Supporting Information

Glycosylation with Ulosonates under Mitsunobu Conditions: Scope and Limitations

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Contents

Experimental 2
General methods 2
General procedure A for the Mitsunobu glycosylations with methyl 3,4,5,7-tetra-*O*-benzoyl-α-D-*gluco*-hept-2-ulopyranosonate 1 2
General procedure B for the Mitsunobu glycosylations with methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonate 33 2
Characterization of the new compounds 3
Copies of the NMR spectra 15

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Experimental

General methods

Reagents were purchased from commercial suppliers (Sigma-Aldrich, TCI, Alfa Aesar) and used without further purification. TLC was carried out on precoated plates (DC-Alurolle Kieselgel 60, F254, Merck), and the spots were visualized under UV light and by gentle heating after treating it with 5% H_2SO_4 and 1% *p*-anisaldehyde solution in ethanol. Column chromatography was performed on silica gel (Kieselgel 60, 63-200 μm, Molar Chemicals). ^1H, ^{13}C NMR spectra were recorded on Bruker Avance DRX 360 and Bruker Avance I 400 spectrometers, ROE and HSQMBC studies were carried out on Bruker Avance II 500 spectrometer. Me_4Si (^1H) or the residual solvent signal (^{13}C) was used as reference. Mass spectra were recorded using a maXis II UHR ESI-TOF MS (Brucker) spectrometer. Optical rotations were determined with a Perkin-Elmer 241 polarimeter at 20°C.

General procedure A for the Mitsunobu glycosylations with methyl 3,4,5,7-tetra-*O*-benzoyl-α-D-*gluco*-hept-2-ulopyranosonate 1

Heptulopyranosonic ester **1** (100 mg, 0.153 mmol) was dissolved in dry THF (3 mL) in a round bottom flask, triphenylphosphine (PPh_3, 120 mg, 3 eq) and the corresponding nucleophile (HNu, 3 eq) were added and the solution was stirred at rt until all materials dissolved. Then, diethylazodicarboxylate (DEAD, 72 μL, 3 eq) was added, and the solution turned dark red. After stirring at rt for 3 h-1 d (specified with the particular compounds), TLC (toluene : EtOAc = 8:1) showed completion of the reactions. The solvent was evaporated under diminished pressure, and the crude mixture was purified by coloumn chromatography (slow gradient elution with toluene : EtOAc from 100 : 0 to 100 : 10).

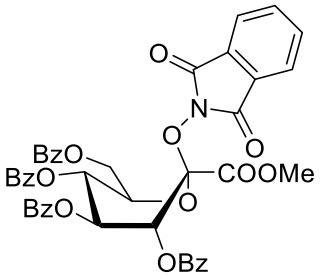
General procedure B for the Mitsunobu glycosylations with methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonate 33

Neuraminic acid ester **33** (200 mg, 0.407 mmol) was dissolved in dry CH_3CN (3 mL) under Ar atmosphere. The solution was cooled to -30 °C and 4Å molecular sieves (100 mg), triphenylphosphine (PPh_3, 320 mg, 3 eq), and a nucleophile (HNu, 3 eq) were added. Diethylazodicarboxylate (DEAD, 190 μL, 3 eq) was added dropwise to this solution, which turned dark orange-red. After 8 hours of stirring at -30 °C, TLC (hexane : acetone = 2 : 1)

showed completion of the reaction. The solvent was evaporated under diminished pressure, and the residue was purified with coloumn chromatography (slow gradient elution with hexane : acetone = 2.5 : 1 to 1.5 : 1).

Characterization of the new compounds

N-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyloxy)onate]-phthalimide (9)



Prepared according to General procedure A from **1** (100 mg, 0.153 mmol) and *N*-hydroxyphthalimide (**5**, 76 mg, 0.459 mmol), reaction time: 6 h.

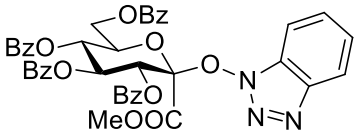
Yield: 72 mg (59%), R_f=0.52 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-23 (c=1.02, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.89 (3×d, 8H, Ar*H*), 7.75-7.69 (m, 2H, Ar*H*), 7.60 (t, *J*=7.4 Hz, 1H, Ar*H*), 7.51-7.25 (m, 12H, Ar*H*), 6.64 (dd, *J*=10.8, 7.8 Hz, 1H, H-5), 6.13 (d, *J*=4.2 Hz, 1H, H-3), 5.97 (dd, *J*=7.8, 4.2 Hz, 1H, H-4), 4.89 (dt, *J*=10.7, 4.2 Hz, 1H, H-6), 4.81 (dd, *J*=12.2, 3.9 Hz, 1H, H-7), 4.61 (dd, *J*=12.2, 4.6 Hz, 1H, H-7'), 3.89 (s, 3H, COOCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.04, 165.36, 165.16, 164.71, 163.90 (4×O*C*OPh, *C*OOMe), 163.66 (2) (N*C*O), 134.80, 133.86, 133.48, 133.40, 132.97, 130.23, 130.09, 130.05, 129.80, 129.59, 129.03, 128.99, 128.95, 128.73, 128.45, 128.38, 128.25, 124.00 (Ar*C*), 102.68 (C-2), 72.99 (2), 71.91, 69.53 (C-3 – C-6), 63.42 (C-7), 53.66 (COO*C*H_3).

HRMS: m/z calcd. for $C_{44}H_{33}NO_{14}Na$: 822.1793, found: 822.1795 ($M+Na^+$).

1-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyloxy)onate]-benzotriazole (10)



Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and *N*-hydroxybenzotriazole (**6**, 63 mg, 0.459 mmol), reaction time: 8 h. This reaction never reached full conversion, even after heating and one week of reaction time. R_f values of **10** and **1** proved to be similar in all attempted eluents, therefore TLC monitoring and column chromatography was difficult and a complete separation could not be achieved.

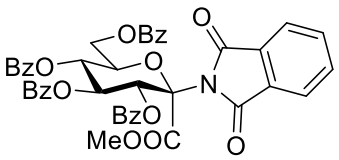
Yield: 40 mg (42%, corrected value for 80% conversion of **1** based on ^{1}H-NMR). R_f=0.50 (toluene:EtOAc=8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.78 (3×d+m, 10H, Ar*H*), 7.65 (m, 1H, Ar*H*), 7.59-7.28 (m, 14H, Ar*H*), 7.13 (m, 2H, Ar*H*), 6.31 (d, *J*=8.4 Hz, 1H, H-3), 6.14 (pt, *J*=8.3, 8.3 Hz, 1H, H-4), 5.89 (pt, *J*=9.9, 8.5 Hz, 1H, H-5), 4.96 (pdt, *J*=9.9, 3.2, 3.2 Hz, 1H, H-6), 4.64 (dd, *J*=12.5, 2.5 Hz, 1H, H-7), 4.43 (dd, *J*=12.5, 4.0 Hz, 1H, H-7'), 3.99 (s, 3H, COOCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.80, 165.40, 164.91, 164.88, 164.08 (4×O*C*OPh, *C*OOMe), 143.04, 133.89, 133.70, 133.57, 133.26, 130.38, 130.10, 130.01, 129.93, 129.63, 129.26, 128.67, 128.56, 128.47, 124.76, 119.96, 110.29 (Ar*C*), 105.02 (C-2), 73.73, 71.24, 69.95, 67.95 (C-3 – C-6), 62.34 (C-7), 53.91 (COO*C*H_3).

HRMS: m/z calcd. for $C_{42}H_{33}N_3O_{12}Na$: 794.1925, found: 794.1922 ($M+Na^+$).

***N*-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-phthalimide (12)**



Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and phthalimide (**11**, 68 mg, 0.459 mmol), reaction time: 16 h.

Yield: 36 mg (30%), R_f=0.34 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-17 (c=1.06, $CHCl_3$)

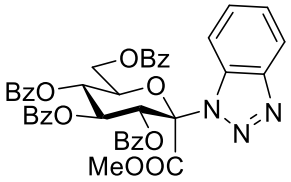
^{1}H NMR (360 MHz, $CDCl_3$) δ 8.09-7.69 (m, 13H, Ar*H*), 7.56-7.23 (m, 14H, Ar*H*), 6.88 (d, *J*=10.2 Hz, 1H, H-3), 6.28 (pt, *J*=10.0, 9.7 Hz, 1H, H-4), 5.93 (pt, *J*=9.7, 10.0 Hz, 1H, H-5), , 4.74 (ddd, *J*=10.1,

4.6, 2.8 Hz, 1H, H-6), 4.61 (dd, *J*=12.3, 2.8 Hz, 1H, H-7), 4.49 (dd, *J*=12.4, 4.7 Hz, 1H, H-7'), 3.98 (s, 3H, COOCH_3).

^{13}C NMR (91 MHz, $CDCl_3$) δ 166.44, 166.27, 165.59 (3), 165.24, 165.20 (4×O*C*OPh, 2×N-*C*O, *C*OOMe), 134.68, 133.58, 133.48, 133.27, 133.16, 131.36, 130.08, 129.99, 129.93, 129.77, 128.92, 128.82, 128.72, 128.52, 128.48, 128.44, 128.34, 123.96 (Ar-*C*), 86.19 (C-2), 73.04, 71.38, 69.30, 69.11 (C-3 – C-6), 63.07 (C-7), 53.51 (COO*C*H_3).

HRMS: m/z calcd. for $C_{44}H_{33}NO_{13}Na$: 806.1844, found: 806.1846 ($M+Na^+$).

1-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-benzotriazole (21)



Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and benzotriazole (**13**, 55 mg, 0.459 mmol), reaction time: 24 h.

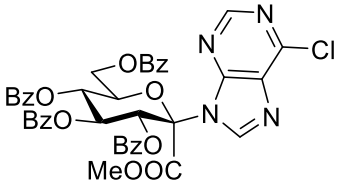
Yield: 34 mg (32%), R_f=0.35 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-19 (c=1.01, $CHCl_3$)

^{1}H NMR (360 MHz, $CDCl_3$) δ 8.06-7.71 (3×d, 2×m, 10H, Ar*H*), 7.59-7.21 (m, 14H, Ar*H*), 6.74 (d, *J*=8.4 Hz, 1H, H-3), 6.37 (pt, *J*=8.3, 7.7 Hz, 1H, H-4), 5.91 (dd, *J*=9.8, 7.7 Hz, 1H, H-5), 4.98 (ddd, *J*=9.7, 4.5, 2.8 Hz, 1H, H-6), 4.86 (dd, *J*=12.7, 2.4 Hz, 1H, H-7), 4.58 (dd, *J*=12.4, 4.8 Hz, 1H, H-7') 3.87 (s, 3H, COOCH_3).

^{13}C NMR (91 MHz, $CDCl_3$) δ 166.07, 165.53, 165.28, 165.16, 164.22 (4×O*C*OPh, *C*OOMe), 146.26, 133.76, 133.72, 133.44, 133.41, 132.28, 130.08, 129.92, 129.86, 129.59, 128.75, 128.62, 128.58, 128.44, 124.73, 120.36, 112.21 (Ar*C*), 91.21 (C-2), 73.76, 71.02, 70.54, 68.77 (C-3 – C-6), 62.85 (C-7), 54.01 (COO*C*H_3).

HRMS: m/z calcd. for $C_{42}H_{33}N_3O_{11}Na$: 778.2007, found: 778.2005 ($M+Na^+$).

6-chloro-9-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-purine (22)



Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and 6-chloropurine (**14**, 71 mg, 0.459 mmol), reaction time: 24 h. The product **22**, still containing significant amounts of DEAD after purification, was re-purified with another coloumn chromatography using toluene:acetonitrile=4:1.

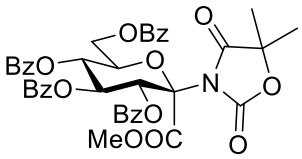
Yield: 38 mg (31%, corrected value based on the integrals from the ^{1}H-NMR spectra of **22** after the first coloumn.), R_f=0.32 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-30 (c=1.02, $CHCl_3$)

^{1}H NMR (360 MHz, $CDCl_3$) δ 8.56 (s, 1H, purine-*H*), 8.27 (s, 1H, purine-*H*), 8.08-7.61 (4×d, 8H, Ar*H*), 7.62-7.22 (m, 12H, Ar*H*), 6.52 (pt, *J*=8.4, 8.4 Hz, H-4), 6.40 (d, *J*=8.8 Hz, 1H, H-3), 5.92 (t, *J*=9.2, 8.8 Hz, 1H, H-5), 4.86-4.78 (m, 2H, H-6, H-7), 4.60 (dd, *J*=12.3, 4.3 Hz, 1H, H-7'), 3.86 (s, 3H, COOCH_3).

^{13}C NMR (91 MHz, $CDCl_3$) δ 166.11, 165.14 (2) , 164.87, 164.57 (4×O*C*OPh, *C*OOMe), 151.92, 151.50, 151.34, 142.25 (4×purine-*C*), 134.00, 133.89, 133.62, 131.93 (purine-*C*), 130.09, 129.88, 129.64, 129.37, 128.72, 128.64, 128.46, 128.03 (Ar*C*), 88.36 (C-2), 73.96, 71.99, 70.93, 68.62 (C-3 – C-6), 62.33 (C-7), 54.08 (COO*C*H_3).

HRMS: m/z calcd. for $C_{41}H_{31}ClN_4O_{11}Na$:813.1570, found: 813.1572($M+Na^+$).

5,5-Dimethyl-3-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-oxazolidin-2,4-dione (23)



Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and 5,5-dimethyloxazolidine-dione (**15**, 59 mg, 0.459 mmol), reaction time: 18 h. The product **23**, still containing traces of unknown impurities, was re-purified with another coloumn chromatography using chloroform:acetonitrile=6:1.

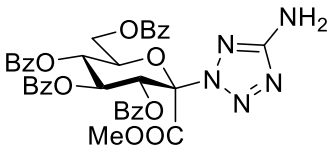
Yield: 39 mg (33%), R_f=0.48 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-22 (c=0.98, $CHCl_3$)

^{1}H NMR (360 MHz, $CDCl_3$) δ 8.10-7.83 (3×d 8H Ar*H*), 7.57-7.23 (m, 14H, Ar*H*), 6.54 (d, *J*=10.1 Hz, 1H, H-3), 6.36 (t, *J*=9.8 Hz, 1H, H-4), 5.89 (t, *J*=9.5 Hz, 1H, H-5), 4.64 (d, *J*=9.6 Hz, 1H, H-7), 4.51 (d+m, *J*=9.3 Hz, 2H, H-6, H-7'), 3.92 (s, 3H, COOCH_3), 1.56 (s, 3H, CH_3), 1.46 (s, 3H, CH_3).

^{13}C NMR (91 MHz, $CDCl_3$) δ 174.09, 166.14, 165.77, 165.43, 165.09, 164.04, 151.09 (4×O*C*OPh, *C*OOMe, 2×N-*C*O), 133.80, 133.61, 133.34, 133.22, 130.08, 129.98, 129.91, 129.83, 129.62, 128.75, 128.63, 128.58, 128.47, 128.35, 128.28 (Ar-*C*), 86.78 (C-2), 82.98 [*C*$(CH_3)_2$], 73.13, 70.85, 69.40, 68.77 (C-3 – C-6), 62.55 (C-7), 53.65 (COO*C*H_3), 23.36, 23.24 (2×*C*H_3).

HRMS: m/z calcd. for $C_{41}H_{35}NO_{14}Na$: 788.1950, found: 788.1960 ($M+Na^+$).

5-Amino-2-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-tetrazole (24)



Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and 5-aminoteteazole (**16**, 39 mg, 0.459 mmol). Instead of THF, 3 mL DMF was used as solvent. Reaction time: 8 h.

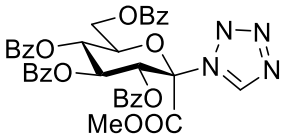
Yield: 35 mg (32%), R_f=0.21 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-25 (c=1.02, $CHCl_3$)

^{1}H NMR (360 MHz, $CDCl_3$) δ 8.04-7.83 (3×d, 8H, Ar*H*), 7.57-7.16 (m, 12H, Ar*H*), 6.79 (d, *J*=8.1 Hz, 1H, H-3), 6.04 (pt, *J*=8.1, 7.2 Hz, 1H, H-4), 5.85 (dd, *J*=9.7, 7.1 Hz, 1H, H-5), 5.09 (ddd, *J*=9.6, 4.90, 3.0 Hz, 1H, H-6) 4.73 (dd, *J*=12.4, 2.90 Hz, 1H, H-7), 4.55 (dd, *J*=12.40, 5.0 Hz, 1H, H-7'), 4.37 (s, 2H, NH_2), 3.91 (s, 3H, COOCH_3).

^{13}C NMR (91 MHz, $CDCl_3$) δ 166.20, 165.87, 165.27, 165.07, 164.59, 163.86 (4×O*C*OPh, *C*OOMe, Tetrazole-*C*), 133.87, 133.69, 133.52, 133.26, 130.05, 130.00, 129.94, 129.65, 128.82, 128.69, 128.49 (Ar*C*), 91.10 (C-2), 73.84, 70.88, 69.62, 68.58 (C-3 – C-6), 63.19 (C-7), 54.16 (COO*C*H_3).

HRMS: m/z calcd. for $C_{37}H_{31}N_5O_{11}Na$: 744.1912, found: 744.1911 ($M+Na^+$).

1-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-tetrazole (25a)



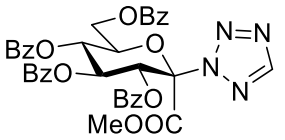
Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and tetrazole (**17**, 32 mg, 0.459 mmol), reaction time: 4 h.

Yield: 32 mg (30%), R_f=0.25 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-27 (c=0.99, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H, tetrazole-C*H*), 8.07, 8.05, 7.93, 7.91, 7.74, 7.72 (3×d, 8H, Ar*H*) 7.60-7.26 (m, 14H, Ar*H*), 6.44 (pt, *J*=8.6, 8.6 Hz, 1H, H-4), 6.30 (d, *J*=8.8 Hz, 1H, H-3), 5.87 (pt, *J*=9.4, 8.4 Hz, 1H, H-5), 4.95 (ddd, *J*=9.8, 4.0, 2.5 Hz, 1H, H-6), 4.90 (dd, *J*=12.4, 4.2 Hz, 1H, H-7), 4.55 (dd, *J*=12.4 Hz, 4.0 Hz, 1H, H-7'), 3.91 (s, 3H, COOC*H*$_3$).
^{13}C NMR (91 MHz, $CDCl_3$) δ 166.18, 165.27, 165.03, 164.31, 164.28 (4×O*C*OPh, *C*OOMe), 141.36 (Tetrazole-*C*) 133.95, 133.87, 133.64, 133.60, 131.27, 130.05, 129.87, 129.82, 129.24, 129.03, 128.70, 128.66, 128.61, 128.47, 128.31, 126.15 (Ar*C*), 89.74 (C-2), 74.59, 71.65, 70.97, 68.07 (C-3 – C-6), 62.05 (C-7), 54.52 (COO*C*H$_3$).

HRMS: m/z calcd. for $C_{37}H_{30}N_4O_{11}Na$: 729.1803, found: 729.1803 ($M+Na^+$).

2-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-tetrazole (25b)



Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and tetrazole (**17**, 32 mg, 0.459 mmol), reaction time: 4 h.

Yield: 35 mg (33%), R_f=0.54 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$= -29 (c=1.00, $CHCl_3$)

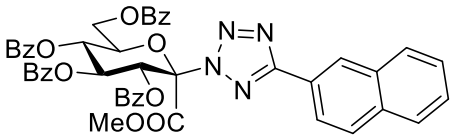
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (Tetrazole-C*H*), 8.03, 8.01, 7.90, 7.88, 7.87, 7.83, 7.81 (3×d, 8H, Ar*H*), 7.54-7.28 (m, 14H, Ar*H*), 6.86 (d, *J*=8.6 Hz, 1H, H-3), 6.19 (pt, *J*=8.1, 8.1 Hz 1H, H-4), 5.91 (pt, *J*=9.3, 8.2 Hz, 1H, H-5), 5.19 (ddd, *J*=9.3, 4.5, 2.9 Hz, 1H, H-6), 4.76 (dd, *J*=12.4, 2.8 Hz, 1H, H-7), 4.57 (dd, *J*=12.5, 4.9 Hz, 1H, H-7'), 3.93 (s, 3H, COOC*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.08, 165.25, 165.00, 164.45, 163.80 (4×O*C*OPh, *C*OOMe), 152.7 (Tetrazole-*C*H) 133.89, 133.70, 133.54, 133.26, 129.94, 129.89, 129.83, 129.48, 128.63, 128.55, 128.50,

128.45, 128.42, 128.25 (Ar*C*), 91.57 (C-2), 74.18, 70.81, 70.12, 68.41 (C-3 – C-6), 62.93 (C-7), 54.28 (COO*C*H$_3$).

HRMS: m/z calcd. for $C_{37}H_{30}N_4O_{11}Na$: 729.1803, found: 729.1800 ($M+Na^+$).

5-(2-naphthyl)-2-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-tetrazole (26)



Prepared according to General Method A from **1** (150 mg, 0.230 mmol) and 5-naphthyltetrazole (**18**, 135 mg, 0.690 mmol), reaction time: 5 h.

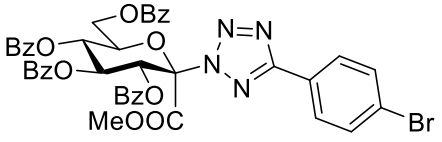
Yield: 75 mg (42%) R_f=0.58 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$ = -30 (c=1.08, $CHCl_3$) value obtained for a sample contaminated by traces of **2**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H, Ar*H*), 8.11-7.86 (m, 12H, Ar*H*), 7.59-7.24 (m, 15H, Ar*H*), 7.03 (d, *J*=8.1 Hz, 1H, H-3), 6.26 (pt, *J*=8.0, 7.2 Hz, 1H, H-4), 6.01 (dd, *J*=9.6, 7.2 Hz, 1H, H-5), 5.31 (ddd, *J*=9.8, 5.2, 3.4 Hz, 1H, H-6), 4.87 (dd, *J*=12.5, 2.8 Hz, 1H, H-7), 4.68 (dd, *J*=12.5, 4.7 Hz, 1H, H-7'), 3.97 (s, 3H, COOC*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.15, 165.26, 165.04, 165.02, 164.70, 163.92 (4×O*C*OPh, *C*OOMe, Tetrazole-*C*), 134.41, 133.92, 133.68, 133.48, 133.22, 133.05, 130.00, 129.97, 129.92, 129.87, 129.56, 128.79, 128.69, 128.61, 128.58, 128.50, 128.43, 128.40, 127.88, 127.35, 127.28, 126.71, 123.95, 123.80 (Ar*C*), 91.67 (C-2), 74.09, 70.81, 70.10, 68.52 (C-3 – C-6), 63.07 (C-7), 54.27 (COO*C*H$_3$).

HRMS: m/z calcd. for $C_{47}H_{36}N_4O_{11}Na$: 855.2273, found: 855.2271 ($M+Na^+$).

5-(4-bromophenyl)-2-[methyl (3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-tetrazole (27)



Prepared according to General Method A from **1** (150 mg, 0.23 mmol) and 5-(*p*-bromophenyl)tetrazole (**19**, 155 mg, 0.69 mmol), reaction time: 4 h.

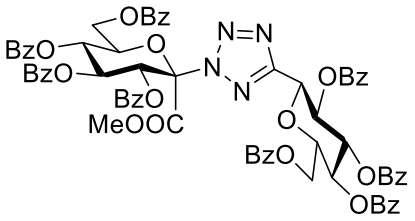
Yield: 79 mg (40%), R_f=0.60 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-24 (c=0.97, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.81 (m, 10H, Ar*H*), 7.57-7.24 (m, 14H, Ar*H*), 6.90 (d, *J*=8.0 Hz, 1H, H-3), 6.15 (pt, *J*=8.1, 7.5 Hz, 1H, H-4), 5.91 (dd, *J*=9.6, 7.2 Hz, 1H, H-5), 5.22 (ddd, *J*=9.7, 5.0, 3.0 Hz, 1H, H-6), 4.79 (dd, *J*=12.4, 2.8 Hz, 1H, H-7), 4.59 (dd, *J*=12.5, 4.7 Hz, 1H, H-7'), 3.91 (s, 3H, COOCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.16, 165.24, 165.07, 164.60, 164.08, 163.89 (4×O*C*OPh, *C*OOMe, Tetrazole-*C*), 133.99, 133.74, 133.58, 133.28, 132.13, 130.01, 129.96, 129.91, 129.58, 128.74, 128.69, 128.62, 128.54, 128.49, 128.45, 128.40, 125.49, 125.24 (Ar*C*), 91.71 (C-2), 74.12, 70.77, 70.00, 68.50 (C-3 – C-6), 63.07 (C-7), 54.32 (COO*C*H_3).

HRMS: m/z calcd. for $C_{43}H_{33}BrN_4O_{11}Na$: 883.1221, 885.1211, found: 883.1219, 885.1205 ($M+Na^+$).

5-(2'',3'',4'',6''-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2-[methyl (3',4',5',7'-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosyl)onate]-tetrazole (28)



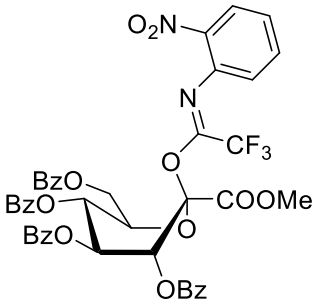
Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and 5-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)tetrazole (**20**, 100 mg, 0.154 mmol). Yield: 70 mg (36%) R_f=0.37 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-62 (c=1.10, $CHCl_3$)

^{1}H NMR (360 MHz, $CDCl_3$) δ 8.00-7.66 (3×d + m, 18H, Ar*H*) 7.54-7.17 (m, 24H, Ar*H*) 6.77 (d, *J*= 8.02 Hz, 1H, H-3'), 6.08-5.92 (m, 3H, H-4', H-2'', H-3''), 5.81-5.75 (m, 2H, H-5', H-4'') 5.18 (m, 1H, H-6'), 5.13 (d, *J*=9.87 Hz, 1H, H-1''), 4.66-4.45 (m, 4H, H-7a', H-7b', H-6a'', H-6b''), 4.26 (m, 1H, H-5''), 3.61 (s, 3H, COOCH_3).

^{13}C NMR (91 MHz, $CDCl_3$) δ 166.30, 166.15, 165.96, 165.28, 165.18, 164.99, 164.48, 164.39, 163.54 (8×O*C*OPh, *C*OOMe), 162.32 (Tetrazole-*C*), 133.81, 133.66, 133.56, 133.35, 133.27, 133.24, 130.00, 129.95, 129.70, 129.65, 129.62, 128.99, 128.93, 128.75, 128.66, 128.49, 128.42, 128.38 (Ar*C*), 91.80 (C-2'), 77.16 (C-1''), 74.44, 74.05, 72.47, 71.14, 70.65, 69.65, 69.60, 68.47 (C-3' – C-6', C-2'' – C-5''), 63.48, 63.21 (C-7', C-6''), 54.01 (COO*C*H_3).

HRMS: m/z calcd. for $C_{71}H_{56}N_4O_{20}Na$: 1307.3380, found: 1307.3381 ($M+Na^+$).

_O_-[methyl (3,4,5,7-tetra-_O_-benzoyl-β-D-_gluco_-hept-2-ulopyranosyl)onate]-_N_-(2-nitrophenyl)-trifluoroacetimidate (30a)



Prepared according to General Method A from **1** (150 mg, 0.23 mmol) and 2-nitrotrifluoroacetanilide (**29a**, 168 mg, 0.69 mmol), reaction time: 3 h.

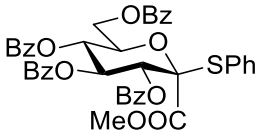
Yield: 105 mg (52%) R_f=0.50 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=-48 (c=1.05, $CHCl_3$)

^{1}H NMR (360 MHz, $CDCl_3$) δ 8.06-7.89 (m, 9H, Ar-H), 7.61 (t, *J*=7.46 Hz, 1H, Ar-H), 7.54-7.26 (m, 13H, Ar-H), 7.14 (t, *J*=7.2 Hz, 1H, Ar-H), 6.66 (d, *J*=9.1 Hz, 1H, Ar-H), 6.07 (dd, *J*=9.4, 6.8 Hz, 1H, H-5), 6.02 (d, *J*=5.0 Hz, 1H, H-3), 5.90 (dd, *J*=6.7, 5.0 Hz, 1H, H-4), 5.18 (pdt, *J*=9.4, 3.8, 3.8 Hz, 1H, H-6), 4.93 (dd, *J*=12.3, 3.3 Hz, 1H, H-7), 4.57 (dd, *J*=12.3, 4.3 Hz, 1H, H-7'), 3.78 (s, 3H, COOC*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.15, 165.23, 165.19, 164.99, 163.91 (4×O*C*OPh, *C*OOMe), 141.80 (q, $^2J_{C\text{-}F}$=38.0 Hz, -*C*=N), 134.10, 134.06, 133.66, 133.26, 130.13, 130.04, 129.96, 129.81, 129.64, 128.77, 128.73, 128.69, 128.51, 128.33, 125.16, 124.76, 121.84 (Ar-C), 115.59 (q, $^1J_{C\text{-}F}$=287.2 Hz, *C*F_3), 98.75 (C-2), 73.33, 71.80, 71.30, 68.06 (C-3 – C-6), 62.73 (C-7), 53.64 (COO*C*H_3).

HRMS: m/z calcd. for $C_{44}H_{33}F_3N_2O_{14}Na$: 893.1776, found: 893.1777 ($M+Na^+$).

Methyl (phenyl 3,4,5,7-tetra-_O_-benzoyl-3-thio-β-D-_gluco_-hept-2-ulopyranoside)onate] (32)



Prepared according to General Method A from **1** (100 mg, 0.153 mmol) and benzenethiol (**31**, 47μL, 0.459 mmol), reaction time: 6 h.

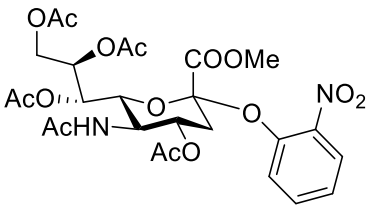
Yield: 45 mg (39%), R_f=0.56 (toluene:EtOAc=8:1) $[\alpha]_D^{20}$=+14 (c=1.04, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, *J*=7.6 Hz, 4H, Ar-H), 7.89 (d, *J*=7.4 Hz, 2H, Ar-H), 7.79 (d, *J*=7.3 Hz, 2H, Ar-H), 7.61-7.16 (m, 17H, Ar-H), 6.03 (pt, *J*=9.6, 9.5 Hz, 1H, H-4), 5.70 (d, *J*=9.6 Hz, 1H, H-3), 5.55 (pt, *J*=10.0, 9.4 Hz, 1H, H-5), 4.81 (ddd, *J*=10.0, 4.4, 2.5 Hz, 1H, H-6), 4.71 (dd, *J*=12.3, 2.4 Hz, 1H, H-7), 4.43 (dd, *J*=12.3, 4.4 Hz, 1H, H-7'), 3.82 (s, 3H, COOC*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.42, 166.22, 165.63, 165.14, 164.84 (4×O*C*OPh, *C*OOMe), 137.31 (2), 133.57 (2), 133.29, 133.23, 130.07, 130.01, 129.98, 129.91, 129.83, 129.14, 128.82, 128.57, 128.50 (2), 128.36, 127.79 (Ar-C), 89.37 (C-2), 73.91, 71.91, 70.98, 68.90 (C-3 – C-6), 63.07 (C-7), 53.28 (COO*C*H$_3$).

HRMS: m/z calcd. for $C_{42}H_{34}O_{11}SNa$: 769.1714, found: 769.1714 ($M+Na^+$).

Methyl (2-nitrophenyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranoside)onate (41α)



Prepared according to General Method B from **33** (200 mg, 0.407 mmol) and 2-nitrophenol (**37**, 170 mg, 1.22 mmol), reaction time: 8 h.

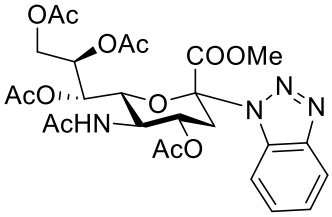
Yield: 143 mg (76%), R_f=0.22 (hexane:acetone=2:1) $[\alpha]_D^{20}$=-3.2 (c=0.97, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J*=8.1 Hz, 1H, ArH), 7.43 (t, *J*=8.0 Hz, 1H, ArH), 7.13 (dd, *J*=7.7, 4.5 Hz, 2H, ArH), 5.58 (d, *J*=10.2 Hz, 1H, NH), 5.49 (dt, *J*=11.0, 4.9 Hz, 1H, H-4), 5.38 (m, 1H, H-7), 4.94 (br, 1H, H-8), 4.65 (dd, *J*=12.5, 2.1 Hz, 1H, H-9), 4.32 (q, *J*=10.5 Hz, 1H, H-5), 4.12 (m, 2H, H-6, H-9'), 3.77 (s, 3H, COOC*H*$_3$), 2.70 (dd, *J*=12.9, 4.8 Hz, 1H, H-3), 2.17 (s, 3H, OCOC*H*$_3$), 2.13 (m, 1H, H-3'), 2.06, 2.04, 1.90 (3×s, 3×3H, OCOC*H*$_3$), 1.75 (s, 3H, NHCOC*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.75, 170.61, 170.57, 170.27, 169.96 (4×O*C*OCH$_3$, *C*OOCH$_3$), 166.66 (NH*C*OCH$_3$), 146.71, 140.59, 134.23, 125.94, 122.74, 117.06 (ArC), 100.03 (C-2), 73.29, 71.09, 68.24, 67.91 (C-4, C-6 – C-8), 61.94 (C-9), 53.64 (COO*C*H$_3$), 48.93 (C-5), 38.09 (C-3), 23.26 (NHCO*C*H$_3$), 20.95, 20.91 (2), 20.82 (4×OCO*C*H$_3$).

HRMS: m/z calcd. for $C_{26}H_{32}N_2O_{15}Na$: 635.1700, found: 635.1695 ($M+Na^+$).

1-[Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate]-benzotriazole (42*α*)



Prepared according to General Method B from **33** (200 mg, 0.407 mmol) and benzotriazole (**13**, 145 mg, , 1.22 mmol), reaction time: 8 h.

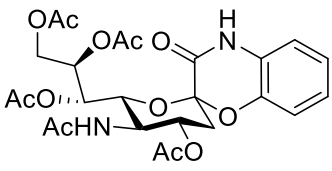
Yield: 151 mg (68%), R_f=0.17 (hexane:acetone=2:1) $[\alpha]_D^{20}$=-7.1 (c=1.02, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dt, *J*=8.37, 0.99 Hz, 1H, ArH), 7.53 (ddd, *J*=8.1, 7.1, 1.1 Hz, 1H, ArH), 7.50 (m, 1H, ArH), 7.39 (ddd, *J*=8.1, 6.7, 1.3 Hz, 1H, ArH), 5.81 (dt, *J*=10.9, 5.2 Hz, 1H, H-4), 5.55 (d, *J*=10.4 Hz, 1H, NH), 5.34 (dd, *J*=4.8, 2.3 Hz, 1H, H-7), 4.94 (m, 1H, H-8), 4.73 (dd, *J*=12.6, 2,3 Hz, 1H, H-9), 4.43 (q, *J*=10.5 Hz, 1H, H-5), 4.19 (dd *J*=12.6, 6.4 Hz, 1H, H-9'), 3.75 (s, 3H, COOC*H*$_3$), 3.49 (dd, *J*=10.7, 2.3 Hz, 1H, H-6), 2.47 (dd, *J*=13.7, 11.2 Hz, 1H, H-3), 2.19 (s, 3H, OCOC*H*$_3$), 2.09 – 2.07 (2×s+1×br, 7H, 2×OCOC*H*$_3$ + H-3'), 1.84 (s, 3H, OCOC*H*$_3$), 1.57 (s, 3H, NHCOC*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.79, 170.64 (2), 170.22, 170.01 (4×O*C*OCH$_3$, *C*OOCH$_3$), 166.04 (NH*C*OCH$_3$), 146.56, 133.47, 129.11, 125.16, 120.44, 111.11 (ArC), 89.22 (C-2), 73.51, 71.60, 69.44, 67.91 (C-4, C-6 – C-8), 62.09 (C-9), 54.01 (COO*C*H$_3$), 49.04 (C-5), 35.70 (C-3), 23.28 (NHCO*C*H$_3$), 21.03, 20.95, 20.94, 20.62 (4×OCO*C*H$_3$).

HRMS: m/z calcd. for $C_{26}H_{32}N_4O_{12}Na$: 615.1914, found: 615.1909 ($M+Na^+$).

(1'*S*)-4-acetamido-3',6',7',8'-tetra-*O*-acetyl-2',4'-dideoxy-spiro-{1',5'-anhydro-D-*glycero*-D-*galacto*-octitol-1',2-benzo[*b*][1,4]oxazin-3(4*H*)-one} (44)



2-Nitroaryl-*O*-glycoside **41** (120 mg, 0.196 mmol) was dissolved in dry EtOAc (5 mL) in a round-bottom flask, and 10w% Pd/C (20 mg) was added while stirring. The flask was placed under hydrogen atmosphere using a gas burette. The reaction mixture was stirred at room temperature for 2 hours, then TLC showed completion of the reaction (hexane:acetone=2:1). The catalyst was filtered over a celite

pad, the solvent was evaporated, and the crude product was purified by column chromatography (hexane:acetone=2.5:1 to 2:1).

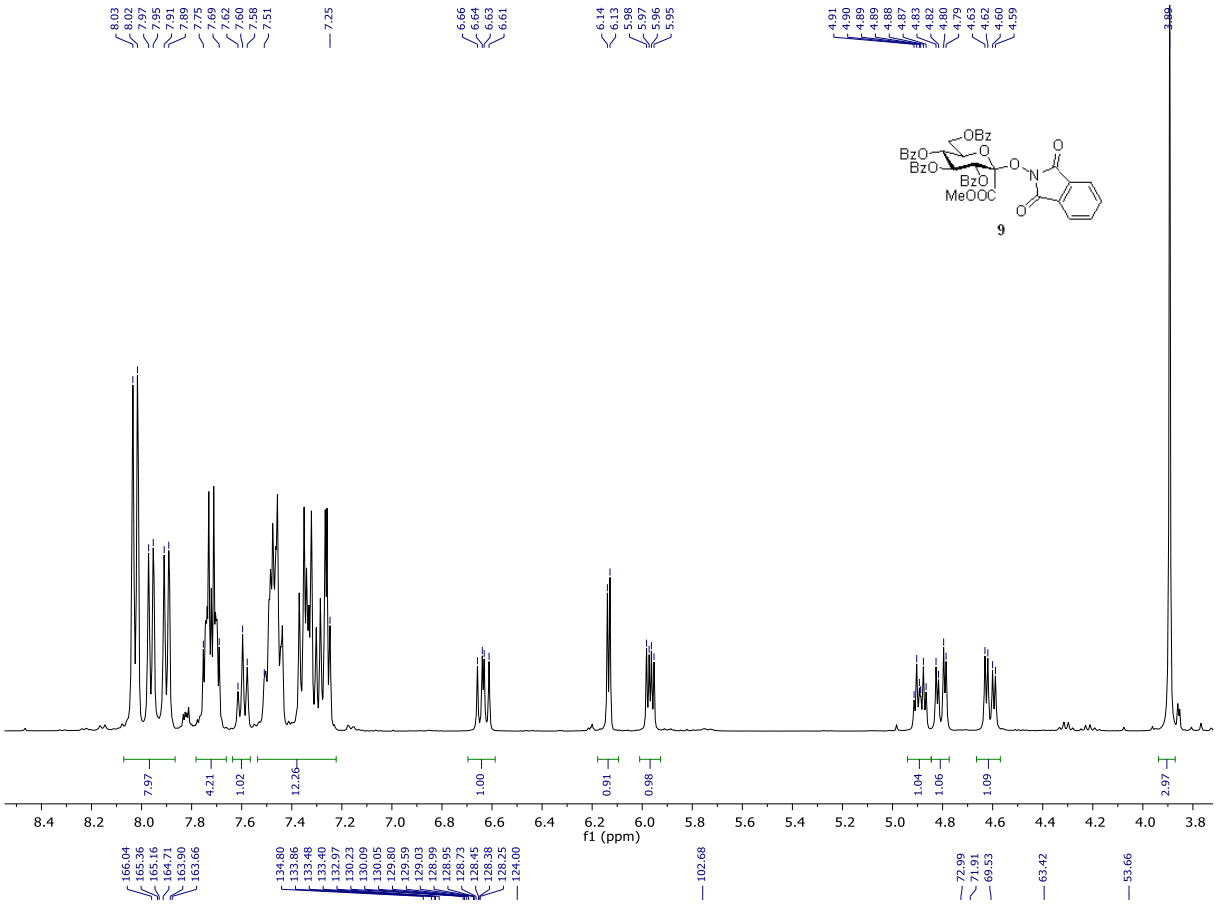
Yield: 73 mg (68%), R_f=0.19 (hexane:acetone=2:1) $[\alpha]_D^{20}$=-11 (c=1.08, $CHCl_3$)

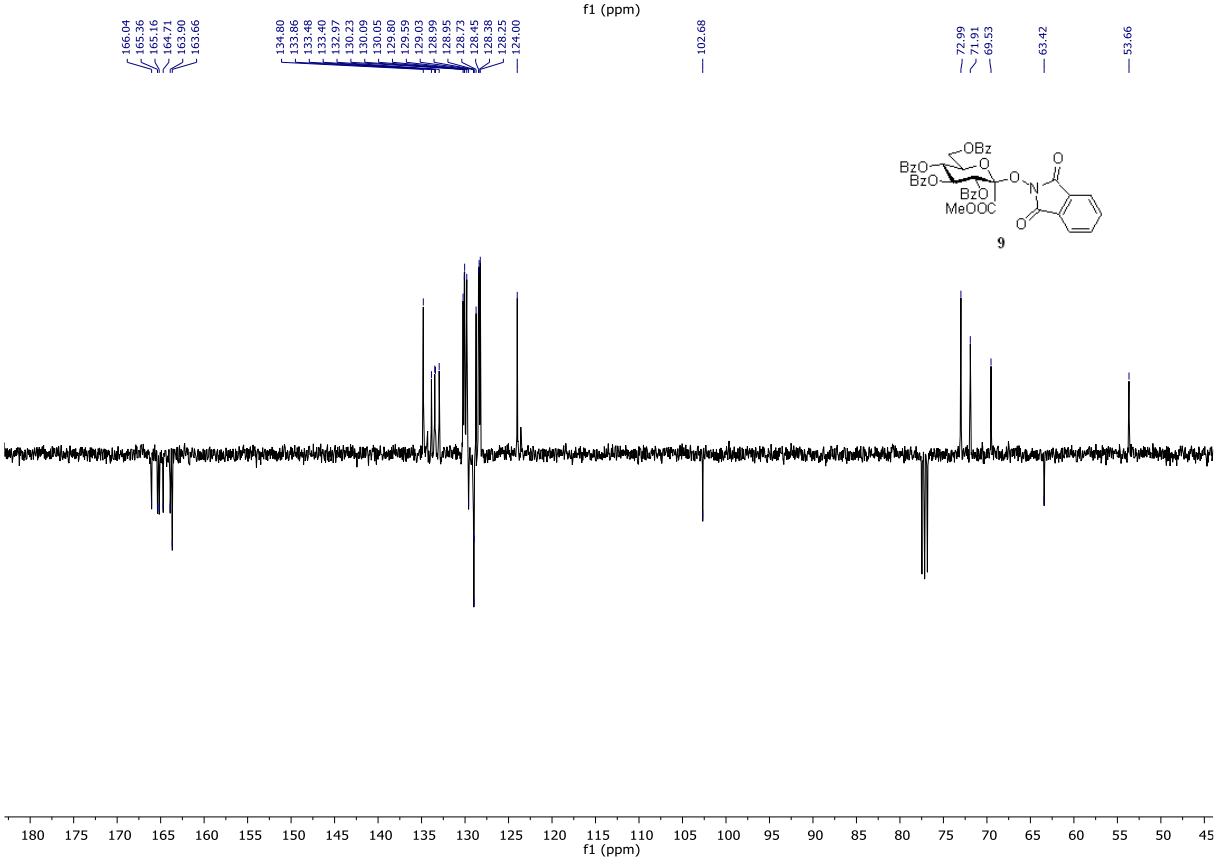
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H, ring-CON*H*), 7.08-6.98 (m, 3H, ArH), 6.93 (d, *J*=7.6 Hz, 1H, ArH), 5.89 (d, *J*=9.2 Hz, 1H, N-acetyl-N*H*), 5.55 (dt, *J*=11.5, 5.2 Hz, 1H, H-3'), 5.31 (d, *J*=2.7 Hz, 1H, H-6'), 4.38 (ddd, *J*=6.8, 4.0, 2.5 Hz, 1H, H-7'), 4.26-4.16 (m, 2H, H-4, H-8a'), 4.06 (dd, *J*=12.3, 2.2 Hz, 1H, H-8b'), 3.8 (dd, *J*=12.3, 7.4 Hz, 1H, H-5'), 2.76 (t, *J*=12.4 Hz, 1H, H-2a'), 2.42 (dd, *J*=13.6, 5.1 Hz, 1H, H-2b'), 2.10, 2.07, 1,95, 1.92, 1.89 (5×s, 5×3H, 4×OCOC*H*$_3$+NHCOC*H*$_3$).

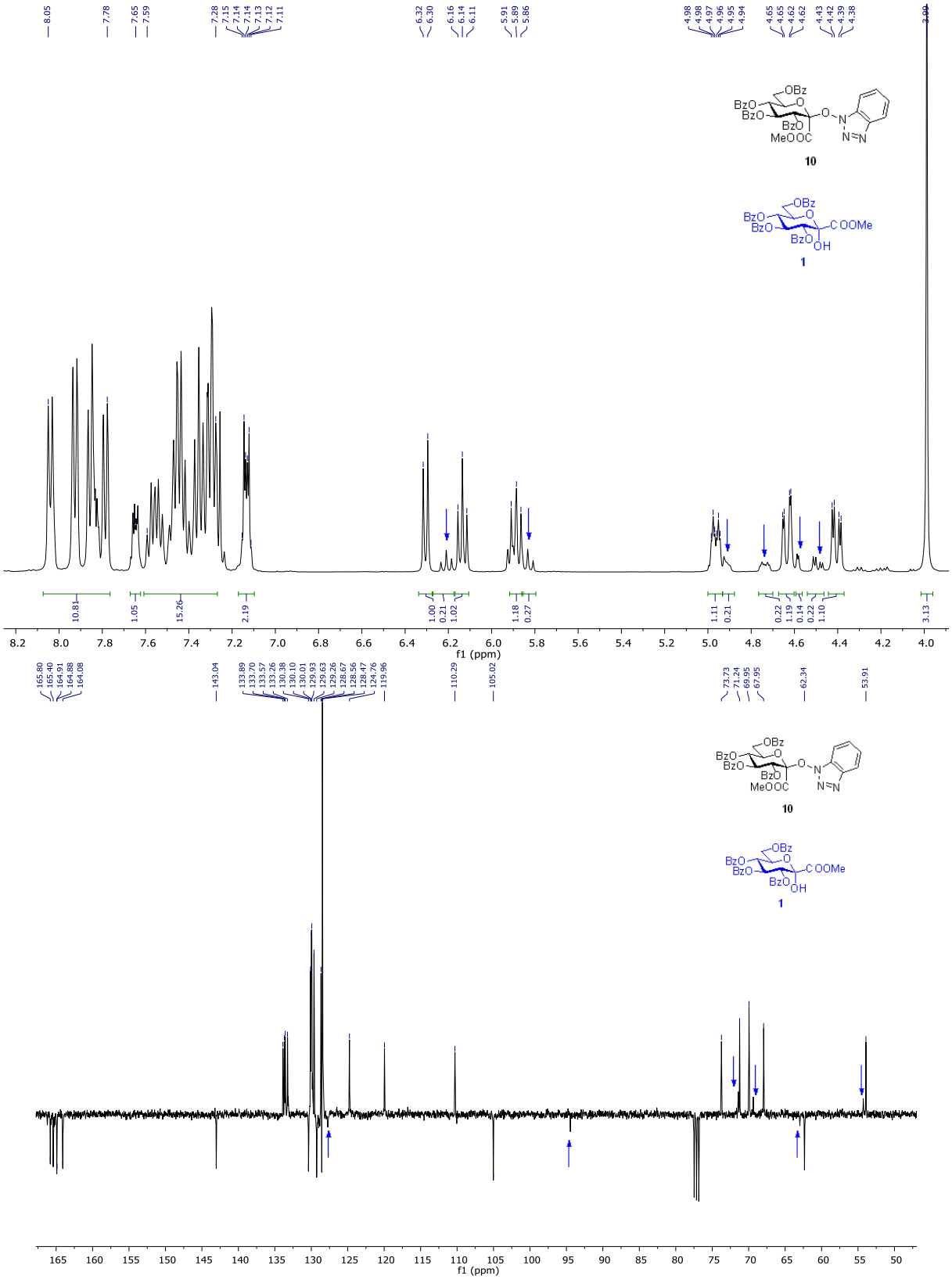
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.39 (ring-*C*ONH), 170.50, 170.46, 170.41, 170.22 (4×O*C*OCH$_3$), 161.07 (NH*C*OCH$_3$), 139.75, 126.56, 124.47, 123.83, 117.25, 116.21 (ArC), 97.32 (C-1'), 72.05, 71.83, 69.10, 67.81 (C-3', C-5' – C-7'), 62.04 (C-8'), 49.44 (C-4'), 33.61 (C-2'), 23.27 (NHCO*C*H$_3$), 21.11, 21.06, 20.91, 20.77 (4×OCO*C*H$_3$*)*.

HRMS: m/z calcd. for $C_{25}H_{30}N_2O_{12}Na$: 573.1696, found: 573.1691 ($M+Na^+$).

Copies of the NMR spectra



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3.99
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15.26
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1.00
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1.18
0.27
1.11
0.21
0.22
1.19
0.14
0.22
1.10
3.13
f1 (ppm)
OBz
BzO
BzO
BzO
MeOOC
O
N
N=N
10
C OOMe
OH
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164.88
164.08
143.04
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67.95
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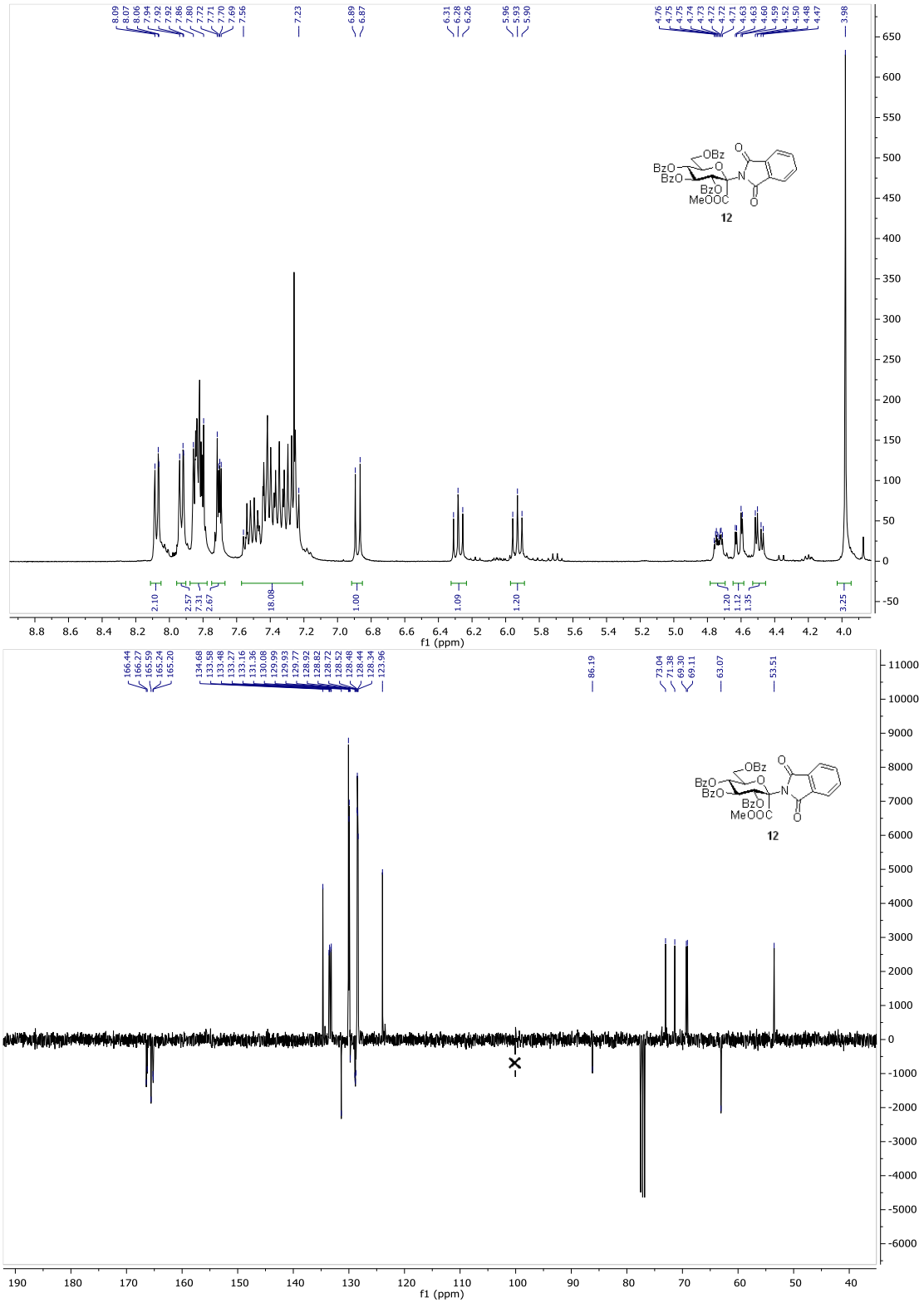
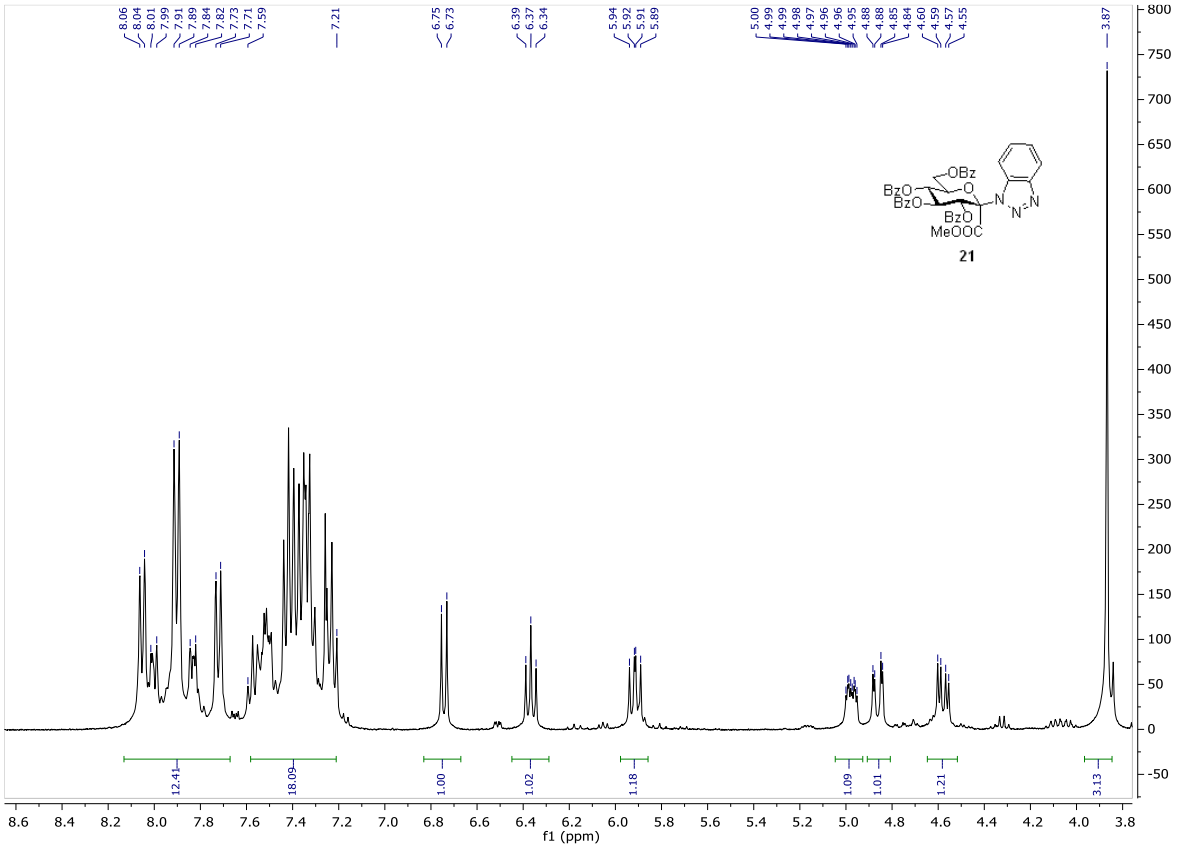
53.91
f1 (ppm)



The signal at 100 ppm is a result of an artifact from the NMR spectrometer, and is not part of the compound's spectrum.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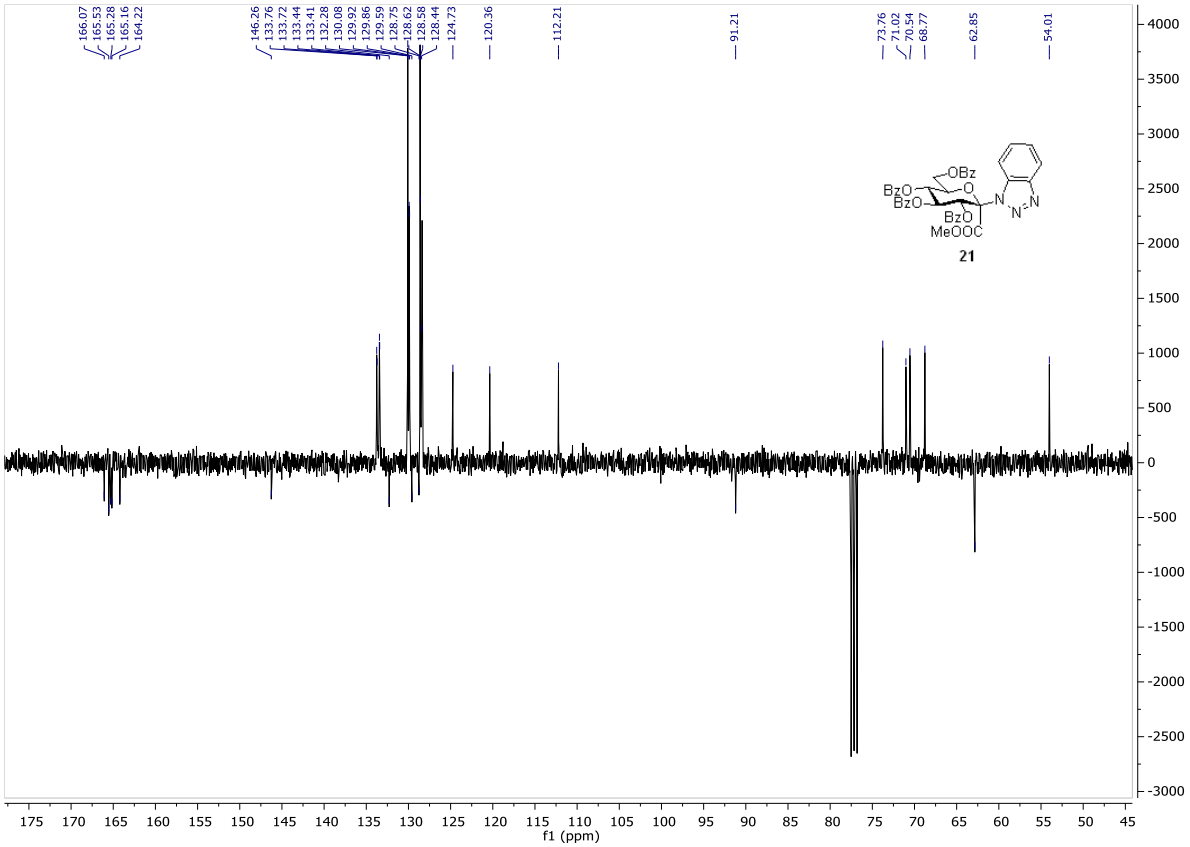
4.88
4.85
4.84
4.60
4.59
4.57
4.55
3.87
12.41
18.09
1.00
1.02
1.18
1.09
1.01
1.21
3.13
f1 (ppm)
OBz
BzO
BzO
BzO
MeOOC
N
N
N
21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133.72
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133.41
132.28
130.08
129.92
129.86
129.59
128.75
128.62
128.58
128.44
124.73
120.36
112.21
91.21
73.76
71.02
70.54
68.77
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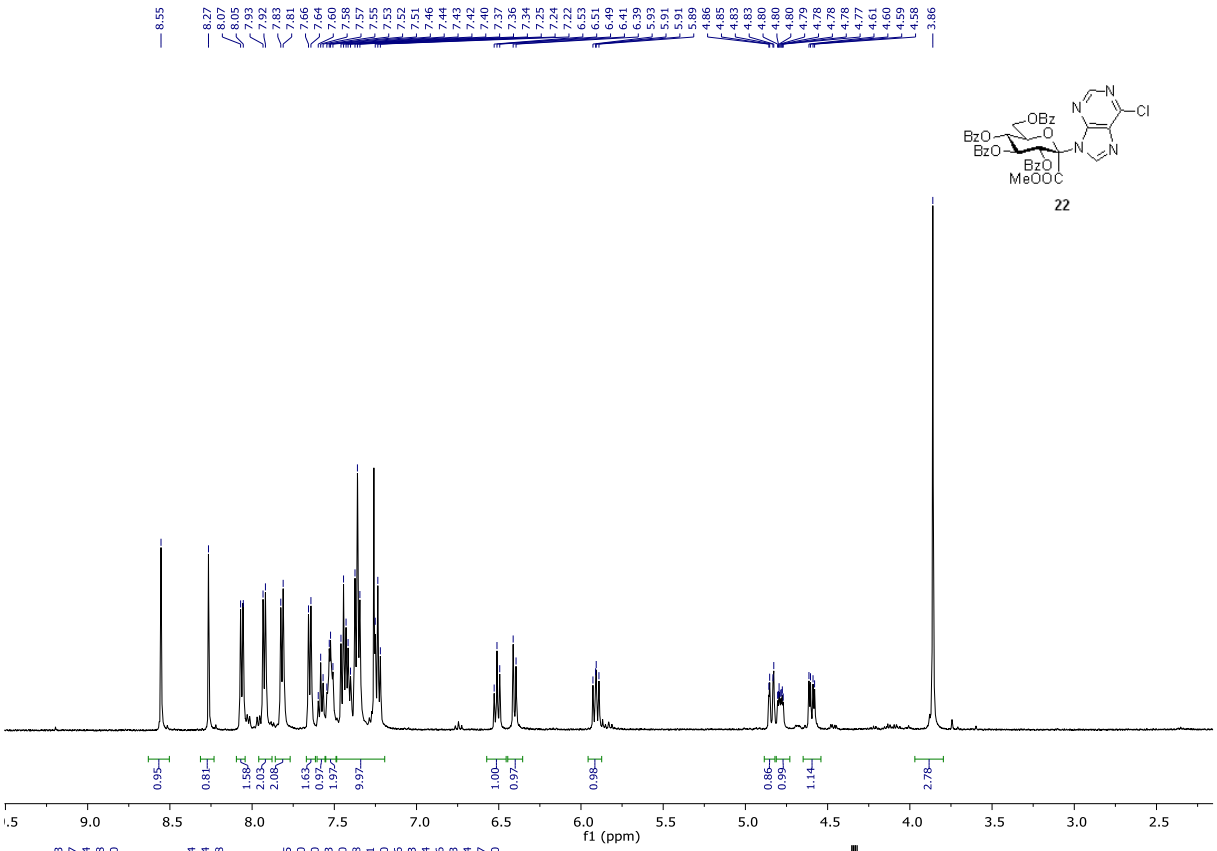
54.01
f1 (ppm)
OBz
BzO
BzO
BzO
MeOOC
N
N
N
21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7.81
7.66
7.64
7.60
7.58
7.57
7.55
7.53
7.52
7.51
7.46
7.44
7.43
7.42
7.40
7.37
7.36
7.34
7.25
7.24
7.22
6.53
6.51
6.49
6.41
6.39
5.93
5.91
5.91
5.89
4.86
4.85
4.83
4.83
4.80
4.80
4.80
4.79
4.78
4.78
4.78
4.77
4.61
4.60
4.59
4.58
3.86
OBz
O
BzO
BzO
BzO
MeOOC
N
N
N
N
Cl
22
0.95
0.81
1.58
2.03
2.08
1.63
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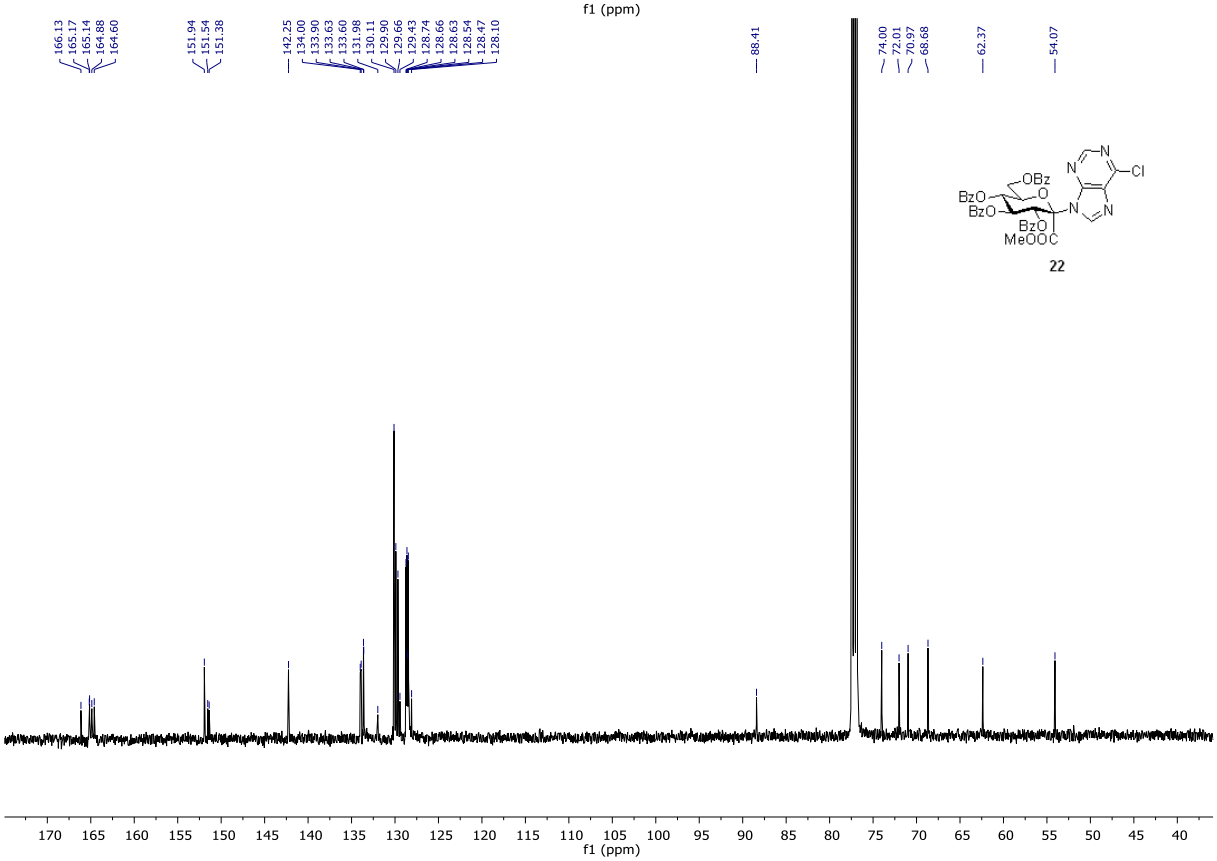
1.97
9.97
1.00
0.97
0.98
0.86
0.99
1.14
2.78
f1 (ppm)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165.17
165.14
164.88
164.60
151.94
151.54
151.38
142.25
134.00
133.90
133.63
133.60
131.98
130.11
129.90
129.66
129.43
128.74
128.66
128.63
128.54
128.47
128.10
88.41
74.00
72.01
70.97
68.68
62.37
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O
BzO
BzO
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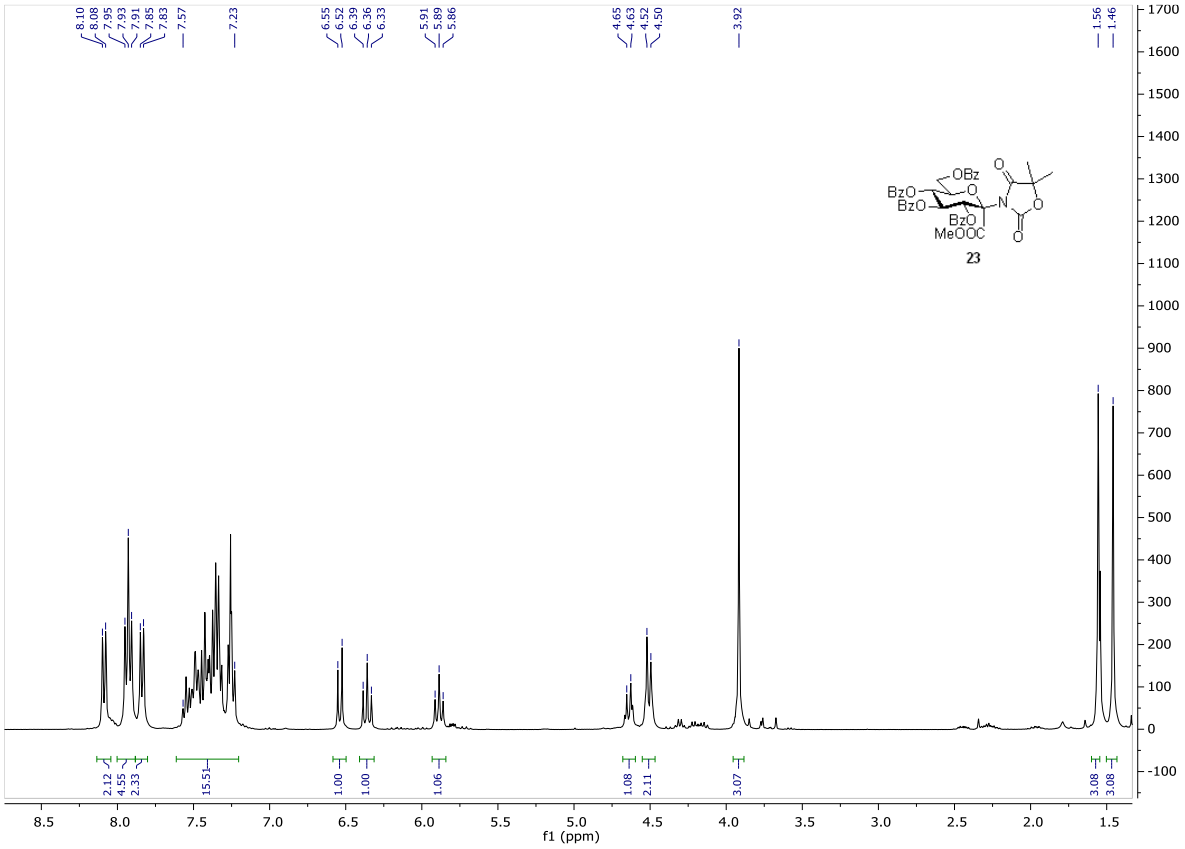
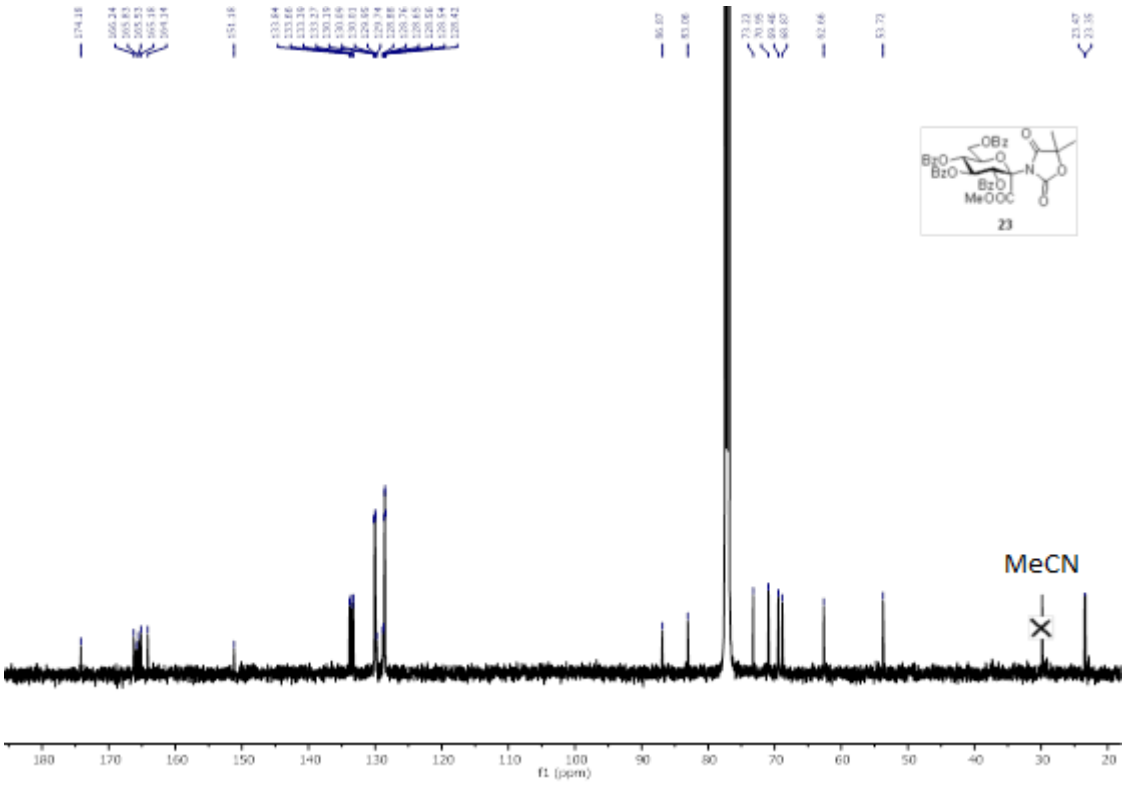
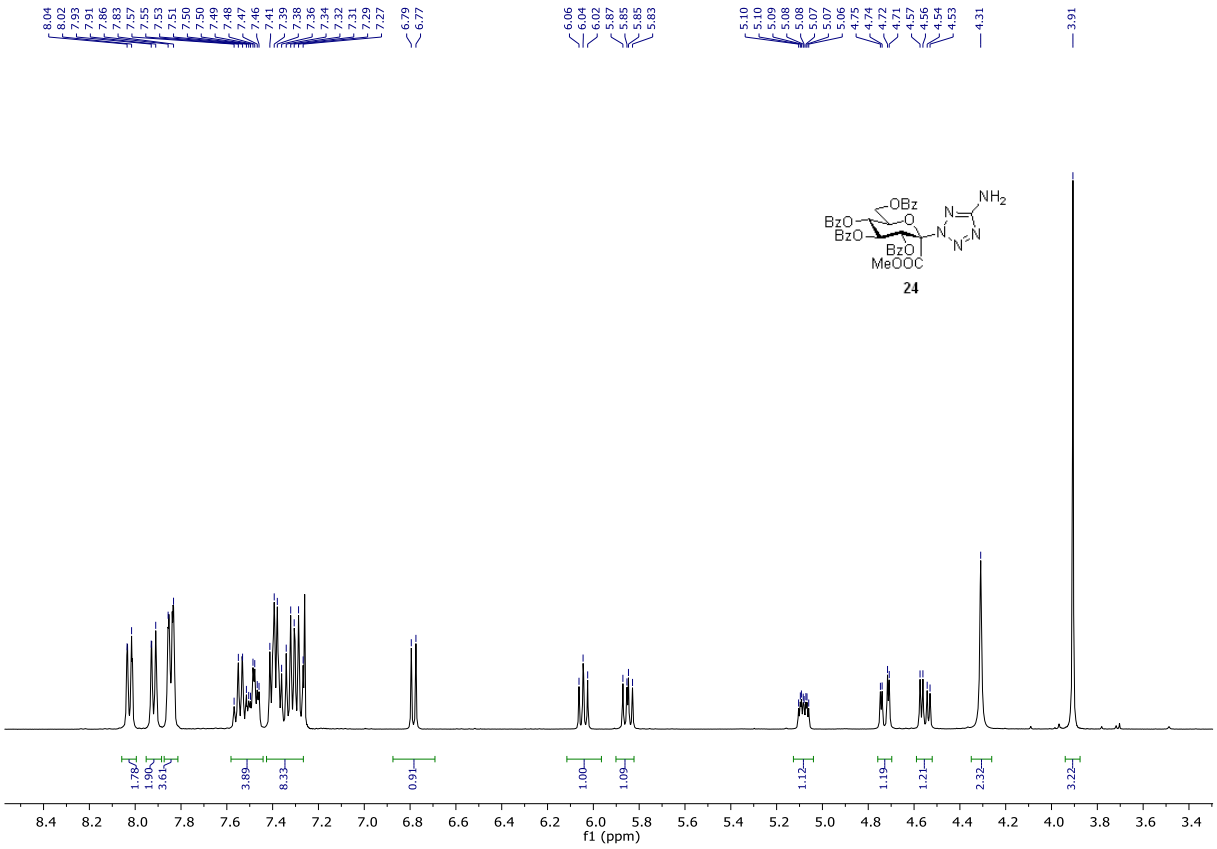
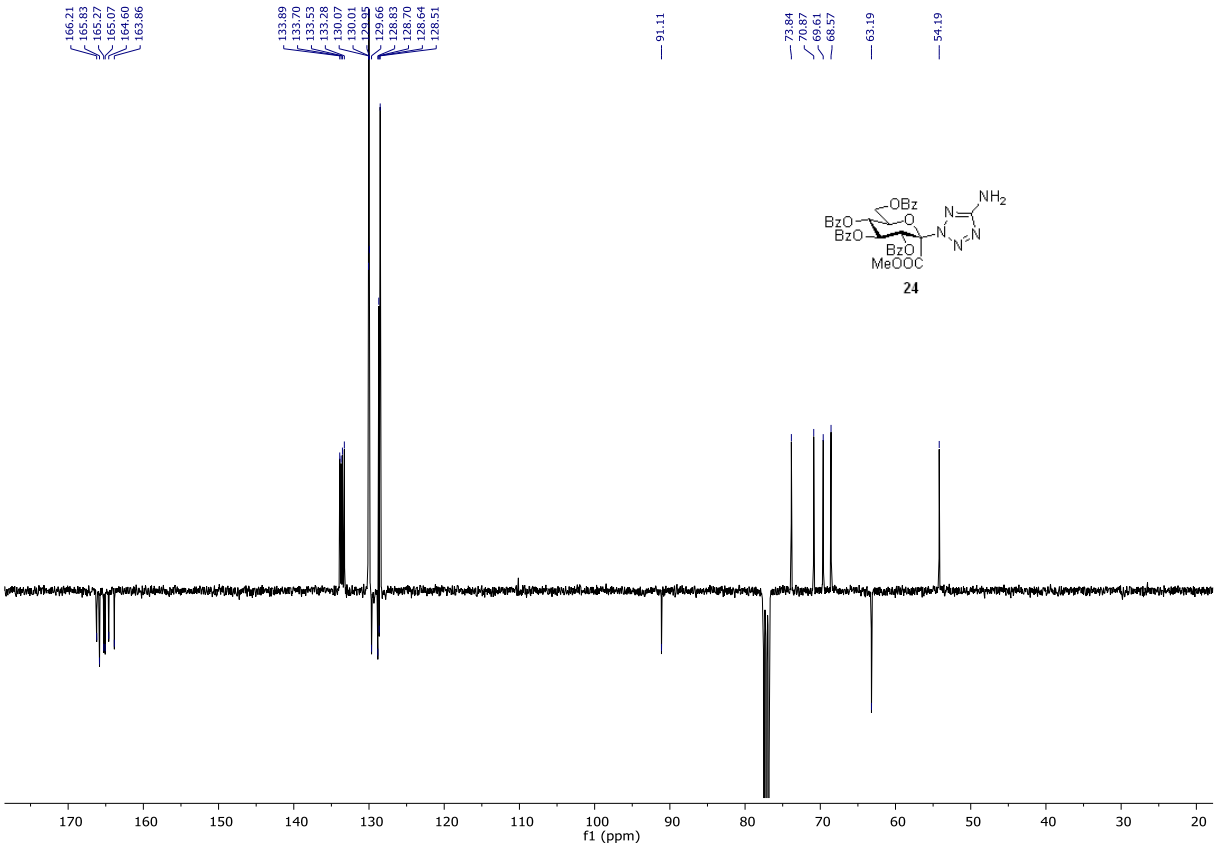
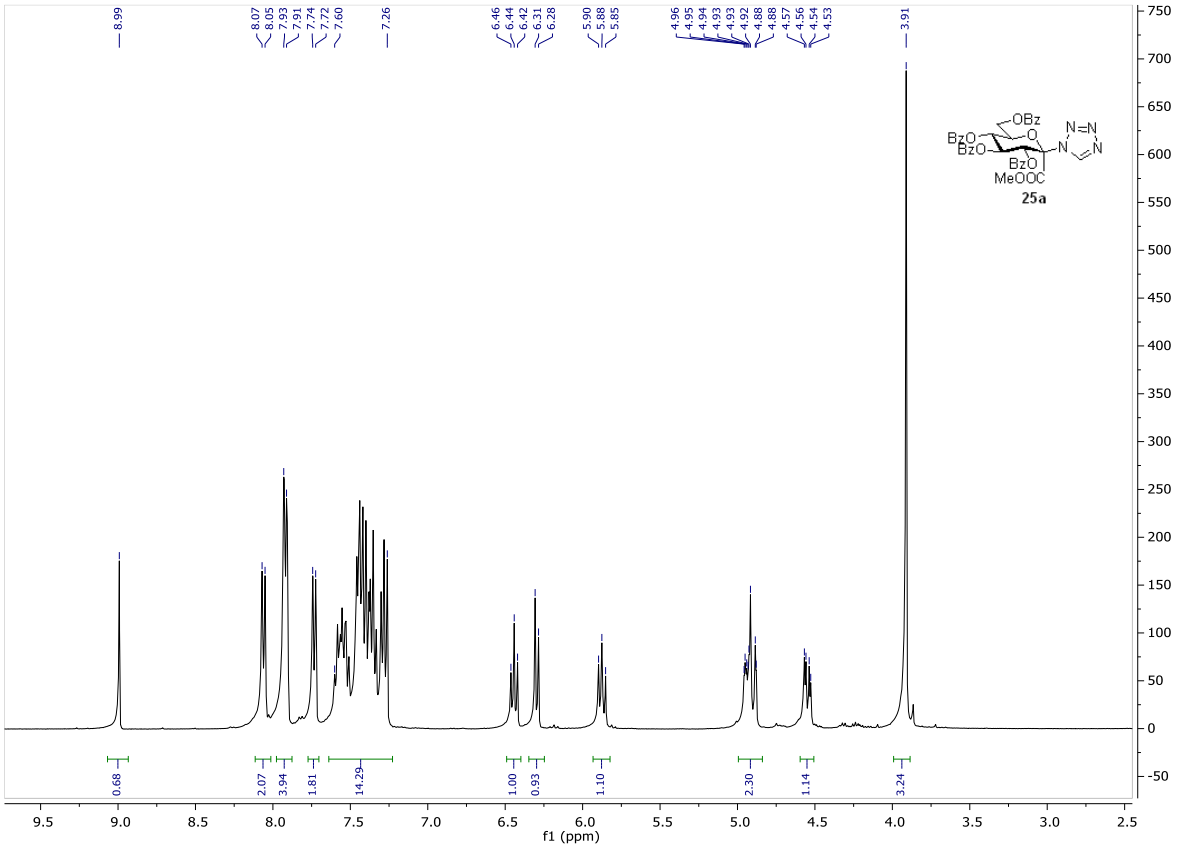
MeOOC
N
N
N
N
Cl
22
f1 (ppm)

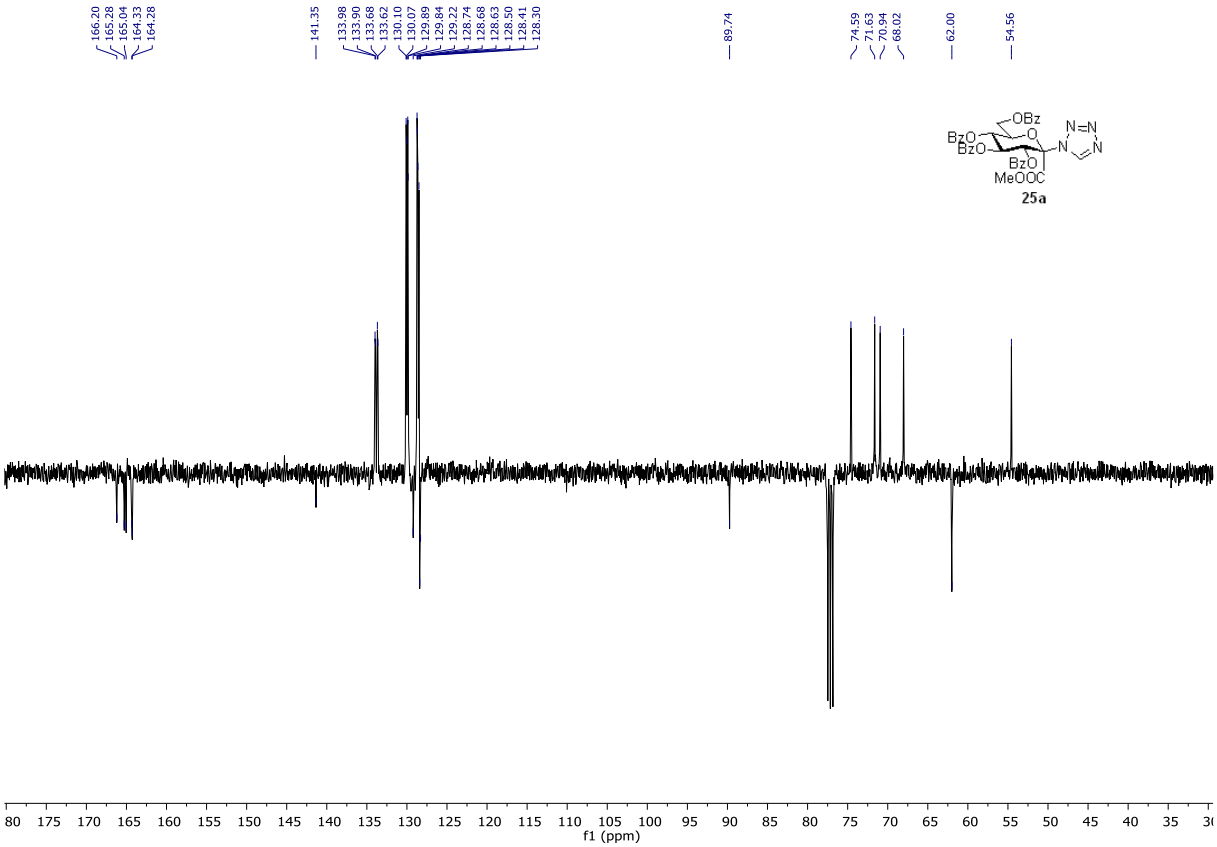

8.10
8.08
7.95
7.93
7.91
7.85
7.83
7.57
7.23
6.55
6.52
6.39
6.36
6.33
5.91
5.89
5.86
4.65
4.63
4.52
4.50
3.92
1.56
1.46
OBz
BzO
BzO
BzO
MeOOC
O
O
N
O
O
23
2.12
4.55
2.33
15.51
1.00
1.00
1.06
1.08
2.11
3.07
3.08
3.08
f1 (ppm)


OBz
BzO
BzO
BzO
MeOOC
O
O
N
O
O
23
MeCN
f1 (ppm)


8.04 8.02 7.93 7.91 7.86 7.83 7.57 7.55 7.53 7.51 7.50 7.50 7.49 7.48 7.47 7.46 7.41 7.39 7.38 7.36 7.34 7.32 7.31 7.29 7.27 6.79 6.77
6.06 6.04 6.02 5.87 5.85 5.85 5.83
5.10 5.10 5.09 5.08 5.08 5.07 5.07 5.06 4.75 4.74 4.72 4.71 4.57 4.56 4.54 4.53 4.31 3.91
OBz
BzO
BzO
BzO
MeOOC
NH2
24
1.78 1.90 3.61 3.89 8.33 0.91 1.00 1.09 1.12 1.19 1.21 2.32 3.22
f1 (ppm)


166.21 165.83 165.27 165.07 164.60 163.86
133.89 133.70 133.53 133.28 130.07 130.01 129.45 129.66 128.83 128.70 128.64 128.51
91.11
73.84 70.87 69.61 68.57
63.19
54.19
OBz
BzO
BzO
BzO
MeOOC
NH2
24
f1 (ppm)


8.99
8.07
8.05
7.93
7.91
7.74
7.72
7.60
7.26
6.46
6.44
6.42
6.31
6.28
5.90
5.88
5.85
4.96
4.95
4.94
4.93
4.93
4.92
4.88
4.88
4.57
4.56
4.54
4.53
3.91
0.68
2.07
3.94
1.81
14.29
1.00
0.93
1.10
2.30
1.14
3.24
f1 (ppm)
OBz
BzO
BzO
BzO
MeOOC
N=N
N
N
25a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165.28
165.04
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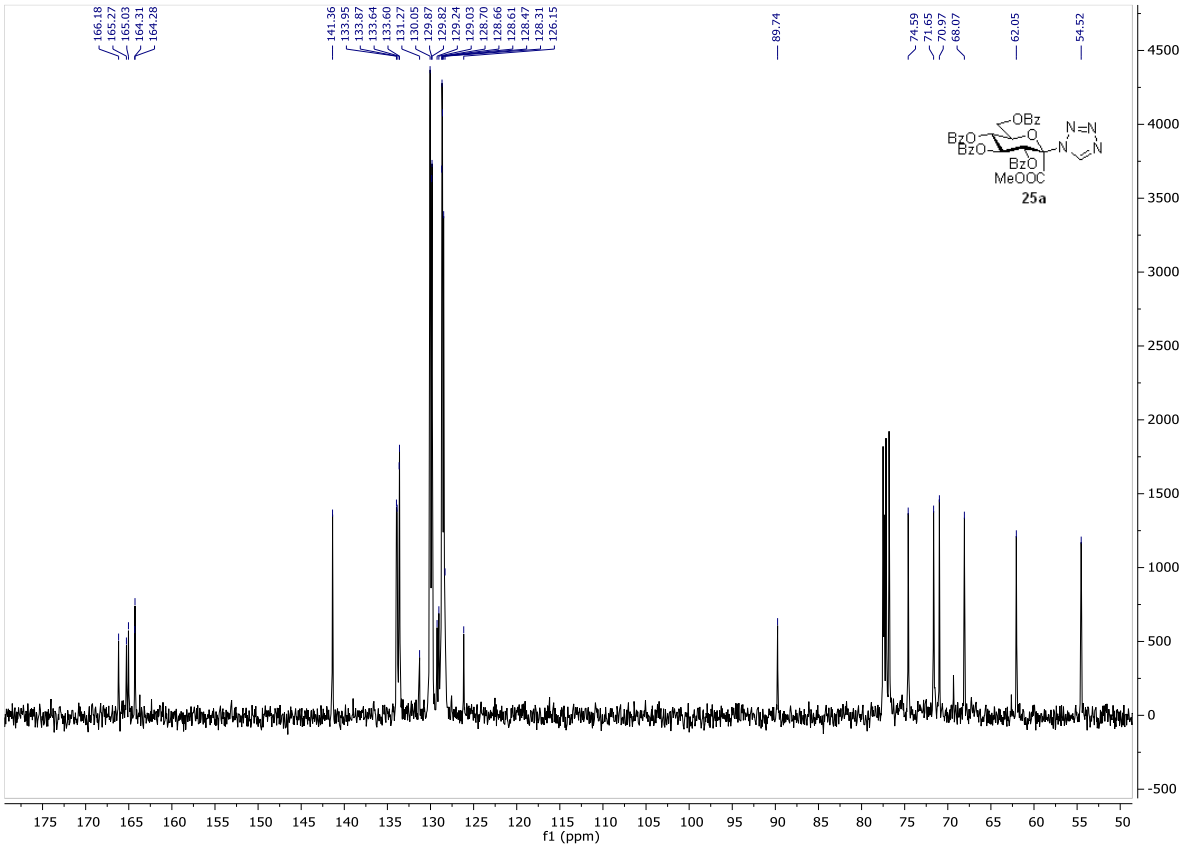
164.28
141.35
133.98
133.90
133.68
133.62
130.10
130.07
129.89
129.84
129.22
128.74
128.68
128.63
128.50
128.41
128.30
89.74
74.59
71.63
70.94
68.02
62.00
54.56
f1 (ppm)
OBz
BzO
BzO
BzO
MeOOC
N=N
N
N
25a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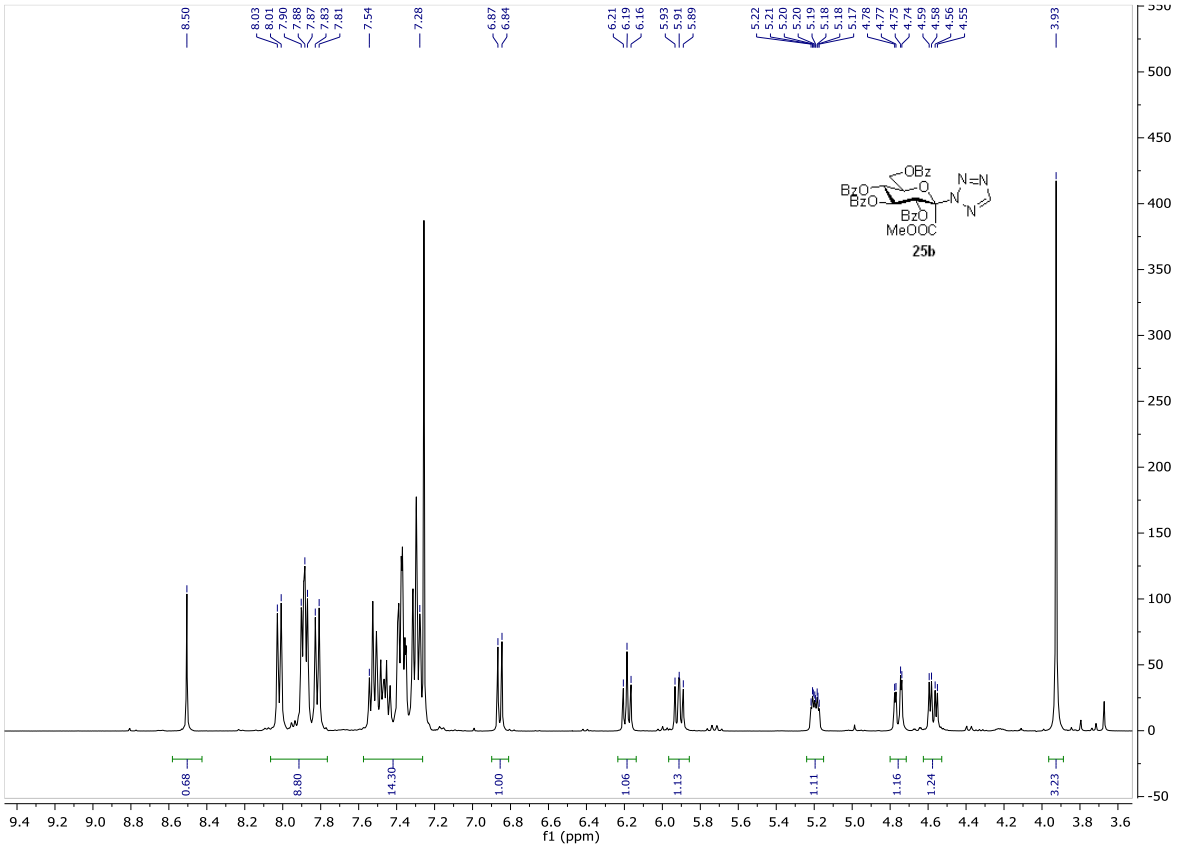
165.27
165.03
164.31
164.28
141.36
133.95
133.87
133.64
133.60
131.27
130.05
129.87
129.82
129.24
129.03
128.70
128.66
128.61
128.47
128.31
126.15
89.74
74.59
71.65
70.97
68.07
62.05
54.52
OBz
BzO
BzO
BzO
MeOOC
N=N
N
N
25a
f1 (ppm)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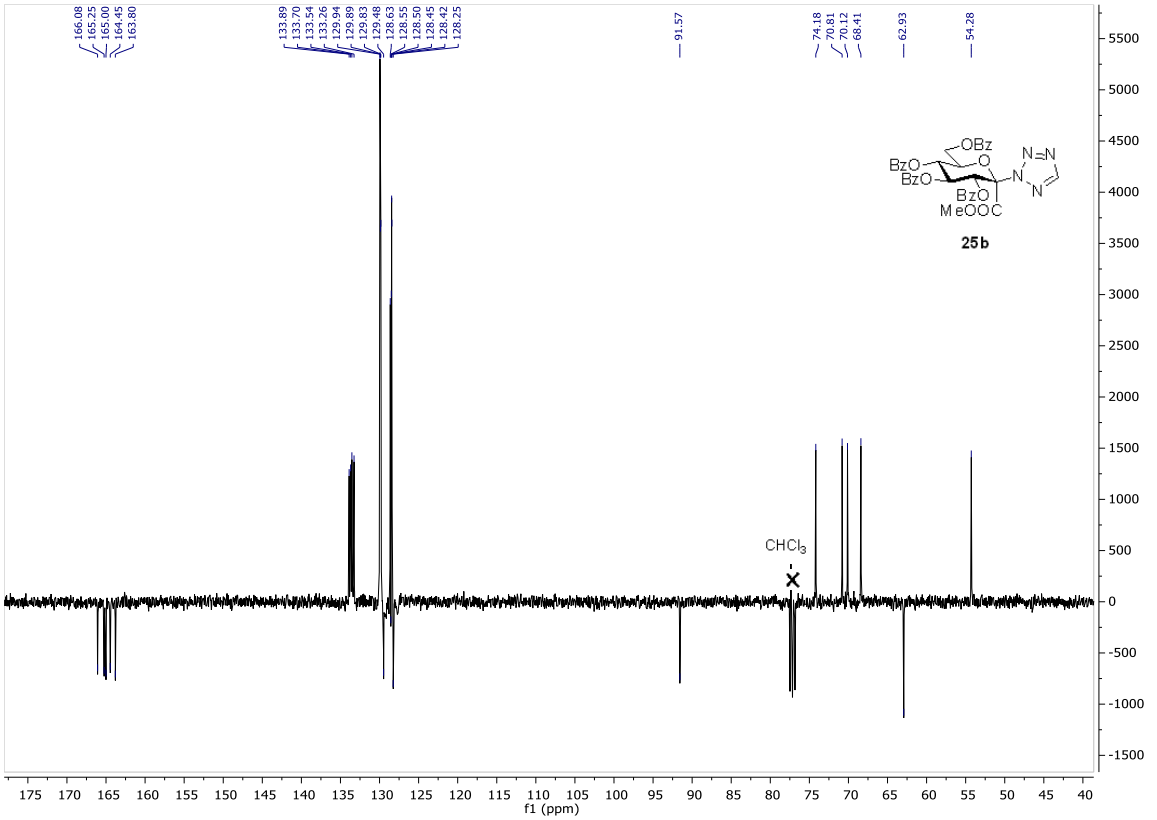
7.87
7.83
7.81
7.54
7.28
6.87
6.84
6.21
6.19
6.16
5.93
5.91
5.89
5.22
5.21
5.20
5.20
5.19
5.18
5.18
5.17
4.78
4.77
4.75
4.74
4.59
4.58
4.56
4.55
3.93
OBz
BzO
BzO
BzO
MeOOC
N=N
25b
0.68
8.80
14.30
1.00
1.06
1.13
1.11
1.16
1.24
3.23
f1 (ppm)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165.00
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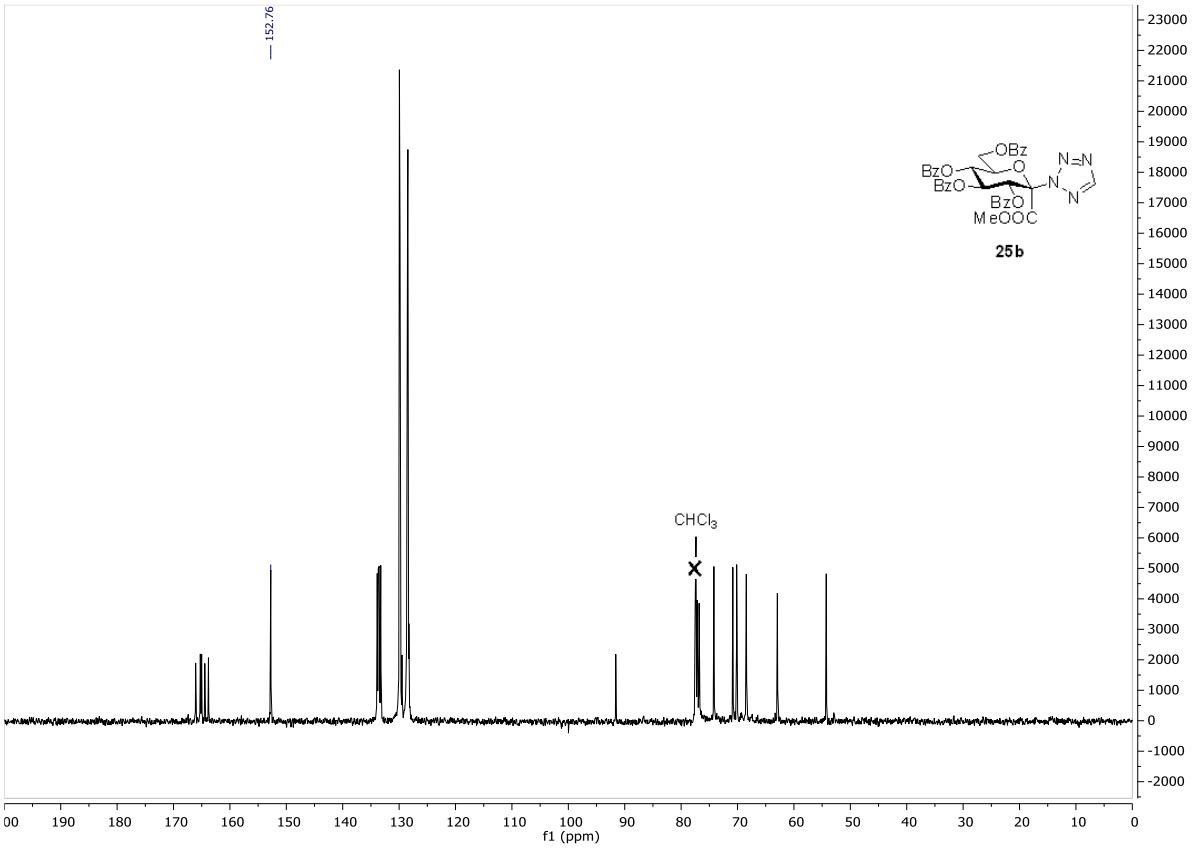
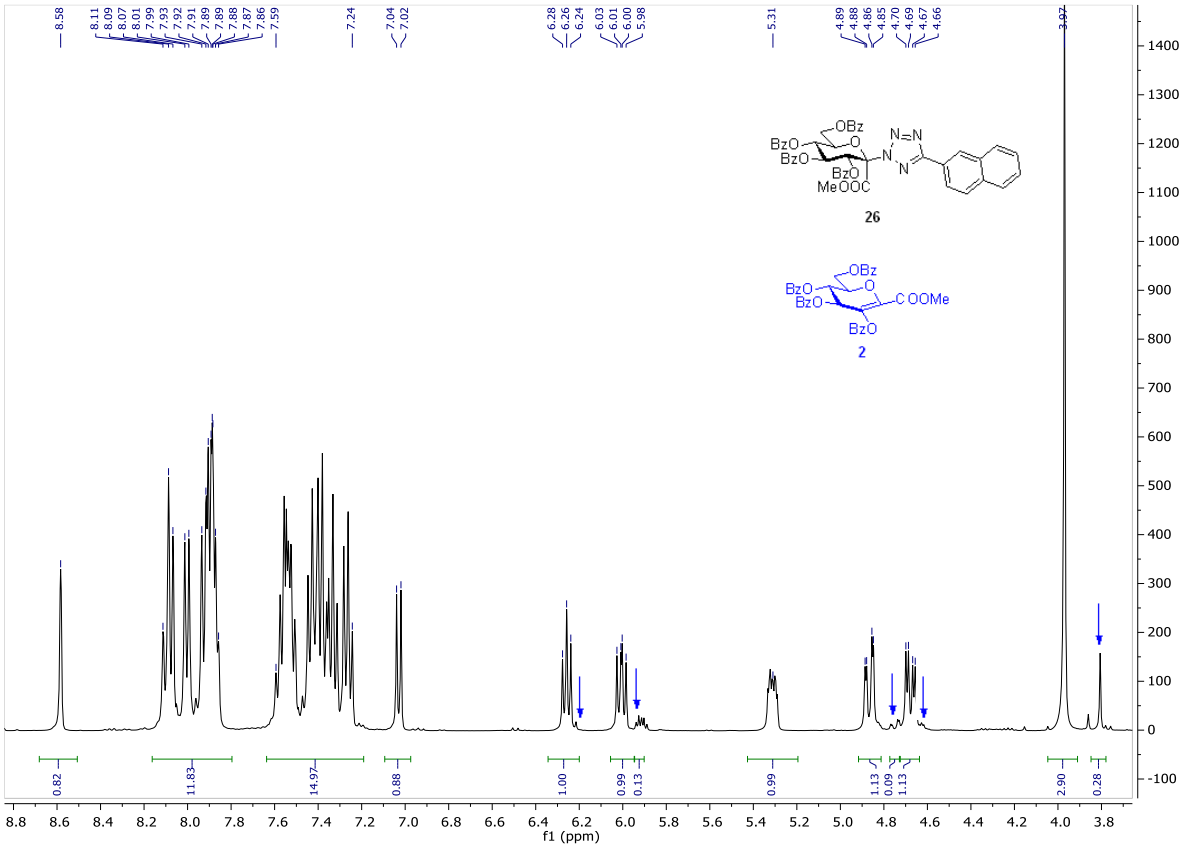
133.89
133.70
133.54
133.26
129.94
129.89
129.83
129.48
128.63
128.55
128.50
128.45
128.42
128.25
91.57
74.18
70.81
70.12
68.41
62.93
54.28
CHCl3
OBz
BzO
BzO
BzO
MeOOC
N=N
25b
f1 (ppm)


152.76
CHCl3
OBz
BzO
BzO
BzO
MeOOC
N=N
N
N
25b
f1 (ppm)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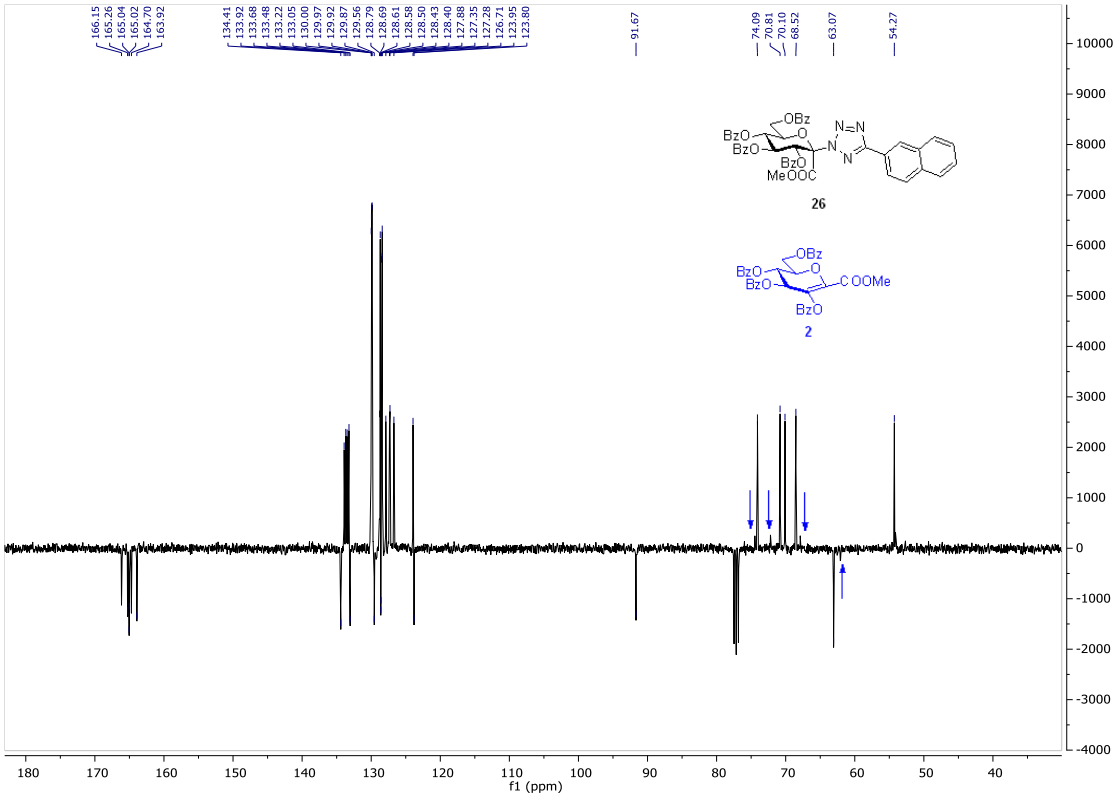
8.09
8.07
8.01
7.99
7.93
7.92
7.91
7.89
7.88
7.87
7.86
7.59
7.24
7.04
7.02
6.28
6.26
6.24
6.03
6.01
6.00
5.98
5.31
4.89
4.88
4.86
4.85
4.70
4.69
4.67
4.66
3.97
OBz
BzO
BzO
BzO
MeOOC
N=N
N
N
26
OBz
BzO
BzO
C OOMe
BzO
2
0.82
11.83
14.97
0.88
1.00
0.99
0.13
0.99
1.13
0.09
1.13
2.90
0.28
f1 (ppm)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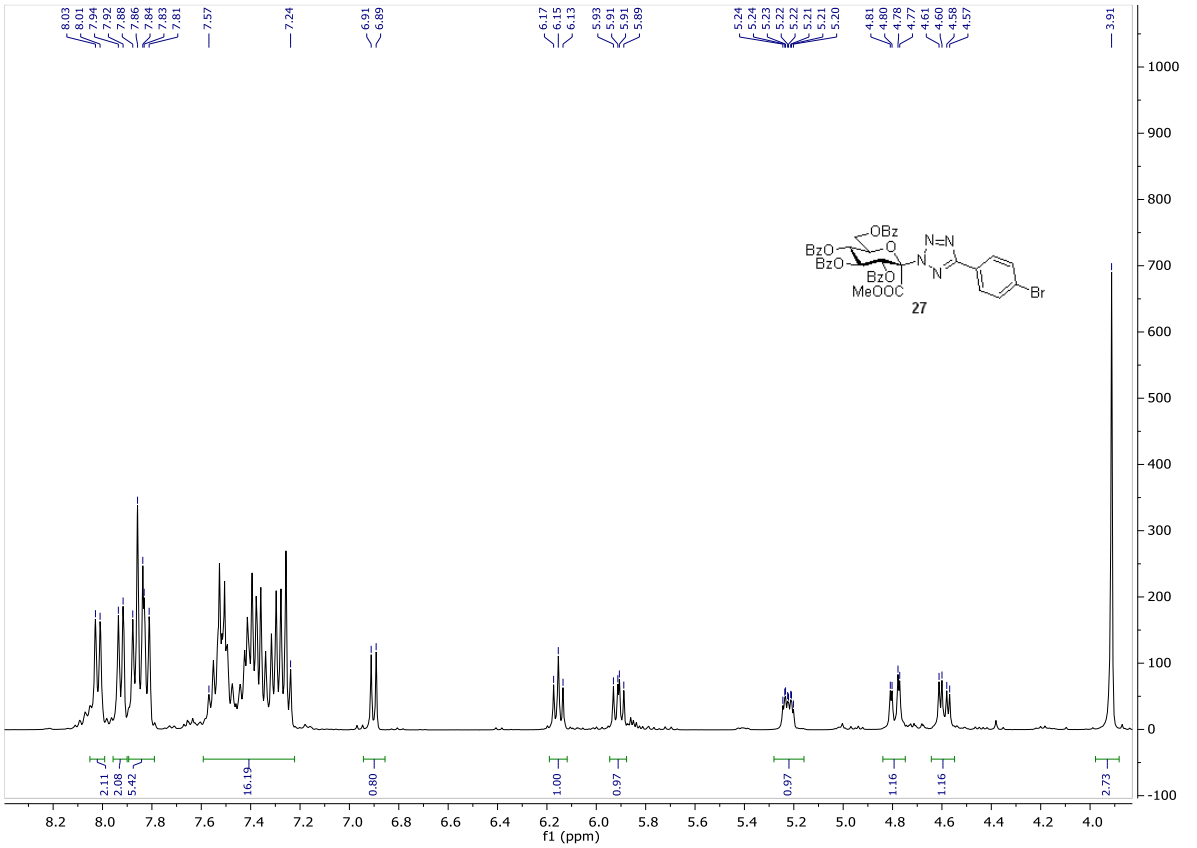
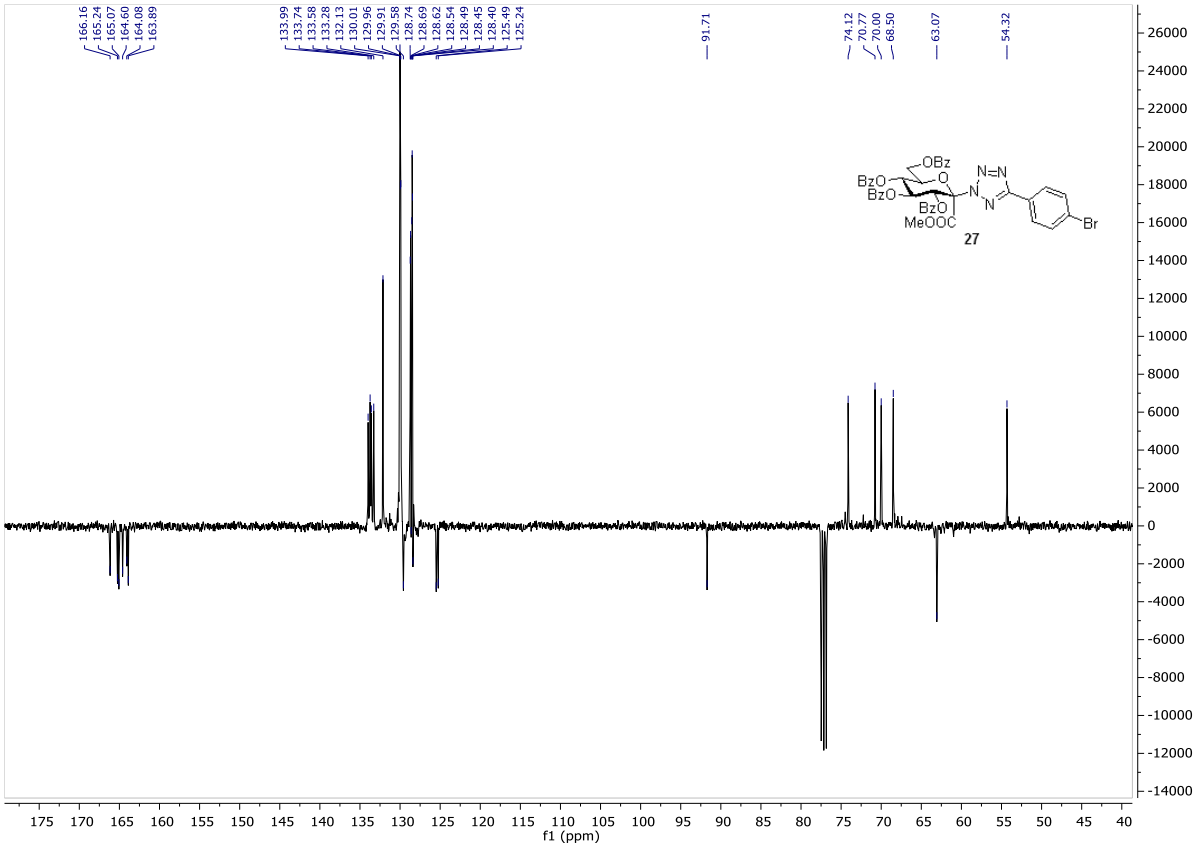
134.41
133.92
133.68
133.48
133.22
133.05
130.00
129.97
129.92
129.87
129.56
128.79
128.69
128.61
128.58
128.50
128.43
128.40
127.88
127.35
127.28
126.71
123.95
123.80
91.67
74.09
70.81
70.10
68.52
63.07
54.27
OBz
BzO
BzO
BzO
MeOOC
N=N
N
N
26
OBz
BzO
BzO
C OOMe
BzO
2
f1 (ppm)


8.03
8.01
7.94
7.92
7.88
7.86
7.84
7.83
7.81
7.57
7.24
6.91
6.89
6.17
6.15
6.13
5.93
5.91
5.91
5.89
5.24
5.24
5.23
5.22
5.22
5.21
5.21
5.20
4.81
4.80
4.78
4.77
4.61
4.60
4.58
4.57
3.91
OBz
BzO
BzO
BzO
MeOOC
N=N
N
N
Br
27
2.11
2.08
5.42
16.19
0.80
1.00
0.97
0.97
1.16
1.16
2.73
f1 (ppm)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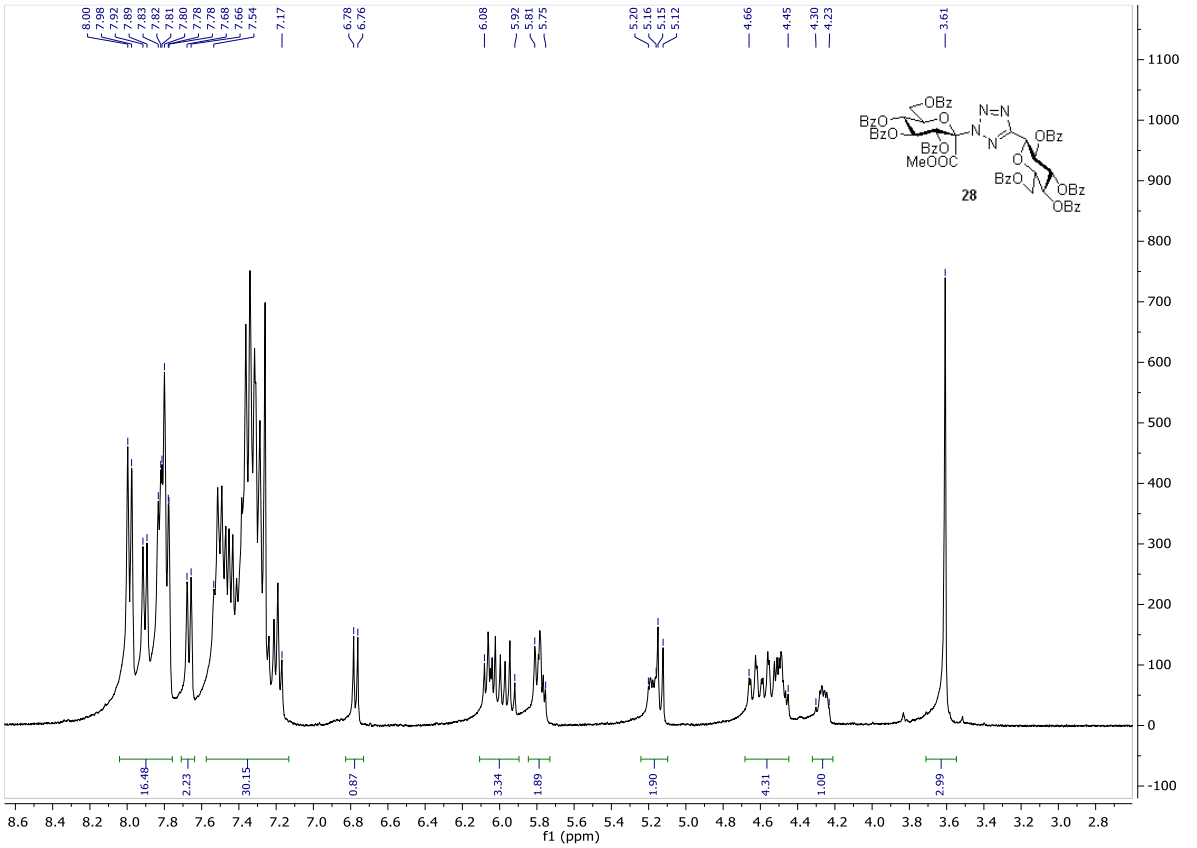
164.08
163.89
133.99
133.74
133.58
133.28
132.13
130.01
129.96
129.91
129.58
128.74
128.69
128.62
128.54
128.49
128.45
128.40
125.49
125.24
91.71
74.12
70.77
70.00
68.50
63.07
54.32
OBz
BzO
BzO
BzO
MeOOC
N=N
N
N
Br
27
f1 (ppm)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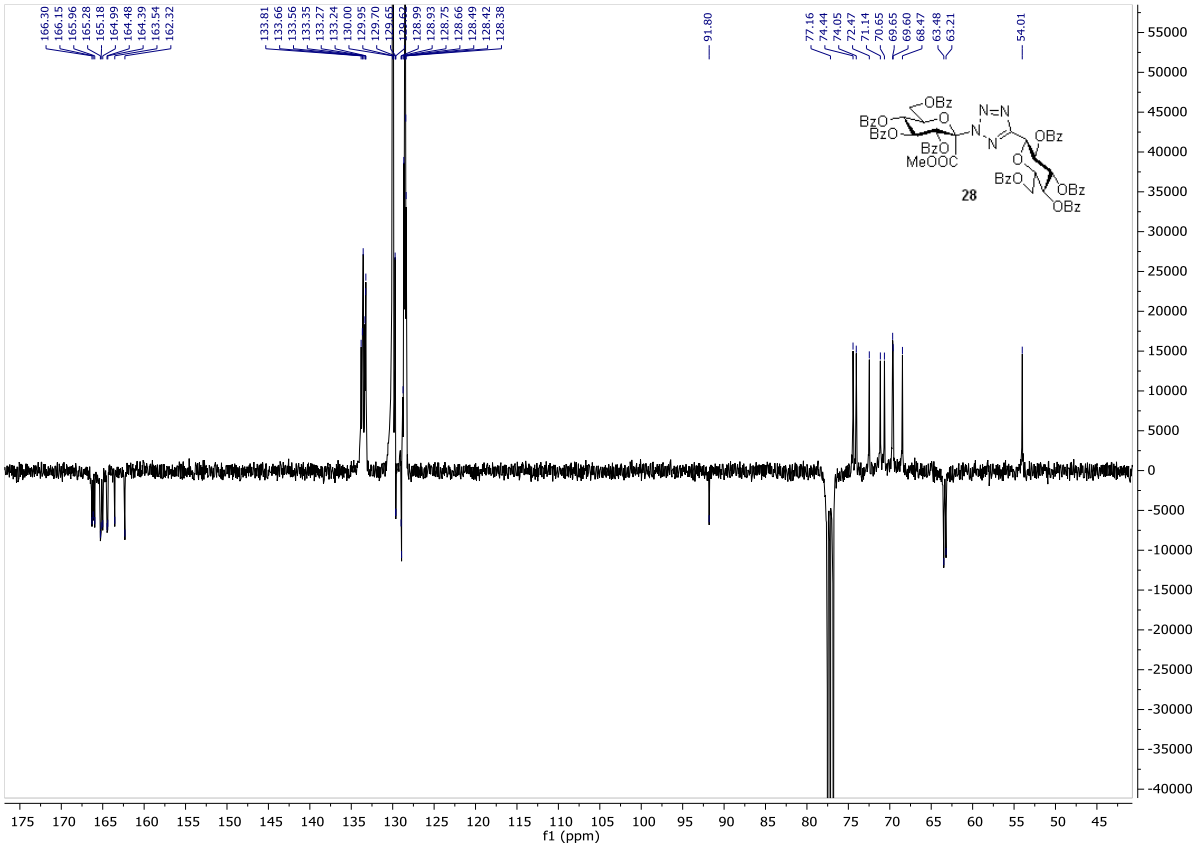
7.98
7.92
7.89
7.83
7.82
7.81
7.80
7.78
7.78
7.68
7.66
7.54
7.17
6.78
6.76
6.08
5.92
5.81
5.75
5.20
5.16
5.15
5.12
4.66
4.45
4.30
4.23
3.61
16.48
2.23
30.15
0.87
3.34
1.89
1.90
4.31
1.00
2.99
f1 (ppm)
28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165.18
164.99
164.48
164.39
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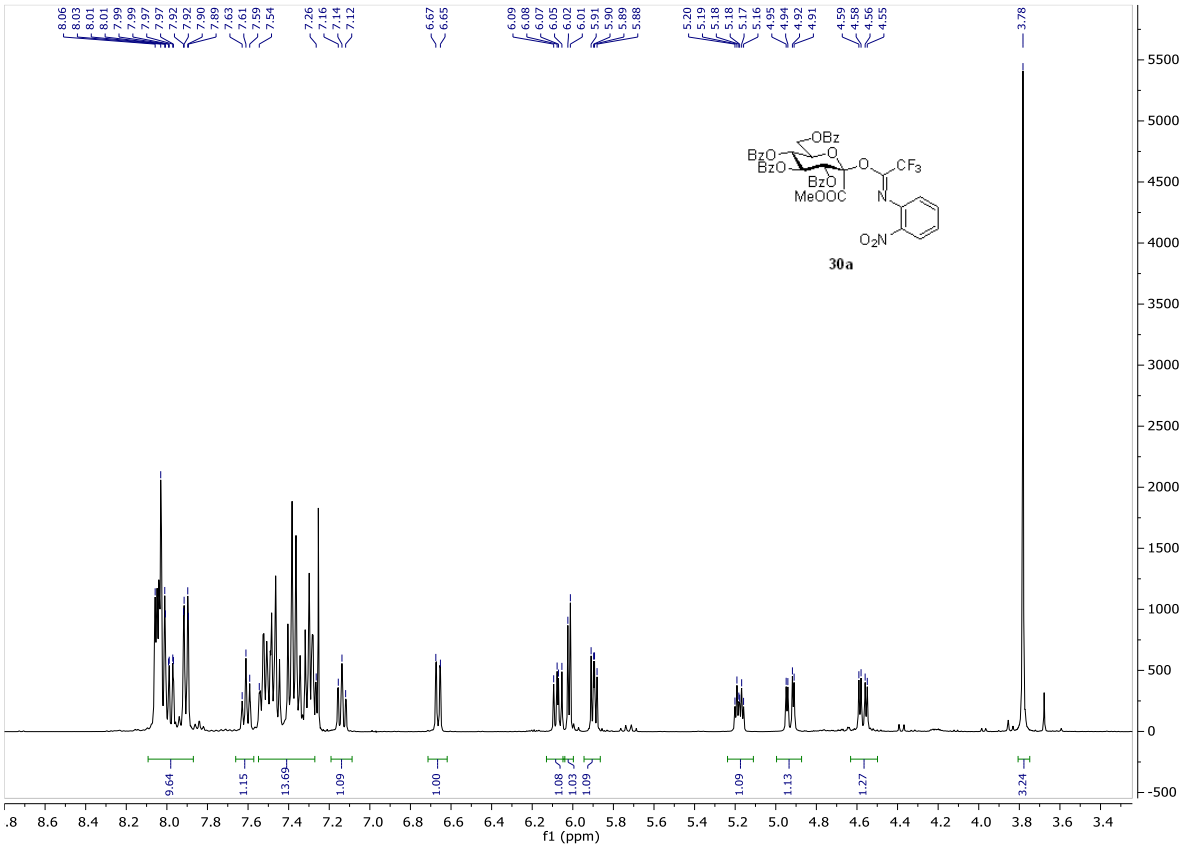
162.32
133.81
133.66
133.56
133.35
133.27
133.24
130.00
129.95
129.70
129.63
129.62
128.99
128.93
128.75
128.66
128.49
128.42
128.38
91.80
77.16
74.44
74.05
72.47
71.14
70.65
69.65
69.60
68.47
63.48
63.21
54.01
f1 (ppm)
28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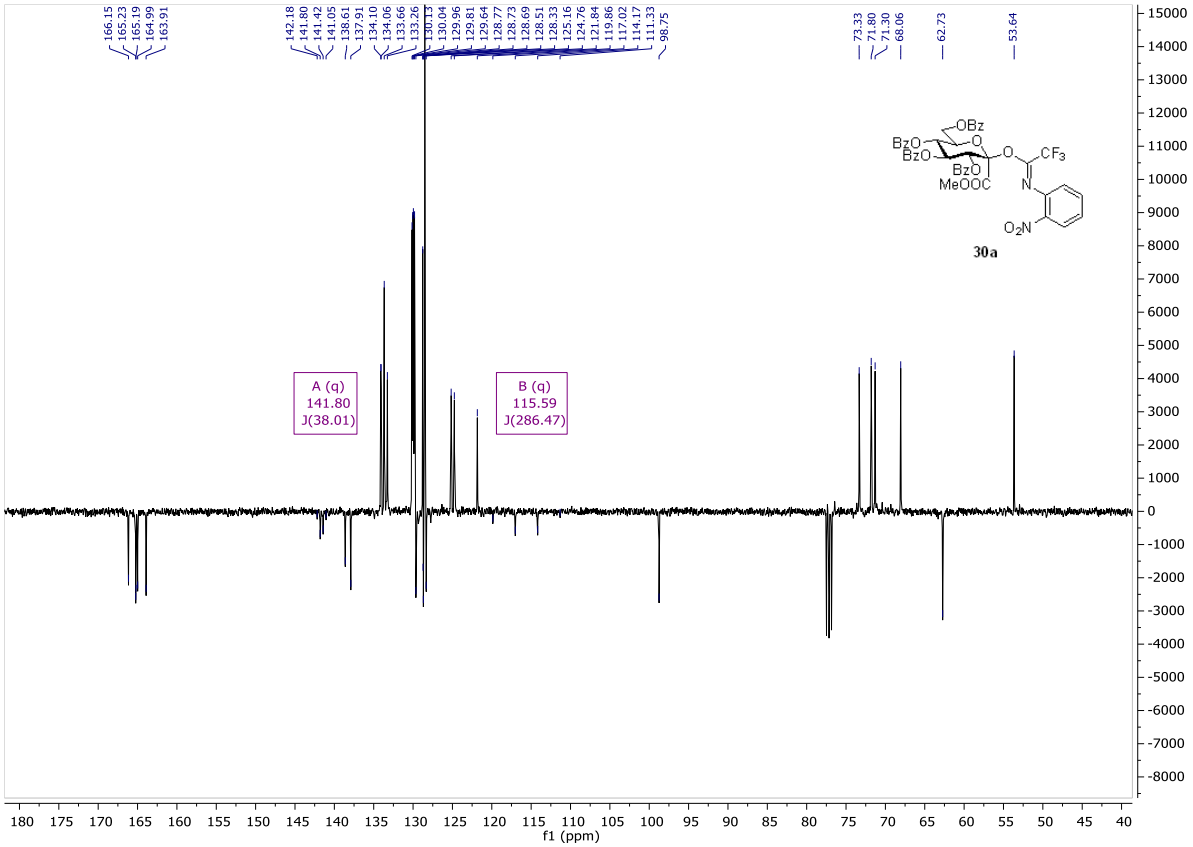
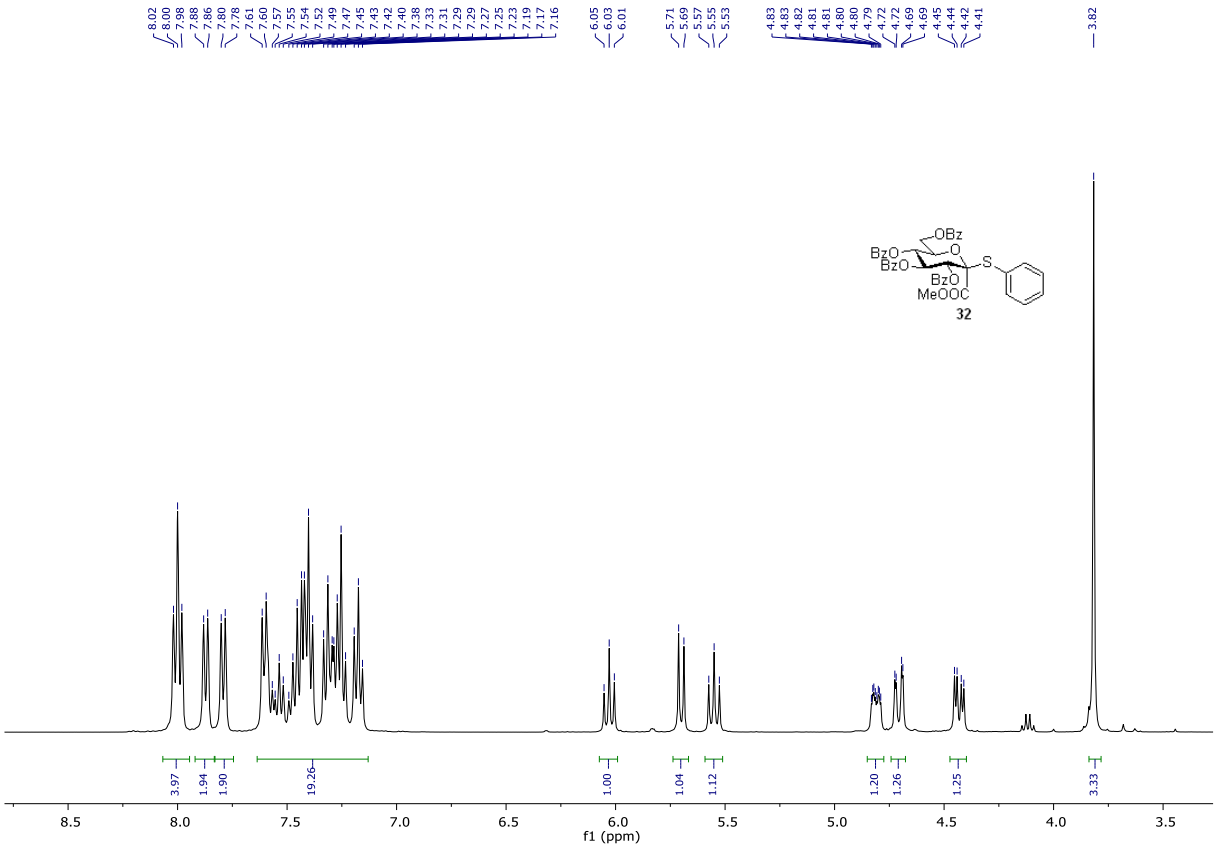
7.26 7.16 7.14 7.12
6.67 6.65
6.09 6.08 6.07 6.05 6.02 6.01 5.91 5.90 5.89 5.88
5.20 5.19 5.18 5.18 5.17 5.16 4.95 4.94 4.92 4.91
4.59 4.58 4.56 4.55
3.78
OBz
BzO
BzO
BzO
MeOOC
O
CF3
N
O2N
30a
9.64 1.15 13.69 1.09 1.00 1.08 1.03 1.09 1.09 1.13 1.27 3.24
f1 (ppm)


166.15 165.23 165.19 164.99 163.91
142.18 141.80 141.42 141.05 138.61 137.91 134.10 134.06 133.66 133.26 130.13 130.04 129.96 129.81 129.64 128.77 128.73 128.69 128.51 128.33 125.16 124.76 121.84 119.86 117.02 114.17 111.33 98.75
73.33 71.80 71.30 68.06 62.73 53.64
A (q)
141.80
J(38.01)
B (q)
115.59
J(286.47)
OBz
BzO
BzO
BzO
MeOOC
O
CF3
N
O2N
30a
f1 (ppm)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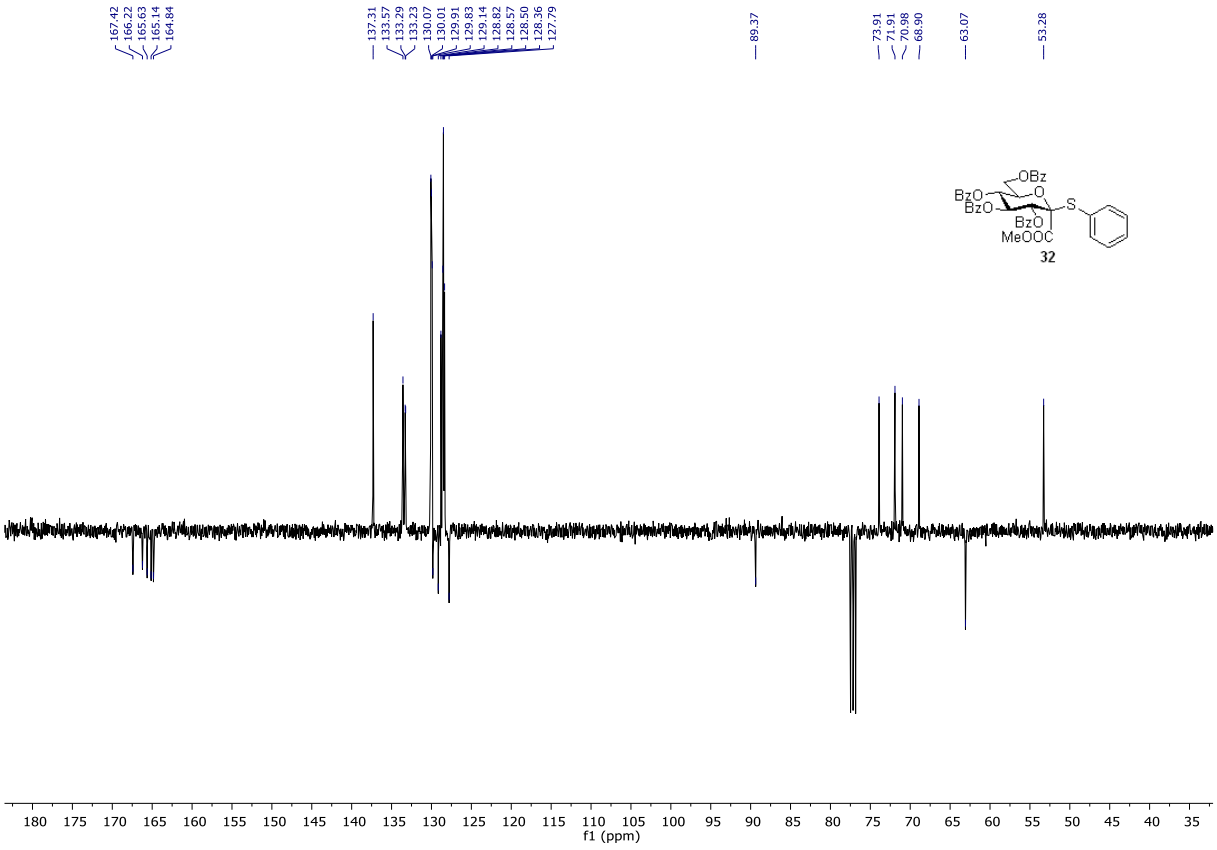
7.98
7.88
7.86
7.80
7.78
7.61
7.60
7.57
7.55
7.54
7.52
7.49
7.47
7.45
7.43
7.42
7.40
7.38
7.33
7.31
7.29
7.27
7.25
7.23
7.19
7.17
7.16
6.05
6.03
6.01
5.71
5.69
5.57
5.55
5.53
4.83
4.83
4.82
4.81
4.81
4.80
4.80
4.79
4.72
4.72
4.69
4.69
4.45
4.44
4.42
4.41
3.82
OBz
BzO
BzO
O
S
BzO
MeOOC
32
3.97
1.94
1.90
19.26
1.00
1.04
1.12
1.20
1.26
1.25
3.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)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133.57
133.29
133.23
130.07
130.01
129.91
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129.14
128.82
128.57
128.50
128.36
127.79
89.37
73.91
71.91
70.98
68.90
63.07
53.28
OBz
BzO
BzO
O
S
BzO
MeOOC
32
180
175
170
165
160
155
150
145
140
135
130
125
120
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110
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100
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80
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65
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55
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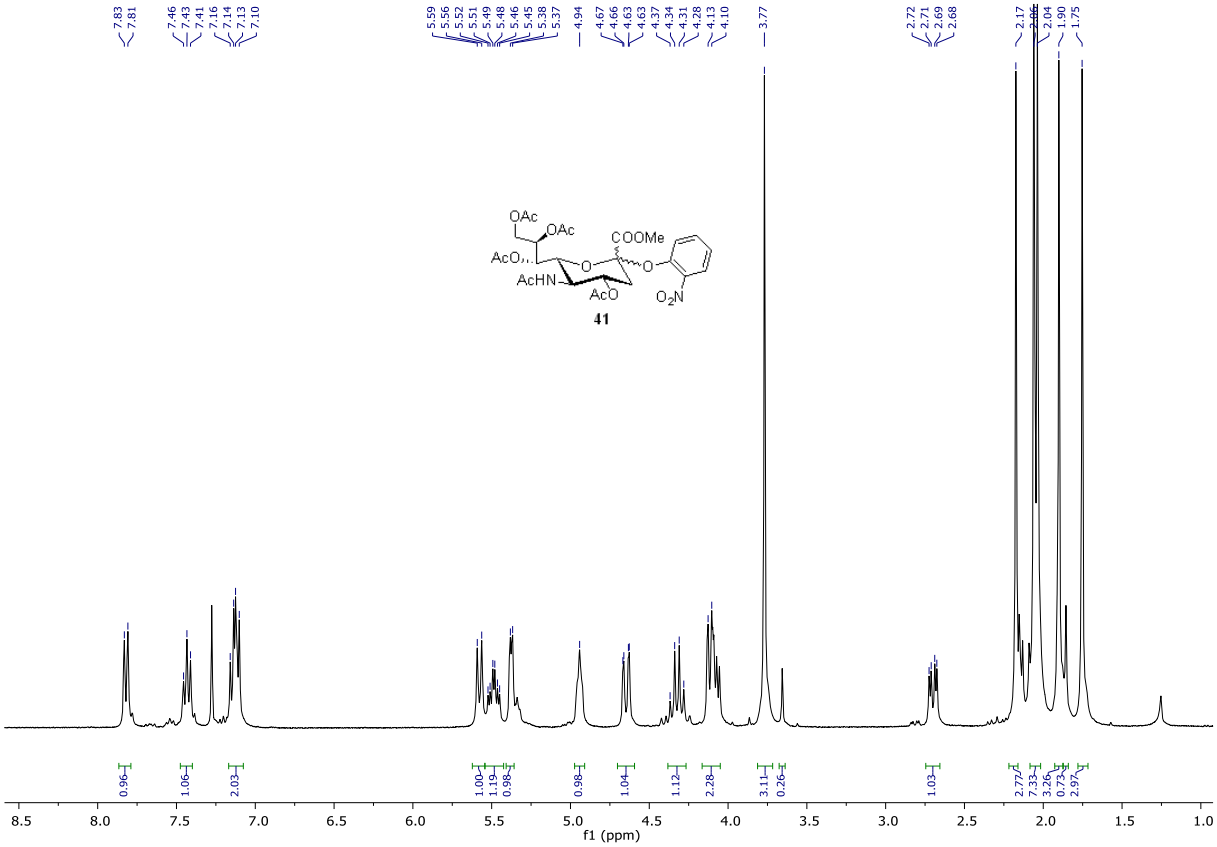
40
35
f1 (ppm)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7.43
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5.51
5.49
5.48
5.46
5.45
5.38
5.37
4.94
4.67
4.66
4.63
4.63
4.37
4.34
4.31
4.28
4.13
4.10
3.77
2.72
2.71
2.69
2.68
2.17
2.04
1.90
1.75
OAc
OAc
COOMe
AcO
AcHN
AcO
O2N
41
0.96
1.06
2.03
1.00
1.19
0.98
0.98
1.04
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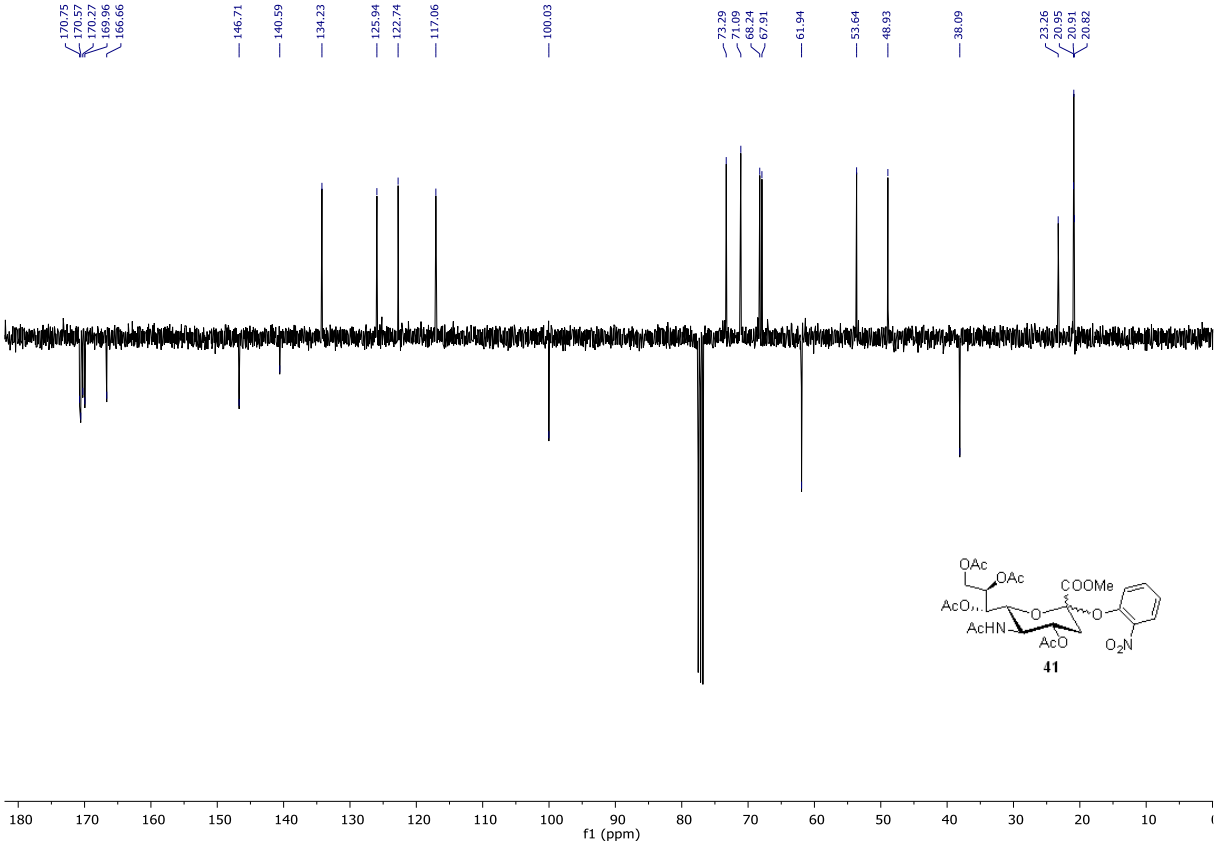
f1 (ppm)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170.27
169.96
166.66
146.71
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122.74
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100.03
73.29
71.09
68.24
67.91
61.94
53.64
48.93
38.09
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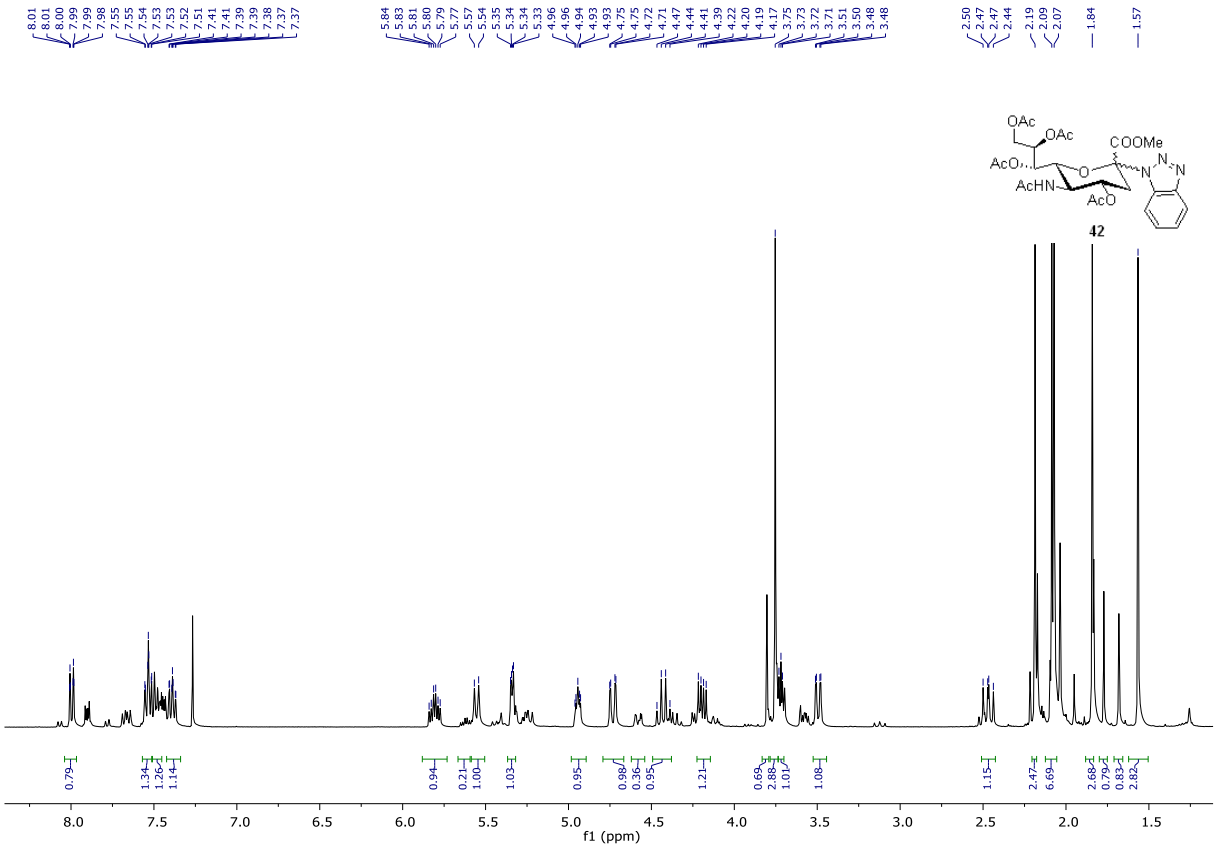
20.82
OAc
OAc
COOMe
AcO
AcHN
AcO
O2N
41
f1 (ppm)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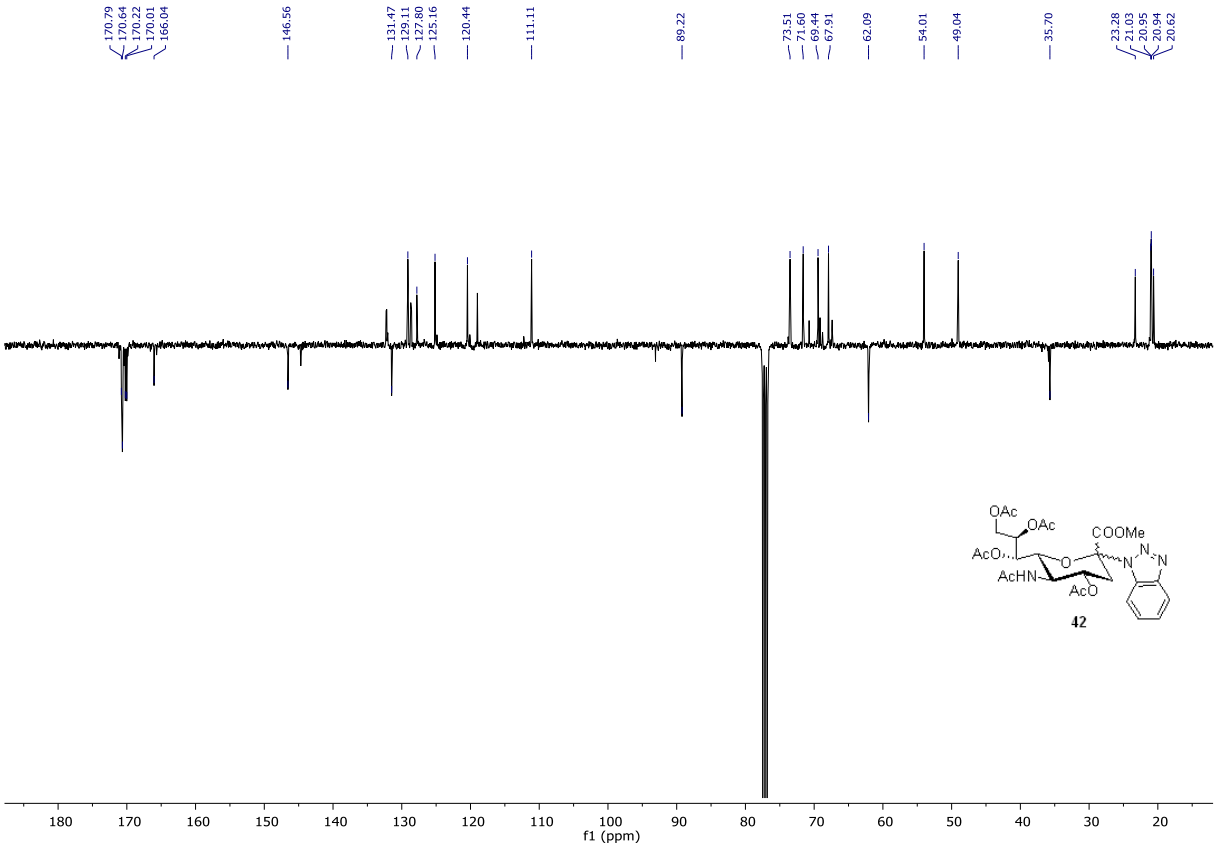
5.84 5.83 5.81 5.80 5.79 5.77 5.57 5.54 5.35 5.34 5.34 5.33 4.96 4.94 4.93 4.93 4.75 4.75 4.72 4.71 4.47 4.44 4.41 4.39 4.22 4.20 4.19 4.17 3.75 3.73 3.72 3.71 3.51 3.50 3.48 3.48
2.50 2.47 2.47 2.44 2.19 2.09 2.07 1.84 1.57
OAc OAc COOMe AcO AcHN AcO O N N N
42
0.79 1.34 1.26 1.14 0.94 0.21 1.00 1.03 0.95 0.98 0.36 0.95 1.21 0.69 2.88 1.01 1.08 1.15 2.47 6.69 2.68 0.79 0.83 2.82
f1 (ppm)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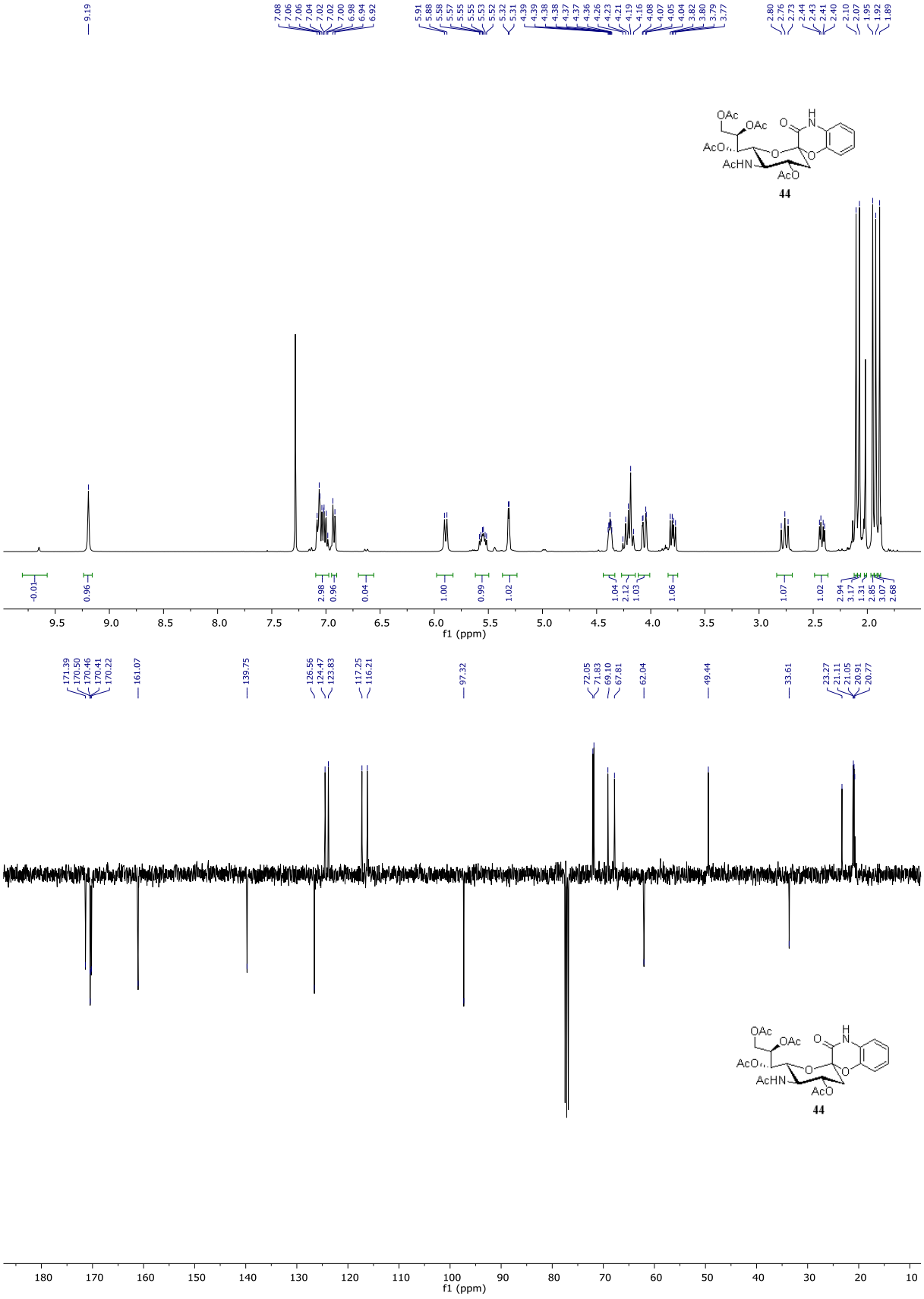
OAc OAc COOMe AcO AcHN AcO O N N N
42
f1 (ppm)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7.08
7.06
7.06
7.04
7.02
7.02
7.00
6.98
6.94
6.92
5.91
5.88
5.58
5.57
5.55
5.55
5.53
5.52
5.32
5.31
4.39
4.39
4.38
4.38
4.37
4.37
4.36
4.26
4.23
4.21
4.19
4.16
4.08
4.07
4.05
4.04
3.82
3.80
3.79
3.77
2.80
2.76
2.73
2.44
2.43
2.41
2.40
2.10
2.07
1.95
1.92
1.89
OAc
OAc
AcO
AcHN
AcO
44
-0.01
0.96
2.98
0.96
0.04
1.00
0.99
1.02
1.04
2.12
1.03
1.06
1.07
1.02
2.94
3.17
1.31
2.85
3.07
2.68
f1 (ppm)
171.39
170.50
170.46
170.41
170.22
161.07
139.75
126.56
124.47
123.83
117.25
116.21
97.32
72.05
71.83
69.10
67.81
62.04
49.44
33.61
23.27
21.11
21.05
20.91
20.77
f1 (ppm)