Defining the S_N1 side of glycosylation reactions: stereoselectivity of glycopyranosyl cations

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Supplementary information

DFT calculations

General procedure I: conformational energy landscape calculation of pyranosyl oxocarbenium ions

To keep the calculation time manageable, large protection groups (OBn) were substituted with electronic comparable smaller groups (OMe). The initial structure for the conformational energy landscape (CEL) mapping of the six-membered oxocarbenium ion was optimised by starting from a 'conformer distribution search' option included in the Spartan 10 program by utilising DFT as the level of theory and B3LYP as hybrid functional in gas phase with 6-31G(d) as the basis set. All generated output geometries were re-optimised with Gaussian 03 or Gaussian 09 by using DFT/B3LYP/6-311G(d,p), their zero-point energy (ZPE) corrections calculated, and further optimised with a polarisable continuum model (PCM) to correct for solvation in CH_2Cl_2. For heavy elements, including iodine, a combination of LANL2DZ and 6-311G(d,p) was used as basis set by utilising the keyword "*genecp*". The geometry with the lowest, ZPE corrected, solvated energy was selected as the starting point for the CEL. A complete survey of the possible conformational space was done by scanning three dihedral angles ranging from −60° to 60°, including the C1-C2-C3-C4 (D1), C3-C4-C5-O (D3) and C5-O-C1-C2 (D5). The resolution of this survey is determined by the step size which was set to 15° per puckering parameter, giving a total of 729 pre-fixed conformations per pyranosyl oxocarbenium ion spanning the entire conformational landscape. All other internal coordinates were unconstrained. Except when a C2-substituent was present on the oxocarbenium ring of interest, then the C2-H2 bond length was fixed based on the optimised structure to counteract rearrangements occurring for higher energy conformers. The 729 structures were computed with Gaussian 03 or Gaussian 09 with DFT/B3LYP/6-311G(d,p). Furthermore, solvation effects of CH_2Cl_2 (or in selected cases Et_2O or MeCN) were taken into account with a PCM function. Dispersion-corrected DFT functionals were also used, including ωB97XD and B3LYP-D3, and showed comparable results (*vide infra*). For pyranosyl oxocarbenium ions bearing a C5-C6 substituent three separate staggered rotamers (*gg*, *gt*, *tg*) of the O5-C5-C6-O6 dihedral angle (-65°, 65°, 175°) were considered. Earlier work showed the importance of these rotamers and their crucial impact on the selectivity and reactivity of the ion.[E. R. van Rijssel *et al.*, Furanosyl Oxocarbenium Ion Stability and Stereoselectivity. *Angew. Chem. Int. Ed.* 53, 10381–10385 (2014)] The CEL maps were calculated separately and the starting geometry was obtained from the method described above in which the lowest, ZPE corrected, solvated energy generated rotamers were used. The three C5-C6 bond rotamers (not constrained) bring the total conformations for each pyranosyl oxocarbenium ion configuration to 2187 geometries. The final denoted free Gibbs energy was calculated using Equation (1) in which ΔE_{gas} is the gas-phase energy (electronic energy), $\Delta G^{T}_{gas,QH}$ (T = reaction temperature and pressure = 1 atm.) is the sum of corrections from the electronic energy to free Gibbs energy in the quasi-harmonic oscillator approximation also including ZPE, and ΔG_{solv} is their corresponding free solvation Gibbs energy. The $\Delta G^{T}_{gas,QH}$ were computed using the quasi-harmonic approximation in the gas phase according to the work of Truhlar.[R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar, Use of Solution-Phase Vibrational Frequencies in Continuum Models for the Free Energy of Solvation. *J. Phys. Chem. B.* 115, 14556–14562 (2011)]

$$\Delta G^{T}_{in\ solution} = \Delta E_{gas} + \Delta G^{T}_{gas,QH} + \Delta G_{solv} \qquad (1)$$

$$= \Delta G^{T}_{gas} + \Delta G_{solv}$$

The quasi-harmonic approximation is the same as the harmonic oscillator approximation except that vibrational frequencies lower than 100 cm^{-1} were raised to 100 cm^{-1} as a way to correct for the breakdown of the harmonic oscillator model for the free energies of low-frequency vibrational modes.

All found minima were checked for imaginary frequencies. To visualise the energy levels of the conformers on the Cremer-Pople sphere, we have generated slices dissecting the sphere that combine closely associated conformers (Figure 1). The OriginPro software was employed to produce the energy heat maps, contoured at 0.5 kcal/mol. For ease of visualisation, the Cremer-Pople globe is turned 180° with respect to its common representation and both poles (the $^{4}C_{1}$ and $^{1}C_{4}$ structures) are omitted as these conformations are very high in energy. Visualisation of conformations of interest was done with CYLview.

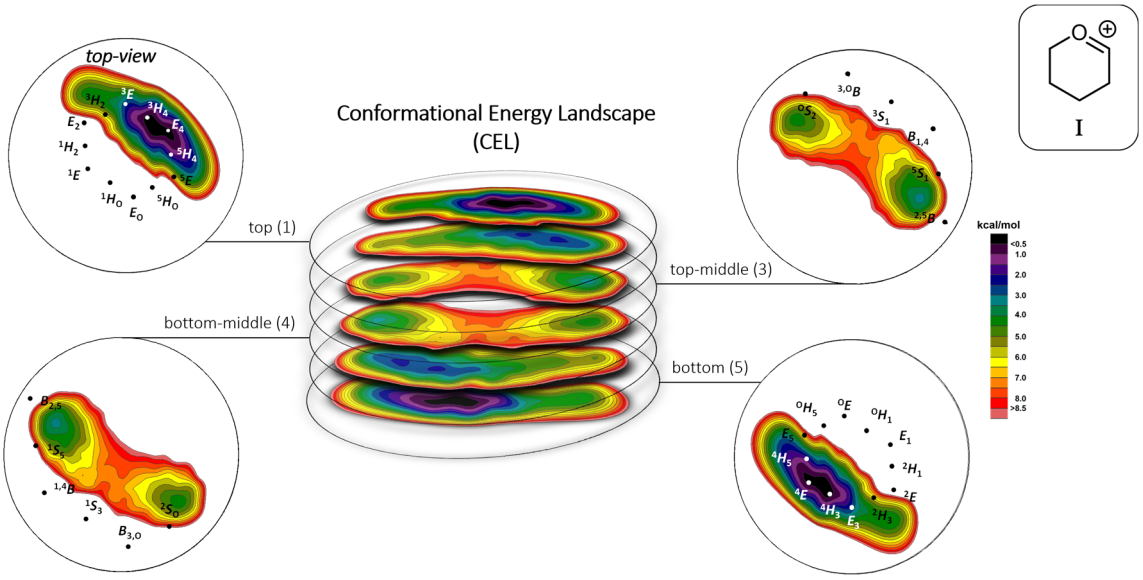


Figure 1| "Deconvolution" of the CEL map of the pyranosyl oxocarbenium ion **I** showing a top view of the most important slices that have been combined to generate the full CEL map.

General procedure II: computation of stereochemical preference based on the calculated CEL

To convert the relative energies of the continuum of conformers into the stereoselectivity of reactions the Boltzmann equation was used (Equation 2). The temperature used in the Boltzmann equation was equal to the reaction temperature. Inspection of the generated energy maps led to the realisation that two families of structures are most relevant: the continuum of (^{3}E, $^{3}H_{4}$, E_{4} and $B_{2,5}$)-like structures and the 'opposite' family of structures, composed of the range of (E_{3}, $^{4}H_{3}$, ^{4}E and $^{2,5}B$)-like conformers.

$$\frac{N_{\mathrm{i}}}{N_{\mathrm{total}}} = \frac{e^{-E_{\mathrm{rel.}}/RT}}{\Sigma_{k=1}^{N_{\mathrm{total}}} e^{-E_{k}/RT}} \qquad (2)$$

To discriminate both families, a selection criterion was set to separate both conformational families. This selection was based on the H2$_{a/b}$-C2-C1-O5 dihedral angle of the oxocarbenium of interest (Figure 2). For the top-half of the CEL map, conformations with an H2$_{a}$-C2-C1-O5 angle larger than 105° were regarded as top face-selective, while a smaller angle was considered as bottom face-selective and *vice versa* for the bottom of the CEL map, but with the H2$_{b}$-C2-C1-O5 dihedral angle. This yields a top face- and bottom face-selective group with a corresponding fractional population, which was considered as the computed stereoselectivity of the calculated pyranosyl oxocarbenium. Only calculated structures with a relative energy of <5 kcal/mol were taken into account for calculating the Boltzmann distribution.

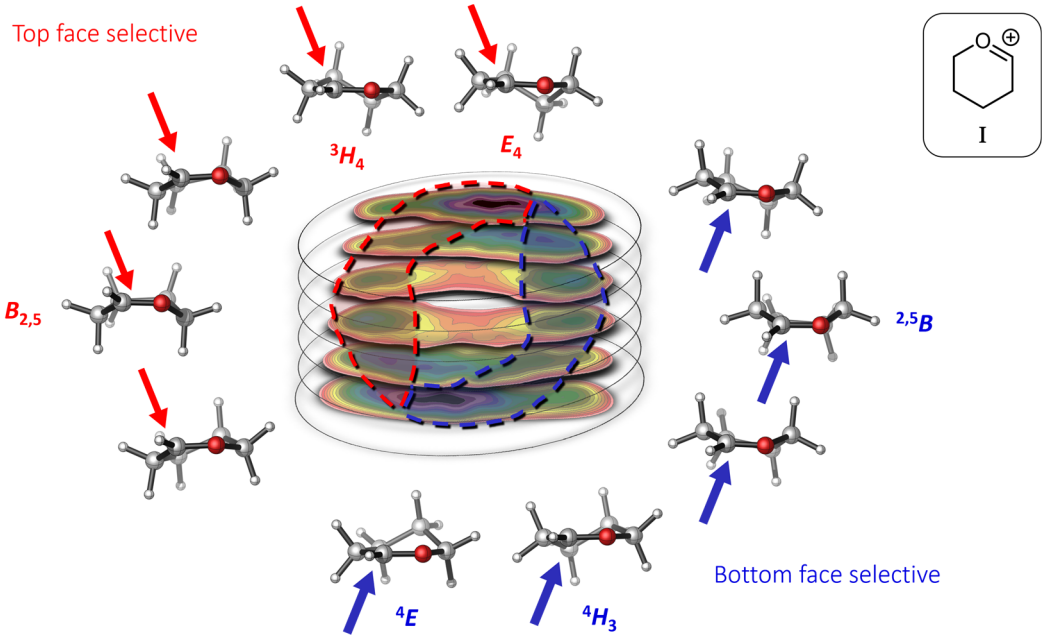


Figure 2| Stereotopic face differentiation of the relevant oxocarbenium ion conformations. CEL map of pyranosyl oxocarbenium ion **I** with marked areas for the top- and bottom face-selective family of conformations.

General procedure III: simulation of NMR spectra based on the calculated CEL map

To convert the relative energies of the continuum of conformers into simulated NMR spectra the Boltzmann equation was used (Equation 2). Based on all relevant geometries ($\Delta G^{T}_{gas/solution} < 2$ kcal/mol) the spin-spin coupling constants were calculated according to the work of Rablen and Bally.[Bally, T.; Rablen, P. R., Quantum-chemical simulation of ^{1}H NMR spectra. Comparison of DFT-based procedures for computing proton–proton coupling constants in organic molecules. *The Journal of organic chemistry* 2011, *76* (12), 4818-4830] with the use of 6-311g(d,p) u+1s as basis set and a scaling factor of 0.92. The computed total nuclear spin-spin coupling terms were used as calculated spin-spin coupling constants. Spectra were simulated with the use of MestReNova 9 with a line width of 4.0 Hz. The used chemical shift in the simulated spectra were acquired from the experimental spectra.

CEL maps

All CEL maps that are described in the article are summarised in the following section. The displayed CEL maps are based on the ΔG^{T}_{DCM} and relevant structures are added with their respective relative energy. Also additional information is given of the found local minima including detailed energy output from Gaussian 03 or Gaussian 09, ring dihedral angles and the geometrical output (coordinates in cartesian style).

Mono-substituted pyranosyl oxocarbenium ions

C-4 Mono-substituted pyranosyl oxocarbenium ions

4-Benzyloxy-pyranosyl oxocarbenium ion (**1**)

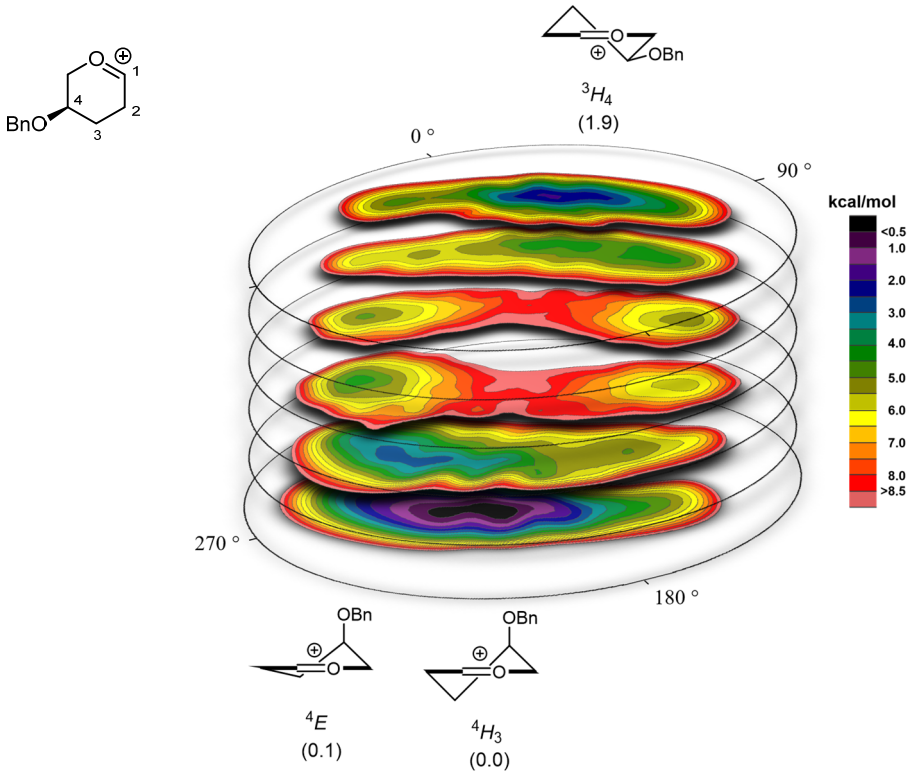


Figure 3| CEL map of 4-benzyloxy-pyranosyl oxocarbenium ion (**1**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -616.623325104 a.u.
E_{solv}(B3LYP) = -616.694267615 a.u.
Zero-point energy correction = 0.247268 a.u.

Atom coordinates

H	1.840685	-1.084953	-1.846118
C	1.880525	-0.580839	-0.873473
C	2.724070	-0.663924	1.464760
O	3.012367	1.381259	0.214744
C	3.064575	0.749351	1.296945
C	2.582456	0.752846	-1.082561
C	2.656488	-1.422841	0.139439
H	1.745329	-0.648037	1.974048
H	3.508946	0.671512	-1.648380
H	3.663420	-1.623958	-0.232881
H	3.413914	-1.096732	2.195663
H	3.368492	1.366726	2.141893
H	1.949570	1.522418	-1.515151
H	2.153289	-2.377619	0.282799
O	0.579209	-0.390756	-0.336668
C	-0.452938	-0.131385	-1.311201
H	-0.470931	-0.957319	-2.031811
H	-0.238844	0.795611	-1.854322
C	-1.767627	-0.020607	-0.588854
C	-4.190109	0.173083	0.803312
C	-2.456843	-1.174498	-0.201102
C	-2.303082	1.229783	-0.269232
C	-3.509716	1.328120	0.421967
C	-3.661480	-1.079742	0.490861
H	-2.049092	-2.149285	-0.447520
H	-1.776395	2.130347	-0.567458
H	-3.918510	2.303588	0.659635
H	-4.190228	-1.980252	0.781824
H	-5.130155	0.247850	1.337995

^{4}E conformation (0.1 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -616.623113259 a.u.
E_{solv}(B3LYP) = -616.694041865 a.u.
Zero-point energy correction = 0.247277 a.u.

Atom coordinates

H	1.875662	-1.356470	-1.671397
C	1.916356	-0.719569	-0.779783
C	2.785724	-0.450575	1.536800
O	2.725997	1.459206	0.038948
C	2.785483	0.974373	1.195516
C	2.645349	0.562483	-1.161400
C	2.699076	-1.405947	0.337540
H	1.939418	-0.560493	2.231955
H	3.674173	0.402558	-1.477580
H	3.696749	-1.664627	-0.019947
H	3.664695	-0.619987	2.173820
H	2.820295	1.730719	1.979266
H	2.123556	1.183297	-1.883024
H	2.197603	-2.325632	0.635174
O	0.620954	-0.444063	-0.277813
C	-0.387450	-0.182366	-1.278096
H	-0.397019	-1.014897	-1.991179
H	-0.152915	0.737579	-1.823449
C	-1.715855	-0.052840	-0.584791
C	-4.166936	0.175035	0.750504
C	-2.399061	-1.196213	-0.156779
C	-2.271686	1.204209	-0.334404
C	-3.492943	1.319354	0.328457
C	-3.617563	-1.084459	0.507122
H	-1.974777	-2.176014	-0.349311
H	-1.749301	2.096579	-0.663433
H	-3.917342	2.299686	0.512776
H	-4.141391	-1.976990	0.829817
H	-5.117992	0.262628	1.263305

$^{3}H_{4}$ conformation (1.9 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -616.616883031 a.u.
E_{solv}(B3LYP) = -616.690653461 a.u.
Zero-point energy correction = 0.246889 a.u.

Atom coordinates

H	1.753783	-0.308573	1.413036
C	1.649078	-0.093552	0.341406
C	3.861995	1.123097	0.083486
O	3.741940	-1.228735	-0.471168
C	4.408465	-0.192991	-0.236428
C	2.247292	-1.247947	-0.452511
C	2.335786	1.236605	0.010203
H	4.381939	1.846489	-0.558333
H	2.016075	-2.223576	-0.036726
H	1.995830	2.020012	0.686675
H	4.267056	1.344078	1.085822
H	5.485170	-0.353561	-0.276411
H	1.960392	-1.205400	-1.502349
H	2.040027	1.523754	-1.001854
O	0.286084	-0.110655	-0.033793
C	-0.628263	0.380529	0.971733
H	-0.430627	1.439197	1.167875
H	-0.470904	-0.181789	1.899249
C	-2.028933	0.190565	0.458188
C	-4.607926	-0.192696	-0.564647
C	-2.693020	1.230530	-0.197906
C	-2.669389	-1.045513	0.594357
C	-3.951969	-1.237254	0.086965
C	-3.977089	1.042227	-0.706128
H	-2.203406	2.192441	-0.308632
H	-2.162610	-1.858757	1.103376
H	-4.441211	-2.197742	0.202343
H	-4.484188	1.857295	-1.209739
H	-5.607676	-0.340342	-0.956960

4-Methoxy-pyranosyl oxocarbenium ion (**S1**)

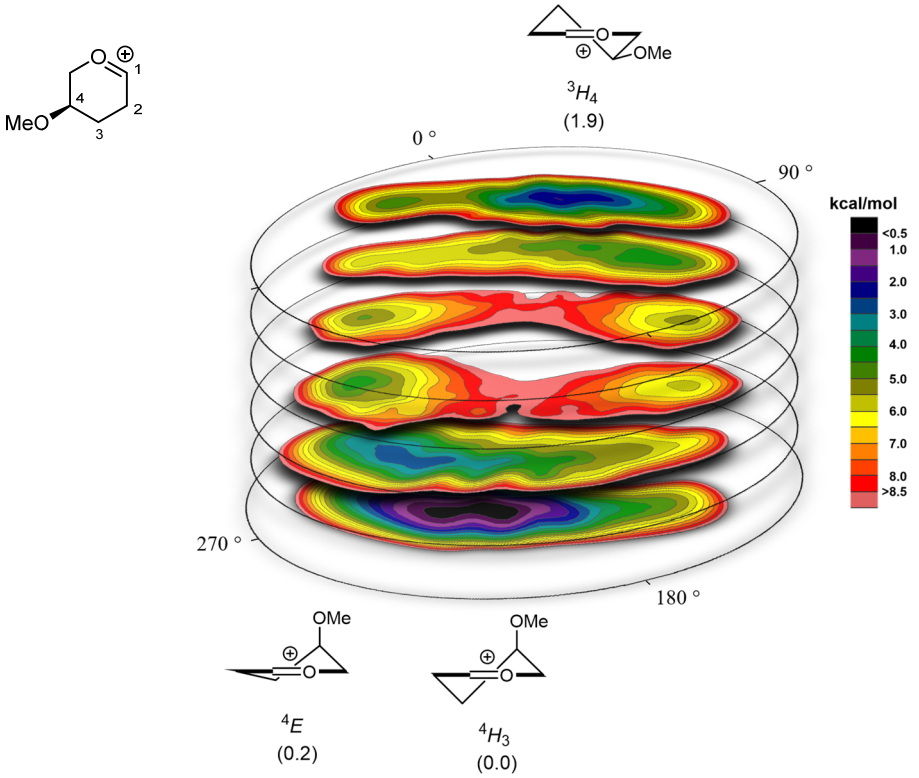


Figure 4| CEL map of 4-methoxy-pyranosyl oxocarbenium ion (**S1**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -385.514115506 a.u.
E_{solv}(B3LYP) = -385.589118697 a.u.
Zero-point energy correction = 0.166311 a.u.

Atom coordinates

H	1.243834	-0.259962	1.594774
C	0.578940	-0.185120	0.721384
C	-1.446453	-1.073113	-0.417436
O	-1.221332	1.318087	-0.184823
C	-1.809794	0.321213	-0.670365
C	-0.040359	1.204011	0.740289
C	-0.522704	-1.242578	0.788004
H	-0.959714	-1.397924	-1.356445
H	-2.631192	0.588245	-1.347337
H	-0.448411	1.480357	1.713950
H	-1.089768	-1.131817	1.716785
H	-2.370615	-1.661490	-0.363401
H	0.616624	1.991683	0.376054
H	-0.076936	-2.237358	0.780254
O	1.286007	-0.409293	-0.490071
C	2.621206	0.094058	-0.513035
H	3.038206	-0.178134	-1.481797
H	3.222285	-0.360219	0.283183
H	2.653259	1.185451	-0.409915

^4E conformation (0.2 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -385.513759513 a.u.
E_{solv}(B3LYP) = -385.588894859 a.u.
Zero-point energy correction = 0.166329 a.u.

Atom coordinates

H	-1.217671	0.619884	1.543509
C	-0.541834	0.360351	0.715003
C	1.573366	0.903727	-0.478872
O	0.955415	-1.414131	-0.113889
C	1.613909	-0.538765	-0.729676

C	0.019326	-1.027578	0.993522
C	0.623136	1.344874	0.643972
H	1.305580	1.334814	-1.459090
H	2.244482	-0.949611	-1.528020
H	0.607601	-1.083305	1.910409
H	1.145440	1.361560	1.603530
H	2.616349	1.226494	-0.332880
H	-0.715048	-1.829724	0.969668
H	0.253509	2.350420	0.441538
O	-1.205682	0.401284	-0.535397
C	-2.546290	-0.091451	-0.529640
H	-2.932255	0.053407	-1.537755
H	-3.162833	0.470527	0.181073
H	-2.592704	-1.158645	-0.283549

$^{3}H_{4}$ conformation (1.9 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -385.508192468 a.u.
E_{solv}(B3LYP) = -385.585504725 a.u.

Zero-point energy correction = 0.166015 a.u.

Atom coordinates

H	-0.649778	-0.053540	1.298088
C	-0.560131	-0.104543	0.201311
C	1.551097	1.293995	0.040984
O	1.738560	-1.116543	0.081990
C	2.258561	0.022810	0.163553
C	0.279099	-1.323680	-0.159228
C	0.068165	1.190506	-0.326420
H	2.132201	1.912057	-0.660700
H	3.338223	-0.003680	0.357479
H	0.048089	-2.200524	0.441499
H	-0.464833	2.061101	0.058368
H	1.726726	1.791188	1.013893
H	0.207954	-1.561233	-1.222228
H	-0.037578	1.193284	-1.415597
O	-1.815276	-0.377786	-0.386730
C	-2.929987	0.212970	0.284867
H	-3.819387	-0.113263	-0.252580
H	-2.881695	1.307060	0.264968
H	-2.987016	-0.130161	1.324324

4-Fluoro-pyranosyl oxocarbenium ion (**2**)

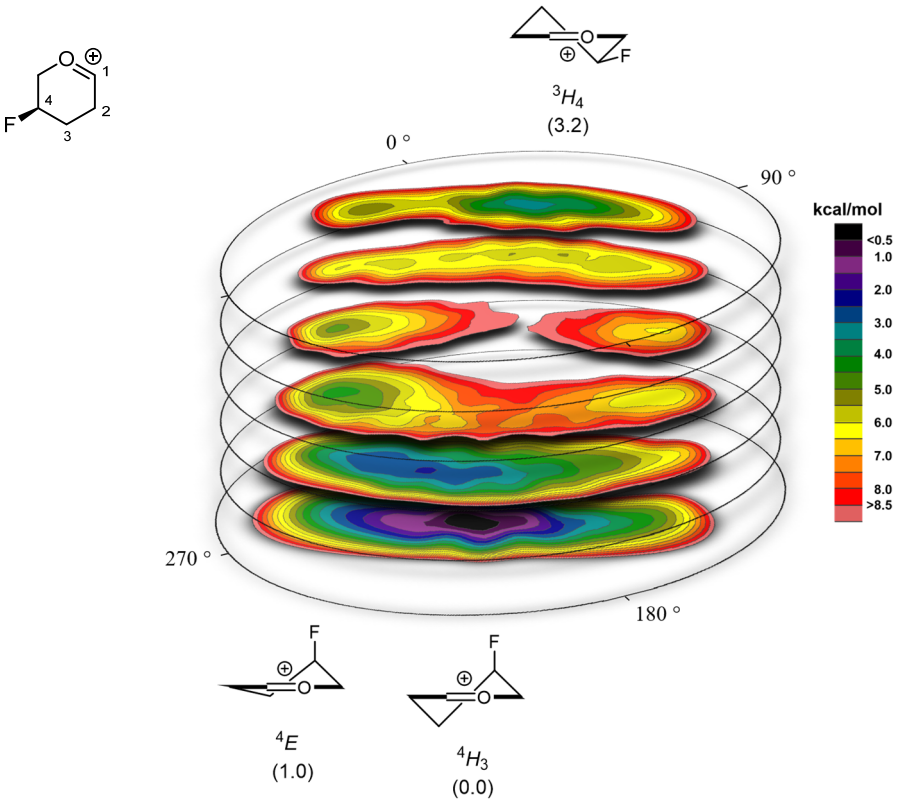


Figure 5| CEL map of 4-fluoro-pyranosyl oxocarbenium ion (**2**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -370.218949634 a.u.
E_{solv}(B3LYP) = -370.301652263 a.u.
Zero-point energy correction = 0.126027 a.u.

Atom coordinates

H	-2.060363	0.022033	0.937700
C	-1.144241	0.037433	0.337076
C	1.060022	1.174897	-0.090185
O	0.959312	-1.242704	-0.063832
C	1.567964	-0.175584	-0.320716
C	-0.414195	-1.265669	0.533045
C	-0.284518	1.253748	0.636194
H	1.029936	1.620098	-1.102500
H	-0.249855	-1.506624	1.584829
H	-0.119400	1.303270	1.717015
H	1.862965	1.737464	0.408952
H	2.555087	-0.335015	-0.773139
H	-0.893553	-2.096152	0.018148
H	-0.822779	2.156413	0.345284
F	-1.520747	0.099022	-1.022013

^4E conformation (1.0 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -370.218283291 a.u.
E_{solv}(B3LYP) = -370.300474245 a.u.
Zero-point energy correction = 0.126221 a.u.

Atom coordinates

H	2.153740	0.101463	-0.707760
C	1.156841	0.078628	-0.253714
C	-1.052658	1.148665	0.050166
O	-0.869551	-1.272591	0.040783
C	-1.496447	-0.221035	0.328253
C	0.460656	-1.200254	-0.650458
C	0.303924	1.267455	-0.663136
H	-1.066372	1.644318	1.036407
H	0.251775	-1.264943	-1.718909
H	0.179073	1.258247	-1.748710
H	-1.879663	1.636530	-0.490305
H	-2.444162	-0.406283	0.849979
H	0.962472	-2.098317	-0.295550
H	0.789041	2.204653	-0.387196
F	1.308512	0.073812	1.141012

$^4H_3$ conformation (3.2 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -370.212239019 a.u.
E_{solv}(B3LYP) = -370.296637511 a.u.
Zero-point energy correction = 0.126128 a.u.

Atom coordinates

H	-1.011443	0.079286	1.469318
C	-0.977200	0.059228	0.373364
C	1.256393	1.172725	0.023041
O	1.123418	-1.240929	-0.031694
C	1.797404	-0.182754	0.024651
C	-0.364593	-1.249401	-0.110044
C	-0.257901	1.279028	-0.178327
H	1.832323	1.743565	-0.721503
H	-0.644770	-2.112108	0.491066
H	-0.638733	2.184199	0.296394
H	1.599996	1.598580	0.985009
H	2.878647	-0.358337	0.093172
H	-0.586998	-1.428999	-1.163866
H	-0.478178	1.344542	-1.248436
F	-2.295867	0.044860	-0.082635

4-*tert*-Butyldimethylsilyloxy-pyranosyl oxocarbenium ion (**3**)

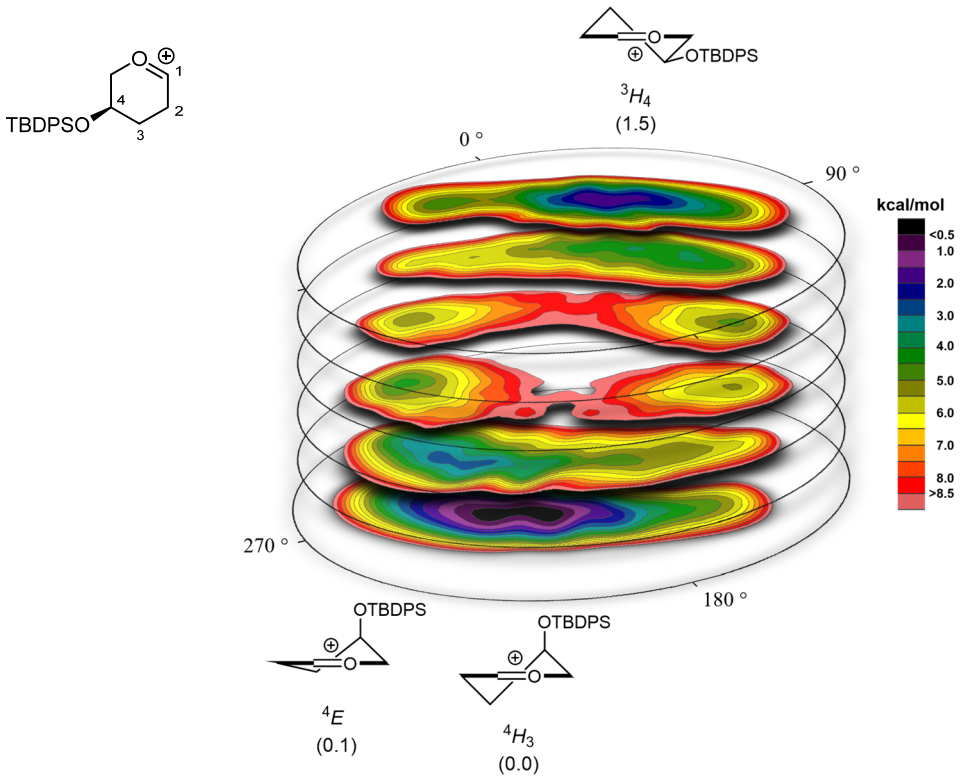


Figure 6| CEL map of 4-*tert*-butyldimethylsilyloxy-pyranosyl oxocarbenium ion (**3**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -1256.49920614 a.u.
E_{solv}(B3LYP) = -1256.56402908 a.u.
Zero-point energy correction = 0.432346 a.u.

Atom coordinates

H	0.824727	-0.752813	-2.056319
C	1.533353	-1.008525	-1.261486
C	3.095865	-2.740874	-0.386737
O	3.903016	-0.476755	-0.602683
C	4.053981	-1.651366	-0.191444
C	2.687936	-0.024704	-1.368582
C	2.054391	-2.434025	-1.462143
H	4.977419	-1.798084	0.368456
H	3.058767	0.094003	-2.385328
H	2.497951	-2.532028	-2.455794
H	3.658574	-3.663525	-0.559854
H	2.475127	0.943533	-0.926123
H	1.230775	-3.142851	-1.394843
H	2.631833	-2.875330	0.605074
O	0.942518	-0.932871	0.025970
Si	-0.366173	0.032815	0.524964
C	-0.414361	-0.242242	2.419123
C	-1.925890	-0.620715	-0.314088
C	-4.296633	-1.646613	-1.450253
C	-2.006183	-1.953988	-0.751345
C	-3.070600	0.183015	-0.459299
C	-4.243441	-0.322502	-1.017758
C	-3.174539	-2.462559	-1.316444
H	-1.148760	-2.609293	-0.642851
H	-3.050323	1.219594	-0.139604
H	-5.113123	0.317318	-1.117972
H	-3.210106	-3.494098	-1.648997
H	-5.207094	-2.040104	-1.888190
C	-0.066200	1.812663	-0.055558
C	0.477607	4.401451	-1.057611
C	0.590969	2.778670	0.728281
C	-0.444059	2.190206	-1.358803
C	-0.174193	3.464141	-1.856327
C	0.857666	4.055946	0.238015
H	0.901041	2.544195	1.738973
H	-0.966769	1.485490	-1.996482
H	-0.478538	3.725142	-2.863788
H	1.359792	4.780889	0.868818

H	0.684472	5.394613	-1.439960
C	-0.903228	-1.683330	2.696643
H	-0.921220	-1.860377	3.778560
H	-0.242024	-2.432381	2.251568
H	-1.912708	-1.854984	2.316174
C	-1.404386	0.746576	3.072690
H	-1.096626	1.787806	2.949433
H	-1.470630	0.546316	4.148549
H	-2.412753	0.644422	2.660470
C	0.984601	-0.084043	3.053930
H	1.392012	0.923224	2.941907
H	1.700558	-0.785444	2.618517
H	0.923848	-0.290730	4.128982

^{4}E conformation (0.1 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -1256.49903868 a.u.
E_{solv}(B3LYP) = -1256.56394510 a.u.
Zero-point energy correction = 0.432431 a.u.

Atom coordinates

H	0.797692	-0.659177	-2.076817
C	1.515299	-0.974998	-1.312138
C	3.065339	-2.783933	-0.577555
O	3.753166	-0.462685	-0.412687
C	3.869914	-1.666190	-0.077213
C	2.714834	-0.046759	-1.416100
C	1.987851	-2.401496	-1.601840
H	4.645493	-1.833871	0.669663
H	3.215787	-0.081412	-2.381742
H	2.389138	-2.453298	-2.615353
H	3.776109	-3.535811	-0.948240
H	2.501868	0.977395	-1.126838
H	1.154675	-3.099456	-1.538436
H	2.652672	-3.249106	0.330122
O	0.972454	-0.918452	-0.006151
Si	-0.330468	0.041060	0.528141
C	-0.329187	-0.219813	2.424212
C	-1.904585	-0.634410	-0.267320
C	-4.287544	-1.684619	-1.355118
C	-1.985118	-1.972825	-0.688546
C	-3.055690	0.161788	-0.403045
C	-4.234467	-0.355737	-0.937531
C	-3.159382	-2.493454	-1.229932
H	-1.122223	-2.621933	-0.587976
H	-3.035462	1.202144	-0.096027
H	-5.108771	0.278700	-1.031429
H	-3.194438	-3.528559	-1.551277
H	-5.202431	-2.087186	-1.775224
C	-0.065570	1.817308	-0.076811
C	0.410466	4.404147	-1.118221
C	0.570147	2.810404	0.690286
C	-0.457939	2.167059	-1.383597
C	-0.221141	3.439689	-1.900781
C	0.803097	4.086703	0.180699
H	0.887804	2.599405	1.703533
H	-0.968265	1.441953	-2.008518
H	-0.536105	3.678618	-2.910433
H	1.288789	4.832863	0.799542
H	0.591134	5.396633	-1.515312
C	-0.742757	-1.680607	2.720230
H	-0.742745	-1.847082	3.803931
H	-0.048105	-2.399330	2.276256
H	-1.745545	-1.906105	2.350485
C	-1.357187	0.726576	3.082746
H	-1.101568	1.780161	2.944348
H	-1.397729	0.535040	4.161464
H	-2.365146	0.571238	2.686703
C	1.067402	0.014572	3.040294
H	1.416492	1.042658	2.925108
H	1.817769	-0.644380	2.597177
H	1.031995	-0.196274	4.115718

$^{3}H_{4}$ conformation (1.5 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -1256.49401966 a.u.
E_{solv}(B3LYP) = -1256.56133477 a.u.
Zero-point energy correction = 0.432301 a.u.

Atom coordinates

H	1.622974	-0.766984	-0.974710
C	1.834967	-1.034754	0.067974
C	3.594085	-2.771444	-0.502930
O	4.307034	-0.523474	0.034006
C	4.545574	-1.666106	-0.422307
C	2.963490	-0.137293	0.573653
C	2.224098	-2.511986	0.131350
H	5.565540	-1.781731	-0.787279
H	2.862666	0.900535	0.270262
H	1.466016	-3.115298	-0.366418
H	3.535202	-2.996302	-1.581310
H	3.077640	-0.209590	1.654264
H	2.246416	-2.812009	1.181778
H	4.100126	-3.655133	-0.092802
O	0.725159	-0.783208	0.899555
Si	-0.623582	0.201808	0.564671

C	-1.339938	0.581391	2.298725
C	-1.835374	-0.806672	-0.474127
C	-3.719413	-2.323928	-1.927047
C	-1.795612	-2.211352	-0.471622
C	-2.849093	-0.183742	-1.223643
C	-3.781940	-0.931279	-1.940523
C	-2.723253	-2.963364	-1.191088
H	-1.035085	-2.727215	0.104514
H	-2.911837	0.898990	-1.257758
H	-4.554472	-0.427373	-2.510708
H	-2.670475	-4.046432	-1.175020
H	-4.442851	-2.906773	-2.486063
C	-0.041371	1.687768	-0.456392
C	0.935852	3.808279	-2.052923
C	0.381540	2.901321	0.116408
C	0.041403	1.574132	-1.857506
C	0.525684	2.616391	-2.646622
C	0.860537	3.949046	-0.668337
H	0.336401	3.045104	1.188696
H	-0.287089	0.663162	-2.345796
H	0.575501	2.499400	-3.723467
H	1.171985	4.875134	-0.198264
H	1.307190	4.623034	-2.664203
C	-1.940289	-0.723095	2.874435
H	-2.345015	-0.527874	3.874551
H	-1.186871	-1.509981	2.971186
H	-2.754722	-1.108068	2.256488
C	-2.461739	1.636610	2.187371
H	-2.092984	2.597017	1.817691
H	-2.905413	1.810551	3.174766
H	-3.266266	1.307321	1.522997
C	-0.251657	1.075997	3.276704
H	0.186550	2.030800	2.977597
H	0.558893	0.350169	3.375906
H	-0.692756	1.222170	4.269918

4-Azido-pyranosyl oxocarbenium ion (**4**)

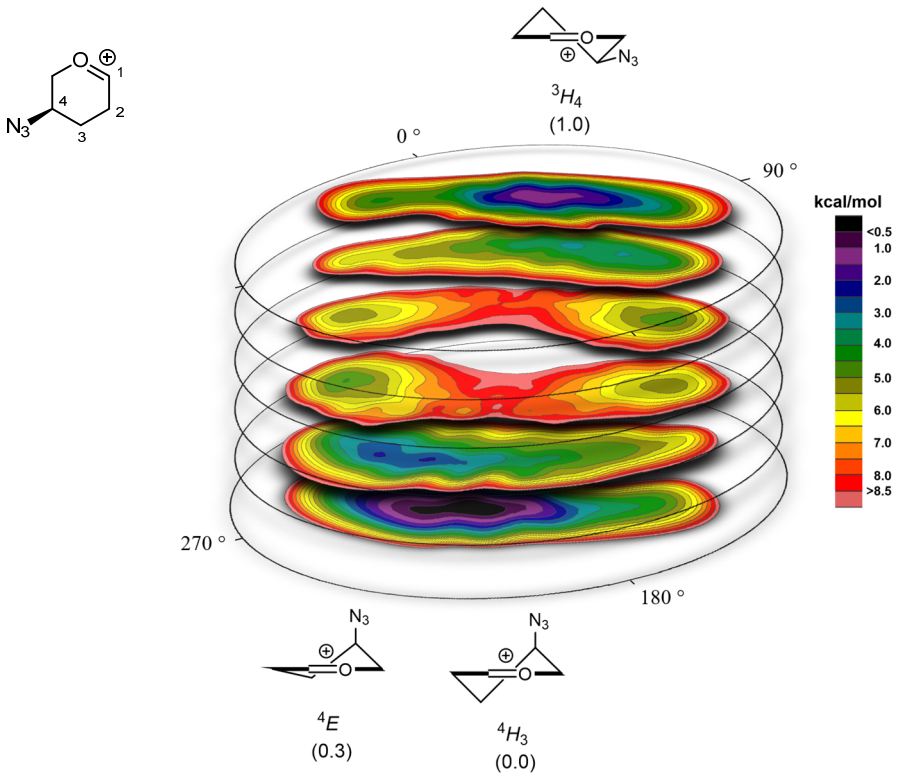


Figure 7| CEL map of 4-azido-pyranosyl oxocarbenium ion (**4**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -434.578260670 a.u.
E_{solv}(B3LYP) = -434.660276705 a.u.
Zero-point energy correction = 0.136964 a.u.

Atom coordinates

H	-0.830507	-0.803989	1.555667
C	-0.258002	-0.413150	0.703537
C	1.197901	1.427977	-0.144349
O	1.924760	-0.849746	-0.465210
C	2.055342	0.377294	-0.696663
C	0.850422	-1.407971	0.425954
C	0.356392	0.953464	1.040449
H	0.576474	1.752466	-1.000252
H	1.388922	-1.697053	1.329113
H	0.979540	0.859446	1.935075
H	1.831755	2.295152	0.080002
H	2.873839	0.605825	-1.391168
H	0.517158	-2.286695	-0.122720
H	-0.425440	1.682576	1.259682
N	-1.106453	-0.336181	-0.512499
N	-2.290108	-0.045016	-0.327751
N	-3.392318	0.204705	-0.287934

^4E conformation (0.3 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -434.577729036 a.u.
E_{solv}(B3LYP) = -434.659826837 a.u.
Zero-point energy correction = 0.137046 a.u.

Atom coordinates

H	-0.780479	-0.819030	1.635075
C	-0.218546	-0.425917	0.776659
C	1.179798	1.444850	-0.105389
O	1.778307	-0.852813	-0.604232
C	1.847562	0.376519	-0.855192
C	0.957753	-1.349681	0.551007
C	0.328433	0.976089	1.084164
H	0.601714	1.994750	-0.867447
H	1.639594	-1.387436	1.400919
H	0.929708	0.928982	1.995622
H	1.969800	2.159657	0.177063
H	2.463257	0.609622	-1.733125
H	0.675491	-2.349919	0.230321
H	-0.482335	1.685229	1.261075
N	-1.040421	-0.455431	-0.454897
N	-2.208849	-0.080323	-0.333655
N	-3.295474	0.231395	-0.350469

$^3H_4$ conformation (1.0 kcal / mol)

D1 = 30°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -434.574088324 a.u.
E_{solv}(B3LYP) = -434.658158122 a.u.
Zero-point energy correction = 0.136706 a.u.

Atom coordinates

H	0.475472	0.066983	-1.181720
C	0.296892	0.043850	-0.098132
C	-1.966480	1.184234	-0.159723
O	-1.873394	-1.230282	-0.098793
C	-2.512508	-0.164742	-0.272827
C	-0.419740	-1.255102	0.259271
C	-0.515338	1.273779	0.319242
H	-2.666140	1.756206	0.469069
H	-0.047545	-2.121720	-0.283473
H	-0.046429	2.175867	-0.075869
H	-2.120445	1.620640	-1.164887
H	-3.563686	-0.325002	-0.544158
H	-0.413199	-1.446294	1.333842
H	-0.495898	1.346503	1.410814
N	1.572952	0.011666	0.644390
N	2.603805	0.012096	-0.034958
N	3.618681	0.015804	-0.532326

4-Chloro-pyranosyl oxocarbenium ion (**5**)

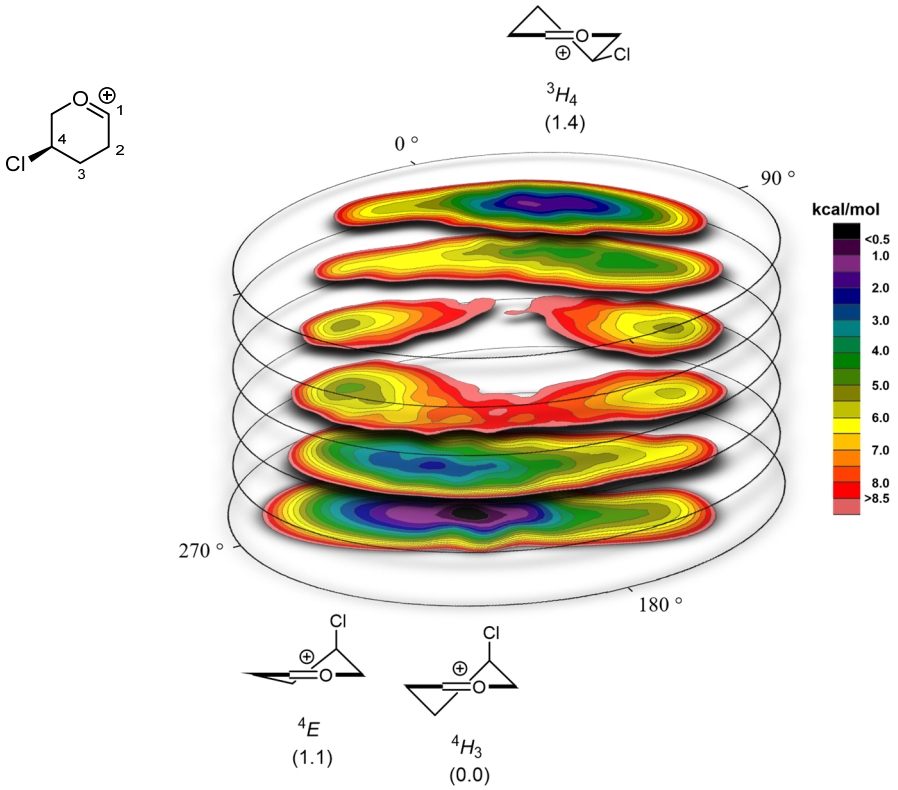


Figure 8| CEL map of 4-chloro-pyranosyl oxocarbenium ion (**5**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -730.576282791 a.u.
E_{solv}(B3LYP) = -730.658978382 a.u.
Zero-point energy correction = 0.124718 a.u.

Atom coordinates

H	-1.295445	-0.125024	1.711806
C	-0.657487	-0.045122	0.828332
C	1.243227	1.223349	-0.256008
O	1.255736	-1.194947	-0.298555
C	1.701269	-0.091422	-0.698916
C	0.163670	-1.306102	0.715928
C	0.211267	1.206645	0.872434
H	0.872281	1.705942	-1.179401
H	0.689588	-1.526551	1.648527
H	0.728453	1.209930	1.838594
H	2.143694	1.807349	-0.011901
H	2.489039	-0.188704	-1.456783
H	-0.397047	-2.176948	0.384380
H	-0.408836	2.101940	0.835274
Cl	-1.814076	0.048680	-0.597216

^4E conformation (1.1 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -730.575364028 a.u.
E_{solv}(B3LYP) = -730.657586289 a.u.
Zero-point energy correction = 0.124901 a.u.

Atom coordinates

H	-1.315598	-0.015801	1.713757
C	-0.648125	0.016723	0.848430
C	1.213003	1.189573	-0.318698
O	1.131314	-1.237439	-0.313033
C	1.546096	-0.155056	-0.802808
C	0.212327	-1.224519	0.870984
C	0.270312	1.233514	0.894618
H	0.816079	1.717191	-1.202502
H	0.860294	-1.257935	1.749027
H	0.839089	1.190290	1.827762

H	2.177134	1.693181	-0.137540
H	2.197837	-0.290894	-1.675285
H	-0.337195	-2.156793	0.761163
H	-0.299050	2.163275	0.891361
Cl	-1.738281	0.029152	-0.610508

$^3H_4$ conformation (1.4 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -730.573210787 a.u.
E_{solv}(B3LYP) = -730.656940733 a.u.
Zero-point energy correction = 0.124818 a.u.

Atom coordinates

H	-0.515606	0.157994	1.474390
C	-0.555851	0.072301	0.384870
C	1.637253	1.179645	0.101365
O	1.538951	-1.224025	-0.074223
C	2.208490	-0.165111	0.002094
C	0.035227	-1.251669	-0.073758
C	0.154989	1.240417	-0.282284
H	2.266359	1.855373	-0.492874
H	-0.193683	-2.089361	0.582635
H	-0.272664	2.188216	0.046938
H	1.822252	1.487098	1.148670
H	3.293139	-0.333183	0.012304
H	-0.215004	-1.494329	-1.107537
H	0.047853	1.178666	-1.369193
Cl	-2.319112	0.022837	-0.029133

4-Bromo-pyranosyl oxocarbenium ion (**6**)

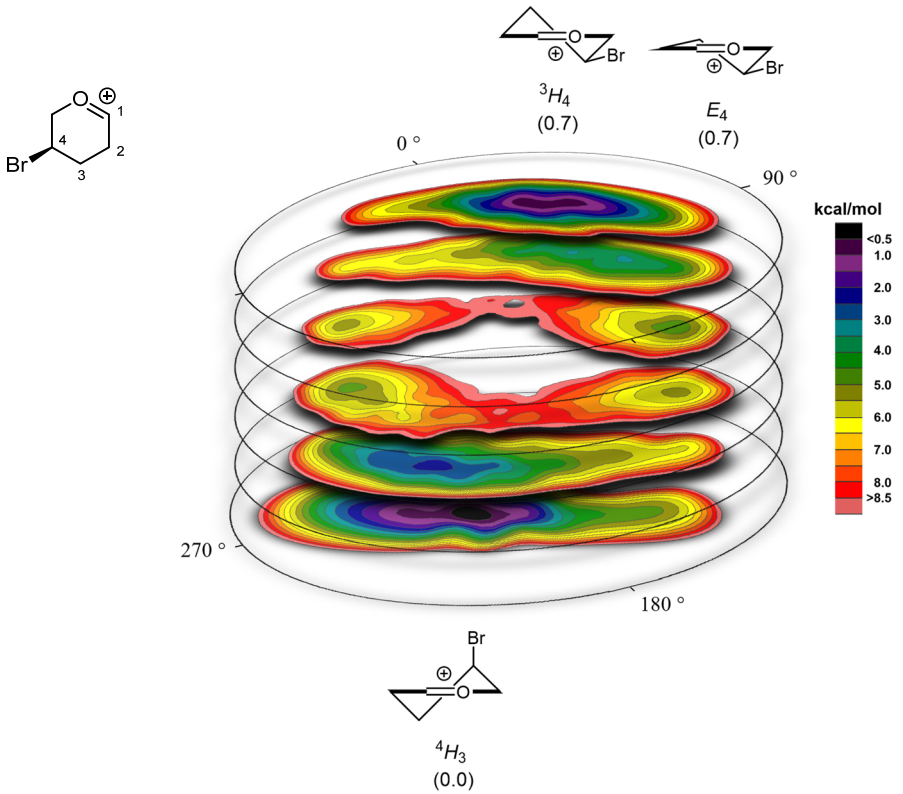


Figure 9| CEL map of 4-bromo-pyranosyl oxocarbenium ion (**6**).

Local minima

$^{4}H_{3}$ conformation (0.0 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -2844.49849824 a.u.
E_{solv}(B3LYP) = -2844.58017057 a.u.
Zero-point energy correction = 0.124093 a.u.

Atom coordinates

H	-0.503970	-0.188831	2.005759
C	-0.022993	-0.080802	1.031329
C	1.638780	1.243284	-0.342427
O	1.681509	-1.173516	-0.437381
C	2.032361	-0.054665	-0.885965
C	0.785507	-1.322824	0.750965
C	0.820848	1.185484	0.947942
H	1.103669	1.735317	-1.175660
H	1.474573	-1.544156	1.571228
H	1.502514	1.175569	1.807179
H	2.559052	1.839221	-0.245487
H	2.677570	-0.122958	-1.771231
H	0.196073	-2.203869	0.509012
H	0.197024	2.073488	1.043413
Br	-1.548160	0.022899	-0.264464

E_{4} conformation (0.7 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -2844.49612987 a.u.
E_{solv}(B3LYP) = -2844.57896606 a.u.
Zero-point energy correction = 0.123992 a.u.

Atom coordinates

H	-0.145821	0.027657	-1.448848
C	-0.051564	0.044970	-0.359372
C	-2.223351	1.177679	-0.013533
O	-2.114057	-1.244366	-0.008776
C	-2.769380	-0.177904	-0.118434
C	-0.628020	-1.210888	0.254677
C	-0.710151	1.267509	0.262121
H	-2.835520	1.698913	0.740632
H	-0.282840	-2.134597	-0.203589
H	-0.316767	2.190123	-0.165570
H	-2.516359	1.668084	-0.959235
H	-3.837050	-0.336973	-0.317614
H	-0.533227	-1.252393	1.340801
H	-0.522276	1.284995	1.338618
Br	1.891346	0.005741	-0.011650

$^{3}H_{4}$ conformation (0.7 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -2844.49634173 a.u.
E_{solv}(B3LYP) = -2844.57874639 a.u.
Zero-point energy correction = 0.124024 a.u.

Atom coordinates

H	0.047769	0.065952	1.512746
C	0.027765	0.046972	0.419314
C	2.240032	1.179175	0.008059
O	2.123460	-1.234728	-0.048332
C	2.790010	-0.173103	-0.010846
C	0.618837	-1.256359	-0.079841
C	0.717754	1.280939	-0.151513
H	2.789782	1.756591	-0.750988
H	0.373891	-2.114568	0.542241
H	0.351766	2.178855	0.346882
H	2.604917	1.603689	0.962622
H	3.875054	-0.338147	0.018459
H	0.393810	-1.464011	-1.127204
H	0.480078	1.373053	-1.215263
Br	-1.893461	0.010019	-0.028968

4-Iodo-pyranosyl oxocarbenium ion (**7**)

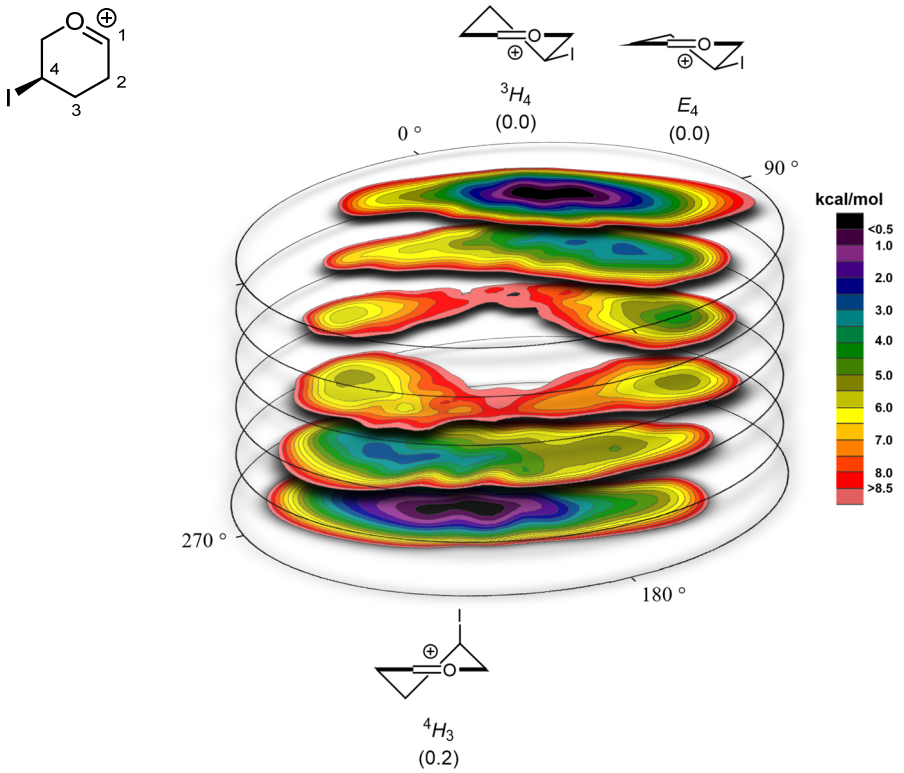


Figure 10| CEL map of 4-iodo-pyranosyl oxocarbenium ion (**7**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -281.732948791 a.u.
E_{solv}(B3LYP) = -281.814132574 a.u.
Zero-point energy correction = 0.123599 a.u.

Atom coordinates

H	0.544334	0.151937	1.497513
C	0.500963	0.067779	0.408846
C	2.686286	1.182236	0.094222
O	2.595785	-1.222210	-0.083201
C	3.260470	-0.161457	-0.016764
C	1.075954	-1.251111	-0.056565
C	1.196666	1.240065	-0.267156
H	3.304598	1.860878	-0.508207
H	0.869764	-2.089545	0.605966
H	0.778668	2.189225	0.069189
H	2.882766	1.486815	1.139959
H	4.346967	-0.321536	-0.026923
H	0.829960	-1.504275	-1.088421
H	1.078560	1.185889	-1.353313
I	-1.655168	0.006664	-0.012182

E_4 conformation (0.0 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -281.732444874 a.u.
E_{solv}(B3LYP) = -281.813970162 a.u.
Zero-point energy correction = 0.123461 a.u.

Atom coordinates

H	-0.603565	0.024959	-1.455880
C	-0.517073	0.043698	-0.366255
C	-2.687423	1.178113	-0.012589
O	-2.582307	-1.244491	-0.007494
C	-3.235467	-0.177583	-0.113845
C	-1.085412	-1.208965	0.249488
C	-1.172452	1.267366	0.256699
H	-3.296414	1.700793	0.743154
H	-0.751075	-2.135314	-0.211155
H	-0.785054	2.191572	-0.172655
H	-2.982637	1.666187	-0.958792
H	-4.305228	-0.332809	-0.307287

H	-0.994349	-1.253598	1.335706
H	-0.983443	1.288572	1.332955
I	1.651834	0.003581	-0.006171

$^4H_3$ conformation (0.2 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -281.732792047 a.u.
E_{solv}(B3LYP) = -281.813862889 a.u.
Zero-point energy correction = 0.123549 a.u.

Atom coordinates

H	0.059911	-0.238655	2.108722
C	0.461607	-0.108357	1.102314
C	1.990779	1.258505	-0.381159
O	2.050487	-1.156046	-0.521649
C	2.351484	-0.025862	-0.978134
C	1.257157	-1.334124	0.734497
C	1.282914	1.168412	0.970550
H	1.384825	1.759621	-1.158710
H	2.019024	-1.553950	1.489322
H	2.036371	1.149853	1.768501
H	2.910193	1.862889	-0.349212
H	2.922862	-0.071886	-1.914100
H	0.668876	-2.225464	0.531402
H	0.667205	2.051757	1.135395
I	-1.379940	0.014392	-0.153331

4-Phenylthio-pyranosyl oxocarbenium ion (**8**)

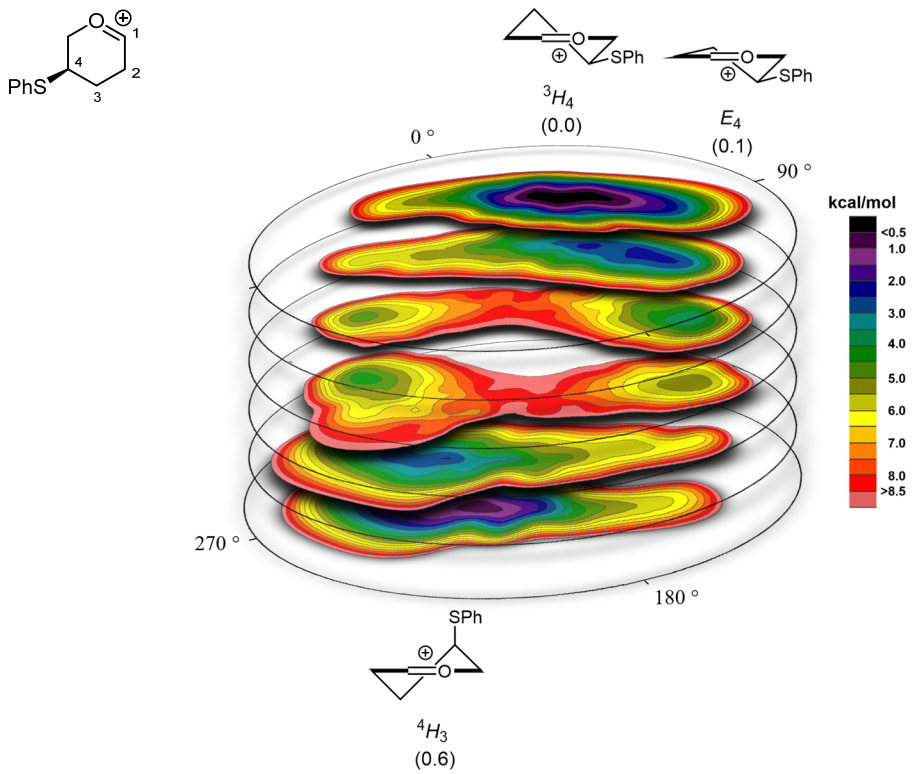


Figure 11| CEL map of 4-phenylthio-pyranosyl oxocarbenium ion (**8**).

Local minima

$^{3}H_{4}$ conformation (0.0 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -900.279025046 a.u.
E_{solv}(B3LYP) = -900.350623170 a.u.
Zero-point energy correction = 0.215238 a.u.

Atom coordinates

H	-0.810749	-0.353051	1.008057
C	-1.211712	-0.337765	-0.007048
C	-3.647725	-0.535002	0.661735
O	-2.735042	1.659389	0.212735
C	-3.643599	0.926838	0.664866
C	-1.479053	1.097053	-0.417888
C	-2.475585	-1.201882	-0.066270
H	-4.627926	-0.847306	0.278758
H	-0.717600	1.798832	-0.092195
H	-2.276189	-2.177209	0.375090
H	-3.697007	-0.806536	1.729520
H	-4.477241	1.481405	1.094997
H	-1.669502	1.211135	-1.483678
H	-2.758646	-1.370256	-1.109050
S	0.096157	-1.044440	-1.104553
C	1.594421	-0.384922	-0.352602
C	3.962101	0.584227	0.756163
C	2.113036	-0.970410	0.807203
C	2.269441	0.674403	-0.965585
C	3.454063	1.155032	-0.409102
C	3.290724	-0.477038	1.363383
H	1.601198	-1.808261	1.265452
H	1.870954	1.117161	-1.870237
H	3.976263	1.975973	-0.886412
H	3.689565	-0.929902	2.263611
H	4.882036	0.960737	1.187933

***E*$_{4}$ conformation (0.1 kcal / mol)**

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -900.278985368 a.u.
E_{solv}(B3LYP) = -900.350630122 a.u.
Zero-point energy correction = 0.215326 a.u.

Atom coordinates

H	-0.921162	-0.139333	1.061495
C	-1.244576	-0.381913	0.048036
C	-3.638613	-0.249820	0.709702
O	-2.516893	1.735758	-0.119435
C	-3.455364	1.192313	0.510314
C	-1.437248	0.882246	-0.759342
C	-2.566167	-1.151766	0.074670
H	-4.659579	-0.478584	0.372581
H	-0.583904	1.552489	-0.759305
H	-2.473943	-2.068047	0.656835
H	-3.701181	-0.371543	1.802560
H	-4.165239	1.901672	0.934868
H	-1.790660	0.705349	-1.773456
H	-2.861000	-1.428533	-0.939790
S	0.083519	-1.400080	-0.734365
C	1.561014	-0.510801	-0.211358
C	3.893158	0.808317	0.562707
C	2.039189	-0.646872	1.096391
C	2.259915	0.271931	-1.134973
C	3.426836	0.927870	-0.744853
C	3.198344	0.021950	1.481811
H	1.511975	-1.275987	1.803598
H	1.893898	0.363901	-2.150275
H	3.967205	1.532979	-1.463371
H	3.564744	-0.081313	2.496526
H	4.798766	1.321431	0.864408

$^{4}H_{3}$ conformation (0.6 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -900.279992470 a.u.
E_{solv}(B3LYP) = -900.350188889 a.u.
Zero-point energy correction = 0.215661 a.u.

Atom coordinates

H	-0.765971	-1.460876	1.299222
C	-1.236735	-0.767092	0.602592
C	-3.468271	-0.171188	-0.465162
O	-2.157312	1.570718	0.584082
C	-3.105222	1.209263	-0.151803
C	-1.241445	0.596258	1.261499
C	-2.660971	-1.238559	0.277247
H	-3.376423	-0.235741	-1.561658
H	-1.618892	0.562545	2.283999
H	-3.164520	-1.475783	1.217563
H	-4.549740	-0.259101	-0.298950
H	-3.664974	2.042087	-0.576302
H	-0.284385	1.108868	1.239163
H	-2.633279	-2.157112	-0.307401

S	-0.255736	-0.790682	-0.982977
C	1.378691	-0.290093	-0.428045
C	3.953954	0.464957	0.333043
C	2.183592	-1.179026	0.293434
C	1.868820	0.972202	-0.777033
C	3.158607	1.343981	-0.398911
C	3.464312	-0.794275	0.680973
H	1.812950	-2.166502	0.541180
H	1.246219	1.654092	-1.343432
H	3.537870	2.320747	-0.675512
H	4.084296	-1.483441	1.242380
H	4.955137	0.756824	0.627715

4-Methylthio-pyranosyl oxocarbenium ion (**9**)

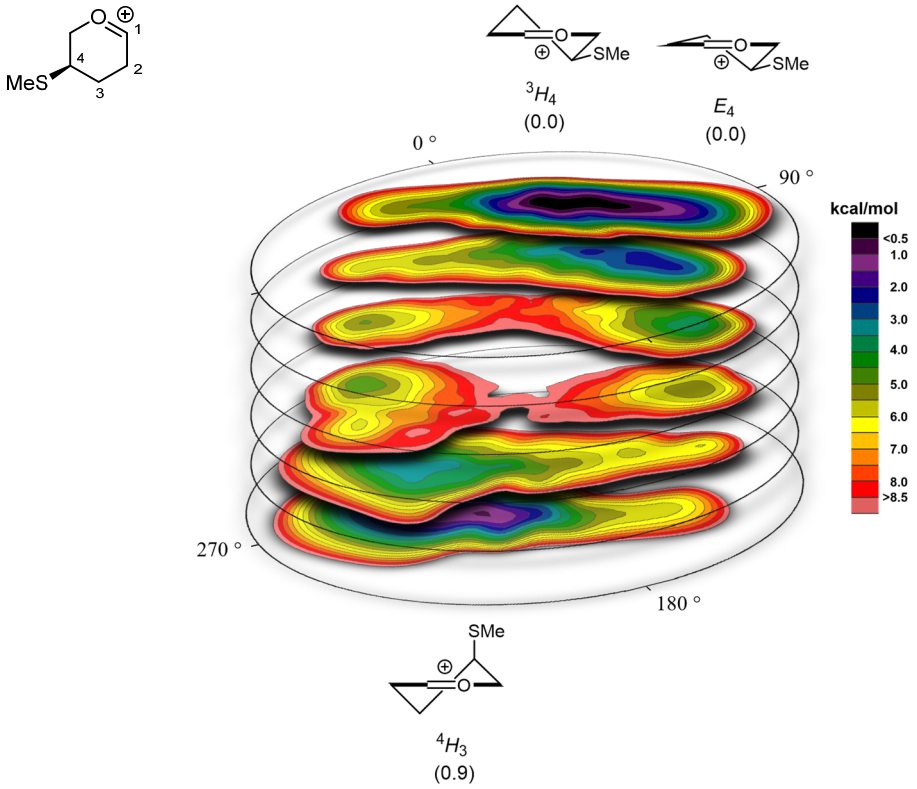


Figure 12| CEL map of 4-methylthio-pyranosyl oxocarbenium ion (**9**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -708.496637991 a.u.
E_{solv}(B3LYP) = -708.574002348 a.u.
Zero-point energy correction = 0.162168 a.u.

Atom coordinates

H	0.318138	-0.023517	1.296666
C	0.215161	-0.140236	0.211274
C	-2.161913	-1.021651	0.288098
O	-1.806618	1.333817	-0.122463
C	-2.563884	0.377217	0.162227
C	-0.326617	1.148007	-0.380258
C	-0.705998	-1.332932	-0.072709
H	-2.888505	-1.612033	-0.290739
H	0.097631	2.052742	0.049675

H	-0.364349	-2.203061	0.488583
H	-2.408695	-1.276804	1.336069
H	-3.606253	0.676631	0.330464
H	-0.262837	1.179850	-1.468997
H	-0.653838	-1.591573	-1.135653
S	1.893350	-0.455060	-0.470036
C	2.943119	0.521156	0.667520
H	3.970692	0.320213	0.362190
H	2.805558	0.188365	1.696448
H	2.752605	1.590236	0.578653

E_4 conformation (0.0 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -708.496343268 a.u.
E_{solv}(B3LYP) = -708.574155241 a.u.
Zero-point energy correction = 0.162239 a.u.

Atom coordinates

H	-0.215831	-0.036695	1.261603
C	-0.191421	0.160251	0.183171
C	2.156225	0.986359	0.315490
O	1.743841	-1.362857	-0.121115
C	2.503413	-0.437183	0.255178
C	0.326409	-1.048804	-0.566503
C	0.727519	1.345031	-0.126706
H	2.939662	1.516417	-0.250554
H	-0.188839	-1.981807	-0.351228
H	0.399072	2.241205	0.401312
H	2.363431	1.275065	1.361464
H	3.499054	-0.780792	0.563802
H	0.404652	-0.890561	-1.642873
H	0.708183	1.562466	-1.198588
S	-1.904677	0.519561	-0.378500
C	-2.873755	-0.634170	0.659018
H	-3.919209	-0.439906	0.416787
H	-2.708472	-0.429330	1.716938
H	-2.647928	-1.675081	0.428368

$^4H_3$ conformation (0.9 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -708.496387444 a.u.
E_{solv}(B3LYP) = -708.572955202 a.u.
Zero-point energy correction = 0.162492 a.u.

Atom coordinates

H	0.778282	-0.279518	1.795293
C	0.234686	-0.190852	0.848345
C	-1.898146	-0.942894	-0.327928
O	-1.339216	1.408320	-0.290454
C	-2.018511	0.453574	-0.738066
C	-0.282888	1.231827	0.756607
C	-0.922512	-1.201667	0.822197
H	-1.634000	-1.476994	-1.259565
H	-0.782871	1.550176	1.675338
H	-1.464216	-1.122652	1.769948
H	-2.918513	-1.298891	-0.117808
H	-2.739146	0.754459	-1.508820
H	0.456369	1.976171	0.472010
H	-0.534207	-2.218722	0.760710
S	1.402790	-0.615947	-0.525373
C	2.835865	0.446735	-0.133059
H	3.615294	0.167085	-0.842616
H	3.190270	0.251368	0.879731
H	2.610859	1.505767	-0.263190

4-Methyl-pyranosyl oxocarbenium ion (**10**)

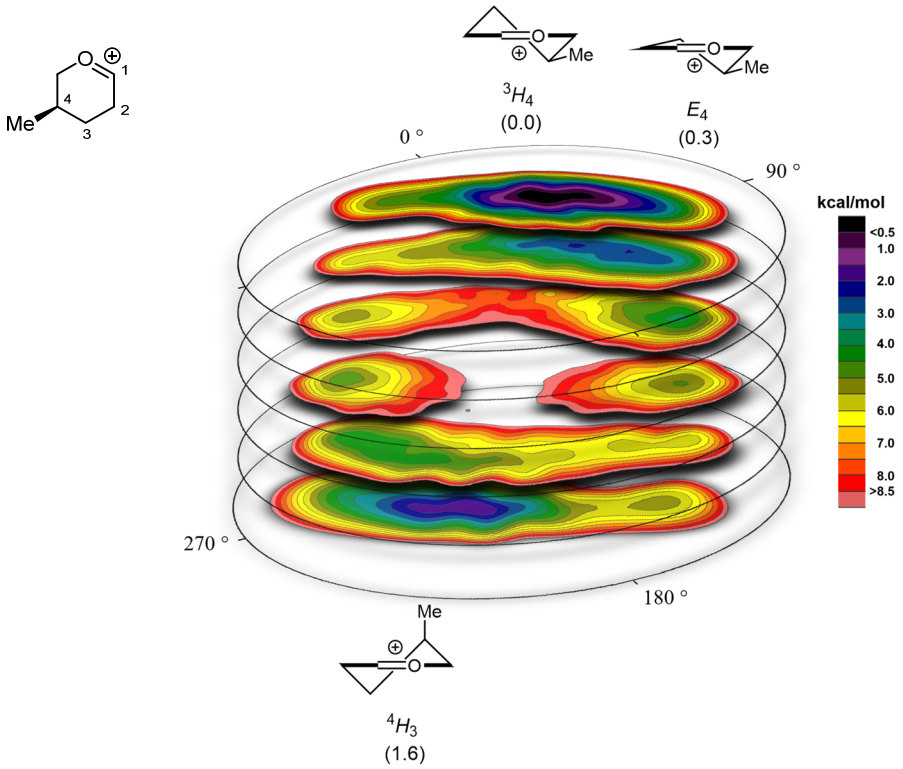


Figure 13| CEL map of 4-methyl-pyranosyl oxocarbenium ion (**10**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -310.290863856 a.u.
E_{solv}(B3LYP) = -310.367104766 a.u.
Zero-point energy correction = 0.161773 a.u.

Atom coordinates

H	0.874308	0.054850	-1.449280
C	0.952939	0.041600	-0.352547
C	-1.300418	1.179986	-0.027732
O	-1.188646	-1.235147	0.025533
C	-1.851307	-0.173193	-0.040309
C	0.313095	-1.246865	0.129587
C	0.210231	1.270856	0.193103
H	-1.890189	1.752425	0.704415
H	0.581321	-2.121062	-0.461272
H	0.594766	2.175864	-0.280598
H	-1.623484	1.605777	-0.996618
H	-2.932957	-0.337663	-0.124795
H	0.483253	-1.448578	1.190214
H	0.405945	1.365192	1.267083
C	2.437680	0.042154	0.028312
H	2.921721	0.937815	-0.367104
H	2.955857	-0.827610	-0.383553
H	2.565306	0.036940	1.114755

E_4 conformation (0.3 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -310.290332509 a.u.
E_{solv}(B3LYP) = -310.366855792 a.u.
Zero-point energy correction = 0.161795 a.u.

Atom coordinates

H	0.734110	0.006967	-1.420984
C	0.920274	0.030887	-0.337861
C	-1.277910	1.183310	-0.017058
O	-1.183993	-1.240400	-0.018640
C	-1.829369	-0.169900	-0.138913
C	0.294958	-1.204126	0.277930
C	0.227458	1.254454	0.278078

H	-1.907439	1.702497	0.724146
H	0.638323	-2.144489	-0.149648
H	0.630850	2.181479	-0.134087
H	-1.553529	1.675919	-0.966823
H	-2.892349	-0.321619	-0.365151
H	0.358189	-1.237561	1.367828
H	0.400582	1.272843	1.358506
C	2.433171	0.022661	-0.090695
H	2.886933	0.909197	-0.539007
H	2.904575	-0.857891	-0.534027
H	2.660204	0.032136	0.979479

$^4H_3$ conformation (1.6 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -310.288319427 a.u.
E_{solv}(B3LYP) = -310.364609593 a.u.
Zero-point energy correction = 0.161825 a.u.

Atom coordinates

H	-1.833313	-0.023515	1.261331
C	-1.094072	0.012726	0.451792
C	1.096034	1.188396	-0.148480
O	1.028649	-1.226608	-0.138487
C	1.599731	-0.151893	-0.437434
C	-0.295555	-1.273223	0.581718
C	-0.189093	1.240489	0.680861
H	1.003148	1.662313	-1.143403
H	-0.001588	-1.501477	1.607946
H	0.083828	1.293479	1.739146
H	1.931309	1.742527	0.307231
H	2.549816	-0.293705	-0.967990
H	-0.771184	-2.143189	0.132164
H	-0.736972	2.155397	0.450179
C	-1.840736	0.084280	-0.891551
H	-2.446909	0.991572	-0.938284
H	-2.506525	-0.773381	-1.013947
H	-1.158657	0.098191	-1.747910

C-3 Mono-substituted pyranosyl oxocarbenium ions

3-Benzyloxy-pyranosyl oxocarbenium ion (**11**)

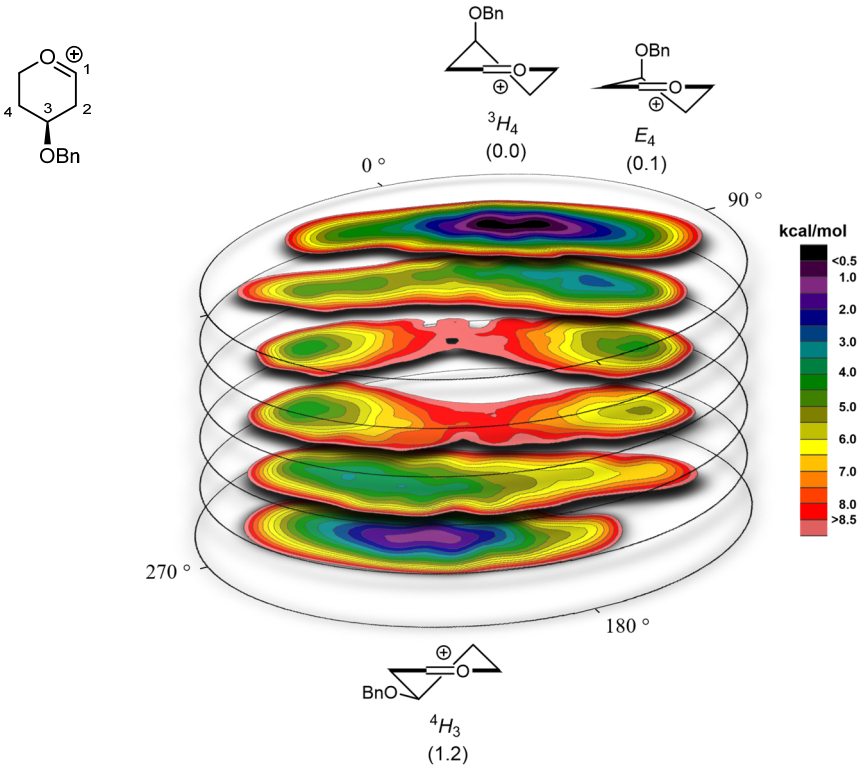


Figure 14| CEL map of 3-benzyloxy-pyranosyl oxocarbenium ion (**11**).

Local minima

$^{3}H_{4}$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -616.624062185 a.u.
E_{solv}(B3LYP) = -616.695303498 a.u.
Zero-point energy correction = 0.247342 a.u.

Atom coordinates

H	-3.602634	0.556832	1.472451
C	-2.601041	0.734254	1.073154
C	-2.647947	-1.429296	-0.154861
O	-3.070097	0.608668	-1.390215
C	-3.052859	-0.641299	-1.327086
C	-2.665171	1.489924	-0.236112
C	-1.876677	-0.605741	0.873011
H	-2.069986	-2.288071	-0.510548
H	-3.413085	2.276837	-0.267208
H	-1.826192	-1.155772	1.817555
H	-3.575443	-1.855229	0.259064
H	-3.388865	-1.127165	-2.242830
H	-1.700622	1.873848	-0.561721
H	-2.075742	1.365543	1.792459
O	-0.578580	-0.428977	0.322016
C	0.438207	-0.067507	1.279329
H	0.456393	-0.824716	2.072456
H	0.207270	0.901165	1.733957
C	1.760934	-0.005475	0.564734
C	4.206218	0.097558	-0.797800
C	2.416930	-1.184701	0.194477
C	2.341351	1.223649	0.242494
C	3.560036	1.276872	-0.433444
C	3.631797	-1.134866	-0.483330
H	1.974965	-2.143923	0.442822
H	1.841072	2.143961	0.526145
H	4.003205	2.236627	-0.673411
H	4.133777	-2.054540	-0.761603
H	5.154623	0.136838	-1.321389

E_{4} conformation (0.1 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -616.623640631 a.u.
E_{solv}(B3LYP) = -616.695139930 a.u.
Zero-point energy correction = 0.247262 a.u.

Atom coordinates

H	-3.553451	0.527176	1.495321
C	-2.563272	0.714966	1.072092
C	-2.595740	-1.424004	-0.201143
O	-3.418832	0.610998	-1.237140
C	-3.357949	-0.639994	-1.181450
C	-2.666463	1.453894	-0.238733
C	-1.812275	-0.604852	0.831486
H	-1.932684	-2.089709	-0.770903
H	-3.254878	2.365067	-0.206356
H	-1.737867	-1.179898	1.759523
H	-3.324264	-2.103159	0.264553
H	-3.945578	-1.140240	-1.950731
H	-1.701127	1.628688	-0.710168
H	-2.025873	1.351029	1.778140
O	-0.523584	-0.386818	0.278511
C	0.493274	-0.042229	1.243560
H	0.498834	-0.803994	2.032320
H	0.270850	0.926360	1.702604
C	1.820447	0.007526	0.536558
C	4.275556	0.086625	-0.809831
C	2.483437	-1.177758	0.199794
C	2.398646	1.230678	0.188366
C	3.621943	1.272069	-0.479840
C	3.703494	-1.139906	-0.469544
H	2.043364	-2.132324	0.468621
H	1.892766	2.155571	0.445703
H	4.063404	2.227324	-0.740014
H	4.211198	-2.064179	-0.720886
H	5.228035	0.116766	-1.326589

$^{4}H_{3}$ conformation (1.2 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -616.618875647 a.u.
E_{solv}(B3LYP) = -616.692839321 a.u.
Zero-point energy correction = 0.246870 a.u.

Atom coordinates

H	1.962885	-1.976196	0.714710
C	2.321618	-1.174853	0.066015
C	2.314036	1.315907	-0.327302
O	4.418047	0.121206	-0.394476
C	3.738576	1.150114	-0.611163
C	3.825877	-1.122247	0.209992
C	1.639370	0.159815	0.410456
H	1.839940	1.460337	-1.313015
H	4.175343	-1.079725	1.240931
H	1.718105	0.337809	1.490958
H	2.185280	2.284915	0.169616
H	4.310305	1.962559	-1.058526

H	4.344812	-1.914617	-0.321031
H	2.055421	-1.438711	-0.961786
O	0.283905	0.190193	0.012070
C	-0.626790	-0.477776	0.908820
H	-0.492229	-0.069632	1.918058
H	-0.411569	-1.550700	0.938491
C	-2.028258	-0.239709	0.415468
C	-4.614077	0.235391	-0.551310
C	-2.659267	0.986796	0.650248
C	-2.704904	-1.222419	-0.311171
C	-3.992926	-0.988767	-0.791079
C	-3.944458	1.224215	0.170451
H	-2.141918	1.755782	1.214405
H	-2.223017	-2.175903	-0.500623
H	-4.509527	-1.760587	-1.350178
H	-4.425910	2.176379	0.362493
H	-5.616314	0.418299	-0.921816

3-Methoxy-pyranosyl oxocarbenium ion (**S2**)

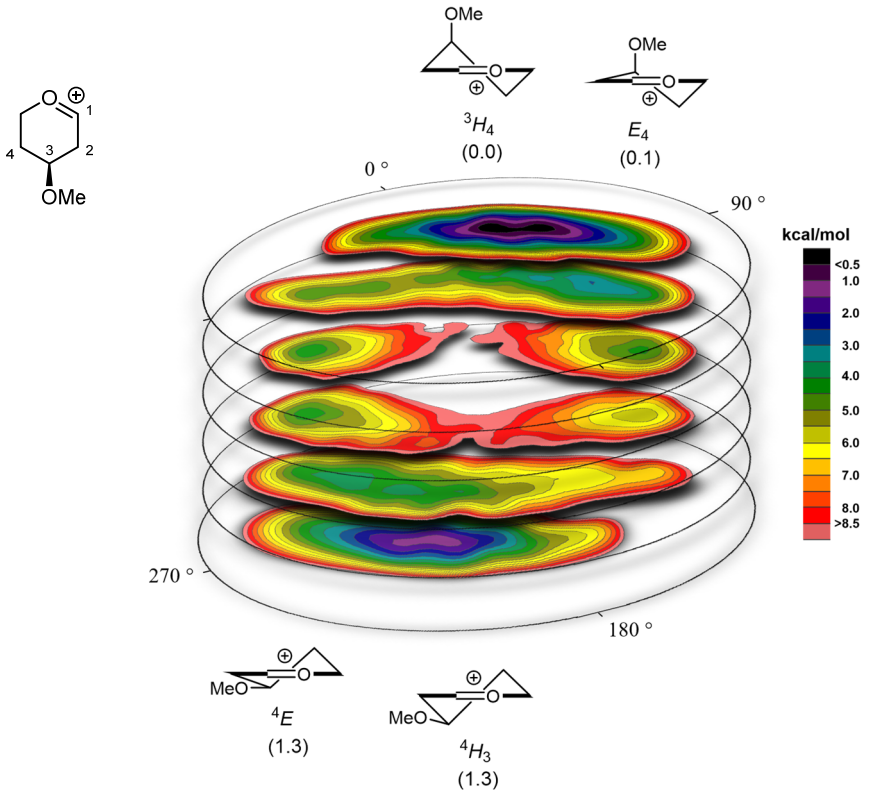


Figure 15| CEL map of 3-methoxy-pyranosyl oxocarbenium ion (**S2**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -385.515056186 a.u.
E_{solv}(B3LYP) = -385.590288877 a.u.
Zero-point energy correction = 0.166313 a.u.

Atom coordinates

H	-0.609748	0.914211	1.922771
C	-0.035280	0.971060	0.992757
C	-0.587752	-1.393454	0.461960
O	-1.822028	0.358500	-0.661015
C	-1.661190	-0.852293	-0.381875
C	-0.907235	1.441925	-0.150683
C	0.558270	-0.409198	0.671152
H	-0.246663	-2.332751	0.008848
H	-2.424070	-1.507761	-0.820901
H	-1.604815	2.235371	0.110849
H	1.190988	-0.754634	1.499087
H	-1.069810	-1.686678	1.411159
H	-0.345607	1.714678	-1.044089

H	0.746131	1.720856	1.143942
O	1.282586	-0.405538	-0.551564
C	2.604308	0.126089	-0.456819
H	3.058939	0.000669	-1.438708
H	3.191116	-0.423676	0.288262
H	2.602348	1.191245	-0.199542

E_4 conformation (0.1 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -385.514657227 a.u.
E_{solv}(B3LYP) = -385.590140865 a.u.
Zero-point energy correction = 0.166238 a.u.

Atom coordinates

H	-0.667092	0.848627	1.857214
C	-0.044202	0.925992	0.959758
C	-0.577558	-1.408868	0.291728
O	-1.953531	0.420991	-0.513535
C	-1.786665	-0.799773	-0.275508
C	-0.856224	1.409915	-0.215414
C	0.567142	-0.439770	0.606122
H	-0.257560	-2.196541	-0.408577
H	-2.655520	-1.420492	-0.528532
H	-1.406865	2.331588	-0.042813
H	1.149122	-0.834294	1.449065
H	-0.919131	-1.962902	1.182206
H	-0.286954	1.465160	-1.143483
H	0.730169	1.669122	1.168671
O	1.365944	-0.373392	-0.565521
C	2.684452	0.135528	-0.356604
H	3.200480	0.056119	-1.312552
H	3.215759	-0.460783	0.394201
H	2.676615	1.185472	-0.043440

^4E conformation (1.3 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -385.510315860 a.u.
E_{solv}(B3LYP) = -385.587882792 a.u.
Zero-point energy correction = 0.165969 a.u.

Atom coordinates

H	0.548260	1.980161	-0.258626
C	-0.055565	1.080951	-0.410128
C	-0.362314	-1.335970	0.055370
O	-2.294256	0.129412	0.005730
C	-1.789749	-1.018230	-0.053781
C	-1.409271	1.333682	0.206159
C	0.577147	-0.142484	0.267618
H	-0.106912	-1.852570	-0.887951
H	-2.526582	-1.816704	-0.207688
H	-1.393674	1.478096	1.288382
H	0.687892	0.055615	1.345060
H	-0.264498	-2.122922	0.819123
H	-1.978938	2.128363	-0.270595
H	-0.146124	0.914780	-1.488877
O	1.814947	-0.525109	-0.291805
C	2.927743	0.258387	0.138753
H	3.812444	-0.191076	-0.310391
H	3.023522	0.234535	1.231002
H	2.851140	1.299276	-0.194774

$^4H_3$ conformation (1.3 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -385.510440376 a.u.
E_{solv}(B3LYP) = -385.587748071 a.u.
Zero-point energy correction = 0.165967 a.u.

Atom coordinates

H	0.540494	2.007755	0.023717
C	-0.026376	1.129733	-0.297023
C	-0.351991	-1.347431	0.027701
O	-2.291510	0.100006	0.011178
C	-1.780758	-1.043507	-0.028185
C	-1.461209	1.348256	0.125359
C	0.578561	-0.162198	0.277503
H	-0.123287	-1.808311	-0.952429
H	-2.518426	-1.850692	-0.120552
H	-1.581135	1.623641	1.175184
H	0.713871	-0.045720	1.364465
H	-0.215534	-2.171441	0.742452
H	-2.001375	2.052579	-0.504193
H	0.034610	1.077767	-1.389861
O	1.807517	-0.499894	-0.331228
C	2.929263	0.247106	0.139151
H	3.807109	-0.178720	-0.345161
H	3.033350	0.152992	1.226819
H	2.857326	1.307494	-0.127075

3-Methyl-pyranosyl oxocarbenium ion (**12**)

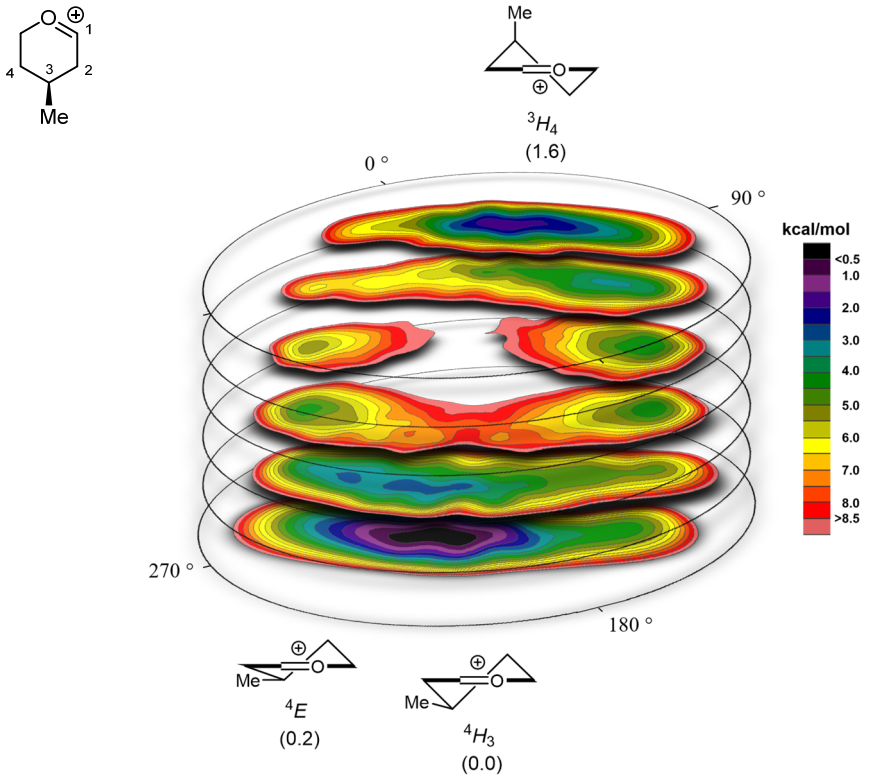


Figure 16| CEL map of 3-methyl-pyranosyl oxocarbenium ion (**12**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -310.290760538 a.u.
E_{solv}(B3LYP) = -310.367315448 a.u.
Zero-point energy correction = 0.161763 a.u.

Atom coordinates

H	0.648671	-2.165604	-0.000874
C	0.215727	-1.208233	0.306390
C	0.267664	1.259978	0.105496
O	-1.871073	0.147186	-0.047841
C	-1.196785	1.199883	0.044291
C	-1.238291	-1.225146	-0.108632
C	0.957200	-0.033158	-0.347336
H	-1.810321	2.108582	0.099424
H	-1.395913	-1.511389	-1.149762
H	0.844771	-0.109447	-1.437335
H	0.583093	2.150148	-0.455142
H	-1.890349	-1.807686	0.540218
H	0.299559	-1.147324	1.397395
H	0.494205	1.506723	1.161424
C	2.447065	-0.018520	-0.003653
H	2.599368	0.040288	1.078587
H	2.947862	0.837224	-0.464076
H	2.932156	-0.927821	-0.366466

^4E conformation (0.2 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -310.290417092 a.u.
E_{solv}(B3LYP) = -310.367082722 a.u.
Zero-point energy correction = 0.161743 a.u.

Atom coordinates

H	-0.623457	-2.167031	-0.122382
C	-0.182480	-1.186451	-0.328392

C	-0.264956	1.259153	0.063121
O	1.882897	0.134807	-0.065141
C	1.188911	1.179579	-0.119261
C	1.226568	-1.196812	0.208959
C	-0.983617	-0.071481	0.358867
H	1.772833	2.082687	-0.337788
H	1.291662	-1.312833	1.292218
H	-0.947757	-0.244903	1.441705
H	-0.436273	2.037228	0.824994
H	1.898714	-1.894075	-0.286960
H	-0.170502	-1.055880	-1.416938
H	-0.624975	1.737242	-0.867458
C	-2.445748	-0.021782	-0.085599
H	-2.523575	0.127276	-1.167232
H	-2.978793	0.794659	0.408717
H	-2.953128	-0.956062	0.166090

$^3H_4$ conformation (1.6 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -310.288704117 a.u.
E_{solv}(B3LYP) = -310.364812938 a.u.
Zero-point energy correction = 0.161837 a.u.

Atom coordinates

H	0.154441	-1.152130	1.746032
C	-0.225477	-1.159892	0.718550
C	-0.185371	1.338107	0.403920
O	1.684126	0.019829	-0.393715
C	1.166274	1.126348	-0.111069
C	0.946157	-1.279583	-0.230318
C	-1.086951	0.096638	0.481298
H	1.841185	1.976417	-0.272461
H	1.727020	-1.953812	0.116207
H	-1.743135	0.218027	1.348117
H	-0.011988	1.801100	1.394893
H	0.673738	-1.534984	-1.255846
H	-0.828807	-2.065925	0.610428
H	-0.618437	2.165662	-0.178521
C	-1.963082	-0.027640	-0.775013
H	-1.365707	-0.139995	-1.686212
H	-2.589404	0.859172	-0.900905
H	-2.621208	-0.896027	-0.696215

C-2 Mono-substituted pyranosyl oxocarbenium ions

2-Benzyloxy-pyranosyl oxocarbenium ion (**13**)

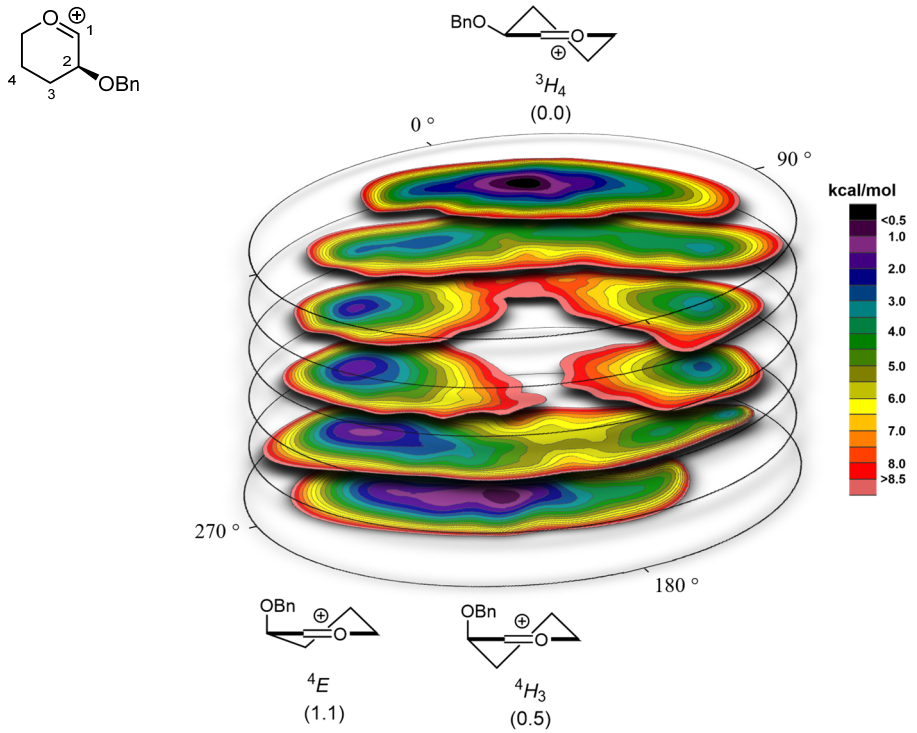


Figure 17| CEL map of 2-benzyloxy-pyranosyl oxocarbenium ion (**13**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -616.619838318 a.u.
E_{solv}(B3LYP) = -616.686921058 a.u.
Zero-point energy correction = 0.247498 a.u.

Atom coordinates

H	2.560292	1.004586	-1.863595
C	3.138842	0.965699	-0.936800
C	1.186977	0.077357	0.321351
O	2.928650	-1.474532	-0.397819
C	1.798185	-1.259791	0.088793
C	3.857405	-0.358796	-0.829914
C	2.229245	1.199615	0.274852
H	4.253274	-0.738027	-1.767642
H	1.730047	2.164796	0.199059
H	0.494458	0.183225	-0.540100
H	1.246856	-2.153860	0.379303
H	4.628259	-0.385809	-0.061083
H	3.901685	1.744531	-1.002350
H	2.799379	1.187075	1.207315
O	0.472393	-0.037492	1.526538
C	-0.727249	0.778583	1.614197
H	-1.053626	0.631101	2.643321
H	-0.465624	1.832704	1.484382
C	-1.795131	0.365613	0.634020
C	-3.781156	-0.415130	-1.181283
C	-2.385743	-0.901903	0.729172
C	-2.210336	1.233067	-0.380758
C	-3.202036	0.846671	-1.283560
C	-3.370185	-1.290349	-0.172875
H	-2.074673	-1.579941	1.516803
H	-1.764498	2.219284	-0.458355
H	-3.519228	1.530456	-2.062365
H	-3.825309	-2.270422	-0.087397
H	-4.552548	-0.717325	-1.880204

$^4H_3$ conformation (0.5 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -616.622587644 a.u.
E_{solv}(B3LYP) = -616.686762545 a.u.
Zero-point energy correction = 0.248108 a.u.

Atom coordinates

H	-4.646680	0.415596	-0.349683
C	-3.583679	0.167833	-0.375451
C	-1.318713	0.652619	0.525424
O	-2.023954	-1.672222	0.331307
C	-1.123120	-0.830649	0.549397
C	-3.452246	-1.288148	0.009641
C	-2.783618	1.048682	0.589833
H	-3.981927	-1.550429	0.924903
H	-3.141393	0.930761	1.617195
H	-0.720538	1.112667	1.339937
H	-0.131886	-1.257380	0.692495
H	-3.702648	-1.992347	-0.778569
H	-3.231738	0.323286	-1.397077
H	-2.871816	2.102977	0.325790
O	-0.764130	0.934227	-0.765237
C	0.525816	1.607211	-0.781701
H	0.620010	1.932925	-1.817689
H	0.468639	2.488138	-0.136078
C	1.674545	0.714916	-0.384165
C	3.788255	-0.968891	0.352827
C	2.030547	-0.373968	-1.192773
C	2.394064	0.953038	0.790355
C	3.447671	0.115473	1.157599
C	3.077877	-1.212442	-0.824407
H	1.487298	-0.559708	-2.113362
H	2.137527	1.800818	1.416979
H	4.000081	0.311449	2.069179
H	3.347993	-2.049175	-1.458165
H	4.607353	-1.619668	0.636113

^4E conformation (1.1 kcal / mol)

D1 = -30°
D3 = -60°
D5 = -15°

E_{gas}(B3LYP) = -616.621695713 a.u.
E_{solv}(B3LYP) = -616.685802355 a.u.
Zero-point energy correction = 0.248223 a.u.

Atom coordinates

H	-4.714414	0.377338	-0.192620
C	-3.658327	0.118919	-0.295090
C	-1.326927	0.617290	0.488872
O	-2.027205	-1.690400	0.053717
C	-1.126138	-0.860746	0.326037
C	-3.478091	-1.295021	0.195691
C	-2.786085	1.066509	0.535004
H	-3.694231	-1.432139	1.254559
H	-3.123389	1.065928	1.575544
H	-0.734969	0.994511	1.349207
H	-0.113980	-1.255811	0.275809
H	-3.987359	-2.047716	-0.397255
H	-3.408544	0.178644	-1.357174
H	-2.834949	2.091431	0.167374
O	-0.735511	0.977598	-0.767427
C	0.557520	1.651335	-0.708854
H	0.678809	2.036339	-1.720932
H	0.472673	2.490994	-0.013375
C	1.696988	0.741092	-0.329395
C	3.785696	-0.986687	0.375759
C	2.145483	-0.235648	-1.229641
C	2.312850	0.846620	0.921323
C	3.353713	-0.013029	1.272976
C	3.180768	-1.096098	-0.877839
H	1.684226	-0.316880	-2.208317
H	1.987867	1.610374	1.619969
H	3.826258	0.080969	2.243712
H	3.523266	-1.844968	-1.582487
H	4.595772	-1.653813	0.646612

2-Methoxy-pyranosyl oxocarbenium ion (**S3**)

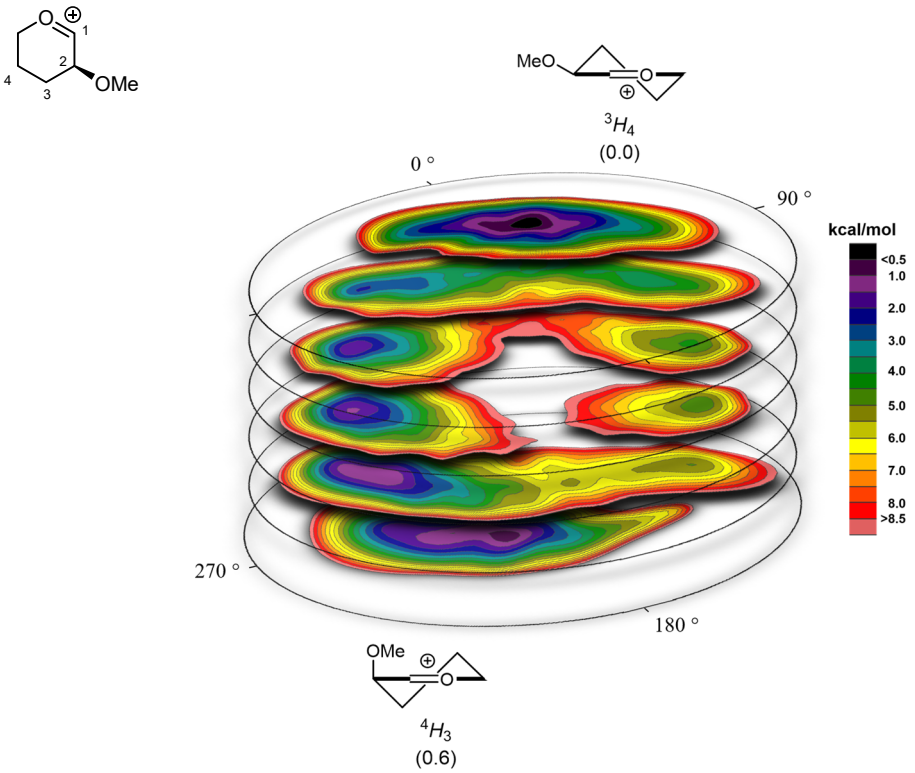


Figure 18| CEL map of 2-methoxy-pyranosyl oxocarbenium ion (**S3**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -385.505750957 a.u.
E_{solv}(B3LYP) = -385.580559380 a.u.
Zero-point energy correction = 0.166162 a.u.

Atom coordinates

H	-1.713098	1.092104	1.422691
C	-1.736480	1.062267	0.328261
C	0.591882	0.185783	0.229276
O	-1.277209	-1.372646	-0.051015
C	-0.055101	-1.158707	0.107044
C	-2.297155	-0.258997	-0.142461
C	-0.337509	1.300887	-0.249218
H	0.559891	-2.067809	0.102771
H	-3.119102	-0.645266	0.457700
H	0.063851	2.263269	0.069985
H	0.805121	0.317515	1.317408
H	-2.564770	-0.276644	-1.200515
H	-2.427436	1.844409	0.000183
H	-0.357630	1.289990	-1.343562
O	1.770567	0.131130	-0.542641
C	2.984558	-0.059831	0.196682
H	3.792380	-0.015538	-0.531665
H	3.003454	-1.034125	0.697509
H	3.109304	0.735820	0.939245

$^4H_3$ conformation (0.6 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -385.506898380 a.u.
E_{solv}(B3LYP) = -385.579980759 a.u.
Zero-point energy correction = 0.166586 a.u.

Atom coordinates

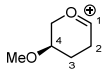
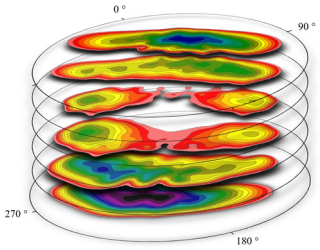
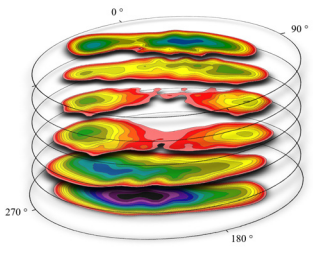
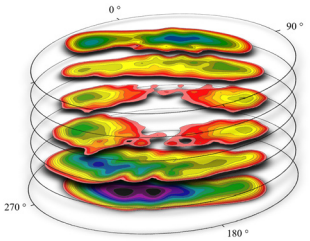
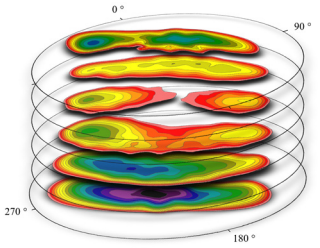
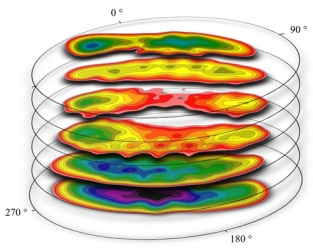
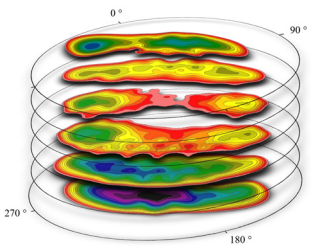
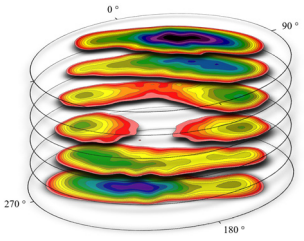
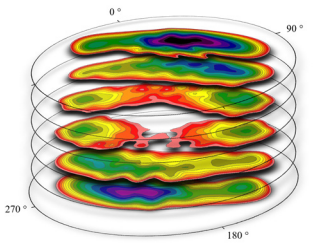
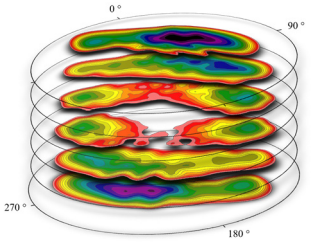
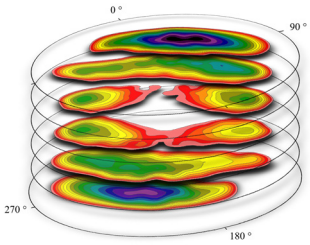
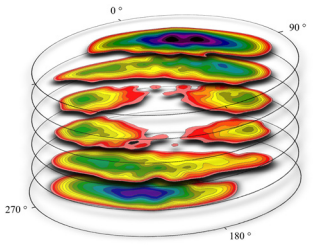
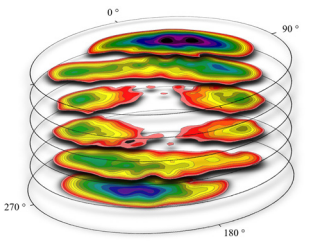
E_{gas}(B3LYP) = -385.506898380 a.u.
E_{solv}(B3LYP) = -385.579980759 a.u.
Zero-point energy correction = 0.166586 a.u.

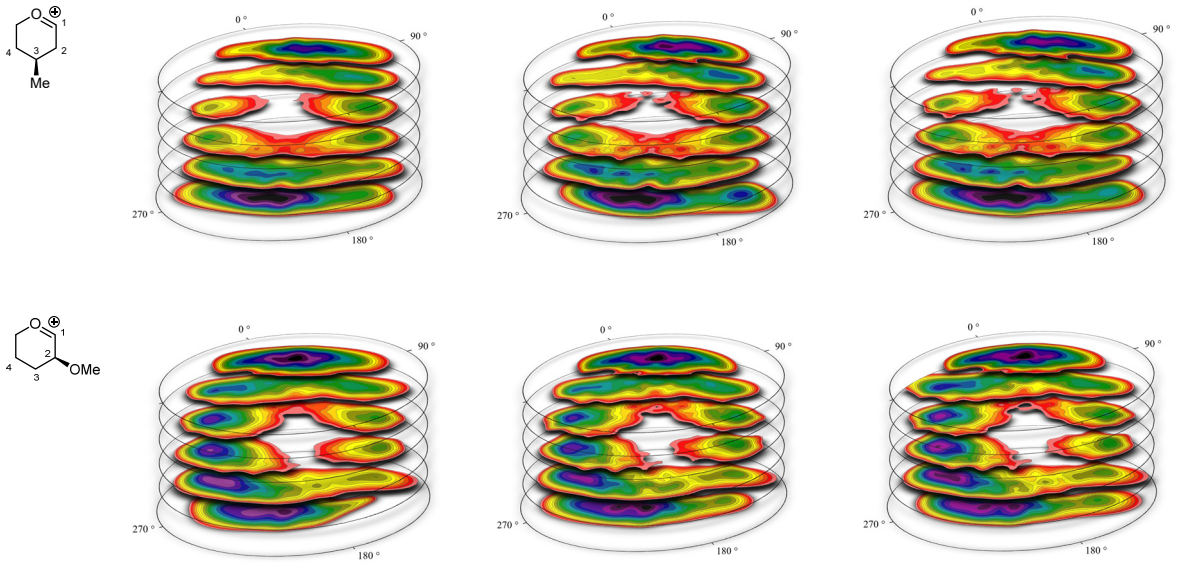
H	-2.087443	1.950834	-0.455062
C	-1.364149	1.130924	-0.466239
C	0.597269	0.080725	0.644810
O	-1.261177	-1.343447	-0.027612
C	-0.089731	-1.225725	0.399128
C	-2.146005	-0.158538	-0.354656
C	-0.370800	1.249126	0.693670
H	0.444745	-2.176223	0.513768
H	-2.866446	-0.164711	0.465723
H	-0.890611	1.237183	1.658656
H	1.207559	0.003183	1.576685
H	-2.626158	-0.484561	-1.275527
H	-0.830671	1.170672	-1.419512
H	0.196954	2.179969	0.633764
O	1.410639	0.110393	-0.532420
C	2.825653	-0.024945	-0.314070
H	3.288027	0.059185	-1.296015
H	3.071627	-0.997349	0.122687
H	3.183299	0.776853	0.339236

Mono-substituted pyranosyl oxocarbenium ions with dispersion-corrected DFT

Novel corrections and functionals, including B3LYP-D3 and ωB97XD, were used to study the effect of dispersion (Van der Waals interactions) on the conformational preference of the studied oxocarbenium ions, because the used B3LYP functional fails to describe adequately this force. All functionals were used in combination with the 6-311(d,p) as basis set and a PCM model (DCM), according to the general procedure previously described. Analysing several mono-substituted oxocarbenium ions one can conclude that these noncovalent interactions have no significant effect on the conformational preference of these reactive intermediates. The CEL maps are based on the ΔE_{DCM} (Equation 3).

$$\Delta E_{DCM} = \Delta E_{gas} + \Delta G_{solv} \tag{3}$$

	B3LYP	B3LYP-D3	ωB97XD
			
			
			
			


Me
OMe
0 °
90 °
180 °
270 °

Probing the influence of the substituent orientation on the oxocarbenium ion stability

To investigate whether the orientation of the substitutions on the ring have a crucial effect on the stability of the oxocarbenium ion, extra DFT calculations were done in which the dihedral angle of the substituent was systematically rotated. Two key conformations were selected as starting point, including the $^{3}H_{4}$ and $^{4}H_{3}$, obtained from the 'conformer distribution search' option included in the Spartan 10 program by utilising DFT as the level of theory and B3LYP as hybrid functional in gas phase with 6-31G(d) as the basis set (*vide supra*). The ring dihdral angles were fixed to counter any conformational changes and the dihedral angle of choice was scanned for a full 360° with a step size of 20°. All calculations were done with Gaussian 09 by using DFT/B3LYP/6-311G(d,p), and further optimised with a polarisable continuum model (PCM) to correct for solvation in CH_2Cl_2. The depicted graphs are based on the relative ΔE_{DCM}.

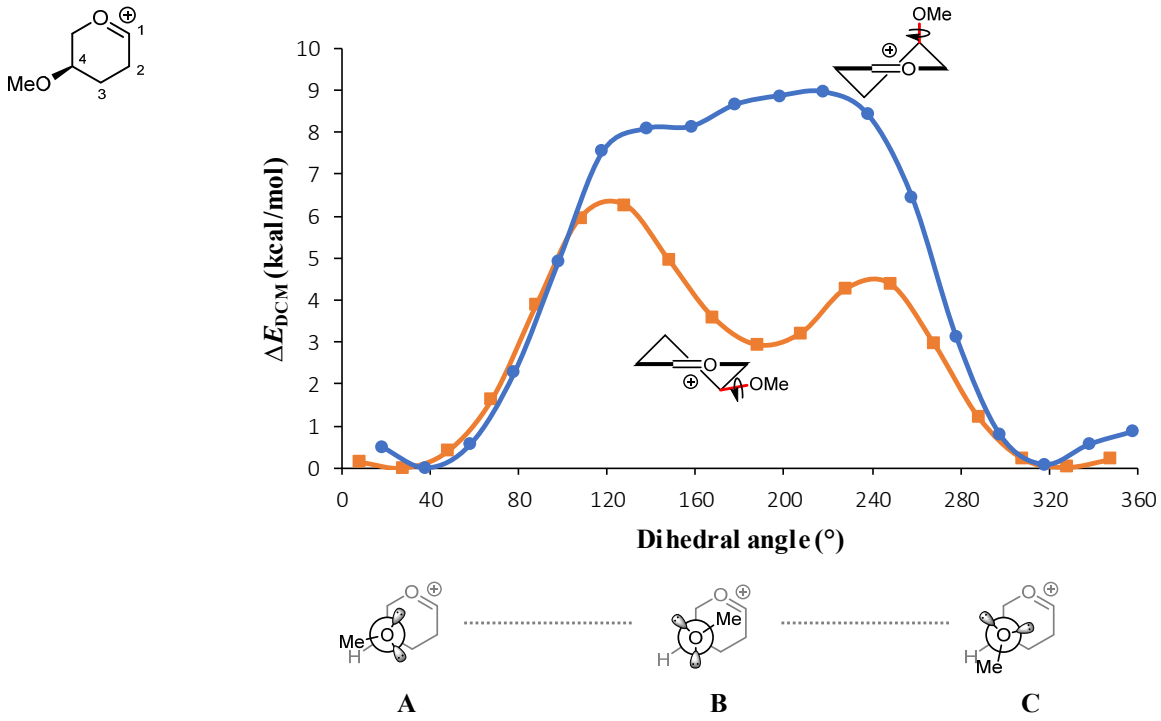


Figure 19| The influence of the orientation of the C-4 substituent on the oxocarbenium ion stability.

Figure 19 shows the result of the scan for the C-4 substituted oxocarbenium ion and it is clear that the orientation of the substituent has an impact on the overall stability of the ion. Both for the $^{3}H_{4}$ and $^{4}H_{3}$ conformation a strong preference for geometry **A** and **B** was found to avoid any steric interactions between the substituent and the ring protons. This behaviour was also found for the C-3 and C-2 substituted oxocarbenium ions (Figure 20 and 21). This shows a general trend, in which the orientation of the substituent is crucial, and for both probed conformations the preference for rotamer **A** and **B** is strong. Concluding, the overall geometry of the substituents will be **A** and **B**, and not very flexible.

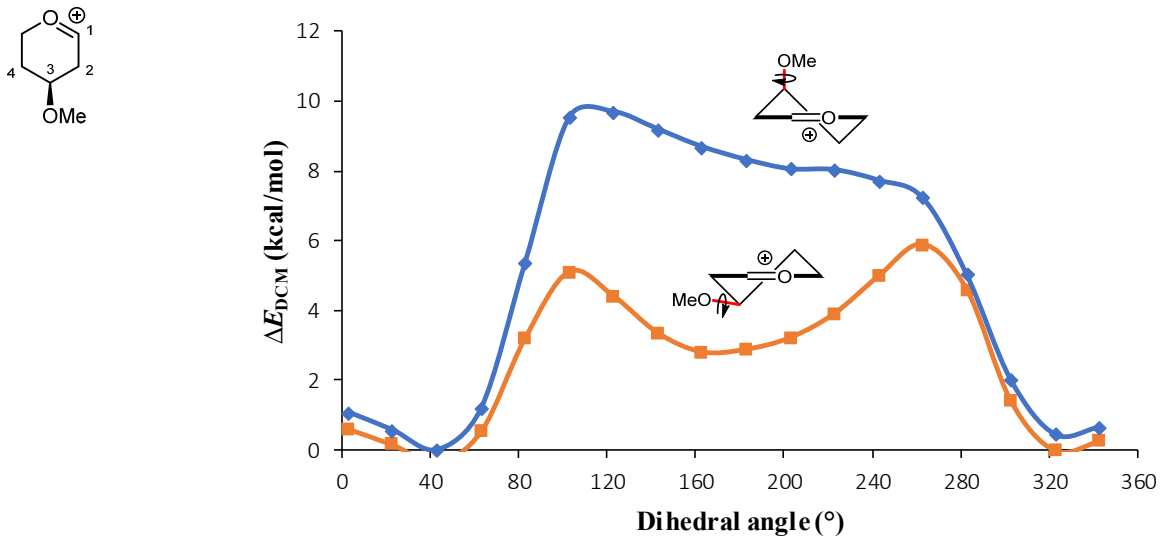


Figure 20| The influence of the orientation of the C-3 substituent on the oxocarbenium ion stability.

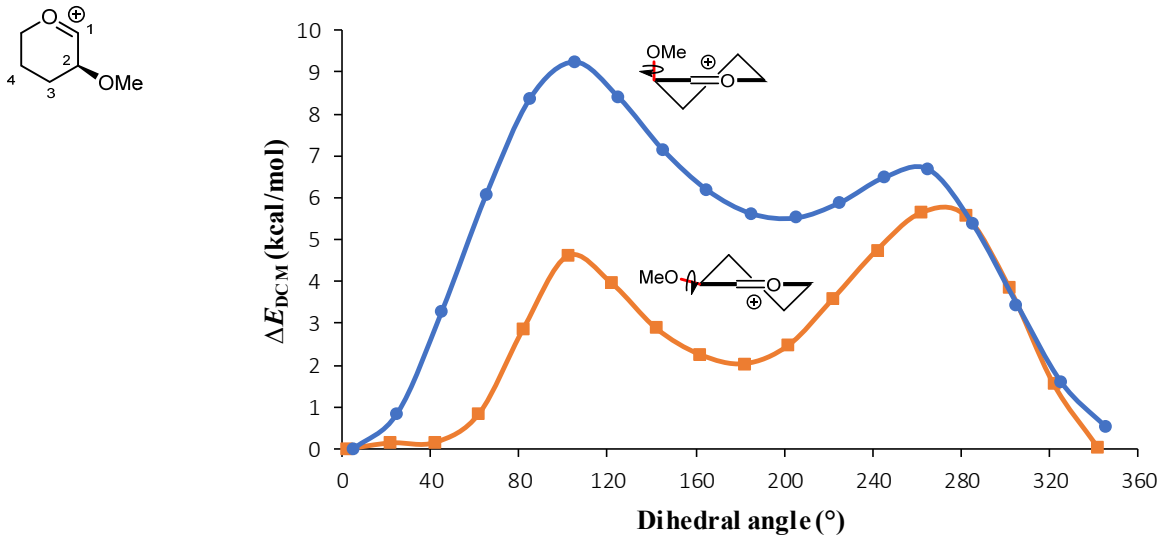


Figure 21| The influence of the orientation of the C-2 substituent on the oxocarbenium ion stability.

Multi-substituted pyranosyl oxocarbenium ions

2,3,4-Tri-*O*-methyl-lyxo-D-pyranosyl oxocarbenium ion (**14**)

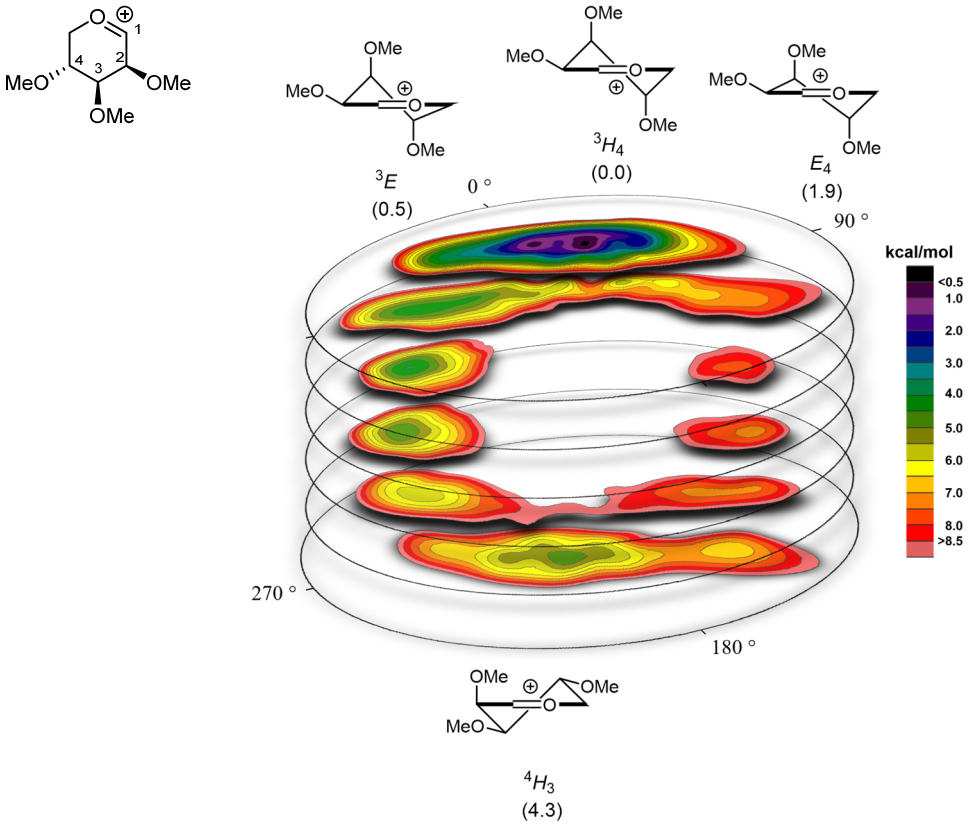


Figure 22| CEL map of 2,3,4-tri-*O*-methyl-lyxo-D-pyranosyl oxocarbenium ion (**14**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -614.607306924 a.u.
E_{solv}(B3LYP) = -614.674748497 a.u.
Zero-point energy correction = 0.230464 a.u.

Atom coordinates

C	1.381784	0.543617	-0.108570
C	-0.796472	-0.678291	-0.182856
O	0.634739	-0.914118	1.786596
C	-0.365438	-1.262252	1.120497
C	1.568255	0.174659	1.350675
C	-0.111249	0.676785	-0.448257
H	-0.973321	-2.039833	1.601917
H	2.548577	-0.237243	1.583268
H	-0.444273	-1.392918	-0.948143
H	1.328019	0.995599	2.027079
H	1.867001	1.517160	-0.272153
O	-2.196367	-0.560104	-0.139178
O	1.900535	-0.461909	-0.963321
C	-2.927368	-1.526070	-0.909483
H	-3.976538	-1.250424	-0.820287
H	-2.783701	-2.538876	-0.518292
H	-2.621329	-1.491466	-1.960445
C	3.298040	-0.345297	-1.243756
H	3.517780	0.619560	-1.714234
H	3.543546	-1.151628	-1.933355
H	3.906997	-0.454477	-0.338969
H	-0.224766	0.943195	-1.505423

O	-0.621952	1.668750	0.416691
C	-1.659527	2.495070	-0.123778
H	-1.871928	3.248882	0.633631
H	-2.560086	1.912722	-0.326846
H	-1.319770	2.989463	-1.040882

^{3}E conformation (0.5 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -614.606750845 a.u.
E_{solv}(B3LYP) = -614.673678097 a.u.
Zero-point energy correction = 0.230219 a.u.

Atom coordinates

C	1.402903	0.439344	-0.238780
C	-0.790596	-0.667196	0.074367
O	0.454713	-0.064387	2.065430
C	-0.568025	-0.561441	1.541391
C	1.601610	0.495473	1.275006
C	-0.086882	0.540213	-0.593692
H	-1.339375	-0.873276	2.257824
H	2.453059	-0.089640	1.620992
H	-0.271682	-1.579377	-0.270676
H	1.660505	1.513551	1.659511
H	1.928467	1.300761	-0.674648
O	-2.169490	-0.678944	-0.175587
O	1.860511	-0.785911	-0.780418
C	-2.710663	-1.946551	-0.574663
H	-3.765084	-1.774359	-0.782332
H	-2.614168	-2.688975	0.225033
H	-2.211048	-2.311937	-1.478201
C	3.247376	-0.807297	-1.128249
H	3.472935	-0.029159	-1.865669
H	3.441716	-1.787525	-1.560739
H	3.888861	-0.671827	-0.249554
H	-0.207559	0.462219	-1.680748
O	-0.556305	1.763412	-0.079976
C	-1.657325	2.355820	-0.784695
H	-1.820712	3.328979	-0.323685
H	-2.557257	1.745000	-0.695002
H	-1.404480	2.492022	-1.841807

E_4 conformation (1.9 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -614.603829673 a.u.
E_{solv}(B3LYP) = -614.672020586 a.u.
Zero-point energy correction = 0.230610 a.u.

Atom coordinates

C	1.331498	0.660684	-0.044764
C	-0.769301	-0.670566	-0.291171
O	0.855790	-1.220249	1.468988
C	-0.109664	-1.535295	0.736782
C	1.475457	0.141006	1.372631
C	-0.159568	0.748896	-0.411225
H	-0.509228	-2.537802	0.934690
H	2.499886	-0.034537	1.692209
H	-0.562751	-1.195357	-1.241082
H	0.940423	0.753176	2.098734
H	1.769753	1.668570	-0.086999
O	-2.139174	-0.670034	0.033523
O	1.916554	-0.221583	-0.984980
C	-2.982963	-1.429923	-0.848683
H	-4.001461	-1.271192	-0.498943
H	-2.746499	-2.497705	-0.804005
H	-2.881453	-1.072200	-1.878414
C	3.336173	-0.116128	-1.125122
H	3.622280	0.909332	-1.383539
H	3.615518	-0.787556	-1.935608
H	3.861554	-0.422058	-0.213726
H	-0.267527	1.110489	-1.440067
O	-0.733181	1.633746	0.525473
C	-1.827167	2.419507	0.044073
H	-2.092864	3.099217	0.852950
H	-2.686410	1.791312	-0.200624
H	-1.527931	3.002188	-0.834737

$^{4}H_3$ conformation (4.3 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -614.597990132 a.u.

E_{solv}(B3LYP) = -614.668104174 a.u.

Zero-point energy correction = 0.230791 a.u.

Atom coordinates

C	0.915843	-0.520975	0.191071
C	-1.402055	0.069881	-0.514874
O	-0.807601	-2.280247	-0.440094
C	-1.658278	-1.392120	-0.687668
C	0.646793	-1.963023	-0.261335
C	0.068251	0.463863	-0.619727
H	-2.672453	-1.768243	-0.865619
H	1.080302	-2.151774	-1.245053
H	-2.026250	0.665946	-1.204430
H	0.979784	-2.715598	0.450383
H	0.659251	-0.400593	1.250329
O	-1.876026	0.118698	0.832058
O	2.289015	-0.281176	-0.035705
C	-2.952215	1.046863	1.080372
H	-3.176980	0.957786	2.141580
H	-3.837086	0.788801	0.492198
H	-2.618214	2.059261	0.843902
C	3.113430	-0.328244	1.135499
H	2.813094	0.441864	1.853384
H	4.131059	-0.134860	0.798705
H	3.076068	-1.311450	1.616648
H	0.358189	0.395244	-1.681476
O	0.181871	1.779800	-0.132444
C	1.096813	2.615260	-0.851633
H	1.084020	3.581596	-0.348802
H	0.772491	2.745017	-1.890867
H	2.107153	2.201361	-0.831621

2,3,4-Tri-*O*-methyl-arabino-D-pyranosyl oxocarbenium ion (**15**)

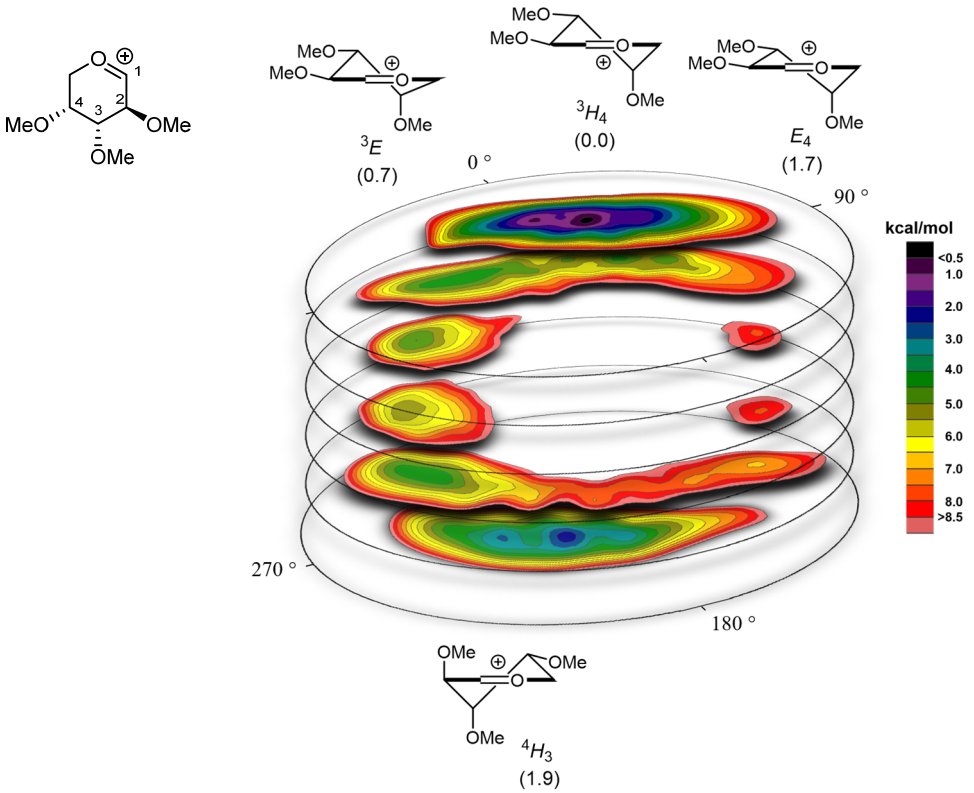


Figure 23| CEL map of 2,3,4-tri-*O*-methyl-arabino-D-pyranosyl oxocarbenium ion (**15**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -614.603576250 a.u.
E_{solv}(B3LYP) = -614.673301059 a.u.
Zero-point energy correction = 0.230291 a.u.

Atom coordinates

C	-1.386226	-0.125715	-0.412006
C	0.983207	-0.553152	0.238091
O	-0.429190	-2.445493	-0.376796
C	0.638464	-1.992588	0.090946
C	-1.540320	-1.561876	-0.867657
C	0.072740	0.350189	-0.602535
H	1.375209	-2.754539	0.376345
H	-2.430520	-2.031110	-0.453518
H	0.765339	-0.343405	1.306496
H	-1.500952	-1.687126	-1.950715
H	-2.066891	0.474617	-1.034895
H	0.359248	0.234629	-1.660789
O	2.344543	-0.428613	-0.069287
O	0.287466	1.669736	-0.165609
O	-1.757970	-0.082968	0.955652
C	3.110691	0.362487	0.856755
H	4.116487	0.414143	0.443466
H	3.144674	-0.116581	1.840774
H	2.687531	1.365583	0.940025
C	0.094503	2.668682	-1.171266
H	0.769787	2.501511	-2.017490
H	0.327152	3.624288	-0.703802
H	-0.940313	2.688554	-1.530906
C	-2.388711	1.128562	1.391249
H	-1.689161	1.966107	1.379815
H	-2.726420	0.944687	2.410613
H	-3.256052	1.357806	0.761443

^3E conformation (0.7 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -614.602235569 a.u.
E_{solv}(B3LYP) = -614.672099100 a.u.
Zero-point energy correction = 0.230156 a.u.

Atom coordinates

C	-1.428789	0.001219	-0.328825
C	0.878386	-0.699189	0.248779
O	-0.661907	-2.421003	-0.462251
C	0.485060	-2.086250	-0.082910
C	-1.793096	-1.447656	-0.629825
C	0.061374	0.260372	-0.649032
H	1.219185	-2.901332	-0.045855
H	-2.558500	-1.822839	0.048198
H	0.551248	-0.529434	1.296212
H	-2.083212	-1.610774	-1.667802
H	-2.062244	0.629244	-0.972992
H	0.267843	0.019883	-1.703784
O	2.261356	-0.597031	0.077125
O	0.453051	1.571267	-0.341206
O	-1.705111	0.228691	1.041391
C	2.944522	0.168105	1.084189
H	3.992441	0.181069	0.789317
H	2.848106	-0.309704	2.065067
H	2.555293	1.187243	1.120725
C	0.559279	2.447675	-1.467933
H	1.305567	2.076055	-2.178060
H	0.879105	3.412295	-1.076800
H	-0.403225	2.566696	-1.977446
C	-2.130854	1.556169	1.381052
H	-1.322818	2.277357	1.251422
H	-2.430332	1.517680	2.427804
H	-2.992854	1.848497	0.770559

***E*$_4$ conformation (1.7 kcal / mol)**

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -614.601932846 a.u.
E_{solv}(B3LYP) = -614.671359043 a.u.
Zero-point energy correction = 0.230576 a.u.

Atom coordinates

C	-1.320131	-0.295807	-0.512648
C	1.049697	-0.273146	0.275526
O	-0.033461	-2.390281	-0.327168
C	0.870455	-1.759988	0.263654
C	-1.079597	-1.658303	-1.123935
C	0.002286	0.501181	-0.532331
H	1.608915	-2.394938	0.769418
H	-1.944296	-2.313194	-1.047414
H	0.947790	0.020621	1.341484
H	-0.689034	-1.635427	-2.142673
H	-2.083803	0.202689	-1.128979
H	0.359944	0.565190	-1.572592
O	2.359710	-0.077388	-0.216341
O	-0.088520	1.782629	0.045854
O	-1.772538	-0.521668	0.810477
C	3.287435	0.516060	0.708652
H	4.210754	0.663770	0.151207
H	3.477352	-0.145139	1.559955

H	2.903721	1.477684	1.061087
C	-0.476679	2.817880	-0.860978
H	0.228988	2.885866	-1.696358
H	-0.457380	3.746856	-0.292911
H	-1.487621	2.659636	-1.252978
C	-2.677008	0.459424	1.333475
H	-2.184483	1.425390	1.459310
H	-3.002751	0.084266	2.303021
H	-3.548386	0.566582	0.677361

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -614.602632241 a.u.
E_{solv}(B3LYP) = -614.670512660 a.u.
Zero-point energy correction = 0.230717 a.u.

Atom coordinates

C	0.801026	-0.708912	0.243411
C	-1.370641	0.458073	-0.129578
O	-0.756133	-1.374095	-1.616861
C	-1.607051	-0.553607	-1.205098
C	0.637895	-1.452338	-1.076274
C	0.116954	0.666055	0.161056
H	-2.603171	-0.676702	-1.647393
H	1.256235	-1.017265	-1.860787
H	-1.838918	1.423041	-0.416815
H	0.808598	-2.523765	-0.995708
H	0.327131	-1.287744	1.049578
H	0.222957	1.217749	1.104642
O	-2.035850	-0.199946	0.944672
O	0.587901	1.412057	-0.947745
O	2.198769	-0.629718	0.425103
C	-3.218957	0.455052	1.441648
H	-3.564784	-0.152251	2.275973
H	-3.996394	0.502111	0.674028
H	-2.971683	1.463654	1.785693
C	1.702920	2.276540	-0.691593
H	1.474178	2.962267	0.132226
H	1.856854	2.850691	-1.604606
H	2.601240	1.702976	-0.457784
C	2.634250	-0.763525	1.781656
H	2.258201	0.052763	2.408029
H	3.722393	-0.725381	1.758909
H	2.311276	-1.722553	2.201301

2,3,4-Tri-*O*-methyl-xylo-D-pyranosyl oxocarbenium ion (**16**)

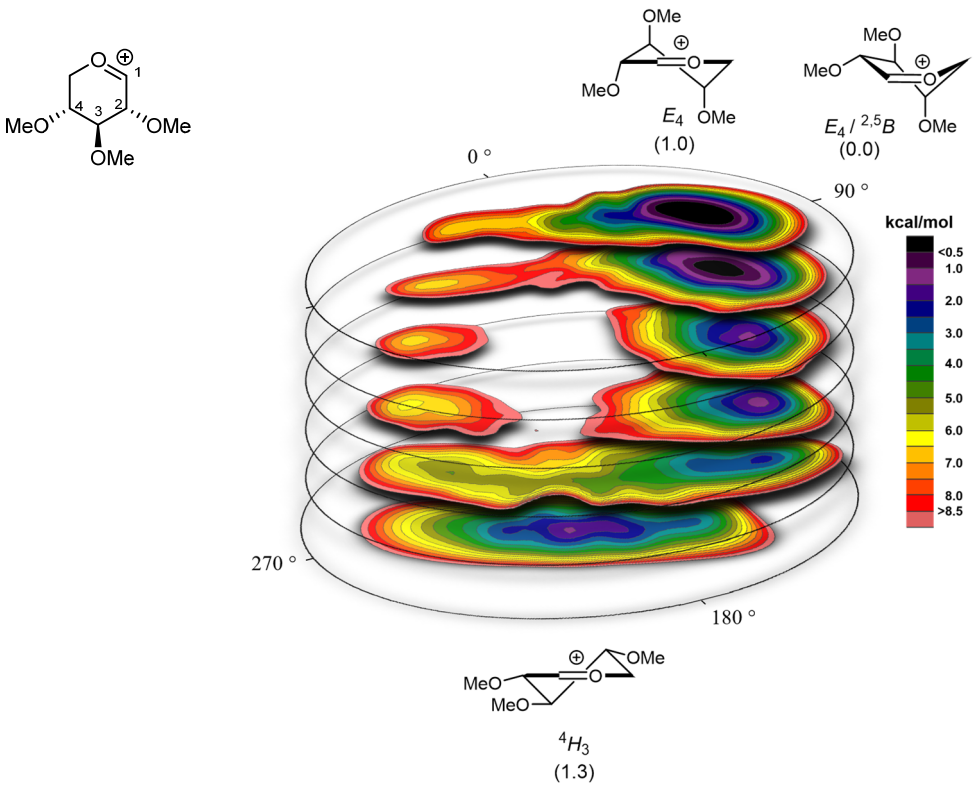
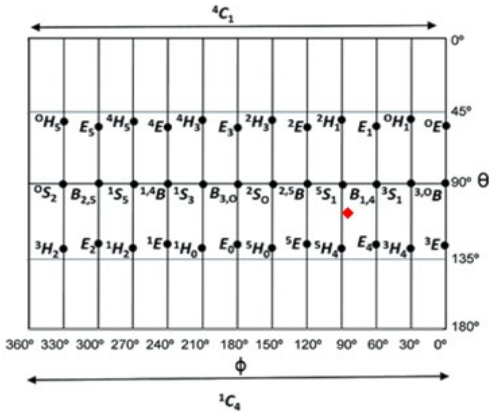


Figure 24| CEL map of 2,3,4-tri-*O*-methyl-xylo-D-pyranosyl oxocarbenium ion (**16**).

Local minima

E_4–$^{2,5}B$ conformation (0.0 kcal / mol)



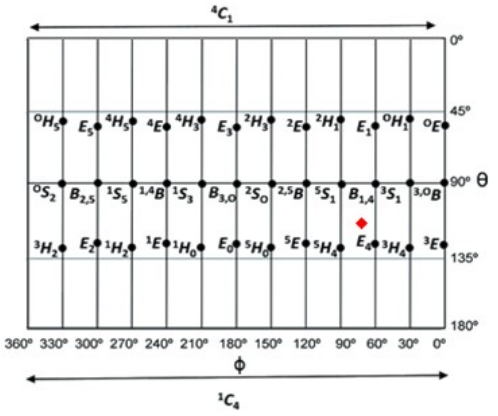
D1 = 0°
D3 = 60°
D5 = -15°

E_{gas}(B3LYP) = -614.603022464 a.u.
E_{solv}(B3LYP) = -614.672507024 a.u.
Zero-point energy correction = 0.230040 a.u.

Atom coordinates

C	-1.127110	0.660270	-0.022565
C	0.943030	-0.808092	-0.241443
O	-1.136779	-1.453326	-1.267601
C	-0.087286	-1.774172	-0.661891
C	-1.567247	-0.025095	-1.310270
C	0.403779	0.600116	0.135568
H	0.084547	-2.852089	-0.550573
H	-2.642036	-0.095350	-1.455539
H	-1.093356	0.416050	-2.190432
H	-1.472250	1.702752	-0.069610
O	-1.623017	-0.016282	1.116025
C	-3.030735	0.086692	1.351445
H	-3.347471	1.135473	1.350002
H	-3.206113	-0.344501	2.335756
H	-3.613194	-0.472683	0.611397
H	1.477765	-0.657478	-1.215755
O	1.760730	-1.428005	0.703479
C	3.091748	-0.896728	0.770702
H	3.579838	-0.952608	-0.208422
H	3.627488	-1.518466	1.485353
H	3.090764	0.139447	1.121953
H	0.631062	0.767684	1.196318
O	1.066019	1.521040	-0.706428
C	1.163899	2.849806	-0.184714
H	1.747306	3.418700	-0.907018
H	1.678680	2.849391	0.782684
H	0.180877	3.319476	-0.070913

E_4–$^{2,5}B$ conformation (0.1 kcal / mol)



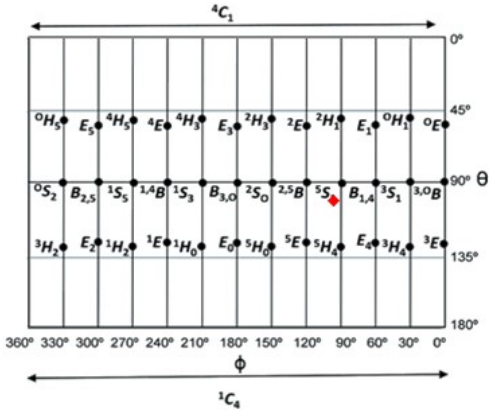
D1 = 15°
D3 = 60°
D5 = -15°

E_{gas}(B3LYP) = -614.603591916 a.u.
E_{solv}(B3LYP) = -614.672267125 a.u.
Zero-point energy correction = 0.230072 a.u.

Atom coordinates

C	1.106815	0.634820	-0.196580
C	-0.963341	-0.692664	0.384366
O	1.089885	-1.000511	1.636381
C	0.037275	-1.470641	1.145189
C	1.596858	0.340423	1.213924
C	-0.431983	0.634115	-0.222234
H	-0.166448	-2.520255	1.391057
H	2.673869	0.236390	1.321401
H	1.207759	1.054979	1.941260
H	1.504710	1.616693	-0.490078
O	1.477875	-0.384830	-1.100873
C	2.855870	-0.418385	-1.485539
H	3.168607	0.552030	-1.886115
H	2.935388	-1.175922	-2.263506
H	3.508222	-0.696907	-0.650994
H	-1.642159	-0.379812	1.220571
O	-1.598728	-1.570185	-0.496146
C	-2.959108	-1.225226	-0.792703
H	-3.560157	-1.199703	0.122634
H	-3.329973	-2.004876	-1.455198
H	-3.022712	-0.258694	-1.303087
H	-0.755210	0.679579	-1.268944
O	-0.966562	1.688112	0.552212
C	-1.095727	2.937632	-0.134083
H	-1.577790	3.620545	0.563761
H	-1.721119	2.825296	-1.026681
H	-0.122707	3.349532	-0.422704

***E*$_4$–^{2,5}*B* conformation (0.4 kcal / mol)**



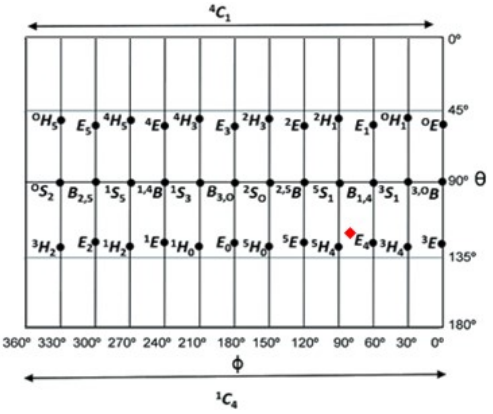
D1 = -15°
D3 = 60°
D5 = -15°

E_{gas}(B3LYP) = -614.601986257 a.u.
E_{solv}(B3LYP) = -614.671966644 a.u.
Zero-point energy correction = 0.229985 a.u.

Atom coordinates

C	1.161587	0.571443	0.192758
C	-0.972450	-0.837615	0.133884
O	1.092456	-1.774912	0.891069
C	0.033834	-1.908851	0.232354
C	1.507822	-0.405411	1.312808
C	-0.353961	0.572063	-0.101682
H	-0.153499	-2.910175	-0.175794
H	2.569978	-0.518659	1.512936
H	0.970336	-0.181702	2.238356
H	1.485700	1.568260	0.523676
O	1.769803	0.184799	-1.023608
C	3.182913	0.388574	-1.111604
H	3.437661	1.431267	-0.891102
H	3.459735	0.156242	-2.138743
H	3.738131	-0.273065	-0.437812
H	-1.367975	-0.805326	1.182897
O	-1.945895	-1.232755	-0.782588
C	-3.225939	-0.607430	-0.609807
H	-3.586815	-0.744232	0.415420
H	-3.897924	-1.106506	-1.305579
H	-3.184243	0.459455	-0.842507
H	-0.478463	0.807605	-1.167085
O	-1.074074	1.456372	0.729482
C	-1.076824	2.816681	0.286551
H	-1.702140	3.365406	0.989162
H	-1.499935	2.896085	-0.721203
H	-0.070758	3.250586	0.290954

***E*$_4$ conformation (1.0 kcal / mol)**



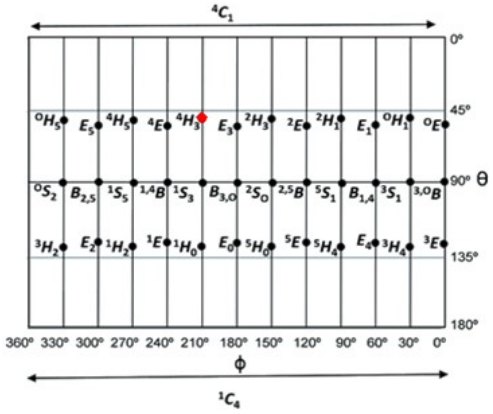
D1 = 15°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -614.602238942 a.u.
E_{solv}(B3LYP) = -614.671115576 a.u.
Zero-point energy correction = 0.229944 a.u.

Atom coordinates

C	1.143054	0.576973	-0.138327
C	-1.040285	-0.632773	0.368997
O	1.010984	-1.205324	1.546984
C	-0.135469	-1.509212	1.149852
C	1.591142	0.139028	1.249397
C	-0.393288	0.658928	-0.195903
H	-0.459844	-2.527299	1.398197
H	2.659921	-0.024519	1.359487
H	1.221672	0.804120	2.032140
H	1.589325	1.562488	-0.332297
O	1.495461	-0.370289	-1.124905
C	2.880031	-0.423289	-1.479247
H	3.245708	0.569559	-1.764279
H	2.950107	-1.095042	-2.333321
H	3.497596	-0.819730	-0.665835
H	-1.746921	-0.278231	1.164531
O	-1.678073	-1.463386	-0.558545
C	-3.018160	-1.066703	-0.885677
H	-3.649874	-1.063052	0.008730
H	-3.385920	-1.806393	-1.594163
H	-3.034552	-0.077663	-1.354886
H	-0.689361	0.755251	-1.247255
O	-0.877695	1.724622	0.599665
C	-0.880787	3.005395	-0.038259
H	-1.344475	3.695189	0.665350
H	-1.468600	2.975433	-0.962505
H	0.132356	3.354813	-0.264491

$^4H_3$ conformation (1.3 kcal / mol)



D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -614.598035080 a.u.
E_{solv}(B3LYP) = -614.670244115 a.u.
Zero-point energy correction = 0.229967 a.u.

Atom coordinates

C	-1.192697	0.512006	0.210599
C	1.292663	0.365227	0.258569
O	0.260004	2.529906	-0.198034
C	1.273825	1.841024	0.056392
C	-1.109798	1.935507	-0.335954
C	0.012686	-0.313503	-0.258539
H	2.214067	2.406118	0.092578
H	-1.303944	1.968426	-1.409126
H	-1.748769	2.644432	0.187443
H	-1.203573	0.532343	1.309643
O	-2.402426	-0.007032	-0.300471
C	-3.262139	-0.613262	0.673221
H	-2.772941	-1.465283	1.153520
H	-4.142166	-0.954634	0.129719
H	-3.566472	0.113276	1.434429
H	1.309336	0.245270	1.373576
O	2.459880	-0.118716	-0.348125
C	3.285905	-0.952733	0.483044
H	3.716779	-0.377110	1.308616
H	4.084441	-1.318027	-0.160309
H	2.705877	-1.792714	0.872548
H	0.044557	-0.324509	-1.357582
O	-0.024115	-1.620145	0.265720
C	-0.360458	-2.642050	-0.681334
H	-0.361643	-3.580798	-0.128728
H	0.387024	-2.692381	-1.480325
H	-1.349236	-2.469811	-1.114693

2-Deoxy-3,4-di-*O*-methyl-xylo-D-pyranosyl oxocarbenium ion (**17**)

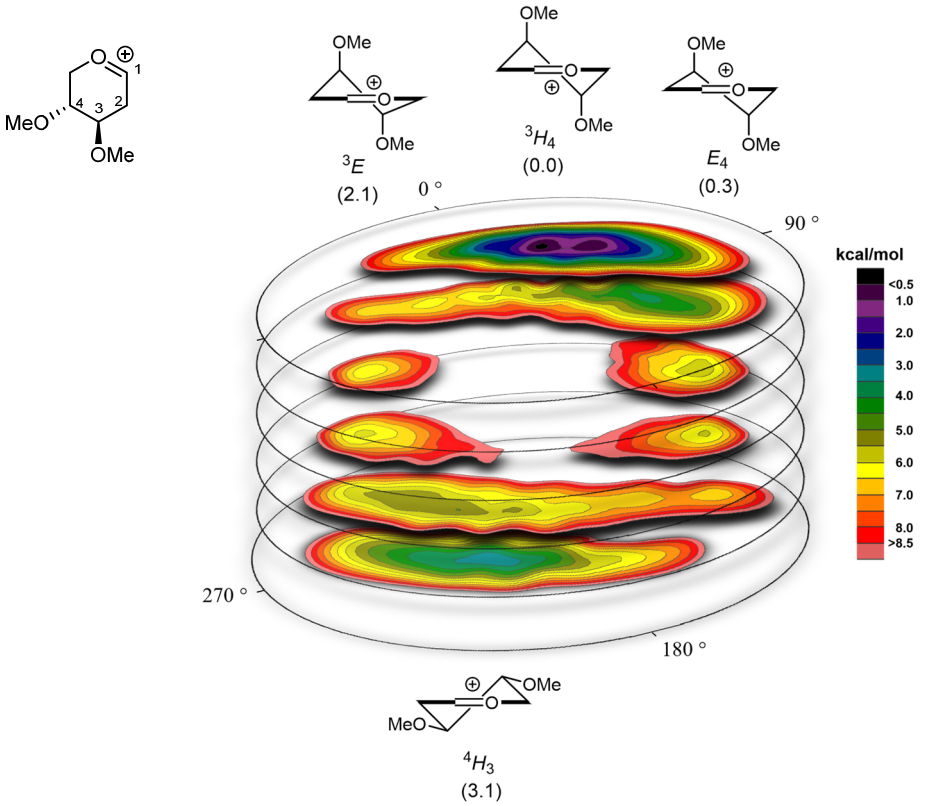


Figure 25| CEL map of 2-deoxy-3,4-di-*O*-methyl-xylo-D-pyranosyl oxocarbenium ion (**17**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -500.065627371 a.u.
E_{solv}(B3LYP) = -500.137159512 a.u.
Zero-point energy correction = 0.198200 a.u.

Atom coordinates

C	-0.328256	1.887274	0.527499
C	-0.661204	-0.581818	0.386349
C	0.740420	0.658596	-1.269496
C	0.664348	-0.571746	-0.383630
O	0.304989	1.903658	-0.554255
C	-0.736337	0.679842	1.251855
H	-0.703446	-1.476230	1.018946
H	1.748303	0.909583	-1.594856
H	0.720826	-1.459072	-1.029816
H	-1.723901	0.857446	1.693144
H	-0.546078	2.889189	0.919048
H	0.063735	0.606007	-2.122682
H	-0.044535	0.619620	2.112059
O	1.685937	-0.557789	0.599651
O	-1.689155	-0.577539	-0.589046
C	-2.924786	-1.152308	-0.160700
H	-2.781328	-2.192216	0.153201
H	-3.594084	-1.121039	-1.019369
H	-3.375917	-0.585090	0.661986
C	2.924274	-1.140870	0.190012
H	2.784662	-2.190642	-0.091501
H	3.593033	-1.080057	1.047463
H	3.373806	-0.597968	-0.649751

E_4 conformation (0.3 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -500.065155452 a.u.
E_{solv}(B3LYP) = -500.136845361 a.u.
Zero-point energy correction = 0.198251 a.u.

Atom coordinates

C	-0.066585	1.904339	-0.467650
C	0.764065	-0.491533	-0.408427
C	-0.710720	0.465435	1.337588
C	-0.561349	-0.671160	0.340687
O	-0.709308	1.770169	0.602003
C	0.736388	0.869467	-1.128070
H	0.878625	-1.296377	-1.144433
H	-1.661123	0.487702	1.865830
H	-0.538914	-1.617929	0.898875
H	1.739706	1.293519	-1.284548
H	-0.162403	2.903330	-0.911650
H	0.124099	0.519711	2.036065
H	0.317995	0.801615	-2.146674
O	-1.580133	-0.643506	-0.638830
O	1.782500	-0.535798	0.573051
C	3.070196	-0.906990	0.080309
H	3.035658	-1.894203	-0.393920
H	3.733776	-0.940731	0.943256
H	3.459911	-0.175453	-0.637910
C	-2.810518	-1.261425	-0.253629
H	-2.648902	-2.312220	0.011056
H	-3.468793	-1.201268	-1.119062
H	-3.282972	-0.743416	0.588475

^3E conformation (2.1 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -500.062694230 a.u.
E_{solv}(B3LYP) = -500.133862557 a.u.
Zero-point energy correction = 0.198229 a.u.

Atom coordinates

C	-0.708963	1.773531	0.573081
C	-0.563346	-0.656986	0.346523
C	0.745275	0.863259	-1.153526
C	0.759051	-0.469219	-0.403403
O	-0.085291	1.934181	-0.503277
C	-0.704283	0.517187	1.331536
H	-0.524897	-1.602968	0.899680
H	1.727440	1.328899	-1.227346
H	0.880310	-1.270849	-1.145236
H	-1.594504	0.470687	1.963835
H	-1.255947	2.667458	0.898208
H	0.286614	0.791971	-2.139523
H	0.168974	0.545729	2.005151
O	1.776215	-0.505221	0.580665
O	-1.597283	-0.643603	-0.616162
C	-2.790733	-1.328388	-0.226349
H	-2.576657	-2.377975	0.002859
H	-3.469227	-1.272722	-1.076326
H	-3.265997	-0.856779	0.641227
C	3.049788	-0.950907	0.110187
H	2.977455	-1.960674	-0.309116
H	3.711932	-0.962340	0.974732
H	3.464636	-0.274152	-0.646242

$^4H_3$ conformation (3.1 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -500.055531412 a.u.
E_{solv}(B3LYP) = -500.131751292 a.u.
Zero-point energy correction = 0.197815 a.u.

Atom coordinates

C	2.346828	0.747767	-0.179737
C	-0.164885	0.636534	0.244368
C	1.345322	-1.396896	0.264593
C	0.000353	-0.826099	-0.173575
O	2.495862	-0.485017	-0.004244
C	1.074858	1.464213	-0.151018
H	-0.279935	0.657826	1.338924
H	1.379415	-1.567878	1.342094
H	-0.083226	-0.883434	-1.269563
H	0.958320	1.870414	-1.174115
H	3.286088	1.278352	-0.381313
H	1.611857	-2.306392	-0.269250
H	1.228372	2.357982	0.471769
O	-0.939580	-1.668572	0.456868
O	-1.325287	1.133604	-0.385238
C	-1.922027	2.256775	0.266306
H	-2.173209	2.017044	1.305796
H	-2.833946	2.484365	-0.283972
H	-1.267143	3.135742	0.245241
C	-2.096739	-1.988052	-0.326416
H	-2.669604	-1.089260	-0.562866
H	-2.697254	-2.661647	0.283856
H	-1.809958	-2.498691	-1.252813

2,3,4-Tri-*O*-methyl-ribo-D-pyranosyl oxocarbenium ion (**18**)

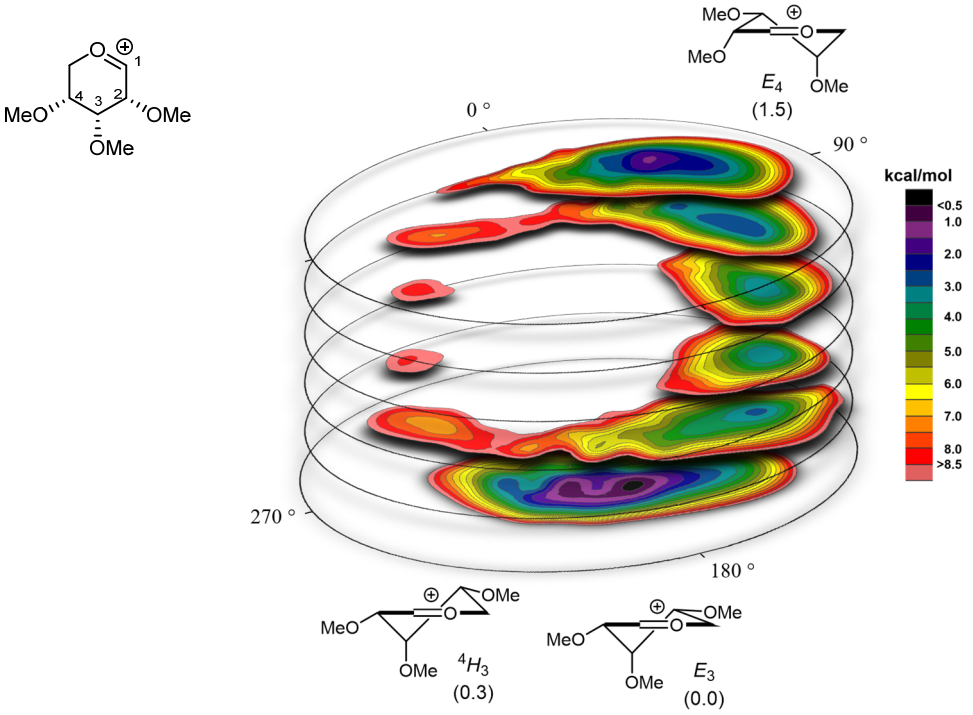


Figure 26| CEL map of 2,3,4-tri-*O*-methyl-ribo-D-pyranosyl oxocarbenium ion (**18**).

Local minima

E_3 conformation (0.0 kcal / mol)

D1 = -60°
D3 = -30°
D5 = 0°

E_{gas}(B3LYP) = -614.598196283 a.u.
E_{solv}(B3LYP) = -614.669534228 a.u.
Zero-point energy correction = 0.230168 a.u.

Atom coordinates

C	1.135426	0.563796	-0.510765
C	-1.302406	0.139065	-0.430078
O	-0.445457	2.016717	0.854317
C	-1.412788	1.313142	0.490269
C	0.964002	1.773955	0.412474
C	0.073489	-0.506240	-0.193506
H	-2.372714	1.600188	0.938637
H	1.489706	1.618771	1.353624
H	1.257019	2.720647	-0.038828
H	1.017175	0.876649	-1.559714
O	2.457990	0.136257	-0.266927
C	3.097775	-0.488681	-1.383728
H	2.594530	-1.418044	-1.671950
H	4.113639	-0.717009	-1.064770
H	3.128784	0.189975	-2.243348
H	0.172056	-1.370555	-0.862215
H	-1.330930	0.539668	-1.464561
O	0.104840	-0.882964	1.166740
O	-2.341322	-0.759702	-0.167928
C	-3.477948	-0.634179	-1.033453
H	-3.964996	0.341228	-0.919562
H	-4.172576	-1.417729	-0.736560
H	-3.184464	-0.775866	-2.079530
C	0.890989	-2.039086	1.473797
H	0.564338	-2.894633	0.871890
H	0.714654	-2.254721	2.527033
H	1.954145	-1.851669	1.310180

$^4H_3$ conformation (0.3 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -614.597765821 a.u.
E_{solv}(B3LYP) = -614.669218656 a.u.
Zero-point energy correction = 0.230189 a.u.

Atom coordinates

C	-1.199125	0.557270	0.397661
C	1.280154	0.223553	0.458149
O	0.366384	2.140871	-0.757184
C	1.343421	1.518617	-0.283709
C	-1.043736	1.658213	-0.641759
C	-0.071717	-0.482080	0.248239
H	2.312954	1.989993	-0.489159
H	-1.278696	1.293745	-1.641759
H	-1.605779	2.560821	-0.412114
H	-1.159049	0.998595	1.406440
O	-2.470787	0.006593	0.137069
C	-3.188845	-0.419486	1.298803
H	-2.661495	-1.220223	1.829030
H	-4.146771	-0.797078	0.944251
H	-3.358091	0.419604	1.982670
H	-0.172725	-1.280890	0.992170
H	1.346058	0.511171	1.527908
O	-0.074427	-0.981832	-1.073114
O	2.360147	-0.569262	0.049146
C	3.459863	-0.628362	0.969740
H	3.938643	0.350024	1.086718
H	4.173802	-1.328573	0.539962
H	3.125136	-0.992708	1.947051
C	-0.565820	-2.313780	-1.229071
H	0.029617	-3.018169	-0.637599
H	-0.459786	-2.556752	-2.285929
H	-1.619529	-2.384198	-0.945292

E_4 conformation (1.5 kcal / mol)

D1 = 30°
D3 = 60°
D5 = -15°

Egas(B3LYP) = -614.595999864 a.u.
Esolv(B3LYP) = -614.667707529 a.u.
Zero-point energy correction = 0.230433 a.u.

Atom coordinates

C	1.113780	-0.982082	-0.247960
C	-0.311461	1.070969	-0.378289
O	2.118834	1.229777	-0.632406
C	1.026190	1.722119	-0.268224
C	2.241255	-0.240199	-0.931878
C	-0.216582	-0.434615	-0.793106
H	1.087731	2.744991	0.122712
H	3.217843	-0.481022	-0.517992
H	2.241593	-0.319751	-2.019543
H	1.204103	-2.051369	-0.497410
O	1.295511	-0.736046	1.130717
C	0.533320	-1.549505	2.034427
H	-0.526129	-1.298674	1.995695
H	0.932056	-1.341259	3.026624
H	0.671124	-2.610893	1.801189
H	-0.168116	-0.481671	-1.891319
H	-0.780503	1.640220	-1.207388
O	-1.308885	-1.172173	-0.311505

O	-0.946746	1.321095	0.844232
C	-2.332990	1.680061	0.756190
H	-2.464052	2.587936	0.157863
H	-2.657112	1.869687	1.778060
H	-2.919883	0.861634	0.334181
C	-2.293301	-1.507633	-1.293250
H	-2.753871	-0.613258	-1.729043
H	-3.057610	-2.086154	-0.776102
H	-1.858164	-2.116330	-2.093303

E_4 conformation (1.5 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -614.595796556 a.u.
E_{solv}(B3LYP) = -614.667617443 a.u.
Zero-point energy correction = 0.230472 a.u.

Atom coordinates

C	1.299365	-0.771383	-0.337215
C	-0.576872	0.920904	-0.426246
O	1.774191	1.639209	-0.473046
C	0.562288	1.882071	-0.277675
C	2.234546	0.274016	-0.902795
C	-0.116639	-0.503445	-0.870891
H	0.364970	2.893374	0.097616
H	3.232971	0.214824	-0.476921
H	2.268070	0.309865	-1.992503
H	1.634002	-1.756505	-0.700920
O	1.412561	-0.653988	1.064472
C	0.928776	-1.757264	1.841888
H	-0.158676	-1.816688	1.810028
H	1.265220	-1.571411	2.861440
H	1.361007	-2.698216	1.482958
H	-0.054860	-0.486453	-1.973385
H	-1.259850	1.350987	-1.187837
O	-0.977867	-1.516457	-0.441431
O	-1.146075	0.929455	0.866708
C	-2.399101	1.617951	0.992756
H	-2.288321	2.691188	0.805973
H	-2.722763	1.462067	2.020235
H	-3.139854	1.201590	0.302626
C	-2.183290	-1.644980	-1.193665
H	-2.844569	-0.781343	-1.061321
H	-2.688024	-2.533634	-0.817675
H	-1.966239	-1.772604	-2.260894

2,3,4-Tri-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**19**)

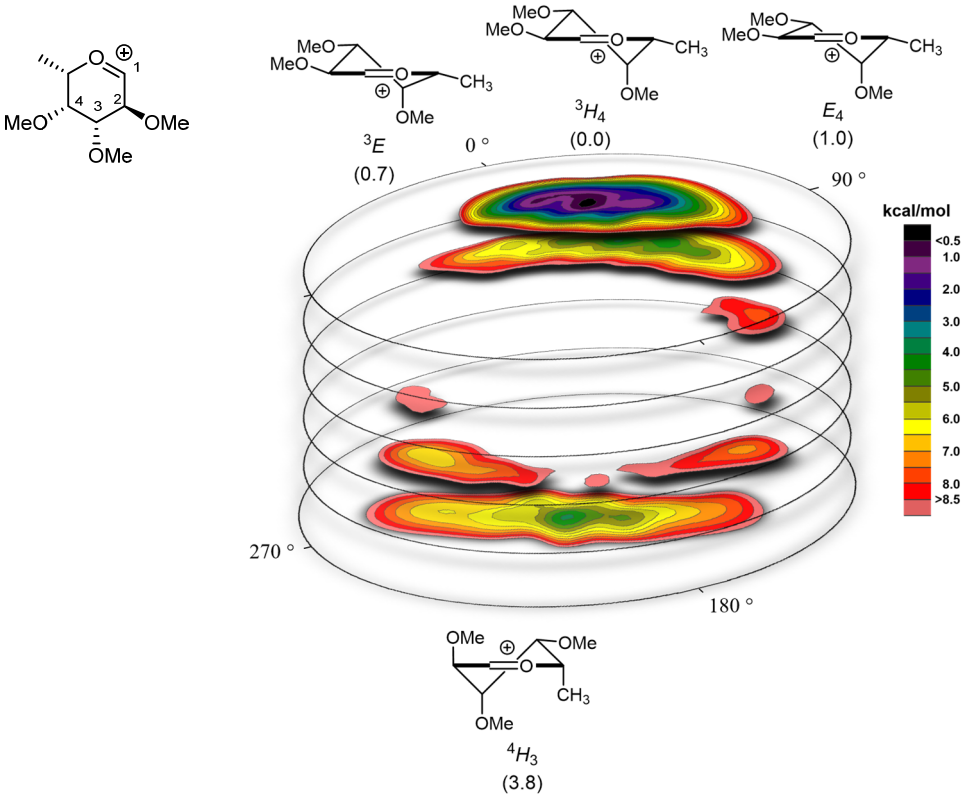


Figure 27| CEL map of 2,3,4-tri-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**19**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -653.937550024 a.u.
E_{solv}(B3LYP) = -654.004885139 a.u.
Zero-point energy correction = 0.257829 a.u.

Atom coordinates

C	-1.109519	0.557784	-0.378878
C	0.944141	-0.715930	0.260106
O	-1.085868	-1.960767	-0.271137
C	0.081855	-1.929327	0.169047
C	-1.827894	-0.721223	-0.798473
C	0.409295	0.439647	-0.599115
H	0.484589	-2.908854	0.458751
H	0.881663	-0.391966	1.315003
H	-1.497612	1.356354	-1.029091
O	2.247047	-1.085562	-0.120408
C	3.203156	-1.160924	0.948747
H	4.161079	-1.383193	0.481908
H	2.949885	-1.959114	1.654403
H	3.259156	-0.204690	1.478651
O	-1.395620	0.809290	0.984520
C	-1.597666	2.186833	1.329450
H	-0.686709	2.766673	1.173021
H	-1.870080	2.198217	2.384267
H	-2.416897	2.614713	0.740463
H	-1.739094	-0.872479	-1.879200
C	-3.247718	-0.878056	-0.316376
H	-3.846591	-0.076000	-0.756284
H	-3.301689	-0.795357	0.768102
H	-3.659707	-1.833084	-0.644505
H	0.593433	0.196323	-1.656397
O	1.047860	1.637480	-0.230397
C	2.032178	2.111652	-1.155852
H	2.832768	1.378927	-1.290478
H	2.442057	3.024102	-0.724615
H	1.579424	2.343164	-2.126568

^3E conformation (0.7 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -653.936656292 a.u.
E_{solv}(B3LYP) = -654.003860538 a.u.
Zero-point energy correction = 0.257842 a.u.

Atom coordinates

C	-1.076667	0.633341	-0.411100
C	0.808724	-0.844221	0.244558
O	-1.226029	-1.917776	-0.491335
C	-0.046700	-2.007751	-0.082421
C	-1.961058	-0.585318	-0.714648
C	0.409008	0.329700	-0.685246
H	0.351301	-3.029658	-0.029072
H	0.551209	-0.530591	1.272656
H	-1.409697	1.432018	-1.089376
O	2.152534	-1.212323	0.097384
C	2.956427	-1.057686	1.277151
H	3.973190	-1.316380	0.986596
H	2.622761	-1.732386	2.072417
H	2.925485	-0.022556	1.630119
O	-1.254562	1.001905	0.943038
C	-1.274334	2.411292	1.207554
H	-0.309168	2.866643	0.981470
H	-1.497023	2.516024	2.268841
H	-2.063118	2.899462	0.623999
H	-2.130220	-0.654655	-1.793423
C	-3.251158	-0.695201	0.058920
H	-3.865114	0.176413	-0.183037
H	-3.071094	-0.696974	1.132771
H	-3.795783	-1.592459	-0.237739
H	0.536833	0.019603	-1.733179
O	1.188011	1.455995	-0.385759
C	2.234454	1.741219	-1.321829
H	2.940031	0.909032	-1.387305
H	2.745996	2.626136	-0.945719
H	1.822615	1.955689	-2.314271

E_4 conformation (1.0 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -653.936490282 a.u.
E_{solv}(B3LYP) = -654.003762077 a.u.
Zero-point energy correction = 0.257957 a.u.

Atom coordinates

C	-1.055066	0.462979	-0.340636
C	1.064782	-0.698484	0.313791
O	-0.998995	-1.982488	0.009899
C	0.151059	-1.872547	0.479313
C	-1.628832	-0.858852	-0.833779
C	0.478942	0.447536	-0.517016
H	0.513924	-2.753732	1.024164
H	1.220003	-0.330814	1.344514
H	-1.496996	1.251676	-0.968297
O	2.242553	-1.243064	-0.240764
C	3.456973	-0.928118	0.462798

H	4.264957	-1.348292	-0.133747
H	3.463500	-1.383031	1.458339
H	3.576095	0.155255	0.545760
O	-1.423842	0.608649	1.017221
C	-1.638169	1.953671	1.462954
H	-0.704694	2.519591	1.472512
H	-2.032600	1.879078	2.475789
H	-2.373776	2.458142	0.826119
H	-1.282971	-1.096897	-1.845047
C	-3.115604	-1.042352	-0.671546
H	-3.622730	-0.330698	-1.328395
H	-3.417875	-0.849198	0.357421
H	-3.413155	-2.050076	-0.964552
H	0.704729	0.244016	-1.576128
O	1.120651	1.628038	-0.088148
C	1.189338	2.659551	-1.075576
H	1.707849	2.303850	-1.972949
H	1.755416	3.475822	-0.629067
H	0.194845	3.025928	-1.353917

$^4H_3$ conformation (3.8 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -653.933492698 a.u.
E_{solv}(B3LYP) = -653.999603265 a.u.
Zero-point energy correction = 0.258614 a.u.

Atom coordinates

C	0.640813	-0.124498	-0.756795
C	-1.510922	-0.028838	0.473331
O	-0.542118	2.053162	-0.353925
C	-1.499430	1.435376	0.158755
C	0.788868	1.406037	-0.747873
C	-0.109345	-0.643569	0.483327
H	-2.401890	2.040907	0.309261
H	-1.996996	-0.186041	1.453476
H	0.042029	-0.397298	-1.638496
O	-2.286416	-0.503530	-0.622228
C	-3.579175	-1.041437	-0.285631
H	-4.006096	-1.393850	-1.222735
H	-4.227188	-0.273828	0.146735
H	-3.469547	-1.874948	0.414587
O	1.955113	-0.629309	-0.874795
C	2.061828	-1.836458	-1.633381
H	1.521300	-2.663321	-1.159426
H	3.122395	-2.080928	-1.672944
H	1.682612	-1.691458	-2.651174
H	0.879576	1.773586	-1.773187
C	1.843566	2.028340	0.141206
H	2.809544	1.623547	-0.163091
H	1.675210	1.789279	1.188967
H	1.858299	3.110363	-0.000460
H	-0.217845	-1.735977	0.429006
O	0.469866	-0.242343	1.709082
C	1.487224	-1.110496	2.225530
H	1.108323	-2.135723	2.307703
H	1.729508	-0.737727	3.220150
H	2.378639	-1.097153	1.595749

2-Deoxy-3,4-di-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**20**)

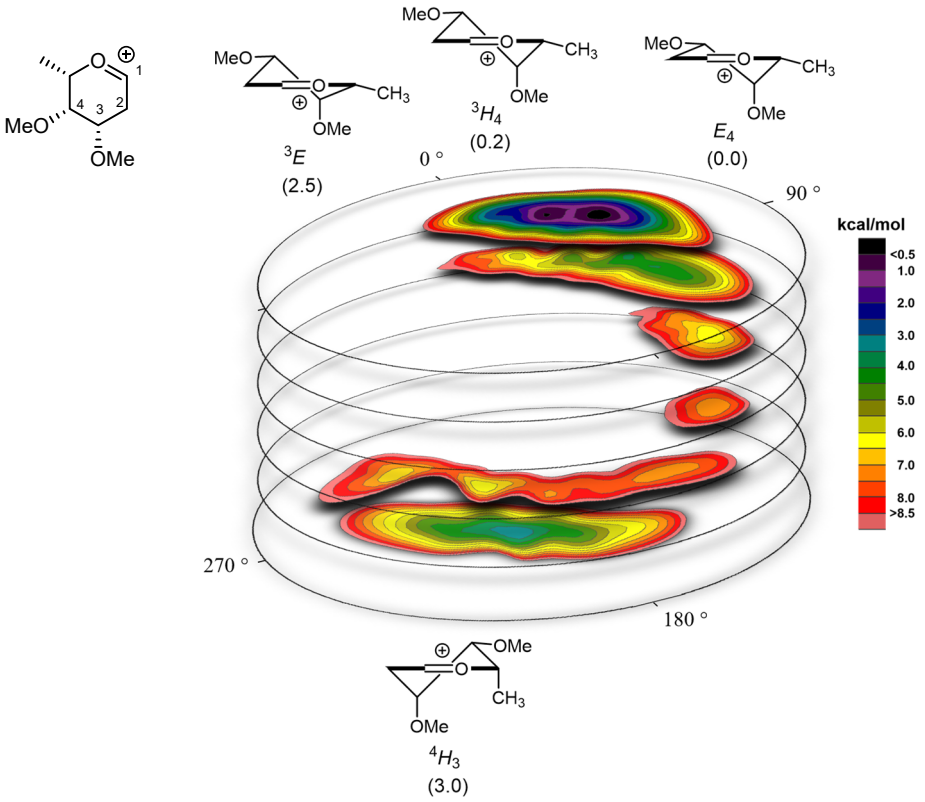


Figure 28| CEL map of 2-deoxy-3,4-di-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**20**).

Local minima

***E*$_4$ conformation (0.0 kcal / mol)**

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -539.394600150 a.u.
E_{solv}(B3LYP) = -539.466437775 a.u.
Zero-point energy correction = 0.225622 a.u.

Atom coordinates

C	-0.088340	0.512189	-0.410407
C	0.252457	-1.734811	0.623367
O	-1.989192	-0.958807	0.145784
C	-1.205027	-1.714629	0.762806
C	-1.474526	0.071974	-0.867634
C	0.834283	-0.725011	-0.369228
H	-1.704100	-2.395406	1.464583
H	0.641602	-1.546079	1.638353
H	0.276953	1.241722	-1.148311
O	-0.242275	1.094300	0.869614
C	0.718871	2.095257	1.224226
H	1.711068	1.661407	1.359226
H	0.374921	2.526770	2.163754
H	0.756990	2.881013	0.460820
H	-1.428615	-0.500342	-1.799749
H	0.851236	-1.169536	-1.376849
O	2.148000	-0.448170	0.065959
C	3.028495	0.010782	-0.960872
H	3.091111	-0.720450	-1.775170
H	4.008754	0.122050	-0.499254
H	2.715463	0.978558	-1.368945
C	-2.534585	1.143376	-0.902724
H	-2.272055	1.861281	-1.684102
H	-2.585583	1.664981	0.052480
H	-3.507548	0.713796	-1.145309
H	0.547764	-2.773108	0.410411

$^3H_4$ conformation (0.2 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -539.394504170 a.u.
E_{solv}(B3LYP) = -539.466327382 a.u.
Zero-point energy correction = 0.225678 a.u.

Atom coordinates

C	0.066668	0.507046	0.430139
C	-0.182123	-1.658282	-0.785276
O	2.006381	-1.050452	0.019493
C	1.268543	-1.794778	-0.664641
C	1.488470	0.135482	0.846741
C	-0.797579	-0.764410	0.285838
H	1.812161	-2.577551	-1.209488
H	-0.344638	-1.212865	-1.784860
H	-0.324664	1.154770	1.228707
O	0.144037	1.196014	-0.804993
C	-0.830764	2.223657	-1.012233
H	-1.829949	1.802605	-1.138948
H	-0.534974	2.745292	-1.922122
H	-0.829316	2.932933	-0.176266
H	1.491856	-0.290256	1.855354
H	-0.792761	-1.302139	1.248511
O	-2.121188	-0.496873	-0.120619
C	-3.016940	-0.180010	0.946251
H	-3.050907	-0.993579	1.680007
H	-4.001246	-0.057960	0.496146
H	-2.739495	0.751180	1.453191
C	2.535405	1.208926	0.682721
H	2.274551	2.042861	1.339902
H	2.562332	1.571689	-0.343596
H	3.516255	0.833571	0.977181
H	-0.633122	-2.655854	-0.831997

^{3}E conformation (2.5 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -539.391476134 a.u.
E_{solv}(B3LYP) = -539.462818424 a.u.
Zero-point energy correction = 0.225834 a.u.

Atom coordinates

C	0.045223	0.516133	0.456900
C	-0.064342	-1.523771	-0.952766
O	2.007831	-1.106550	0.168991
C	1.319357	-1.829271	-0.589283
C	1.503128	0.193173	0.820819
C	-0.745102	-0.786620	0.203802
H	1.852469	-2.710978	-0.967087
H	-0.033759	-0.859790	-1.834816
H	-0.366295	1.064118	1.316893
O	0.044225	1.320674	-0.706845
C	-0.992984	2.304010	-0.789282
H	-1.967748	1.839344	-0.948581
H	-0.744810	2.937430	-1.640497
H	-1.016687	2.917486	0.118952
H	1.560982	-0.098692	1.873764
H	-0.707448	-1.416833	1.108214
O	-2.079193	-0.556860	-0.180540
C	-2.995007	-0.422150	0.908287
H	-2.983498	-1.318448	1.539086
H	-3.983396	-0.303500	0.466508
H	-2.771402	0.455830	1.524915
C	2.534404	1.239075	0.476677
H	2.288503	2.150616	1.027761
H	2.522034	1.470942	-0.587093
H	3.527487	0.907916	0.783051
H	-0.587398	-2.437030	-1.244848

$^{4}H_{3}$ conformation (3.0 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -539.389291385 a.u.
E_{solv}(B3LYP) = -539.461442255 a.u.
Zero-point energy correction = 0.226035 a.u.

Atom coordinates

C	-0.267643	-0.586969	-0.565264
C	1.327824	1.323978	-0.964039
O	2.178727	-0.753512	-0.054937
C	2.364402	0.370148	-0.573494
C	0.800669	-1.319370	0.259591
C	-0.107498	0.947992	-0.586872
H	3.424012	0.613757	-0.728124
H	1.599849	2.299964	-0.536710
H	-0.151650	-0.929216	-1.608427
O	-1.507869	-1.018300	-0.049732
C	-2.535307	-1.189912	-1.028800
H	-2.796736	-0.243084	-1.514124
H	-3.406267	-1.569533	-0.496152
H	-2.229853	-1.915404	-1.790924
H	0.912860	-2.345076	-0.098144
H	-0.796223	1.376277	-1.327313
O	-0.326230	1.536079	0.690208
C	-1.679174	1.888647	0.993686
H	-2.113290	2.484911	0.181997
H	-1.639678	2.496082	1.897871
H	-2.294578	1.005117	1.170886
C	0.666760	-1.272181	1.768131
H	-0.280752	-1.743659	2.031097
H	0.655180	-0.245709	2.132112
H	1.478904	-1.831119	2.236113
H	1.461010	1.458553	-2.052111

2-Azido-2-deoxy-3,4-di-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**21**)

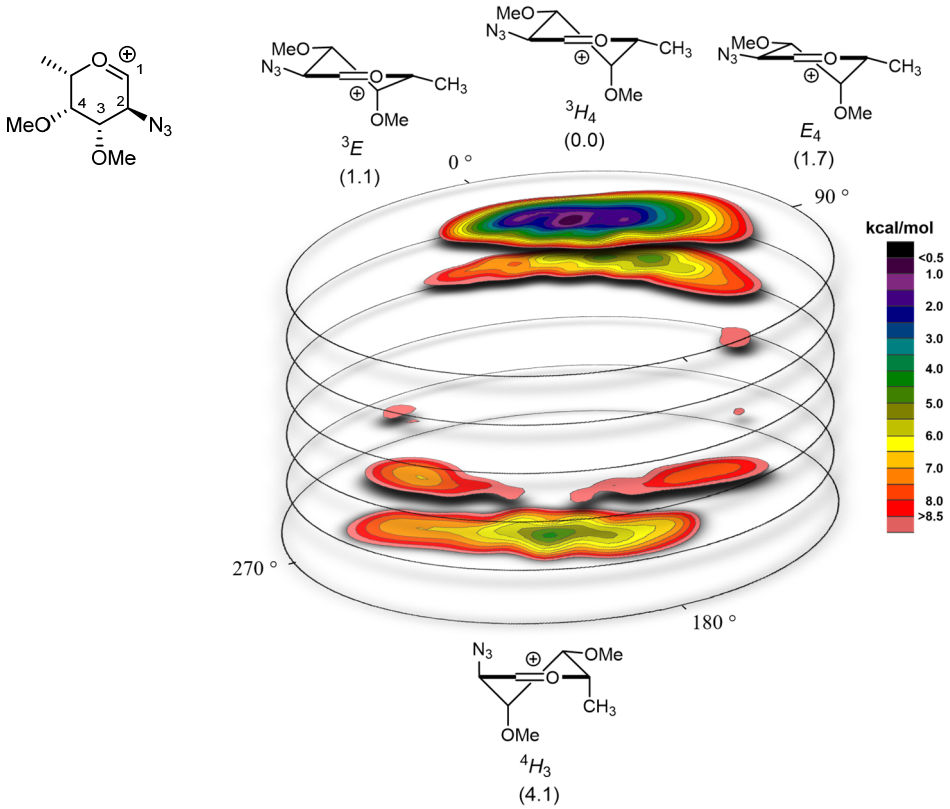


Figure 29| CEL map of 2-azido-2-deoxy-3,4-di-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**21**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -703.004107311 a.u.
E_{solv}(B3LYP) = -703.077766456 a.u.
Zero-point energy correction = 0.228553 a.u.

Atom coordinates

C	-1.224333	0.543950	-0.339545
C	0.756787	-0.883029	0.194212
O	-1.371963	-1.967060	-0.212355
C	-0.185443	-2.026241	0.164119
C	-2.055089	-0.679170	-0.712345
C	0.272801	0.308626	-0.640861
H	0.155862	-3.021960	0.478003
H	0.728780	-0.570739	1.260705
H	-1.604172	1.369187	-0.960808
O	-1.409689	0.799536	1.040003
C	-1.459905	2.179597	1.422090
H	-0.492566	2.664348	1.277166
H	-1.721149	2.192584	2.479674
H	-2.233043	2.708931	0.853781
H	-2.036113	-0.841551	-1.795240
C	-3.452910	-0.738073	-0.151304
H	-4.017130	0.104737	-0.560033
H	-3.441963	-0.654394	0.934355
H	-3.947459	-1.661305	-0.455264
H	0.392838	0.058080	-1.707618
O	1.091208	1.393106	-0.282401
C	1.314248	2.351012	-1.322447
H	1.764125	1.872764	-2.199224
H	2.004779	3.088120	-0.915659
H	0.386194	2.852719	-1.617480
N	2.079676	-1.380133	-0.184899
N	3.036068	-0.823799	0.373070
N	3.996775	-0.411239	0.794994

^3E conformation (1.1 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -703.002618569 a.u.
E_{solv}(B3LYP) = -703.075929457 a.u.
Zero-point energy correction = 0.228455 a.u.

Atom coordinates

C	1.200484	0.619560	0.348166
C	-0.632427	-0.973931	-0.186238
O	1.491589	-1.918203	0.428301
C	0.301505	-2.085016	0.090950
C	2.167418	-0.543682	0.607053
C	-0.250882	0.226889	0.708208
H	-0.028362	-3.131017	0.031932
H	-0.454586	-0.678126	-1.242926
H	1.536515	1.441498	0.998149
O	1.280206	0.977160	-1.015863
C	1.157400	2.374541	-1.311291
H	0.142578	2.729489	-1.124839
H	1.397699	2.482491	-2.368394
H	1.871992	2.956694	-0.718524
H	2.401191	-0.600235	1.674772
C	3.411677	-0.594665	-0.243150
H	3.981228	0.320409	-0.060266
H	3.166042	-0.636071	-1.303072
H	4.029453	-1.447940	0.039337
H	-0.310014	-0.082307	1.764483
O	-1.171234	1.245659	0.425491
C	-1.518672	2.076179	1.539458
H	-1.944261	1.476233	2.350817
H	-2.266848	2.778034	1.174650
H	-0.652278	2.633118	1.912036
N	-1.988229	-1.470638	0.032773
N	-2.883935	-0.866200	-0.570910
N	-3.798387	-0.417226	-1.054795

E_4 conformation (1.7 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -703.000782352 a.u.
E_{solv}(B3LYP) = -703.074918892 a.u.
Zero-point energy correction = 0.228415 a.u.

Atom coordinates

C	-1.234525	0.483372	-0.364164
C	0.832915	-0.826341	0.233500
O	-1.325698	-1.930915	0.131494
C	-0.113032	-1.954687	0.417413
C	-1.909811	-0.818043	-0.769450
C	0.293812	0.369375	-0.567738
H	0.238243	-2.870111	0.913000
H	0.924807	-0.484985	1.287421
H	-1.635912	1.273293	-1.017405
O	-1.553545	0.712368	0.994691
C	-1.695244	2.083891	1.385396
H	-0.739956	2.609298	1.334485
H	-2.050728	2.069807	2.415080
H	-2.435587	2.589664	0.755355
H	-1.604466	-1.144897	-1.769061
C	-3.399034	-0.891182	-0.561179
H	-3.876859	-0.195823	-1.256515
H	-3.660303	-0.608166	0.457750
H	-3.767539	-1.895063	-0.776455
H	0.485678	0.178087	-1.635993
O	1.020752	1.487482	-0.120397
C	1.189387	2.526799	-1.090685
H	1.682908	2.140736	-1.989119
H	1.821645	3.280363	-0.623723
H	0.232780	2.982572	-1.368134
N	2.106710	-1.359674	-0.253147
N	3.120837	-0.803038	0.193938
N	4.124798	-0.396625	0.506131

$^4H_3$ conformation (4.1 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -702.999173767 a.u.
E_{solv}(B3LYP) = -703.071494144 a.u.
Zero-point energy correction = 0.229030 a.u.

Atom coordinates

C	0.807293	-0.167990	-0.765243
C	-1.296449	0.169238	0.517397
O	-0.135216	2.124090	-0.368938
C	-1.138498	1.618530	0.176424
C	1.113490	1.338892	-0.784265
C	0.038343	-0.586504	0.501909
H	-1.962395	2.320560	0.358977
H	-1.773017	0.087319	1.518341
H	0.171255	-0.391371	-1.634185
O	2.060098	-0.807802	-0.891696
C	2.028550	-2.038689	-1.619406
H	1.412318	-2.792260	-1.116852
H	3.057322	-2.393045	-1.665361
H	1.651377	-1.880063	-2.635752
H	1.215543	1.681051	-1.817351
C	2.246549	1.864516	0.069584
H	3.157899	1.357296	-0.249583
H	2.081367	1.661213	1.125191
H	2.368315	2.936646	-0.093885
H	-0.183780	-1.662042	0.473480
O	0.689637	-0.223540	1.701480
C	1.592713	-1.202895	2.232825
H	1.081948	-2.164171	2.359290
H	1.903915	-0.831330	3.208451
H	2.464076	-1.329709	1.587875
N	-2.181412	-0.289116	-0.581202
N	-3.360644	-0.529260	-0.271469
N	-4.445691	-0.797719	-0.136008

2,3,4-Tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**22**)

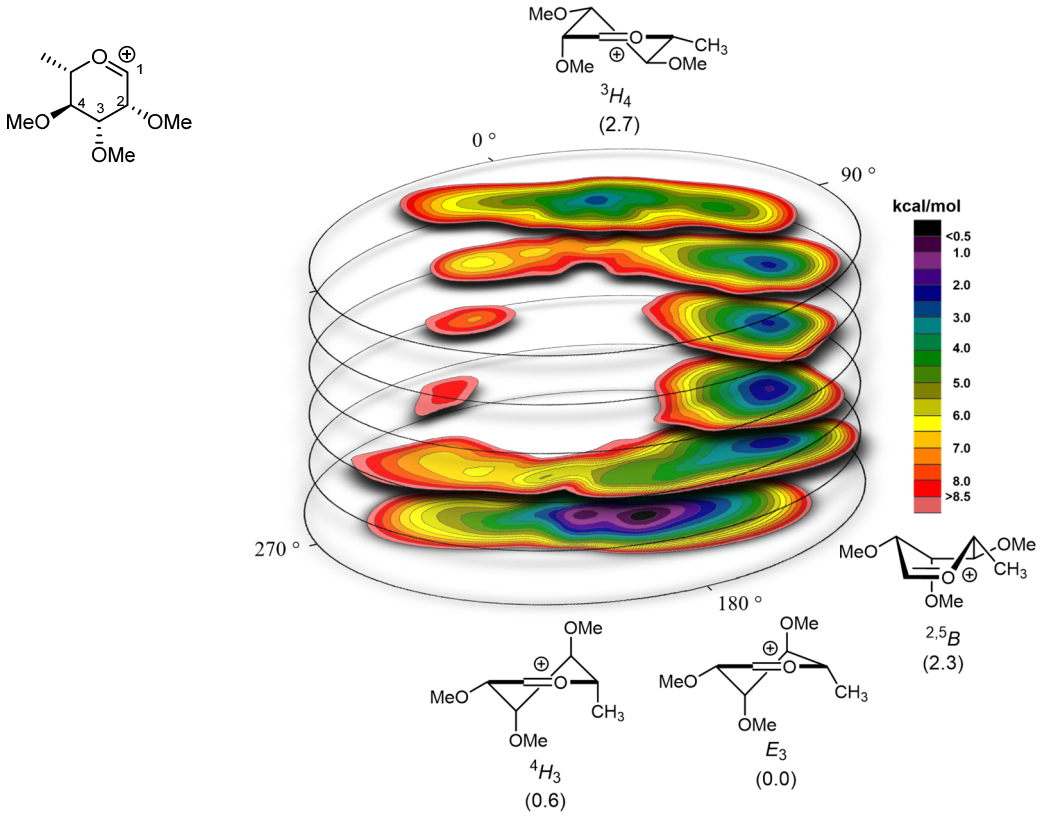


Figure 30| CEL map of 2,3,4-tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**22**).

Local minima

E_3 conformation (0.0 kcal / mol)

D1 = -60°
D3 = -30°
D5 = 0°

E_{gas}(B3LYP) = -653.939524019 a.u.
E_{solv}(B3LYP) = -654.003898257 a.u.
Zero-point energy correction = 0.257893 a.u.

Atom coordinates

C	1.156921	0.261115	-0.566465
C	-1.024251	0.473642	0.588102
O	0.713340	-0.766234	1.721549
C	-0.455900	-0.330284	1.697436
C	1.748787	-0.539999	0.607686
C	-0.351516	0.011881	-0.728277
H	-1.077449	-0.606330	2.559948
H	2.482162	0.060231	1.151514
C	2.278445	-1.921773	0.291901
H	3.146751	-1.811501	-0.362894
H	1.526434	-2.520398	-0.220076
H	2.601454	-2.425316	1.204220
H	-0.714312	0.624415	-1.562676
O	-0.549530	-1.363851	-0.950148
C	-1.709468	-1.712439	-1.718091
H	-2.626917	-1.493883	-1.168242
H	-1.638504	-2.783084	-1.904959
H	-1.710491	-1.177102	-2.673944
H	-0.703159	1.515850	0.790574
O	-2.417315	0.319122	0.633221
C	-3.159840	1.481893	0.239694
H	-2.927444	2.328672	0.894212
H	-4.211009	1.219046	0.343114
H	-2.954902	1.753233	-0.800992
H	1.660937	-0.066479	-1.485820
O	1.299899	1.654652	-0.368066
C	2.548158	2.201619	-0.800540
H	2.490172	3.275306	-0.628862
H	2.706160	2.008698	-1.867345
H	3.390939	1.795213	-0.228901

$^4H_3$ conformation (0.6 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -653.938825988 a.u.
E_{solv}(B3LYP) = -654.003204182 a.u.
Zero-point energy correction = 0.258186 a.u.

Atom coordinates

C	-1.235346	0.006902	-0.580902
C	1.009534	-0.683216	0.234940
O	-0.707993	-0.068025	1.867185
C	0.415799	-0.541889	1.596622
C	-1.684830	0.459551	0.809311
C	0.276820	0.190281	-0.808768
H	1.007286	-0.831339	2.475506
H	-2.586209	-0.082051	1.104816
C	-1.832493	1.941298	1.084544
H	-2.621742	2.326831	0.433736
H	-0.912330	2.480575	0.873207
H	-2.138125	2.100899	2.119872
H	0.525233	-0.175095	-1.812199
O	0.588223	1.552333	-0.652630
C	1.650129	2.045464	-1.478415
H	2.604784	1.596078	-1.199644
H	1.687525	3.121583	-1.313473
H	1.438189	1.848091	-2.535256
H	0.826282	-1.743165	-0.035650
O	2.375178	-0.371867	0.340557
C	3.277595	-1.477213	0.181429
H	3.155072	-2.208721	0.987063
H	4.280604	-1.056688	0.225598
H	3.122727	-1.965632	-0.786383
H	-1.771839	0.614628	-1.322940
O	-1.487358	-1.378061	-0.754365
C	-2.782508	-1.694453	-1.272149
H	-2.817014	-2.777893	-1.376263
H	-2.931649	-1.226722	-2.251543
H	-3.581384	-1.376766	-0.592099

$^{2,5}B$ conformation (2.3 kcal / mol)

D1 = -30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -653.933945356 a.u.
E_{solv}(B3LYP) = -654.000684588 a.u.
Zero-point energy correction = 0.257632 a.u.

Atom coordinates

C	-1.179772	0.421889	0.089689
C	1.051844	-0.625475	-0.551192
O	-0.661600	-2.023470	0.329483
C	0.563316	-1.821501	0.168203
C	-1.643689	-1.014834	-0.228636
C	0.357628	0.569935	0.186605
H	1.238238	-2.568343	0.604947
H	-1.580694	-1.162803	-1.312902
C	-2.993831	-1.395884	0.320128
H	-3.729297	-0.694605	-0.080113
H	-3.006982	-1.333351	1.410345
H	-3.272848	-2.403329	0.008501
H	0.660939	1.507690	-0.290499
O	0.700192	0.538318	1.557196
C	1.877763	1.264545	1.936367
H	2.783002	0.776504	1.570907
H	1.883606	1.282307	3.025482
H	1.830297	2.293028	1.560451
H	0.657550	-0.676514	-1.586673
O	2.448052	-0.626192	-0.510655
C	3.075828	0.108326	-1.570140
H	2.760218	-0.276558	-2.545878
H	4.146825	-0.042172	-1.448524
H	2.852664	1.178261	-1.506756
H	-1.589069	0.741274	1.056976
O	-1.722844	1.170724	-0.979379
C	-2.016665	2.533994	-0.659894
H	-2.454007	2.970206	-1.556604
H	-1.111858	3.093261	-0.395818
H	-2.733530	2.594139	0.166219

$^{3}H_4$ conformation (2.7 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -653.931740606 a.u.
E_{solv}(B3LYP) = -653.999803772 a.u.
Zero-point energy correction = 0.258116 a.u.

Atom coordinates

C	-0.896299	0.089624	0.117872
C	1.442166	-0.523381	-0.480336
O	-0.276508	-2.231737	-0.672642
C	0.932184	-1.912928	-0.682426
C	-1.421803	-1.235356	-0.450017
C	0.357998	0.542471	-0.636450
H	1.629764	-2.753805	-0.776948
H	-1.788585	-1.080066	-1.470170
C	-2.420279	-1.971976	0.407438
H	-3.297006	-1.331726	0.525131
H	-2.009557	-2.192253	1.395269
H	-2.735797	-2.899613	-0.071909
H	0.116174	0.631301	-1.706873
O	0.856759	1.754673	-0.115921
C	0.645731	2.898202	-0.951015
H	1.170430	2.789688	-1.907267
H	1.057711	3.750466	-0.411776
H	-0.419670	3.061123	-1.135617
H	2.292278	-0.338919	-1.168505
O	1.858037	-0.660337	0.876725

C	3.223986	-0.294049	1.145761	O	-1.952724	1.013995	-0.062357
H	3.919257	-0.936085	0.597063	C	-2.309238	1.760718	1.107122
H	3.362960	-0.435252	2.216193	H	-3.112272	2.432474	0.806014
H	3.380564	0.753381	0.878551	H	-1.459934	2.343850	1.473830
H	-0.646782	-0.027845	1.179515	H	-2.670723	1.100590	1.903365

2-Deoxy-3,4-tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**23**)

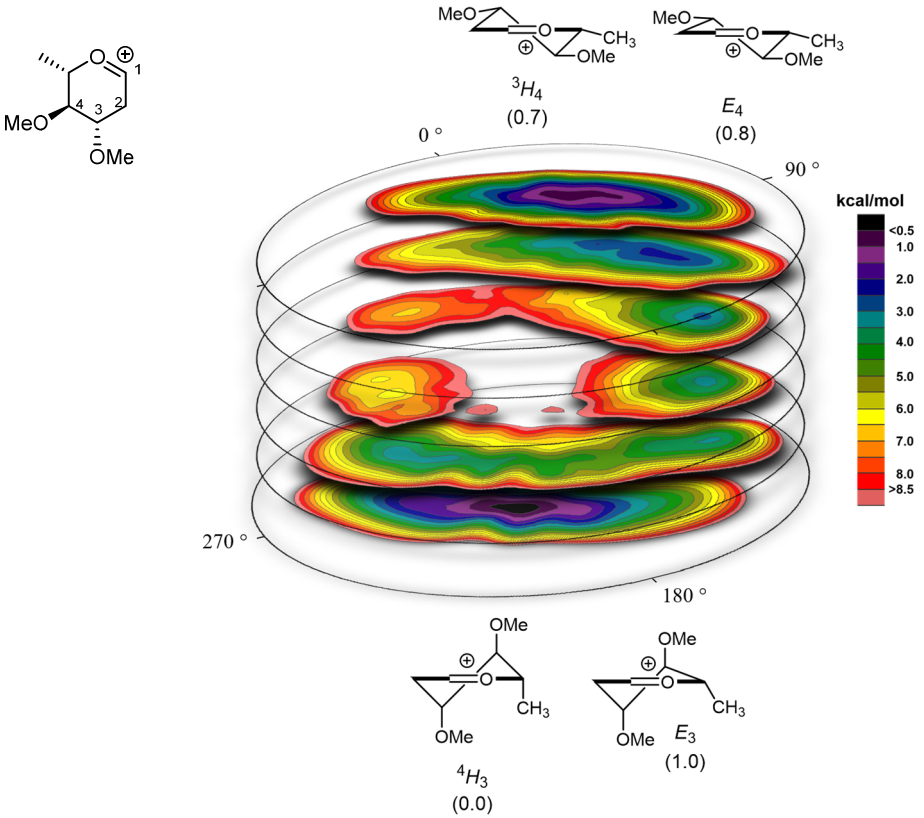


Figure 31| CEL map of 2-deoxy-3,4-di-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**23**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -539.397133128 a.u.
E_{solv}(B3LYP) = -539.465375771 a.u.
Zero-point energy correction = 0.225984 a.u.

Atom coordinates

C	-0.656644	-0.394021	-0.517103	C	0.687313	-0.869546	0.056913
C	0.731891	-0.463397	1.536165	H	0.481682	1.421085	2.720977
O	-0.374886	1.610904	0.960640	H	1.715839	-0.586573	2.002962
C	0.279080	0.913186	1.768881	H	-1.872530	1.390249	-0.381525
C	-0.813380	1.126190	-0.426031	H	0.722826	-1.963181	-0.020803
				O	1.729436	-0.267954	-0.681004
				C	2.970079	-0.975209	-0.648861
				H	3.396935	-1.006486	0.360279
				H	3.651197	-0.433974	-1.303901
				H	2.842329	-1.998547	-1.019261
				C	-0.087047	1.998569	-1.427847
				H	-0.482619	1.769622	-2.421036
				H	0.982806	1.805398	-1.426888
				H	-0.283268	3.051622	-1.219212
				H	0.049002	-1.088851	2.138524
				H	-0.718668	-0.680911	-1.575727
				O	-1.648049	-1.039896	0.264201
				C	-2.871169	-1.319284	-0.419459
				H	-3.515131	-1.828515	0.296171

H	-2.693776	-1.971927	-1.281465
H	-3.369373	-0.402379	-0.755741

$^3H_4$ conformation (0.7 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -539.389999063 a.u.
E_{solv}(B3LYP) = -539.463534576 a.u.
Zero-point energy correction = 0.225313 a.u.

Atom coordinates

C	0.267979	0.528489	-0.109194
C	-0.466720	-1.898833	-0.160312
O	1.882533	-1.400219	0.088808
C	0.959077	-2.213537	-0.140107
C	1.644076	0.073198	0.386905
C	-0.844458	-0.462591	0.246338
H	1.309490	-3.232177	-0.351972
H	-0.786652	-2.103718	-1.199516
H	1.671798	0.096985	1.481671
H	-0.987358	-0.419532	1.336745
O	-2.014952	-0.042430	-0.421563
C	-3.234221	-0.489108	0.174324
H	-3.336100	-1.579684	0.126710
H	-4.042036	-0.035135	-0.398038
H	-3.300166	-0.164601	1.219132
C	2.819841	0.798698	-0.220968
H	2.726037	1.857042	0.027584
H	2.831598	0.691194	-1.308009
H	3.759085	0.427910	0.191523
H	-0.973148	-2.675483	0.431546
H	0.293358	0.641538	-1.204550
O	0.069516	1.772924	0.528892
C	-0.563829	2.781317	-0.269118
H	-0.617563	3.670935	0.357469
H	-1.567988	2.472669	-0.565007
H	0.032401	3.004057	-1.161581

***E*$_4$ conformation (0.8 kcal / mol)**

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -539.388955002 a.u.
E_{solv}(B3LYP) = -539.463089711 a.u.
Zero-point energy correction = 0.225172 a.u.

Atom coordinates

C	0.289425	0.499281	-0.146374
C	-0.501419	-1.865898	-0.241027
O	1.866499	-1.412248	-0.046846
C	0.923801	-2.183979	-0.342515
C	1.600519	-0.003219	0.470671
C	-0.840087	-0.446428	0.271818
H	1.252107	-3.163115	-0.714888
H	-0.905661	-2.010052	-1.259202
H	1.497960	-0.146323	1.551739
H	-0.903884	-0.439740	1.369590
O	-2.045098	0.008612	-0.300153
C	-3.226369	-0.444129	0.363228
H	-3.343700	-1.531890	0.290292
H	-4.065907	0.034925	-0.138631
H	-3.217537	-0.151105	1.419331
C	2.835088	0.789113	0.119509
H	2.720478	1.793428	0.528208
H	2.962810	0.862181	-0.962940
H	3.722587	0.331460	0.559113
H	-0.959892	-2.678490	0.344565
H	0.377721	0.522609	-1.244593
O	0.107935	1.791259	0.388061
C	-0.512052	2.738482	-0.490795
H	-0.545629	3.679824	0.056601
H	-1.523533	2.424365	-0.753573
H	0.083958	2.871595	-1.401190

***E*$_3$ conformation (1.0 kcal / mol)**

D1 = -60°
D3 = -30°
D5 = 0°

E_{gas}(B3LYP) = -539.395659340 a.u.
E_{solv}(B3LYP) = -539.463759636 a.u.
Zero-point energy correction = 0.225934 a.u.

Atom coordinates

C	-0.730242	-0.360079	-0.440486
C	0.784657	-0.589863	1.503562
O	0.041258	1.627183	0.963393
C	0.718855	0.865175	1.690747
C	-0.817720	1.162820	-0.225683
C	0.632311	-0.905970	0.005919
H	1.259005	1.386075	2.492055
H	1.704732	-0.973582	1.951145
H	-1.808615	1.443046	0.139811
H	0.630861	-1.992776	-0.140596
O	1.638222	-0.271634	-0.755473
C	2.844677	-1.024228	-0.902330
H	3.343634	-1.182585	0.060508
H	3.496650	-0.438049	-1.548268
H	2.641039	-1.993588	-1.370064
C	-0.374880	2.037223	-1.378249
H	-1.073324	1.889260	-2.206220
H	0.625934	1.765509	-1.710788
H	-0.402594	3.089985	-1.093154

H	-0.056949	-1.029262	2.064637	H	-3.584147	-1.774774	0.408401
H	-0.862832	-0.561284	-1.511786	H	-2.874540	-1.755110	-1.228764
O	-1.694113	-1.045462	0.338072	H	-3.451745	-0.238259	-0.477711
C	-2.969331	-1.204294	-0.286339				

2,3,4,6-Tera-*O*-methyl-gluco-D-pyranosyl oxocarbenium ion (**24**)

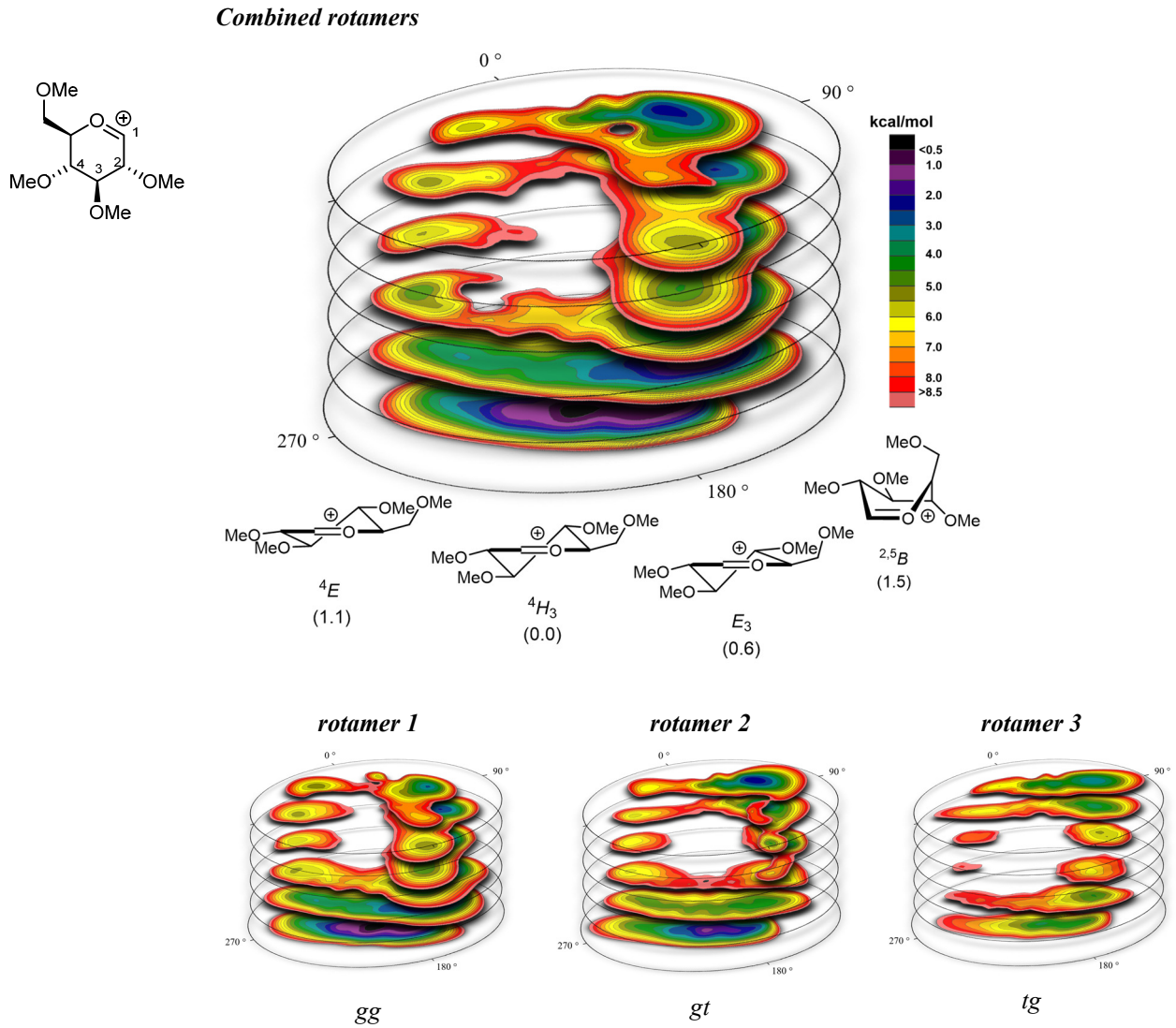


Figure 32| CEL map of 2,3,4,6-tera-*O*-methyl-gluco-D-pyranosyl oxocarbenium ion (**24**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -768.481443857 a.u.
E_{solv}(B3LYP) = -768.548553062 a.u.
Zero-point energy correction = 0.290971 a.u.

Atom coordinates

O	0.651059	-1.733318	-0.884135
C	0.381414	0.653796	-0.134379
C	-1.432131	-1.030159	0.174952
C	-1.125651	0.405817	-0.277891
C	-0.457446	-2.011849	-0.379856
C	1.186015	-0.312838	-1.010689
H	0.670689	0.520400	0.914827
H	-1.283967	-1.073373	1.264691
H	-1.416294	0.507283	-1.333172
H	-0.714793	-3.079063	-0.396520

H	1.037510	-0.092859	-2.073329
O	-2.712345	-1.461548	-0.207424
O	-1.863072	1.283372	0.541608
O	0.723251	1.946078	-0.595082
C	2.657499	-0.417385	-0.687472
H	3.120546	0.544753	-0.950821
H	3.112939	-1.196492	-1.314613
C	-3.651022	-1.627657	0.868851
H	-3.353139	-2.451179	1.525961
H	-4.604775	-1.864321	0.400419
H	-3.737446	-0.701879	1.443473
C	-2.568548	2.314736	-0.159284
H	-3.311752	1.884412	-0.839026
H	-1.880678	2.951162	-0.722445
H	-3.076140	2.907558	0.600788
C	1.116259	2.866006	0.431871
H	1.350673	3.802817	-0.072072
H	2.004914	2.505961	0.960979
H	0.304595	3.025082	1.146878
O	2.792970	-0.712766	0.684297
C	4.151536	-0.854381	1.090749
H	4.713167	0.072687	0.921818
H	4.641078	-1.673984	0.550582
H	4.140441	-1.080042	2.156359

E_3 conformation (0.6 kcal / mol)

D1 = -60°
D3 = -30°
D5 = 0°

E_{gas}(B3LYP) = -768.481953982 a.u.
E_{solv}(B3LYP) = -768.547437087 a.u.
Zero-point energy correction = 0.290852 a.u.

Atom coordinates

O	0.760757	-1.335070	-1.355792
C	0.405879	0.880203	-0.129210
C	-1.184427	-1.011973	0.047910
C	-1.067415	0.497668	-0.309685
C	-0.306791	-1.776855	-0.877799
C	1.314613	0.051606	-1.057147
H	0.688186	0.716564	0.917318
H	-0.813054	-1.139411	1.076109
H	-1.374385	0.654514	-1.353726
H	-0.594937	-2.772293	-1.241254
H	1.335066	0.505337	-2.052069
O	-2.502932	-1.464358	-0.114233
O	-1.843891	1.256402	0.576503
O	0.661686	2.212039	-0.521842
C	2.712253	-0.193043	-0.539124
H	3.207351	0.786067	-0.455084
H	3.274447	-0.799210	-1.262748
C	-2.994196	-2.312902	0.933772
H	-2.438090	-3.255953	0.976984
H	-4.035459	-2.519523	0.693385
H	-2.930251	-1.803202	1.900756
C	-3.115493	1.682406	0.068946
H	-3.742571	0.825778	-0.187656
H	-2.986082	2.324140	-0.809312
H	-3.584659	2.254142	0.868634
C	0.683811	3.170207	0.544982
H	0.930737	4.126048	0.084481
H	1.454038	2.913689	1.281307
H	-0.288142	3.233394	1.036928
O	2.603505	-0.844768	0.706322
C	3.868640	-1.146284	1.290680
H	4.444768	-0.231509	1.475610
H	4.451168	-1.814132	0.644574
H	3.667625	-1.644598	2.238154

E_4 conformation (1.1 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -768.479138867 a.u.
E_{solv}(B3LYP) = -768.546681915 a.u.
Zero-point energy correction = 0.290948 a.u.

Atom coordinates

O	-0.458169	-1.879795	0.365359
C	-0.372616	0.571380	0.041660
C	1.659997	-0.840014	-0.300235
C	1.154762	0.522304	0.197994
C	0.685947	-1.964019	-0.132434
C	-0.999228	-0.552279	0.876461
H	-0.645876	0.436935	-1.012690
H	1.816969	-0.748228	-1.385724
H	1.404604	0.616182	1.264745
H	0.982564	-2.981202	-0.417272
H	-0.664726	-0.519466	1.919857
O	2.822781	-1.271419	0.374988
O	1.801507	1.512803	-0.567329
O	-0.863715	1.793213	0.549116
C	-2.500634	-0.679815	0.807656
H	-2.931398	0.168570	1.358408
H	-2.804950	-1.604329	1.318500
C	3.970610	-1.512836	-0.456745
H	3.801876	-2.356452	-1.133550
H	4.786591	-1.752215	0.222919
H	4.214031	-0.615696	-1.033330
C	2.208915	2.676170	0.163232
H	2.925793	2.408937	0.947758
H	1.351499	3.185894	0.607959
H	2.694009	3.332796	-0.558197
C	-1.640011	2.565413	-0.377645
H	-1.980723	3.444331	0.168096
H	-2.501703	1.995092	-0.735414

H	-1.027445	2.878242	-1.229062
O	-2.893898	-0.684743	-0.546536
C	-4.290857	-0.910379	-0.716906
H	-4.881743	-0.122660	-0.233237
H	-4.584509	-1.883171	-0.303936
H	-4.484227	-0.899573	-1.788841

$^{2,5}B$ conformation (1.5 kcal / mol)

D1 = -60°
D3 = 15°
D5 = 0°

E_{gas}(B3LYP) = -768.481923549 a.u.
E_{solv}(B3LYP) = -768.546076522 a.u.
Zero-point energy correction = 0.290857 a.u.

Atom coordinates

O	1.144374	0.025920	1.845453
C	-0.071877	-1.309348	0.042607
C	-0.343767	1.198105	0.375680
C	-1.098768	-0.162512	0.165753
C	0.431004	1.034170	1.622429
C	1.243411	-1.090947	0.822475
H	0.179288	-1.378673	-1.024234
H	0.362910	1.305314	-0.461258
H	-1.734659	-0.348491	1.043132
H	0.377436	1.760932	2.443412
H	1.409078	-1.954506	1.468779
O	-1.249713	2.255899	0.489627
O	-1.852225	-0.111371	-1.013761
O	-0.584866	-2.540406	0.511794
C	2.485880	-0.828886	0.000551
H	2.675003	-1.738188	-0.590273
H	3.343125	-0.672258	0.669900
C	-0.873282	3.443984	-0.222355
H	0.055385	3.867888	0.175565
H	-1.684329	4.155342	-0.077612
H	-0.755488	3.232745	-1.290340
C	-3.235284	0.237546	-0.857279
H	-3.344232	1.237174	-0.434291
H	-3.748197	-0.491722	-0.219882
H	-3.666242	0.209135	-1.857107
C	-1.474901	-3.213761	-0.383559
H	-1.619447	-4.211623	0.028998
H	-1.034417	-3.291578	-1.384071
H	-2.441999	-2.709132	-0.456655
O	2.272351	0.295824	-0.826091
C	3.397032	0.610709	-1.648869
H	3.630916	-0.220955	-2.323023
H	4.276138	0.840899	-1.036112
H	3.123677	1.486408	-2.235697

Methyl (2,3,4-tri-*O*-benzyl-gluco-D-pyranosyl uronate) oxocarbenium ion (**25**)

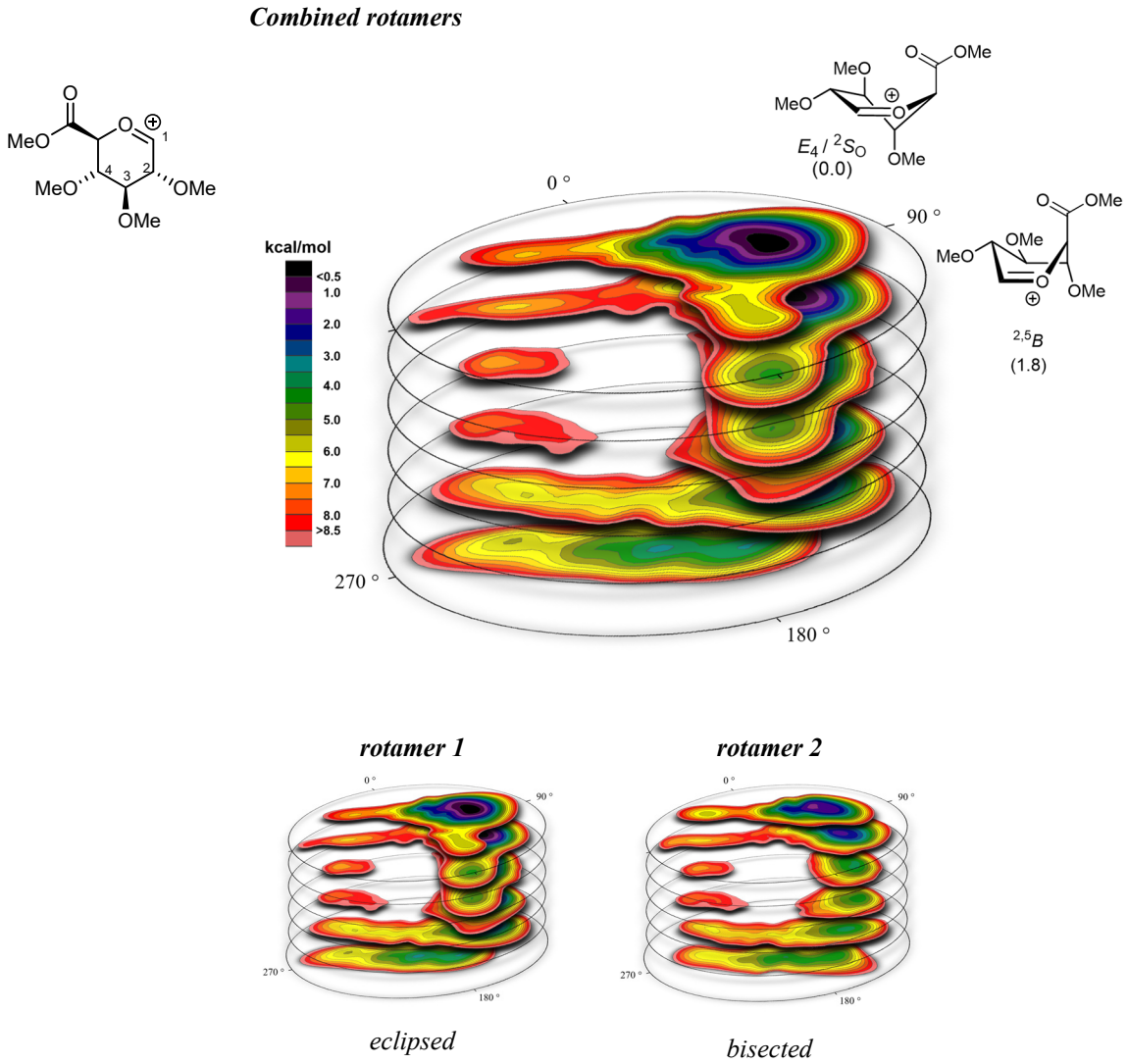
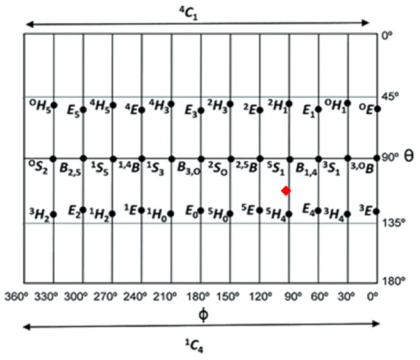


Figure 33| CEL map of methyl (2,3,4-tri-*O*-benzyl-gluco-D-pyranosyl uronate) oxocarbenium ion (**25**).

Local minima

E_4–^2S_O conformation (0.0 kcal / mol)



D1 = 0°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -842.539064707 a.u.
E_{solv}(B3LYP) = -842.601075573 a.u.
Zero-point energy correction = 0.272595 a.u.

Atom coordinates

O	0.030443	1.035705	-1.782321
C	0.122987	1.037243	0.663343
C	-1.512001	-0.455523	-0.643722
C	-0.878285	-0.132307	0.741002
C	-1.049131	0.398558	-1.757264
C	0.955534	0.964999	-0.633065
H	0.821417	0.990167	1.504777
H	-1.691821	0.184930	1.400547
H	-1.675491	0.516609	-2.639952

H	1.592187	1.835045	-0.763481
O	-0.262487	-1.321300	1.189352
O	-0.652646	2.210011	0.677055
C	1.773195	-0.323895	-0.786968
C	-0.122471	-1.426323	2.611351
H	0.541265	-0.656064	3.016288
H	0.313739	-2.405094	2.800702
H	-1.099572	-1.359480	3.100371
C	0.047436	3.421107	0.987903
H	0.592386	3.319733	1.931501
H	-0.712966	4.193057	1.085810
H	0.742067	3.707444	0.191789
O	2.822744	-0.269840	0.011588
C	3.686082	-1.442824	0.030621
H	3.113028	-2.311427	0.350744
H	4.468037	-1.204995	0.744616
H	4.100256	-1.607107	-0.962675
O	1.460932	-1.220703	-1.526548
H	-1.087682	-1.442652	-0.927603
O	-2.907042	-0.459604	-0.686833
C	-3.509830	-1.657732	-0.171134
H	-3.134363	-2.536659	-0.703979
H	-4.578822	-1.551940	-0.340616
H	-3.320311	-1.765542	0.900407

E_4 conformation (1.4 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -842.534003734 a.u.
E_{solv}(B3LYP) = -842.598907186 a.u.
Zero-point energy correction = 0.272732 a.u.

Atom coordinates

O	0.285930	0.579776	-1.750454
C	-0.262877	1.225468	0.556343
C	-1.226652	-0.861564	-0.451523
C	-0.688122	-0.223929	0.857968
C	-0.595125	-0.310204	-1.690465
C	0.828917	1.220695	-0.510362
H	0.160205	1.681856	1.457663
H	-1.499620	-0.237826	1.591189
H	-0.961137	-0.642383	-2.660716
H	1.009927	2.238683	-0.849331
O	0.449969	-0.902116	1.325016
O	-1.313426	1.979036	0.004718
C	2.171955	0.609383	-0.108052
C	0.183060	-2.036721	2.156636
H	-0.378902	-1.736166	3.045965
H	1.150948	-2.436113	2.452127
H	-0.374541	-2.810350	1.617289
C	-2.304962	2.429665	0.936660
H	-2.925204	1.604356	1.295304
H	-2.930726	3.133673	0.391777
H	-1.834030	2.938503	1.783448
O	2.513345	-0.422429	-0.861351
C	3.787830	-1.048742	-0.552725
H	4.589382	-0.316957	-0.639677
H	3.900983	-1.838725	-1.288758
H	3.758907	-1.457098	0.456514
O	2.813529	1.111882	0.775471
H	-0.959213	-1.928939	-0.438228
O	-2.604650	-0.665459	-0.661605
C	-3.398904	-1.866637	-0.669918
H	-3.128759	-2.511112	-1.510981
H	-4.430991	-1.540677	-0.776387
H	-3.275528	-2.410719	0.271081

$^{2,5}B$ conformation (1.8 kcal / mol)

D1 = -30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -842.536153625 a.u.
E_{solv}(B3LYP) = -842.598247786 a.u.
Zero-point energy correction = 0.272354 a.u.

Atom coordinates

O	0.335422	-0.385625	-2.023409
C	0.395760	1.131681	-0.054027
C	-1.501180	-0.608526	-0.477297
C	-1.046069	0.661848	0.290200
C	-0.858688	-0.704544	-1.802530
C	1.181438	0.119823	-0.919928
H	0.960990	1.253887	0.876722
H	-1.713417	1.473092	-0.017058
H	-1.413203	-1.055005	-2.671702
H	2.006939	0.600572	-1.436023
O	-1.211635	0.347181	1.651899
O	0.260377	2.353160	-0.744786
C	1.697392	-1.100390	-0.145156
C	-1.407663	1.487423	2.496144
H	-0.529572	2.141798	2.502692
H	-1.569984	1.099393	3.499752
H	-2.283953	2.059759	2.174755
C	1.411352	3.203169	-0.719122
H	1.727615	3.393397	0.311539
H	1.108653	4.137498	-1.187602
H	2.248775	2.780883	-1.284929
O	2.751338	-0.743556	0.562957
C	3.349704	-1.766193	1.411782
H	2.610698	-2.128995	2.124199
H	4.168672	-1.265620	1.918159
H	3.714042	-2.584185	0.792686
O	1.178709	-2.187122	-0.184753
H	-1.099937	-1.480729	0.082456
O	-2.886076	-0.663861	-0.641741

C	-3.570329	-1.564242	0.248855
H	-3.260397	-2.597551	0.066858
H	-4.629188	-1.457849	0.023507
H	-3.382118	-1.292069	1.289135

$^4H_3$ conformation (2.1 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -842.532838889 a.u.
E_{solv}(B3LYP) = -842.597438836 a.u.
Zero-point energy correction = 0.272482 a.u.

Atom coordinates

O	-0.188439	0.209187	-1.864975
C	0.029419	0.886125	0.549106
C	-1.745488	-0.766334	-0.253529
C	-0.810568	-0.357845	0.892537
C	-1.233494	-0.429957	-1.610457
C	0.722042	0.742032	-0.815226
H	0.818374	1.015216	1.296320
H	-1.428703	-0.129112	1.764804
H	-1.823107	-0.686902	-2.488604
H	1.003205	1.713284	-1.216556
O	0.047774	-1.463371	1.109096
O	-0.859733	1.980371	0.531042
C	1.941945	-0.191782	-0.837207
C	0.495492	-1.619644	2.461073
H	1.070614	-0.753018	2.802319
H	1.136841	-2.498729	2.469938
H	-0.355309	-1.778999	3.130876
C	-0.262982	3.251564	0.804112
H	0.222280	3.247174	1.785611
H	-1.073663	3.977495	0.800536
H	0.468980	3.533789	0.039262
O	2.872466	0.308382	-0.034919
C	4.119777	-0.434424	0.051705
H	3.925792	-1.435635	0.433507
H	4.738913	0.131522	0.740738
H	4.582661	-0.490207	-0.932396
O	2.019064	-1.189385	-1.500748
H	-1.872860	-1.869102	-0.201212
O	-2.976423	-0.067964	-0.246652
C	-4.151582	-0.900219	-0.206730
H	-4.226773	-1.525756	-1.100017
H	-4.996671	-0.216804	-0.168103
H	-4.135618	-1.529063	0.687931

2-Deoxy-3,4,6-tri-*O*-methyl-gluco-D-pyranosyl oxocarbenium ion (**26**)

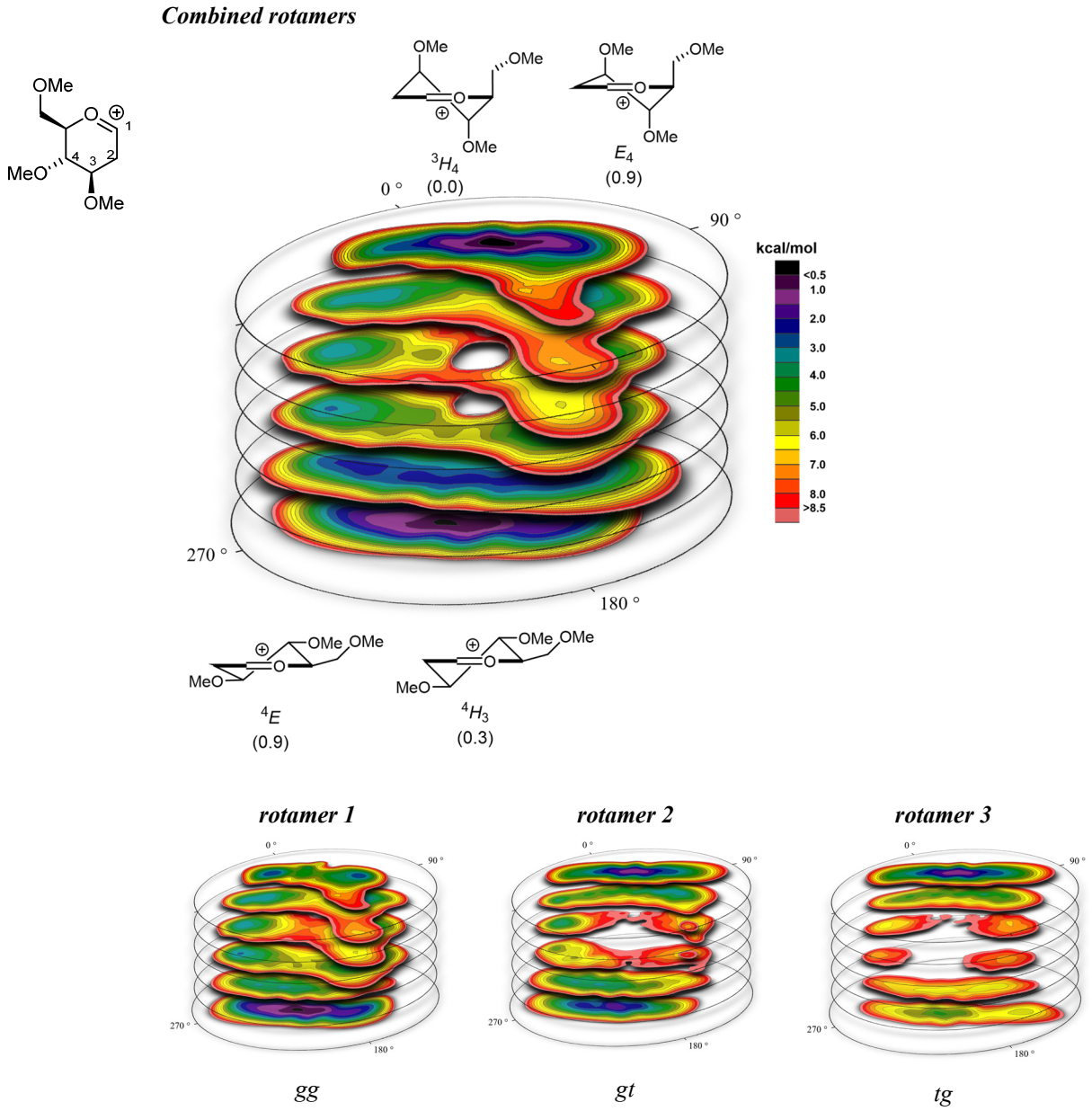


Figure 34| CEL map of 2-deoxy-3,4,6-tri-*O*-methyl-gluco-D-pyranosyl oxocarbenium ion (**26**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -653.940719901 a.u.
E_{solv}(B3LYP) = -654.005899169 a.u.
Zero-point energy correction = 0.258732 a.u.

Atom coordinates

C	-0.905957	-0.397201	-0.612304
C	-1.677380	0.610118	1.518403
O	0.396425	-0.637875	1.522852
C	-0.523274	-0.050689	2.136742
C	0.448934	-0.752587	0.004925
C	-1.492451	0.877176	0.027408
H	-1.899421	1.522502	2.079267
H	-0.411506	-0.083712	3.220420
H	0.655496	-1.815870	-0.104386
H	-2.467495	1.074645	-0.426381
H	-0.757397	-0.246834	-1.687256
H	-2.526078	-0.067650	1.698337

C	1.671817	0.025794	-0.440222
H	1.631589	1.056968	-0.074265
H	1.658416	0.054435	-1.539858
O	2.807253	-0.658219	0.040480
C	4.025321	0.004351	-0.284036
H	4.831930	-0.594078	0.136765
H	4.056394	1.011151	0.150005
H	4.159739	0.079567	-1.370229
O	-1.852832	-1.417977	-0.363793
C	-1.833526	-2.507985	-1.290376
H	-2.025361	-2.153882	-2.308499
H	-2.629208	-3.184423	-0.984005
H	-0.880328	-3.046787	-1.266556
O	-0.630519	1.987921	-0.104633
C	-0.814522	2.747026	-1.305201
H	-0.604527	2.153447	-2.200722
H	-0.112517	3.577236	-1.254469
H	-1.836105	3.136472	-1.359441

$^4H_3$ conformation (0.3 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -653.938077008 a.u.
Es_{olv}(B3LYP) = -654.005348088 a.u.
Zero-point energy correction = 0.258481 a.u.

Atom coordinates

C	-0.215081	0.398372	-0.192133
C	-1.466094	-1.748800	0.304141
O	0.798479	-1.887665	-0.525157
C	-0.205603	-2.419674	-0.001694
C	0.846213	-0.427435	-0.926580
C	-1.582751	-0.287751	-0.170613
H	-1.557945	-1.801109	1.402256
H	-0.066256	-3.473468	0.238721
H	0.640937	-0.456026	-1.997114
H	-1.982430	-0.269130	-1.192363
H	0.116027	0.559167	0.839139
H	-2.271949	-2.397887	-0.059507
C	2.274046	0.003588	-0.679911
H	2.391326	1.001814	-1.121950
H	2.955279	-0.682950	-1.198971
O	2.507648	0.010617	0.709404
C	3.827921	0.427575	1.047227
H	4.021928	1.447215	0.693801
H	4.576959	-0.248916	0.618847
H	3.898879	0.402432	2.133437
O	-0.264785	1.613783	-0.908948
C	-0.350198	2.794254	-0.098485
H	-1.257596	2.784982	0.508092
H	-0.376661	3.634177	-0.791046
H	0.528235	2.886094	0.548958
O	-2.412794	0.456889	0.692664
C	-3.813525	0.300252	0.454154
H	-4.146007	-0.726268	0.643072
H	-4.067865	0.580406	-0.573788
H	-4.320802	0.968185	1.148085

^4E conformation (0.9 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -653.936673013 a.u.
Es_{olv}(B3LYP) = -654.004369853 a.u.
Zero-point energy correction = 0.258422 a.u.

Atom coordinates

C	0.207026	0.337184	0.085454
C	1.574855	-1.691383	-0.391445
O	-0.743659	-1.945172	0.260096
C	0.297061	-2.396768	-0.272684
C	-0.771712	-0.551286	0.861629
C	1.610288	-0.260361	0.200105
H	1.791865	-1.658225	-1.471322
H	0.181332	-3.402482	-0.675943
H	-0.463239	-0.696405	1.897102
H	1.890951	-0.291947	1.259300
H	-0.105008	0.391954	-0.962096
H	2.342960	-2.364812	0.012539
C	-2.219283	-0.123925	0.797104
H	-2.312246	0.805111	1.373356
H	-2.843815	-0.889989	1.275449
O	-2.570765	0.058590	-0.555300
C	-3.928435	0.454904	-0.727644
H	-4.127184	1.410834	-0.228801
H	-4.614313	-0.304560	-0.333626
H	-4.091363	0.566346	-1.798514
O	0.139440	1.598846	0.710367
C	0.144996	2.715155	-0.189704
H	1.067589	2.738646	-0.773152
H	0.080188	3.606399	0.432595
H	-0.720276	2.675420	-0.859501
O	2.502430	0.552667	-0.524000
C	3.861140	0.488489	-0.084259
H	4.290334	-0.509207	-0.228039
H	3.941780	0.769306	0.971446
H	4.415261	1.202098	-0.691434

E_4 conformation (0.9 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -653.939271652 a.u.
E_{solv}(B3LYP) = -654.004592687 a.u.
Zero-point energy correction = 0.258858 a.u.

Atom coordinates

C	-0.957176	-0.240547	-0.644650
C	-1.419349	0.527189	1.660660
O	0.299355	-1.154329	1.268203
C	-0.506098	-0.564796	2.026650
C	0.410219	-0.764846	-0.198374
C	-1.360011	0.985669	0.196209
H	-1.226285	1.360054	2.349758
H	-0.498456	-0.944959	3.048200
H	0.609206	-1.738947	-0.641733
H	-2.360375	1.303247	-0.111041
H	-0.881992	0.030931	-1.704029
H	-2.417817	0.163697	1.940419
C	1.652926	0.085195	-0.370357
H	1.655534	0.939060	0.313163
H	1.642305	0.480172	-1.396813
O	2.761809	-0.762102	-0.157941
C	4.005147	-0.078094	-0.275323
H	4.788021	-0.813034	-0.094113
H	4.086439	0.727674	0.464481
H	4.131990	0.345314	-1.279380
O	-1.959455	-1.209456	-0.427195
C	-2.107391	-2.185447	-1.464740
H	-2.344617	-1.701042	-2.417180
H	-2.934879	-2.825660	-1.165177
H	-1.207130	-2.797211	-1.580713
O	-0.439062	2.047442	0.089404
C	-0.719638	2.973854	-0.966512
H	-0.691004	2.493240	-1.949535
H	0.055470	3.736469	-0.919266
H	-1.699348	3.439488	-0.818185

2-Azido-2-deoxy-3,4,6-tri-*O*-methyl-gluco-D-pyranosyl oxocarbenium ion (**27**)

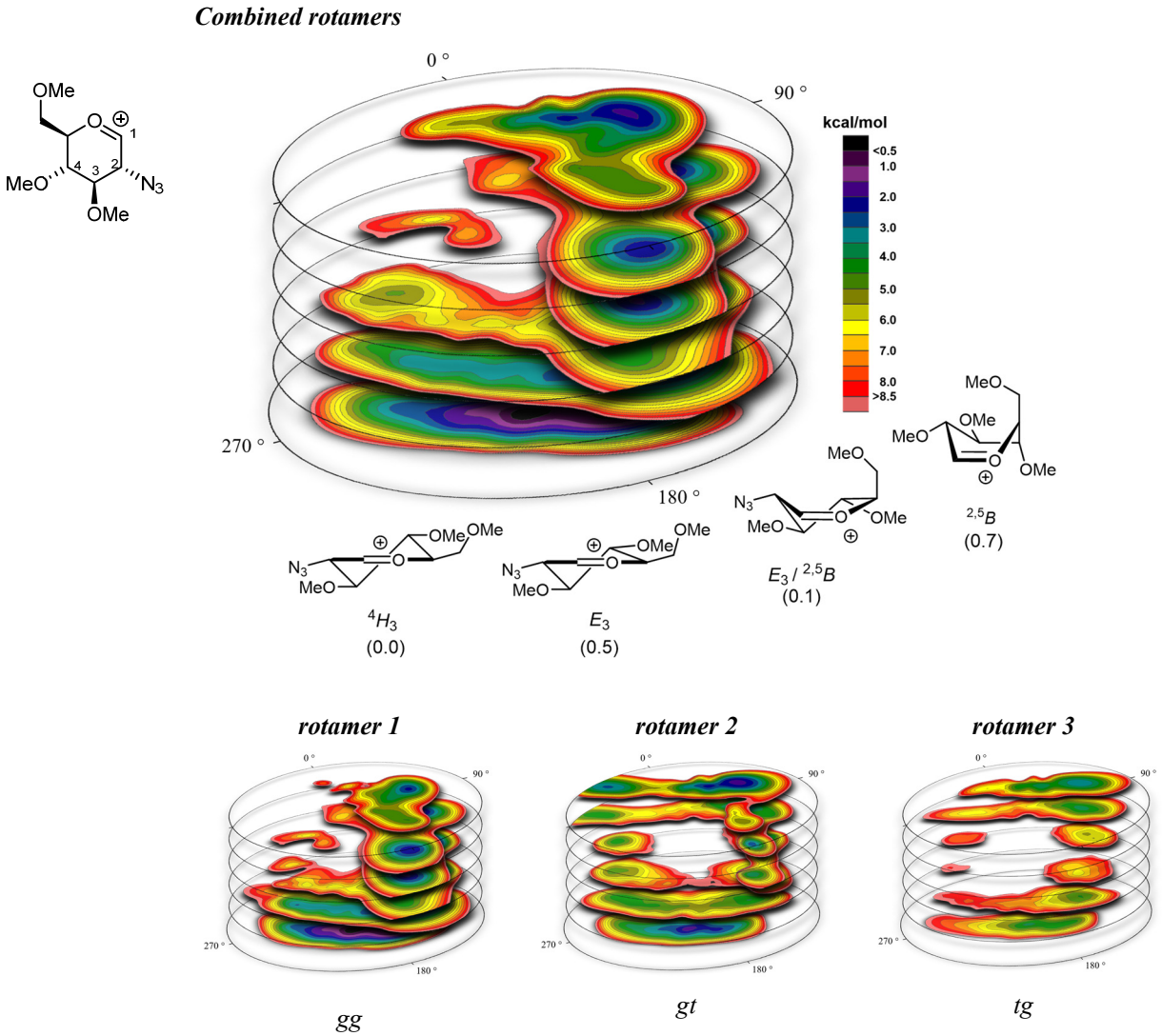


Figure 35| CEL map of 2-azido-2-deoxy-3,4,6-tri-*O*-methyl-gluco-D-pyranosyl oxocarbenium ion (**27**).

Local minima

$^{4}H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

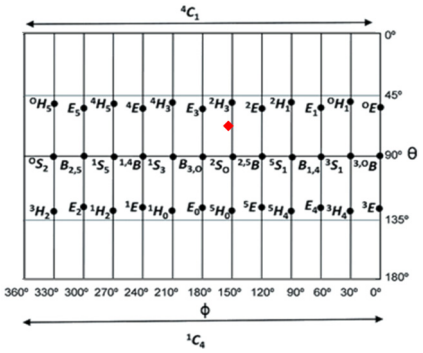
E_{gas}(B3LYP) = -768.481443857 a.u.
E_{solv}(B3LYP) = -768.548553062 a.u.
Zero-point energy correction = 0.290971 a.u.

Atom coordinates

O	0.651059	-1.733318	-0.884135
C	0.381414	0.653796	-0.134379
C	-1.432131	-1.030159	0.174952
C	-1.125651	0.405817	-0.277891
C	-0.457446	-2.011849	-0.379856
C	1.186015	-0.312838	-1.010689
H	0.670689	0.520400	0.914827
H	-1.283967	-1.073373	1.264691
H	-1.416294	0.507283	-1.333172
H	-0.714793	-3.079063	-0.396520
H	1.037510	-0.092859	-2.073329
O	-2.712345	-1.461548	-0.207424
O	-1.863072	1.283372	0.541608
O	0.723251	1.946078	-0.595082
C	2.657499	-0.417385	-0.687472
H	3.120546	0.544753	-0.950821
H	3.112939	-1.196492	-1.314613
C	-3.651022	-1.627657	0.868851
H	-3.353139	-2.451179	1.525961
H	-4.604775	-1.864321	0.400419
H	-3.737446	-0.701879	1.443473
C	-2.568548	2.314736	-0.159284

H	-3.311752	1.884412	-0.839026
H	-1.880678	2.951162	-0.722445
H	-3.076140	2.907558	0.600788
C	1.116259	2.866006	0.431871
H	1.350673	3.802817	-0.072072
H	2.004914	2.505961	0.960979
H	0.304595	3.025082	1.146878
O	2.792970	-0.712766	0.684297
C	4.151536	-0.854381	1.090749
H	4.713167	0.072687	0.921818
H	4.641078	-1.673984	0.550582
H	4.140441	-1.080042	2.156359

***E*$_3$–^{2,5}*B* conformation (0.1 kcal / mol)**



D1 = -60°
D3 = 0°
D5 = 0°

E_{gas}(B3LYP) = -817.548654667 a.u.
E_{solv}(B3LYP) = -817.614041779 a.u.
Zero-point energy correction = 0.261647 a.u.

Atom coordinates

O	-1.053045	-0.871979	1.775744
C	-0.707367	0.999658	0.037300
C	0.956834	-0.847524	0.476540
C	0.769968	0.690757	0.323637
C	0.110716	-1.287242	1.600834
C	-1.716889	0.133498	0.842128
H	-0.870008	0.804203	-1.027714
H	0.545438	-1.331351	-0.424746
H	1.065541	1.180580	1.258553
H	0.471933	-1.992970	2.348683
H	-2.263123	0.751698	1.550674
O	1.585926	1.091623	-0.740037
O	-0.888831	2.368523	0.329698
C	-2.650397	-0.714108	0.001645
H	-3.289907	-0.038385	-0.582825
H	-3.296768	-1.319567	0.649079
C	2.295626	2.325712	-0.544593
H	1.601618	3.158048	-0.414960
H	2.890186	2.474616	-1.443903
H	2.959199	2.255458	0.323015
C	-1.914238	3.022684	-0.425951
H	-1.758053	2.878892	-1.500013
H	-1.841490	4.081828	-0.186107
H	-2.913166	2.666769	-0.151748
O	-1.842554	-1.524599	-0.824201
C	-2.587429	-2.415377	-1.657570
H	-3.186769	-3.104117	-1.052507
H	-1.861772	-2.980057	-2.239806
H	-3.244056	-1.858528	-2.334255
N	2.328333	-1.246206	0.764774
N	3.092462	-1.297153	-0.207291
N	3.898960	-1.397214	-0.989608

***E*$_3$ conformation (0.5 kcal / mol)**

D1 = -60°
D3 = -30°
D5 = 0°

E_{gas}(B3LYP) = -817.547901163 a.u.
E_{solv}(B3LYP) = -817.613421185 a.u.
Zero-point energy correction = 0.261410 a.u.

Atom coordinates

O	0.995051	-1.364408	-1.397986
C	0.564843	0.825836	-0.152698
C	-1.029374	-1.070711	-0.131416
C	-0.892928	0.446485	-0.440214
C	-0.098273	-1.819424	-1.007982
C	1.536020	0.020167	-1.035401
H	0.780377	0.630626	0.901514
H	-0.683649	-1.243305	0.901855
H	-1.138243	0.628959	-1.491675
H	-0.347327	-2.814311	-1.377104
H	1.625617	0.487897	-2.014369
O	-1.768919	1.132159	0.413449
O	0.825767	2.173867	-0.480327
C	2.892264	-0.249238	-0.425840
H	3.385401	0.723329	-0.287721
H	3.499845	-0.844803	-1.118341
C	-2.625026	2.091158	-0.227796
H	-2.039156	2.877078	-0.710756
H	-3.238189	2.522819	0.560841
H	-3.269989	1.604130	-0.965000
C	0.900887	3.066764	0.641725
H	-0.045218	3.096627	1.186316
H	1.119008	4.050005	0.228776
H	1.706405	2.771296	1.321270
O	2.686766	-0.921912	0.794736
C	3.899689	-1.228180	1.481108
H	4.537771	-1.883355	0.877247
H	3.619760	-1.742093	2.399089
H	4.452383	-0.314810	1.728956
N	-2.369077	-1.606631	-0.351220
N	-3.168328	-1.455274	0.582388

N	-4.000126	-1.395934	1.341861

$^{2,5}B$ conformation (0.7 kcal / mol)

D1 = -45°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -817.547543994 a.u.
E_{solv}(B3LYP) = -817.613274348 a.u.
Zero-point energy correction = 0.261447 a.u.

Atom coordinates

O	1.018495	0.847445	1.839282
C	1.091215	-0.833848	-0.051307
C	-1.049309	0.400323	0.718091
C	-0.450869	-0.897859	0.117106
C	-0.231616	0.844970	1.859141
C	1.781815	0.380649	0.607255
H	1.294619	-0.756772	-1.126131
H	-0.928803	1.185959	-0.047230
H	-0.651011	-1.715397	0.819418
H	-0.684694	1.193195	2.786964
H	2.717748	0.068410	1.064243
O	-1.139839	-1.093418	-1.087558
O	1.593086	-2.047321	0.472400
C	2.043818	1.593945	-0.259765
H	2.801979	1.293156	-0.996949
H	2.469346	2.400271	0.351224
C	-1.218624	-2.458907	-1.517473
H	-0.232527	-2.855041	-1.775657
H	-1.852573	-2.461585	-2.401875
H	-1.669313	-3.082962	-0.739104
C	2.852267	-2.457003	-0.067986
H	2.796454	-2.545839	-1.158306
H	3.070150	-3.430412	0.367100
H	3.659060	-1.764234	0.196387
O	0.846806	2.000825	-0.884747
C	1.010146	3.146573	-1.725028
H	1.356377	4.008335	-1.144562
H	0.033253	3.363187	-2.152837
H	1.723056	2.938433	-2.529585
N	-2.425144	0.241835	1.177296
N	-3.296596	0.302840	0.300719
N	-4.196056	0.339325	-0.379205

2,3,4,6-Tetra-*O*-methyl-manno-D-pyranosyl oxocarbenium ion (**28**)

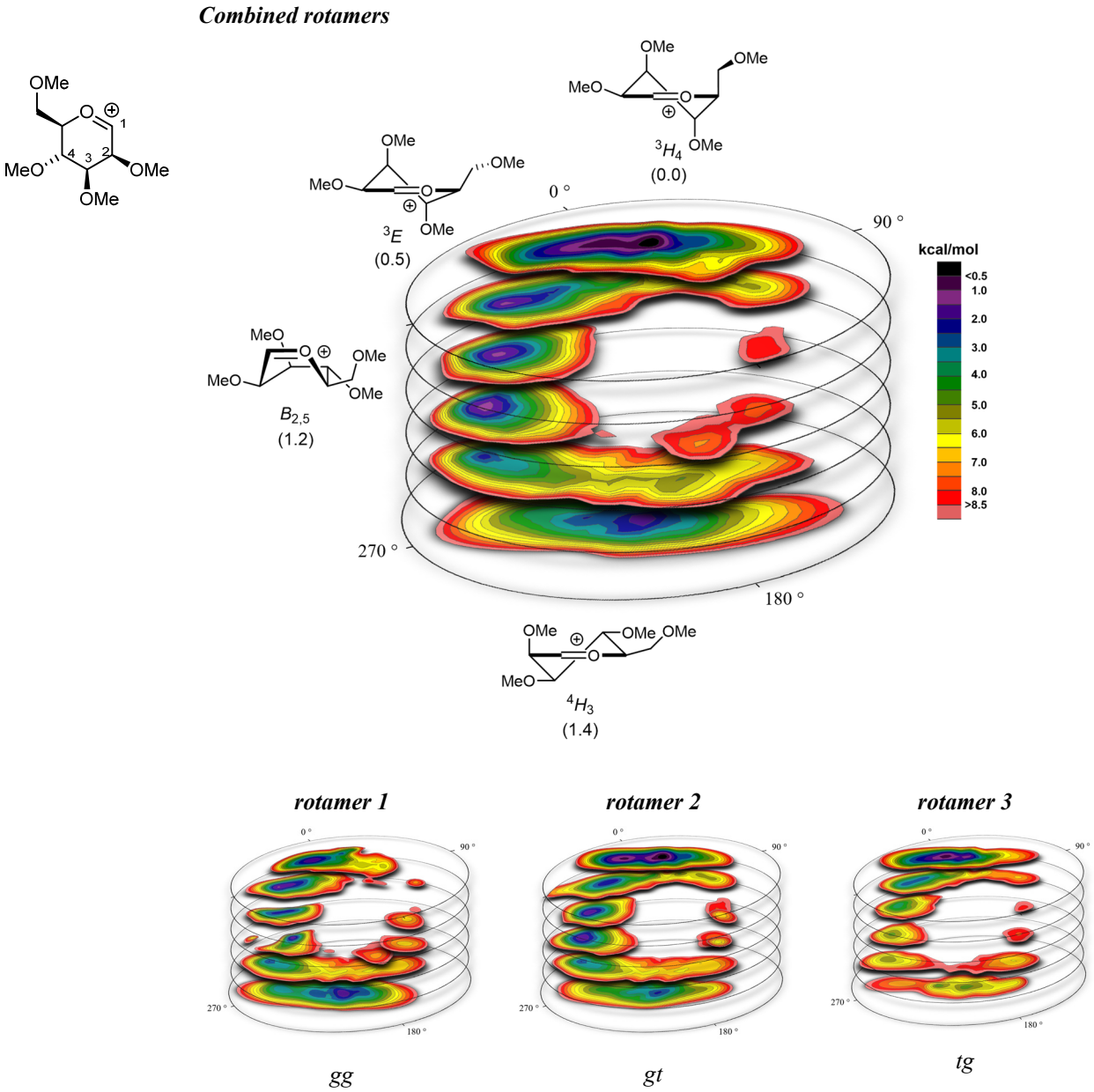


Figure 36| CEL map of 2,3,4,6-tera-*O*-methyl-manno-D-pyranosyl oxocarbenium ion **(28)**.

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -768.482709395 a.u.
E_{solv}(B3LYP) = -768.547141086 a.u.
Zero-point energy correction = 0.290949 a.u.

Atom coordinates

O	0.596455	-0.029300	-1.501483
C	0.178757	1.157486	0.665932
C	-1.660193	0.001576	-0.549232
C	-1.023165	0.213938	0.840498
C	-0.628419	-0.258707	-1.596244
C	1.244205	0.571358	-0.260386
H	0.635564	1.326134	1.651037
H	-1.757116	0.690950	1.500189
H	-0.922110	-0.738241	-2.539431
H	1.850437	1.360055	-0.712096
O	-0.539482	-0.996637	1.371425

O	-0.341955	2.355720	0.116462
C	2.173794	-0.495541	0.287488
H	1.632846	-1.429771	0.468810
H	2.554135	-0.130317	1.254163
C	-1.419399	-1.676887	2.275016
H	-0.861980	-2.532561	2.653999
H	-2.318752	-2.020503	1.760894
H	-1.691904	-1.022776	3.110646
C	0.393837	3.538413	0.442719
H	-0.140896	4.369586	-0.014341
H	1.413116	3.507042	0.041024
H	0.434411	3.679775	1.528255
O	3.219287	-0.662423	-0.645654
C	4.157801	-1.654856	-0.244263
H	4.914910	-1.708232	-1.025829
H	3.677390	-2.635745	-0.137753
H	4.637097	-1.386959	0.706156
H	-2.134565	0.953034	-0.847796
O	-2.550256	-1.085950	-0.562961
C	-3.834557	-0.828582	-1.151181
H	-4.413324	-1.741486	-1.023361
H	-3.745250	-0.602590	-2.219078
H	-4.332359	0.002138	-0.639887

^3E conformation (0.5 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -768.484150842 a.u.
E_{solv}(B3LYP) = -768.546476586 a.u.
Zero-point energy correction = 0.290902 a.u.

Atom coordinates

O	-0.051107	-0.062023	1.833002
C	-0.465729	0.723254	-0.545126
C	1.805523	0.243840	0.302398
C	0.796299	-0.107149	-0.819134
C	1.178705	-0.117464	1.601725
C	-1.082100	0.382336	0.820207
H	-1.216905	0.488020	-1.307808
H	1.223893	0.200725	-1.780767
H	1.776994	-0.513852	2.432727
H	-1.494734	1.275150	1.297292
O	0.447313	-1.469121	-0.795136
O	-0.069472	2.079889	-0.607198
C	-2.127337	-0.730804	0.827420
H	-2.420114	-0.943801	1.864775
H	-1.718629	-1.641020	0.374922
C	1.236165	-2.329505	-1.630267
H	1.215634	-1.977667	-2.667335
H	0.772116	-3.313135	-1.573083
H	2.267395	-2.382762	-1.277231
C	-1.101680	2.983459	-1.013961
H	-1.461572	2.730900	-2.017271
H	-0.654901	3.976408	-1.024757
H	-1.945948	2.976478	-0.315356
O	-3.207183	-0.214086	0.080159
C	-4.289826	-1.133243	-0.032550
H	-5.058937	-0.642089	-0.627448
H	-4.698414	-1.383750	0.954236
H	-3.974762	-2.055903	-0.535457
H	1.931710	1.341687	0.293997
O	3.009407	-0.460389	0.164667
C	4.199209	0.315171	0.366921
H	4.231656	1.160728	-0.328610
H	5.034998	-0.353872	0.170910
H	4.263475	0.684227	1.396520

$B_{2,5}$ conformation (1.2 kcal / mol)

D1 = 60°
D3 = -30°
D5 = 0°

E_{gas}(B3LYP) = -768.479805022 a.u.
E_{solv}(B3LYP) = -768.545066139 a.u.
Zero-point energy correction = 0.290500 a.u.

Atom coordinates

O	0.523701	-1.702829	-0.498390
C	0.470340	0.783181	-0.156152
C	-1.600089	-0.630276	-0.602733
C	-0.986986	0.509726	0.283185
C	-0.716331	-1.788964	-0.351569
C	1.107092	-0.382410	-0.940710
H	1.051839	0.965504	0.751453
H	-1.576814	1.421765	0.142928
H	-1.096678	-2.760445	-0.011172
H	0.832679	-0.298605	-1.998898
O	-0.963028	0.094863	1.631962
O	0.560858	1.862887	-1.065298
C	2.601537	-0.518976	-0.784005
H	3.059563	0.363333	-1.256990
H	2.944970	-1.410569	-1.327856
C	-2.114044	0.429749	2.419188
H	-1.858255	0.181163	3.448376
H	-2.989788	-0.143265	2.109065
H	-2.326278	1.502911	2.350405
C	0.692432	3.144894	-0.442676
H	-0.191820	3.398204	0.153209
H	0.795623	3.868078	-1.250228
H	1.581182	3.177280	0.196742
O	2.902669	-0.600424	0.588019
C	4.295924	-0.742493	0.846630
H	4.410452	-0.808749	1.927805
H	4.857494	0.123281	0.473729
H	4.692634	-1.654153	0.382893
H	-1.488205	-0.345553	-1.664006

O	-2.907771	-0.998933	-0.279826
C	-3.923852	-0.242952	-0.952668
H	-4.874181	-0.678628	-0.650278
H	-3.810970	-0.326946	-2.038942
H	-3.901028	0.812003	-0.660906

$^4H_3$ conformation (1.4 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -768.478915880 a.u.
E_{solv}(B3LYP) = -768.545232706 a.u.
Zero-point energy correction = 0.291077 a.u.

Atom coordinates

O	0.825245	-1.394974	-1.381401
C	0.105945	0.710095	-0.184982
C	-1.427505	-1.224709	-0.479343
C	-1.316311	0.297768	-0.569780
C	-0.266166	-1.934249	-1.097099
C	1.130849	0.078211	-1.136240
H	0.305429	0.376134	0.836242
H	-1.509887	0.597248	-1.611395
H	-0.302337	-3.016565	-1.268938
H	1.047384	0.515384	-2.137375
O	-2.261302	0.860738	0.313968
O	0.288059	2.106708	-0.313509
C	2.565414	0.108988	-0.665775
H	2.894762	1.158093	-0.697025
H	3.189166	-0.462303	-1.367795
C	-3.052678	1.913895	-0.245397
H	-3.712597	2.256511	0.550861
H	-3.658629	1.550387	-1.083380
H	-2.423757	2.742895	-0.582006
C	0.474940	2.797192	0.928806
H	-0.398832	2.680608	1.575849
H	0.607249	3.848760	0.676878
H	1.366762	2.433058	1.449563
O	2.628156	-0.425715	0.635867
C	3.954877	-0.473049	1.150956
H	3.889186	-0.890683	2.154851
H	4.395508	0.530447	1.203213
H	4.595793	-1.113468	0.532215
H	-2.362760	-1.588794	-0.940455
O	-1.260783	-1.690057	0.856158
C	-2.429385	-2.276109	1.457785
H	-2.137639	-2.541693	2.472369
H	-2.741145	-3.175044	0.917746
H	-3.238536	-1.542774	1.476322

Methyl (2,3,4-tri-*O*-benzyl-manno-D-pyranosyl uronate) oxocarbenium ion (**29**)

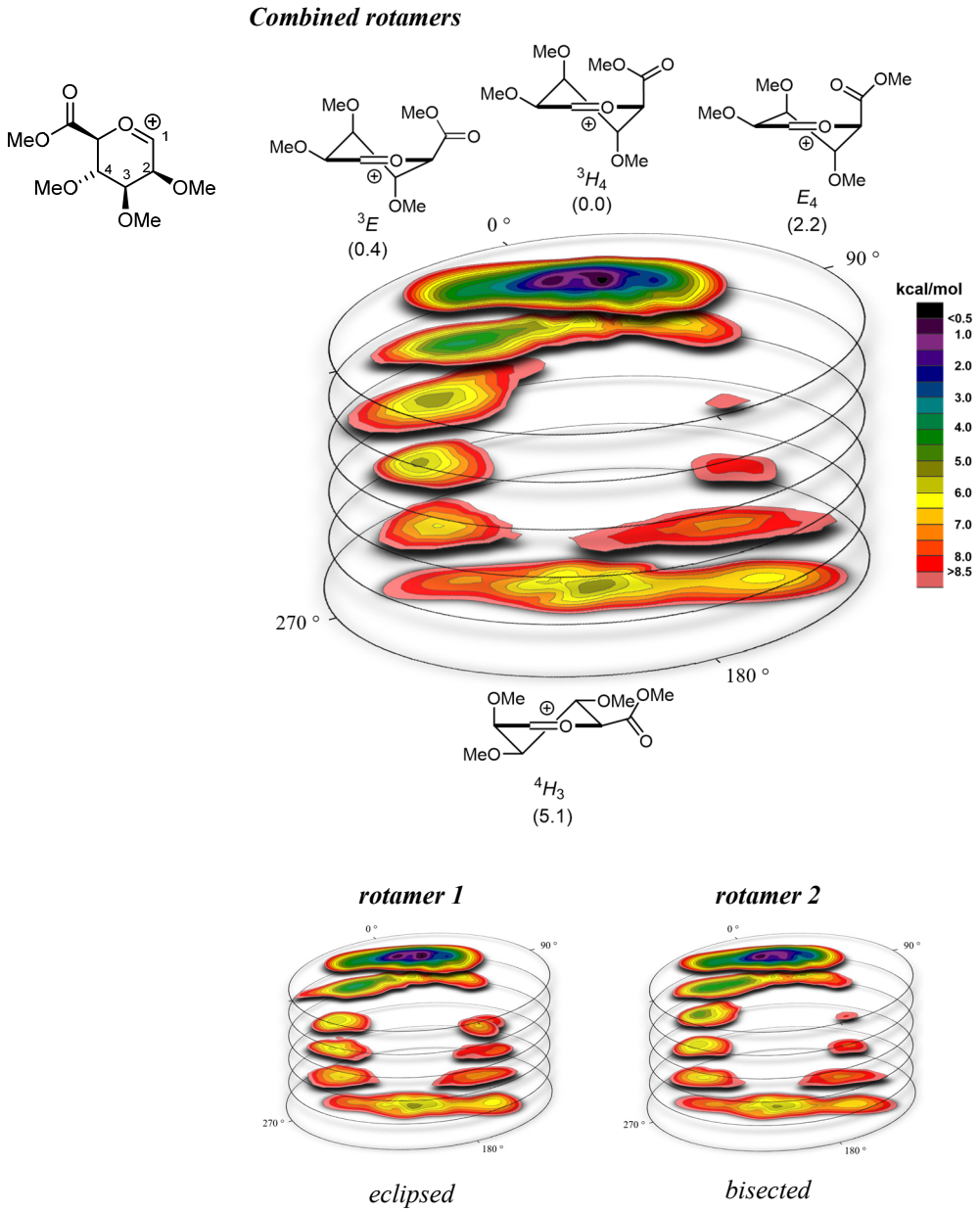


Figure 37| CEL map of methyl (2,3,4-tri-*O*-benzyl-manno-D-pyranosyl uronate) oxocarbenium ion (**29**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -842.537764049 a.u.
E_{solv}(B3LYP) = -842.601711538 a.u.
Zero-point energy correction = 0.272579 a.u.

Atom coordinates

O	0.300595	0.231586	-1.717711
C	0.062147	1.294336	0.539838
C	-1.739958	-0.137622	-0.415307
C	-0.921384	0.157743	0.857246
C	-0.871972	-0.199303	-1.623165
C	1.019931	0.893180	-0.588183
H	0.669243	1.508026	1.423829
H	-1.592511	0.471549	1.659725
H	-1.236207	-0.694880	-2.522805
H	1.446008	1.773911	-1.065950

O	-0.141930	-0.959432	1.215179
O	-0.722756	2.399949	0.144540
C	2.179429	-0.000724	-0.133243
C	-0.696661	-1.812246	2.226205
H	-0.896088	-1.243195	3.139818
H	0.057754	-2.569914	2.430196
H	-1.612898	-2.288919	1.873706
C	-0.140078	3.683543	0.398758
H	0.066010	3.806266	1.466291
H	-0.873555	4.421073	0.079429
H	0.783801	3.829849	-0.170481
O	2.270271	-1.127714	-0.814967
C	3.353679	-2.020994	-0.438730
H	3.271413	-2.865231	-1.116262
H	3.224606	-2.337468	0.595294
H	4.309740	-1.514227	-0.560628
H	-2.382648	0.742202	-0.591101
O	-2.461857	-1.335234	-0.344695
C	-3.876808	-1.216190	-0.578894
H	-4.290120	-2.210067	-0.423265
H	-4.083206	-0.892289	-1.602892
H	-4.325113	-0.513821	0.129765
O	2.912403	0.381696	0.741177

^3E conformation (0.4 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -842.537379074 a.u.
E_{solv}(B3LYP) = -842.601023271 a.u.
Zero-point energy correction = 0.272393 a.u.

Atom coordinates

O	0.279054	-0.199856	-1.606409
C	0.082300	1.203541	0.509645
C	-1.823664	-0.099752	-0.396155
C	-0.953146	0.128756	0.859893
C	-0.918161	-0.549504	-1.485919
C	0.972784	0.728762	-0.661081
H	0.736579	1.370532	1.368743
H	-1.590601	0.488480	1.670826
H	-1.248716	-1.272226	-2.231259
H	1.248004	1.565465	-1.302090
O	-0.236376	-1.032162	1.205211
O	-0.636980	2.364784	0.161464
C	2.262153	0.042960	-0.192176
C	-0.856878	-1.886194	2.179400
H	-1.055681	-1.330183	3.100914
H	-0.140569	-2.679879	2.382810
H	-1.784329	-2.311737	1.792831
C	0.070946	3.594181	0.360548
H	0.361098	3.705174	1.409862
H	-0.615416	4.391147	0.082479
H	0.963907	3.653654	-0.270738
O	2.461204	-1.141997	-0.737480
C	3.673068	-1.838570	-0.335634
H	3.653851	-2.775398	-0.883698
H	3.655285	-2.014643	0.738913
H	4.545913	-1.246036	-0.605575
H	-2.231916	0.882726	-0.689600
O	-2.808033	-1.071592	-0.185618
C	-4.099391	-0.757792	-0.732552
H	-4.755783	-1.576168	-0.445872
H	-4.062094	-0.687278	-1.823712
H	-4.474216	0.181842	-0.315326
O	2.982959	0.612847	0.585917

***E_4* conformation (2.2 kcal / mol)**

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -842.534310988 a.u.
E_{solv}(B3LYP) = -842.598235307 a.u.
Zero-point energy correction = 0.272706 a.u.

Atom coordinates

O	-0.026190	0.823298	-1.742965
C	0.293185	1.168117	0.675508
C	-1.787804	0.100725	-0.175068
C	-0.763218	0.098910	0.993226
C	-1.211831	0.496351	-1.499273
C	0.987764	0.848403	-0.655437
H	1.055214	1.169771	1.460500
H	-1.275881	0.363994	1.921194
H	-1.849360	0.462464	-2.381714
H	1.639347	1.666331	-0.957071
O	-0.085588	-1.124118	1.102193
O	-0.393147	2.395846	0.584613
C	1.773062	-0.466363	-0.757358
C	-0.650133	-2.066763	2.021945
H	-0.704551	-1.635820	3.027273
H	0.022815	-2.922247	2.030796
H	-1.642063	-2.385114	1.696442
C	0.399321	3.563173	0.837787
H	0.846365	3.511774	1.835150
H	-0.280569	4.410765	0.783914
H	1.187390	3.689241	0.088872
O	2.799216	-0.404983	0.079245
C	3.663473	-1.571938	0.125800
H	4.435187	-1.324517	0.848184
H	4.094337	-1.752646	-0.857863
H	3.090079	-2.439091	0.450574
H	-2.524458	0.894821	0.038083
O	-2.394367	-1.147961	-0.392381
C	-3.832058	-1.132208	-0.468805
H	-4.135370	-2.171929	-0.568047

H	-4.177540	-0.569389	-1.340002
H	-4.256366	-0.703029	0.443362
O	1.505684	-1.354060	-1.519403

$^4H_3$ conformation (5.1 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 15°

E_{gas}(B3LYP) = -842.528098534 a.u.
E_{solv}(B3LYP) = -842.593836183 a.u.
Zero-point energy correction = 0.272826 a.u.

Atom coordinates

O	0.734768	-1.505565	-0.807503
C	-0.148578	0.732155	-0.004126
C	-1.653290	-1.201430	-0.485052
C	-1.491928	0.313787	-0.606105
C	-0.433048	-1.969677	-0.868850
C	1.004640	-0.033180	-0.656695
H	-0.159278	0.533018	1.069945
H	-1.502227	0.577903	-1.670772
H	-0.478389	-3.041774	-1.045636
H	1.172526	0.307094	-1.677757
O	-2.536826	0.950533	0.092130
O	0.126911	2.087601	-0.280544
C	2.315325	0.040833	0.142276
C	-3.427317	1.721525	-0.723175
H	-2.889892	2.526061	-1.233930
H	-4.164615	2.150673	-0.046798
H	-3.939467	1.095345	-1.461169
C	0.101765	2.957690	0.861508
H	-0.887032	2.956414	1.326598
H	0.327873	3.953805	0.484460
H	0.860196	2.658904	1.589822
O	3.313654	-0.448553	-0.576937
C	4.618330	-0.484786	0.062607
H	5.280680	-0.935623	-0.669839
H	4.568868	-1.088609	0.967809
H	4.936831	0.528279	0.304575
H	-2.551023	-1.567347	-1.012521
O	-1.611159	-1.627147	0.877482
C	-2.713328	-2.450664	1.317299
H	-2.527539	-2.645123	2.370897
H	-2.746718	-3.394099	0.768443
H	-3.647462	-1.900965	1.189757
O	2.386558	0.484196	1.258871

Methyl (2-azido-2-deoxy-3,4-di-*O*-benzyl-manno-D-pyranosyl uronate) oxocarbenium ion (**30**)

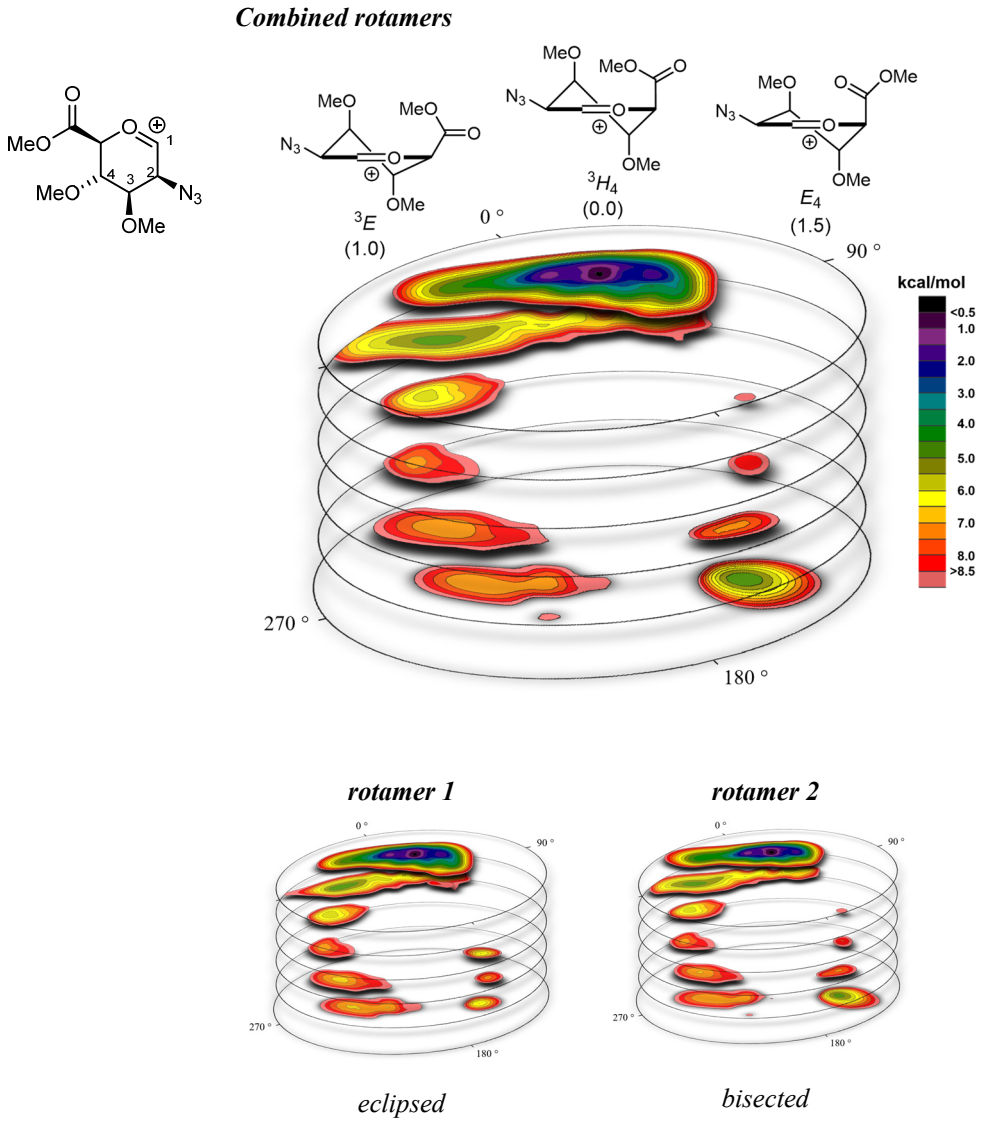


Figure 38| CEL map of methyl (2-azido-2-deoxy-3,4-di-*O*-benzyl-manno-D-pyranosyl uronate) oxocarbenium ion (**30**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -891.604002017 a.u.
E_{solv}(B3LYP) = -891.671480132 a.u.
Zero-point energy correction = 0.243664 a.u.

Atom coordinates

O	-0.433355	-0.109633	-1.784601
C	-0.893848	-1.189376	0.433919
C	1.390905	-1.177932	-0.564887
C	0.599362	-0.951544	0.731178
C	0.745551	-0.524029	-1.736410
C	-1.389752	-0.214973	-0.639756
H	-1.489433	-1.008450	1.333054
H	0.938779	-1.658978	1.491468
H	1.311885	-0.366827	-2.654605
H	-2.290854	-0.587337	-1.125015
O	0.824856	0.387238	1.111358
O	-0.998414	-2.521866	-0.015741
C	-1.680667	1.192729	-0.102852
C	0.727440	0.654247	2.520285
H	-0.304394	0.563487	2.869088
H	1.066360	1.678680	2.658592
H	1.374105	-0.026420	3.080384
C	-2.244920	-3.171087	0.268970
H	-2.427579	-3.192951	1.347378

H	-2.151715	-4.187332	-0.108014
H	-3.082153	-2.677250	-0.234606
O	-1.165354	2.149820	-0.850602
C	-1.424304	3.515912	-0.420527
H	-0.954282	4.141238	-1.172982
H	-0.977687	3.681587	0.558691
H	-2.497997	3.691614	-0.380754
H	1.303639	-2.249508	-0.804805
O	-2.358148	1.324327	0.883664
N	2.823821	-0.911972	-0.521511
N	3.195955	0.231384	-0.195528
N	3.729660	1.188543	0.067035

^{3}E conformation (1.0 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -891.601503203 a.u.
E_{solv}(B3LYP) = -891.669393790 a.u.
Zero-point energy correction = 0.243216 a.u.

Atom coordinates

O	0.381505	-0.113440	-1.701369
C	0.433512	1.303320	0.421339
C	-1.680295	0.661891	-0.700001
C	-0.926601	0.617735	0.639270
C	-0.867949	-0.065290	-1.712875
C	1.236671	0.554514	-0.665748
H	1.028003	1.267055	1.338045
H	-1.493963	1.177852	1.386546
H	-1.331280	-0.611839	-2.534573
H	1.825113	1.252422	-1.260272
O	-0.776652	-0.741463	0.978347
O	0.150657	2.626706	0.033104
C	2.184288	-0.509394	-0.095800
C	-0.743849	-1.026568	2.387133
H	0.119498	-0.560140	2.868591
H	-0.665904	-2.108011	2.473650
H	-1.665855	-0.684452	2.865242
C	1.157031	3.592089	0.366965
H	1.324182	3.613868	1.447898
H	0.775917	4.555386	0.035024
H	2.102326	3.383555	-0.144521
O	2.109074	-1.669200	-0.718714
C	3.003665	-2.715548	-0.245878
H	2.784476	-3.575377	-0.871033
H	2.796088	-2.930348	0.801242
H	4.037769	-2.397178	-0.367909
H	-1.694542	1.712432	-1.031076
O	2.915952	-0.221122	0.816136
N	-3.069409	0.220943	-0.692365
N	-3.322179	-0.888457	-0.189232
N	-3.746263	-1.850137	0.219696

E_4 conformation (1.5 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -891.602001498 a.u.
E_{solv}(B3LYP) = -891.669071612 a.u.
Zero-point energy correction = 0.243505 a.u.

Atom coordinates

O	-0.423797	-0.763957	-1.820348
C	-1.126755	-0.851123	0.541452
C	1.177531	-1.519684	-0.114411
C	0.345231	-0.837185	0.997562
C	0.623989	-1.368017	-1.496153
C	-1.267381	-0.098852	-0.789168
H	-1.751158	-0.337821	1.279411
H	0.449307	-1.415126	1.918586
H	1.167589	-1.803327	-2.334231
H	-2.269550	-0.210351	-1.198527
O	0.798827	0.483180	1.150472
O	-1.481755	-2.203909	0.387670
C	-0.894268	1.390502	-0.812885
C	0.781160	0.989599	2.494262
H	1.176331	2.001698	2.440023
H	1.419457	0.378810	3.138655
H	-0.234976	1.017562	2.897491
C	-2.878560	-2.501941	0.524518
H	-3.249437	-2.154590	1.493310
H	-2.964396	-3.584764	0.465770
H	-3.469030	-2.051870	-0.279091
O	-1.721066	2.041991	-0.008158
C	-1.551325	3.485150	0.060140
H	-2.303590	3.824964	0.765086
H	-1.715209	3.920415	-0.924544
H	-0.548842	3.720410	0.414097
H	1.067434	-2.605478	0.041895
O	-0.031912	1.856853	-1.505377
N	2.620512	-1.301423	-0.113824
N	3.035911	-0.129048	-0.203588
N	3.607286	0.838404	-0.280289

$^{4}H_3$ conformation (7.1 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -891.590367190 a.u.
E_{solv}(B3LYP) = -891.659829888 a.u.
Zero-point energy correction = 0.243244 a.u.

Atom coordinates

O	0.855813	-1.522796	-0.864411
C	-0.057794	0.728202	-0.168837
C	-1.573563	-1.230683	-0.829078
C	-1.383760	0.319087	-0.819096
C	-0.300183	-2.002699	-0.902980
C	1.123769	-0.048873	-0.733534
H	-0.105933	0.565344	0.912926
H	-1.360400	0.648888	-1.865388
H	-0.332996	-3.089695	-0.955061
H	1.357813	0.264422	-1.750265
O	-2.407103	0.958598	-0.110578
O	0.259148	2.067622	-0.466672
C	2.381534	0.033627	0.150075
C	-3.654190	1.059978	-0.811207
H	-4.306342	1.664971	-0.185012
H	-4.109796	0.075403	-0.957389
H	-3.514031	1.550744	-1.779357
C	0.044658	3.000146	0.606182
H	-1.007483	3.018608	0.896091
H	0.338614	3.973242	0.217021
H	0.670368	2.745070	1.466134
O	3.437303	-0.374743	-0.532316
C	4.704673	-0.399556	0.181450
H	5.428931	-0.761945	-0.541194
H	4.632678	-1.073407	1.034006
H	4.955745	0.605699	0.516460
H	-2.167670	-1.535140	-1.706487
O	2.360192	0.412752	1.291498
N	-2.276589	-1.839342	0.322164
N	-2.054252	-1.360141	1.449703
N	-1.988187	-1.048954	2.530918

2,3,4,6-Tetra-*O*-methyl-galacto-D-pyranosyl oxocarbenium ion (**31**)

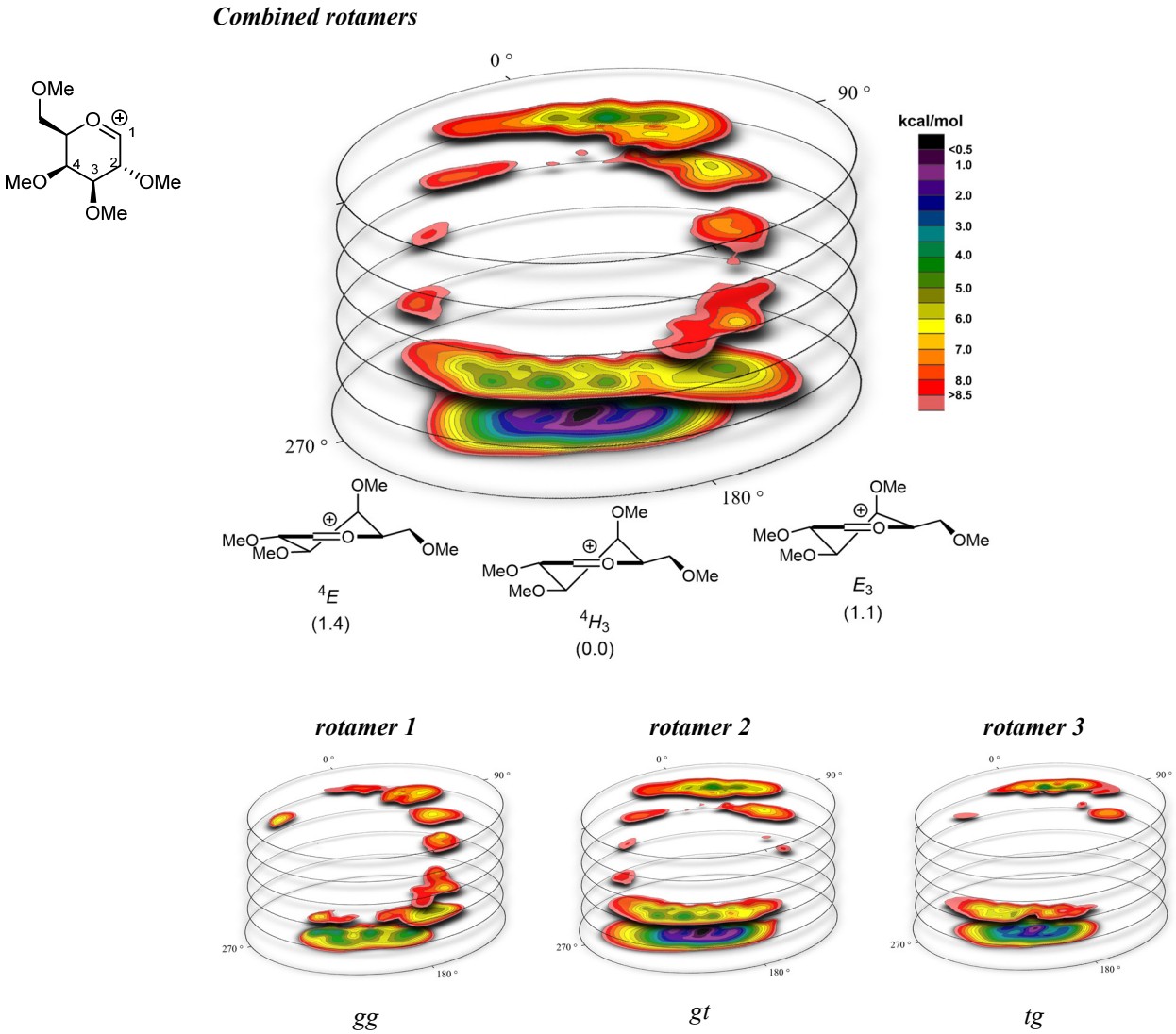


Figure 39| CEL map of 2,3,4,6-tera-*O*-benzyl-galacto-D-pyranosyl oxocarbenium ion (**31**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -768.481861353 a.u.
E_{solv}(B3LYP) = -768.549528278 a.u.
Zero-point energy correction = 0.290585 a.u.

Atom coordinates

O	0.998973	-1.493676	-0.053771
C	0.175536	0.876697	-0.271708
C	-1.367855	-1.015142	0.277397
C	-1.194586	0.235243	-0.592639
C	-0.141703	-1.855910	0.301383
C	1.307212	-0.092002	-0.579785
H	-1.475372	-0.678753	1.328608
H	-1.207414	-0.080434	-1.648656
H	-0.215298	-2.902506	0.625135
H	1.400268	-0.276677	-1.655120
O	-2.423357	-1.840120	-0.136000
O	-2.279325	1.085331	-0.306555
C	2.650040	0.265715	0.012560
H	2.625314	0.148870	1.103279
H	2.830818	1.329884	-0.207457
C	-3.615259	-1.757798	0.664992
H	-3.429973	-2.131397	1.677398
H	-4.349818	-2.392769	0.172664
H	-3.976489	-0.727899	0.703057
C	-2.702846	1.902172	-1.402548

H	-1.914287	2.592014	-1.723078
H	-3.555782	2.477577	-1.045858
H	-3.009263	1.281042	-2.251173
O	3.622236	-0.559873	-0.584981
C	4.923600	-0.353776	-0.044758
H	5.593232	-1.038087	-0.564372
H	4.944585	-0.571608	1.030514
H	5.261893	0.677487	-0.207377
H	0.338769	1.750832	-0.920858
O	0.268204	1.222923	1.099406
C	-0.143010	2.554823	1.438066
H	0.398865	3.288996	0.830902
H	0.117413	2.694903	2.486583
H	-1.218080	2.681716	1.303248

E_3 conformation (1.1 kcal / mol)

D1 = -60°
D3 = -30°
D5 = 0°

E_{gas}(B3LYP) = -768.480424531 a.u.
E_{solv}(B3LYP) = -768.547799841 a.u.
Zero-point energy correction = 0.290586 a.u.

Atom coordinates

O	1.004921	-1.480539	-0.445721
C	0.195679	0.943194	-0.409261
C	-1.242905	-0.963891	0.269588
C	-1.157843	0.259689	-0.680847
C	-0.113113	-1.868545	-0.036027
C	1.358550	-0.013874	-0.687634
H	-1.070388	-0.577993	1.294811
H	-1.189004	-0.090659	-1.723759
H	-0.228775	-2.958158	0.037664
H	1.584307	-0.047319	-1.757853
O	-2.442304	-1.673265	0.141020
O	-2.210716	1.142924	-0.406461
C	2.623735	0.250054	0.095573
H	2.471970	0.025893	1.159254
H	2.836620	1.326731	0.009249
C	-3.311261	-1.606845	1.283299
H	-2.854453	-2.093569	2.151210
H	-4.218027	-2.140728	1.004290
H	-3.552687	-0.567392	1.522266
C	-3.267416	1.149127	-1.374838
H	-2.897568	1.472486	-2.353908
H	-4.006272	1.863463	-1.014398
H	-3.724783	0.159979	-1.461797
O	3.653494	-0.529128	-0.466947
C	4.893936	-0.368946	0.213686
H	5.616631	-1.007954	-0.292472
H	4.812253	-0.675508	1.264161
H	5.238596	0.672175	0.170901
H	0.315932	1.788958	-1.101582
O	0.279729	1.368169	0.939493
C	-0.114701	2.725350	1.191182
H	0.474965	3.414285	0.575950
H	0.099153	2.910175	2.243243
H	-1.177433	2.867967	0.993350

^4E conformation (1.4 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -768.480247688 a.u.
E_{solv}(B3LYP) = -768.547528113 a.u.
Zero-point energy correction = 0.290718 a.u.

Atom coordinates

O	0.958070	-1.358036	0.392975
C	0.171334	0.907805	-0.202221
C	-1.452870	-0.922642	0.331100
C	-1.211338	0.310546	-0.544142
C	-0.208731	-1.659683	0.717895
C	1.239606	-0.136692	-0.480920
H	-1.889403	-0.584639	1.292846
H	-1.193229	-0.022298	-1.594341
H	-0.295652	-2.580384	1.308625
H	1.184182	-0.536791	-1.498869
O	-2.252676	-1.894155	-0.309602
O	-2.290225	1.187915	-0.314943
C	2.653529	0.268710	-0.141416
H	2.758711	0.389764	0.944334
H	2.837693	1.246743	-0.613777
C	-3.529569	-2.147845	0.300937
H	-3.412519	-2.599987	1.290874
H	-4.041583	-2.846793	-0.358201
H	-4.101586	-1.219168	0.379542
C	-2.601938	2.048325	-1.413552
H	-1.782317	2.740762	-1.636074
H	-3.479048	2.621155	-1.115934
H	-2.834805	1.463092	-2.310069
O	3.520932	-0.720153	-0.646715
C	4.884665	-0.474686	-0.318285
H	5.464545	-1.291562	-0.746400
H	5.032615	-0.455264	0.768799
H	5.230434	0.476231	-0.743370
H	0.382713	1.763918	-0.860675
O	0.277284	1.262378	1.164143
C	-0.108880	2.604391	1.490097
H	0.448820	3.323395	0.879335
H	0.149814	2.747793	2.538526
H	-1.181308	2.751070	1.351017

2-Deoxy-3,4,6-tri-*O*-methyl-galacto-D-pyranosyl oxocarbenium ion (**32**)

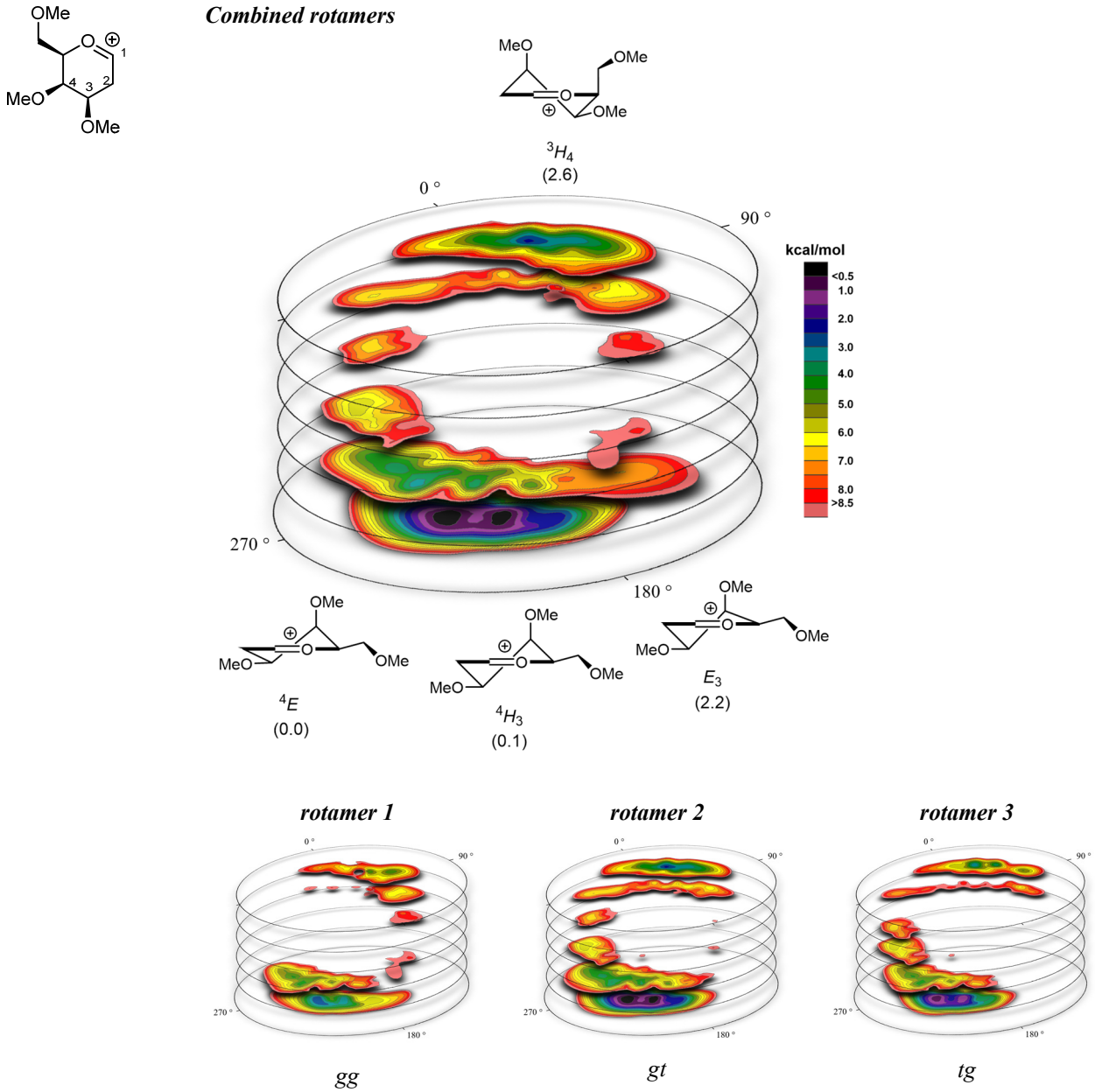


Figure 40| CEL map of 2-deoxy-3,4,6-tri-*O*-benzyl-galacto-D-pyranosyl oxocarbenium ion (**32**).

Local minima

^4E conformation (0.0 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -653.938644071 a.u.
E_{solv}(B3LYP) = -654.005633226 a.u.
Zero-point energy correction = 0.258487 a.u.

Atom coordinates

C	0.467399	-0.464320	-0.228275
C	1.429208	1.740408	0.445728
O	-0.969961	1.412716	0.474077
C	0.050776	2.036323	0.842838
C	-0.867241	0.222848	-0.474015
C	1.598745	0.550625	-0.504643
H	1.966708	1.553954	1.388003
H	-0.160484	2.854563	1.531040
H	-0.933702	0.676399	-1.462479
H	1.501425	0.894292	-1.542968
H	1.871094	2.668383	0.061497
C	-2.095868	-0.608884	-0.194310

H	-2.160119	-0.832848	0.876888
H	-1.978610	-1.560050	-0.734144
O	-3.216518	0.111261	-0.651355
C	-4.446832	-0.555332	-0.385603
H	-4.488254	-1.527662	-0.891645
H	-5.241003	0.083408	-0.769154
H	-4.590886	-0.706349	0.691082
O	2.891654	0.037697	-0.280851
C	3.464727	-0.638354	-1.403306
H	3.519002	0.029037	-2.270229
H	2.900907	-1.537346	-1.673291
H	4.471199	-0.927465	-1.106081
H	0.536955	-1.309435	-0.923392
O	0.459813	-0.897118	1.118145
C	1.255291	-2.054649	1.409177
H	2.318967	-1.842819	1.293784
H	0.968779	-2.889576	0.760885
H	1.040902	-2.314930	2.444522

$^4H_3$ conformation (0.1 kcal / mol)

D1 = -45°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -653.938549836 a.u.
E_{solv}(B3LYP) = -654.005666625 a.u.
Zero-point energy correction = 0.258548 a.u.

Atom coordinates

C	0.483814	-0.442560	-0.289161
C	1.401901	1.666708	0.675956
O	-0.968363	1.544279	0.248566
C	0.017077	2.131197	0.749103
C	-0.860645	0.233050	-0.525125
C	1.623946	0.595501	-0.387256
H	1.614985	1.246969	1.674286
H	-0.243823	3.041148	1.289321
H	-0.966348	0.572661	-1.555340
H	1.587928	1.061513	-1.382295
H	2.066432	2.528282	0.572019
C	-2.075608	-0.568180	-0.118819
H	-2.123061	-0.655616	0.972667
H	-1.951349	-1.580162	-0.531567
O	-3.211176	0.074262	-0.648358
C	-4.429874	-0.559941	-0.273339
H	-4.469670	-1.592785	-0.640628
H	-5.236347	0.014007	-0.727289
H	-4.555839	-0.562876	0.816140
O	2.897555	0.044253	-0.151902
C	3.521038	-0.526464	-1.305671
H	3.619239	0.219200	-2.101946
H	2.966752	-1.391258	-1.685109
H	4.510879	-0.851279	-0.990100
H	0.593131	-1.205278	-1.069173
O	0.441775	-1.027650	0.999855
C	1.188092	-2.241081	1.160871
H	2.261322	-2.055659	1.098865
H	0.892013	-2.977364	0.405852
H	0.936982	-2.622041	2.149653

***E*$_3$ conformation (2.2 kcal / mol)**

D1 = -60°
D3 = -30°
D5 = 0°

E_{gas}(B3LYP) = -653.935432424 a.u.
E_{solv}(B3LYP) = -654.002451004 a.u.
Zero-point energy correction = 0.258607 a.u.

Atom coordinates

C	-0.506770	-0.442225	0.358701
C	-1.269850	1.544921	-0.909317
O	0.955497	1.623906	-0.028755
C	0.028688	2.173745	-0.669270
C	0.854150	0.227276	0.585611
C	-1.618538	0.626552	0.266880
H	-1.174325	0.927815	-1.817812
H	0.282189	3.165300	-1.043056
H	0.997513	0.471244	1.637582
H	-1.640453	1.211238	1.197079
H	-2.029003	2.303002	-1.100248
C	2.053579	-0.538564	0.074396
H	2.058742	-0.554512	-1.021702
H	1.943938	-1.576621	0.420476
O	3.210140	0.067413	0.600371
C	4.410157	-0.549951	0.145107
H	4.451866	-1.604976	0.442611
H	5.236303	-0.012959	0.608694
H	4.501169	-0.482585	-0.945811
O	-2.886244	0.081601	0.003544
C	-3.617432	-0.315657	1.167649
H	-3.734138	0.526272	1.858297
H	-3.134217	-1.148818	1.688578
H	-4.597533	-0.635859	0.818934
H	-0.674998	-1.103570	1.215940
O	-0.435586	-1.183257	-0.845121
C	-1.190151	-2.401895	-0.872452
H	-2.262559	-2.202143	-0.878910
H	-0.932031	-3.031616	-0.014203
H	-0.905915	-2.913727	-1.790593

$^3H_4$ conformation (2.6 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -653.934541622 a.u.
E_{solv}(B3LYP) = -654.002140692 a.u.
Zero-point energy correction = 0.258992 a.u.

Atom coordinates

C	-0.864361	-0.242084	0.841270
C	-1.443998	2.061056	0.127774
O	0.825050	1.617304	0.846774
C	-0.075760	2.421874	0.518669
C	0.632614	0.109220	0.890731
C	-1.598489	0.581431	-0.232465
H	-1.739801	2.711056	-0.701981
H	0.238580	3.464803	0.556595
H	1.055810	-0.126836	1.865069
H	-2.662747	0.324476	-0.227286
H	-2.086540	2.362002	0.969442
C	1.536759	-0.464344	-0.183617
H	1.346165	0.015204	-1.149356
H	1.291832	-1.529435	-0.271039
O	2.868511	-0.268766	0.245318
C	3.819473	-0.787770	-0.677351
H	3.694690	-1.869711	-0.810300
H	4.806175	-0.588548	-0.261407
H	3.733665	-0.297394	-1.655038
O	-1.049690	0.416144	-1.525291
C	-1.632194	-0.633351	-2.310574
H	-2.713625	-0.485823	-2.402858
H	-1.429666	-1.614459	-1.877880
H	-1.176202	-0.563306	-3.296882
H	-1.300567	0.013825	1.816156
O	-0.925630	-1.635231	0.633974
C	-2.025570	-2.286143	1.279266
H	-2.986666	-1.940633	0.886215
H	-1.991686	-2.121458	2.361201
H	-1.916204	-3.348710	1.070934

Solvent effect on multi-substituted pyranosyl oxocarbenium ions

2,3,4-Tri-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**19**) in Et_2O

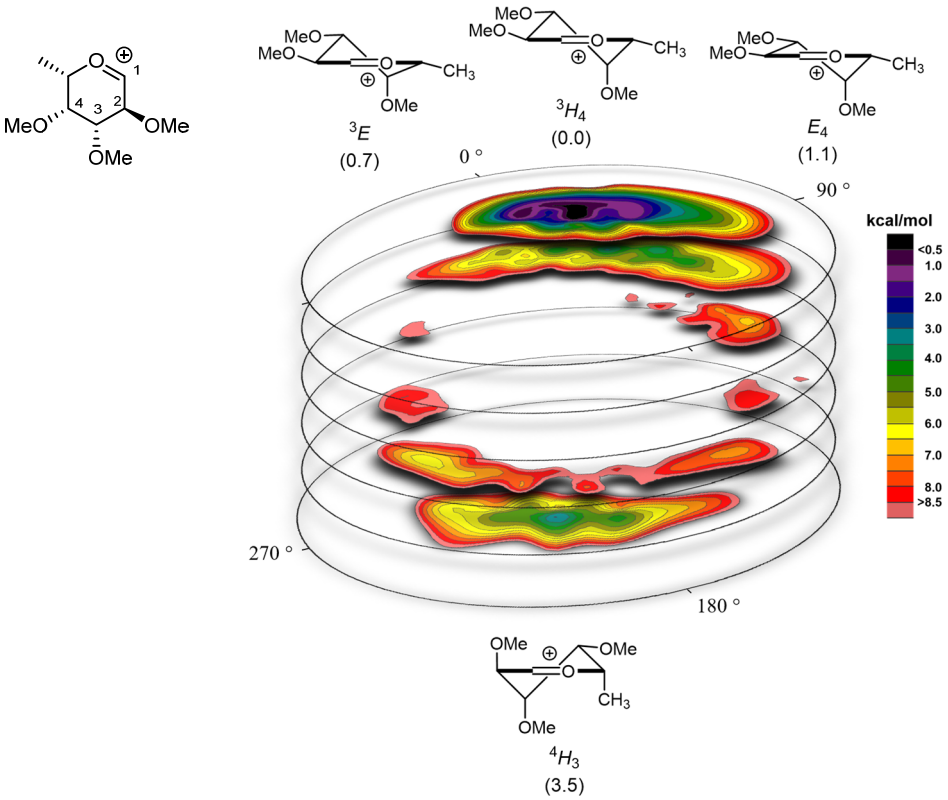


Figure 41| CEL map of 2,3,4-tri-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**19**) in Et_2O.

2,3,4-Tri-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**19**) in MeCN

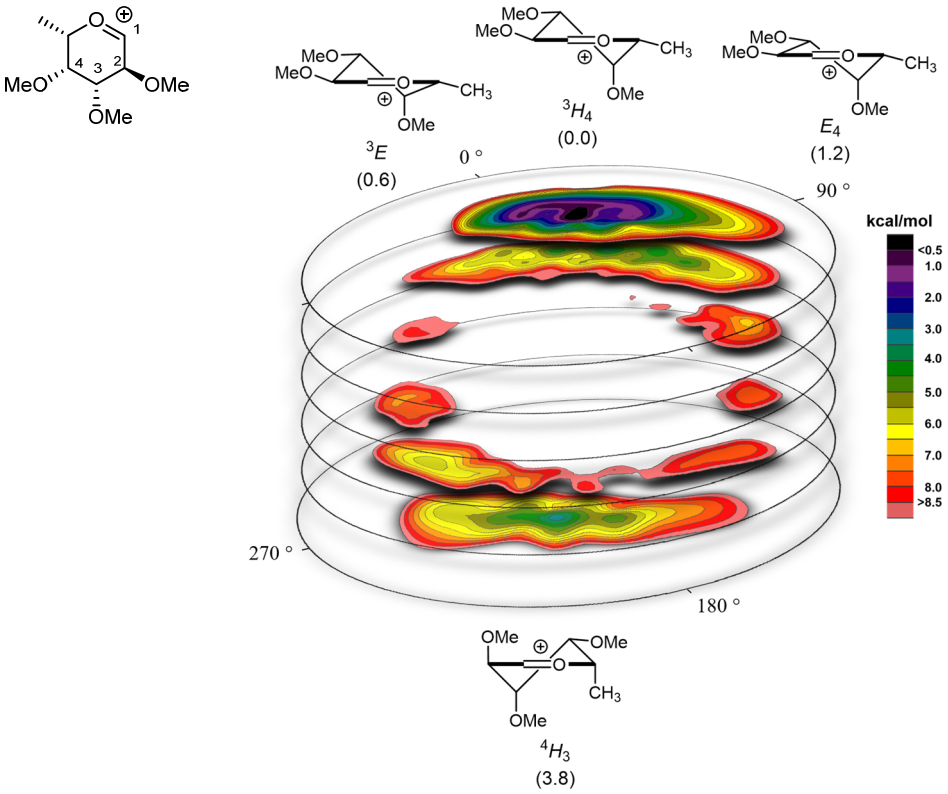


Figure 42| CEL map of 2,3,4-tri-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**19**) in MeCN.

2,3,4-Tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**22**) in Et_2O

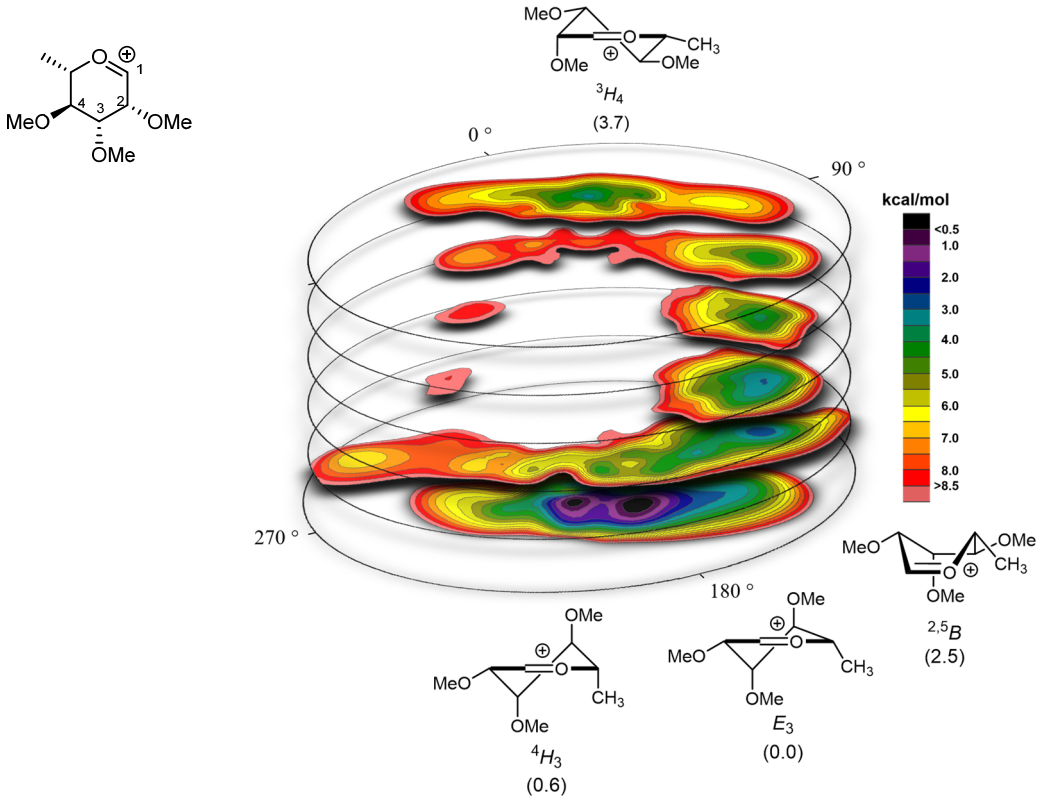


Figure 43| CEL map of 2,3,4-tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**22**) in Et_2O.

2,3,4-Tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**22**) in MeCN

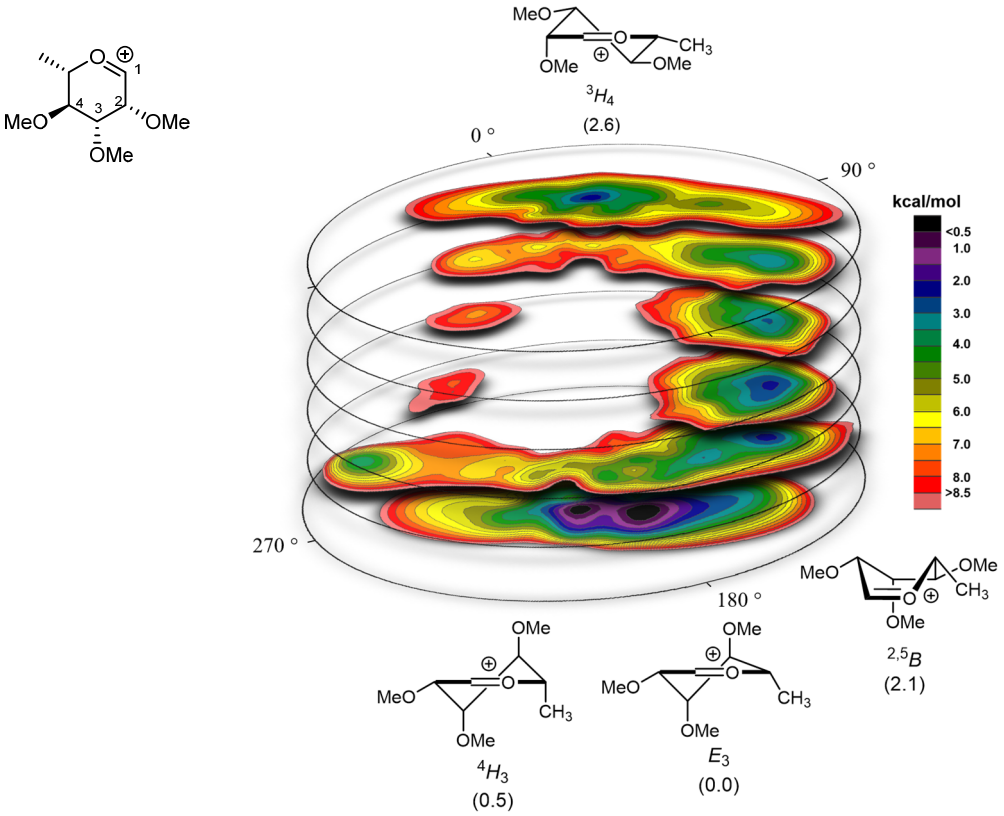


Figure 44| CEL map of 2,3,4-tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**22**) in MeCN.

Additional information

Top views per slice

4-Benzyloxy-pyranosyl oxocarbenium ion (**1**)

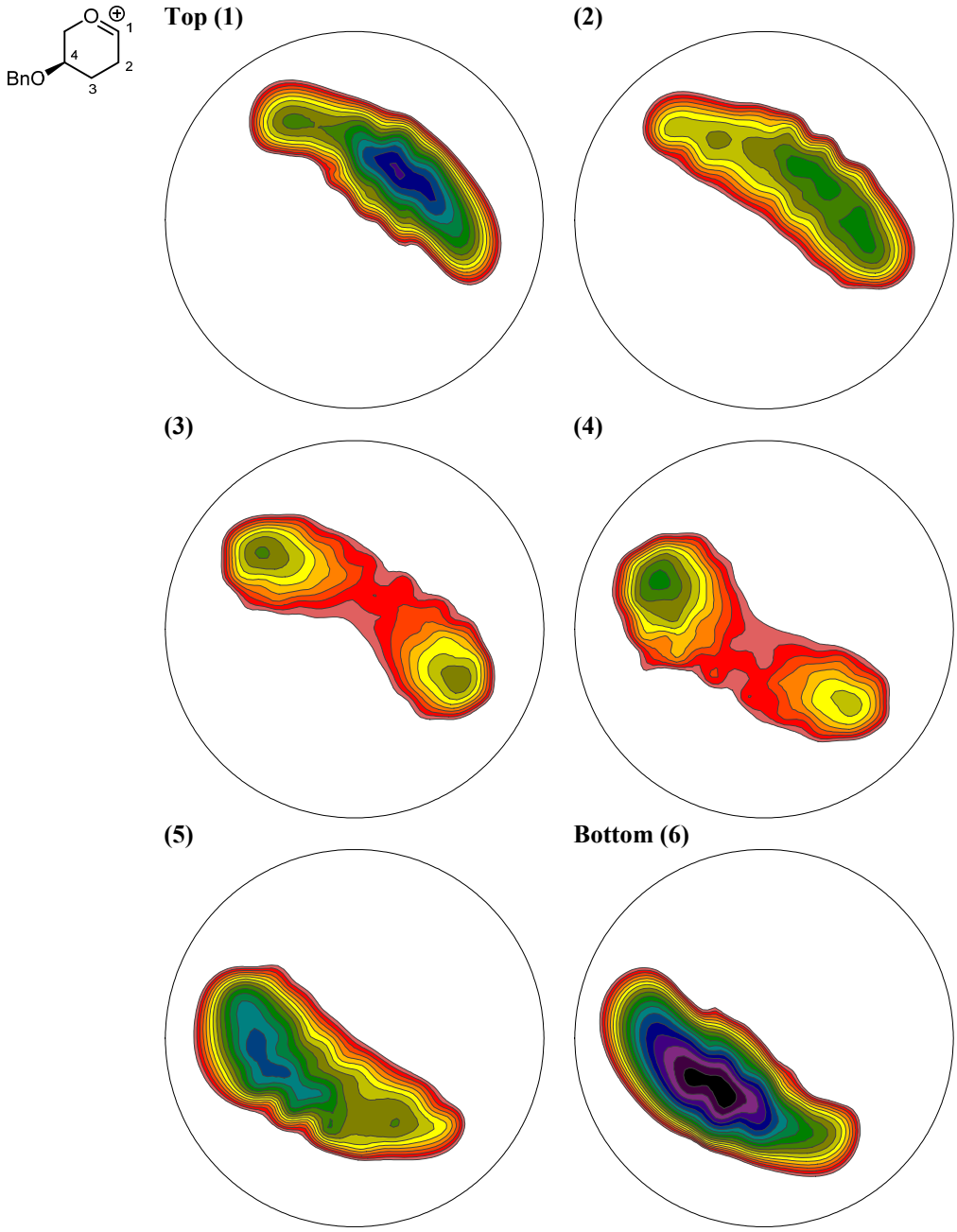


Figure 45| Top views of the CEL map of 4-benzyloxy-pyranosyl oxocarbenium ion (**1**).

3-Benzyloxy-pyranosyl oxocarbenium ion (**11**)

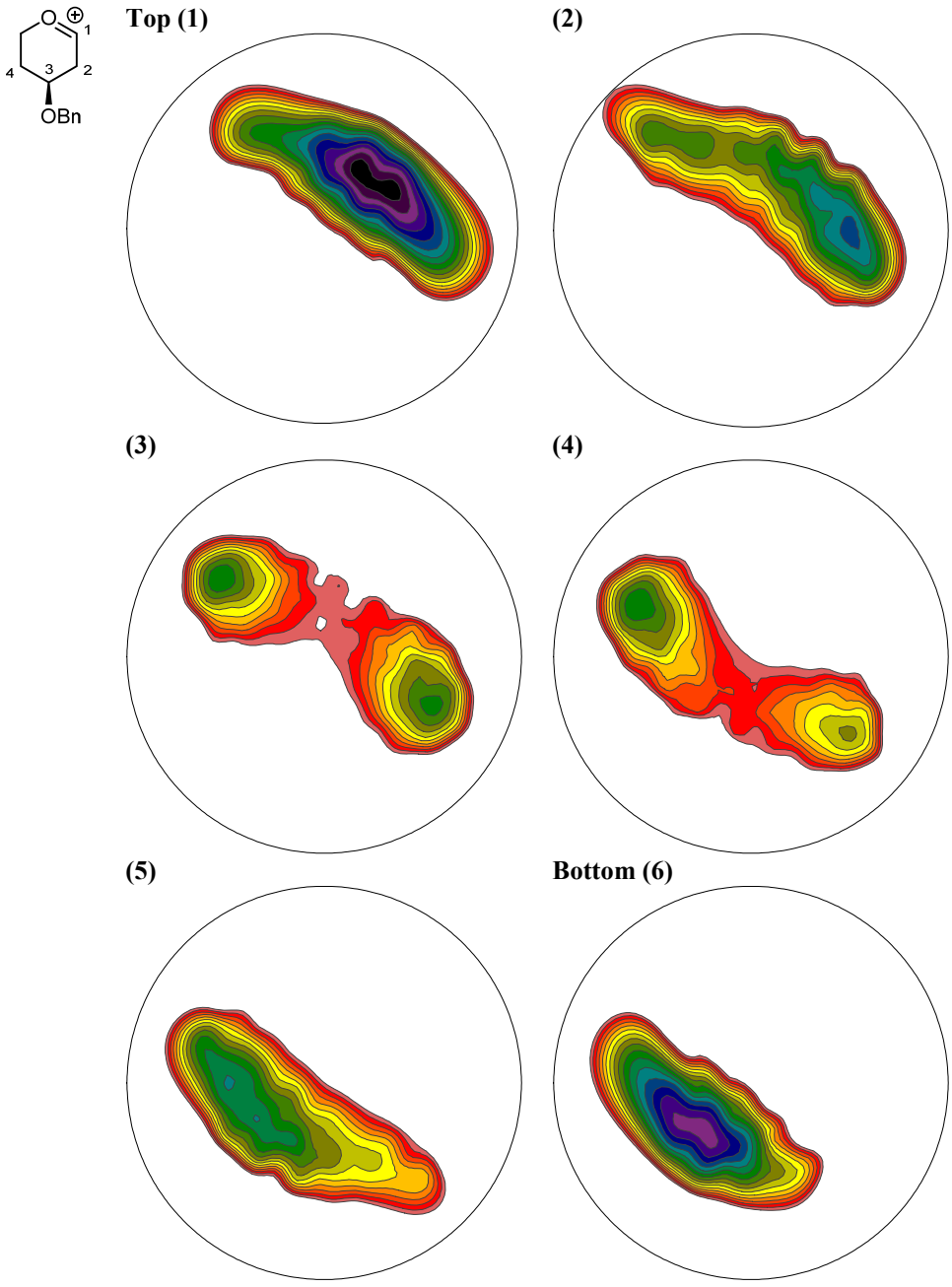


Figure 46| Top views of the CEL map of 3-benzyloxy-pyranosyl oxocarbenium ion (**11**).

3-Benzyloxy-pyranosyl oxocarbenium ion (**13**)

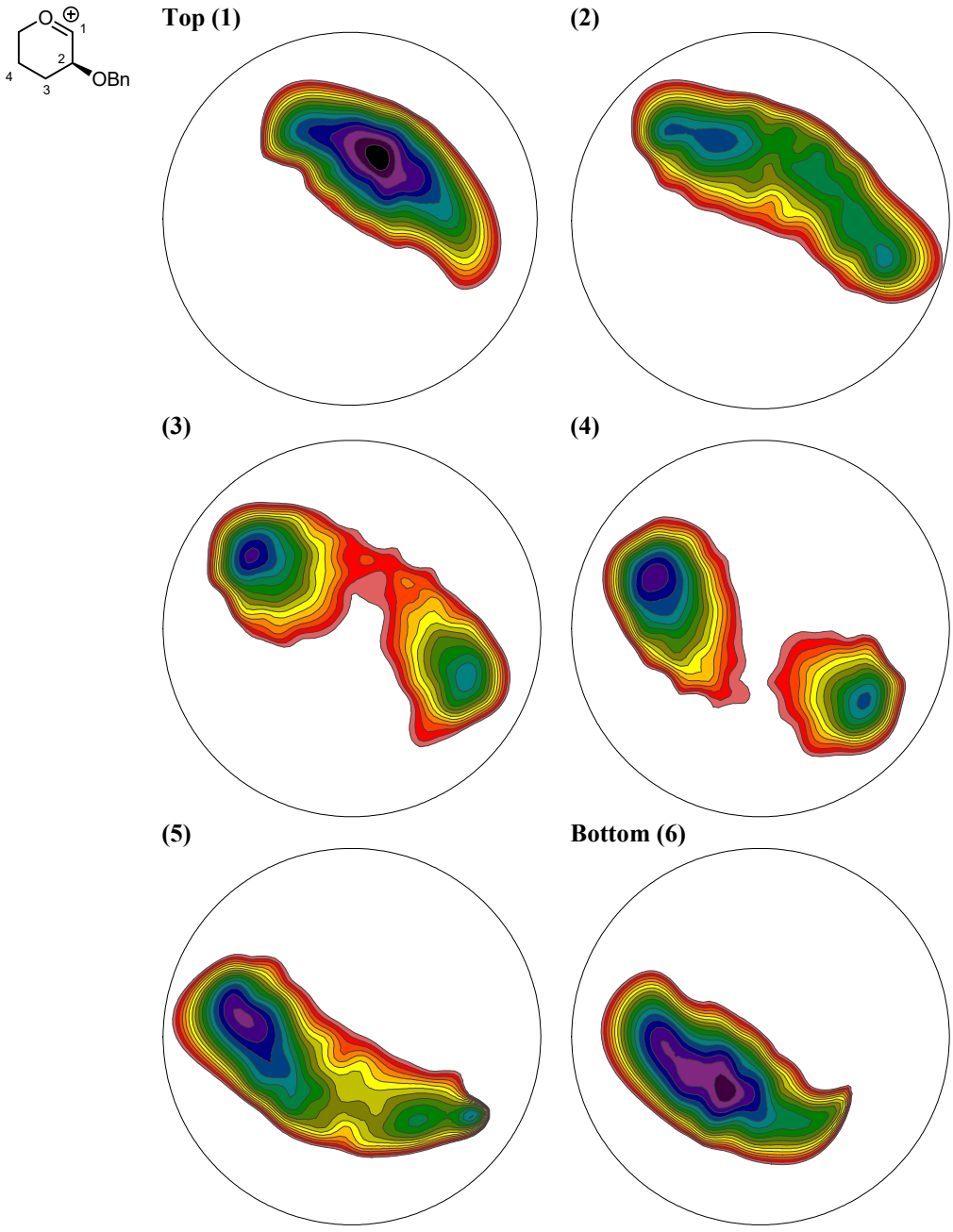


Figure 47| Top views of the CEL map of 2-benzyloxy-pyranosyl oxocarbenium ion (**13**).

2,3,4-Tri-*O*-methyl-lyxo-D-pyranosyl oxocarbenium ion (**14**)

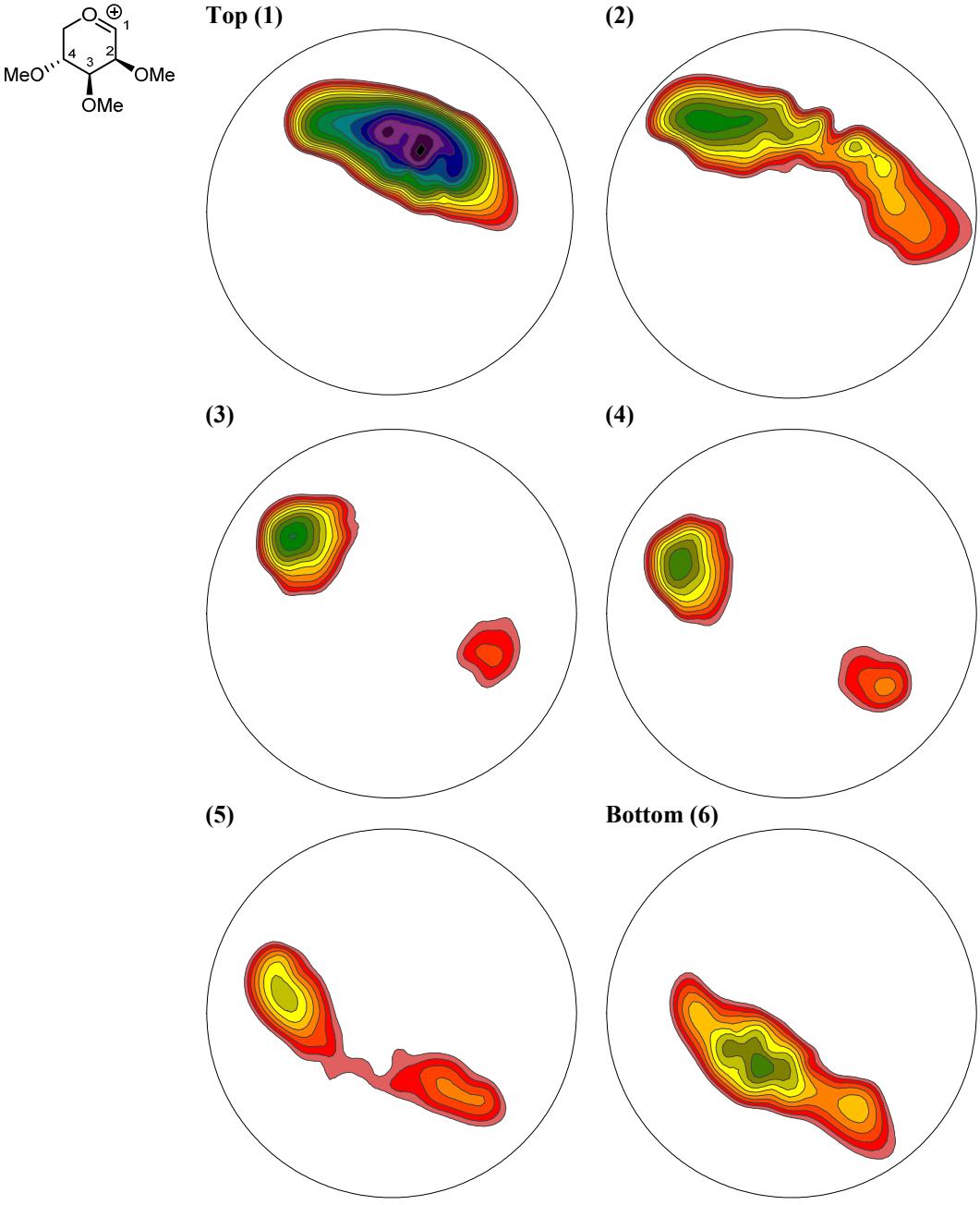


Figure 48| Top views of the CEL map of 2,3,4-tri-*O*-methyl-lyxo-D-pyranosyl oxocarbenium ion (**14**).

2,3,4-Tri-*O*-methyl-xylo-D-pyranosyl oxocarbenium ion (**16**)

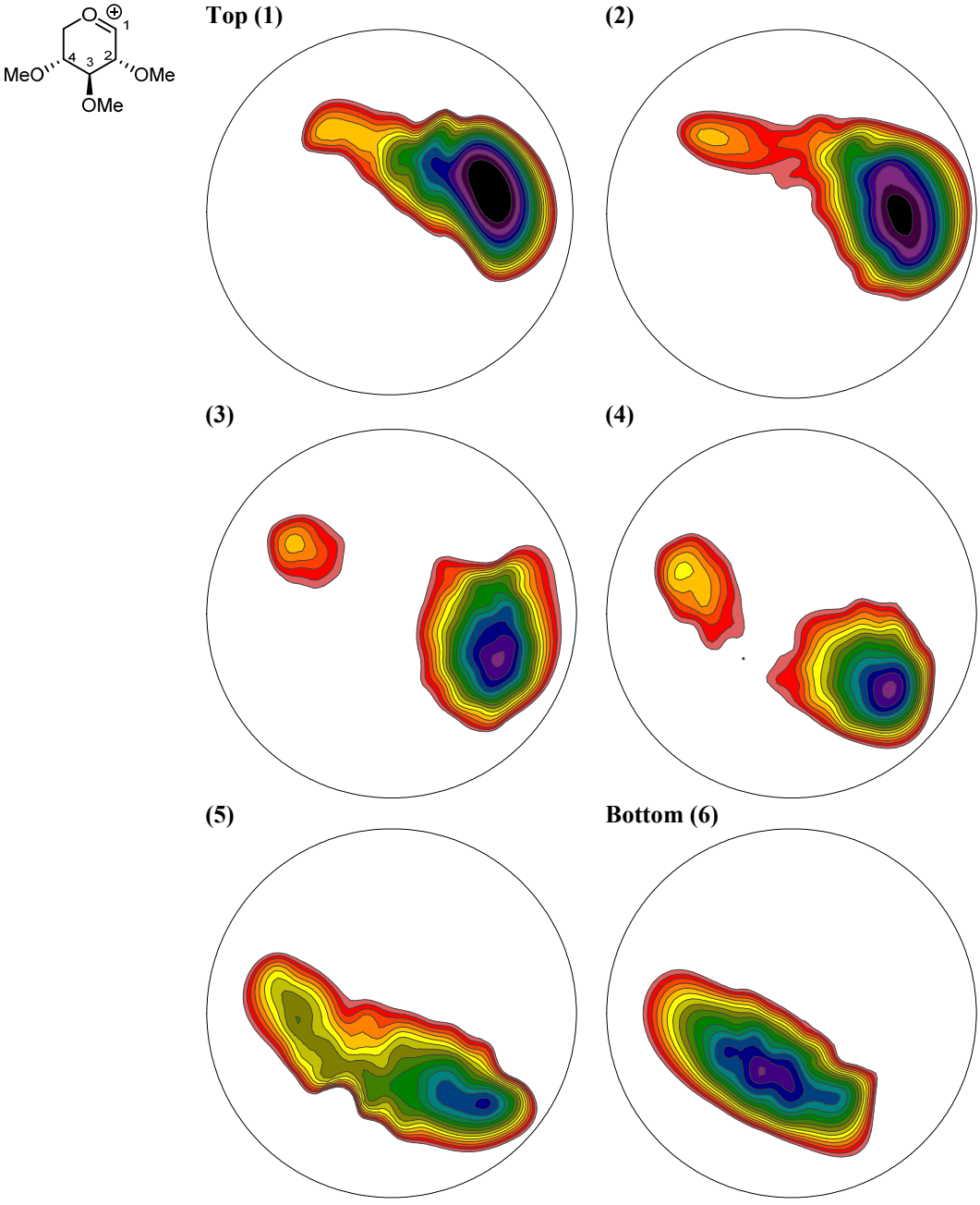


Figure 49| Top views of the CEL map of 2,3,4-tri-*O*-methyl-xylo-D-pyranosyl oxocarbenium ion (**16**).

2,3,4-Tri-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**20**)

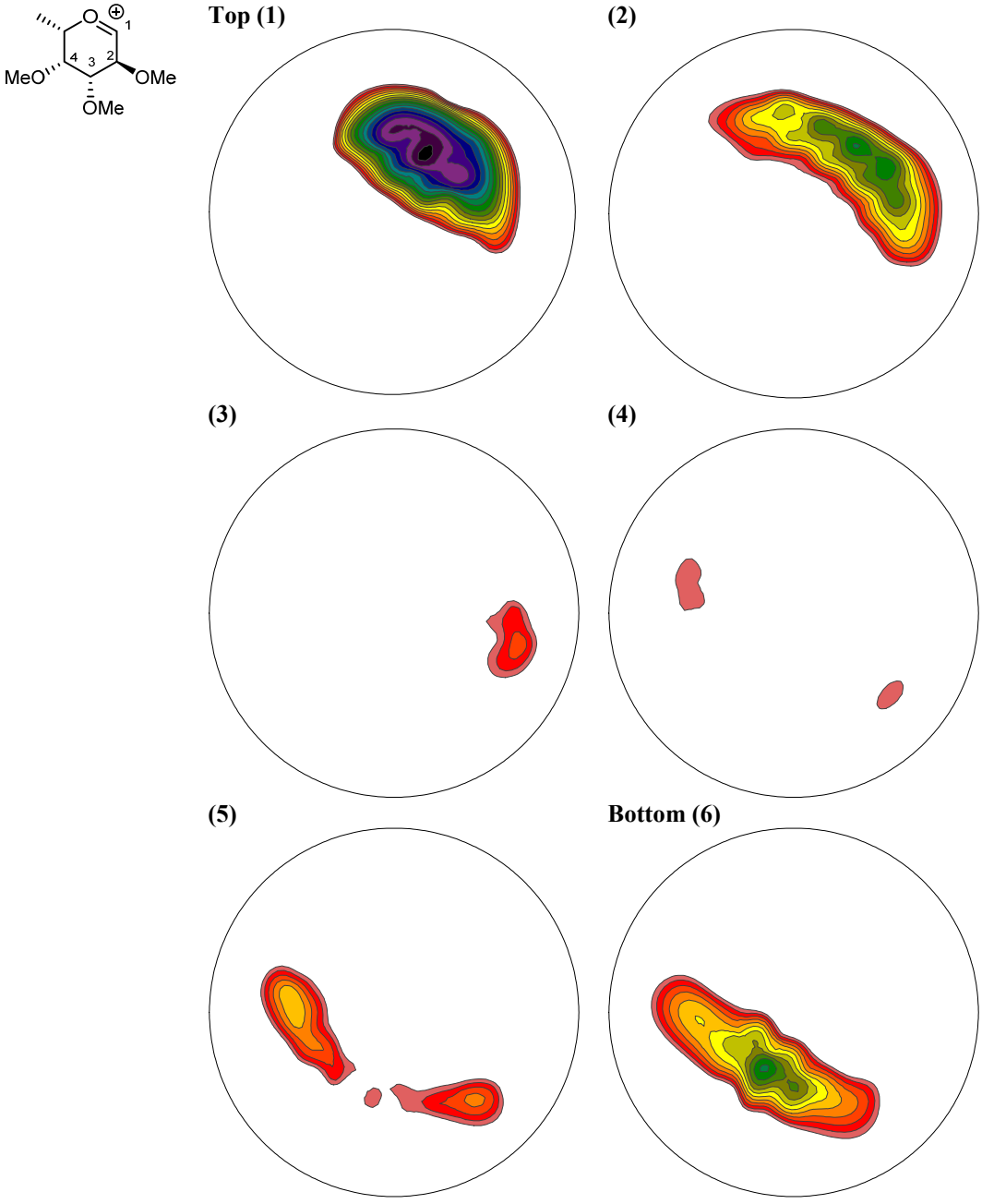


Figure 50| Top views of the CEL map of 2,3,4-tri-*O*-methyl-fuco-L-pyranosyl oxocarbenium ion (**20**).

2,3,4-Tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**22**)

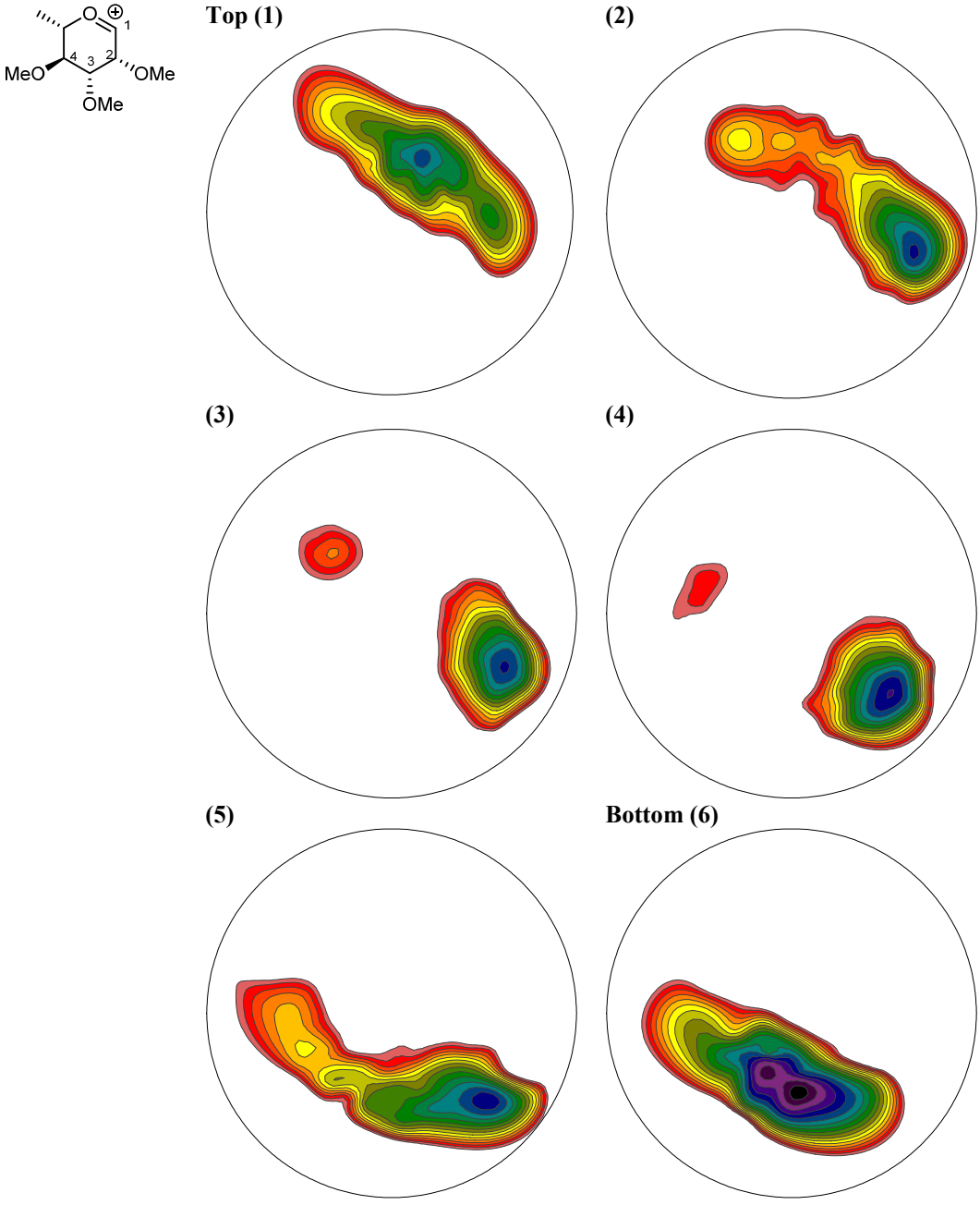


Figure 51| Top views of the CEL map of 2,3,4-tri-*O*-methyl-rhamno-L-pyranosyl oxocarbenium ion (**22**).

2,3,4,6-Tetra-*O*-methyl-gluco-D-pyranosyl oxocarbenium ion (*overall*) (**24**)

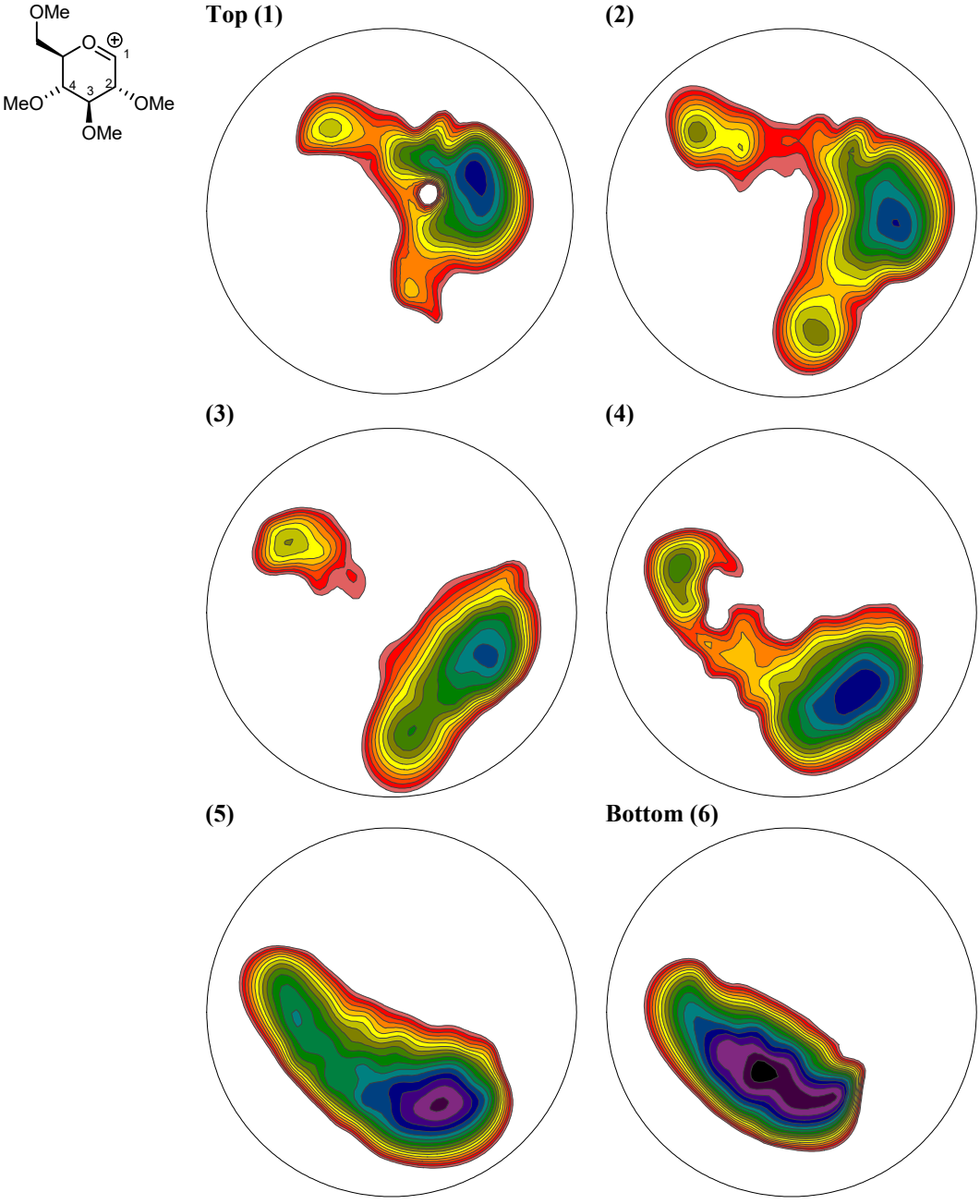


Figure 52| Top views of the CEL map of 2,3,4-tri-*O*-methyl-gluco-D-pyranosyl oxocarbenium ion (**24**).

2,3,4,6-Tetra-*O*-methyl-manno-D-pyranosyl oxocarbenium ion (*overall*) (**28**)

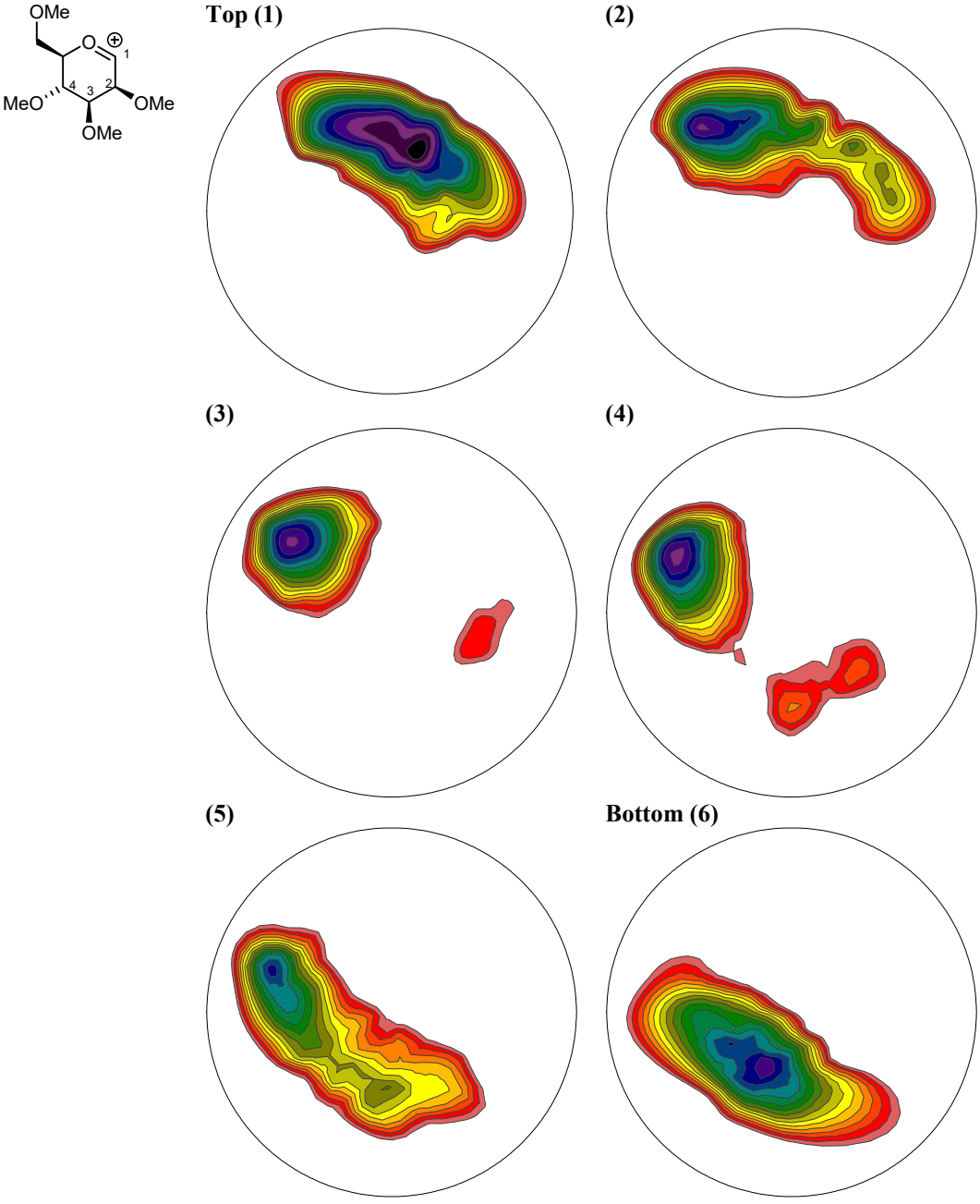


Figure 53| Top views of the CEL map of 2,3,4-tri-*O*-methyl-manno-D-pyranosyl oxocarbenium ion (**28**).

CEL maps

All CEL maps that are described in the superacid section of the article are summarised in the following section. The displayed CEL maps are based on the ΔG^{T}_{gas} and relevant structures are added with their corresponding energy. Also additional information is given of the found local minima including detailed energy output from Gaussian 03 or Gaussian 09, ring dihedral angles and the geometrical output (coordinates in cartesian style).

Protonated mono-substituted pyranosyl oxocarbenium ions

Protonated 4-*O*-acetyl-pyranosyl oxocarbenium ion (**S4**)

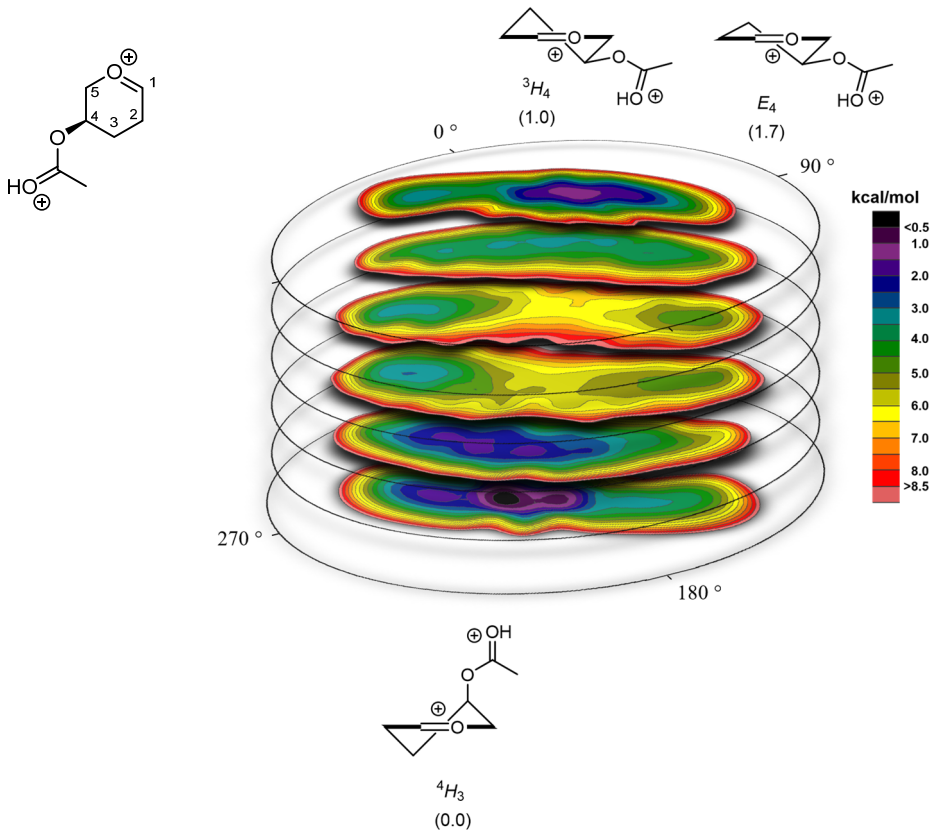


Figure 54| CEL map of protonated 4-*O*-acetyl-pyranosyl oxocarbenium ion (**S4**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -499.099060373 a.u.
Zero-point energy correction = 0.187858 a.u.

Atom coordinates

H	3.264281	-1.205469	-0.960123
C	2.491631	-0.580907	-0.504932
C	1.089479	-0.303471	1.450486
C	0.934657	1.414154	-0.385061
C	0.163254	0.559489	0.617638
C	1.940128	0.584928	-1.200092
O	2.138810	-0.977969	0.634047
H	0.256821	1.950139	-1.050196
H	-0.434515	1.170385	1.293479
H	2.795784	1.185929	-1.545405
H	1.639636	0.295356	2.178337
H	1.464380	2.176237	0.194199
H	1.529722	0.191938	-2.146302
H	0.598647	-1.131694	1.957379
O	-0.751549	-0.370509	-0.114955
C	-2.038968	-0.235138	-0.163493
H	-2.135729	-1.847670	-1.181983

O	-2.683253	-1.130161	-0.806249
C	-2.830712	0.846250	0.462160
H	-2.840412	0.708071	1.551332
H	-3.857199	0.793065	0.102068
H	-2.410297	1.831002	0.244230

$^3H_4$ conformation (1.0 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -499.097390783 a.u.
Zero-point energy correction = 0.187958 a.u.

Atom coordinates

H	4.053828	-0.076334	0.414683
C	2.986497	-0.024223	0.186708
C	0.943016	-1.323287	0.111902
C	0.865850	1.113371	-0.619626
C	0.170766	0.000144	0.164142
C	2.352778	1.223472	-0.235241
O	2.393387	-1.122163	0.339155
H	0.784999	0.887426	-1.686293
H	-0.027237	0.287472	1.197237
H	2.544125	1.936266	0.587108
H	0.662775	-2.031340	0.889062
H	0.372452	2.071434	-0.452032
H	2.962454	1.636979	-1.053446
H	0.874733	-1.800182	-0.866940
O	-1.113184	-0.310625	-0.496833
C	-2.285827	-0.018686	-0.026447
H	-3.051190	-0.795393	-1.592247
O	-3.280441	-0.350091	-0.751222
C	-2.572734	0.648436	1.261976
H	-2.260549	0.004435	2.092809
H	-3.643372	0.830133	1.341162
H	-2.033195	1.596768	1.339617

***E*$_4$ conformation (1.7 kcal / mol)**

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -499.096455938 a.u.
Zero-point energy correction = 0.188106 a.u.

Atom coordinates

H	3.936540	0.020627	0.747184
C	2.921698	0.011262	0.342338
C	0.962056	-1.326953	-0.023062
C	0.880826	1.040078	-0.786279
C	0.189306	-0.009632	0.076728
C	2.327381	1.207367	-0.264088
O	2.349038	-1.104769	0.459849
H	0.884845	0.707668	-1.826360
H	0.060924	0.299024	1.114963
H	2.429778	2.005112	0.491252
H	0.591463	-2.116605	0.626895
H	0.368699	2.002244	-0.744375
H	3.023266	1.537912	-1.052941
H	1.048033	-1.689824	-1.047703
O	-1.129404	-0.322114	-0.508159
C	-2.274232	-0.008064	0.012122
H	-3.124303	-0.814310	-1.493815
O	-3.307040	-0.347001	-0.653276
C	-2.488801	0.693375	1.296370
H	-2.130469	0.072038	2.125710
H	-3.553141	0.879669	1.430510
H	-1.945793	1.642916	1.316598

Protonated 3-*O*-acetyl-pyranosyl oxocarbenium ion (**S5**)

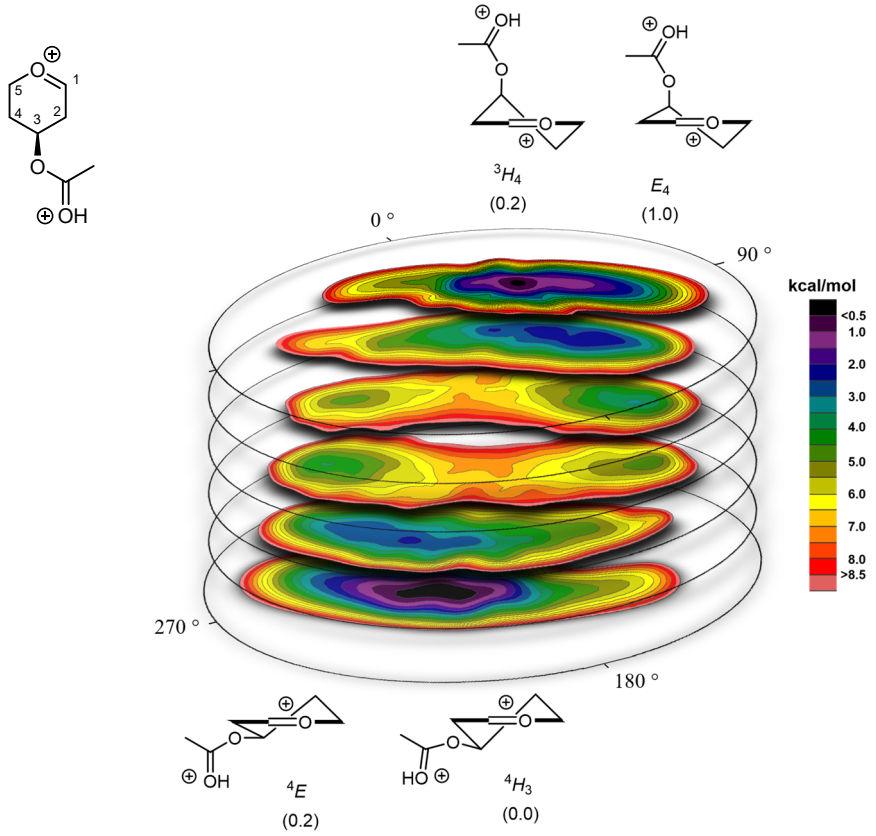


Figure 55| CEL map of protonated 3-*O*-acetyl-pyranosyl oxocarbenium ion (**S5**).

Local minima

$^4H_3$ conformation (0.0 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -499.100254820 a.u.
Zero-point energy correction = 0.188163 a.u.

Atom coordinates

H	-3.131630	-1.927956	0.419509
C	-2.451136	-1.085951	0.269165
C	-2.289456	1.281855	-0.213193
C	-0.156258	-0.009000	0.237258
C	-0.844892	1.047706	-0.629492
C	-0.988866	-1.291036	0.353351
O	-3.023188	-0.004386	0.030280
H	-0.326705	2.008271	-0.575131
H	-0.789609	-1.860538	1.271140
H	-2.418306	1.821883	0.726087
H	0.085967	0.376138	1.227545
H	-0.749586	-1.996680	-0.460080
H	-2.882435	1.762020	-0.988592
H	-0.814825	0.719032	-1.673017
O	1.107032	-0.403522	-0.428783
C	2.292336	-0.044200	-0.050004
H	3.007368	-1.019844	-1.525383
O	3.263767	-0.464341	-0.761655
C	2.623508	0.788195	1.127300
H	2.050234	1.719002	1.127407
H	3.688763	1.013665	1.118959
H	2.388456	0.237586	2.046505

$^3H_4$ conformation (0.2 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -499.100052227 a.u.
Zero-point energy correction = 0.188070 a.u.

Atom coordinates

H	3.017820	-1.856128	0.382946
C	2.313844	-1.047673	0.168395
C	1.829327	1.308137	0.479313

C	0.153064	-0.115736	-0.791830
C	0.899541	1.213750	-0.717418
C	1.109906	-1.302360	-0.654417
O	2.638087	0.052220	0.659344
H	1.469868	1.315225	-1.647173
H	1.486791	-1.607639	-1.645406
H	2.592788	2.076343	0.376047
H	-0.424064	-0.201036	-1.709407
H	0.622893	-2.209342	-0.273761
H	1.330948	1.420962	1.442014
H	0.211691	2.062576	-0.686190
O	-0.797346	-0.207590	0.363069
C	-2.080180	-0.061383	0.262178
H	-2.229171	-0.386124	2.138252
O	-2.754479	-0.180008	1.339795
C	-2.837197	0.214835	-0.978394
H	-2.398942	1.042534	-1.541213
H	-3.870434	0.446242	-0.723617
H	-2.830109	-0.678003	-1.617129

^{4}E conformation (0.2 kcal / mol)

D1 = -30°
D3 = -60°
D5 = 0°

E_{gas}(B3LYP) = -499.100042765 a.u.
Zero-point energy correction = 0.188197 a.u.

Atom coordinates

H	-3.148373	-1.897632	0.419182
C	-2.465215	-1.054508	0.288550
C	-2.229266	1.286420	-0.185712
C	-0.157205	0.010428	0.213454
C	-0.874949	0.931760	-0.770596
C	-1.001808	-1.257822	0.429297
O	-3.029844	0.027448	0.024151
H	-0.324798	1.862788	-0.931182
H	-0.838048	-1.741912	1.403023
H	-2.211465	1.763596	0.795322
H	0.063940	0.509996	1.155714
H	-0.740627	-2.035625	-0.306219
H	-2.854382	1.864217	-0.862434
H	-0.992318	0.443688	-1.742329
O	1.115070	-0.451587	-0.386718
C	2.294871	-0.048305	-0.037114
H	3.029217	-1.172581	-1.392279
O	3.275517	-0.538255	-0.689037
C	2.610014	0.909521	1.045492
H	2.060558	1.845873	0.913113
H	3.679849	1.111878	1.045377
H	2.331850	0.479900	2.015323

***E*$_4$ conformation (1.0 kcal / mol)**

D1 = 15°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -499.098909098 a.u.
Zero-point energy correction = 0.188090 a.u.

Atom coordinates

H	3.228058	1.532962	-0.840944
C	2.438450	0.866711	-0.483868
C	1.792240	-1.371229	0.063332
C	0.143624	0.444107	0.580497
C	0.908791	-0.757667	1.129101
C	1.099609	1.410630	-0.147747
O	2.776788	-0.333030	-0.405260
H	1.514759	-0.423709	1.978336
H	1.276624	2.316854	0.449446
H	2.432812	-2.169457	0.429156
H	-0.398602	0.971878	1.361123
H	0.675521	1.802393	-1.085289
H	1.276718	-1.692730	-0.841535
H	0.231352	-1.524072	1.514154
O	-0.848199	-0.035523	-0.427993
C	-2.128977	-0.062451	-0.232954
H	-2.344836	-0.770396	-1.993623
O	-2.842225	-0.503196	-1.195258
C	-2.840160	0.376630	0.987779
H	-2.437035	-0.114540	1.878083
H	-3.899206	0.143820	0.888780
H	-2.728547	1.460606	1.113556

Protonated multi-substituted pyranosyl oxocarbenium ions

Protonated 2-deoxy-3,4-di-*O*-actyl-fucose-L-pyranosyl oxocarbenium ion (**35**)

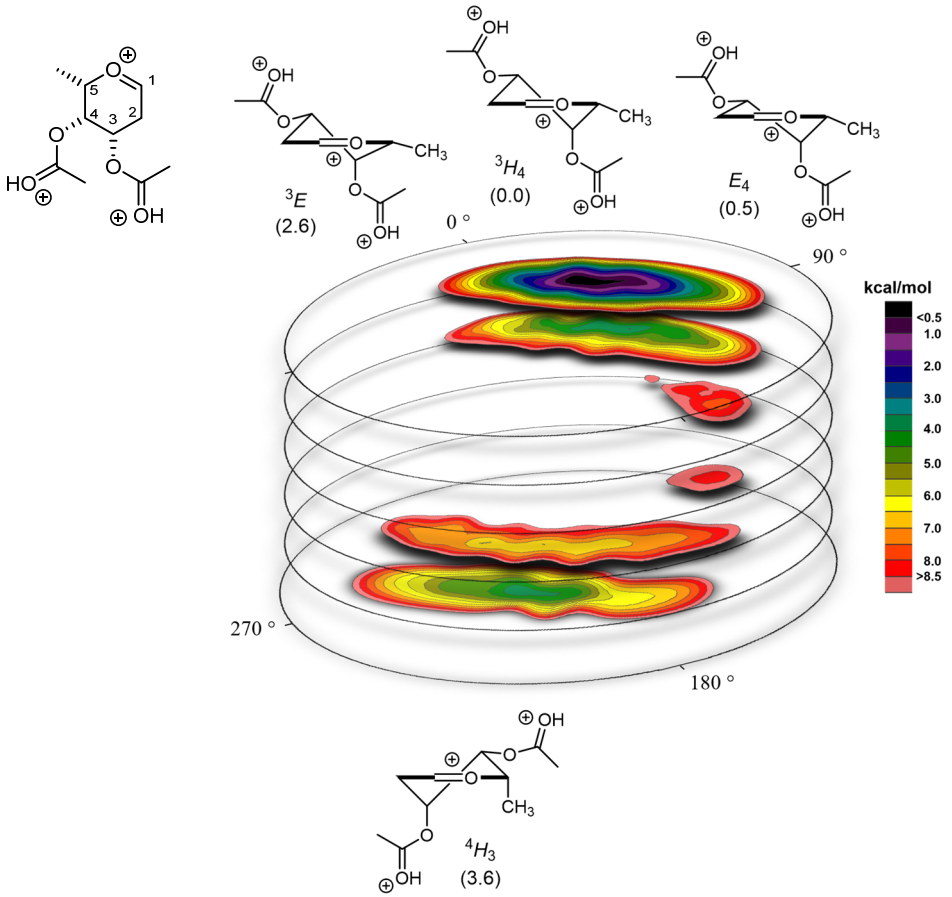


Figure 56| CEL map of protonated 2-deoxy-3,4-di-O-actyl-fucose-L-pyranosyl oxocarbenium ion (**35**).

Local minima

$^3H_4$ conformation (0.0 kcal / mol)

D1 = 45°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -766.463235721 a.u.
Zero-point energy correction = 0.267880 a.u.

Atom coordinates

C	-0.522096	-0.179443	-0.580829
C	0.692085	-1.504074	1.203340
O	-1.307312	-2.440038	0.221793
C	-0.422920	-2.477028	1.101436
C	-1.406996	-1.400116	-0.900443
C	0.847557	-0.674404	-0.078067
H	-0.537236	-3.286631	1.829973
H	0.480715	-0.875915	2.083846
H	-0.418394	0.410401	-1.492060
O	-1.139464	0.635150	0.475203
H	-0.970118	-1.937683	-1.746650
H	1.287451	-1.269740	-0.880229
O	1.714405	0.474827	0.193854
C	-2.885165	-1.174105	-1.115588
H	-3.025944	-0.556047	-2.007398
H	-3.370669	-0.708215	-0.256923
H	-3.374537	-2.129820	-1.312444
H	1.600672	-2.060485	1.466359
C	-1.735017	1.789969	0.293066
C	2.983665	0.536559	-0.145432
C	-1.843628	2.542787	-0.972869
H	-0.959022	2.457674	-1.604620
H	-2.043194	3.591432	-0.743524
H	-2.712697	2.167793	-1.533416
C	3.732870	-0.474075	-0.920786
H	4.789880	-0.205701	-0.927152
H	3.376222	-0.485948	-1.960051
H	3.617184	-1.478342	-0.502518

H	3.109093	2.242439	0.733446
O	3.609721	1.576934	0.218189
H	-2.254987	1.788170	2.146961
O	-2.281920	2.305651	1.316390

E_4 conformation (0.5 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

E_{gas}(B3LYP) = -766.462378131 a.u.
Zero-point energy correction = 0.267959 a.u.

Atom coordinates

C	0.509972	-0.179866	0.577268
C	-0.708558	-1.551461	-1.166817
O	1.487187	-2.238327	-0.394692
C	0.583305	-2.275748	-1.255944
C	1.368780	-1.417288	0.894310
C	-0.865482	-0.687403	0.102993
H	0.805007	-2.905750	-2.123819
H	-0.785739	-0.946636	-2.083745
H	0.411947	0.417362	1.484345
O	1.137586	0.613171	-0.482895
H	0.825729	-2.079281	1.573871
H	-1.292473	-1.259342	0.927058
O	-1.744393	0.446266	-0.195040
C	2.784480	-1.198860	1.370660
H	2.763378	-0.715626	2.352024
H	3.377271	-0.602928	0.674564
H	3.279401	-2.163463	1.499965
H	-1.501648	-2.307046	-1.276155
C	1.744115	1.763968	-0.299708
C	-3.014432	0.500578	0.142894
C	1.836656	2.517413	0.967485
H	0.878126	2.570662	1.489298
H	2.199835	3.523964	0.755901
H	2.565057	2.030561	1.630427
C	-3.754288	-0.506847	0.931078
H	-4.815206	-0.254221	0.925078
H	-3.405768	-0.493155	1.973192
H	-3.619938	-1.516839	0.533053
H	-3.155293	2.193903	-0.757718
O	-3.650420	1.529626	-0.235650
H	2.277712	1.753923	-2.149918
O	2.305704	2.270138	-1.318316

^3E conformation (2.6 kcal / mol)

D1 = 60°
D3 = 30°
D5 = 0°

E_{gas}(B3LYP) = -766.459239192 a.u.
Zero-point energy correction = 0.267889 a.u.

Atom coordinates

C	0.543705	0.176585	-0.579182
C	-0.658818	1.448504	1.230870
O	1.077821	2.605385	0.053891
C	0.199765	2.626676	0.941125
C	1.425885	1.421799	-0.864140
C	-0.829400	0.645671	-0.066316
H	0.134439	3.564804	1.501975
H	-0.174628	0.863696	2.026996
H	0.456349	-0.391525	-1.505256
O	1.151565	-0.666921	0.459953
H	1.125534	1.834275	-1.830959
H	-1.288709	1.252581	-0.849272
O	-1.672872	-0.523845	0.190363
C	2.928096	1.273584	-0.789965
H	3.254415	0.568297	-1.560474
H	3.272141	0.939805	0.189654
H	3.399885	2.230302	-1.021664
H	-1.610405	1.796049	1.644660
C	1.760752	-1.809467	0.250394
C	-2.944853	-0.601055	-0.134692
C	1.909936	-2.514847	-1.038811
H	1.051370	-2.400313	-1.700687
H	2.095324	-3.572819	-0.841989
H	2.802764	-2.126774	-1.551231
C	-3.720493	0.410989	-0.881696
H	-4.771751	0.120968	-0.886820
H	-3.371667	0.455571	-1.922644
H	-3.622899	1.406955	-0.439393
H	-3.031296	-2.323844	0.715457
O	-3.548770	-1.658435	0.216978
H	2.234833	-1.871911	2.115615
O	2.286863	-2.358277	1.267630

$^4H_3$ conformation (3.6 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -766.457840733 a.u.
Zero-point energy correction = 0.268235 a.u.

Atom coordinates

C	0.738537	0.450815	-0.380680
C	-1.362699	1.500321	-1.288963
O	0.088714	2.783191	0.171225
C	-0.864151	2.729589	-0.633060
C	0.924612	1.608337	0.637647
C	-0.714341	0.181716	-0.824452
H	-1.331537	3.697950	-0.841449
H	-2.456815	1.488803	-1.192480

H	1.271100	0.707501	-1.301073	C	3.449866	-0.631456	-1.120461
O	1.320498	-0.765917	0.174395	H	3.062818	-0.793376	-2.136298
H	1.927185	2.026653	0.537045	H	4.413735	-1.135846	-1.041550
H	-0.724055	-0.555696	-1.626095	H	3.589221	0.442708	-0.969039
O	-1.477538	-0.359657	0.317660	C	-2.803504	-1.970490	-1.042261
C	0.588090	1.386368	2.098163	H	-3.661849	-2.610435	-0.836054
H	1.276372	0.652335	2.522728	H	-1.982710	-2.599654	-1.410276
H	-0.435482	1.045867	2.247898	H	-3.066407	-1.256337	-1.829121
H	0.739686	2.318987	2.645724	H	-2.734905	-1.159088	2.095564
H	-1.209452	1.656409	-2.371659	O	-2.997589	-1.619963	1.272589
C	2.519248	-1.215682	-0.132780	H	2.269776	-2.649158	1.125089
C	-2.401266	-1.283903	0.204076	O	2.891785	-2.264068	0.473839

Protonated 2-deoxy-3,4-di-*O*-actyl-rhamnose-L-pyranosyl oxocarbenium ion (**36**)

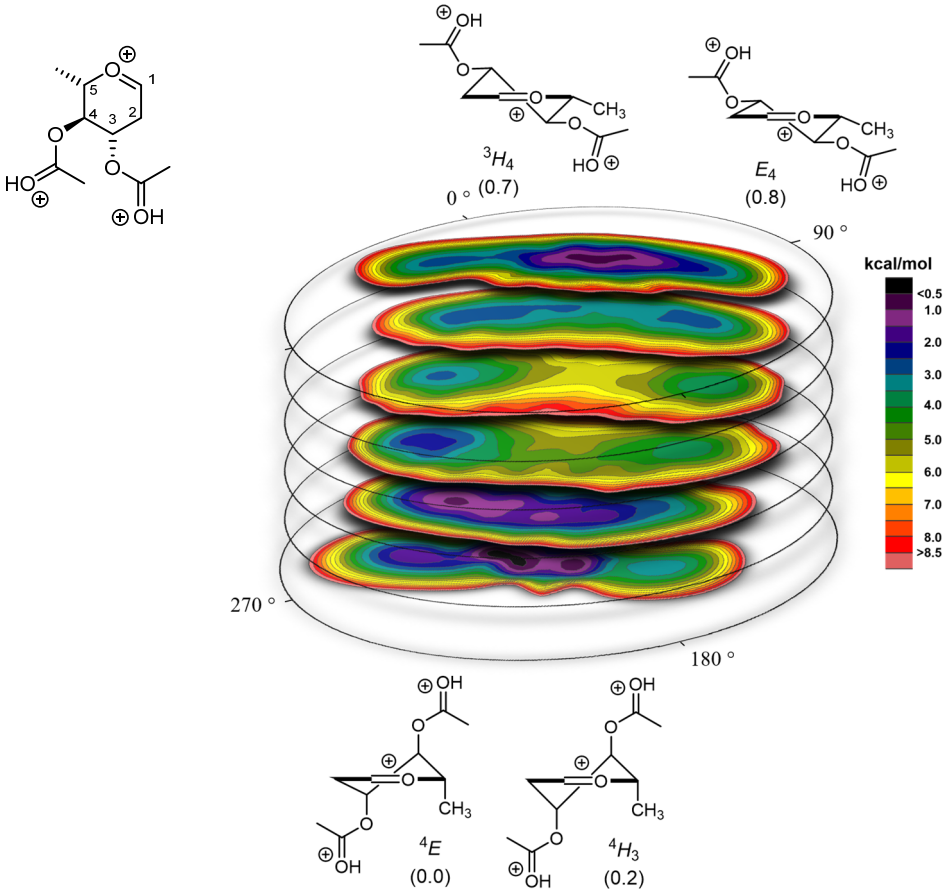


Figure 57| CEL map of protonated 2-deoxy-3,4-di-O-actyl-fucose-L-pyranosyl oxocarbenium ion (**36**).

Local minima

^4H conformation (0.0 kcal / mol)

D1 = -15°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -766.476918682 a.u.
Zero-point energy correction = 0.268087 a.u.

Atom coordinates

C	-0.536601	0.025026	-0.373594
C	0.734569	0.792141	1.731478
O	-0.794635	2.305601	0.605951
C	-0.120128	1.993592	1.608057

C	-0.852363	1.491765	-0.675187
C	0.680527	-0.211887	0.563988
H	-0.186505	2.706111	2.436645
H	1.754746	1.159554	1.924251
H	-1.902159	1.610735	-0.942508
H	0.634900	-1.232496	0.939298
O	1.877613	-0.068058	-0.279963
C	0.030154	2.190333	-1.694028
H	-0.118133	1.721940	-2.671043
H	1.087980	2.151768	-1.434146
H	-0.276264	3.234288	-1.783109
H	0.455851	0.315216	2.683832
C	2.916583	-0.869710	-0.229936
C	3.073436	-2.044347	0.652548
H	4.109517	-2.382859	0.612618
H	2.437710	-2.863424	0.287821
H	2.797994	-1.823906	1.687034
H	3.751106	0.162703	-1.622375
O	3.866454	-0.606940	-1.027719
H	-0.412020	-0.515736	-1.311918
O	-1.660445	-0.576689	0.390846
C	-2.697282	-1.122225	-0.172526
C	-3.745588	-1.705601	0.680888
H	-4.700920	-1.199652	0.480910
H	-3.496930	-1.618939	1.736423
H	-3.887220	-2.762649	0.415653
O	-2.720166	-1.100481	-1.454320
H	-3.500086	-1.524627	-1.867876

$^{4}H_{3}$ conformation (0.2 kcal / mol)

D1 = -30°
D3 = -45°
D5 = 0°

E_{gas}(B3LYP) = -766.476748918 a.u.
Zero-point energy correction = 0.268236 a.u.

Atom coordinates

C	-0.552945	0.012045	-0.388668
C	0.593114	0.480271	1.826852
O	-0.594850	2.267904	0.690158
C	-0.034410	1.817988	1.711169
C	-0.733191	1.515037	-0.626356
C	0.647602	-0.344315	0.531063
H	-0.041072	2.501377	2.566572
H	1.579185	0.614387	2.292777
H	-1.774749	1.733007	-0.866195
H	0.617553	-1.408372	0.758898
O	1.871420	-0.051309	-0.221346
C	0.175440	2.194620	-1.633322
H	-0.008079	1.764340	-2.621923
H	1.230629	2.095000	-1.386221
H	-0.078673	3.254889	-1.686517
H	0.017409	-0.052374	2.602373
C	2.921504	-0.841880	-0.245958
C	3.054304	-2.140410	0.446363
H	4.092410	-2.469474	0.387386
H	2.431692	-2.892145	-0.058721
H	2.746697	-2.081190	1.493815
H	3.810696	0.406511	-1.411122
O	3.905339	-0.447220	-0.940897
H	-0.474392	-0.492404	-1.351976
O	-1.715200	-0.530269	0.352417
C	-2.780390	-0.996157	-0.232845
C	-3.868492	-1.537161	0.598011
H	-4.792223	-0.974905	0.400254
H	-3.626967	-1.488719	1.657576
H	-4.065645	-2.578859	0.307775
O	-2.792453	-0.937845	-1.512756
H	-3.593736	-1.301374	-1.943209

$^{3}H_{4}$ conformation (0.7 kcal / mol)

D1 = 30°
D3 = 45°
D5 = 0°

E_{gas}(B3LYP) = -766.476748918 a.u.
Zero-point energy correction = 0.268236 a.u.

Atom coordinates

C	-0.552945	0.012045	-0.388668
C	0.593114	0.480271	1.826852
O	-0.594850	2.267904	0.690158
C	-0.034410	1.817988	1.711169
C	-0.733191	1.515037	-0.626356
C	0.647602	-0.344315	0.531063
H	-0.041072	2.501377	2.566572
H	1.579185	0.614387	2.292777
H	-1.774749	1.733007	-0.866195
H	0.617553	-1.408372	0.758898
O	1.871420	-0.051309	-0.221346
C	0.175440	2.194620	-1.633322
H	-0.008079	1.764340	-2.621923
H	1.230629	2.095000	-1.386221
H	-0.078673	3.254889	-1.686517
H	0.017409	-0.052374	2.602373
C	2.921504	-0.841880	-0.245958
C	3.054304	-2.140410	0.446363
H	4.092410	-2.469474	0.387386
H	2.431692	-2.892145	-0.058721
H	2.746697	-2.081190	1.493815
H	3.810696	0.406511	-1.411122
O	3.905339	-0.447220	-0.940897
H	-0.474392	-0.492404	-1.351976
O	-1.715200	-0.530269	0.352417
C	-2.780390	-0.996157	-0.232845
C	-3.868492	-1.537161	0.598011
H	-4.792223	-0.974905	0.400254

H	-3.626967	-1.488719	1.657576
H	-4.065645	-2.578859	0.307775
O	-2.792453	-0.937845	-1.512756
H	-3.593736	-1.301374	-1.943209

E_4 conformation (0.8 kcal / mol)

D1 = 30°
D3 = 60°
D5 = 0°

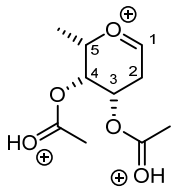
E_{gas}(B3LYP) = -766.475391638 a.u.
Zero-point energy correction = 0.267910 a.u.

Atom coordinates

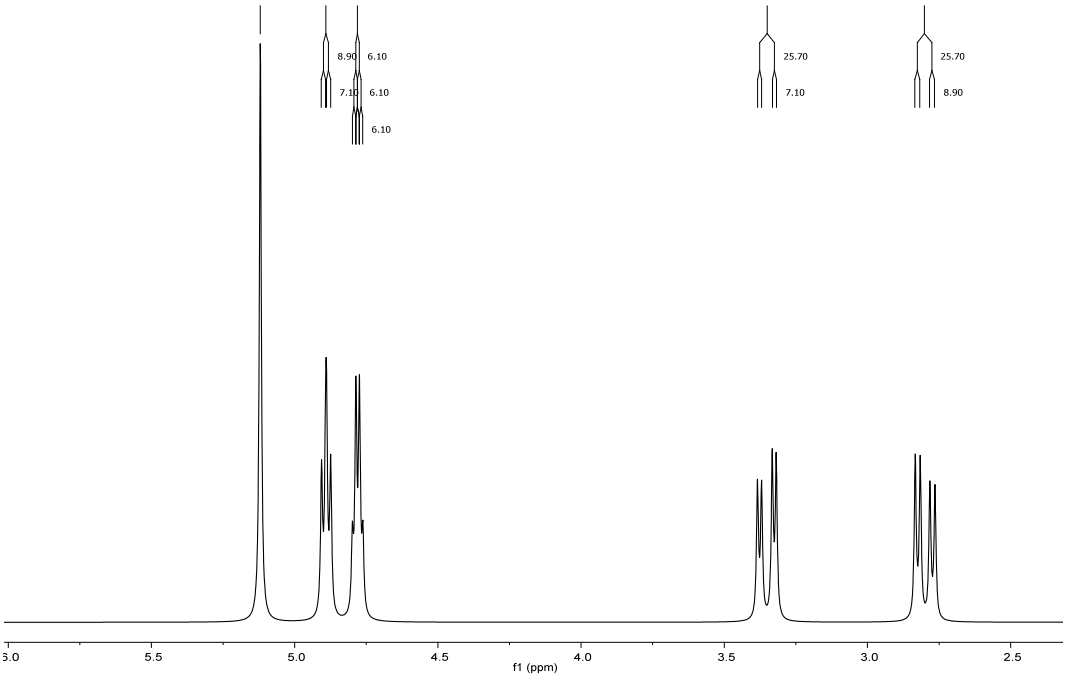
C	-0.660331	0.275054	-0.146336
C	0.963346	2.174804	-0.333545
O	-1.388532	2.626052	0.019790
C	-0.259806	3.007088	-0.355135
C	-1.660622	1.229066	0.558651
C	0.767914	0.730466	0.186188
H	-0.222544	4.040908	-0.714003
H	1.348142	2.175867	-1.366603
H	-1.434234	1.319218	1.624286
H	0.946920	0.648380	1.258172
O	1.714992	-0.135551	-0.528584
C	-3.133251	0.988883	0.322797
H	-3.450090	0.088701	0.855171
H	-3.377424	0.902870	-0.737246
H	-3.703829	1.815220	0.752413
H	1.717920	2.737559	0.236937
C	2.868817	-0.534649	-0.050146
C	3.387592	-0.284854	1.310772
H	4.305964	-0.855151	1.452607
H	2.659620	-0.564658	2.078131
H	3.626126	0.780186	1.430960
H	3.265848	-1.320161	-1.757327
O	3.602315	-1.198251	-0.845235
H	-0.835806	0.220369	-1.222246
O	-0.844623	-1.054148	0.457665
C	-1.524443	-2.017592	-0.088881
C	-1.685340	-3.274915	0.661948
H	-2.750555	-3.407144	0.905182
H	-1.107537	-3.267013	1.583854
H	-1.398673	-4.128959	0.035376
O	-2.015639	-1.790070	-1.249945
H	-2.521208	-2.530561	-1.643065

DFT computed NMR simulations

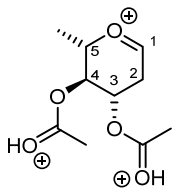
Protonated 2-deoxy-3,4-di-*O*-actyl-fucose-L-pyranosyl oxocarbenium ion (**35**)



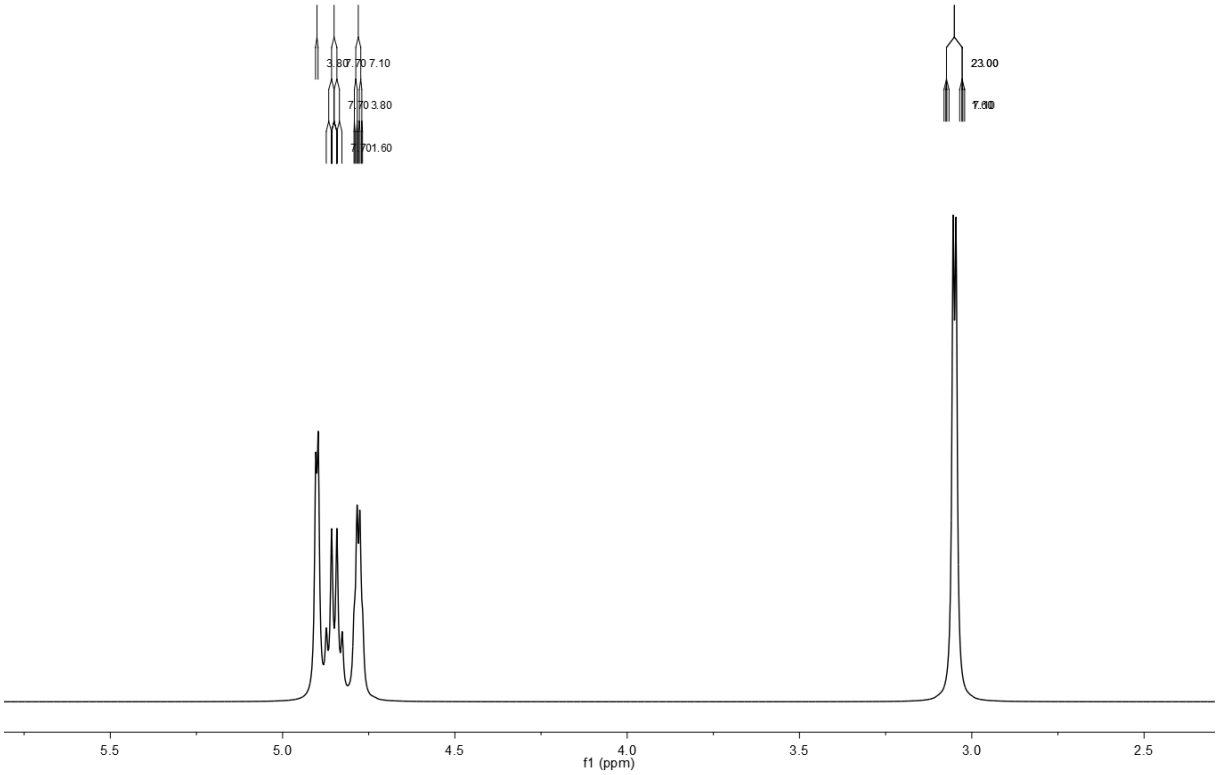
Geometry	**Coupling constant (Hz)**						
	H1-H2$_a$	**H1-H2$_b$**	**H2$_a$-H3**	**H2$_b$-H3**	**H3-H4**	**H4-H5**	**H5-CH$_3$**
D1_15_D3_60_D5_0	2.9	0.4	5.5	11.1	4.8	0.8	6.5
D1_15_D3_60_D5_15	2.4	0.1	5.9	10.7	5.3	0.7	6.3
D1_30_D3_45_D5_0	0.8	1.4	8.7	9.0	4.4	2.4	6.5
D1_30_D3_45_D5_15	0.4	1.8	9.1	8.7	4.8	2.2	6.4
D1_30_D3_45_D5_-15	1.1	0.8	8.2	9.2	3.8	2.6	6.7
D1_30_D3_60_D5_0	1.3	0.6	8.3	8.6	3.1	0.8	6.6
D1_30_D3_60_D5_15	0.9	1.1	8.6	8.3	3.6	0.7	6.4
D1_45_D3_30_D5_0	0.5	3.5	11.3	6.6	4.1	4.4	6.9
D1_45_D3_30_D5_-15	0.4	2.9	10.8	6.7	3.6	4.7	6.9
D1_45_D3_45_D5_0	0.3	2.7	11.0	6.4	2.8	2.4	6.7
D1_45_D3_45_D5_15	0.5	3.1	11.4	6.2	3.2	2.2	6.5
D1_45_D3_45_D5_-15	0.1	2.1	10.4	6.6	2.3	2.6	6.8
Boltzmann corrected scaled H-H couplings	**0.7**	**1.7**	**8.9**	**7.1**	**3.1**	**1.9**	**6.1**
Experimental data	-	-	**8.5**	**6.8**	**3.0**	-	**6.4**

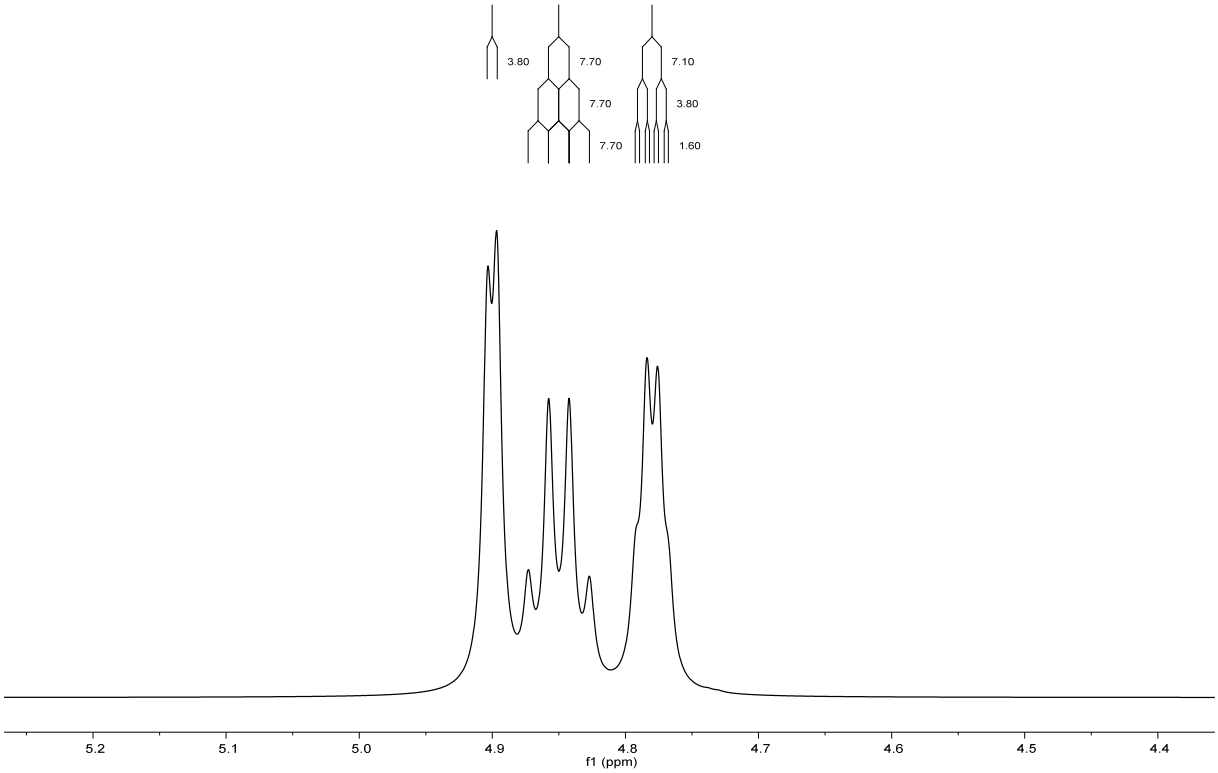


Protonated 2-deoxy-3,4-di-*O*-actyl-rhamnose-L-pyranosyl oxocarbenium ion (**36**)



Geometry	**Coupling constant (Hz)**						
	H1-H2$_a$	**H1-H2$_b$**	**H2$_a$-H3**	**H2$_b$-H3**	**H3-H4**	**H4-H5**	**H5-CH$_3$**
D1_-15_D3_-45_D5_0	0.7	1.5	0.1	9.0	2.8	0.6	8.7
D1_-30_D3_-30_D5_0	2.6	0.0	0.5	7.6	3.1	0.1	8.4
D1_-30_D3_-45_D5_0	1.9	0.3	0.4	7.5	4.3	0.6	9.1
D1_-15_D3_-45_D5_-15	1.1	1.1	0.0	8.6	2.3	0.7	8.6
D1_-45_D3_-30_D5_0	3.5	0.5	1.7	5.5	4.4	0.1	8.4
D1_-30_D3_-45_D5_-15	2.2	0.0	0.6	7.0	3.8	0.7	8.9
D1_30_D3_45_D5_0	0.7	1.4	6.8	9.0	9.0	9.6	7.4
D1_0_D3_-45_D5_0	0.3	2.9	1.2	9.9	1.4	0.6	8.5
D1_-30_D3_-30_D5_-15	2.9	0.3	0.6	7.2	2.6	0.1	8.3
D1_45_D3_45_D5_0	0.3	2.6	9.3	6.4	9.7	9.4	7.3
D1_30_D3_60_D5_0	1.1	0.8	6.6	8.3	9.8	10.0	7.4
D1_-30_D3_-30_D5_15	2.1	0.1	0.3	7.9	3.6	0.2	8.4
D1_-45_D3_-15_D5_0	4.0	0.5	1.8	5.5	2.9	0.6	8.2
D1_15_D3_60_D5_0	2.6	0.2	3.8	10.6	9.2	10.4	7.4
D1_-15_D3_-30_D5_0	1.5	1.0	0.1	9.4	1.7	0.1	8.3
D1_-45_D3_-30_D5_-15	3.7	0.5	2.0	5.2	3.9	0.0	8.4
D1_0_D3_-45_D5_-15	0.0	2.4	0.8	9.6	1.1	0.7	8.5
D1_30_D3_60_D5_15	0.7	1.1	7.0	8.2	9.6	10.3	7.5
D1_15_D3_-45_D5_0	0.8	4.1	3.7	9.9	0.5	0.6	8.4
D1_-15_D3_-45_D5_15	0.3	1.8	0.2	9.3	3.2	0.5	8.9
D1_-45_D3_-30_D5_15	3.1	0.5	1.4	5.8	4.9	0.1	8.4
D1_45_D3_30_D5_0	0.5	3.3	9.7	7.0	8.9	7.7	7.5
D1_30_D3_45_D5_-15	1.0	0.9	6.3	8.9	9.4	9.4	7.3
D1_30_D3_45_D5_15	0.4	1.8	7.3	9.0	8.5	9.8	7.4
D1_-45_D3_-15_D5_15	3.7	0.5	1.5	5.8	3.4	0.8	8.2
45_D3_30_D5_-15	0.4	2.8	9.1	6.8	9.3	7.7	7.4
D1_15_D3_60_D5_15	2.2	0.0	4.3	10.6	8.8	10.7	7.6
D1_0_D3_-60_D5_0	0.7	3.4	0.9	9.3	2.2	1.9	9.1
D1_45_D3_45_D5_-15	0.1	2.2	8.7	6.2	9.9	9.2	7.2
D1_-30_D3_-15_D5_0	3.2	0.3	0.5	7.8	1.7	0.7	8.2
D1_-15_D3_-30_D5_-15	1.8	0.6	0.1	9.1	1.3	0.1	8.2
D1_-30_D3_-45_D5_15	1.3	0.5	0.2	7.8	4.8	0.5	9.2
D1_15_D3_-45_D5_-15	0.8	3.7	3.1	9.6	0.3	0.7	8.4
D1_15_D3_45_D5_0	2.2	0.2	3.9	11.1	7.7	9.8	7.4
Boltzmann corrected scaled H-H couplings	**1.6**	**0.8**	**1.5**	**7.3**	**3.8**	**1.7**	**7.7**
Experimental data	-	-	-	-	**3.5**	**-**	**7.5**


3.80
7.70
7.10
7.70
3.80
7.70
1.60
23.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)


3.80
7.70
7.70
7.70
7.10
3.80
1.60
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
f1 (ppm)

NMR experiments

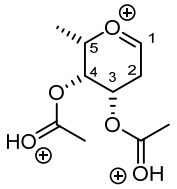
General experimental procedures

The authors want to draw the reader's attention to the dangerous features of superacidic chemistry. Handling of hydrogen fluoride and antimony pentafluoride must be done by experienced chemists with all the necessary safety arrangements in place. Experiments performed in superacid were carried out in a sealed Teflon® flask with a magnetic stirrer. No further precautions have to be taken to prevent reaction mixture from moisture (test reaction performed in anhydrous conditions leads to the same results). ^{1}H, ^{13}C NMR were recorded on a 400 MHz Bruker Advance DPX spectrometer using CD_3COCD_3 as external reference. To get better resolution of signals with small coupling constants or overlapping signals a gaussian window function (LB ± -1 and GB ± 0.5) was used on the ^{1}H NMR spectrum. COSY ^{1}H-^{1}H and HSQC ^{1}H-^{13}C experiments were used to confirm the NMR peak assignments.

General procedure in superacidic media for NMR experiments

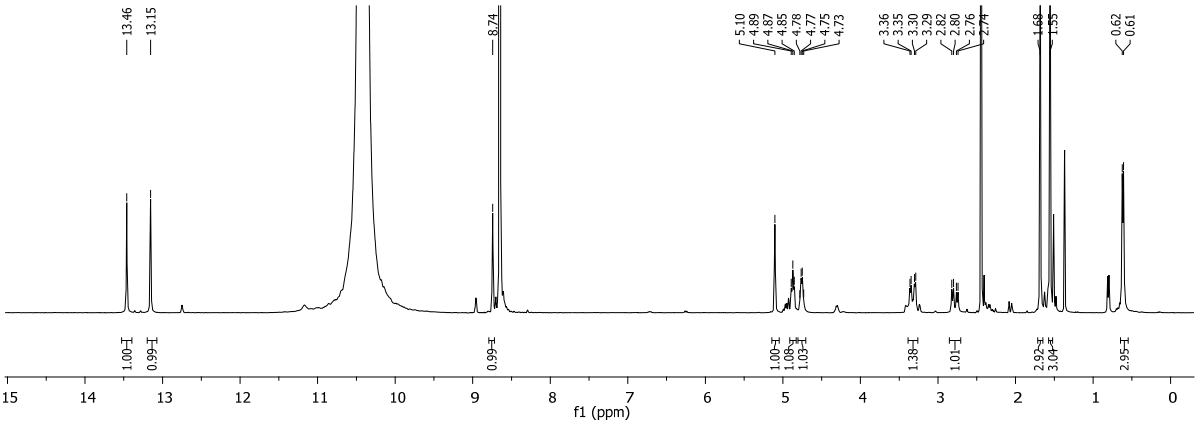
To a magnetically stirred mixture of HF/SbF_5 (1 mL, SbF_5 22 mol %) maintained at -40 °C, was added substrate. After 5 minutes, the mixture was introduced in a Teflon® NMR tube which was inserted into a classical glass NMR tube containing acetone-d_6 as external standard.

Protonated pyranosyl oxocarbenium ions

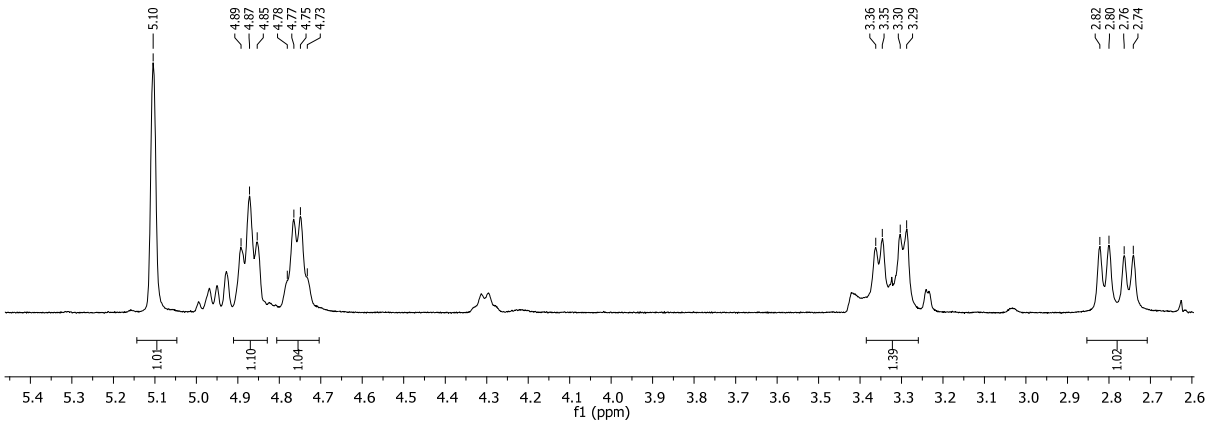


Protonated 2-deoxy-3,4-di-*O*-acetyl-fucose-L-pyranosyl oxocarbenium ion (35). The ion **35** was obtained from glycosyl donor **33** according to general procedure in superacidic media. ^{1}H NMR (400 MHz, Acetone-d_6): δ 13.46 (s, 1H, H'), 13.15 (s, 1H, H'), 8.74 (s, 1H, H-1), 5.10 (d, J = 3.0 Hz, H-4), 4.87 (t, J = 8.5 Hz, 1H, H-3), 4.76 (q, J = 6.4 Hz, 1H, H-5), 3.33 (dd, J = 23.7, 6.8 Hz, 1H, H-2b), 2.78 (dd, J = 23.7, 9.8 Hz, 1H, H-2a), 1.68 (s, 3H, CH_3Ac), 1.55 (s, 3H, CH_3 Ac), 0.62 (d, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, Acetone-d_6): δ 224.8 (CH, C-1), 194.2 (C=O), 193.3 (C=O), 94.7 (CH, C-5), 75.8 (CH, C-4), 69.6 (CH, C-3), 35.6 (CH_2, C-2), 19.6 (CH_3 Ac), 19.5 (CH_3 Ac), 13.0 (CH_3).

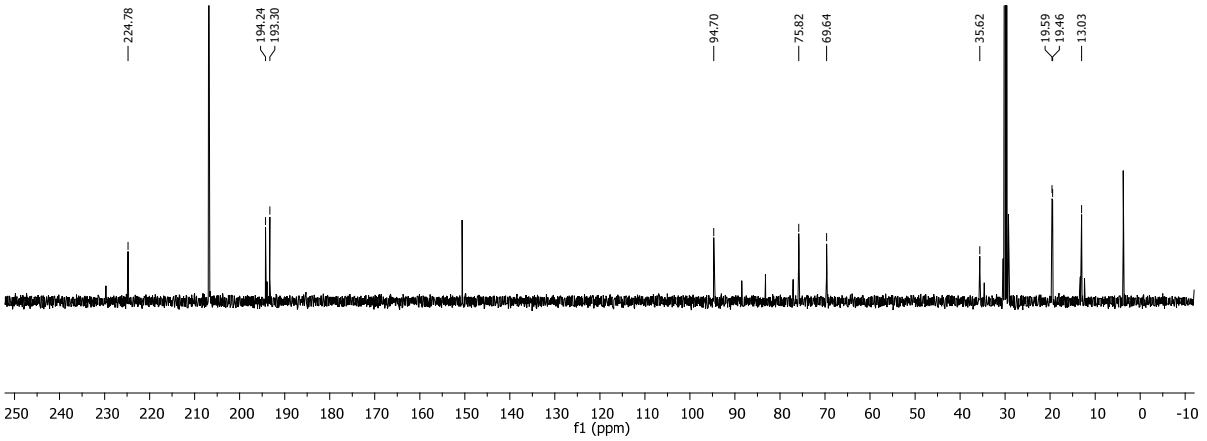
^{1}H NMR, Acetone-d_6 of oxocarbenium ion **35**



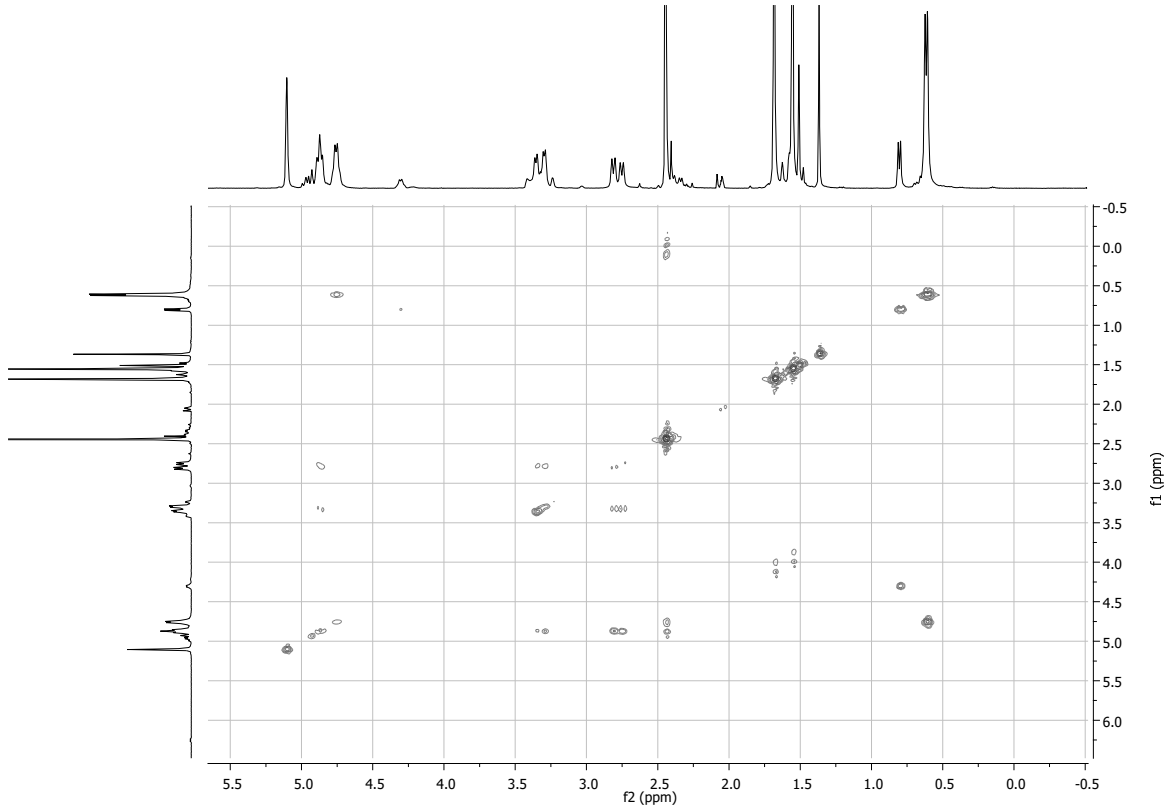
^{1}H NMR, Acetone-d_6 of oxocarbenium ion **35** (cropped)



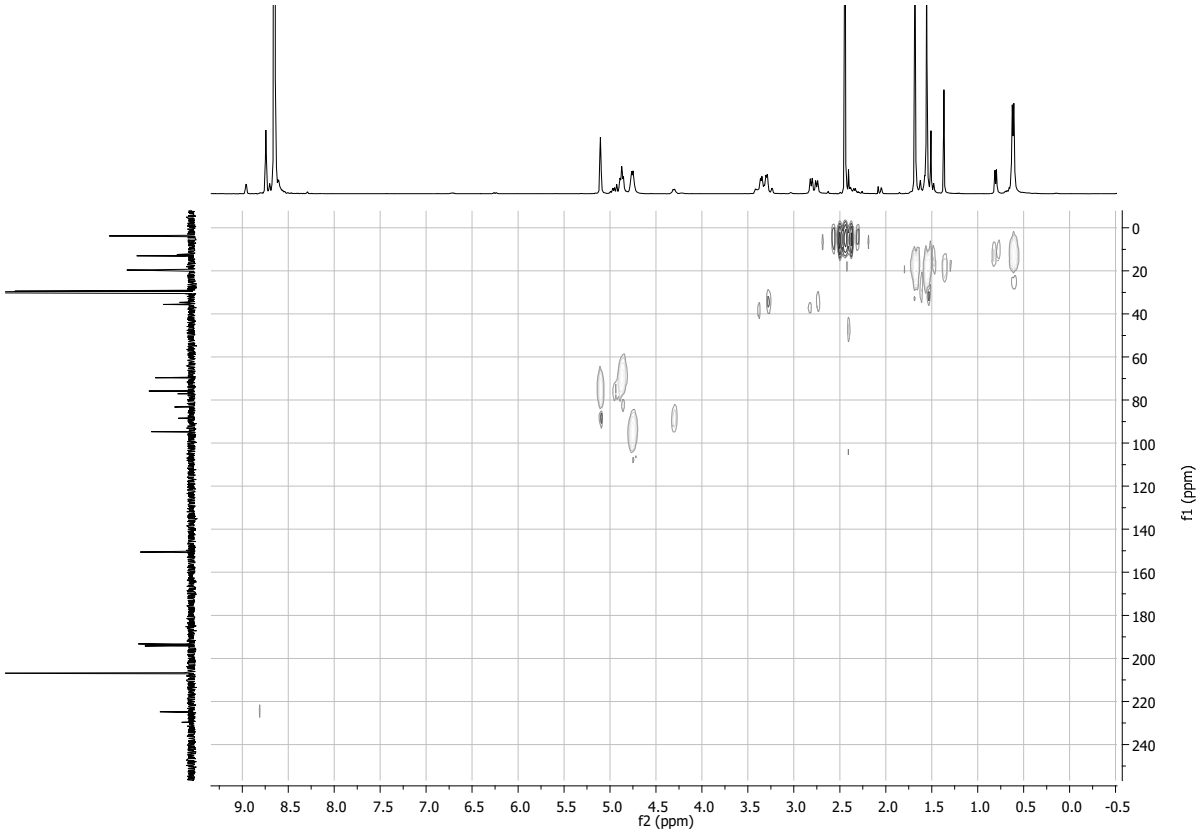
^{13}C NMR, Acetone-d_6 of oxocarbenium ion **35**

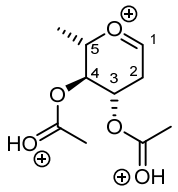


COSY NMR, Acetone-d_6 of oxocarbenium ion **35**



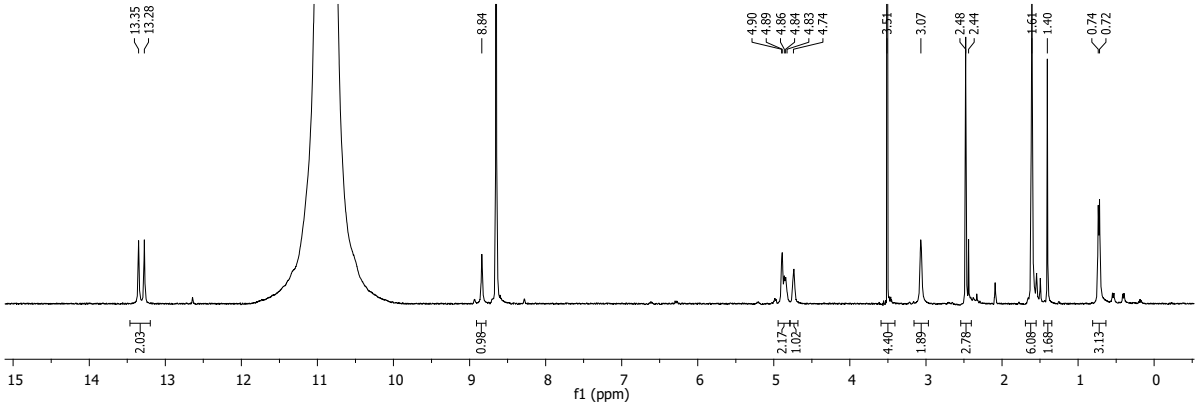
HSQC NMR, Acetone-d_6 of oxocarbenium ion **35**



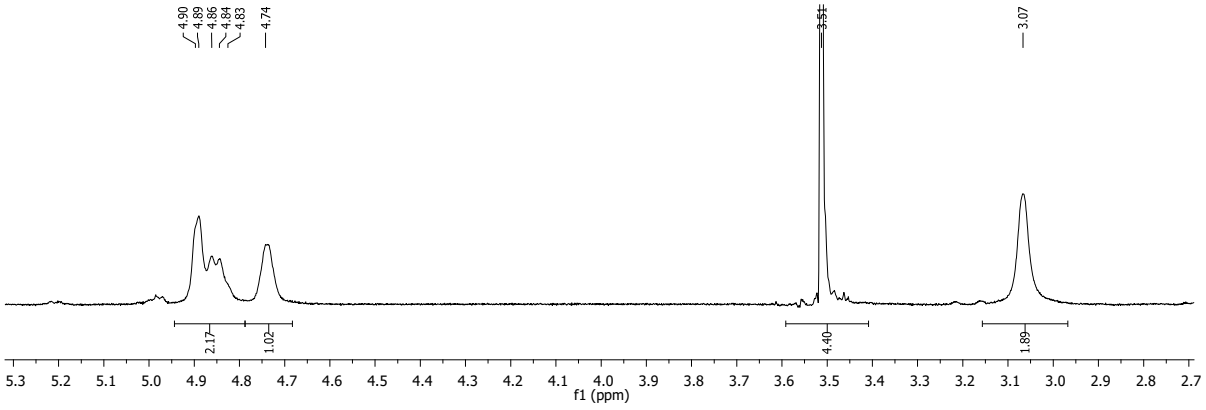


Protonated 2-deoxy-3,4-di-*O*-acetyl-rhamnose-L-pyranosyl oxocarbenium ion (36). The ion **36** was obtained from glycosyl donor **34** according to general procedure in superacidic media. ^{1}H NMR (400 MHz, Acetone-d_6): δ 13.35 (s, 1H, H'), 13.28 (s, 1H, H'), 8.84 (s, 1H, H-1), 4.89 (d, J = 3.5 Hz, 1H, H-4), 4.85 (q, J = 7.5 Hz, 1H H-5), 4.74 (bs, 1H, H-3), 3.07 (bs, 2H, H-2), 1.61 (s, 6H, 2x CH_3 Ac), 0.73 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, Acetone-d_6): δ 224.0 (CH, C-1), 193.5 (C=O), 193.4 (C=O), 92.3 (CH, C-5), 73.5 (CH, C-4), 61.2 (CH, C-3), 35.8 (CH_2, C-2), 19.9 (CH_3 Ac), 19.8 (CH_3 Ac), 15.2 (CH_3).

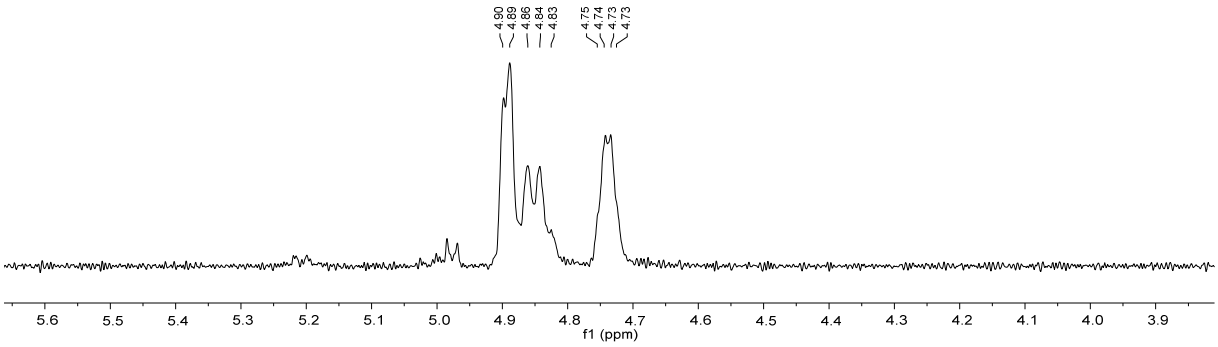
^{1}H NMR, Acetone-d_6 of oxocarbenium ion **36**



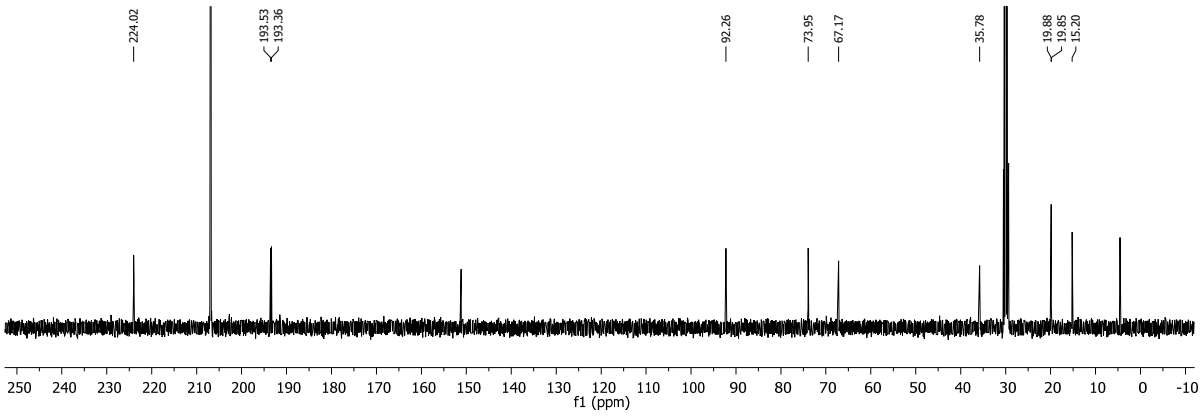
^{1}H NMR, Acetone-d_6 of oxocarbenium ion **36** (cropped)



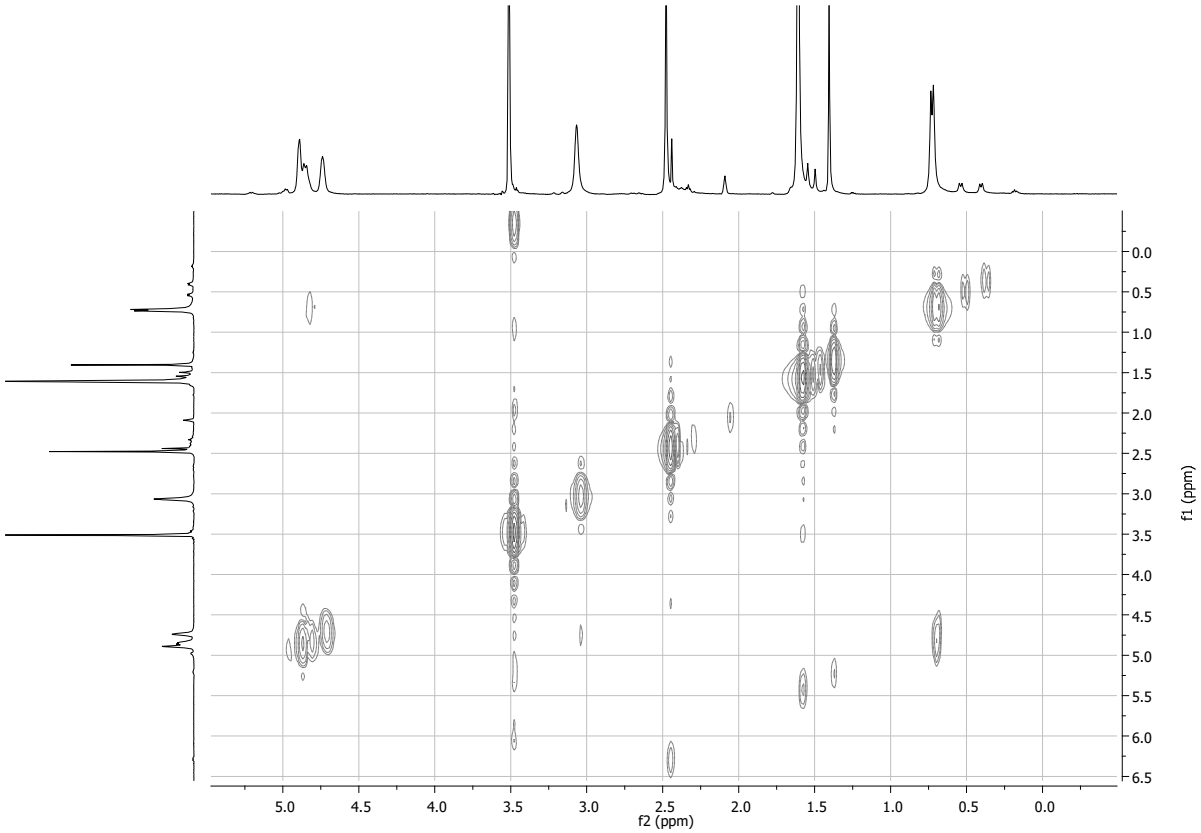
^{1}H NMR, Acetone-d_6 of oxocarbenium ion **36** (cropped; LB ± -2 and GB ± 4)



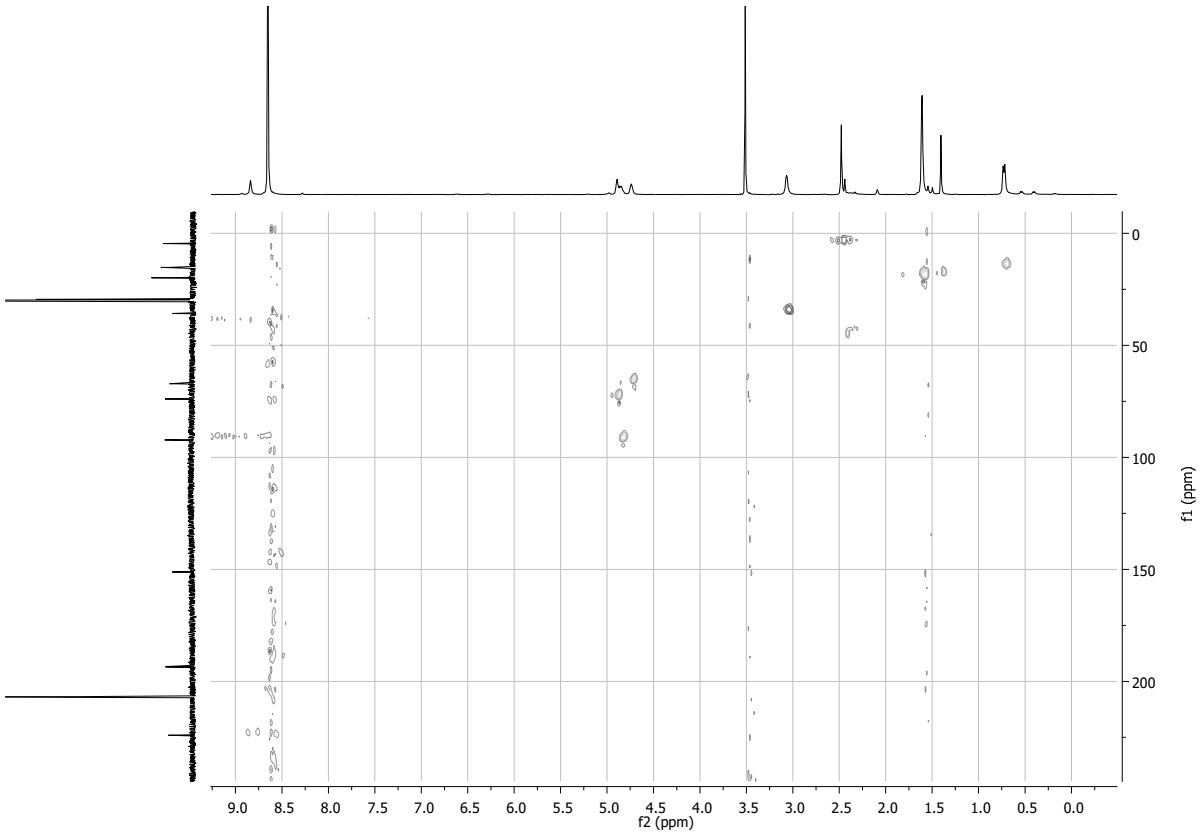
^{13}C NMR, Acetone-d_6 of oxocarbenium ion **36**



COSY NMR, Acetone-d_6 of oxocarbenium ion **36**



HSQC NMR, Acetone-d_6 of oxocarbenium ion **36**



Organic synthesis

General experimental procedures

All chemicals (Acros, Fluka, Merck, and Sigma-Aldrich) were used as received unless stated otherwise. Dichloromethane was stored over activated 4 Å molecular sieves (beads, 8-12 mesh, Sigma-Aldrich). Before use traces of water present in the donor, diphenyl sulfoxide (Ph_2SO) and tri-*tert*-butylpyrimidine (TTBP) were removed by co-evaporation with dry toluene. The acceptor (TES-*D*) was stored in stock solutions (DCM, 0.5 M) over activated 4 Å molecular sieves. Trifluoromethanesulfonic anhydride (Tf_2O) was distilled over P_2O_5 and stored at -20 °C under a nitrogen atmosphere. Overnight temperature control was achieved by an FT902 Immersion Cooler (Julabo). Column chromatography was performed on silica gel 60 Å (0.04 – 0.063 mm, Screening Devices B.V.). Size exclusion chromatography was carried out on Sephadex™ (LH-20, GE Healthcare Life Sciences) by isocratic elution with DCM:MeOH (1:1, v:v). TLC-analysis was conducted on TLC Silica gel 60 (Kieselgel 60 F_{254}, Merck) with UV detection by (254 nm) and by spraying with 20% sulfuric acid in ethanol followed by charring at ±150 °C or by spraying with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}H_2O$ (25 g/l) and $(NH_4)_4Ce(SO_4)_4{\cdot}{}_2H_2O$ (10 g/l) in 10% sulfuric acid in water followed by charring at ±250 °C. High-resolution mass spectra were recorded on a Thermo Finnigan LTQ Orbitrap mass spectrometer equipped with an electrospray ion source in positive mode (source voltage 3.5 kV, sheath gas flow 10, capillary temperature 275 °C) with resolution R=60.000 at m/z=400 (mass range = 150-4000). ^1H, ^2H and ^{13}C NMR spectra were recorded on a Bruker AV-400 NMR instrument (400, 61 and 101 MHz respectively), a Bruker AV-500 NMR instrument (500, 75 and 126 MHz respectively), or a AV-600 NMR instrument (600, 92 and 150 MHz respectively). For samples measured in $CDCl_3$ chemical shifts (δ) are given in ppm relative to tetramethylsilane as an internal standard or the residual signal of the deuterated solvent. Coupling constants (*J*) are given in Hz. To get better resolution of signals with small coupling constants or overlapping signals a gaussian window function (LB ± -1 and GB ± 0.5) was used on the ^1H NMR spectrum. All given ^{13}C APT spectra are proton decoupled. NMR peak assignment was made using COSY, HSQC. If necessary additional NOESY, HMBC and HMBC-GATED experiments were used to elucidate the structure further. The anomeric product ratios were based on the integration of ^1H NMR. If the stereochemistry of the coupled product was not completely clear a deprotection step was used to verify the stereochemistry. IR spectra were recorded on a Shimadzu FTIR-8300 IR spectrometer with a resolution of 4 cm^{-1} and are reported in cm^{-1}. Specific rotations were measured on an MCP 100 Anton Paar polarimeter in $CHCl_3$ (10 mg/mL) at 589 nm unless stated otherwise.

General procedure IV: synthesis of phenyl 2,3,4-tri-*O*-benzyl/methyl-1-thio-pentopyranoses

To a suspension of the corresponding pentose (10 mmol – 40 mmol) in pyridine (0.40 M), Ac_2O (12 eq.) was added dropwise at 0 °C. The mixture was allowed to warm to rt. and stirred for 16 h. The reaction was quenched with sat. aq. $NaHCO_3$ and diluted with H_2O. The resulting product was extracted with DCM (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was dissolved in DCM (0.15 M) and cooled to 0 °C. Hydrogen bromide (33 wt% in AcOH, 4.4 eq.) was added dropwise, and the reaction was allowed to warm to rt. and stirred for an additional 16 h. Subsequently, the reaction mixture was concentrated under reduced pressure and co-evaporated with toluene (3x). To a solution of the crude product and thiophenol (1.05 eq.) in DMF (0.5 M), NaH (60% dispersion in mineral oil, 1.05 eq.) was added portionwise at 0 °C. After stirring for 16 h, the reaction was quenched by the addition of aqueous HCl (0.02 M) and diluted with H_2O. The resulting crude product was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography yielded an inseparable pyranose/furanose mixture. To a solution of the crude product in MeOH (0.2 M), NaOMe (0.2 eq.)

was added portionwise. The reaction mixture was stirred for 1 h after which Amberlite IR120 H^+ was added until pH 6 was reached. The resulting suspension was filtered, concentrated under reduced pressure and co-evaporated with toluene (3x). The crude product was dissolved in DMF (0.25 M) and cooled to 0 °C. NaH (60% dispersion in mineral oil, 4 eq.) was added, and the resulting mixture was stirred for 10 minutes. Subsequently, benzyl bromide (4 eq.) or methyl iodine (4 eq.) was added, and the reaction mixture was allowed to warm up to rt. and stirred for an additional 16 h. The reaction was quenched with MeOH and diluted with H_2O, after which the resulting mixture was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure.

General procedure V: pre-activation Tf_2O/Ph_2SO based *D*-glycosylation

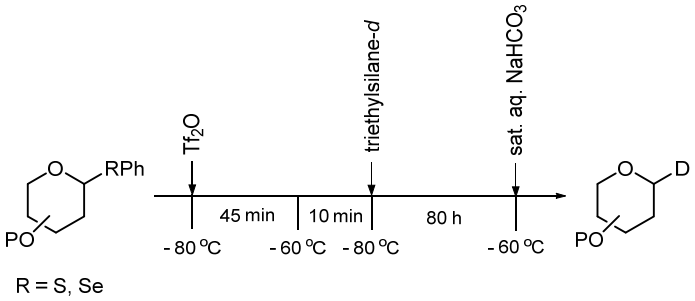


Figure 58| Schematic representation of the reaction procedure during pre-activation Ph_2SO/Tf_2O mediated glycosylation.

A solution of the donor (100 µmol), Ph_2SO (26 mg, 130 µmol, 1.3 eq.) and TTBP (62 mg, 250 µmol, 2.5 eq.) in DCM (2 mL, 0.05 M) was stirred over activated 3Å molecular sieves (rods, size 1/16 in., Sigma-Aldrich) for 30 min under an atmosphere of N_2. The solution was cooled to −80 °C and Tf_2O (22 µl, 130 µmol, 1.3 eq.) was slowly added to the reaction mixture. The reaction mixture was allowed to warm to −60 °C in approximately 45 min, followed by cooling to −80 °C and the addition of the acceptor (200 µmol, 2 eq.) in DCM (0.4 mL, 0.5 M). The reaction was allowed to warm up to −60 °C and stirred for an additional 80 h at this temperature to ensure reaction completion. The reaction was quenched with sat. aq. $NaHCO_3$ at −60 °C and diluted with DCM (5 mL). The resulting solution was washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography yielded the corresponding *D*-coupled glycoside.

General procedure VI: debenzylation of *D*-coupled pyranoses

The *D*-coupled pyranose was dissolved in MeOH (0.02 M) under an atmosphere of N_2, and Pd/C (10 mol%) was added. Subsequently, H_2 was bubbled through the reaction mixture for approximately 15 min., and the reaction was stirred for an additional 32 h. The reaction was filtered over Celite® 545 (Sigma-Aldrich) and concentrated under reduced pressure. Purification by column chromatography yielded the corresponding deprotected *D*-coupled glycoside.

General procedure VII: pre-activation Tf_2O/Ph_2SO based *D*-glycosylation in Et_2O or CH_3CN

A solution of the donor (100 µmol), Ph_2SO (26 mg, 130 µmol, 1.3 eq.) and TTBP (62 mg, 250 µmol, 2.5 eq.) in Et_2O (1.7 mL) or CH_3CN (1.7 mL) and DCM (0.7 mL) was stirred over activated 3Å molecular sieves (rods, size 1/16 in., Sigma-Aldrich) for 30 min under an atmosphere of N_2. The solution was cooled to −80 °C and Tf_2O (22 µl, 130 µmol, 1.3 eq.) was slowly added to the reaction mixture. The reaction mixture was allowed to warm to −60

°C in approximately 45 min, followed by cooling to −80 °C and the addition of the acceptor (200 µmol, 2 eq.). The reaction was allowed to warm up to −60 °C and stirred for an additional 80 h at this temperature to ensure reaction completion. The reaction was quenched with sat. aq. $NaHCO_3$ at −60 °C and diluted with DCM (5 mL). The resulting solution was washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography yielded the corresponding *D*-coupled glycoside.

General procedure VIII: TMSOTf activation based *D*-glycosylation

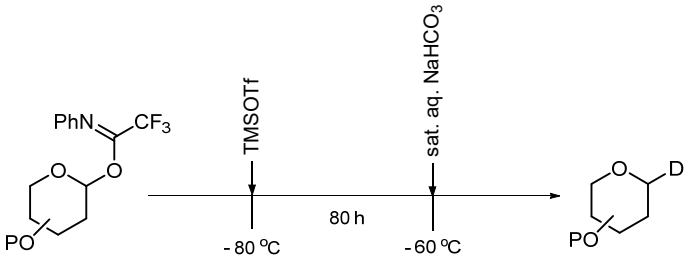
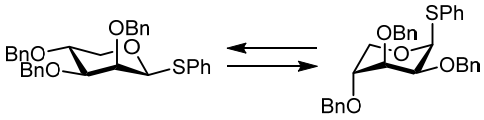


Figure 59| Schematic representation of the reaction procedure during TMSOTf activation glycosylation.

The imidate donor (100 µmol, 1 eq.) was co-evaporated twice with dry toluene and then dissolved in dry DCM (1 mL, 0.1 M). Activated 3 Å molecular sieves and the acceptor (200 µmol, 2 eq.) were added and the solution was stirred for 30 min at room temperature under an inert atmosphere (N_2). The reaction mixture was cooled to the −80 °C and a freshly prepared stock solution of TMSOTf in DCM (0.5 M) of was introduced via syringe (50 µL, 0.01 mmol, 0.1 eq.). The reaction was allowed to warm up to −60 °C and stirred for an additional 80 h, and was then quenched by the addition of sat. aq. $NaHCO_3$. The mixture was diluted with DCM and H_2O and twice extracted with DCM. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by column chromatography yielded the corresponding *D*-coupled glycoside.

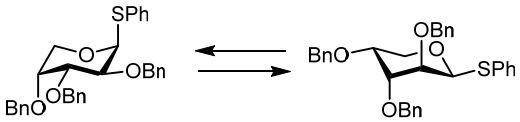
OBn-protected glycosyl donors

Preparation of Donor S6



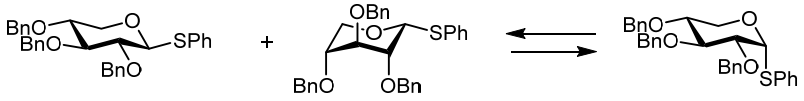
Phenyl 2,3,4-tri-*O*-benzyl-1-thio-D-lyxopyranoside (S6). The title compound was prepared according to general procedure IV from D-lyxose. Column chromatography (100:0 → 95:5, pentane:EtOAc) yielded compound **S6** (643 mg, 1.22 mmol, 52% over 5 steps, average of 88% per step, colourless solid). TLC: R_f 0.21 (pentane:EtOAc, 9.5:0.5, v:v); $[\alpha]_D^{20}$ –87.0°; IR (thin film, cm^{-1}): 693, 748, 1049, 1217, 1367, 1438, 1743; ^{1}H NMR (400 MHz, Chloroform-*d,* HH-COSY, HSQC, HMBC, HH-NOESY, HMBC-Gated): δ 7.54 – 7.15 (m, 20H, CH_{arom}), 5.30 (d, *J* = 4.0 Hz, 1H, H-1), 4.88 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.77 – 4.71 (m, 2H, CH_2 Bn), 4.68 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.55 (s, 2H, CH_2 Bn), 4.33 (dd, *J* = 12.3, 2.5 Hz, 1H, H-5), 4.18 (dd, *J* = 4.1, 2.5 Hz, 1H, H-2), 3.79 – 3.69 (m, 2H, H-3, H-4), 3.51 (dd, *J* = 12.2, 4.3 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 138.6, 138.1, 137.5 ($C_{q\text{-}arom}$), 130.6, 128.9, 128.5, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 127.7, 126.7 (CH_{arom}), 87.9 (C-1), 77.2 (C-3), 75.7 (C-2), 75.2 (C-4), 73.4, 72.9, 72.0 (CH_2 Bn), 62.1 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 87.9 ($J_{C1\text{-}H1}$= 160 Hz, 1,2-*cis*); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{36}NO_4S$ 530.23596, found 530.23568.

Preparation of Donor S7



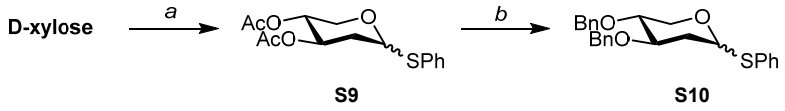
Phenyl 2,3,4-tri-*O*-benzyl-1-thio-D-arabinopyranoside (S7). The title compound was prepared according to general procedure IV from D-arabinose. Column chromatography (100:0 → 95:5, pentane:EtOAc) yielded compound **S7** (2.21 g, 4.31 mmol, 50% over 5 steps, average of 87% per step, off-white solid). TLC: R_f 0.45 (pentane:EtOAc, 9.5:0.5, v:v); $[\alpha]_D^{20}$ –49.8°; IR (thin film, cm^{-1}): 731, 775, 1026, 1042, 1082, 1125, 1452, 2862; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC, HH-NOESY, HMBC-Gated): δ 7.56 – 7.19 (m, 20H, CH_{arom}), 4.91 (d, *J* = 6.1 Hz, 1H, H-1), 4.70 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.68 – 4.61 (m, 4H, CH_2 Bn, CH_2 Bn), 4.59 (d, *J* = 12.3 Hz, 1H, CH*H* Bn), 4.26 (dd, *J* = 12.0, 5.8 Hz, 1H, H-5), 3.94 (t, *J* = 6.5 Hz, 1H, H-2), 3.82 (dt, *J* = 5.8, 2.8 Hz, 1H, H-4), 3.67 (dd, *J* = 6.9, 3.1 Hz, 1H, H-3), 3.44 (dd, *J* = 12.0, 2.6 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 138.3, 138.2, 138.1, 135.6 ($C_{q\text{-}arom}$), 131.3, 128.9, 128.5, 128.5, 128.4, 128.1, 127.9, 127.9, 127.9, 127.8, 127.1 (CH_{arom}), 87.3 (C-1), 78.6 (C-3), 77.4 (C-2), 74.3 (CH_2 Bn), 72.4 (C-4), 72.4, 71.2 (CH_2 Bn), 63.3 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 83.3 ($J_{C1\text{-}H1}$= 158 Hz, 1,2-*trans*); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{36}NO_4S$ 530.23596, found 530.23588.

Preparation of Donor S8

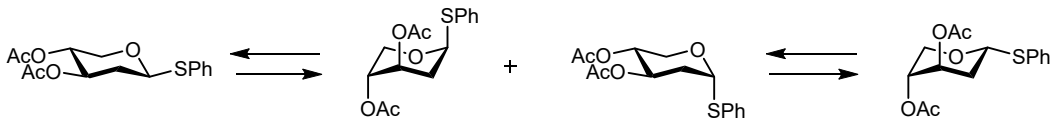


Phenyl 2,3,4-tri-*O*-benzyl-1-thio-D-xylopyranoside (S8). The title compound was prepared according to general procedure IV from D-xylose. Column chromatography (100:0 → 95:5, pentane:EtOAc) yielded compound **S8** (2.33 g, 4.40 mmol, 48% over 5 steps, average of 86% per step, yellow wax, 1,2-*cis*:1,2-*trans*; 23:77). TLC: R_f 0.42 (pentane:EtOAc, 9.5:0.5, v:v); IR (thin film, cm^{-1}): 694, 735, 1026, 1070, 1120, 1454, 2864, 3030; Data of the major stereoisomer (1,2-*trans* product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC, HH-NOESY, HMBC-Gated): δ 7.54 – 7.25 (m, 20H, CH_{arom}), 4.89 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.85 (d, *J* = 10.1 Hz, 1H, C*H*H Bn), 4.83 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.75 (d, *J* = 10.0 Hz, 1H, CH*H* Bn), 4.71 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.67 (d, *J* = 9.5 Hz, 1H, H-1), 4.62 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.09 – 4.02 (m, 1H, H-5_{eq}), 3.67 – 3.60 (m, 2H, H-3, H-4), 3.44 (t, *J* = 8.7 Hz, 1H, H-2), 3.24 (dd, *J* = 11.5, 9.6 Hz, 1H, H-5_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 138.6, 138.2, 133.8, 132.0 ($C_{q\text{-}arom}$), 129.1, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 128.0, 128.0, 127.9, 127.7 (CH_{arom}), 88.5 (C-1), 85.4 (C-3), 80.5 (C-2), 77.8 (C-4), 75.8, 75.6, 73.4 (CH_2 Bn), 67.6 (C-5); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 88.5 ($J_{C1\text{-}H1}$= 157 Hz, 1,2-*trans*); Data of the minor stereoisomer (1,2-*cis* product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC, HH-NOESY, HMBC-Gated): δ 7.47 – 7.44 (m, 20H, CH_{arom}), 5.54 (d, *J* = 4.4 Hz, 1H, H-1), 4.93 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.76 (d, *J* = 10.6 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.82 – 3.78 (m, 2H, H-2, H-3), 3.71 – 3.66 (m, 2H, H-5, H-5). 3.61 – 3.53 (m, 1H, H-4); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 138.8, 138.4, 137.9, 134.6 ($C_{q\text{-}arom}$), 131.7, 129.1, 128.6, 128.5, 128.2, 128.2, 127.9, 127.8, 127.2 (CH_{arom}), 87.5 (C-1), 81.8 (C-3), 79.6 (C-2), 77.7 (C-4), 75.9, 73.7, 72.8 (CH_2 Bn), 61.2 (C-5); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 87.5 ($J_{C1\text{-}H1}$= 165 Hz, 1,2-*cis*); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{36}NO_4S$ 530.23596, found 530.23589.

Preparation of Donor S10

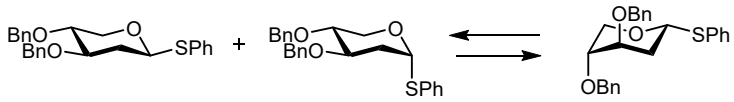


Scheme S-1. Donor **S10** synthesis. *Reagents and conditions:* a) *i.* Ac_2O, pyridine; *ii.* HBr, AcOH, DCM; *iii.* Bu_3SnH, AIBN, toluene; *iv.* PhSH, $BF_3{\cdot}OEt_2$, DCM **S9**: 69%; b) *i.* NaOMe, MeOH, *ii.* BnBr, NaH, DMF, **S10**: 92%.



Phenyl 2-deoxy-3,4-di-*O*-benzyl-1-thio-D-xylopyranoside (S9). To a suspension of L-xylose (4.46 g, 29.7 mmol) in pyridine (72 mL), Ac_2O (34 mL, 356 mmol, 12 eq.) was added dropwise at 0 °C. After stirring for an additional 16 h at rt. the mixture was concentrated *in vacuo* and co-evaporated three times with heptane. The crude product was dissolved in a mixture of DCM (55 mL) and Ac_2O (0.28 mL, 3.0 mmol, 0.1 eq.), HBr (33 wt% in AcOH, 23 mL, 127 mmol, 4.3 eq.) was added dropwise at 0 °C. The mixture was stirred for an additional 16 h at rt. and subsequently concentrated under reduced pressure. The crude product was three times co-evaporated with toluene. The crude product was dissolved in toluene (1.2 L, 0.025 M) and AIBN (0.49 g, 2.97 mmol, 0.1 eq.) was added. The reaction was stirred at 80 °C for 30 minutes and Bu_3SnH (9.6 mL, 35.6 mmol, 1.2 eq.) was added dropwise over 16 h. The reaction mixture was concentrated and column chromatography (80:20 → 70:30, pentane:EtOAc)

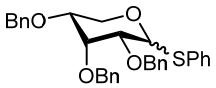
afforded the crude product. The crude product was dissolved in DCM (250 mL, 0.10 M) and cooled to −80 °C. Subsequently, thiophenol (3.4 mL, 32.7 mmol, 1.1 eq.) and $BF_3{\cdot}OEt_2$ (4.5 mL, 35.6 mmol, 1.2 eq.) were added dropwise to the solution and the reaction was allowed to warm up to rt. in 4 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$ and extracted with DCM (3x). The combined organic layers were dried with $MgSO_4$ and concentrated *in vacuo.* The residue was purified using column chromatography (pentane:EtOAc, 90:10 → 70:30) affording title compound **S9**. (6.36 g, 20.5 mmol, 69% over 4 steps, average of 91% per step, colourless oil, 1,3-*cis*:1,3-*trans*; 66:34). TLC: R_f 0.42 (pentane:EtOAc, 7:3, v:v); IR (thin film, cm^{-1}): 693, 743, 1026, 1049, 1220, 1368, 1736; Data of the major stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.65 – 7.18 (m, 5H, CH_{arom}), 5.10 (dd, *J* = 7.4, 4.0 Hz, 1H, H-1), 5.00 (td, *J* = 7.5, 4.5 Hz, 1H, H-3), 4.85 (td, *J* = 7.0, 4.0 Hz, 1H, H-4), 4.36 (dd, *J* = 12.2, 3.9 Hz, 1H, H-5), 3.49 (dd, *J* = 12.2, 6.7 Hz, 1H, H-5), 2.52 (dt, *J* = 13.9, 4.3 Hz, 1H, H-2), 2.11 (s, 3H, CH_3 Ac), 2.08 (s, 3H, CH_3 Ac), 1.95 (dt, *J* = 13.9, 7.6 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 170.1, 170.1 (C=O), 134.4 ($C_{q\text{-}arom}$), 131.8, 129.1, 127.7 (CH_{arom}), 82.8 (C-1), 69.0 (C-3), 68.5 (C-4), 63.6 (C-5), 34.1 (C-2), 21.3, 21.1 (CH_3 Ac); Data of the minor stereoisomer (1,3-*trans* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 5.33 (dd, *J* = 6.6, 3.9 Hz, 1H, H-1), 5.17 (td, *J* = 6.9, 4.2 Hz, 1H, H-3), 4.80 (td, *J* = 6.7, 4.1 Hz, 1H, H-4), 4.09 (dd, *J* = 12.2, 6.2 Hz, 1H, H-5), 3.89 (dd, *J* = 12.2, 3.7 Hz, 1H, H-5), 2.34 (ddd, *J* = 14.0, 6.6, 4.2 Hz, 1H, H-2), 2.09 (s, 3H, CH_3 Ac), 2.08 (s, 3H, CH_3 Ac); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 170.2, 169.8 (C=O), 134.2 ($C_{q\text{-}arom}$), 131.5, 127.7 (CH_{arom}), 82.2 (C-1), 68.3 (C-4), 68.2 (C-3), 63.1 (C-5), 33.9 (C-2), 21.2, 21.1 (CH_3 Ac); HRMS: $[M+Na]^+$ calcd for $C_{15}H_{18}NaO_5S$ 333.0767, found 333.0771.



Phenyl 2-deoxy-3,4-di-*O*-benzyl-1-thio-D-xylopyranoside (S10). Compound **S9** (150 mg, 0.48 mmol) was dissolved in MeOH (4.8 mL, 0.1 M) and subsequently NaOMe (2.6 mg, 48 µmol 0.1 eq.) was added portionwise. The reaction mixture was stirred for 1 h after which Amberlite IR120 H^+ was added until pH 6 was reached. The resulting suspension was filtered, concentrated under reduced pressure and co-evaporated with toluene (3x). The crude product was dissolved in DMF (4.8 mL, 0.1 M) and cooled to 0 °C. benzyl bromide (0.14 mL, 1.2 mL, 2.4 eq.) was added, and subsequently, NaH (60% dispersion in mineral oil, 46 mg, 1.2 mmol, 2.4 eq.) was added. The reaction mixture was allowed to warm up to rt. and stirred for an additional 16 h. The reaction was quenched with MeOH and diluted with H_2O, after which the resulting mixture was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (95:5 → 85:15, pentane:EtOAc) gave the title compound **S10** (180 mg, 0.44 mmol, 92%, over 2 steps, average of 97% per step, colourless oil, 1,3-*cis*:1,3-*trans*; 62:38). TLC: R_f 0.31 (pentane:EtOAc, 8:2, v:v); IR (thin film, cm^{-1}): 694, 695, 735, 1026, 1077, 1089, 1206, 1440, 1454, 1480, 2846; Data of the major stereoisomer (1,3-*cis* product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.53 – 7.17 (m, 15H, CH_{arom}), 4.96 (dd, *J* = 8.9, 3.3 Hz, 1H, H-1), 4.72 (dd, *J* = 11.8, 3.3 Hz, 1H, C*H*H Bn), 4.65 – 4.55 (m, 3H, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.21 (dd, *J* = 11.9, 4.1 Hz, 1H, H-5_{eq}), 3.65 (ddd, *J* = 8.8, 7.1, 4.6 Hz, 1H, H-3), 3.51 (ddd, *J* = 14.2, 7.3, 4.0 Hz, 1H, H-4), 3.36 (dd, *J* = 11.9, 7.9 Hz, 1H, H-5_{ax}), 2.47 (ddd, *J* = 13.5, 4.6, 3.3 Hz, 1H, H-2_{eq}), 1.86 (dt, *J* = 13.5, 8.8 Hz, 1H, H-2_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.4, 138.4, 135.0 ($C_{q\text{-}arom}$), 131.3, 129.0, 128.6, 128.6, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.3, 127.2 (CH_{arom}), 83.2 (C-1), 77.1 (C-3), 76.5 (C-4), 72.8, 71.9 (CH_2 Bn), 65.5 (C-5), 35.2 (C-2); Data of the minor stereoisomer (1,3-*trans* product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 5.43 (t, *J* = 4.7 Hz, 1H, H-1), 4.04 (dd, *J* = 11.9, 7.4 Hz, 1H, H-5), 3.83 (dd, *J* = 11.9, 4.0 Hz, 1H, H-3), 2.35 (ddd, *J* = 13.7, 5.2, 4.3 Hz, 1H, H-2), 2.04 (ddd, *J* = 13.2, 8.6, 4.4 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.5, 138.5, 134.9 ($C_{q\text{-}arom}$), 83.0 (C-1), 76.3 (C-3),

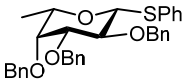
75.6 (C-4), 72.5, 72.0 (CH_2 Bn), 63.1 (C-5), 34.9 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{25}H_{26}O_3SNa$ 429.1495, found 429.1499.

Preparation of Donor S11



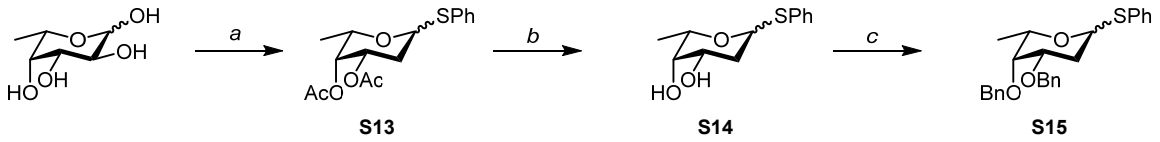
Phenyl 2,3,4-tri-*O*-benzyl-1-thio-D-ribopyranoside (S11). The title compound was prepared according to general procedure IV from D-ribose. Column chromatography (95:5 → 90:10, pentane:EtOAc) yielded compound **S11** (1.02 g, 2.00 mmol, 25% over 5 steps, average of 76% per step yellow oil, 1,2-*cis*:1,2-*trans*; 32:68). TLC: R_f 0.39, 0.54 (pentane:EtOAc, 9.5:0.5, v:v); IR (thin film, cm^{-1}): 694, 735, 1026, 1060, 1087, 1454, 2873, 2926; Data of the major stereoisomer (1,2-*trans* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC, HH-NOESY, HMBC-Gated): δ 7.55 – 7.19 (m, 20H, CH_{arom}), 5.22 (d, J = 9.0 Hz, 1H, H-1), 4.81 (s, 2H, CH_2 Bn), 4.61 – 4.54 (m, 4H, CH_2 Bn, CH_2 Bn), 4.13 (t, J = 2.5 Hz, 1H, H-3), 3.90 – 3.83 (m, 2H, H-5_{ax}, H-5_{eq}), 3.52 (ddd, J = 8.3, 5.9, 2.3 Hz, 1H, H-4), 3.33 (dd, J = 9.1, 2.5 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.9, 138.2, 137.9 ($C_{q\text{-}arom}$), 133.9, 131.8, 128.9, 128.6, 128.5, 128.3, 128.1, 128.0, 127.6 (CH_{arom}), 84.4 (C-1), 77.8 (C-2), 75.3 (C-4), 74.4 (C-3), 74.1, 72.4, 71.5 (CH_2 Bn), 64.6 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 84.4 ($J_{C1\text{-}H1}$ = 161 Hz); Data of the minor stereoisomer (1,2-*cis* isomer product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC, HH-NOESY, HMBC-Gated): δ 7.56 – 7.18 (m, 20H, CH_{arom}), 5.46 (d, J = 5.5 Hz, 1H, H-1), 5.03 (d, J = 12.4 Hz, 1H, C*H*H Bn), 4.89 (d, J = 12.5 Hz, 1H, CH*H* Bn), 4.71 (d, J = 11.9 Hz, 1H, C*H*H Bn), 4.61 (d, J = 11.7 Hz, 1H, C*H*H Bn), 4.51 (m, 1H, C*H*H Bn), 4.45 (d, J = 12.1 Hz, 1H, CH*H* Bn), 4.40 (t, J = 10.8 Hz, 1H, H-5_{ax}), 4.16 (d, J = 2.5 Hz, 1H, H-3), 3.70 (dd, J = 5.5, 2.2 Hz, 1H, H-2), 3.63 (dd, J = 10.9, 5.0 Hz, 1H, H-5_{eq}), 3.49 – 3.44 (m, 1H, H-4); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 139.1, 138.6 , 138.2, 137.9 ($C_{q\text{-}arom}$), 131.1, 128.9, 128.6, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6, 127.6, 127.3, 126.8 (CH_{arom}), 87.0 (C-1), 77.0 (C-2), 74.4 (C-4), 74.0 (C-3), 74.0, 71.2, 70.9 (CH_2 Bn), 58.2 (C-5); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 87.0 ($J_{C1\text{-}H1}$ = 162 Hz); HRMS: $[M+NH_4]^+$ calcd for $C_{32}H_{36}NO_4S$ 530.23596, found 530.23579.

Preparation of Donor S12

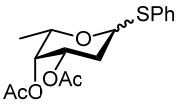


Phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside (S12). Compound **S12** was obtained from L-fucose, according to a literature procedure.[Chervin, S. M., Lowe, J. B. & Koreeda, M. Synthesis and Biological Evaluation of a New Sialyl Lewis X Mimetic Derived from Lactose. *J. Org. Chem.* 67, 5654–5662 (2002).] TLC: R_f 0.53 (pentane:Et_2O, 8:2, v:v); IR (thin film, cm^{-1}): 736, 868, 1043, 1053, 1059, 1441, 1479, 1584, 2855, 2897; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.65 – 7.16 (m, 20H, CH_{arom}), 5.01 (d, J = 11.6 Hz, 1H, C*H*H Bn), 4.79 (d, J = 10.2 Hz, 1H, CH*H* Bn), 4.75 – 4.64 (m, 4H, CH_2 Bn, CH_2 Bn), 4.60 (d, J = 9.6 Hz, 1H, H-1), 3.93 (t, J = 9.4 Hz, 1H, H-2), 3.64 (dd, J = 2.9, 0.9 Hz, 1H, H-4), 3.59 (dd, J = 9.2, 2.8 Hz, 1H, H-3), 3.53 (qd, J = 6.4, 1.0 Hz, 1H, H-5), 1.27 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.9, 138.5, 138.5 ($C_{q\text{-}arom}$), 134.5, 131.6, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 127.8, 127.7, 127.6, 127.1 (CH_{arom}), 87.7 (C-1), 84.7 (C-3), 77.3 (C-2), 76.8 (C-4), 75.7 (CH_2 Bn), 74.8 (C-5), 74.7, 73.0 (CH_2 Bn), 17.5 (CH_3); HRMS: $[M+H]^+$ calcd for $C_{33}H_{35}O_4S$ 527.22506, found 527.22479.

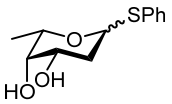
Preparation of Donor S15



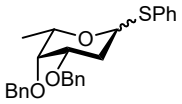
Scheme S-2. Donor **S15** synthesis. *Reagents and conditions:* a) *i.* Ac_2O, pyridine; *ii.* HBr, AcOH, DCM; *iii.* Bu_3SnH, AIBN, toluene; *iv.* PhSH, $BF_3{\cdot}OEt_2$, DCM, **S13**: 61%; b) NaOMe, MeOH, **S14**: 97%; c) BnBr, NaH, DMF, **S15**: 92%.



Phenyl 2-deoxy-3,4-di-*O*-acetyl-1-thio-L-fucopyranoside (S13). To a suspension of L-fucose (928 mg, 5.7 mmol) in pyridine (2.5 mL), Ac_2O (5 mL, 53 mmol, 12 eq.) was added dropwise at 0 °C. After stirring for an additional 16 h at rt. the mixture was concentrated *in vacuo* and co-evaporated three times with heptane. The crude product was dissolved in a mixture of DCM (4 mL) and Ac_2O (0.25 mL, 2.6 mmol, 0.5 eq.), HBr (33 wt% in AcOH, 1.6 mL, 9.9 mmol, 1.8 eq.) was added dropwise at 0 °C. The mixture was stirred for an additional 4 h at rt. and subsequently concentrated under reduced pressure. The crude product was dissolved in toluene (500 mL, 0.01 M) and AIBN (123 mg, 0.75 mmol, 0.1 eq.) was added. The reaction was stirred at 80 °C for 30 minutes and Bu_3SnH (3 mL, 11.3 mmol, 2 eq.) was added dropwise over 16 h. The reaction mixture was concentrated and column chromatography (90:10 → 80:20, pentane:EtOAc) afforded the crude product. The crude product was dissolved in DCM (40 mL, 0.15 M) and cooled to –80 °C. Subsequently, thiophenol (0.6 mL, 5.9 mmol, 1.05 eq.) and $BF_3{\cdot}OEt_2$ (0.79 mL, 6.2 mmol, 1.1 eq.) were added dropwise to the solution and the reaction was allowed to warm up to rt. in 4 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$ and extracted with DCM (3x). The combined organic layers were dried with $MgSO_4$ and concentrated *in vacuo.* The residue was purified using column chromatography (pentane:EtOAc, 90:10 → 70:30) affording title compound **S13**. (1.43 g, 3.4 mmol, 61% over 4 steps, average of 85% per step, colourless oil, 1,3-*cis*:1,3-*trans*; 20:80). TLC: R_f 0.45 (pentane:EtOAc, 8:2, v:v); IR (thin film, cm^{-1}): 884, 1024, 1060, 1224, 1366, 1440, 1480, 1742; Data of the major stereoisomer (1,3-*trans* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.55 – 7.22 (m, 5H, CH_{arom} SPh), 5.74 (d, *J* = 5.7 Hz, 1H, H-1), 5.28 (ddd, *J* = 12.6, 4.9, 3.0 Hz, 1H, H-3), 5.23 (d, *J* = 3.1 Hz, 1H, H-4), 4.56 (dt, *J* = 7.5, 6.0 Hz, 1H, H-5), 2.46 (td, *J* = 12.9, 5.9 Hz, 1H, H-2), 2.16 (s, 3H, CH_3 Ac), 2.10 – 2.02 (m, 1H, H-2), 2.01 (s, 3H, CH_3 Ac), 1.15 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 170.8, 170.1 (C=O Ac), 131.1, 129.1, 127.3 (C_{arom} SPh), 83.8 (C-1), 69.8 (C-3), 67.4 (C-4), 65.9 (C-5), 30.7 (C-2), 20.9 (CH_3 Ac), 16.6 (C-6); Data of the minor stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.55 – 7.22 (m, 5H, CH_{arom} SPh), 5.13 (d, *J* = 3.2 Hz, 1H, H-4), 5.01 (ddd, *J* = 10.1, 7.4, 3.1 Hz, 1H, H-3), 4.83 (dd, *J* = 8.3, 5.8 Hz, 1H, H-1), 3.73 (qd, *J* = 6.3, 0.9 Hz, 1H, H-5), 2.16 (s, 3H, CH_3 Ac), 2.12 – 2.02 (m, 2H, H-2, H-2), 2.00 (s, 3H, CH_3 Ac), 1.24 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 131.8, 129.0, 127.7 (C_{arom} SPh), 82.5 (C-1), 73.4 (C-5), 70.0 (C-3), 68.7 (C-4), 31.5 (C-2), 21.1 (CH_3 Ac), 17.1 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{16}H_{20}NaO_5S$ 347.0929, found 347.0925.



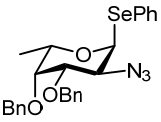
Phenyl 2-deoxy-1-thio-L-fucopyranoside (S14). Compound **S13** (243 mg, 0.75 mmol) was dissolved in MeOH (3 mL, 0.25 M), NaOMe (8 mg, 750 μmol, 0.1 eq.) was added portionwise to the stirred solution. After 4 h of stirring the reaction was quenched with Amberlite IR120 H^+. Filtration followed by column chromatography (50:50 → 20:80, pentane:EtOAc) afforded the title compound **S14** (0.78 g, 3.3 mmol, 97%, white solid, 1,3-*cis*:1,3-*trans*; 20:80). TLC: R_f 0.43 (pentane:EtOAc, 2:8, v:v); IR (neat, cm^{-1}): 733, 876, 968, 1092, 1165, 1373, 1585, 2882, 3348; Data of the major stereoisomer (1,3-*trans* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.56 – 7.17 (m, 5H, CH_{arom}), 5.65 (d, *J* = 5.7 Hz, 1H, H-1), 4.03 (ddd, *J* = 12.1, 5.3, 3.2 Hz, 1H, H-3), 3.79 – 3.53 (m, 2H, H-4, H-5), 2.84 – 2.29 (m, 2H, 3-OH, 4-OH), 2.29 – 2.04 (m, 1H, H-2), 2.18 – 1.70 (m, 1H, H-2), 1.28 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 135.1 ($C_{q\text{-}arom}$), 131.6, 131.1, 129.1, 127.2 (CH_{arom}), 84.0 (C-1), 71.4 (C-4), 67.0 (C-5), 66.7 (C-3), 33.6 (C-2), 16.8 (CH_3). Data of the minor stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.56 – 7.17 (m, 5H, CH_{arom}), 4.72 (dd, *J* = 12.0, 2.2 Hz, 1H, H-1'), 4.43 (q, *J* = 6.8 Hz, 1H, H-5'), 3.79 – 3.53 (m, 2H, H-3', H-4'), 2.84 – 2.29 (m, 2H, 3-OH, 4-OH), 2.29 – 2.04 (m, 1H, H-2), 2.18 – 1.70 (m, 1H, H-2), 1.35 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 134.0 ($C_{q\text{-}arom}$), 131.6, 129.1, 129.0, 127.6 (CH_{arom}), 82.5 (C-1), 74.8 (C-4), 70.6 (C-5), 69.8 (C-3), 34.7 (C-2), 17.3 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{12}H_{16}NaO_3S$ 263.0719, found 263.0717.



Phenyl 2-deoxy-3,4-di-*O*-benzyl-1-thio-L-fucopyranoside (S15). Compound **S14** (120 mg, 0.5 mmol) was dissolved in DMF (2.5 mL, 0.25 M) and cooled to 0 °C. NaH (60% dispersion in mineral oil, 44 mg, 1.1 mmol, 2.2 eq.) was added portionwise and the resulting mixture was stirred for 15 minutes. Subsequently, benzyl bromide (131 μL, 1.1 mmol, 2.2 eq.) was added and the reaction mixture was allowed to warm up to rt. and stirred for an additional 16 h. The reaction was quenched with MeOH and diluted with H_2O, after which the resulting mixture was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (95:5 → 85:15, pentane:Et_2O) gave the title compound **S15** (194 mg, 0.46 mmol, 92%, white solid, 1,3-*cis*:1,3-*trans*; 39:61). TLC: R_f 0.42 and 0.62 (pentane:Et_2O, 9:1, v:v); IR (thin film, cm^{-1}): 691, 733, 957, 1026, 1057, 1099, 1362, 2866; Data of the major stereoisomer (1,3-*trans* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.63 – 7.16 (m, 15H, CH_{arom}), 5.76 (d, *J* = 5.6 Hz, 1H, H-1), 4.98 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.71 (m, 1H, CH*H* Bn) 4.66 (d, *J* = 12.8 Hz, 1H, C*H*H Bn), 4.62 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.27 (q, *J* = 6.5 Hz, 1H, H-5), 3.91 (ddd, *J* = 12.3, 4.4, 2.5 Hz, 1H, H-3), 3.70 – 3.63 (m, 1H, H-4), 2.60 (td, *J* = 12.7, 5.8 Hz, 1H, H-2_{ax}), 2.16 (dd, *J* = 13.0, 4.5 Hz, 1H, H-2_{eq}), 1.19 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.9, 138.4, 135.7 ($C_{q\text{-}arom}$), 131.3, 130.6, 129.0, 128.8, 128.6, 128.4, 128.3, 127.8, 127.5 (CH_{arom}), 84.4 (C-1), 76.1 (C-3/C-4), 76.0 (C-3/C-4), 74.6 (CH_2 Bn), 70.6 (CH_2 Bn), 68.0 (C-5), 31.7 (C-2), 17.3 (CH_3); Data of the minor stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 4.98 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.74 – 4.68 (m, 1H, H-1), 4.69 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.57 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 3.59 (ddd, *J* = 11.5, 4.6, 2.5 Hz, 1H, H-3), 3.54 (dt, *J* = 2.5, 1.2 Hz, 1H, H-4), 3.46 (q, *J* = 5.7 Hz, 1H, H-5), 2.28 (q, *J* = 11.9 Hz, 1H, H-2_{ax}), 2.20 – 2.10 (m, 1H, H-2_{eq}), 1.26 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 139.0, 138.4 ($C_{q\text{-}arom}$), 134.7, 131.3, 128.8, 128.6, 128.3, 128.2, 127.7, 127.5, 127.4, 127.1, 127.0,

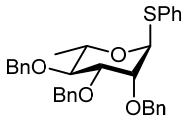
126.8 (CH_{arom}), 82.7 (C-1), 79.0 (C-3), 75.1 (C-5), 74.6 (C-4), 74.3 (CH_2 Bn), 70.3 (CH_2 Bn), 68.0 (CH_2 Bn), 32.1 (C-2), 17.8 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{26}H_{28}NaO_3S$ 443.1657, found 443.1651.

Preparation of Donor S16



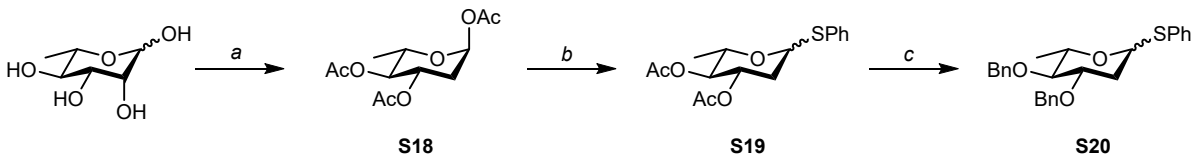
Phenyl 2-azido-2-deoxy-3,4-di-*O*-benzyl-1-seleno-β-L-fucopyranoside (S16). Compound **S16** was obtained from L-fucose, according to a literature procedure.[Hagen, B., Ali, S., Overkleeft, H. S., van der Marel, G. A. & Codée, J. D. C. Mapping the Reactivity and Selectivity of 2-Azidofucosyl Donors for the Assembly of N-Acetylfucosamine-Containing Bacterial Oligosaccharides. *J. Org. Chem.* 82, 848–868 (2017).] TLC: R_f 0.68 (pentane:Et_2O, 8:2, v:v); IR (thin film, cm^{-1}): 694, 737, 1064, 1105, 1454, 1744, 2106, 2855, 2922; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.63 – 7.18 (m, 15H, CH_{arom}), 5.93 (d, *J* = 5.3 Hz, 1H, H-1), 4.93 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.78 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.75 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.60 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.35 (dd, *J* = 9.9, 5.3 Hz, 1H, H-2), 4.22 (q, *J* = 6.5 Hz, 1H, H-5), 3.75 – 3.69 (m, 2H, H-3, H-4), 1.13 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.3, 137.6, 134.5 ($C_{q\text{-}arom}$), 129.1, 128.7, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8 (CH_{arom}), 85.7 (C-1), 80.8 (C-3), 75.9 (C-4), 75.1, 72.7 (CH_2 Bn), 69.5 (C-5), 61.1 (C-2), 16.7 (CH_3); HRMS: $[M\text{-}N_2+NH_4]^+$ calcd for $C_{26}H_{28}NO_3Se$ 482.12289, found 482.12287.

Preparation of Donor S17

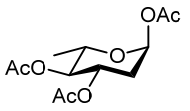


Phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-rhamnopyranoside (S17). Compound **S17** was obtained from L-rhamnose, according to a literature procedure.[Tanikawa, T. *et al.* Using Biological Performance Similarity To Inform Disaccharide Library Design. *J. Am. Chem. Soc.* 131, 5075–5083 (2009).] TLC: R_f 0.63 (pentane:Et_2O, 8:2, v:v); IR (thin film, cm^{-1}): 692, 732, 843, 908, 1024, 1070, 1082, 1205, 1452, 2868; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.48 – 7.10 (m, 20H, CH_{arom}), 5.49 (d, *J* = 1.6 Hz, 1H, H-1), 4.97 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.72 (d, *J* = 12.4 Hz, 1H, C*H*H Bn), 4.68 – 4.58 (m, 4H, CH_2 Bn, CH_2 Bn), 4.14 (dq, *J* = 9.3, 6.2 Hz, 1H, H-5), 3.99 (dd, *J* = 3.1, 1.7 Hz, 1H, H-2), 3.83 (dd, *J* = 9.3, 3.1 Hz, 1H, H-3), 3.68 (t, *J* = 9.3 Hz, 1H, H-4), 1.35 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.6, 138.3, 138.0, 134.8 ($C_{q\text{-}arom}$), 131.4, 129.1, 128.5, 128.5, 128.1, 128.1, 127.9, 127.9, 127.8, 127.4 (CH_{arom}), 85.9 (C-1), 80.6 (C-4), 80.1 (C-3), 76.6 (C-2), 75.6, 72.2, 72.2 (CH_2 Bn), 69.4 (C-5), 18.1 (CH_3); HRMS: $[M+H]^+$ calcd for $C_{33}H_{35}O_4S$ 527.22506, found 527.22483.

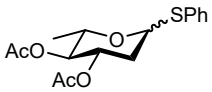
Preparation of Donor S20



Scheme S-3. Donor **S20** synthesis. *Reagents and conditions:* a) *i.* Ac_2O, pyr; *ii.* HBr, AcOH, DCM; *iii.* $CuSO_4{\cdot}5H_2O$, Ac_2O, NaOAc, AcOH, Zn; *iv.* Ac_2O, HBr, AcOH, **S18**: 60%; b) PhSH, $BF_3{\cdot}Et_2O$, DCM, **S19**: 97%; c) *i.* NaOMe, MeOH, *ii.* BnBr, NaH, DMF, **S20**: 95%.

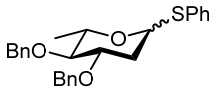


2-deoxy-1,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (S18). To suspension of L-rhamnose (4.5 g, 27.5 mmol) in pyridine (25 mL), Ac_2O (32 mL, 340 mmol, 12 eq.) at 0 °C. After stirring for an additional 16 h at rt. the mixture was concentrated *in vacuo* and co-evaporated three times with heptane. The resulting colourless oil was used in the next step without further purification. The crude product was dissolved in DCM (18 mL), followed by the addition of Ac_2O (1.0 mL, 11 mmol, 0.4 eq.). To the solution HBr (33 wt% in AcOH, 8.5 mL, 55.0 mmol, 2.0 eq.) was added dropwise at 0 °C and stirred for an additional 4 h at rt. The mixture was then concentrated under reduced pressure and the yellow oil was used as a crude product in the next step. Copper sulfate pentahydrate (0.88 g), Ac_2O (3.6 mL, 38 mmol, 1.4 eq.), sodium acetate (4.5 g, 55 mmol, 2 eq.), AcOH (3.2 mL) were suspended in acetonitrile (12 mL), and subsequently Zn (dust, 3.6 g, 55 mmol, 2 eq.) was added. After 45 minutes of stirring the rhamnosyl bromide was added in 60 mL acetonitrile via a dropping funnel over 40 minutes. The reaction was allowed to stir for an additional 2 h. After reaction completion the mixture was diluted with DCM and filtrated over Celite® 545 (Sigma-Aldrich) and transferred to a separatory funnel. The organic phase was washed with saturated sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated *in vacuo*. The crude rhamnal was dissolved in DCM (40 mL) and AcOH (15.8 mL, 276 mmol, 10 eq.), Ac_2O (22.2 mL, 233 mmol, 8.5 eq.) were added at 0 °C. After 15 min stirring, HBr (33 wt% in AcOH, 1.5 mL, 9.1 mmol, 0.3 eq.) was dropwise added at 0 °C and the reaction was stirred for an additional 5 h. After reaction completion the mixture was diluted with ice-cold water and extracted DCM (3x). The combined organic layers were washed with sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated *in vacuo*. Column chromatography (95:5 → 85:15, pentane:EtOAc) gave the title compound **S18** (4.5 g, 16.4 mmol, 60% over 4 steps, average of 88% per step, white solid). TLC: R_f 0.26 (pentane:EtOAc, 8:2, v:v); IR (neat, cm^{-1}): 922, 1037, 1134, 1157, 1369, 1732, 2994; ^1H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 6.19 (dd, *J* = 3.8, 1.4 Hz, 1H, H-1), 5.27 (ddd, *J* = 11.6, 9.5, 5.3 Hz, 1H, H-3), 4.80 (t, *J* = 9.7 Hz, 1H, H-4), 3.94 (dq, *J* = 9.8, 6.2 Hz, 1H, H-5), 2.26 (ddd, *J* = 13.5, 5.3, 1.5 Hz, 1H, H-2), 2.12 (s, 3H, CH_3 Ac), 2.07 (s, 3H, CH_3 Ac), 2.03 (s, 3H, CH_3 Ac), 1.92 (ddd, *J* = 13.5, 11.7, 3.7 Hz, 1H, H-2), 1.19 (d, *J* = 6.3 Hz, 3H, CH_3); ^{13}C NMR (126 MH, $CDCl_3$, HSQC): δ 170.4, 170.1, 169.3 (C=O, Ac), 90.9 (C-1), 74.2 (C-4), 68.5 (C-3), 68.3 (C-5), 34.3 (C-2), 21.2 (CH_3 Ac), 21.1 (CH_3 Ac), 20.9 (CH_3 Ac), 17.7 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{12}H_{18}NaO_7$ 297.0950, found 297.0951.



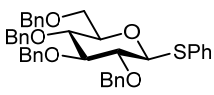
Phenyl 2-deoxy-3,4-di-*O*-acetyl-1-thio-L-rhamnopyranoside (S19). Compound **S18** (400 mg, 1.46 mmol) was dissolved in DCM (10 mL, 0.15M), and thiophenol (0.20 mL, 1.90 mmol, 1.3 eq.) was added, followed by the dropwise addition of $BF_3{\cdot}OEt_2$ (0.21 mL, 1.63 mmol, 1.1 eq.) at −80 °C. The reaction mixture was allowed to warm to room temperature in approximately 4 h. After 4 h, the reaction mixture quenched with sat. aq. $NaHCO_3$. The water layer was extracted with DCM (2x). The combined organic layer layers were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$ and concentrated *in vacuo*. Column chromatography (95:5 → 85:15, pentane:EtOAc) gave the title compound **S19** (460 mg, 1.42 mmol, 97%, colourless oil, 1,3-*cis*:1,3-*trans*; 36:64). TLC: R_f 0.52 (pentane:EtOAc, 8:2, v:v); IR (thin film, cm^{-1}): 741, 910, 1049, 1219, 1366, 1740, 2982; Data of the major stereoisomer (1,3-*trans* product): ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.56 – 7.20 (m, 5H, CH_{arom} SPh), 5.60 (d, *J* = 5.6 Hz, 1H, H-1), 5.26 (ddd, *J* = 11.8, 9.3, 5.2 Hz, 1H, H-3), 4.83 – 4.71 (m, 1H, H-4), 4.37 (dq, *J* = 9.6, 6.2 Hz, 1H, H-5), 2.45 (ddd, *J* = 13.4, 5.2, 1.2 Hz, 1H, H-2_{eq}), 2.20 (ddd, *J* = 13.4, 11.8, 5.9 Hz, 1H, H-2_{ax}), 2.08 (s, 3H, Ac CH_3), 2.03 (s, 3H, Ac CH_3), 1.19 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 170.35, 170.31 (C=O, Ac), 134.67 ($C_{q\text{-}arom}$), 133.02, 132.41, 131.34, 129.14, 129.07, 127.41

(CH_{arom}), 83.14 (C-1), 74.91 (C-4), 69.45 (C-3), 66.90 (C-5), 36.01 (CH_3 Ac), 21.15 (CH_3 Ac), 21.01 (CH_3 Ac), 17.57 (CH_3); Data of the minor stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 4.98 (ddd, *J* = 11.4, 9.5, 5.4 Hz, 1H, H-3), 3.52 (dq, *J* = 9.6, 6.2 Hz, 1H, H-4), 2.05 (s, 3H, Ac CH_3), 2.01 (s, 3H, Ac CH_3), 1.83 (dt, *J* = 12.7, 11.6 Hz, 1H, Ac CH_3), 1.26 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 170.50, 170.21 (C=O, Ac), 81.69 (C-1), 74.46 (C-5), 73.89 (C-4), 71.88 (C-3), 36.69 (CH_3 Ac), 21.10 (CH_3 Ac), 20.98 (CH_3 Ac), 18.05 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{16}H_{20}NaO_5S$ 347.0929, found 347.0928.



Phenyl 2-deoxy-3,4-di-*O*-benzyl-1-thio-L-rhamnopyranoside (S20). Compound **S19** (400 mg, 1.2 mmol) was dissolved in MeOH (6 mL, 0.2 M), and NaOMe (7 mg, 120 μmol, 0.1 eq.) was added. The reaction mixture was stirred for 4 h, and subsequently quenched with Amberlite IR120 H^+ and filtrated. The resulting filtrate was concentrated *in vacuo.* The crude product was dissolved in DMF (6 mL, 0.2 M) and cooled to 0 ºC, and NaH (60% dispersion in mineral oil, 109 mg, 2.7 mmol, 2.2 eq.). The resulting suspension was stirred for 15 minutes, and benzyl bromide (323 μL, 2.7 mmol, 2.2 eq.) was dropwise added. The reaction mixture was allowed to warm up to rt. and stirred for an additional 16 h. The reaction was quenched with MeOH and diluted with H_2O. The resulting reaction mixture was extracted with Et_2O (3x), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (95:5 → 85:15, pentane:Et_2O) gave the title compound **S20** (495 mg, 1.18 mmol, 95%, white solid, 1,3-*cis*:1,3-*trans*; 35:65). TLC: R_f 0.46 and 0.59 (pentane:Et_2O, 9:1, v:v); IR (thin film, cm^{-1}): 694, 737, 995, 1072, 2866; Data of the major stereoisomer (1,3-*trans* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.54 – 7.14 (m, 15H, CH_{arom}), 5.58 (dd, *J* = 5.8, 1.3 Hz, 1H, H-1), 4.96 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.70 – 4.64 (m, 4H, CH*H* Bn, CH_2 Bn), 4.23 (dq, *J* = 9.4, 6.2 Hz, 1H, H-5), 3.94 (ddd, *J* = 11.5, 8.6, 4.8 Hz, 1H, H-3), 3.17 (t, *J* = 9.0 Hz, 1H, H-4), 2.47 (ddd, *J* = 13.2, 4.7, 1.3 Hz, 1H, H-2_{eq}), 2.09 (ddd, *J* = 13.4, 11.6, 5.7 Hz, 1H, H-2_{ax}), 1.29 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.6, 138.5 ($C_{q\text{-}arom}$), 131.3, 129.0, 128.6, 128.5, 128.1, 127.9, 127.2 (CH_{arom}), 84.5 (C-4), 83.9 (C-1), 77.8 (C-3), 75.4 (CH_2 Bn), 72.0 (CH_2 Bn), 68.5 (C-5), 36.7 (C-2), 18.2 (CH_3); Data of the minor stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 4.94 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.73 (dd, *J* = 11.9, 2.0 Hz, 1H, H-1), 4.61 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 3.65 (ddd, *J* = 11.1, 8.7, 5.2 Hz, 1H, H-3), 3.39 (dq, *J* = 9.3, 6.1 Hz, 1H, H-5), 3.15 (t, *J* = 9.0 Hz, 1H, H-4), 1.79 (dt, *J* = 12.8, 11.6 Hz, 1H, H-2_{ax}), 1.36 (d, *J* = 6.2 Hz, 1H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.5, 138.3 ($C_{q\text{-}arom}$), 134.2, 131.4, 129.0, 128.2, 127.9, 127.5 (CH_{arom}), 83.5 (C-4), 82.0 (C-1), 80.6 (C-3), 75.8 (C-5), 75.5 (CH_2 Bn), 71.8 (CH_2 Bn), 37.3 (C-2), 18.6 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{26}H_{28}NaO_3S$ 443.1657, found 443.1651.

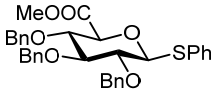
Preparation of Donor S21



Phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (S21). Compound **S21** was obtained from D-glucose, according to a literature procedure.[Dinkelaar, J. *et al.* Stereodirecting Effect of the Pyranosyl C-5 Substituent in Glycosylation Reactions. *J. Org. Chem.* 74, 4982–4991 (2009)] TLC: R_f 0.73 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ = 15.2° (*c* 1, DCM); IR (thin film, cm^{-1}): 714, 781, 1063, 1359, 1453, 2858, 2922; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.68 – 7.09 (m, 25H, CH_{arom}), 4.90 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.89 (d, *J* = 10.3 Hz, 1H, C*H*H Bn), 4.84 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.82 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.73 (d, *J* = 10.3 Hz, 1H

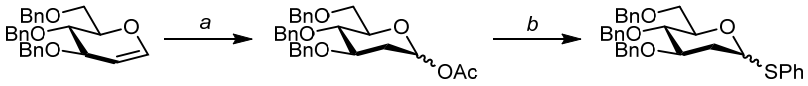
CH*H* Bn), 4.67 (dd, *J* = 9.8, 0.9 Hz, 1H, H-1), 4.61 (d, *J* = 12.0 Hz, 1H C*H*H Bn), 4.59 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 4.54 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 3.79 (dd, *J* = 10.9, 1.9 Hz, 1H, H-6), 3.75 – 3.61 (m, 3H, H-3, H-4, H-6), 3.55 – 3.47 (m, 2H, H-2, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.5, 138.4, 138.2, 134.0 ($C_{q\text{-}arom}$), 132.1, 129.0, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6 (CH_{arom}), 87.6 (C-1), 86.9 (C-3), 81.0 (C-5), 79.2 (C-2), 78.0 (C-4), 76.0, 75.6, 75.2, 73.6 (CH_2 Bn), 69.2 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{40}H_{40}NaO_5S$ 655.2494, found 655.2496.

Preparation of Donor S22



Methyl (phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranosyl uronate) (S22). Compound **S22** was obtained from D-glucose, according to a literature procedure.[Dinkelaar, J. *et al.* Stereodirecting Effect of the Pyranosyl C-5 Substituent in Glycosylation Reactions. *J. Org. Chem.* 74, 4982–4991 (2009)] TLC: R_f 0.56 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 697, 738, 1026, 1073, 1209, 1439, 1453, 1750, 2856, 2924; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.71 – 7.08 (m, 20H, CH_{arom}), 4.88 (d, *J* = 10.3 Hz, 1H, C*H*H Bn), 4.88 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.84 (d, *J* = 10.9 Hz, 1H, CH*H* Bn), 4.78 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.73 (d, *J* = 10.2 Hz, 1H, CH*H* Bn), 4.68 (d, *J* = 9.8 Hz, 1H, H-1), 4.61 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 3.92 (d, *J* = 9.7 Hz, 1H, H-5), 3.84 (t, *J* = 9.4 Hz, 1H, H-4), 3.73 (s, 3H, CH_3 COOMe), 3.71 (t, *J* = 8.9 Hz, 1H, H-3), 3.52 (dd, *J* = 9.8, 8.7 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 168.8 (C=O), 138.2, 137.9, 137.8, 133.3 ($C_{q\text{-}arom}$), 132.3, 129.1, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 128.0, 127.9 (CH_{arom}), 88.4 (C-1), 86.0 (C-3), 80.4 (C-2), 79.3 (C-4), 78.1 (C-5), 76.0, 75.6, 75.2 (CH_2 Bn), 52.6 (CH_3 COOMe); HRMS: $[M+Na]^+$ calcd for $C_{34}H_{34}NaO_6S$ 593.1968, found 593.1977.

Preparation of Donor S24



S23 **S24**

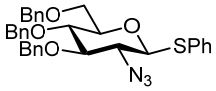
Scheme S-4. Donor **S24** synthesis. *Reagents and conditions:* a) HBr·PPh_3, AcOH, **S23**: 83%. b) PhSH, *p*TsOH, DCM, **S24**: 91%.

Phenyl 2-deoxy-3,4,6-tri-*O*-benzyl-1-thio-D-glucopyranoside (S23). Compound **S23** was obtained from 2-deoxy-tri-*O*-benzyl-D-glucal, according to a literature procedure as a mixture of stereoisomers (1,3-*cis*:1,3-*trans*; 10:90).[Beaver, M. G. & Woerpel, K. A. Erosion of Stereochemical Control with Increasing Nucleophilicity: *O*-Glycosylation at the Diffusion Limit. *J. Org. Chem.* 75, 1107–1118 (2010)] TLC: R_f 0.30 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 694, 734, 1026, 1078, 1362, 1454, 2863; Data of the major stereoisomer (1,3-*trans* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.47 – 7.06 (m, 15H, CH_{arom}), 6.25 (dd, *J* = 3.5, 1.5 Hz, 1H, H-1), 4.90 (d, *J* = 10.6 Hz, 1H, C*H*H Bn), 4.68 – 4.60 (m, 2H, C*H*H Bn, CH*H* Bn), 4.54 (d, *J* = 10.7 Hz, 1H, C*H*H Bn), 4.51 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.00 – 3.92 (m, 1H, CH*H* Bn), 3.96 (ddd, *J* = 11.4, 8.8, 4.9 Hz, 1H, H-3), 3.84 (dq, *J* = 9.9, 1.9 Hz, 1H, H-5), 3.78 (dd, *J* = 10.7, 3.5 Hz, 1H, H-6) 3.71 (dd, *J* = 9.8, 8.9 Hz, 1H, H-4), 3.66 (dd, *J* = 10.7, 1.9 Hz, 1H, H-6), 2.28 (ddd, *J* = 13.6, 5.0, 1.7 Hz, 1H, H-2_{eq}), 2.04 (s, 3H, CH_3 Ac), 1.84 (ddd, *J* = 13.6, 11.5, 3.5 Hz, 1H, H-2_{ax}); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 169.4 (C=O), 138.4, 138.3, 138.1 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.1, 128.0, 127.8, 127.8, 127.8, 127.7 (CH_{arom}), 92.3 (C-1), 77.6 (C-

4), 76.9 (C-3), 75.3 (CH_2 Bn), 73.6 (CH_2 Bn), 73.5 (C-5), 71.9 (CH_2 Bn), 68.5 (C-6), 34.3 (C-2), 21.2 (CH_3 Ac); Data of the minor stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 5.67 (dd, *J* = 10.0, 2.2 Hz, 1H, H-1), 2.36 (ddd, *J* = 12.5, 4.9, 2.2 Hz, 1H, H-2_{eq}), 2.10 (s, 3H, CH_3 Ac). ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 169.4 (C=O), 92.9 (C-1), 75.1 (CH_2 Bn), 73.6 (CH_2 Bn), 71.8 (CH_2 Bn), 35.5 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{29}H_{32}NaO_6$ 499.2091, found 499.2096.

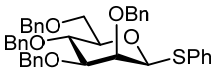
Phenyl 2-deoxy-3,4,6-tri-*O*-benzyl-1-thio-D-glucopyranoside (S24). Compound **S23** (0.7 g, 1.5 mmol) was dissolved in DCM (14 mL, 0.1 M), followed by the addition of thiophenol (0.3 mL, 3.0 mmol, 2 eq.) and *p*TsOH (0.56 g, 3.0 mmol, 2 eq.). After 16 h of stirring the reaction was quenched with sat. aq. $NaHCO_3$ and extracted with DCM (3x). The combined organic layers were washed with brine and dried over $MgSO_4$. Column chromatography (95:5 → 80:20, pentane:Et_2O) gave the title compound **S24** (702 mg, 1.33 mmol, 91%, colourless oil, 1,3-*cis*:1,3-*trans*; 40:60). TLC: R_f 0.60 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 694, 734, 1026, 1078, 1362, 1454, 2863; Data of the major stereoisomer (1,3-*trans* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.70 – 6.94 (m, 20H, CH_{arom}), 5.69 (dd, *J* = 5.6, 1.2 Hz, 1H, H-1), 4.90 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.74 – 4.51 (m, 4H, CH_2 Bn, CH_2 Bn, CH_2 Bn, CH_2 Bn), 4.46 (d, *J* = 12.0 Hz, 1H, CH*H* Bn), 4.30 (ddd, *J* = 9.8, 4.1, 2.0 Hz, 1H, H-5), 3.97 (ddd, *J* = 11.6, 8.7, 4.9 Hz, 1H, H-3), 3.90 – 3.76 (m, 1H, H-6), 3.73 (dd, *J* = 10.8, 4.6 Hz, 1H, H-5), 3.66 (ddd, *J* = 8.8, 5.0, 2.9 Hz, 1H, H-4), 2.49 – 2.41 (m, 1H, H-2_{eq}), 2.13 (ddd, *J* = 13.4, 11.7, 5.7 Hz, 1H, H-2_{ax}); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.5, 138.5, 138.2 ($C_{q\text{-}arom}$), 131.3, 129.0, 129.0, 128.6, 128.5, 128.5, 128.1, 128.0, 127.9, 127.8, 127.8 (CH_{arom}), 84.2 (C-1), 78.1 (C-4), 78.0 (C-3), 75.2, 73.5, 72.0 (CH_2 Bn), 71.8 (C-5), 68.9 (C-6), 36.4 (C-2). Data of the minor stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 4.75 (dd, *J* = 11.9, 1.9 Hz, 1H, H-1), 1.88 – 1.74 (m, 1H, H-2). ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 82.2 (C-1), 37.0 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{33}H_{34}NaO_4S$ 549.2070, found 549.2081.

Preparation of Donor S25



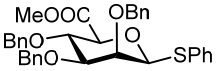
Phenyl 2-azido-2-deoxy-3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (S25). Compound **S25** was obtained from D- glucosamine, according to a literature procedure.[Greenberg, W. A. *et al.* Design and Synthesis of New Aminoglycoside Antibiotics Containing Neamine as an Optimal Core Structure: Correlation of Antibiotic Activity with in Vitro Inhibition of Translation. *J. Am. Chem. Soc.* 121, 6527–6541 (1999)] TLC: R_f 0.61 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 697, 1101, 1105, 1146, 1276, 1453, 2109, 2856, 2919; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.60 (m, 2H, CH_{arom}), 7.35- 7.19 (m, 18H, CH_{arom}), 4.86 (d, *J* = 10.5 Hz, 1H, C*H*H Bn), 4.83 (d, *J* = 10.5 Hz, 1H, CH*H* Bn), 4.79 (d, *J* = 11.0 Hz, 1H, CH*H* Bn), 4.62 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.58 (d, *J* = 10.5 Hz, 1H, CH*H* Bn), 4.54 (d, *J* = 12.0 Hz, 1H, C*H*H Bn), 4.41 (d, *J* = 10.0 Hz, 1H, H-1), 3.80 – 3.71 (m, 2H, H-6), 3.61 (t, *J* = 9.5 Hz, 1H, H-4), 3.51 (t, *J* = 9.5 Hz, 1H, H-3), 3.47 (ddd, *J* = 2.0, 4.0, 9.5 Hz, 1H, H-5), 3.34 (t, *J* = 9.5 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.2, 137.8, 137.6 ($C_{q\text{-}arom}$), 133.6, 131.1, 129.0, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5 (CH_{arom}), 85.9 (C-1), 85.0 (C-3), 79.3 (C-5), 77.5 (C-4), 75.9, 75.0, 73.4 (CH_2 Bn), 68.7 (C-6), 65.0 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{33}H_{33}N_3NaO_4S$ 590.2084, found 590.2094.

Preparation of Donor S26



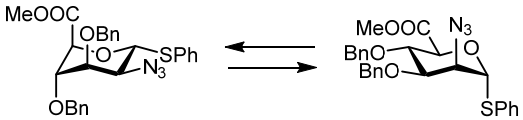
Phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-mannopyranoside (S26). Compound **S26** was obtained from D-mannose, according to a literature procedure.[S. van der Vorm, T. Hansen, H. S. Overkleeft, G. A. van der Marel, J. D. C. Codée, The influence of acceptor nucleophilicity on the glycosylation reaction mechanism. *Chem. Sci.* 8, 1867–1875 (2017)] TLC: R_f 0.81 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 694, 731, 1026, 1064, 1362, 1454, 2863, 3029; ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 7.53 – 7.17 (m, 25H, CH_{arom}), 5.05 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.89 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.87 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.77 (d, *J* = 0.9 Hz, 1H, H-1), 4.73 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.69 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.60 (m, 2H, CH*H* Bn, C*H*H Bn), 4.55 (d, *J* = 11.8 Hz, 1H, CH*H* Bn), 4.15 (d, *J* = 2.2 Hz, 1H, H-2), 3.94 (t, *J* = 9.5 Hz, 1H, H-4), 3.84 (dd, *J* = 10.9, 1.8 Hz, 1H, H-6), 3.74 (dd, *J* = 10.9, 6.5 Hz, 1H, H-6), 3.63 (dd, *J* = 9.4, 2.9 Hz, 1H, H-3), 3.54 (ddd, *J* = 9.5, 6.5, 1.8 Hz, 1H, H-5); ^{13}C NMR ($CDCl_3$, 101 MHz, HSQC): δ 138.7, 138.4, 138.3, 138.2, 135.8 ($C_{q\text{-}arom}$), 130.7, 129.0, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.5, 127.1 (CH_{arom}), 87.8 (C-1), 84.5 (C-3), 80.3 (C-5), 77.7 (C-2), 75.3 (CH_2 Bn), 75.2 (CH_2 Bn), 75.1 (C-4), 73.6 (CH_2 Bn), 72.7 (CH_2 Bn), 70.0 (C-6); ^{13}C-GATED NMR (101 MHz, $CDCl_3$): δ 87.8 ($J_{C1,H1}$ = 154 Hz, C-1 β); HRMS: $[M+NH_4]^+$ calcd for $C_{40}H_{44}NO_5S$ 650.29347, found 650.29381.

Preparation of Donor S27



Methyl (phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-mannopyranosyl uronate) (S27). Compound **S27** was obtained from D-mannose, according to a literature procedure.[Dinkelaar, J. *et al.* Stereodirecting Effect of the Pyranosyl C-5 Substituent in Glycosylation Reactions. *J. Org. Chem.* 74, 4982–4991 (2009)] TLC: R_f 0.40 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 695, 734, 1025, 1067, 1131, 1200, 1286, 1438, 1453, 1747, 2850; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.53 – 7.24 (m, 20H, CH_{arom}), 5.05 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.87 (d, *J* = 11.4 Hz, 1H, CH*H* Bn), 4.86 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.78 (d, *J* = 1.2 Hz, 1H, H-1), 4.74 – 4.67 (m, 3H, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.31 (t, *J* = 9.5 Hz, 1H, H-4), 4.14 (dd, *J* = 2.9, 1.2 Hz, 1H, H-2), 3.87 (d, *J* = 9.5 Hz, 1H, H-5), 3.72 (s, 3H, CH_3 COOMe), 3.62 (dd, *J* = 9.5, 2.9 Hz, 1H, H-3); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 168.4 (C=O), 138.2, 138.0, 135.2 ($C_{q\text{-}arom}$), 131.0, 129.1, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5 (CH_{arom}), 89.0 (C-1), 83.5 (C-3), 78.9 (C-5), 77.4 (C-2), 75.7 (C-4), 75.4, 75.3, 72.9 (CH_2 Bn), 52.5 (C-5); HRMS: $[M+Na]^+$ calcd for $C_{34}H_{34}NaO_6S$ 593.1968, found 593.1981.

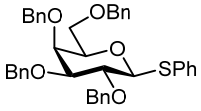
Preparation of Donor S28



Methyl (phenyl 2-azido-2-deoxy-3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranosyl uronate) (S28). Compound **S28** was obtained from D-mannosamine, according to a literature procedure. TLC: R_f 0.45 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 695, 736, 1025, 1119, 1206, 1439, 1453, 1750, 2102; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.65 – 7.26 (m, 15H, CH_{arom}), 5.61 (d, *J* = 7.6 Hz, 1H, H-1), 4.68 (d, *J* = 11.4 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 4.4 Hz, 1H, H-5), 4.59 (s, 2H, CH_2 Bn, CH_2 Bn), 4.21 (dd, *J* = 5.7, 4.4 Hz, 1H, H-4), 3.93 (dd, *J* = 5.7, 3.0 Hz, 1H, H-3), 3.72 (dd, *J* = 9.4, 3.5 Hz, 1H, H-2), 3.54 (s, 3H, CH_3 COOMe); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 169.5 (C=O), 137.5, 137.0 ($C_{q\text{-}arom}$),

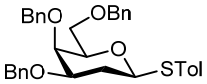
132.6 (CH_{arom}), 132.2 ($C_{q\text{-}arom}$), 129.1, 128.6, 128.6, 128.3, 128.2, 128.2, 128.0, 127.9 (CH_{arom}), 82.3 (C-1), 77.2 (C-3), 74.9 (C-4), 73.2 (CH_2 Bn), 73.1 (C-5), 58.9 (C-2), 52.4 (CH_3 COOMe); HRMS: $[M+Na]^+$ calcd for $C_{27}H_{27}N_3NaO_5S$ 528.1564, found 528.1574.

Preparation of Donor S29



Phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (S29). Compound **S29** was obtained from D-galactose, according to a literature procedure.[Whitman, C. P.; Hajipour, G.; Watson, R. J.; Johnson, W. H.; Bembenek, M. E.; Stolowicht, N. J. *J. Am. Chem. Soc.* 1992, 114, 10104-10110] TLC: R_f 0.75 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 714, 782, 1060, 1360, 1452, 2855, 2927; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC) δ 7.63 – 7.11 (m, 30H, CH_{arom}), 4.97 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.78 (d, *J* = 10.2 Hz, 1H, C*H*H Bn), 4.76 – 4.70 (m, 3H, CH*H* Bn, CH*H* Bn, C*H*H Bn), 4.64 (d, *J* = 9.7 Hz, 1H, H-1), 4.60 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.47 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.41 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.98 (dd, *J* = 2.8, 0.8 Hz, 1H, H-4), 3.93 (t, *J* = 9.4 Hz, 1H, H-2), 3.68 – 3.58 (m, 4H, H-3, H-5, H-6, H-6); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.9, 138.5, 138.4, 138.0, 134.3 ($C_{q\text{-}arom}$), 131.7, 128.9, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.2 (CH_{arom}), 87.9 (C-1), 84.3 (C-3), 76.9 (C-5), 76.8 (C-2), 75.8, 74.6 (CH_2 Bn), 73.7 (C-4), 72.9 (CH_2 Bn), 68.9 (C-6); HRMS: $[M+NH_4]^+$ calcd for $C_{40}H_{44}NO_5S$ 650.29347, found 650.29380.

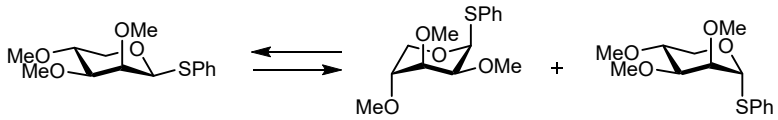
Preparation of Donor S30



***p*-Tolyl 2-deoxy-3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (S30).** Compound **S30** was obtained from D-galactose, according to a literature procedure.[Chen, J. H., Ruei, J. H. & Mong, K. K. T. Iterative α-Glycosylation Strategy for 2-Deoxy- and 2,6-Dideoxysugars: Application to the One-Pot Synthesis of Deoxysugar-Containing Oligosaccharides. *European Journal of Organic Chemistry* 2014, 1827–1831] TLC: R_f 0.65 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 656, 733, 808, 1027, 1061, 1093, 1360, 1454, 1493, 2862, 3029; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.45 – 6.99 (m, 20H, CH_{arom}), 4.93 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.68 (dd, *J* = 11.8, 2.2 Hz, 1H, H-1), 4.62 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.60 – 4.54 (m, 2H, CH*H* Bn, CH*H* Bn), 4.46 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.41 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.85 (s, 1H, H-4), 3.65 (m, 2H, H-6), 3.58 (ddd, *J* = 11.6, 4.5, 2.4 Hz, 1H, H-3), 3.53 (t, *J* = 6.1 Hz, 1H, H-5), 2.27 (q, *J* = 11.9 Hz, 1H, H-2_{ax}), 2.15 (dt, *J* = 12.9, 2.9 Hz, 1H, H-2_{eq}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.1, 138.3, 138.2 ($C_{q\text{-}arom}$), 137.4 (CH_{arom}), 132.0 ($C_{q\text{-}arom}$), 130.6, 129.6, 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 127.8, 127.5, 127.5 (CH_{arom}), 83.4 (C-1), 78.5 (C-3), 78.1 (C-5), 74.2, 73.7 (CH_2 Bn), 71.9 (C-4), 70.3 (CH_2 Bn), 69.6, (C-6) 32.6 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{27}H_{29}NaO_4$ 440.1958, found 440.1960.

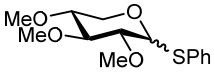
OMe-protected glycosyl donors

Preparation of Donor S31



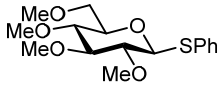
Phenyl 2,3,4-tri-*O*-methyl-1-thio-D-lyxopyranoside (S31). The title compound was prepared according to general procedure IV from D-lyxose. Column chromatography (95:5 → 85:15, pentane:EtOAc) yielded compound **S31** (334 mg, 1.17 mmol, 27% over 5 steps, average of 77% per step, colourless oil, 1,2-*cis*:1,2-*trans*; 72:28). TLC: R_f 0.21 (pentane:EtOAc, 8:2, v:v); IR (thin film, cm^{-1}): 692, 743, 934, 1045, 1069, 1196, 1439, 1584, 2825, 2927; Data of the major stereoisomer (1,2-*cis* isomer product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC, HH-NOESY, HMBC-Gated): δ 7.53 – 7.16 (m, 5H, CH_{arom} SPh), 5.29 (d, *J* = 4.1 Hz, 1H, H-1), 4.26 (dd, *J* = 9.8, 3.9 Hz, 1H, H-5), 3.88 (dd, *J* = 4.3, 2.5 Hz, 1H, H-2), 3.56 – 3.47 (m, 9H, H-3, H-4, H-5, CH_3 Me, CH_3 Me), 3.42 (d, *J* = 0.9 Hz, 3H, CH_3 Me); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 136.9 ($C_{q\text{-}arom}$ SPh), 130.2, 128.5, 126.4 (CH_{arom} SPh), 87.2 (C-1), 78.7 (C-3), 76.8 (C-2), 75.9 (C-4), 60.4 (C-5), 58.7, 57.9, 57.1 (CH_3 Me); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 87.2 ($J_{C1\text{-}H1}$= 158 Hz, 1,2-*cis*); Data of the minor stereoisomer (1,2-*trans* isomer product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC, HH-NOESY, HMBC-Gated): δ 7.53 – 7.16 (m, 5H, CH_{arom} SPh), 5.47 (d, *J* = 3.4 Hz, 1H, H-1), 3.92 – 3.80 (m, 2H, H-5_{ax}, H-5_{eq}), 3.76 (t, *J* = 3.3 Hz, 1H, H-2), 3.62 (td, *J* = 8.4, 4.8 Hz, 1H, H-4), 3.56 – 3.47 (m, 4H, H-3, CH_3 Me), 3.46 (s, 3H, CH_3 Me), 3.45 (s, 3H, CH_3 Me); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC, HMBC-Gated): δ 134.1 ($C_{q\text{-}arom}$ SPh), 130.9, 128.7, 127.0 (CH_{arom} SPh), 84.8 (C-1), 79.4 (C-3), 78.1 (C-2), 75.8 (C-4), 61.7 (C-5), 58.4, 58.2, 57.8 (CH_3 Me); ^{13}C-GATED NMR (126 MHz, $CDCl_3$): δ 84.8 ($J_{C1\text{-}H1}$= 164 Hz, 1,2-*trans*); HRMS: $[M+Na]^+$ calcd for $C_{14}H_{20}NaO_4S$ 307.09745, found 307.09752.

Preparation of Donor S32



Phenyl 2,3,4-tri-*O*-methyl-1-thio-D-xylopyranoside (S32). The title compound was prepared according to general procedure IV from D-xylose. Column chromatography (95:5 → 85:15, pentane:EtOAc) yielded compound **S32** (1.24 g, 4.35 mmol, 79%, colourless oil, 1,2-*cis*:1,2-*trans*; 18:82). TLC: R_f 0.29 (pentane:EtOAc, 8.5:1.5, v:v); IR (thin film, cm^{-1}): 692, 745, 1051, 1094, 1130, 1157, 1439, 1462, 2831, 2899, 2931; Data of the minor stereoisomer (1,2-*trans* isomer product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC): δ 7.54 – 7.23 (m, 5H, CH_{arom} SPh), 4.59 (d, *J* = 8.9 Hz, 1H, H-1), 4.11 (dd, *J* = 11.3, 4.6 Hz, 1H, H-5_{eq}), 3.62 (s, 3H, CH_3 Me), 3.59 (s, 3H, CH_3 Me), 3.46 (s, 3H, CH_3 Me), 3.26 (ddd, *J* = 9.2, 8.2, 4.6 Hz, 1H, H-4), 3.23– 3.15 (m, 2H, H-3, H-5_{ax}), 3.07 (dd, *J* = 8.9, 7.9 Hz, 1H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC): δ 133.9 ($C_{q\text{-}arom}$), 131.9, 129.0, 127.5 (CH_{arom}), 87.8 (C-1), 86.5 (C-3), 82.0 (C-2), 79.1 (C-4), 66.4 (C-5), 60.7 (CH_3 Me, CH_3 Me), 58.7 (CH_3 Me); Data of the minor stereoisomer (1,2-*cis* isomer product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, HMBC): δ 5.65 (d, *J* = 5.3 Hz, 1H, H-1), 4.03 – 3.94 (m, 1H, H-5), 3.79 (dd, *J* = 11.5, 5.5 Hz, 1H, H-5), 3.64 (s, 3H, CH_3 Me), 3.52 (s, 3H, CH_3 Me), 3.50 (s, 3H, CH_3 Me), 3.35 (t, *J* = 9.0 Hz, 1H, H-3); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC, HMBC): δ 134.6 ($C_{q\text{-}arom}$), 131.6, 129.1, 127.3 (CH_{arom}), 87.0 (C-1), 82.9 (C-3), 61.1 (CH_3 Me), 60.7 (C-5), 59.1, 58.4 (CH_3 Me); HRMS: $[M+Na]^+$ calcd for $C_{14}H_{20}NaO_4S$ 307.09745, found 307.09757.

Preparation of Donor S33



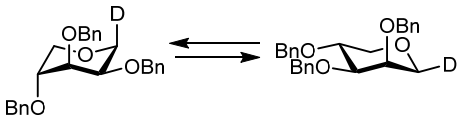
Phenyl 2,3,4,6-tetra-*O*-methyl-1-thio-β-D-glucopyranoside (S33). Phenyl 1-thio-β-D-glucose (1.36 g, 5.0 mmol) [S. van der Vorm, T. Hansen, H. S. Overkleeft, G. A. van der Marel, J. D. C. Codée, The influence of acceptor nucleophilicity on the glycosylation reaction mechanism. *Chem. Sci.* 8, 1867–1875 (2017)] was dissolved in DMF (25 mL, 0.25 M) and cooled to 0 °C. NaH (60% dispersion in mineral oil, 0.96 g, 24.0 mmol, 4.8 eq.) was added, and the resulting mixture was stirred for 10 minutes. Subsequently, methyl iodide (1.5 mL, 24.0 mmol, 4.8 eq.) was added, and the reaction mixture was allowed to warm up to rt. and stirred for an additional 16 h. The reaction was quenched with MeOH and diluted with H_2O, after which the resulting mixture was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (75:15 → 80:20, pentane:EtOAc) yielded compound **S33** (1.05 g, 3.2 mmol, 64%, colourless solid). TLC: R_f 0.33 (pentane:EtOAc, 8:2, v:v); IR (thin film, cm^{-1}): 2932, 2833, 1097; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.64 – 7.21 (m, 5H, CH_{arom}), 4.52 (d, J = 9.8 Hz, 1H, H-1), 3.71 – 3.63 (m, 4H, CH_3, H-6), 3.63 (s, 3H, CH_3), 3.59 (dd, J = 10.8, 4.7 Hz, 1H, H-6), 3.56 (s, 3H, CH_3), 3.42 (s, 3H, CH_3), 3.32 (ddd, J = 9.4, 4.7, 2.0 Hz, 1H, H-5), 3.24 (t, J = 8.6 Hz, 1H, H-3), 3.19 (t, J = 9.3 Hz, 1H, H-4), 3.08 (dd, J = 9.8, 8.3 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 134.1 ($C_{q\text{-}arom}$), 131.8, 128.9, 127.4 (CH_{arom}), 88.8 (C-4), 87.5 (C-1), 82.7 (C-2), 79.4 (C-3), 78.9 (C-5), 71.5 (C-6), 61.1 (CH_3), 61.0 (CH_3), 60.6 (CH_3), 59.5 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{16}H_{24}NaO_5S$ 351.1237, found 351.1239.

Preparation of Donor S34

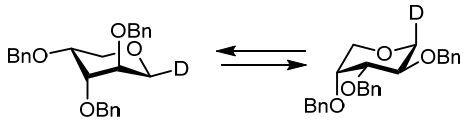
Phenyl 2,3,4,6-tetra-*O*-methyl-1-thio-β-D-mannopyranoside (S34). Phenyl 1-thio-β-D-mannose (0.5 g, 1.8 mmol) [S. van der Vorm, T. Hansen, H. S. Overkleeft, G. A. van der Marel, J. D. C. Codée, The influence of acceptor nucleophilicity on the glycosylation reaction mechanism. *Chem. Sci.* 8, 1867–1875 (2017)] was dissolved in DMF (9.2 mL, 0.2 M) and cooled to 0 °C. NaH (60% dispersion in mineral oil, 0.35 g, 8.8 mmol, 4.8 eq.) was added, and the resulting mixture was stirred for 10 minutes. Subsequently, methyl iodide (0.55 mL, 8.8 mmol, 4.8 eq.) was added, and the reaction mixture was allowed to warm up to rt. and stirred for an additional 16 h. The reaction was quenched with MeOH and diluted with H_2O, after which the resulting mixture was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (75:15 → 80:20, pentane:EtOAc) yielded compound **S34** (0.5 g, 1.5 mmol, 83%, colourless solid). TLC: R_f 0.30 (pentane:EtOAc, 8:2, v:v); IR (thin film, cm^{-1}): 2982, 2907, 1069, 737; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.74 – 7.04 (m, 5H, CH_{arom} SPh), 4.71 (d, J = 1.0 Hz, 1H, H-1), 3.89 (dd, J = 3.2, 1.0 Hz, 1H, H-2), 3.74 – 3.58 (m, 5H, CH_3, H-6), 3.53 (s, 6H, CH_3, CH_3), 3.45 (t, J = 9.5 Hz, 1H, H-4), 3.39 (s, 3H, CH_3), 3.31 (ddd, J = 9.7, 5.9, 1.9 Hz, 1H, H-5), 3.24 (dd, J = 9.3, 3.1 Hz, 1H, H-3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 135.5 ($C_{q\text{-}arom}$), 130.7, 128.9, 127.1 (CH_{arom}), 87.5 (C-1), 86.1 (C-3), 79.7 (C-5), 79.1 (C-2), 76.4 (C-4), 71.9 (C-6), 62.1 (CH_3), 60.9 (CH_3), 59.4 (CH_3), 58.1 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{16}H_{24}NaO_5S$ 351.1237, found 351.1240.

Model glycosylation reactions

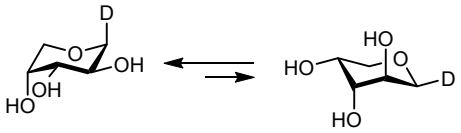
OBn-protected glycosyl donors



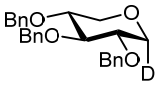
1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-D-lyxopyranoside (S35). The title compound was prepared according to general procedure V yielding compound **S35** (33 mg, 81 µmol, 81%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.57 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ –30.2° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 731, 1026, 1096, 1350, 1452, 2875, 2916; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.38 – 7.26 (m, 15H, CH_{arom}), 4.71 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.65 – 4.58 (m, 5H, CH*H* Bn, CH_2 Bn, CH_2 Bn), 3.88 (dd, *J* = 11.8, 3.5 Hz, 1H, H-5), 3.82 (t, *J* = 3.0 Hz, 1H, H-2), 3.78 (td, *J* = 6.4, 3.5 Hz, 1H, H-4), 3.68 (dd, *J* = 6.7, 3.0 Hz, 1H, H-3), 3.47 (d, *J* = 2.8 Hz, 1H, H-1), 3.41 (dd, *J* = 11.7, 6.1 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.7, 138.4, 138.4 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.5, 127.9, 127.9, 127.8, 127.8, 127.7 (CH_{arom}), 77.9 (C-3), 75.2 (C-4), 73.2 (C-2), 72.6, 71.6 (CH_2 Bn), 67.3 (C-5), 66.2 (t, *J* = 23.0 Hz, C-1); ^2H NMR (77 MHz, $CHCl_3$) δ 3.86 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{26}H_{31}DNO_4$ 423.23941, found 423.23876.



1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-D-arabinopyranoside (S36). The title compound was prepared according to general procedure V yielding compound **S36** (35 mg, 86 µmol, 86%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.52 (pentane:EtOAc, 9:1, v:v); ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.38 – 7.26 (m, 15H, CH_{arom}), 4.71 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.68 – 4.57 (m, 5H, CH*H* Bn, CH_2 Bn, CH_2 Bn), 3.89 – 3.79 (m, 3H, H-1, H-2, H-5), 3.76 (dd, *J* = 6.6, 3.4 Hz, 1H, H-3), 3.68 (dd, *J* = 6.6, 2.4 Hz, 1H, H-4), 3.51 (t, *J* = 7.9 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.7, 138.4 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.5, 127.9, 127.8, 127.8, 127.8, 127.7 (CH_{arom}), 77.7 (C-4), 75.1 (C-3), 73.3 (C-2), 72.6, 72.5, 71.5 (CH_2 Bn), 66.8 (t, *J* = 23.4 Hz, C-1), 66.4 (C-5); ^2H NMR (77 MHz, $CHCl_3$): δ 3.44 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{26}H_{31}DNO_4$ 423.23941, found 423.23876.

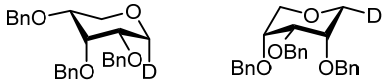


1-Deutero-1-deoxy-D-arabinopyranoside (S37). The title compound was prepared according to general procedure VI yielding compound **S37** (12 mg, 89 µmol, 89%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.53 (DCM:MeOH, 8:2, v:v); $[\alpha]_D^{20}$ –6.1° (*c* 0.25, MeOH); IR (thin film, cm^{-1}): 1014, 1410, 1449, 1647, 2951, 3294; ^1H NMR (400 MHz, Methanol-d_4, HH-COSY, HSQC, NOESY): δ 3.87 (dt, *J* = 5.8, 2.9 Hz, 1H, H-4), 3.79 (d, *J* = 3.8 Hz, 1H, H-1), 3.74 (dd, *J* = 7.4, 4.1 Hz, 1H, H-2), 3.72 (dd, *J* = 11.7, 5.2 Hz, 1H, H-5), 3.56 (dd, *J* = 7.4, 3.4 Hz, 1H, H-3), 3.50 (dd, *J* = 11.7, 2.6 Hz, 1H, H-5); ^{13}C NMR (101 MHz, MeOD, HSQC): δ 74.2 (C-3), 70.4 (C-5), 69.98 (t, *J* = 21.9 Hz, C-1), 69.3 (C-2), 69.0 (C-4); ^2H NMR (77 MHz, MeOH): δ 3.15 (D-1); HRMS: $[M+H]^+$ calcd for $C_5H_{10}DO_4$ 136.07201, found 136.07146.

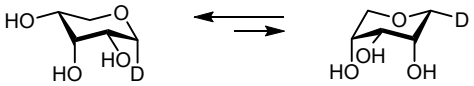


1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-D-xylopyranoside (S38). The title compound was prepared according to general procedure V yielding compound **S38** (35 mg, 86 µmol, 86%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.44 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ –121.8° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 733, 1026, 1070, 1454, 1497, 2851, 2916; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.45 – 7.18 (m, 15H, CH_{arom}), 4.89 (s, 2H, CH_2 Bn), 4.73 (d, *J* = 11.6 Hz, 2H, CH_2 Bn), 4.63 (d, *J* = 11.6 Hz, 2H, CH_2 Bn), 3.96 – 3.90 (m, 2H, H-1, H-5_{eq}), 3.60 – 3.47 (m, 3H, H-2, H-3, H-4), 3.14 (dd, *J* = 11.1, 9.9 Hz, 1H, H-5_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.9, 138.4 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.1, 127.9, 127.7 (CH_{arom}), 85.3 (C-3), 78.1, 78.1 (C-2/C-4), 75.6, 73.5, 73.5 (CH_2 Bn), 68.9 (C-5), 68.7, (t, *J* = 22.5 Hz, C-1); ^{2}H NMR (77 MHz, $CHCl_3$) δ 3.16 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{26}H_{31}DNO_4$ 423.23941, found 423.23871.

1-Deutero-1,2-di-deoxy-3,4-di-*O*-benzyl-D-xylopyranoside (S39). The title compound was prepared according to general procedure V yielding compound **S39** (22 mg, 74 µmol, 74%, colourless oil, 1,3-*cis*:1,3-*trans*; >98:2). TLC: R_f 0.63 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{25}$ –16.2° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 730, 1020, 1077, 1456, 1496, 2850, 2910; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.65 – 6.57 (m, 10H, CH_{arom}), 4.74 (d, *J* = 11.8 Hz, 1H, C*H*H Bn), 4.71 – 4.63 (m, 3H, CH*H* Bn, C*H*H Bn, CH*H* Bn), 3.95 (dd, *J* = 11.5, 4.3 Hz, 1H, H-5), 3.58 (ddd, *J* = 9.1, 7.3, 4.5 Hz, 1H, H-3), 3.47 (ddd, *J* = 8.1, 7.3, 4.3 Hz, 1H, H-4), 3.39 (dd, *J* = 9.9, 2.8 Hz, 1H, H-1), 3.29 (dd, *J* = 11.5, 8.2 Hz, 1H, H-5), 2.06 (ddd, *J* = 13.4, 4.5, 2.9 Hz, 1H, H-2_{eq}), 1.64 (ddd, *J* = 13.4, 9.9, 9.2 Hz, 1H, H-2_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.8, 138.6 ($C_{q\text{-}arom}$), 128.5, 128.5, 127.9, 127.8, 127.7, 127.7 (CH_{arom}), 78.0 (C-3), 77.3 (C-4), 72.8, 71.7 (CH_2 Bn), 68.2 (C-5), 65.24 (t, *J* = 22.3 Hz, C-1), 30.3 (C-2); ^{2}H NMR (77 MHz, $CHCl_3$): δ 3.89 (D-1); HRMS: $[M+Na]^+$ calcd for $C_{19}H_{21}NaDO_3$ 322.1524, found 322.1526.

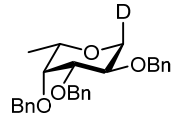


1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-D-ribopyranoside (S40). The title compound was prepared according to general procedure V yielding compound **S40** (28 mg, 69 µmol, 69%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.62 (pentane:EtOAc, 9:1, v:v); ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.56 – 7.17 (m, 15H, CH_{arom}), 4.88 (s, 2H, CH_2 Bn), 4.56 (d, *J* = 12.1 Hz, 2H, CH_2 Bn), 4.52 (d, *J* = 12.1 Hz, 2H, CH_2 Bn), 4.21 (t, *J* = 2.1 Hz, 1H, H-3), 3.74 – 3.68 (m, 3H, H-1, H-5, H-5), 3.48 – 3.43 (m, 3H, H-2, H-4); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 139.4, 138.3 ($C_{q\text{-}arom}$), 128.6, 128.3, 127.9, 127.8, 127.6, 127.4 (CH_{arom}), 75.8, 75.7 (C-2/C-4), 74.0 (C-3), 73.8, 71.2, 71.2 (CH_2 Bn), 64.5 (C-5), 64.2 (t, *J* = 22.7 Hz, C-1); ^{2}H NMR (77 MHz, $CHCl_3$): δ 3.71 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{26}H_{31}DNO_4$ 423.23941, found 423.23877.

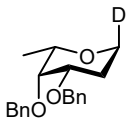


1-Deutero-1-deoxy-D-ribopyranoside (S41). The title compound was prepared according to general procedure VI yielding compound **S41** (12 mg, 89 µmol, 89%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.50 (DCM:MeOH, 8:2, v:v); $[\alpha]_D^{20}$ 10.5° (*c* 1, MeOH); IR (thin film, cm^{-1}): 1013, 1043, 1105, 1412, 1448, 1645, 2920,

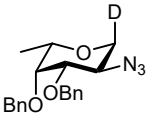
3368; ^{1}H NMR (500 MHz, Methanol-d_4, HH-COSY, HSQC, NOESY): δ 3.86 (t, J = 2.9 Hz, 1H, H-3), 3.70 – 3.65 (m, 2H, H-2, H-4), 3.62 (dd, J = 11.0, 7.3 Hz, 1H, H-5), 3.54 – 3.48 (m, 2H, H-1, H-5); ^{13}C NMR (126 MHz, MeOD, HSQC): δ 68.9 (C-3), 67.9 (C-2, C-4), 67.8 (C-5), 66.61 (t, J = 21.5 Hz, C-1); ^{2}H NMR (77 MHz, MeOH): δ 3.57 (D-1); HRMS: $[M+H]^+$ calcd for $C_5H_{10}DO_4$ 136.07201, found 136.07141.



1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-α-L-fucopyranoside (S42). The title compound was prepared according to general procedure V yielding compound **S42** (31 mg, 74 µmol, 74%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.54 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ –35.0° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 694, 733, 1026, 1070, 1088, 1360, 1454, 1497, 2851, 2916; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.42 – 7.24 (m, 15H, CH_{arom}), 4.99 (d, J = 11.6 Hz, 1H, C*H*H Bn), 4.86 – 4.75 (m, 3H, CH*H* Bn, CH_2 Bn), 4.71 – 4.63 (m, 2H, CH_2 Bn), 4.06 – 4.00 (m, 2H, H-1, H-2), 3.64 (dd, J = 2.9, 1.1 Hz, 1H, H-4), 3.54 (dd, J = 8.7, 2.9 Hz, 1H, H-3), 3.40 (qd, J = 6.4, 1.1 Hz, 1H, H-5), 1.14 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.8, 138.6 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.3, 127.9, 127.8, 127.7, 127.7, 127.6 (CH_{arom}), 84.2 (C-3), 77.1 (C-4), 75.2 (C-5), 75.1 (CH_2 Bn), 74.9 (C-2), 73.6, 72.9 (CH_2 Bn), 66.75 (t, J = 23.5 Hz, C-1), 17.3 (CH_3); ^{2}H NMR (77 MHz, $CHCl_3$): δ 3.17 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{33}DNO_4$ 437.25506, found 437.25445.

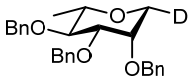


1-Deutero-1,2-di-deoxy-3,4-di-*O*-benzyl-α-L-fucopyranoside (S43). The title compound was prepared according to general procedure V yielding compound **S43** (26 mg, 83 µmol, 83%, colourless oil, 1,3-*cis*:1,3-*trans*; <2:98). TLC: R_f 0.21 (pentane:EtOAc, 9:1, v:v); IR (thin film, cm^{-1}): 696, 733, 1028, 1063, 1082, 1105, 1175, 1364, 1454, 2855, 2927, 2949; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.54 – 7.18 (m, 10H, CH_{arom}), 4.98 (d, J = 11.7 Hz, 1H, C*H*H Bn), 4.71 (d, J = 11.7 Hz, 1H, CH*H* Bn), 4.65 (d, J = 12.1 Hz, 1H, C*H*H Bn), 4.60 (d, J = 12.2 Hz, 1H, CH*H* Bn), 4.01 (dd, J = 5.0, 1.7 Hz, 1H, H-1), 3.58 (dt, J = 2.5, 1.2 Hz, 1H, H-4), 3.55 (ddd, J = 11.7, 4.5, 2.5 Hz, 1H, H-3), 3.34 (qd, J = 6.4, 1.1 Hz, 1H, H-5), 2.16 (td, J = 12.2, 4.9 Hz, 1H, H-2_{ax}), 1.76 (ddt, J = 12.6, 4.5, 1.6 Hz, 1H, H-2_{eq}), 1.17 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 139.0, 138.7 ($C_{q\text{-}arom}$), 128.6, 128.6, 128.3, 127.7, 127.6, 127.4 (CH_{arom}), 79.2 (C-3), 76.0 (C-4), 75.1 (C-5), 74.6 (CH_2 Bn), 70.1 (CH_2 Bn), 65.84 (t, J = 21.2 Hz, C-1), 26.9 (C-2), 18.0 (CH_3); ^{2}H NMR (77 MHz, $CHCl_3$): δ 3.40 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{20}H_{27}DNO_3$ 331.21320, found 331.21289.

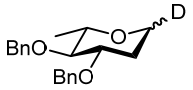


1-Deutero-2-azido-2-deoxy-3,4-di-*O*-benzyl-α-L-fucopyranoside (S44). The title compound was prepared according to general procedure V yielding compound **S44** (23 mg, 65 µmol, 65%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.35 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ –2.1° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 1123, 1265, 1724, 2106; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.47 – 7.27 (m, 10H, CH_{arom}), 4.95 (d, J = 11.5 Hz, 1H, C*H*H Bn), 4.76 (d, J = 11.6 Hz, 1H, C*H*H Bn), 4.71 (d, J = 11.6 Hz, 1H, CH*H* Bn), 4.64 (d, J =

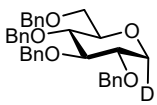
11.5 Hz, 1H, CH*H* Bn), 4.02 (dd, *J* = 9.6, 5.5 Hz, 1H, H-2), 3.97 (d, *J* = 5.5 Hz, 1H, H-1), 3.65 (d, *J* = 2.7 Hz, 1H, H-4), 3.43 (dd, *J* = 9.6, 2.7 Hz, 1H, H-3), 3.38 (q, *J* = 6.5 Hz, 1H, H-5), 1.17 (d, *J* = 6.3 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.3, 137.7 ($C_{q\text{-}arom}$), 128.7, 128.5, 128.4, 128.1, 128.0, 127.9 (CH_{arom}), 83.3 (C-3), 75.5 (C-2), 75.2 (C-5), 75.0, 72.2 (CH_2 Bn), 68.2 (t, *J* = 21.2 Hz, C-1), 58.3 (C-4), 17.5 (CH_3); ^2H NMR (77 MHz, $CHCl_3$): δ 3.08 (D-1); HRMS: $[M\text{-}N_2\text{+}H]^+$ calcd for $C_{20}H_{23}DNO_3$ 327.18135, found 327.18146.



1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-β-L-rhamnopyranoside (S45). The title compound was prepared according to general procedure V yielding compound **S45** (33 mg, 79 µmol, 79%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.38 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ 26.1° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 694, 733, 1026, 1092, 1113, 1354, 1452, 1497, 2860; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.46 – 7.26 (m, 15H, CH_{arom}), 4.99 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.81 (d, *J* = 12.7 Hz, 1H, CH*H* Bn), 4.72 – 4.61 (m, 3H, CH_2 Bn, C*H*H Bn), 4.57 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 3.75 (dd, *J* = 3.3, 1.0 Hz, 1H, H-2), 3.62 (t, *J* = 9.2 Hz, 1H, H-4), 3.53 (dd, *J* = 9.3, 3.2 Hz, 1H, H-3), 3.28 (dq, *J* = 9.0, 6.0 Hz, 1H, H-5), 3.24 (s, 1H, H-1), 1.36 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.7, 138.5, 138.4 ($C_{q\text{-}arom}$), 128.5, 128.2, 127.8, 127.7 (CH_{arom}), 82.8 (C-4), 80.8 (C-3), 76.5 (C-5), 75.7 (CH_2 Bn), 72.6 (C-2), 71.7, 71.3 (CH_2 Bn), 66.8 (t, *J* = 23.5 Hz, C-1), 18.4 (CH_3); ^2H NMR (77 MHz, $CHCl_3$): δ 4.03 (D-1); HRMS: $[M\text{+}NH_4]^+$ calcd for $C_{27}H_{33}DNO_4$ 437.25506, found 437.25446.

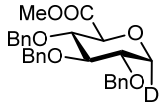


1-Deutero-1,2-di-deoxy-3,4-di-*O*-benzyl-L-rhamnopyranoside (S46). The title compound was prepared according to general procedure V yielding compound **S46** (27 mg, 86 µmol, 86%, colourless oil, 1,3-*cis*:1,3-*trans*; 66:34). TLC: R_f 0.24 (pentane:Et_2O, 8:2, v:v); IR (thin film, cm^{-1}): 696, 735, 1089, 1107, 1360, 1454, 2855, 2924. Data of the major stereoisomer (1,3-*cis* product): ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.38 – 7.21 (m, 10H, CH_{arom}), 4.96 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.70 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 4.66 (d, *J* = 10.9 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 11.7 Hz, 1H, CH*H* Bn), 3.59 (ddd, *J* = 11.4, 8.6, 5.1 Hz, 1H, H-3), 3.33 (dd, *J* = 12.8, 2.0 Hz, 0. 66H, H-1), 3.27 (dq, *J* = 9.2, 6.1 Hz, 1H, H-5), 3.10 (t, *J* = 8.9 Hz, 1H, H-4), 2.08 (ddd, *J* = 13.0, 5.1, 2.0 Hz, 1H, $H\text{-}2_{eq}$), 1.67 (td, *J* = 12.9, 11.3 Hz, 1H, $H\text{-}2_{ax}$), 1.30 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CHCl_3$, HSQC): δ 138.7 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.2, 127.8, 127.7 (CH_{arom}), 84.5 (C-4), 81.1 (H-3), 76.1 C-5), 75.5 (CH_2 Bn), 71.5 (CH_2 Bn), 65.21 (t, *J* = 22.4 Hz, C-1), 31.8 (C-2), 18.7 (CH_3); ^2H NMR (77 MHz, $CHCl_3$): δ 3.91 (D-1); Data of the minor stereoisomer (1,3-*trans* product): ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): 3.88 (dd, *J* = 5.0, 1.7 Hz, 0.34 H, H-1'); ^2H NMR (77 MHz, $CHCl_3$): δ 3.36 (D-1'); HRMS: $[M\text{+}NH_4]^+$ calcd for $C_{20}H_{27}DNO_3$ 331.21320, found 331.21269.

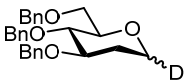


1-Deutero-1-deoxy-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (S47). The title compound was prepared according to general procedure V yielding compound **S47** (37 mg, 70 µmol, 70%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.69 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{20}$ 5.3° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 698, 731, 1024, 1093, 1123, 1353, 1451, 1499, 2867; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.61 – 6.96 (m,

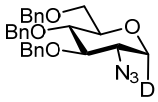
20H, CH_{arom}), 4.97 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.84 (d, *J* = 11.0 Hz, 1H, CH*H* Bn), 4.83 (d, *J* = 10.7 Hz, 1H, C*H*H Bn), 4.71 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.59 (d, *J* = 12.2 Hz, 1H, C*H*H Bn), 4.50 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.48 (d, *J* = 10.7 Hz, 1H, CH*H* Bn), 4.01 (d, *J* = 4.5 Hz, 1H, H-1), 3.74 – 3.59 (m, 4H, H-2, H-6, H-6, H-5), 3.56 (ddd, *J* = 9.2, 5.7, 3.5 Hz, 1H, H-4), 3.37 (ddd, *J* = 9.5, 4.3, 2.1 Hz, 1H, H-3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.8, 138.3, 138.2, 138.0 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 86.5 (C-2/C-5), 79.3 (C-3), 78.5 (C-5/C-2), 77.9 (C-4), 75.7 (CH_2 Bn), 75.3 (CH_2 Bn), 73.7 (CH_2 Bn), 73.4 (CH_2 Bn), 69.1 (C-6), 67.9 (t, *J* = 21.5 Hz, C-1); HRMS: $[M+Na]^+$ calcd for $C_{34}H_{35}NaDO_5$ 548.2518, found 548.2521.



Methyl (2,3,4-tri-*O*-benzyl-1-deoxy-α-deuterio-D-glucopyranosyl uronate) (S48). The title compound was prepared according to general procedure V yielding compound **S48** (20 mg, 43 μmol, 43%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.73 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{25}$ 54.5° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 695, 734, 1027, 1070, 1211, 1438, 1454, 1747, 2950; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.13 (m, 20H, CH_{arom}), 4.93 (d, *J* = 11.0 Hz, 1H, C*H*H Bn), 4.84 (d, *J* = 11.0 Hz, 1H, CH*H* Bn), 4.79 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.72 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.62 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.57 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 4.02 (d, *J* = 4.4 Hz, 1H, H-1), 3.84 (d, *J* = 9.4 Hz, 1H, H-5), 3.70 (s, 3H, CH_3 COOMe), 3.75 – 3.64 (m, 3H, H-2, H-3, H-4); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 169.8 (C=O), 138.6, 138.1, 137.9 ($C_{q\text{-}arom}$), 128.7, 128.6, 128.5, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9 (CH_{arom}), 85.3 (C-3), 79.5 (C-4), 78.7 (C-5), 77.7 (C-2), 75.7, 75.3, 73.6 (CH_2 Bn), 67.95 (t, *J* = 21.1 Hz, C-1), 52.6 (CH_3 COOMe); ^{2}H NMR (77 MHz, $CHCl_3$): δ 3.26 (D-1); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}DO_6Na$ 486.1997, found 486.2004.

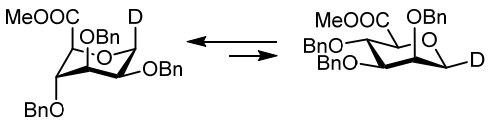


1-Deutero-1,2-di-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranoside (S49). The title compound was prepared according to general procedure V yielding compound **S49** (32 mg, 43 μmol, 43%, colourless oil, 1,3-*cis*:1,3-*trans*; 52:48). TLC: R_f 0.62 (pentane:EtOAc, 8:2, v:v); IR (thin film, cm^{-1}): 734, 1027, 1086, 1360, 1452, 2862, 2922; Data of the major stereoisomer (1,3-*cis* product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.40 – 7.11 (m, 15H, CH_{arom}), 4.90 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.70 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.63 (d, *J* = 10.3 Hz, 1H, CH*H* Bn), 4.60 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.53 (d, *J* = 12.2 Hz, 1H, CH*H* Bn), 4.52 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), , 3.72 – 3.59 (m, 3H, H-3, H-6, H-6), 3.49 (t, *J* = 9.1 Hz, 1H, H-4), 3.39 – 3.31 (m, 1.52H, H-1, H-5), 2.07 (ddd, *J* = 13.0, 5.0, 1.9 Hz, 1H, H-2_{eq}), 1.70 (dddd, *J* = 16.3, 12.9, 9.5, 3.9 Hz, 1H, H-2_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.7, 138.6, 138.2 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.5, 128.1, 128.1, 127.8, 127.7, 127.7 (CH_{arom}), 81.3 (C-3), 79.4 (C-5), 78.6 (C-4), 75.2, 73.7, 71.5 (CH_2 Bn), 69.6 (C-6), 65.5 (t, *J* = 22.5 Hz, C-1), 31.5 (C-2); ^{2}H NMR (77 MHz, $CHCl_3$): δ 4.05 (D-1); Data of the minor stereoisomer (1,3-*trans* product): ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): 3.98 (dd, *J* = 5.0, 1.7 Hz, 0.48 H, H-1'); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 65.5 (t, *J* = 22.5 Hz, C-1); ^{2}H NMR (77 MHz, $CHCl_3$): δ 3.36 (D-1'); HRMS: $[M+Na]^+$ calcd for $C_{27}H_{29}DO_4Na$ 442.2099, found 442.2103.

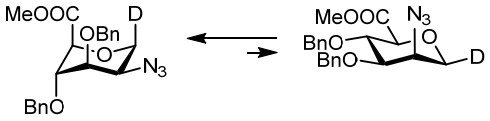


1-Deutero-2-azido-1,2-di-deoxy-3,4,6-tri-*O*-benzyl-1-α-D-glucopyranoside (S50). The title compound was prepared according to general procedure V yielding compound **S50** (24 mg, 52 µmol, 52%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.77 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{25}$ –9.2° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 697, 735, 1027, 1059, 1109, 1137, 1261, 1362, 1454, 1497, 2104, 2866; ^1H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.51 – 6.88 (m, 15H, CH_{arom}), 4.88 (s, 2H, CH_2 Bn), 4.80 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.60 (d, *J* = 12.1 Hz, 1H, C*H*H Bn), 4.52 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 4.51 (d, *J* = 12.1 Hz, 1H, CH*H* Bn), 4.01 (d, *J* = 5.4 Hz, 1H, H-1), 3.71 – 3.57 (m, 4H, H-2, H-4, H-6, H-6), 3.51 (dd, *J* = 9.5, 8.9 Hz, 1H, H-3), 3.36 (ddd, *J* = 9.7, 4.1, 2.3 Hz, 1H, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.0, 137.9, 137.9 ($C_{q\text{-}arom}$), 128.6, 128.6, 128.6, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9 (CH_{arom}), 85.5 (C-3), 79.7 (C-5), 78.3 (C-4), 75.7, 75.2, 73.7 (CH_2 Bn), 68.8 (C-6), 68.0 (t, *J* = 21.5 Hz, C-1), 61.9 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{27}H_{28}DN_3NaO_4$ 483.2113, found 483.2118.

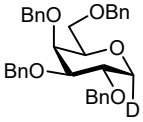
1-Deutero-1-deoxy-2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranoside (S51). The title compound was prepared according to general procedure V yielding compound **S51** (49 mg, 93 µmol, 93%, colourless oil, 1,2-*cis*:1,2-*trans*; 95:5). TLC: R_f 0.60 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{20}$ –28.3° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 699, 723, 1020, 1090, 1128, 1356, 1454, 1498, 2860; Data of the major stereoisomer (1,2-*cis* product): ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.66 – 7.03 (m, 20H, CH_{arom}), 4.92 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.80 (d, *J* = 12.6 Hz, 1H, C*H*H Bn), 4.65 (d, *J* = 12.4 Hz, 1H, C*H*H Bn), 4.63 – 4.54 (m, 4H, C*H*H Bn, CH*H* Bn, CH*H* Bn, CH*H* Bn), 4.52 (d, *J* = 10.8 Hz, 1H, CH*H* Bn), 3.89 (t, *J* = 9.4 Hz, 1H, H-4), 3.79 – 3.64 (m, 3H, H-2, H-6, H-6), 3.57 (dd, *J* = 9.3, 3.3 Hz, 1H, H-3), 3.42 (ddd, *J* = 9.6, 5.9, 2.1 Hz, 1H, H-5), 3.27 (s, 0.95H, H-1); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.5, 138.4, 138.3, 138.3 ($C_{q\text{-}arom}$), 129.4, 128.5, 128.5, 128.4, 128.4, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7 (CH_{arom}), 82.9 (C-3), 79.8 (C-5), 75.4 (CH_2 Bn), 75.3 (C-4), 73.6 (CH_2 Bn), 72.3 (C-2), 71.6, 71.0 (CH_2 Bn), 69.8 (C-6), 66.5 (t, *J* = 22.2 Hz, C-1); Data of the minor stereoisomer (1,2-*trans* product): ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 4.11 (d, *J* = 2.3 Hz, 0.05H); HRMS: $[M+Na]^+$ calcd for $C_{34}H_{35}NaDO_5$ 548.2518, found 548.2521.



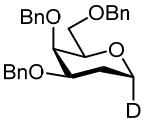
Methyl (2,3,4-tri-*O*-benzyl-1-deoxy-β-deuterio-D-mannopyranosyl uronate) (S52). The title compound was prepared according to general procedure V yielding compound **S52** (35 mg, 76 µmol, 76%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.72 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{25}$ –8.3° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 696, 735, 1027, 1091, 1104, 1205, 1454, 1750, 2869; ^1H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.80 – 7.15 (m, 15H, CH_{arom}), 4.66 (s, 2H, CH_2 Bn), 4.62 (d, *J* = 12.2 Hz, 1H. C*H*H Bn), 4.60 – 4.52 (m, 3H, C*H*H Bn, CH*H* Bn, CH*H* Bn), 4.26 (dd, *J* = 6.3, 4.9 Hz, 1H, H-4), 4.13 (d, *J* = 4.8 Hz, 1H, H-5), 3.88 (t, *J* = 3.2 Hz, 1H, H-2), 3.74 (dd, *J* = 6.1, 2.9 Hz, 1H, H-3), 3.63 (s, 3H, CH_3 COOMe), 3.58 (d, *J* = 3.5 Hz, 1H, H-1); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 170.0 (C=O), 138.3, 138.2, 138.0 ($C_{q\text{-}arom}$), 131.2, 128.6, 128.5, 128.4, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 124.9 (CH_{arom}), 76.7 (C-3), 76.2 (C-4), 75.4 (C-5), 73.6, 72.2 (CH_2 Bn), 71.9 (C-2), 71.4 (CH_2 Bn), 63.7 (td, *J* = 21.5 Hz, C-1), 52.3 (CH_3 COOMe); ^2H NMR (77 MHz, $CHCl_3$): δ 4.21 (D-1); HRMS: $[M+Na]^+$ calcd for $C_{28}H_{29}DO_6Na$ 486.1997, found 486.1998.



Methyl (2-azido-3,4-di-*O*-benzyl-1,2-dideoxy-β-deuterio-D-glucopyranosyl uronate) (S53). The title compound was prepared according to general procedure V yielding compound **S53** (21 mg, 53 µmol, 53%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.56 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{25}$ –4.1° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 698, 738, 1026, 1100, 1133, 1278, 1454, 1750, 2102, 2880; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.38 – 7.24 (m, 10H, CH_{arom}), 4.68 (s, 2H, CH_2 Bn), 4.61 (s, 2H, CH_2 Bn), 4.20 (dd, *J* = 6.0, 5.0 Hz, 1H, H-4), 4.13 (d, *J* = 5.0 Hz, 1H, H-5), 3.84 – 3.76 (m, 2H, H-2, H-3), 3.65 (d, *J* = 1.5 Hz, 1H, H-1), 3.59 (s, 3H, CH_3 COOMe); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 169.5 (C=O), 137.6, 137.2 ($C_{q\text{-}arom}$), 128.7, 128.6, 128.2, 128.2, 128.1, 128.0 (CH_{arom}), 77.7 (C-3), 75.1 (C-4/C-5), 75.1 (C-5/C-4), 73.7, 72.6 (CH_2 Bn), 63.7 (bs, C-1), 56.2 (C-2), 52.4 (CH_3 COOMe); HRMS: $[M+Na]^+$ calcd for $C_{21}H_{22}DN_3NaO_5$ 421.1593, found 421.1591.



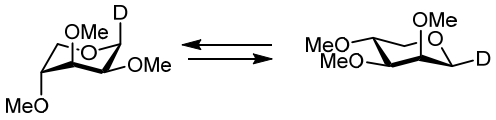
1-Deutero-1-deoxy-2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranoside (S54). The title compound was prepared according to general procedure V yielding compound **S54** (45 mg, 86 µmol, 86%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.65 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{20}$ 1.2° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 690, 730, 1029, 1092, 1129, 1350, 1449, 1493, 2867; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.43 – 7.21 (m, 20H, CH_{arom}), 4.94 (d, *J* = 11.5 Hz, 1H, C*H*H Bn), 4.81 – 4.73 (m, 3H, CH*H* Bn, C*H*H Bn, C*H*H Bn), 4.64 (d, *J* = 11.5 Hz, 1H, CH*H* Bn), 4.59 (d, *J* = 11.6 Hz, 1H, CH*H* Bn), 4.47 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.39 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.08 – 3.99 (m, 2H, H-1, H-3), 3.93 (dd, *J* = 2.9, 1.1 Hz, 1H, H-4), 3.59 – 3.50 (m, 2H, H-6, H-2), 3.49 (td, *J* = 6.0, 1.1 Hz, 1H, H-5), 3.43 (dd, *J* = 8.9, 6.1 Hz, 1H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.7, 138.7, 138.6, 138.0 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.4, 128.4, 128.1, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6 (CH_{arom}), 83.8 (C-2), 78.0 (C-5), 75.3 (C-3), 74.8 (CH_2 Bn), 74.5 (C-4), 73.7, 73.7, 72.8 (CH_2 Bn), 69.4 (C-6), 68.3 (t, *J* = 21.2 Hz, C-1); HRMS: $[M+Na]^+$ calcd for $C_{34}H_{35}NaDO_5$ 548.2518, found 548.2518.



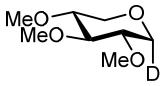
1-Deutero-1,2-di-deoxy-3,4,6-tri-*O*-benzyl-1-α-D-galactopyranoside (S55). The title compound was prepared according to general procedure V yielding compound **S55** (38 mg, 91 µmol, 91%, colourless oil, 1,3-*cis*:1,3-*trans*; <2:98). TLC: R_f 0.52 (pentane:EtOAc, 8:2, v:v); IR (thin film, cm^{-1}): 730, 1025, 1080, 1368, 1450, 2863, 2920; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.05 (m, 15H, CH_{arom}), 4.93 (d, *J* = 11.7 Hz, 1H, C*H*H Bn), 4.66 – 4.56 (m, 3H, CH*H* Bn, C*H*H Bn, CH*H* Bn), 4.49 (d, *J* = 11.9 Hz, 1H, C*H*H Bn), 4.41 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 4.04 (dd, *J* = 5.0, 1.8 Hz, 1H, H-1), 3.85 (dt, *J* = 2.4, 1.1 Hz, 1H, H-4), 3.63 – 3.56 (m, 1H, H-6), 3.54 (ddd, *J* = 11.7, 4.5, 2.5 Hz, 1H, H-3), 3.50 – 3.42 (m, 2H, H-5, H-6), 2.19 (td, *J* = 12.2, 4.9 Hz, 1H, H-2_{ax}), 1.77 (ddt, *J* = 12.6, 4.5, 1.6 Hz, 1H, H-2_{eq}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 138.9, 138.6, 138.1 ($C_{q\text{-}arom}$), 128.5, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.4 (CH_{arom}),

78.6 (C-3), 78.1 (C-5), 74.4, 73.6 (CH_2 Bn), 73.4 (C-4), 70.2 (CH_2 Bn), 70.0 (C-6), 66.0 (t, J = 21.5 Hz, C-1), 27.3 (C-2); HRMS: $[M+Na]^+$ calcd for $C_{27}H_{29}NaDO_4$442.2099, found 442.2106.

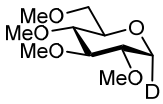
OMe-protected glycosyl donors



1-Deutero-1-deoxy-2,3,4-tri-*O*-methyl-D-lyxopyranoside (S56). The title compound was prepared according to general procedure V yielding compound **S56** (16 mg, 90 µmol, 90%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.28 (pentane:EtOAc, 5:5, v:v); $[\alpha]_D^{20}$ −133.7° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 733, 953, 1072, 1096, 1357, 1462, 2824, 2897; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 3.88 (dd, J = 11.7, 3.7 Hz, 1H, H-5), 3.62 (t, J = 2.9 Hz, 1H, H-2), 3.54 (dt, J = 6.9, 3.4 Hz, 1H, H-4), 3.51 (s, 3H, CH_3), 3.47 (s, 3H, CH_3), 3.45 (m, 4H, H-1, CH_3), 3.42 (dd, J = 7.1, 3.2 Hz, 1H, H-3), 3.35 (dd, J = 11.8, 6.8 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 80.2 (C-3), 76.3 (C-4), 75.0 (C-2), 66.6 (C-5), 65.33 (t, J = 22.5 Hz, C-1), 58.3, 58.0, 57.4 (CH_3 Me); ^{2}H NMR (77 MHz, $CHCl_3$): δ 3.85 (D-1); HRMS: $[M+H]^+$ calcd for $C_8H_{16}DO_4$ 178.11896, found 178.11840.



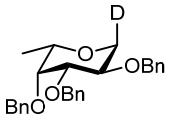
1-Deutero-1-deoxy-2,3,4-tri-*O*-methyl-D-xylopyranoside (S57). The title compound was prepared according to general procedure V yielding compound **S57** (15 mg, 85 µmol, 85%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.62 (pentane:EtOAc, 5:5, v:v); $[\alpha]_D^{20}$ −1.8° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 841, 922, 1022, 1099, 1161, 1462, 2827, 2932; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 4.00 (dd, J = 5.0, 1.2 Hz, 1H, H-5_{eq}), 3.97 (td, J = 4.9, 1.2 Hz, 1H, H-1), 3.63 (s, 3H, CH_3), 3.48 (s, 6H, CH_3, CH_3), 3.26 – 3.19 (m, 2H, H-2, H-4), 3.12 (t, J = 8.3 Hz, 1H, H-3), 3.09 (dd, J = 11.2, 9.9 Hz, 1H, H-5_{ax}); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 86.0 (C-3), 79.6, 79.5 (C-2/C-4), 68.2 (C-5), 67.9 (t, J = 21.5 Hz, C-1), 60.7 (CH_3 Me), 58.9 (CH_3 Me, CH_3 Me; ^{2}H NMR (77 MHz, $CDCl_3$): δ 3.08 (D-1); HRMS: $[M+H]^+$ calcd for $C_8H_{16}DO_4$ 178.11896, found 178.11847.



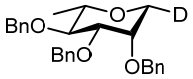
1-Deuterio-1-deoxy-2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside (S58). The title compound was prepared according to general procedure V yielding compound **S58** (21 mg, 95 µmol, 95%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.69 (pentane:EtOAc, 5:5, v:v); $[\alpha]_D^{20}$ 4.2° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 830, 920, 1031, 1086, 1464, 2821, 2940; ^{1}H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 4.04 (d, J = 5.2 Hz, 1H, H-1), 3.64 (s, 3H, CH_3), 3.60 (dd, J = 10.4, 2.1 Hz, 1H, H-6), 3.54 (s, 4H, CH_3, H-6), 3.47 (s, 3H, CH_3), 3.40 (s, 3H, CH_3), 3.29 – 3.18 (m, 2H, H-2, H-5), 3.18 – 3.05 (m, 2H, H-3, H-4); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 87.9 (C-3), 80.0 (C-2), 79.7 (C-4), 79.1 (C-5), 71.8 (C-6), 67.42 (t, J = 21.7 Hz, C-1), 60.8, 60.6, 59.4, 58.9 (CH_3); HRMS: $[M+H]^+$ calcd for $C_{10}H_{19}NaDO_5$ 244.1256, found 244.1267.

1-Deuterio-1-deoxy-2,3,4,6-tetra-*O*-methyl-β-D-mannopyranoside (S59). The title compound was prepared according to general procedure V yielding compound **S59** (22 mg, 99 µmol, 99%, colourless oil, 1,2-*cis*:1,2-*trans*; 96:4). TLC: R_f 0.71 (pentane:EtOAc, 5:5, v:v); $[\alpha]_D^{20}$ −16.1° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 833, 923, 1028, 1090, 1465, 2825, 2930; Data of the major stereoisomer (1,2-*cis* product): ^1H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 3.65 (dd, *J* = 10.3, 2.0 Hz, 1H, H-6), 3.62 (dd, *J* = 3.4, 0.9 Hz, 1H, H-2), 3.56 (dd, *J* = 10.3, 6.4 Hz, 1H, H-6), 3.53 (s, 3H, CH_3), 3.50 (s, 3H, CH_3), 3.45 (s, 3H, CH_3), 3.41 (s, 3H, CH_3), 3.36 (t, *J* = 9.3 Hz, 1H, H-4), 3.31 – 3.23 (m, 2.96H, H-1, H-3, H-5); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 84.6 (C-3), 79.5 (C-5), 77.0 (C-4), 75.2 (C-2), 72.4 (C-6), 65.51 (t, *J* = 22.7 Hz, C-1), 61.0, 59.4, 57.4, 57.3 (CH_3); Data of the major stereoisomer (1,2-*trans* product): ^1H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): 4.17 (d, *J* = 1.5 Hz, 0.04H); HRMS: $[M+H]^+$ calcd for $C_{10}H_{19}NaDO_5$ 244.1256, found 244.1269.

Model glycosylation reactions in Et_2O or MeCN



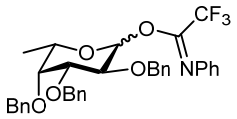
1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-α-L-fucopyranoside (S42). The title compound was prepared according to general procedure VII yielding compound **S42** (40 mg, 95 µmol, 95%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2) in Et_2O or yielding compound **S42** (23 mg, 55 µmol, 55%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2) in MeCN. TLC: R_f 0.54 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ −35.0° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 694, 733, 1026, 1070, 1088, 1360, 1454, 1497, 2851, 2916; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.42 – 7.24 (m, 15H, CH_{arom}), 4.99 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.86 – 4.75 (m, 3H, CH*H* Bn, CH_2 Bn), 4.71 – 4.63 (m, 2H, CH_2 Bn), 4.06 – 4.00 (m, 2H, H-1, H-2), 3.64 (dd, *J* = 2.9, 1.1 Hz, 1H, H-4), 3.54 (dd, *J* = 8.7, 2.9 Hz, 1H, H-3), 3.40 (qd, *J* = 6.4, 1.1 Hz, 1H, H-5), 1.14 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.8, 138.6 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.3, 127.9, 127.8, 127.7, 127.7, 127.6 (CH_{arom}), 84.2 (C-3), 77.1 (C-4), 75.2 (C-5), 75.1 (CH_2 Bn), 74.9 (C-2), 73.6, 72.9 (CH_2 Bn), 66.75 (t, *J* = 23.5 Hz, C-1), 17.3 (CH_3); ^2H NMR (77 MHz, $CHCl_3$): δ 3.17 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{33}DNO_4$ 437.25506, found 437.25445.



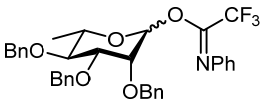
1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-β-L-rhamnopyranoside (S45). The title compound was prepared according to general procedure VII yielding compound **S45** (36 mg, 86 µmol, 86%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2) in Et_2O or yielding compound **S45** (25 mg, 60 µmol, 60%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2) in MeCN. TLC: R_f 0.38 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ 26.1° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 694, 733, 1026, 1092, 1113, 1354, 1452, 1497, 2860; ^1H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.46 – 7.26 (m, 15H, CH_{arom}), 4.99 (d, *J* = 10.8 Hz, 1H, C*H*H Bn), 4.81 (d, *J* = 12.7 Hz, 1H, CH*H* Bn), 4.72 – 4.61 (m, 3H, CH_2 Bn, C*H*H Bn), 4.57 (d, *J* = 11.9 Hz, 1H, CH*H* Bn), 3.75 (dd, *J* = 3.3, 1.0 Hz, 1H, H-2), 3.62 (t, *J* = 9.2 Hz, 1H, H-4), 3.53 (dd, *J* = 9.3, 3.2 Hz, 1H, H-3), 3.28 (dq, *J* = 9.0, 6.0 Hz, 1H, H-5), 3.24 (s, 1H, H-1), 1.36 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.7, 138.5, 138.4 ($C_{q\text{-}arom}$), 128.5, 128.2, 127.8, 127.7 (CH_{arom}), 82.8 (C-4), 80.8 (C-3), 76.5 (C-5), 75.7 (CH_2 Bn), 72.6 (C-2), 71.7, 71.3 (CH_2 Bn), 66.8 (t, *J* =

23.5 Hz, C-1), 18.4 (CH_3); ^{2}H NMR (77 MHz, $CHCl_3$): δ 4.03 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{33}DNO_4$ 437.25506, found 437.25446.

Preparation of *N*-phenyl trifluoroacetimidate donors and their model glycosylations

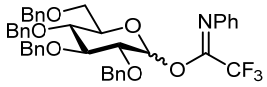


2,2,2-trifluoro-*N*-phenylacetimidoyl 2,3,4-tri-*O*-benzyl-α/β-D-fucopyranoside (S60). 2,3,4-tri-*O*-benzyl-α/β-D-fucopyranoside (87 mg, 0.2 mmol) was dissolved in acetone (2 mL, 0.1 M) and water (0.2 mL, 50 eq.) and cooled on ice. Subsequently, $CsCO_3$ (130 mg, 0,4 mmol, 1.8 eq.) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (83 mg, 0.4 mmol, 1.8 mmol) was added and the solution was allowed to attain rt. After stirring for 18 hours, the solution was diluted with H_2O and EtOAc. The aqueous layer was extracted (3x) with EtOAc followed by washing the combined organic layer with H_2O, sat. aq. $NaHCO_3$ and brine respectively. Subsequently, the organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield the crude product as a colourless oil. Flash column chromatography (95:5 → 80:20; pentane:Et_2O) yielded the title compound **S60** (102 mg, 0.17 mmol, 76% in a 33:66 α:β ratio) as a colourless oil. Spectroscopic data was in accordance with literature.[M. Adinolfi, A. Iadonisi, A. Ravidà, M. Schiattarella, Versatile Use of Ytterbium(III) Triflate and Acid Washed Molecular Sieves in the Activation of Glycosyl Trifluoroacetimidate Donors. Assemblage of a Biologically Relevant Tetrasaccharide Sequence of Globo H. *The Journal of Organic Chemistry*. 70, 5316–5319 (2005).] TLC: R_f 0.4 (pentane: Et_2O, 9:1, v:v); Data for the anomeric mixture: (500 MHz, Chloroform-*d*, 60 °C, HH-COSY, HSQC): δ 7.64 – 6.60 (m, 30H, CH_{arom}), 6.38 (s, 0.5H, H-1$_\alpha$), 5.54 (s, 1H, H-1$_\beta$), 5.06 – 4.61 (m, 9H, CH_2 Bn$_\alpha$, CH_2 Bn$_\alpha$, CH_2 Bn$_\alpha$, CH_2 Bn$_\beta$, CH_2 Bn$_\beta$, CH_2 Bn$_\beta$), 4.16 (dd, *J* = 10.1, 3.5 Hz, 0.5H, H-2$_\alpha$), 4.08 – 3.98 (m, 1.5H, H-2$_\beta$, H-5$_\alpha$), 3.96 (dd, *J* = 10.1, 2.8 Hz, 0.5H, H-3$_\alpha$), 3.67 (dd, *J* = 2.8, 1.3 Hz, 0.5H, H-4$_\alpha$), 3.63 – 3.47 (m, 2H, H-3$_\beta$, H-4$_\beta$), 3.41 (s, 1H, H-5$_\beta$), 1.18 (m, 4.5H, $CH_{3\alpha}$, $CH_{3\beta}$); ^{13}C NMR (101 MHz, $CDCl_3$, 60 °C, HSQC): δ 144.1, 144.0, 138.9, 138.7, 138.7, 138.6, 138.5, 135.4 ($C_{q\text{-}arom}$), 129.5, 128.8, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 127.9, 127.8, 127.8, 127.8, 127.7, 126.6, 124.3, 124.2, 120.8, 119.8, 119.6 (CH_{arom}), 98.0 (C-1$_\beta$), 95.4 (bs, C-1$_\alpha$), 82.8 (C-3$_\beta$), 78.9 (C-3$_\alpha$), 78.4 (C-2$_\beta$), 78.0 (C-4$_\alpha$), 76.7 (C-4$_\beta$), 76.0 (C-2$_\alpha$), 75.5, 75.2, 75.1, 73.6, 73.6, 73.5 (CH_2 Bn), 71.9 (C-5$_\beta$), 69.9 (C-5$_\alpha$), 16.8 ($CH_{3\beta}$), 16.8 ($CH_{3\alpha}$).

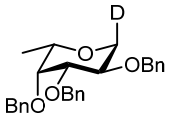


2,2,2-trifluoro-*N*-phenylacetimidoyl 2,3,4-tri-*O*-benzyl-α/β-D-rhamnopyranoside (S61). 2,3,4-tri-*O*-benzyl-α/β-D-rhamnopyranoside (87 mg, 0.2 mmol) was dissolved in acetone (2 mL, 0.1 M) and water (0.2 mL, 50 eq.) and cooled on ice. Subsequently, $CsCO_3$ (130 mg, 0,4 mmol, 1.8 eq.) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (83 mg, 0.4 mmol, 1.8 mmol) was added and the solution was allowed to attain rt. After stirring for 18 hours, the solution was diluted with H_2O and EtOAc. The aqueous layer was extracted (3x) with EtOAc followed by washing the combined organic layer with H_2O, sat. aq. $NaHCO_3$ and brine respectively. Subsequently, the organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield the crude product as a colourless oil. Flash column chromatography (95:5 → 80:20; pentane:Et_2O) yielded the title compound **S60** (109 mg, 0.18 mmol, 81% in a 71:29 α:β ratio) as a colourless oil. Spectroscopic data was in accordance with literature.[M. Adinolfi, G. Barone, A. Iadonisi, M. Schiattarella, Activation of Glycoyl Trihaloacetimidates with Acid-Washed Molecular Sieves in the Glycosidation Reaction. *Org. Lett.* 5, 987–989

(2003).] TLC: R_f 0.4 (pentane: Et_2O, 9:1, v:v); Data for the anomeric mixture: (500 MHz, Chloroform-*d*, 60 °C, HH-COSY, HSQC): δ 7.74 – 6.66 (m, 28H, CH_{arom}), 6.09 (bs, 1H, H-1_α), 5.52 (bs, 0.4H, H-1_β), 4.96 – 4.46 (m, 8.4H, CH_2 Bn$_\alpha$, CH_2 Bn$_\alpha$, CH_2 Bn$_\alpha$, CH_2 Bn$_\beta$, CH_2 Bn$_\beta$, CH_2 Bn$_\beta$), 4.05 (d, *J* = 2.9 Hz, 0.4H, H-3_β), 3.91 – 3.72 (m, 3H, H-2_α, H-3_α, H-5_α), 3.74 – 3.58 (m, 1.4H, H-2_β, H-4_α), 3.48 (d, *J* = 9.1 Hz, 0.4H, H-4_β), 3.25 (bs, 0.4H, H-5_β), 1.34 (m, 4.2H, $CH_{3\alpha}$, $CH_{3\beta}$); ^{13}C NMR (101 MHz, $CDCl_3$, 60 °C, HSQC): δ 143.9, 138.7, 138.5, 138.1 ($C_{q\text{-}arom}$), 129.6, 128.9, 128.9, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 126.6, 124.5, 120.8, 119.7, 119.6 (CH_{arom}), 96.5 (C-1_β), 96.2 (C-1_α), 82.4 (C-4_β), 80.1 (C-4_α), 79.9 (C-2_β), 79.3 (C-2_α), 75.6, 75.5, 74.4 (CH_2 Bn), 74.2 (C-3_α), 73.7 (C-3_β), 73.2 (C-5_β), 73.1, 72.9, 72.4 (CH_2 Bn), 71.3 (C-5_α), 18.2 ($CH_{3\alpha}$), 18.1 ($CH_{3\beta}$).

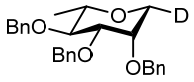


2,2,2-trifluoro-*N*-phenylacetimidoyl 2,3,4-tri-*O*-benzyl-α/β-D-rhamnopyranoside (S62). 2,3,4-tri-*O*-benzyl-α/β-D-rhamnopyranoside (108 mg, 0.2 mmol) was dissolved in acetone (2 mL, 0.1 M) and water (0.2 mL, 50 eq.) and cooled on ice. Subsequently, $CsCO_3$ (130 mg, 0,4 mmol, 1.8 eq.) and 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride (83 mg, 0.4 mmol, 1.8 mmol) was added and the solution was allowed to attain rt. After stirring for 18 hours, the solution was diluted with H_2O and EtOAc. The aqueous layer was extracted (3x) with EtOAc followed by washing the combined organic layer with H_2O, sat. aq. $NaHCO_3$ and brine respectively. Subsequently, the organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield the crude product as a colourless oil. Flash column chromatography (95:5 → 80:20; pentane:Et_2O) yielded the title compound **S60** (142 mg, 197 µmol, 98% in a 50:50 α:β ratio) as a colourless syrup. Spectroscopic data was in accordance with literature.[L. Wang, H. S. Overkleeft, G. A. van der Marel, J. D. C. Codée, Reagent Controlled Stereoselective Synthesis of α-Glucans. *Journal of the American Chemical Society* (2018).] TLC: R_f 0.4 (pentane: Et_2O, 9:1, v:v); Data for the anomeric mixture: (500 MHz, Chloroform-*d*, 60 °C, HH-COSY, HSQC) δ 7.78 – 6.70 (m, 50H, CH_{arom}), 6.44 (bs, 1H, H-1_α), 5.59 (bs, 1H, H-1_β), 4.99 – 4.49 (m, 16H, CH_2 Bn$_\alpha$, CH_2 Bn$_\alpha$, CH_2 Bn$_\alpha$, CH_2 Bn$_\alpha$, CH_2 Bn$_\beta$, CH_2 Bn$_\beta$, CH_2 Bn$_\beta$, CH_2 Bn$_\beta$), 4.06 (t, *J* = 9.3 Hz, 1H, H-4_α), 3.99 (m, 1H, H-6_α), 3.80 – 3.32 (m, 10H, H-2_α, H-3_α, H-5_α, H-6_α, H-2_β, H-3_β, H-4_β, H-5_β, H-6_β, H-6_β); ^{13}C NMR (101 MHz, $CDCl_3$, 60 °C, HSQC): δ 143.9, 143.7, 143.4, 138.9, 138.7, 138.3, 138.2, 138.1, 138.1, 135.9, 135.8, 133.5, 133.5, 133.2, 133.2 ($C_{q\text{-}arom}$), 129.4, 128.8, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.9, 127.90, 127.80, 127.7, 127.7, 127.6, 126.7, 126.7, 126.4, 126.1, 126.0, 126.0, 124.4, 124.3, 120.7, 119.6, 119.6 (CH_{arom}), 116.5 (q, CF_3), 97.6 (C-1_β), 93.9 (C-1_α), 84.7, 81.7, 81.2, 79.7, 77.6, 77.6, 76.0, 75.7, 75.6, 75.3, 75.0, 75.0, 73.7, 73.6, 73.5, 73.5, 68.6.

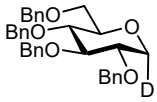


1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-α-L-fucopyranoside (S42). The title compound was prepared according to general procedure VIII yielding compound **S42** (38 mg, 91 µmol, 91%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.54 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ −35.0° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 694, 733, 1026, 1070, 1088, 1360, 1454, 1497, 2851, 2916; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.42 – 7.24 (m, 15H, CH_{arom}), 4.99 (d, *J* = 11.6 Hz, 1H, C*H*H Bn), 4.86 – 4.75 (m, 3H, CH*H* Bn, CH_2 Bn), 4.71 – 4.63 (m, 2H, CH_2 Bn), 4.06 – 4.00 (m, 2H, H-1, H-2), 3.64 (dd, *J* = 2.9, 1.1 Hz, 1H, H-4), 3.54 (dd, *J* = 8.7, 2.9 Hz, 1H, H-3), 3.40 (qd, *J* = 6.4, 1.1 Hz, 1H, H-5), 1.14 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.8, 138.6 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.3, 127.9, 127.8, 127.7, 127.7, 127.6 (CH_{arom}), 84.2 (C-3), 77.1 (C-

4), 75.2 (C-5), 75.1 (CH_2 Bn), 74.9 (C-2), 73.6, 72.9 (CH_2 Bn), 66.75 (t, J = 23.5 Hz, C-1), 17.3 (CH_3); ^{2}H NMR (77 MHz, $CHCl_3$): δ 3.17 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{33}DNO_4$ 437.25506, found 437.25445.



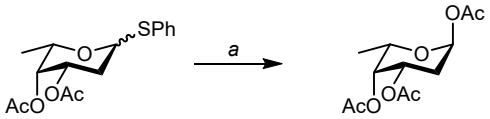
1-Deutero-1-deoxy-2,3,4-tri-*O*-benzyl-β-L-rhamnopyranoside (S45). The title compound was prepared according to general procedure VIII yielding compound **S45** (39 mg, 93 µmol, 93%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.38 (pentane:EtOAc, 9:1, v:v); $[\alpha]_D^{20}$ 26.1° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 694, 733, 1026, 1092, 1113, 1354, 1452, 1497, 2860; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC, NOESY): δ 7.46 – 7.26 (m, 15H, CH_{arom}), 4.99 (d, J = 10.8 Hz, 1H, C*H*H Bn), 4.81 (d, J = 12.7 Hz, 1H, CH*H* Bn), 4.72 – 4.61 (m, 3H, CH_2 Bn, C*H*H Bn), 4.57 (d, J = 11.9 Hz, 1H, CH*H* Bn), 3.75 (dd, J = 3.3, 1.0 Hz, 1H, H-2), 3.62 (t, J = 9.2 Hz, 1H, H-4), 3.53 (dd, J = 9.3, 3.2 Hz, 1H, H-3), 3.28 (dq, J = 9.0, 6.0 Hz, 1H, H-5), 3.24 (s, 1H, H-1), 1.36 (d, J = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.7, 138.5, 138.4 ($C_{q\text{-}arom}$), 128.5, 128.2, 127.8, 127.7 (CH_{arom}), 82.8 (C-4), 80.8 (C-3), 76.5 (C-5), 75.7 (CH_2 Bn), 72.6 (C-2), 71.7, 71.3 (CH_2 Bn), 66.8 (t, J = 23.5 Hz, C-1), 18.4 (CH_3); ^{2}H NMR (77 MHz, $CHCl_3$): δ 4.03 (D-1); HRMS: $[M+NH_4]^+$ calcd for $C_{27}H_{33}DNO_4$ 437.25506, found 437.25446.



1-Deutero-1-deoxy-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (S47). The title compound was prepared according to general procedure VIII yielding compound **S47** (48 mg, 91 µmol, 91%, colourless oil, 1,2-*cis*:1,2-*trans*; >98:2). TLC: R_f 0.69 (pentane:EtOAc, 8:2, v:v); $[\alpha]_D^{20}$ 5.3° (*c* 1, $CHCl_3$); IR (thin film, cm^{-1}): 698, 731, 1024, 1093, 1123, 1353, 1451, 1499, 2867; ^{1}H NMR (400 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 7.61 – 6.96 (m, 20H, CH_{arom}), 4.97 (d, J = 11.0 Hz, 1H, C*H*H Bn), 4.84 (d, J = 11.0 Hz, 1H, CH*H* Bn), 4.83 (d, J = 10.7 Hz, 1H, C*H*H Bn), 4.71 (d, J = 11.6 Hz, 1H, C*H*H Bn), 4.63 (d, J = 11.6 Hz, 1H, CH*H* Bn), 4.59 (d, J = 12.2 Hz, 1H, C*H*H Bn), 4.50 (d, J = 12.2 Hz, 1H, CH*H* Bn), 4.48 (d, J = 10.7 Hz, 1H, CH*H* Bn), 4.01 (d, J = 4.5 Hz, 1H, H-1), 3.74 – 3.59 (m, 4H, H-2, H-6, H-6, H-5), 3.56 (ddd, J = 9.2, 5.7, 3.5 Hz, 1H, H-4), 3.37 (ddd, J = 9.5, 4.3, 2.1 Hz, 1H, H-3); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 138.8, 138.3, 138.2, 138.0 ($C_{q\text{-}arom}$), 128.6, 128.5, 128.5, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7 (CH_{arom}), 86.5 (C-2/C-5), 79.3 (C-3), 78.5 (C-5/C-2), 77.9 (C-4), 75.7 (CH_2 Bn), 75.3 (CH_2 Bn), 73.7 (CH_2 Bn), 73.4 (CH_2 Bn), 69.1 (C-6), 67.9 (t, J = 21.5 Hz, C-1); HRMS: $[M+Na]^+$ calcd for $C_{34}H_{35}NaDO_5$ 548.2518, found 548.2521.

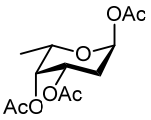
Preparation of the donors for the HF/SbF_5 experiments

Preparation of Donor 33



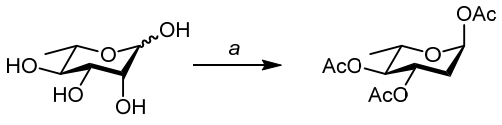
S13 **33**

Scheme S-5. Donor **33** synthesis. *Reagents and conditions:* a) NIS, AcOH, Et_2O, 1,2-dichloroethane, **33**: 67%.



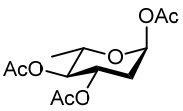
Acetyl 3,4-di-*O*-acetyl-2-deoxy-α-L-fucopyranoside (33). Glacial acetic acid (11.9 mL, 208 mmol, 100 eq.) was added to a mixture of NIS (0.52 g, 2.29 mmol, 1.1 eq.) in Et_2O (10.4 mL) and 1,2-dichloroethane (10.4 mL). The formed solution was added to compound **S13** (0.69 g, 2.1 mmol). After 45 minutes of stirring, the reaction was quenched with sat. aq. NaS_2O_3. The aqueous mixture was extracted with DCM (3x), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography (pentane:EtOAc, 10:90 → 70:30) was performed to yield title compound **33** as an 1:4 1,3-*cis*/1,3-*trans* mixture (0.49 g, 1.8 mmol, 86%, colourless oil). Additional purification by column made it possible to solely isolate the 1,3-*trans* product (0.38 g, 1.4 mmol, 67%, colourless solid). TLC: R_f 0.45 (pentane:EtOAc, 3:7, v:v); IR (neat, cm^{-1}): 802, 927, 987, 1011, 1038, 1194, 1222, 1368, 1441, 1739; Data for the major stereoisomer (1,3-*trans* product): ^{1}H NMR (400 MHz, $CDCl_3$, HH-COSY, HSQC): δ 6.32 (d, *J* = 2.7 Hz, 1H, H-1), 5.32 (ddd, *J* = 12.5, 5.1, 3.0 Hz, 1H, H-3), 5.28 – 5.22 (m, 1H, H-4), 4.20 (q, *J* = 6.5 Hz, 1H, H-5), 2.21 (td, *J* = 13.0, 3.6 Hz, 1H, H-2), 2.20 (s, 3H, CH_3 Ac), 2.14 (s, 3H, CH_3 Ac), 2.04 (s, 3H, CH_3 Ac), 1.91 (ddt, *J* = 13.4, 5.1, 1.2 Hz, 1H, H2), 1.18 (d, *J* = 6.5 Hz, 3H, H-6, H-6, H-6); ^{13}C NMR (101 MHz, $CDCl_3$, HSQC): δ 170.8, 170.3, 169.5 (C=O Ac), 92.1 (C-1), 69.4 (C-4), 67.5 (C-5), 66.4 (C-3), 28.9 (C-2), 21.3, 21.1, 20.9 (CH_3 Ac), 16.7 (C-6); Data for the minor stereoisomer (1,3-*cis* product): ^{1}H NMR (400 MHz, CDCl3, HH-COSY, HSQC): δ 5.77 (dd, *J* = 9.3, 3.3 Hz, 1H, H-1), 5.14 (d, *J* = 3.1 Hz, 1H, H-4), 5.04 (ddd, *J* = 11.7, 5.8, 3.2 Hz, 1H, H3), 3.82 (q, *J* = 6.4 Hz, 1H, H-5), 2.18 (s, 3H, CH_3 Ac), 2.14 (s, 3H, CH_3 Ac), 2.03 – 2.00 (m, 5H, H2, H-2, CH_3 Ac), 1.23 (d, *J* = 6.4 Hz, 3H, H-6, H-6, H-6); ^{13}C NMR (126 MHz, $CDCl_3$, HSQC): δ 91.8 (C-1), 70.5 (C-5), 68.7 (C-4), 68.4 (C-3), 30.5 (C-2), 21.2 (CH_3 Ac), 20.9 (CH_3 Ac), 16.5 (C-6); HRMS: $[M+Na]^+$ calcd for $C_{12}H_{18}NaO_7$ 297.09447, found 297.09439.

Preparation of Donor 34



34

Scheme S-6. Donor **34** synthesis. *Reagents and conditions:* a) *i.* Ac_2O, pyr; *ii.* HBr, AcOH, DCM; *iii.* $CuSO_4 \cdot 5H_2O$, Ac_2O, NaOAc, AcOH, Zn; *iv.* Ac_2O, HBr, AcOH, **34**: 60%.



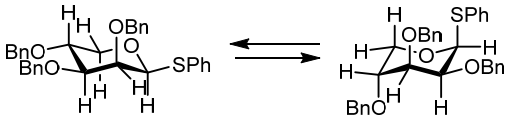
2-deoxy-1,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (34). To suspension of L-rhamnose (4.5 g, 27.5 mmol) in pyridine (25 mL), Ac_2O (32 mL, 340 mmol, 12 eq.) at 0 °C. After stirring for an additional 16 h at rt. The mixture

was concentrated *in vacuo* and co-evaporated three times with heptane. The resulting colourless oil was used in the next step without further purification. The crude product was dissolved in DCM (18 mL), followed by the addition of Ac_2O (1 mL, 10.6 mmol, 0.4 eq.). To the solution HBr (33 wt% in AcOH, 8.5 mL, 55.0 mmol, 2.0 eq.) was added dropwise at 0 °C and stirred for an additional 4 h at rt. The mixture was then concentrated under reduced pressure and the yellow oil was used as a crude product in the next step. $CuSO_4 \cdot 5H_2O$ (0.88 g), Ac_2O (3.6 mL, 38 mmol, 1.4 eq.), sodium acetate (4.5 g, 55 mmol, 2 eq.), AcOH (3.2 mL) were suspended in acetonitrile (12 mL), and subsequently Zn (dust, 3.6 g, 55 mmol, 2 eq.) was added. After 45 minutes of stirring the rhamnosyl bromide was added in 60 mL acetonitrile via a dropping funnel over 40 minutes. The reaction was allowed to stir for an additional 2 h. After reaction completion the mixture was diluted with DCM and filtrated over Celite® 545 (Sigma-Aldrich) and transferred to a separatory funnel. The organic phase was washed with saturated sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated *in vacuo*. The crude rhamnal was dissolved in DCM (40 mL) and AcOH (15.8 mL, 276 mmol, 10 eq.), Ac_2O (22.2 mL, 233 mmol, 8.5 eq.) were added at 0 °C. After 15 min stirring, HBr (33 wt% in AcOH, 1.5 mL, 9.1 mmol, 0.3 eq.) was dropwise added at 0 °C and the reaction was stirred for an additional 5 h. After reaction completion the mixture was quenched with ice-cold water and extracted DCM (3x). The combined organic layers were washed with sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated *in vacuo*. Column chromatography (95:5 → 85:15, pentane:EtOAc) gave the title compound **34** (4.5 g, 16.4 mmol, 60% over 4 steps, average of 88% per step, white solid). TLC: R_f 0.26 (pentane:EtOAc, 8:2, v:v). IR (neat, cm^{-1}): 922, 1037, 1134, 1157, 1369, 1732, 2994; ^1H NMR (500 MHz, Chloroform-*d*, HH-COSY, HSQC): δ 6.19 (dd, J = 3.8, 1.4 Hz, 1H, H-1), 5.27 (ddd, J = 11.6, 9.5, 5.3 Hz, 1H, H-3), 4.80 (t, J = 9.7 Hz, 1H, H-4), 3.94 (dq, J = 9.8, 6.2 Hz, 1H, H-5), 2.26 (ddd, J = 13.5, 5.3, 1.5 Hz, 1H, H-2), 2.12 (s, 3H, CH_3 Ac), 2.07 (s, 3H, CH_3 Ac), 2.03 (s, 3H, CH_3 Ac), 1.92 (ddd, J = 13.5, 11.7, 3.7 Hz, 1H, H-2), 1.19 (d, J = 6.3 Hz, 3H, CH_3); ^{13}C NMR (126 MH, $CDCl_3$, HSQC): δ 170.4, 170.1, 169.3 (C=O, Ac), 90.9 (C-1), 74.2 (C-4), 68.5 (C-3), 68.3 (C-5), 34.3 (C-2), 21.2 (CH_3 Ac), 21.1 (CH_3 Ac), 20.9 (CH_3 Ac), 17.7 (CH_3); HRMS: $[M+Na]^+$ calcd for $C_{12}H_{18}NaO_7$ 297.0950, found 297.0951.

Stereochemical proofs

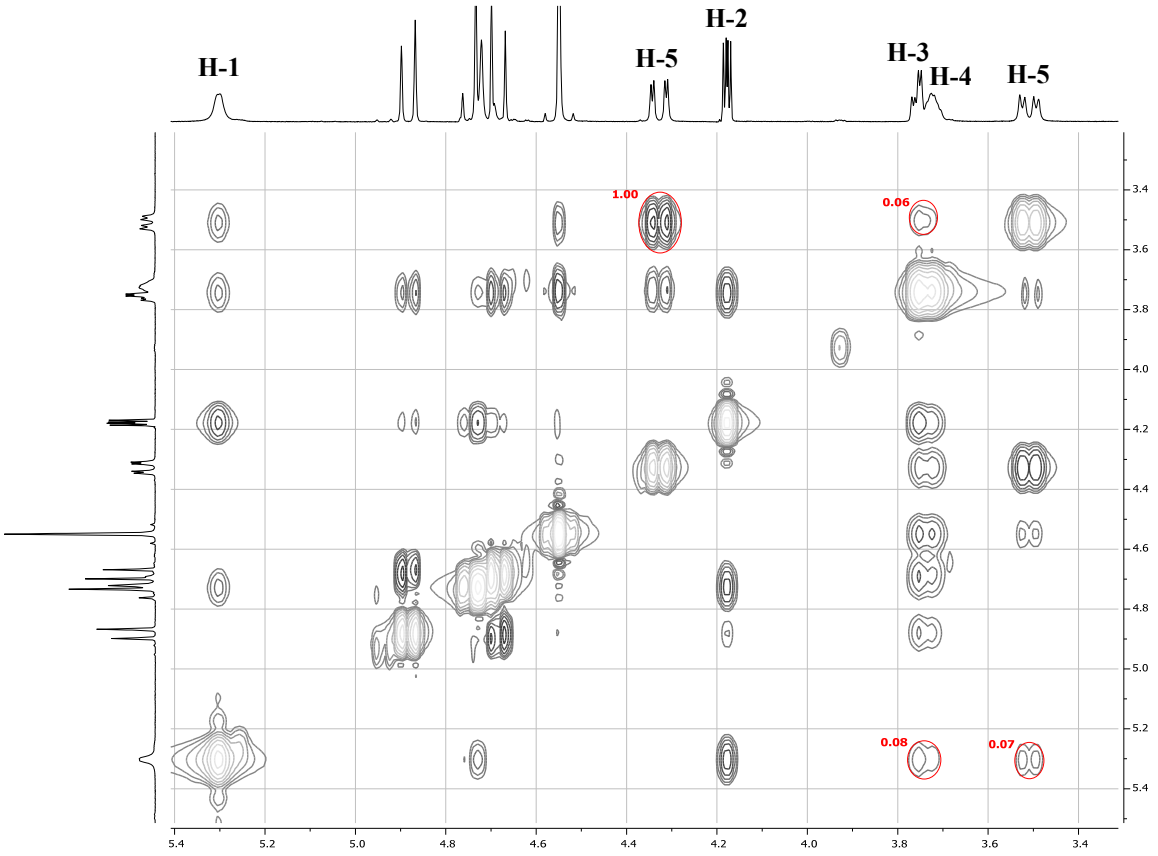
Donor S6

^{1}H NMR H-H coupling constants



H-1: d, *J* = 4.0 Hz (H-1−H-2)
H-2: dd, *J* = 4.1, Hz (H-2−H-1), 2.5 Hz (H-2−H-3)
H-3: dd, *J* = 5.7 Hz (H-3−H-4) 2.6 Hz (H-3−H-2)
H-4: signal overlaps with H-3
H-5$_{eq}$: dd, *J* = 12.2 Hz (geminal), 4.3 Hz (H-5−H-4)
H-5$_{ax}$: dd, *J* = 12.3 Hz (geminal), 2.5 Hz (H-5−H-4)

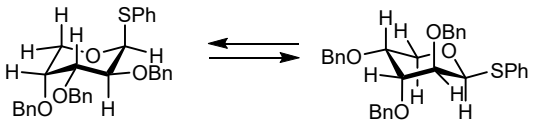
NOESY NMR: H-H long range NOE coupling interaction



The vicinal long range NOE interactions are very weak, which is extra indication that a conformational equilibrium is present. For further structure elucidation see section *"NMR simulations of selected glycosides"*.

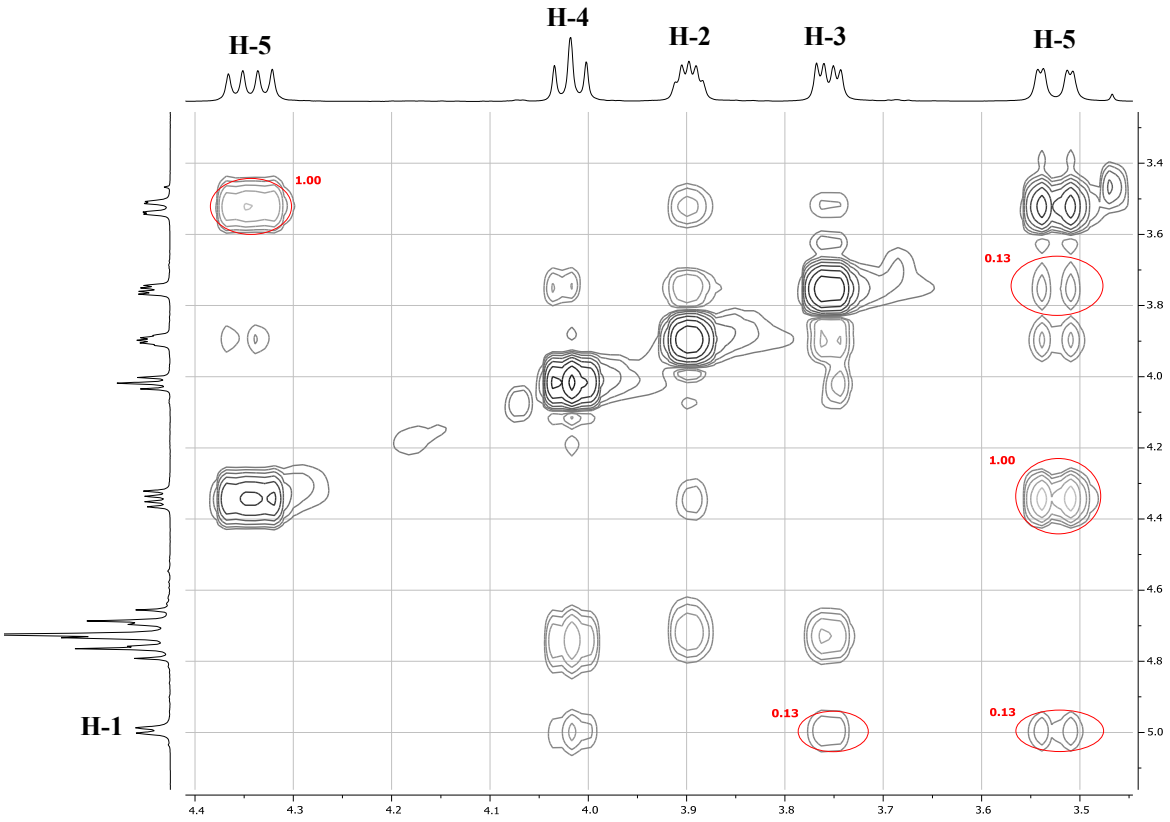
Donor S7

^{1}H NMR H-H coupling constants



H-1: d, *J* = 6.1 Hz (H-1−H-2)
H-2: t, *J* = 6.5 Hz (H-2−H-1 and H-2−H-3)
H-3: dd, *J* = 6.9 Hz (H-3−H-2) 3.1 Hz (H-3−H-4)
H-4: dt, *J* = 5.8 Hz (H-4−H-5), 2.8 Hz (H-4−H-3 and H-4−H-5)
H-5$_{eq}$: dd, *J* = 12.0 Hz (geminal), 5.8 Hz (H-5−H-4)
H-5$_{ax}$: dd, *J* = 12.0 Hz (geminal), 2.6 Hz (H-5−H-4)

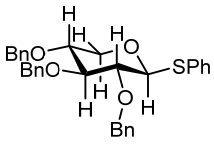
NOESY NMR: H-H long range NOE coupling interaction



The vicinal long range NOE interactions are very weak, which is extra indication that a conformational equilibrium is present. For further structure elucidation see section *"NMR simulations of selected glycosides"*.

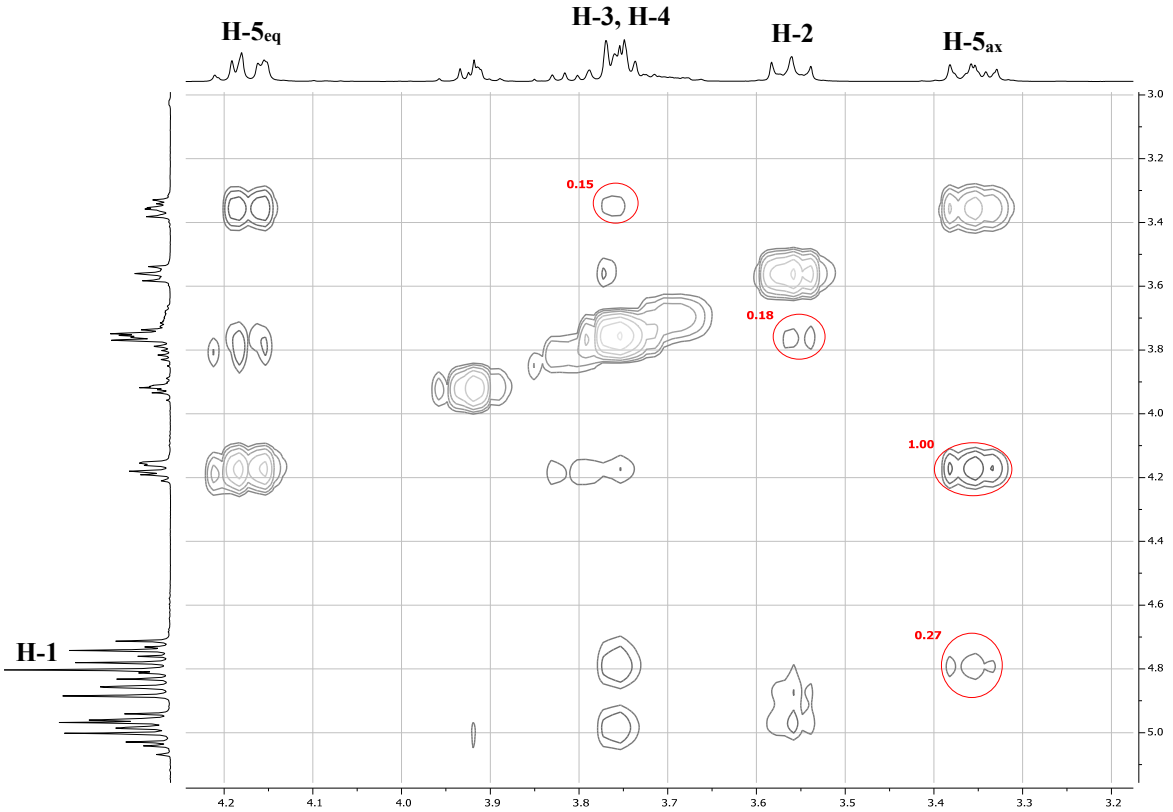
Donor S8; major isomer 1,2-*trans*

^{1}H NMR H-H coupling constants



H-1: d, J = 9.5 Hz (ax^{H-1}–ax^{H-2})
H-2: t, J = 8.7 H (ax^{H-2}–ax^{H-1} and ax^{H-2}–ax^{H-3})
H-3: signal overlaps with H-4
H-4: signal overlaps with H-3
H-5$_{eq}$: signal overlaps with H-5$_{ax}$ of 1,2-*cis* anomer
H-5$_{ax}$: dd, J = 11.5 Hz (geminal), 9.6 Hz (ax^{H-5}–ax^{H-4})

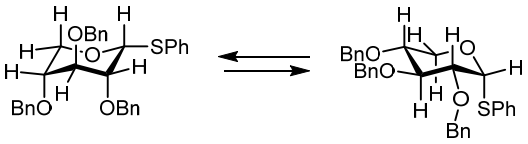
NOESY NMR: H-H long range NOE coupling interaction



No clear visible vicinal H1-H3 long range NOE interactions as a result of overlap with other NOE signals**.** As expected the vicinal H1-H5$_{ax}$ long range NOE interaction is present at medium intensity.

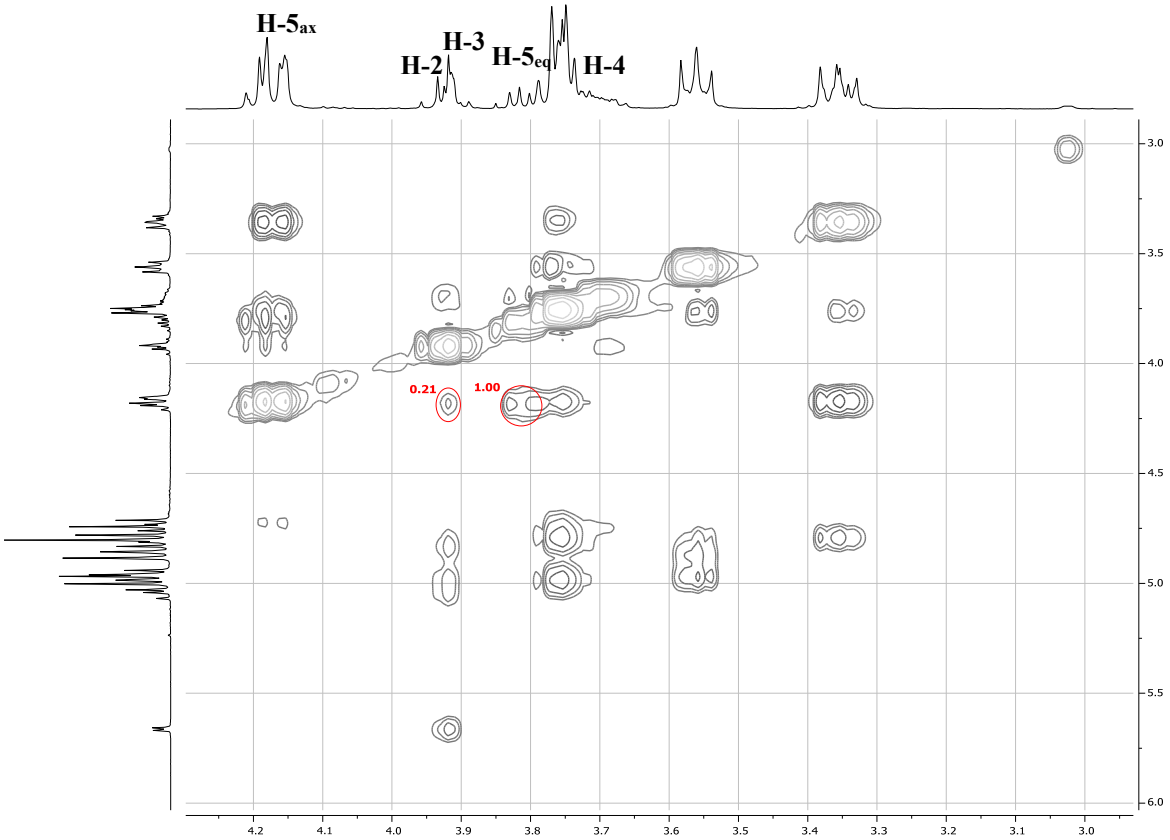
Donor S8; minor isomer 1,2-*cis*

^{1}H NMR H-H coupling constants



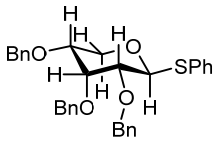
H-1: d, *J* = 4.4 Hz (H-1−H-2)
H-2: t, *J* = 3.0 Hz (H-2−H-1 and H-2−H-3)
H-3: dd, *J* = 5.9 Hz (H-3−H-4) 3.1 Hz (H-3−H-2)
H-4: signal overlaps with H-3, H-4 of 1,2-*trans* anomer
H-5$_{eq}$: dd, *J* = 11.4 Hz (geminal), 5.7 Hz (H-5−H-4)
H-5$_{ax}$: signal overlaps with H-5$_{eq}$ of 1,2-*cis* anomer

NOESY NMR: H-H long range NOE coupling interaction



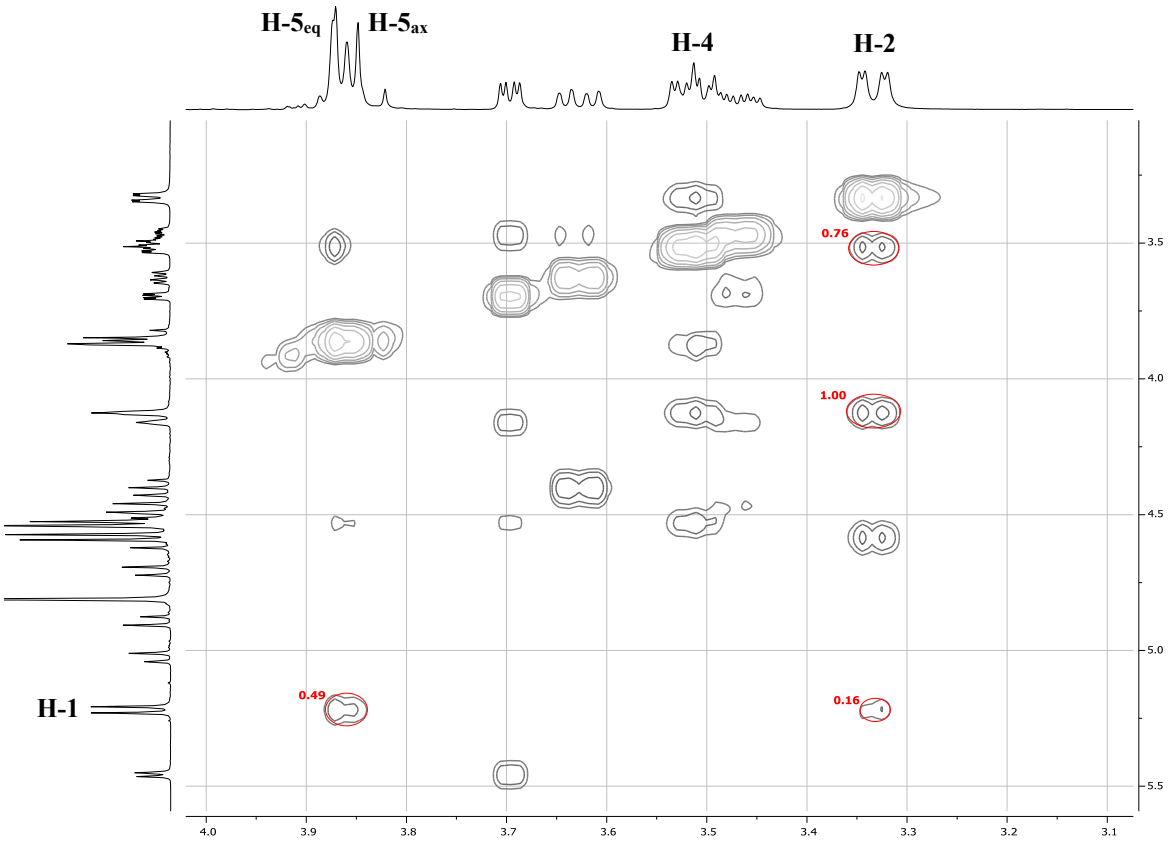
Donor S11; major isomer 1,2-*trans*

^{1}H NMR H-H coupling constants



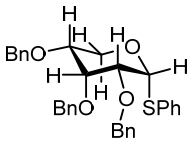
H-1: d, J = 9.0 Hz (ax^{H-1}–ax^{H-2})
H-2: dd, J = 9.1 Hz (ax^{H-2}–ax^{H-1}), 2.5 Hz (ax^{H-2}–eq^{H-3})
H-3: t, J = 2.5 Hz (eq^{H-3}–ax^{H-2} and eq^{H-3}–ax^{H-4})
H-4: ddd, J = 8.3 (ax^{H-4}–ax^{H-5}) 5.9 Hz (ax^{H-4}–eq^{H-5}), 2.3 Hz (ax^{H-4}–eq^{H-3})
H-5$_{eq}$: signal overlaps with H-5$_{ax}$
H-5$_{ax}$: signal overlaps with H-5$_{eq}$

NOESY NMR: H-H long range NOE coupling interaction



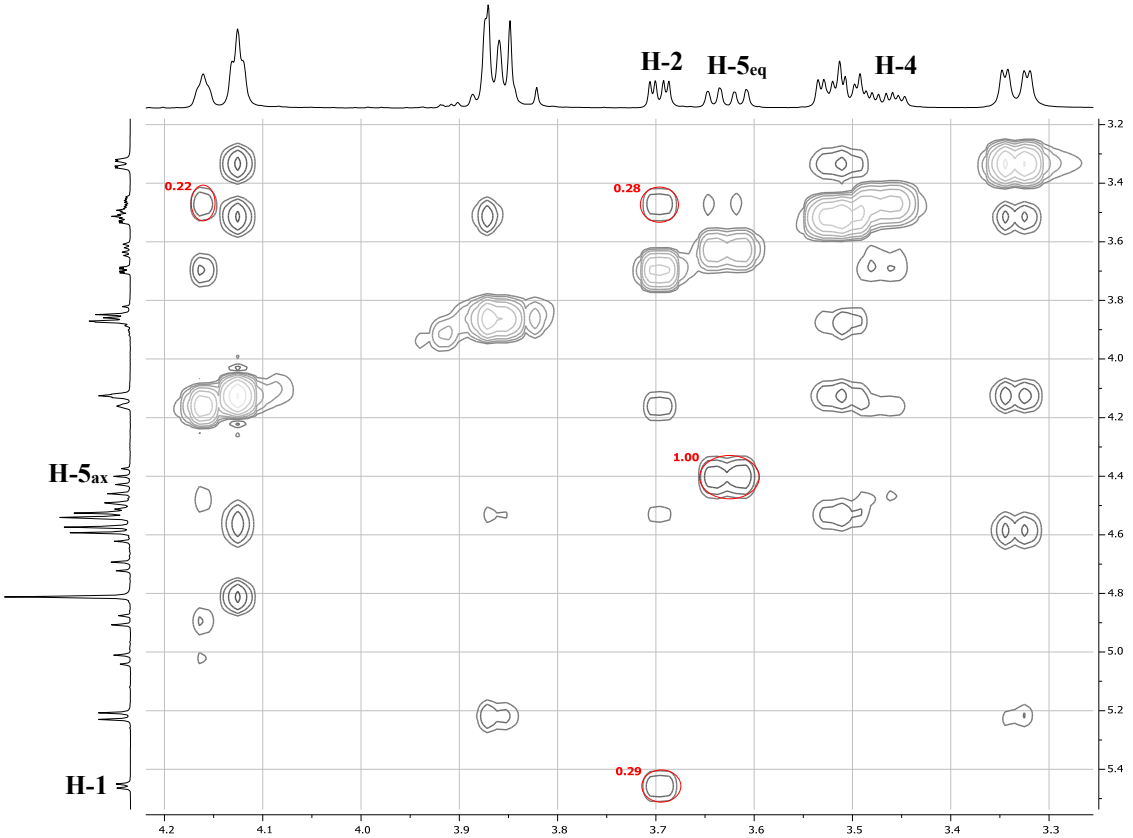
Donor S11; minor isomer 1,2-*cis*

^{1}H NMR H-H coupling constants



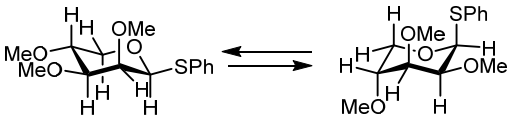
H-1: d, *J*= 5.5 Hz (eq^{H-1}–ax^{H-2})
H-2: dd *J* = 5.5 Hz (ax^{H-2}–eq^{H-1}), 2.2 Hz (ax^{H-2}–eq^{H-3})
H-3: t, *J* = 2.4 Hz (eq^{H-3}–ax^{H-2} and eq^{H-3}–ax^{H-4})
H-4: m
H-5$_{eq}$: dd, *J* = 10.9 Hz (geminal), 5.0 Hz (eq^{H-5}–ax^{H-4})
H-5$_{ax}$: t, *J* = 10.8 Hz (geminal and ax^{H-5}–ax^{H-4})

NOESY NMR: H-H long range NOE coupling interaction



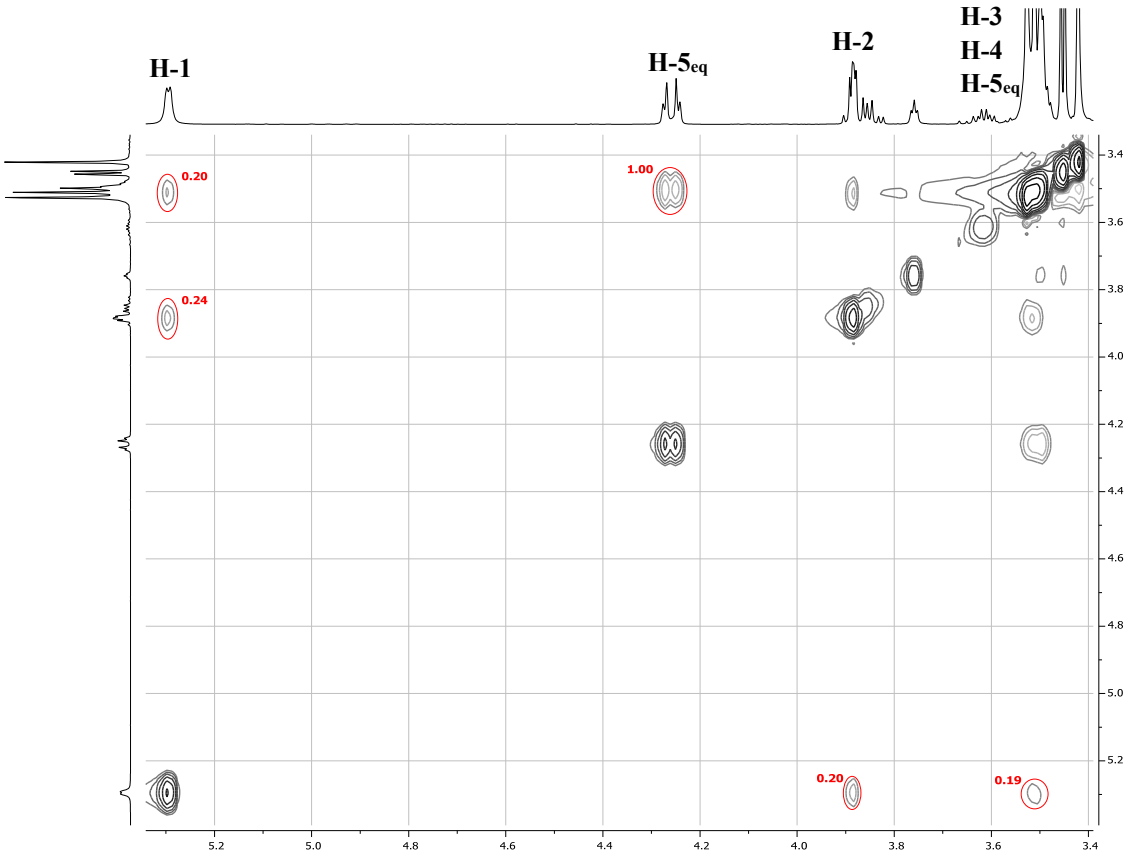
Donor S31; major isomer 1,2-*cis*

^{1}H NMR H-H coupling constants



H-1: d, J = 4.1 Hz (H-1−H-2)
H-2: dd, J = 4.3 Hz (H-2−H-1), 2.5 Hz (H-2−H-3)
H-3: signal overlaps with H-4, H-5 and CH_3
H-4: signal overlaps with H-3, H-5 and CH_3
H-5$_{ax}$: signal overlaps with H-3, H-4 and CH_3
H-5$_{eq}$: dd, J = 9.8 Hz (geminal), 3.9 Hz (H-5−H-4)

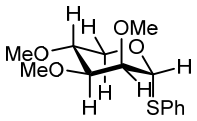
NOESY NMR: H-H long range NOE coupling interaction



The vicinal long range NOE interactions are very weak, which is extra indication for a conformational equilibrium. For further structure elucidation see section *"NMR simulations of selected glycosides"*.

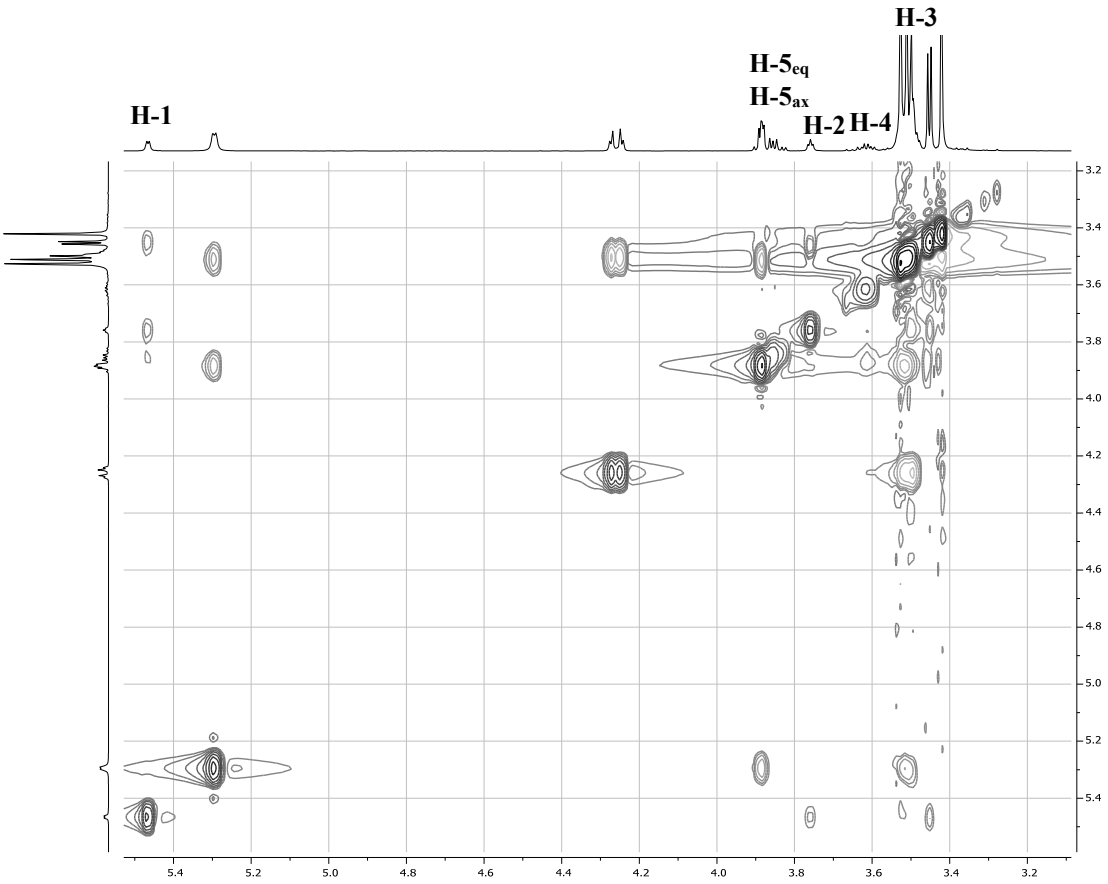
Donor S31; minor isomer 1,2-*trans*

^{1}H NMR H-H coupling constants



H-1: d, J = 3.4 Hz (eq^{H-1}–eq^{H-2})
H-2: t, J = 3.3 Hz (eq^{H-2}–ax^{H-1} and eq^{H-2}–ax^{H-3})
H-3: signal overlaps with CH_3
H-4: td, J = 8.4 Hz (ax^{H-4}–ax^{H-5} and ax^{H-4}–ax^{H-3}), 4.8 Hz (ax^{H-4}–eq^{H-5})
H-5$_{eq}$: signal overlaps with H-5$_{ax}$
H-5$_{ax}$: signal overlaps with H-5$_{eq}$

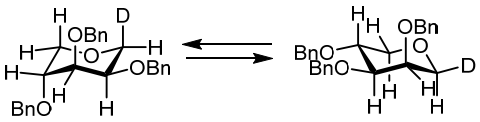
NOESY NMR: H-H long range NOE coupling interaction



No clear visible vicinal H3-H5 long range NOE interactions as a result of overlap with 1,2-*cis* anomer NOE signals.

Compound S35

^{1}H NMR H-H coupling constants



H-1: d, *J* = 2.8 Hz (H-1–H-2)

H-2: t, *J* = 3.0 Hz (H-2–H-1 and H-2–H-3)

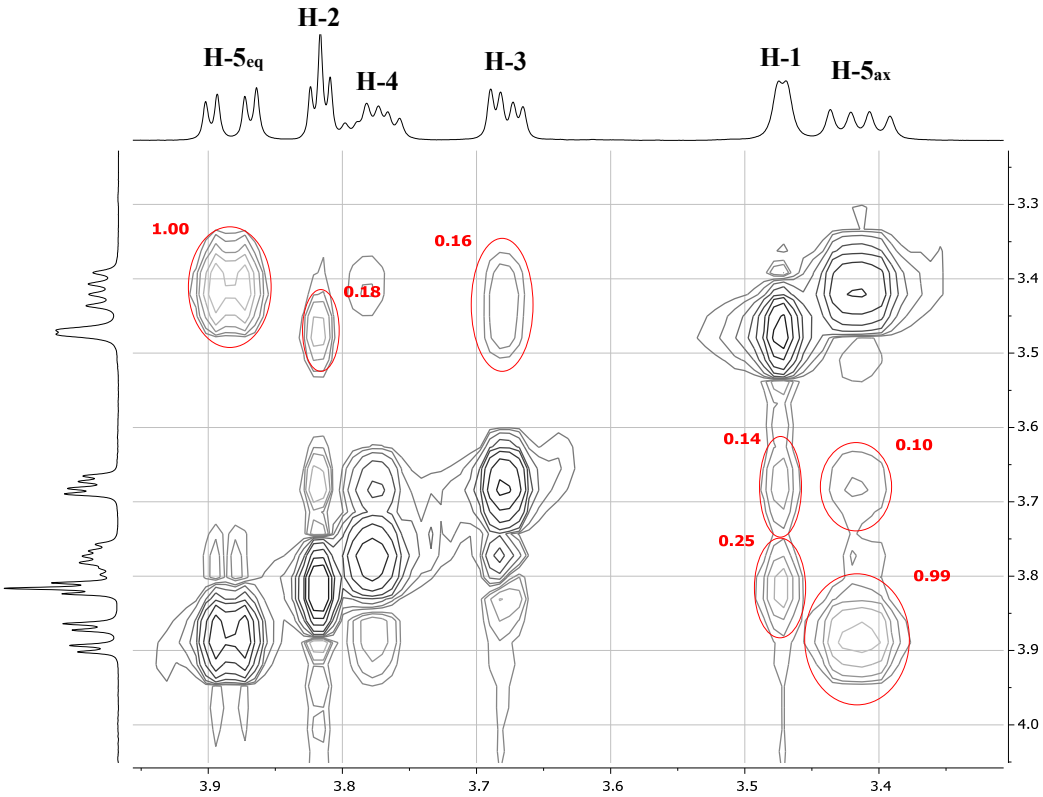
H-3: dd, *J* = 6.7 Hz (H-3–H-4 and H-3–H-5), 3.0 Hz (H-3–H-2)

H-4: td, *J* = 6.4 Hz (H-4–H-3 and H-4 and H-5), 3.5 Hz (H-4–H-5)

H-5$_{ax}$: dd, *J* = 11.7 Hz (geminal), 6.1 Hz (H-5–H-4), signal almost overlaps with H-1, indicating H-1 has to be axial oriented (which is confirmed by NOESY):

H-5$_{eq}$: dd, *J* = 11.8 Hz (geminal), 3.5 Hz (H-5–H-4)

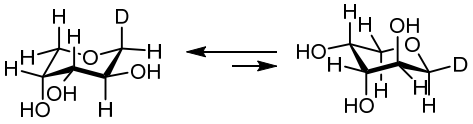
NOESY NMR: H-H long range NOE coupling interaction



For further structure elucidation see section *"NMR simulations of selected glycosides"*.

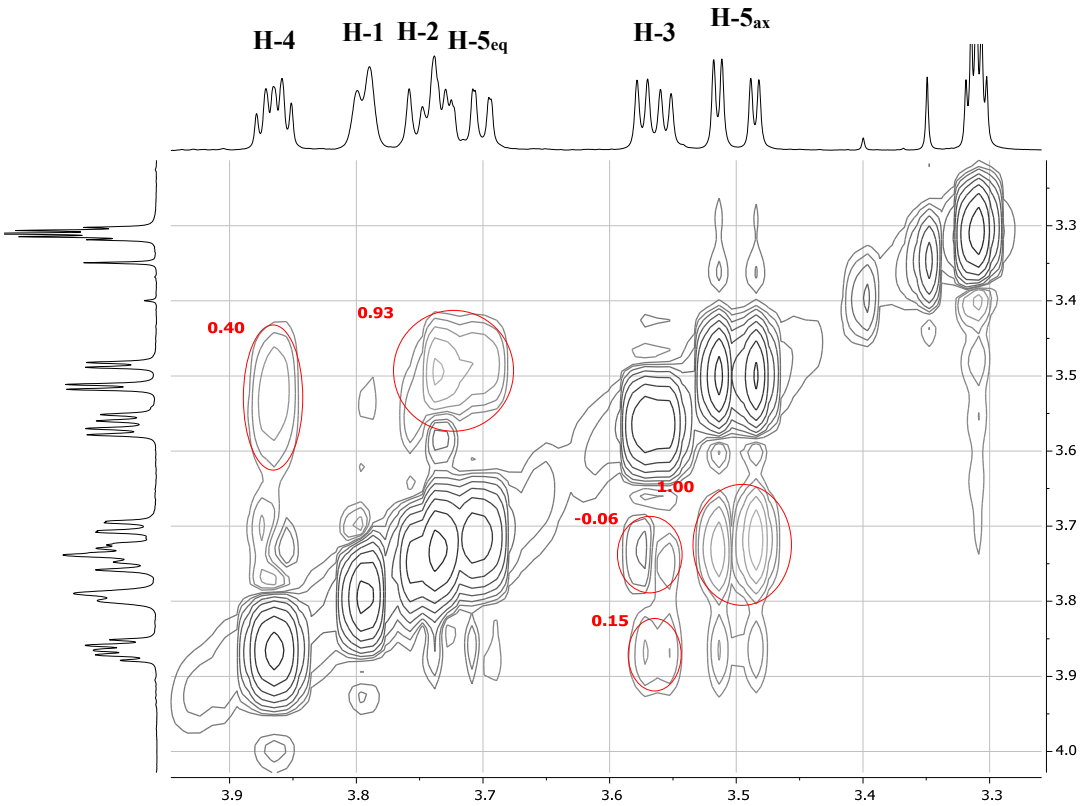
Compound S37

^{1}H NMR: H-H coupling constants

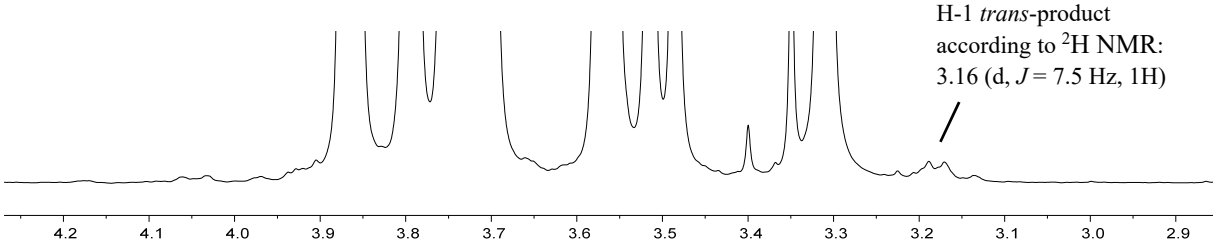


H-1: d, J = 3.8 Hz (H-1–H-2)
H-2: dd, J = 7.4 Hz (H-2–H-3), 4.1 Hz (H-2–H-1)
H-3: dd, J = 7.4 (H-3–H-2), 3.4 Hz (H-3–H-4)
H-4: dt, J = 5.8 (H-4–H-5), 2.9 Hz (H-4–H-3 and H-4–H-5)
H-5$_{ax}$: 11.7 Hz (geminal), 2.6 Hz (H-5–H-4)
H-5$_{eq}$: 11.7 Hz (geminal), 5.2, Hz (H-5–H-4)

NOESY-NMR: H-H long range NOE coupling interaction

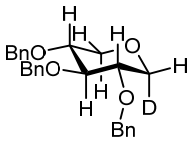


^{1}H NMR: H-H coupling constants of the minor anomer



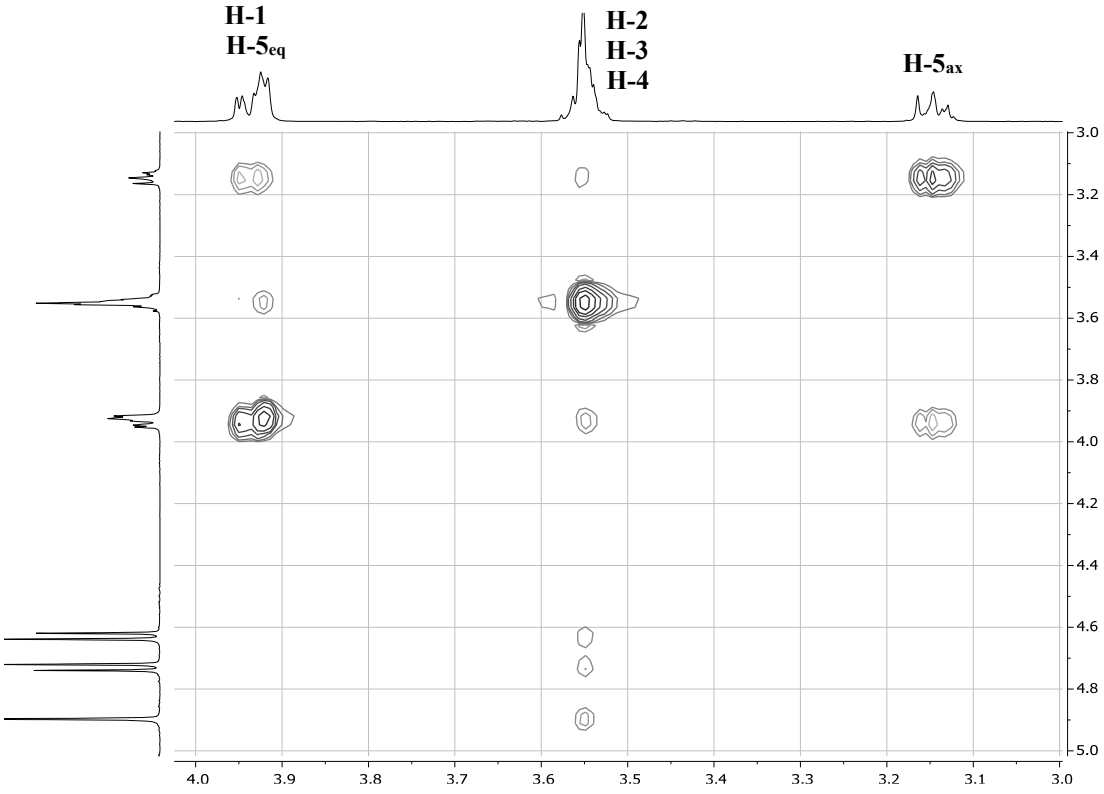
Compound S38

^{1}H NMR: H-H coupling constants



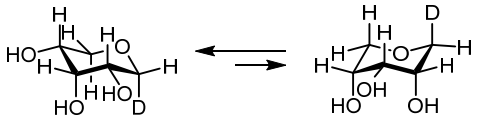
H-1: signal overlaps with H-5$_{eq}$ (H-1 is most likely a singlet or very small coupling constant)
H-2: signal overlaps with H-3 and H-4
H-3: signal overlaps with H-2 and H-4
H-4: signal overlaps with H-2 and H-3
H-5$_{ax}$: dd, J = 11.1 (geminal) and 9.9 Hz (ax^{H-5}–ax^{H-4})
H-5$_{eq}$: signal overlaps with H-1, and therefore H-1 can only be an equatorial hydrogen (as result of the symmetry in the molecule)

NOESY-NMR: H-H long range NOE coupling interaction



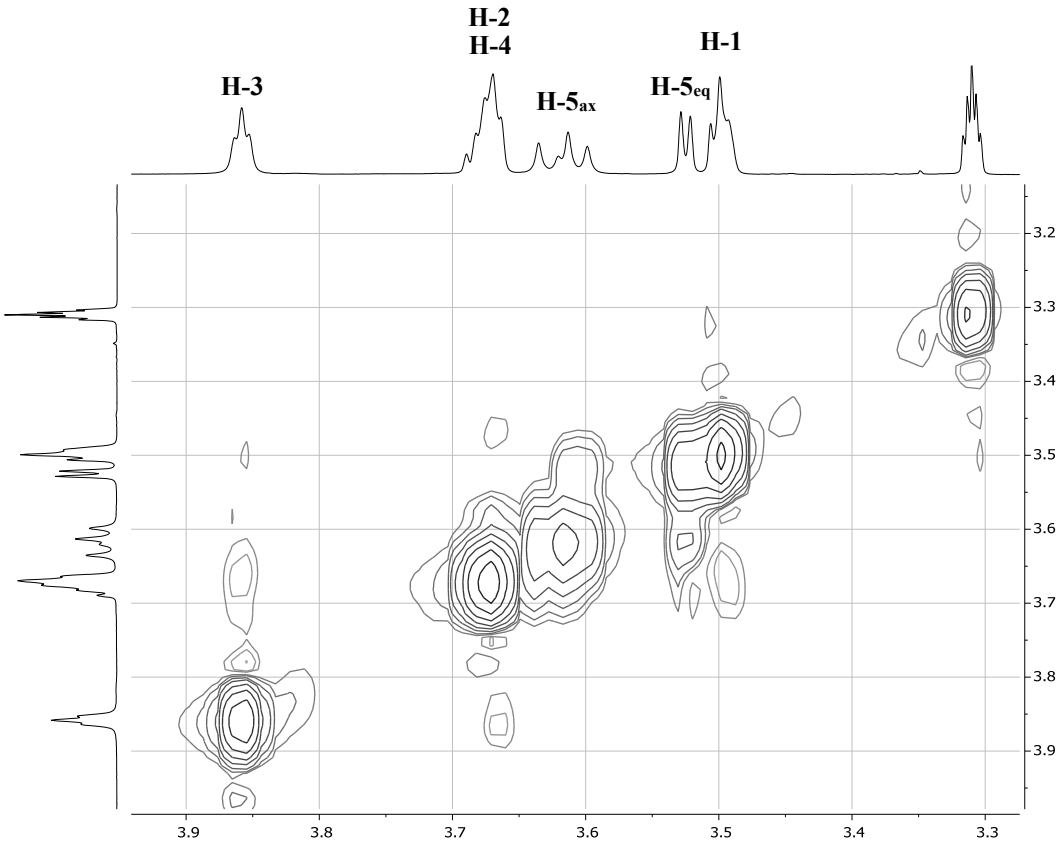
Compound S41

^{1}H NMR: H-H coupling constants



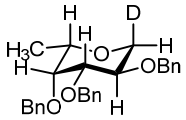
H-1: s
H-2: signal overlaps with H-4
H-3: t, *J* = 2.9 Hz (H-3–H-2 and H-3–H-4)
H-4: signal overlaps with H-2
H-5$_{ax}$: dd, *J* = 11.0 Hz (geminal), 7.3 Hz (H-5–H-4)
H-5$_{eq}$: dd, *J* = 11.2 Hz (geminal), 3.5 Hz (H-5–H-4), signal overlaps with H-1, and therefore H-1 can only be an equatorial hydrogen (as result of the symmetry in the molecule)

NOESY-NMR: H-H long range NOE coupling interaction



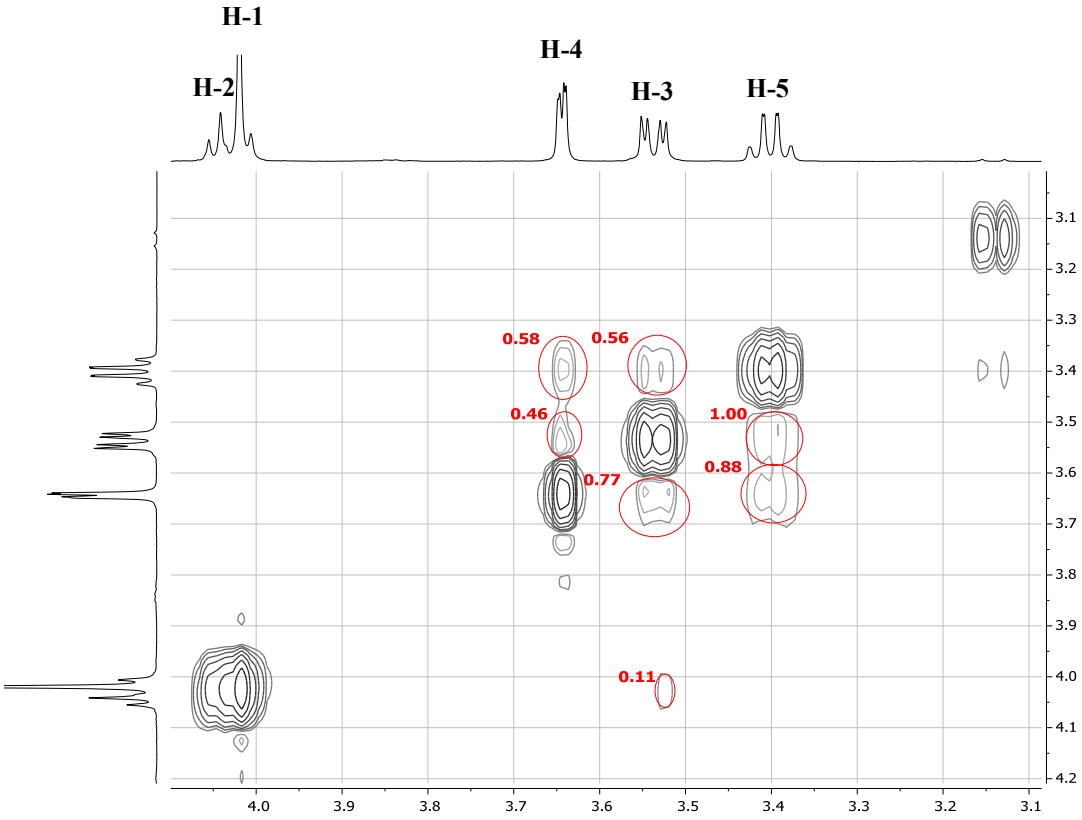
Compound S42

^{1}H NMR: H-H coupling constants

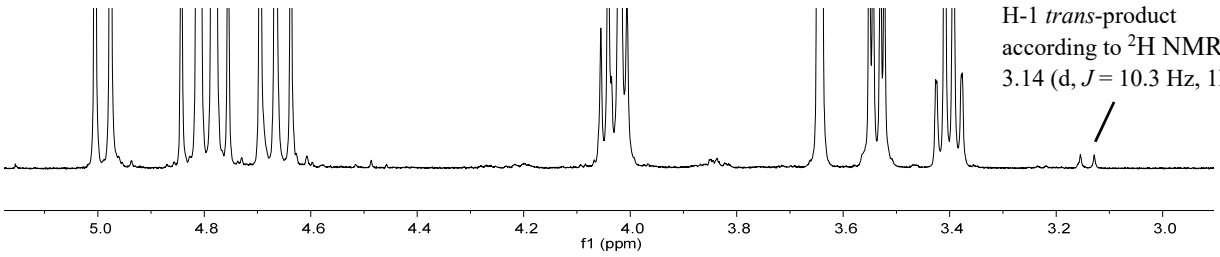


H-1: s
H-2: signal overlaps with H-1
H-3: dd, J = 8.7 Hz (ax^{H-3}–ax^{H-2}), 2.9 Hz (ax^{H-3}–eq^{H-4})
H-4: dd, J = 2.9 Hz (eq^{H-4}–ax^{H-3}), 1.1 Hz (eq^{H-4}–ax^{H-5})
H-5: qd, J = 6.4 Hz (ax^{H-5}–CH$_3$), 1.1 Hz (ax^{H-5}–eq^{H-4})

NOESY-NMR: H-H long range NOE coupling interaction

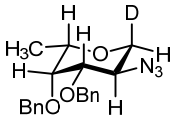


^{1}H NMR: H-H coupling constants of the minor anomer



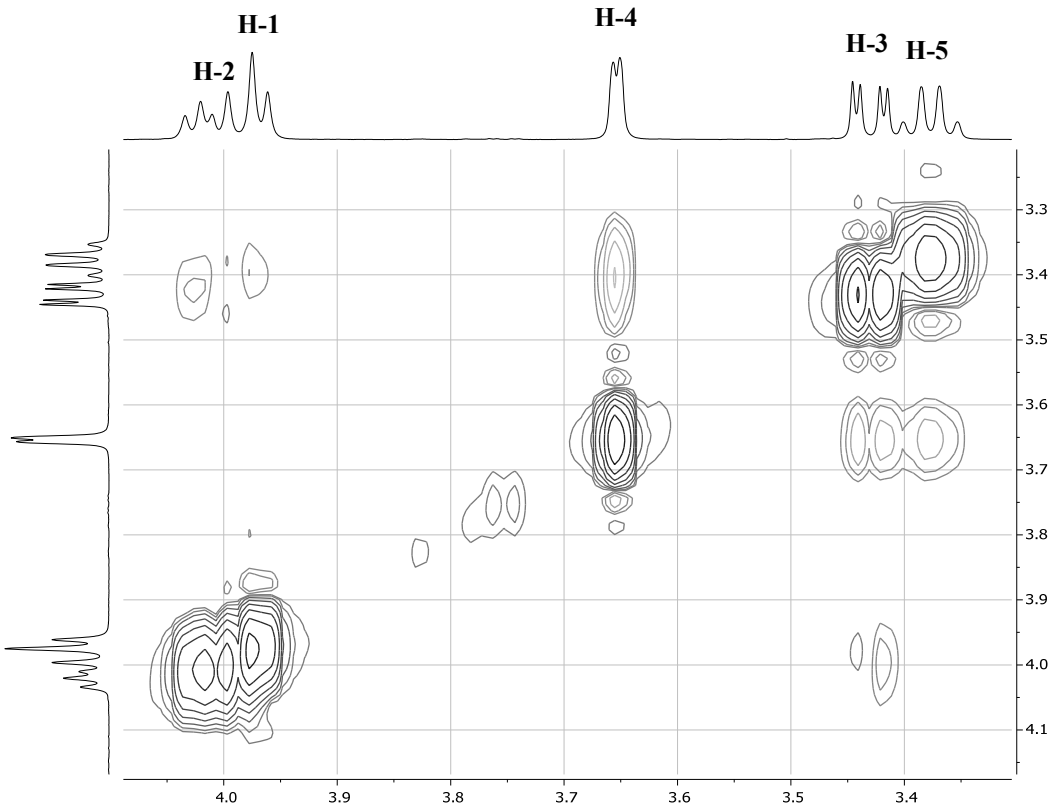
Compound S44

^{1}H NMR: H-H coupling constants



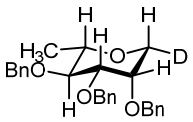
H-1: d, J = 5.5 Hz (eq^{H-1}–ax^{H-2})
H-2: dd, J = 9.6 Hz (ax^{H-2}–ax^{H-3}), 5.5 Hz (ax^{H-2}–eq^{H-1})
H-3: dd, J = 9.6 Hz (ax^{H-3}–ax^{H-2}), 2.7 Hz (ax^{H-3}–eq^{H-4})
H-4: d, J = 2.7 Hz (eq^{H-4}–ax^{H-3})
H-5: q, J = 6.5 Hz (ax^{H-5}–CH_3)

NOESY-NMR: H-H long range NOE coupling interaction



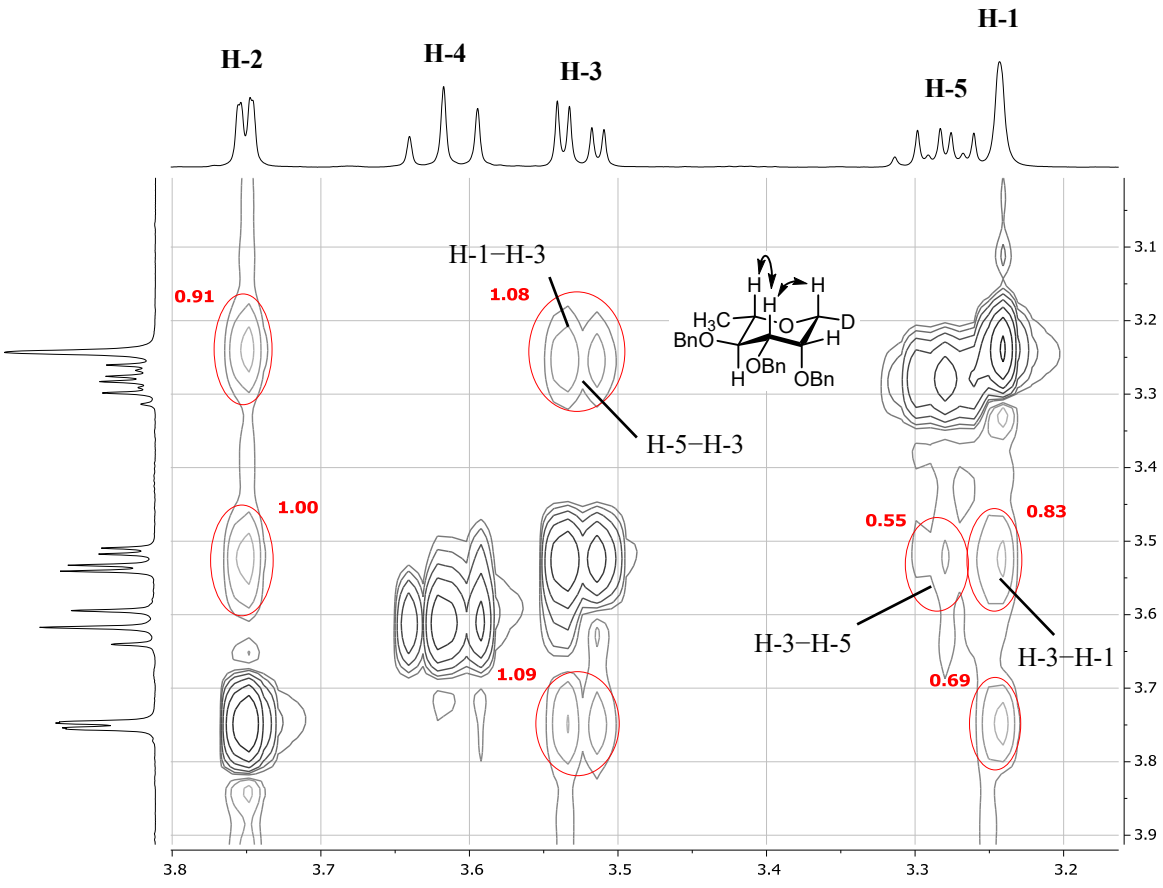
Compound S45

^{1}H NMR: H-H coupling constants



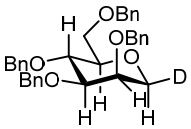
H-1: s
H-2: dd, J = 3.3 Hz (eq^{H-2}–ax^{H-3}), 1.0 Hz (eq^{H-2}–ax^{H-1})
H-3: dd, J = 9.3 Hz (ax^{H-3}–ax^{H-4}), 3.2 Hz (ax^{H-3}–eq^{H-2})
H-4: t, J = 9.2 Hz (ax^{H-3}–ax^{H-4} and ax^{H-4}–ax^{H-5})
H-5: dq, J = 9.0 Hz (ax^{H-5}–ax^{H-4}), 6.0 Hz (ax^{H-5}–CH_3)

NOESY-NMR: H-H long range NOE coupling interaction



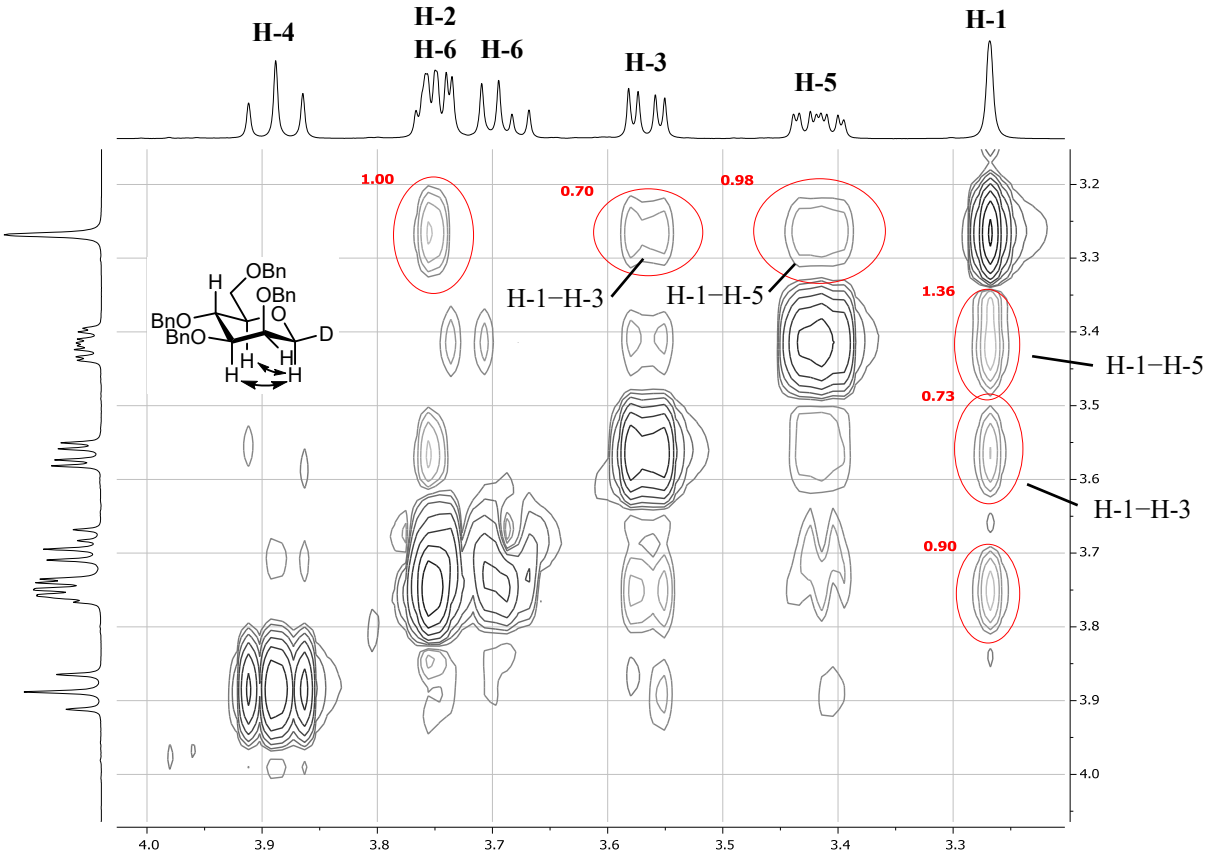
Compound S51

^{1}H NMR: H-H coupling constants



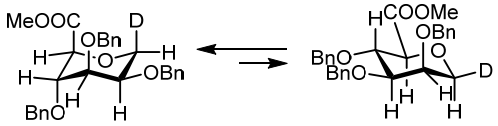
H-1: s
H-2: signal overlaps with H-6
H-3: dd, J = 9.3 Hz (ax^{H-3}–ax^{H-4}), 3.3 Hz (ax^{H-3}–eq^{H-2})
H-4: t, J = 9.4 Hz (ax^{H-3}–ax^{H-4} and ax^{H-4}–ax^{H-5})
H-5: ddd, J = 9.0 Hz (ax^{H-5}–ax^{H-4}), 6.0 Hz (ax^{H-5}–H-6), 2.1 (ax^{H-5}–H-6)

NOESY-NMR: H-H long range NOE coupling interaction



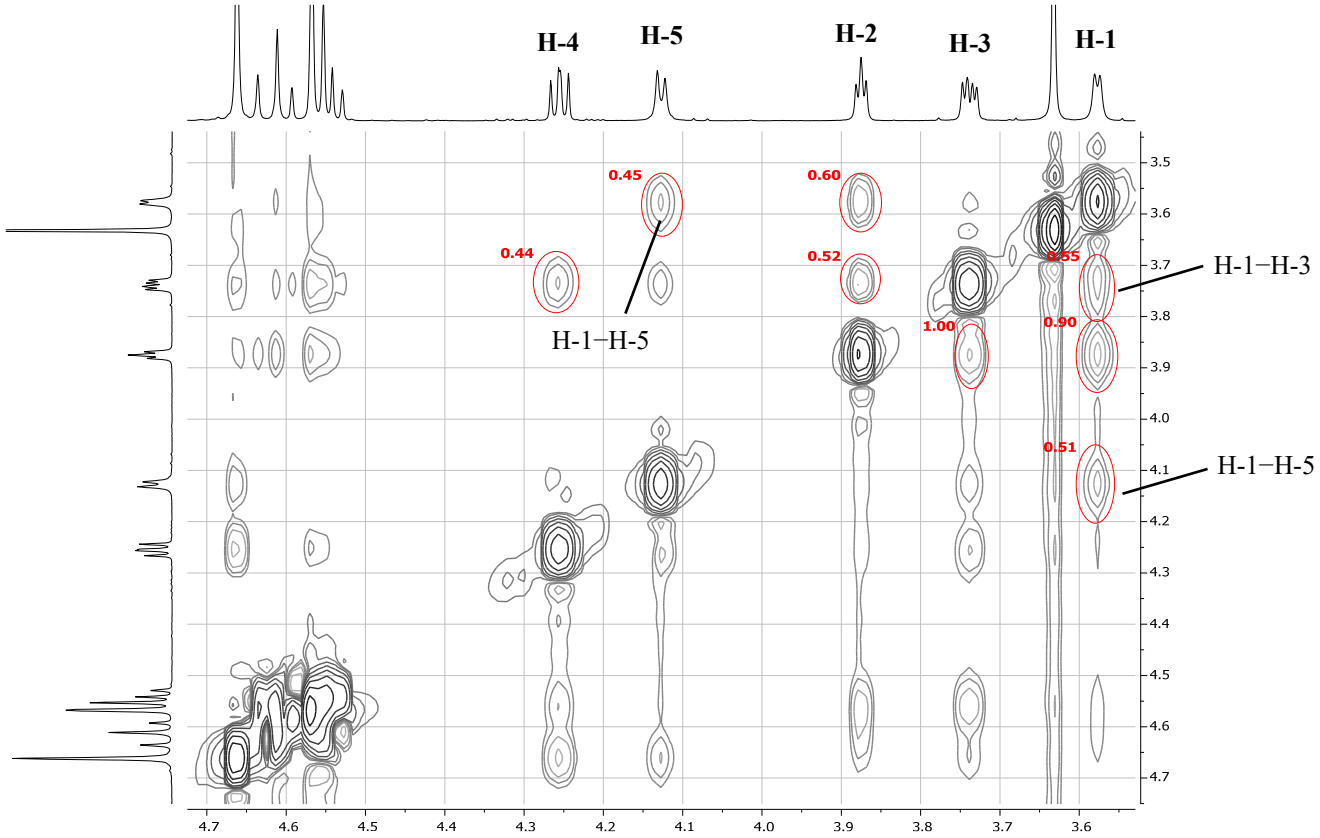
Compound S52

^{1}H NMR: H-H coupling constants



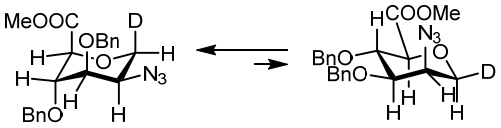
H-1: d, J = 3.5 Hz (H-1–H-2)
H-2: t, J = 3.2 Hz (H-2–H-1 and H-2–H-3)
H-3: dd, J = 6.1 Hz (H-3–H-4), 2.9 Hz (H-3–H-2)
H-4: dd, J = 6.3 Hz (H-4–H-3), 4.9 Hz (H-4–H-5)
H-5: d, J = 4.8 Hz (H-5–H-4)

NOESY-NMR: H-H long range NOE coupling interaction



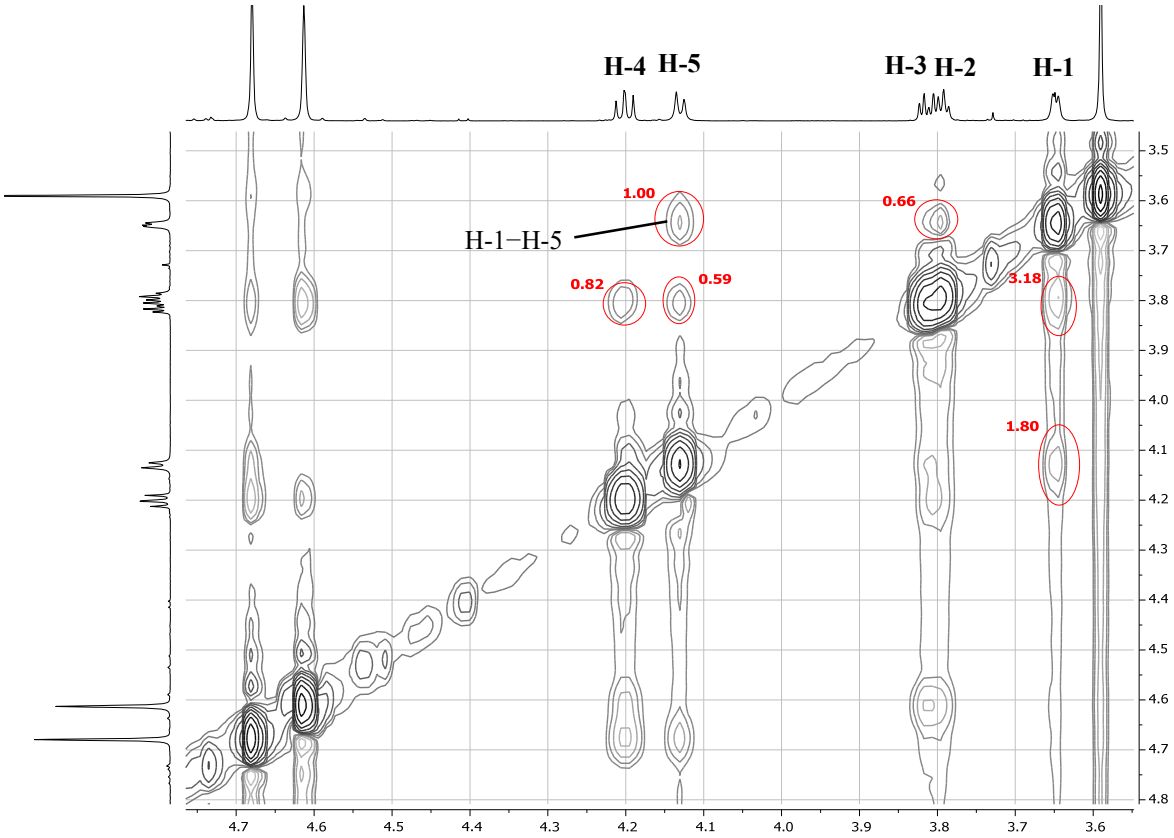
Compound S53

^{1}H NMR: H-H coupling constants



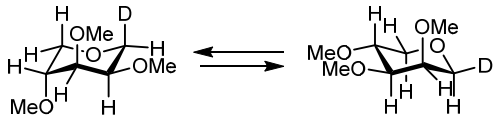
H-1: d, J = 1.5 Hz (eq^{H-1}–ax^{H-2})
H-2: signal overlaps with H-3
H-3: signal overlaps with H-2
H-4: dd, J = 6.0 Hz (eq^{H-4}–eq^{H-3}), 5.0 Hz (eq^{H-4}–eq^{H-5})
H-5: d, J = 5.0 Hz (eq^{H-5}–eq^{H-4})

NOESY-NMR: H-H long range NOE coupling interaction



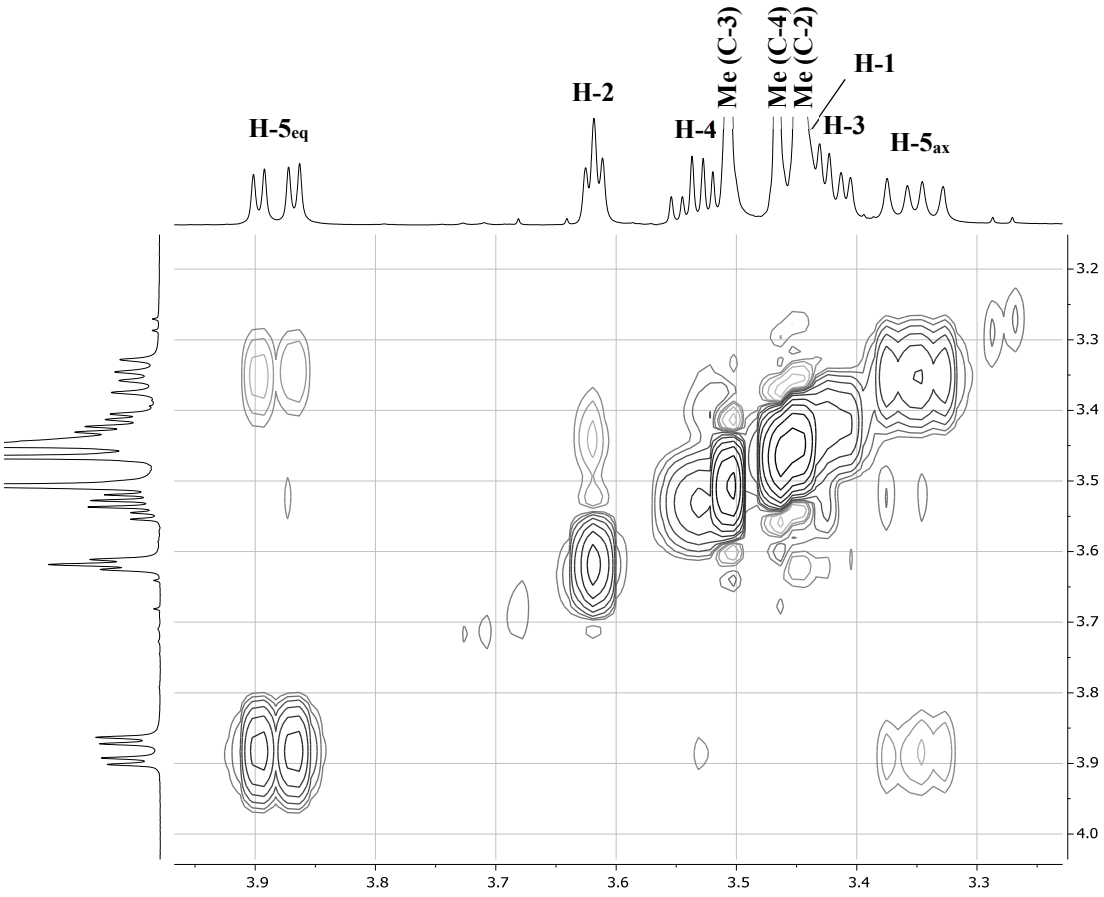
Compound S56

^{1}H NMR: H-H coupling constants



H-1: signal overlaps with Me (C-2)
H-2: t, *J* = 2.9 Hz (H-2–H-1 and H-2–H-3)
H-3: dd, *J* = 7.1 Hz (H-3–H-4), 3.2 Hz (H-3–H-2)
H-4: dt, *J* = 6.9 Hz (H-4–H-3 and H-4–H-5), 3.4 Hz (H-4–H-5)
H-5$_{ax}$: dd, *J* = 11.8 Hz (geminal), 6.8 Hz (H-5–H-4), signal in close proximity with H-1, indicating H-1 to be axial oriented (which is confirmed by NOESY):
H-5$_{eq}$: dd, *J* = 11.7 Hz (geminal), 3.7 Hz (H-5–H-4)

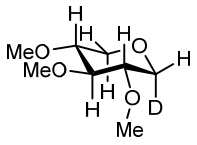
NOESY-NMR: H-H long range NOE coupling interaction



For further structure elucidation see section *"NMR simulations of selected glycosides"*.

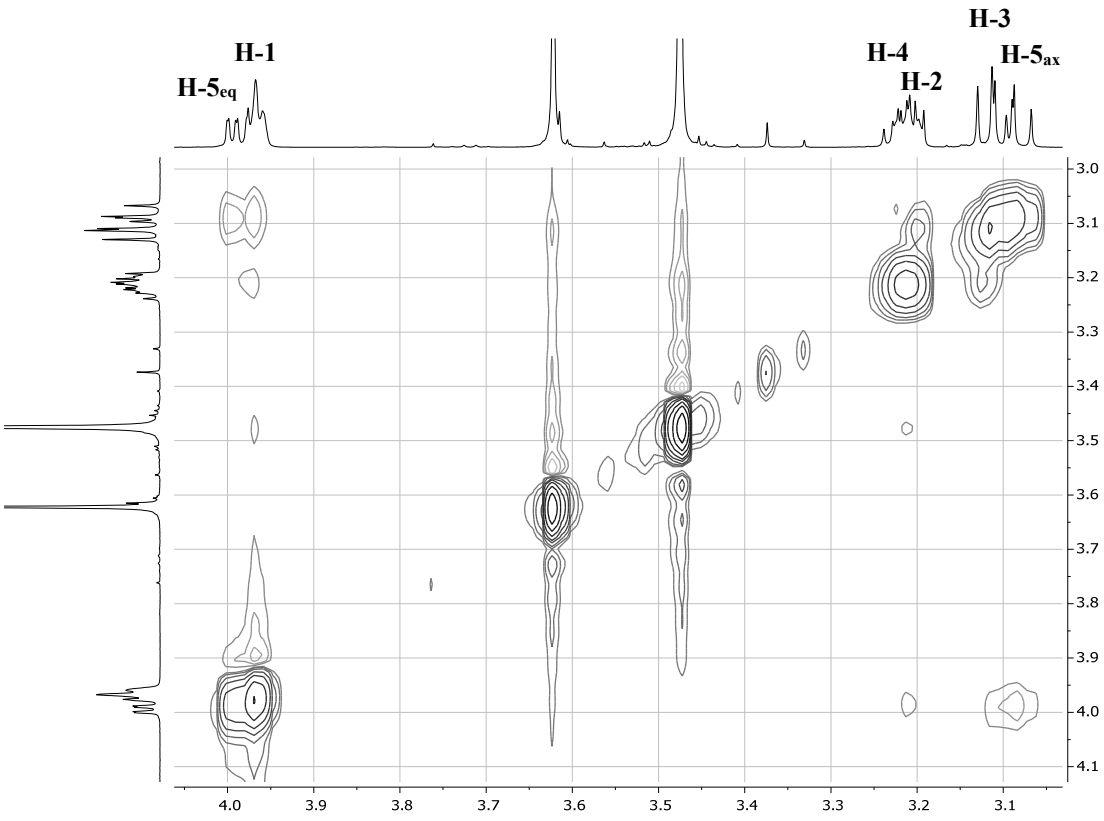
Compound S57

^{1}H NMR: H-H coupling constants



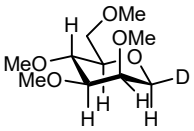
H-1: s (signal overlaps partly with H-5_{eq})
H-2: signal overlaps with H-4
H-3: t, J = 8.3 Hz (ax^{H-3}–ax^{H-2} and ax^{H-3}–ax^{H-4})
H-4: signal overlaps with H-2
H-5_{ax}: dd, J = 11.2 Hz (geminal), 9.9 Hz (ax^{H-5}–ax^{H-4})
H-5_{eq}: dd, J = 11.0 Hz (geminal) 5.0 Hz (eq^{H-5}–ax^{H-4}), signal overlaps with H-1, and therefore H-1 can only be also an equatorial hydrogen (as result of the symmetry in the molecule)

NOESY-NMR: H-H long range NOE coupling interaction



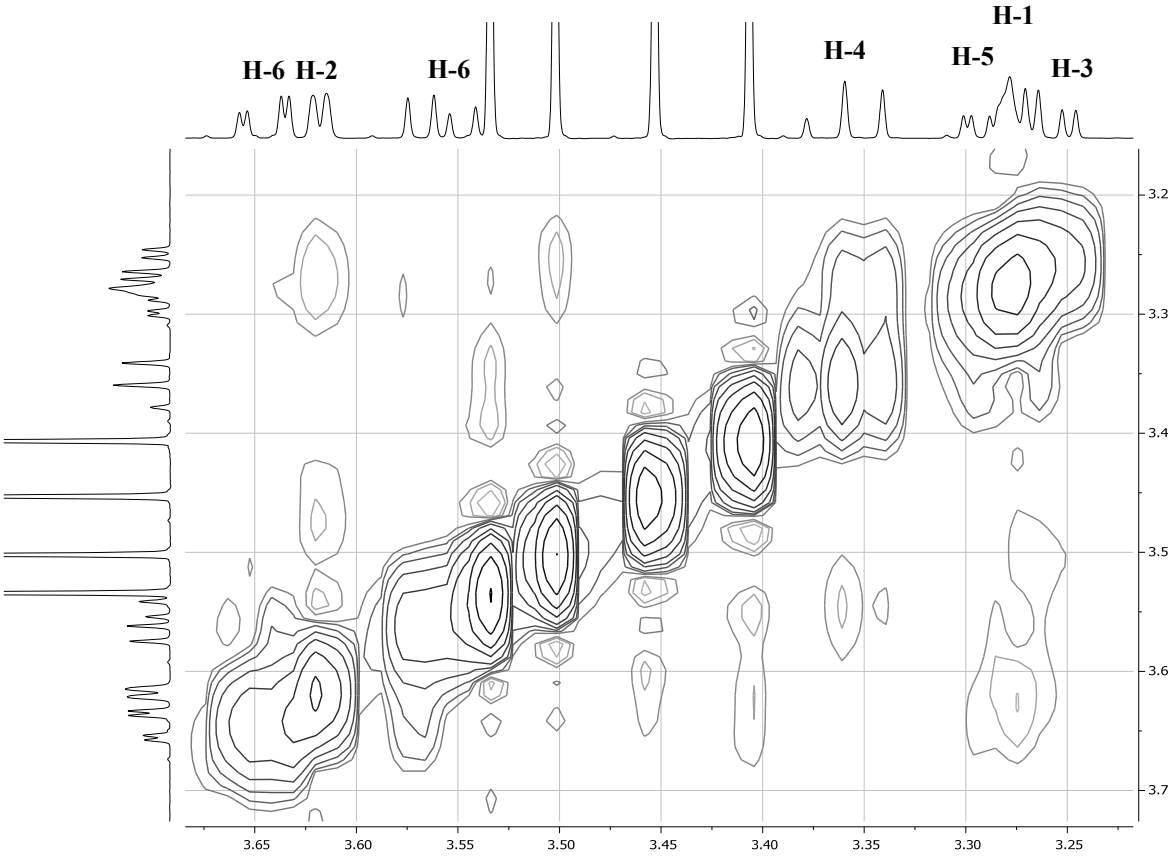
Compound S59

^{1}H NMR: H-H coupling constants



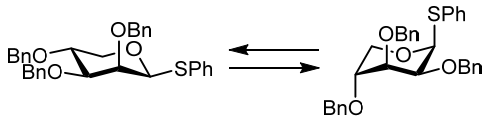
H-1: d J = ±0.5 Hz (ax^{H-1}–eq^{H-2})
H-2: dd, J = 3.4 Hz (eq^{H-2}–ax^{H-3}), 0.9 Hz (eq^{H-2}–ax^{H-1})
H-3: dd, J = 3.5 Hz (ax^{H-3}–eq^{H-2}), 9.5 Hz (ax^{H-3}–ax^{H-4})
H-4: t, J = 9.3 Hz (ax^{H-3}–ax^{H-4} and ax^{H-4}–ax^{H-5})
H-5: signal overlaps with H-1 and H-3

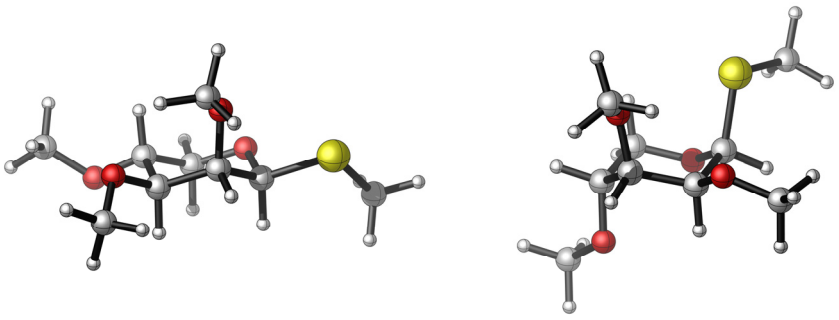
NOESY-NMR: H-H long range NOE coupling interaction



DFT computed NMR simulations of selected glycosides

Donor S6





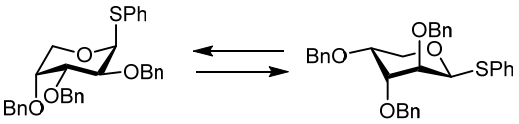
$^4C_1$ $^1C_4$

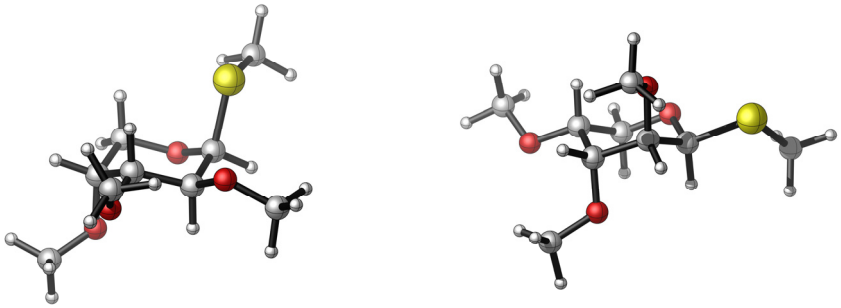
Gibbs free energy	0.00	0.23

H-H coupling	**Exp.**	**DFT Calcs.[1]**
H-1−H-2	4.0 Hz	3.3 Hz
H-2−H-3	2.6 Hz	3.1 Hz
H-3−H-4	5.7 Hz	6.4 Hz
H-4−H-5	2.5 Hz	3.9 Hz
H-4−H-5	4.3 Hz	6.7 Hz
H-5−H-5	12.3 Hz	12.5 Hz

[1]Boltzmann weighted averaged coupling constants based on the $^4C_1$ and $^1C_4$. Computed using B3LYP/6-311g(d,p) u+1s (*T*=293.15 K) PCM=chloroform and a scaling factor of 0.92.

Donor S7





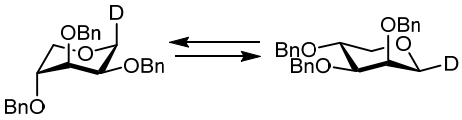
$^{1}C_4$ $^{4}C_1$

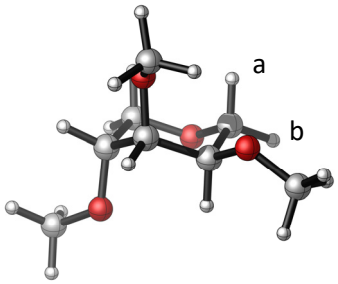
Gibbs free energy	0.00	0.21

H-H coupling	**Exp.**	**DFT Calcs.[1]**
H-1−H-2	6.1 Hz	5.0 Hz
H-2−H-3	6.5 Hz	7.1 Hz
H-3−H-4	3.1 Hz	3.3 Hz
H-4−H-5	2.8 Hz	3.1 Hz
H-4−H-5	5.8 Hz	5.3 Hz
H-5−H-5	12.0 Hz	11.2 Hz

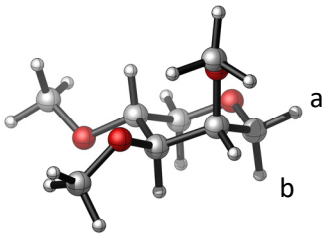
[1]Boltzmann weighted averaged coupling constants based on the $^{4}C_1$ and $^{1}C_4$. Computed using B3LYP/6-311g(d,p) u+1s (*T*=293.15 K) PCM=chloroform and a scaling factor of 0.92.

Compound S35





$^4C_1$



$^1C_4$

Gibbs free energy	0.00	0.12

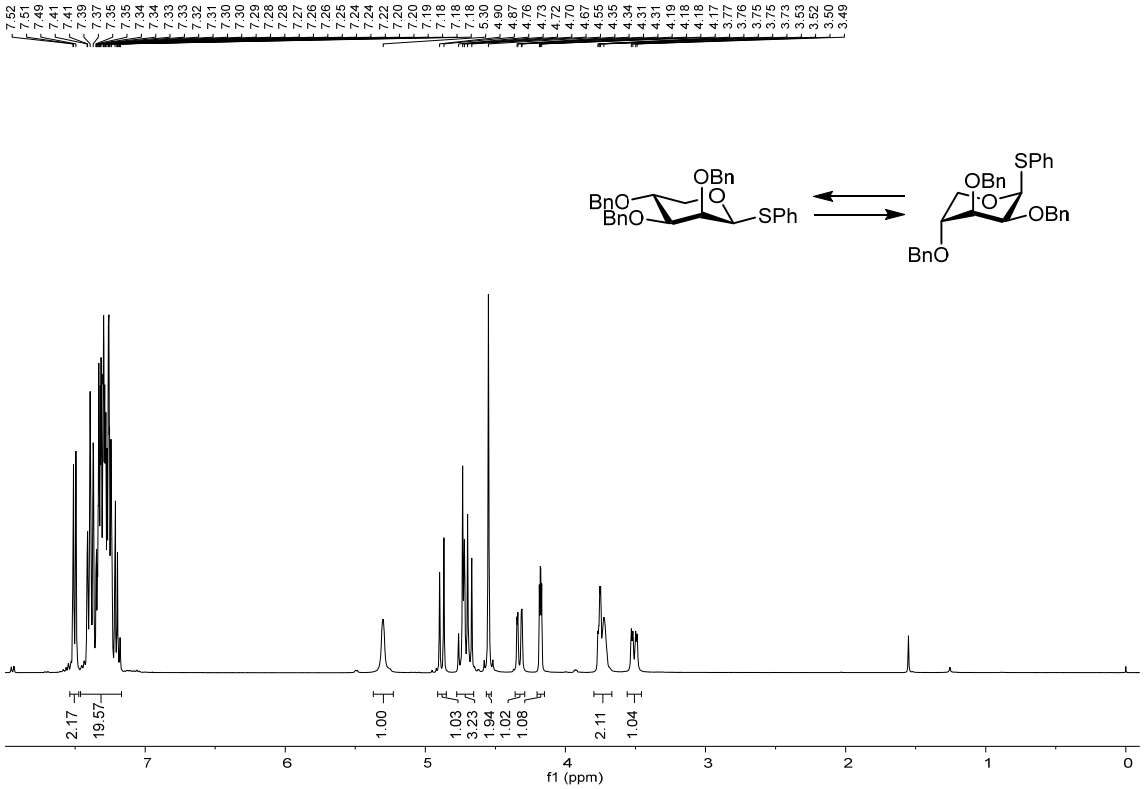
H-H coupling	**Exp.**	**DFT Calcs.**[1]
H-1$_b$–H-2	2.8 Hz	3.5 Hz
H-2–H-3	3.0 Hz	3.1 Hz
H-3–H-4	6.4 Hz	6.1 Hz
H-4–H-5	3.5 Hz	3.1 Hz
H-4–H-5	6.1 Hz	5.0 Hz
H-5–H-5	11.8 Hz	12.0 Hz

[1]Boltzmann weighted averaged coupling constants based on the $^4C_1$ and $^1C_4$. Computed using B3LYP/6-311g(d,p) u+1s (*T*=293.15 K) PCM=chloroform and a scaling factor of 0.92.

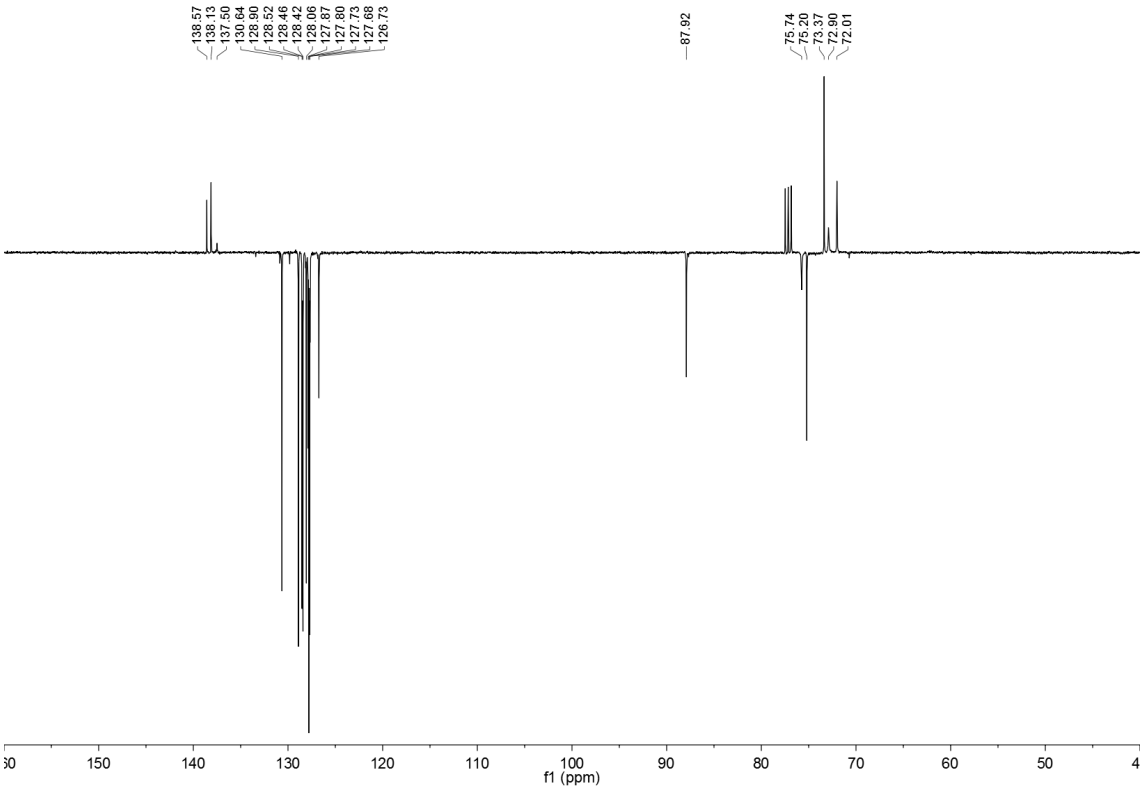
If H-1$_a$ was present:
H-1$_a$–H-2: 6.7 Hz

NMR spectra of new and selected compounds

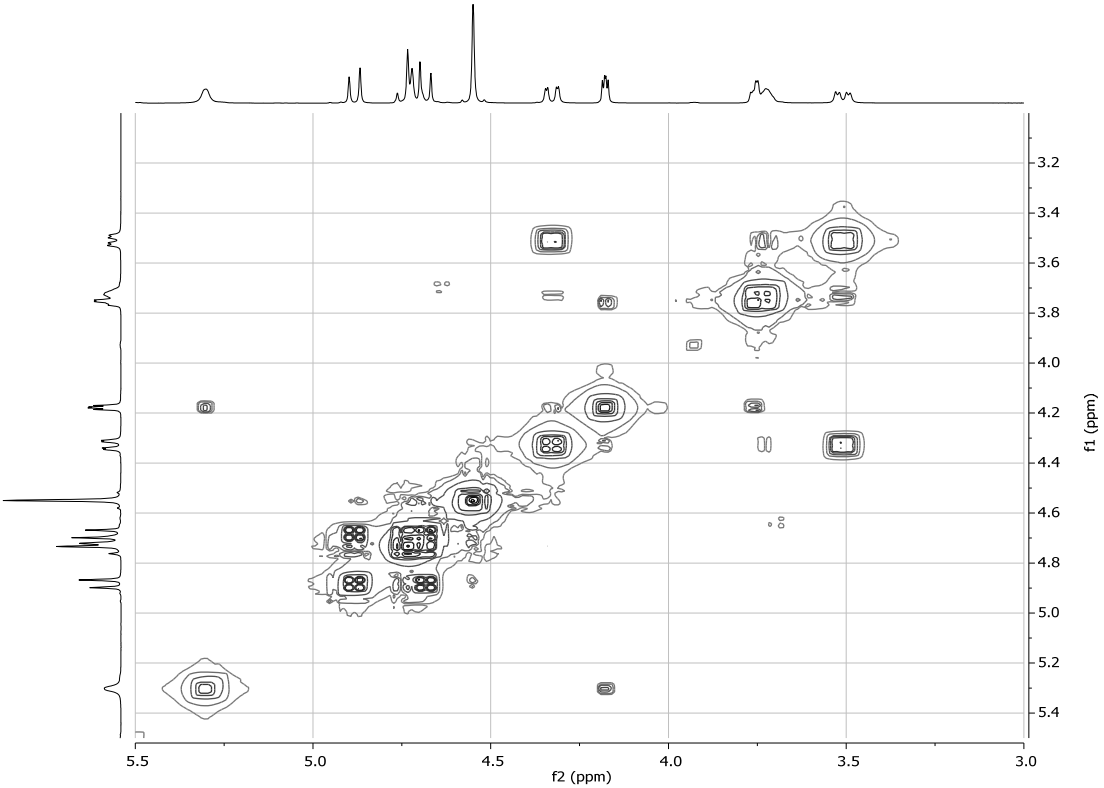
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S6**



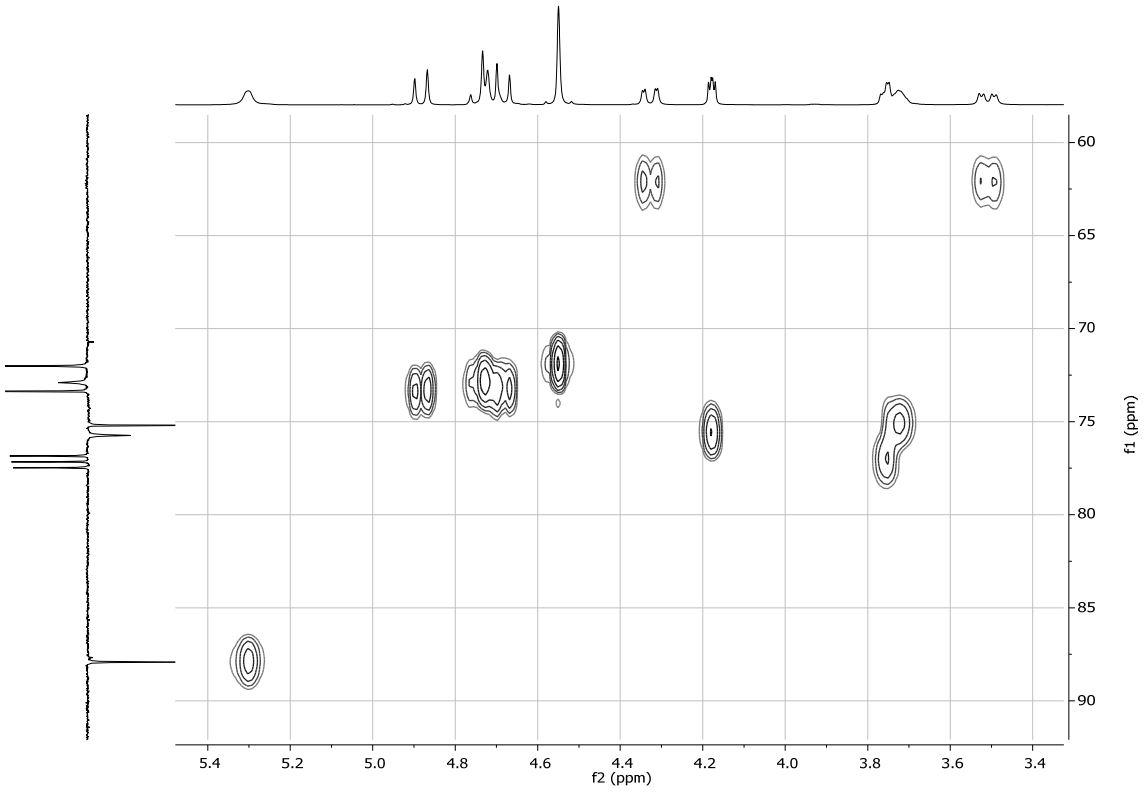
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S6**



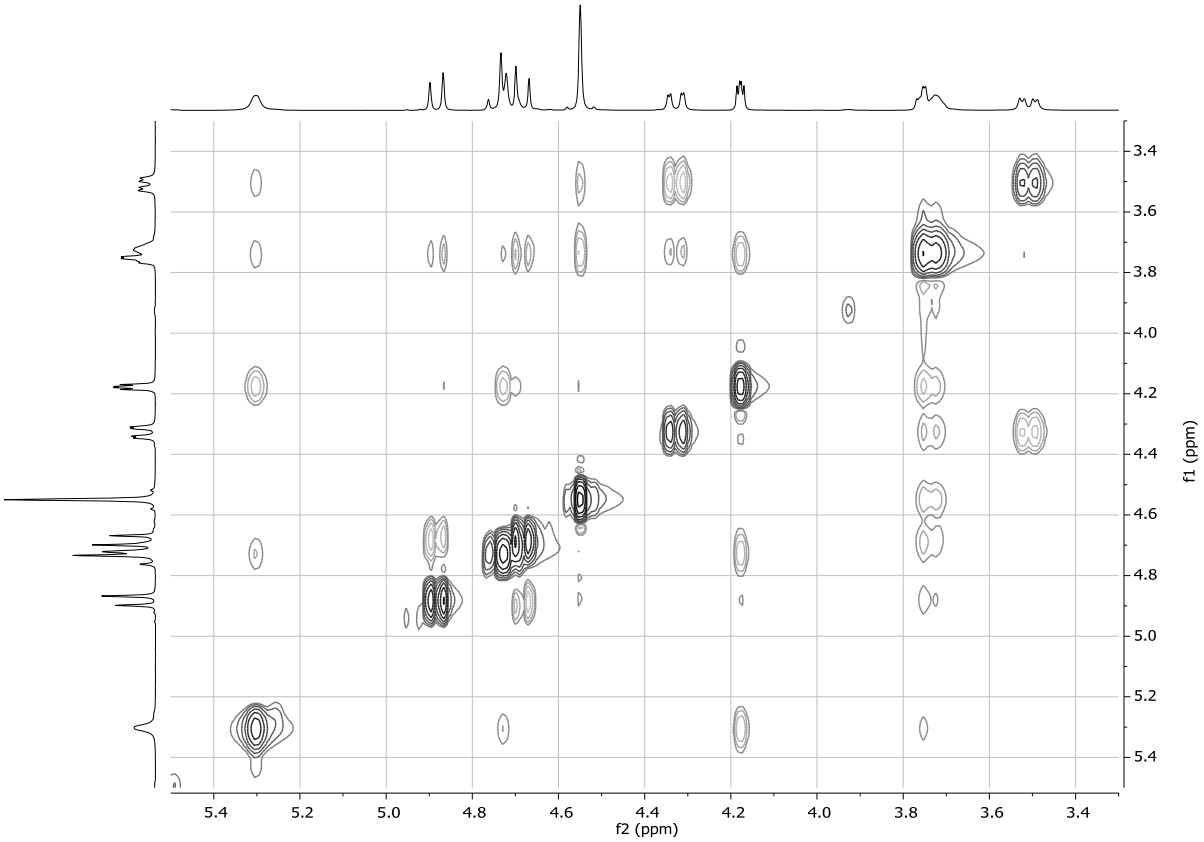
HH-COSY NMR, $CDCl_3$ of Donor **S6**



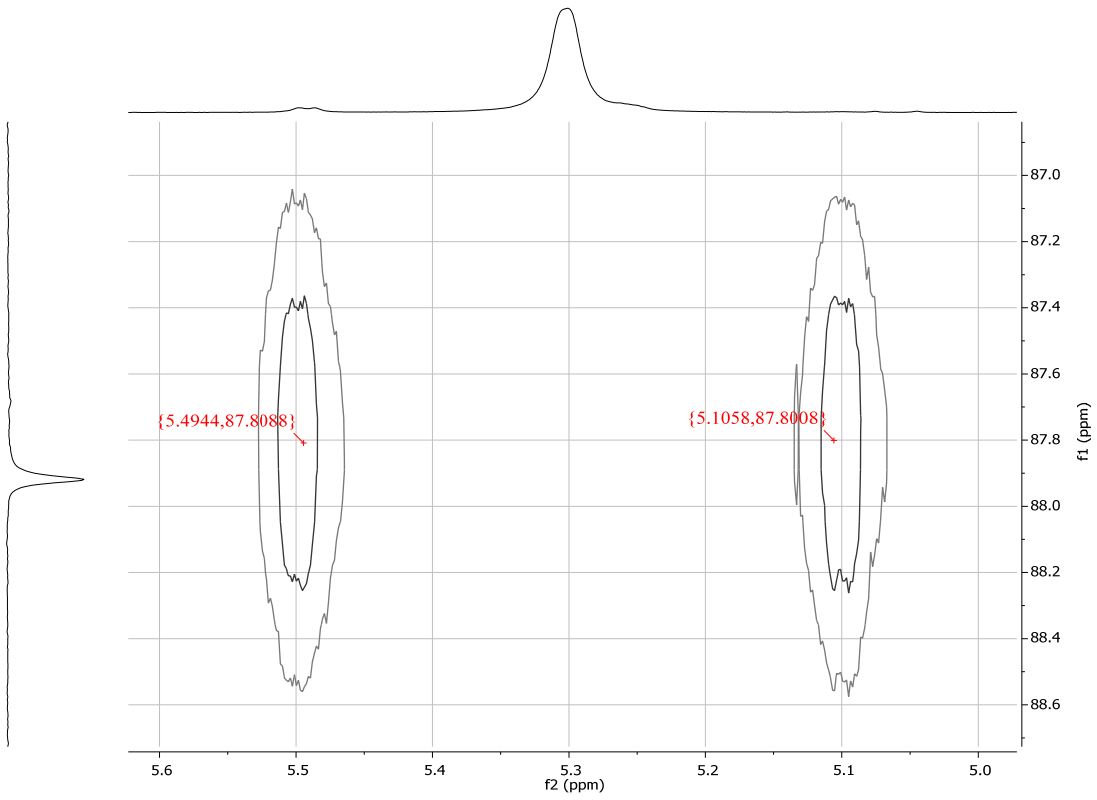
HSQC NMR, $CDCl_3$ of Donor **S6**



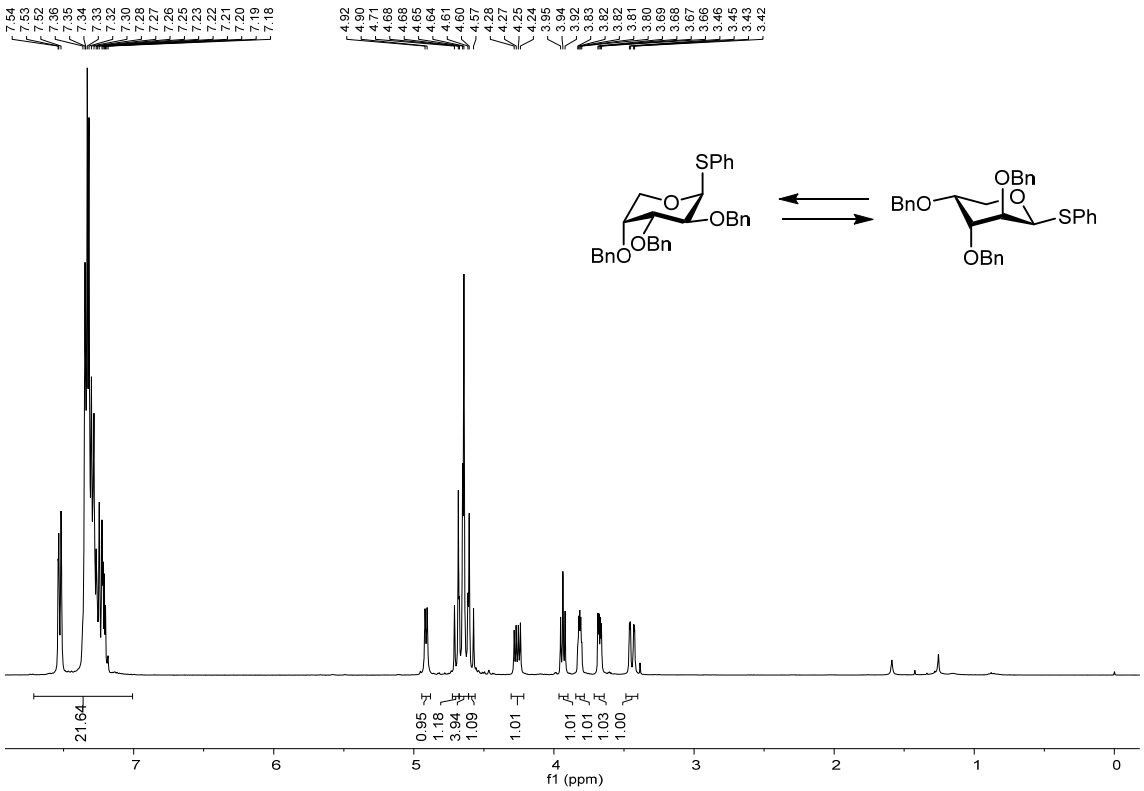
NOESY NMR, $CDCl_3$ of Donor **S6**



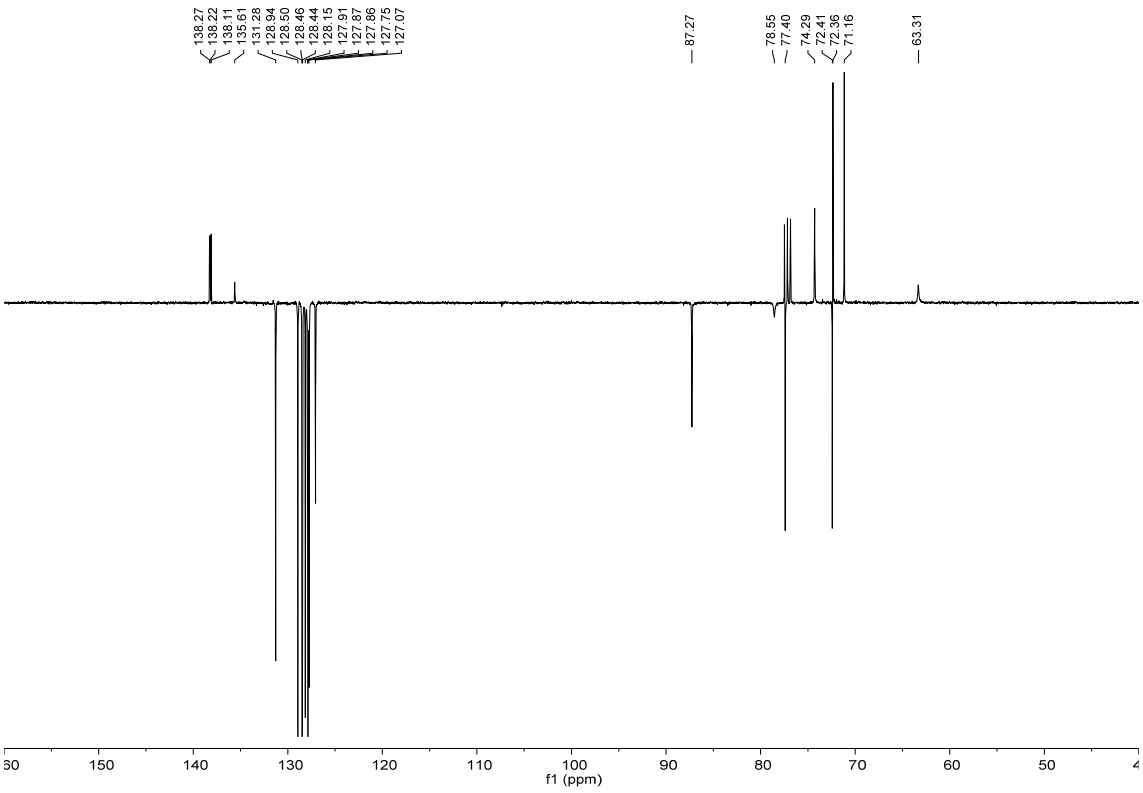
HMBC-GATED NMR, $CDCl_3$ of Donor **S6**



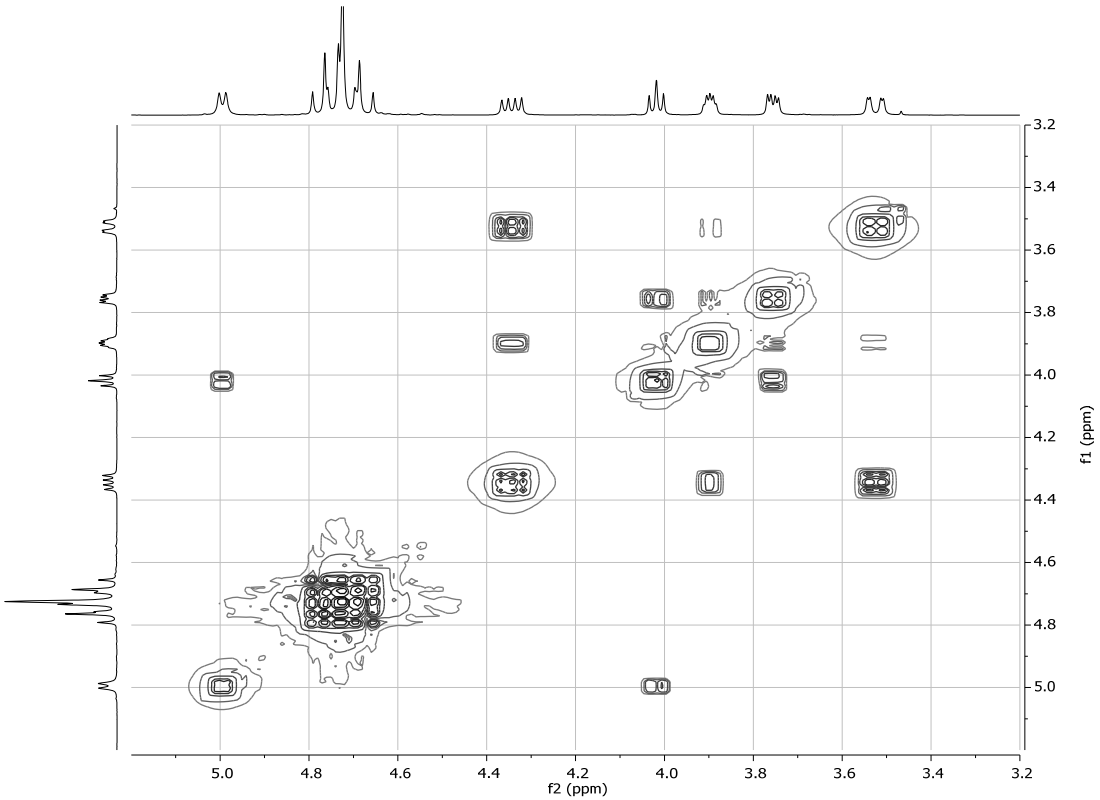
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S7**



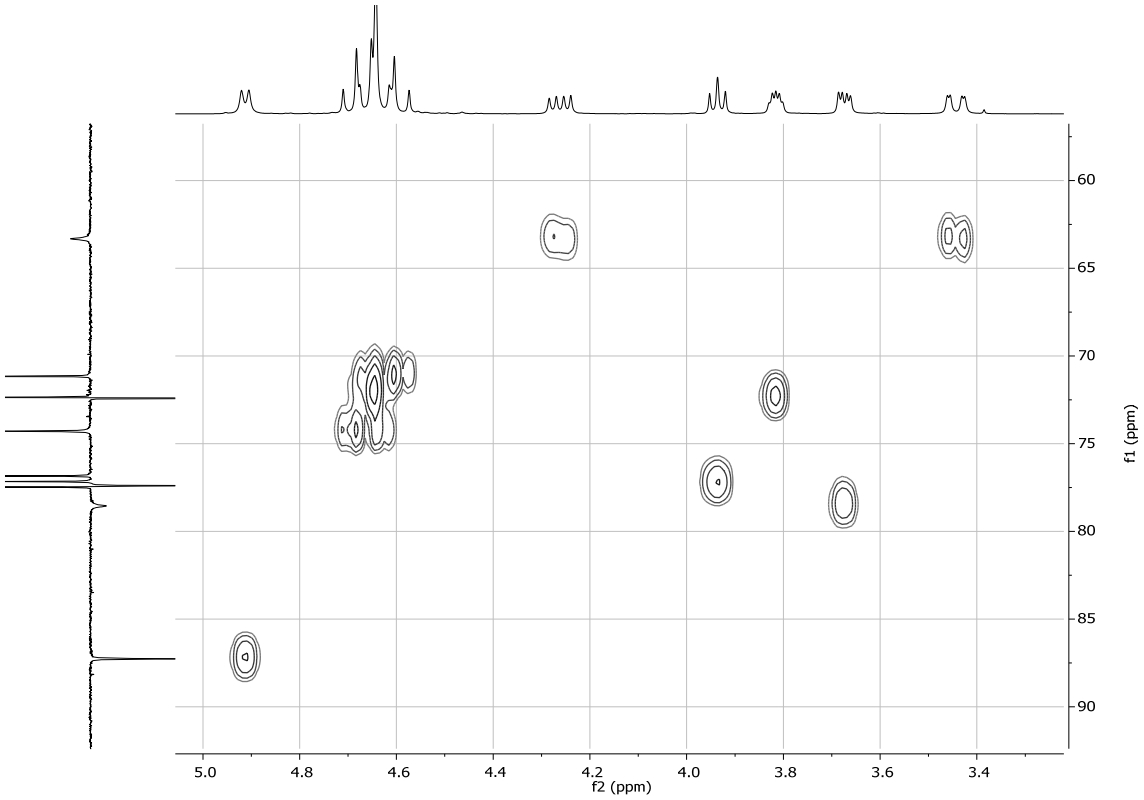
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S7**



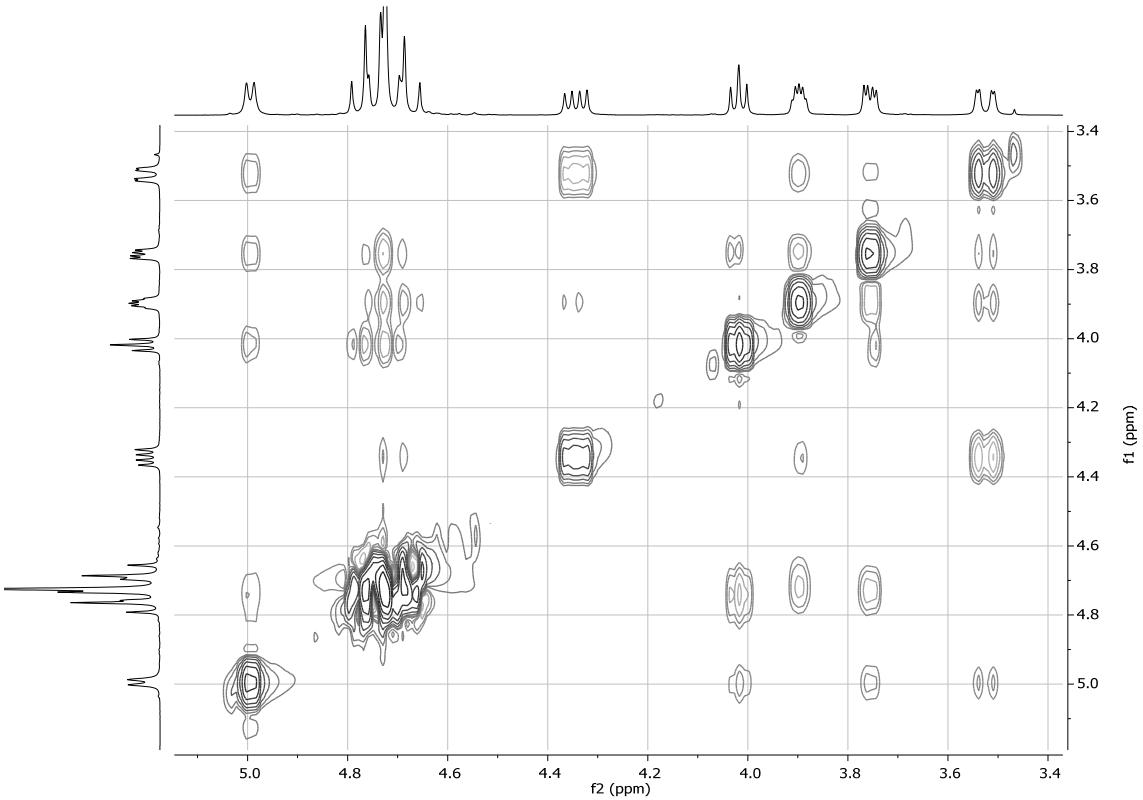
HH-COSY NMR, $CDCl_3$ of Donor **S7**



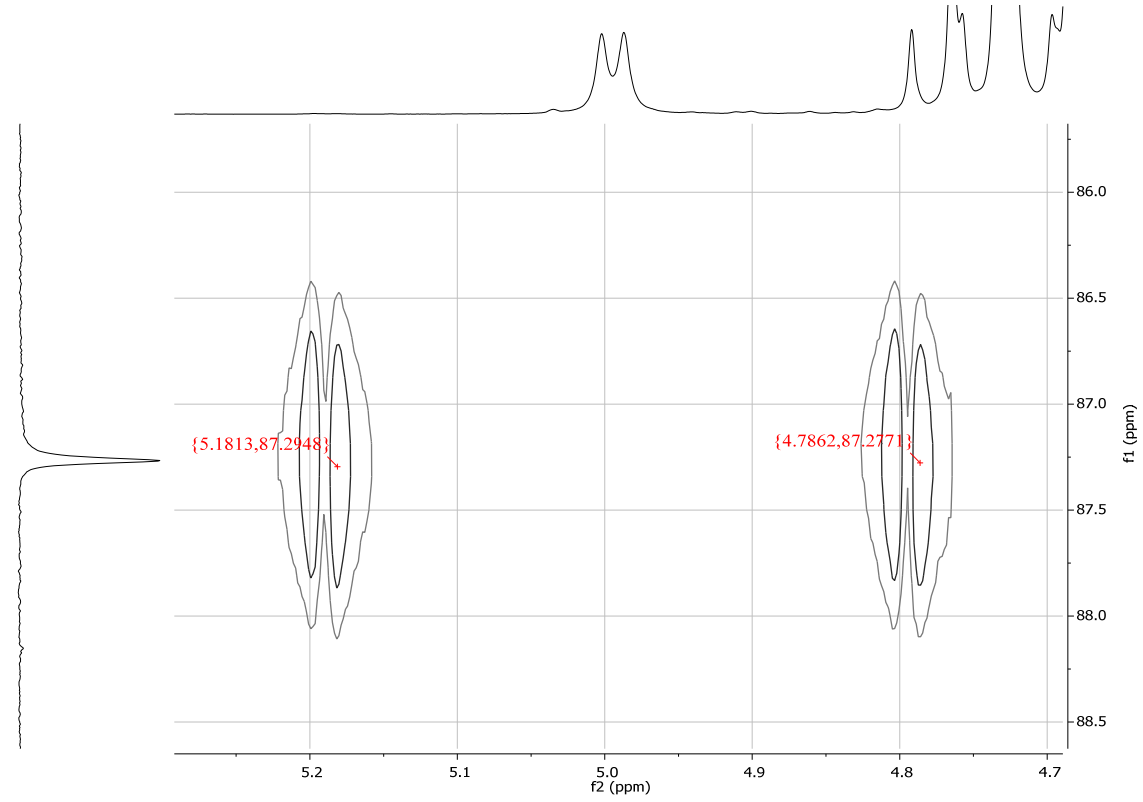
HSQC NMR, $CDCl_3$ of Donor **S7**



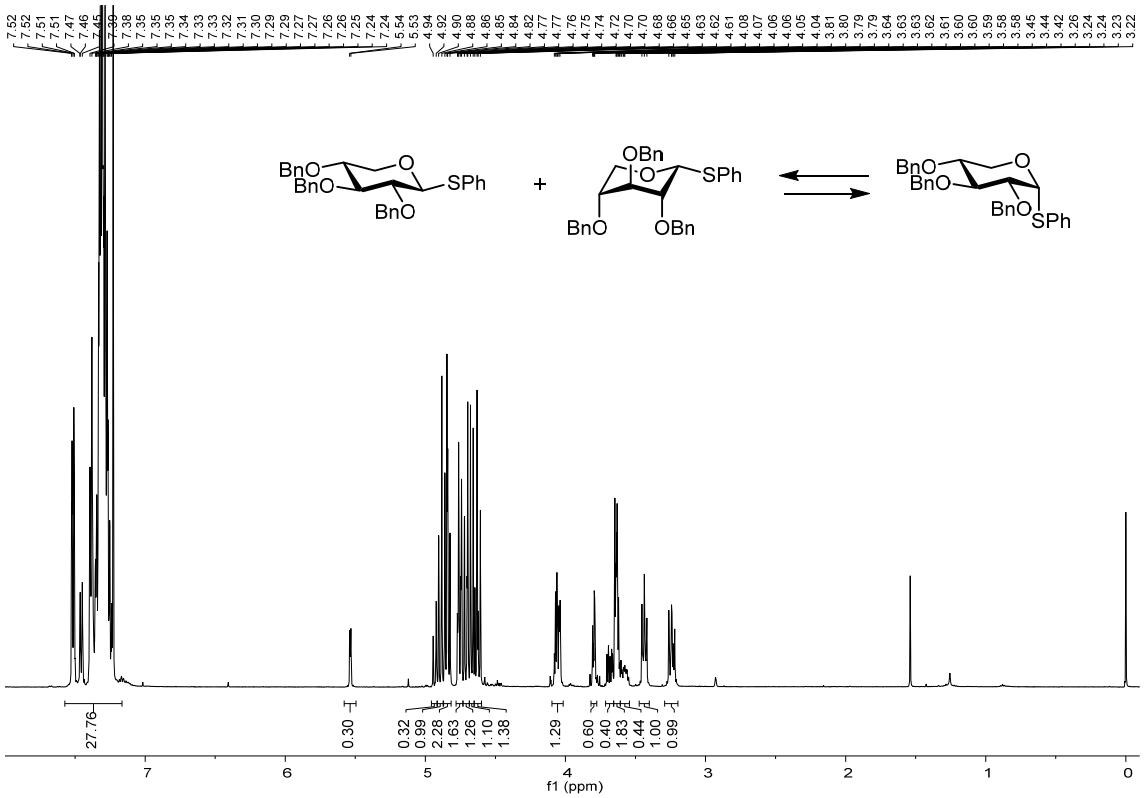
NOESY NMR, $CDCl_3$ of Donor **S7**



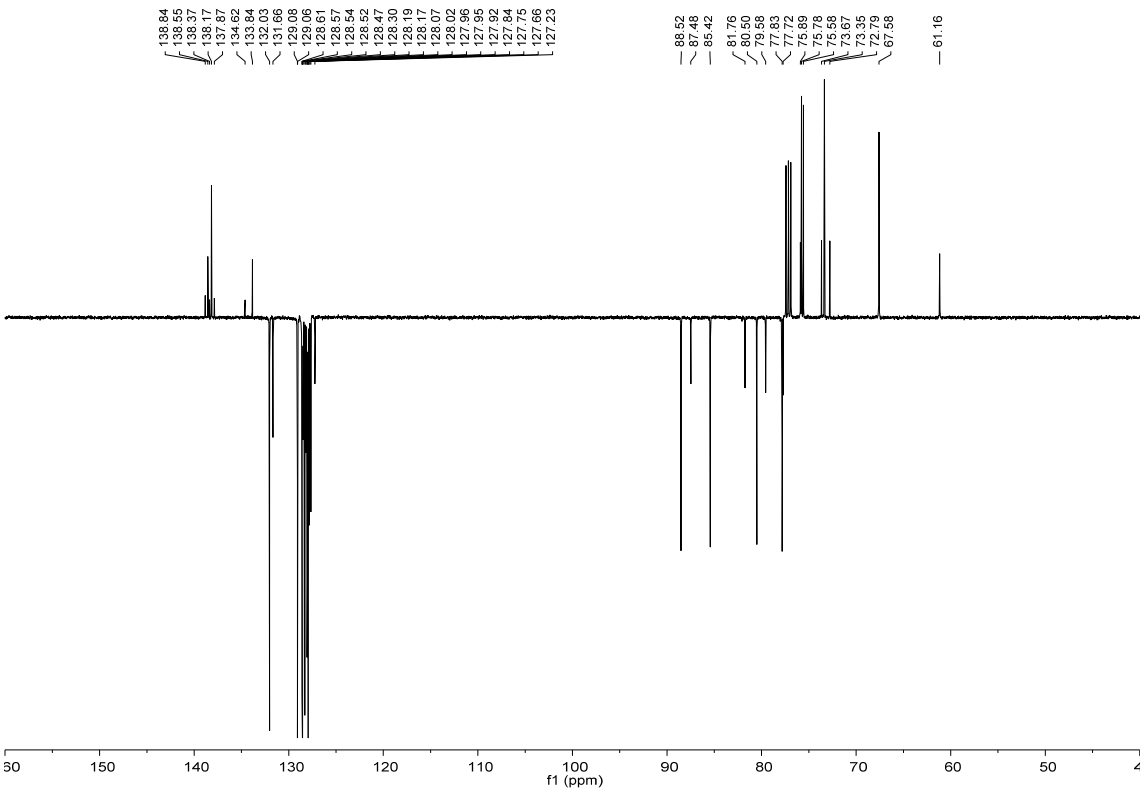
HMBC-GATED NMR, $CDCl_3$ of Donor **S7**



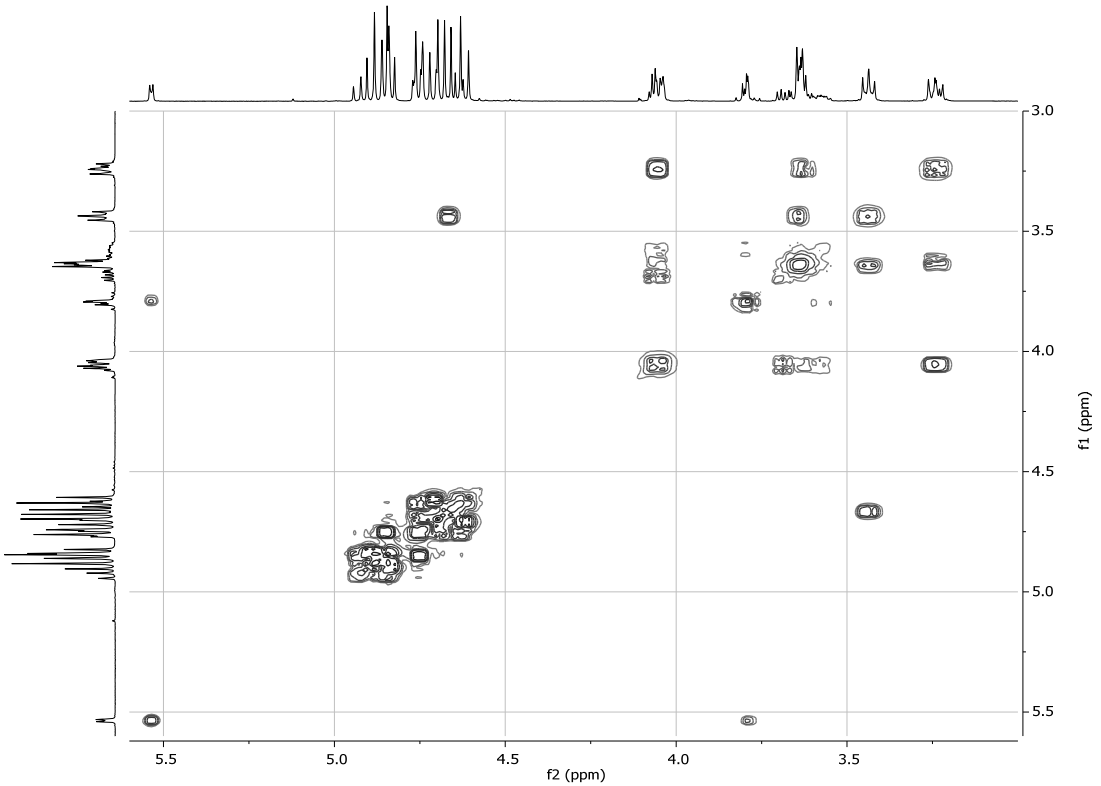
^{1}H NMR, 500 MHz, $CDCl_3$ of Donor **S8**



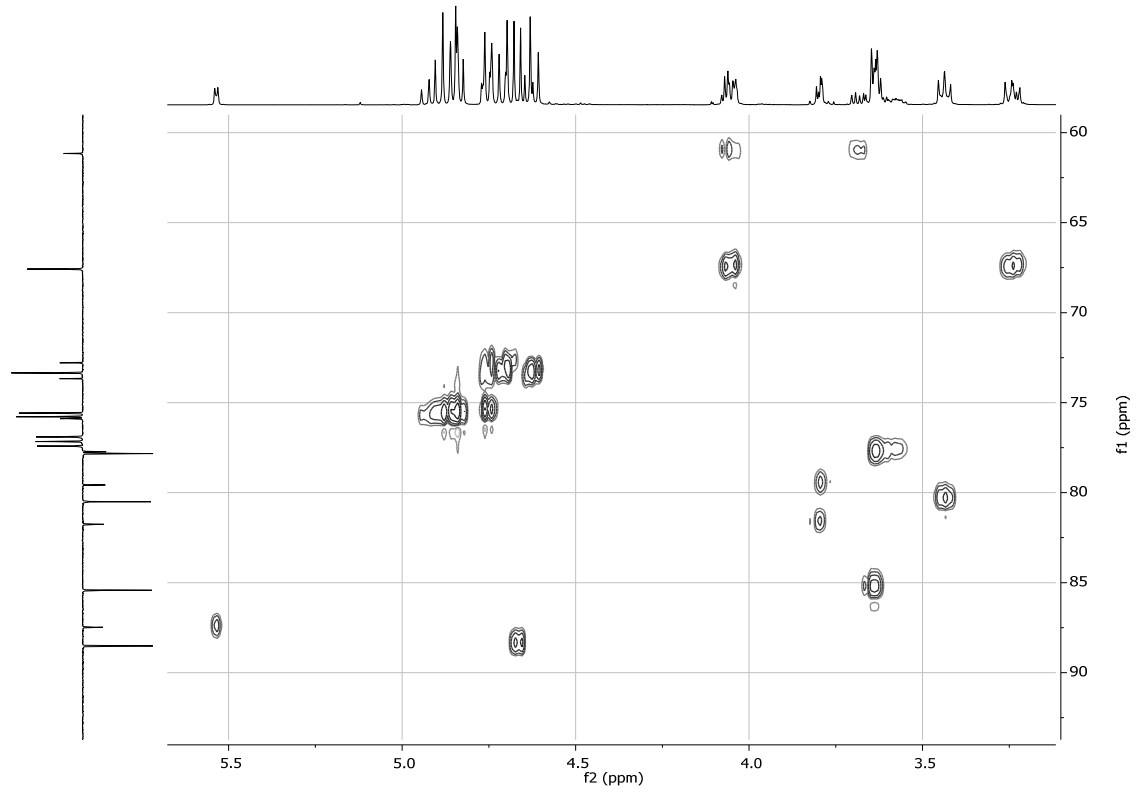
^{13}C NMR, 126 MHz, $CDCl_3$ of Donor **S8**



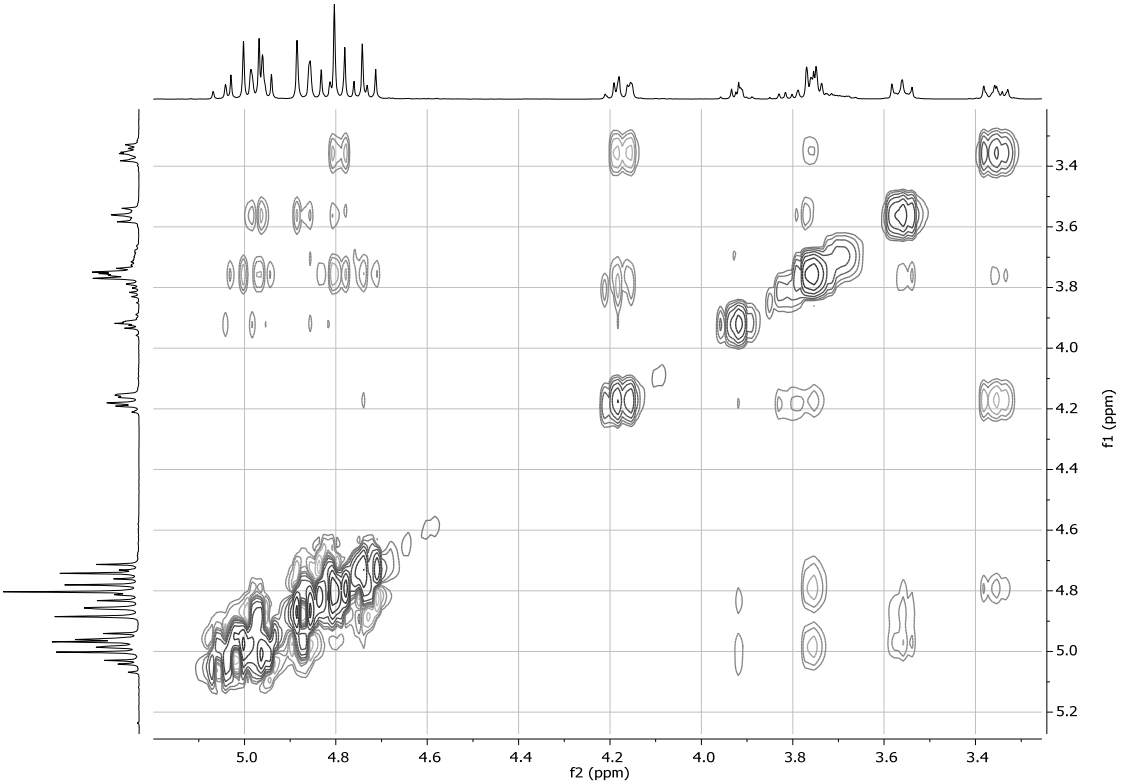
HH-COSY NMR, $CDCl_3$ of Donor **S8**



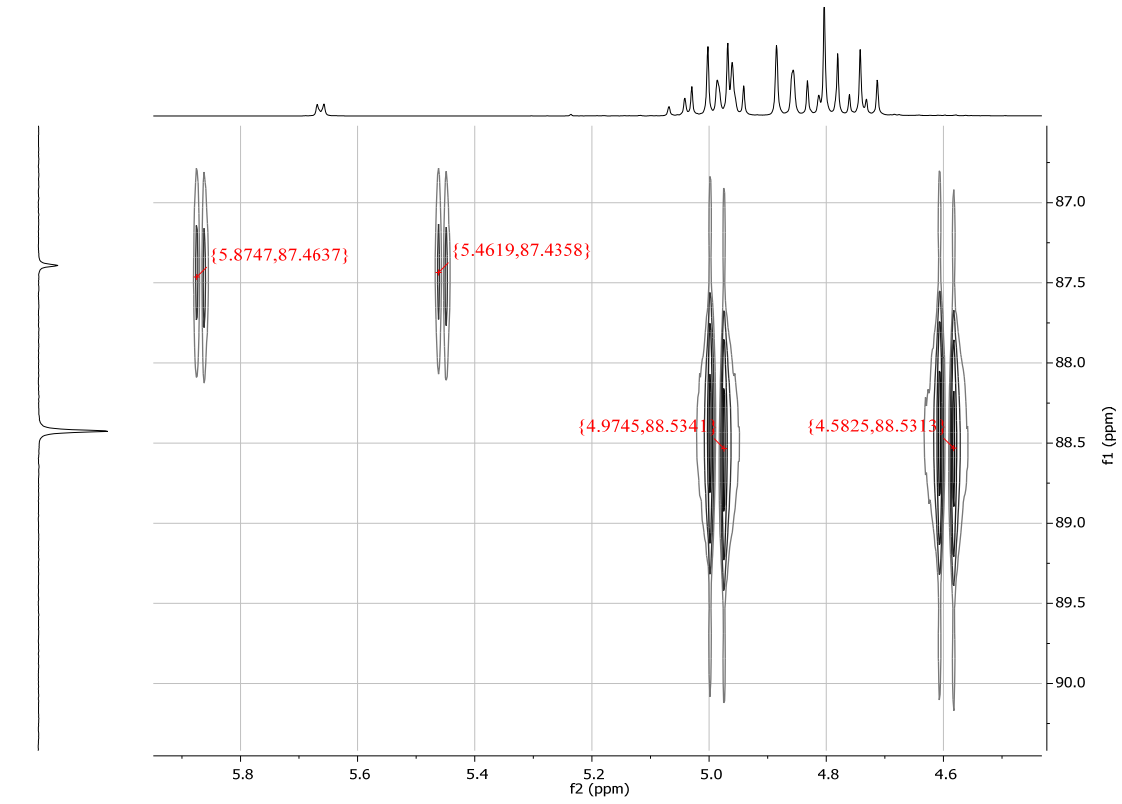
HSQC NMR, $CDCl_3$ of Donor **S8**



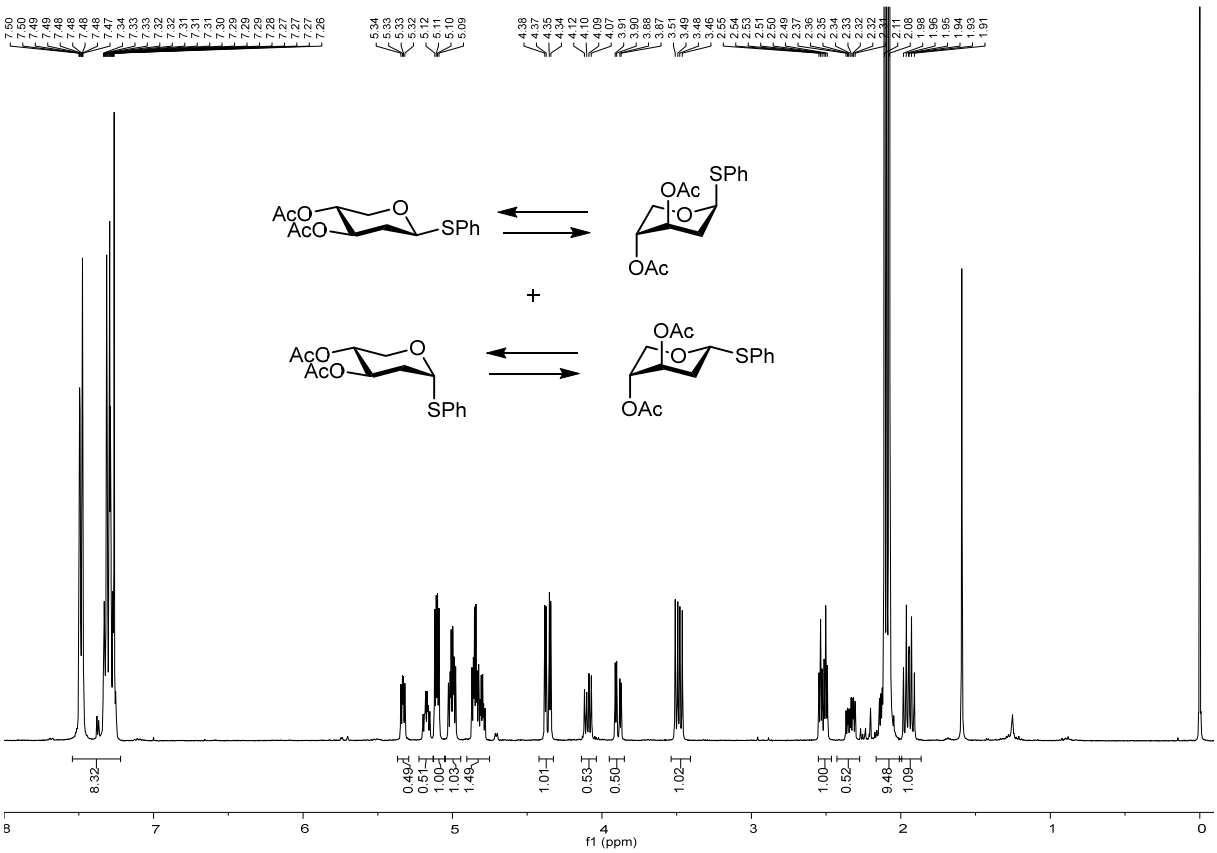
NOESY NMR, $CDCl_3$ of Donor **S8**



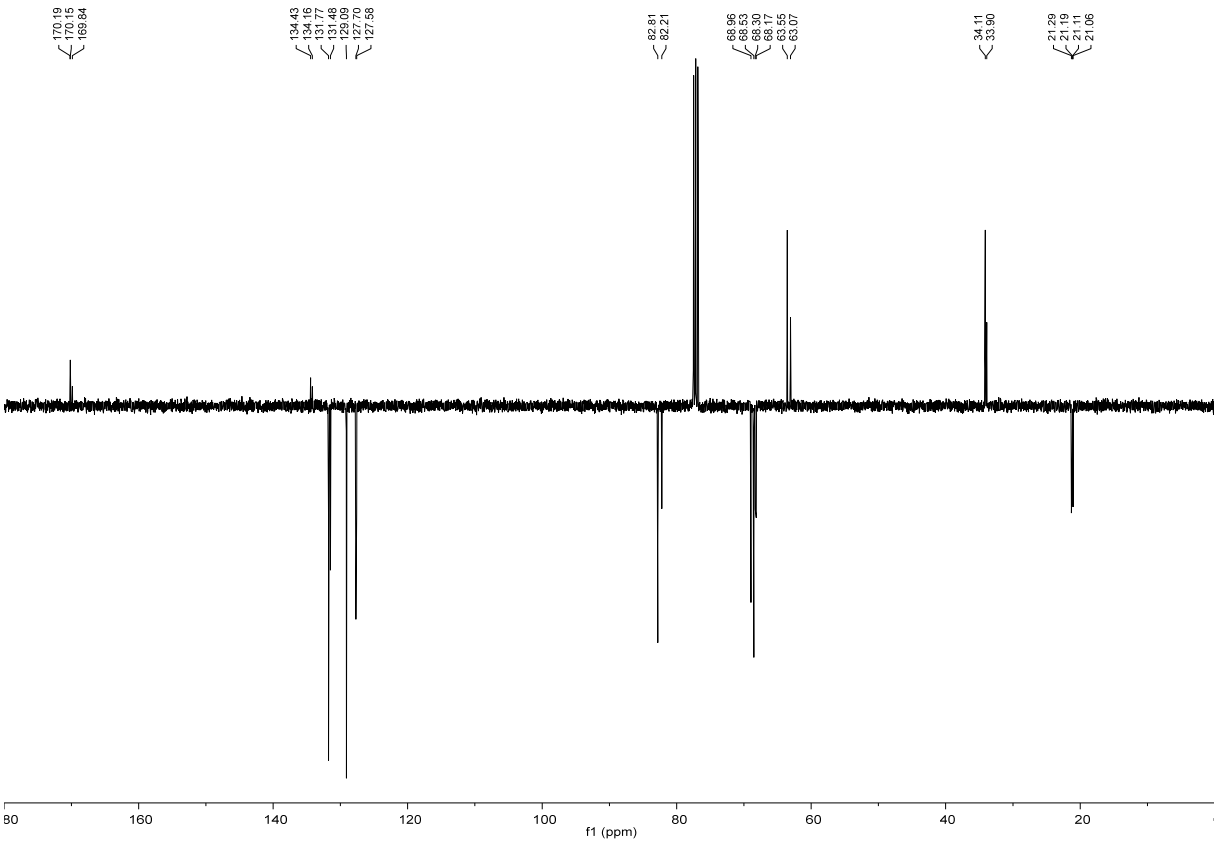
HMBC-GATED NMR, $CDCl_3$ of Donor **S8**



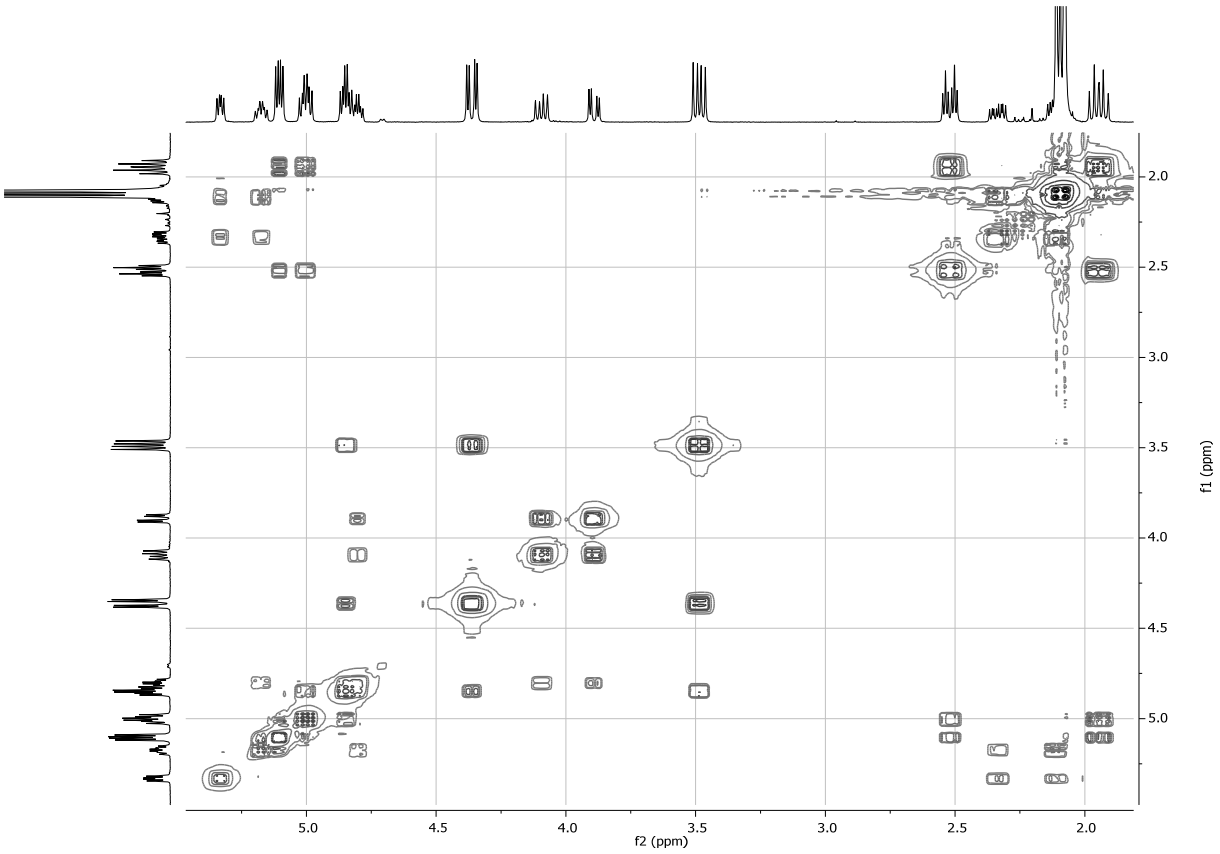
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S9**



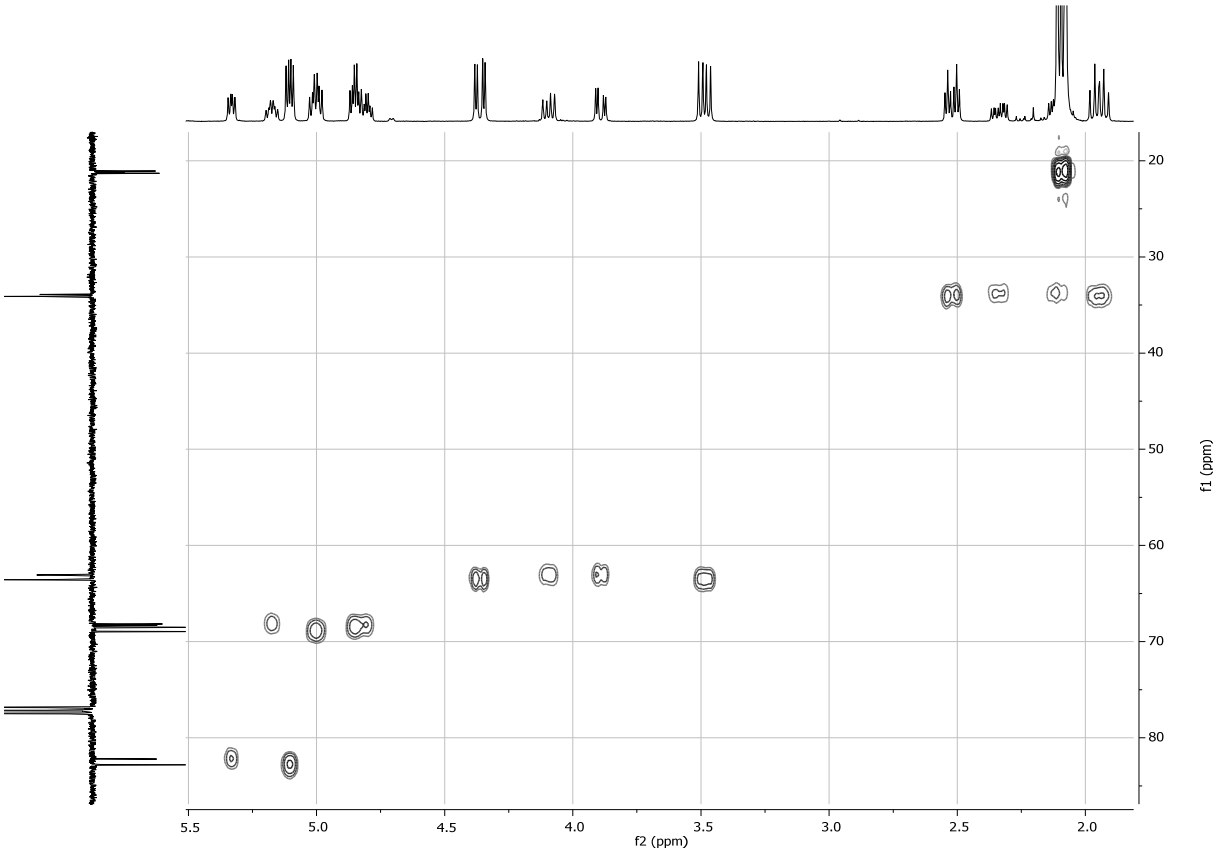
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S9**



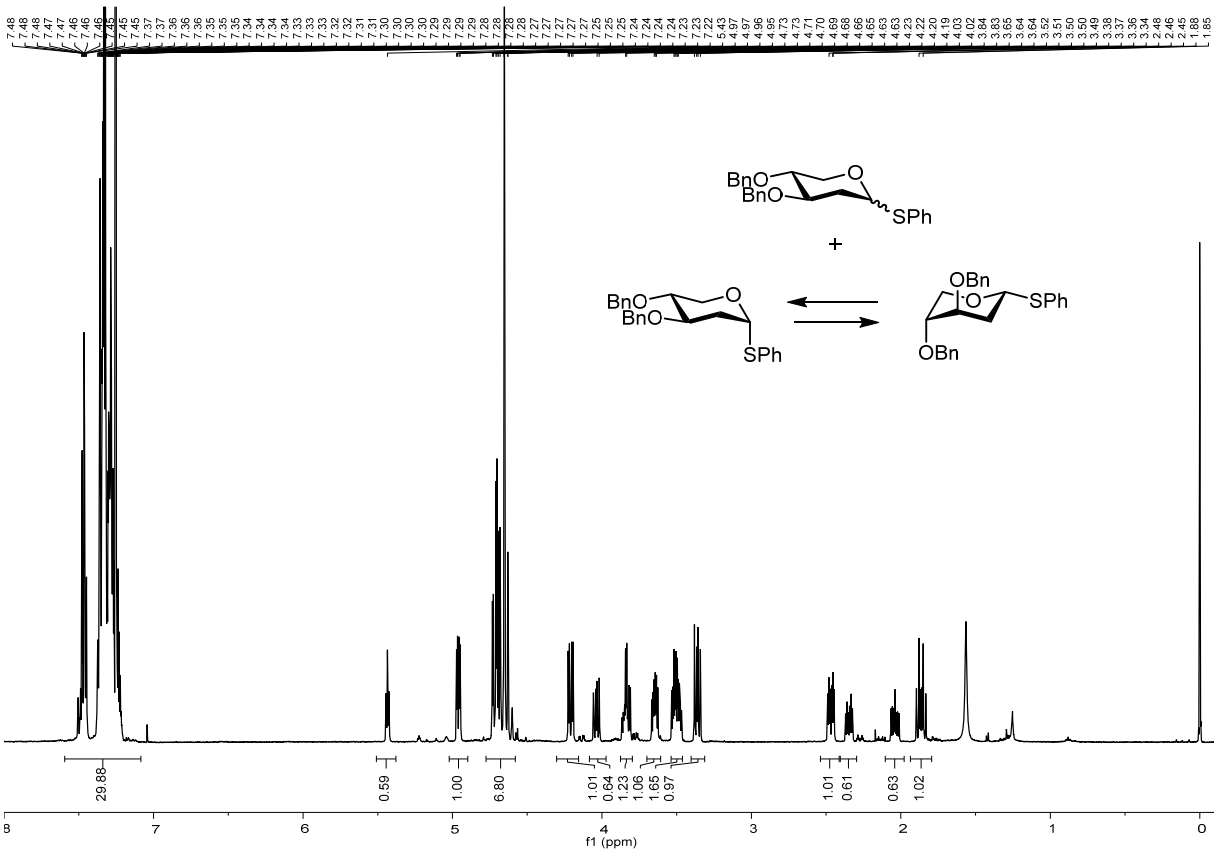
HH-COSY NMR, $CDCl_3$ of Donor **S9**



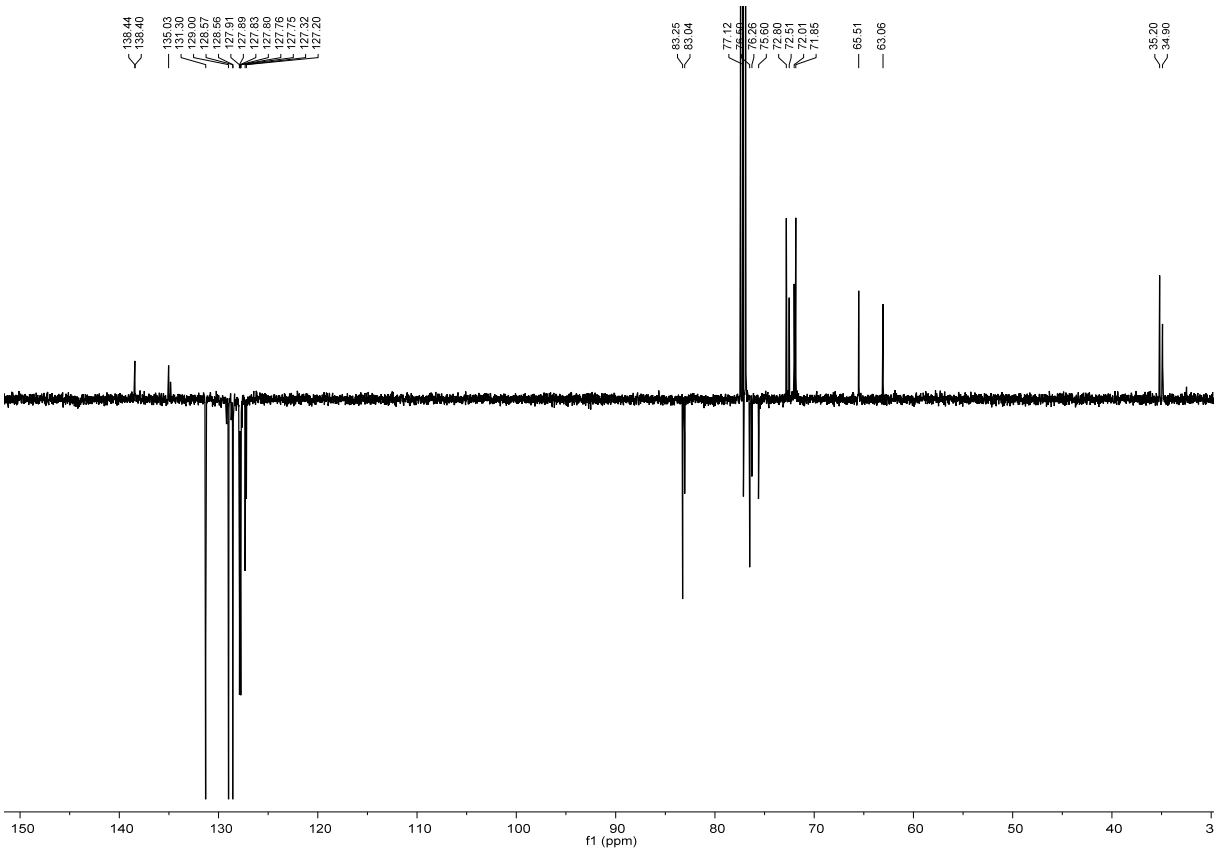
HSQC NMR, $CDCl_3$ of Donor **S9**



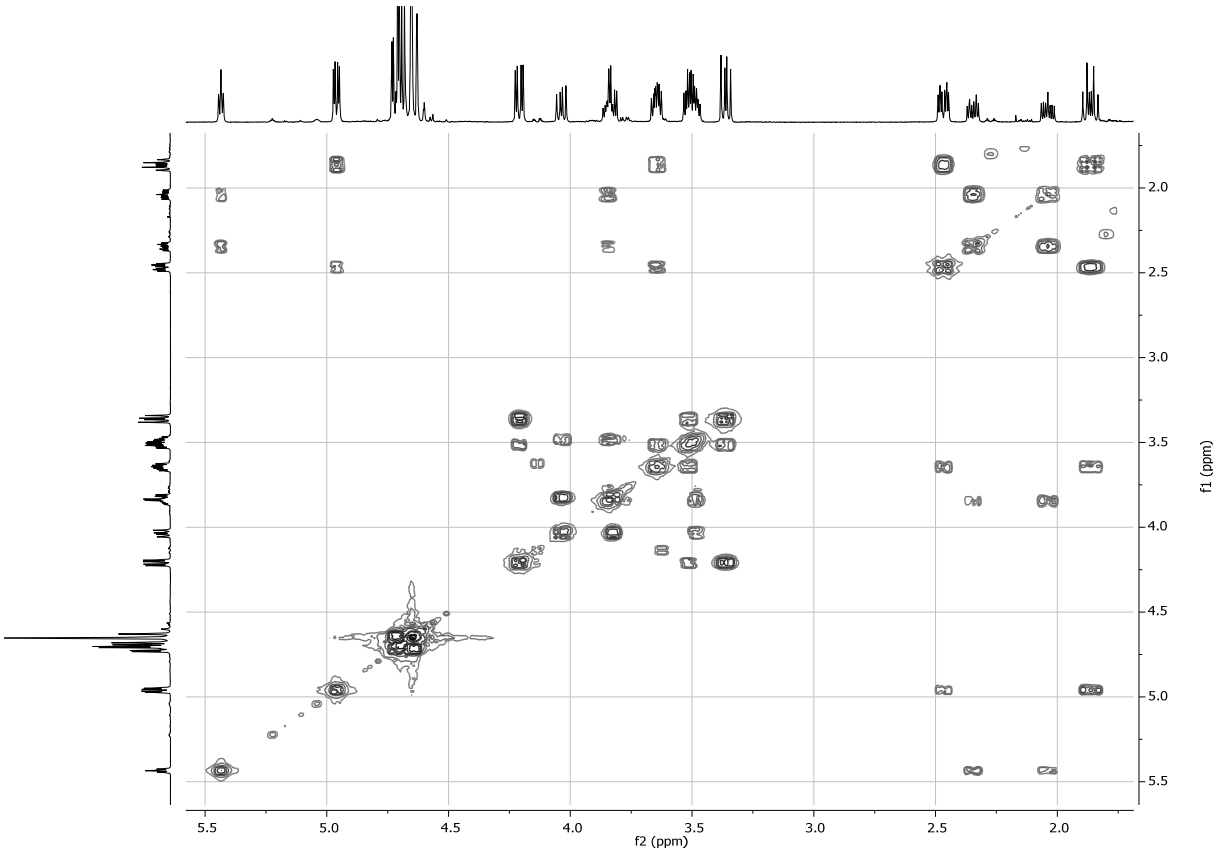
^{1}H NMR, 500 MHz, $CDCl_3$ of Donor **S10**



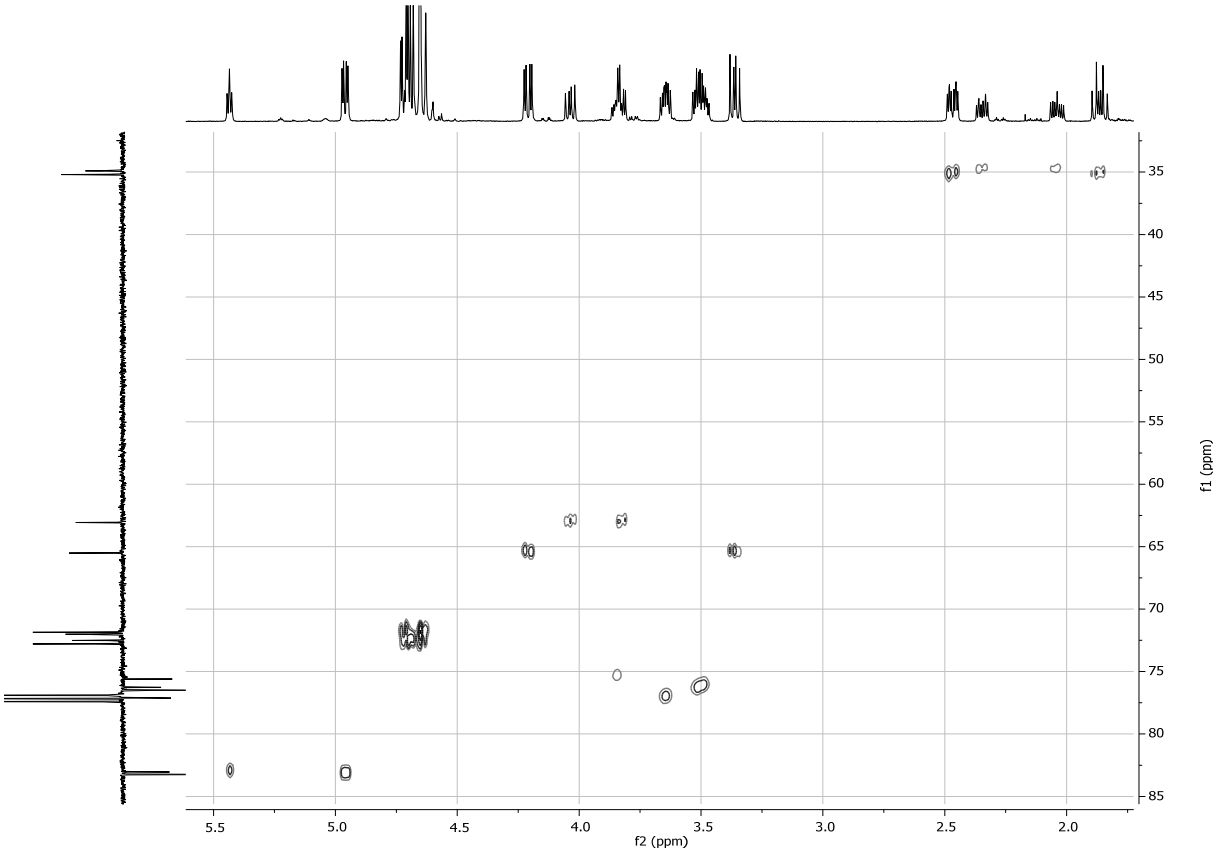
^{13}C NMR, 126 MHz, $CDCl_3$ of Donor **S10**



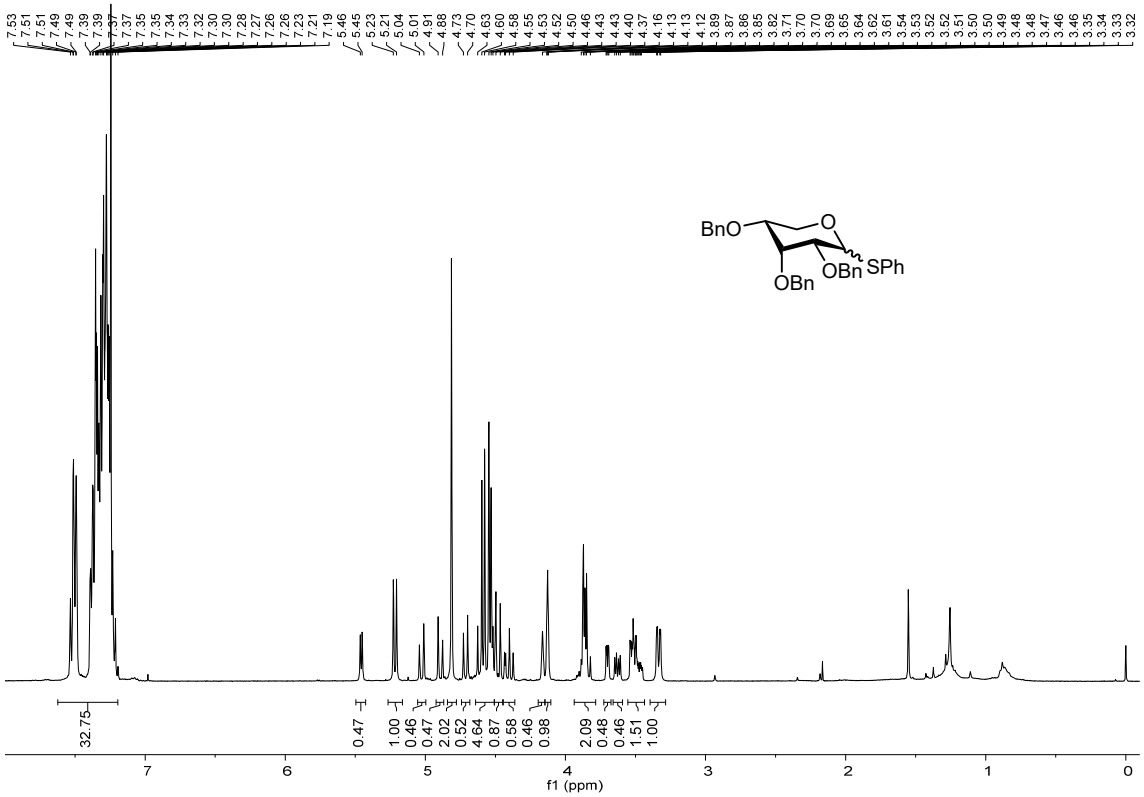
HH-COSY NMR, $CDCl_3$ of Donor **S10**



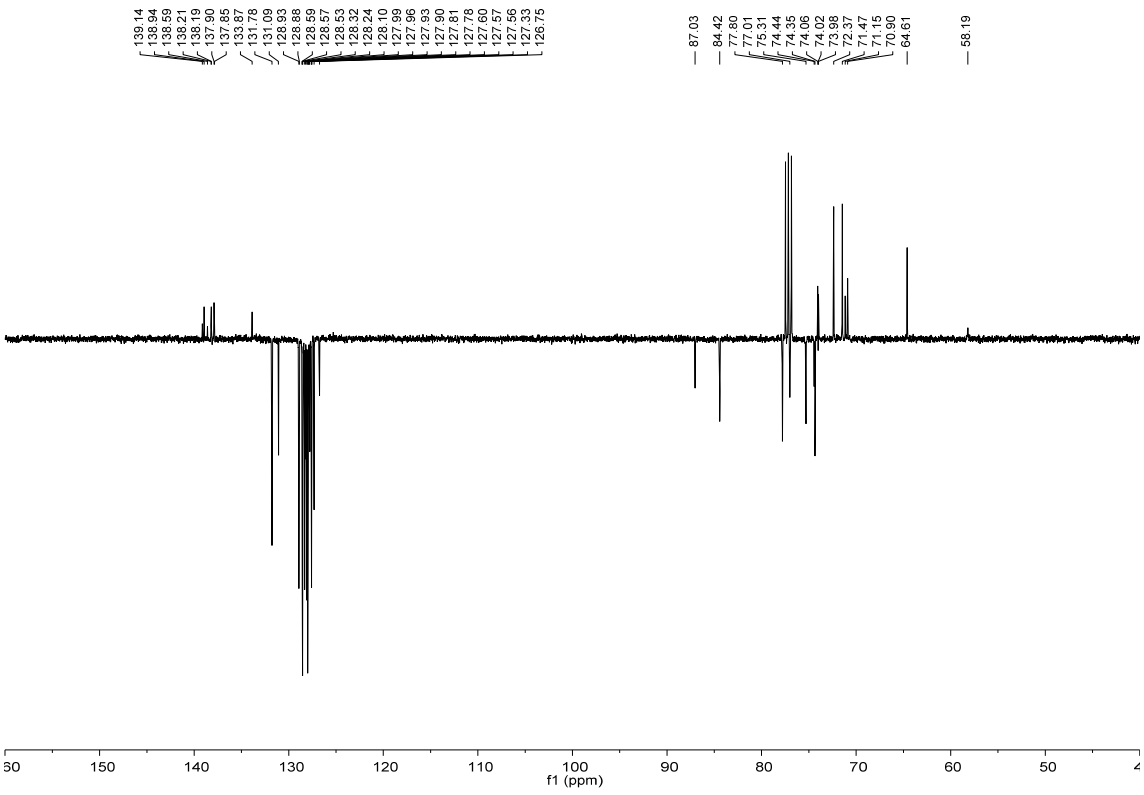
HSQC NMR, $CDCl_3$ of Donor **S10**



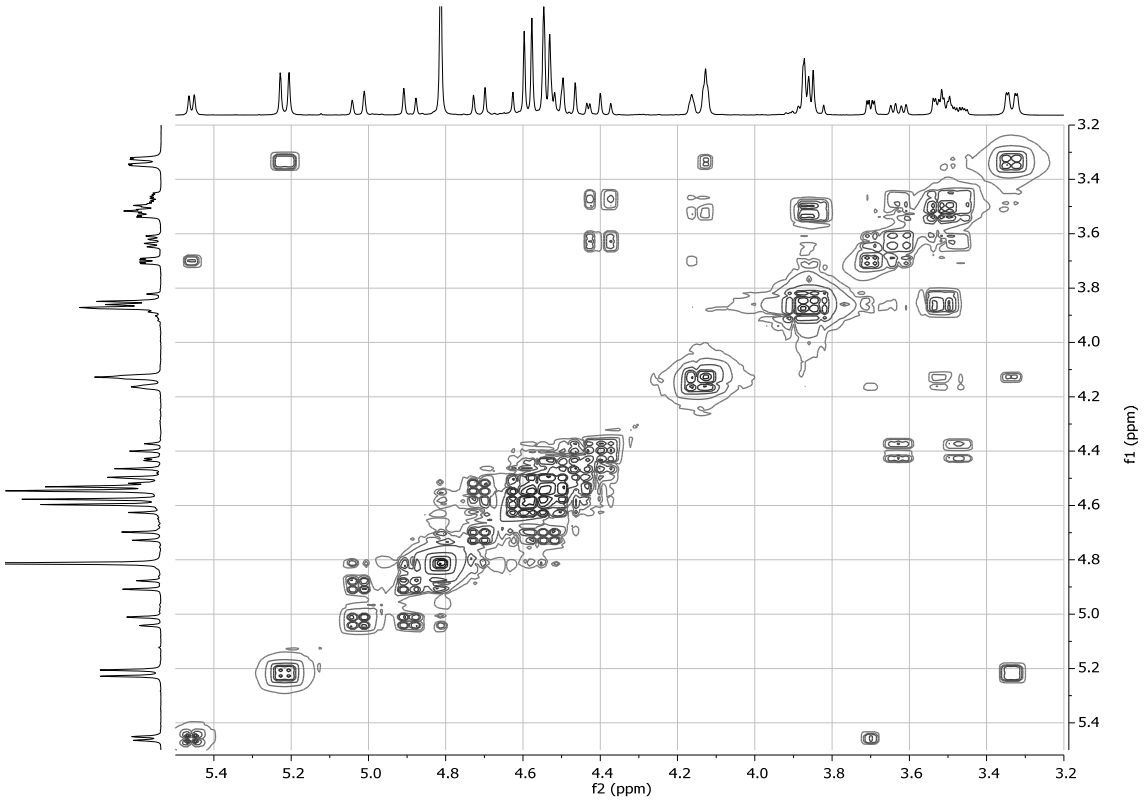
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S11**



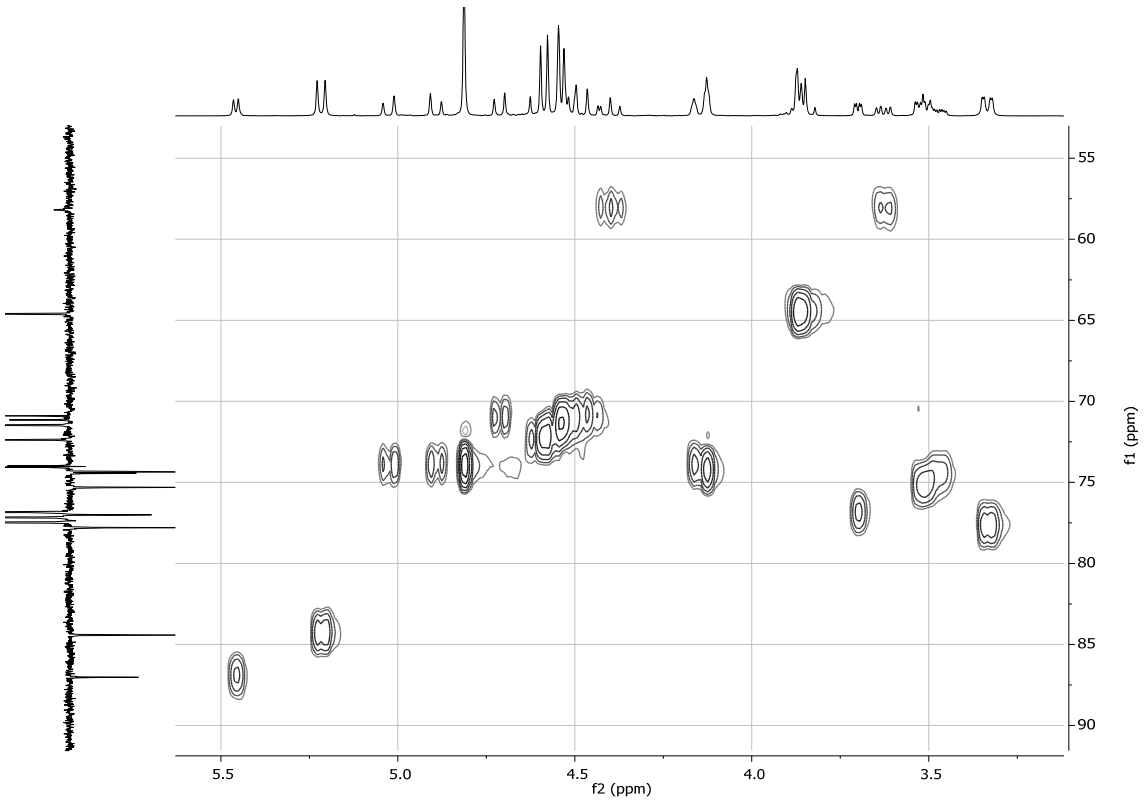
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S11**



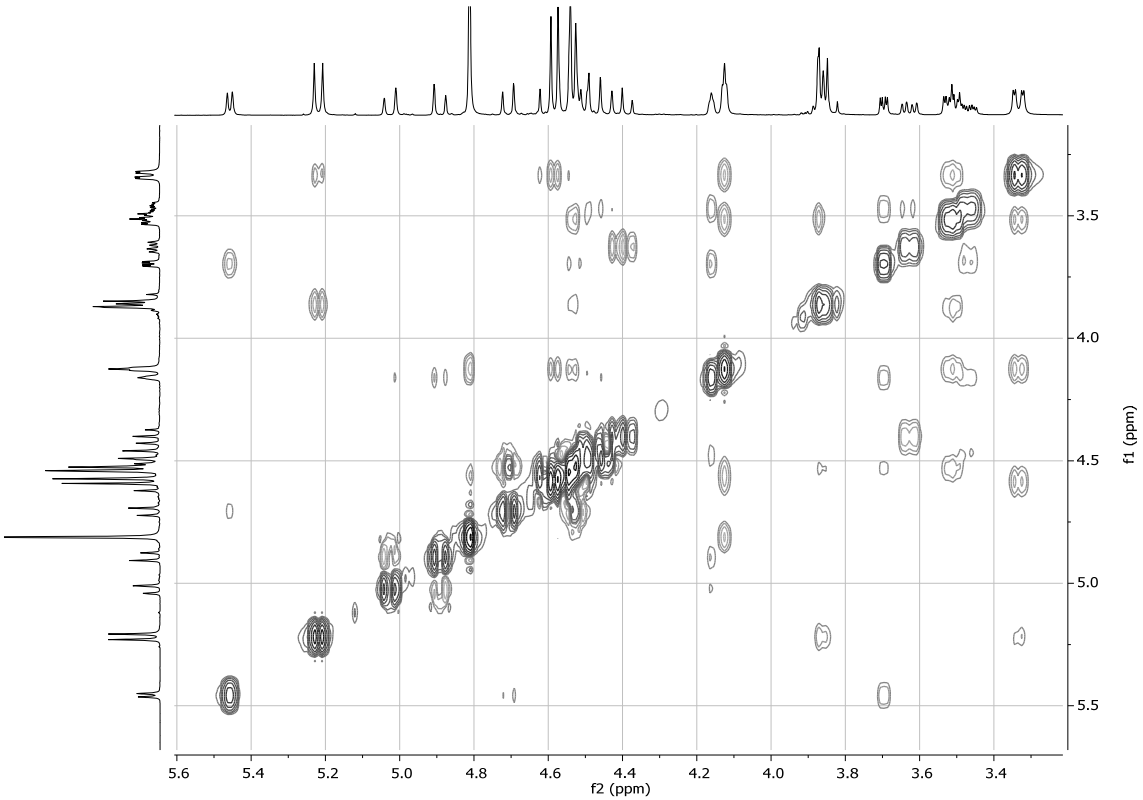
HH-COSY NMR, $CDCl_3$ of Donor **S11**



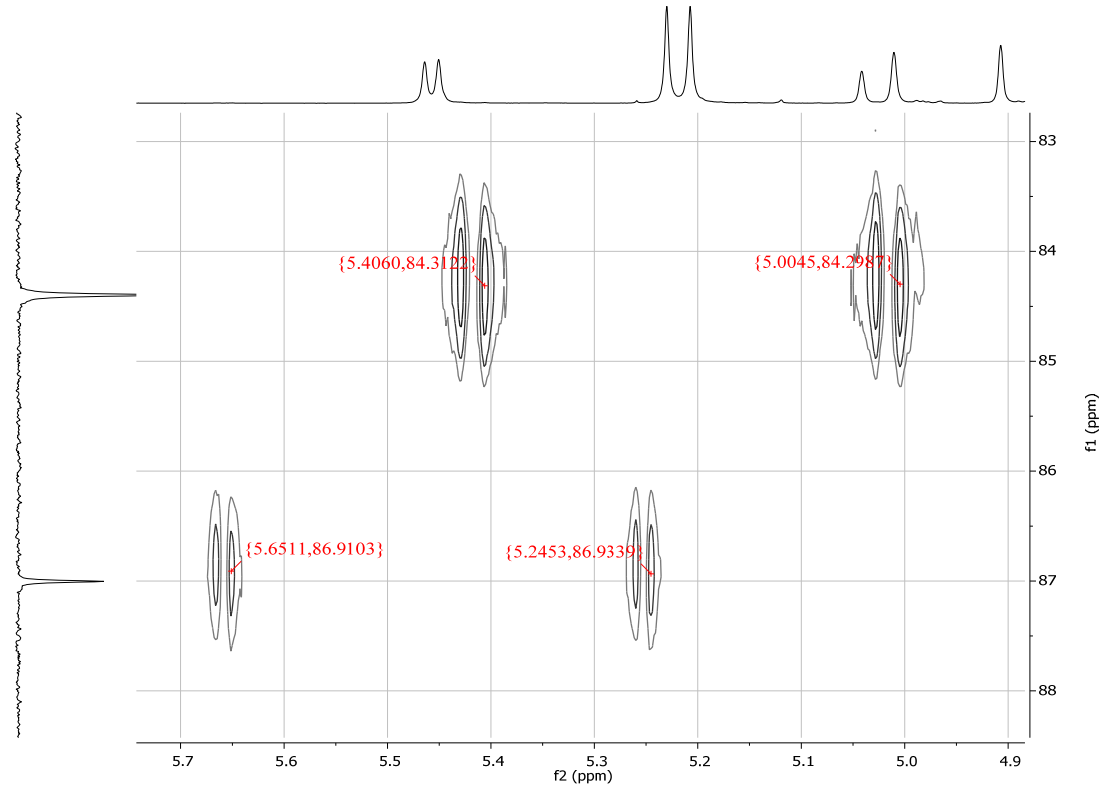
HSQC NMR, $CDCl_3$ of Donor **S11**



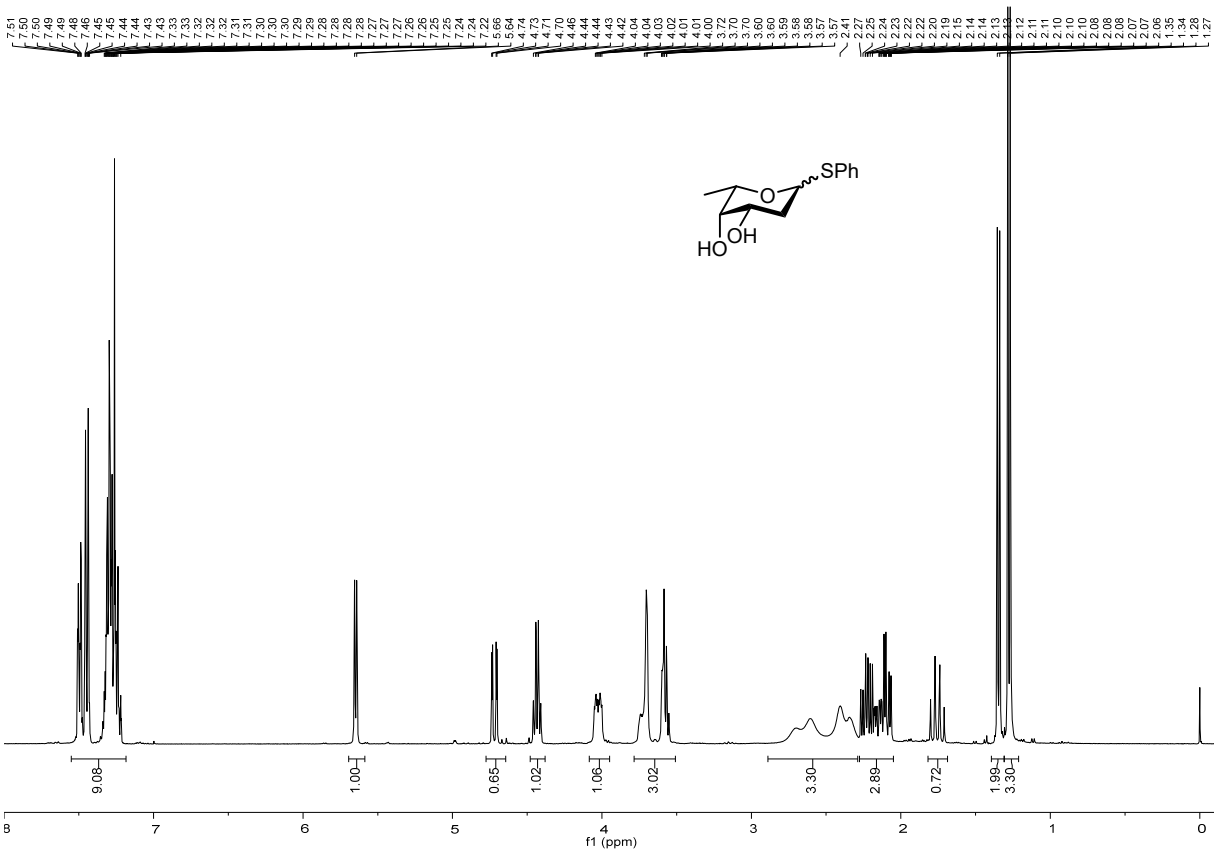
NOESY NMR, $CDCl_3$ of Donor **S11**



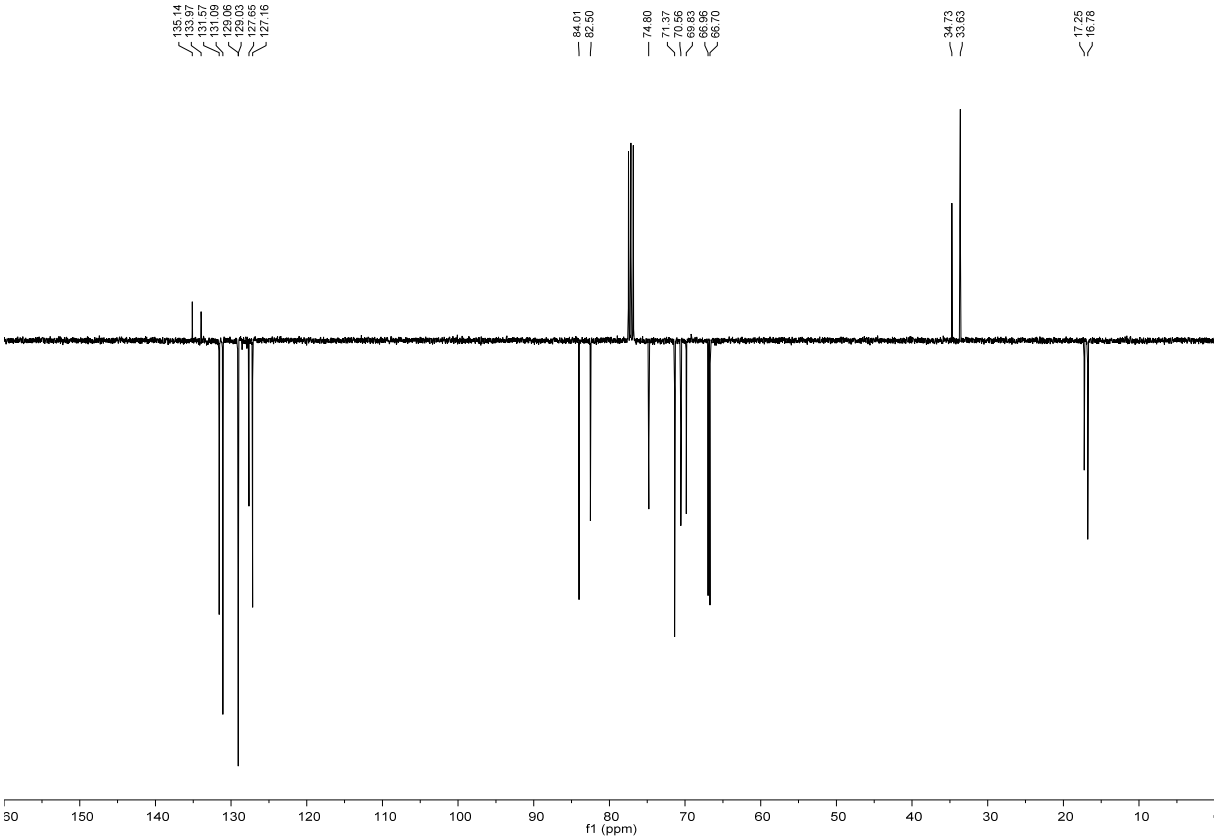
HMBC-GATED NMR, $CDCl_3$ of Donor **S11**



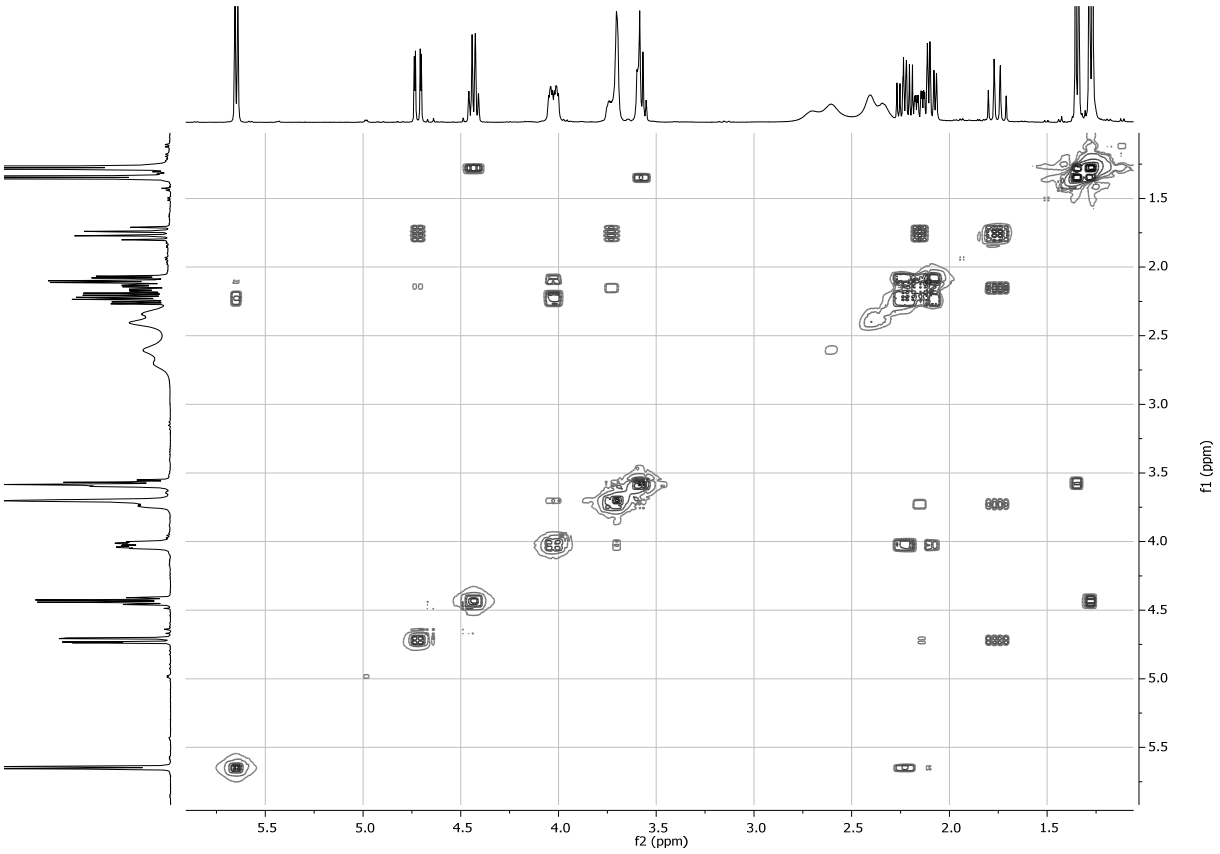
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S14**



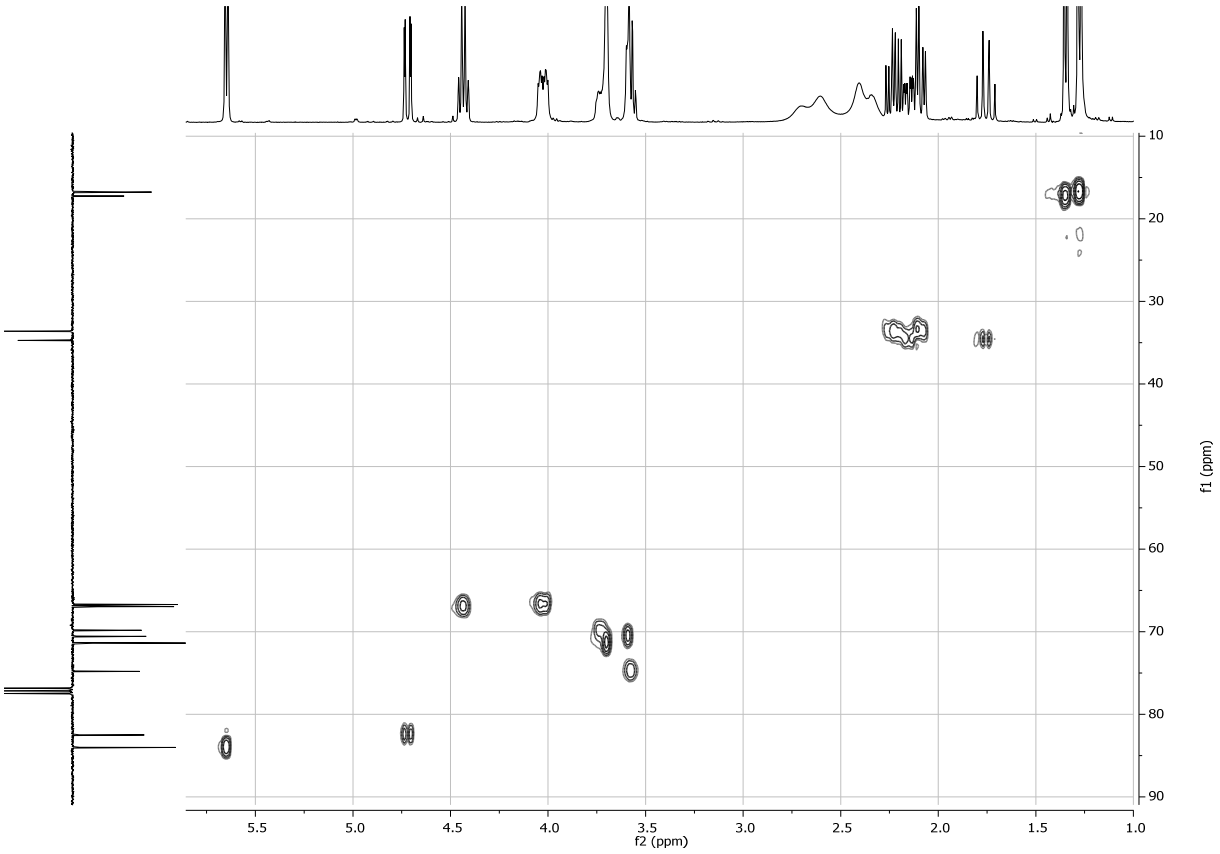
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S14**



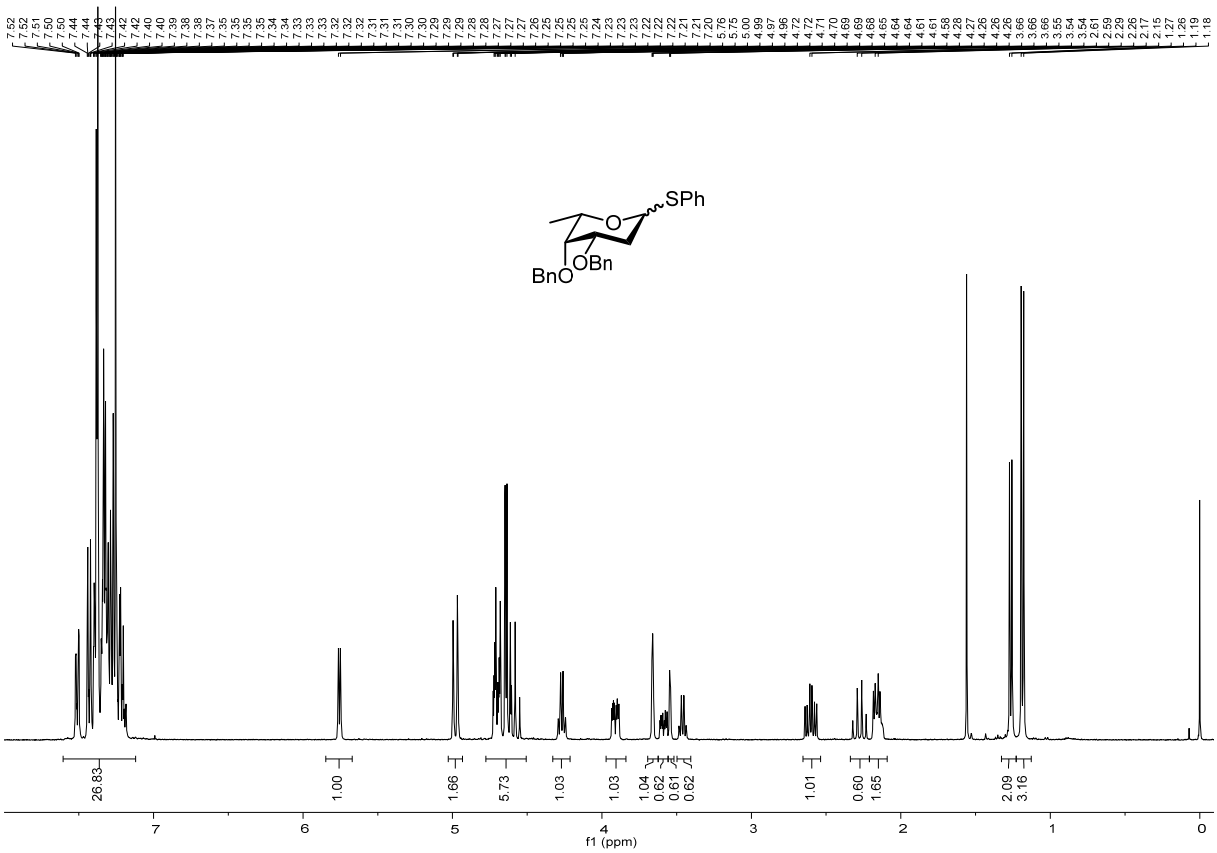
HH-COSY NMR, $CDCl_3$ of Donor **S14**



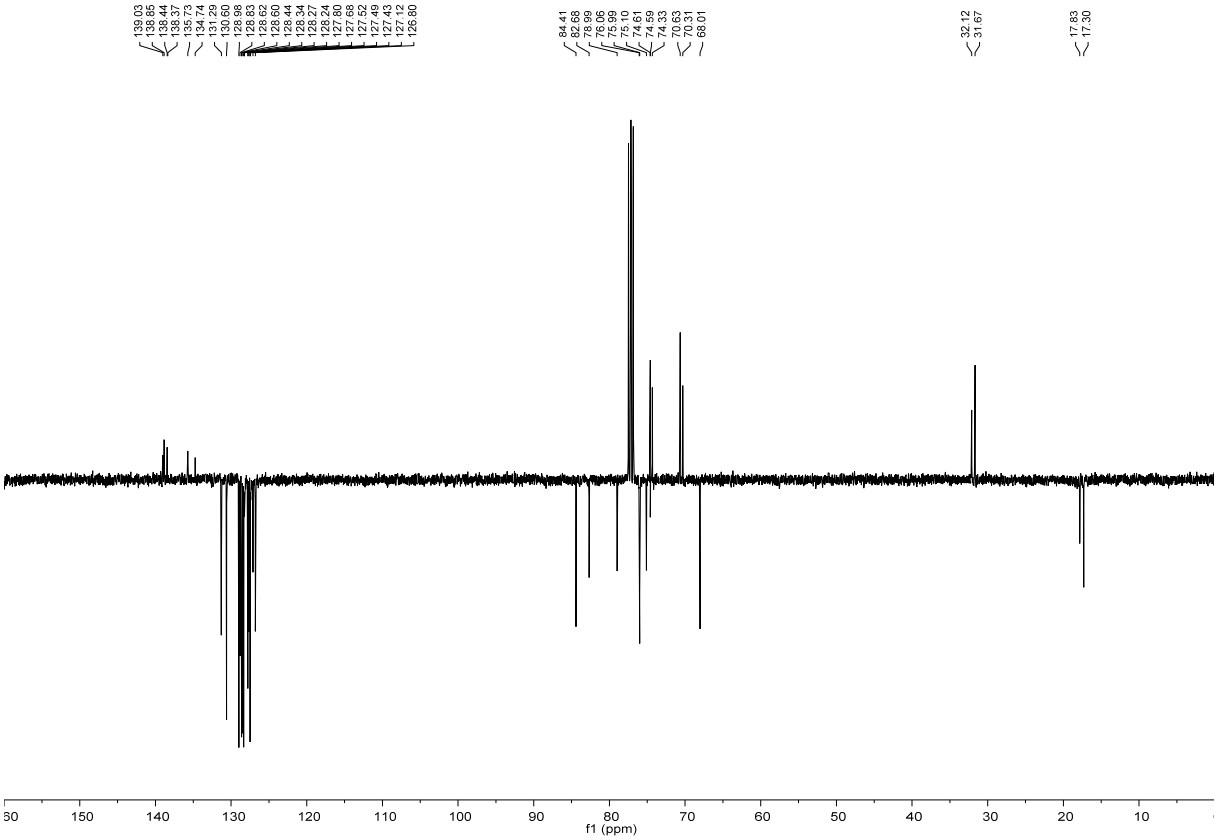
HSQC NMR, $CDCl_3$ of Donor **S14**



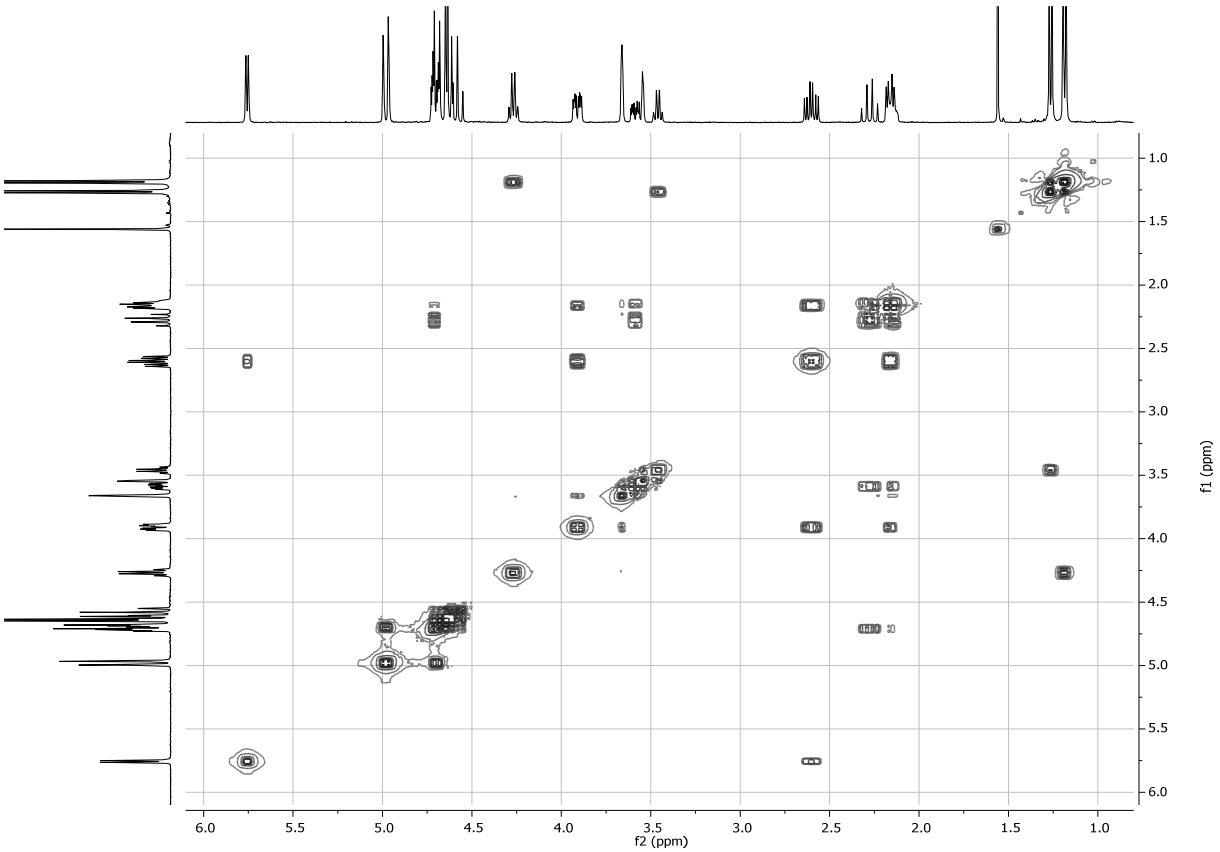
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S15**



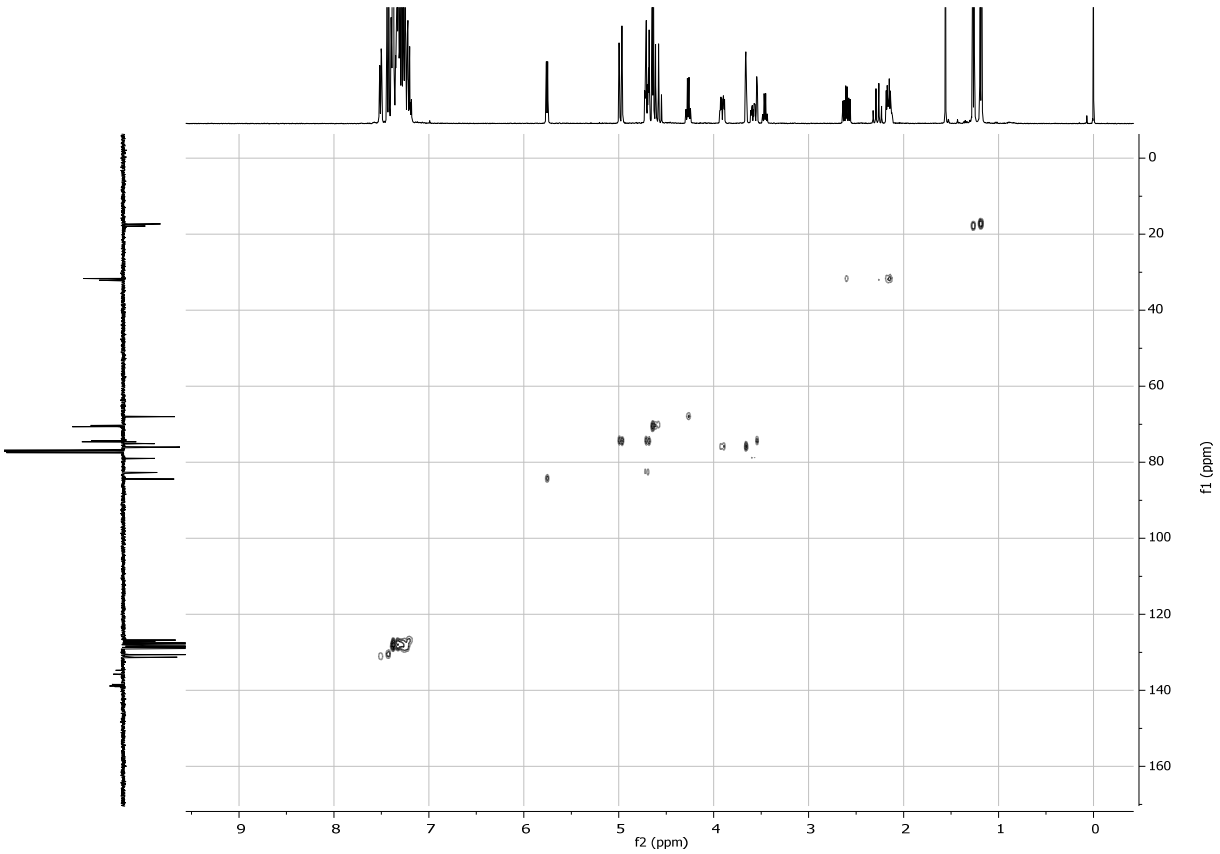
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S15**



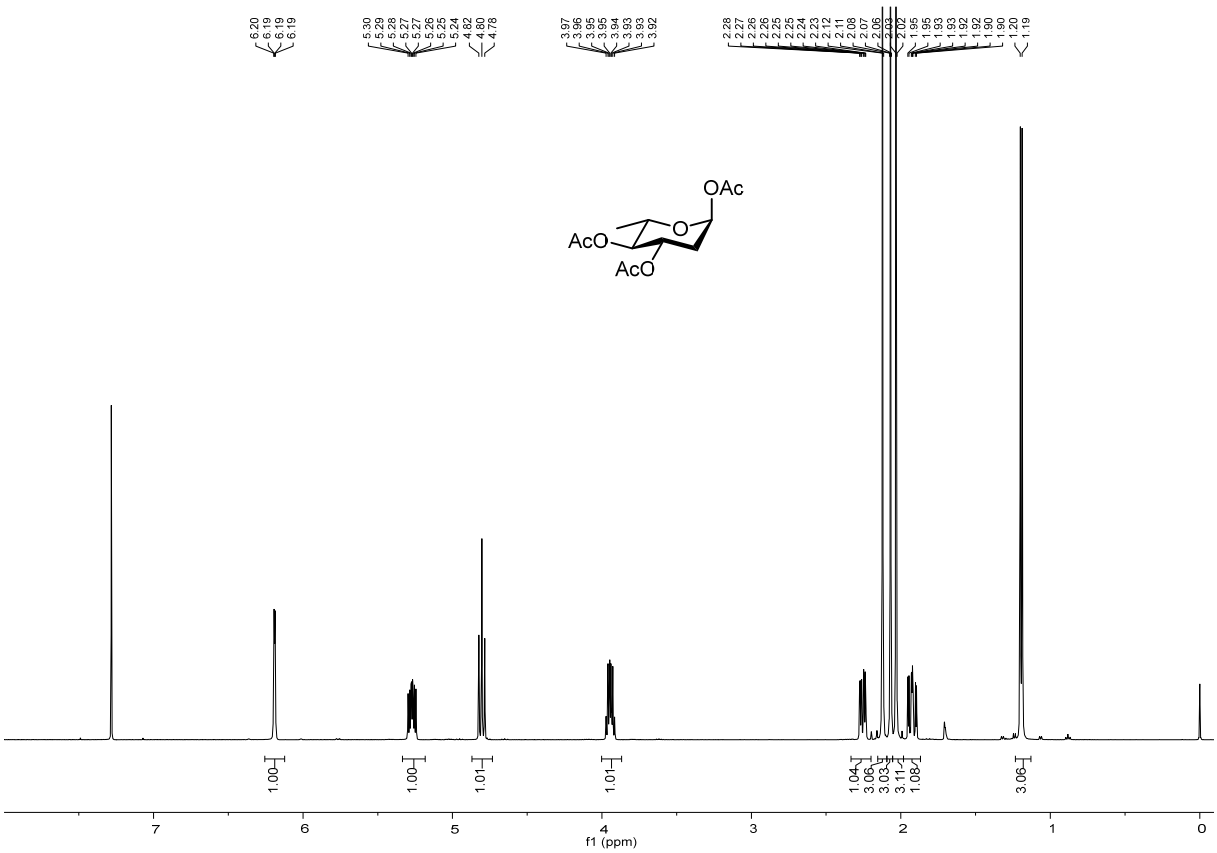
HH-COSY NMR, $CDCl_3$ of Donor **S15**



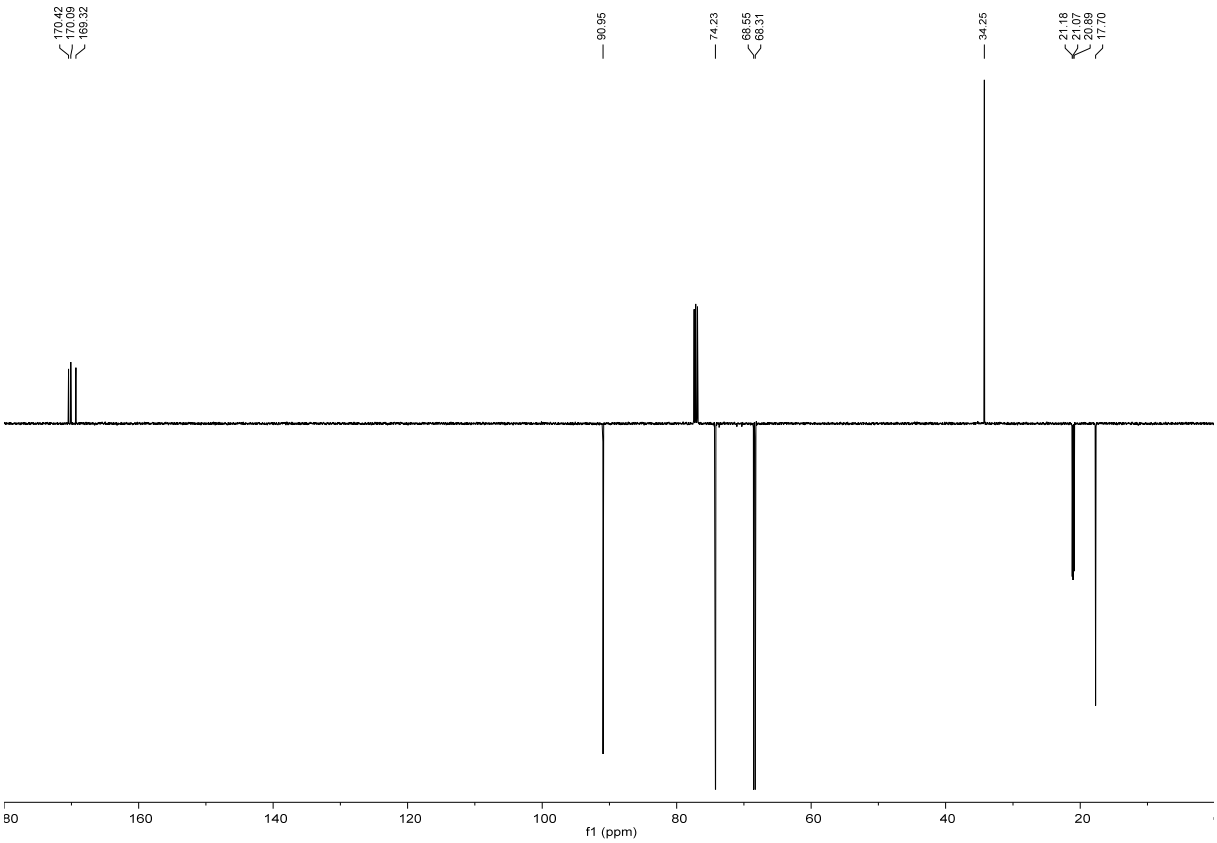
HSQC NMR, $CDCl_3$ of Donor **S15**



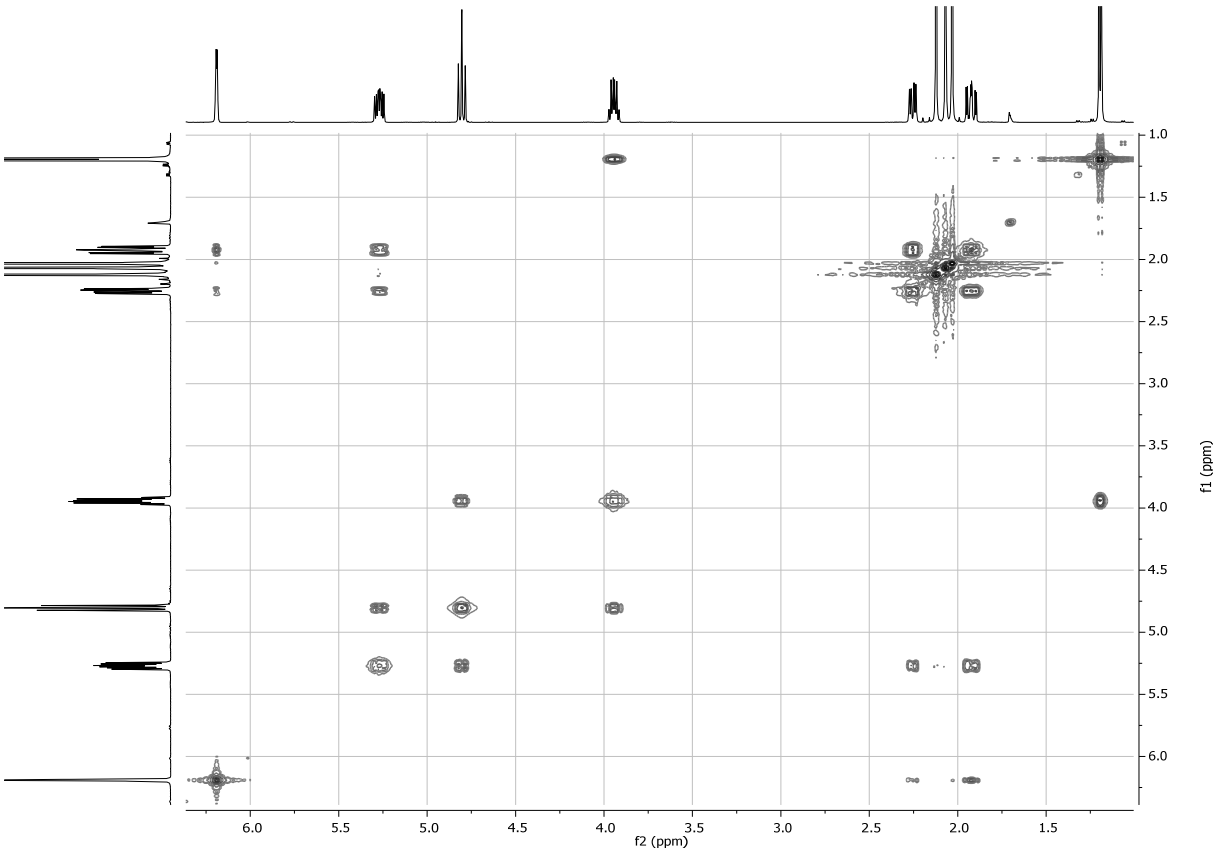
^{1}H NMR, 500 MHz, $CDCl_3$ of Donor **S18**



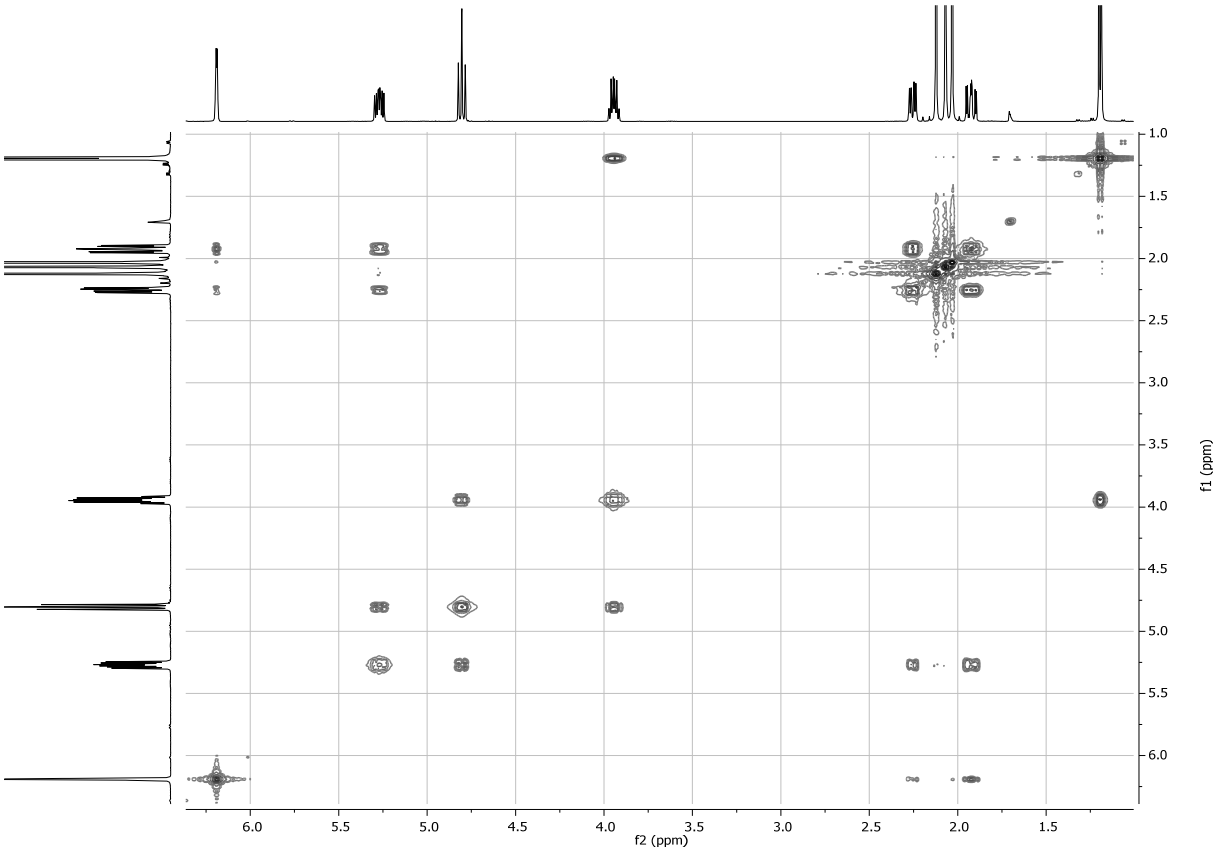
^{13}C NMR, 126 MHz, $CDCl_3$ of Donor **S18**



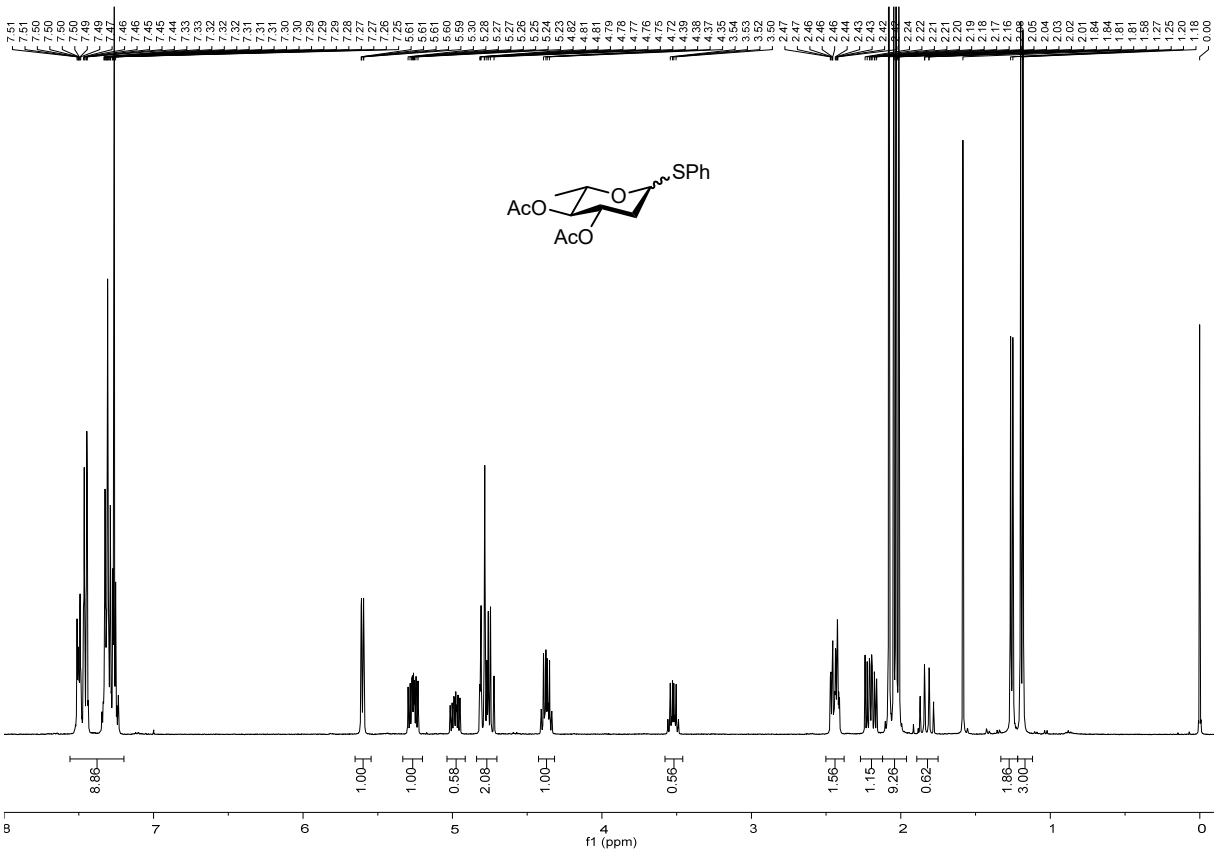
HH-COSY NMR, $CDCl_3$ of Donor **S18**



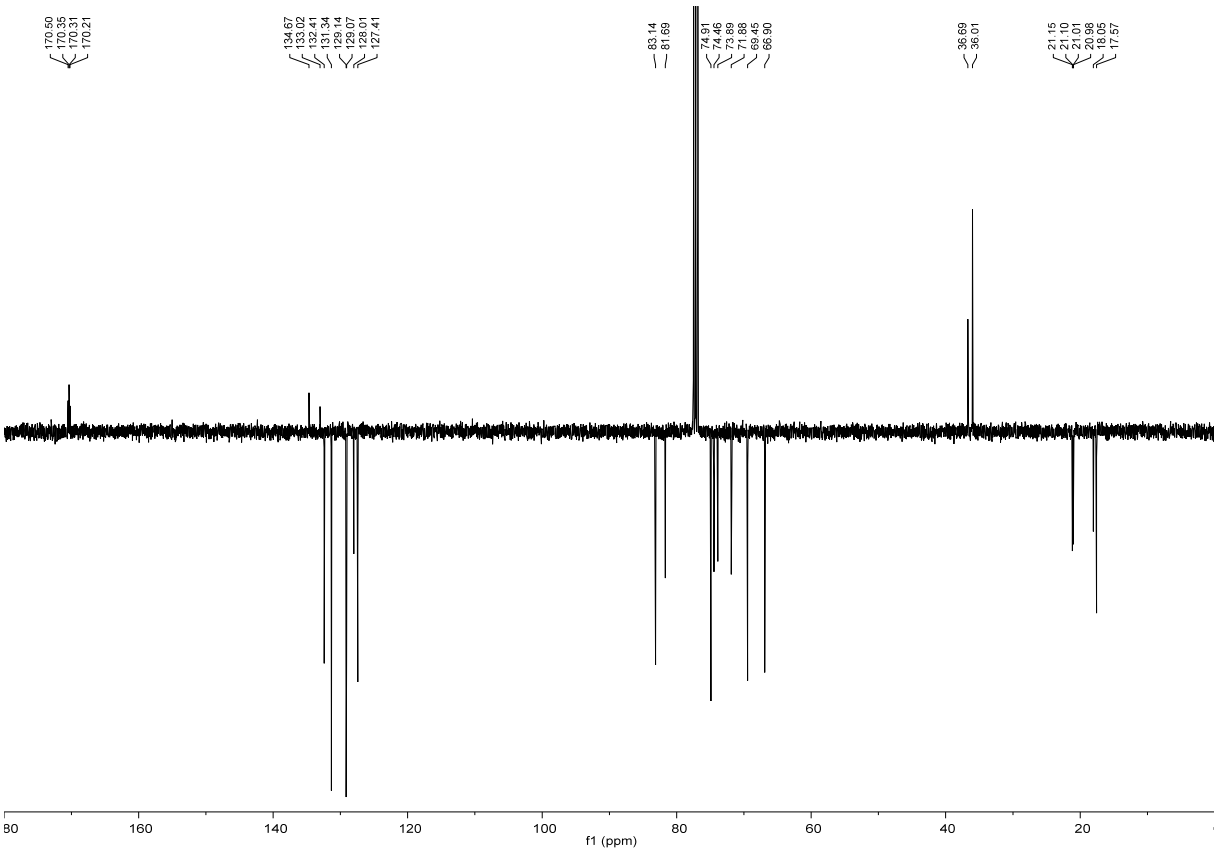
HSQC NMR, $CDCl_3$ of Donor **S18**



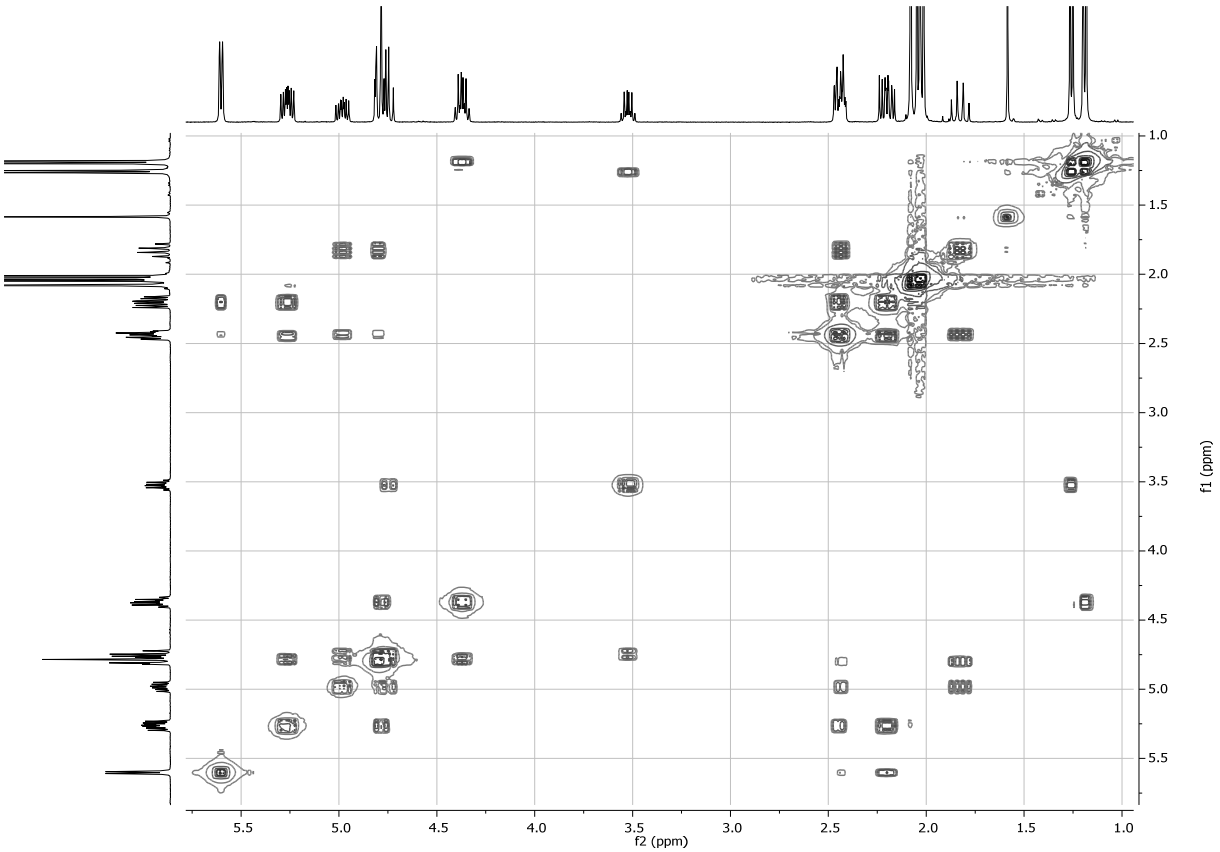
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S19**



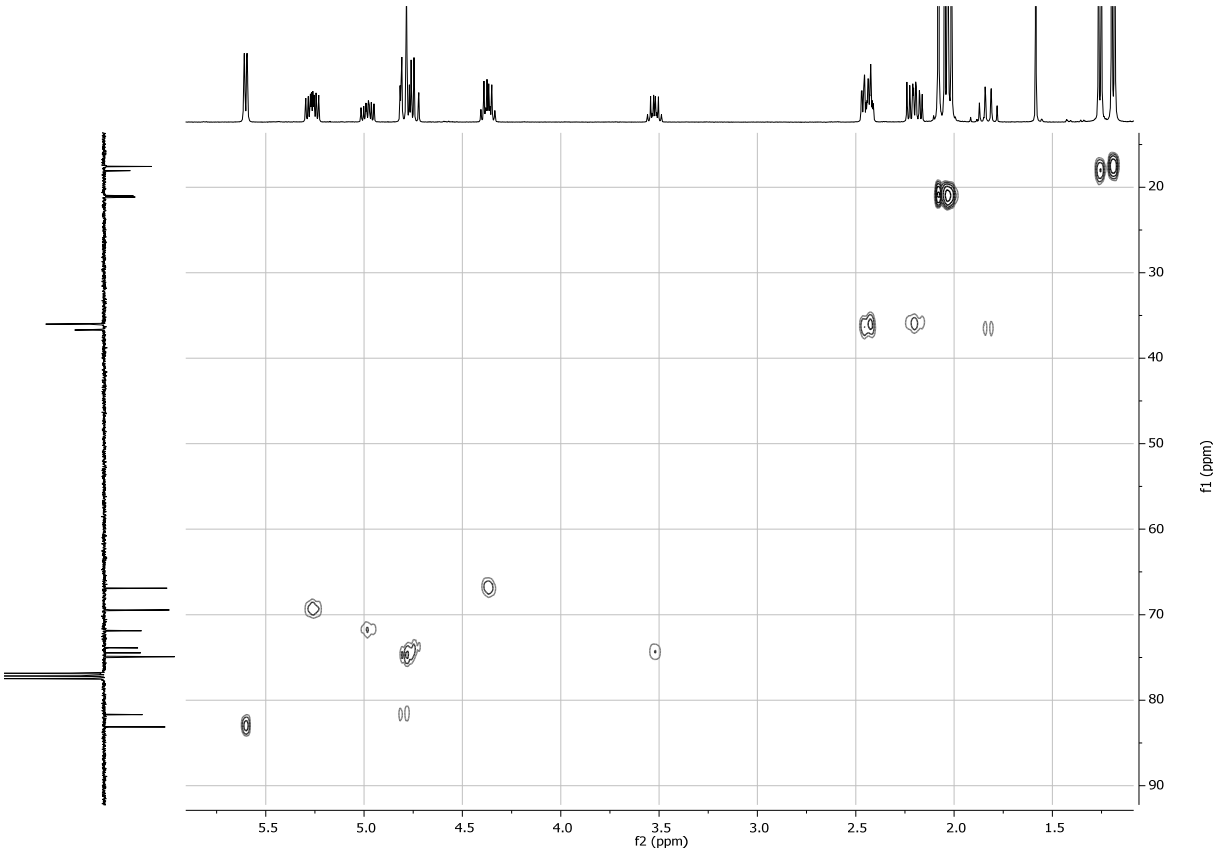
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S19**



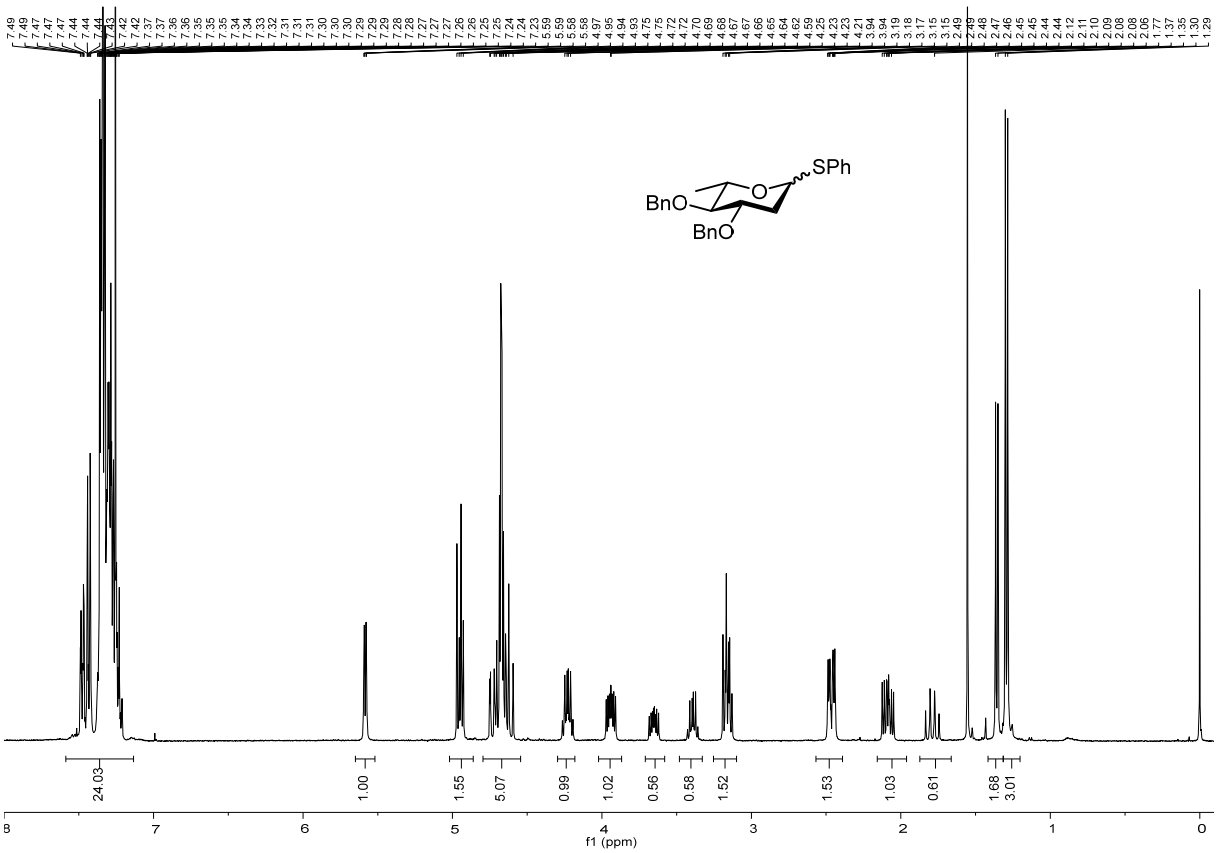
HH-COSY NMR, $CDCl_3$ of Donor **S19**



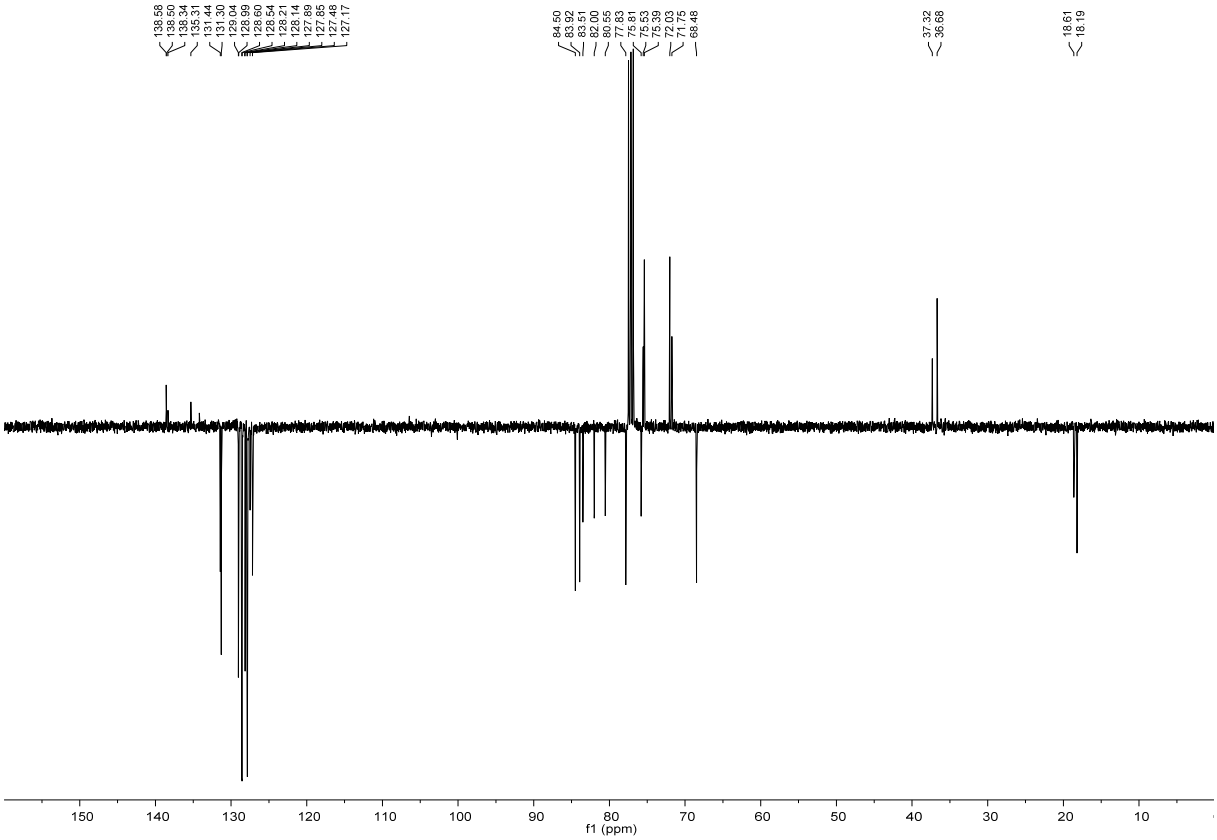
HSQC NMR, $CDCl_3$ of Donor **S19**



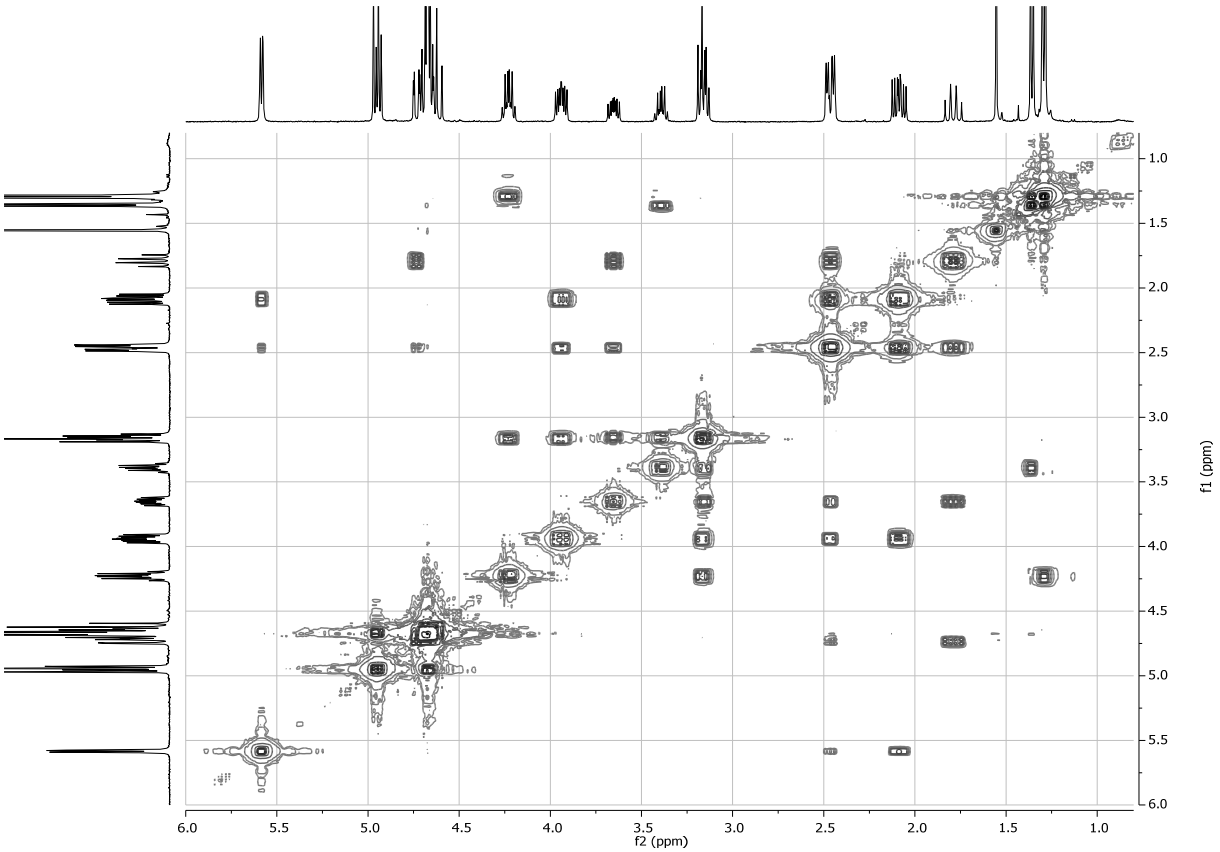
^{1}H NMR, 500 MHz, $CDCl_3$ of Donor **S20**



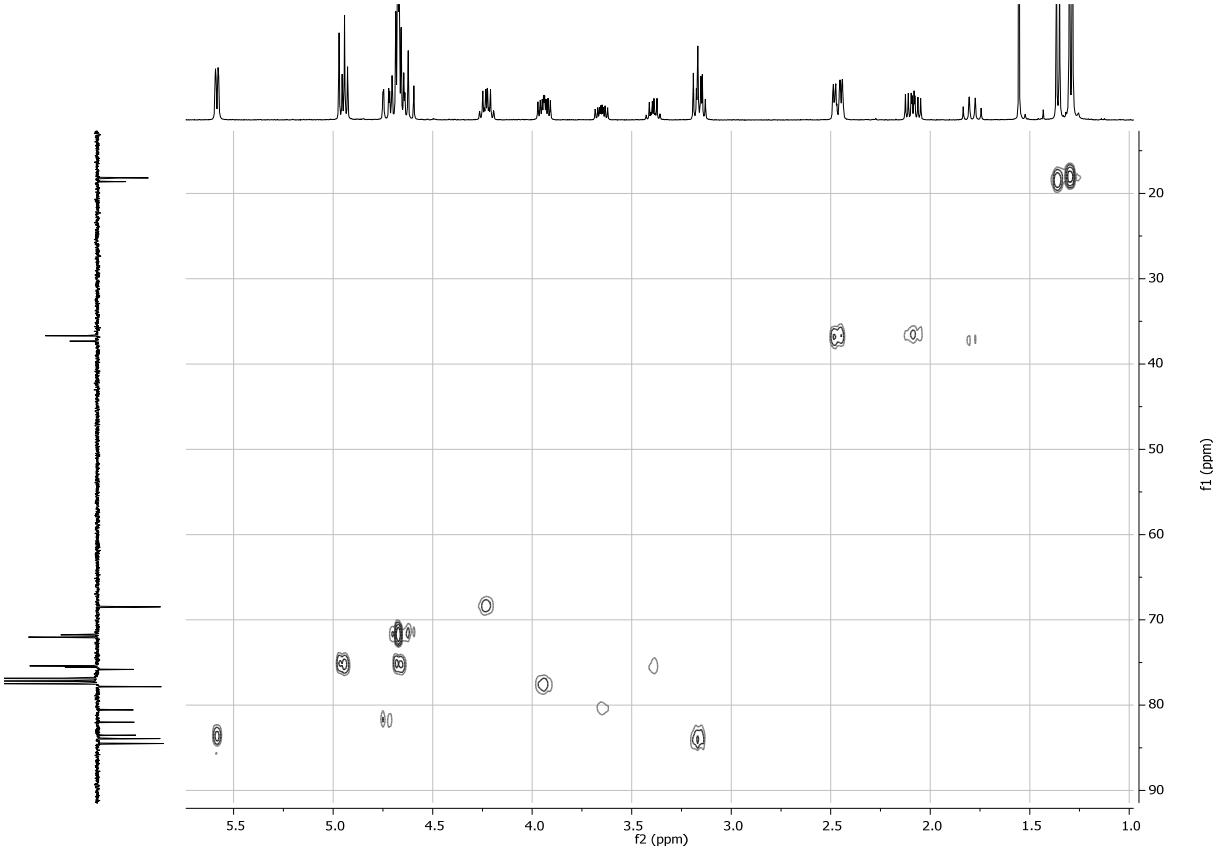
^{13}C NMR, 126 MHz, $CDCl_3$ of Donor **S20**



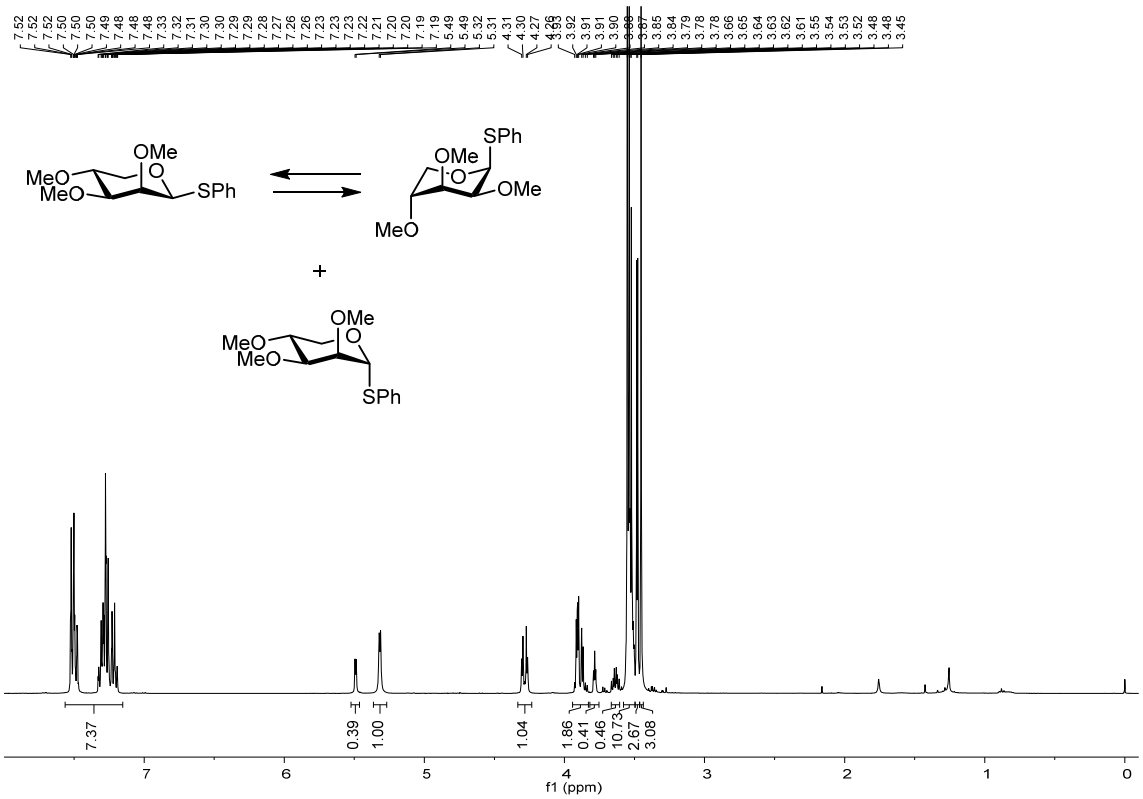
HH-COSY NMR, $CDCl_3$ of Donor **S20**



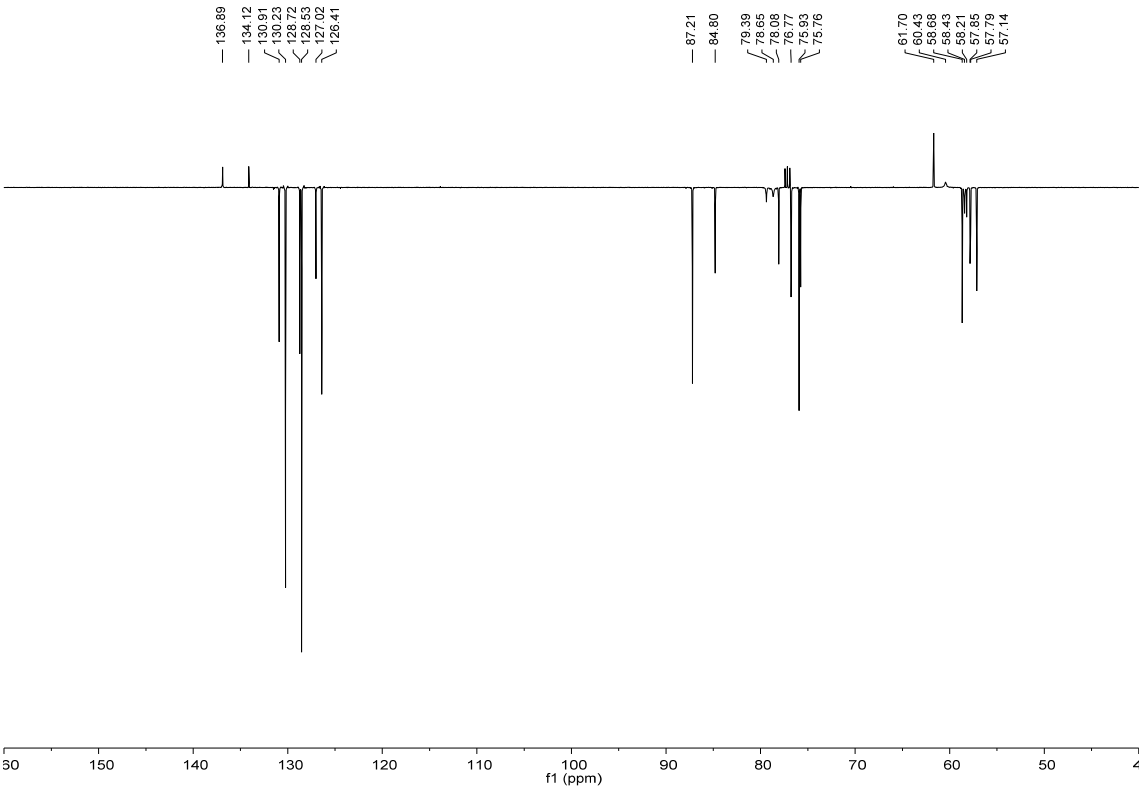
HSQC NMR, $CDCl_3$ of Donor **S20**



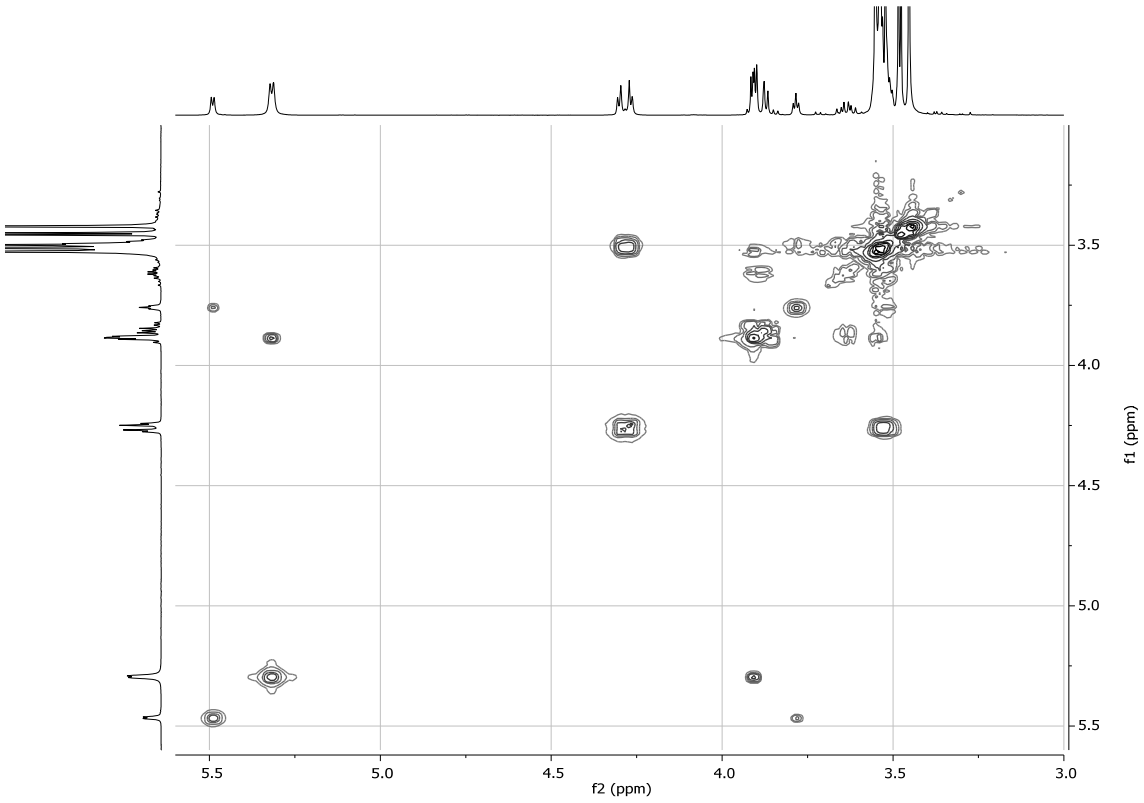
^{1}H NMR, 500 MHz, $CDCl_3$ of Donor **S31**



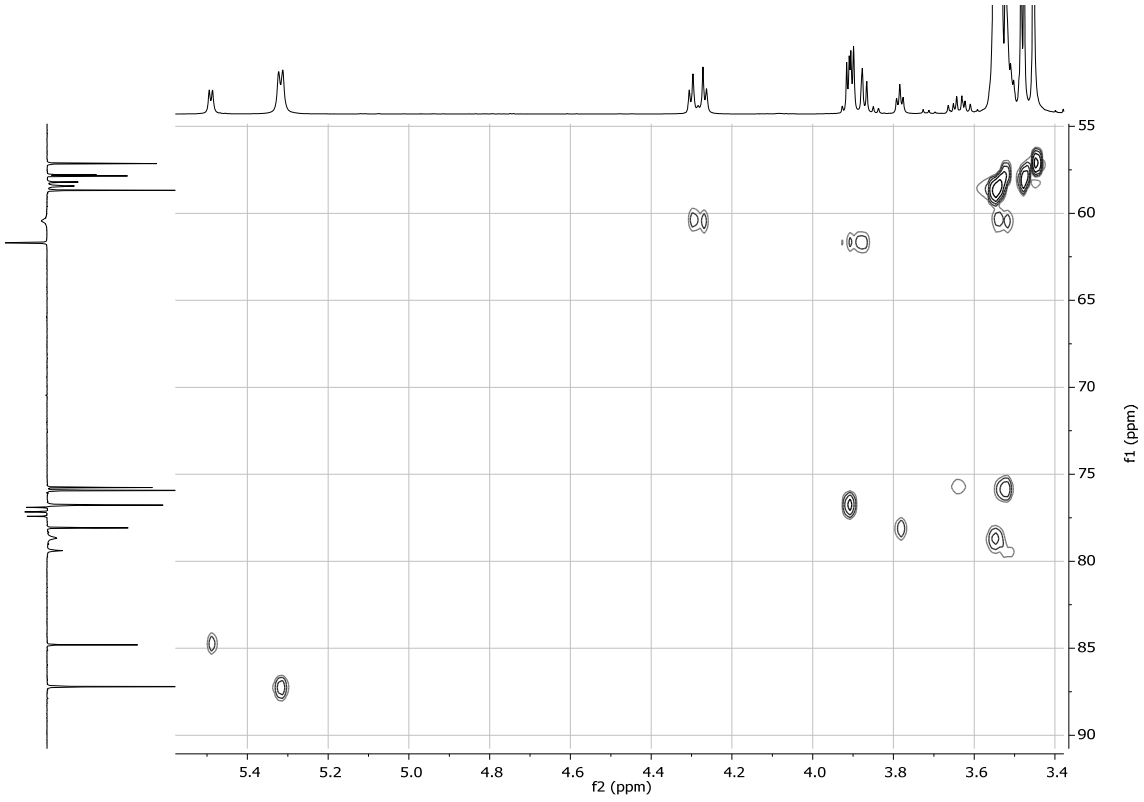
^{13}C NMR, 126 MHz, $CDCl_3$ of Donor **S31**



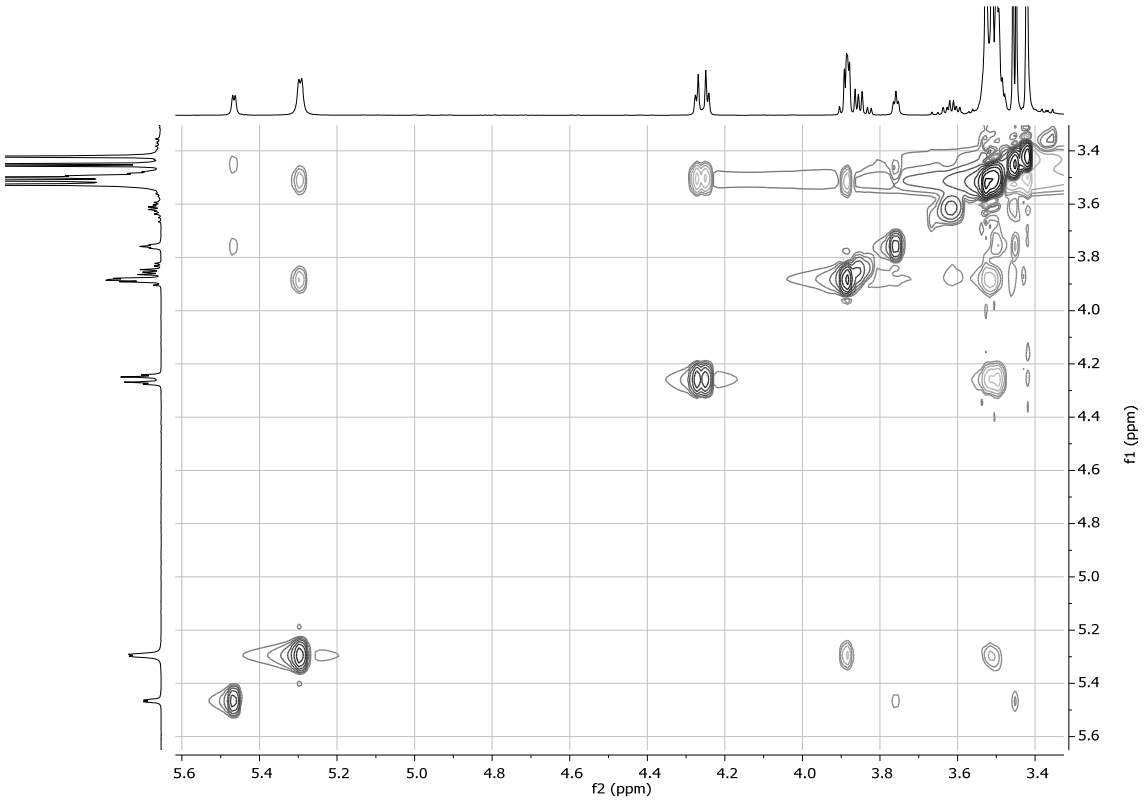
HH-COSY NMR, $CDCl_3$ of Donor **S31**



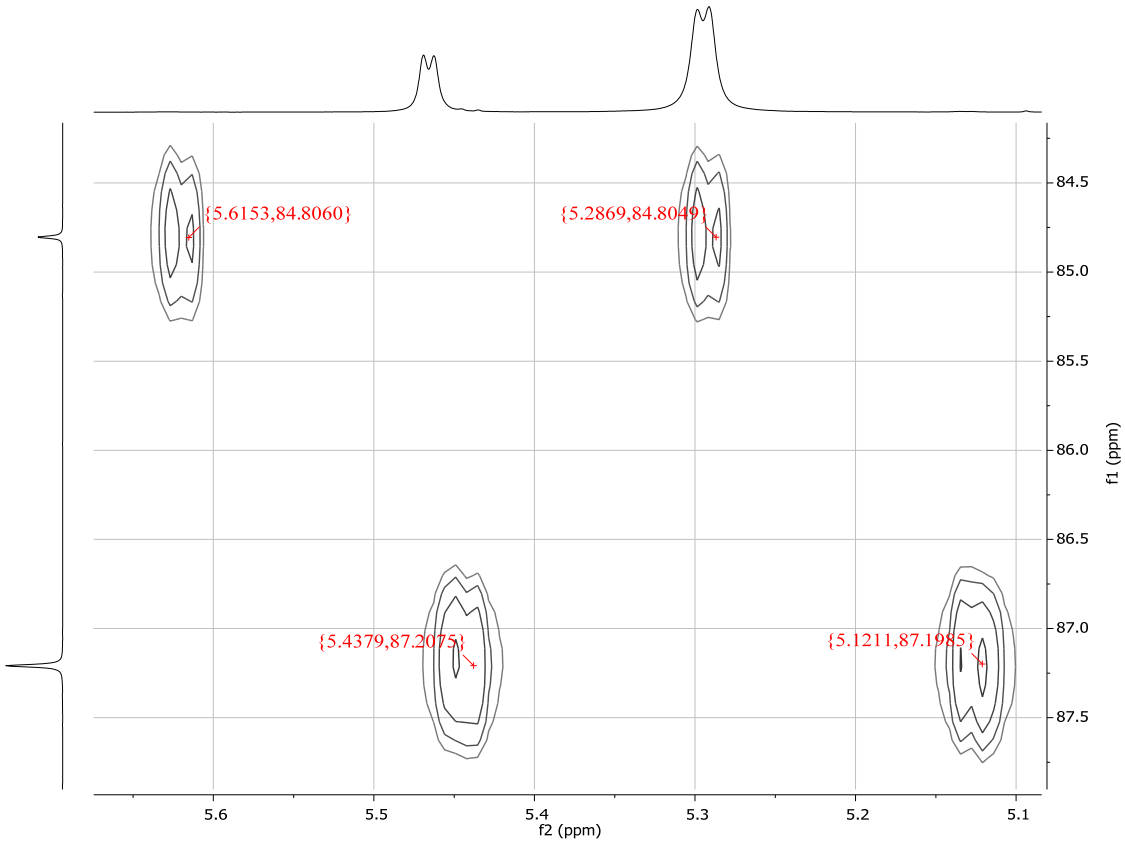
HSQC NMR, $CDCl_3$ of Donor **S31**



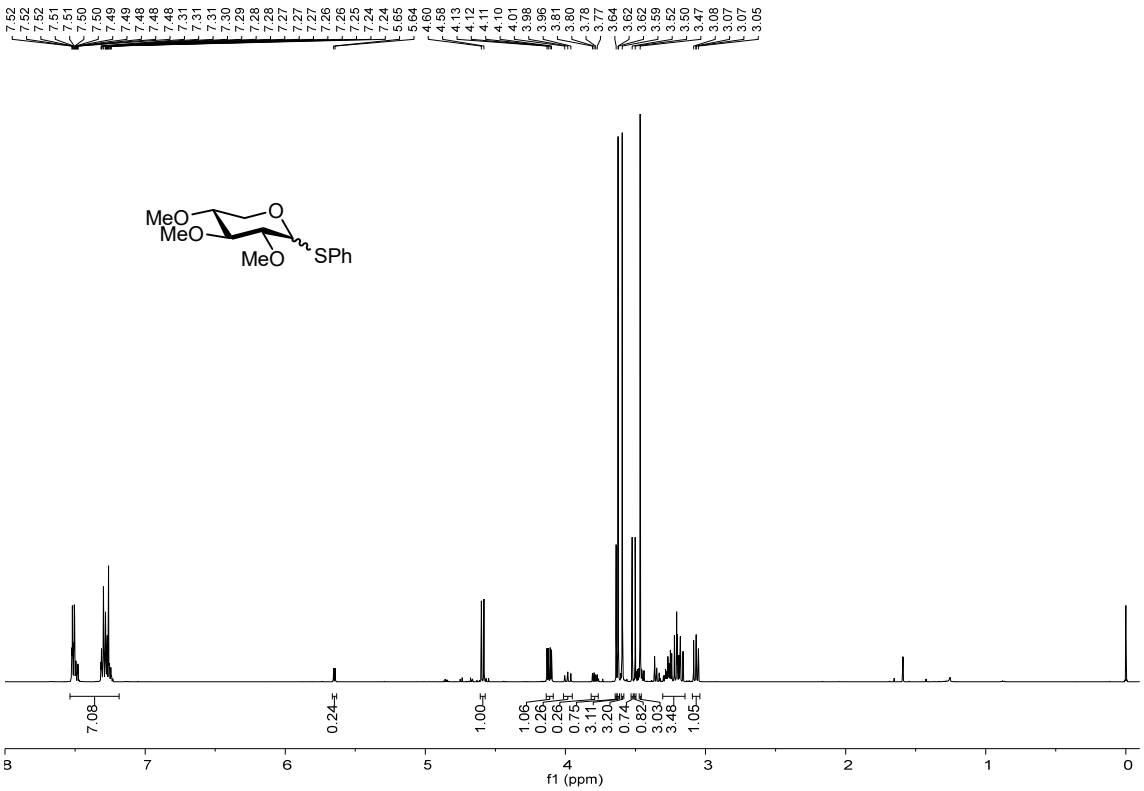
NOESY NMR, $CDCl_3$ of Donor **S31**



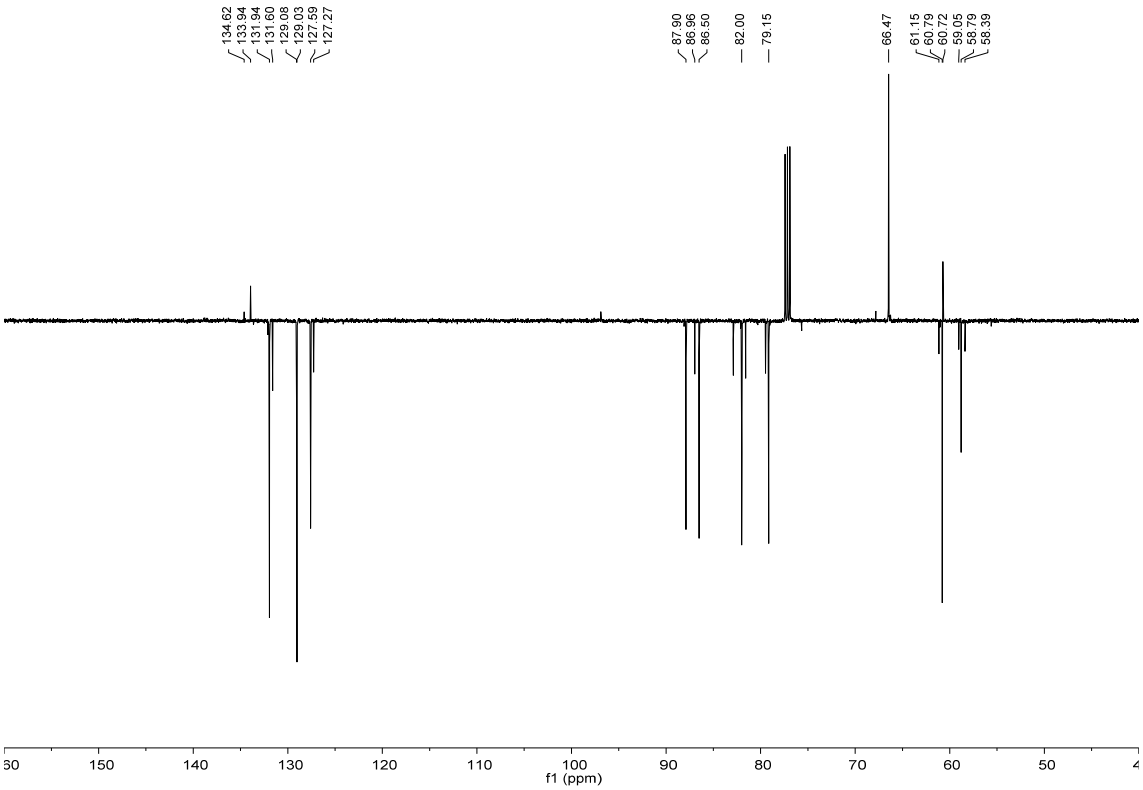
HMBC-GATED NMR, $CDCl_3$ of Donor **S31**



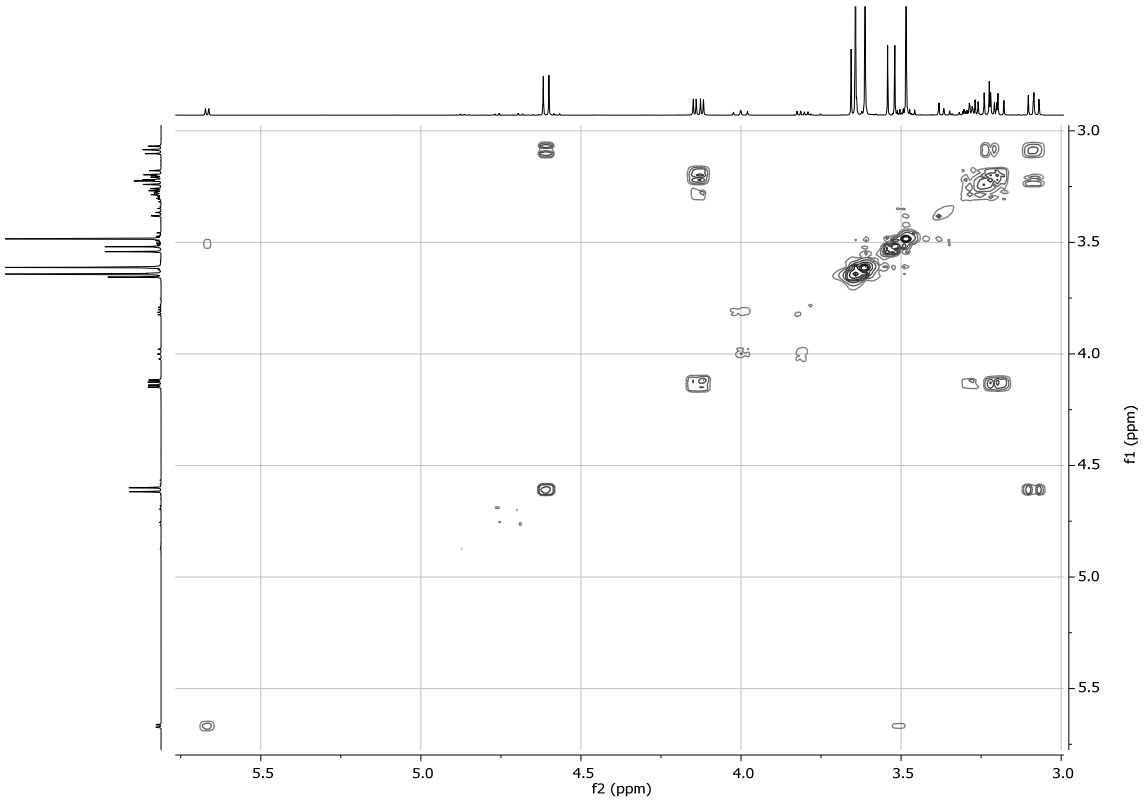
^{1}H NMR, 500 MHz, $CDCl_3$ of Donor **S32**



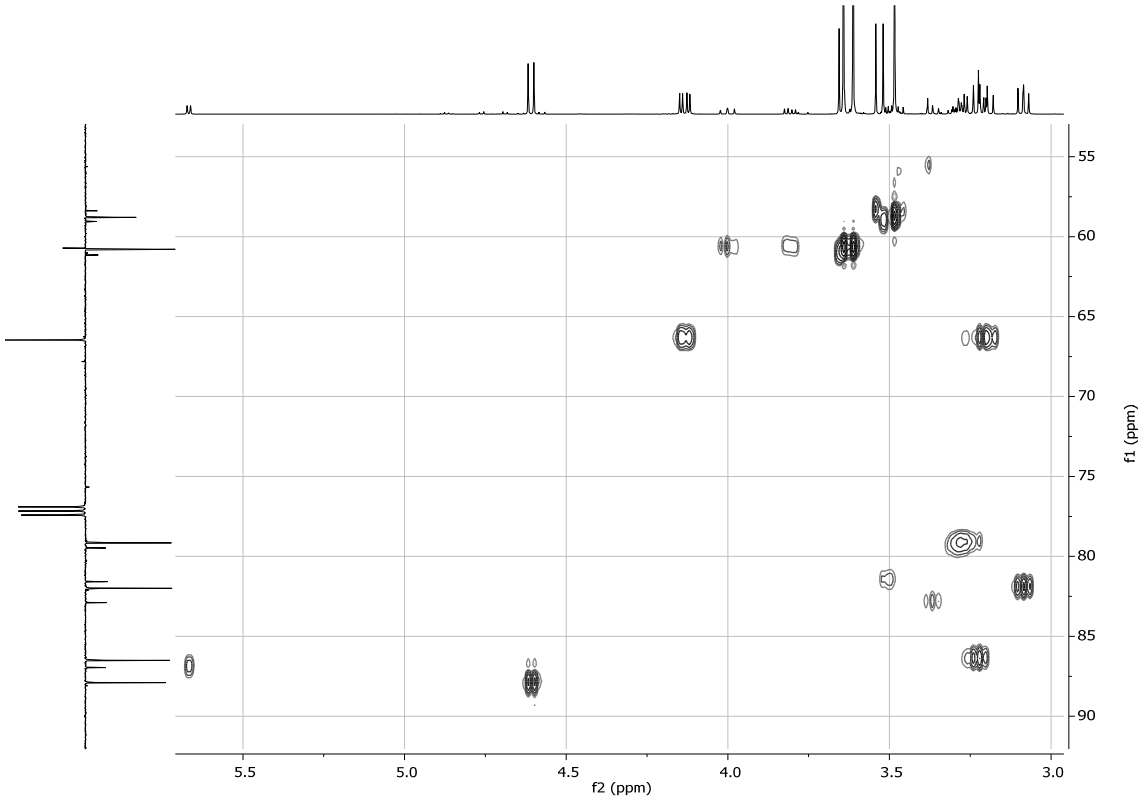
^{13}C NMR, 126 MHz, $CDCl_3$ of Donor **S32**



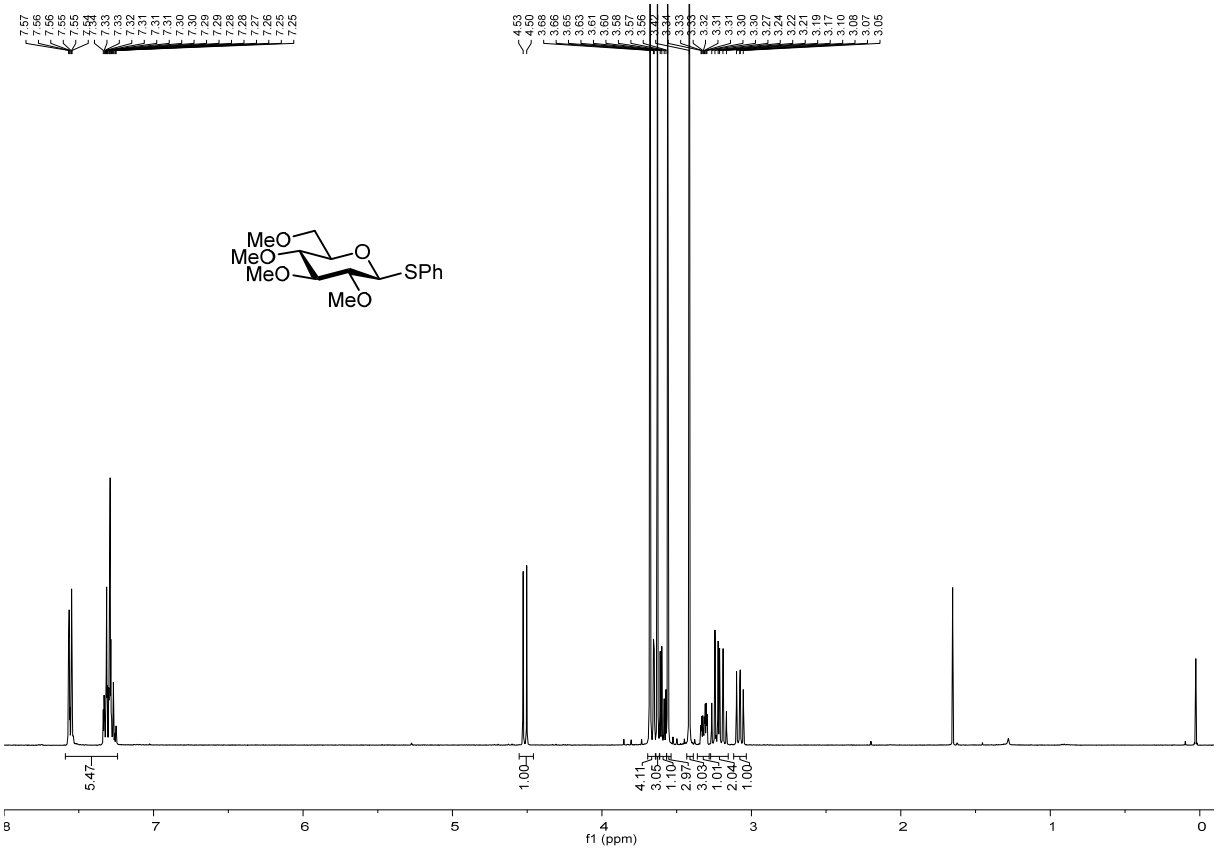
HH-COSY NMR, $CDCl_3$ of Donor **S32**



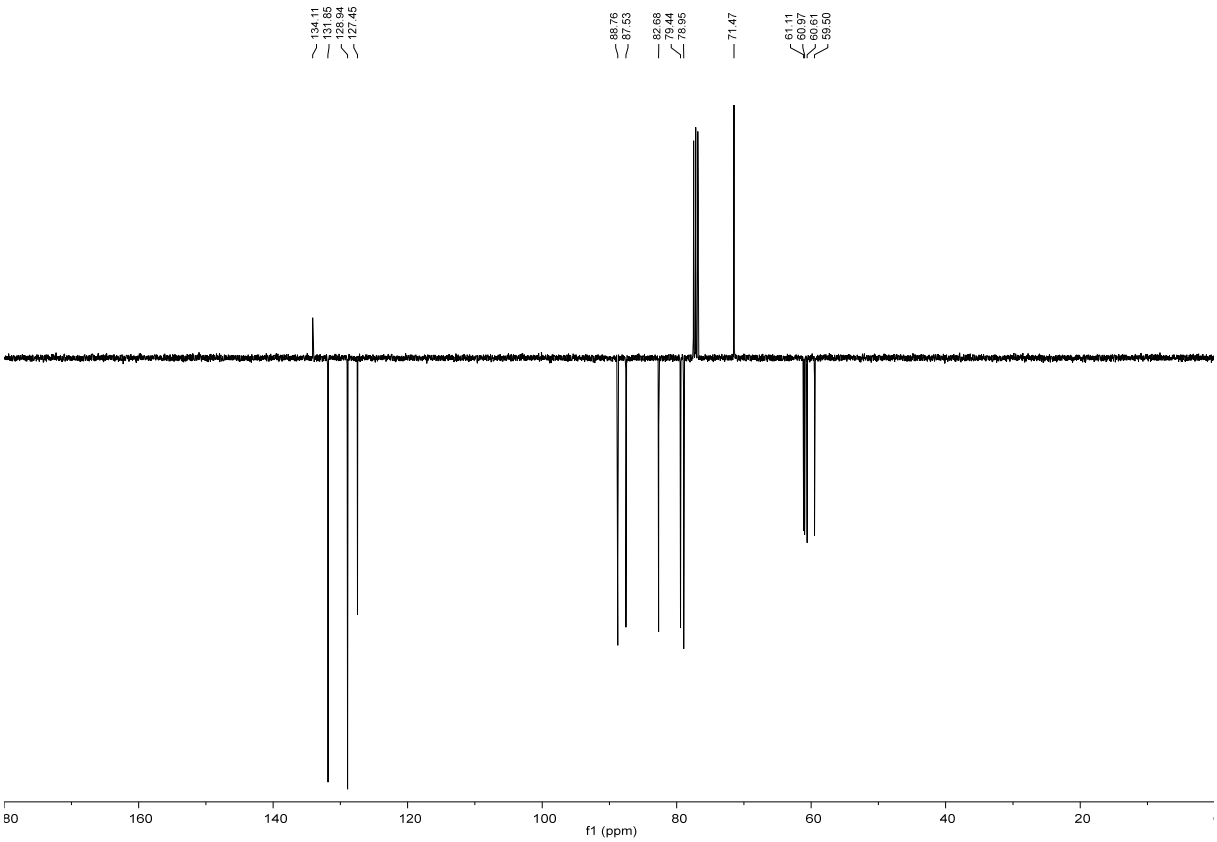
HSQC NMR, $CDCl_3$ of Donor **S32**



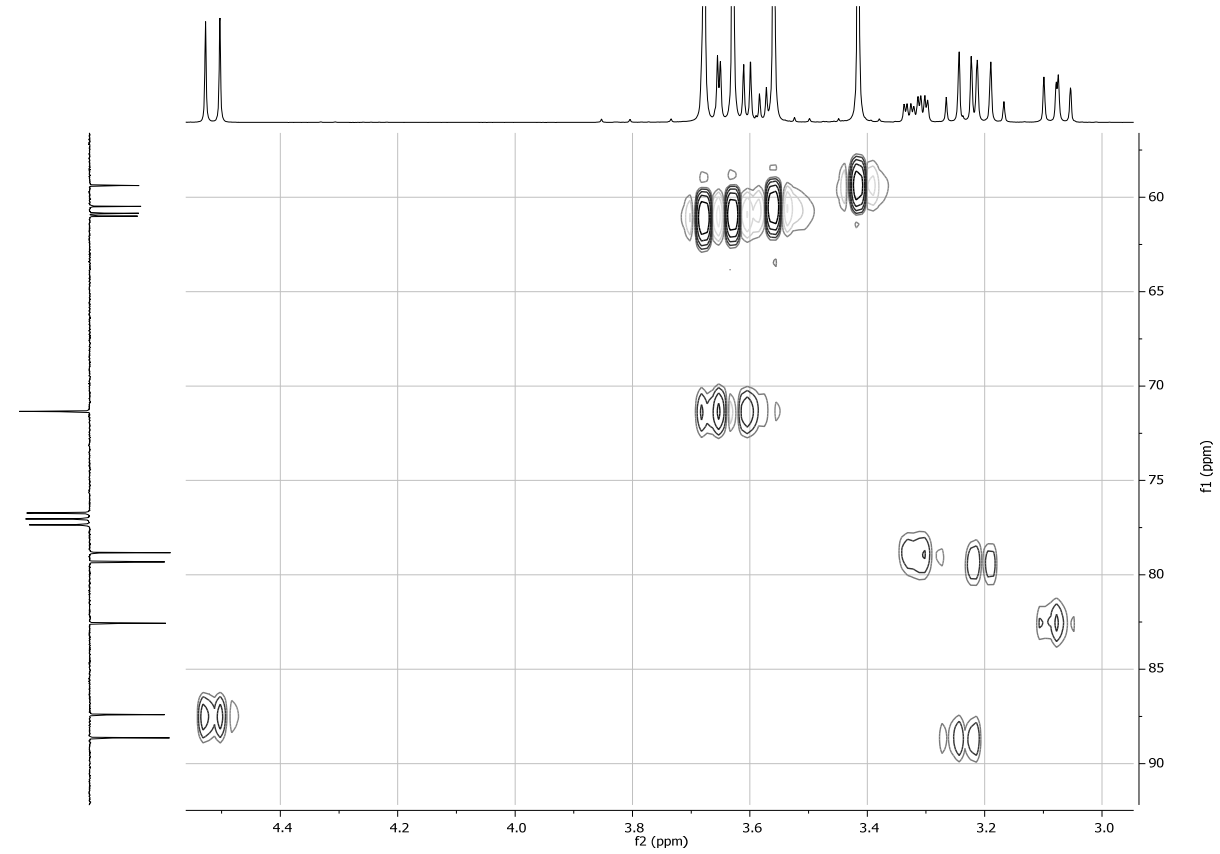
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S33**



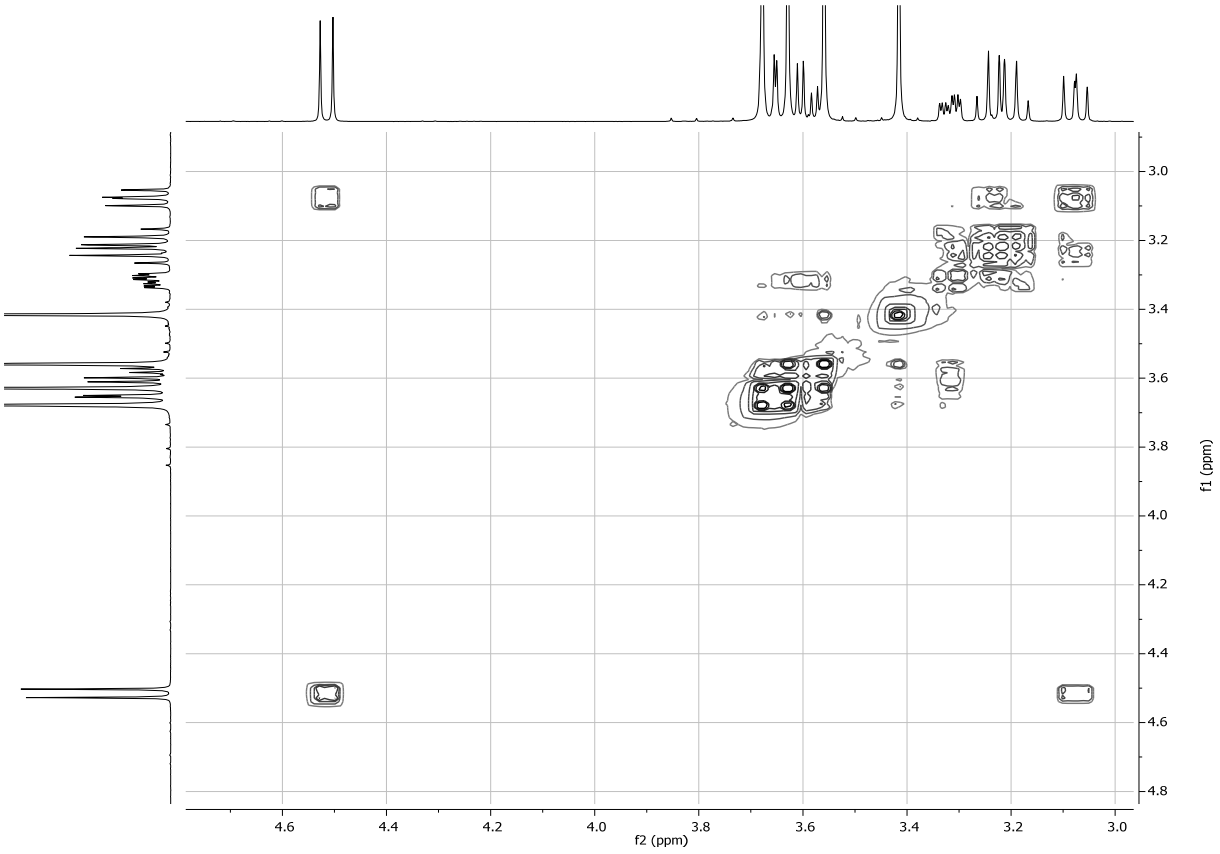
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S33**



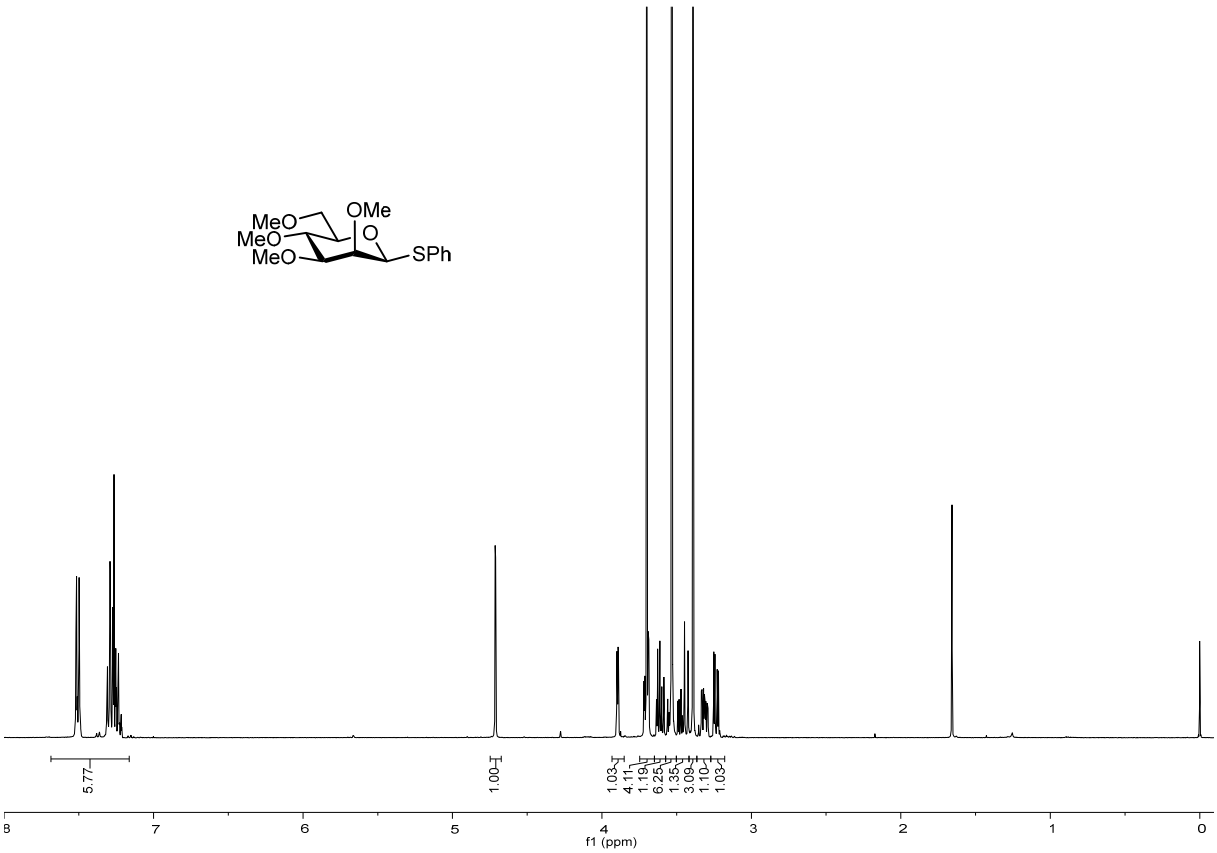
HH-COSY NMR, $CDCl_3$ of Donor **S33**



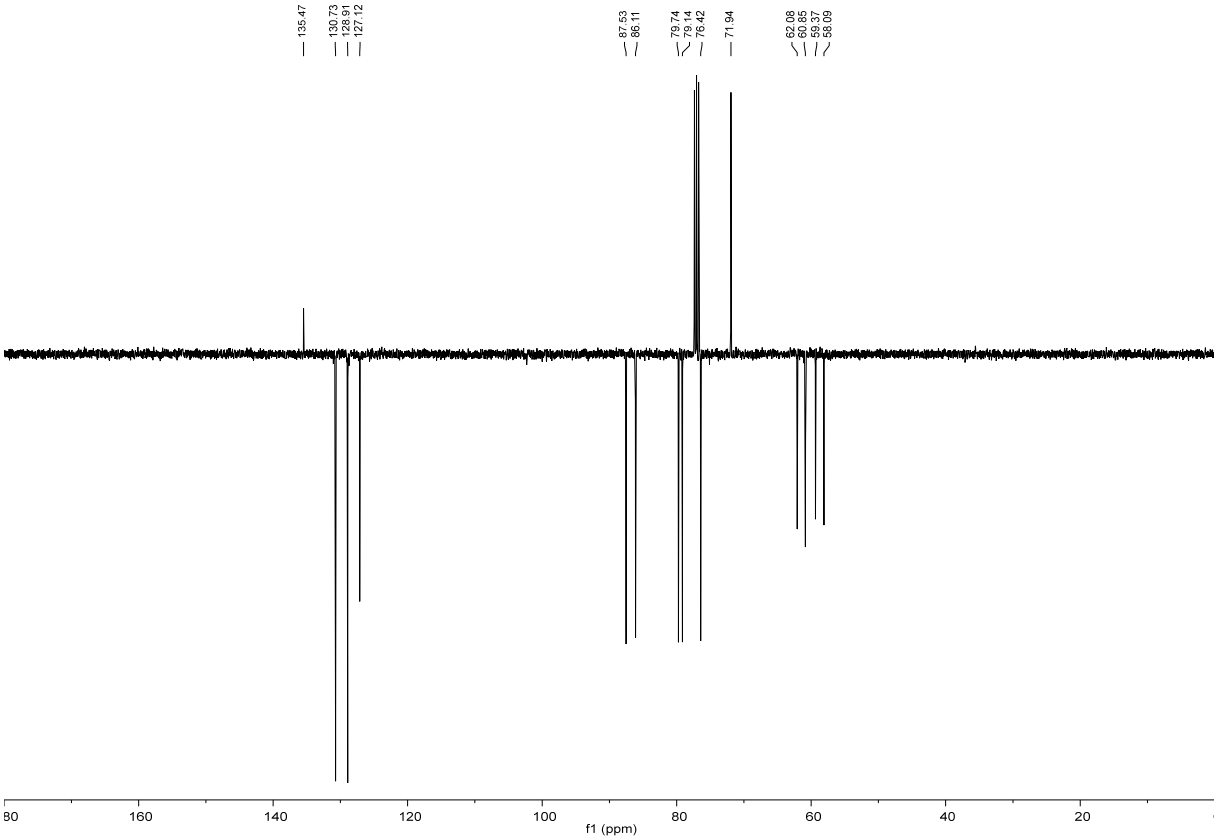
HSQC NMR, $CDCl_3$ of Donor **S33**



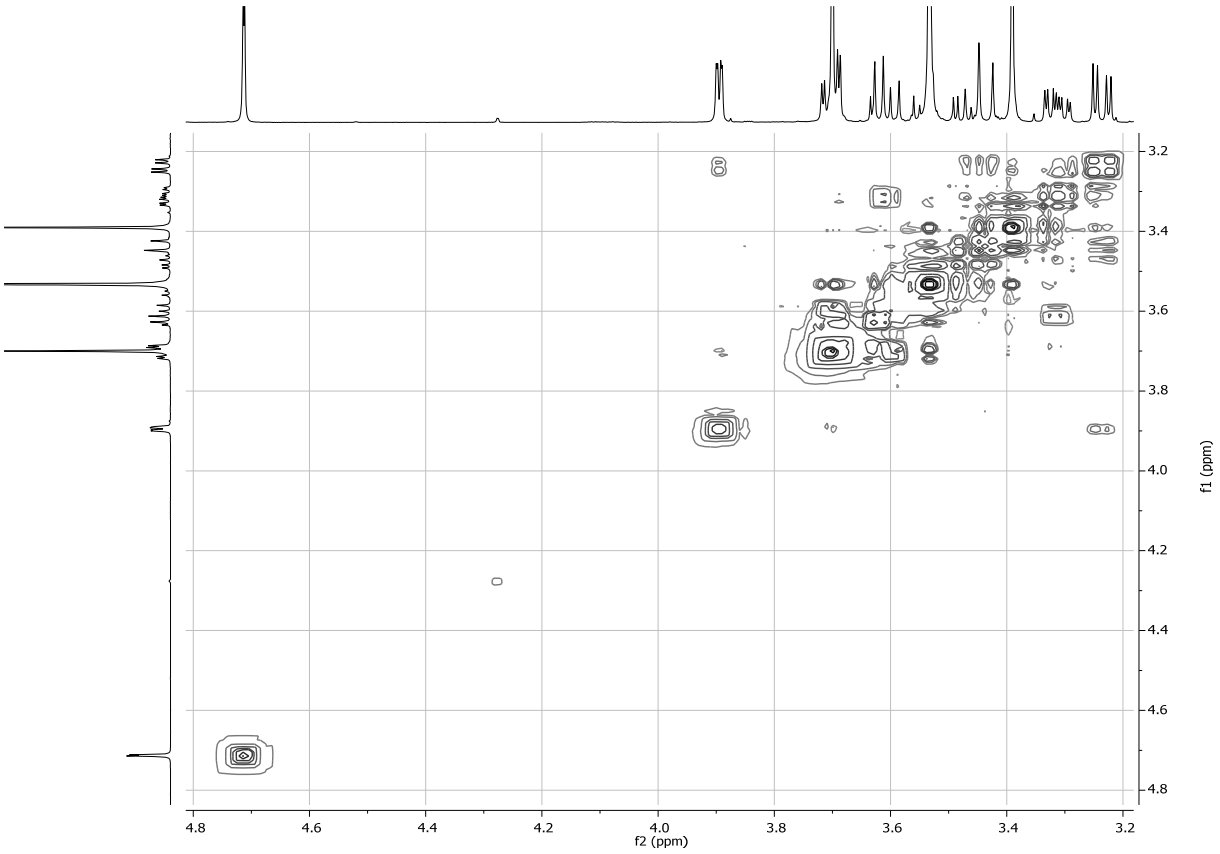
^{1}H NMR, 400 MHz, $CDCl_3$ of Donor **S34**



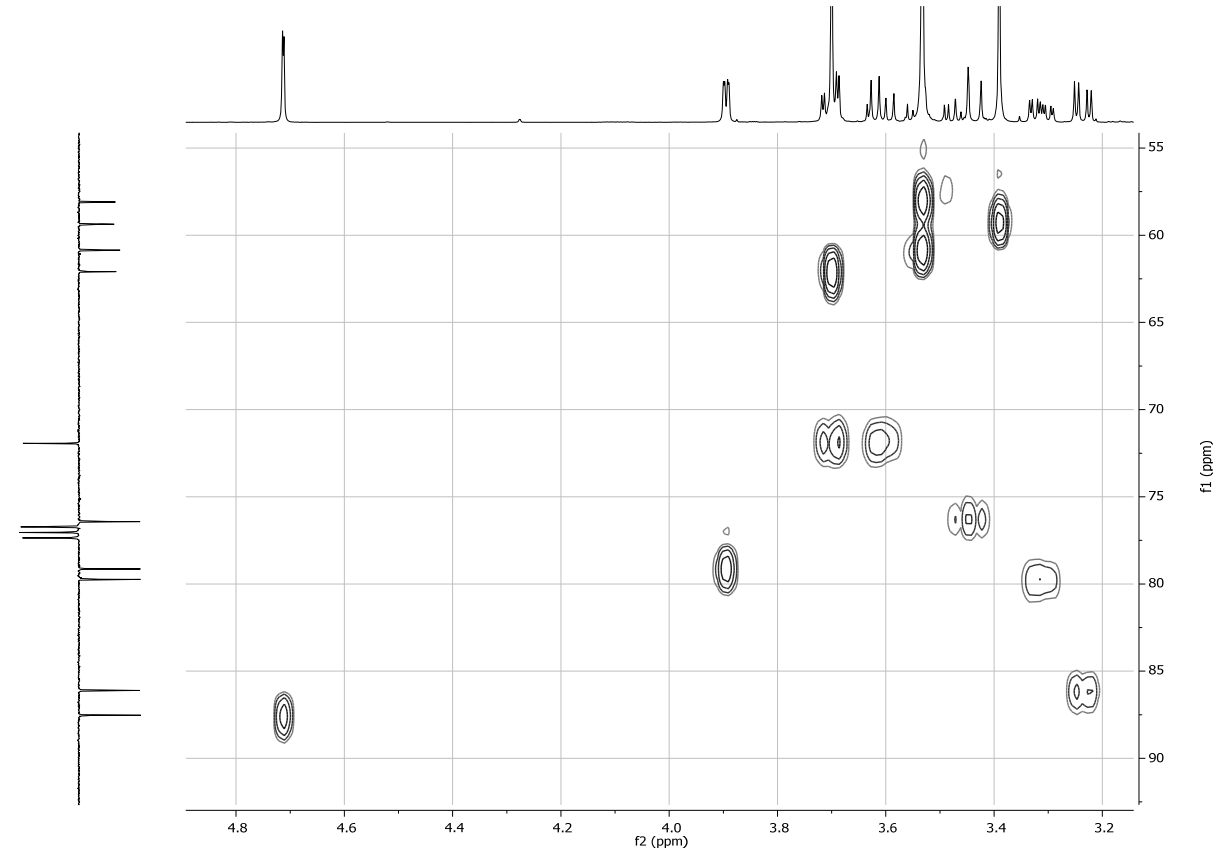
^{13}C NMR, 101 MHz, $CDCl_3$ of Donor **S34**



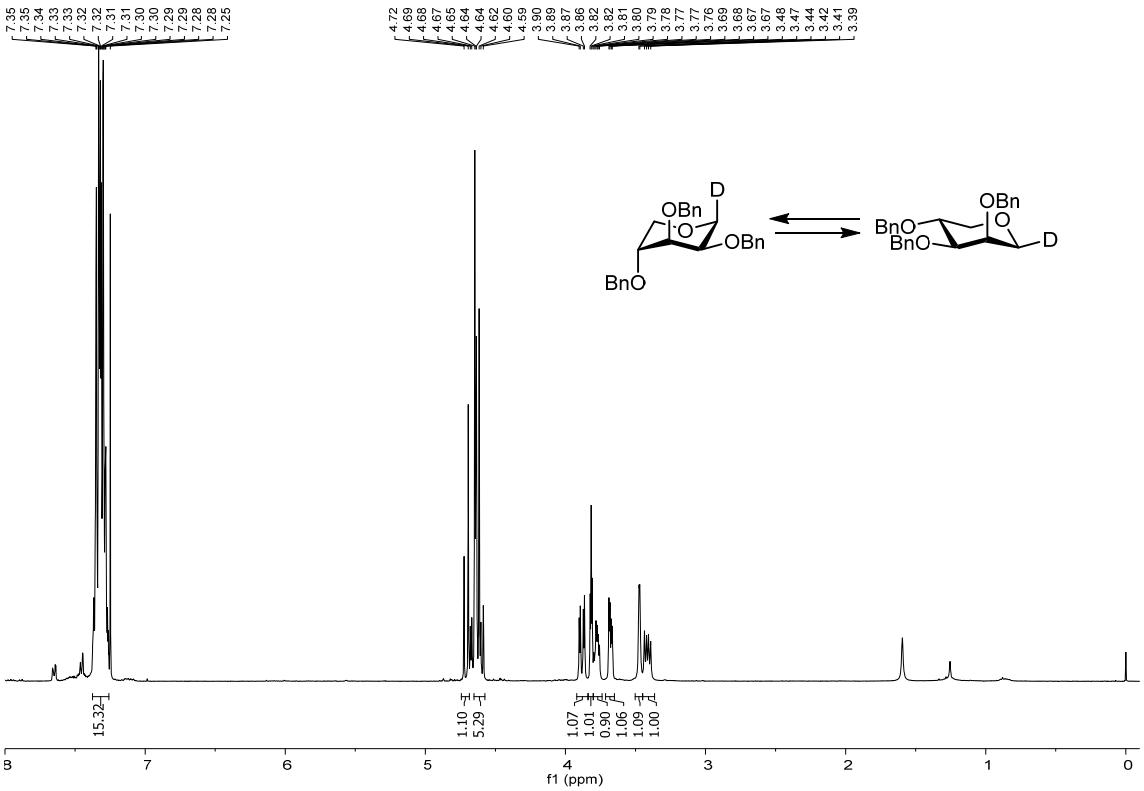
HH-COSY NMR, $CDCl_3$ of Donor **S34**



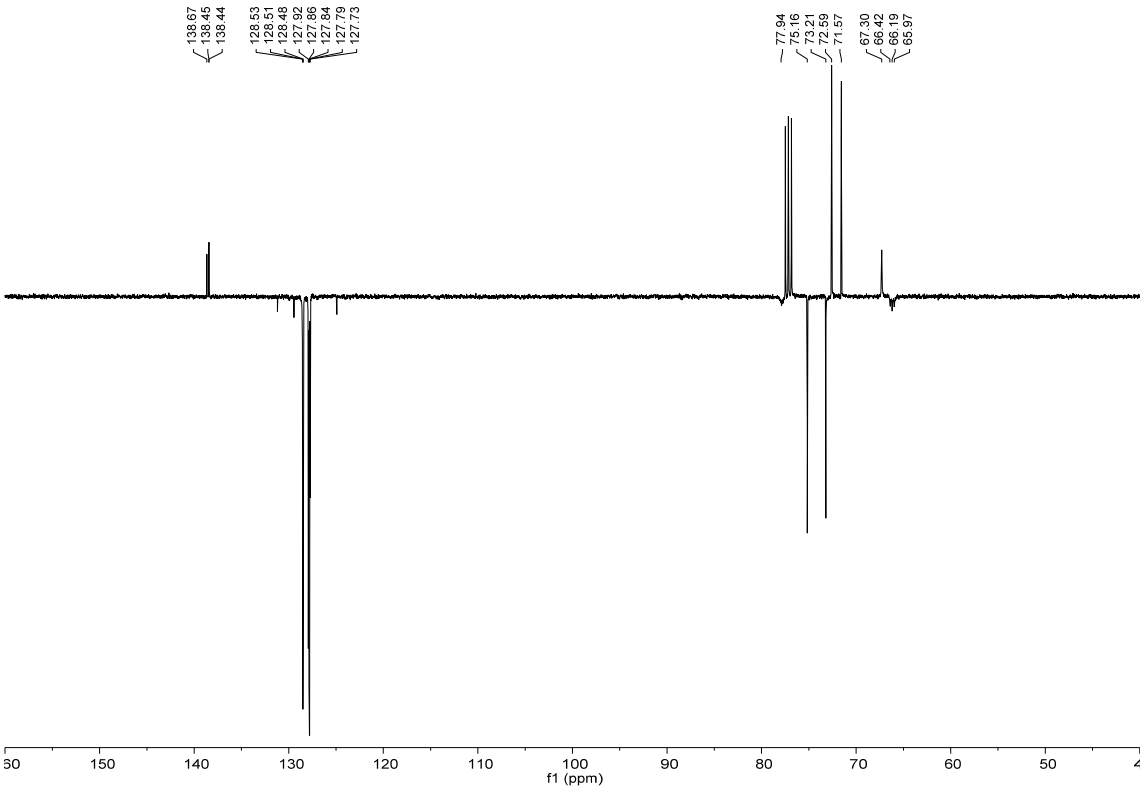
HSQC NMR, $CDCl_3$ of Donor **S34**



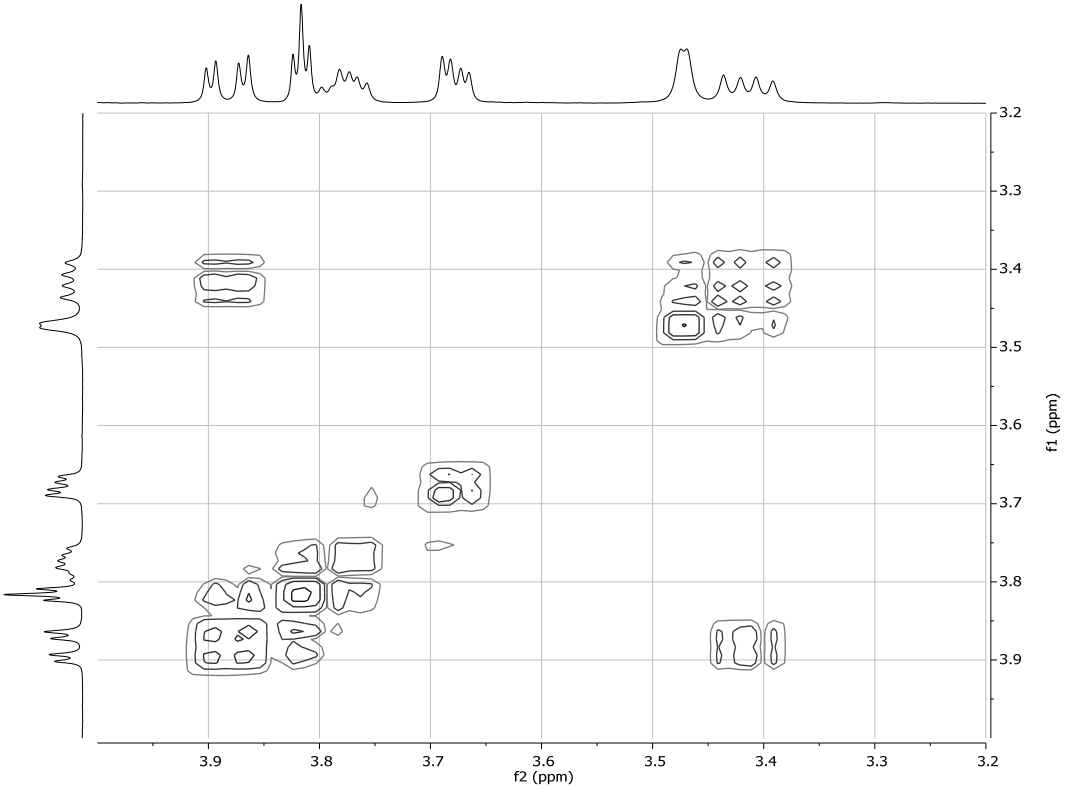
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S35**



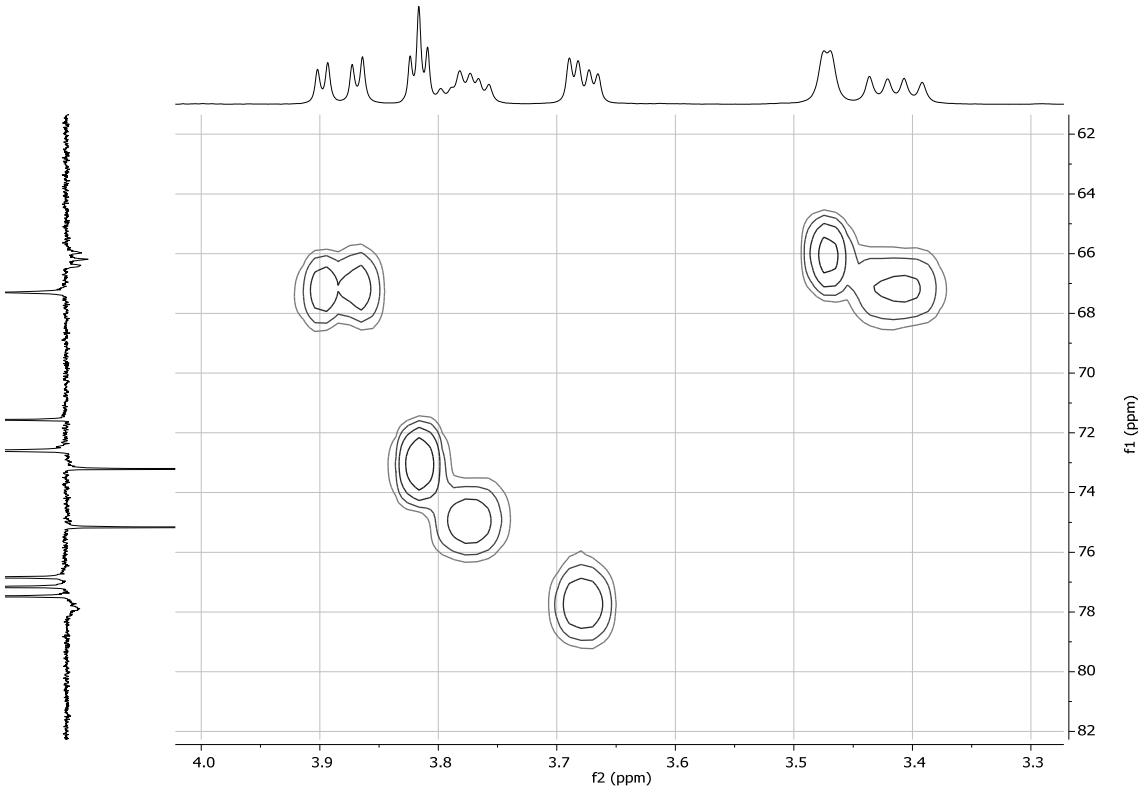
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S35**



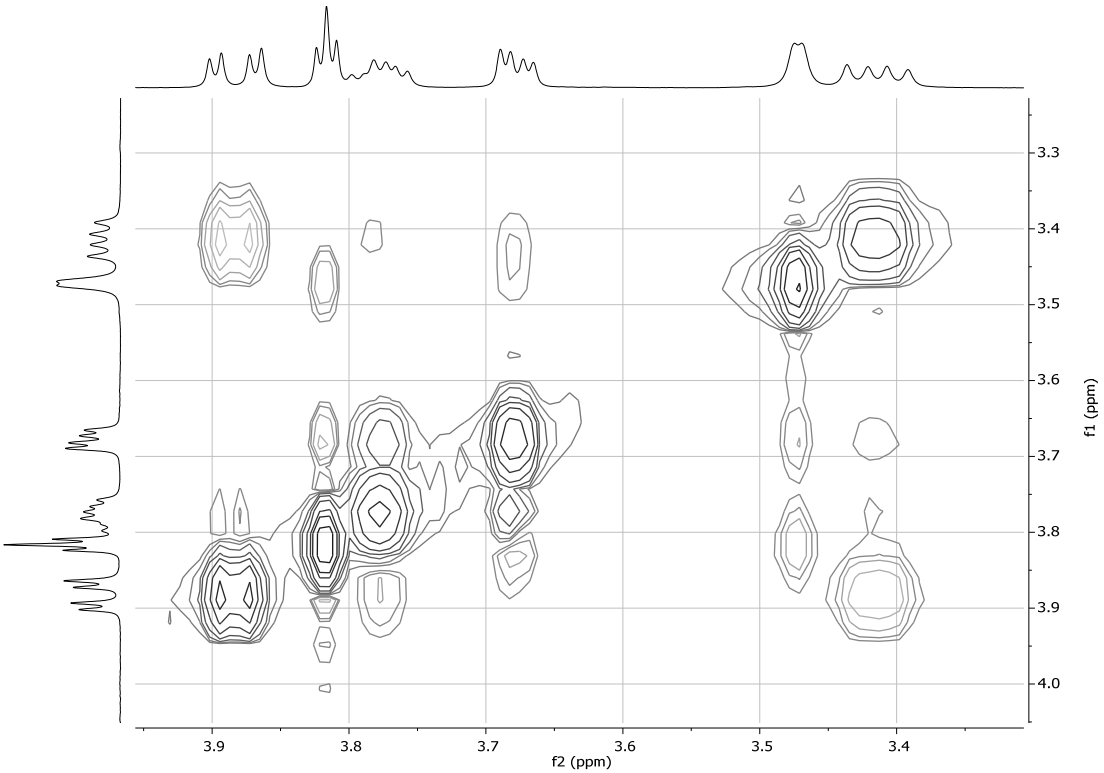
HH-COSY NMR, $CDCl_3$ of compound **S35**



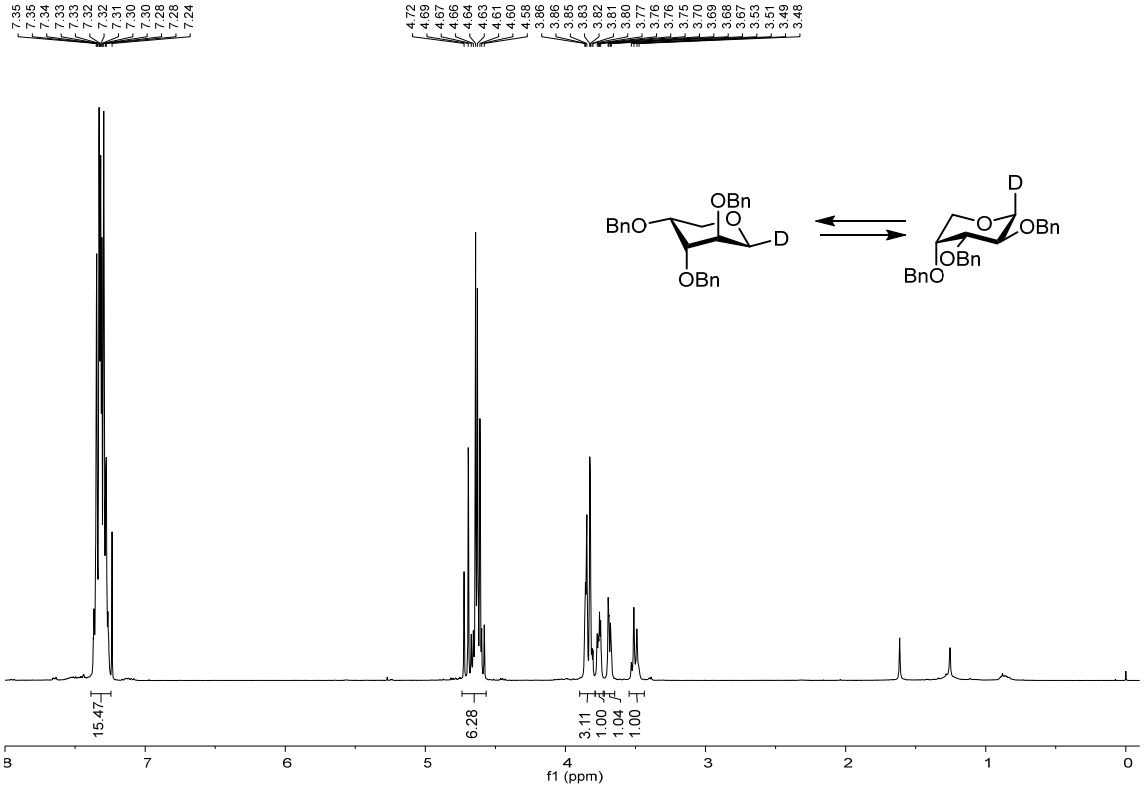
HSQC NMR, $CDCl_3$ of compound **S35**



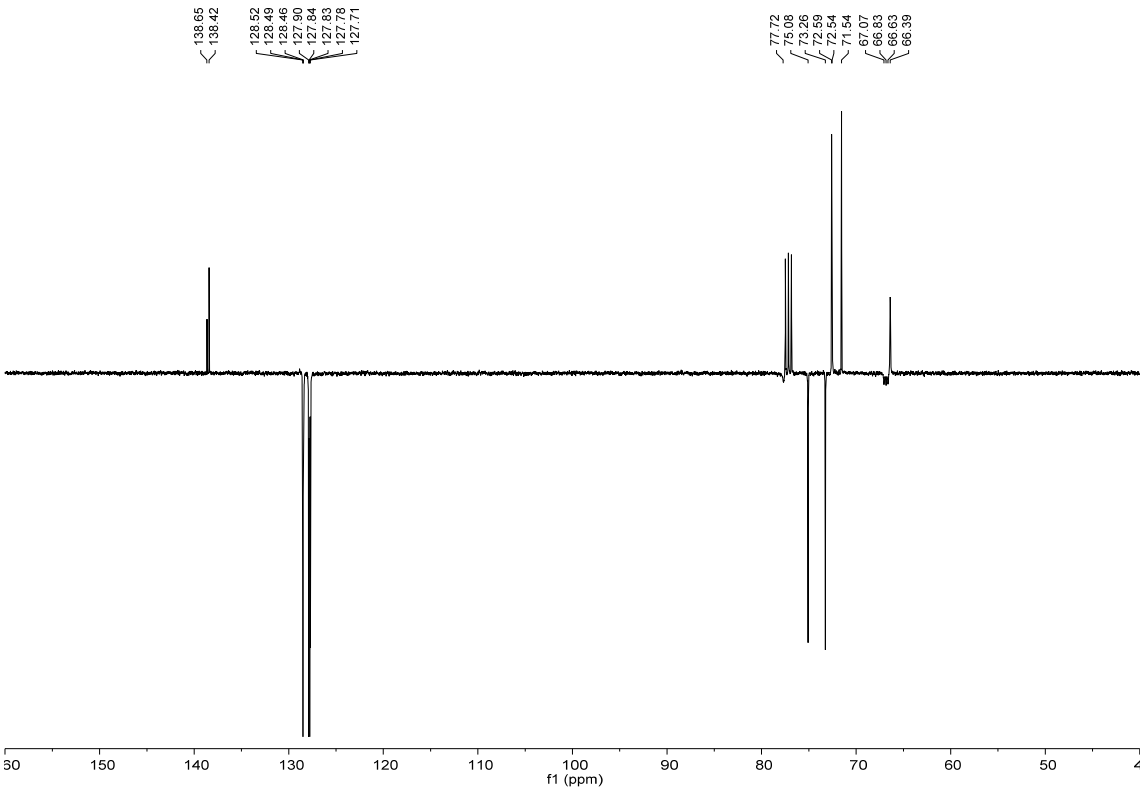
NOESY NMR, $CDCl_3$ of compound **S35**



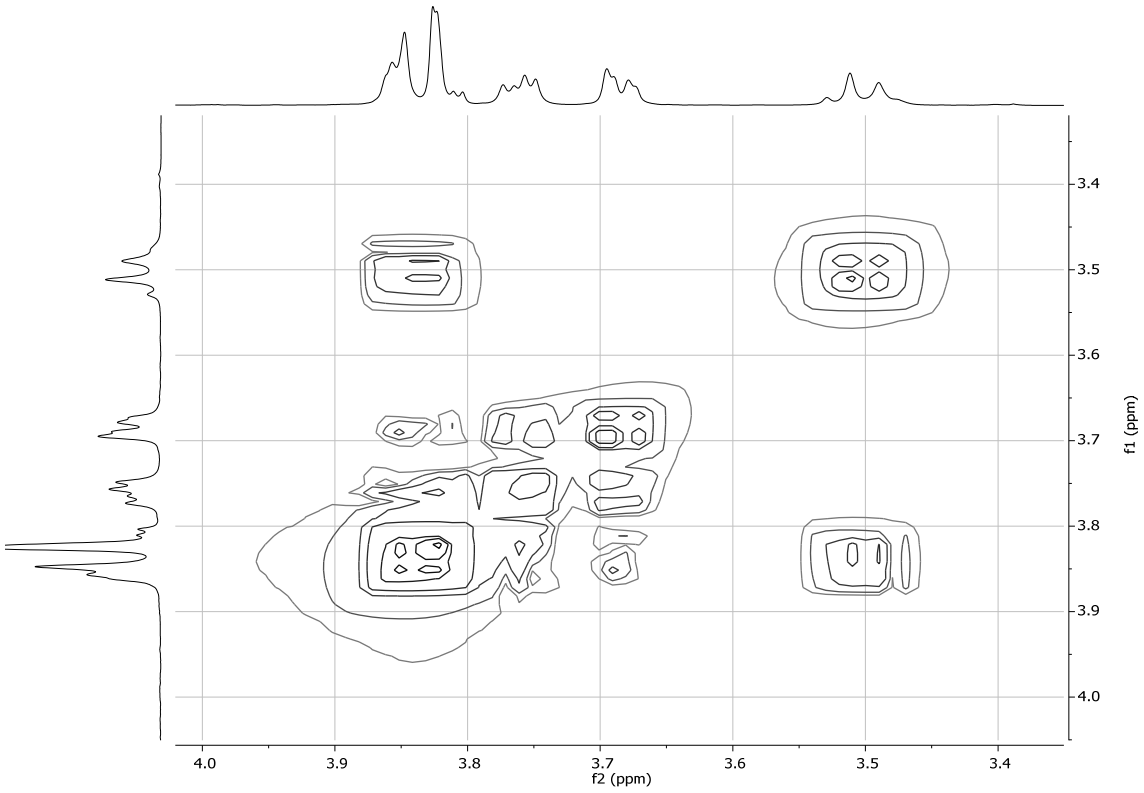
^1H NMR, 400 MHz, $CDCl_3$ of compound **S36**



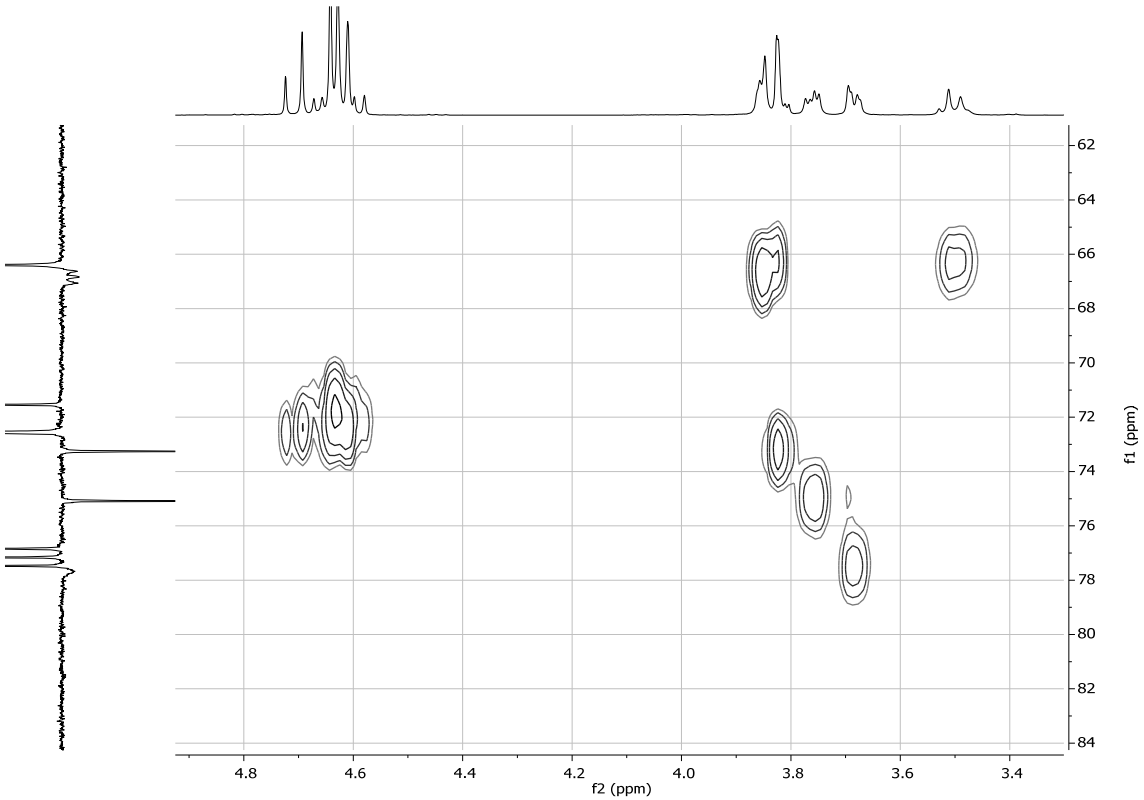
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S36**



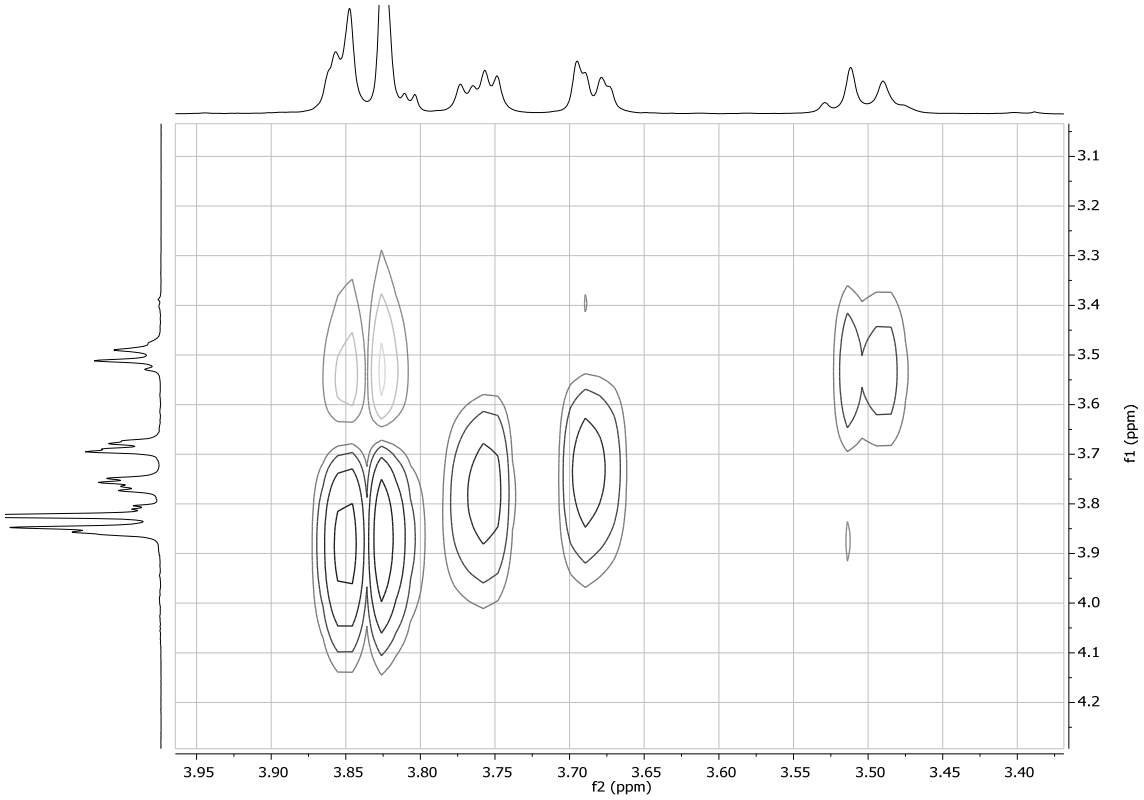
HH-COSY NMR, $CDCl_3$ of compound **S36**



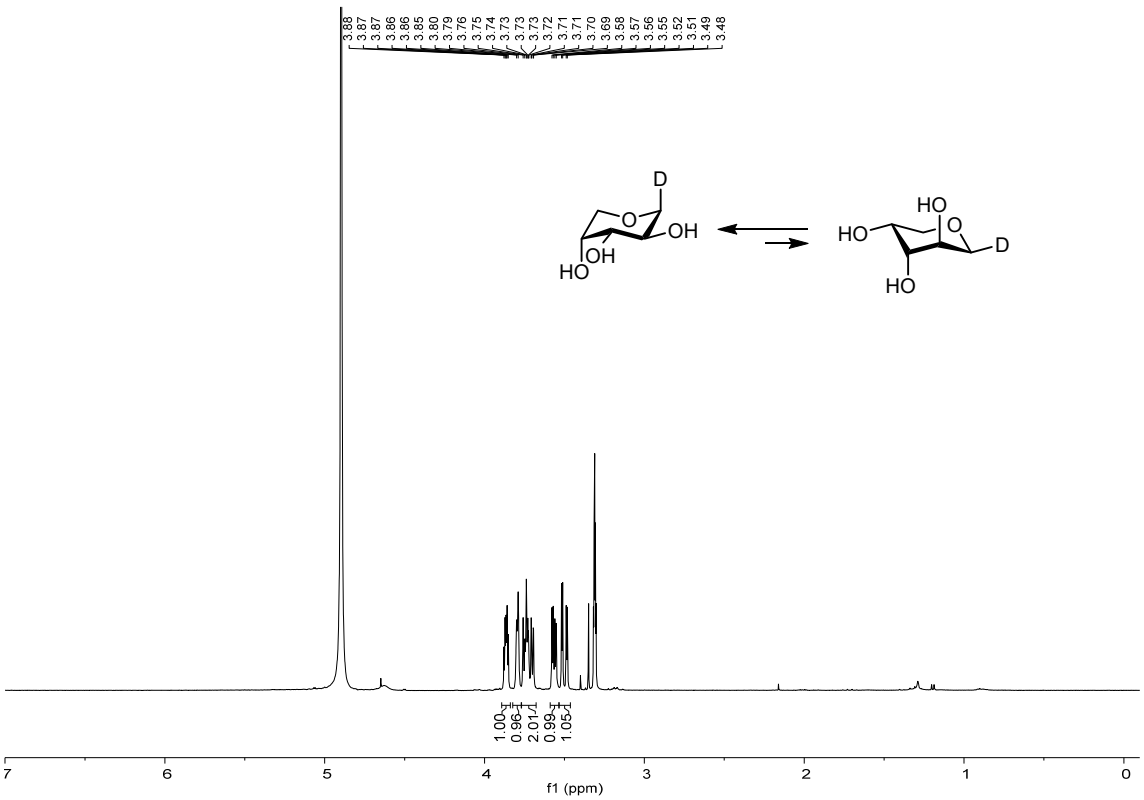
HSQC NMR, $CDCl_3$ of compound **S36**



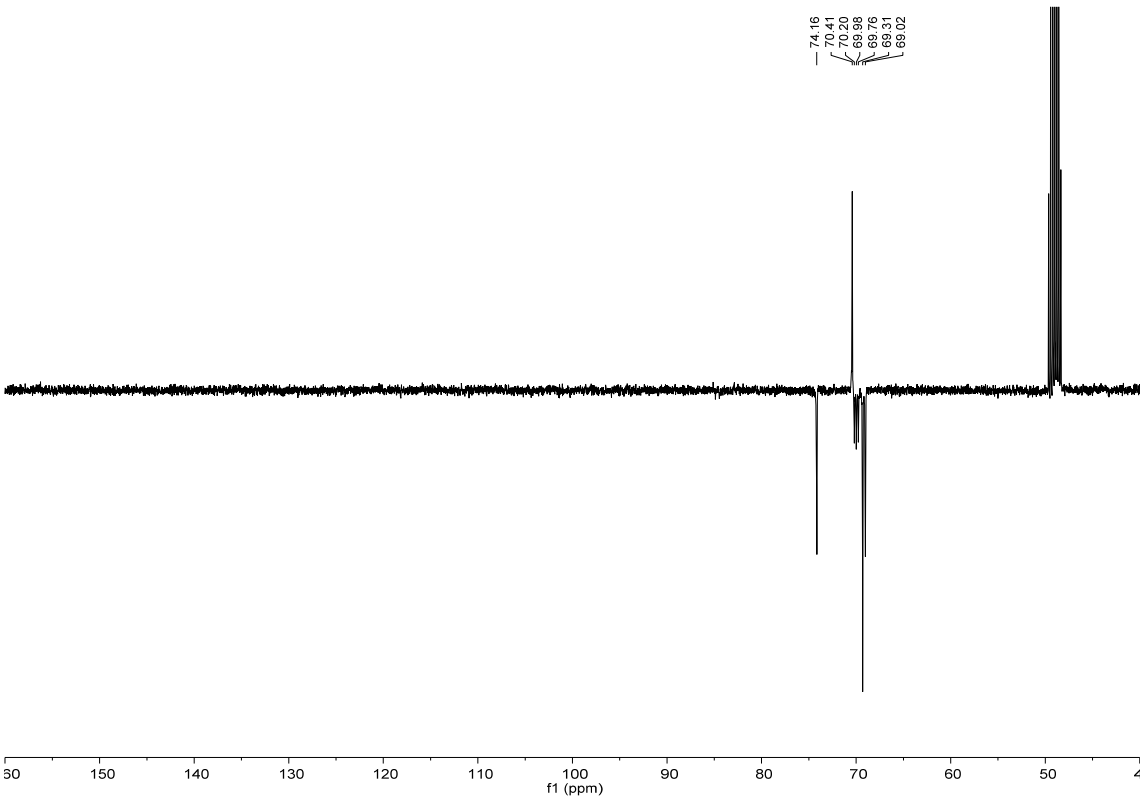
NOESY NMR, $CDCl_3$ of compound **S36**



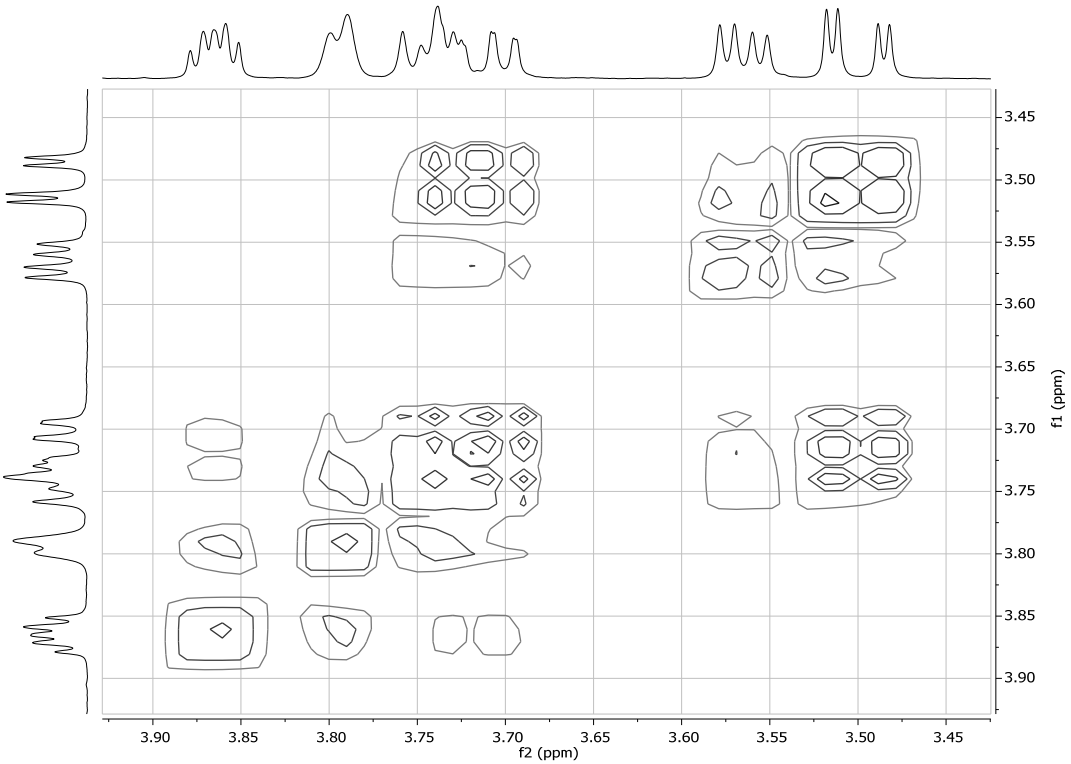
^{1}H NMR, 400 MHz, MeOD of compound **S37**



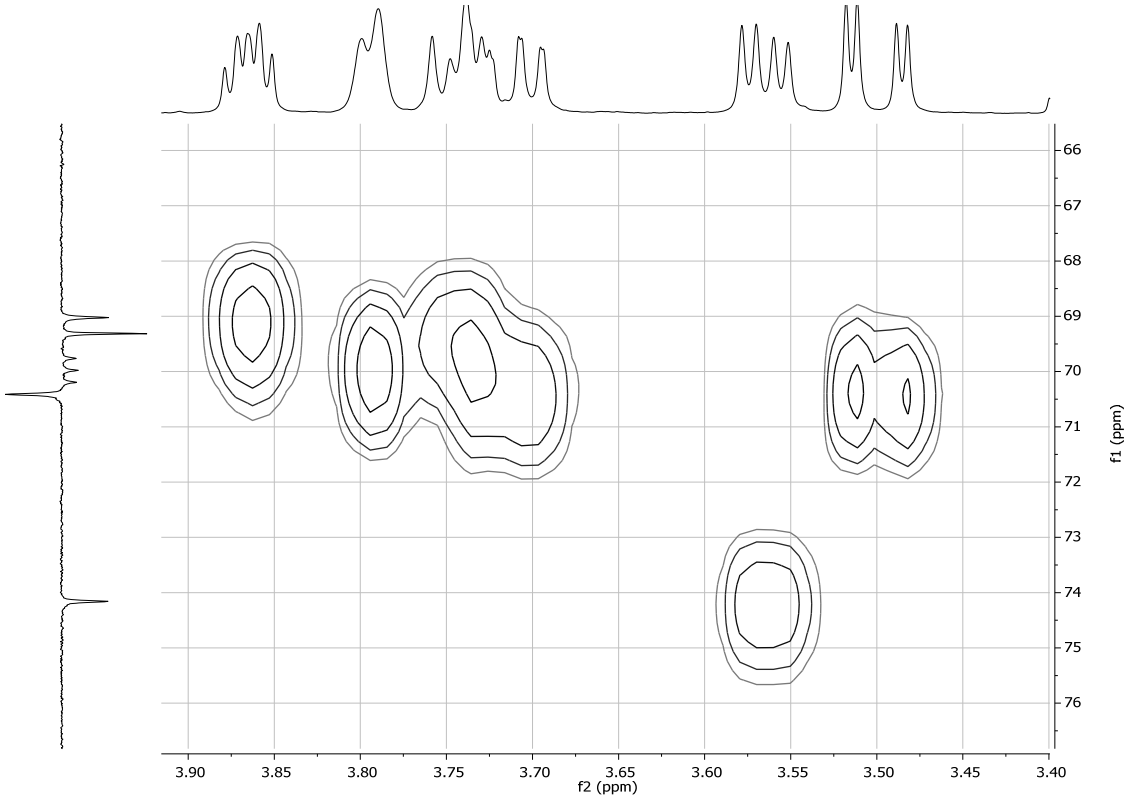
^{13}C NMR, 101 MHz, MeOD of compound **S37**



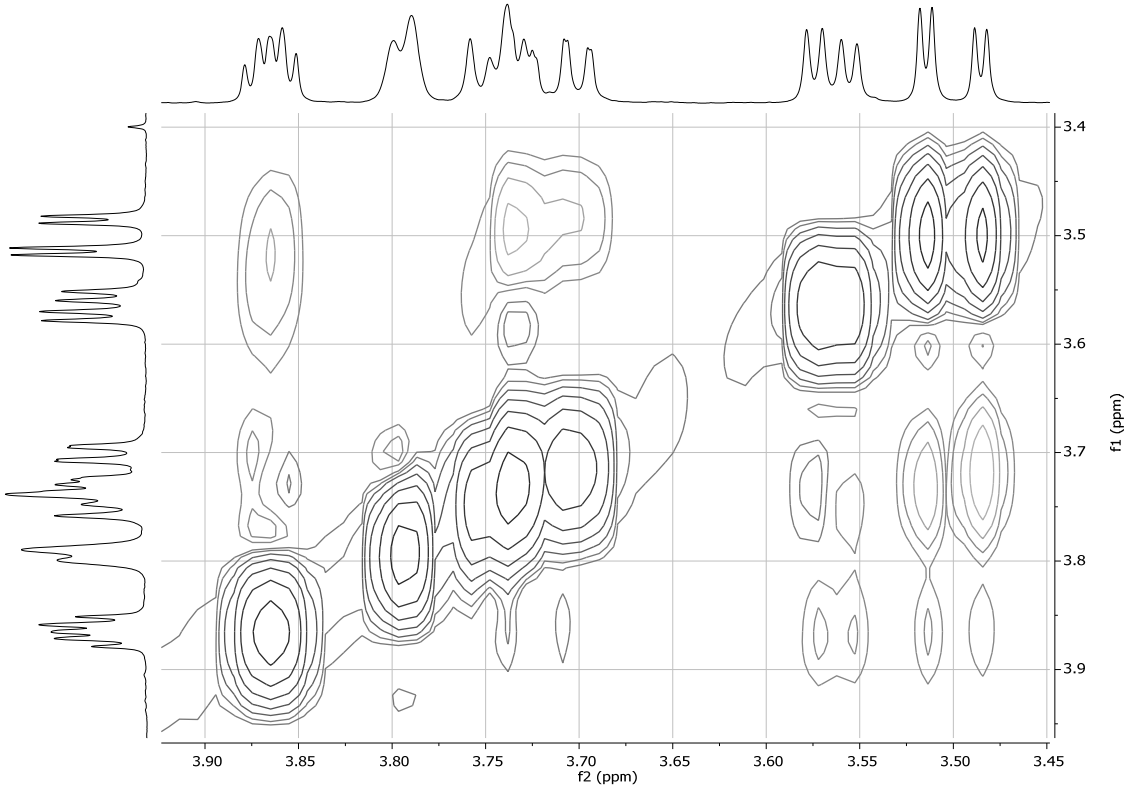
HH-COSY NMR, MeOD of compound **S37**



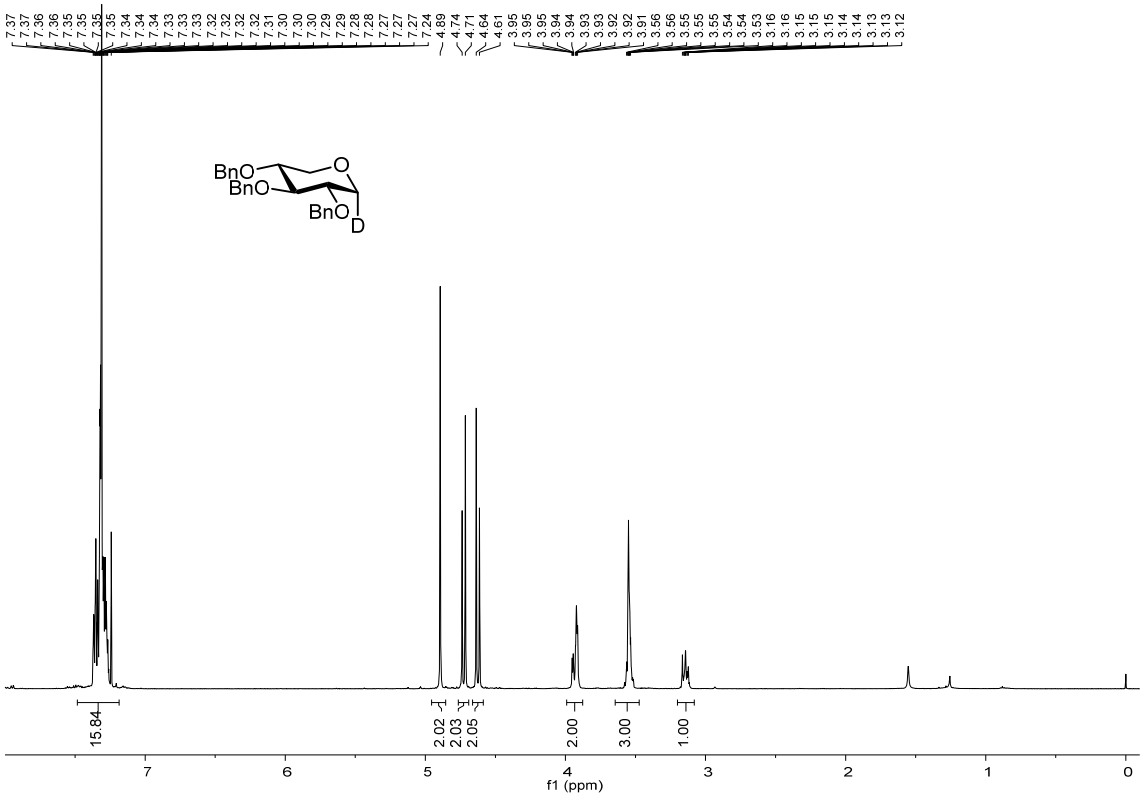
HSQC NMR, MeOD of compound **S37**



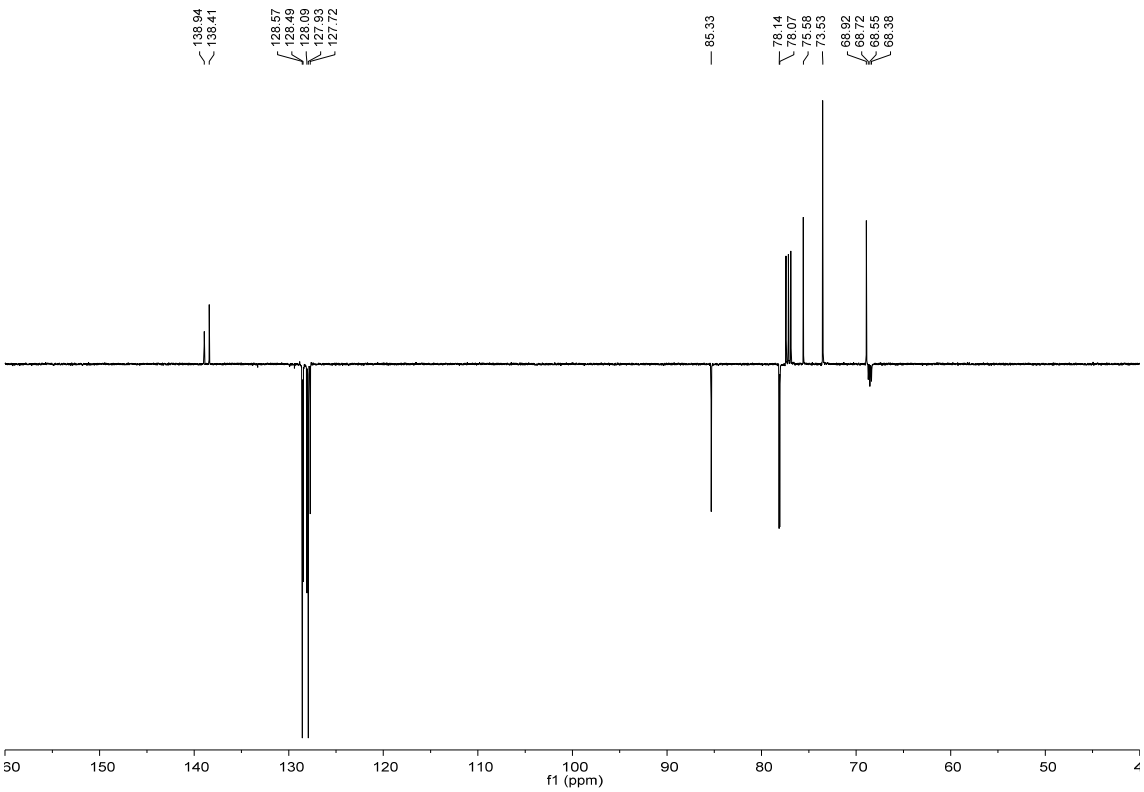
NOESY NMR, MeOD of compound **S37**



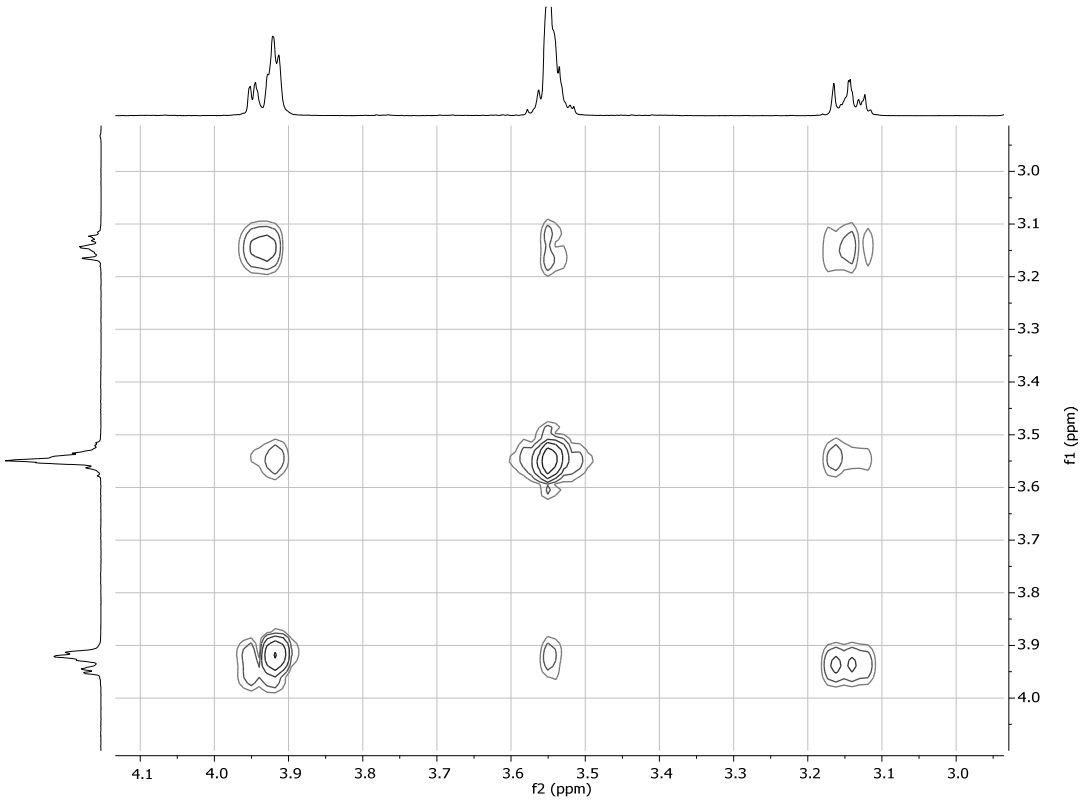
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S38**



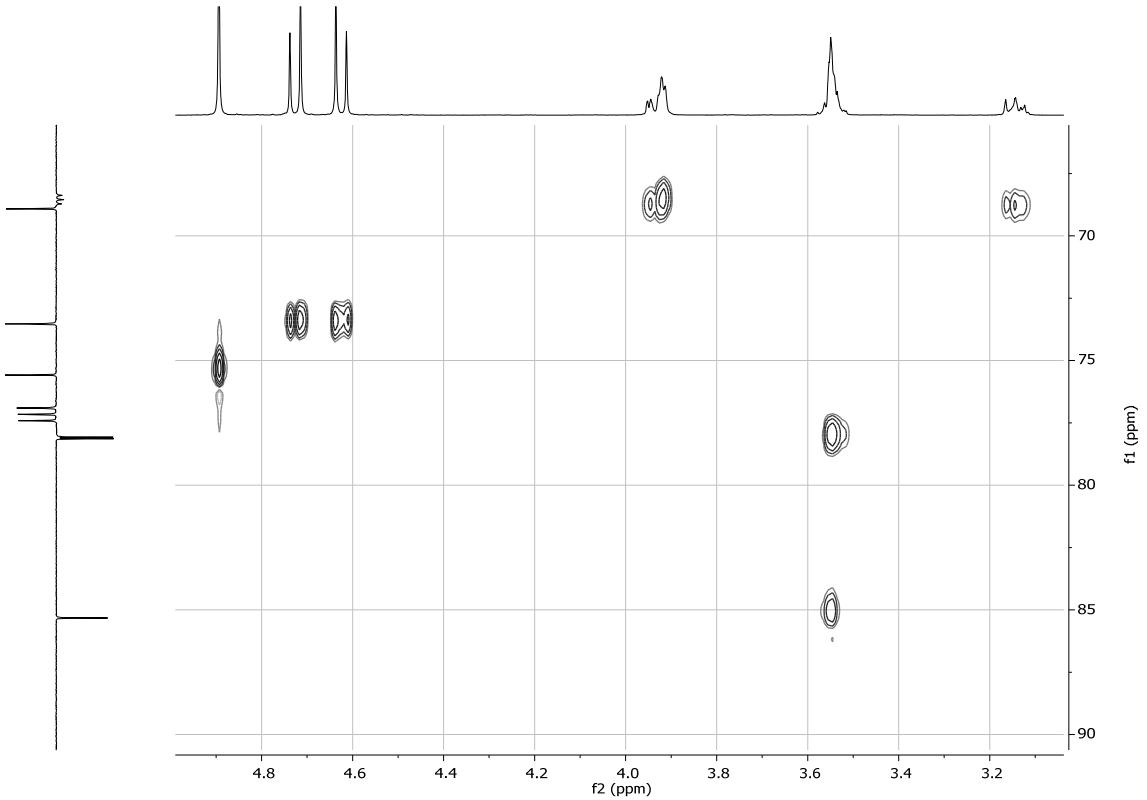
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S38**



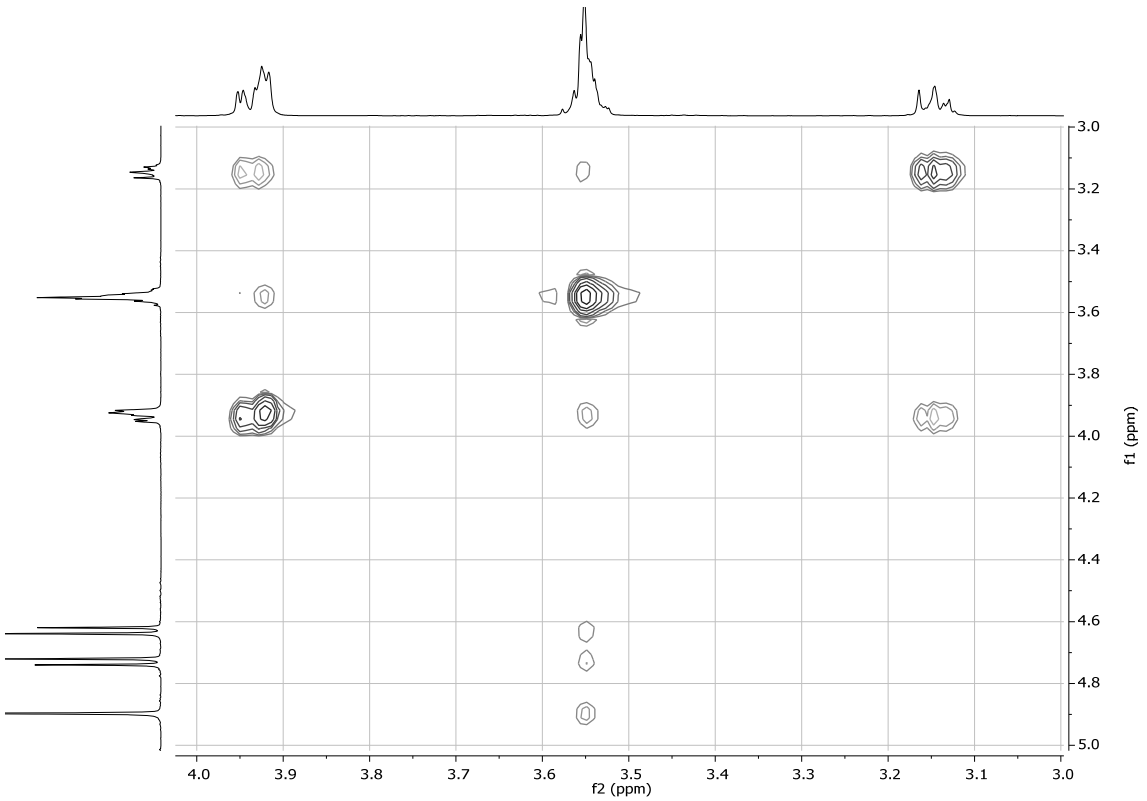
HH-COSY NMR, $CDCl_3$ of compound **S38**



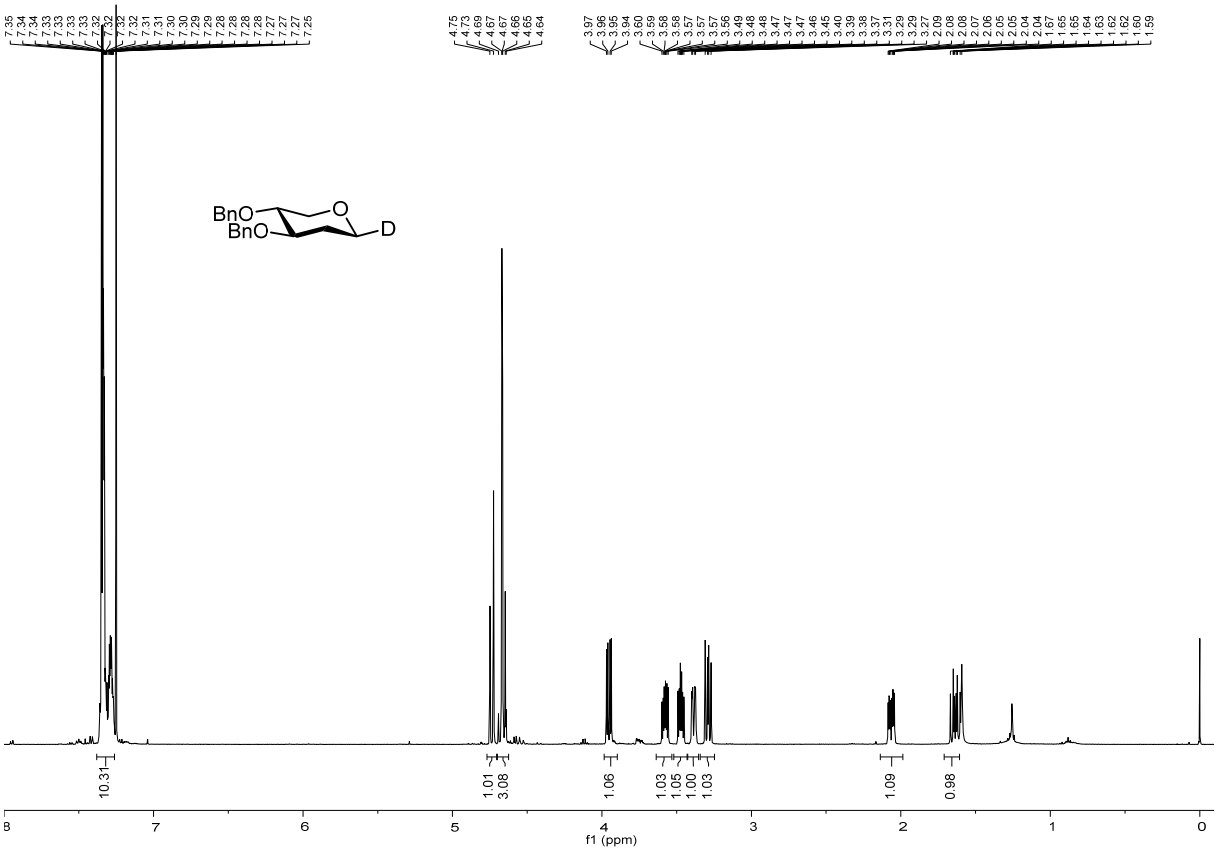
HSQC NMR, $CDCl_3$ of compound **S38**



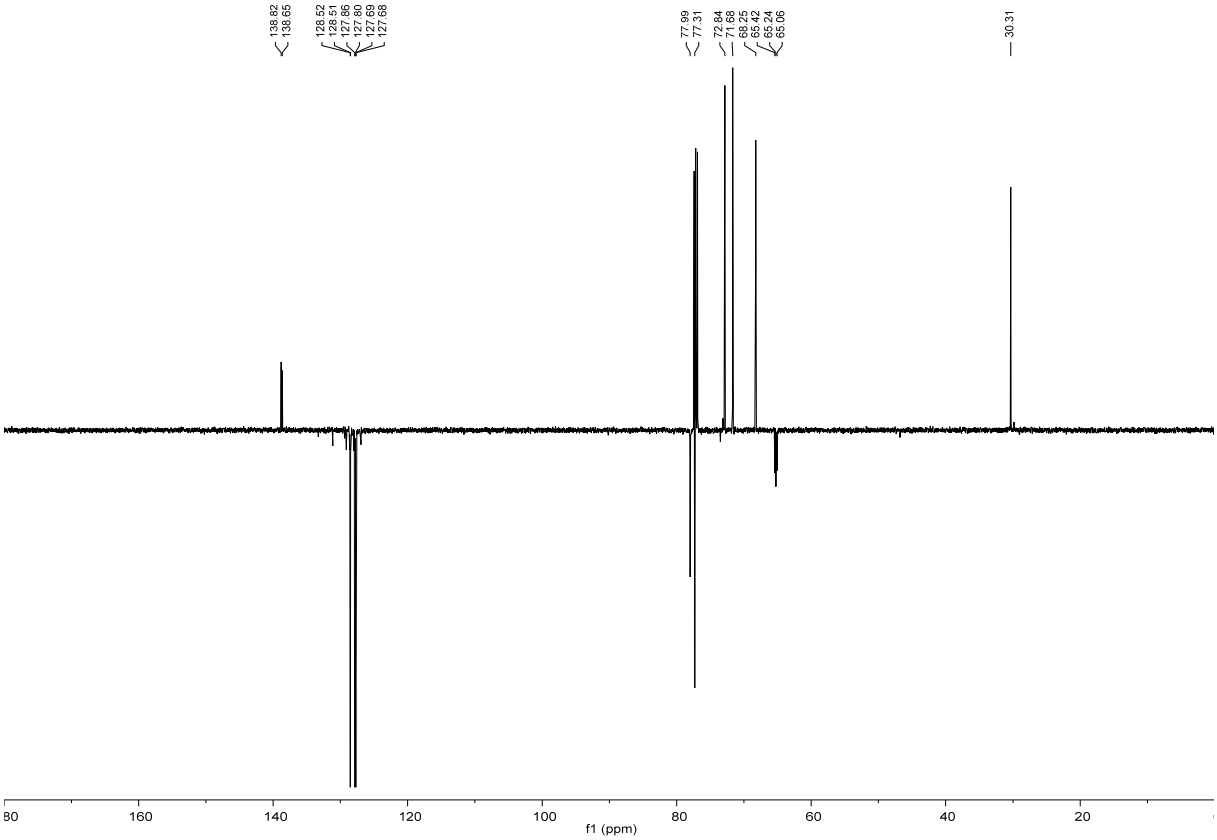
NOESY NMR, $CDCl_3$ of compound **S38**



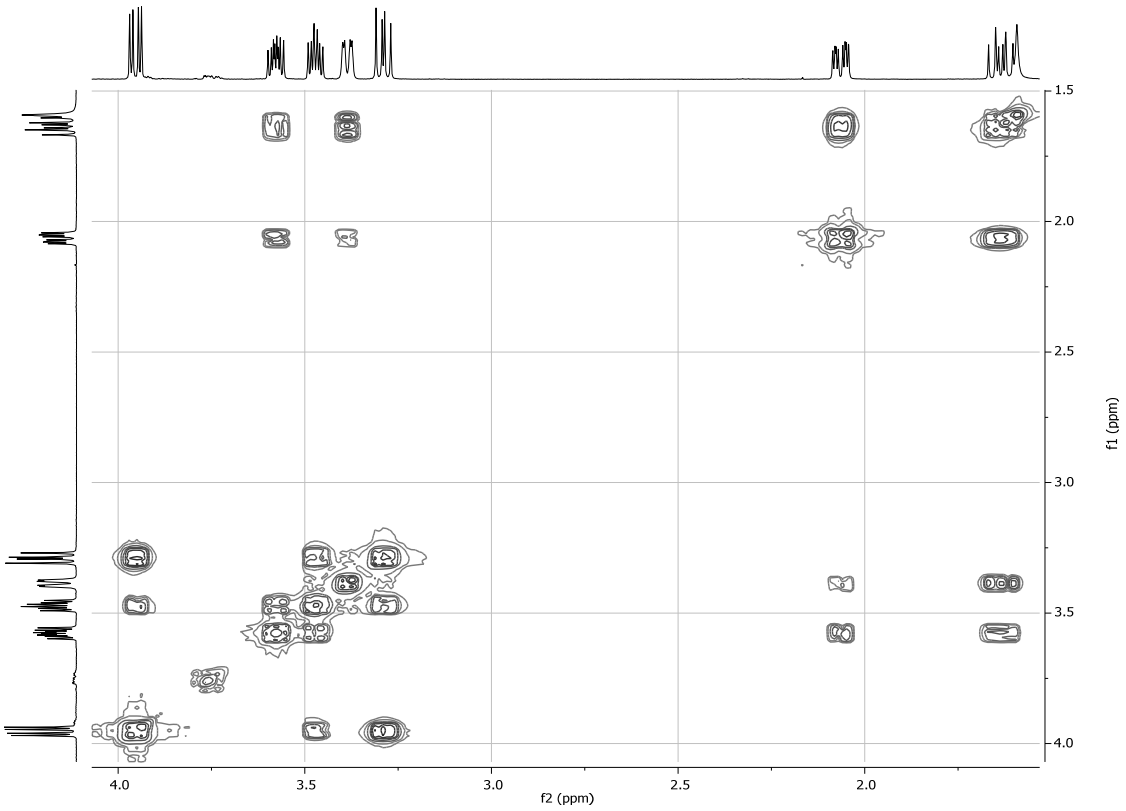
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S39**



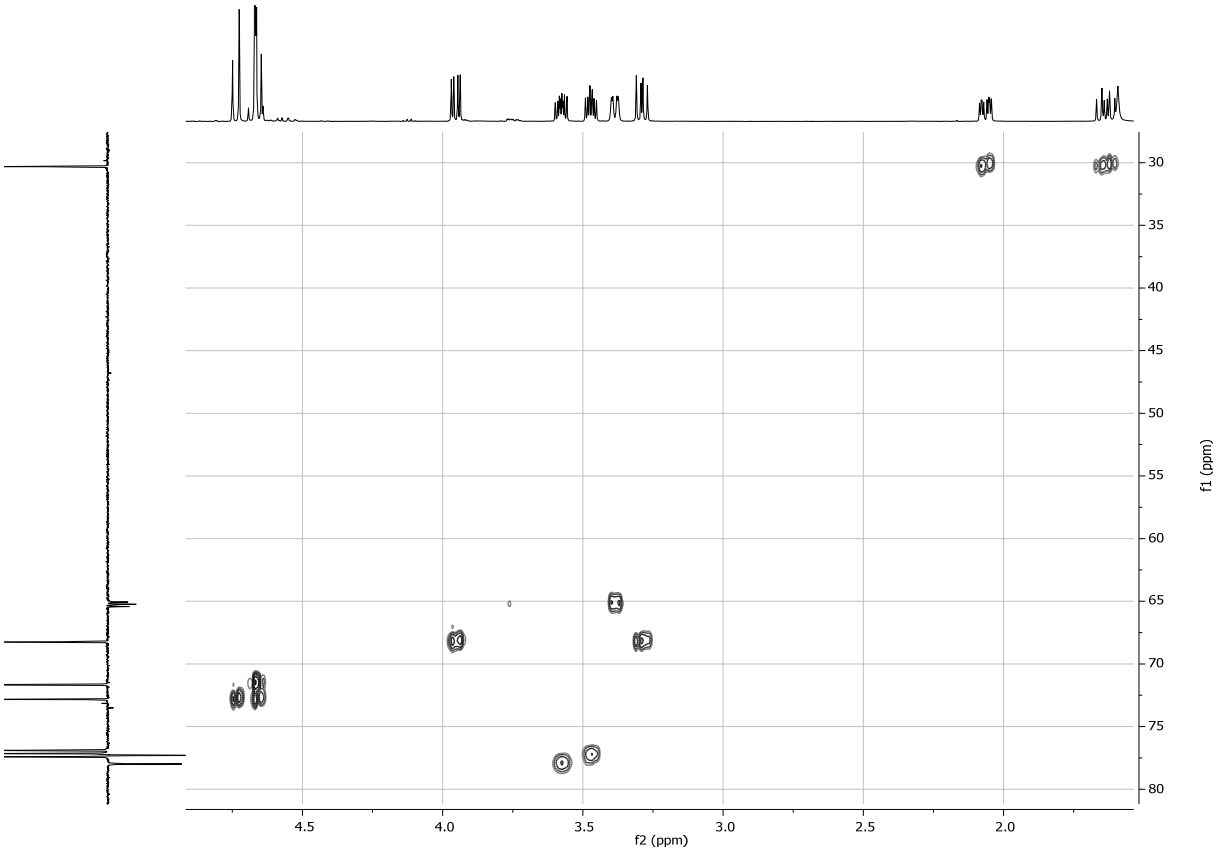
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S39**



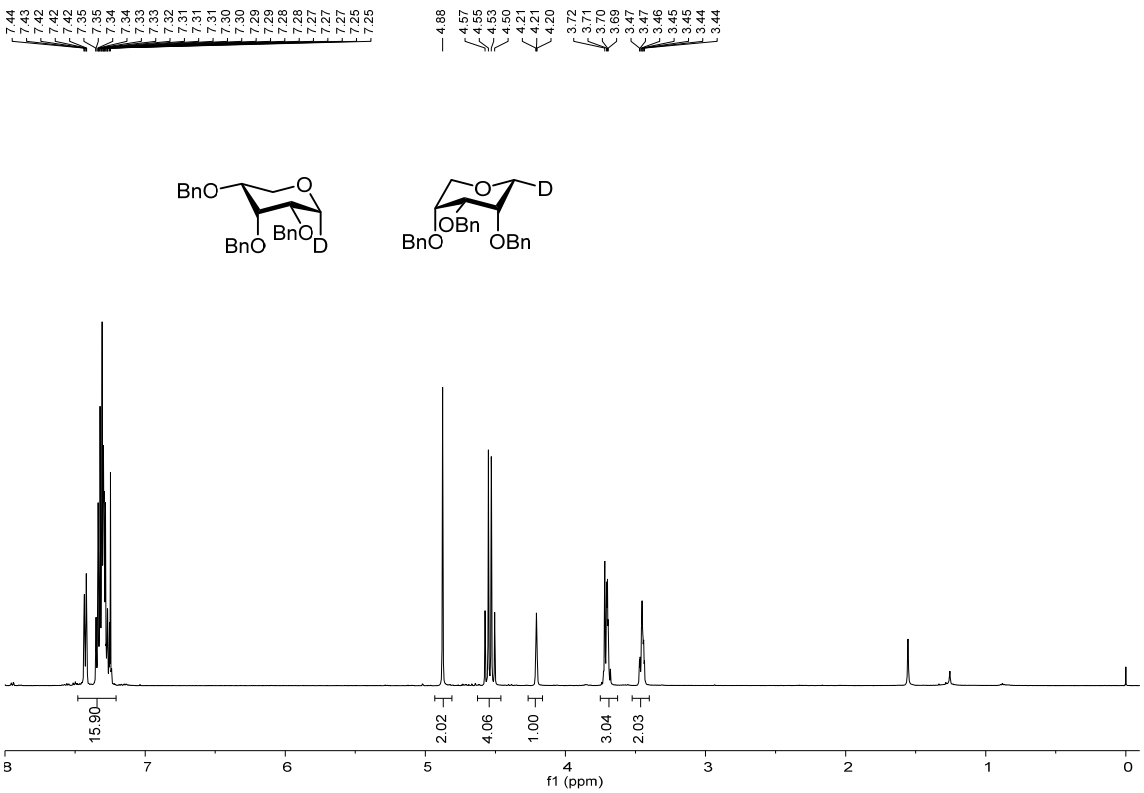
HH-COSY NMR, $CDCl_3$ of compound **S39**



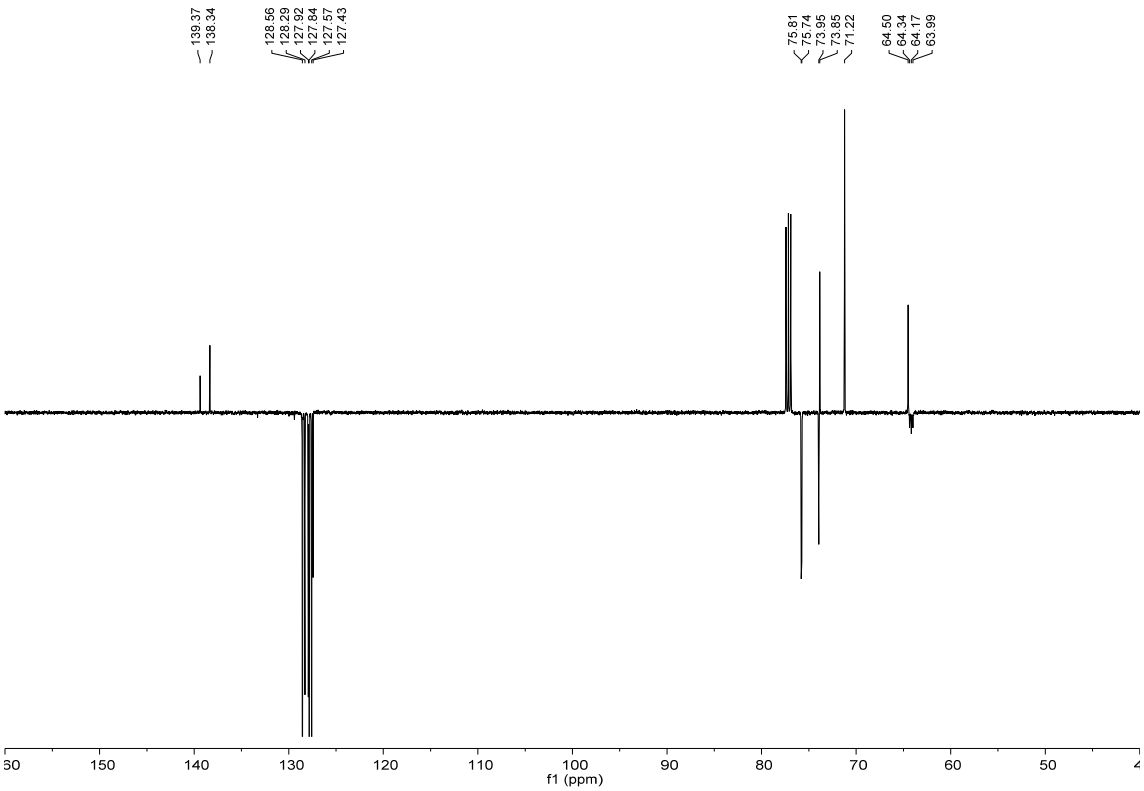
HSQC NMR, $CDCl_3$ of compound **S39**



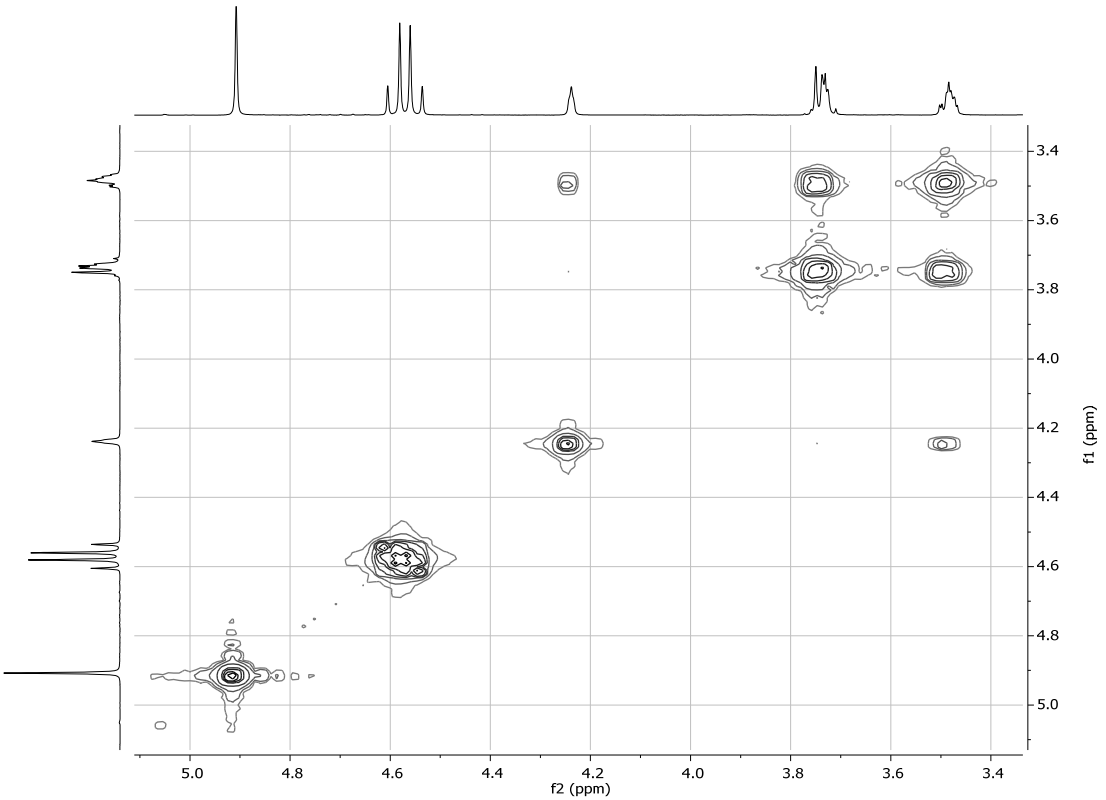
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S40**



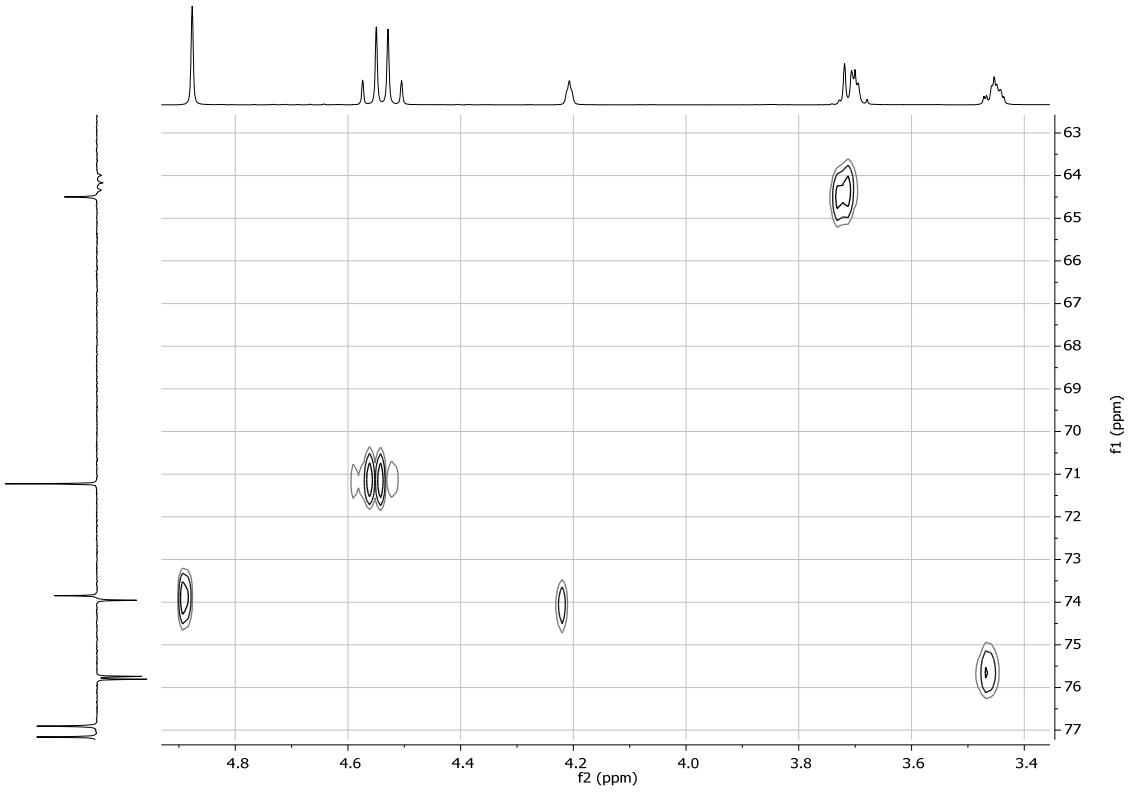
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S40**



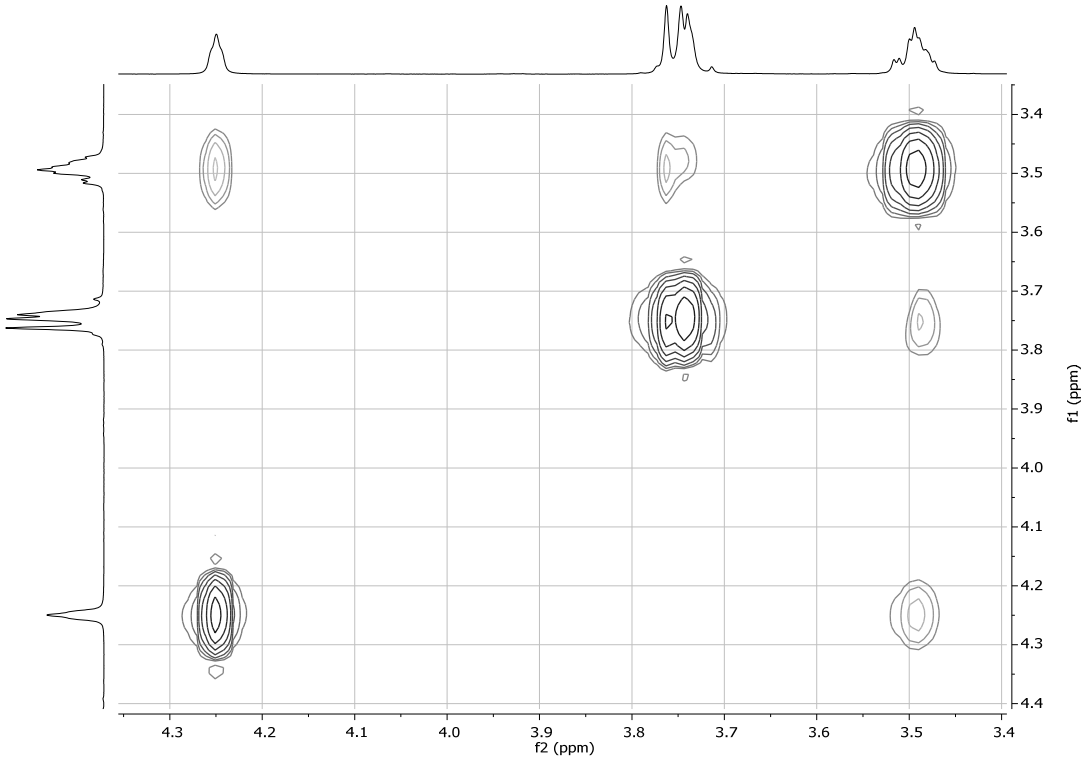
HH-COSY NMR, $CDCl_3$ of compound **S40**



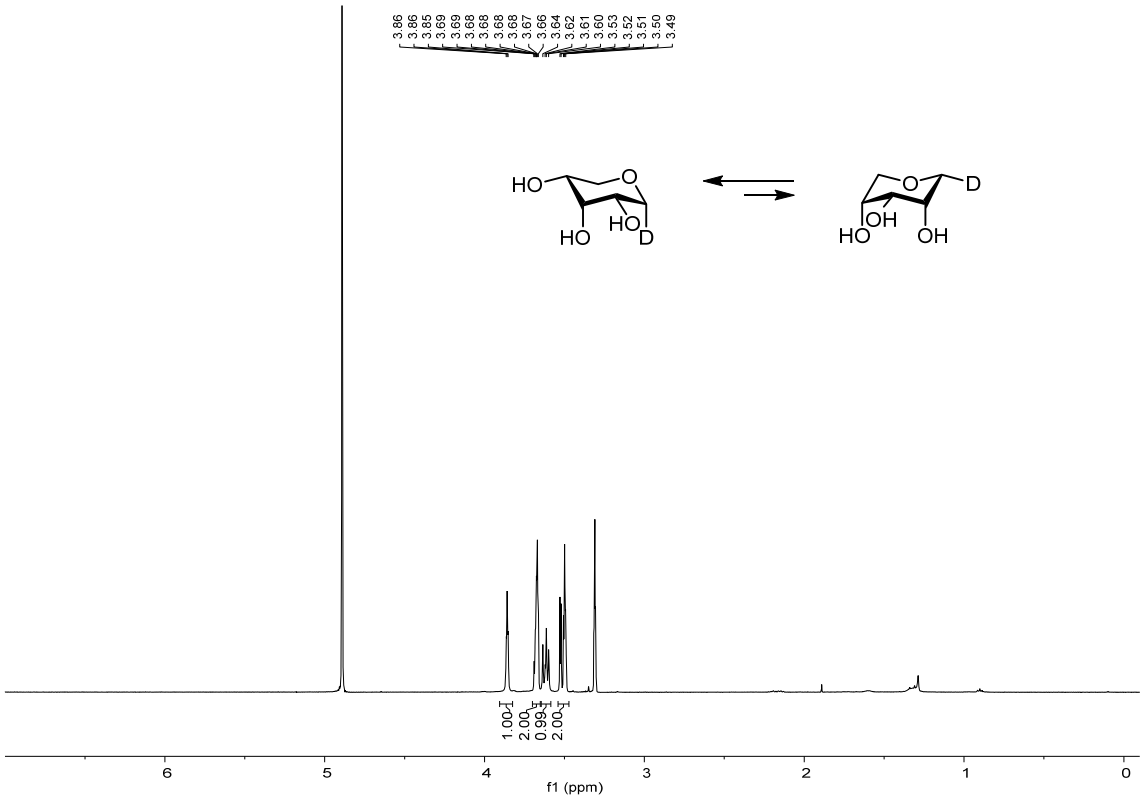
HSQC NMR, $CDCl_3$ of compound **S40**



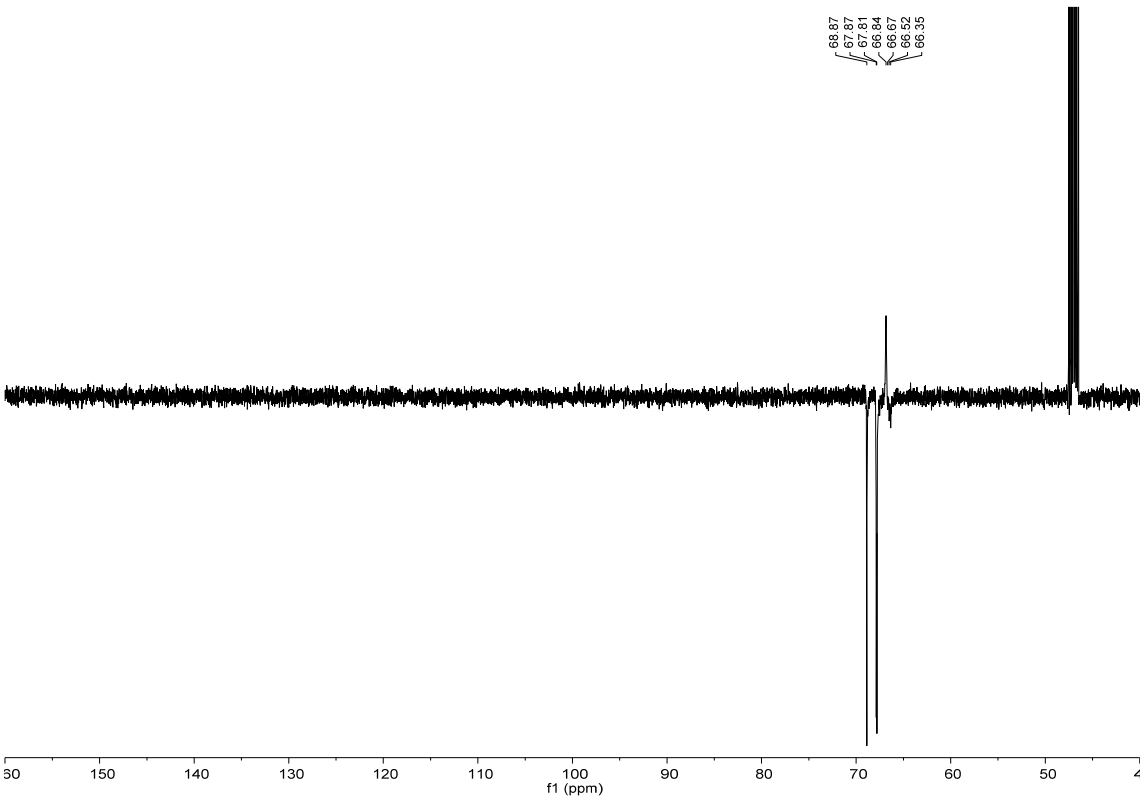
NOESY NMR, $CDCl_3$ of compound **S40**



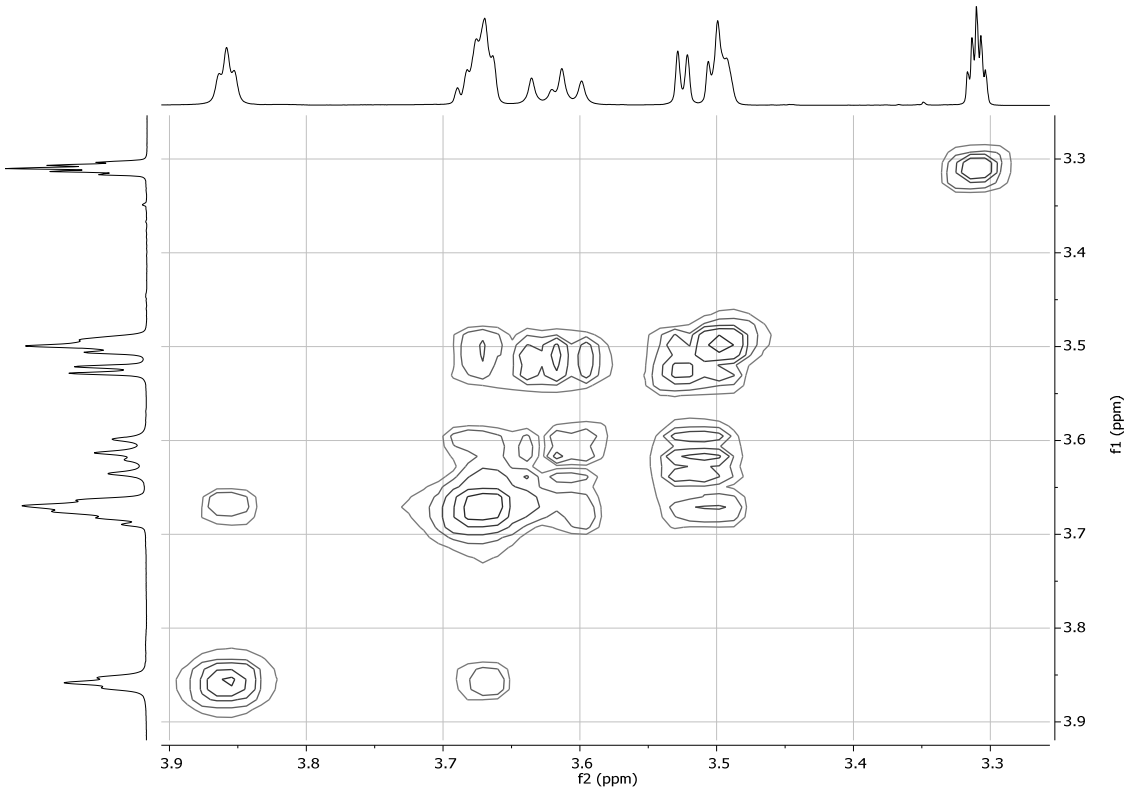
^{1}H NMR, 500 MHz, MeOD of compound **S41**



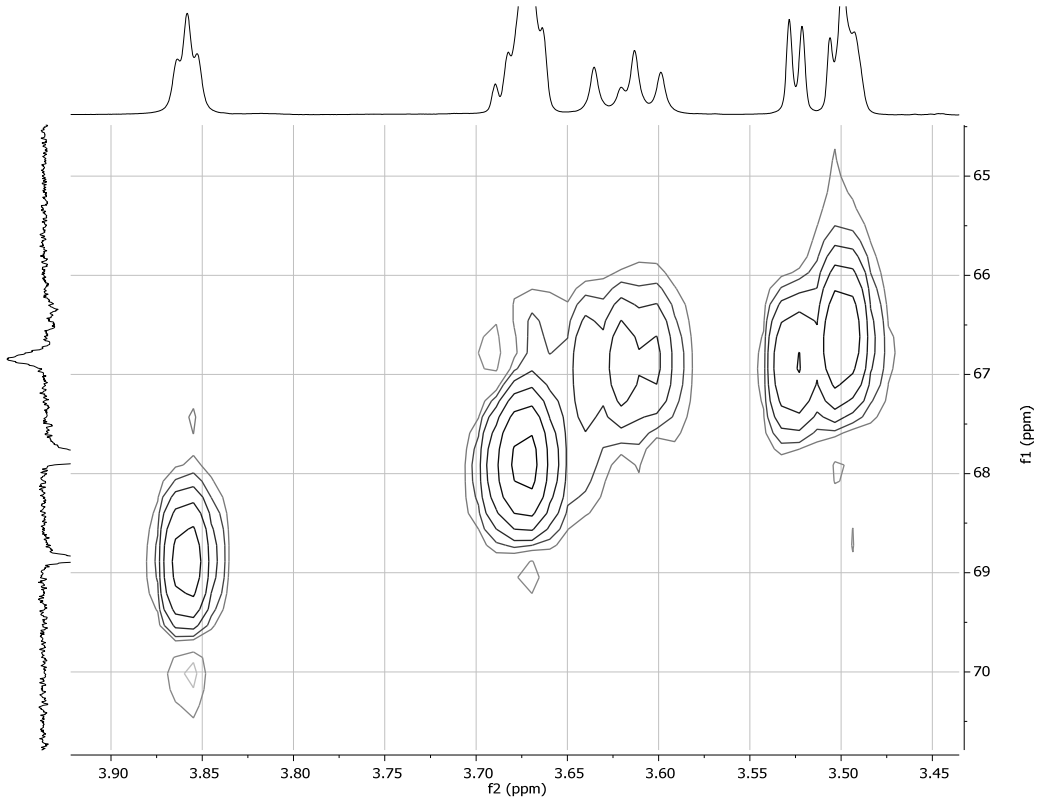
^{13}C NMR, 126 MHz, MeOD of compound **S41**



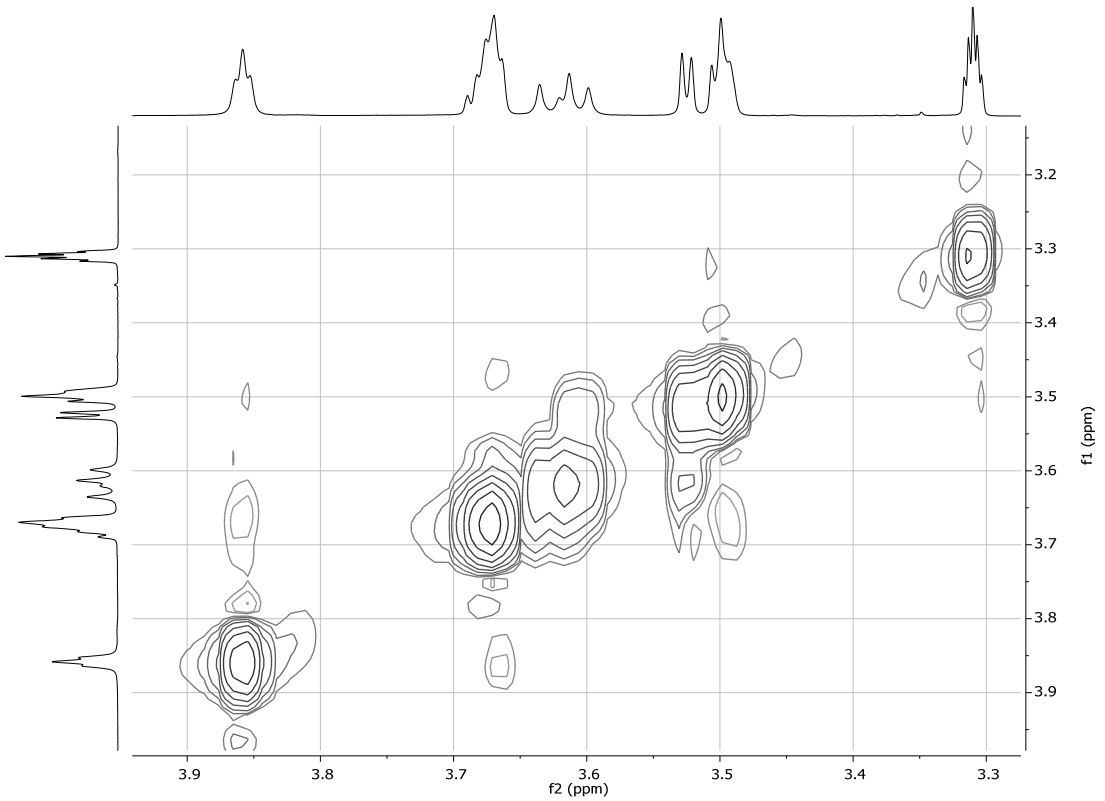
HH-COSY NMR, MeOD of compound **S41**



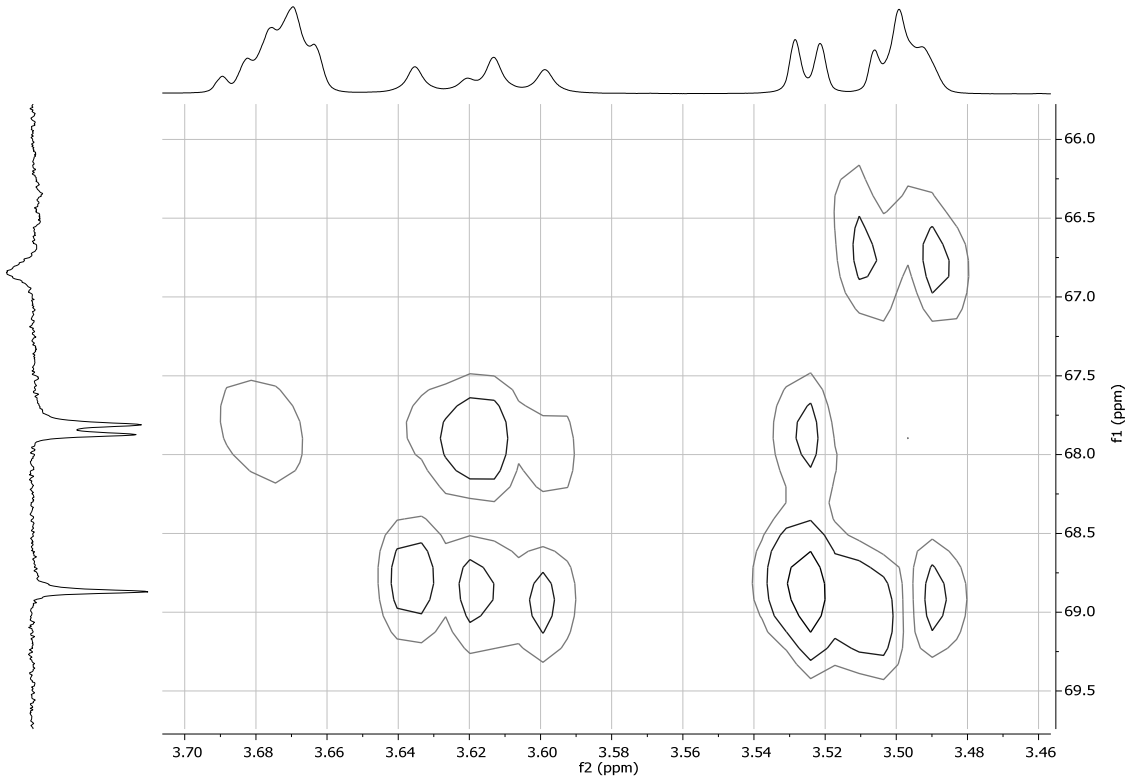
HSQC NMR, MeOD of compound **S41**



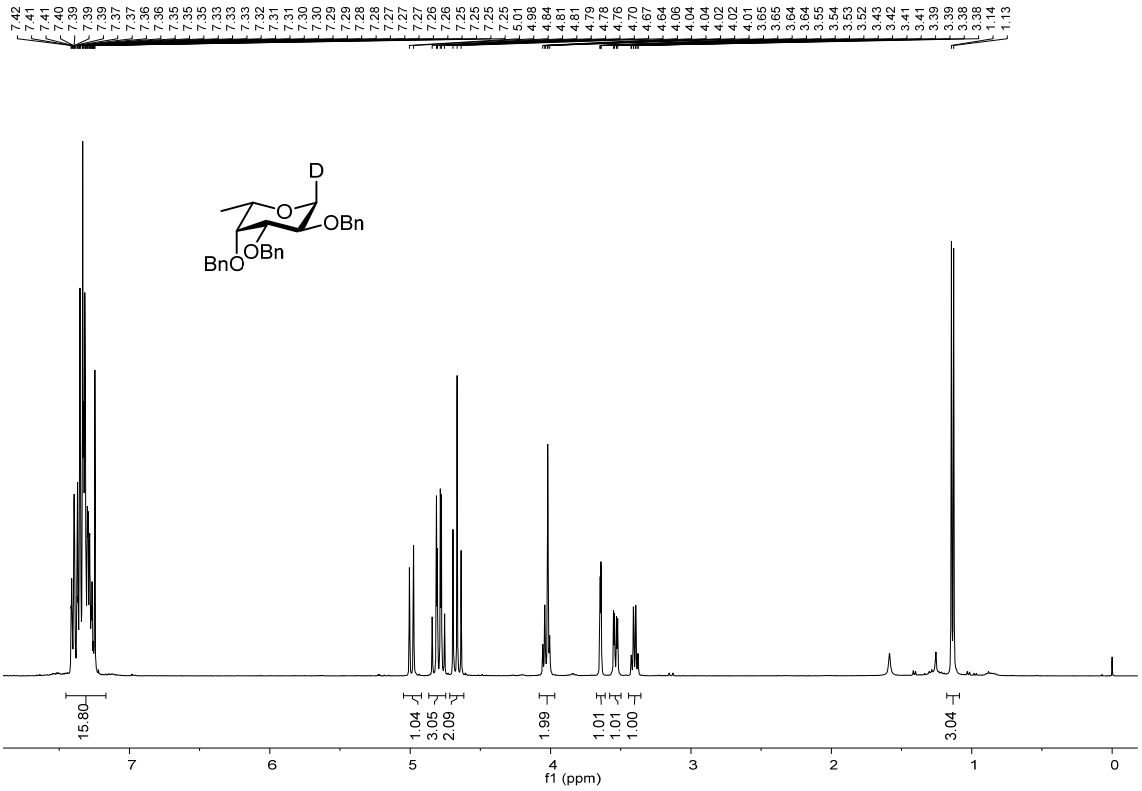
NOESY NMR, MeOD of compound **S41**



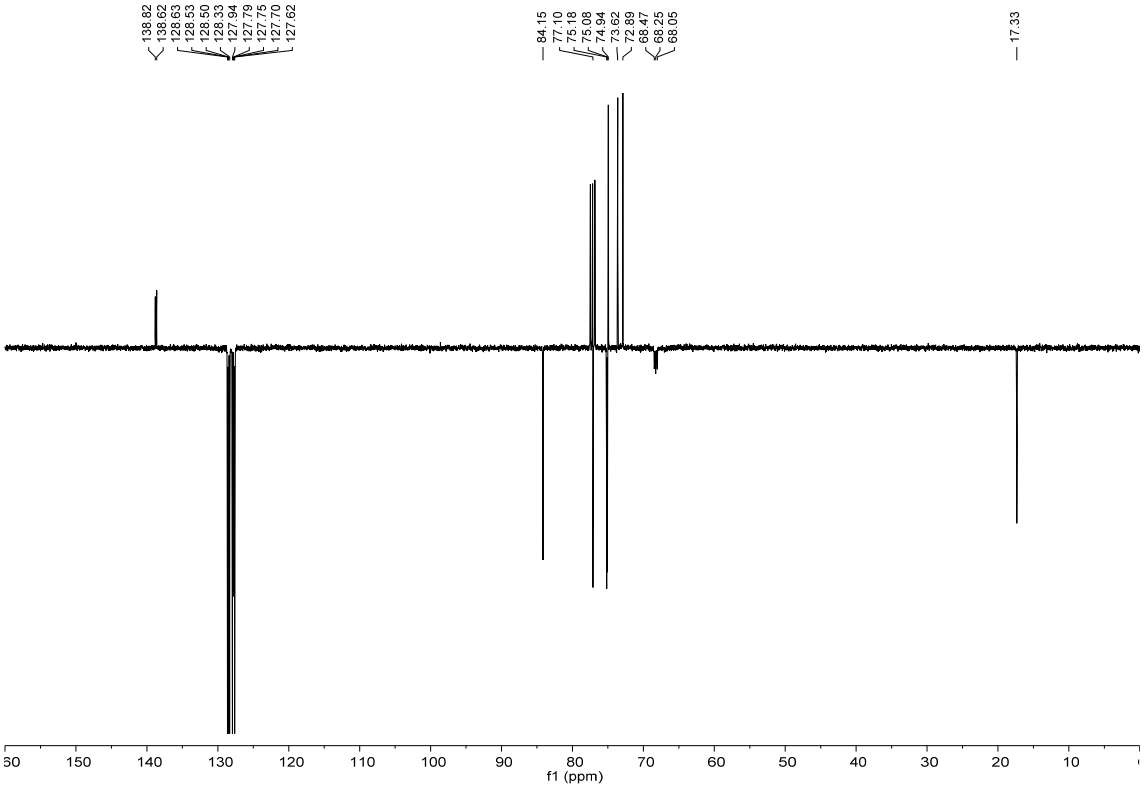
HMBC NMR, MeOD of compound **S41**



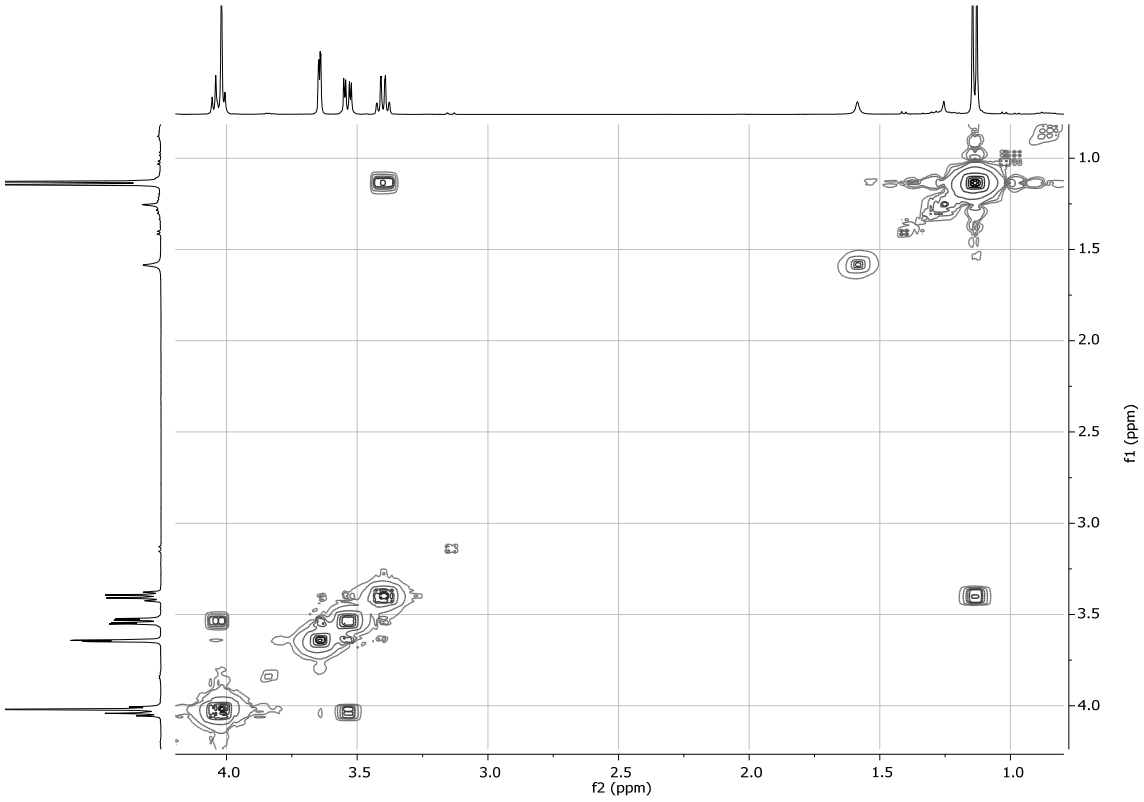
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S42** (pre-activation Tf_2O/Ph_2SO based *D*-glycosylation in DCM)



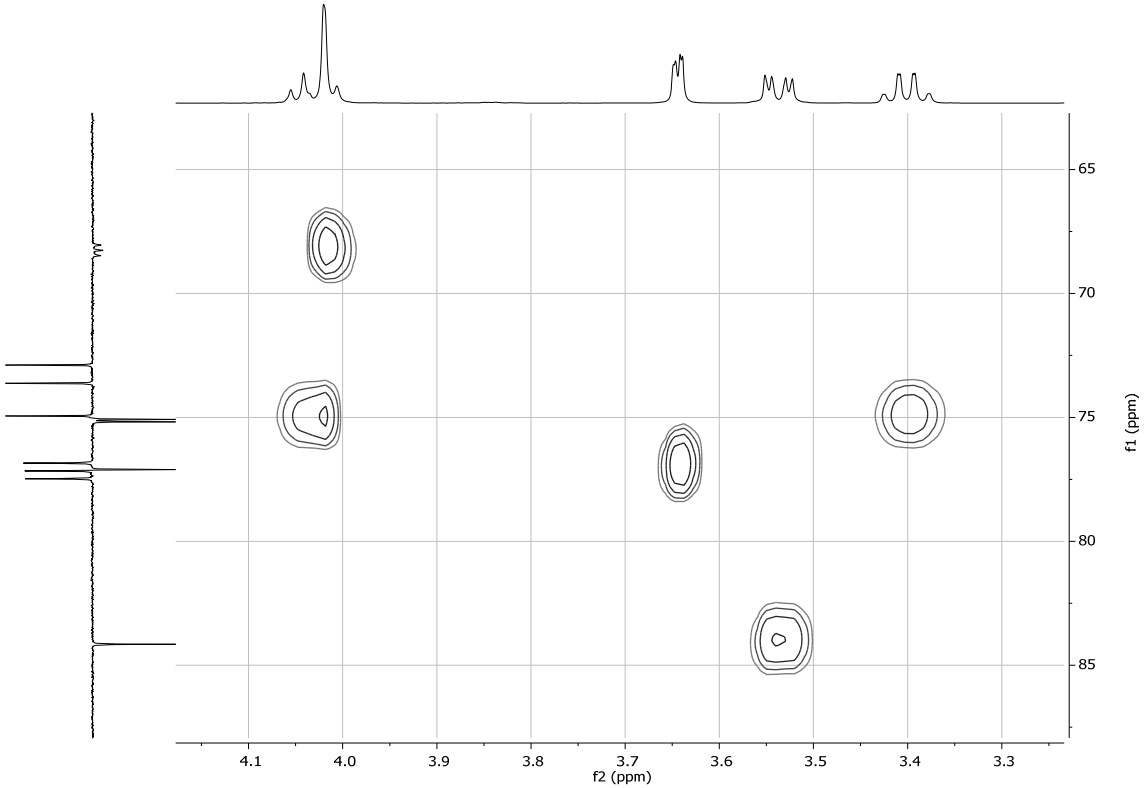
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S42**



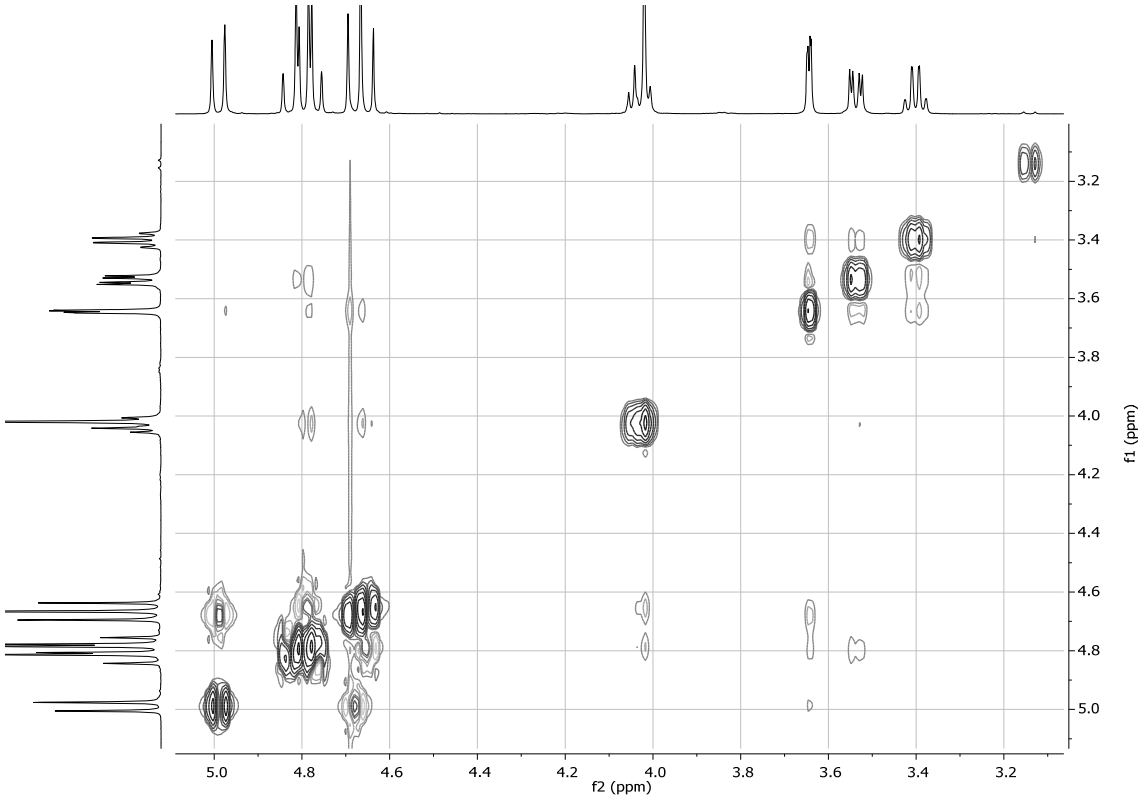
HH-COSY NMR, $CDCl_3$ of compound **S42**



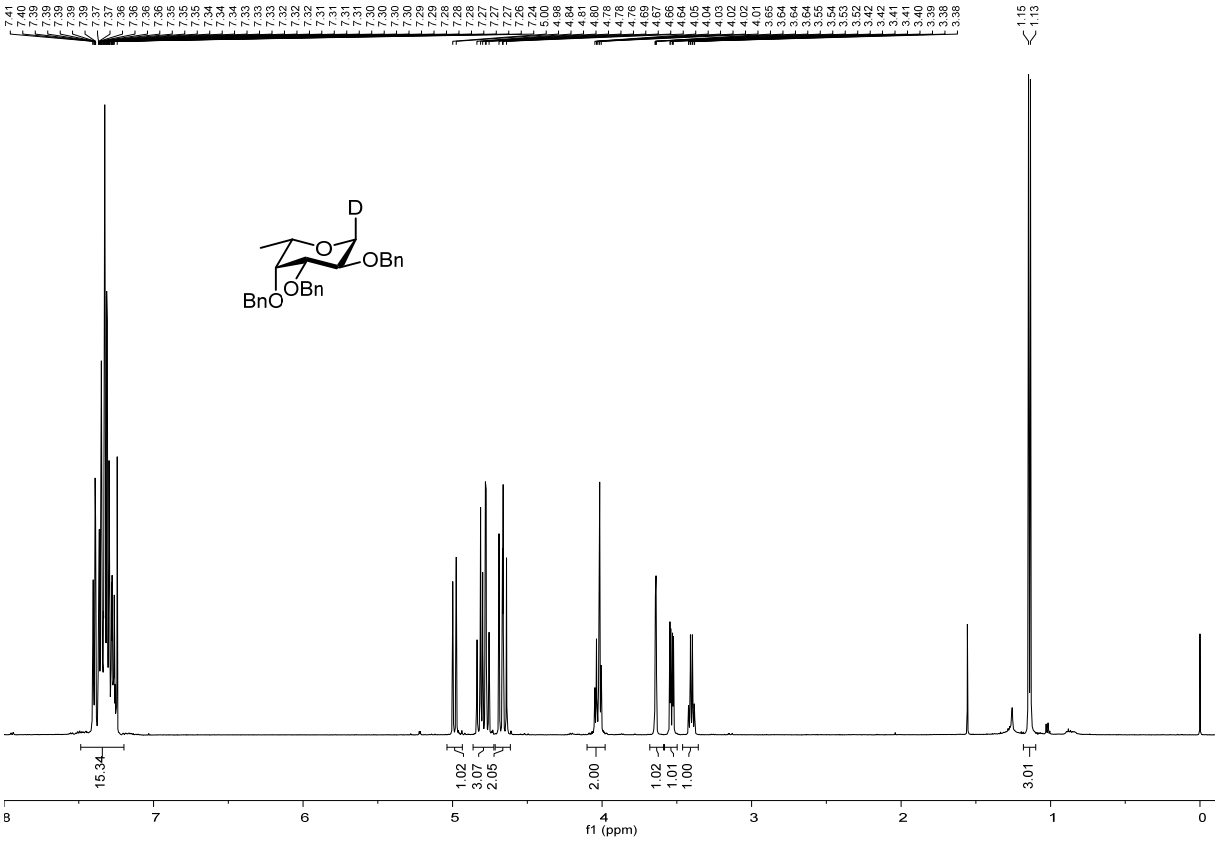
HSQC NMR, $CDCl_3$ of compound **S42**



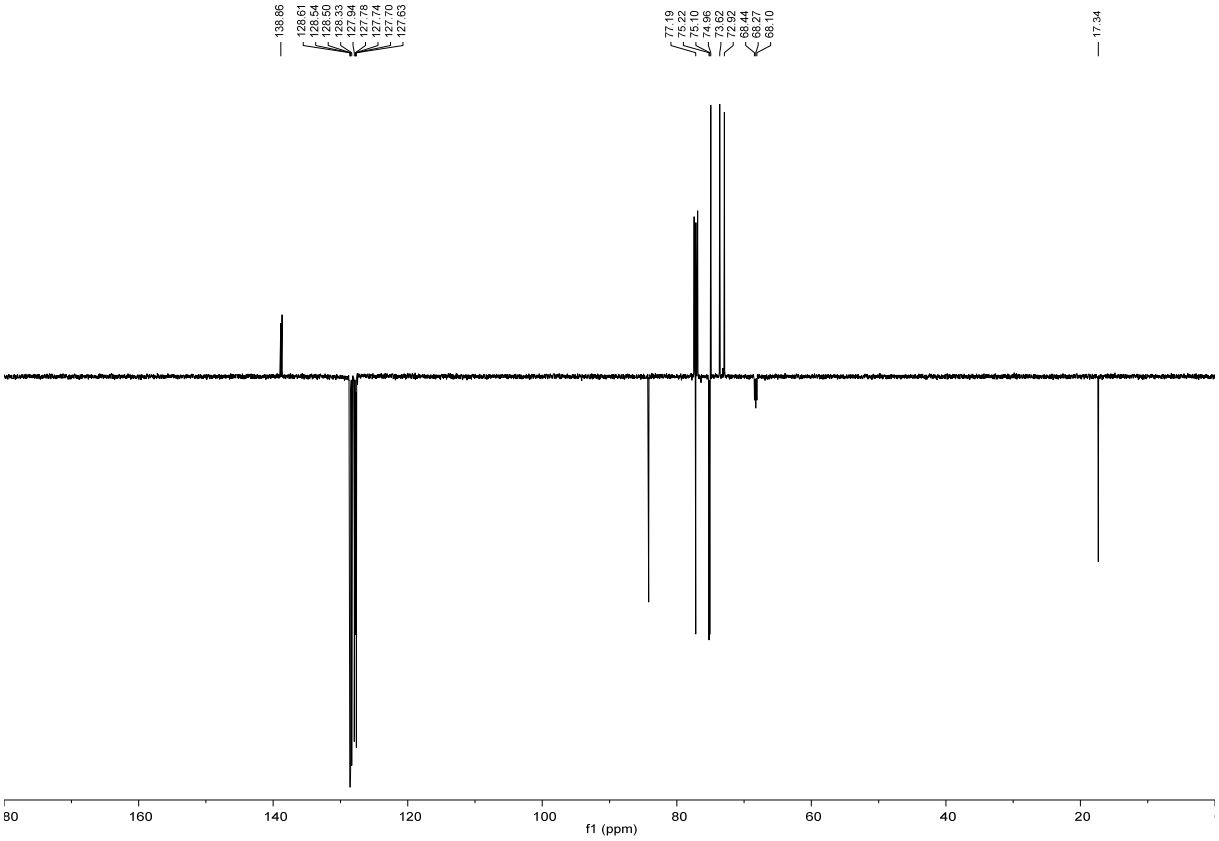
NOESY NMR, $CDCl_3$ of compound **S42**



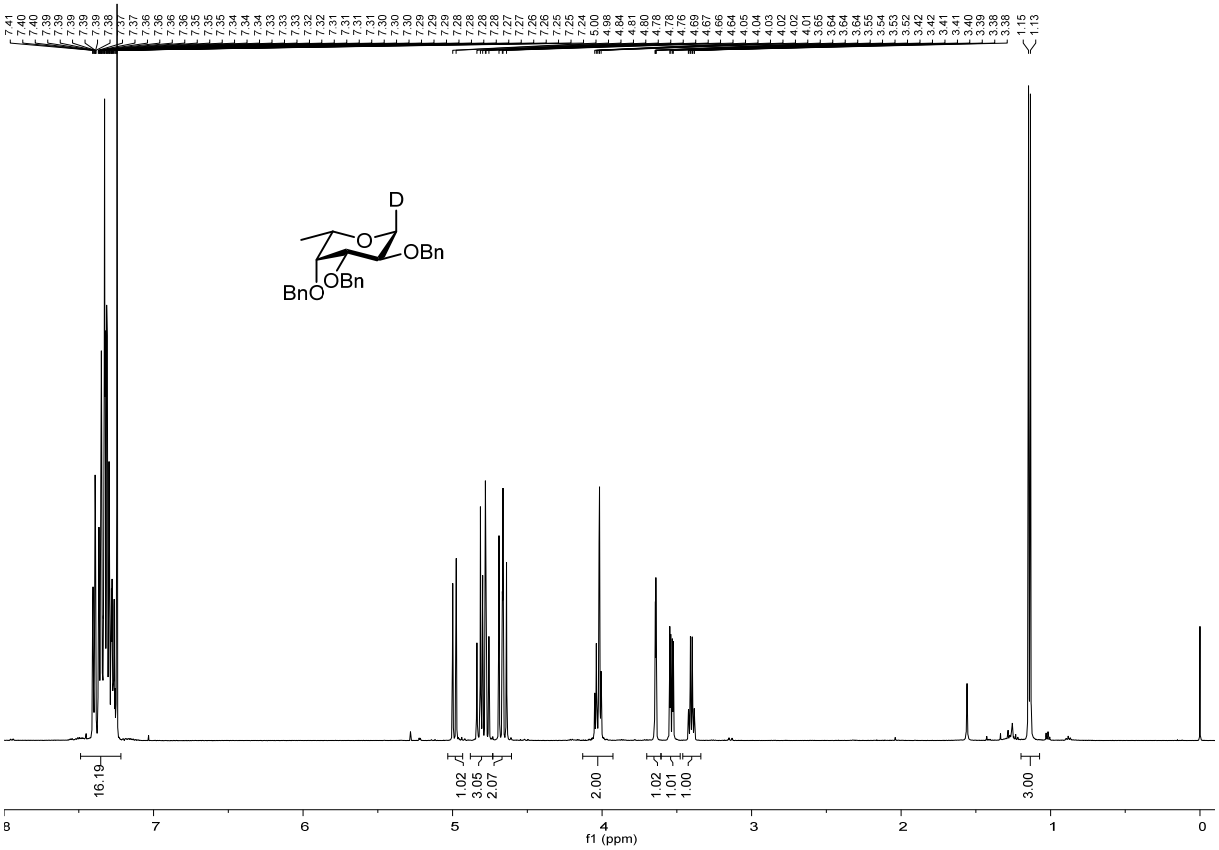
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S42** (pre-activation Tf_2O/Ph_2SO based *D*-glycosylation in Et_2O)



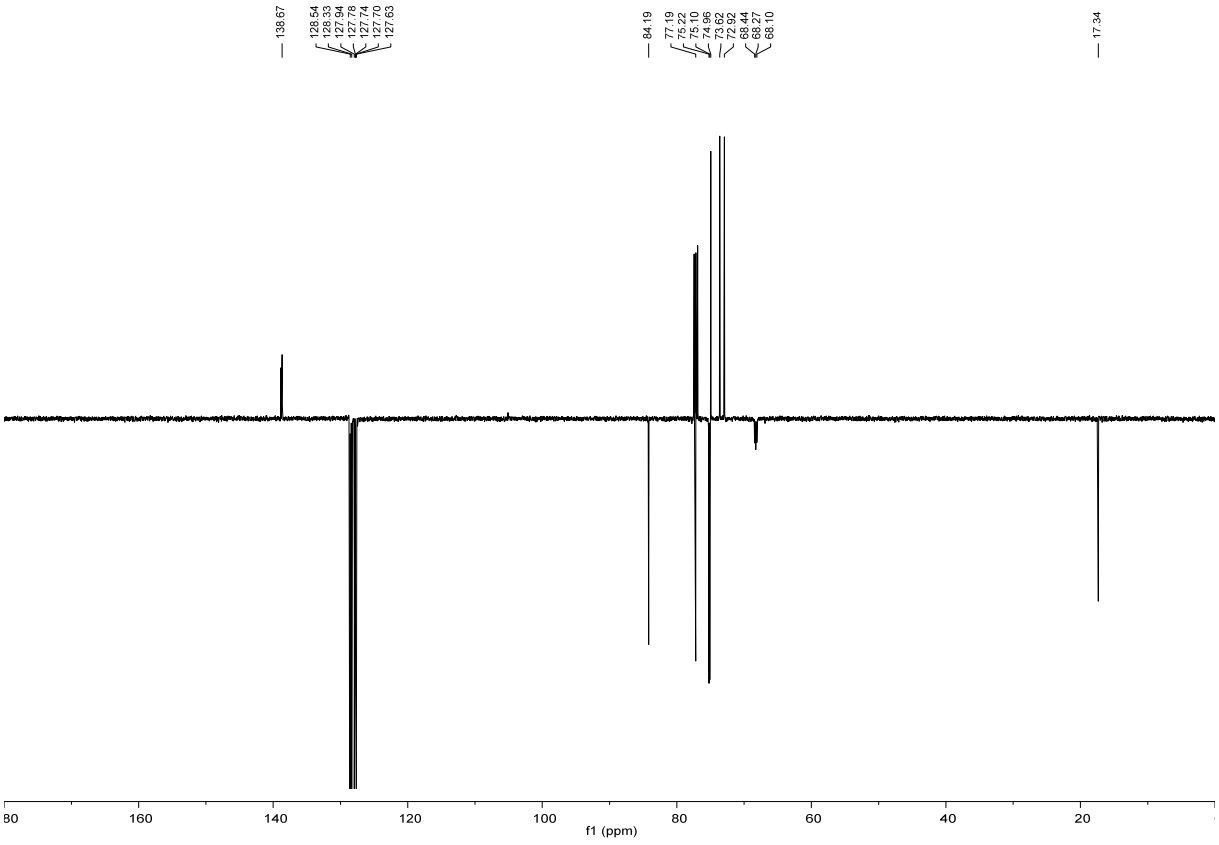
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S42**



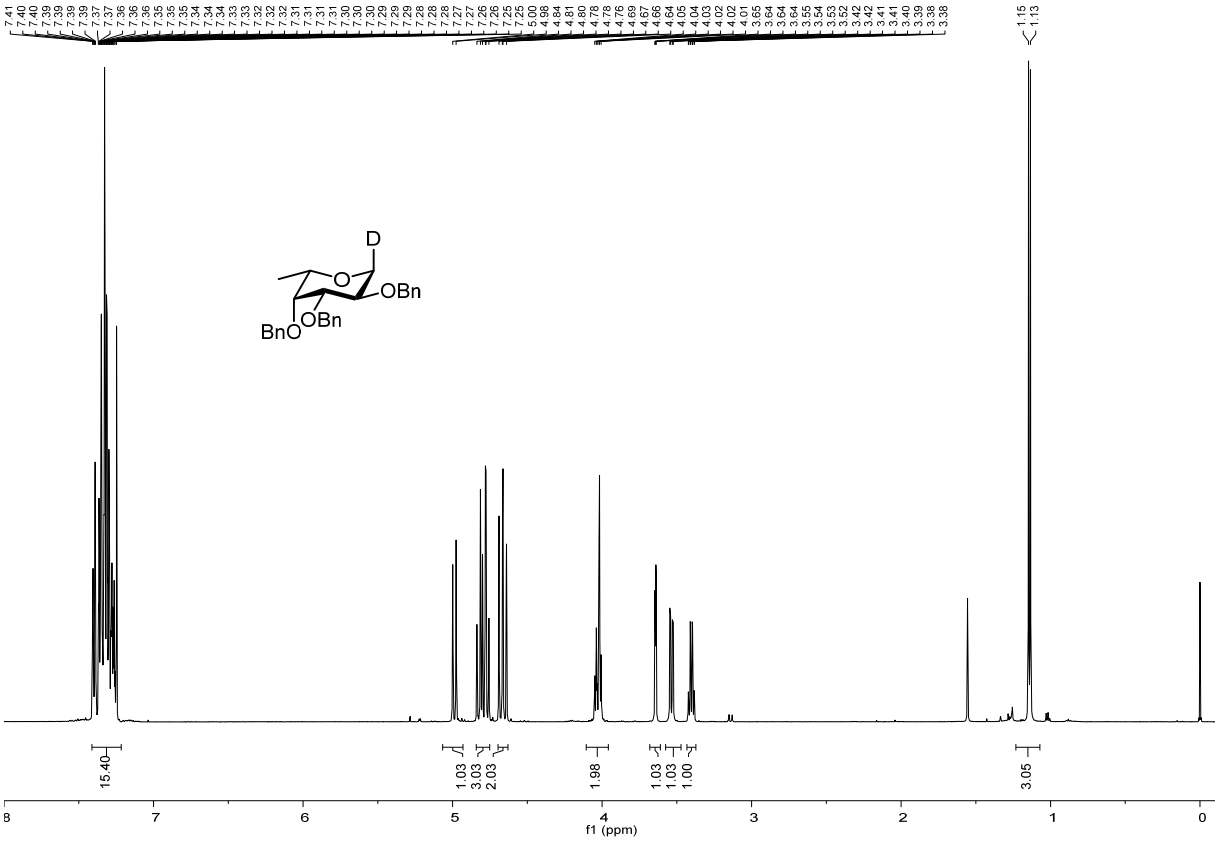
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S42** (pre-activation Tf_2O/Ph_2SO based *D*-glycosylation in MeCN)



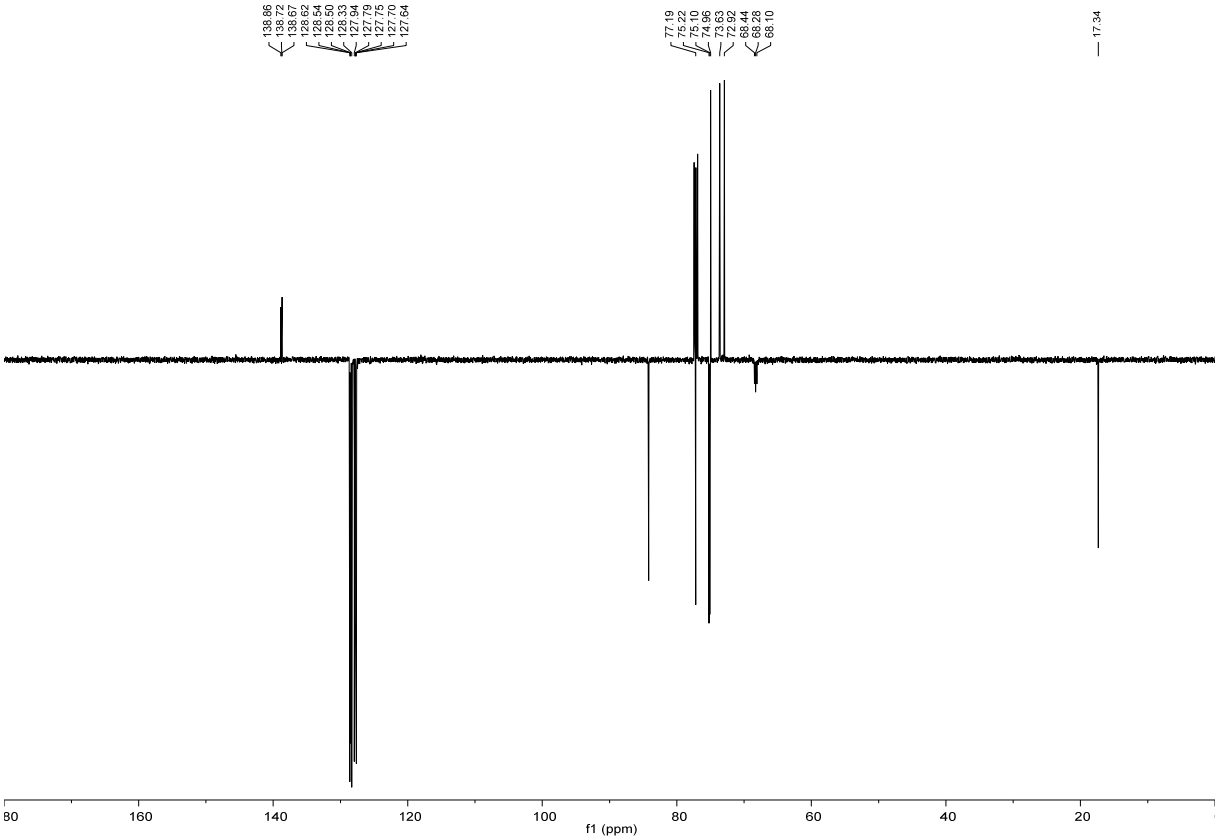
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S42**



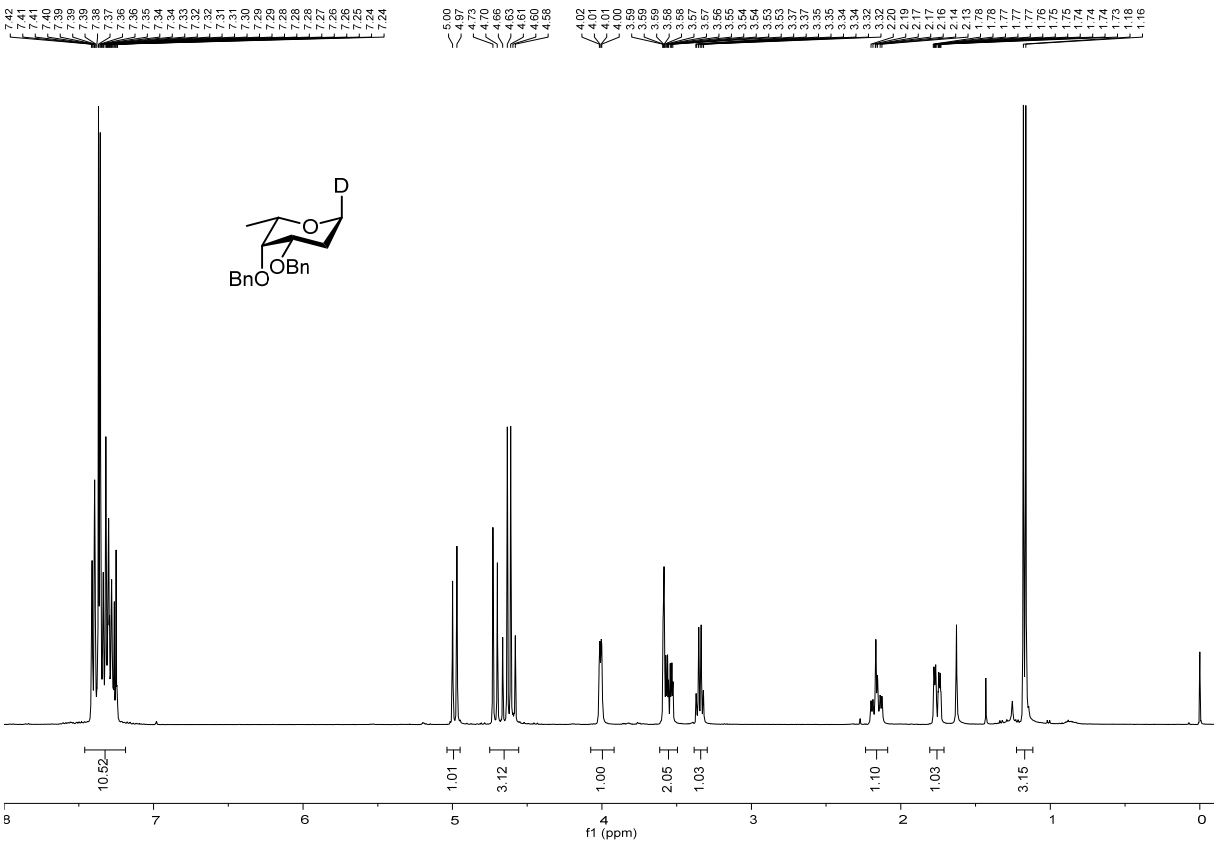
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S42** (TMSOTf activation based *D*-glycosylation)



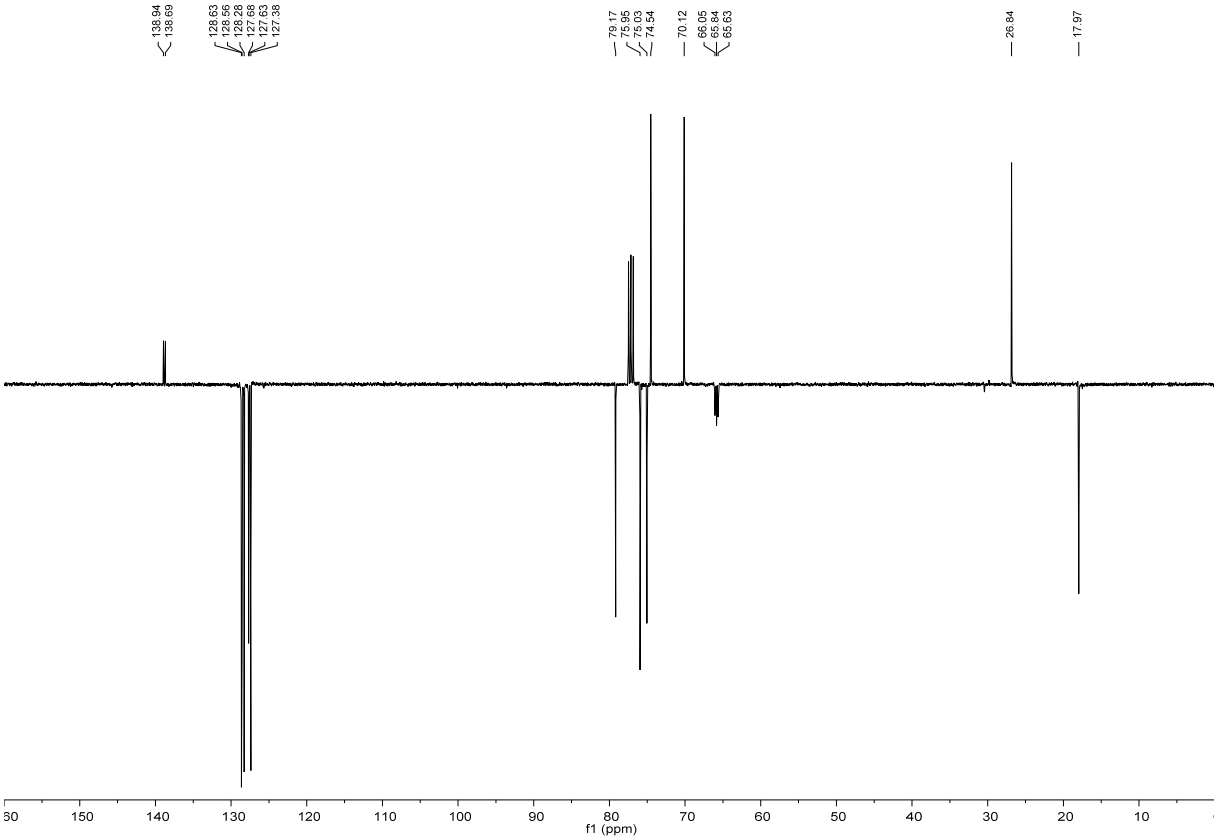
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S42**



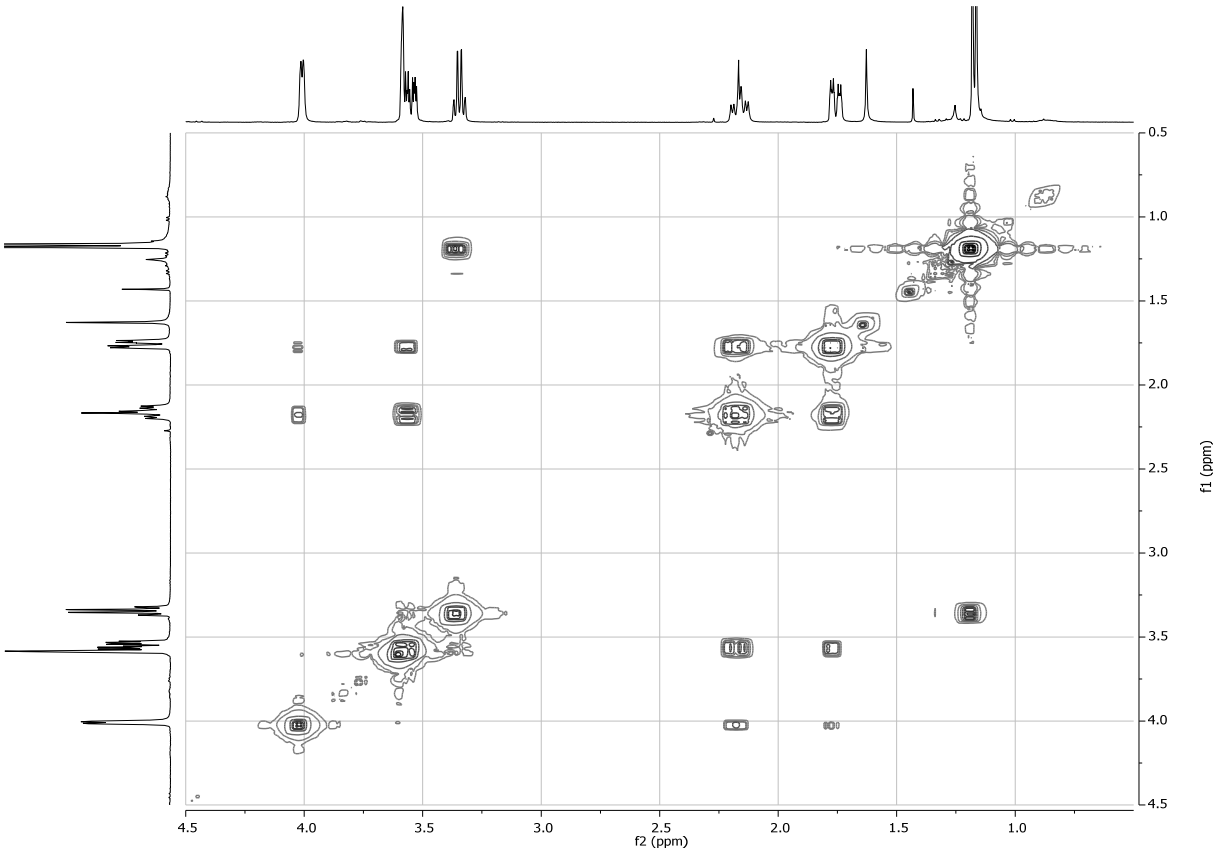
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S43**



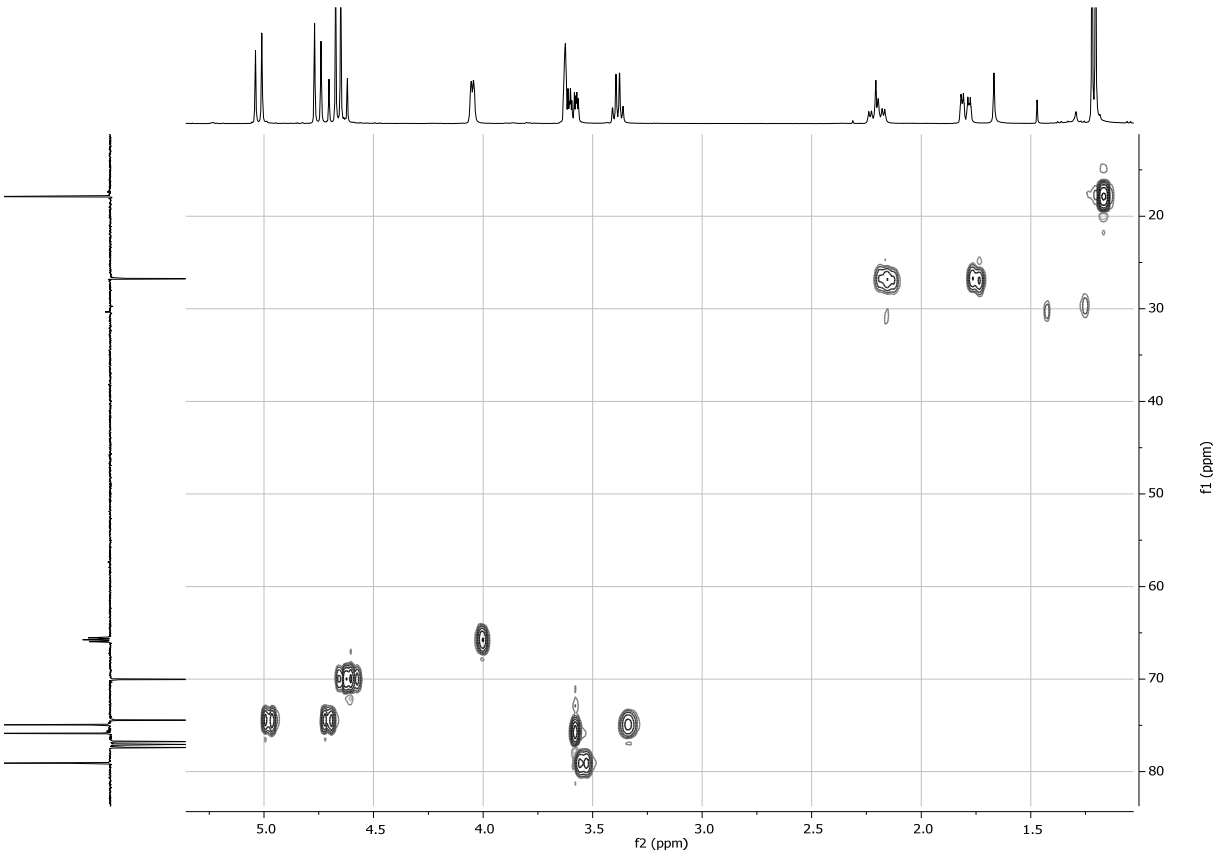
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S43**



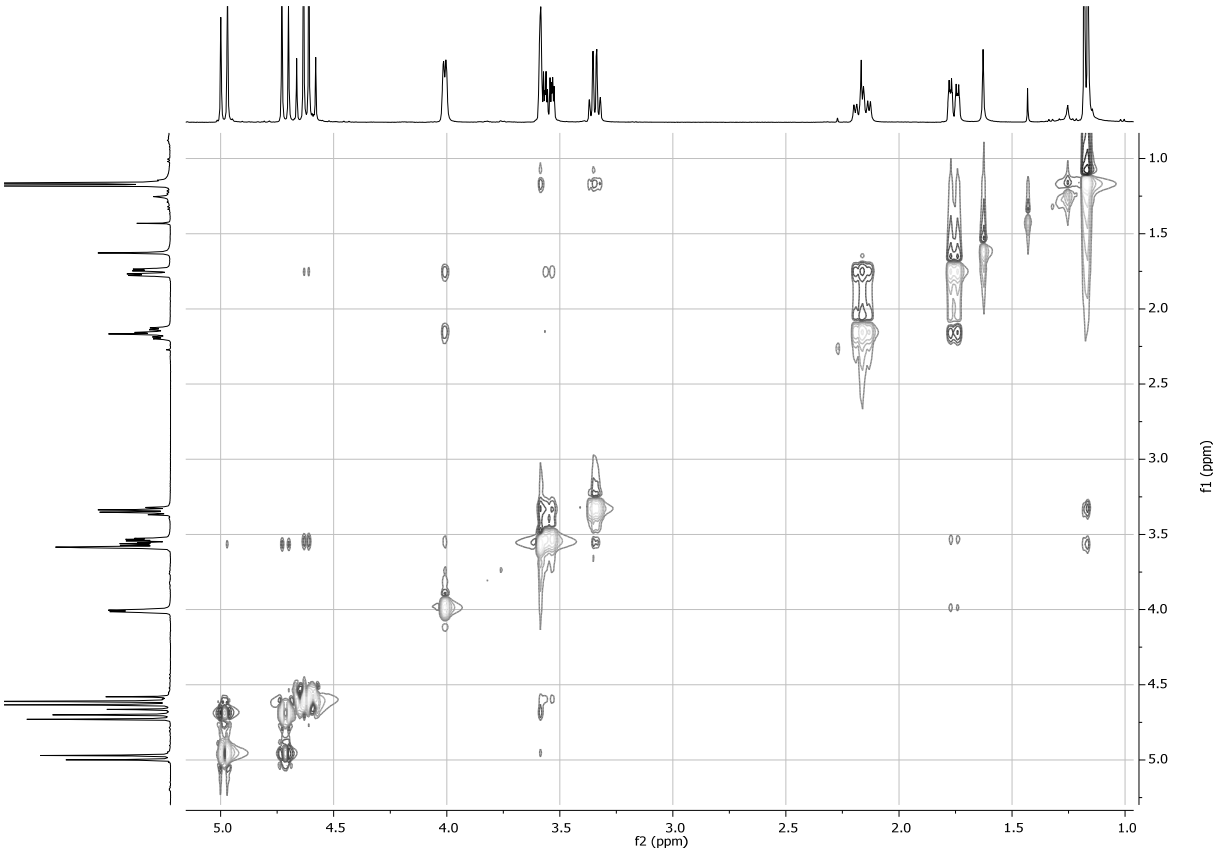
HH-COSY NMR, $CDCl_3$ of compound **S43**



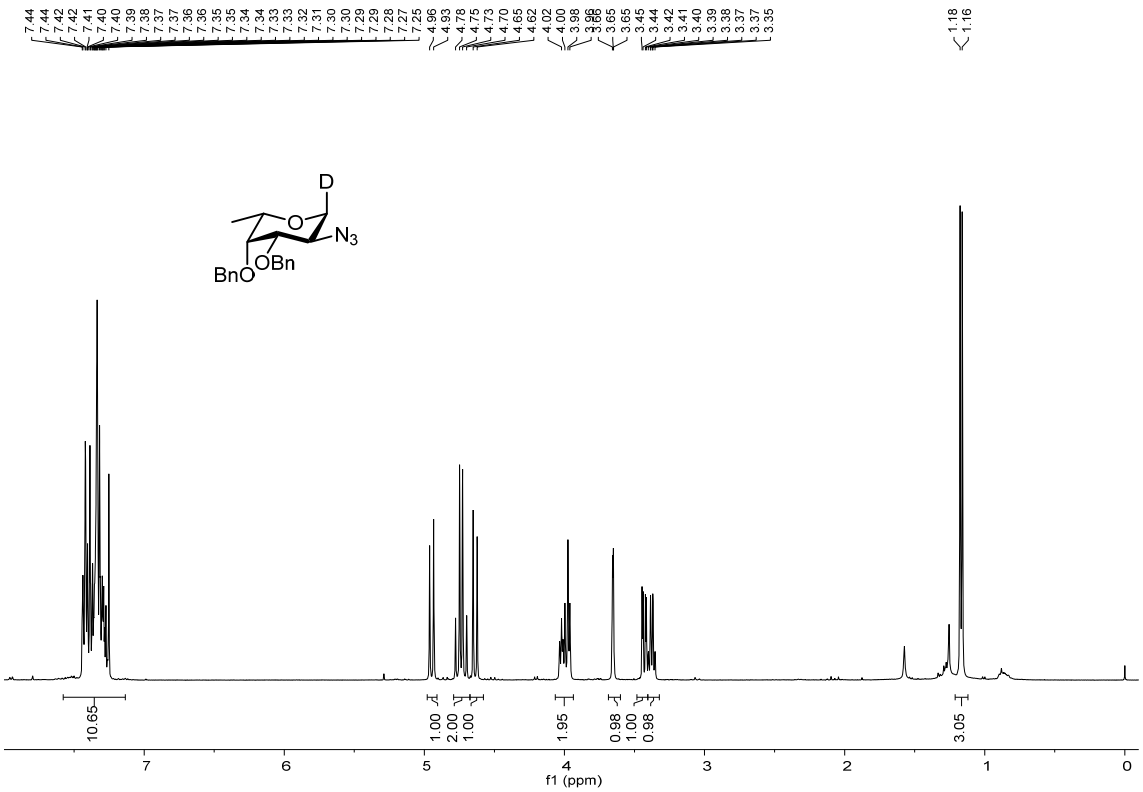
HSQC NMR, $CDCl_3$ of compound **S43**



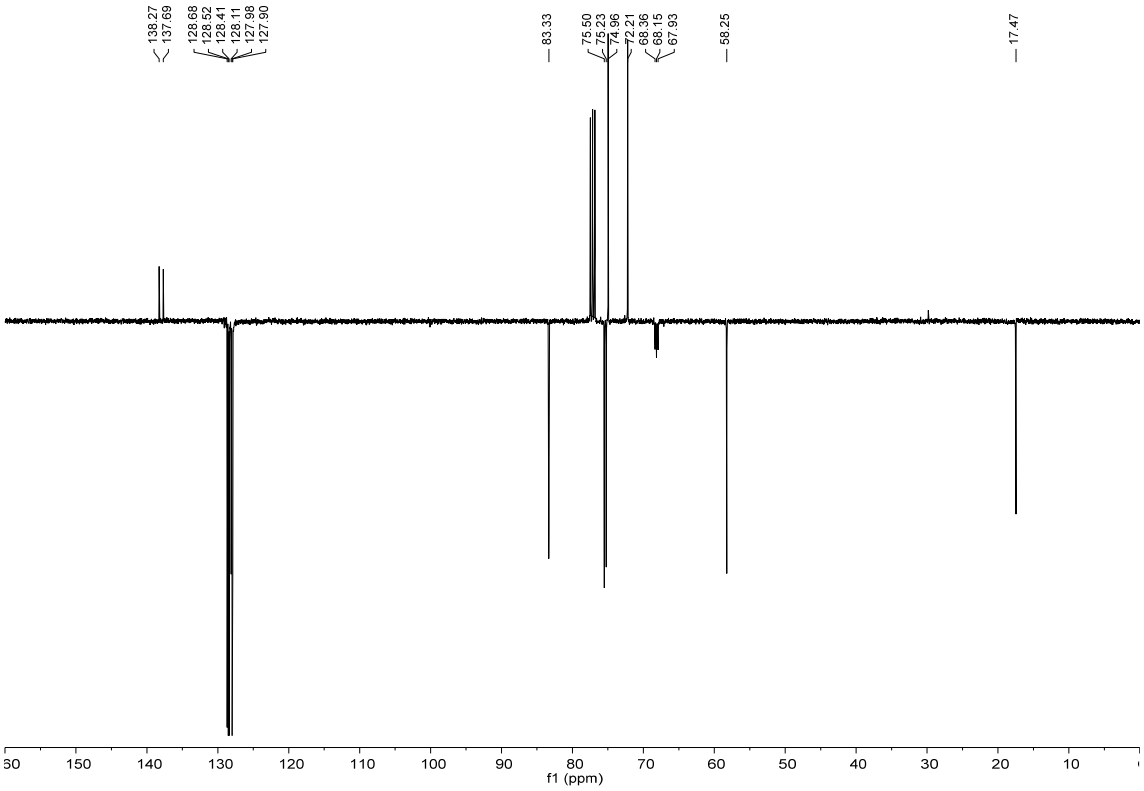
NOESY NMR, $CDCl_3$ of compound **S43**



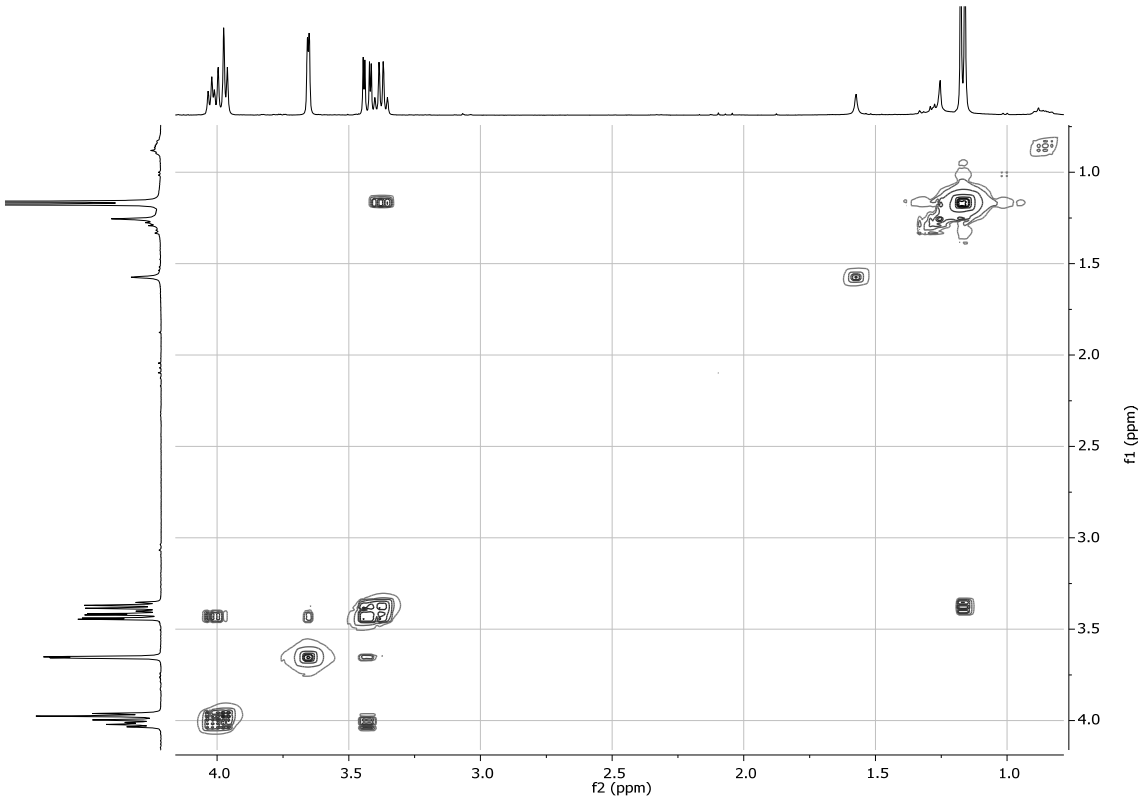
^1H NMR, 400 MHz, $CDCl_3$ of compound **S44**



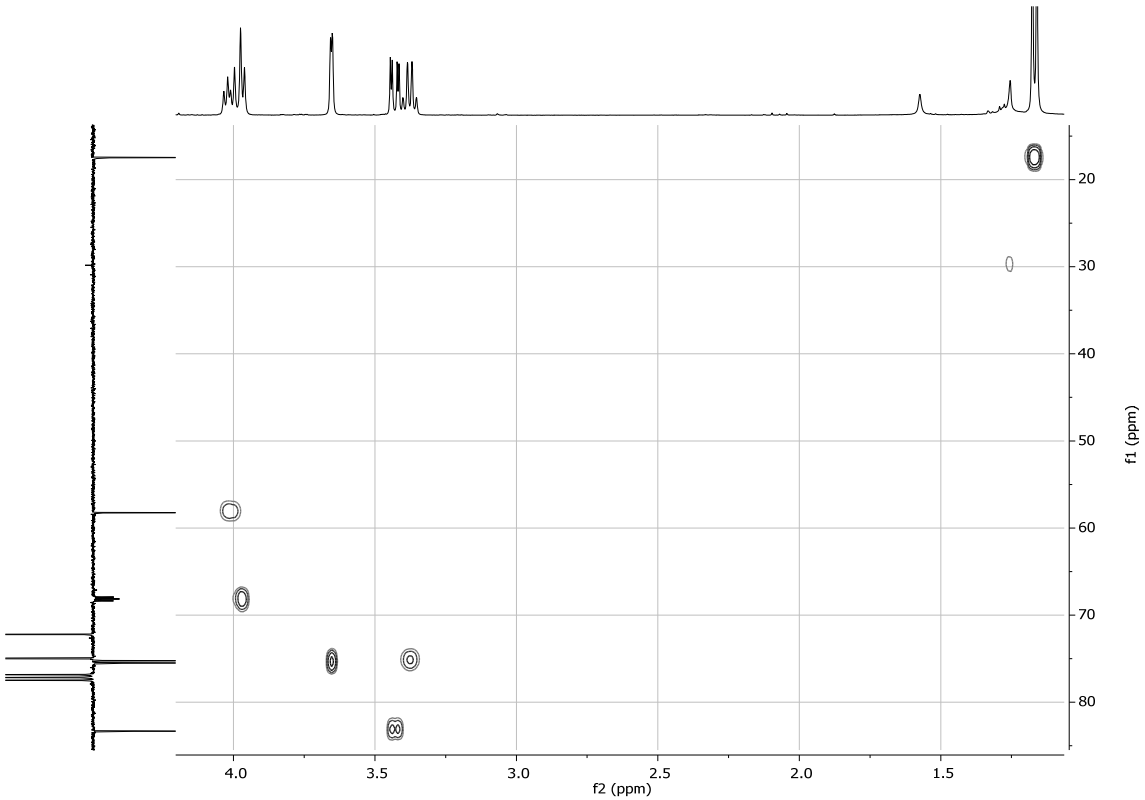
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S44**



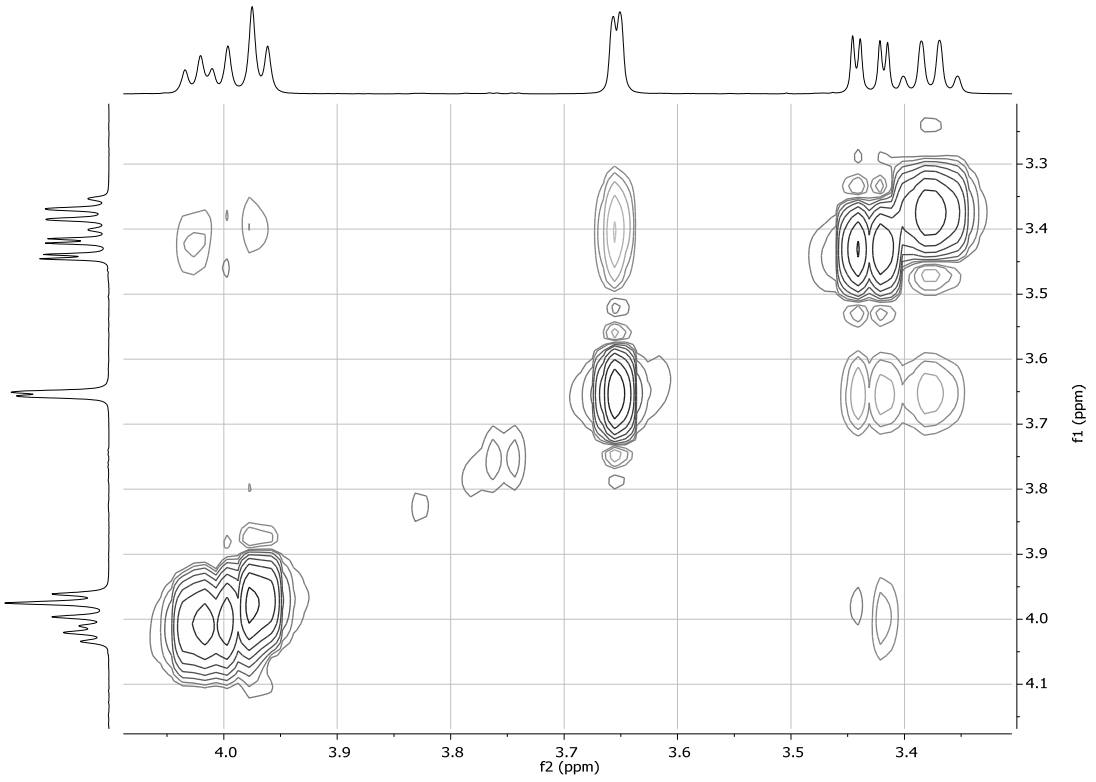
HH-COSY NMR, $CDCl_3$ of compound **S44**



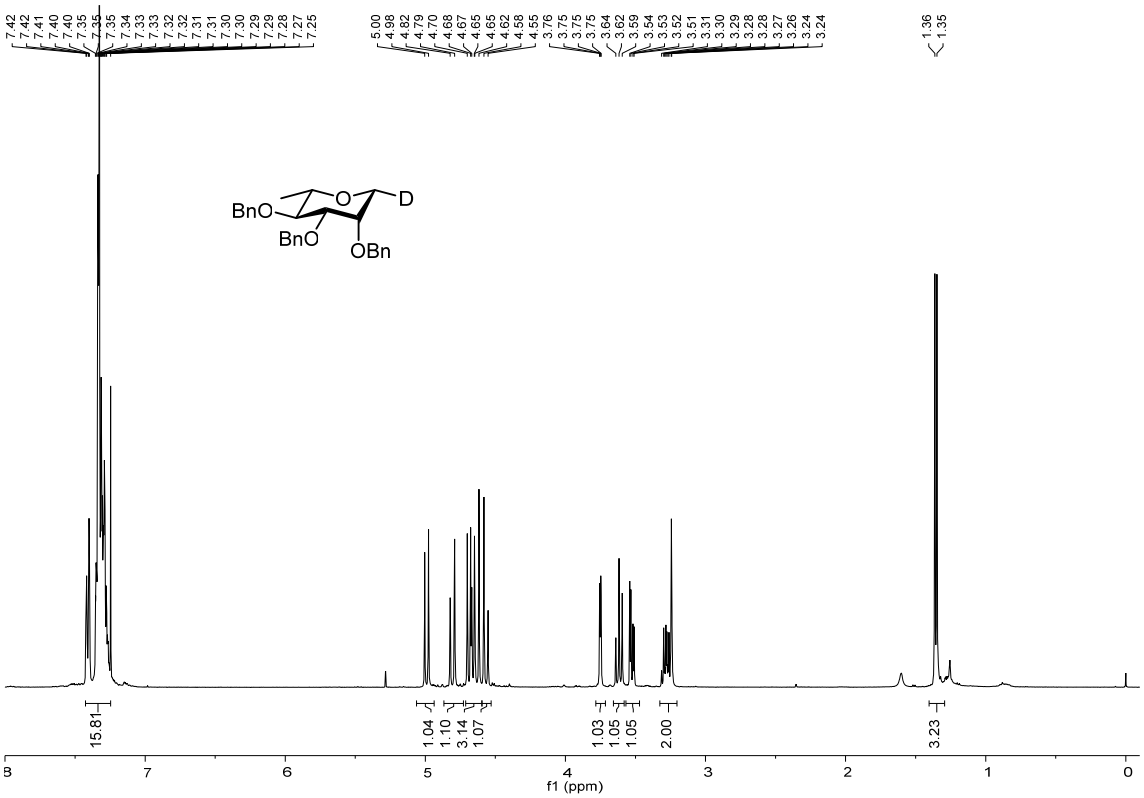
HSQC NMR, $CDCl_3$ of compound **S44**



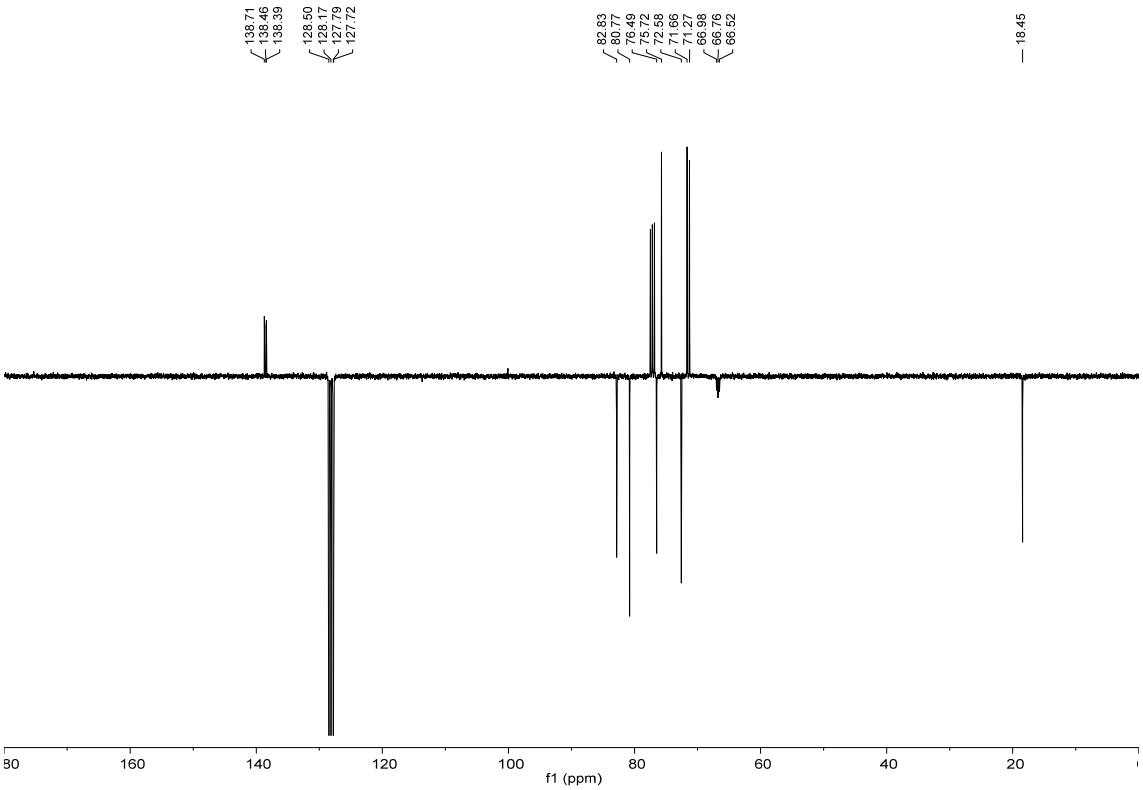
NOESY NMR, $CDCl_3$ of compound **S44**



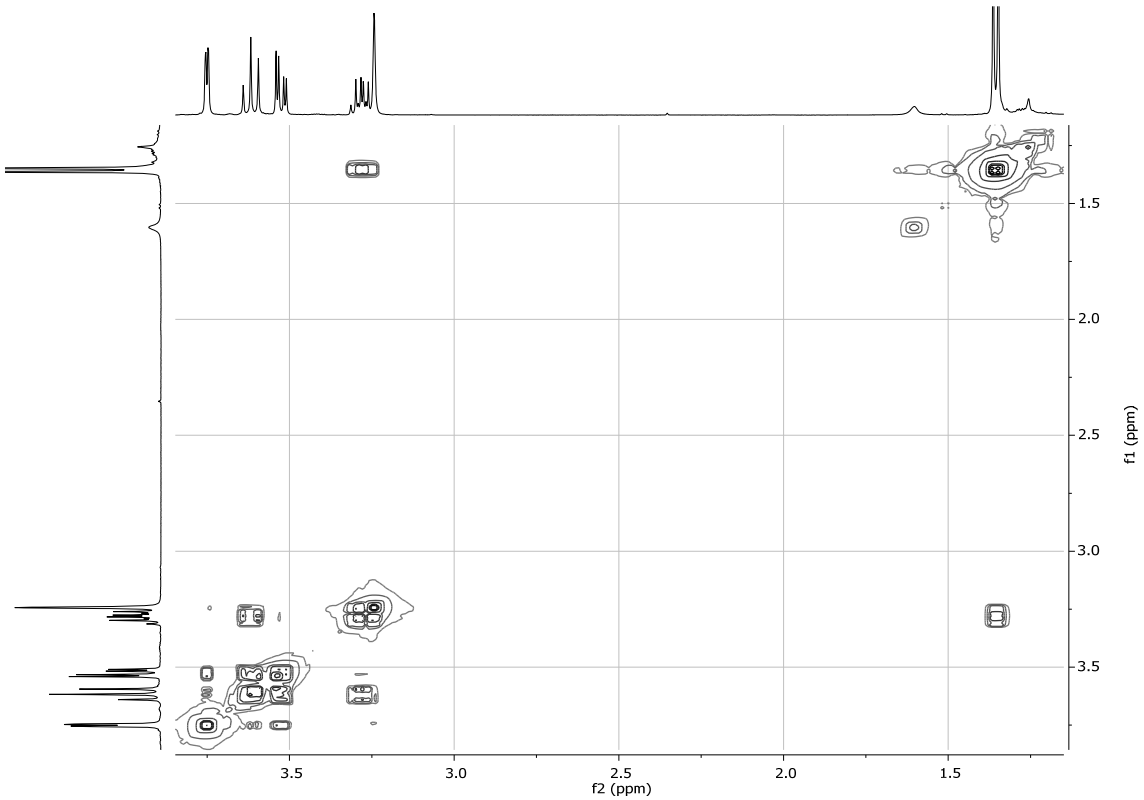
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S45** (pre-activation Tf_2O/Ph_2SO based *D*-glycosylation in DCM)



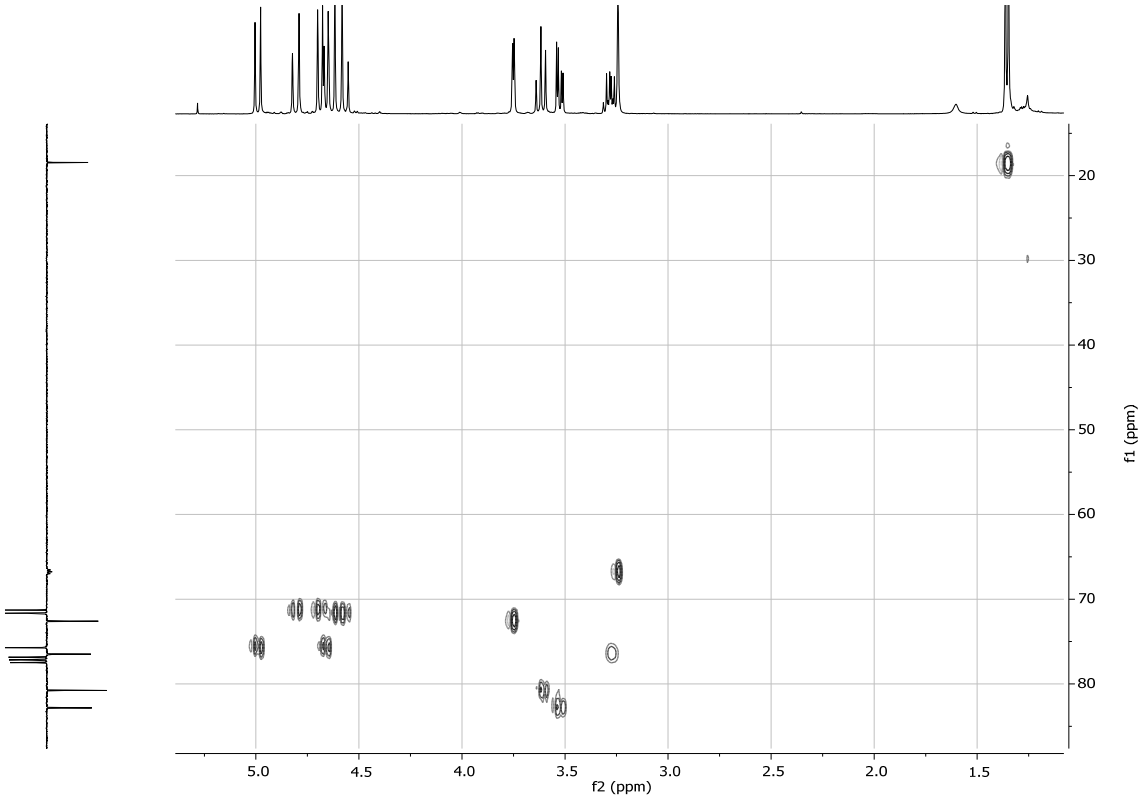
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S45**



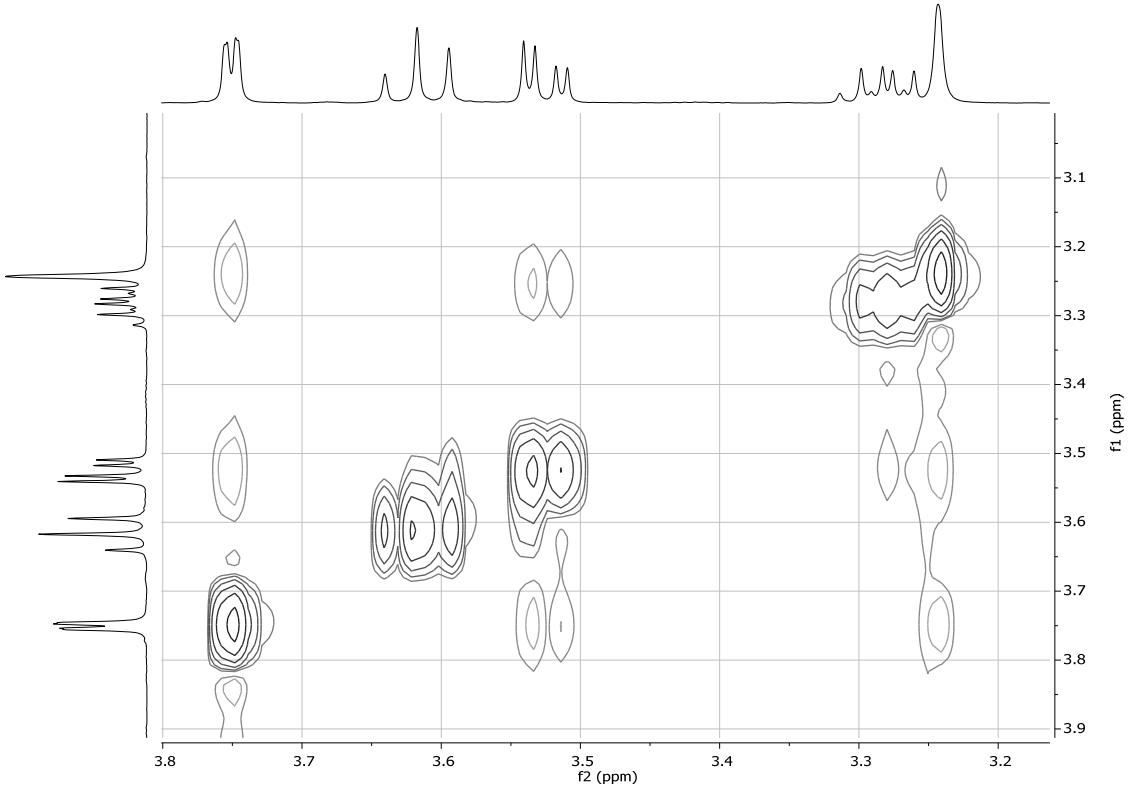
HH-COSY NMR, $CDCl_3$ of compound **S45**



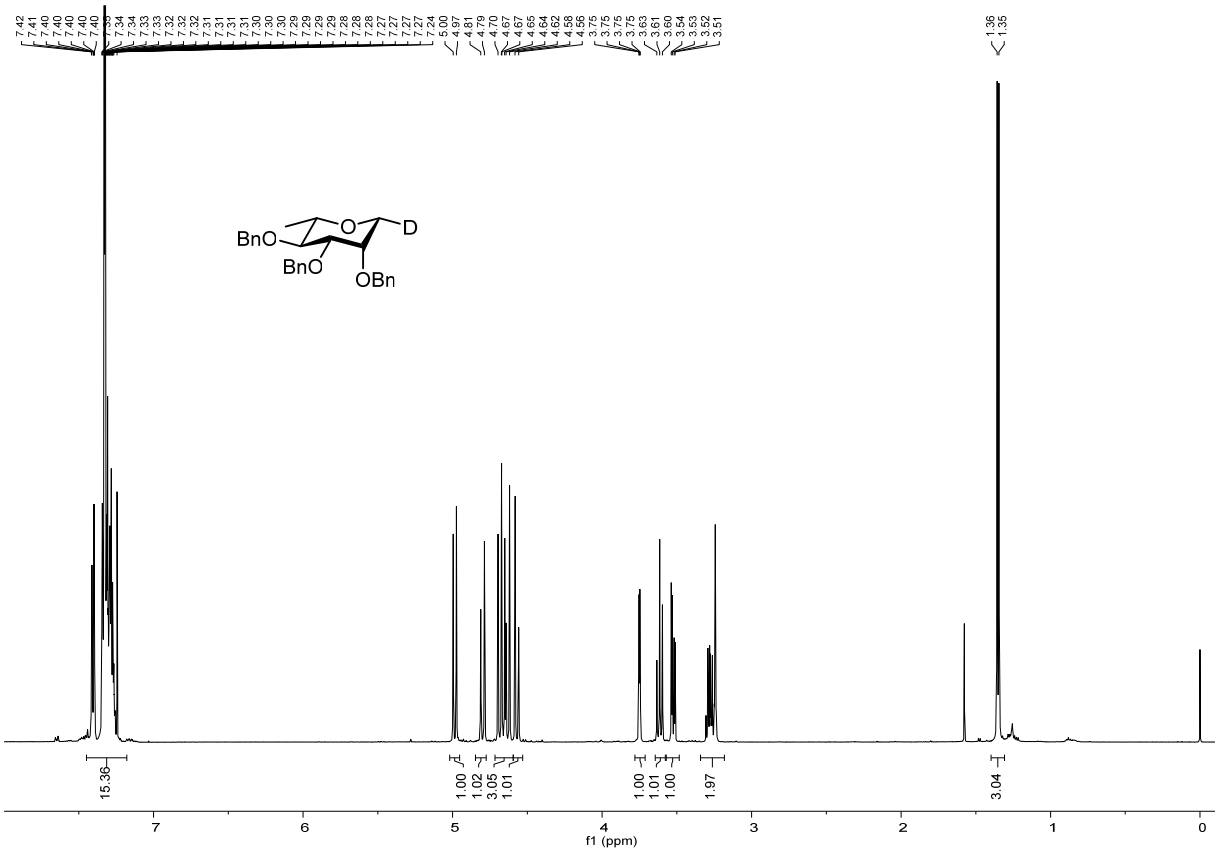
HSQC NMR, $CDCl_3$ of compound **S45**



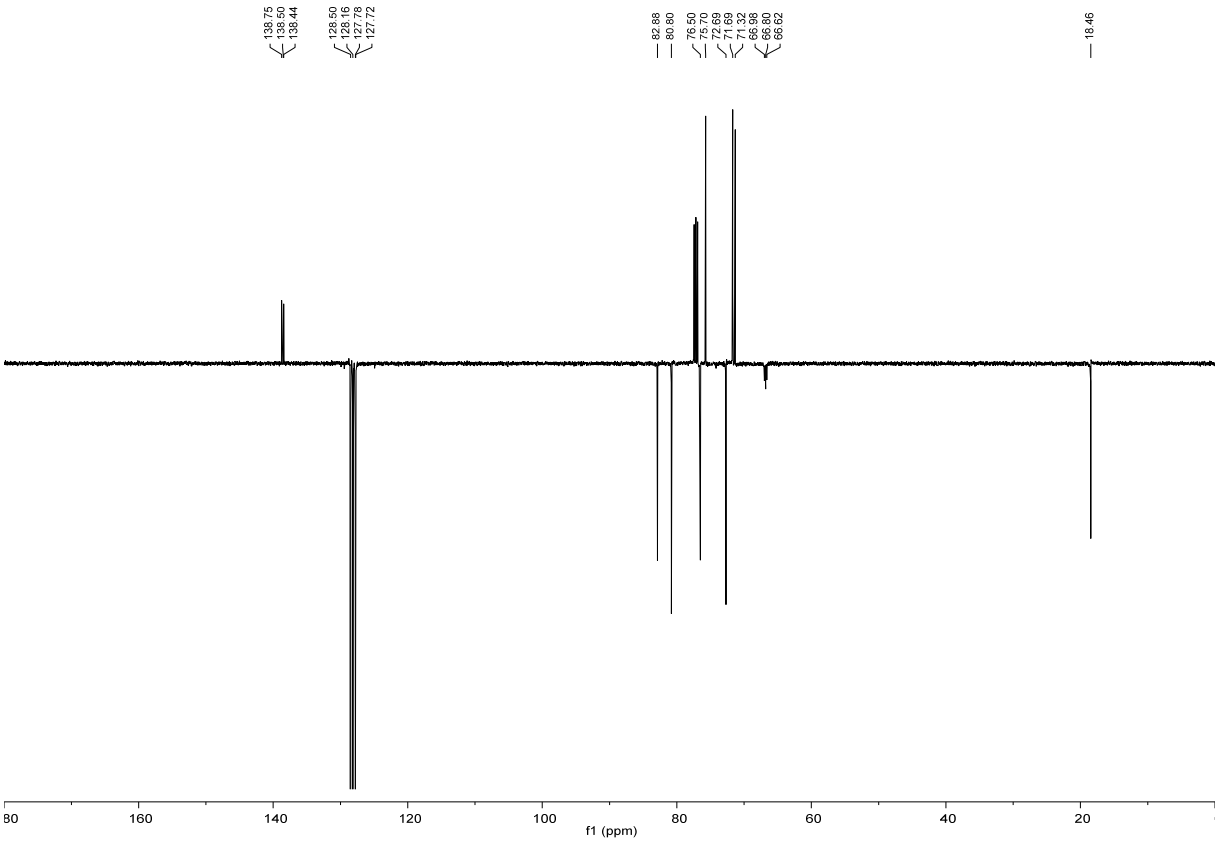
NOESY NMR, $CDCl_3$ of compound **S45**



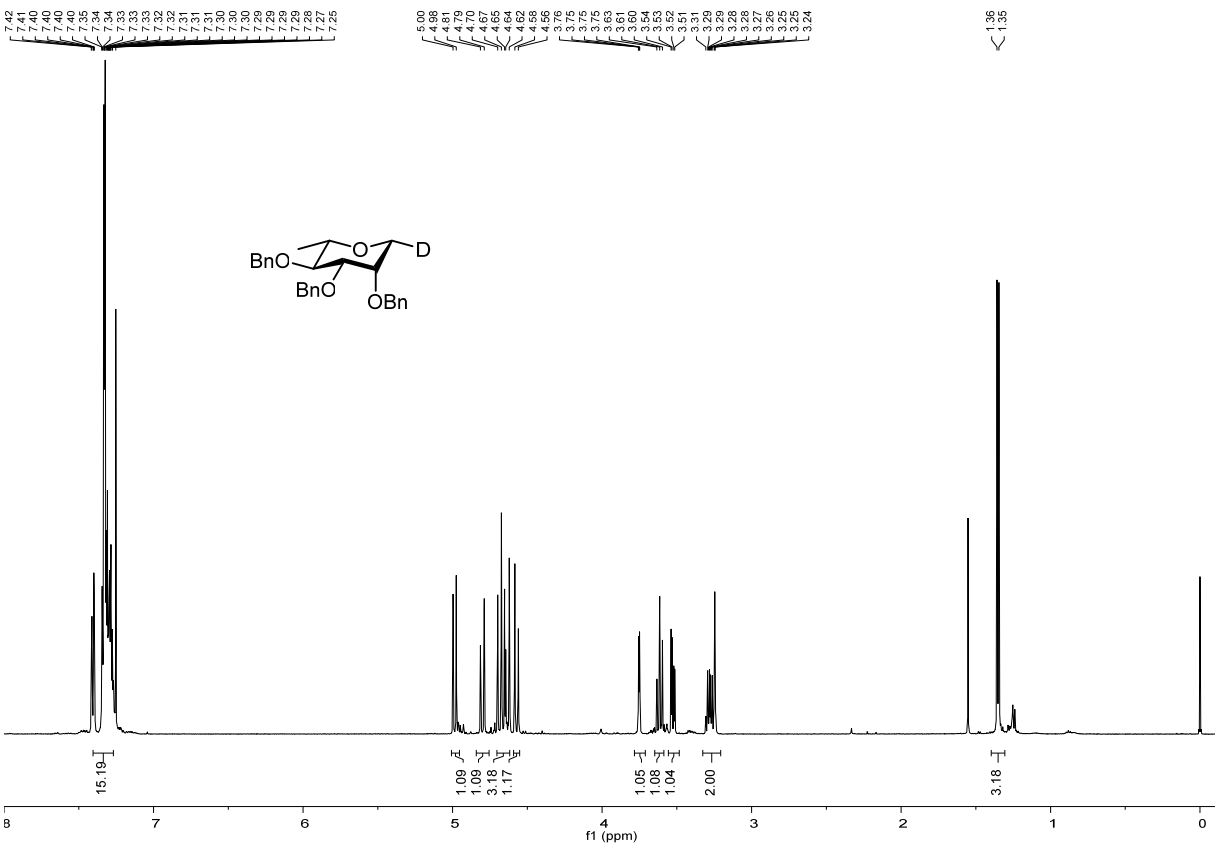
^1H NMR, 400 MHz, $CDCl_3$ of compound **S45** (pre-activation Tf_2O/Ph_2SO based *D*-glycosylation in Et_2O)



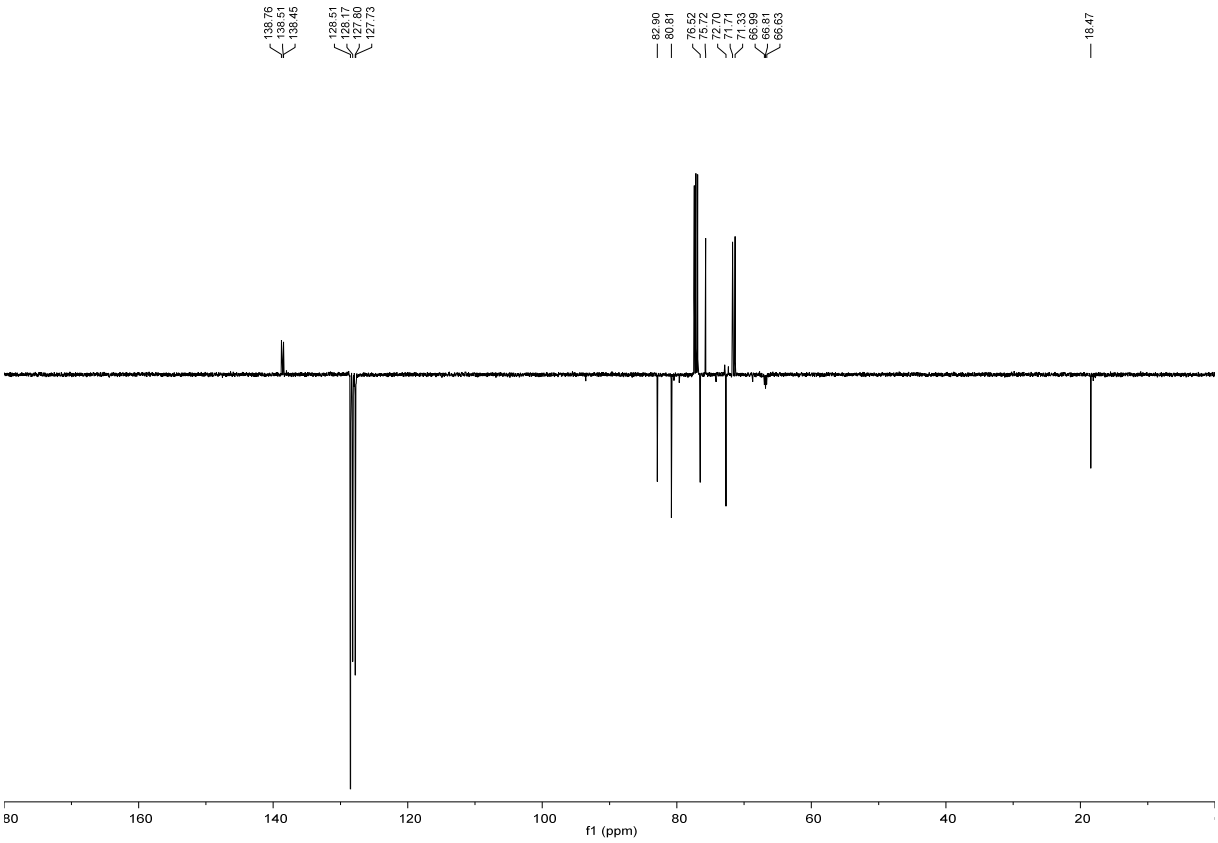
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S45**



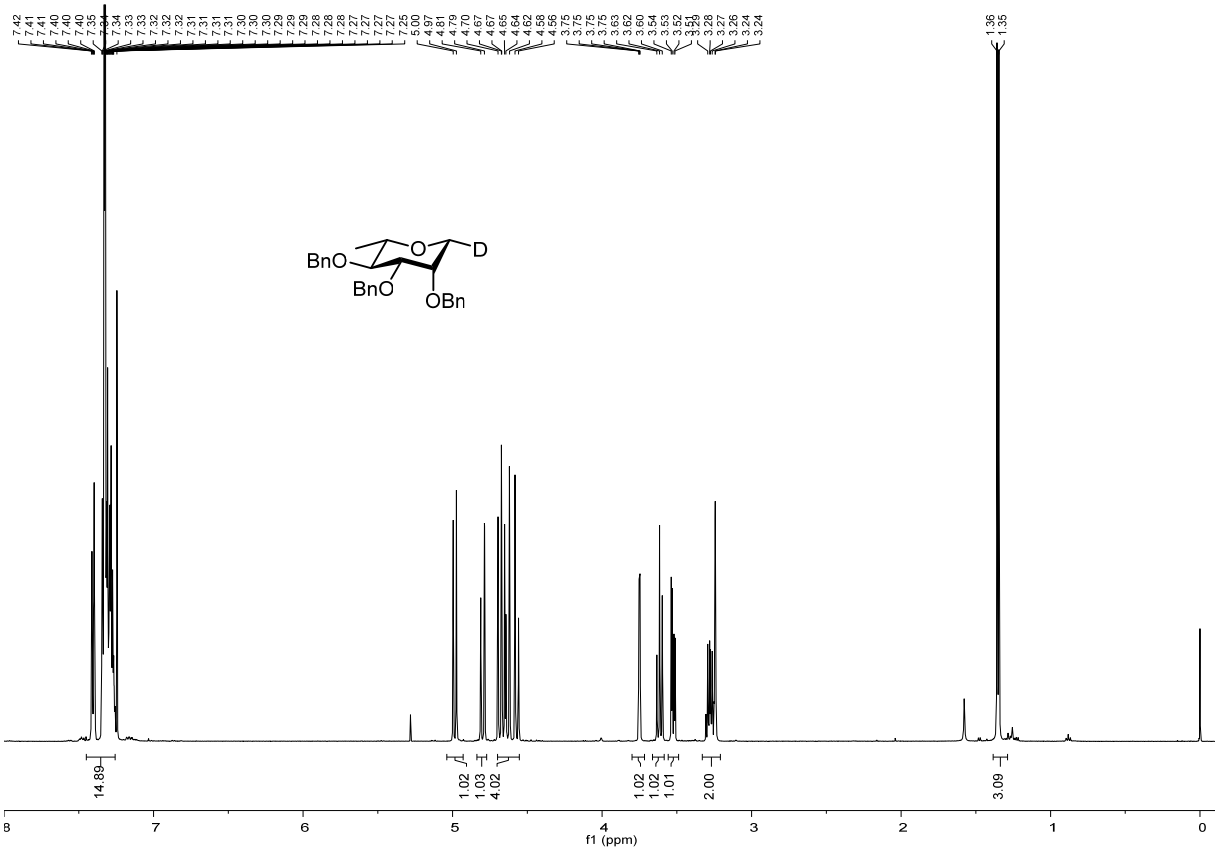
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S45** (pre-activation Tf_2O/Ph_2SO based *D*-glycosylation in MeCN)



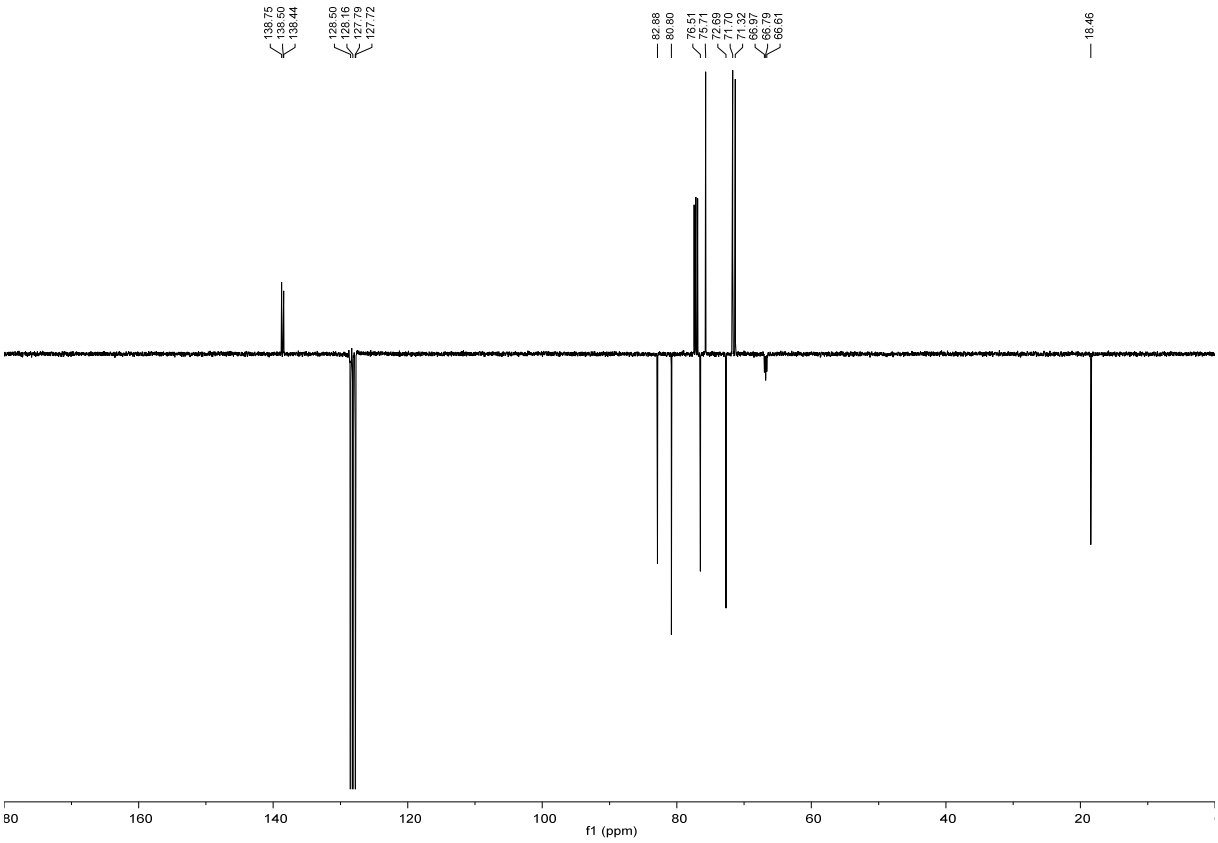
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S45**



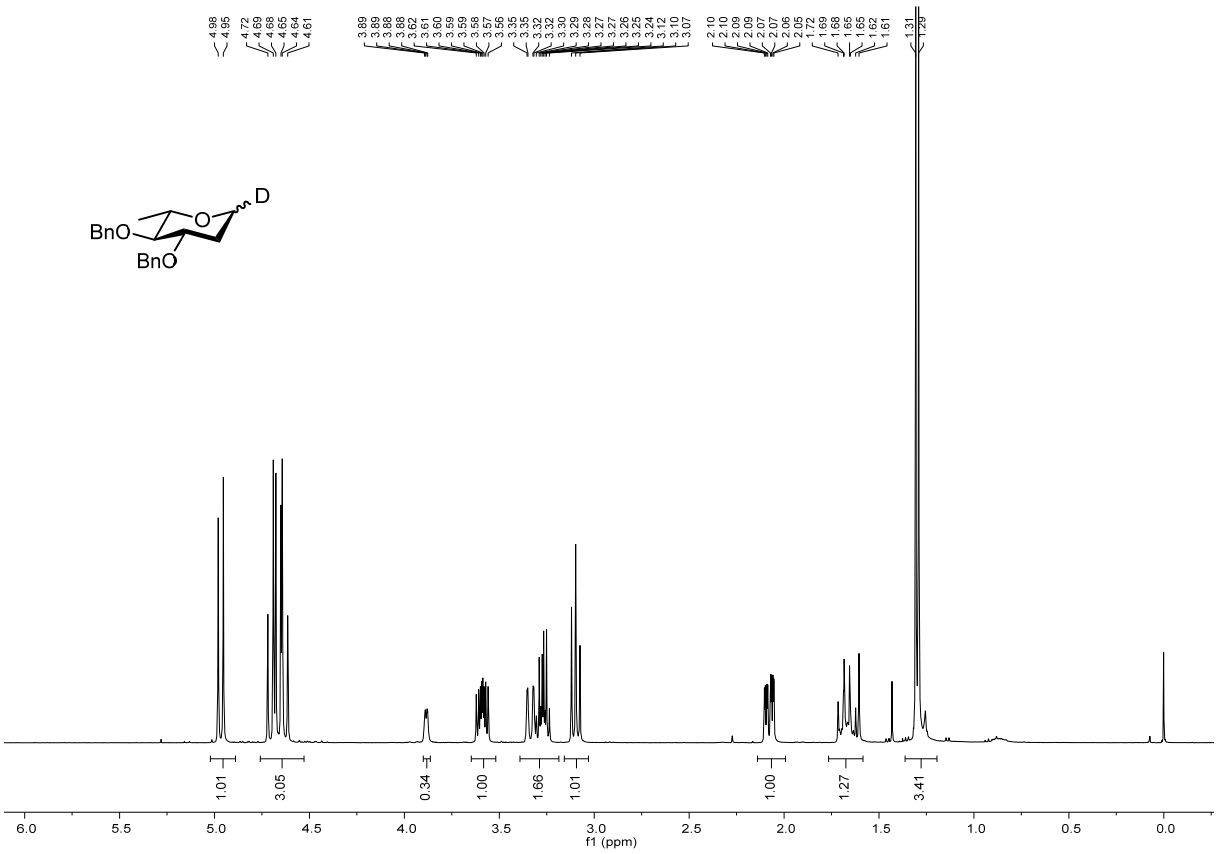
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S45** (TMSOTf activation based *D*-glycosylation)



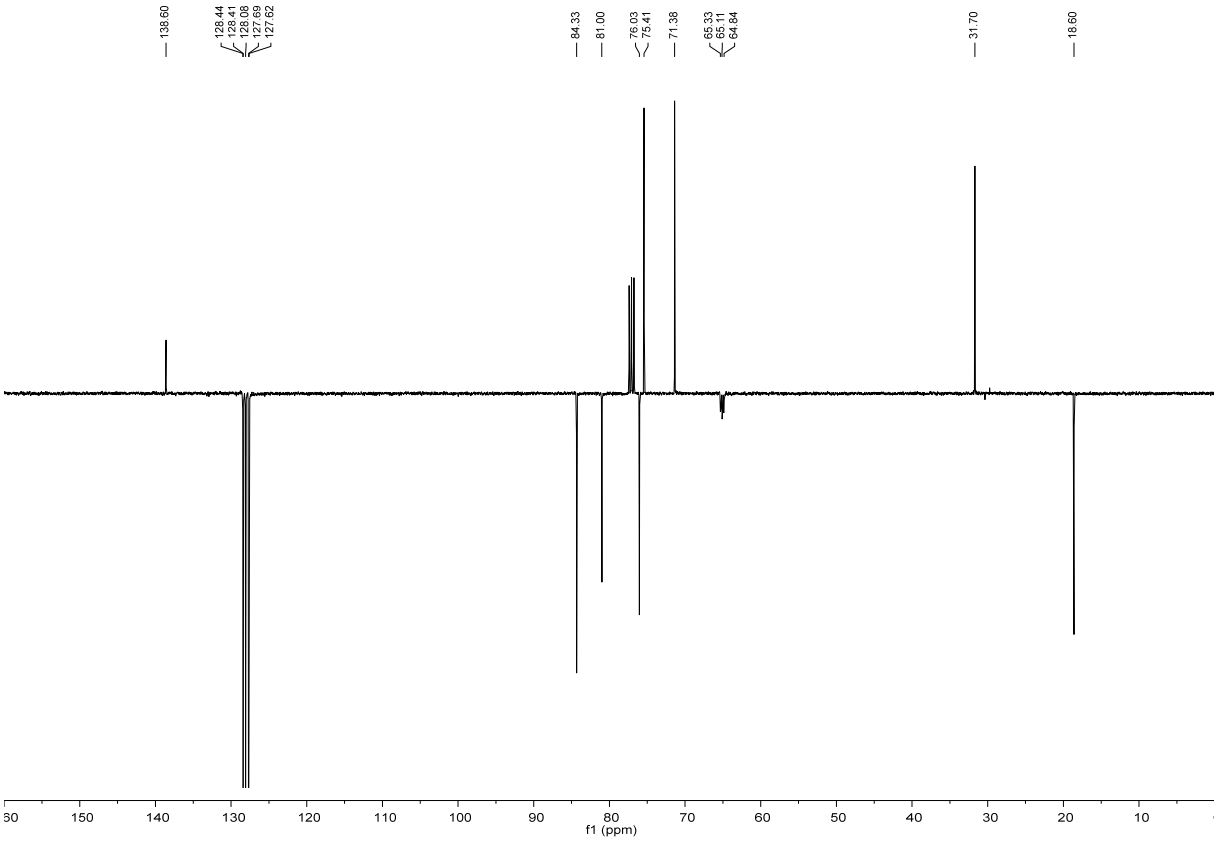
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S45**



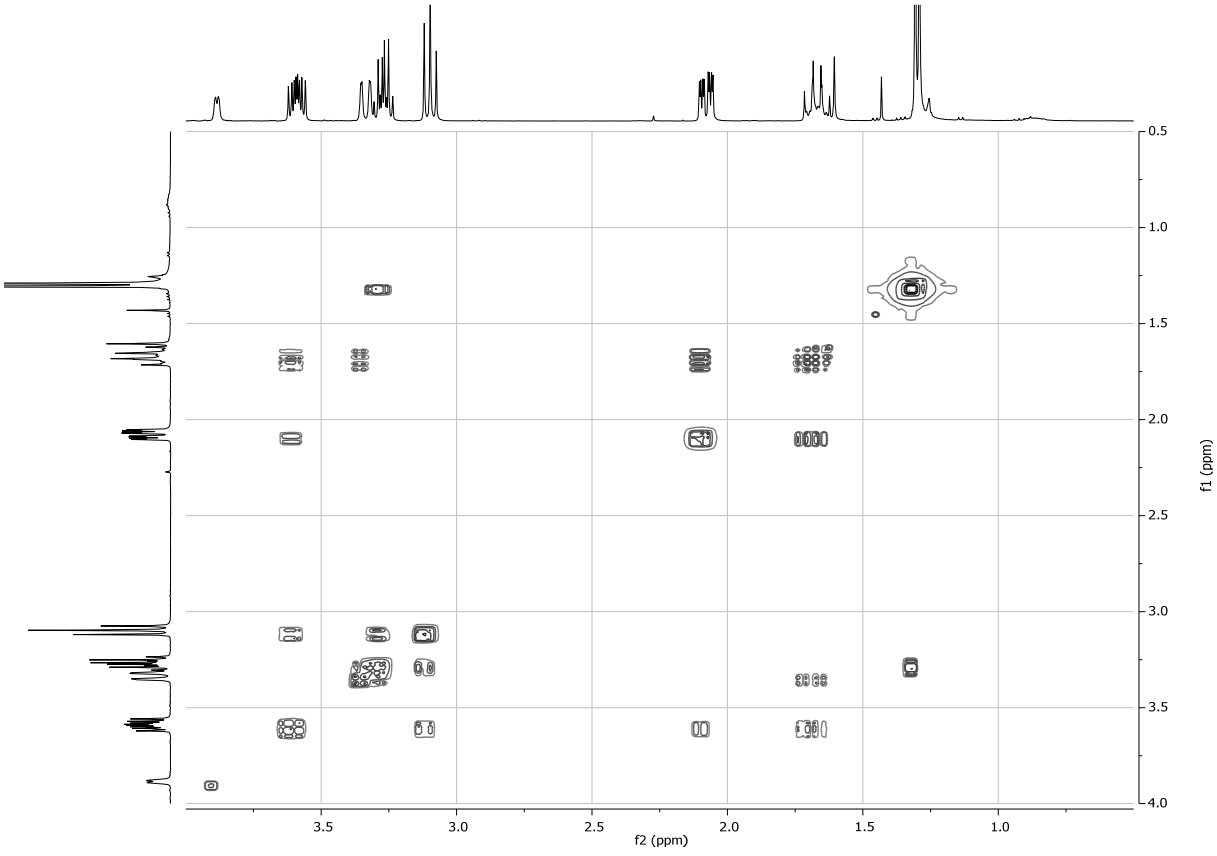
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S46**



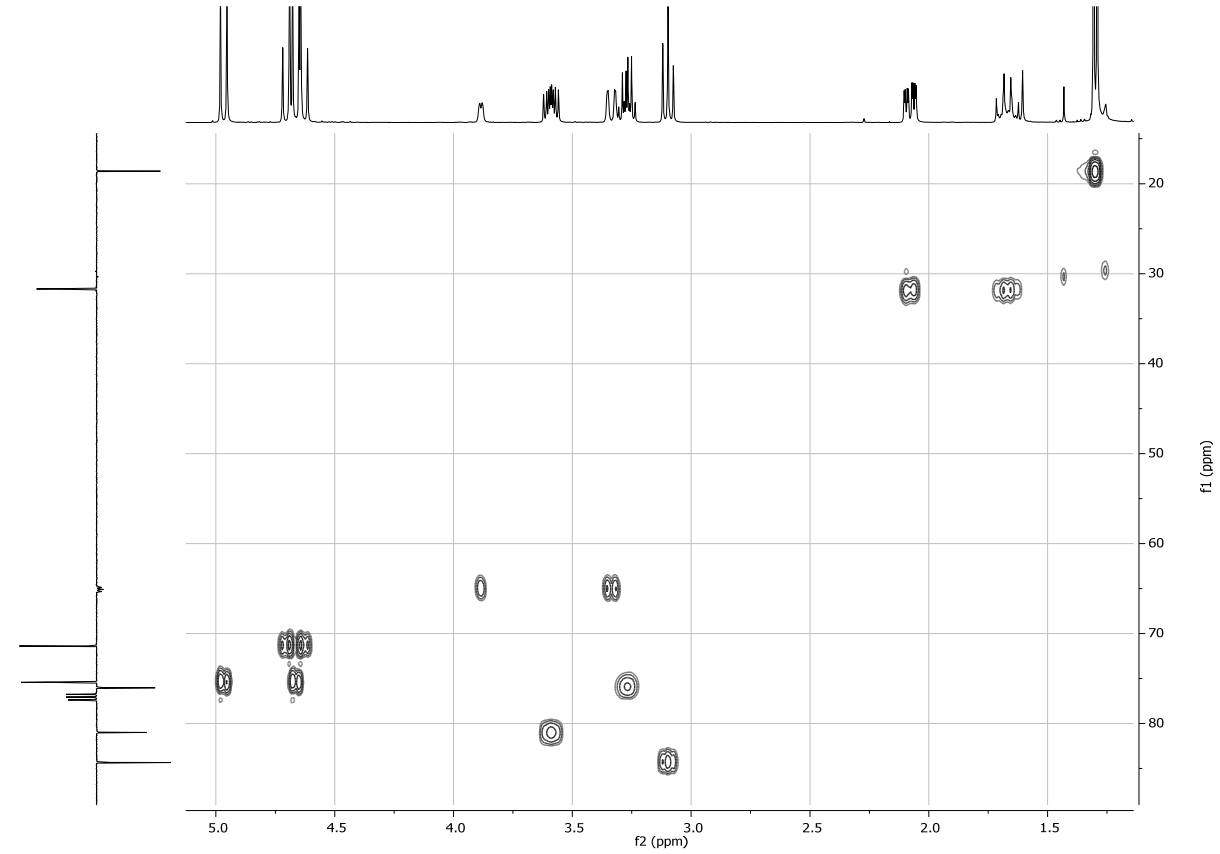
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S46**



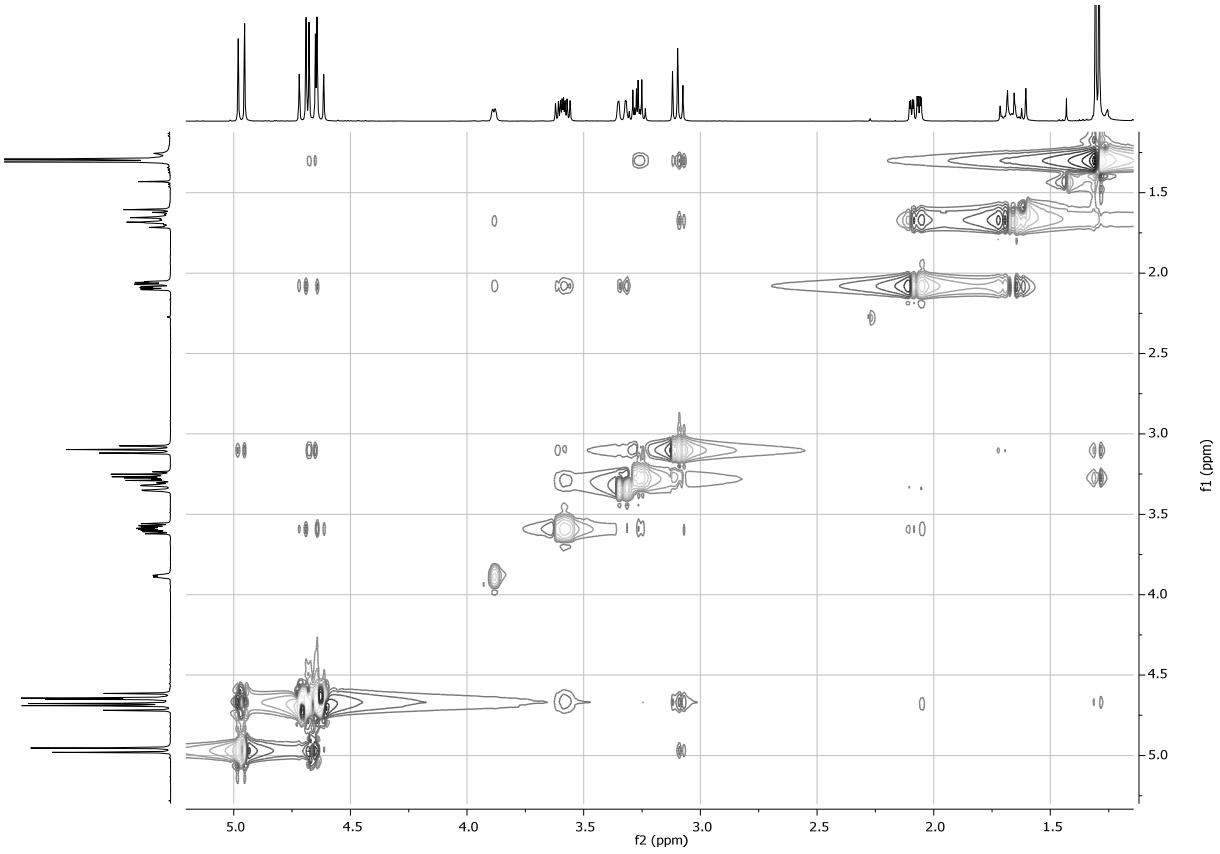
HH-COSY NMR, $CDCl_3$ of compound **S46**



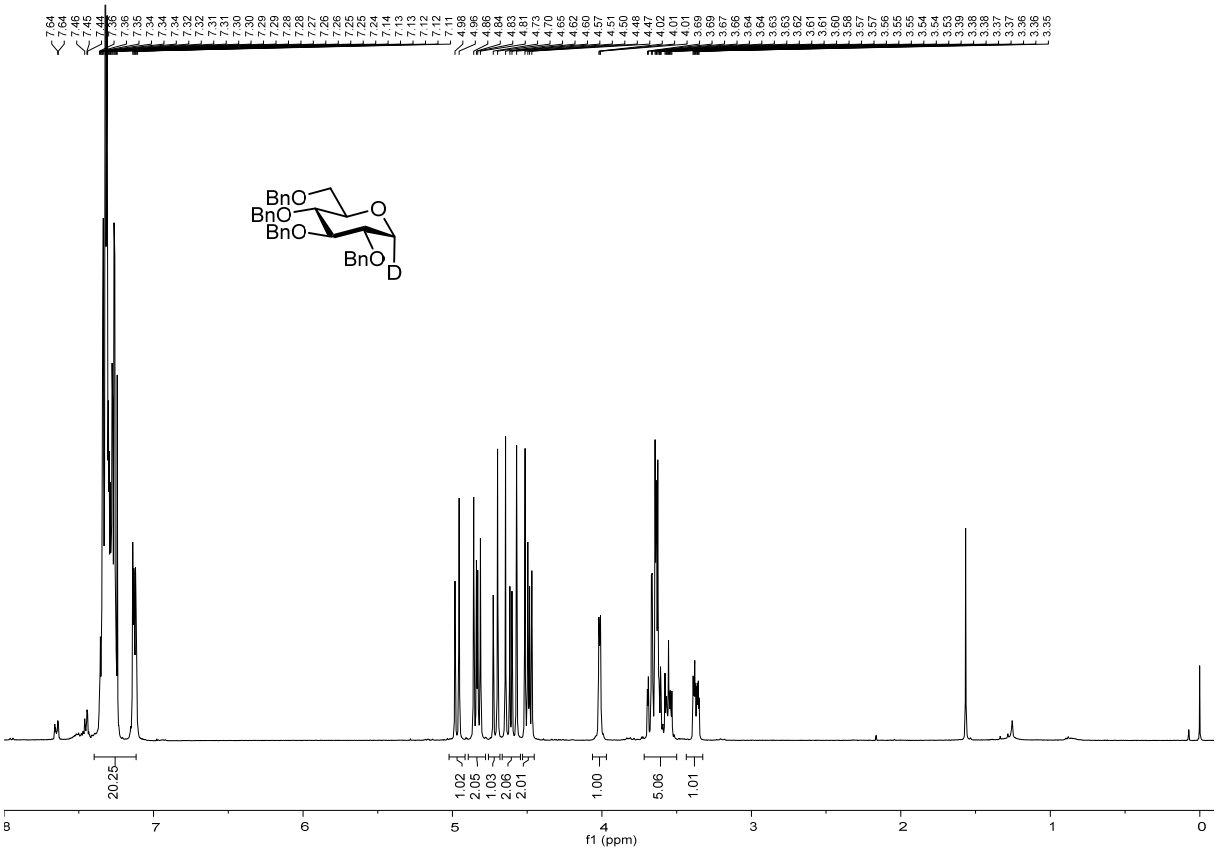
HSQC NMR, $CDCl_3$ of compound **S46**



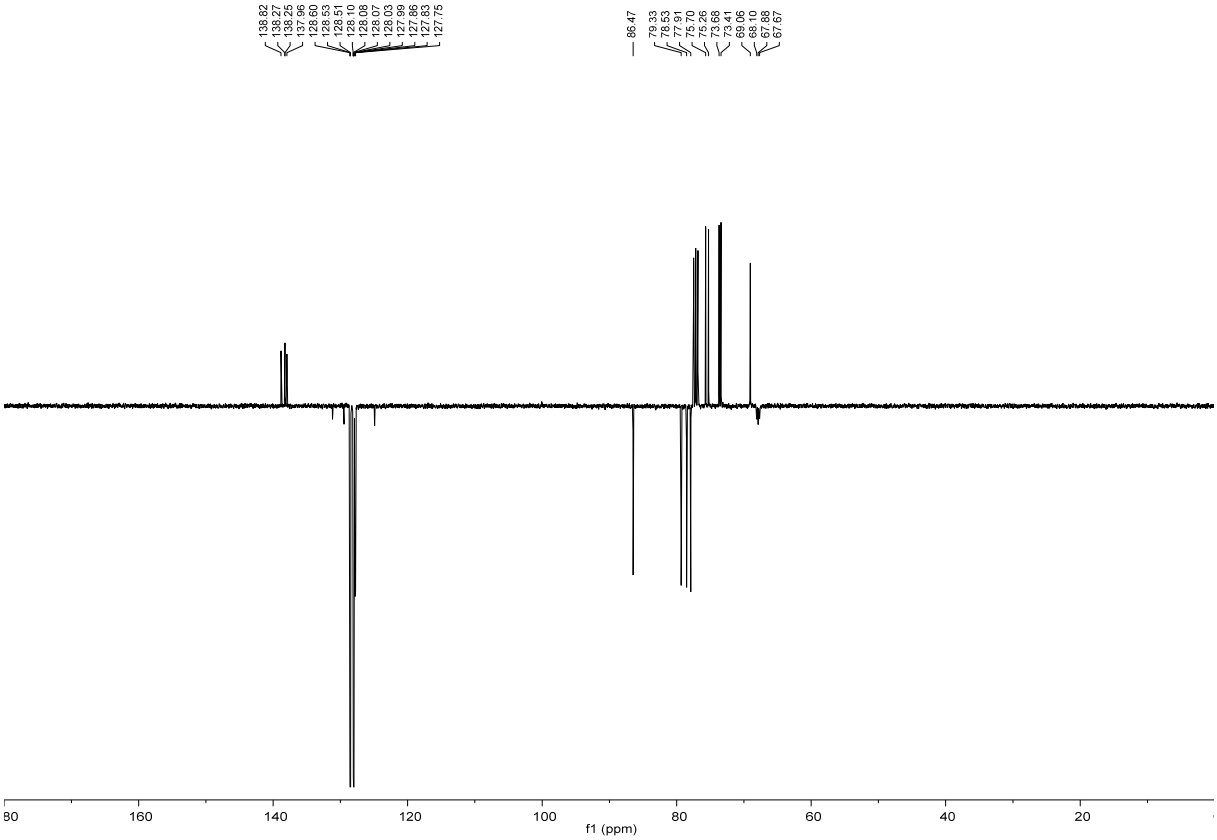
NOESY NMR, $CDCl_3$ of compound **S46**



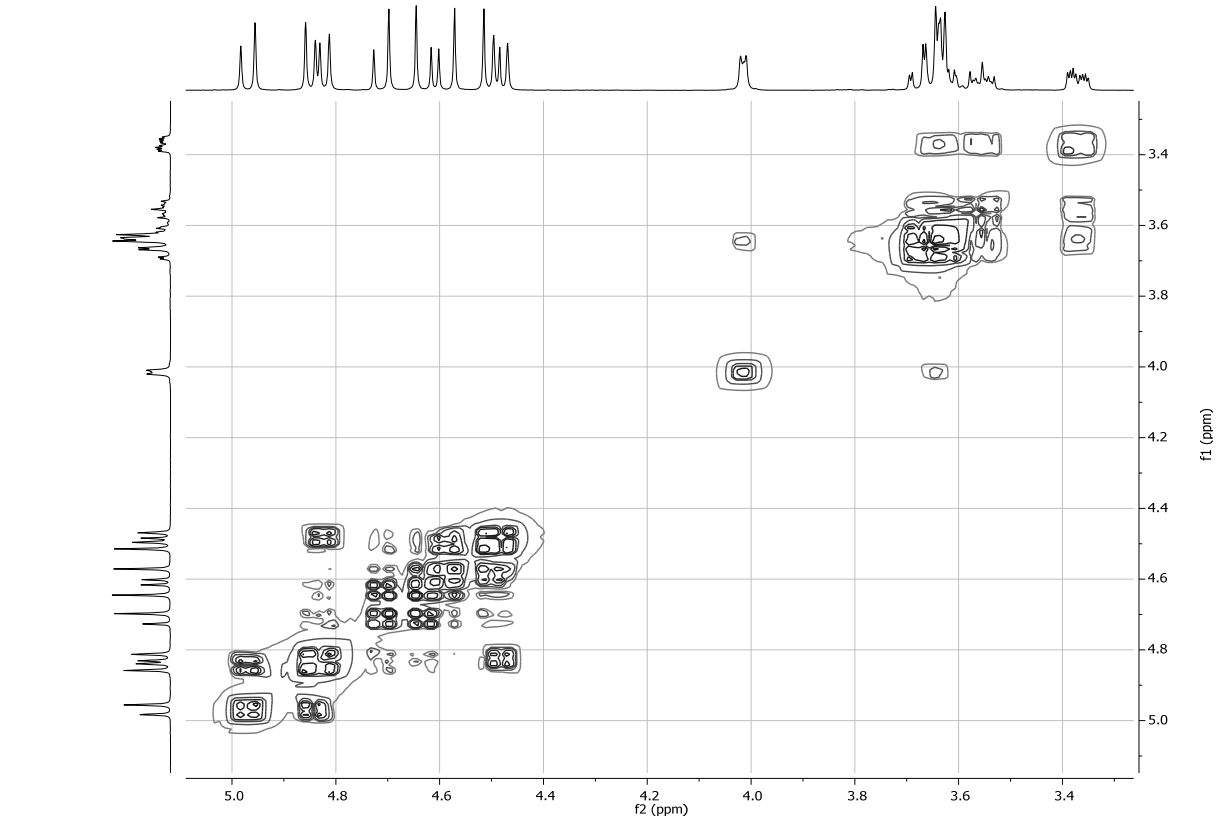
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S47** (pre-activation Tf_2O/Ph_2SO based *D*-glycosylation in DCM)



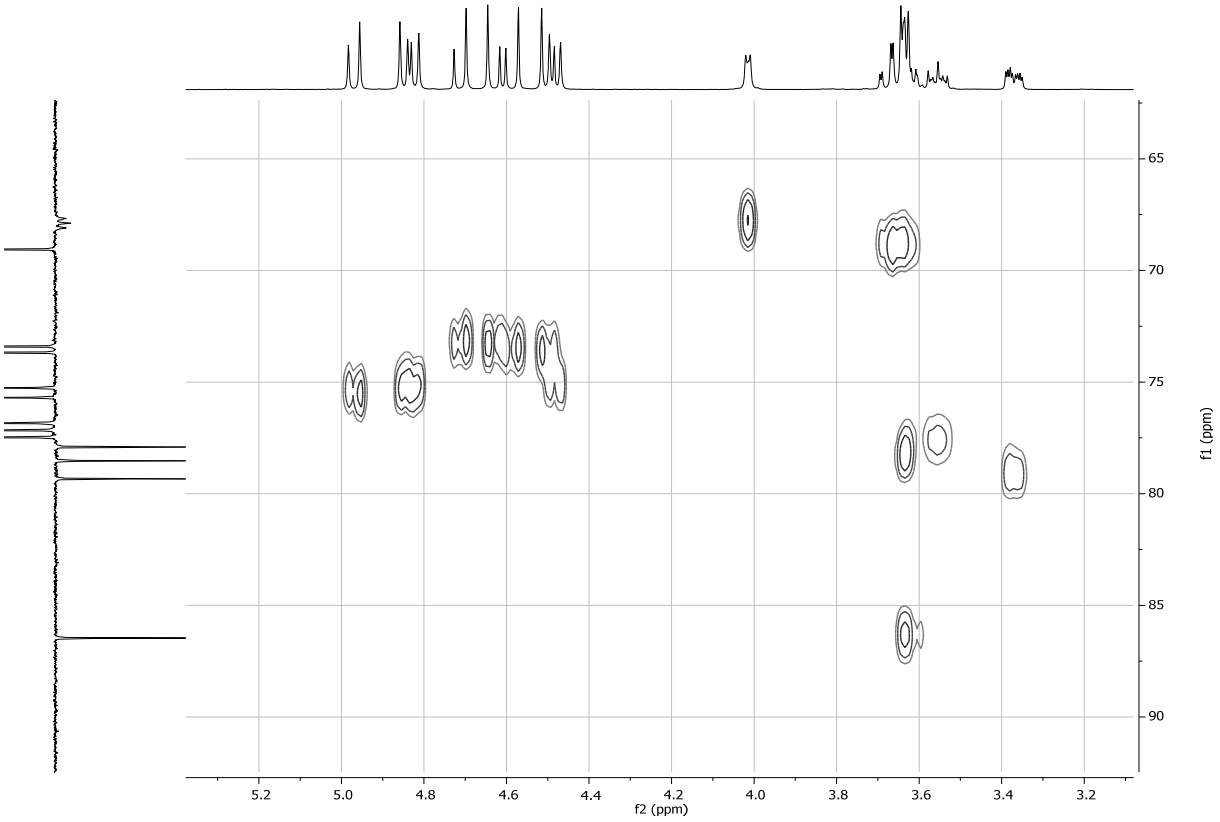
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S47**



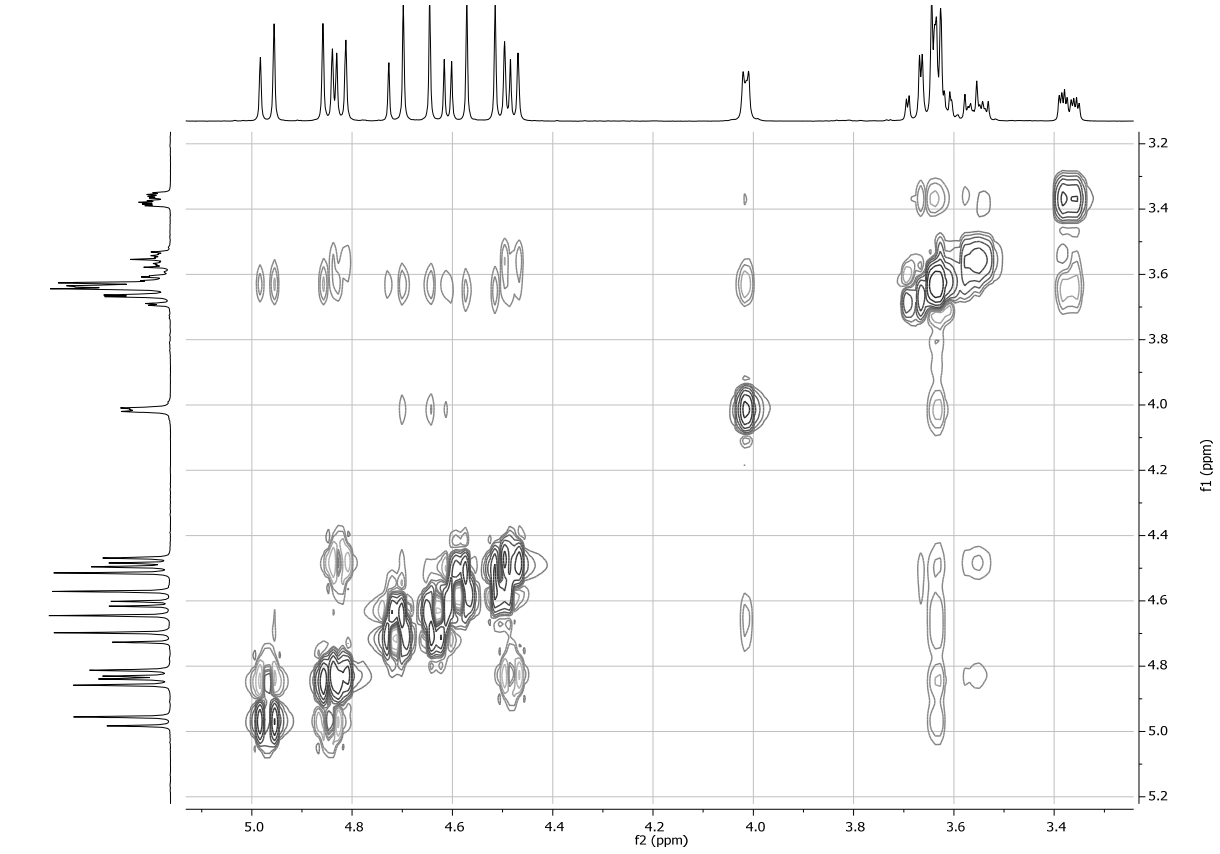
HH-COSY NMR, $CDCl_3$ of compound **S47**



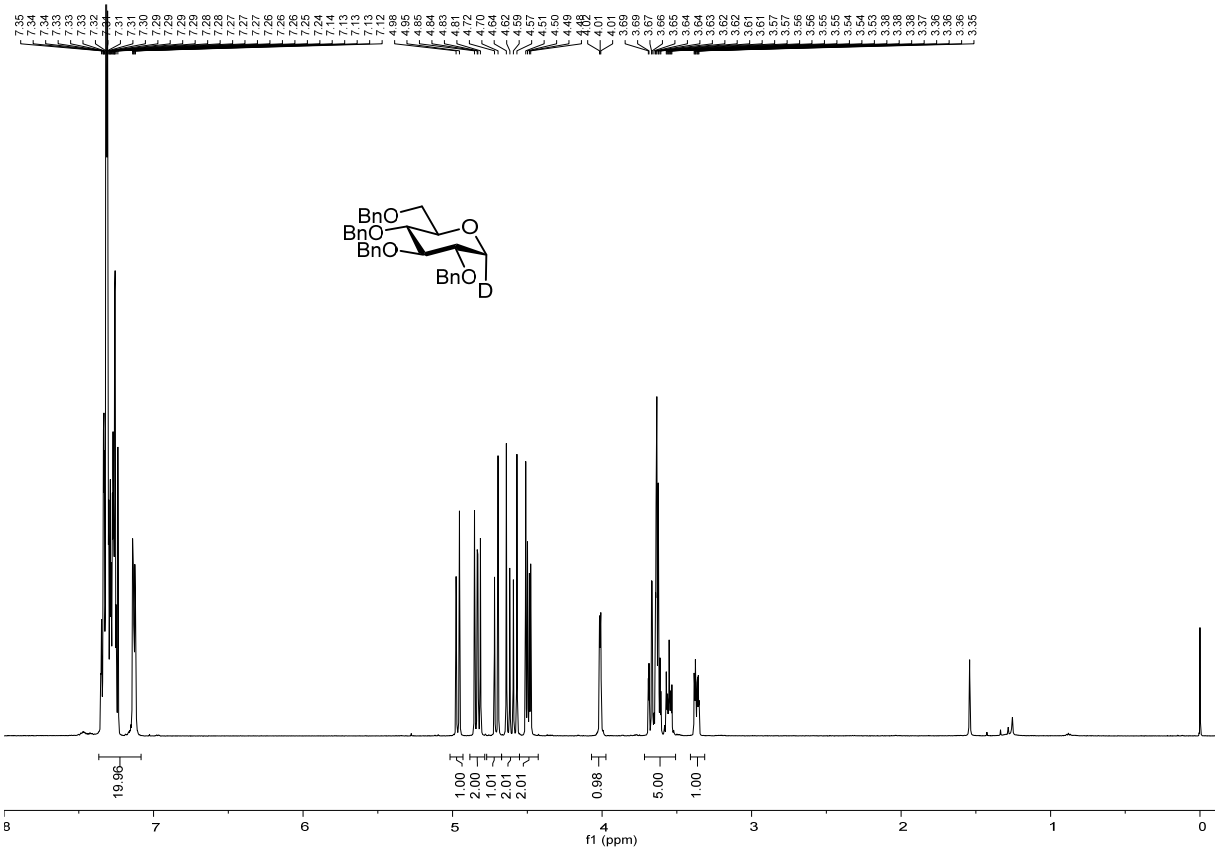
HSQC NMR, $CDCl_3$ of compound **S47**



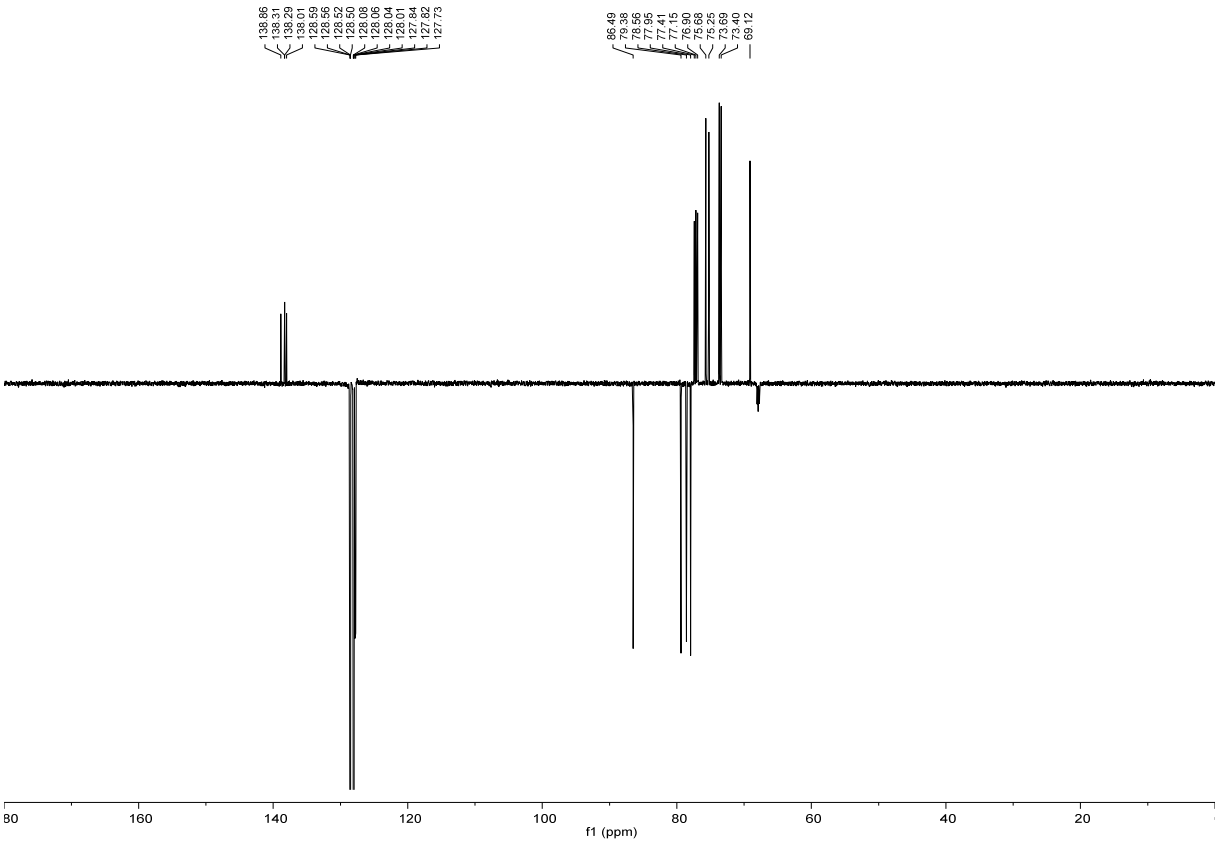
NOESY NMR, $CDCl_3$ of compound **S47**



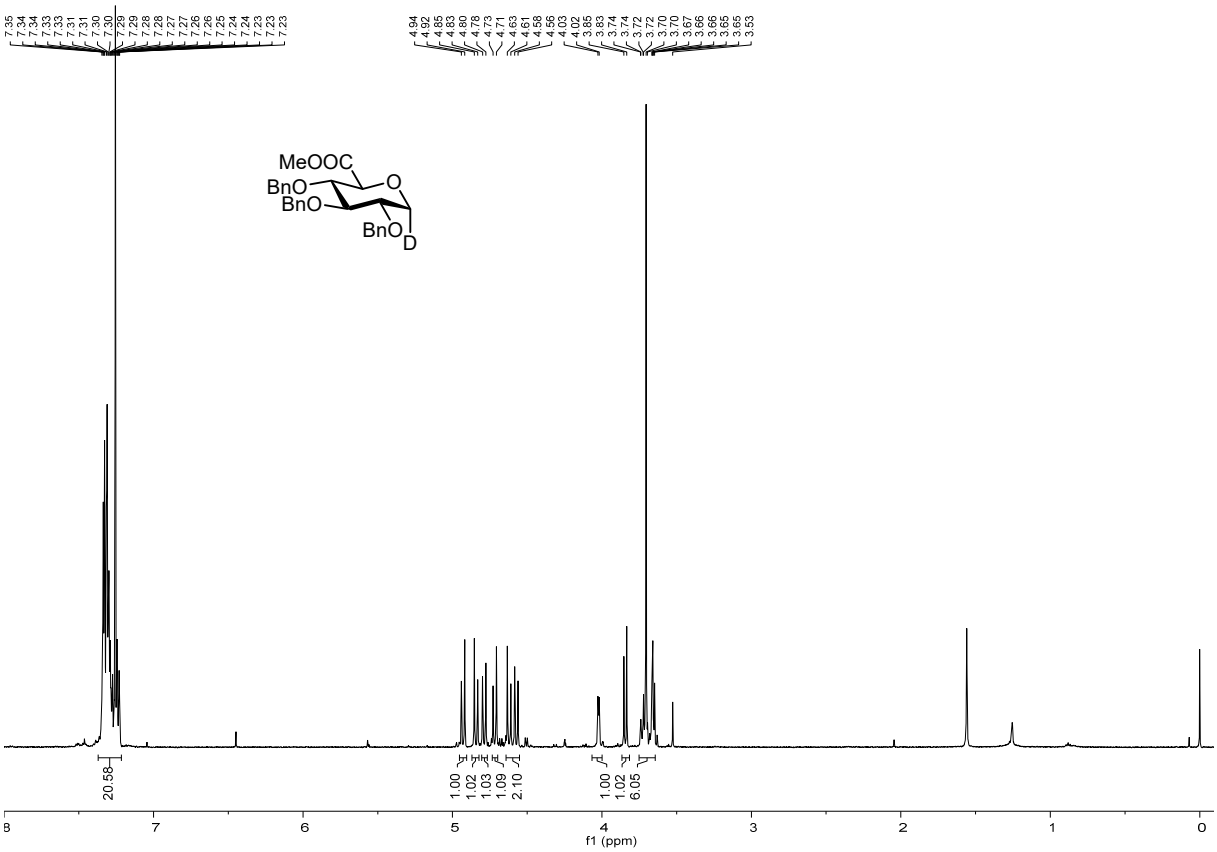
^1H NMR, 400 MHz, $CDCl_3$ of compound **S47** (TMSOTf activation based *D*-glycosylation)



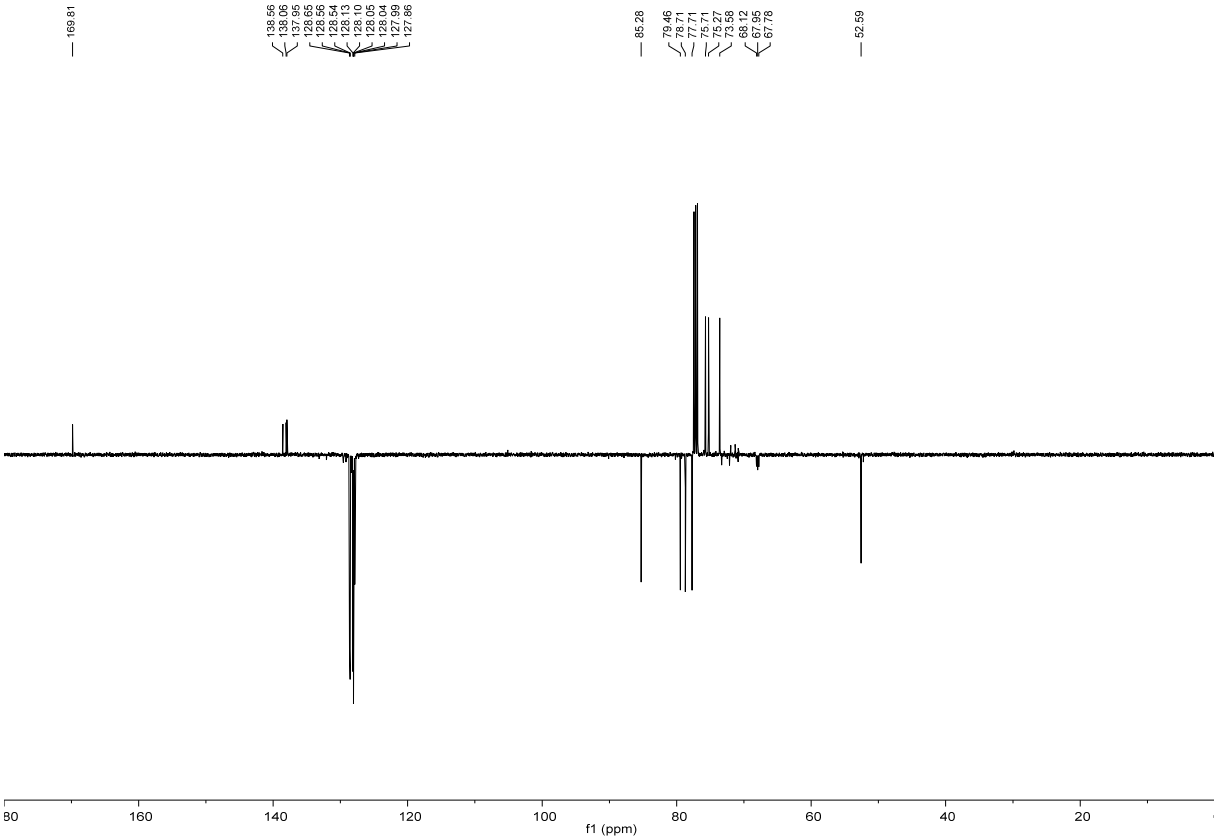
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S47**



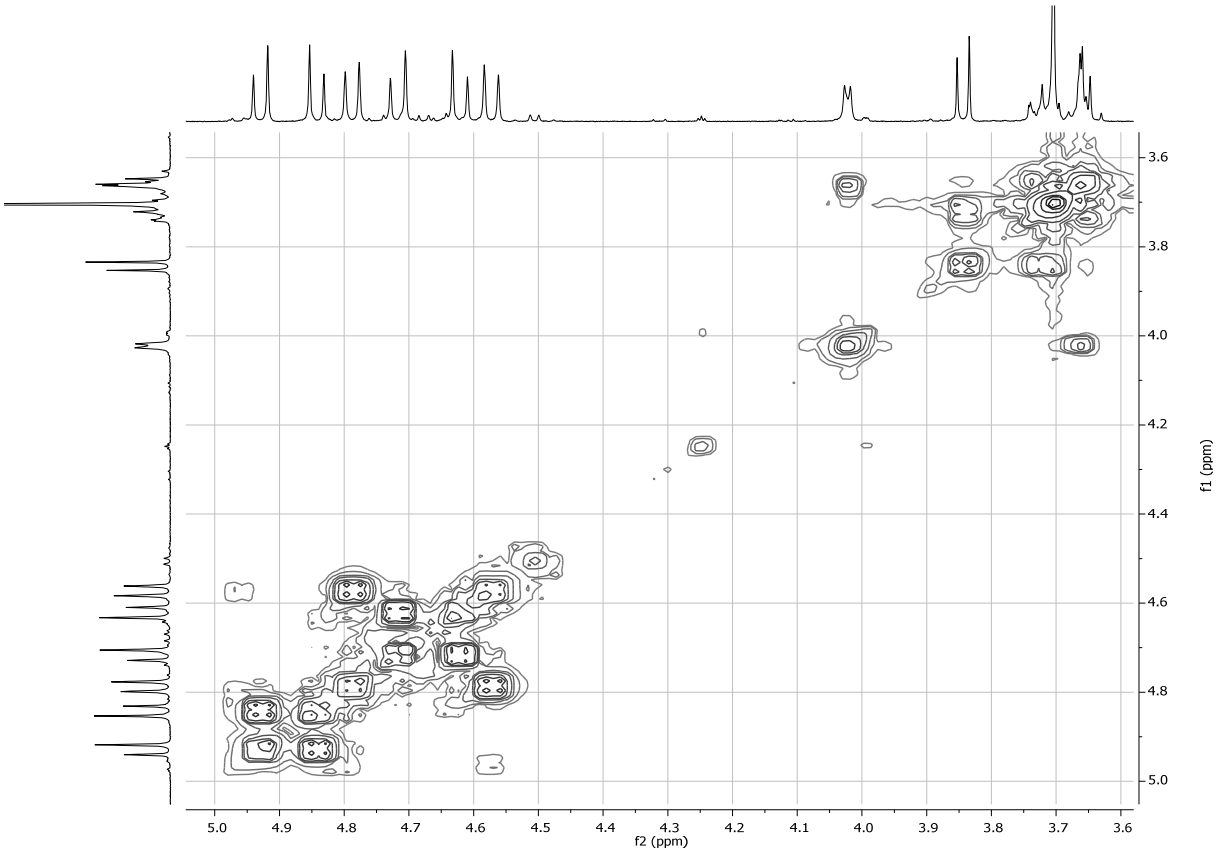
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S48**



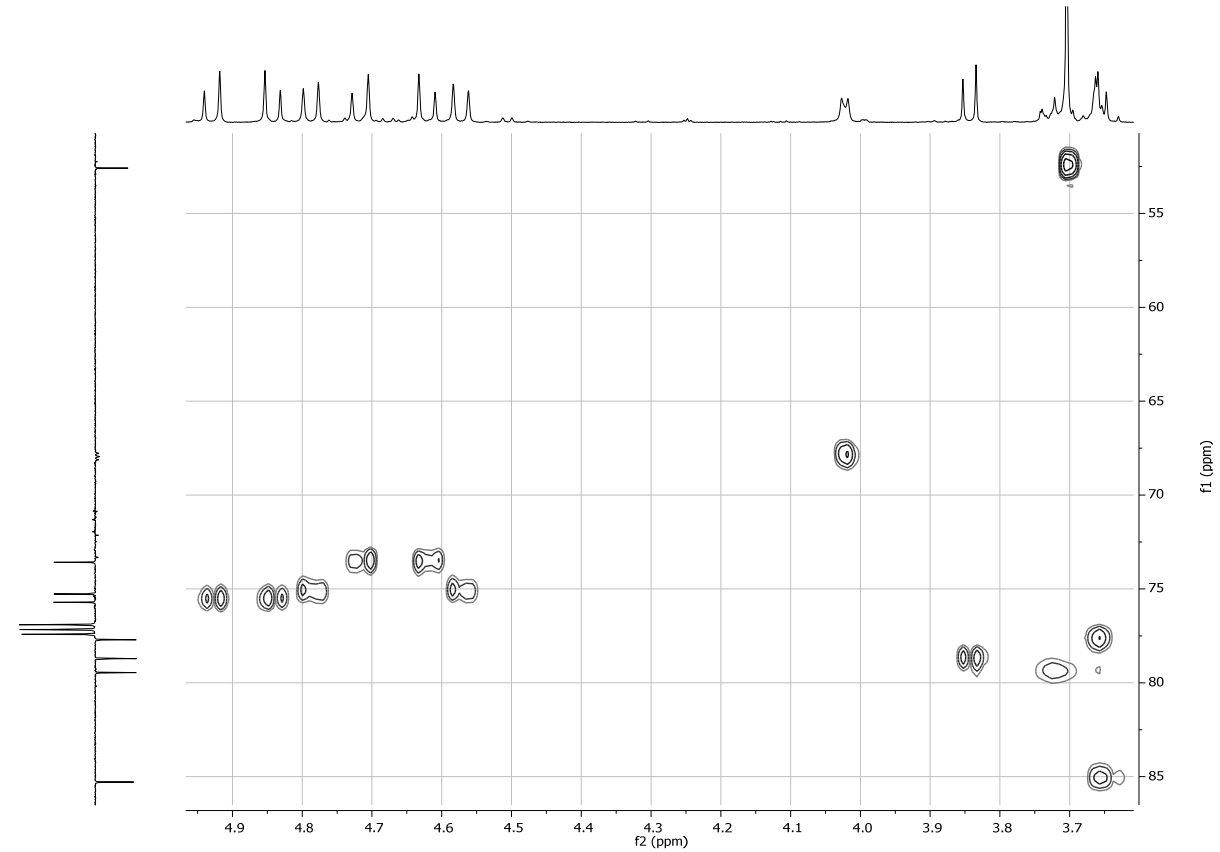
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S48**



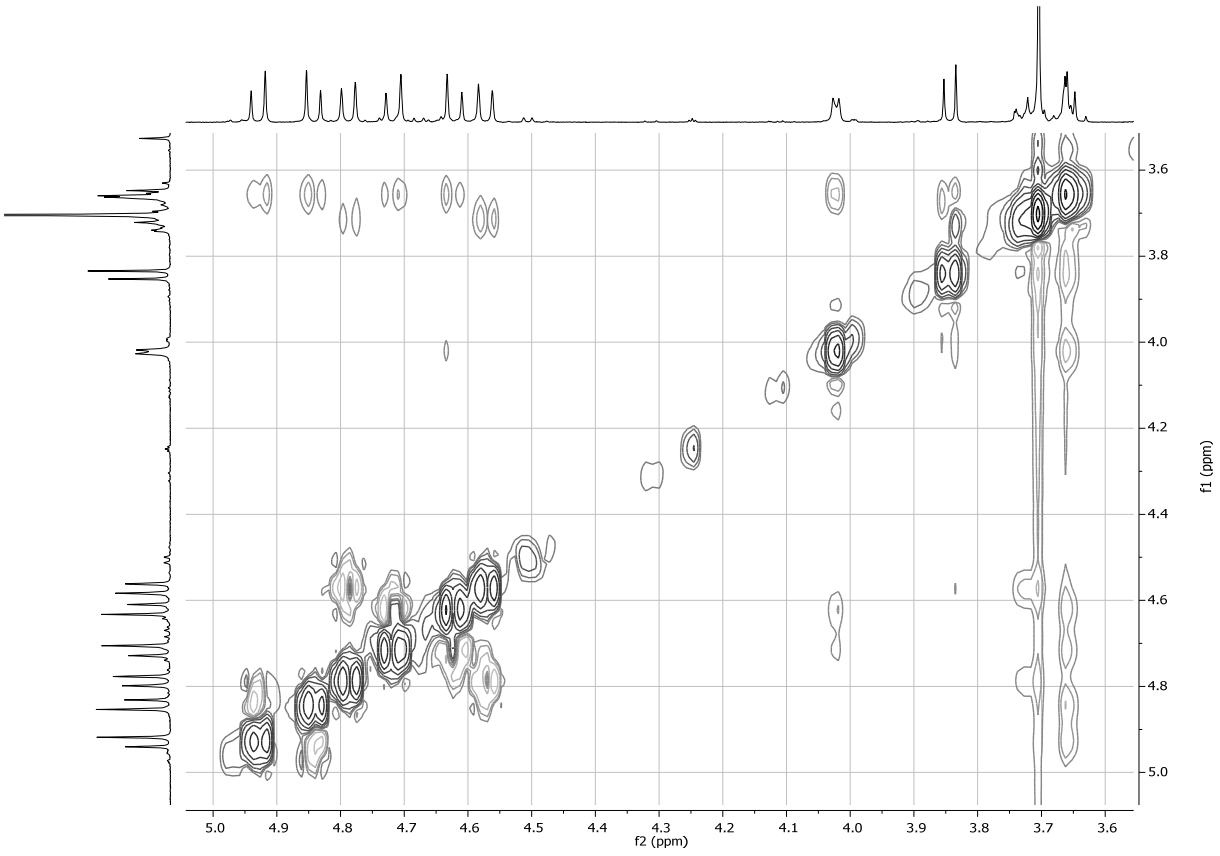
HH-COSY NMR, $CDCl_3$ of compound **S48**



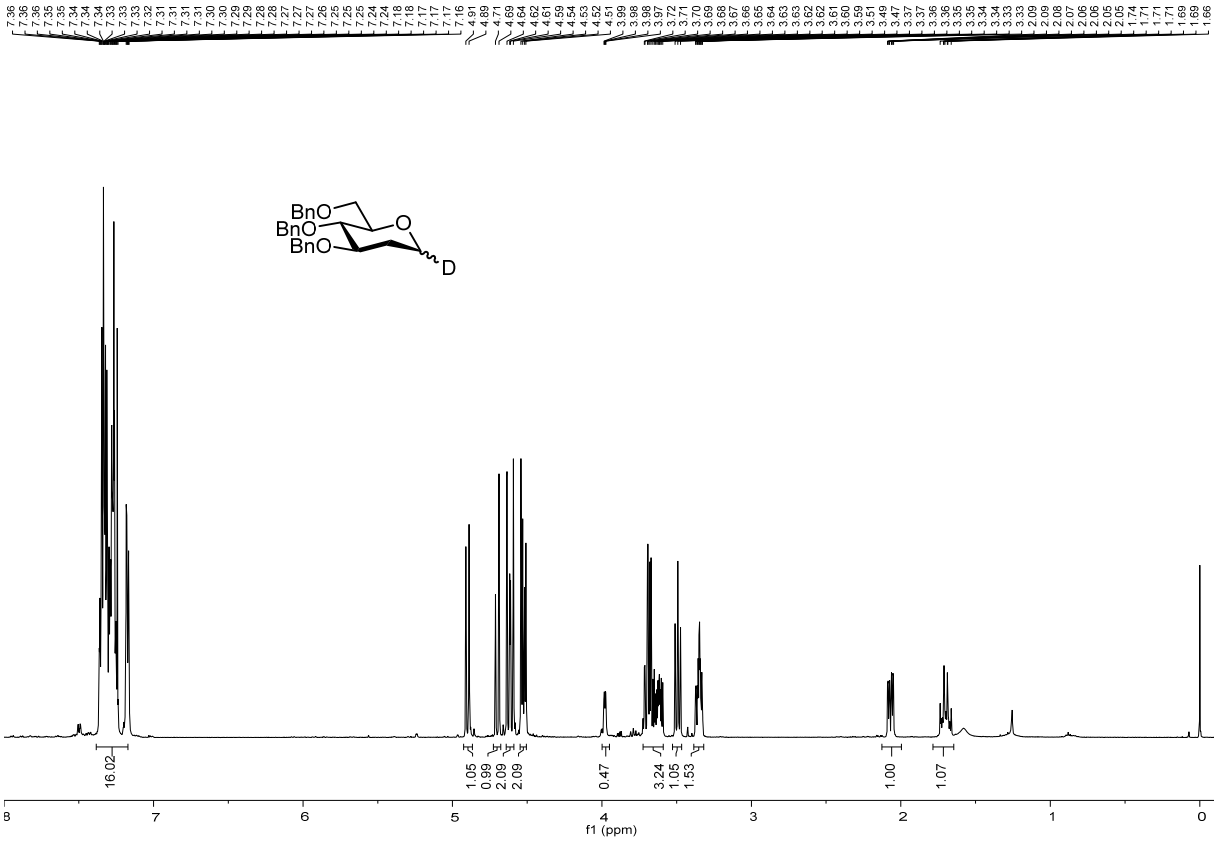
HSQC NMR, $CDCl_3$ of compound **S48**



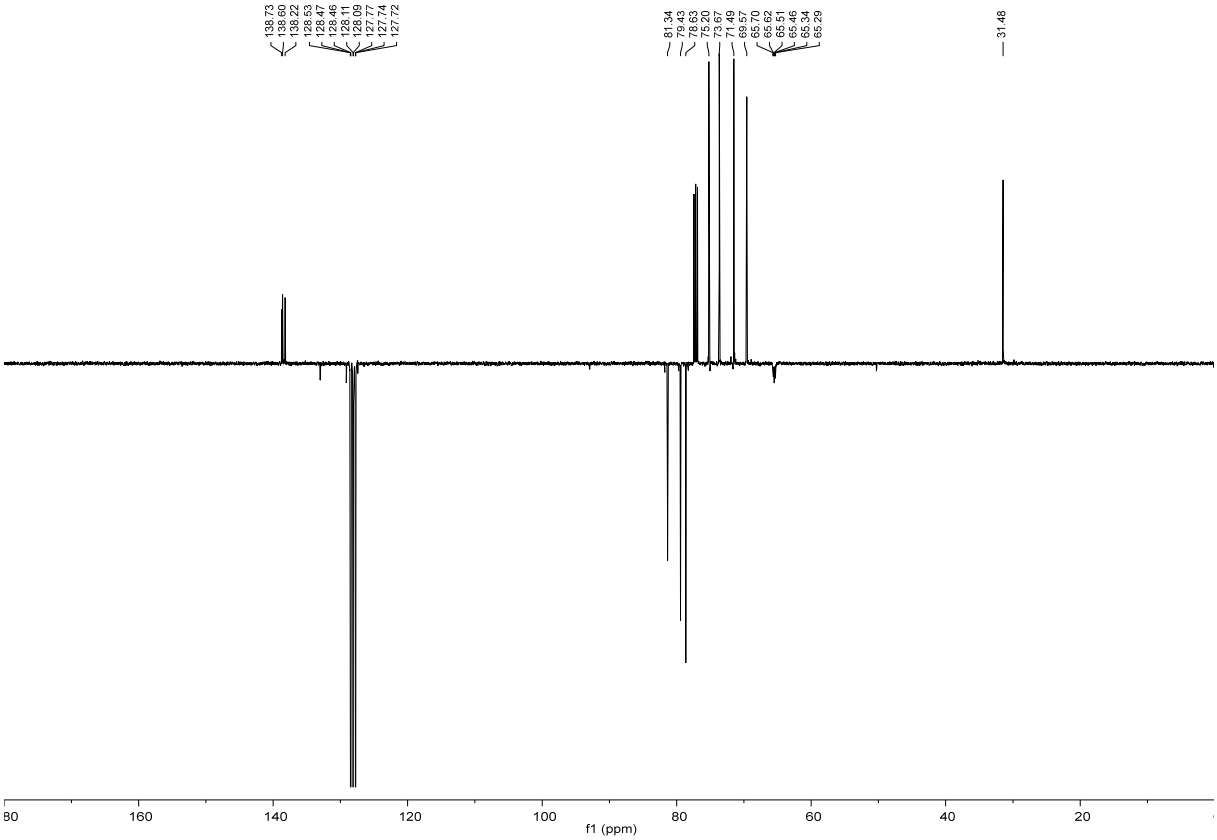
NOESY NMR, $CDCl_3$ of compound **S48**



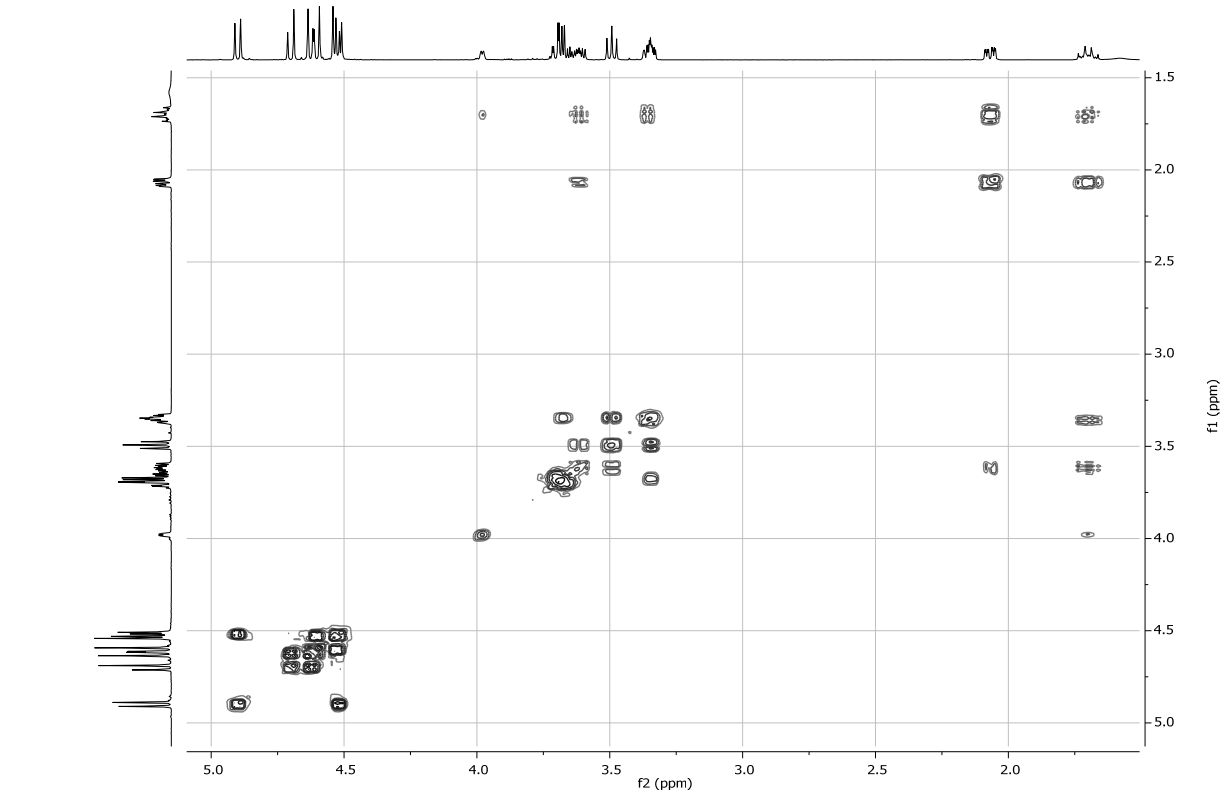
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S49**



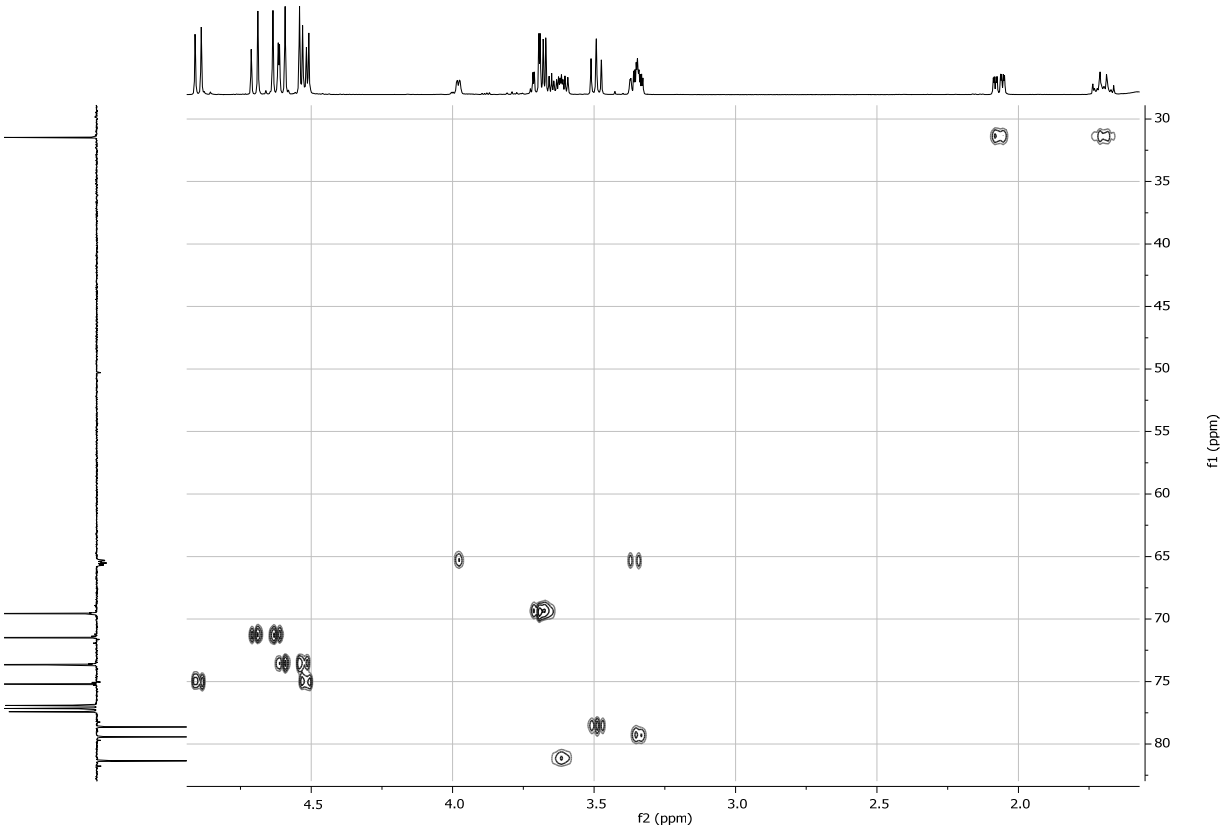
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S49**



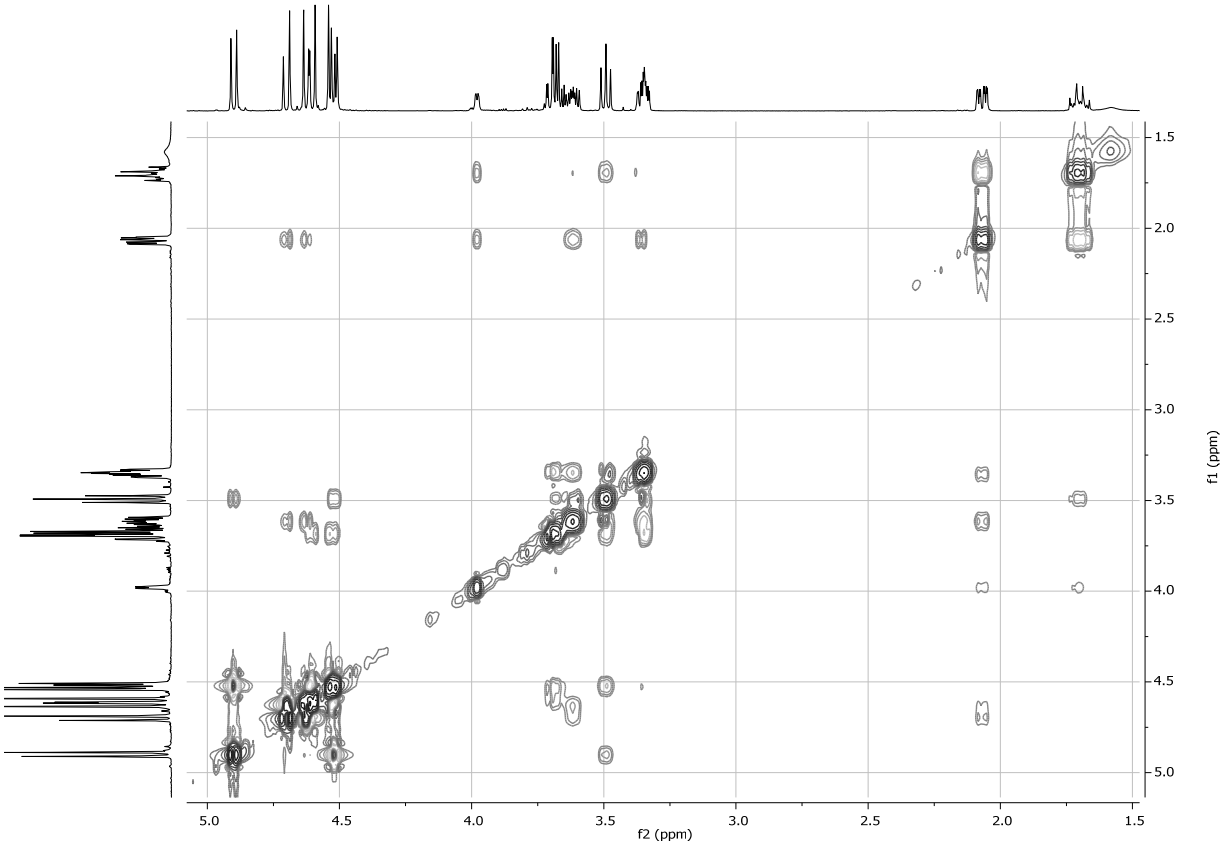
HH-COSY NMR, $CDCl_3$ of compound **S49**



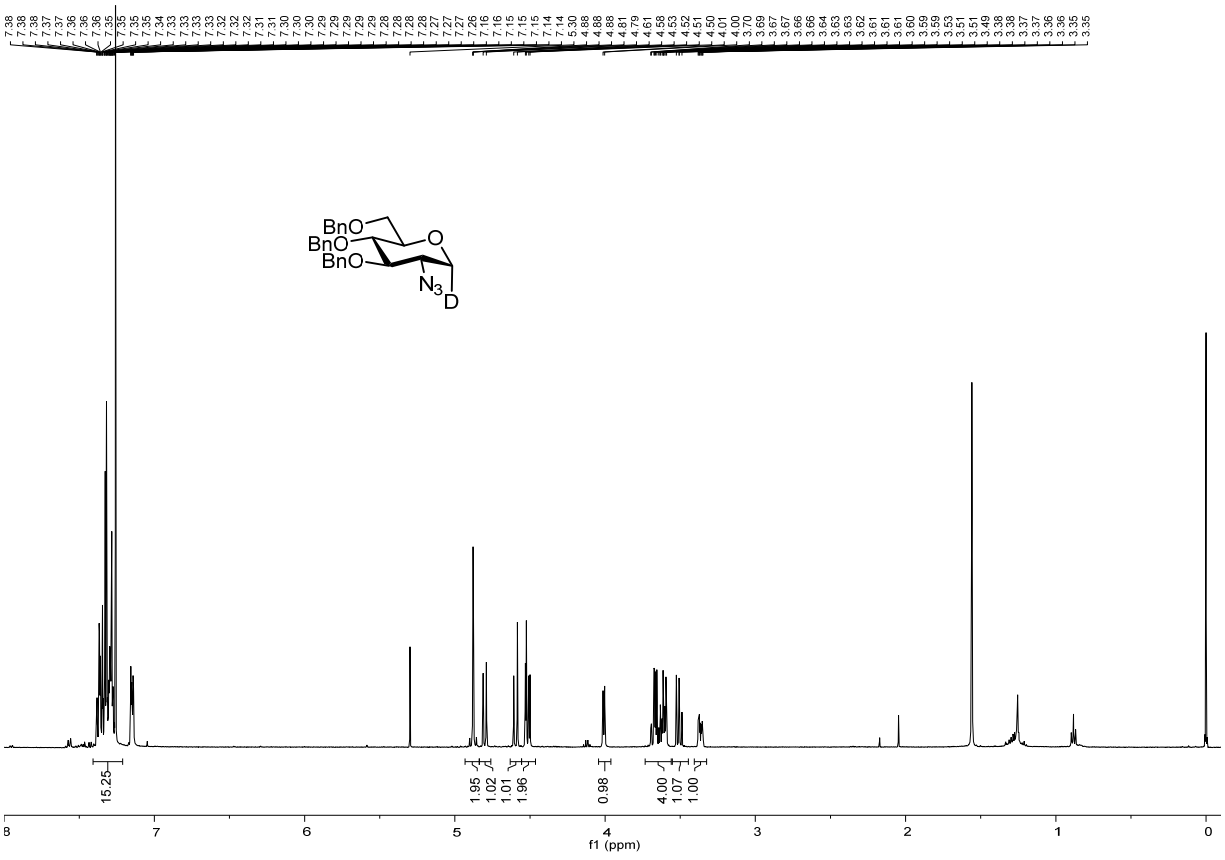
HSQC NMR, $CDCl_3$ of compound **S49**



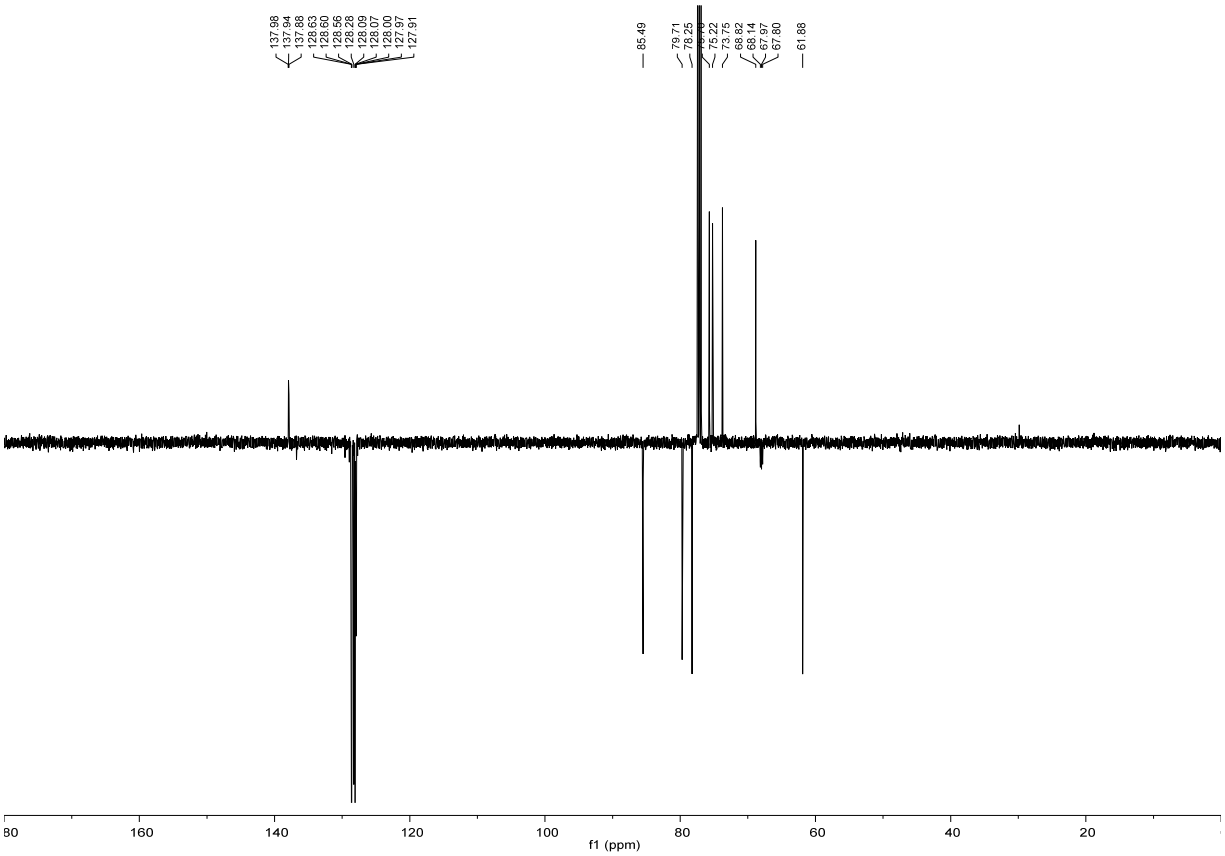
NOESY NMR, $CDCl_3$ of compound **S49**



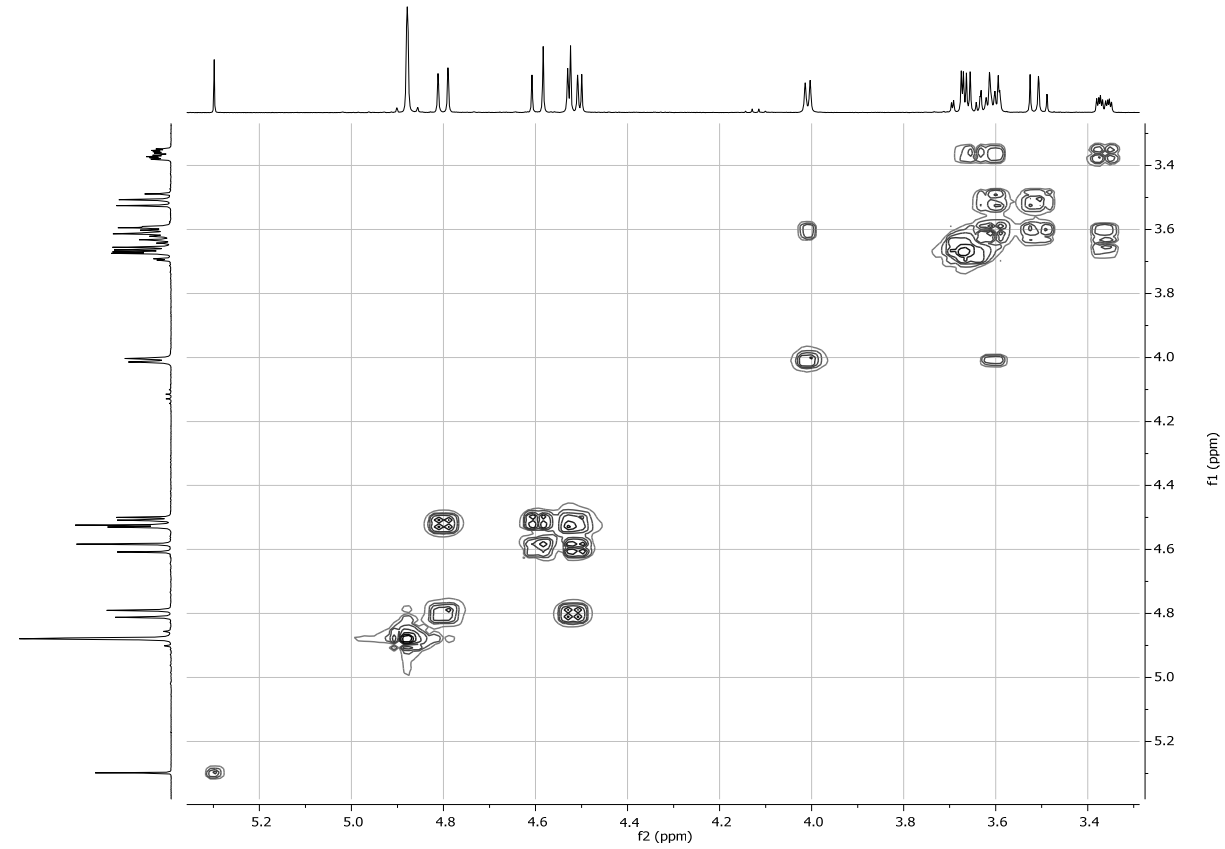
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S50**



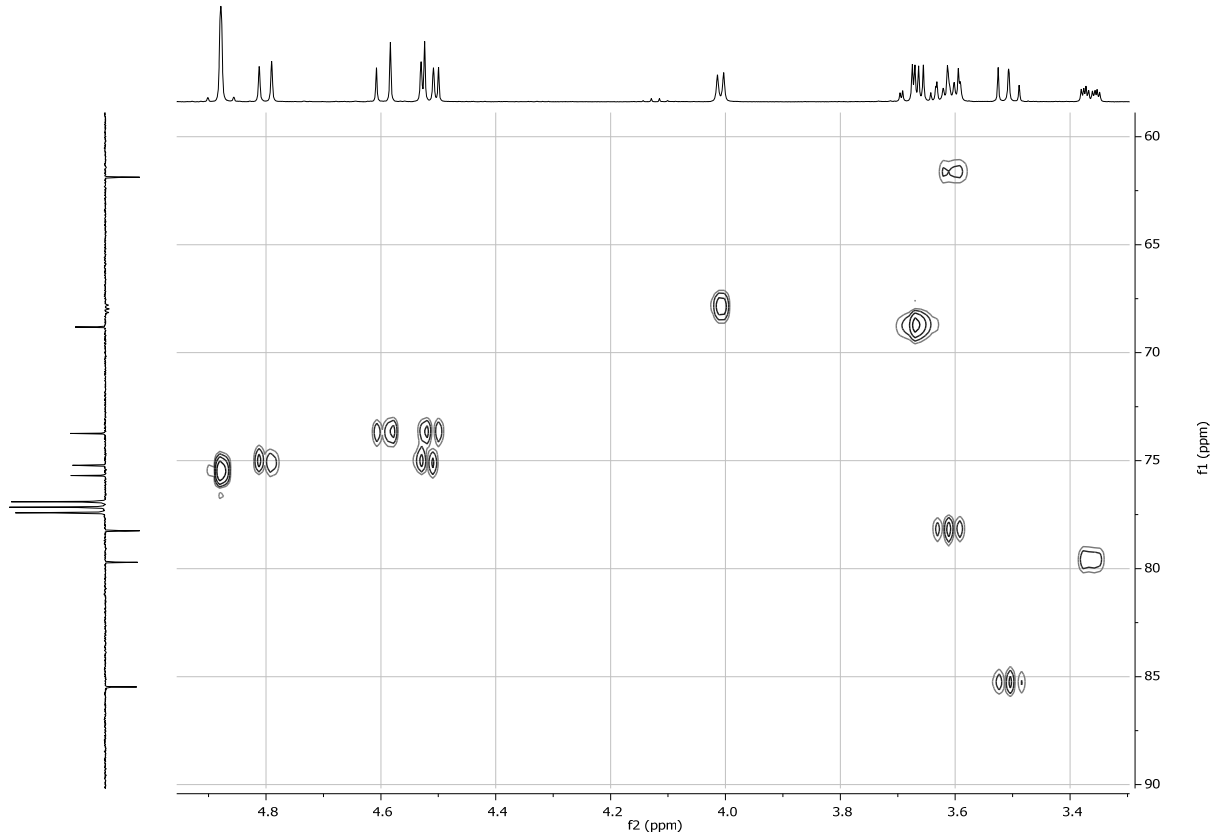
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S50**



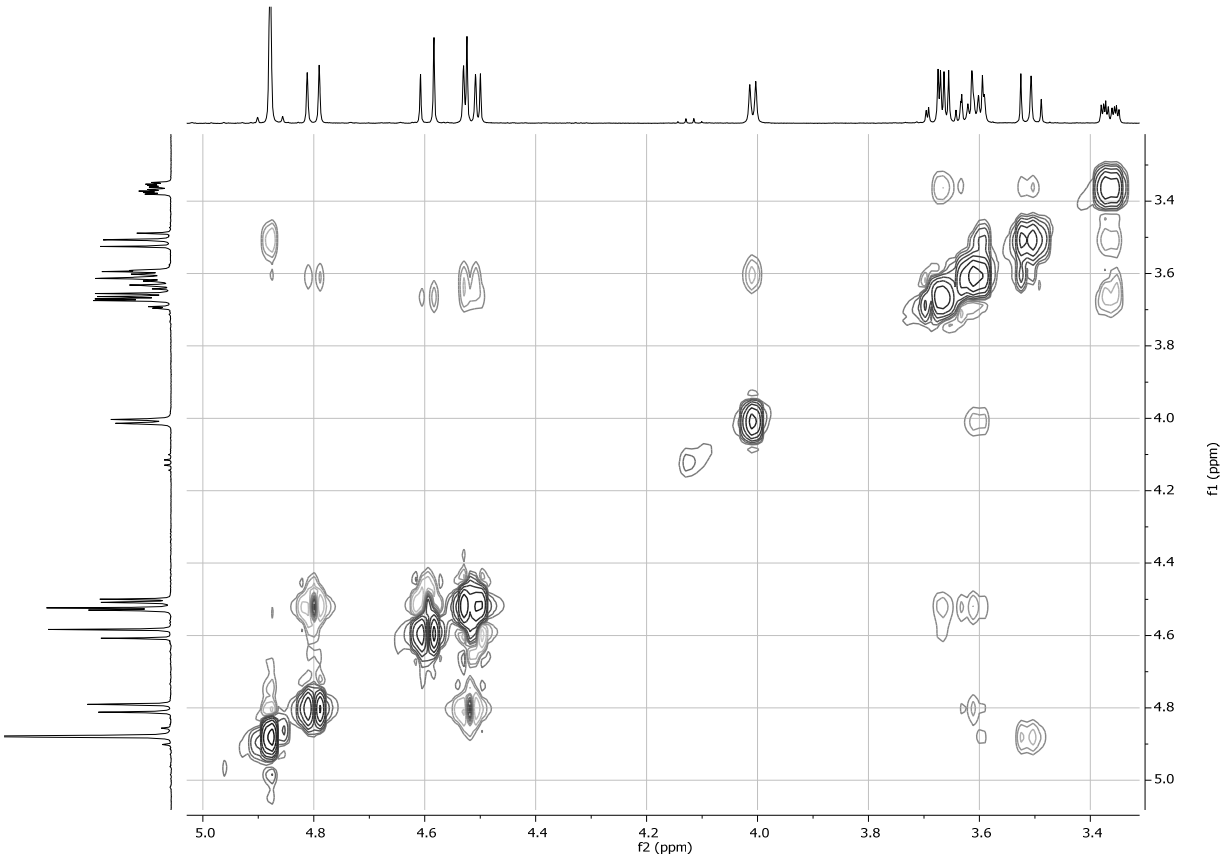
HH-COSY NMR, $CDCl_3$ of compound **S50**



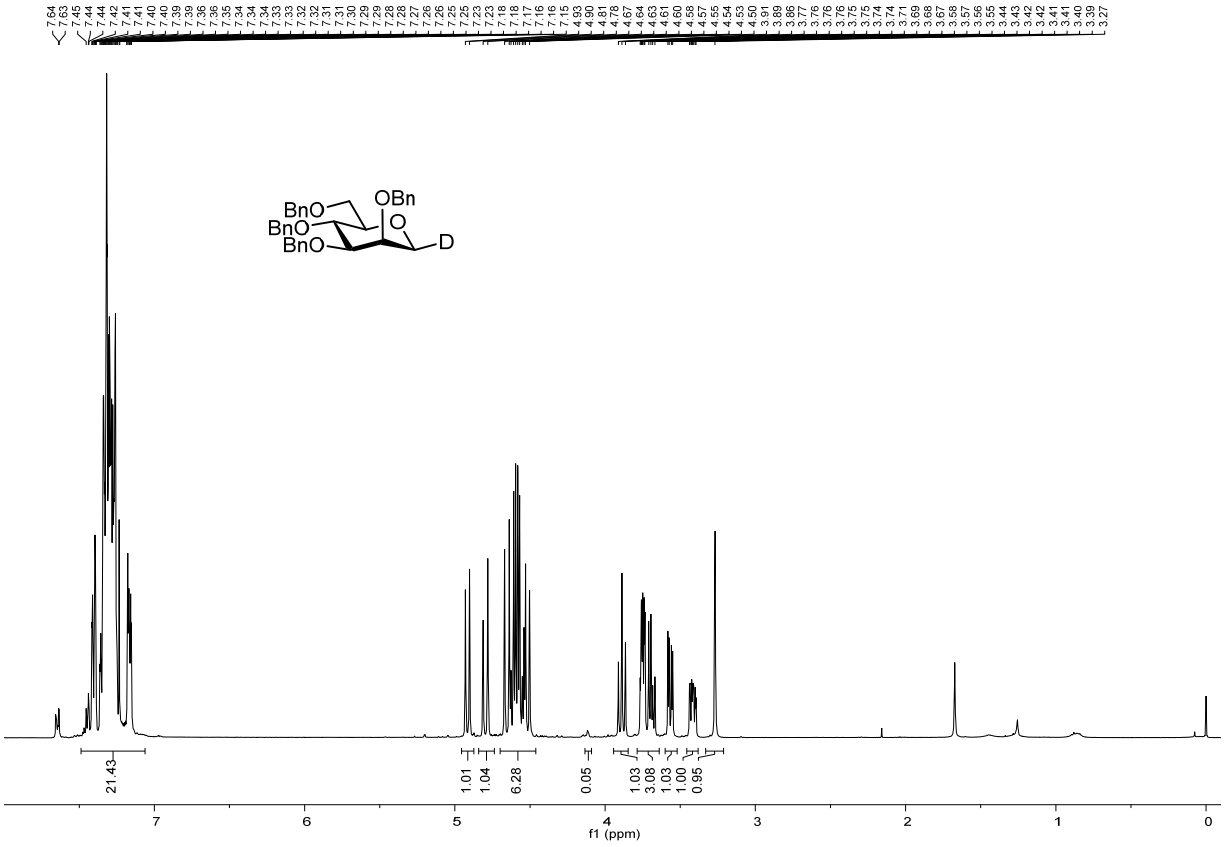
HSQC NMR, $CDCl_3$ of compound **S50**



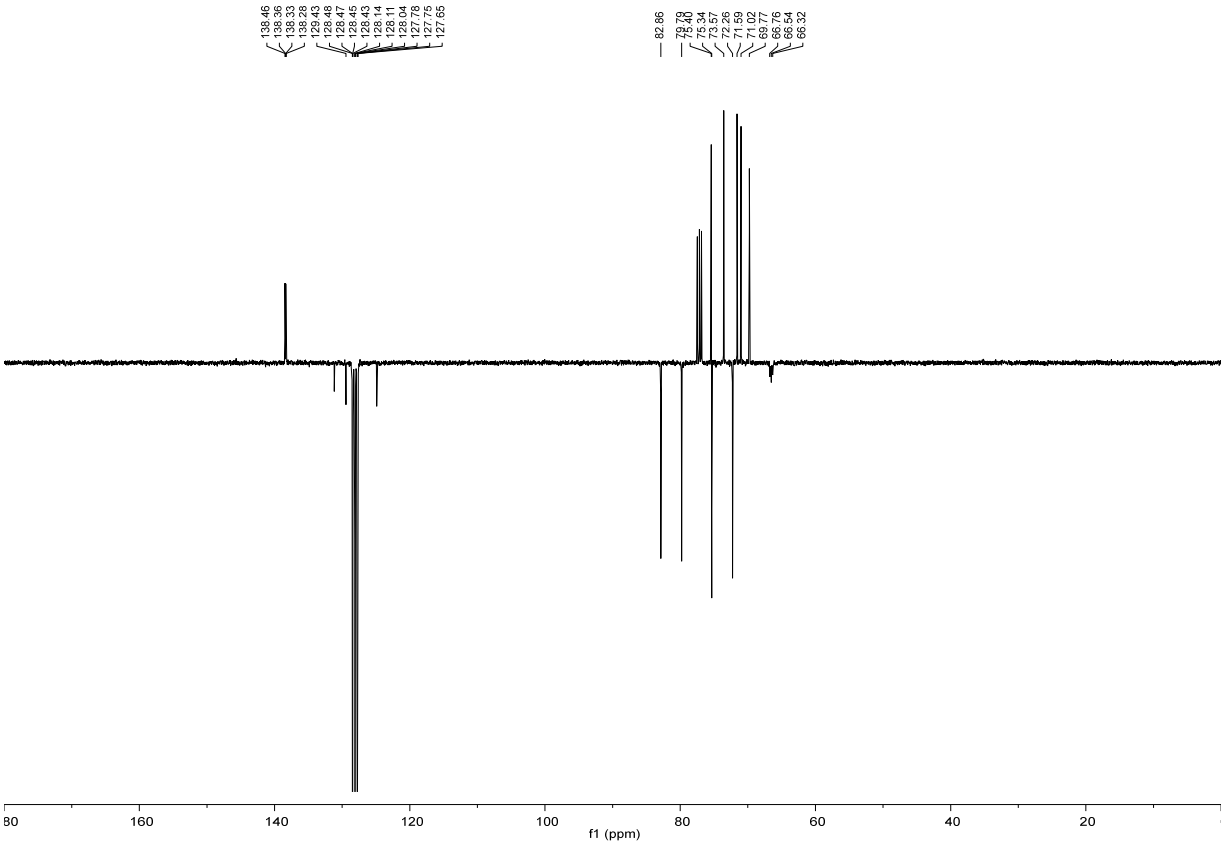
NOESY NMR, $CDCl_3$ of compound **S50**



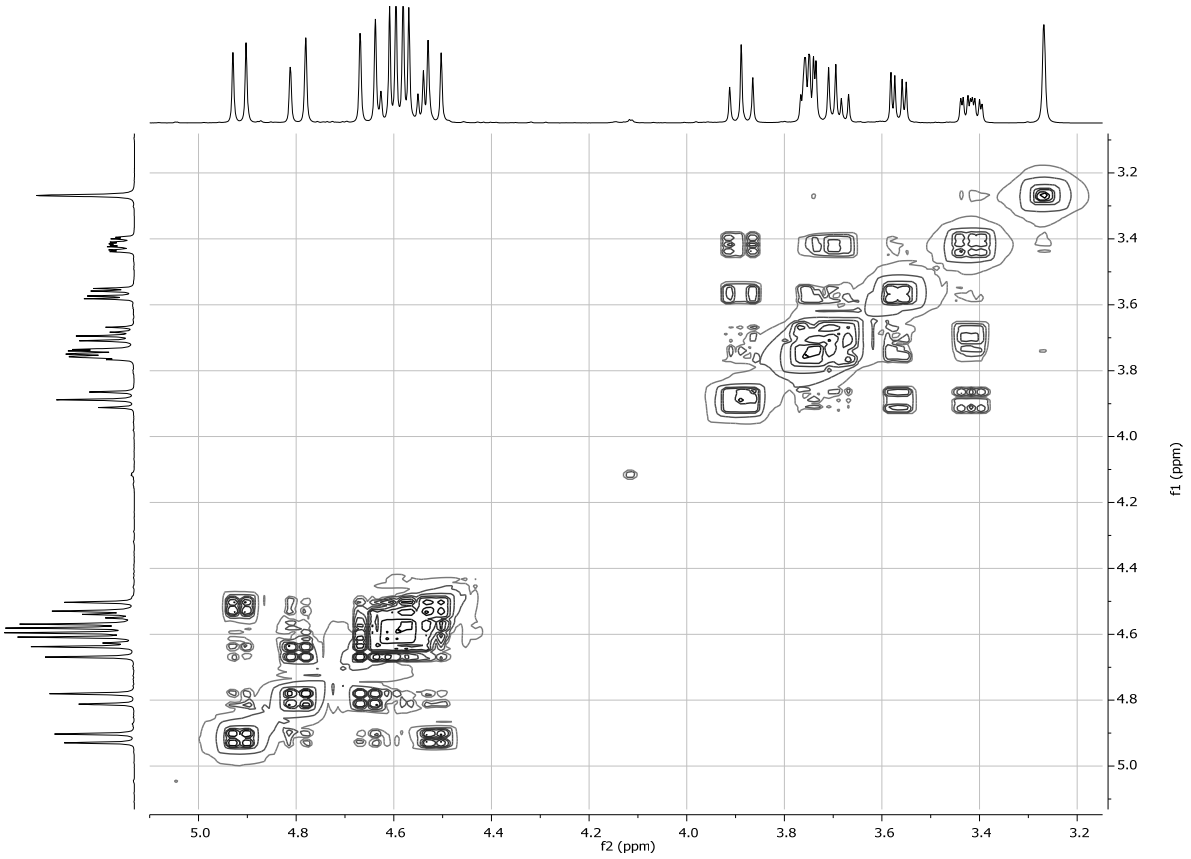
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S51**



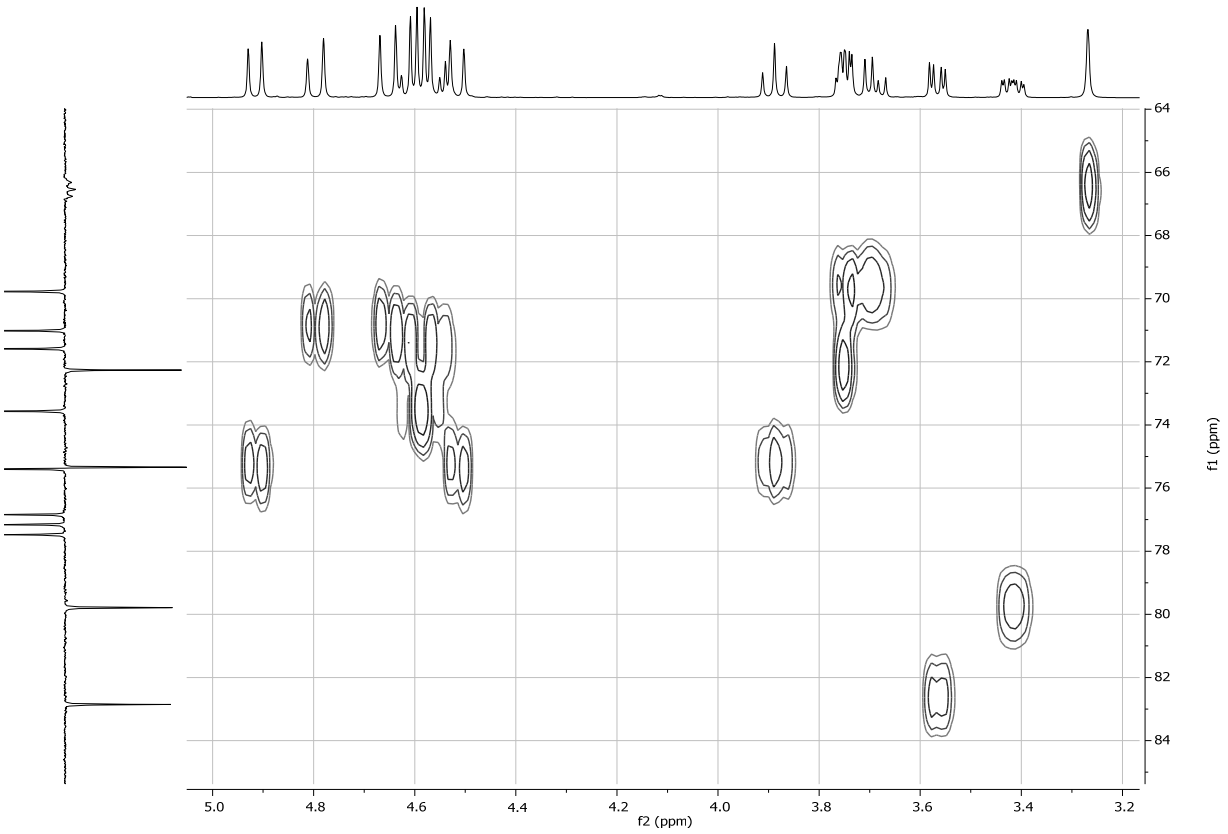
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S51**



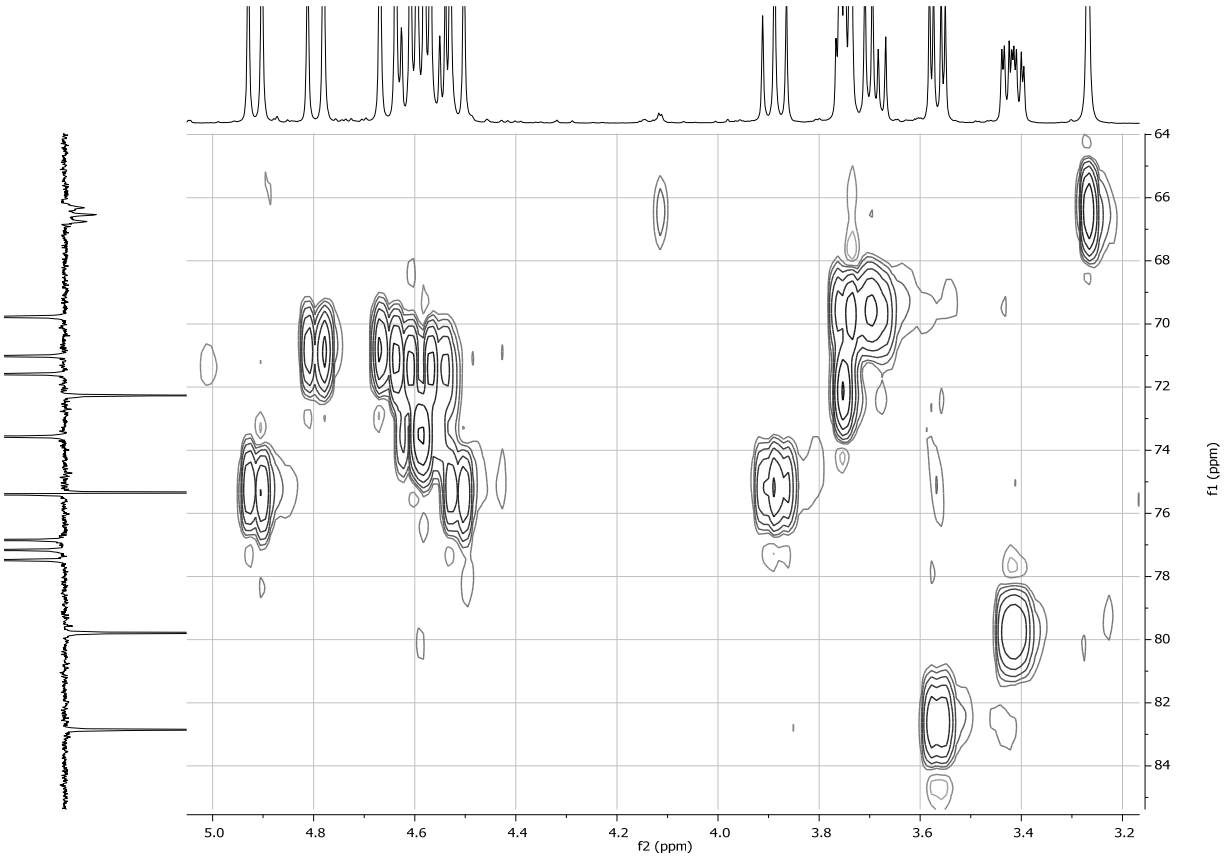
HH-COSY NMR, $CDCl_3$ of compound **S51**



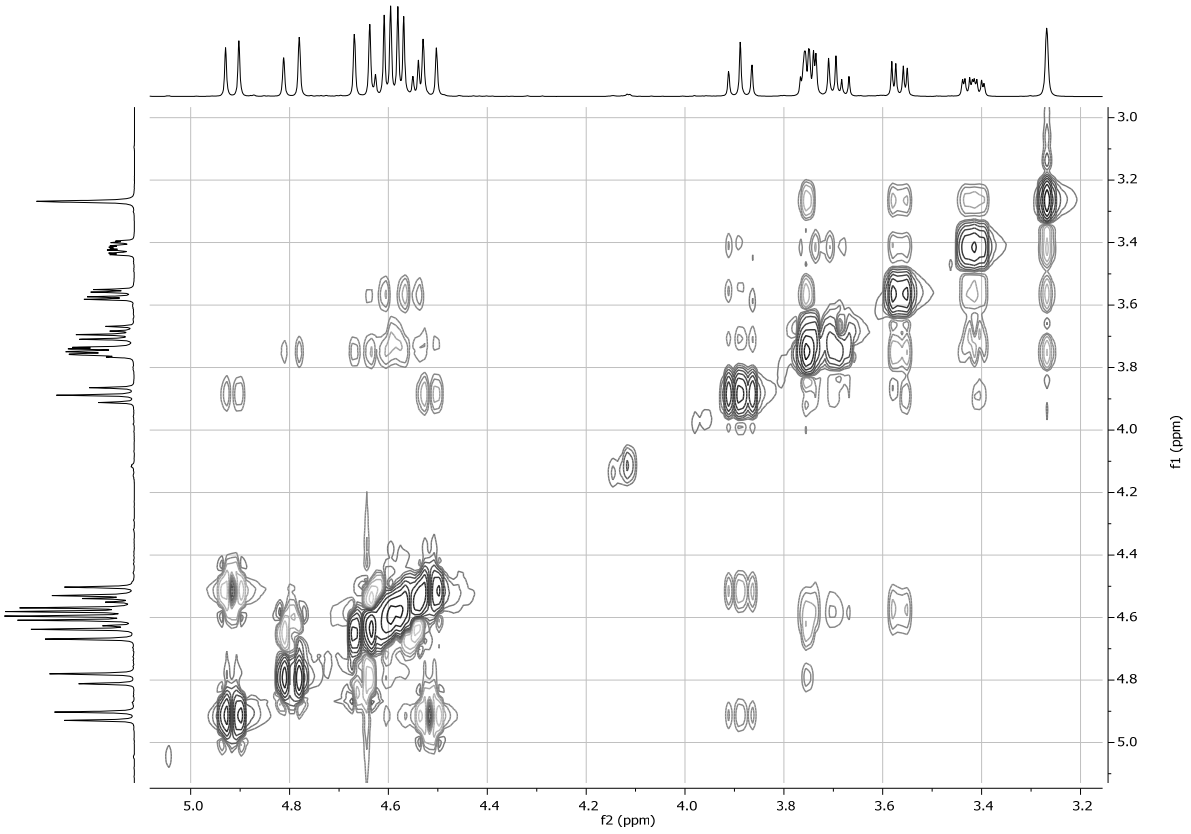
HSQC NMR, $CDCl_3$ of compound **S51**



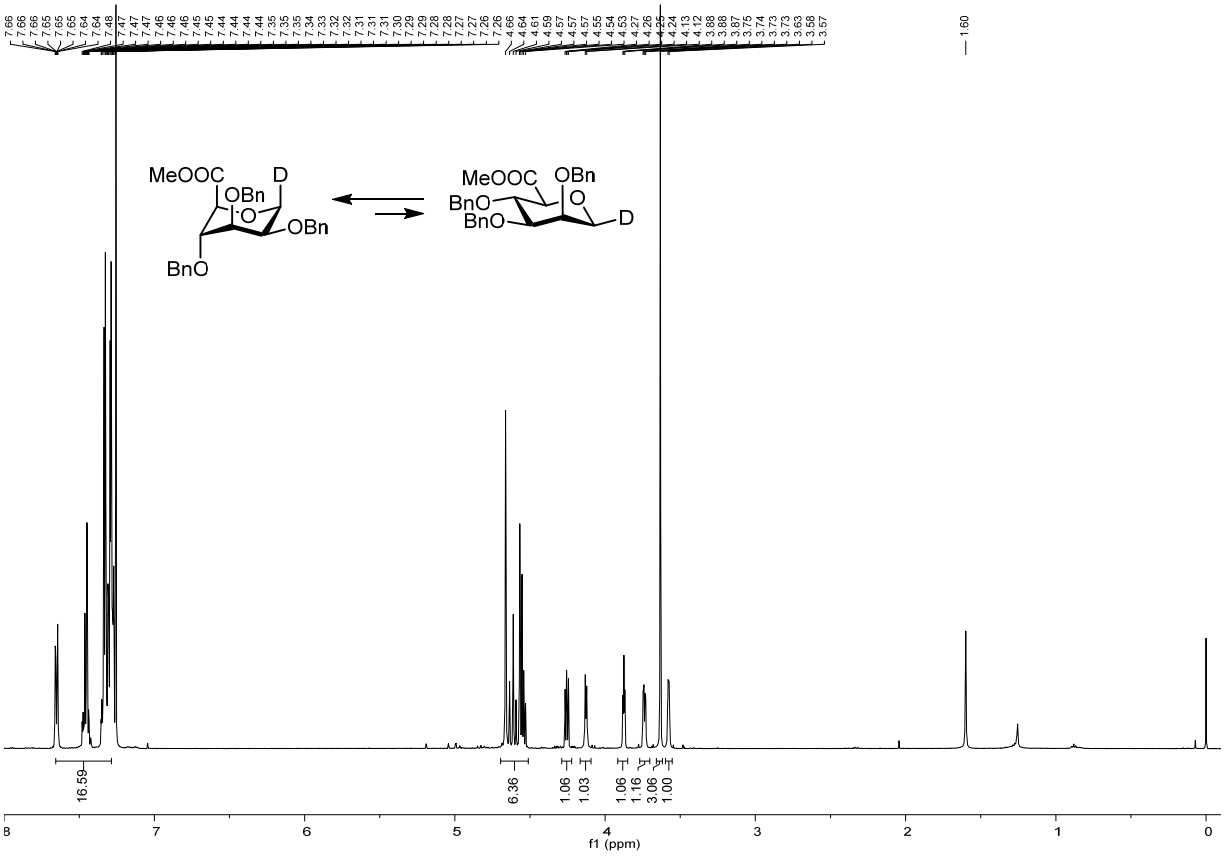
HSQC NMR, $CDCl_3$ of compound **S51** (cropped)



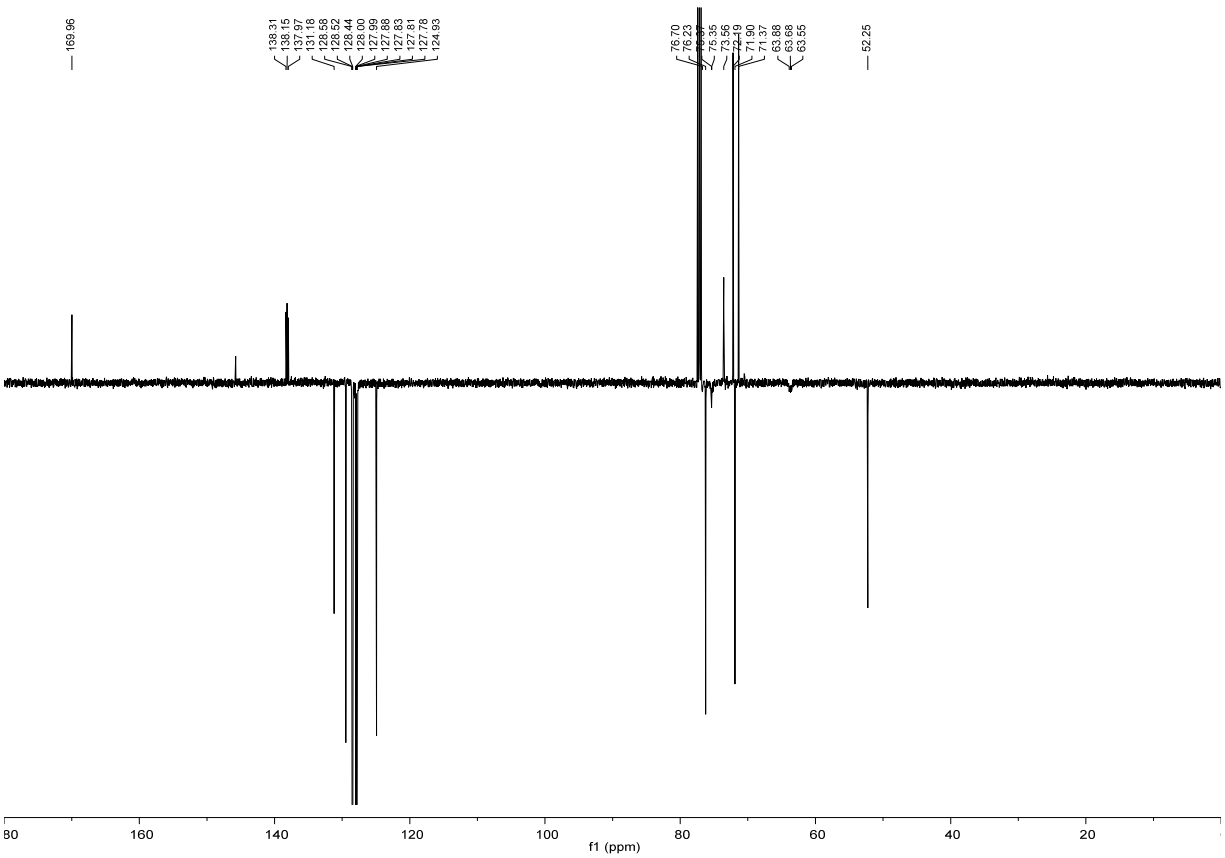
NOESY NMR, $CDCl_3$ of compound **S51**



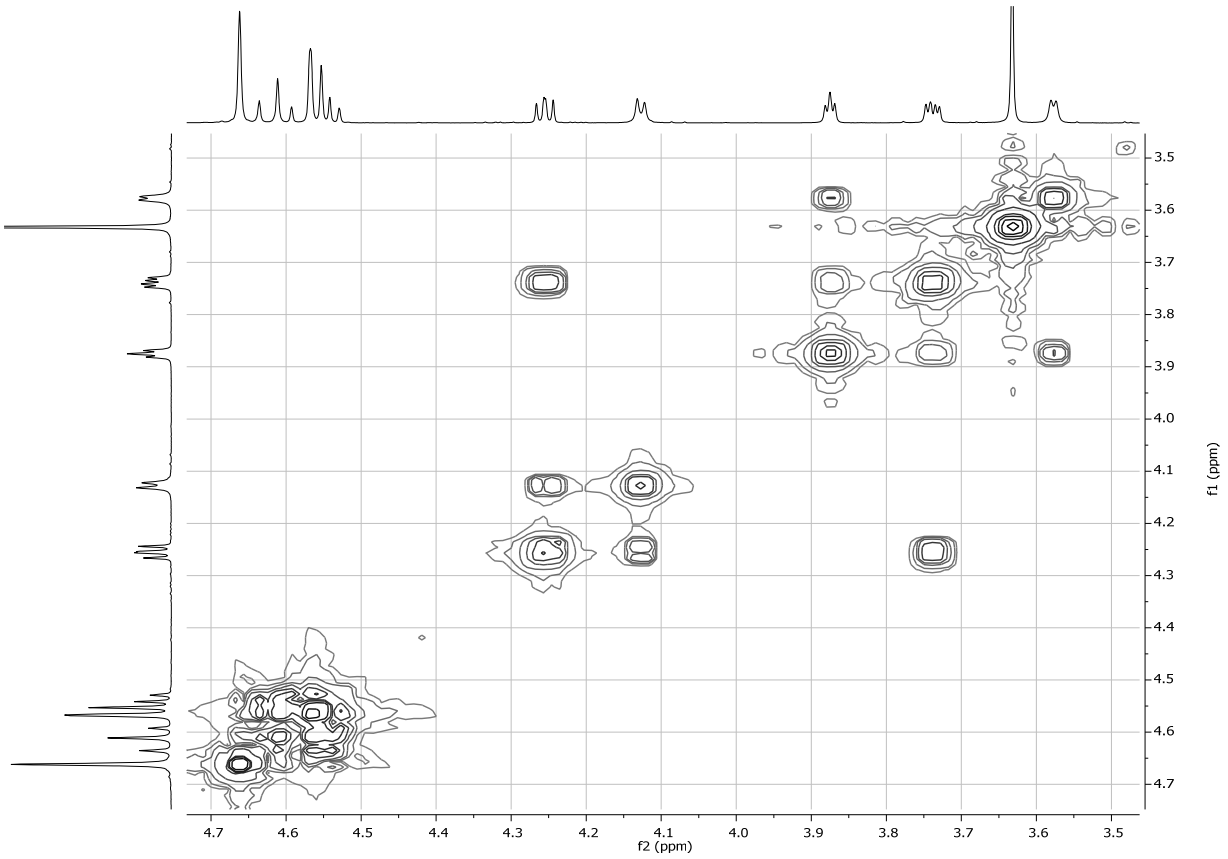
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S52**



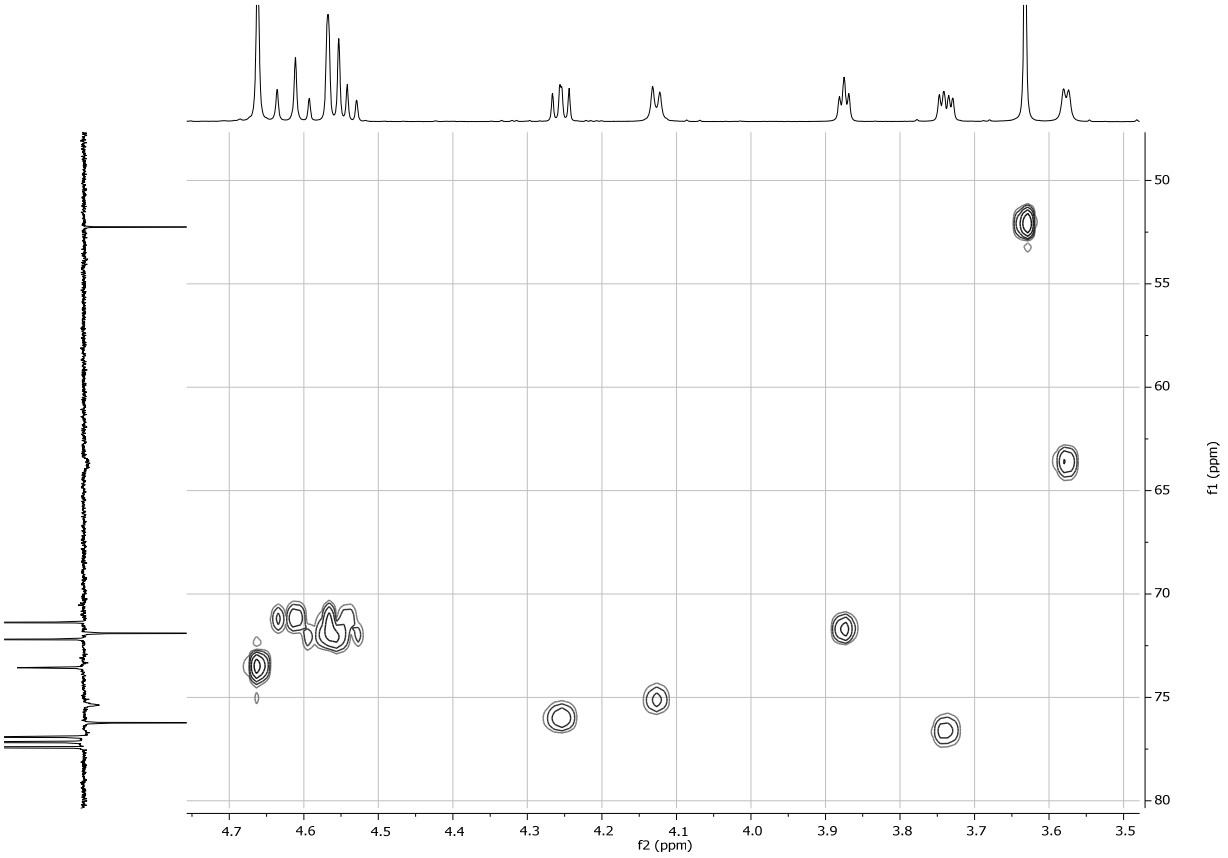
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S52**



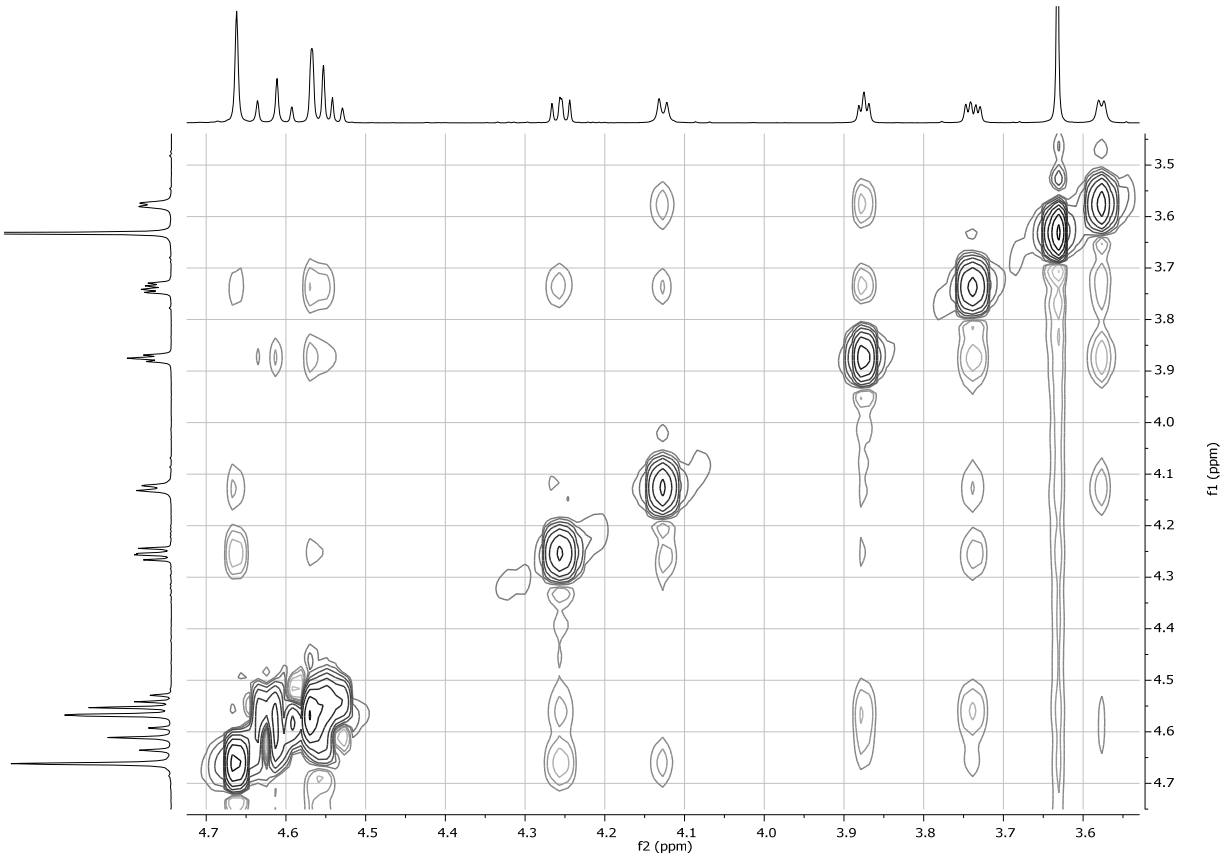
HH-COSY NMR, $CDCl_3$ of compound **S52**



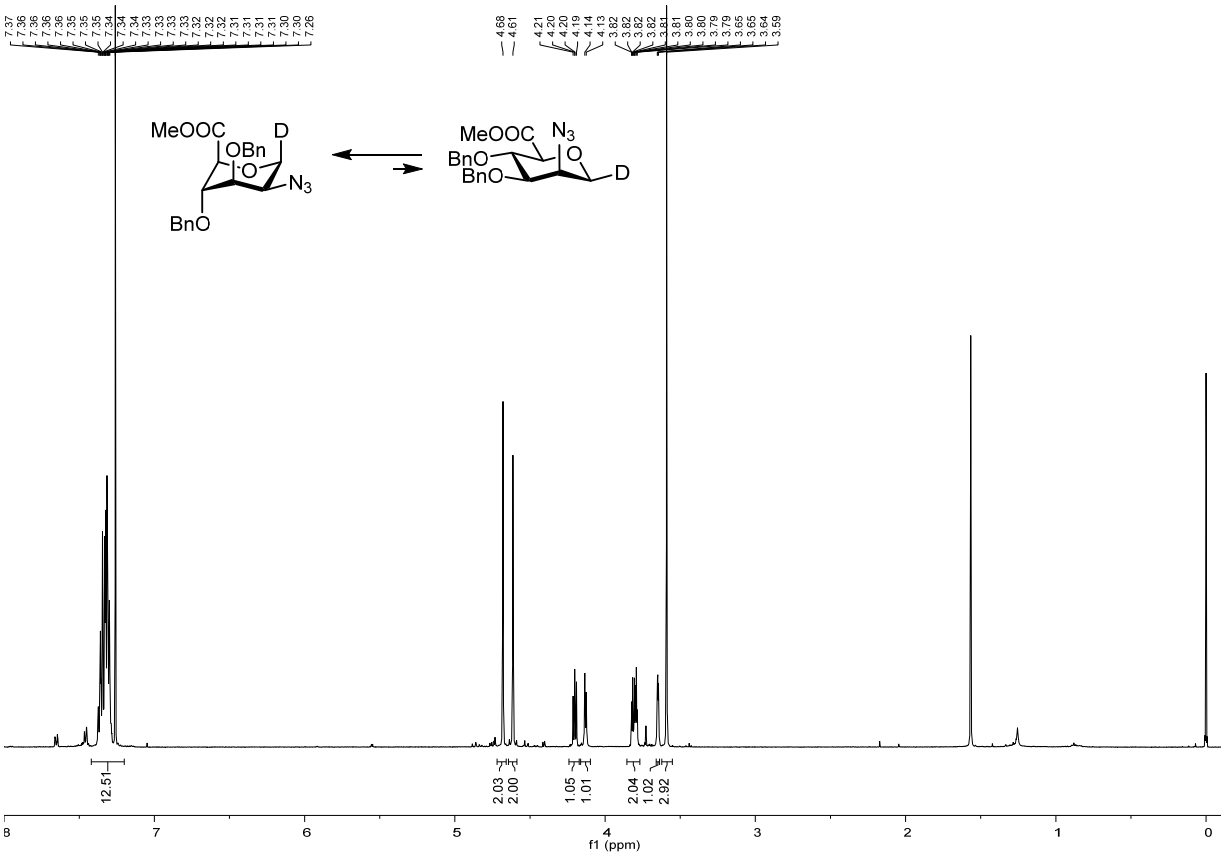
HSQC NMR, $CDCl_3$ of compound **S52**



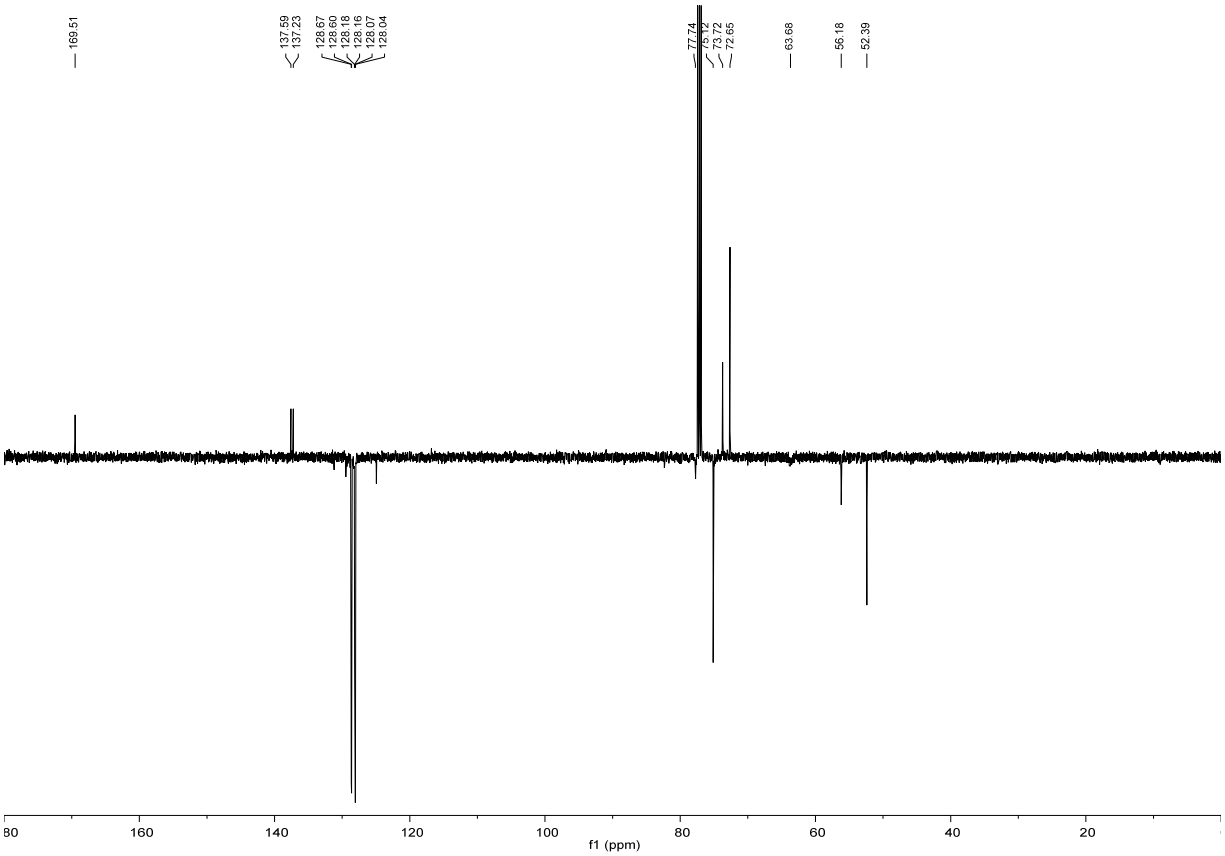
NOESY NMR, $CDCl_3$ of compound **S52**



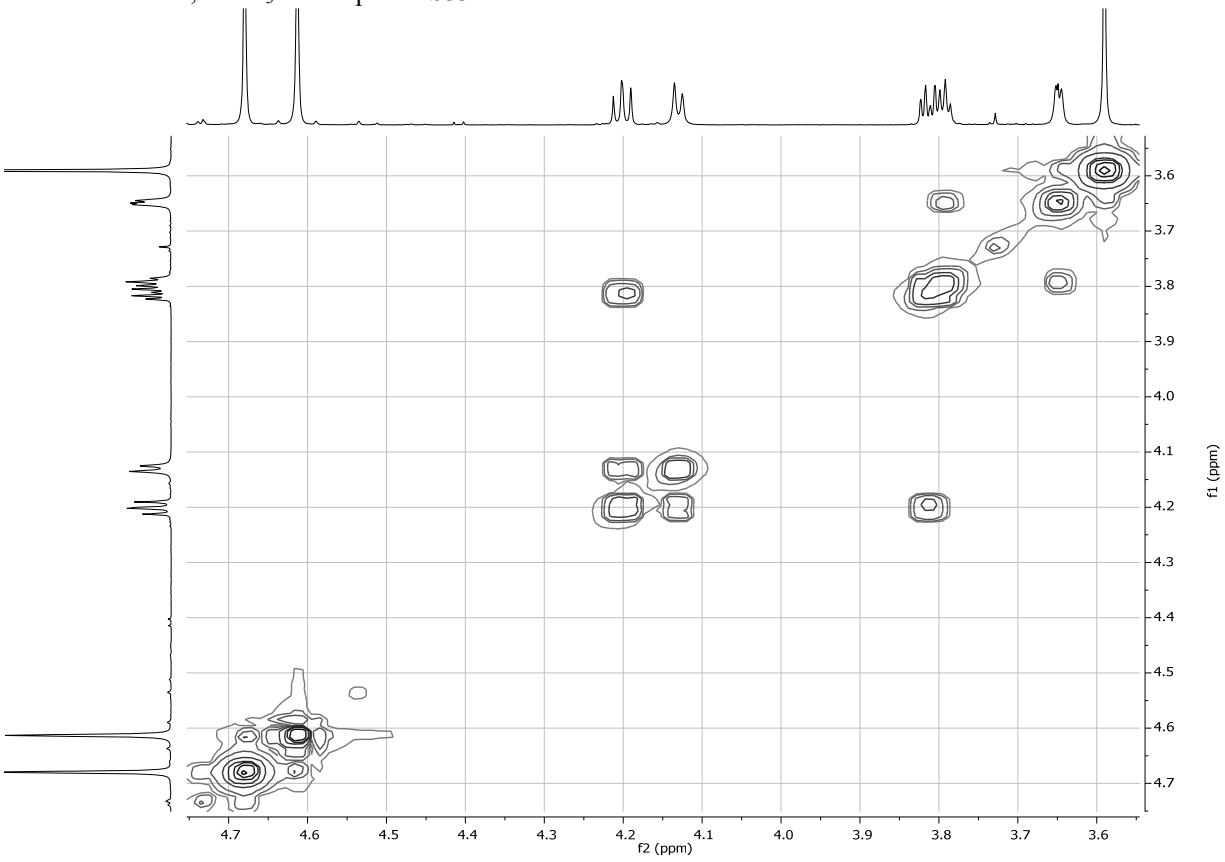
^1H NMR, 500 MHz, $CDCl_3$ of compound **S53**



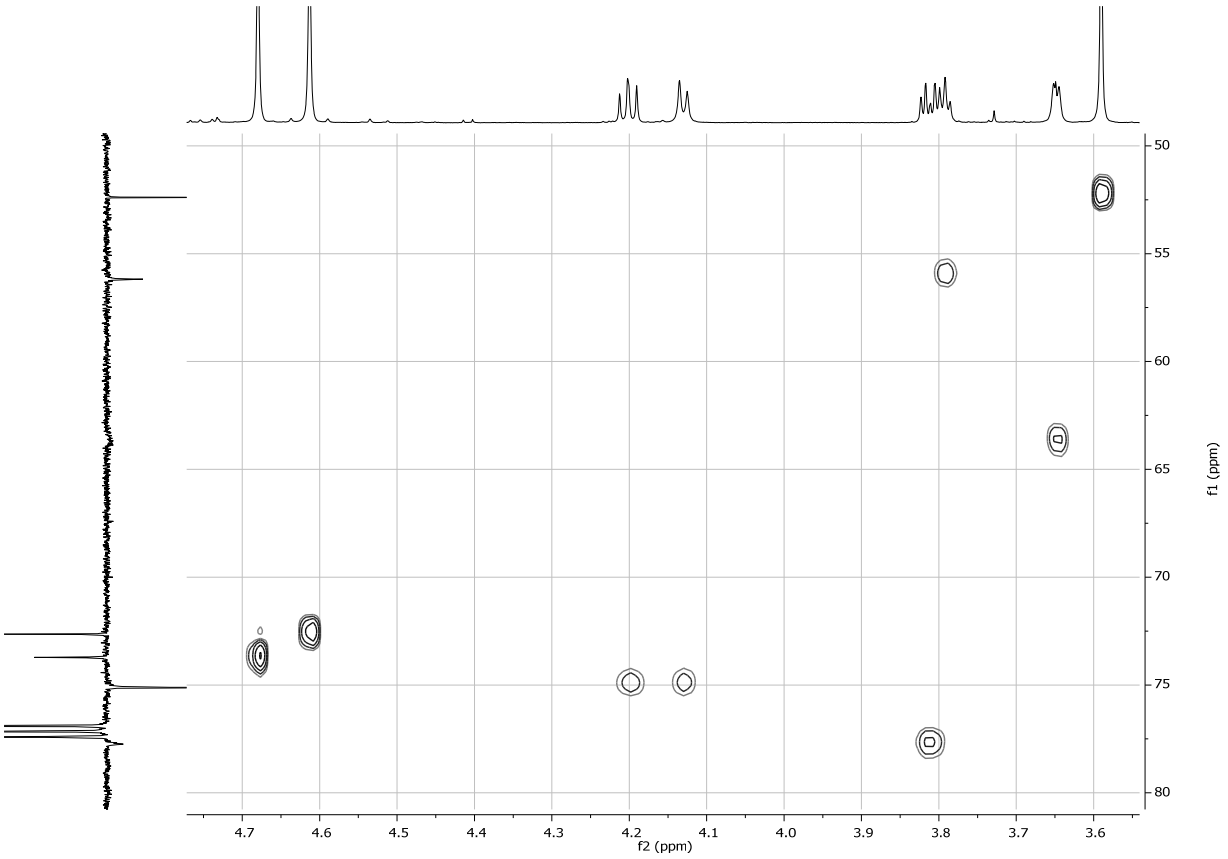
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S53**



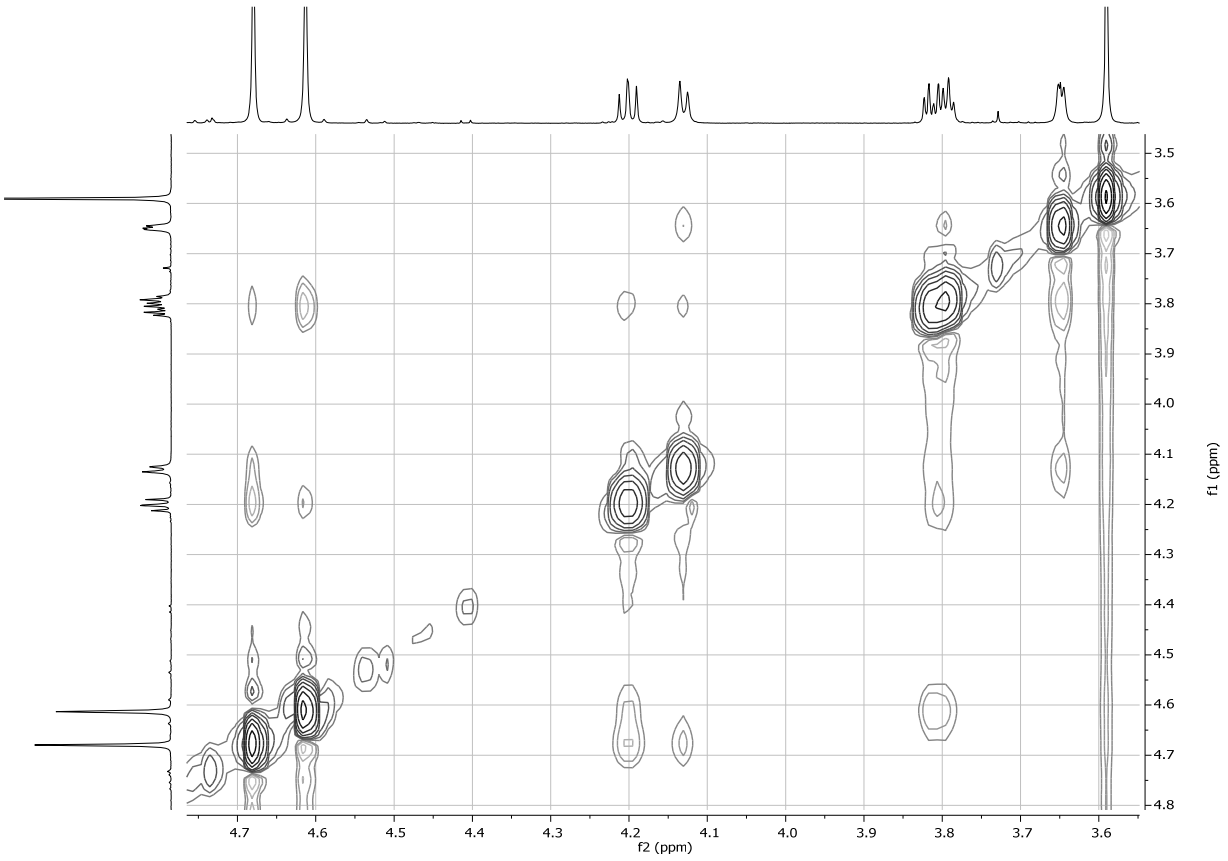
HH-COSY NMR, $CDCl_3$ of compound **S53**



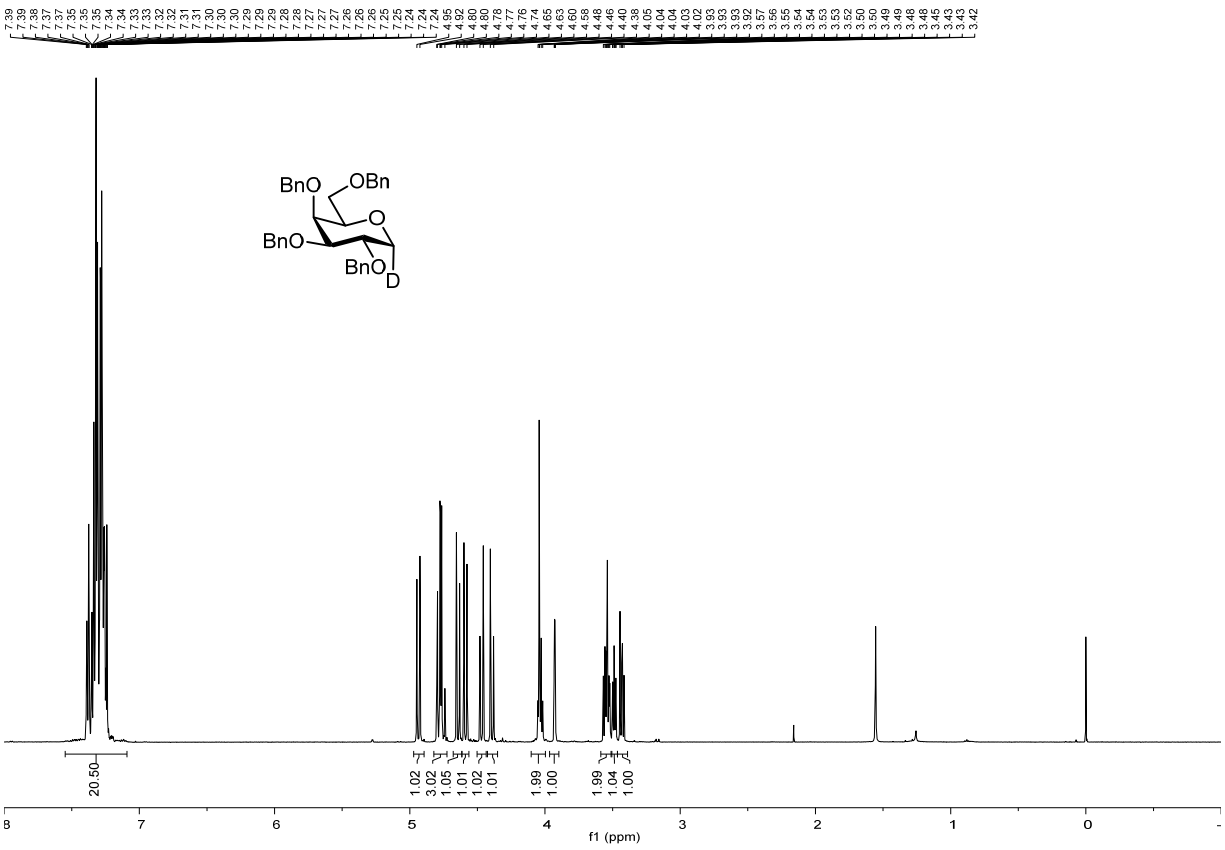
HSQC NMR, $CDCl_3$ of compound **S53**



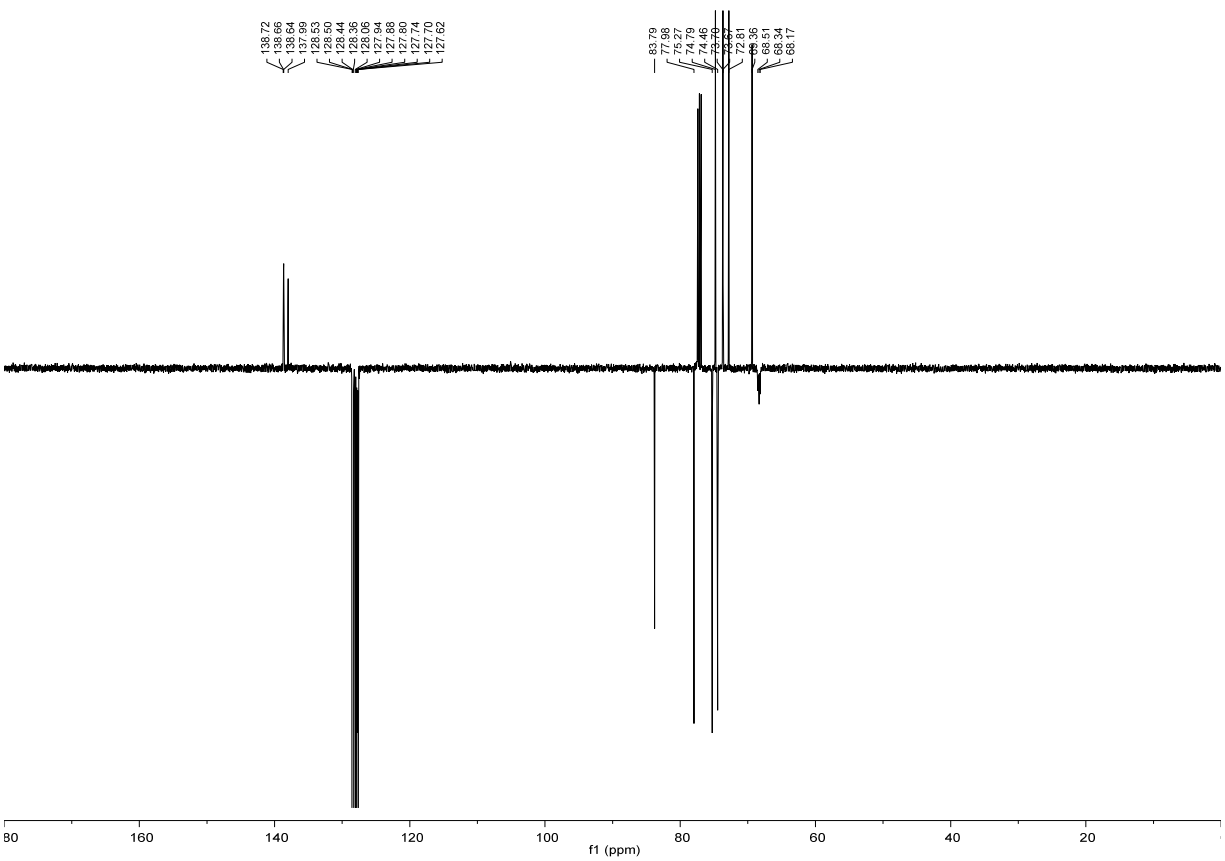
NOESY NMR, $CDCl_3$ of compound **S53**



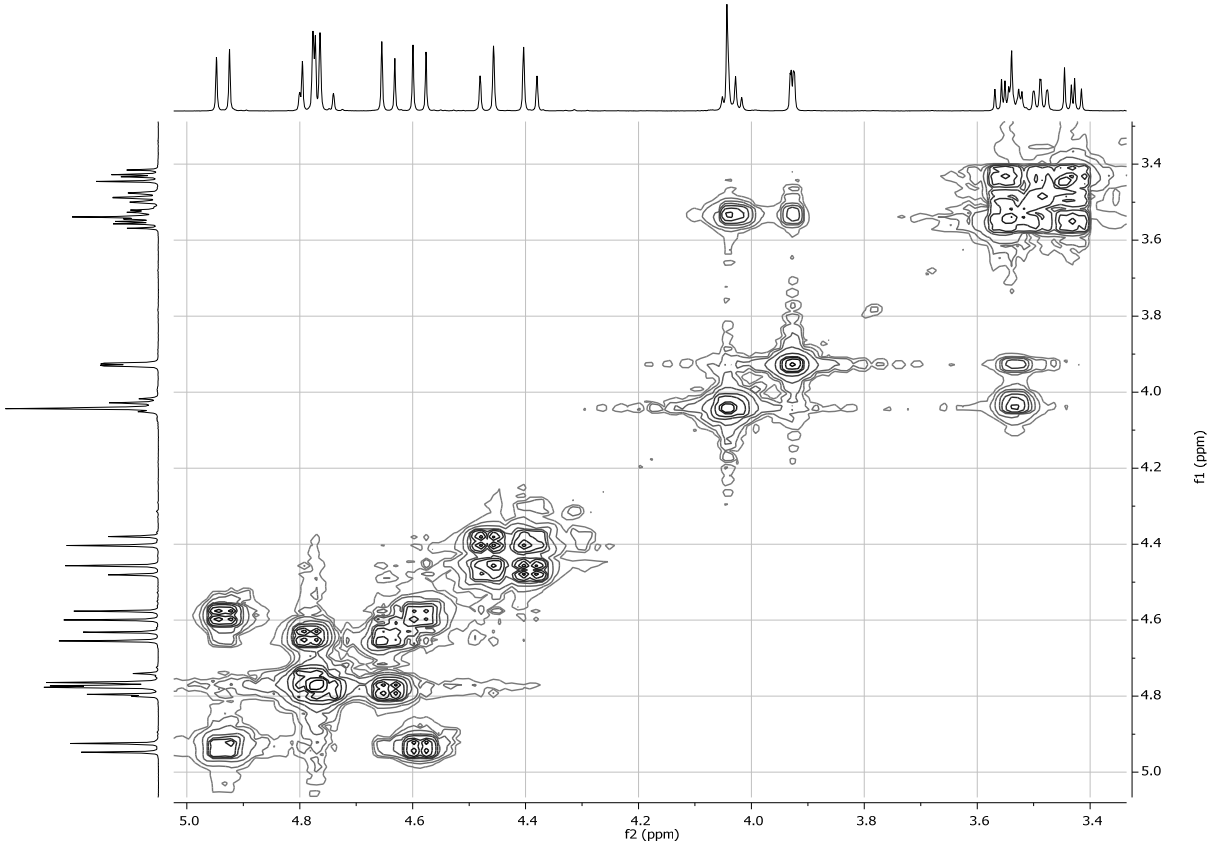
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S54**



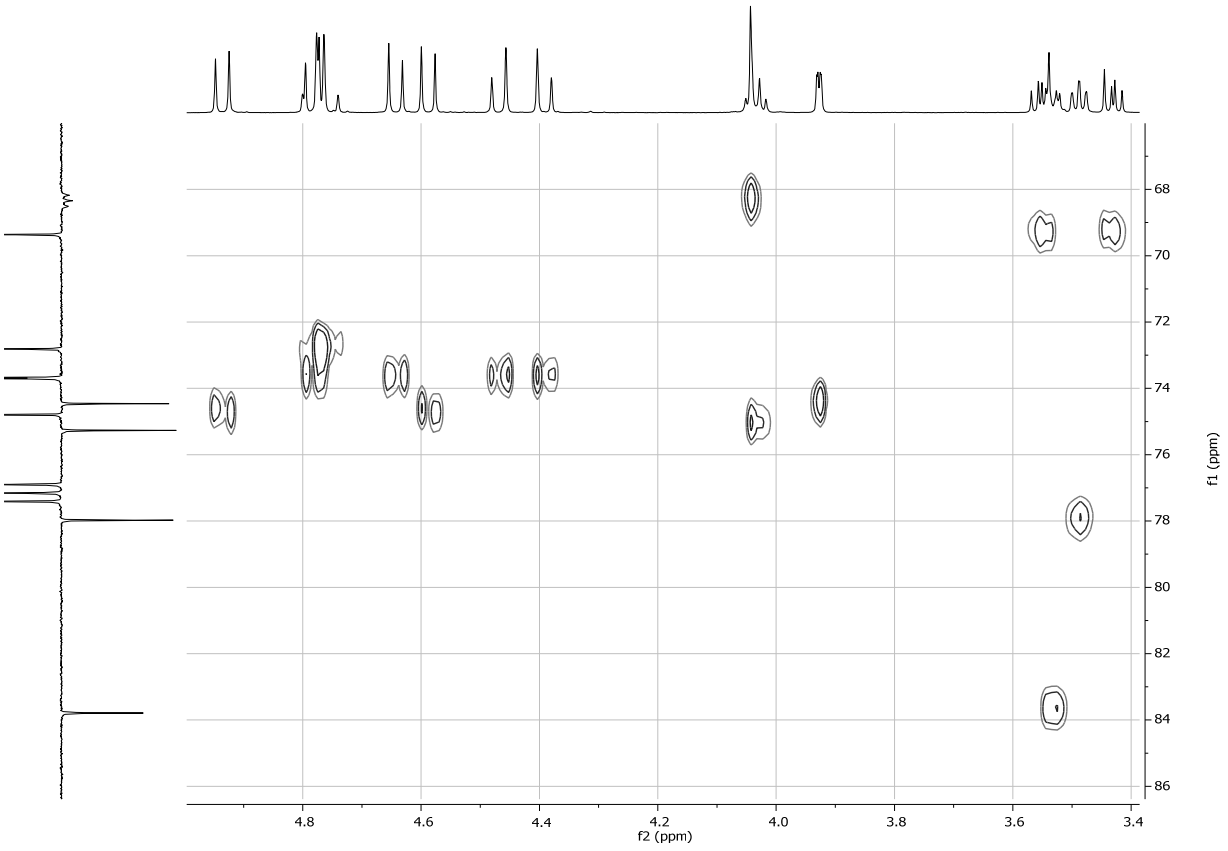
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S54**



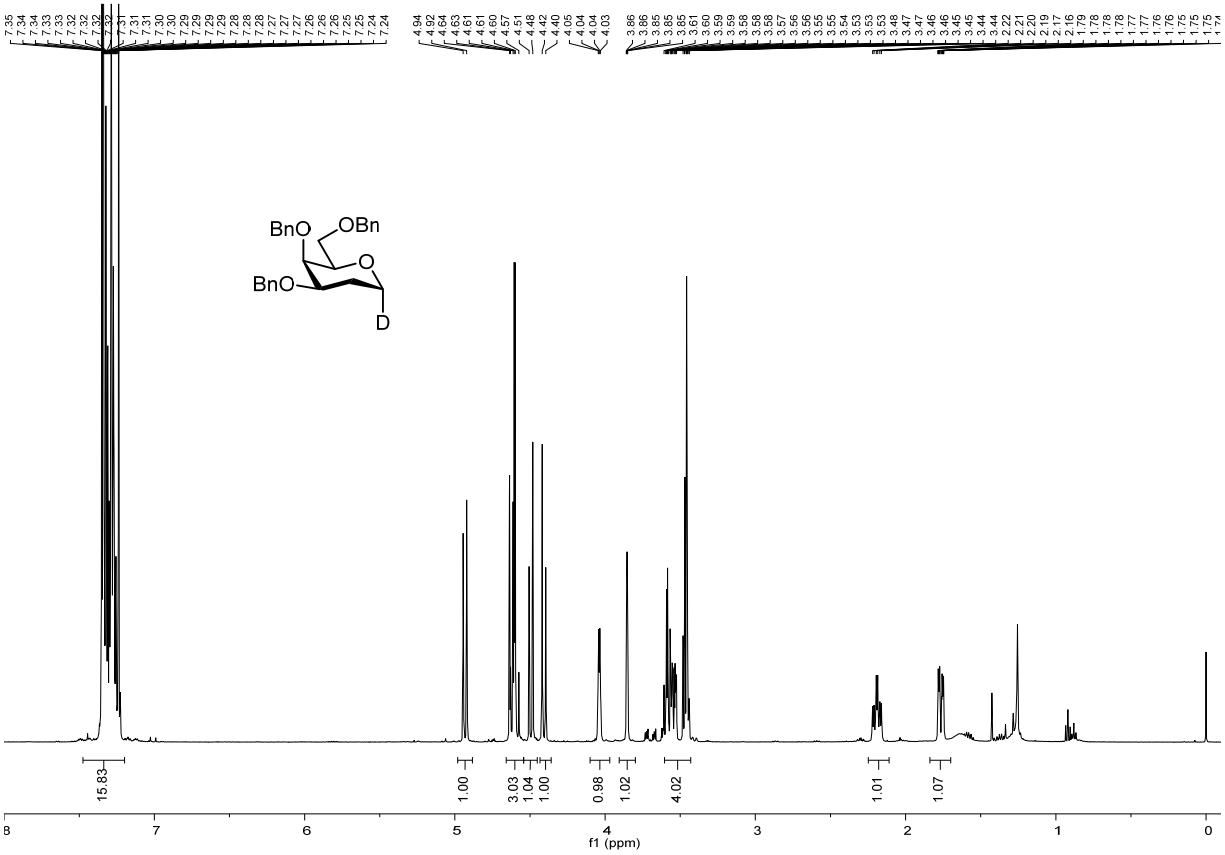
HH-COSY NMR, $CDCl_3$ of compound **S54**



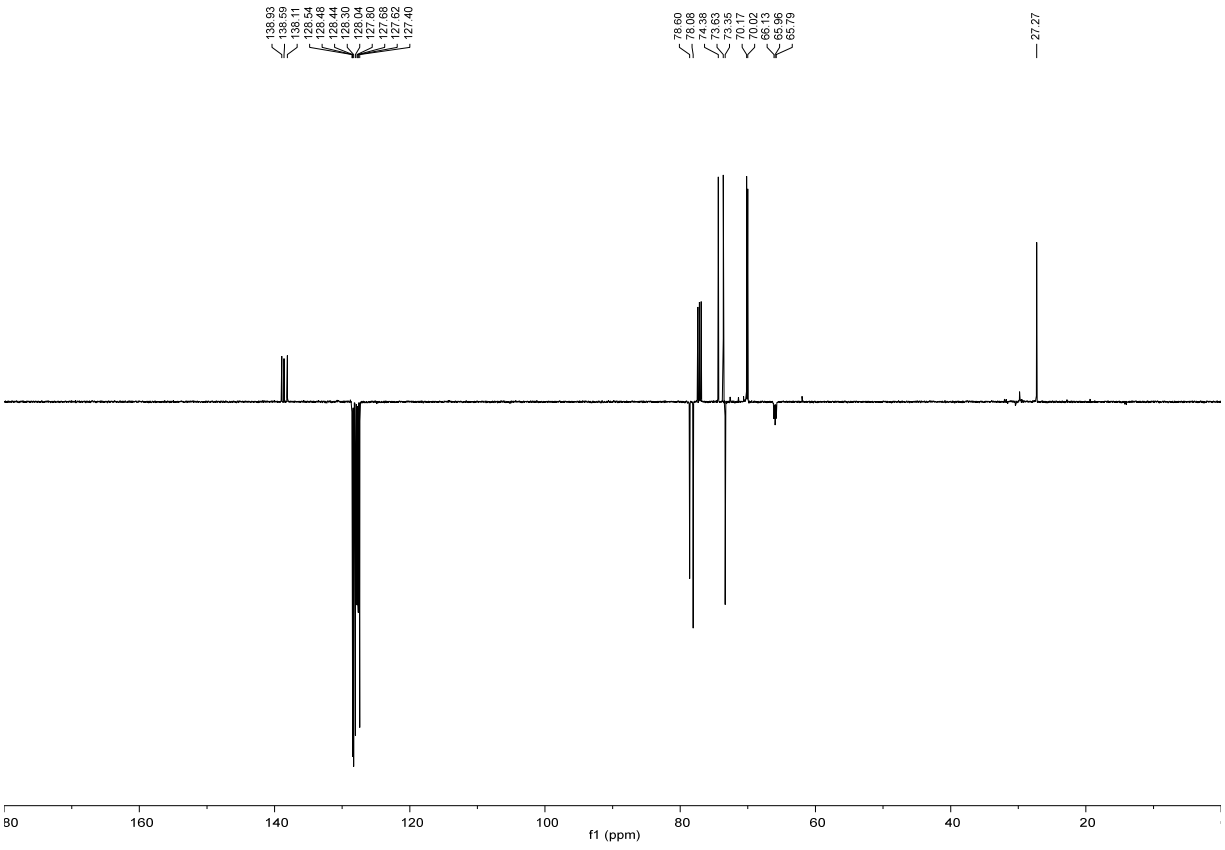
HSQC NMR, $CDCl_3$ of compound **S54**



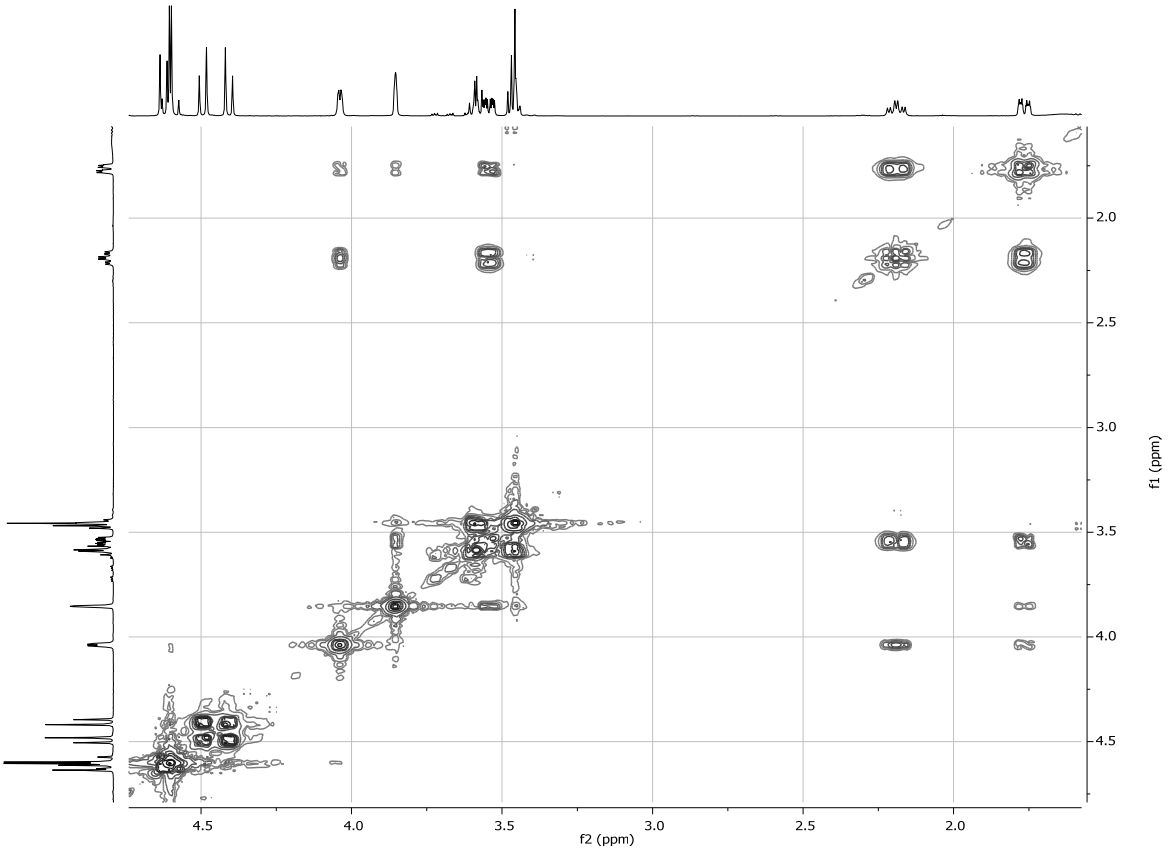
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S55**



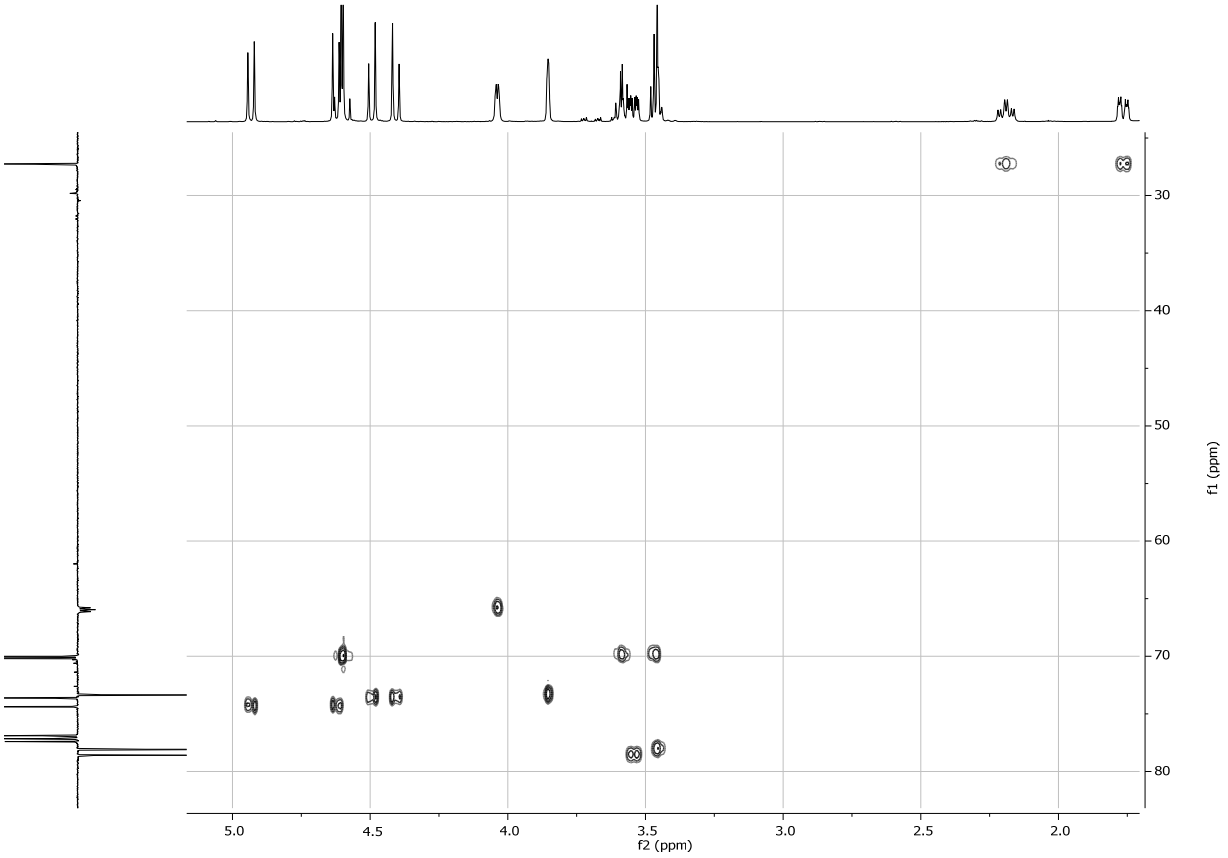
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S55**



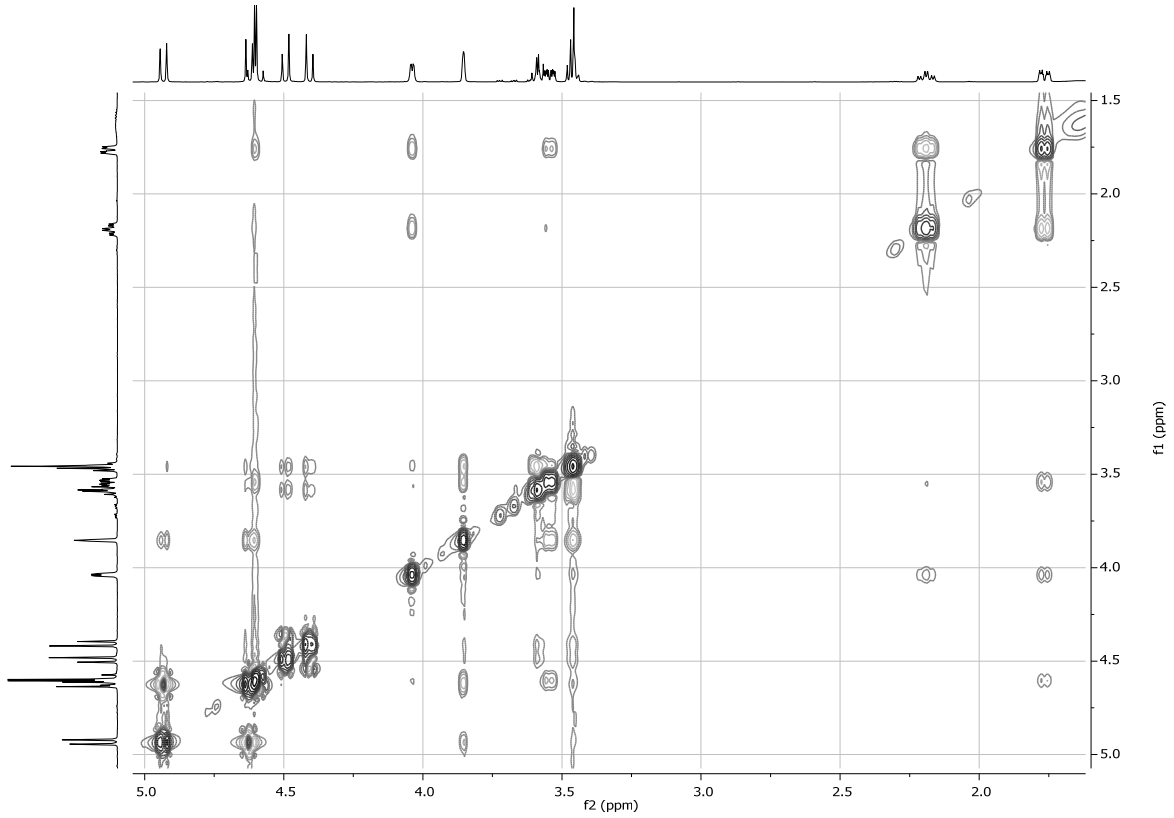
HH-COSY NMR, $CDCl_3$ of compound **S55**



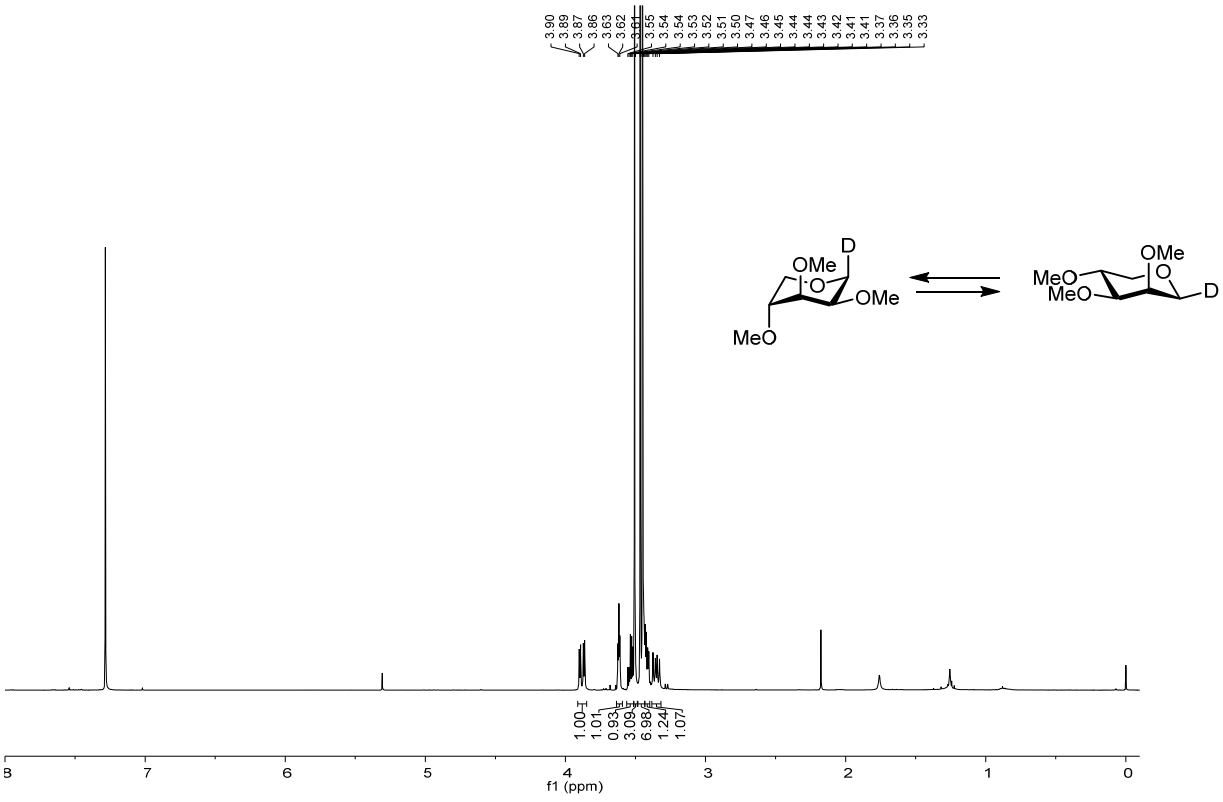
HSQC NMR, $CDCl_3$ of compound **S55**



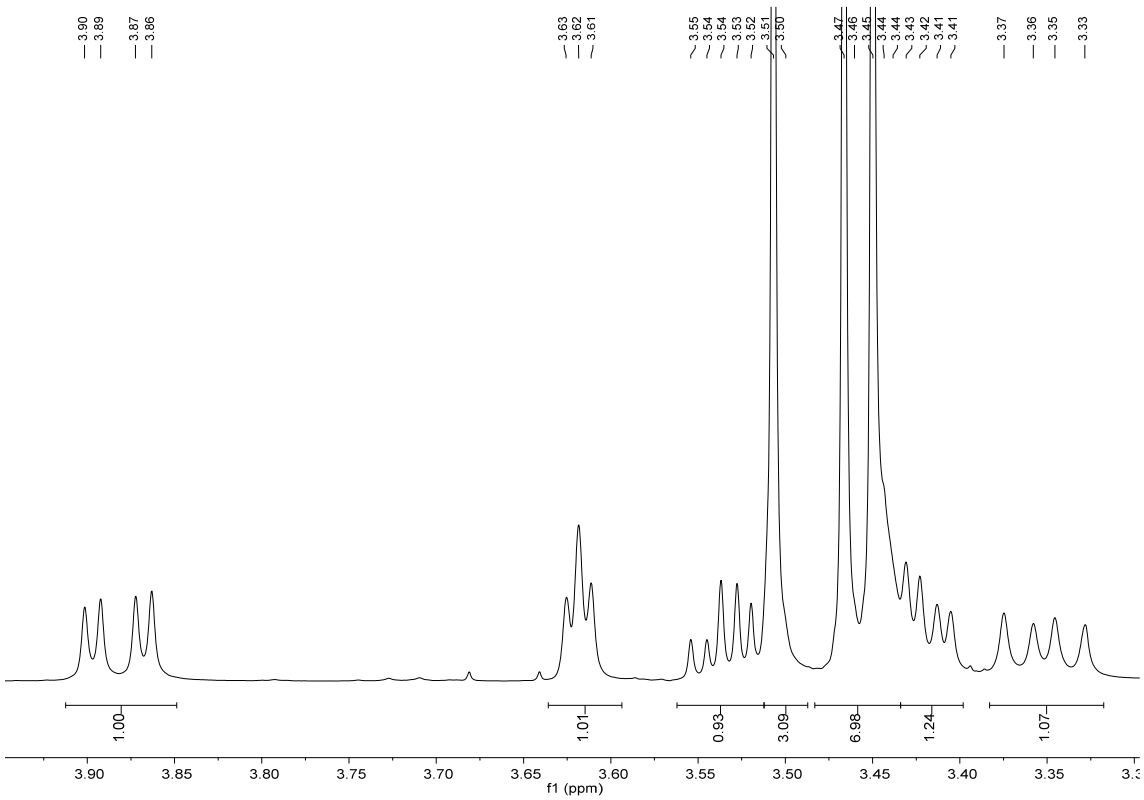
NOESY NMR, $CDCl_3$ of compound **S55**



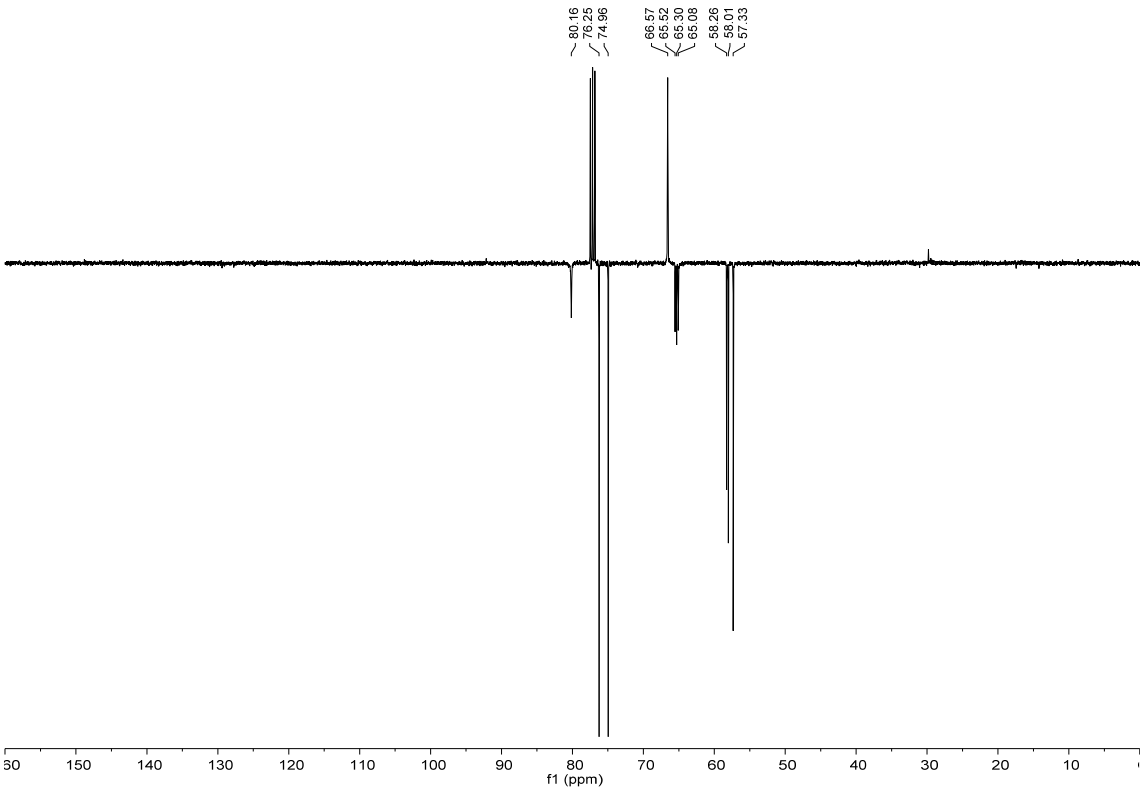
^1H NMR, 400 MHz, $CDCl_3$ of compound **S56**



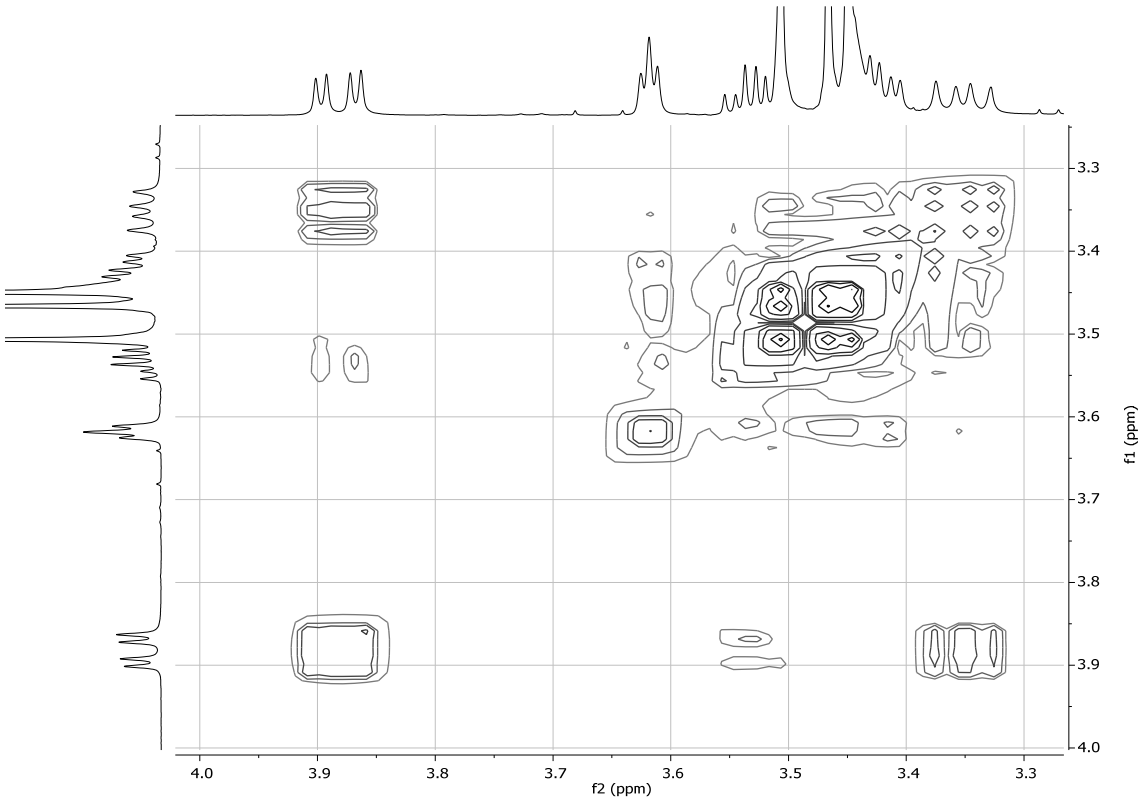
^{1}H NMR, 400 MHz, $CDCl_3$ of compound **S56** (cropped)



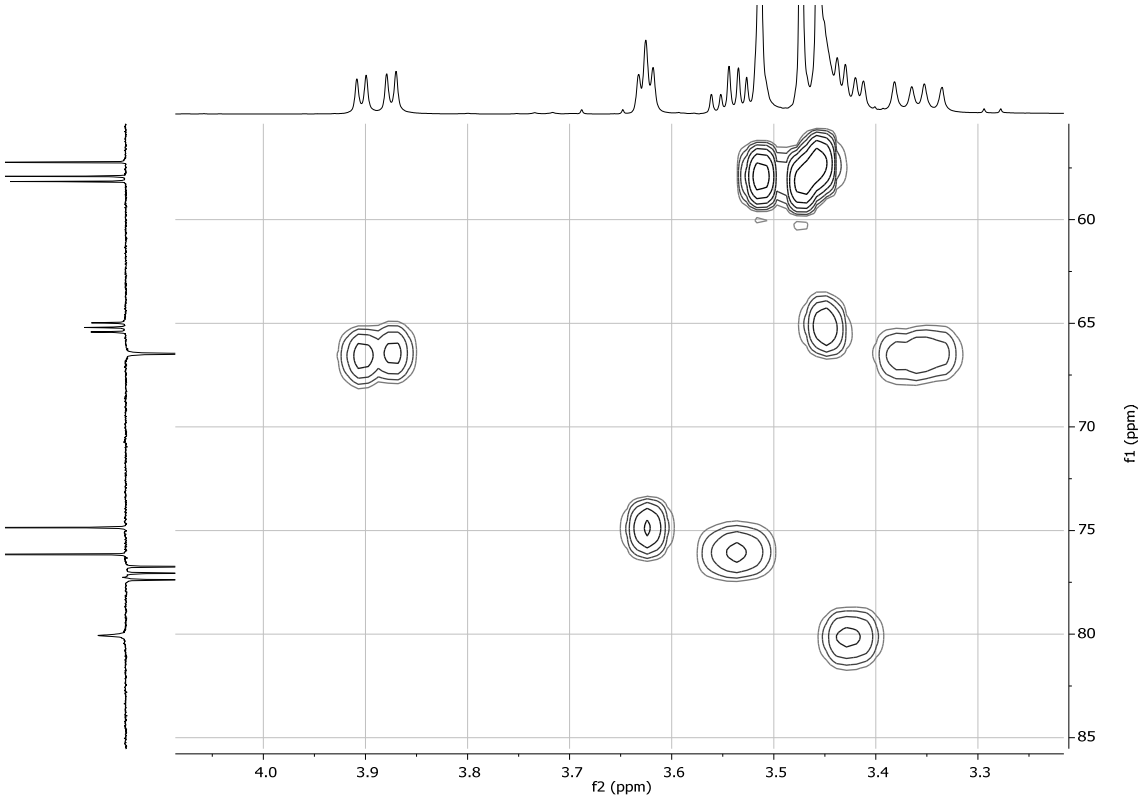
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S56**



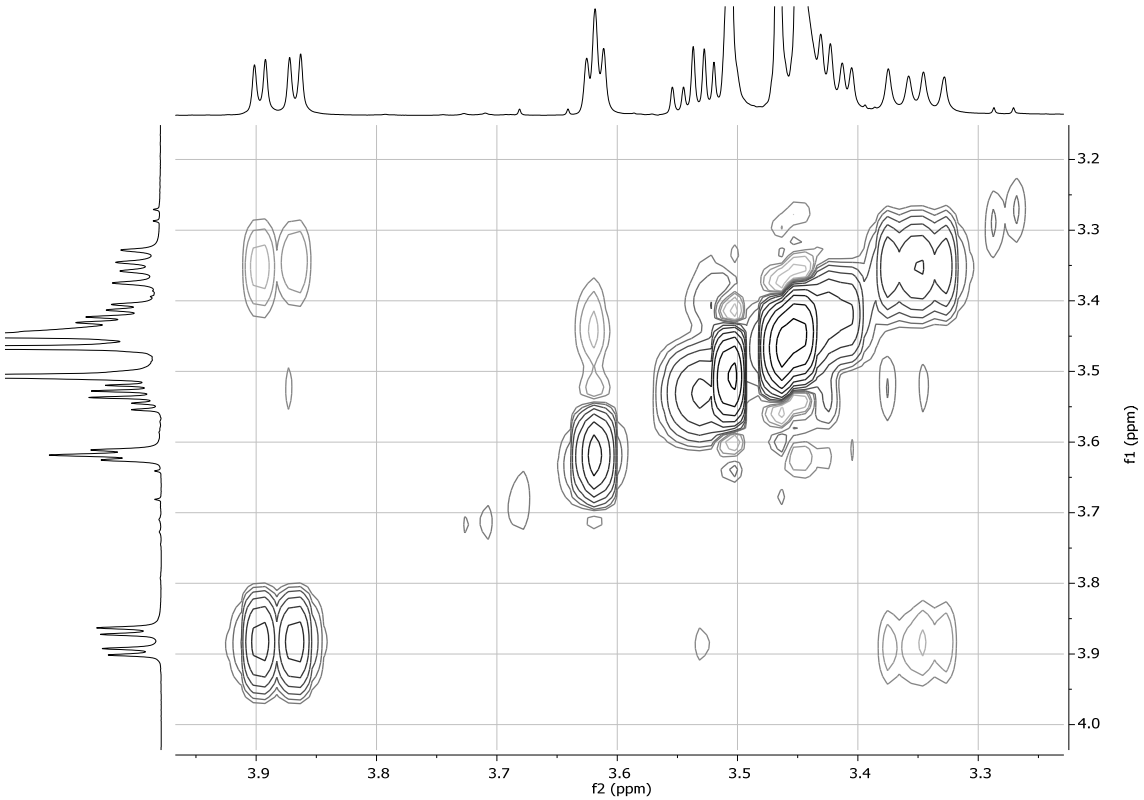
HH-COSY NMR, $CDCl_3$ of compound **S56**



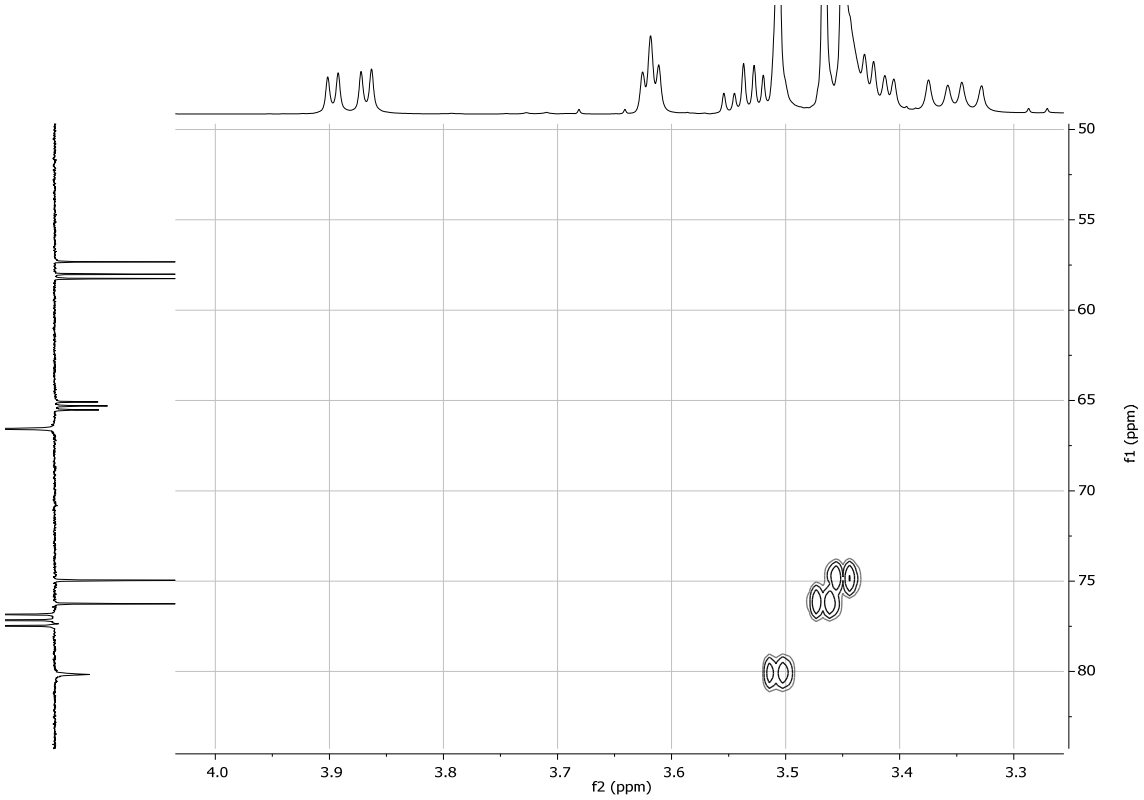
HSQC NMR, $CDCl_3$ of compound **S56**



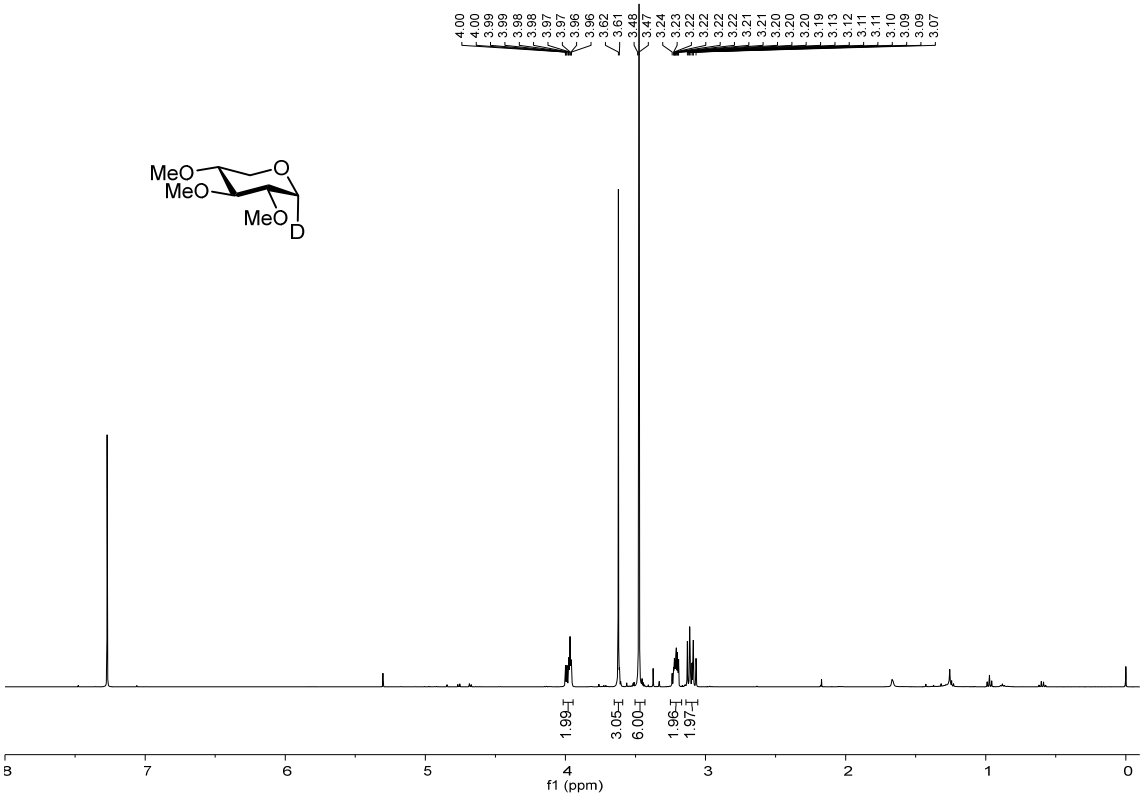
NOESY NMR, $CDCl_3$ of compound **S56**



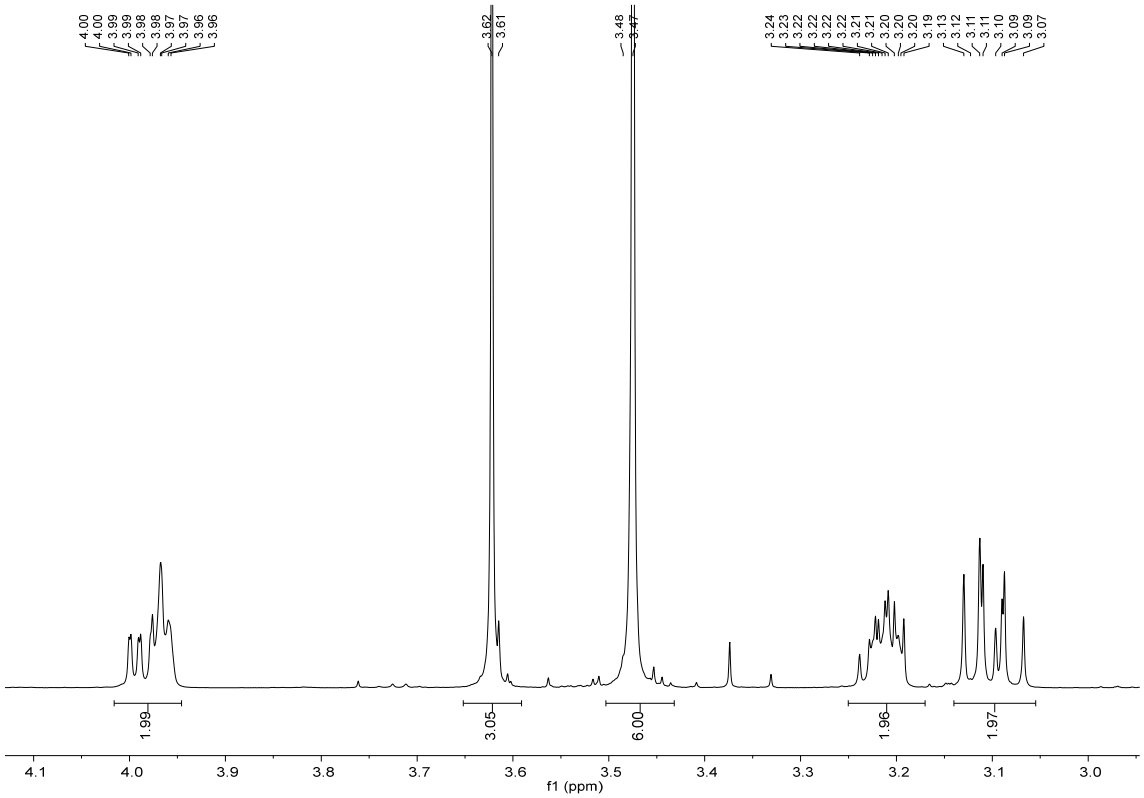
HMBC NMR, $CDCl_3$ of compound **S56**



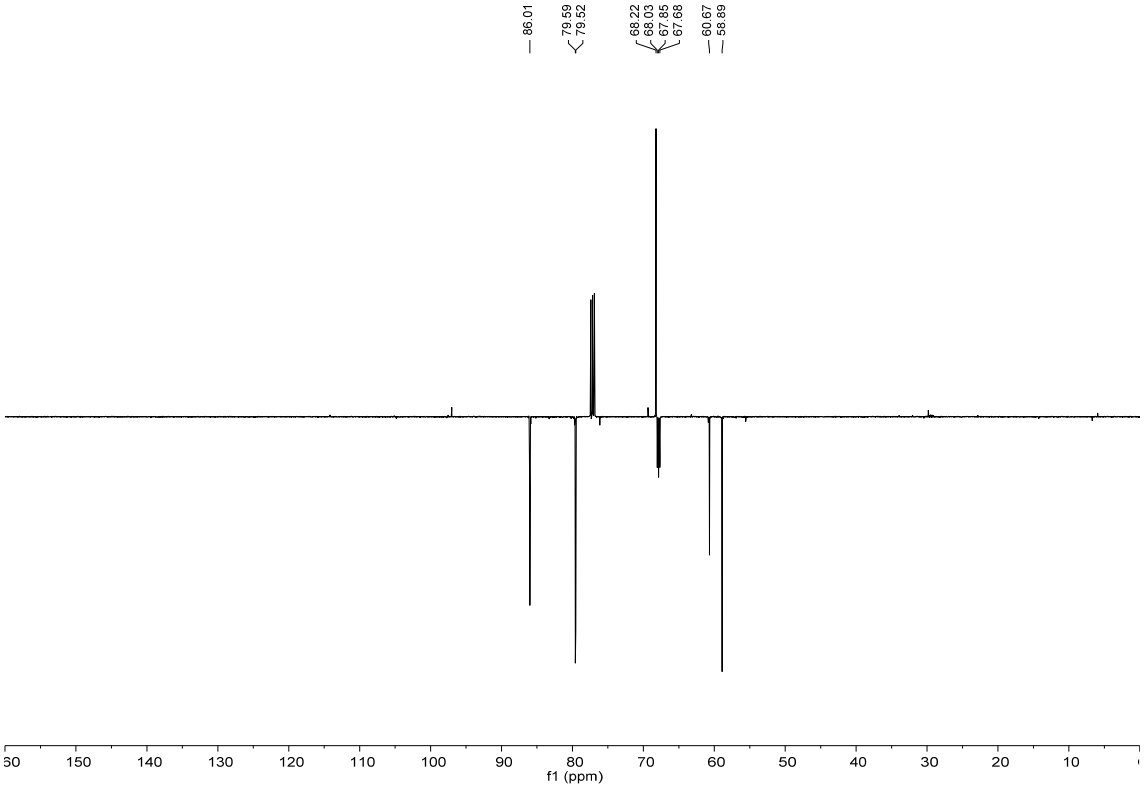
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S57**



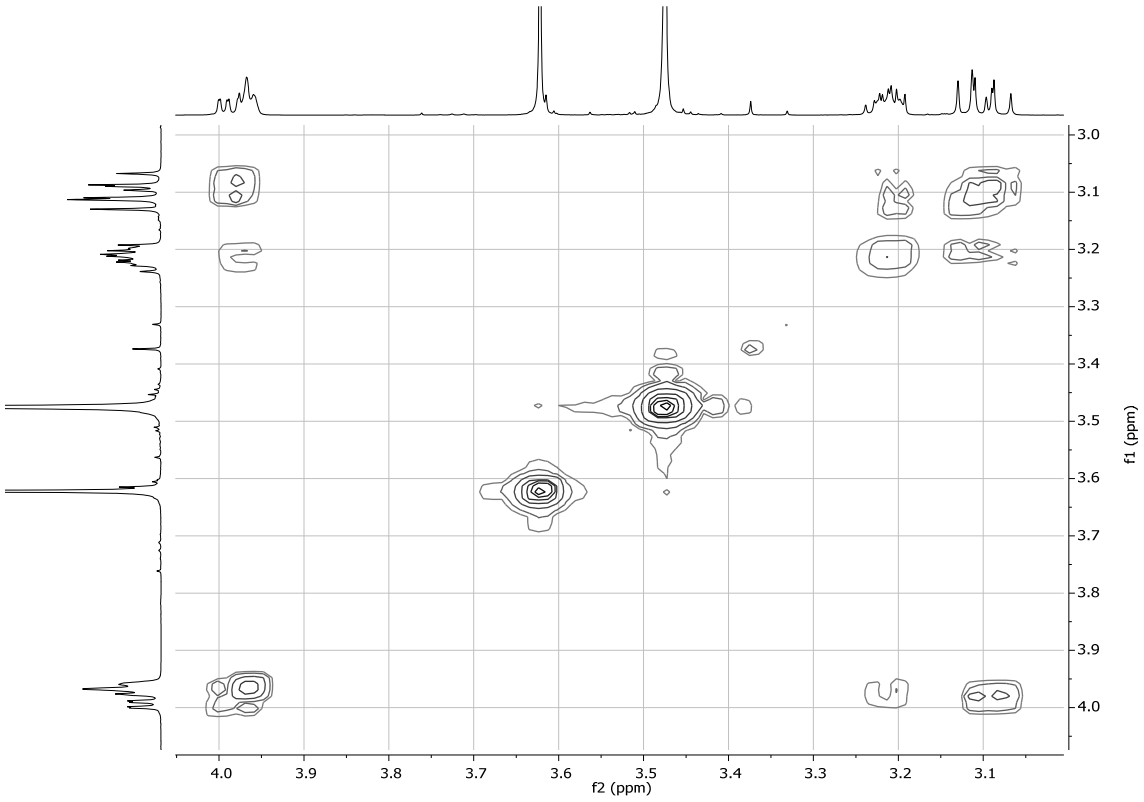
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S57** (cropped)



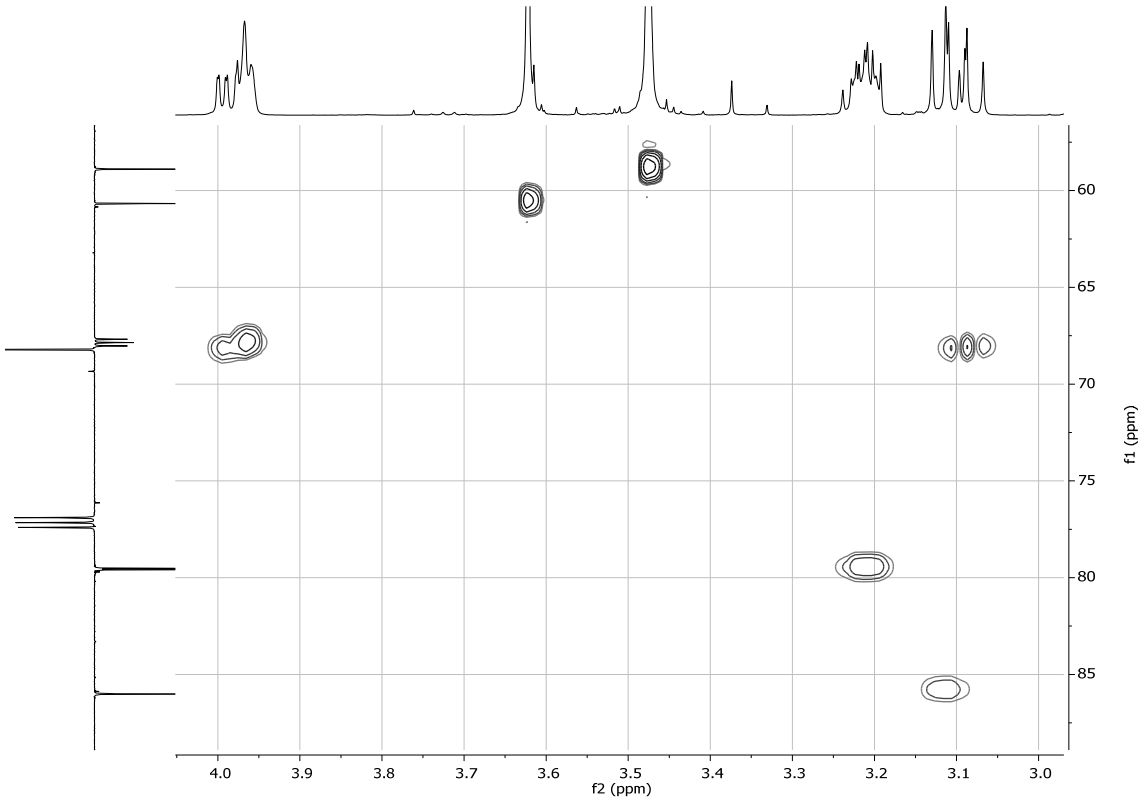
^{13}C NMR, 101 MHz, $CDCl_3$ of compound **S57**



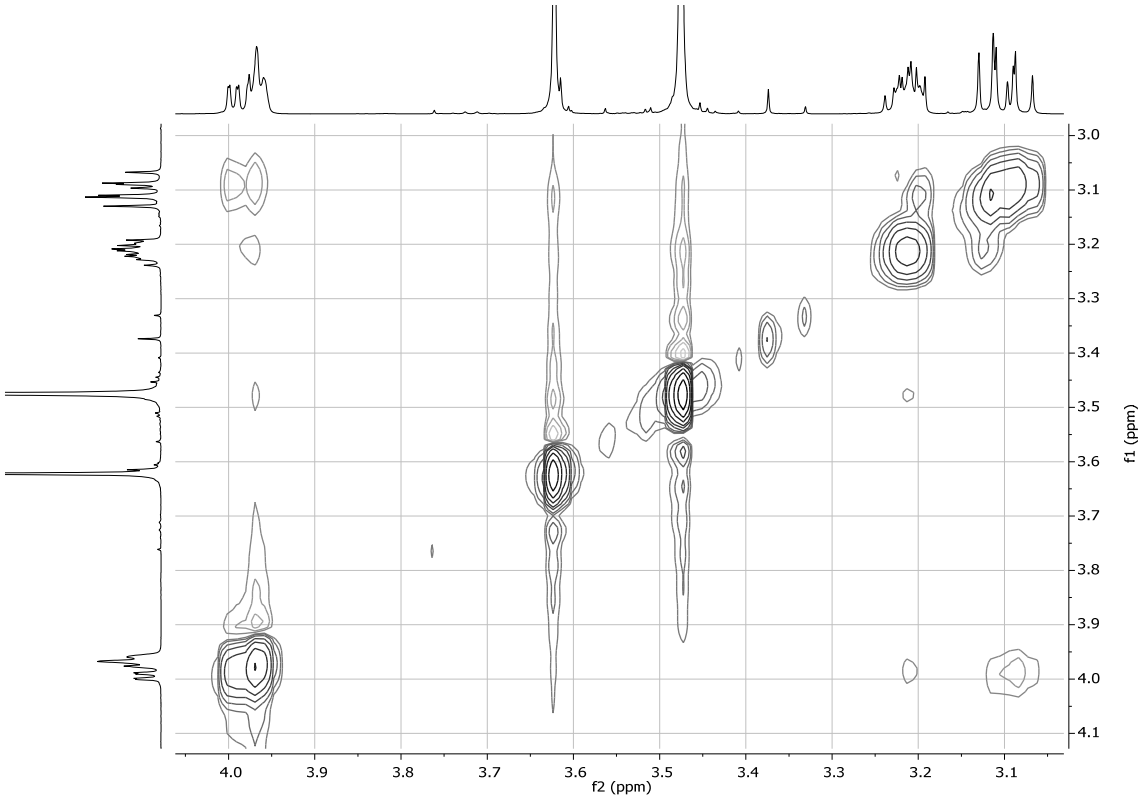
HH-COSY NMR, $CDCl_3$ of compound **S57**



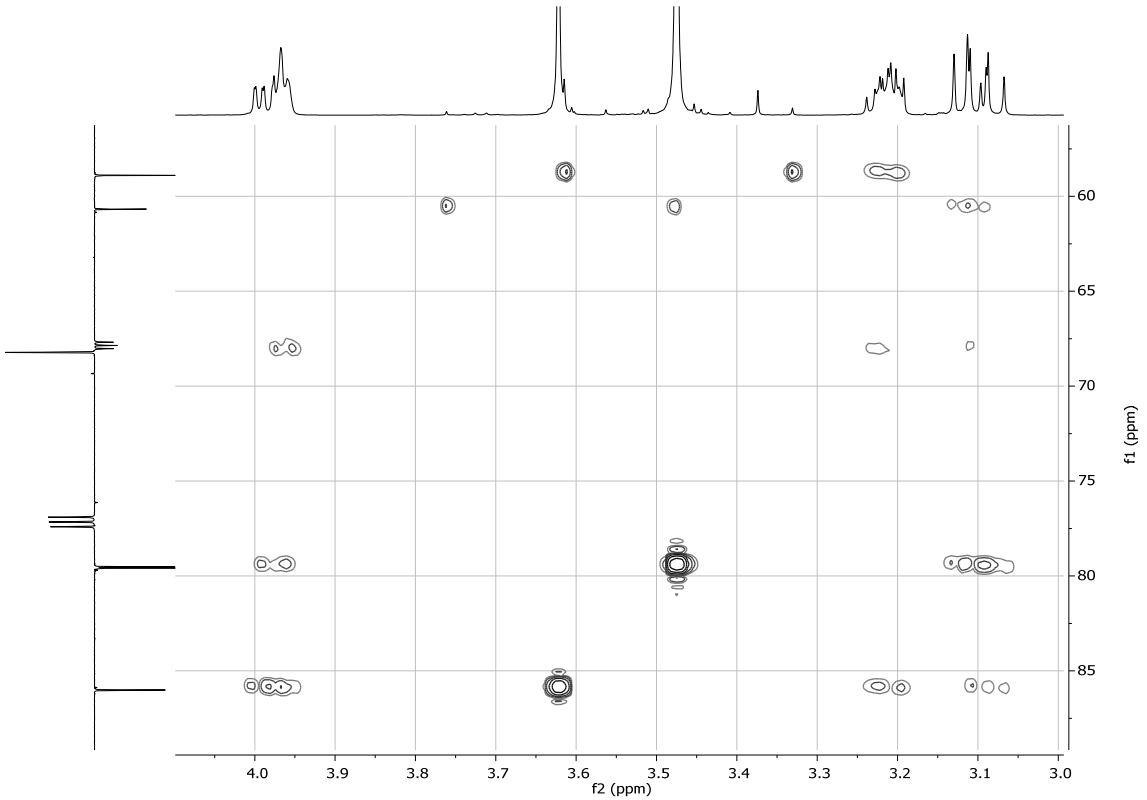
HSQC NMR, $CDCl_3$ of compound **S57**



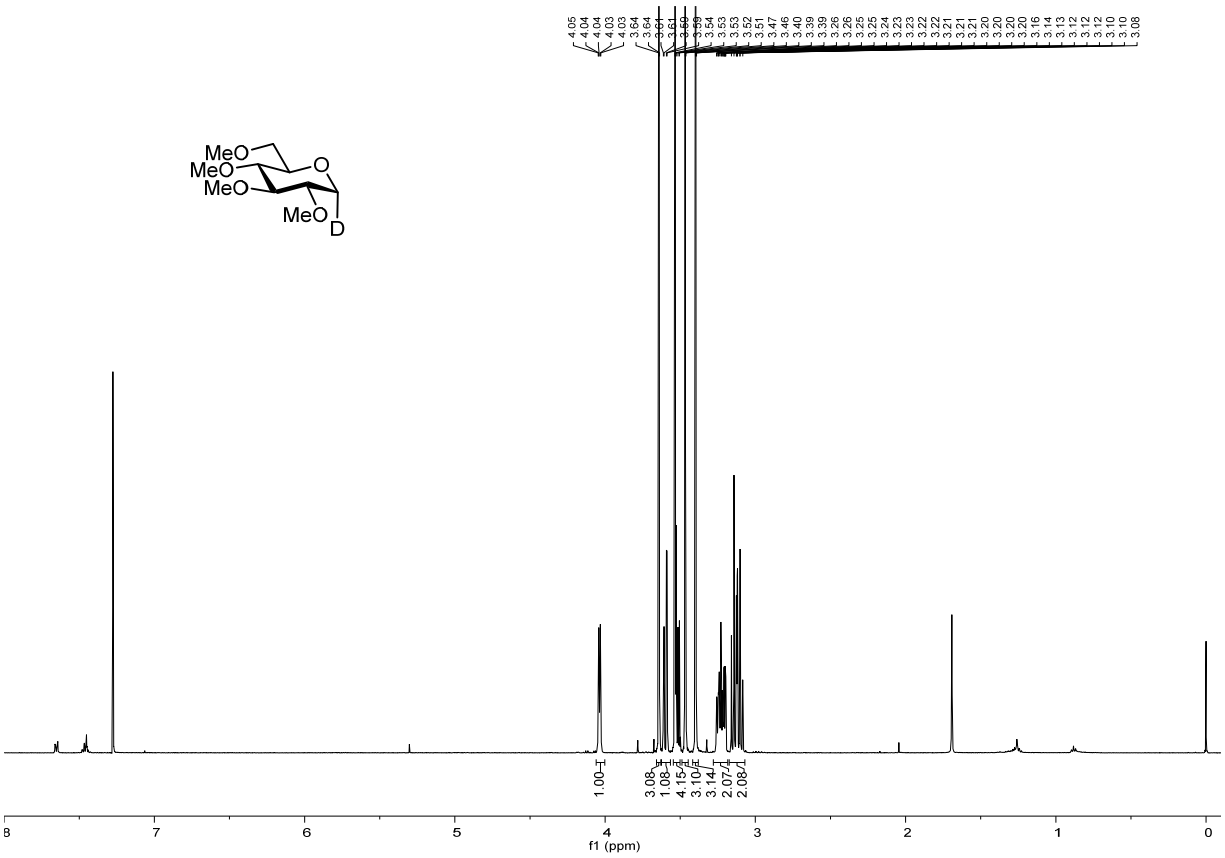
NOESY NMR, $CDCl_3$ of compound **S57**



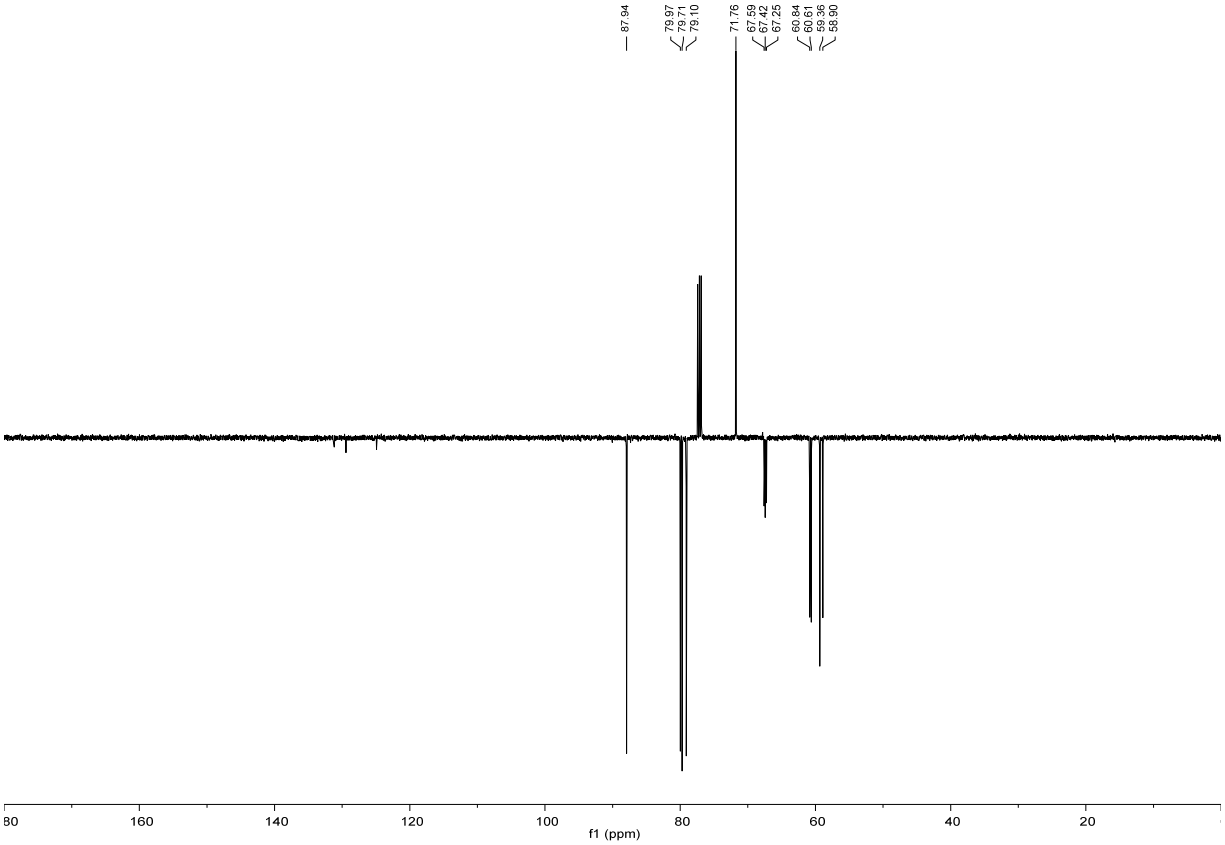
HMBC NMR, $CDCl_3$ of compound **S57**



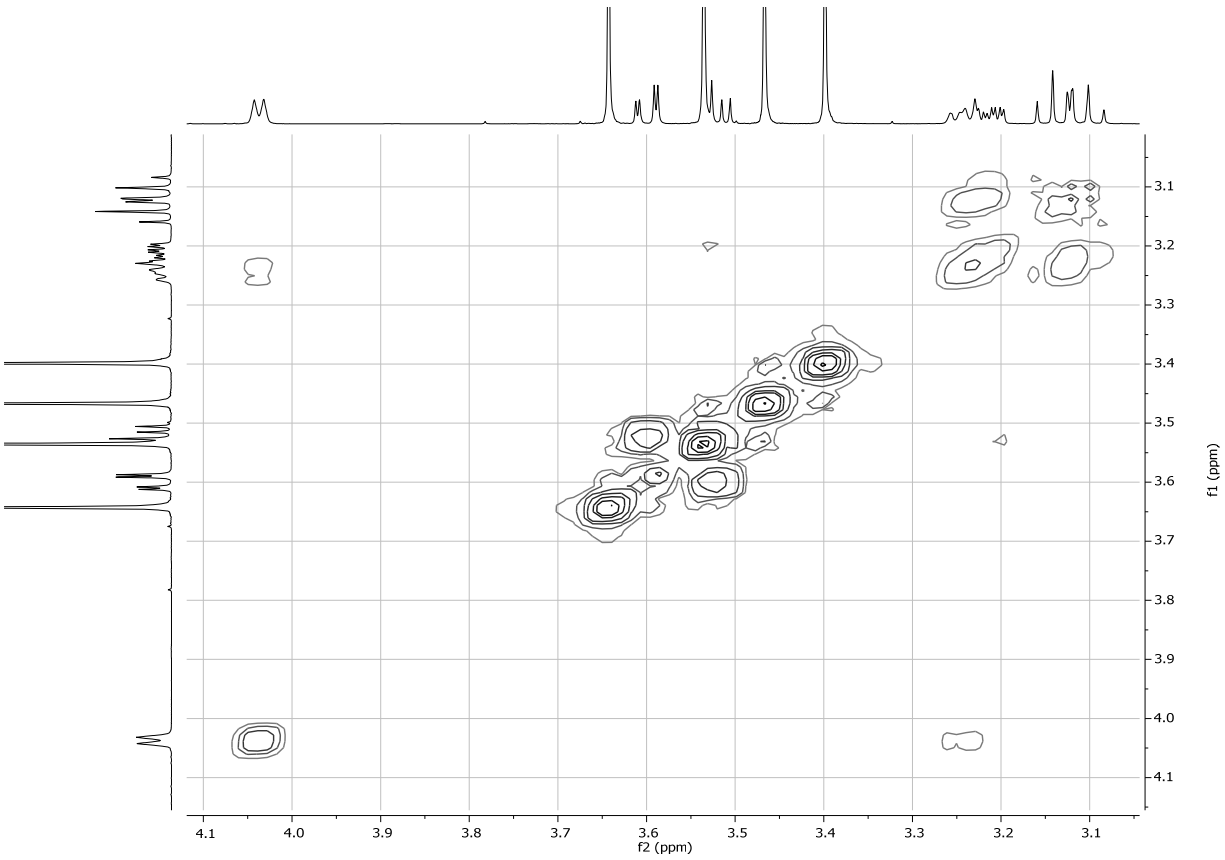
^1H NMR, 500 MHz, $CDCl_3$ of compound **S58**



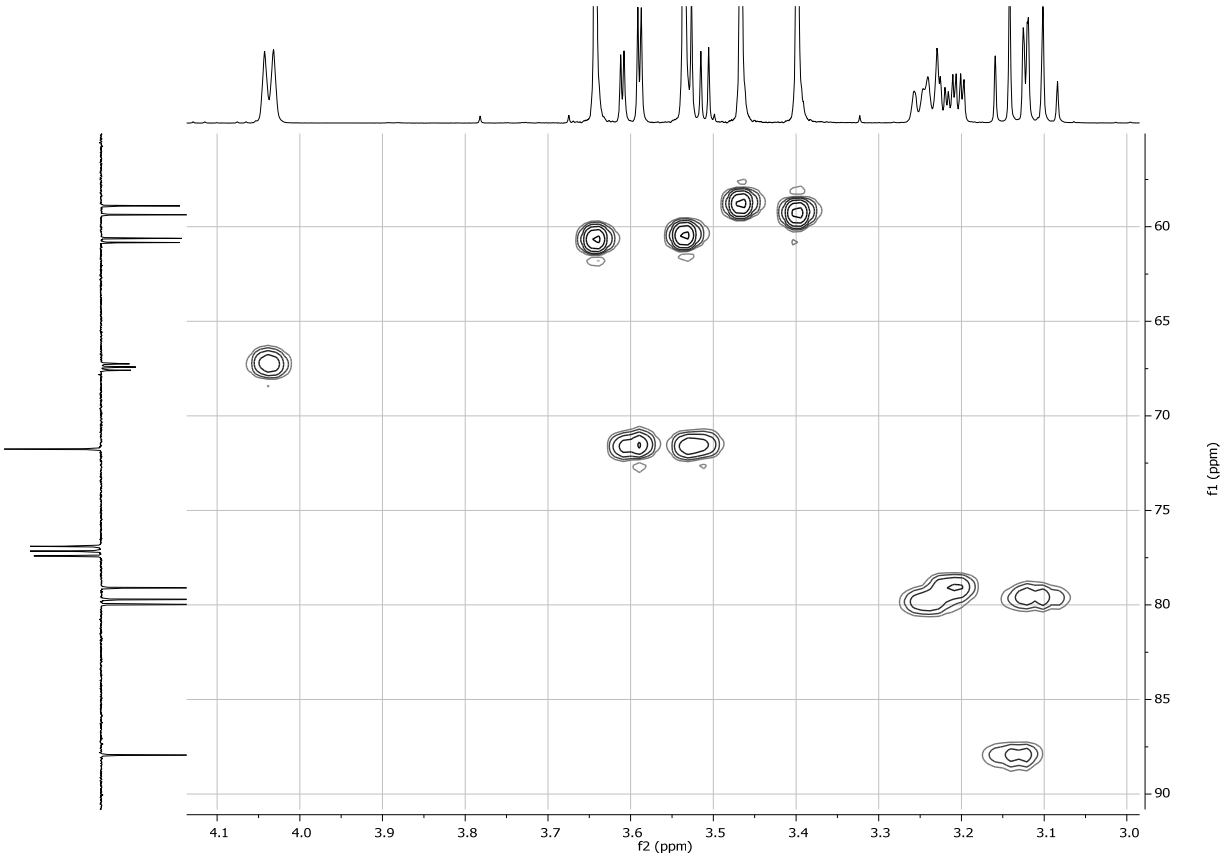
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S58**



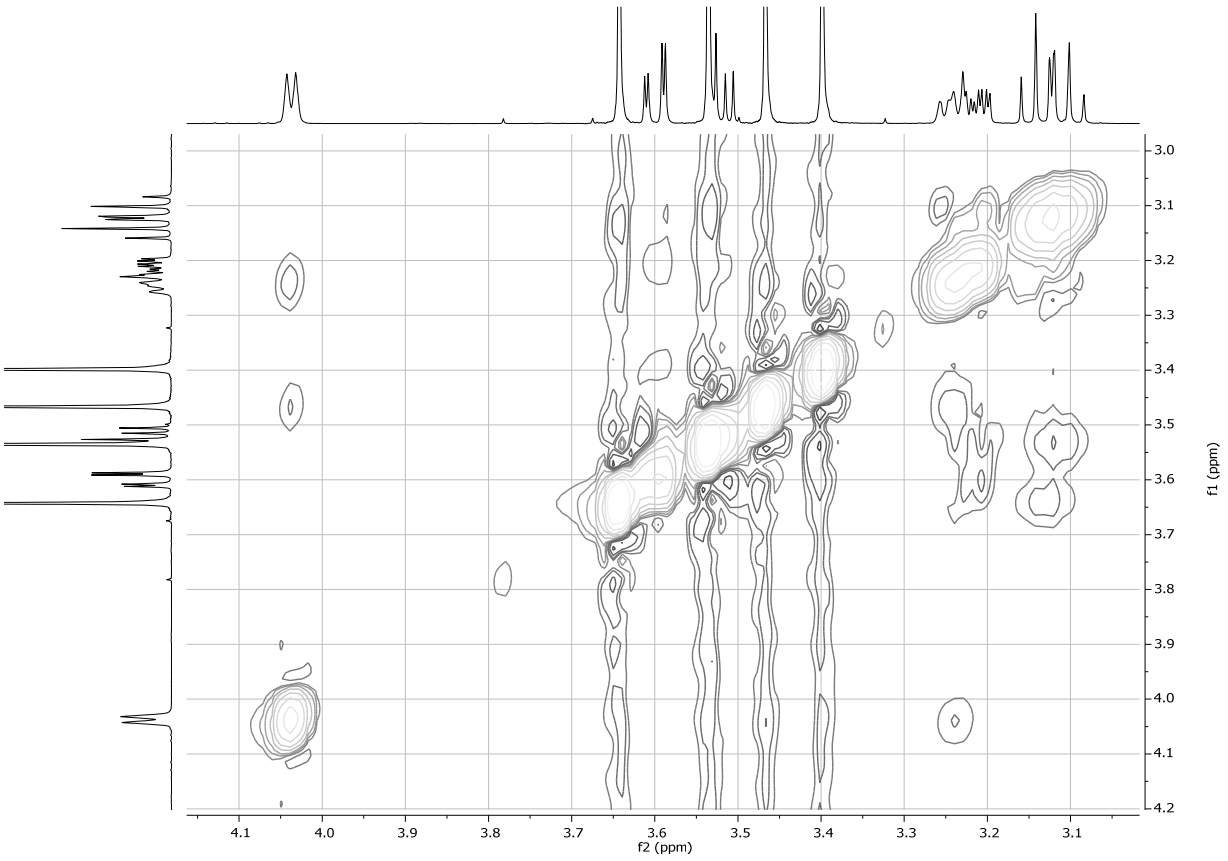
HH-COSY NMR, $CDCl_3$ of compound **S58**



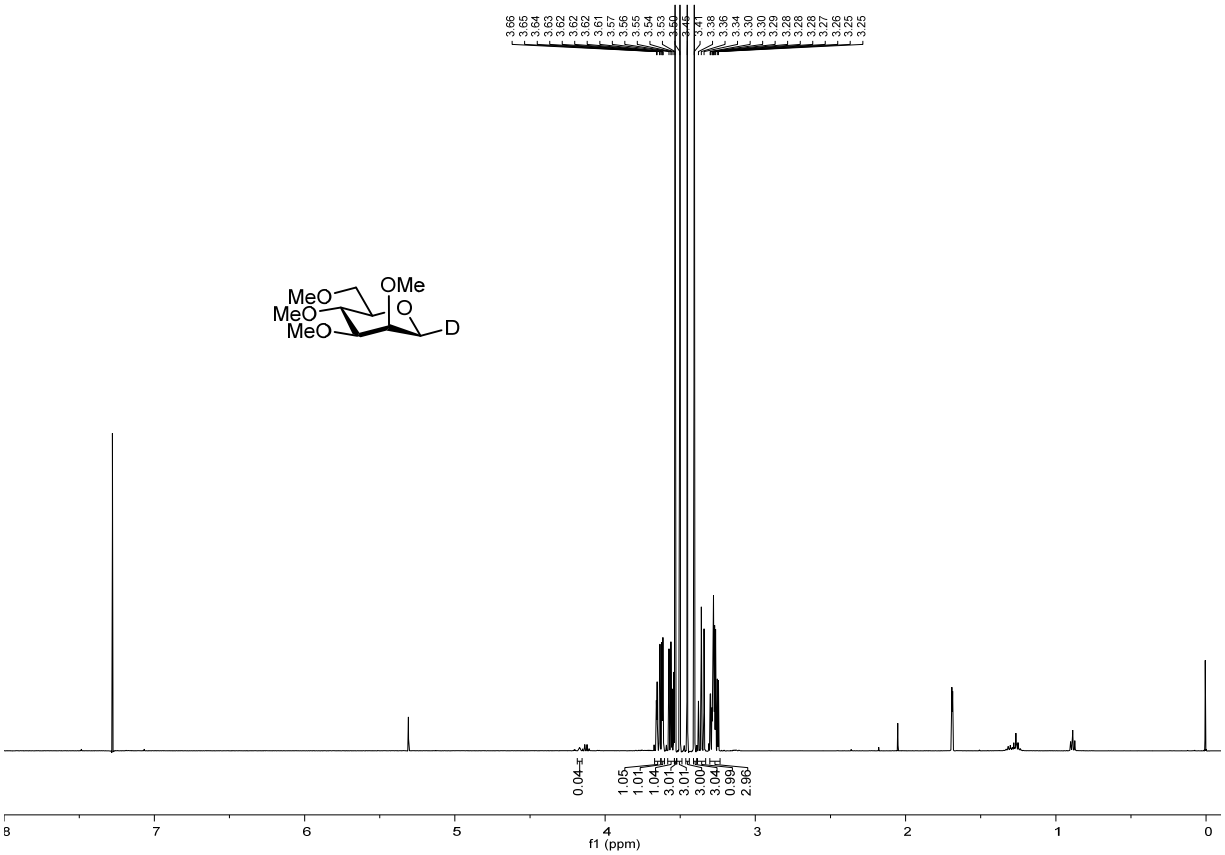
HSQC NMR, $CDCl_3$ of compound **S58**



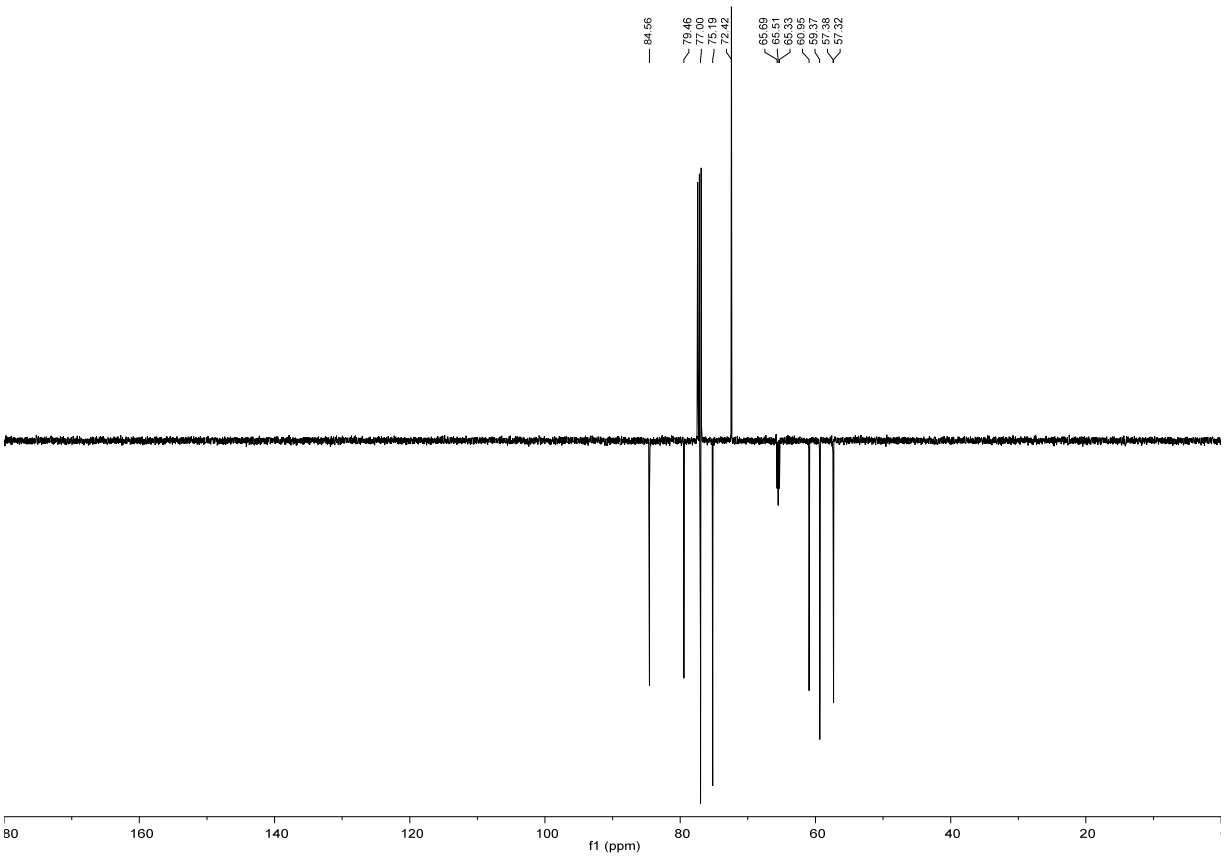
NOESY NMR, $CDCl_3$ of compound **S58**



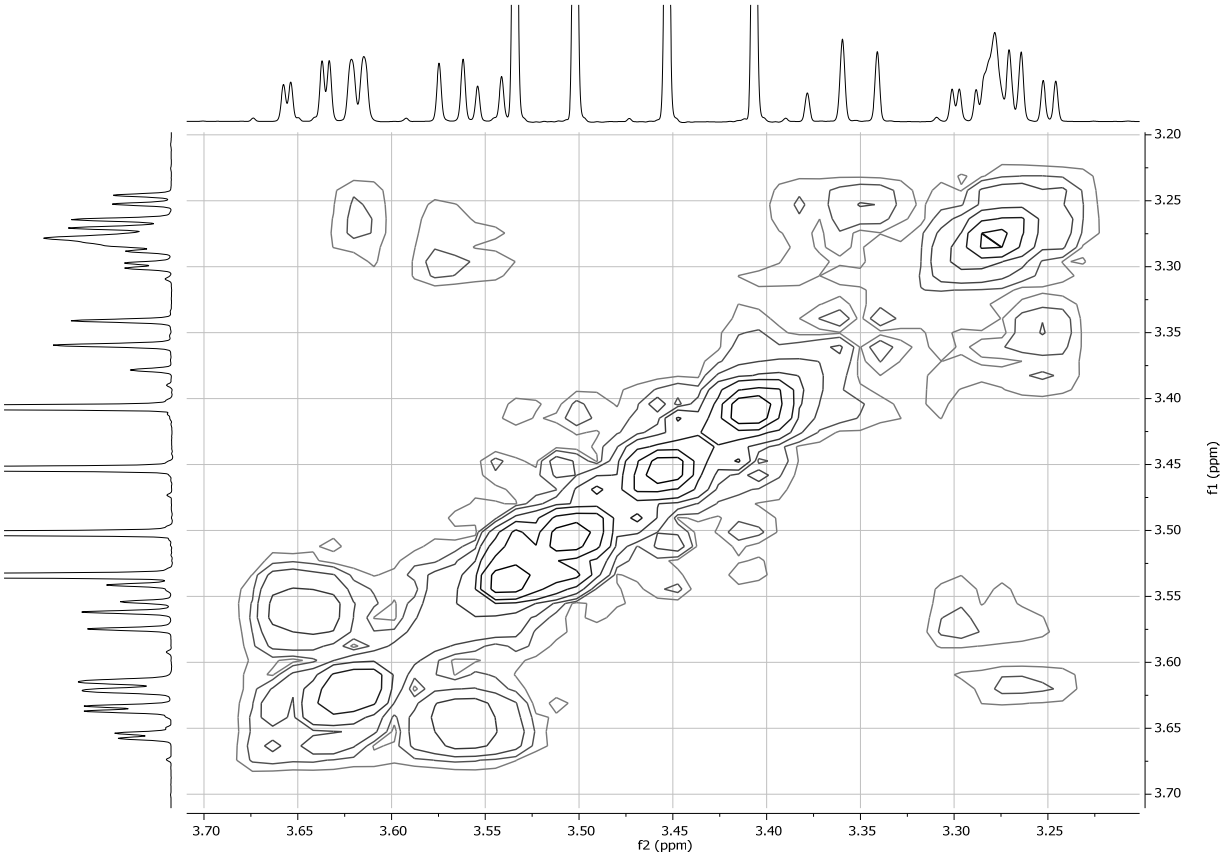
^{1}H NMR, 500 MHz, $CDCl_3$ of compound **S59**



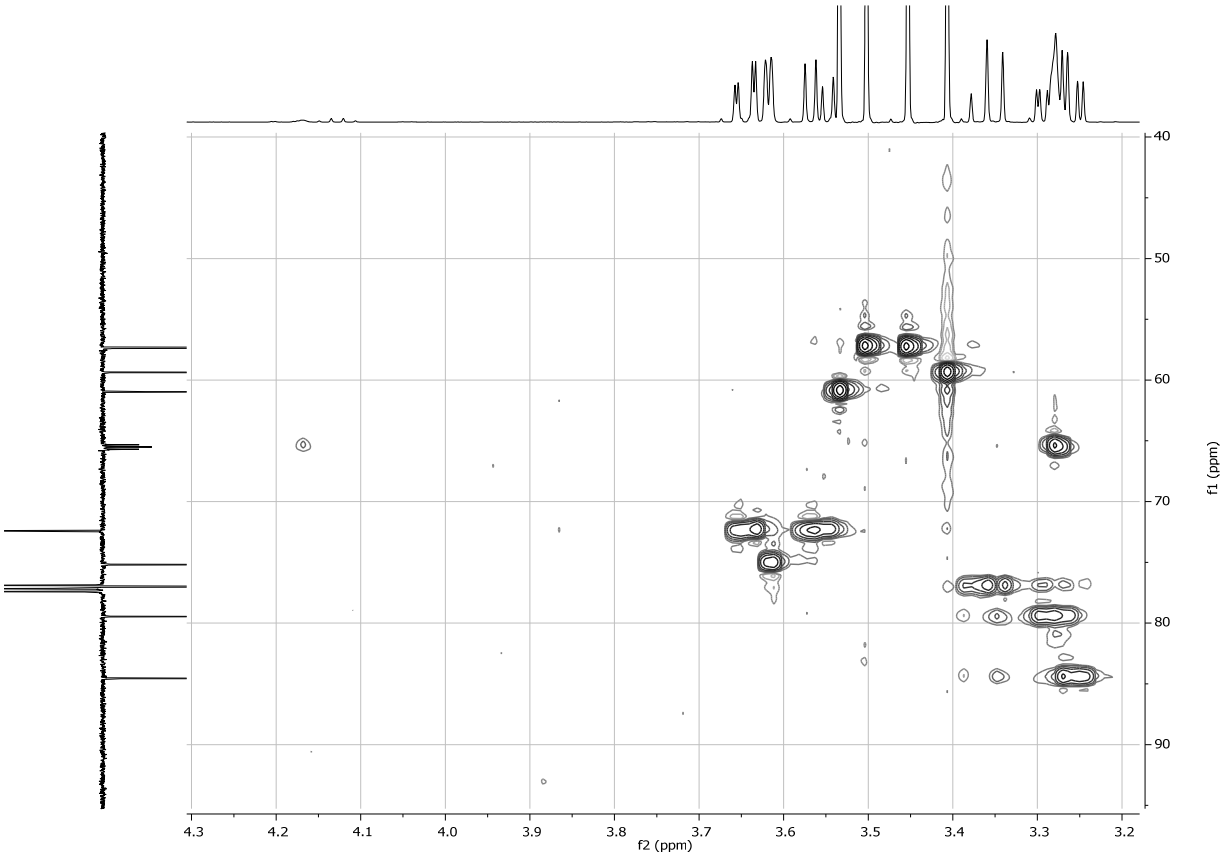
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **S58**



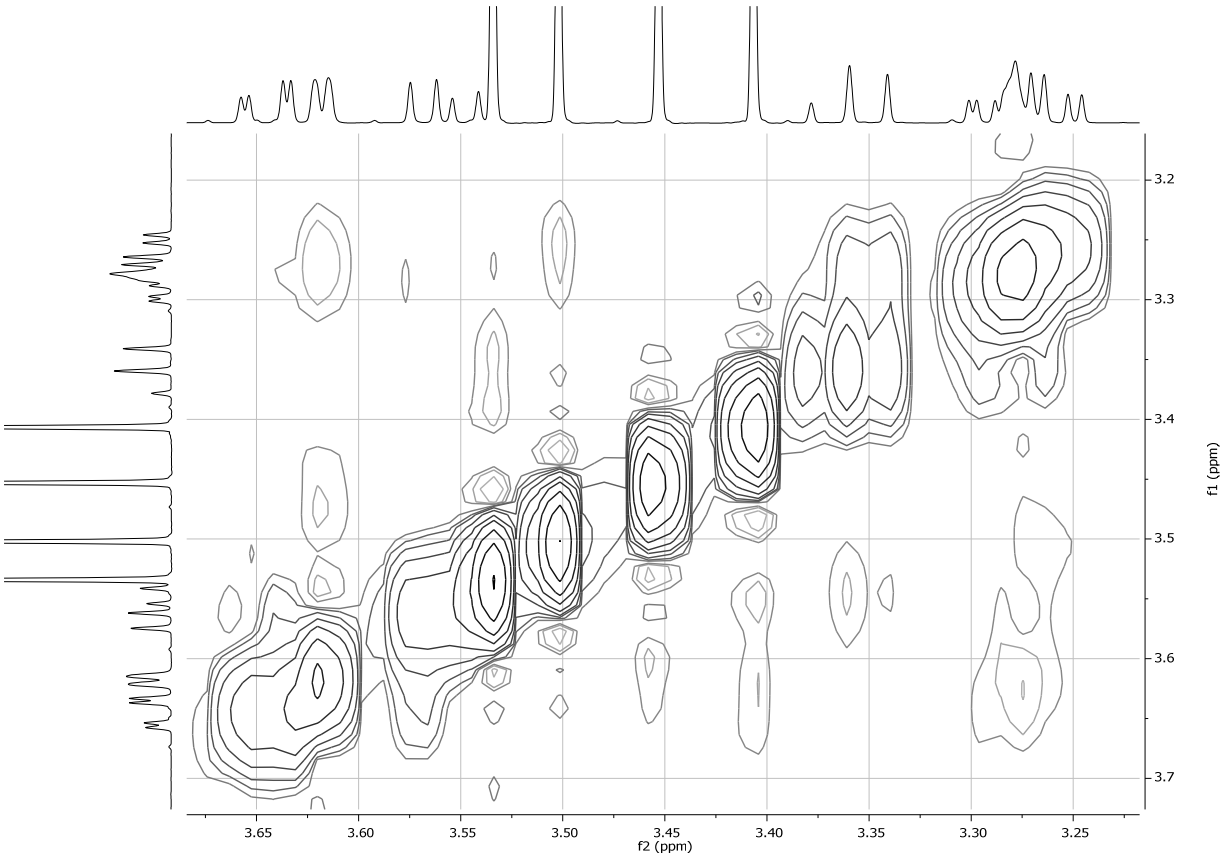
HH-COSY NMR, $CDCl_3$ of compound **S58**



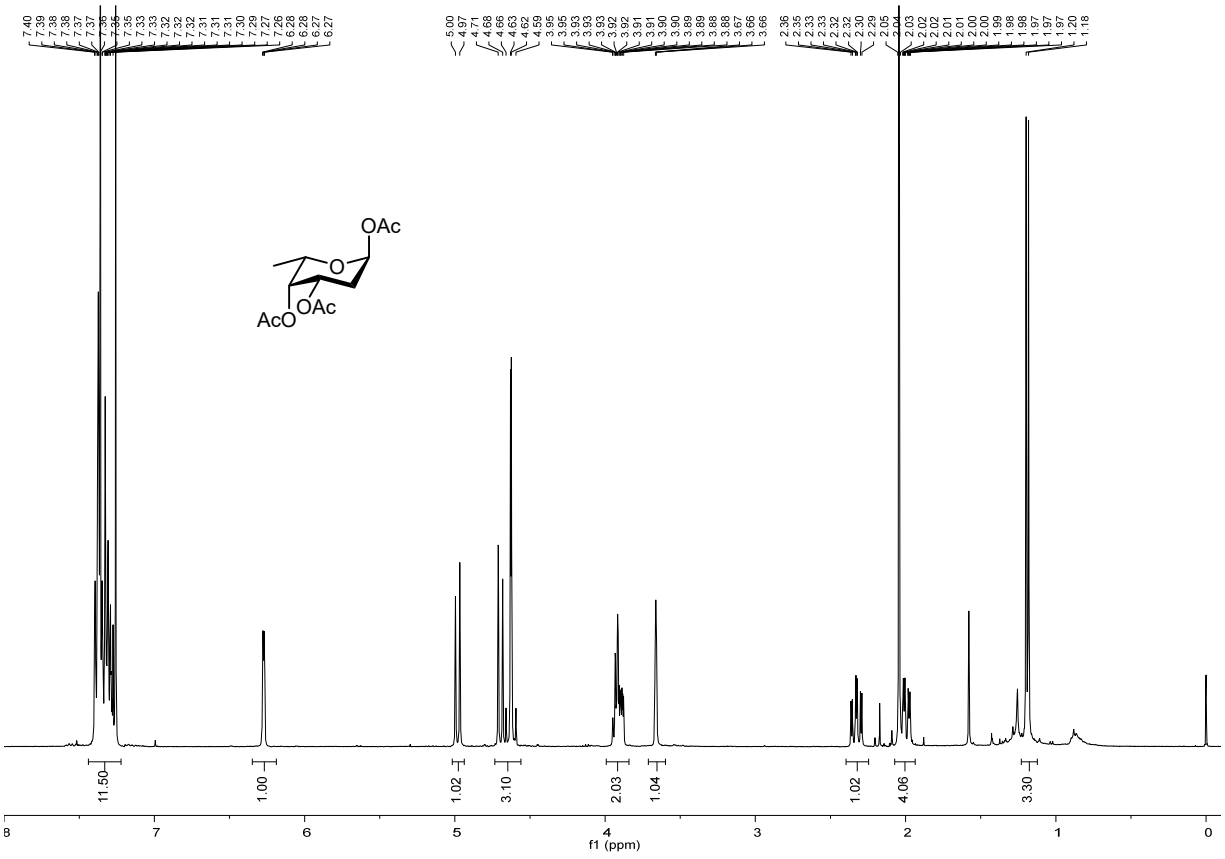
HSQC NMR, $CDCl_3$ of compound **S58**



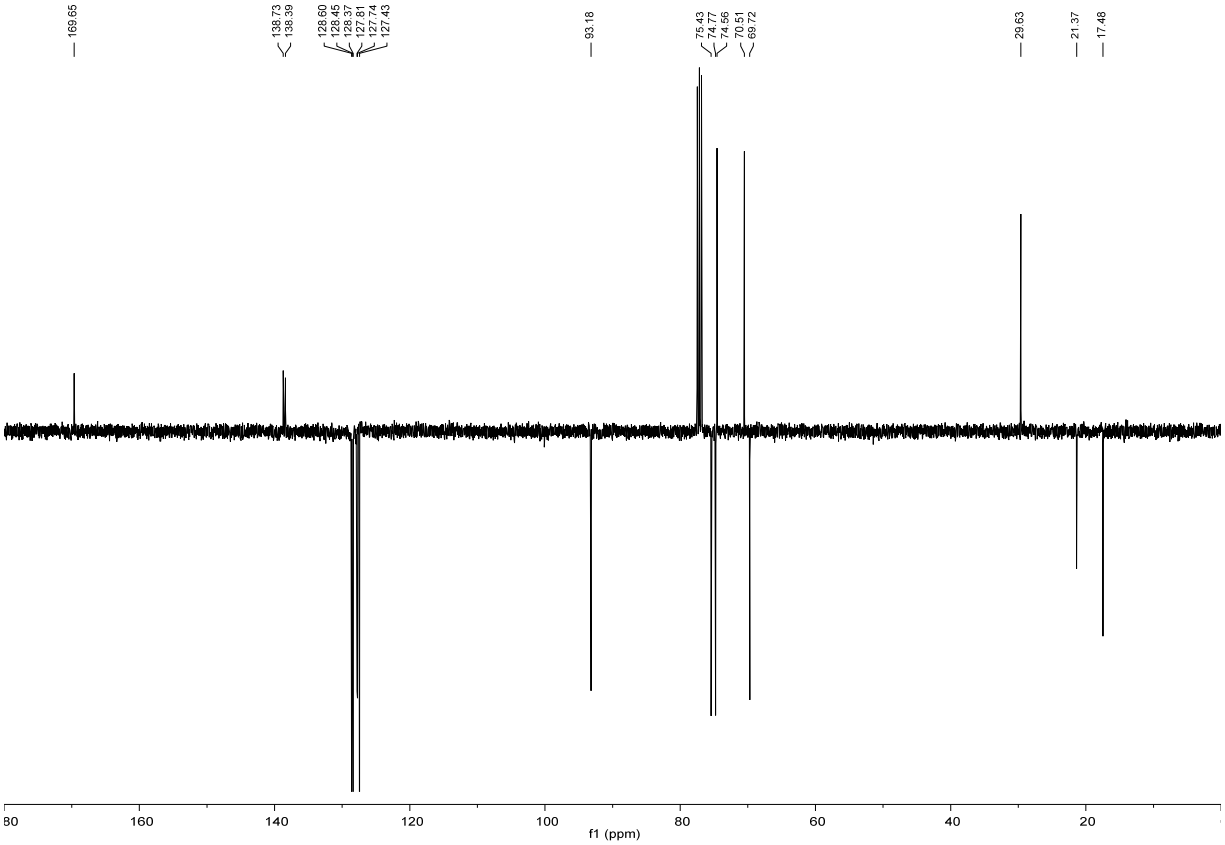
NOESY NMR, $CDCl_3$ of compound **S58**



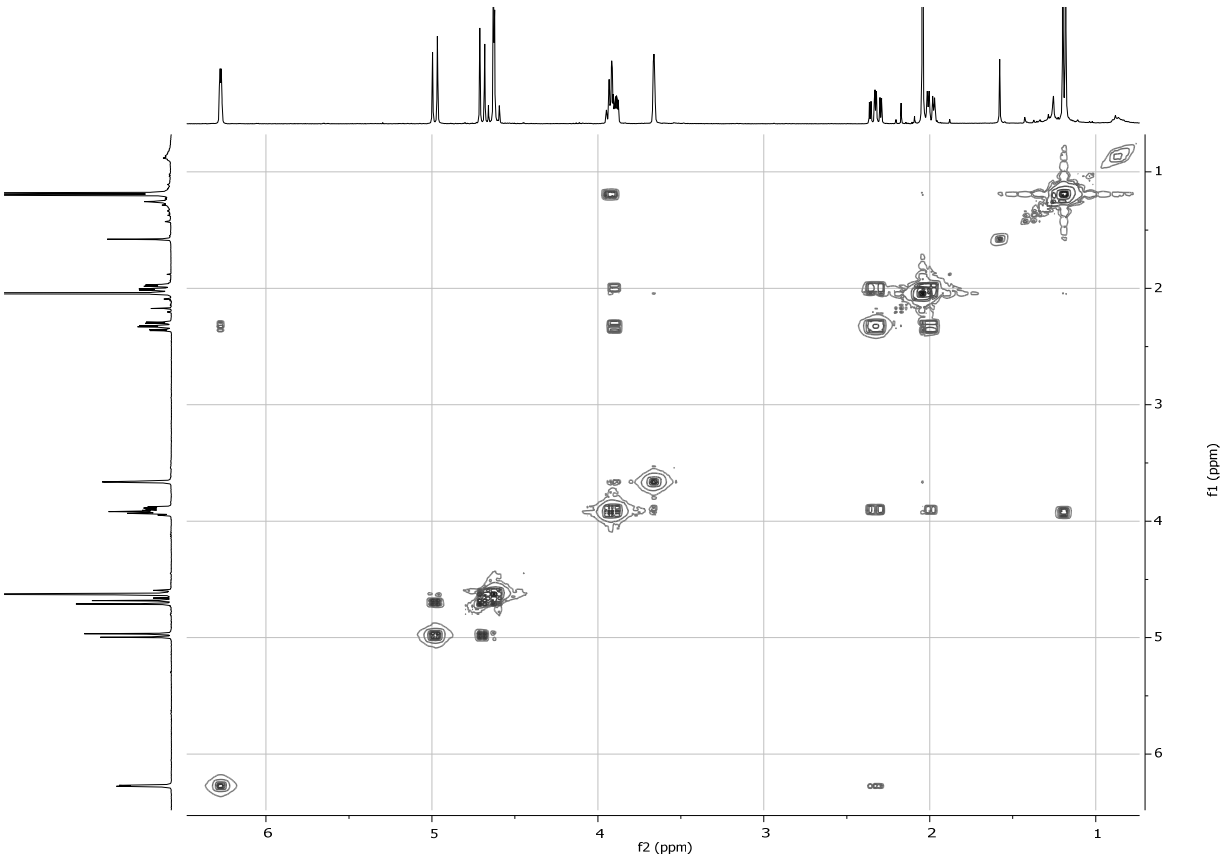
^1H NMR, 500 MHz, $CDCl_3$ of compound **33**



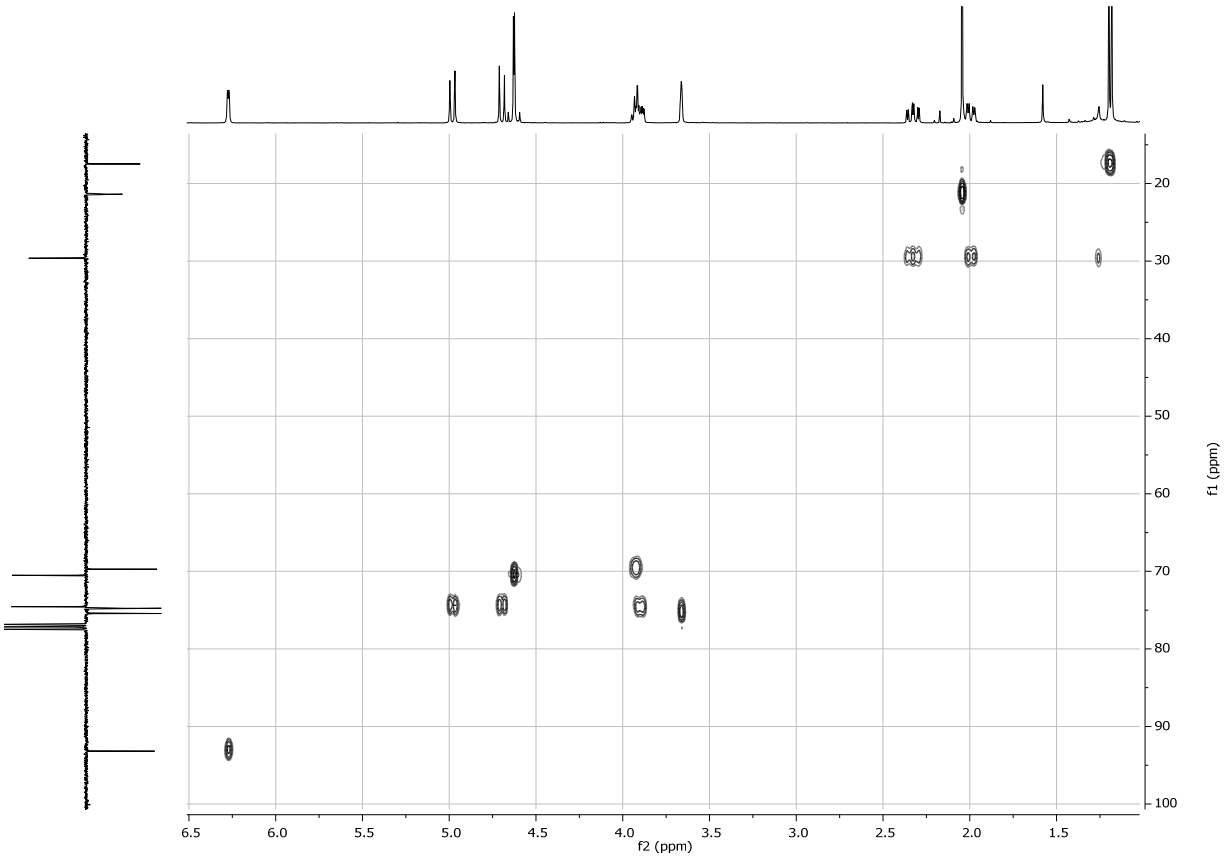
^{13}C NMR, 126 MHz, $CDCl_3$ of compound **33**



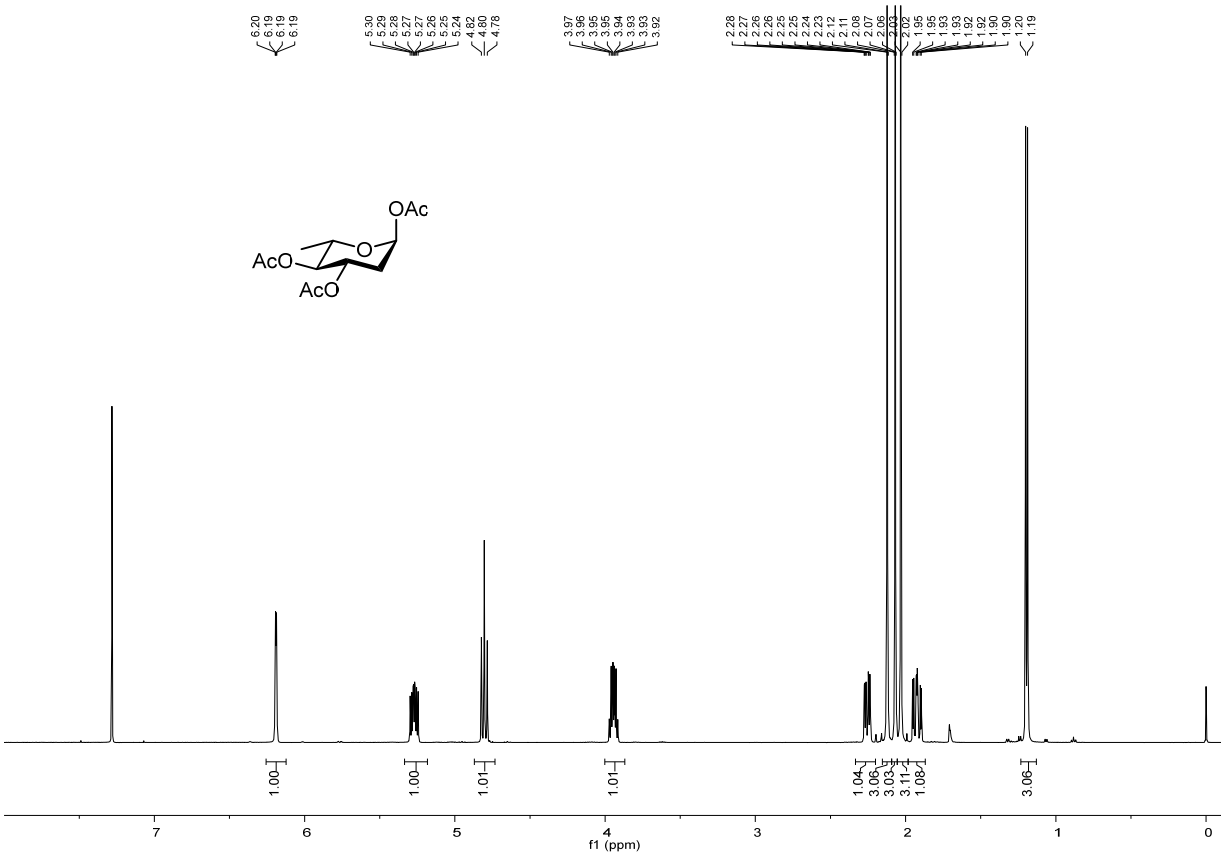
HH-COSY NMR, $CDCl_3$ of compound **33**



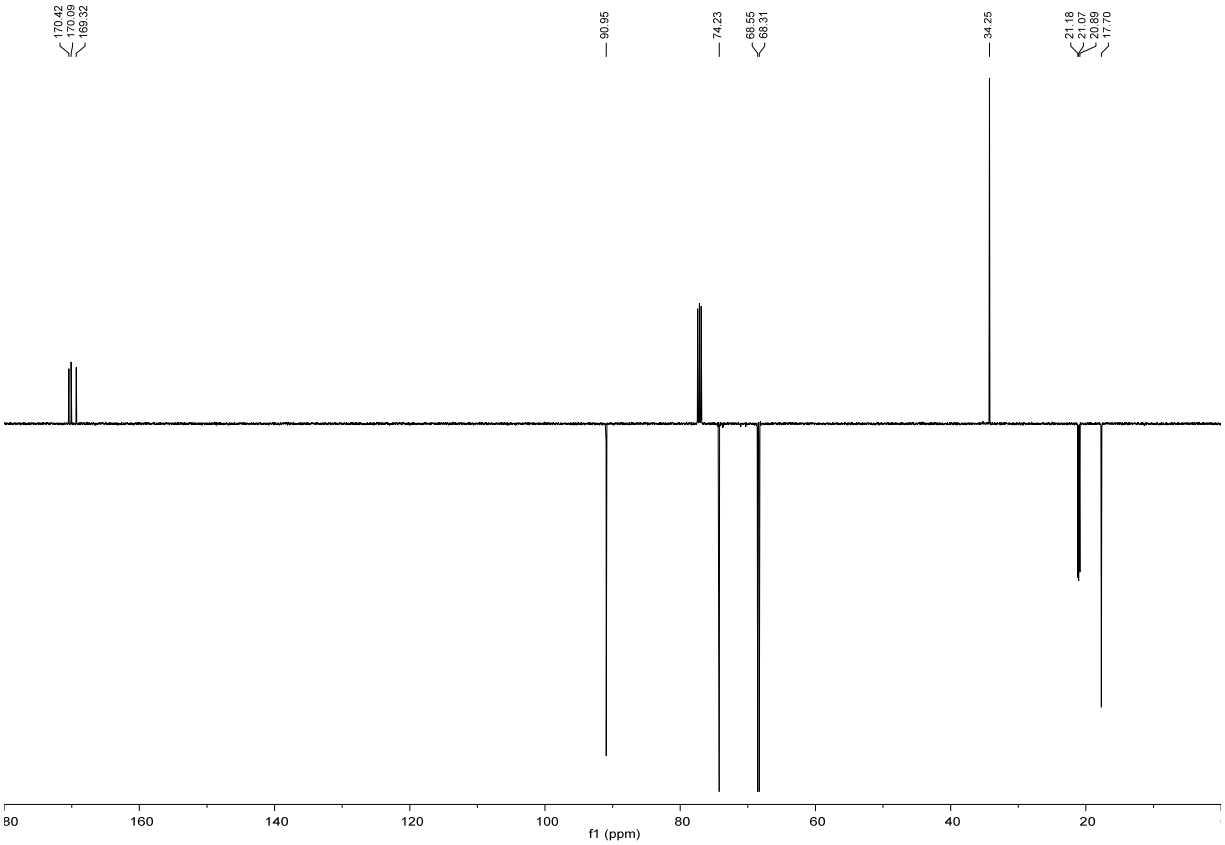
HSQC NMR, $CDCl_3$ of compound **33**



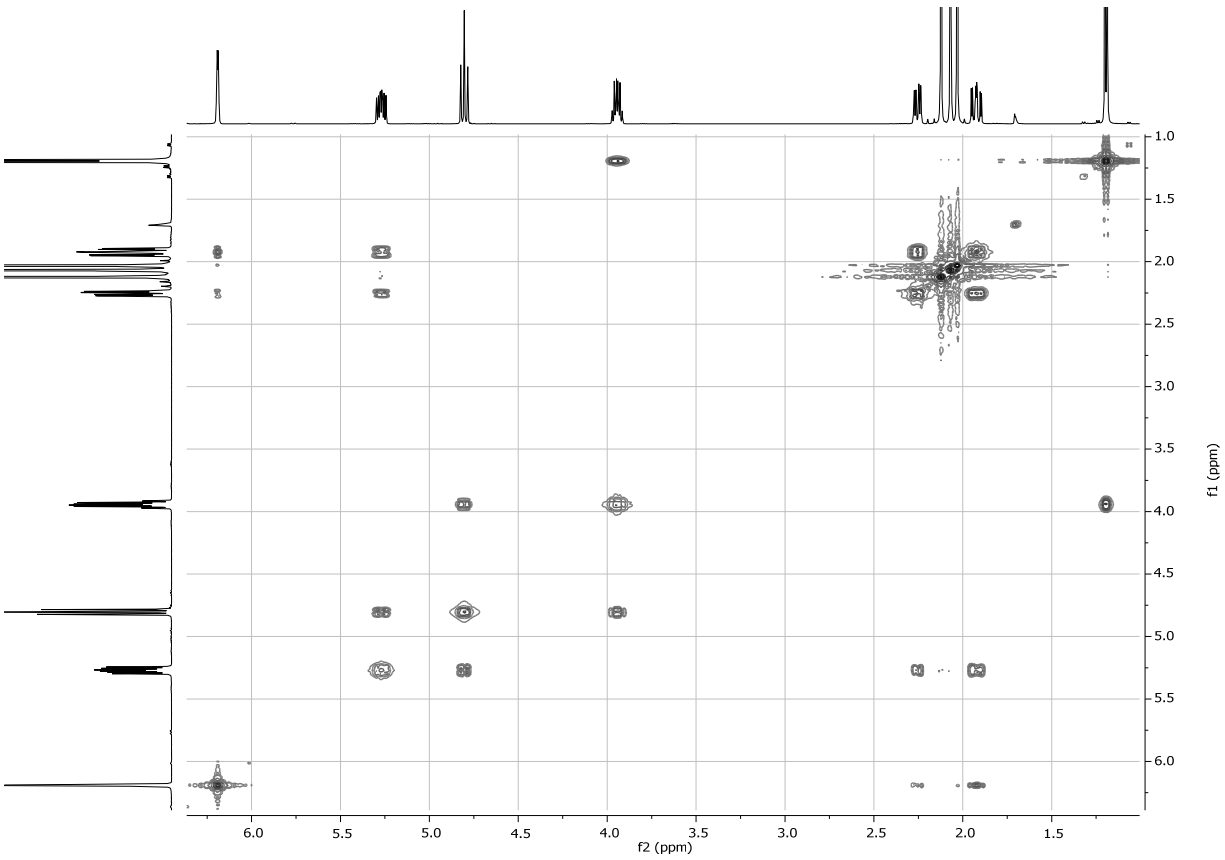
^1H NMR, 500 MHz, $CDCl_3$ of Donor **34**



^{13}C NMR, 126 MHz, $CDCl_3$ of Donor **34**



HH-COSY NMR, $CDCl_3$ of Donor **34**



HSQC NMR, $CDCl_3$ of Donor **34**