Electronic Supplementary Material (ESI) for ChemComm.

Catalytic Stereospecific *O*-Glycosylation

Karolina Kowalska and Christian Marcus Pedersen*

Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark.

cmp@chem.ku.dk

Table of contents

General Information:

All reagents were used as purchased without further purification. Dry solvents were taken from a purification solvent systems. All inert reactions were carried out under argon atmosphere using flame-dried flasks. Columns were packed with pre-neutralized silica gel LC-60A (40 – 63 μM, pre-neutralized from the manufacturer to a pH of 6.0 to 8.0). TLC analysis was performed on plates (Merck 60, F254) and visualized by spraying with 10% sulphuric acid in ethanol followed by charring at ≈300 ^{o}C. ^{1}H and ^{13}C NMR spectra were acquired using a 500 MHz Avance III HD equipped with a cryogenically cooled 5 mm observe probe optimized for ^{13}C. Chemical shifts are reported in parts per million (ppm) relative to residual solvents signals (δ = 7.26 for ^{1}H-NMR and 77.16 for ^{13}C-NMR) as the internal standard. High resolution mass spectral (HRMS) data were obtained by MALDI – MS using a SolariX XR 7 T ESI/MALDI – FT – ICR MS instrument. Optical rotation data were obtained on an Anton-Paar Polarimeter.

Trichloroacetamidates **1**[1], **2**[1], **3**[2], **4**[2], **5**[3], **6**[3], **7**[4] were prepared according to the literature procedures.

Glycosylation procedures:

General procedure A for glycosylations:

A mixture of glycosyl donor (0.2 mmol) and acceptor (0.3 mmol) were dissolved in dry CH_2Cl_2 (0.05 M with respect to donor), containing freshly activated 3 Å molecular sieves (~200 mg), and stirred under an inert atmosphere for 1h. Subsequently, the reaction mixture was cooled to –78°C and $TMSNTf_2$ (0.02 mmol) was added. Upon completion (judged by TLC), the reaction was quenched with Et_3N. The solid was filtered off and the filtrate was washed with brine. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography to afford the corresponding glycoside. Anomeric ratios were measured by comparison of integral intensities of the anomeric protons from ^{1}H-NMR spectra of crude reaction mixtures.

General procedure B for glycosylations:

A mixture of acceptor (0.3 mmol) and freshly activated 3 Å molecular sieves (~200 mg) were storred in dry CH_2Cl_2 (0.05 M with respect to donor) under an inert atmosphere for 1h. Subsequently, the reaction mixture was cooled to –78°C and $TMSNTf_2$ (0.02 mmol) was added followed by dropwise addition of the donor (0.2 mmol in 1 mL of CH_2Cl_2) by a syringe pump over 1h. Upon completion (judged by TLC), the reaction was quenched with Et_3N. The solid was filtered off and the filtrate was washed with brine. The organic layer was dried over $MgSO_4$, filtrated and concentrated in vacuo. The residue was purified by flash column chromatography to afford the corresponding glycoside. Anomeric ratios were measured by comparison of integral intensities of the anomeric protons from ^{1}H-NMR spectra of the crude reaction mixtures.

General procedure C for glycosylations:

A mixture of glycosyl donor (0.2 mmol), acceptor (0.3 mmol) and freshly activated 3 Å molecular sieves (~200 mg) were stirred in dry CH_2Cl_2 (0.05 M with respect to donor) under an inert atmosphere for 1h. Subsequently, the reaction mixture was cooled to –78°C and Tf_2NH (0.02 mmol in CH_2Cl_2) was added. Upon completion (judged by TLC), the reaction was quenched with Et_3N. The solid was filtered off and the filtrate was washed with brine. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography to afford the corresponding glycoside. Anomeric ratios were measured by comparison of integral intensities of the anomeric protons from ^{1}H-NMR spectra of crude reaction mixtures.

Table 1. Glycosylations according to the procedure A

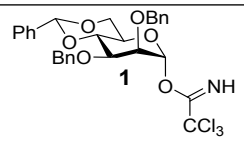
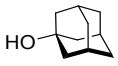
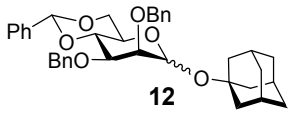
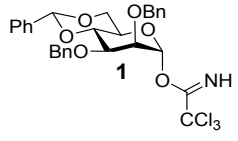
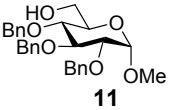
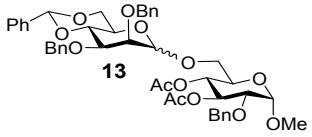
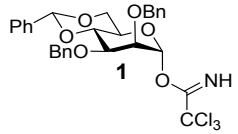
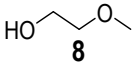
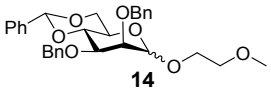
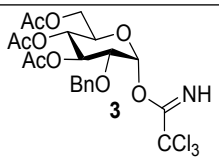
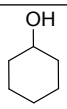
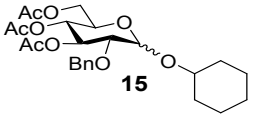
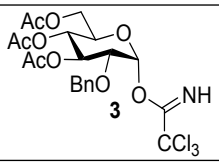
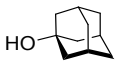
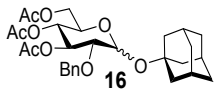
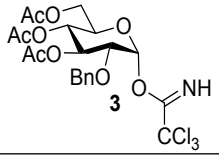
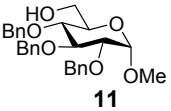
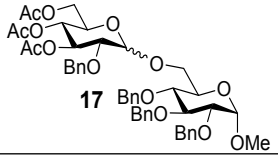
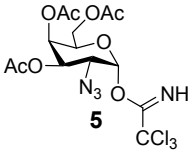
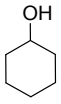
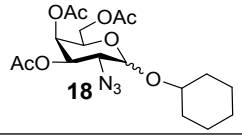
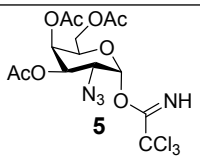
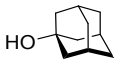
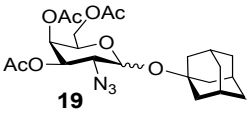
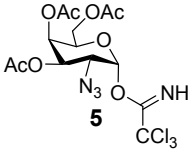
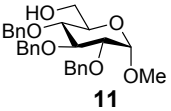
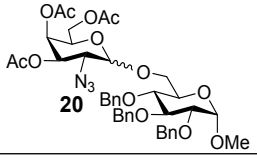
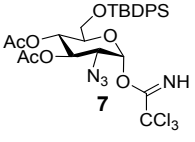
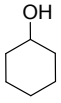
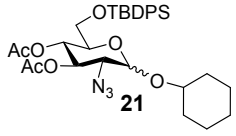
Entry	Donor	Acceptor	Product	β/α (yield%)
1	 **1**	 **10**	 **12**	>10:1[5, 6] (93)
2	 **1**	 **11**	 **13**	4:1[6] (n.d.)
3	 **1**	 **8**	 **14**	4:1[6] (n.d.)
4	 **3**	 **9**	 **15**	>10:1 (85)
5	 **3**	 **10**	 **16**	4:1 (81)
6	 **3**	 **11**	 **17**	>10:1 (70)
7	 **5**	 **9**	 **18**	>10:1 (71)
8	 **5**	 **10**	 **19**	>10:1 (90)
9	 **5**	 **11**	 **20**	>10:1 (68)
10	 **7**	 **9**	 **21**	>10:1 (77)

Table 1 (continued). Glycosylations according to the procedure A

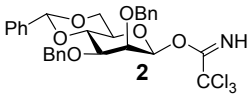
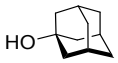
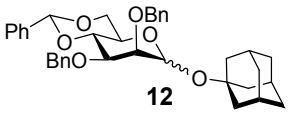
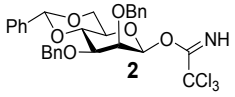
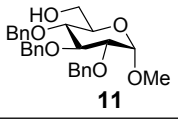
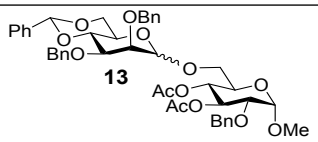
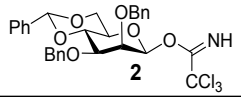
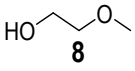
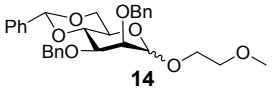
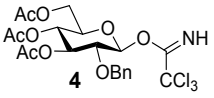
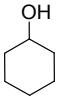
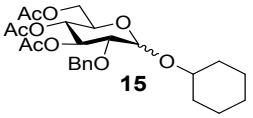
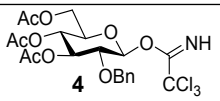
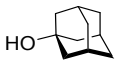
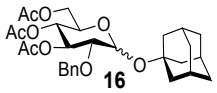
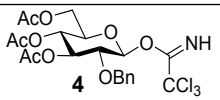
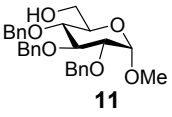
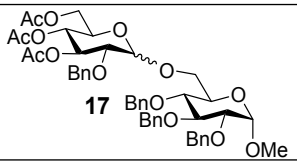
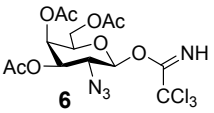
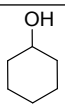
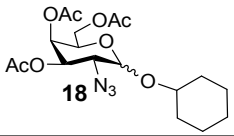
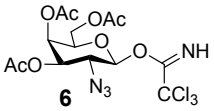
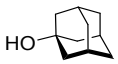
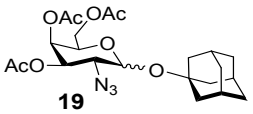
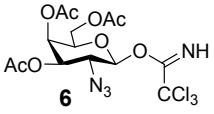
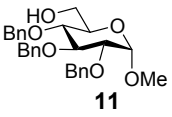
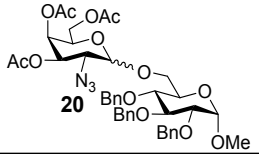
Entry	Donor	Acceptor	Product	β/α (yield%)
11	 **2**	 **10**	 **12**	1:5[5, 6] (n.d.)
12	 **2**	 **11**	 **13**	1:7[6] (n.d.)
13	 **2**	 **8**	 **14**	1:10[6] (n.d.)
14	 **4**	 **9**	 **15**	1:4 (71)
15	 **4**	 **10**	 **16**	2:1 (82)
16	 **4**	 **11**	 **17**	2:1 (69)
17	 **6**	 **9**	 **18**	2:1[7] (72)
18	 **6**	 **10**	 **19**	1:1 (78)
19	 **6**	 **11**	 **20**	2:1[8] (50)

Table 2. Glycosylations according to the procedure B

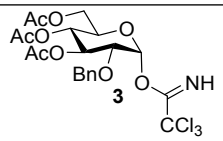
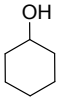
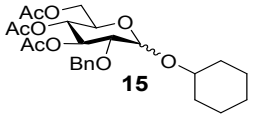
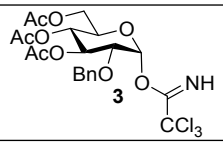
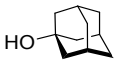
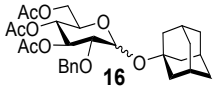
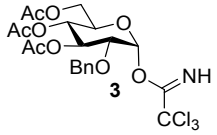
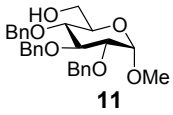
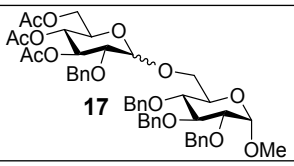
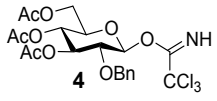
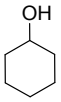
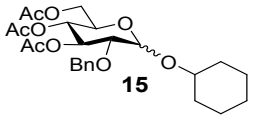
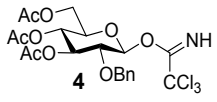
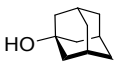
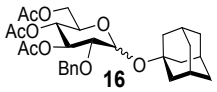
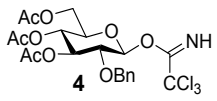
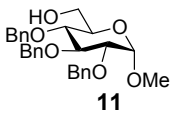
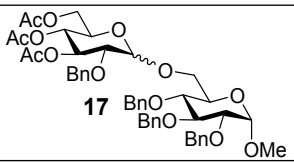
Entry	Donor	Acceptor	Product	β/α (yield%)
1	 **3**	 **9**	 **15**	4:1 (59)
2	 **3**	 **10**	 **16**	2:1 (61)
3	 **3**	 **11**	 **17**	5:1 (46)
4	 **4**	 **9**	 **15**	2:1 (68)
5	 **4**	 **10**	 **16**	2:1 (74)
6	 **4**	 **11**	 **17**	5:1 (61)

Table 3. Glycosylations according to the procedure C

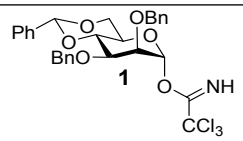
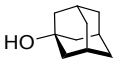
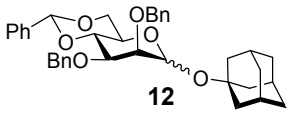
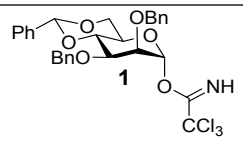
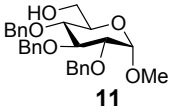
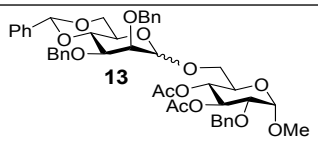
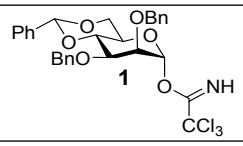
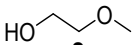
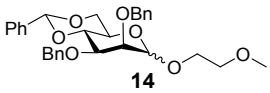
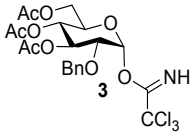
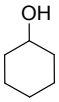
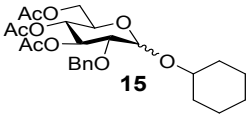
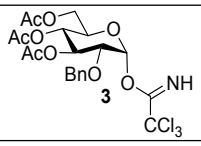
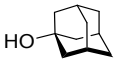
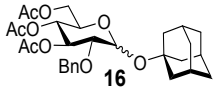
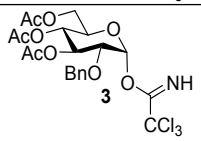
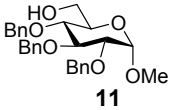
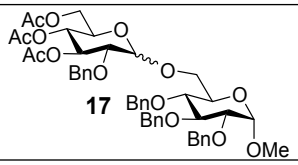
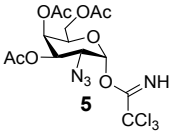
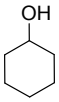
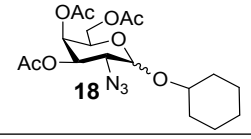
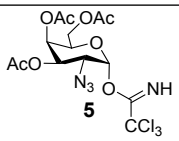
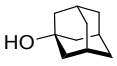
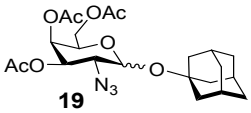
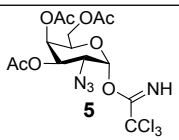
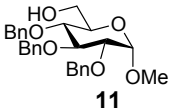
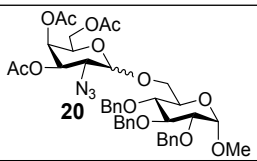
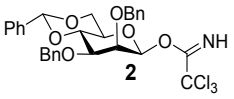
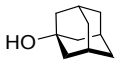
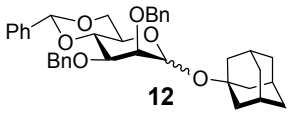
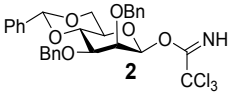
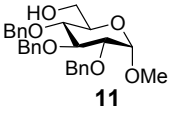
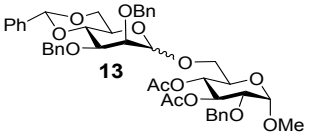
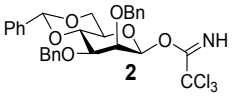
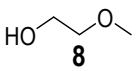
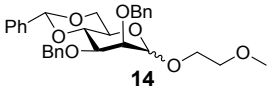
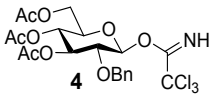
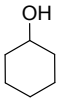
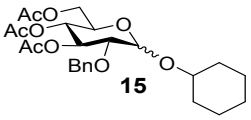
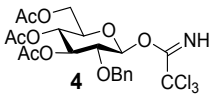
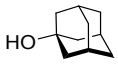
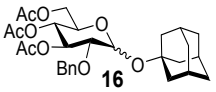
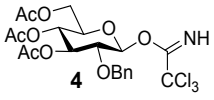
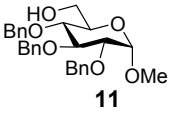
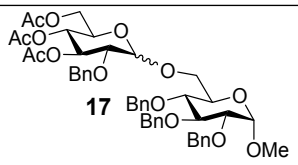
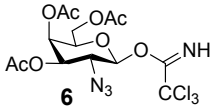
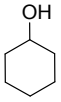
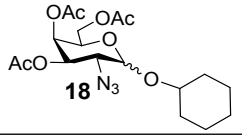
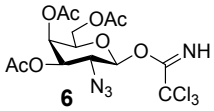
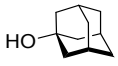
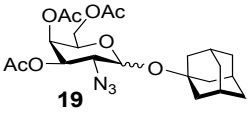
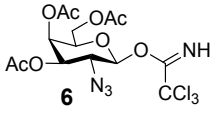
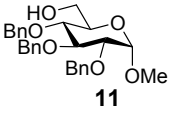
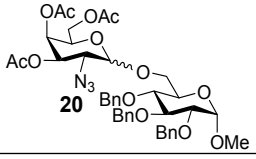
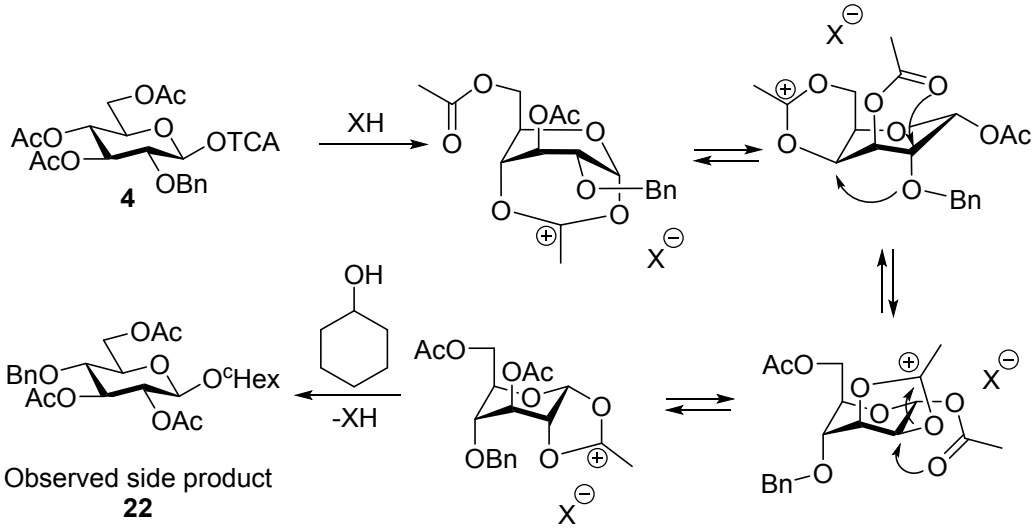
Entry	Donor	Acceptor	Product	α/β (yield%)
1	 **1**	 **10**	 **12**	>10:1[5, 6] (91)
2	 **1**	 **11**	 **13**	4:1[6] (74)
3	 **1**	 **8**	 **14**	4:1[6] (82)
4	 **3**	 **9**	 **15**	>10:1 (87)
5	 **3**	 **10**	 **16**	5:1 (81)
6	 **3**	 **11**	 **17**	>10:1 (71)
7	 **5**	 **9**	 **18**	>10:1[7] (81)
8	 **5**	 **10**	 **19**	>10:1 (91)
9	 **5**	 **11**	 **20**	>10:1 (70)[7]

Table 3 (continued). Glycosylations according to the procedure C

Entry	Donor	Acceptor	Product	β/α (yield%)
10	 **2**	 **10**	 **12**	2:1[5, 6] (88%)
11	 **2**	 **11**	 **13**	>1:10[6] (79)
12	 **2**	 **8**	 **14**	>1:10[6] (88)
13	 **4**	 **9**	 **15**	1:4.5 (67)
14	 **4**	 **10**	 **16**	2:1 (86)
15	 **4**	 **11**	 **17**	2:1 (66)
16	 **6**	 **9**	 **18**	3:1 (71)[6]
17	 **6**	 **10**	 **19**	1:1 (80)
18	 **6**	 **11**	 **20**	2:1[8] (52)

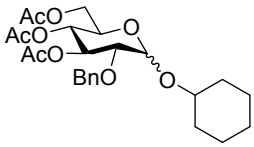
When the donor **4** was activated in the presence of c-hexanol a side product, **22**, was isolated besides the expected glycosides. In this product the benzyl group has exchanged place with the acetyl at the 4-O-position. A plausible reaction pathway for the formation of 1-cyclohexyl 2,3,6-tri-*O*-acetyl-4-*O*-benzyl- D-glucopyranoside **22** is shown below. Participation of an 4-O-acetyl in the glycosylation reaction has been observed before and proposed to be responsible for increased β-selectivity in glycosylations.[9]



Scheme 1 Proposed mechanism for the formation of 22 from 4.

Compounds Characterization Data

1-cyclohexyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranoside (15)



The α anomer could not be separated from α/β mixture. ***α*-anomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H, Ph), 5.44 (t, *J* = 9.7 Hz, 1H, H-3), 4.96 (d, *J* = 9.5 Hz, 1H, H-4), 4.95 (d, *J* = 3.7 Hz, 1H, H-1), 4.62 (d, *J* = 12.1 Hz, 1H, PhC*(H)*H) 4.58 (d, *J* = 12.1 Hz, 1H, PhC*(H)*H), 4.24 (dd, *J* = 12.1, 4.7 Hz, 1H, H-6), 4.11-4.06 (m, 1H, H-5), 4.04 (dd, *J* = 12.1, 2.3 Hz, 1H, H-6), 3.55 (dd, *J* = 9.8, 3.7, 1H, H-2), 3.53– 3.48 (m, 1H, C*H*$_{\text{-cyclohexanol}}$), 2.06 (s, 3H, C*H*$_3$), 2.02 (s, 3H, C*H*$_3$), 2.01 (s, C*H*$_3$), 1.28–1.23 (m, 10H, H$_{\text{-cyclohexanol}}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C = O), 170.3 (C = O), 170.0 (C = O), 138.0 (C_{Ph}), 128.6 (C_{Ph}), 128.1 (C_{Ph}), 128.0 (C_{Ph}), 94.9 (C-1), 76.7 (*C*H-O), 76.7 (C-2), 72.7 (C_{Bn}), 72.1 (C-3), 69.1. (C-4), 62.4 (C-5), 62.1 (C-6), 33.4 (*C*H$_{2\text{-cyclohexanol}}$), 31.6 (*C*H$_{2\text{-cyclohexanol}}$), 29.9 (*C*H$_{2\text{-cyclohexanol}}$), 25.7 (*C*H$_{2\text{-cyclohexanol}}$), 21.0 (*C*H$_3$), 20.9 (2 x *C*H$_3$).

HRMS (MALDI) *m/z*: [M+Na$^+$] Calcd for $C_{25}H_{34}O_9Na^+$ 501.2101; found 501.2107.

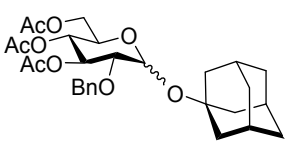
***β*-anomer**:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 5H, Ph), 5.13 (t, *J* = 9.5 Hz, 1H, H-3), 4.95 (t, *J* = 9.5 Hz, 1H, H-4), 4.86 (d, *J* = 11.8 Hz, 1H, PhC*(H)*H), 4.62 (d, *J* = 11.8 Hz, 1H, PhC*(H)*H), 4.59 (d, *J* = 7.8 Hz, 1H, H-1), 4.26 (dd, *J* = 12.2, 5.1 Hz, 1H, H-6), 4.07 (dd, *J* = 12.1, 2.5 Hz, 1H, H-6), 3.73–3.67 (m, 1H, C*H*$_{\text{-cyclohexanol}}$), 3.64 (ddd, *J* = 10.1, 5.1, 2.5 Hz, 1H, H-5), 3.41 (dd, *J* = 9.5, 7.8 Hz, 1H, H-2), 2.06 (s, 3H, C*H*$_3$), 1.99 (s, 3H, C*H*$_3$), 1.89 (s, C*H*$_3$), 1.34–1.18 (m, 10H, H$_{\text{-cyclohexanol}}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9 (C = O), 170.4 (C = O), 169.8 (C = O), 138.2 (C_{Ph}), 128.5 (C_{Ph}), 128.3 (C_{Ph}), 127.9 (C_{Ph}), 102.1 (C-1), 78.7 (C-2), 78.5 (C*H*-O), 74.5 (C_{Bn}), 74.1 (C-3), 71.6 (C-5), 69.0 (C-4), 62.5 (C-6), 33.7 (*C*H$_{2\text{-cyclohexanol}}$), 32.0 (*C*H$_{2\text{-cyclohexanol}}$), 29.8 (*C*H$_{2\text{-cyclohexanol}}$), 25.7 (*C*H$_{2\text{-cyclohexanol}}$), 20.9 (*C*H$_3$), 20.9 (*C*H$_3$), 20.8 (*C*H$_3$).

HRMS (MALDI) *m/z*: [M+Na$^+$] Calcd for $C_{25}H_{34}O_9Na^+$ 501.2101; found 501.2108.

$[\alpha]_D^{25}$ = +18.1 (c = 1.0 $CHCl_3$)

1-adamantanyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranoside (16)



***α*–anomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.26 (m, 4H, Ph), 7.18-7.14 (m, 1H, Ph), 5.44 (t, *J* = 9.7 Hz, 1H, H-3), 5.29 (d, *J* = 3.7 Hz, 1H, H-1), 4.93 (d, *J* = 9.7 Hz, 1H, H-4), 4.60 (d, *J* = 11.9 Hz, 1H, PhC*(H)*H), 4.54 (d, *J* = 12.1 Hz, 1H, PhC*(H)*H), 4.26 (dd, *J* = 12.1, 4.8 Hz, 1H, H-6), 3.99 (dd, *J* = 12.1, 2.2 Hz, 1H, H-6), 4.22-4.17 (m, 1H, H-5), 3.53 (dd, *J* = 9.7, 3.7 Hz, 1H, H-2), 2.19-2.13 (m, 3H, H$_{\text{-adamantanol}}$), 2.05 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.99 (m, 3H, H$_{\text{-adamantanol}}$), 1.87 (s, 3H, Ac), 1.84-1.76 (m, 3H, H$_{\text{-adamantanol}}$), 1.68-1.60 (m, 6H, H$_{\text{-adamantanol}}$).

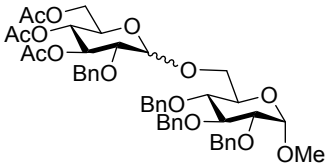
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C = O), 170.4 (C = O), 170.1 (C = O), 137.9 (C_{Ph}), 128.6 (C_{Ph}), 128.1 (C_{Ph}), 128.0 (C_{Ph}), 89.8 (C-1), 76.6 (C-2), 75.4 (*C*H-O), 72.6 (C_{Bn}), 72.2 (C-3), 69.3 (C-4), 66.8 (C-5), 62.2 (C-6), 42.5 ($C_{\text{-adamantanol}}$), 36.2 ($C_{\text{-adamantanol}}$), 30.7 ($C_{\text{-adamantanol}}$), 21.0 (*C*H_3), 20.8 (*C*H_3), 20.8 (*C*H_3).

***β*-anomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.26 (m, 4H, Ph), 7.18-7.14 (m, 1H, Ph) 5.13 (t, *J* = 9.5 Hz, 1H, H-3), 4.90 (t, *J* = 9.7 Hz, 1H, H-4), 4.84 (d, *J* = 11.9 Hz, 1H, PhC*(H)*H), 4.76 (d, *J* = 7.9 Hz, 1H, H-1), 4.62 (d, *J* = 11.9 Hz, 1H, PhC*(H)*H), 4.22 (dd, *J* = 12.0, 5.9 Hz, 1H, H-6), 4.05 (dd, *J* = 12.0, 2.5 Hz, 1H, H-6), 3.64 (ddd, *J* = 10.1, 5.9, 2.5 Hz, 1H, H-5), 3.39 (dd, *J* = 9.6, 7.8 Hz, 1H, H-2), 2.19-2.13 (m, 3H, $H_{\text{-adamantanol}}$), 2.04 (s, 3H), 1.99 (s, 3H), 1.94-1.98 (m, 2H, $H_{\text{-adamantanol}}$), 1.87 (s, 3H), 1.83-1.78 (m, 2H, $H_{\text{-adamantanol}}$), 1.94-1.98 (m, 3H, $H_{\text{-adamantanol}}$), 1.87 (s, 3H), 1.84-1.76 (m, 3H, $H_{\text{-adamantanol}}$), 1.68-1.60 (m, 6H, $H_{\text{-adamantanol}}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C = O), 170. (C = O), 169.8 (C = O), 138.2 (C_{Ph}), 128.5 (C_{Ph}), 128.3 (C_{Ph}), 127.9 (C_{Ph}), 96.5 (C-1), 78.7 (C-2), 76.1 (*C*H-O), 74.5 (C_{Bn}), 74.2 (C-3), 71.4 (C-5), 69.2 (C-4), 62.7 (C-6), 42.8 ($C_{\text{-adamantanol}}$), 36.3 ($C_{\text{-adamantanol}}$), 30.8 ($C_{\text{-adamantanol}}$), 20.9 (*C*H_3), 20.8 (*C*H_3), 20.8 (*C*H_3).

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{29}H_{38}O_9Na^+$ 553.2414; found 553.2421.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-*α*-D-glucopyranoside (17)



The α-anomer could not be separated from α/β mixture.

***α*–anomer**: ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.38-7.28 (m, 13H, Ph), 7.27-7.21 (m, 5H, Ph), 7.21-7.14 (m, 2H, Ph), 6.35 (d, *J* = 3.6 Hz, 1H, H-1'), 5.40 (t, *J* = 9.6 Hz, 1H, H-3'), 5.03 (t, *J* = 9.6 Hz, 1H, H-4'), 4.82–4.70 (m, 1H, PhC*(H)*H), 4.72–4.58 (m, 5H, PhC*(H)*H), 4.55 (d, *J* = 3.7 Hz, 1H, H-1) 4.54 (d, *J* =11.4 Hz, 1H, PhC*(H)*H), 4.28 (dd, *J* = 12.3, 4.0 Hz, 1H, H-6'), 4.06 (dd, *J* = 11.2, 2.4 Hz, 1H, H-6), 4.02 (dd, *J* = 12.3, 2.4 Hz, 1H, H-6'), 4.02–3.98 (m, 1H, H-5'), 3.93 (t, 1H, *J* = 9.5 Hz, H-3), 3.76 (ddd, 1H, *J* = 10.1, 4.9, 2.1, H-5), 3.74–3.67 (m, 2H, H-6, H-2'), 3.54-3.45 (m, 2H, H-4, H-2), 3.37 (s, 3H, OC*H*$_3$), 2.19 (s, 3H, C*H*$_3$), 2.04 (s, 3H, C*H*$_3$), 2.02 (s, C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7 (C = O), 169.8 (C = O), 169.2 (C = O), 138.8 (C_{Ph}), 138.4 (C_{Ph}), 138.2 (C_{Ph}), 137.2 (C_{Ph}), 128.7 (C_{Ph}), 128.6 (C_{Ph}), 128.5 (C_{Ph}), 128.5 (C_{Ph}), 128.4 (C_{Ph}), 128.3 (C_{Ph}), 128.22 (C_{Ph}), 128.11 (C_{Ph}), 128.0 (C_{Ph}), 127.9 (C_{Ph}), 127.897 (C_{Ph}), 127.8 (C_{Ph}), 98.2 (C-1), 89.3 (C-1'), 82.1 (C-3), 79.9 (C-2), 78.1 (C-4), 75.9 (C_{Bn}), 75.1 (C_{Bn}), 73.5 (C_{Bn}), 73.1 (C_{Bn}), 71.7 (C-3'), 70.0 (C-5), 69.8 (C-5'), 68.7 (C-6), 68.1 (C-4'), 62.2 (C-6'), 55.3 (O*C*H_3), 21.1 (*C*H_3), 20.9 (*C*H_3), 20.7 (*C*H_3).

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{47}H_{54}O_{14}Na^+$ 865.3411; found 865.3430.

***β*-anomer**: ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.37-7.27 (m, 15H, Ph), 7.25-7.18 (m, 5H, Ph), 5.13 (t, *J* = 9.5 Hz, 1H, H-3'), 4.97 (d, 1H, *J* = 11.2 Hz, PhC*(H)*H), 4.95 (d, 1H, *J* = 9.6 Hz, H-4'),

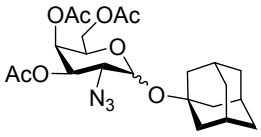
4.84 (d, *J* = 11.6 Hz, 1H, PhC*(H)*H), 4.79 (d, *J* = 10.8 Hz, 1H, PhC*(H)*H), 4.78 (d, *J* = 12.1 Hz, 1H, PhC*(H)*H), 4.76 (d, *J* = 11.2 Hz, 1H, PhC*(H)*H), 4.66 (d, *J* = 12.1 Hz, 1H, PhC*(H)*H), 4.62 (d, *J* = 3.7 Hz 1H, H-1), 4.60 (d, *J* = 11.2 Hz, 1H, PhC*(H)*H), 4.51 (d, *J* = 11.2 Hz, 1H, PhC*(H)*H), 4.41 (d, *J* = 7.8 Hz, 1H, H-1'), 4.13 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6'), 4.09 (dd, *J* = 12.3, 2.4 Hz, 1H, H-6), 3.99 (t, *J* = 9.3 Hz, 1H, H-3), 3.83 (ddd, 1H, *J* = 10.1, 4.9, 2.0, H-5), 3.69 (dd, *J* = 11.0, 4.8 Hz, 1H, H-6), 3.59 (ddd, *J* = 10.0, 4.7, 2.5 Hz, 1H, H-5'), 3.51 (dd, *J* = 9.6, 3.5 Hz, 1H, H-2), 3.47 (t, *J* = 9.5 Hz, 1H, H-4), 3.51 (dd, *J* = 9.6, 3.5 Hz, 1H, H-2), 3.51 (3.47, dd, *J* = 9.7, 7.7 Hz, 1H, H-2'), 3.35 (s, 3H, OCH_3), 2.04 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.88 (s, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C = O), 170.3 (C = O), 169.8 (C = O), 138.9 (C_{Ph}), 138.2 (C_{Ph}), 137.9 (C_{Ph}), 128.6 (C_{Ph}), 128.6 (C_{Ph}), 128.5 (C_{Ph}), 128.5 (C_{Ph}), 128.3 (C_{Ph}), 128.1 (C_{Ph}), 128.1 (C_{Ph}), 128.0 (C_{Ph}), 127.9 (C_{Ph}), 127.8 (C_{Ph}), 127.8 (C_{Ph}), 127.7 (C_{Ph}), 103.8 (C-1'), 98.3 (C-1), 82.1 (C-3), 79.9 (C-2), 78.8 (C-2'), 78.1 (C-4), 75.9 (C_{Bn}), 75.1 (C_{Bn}), 74.8 (C_{Bn}), 74.1 (C-3'), 73.7 (C_{Bn}), 71.7 (C-5'), 70.0 (C-5), 68.9 (C-4'), 68.8 (C-6), 62.2 (C-6'), 55.4 (O*C*H_3), 20.9 (*C*H_3), 20.8 (*C*H_3), 20.8 (*C*H_3).

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{47}H_{54}O_{14}Na^+$ 865.3411; found 865.3427.

$[\alpha]_D^{25}$ = +25.1 (c = 1.0 $CHCl_3$)

1-adamantanyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranoside (19)



***α*-anomer:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.45 (dd, 1H, *J* = 3.4 Hz, H-4), 5.42 (dd, 1H, *J* = 11.0, 3.4 Hz, H-3), 5.41 (dd, 1H, *J* = 3.5 Hz, H-1), 4.42 (td, *J* = 6.7, 1.4 Hz, 1H, H-5), 4.07 (dd, *J* = 6.7, 4.6 Hz, 2H, H-6), 3.47 (dd, *J* = 11.1, 3.6 Hz, 1H, H-2), 2.18 (s, 4H, $H_{\text{-adamantanol}}$), 2.13 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.91-1.82 (m, 6H, $H_{\text{-adamantanol}}$), 1.67-1.60 (m, 5H, $H_{\text{-adamantanol}}$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.8 (C = O), 170.6 (C = O), 170.4 (C = O), 92.0 (C-1), 76.4 (*C*H-O), 68.3 (C-3), 68.3 (C-4), 66.7 (C-5), 62.2 (C-6), 57.6 (C-2), 42.7 ($C_{\text{-adamantanol}}$), 36.6 ($C_{\text{-adamantanol}}$), 31.1 ($C_{\text{-adamantanol}}$), 21.1 CH_3), 21.1 (CH_3), 21.1 (CH_3).

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{22}H_{31}N_3O_9Na^+$ 488.2009; found 488.2006.

$[\alpha]_D^{25}$ = +42.2 (c = 0.9 $CHCl_3$)

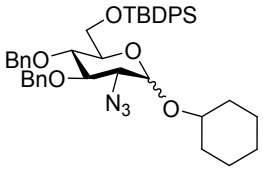
***β*-anomer:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (d, *J* = 3.5 Hz, 1H, H-4), 4.76 (dd, *J* = 10.9, 3.4 Hz, 1H, H-3), 4.66 (d, *J* = 7.9 Hz, 1H, H-1), 4.17 (dd, *J* = 11.2, 6.9 Hz, 1H, H-6), 4.07 (dd, *J* = 11.3, 6.6 Hz, 1H, H-6), 3.83 (t, *J* = 6.8 Hz, 1H, H-5), 3.67 (dd, *J* = 10.9, 8.0 Hz, 1H, H-2), 2.18 (s, 4H, $H_{\text{-adamantanol}}$), 2.14 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.94 – 1.89 (m, 3H, $H_{\text{-adamantanol}}$), 1.84–1.79 (m, 3H, $H_{\text{-adamantanol}}$), 1.67 – 1.61 (m, 5H, $H_{\text{-adamantanol}}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C = O), 170.4 (C = O), 170.1 (C = O), 137.9 (C_{Ph}), 128.6 (C_{Ph}), 128.1 (C_{Ph}), 128.0 (C_{Ph}), 89.8 (C-1), 76.6 (C-2), 75.4 (*C*H-O), 72.6 (C_{Bn}), 72.2 (C-3), 69.3 (C-4), 66.9 (C-5), 62.2 (C-6), 42.5 ($C_{\text{-adamantanol}}$), 36.2 ($C_{\text{-adamantanol}}$), 30.7 ($C_{\text{-adamantanol}}$), 21.0 (CH_3), 20.8 (CH_3), 20.8 (CH_3).

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{22}H_{31}N_3O_9Na^+$ 488.2009; found 488.2006.

$[\alpha]_D^{25}$ = +9.8 (c = 1.0 $CHCl_3$)

1-cyclohexyl 2-azido-3,4-di-*O*-acetyl-6-*O-tert*-butyldiphenylsilyl-2-deoxy-β-D-glucopyranoside (21)



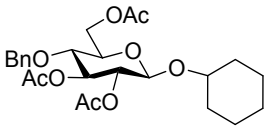
***β*-anomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.72 (m, 2H, Ph), 7.71–7.67 (m, 2H, Ph), 7.48–7.36 (m, 12H, Ph), 7.32–7.28 (m, 2H, Ph), , 7.19-7.15 (m, 2H, Ph), 4.91 (d, *J* = 10.7 Hz, 1H, PhC*(H)*H), 4.87 (d, *J* = 10.7 Hz, 1H, PhC*(H)*H), 4.82 (d, *J* = 10.7 Hz, 1H, PhC*(H)*H), 4.67 (d, *J* = 10.8 Hz, 1H, PhC*(H)*H), 4.42 (d, *J* = 7.6 Hz, 1H, H-1), 3.90 (dd, *J* = 4.6, 3.1 Hz, 2H, H-6), 3.74 (t, *J* = 9.2 Hz, 1H, H-4), 3.49 – 3.39 (m, 2H, H-2, H-3), 3.33 (ddd, *J* = 9.7, 4.0, 2.1 Hz, 1H, H-5), 2.07-1.92 (m, 2H, $H_{\text{-cyclohexanol}}$), 1.84-1.77 (m, 2H, $H_{\text{-cyclohexanol}}$), 1.58-1.53 (m, 3H, $H_{\text{-cyclohexanol}}$), 1.34-1.25 (m, 5H, $H_{\text{-cyclohexanol}}$), 1.06 (s, 9H, C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2 (C_{Ph}), 138.1 (C_{Ph}), 136.0 (C_{Ph}), 135.7 (C_{Ph}), 133.7 (C_{Ph}), 133.2 (C_{Ph}), 129.8 (C_{Ph}), 128.6–127.5 (9 x C_{Ph}), 100.7 (C-1), 83.4 (C-3), 78.0 (C*H*-O), 77.8 (C-4), 76.0 (C_{Bn}), 75.7 (C-5), 75.3 (C_{Bn}), 66.7 (C-2), 62.8 (C-6), 33.9 ($CH_{2\text{-cyclohexanol}}$), 31.9 ($CH_{2\text{-cyclohexanol}}$), 26.9 (3 x CH_3), 25.8 ($CH_{2\text{-cyclohexanol}}$), 24.2 ($CH_{2\text{-cyclohexanol}}$), 24.0 ($CH_{2\text{-cyclohexanol}}$), 19.4 ($C_q$).

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{42}H_{51}N_3O_5SiNa^+$ 728.3496; found 728.3480.

$[\alpha]_D^{25}$ = -11.5 (c = 1.0 $CHCl_3$)

1-cyclohexyl 2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-glucopyranoside (22)



***β*-anomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.27 (m, 4H, Ph), 7.25–7.21 (m, 1H, Ph), 5.25 (t, 1H, *J* = 9.5 Hz, H-3), 4.87 (dd, 1H, *J* = 9.7, 8.0, H-2), 4.60 (d, *J* = 11.2 Hz, 1H, PhC*(H)*H), 4.56 (d, 1H, *J* = 7.8 Hz, H-1), 4.55 (d, *J* = 11.2 Hz, 1H, PhC*(H)*H), 4.35 (dd, *J* = 11.9, 2.3 Hz, 1H, H-6), 4.21 (dd, *J* = 11.9, 4.8 Hz, 1H, H-6), 3.66 (t, *J* = 9.4 Hz, 1H, H-4), 3.62 – 3.55 (m, 2H, C*H*-O, H-5), 2.06 (s, 3H, C*H*$_3$), 2.02 (s, 3H, C*H*$_3$), 2.01 (s, 3H, C*H*$_3$), 1.43-1.28 (m, 10H, $H_{\text{-cyclohexanol}}$),

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C = O), 170.3 (C = O), 169.8 (C = O), 137.4 (C_{Ph}), 128.7 (C_{Ph}), 128.3 (C_{Ph}), 128.2 (C_{Ph}), 99.4 (C-1), 78.1 (*C*H-O), 76.0 (C-4), 75.3 (C-3), 74.9 (C_{Bn}), 72.9 (C-5), 72.2 (C-2), 62.9 (C-6), 33.4 ($CH_{2\text{-cyclohexanol}}$), 32.1 ($CH_{2\text{-cyclohexanol}}$), 29.9 ($CH_{2\text{-cyclohexanol}}$), 21.0 (2 x CH_3), 20.9 (CH_3), 20.8 (CH_3).

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{25}H_{34}O_9Na^+$ 501.2101; found 501.2108.

$[\alpha]_D^{25}$ = +1.4 (c = 0.8 $CHCl_3$)

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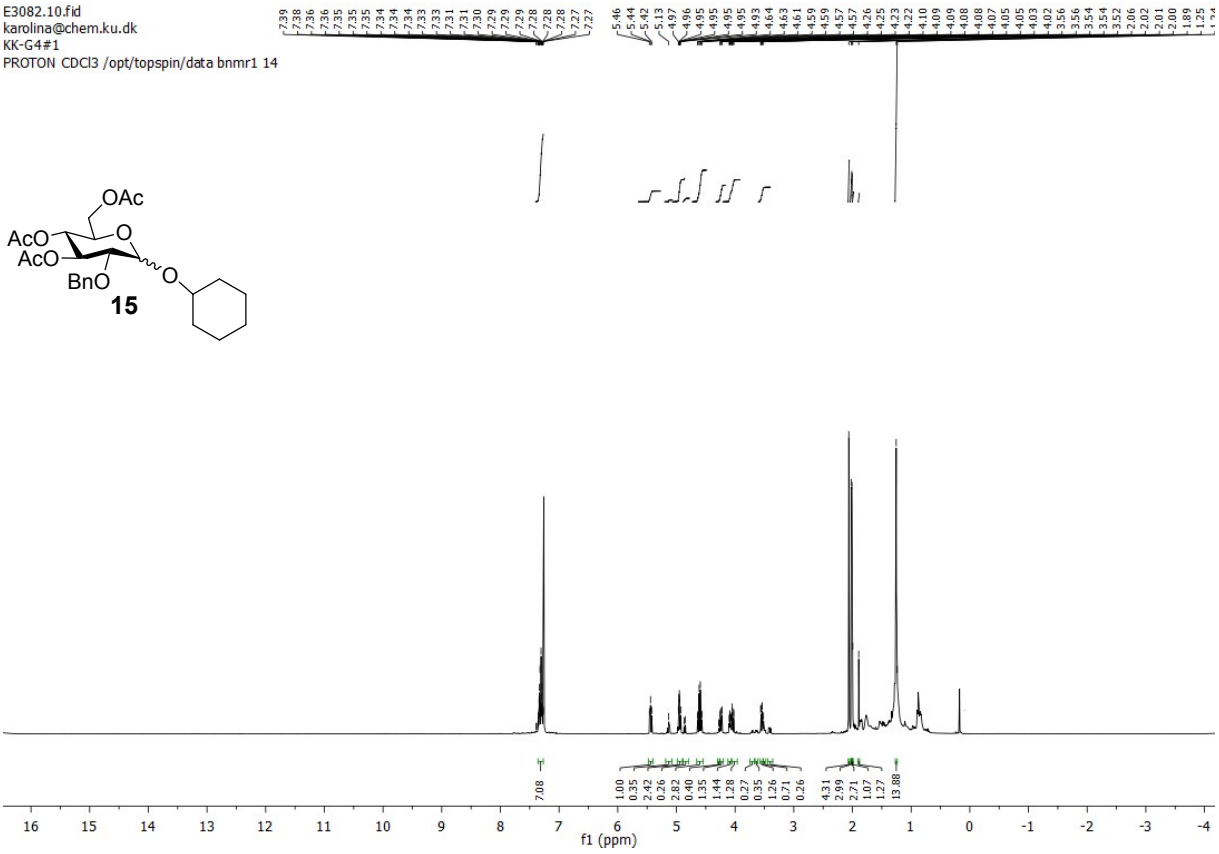
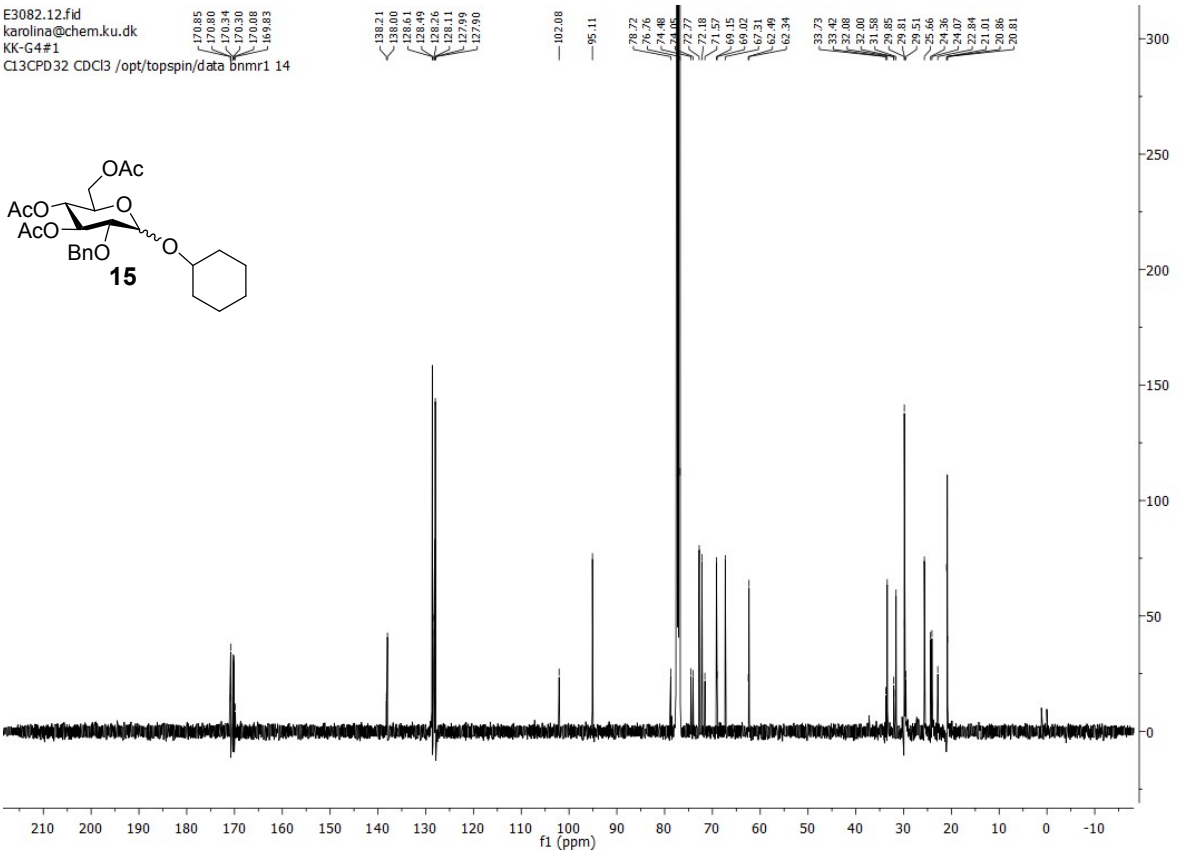
^{1}H-NMR and ^{13}C-NMR spectra of compounds

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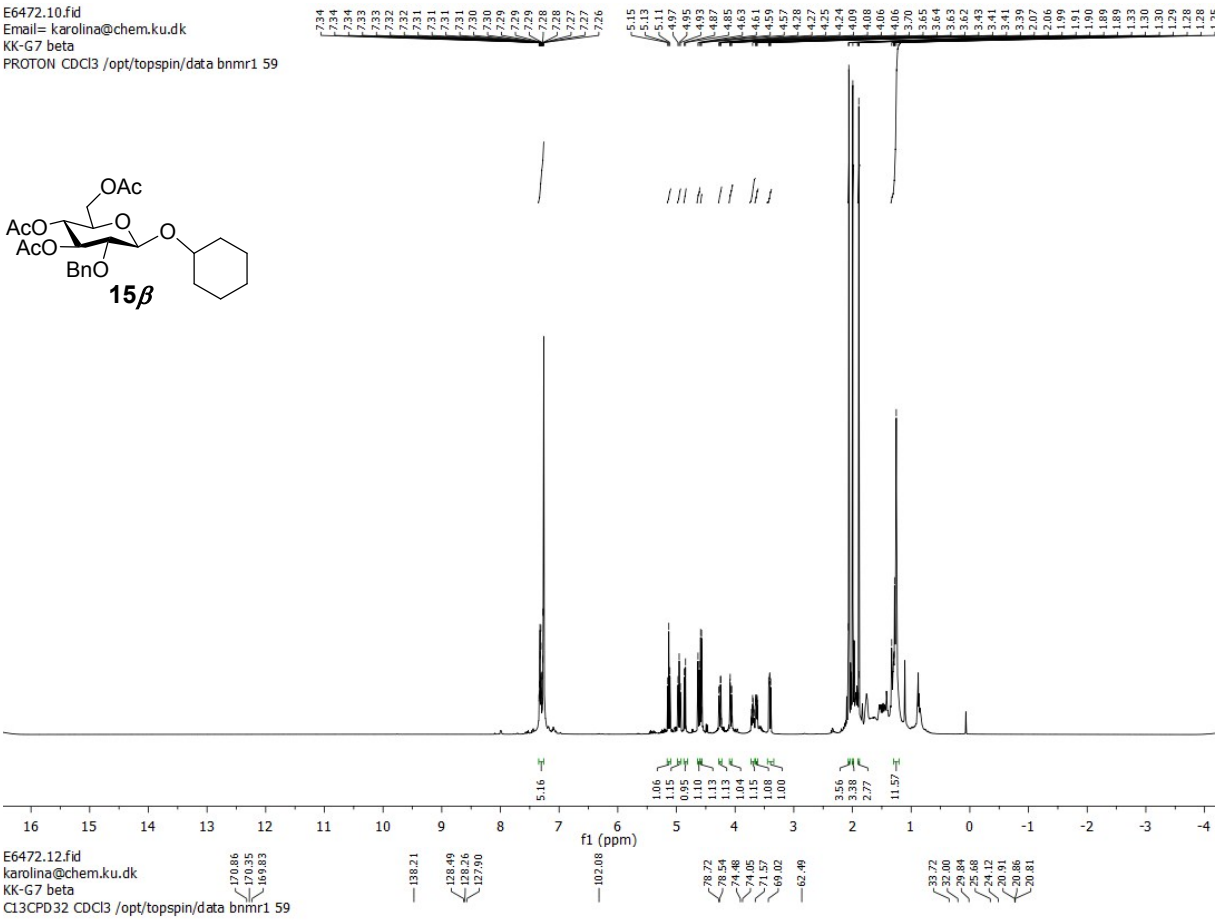
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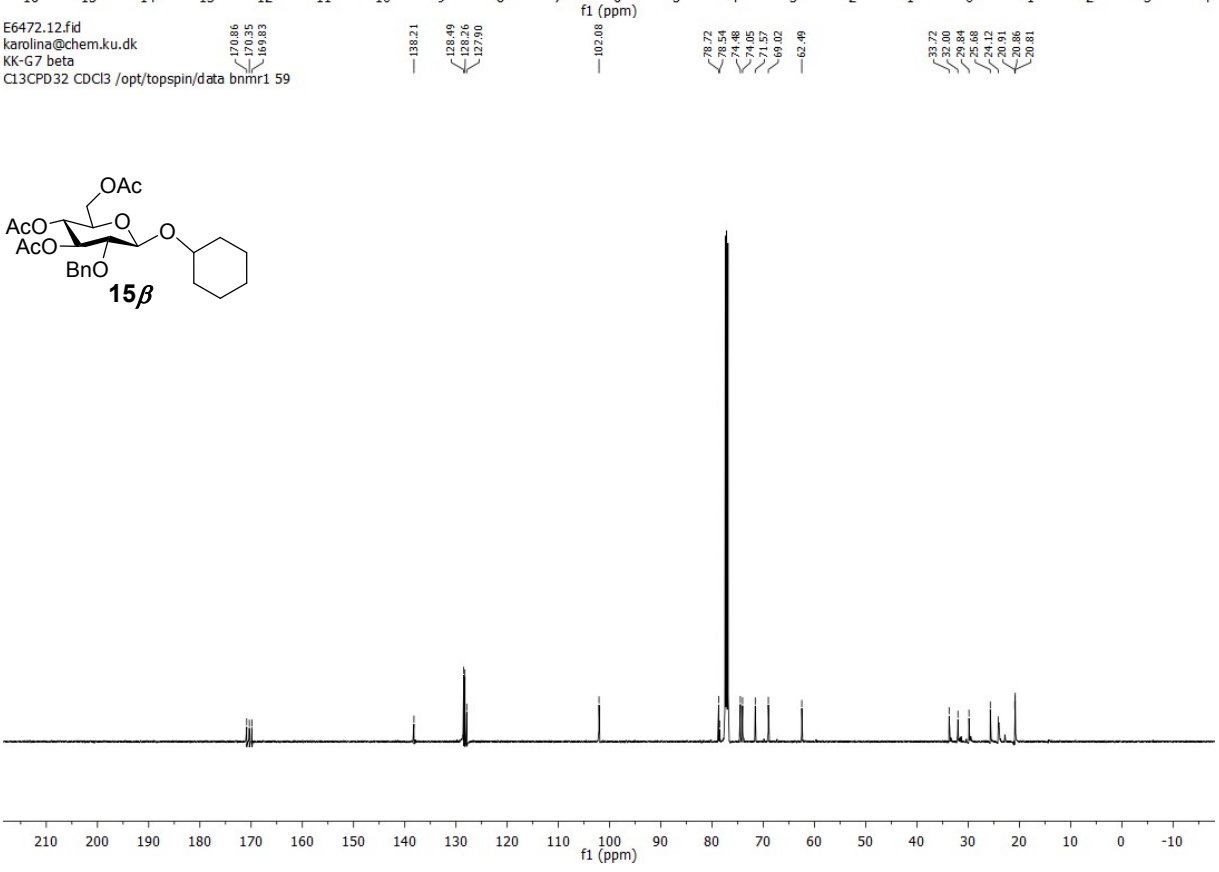
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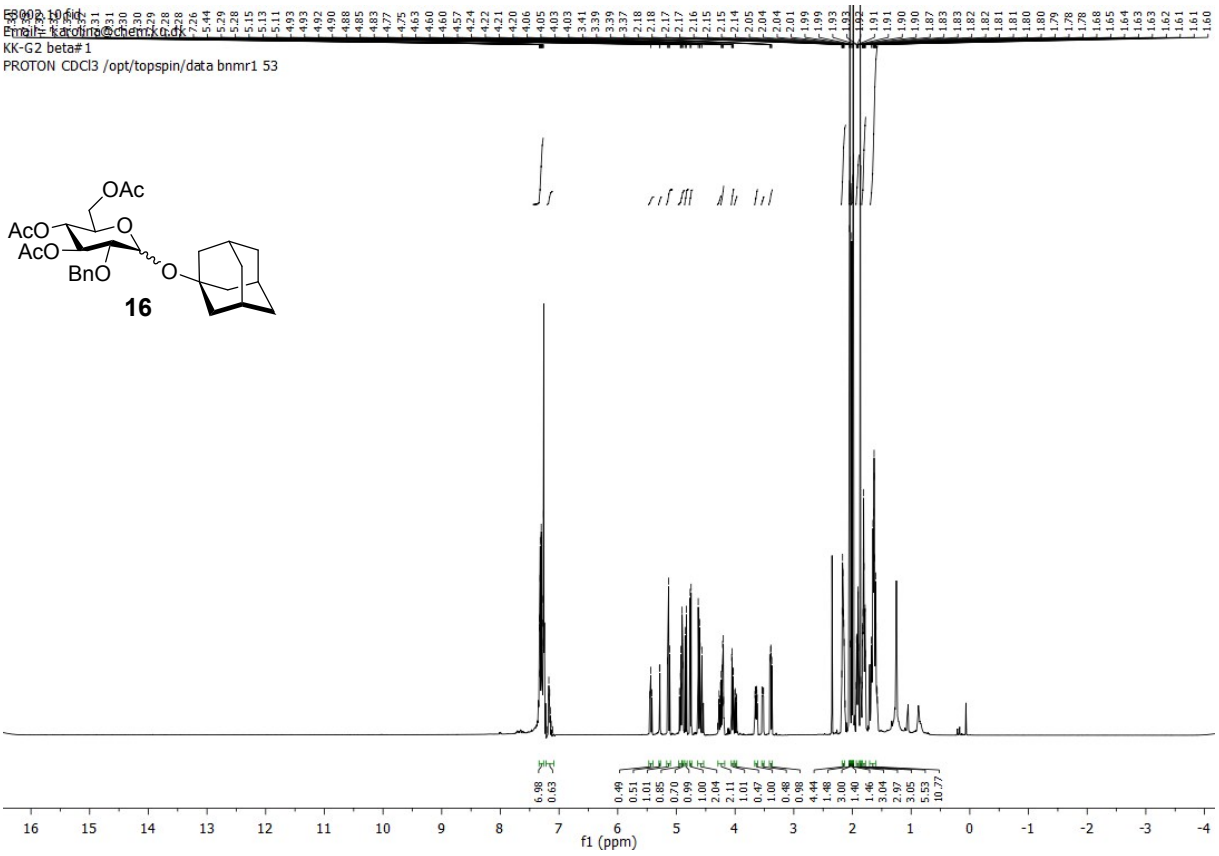
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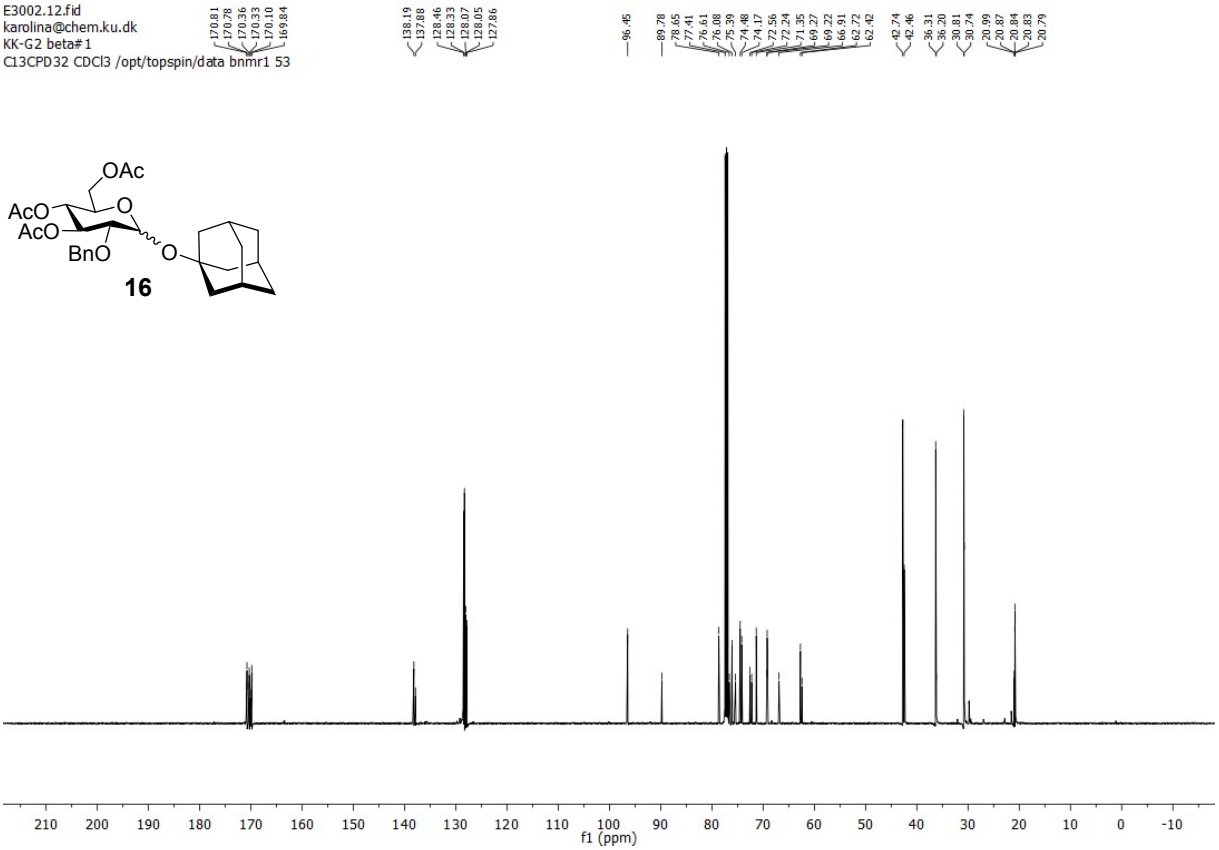
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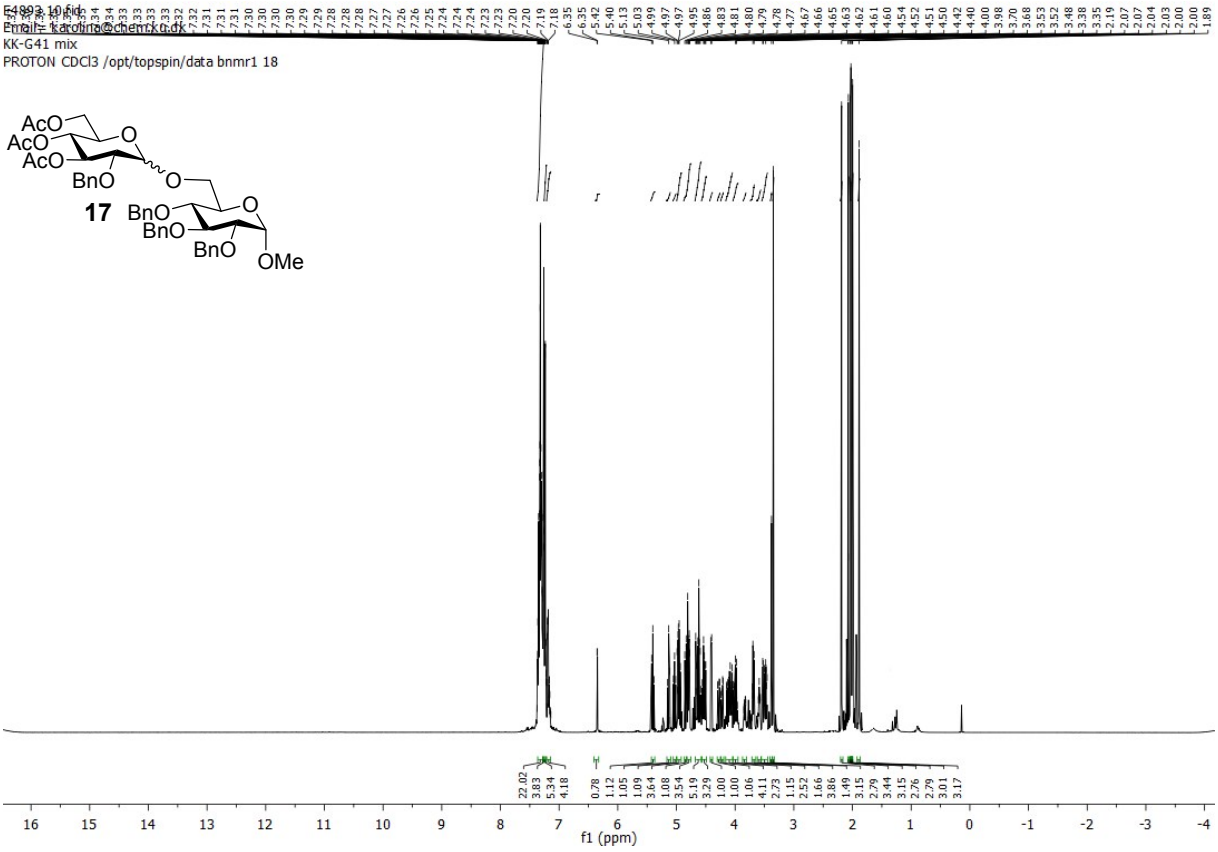
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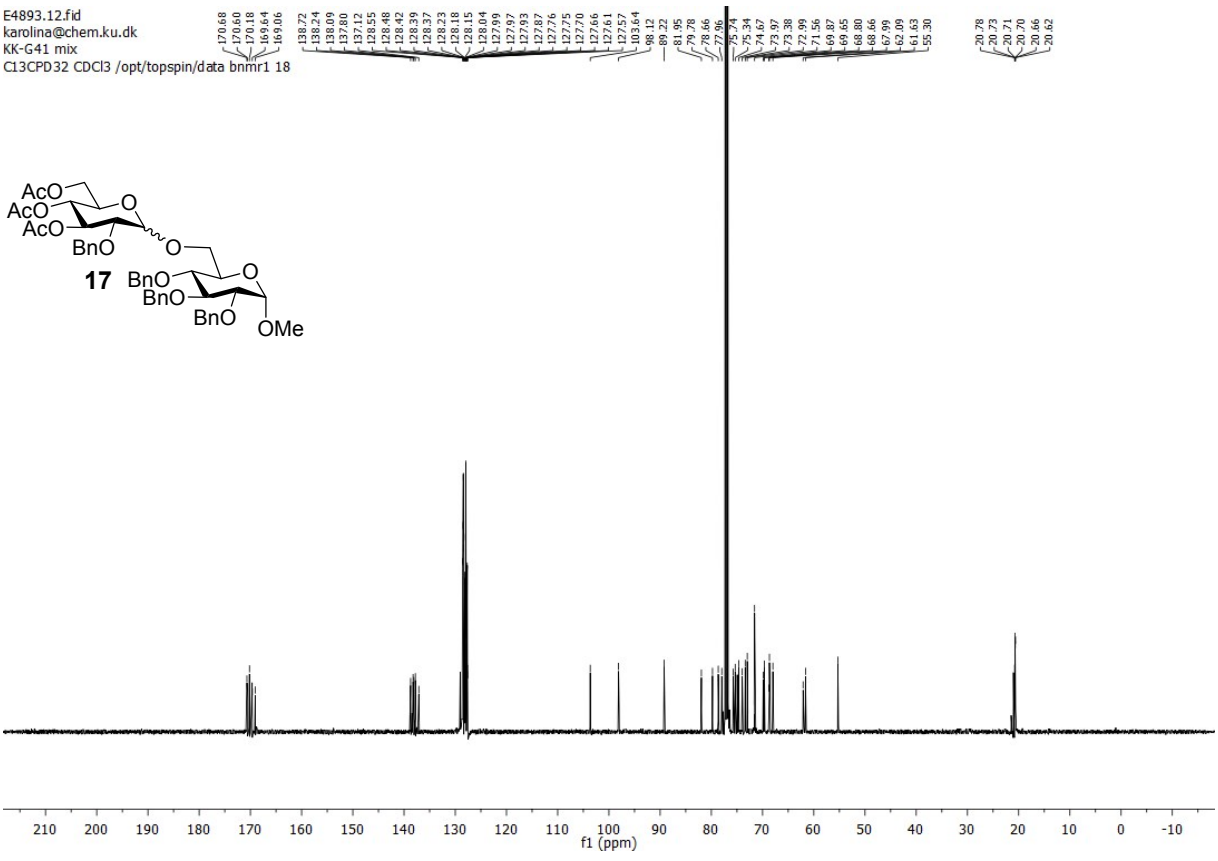
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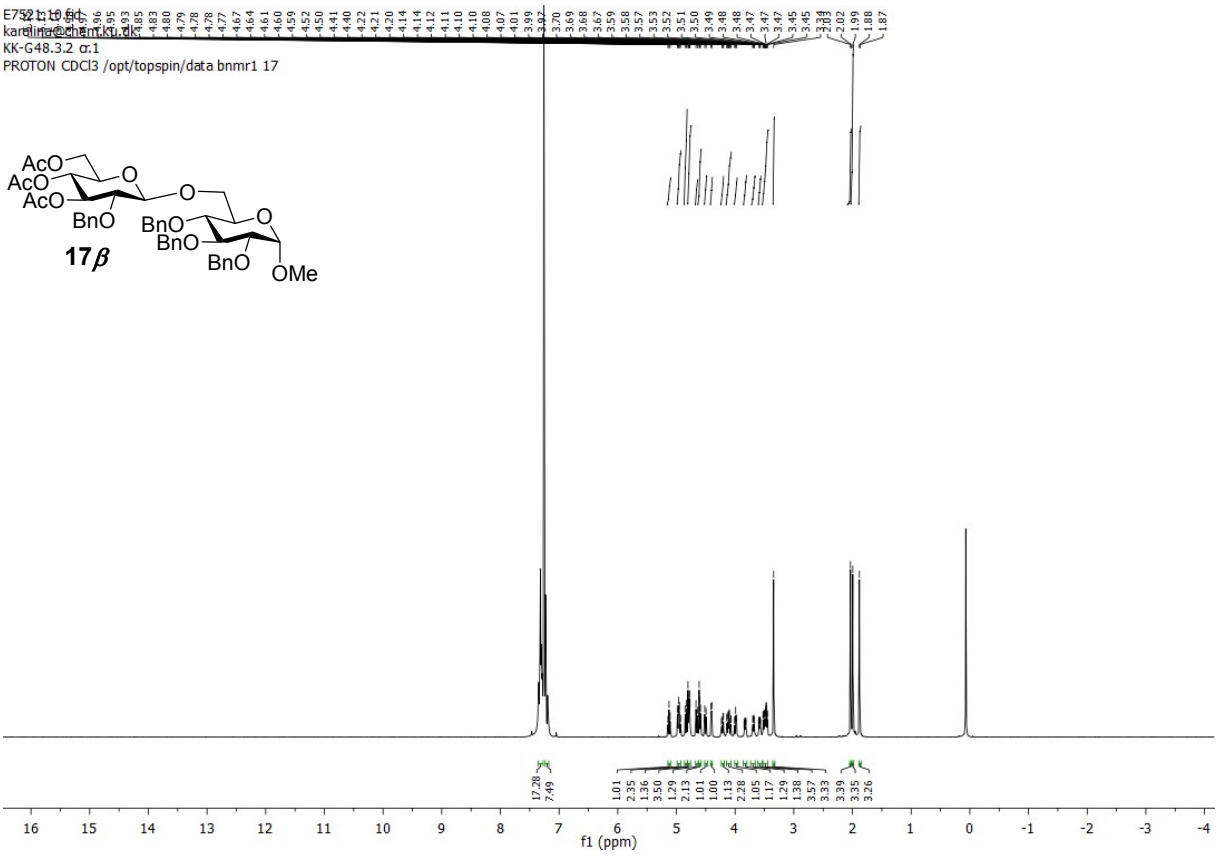
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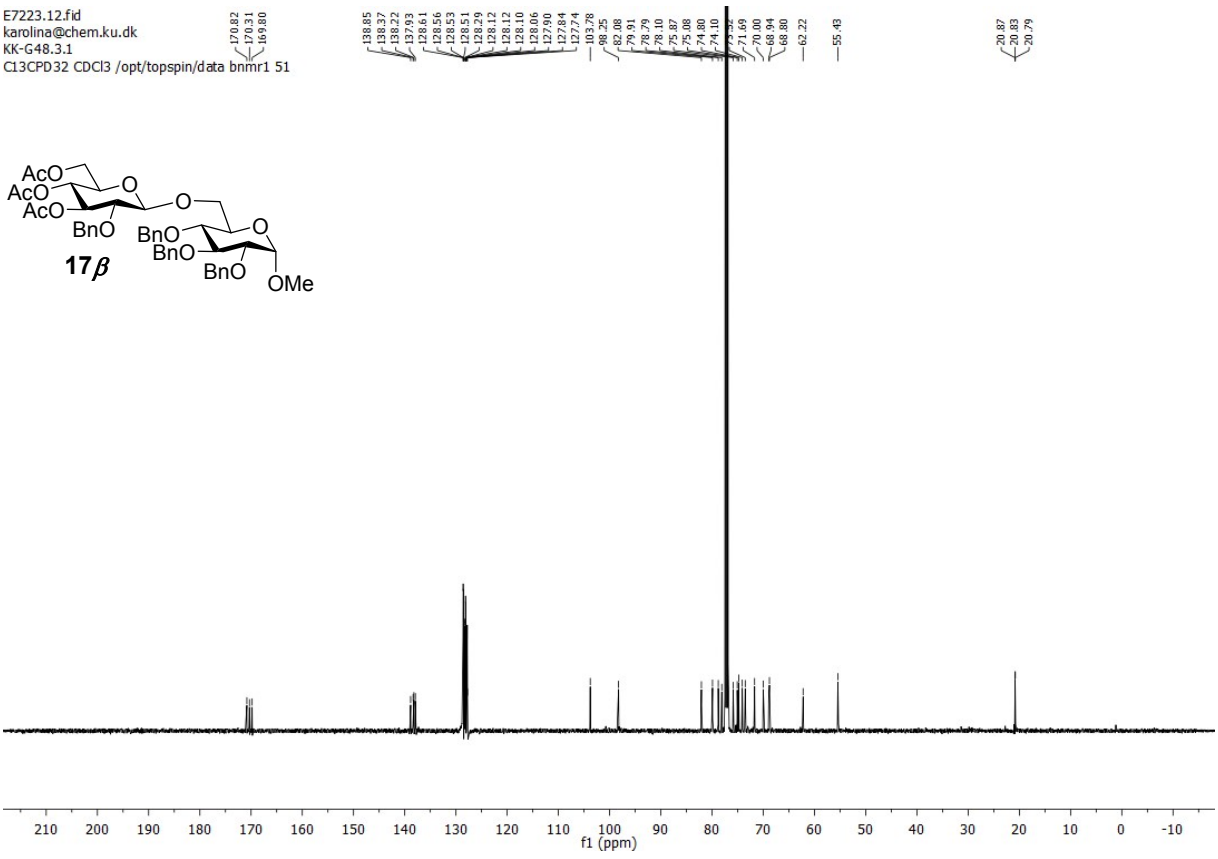
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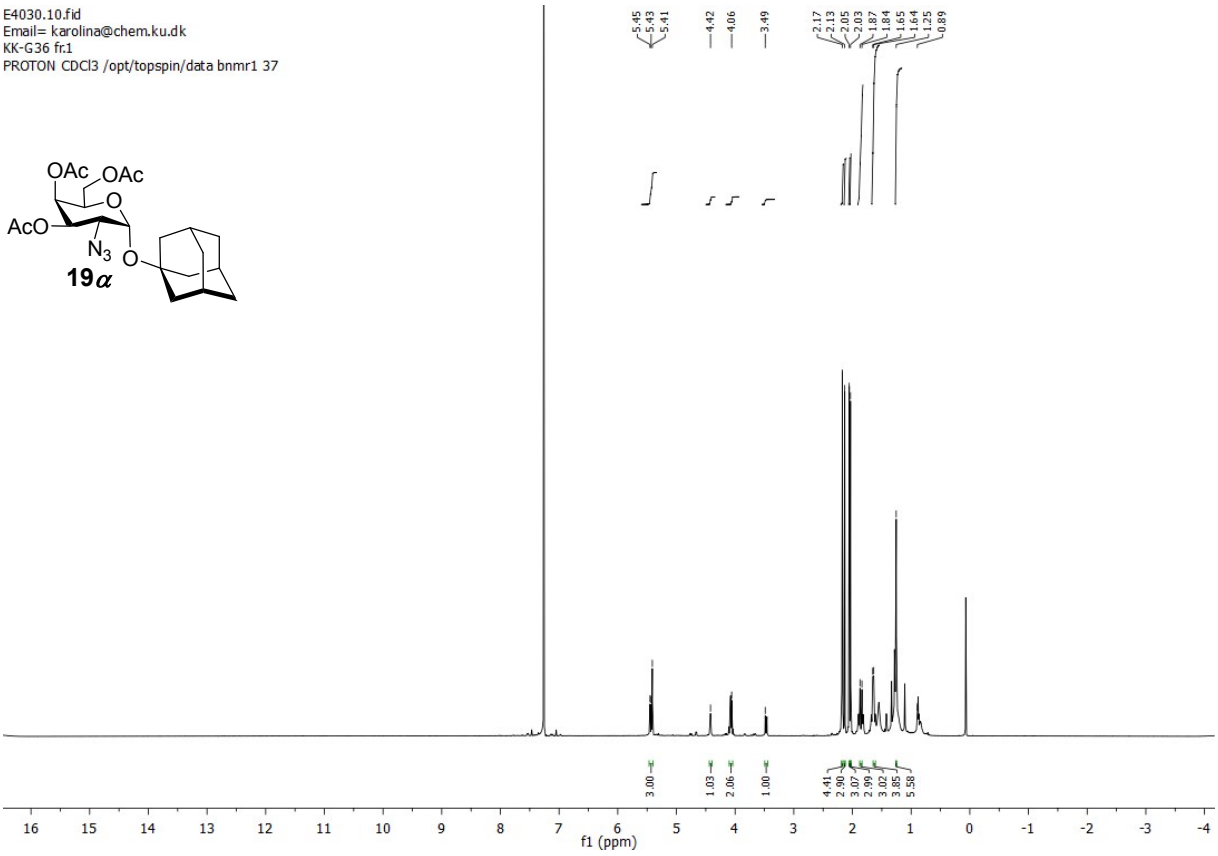
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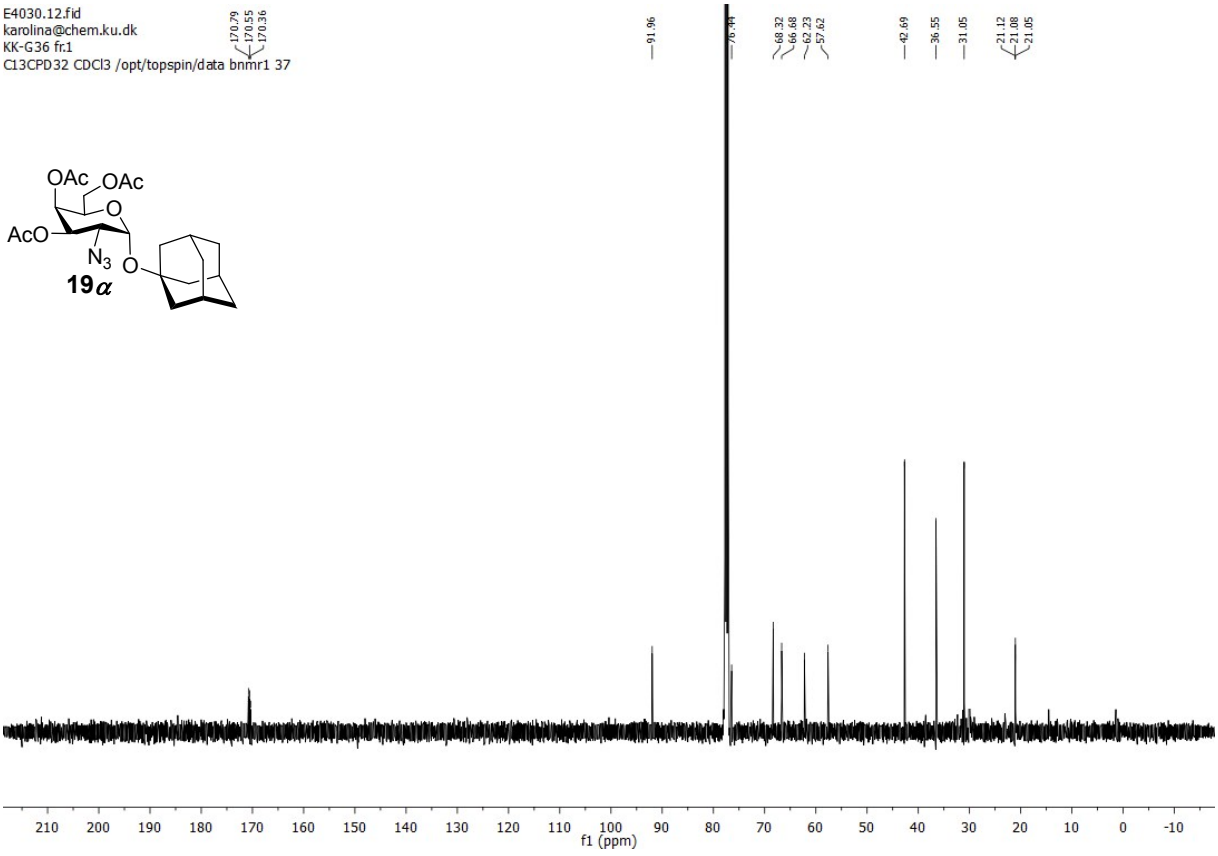
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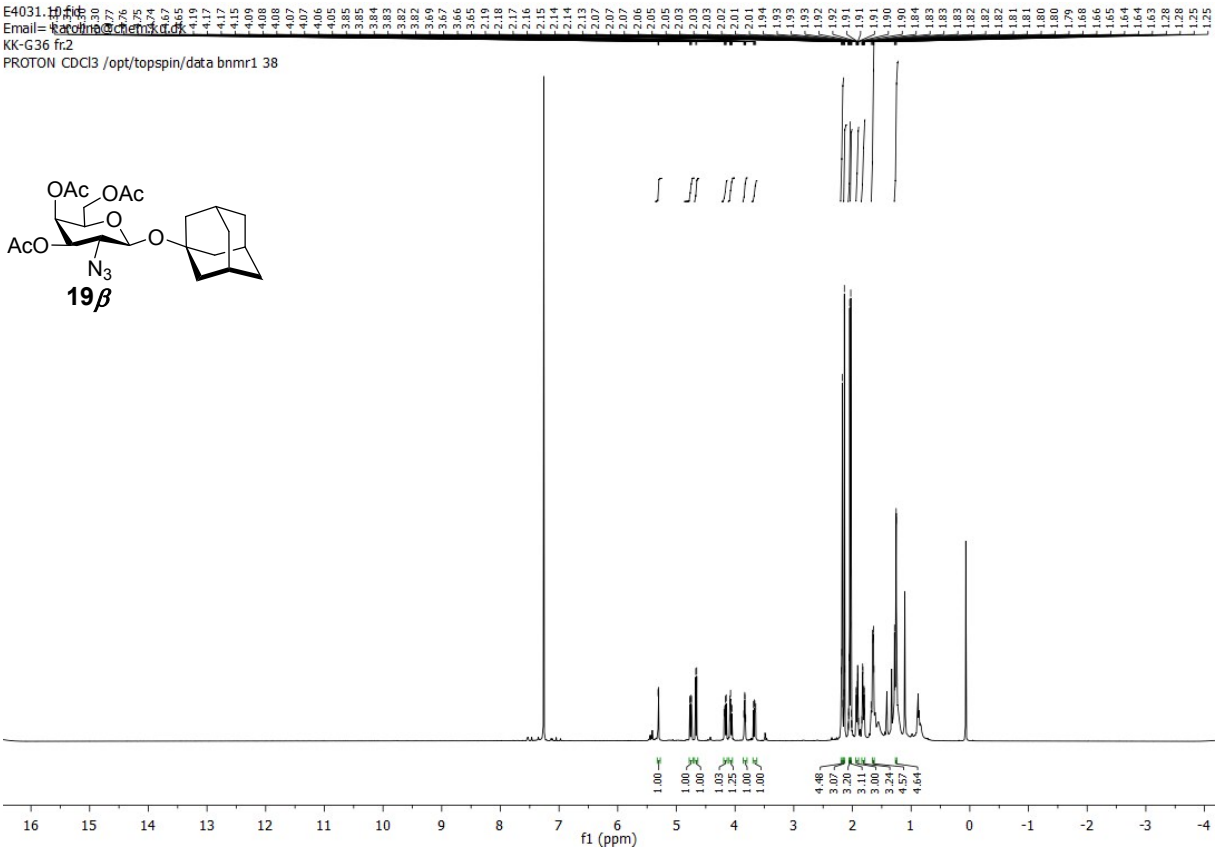
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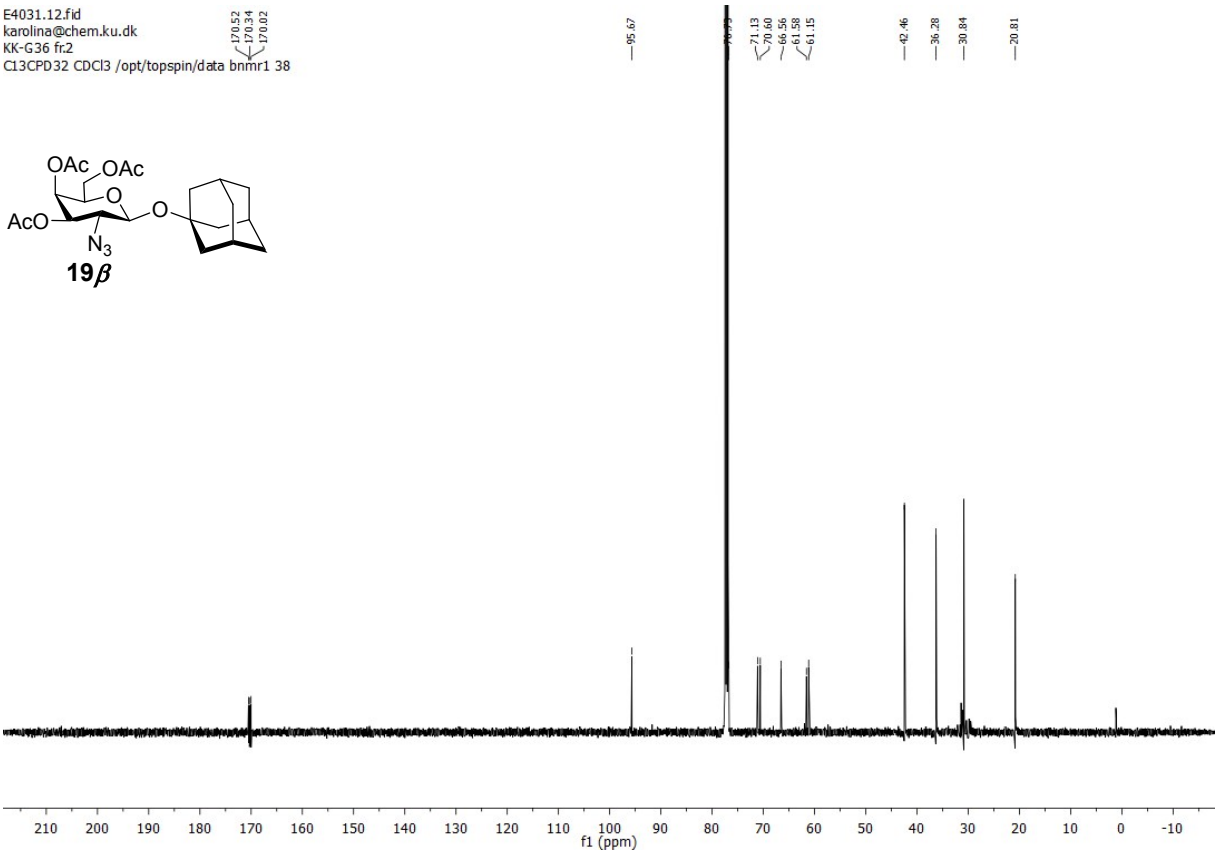
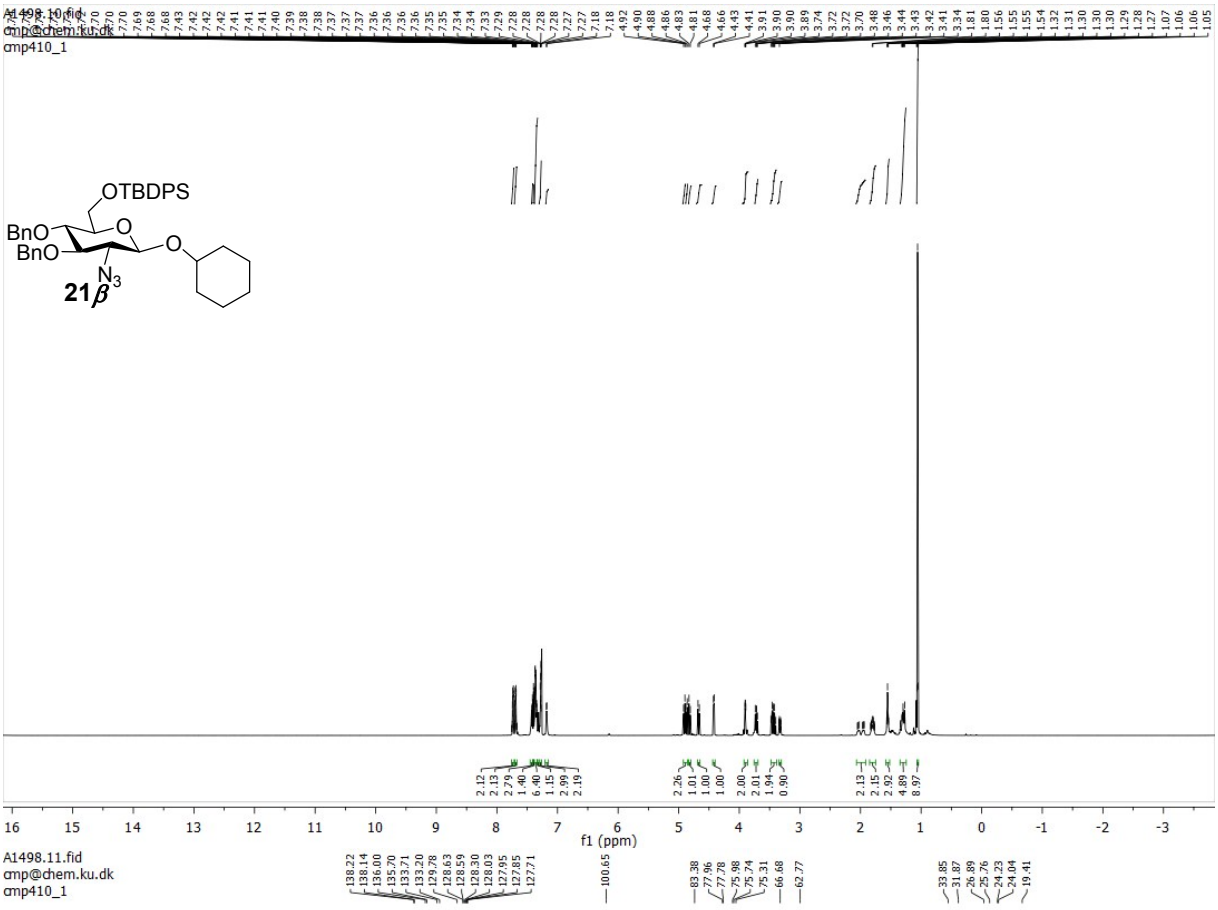
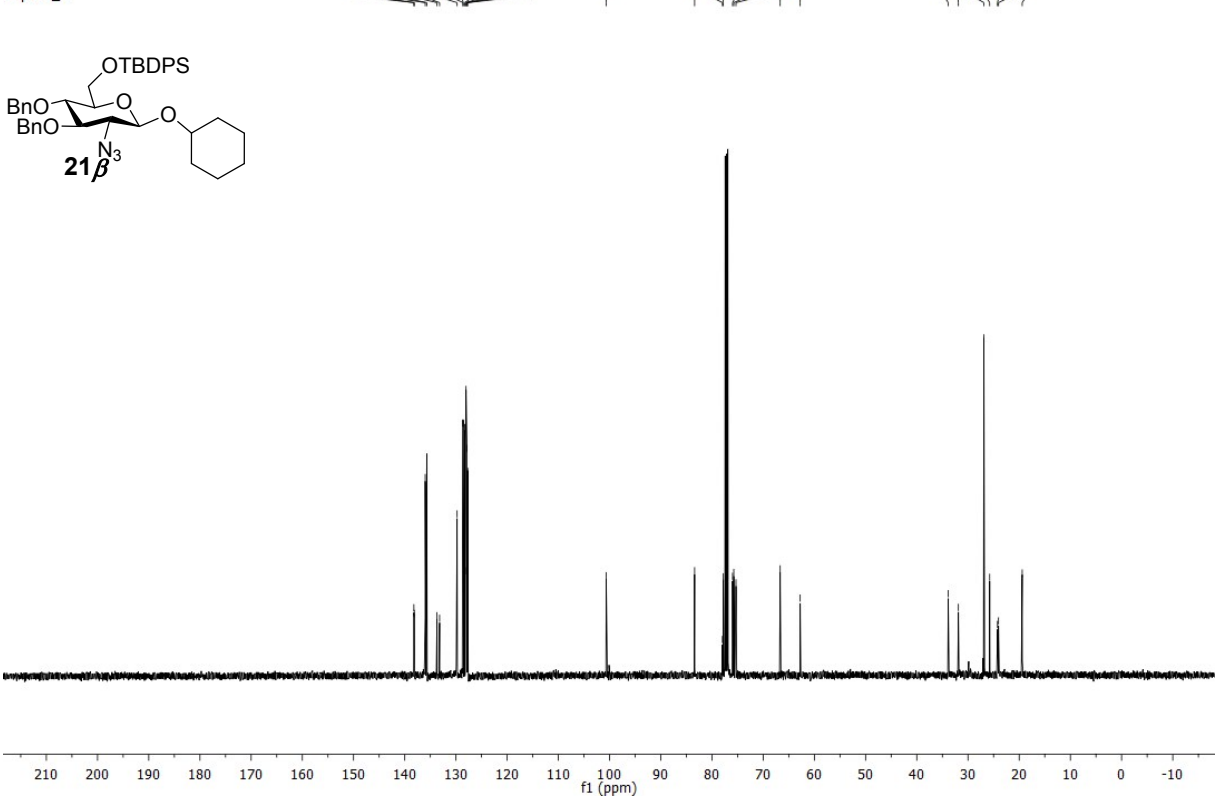
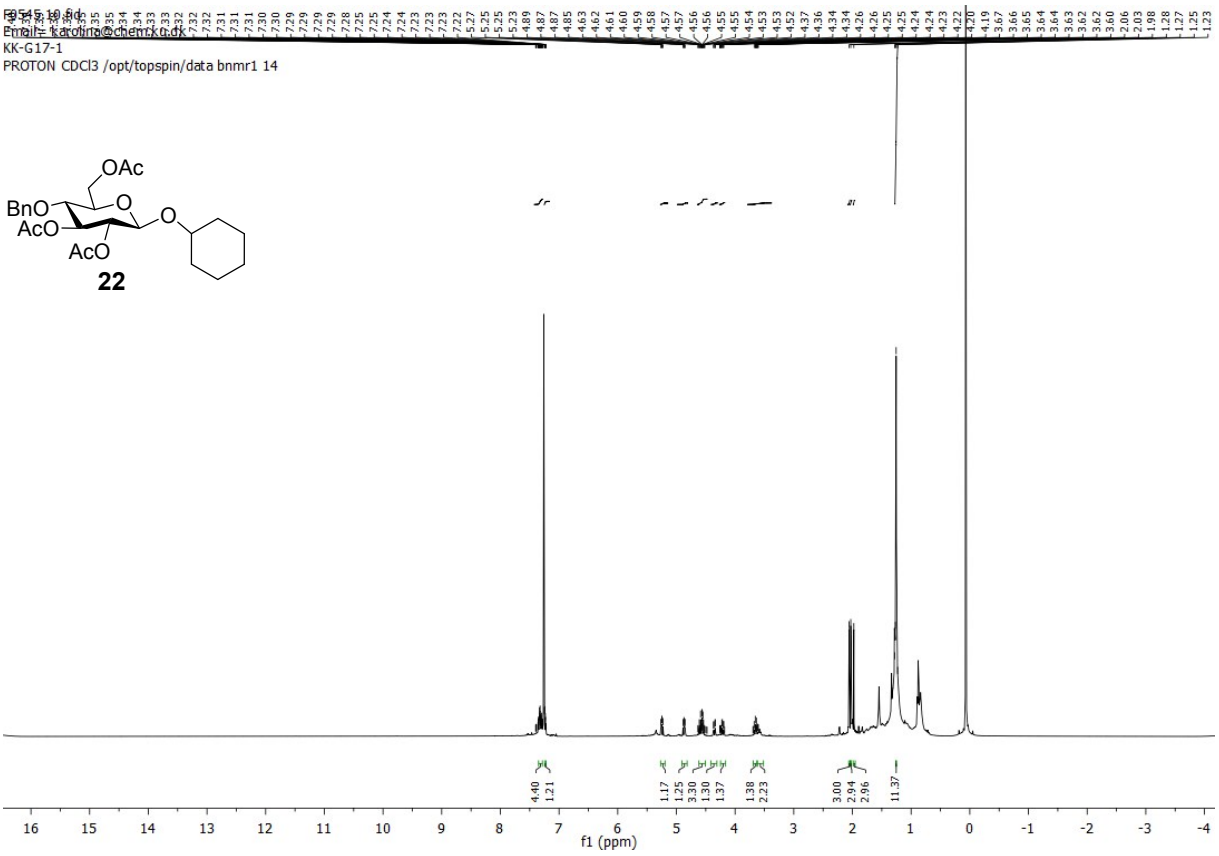
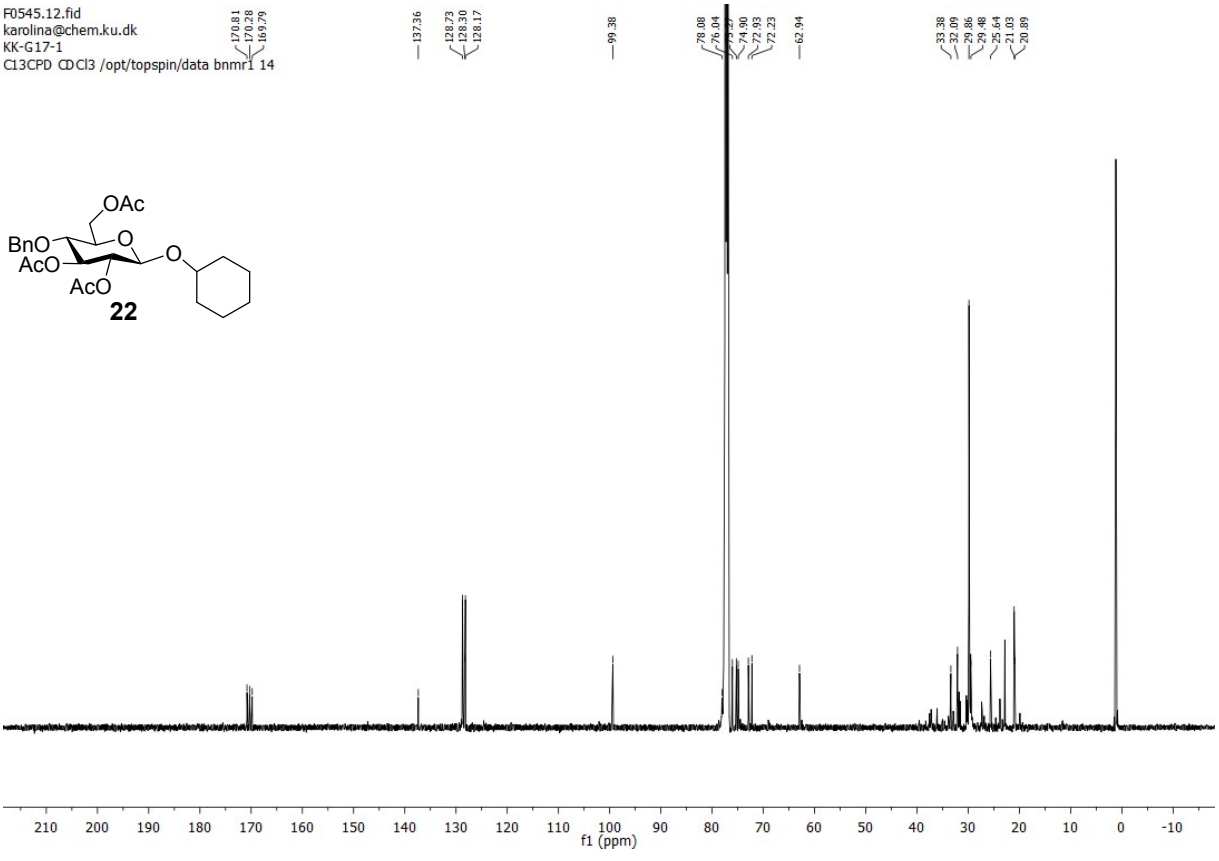

E4031.12.fid
karolina@chem.ku.dk
KK-G36 fr.2
C13CPD32 CDCl3 /opt/topspin/data bnmr1 38
170.52
170.34
170.02
95.67
76.73
71.13
70.60
66.56
61.58
61.15
42.46
36.28
30.84
20.81
OAc
OAc
O
AcO
O
N3
19β
f1 (ppm)


A1498.10.fid
cmp@chem.ku.dk
cmp410_1
OTBDPS
BnO
BnO
O
O
N3
21β
f1 (ppm)


A1498.11.fid
cmp@chem.ku.dk
cmp410_1
OTBDPS
BnO
BnO
O
O
N3
21β
f1 (ppm)


F0545.10.fid
Email: karolina@chem.ku.dk
KK-G17-1
PROTON CDCl3 /opt/topspin/data bnmr1 14
OAc
BnO
AcO
AcO
O
O
22
4.40
1.21
1.17
1.25
3.30
1.30
1.37
1.38
2.23
3.00
2.94
2.96
11.37
f1 (ppm)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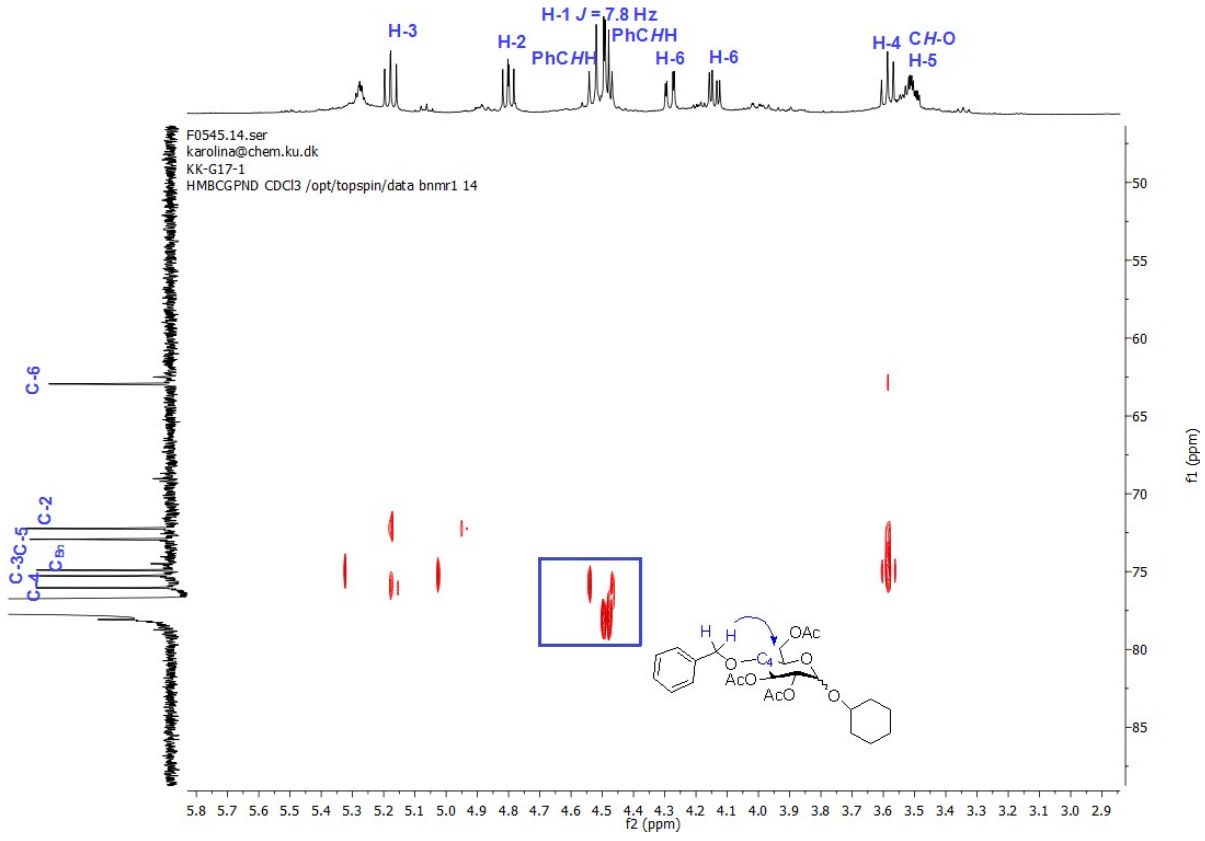
karolina@chem.ku.dk
KK-G17-1
C13CPD CDCl3 /opt/topspin/data bnmr1 14
170.81
170.38
169.79
137.36
128.73
128.30
128.17
99.38
78.08
76.04
74.90
72.93
72.23
62.94
33.38
32.09
29.86
29.48
25.64
21.03
20.89
OAc
BnO
AcO
AcO
O
O
22
f1 (ppm)


H-3
H-2
PhCHH
H-1 J = 7.8 Hz
PhCHH
H-6
H-6
H-4
CH-O
H-5
F0545.14.ser
karolina@chem.ku.dk
KK-G17-1
HMBCGPND CDCl3 /opt/topspin/data bnmr1 14
C-6
C-2
C-3
C-5
C-4
CBn
f1 (ppm)
f2 (ppm)
OAc
AcO
AcO
O
C4