Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Intercepted dehomologation of aldoses by *N*-heterocyclic carbene catalysis – a novel transformation in carbohydrate chemistry

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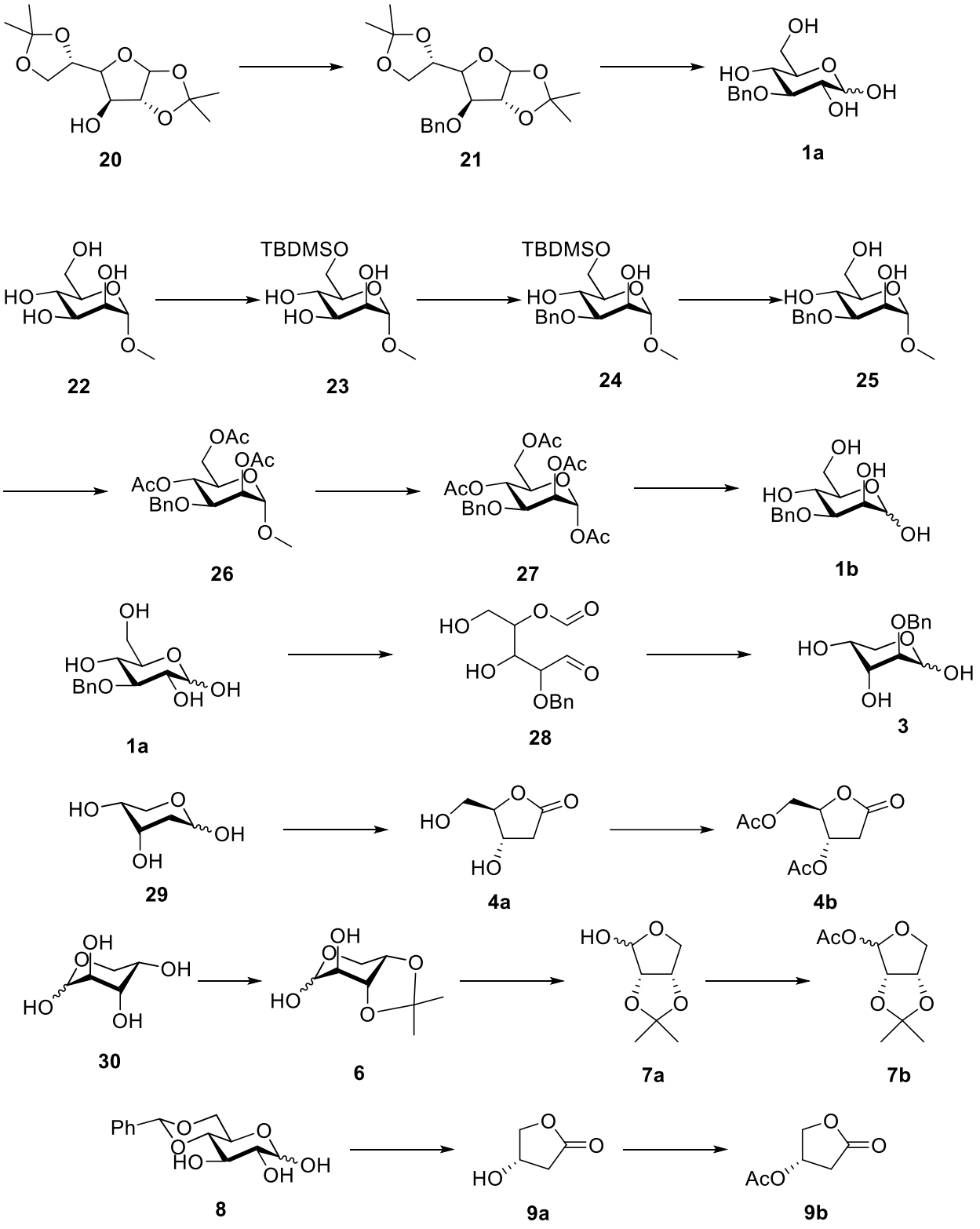

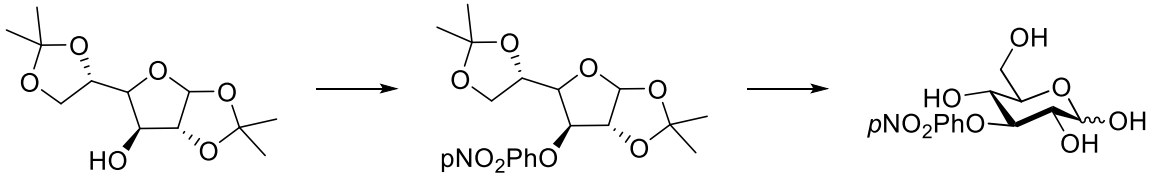

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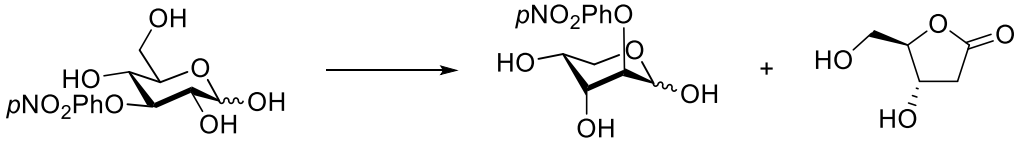
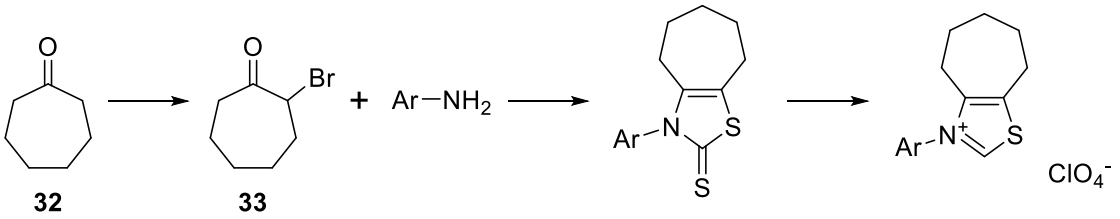


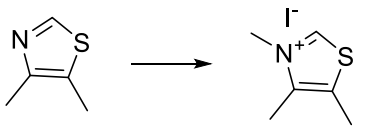
10 **11** **4a**



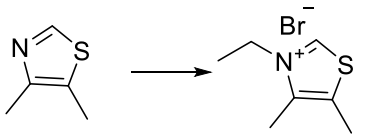
32 **33**

34 (Ar = Ph)
35 (Ar = *p*-MeOPh)
36 (Ar = *p*-NO_2Ph)
37 (Ar = Mes)
38 (Ar = dipp)

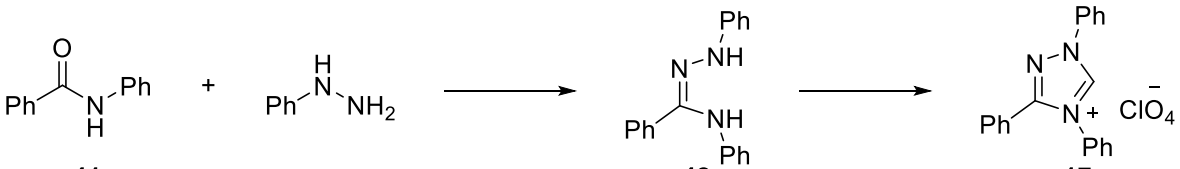
12 (Ar = Ph)
13 (Ar = *p*-MeOPh)
14 (Ar = *p*-NO_2Ph)
15 (Ar = Mes)
16 (Ar = dipp)



39 **2**



39 **40**



41 **42** **17**

2 General information

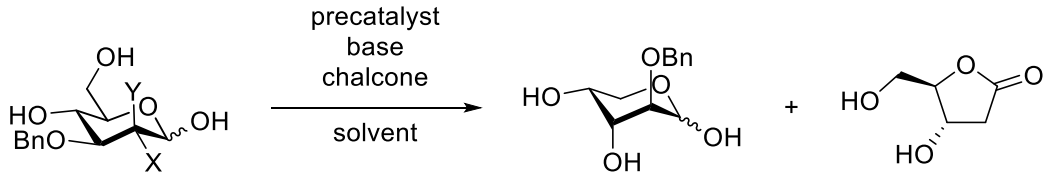
All chemicals were used directly from commercial sources and used without further purification. Water-free solvents were available at the institute from a PureSolv EN 1-4 Enclosed solvent drying plant. Light petrol for column chromatography was distilled prior to use. MeCN was dried by refluxing it over CaH_2 for several hours, before collecting it by distillation. Amberlyst 15 was washed with the respective solvent prior to use. TLC analysis for reaction monitoring and analyzing fraction from column chromatography was performed on silica gel 60 F254-plates or HPTLC-plates (silica gel 60 F_{254} with concentration zone 20 × 2.5 cm). The reverse phase columns LiChrolut® RP18 (100 mg) used for the removal of aliphatic residues in the derivatisation step of the dehomologation experiments were purchased from VWR. The spots were visualized using UV light (254 nm) followed by staining the plates with anisaldehyde solution (180 ml EtOH, 10 ml anisaldehyde, 10 ml H_2SO_4 conc., 2 ml AcOH), potassium permanganate solution (3.0 g $KMnO_4$, 20.0 g K_2CO_3, 250 mg KOH, 300 ml H_2O) or cerium molybdate solution ("Mostain", 21 g $(NH_4)_6Mo_7O_{24}{\cdot}4\,H_2O$, 1 g $Ce(SO_4)_2$ 31 ml H_2SO_4 conc., 500 ml H_2O). NMR spectra were recorded at 297 K in the solvent indicated with an Avance UltraShield 400 and an Avance III HD 600 spectrometer. All spectra were calibrated to the solvent residual peak. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. GC analysis was carried out on a Thermo Finnigan Focus GC/DSQ II equipped with a standard capillary column (BGB5, 30 m x 0.25 mm ID, 0.50 µm film) with FID detector. Carrier gas: helium, injector: 230 °C; column flow: 2.0 mL/min; method for quantification: 50−180 °C (60 °C/min) → 180−310 °C (20 °C/min) → 310 °C (2 min). Accurate mass analysis was obtained on an Agilent 6230 AJS ESI-TOF mass spectrometer with ESI ionization method or (for the cases denoted with a *) Q Exactive Focus, ESI, FIA injection, mobile phase 18% MeCN with 0.1% formic acid. GC-MS spectra were measured on a Thermo Trace 1300 / ISQ LT (single quadrupole MS (EI)) using a standard capillary column BGB 5 (30 m x 0.25 mm ID). Optical rotation was measured on an Anton Paar MCP 500 at the specified conditions, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Melting points were recorded on a Kofler-type Leica Galen III or a BÜCHI Melting Point B-545 with a 40%/90% threshold. For DMSO removal a vacuum concentrator RVC 2-25 CDPLUS with an Alpha 2-4 LDplus freeze-dryer was used. Precatalysts **18** and **19** were prepared according to literature procedure.[1]

3 Analytical dehomologation experiments

3.1 Calibration method for reducing sugars

Stock solutions (100 mM) in H_2O of the synthesized carbohydrates **1a**, **3** and **4a** (*vide infra*) as well as erythritol were prepared and aliquots of 40 µL were taken out, combined and evaporated to dryness. Then, a solution of *O*-methylhydroxyl amine hydrochloride in pyridine (400 µL, 40 mg/mL) was added and heated to 70 °C for 1 h. Subsequently, a solution of DMAP in pyridine (400 µL, 1.5 mg/mL) as well as BSTFA (400 µL, + 1% TMSCl) were added and heated to 70 °C for another 2 h. To this mixture, a solution of methylbenzoate (MB) in EtOAc (800 µL, 2.5 mM) was added to reach following concentrations: MB 1.00 mM, all other analytes 5.00 mM. Then, 800 µL were taken out and diluted with a solution of MB in EtOAc (200 µL, 1.00 mM) leading to a concentration of all analytes of 4.00 mM and keeping the concentration of MB at 1.00 mM. From these, 500 µL were taken out and diluted in a ratio of 1:1 with a solution of methylbenzoate in EtOAc (1.00 mM), halving the concentration of the analytes while maintaining a concentration of MB of 1.00 mM. This step was repeated three times to generate a total of ten samples with concentrations of 5.00, 4.00, 2.50, 2.00, 1.25, 1.00, 0.63, 0.50, 0.31 and 0.25 mM, which were filtered *via* syringe filter and submitted to analysis by GC.

3.2 General procedure for the dehomologation reaction and analysis thereof



1a (X = OH, Y = H)
1b (X = H, Y = OH)

3

4a

Stock solutions were prepared for all reactions in DMSO of the sugars, the precatalysts and chalcone. A significant dependence on the grain size of the used K_2CO_3 on the reaction outcome was observed. If not noted otherwise, granulated K_2CO_3 (Alfa Aesar, product number A16625) was used. If fine, powdered K_2CO_3 is used, the formed products are not stable in the reaction mixture leading to substantially lower recovery of identified products. A decline in detectable carbohydrate-based substrates and products over time was given throughout the majority of all conducted experiments (see 3.3 to 3.10 for a selection of the timecourses that have been performed. Decomposition of the formed products and not reacted substrates is very likely, given the forcing conditions. The formation of a defined side product, which would explain the loss of material, was not observed *via* TLC, NMR, HPLC-MS or GC (upon derivatization). For

representative values, 20 minutes was chosen as the usually ideal time point for comparison of different reaction parameters.

Transformation with NHCs

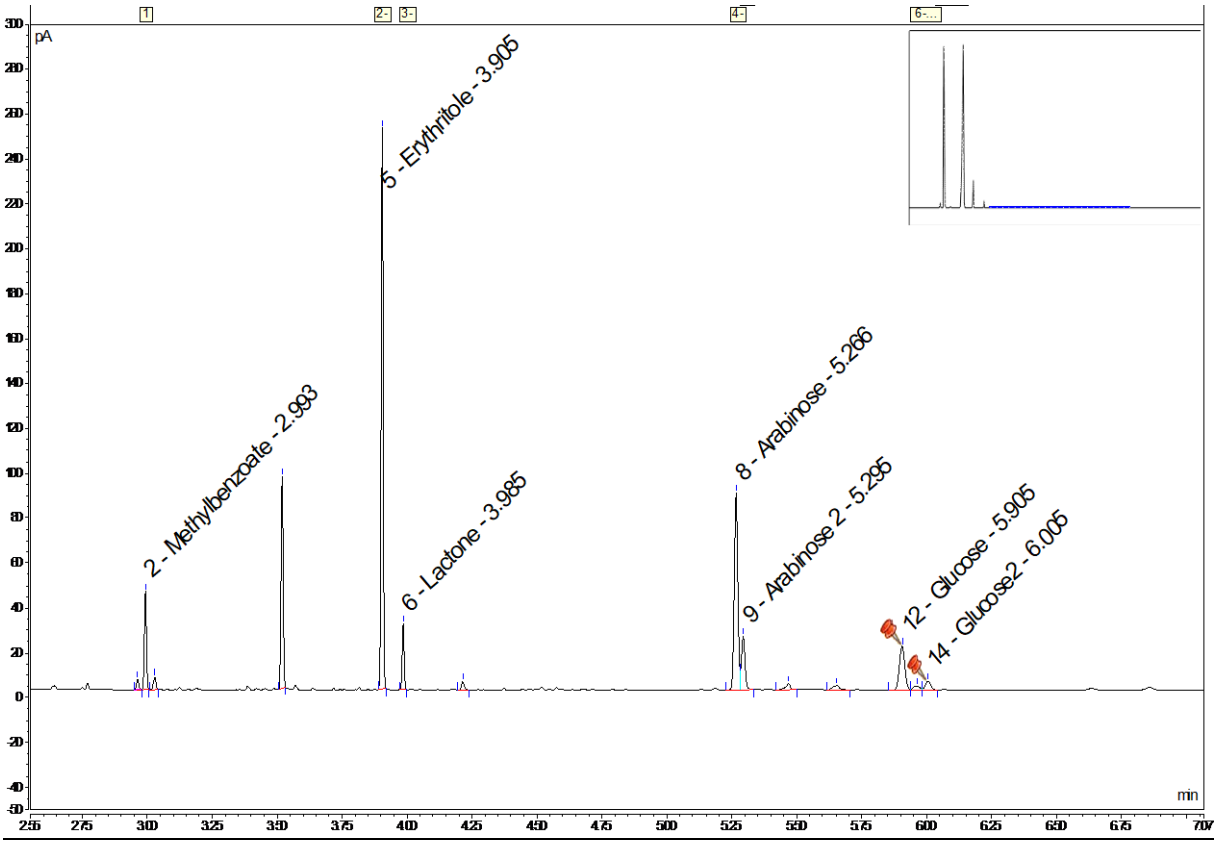
The base (0.20, 0.08 or 0.04 equiv.) was charged into a microwave vial. Appropriate amounts of the stock solutions of benzylated-sugar (0.16 mmol, 1.00 equiv.), the precatalyst (0.25, 0.10 or 0.05 equiv.) and the chalcone (2.0 equiv.), as well as the respective solvent (anh., totaling: 2.0 mL) were added. The microwave vial was capped and the reaction mixture was set under Ar atmosphere *via* Schlenk technique. After stirring for 2 min at rt a t0 sample was taken to later correct for the actual initial benzyl hexose concentration. The reaction mixture was heated in a heating block at the temperature and time indicated with samples of roughly 0.2 ml being taken at several time points and were directly processed further or stored at -18 °C.

Processing of aliquots and derivatisation

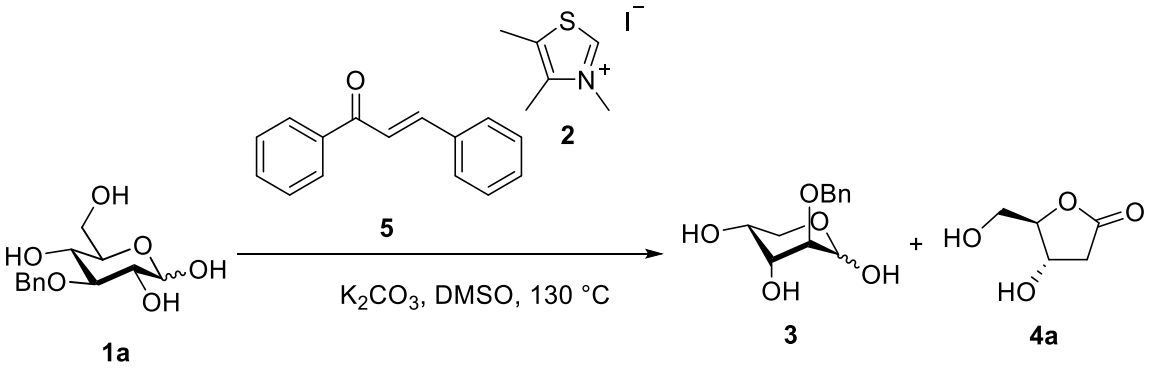
Exactly 125 µl from each sample were transferred to an Eppendorf vial, a solution of erythritol in H_2O (60 µl, 100 mM, 0.012 mmol) was added (as silylation standard) and volatiles were removed in the vacuum concentrator (0.7 mbar, 26.5 °C, ~ 2 h). For each of the samples obtained in this manner the following procedure was applied:

The residue was transferred in MeCN:H_2O=1:4 (2 × 0.5 mL), onto a LiChrolut® RP18 (100 mg). The vial was once rinsed with MeCN (0.2 ml) onto the column and eluted with MeCN:H_2O 1:4 (0.5 ml). The obtained eluent was concentrated *in vacuo*. Following a modified literature procedure[2], a solution of *O*-methylhydroxylamin in pyridine (anh., 200 µl, 40 mg/ml) was added to the residue and heated to 70 °C for 1 h. Next, a solution of DMAP in pyridine (anh., 200 µl, 1.5 mg/ml) was added as well as BSTFA (+1% TMSCl, 200 µl). The mixture was stirred at 70 °C for another 2 h. Upon cooling to rt, EtOAc (400 µl) was added, resulting in a maximum concentration of starting material derived components of 10 mM and 6 mM of erythritol. 600 µl were taken out and diluted with a solution of methylbenzoate in EtOAc (600 µl, 2 mM). The sample was filtered *via* syringe filter and subjected to GC analysis. Thereby, a peak area each for methyl benzoate, the silylated erythritol, lactone and the two sugar species (as the sum of the two respective peaks) was obtained. The measured concentration of the analysts in the sample was obtained by comparing the ratio of the areas of the three analysts to the area of the methyl benzoate with the calibration curve. Finally, the values were corrected for the actual concentration in the t0-sample to consider minor weighing errors.

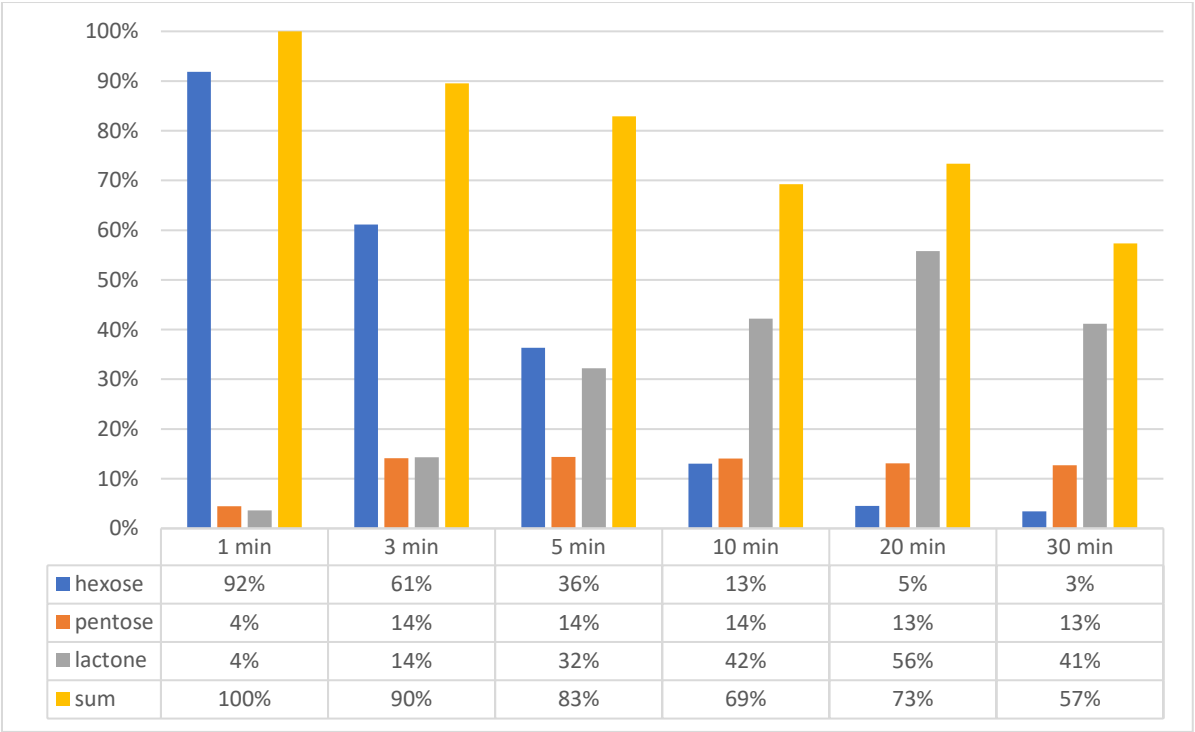
GC-Chromatogramm after 20 min:



3.3 Time resolved dehomologation of 3-*O*-Bn-glucose 1a with catalyst 2

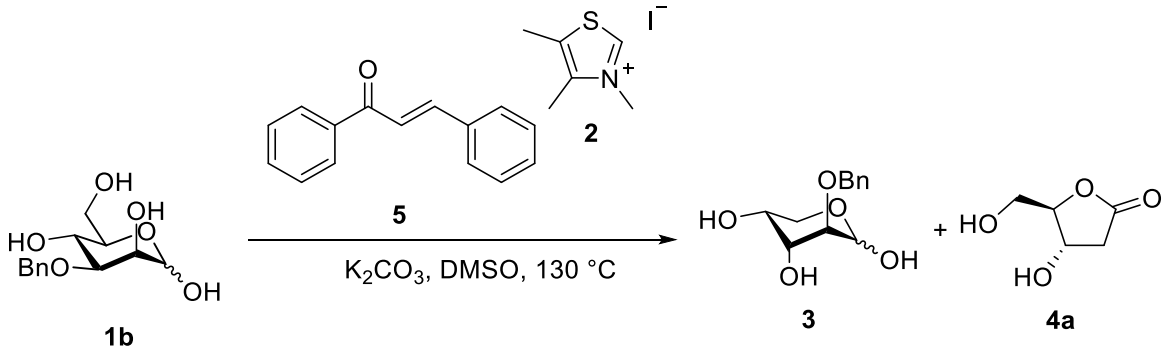


Reaction conditions: **1a**/**2**/K_2CO_3/**5** = 1.00 : 0.25 : 0.20 : 2.00 (molar ratio)

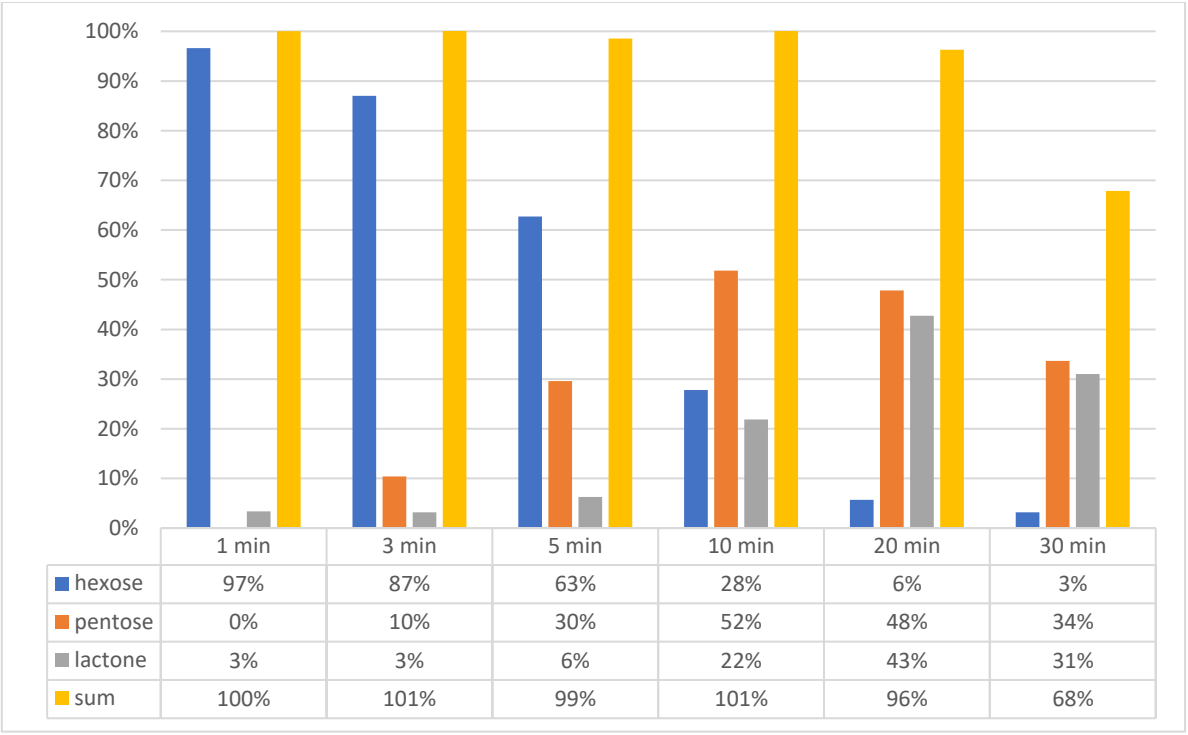


	1 min	3 min	5 min	10 min	20 min	30 min
hexose	92%	61%	36%	13%	5%	3%
pentose	4%	14%	14%	14%	13%	13%
lactone	4%	14%	32%	42%	56%	41%
sum	100%	90%	83%	69%	73%	57%

3.4 Time resolved dehomologation of 3-*O*-Bn-mannose 1b with catalyst 2

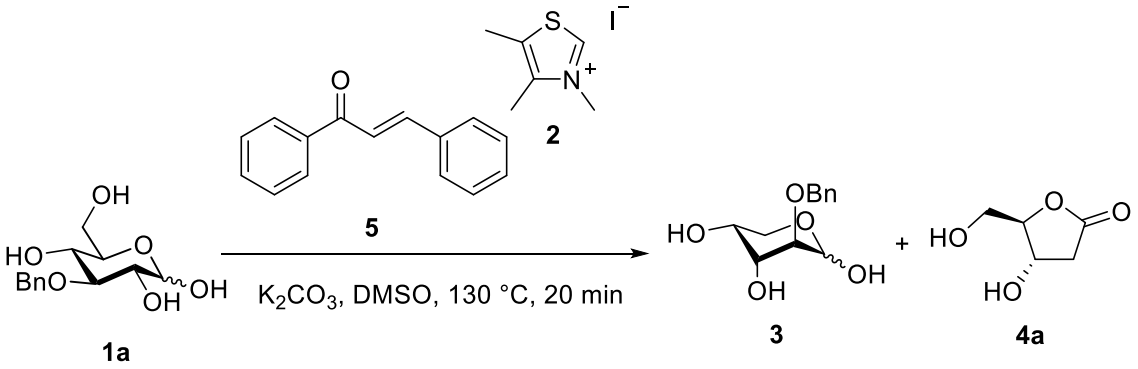


Reaction conditions: **1b**/**2**/K_2CO_3/**5** = 1.00 : 0.25 : 0.20 : 2.00 (molar ratio)



	1 min	3 min	5 min	10 min	20 min	30 min
hexose	97%	87%	63%	28%	6%	3%
pentose	0%	10%	30%	52%	48%	34%
lactone	3%	3%	6%	22%	43%	31%
sum	100%	101%	99%	101%	96%	68%

3.5 Screening of reaction conditions with 3-*O*-Bn-Glucose 1a as starting material

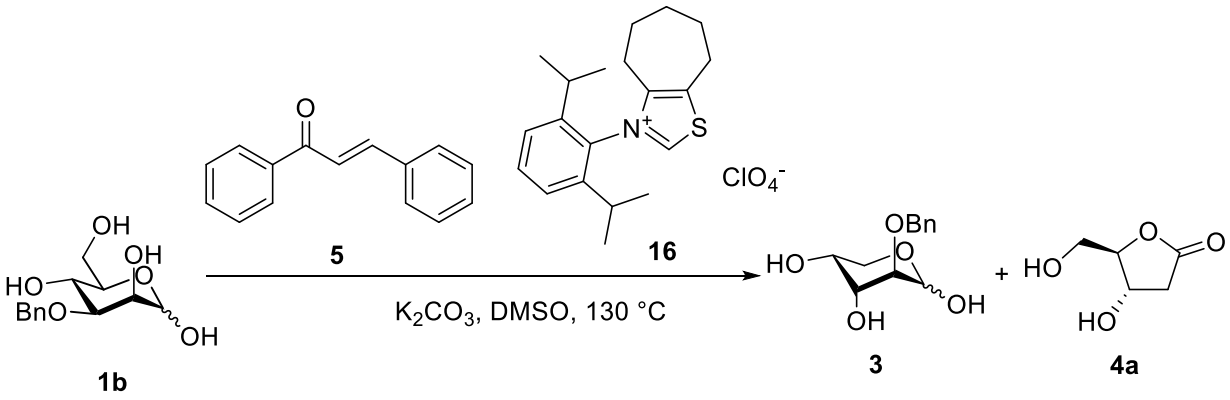


Reaction conditions: **1a**/**2**/base/**5** = 1.00 : 0.25 : 0.20 : 2.00 (molar ratio), 20 min. GC yields based on calibrated GC. [a]reactions performed under µW irradiation. Powdered K_2CO_3 was used in all cases except entry 5 & 6.

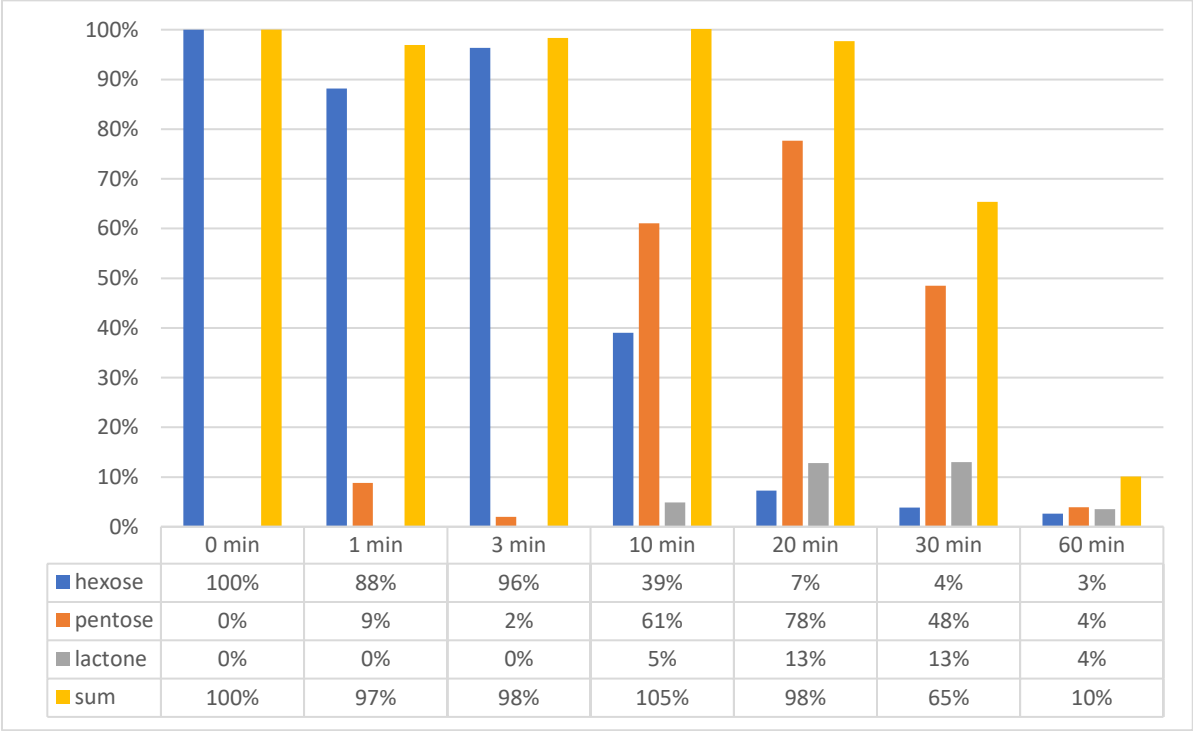
Table 1 Screening of reaction conditions

Entry	Deviation from standard conditions	**1a** [%]	**3** [%]	**4a** [%]	Sum [%]
1	none	5	13	56	73
2	Solvent: MeCN[a]	0	4	40	45
3	Solvent: DMF[a]	0	12	56	69
4	Solvent: EtOH[a]	0	4	13	17
5	Base: Li_2CO_3	46	34	16	96
6	Base: DBU	96	0	1	97
7	T = 90 °C / 320 min	30	5	39	74
8	T = 110 °C / 80 min	2	5	33	39
9	T = 150 °C / 10 min	8	4	22	33

3.6 Time resolved dehomologation of 3-*O*-Bn-mannose 1b with catalyst 16

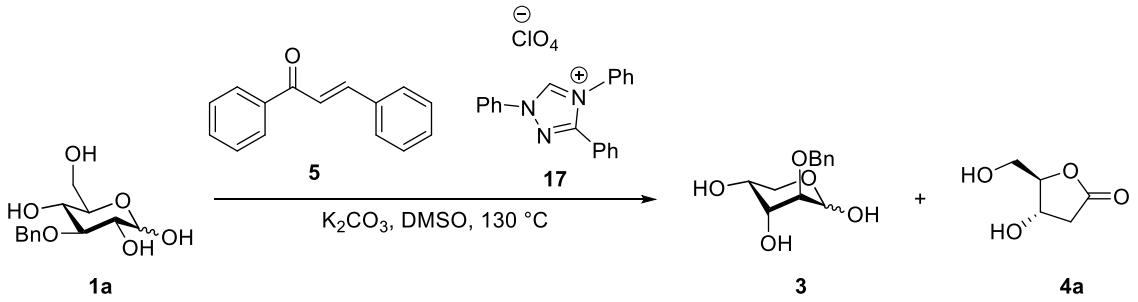


Reaction conditions: **1b**/**16**/K_2CO_3/**5** = 1.00 : 0.25 : 0.20 : 2.00 (molar ratio)

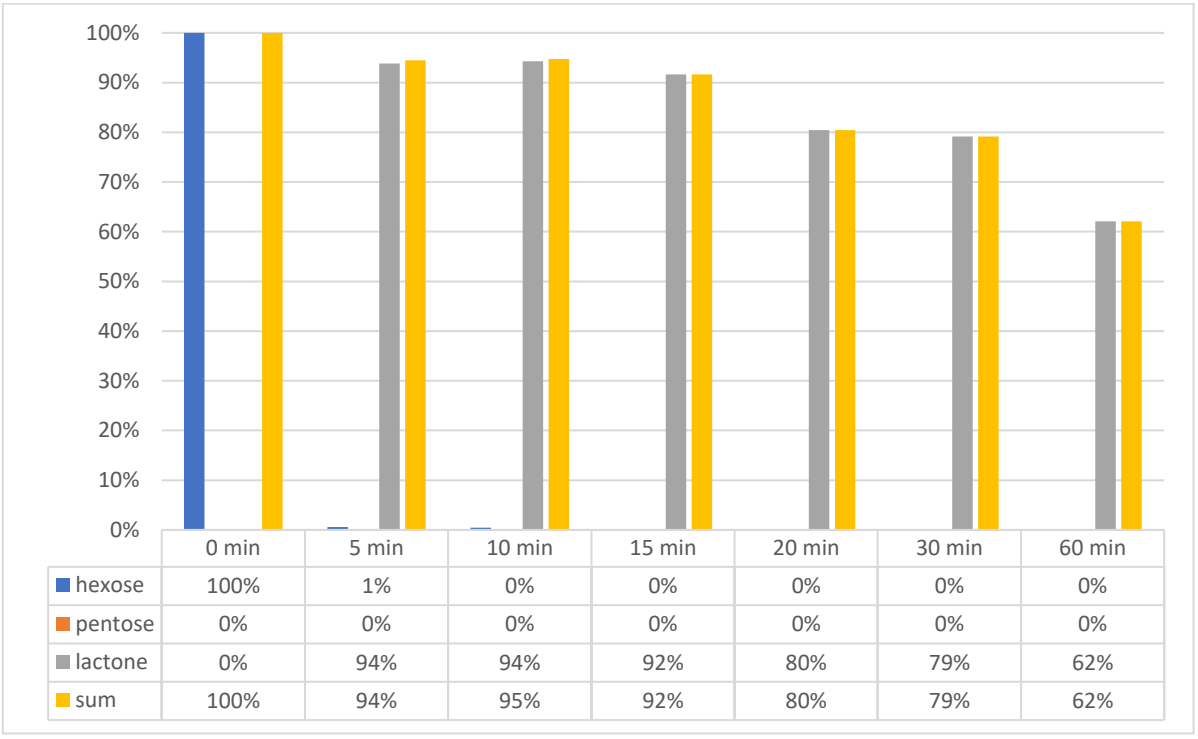


	0 min	1 min	3 min	10 min	20 min	30 min	60 min
hexose	100%	88%	96%	39%	7%	4%	3%
pentose	0%	9%	2%	61%	78%	48%	4%
lactone	0%	0%	0%	5%	13%	13%	4%
sum	100%	97%	98%	105%	98%	65%	10%

3.7 Time resolved dehomologation of 3-*O*-Bn-glucose 1a with catalyst 17

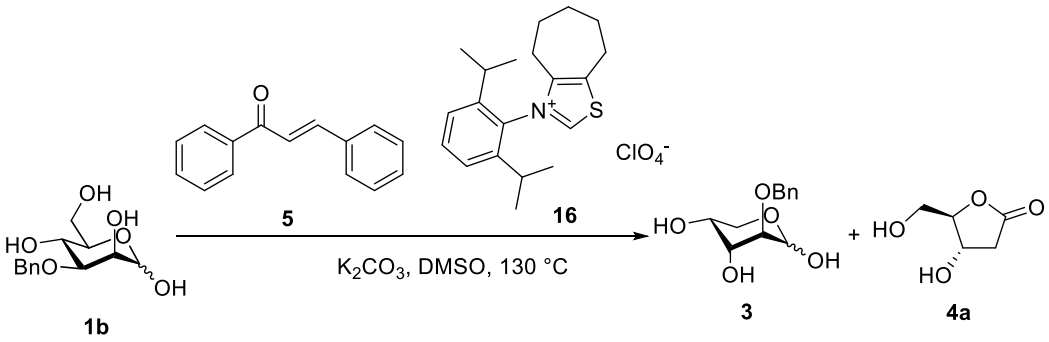


Reaction conditions: **1a**/**17**/K_2CO_3(powdered)/**5** = 1.00 : 0.25 : 0.20 : 2.00 (molar ratio)

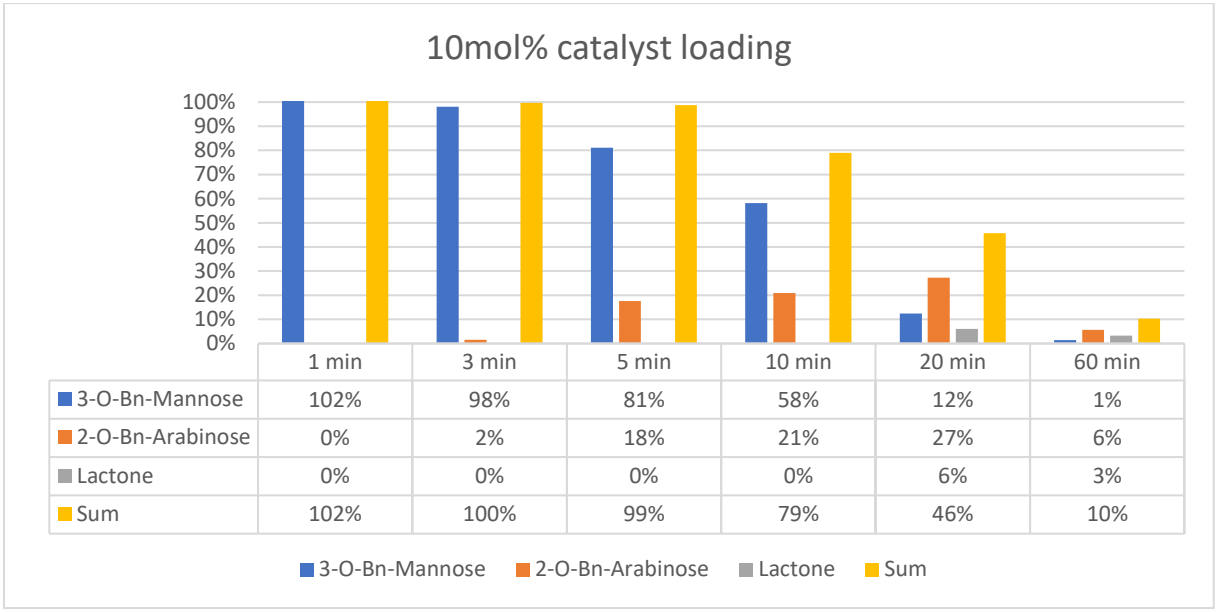


	0 min	5 min	10 min	15 min	20 min	30 min	60 min
hexose	100%	1%	0%	0%	0%	0%	0%
pentose	0%	0%	0%	0%	0%	0%	0%
lactone	0%	94%	94%	92%	80%	79%	62%
sum	100%	94%	95%	92%	80%	79%	62%

3.8 Time resolved dehomologation of 3-*O*-Bn-mannose 1b with catalyst 16 – different catalyst loading

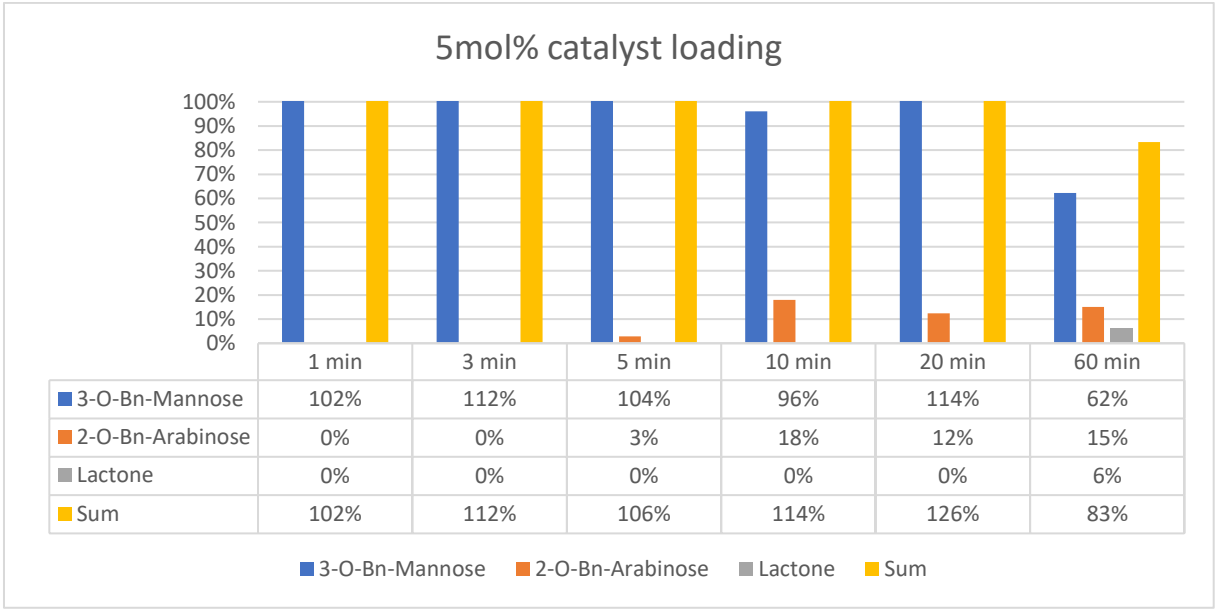


Reaction conditions: **1b**/**16**/K_2CO_3/**5** = 1.00 : 0.10 : 0.08 : 2.00 (molar ratio)



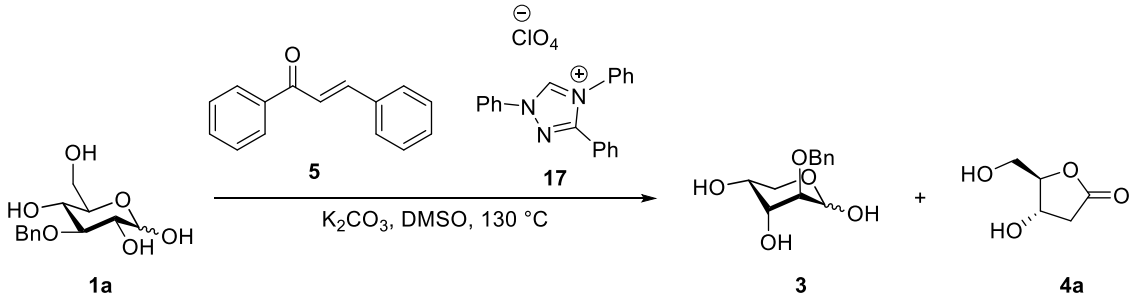
	1 min	3 min	5 min	10 min	20 min	60 min
3-O-Bn-Mannose	102%	98%	81%	58%	12%	1%
2-O-Bn-Arabinose	0%	2%	18%	21%	27%	6%
Lactone	0%	0%	0%	0%	6%	3%
Sum	102%	100%	99%	79%	46%	10%

Reaction conditions: **1b**/**16**/K_2CO_3/**5** = 1.00 : 0.05 : 0.04 : 2.00 (molar ratio)

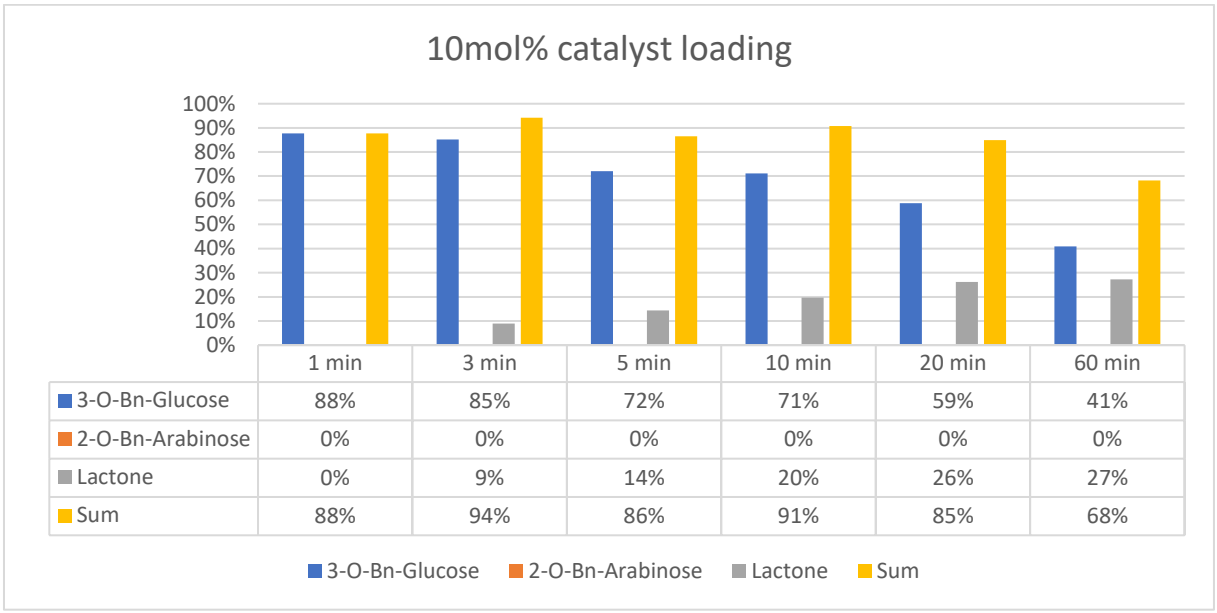


	1 min	3 min	5 min	10 min	20 min	60 min
3-O-Bn-Mannose	102%	112%	104%	96%	114%	62%
2-O-Bn-Arabinose	0%	0%	3%	18%	12%	15%
Lactone	0%	0%	0%	0%	0%	6%
Sum	102%	112%	106%	114%	126%	83%

3.9 Time resolved dehomologation of 3-*O*-Bn-glucose 1a with catalyst 17 – different catalyst loading

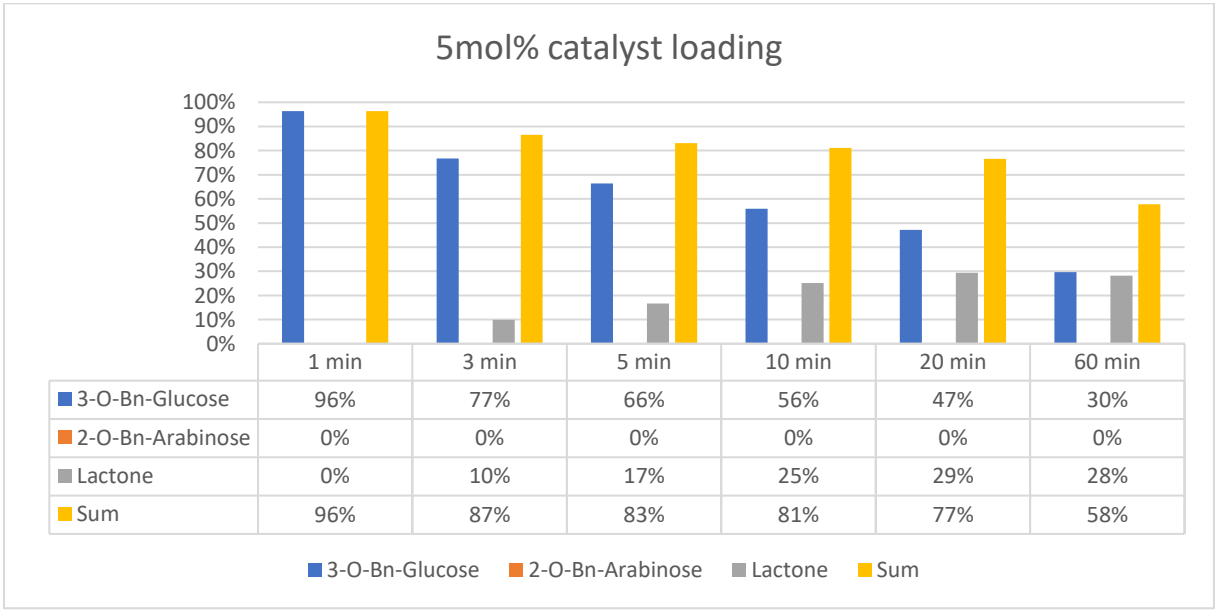


Reaction conditions: **1a**/**17**/K_2CO_3(powdered)/**5** = 1.00 : 0.10 : 0.08 : 2.00 (molar ratio)



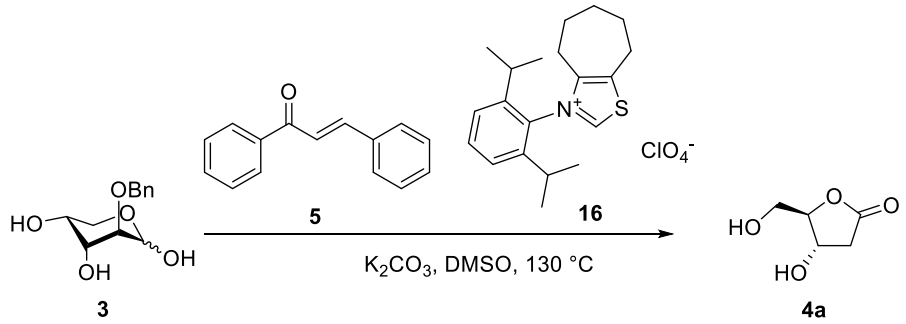
	1 min	3 min	5 min	10 min	20 min	60 min
3-O-Bn-Glucose	88%	85%	72%	71%	59%	41%
2-O-Bn-Arabinose	0%	0%	0%	0%	0%	0%
Lactone	0%	9%	14%	20%	26%	27%
Sum	88%	94%	86%	91%	85%	68%

Reaction conditions: **1a**/**17**/K_2CO_3(powdered)/**5** = 1.00 : 0.05 : 0.04 : 2.00 (molar ratio)

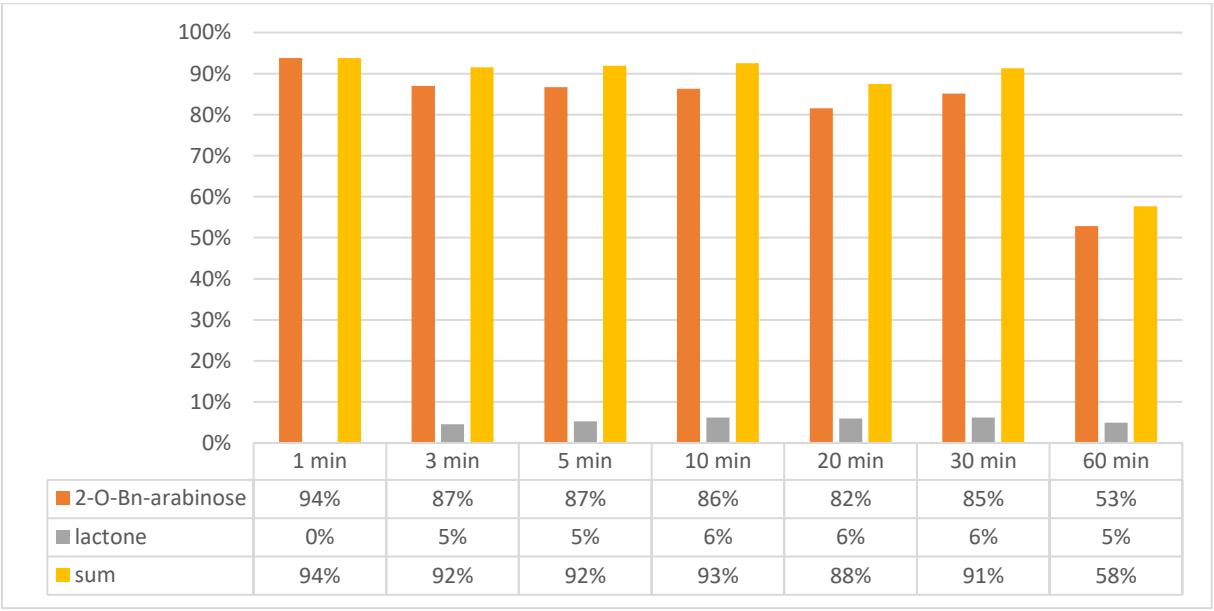


	1 min	3 min	5 min	10 min	20 min	60 min
3-O-Bn-Glucose	96%	77%	66%	56%	47%	30%
2-O-Bn-Arabinose	0%	0%	0%	0%	0%	0%
Lactone	0%	10%	17%	25%	29%	28%
Sum	96%	87%	83%	81%	77%	58%

3.10 Time resolved dehomologation of 2-O-Bn-arabinose 3 with catalyst 16



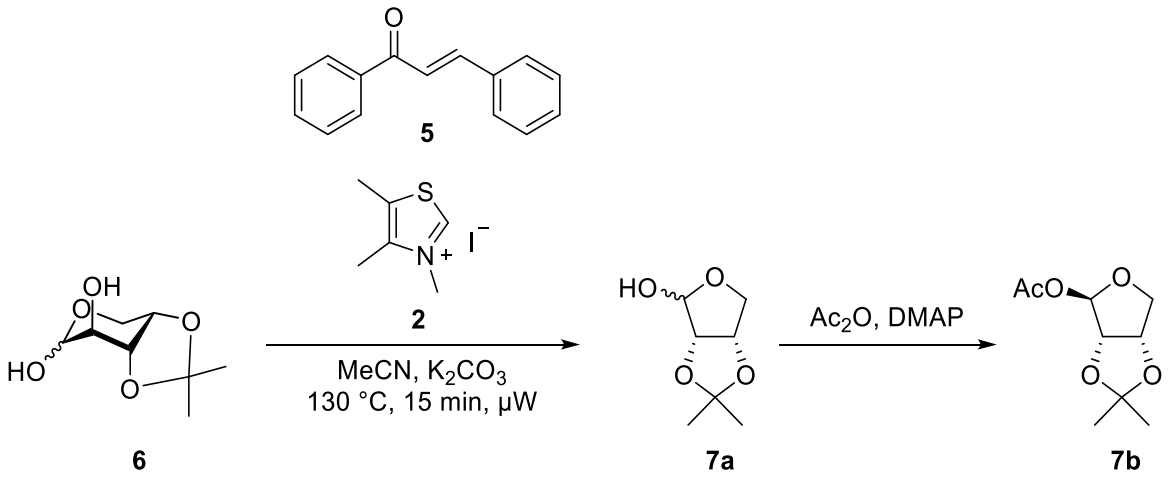
Reaction conditions: **3**/**16**/K_2CO_3/**5** = 1.00 : 0.25 : 0.20 : 2.00 (molar ratio)



	1 min	3 min	5 min	10 min	20 min	30 min	60 min
2-O-Bn-arabinose	94%	87%	87%	86%	82%	85%	53%
lactone	0%	5%	5%	6%	6%	6%	5%
sum	94%	92%	92%	93%	88%	91%	58%

4 Synthesis and characterisation *via* preparative dehomologation experiments

4.1 1-*O*-Acetyl-2,3-*O*-isopropylidene-L-erythrose 7b *via* preparative dehomologation



Total amounts of 3,4-*O*-isopropylidene L-arabinose **6** (612 mg, 3.2 mmol, 1.0 equiv.), 3,4,5-trimethylthiazolium iodide **2** (205 mg, 0.8 mmol, 0.25 equiv.), K_2CO_3 (89.0 mg, 0.64 mmol, 0.2 equiv.) and chalcone **5** (668 mg, 3.2 mmol, 1.0 equiv.) were equally split into two 20 ml microwave vials and dissolved in MeCN (20 ml each). The vial was three times purged with Ar *via* Schlenk technique. The suspension was heated under microwave irradiation for 15 min at 130 °C (very high absorption). After cooling to rt, TLC showed nearly complete reaction. The solvent was evaporated, and the residue was taken up in DCM and purification of the crude mixture was achieved by column chromatography using SiO_2 (90 g) and a gradient of EtOAc in LP from 15-50%. The product **7a** containing fractions were united, concentrated under reduced pressure for acetylation to yield ~800 mg of material.

Acetylation of lactol **7a**:

About 800 mg of erythrose acetonide **7a** were dissolved in pyridine (1.5 ml). Ac_2O (1 ml) was added portionwise under cooling with an ice bath due to exothermic reactions. Then a small portion of DMAP was added. After 3h of stirring, Ac_2O was quenched with MeOH (1 ml). EtOAc (10 ml) were added and the mixture was washed with ice cold HCl solution (1N), until the mixture had turned acidic (monitored *via* pH-paper). The organic layer was washed with $NaHCO_3$ solution (sat.) until the solution was basic. The organic layer was dried with brine and Na_2SO_4. The solvent was evaporated (90 mbar, 50 °C) yielding a highly viscous liquid. After 16 h, brown crystals (372 mg, 53%) were observed, which was confirmed to be the acetylation product of erythrose acetonide **7b** by NMR.

m.p. 63.8-64.2 °C (EtOAc).

R_f (LP:EtOAc = 7:3, anisaldehyde stain): 0.41.

Optical rotation $[\alpha]_D^{20}$ = +108 (c = 1.0, $CHCl_3$), (lit.[3] $[\alpha]_D^{20}$ = -104.5, D-form, c = 1.0, MeOH).

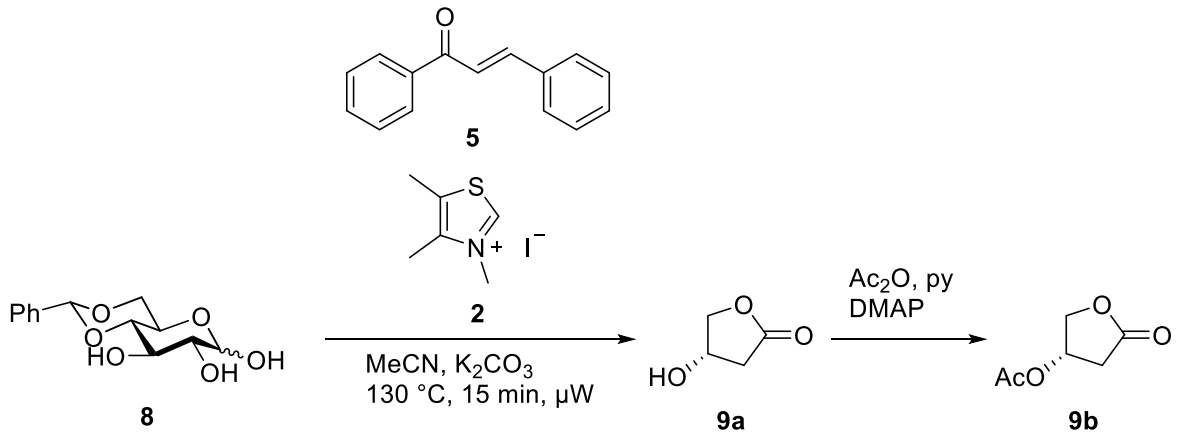
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 1H, H1), 4.86 (dd, *J* = 5.9, 3.7 Hz, 1H, H3), 4.65 (d, *J* = 5.9 Hz, 1H, H2), 4.11 (d, *J* = 10.5 Hz, 1H, H4a), 3.98 (dd, *J* = 10.5, 3.7 Hz, 1H, H4b), 2.05 (s, 3H, $COCH_3$), 1.47, 1.32 (2 × s, 2 × 1H, $C(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7 ($\underline{\mathbf{C}}OCH_3$), 113.0 ($\underline{\mathbf{C}}(CH_3)_2$), 101.6 (C1), 84.8 (C2), 79.7 (C3), 73.8 (C4), 26.4, 25.0 (2 × $C(\underline{\mathbf{C}}H_3)_2$), 21.2 ($CO\underline{\mathbf{C}}H_3$).

GC-MS t_R = 4.24 min, main fragments 188 (4.1, M-Me$^+$), 187 (49, M-Me$^+$), 143 (49), 101 (81), 85 (100), 59 (47).

Spectral data in accordance with literature.[3]

4.2 (3*S*)-β-Acetoxy-γ-butyrolactone 9b *via* preparative dehomologation



4,6-Benzylidene-D-glucose **8** (268 mg, 1.00 mmol, 1.00 equiv.), 3,4,5-trimethylthiazol-3-ium iodide **2** (63.8 mg, 0.25 mmol, 0.25 equiv.), K_2CO_3 (27.6 mg, 0.20 mmol, 0.20 equiv.) and chalcone **5** (416 mg, 2.00 mmol, 2.00 equiv.) were weighted into a microwave vial and MeCN (12.5 ml) was added. The vial was flushed with Ar *via* Schlenk technique and heated in the microwave for 15 min at 130 °C. Reaction monitoring at this point indicated complete conversion of starting material to a less polar spot, staining differently (starting material with anisaldehyde, product only with $KMnO_4$). Reaction mixture was evaporated to dryness and taken up in H_2O. The aq. layer was extracted with Et_2O (2 x 50 ml) and evaporated to dryness, yielding 150 mg of a yellow, high viscous oil containing lactone **9a**. This was taken up in pyridine (1.5 ml) and Ac_2O (0.6 ml) added. A small portion of DMAP was added and it was

stirred at rt overnight. The next day, MeOH (0.5 ml) was added to quench excessive reagent. The mixture was diluted with DCM and washed with ice cold 1N HCl, sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$ and solvent evaporated, yielding 100 mg of a yellow-orange oil, according to NMR the desired compound in 80-90% purity. Product was purified *via* flash column chromatography (5 g SiO_2, LP/EtOAc 2:1, 5 ml fractions). Fractions containing the product were pooled and solvent evaporated affording the target compound as a colourless oil (77 mg), that primarily contained the target compound **9b** (59 mg, 41%) as a mixture containing an impurity of 23% EtOAc according to ^{1}H-NMR.

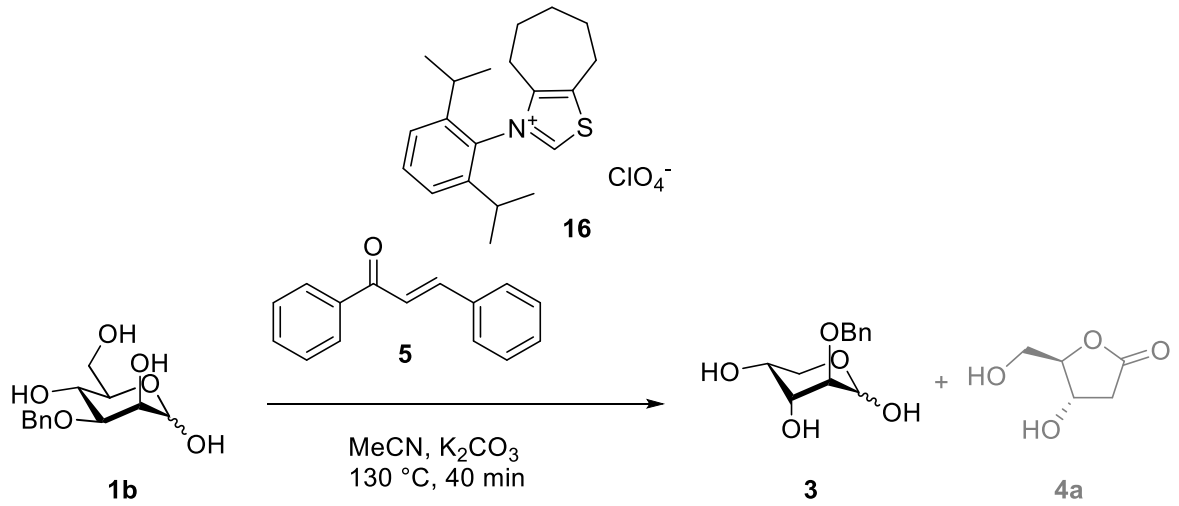
R_f (LP:EtOAc = 1:1, potassium permanganate stain): 0.51.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (ddt, *J* = 6.6, 4.8, 1.6 Hz, 1H, H3), 4.48 (dd, *J* = 11.0, 4.8 Hz, 1H, H4a), 4.34 (dt, *J* = 11.0, 1.2 Hz, 1H, H4b), 2.84 (dd, *J* = 18.4, 6.7 Hz, 1H, H2a), 2.58 (dt, *J* = 18.4, 1.3 Hz, 1H, H2b), 2.07 (s, 2H, $COCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6 (C1), 170.4 (**C**OCH_3), 73.1 (C4), 69.9 (C3), 34.6 (C2), 20.9 (CO**C**H_3).

Spectral data in accordance with literature.[4]

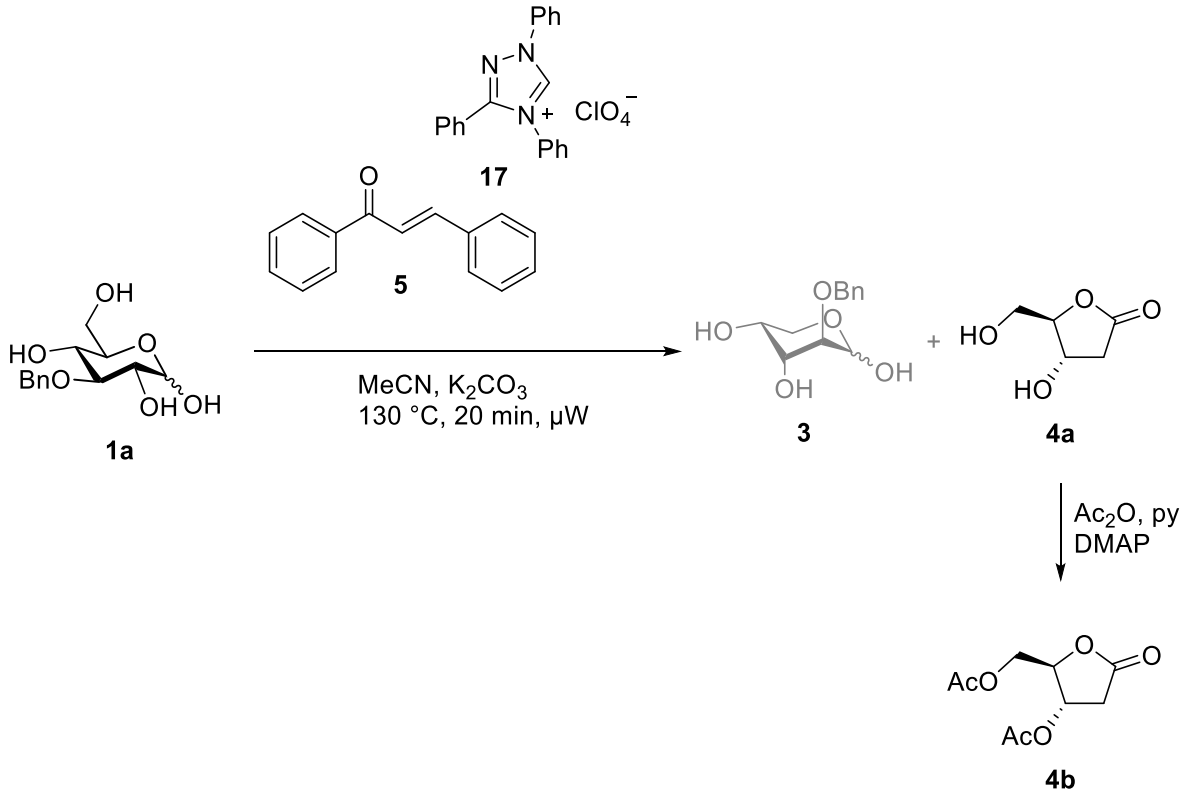
4.3 2-*O*-Benzyl-D-arabinose 3 *via* preparative dehomologation



To avoid upscaling problems 3-*O*-benzyl-D-mannose **1b** (270 mg, 1.00 mmol, 1.00 equiv.), chalcone **5** (417 mg, 2.00 mmol, 2.00 equiv.), dipp thiazolium precatalyst **16** (104 mg, 0.25 mmol, 0.25 equiv.) and K_2CO_3 (27.6 mg, 0.20 mmol, 0.20 equiv.) were partitioned in five identical batches in five 2-5 ml microwave vials. Then, MeCN (2.5 mL) was added, the vial was three times purged with Ar *via* Schlenk technique and the reaction mixture was heated in a heating block at 130 °C for 40 minutes (as after 20 min still significant amounts of starting

material were present according to TLC), when TLC indicated nearly full conversion. A small sample was drawn and derivatized as described in **3.2**, indicating the formation of 78% 2-*O*-benzyl-D-arabinose. The solvent was removed under reduced pressure and the residue was distributed between H_2O (40 ml) and Et_2O (50 ml) and the aqueous phase was washed with Et_2O (2 × 50 ml). The aqueous phase was lyophilized overnight yielding 211 mg. Purification of the crude mixture was achieved by column chromatography using SiO_2 (12 g) and a gradient of MeOH in DCM from 5-20% and afforded the target compound as a yellowish crystals (161.4 mg), that primarily contained 2-*O*-benzyl-arabionse **3** (152 mg, 63%) as a mixture containing an impurity of 6% lactone **4a** according to ^{1}H-NMR.

4.4 3,5-*O*-Diacetyl-2-deoxy-D-ribono-1,4-lactone 4b *via* preparative dehomologation



3-*O*-benzyl-D-glucose **1a** (1.35 g, 5.00 mmol, 1.00 equiv.), chalcone **5** (2.08 g, 10.0 mmol, 2.00 equiv.), triphenyl triazolium precatalyst **17** (470 mg, 1.25 mmol, 0.25 equiv.) and K_2CO_3 (powdered, 138 mg, 1.00 mmol, 0.20 equiv.) were weighted into a microwave vial. Then, MeCN (20 mL) was added, the vial was three times purged with Ar *via* Schlenk technique and the reaction mixture was heated under microwave irradiation to 130 °C for 20 min (absorbance high). Then, reaction monitoring *via* TLC (DCM/MeOH 5:1; starting material anisaldehyde stain; product $KMnO_4$ stain) indicated full conversion of the starting material to the desired product. It was evaporated to dryness, taken up in H_2O (approx. 100 ml), extracted with Et_2O

(2 × 200 ml), the aq. layer was evaporated again to obtain ca. 1.00 g of a crude mixture. This was taken up in pyridine (10 ml), Ac_2O (2.83 ml) added and after the addition of DMAP (spatula) stirred overnight at rt to allow full conversion to the peracetylated compound, as observed with TLC (DCM/MeOH 5:1; LP/EtOAc 1:1). Acetylation was worked up by quenching with MeOH (5 ml), extraction with DCM against 1N HCl (ice cold), sat. aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and evaporated to obtain ca. 1.00 g of a dark yellow – orange liquid, according to the NMR the desired product (80-90% pure).

Purification of the crude mixture was achieved by flash column chromatography using SiO_2 (45 g) and a gradient of EtOAc in DCM from 0-100% and afforded the target compound **4b** as a colourless oil (590 mg, 55%) and pure according to ^{1}H-NMR.

R_f (LP:EtOAc = 7:3, potassium permanganate stain): 0.52.

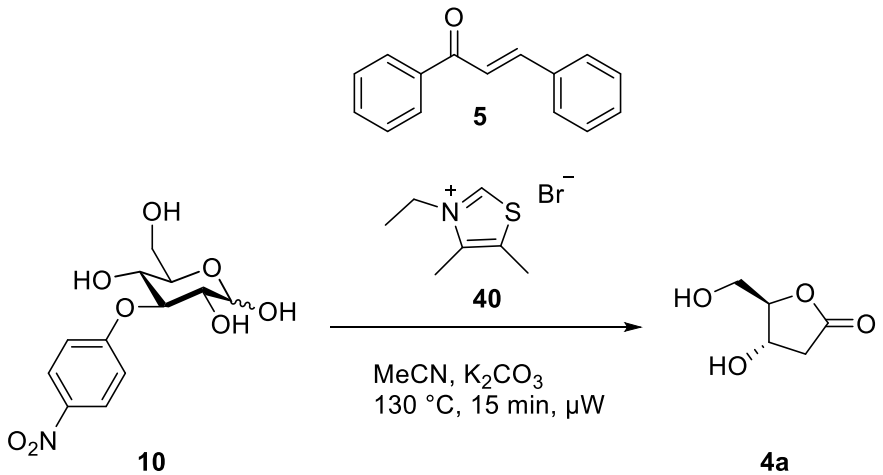
Optical rotation $[\alpha]_D^{20}$ = -5.3 (c = 1.25, EtOH), (lit.[5]: -5.3, c = 1.25, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (dt, *J* = 7.5, 1.9 Hz, 1H, H3), 4.65 (td, *J* = 3.5, 1.7 Hz, 1H, H4), 4.36 (dd, *J* = 12.3, 3.4 Hz, 1H, H5a), 4.26 (dd, *J* = 12.3, 3.6 Hz, 1H, H5b), 2.98 (dd, *J* = 18.7, 7.5 Hz, 1H, H2a), 2.59 (dd, *J* = 18.7, 2.1 Hz, 1H, H2b), 2.09, 2.07 (2 × s, 2 × 3H, 2 × $COCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9 (C1), 170.4, 170.1 (2 × $\underline{C}OCH_3$), 82.1 (C4), 71.2 (C3), 63.4 (C5), 34.9 (C2), 20.9, 20.7 (2 × $CO\underline{C}H_3$).

Spectral data in accordance with literature.[6]

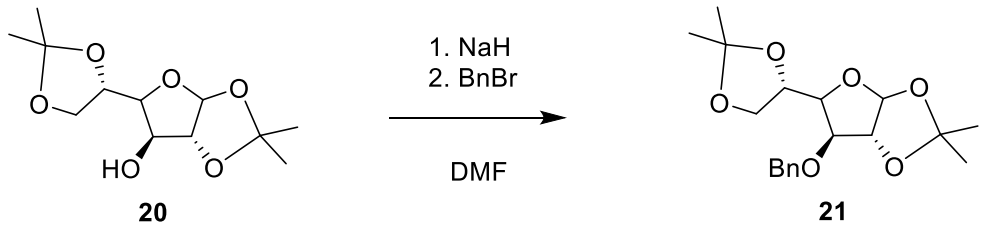
4.5 3,5-*O*-Diacetyl-2-deoxy-D-ribono-1,4-lactone 4a *via* preparative dehomologation from 3-*O*-(4-nitrophenyl)-D-glucose 10



3-O-(4-nitrophenyl)-D-glucose **10** (0.300 g, 1.00 mmol, 1.00 equiv.), 3-ethyl-4,5-dimethylthiazolium bromide **40** (44 mg, 0.20 mmol, 0.20 equiv.), K_2CO_3 (28 mg, 0.20 mmol, 0.20 equiv.) and chalcone **5** (414 mg, 2.00 mmol, 2.00 equiv.) were added to a microwave vial and heated at 130 °C for 15 min under microwave irradiation. This led to full conversion to the desired product and therefore the solvent was evaporated. Purification of the crude mixture was achieved by flash column chromatography using SiO_2 (90 g) and a gradient of MeOH in EtOAc from 0-10% and afforded the target compound **4a** as a slightly yellow oil (70 mg, 53%) containing 6% of *p*-nitrophenol as an impurity according to ^{1}H-NMR.

5 Synthesis and characterization of substrates and reference materials

5.1 3-*O*-Benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 21



20 **21**

Diacetone glucose **20** (20.42 g, 78.5 mmol, 1.0 equiv.) was dissolved in dry DMF (80 mL) and a continuous flow of argon was applied to the reaction flask. The reaction mixture was stirred and cooled in an ice bath, before NaH (9.22 g, 60 % in paraffin oil, 231 mmol, 2.9 equiv.) was added portionwise and the formation of H_2 gas was observed. After stirring at 0 °C for 20 min, benzyl bromide (11.2 mL, 94.1 mmol, 1.2 equiv.) was added, so that the reaction temperature did not rise above 20 °C. During that process, a white solid material was formed and more DMF (10 mL) was added, so that the reaction mixture could be stirred more efficiently. The reaction mixture was allowed to reach rt and TLC (LP:EtOAc 6:1) confirmed the clean formation of the target compound **21**. Foaming occurred, as MeOH (10 mL) was added carefully to quench the reaction. The mixture was distributed between aqueous NH_4Cl (10 %, 300 mL) and Et_2O (300 mL) and the aqueous phase was then extracted with Et_2O (2 × 150 mL, 1 × 100 mL). The pooled organic phases were washed with water (3 × 150 mL), brine (1 × 150 mL), dried over Na_2SO_4 and filtered. The solvent was evaporated and crude material was subsequently distributed between acetonitrile (200 mL) and n-hexane (4 × 50 mL), to remove the paraffin oil, which has been introduced with the NaH. The combined hexane phases were extracted with acetonitrile (2 × 50 mL) and the collected acetonitrile fractions were evaporated to obtain target product **21** as a viscous syrup (27.12 g, 98%), pure according to ^{1}H-NMR.

R_f (LP:EtOAc = 4:1, anisaldehyde stain): 0.31.

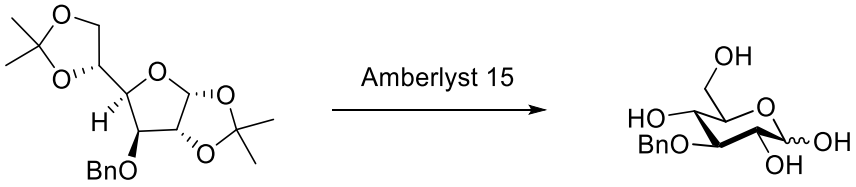
Optical rotation $[\alpha]_D^{20}$ = -28 (c = 1.0 in EtOH), (lit.[7] $[\alpha]_D^{28}$ = -28.3, c = 1.3, EtOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H, PhH), 5.90 (d, *J* = 3.7 Hz, 1H, H1), 4.69 (d, *J* = 11.8 Hz, 1H, Ph-C**H**H), 4.64 (d, *J* = 11.9 Hz, 1H, Ph-CH**H**), 4.59 (d, *J* = 3.7 Hz, 1H, H2), 4.38 (dt, *J* = 7.7, 6.0 Hz, 1H, H5), 4.16 (dd, *J* = 7.7, 3.1 Hz, 1H, H4), 4.12 (dd, *J* = 8.6, 6.2 Hz, 1H, H6a), 4.03 (d, *J* = 3.1 Hz, 1H, H3), 4.01 (dd, *J* = 8.6, 5.9 Hz, 1H, H6b), 1.50, 1.43, 1.38, 1.31 (4 × s, 4 × 3H, 4 × CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7 (PhC1), 128.5 (PhC2/6 or PhC3/5), 127.9 (PhC4), 127.7 (PhC2/6 or PhC3/5), 111.9, 109.1 (2 × **C**$(CH_3)_2$), 105.4 (C1), 82.7 (C2), 81.8 (C3), 81.4 (C4), 72.6 (C5), 72.5 (Ph-CH_2), 67.5 (C6), 27.0, 26.9, 26.4, 25.6 (4 × CH_3).

Spectral data in accordance with literature.[8]

5.2 3-*O*-Benzyl-D-glucose 1a



21 **1a**

Procedure:

3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **21** (6.13 g, 17.5 mmol, 1 equiv.) was stirred in H_2O (31 ml) and heated to 70 °C. Amberlyst 15 (hydrogen form, 12.3 g) was first washed with water (3x 80 mL) and then added to the reaction mixture. TLC (3:2 EtOAc/LP for the starting material, 6:1 DCM/MeOH for the product) showed after approx. 4.5 h complete reaction. The liquid phase was vacuum-filtered over Celite® resulting in 4 fractions of each 100 mL containing product. The remaining residue was washed with water. The united aqueous fractions were extracted once with Et_2O (250 mL) to remove lipophilic traces. The aqueous solution was then lyophilized yielding the target compound **1a** as a colourless solid (4.20 g, 89%).

m.p. 133.7-136.6 °C (H_2O), (lit.[9] 135-137 °C).

R_f (DCM:MeOH = 4:1, anisaldehyde stain): 0.46.

Optical rotation $[\alpha]_D^{20}$ = +42 (c = 1.0, H_2O, 12 h), (lit.[7] $[\alpha]_D^{29}$ = +41.3, c = 0.9, H_2O).

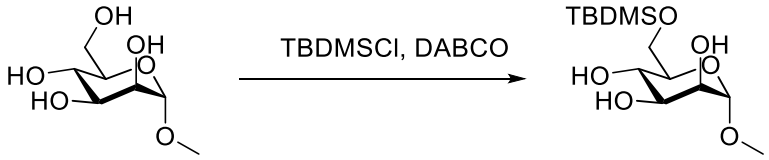
^{1}H NMR (400 MHz, DMSO-d_6) beta-anomer: δ 7.41 (d, *J* = 7.0 Hz, 2H, PhH2/H6), 7.31 (t, *J* = 7.3 Hz, 2H, PhH3/H5), 7.24 (t, *J* = 7.3 Hz, 1H, PhH4), 6.68 (d, *J* = 6.4 Hz, 1H, OH1), 5.09 – 5.04 (m, 2H, OH2, OH4), 4.81 (d, *J* = 11.7 Hz, 1H, Ph-C**H**H), 4.77 (d, *J* = 11.7 Hz, 1H, Ph-CH**H**), 4.52 (t, *J* = 5.8 Hz, 1H, OH6), 4.33 (app. t, *J* = 7.0 Hz, 1H, H1), 3.68 (ddd, *J* = 11.7, 5.5, 2.1 Hz, 1H, H6a), 3.45 (dt, *J* = 11.8, 6.0 Hz, 1H, H6b), 3.28 – 3.17 (m, 2H, H4, H3), 3.16 – 3.03 (m, 2H, H5, H2).

^{13}C NMR (101 MHz, $CDCl_3$) beta-anomer: δ 139.7 (PhC1), 127.9 (PhC3/C5), 127.4 (PhC2/C6), 127.0 (PhC4), 96.9 (C1), 85.3 (C3), 76.7 (C5), 74.8 (C2), 73.6 (Ph-**C**H_2), 69.9 (C4), 61.1 (C6).

HRMS (ESI$^+$) Exact mass calc. for $C_{13}H_{18}O_6Na$ $[M+Na]^+$: 293.0996, found: 293.0995 (- 0.11 ppm).

Spectral data in accordance with literature.[8]

5.3 Methyl 6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside 23



22 **23**

Procedure adapted from literature protocol. [10]

Methyl-α-D-mannopyranoside **22** (10.0 g, 51.5 mmol, 1.00 equiv.) was dispersed in MeCN (anh., 180 ml) and DABCO (6.64 g, 59.6 mmol, 1.15 equiv.) was added at rt. The mixture was cooled to 5 °C *via* ice bath. TBDMSCl (8.54 g, 56.6 mmol, 1.10 equiv.) was added dropwise and the mixture was stirred for 18 h and when TLC (DCM:MeOH 6:1) indicated still incomplete conversion further DABCO (1.44 g, 12.9 mmol, 0.25 equiv.) was added at rt. Again, the mixture was cooled to 5 ºC *via* ice bath, and then TBDMSCl (1.55 g, 10.3 mmol, 0.20 equiv.) was added dropwise. The mixture was stirred for 1 h when TLC (DCM:MeOH 6:1) showed complete conversion. MeOH (12.5 ml, 6 equiv.) was added and the solution was stirred for 30 min and concentrated *in vacuo*. The residue was taken up in H_2O (200 ml) and extracted with DCM (600 ml) until no further product was detected in the extract using TLC. Then the organic layer was dried with Na_2SO_4, concentrated *in vacuo* and crystallized overnight. The crude yield was 15.65 g (98.5%) of a colourless solid. An aliquot of 7.30 g of crude product was purified *via* column chromatography using SiO_2 (180 g) and a gradient of MeOH in DCM from 0-20% and afforded the target compound **23** as a colourless solid (4.86 g, 82%) and pure according to ^{1}H-NMR.

m.p. 102.8 – 103.1 ºC (DCM), (lit.[11] 98-100 °C).

R_f (DCM:MeOH = 7:1, anisaldehyde stain): 0.60.

Optical rotation $[\alpha]_D^{20}$ = +49.0 (c 1.0, $CHCl_3$), (lit.[12] $[\alpha]_D^{23}$= +57, c 0.3, $CHCl_3$).

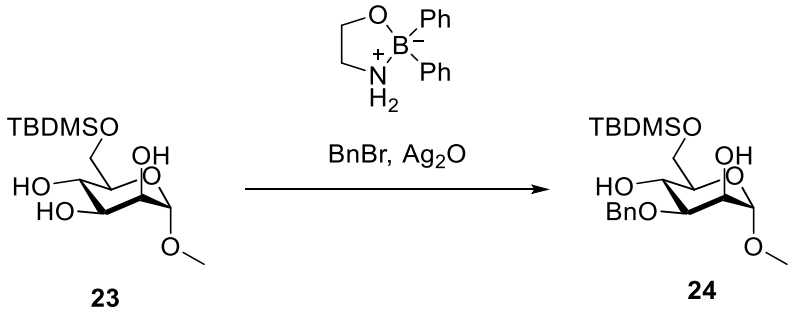
^{1}H NMR (600 MHz, MeOD) δ 4.61 (d, *J* = 1.6 Hz, 1H, H1), 3.98 (dd, *J* = 11.1, 2.0 Hz, 1H, H6a), 3.81 – 3.74 (m, 2H, H2, H6b), 3.64 (dd, *J* = 9.1, 3.5 Hz, 1H, H3), 3.53 (t, *J* = 9.5 Hz, 1H, H4), 3.51 – 3.45 (m, 1H, H5), 3.36 (s, 3H, OMe), 0.92 (s, 9H, $C(CH_3)_3$), 0.10 (d, *J* = 2.1 Hz, 6H, $Si(CH_3)_2$).

^{13}C NMR (101 MHz, MeOD) δ 102.6 (C1), 75.0 (C5), 72.8 (C3), 72.0 (C2), 68.8 (C4), 64.6 (C6), 55.0 (OMe), 26.4 ($C(\underline{C}H_3)_3$), 19.2 ($Si(CH_3)_2$), -5.1 ($\underline{C}(CH_3)_3$).

HRMS (ESI^{+}) Exact mass calc. for $C_{13}H_{28}O_6SiNa$ $[M+Na]^+$: 331.1547, found: 331.1566 (5.51 ppm).

Spectral data in accordance with literature.[11]

5.4 Methyl 6-*O*-(*tert*-butyldimethylsilyl)-3-*O*-benzyl-α-D-mannopyranoside 24



Methyl 6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside **23** (10.0 g, 32.4 mmol, 1.00 equiv.), Ag_2O (8.26 g, 35.7 mmol, 1.10 equiv.) and 2-aminoethyl diphenylborinate (730 mg, 3.2 mmol, 0.1 equiv.) were dispersed in MeCN (325 ml, anh.). The flask was purged with Ar, benzylbromide (8.32 g, 48.6 mmol, 1.5 equiv.) was added slowly and the solution was heated to 40 ºC. The mixture was stirred vigorously for 28 h when TLC (LP:EtOAc = 7:3, anisaldehyde stain) indicated complete conversion. The suspension was filtered through Celite®, rinsed with DCM (400 ml) until no further product was detected in the extract using TLC (LP:EtOAc = 7:3, anisaldehyde stain). The yellow solution was dried over Na_2SO_4 and concentrated *in vacuo*. Purification of the crude mixture was achieved by column chromatography using SiO_2 (300 g) and a gradient of EtOAc in LP from 5-25% and afforded the target compound **24** as a colourless solid (9.12 g, 71%) and pure according to ^{1}H-NMR.

m.p. 84.3 – 85.5 ºC (EtOAc).

R_f (LP:EtOAc = 1:1, anisaldehyde stain): 0.57.

Optical rotation $[\alpha]_D^{20}$ = +30.4 (c 1.0, $CHCl_3$), (lit.[13]: +34.6, c = 0.1, $CHCl_3$).

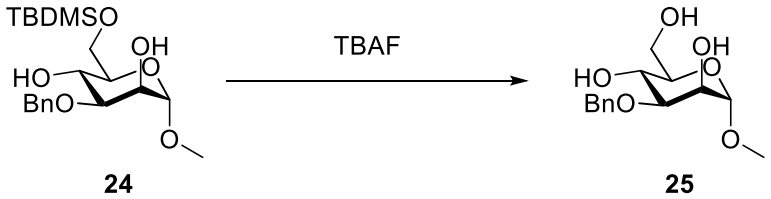
^{1}H NMR (600 MHz, MeOD) δ 7.43 (d, *J* = 7.0 Hz, 2H, PhH2/H6), 7.32 (t, *J* = 7.5 Hz, 2H, PhH3/H5), 7.26 (t, *J* = 7.4 Hz, 1H, PhH4), 4.71 (d, *J* = 11.8 Hz, 1H, PhC**H**H), 4.64 (d, *J* = 11.3 Hz, 1H, PhCH**H**), 4.63 (s, 1H, H1), 3.98 (dd, *J* = 11.1, 2.0 Hz, 1H, H6a), 3.94 (dd, *J* = 3.2, 1.8 Hz, 1H, H2), 3.78 (dd, *J* = 11.1, 6.7 Hz, 1H, H6b), 3.70 (t, *J* = 9.7 Hz, 1H, H4), 3.56 (dd, *J* = 9.3, 3.3 Hz, 1H, H3), 3.51 (ddd, *J* = 9.5, 6.7, 1.9 Hz, 1H, H5), 3.35 (s, 3H, OMe), 0.92 (s, 9H, $C(CH_3)_3$), 0.10 (d, *J* = 2.1 Hz, 6H, $Si(CH_3)_2$).

^{13}C NMR (101 MHz, MeOD) δ 139.98 (PhC1), 129.26 (PhC3/C5), 129.06 (PhC2/C6), 128.59 (PhC4), 102.57 (C1), 80.54 (C3), 75.03 (C5), 72.65 (Ph**C**H_2), 68.88 (C2), 67.85 (C4), 64.60 (C6), 55.05 (OMe), 26.41 ($C(CH_3)_3$), 19.23 ($Si(CH_3)_2$), -5.12 ($C(CH_3)_3$).

HRMS (ESI$^+$) Exact mass calc. for $C_{20}H_{34}O_6SiNa$ $[M+Na]^+$: 421.2017, found: 421.2035 (4.34 ppm).

Spectral data in accordance with literature.[14]

5.5 Methyl 3-*O*-benzyl-α-D-mannopyranoside 25



24 **25**

Methyl 3-*O*-Bn-6-TBDMS-mannopyranoside **24** (5.00 g, 12.5 mmol, 1.00 equiv.) and tetrabutylammonium fluoride solution (14.3 ml, 14.3 mmol, 1.14 equiv., 1 M in THF) in THF (71 ml, anh.) were left stirring at rt under Ar. After 1 h TLC (DCM:MeOH = 6:1, anisaldehyde stain) indicated complete conversion and the reaction mixture was concentrated *in vacuo*. The crude yield was 3.34 g of a colourless oil. Purification of the crude mixture was achieved by column chromatography using solid loading (10 g SiO_2) on SiO_2 (90 g) and a gradient of MeOH in DCM from 5-25% and afforded the target compound **25** as a colourless oil (2.49 g, 70%) and pure according to ^{1}H-NMR.

R_f (DCM:MeOH = 7:1, anisaldehyde stain): 0.58.

Optical rotation $[\alpha]_D^{20}$ = +35.9 (c = 1.0, EtOH), (lit.[15] +35.2, c = 1, EtOH).

^{1}H NMR (600 MHz, MeOD) δ 7.43 (d, *J* = 7.0 Hz, 2H, PhH2/H6), 7.33 (t, *J* = 7.5 Hz, 2H, PhH3/H5), 7.26 (t, *J* = 7.3 Hz, 1H, PhH4), 4.72 (d, *J* = 11.8 Hz, 1H, PhC**H**H), 4.66 – 4.63 (m, 1H, H1, PhCH**H**), 3.95 (dd, *J* = 3.2, 1.9 Hz, 1H, H2), 3.84 (dd, *J* = 11.8, 2.3 Hz, 1H, 6a), 3.76

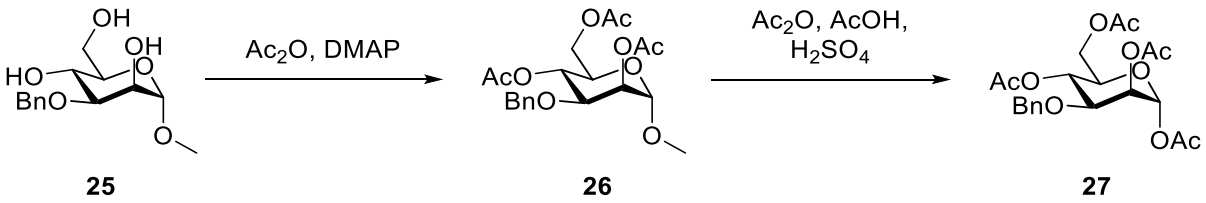
(t, *J* = 9.7 Hz, 1H, H4), 3.71 (dd, *J* = 11.8, 6.0 Hz, 1H, 6b), 3.57 (dd, *J* = 9.4, 3.3 Hz, 1H, H3), 3.50 (ddd, *J* = 9.8, 6.0, 2.2 Hz, 1H, H5), 3.36 (s, 3H, OMe).

^{13}C NMR (101 MHz, MeOD) δ 138.60 (PhC1), 127.87 (PhC3/C5), 127.67 (PhC2/C6), 127.20 (PhC4), 101.26 (C1), 78.97 (C3), 73.16 (C5), 71.27 ($PhCH_2$), 67.60 (C2), 66.28 (C4), 61.54 (C6), 53.80 (OMe).

HRMS (ESI$^+$) Exact mass calc. for $C_{14}H_{20}O_6Na$ $[M+Na]^+$: 307.1152, found: 307.1168 (5.26 ppm).

Spectral data in accordance with literature.[16]

5.6 1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranose 27



25 **26** **27**

Procedure adapted from literature protocol.[15]

The acetylation step was performed separately from the acetolysis step, as the exothermic reaction of the first step leads to partial debenzylation under acetolysis conditions. Methyl 3-*O*-benzyl-mannopyranoside **25** (2.00 g, 7.04 mmol, 1.00 equiv.) was dissolved in pyridine (20.4 ml). Acetic anhydride (6.0 ml, 63 mmol, 1.1 equiv.) and DMAP (43.0 mg 0.352 mmol, 0.05 equiv.) were added carefully and the mixture was stirred at rt for 2 h, when TLC (LP:EA = 7:3) indicated full conversion. MeOH (2.6 ml) was added and the mixture was diluted with EtOAc (200 ml). The solution was transferred into a separating funnel and was washed with 1N HCl (400 ml) until TLC showed no more pyridine in the organic phase. After extracting the 1N HCl phase again with EtOAc, the combined organic phases washed with aq. $NaHCO_3$ (100 ml) and brine (50 ml). The organic layer was concentrated in vacuo yielding the intermediate **26** as a colourless oil (2.75 g) as crude, which was used without further purification.

An aliquot of intermediate **26** (2.65 g, 6.46 mmol, 1.00 equiv.) in Ac_2O:AcOH:H_2SO_4 (23.2 ml, 50:20:0.5 v/v) was stirred at rt for 5 h when TLC (LP:EtOAc = 4:3) indicated full conversion. The solution was dropwise added to ice water (150 ml) for better heat distribution until the excess of Ac_2O was hydrolyzed. Then NaOAc (790 mg) was added to quench the H_2SO_4. The product was extracted with EtOAc (3 × 100 ml) using TLC as indicator for completion. The

combined organic phases were washed with aq. $NaHCO_3$ and dried first with brine and, afterwards, with Na_2SO_4 and concentrated *in vacuo*. Purification of the crude mixture was achieved by column chromatography using SiO_2 (90 g) and a gradient of EtOAc in LP from 15-40% and afforded the target compound **27** as a colourless oil (2.57 g, 91%), pure according to ^{1}H-NMR.

R_f (LP:EtOAc = 1:1, anisaldehyde stain): 0.45.

Optical rotation $[\alpha]_D^{20}$ = +4.7 (c = 0.9, $CHCl_3$), (lit.[15] +0.20, c ~1, $CHCl_3$).

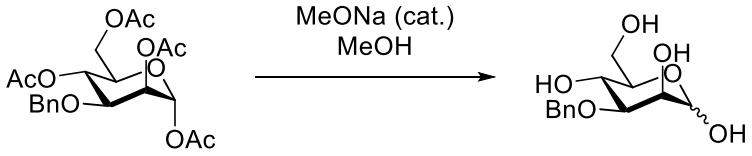
^{1}H NMR (400 MHz, MeOD) δ 7.37 – 7.26 (m, 5H, Ph), 6.03 (d, *J* = 1.8 Hz, 1H, H1), 5.37 (dd, *J* = 3.2, 2.1 Hz, 1H, H2), 5.23 (appt. t, *J* = 10.1 Hz, 1H, H4), 4.65 (d, *J* = 11.8 Hz, 1H, PhC**H**H), 4.48 (d, *J* = 11.8 Hz, 1H, PhCH**H**), 4.22 (dd, *J* = 12.5, 4.9 Hz, 1H, H6a), 4.03 (dd, *J* = 12.1, 2.3 Hz, 1H, H6b), 4.03 – 3.97 (m, 1H, H5), 3.97 (dd, *J* = 9.8, 3.4 Hz, 1H, H3), 2.14, 2.13, 2.04, 2.01 (4 × s, 4 × 3H, 4 × $COCH_3$).

^{13}C NMR (101 MHz, MeOD) δ 172.4, 171.5, 171.4, 169.9 (4 × s, 4 × **C**OCH_3), 139.1 (s, PhC1), 129.4 (d, PhC3/C5), 129.1 (d, PhC2/C6), 128.9 (d, PhC4), 92.3 (d, C1), 75.9 (d, C3), 72.8 (t, $PhCH_2$), 72.0 (d, C5), 68.8 (d, C2), 68.2 (d, C4), 63.4 (t, C6), 20.8, 20.7, 20.64, 20.61 (4 × q, 4 × CO**C**H_3).

HRMS (ESI$^+$) calc. for $C_{21}H_{26}O_{10}Na$ $[M+Na]^+$: 461.1418, found: 461.1444 (– 5.51 ppm).

Spectral data in accordance with literature.[17]

5.7 3-*O*-Benzyl-α-D-mannose 1b



27 **1b**

The 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-mannopyranoside **27** (600 mg, 1.37 mmol, 1.00 equiv.) was dissolved in MeOH (5 ml, anh.). NaOMe (0.23 ml, 0.05 equiv., 30% solution in MeOH) was added and the pH was checked to be ~10. The solution was stirred at room temperature for 3 h, when full conversion was observed by TLC (DCM/MeOH = 10:1, anisaldehyde stain). Acidic ion exchange resin (Amberlyst 15, 0.6 g) was added and the mixture was stirred for a few minutes. After neutralization (checked using pH paper) the resin was filtered off, washed with methanol, the filtrate was dried using Na_2SO_4 and concentrated *in vacuo*. Purification of the crude mixture was achieved by column chromatography using SiO_2 (12 g) and a gradient

of MeOH in DCM from 5-25% and afforded the target compound **1b** as a colourless oil (188 mg, 51%) and pure according to ^{1}H-NMR.

R$_f$ ($CHCl_3$:MeOH:H_2O = 7:3:0.5, anisaldehyde stain): 0.45.

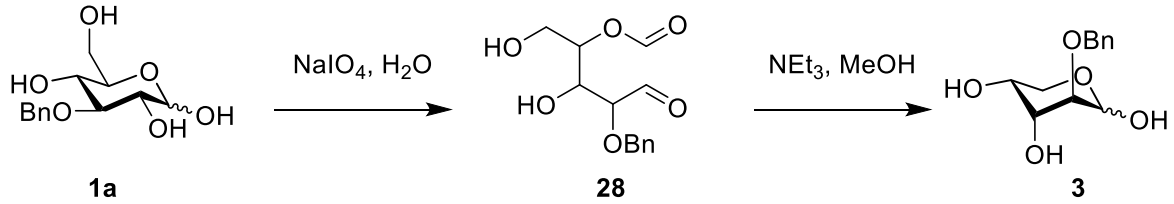
Optical rotation $[\alpha]_D^{20}$ = -0.80 (c = 1.0, MeOH, 12 h), (lit.[18] -16, c = 1.0, $CHCl_3$; lit.[15] +3.0, c = 1, $CHCl_3$).

^{1}H NMR (400 MHz, MeOD) α- and β-isomer were obtained in a ratio of ~ 7:3. δ 7.45 (d, *J* = 6.8 Hz, 2H, PhH2/H6), 7.33 (t, *J* = 7.3 Hz, 2H, PhH3/H5), 7.27 (d, *J* = 7.1 Hz, 1H, PhH4), 5.08 (d, *J* = 1.8 Hz, 0.7H, α H1), 4.74 (d, *J* = 11.6 Hz, 1H, PhC**H**H), 4.70 (d, *J* = 0.9 Hz, 0.3H, β H1), 4.66 (d, *J* = 11.7 Hz, 1H, PhCH**H**), 3.99 (d, *J* = 2.3 Hz, 0.3H, β H2), 3.96 (dd, *J* = 3.0, 2.0 Hz, 0.7H, α H2), 3.86 (dd, *J* = 11.8, 2.4 Hz, 0.3H, β H6a), 3.83 – 3.73 (m, 3.4H, α H4, β H4, α H5, α H6a, α H6b, H6b β), 3.69 (dd, *J* = 8.9, 3.0 Hz, 0.7H, α H3), 3.38 (dd, *J* = 9.4, 3.1 Hz, 0.3H, β H3), 3.24 (ddd, *J* = 9.6, 5.8, 2.4 Hz, 1H, β H5).

^{13}C NMR (101 MHz, MeOD) α-anomer: δ 140.1 (PhC1), 129.3 (PhC3/C5), 129.1 (PhC2/6), 128.6 (PhC4), 95.8 (C1), 80.3 (C3), 74.1 (C5), 72.7 ($PhCH_2$), 69.9 (C2), 67.8 (C4), 63.0 (C6). β-anomer: δ 140.1 (PhC1), 129.3 (PhC3/C5), 129.1 (PhC2/C6), 128.6 (PhC4), 95.6 (C1), 82.9 (C3), 78.1 (C4 or C5), 72.4 (Ph-CH_2), 70.0 (C2), 67.4 (C4 or C5), 63.0 (C6).

HRMS (ESI+) calc. for $C_{13}H_{18}O_6Na$ [M+Na]+: 293.0996, found: 293.1009 (– 4.43 ppm).

5.8 2-*O*-Benzyl-D-arabinose 3[19]



1a **28** **3**

3-*O*-Benzyl-α-D-glucose **1a** (5.00 g, 18.5 mmol, 1.00 equiv.) was dissolved in water (15 mL). sodium periodate (4.16 g, 19.4 mmol, 1.05 equiv.) was dissolved in water (15 mL), under heating in a water bath, then rapidly cooled in an ice bath and added to the glucose solution. The mixture was cooled in an ice bath instantly for about 1 min and then stirred at rt for 15 min. A white solid precipitated, and the reaction mixture turned solid. The formed precipitate was then collected *via* vacuum filtration and washed with cold water, yielding 4 g of intermediate **28**. MeOH (50 mL) was added to the filtrate and it was placed in the refrigerator for 3h, where further precipitation occurred, which was again collected *via* vacuum filtration, yielding another

2.5 g of **28**. Both parts of **28** were combined, dissolved in MeOH (28 mL), mixed with NEt_3 (9 mL) and stirred overnight. After saponification, a precipitate formed, which was filtered off and washed with MeOH. The filtrate was concentrated under reduced pressure. Purification of the crude mixture was achieved first by column chromatography using solid loading (Celite®, 10 g) on SiO_2 (90 g) and a gradient of MeOH in DCM from 6-21%, collecting the product fractions. After solvent removal these were refluxed in EtOAc (4 ml). After cooling down the precipitate was collected by vacuum filtration and washed with EtOAc, yielding the target compound **3** as a slightly beige solid (2.71 g, 61%).

m.p. 111.3-112.1 °C (EtOAc), (lit.[19] 111-113 °C).

R_f (DCM:MeOH = 9:1, anisaldehyde stain): 0.29.

Optical rotation $[\alpha]_D^{20}$ = -71.8 (c = 1.0, H_2O, 12 h), (lit.[19] -73, c = 2.1, H_2O).

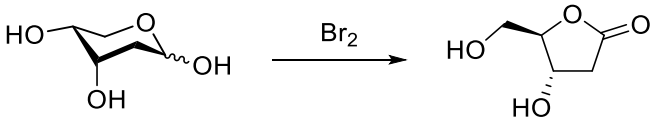
^{1}H NMR (400 MHz, MeOD) the isomers were obtained in a ratio of furanosides : α-pyranoside : β-pyranoside ~ 37:30:33. δ 9.02 – 8.77 (m, 5H, PhH), 6.82, 6.81 (d, *J* = 2.2 Hz, 0.37H, αf H1, βf H1), 6.71 (d, *J* = 3.3 Hz, 0.3H, αp H1), 6.45 – 6.17 (m, 2H, $PhCH_2$), 6.11 (d, *J* = 6.8 Hz, 0.33H, βp H1), 5.73 (dd, *J* = 7.0, 6.3 Hz, 0.1H, CHOH), 5.61 – 5.47, 5.45 – 5.35, 5.33 – 5.28, 5.27 – 5.14, 5.14 – 5.08, 5.06 – 5.00 (6 × m, 5.14H, CH(OH)).

^{13}C NMR (101 MHz, MeOD) δ 140.3, 140.0, 139.4 (PhC1), 129.3, 129.3, 129.2, 129.2, 129.1, 129.1, 128.9, 128.8, 128.7, 128.7, 128.5 (PhC2-6), 101.9 (αf C1), 98.5 (βp C1), 92.8 (αp C1), 91.9, 85.7, 84.4, 83.9, 81.7, 78.3, 76.7, 75.4, 75.1, 73.8, 73.7, 73.2, 72.8, 70.5, 69.8, 69.8, 66.5, 64.6, 63.7, 62.9 (C2-C5, Ph**C**H_2).

HRMS (ESI$^+$) Exact mass calc. for $C_{12}H_{16}O_5Na$ $[M+Na]^+$: 263.0890, found: 263.0899 (3.27 ppm).

Hydrogenation (H_2, Pd/C, MeOH) led to clean conversion to D-arabinose.

5.9 2-Deoxy-D-ribono-1,4-lactone 4a[20]



29 **4a**

2-Deoxy-D-ribose **29** (2.00 g, 14.9 mmol, 1.00 equiv.) was dissolved in H_2O (12 ml) in a round bottom flask. To this solution, Br_2 (4.0 ml, 77.6 mmol, 5.20 equiv.) was added, which led to the

formation of a biphasic system. The flask was sealed and stirring was continued at rt for 24 h, when TLC ($CHCl_3$:MeOH:H_2O = 7:3:0.5, starting material staining with anisaldehyde, product with $KMnO_4$ solution) showed complete conversion to the desired product. Ag_2CO_3 was added until the supernatant decolourized, which led to the formation of gas and a yellow-white precipitate. The reaction mixture was filtered through a bed of Celite® and the solvent was lyophilized. Purification of the crude mixture was achieved by column chromatography using SiO_2 (30 g) and a gradient of MeOH in EtOAc from 0-10% and afforded the target compound **4a** as a colourless oil (1.50 g, 76%) and pure according to ^{1}H-NMR.

R_f (DCM:MeOH = 6:1, $KMnO_4$ stain): 0.48.

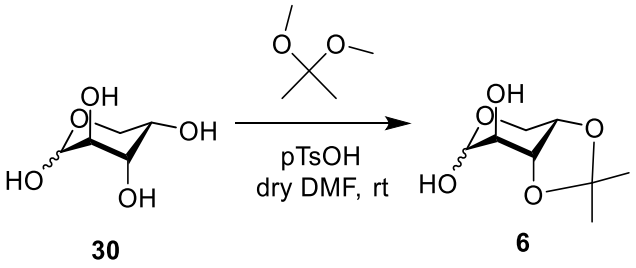
Optical rotation $[\alpha]_D^{20}$ = +4.7 (c = 1.0, MeOH), (lit.[20] +3.05, c = 1.14, MeOH).

^{1}H NMR (400 MHz, MeOD) δ 4.43 (dt, *J* = 6.7, 2.2 Hz, 1H, H3), 4.37 (q, *J* = 3.2 Hz, 1H, H4), 3.76 (dd, *J* = 12.4, 3.2 Hz, 1H, H5a), 3.69 (dd, *J* = 12.4, 3.6 Hz, 1H, H5b), 2.91 (dd, *J* = 18.0, 6.7 Hz, 1H, H2a), 2.37 (dd, *J* = 18.0, 2.4 Hz, 1H, H2b).

^{13}C NMR (101 MHz, MeOD) δ 177.2 (C1), 88.8 (C4), 68.3 (C3), 61.1 (C5), 37.8 (C2).

Spectral data in accordance with literature.[21]

5.10 3,4-*O*-Isopropylidene L-arabinose 6[22]



30 **6**

A suspension of L-arabinose **30** (5.00 g, 33.8 mmol, 1.00 equiv.) in DMF (anh., 20 mL) was prepared. Dimethoxypropane (10.5 g, 101 mmol, 3.00 equiv.) and pTsOH·H_2O (96 mg, 0.5 mmol, 0.02 equiv.) were added while stirring at rt. After 160 minutes the starting material was fully converted to a less polar spot (TLC (LP/EtOAc = 1:2 and $CHCl_3$/MeOH/H_2O = 7:3:0.5, anisaldehyde stain). triethylamine (0.17 g, 1.70 mmol, 0.05 equiv.) was added and the mixture was stirred overnight. The next day, the clear solution was co-evaporated with toluene (5 × 40 mL). The residue was dried under high vacuum. Purification of the crude mixture was achieved by column chromatography using SiO_2 (90 g) and a gradient of EtOAc in LP from

20-100% and afforded the target compound **6** as a colourless solid (4.67 g, 73%) and pure according to ^{1}H-NMR.

m.p. 124.4-124.5 °C (EtOAc), (lit.[23] 110 °C).

R_f (LP:EtOAc = 1:3, anisaldehyde stain): 0.22.

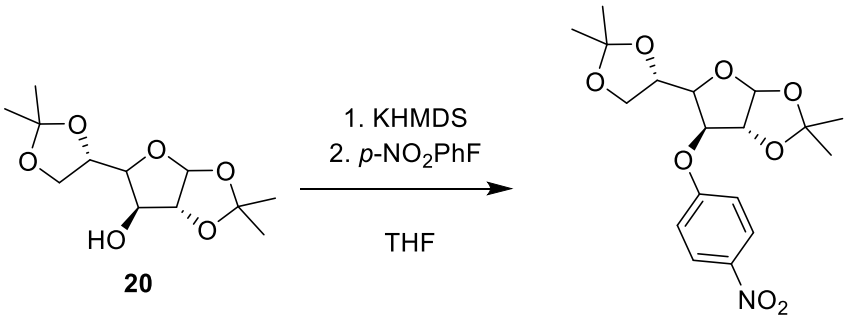
Optical rotation $[\alpha]_D^{20}$ = +118 (c = 1.0, H_2O, 12 h), (lit.[23] +128.8, c = 1.0, H_2O).

^{1}H NMR (400 MHz, MeOD) The anomeric ratio is according to ^{1}H-NMR α:β = 0.17 :0.83. δ 5.01 (d, *J* = 3.3 Hz, 1H, β H1), 4.37 (d, *J* = 7.9 Hz, 1H, α H1), 4.27 – 4.20 (m, 1H, β H4), 4.21 – 4.16 (m, 2H, β H3 + α H4), 4.17 – 4.14 (m, 1H, α+β H5a), 4.00 (t, *J* = 6.5 Hz, 1H, α H3), 3.85 – 3.76 (m, 2H, α+β H5b), 3.62 (dd, *J* = 7.0, 3.3 Hz, 1H, β H2), 3.41 (t, *J* = 7.6 Hz, 1H, α H2), 1.48 (s, 3H, CH_3), 1.34 (s, 3H, CH_3).

^{13}C NMR (101 MHz, MeOD) δ 110.7 (α **C**$(CH_3)_2$,), 109.9 (β **C**$(CH_3)_2$), 97.7 (α C1), 93.7 (β C1), 80.5 (α C3), 77.4 (β C3), 75.6 (α C2), 75.0 (α C4), 74.6 (β C4), 71.7 (β C2), 64.0 (α C5), 59.9 (β C5), 28.4 (α C(**C**$H_3)_2$), 26.4 (β C(**C**$H_3)_2$).

Spectral data is in accordance with literature.[24]

5.11 3-*O*-(4-Nitrophenyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 31



20 **31**

p-Fluoronitrobenzene was distilled by Kugelrohr distillation at 100 °C and 0.35 mbar for about 30 minutes to give a clear liquid from a brown liquid.

A vial with diacetone glucose **20** (1000 mg, 3.84 mmol, 1.10 equiv.) was evacuated and purged with Ar three times. Then, anhydrous THF (17.5 mL) and p-NO_2PhF (492 mg, 3.49 mmol, 1.00 equiv.) were added via syringe. The reaction mixture was cooled in an ice bath and KHMDS (anh., 0.7 M solution in toluene, 7.68 mL, 3.84 mmol, 1.10 equiv.) was added dropwise to the cooled reaction mixture. After 2.5 h, a first TLC analysis (LP/EtOAc 4:1) showed the formation of a new, less polar spot with still both starting material and *p*-NO_2PhF left. The reaction was stirred overnight with no further reaction having occurred according to

TLC. Aq. $NaHCO_3$ (sat., 5 mL) was added. After 15 minutes brine (30 mL) was added and the reaction mixture was extracted with EtOAc (2 × 70 mL, 1 × 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated to give the desired product as crude material as yellow liquid. Purification of the crude mixture was achieved by column chromatography using SiO_2 (90 g) and a gradient of EtOAc in LP from 9-20% and afforded the target compound **31** as colourless crystals (1418 mg, 97%) and pure according to ^{1}H-NMR.

m.p. 134-136 °C ($CHCl_3$), (lit.[25] 136-137 °C).

R_f (LP:EtOAc = 4:1, anisaldehyde stain): 0.22.

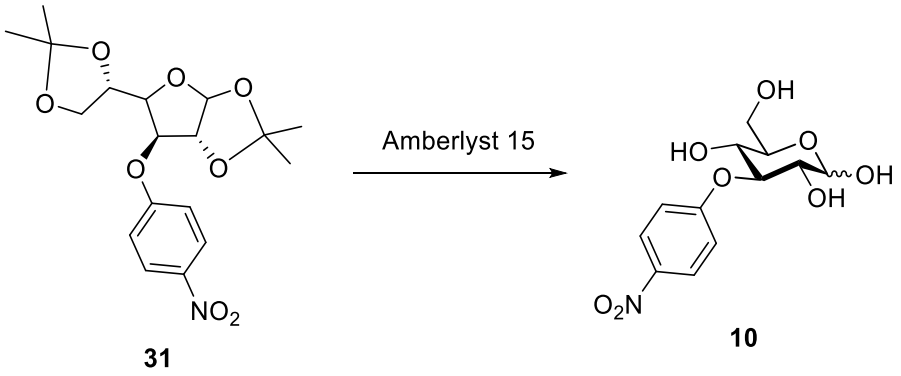
Optical rotation $[\alpha]_D^{20}$ = -35.6 (c = 1.0, $CHCl_3$), (lit.[26] $[\alpha]_D^{21}$ = -45, c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.20 (m, 2H, PhH3/H5), 7.11 – 7.05 (m, 2H, PhH2/H6), 5.95 (d, *J* = 3.8 Hz, 1H, H1), 4.82 (d, *J* = 3.0 Hz, 1H, H3), 4.57 (d, *J* = 3.9 Hz, 1H, H2), 4.41 (ddd, *J* = 8.3, 6.0, 5.1 Hz, 1H, H5), 4.29 (dd, *J* = 8.3, 3.0 Hz, 1H, H4), 4.15 (dd, *J* = 8.7, 6.0 Hz, 1H, H6a), 4.09 (dd, *J* = 8.7, 5.0 Hz, 1H, H6b), 1.56, 1.43, 1.32, 1.29 (4×s, 4×3H, 2×C(CH_3)$_2$) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (PhC1), 142.4 (PhC4), 126.1 (PhC3/C5), 115.6 (PhC2/C6), 112.6 (**C**(CH_3)$_2$(O1/O2)), 109.6 (**C**(CH_3)$_2$(O5/O6)), 105.4 (C1), 82.4 (C2), 80.8 (C3), 80.5 (C4), 72.0 (C5), 67.4 (C6), 27.1, 26.8, 26.4, 25.3 (2×C(**C**H_3)$_2$) ppm.

Spectral data in accordance with literature.[26]

5.12 3-*O*-(4-Nitrophenyl)-D-glucose 10



31 **10**

Amberlyst 15 (hydrogen form, 3.57 g) was first washed with water (3x 50 mL) and then added to the reaction mixture. 3-*O*-(4-Nitrophenyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **31** (1.39 g, 3.64 mmol, 1.00 equiv.) was stirred in H_2O (14 ml) and heated to 70 °C. TLC

(4:1 DCM/MeOH) showed after approx. 2.5 h complete reaction. The reaction mixture was filtered over Celite in a glassinter funnel and washed several times with water. The pooled aqueous fractions (~70 mL) were washed with Et_2O (2 x 10 mL) whereby most of the *p*-NO_2PhF from the reaction before was removed. Then, it was evaporated *in vacuo* to give the product **10** as yellow powder (556 mg, 51%) due to small leftover impurities of *p*-NO_2PhF. According to NMR analysis the obtained product **10** was pure.

m.p. 172-175 °C (H_2O). **R_f** (DCM:MeOH = 4:1, anisaldehyde stain): 0.50.

Optical rotation $[\alpha]_D^{20}$ = +51.2 (c = 1.0, H_2O, 12 h).

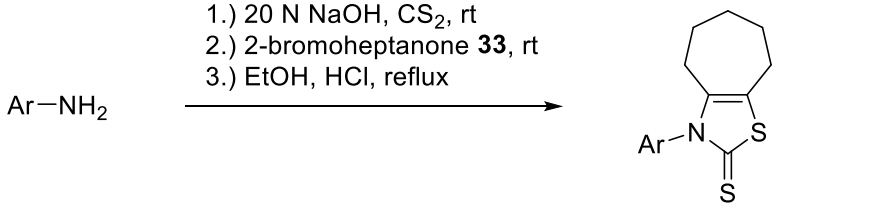
^{1}H NMR (400 MHz, D_2O) α- and β-isomer were obtained in a ratio of ~ 4:6. (400 MHz, D_2O) δ 8.24 (d, *J* = 9.1 Hz, 2H, α,β PhH3/H5), 7.27 (d, *J* = 9.1 Hz, 2H, α,β PhH2/H6), 5.33 (d, *J* = 3.7 Hz, 0.4H, α H1), 4.82 (d, *J* = 8.1 Hz, 0.6H, β H1), 4.81 – 4.73 (m, 0.4H, α H3), 4.60 (t, *J* = 9.1 Hz, 0.6H, β H3), 4.03 – 3.94 (m, 0.4H, α H5), 3.93 (dd, *J* = 12.3, 2.0 Hz, 0.6H, β H6a), 3.90 – 3.70 (m, 2.8H, α H2, α H4, β H4, α H6a, α H6b, β H6b), 3.62 (ddd, *J* = 10.0, 5.6, 2.1 Hz, 0.6H, β H5), 3.57 (s, 0.6H, β H2) ppm.

^{13}C NMR (101 MHz, D_2O) δ 165.9, 165.7 (α,β PhC1), 142.1, 142.0 (α,β PhC4), 126.7 (α,β PhC3/C5), 117.03 (β PhC2/C6), 116.95 (α PhC2/C6), 96.3 (β C1), 92.8 (α C1), 84.3 (β C3), 81.9 (α C3), 76.2 (β C5), 74.1 (β C2), 71.9 (α C5), 71.5 (α C2), 69.7, 69.6 (α, β C4), 61.2 (β C6), 61.0 (α C6) ppm.

HRMS (ESI$^-$) Exact mass calc. for $C_{14}H_{18}NO_{10}$ $[M+COO]^-$: 360.0936, found: 360.0964 (- 7.78 ppm).

6 Synthesis and characterization of precatalysts

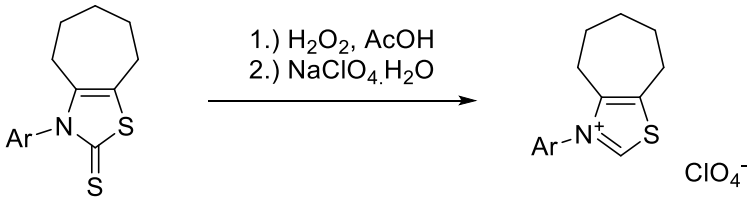
6.1 General procedure for the synthesis of cyclohepta[*d*]thiazole-2-thiones 34, 35, 36, 37 and 38 (procedure A)[27]



34 (Ar = Ph)
35 (Ar = *p*-MeOPh)
36 (Ar = *p*-NO_2Ph)
37 (Ar = Mes)
38 (Ar = dipp)

A solution of the respective aniline (1.00 equiv.) in DMSO (0.5 ml/mmol) was treated with aqueous NaOH solution (20 N, 1.00 equiv.). At 0 °C CS_2 (1.00 equiv.) was added dropwise and stirred for 1 h at room temperature. Then, 2-bromocycloheptanone **33** (1.00 equiv.) was added slowly at 0 °C, which led to a colour change of the solution and the mixture was stirred for 20 h at rt. H_2O (1 mL/mmol) was added, the mixture was stirred for 10 min at 0 °C and the supernatant solution was decanted. Depending on the substrate either a slurry or a precipitate remained, that was suspended in EtOH (1 mL/mmol). Concentrated HCl (0.05 mL/mmol, 0.58 equiv.) was added dropwise and the mixture was heated to reflux for 1 h. After cooling to room temperature, the mixture was placed in the fridge, where crystals precipitated. The solid was collected by suction filtration, washed with small amounts of *n*-pentane before being dried by first purging with air and then under reduced pressure on the rotary evaporator. Purification by column chromatography was performed when products were not already obtained pure according to ^{1}H-NMR.

6.2 General procedure for the synthesis of cyclohepta[*d*]thiazole precatalysts 12, 13, 14, 15 and 16 (procedure B)[27]

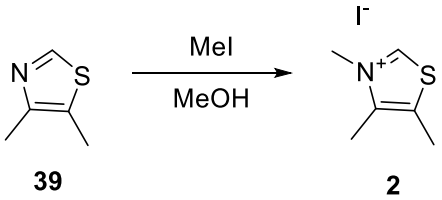


34 (Ar = Ph)
35 (Ar = *p*-MeOPh)
36 (Ar = *p*-NO_2Ph)
37 (Ar = Mes)
38 (Ar = dipp)

12 (Ar = Ph)
13 (Ar = *p*-MeOPh)
14 (Ar = *p*-NO_2Ph)
15 (Ar = Mes)
16 (Ar = dipp)

A solution or suspension of the thione (1.00 equiv.) in glacial acetic acid (4.1 ml/mmol) was cooled with a water bath, then H_2O_2 (30%, aqueous solution, 3.30 equiv.) was added dropwise and the reaction mixture was stirred for 1 h. The volatile components were removed under reduced pressure and the residue was dissolved in MeOH (0.69 ml/mmol). It was cooled to 0 °C and a mixture of sodium perchlorate monohydrate (4.10 equiv.) in MeOH/H_2O = 2/1 (3.61 ml/mmol) was added and the solution was stirred for 30 min. H_2O (50 mL) was added and the mixture was extracted three times with DCM. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification was performed by column chromatography or trituration when required.

6.3 3,4,5-Trimethylthiazol-3-ium iodide 2[28]



39 **2**

4,5-Dimethylthiazole **39** (2.15 g, 19.0 mmol, 1.00 equiv.) was dissolved in MeOH (12.1 ml), iodomethane (22.9 g, 162 mmol, 8.5 equiv.) was added and the solution was stirred in a closed flask at rt for 4 days, leading to the formation of a first slightly yellow, then brown solution with a white precipitate. EtOAc (50 mL) was added to the solution to decrease the solubility of the already precipitating product. The formed precipitate was filtered, washed with EtOAc (30 ml) and was consequently dried on a suction filter. Remaining solvent was evaporated *in vacuo* (6 mbar, 40°C) yielding the target compound **2** slightly yellow crystalline solid (4.51 g, 93%) pure according to ^{1}H-NMR.

m.p. 227.8-228.9 °C (EtOAc), (lit.[29]: 228 - 230 °C).

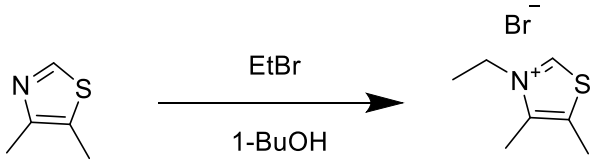
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.94 (d, *J* = 0.9 Hz, 1H, H2), 4.08 (d, *J* = 0.8 Hz, 3H, N-CH_3), 2.49 (d, *J* = 0.8 Hz, 3H, CH_3), 2.40 (d, *J* = 0.9 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 155.6 (C2), 142.1 (C4), 132.3 (C5), 40.4 (N-CH_3), 12.0,11.1 (2 × CH_3).

HRMS (ESI$^+$) Exact mass calc. for $C_6H_{10}NS$ $[M-I]^+$: 128.0543, found: 128.0534 (7.11 ppm).

Spectral data in accordance with literature.[30]

6.4 3-Ethyl-4,5-dimethylthiazol-3-ium bromide 40[28]



39 **40**

4,5-Dimethylthiazole **39** (1.0 mL, 8.80 mmol, 1.00 equiv.) was dissolved in 1-butanol (1.0 mL). Then, EtBr (925 µL, 13.2 mmol, 1.50 equiv.) was added and the vial was closed. The reaction vial was heated to 110 °C and stirred for 20 minutes. Then, the vial was allowed to cool down to room temperature. Two layers formed of which the lower one contained beige floating solid,

which was collected and washed with EtOAc (~30 mL) to give the product **40** as a white powder (443 mg, 24%), pure according to NMR analysis.

m.p.: 162-164 °C (BuOH/EtOAc)

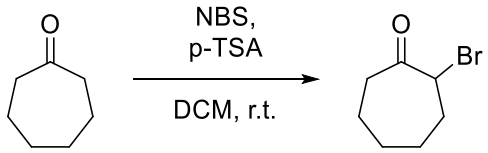
^{1}H NMR (400 MHz, MeOD) δ 9.97 (s, 1H, H2), 4.55 (q, *J* = 7.3 Hz, 2H, CH_2), 2.60 (s, 3H, CH_3*), 2.56 (s, 3H, CH_3*), 1.63 (t, *J* = 7.3 Hz, 3H, ***CH*$_3$**-CH_2) ppm.

^{13}C NMR (101 MHz, MeOD) δ 155.2 (C2), 143.5 (C4), 135.1 (C5), 50.3 (CH_2), 14.9 (**C**H_3-CH_2), 12.3 (CH_3*), 11.4 (CH_3*) ppm.

HRMS (ESI$^+$) Exact mass calc. for $C_7H_{12}NS$ $[M\text{-}Br]^+$: 142.0685, found: 142.0697 (8.11 ppm).

Spectral data in accordance with literature.[28]

6.5 2-Bromocycloheptanone 33[31]



32 **33**

Under Ar atmosphere cycloheptanone **32** (5.00 g, 44.6 mmol, 1.00 equiv.) was dissolved in DCM (anh., 11 ml) in a three-neck round bottom flask. *p*-Toluenesulfonic acid monohydrate (0.85 g, 4.5 mmol, 0.10 equiv.) was added in one portion and *N*-bromosuccinimide (7.93 g, 44.6 mmol, 1.00 equiv.) was added in several small portions while cooling with ice-water, preventing the reaction from exceeding 5 °C. After slowly warming to rt, the reaction mixture was stirred for 20 h at this temperature, when GC-MS (2.74 min: starting material with m/z = 112.09, 4.24 min: product with m/z = 190.0 and 192.0, 5.56 min: dibromo-product with m/z = 267.94, 269.90, 271.88) and TLC (LP:EtOAc = 10:1, cerium molybdate stain) indicated dominant product formation. The reaction was diluted by adding LP (25 ml) and was stirred for 5-10 min to improve precipitation of the formed succinimide.

The beige solid was filtered off and the filtrate was washed with aqueous $Na_2S_2O_3$ (satd., 2 × 75 ml), aqueous $NaHCO_3$ (satd., 2 × 75 ml) and brine (2 × 75 ml), dried over Na_2SO_4 and evaporated yielding 8.08 g (95%) of a slightly yellowish liquid. Analysis by ^{1}H-NMR confirmed predominant product formation with 12% of what is assumed to be the 2,7-dibrominated product. Distillation at 106 °C, 7 mbar afforded product **33** as a yellowish liquid **(**6.48 g, 76%) pure according to ^{1}H-NMR.

b.p. 106 °C (7 mbar).

R_f (LP/EtOAc 10:1, cerium molybdate stain): 0.61

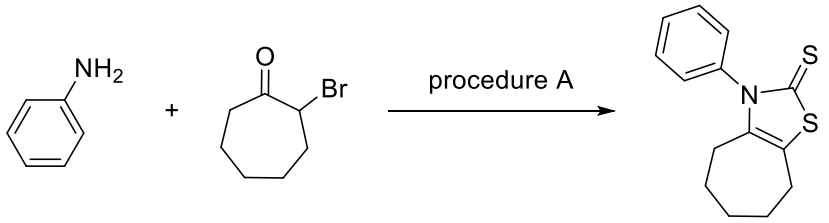
GC-MS t_R = 4.24 min, main fragments 192 (1.5, M^+), 190 (1.5, M^+), 111 (45), 93 (46), 55 (100).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (dd, *J* = 9.6, 5.1 Hz, 1H, H2), 2.92 – 2.80 (m, 1H, H7a), 2.56 – 2.42 (m, 2H, H7b), 2.42 – 2.28 (m, 1H, H3a), 2.13 – 1.86 (m, 4H, H3b, H4a, H6a), 1.81 – 1.64 (m, 2H, H5a), 1.63 – 1.47 (m, 4H, H5b, H6b), 1.44 – 1.31 (m, 2H, H4b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4 (C1), 53.9 (C2), 39.5 (C7), 34.4 (C3), 29.7 (C5), 27.0 (C4), 25.1 (C6).

Spectral data in accordance with literature.[32]

6.6 3-Phenyl-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]thiazole-2-thione 34



33 **34**

Thione **34** was prepared according to general **procedure A** from aniline (487 mg, 5.23 mmol, 1.00 equiv.). It was further purified using column chromatography (SiO_2, 12 g, EtOAc in LP = 5-50%) yielding a bright beige solid (228 mg, 17%) pure according to ^{1}H-NMR.

m.p. 197.2-197.6 °C. (EtOAc).

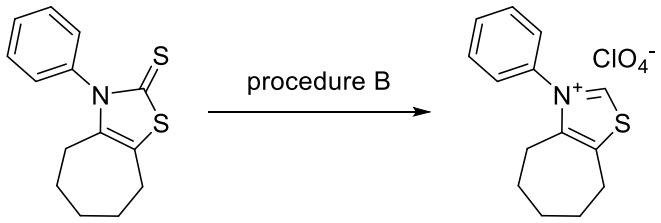
R_f (LP:EtOAc = 5:1, potassium permanganate stain): 0.27.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H, PhH3/H5), 7.52 – 7.45 (m, 1H, PhH4), 7.22 (m, 2H, PhH2/H6), 2.66 – 2.53 (m, 2H, H8), 2.42 – 2.19 (m, 2H, H4), 1.87 – 1.73 (m, 4H, H6, H7), 1.65 – 1.45 (m, 2H, H5).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3 (C2), 141.8 (C3a), 138.8 (Ph C1), 130.0 (Ph C3/C5), 129.6 (Ph C4), 128.5 (Ph C2/C6), 124.3 (C8a), 30.8 (C6 or C7), 29.8 (C4), 27.2 (C8 & C6 or C7), 27.1 (C8 & C6 or C7), 26.0 (C5).

HRMS (ESI^+) calc. for $C_{14}H_{16}NS_2$ $[M+H]^+$: 262.0719, found: 262.0725 (- 2.32 ppm).

6.7 3-Phenyl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate 12



34 **12**

Thiazol-3-ium perchlorate **12** was prepared according to general **procedure B** from thione **34** (200 mg, 0.77 mmol, 1.00 equiv.). The product was not obtained pure after precipitation and purification *via* column chromatography with SiO_2 (12 g) and a gradient of MeOH in DCM from 0-20% and a second column using 5-10% afforded the target compound **12** as a brown oil (97 mg, 39%) and pure according to ^{1}H-NMR.

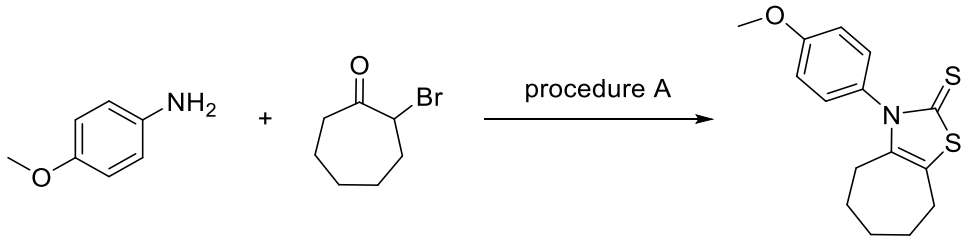
R_f (DCM:MeOH = 9:1, potassium permanganate stain): 0.28.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H, H2), 7.71 – 7.57 (m, 3H, PhH3/H5, PhH4), 7.54 – 7.48 (m, 2H, PhH2/H6), 3.13 – 3.01 (m, 2H, H8), 2.78 – 2.69 (m, 2H, H4), 2.02 – 1.83 (m, 4H, H6 & H7), 1.76 – 1.65 (m, 2H, H5).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4 (C2), 148.5 (C3a), 140.3 (C8a), 136.9 (PhC1), 131.9 (PhC4), 130.6 (PhC3/C5), 126.2 (PhC2/C6), 30.8 (C6), 28.2 (C8), 28.0 (C4), 26.4 (C7), 25.2 (C5).

HRMS (ESI$^+$) calc. for $C_{14}H_{16}NS$ $[M\text{-}ClO_4]^+$: 230.0998, found: 230.0998 (± 0.00 ppm).

6.8 3-(4-Methoxyphenyl)-3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione 35



33 **36**

3-(4-Methoxyphenyl)-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]thiazole-2-thione **35** was prepared according to general **procedure A** from 4-methoxyaniline (645 mg, 5.23 mmol, 1.00 equiv.) yielding a beige solid (619 mg, 41%) pure product according to ^{1}H-NMR directly after precipitation.

m.p. 119.2-120.1 °C (H_2O).

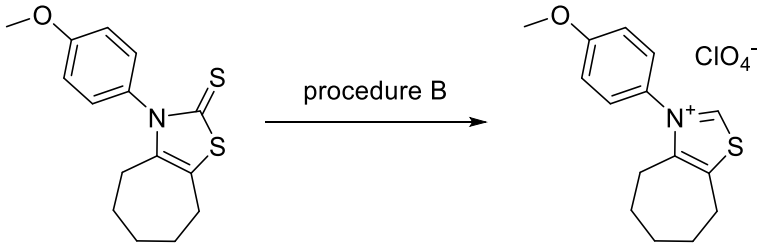
R_f (LP:EtOAc = 5:1, permanganate stain): 0.23.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12, 7.03 (2 × d, *J* = 8.5 Hz, 2 × 2H, PhH2/H6 & PhH3/H5), 3.85 (s, 3H, OCH_3), 2.64 – 2.57 (m, 2H, H8), 2.34 – 2.26 (m, 2H, H4), 1.82 – 1.71 (m, 4H, H6 & H7), 1.65 – 1.53 (m, 2H, H5).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3 (C2), 160.0 (PhC4), 142.1 (C3a), 131.2 (PhC1), 129.4, 115.0 (PhC2/C6, PhC3/C5), 123.8 (C8a), 55.5 (OCH_3), 30.7 (C6 or C7), 29.7 (C4), 27.1, 27.0 (C8 & C6 or C7), 25.8 (C5).

HRMS (ESI$^+$) calc. for $C_{15}H_{18}NOS_2$ $[M+H]^+$: 292.0824, found: 292.0829 (- 1.63 ppm).

6.9 3-(4-Methoxyphenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[d]thiazol-3-ium perchlorate 13



36 **13**

3-(4-Methoxyphenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate **13** was prepared according to general **procedure B** from **36** (475 mg, 1.63 mmol, 1.00 equiv.) yielding the target compound **13** (512 mg, 87%) pure according to ^{1}H-NMR.

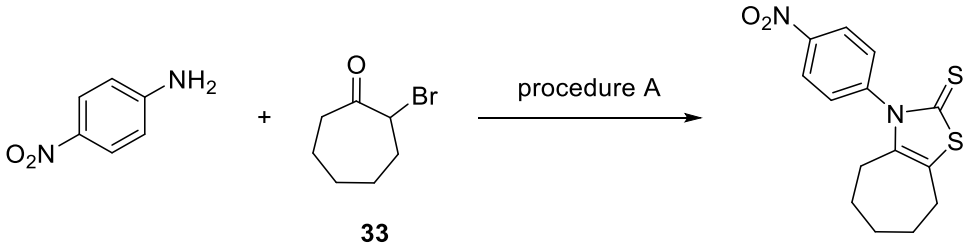
R_f (DCM:MeOH = 9:1, permanganate stain): 0.36.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H, H2), 7.43, 7.05 (2×d, *J* = 8.6 Hz, 2×2H, PhH2/H6 & PhH3/H5), 3.87 (s, 3H, OCH_3), 3.18 – 2.96 (m, 2H, H8), 2.83 – 2.68 (m, 2H, H4), 1.96 – 1.81 (m, 4H, H6 & H7), 1.71 – 1.61 (m, 2H, H5).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (PhC4), 154.4 (C2), 148.7 (C3a), 139.9 (C8a), 129.5 (PhC1), 127.5, 115.5 (PhC2/C6 & PhC3/C5), 56.0 (OCH_3), 30.8 (C6), 28.2 (C8), 27.9 (C4), 26.5 (C7), 25.2 (C5).

HRMS (ESI$^+$) calc. for $C_{15}H_{18}NOS$ $[M-ClO_4]^+$: 260.1104, found: 260.1119 (– 5.99 ppm).

6.10 3-(4-Nitrophenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate 14



33 **36**

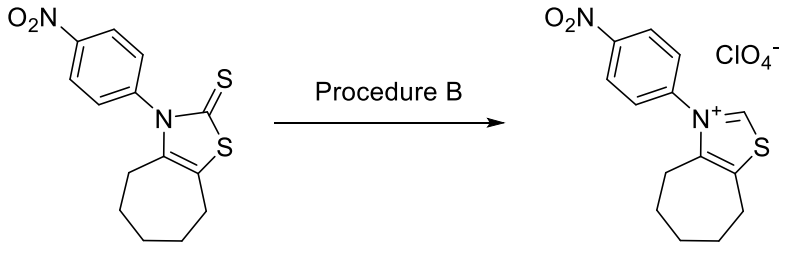
3-(4-Nitrophenyl)-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]thiazole-2-thione **36** was prepared according to general **procedure A** from 4-nitroaniline (723 mg, 5.23 mmol, 1.00 equiv.). It was further purified using column chromatography yielding an orange solid (361.0 mg), however still containing an unidentified impurity (^{1}H-NMR). The material was used without further purification in the next step.

R_f (LP:EtOAc = 5:1, permanganate stain): 0.33.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.36, 7.52 – 7.40 (2 × m, 2 × 2H, PhH2/H6, PhH3/H5), 2.63 (dd, *J* = 15.8, 9.2 Hz, 2H, H8), 2.31 (td, *J* = 11.4, 5.8 Hz, 2H, H4), 1.90 – 1.75 (m, 4H, H6, H7), 1.64 (dt, *J* = 16.9, 5.4 Hz, 2H, H5).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4 (s, C2), 148.0, 143.9 (2×s, PhC1 & PhC4), 140.6 (s, H3a), 130.1 (d, PhC2/C6), 125.5 (s, H8a), 125.2 (d, PhC3/C5), 30.5 (t, C6), 29.7 (t, C4), 27.1 (t, C8), 26.9 (t, C7), 25.8 (t, C5).

HRMS (ESI$^+$) calc. for $C_{14}H_{15}N_2O_2S_2$ $[M+H]^+$: 307.0568, found: 307.0568 (± 0.00 ppm).



35 **14**

3-(4-Nitroxyphenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate **14** was prepared according to general **procedure B** from the crude mixture of **36** (170.6 mg, stoichiometric calculations assuming a content of 1.63 mmol, 1.00 equiv.). Purification was achieved through trituration of the obtained crude oil with Et_2O resulting in the precipitation of the target compound **13** which was washed with $CHCl_3$ to yield a beige solid (60 mg, 29%) which were pure according to ^{1}H-NMR.

m.p. 173-175 °C (MeOH).

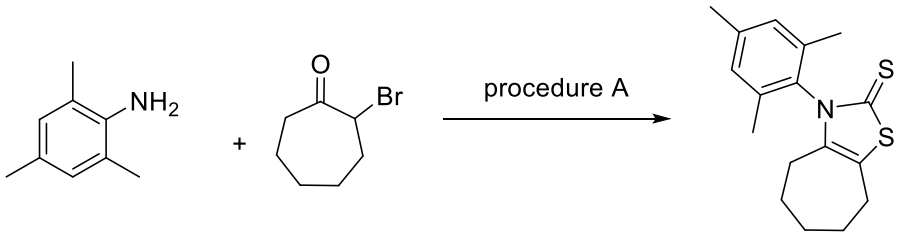
R_f (DCM:MeOH = 9:1, permanganate stain): 0.36.

^{1}H NMR (600 MHz, MeOD) δ 10.08 (s, 1H, H2), 8.58 (d, *J* = 9.0 Hz, 2H, PhH2/H6 or PhH3/H5), 7.92 (d, *J* = 9.0 Hz, 2H, PhH2/H6 or PhH3/H5), 3.23 – 3.11 (m, 2H, H8), 2.90 – 2.74 (m, 2H, H4), 2.05 – 1.97 (m, 2H, H6), 1.94 – 1.88 (m, 2H, H7), 1.81 – 1.73 (m, 2H, H5).

^{13}C NMR (151 MHz, MeOD) δ 149.6 (s, PhC1 or PhC4), 148.6 (s, C3a), 141.3 (s, PhC1 or PhC4), 140.1 (s, C8a), 127.8, 125.2 (2×d, PhC2/C6 & PhC3/C5), 30.3 (t, C6), 27.3 (t, C4), 27.1 (t, C8), 26.1 (t, C7), 24.6 (t, C5). C2 is not visible, presumably due to neighboring D exchange resulting in broadening of the signal.

HRMS (ESI$^+$) calc. for $C_{17}H_{22}NO_2$ $[M\text{-}ClO_4]^+$: 275.0849, found: 275.0848 (- 0.36 ppm).

6.11 3-Mesityl-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]thiazole-2-thione 37[27]



33 **37**

Thione **37** was prepared according to general **procedure A** from 2,4,6-trimethylaniline (707 mg, 5.23 mmol, 1.00 equiv.) yielding a beige solid (596 mg, 38%) pure according to ^{1}H-NMR directly after precipitation.

m.p. 135.3-137.0 °C (*n*-pentane).

R_f (LP:EtOAc = 5:1, potassium permanganate stain): 0.33.

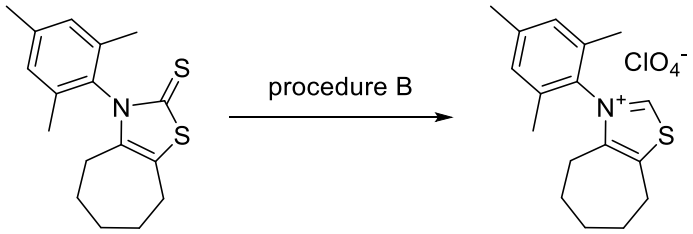
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 2H, Ph H3/5), 2.66 – 2.60 (m, 2H, H8), 2.33 (s, 3H, PhC**H$_3$**(C4)), 2.24 – 2.16 (m, 2H, H4), 2.01 (s, 6H, $PhCH_3$(C2/C6)), 1.85-1.74 (m, 4H, H6 & H7), 1.62-1.53 (m, 2H, H5).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.4 (C2), 140.8 (C3a), 139.6 (PhC4), 135.7 (PhC1), 134.2 (Ar C2/6), 129.7 (Ar C3/C5), 124.5 (C8a), 31.1 (C6 or C7), 28.9 (C4), 27.5 (C8), 27.4 (C6 or C7), 26.5 (C5), 21.4 (PhC4-CH_3), 17.8 (PhC2/C6-CH_3).

HRMS (ESI$^+$) calc. for $C_{17}H_{22}NO_2$ $[M+H]^+$: 304.1188, found: 304.1203 (- 4.93 ppm).

Spectral data in accordance with literature.[27]

6.12 3-Mesityl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate 15[27]



37 **15**

Thiazol-3-ium perchlorate **15** was prepared according to general **procedure B** from thione **37** (700 mg, 2. 31 mmol, 1.00 equiv.) yielding a beige-brown solid (776 mg, 90%) pure according to ^{1}H-NMR directly upon precipitation.

m.p. 135.6-135.7 °C (DCM).

R_f (DCM:MeOH = 9:1, potassium permanganate stain): 0.43.

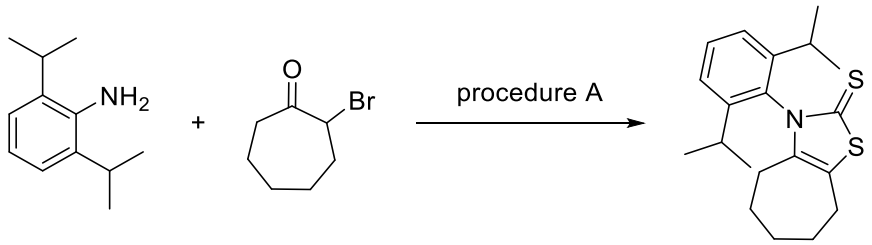
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H, H2), 7.06 (s, 2H, Ph-H3/H5), 3.28 – 3.04 (m, 2H, H8), 2.58 – 2.48 (m, 2H, H4), 2.37 (s, 3H, $PhCH_3$(C4)), 2.00 – 1.93 (m, 8H, $PhCH_3$(C2/5), H6), 1.91 – 1.82 (m, 2H, H7), 1.70 – 1.61 (m, 2H, H5).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5 (C2), 148.0 (C3a), 142.2 (PhC4), 141.1 (C8a), 134.1 (PhC2/C6), 132.9 (PhC1), 130.3 (PhC3/C5), 30.9 (C6), 28.3 (C8), 27.0 (C4), 26.8 (C7), 25.7 (C5), 21.3 ($PhCH_3$(C4)), 17.4 ($PhCH_3$(C2/C6)).

HRMS (ESI$^+$) calc. for $C_{17}H_{22}NS^+$ $[M\text{-}ClO_4]^+$: 272.1467, found: 272.1479 (-4.22 ppm).

Spectral data in accordance with literature.[27]

6.13 3-(2,6-Diisopropylphenyl)-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]thiazole-2-thione 38[27]



33 **38**

Thione **38** was prepared according to general **procedure A** from 2,6-diisopropylaniline (928 mg, 5.23 mmol, 1.00 equiv.) yielding a slightly yellow solid (972 mg, 54%) pure according to ^{1}H-NMR directly after precipitation.

m.p. 165.0-165.1 °C (*n*-pentane).

R_f (LP:EtOAc = 10:1, potassium permanganate stain): 0.31.

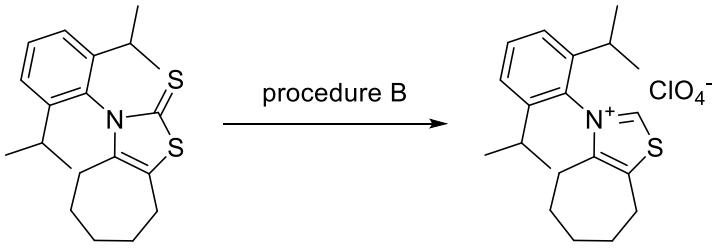
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.8 Hz, 1H, PhH4), 7.29 (d, *J* = 7.8 Hz, 2H, PhH3/H5), 2.68 – 2.62 (m, 2H, H8), 2.46 (sept, *J* = 6.8 Hz, 2H, Ph-CH), 2.26 – 2.14 (m, 2H, H4), 1.88 – 1.70 (m, 4H, H6 & H7), 1.59 – 1.50 (m, 2H, H5), 1.28 (d, *J* = 6.8 Hz, 6H, C**H**$(CH_3)_2$), 1.13 (d, *J* = 6.9 Hz, 6H, CH(C**H**$_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.8 (C2), 146.5 (PhC2/C6), 141.9 (C3a), 133.8 (PhC1), 130.4 (PhC4), 124.7 (PhC3/C5), 124.2 (C8a), 31.1 (C6), 29.5 (C4), 28.9 (**C**H$(CH_3)_2$), 27.6 (C8), 27.3 (C7), 26.4 (C5), 24.5, 24.0 (2 × CH(**C**$H_3)_2$).

HRMS (ESI^+) calc. for $C_{20}H_{28}NS_2$ $[M+H]^+$: 346.1658, found: 346.1675 (- 5.11 ppm).

Spectral data in accordance with literature.[27]

6.14 3-(2,6-Diisopropylphenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate 16[27]



38 **16**

3-(2,6-Diisopropylphenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate **16** was prepared according to general **procedure B** from **38** (700 mg, 2.03 mmol, 1.00 equiv.) yielding a beige foam (696 mg, 83%) of the target compound pure according to ^{1}H-NMR directly upon evaporation.

m.p. 96.7-97.2 °C (DCM).

R_f (DCM:MeOH = 9:1, potassium permanganate stain): 0.49.

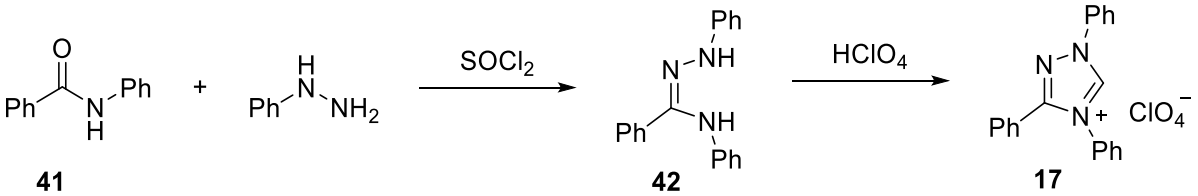
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H, H2), 7.59 (t, *J* = 7.9 Hz, 1H, Ph H4), 7.35 (d, *J* = 7.9 Hz, 2H, Ph H3/H5), 3.22 – 3.14 (m, 1H, H8), 2.59 – 2.46 (m, 1H, H4), 2.05 (sept, *J* = 6.8 Hz, 2H, C**H**$(CH_3)_2$), 1.99 – 1.92 (m, 1H, H6), 1.90 (q, *J* = 4.7, 4.1 Hz, 1H, H7), 1.62 (pent, *J* = 5.1 Hz, 1H, H5), 1.16 (d, *J* = 6.9 Hz, 6H, C**H**$_3$-CH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4 (C2), 148.8 (C3a), 145.0 (PhC2/C6), 141.2 (C8a), 132.6 (PhC4), 132.2 (PhC1), 125.3 (PhC3/C5), 30.9 (C6), 28.9 (**C**H$(CH_3)_2$), 28.3 (C8), 27.4 (C4), 26.7 (C7), 25.6 (C5), 24.9, 23.3 (2 × CH(**C**$H_3)_2$).

HRMS (ESI$^+$) calc. for $C_{10}H_{28}NS$ $[M\text{-}ClO_4]^+$: 314.1937, found: 314.1951 (-4.61 ppm).

Spectral data in accordance with literature.[27]

6.15 1,3,4-Triphenyl-1,2,4-triazol-1-ium perchlorate 17[33]



Benzanilide **41** (4.00 g, 20.3 mmol, 1.00 equiv.) was dissolved in toluene (20 ml) in a flask equipped with a reflux condenser with dry tube ($CaCl_2$). The suspension was stirred for several minutes and then thionyl chloride (7.24 g, 60.8 mmol, 3.00 equiv.) was added at once with a syringe. Then the reaction mixture was heated to 80 °C and stirred there overnight with the solution turning yellow. The reflux condenser was removed, and a distillation head was added. The solvent was evaporated (up to 5 mbar at 60 °C). a yellow solution remained, which solidified upon cooling to rt. THF (anh., 20 ml) was added with the solution turning yellow again. NEt_3 (4.24 ml, 30.4 mmol, 1.5 equiv.) was added slowly and phenylhydrazine (1.99 ml, 20.3 mmol, 1.1 equiv.) was added in a way to keep the temperature under 40 °C. A colourless solid precipitated and the yellow colour got more intense. The suspension was stirred at rt for 3 h, when reaction monitoring *via* TLC (LP/EtOAc 9:1) showed complete conversion of starting material and formation of a new, not smearing spot. The reagents and the solvent were removed *in vacuo* (40 °C, 40 mbar) and a thick, honey like, orange-yellow coloured residue remained with the crude NMR being reported in 9.6 and matching intermediate **42**. The residue was treated with 2% HOAc (36 ml) and heated up to 70°C under stirring for 30 min, until a homogenous suspension was observed. The precipitate was vacuum filtered and washed with H_2O and MeOH. After washing with MeOH, a slightly yellow solid (2.80 g, 48%) was observed.

Formic acid (8.46 ml, 224 mmol, 23 equiv.) and Ac_2O (16.6 ml, 175 mmol, 18 equiv.) were mixed and heated up to 60 °C for 15 min. After cooling to rt, the intermediate **42** (2.80 g, 9.74 mmol, 1.00 equiv.) was added portionwise under cooling with a water bath over 10 min. The solution was stirred for 20 h. The solvent was evaporated (60 °C, up to 45 mbar) and $HClO_4$

solution (35%, 16.8 ml) was added. A solid precipitated and the rm was stirred for 30 min. After adding 5 ml H_2O the reaction mixture was stirred for 10 min. The precipitate was vacuum filtered and washed with H_2O and MeOH. The target compound **17** was obtained as a slightly beige solid (2.50 g, 65%, over 2 steps: 31%) pure according to ^{1}H-NMR.

m.p. 232-233 °C (MeOH), (lit.[33] 220 °C).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.35 (s, 1H, H2), 8.09 (d, *J* = 7.9 Hz, 2H, PhH), 7.79 (t, *J* = 7.7 Hz, 3H, PhH), 7.73 – 7.67, 7.66 – 7.61, 7.57 – 7.51 (3 × m, 7H; 2H; 6H, PhH).

^{13}C NMR (101 MHz, DMSO-d_6) δ 153.29, 143.18, 134.87, 132.37, 132.07, 131.57, 130.92, 130.46, 130.25, 129.33, 129.27, 126.58, 122.39, 120.66.

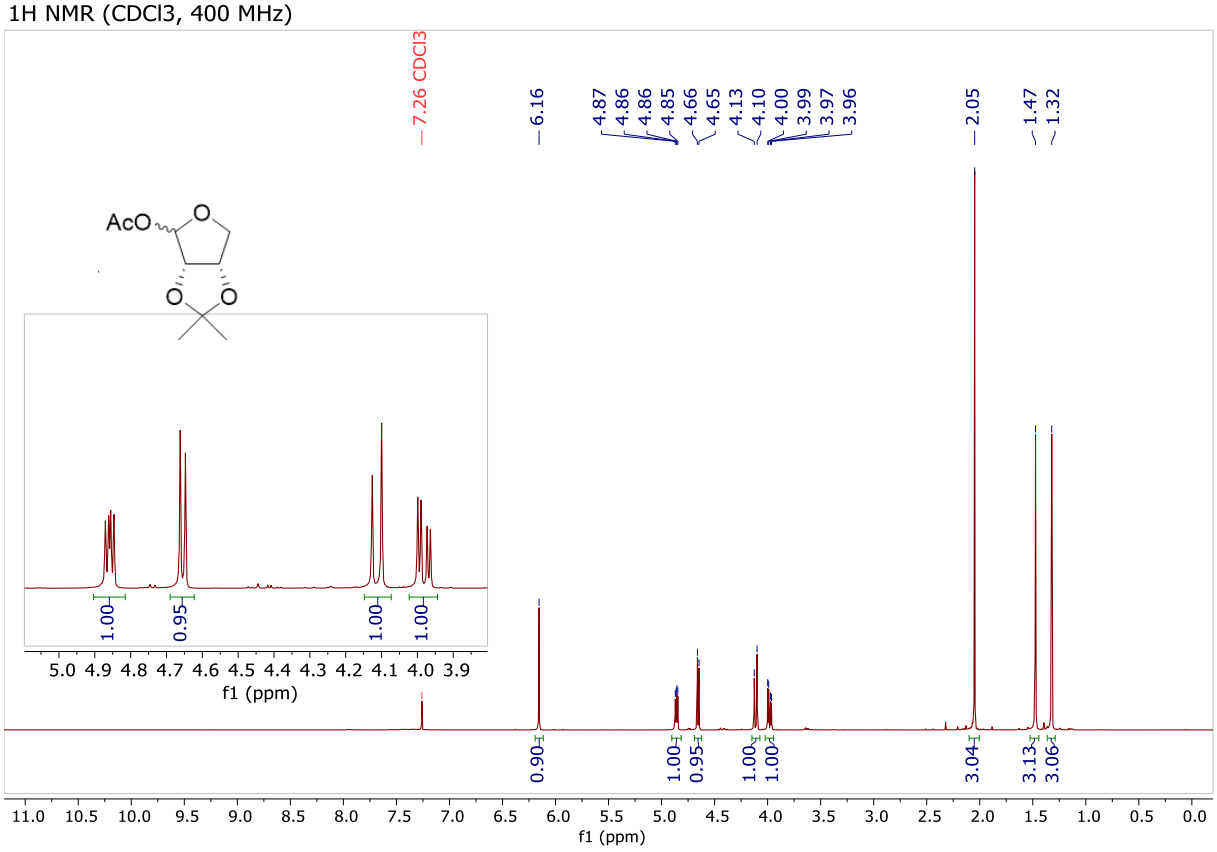
HRMS (ESI$^+$) Exact mass calc. for $C_{20}H_{16}N_3$ $[M\text{-}ClO_4]^+$: 298.1361, found: 298.1344 (5.49 ppm).

Spectral data in accordance with literature.[33]

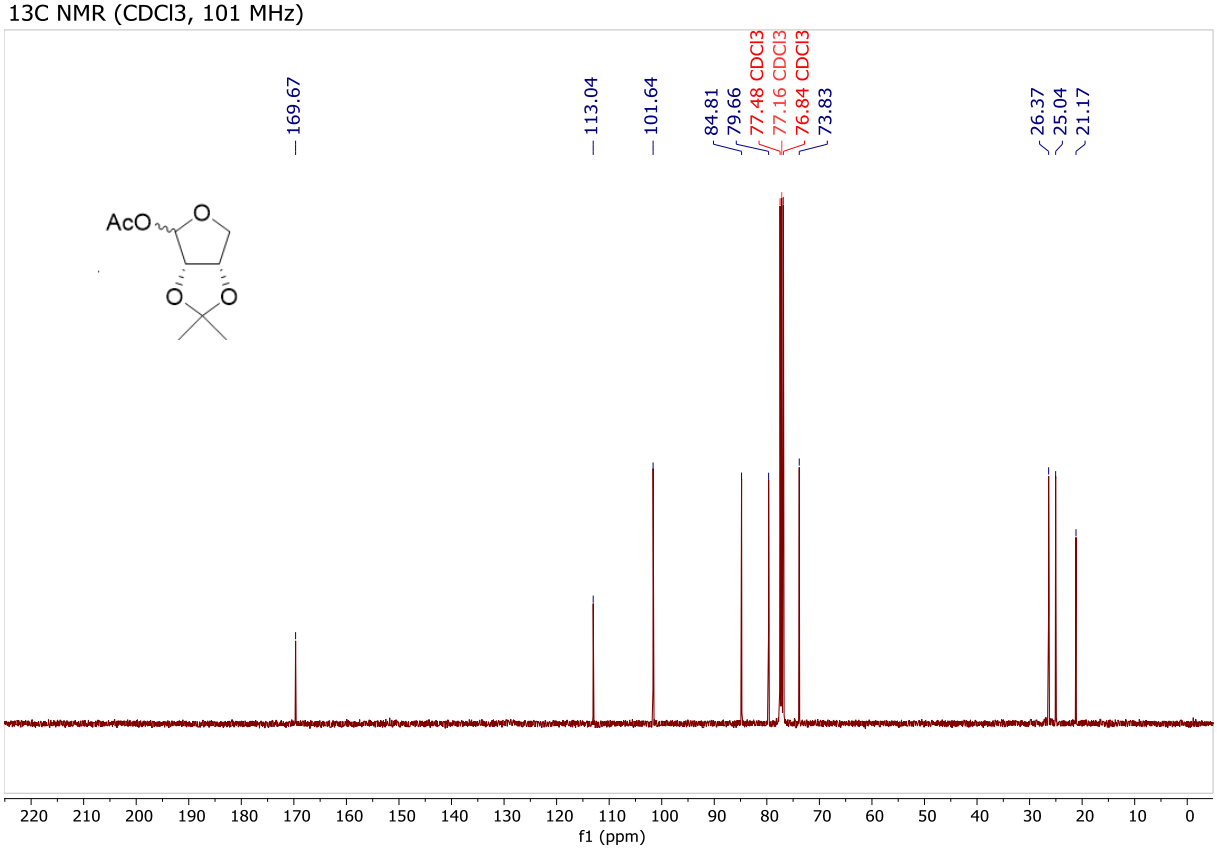
7 NMR spectra of dehomologation products

7.1 1-*O*-Acetyl-2,3-*O*-isopropylidene-L-erythrose 7b

1H NMR (CDCl3, 400 MHz)

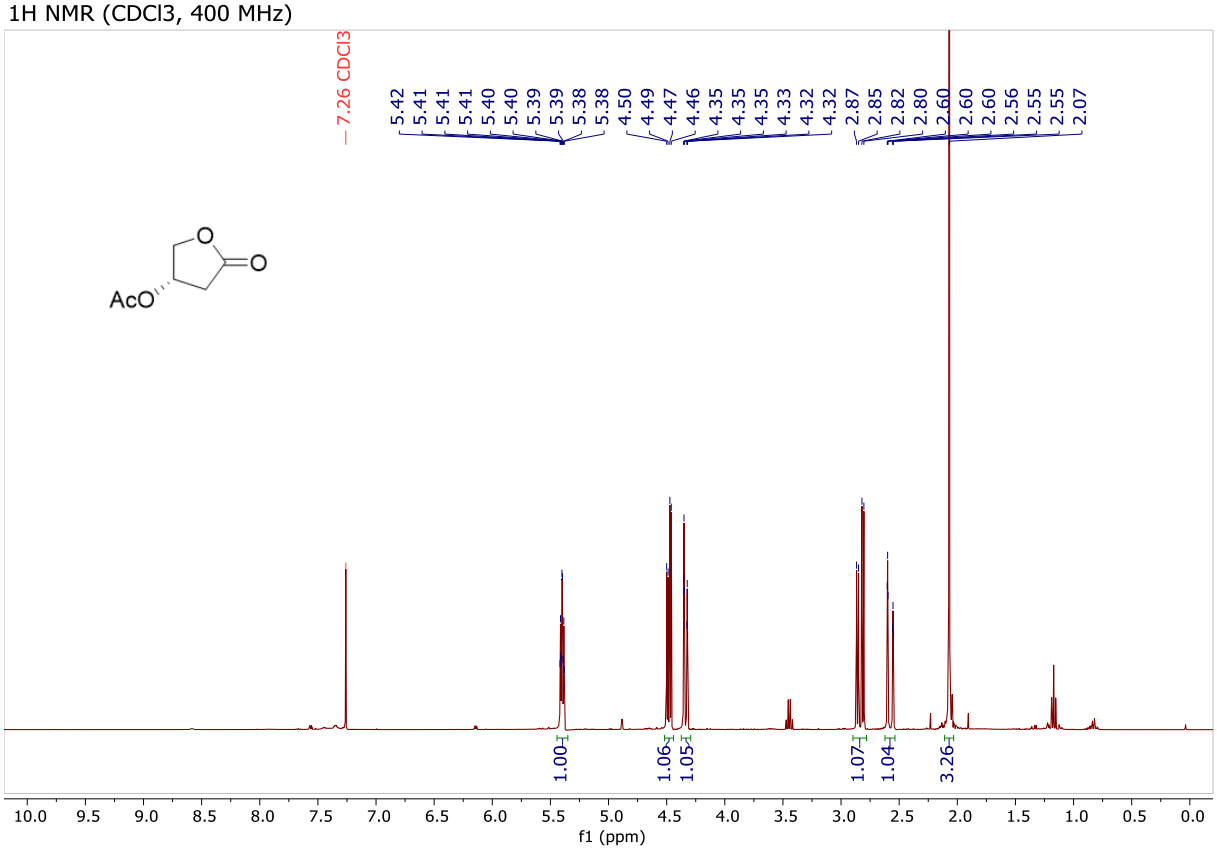


13C NMR (CDCl3, 101 MHz)

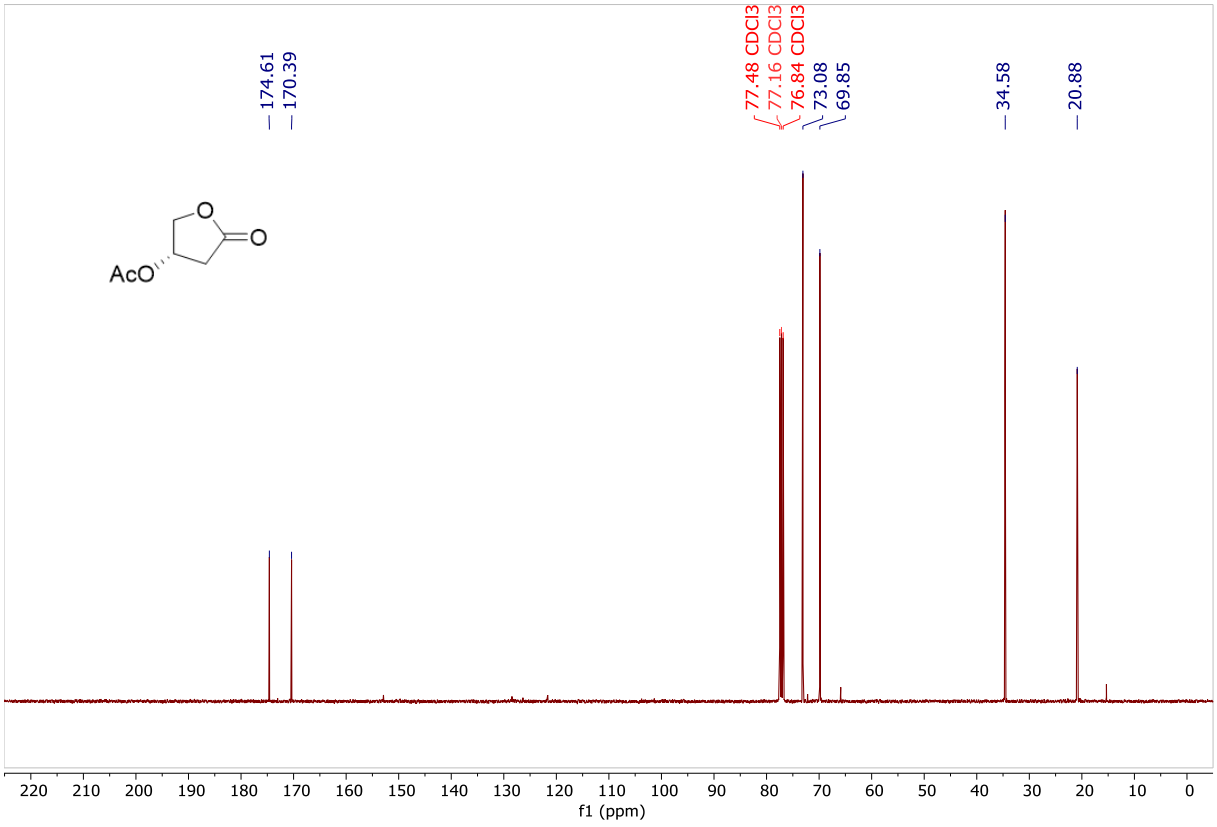


7.2 (3*S*)-β-acetoxy-γ-butyrolactone 9b

1H NMR (CDCl3, 400 MHz)

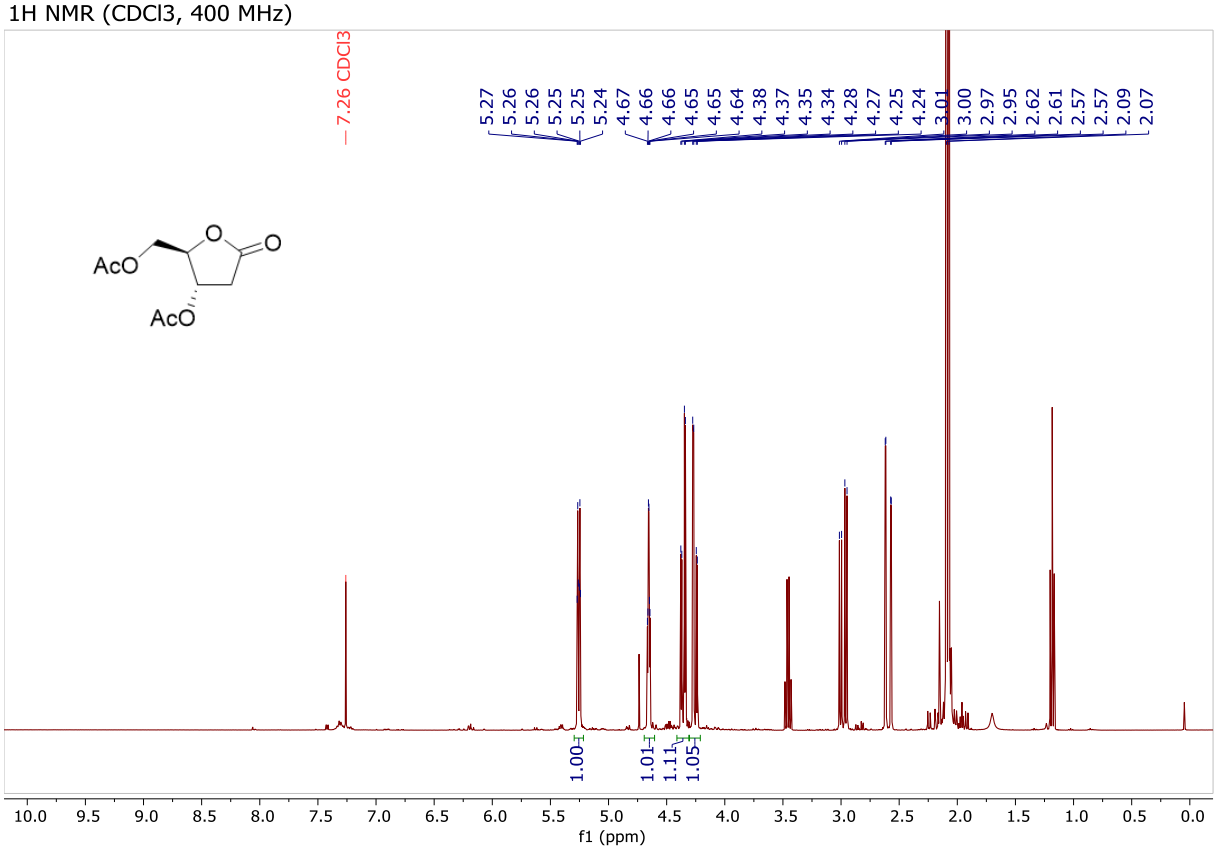


13C NMR (CDCl3, 101 MHz)

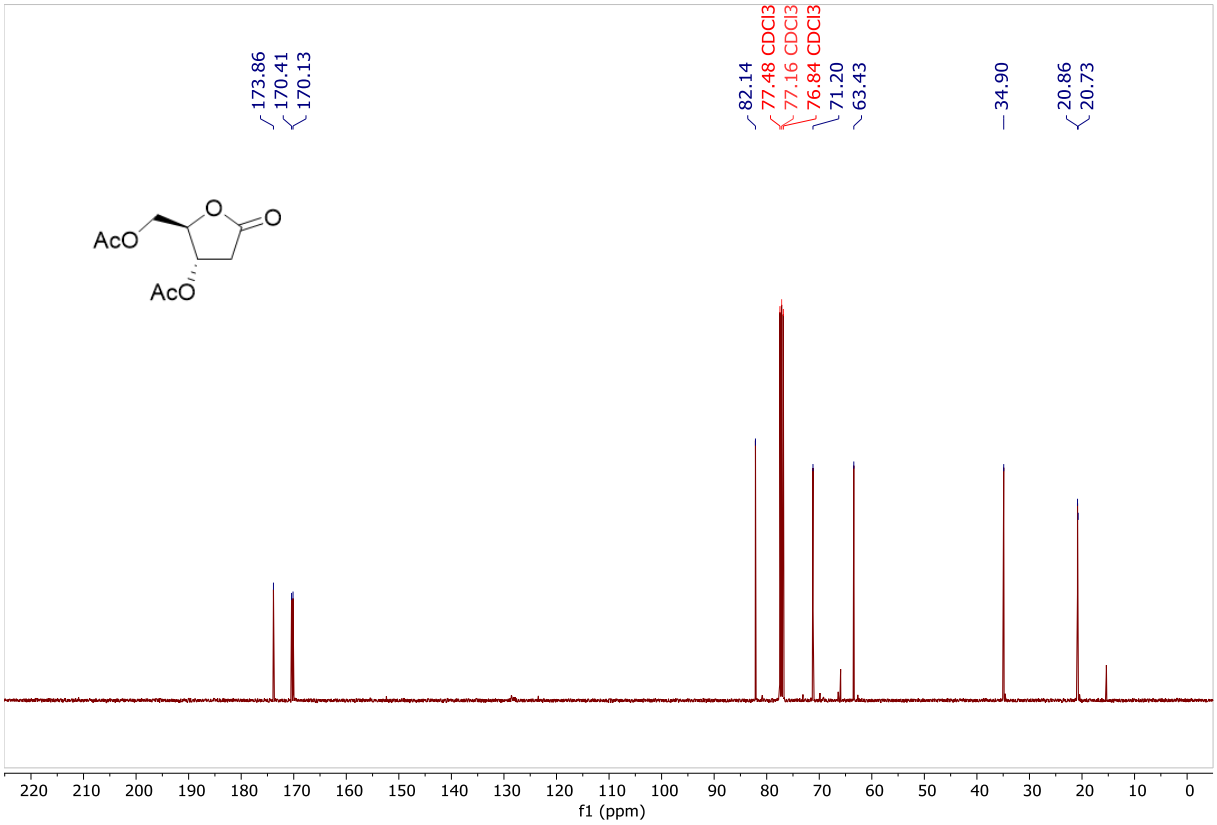


7.3 3,5-*O*-Diacetyl-2-deoxy-D-ribono-1,4-lactone 4b

1H NMR (CDCl3, 400 MHz)



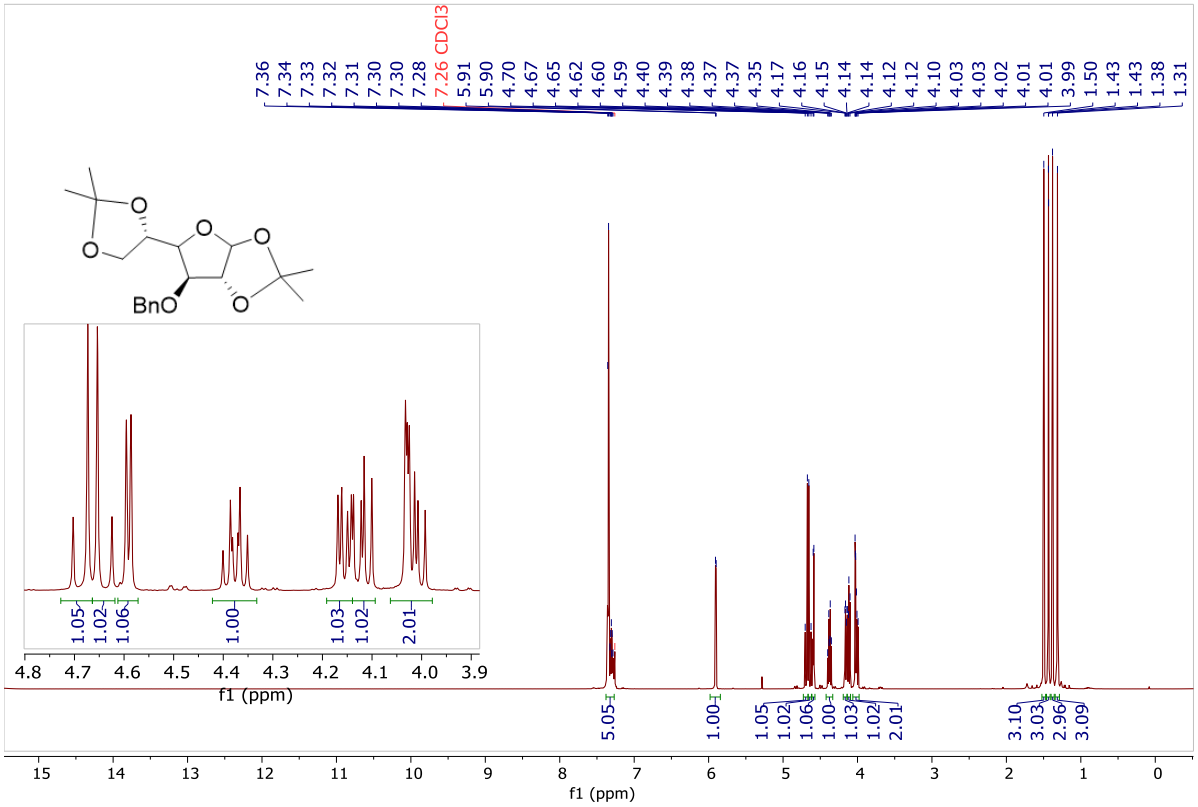
13C NMR (CDCl3, 101 MHz)



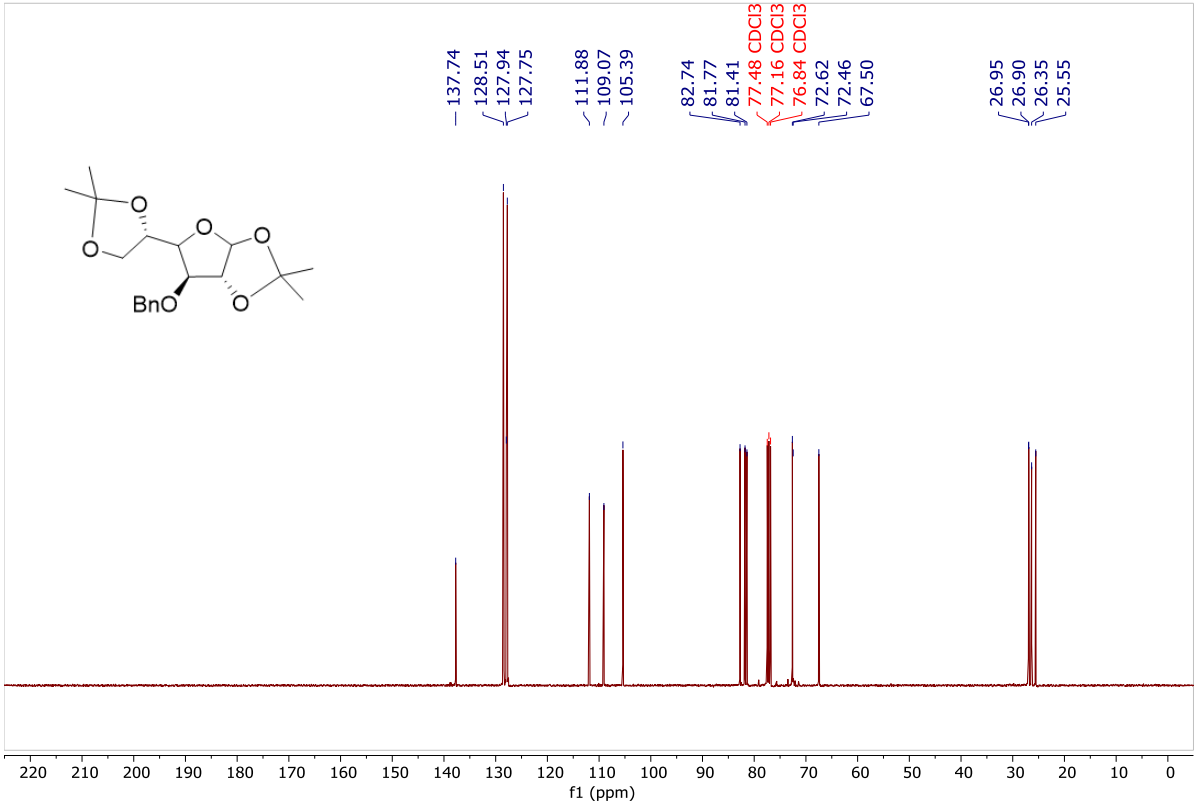
8 NMR spectra of sugar substrates

8.1 NMR-spectra of isolated 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 21

1H NMR (CDCl3, 400 MHz)

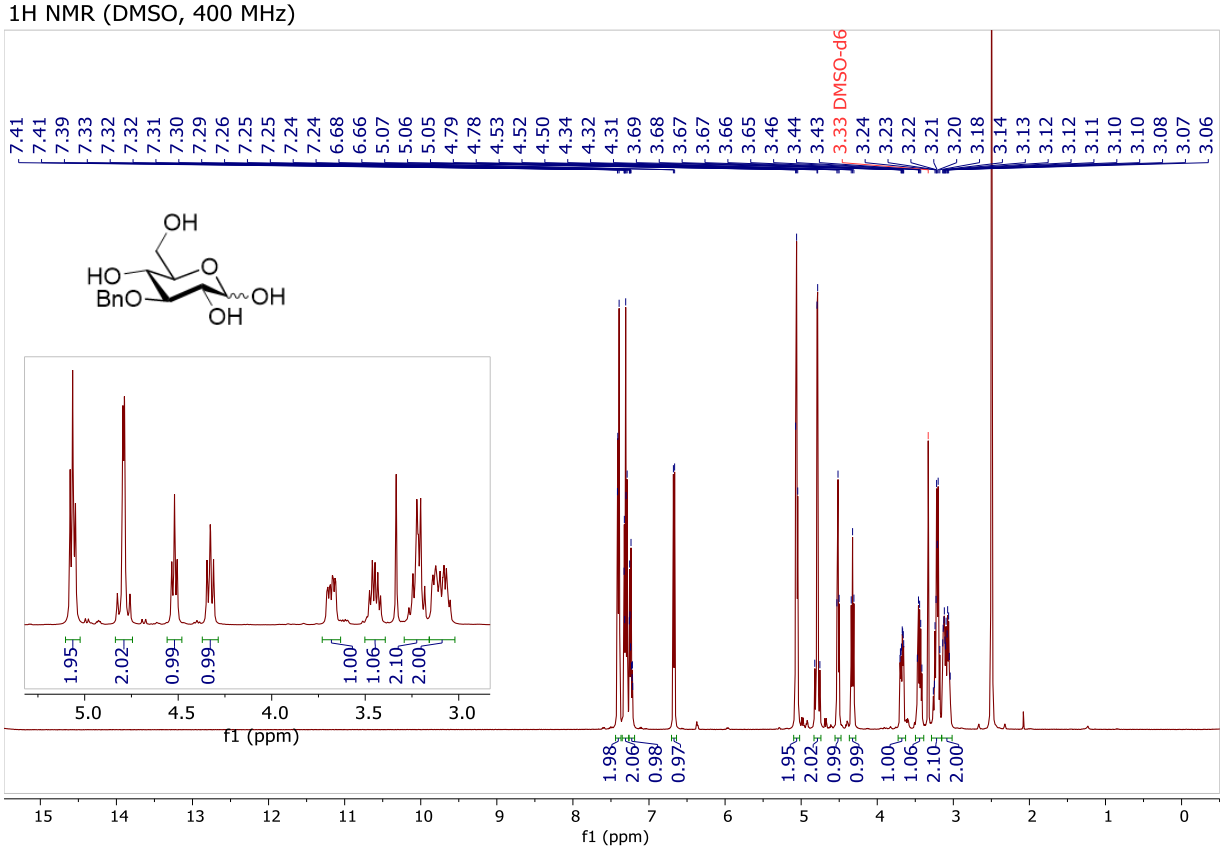


13C NMR (CDCl3, 101 MHz)

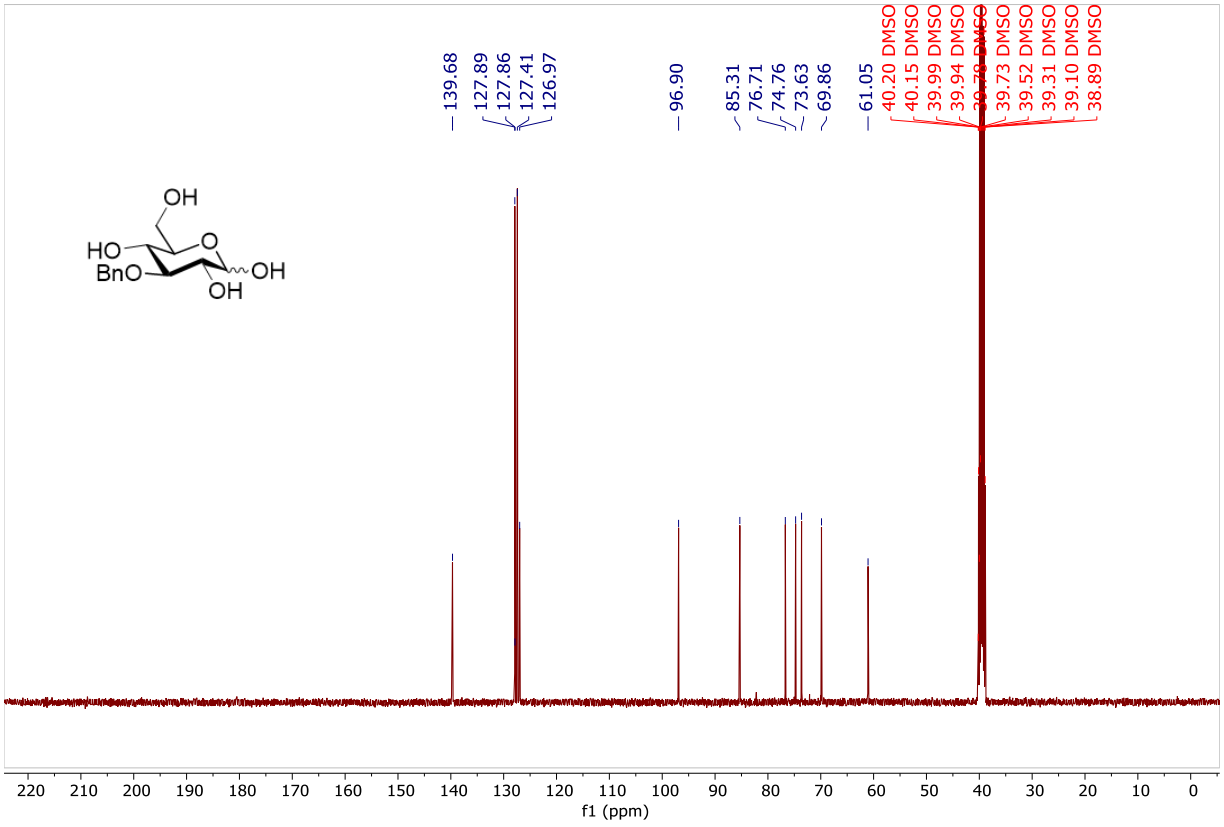


8.2 NMR-spectra of isolated 3-*O*-benzyl-D-glucose 1a

1H NMR (DMSO, 400 MHz)

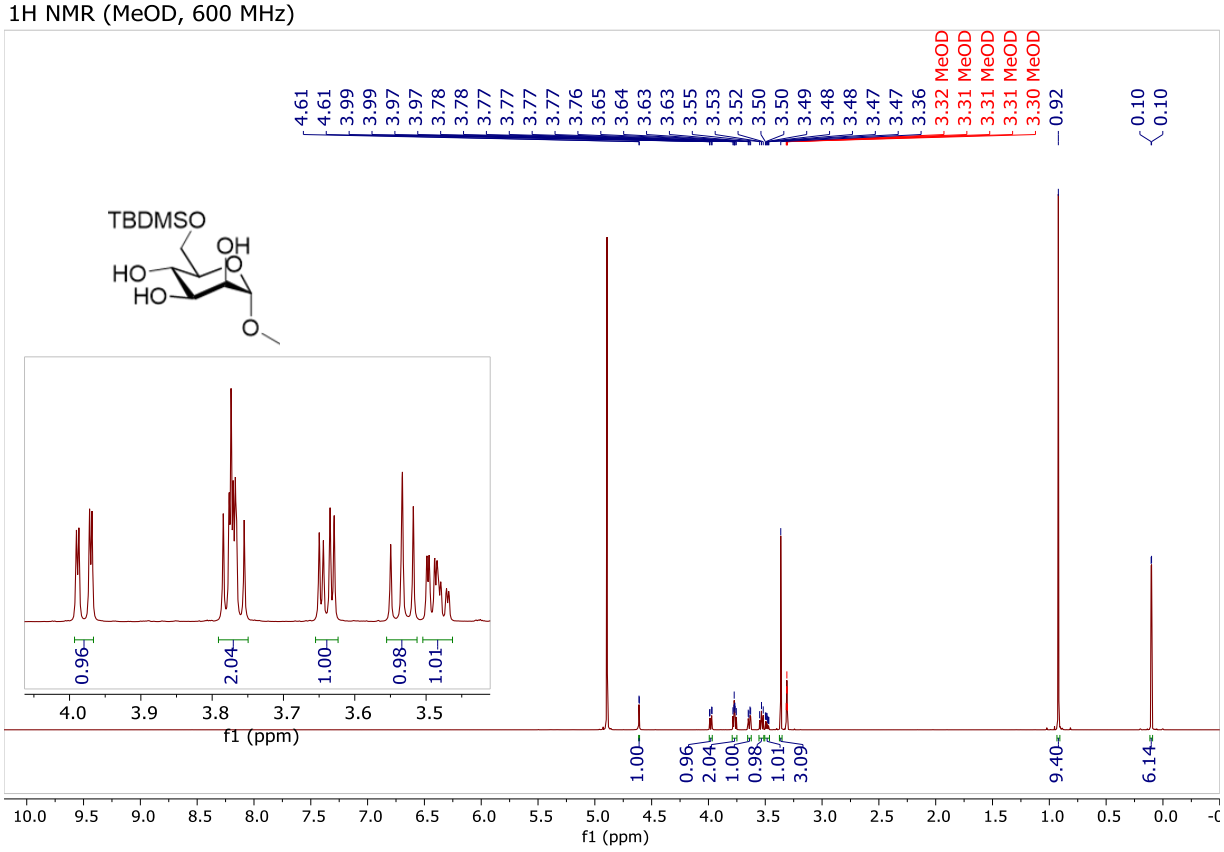


13C NMR (DMSO, 101 MHz)

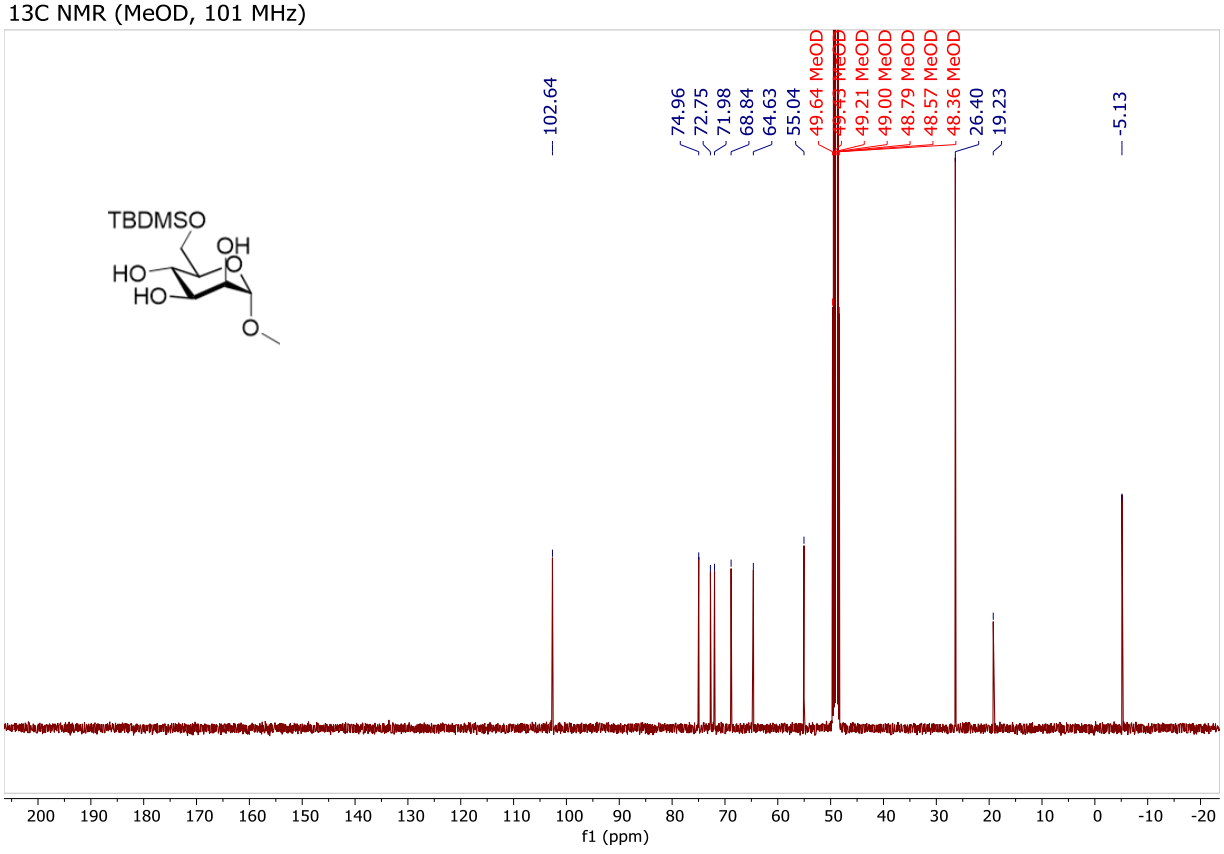


8.3 NMR-spectra of isolated methyl 6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside 23

1H NMR (MeOD, 600 MHz)

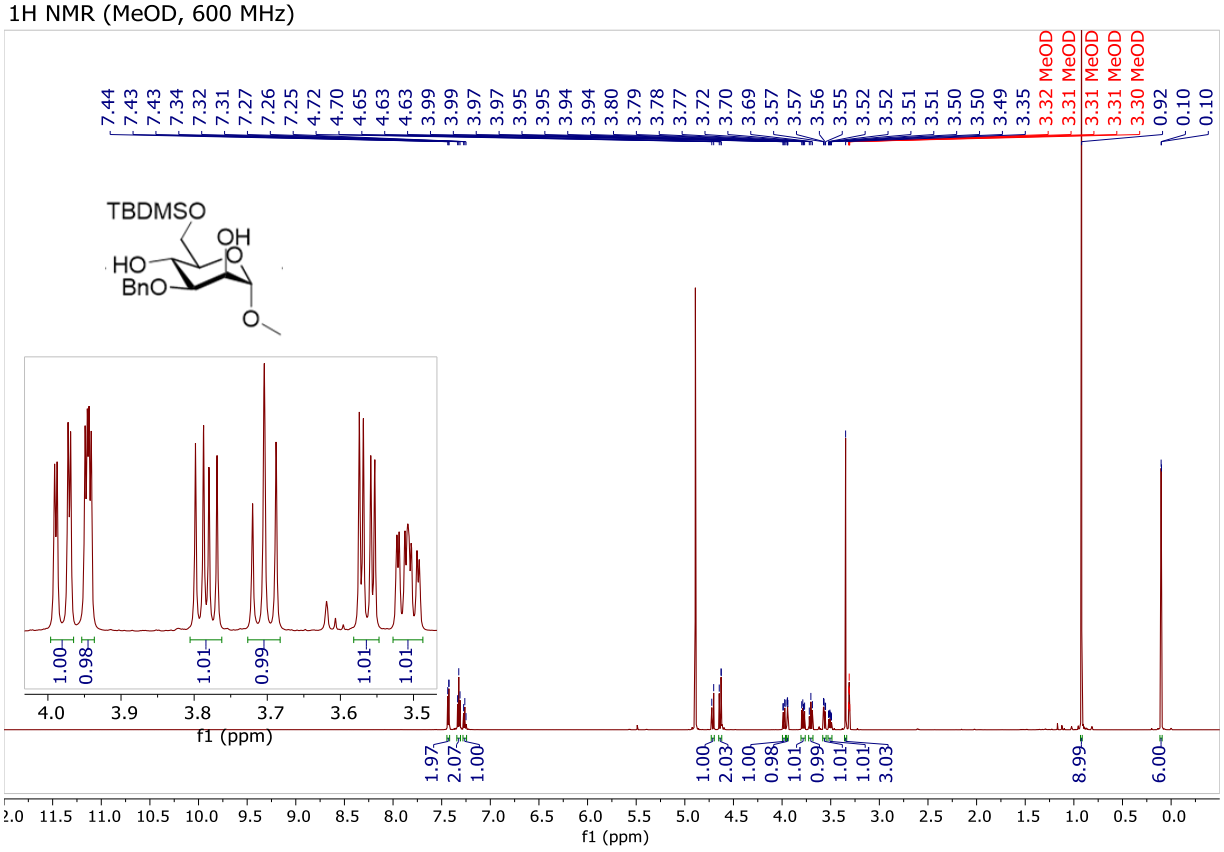


13C NMR (MeOD, 101 MHz)

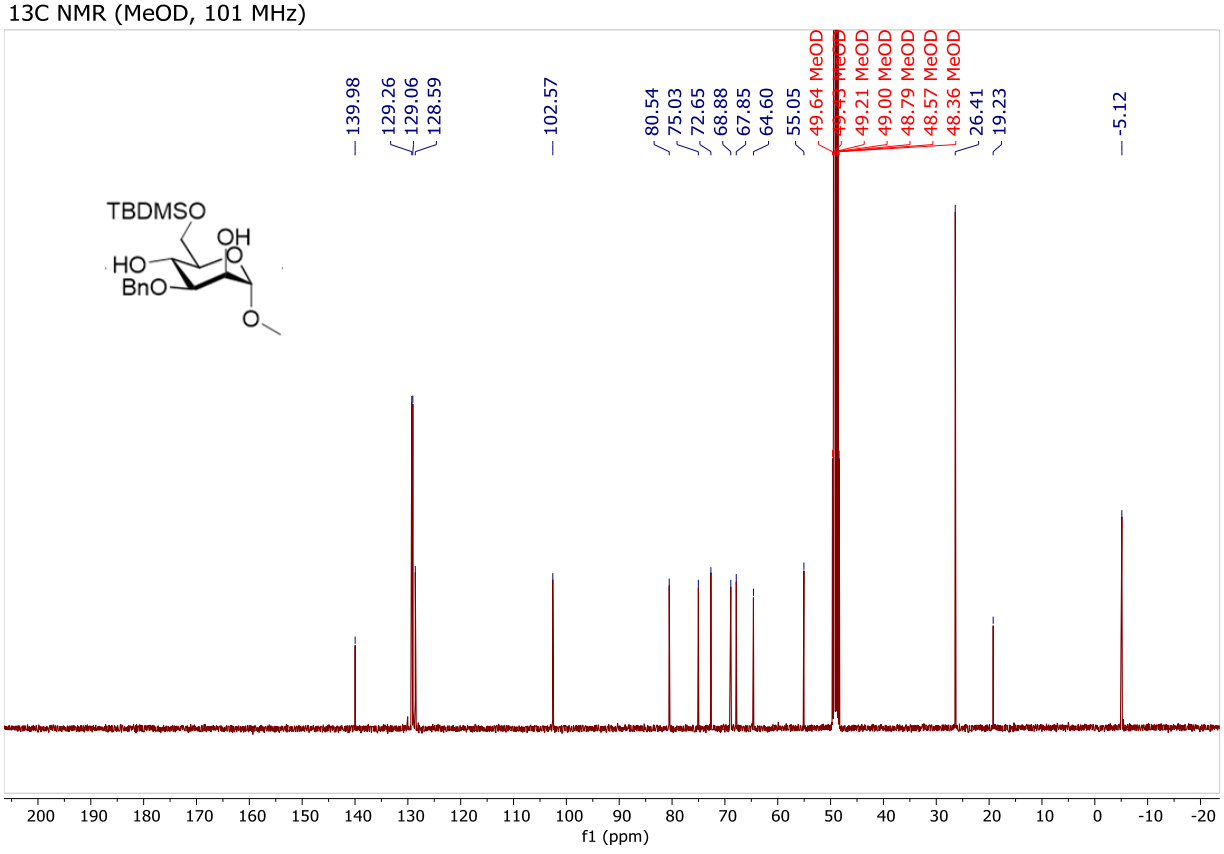


8.4 NMR-spectra of isolated methyl 6-*O*-(*tert*-butyldimethylsilyl)-3-*O*-benzyl-α-D-mannopyranoside 24

1H NMR (MeOD, 600 MHz)

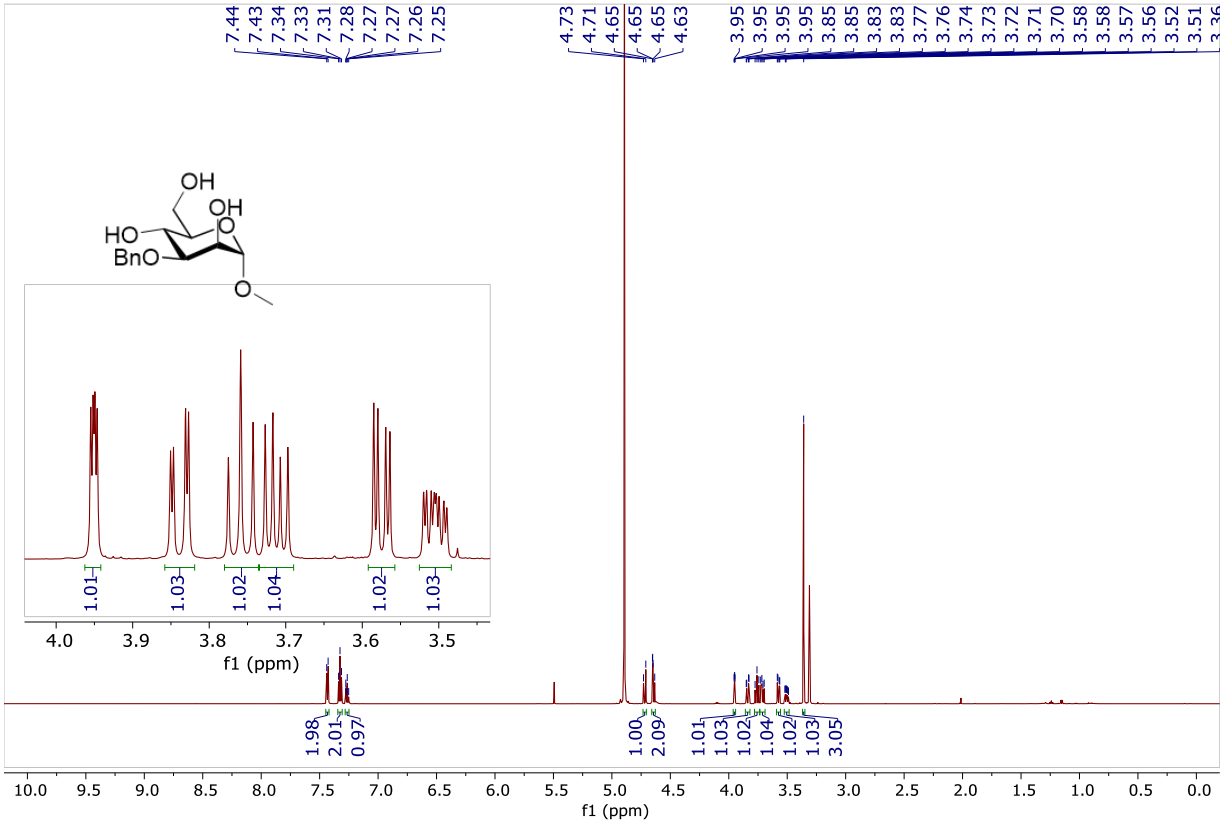


13C NMR (MeOD, 101 MHz)

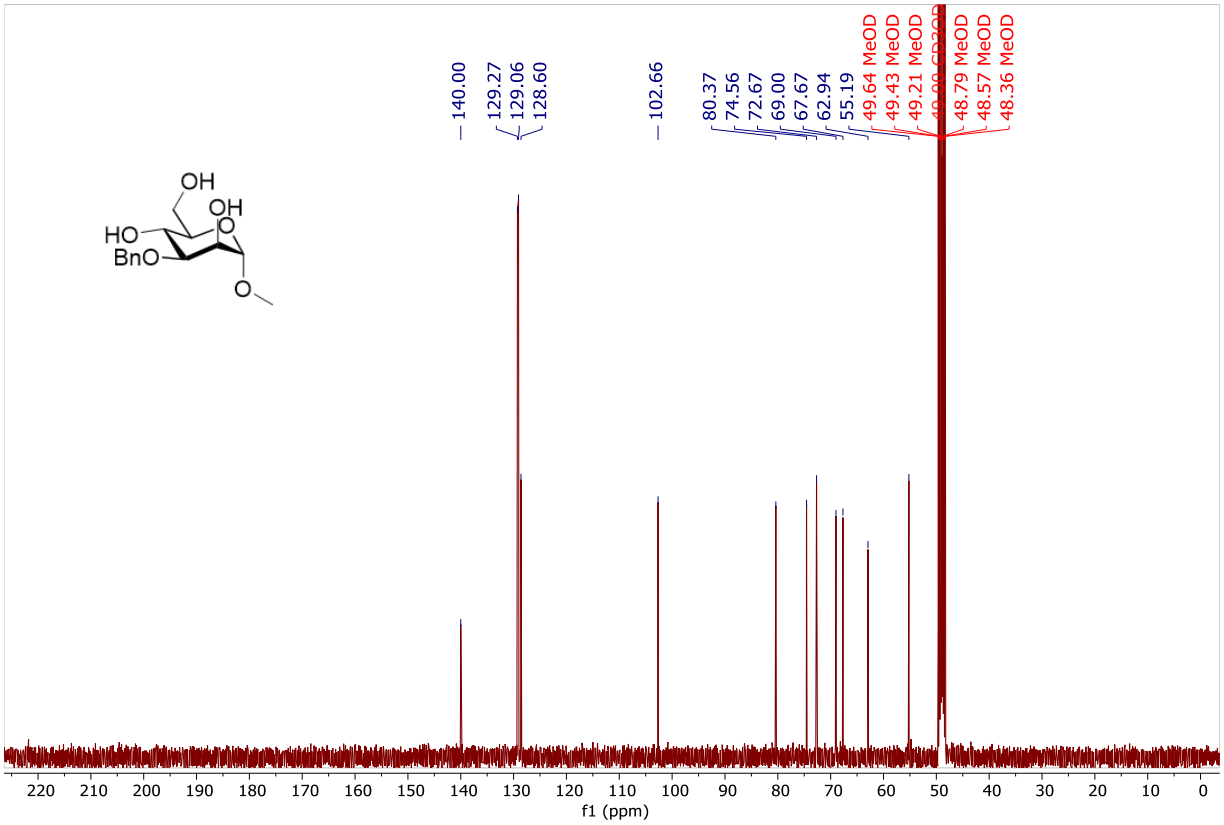


8.5 NMR-spectra of isolated methyl 3-*O*-benzyl-α-D-mannopyranoside 25

1H NMR (MeOD, 600 MHz)

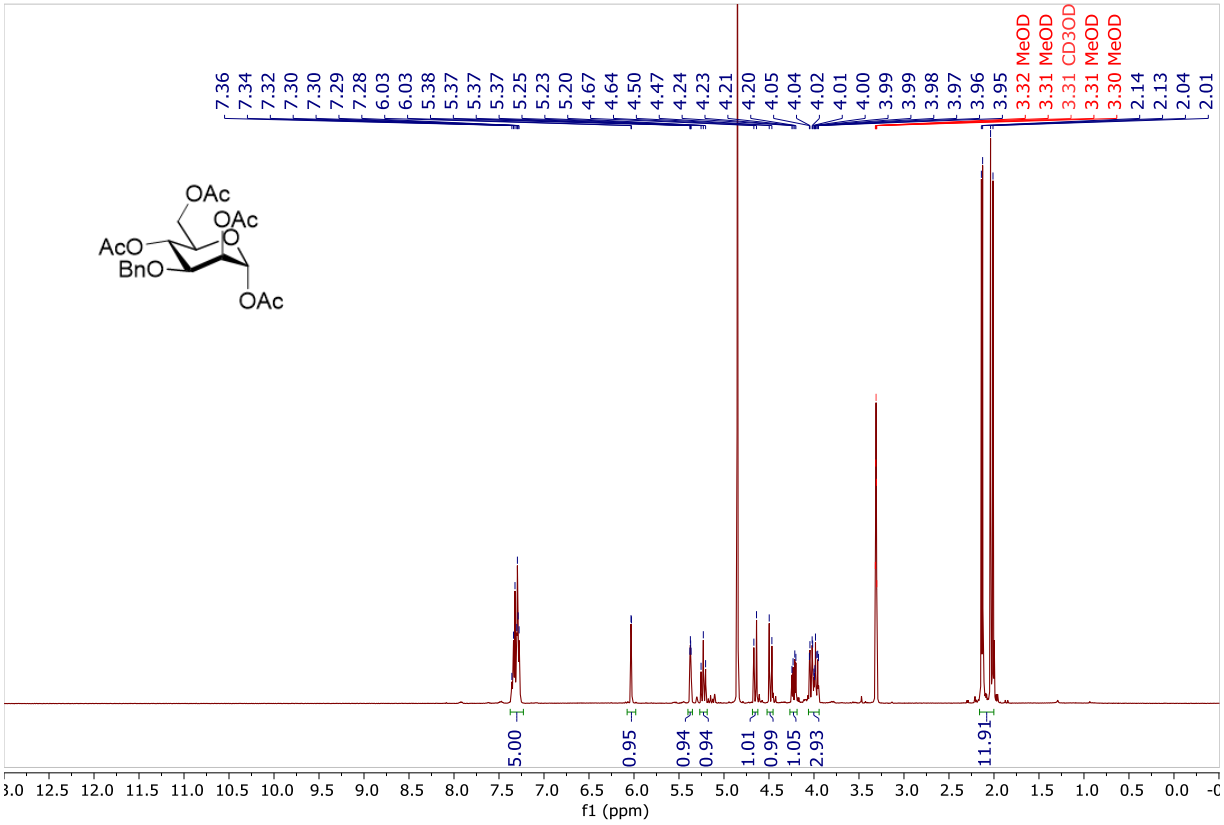


13C NMR (MeOD, 101 MHz)

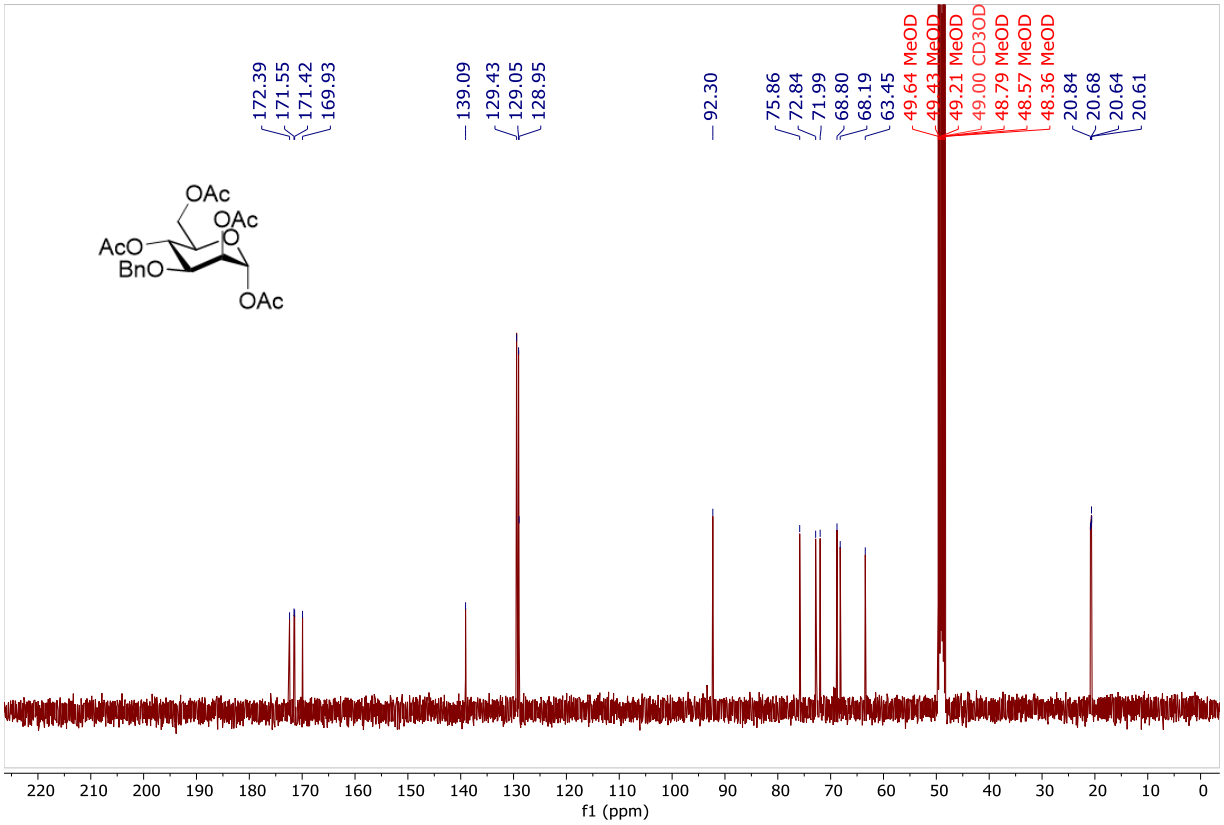


8.6 NMR-spectra of isolated 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranose 27

1H NMR (MeOD, 400 MHz)

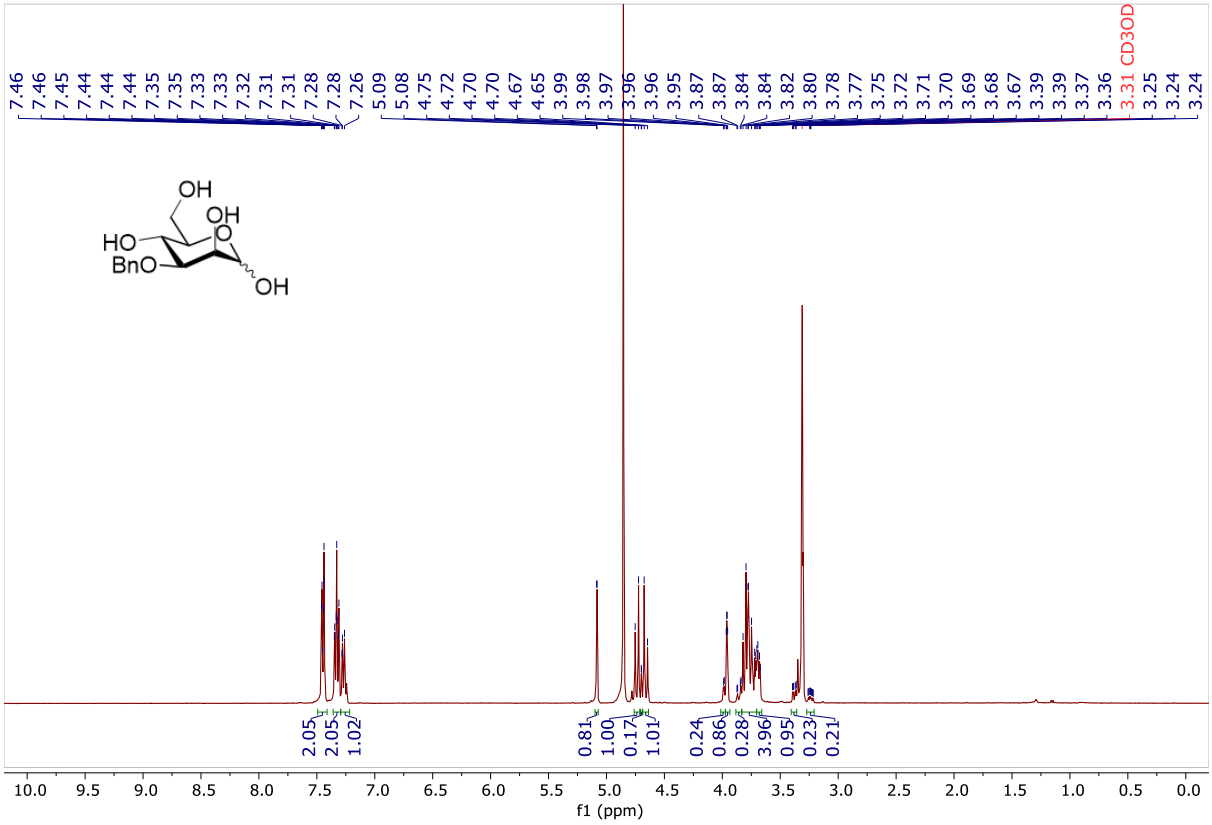


13C NMR (MeOD, 101 MHz)

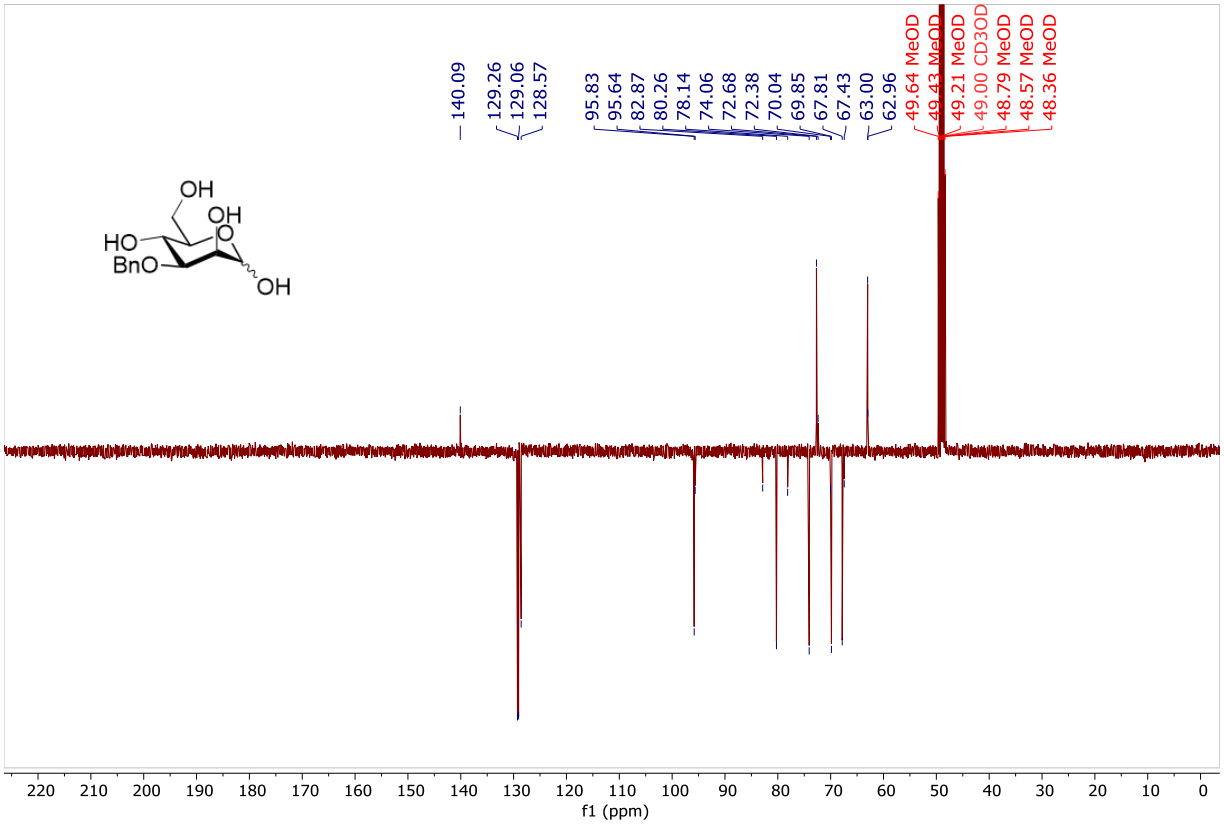


8.7 NMR-spectra of isolated 3-*O*-benzyl-α-D-mannose 1b

1H NMR (MeOD, 400 MHz)

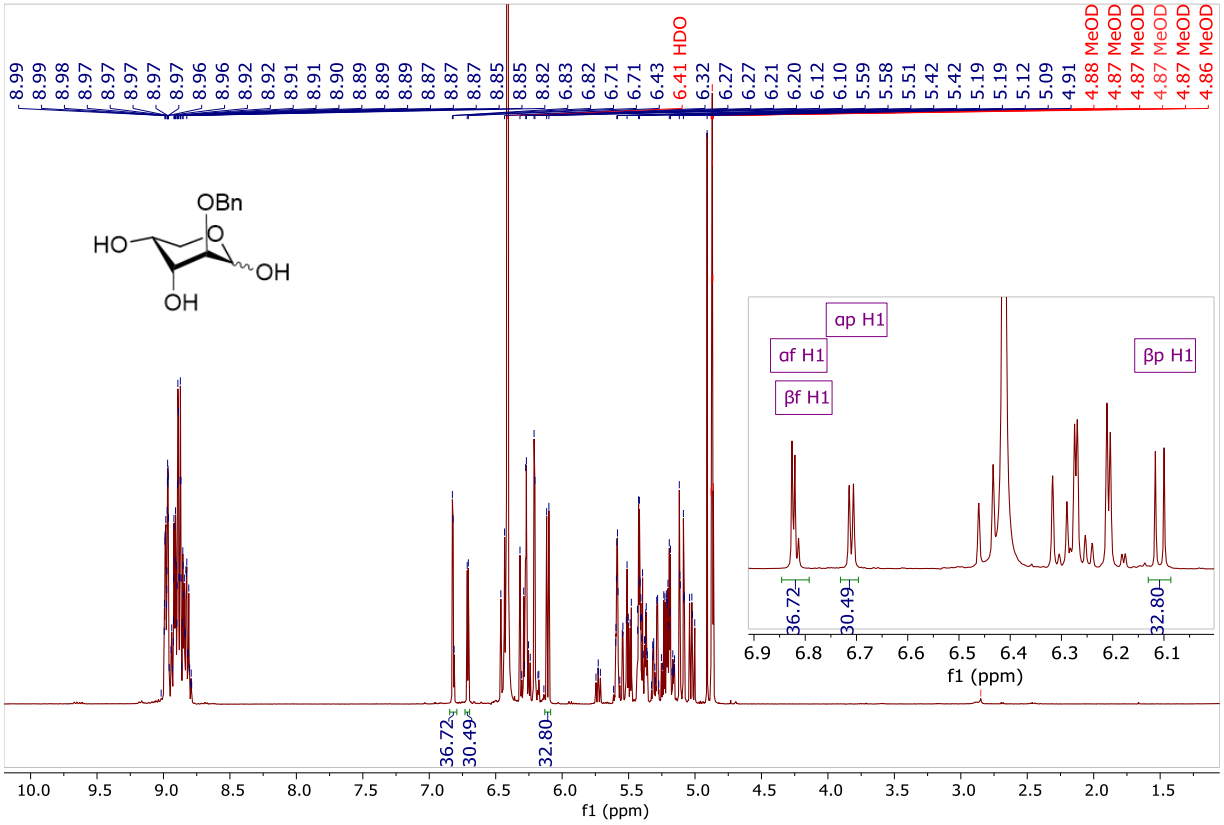


13C NMR (MeOD, 101 MHz)

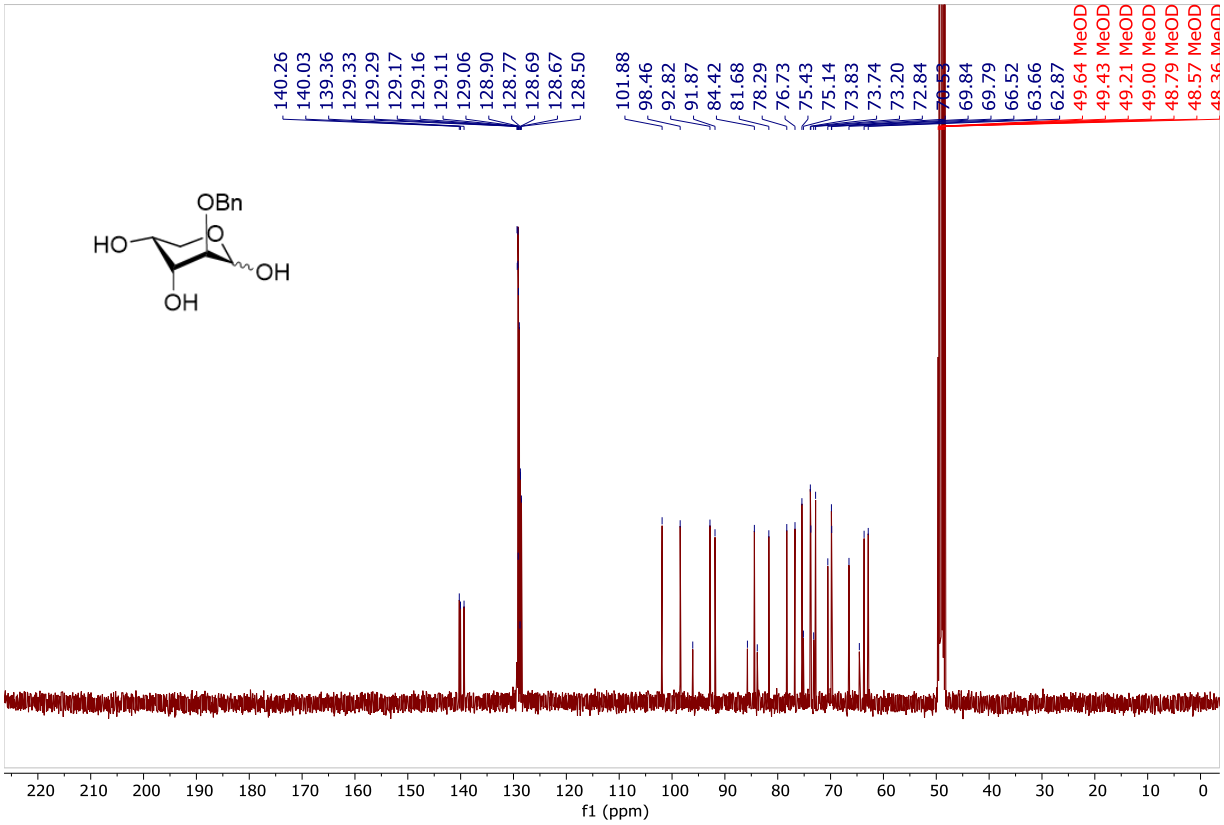


8.8 NMR-spectra of isolated 2-*O*-benzyl-D-arabinose 3

1H NMR (MeOD, 400 MHz)

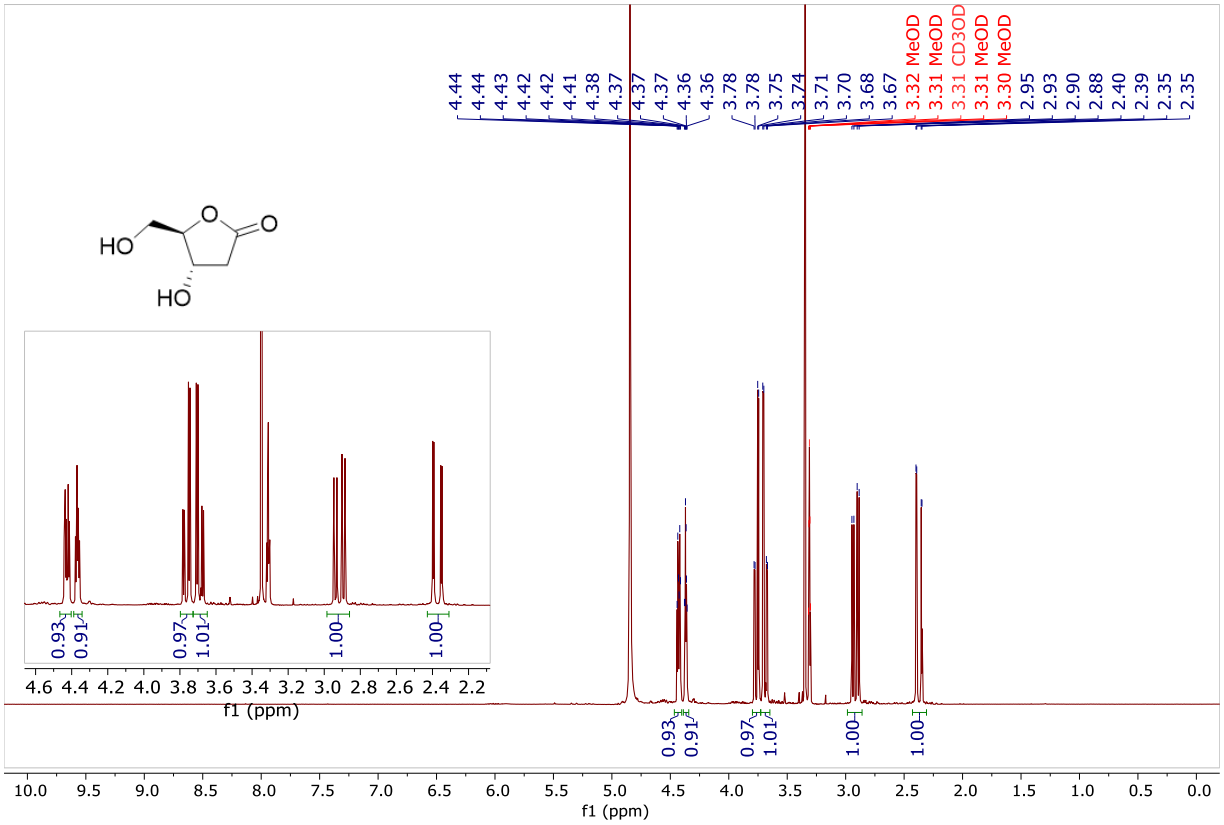


13C NMR (MeOD, 101 MHz)

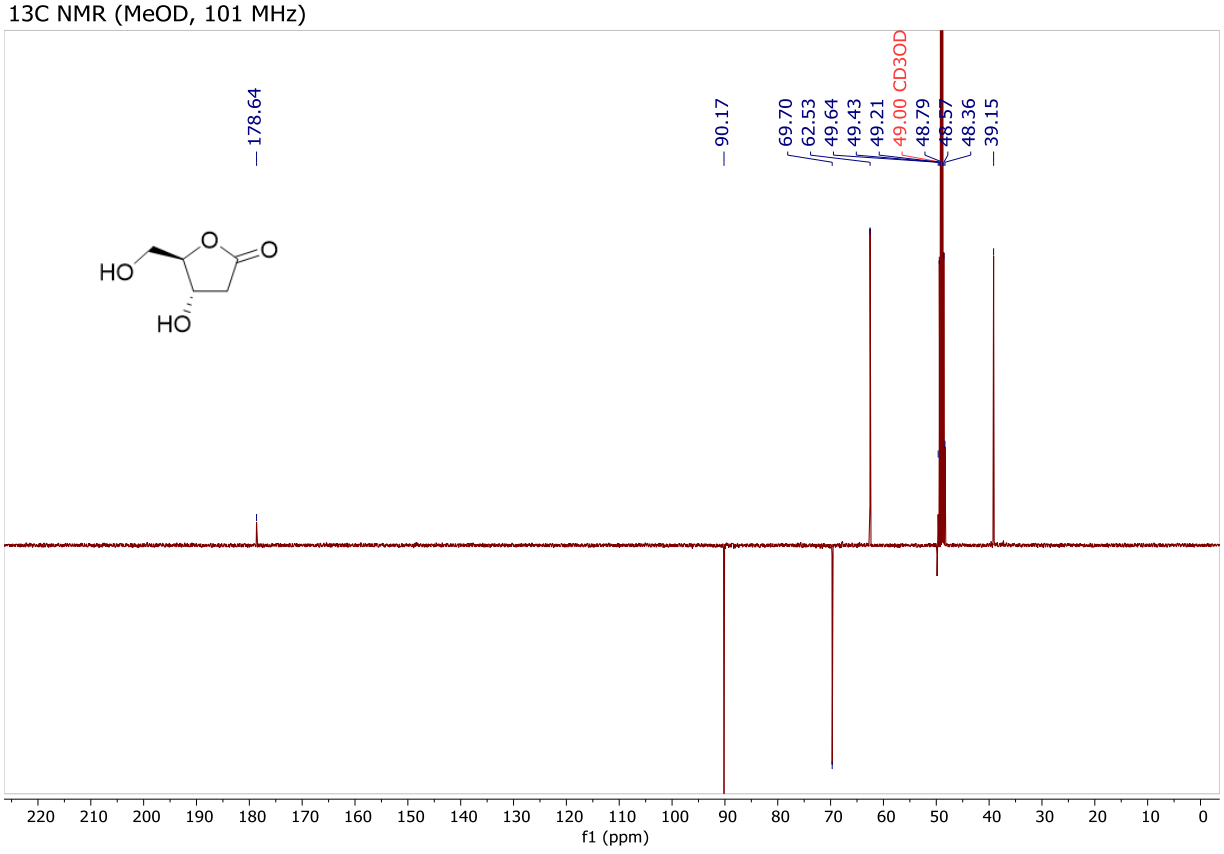


8.9 NMR-spectra of isolated 2-deoxy-D-ribono-1,4-lactone 4a

1H NMR (MeOD, 400 MHz)

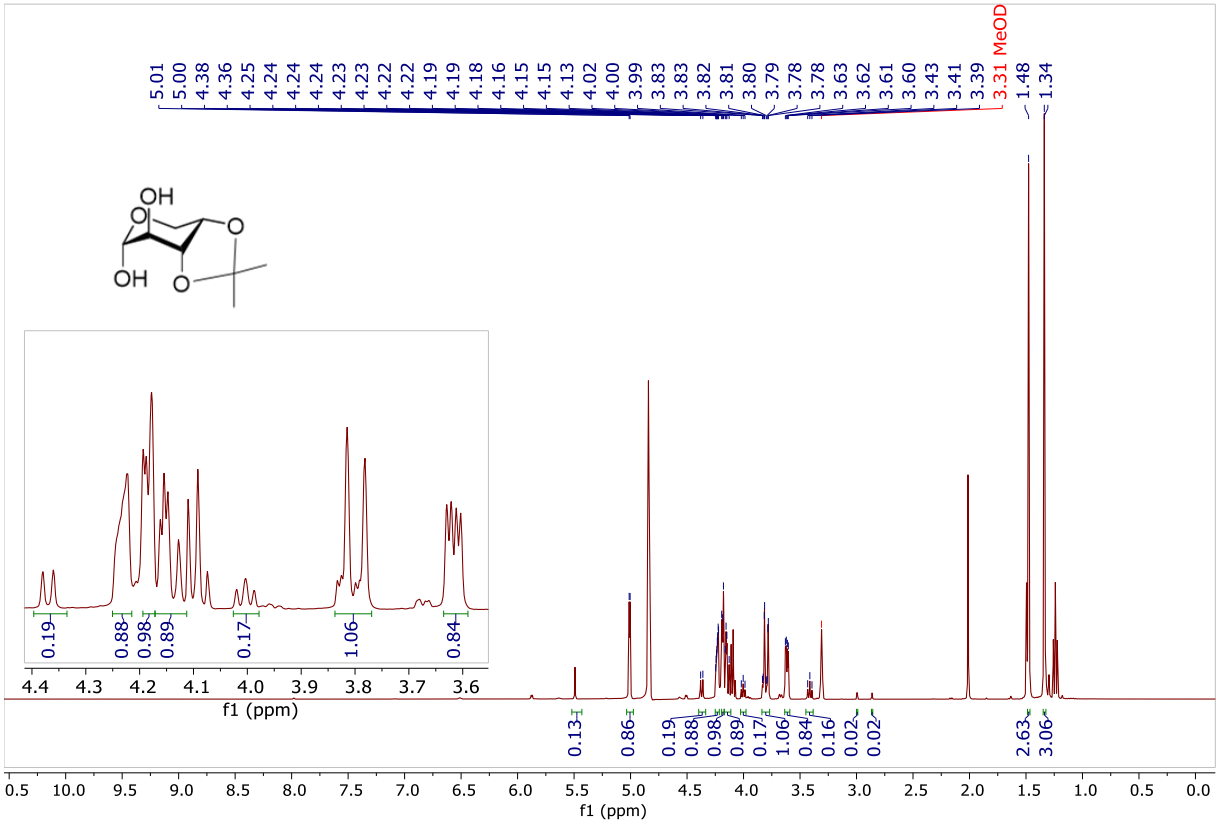


13C NMR (MeOD, 101 MHz)

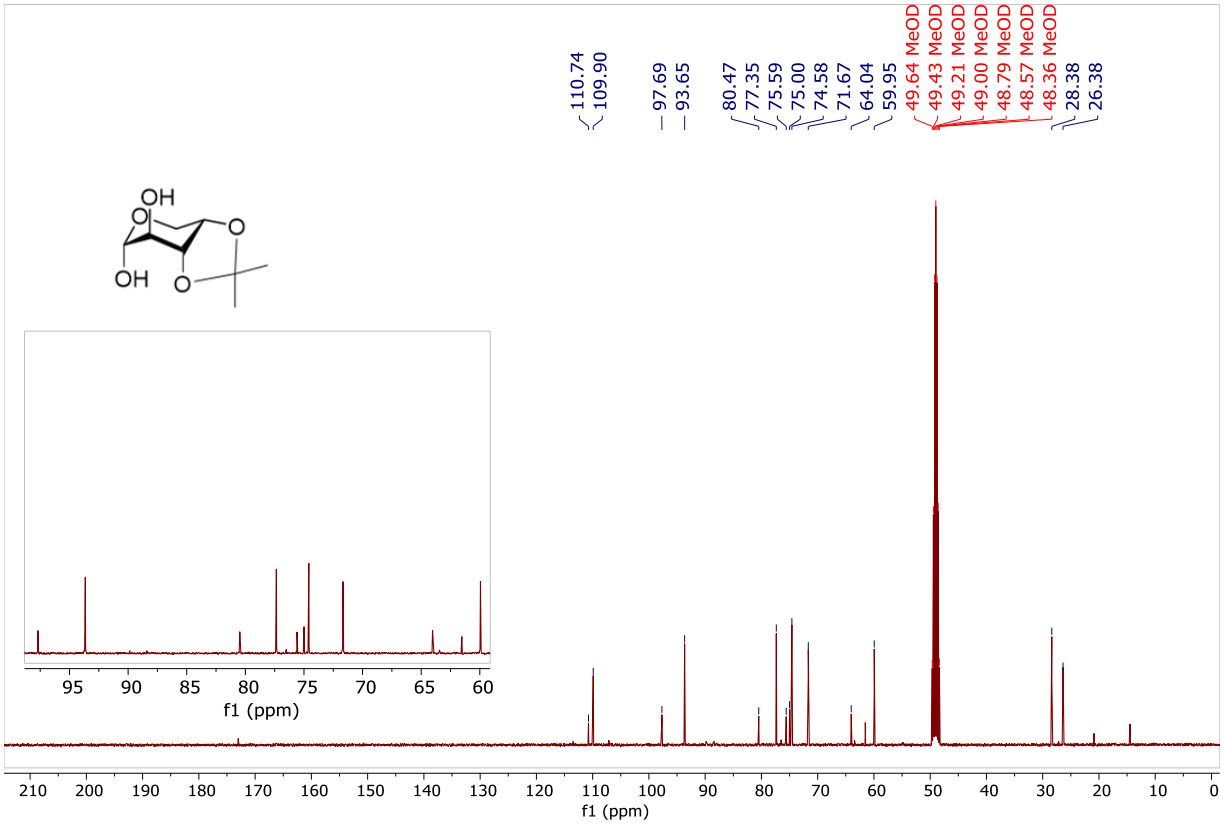


8.10 NMR-spectra of isolated 3,4-*O*-isopropylidene L-arabinose 6

1H NMR (MeOD, 400 MHz)

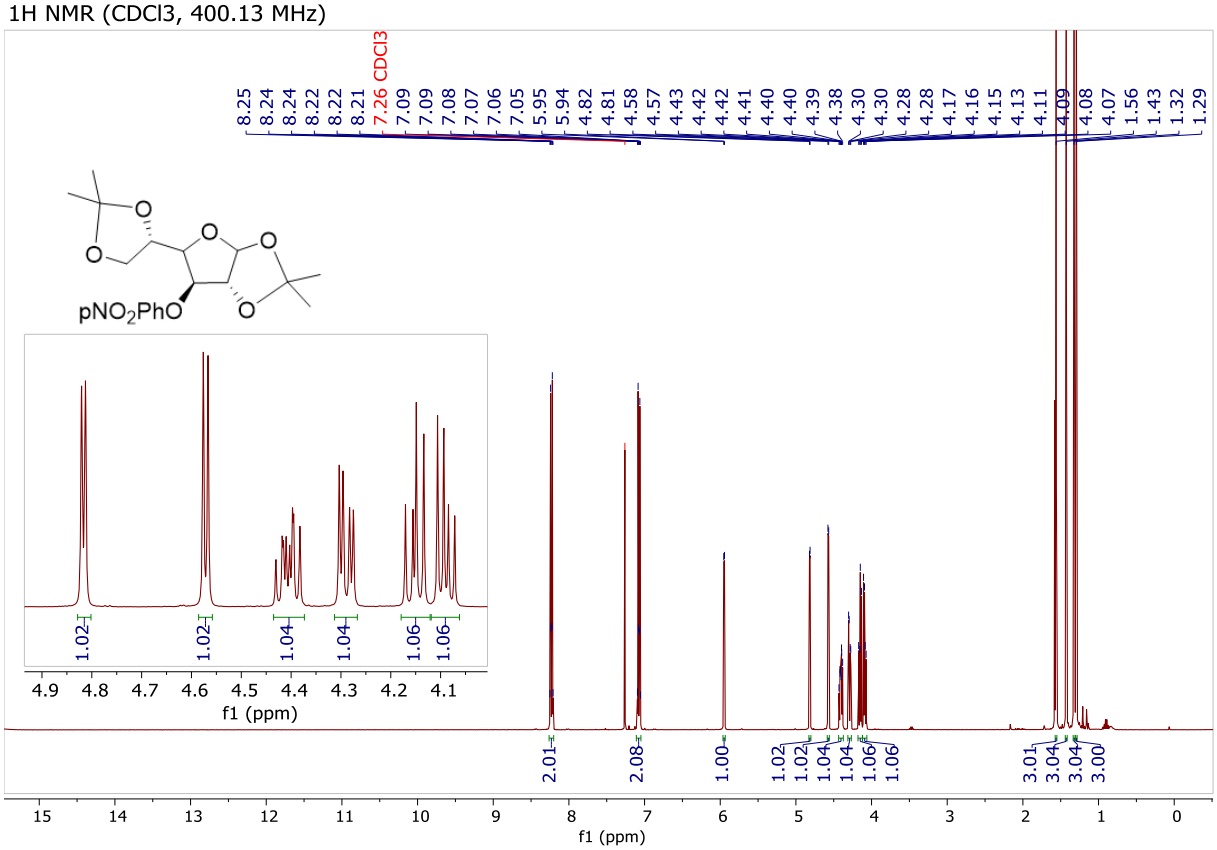


13C NMR (MeOD, 101 MHz)

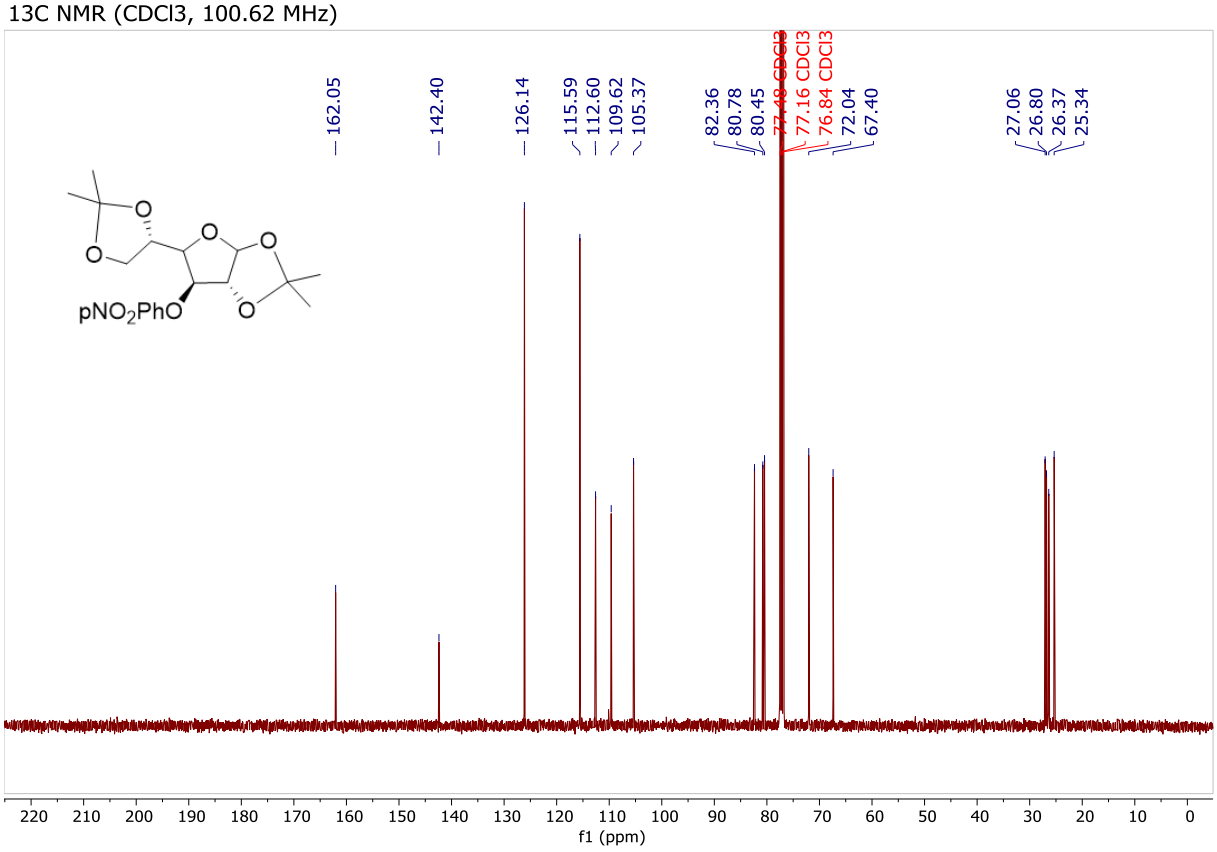


8.11 NMR-spectra of isolated 3-*O*-(4-nitrophenyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 31

1H NMR (CDCl3, 400.13 MHz)

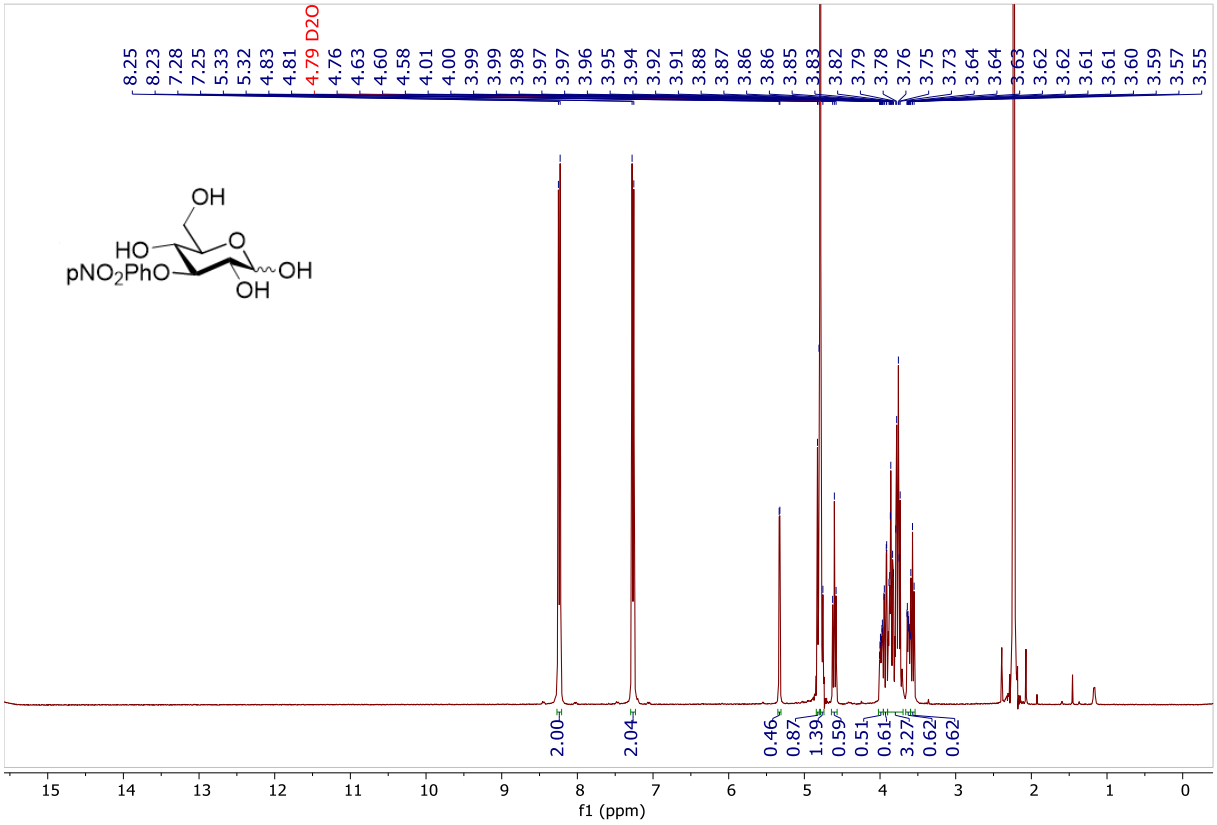


13C NMR (CDCl3, 100.62 MHz)

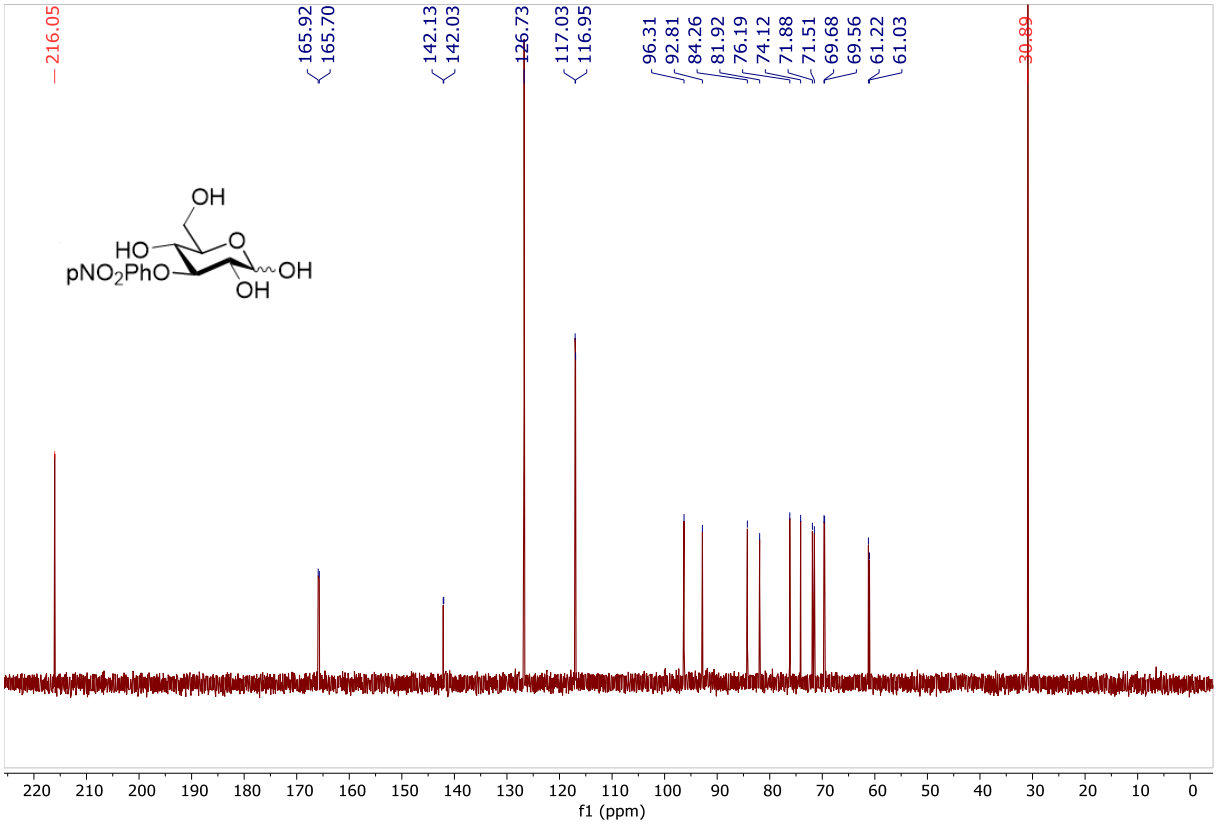


8.12 NMR-spectra of isolated 3-*O*-(4-nitrophenyl)-D-glucose 10

1H NMR (D2O, 400.13 MHz)



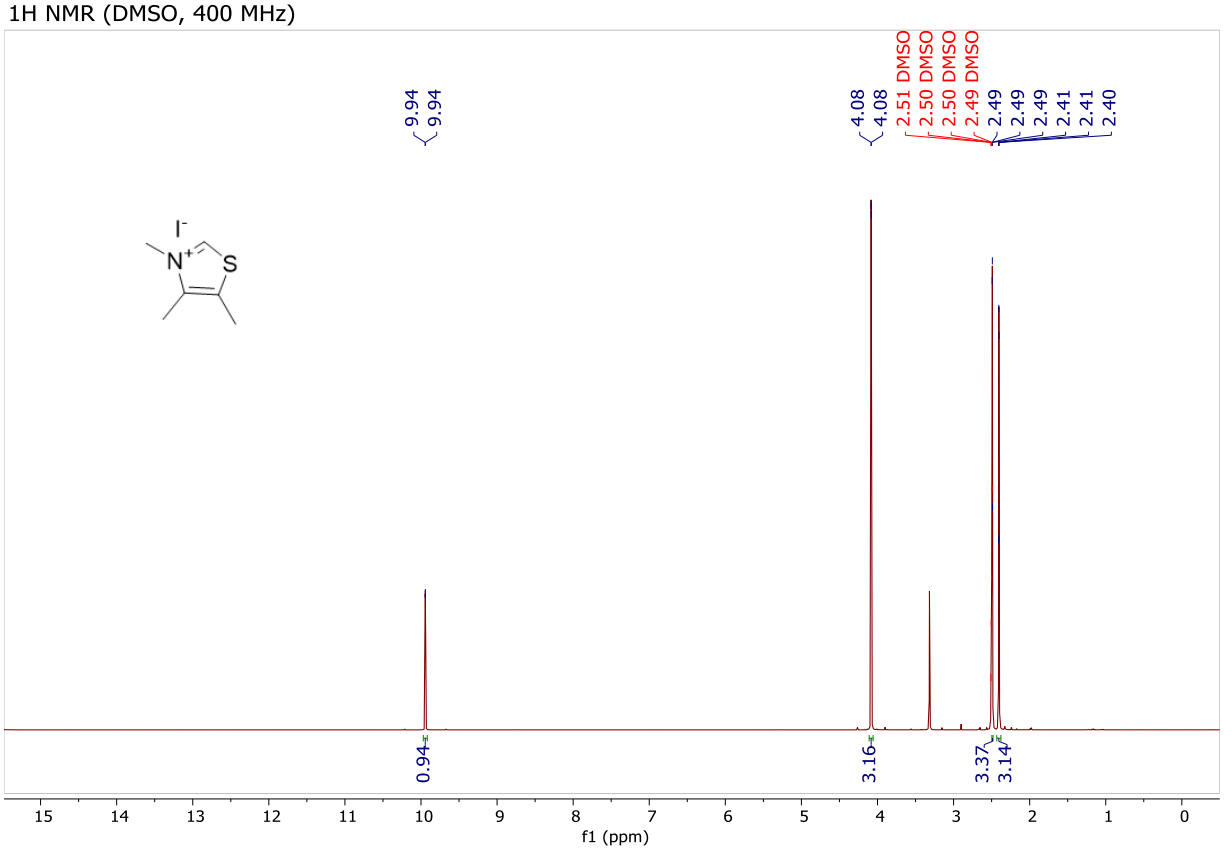
13C NMR (D2O, 100.62 MHz)



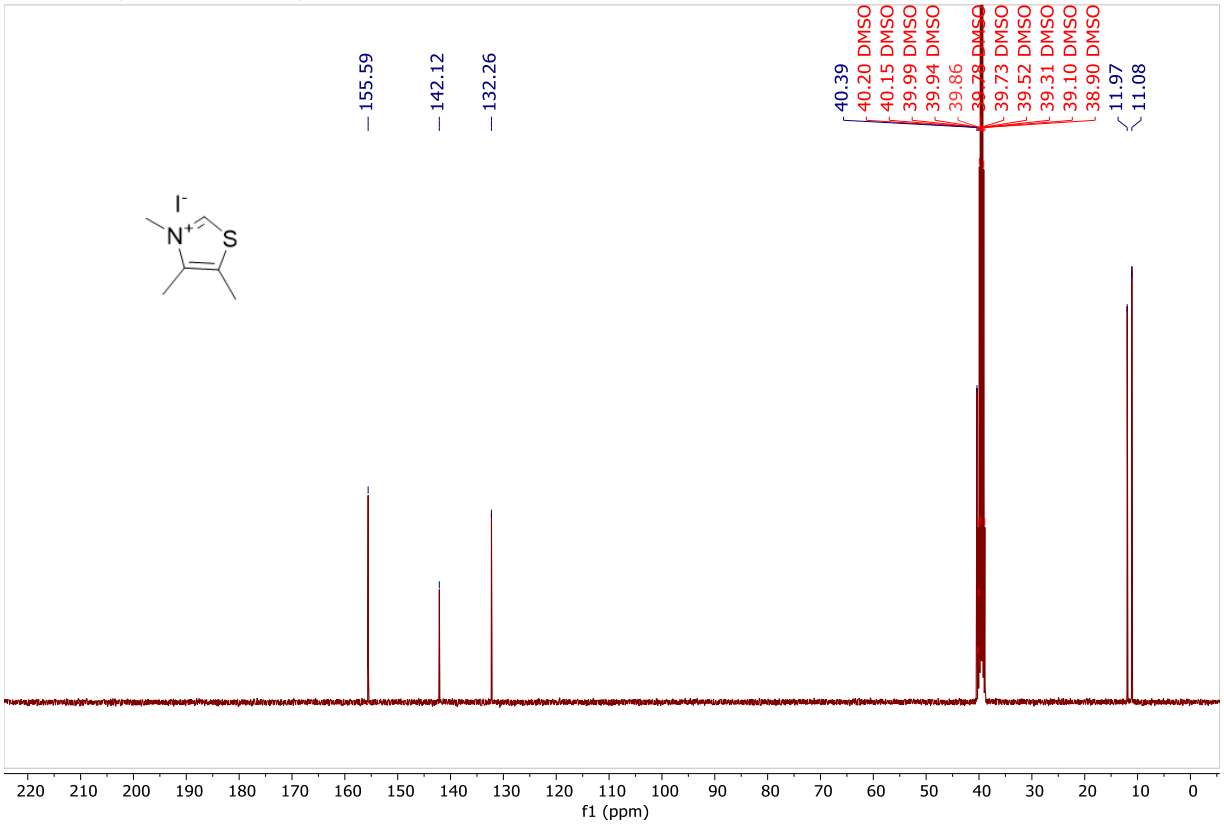
9 NMR spectra of precatalysts

9.1 NMR-spectra of isolated 3,4,5-trimethylthiazol-3-ium iodide 2

1H NMR (DMSO, 400 MHz)

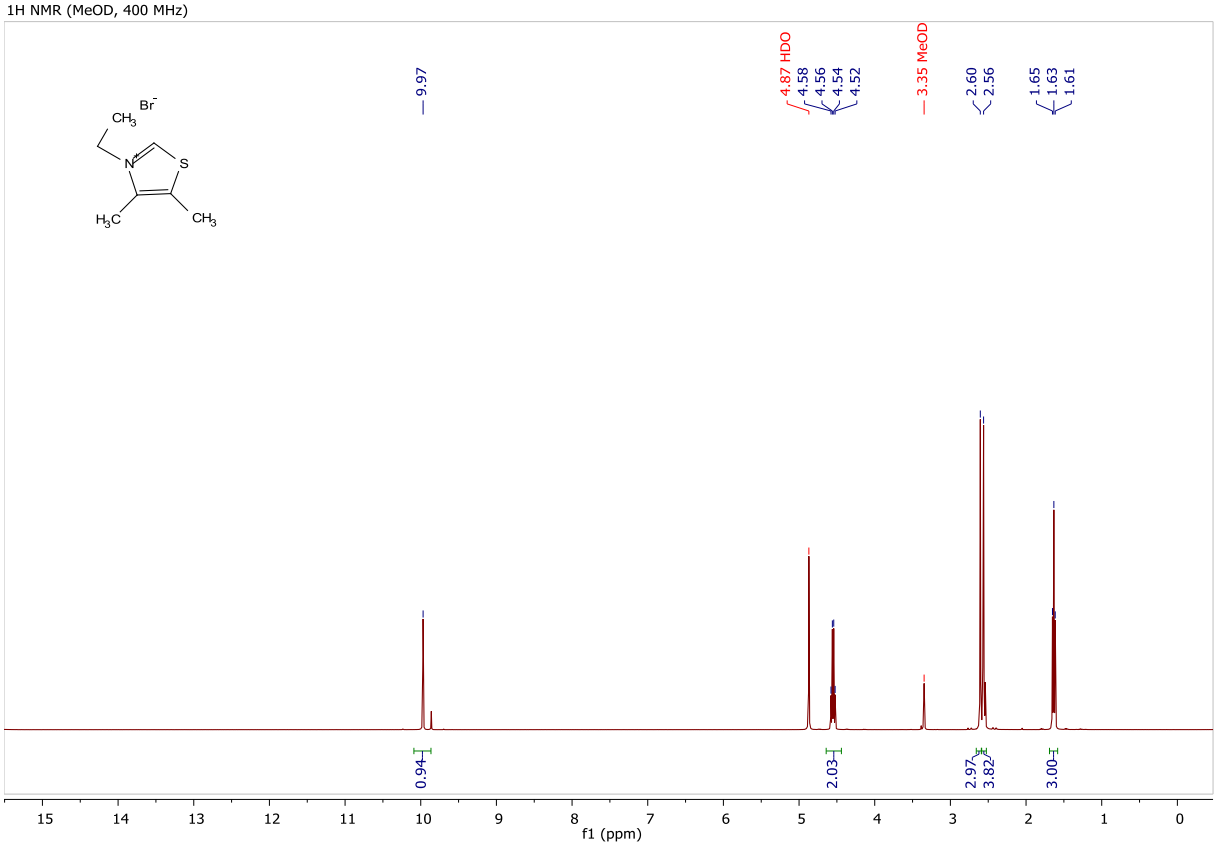


13C NMR (DMSO, 101 MHz)

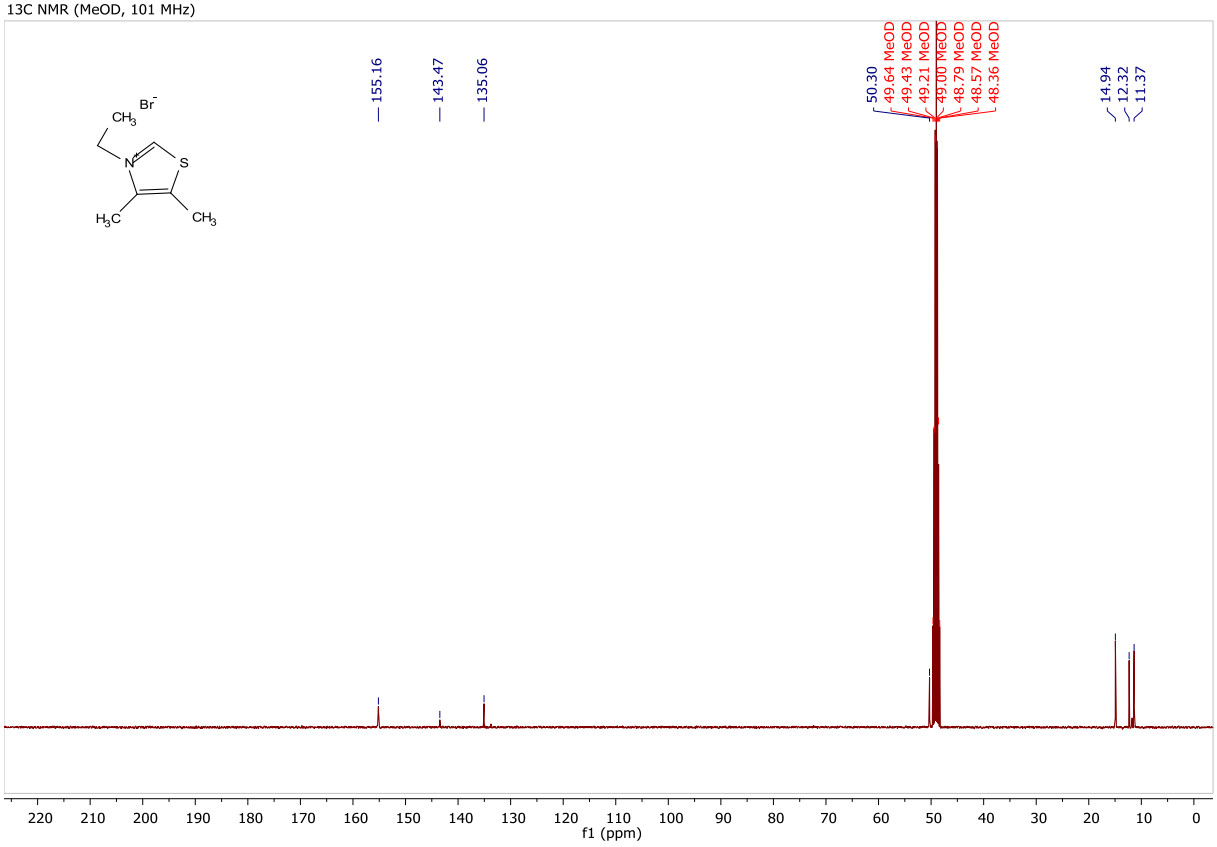


9.2 NMR-spectra of isolated 3-Ethyl-4,5-dimethylthiazol-3-ium iodide 40

1H NMR (MeOD, 400 MHz)

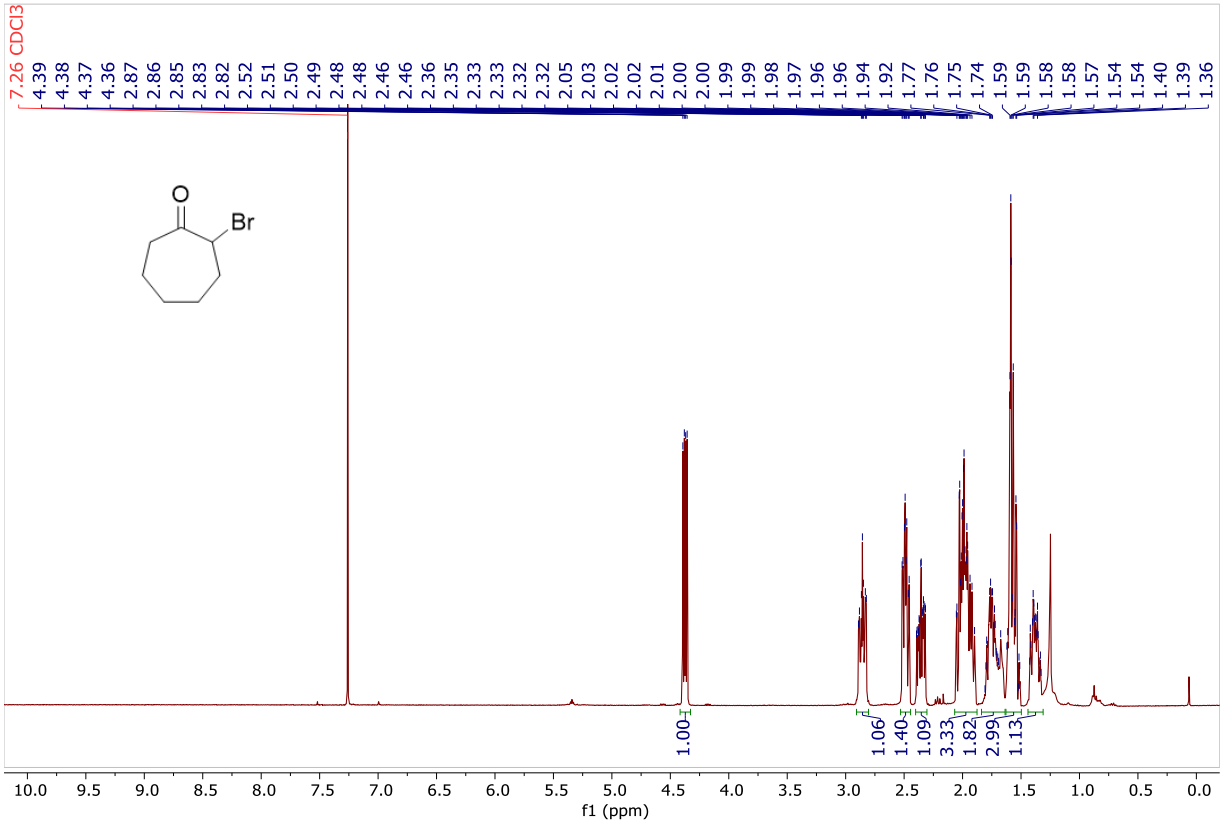


13C NMR (MeOD, 101 MHz)

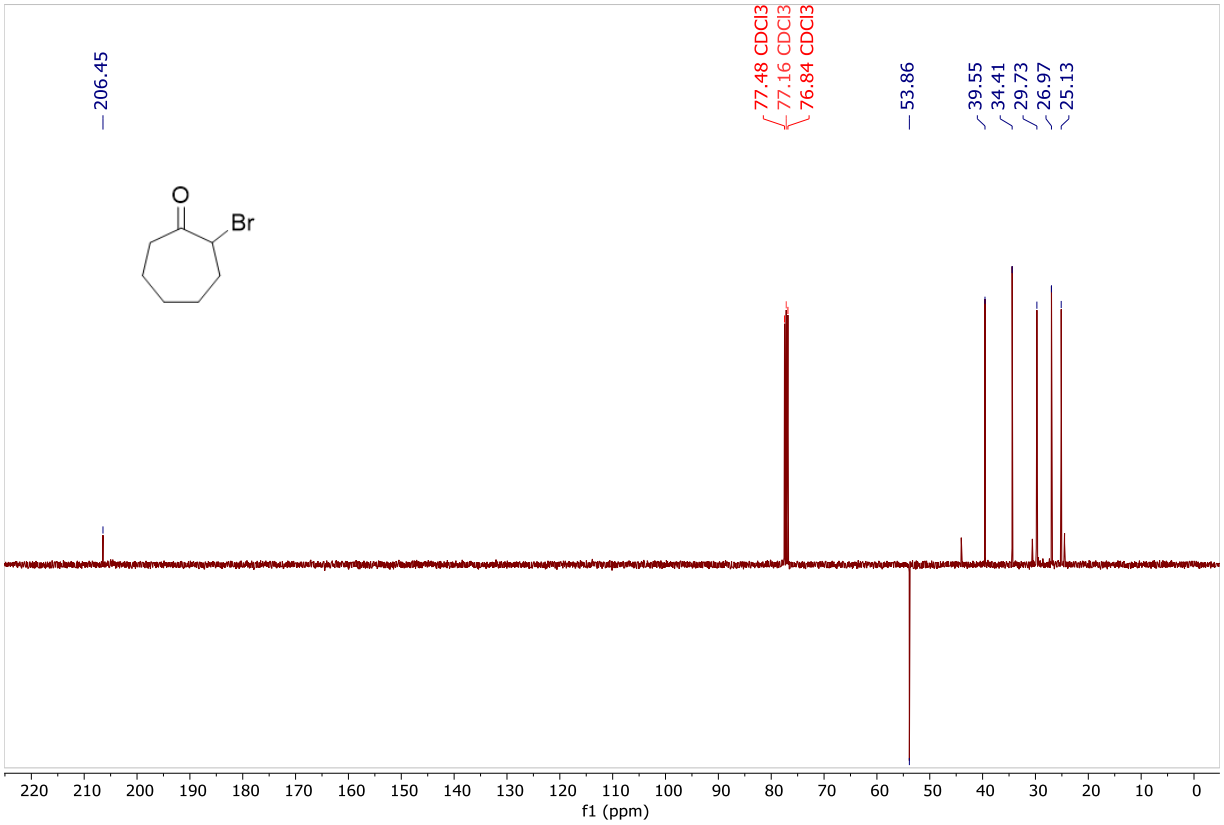


9.3 NMR-spectra of isolated 2-bromocycloheptanone 33

1H NMR (CDCl3, 400 MHz)

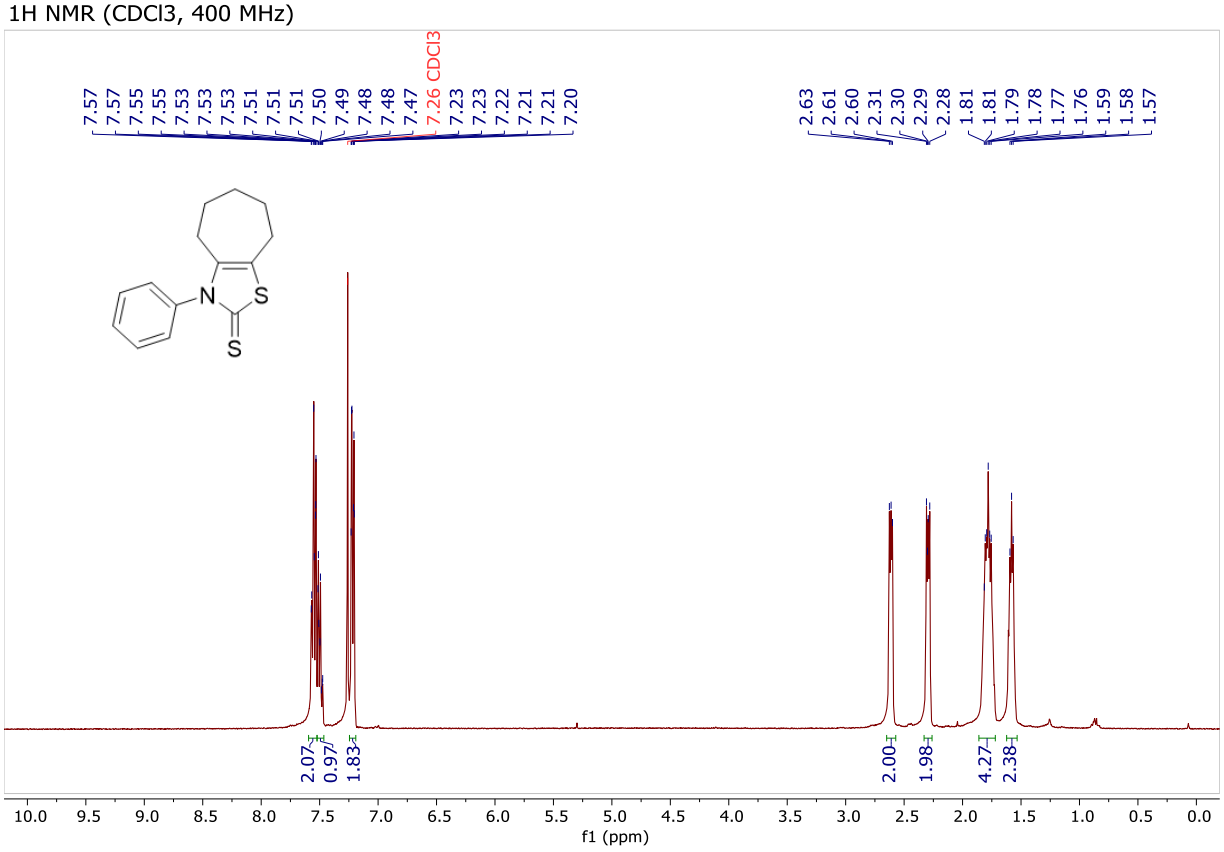


13C NMR (CDCl3, 101 MHz)

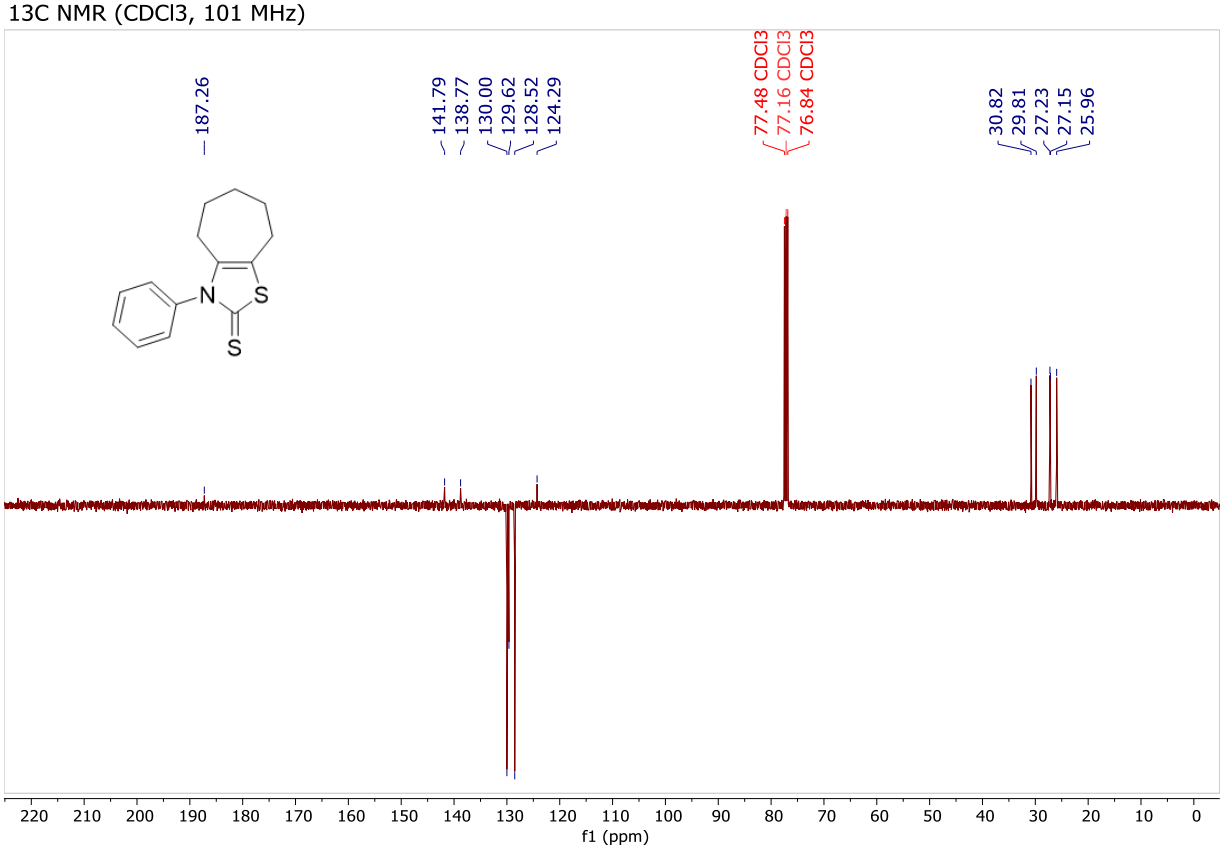


9.4 NMR-spectra of isolated 3-phenyl-3,4,5,6,7,8-hexahydro-2*H*-cyclohepta[*d*]thiazole-2-thione 34

1H NMR (CDCl3, 400 MHz)

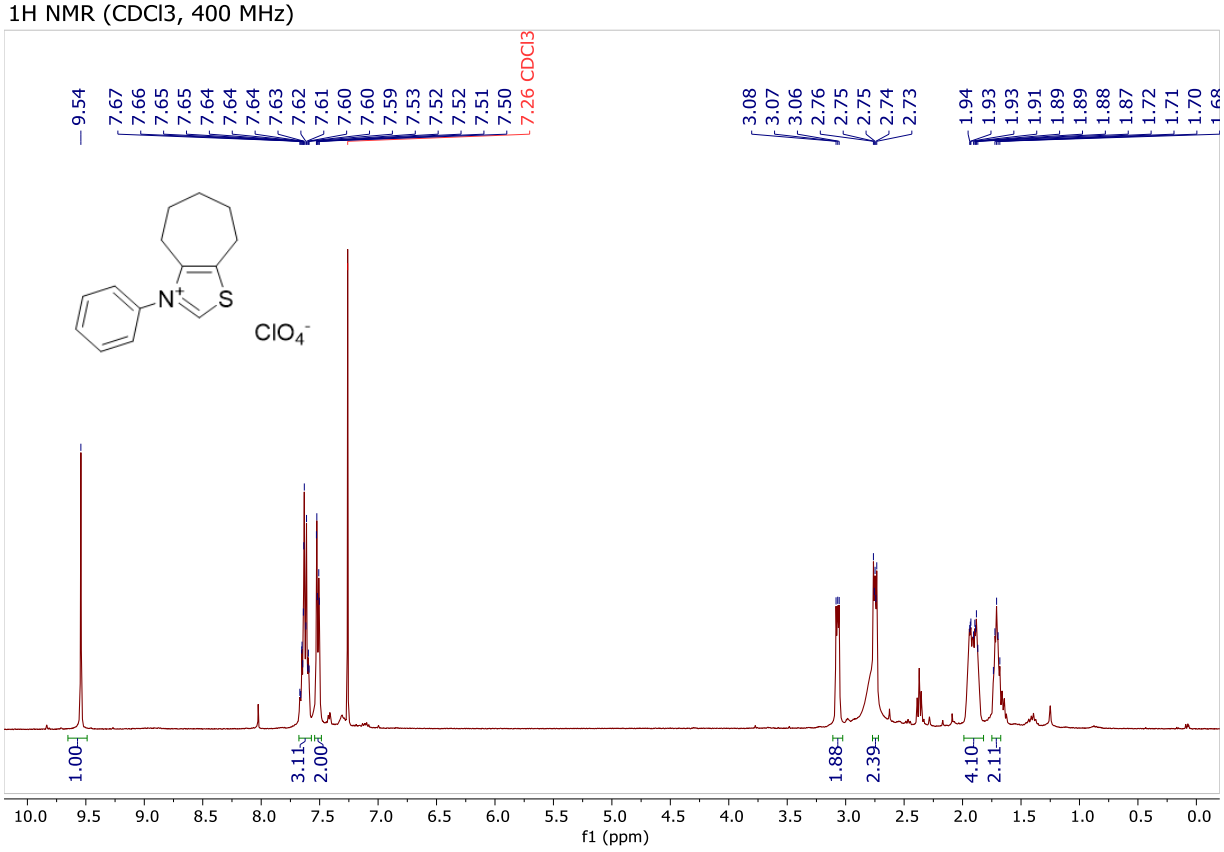


13C NMR (CDCl3, 101 MHz)

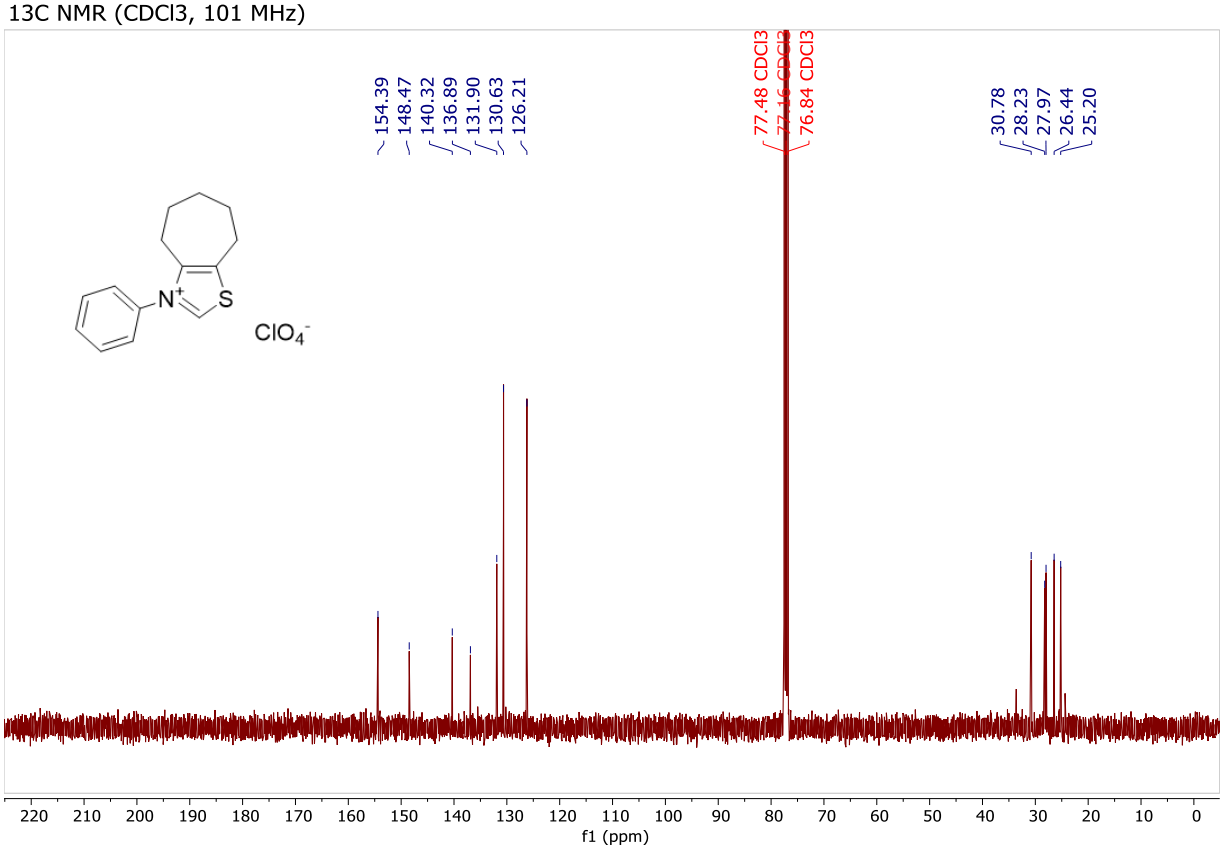


9.5 NMR-spectra of isolated 3-phenyl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate 12

1H NMR (CDCl3, 400 MHz)

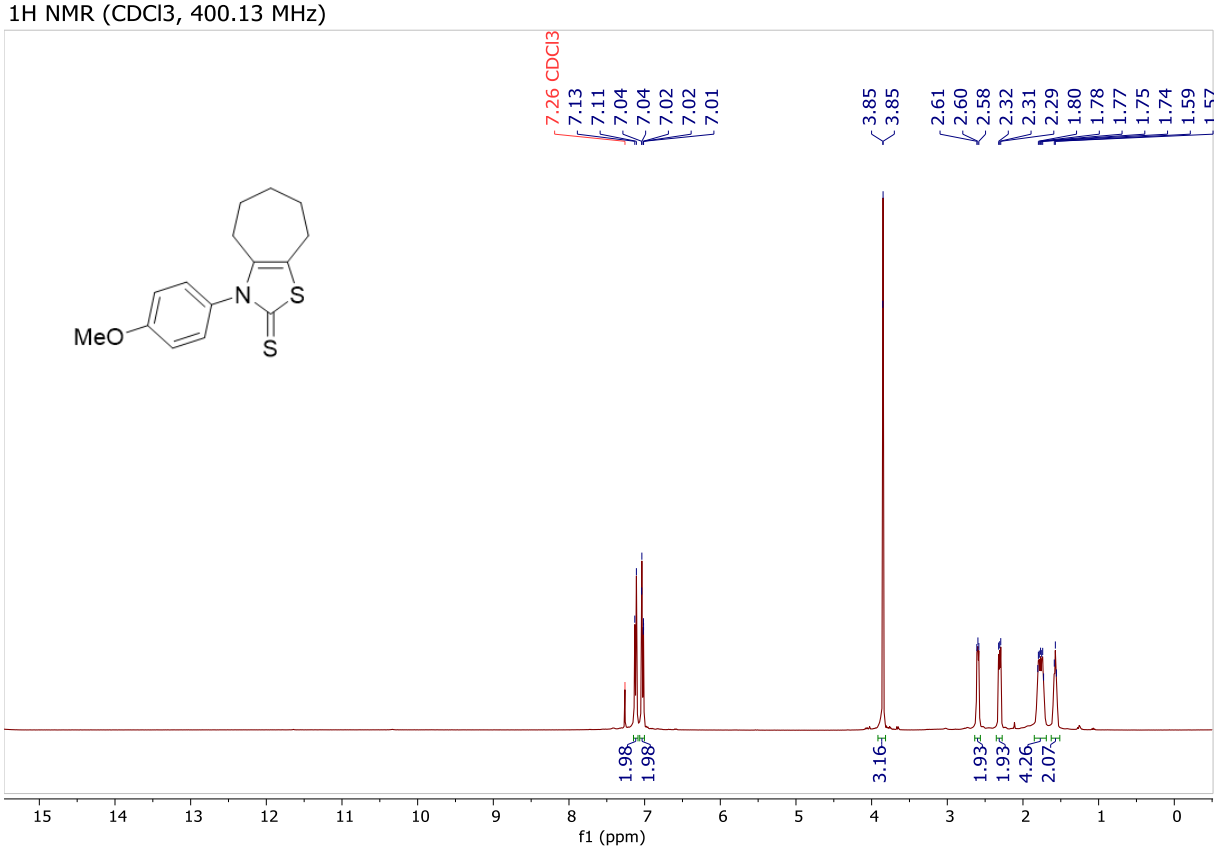


13C NMR (CDCl3, 101 MHz)

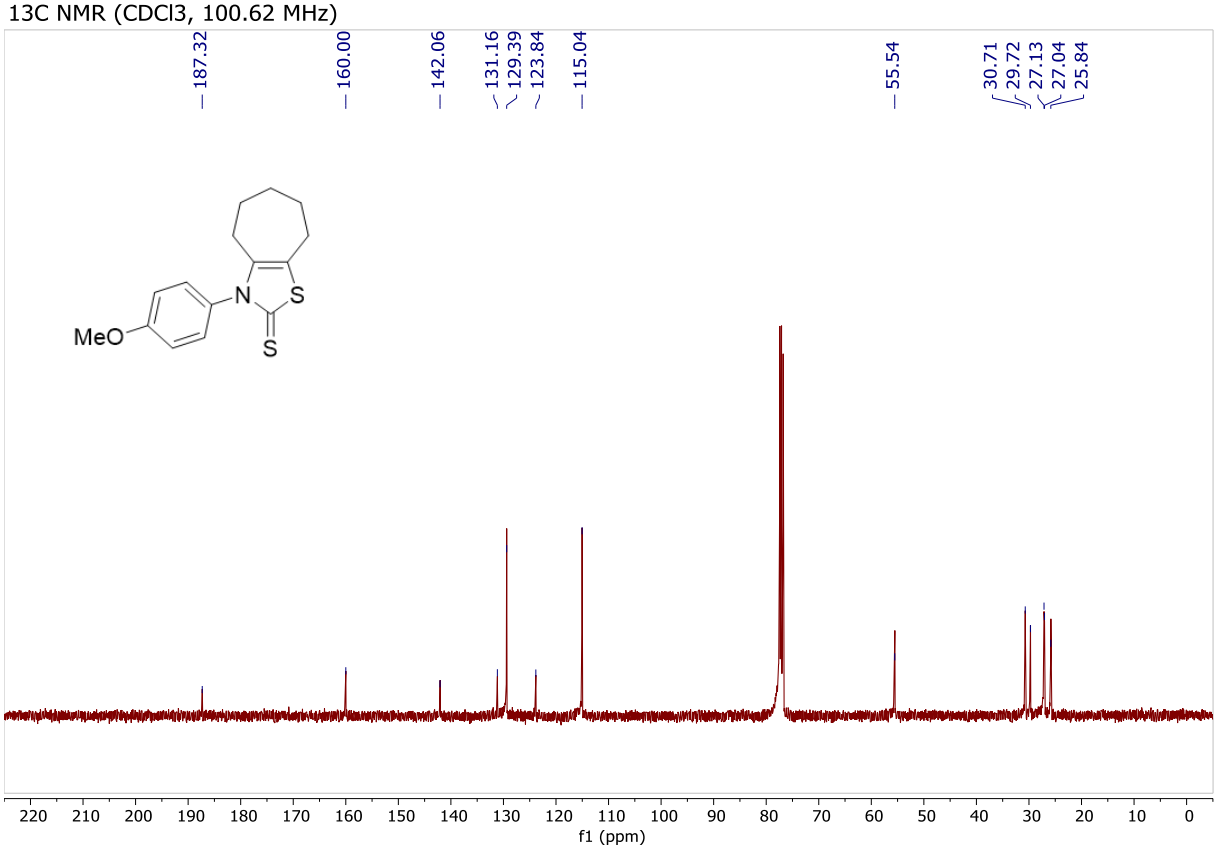


9.6 NMR-spectra of isolated 3-(4-methoxyphenyl)-3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione 35

1H NMR (CDCl3, 400.13 MHz)

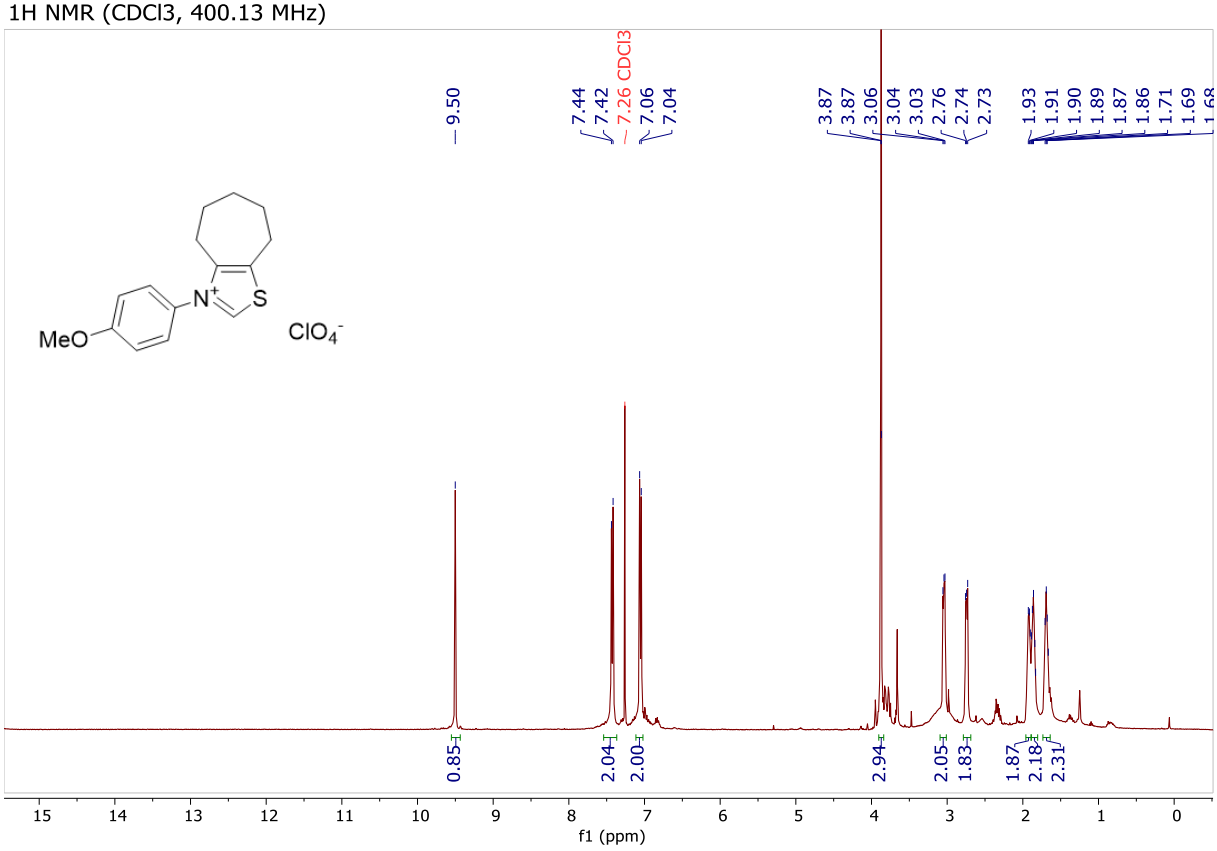


13C NMR (CDCl3, 100.62 MHz)

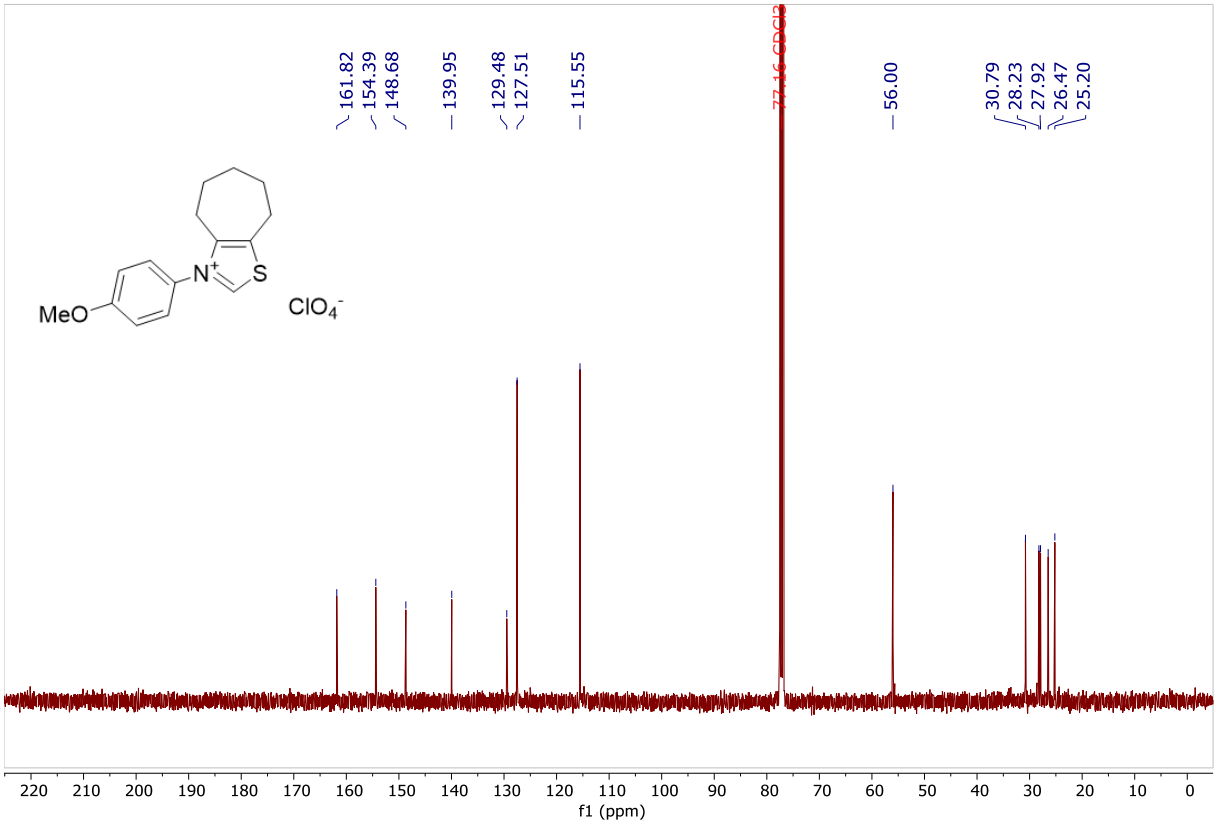


9.7 NMR-spectra of isolated 3-(4-methoxyphenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[d]thiazol-3-ium perchlorate 13

1H NMR (CDCl3, 400.13 MHz)

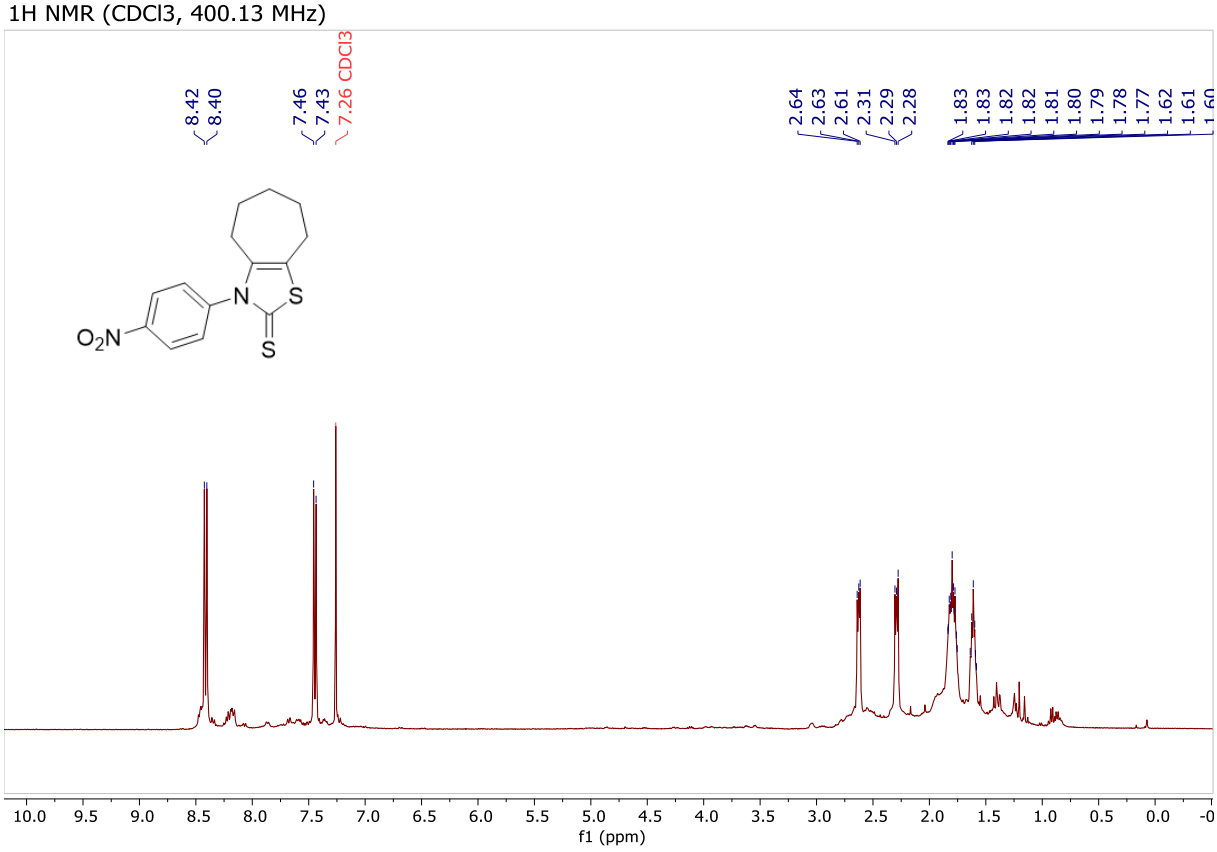


13C NMR (CDCl3, 100.62 MHz)

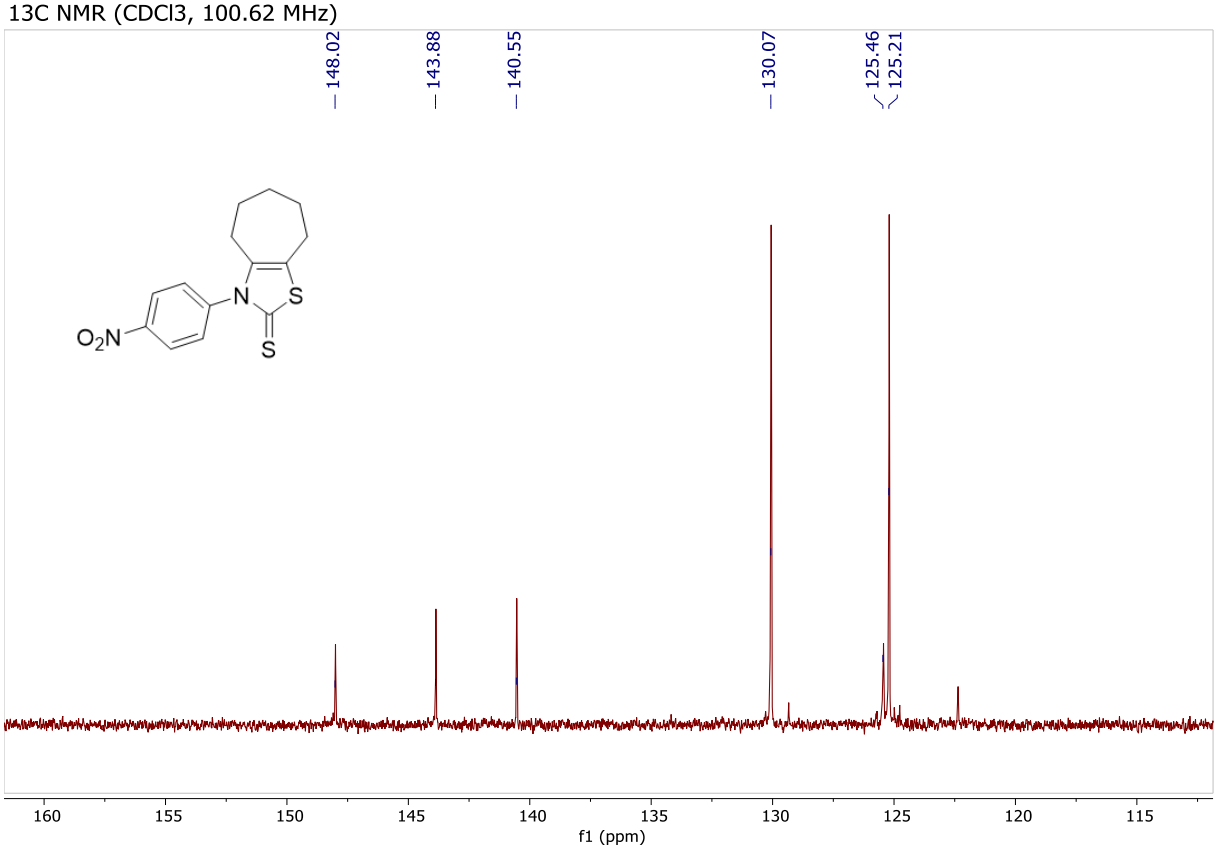


9.8 NMR-spectra of crude 3-(4-nitroxyphenyl)-3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione 36

1H NMR (CDCl3, 400.13 MHz)

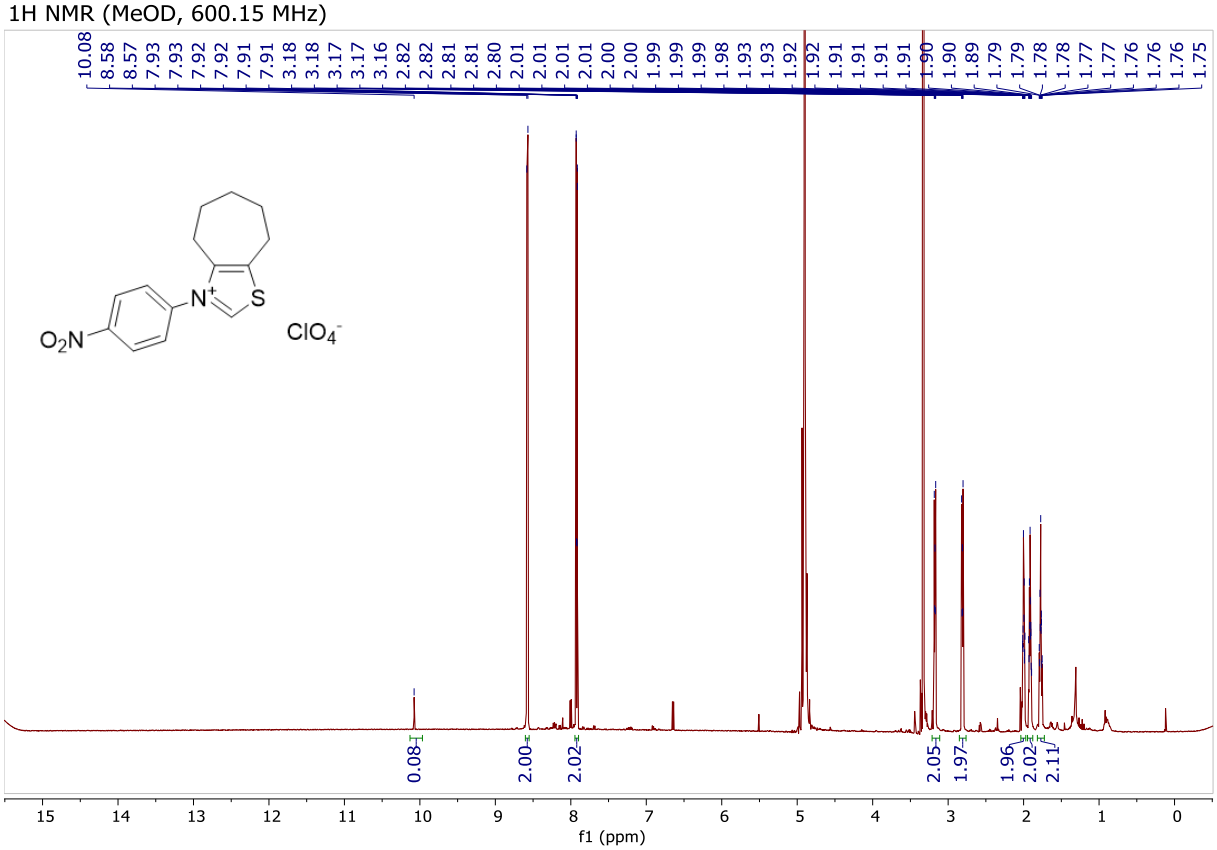


13C NMR (CDCl3, 100.62 MHz)

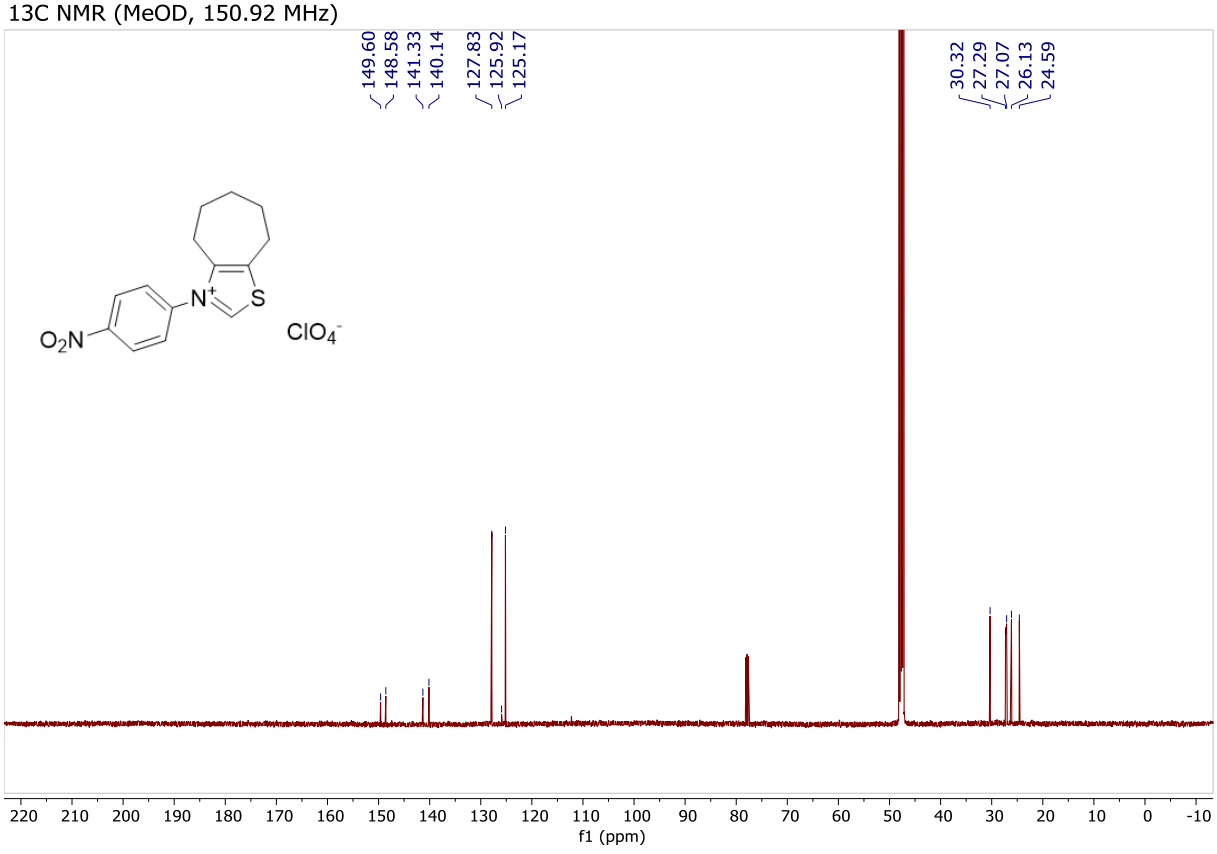


9.9 NMR-spectra of isolated 3-(4-nitrophenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate 14

1H NMR (MeOD, 600.15 MHz)

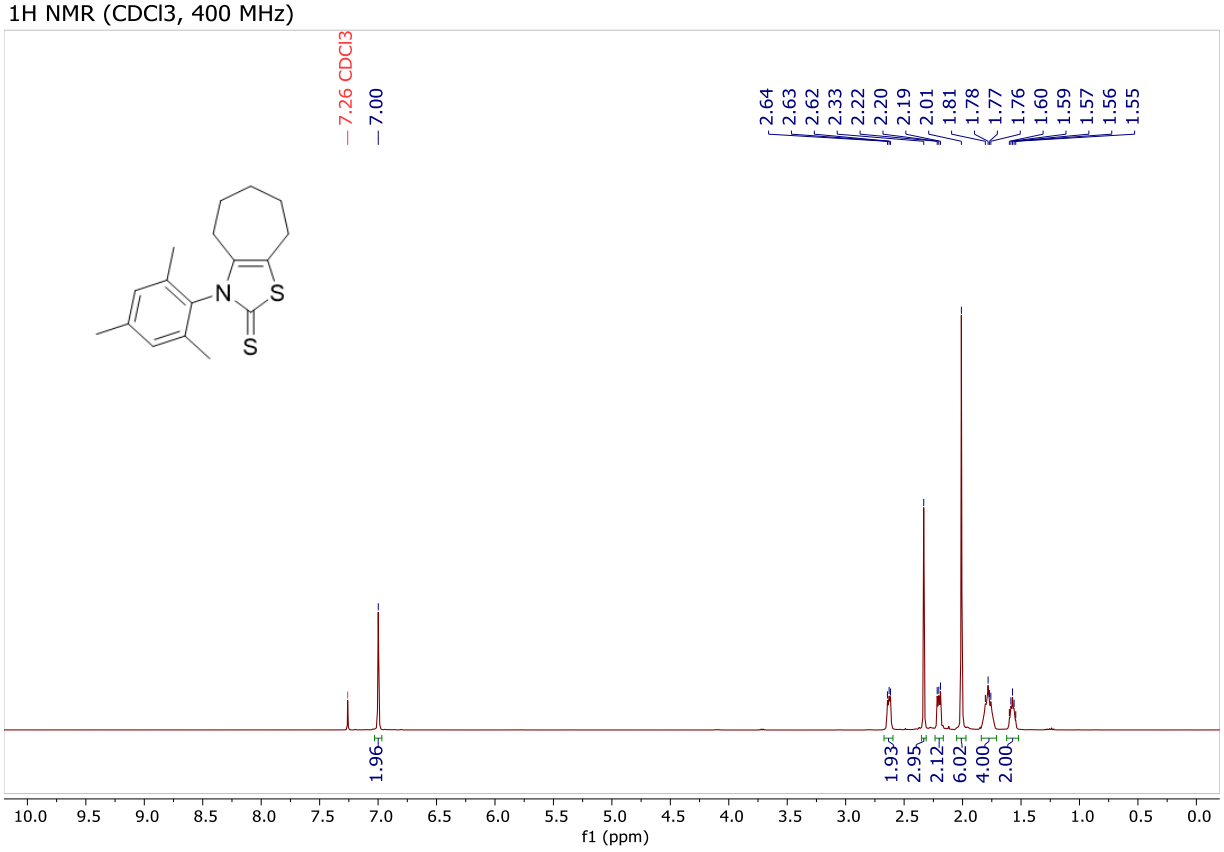


13C NMR (MeOD, 150.92 MHz)

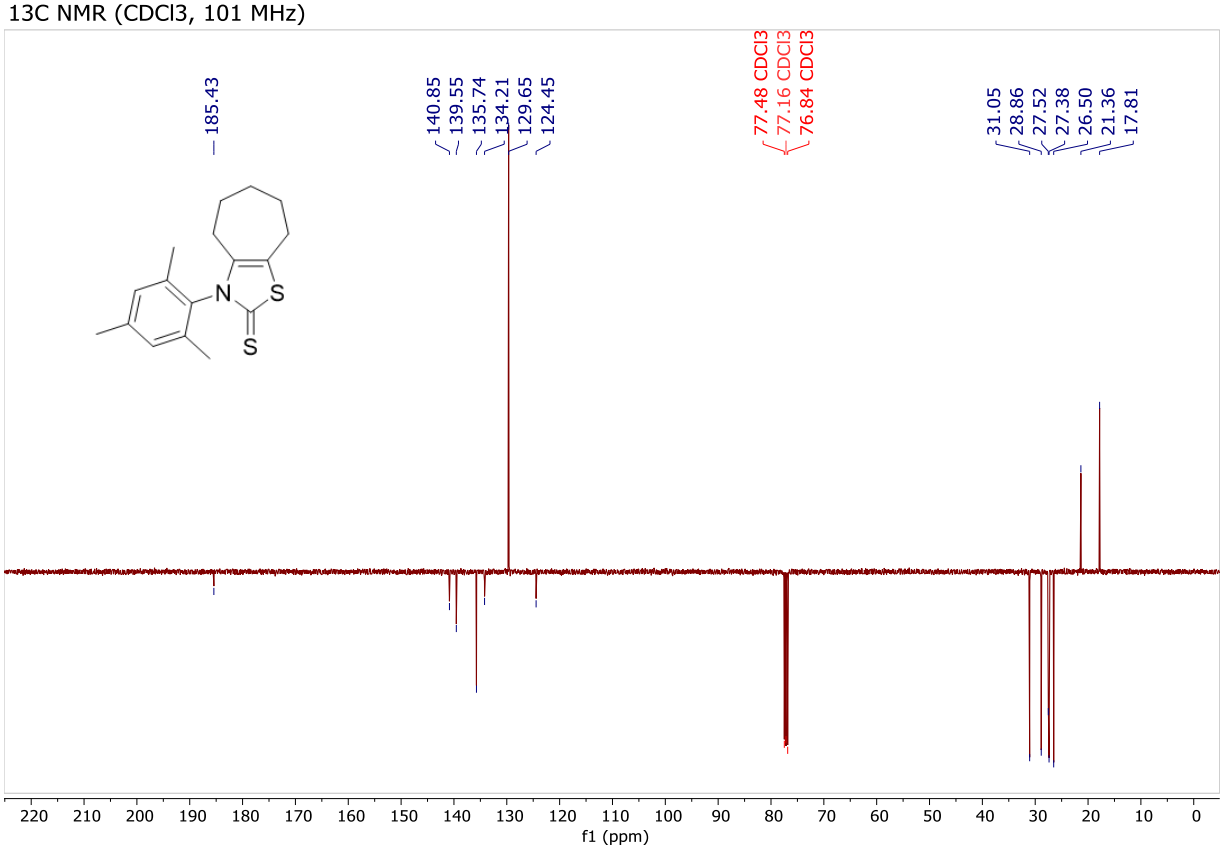


9.10 NMR-spectra of isolated 3-mesityl-3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione 37

1H NMR (CDCl3, 400 MHz)

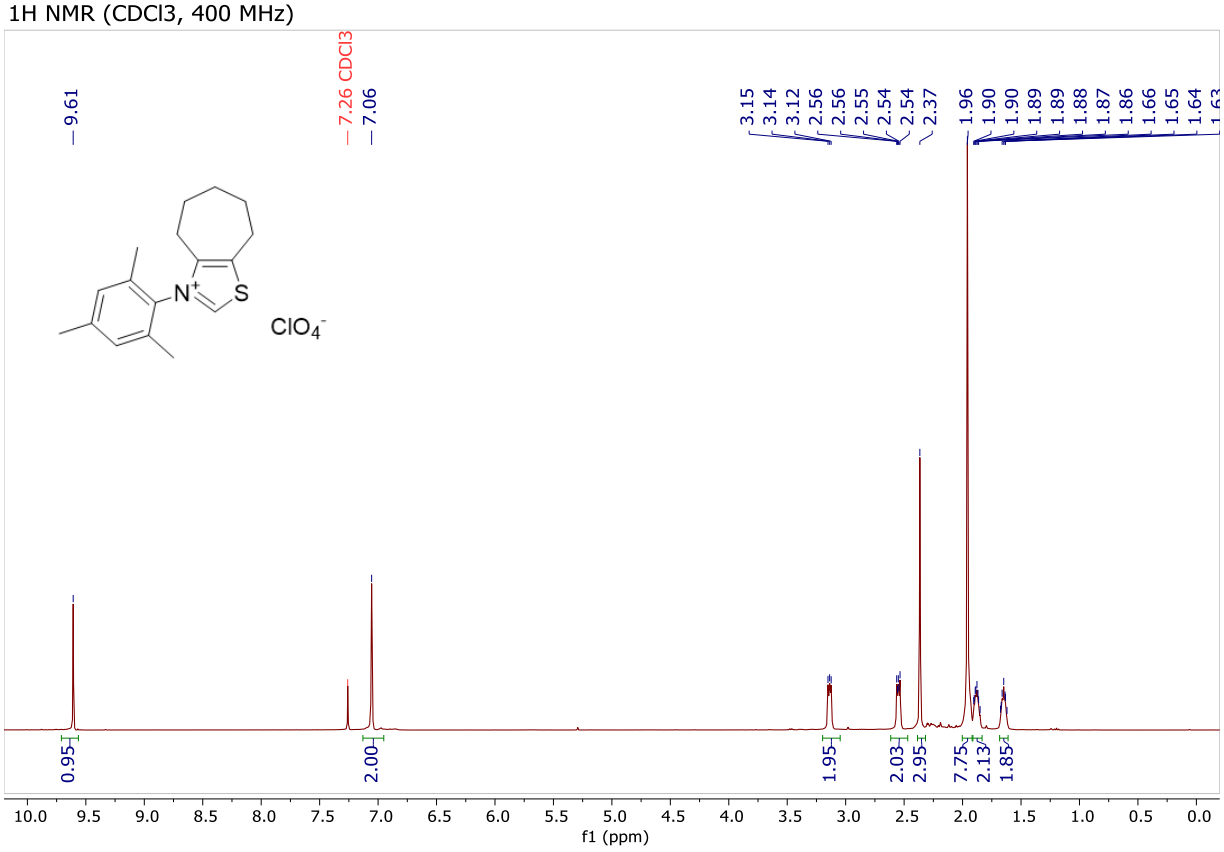


13C NMR (CDCl3, 101 MHz)

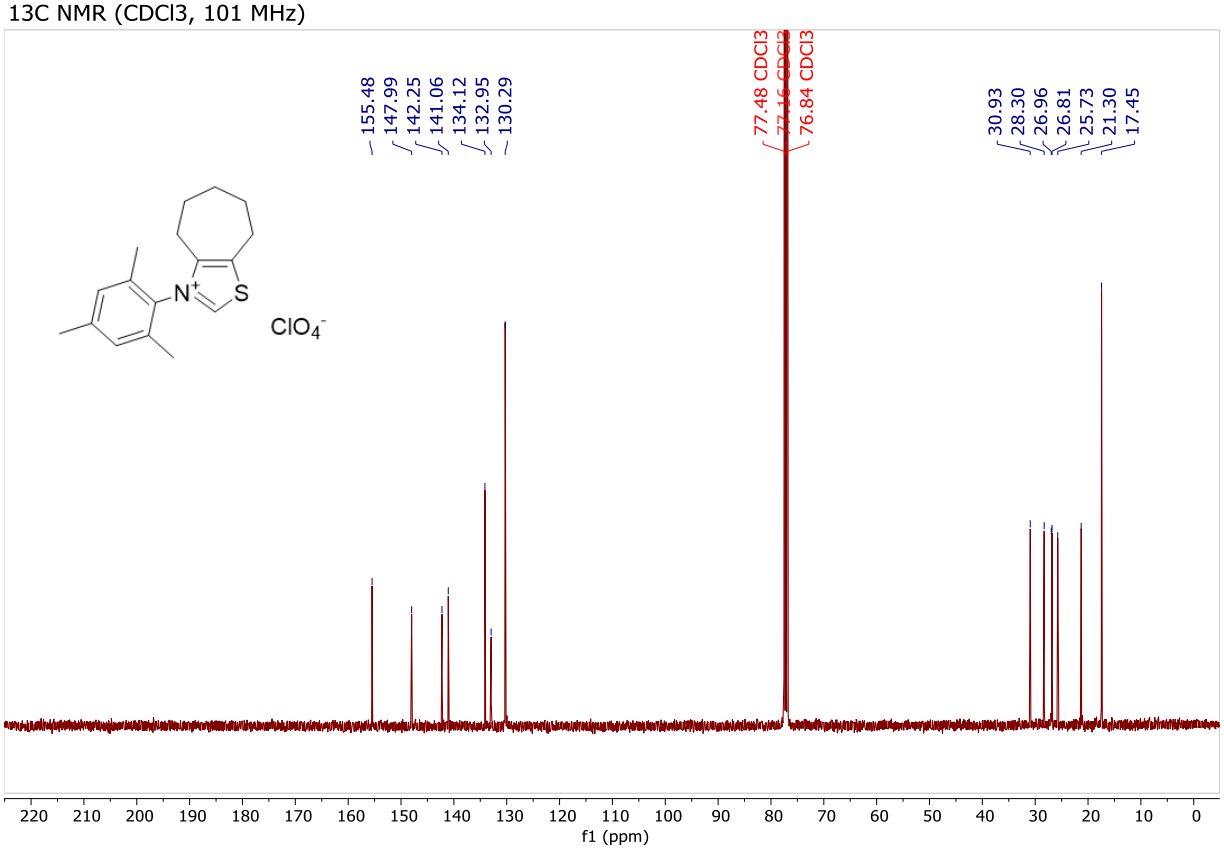


9.11 NMR-spectra of isolated 3-mesityl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate 15

1H NMR (CDCl3, 400 MHz)

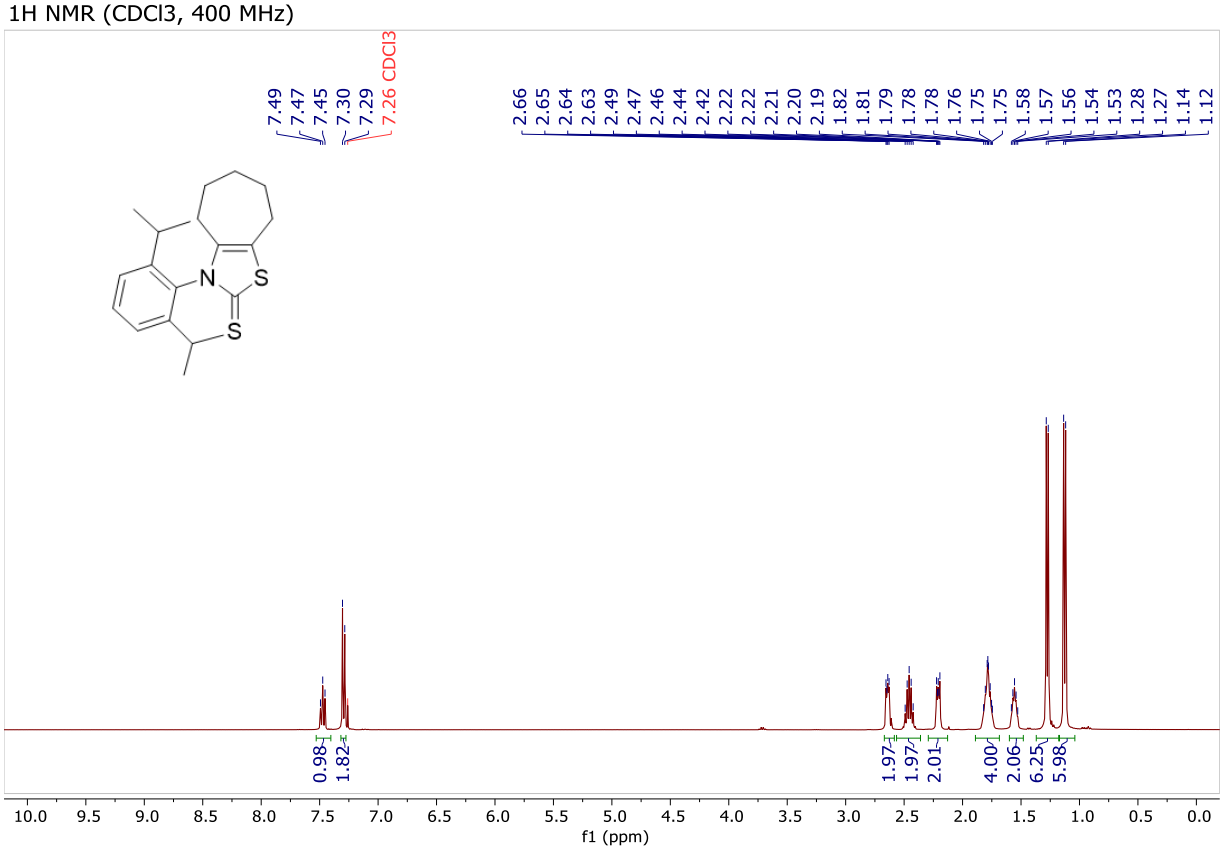


13C NMR (CDCl3, 101 MHz)

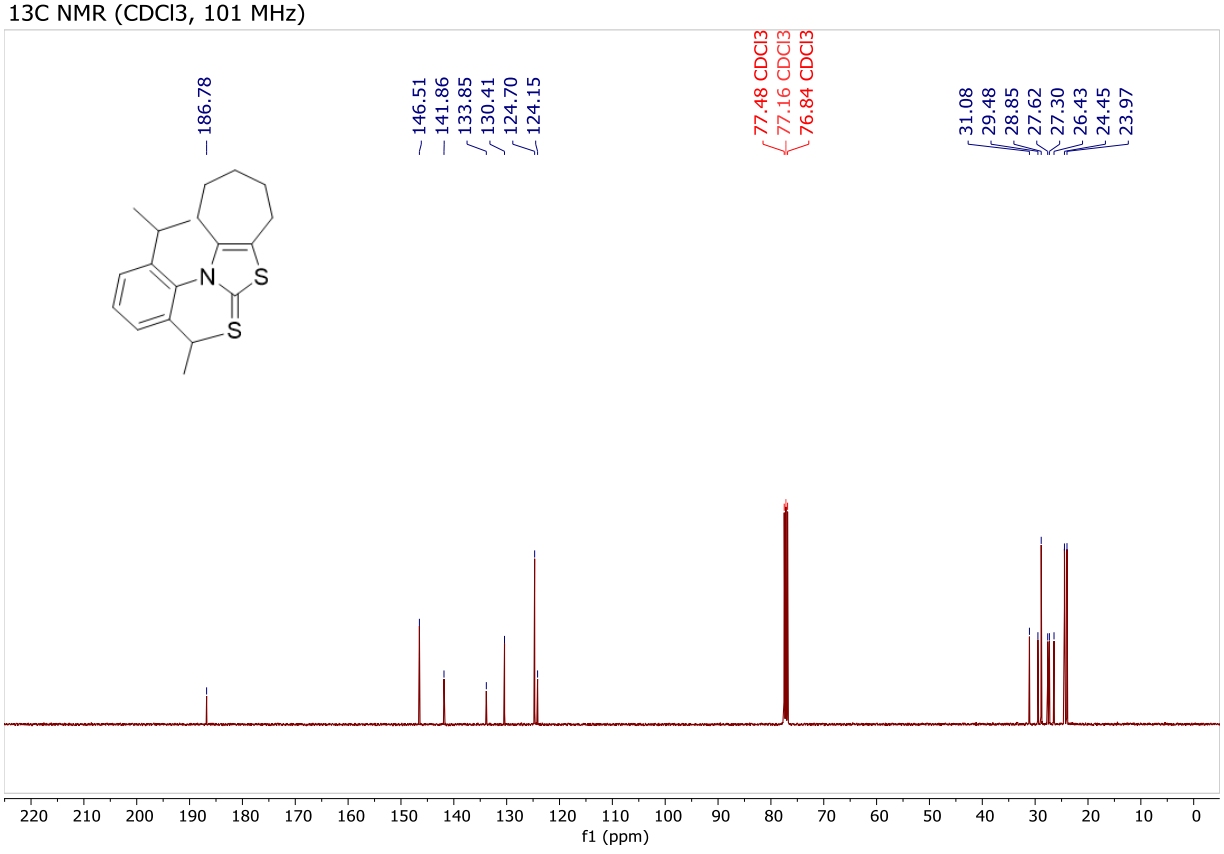


9.12 NMR-spectra of isolated 3-(2,6-diisopropylphenyl)-3,4,5,6,7,8-hexahydro-2H-cyclohepta[d]thiazole-2-thione 38

1H NMR (CDCl3, 400 MHz)

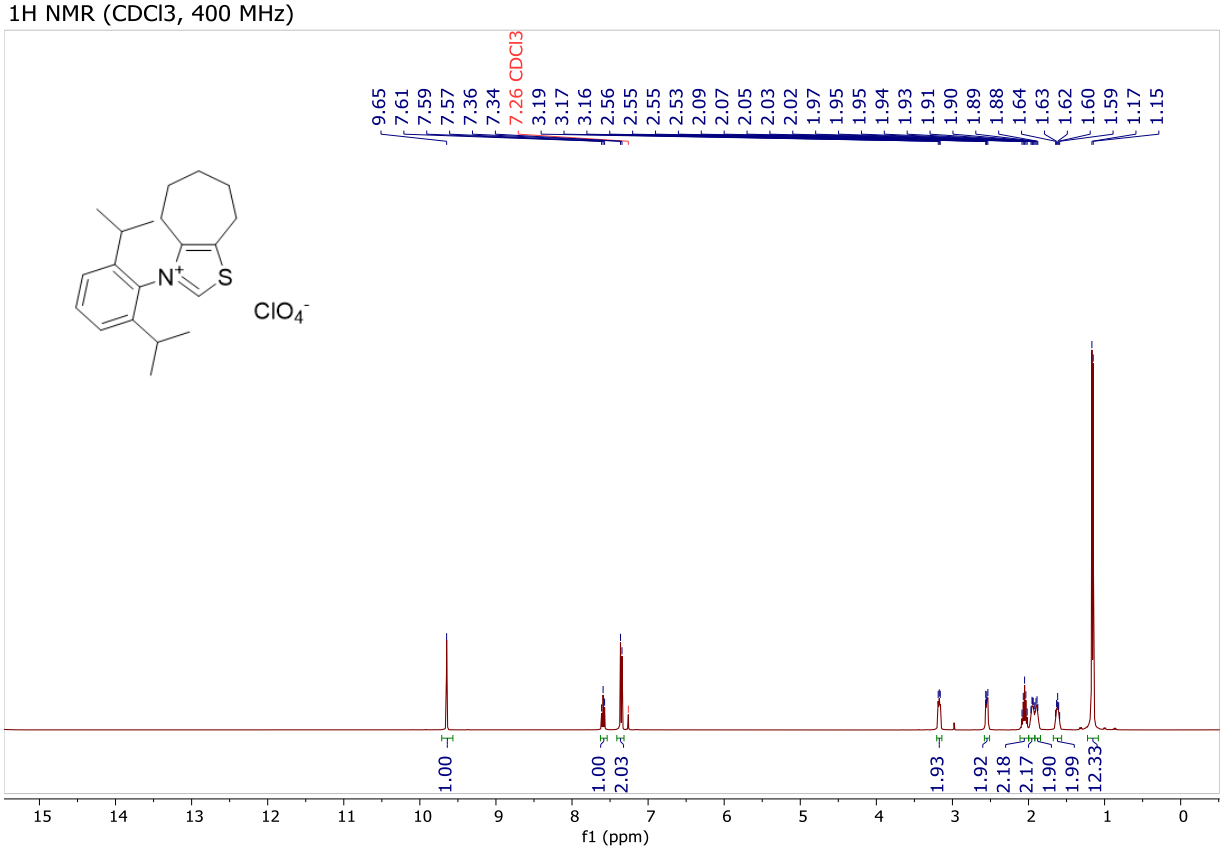


13C NMR (CDCl3, 101 MHz)

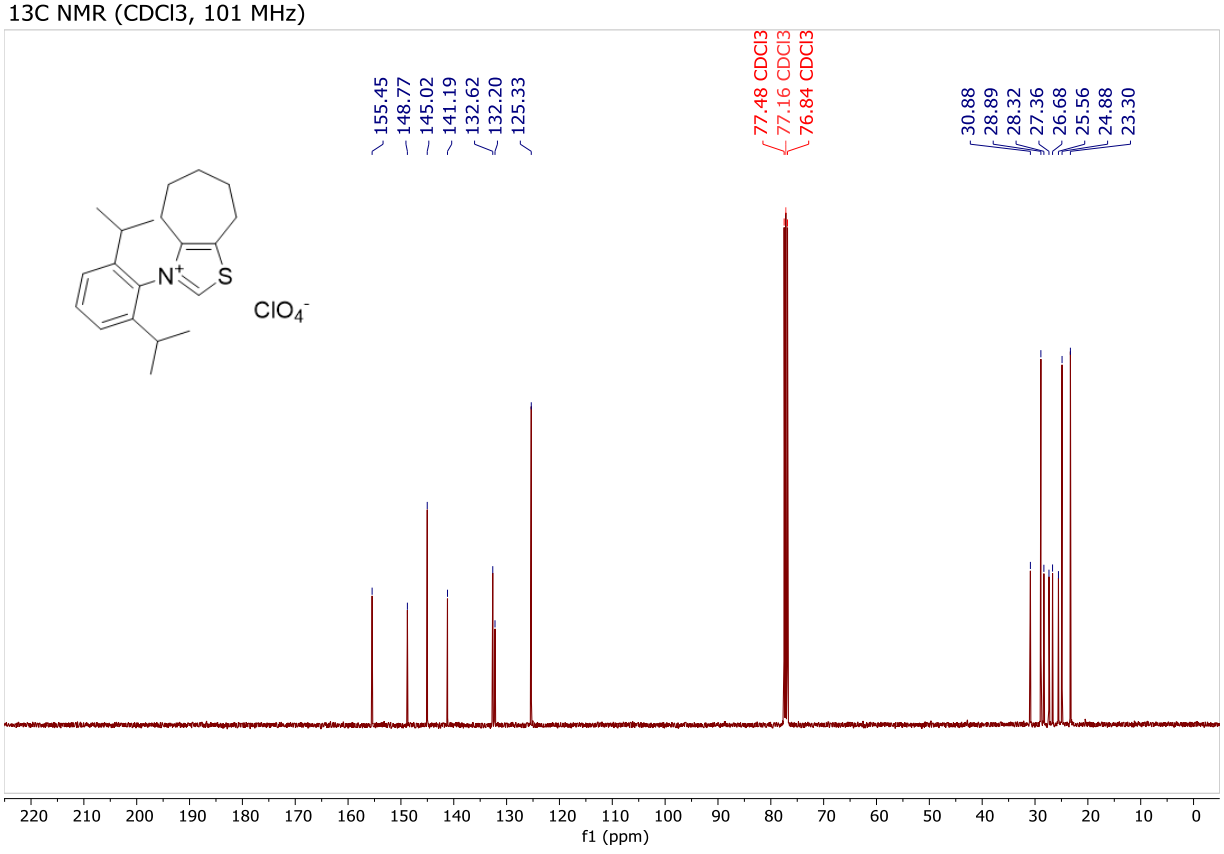


9.13 NMR-spectra of isolated 3-(2,6-diisopropylphenyl)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-3-ium perchlorate 16

1H NMR (CDCl3, 400 MHz)

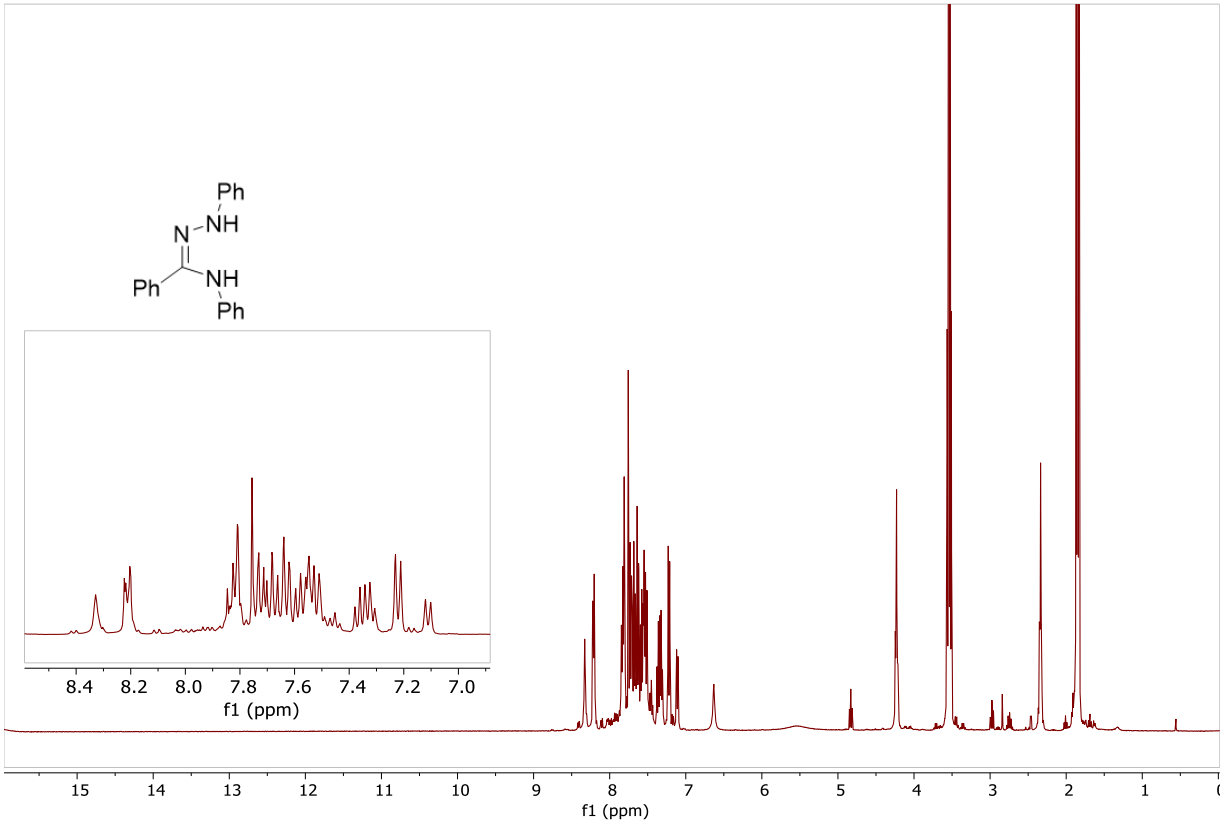


13C NMR (CDCl3, 101 MHz)

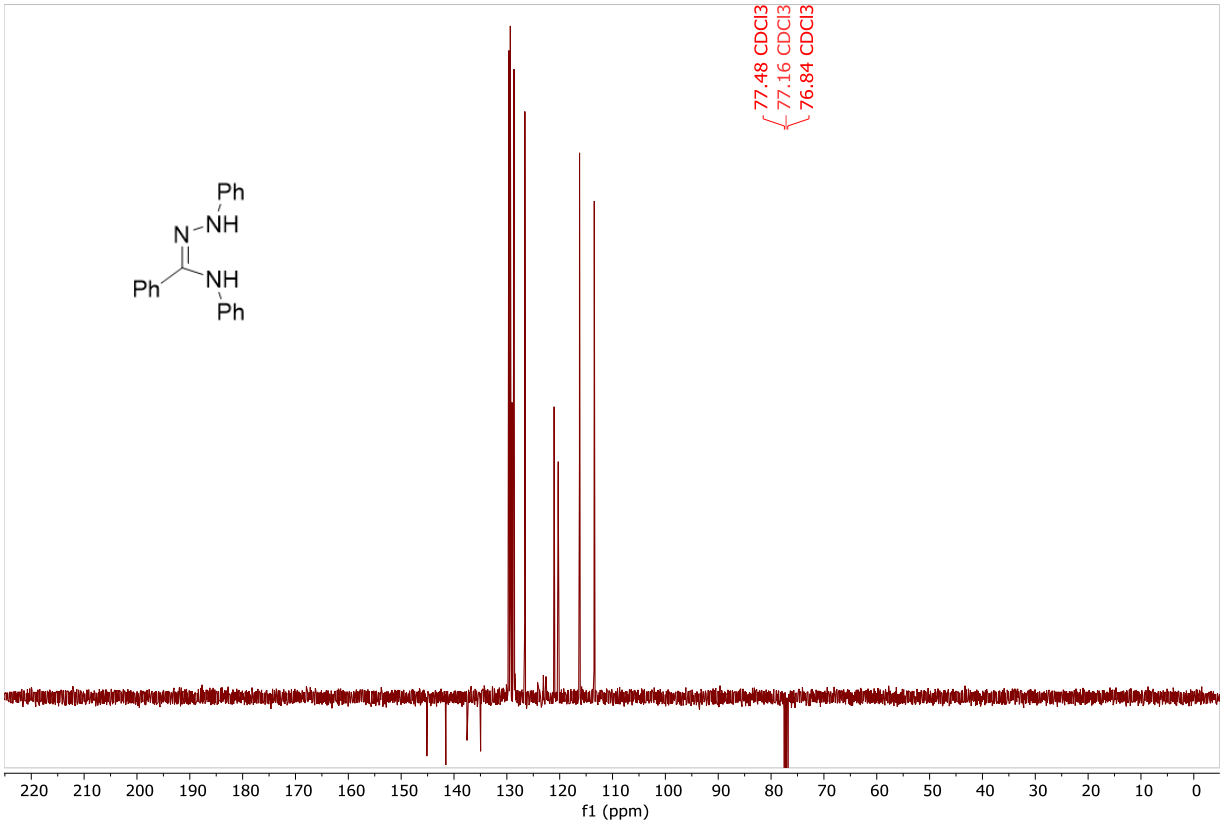


9.14 NMR-spectra of crude *N*,*N*'-diphenylbenzohydrazonamide 42

1H NMR (CDCl3, 400 MHz)

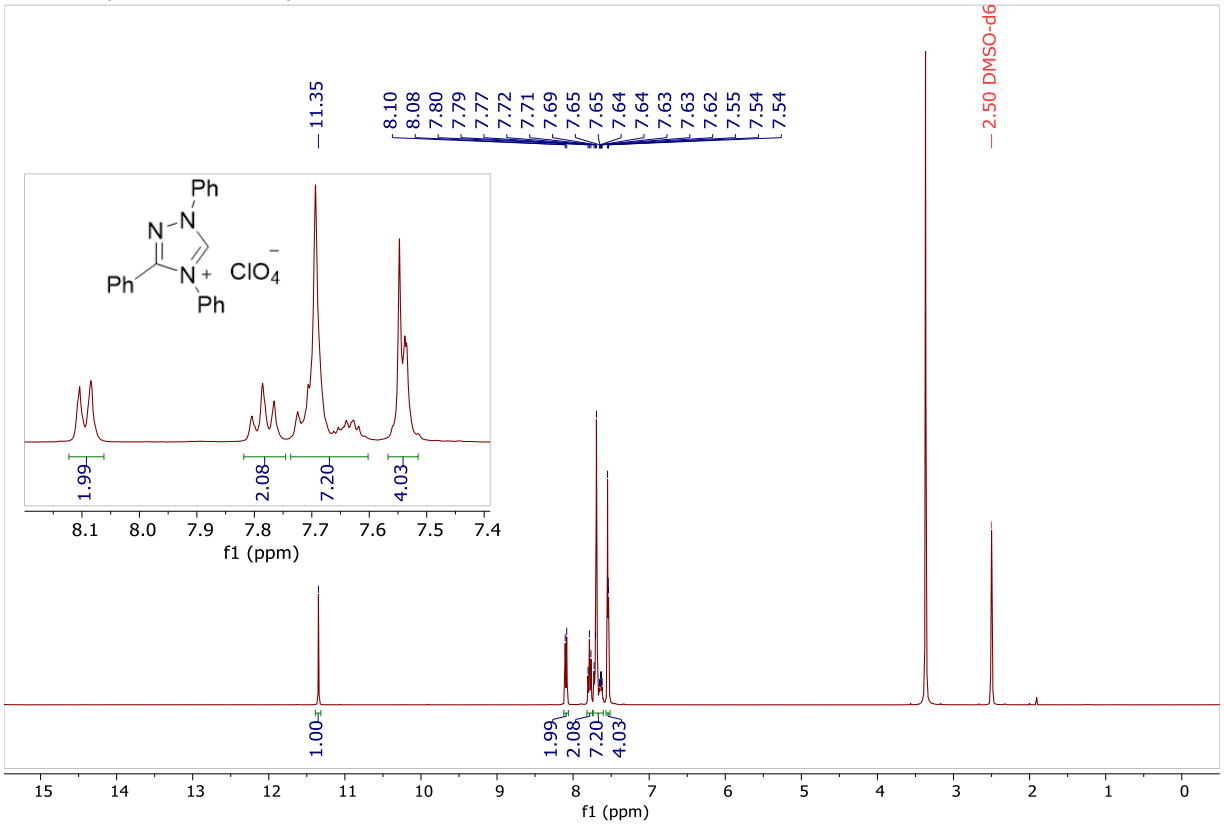


13C NMR (CDCl3, 101 MHz)

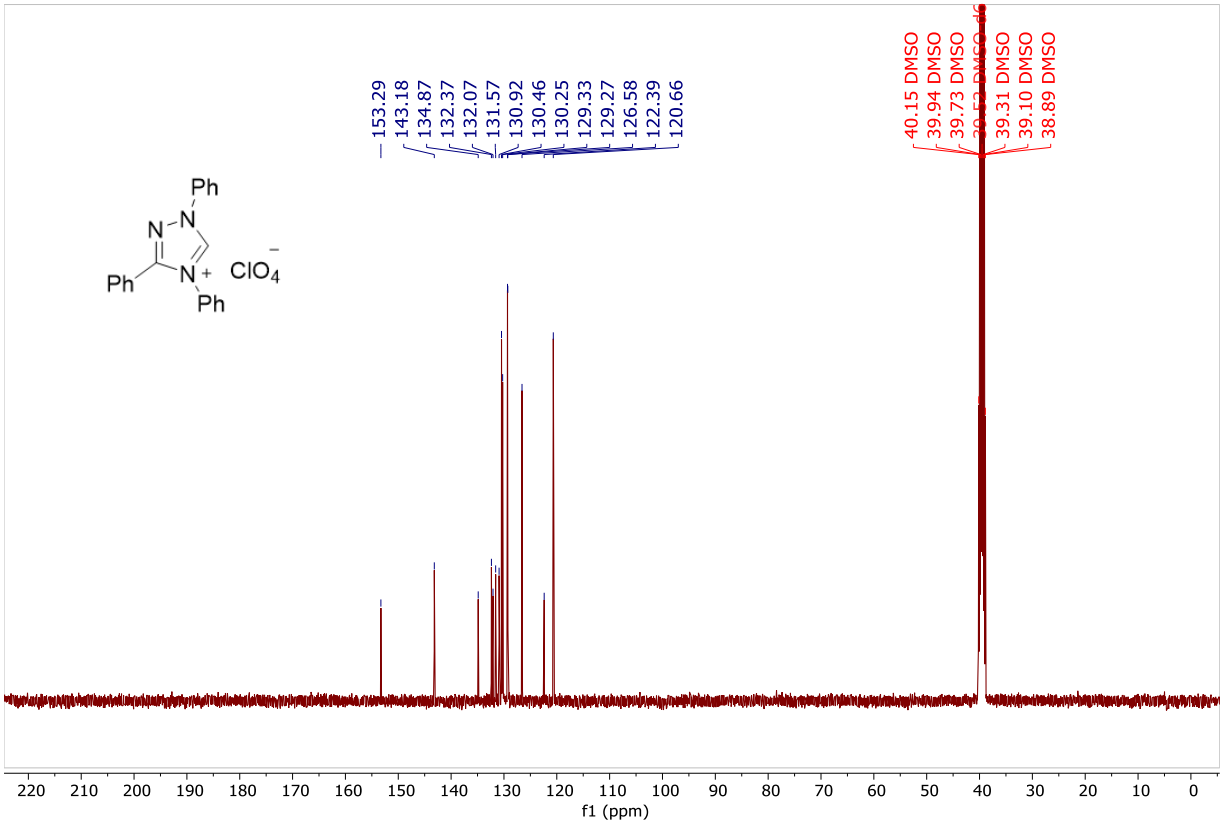


9.15 NMR-spectra of isolated 1,3,4-triphenyl-1,2,4-triazol-1-ium perchlorate 17

1H NMR (DMSO, 400 MHz)



13C NMR (DMSO, 101 MHz)



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