Supporting Information

Transient imine as a directing group for the Pd-catalyzed anomeric C(*sp*³)–H arylation of 3-aminosugars

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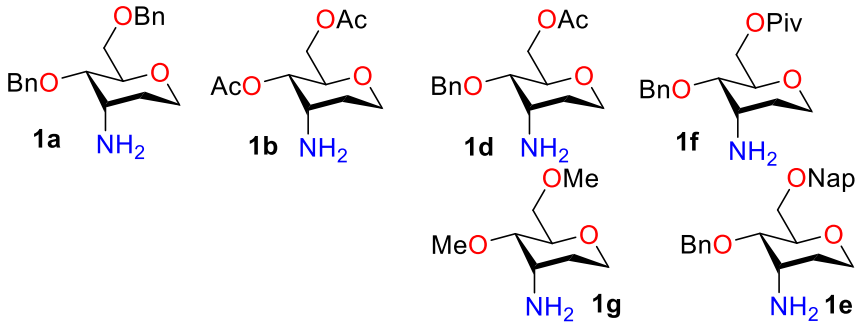
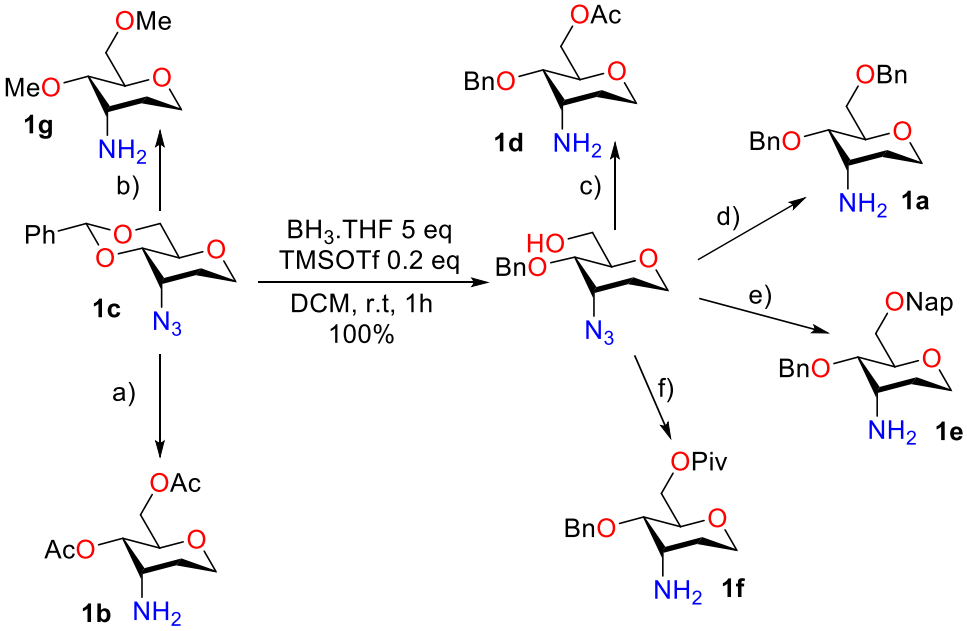
General information

All reactions were carried out under an argon atmosphere in oven-dried glassware unless otherwise noted. All solvents and reagents were used as obtained from suppliers unless otherwise noted. Analytical TLC was performed using Merck silica gel F254 (230-400 mesh) plates and analyzed by UV light or by staining upon heating with vanillin solution (15 g of vanillin, 250 mL of EtOH, 2.5 mL conc. H_2SO_4). For silica gel chromatography, the flash chromatography technique was used, with Merck silica gel 60 (230- 400 mesh) or RediSep Rf Gold Silica Cartridges and p.a. grade solvents.

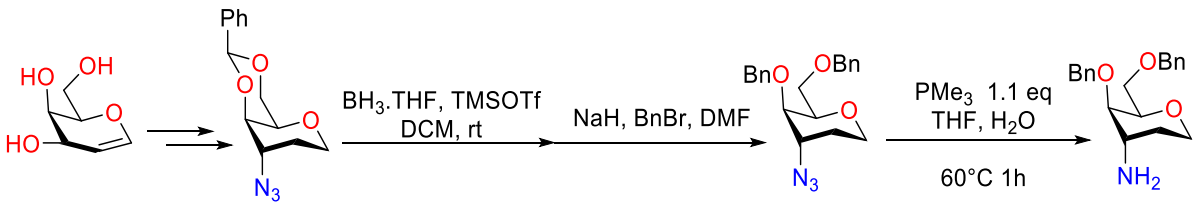
The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ or CD_3OD on Bruker Avance 200, 300 and 400 spectrometers. The chemical shifts of ^{1}H are reported in ppm relative to the solvent residual peak in $CDCl_3$ (δ 7.26) or in CD_3OD (δ 3.31) for ^{1}H NMR. For the ^{13}C NMR spectra, the solvent signals of $CDCl_3$ (δ 77.16) and CD_3OD (δ 49.00) were used as the internal standards. IR spectra were recorded on a Tensor 27 FT-IR spectrometer. Optical rotations were obtained with a Polarimeter-MCP 100. High-resolution mass spectrometric data were measured using MicroMass LCT Premier Spectrometer.

a) *List of Substrates:*





a) i) AcOH aq 80%, 1h, 80°C, ii) Py, Ac_2O, iii) PMe_3, THF/H_2O (95:5), 60°C.
b) i) AcOH aq 80%, 1h, 80°C, ii) NaH, MeI, DMF, rt, iii) PMe_3, THF/H_2O (95:5), 60°C.
c) i) Py, Ac_2O, ii) PMe_3, THF/H_2O (95:5), 60°C.
d) i) NaH, BnBr, DMF, rt, ii) PMe_3, THF/H_2O (95:5), 60°C.
e) i) NaH, NapBr, DMF, rt, ii) PMe_3, THF/H_2O (95:5), 60°C.
f) i) PivCl, NEt_3,DCM, rt, ii) PMe_3, THF/H_2O (95:5), 60°C.



All the experimental procedures are described in the reference[1]

[1] J. Ghouilem, C. Tran, N. Grimblat, P. Retailleau, M. Alami, V. Gandon, S. Messaoudi. *ACS Catal.* 2021, ***11***, 1818

b) *General procedure for C-H activation*

A reaction tube was charged with starting material (1.0 equiv), Pd $(OAc)_2$ (10 mol%), TDG 1 (50 mol%), L7 (50 mol%), AgTFA (2.0 equiv), aryl iodide (3.0 equiv), H_2O (10 equiv), and HFIP 19:1 AcOH (0.1 M, relative to starting material). The reaction vessel was purged with argon and sealed, then placed in an oil bath (preheated at 90 °C) for 16h. The reaction mixture was then allowed to cool to rt and EtOAc 1: 1 MeOH (10 mL) was added. The resulting solution was filtered through a pad of Celite, eluting with further EtOAc (2 × 10 mL). The solvent was removed under reduced pressure, and the crude material dried over vacuum for 1h, then added Imidazole-1-sulfonyl Azide Hydrochloride (1.5 equiv), $CuSO_4.5H_2O$ (2 mol%), K_2CO_3 (3 equiv) (in some cases Et_3N was used instead of K_2CO_3) and MeOH (0.2 M, relative to starting material), for 1h. the crude material was purified by flash column chromatography (0% grading to 4% AcOEt/Cyclohexane).

c) *General procedure CuAAc*[2]

1) To a stirred solution of Alkyne[3] (1 eq) and azide (1.5 equiv.) in tert-butanol and water (2 :1) 0.1M, were added $CuSO_4.5H_2O$ (10 mol%) and sodium ascorbate (40 mol%). The reaction mixture was stirred at room temperature until TLC monitoring showed complete conversion of the starting material (48 h). The reaction mixture was evaporated to dryness, then dissolved in CH_2Cl_2 and was filtered, the filtrate was evaporated to dryness and purified by flash column chromatography (25% grading to 45% AcOEt/Cyclohexane).

2) To a solution of 3-azido- (1 equiv) and CuI (0.5 equiv) in MeCN (0.1M)[4] were the corresponding acetylene derivative (2 equiv) and diisopropylethylamine (DIPEA) (1.2 equiv) added. The mixture was stirred (t) h at 50 °C before quenching with sat. aq. NH_4Cl followed by evaporation of the solvent. The residue was extracted twice with EtOAc and the organic phases were washed with brine, dried, evaporated and purified by flash column chromatography.

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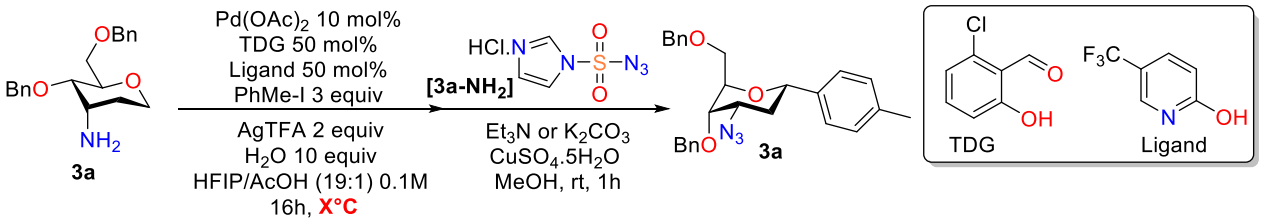
[2] S. M. Park, Y. Shen and B. H. Kim, *Org. Biomol. Chem*., 2007, ***5***, 610.

[3] a) D. H. Hilko, L. F. Bornaghi, S.-A. Poulsen *J. Org. Chem.* 2018, ***83***, 11944; b) G. T. Crisp and B. L. Flynn *J. Org. Chem*. 1993, ***58***, 6614.

[4] K. Peterson, R. Kumar, O. Stenström, P. Verma, P. R. Verma, M. Hakansson, ° B. Kahl-Knutsson, F. Zetterberg, H. Leffler, M. Akke,D. T. Logan, U. J. Nilsson, *J. Med. Chem*. 2018**,** ***61***, 3, 1164.

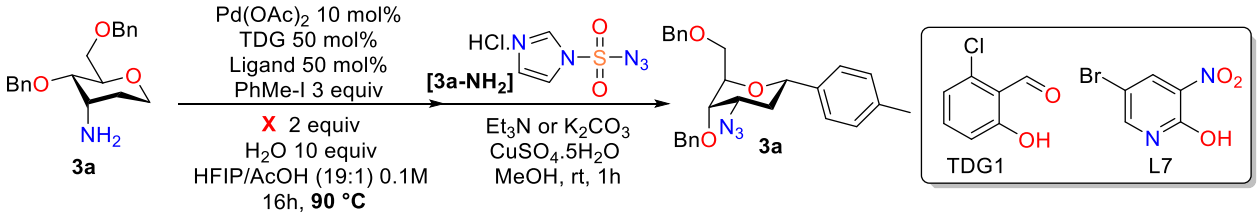
d) Optimization of the reaction conditions with the model substrate 3a

Temperature screening



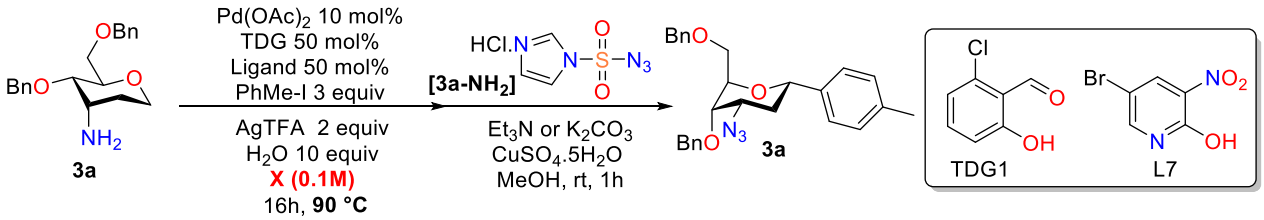
entry	Conditions	yield
1	110°C	31%
2	90°C	32%
3	80°C	29%
4	70°C	0%

Oxidant screening

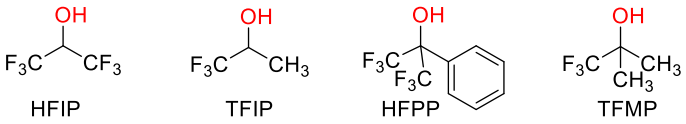


entry	Conditions	yield
1	AgTFA	51%
2	AgOMs	0%
3	AgOAc	0%
4	Ag_2O	0%
5	NFSI OTf	0%
6	NFSI BF_4	0%
7	$K_2S_2O_8$	0%
8	$Cu(TFA)_2$	18%

Solvant screening

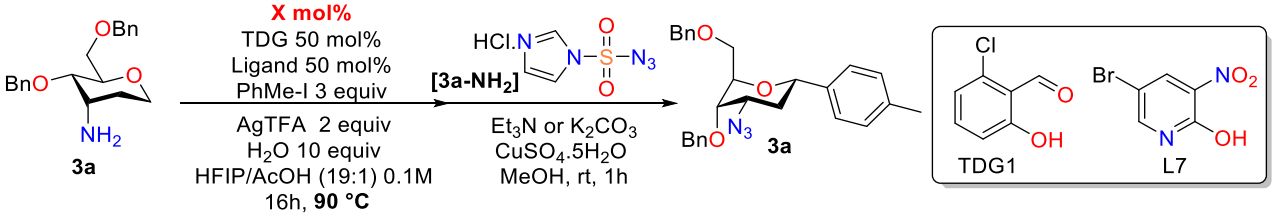


Solvant:



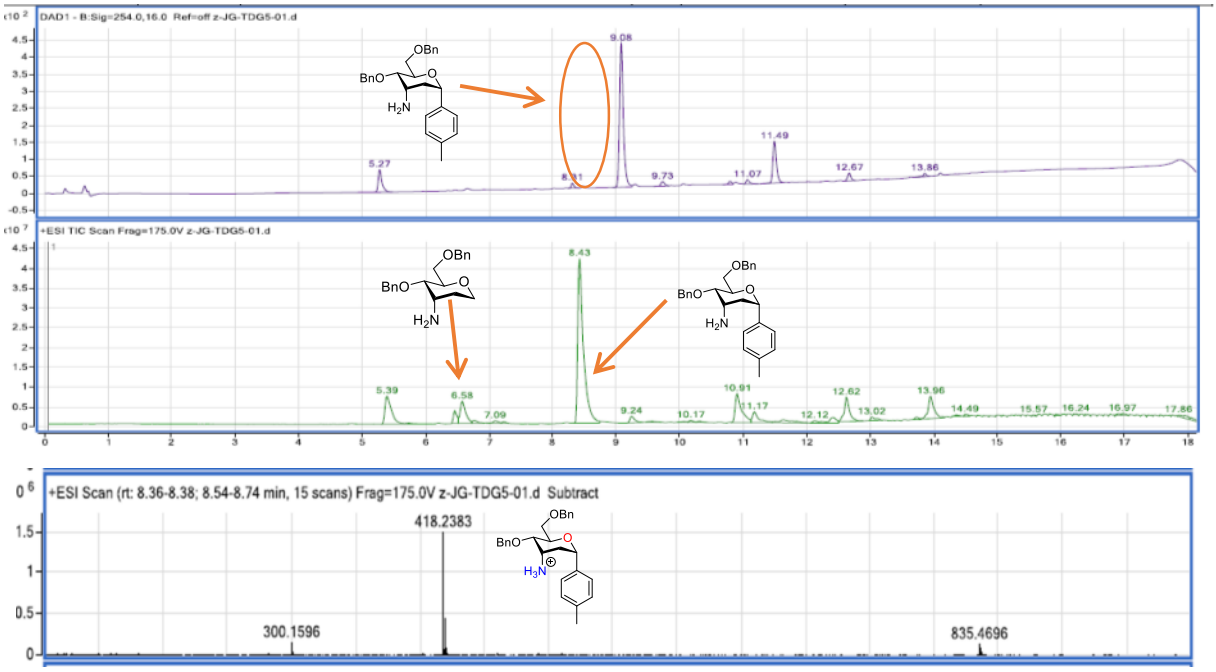
entry	Conditions	yield
1	HFIP 19 :1 AcOH	51%
2	HFIP 3 :1 AcOH	0%
3	HFIP 100%	27%
4	without H_2O	30%
5	HFIP 1 :1 PhCl	35%
6	TFIP 19 :1 AcOH	25%
7	HFPP 19 :1 AcOH	22%
8	TFMP 19 :1 AcOH	16%

Catalyst screening

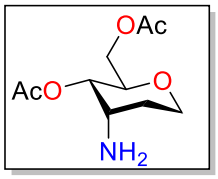


entry	Conditions	yield
1	$Pd(OAc)_2$ 10 mol%	51%
2	$Pd(OAc)_2$ 20 mol%	35%
3	$PdCl_2$ 10 mol%	25%
4	$Pd(OAc)_2$ 7.5 mol% & $Pd(TFA)_2$ 7.5 mol%	46%
5	$Pd(PhCN)_2Cl_2$ 7,5 mol% & $Pd(TFA)_2$ 7.5 mol%	32%
6	$Pd(OAc)_2$ 7.5 mol% & $Pd(PhCN)_2Cl_2$ 7.5 mol%	40%

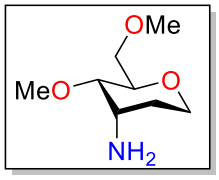
LCMS Analysis of the [NH_2-3a] intermediate (No absorption at 254 nm wavelength)



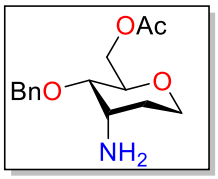
e) *Characterization of compounds:*



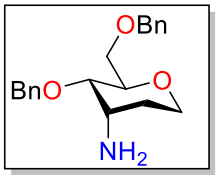
^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.10 (d, *J* = 5.1 Hz, 1H), 4.44 – 4.12 (m, 3H), 3.89 – 3.74 (m, 1H), 3.69 – 3.48 (m, 3H), 3.06 (s, 2H), 2.10 (s, 3H), 2.04 (s, 3H), 1.97 – 1.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 171.6, 75.2, 68.0, 64.0, 62.3, 48.4, 29.4, 23.5, 21.0. HRMS (ESI-TOF): m/z calculated for $C_{10}H_{17}NO_5^+$ [M+Na]$^+$ 254.0999, found 254.1000.



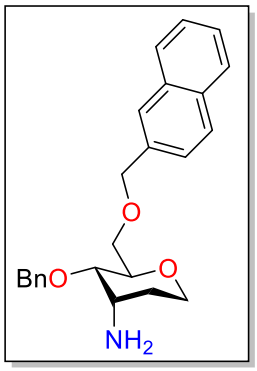
^{1}H NMR (300 MHz, Methanol-d^4) δ 3.92 – 3.71 (m, 4H), 3.64 (d, J = 3.6 Hz, 3H), 3.46 (m, 6H), 3.36 (s, 3H), 2.06 – 1.90 (m, 2H). ^{13}C NMR (75 MHz, MeOD) δ 75.1, 74.6, 72.8, 62.0, 59.5, 58.0, 47.8, 28.2. HRMS (ESI-TOF): m/z calculated for $C_8H_{18}NO_3^+$ [M+H]$^+$ 176.1281, found 176.1281.



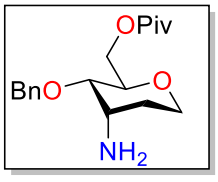
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 (s, 5H), 4.67 (d, J = 11.5 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 4.37 – 4.27 (m, 1H), 4.27 – 4.16 (m, 2H), 3.92 – 3.80 (m, 1H), 3.76 – 3.59 (m, 2H), 3.53 (dd, J = 9.5, 3.1 Hz, 1H), 2.02 (s, 3H), 1.87 – 1.72 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 128.8, 128.5, 128.4, 128.3, 73.4, 73.1, 71.7, 64.3, 64.0, 63.6, 62.6, 62.5, 21.0. HRMS (ESI-TOF): m/z calculated for $C_{15}H_{22}NO_4^+$ [M+H]$^+$ 280.1543, found 280.1545.



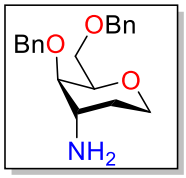
^{1}H NMR (200 MHz, Chloroform-*d*) δ 7.36 – 7.23 (m, 10H), 4.52 (m, 4H), 3.96 – 3.44 (m, 7H), 2.17 (s, 2H), 2.02 – 1.79 (m, 1H), 1.76 – 1.59 (m, 1H). ^{13}C NMR (75 MHz, CDCl3) δ 138.3, 137.9, 128.5, 128.4, 128.1, 128.0, 127.7, 74.5, 73.7, 73.6, 71.5, 69.8, 61.7, 45.8, 30.7. HRMS (ESI-TOF): m/z calculated for $C_{20}H_{25}NO_3^+$ [M+H]$^+$ 328.1907, found 328.1912.



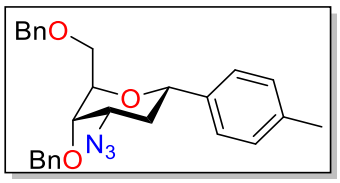
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.86 – 7.71 (m, 4H), 7.53 – 7.40 (m, 3H), 7.25 – 7.10 (m, 5H), 4.85 – 4.62 (m, 2H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 3.95 – 3.49 (m, 7H), 1.86 (s, 2H), 1.71 – 1.59 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.5, 128.3, 128.1, 128.0, 128.0, 127.8, 126.9, 126.2, 126.1, 126.0, 126.0, 74.3, 73.8, 73.7, 71.6, 69.8, 61.7, 46.0, 30.6. HRMS (ESI-TOF): m/z calculated for $C_{24}H_{27}NO_3^+$ [M+H]$^+$ 378.2064, found 378.2069.



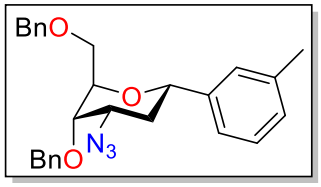
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.32 (s, 5H), 4.60 (d, *J* = 11.3 Hz, 1H), 4.46 (d, *J* = 11.4 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.19 (dd, *J* = 11.6, 4.7 Hz, 1H), 3.96 – 3.74 (m, 2H), 3.73 – 3.55 (m, 2H), 3.43 (d, *J* = 7.6 Hz, 1H), 1.92 – 1.60 (m, 4H), 1.20 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 128.7, 128.1, 73.6, 72.3, 71.3, 64.1, 61.5, 27.4. HRMS (ESI-TOF): m/z calculated for $C_{18}H_{27}NO_4^+$ [M+H] $^+$ 322.2013, found 322.2019.



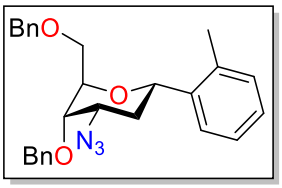
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 – 7.23 (m, 10H), 4.60 – 4.43 (m, 4H), 4.14 – 4.00 (m, 1H), 3.81 – 3.64 (m, 3H), 3.54 (dd, *J* = 10.1, 4.8 Hz, 1H), 3.26 – 3.12 (m, 2H), 2.15 – 2.05 (m, 1H), 1.65 (s, 2H), 1.43 – 1.31 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 138.2, 128.5, 128.1, 127.9, 127.7, 78.2, 73.5, 73.2, 72.5, 68.5, 61.3, 46.5, 30.2. HRMS (ESI-TOF): m/z calculated for $C_{20}H_{25}NO_3^+$ [M+H] $^+$ 328.1907, found 328.1910.



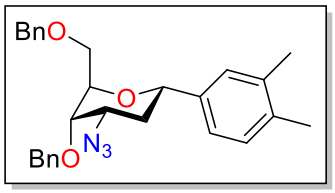
Compound 3a was obtained (25 mg, 51%) as a yellow oil. $[\alpha]^{25}_{D}$= -16.8 ° (c 0,5 EtOH). IR (neat, cm^{-1}): 2924, 2854, 2096, 1454, 1263, 1091, 1049.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 6.7 Hz, 2H), 7.43 – 7.29 (m, 10H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.80 (dd, *J* = 10.7, 3.0 Hz, 1H), 4.75 (d, *J* = 4.7 Hz, 1H), 4.58 (s, 2H), 4.40 – 4.34 (m, 1H), 3.84 (m, 1H), 3.78 – 3.70 (m, 3H), 2.45 – 2.34 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.1, 137.9, 137.6, 129.2, 128.7, 128.5, 128.1, 128.0, 127.9, 127.8, 126.1, 74.7, 74.1, 73.6, 73.4, 72.1, 69.6, 56.8, 32.7, 21.3. HRMS (ESI-TOF): m/z calculated for $C_{27}H_{29}N_3O_3^+$ [M+Na] $^+$ 466.2101, found 466.2106.



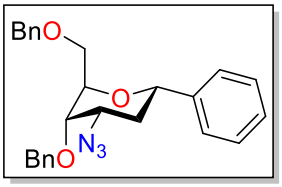
Compound 3b was obtained (15 mg, 32%) as a yellow oil. $[\alpha]^{25}_{D}$ = -7.8 ° (c 0,5 EtOH). IR (neat, cm^{-1}): 2924, 2854, 2098, 1456, 1261, 1087, 1047.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.09 (m, 14H), 4.78 – 4.72 (m, 1H), 4.71 (d, *J* = 5.0 Hz, 2H), 4.53 (d, *J* = 1.7 Hz, 2H), 4.34 (td, *J* = 5.4, 2.3 Hz, 1H), 3.80 (t, *J* = 2.8 Hz, 1H), 3.75 – 3.65 (m, 3H), 2.41 – 2.31 (m, 4H), 1.95 (dt, *J* = 12.7, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 138.3, 138.1, 137.9, 128.7, 128.5, 128.5, 128.1, 128.0, 127.9, 127.8, 126.8, 123.3, 74.7, 74.2, 73.6, 73.6, 72.2, 69.6, 56.7, 32.7, 29.9, 21.6. HRMS (ESI-TOF): m/z calculated for $C_{27}H_{29}N_3O_3^+$ $[M+NH_4]^+$ 461.2547, found 461.2560.



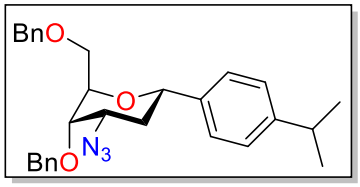
Compound 3c was obtained (19 mg, 40%) as a yellow oil. $[\alpha]^{25}_{D}$ = -15.33 ° (c 0,75 EtOH). IR (neat, cm^{-1}): 2970, 2926, 2096, 1454, 1361, 1265, 1087, 1045.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.40 – 7.24 (m, 9H), 7.24 – 7.11 (m, 3H), 5.02 (dd, *J* = 11.3, 2.1 Hz, 1H), 4.72 (q, *J* = 11.9 Hz, 2H), 4.52 (s, 2H), 4.37 (td, *J* = 5.3, 1.5 Hz, 1H), 3.81 (d, *J* = 1.8 Hz, 1H), 3.78 – 3.65 (m, 3H), 2.42 – 2.27 (m, 4H), 1.94 – 1.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 138.1, 137.8, 134.8, 130.5, 128.7, 128.5, 128.1, 128.1, 127.9, 127.8, 127.8, 126.5, 126.1, 75.0, 74.8, 73.7, 72.2, 70.7, 70.2, 56.9, 31.2, 19.1. HRMS (ESI-TOF): m/z calculated for $C_{27}H_{29}N_3O_3^+$ $[M+Na]^+$ 466.2101, found 466.2104.



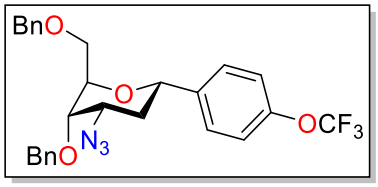
Compound 3d was obtained (15.5 mg, 37%) as a yellow oil. $[\alpha]^{25}_{D}$ = -12.2 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}) : 2924, 2854, 2098, 1454, 1259, 1091, 1026.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 11H), 7.18 – 7.04 (m, 3H), 4.74 (d, *J* = 3.2 Hz, 1H), 4.70 (d, *J* = 5.8 Hz, 2H), 4.53 (s, 2H), 4.33 (td, *J* = 5.4, 2.2 Hz, 1H), 3.79 (t, *J* = 2.4 Hz, 1H), 3.72 – 3.66 (m, 3H), 2.42 – 2.31 (m, 1H), 2.25 (d, *J* = 7.2 Hz, 6H), 1.93 (dt, *J* = 12.6, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.1, 137.9, 136.8, 136.2, 129.8, 128.7, 128.5, 128.1, 128.0, 127.9, 127.8, 127.4, 123.6, 74.2, 73.6, 72.1, 56.8, 32.7, 29.8, 19.9, 19.6. HRMS (ESI-TOF): m/z calculated for $C_{28}H_{35}N_3O_3^+$ $[M+NH_4]^+$ 475.2704, found 475.2712.



Compound 3e was obtained (22 mg, 35%) as a yellow oil. $[\alpha]^{25}_{D}$ = -7 ° (c 0,5 EtOH). IR (neat, cm^{-1}): 2926, 2856, 2096, 1496, 1454, 1261, 1089, 1045, 1026.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.22 (m, 15H), 4.80 (dd, *J* = 10.6, 3.0 Hz, 1H), 4.71 (d, *J* = 4.1 Hz, 2H), 4.54 (d, *J* = 2.2 Hz, 2H), 4.39 – 4.29 (m, 1H), 3.80 (t, *J* = 2.9 Hz, 1H), 3.76 – 3.68 (m, 3H), 2.43 – 2.29 (m, 1H), 2.03 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 138.1, 137.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 126.2, 74.8, 74.2, 73.6, 73.5, 72.2, 69.6, 69.6, 56.7, 32.7. HRMS (ESI-TOF): m/z calculated for $C_{26}H_{27}N_3O_3^+$ $[M+Na]^+$ 452.1945, found 452.1946.

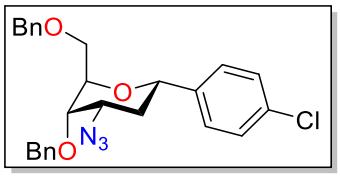


Compound 3f was obtained (23 mg, 45%) as a yellow oil. $[\alpha]^{25}_{D}$ = -7.7 ° (c 1, CHCl3). IR (neat, cm^{-1}):2958, 2926, 2096, 1454, 1363, 1265, 1091. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.28 (m, 10H), 7.21 (d, *J* = 8.2 Hz, 2H), 4.76 (dd, *J* = 10.7, 2.9 Hz, 1H), 4.70 (d, *J* = 5.2 Hz, 2H), 4.53 (s, 2H), 4.33 (td, *J* = 5.4, 2.3 Hz, 1H), 3.85 – 3.78 (m, 1H), 3.75 – 3.63 (m, 3H), 2.94 – 2.85 (m, 1H), 2.44 – 2.31 (m, 1H), 1.99 – 1.92 (m, 1H), 1.25 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 139.0, 138.1, 137.9, 128.7, 128.5, 128.0, 128.0, 127.9, 127.8, 126.6, 126.2, 74.8, 74.2, 73.6, 73.5, 72.1, 69.6, 56.8, 34.0, 32.5, 24.1. HRMS (ESI-TOF): m/z calculated for $C_{29}H_{33}N_3O_3^+$ $[M+Na]^+$ 494.2414, found 494.2418.

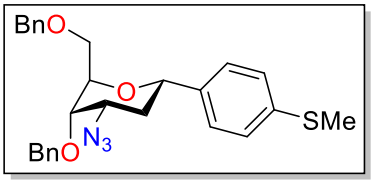


Compound 3g was obtained (20 mg, 38%) as a yellow oil. $[\alpha]^{25}_{D}$ = -0.9 ° (c 1, CH_2Cl_2). IR (neat, cm^{-1}): 2958, 2926, 2096, 1456, 1361, 1219, 1089. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.16 (m, 14H), 4.81 (dd, *J* = 10.5, 3.0 Hz, 1H), 4.69 (d, *J* = 1.4 Hz, 2H), 4.62 – 4.55 (m, 1H), 4.53 (d, *J* = 2.9 Hz, 2H), 4.35 – 4.27 (m, 1H), 3.79 (t, *J* = 3.0 Hz, 1H), 3.76 – 3.70 (m, 1H), 3.68 (dd, *J* = 5.2, 2.5 Hz, 2H), 2.37 – 2.25 (m, 1H), 2.01 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 137.9, 137.8, 128.7, 128.6, 128.1, 128.0,

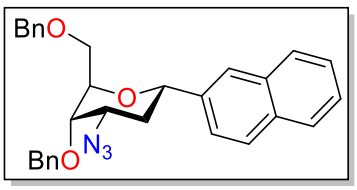
127.8, 127.6, 74.7, 73.7, 72.8, 72.3, 69.6, 56.6, 32.7. ^{19}F NMR (188 MHz, $CDCl_3$) δ -57.9. HRMS (ESI-TOF): m/z calculated for $C_{27}H_{26}F_3N_3O_4^+$ $[M+Na]^+$ 536.1768, found 536.1777.



Compound 3h was obtained (12.5 mg, 22%) as a yellow oil. $[\alpha]^{25}_D$ = -25.2 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 2926, 2856, 2098, 1718, 1490, 1454, 1261, 1087, 1026, 1014.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.18 (m, 14H), 4.72 (dd, *J* = 10.3, 3.1 Hz, 1H), 4.64 (d, *J* = 1.5 Hz, 2H), 4.53 – 4.42 (m, 2H), 4.28 – 4.21 (m, 1H), 3.73 (t, *J* = 2.6 Hz, 1H), 3.71 – 3.64 (m, 1H), 3.62 (dd, *J* = 5.2, 1.8 Hz, 2H), 2.31 – 2.17 (m, 1H), 1.95 – 1.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 137.9, 137.8, 133.5, 128.7, 128.6, 128.1, 128.1, 128.0, 127.8, 127.5, 74.7, 74.1, 73.6, 72.8, 72.2, 69.6, 56.6, 32.7. HRMS (ESI-TOF): m/z calculated for $C_{26}H_{26}ClN_3O_3^+$ $[M+NH_4]^+$ 481.2001, found 481.2001.

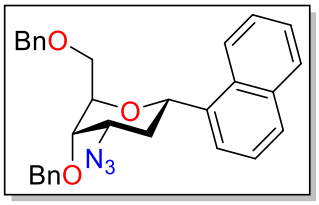


Compound 3i was obtained (10.5 mg, 18%) as a yellow oil. $[\alpha]^{25}_D$ = -8 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 2922, 2852, 2096, 1496, 1456, 1261, 1089, 1049, 1026.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.29 (m, 14H), 4.76 (dd, *J* = 10.5, 3.0 Hz, 1H), 4.69 (d, *J* = 2.9 Hz, 2H), 4.66 – 4.59 (m, 1H), 4.58 – 4.49 (m, 2H), 4.34 – 4.27 (m, 1H), 3.82 – 3.76 (m, 1H), 3.75 – 3.70 (m, 1IIJH), 3.70 – 3.66 (m, 1H), 2.47 (s, 3H), 2.39 – 2.26 (m, 1H), 1.99 – 1.89 (m, 1H). 13C NMR (101 MHz, CDCl3) δ 138.7, 138.2, 138.0, 138.0, 137.9, 137.7, 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.0, 126.7, 73.8, 73.6, 73.1, 72.2, 72.1, 69.6, 62.4, 56.7, 32.6, 29.8, 16.3. HRMS (ESI-TOF): m/z calculated for $C_{27}H_{29}N_3O_3S^+$ $[M+NH_4]^+$ 493.2268, found 493.2275.

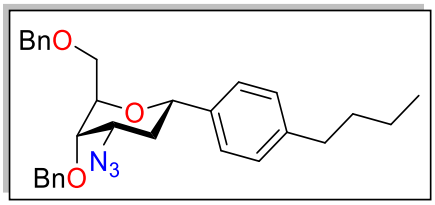


Compound 3j was obtained (19 mg, 33%) as a yellow oil. $[\alpha]^{25}_D$ = -46.13 ° (c 0,75 CH_2Cl_2). IR (neat, cm^{-1}): 2924, 2860, 2096, 1508, 1496, 1454, 1361, 1261, 1089, 1047, 1026.^{1}H NMR (400 MHz, Chloroform-

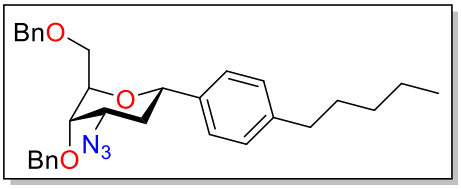
d) δ 7.89 – 7.78 (m, 4H), 7.57 – 7.41 (m, 5H), 7.40 – 7.29 (m, 10H), 4.96 (dd, *J* = 10.5, 3.0 Hz, 1H), 4.73 (d, *J* = 4.1 Hz, 2H), 4.56 (d, *J* = 3.5 Hz, 2H), 4.44 – 4.35(m, 1H), 3.87 – 3.65 (m, 4H), 2.52 –2.39 (m, 1H), 2.11 – 2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.1, 137.9, 133.4, 133.2, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 126.2, 126.0, 124.9, 124.3, 74.8, 74.3, 73.6, 73.6, 72.2, 69.6, 56.8, 32.7. HRMS (ESI-TOF): m/z calculated for $C_{30}H_{29}N_3O_3^+$ [M+Na] $^+$ 502.2101, found 502.2102.



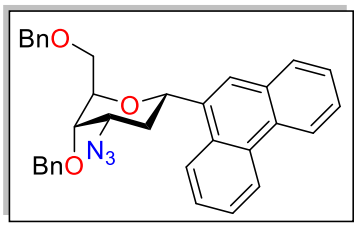
Compound 3k was obtained (14 mg, 26%) as a yellow oil. $[\alpha]^{25}_D$ = -22.8 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 2960, 2926, 2856, 2096, 1454, 1259, 1085, 1045, 1026.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.66 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.44 – 7.30 (m, 10H), 5.53 (dd, *J* = 11.6, 2.5 Hz, 1H), 4.84 – 4.69 (m, 2H), 4.58 (s, 2H), 4.48 (td, *J* = 5.4, 1.6 Hz, 1H), 3.92 – 3.74 (m, 4H), 2.71 – 2.55 (m, 1H), 2.18 – 2.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.8, 137.1, 134.1, 130.7, 129.0, 128.7, 128.7, 128.6, 128.1, 127.9, 127.9, 126.2, 125.6, 125.6, 124.1, 123.7, 75.2, 74.9, 73.8, 72.3, 71.7, 69.9, 56.8, 31.8. HRMS (ESI-TOF): m/z calculated for $C_{30}H_{29}N_3O_3^+$ [M+NH_4] $^+$ 497.2547, found 497.2551.



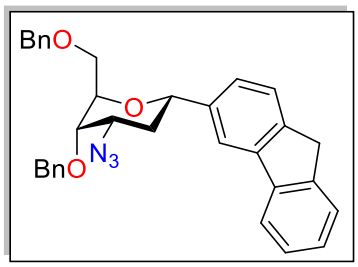
Compound 3l was obtained (18 mg, 25%) as a yellow oil. $[\alpha]^{25}_D$ = -6 ° (c 0,75 CH_2Cl_2). IR (neat, cm^{-1}): 2926, 2856, 2098, 1456, 1259, 1089, 1018.^{1}H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.40 (m, 2H), 7.38 – 7.27 (m, 10H), 7.16 (d, J = 8.0 Hz, 2H), 4.76 (dd, J = 11.0, 3.0 Hz, 1H), 4.70 (d, J = 5.2 Hz, 2H), 4.53 (s, 2H), 4.33 (dt, J = 5.2, 2.5 Hz, 1H), 3.79 (d, J = 2.9 Hz, 1H), 3.74 – 3.62 (m, 3H), 2.65 – 2.55 (m, 1H), 2.37 (q, J = 11.9 Hz, 1H), 1.95 (dt, J = 12.6, 3.3 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.39 – 1.30 (m, 3H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 142.7, 138.8, 138.1, 137.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 126.2, 74.8, 74.2, 73.6, 73.5, 72.2, 69.6, 56.8, 35.5, 33.8, 32.6, 29.9, 22.4, 14.1. HRMS (ESI-TOF): m/z calculated for $C_{30}H_{35}N_3O_3^+$ [M+Na] $^+$ 508.2571, found 508.2570.



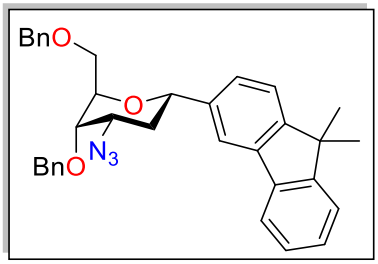
Compound 3m was obtained (14.5 mg, 18%) as a yellow oil. $[\alpha]^{25}_{D}$ = -11.2 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 2926, 2854, 2098, 1456, 1363, 1259, 1089, 1045, 1026, 800, 734.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.27 (m, 12H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.74 (d, *J* = 3.1 Hz, 1H), 4.70 (d, *J* = 5.2 Hz, 2H), 4.53 (s, 2H), 4.33 (dt, *J* = 5.3, 2.6 Hz, 1H), 3.80 (s, 1H), 3.74 – 3.67 (m, 3H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.37 (q, *J* = 11.8 Hz, 1H), 1.95 (d, *J* = 12.6 Hz, 1H), 1.64 – 1.57 (m, 2H), 1.34 – 1.30 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 142.7, 138.8, 138.1, 137.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 126.1, 74.8, 74.2, 73.6, 73.5, 72.2, 69.6, 35.8, 32.6, 31.6, 31.3, 22.7, 14.2. HRMS (ESI-TOF): m/z calculated for $C_{31}H_{37}N_3O_3^+$ $[M+NH_4]^+$ 517.3173, found 517.3179.



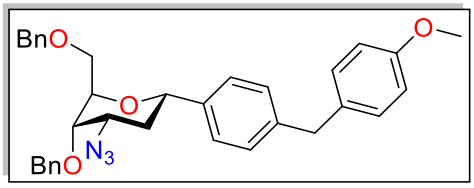
Compound 3n was obtained (20 mg, 34%) as a yellow oil. $[\alpha]^{25}_{D}$ = -11 ° (c 1 CH_2Cl_2). IR (neat, cm^{-1}): 2960, 2926, 2866, 2094, 1496, 1452, 1363, 1263, 1085, 1066, 1049, 1028.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.16 – 8.07 (m, 1H), 7.87 – 7.78 (m, 1H), 7.59 – 7.46 (m, 3H), 7.45 – 7.38 (m, 3H), 7.33 – 7.22 (m, 9H), 7.17 (s, 1H), 5.46 (dd, *J* = 11.5, 2.5 Hz, 1H), 4.70 (d, *J* = 7.2 Hz, 2H), 4.50 (s, 2H), 4.47 – 4.38 (m, 1H), 3.87 – 3.72 (m, 4H), 2.57 (q, *J* = 12 Hz, 1H), 2.17 – 2.03 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 137.8, 135.2, 131.6, 131.0, 130.4, 129.7, 129.1, 128.8, 128.6, 128.1, 128.0, 127.9, 126.9, 126.8, 126.7, 126.4, 125.1, 124.4, 123.4, 122.6, 75.3, 75.0, 73.8, 72.3, 71.7, 69.9, 56.9, 31.6. HRMS (ESI-TOF): m/z calculated for $C_{34}H_{31}N_3O_3^+$ $[M+Na]^+$ 552.2258, found 552.2257.



Compound 3o was obtained (18 mg, 25%) as a yellow oil. $[\alpha]^{25}_{D}$ = -6.4 ° (c 0,75 CH_2Cl_2). IR (neat, cm^{-1}): 2924, 2854, 2100, 1456, 1261, 1091, 1049, 1026.^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (dd, J = 11.4, 7.7 Hz, 2H), 7.69 – 7.58 (m, 1H), 7.54 (d, J = 7.4 Hz, 2H), 7.41 – 7.29 (m, 12H), 4.86 (dd, J = 10.7, 2.9 Hz, 1H), 4.78 – 4.68 (m, 2H), 4.55 (d, J = 2.4 Hz, 2H), 4.41 – 4.35 (m, 1H), 3.89 (s, 1H), 3.82 (t, J = 2.7 Hz, 1H), 3.76 – 3.70 (m, 2H), 3.49 (s, 2H), 2.42 (q, J = 11.7 Hz, 1H), 2.05 – 1.97 (m, 1H). 13C NMR (101 MHz, CDCl3) δ 143.7, 143.6, 141.6, 141.6, 140.3, 138.1, 137.9, 134.3, 128.7, 128.5, 128.1, 128.0, 127.9, 127.8, 126.9, 126.8, 125.2, 125.0, 122.8, 120.1, 119.9, 74.8, 74.4, 73.9, 73.6, 72.2, 69.6, 56.8, 37.1, 32.9, 29.8. HRMS (ESI-TOF): m/z calculated for $C_{33}H_{31}N_3O_3^+$ $[M+Na]^+$ 540.2258, found 568.2258.

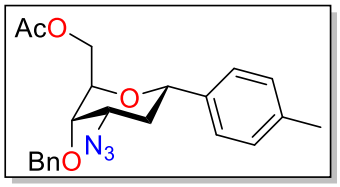


Compound 3p was obtained (18 mg, 25%) as a yellow oil. $[\alpha]^{25}_{D}$ = - 9.6 ° (c 0,75 CH_2Cl_2). IR (neat, cm^{-1}): 2924, 2854, 2098, 1456, 1261, 1209, 1091, 1043, 1026.^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 – 7.67 (m, 2H), 7.48 – 7.42 (m, 3H), 7.42 – 7.38 (m, 2H), 7.38 – 7.29 (m, 10H), 4.86 (dd, J = 10.6, 2.8 Hz, 1H), 4.74 (d, J = 4.1 Hz, 2H), 4.55 (d, J = 1.9 Hz, 2H), 4.43 – 4.33 (m, 1H), 3.83 (s, 1H), 3.79 – 3.68 (m, 3H), 2.42 (q, J = 11.7 Hz, 1H), 2.02 (dt, J = 12.7, 3.5 Hz, 1H), 1.53 – 1.44 (m, 6H). 13C NMR (101 MHz, CDCl3) δ 154.0, 140.8, 139.1, 138.1, 137.9, 134.3, 128.7, 128.6, 128.1, 128.0, 127.9, 127.9, 127.4, 127.3, 127.1, 125.2, 122.7, 120.5, 120.1, 120.0, 74.8, 74.2, 74.0, 73.6, 72.2, 69.6, 56.9, 47.1, 32.9, 29.8, 27.4. HRMS (ESI-TOF): m/z calculated for $C_{35}H_{35}N_3O_3^+$ $[M+Na]^+$ 568.2571, found 568.2571.

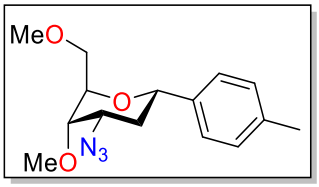


Compound 3q was obtained (17 mg, 30%) as a yellow oil. $[\alpha]^{25}_{D}$ = -5.46 ° (c 0,75 CH_2Cl_2). IR (neat, cm^{-1}): 2954, 2924, 2854, 2100, 1510, 1456, 1246, 1097, 1028.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.19 (m, 14H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.79 – 4.72 (m, 1H), 4.70 (d, *J* = 3.9 Hz, 2H), 4.52 (d, *J* = 2.7 Hz, 2H), 4.35 – 4.28 (m, 1H), 3.93 (s, 2H), 3.78 (s, 3H), 3.71 – 3.65 (d, *J* = 5.5 Hz, 3H), 2.40 – 2.28 (m, 1H), 1.99 – 1.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 141.8, 141.8, 133.3, 130.1,

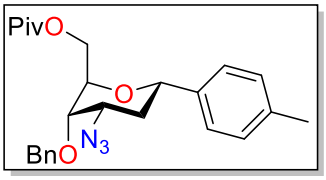
128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 126.7, 123.8, 114.0, 74.7, 74.1, 73.6, 73.5, 72.2, 69.5, 62.4, 57.8, 56.8, 55.4, 41.2, 32.7, 29.8. HRMS (ESI-TOF): m/z calculated for $C_{27}H_{26}F_3N_3O_4^+$ $[M+NH_4]^+$ 567.2966, found 567.2972.



Compound 3r was obtained (9.5 mg, 16%) as a yellow oil. $[\alpha]^{25}_D$ = -5.4 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}) : 2926, 2856, 2100, 1735, 1456, 1367, 1230, 1093, 1039.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.35 (m, 4H), 7.30 – 7.25 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.75 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.71 (d, *J* = 2.1 Hz, 2H), 4.46 – 4.39 (m, 1H), 4.38 – 4.32 (m, 1H), 4.12 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.68 – 3.57 (m, 2H), 2.49 – 2.38 (m, 1H), 2.34 (s, 3H), 2.05 (s, 3H), 2.04 – 1.97(dt, *J* = 12.0, 3.3 Hz, 1H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 138.0, 137.8, 137.7, 129.3, 128.6, 128.2, 126.2, 73.9, 72.8, 72.6, 72.1, 61.8, 56.5, 32.3, 21.3, 21.0. HRMS (ESI-TOF): m/z calculated for $C_{22}H_{25}N_3O_4^+$ $[M+Na]^+$ 418.1737, found 418.1739.

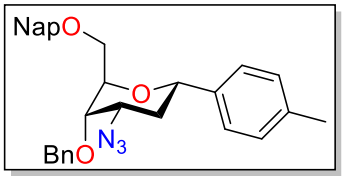


Compound 3s was obtained (11 mg, 15%) as a yellow oil. $[\alpha]^{25}_D$ = -52.6 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 2926, 2854, 2096, 1456, 1261, 1112, 1089, 1041.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.77 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.28 – 4.22 (m, 1H), 3.76 (dt, *J* = 11.6, 3.8 Hz, 1H), 3.65 (dd, *J* = 5.3, 2.9 Hz, 2H), 3.51 (s, 4H), 3.39 (s, 3H), 2.33 (s, 3H), 2.28 (ddd, *J* = 12.8, 11.7, 10.5 Hz, 1H), 2.00 – 1.89 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 137.5, 129.2, 126.1, 77.4, 73.7, 73.4, 72.6, 59.5, 58.0, 56.7, 32.7, 21.3. HRMS (ESI-TOF): m/z calculated for $C_{15}H_{21}N_3O_4^+$ $[M+Na]^+$ 314.1475, found 314.1487.

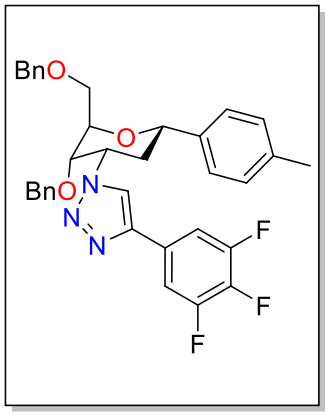


Compound 3t was obtained (16 mg, 28%) as a yellow oil. $[\alpha]^{25}_D$ = -5.8° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}) : 2960, 2927, 2870, 2098, 1730, 1456, 1280, 1261, 1157, 1122, 1095, 1047.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.15 (m, 7H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.70 – 4.55 (m, 3H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.14 – 4.02 (m, 1H), 3.65 – 3.49 (m, 2H), 2.41 – 2.27 (m, 1H), 2.25 (s, 3H), 1.93 (d, *J* = 12.8 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 138.0, 137.7, 129.2, 128.6, 128.1, 126.2, 74.2, 72.9,

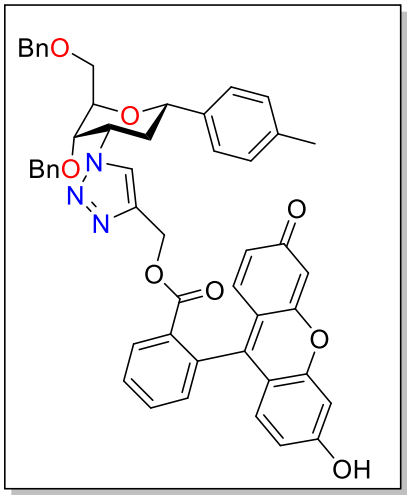
72.6, 72.2, 62.0, 56.5, 32.2, 27.3, 21.3. HRMS (ESI-TOF): m/z calculated for $C_{25}H_{35}N_4O_4^+$ $[M+NH_4]^+$ 455.2653, found 455.5654.



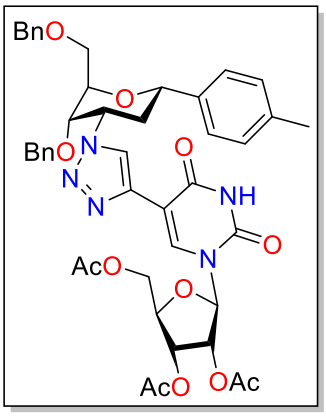
Compound 3u was obtained (12 mg, 16%) as a yellow oil. $[\alpha]^{25}_D$ = -23.2 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 2924, 2858, 2096, 1508, 1456, 1261, 1089, 1047.^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 – 7.76 (m, 3H), 7.73 (s, 1H), 7.51 – 7.45 (m, 2H), 7.45 – 7.35 (m, 3H), 7.35 – 7.22 (m, 5H), 7.14 (d, J = 7.8 Hz, 2H), 4.78 – 4.63 (m, 5H), 4.34 (dd, J = 5.3, 2.9 Hz, 1H), 3.80 (s, 1H), 3.71 (d, J = 5.3 Hz, 3H), 2.40 – 2.26 (m, 4H), 1.96 – 1.88 (m, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 138.7, 138.1, 137.6, 135.4, 133.4, 133.2, 129.2, 128.6, 128.5, 128.0, 127.9, 127.9, 126.7, 126.4, 126.2, 126.1, 125.7, 74.8, 74.1, 73.7, 73.4, 72.2, 69.5, 56.8, 32.7, 21.3. HRMS (ESI-TOF): m/z calculated for $C_{31}H_{35}N_4O_3^+$ $[M+NH_4]^+$ 511.2704, found 511.2706.



Compound **4a** was obtained (31 mg, 61%) as a yellow solid according to the general procedure (C). $[\alpha]^{25}_D$ = - 56.2 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 3049, 2925, 2854, 1642, 1454, 1241, 1047. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.34 – 7.14 (m, 12H), 7.12 – 6.95 (m, 4H), 5.43 (dt, J = 13.1, 3.8 Hz, 1H), 4.89 (dd, J = 11.4, 2.5 Hz, 1H), 4.63 – 4.46 (m, 3H), 4.39 (t, J = 5.3 Hz, 1H), 4.10 (d, J = 11.3 Hz, 1H), 3.90 (t, J = 2.0 Hz, 1H), 3.83 (dd, J = 10.2, 5.5 Hz, 1H), 3.73 (dd, J = 10.2, 5.0 Hz, 1H), 2.46 (q, J = 12.2 Hz, 1H), 2.26 (s, 3H), 1.99 (dt, J = 12.2, 3.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 151.1, 149.9, 144.6, 141.1, 140.8, 138.3, 137.8, 137.5, 137.1, 129.3, 129.2, 129.2, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.1, 128.1, 128.0, 127.8, 127.8, 127.0, 126.2, 125.9, 120.2, 117.4, 109.7, 109.6, 109.5, 109.4, 74.9, 74.2, 74.1, 73.7, 72.3, 72.2, 70.0, 57.9, 34.0, 21.1. HRMS (ESI-TOF): m/z calculated for $C_{35}H_{33}F_3N_3O_3^+$ $[M+H]^+$ 600.2469, found 600.2475.



Compound **4b** was obtained (21 mg, 59%) as an orange solid according to the general procedure (C). $[\alpha]^{25}_{D}$ = - 21.6 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 3624, 3190, 2927, 2919, 2851, 1403, 1365, 1241, 1218, 1039. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 5.3 Hz, 1H), 7.73 – 7.61 (m, 2H), 7.36 (t, *J* = 3.4 Hz, 2H), 7.26 (s, 10H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.09 (s, 2H), 7.01 – 6.93 (m, 1H), 6.93 – 6.80 (m, 2H), 6.77 – 6.63 (m, 2H), 5.48 (d, *J* = 12.3 Hz, 1H), 5.22 (d, *J* = 2.7 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 4.75 – 4.63 (m, 1H), 4.63 – 4.50 (m, 2H), 4.48 – 4.34 (m, 2H), 4.23 – 4.14 (m, 1H), 4.04 – 3.93 (m, 1H), 3.85 (d, *J* = 5.3 Hz, 1H), 3.83 – 3.71 (m, 1H), 2.57 – 2.46 (m, 1H), 2.40 – 2.25 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 160.2, 153.0, 152.0, 148.6, 138.4, 138.0, 137.7, 137.3, 135.4, 130.1, 129.3, 128.8, 128.7, 128.6, 128.1, 127.9, 126.0, 125.3, 124.1, 123.0, 116.7, 109.9, 103.4, 102.2, 77.3, 74.7, 74.4, 73.8, 72.2, 70.1, 62.4, 58.0, 29.8, 21.3. HRMS (ESI-TOF): m/z calculated for $C_{50}H_{44}N_3O_8^+$ $[M+H]^+$ 814.3121, found 814.3125.

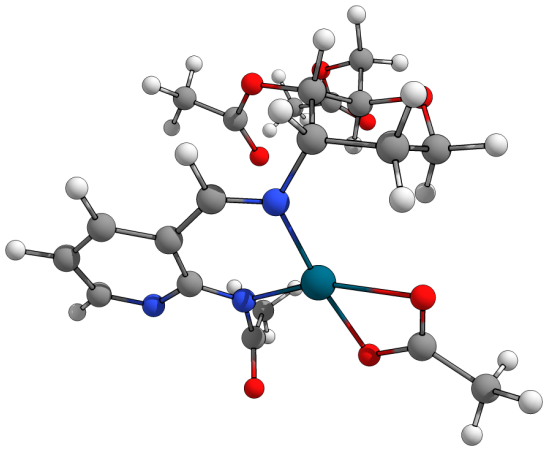


Compound 4c was obtained (72 mg, 65%) as a yellow oil according to the general procedure (C). $[\alpha]^{25}_{D}$ = - 37.8 ° (c 0,5 CH_2Cl_2). IR (neat, cm^{-1}): 3064, 2926, 2856, 1747, 1716, 1685, 1456, 1367, 1219, 1041.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 8.47 (s, 1H), 8.28 (s, 1H), 7.31 – 7.18 (m, 7H), 7.16 – 7.12 (m, 3H), 7.09 (d, J = 7.9 Hz, 2H), 7.06 – 7.02 (m, 2H), 6.16 (d, J = 5.9 Hz, 1H), 5.45 – 5.28 (m, 3H), 4.85 (d, J = 11.1 Hz, 1H), 4.57 – 4.47 (m, 2H), 4.38 – 4.29 (m, 5H), 4.18 (d, J = 11.8 Hz, 1H), 3.88 (s, 1H), 3.81 – 3.75 (m, 1H), 3.73 – 3.65 (m, 1H), 2.65 – 2.52 (m, 1H), 2.26 (s, 6H), 2.07 (s, 3H), 2.02 (s, 3H). ^{13}C NMR

(101 MHz, CDCl3) δ 171.0, 169.8, 169.7, 160.3, 149.6, 138.4, 138.2, 137.9, 137.8, 137.2, 135.4, 129.3, 128.7, 128.4, 128.2, 128.1, 127.9, 127.9, 126.2, 107.5, 87.4, 80.7, 74.6, 74.5, 73.9, 73.7, 73.1, 72.3, 70.9, 70.0, 63.5, 58.1, 33.5, 28.7, 21.3, 21.1, 20.7, 20.5. HRMS (ESI-TOF): m/z calculated for $C_{44}H_{48}N_5O_{12}^+$ $[M+H]^+$ 832.3294, found 832.3294.

f) *DFT calculations*

The calculations were performed using the Gaussian '09 software package, revision D01.[5] Geometries were optimized with the B3LYP[6] functional and the 6-31+G(d,p) basis set for H, C, O and N, and LANL2DZ ECP basis set for Pd.



Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.445347 (Hartree/Particle)
Thermal correction to Energy= 0.478797
Thermal correction to Enthalpy= 0.479742
Thermal correction to Gibbs Free Energy= 0.375271
Sum of electronic and zero-point Energies= -1669.654480
Sum of electronic and thermal Energies= -1669.621030
Sum of electronic and thermal Enthalpies= -1669.620086
Sum of electronic and thermal Free Energies= -1669.724556

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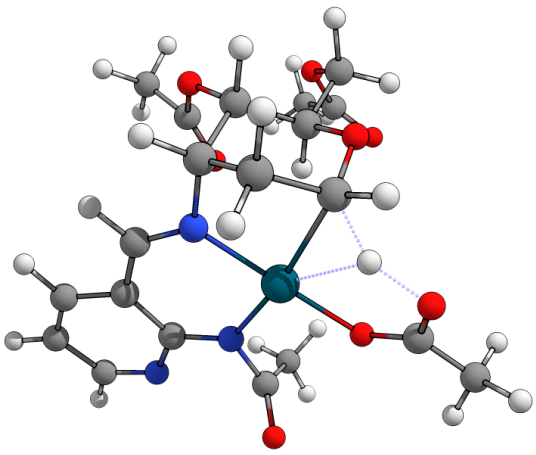
Pd	1.460227	-1.021685	-0.155345
O	1.349559	-3.159387	-0.563127



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Sum of electronic and thermal Enthalpies= -1669.591816
Sum of electronic and thermal Free Energies= -1669.693505

H	0.088384	-2.646202	-1.26947
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O	0.579888	-3.839686	-0.904806

[5] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[6] (a) Becke, A. D. *Phys. Rev.* 1988, ***A 38***, 3098. (b) Lee, C., Yang, W. & Parr, R. G. *Phys. Rev. B Condens. Matter Mater. Phys.* 1988, **37,** 785. (c) Becke, A. D. *J. Chem. Phys.* 1993, ***98***, 5648. (d) Stephens, P. J., Devlin, F. J., Chabalowski, C. F. & Frisch, M. J. *J. Phys. Chem.* 1994, ***98***, 11623.

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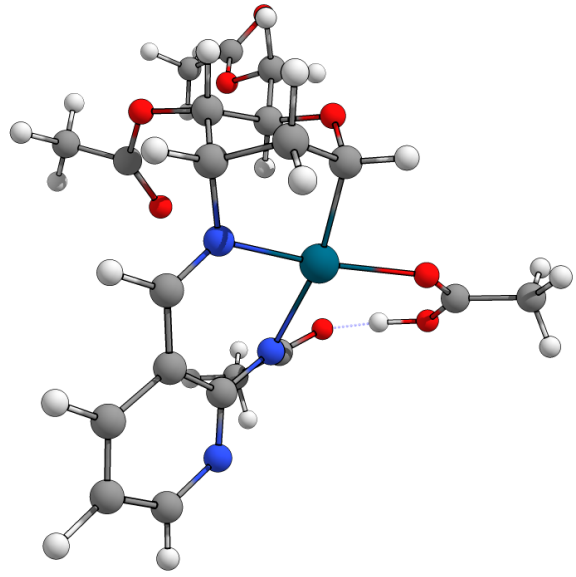
C	-2.274954	-0.161353	-1.629552	C	-2.314449	0.506591	-1.611068
H	-2.981317	-0.348929	-2.446353	H	-3.088374	0.293994	-2.356721
C	-2.790533	-1.030564	-0.462142	C	-2.386202	-0.635851	-0.572076
H	-2.137869	-0.972306	0.414586	H	-1.650458	-0.49085	0.226146
C	0.587668	1.205203	-1.871945	C	0.727246	1.934928	-1.488111
C	2.137719	1.901417	0.002176	C	2.521595	1.524793	0.257478
C	1.477174	2.130522	-1.259955	C	1.816321	2.365703	-0.685144
C	2.907195	4.089661	0.029498	C	3.873094	3.321098	0.864925
C	2.380058	4.38684	-1.246927	C	3.265283	4.212071	-0.047032
H	3.446265	4.857585	0.58396	H	4.682883	3.671452	1.50499
H	2.524967	5.363532	-1.694146	H	3.599398	5.240028	-0.128288
H	0.056734	1.596971	-2.74402	H	0.281418	2.700089	-2.130831
C	1.644175	3.396584	-1.866312	C	2.231452	3.711761	-0.810357
H	1.168431	3.581417	-2.827249	H	1.713963	4.350361	-1.523363
N	2.793735	2.923607	0.638442	N	3.534903	2.055683	1.019184
N	2.141534	0.713182	0.601647	N	2.252378	0.231168	0.441444
C	2.867858	0.582587	1.860322	C	3.122839	-0.484535	1.36752
O	4.024115	0.236647	1.871749	O	4.093312	-1.081345	0.964129
C	2.034782	0.83686	3.09021	C	2.665162	-0.468597	2.803407
H	1.205634	0.121704	3.124066	H	1.701899	-0.984413	2.872646
H	2.652268	0.736871	3.984237	H	3.401992	-0.972772	3.431333
H	1.601134	1.840109	3.0368	H	2.525383	0.563107	3.138023



Temperature 298.150 Kelvin. Pressure 1.00000 Atm. Zero-point correction= 0.443163 (Hartree/Particle) Thermal correction to Energy= 0.476229 Thermal correction to Enthalpy= 0.477173 Thermal correction to Gibbs Free Energy= 0.373473 Sum of electronic and zero-point Energies= -1669.680079 Sum of electronic and thermal Energies= -1669.647012 Sum of electronic and thermal Enthalpies= -1669.646068 Sum of electronic and thermal Free Energies= -1669.749768				
H	1.826965	-2.430225	1.924443	
Pd	0.935148	-0.925667	-0.649016	
O	2.039901	-3.456694	1.647641	
N	0.391073	0.909573	-1.361048	
O	1.495891	-2.980795	-0.495957	
C	1.887455	-3.757531	0.402546	
O	-1.746368	-1.69133	-1.374847	
O	-4.081963	0.000343	0.771854	
O	-2.615487	1.938397	-1.02476	
O	-1.346083	1.932313	0.869777	
O	-5.957675	-1.236755	1.024068	
C	-5.273869	-0.288181	1.348745	
C	-2.202953	2.429984	0.175197	
C	2.217253	-5.18823	0.049411	
H	2.116633	-5.350938	-1.023507	
H	1.542316	-5.857557	0.592359	
H	3.235936	-5.419667	0.374284	
C	-2.971355	3.687388	0.506606	
H	-2.561112	4.133253	1.412704	
H	-4.02568	3.438436	0.662404	
H	-2.922623	4.399349	-0.322419	
C	-5.627936	0.722503	2.412347	
H	-5.957214	1.652087	1.934849	
H	-4.75934	0.953857	3.03403	
H	-6.44257	0.332132	3.022609	
C	-3.638595	-0.914124	-0.252506	

H	-4.33039	-0.877215	-1.100646
H	-3.635723	-1.932664	0.142608
C	-0.472624	-1.558477	-1.997455
H	-0.214042	-2.550948	-2.368764
C	-0.525257	-0.466442	-3.06672
H	0.418192	-0.415642	-3.618928
H	-1.339094	-0.644944	-3.783551
C	-0.755592	0.836746	-2.283568
H	-0.787079	1.730126	-2.922012
C	-2.128525	0.694708	-1.587105
H	-2.840674	0.531083	-2.402783
C	-2.215126	-0.539821	-0.657872
H	-1.605186	-0.384085	0.236564
C	1.131311	1.963432	-1.331609
C	2.862566	1.314404	0.456133
C	2.367398	2.157926	-0.595752
C	4.724555	2.681876	0.705223
C	4.322955	3.568823	-0.299476
H	5.65753	2.846747	1.242543
H	4.926541	4.431267	-0.560157
H	0.829014	2.810269	-1.958322
C	3.123381	3.292516	-0.940582
H	2.756026	3.953433	-1.722655
N	4.031735	1.604186	1.071141
N	2.184545	0.185267	0.853876
C	2.037232	-0.103985	2.158145
O	1.631738	-1.237835	2.54559
C	2.238799	0.921607	3.259232
H	1.505632	0.710219	4.040642
H	3.239906	0.806355	3.684245
H	2.131699	1.950882	2.913864

g) Crystallographic data collection, structure determination and refinement for 3a.

Single crystals of ***3a*** suitable for X-ray diffraction analysis were obtained after slow evaporation of mixture of saturated deuterated chloroform solution and dichloromethane. A colourless small parallelepipedic crystal was reserved under a binocular and mounted upon a nylon loop to be placed at the intersection of a Mo $K\alpha$ microfocused X-ray beam and the angles of the kappa goniometer that constitute altogether with a HPAD PILATUS3R 200K detector a RIGAKU XtaLabPro diffractometer. The crystal was kept at 123 K using nitrogen cryostream during a complete data collection that optimized the Bijvoet pair measurement. *CrysAlisPro 1.171.42.75a* [7] was employed for the data processing, with an empirical absorption correction using a combination of spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm and numerical absorption correction based on gaussian integration over multifaceted crystal models. Structure solution was readily obtained using intrinsic phasing methods (*SHELXT* program),[8] and the molecular model was then refined by full-matrix least-squares methods on F^2 using *SHELX-L*[9] satisfactorily. All non-hydrogen atoms of the molecules of interest were subjected to anisotropic refinement. H atoms bound to carbon atoms were identified in Fourier difference maps, nevertheless they were positioned geometrically and refined with U_{iso} set to either $1.2U_{eq}$(C) or 1.5 for methyl carbons. Regarding the relative stereochemistry of the fourth tolyl substituent to the sugar moiety, the crystal structure brings evidence that its stereodescriptor is S, (see Figure S1) disregarding the unreliable statistics based on Bijvoet pairs analyses at this Mo radiation. Later on further data from another thicker crystal were recorded using a RIGAKU MM007HF copper rotating anode and processed with *FS_Process* option in the *CrystalClear 2.0* suite[10] allowed us to rely on the weak dispersion signal to confirm the absolute configuration if ever needed.[11,12] The Cremer & Pople puckering parameters[13] for the chair-form adopted by the sugar ring are as following: Q(2) = 0.054(2) Å, Q(3) = 0.545(2) Å, Puckering Amplitude (Q) = 0.548(2) Å, Theta = 5.8(2)°, Phi = 251(2)°. Additionally the disorder of the phenyl ring from the benzyloxy-methyl substituent at C1 was taken into account by splitting it over two sites (with a benzyl flip of ca 54° (ca 49° at rt for the second structure model) relatively to the benzyloxy-methyl mean plane of the major conformer) with occupancy ratio refined at 0.543(5):0457(3) (0.58(2):0.42(2) at room temperature regarding the second model).

Crystal data, data collection and structure refinement details are summarized in Table S1.

CCDC 2225278 (Mo-lowT **3a** model)-2225279(Cu-rT **3a** model) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

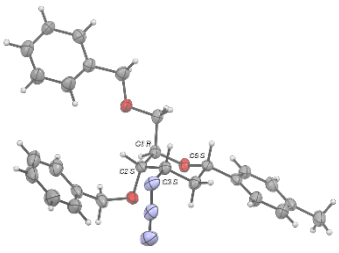


Figure S1 Ortep view of **3a** showing the displacement ellipsoids at the 50% of probability level, the hydrogen atoms as small spheres with arbitrary radius and the major conformer for clarity regarding the benzyl disorder.

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[7] Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England

[8] Sheldrick, G. M. *Acta Cryst.*, 2015, ***C71***, 3-8.

[9] Sheldrick, G. M. *Acta Cryst.*, 2015, ***A71***, 3-8.

[10] Rigaku (2009) CrystalClear-SM Expert 2.0 r4 Rigaku Corporation, Tokyo, Japan.

[11] Hooft, R.W.W., Straver, L.H., Spek, A.L. *J. Appl. Cryst.*, 2008; ***41***, 96-103.

[12] Spek, A. L. *Acta Cryst.* 2009, ***D65***, 148-155.

[13] Cremer, D. & Pople, J.A. *J. Amer. Chem. Soc.*, 1975, ***97***, 1354-1358.

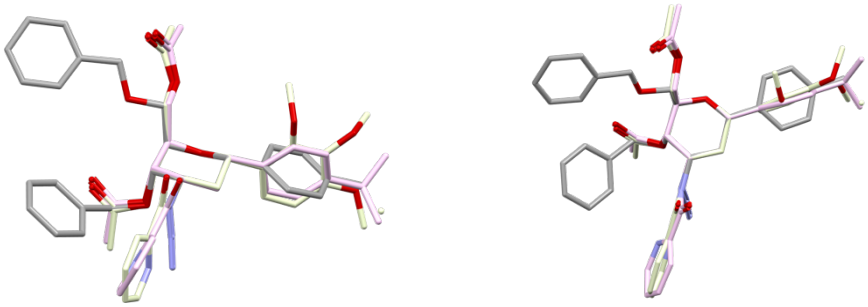
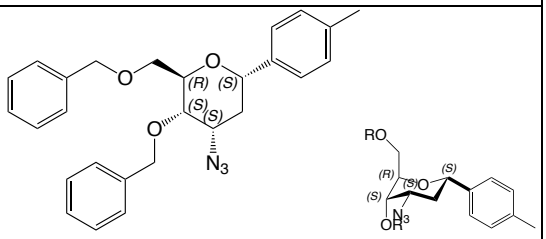


Figure S2 side (left) and top (right) views of overlay of CSD[14] *Refcode* JAQMAT (carbons in yellow) and JAQMEX (carbons in pink) from *Ref* [15] over the sugar ring of ***3a*** compound.

Table S1 Crystal data, data collection and structure refinement details for ***3a***.

Compound	***3a*** (2*R*,3*S*,4*S*,6*S*)-4-azido-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(*p*-tolyl)tetrahydro-2*H*-pyran	
2D-scheme		
Empirical formula	$C_{27}H_{29}N_3O_3$,	
Formula weight	443.53	
Temperature (K)	123(2)	293(2)
Diffractometer Rigaku®	*μS* mm003, double-bounce max flux optic, HPAD Pilatus 200K	mm007HF, CMF optics, SuperRapid2 IP detector
Wavelength (Å)	0.71073	1.54187
Crystal system, space group	Orthorhombic, $P\ 2_12_12_1$	

[14] Groom, C. R. & Allen, F. H. *Angew. Chem. Int. Ed.* 2014, ***53***, 662

[15] J. Ghouilem, C. Tran, N. Grimblat, P. Retailleau, M. Alami, V. Gandon, S. Messaoudi. *ACS Catal.* 2021, ***11***, 1818

Unit cell dimensions | (Å)		4.8747(2) 10.5771(4) 44.7202(16)	4.9654(3) 10.7233(8) 44.847(3)
Volume ($Å^3$)		2305.78(15)	2387.9(3)
Z, Calculated density (Mg/m^3)		4, 1.278	4, 1.234
Absorption coefficient (mm^{-1})		0.084	0.649
F(000)		944	944
Crystal size (mm)		0.15 x 0.06 x 0.03	0.55 x 0.13 x 0.07
θ range for data collection (°)		2.130 to 25.341	7.223 to 65.083
Limiting indices		-5 ≤ h ≤ 5, -12 ≤ k ≤ 11, -53 ≤ l ≤ 53	-5 ≤ h ≤ 5, -12 ≤ k ≤ 12, -52 ≤ l ≤ 52
Reflections collected / unique R(int)		25032 / 4183 0.0558	21847 / 4045 0.1014
Completeness to θ=25.2/65.1° (%)		99.7	99.4
Absorption correction		Semi-empirical from equivalents	
		& Gaussian	-
Max. and min. transmission		1.000 and 0.812	1.000 and 0.592
Refinement method		Full-matrix least-squares on F^2	
Data / restraints / parameters		4181 / 37 / 337	4045 / 183 / 337
Goodness-of-fit on F^2		1.033	0.810
Final R indices [$I>2\sigma I$)]	R1 wR2	0.0405, 0.0896	0.0521, 0.1056
Final R indices *[all]*	R1 wR2	0.0536, 0.09448	0.0820, 0.1197
Absolute Structure Parameter	Flack x [16]	-	-0.1(3)

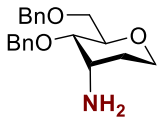
[16] Flack, H.D. (1983). Acta Cryst. A39, 876-881.

	Parsons z [17]	-	0.0(2)
	Hooft y [11]	-	0.0(2)
	$P2_{(true)}$	-	1.000
	$P2_{(false)}$	-	10^{-4}
	$P3_{(true)}$	-	0.918
	$P3_{(rac\text{-}twin)}$	-	0.082
	$P3_{(false)}$	-	9.10^{-5}
Largest Δ peak and hole (e.Å^{-3})		0.152 and -0.159	0.193 and -0.186
CCDC deposit number		2225278	2225279

[17] Parsons, S., Flack, H.D. & Wagner, T. (2013) Acta Cryst. B69, 249-259.

h) *NMR Spectra*

^{1}H NMR, $CDCl_3$, 400 MHz



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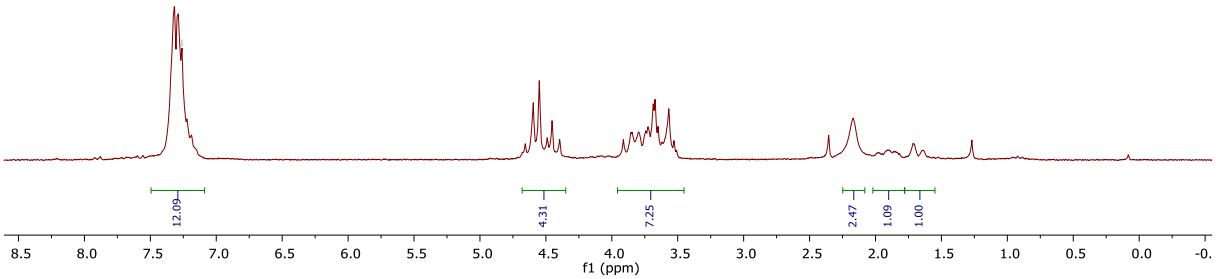
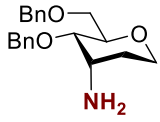
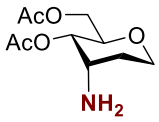


^{13}C NMR, $CDCl_3$, 100 MHz



1a

^{1}H NMR, $CDCl_3$, 400 MHz



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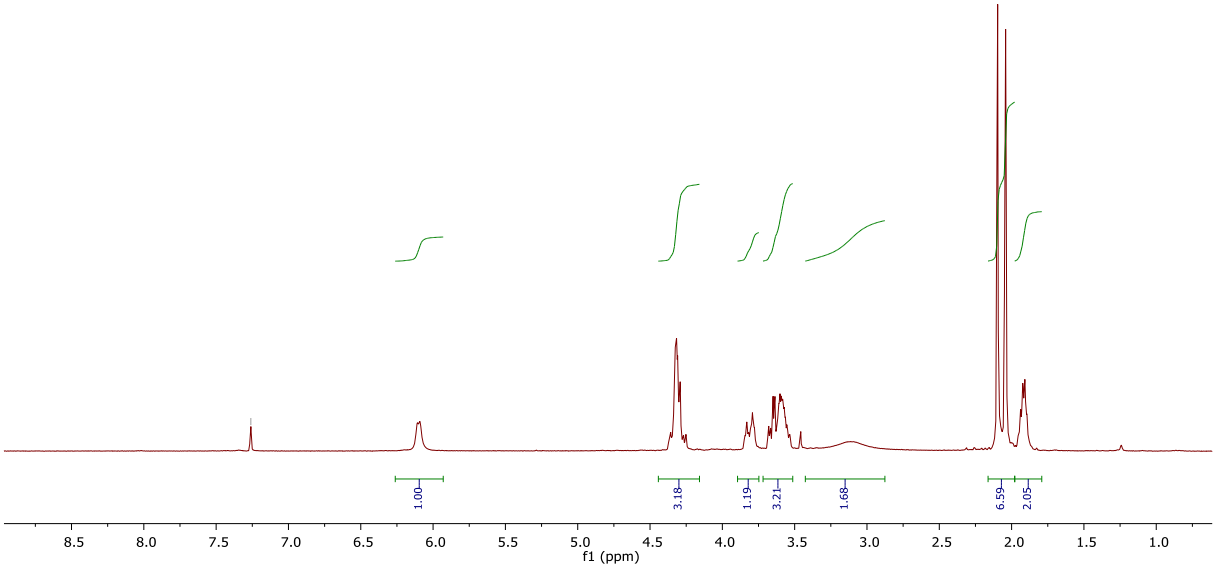
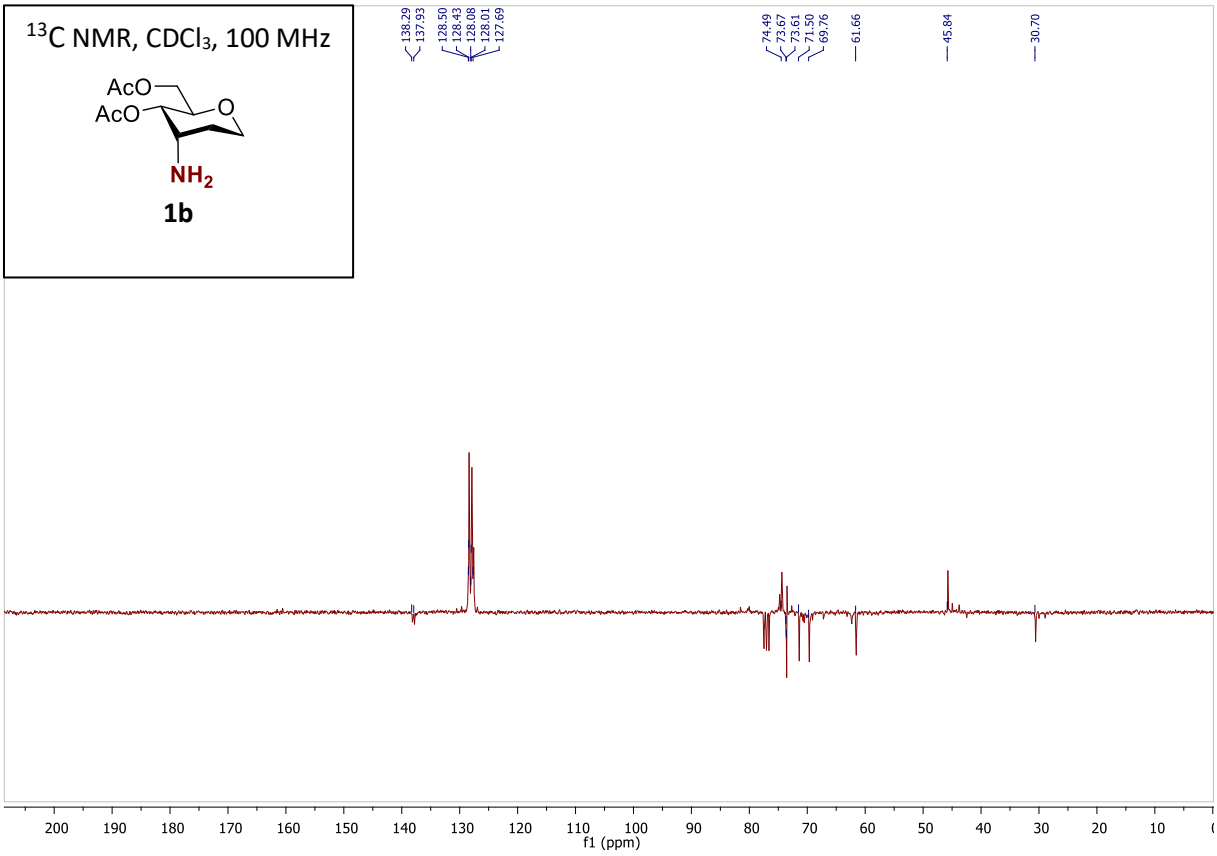
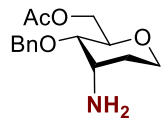


^{13}C NMR, $CDCl_3$, 100 MHz

1b



^{1}H NMR, $CDCl_3$, 400 MHz



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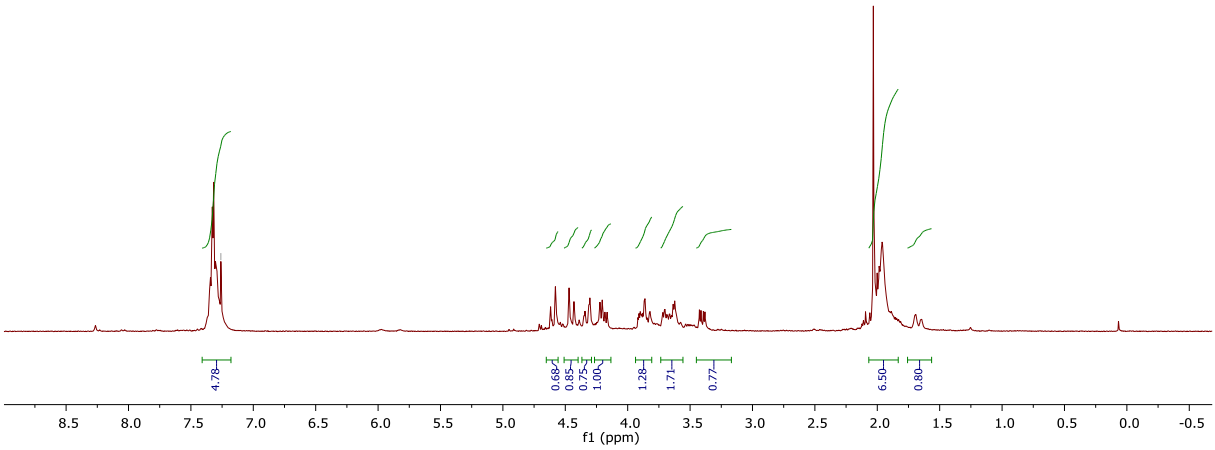
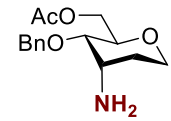
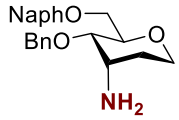


^{13}C NMR, $CDCl_3$, 100 MHz



1d

^{1}H NMR, $CDCl_3$, 400 MHz



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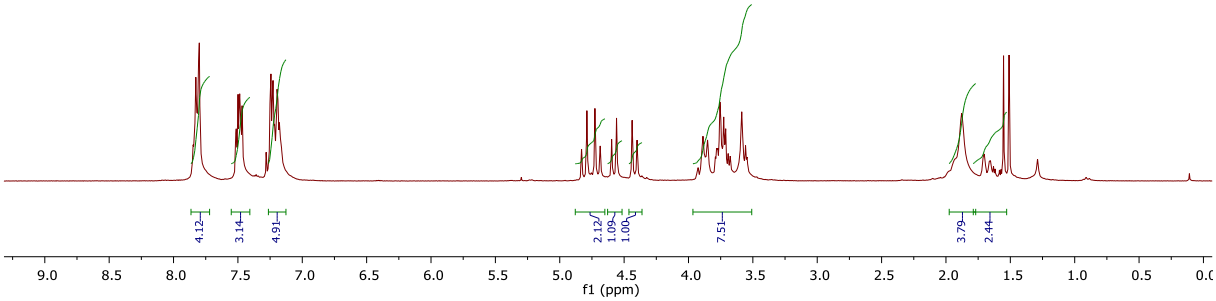
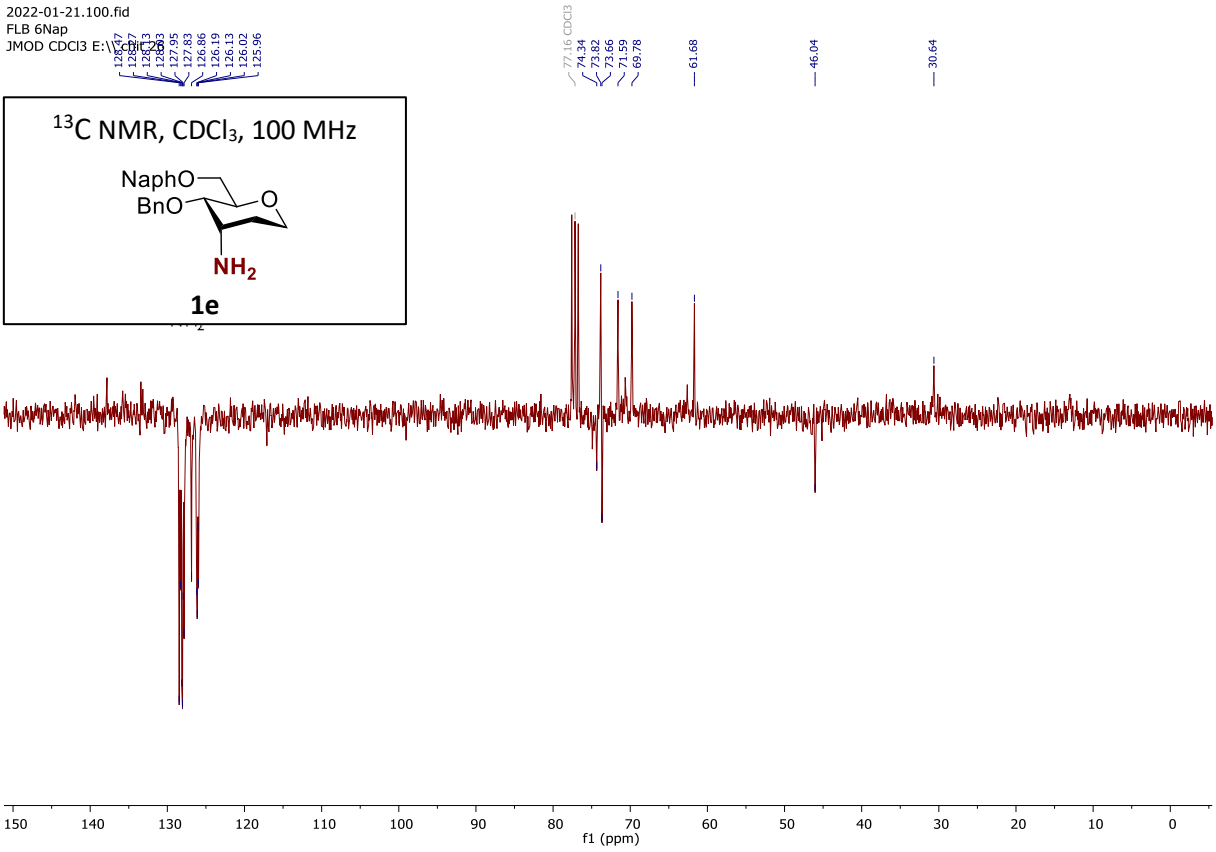
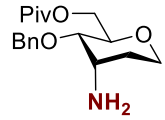




^{13}C NMR, $CDCl_3$, 100 MHz

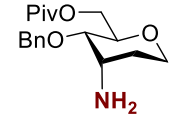
1e

^{1}H NMR, $CDCl_3$, 400 MHz



1f

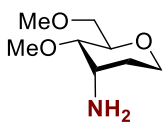
^{13}C NMR, $CDCl_3$, 100 MHz



1f

JG 46OMe3NH2.2.fid

^{1}H NMR, $CDCl_3$, 400 MHz



1g

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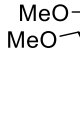
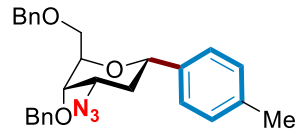
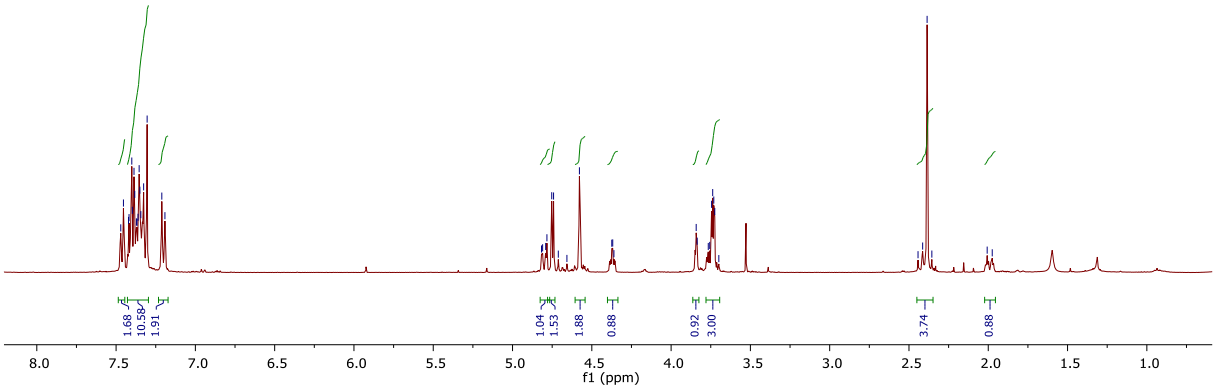


1g

^{1}H NMR, $CDCl_3$, 400 MHz



3a



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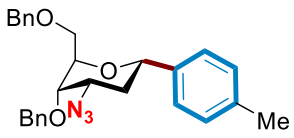
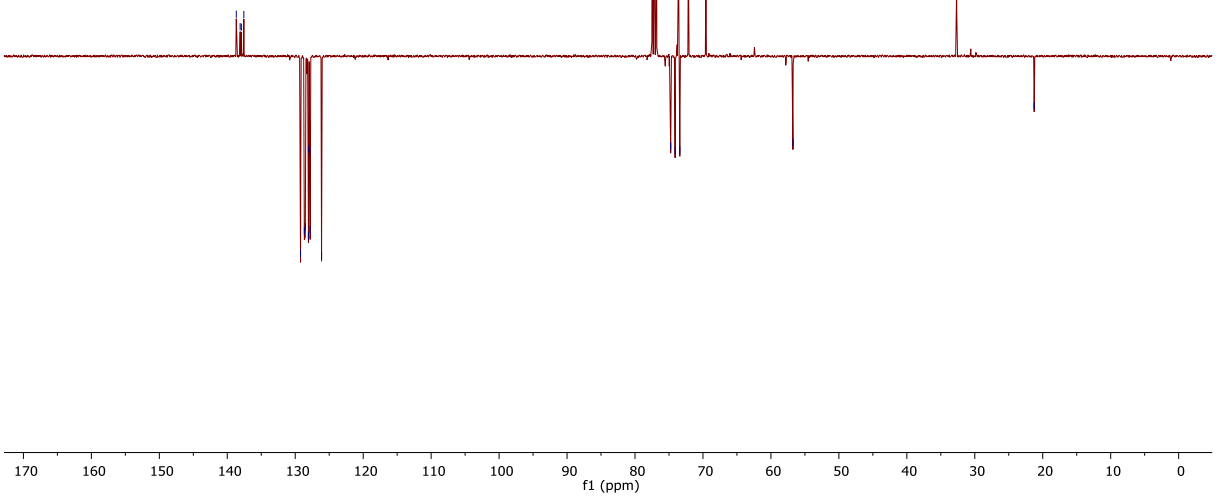
jg scn3
CDCl3 5 mm

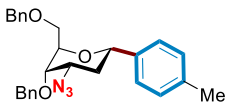
^{13}C NMR, $CDCl_3$, 100 MHz



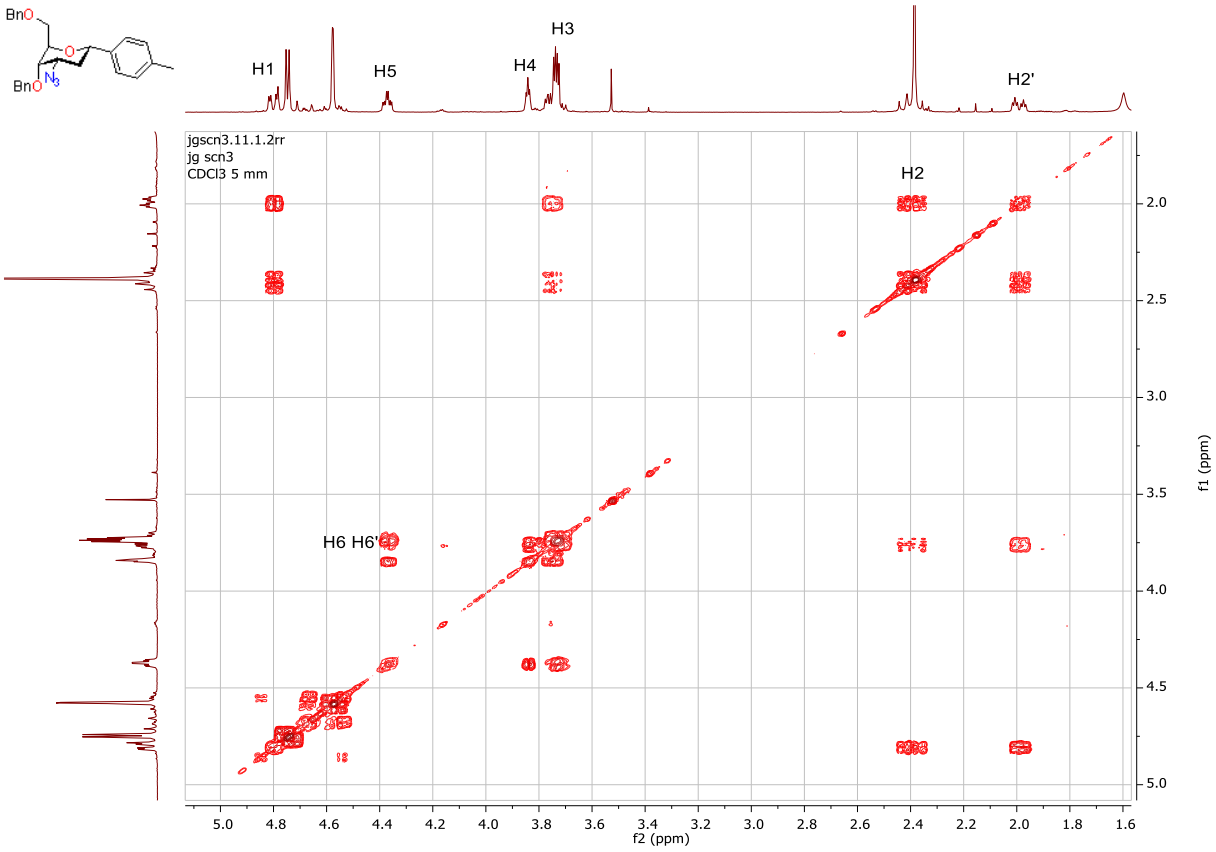
3a

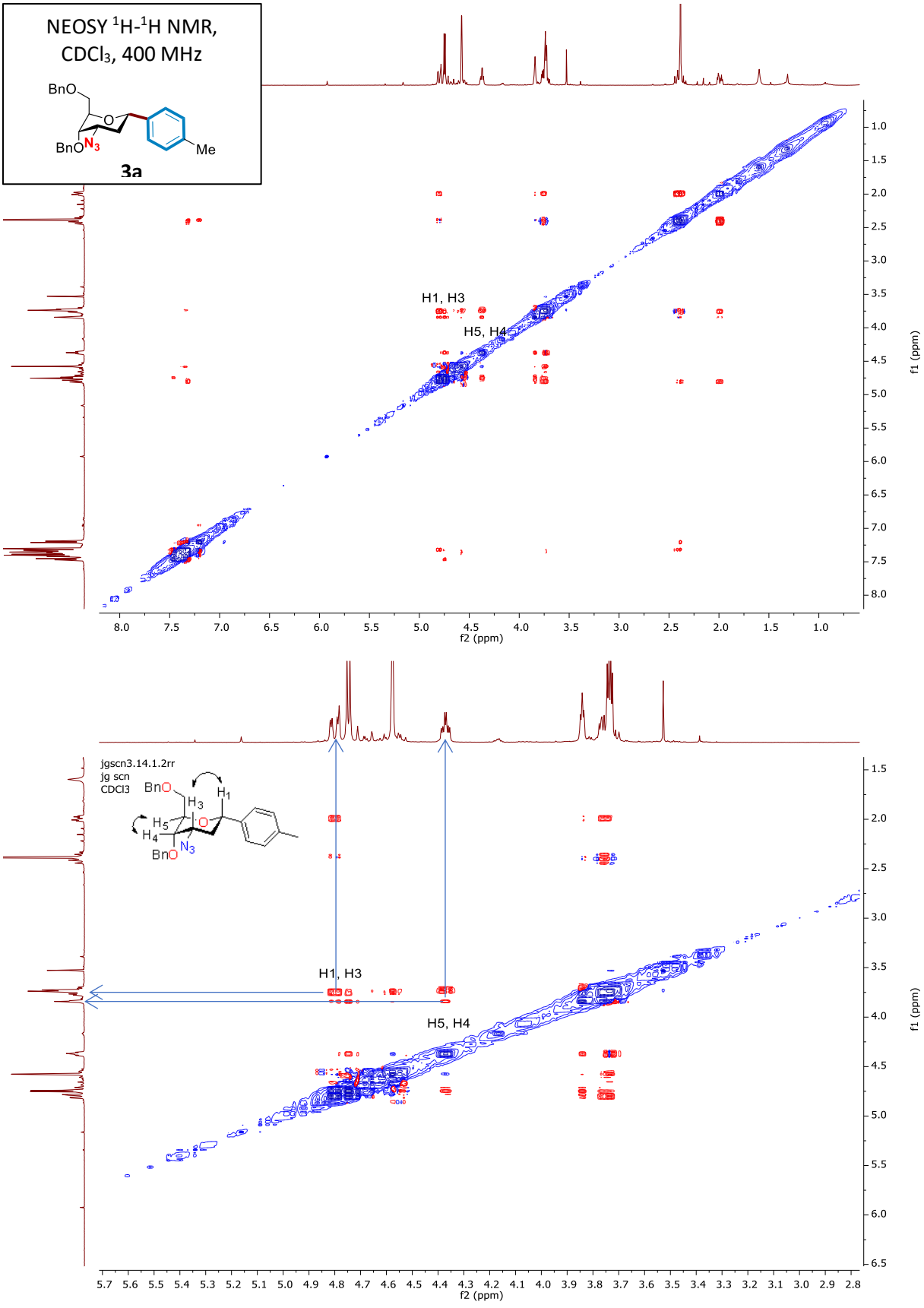


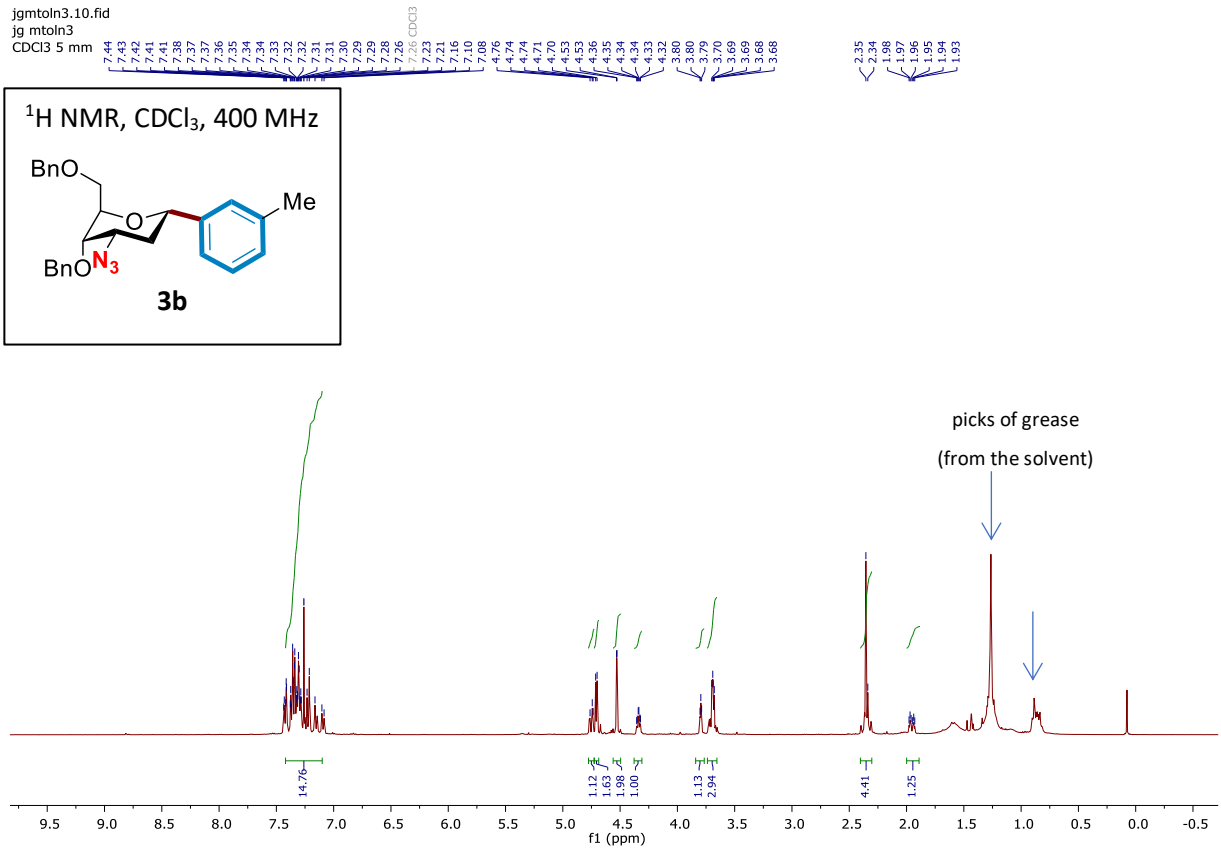
COSY ^{1}H-^{1}H NMR, $CDCl_3$, 400 MHz

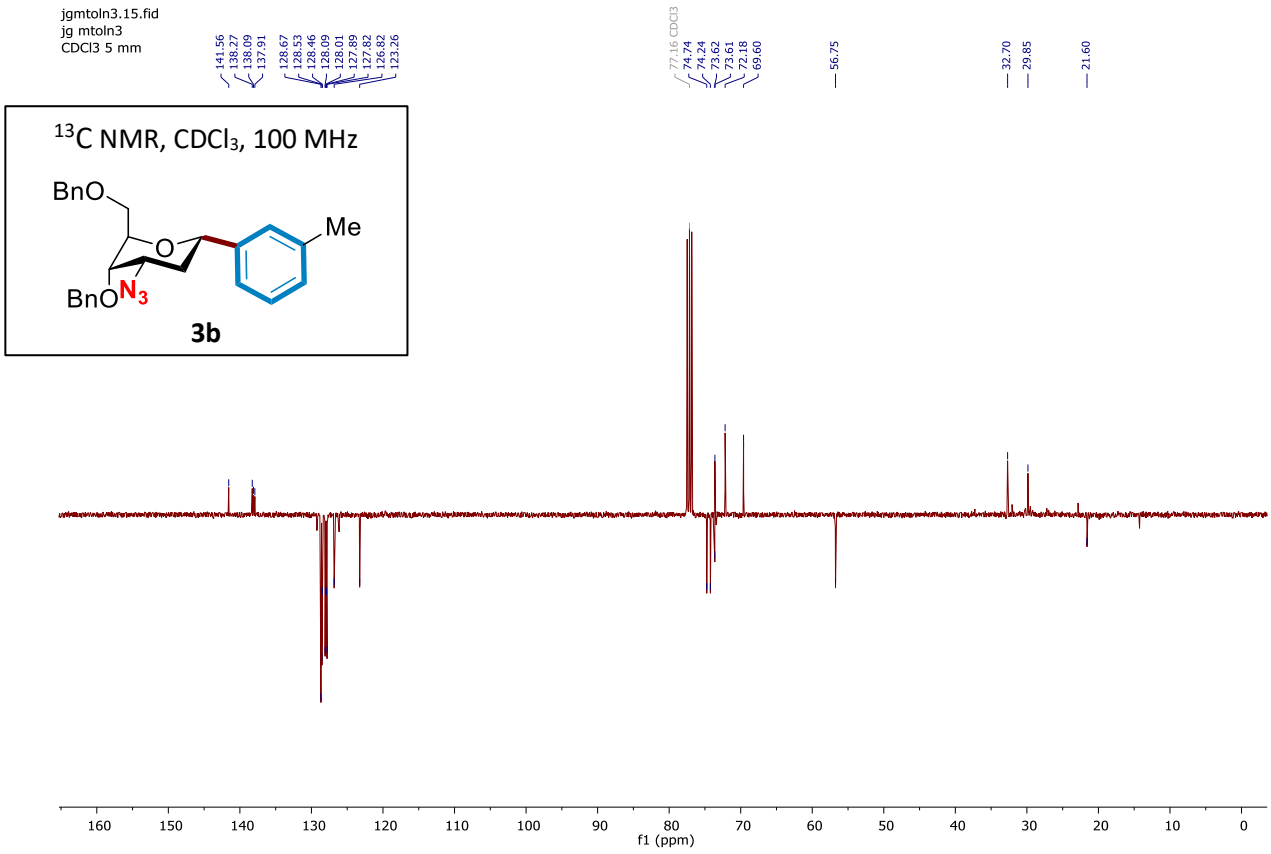


3a



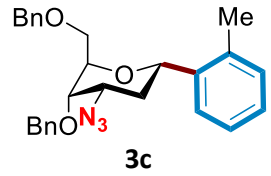

NEOSY ^{1}H-^{1}H NMR,
$CDCl_3$, 400 MHz
BnO
BnO
N3
Me
3a
H1, H3
H5, H4
f2 (ppm)
f1 (ppm)
jgscn3.14.1.2rr
jg scn
CDCl3
H1, H3
H5, H4
f2 (ppm)
f1 (ppm)


jgmtoln3.10.fid
jg mtoln3
CDCl3 5 mm
^{1}H NMR, CDCl$_3$, 400 MHz
BnO
Me
O
BnO
N$_3$
3b
picks of grease
(from the solvent)
14.76
1.12
1.63
1.98
1.00
1.13
2.94
4.41
1.25
f1 (ppm)

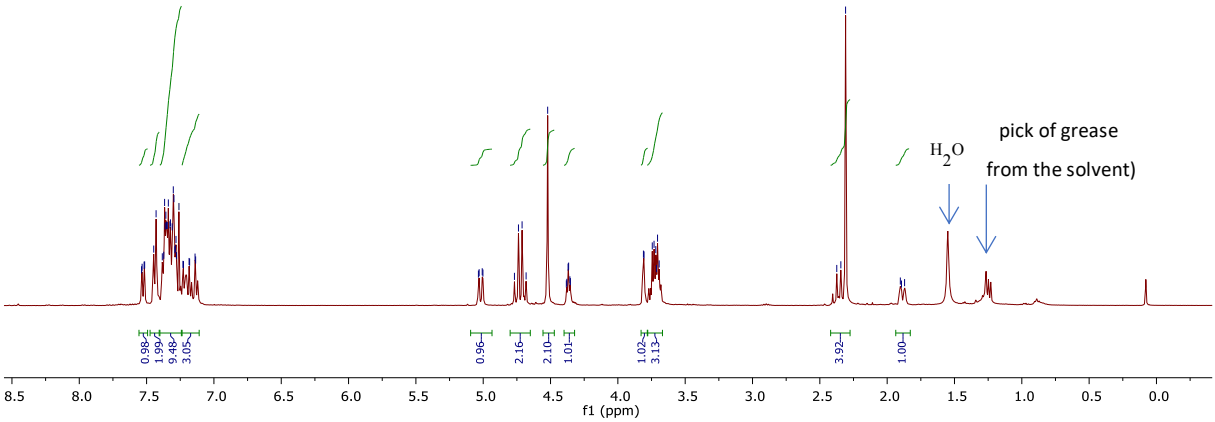

jgmtoln3.15.fid
jg mtoln3
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
BnO
Me
O
BnO
N$_3$
3b
f1 (ppm)

jgotolyln3.10.fid
JG OTolyl N3
CDCl3 5 mm

^{1}H NMR, $CDCl_3$, 400 MHz

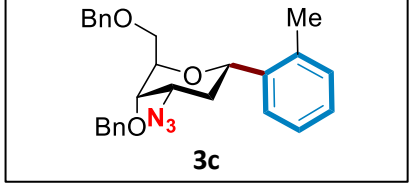


3c

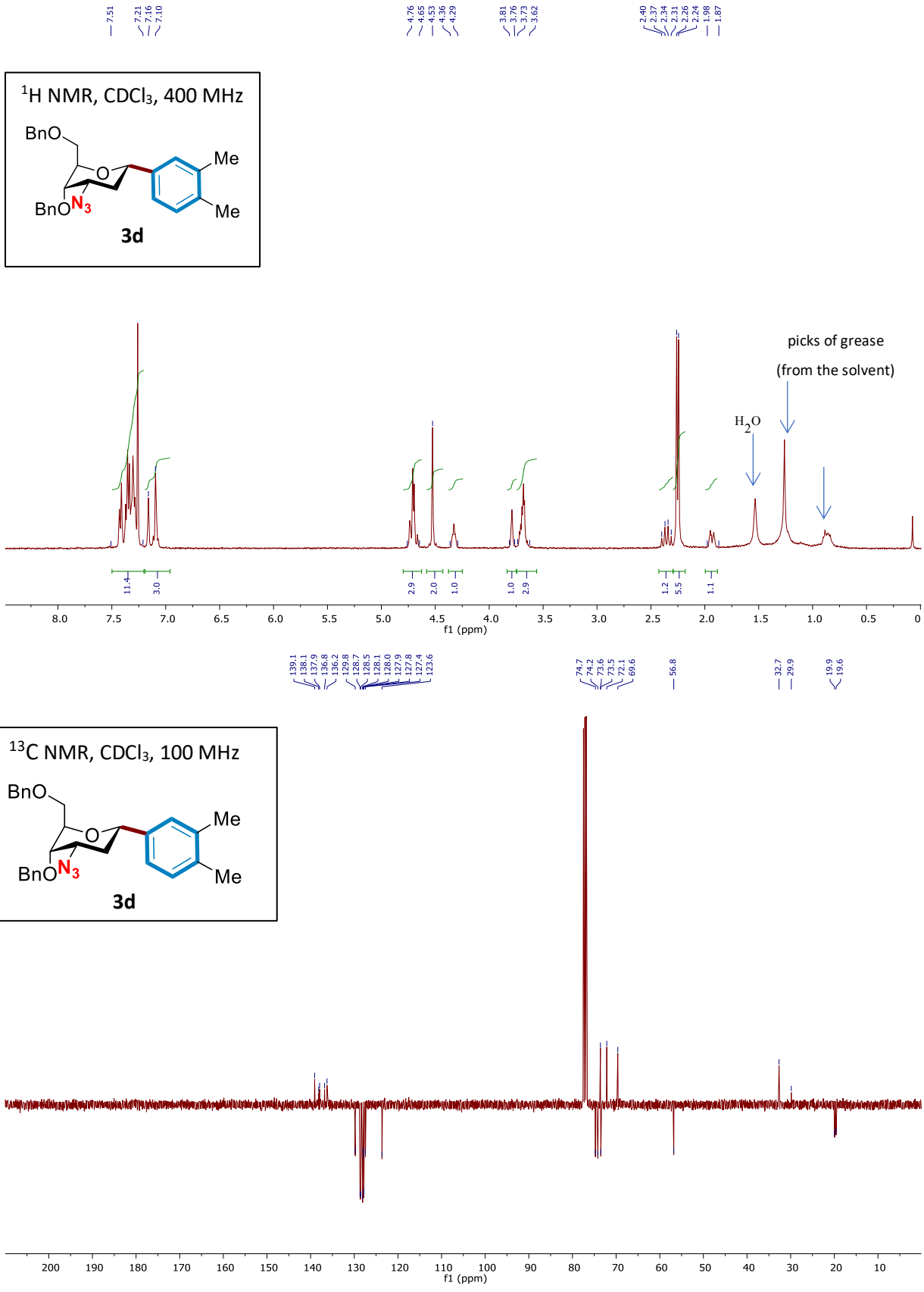


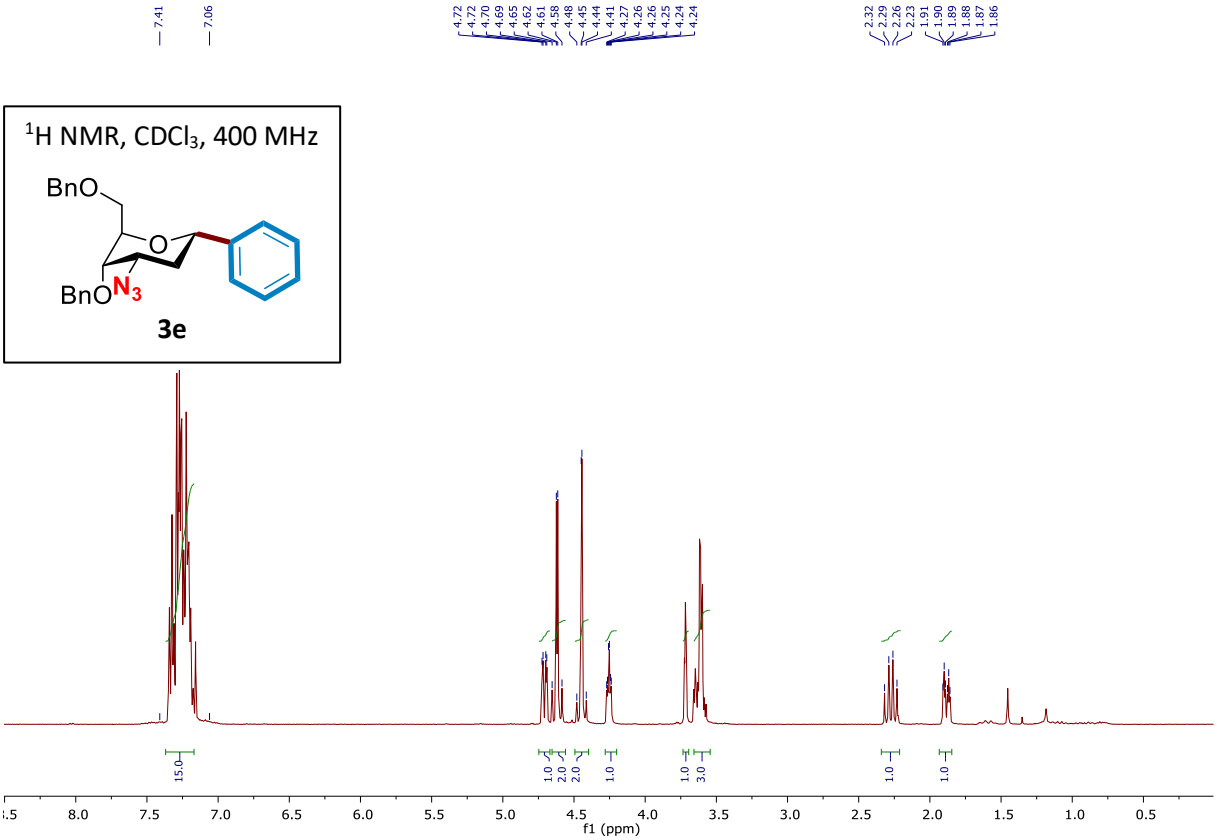
jgotolyln3.15.fid
JG OTolyl N3
CDCl3 5 mm

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

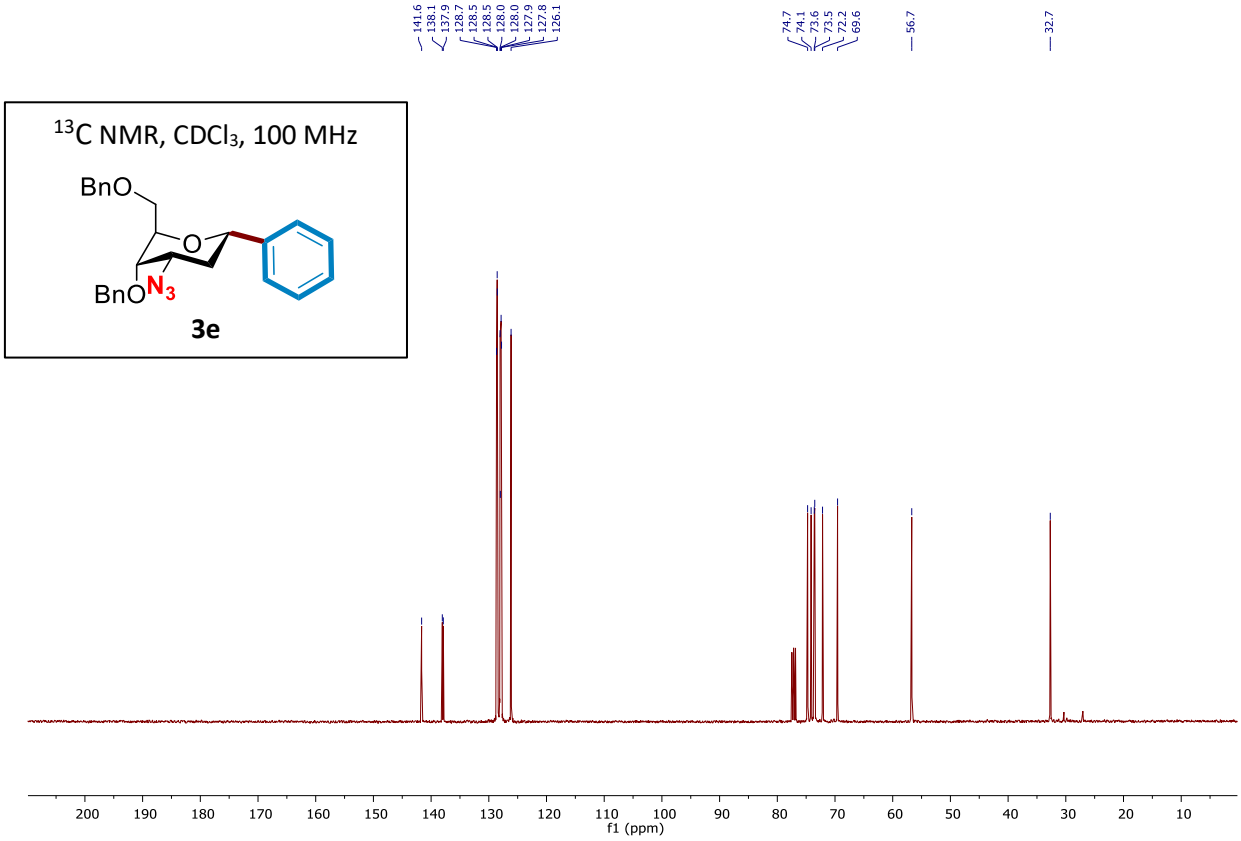


3c


7.51
7.21
7.16
7.10
4.76
4.65
4.53
4.36
4.29
3.81
3.76
3.73
3.62
2.40
2.37
2.34
2.31
2.26
2.24
1.98
1.87
^{1}H NMR, CDCl$_3$, 400 MHz
BnO
O
BnO
N$_3$
Me
Me
3d
picks of grease
(from the solvent)
H$_2$O
11.4
3.0
2.9
2.0
1.0
1.0
2.9
1.2
5.5
1.1
f1 (ppm)
139.1
138.1
137.9
136.8
136.2
129.8
128.7
128.5
128.1
128.0
127.9
127.8
127.4
123.6
74.7
74.2
73.6
73.5
72.1
69.6
56.8
32.7
29.9
19.9
19.6
^{13}C NMR, CDCl$_3$, 100 MHz
BnO
O
BnO
N$_3$
Me
Me
3d
f1 (ppm)

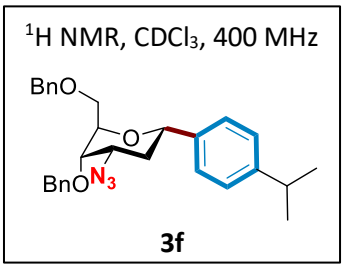

7.41
7.06
4.72
4.72
4.70
4.69
4.65
4.62
4.61
4.58
4.48
4.45
4.44
4.41
4.27
4.26
4.26
4.25
4.24
4.24
2.32
2.29
2.26
2.23
1.91
1.90
1.89
1.88
1.87
1.86
1H NMR, CDCl3, 400 MHz
BnO
O
BnO
N3
3e
15.0
1.0
2.0
2.0
1.0
1.0
3.0
1.0
1.0
f1 (ppm)

i

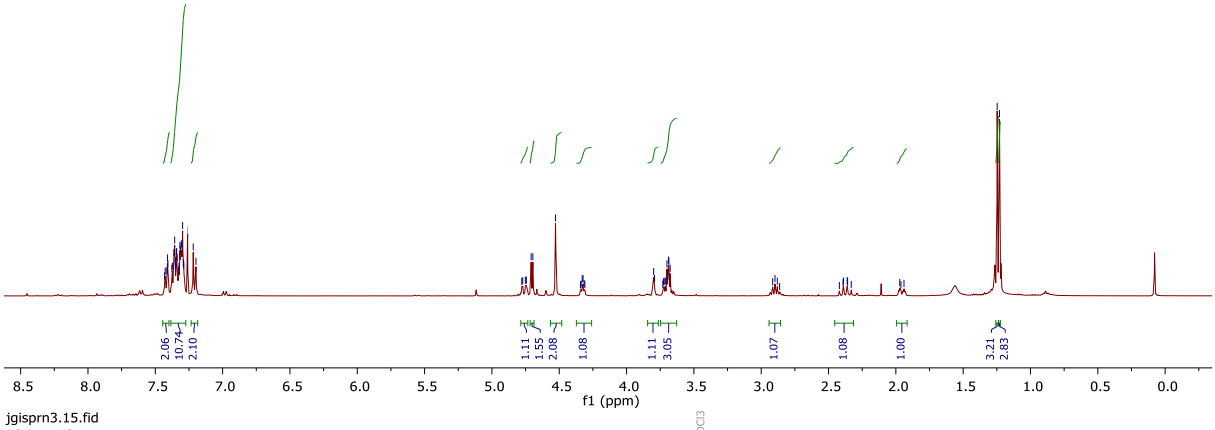

141.6
138.1
137.9
128.7
128.5
128.5
128.0
128.0
127.9
127.8
126.1
74.7
74.1
73.6
73.5
72.2
69.6
56.7
32.7
13C NMR, CDCl3, 100 MHz
BnO
O
BnO
N3
3e
f1 (ppm)

jgisprn3.10.fid
JG Ispr N3
CDCl3 5 mm

^{1}H NMR, $CDCl_3$, 400 MHz

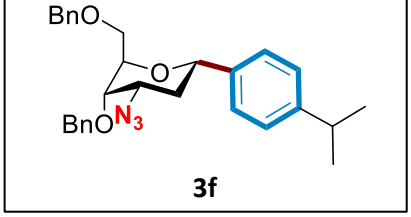


3f

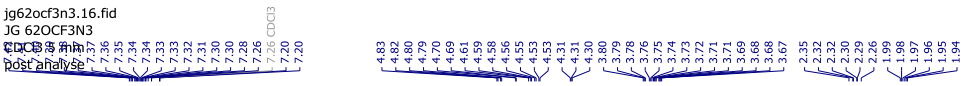


jgisprn3.15.fid
JG Ispr N3
CDCl3 5 mm

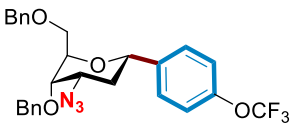
^{13}C NMR, $CDCl_3$, 100 MHz



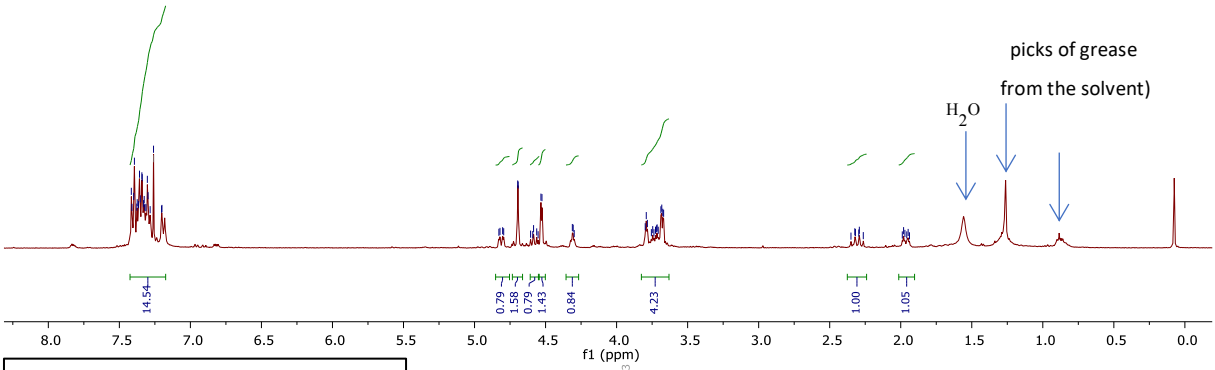
3f



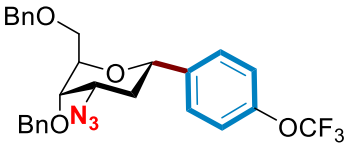
^{1}H NMR, $CDCl_3$, 400 MHz



3g

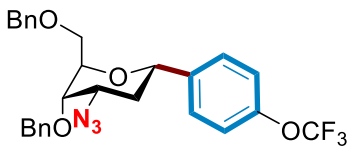


^{13}C NMR, $CDCl_3$, 100 MHz

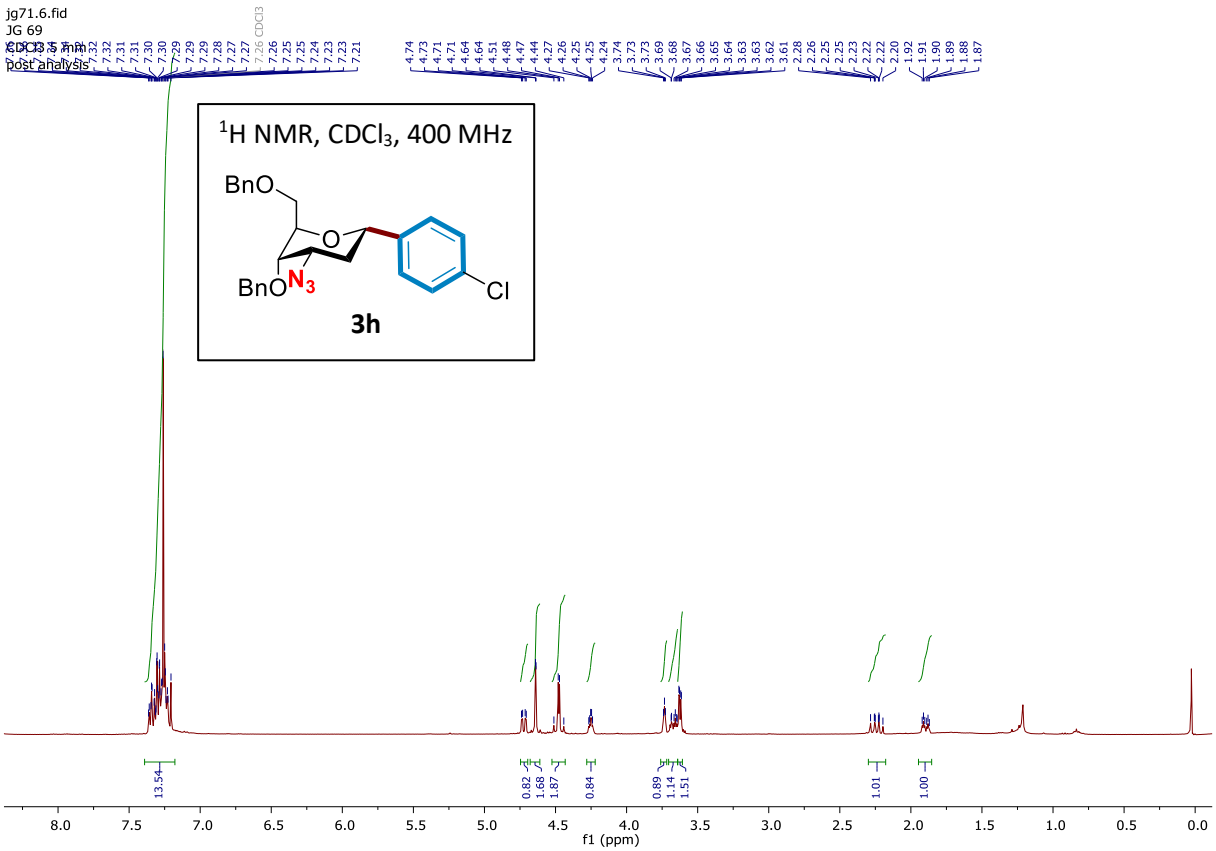


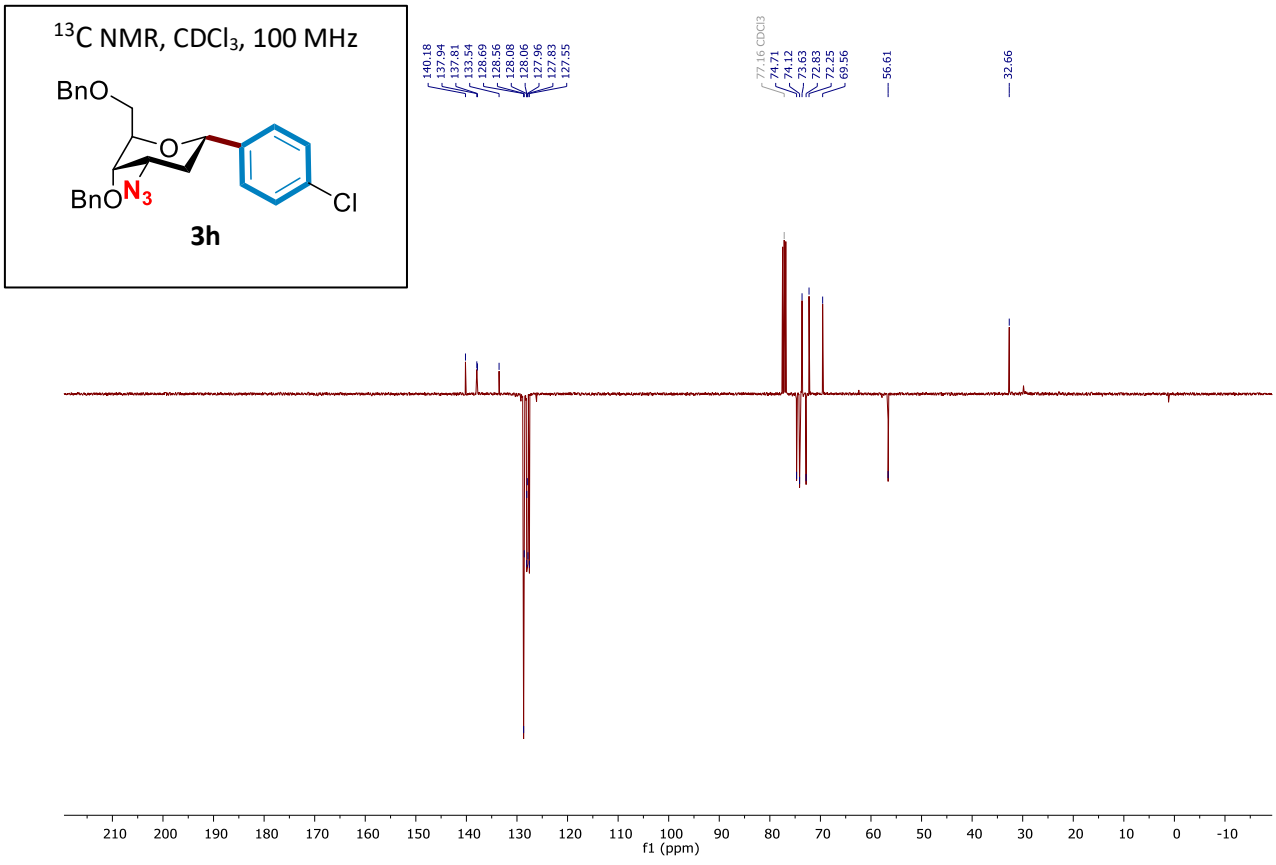
3g

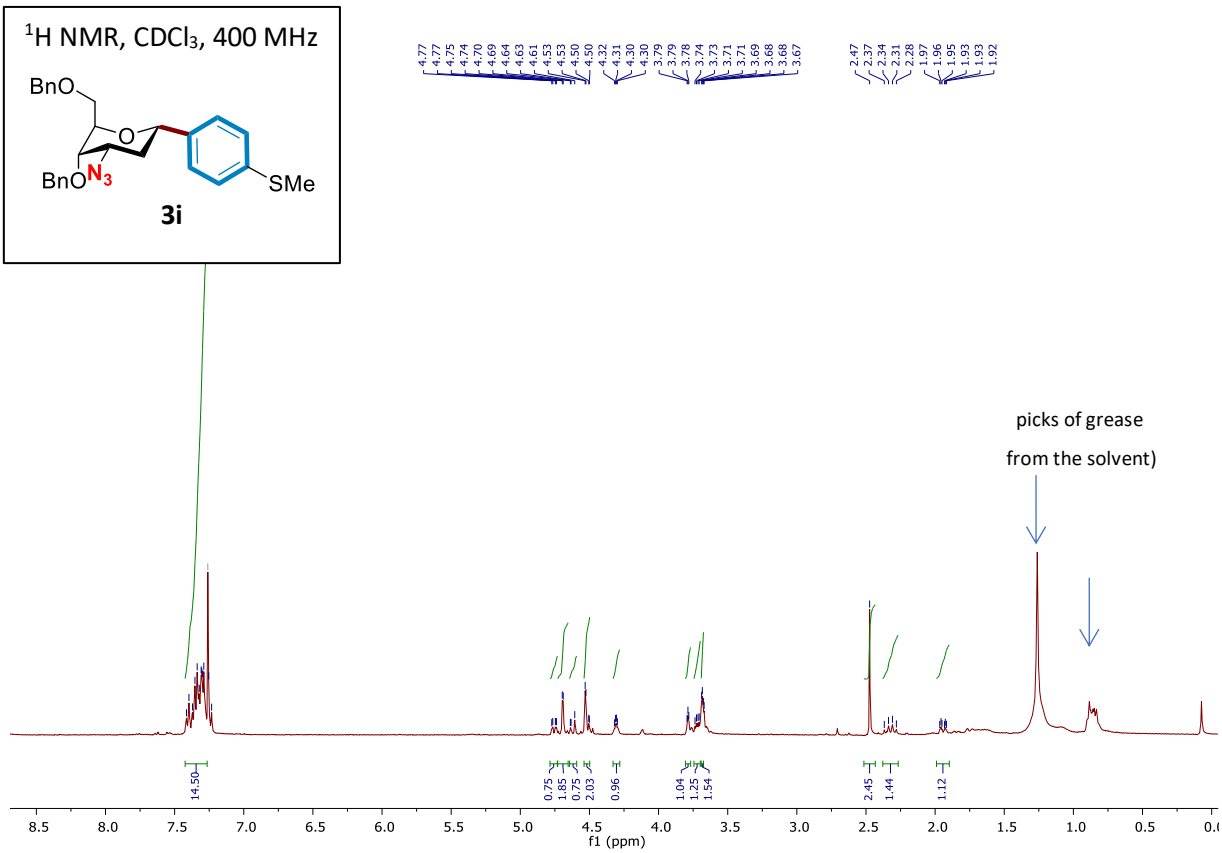
^{19}F NMR, $CDCl_3$, 376 MHz

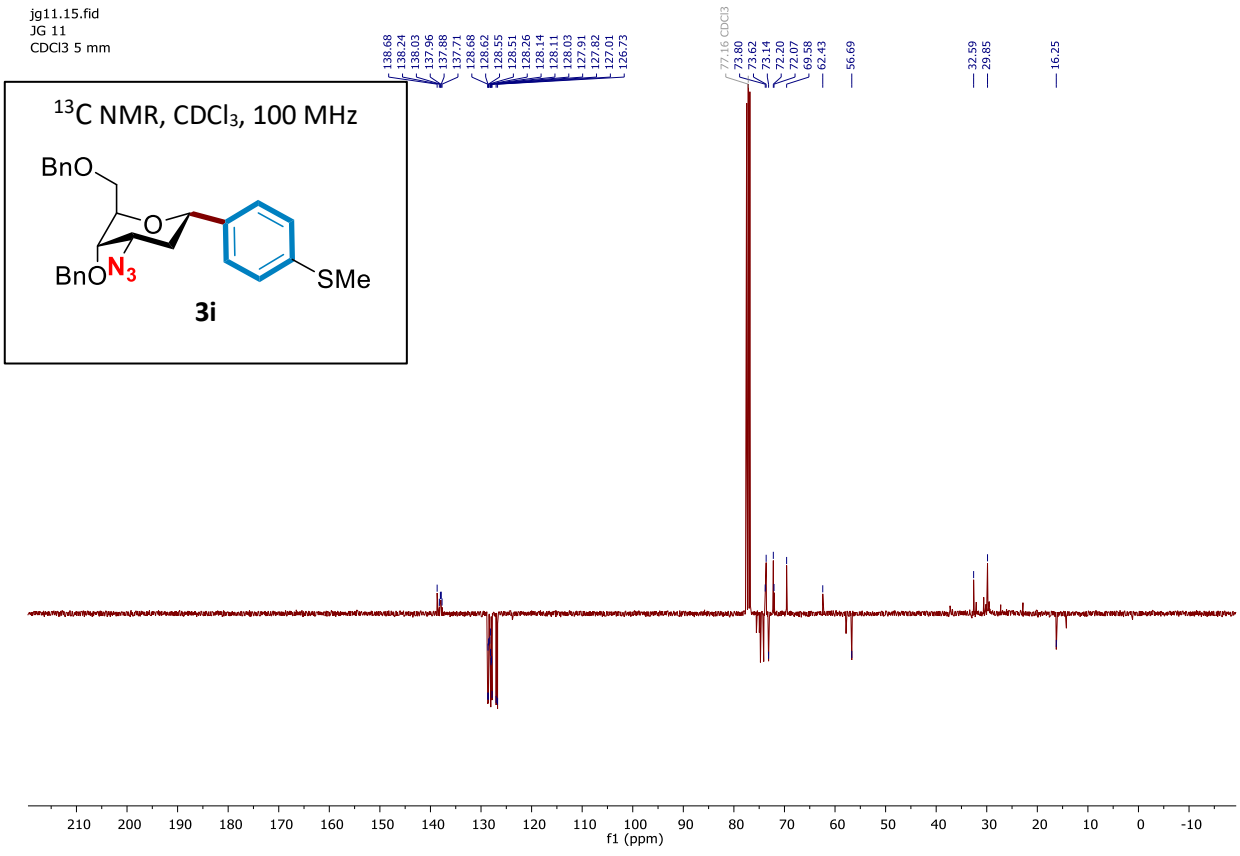


3g


jg71.6.fid
JG 69
CDCl3 5 mm
post analysis
^{1}H NMR, CDCl$_3$, 400 MHz
BnO
O
BnO
N$_3$
Cl
3h
f1 (ppm)

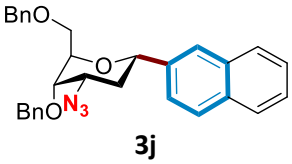

^{13}C NMR, CDCl$_3$, 100 MHz
BnO
O
BnO
N$_3$
Cl
3h
f1 (ppm)


^{1}H NMR, CDCl$_3$, 400 MHz
BnO
BnO
N$_3$
SMe
3i
picks of grease
from the solvent)
f1 (ppm)


jg11.15.fid
JG 11
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
BnO
BnO
N$_3$
SMe
3i
f1 (ppm)

jgnapn3.10.fid
JG Nap N3
CDCl3 5 mm

^{1}H NMR, $CDCl_3$, 400 MHz



3j

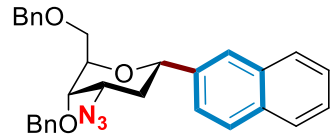
picks of grease

from the solvent)

H_2O

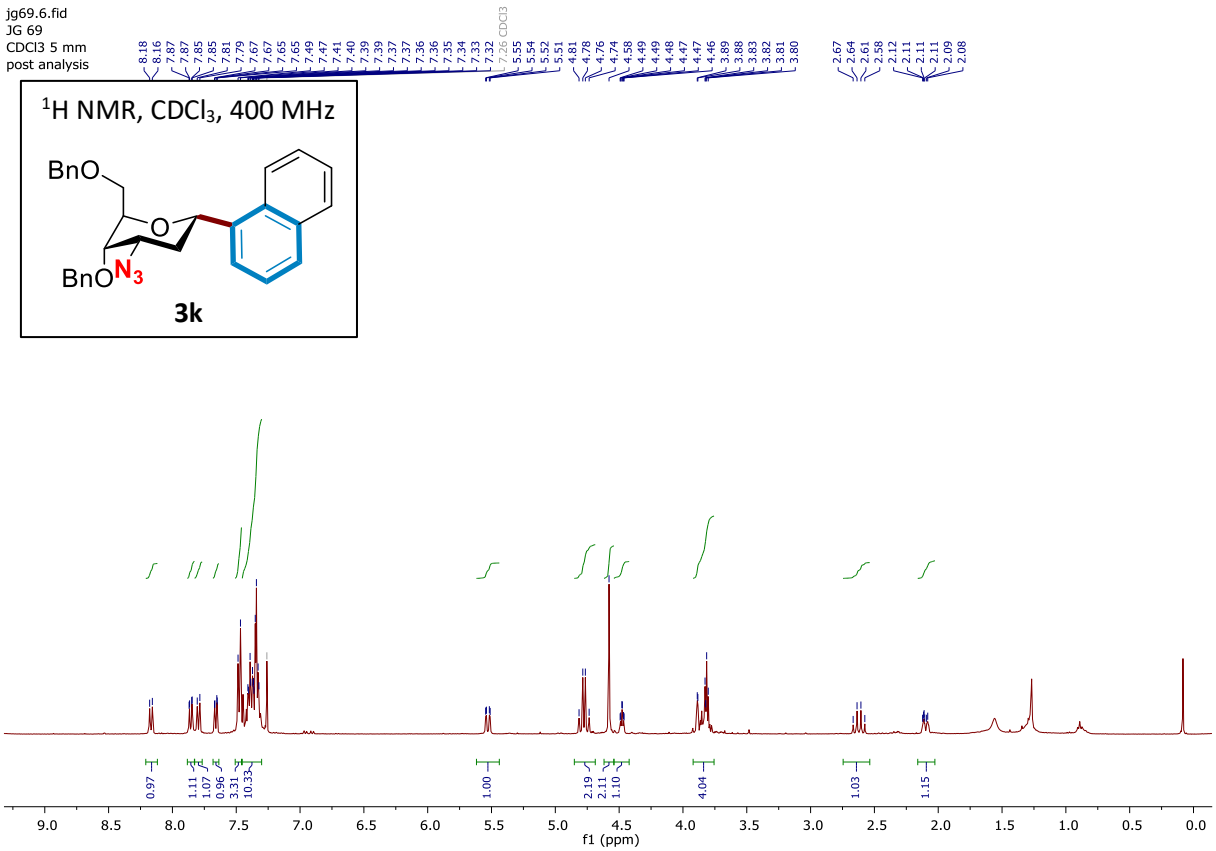
f1 (ppm)

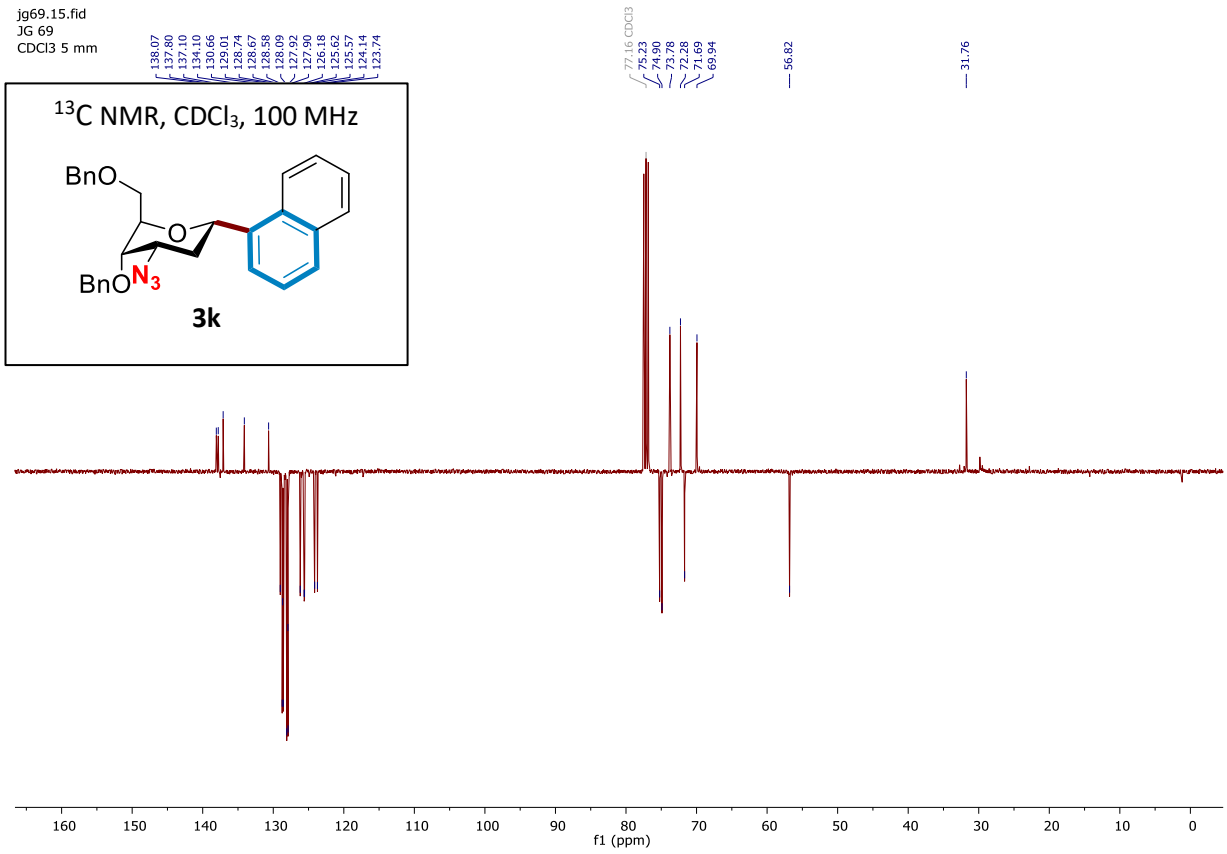
^{13}C NMR, $CDCl_3$, 100 MHz

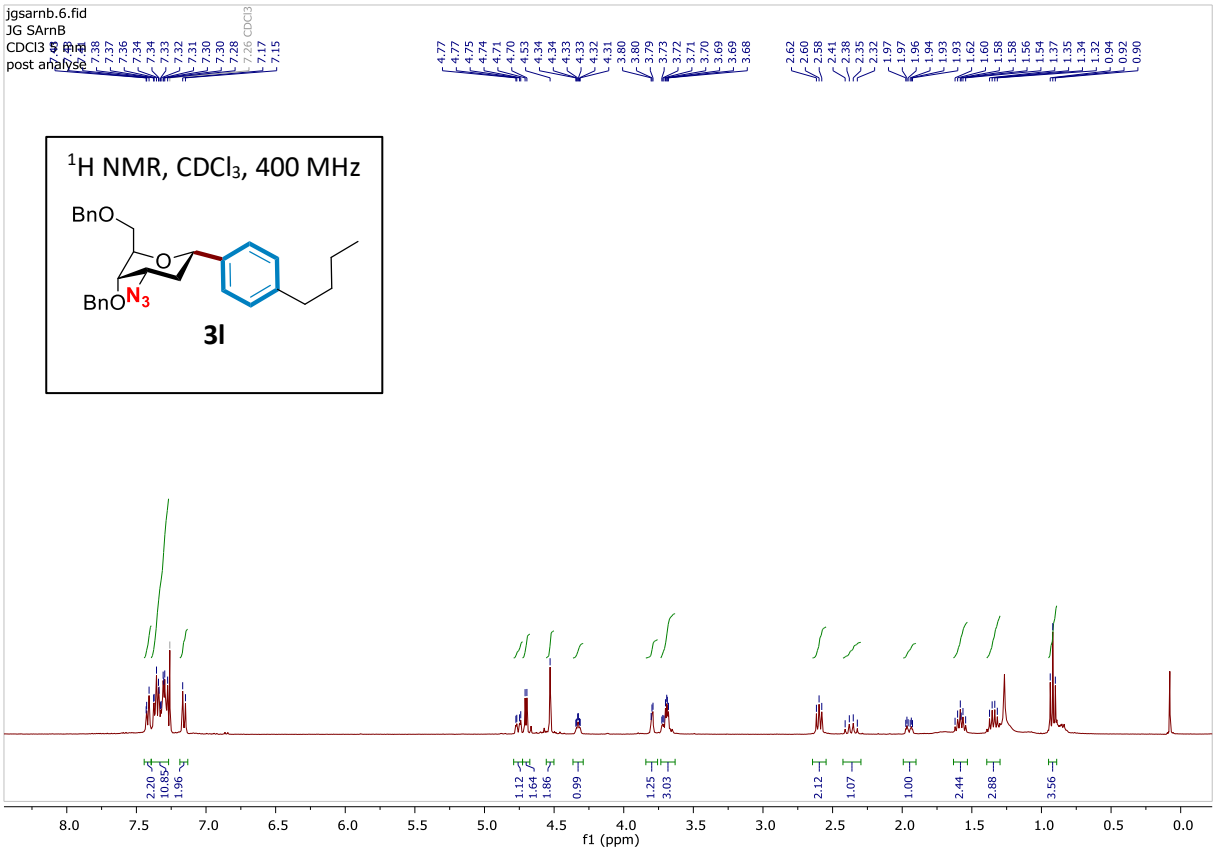


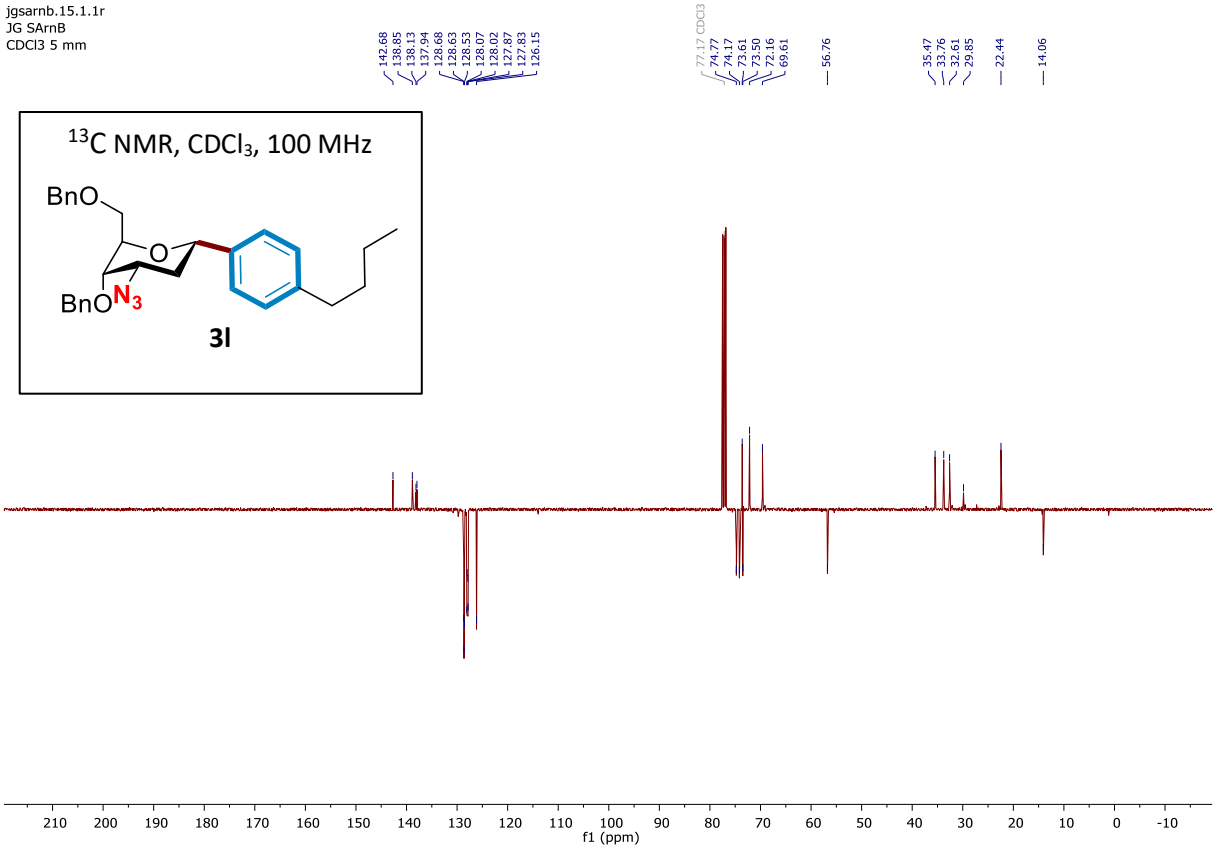
3j

f1 (ppm)


jg69.6.fid
JG 69
CDCl3 5 mm
post analysis
^{1}H NMR, CDCl$_3$, 400 MHz
BnO
BnO
N$_3$
3k
f1 (ppm)

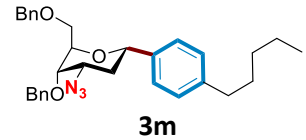

jg69.15.fid
JG 69
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
BnO
BnO
N$_3$
3k
f1 (ppm)


jgsarnb.6.fid
JG SArnB
CDCl3 5 mm
post analyse
^{1}H NMR, CDCl$_3$, 400 MHz
BnO
BnO
N$_3$
3l
f1 (ppm)

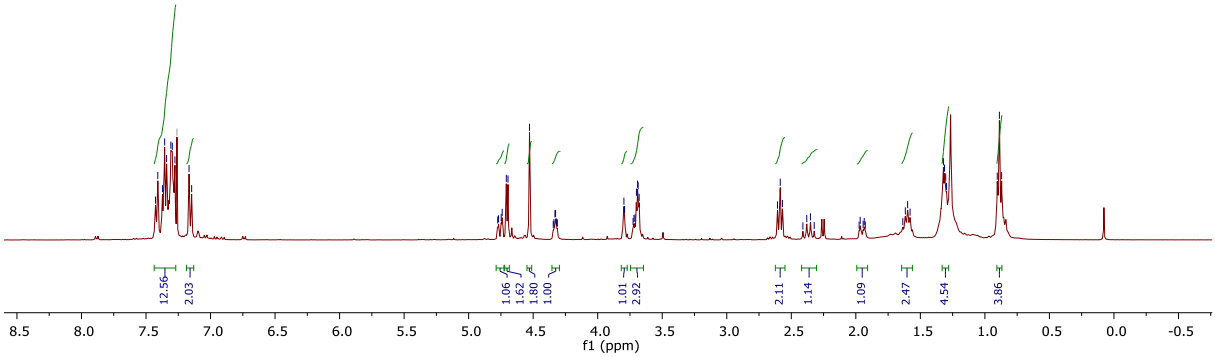

jgsarnb.15.1.1r
JG SArnB
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
BnO
BnO
N$_3$
3l
f1 (ppm)

jg14.10.fid
JG 14
CDCl3 5 mm

^{1}H NMR, $CDCl_3$, 400 MHz

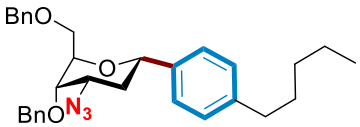


3m

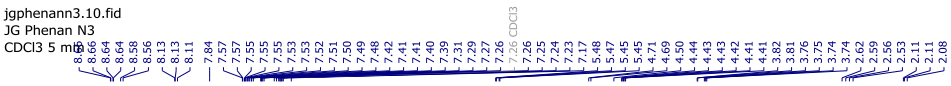


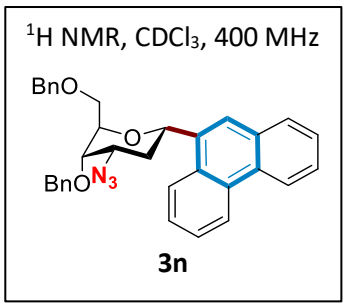
jg14.15.fid
JG 14
CDCl3 5 mm

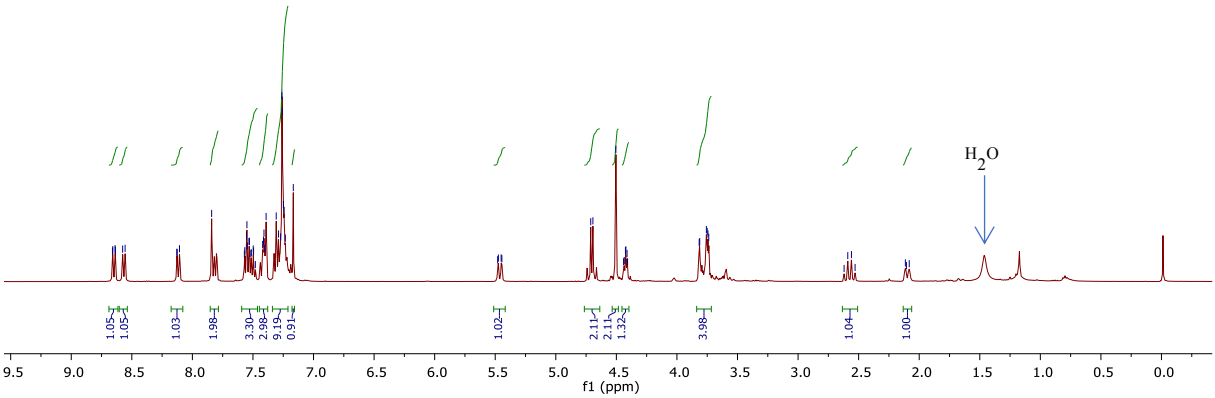
^{13}C NMR, $CDCl_3$, 100 MHz

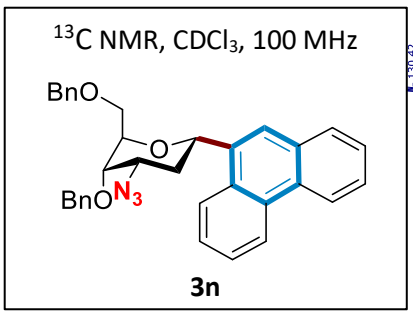


3m


jgphenann3.10.fid
JG Phenan N3
CDCl3 5 mm


1H NMR, CDCl3, 400 MHz
BnO
BnO
N3
3n

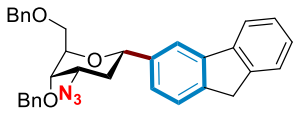

H2O
f1 (ppm)


13C NMR, CDCl3, 100 MHz
BnO
BnO
N3
3n

f1 (ppm)

jg9n3.10.fid
jg9n3
CDCl3 5 mm

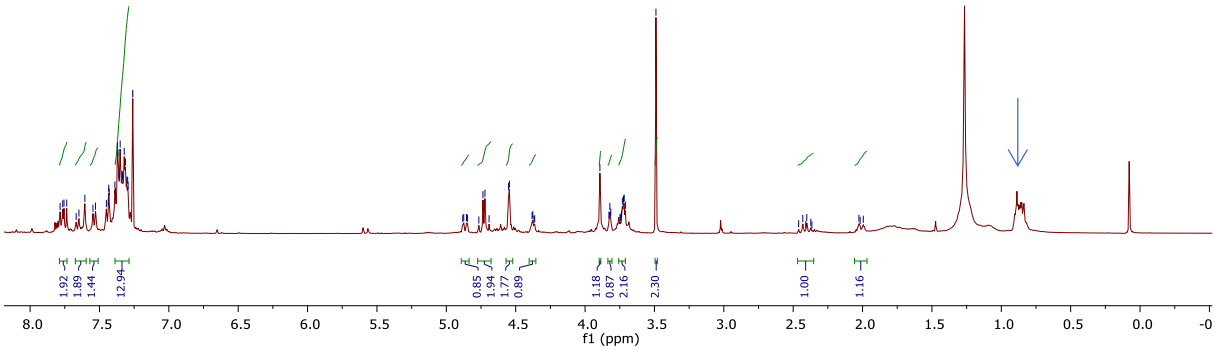
^{1}H NMR, $CDCl_3$, 400 MHz



3o

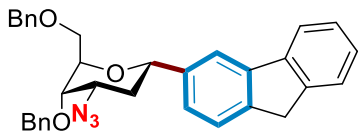
picks of grease

(from the solvent)

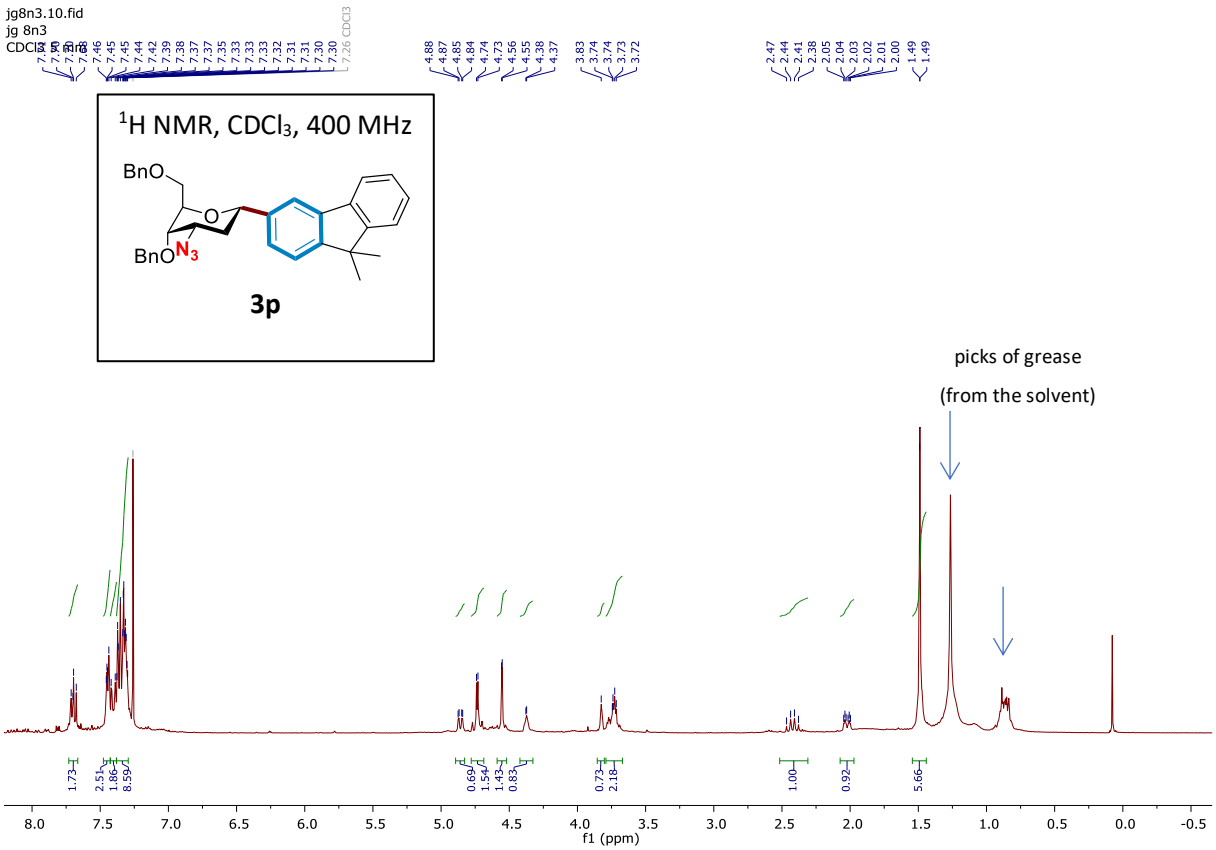


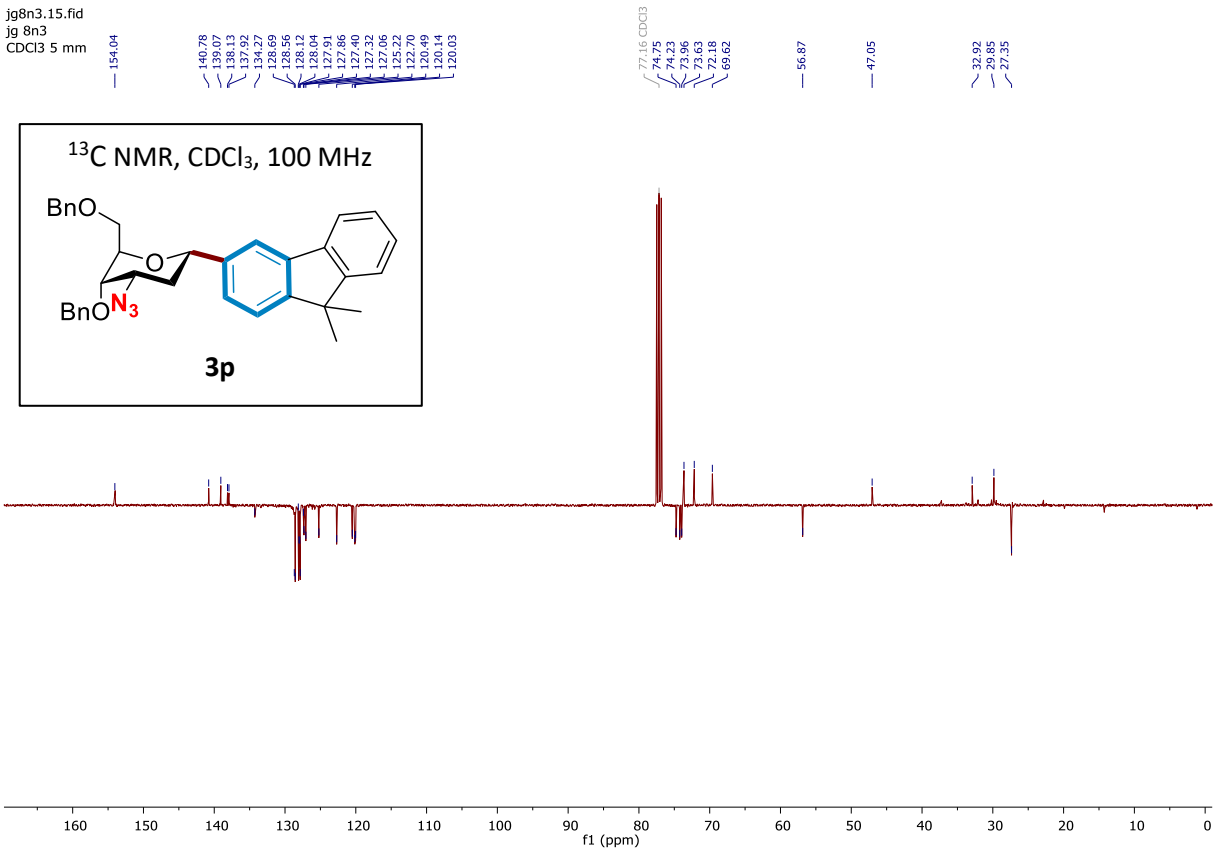
jg9n3.15.fid
jg9n3
CDCl3 5 mm

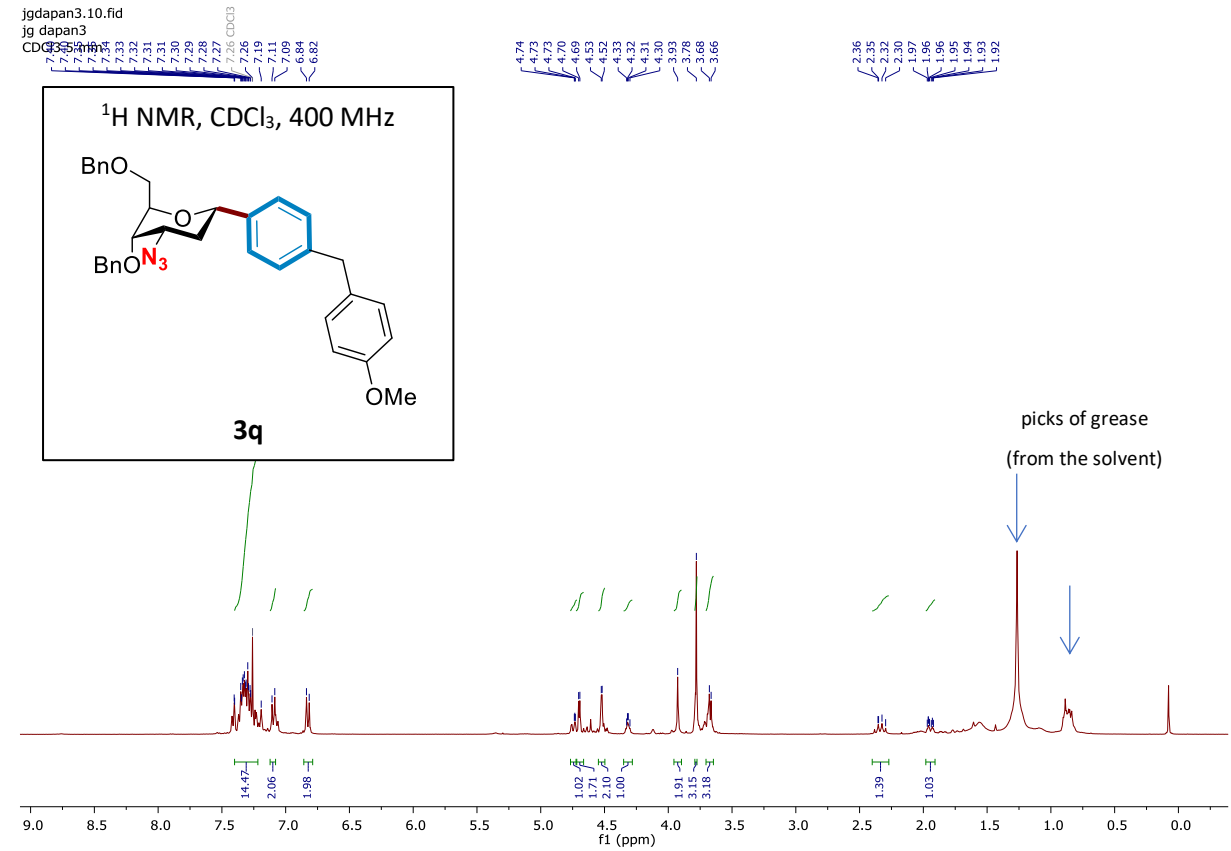
^{13}C NMR, $CDCl_3$, 100 MHz

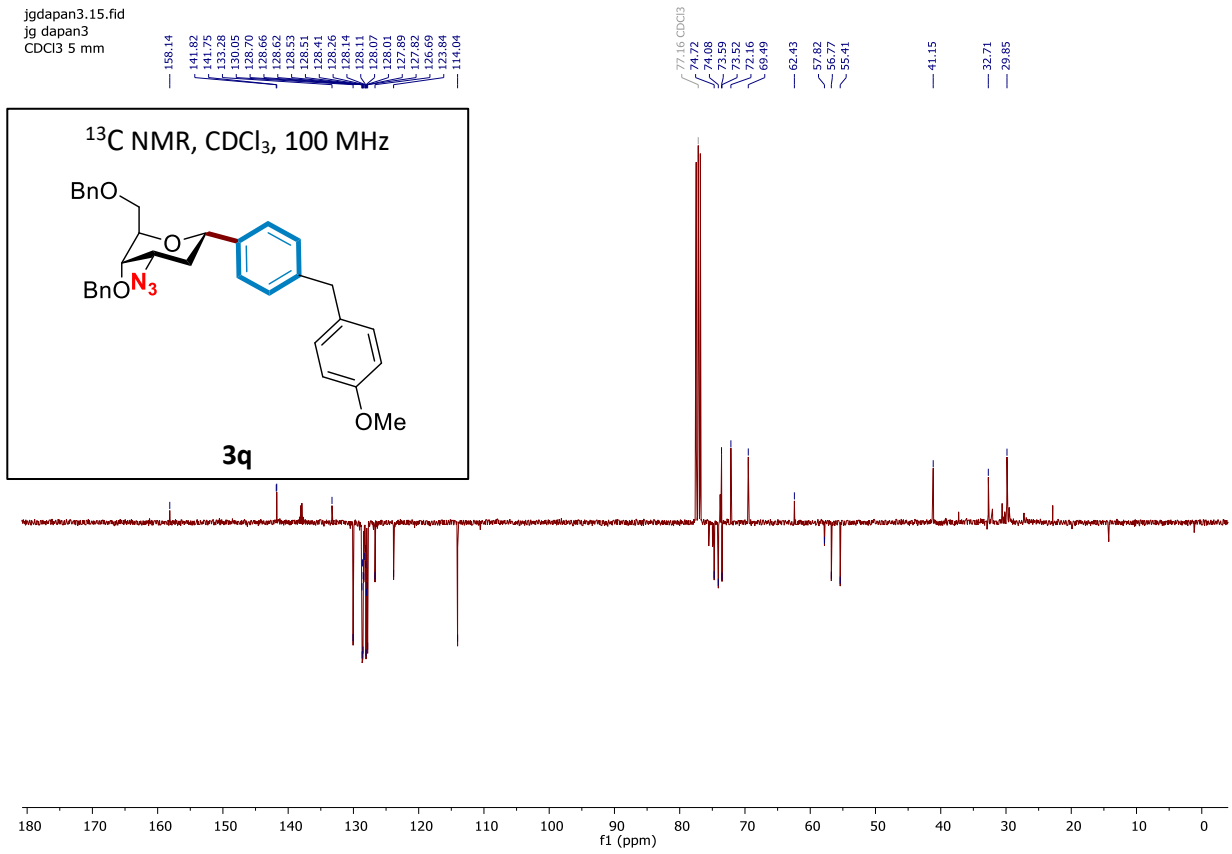


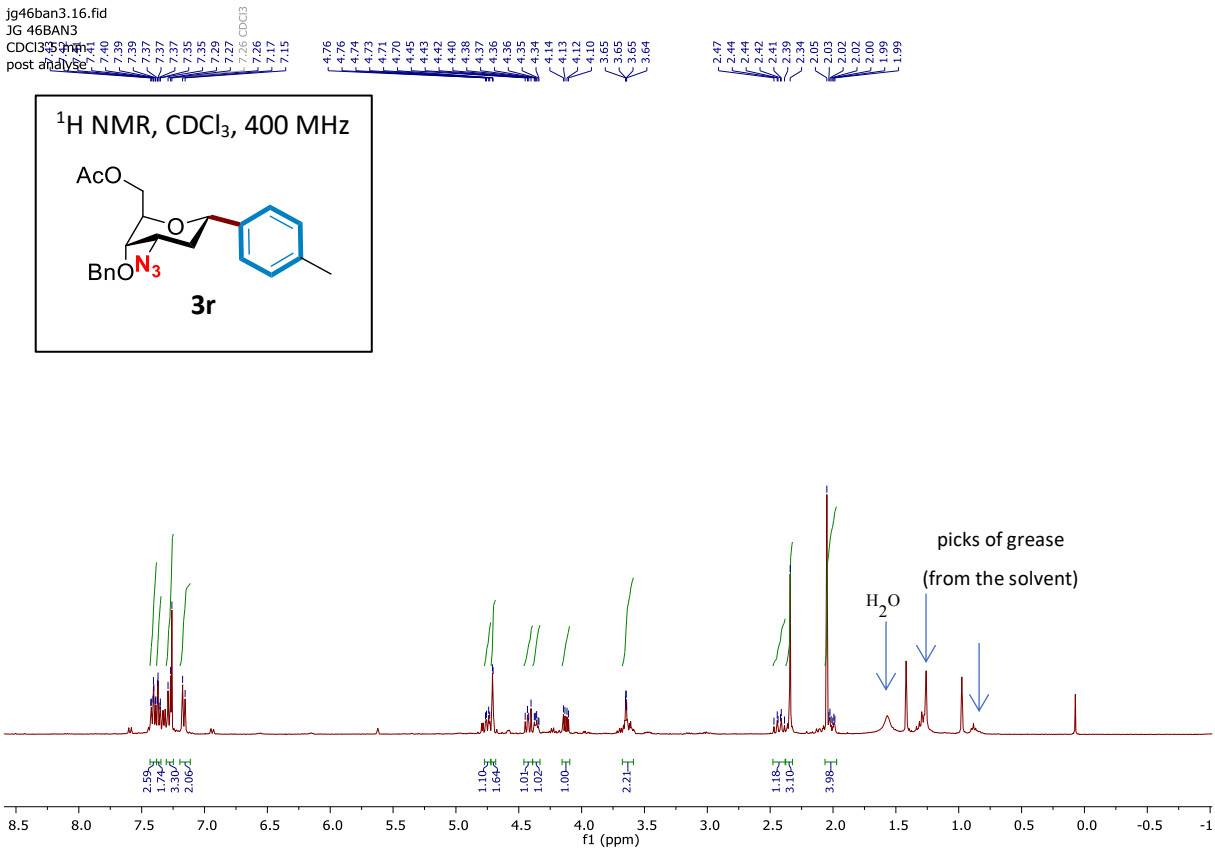
3o

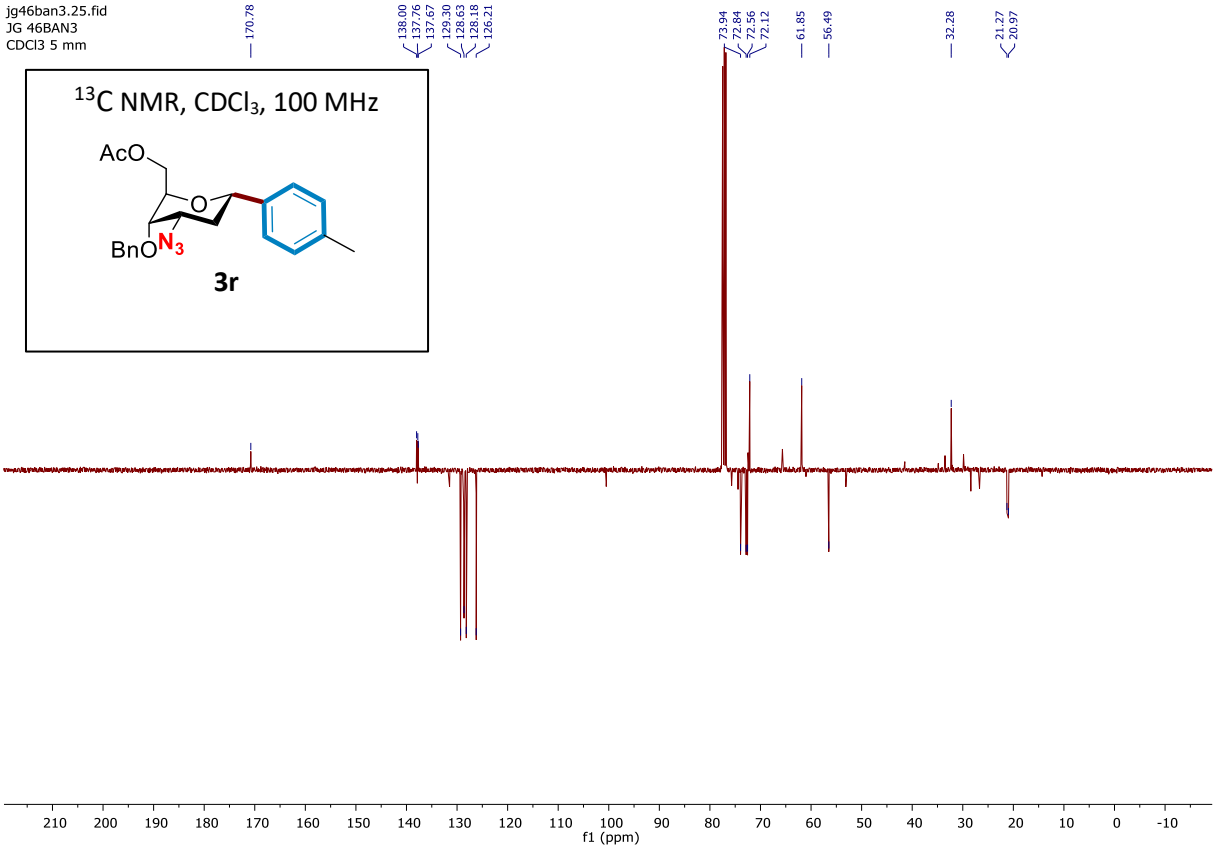

jg8n3.10.fid
jg 8n3
CDCl3 5 mm
^{1}H NMR, CDCl$_3$, 400 MHz
BnO
BnO
N$_3$
3p
picks of grease
(from the solvent)
f1 (ppm)

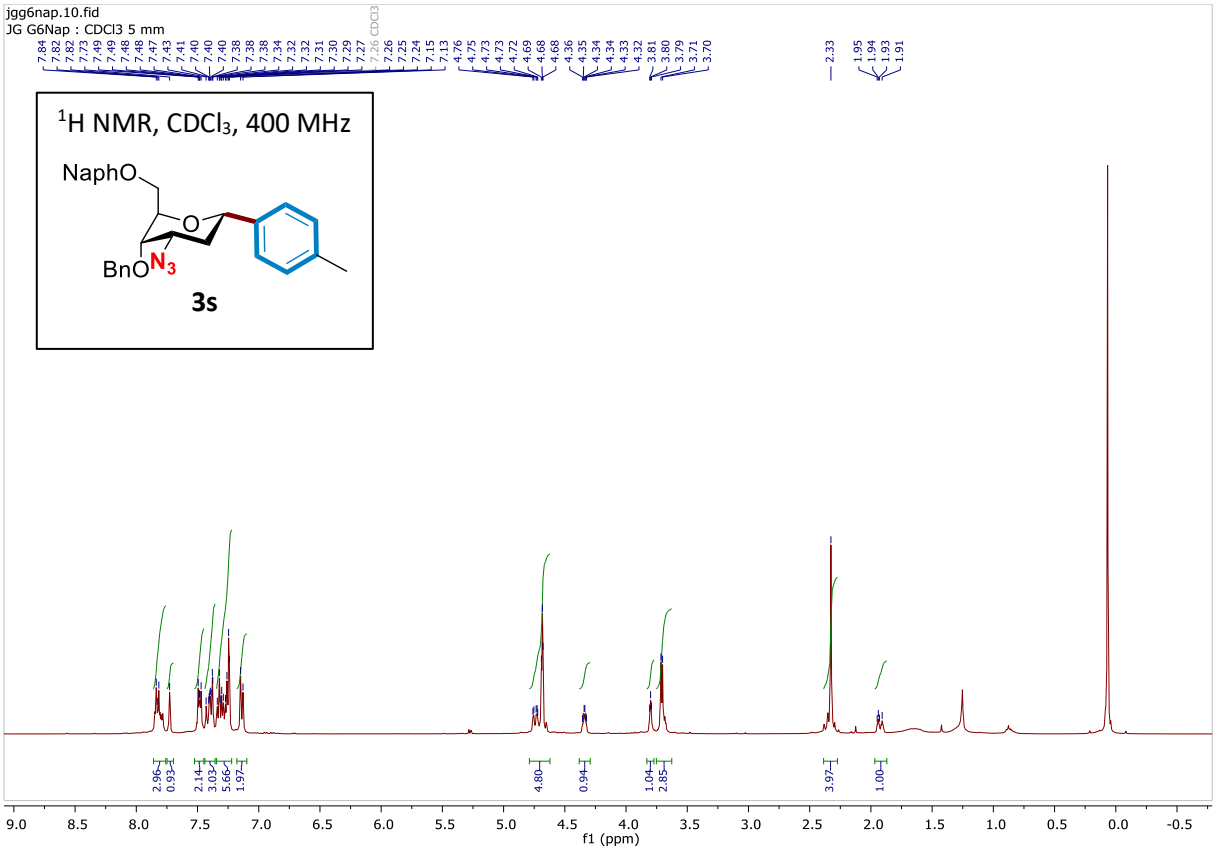

jg8n3.15.fid
jg 8n3
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
BnO
BnO
N$_3$
3p
f1 (ppm)

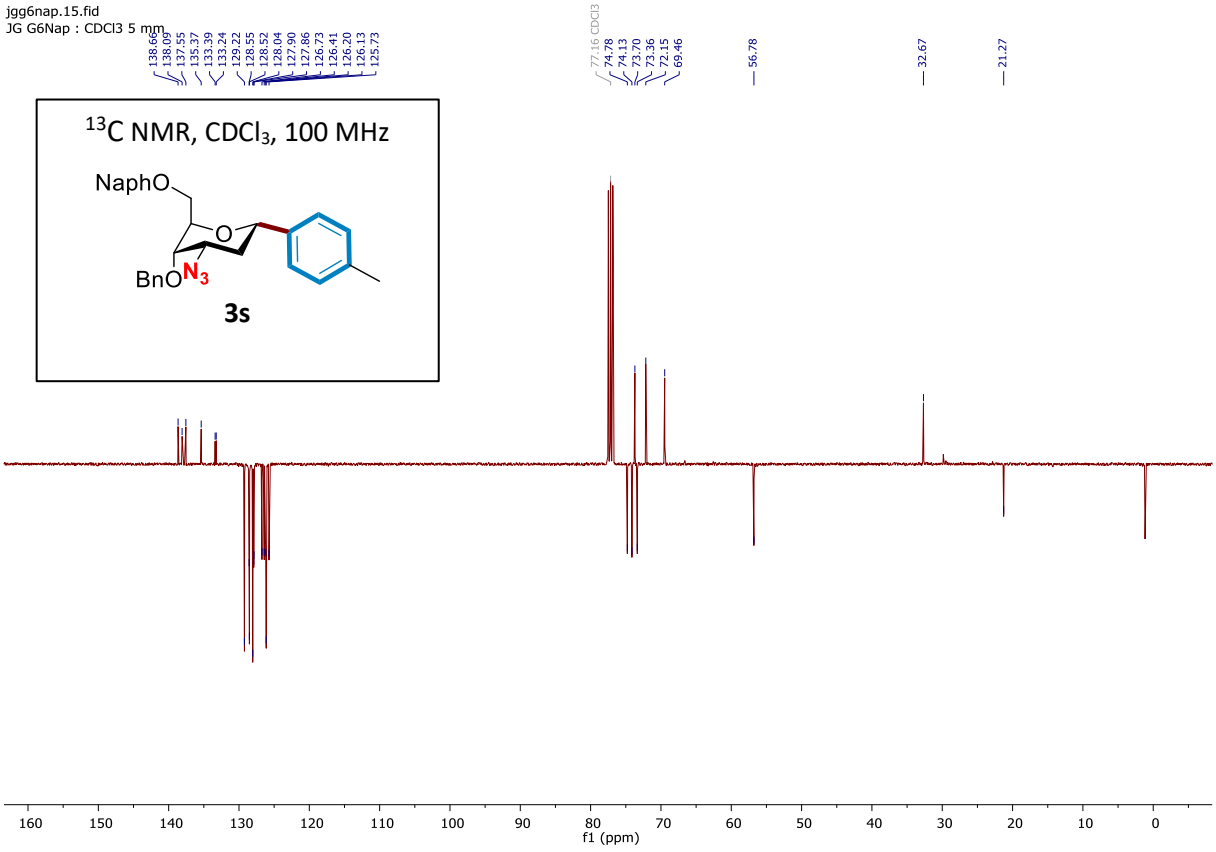

jgdapan3.10.fid
jg dapan3
CDCl3 5 mm
^{1}H NMR, CDCl$_3$, 400 MHz
BnO
BnO
N$_3$
O
OMe
3q
picks of grease
(from the solvent)
f1 (ppm)

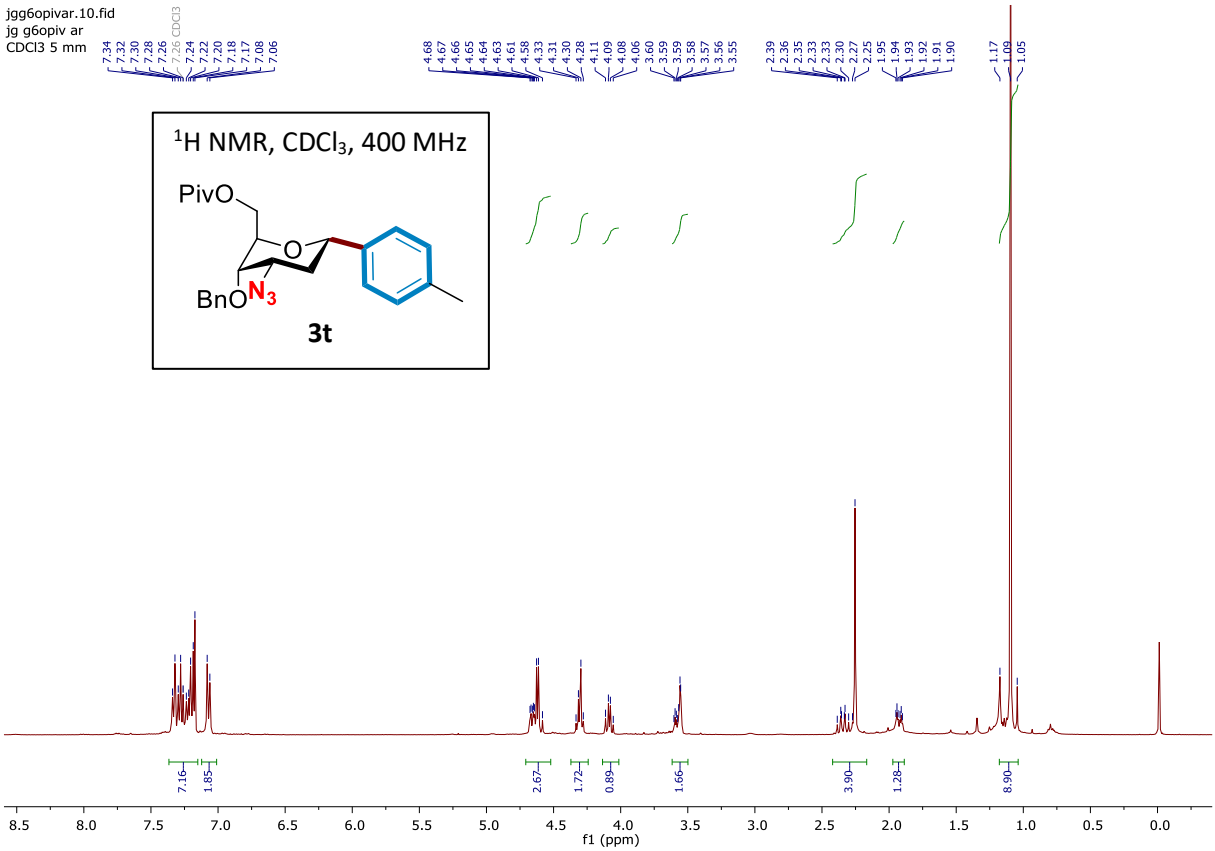

jgdapan3.15.fid
jg dapan3
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
BnO
BnO
N$_3$
O
OMe
3q
f1 (ppm)

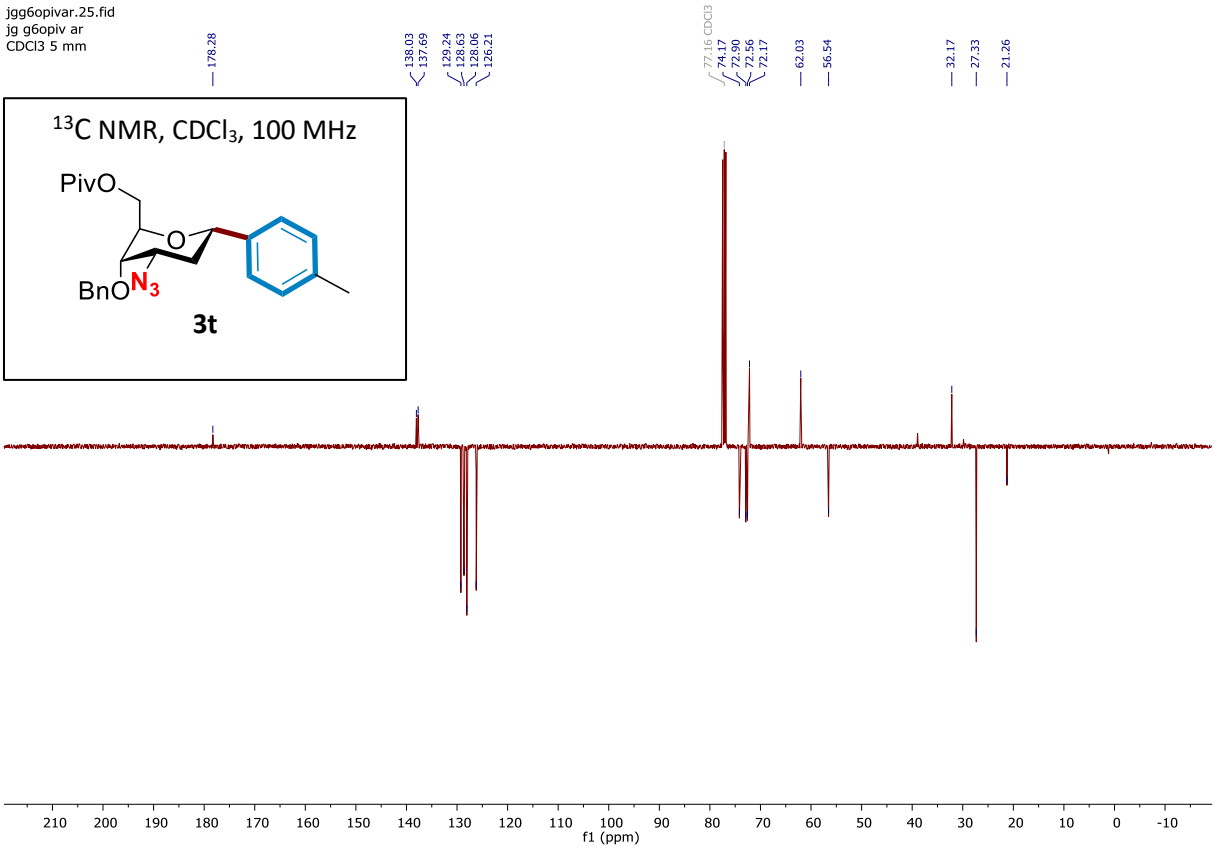

jg46ban3.16.fid
JG 46BAN3
CDCl3 5 mm
post analyse
^{1}H NMR, CDCl$_3$, 400 MHz
AcO
O
BnO
N$_3$
3r
picks of grease
(from the solvent)
H$_2$O
f1 (ppm)

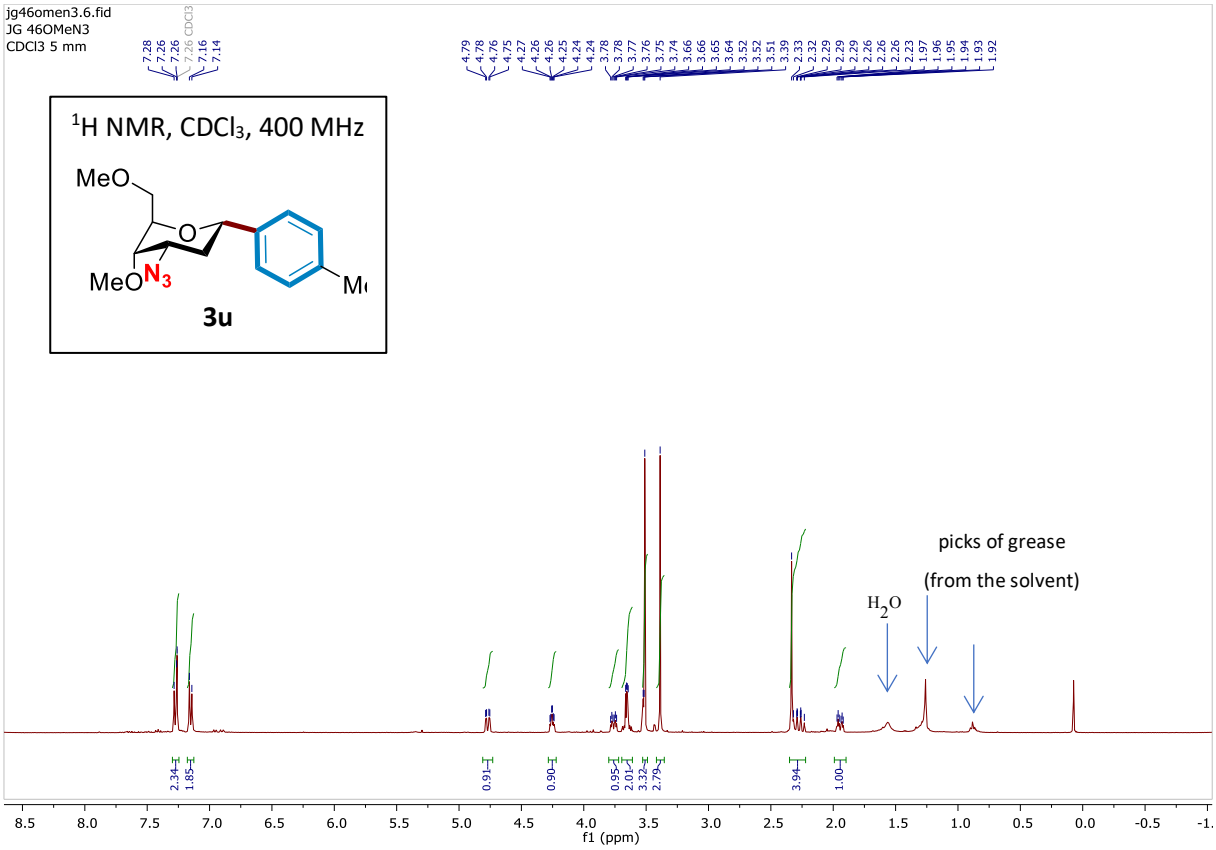

jg46ban3.25.fid
JG 46BAN3
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
AcO
O
BnO
N$_3$
3r
f1 (ppm)

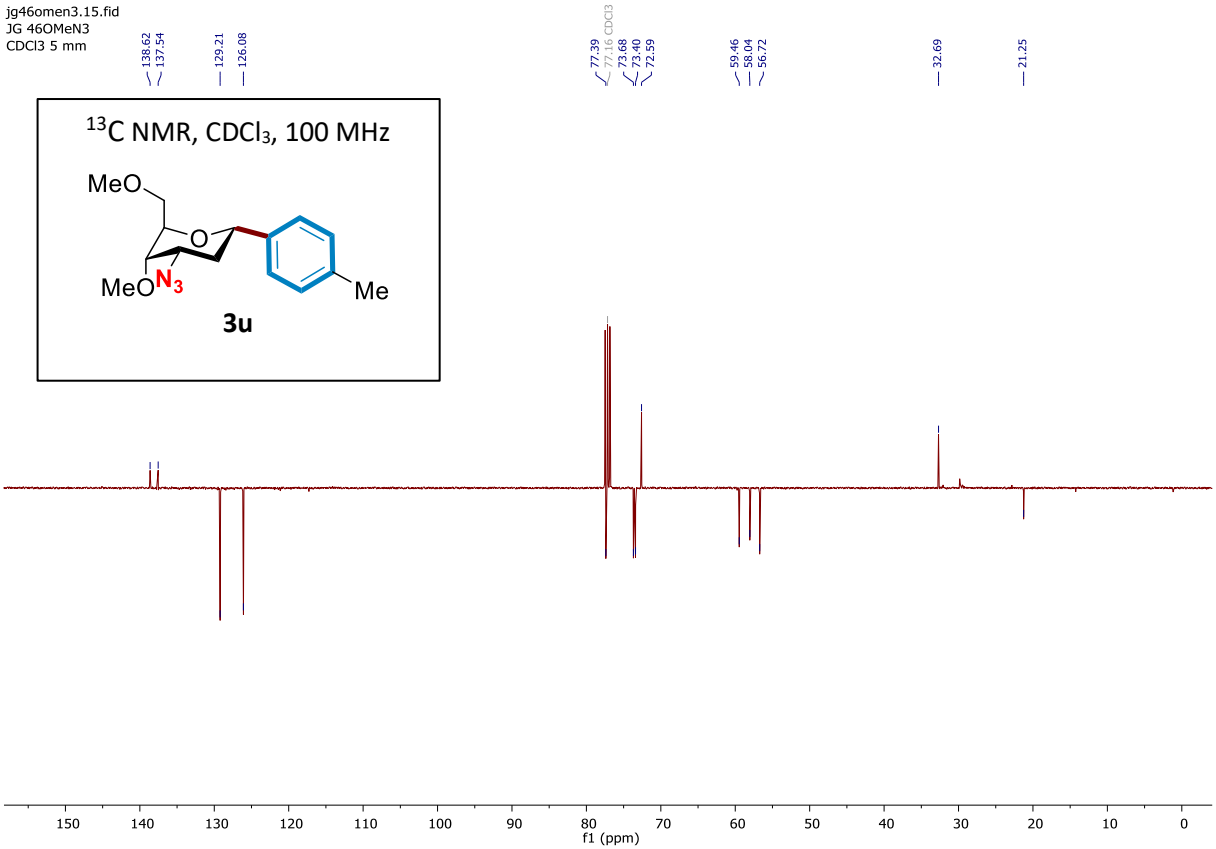

jgg6nap.10.fid
JG G6Nap : CDCl3 5 mm
^{1}H NMR, CDCl$_3$, 400 MHz
NaphO
BnO
N$_3$
3s
f1 (ppm)

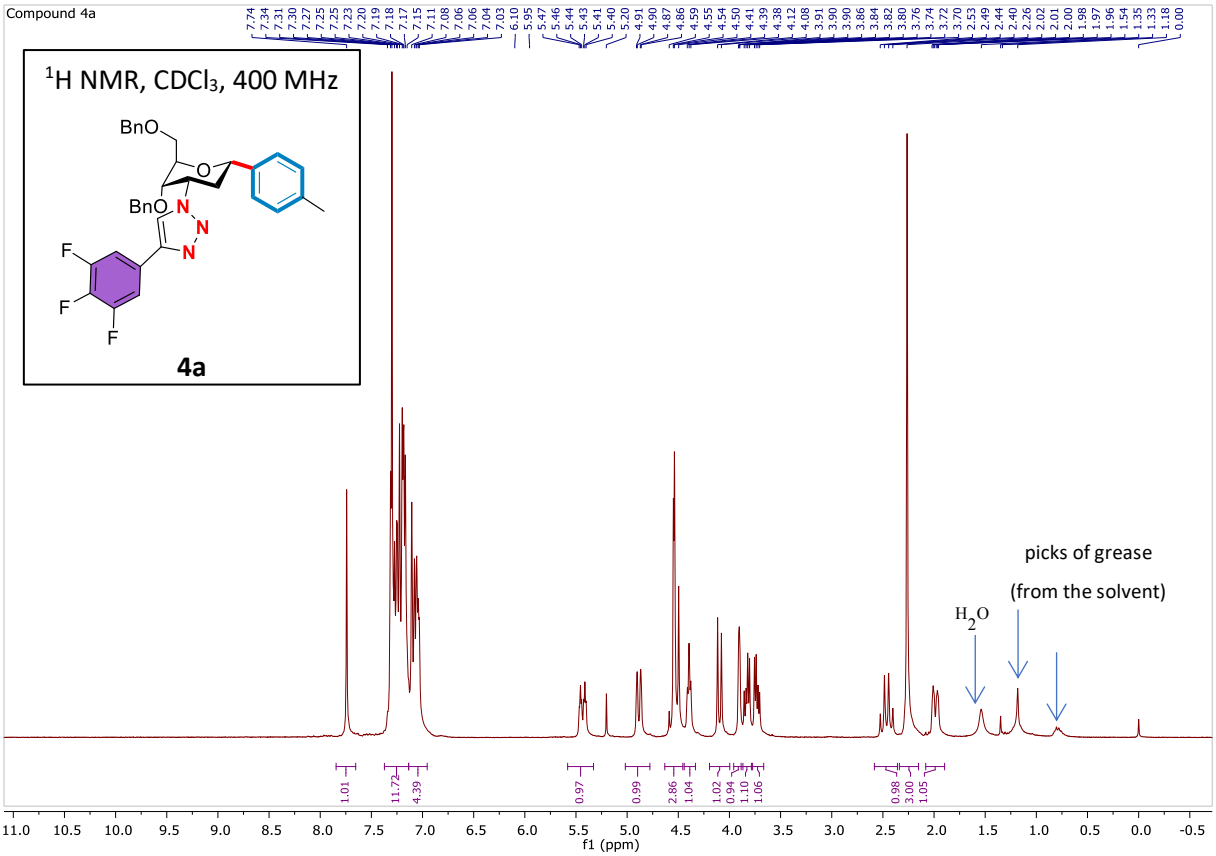

jgg6nap.15.fid
JG G6Nap : CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
NaphO
BnO
N$_3$
3s
f1 (ppm)

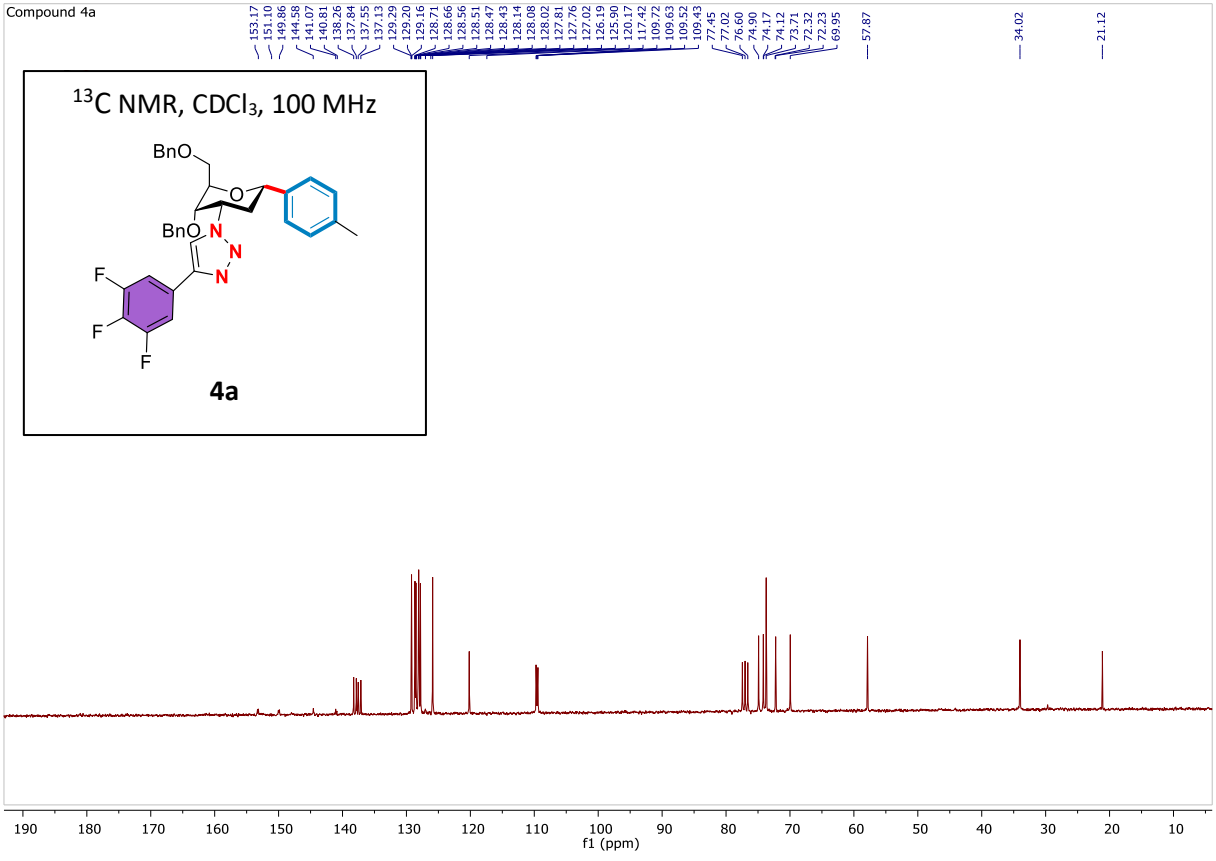

jgg6opivar.10.fid
jg g6opiv ar
CDCl3 5 mm
^{1}H NMR, $CDCl_3$, 400 MHz
PivO
BnO
N_3
3t
f1 (ppm)

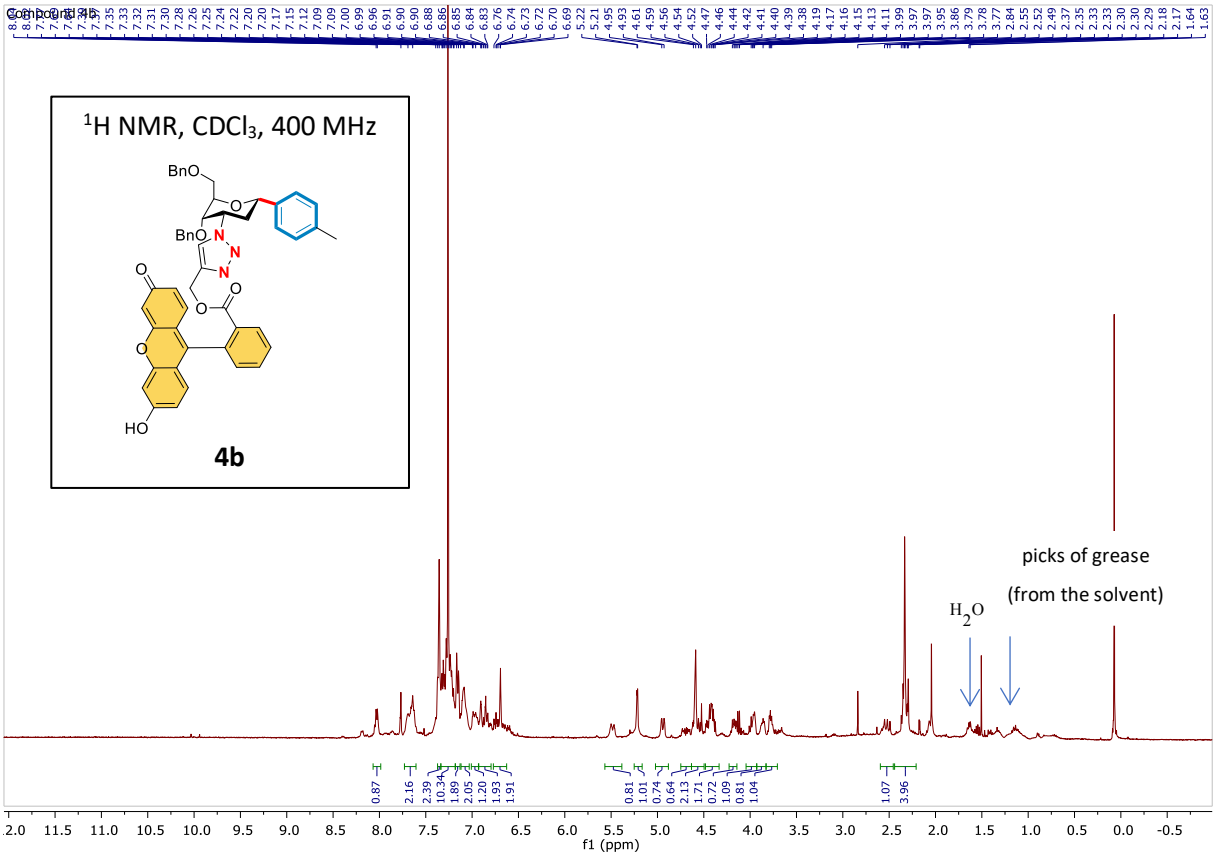

jgg6opivar.25.fid
jg g6opiv ar
CDCl3 5 mm
^{13}C NMR, $CDCl_3$, 100 MHz
PivO
BnO
N_3
3t
f1 (ppm)

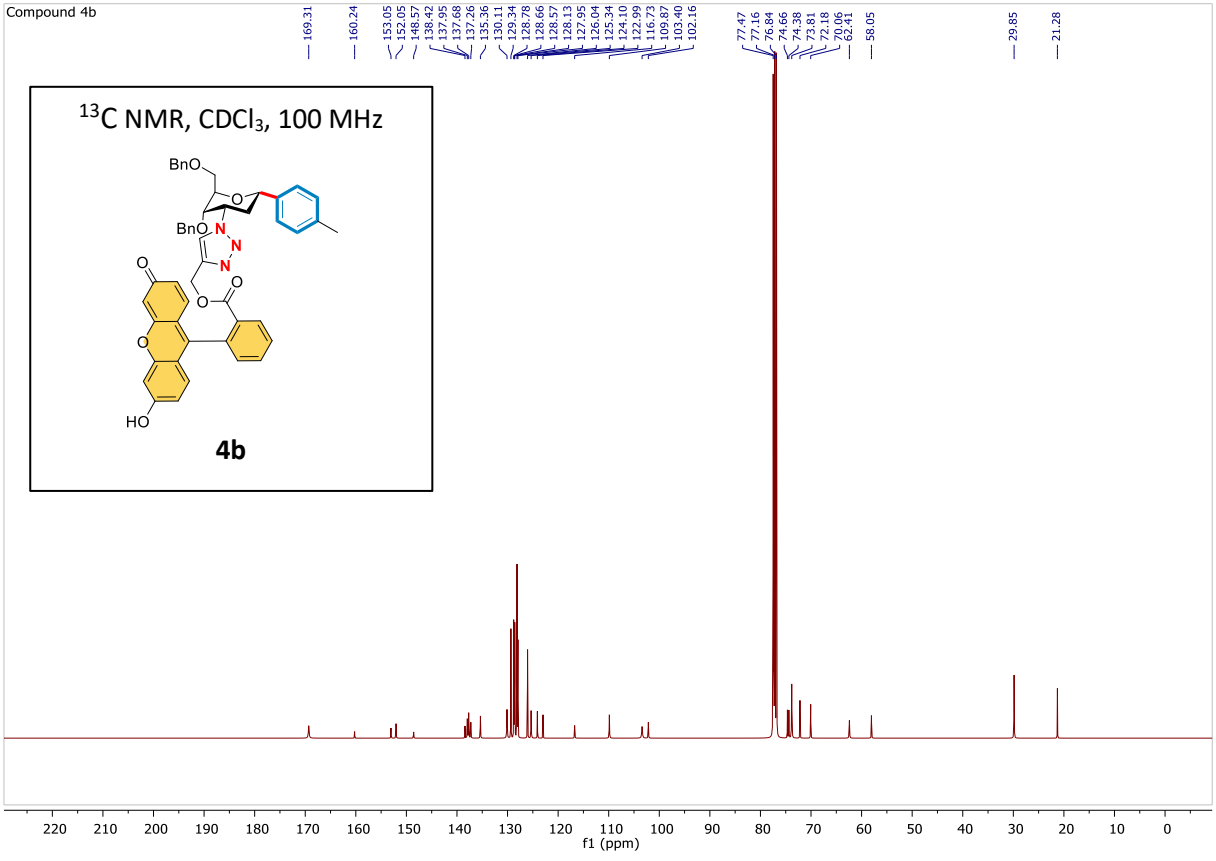

jg46omen3.6.fid
JG 46OMeN3
CDCl3 5 mm
^{1}H NMR, CDCl$_3$, 400 MHz
MeO
MeO
N$_3$
3u
picks of grease
(from the solvent)
H$_2$O
f1 (ppm)

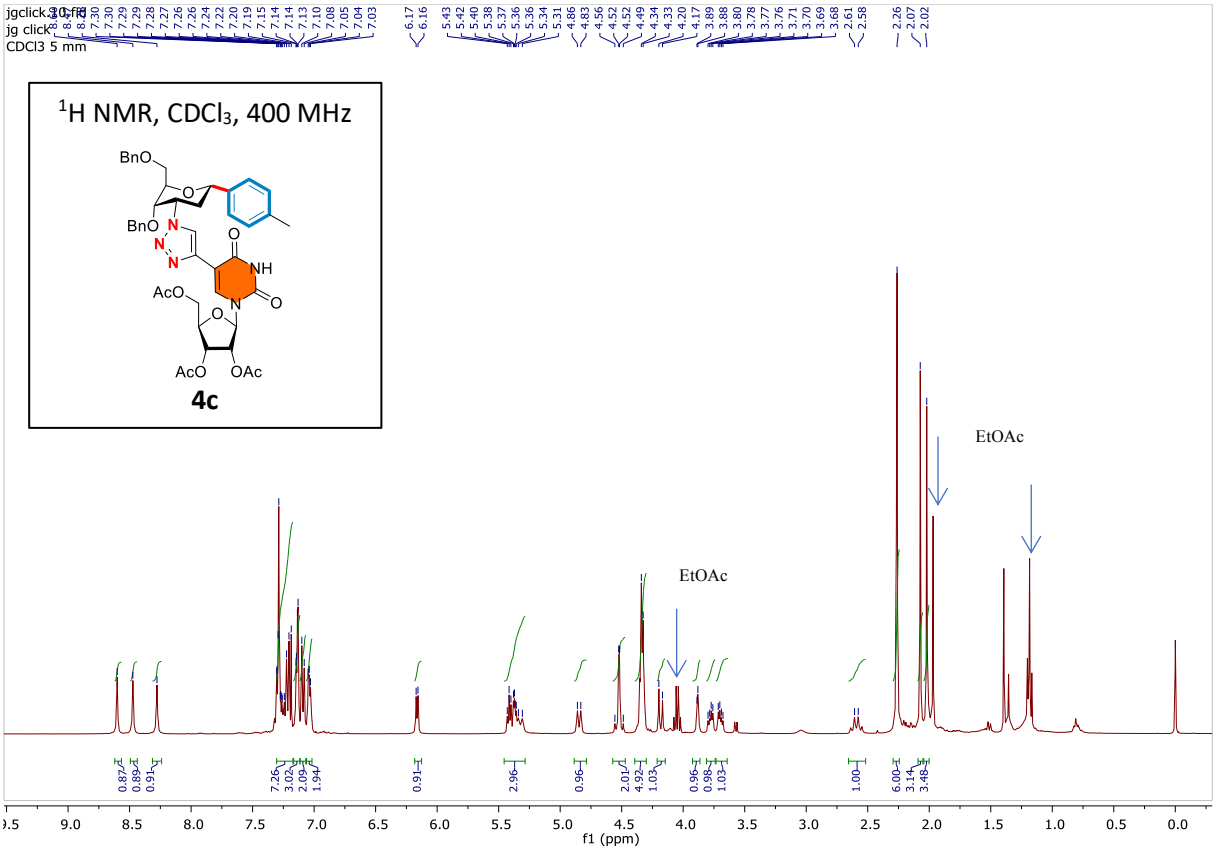

jg46omen3.15.fid
JG 46OMeN3
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
MeO
MeO
N$_3$
Me
3u
f1 (ppm)

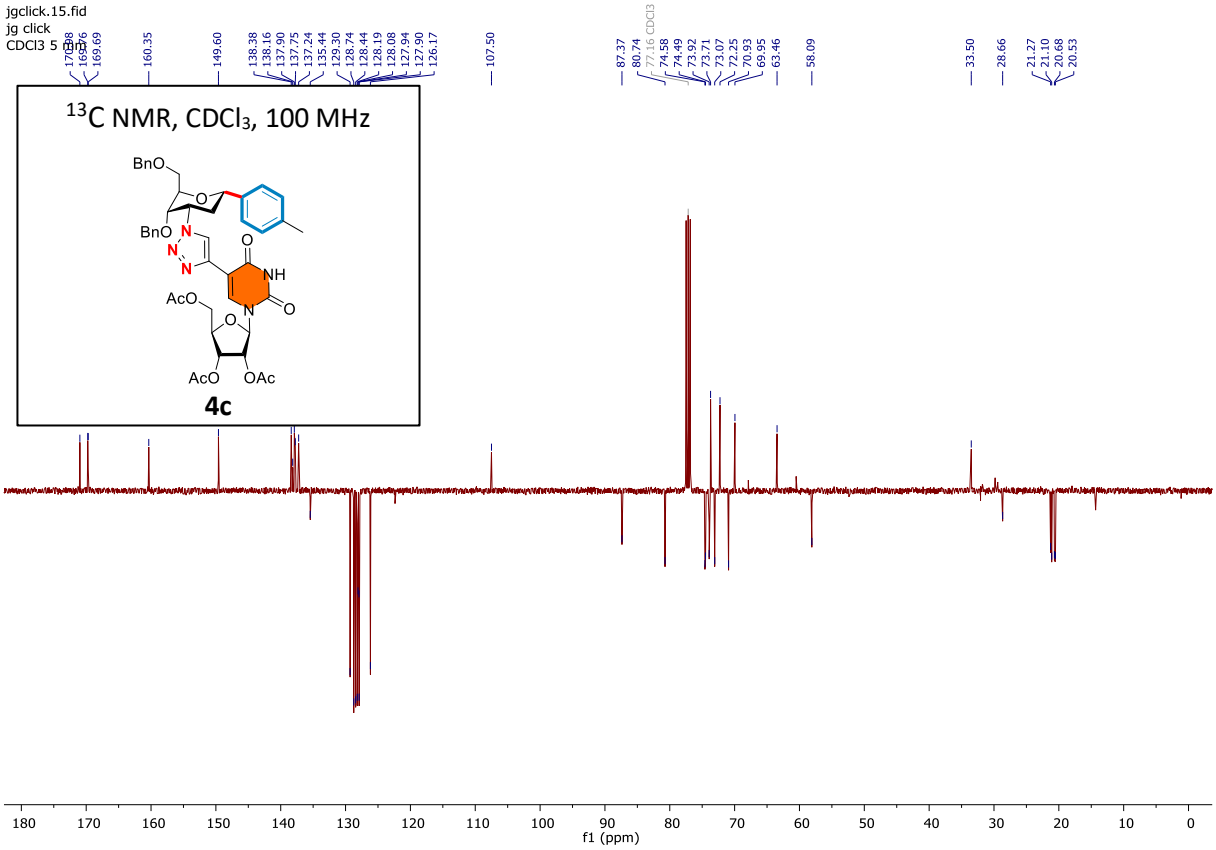

Compound 4a
^{1}H NMR, CDCl$_3$, 400 MHz
BnO
O
BnO
N
N
N
F
F
F
4a
picks of grease
(from the solvent)
H$_2$O
f1 (ppm)


Compound 4a
^{13}C NMR, CDCl$_3$, 100 MHz
BnO
O
BnO
N
N
N
F
F
F
4a
f1 (ppm)


Compound 4b
^{1}H NMR, $CDCl_3$, 400 MHz
BnO
BnO
N
N
O
O
O
O
HO
4b
picks of grease
(from the solvent)
H_2O
f1 (ppm)


Compound 4b
^{13}C NMR, $CDCl_3$, 100 MHz
BnO
BnO
N
N
O
O
O
O
HO
4b
f1 (ppm)


jgclick.30.fid
jg click
CDCl3 5 mm
^{1}H NMR, CDCl$_3$, 400 MHz
4c
EtOAc
EtOAc
f1 (ppm)


jgclick.15.fid
jg click
CDCl3 5 mm
^{13}C NMR, CDCl$_3$, 100 MHz
4c
f1 (ppm)