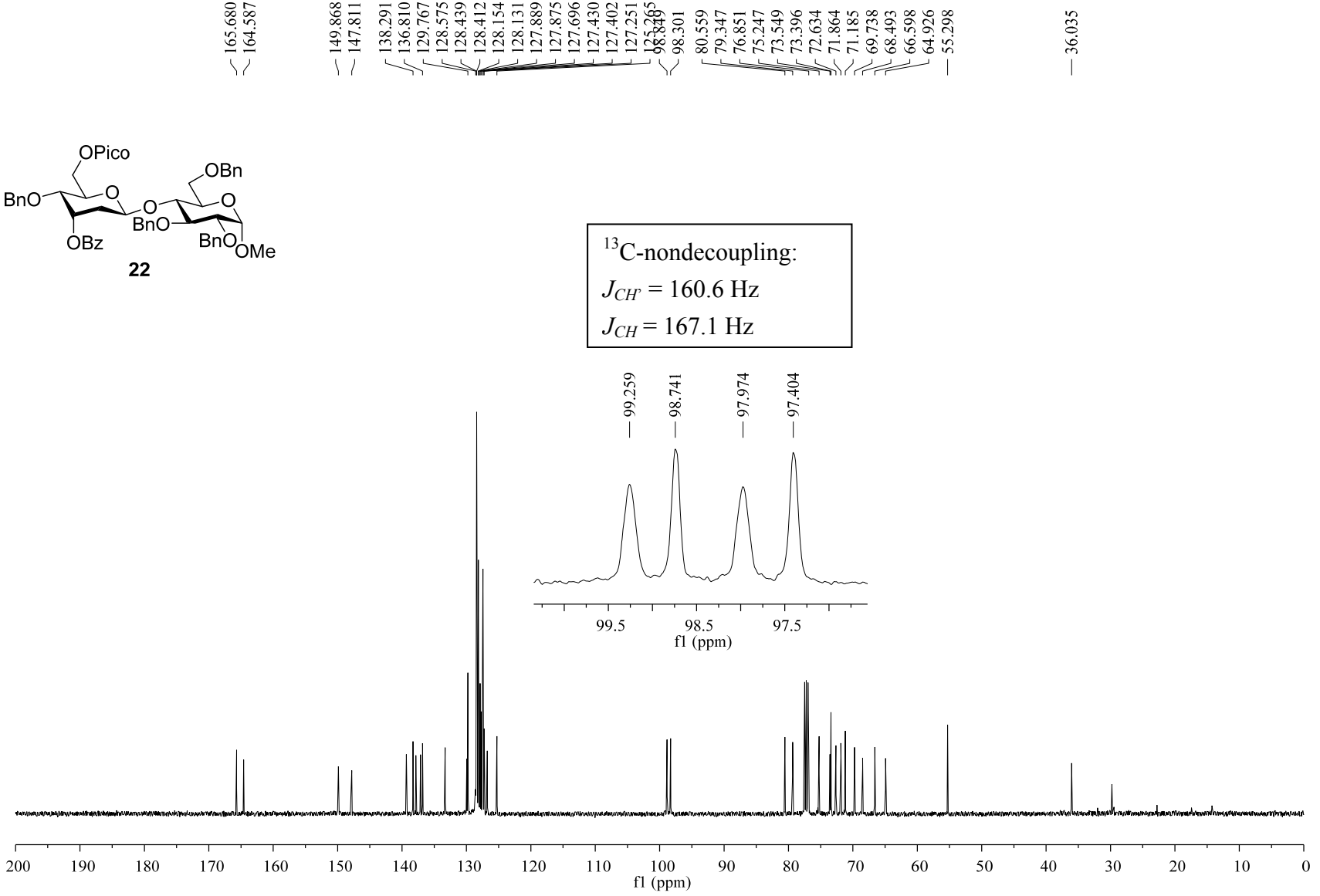
21

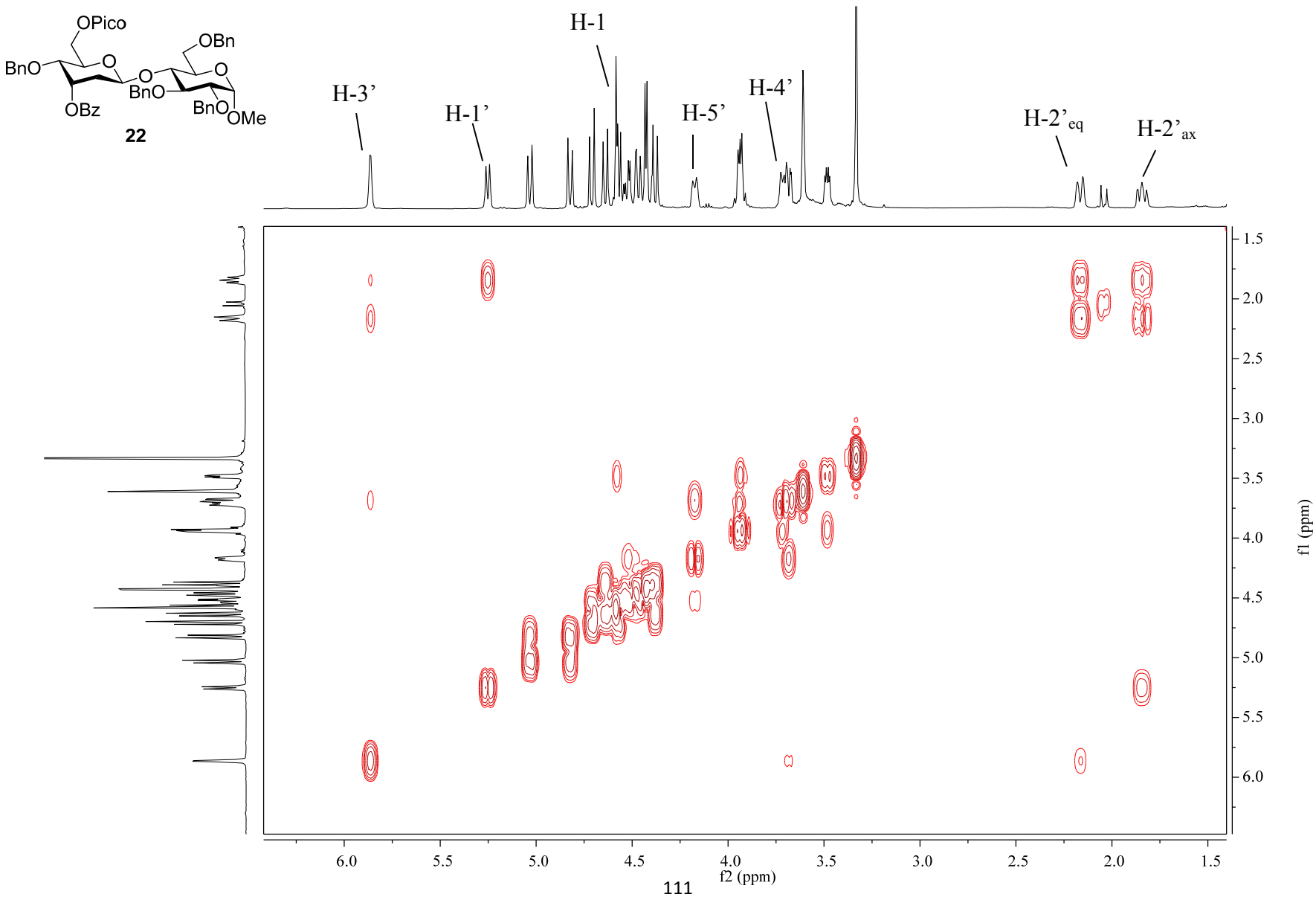
164.697
149.806
147.814
136.786
128.391
128.333
128.294
128.191
127.780
127.690
127.664
127.642
126.132
125.956
125.847
125.317
99.936
97.975
84.178
77.255
77.000
76.746
75.061
74.585
74.116
70.572
66.789
54.259
37.265
31.647
29.519
18.077
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

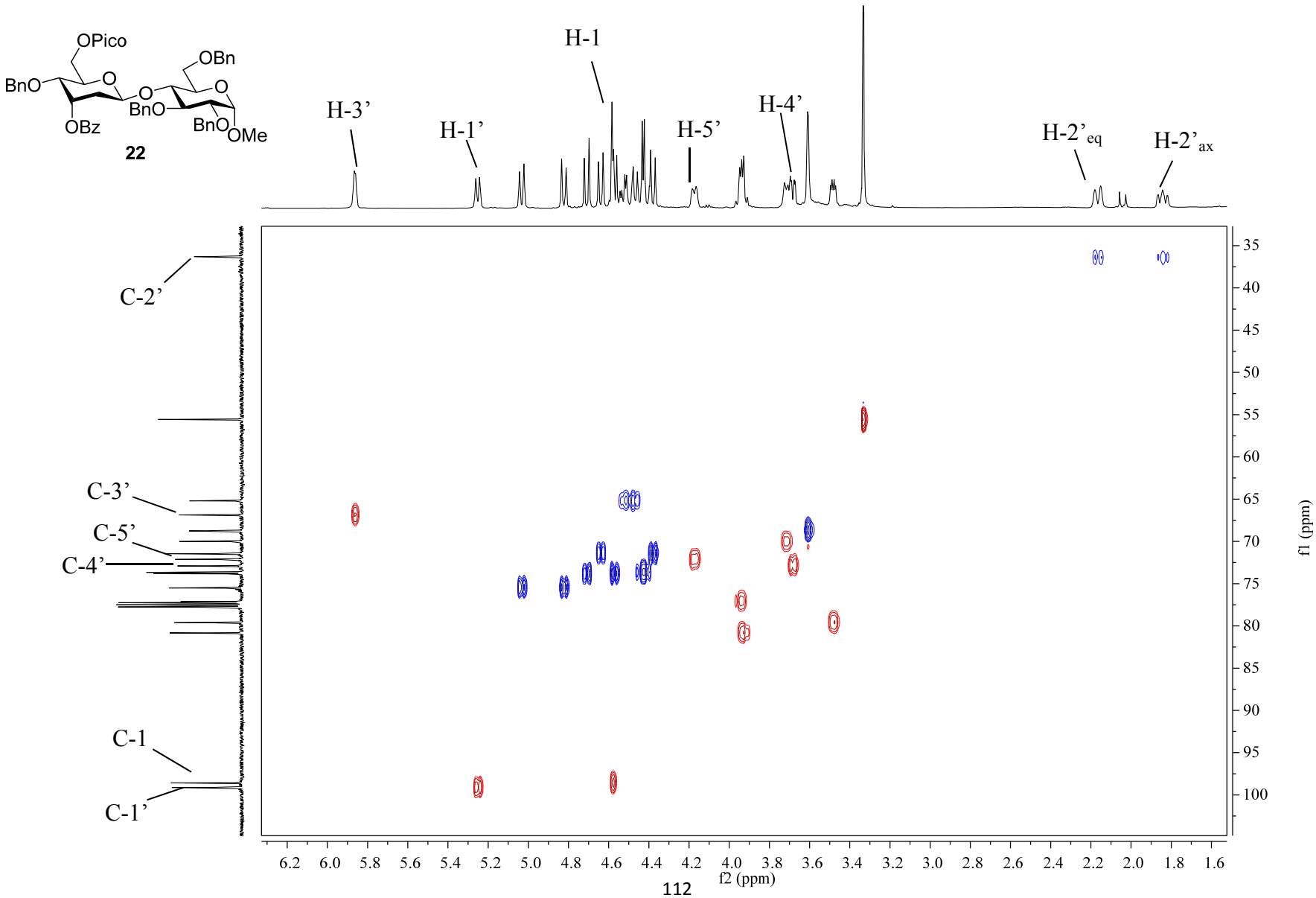

BnO
OPico
O
BnO
O
NapO
O
OMe
21
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)

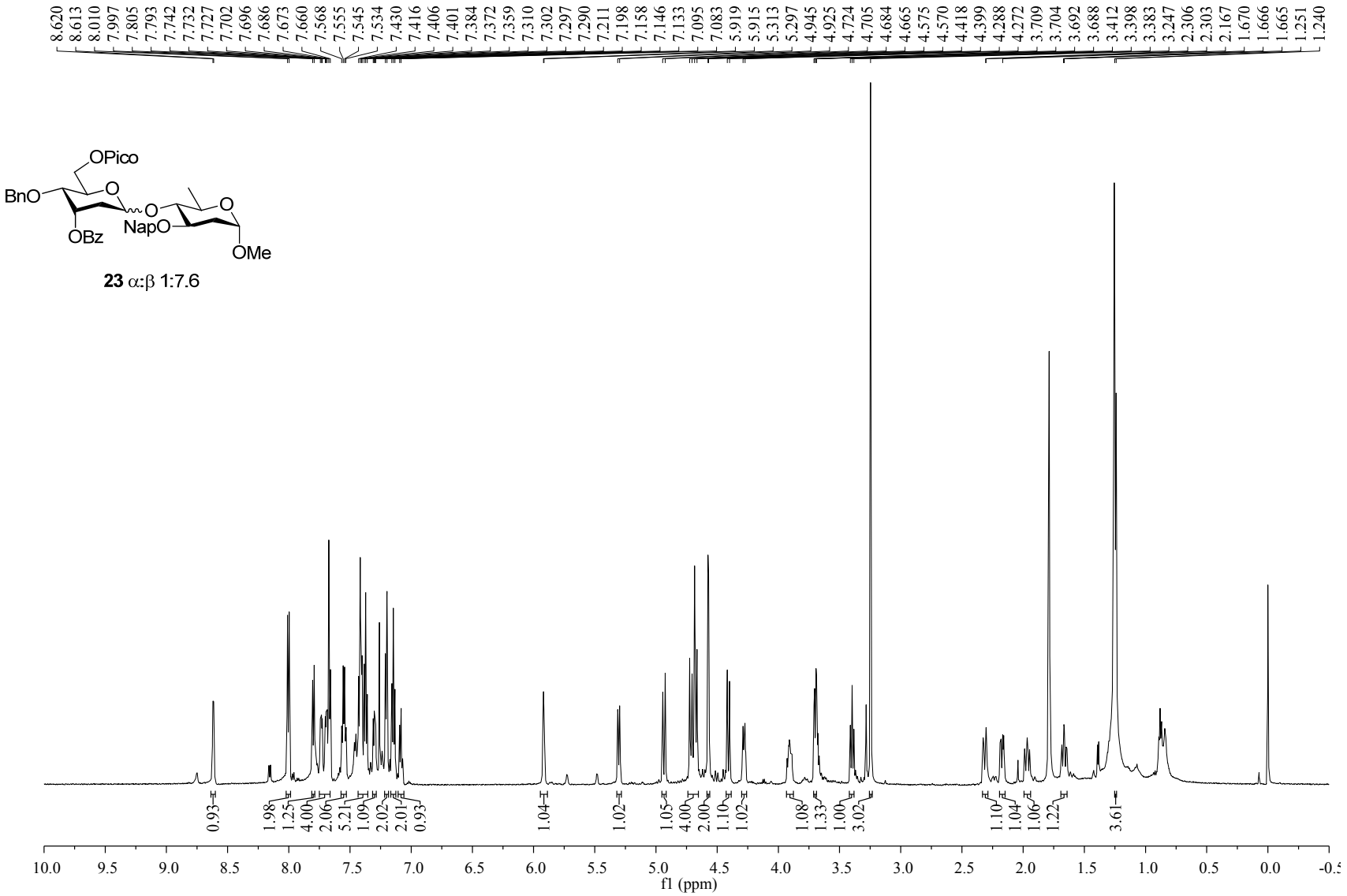

BnO
OPico
O
BnO
O
NapO
O
OMe
21
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)

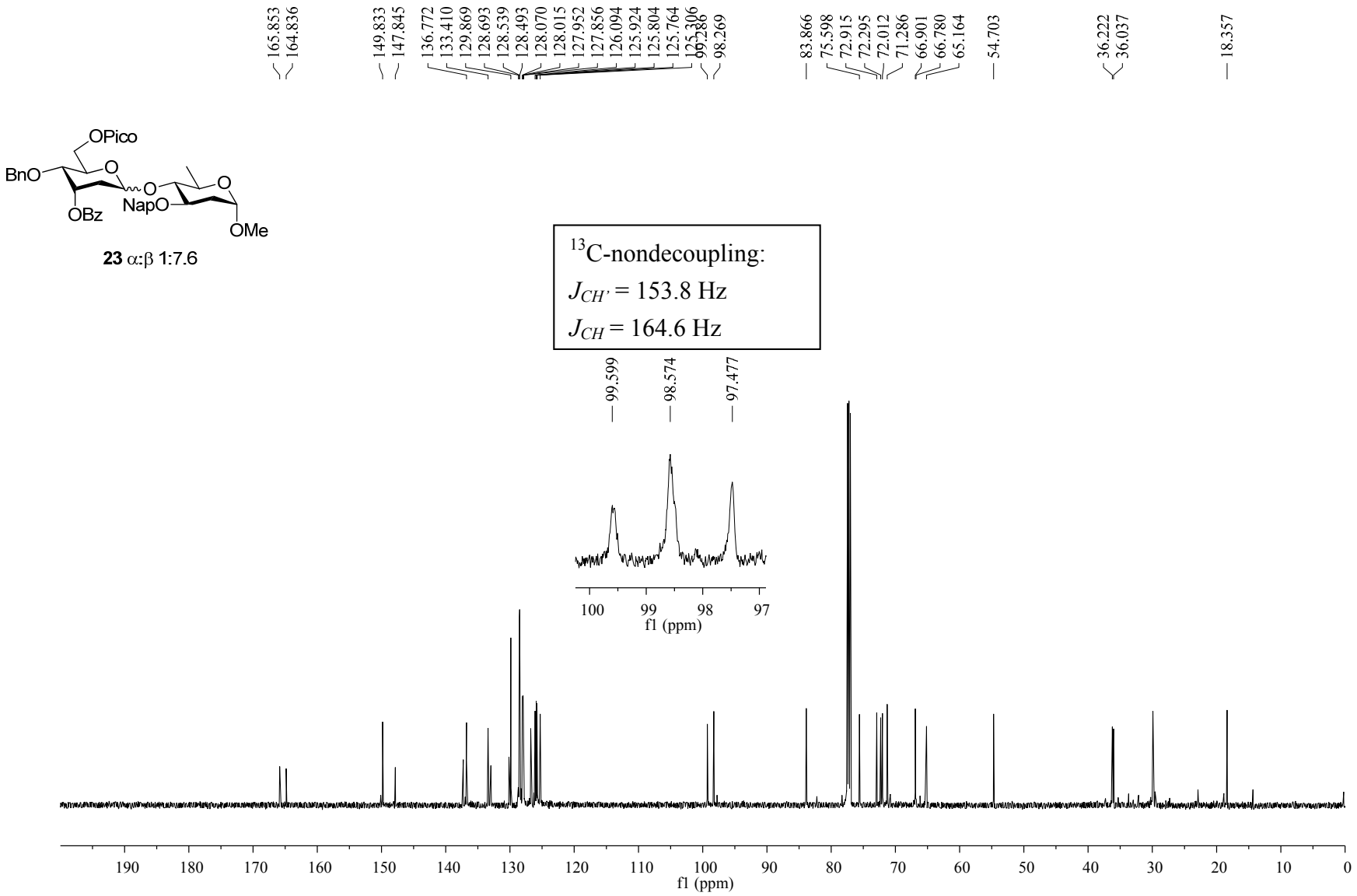

OPico
OBn
BnO
O
O
O
BnO
BnO
OMe
OBz
22
8.712
8.703
7.979
7.978
7.964
7.847
7.832
7.616
7.613
7.511
7.391
7.381
7.376
7.322
7.307
7.291
7.258
7.252
7.249
7.248
7.235
7.221
7.217
7.209
7.199
7.195
7.187
7.173
7.152
7.137
7.134
7.131
7.127
7.115
7.100
7.063
7.049
5.866
5.861
5.243
5.044
5.022
4.834
4.812
4.722
4.697
4.651
4.628
4.584
4.575
4.560
4.519
4.511
4.481
4.478
4.458
4.433
4.423
4.391
4.368
3.948
3.938
3.928
3.696
3.691
3.610
3.606
3.332
0.95
1.96
0.97
1.03
1.04
1.10
4.03
8.01
4.04
5.00
0.93
0.98
0.97
0.99
0.96
1.06
1.03
2.16
1.09
1.12
1.81
1.10
1.01
2.07
2.06
2.00
1.08
3.00
1.06
1.01
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
f1 (ppm)

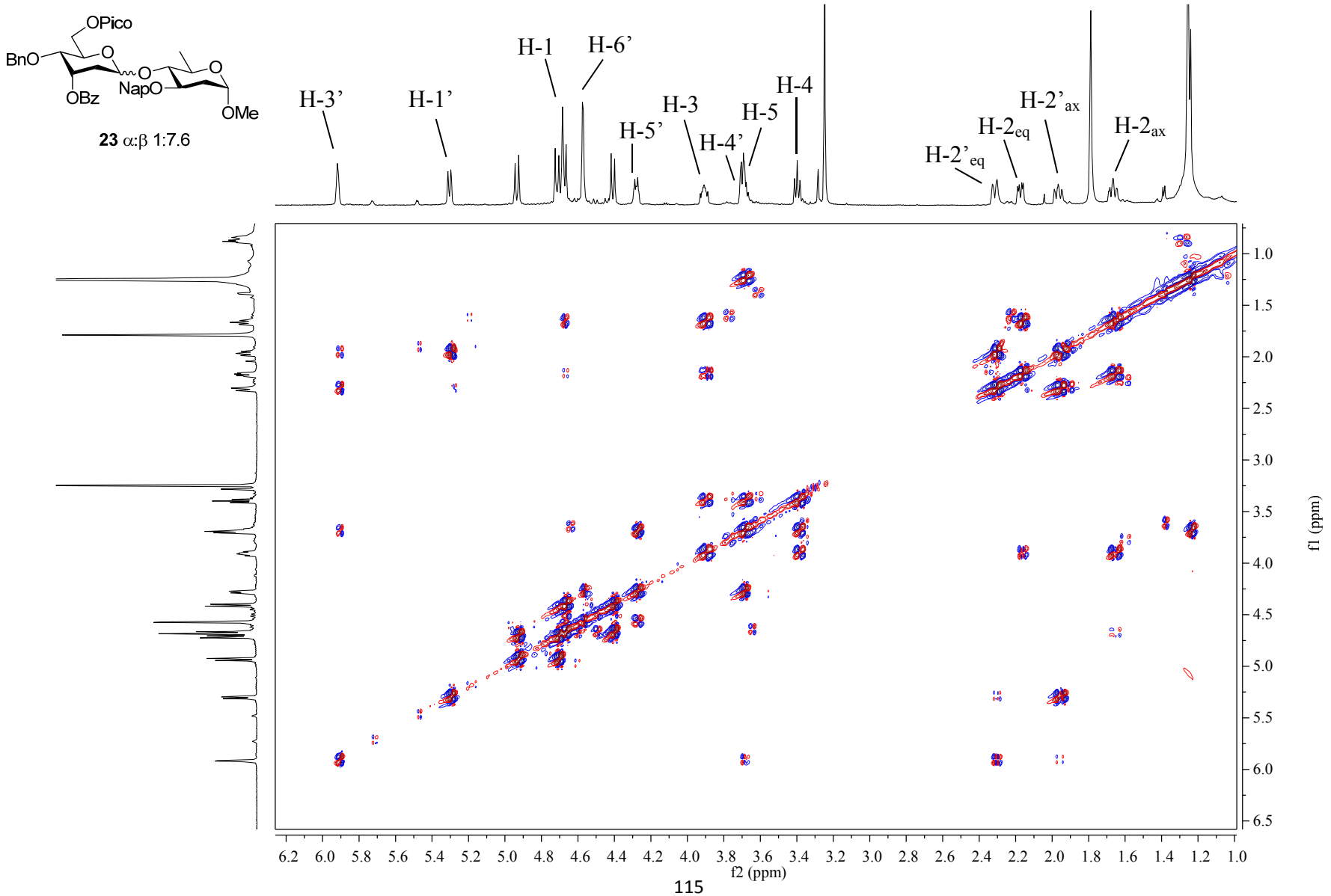

165.680
164.587
149.868
147.811
138.291
136.810
129.767
128.575
128.439
128.412
128.154
128.131
127.889
127.875
127.696
127.430
127.402
127.251
98.849
98.301
80.559
79.347
76.851
75.247
73.549
73.396
72.634
71.864
71.185
69.738
68.493
66.598
64.926
55.298
36.035
OPico
OBn
BnO
O
O
O
BnO
BnO
OMe
OBz
22
^{13}C-nondecoupling:
$J_{CH'}$ = 160.6 Hz
J_{CH} = 167.1 Hz
99.259
98.741
97.974
97.404
99.5
98.5
97.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

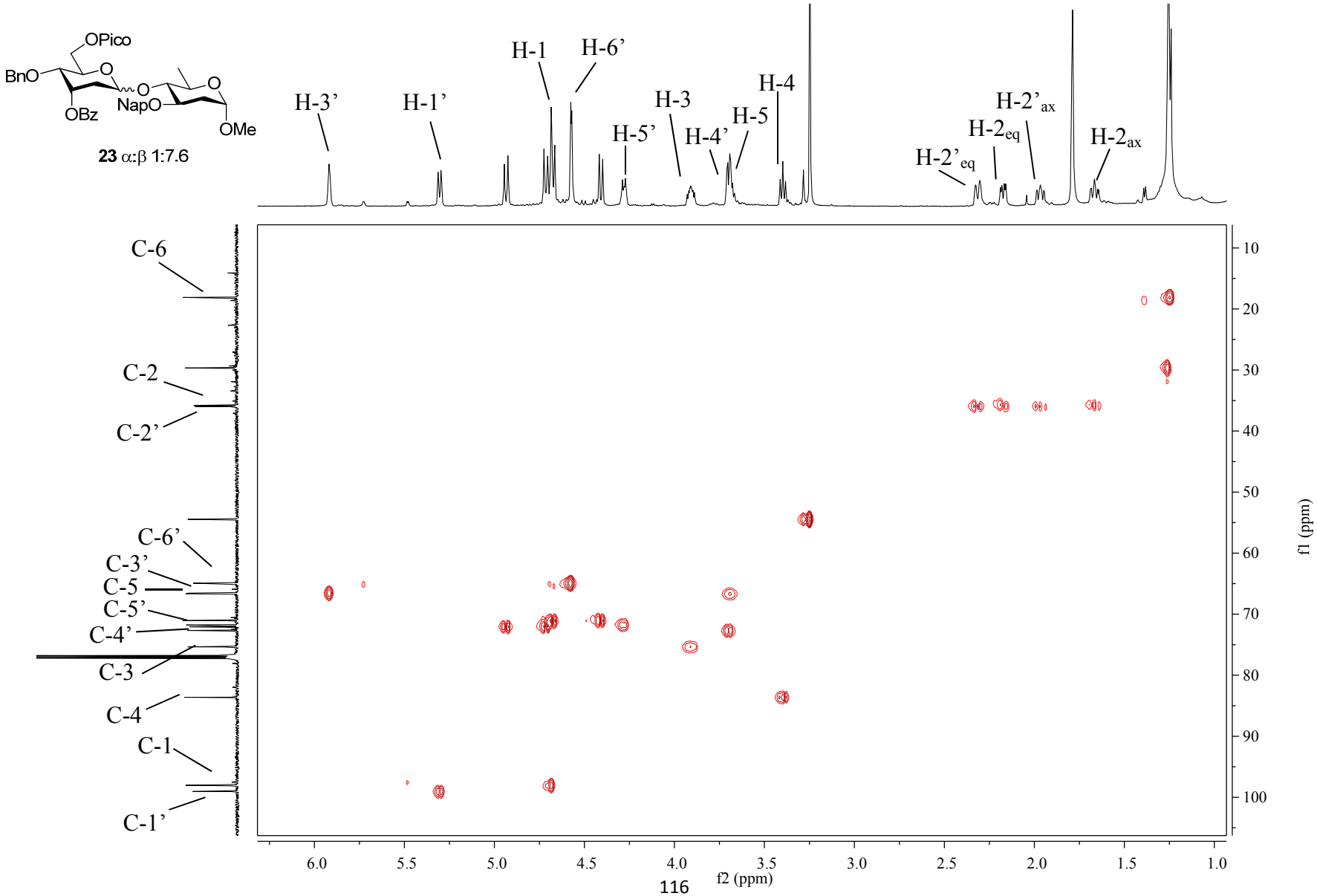

OPico
OBn
BnO
O
O
O
BnO
BnO
OBz
OMe
22
H-3'
H-1'
H-1
H-5'
H-4'
H-2'eq
H-2'ax
f1 (ppm)
f2 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

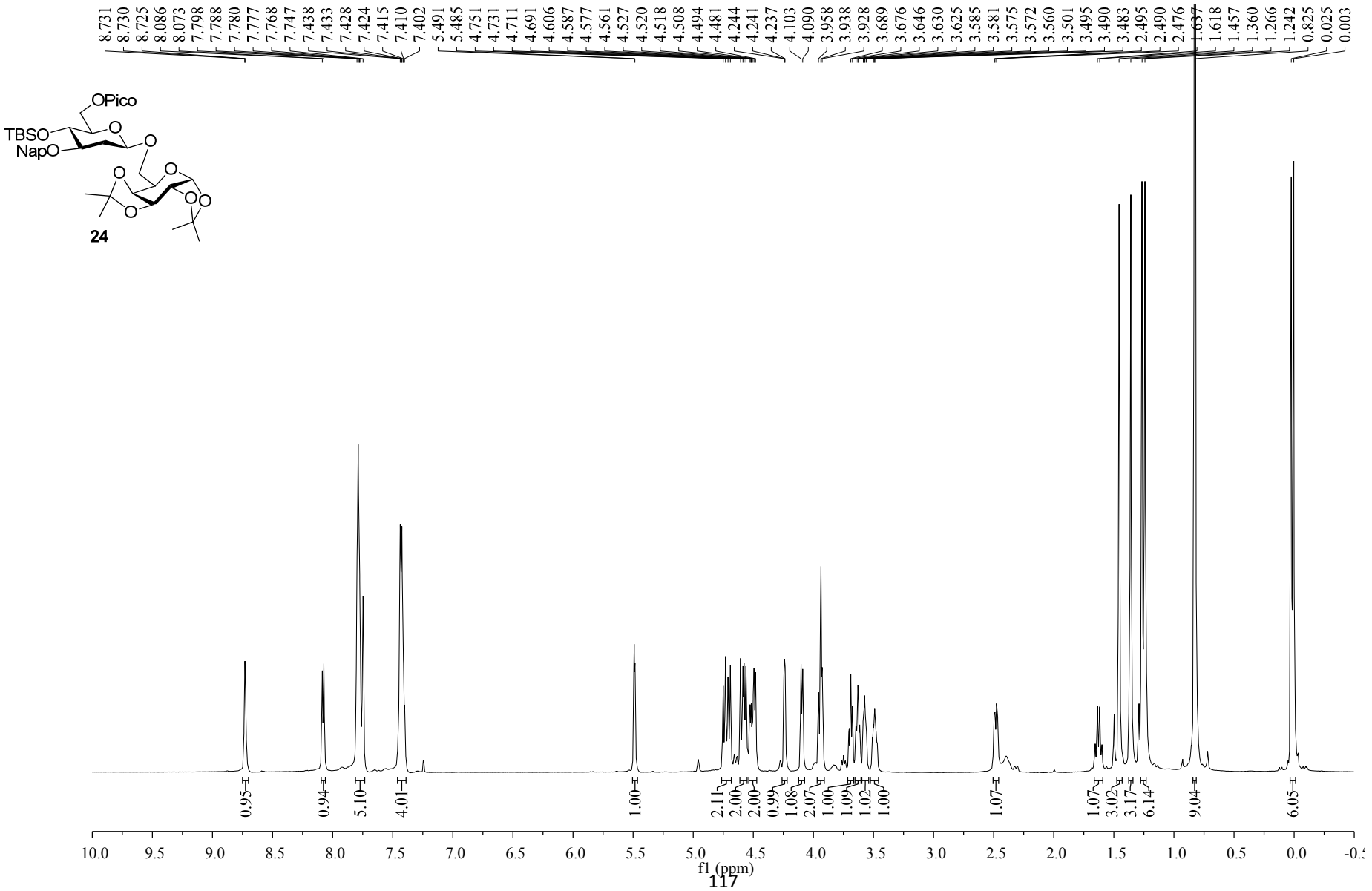

OPico
OBn
BnO
BnO
BnO
OBz
OMe
22
H-3'
H-1'
H-1
H-5'
H-4'
H-2'eq
H-2'ax
C-2'
C-3'
C-5'
C-4'
C-1
C-1'
f2 (ppm)
f1 (ppm)

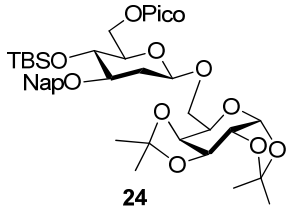

OPico
BnO
O
O
O
NapO
OBz
OMe
23 α:β 1:7.6
fl (ppm)


165.853
164.836
149.833
147.845
136.772
133.410
129.869
128.693
128.539
128.493
128.070
128.015
127.952
127.856
126.094
125.924
125.804
125.764
125.306
99.286
98.269
83.866
75.598
72.915
72.295
72.012
71.286
66.901
66.780
65.164
54.703
36.222
36.037
18.357
OPico
BnO
O
O
O
NapO
OBz
OMe
23 α:β 1:7.6
13C-nondecoupling:
JCH' = 153.8 Hz
JCH = 164.6 Hz
99.599
98.574
97.477
100
99
98
97
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OPico
BnO
O
O
NapO
O
OBz
OMe
23 α:β 1:7.6
H-3'
H-1'
H-1
H-6'
H-5'
H-3
H-4'
H-5
H-4
H-2'eq
H-2eq
H-2'ax
H-2ax
f2 (ppm)
f1 (ppm)


OPico
BnO
O
O
NapO
O
OBz
OMe
23 α:β 1:7.6
H-3'
H-1'
H-1
H-6'
H-5'
H-3
H-4'
H-5
H-4
H-2'eq
H-2eq
H-2'ax
H-2ax
C-6
C-2
C-2'
C-6'
C-3'
C-5
C-5'
C-4'
C-3
C-4
C-1
C-1'
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
f1 (ppm)


OPico
TBSO
NapO
24
8.731
8.730
8.725
8.086
8.073
7.798
7.788
7.780
7.777
7.768
7.747
7.438
7.433
7.428
7.424
7.415
7.410
7.402
5.491
5.485
4.751
4.731
4.711
4.691
4.606
4.587
4.577
4.561
4.527
4.520
4.518
4.508
4.494
4.481
4.244
4.241
4.237
4.103
4.090
3.958
3.938
3.928
3.689
3.676
3.646
3.630
3.625
3.585
3.581
3.575
3.572
3.560
3.501
3.495
3.490
3.483
2.495
2.490
2.476
1.637
1.618
1.457
1.360
1.266
1.242
0.825
0.025
0.003
0.95
0.94
5.10
4.01
1.00
2.11
2.00
2.00
0.99
1.08
2.07
1.00
1.09
1.02
1.00
1.07
1.07
3.02
3.17
6.14
9.04
6.05
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
f1 (ppm)



24

164.905
150.037
148.108
136.965
135.727
128.106
127.965
127.787
126.869
126.574
126.150
126.054
125.931
108.700
100.557
96.378
79.294
74.717
71.629
71.492
70.857
70.763
70.463
68.923
67.980
65.243
36.050
26.125
26.041
25.068
24.486
18.269
-3.562
-4.926

^{13}C-nondecoupling:

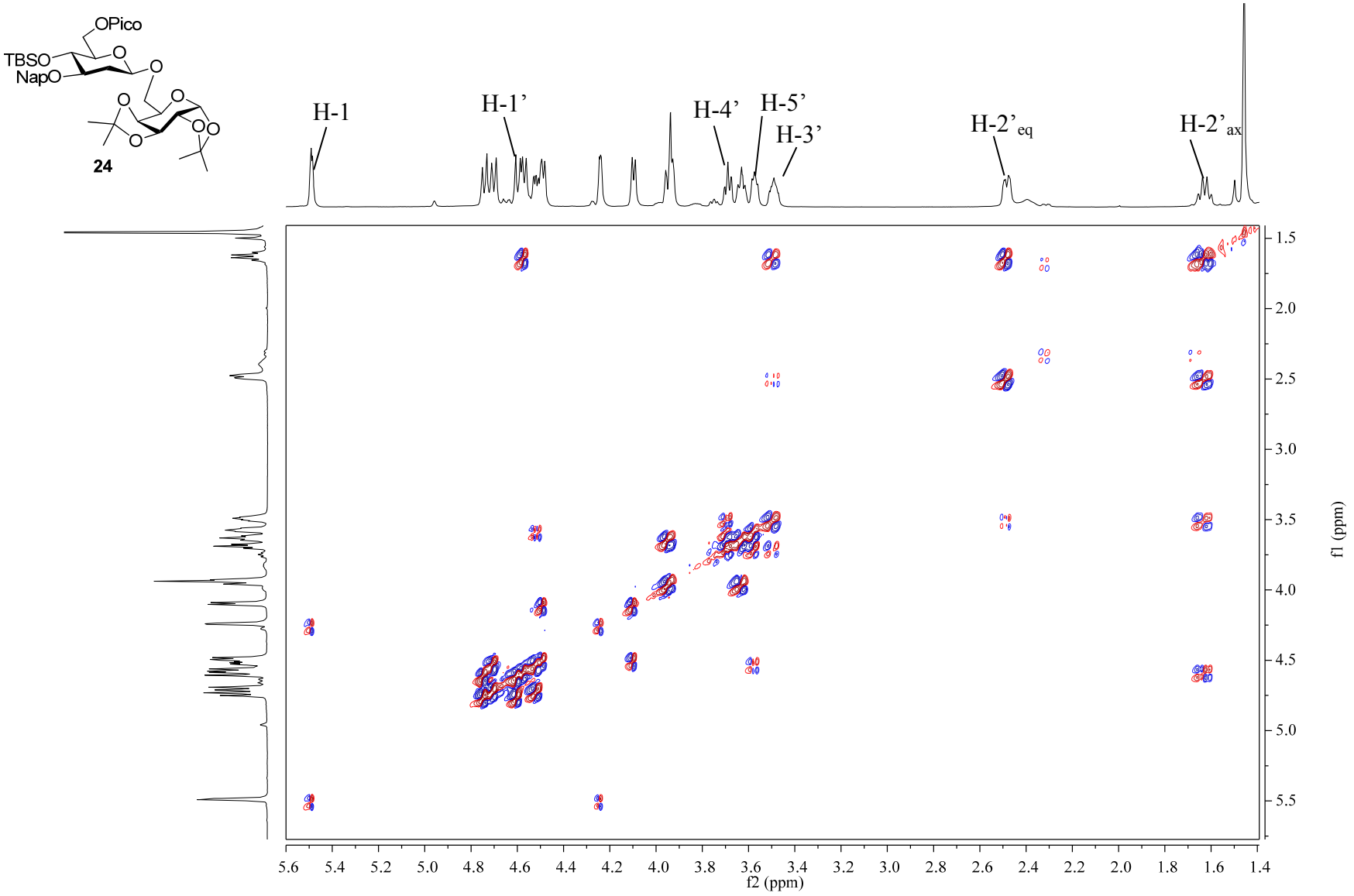
$J_{CH'}$ = 157.1 Hz

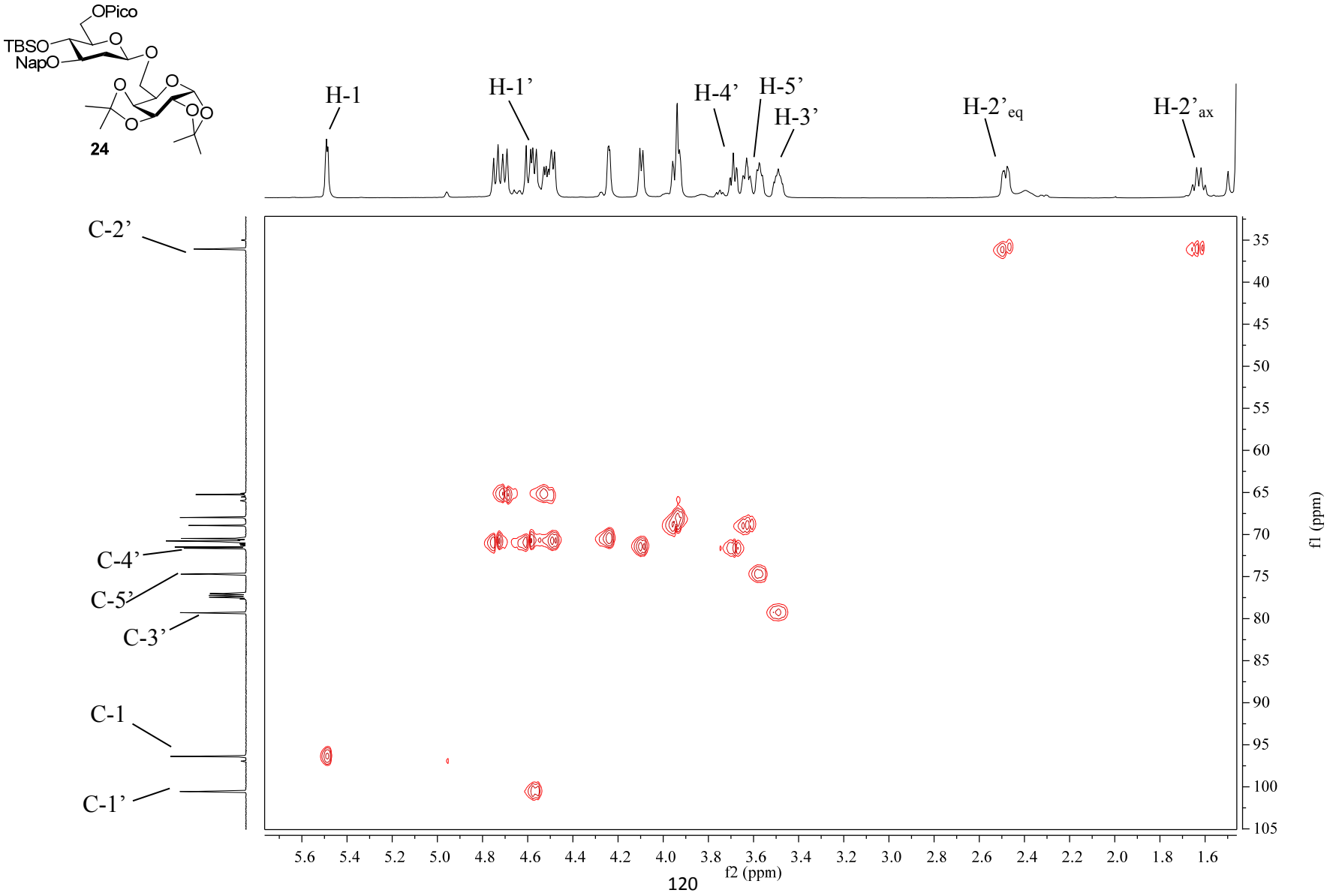
J_{CH} = 178.5 Hz

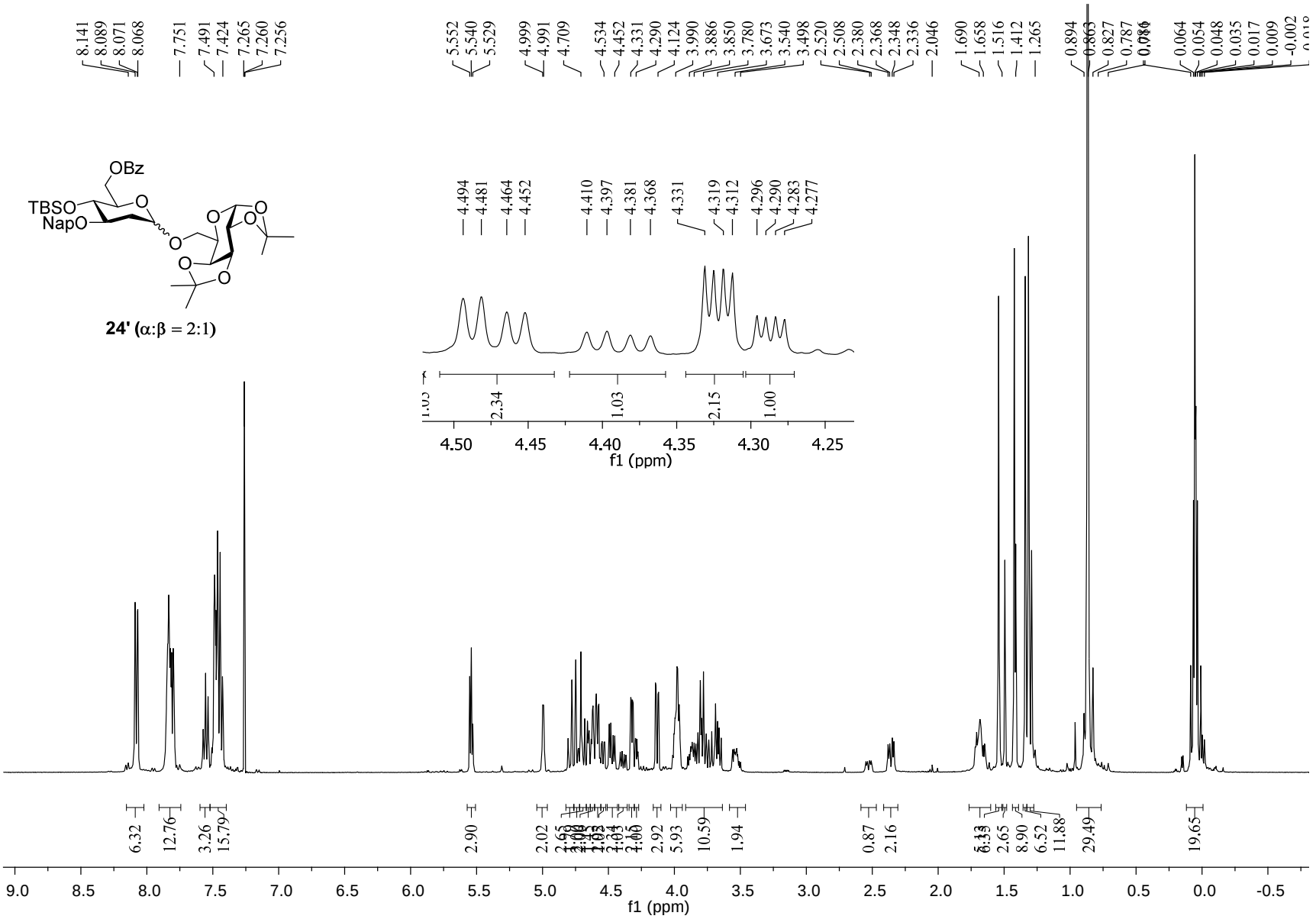
100.955
99.908
96.844
95.654

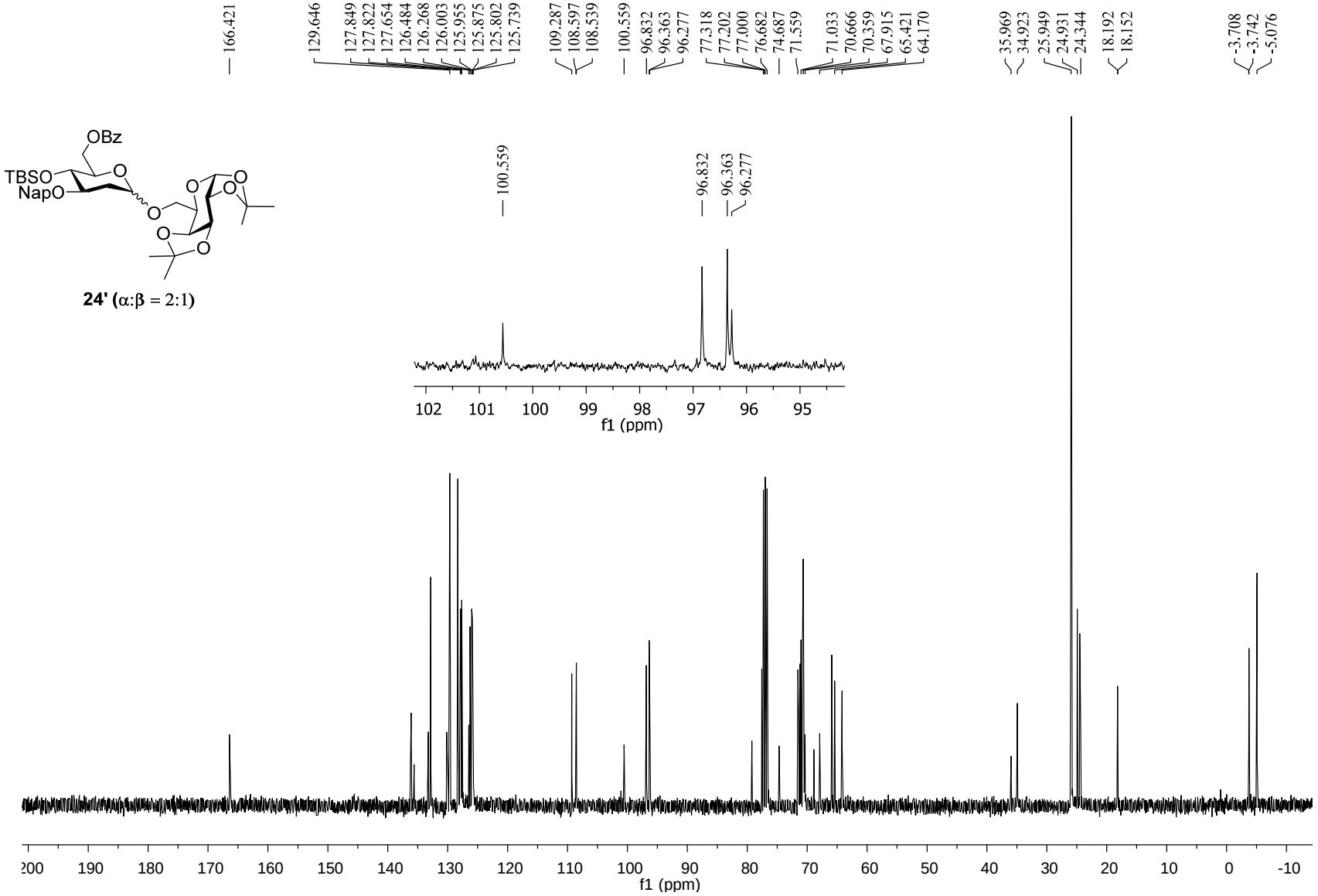
102 100 98 96
f1 (ppm)

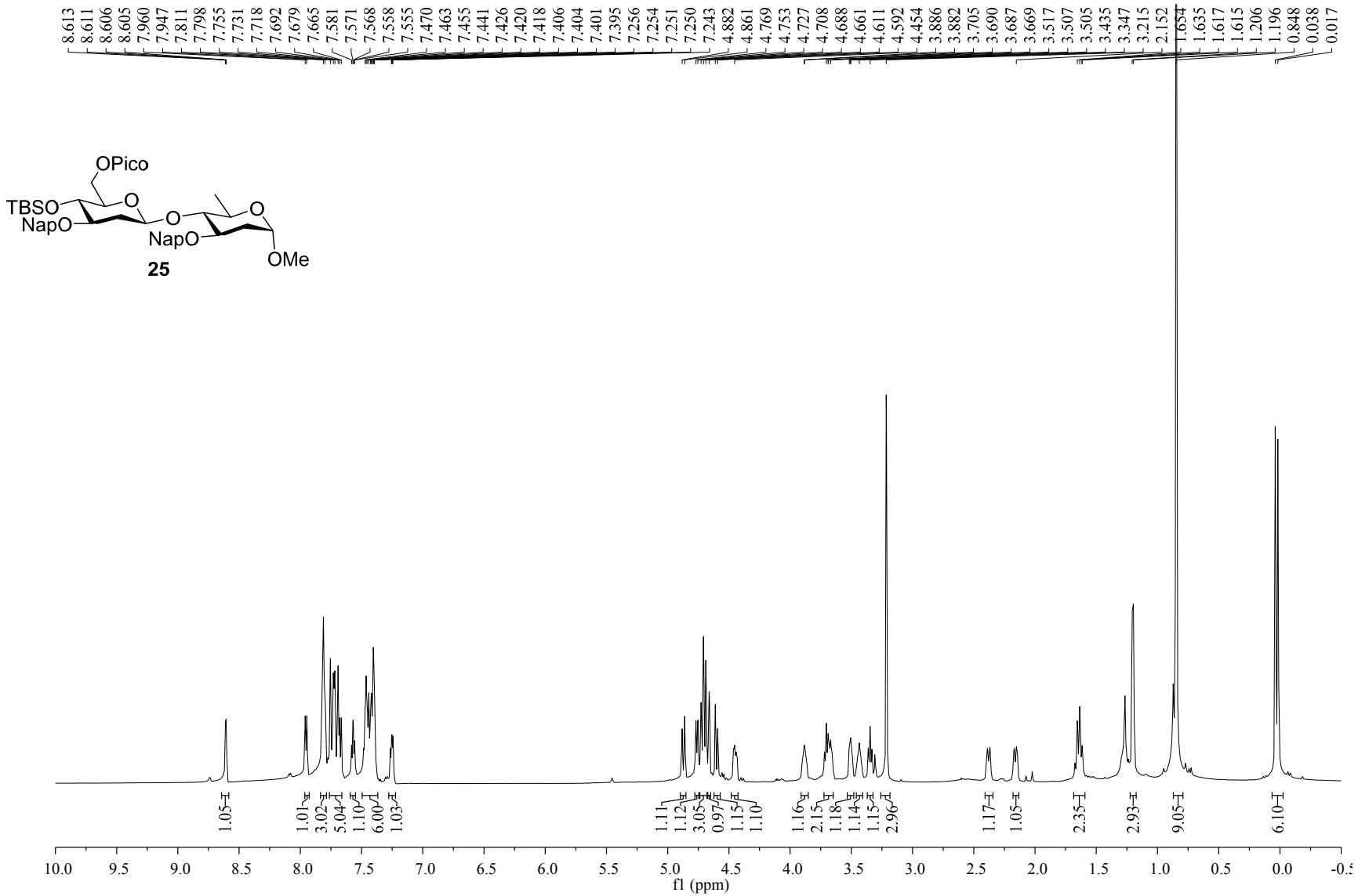
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

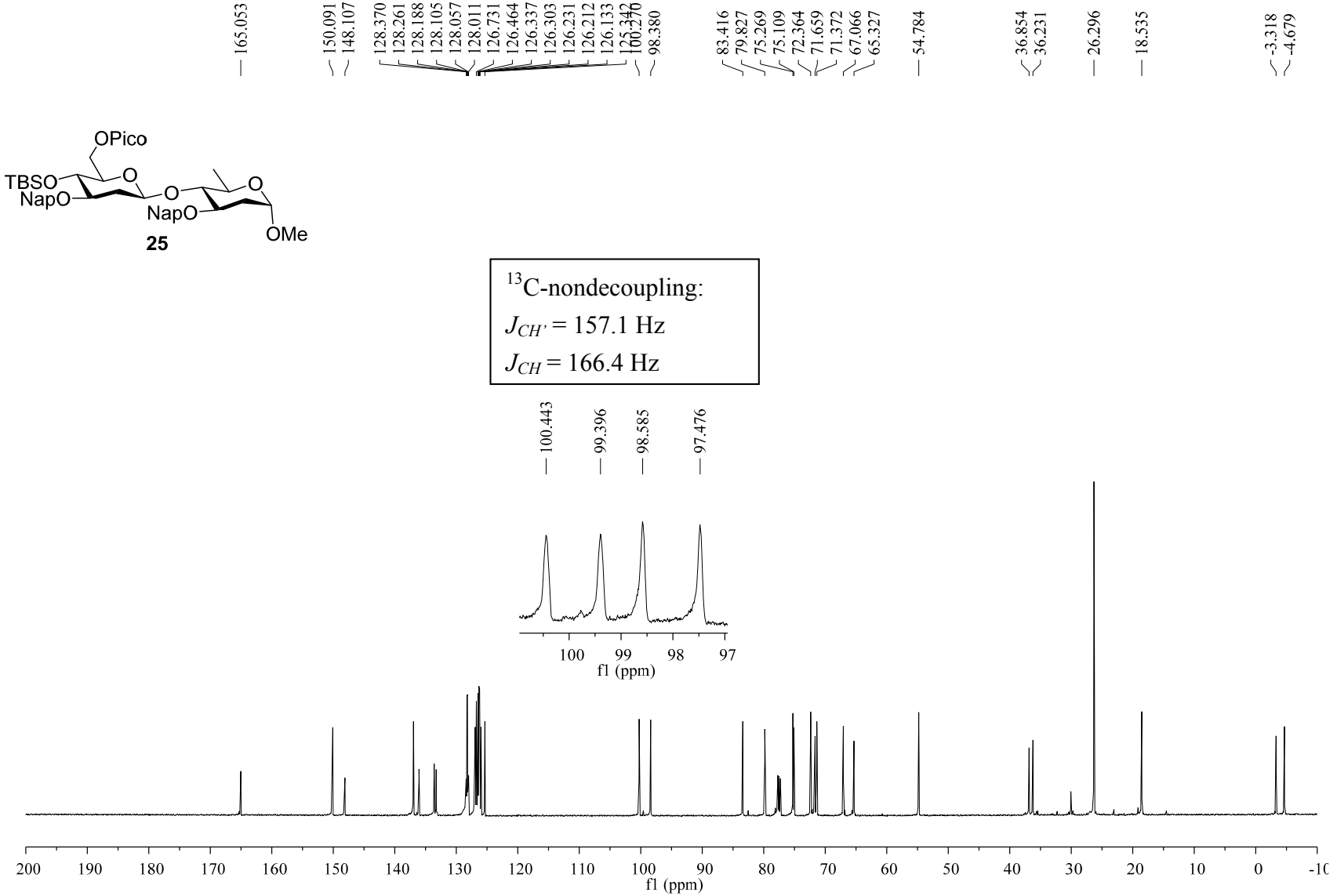

OPico
TBSO
NapO
24
H-1
H-1'
H-4'
H-5'
H-3'
H-2'eq
H-2'ax
f1 (ppm)
f2 (ppm)

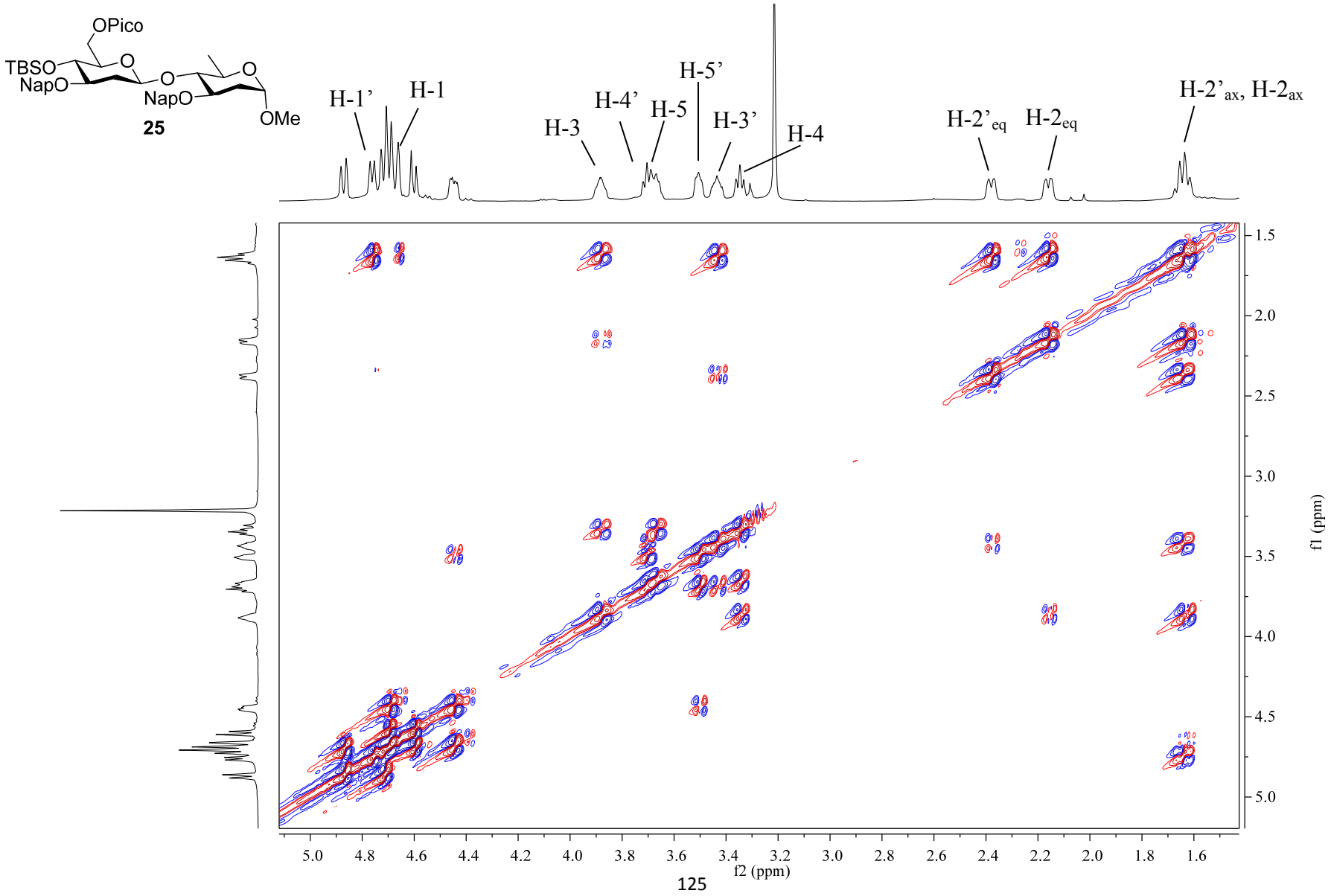

OPico
TBSO
NapO
24
H-1
H-1'
H-4'
H-5'
H-3'
H-2'eq
H-2'ax
C-2'
C-4'
C-5'
C-3'
C-1
C-1'
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f2 (ppm)
35 40 45 50 55 60 65 70 75 80 85 90 95 100 105
f1 (ppm)

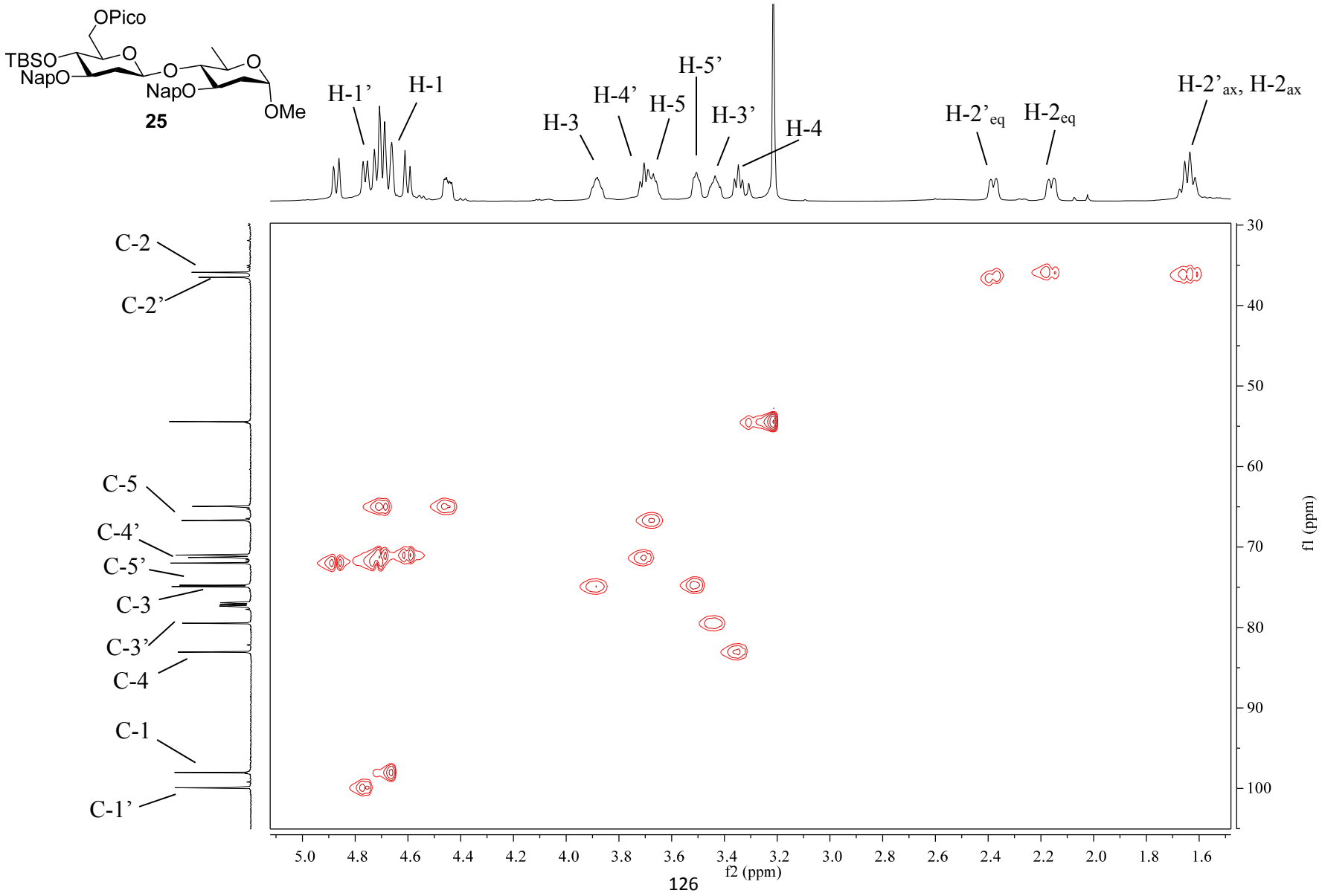

OBz
TBSO
NapO
O
O
O
O
O
O
O
O
24' (α:β = 2:1)
8.141
8.089
8.071
8.068
7.751
7.491
7.424
7.265
7.260
7.256
5.552
5.540
5.529
4.999
4.991
4.709
4.534
4.452
4.331
4.290
4.124
3.990
3.886
3.850
3.780
3.673
3.540
3.498
2.520
2.508
2.380
2.368
2.348
2.336
2.046
1.690
1.658
1.516
1.412
1.265
0.894
0.863
0.827
0.787
0.064
0.054
0.048
0.035
0.017
0.009
-0.002
4.494
4.481
4.464
4.452
4.410
4.397
4.381
4.368
4.331
4.319
4.312
4.296
4.290
4.283
4.277
2.34
1.03
2.15
1.00
4.50
4.45
4.40
4.35
4.30
4.25
f1 (ppm)
6.32
12.76
3.26
15.79
2.90
2.02
2.92
5.93
10.59
1.94
0.87
2.16
2.65
8.90
6.52
11.88
29.49
19.65
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)

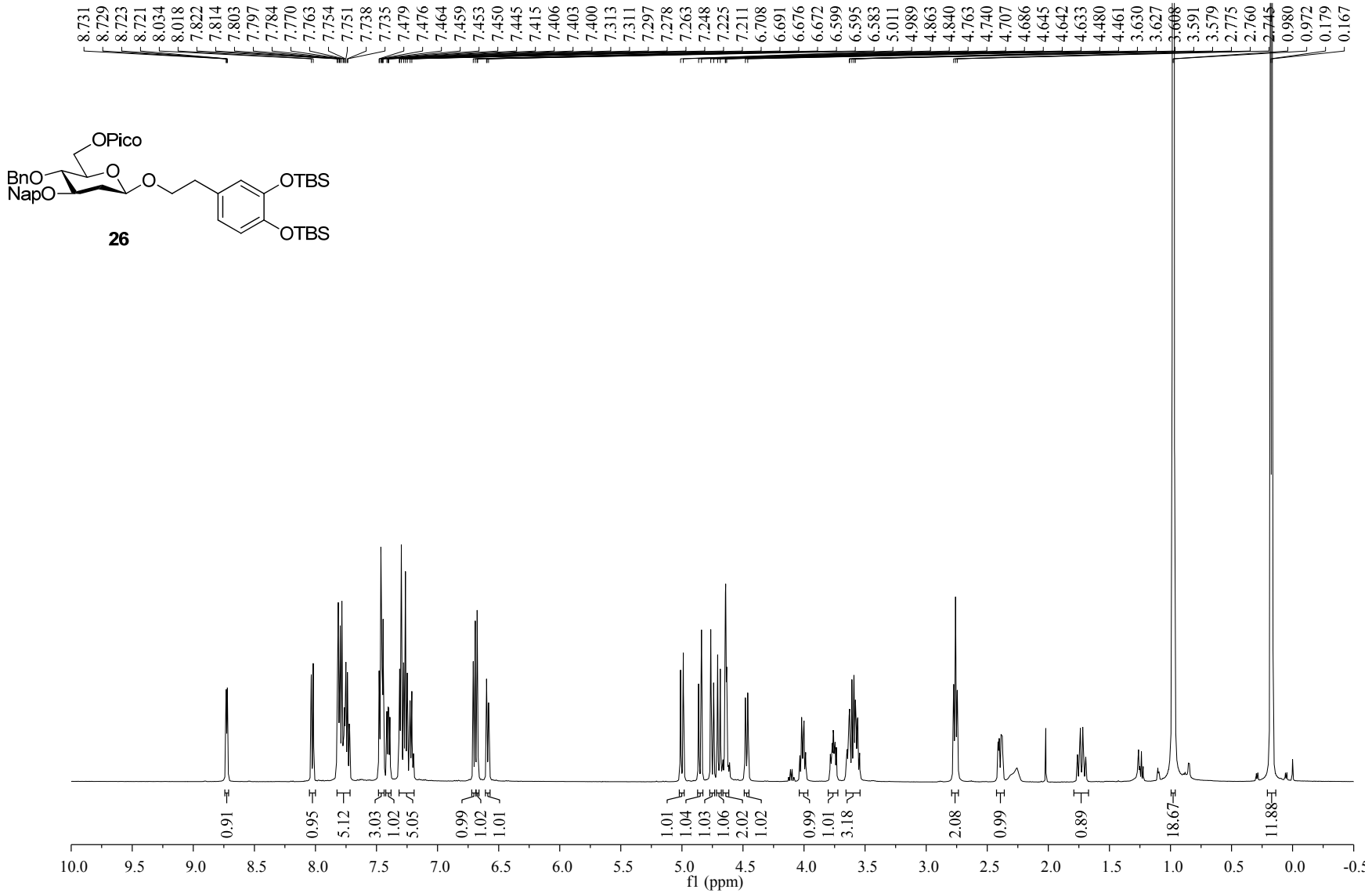

166.421
129.646
127.849
127.822
127.654
126.484
126.268
126.003
125.955
125.875
125.802
125.739
109.287
108.597
108.539
100.559
96.832
96.363
96.277
77.318
77.202
77.000
76.682
74.687
71.559
71.033
70.666
70.359
67.915
65.421
64.170
35.969
34.923
25.949
24.931
24.344
18.192
18.152
-3.708
-3.742
-5.076
OBz
TBSO
NapO
O
24' (α:β = 2:1)
f1 (ppm)

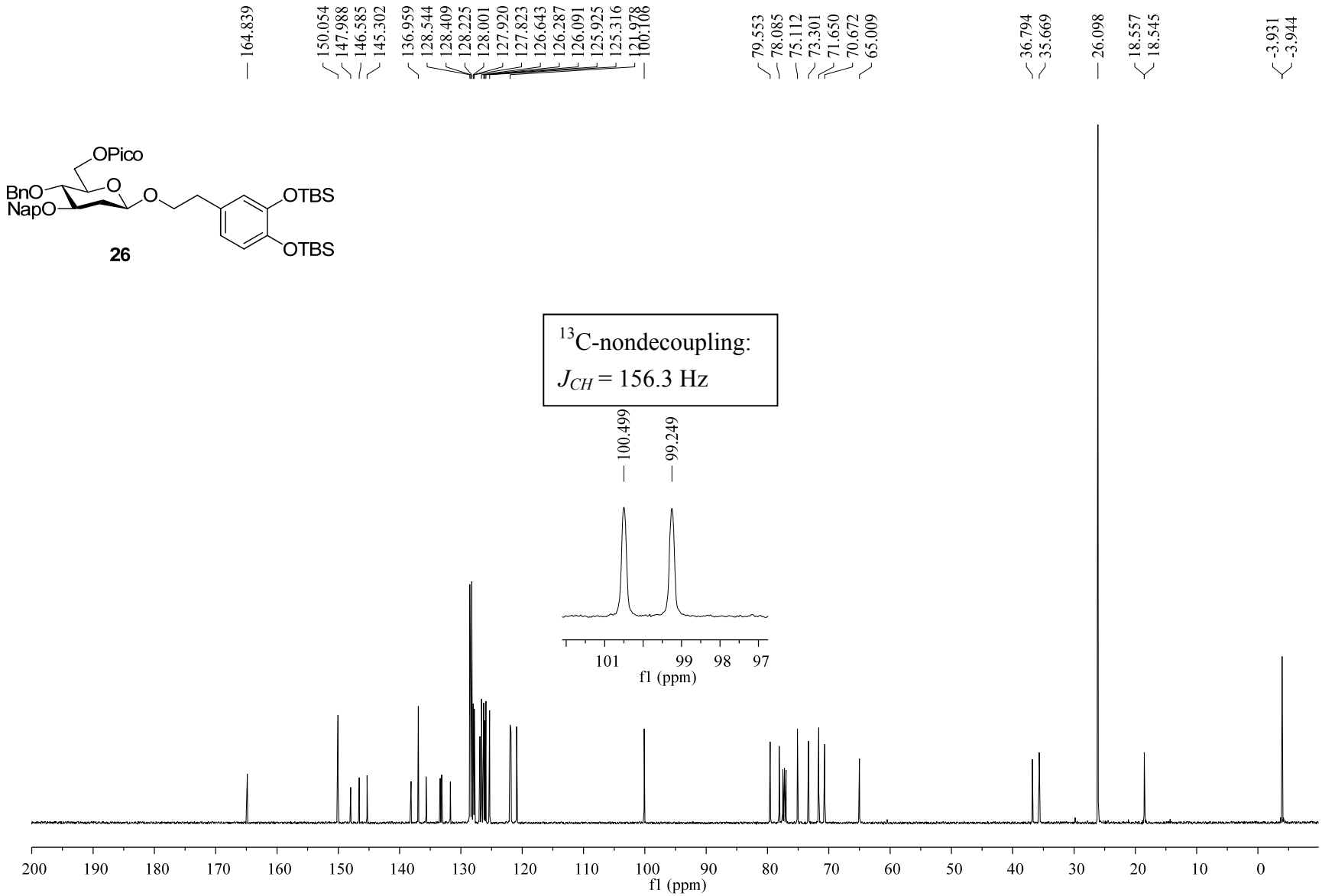

8.613
8.611
8.606
8.605
7.960
7.947
7.811
7.798
7.755
7.731
7.718
7.692
7.679
7.665
7.581
7.571
7.568
7.558
7.555
7.470
7.463
7.455
7.441
7.426
7.420
7.418
7.406
7.404
7.401
7.395
7.256
7.254
7.251
7.250
7.243
4.882
4.861
4.769
4.753
4.727
4.708
4.688
4.661
4.611
4.592
4.454
3.886
3.882
3.705
3.690
3.687
3.669
3.517
3.507
3.505
3.435
3.347
3.215
2.152
1.654
1.635
1.617
1.615
1.206
1.196
0.848
0.038
0.017
OPico
TBSO
NapO
O
O
O
NapO
OMe
25
1.05
1.01
3.02
5.04
1.10
6.00
1.03
1.11
1.12
3.05
0.97
1.15
1.10
1.16
2.15
1.18
1.14
1.15
2.96
1.17
1.05
2.35
2.93
9.05
6.10
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
f1 (ppm)

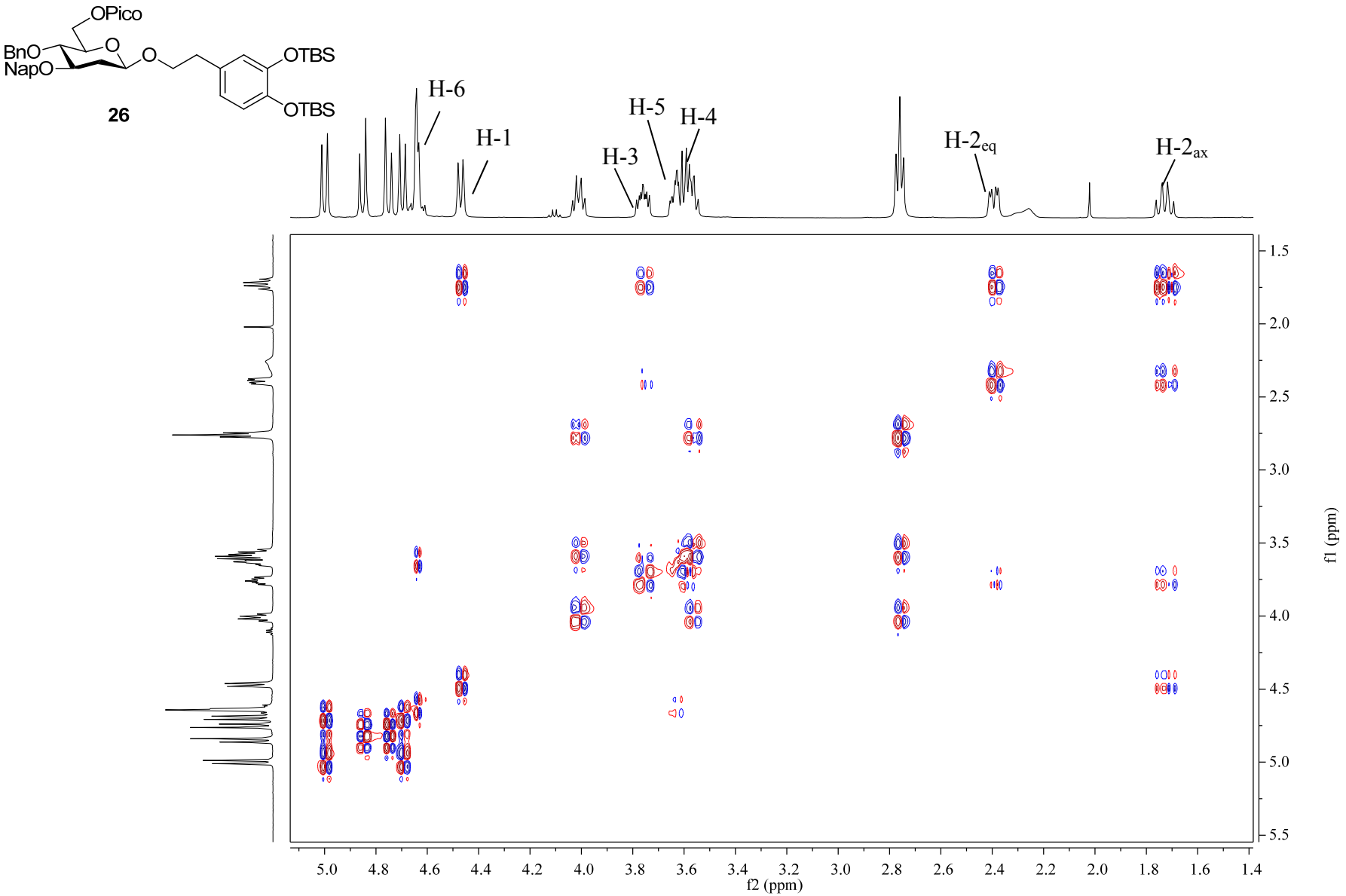

165.053
150.091
148.107
128.370
128.261
128.188
128.105
128.057
128.011
126.731
126.464
126.337
126.303
126.231
126.212
126.133
125.342
100.270
98.380
83.416
79.827
75.269
75.109
72.364
71.659
71.372
67.066
65.327
54.784
36.854
36.231
26.296
18.535
-3.318
-4.679
OPico
TBSO
NapO
NapO
OMe
25
13C-nondecoupling:
JCH' = 157.1 Hz
JCH = 166.4 Hz
100.443
99.396
98.585
97.476
100
99
98
97
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

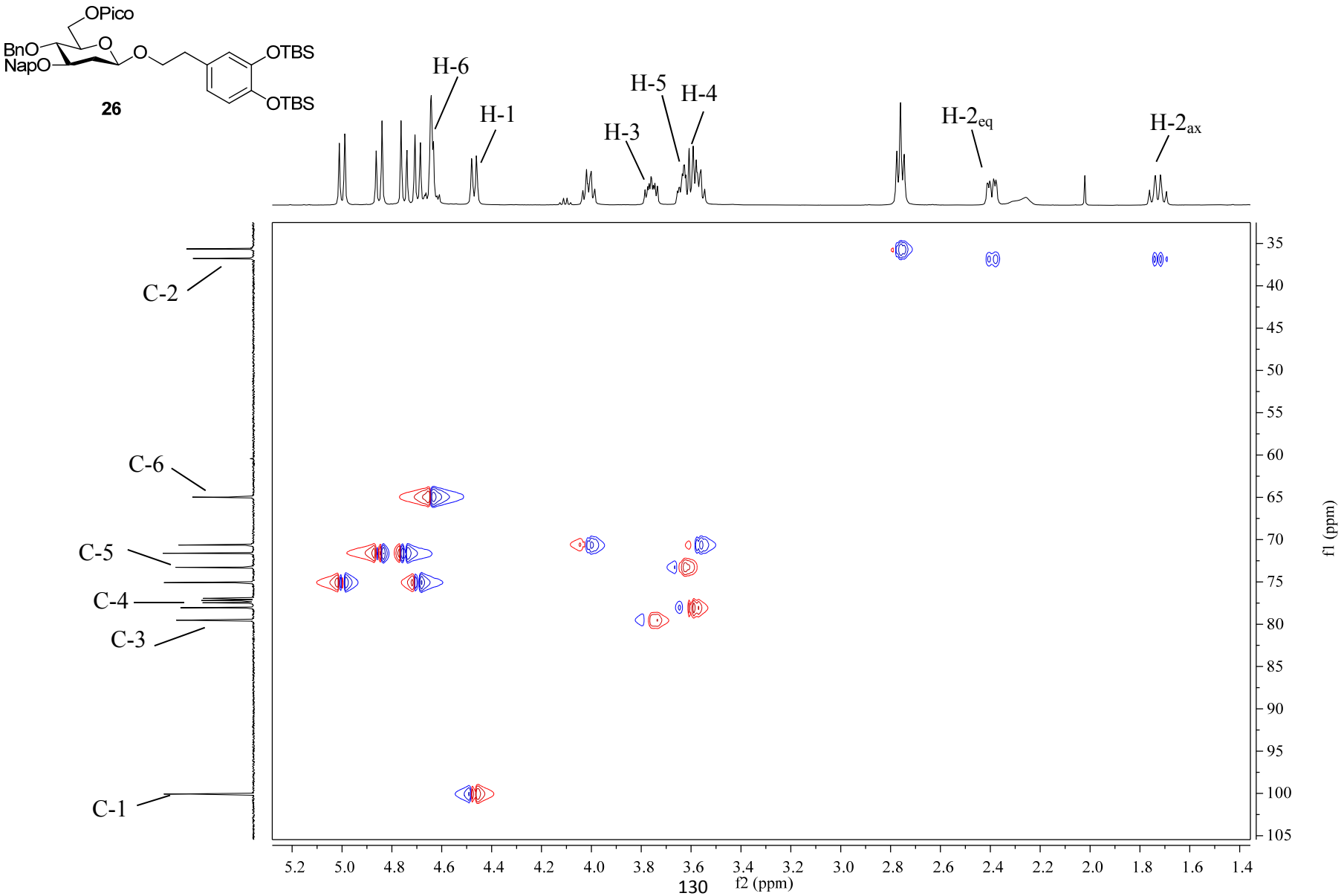

OPico
TBSO
NapO
NapO
OMe
25
H-1'
H-1
H-3
H-4'
H-5
H-5'
H-3'
H-4
H-2'eq
H-2eq
H-2'ax, H-2ax
f2 (ppm)
f1 (ppm)

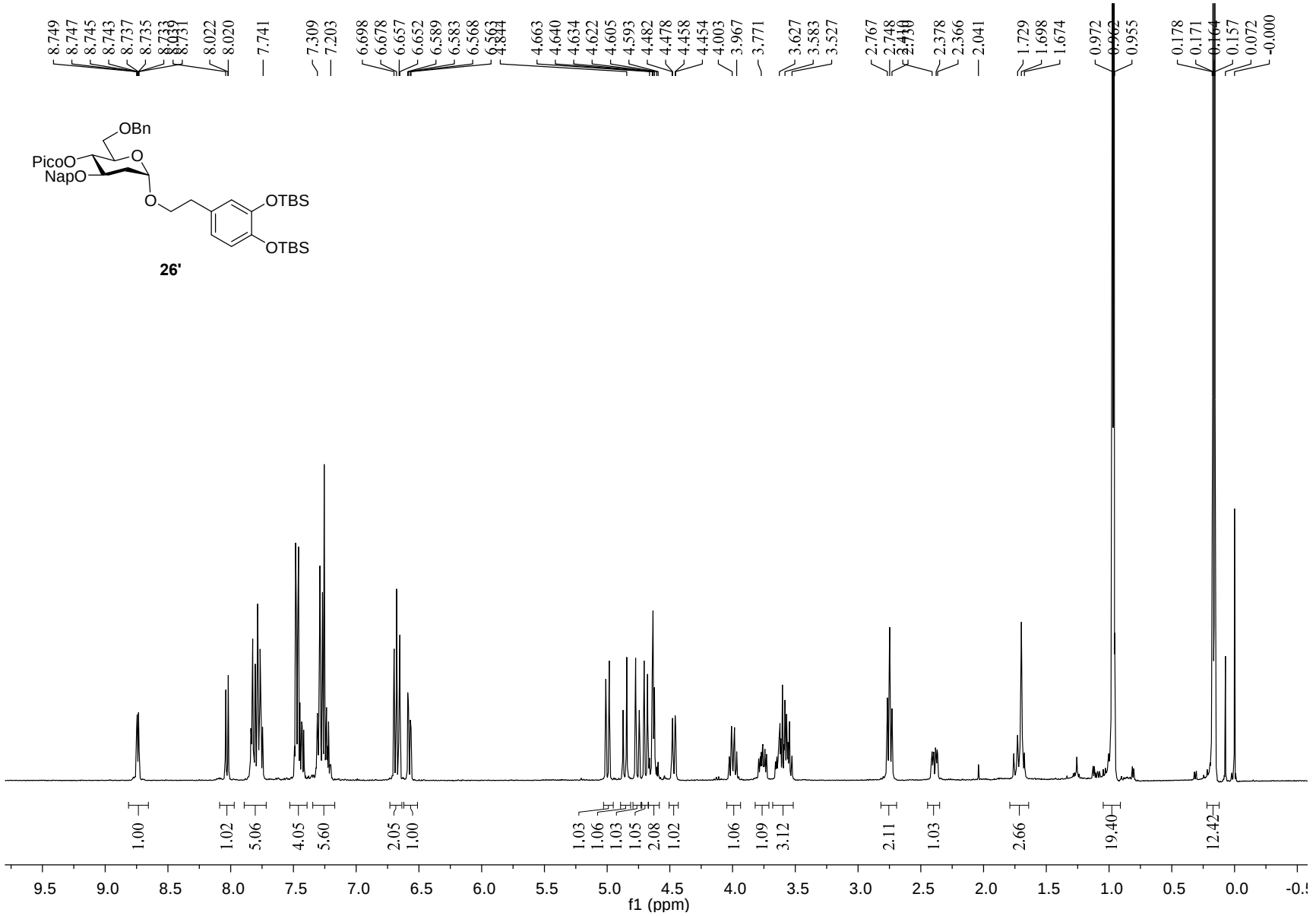

OPico
TBSO
NapO
NapO
OMe
25
H-1'
H-1
H-3
H-4'
H-5
H-5'
H-3'
H-4
H-2'eq
H-2eq
H-2'ax, H-2ax
C-2
C-2'
C-5
C-4'
C-5'
C-3
C-3'
C-4
C-1
C-1'
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
30
40
50
60
70
80
90
100
f1 (ppm)

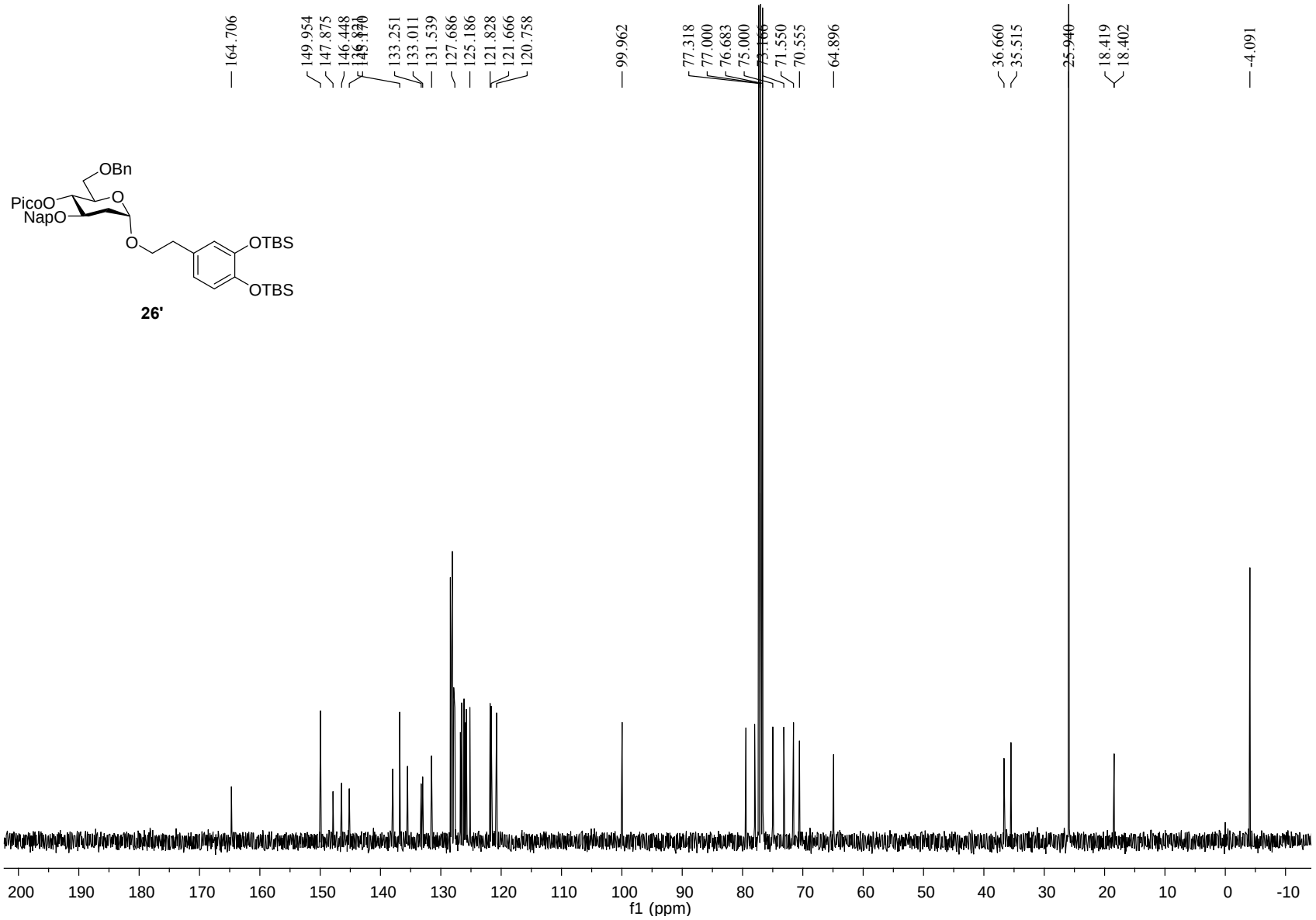

OPico
BnO
NapO
O
O
OTBS
OTBS
26
8.731
8.729
8.723
8.721
8.034
8.018
7.822
7.814
7.803
7.797
7.784
7.770
7.763
7.754
7.751
7.738
7.735
7.479
7.476
7.464
7.459
7.453
7.450
7.445
7.415
7.406
7.403
7.400
7.313
7.311
7.297
7.278
7.263
7.248
7.225
7.211
6.708
6.691
6.676
6.672
6.599
6.595
6.583
5.011
4.989
4.863
4.840
4.763
4.740
4.707
4.686
4.645
4.642
4.633
4.480
4.461
3.630
3.627
3.608
3.591
3.579
2.775
2.760
2.745
0.980
0.972
0.179
0.167
0.91
0.95
5.12
3.03
1.02
5.05
0.99
1.02
1.01
1.01
1.04
1.03
1.06
2.02
1.02
0.99
1.01
3.18
2.08
0.99
0.89
18.67
11.88
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
f1 (ppm)

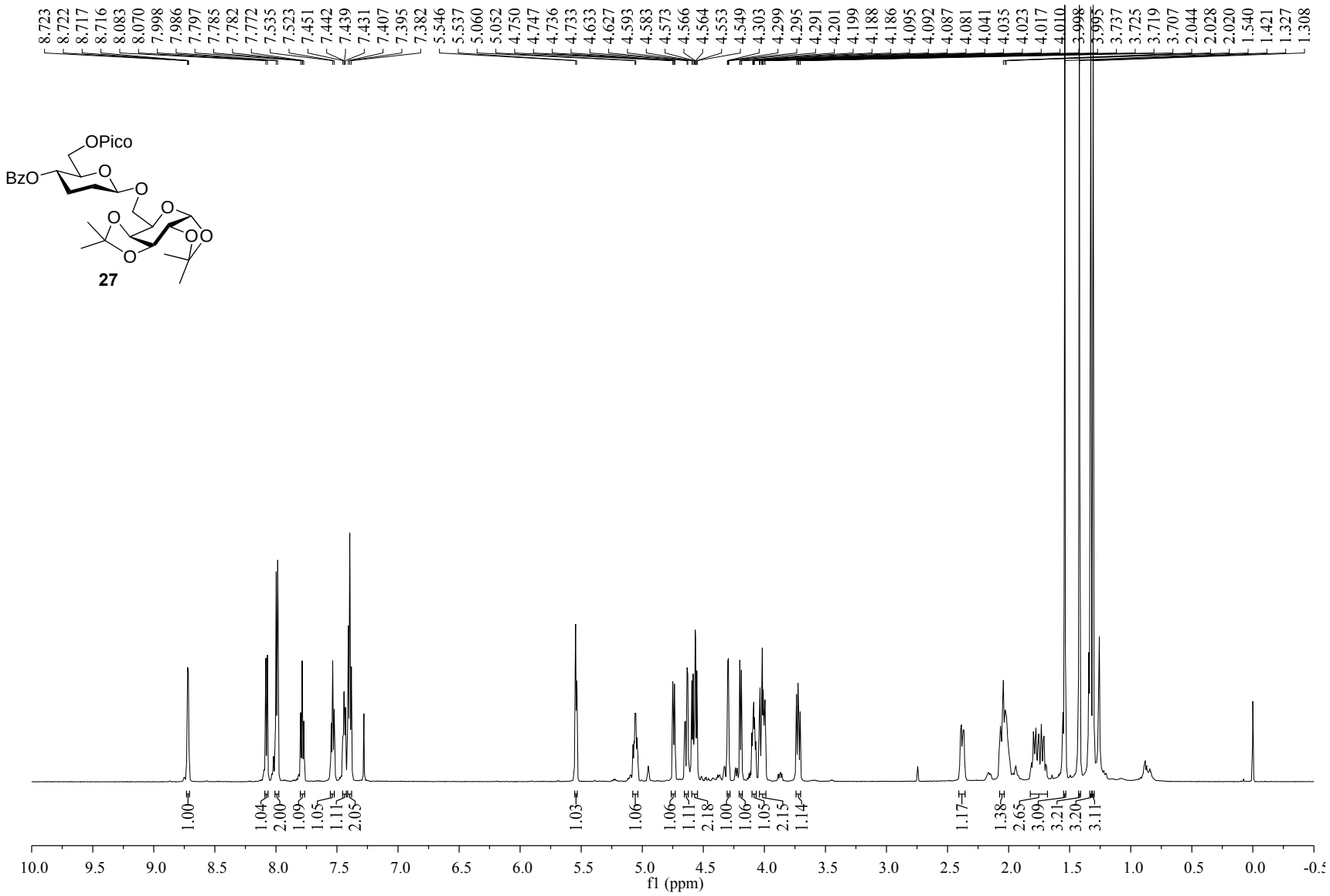

164.839
150.054
147.988
146.585
145.302
136.959
128.544
128.409
128.225
128.001
127.920
127.823
126.643
126.287
126.091
125.925
125.316
121.978
100.106
79.553
78.085
75.112
73.301
71.650
70.672
65.009
36.794
35.669
26.098
18.557
18.545
-3.931
-3.944
OPico
BnO
NapO
O
O
OTBS
OTBS
26
13C-nondecoupling:
JCH = 156.3 Hz
100.499
99.249
101
99
98
97
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

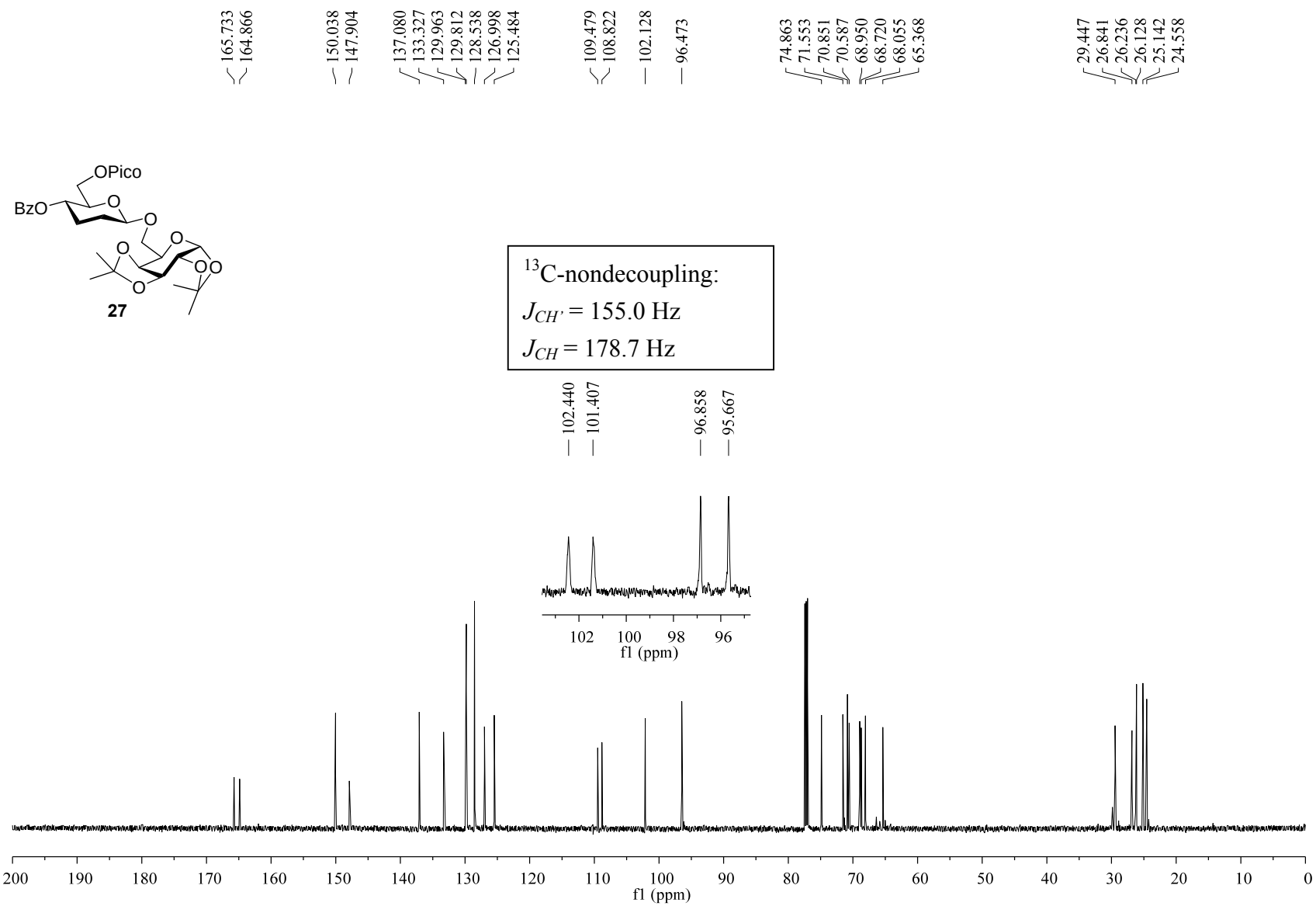

OPico
BnO
NapO
O
O
OTBS
OTBS
26
H-6
H-1
H-3
H-5
H-4
H-2eq
H-2ax
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)

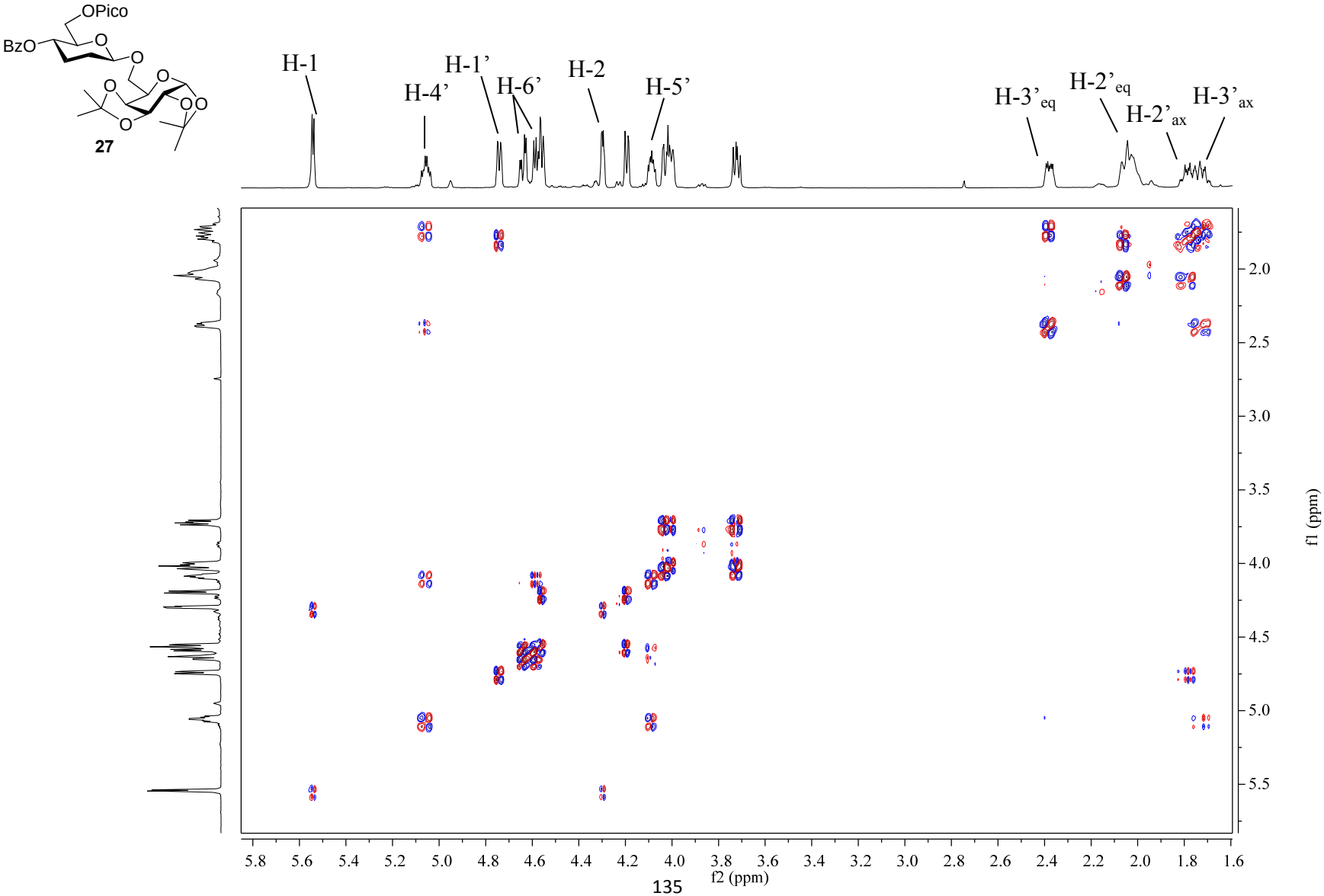

OPico
BnO
NapO
O
O
OTBS
OTBS
26
H-6
H-1
H-3
H-5
H-4
H-2eq
H-2ax
C-2
C-6
C-5
C-4
C-3
C-1
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)

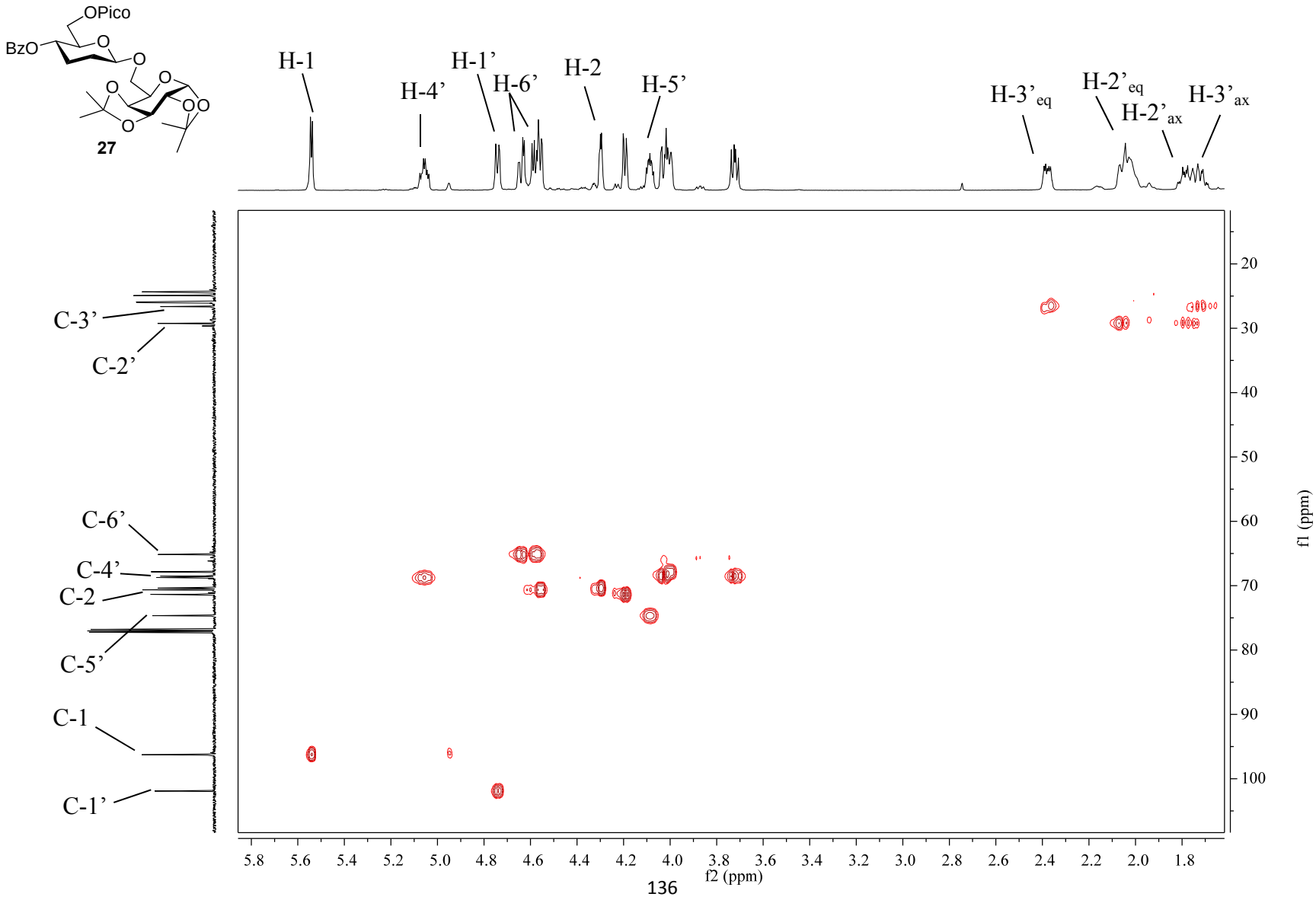

OBn
PicoO
NapO
O
O
OTBS
OTBS
26'
f1 (ppm)

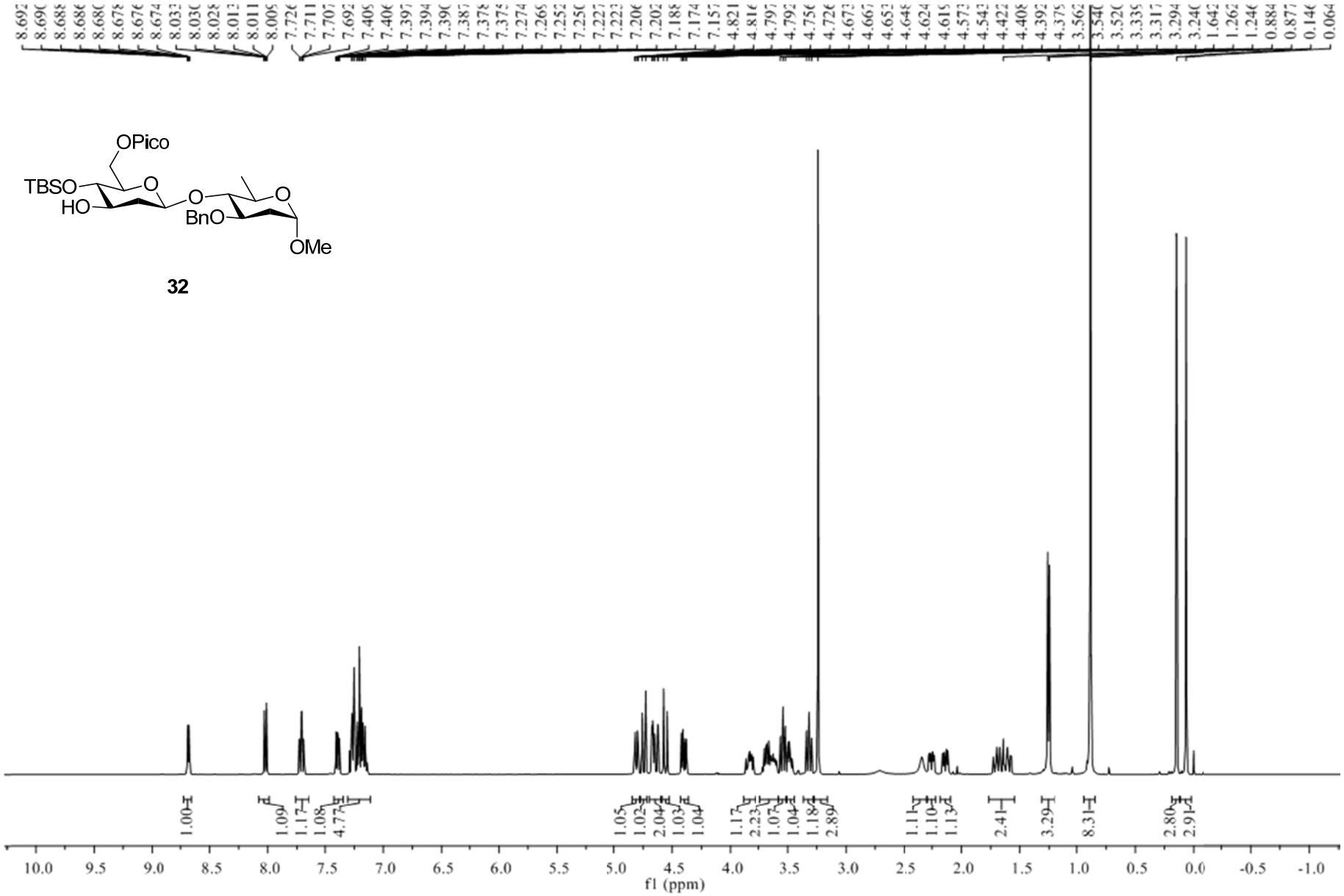

164.706
149.954
147.875
146.448
133.251
133.011
131.539
127.686
125.186
121.828
121.666
120.758
99.962
77.318
77.000
76.683
75.000
73.166
71.550
70.555
64.896
36.660
35.515
25.940
18.419
18.402
-4.091
OBn
PicoO
NapO
O
O
OTBS
OTBS
26'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

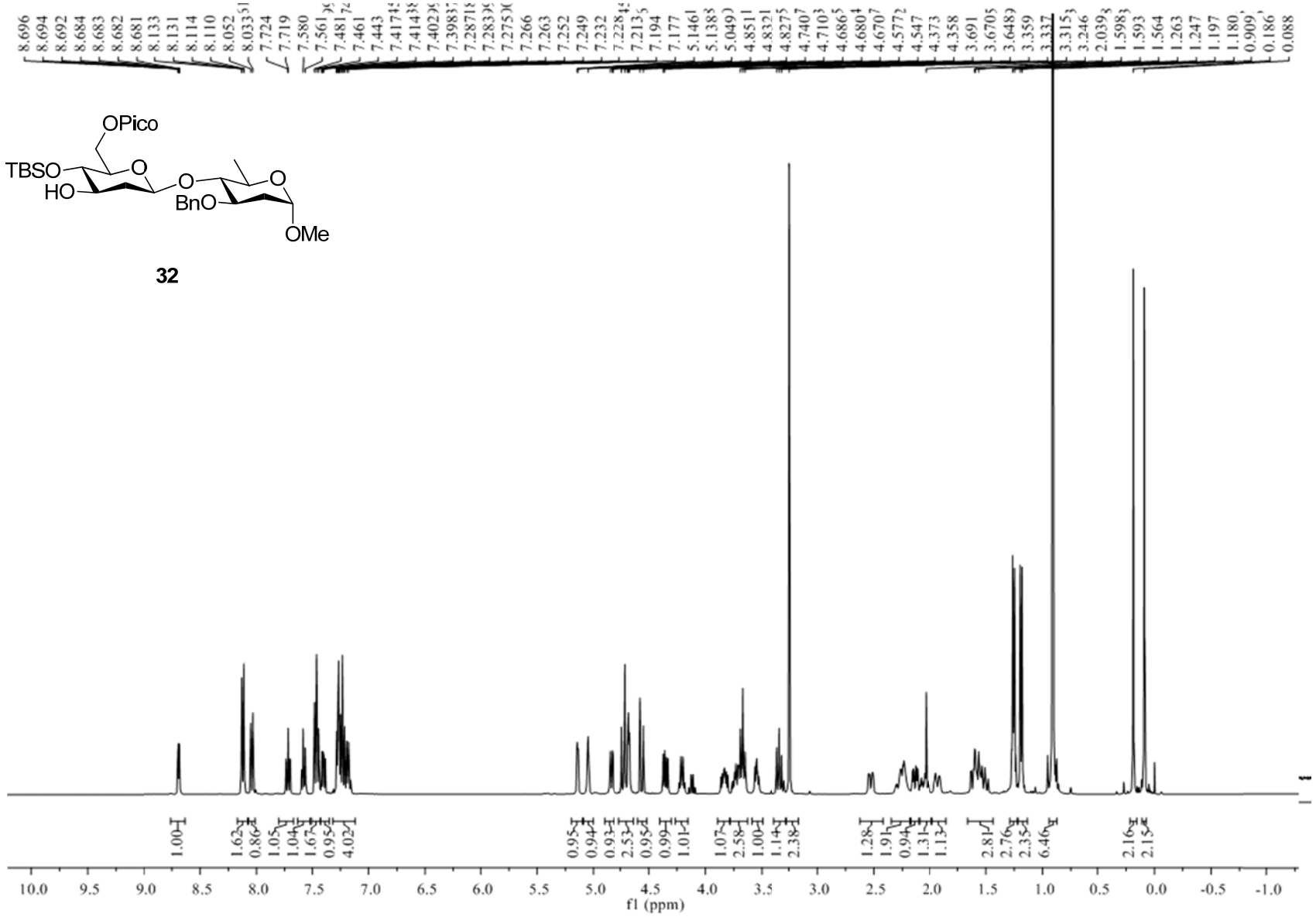

OPico
BzO
O
O
O
O
O
O
O
O
27
8.723
8.722
8.717
8.716
8.083
8.070
7.998
7.986
7.797
7.785
7.782
7.772
7.535
7.523
7.451
7.442
7.439
7.431
7.407
7.395
7.382
5.546
5.537
5.060
5.052
4.750
4.747
4.736
4.733
4.633
4.627
4.593
4.583
4.573
4.566
4.564
4.553
4.549
4.303
4.299
4.295
4.291
4.201
4.199
4.188
4.186
4.095
4.092
4.087
4.081
4.041
4.035
4.023
4.017
4.010
3.998
3.995
3.737
3.725
3.719
3.707
2.044
2.028
2.020
1.540
1.421
1.327
1.308
1.00
1.04
2.00
1.09
1.05
1.11
2.05
1.03
1.06
1.06
1.11
2.18
1.00
1.06
1.05
2.15
1.14
1.17
1.38
2.65
3.09
3.21
3.20
3.11
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
f1 (ppm)


165.733
164.866
150.038
147.904
137.080
133.327
129.963
129.812
128.538
126.998
125.484
109.479
108.822
102.128
96.473
74.863
71.553
70.851
70.587
68.950
68.720
68.055
65.368
29.447
26.841
26.236
26.128
25.142
24.558
OPico
BzO
O
O
O
O
O
O
O
O
27
13C-nondecoupling:
JCH' = 155.0 Hz
JCH = 178.7 Hz
102.440
101.407
96.858
95.667
102
100
98
96
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

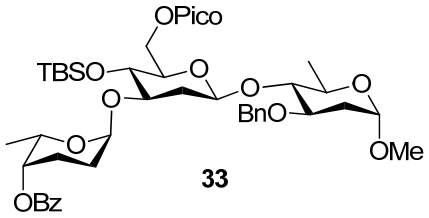

OPico
BzO
O
O
O
O
O
O
O
O
27
H-1
H-4'
H-1'
H-6'
H-2
H-5'
H-3'eq
H-2'eq
H-2'ax
H-3'ax
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)


OPico
BzO
27
H-1
H-4'
H-1'
H-6'
H-2
H-5'
H-3'eq
H-2'eq
H-2'ax
H-3'ax
C-3'
C-2'
C-6'
C-4'
C-2
C-5'
C-1
C-1'
f2 (ppm)
f1 (ppm)


OPico
TBSO
HO
O
O
BnO
O
OMe
32
fl (ppm)

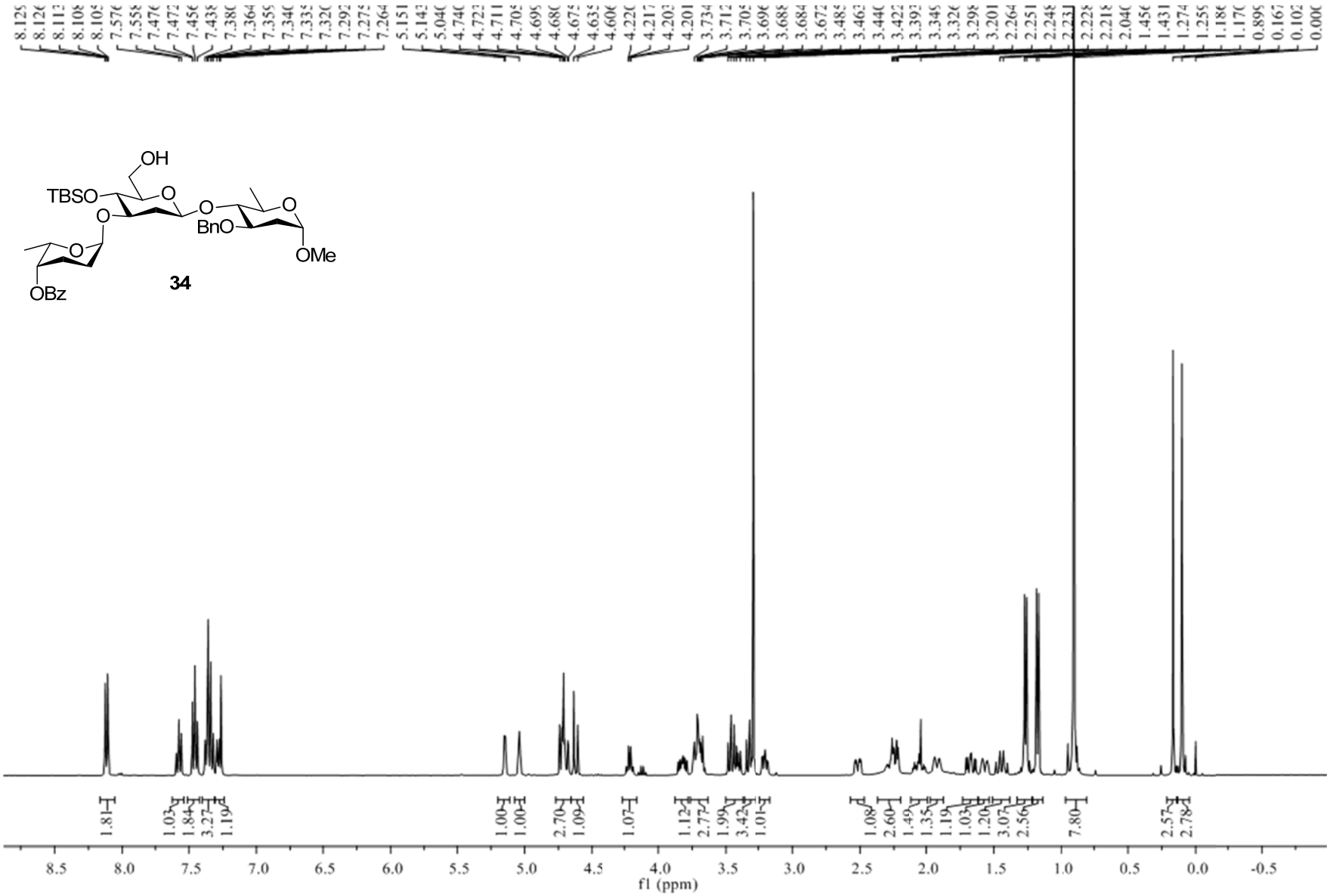


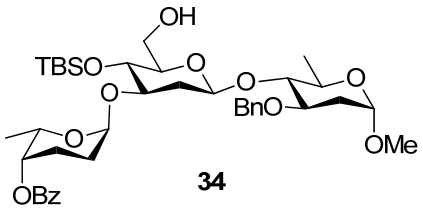
32


OPico
TBSO
O
O
O
O
BnO
O
OMe
OBz

33

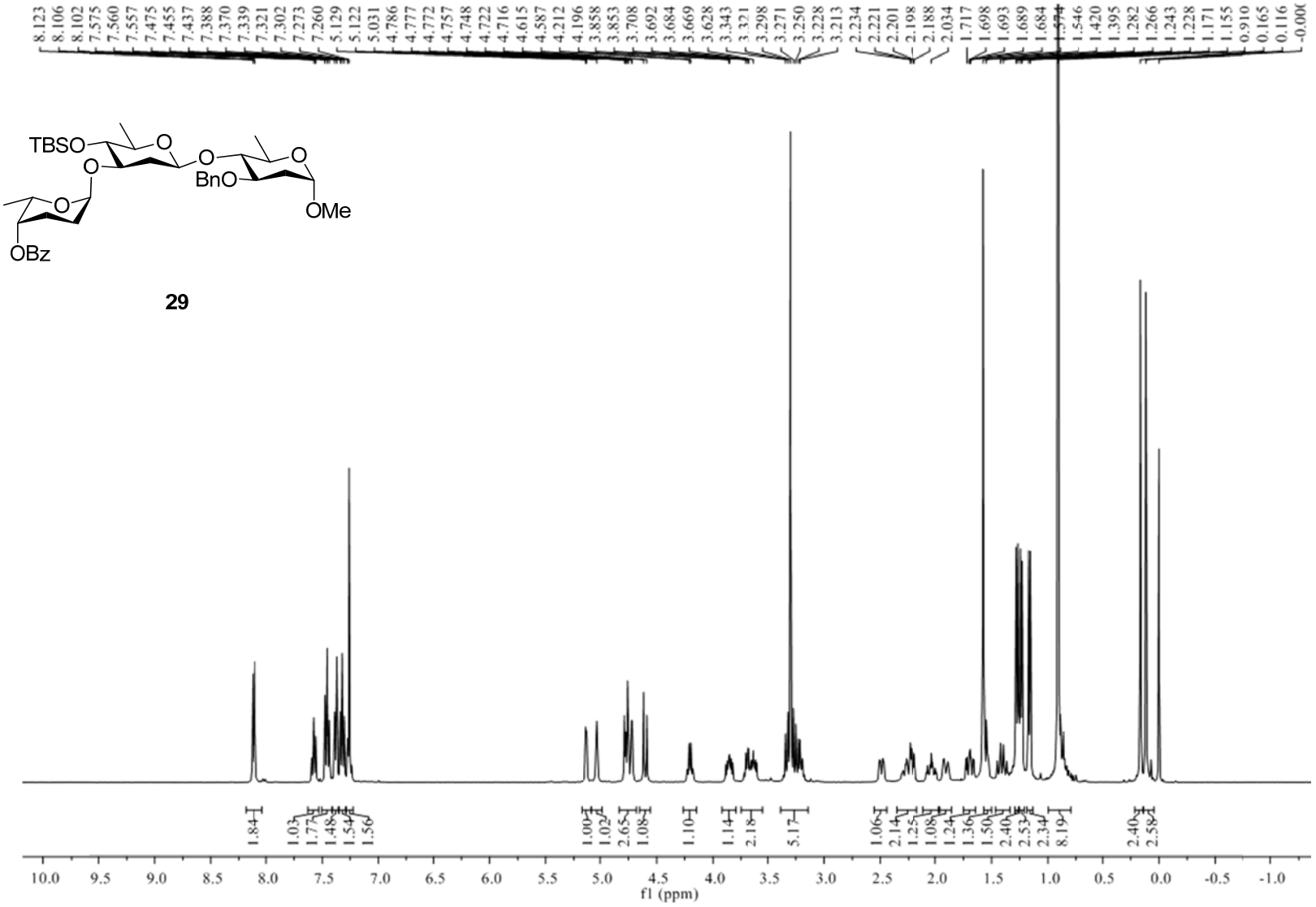
166.0
164.71
149.7
147.8
139.01
136.6
132.9
130.2
129.61
128.3
128.0
127.3
127.1
126.6
125.0
99.91
97.97
91.31
82.91
77.32
77.00
76.68
74.98
74.81
73.23
71.87
70.92
69.74
66.66
54.40
35.73
34.68
25.78
23.83
22.90
18.16
17.93
17.12
-3.35
-4.42
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OH
TBSO
O
O
O
BnO
O
OMe
OBz
34
fl (ppm)

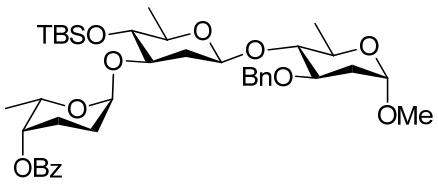

OH
TBSO
O
O
O
O
BnO
O
OMe
OBz

34

166.083
138.81
133.00
130.27
129.64
128.36
128.26
127.50
127.44
100.10
98.120
91.349
83.680
77.317
77.000
76.683
74.890
72.188
71.229
69.789
66.832
54.513
35.904
34.808
25.803
23.879
22.903
18.037
17.938
17.149
-3.353
-4.324
f1 (ppm)

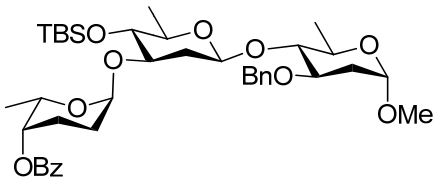


29

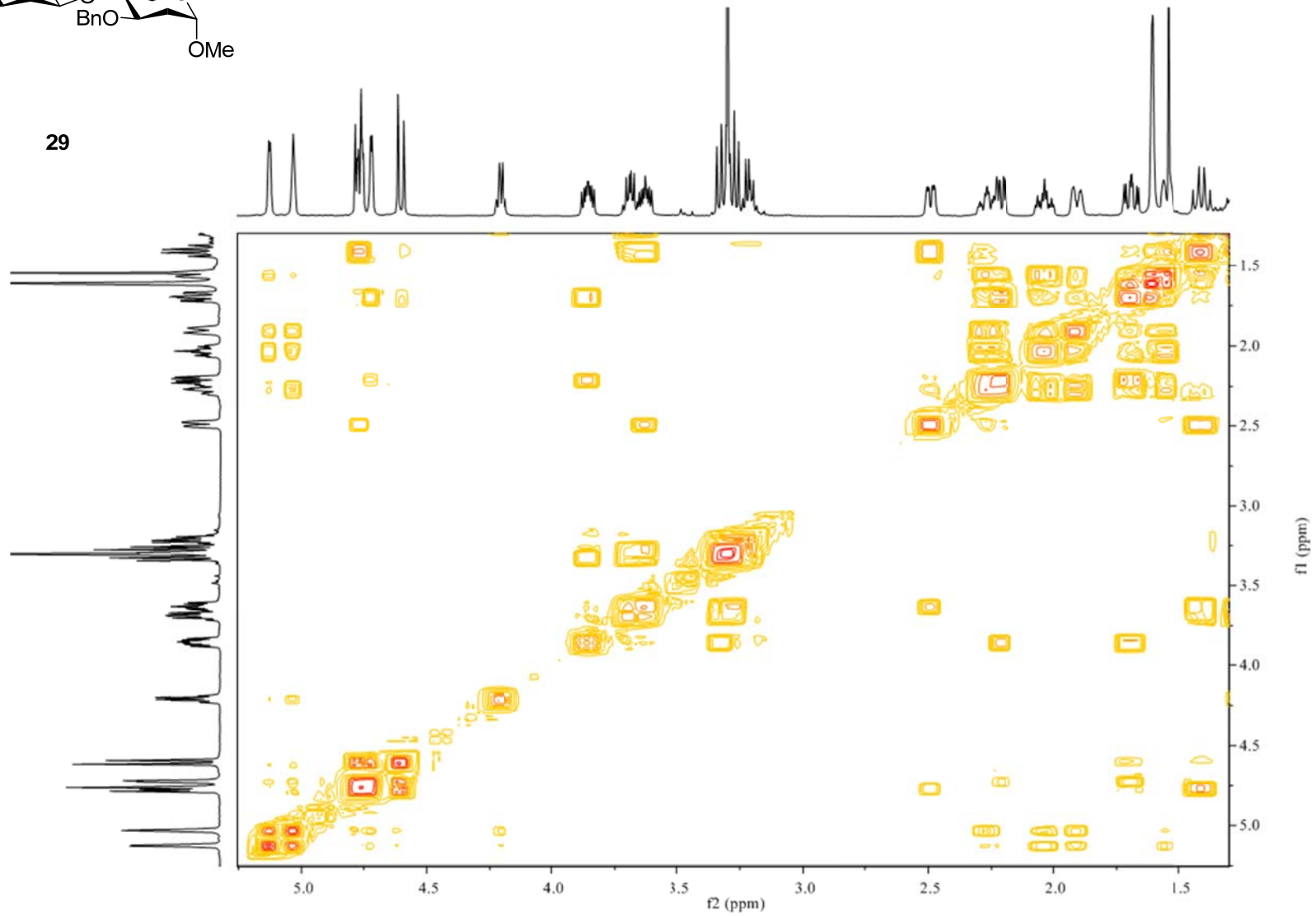

TBSO
O
O
O
O
BnO
O
OMe
OBz

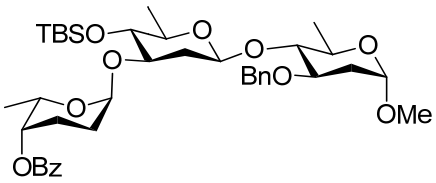
29

166.1
139.1
133.0
130.3
129.6
128.3
128.1
127.5
127.3
100.1
98.13
91.28
83.02
77.32
77.00
76.68
75.93
75.75
73.05
73.03
72.12
66.76
54.58
35.74
35.24
25.91
23.92
23.45
22.97
18.81
18.28
18.05
17.18
-3.15
-3.60
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



29




TBSO
O
O
O
O
BnO
O
OMe
OBz

29

10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)