Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Construction of 1,2-*cis* Rhamnosidic Linkages and Synthesis of Core Tetrasaccharide Repeating Unit of *Streptococcus pneumoniae* Serotype 23F

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Density Functional Theory (DFT)

For understanding of mechanism of this β-rhamnosylation, DFT calculations were conducted using the Gaussian 09 program package[1]. All the geometries were optimized with the B3LYP[2] functional and basis set BS1 (BS1 = 6-31G(d)[3] for main group elements and Lanl2dz[4] for Zn and I) in the gas phase. Solvation free energies were calculated using the SMD[5] solvation model (solvent = diethyl ether) under ωB97XD[6]/BS2 (BS2 = 6-311 + G**[3] for main group elements and SDD[7] for Zn and I). Gibbs free energy present in this paper is the sum of single point energy at ωB97XD[6]/BS2, thermodynamic correction at B3LYP/BS1, and solvation free energy. Frequency analysis was conducted for optimized structure at the same level of theory at default temperature (298.15K) to ensure that the optimized ground state structures have no imaginary frequency, while the optimized transition state structures each has exactly 1 imaginary frequency, with the direction of vibration of the imaginary frequency aligned along the direction of formation or dissociation of the chemical bond of interest. Short intrinsic reaction coordinate scans (IRC) were performed on the optimized TS structures at the same level of theory to ensure that the TS structures correspond to energy maxima along the reaction routes connecting the immediately reacting intermediates and product structures.

To obtain a reliable description of the mechanism of ZnI_2-catalyzed 1,2-*cis*-rhamnosylation, we proposed the possible mechanism and conducted computational studies. The starting material has two possible isomers as R1 and R1' depending on the orientations of the substituent. Our calculations indicate that R1 is 5.3 kcal/mol more stable than the R1' (see Figure S1 in the Supporting Information). Therefore, in the following discussion, we will only refer to the more stable starting material R1. The model reaction was simplified as the reaction between R1 and methanol.

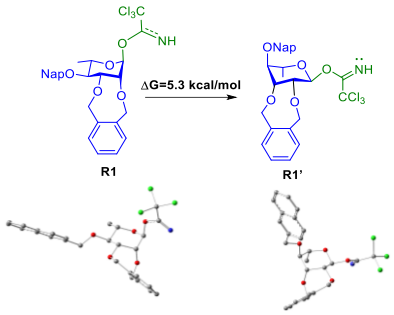


Figure S1. Transformation of the isomers of the starting material. For the optimized structures, irrelevant hydrogen atoms are omitted for clarity.

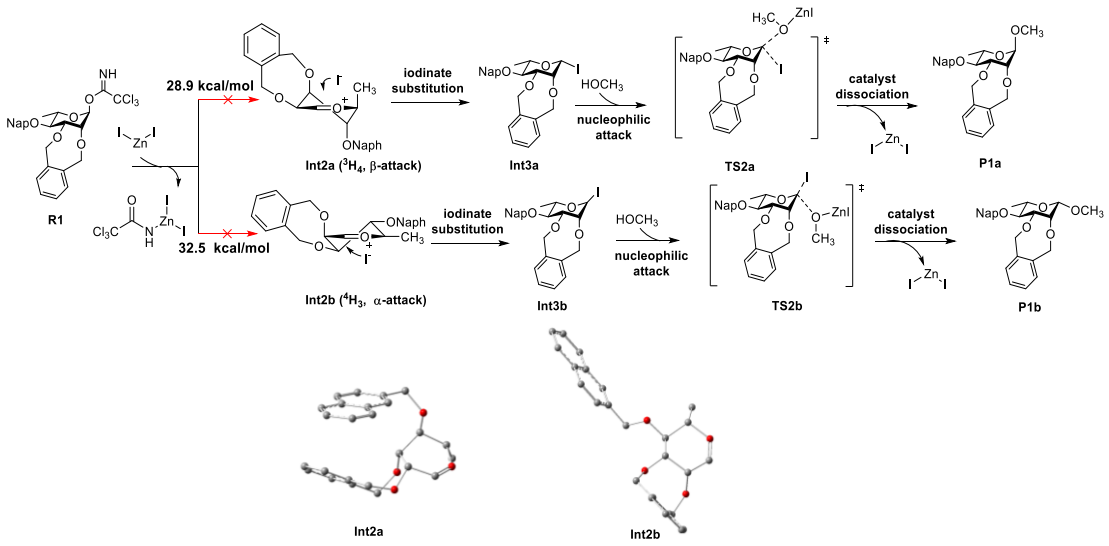


Figure S2. The pathway of the S_N1-type mechanism via generating glycosyl cations. For the optimized structures, irrelevant hydrogen atoms are omitted for clarity.

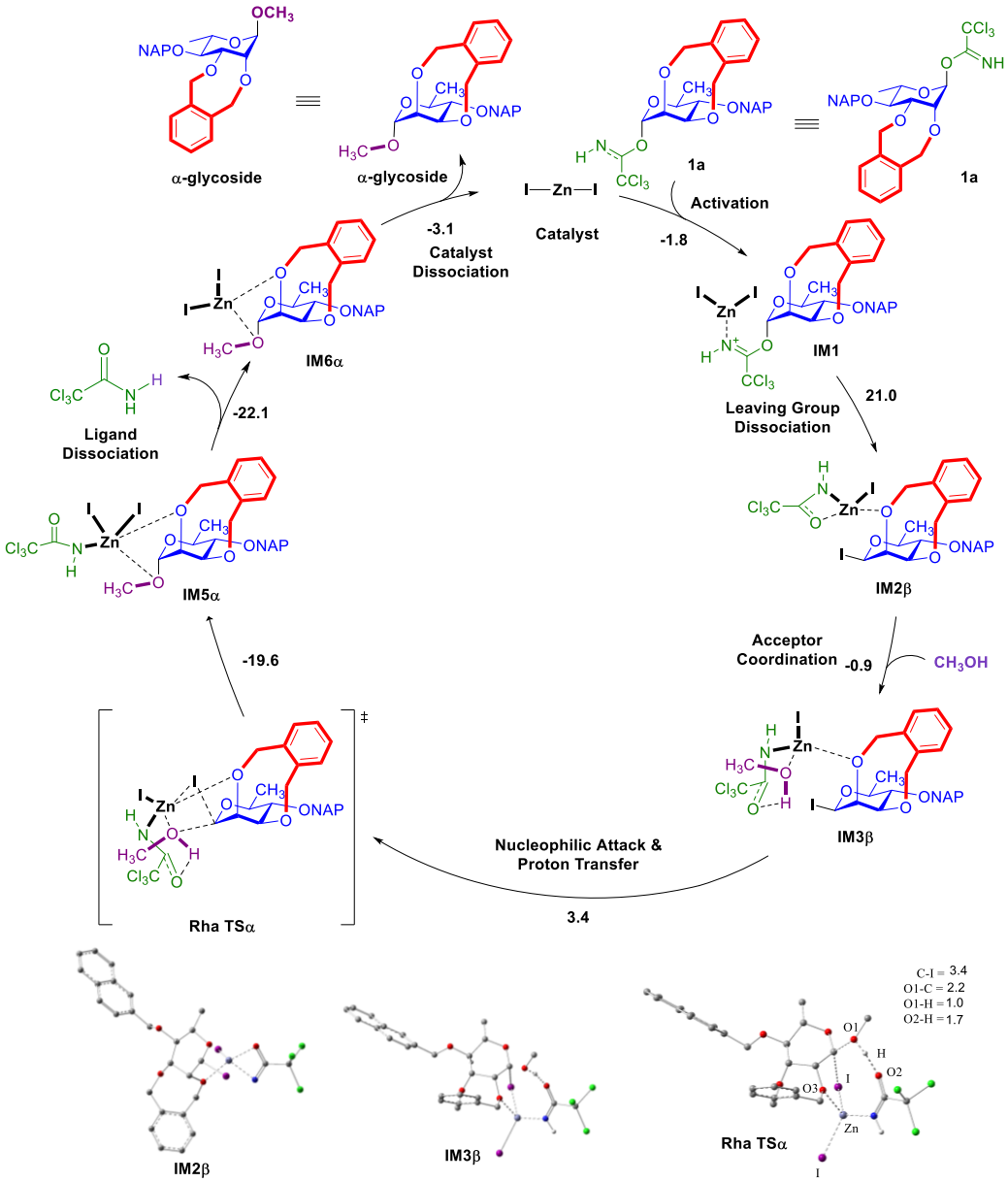


Figure S3. Proposed α-selective catalytic cycle of the zinc iodide catalyzed rhamnosylation of alcohol with **R1**. For optimized structures of the important intermediates, and TS along the reaction direction, irrelevant hydrogen atoms are omitted for clarity. The bond lengths are given in Å and the energy of each step is given in kcal/mol.

Number of Imaginary Frequencies: 0
Electronic energy (Hartree): -250.149995354
Charge = 0 Multiplicity = 1
Coordinates of Optimized Structure:

C	2.5067	-3.72647	1.13078
H	1.7528	-3.44367	1.89521
H	2.2601	-4.74441	0.7891
H	3.492	-3.71984	1.59831

O	2.55597	-2.81899	0.02671
H	1.67215	-2.69732	-0.32778

CH_3OH

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -115.739123457

Coordinates of Optimized Structure:

C	2.5067	-3.72647	1.13078
H	1.7528	-3.44367	1.89521
H	2.2601	-4.74441	0.7891
H	3.492	-3.71984	1.59831
O	2.55597	-2.81899	0.02671
H	1.67215	-2.69732	-0.32778

Cl_3C-CO-NH_2

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -1588.05172065

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

N	-4.58949	0.76443	-2.17844
H	-4.95901	0.88908	-1.25761
C	-4.88794	1.80917	-2.91476
O	-4.07502	2.16332	-3.82815
C	-6.17402	2.65726	-2.75491
Cl	-7.08576	2.58584	-4.29656
Cl	-7.22266	2.04617	-1.42097
Cl	-5.69083	4.34496	-2.39339
H	-3.59571	0.66498	-2.12817

Cl_3C-CO-NHZnI_2

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -1837.73634521

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

Charge = -1 Multiplicity = 1

Zn	-2.9056	0.39079	-3.27868
I	-2.91694	-2.07	-2.32371
N	-3.96288	1.79868	-2.13985
H	-4.04251	2.4081	-1.33562
C	-4.9582	1.73243	-2.98091
O	-4.91545	0.99485	-3.99395
C	-6.29579	2.48391	-2.74397
Cl	-6.96041	3.08822	-4.27739
Cl	-7.43758	1.31018	-2.01537
Cl	-6.1114	3.8791	-1.61668

I	-0.92914	1.37299	-4.72856

R1

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -2856.08334030

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.41408	-3.07383	-1.7709
C	3.90172	-3.03757	-1.4625
C	3.66495	-1.16044	-0.01785
C	2.18359	-1.03665	-0.36617
C	1.60159	-2.40486	-0.66552
H	4.48749	-3.38018	-2.32727
H	2.12152	-4.13315	-1.84835
H	3.75165	-1.75372	0.90975
H	2.08853	-0.40352	-1.26727
H	1.65698	-3.01274	0.26112
O	1.53294	-0.46587	0.7385
C	0.58445	0.53726	0.42631
C	-0.44315	0.60971	1.51214
C	-1.06135	-0.58732	1.95512
C	-2.04431	-0.55204	2.90733
C	-2.47352	0.67818	3.46761
C	-1.85623	1.88412	3.02587
C	-0.83512	1.81124	2.0469
C	-3.4912	0.74867	4.44828
C	-3.88466	1.95731	4.96718
C	-3.27351	3.15245	4.52858
C	-2.28127	3.11472	3.58094
H	1.08813	1.51338	0.29786
H	0.09169	0.29092	-0.52868
H	-0.72626	-1.53127	1.52473
H	-2.5165	-1.47324	3.25088
H	-0.35881	2.73724	1.71744
H	-3.9582	-0.17794	4.78384
H	-4.67016	1.99941	5.71982
H	-3.5945	4.10558	4.94552
H	-1.80583	4.03432	3.23816
C	4.32169	0.18446	0.15524
H	4.25188	0.75912	-0.77788
H	3.82272	0.74012	0.95637
H	5.38073	0.06727	0.40888
C	4.01865	-5.26201	-0.44129
N	3.77655	-5.94747	-1.49422

C	4.12984	-5.88559	0.97095
Cl	5.50025	-5.19136	1.84951
Cl	2.5893	-5.46597	1.79318
H	3.75479	-6.94702	-1.27173
O	4.13061	-3.96958	-0.33841
Cl	4.29768	-7.65296	0.90758
O	4.38141	-1.8319	-1.06855
O	0.25235	-2.23436	-1.03978
O	2.27386	-2.42238	-2.99848
C	-0.51169	-3.41075	-1.12857
H	-0.39868	-3.99931	-0.19647
H	-1.55738	-3.07121	-1.16026
C	1.015	-2.55883	-3.66757
H	1.24974	-2.39503	-4.72646
H	0.33554	-1.76395	-3.33701
C	0.2122	-6.19607	-4.35549
C	0.63734	-4.87835	-4.49198
C	0.41075	-3.92511	-3.49001
C	-0.23768	-4.32399	-2.31003
C	-0.65275	-5.65307	-2.18009
C	-0.43861	-6.58403	-3.18657
H	0.39493	-6.91827	-5.1492
H	1.15207	-4.56551	-5.40122
H	-1.14059	-5.96419	-1.25474
H	-0.75189	-7.6176	-3.05376
Zn	3.33365	-6.12967	-3.62942
I	2.94544	-8.70496	-3.59435
I	4.45392	-4.44202	-5.21254

R1’

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -2856.07660730

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	-2.42359	0.9917	-2.45777
C	-1.05779	0.61117	-1.88894
C	-0.51704	1.63304	-0.88258
C	-1.6056	2.01621	0.13035
C	-2.8504	2.42818	-0.62629
O	-3.30226	1.36701	-1.40362
C	-2.37548	2.02914	-3.56734
O	-1.1975	-0.62696	-1.22038
O	-0.04015	2.73538	-1.61423
O	-1.23483	3.09664	0.9496

C	0.65573	3.76514	-0.90758
C	-0.24027	2.8346	1.90011
C	1.60948	3.25962	0.14282
C	2.96898	3.19334	-0.17538
C	3.91061	2.7161	0.72667
C	3.49199	2.27151	1.97595
C	2.14278	2.31374	2.30033
C	1.19203	2.80731	1.40523
C	-0.04331	-1.43669	-1.26494
C	-0.09139	-2.43035	-0.14653
C	-0.22571	-1.95587	1.18265
C	-0.24849	-2.82677	2.23794
C	-0.13668	-4.22474	2.02791
C	-0.00117	-4.70952	0.69505
C	0.01383	-3.7792	-0.37368
C	-0.15614	-5.15225	3.09629
C	-0.04634	-6.49979	2.85874
C	0.08714	-6.98041	1.53779
C	0.10856	-6.1041	0.48131
H	-2.86687	0.06447	-2.84464
H	-0.33403	0.53163	-2.72081
H	0.31473	1.14759	-0.34013
H	-1.8597	1.12609	0.73762
H	-1.93204	1.5912	-4.47094
H	-1.77861	2.90684	-3.29965
H	-3.3969	2.35272	-3.80049
H	1.22621	4.28744	-1.68652
H	-0.0638	4.47714	-0.48507
H	-0.3432	3.62859	2.65476
H	-0.45561	1.88113	2.42142
H	3.28951	3.53328	-1.1609
H	4.9638	2.68564	0.4537
H	4.21282	1.8836	2.69382
H	1.80906	1.95388	3.27566
H	0.03182	-1.9488	-2.2416
H	0.86382	-0.81054	-1.16205
H	-0.31563	-0.88064	1.34477
H	-0.35391	-2.45867	3.25894
H	0.10762	-4.15568	-1.39445
H	-0.26136	-4.77395	4.11362
H	-0.06316	-7.20384	3.68899
H	0.17244	-8.05126	1.36054
H	0.20974	-6.46998	-0.54096
O	-3.86561	2.69743	0.31528

C	-4.91204	3.40679	-0.12235
C	-5.9239	3.52707	1.03277
Cl	-5.14833	4.36558	2.40476
Cl	-6.4501	1.89971	1.53188
Cl	-7.35777	4.46568	0.52418
H	-2.66314	3.33849	-1.2202
N	-5.00079	3.88529	-1.28362
H	-5.86469	4.40631	-1.42105

Int2a

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -1268.44334164

Charge = 1 Multiplicity = 1

Coordinates of Optimized Structure:

C	-1.75655	1.35965	-3.36335
C	-0.64566	0.64864	-2.60996
C	-0.53619	1.09689	-1.14712
C	-1.8726	0.77312	-0.46202
C	-2.99963	1.29897	-1.25721
O	-2.98748	1.5142	-2.48708
C	-1.47743	2.7328	-3.90923
O	-0.93768	-0.72092	-2.70057
O	-0.27237	2.46101	-1.12539
O	-2.05373	1.31034	0.80597
C	0.0246	3.05558	0.16043
C	-1.25414	0.75377	1.84306
C	0.7952	2.17376	1.10167
C	2.17095	2.39256	1.22213
C	2.9549	1.64945	2.09476
C	2.3623	0.65372	2.86196
C	1.0038	0.3996	2.72917
C	0.20808	1.14252	1.85706
C	0.17493	-1.61265	-2.60376
C	0.57936	-1.93617	-1.19207
C	1.91657	-1.73964	-0.77165
C	2.30187	-2.06475	0.50495
C	1.371	-2.58384	1.43507
C	0.0139	-2.75727	1.0293
C	-0.34542	-2.43737	-0.30097
C	1.74045	-2.92655	2.75898
C	0.80658	-3.3949	3.6485
C	-0.54243	-3.54948	3.25181
C	-0.92787	-3.24452	1.97055
H	-2.14123	0.67904	-4.13106

H	0.30373	0.89825	-3.11896
H	0.25744	0.51316	-0.65518
H	-1.98833	-0.33882	-0.47842
H	-0.70907	2.64444	-4.68631
H	-1.10716	3.40309	-3.12881
H	-2.37573	3.15363	-4.37273
H	0.62152	3.93961	-0.08926
H	-0.91476	3.40089	0.60828
H	-1.7436	1.09119	2.76587
H	-1.33775	-0.34914	1.81652
H	2.62854	3.1828	0.62675
H	4.01978	1.85447	2.18113
H	2.9579	0.06565	3.55846
H	0.54561	-0.4002	3.31466
H	-0.15327	-2.51674	-3.13175
H	1.02674	-1.19333	-3.16542
H	2.64376	-1.33758	-1.47794
H	3.33448	-1.91981	0.82246
H	-1.37248	-2.62412	-0.62765
H	2.78282	-2.81009	3.05696
H	1.10071	-3.65746	4.6627
H	-1.27145	-3.92835	3.96538
H	-1.96234	-3.38498	1.65444
H	-3.94109	1.54446	-0.75007

Int2b

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -1268.43543472

Charge = 1 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.45343	-3.2385	-1.67468
C	3.90582	-3.10513	-1.22702
C	3.45415	-1.17627	0.08721
C	1.98894	-1.18162	-0.34362
C	1.53356	-2.59799	-0.63602
H	4.57887	-3.44817	-2.01959
H	2.22977	-4.31629	-1.77414
H	3.52657	-1.71751	1.04669
H	1.88792	-0.57411	-1.26159
H	1.59742	-3.1777	0.30659
O	1.23099	-0.64126	0.71145
C	0.32089	0.37057	0.33254
C	-0.64841	0.58899	1.45126
C	-1.40266	-0.51589	1.92167

C	-2.31757	-0.35837	2.9274
C	-2.53241	0.91012	3.52403
C	-1.77436	2.02367	3.05919
C	-0.83411	1.82466	2.01797
C	-3.47057	1.10663	4.56482
C	-3.65016	2.3471	5.12506
C	-2.89624	3.44962	4.66713
C	-1.98007	3.28948	3.65726
H	0.85854	1.30767	0.09324
H	-0.21991	0.05755	-0.57797
H	-1.22799	-1.4906	1.46659
H	-2.89765	-1.20897	3.28715
H	-0.24882	2.67885	1.6707
H	-4.04907	0.25056	4.91384
H	-4.37598	2.48528	5.92478
H	-3.0446	4.4291	5.11907
H	-1.39463	4.13747	3.30019
C	3.99639	0.22243	0.23644
H	3.9247	0.75752	-0.72025
H	3.42562	0.76762	0.99622
H	5.04972	0.19557	0.53643
O	4.27171	-1.8313	-0.88651
O	0.18532	-2.53951	-1.05248
O	2.39946	-2.6004	-2.92271
C	-0.44746	-3.78033	-1.21649
H	-0.14362	-4.46778	-0.40198
H	-1.52184	-3.58841	-1.07497
C	1.16132	-2.62789	-3.62826
H	1.43371	-2.3626	-4.65778
H	0.49469	-1.84279	-3.24835
C	-0.03178	-5.99165	-4.89973
C	0.57017	-4.74582	-4.79527
C	0.46966	-3.96718	-3.63764
C	-0.24721	-4.48176	-2.54525
C	-0.84452	-5.73969	-2.6565
C	-0.7485	-6.4924	-3.81791
H	0.05906	-6.56847	-5.81821
H	1.13906	-4.35064	-5.63753
H	-1.39886	-6.13391	-1.80211
H	-1.2266	-7.46882	-3.87624

IM1

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -3106.25316183

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.41408	-3.07383	-1.7709
C	3.90172	-3.03757	-1.4625
C	3.66495	-1.16044	-0.01785
C	2.18359	-1.03665	-0.36617
C	1.60159	-2.40486	-0.66552
H	4.48749	-3.38018	-2.32727
H	2.12152	-4.13315	-1.84835
H	3.75165	-1.75372	0.90975
H	2.08853	-0.40352	-1.26727
H	1.65698	-3.01274	0.26112
O	1.53294	-0.46587	0.7385
C	0.58445	0.53726	0.42631
C	-0.44315	0.60971	1.51214
C	-1.06135	-0.58732	1.95512
C	-2.04431	-0.55204	2.90733
C	-2.47352	0.67818	3.46761
C	-1.85623	1.88412	3.02587
C	-0.83512	1.81124	2.0469
C	-3.4912	0.74867	4.44828
C	-3.88466	1.95731	4.96718
C	-3.27351	3.15245	4.52858
C	-2.28127	3.11472	3.58094
H	1.08813	1.51338	0.29786
H	0.09169	0.29092	-0.52868
H	-0.72626	-1.53127	1.52473
H	-2.5165	-1.47324	3.25088
H	-0.35881	2.73724	1.71744
H	-3.9582	-0.17794	4.78384
H	-4.67016	1.99941	5.71982
H	-3.5945	4.10558	4.94552
H	-1.80583	4.03432	3.23816
C	4.32169	0.18446	0.15524
H	4.25188	0.75912	-0.77788
H	3.82272	0.74012	0.95637
H	5.38073	0.06727	0.40888
C	4.01865	-5.26201	-0.44129
N	3.77655	-5.94747	-1.49422
C	4.12984	-5.88559	0.97095
Cl	5.50025	-5.19136	1.84951
Cl	2.5893	-5.46597	1.79318
H	3.75479	-6.94702	-1.27173
O	4.13061	-3.96958	-0.33841

Cl	4.29768	-7.65296	0.90758
O	4.38141	-1.8319	-1.06855
O	0.25235	-2.23436	-1.03978
O	2.27386	-2.42238	-2.99848
C	-0.51169	-3.41075	-1.12857
H	-0.39868	-3.99931	-0.19647
H	-1.55738	-3.07121	-1.16026
C	1.015	-2.55883	-3.66757
H	1.24974	-2.39503	-4.72646
H	0.33554	-1.76395	-3.33701
C	0.2122	-6.19607	-4.35549
C	0.63734	-4.87835	-4.49198
C	0.41075	-3.92511	-3.49001
C	-0.23768	-4.32399	-2.31003
C	-0.65275	-5.65307	-2.18009
C	-0.43861	-6.58403	-3.18657
H	0.39493	-6.91827	-5.1492
H	1.15207	-4.56551	-5.40122
H	-1.14059	-5.96419	-1.25474
H	-0.75189	-7.6176	-3.05376
Zn	3.33365	-6.12967	-3.62942
I	2.94544	-8.70496	-3.59435
I	4.45392	-4.44202	-5.21254

IM2*α*

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -3106.22216093

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.00224	-3.82456	-1.87861
C	3.48605	-3.8045	-1.56943
C	3.30187	-1.68136	-0.4513
C	1.79448	-1.62824	-0.69239
C	1.20103	-3.01906	-0.85464
H	4.05394	-4.27605	-2.37818
H	1.65573	-4.86686	-1.93775
H	3.49146	-2.17828	0.5145
H	1.60598	-1.06689	-1.62454
H	1.24361	-3.53793	0.12252
O	1.2016	-0.98113	0.40012
C	0.39323	0.13458	0.0504
C	-0.48191	0.47552	1.21302
C	-1.37701	-0.51009	1.70158
C	-2.21656	-0.23273	2.74595

C	-2.21131	1.04407	3.36442
C	-1.31031	2.03677	2.88148
C	-0.45317	1.71517	1.80029
C	-3.06889	1.36427	4.44321
C	-3.03614	2.60907	5.02138
C	-2.14099	3.59158	4.54502
C	-1.29819	3.31027	3.49893
H	1.02581	0.99369	-0.23835
H	-0.22367	-0.12911	-0.82589
H	-1.37606	-1.49112	1.22549
H	-2.90721	-0.98933	3.12002
H	0.23818	2.47671	1.43354
H	-3.75742	0.60132	4.80794
H	-3.70045	2.84338	5.85149
H	-2.12223	4.57506	5.01162
H	-0.60493	4.06455	3.12532
C	3.95558	-0.32505	-0.47925
H	3.77196	0.19145	-1.43326
H	3.54094	0.2901	0.32705
H	5.03746	-0.41806	-0.33364
O	3.93913	-2.4899	-1.47362
O	-0.14178	-2.83755	-1.23788
O	1.94128	-3.22472	-3.17072
C	-0.92916	-3.9992	-1.29263
H	-0.70202	-4.64858	-0.4252
H	-1.96641	-3.65752	-1.16235
C	0.654	-3.18361	-3.84183
H	0.91522	-3.00491	-4.89126
H	0.09284	-2.31639	-3.47942
C	-0.82974	-6.53078	-4.78791
C	-0.12605	-5.33523	-4.80974
C	-0.12422	-4.46225	-3.71646
C	-0.83751	-4.82457	-2.5613
C	-1.53525	-6.0337	-2.5466
C	-1.54269	-6.88037	-3.64615
H	-0.82014	-7.18635	-5.65626
H	0.43911	-5.05621	-5.69923
H	-2.08624	-6.31239	-1.64623
H	-2.09879	-7.81542	-3.60859
Zn	3.62611	-1.74374	-3.64374
I	2.13475	0.2785	-4.30624
N	5.72573	-1.48224	-3.78754
H	6.58518	-0.96029	-3.65611
C	5.79824	-2.71578	-4.18661

O	4.73292	-3.38664	-4.3627
C	7.11639	-3.49195	-4.35724
Cl	7.06677	-4.49703	-5.816
Cl	8.53712	-2.41073	-4.43978
Cl	7.25454	-4.52983	-2.89848
I	3.96628	-5.05114	0.19398

IM3α

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -3221.99142600

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.05445	-3.49381	-1.93521
C	3.52761	-3.51402	-1.56036
C	3.32714	-1.60704	-0.1569
C	1.86027	-1.43259	-0.533
C	1.22689	-2.7718	-0.86968
H	4.14624	-3.89978	-2.37732
H	1.70591	-4.52501	-2.08648
H	3.38844	-2.24241	0.7458
H	1.81294	-0.78134	-1.4267
H	1.22682	-3.39469	0.04587
O	1.195	-0.85464	0.55681
C	0.43448	0.29881	0.24428
C	-0.49962	0.58896	1.37536
C	-1.38765	-0.42788	1.80958
C	-2.28034	-0.18893	2.81928
C	-2.34125	1.07881	3.45284
C	-1.44997	2.10359	3.02171
C	-0.53466	1.82096	1.97843
C	-3.25421	1.35906	4.49671
C	-3.28505	2.59689	5.08969
C	-2.40073	3.61195	4.66337
C	-1.50414	3.36917	3.65291
H	1.10085	1.16069	0.05627
H	-0.13912	0.11331	-0.68061
H	-1.33293	-1.40282	1.32496
H	-2.96209	-0.97166	3.15381
H	0.15237	2.6065	1.65681
H	-3.93382	0.57065	4.82183
H	-3.99259	2.80035	5.89172
H	-2.43408	4.59006	5.14035
H	-0.81859	4.14881	3.31933
C	4.01531	-0.28916	0.08781

H	3.79002	0.4262	-0.71392
H	3.66166	0.13615	1.03288
H	5.10137	-0.42155	0.13368
O	4.01982	-2.29211	-1.21211
O	-0.09964	-2.51689	-1.26381
O	2.00122	-2.80521	-3.19295
C	-0.93153	-3.64085	-1.39939
H	-0.75981	-4.34058	-0.55909
H	-1.95744	-3.2612	-1.28443
C	0.70392	-2.70716	-3.8574
H	0.96449	-2.47509	-4.89757
H	0.1664	-1.85872	-3.42561
C	-0.77581	-5.97583	-5.02646
C	-0.06439	-4.78592	-4.96535
C	-0.08673	-3.98048	-3.82123
C	-0.82507	-4.40288	-2.70388
C	-1.53003	-5.60534	-2.77446
C	-1.51684	-6.38526	-3.92274
H	-0.74945	-6.58136	-5.93
H	0.52598	-4.45913	-5.82289
H	-2.10082	-5.93285	-1.90349
H	-2.07817	-7.31755	-3.95139
Zn	3.62564	-1.91209	-4.31755
I	3.31634	-2.88817	-6.71504
N	3.62454	0.01739	-3.80657
H	2.90935	0.66601	-4.12218
C	4.64752	0.58413	-3.18454
O	5.65426	0.01783	-2.74718
C	4.6066	2.14465	-3.02486
Cl	4.99933	2.84585	-4.62679
Cl	2.96369	2.69899	-2.5306
Cl	5.77751	2.7037	-1.82759
I	3.8513	-5.09168	0.02032
C	6.54562	-2.52908	-4.59815
H	7.48777	-2.81296	-4.11648
H	6.2626	-3.28831	-5.33243
O	5.5079	-2.45841	-3.61763
H	6.66712	-1.56191	-5.10657
H	5.68266	-1.6451	-3.06219

IM4α

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -3472.15586611

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.36749	-3.57341	-1.45767
C	3.719	-3.78418	-0.79351
C	3.36073	-2.03974	0.78075
C	2.12199	-1.57513	0.02189
C	1.39933	-2.76526	-0.5851
H	4.47201	-4.19585	-1.47977
H	1.95469	-4.55755	-1.71154
H	3.05108	-2.74806	1.57187
H	2.44465	-0.89933	-0.79089
H	1.02392	-3.40488	0.23865
O	1.28073	-0.91043	0.92013
C	0.87751	0.38218	0.48067
C	-0.18029	0.89944	1.39947
C	-1.32613	0.10242	1.6487
C	-2.33224	0.56118	2.45535
C	-2.25573	1.84362	3.05606
C	-1.10792	2.65052	2.80846
C	-0.08182	2.14208	1.97438
C	-3.27934	2.34764	3.89306
C	-3.17299	3.59301	4.46099
C	-2.03494	4.39217	4.21634
C	-1.02625	3.92981	3.40834
H	1.74626	1.0623	0.44293
H	0.48001	0.30412	-0.5477
H	-1.38237	-0.88444	1.18892
H	-3.21227	-0.05287	2.64964
H	0.80082	2.75854	1.79061
H	-4.15532	1.72577	4.08017
H	-3.96684	3.96927	5.10406
H	-1.96031	5.37816	4.67194
H	-0.14494	4.54183	3.21395
C	4.14739	-0.90351	1.37673
H	4.42266	-0.18074	0.59876
H	3.53527	-0.39412	2.12769
H	5.05904	-1.2761	1.85807
O	4.2391	-2.76356	-0.10855
O	0.32553	-2.25781	-1.33426
O	2.63885	-2.87711	-2.67249
C	-0.6968	-3.16226	-1.67729
H	-1.06226	-3.67887	-0.77031
H	-1.52127	-2.52704	-2.0336
C	1.57306	-2.83713	-3.67532
H	2.11269	-2.79259	-4.63208

H	1.02246	-1.90192	-3.53007
C	0.12762	-6.18896	-4.64489
C	0.91879	-5.04787	-4.60093
C	0.67985	-4.03685	-3.66752
C	-0.35706	-4.19467	-2.73146
C	-1.13389	-5.35104	-2.7748
C	-0.90693	-6.33724	-3.72821
H	0.32346	-6.96127	-5.38564
H	1.74354	-4.92822	-5.30483
H	-1.93055	-5.48107	-2.04075
H	-1.52941	-7.23001	-3.74242
Zn	4.1844	-1.47669	-3.38951
O	5.12797	-0.64895	-1.78875
H	4.7087	0.23861	-1.64568
C	6.49018	-0.76378	-1.39786
H	6.58561	-0.61103	-0.31583
H	6.81168	-1.78159	-1.6408
N	2.95664	0.06532	-3.75579
H	2.37965	0.10341	-4.59165
C	2.69435	1.0124	-2.86985
O	3.29068	1.20991	-1.80255
C	1.48873	1.96124	-3.19767
Cl	0.00666	0.95187	-3.41199
Cl	1.20027	3.12651	-1.90377
Cl	1.82791	2.83144	-4.72501
I	5.62826	-3.04302	-4.82281
H	7.12031	-0.04663	-1.93712
I	7.41562	-4.89064	-1.03465
Zn	6.37094	-5.75514	1.12899
I	3.45328	-5.62797	0.63478
I	6.65029	-6.68773	3.47311

Rha TSβ

Number of Imaginary Frequencies: 1 (-182.29cm^{-1})

Electronic energy (Hartree): -3472.14635687

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.66166	-3.71994	-1.88712
C	4.10355	-3.53421	-1.48275
C	3.51792	-2.05487	0.37246
C	2.32397	-1.60804	-0.48459
C	1.64464	-2.83073	-1.10552
H	4.81874	-4.27318	-1.83911
H	2.50129	-4.76781	-1.58864

H	3.16188	-2.69352	1.18602
H	2.66901	-0.91978	-1.26815
H	1.25616	-3.43251	-0.27469
O	1.45653	-0.95333	0.41846
C	0.75089	0.17947	-0.1181
C	-0.23655	0.67452	0.90684
C	-1.10011	-0.24423	1.56524
C	-2.04543	0.19923	2.45885
C	-2.19258	1.58457	2.74468
C	-1.32392	2.51583	2.08887
C	-0.35048	2.02132	1.17907
C	-3.1647	2.07579	3.65622
C	-3.27515	3.42539	3.90883
C	-2.41529	4.34647	3.26133
C	-1.46161	3.90103	2.37297
H	1.46514	0.97333	-0.37824
H	0.237	-0.12708	-1.03783
H	-0.98913	-1.30618	1.36774
H	-2.69708	-0.51077	2.96264
H	0.3108	2.73392	0.6894
H	-3.82242	1.36656	4.15311
H	-4.02318	3.78931	4.60775
H	-2.51171	5.40853	3.46937
H	-0.80061	4.60659	1.87491
C	4.38158	-0.92274	0.89058
H	4.76317	-0.30677	0.07009
H	3.76689	-0.29753	1.54327
H	5.22026	-1.31587	1.47173
O	4.43223	-2.96068	-0.38998
O	0.59829	-2.42044	-1.96369
O	2.5409	-3.6359	-3.30386
C	-0.58002	-3.2427	-1.92197
H	-1.10662	-3.07751	-0.97244
H	-1.20964	-2.84073	-2.72423
C	1.36628	-4.30084	-3.94705
H	1.80024	-4.84312	-4.78801
H	0.7492	-3.48138	-4.32111
C	0.05848	-7.50278	-2.39237
C	0.78141	-6.60606	-3.18011
C	0.59036	-5.22257	-3.05625
C	-0.33368	-4.72827	-2.10789
C	-1.04206	-5.63764	-1.3174
C	-0.85806	-7.01426	-1.4611
H	0.22473	-8.57076	-2.49036

H	1.50773	-6.98045	-3.89648
H	-1.73887	-5.26471	-0.57101
H	-1.41115	-7.70275	-0.82971
Zn	3.64429	-2.35896	-4.58913
O	4.91347	-2.25473	-2.93992
H	4.76444	-1.11017	-2.71323
C	6.32779	-2.55064	-3.03259
H	6.7703	-2.52862	-2.03208
H	6.45921	-3.53979	-3.47702
N	3.2048	-0.33885	-4.45797
H	2.65854	0.11896	-5.18175
C	3.78482	0.47851	-3.62384
O	4.53582	0.11109	-2.65658
C	3.66109	2.02886	-3.76187
Cl	2.34655	2.5137	-4.89142
Cl	3.33755	2.75299	-2.15573
Cl	5.23498	2.62004	-4.3963
I	2.55868	-5.90989	1.41017
I	4.07512	-3.40476	-6.91607
Zn	3.29636	-7.95192	-0.20648
I	4.96445	-7.16587	-2.18683
I	2.32156	-10.37093	-0.01566
H	6.81221	-1.79967	-3.66372

IM5β

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -3222.00737665

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.56792	-2.94571	-1.90777
C	4.01337	-2.5187	-1.66184
C	3.4666	-0.47362	-0.66757
C	1.96874	-0.73349	-0.79284
C	1.68935	-2.22786	-0.88262
H	2.48827	-4.03776	-1.75664
H	3.80247	-0.88754	0.30483
H	1.60983	-0.23223	-1.71084
H	1.96672	-2.65691	0.10517
O	1.35009	-0.21157	0.3523
C	0.15498	0.51915	0.12465
C	-0.67276	0.48743	1.37036
C	-1.11494	-0.7689	1.85851
C	-1.8844	-0.84571	2.98726
C	-2.25631	0.32521	3.69612

C	-1.81282	1.59028	3.21321
C	-1.01592	1.63352	2.04221
C	-3.05069	0.2785	4.86574
C	-3.38979	1.43021	5.53145
C	-2.94777	2.68357	5.05505
C	-2.17744	2.76005	3.92139
H	0.39616	1.55895	-0.16284
H	-0.40076	0.05714	-0.70742
H	-0.82743	-1.66868	1.31375
H	-2.22807	-1.81111	3.36041
H	-0.6711	2.60355	1.67757
H	-3.38957	-0.69224	5.22905
H	-4.00169	1.38176	6.43064
H	-3.22101	3.5905	5.59184
H	-1.83229	3.72495	3.54838
C	3.80139	0.99267	-0.75459
H	3.49319	1.39109	-1.73015
H	3.27622	1.53968	0.03595
H	4.87889	1.15357	-0.64022
O	4.15134	-1.13992	-1.72101
O	0.31065	-2.38287	-1.09053
O	2.32993	-2.64724	-3.27097
C	-0.17636	-3.70509	-1.18419
H	0.51899	-4.40668	-0.68685
H	-1.10925	-3.73377	-0.60132
C	0.98995	-2.40271	-3.7593
H	1.17044	-2.08283	-4.79259
H	0.56546	-1.55758	-3.20899
C	-1.06191	-5.27044	-5.09971
C	-0.2307	-4.16485	-4.99221
C	0.08593	-3.60138	-3.75186
C	-0.46019	-4.17156	-2.59117
C	-1.3012	-5.27786	-2.71074
C	-1.59783	-5.83314	-3.9476
H	-1.28362	-5.69269	-6.07761
H	0.20262	-3.72354	-5.89121
H	-1.72767	-5.71471	-1.80589
H	-2.25128	-6.70145	-4.00996
H	4.35887	-2.88852	-0.67105
I	3.59465	-2.70177	-6.69694
O	6.31904	-5.53795	-2.67782
C	6.44819	-5.62839	-3.98561
C	7.62763	-6.53876	-4.34742
Cl	9.11555	-5.67932	-3.83781

Cl	7.69817	-6.84079	-6.09788
Cl	7.47554	-8.07918	-3.48465
Zn	3.68892	-4.06179	-4.45904
N	5.70999	-4.98976	-4.80097
H	5.91928	-5.15566	-5.785
I	2.77343	-6.37141	-3.46032
O	4.81986	-3.09577	-2.67164
C	6.08625	-2.44068	-2.86055
H	6.60853	-3.00068	-3.63894
H	5.9341	-1.41112	-3.18893
H	6.65928	-2.46079	-1.92405
H	5.56274	-4.94517	-2.47627

IM6β

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -1633.96981786

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	1.81112	-4.12096	-1.88092
C	3.27827	-4.11303	-1.4412
C	3.08746	-1.99687	-0.33979
C	1.59407	-1.8696	-0.70154
C	0.96534	-3.25486	-0.92674
H	1.46113	-5.15902	-1.87728
H	3.16266	-2.52026	0.62737
H	1.50354	-1.28475	-1.62621
H	0.91623	-3.76968	0.04924
O	0.97162	-1.2082	0.38741
C	-0.03078	-0.24674	0.02963
C	-0.48628	0.46753	1.2765
C	-0.90954	-0.28256	2.40897
C	-1.35929	0.34964	3.54341
C	-1.42038	1.76886	3.61685
C	-0.9959	2.53192	2.48132
C	-0.52828	1.8445	1.32833
C	-1.88306	2.45468	4.77139
C	-1.9249	3.83126	4.80475
C	-1.50418	4.58609	3.6822
C	-1.0502	3.95008	2.54784
H	0.37931	0.47326	-0.69238
H	-0.86975	-0.76337	-0.45449
H	-0.85949	-1.36666	2.36769
H	-1.67763	-0.23223	4.40553
H	-0.19925	2.43055	0.47225

H	-2.20495	1.87282	5.63209
H	-2.28113	4.34427	5.69399
H	-1.5414	5.67143	3.71997
H	-0.72677	4.52727	1.68469
C	3.7938	-0.65438	-0.25469
H	3.75625	-0.13957	-1.22054
H	3.30083	-0.03427	0.49811
H	4.84056	-0.7926	0.0353
O	3.77202	-2.79007	-1.33478
O	-0.3493	-3.03873	-1.41762
O	1.8062	-3.62629	-3.21737
C	-1.22317	-4.15574	-1.45807
H	-1.17055	-4.70756	-0.50552
H	-2.22598	-3.71595	-1.51562
C	0.54208	-3.63307	-3.96712
H	0.86415	-3.55662	-5.00609
H	-0.00831	-2.7332	-3.70008
C	-0.90847	-7.07339	-4.6547
C	-0.19693	-5.88098	-4.76167
C	-0.25989	-4.89595	-3.76289
C	-1.04301	-5.13681	-2.61492
C	-1.74447	-6.34602	-2.5134
C	-1.68978	-7.30558	-3.52209
H	-0.84802	-7.81562	-5.44522
H	0.42666	-5.70048	-5.63343
H	-2.3463	-6.53607	-1.62635
H	-2.24728	-8.2325	-3.41849
H	3.38985	-4.63877	-0.47799
I	2.87591	-0.43034	-4.58371
Zn	3.69396	-2.97929	-4.14799
I	3.95614	-4.74609	-6.23012
O	4.01712	-4.73614	-2.44791
C	5.30206	-5.23358	-2.05053
H	5.76254	-5.63205	-2.95475
H	5.92317	-4.43674	-1.63179
H	5.17553	-6.03828	-1.31652

β-product

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -1383.79708842

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.53404	-3.08543	-1.6388
C	3.97613	-3.00565	-1.12571

C	3.6076	-0.98207	0.01094
C	2.11913	-0.99134	-0.34364
C	1.63808	-2.40854	-0.6024
H	2.28051	-4.158	-1.72638
H	3.71304	-1.50086	0.98708
H	1.97547	-0.39663	-1.26388
H	1.70703	-2.9713	0.35272
O	1.40677	-0.43889	0.73726
C	0.47058	0.56209	0.39717
C	-0.56099	0.65533	1.47802
C	-1.27063	-0.51782	1.84106
C	-2.24989	-0.47243	2.79589
C	-2.57757	0.74508	3.44605
C	-1.86297	1.92572	3.09124
C	-0.85375	1.84266	2.09992
C	-3.58668	0.82633	4.43452
C	-3.87609	2.02009	5.04791
C	-3.16521	3.18911	4.69934
C	-2.18162	3.14094	3.74296
H	0.97579	1.53618	0.25471
H	-0.01791	0.30067	-0.55759
H	-1.00951	-1.451	1.34192
H	-2.79753	-1.37409	3.07292
H	-0.30342	2.74796	1.83451
H	-4.13161	-0.08025	4.70022
H	-4.65519	2.0701	5.80683
H	-3.40072	4.13046	5.19324
H	-1.62849	4.04019	3.46949
C	4.14718	0.42264	0.11538
H	4.0437	0.93493	-0.85089
H	3.59604	0.98379	0.87835
H	5.20939	0.40695	0.38308
O	4.3655	-1.66427	-0.96722
O	0.28194	-2.32607	-0.98937
O	2.46497	-2.45272	-2.89053
C	-0.38647	-3.54979	-1.1318
H	-0.09793	-4.23458	-0.30983
H	-1.45374	-3.32445	-0.98401
C	1.21547	-2.46567	-3.57511
H	1.47356	-2.21643	-4.61262
H	0.56943	-1.66413	-3.19423
C	-0.05799	-5.82171	-4.78735
C	0.57129	-4.58749	-4.70605
C	0.49751	-3.79078	-3.55896

C	-0.2182	-4.27503	-2.4523
C	-0.84431	-5.52054	-2.54041
C	-0.77605	-6.29087	-3.69239
H	0.01158	-6.41362	-5.69806
H	1.13993	-4.21595	-5.55949
H	-1.39932	-5.89041	-1.67562
H	-1.27635	-7.25699	-3.73264
H	3.98947	-3.50838	-0.13635
O	4.90837	-3.68599	-1.87455
C	5.20141	-3.19769	-3.17194
H	6.18967	-3.59373	-3.4276
H	4.4656	-3.54533	-3.90813
H	5.23331	-2.10266	-3.19027

IM2β

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -3106.22026149

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.86104	-2.90362	-1.80808
C	4.28754	-2.46994	-1.46843
C	3.62223	-1.4127	0.60435
C	2.32161	-1.1031	-0.12533
C	1.82009	-2.36948	-0.78963
H	5.02658	-3.15989	-1.88033
H	2.94291	-3.99849	-1.71201
H	3.35132	-2.02221	1.47993
H	2.47593	-0.32101	-0.89128
H	1.69154	-3.12134	0.01334
O	1.42337	-0.66478	0.85835
C	0.6041	0.42311	0.46094
C	-0.52469	0.5753	1.43171
C	-1.2254	-0.57538	1.87167
C	-2.30388	-0.45977	2.70719
C	-2.75183	0.81079	3.14698
C	-2.04982	1.97229	2.71157
C	-0.932	1.81591	1.85613
C	-3.86791	0.96425	4.0035
C	-4.27366	2.21019	4.4114
C	-3.57715	3.36124	3.98141
C	-2.49044	3.24353	3.15158
H	1.20412	1.35052	0.41274
H	0.21073	0.23035	-0.55047
H	-0.87381	-1.55343	1.54586

H	-2.83849	-1.34747	3.04713
H	-0.39318	2.70871	1.53146
H	-4.40111	0.07145	4.33184
H	-5.13455	2.3159	5.06931
H	-3.90763	4.34455	4.31178
H	-1.9493	4.12894	2.81655
C	4.37384	-0.18333	1.05522
H	4.66328	0.4503	0.20771
H	3.72536	0.40102	1.7191
H	5.2783	-0.46299	1.60597
O	4.50572	-2.26508	-0.16797
O	0.58725	-2.10858	-1.40504
O	2.49109	-2.59955	-3.13291
C	-0.35443	-3.16275	-1.35019
H	-0.73461	-3.27576	-0.31913
H	-1.19537	-2.81639	-1.96794
C	1.4166	-3.39144	-3.73106
H	1.79964	-3.71423	-4.7105
H	0.58603	-2.69522	-3.89553
C	1.12493	-6.99862	-2.6328
C	1.48877	-5.85093	-3.32819
C	1.0027	-4.59897	-2.9503
C	0.1613	-4.49441	-1.82962
C	-0.18612	-5.64912	-1.13235
C	0.27744	-6.89751	-1.53624
H	1.51346	-7.96603	-2.94436
H	2.17467	-5.91965	-4.17323
H	-0.82844	-5.56675	-0.25476
H	-0.00812	-7.78794	-0.979
I	5.00817	-0.57695	-2.71266
O	4.5827	-4.52621	-3.61483
C	4.69627	-4.44795	-4.8342
C	5.09867	-5.75587	-5.60899
Cl	5.55263	-7.04742	-4.49083
Cl	6.45292	-5.43789	-6.73434
Cl	3.65731	-6.28284	-6.5609
Zn	3.58958	-1.77889	-4.81498
N	4.44917	-3.37902	-5.58254
H	4.59508	-3.49369	-6.58106
I	2.12795	-0.11336	-6.12906

IM3β

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -3221.97759374

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	3.12339	-2.67498	-1.71605
C	4.52181	-2.11233	-1.75453
C	4.15377	-1.17631	0.44636
C	2.8108	-0.72378	-0.11225
C	2.11931	-1.8522	-0.86341
H	5.22528	-2.72128	-2.32742
H	3.30785	-3.6568	-1.23884
H	3.96762	-1.98007	1.17821
H	2.97013	0.12357	-0.80085
H	1.70726	-2.52302	-0.08782
O	2.03812	-0.32993	0.99133
C	1.12349	0.72973	0.75539
C	-0.17757	0.46909	1.45443
C	-0.71232	-0.84252	1.49725
C	-1.93577	-1.0792	2.06757
C	-2.7015	-0.0231	2.62065
C	-2.16719	1.29727	2.58659
C	-0.89484	1.50511	2.0015
C	-3.97135	-0.23489	3.20815
C	-4.68376	0.81226	3.73676
C	-4.15435	2.12138	3.70374
C	-2.92389	2.35672	3.14295
H	1.56074	1.68111	1.10458
H	0.94432	0.8238	-0.32576
H	-0.1261	-1.66507	1.08735
H	-2.3381	-2.0928	2.11353
H	-0.48735	2.5185	1.98528
H	-4.37408	-1.24805	3.23177
H	-5.66105	0.63842	4.18398
H	-4.72768	2.94486	4.1261
H	-2.51042	3.3653	3.11366
C	4.93123	-0.05008	1.07826
H	5.11771	0.74152	0.33968
H	4.35915	0.37095	1.9113
H	5.89582	-0.409	1.4529
O	5.0127	-1.75399	-0.57402
O	1.1033	-1.27282	-1.6247
O	2.6187	-2.92241	-3.01403
C	0.04318	-2.09689	-2.1325
H	-0.89149	-1.59565	-1.8463
H	0.10539	-2.06908	-3.23039
C	1.92928	-4.18116	-3.1701

H	2.67825	-4.98213	-3.23309
H	1.42643	-4.09218	-4.1454
C	0.02331	-6.09071	-0.52814
C	0.94814	-5.74548	-1.50865
C	0.94577	-4.47182	-2.07543
C	0.02388	-3.51004	-1.62313
C	-0.89024	-3.86882	-0.63355
C	-0.90379	-5.15155	-0.09355
H	0.03628	-7.09059	-0.09859
H	1.69757	-6.46659	-1.8349
H	-1.60432	-3.12113	-0.28507
H	-1.63023	-5.41044	0.67471
I	4.60832	-0.23808	-3.27799
O	5.18685	-4.04948	-3.96551
C	4.89842	-4.16114	-5.16385
C	5.44898	-5.44383	-5.87332
Cl	7.07353	-5.83447	-5.2802
Cl	5.49806	-5.3146	-7.65555
Cl	4.31269	-6.76325	-5.41488
Zn	3.07096	-1.9445	-4.88334
N	4.10357	-3.3543	-5.83543
H	3.9775	-3.56419	-6.8206
I	1.00179	-0.87536	-5.99214
O	4.51168	-5.50659	-1.72902
C	5.60318	-5.78466	-0.88897
H	5.21043	-6.20814	0.04239
H	6.29537	-6.51799	-1.33115
H	6.18041	-4.87934	-0.63288
H	4.86587	-5.19091	-2.58403

Rha TSα

Number of Imaginary Frequencies: 1 (-182.29 cm^{-1})

Electronic energy (Hartree): -3221.97493435

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.7304	-3.17663	-1.80277
C	4.10749	-2.69762	-1.41189
C	3.29679	-1.6673	0.62933
C	2.03275	-1.32228	-0.17206
C	1.57417	-2.57262	-0.9231
H	4.89855	-2.69537	-2.15365
H	2.7598	-4.25823	-1.63114
H	3.10664	-2.53198	1.27546
H	2.26927	-0.51926	-0.88463

H	1.30662	-3.31761	-0.15974
O	1.06556	-0.91661	0.774
C	0.21631	0.16356	0.34162
C	-0.74848	0.49774	1.44925
C	-1.50596	-0.53429	2.06983
C	-2.41984	-0.241	3.05349
C	-2.64081	1.09986	3.4732
C	-1.88271	2.14511	2.853
C	-0.93797	1.80402	1.84746
C	-3.58135	1.43853	4.48207
C	-3.76616	2.74982	4.8615
C	-3.01632	3.7837	4.24844
C	-2.0959	3.48715	3.26764
H	0.82944	1.04002	0.09037
H	-0.3147	-0.14556	-0.56707
H	-1.34115	-1.56342	1.76431
H	-2.99142	-1.03708	3.52524
H	-0.35996	2.60251	1.3862
H	-4.15576	0.64296	4.95099
H	-4.48948	2.99672	5.63384
H	-3.17143	4.81427	4.55574
H	-1.51988	4.27925	2.79501
C	3.88449	-0.51332	1.41532
H	4.13836	0.31551	0.74762
H	3.14396	-0.1745	2.14363
H	4.78782	-0.82899	1.94514
O	4.36213	-2.08724	-0.31559
O	0.45601	-2.26766	-1.7229
O	2.57421	-2.93719	-3.19149
C	-0.54997	-3.28259	-1.79316
H	-1.09367	-3.32952	-0.8384
H	-1.24734	-2.91365	-2.55352
C	1.54329	-3.72185	-3.90212
H	2.04793	-4.09387	-4.7957
H	0.7854	-3.00091	-4.21
C	0.80262	-7.27593	-2.77472
C	1.36388	-6.17672	-3.42574
C	0.94783	-4.87083	-3.13328
C	-0.04424	-4.66861	-2.14837
C	-0.58855	-5.77694	-1.49201
C	-0.18051	-7.07458	-1.80683
H	1.13421	-8.28029	-3.02126
H	2.13376	-6.32912	-4.17795
H	-1.34629	-5.62207	-0.72728

H	-0.62281	-7.92138	-1.28966
I	4.67375	0.27956	-3.12684
O	5.61204	-4.0416	-3.52552
C	5.4616	-4.0472	-4.76605
C	6.14076	-5.27849	-5.49094
Cl	7.86732	-5.35537	-5.01354
Cl	6.03961	-5.23625	-7.28913
Cl	5.29167	-6.77369	-4.9104
Zn	3.67683	-1.59453	-4.77665
N	4.79791	-3.16163	-5.4718
H	4.81042	-3.31758	-6.47478
I	1.82029	-0.97734	-6.5852
O	4.94092	-4.71323	-1.07228
C	6.13462	-4.71018	-0.28415
H	5.86666	-4.38056	0.72254
H	6.54908	-5.72352	-0.22866
H	6.88919	-4.03285	-0.70043
H	5.21248	-4.78776	-2.0232

IM5α

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -3222.01214127

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	2.90975	-3.60969	-0.83767
C	4.41203	-3.43749	-0.80303
C	4.46239	-2.42711	1.33276
C	3.24121	-1.66439	0.79437
C	2.23266	-2.60118	0.13417
H	4.71354	-2.44465	-1.20079
H	2.70236	-4.64937	-0.54974
H	4.17271	-2.82756	2.31556
H	3.57317	-0.93067	0.04031
H	1.70457	-3.13838	0.93802
O	2.69718	-0.98546	1.897
C	2.10348	0.28263	1.64966
C	0.60399	0.21618	1.6121
C	-0.07656	-0.4698	2.65006
C	-1.44534	-0.55225	2.65521
C	-2.21344	0.04228	1.62177
C	-1.53457	0.72897	0.57196
C	-0.11922	0.79823	0.59959
C	-3.62645	-0.03626	1.5895
C	-4.3355	0.52959	0.55957

C	-3.66219	1.19639	-0.48778
C	-2.29322	1.29445	-0.48173
H	2.42883	0.9286	2.47943
H	2.49635	0.71946	0.71694
H	0.5102	-0.93776	3.44038
H	-1.966	-1.07571	3.45856
H	0.39686	1.30194	-0.22226
H	-4.1403	-0.55572	2.39938
H	-5.42208	0.46219	0.5436
H	-4.23415	1.63184	-1.3051
H	-1.7657	1.79596	-1.29343
C	5.66367	-1.51751	1.46731
H	5.99379	-1.16466	0.47937
H	5.40706	-0.64034	2.07413
H	6.49661	-2.04577	1.94479
O	4.78854	-3.57177	0.53943
O	1.29943	-1.83253	-0.61211
O	2.45902	-3.38978	-2.17509
C	-0.05575	-2.28733	-0.50195
H	-0.45081	-1.92457	0.45705
H	-0.59814	-1.76624	-1.30342
C	1.28111	-4.12677	-2.61025
H	1.64361	-4.98112	-3.19984
H	0.75642	-3.44877	-3.29995
C	-0.80524	-6.5333	-0.58863
C	0.08437	-5.98703	-1.50627
C	0.36274	-4.61908	-1.52981
C	-0.25195	-3.77861	-0.58035
C	-1.11931	-4.34656	0.35331
C	-1.41186	-5.70584	0.34651
H	-1.01113	-7.60163	-0.59953
H	0.57334	-6.63656	-2.2328
H	-1.5788	-3.69555	1.09876
H	-2.1023	-6.11643	1.08081
I	4.32925	0.22734	-2.45607
O	4.28619	-3.74014	-4.26772
C	3.71321	-2.87757	-5.07376
C	4.3795	-2.93805	-6.4592
Cl	6.08392	-2.46316	-6.25787
Cl	3.59365	-1.83884	-7.61509
Cl	4.27054	-4.60914	-7.07409
Zn	2.13431	-1.22178	-2.79249
N	2.76054	-2.10032	-4.74075
H	2.43705	-1.50088	-5.50039

I	-0.14098	-0.22366	-3.68332
O	4.97595	-4.43298	-1.57179
C	6.34932	-4.20592	-1.84143
H	6.93401	-4.2067	-0.91247
H	6.68342	-5.01732	-2.49278
H	6.48537	-3.24385	-2.36281
H	3.86795	-3.72664	-3.37356

IM6*α*

Number of Imaginary Frequencies: 0

Electronic energy (Hartree):-1633.97136819

Charge = 0 Multiplicity = 1

Coordinates of Optimized Structure:

C	1.95581	-3.67701	-1.9216
C	3.46026	-3.62771	-1.67249
C	3.30238	-1.4759	-0.66219
C	1.77963	-1.46005	-0.78069
C	1.2112	-2.86942	-0.86471
H	3.98957	-4.13524	-2.50175
H	1.62049	-4.72633	-1.93505
H	3.57712	-1.95281	0.28984
H	1.50551	-0.921	-1.70432
H	1.33757	-3.36157	0.12091
O	1.26471	-0.80555	0.3505
C	0.36502	0.25186	0.06123
C	-0.41814	0.5623	1.29744
C	-1.0981	-0.49601	1.95187
C	-1.84862	-0.25704	3.07083
C	-1.9669	1.05293	3.60146
C	-1.28674	2.12127	2.9485
C	-0.51321	1.83728	1.79555
C	-2.73498	1.33359	4.75614
C	-2.82764	2.61302	5.24516
C	-2.1533	3.67159	4.59881
C	-1.40036	3.42945	3.47681
H	0.91407	1.14194	-0.29709
H	-0.31486	-0.06017	-0.75014
H	-0.99908	-1.50169	1.54351
H	-2.37005	-1.07212	3.57427
H	0.0132	2.65685	1.3017
H	-3.25291	0.51138	5.25135
H	-3.42208	2.81703	6.13426
H	-2.23366	4.68257	4.99493
H	-0.87772	4.24313	2.9727

C	3.91439	-0.10212	-0.74543
H	3.64589	0.39947	-1.686
H	3.54673	0.50495	0.08971
H	5.00722	-0.16713	-0.67449
O	3.8256	-4.16296	-0.44324
O	3.86811	-2.28345	-1.72746
O	-0.16261	-2.73468	-1.15934
O	1.80209	-3.11252	-3.20826
C	-0.91482	-3.91911	-1.1574
H	-0.62218	-4.54788	-0.29282
H	-1.95345	-3.60678	-0.9741
C	0.49317	-3.12798	-3.82356
H	0.70689	-2.98361	-4.88975
H	-0.07409	-2.26175	-3.46582
C	-0.93154	-6.54547	-4.58628
C	-0.27037	-5.32907	-4.68304
C	-0.24023	-4.42213	-3.61838
C	-0.87212	-4.7714	-2.41261
C	-1.52732	-6.00129	-2.32416
C	-1.56938	-6.88127	-3.39687
H	-0.9455	-7.22775	-5.43379
H	0.24223	-5.06131	-5.60733
H	-2.01681	-6.27004	-1.38571
H	-2.09073	-7.83218	-3.29997
C	3.74607	-5.56634	-0.3786
H	4.2889	-5.87621	0.51869
H	2.70576	-5.92117	-0.29931
H	4.21124	-6.0348	-1.26088
I	1.99991	0.39389	-4.40488
Zn	3.46698	-1.78469	-3.98859
I	4.23336	-3.6414	-5.73406

α-product

Number of Imaginary Frequencies: 0

Electronic energy (Hartree): -1383.80526067

Charge = 0 Multiplicity = 1

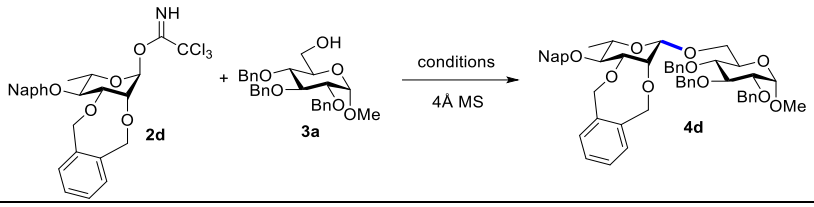
Coordinates of Optimized Structure:

C	1.67925	-3.92656	-2.06202
C	3.15689	-3.97852	-1.68373
C	3.03155	-1.82931	-0.58317
C	1.50655	-1.73368	-0.79535
C	0.87541	-3.11638	-1.03214
H	3.74091	-4.46064	-2.47715
H	1.30256	-4.95065	-2.14034

H	3.21178	-2.37237	0.34933
H	1.30824	-1.10627	-1.67388
H	0.8674	-3.66782	-0.07975
O	0.98482	-1.13062	0.38002
C	-0.0803	-0.19717	0.15941
C	-0.53749	0.34956	1.48829
C	-0.8029	-0.53833	2.56765
C	-1.26705	-0.06358	3.77111
C	-1.5014	1.32498	3.97098
C	-1.2351	2.22627	2.88987
C	-0.74638	1.70117	1.66279
C	-1.98619	1.84891	5.19896
C	-2.19919	3.20107	5.35432
C	-1.93499	4.0928	4.28567
C	-1.46337	3.61543	3.08272
H	0.26281	0.61921	-0.4922
H	-0.90578	-0.70771	-0.35309
H	-0.61894	-1.59925	2.42857
H	-1.46381	-0.75011	4.59165
H	-0.53809	2.39251	0.84831
H	-2.18788	1.16183	6.01767
H	-2.57132	3.58937	6.2986
H	-2.10685	5.15747	4.4193
H	-1.26015	4.2981	2.26078
C	3.71524	-0.47448	-0.52733
H	3.54965	0.09728	-1.44592
H	3.30068	0.0902	0.31195
H	4.79164	-0.597	-0.3727
O	3.297	-4.63029	-0.46902
O	3.64871	-2.61778	-1.65345
O	-0.45997	-2.87937	-1.46976
O	1.67555	-3.30204	-3.34614
C	-1.31079	-4.00591	-1.58935
H	-1.19484	-4.66089	-0.71052
H	-2.3258	-3.59294	-1.54527
C	0.41116	-3.23307	-4.08013
H	0.72523	-3.0633	-5.1108
H	-0.13966	-2.35941	-3.73463
C	-1.12247	-6.55629	-5.09773
C	-0.38827	-5.37308	-5.08892
C	-0.40897	-4.49971	-3.9896
C	-1.17703	-4.84861	-2.85862
C	-1.90382	-6.04715	-2.87538
C	-1.88823	-6.89403	-3.98124

H	-1.09272	-7.20948	-5.96503
H	0.21838	-5.10912	-5.95131
H	-2.49362	-6.31973	-2.00178
H	-2.46405	-7.81548	-3.96656
C	4.64067	-5.00702	-0.16217
H	4.60554	-5.51307	0.8042
H	5.03266	-5.69421	-0.92346
H	5.2945	-4.12997	-0.0976

Table S1: Optimization of Glycosylation under Various Conditions.



Entry	Promotor	Time	[M]	Solvent	Temp.	Yield (%)[b]	α: β[c]
1	ZnI_2	12 h	0.01	Et_2O	r.t.	95	1:6
2	$ZnBr_2$	12 h	0.01	Et_2O	r.t.	87	1:3
3	$ZnCl_2$	12 h	0.01	Et_2O	r.t.	94	1:2
4	$Zn(OTf)_2$	12 h	0.01	Et_2O	r.t.	73	1:1
5	$Cu(OTf)_2$	12 h	0.01	Et_2O	r.t.	63	1:1
6	$FeCl_3$	12 h	0.01	Et_2O	r.t.	40	1:1
7	$AuCl_3$	12 h	0.01	Et_2O	r.t.	51	1:1
8	TMSOTf	12 h	0.01	Et_2O	r.t.	47	1:1
9	$B(C_6F_5)_3$	12 h	0.01	Et_2O	r.t.	43	1:3
10	TfOH	12 h	0.01	Et_2O	r.t.	65	1:1
11	ZnI_2	12 h	0.01	Toluene	r.t.	64	3:1
12	ZnI_2	12 h	0.01	DCM	r.t.	98	2:1
13	ZnI_2	12 h	0.01	MeCN	r.t.	89	3:1
14	ZnI_2	12 h	0.01	THF	r.t.	64	1:1
15	ZnI_2	12 h	0.01	1,4-dioxane	r.t.	74	1:3
16	ZnI_2	12 h	0.01	Et_2O	− 20 ℃	54	1:3
17	ZnI_2	12 h	0.01	Et_2O	–5 ℃	89	1:10
18	ZnI_2	12 h	0.01	Et_2O	0 ℃	72	1:10
19	ZnI_2	20 min	0.01	Et_2O	60 ℃	65	1:5
20	ZnI_2	24 h	0.01	Et_2O	–5 ℃	91	1:11
21	ZnI_2	24 h	0.005	Et_2O	–5 ℃	61	1:8
22	ZnI_2	24 h	0.02	Et_2O	–5 ℃	73	1:12
23	ZnI_2	24 h	0.08	Et_2O	− 5 ℃	55	1:10

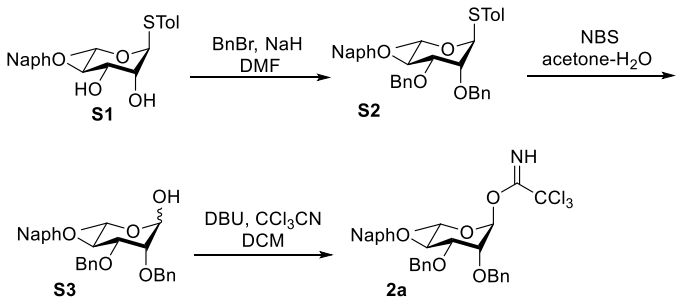
[a]Reaction conditions: donor **2d** (1.5 equiv.), acceptor **3a** (1.0 equiv.), promotor (0.5 equiv.), MS 4Å (100 mg/mL); [b]Combined yield of the anomeric mixture of the corresponding glycoside; [c]Determined by the integration ratio obtained from ^{1}H-NMR of crude mixture.

General experimental

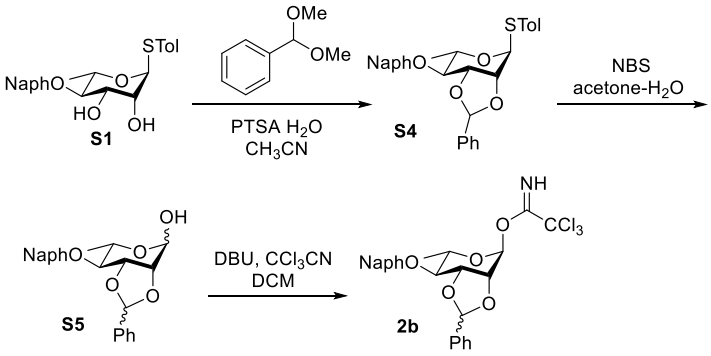
All reactions sensitive to air and/or moisture were carried out under a nitrogen or argon atmosphere with anhydrous solvents. Substrates of glycosylations were dried by azeotropic removal with toluene. Column chromatography was performed on silica gel, 300–400 mesh). Reactions were monitored by thin-layer chromatography (TLC) on glassplates coated with silica gel 60 F254, 0.2 mm thickness and compounds were detected by examination under UV light and by charring with 10% sulfuric acid in MeOH. Solvents were removed under reduced pressure at <40 °C. CH_2Cl_2 was freshly distilled from calcium hydride under nitrogen prior to use. Molecular sieves (4 Å) were activated in an oil bath at 170 °C for 2–3 h under reduced pressure prior to application. All experiments were performed using standard Schlenk techniques under an argon atmosphere. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker spectrometers at 400, 500 or 600 MHz. The ^{1}H NMR spectra were referenced to $CDCl_3$ at 7.26 ppm, MeOD at 3.31 ppm and C_6D_6 at 7.15 ppm, and the ^{13}C NMR spectra were referenced to $CDCl_3$ at 77.0 ppm, MeOD at 47.67 ppm, and C_6D_6 at 128.01 ppm or a native scale. Assignments were made by standard 2D experiments. Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. Optical rotations were measured with 'Insmark IP-digi300/1' polarimeter. High Resolution Mass Spectra (HRMS) were recorded on Shimadzu (LCMS-IT-TOF). All other reagents were purchased from Adamas-Beta Co. or Bidepharm Co.

Synthetic procedures.

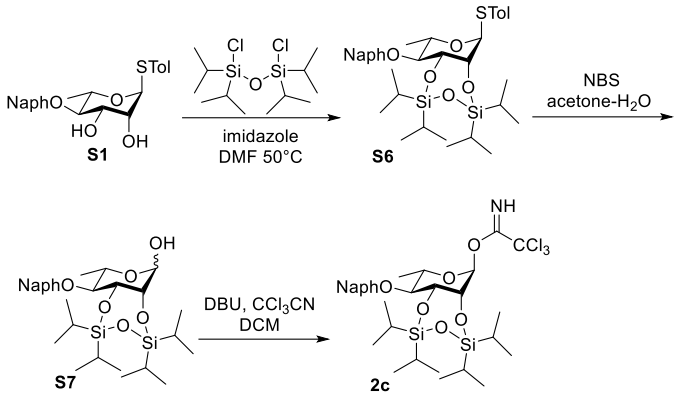
Scheme S1. Synthesis of rhamnosyltrichloroacetimidate donor **2a**.



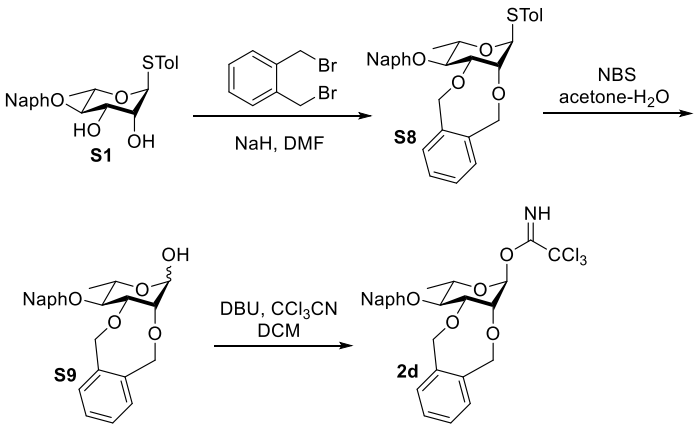
Scheme S2. Synthesis of rhamnosyltrichloroacetimidate donor **2b**.



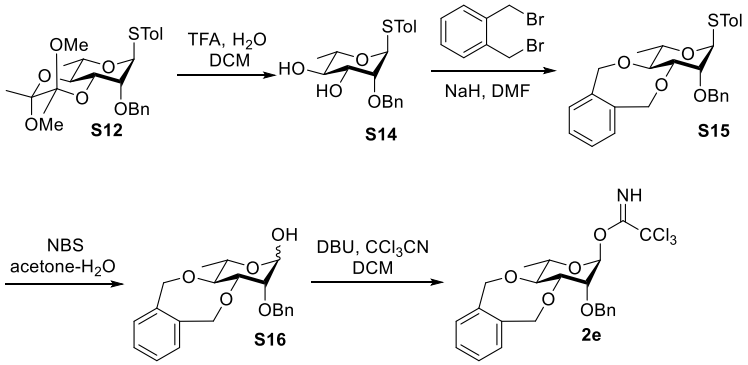
Scheme S3. Synthesis of rhamnosyltrichloroacetimidate donor **2c**.



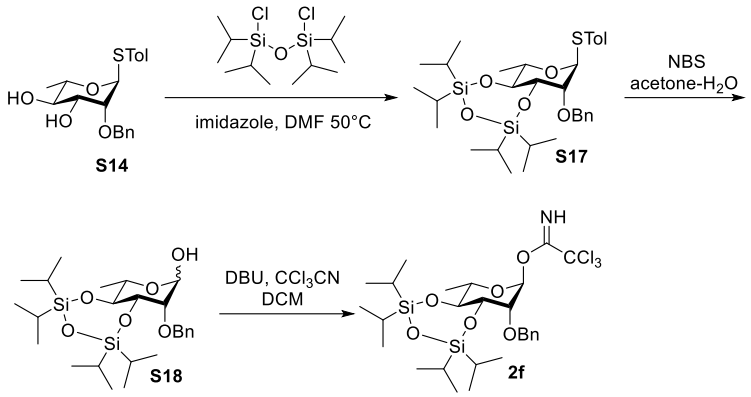
Scheme S4. Synthesis of rhamnosyltrichloroacetimidate donor **2d**.



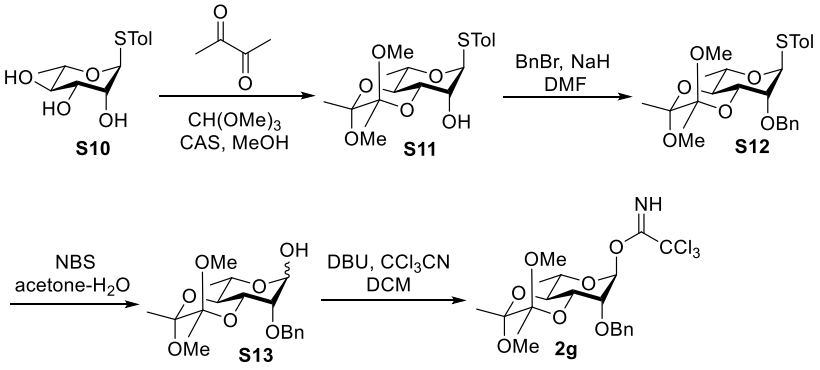
Scheme S5. Synthesis of rhamnosyltrichloroacetimidate donor **2e**.



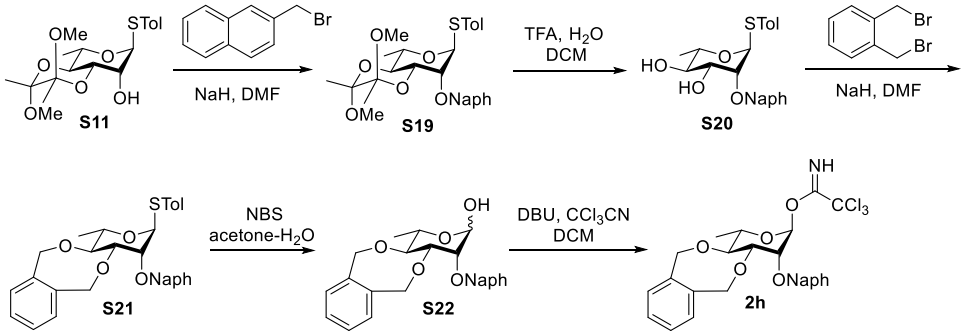
Scheme S6. Synthesis of rhamnosyltrichloroacetimidate donor **2f**.



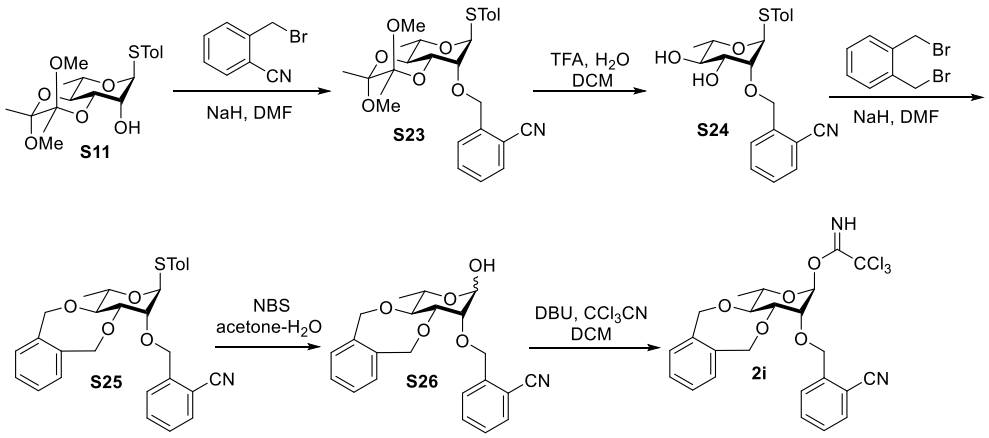
Scheme S7. Synthesis of rhamnosyltrichloroacetimidate donor **2g**.



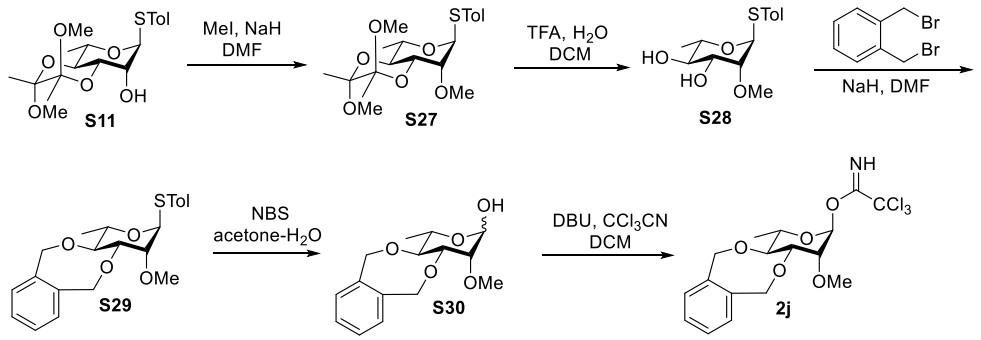
Scheme S8. Synthesis of rhamnosyltrichloroacetimidate donor **2h**.



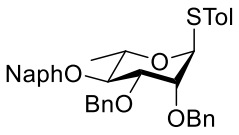
Scheme S9. Synthesis of rhamnosyltrichloroacetimidate donor **2i**.



Scheme S10. Synthesis of rhamnosyltrichloroacetimidate donor **2j**.

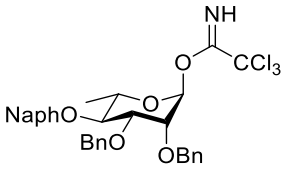


Tolyl 2,3-*O*-dibenzyl-4-*O*-(2-naphthylmethyl)-1-thio-α-L-rhamnopyranoside (S2):



To a magnetically stirred solution of **S1**[8] (400 mg, 1.0 mmol) in anhydrous DMF (5 mL) was added sodium hydride (60% dispersion in oil, 270 mg, 4.0 mmol, 4.0 equiv.) in small portions at 0 °C. After 15 min, benzyl bromide (360 μL, 3.0 mmol, 3.0 equiv.) was added dropwise for 1 min and stirred at room temperature. Complete consumption of starting materials was observed after 2 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 30 mL), washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S2** (573.5 mg, 98% yield) as a coloreless oil. TLC (hexane–EtOAc, 5:1): R_f = 0.72; $[\alpha]_D^{21}$ = –65.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79–7.04 (m, 21H, ArH), 5.45 (d, 1H, *J* = 1.6 Hz, C1^{Rha}-H), 5.10 (d, 1H, *J* = 11.1 Hz, OC$\underline{H_2}$Ph), 4.80 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.70 (d, 1H, *J* = 12.4 Hz, OC$\underline{H_2}$Ph), 4.62 (d, 1H, *J* = 12.3 Hz, OC$\underline{H_2}$Ph), 4.59 (s, 2H, OC$\underline{H_2}$Ph), 4.23–4.19 (m, 1H, C5^{Rha}-H), 4.00 (dd, 1H, *J* = 1.7, 3.1 Hz, C2^{Rha}-H), 3.89 (dd, 1H, *J* = 3.0, 9.3 Hz, C3^{Rha}-H), 3.75 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 2.27 (s, 3H, $\underline{Me}$ of Tol), 1.37 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5, 138.1, 137.7, 136.3, 133.5, 133.2, 132.2, 131.0, 130.0, 128.6, 128.6, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 126.7, 126.3, 126.2, 126.0, 86.3 (C1^{Rha}), 80.8, 80.2, 77.6, 77.3, 77.0, 76.7, 75.6, 72.3, 72.2, 69.5, 21.3, 18.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{38}H_{38}O_4SNa$, 613.2389; found, 613.2395.

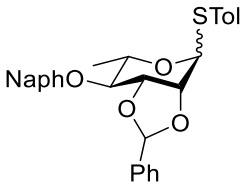
2,3-*O*-dibenzyl-4-*O*-(2-naphthylmethyl)-α-L-rhamnopyranosyltrichloroacetimidate (2a):



To a magnetically stirred solution of **S2** (573.5 mg, 1.0 mmol) in acetone–H_2O (20:1, 21 mL) was added NBS (531 mg, 3.0 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (50 mL), washed with saturated aq. $Na_2S_2O_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 5:1) afforded the mixture of isomers **S3** (449 mg, 96% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.27. To a magnetically stirred solution of **S3** (136 mg, 0.29 mmol) and CCl_3CN (234 μL, 2.32 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (5.8 mL), DBU (17 μL, 0.12 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (eluent: hexane–EtOAc, 20:1) to afford compound **2a** (50 mg, 28% yield) as a white powder. TLC (hexane–EtOAc, 4:1): R_f = 0.71; $[\alpha]_D^{21}$ = –41.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.44 (s, 1H, N$\underline{H}$), 7.72–7.06 (m, 17H, ArH), 6.66 (d, 1H, *J* = 2.0 Hz, C1^{Rha}-H), 5.09 (d, 1H, *J* = 11.4 Hz, OC$\underline{H_2}$Ph), 4.67 (d, 1H, *J* = 11.5 Hz, OC$\underline{H_2}$Ph), 4.61 (s, 2H, OC$\underline{H_2}$Ph), 4.50 (s, 2H, OC$\underline{H_2}$Ph), 4.28–4.22 (m, 1H, C5^{Rha}-H), 4.12 (dd, 1H, *J* = 3.1, 9.4 Hz, C3^{Rha}-H), 4.00 (t, 1H, *J* = 9.5 Hz, C4^{Rha}-H), 4.00–3.99 (m, 1H, C2^{Rha}-H), 1.39 (d, 3H, *J* = 6.3 Hz, C6^{Rha}-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 160.4, 138.5, 138.3, 136.4, 133.6, 133.1, 128.3, 127.9, 127.8, 127.7, 127.5, 126.5, 126.1, 125.9,

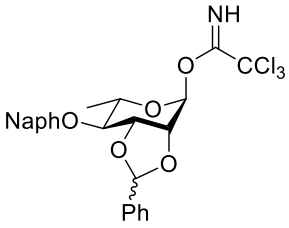
125.7, 96.5 ($C1^{Rha}$), 91.3, 80.0, 79.4, 75.3, 74.3, 72.8, 72.0, 71.5, 31.3, 30.1, 29.9, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{33}H_{32}Cl_3NO_5Na$, 650.1244; found, 650.1240.

Tolyl 2,3-*O*-(phenylmethylene)-4-*O*-(2-naphthylmethyl)-1-thio-α/β-L-rhamnopyranoside (S4α,β):



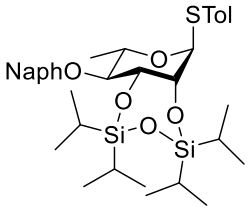
S1[8] (500 mg, 1.26 mmol) was dissolved in anhydrous acetonitrile (10 mL). After 10 min, benzaldehyde dimethyl acetal (568 μL, 3.79 mmol, 3.0 equiv.) and *p*-Toluenesulfonic acid monohydrate (12 mg, 0.06 mmol, 0.05 equiv.) was added and stirred at room temperature overnight. The reaction mixture was concentrated under vacuum. The reaction mixture was dissolved in EtOAc (40 mL), washed with saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S4α,β** (601.7 mg, 98% yield) as a coloreless oil. TLC (hexane–EtOAc, 5:1): R_f = 0.73; α:β = 0.6:0.4; ^{1}H NMR (C_6D_6, 400 MHz): δ 7.76–6.81 (m, 16H, ArH), 6.01 (s, 1H, $C1^{Rhaβ}$-H and ArCH), 5.93 (s, 0.4H, ArCH), 5.71 (s, 0.4H, $C1^{Rhaα}$-H), 5.06 (d, 0.4H, *J* = 11.6 Hz, OCH_2Ph), 5.03 (d, 0.6H, *J* = 11.7 Hz, OCH_2Ph), 4.78 (d, 0.4H, *J* = 12.0 Hz, OCH_2Ph), 4.70 (d, 0.6H, *J* = 12.1 Hz, OCH_2Ph), 4.57 (dd, 0.4H, *J* = 5.4, 7.2 Hz, $C3^{Rhaβ}$-H), 4.51–4.39 (m, 2H, $C5^{Rhaβ}$-H, $C5^{Rhaα}$-H, $C3^{Rhaα}$-H and $C2^{Rhaβ}$-H), 4.25 (dd, 0.6H, *J* = 0.8, 6.3 Hz, $C3^{Rhaα}$-H), 3.57–3.49 (m, 1H, $C4^{Rhaα}$-H and $C4^{Rhaβ}$-H), 1.98 (s, 3H, Me of Tol), 1.39 (d, 1.2H, *J* = 6.2 Hz, $C6^{Rhaβ}$-H), 1.29 (d, 1.8H, *J* = 6.2 Hz, $C6^{Rhaα}$-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 139.2, 137.8, 137.5, 137.5, 136.0, 135.9, 133.5, 133.3, 133.2, 132.7, 132.7, 130.0, 129.9, 129.8, 129.8, 129.1, 129.0, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 126.9, 126.8, 126.8, 126.5, 126.1, 126.0, 125.8, 125.8, 125.7, 103.9 ($C1^{Rhaβ}$), 103.1 ($C1^{Rhaα}$), 84.7, 84.1, 81.7, 79.5, 79.0, 78.1, 78.1, 76.5, 72.7, 72.4, 66.2, 65.9, 20.6, 17.8, 17.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{30}O_4SNa$, 521.1762; found, 521.1769.

2,3-*O*-(phenylmethylene)-4-*O*-(2-naphthylmethyl)-α-L-rhamnopyranosyltrichloroacetimidate (2b):



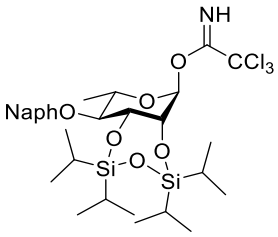
To a magnetically stirred solution of **S4α,β** (400 mg, 0.82 mmol) in acetone–H_2O (20:1, 15 mL) was added NBS (440 mg, 2.5 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (50 mL), washed with saturated aq. $Na_2S_2O_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 10:1) afforded the mixture of isomers **S5** (223 mg, 71% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.35. To a magnetically stirred solution of **S5** (77 mg, 0.20 mmol) and CCl_3CN (165 μL, 1.63 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (4 mL), DBU (12 μL, 0.08 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (eluent: hexane–EtOAc, 10:1) to afford compound **2b** (100 mg, 94% yield) as a white powder. TLC (hexane–EtOAc, 10:1): R_f = 0.64; *exo*:*endo* = 0.3:0.7; ^{1}H NMR (C_6D_6, 400 MHz): δ 8.55 (s, 0.3H, NH), 8.51 (s, 0.7H, NH), 7.72–7.12 (m, 11H, ArH), 6.90 (s, 0.3H, $C1^{Rha}$-H), 6.83 (s, 0.7H, $C1^{Rha}$-H), 5.97 (s, 0.7H, ArCH), 5.72 (s, 0.3H, ArCH), 5.03 (d, 0.7H, *J* = 12.2 Hz, OCH_2Ph), 4.99 (d, 0.3H, *J* = 12.9 Hz, OCH_2Ph), 4.75 (d, 0.7H, *J* = 11.9 Hz, OCH_2Ph), 4.65 (d, 0.3H, *J* = 12.0 Hz, OCH_2Ph), 4.60 (dd, 0.7H, *J* = 5.5, 7.3 Hz, $C3^{Rha}$-H), 4.40 (t, 0.3H, *J* = 6.6 Hz, $C4^{Rha}$-H), 4.21 (d, 0.7H, *J* = 5.6 Hz, $C2^{Rha}$-H), 4.19–4.13 (m, 1.3H, $C5^{Rha}$-H, $C5^{Rha}$-H and $C2^{Rha}$-H), 3.52–3.43 (m, 1H, $C3^{Rha}$-H and $C4^{Rha}$-H), 1.42 (d, 2.1H, *J* = 6.2 Hz, $C6^{Rha}$-H), 1.31 (d, 0.9H, *J* = 6.2 Hz, $C6^{Rha}$-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 159.9, 159.8, 138.7, 137.5, 135.8, 135.7, 133.5, 133.4, 133.3, 133.2, 129.2, 129.2, 129.1, 128.3, 128.3, 128.1, 127.9, 127.7, 127.5, 127.0, 126.8, 126.7, 126.6, 126.5, 126.4, 126.1, 126.1, 125.9, 125.7, 104.9, 104.1, 103.1, 95.4 ($C1^{Rha}$), 95.0 ($C1^{Rha}$), 91.3, 91.2, 80.5, 79.5, 78.0, 77.0, 76.9, 76.6, 74.5, 73.1, 72.8, 72.5, 72.0, 70.7, 67.8, 67.6, 46.3, 31.3, 31.2, 30.1, 29.9, 22.8, 19.9, 17.8, 17.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{24}Cl_3NO_5Na$, 558.0618; found, 558.0610.

Tolyl 2,3-*O*-[1,1,3,3-tetrakis(1-methylethyl)-1,3-disiloxanediyl]-4-*O*-(2-naphthylmethyl)-1-thio-α-L-rhamnopyranoside (S6):



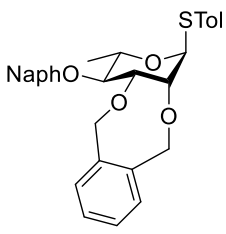
To a magnetically stirred solution of **S1**[8] (100 mg, 0.25 mmol) in anhydrous DMF (2.5 mL) was added 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (242 μL, 0.76 mmol, 3 equiv.) and imidazole (103 mg, 1.52 mmol, 6 equiv.) in small portions. Starting materials were consumed at 50 °C after 30 min. The reaction mixture was quenched by saturated aqueous $NaHCO_3$ (10 mL) at 0 °C. The reaction mixture was extracted with EtOAc (2 × 20 mL), washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded compound **S6** (153 mg, 95% yield) as a coloreless oil. TLC (hexane–EtOAc, 50:1): R_f = 0.80; $[\alpha]_D^{21}$ = –84.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81–7.06 (m, 11H, ArH), 5.38 (d, 1H, *J* = 1.6 Hz, C1^{Rha}-H), 5.15 (d, 1H, *J* = 11.1 Hz, OC$\underline{H_2}$Ph), 4.80 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.52 (dd, 1H, *J* = 1.7, 3.2 Hz, C2^{Rha}-H),), 4.40 (dd, 1H, *J* = 3.1, 9.0 Hz, C3^{Rha}-H), 4.26–4.19 (m, 1H, C5^{Rha}-H), 3.54 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 2.28 (s, 3H, $\underline{Me}$ of Tol), 1.33 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H), 1.63–1.00 (m, 24H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.5, 136.3, 133.4, 133.1, 131.9, 130.9, 129.9, 128.2, 128.0, 127.8, 126.7, 126.3, 126.1, 125.9, 88.7 (C1^{Rha}), 81.7, 77.5, 77.2, 76.9, 76.0, 75.4, 74.2, 69.1, 21.2, 18.2, 17.9, 17.7, 17.6, 17.5, 17.4, 17.2, 17.2, 14.6, 13.8, 13.2, 12.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{36}H_{52}O_5SSi_2Na$, 675.2972; found, 675.2981.

2,3-*O*-[1,1,3,3-tetrakis(1-methylethyl)-1,3-disiloxanediyl]-4-*O*-(2-naphthylmethyl)-α-L-rhamnopyranosyl-trichloroacetimidate (2c):



To a magnetically stirred solution of **S6** (153 mg, 0.24 mmol) in acetone–H_2O (20:1, 5.7 mL) was added NBS (128 mg, 0.72 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (50 mL), washed with saturated aq. $Na_2S_2O_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 10:1) afforded the mixture of isomers **S7** (102 mg, 80% yield) as a white solid. TLC (hexane–EtOAc, 10:1): R_f = 0.20. To a magnetically stirred solution of **S7** (143 mg, 0.27 mmol) and CCl_3CN (218 μL, 2.15 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (5.4 mL), DBU (16 μL, 0.11 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (eluent: hexane–EtOAc, 50:1) to afford compound **2c** (169 mg, 93% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.70; $[\alpha]_D^{21}$ = –32.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.16 (s, 1H, N$\underline{H}$), 7.65–6.94 (m, 7H, ArH), 6.36 (s, 1H, C1^{Rha}-H), 5.10 (d, 1H, *J* = 11.4 Hz, OC$\underline{H_2}$Ph), 4.65 (d, 1H, *J* = 11.4 Hz, OC$\underline{H_2}$Ph), 4.54–4.50 (m, 2H, C2^{Rha}-H and C3^{Rha}-H), 4.14–4.07 (m, 1H, C5^{Rha}-H), 3.61 (t, 1H, *J* = 8.9 Hz, C4^{Rha}-H), 1.21 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H), 1.05–0.88 (m, 24H, CH_3); ^{13}C NMR (C_6D_6, 100 MHz): δ 160.3, 136.5, 133.6, 133.2, 127.9, 127.7, 127.5, 126.5, 126.4, 126.1, 126.0, 126.0, 125.7, 98.9 (C1^{Rha}), 91.2, 81.2, 81.0, 75.9, 75.4, 71.1, 71.0, 46.4, 18.2, 17.5, 17.4, 17.3, 17.3, 17.2, 17.1, 17.0, 14.4, 13.8, 13.0, 12.9, 12.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{46}Cl_3NO_6Si_2Na$, 712.1827; found, 712.1821.

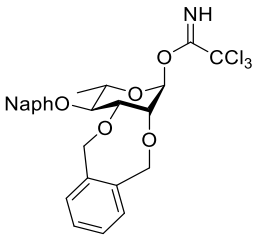
Tolyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-1-thio-α-L-rhamnopyranoside (S8):



To a magnetically stirred solution of **S1**[8] (100 mg, 0.25 mmol) in anhydrous DMF (5 mL) was added sodium hydride (60% dispersion in oil, 50 mg, 1.26 mmol, 5.0 equiv.) in small portions at 0 °C. After 30 min, 1,2-bis(bromomethyl)benzene (67 mg, 0.25 mmol, 1.0 equiv.) was added and stirred at room temperature. Complete consumption of starting materials was observed after 2 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 30 mL), washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and

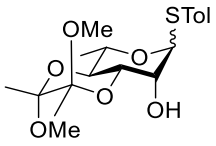
concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 20:1) afforded the title compound **S8** (96 mg, 76% yield) as a coloreless oil. TLC (hexane–EtOAc, 4:1): R_f = 0.85; $[\alpha]_D^{21}$ = –4.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80–6.96 (m, 15H, ArH), 5.45 (d, 1H, *J* = 1.6 Hz, C1^{Rha}-H), 5.16 (d, 1H, *J* = 10.9 Hz, OC$\underline{H_2}$Ph), 4.87 (d, 1H, *J* = 12.6 Hz, OC$\underline{H_2}$Ph), 4.85 (d, 1H, *J* = 11.1 Hz, OC$\underline{H_2}$Ph), 4.78 (d, 1H, *J* = 12.5 Hz, OC$\underline{H_2}$Ph), 4.76 (d, 1H, *J* = 12.0 Hz, OC$\underline{H_2}$Ph), 4.72 (d, 1H, *J* = 12.0 Hz, OC$\underline{H_2}$Ph), 4.25–4.18 (m, 1H, C5^{Rha}-H), 4.05 (dd, 1H, *J* = 1.8, 3.1 Hz, C2^{Rha}-H),), 3.97 (dd, 1H, *J* = 3.1, 9.3 Hz, C3^{Rha}-H), 3.81 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 2.26 (s, 3H, $\underline{Me}$ of Tol), 1.40 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.6, 136.2, 135.9, 135.5, 133.5, 133.4, 133.3, 133.2, 133.1, 132.1, 130.8, 129.9, 128.4, 128.3, 128.2, 128.1, 128.1, 127.8, 127.8, 127.0, 126.7, 126.6, 126.2, 126.2, 126.2, 126.1, 126.1, 126.0, 125.9, 86.4 (C1^{Rha}), 80.8, 80.2, 77.5, 77.2, 76.9, 76.6, 75.6, 72.4, 72.3, 69.6, 21.2, 18.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{32}H_{32}O_4SNa$, 535.1919; found, 535.1912.

2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-α-L-rhamnopyranosyltrichloroacetimidate (2d):



To a magnetically stirred solution of **S8** (139 mg, 0.28 mmol) in acetone–H_2O (20:1, 5.2 mL) was added NBS (149 mg, 0.84 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (50 mL), washed with saturated aq. $Na_2S_2O_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 10:1) afforded the mixture of isomers **S9** (66 mg, 60% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.20. To a magnetically stirred solution of **S9** (400 mg, 1.02 mmol) and CCl_3CN (824 μL, 8.15 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (20 mL), DBU (61 μL, 0.41 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (preconditioned with Et_3N; eluent: hexane–EtOAc, 50:1) to afford compound **2d** (535 mg, 98% yield) as a coloreless oil. TLC (hexane–EtOAc, 4:1): R_f = 0.62; $[\alpha]_D^{21}$ = +26.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.36 (s, 1H, N$\underline{H}$), 7.84–6.83 (m, 11H, ArH), 6.53 (d, 1H, *J* = 2.0 Hz, C1^{Rha}-H), 5.60 (d, 1H, *J* = 12.8 Hz, OC$\underline{H_2}$Ph), 5.27 (d, 1H, *J* = 14.6 Hz, OC$\underline{H_2}$Ph), 5.19 (d, 1H, *J* = 11.4 Hz, OC$\underline{H_2}$Ph), 4.76 (d, 1H, *J* = 11.5 Hz, OC$\underline{H_2}$Ph), 4.45 (d, 1H, *J* = 12.9 Hz, OC$\underline{H_2}$Ph), 4.37 (d, 1H, *J* = 14.6 Hz, OC$\underline{H_2}$Ph), 4.37–4.34 (m, 1H, C5^{Rha}-H), 4.29 (dd, 1H, *J* = 6.2, 9.4 Hz, C3^{Rha}-H), 4.13 (t, 1H, *J* = 2.5 Hz, C4^{Rha}-H), 3.98 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 1.46 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 159.9, 139.3, 136.5, 134.0, 133.6, 133.2, 130.6, 126.6, 126.2, 126.0, 125.7, 97.4 (C1^{Rha}), 91.2, 80.5, 78.6, 75.2, 72.6, 71.8, 70.8, 69.3, 59.7, 20.2, 18.2, 13.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{26}Cl_3NO_5Na$, 572.0774; found, 572.0785.

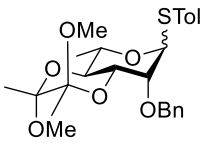
Tolyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-1-thio-α/β-L-rhamnopyranoside (S11α,β):



To a magnetically stirred solution of **S10**[9] (500 mg, 1.85 mmol) in methanol (5.9 mL) were added 2,3-butanedione (178 μL, 2.03 mmol, 1.1 equiv.), trimethylorthoformate (607 μL, 5.55 mmol, 3.0 equiv.) and camphorsulfonic acid (64 mg, 0.28 mmol, 0.15 equiv.). The reaction mixture was stirred under reflux for 8 h. After quenching with triethylamine (3 mL) and concentrated under reduced pressure. The obtained residue was diluted with EtOAc (20 mL) and washed with saturated aqueous $NaHCO_3$ (2 x 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 10:1) afforded the title compound **S11α,β** (516.2 mg, 73% yield) as a coloreless oil. TLC (hexane–EtOAc, 2:1): R_f = 0.70; α:β = 1:0.88; ^{1}H NMR (C_6D_6, 400 MHz): δ 7.50 (d, 2H, *J* = 8.1 Hz, ArH), 7.35 (d, 2H, *J* = 8.1 Hz, ArH), 6.87 (d, 2H, *J* = 8.4 Hz, ArH), 6.80 (d, 2H, *J* = 8.4 Hz, ArH), 5.70 (t, 1H, *J* = 0.8 Hz, C1^{Rhaα}-H), 4.63 (t, 1H, *J* = 1.0 Hz, C1^{Rhaβ}-H), 4.53–4.49 (m, 1H, C5^{Rhaα}-H), 4.30–4.25 (m, 2H, C2^{Rhaα}-H and C3^{Rhaα}-H), 4.07 (t, 1H, *J* = 9.6 Hz, C4^{Rhaα}-H), 4.06–4.04 (m, 1H, C2^{Rhaβ}-H), 3.91 (t, 1H, *J* = 9.7 Hz, C4^{Rhaβ}-H), 3.56 (dd, 1H, *J* = 3.1, 10.0 Hz, C3^{Rhaβ}-H), 3.28–3.24 (m, 1H, C5^{Rhaβ}-H), 3.04 (s, 3H, OMe), 3.01 (s, 6H, OMe), 2.99 (s, 3H, OMe), 2.53–2.49 (m, 2H, C2^{Rhaα}-OH and C2^{Rhaβ}-OH), 2.02 (s, 3H, $\underline{Me}$ of Tol), 1.98

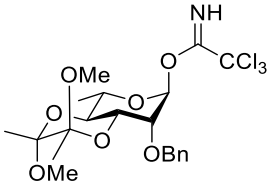
(s, 3H, Me of Tol), 1.33 (d, 3H, *J* = 6.1 Hz, C6$^{Rha\alpha}$-H), 1.32 (d, 3H, *J* = 6.7 Hz, C6$^{Rha\beta}$-H), 1.31 (s, 3H, CH_3), 1.30 (s, 3H, CH_3); ^{13}C NMR (C_6D_6, 100 MHz): δ 137.0, 136.6, 132.6, 132.1, 131.3, 130.9, 129.7, 129.5, 127.9, 127.8, 127.7, 127.6, 127.5, 100.3, 100.2, 99.8, 99.7, 88.4 (C1$^{Rha\alpha}$), 87.6 (C1$^{Rha\beta}$), 74.4, 71.5, 71.4, 71.3, 69.1, 68.8, 68.0, 67.8, 47.4, 47.3, 47.1, 47.0, 20.6, 17.7, 17.6, 17.6, 16.9, 16.5; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{19}H_{28}O_6SNa$, 407.1504; found, 407.1511.

Tolyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-benzyl-1-thio-α/β-L-rhamnopyranoside (S12α,β):



To a magnetically stirred solution of **S11α,β** (516.2 mg, 1.34 mmol) in anhydrous DMF (6.7 mL) was added sodium hydride (60% dispersion in oil, 107 mg, 2.69 mmol, 2.0 equiv.) in small portions at 0 °C. After 5 min, benzyl bromide (239 μL, 2.01 mmol, 1.5 equiv.) was added dropwise for 1 min and stirred at room temperature. Complete consumption of starting materials was observed after 3 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 20 mL), washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S12α,β** (510.3 mg, 80% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.50; $[\alpha]_D^{21}$ = –188.8 (*c* = 1.0, $CHCl_3$); (**α**) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42–7.07 (m, 9H, ArH), 5.37 (d, 1H, *J* = 1.4 Hz, C1^{Rha}-H), 4.87 (d, 1H, *J* = 12.1 Hz, OCH$_2$Ph), 4.68 (d, 1H, *J* = 12.1 Hz, OCH$_2$Ph), 4.25–4.21 (m, 1H, C5^{Rha}-H), 4.00 (dd, 1H, *J* = 2.9, 10.2 Hz, C3^{Rha}-H), 3.93 (dd, 1H, *J* = 1.4, 2.9 Hz, C2^{Rha}-H), 3.90 (t, 1H, *J* = 9.7 Hz, C4^{Rha}-H), 3.30 (s, 3H, OMe), 3.28 (s, 3H, OMe), 2.31 (s, 3H, Me of Tol), 1.35 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.28 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5, 137.4, 131.8, 131.0, 129.8, 128.2, 128.0, 127.5, 99.9, 99.6, 87.6 (C1^{Rha}), 77.7, 77.4, 77.1, 76.8, 72.9, 69.4, 69.0, 68.1, 48.0, 47.7, 21.1, 21.1, 17.9, 17.8, 16.6; $[\alpha]_D^{21}$ = –77.7 (*c* = 1.0, $CHCl_3$); (**β**) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55–7.08 (m, 9H, ArH), 5.03 (d, 1H, *J* = 11.4 Hz, OCH$_2$Ph), 4.79 (d, 1H, *J* = 11.3 Hz, OCH$_2$Ph), 4.75 (d, 1H, *J* = 1.3 Hz, C1^{Rha}-H), 3.97 (dd, 1H, *J* = 1.4, 2.8 Hz, C2^{Rha}-H), 3.94 (t, 1H, *J* = 9.9 Hz, C4^{Rha}-H), 3.73 (dd, 1H, *J* = 2.4, 9.8 Hz, C3^{Rha}-H), 3.48–3.42 (m, 1H, C5^{Rha}-H), 3.27 (s, 3H, OMe), 3.25 (s, 3H, OMe), 2.32 (s, 3H, Me of Tol), 1.34 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H), 1.33 (s, 3H, CH_3), 1.30 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ138.5, 137.32, 131.74, 129.60, 128.84, 128.01, 127.50, 99.77, 99.55, 88.36 (C1^{Rha}), 77.57, 77.35, 77.03, 76.72, 74.92, 74.60, 72.94, 68.4, 48.0, 47.7, 21.1, 17.8, 17.8, 16.9; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{26}H_{34}O_6SNa$, 497.1974; found, 497.1971.

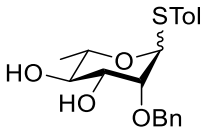
3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-benzyl-α-L-rhamnopyranosyltrichloroacetimidate (2g):



To a magnetically stirred solution of **S12α,β** (131 mg, 0.28 mmol) in acetone–H_2O (20:1, 5.2 mL) was added NBS (147 mg, 0.83 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (30 mL), washed with saturated aq. $Na_2S_2O_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 5:1) afforded the mixture of isomers **S13** (91 mg, 89% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.30. To a magnetically stirred solution of **S13** (129 mg, 0.35 mmol) and CCl_3CN (282 μL, 2.80 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (7.0 mL), DBU (21 μL, 0.14 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (preconditioned with Et_3N; eluent: hexane–EtOAc, 50:1) to afford compound **2g** (167 mg, 93% yield) as a coloreless oil. TLC (hexane–EtOAc, 5:1): R_f = 0.80; $[\alpha]_D^{21}$ = –77.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.23 (s, 1H, NH), 7.26–6.42 (m, 5H, ArH), 6.41 (d, 1H, *J* = 1.2 Hz, C1^{Rha}-H), 4.69 (d, 1H, *J* = 11.9 Hz, OCH$_2$Ph), 4.40 (d, 1H, *J* = 11.8 Hz, OCH$_2$Ph), 4.16 (dd, 1H, *J* = 2.9, 9.9 Hz, C3^{Rha}-H), 4.10–4.04 (m, 1H, C5^{Rha}-H), 4.02 (t, 1H, *J* = 9.8 Hz, C4^{Rha}-H), 3.80 (dd, 1H, *J* = 1.8, 3.0 Hz, C2^{Rha}-H), 2.89 (s, 3H, OMe), 2.84 (s, 3H, OMe), 1.18 (d, 3H, *J* = 5.9 Hz, C6^{Rha}-H), 1.17 (s, 3H, CH_3), 1.10 (s, 3H, CH_3); ^{13}C NMR (C_6D_6, 100 MHz): δ 160.1, 138.7, 128.2,

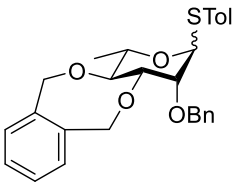
128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 99.8, 99.6, 97.5 ($C1^{Rha}$), 75.1, 73.4, 70.5, 68.9, 68.4, 47.2, 47.1, 46.4, 17.7, 17.6, 16.7, 12.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{28}Cl_3NO_7Na$, 534.0829; found, 534.0836.

Tolyl 2-*O*-benzyl-1-thio-α/β-L-rhamnopyranoside (S14α,β):



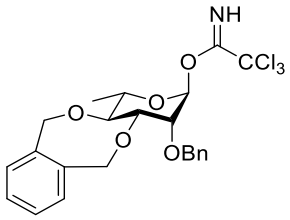
To a magnetically stirred solution of **S12α,β** (510.3 mg, 1.08 mmol) in CH_2Cl_2 (2.5 mL) were added trifluoroacetic acid / water (550 µL, 10:1, v/v) at room temperature and reaction mixture was stirred for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 3:1) afforded the title compound **S14α,β** (308.9 mg, 80% yield) as a coloreless oil. TLC (hexane–EtOAc, 1:1): R_f = 0.50; $[\alpha]_D^{21}$ = –160.0 (*c* = 1.0, $CHCl_3$); (**α**) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33–7.09 (m, 9H, ArH), 5.48 (d, 1H, *J* = 1.3 Hz, $C1^{Rha}$-H), 4.69 (d, 1H, *J* = 11.7 Hz, O$\underline{CH_2}$Ph), 4.48 (d, 1H, *J* = 11.7 Hz, O$\underline{CH_2}$Ph), 4.13–4.08 (m, 1H, $C5^{Rha}$-H), 3.97 (dd, 1H, *J* = 1.4, 3.7 Hz, $C2^{Rha}$-H), 3.78–3.75 (m, 1H, $C3^{Rha}$-H), 3.51 (t, 1H, *J* = 9.4 Hz, $C4^{Rha}$-H), 3.17 (s, 1H, OH), 2.85 (d, 1H, *J* = 9.2 Hz, OH), 2.32 (s, 3H, $\underline{Me}$ of Tol), 1.31 (d, 3H, *J* = 6.2 Hz, $C6^{Rha}$-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 137.4, 132.2, 130.5, 129.9, 128.6, 128.1, 128.0, 85.5 ($C1^{Rha}$), 79.6, 74.1, 72.3, 72.0, 69.2, 68.5, 21.2, 21.1, 17.6, 14.2; $[\alpha]_D^{21}$ = +125.2 (*c* = 1.0, $CHCl_3$); (**β**) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45–7.11 (m, 9H, ArH), 5.06 (d, 1H, *J* = 11.5 Hz, O$\underline{CH_2}$Ph), 4.74 (d, 1H, *J* = 1.2 Hz, $C1^{Rha}$-H), 4.70 (d, 1H, *J* = 11.5 Hz, O$\underline{CH_2}$Ph), 4.03 (dd, 1H, *J* = 1.4, 3.2 Hz, $C2^{Rha}$-H), 3.47–3.43 (m, 2H, $C4^{Rha}$-H and $C3^{Rha}$-H), 3.27–3.22 (m, 1H, $C5^{Rha}$-H), 2.34 (s, 3H, $\underline{Me}$ of Tol), 1.36 (d, 3H, *J* = 6.1 Hz, $C6^{Rha}$-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 137.7, 131.6, 131.2, 129.8, 128.7, 128.3, 128.2, 88.1 ($C1^{Rha}$), 80.8, 76.5, 76.3, 75.3, 73.6, 21.1, 17.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{24}O_4SNa$, 383.1293; found, 383.1299.

Tolyl 3,4-*O*-(o-xylylene)-2-*O*-benzyl-1-thio-α/β-L-rhamnopyranoside (S15α,β):



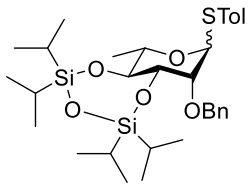
To a magnetically stirred solution of **S14α,β** (200 mg, 0.55 mmol) in anhydrous DMF (11 mL) was added sodium hydride (60% dispersion in oil, 110 mg, 12.1 mmol, 5.0 equiv.) in small portions at 0 °C. After 30 min, 1,2-bis(bromomethyl)benzene (146 mg, 0.55 mmol, 1.0 equiv.) was added and stirred at room temperature. Complete consumption of starting materials was observed after 2 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 30 mL), washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 50:1) afforded the title compound **S15α,β** (89 mg, 35% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.60; α:β = 0.8:0.2; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81–7.04 (m, 13H, ArH), 5.45 (d, 0.8H, *J* = 1.6 Hz, $C1^{Rha\alpha}$-H), 5.20 (s, 0.2H, O$\underline{CH_2}$Ph), 5.13 (d, 0.8H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 5.09 (d, 0.4H, *J* = 11.6 Hz, O$\underline{CH_2}$Ph), 4.92 (d, 0.2H, *J* = 11.5 Hz, O$\underline{CH_2}$Ph), 4.84 (d, 0.2H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.83 (d, 0.8H, *J* = 11.6 Hz, O$\underline{CH_2}$Ph), 4.80 (d, 0.2H, *J* = 12.8 Hz, O$\underline{CH_2}$Ph), 4.75 (s, 1.6H, O$\underline{CH_2}$Ph), 4.73 (d, 0.8H, *J* = 12.5 Hz, O$\underline{CH_2}$Ph), 4.68 (s, 0.2H, $C1^{Rha\beta}$-H), 4.64 (d, 0.8H, *J* = 12.4 Hz, O$\underline{CH_2}$Ph), 4.24–4.19 (m, 0.8H, $C5^{Rha\alpha}$-H), 4.16 (d, 0.2H, *J* = 3.5 Hz, $C2^{Rha\beta}$-H), 4.04–4.03 (m, 0.8H, $C2^{Rha\alpha}$-H), 3.95 (dd, 0.8H, *J* = 3.1, 9.3 Hz, $C3^{Rha\alpha}$-H), 3.79 (t, 0.2H, *J* = 8.8 Hz, $C4^{Rha\beta}$-H), 3.77 (t, 0.8H, *J* = 9.2 Hz, $C4^{Rha\alpha}$-H), 3.62 (dd, 0.2H, *J* = 2.9, 9.44 Hz, $C3^{Rha\beta}$-H), 3.40–3.34 (m, 0.2H, $C5^{Rha\beta}$-H), 2.29 (s, 3H, $\underline{Me}$ of Tol), 1.41 (d, 0.6H, *J* = 6.1 Hz, $C6^{Rha\beta}$-H), 1.38 (d, 2.4H, *J* = 6.2 Hz, $C6^{Rha\alpha}$-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5, 138.0, 137.6, 137.4, 136.2, 136.0, 135.9, 135.7, 133.4, 133.4, 133.4, 133.1, 132.1, 131.5, 130.9, 129.9, 129.7, 128.5, 128.5, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 126.9, 126.6, 126.6, 126.4, 126.3, 126.2, 126.2, 126.1, 126.1, 126.1, 126.0, 125.9, 125.7, 88.1 ($C1^{Rha\beta}$), 86.2 ($C1^{Rha\alpha}$), 84.2, 80.7, 80.2, 77.9, 77.5, 77.2, 76.8, 76.6, 76.4, 75.7, 75.6, 75.3, 72.6, 72.2, 72.2, 69.5, 21.2, 18.4, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{30}O_4SNa$, 485.1762; found, 485.1773.

3,4-*O*-(o-xylylene)-2-*O*-benzyl-α-L-rhamnopyranosyltrichloroacetimidate (2e):



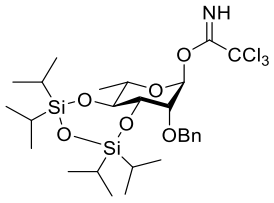
To a magnetically stirred solution of **S15α,β** (89 mg, 0.19 mmol) in acetone–H_2O (20:1, 3.5 mL) was added NBS (102 mg, 0.58 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (30 mL), washed with saturated aq. $Na_2S_2O_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 2:1) afforded the mixture of isomers **S16** (65 mg, 95% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.30. To a magnetically stirred solution of **S16** (65 mg, 0.18 mmol) and CCl_3CN (148 μL, 1.46 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (3.7 mL), DBU (11 μL, 0.07 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (preconditioned with Et_3N; eluent: hexane–EtOAc, 50:1) to afford compound **2e** (81 mg, 88% yield) as a coloreless oil. TLC (hexane–EtOAc, 4:1): R_f = 0.85; $[\alpha]_D^{21}$ = +24.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.40 (s, 1H, NH), 7.74–7.10 (m, 9H, ArH), 6.65 (d, 1H, *J* = 1.9 Hz, C1^{Rha}-H), 5.13 (d, 1H, *J* = 11.4 Hz, OC$\underline{H_2}$Ph), 4.71 (d, 1H, *J* = 11.5 Hz, OC$\underline{H_2}$Ph), 4.66 (s, 2H, OC$\underline{H_2}$Ph), 4.64 (s, 2H, OC$\underline{H_2}$Ph), 4.27–4.23 (m, 1H, C5^{Rha}-H), 4.17 (dd, 1H, *J* = 3.2, 9.5 Hz, C3^{Rha}-H), 4.03 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 4.00 (dd, 1H, *J* = 2.0, 3.0 Hz, C2^{Rha}-H), 1.41 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 160.3, 138.4, 136.5, 135.9, 133.6, 133.5, 133.2, 133.1, 128.3, 127.9, 127.7, 127.5, 126.8, 126.4, 126.0, 126.0, 125.9, 125.8, 125.7, 96.4 (C1^{Rha}), 80.1, 79.1, 75.4, 74.5, 72.8, 72.2, 71.5, 46.4, 18.1, 11.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{24}Cl_3NO_5Na$, 522.0618; found, 522.0624.

Tolyl 3,4-*O*-[1,1,3,3-tetrakis(1-methylethyl)-1,3-disiloxanediyl]-2-*O*-benzyl-1-thio-α/β-L-rhamnopyranoside (S17α,β):



To a magnetically stirred solution of **S14α,β** (116 mg, 0.32 mmol) in anhydrous DMF (3.2 mL) was added 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (308 μL, 0.96 mmol, 3 equiv.) and imidazole (131 mg, 1.92 mmol, 6 equiv.) in small portions. Starting materials were consumed at 50 °C after 30 min. The reaction mixture was quenched by saturated aqueous $NaHCO_3$ (10 mL) at 0 °C. The reaction mixture was extracted with EtOAc (2 × 20 mL), washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the mixture of isomers **S17α,β** (170 mg, 88% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.85; α:β = 0.8:0.2; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49–7.07 (m, 9H, ArH), 5.37 (d, 0.8H, *J* = 1.4 Hz, C1^{Rhaα}-H), 5.09 (d, 0.2H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.84 (d, 0.8H, *J* = 12.3 Hz, OC$\underline{H_2}$Ph), 4.82 (d, 0.2H, *J* = 11.3 Hz, OC$\underline{H_2}$Ph), 4.72 (d, 0.2H, *J* = 1.2 Hz, C1^{Rhaβ}-H), 4.71 (d, 0.8H, *J* = 12.3 Hz, OC$\underline{H_2}$Ph), 4.12–4.04 (m, 0.8H, C5^{Rhaα}-H), 4.03 (d, 0.2H, *J* = 2.7 Hz, C2^{Rhaβ}-H), 4.00 (dd, 0.8H, *J* = 3.2, 8.9 Hz, C3^{Rhaα}-H), 3.93 (dd, 0.8H, *J* = 1.6, 3.2 Hz, C2^{Rhaα}-H), 3.86 (t, 0.2H, *J* = 8.9 Hz, C4^{Rhaβ}-H), 3.85 (t, 0.8H, *J* = 9.0 Hz, C4^{Rhaα}-H), 3.75 (dd, 0.2H, *J* = 3.1, 8.9 Hz, C3^{Rhaβ}-H), 3.31–3.24 (m, 0.2H, C5^{Rhaβ}-H), 2.31 (s, 3H, $\underline{Me}$ of Tol), 1.39 (d, 0.6H, *J* = 6.2 Hz, C6^{Rhaβ}-H), 1.34 (d, 2.4H, *J* = 6.2 Hz, C6^{Rhaα}-H), 1.12–0.99 (m, 24H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.6, 138.5, 137.4, 137.1, 132.2, 131.8, 131.3, 131.0, 129.8, 129.6, 128.5, 128.3, 128.1, 127.7, 127.5, 127.5, 88.2 (C1^{Rhaβ}), 87.5 (C1^{Rhaα}), 80.6, 80.0, 79.3, 77.4, 77.1, 77.0, 76.8, 75.9, 75.8, 75.4, 75.3, 73.6, 70.2, 21.1, 18.1, 17.7, 17.7, 17.7, 17.5, 17.4, 17.4, 17.4, 17.4, 17.3, 17.3, 17.3, 12.9, 12.9, 12.8, 12.7, 12.4, 12.3, 12.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{32}H_{50}O_5SSi_2Na$, 625.2815; found, 625.2820.

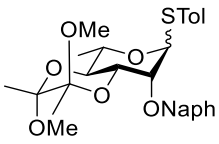
3,4-*O*-[1,1,3,3-tetrakis(1-methylethyl)-1,3-disiloxanediyl]-2-*O*-benzyl-α-L-rhamnopyranosyltrichloroacetimidate (2f):



To a magnetically stirred solution of **S17α,β** (169 mg, 0.28 mmol) in acetone–H_2O (20:1, 5.2 mL) was added NBS (149 mg, 0.84 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (30 mL), washed with saturated aq. $Na_2S_2O_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and

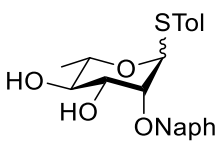
concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 10:1) afforded the mixture of isomers **S18** (106 mg, 78% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.30. To a magnetically stirred solution of **S18** (106 mg, 0.30 mmol) and CCl_3CN (241 μL, 2.39 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (6.0 mL), DBU (18 μL, 0.12 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (preconditioned with Et_3N; eluent: hexane–EtOAc, 50:1) to afford compound **2f** (109 mg, 57% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.80; $[\alpha]_D^{21}$ = –56.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.22 (s, 1H, NH), 7.18–6.84 (m, 5H, ArH), 6.41 (d, 1H, *J* = 1.8 Hz, C1^{Rha}-H), 4.60 (d, 1H, *J* = 12.0 Hz, O$\underline{CH_2}$Ph), 4.40 (d, 1H, *J* = 12.0 Hz, O$\underline{CH_2}$Ph), 4.17 (dd, 1H, *J* = 3.2, 8.6 Hz, C3^{Rha}-H), 3.96 (t, 1H, *J* = 9.0 Hz, C4^{Rha}-H), 3.95–3.92 (m, 1H, C5^{Rha}-H), 3.78 (dd, 1H, *J* = 1.9, 3.3 Hz, C2^{Rha}-H), 1.23 (d, 3H, *J* = 5.8 Hz, C6^{Rha}-H), 1.00–0.81 (m, 24H, CH_3); ^{13}C NMR (C_6D_6, 100 MHz): δ 160.1, 138.5, 128.2, 128.1, 127.9, 127.8, 127.9, 127.6, 127.5, 127.4, 97.0 (C1^{Rha}), 77.4, 75.5, 74.8, 73.9, 72.2, 17.9, 17.5, 17.3, 17.3, 17.3, 17.3, 17.2, 17.1, 12.9, 12.9, 12.5, 12.4; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{44}Cl_3NO_6Si_2Na$, 662.1670; found, 662.1665.

Tolyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-(2-naphthylmethyl)-1-thio-α/β-L-rhamnopyranoside (S19α,β):



To a magnetically stirred solution of **S11α,β** (200 mg, 0.5 mmol) in anhydrous DMF (2.5 mL) was added sodium hydride (60% dispersion in oil, 40 mg, 1.0 mmol, 2.0 equiv.) in small portions at 0 °C. After 15 min, 2-(bromomethyl)naphthalene (166 mg, 0.75 mmol, 1.5 equiv.) was added and stirred at room temperature. Complete consumption of starting materials was observed after 3 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 20 mL), washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S19α,β** (248.8 mg, 97% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.45; $[\alpha]_D^{21}$ = –178.4 (*c* = 1.0, $CHCl_3$); (**α**) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87–7.01 (m, 11H, ArH), 5.38 (t, 1H, *J* = 1.6 Hz, C1^{Rha}-H), 5.00 (d, 1H, *J* = 12.2 Hz, O$\underline{CH_2}$Ph), 4.85 (d, 1H, *J* = 12.5 Hz, O$\underline{CH_2}$Ph), 4.25–4.21 (m, 1H, C5^{Rha}-H), 4.00 (dd, 1H, *J* = 2.8, 10.2 Hz, C3^{Rha}-H), 3.98 (dd, 1H, *J* = 1.4, 2.9 Hz, C2^{Rha}-H), 3.94 (t, 1H, *J* = 9.6 Hz, C4^{Rha}-H), 3.30 (s, 6H, OMe), 2.29 (s, 3H, $\underline{Me}$ of Tol), 1.40 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.29 (d, 3H, *J* = 6.3 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.4, 136.0, 133.3, 133.0, 131.8, 130.9, 129.8, 128.0, 127.9, 127.7, 126.7, 126.1, 126.0, 125.8, 100.0, 99.7, 87.7 (C1^{Rha}), 77.8, 77.4, 77.3, 77.1, 76.7, 73.0, 69.3, 69.1, 68.2, 48.0, 47.8, 21.1, 17.9, 17.9, 16.6; $[\alpha]_D^{21}$ = –12.6 (*c* = 1.0, $CHCl_3$); (**β**) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96–7.08 (m, 11H, ArH), 5.16 (d, 1H, *J* = 11.4 Hz, O$\underline{CH_2}$Ph), 4.99 (d, 1H, *J* = 11.6 Hz, O$\underline{CH_2}$Ph), 4.77 (d, 1H, *J* = 1.3 Hz, C1^{Rha}-H), 4.03 (dd, 1H, *J* = 1.3, 2.8 Hz, C2^{Rha}-H), 3.99 (t, 1H, *J* = 9.8 Hz, C4^{Rha}-H), 3.75 (dd, 1H, *J* = 2.8, 10.16 Hz, C3^{Rha}-H), 3.49–3.42 (m, 1H, C5^{Rha}-H), 3.30 (s, 3H, OMe), 3.26 (s, 3H, OMe), 2.32 (s, 3H, $\underline{Me}$ of Tol), 1.37 (s, 3H, CH_3), 1.34 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H), 1.32 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.4, 136.0, 133.3, 133.1, 131.8, 131.7, 129.6, 128.0, 127.7, 127.4, 127.0, 125.7, 125.6, 99.8, 99.6, 88.4 (C1^{Rha}), 77.7, 77.4, 77.2, 77.0, 76.7, 74.9, 74.8, 72.9, 68.4, 48.0, 47.7, 29.7, 21.1, 17.9, 17.8, 16.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{36}O_6SNa$, 547.2130; found, 547.2138.

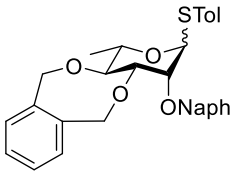
Tolyl 2-*O*-(2-naphthylmethyl)-1-thio-α/β-L-rhamnopyranoside (S20α,β):



To a magnetically stirred solution of **S19α,β** (248.8 mg, 0.49 mmol) in CH_2Cl_2 (1.2 mL) were added trifluoroacetic acid / water (247 μL, 10:1, v/v) at room temperature and reaction mixture was stirred for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 3:1) afforded the title compound **S20α,β** (175.5 mg, 91% yield) as a white powder. TLC (hexane–EtOAc, 2:1): R_f = 0.40; (**α**) $[\alpha]_D^{21}$ = –47.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.82–7.05 (m, 11H, ArH),

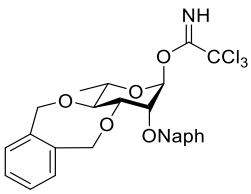
5.48 (d, 1H, *J* = 1.2 Hz, C1^{Rha}-H), 4.84 (d, 1H, *J* = 11.7 Hz, OCH$_2$Ph), 4.63 (d, 1H, *J* = 11.7 Hz, OCH$_2$Ph), 4.15–4.08 (m, 1H, C5^{Rha}-H), 4.02 (dd, 1H, *J* = 1.3, 3.6 Hz, C2^{Rha}-H), 3.76 (dd, 1H, *J* = 3.6, 9.6 Hz, C3^{Rha}-H), 3.53 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 2.72 (s, 1H, OH), 2.58 (s, 1H, OH), 2.31 (s, 3H, Me of Tol), 1.32 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 134.6, 133.2, 133.2, 132.3, 130.4, 129.9, 128.6, 128.0, 127.8, 127.1, 126.4, 126.2, 125.8, 85.6 (C1^{Rha}), 79.6, 77.4, 77.1, 76.8, 74.3, 72.5, 72.0, 69.1, 21.2, 17.5, 0.0; (**β**) $[\alpha]_D^{21}$ = +71.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88–7.13 (m, 11H, ArH), 5.25 (d, 1H, *J* = 11.6 Hz, OCH$_2$Ph), 4.86 (d, 1H, *J* = 11.7 Hz, OCH$_2$Ph), 4.79 (d, 1H, *J* = 1.1 Hz, C1^{Rha}-H), 4.11 (dd, 1H, *J* = 1.1, 3.4 Hz, C2^{Rha}-H), 3.49 (t, 1H, *J* = 9.2 Hz, C4^{Rha}-H), 3.47–3.43 (m, 1H, C3^{Rha}-H), 3.29–3.26 (m, 1H, C5^{Rha}-H), 2.34 (s, 3H, Me of Tol), 2.29 (s, 1H, OH), 2.12 (s, 1H, OH), 1.38 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 135.2, 133.3, 133.2, 131.7, 131.2, 129.8, 128.6, 128.1, 127.8, 127.3, 126.3, 126.2, 126.1, 88.1 (C1^{Rha}), 80.7, 77.4, 77.0, 76.7, 76.6, 76.3, 75.3, 73.7, 31.5, 30.2, 21.1, 17.8; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{24}H_{26}O_4SNa$, 433.1449; found, 433.1441.

Tolyl 3,4-*O*-(o-xylylene)-2-*O*-(2-naphthylmethyl)-1-thio-α/β-L-rhamnopyranoside (S21α,β):



To a magnetically stirred solution of **S20α,β** (175.5 mg, 0.44 mmol) in anhydrous DMF (8.8 mL) was added sodium hydride (60% dispersion in oil, 89 mg, 2.20 mmol, 5.0 equiv.) in small portions at 0 °C. After 30 min, 1,2-bis(bromomethyl)benzene (232 mg, 0.88 mmol, 2.0 equiv.) was added and stirred at room temperature. Complete consumption of starting materials was observed after 2 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 30 mL), washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S21α,β** (122 mg, 56% yield) as a coloreless oil. TLC (hexane–EtOAc, 4:1): R_f = 0.30; α:β = 0.8:0.2 ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81–6.97 (m, 15H, ArH), 5.44 (d, 0.8H, *J* = 1.6 Hz, C1^{Rhaα}-H), 5.21 (d, 0.2H, *J* = 11.7 Hz, OCH$_2$Ph), 5.16 (d, 0.8H, *J* = 11.2 Hz, OCH$_2$Ph), 5.11 (d, 0.2H, *J* = 11.1 Hz, OCH$_2$Ph), 5.10 (d, 0.2H, *J* = 11.7 Hz, OCH$_2$Ph), 4.88 (d, 0.8H, *J* = 12.6 Hz, OCH$_2$Ph), 4.87 (d, 0.2H, *J* = 11.4 Hz, OCH$_2$Ph), 4.86 (d, 0.8H, *J* = 11.4 Hz, OCH$_2$Ph), 4.83 (d, 0.8H, *J* = 10.0 Hz, OCH$_2$Ph), 4.79 (d, 0.2H, *J* = 12.5 Hz, OCH$_2$Ph), 4.77 (d, 0.8H, *J* = 11.8 Hz, OCH$_2$Ph), 4.76 (d, 0.8H, *J* = 11.6 Hz, OCH$_2$Ph), 4.73 (d, 0.2H, *J* = 12.0 Hz, OCH$_2$Ph), 4.69 (d, 0.2H, *J* = 1.1 Hz, C1^{Rhaβ}-H), 4.24–4.17 (m, 1H, C5^{Rhaα}-H and C2^{Rhaβ}-H), 4.06 (dd, 0.8H, *J* = 1.7, 3.1 Hz, C2^{Rhaα}-H), 3.97 (dd, 0.8H, *J* = 3.1, 9.3 Hz, C3^{Rhaα}-H), 3.84 (t, 0.2H, *J* = 9.3 Hz, C4^{Rhaβ}-H), 3.81 (t, 0.8H, *J* = 9.3 Hz, C4^{Rhaα}-H), 3.63 (dd, 0.2H, *J* = 2.9, 12.6 Hz, C3^{Rhaβ}-H), 3.40–3.37 (m, 0.2H, C5^{Rhaβ}-H), 2.29 (s, 0.6H, Me of Tol), 2.27 (s, 2.4H, Me of Tol), 1.42 (d, 0.6H, *J* = 6.1 Hz, C6^{Rhaβ}-H), 1.40 (d, 2.4H, *J* = 6.2 Hz, C6^{Rhaα}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.6, 136.2, 135.93, 135.85, 135.4, 133.42, 133.38, 133.34, 133.27, 133.19, 133.15, 133.1, 133.0, 132.1, 131.6, 130.8, 129.9, 129.7, 128.3, 128.24, 128.20, 128.18, 128.09, 128.07, 128.04, 128.01, 127.78, 127.75, 127.1, 127.0, 126.9, 126.7, 126.61, 126.58, 126.4, 126.18, 126.16, 126.10, 126.08, 126.05, 125.9, 125.8, 125.7, 88.1 (C1^{Rhaβ}), 86.4 (C1^{Rhaα}), 84.3, 80.8, 80.2, 77.8, 77.5, 77.4, 77.2, 76.8, 76.5, 76.4, 75.7, 75.6, 75.3, 72.7, 72.4, 72.3, 69.6, 60.5, 34.6, 31.6, 31.5, 30.3, 30.2, 29.8, 21.2, 21.1, 18.4, 18.1, 14.3; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{32}H_{32}O_4SNa$, 535.1919; found, 535.1924.

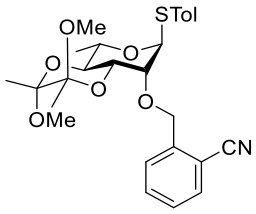
3,4-*O*-(o-xylylene)-2-*O*-(2-naphthylmethyl)-α-L-rhamnopyranosyltrichloroacetimidate (2h):



To a magnetically stirred solution of **S21α,β** (104 mg, 0.20 mmol) in acetone–H_2O (20:1, 3.7 mL) was added NBS (108 mg, 0.61 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (30 mL), washed with saturated aq. $Na_2S_2O_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 5:1) afforded the mixture of isomers **S22** (69 mg, 83% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.25. To a magnetically stirred solution of **S22** (112 mg, 0.28 mmol) and CCl_3CN (223 μL, 2.20 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (5.5 mL), DBU (16 μL, 0.11 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was

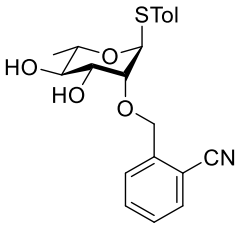
stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (preconditioned with Et_3N; eluent: hexane–EtOAc, 50:1) to afford compound **2h** (145 mg, 96% yield) as a coloreless oil. TLC (hexane–EtOAc, 5:1): R_f = 0.55; $[\alpha]_D^{21}$ = +5.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.40 (s, 1H, NH), 7.80–7.15 (m, 11H, ArH), 6.72 (d, 1H, *J* = 1.9 Hz, C1^{Rha}-H), 5.17 (d, 1H, *J* = 11.4 Hz, OCH$_2$Ph), 4.82 (d, 1H, *J* = 12.3 Hz, OCH$_2$Ph), 4.77 (d, 1H, *J* = 12.4 Hz, OCH$_2$Ph), 4.75 (d, 1H, *J* = 11.5 Hz, OCH$_2$Ph), 4.66 (d, 1H, *J* = 11.9 Hz, OCH$_2$Ph), 4.63 (d, 1H, *J* = 12.0 Hz, OCH$_2$Ph), 4.30–4.25 (m, 1H, C5^{Rha}-H), 4.20 (dd, 1H, *J* = 3.1, 9.5 Hz, C3^{Rha}-H), 4.10 (t, 1H, *J* = 9.7 Hz, C4^{Rha}-H), 4.08 (dd, 1H, *J* = 2.8, 3.8 Hz, C2^{Rha}-H), 1.44 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 160.4, 136.4, 135.9, 135.8, 133.6, 133.52, 133.45, 133.3, 133.19, 133.16, 127.9, 127.7, 127.5, 126.8, 126.5, 126.1, 126.01, 125.99, 125.96, 125.9, 125.8, 125.7, 96.4 (C1^{Rha}), 91.2, 80.2, 79.2, 75.39, 74.36, 72. 8, 72.2, 71.6, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{26}Cl_3NO_5Na$, 572.0774; found, 572.0784.

Tolyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-(2-cyanobenzyl)-1-thio-α-L-rhamnopyranoside (S23):



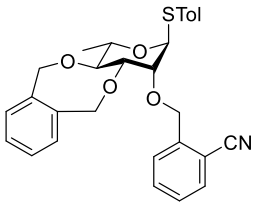
To a magnetically stirred solution of **S11*α*,*β*** (200 mg, 0.5 mmol) in anhydrous DMF (2.5 mL) was added sodium hydride (60% dispersion in oil, 40 mg, 1.0 mmol, 2.0 equiv.) in small portions at 0 °C. After 15 min, 2-cyanobenzyl bromide (148 mg, 0.75 mmol, 1.5 equiv.) was added and stirred at room temperature. Complete consumption of starting materials was observed after 3 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 20 mL), washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S23** (232.8 mg, 96% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.50; $[\alpha]_D^{21}$ = –20.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82–7.10 (m, 8H, ArH), 5.45 (d, 1H, *J* = 1.3 Hz, C1^{Rha}-H), 5.04 (d, 1H, *J* = 13.1 Hz, OCH$_2$Ph), 4.93 (d, 1H, *J* = 13.2 Hz, OCH$_2$Ph), 4.31–4.24 (m, 1H, C5^{Rha}-H), 4.05 (dd, 1H, *J* = 2.8, 10.1 Hz, C3^{Rha}-H), 4.01 (dd, 1H, *J* = 1.4, 2.8 Hz, C2^{Rha}-H), 3.90 (t, 1H, *J* = 9.8 Hz, C4^{Rha}-H), 3.31 (s, 3H, OMe), 3.27 (s, 3H, OMe), 2.32 (s, 3H, Me of Tol), 1.32 (s, 6H, CH_3), 1.29 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.6, 137.7, 132.8, 132.4, 132.1, 130.6, 129.9, 129.0, 127.8, 117.4, 110.9, 99.9, 99.7, 87.6 (C1^{Rha}), 79.2, 77.4, 77.1, 76.7, 70.8, 69.4, 69.0, 68.1, 48.1, 47.7, 31.5, 21.1, 17.8, 17.7, 16.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{33}NO_6SNa$, 522.1926; found, 522.1933.

Tolyl 2-*O*-(2-cyanobenzyl)-1-thio-α-L-rhamnopyranoside (S24):



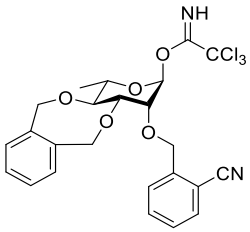
To a magnetically stirred solution of **S23** (232.8 mg, 0.48 mmol) in CH_2Cl_2 (1.1 mL) were added trifluoroacetic acid / water (243 μL, 10:1, v/v) at room temperature and reaction mixture was stirred for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 2:1) afforded the title compound **S24** (156.3 mg, 88% yield) as a white powder. TLC (hexane–EtOAc, 2:1): R_f = 0.35; $[\alpha]_D^{21}$ = –81.4 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65–7.11 (m, 8H, ArH), 5.54 (d, 1H, *J* = 1.3 Hz, C1^{Rha}-H), 4.80 (s, 2H, OCH$_2$Ph), 4.18–4.09 (m, 1H, C5^{Rha}-H), 4.06 (dd, 1H, *J* = 1.4, 3.5 Hz, C2^{Rha}-H), 3.87–3.82 (m, 1H, C3^{Rha}-H), 3.60 (t, 1H, *J* = 9.9 Hz, C4^{Rha}-H), 3.28 (t, 1H, *J* = 3.2 Hz, OH), 3.17 (t, 1H, *J* = 9.1 Hz, OH), 2.33 (s, 3H, Me of Tol), 1.32 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.3, 141.2, 137.8, 133.1, 133.0, 132.2, 130.1, 129.9, 129.0, 128.5, 1181, 111.4, 85.3 (C1^{Rha}), 80.6, 77.4, 77.1, 76.8, 73.9, 72.4, 70.2, 69.3, 60.5, 21.1, 21.1, 17.5, 14.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{23}NO_4SNa$, 408.1245; found, 408.1253.

Tolyl 3,4-*O*-(o-xylylene)-2-*O*-(2-cyanobenzyl)-1-thio-α-L-rhamnopyranoside (S25):



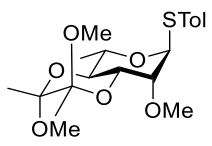
To a magnetically stirred solution of **S24** (155 mg, 0.42 mmol) in anhydrous DMF (8.3 mL) was added sodium hydride (60% dispersion in oil, 137 mg, 2.08 mmol, 5.0 equiv.) in small portions at 0 °C. After 30 min, 1,2-bis(bromomethyl)benzene (220 mg, 0.83 mmol, 2.0 equiv.) was added and stirred at room temperature. Complete consumption of starting materials was observed after 2 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 30 mL), washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S25** (144 mg, 73% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.45; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56–7.09 (m, 12H, ArH), 5.46 (d, 1H, *J* = 1.52 Hz, C1^{Rha}-H), 5.17 (d, 1H, *J* = 13.5 Hz, O$\underline{CH_2}$Ph), 5.07 (d, 1H, *J* = 14.3 Hz, O$\underline{CH_2}$Ph), 5.01 (d, 1H, *J* = 14.4 Hz, O$\underline{CH_2}$Ph), 4.92 (d, 1H, *J* = 13.5 Hz, O$\underline{CH_2}$Ph), 4.88 (d, 2H, *J* = 2.2 Hz, O$\underline{CH_2}$Ph), 4.17–4.11 (m, 1H, C5^{Rha}-H), 4.10 (dd, 1H, *J* = 1.4, 3.0 Hz, C2^{Rha}-H), 3.85 (dd, 1H, *J* = 3.0, 9.3 Hz, C3^{Rha}-H), 3.64 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 2.31 (s, 3H, $\underline{Me}$ of Tol), 1.37 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.3, 137.7, 137.0, 136.9, 132.8, 132.4, 132.0, 130.6, 130.5, 129.9, 129.1, 128.6, 128.0, 127.9, 127.8, 117.4, 110.8, 86.8 (C1^{Rha}), 80.9, 80.2, 79.5, 77.4, 77.1, 76.8, 73.5, 72.4, 70.9, 68.8, 21.1, 17.5; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{29}H_{29}NO_4SNa$, 510.1715; found, 510.1726.

3,4-*O*-(o-xylylene)-2-*O*-(2-cyanobenzyl)-α-L-rhamnopyranosyltrichloroacetimidate (2i):



To a magnetically stirred solution of **S25** (125 mg, 0.26 mmol) in acetone–H_2O (20:1, 4.8 mL) was added NBS (136 mg, 0.77 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (30 mL), washed with saturated aq. $Na_2S_2O_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 5:1) afforded the mixture of isomers **S26** (59 mg, 60% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.30. To a magnetically stirred solution of **S26** (59 mg, 0.15 mmol) and CCl_3CN (124 μL, 1.23 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (3.1 mL), DBU (9 μL, 0.06 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (preconditioned with Et_3N; eluent: hexane–EtOAc, 50:1) to afford compound **2i** (57 mg, 70% yield) as a coloreless oil. TLC (hexane–EtOAc, 5:1): R_f = 0.70; $[\alpha]_D^{21}$ = –51.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.14 (s, 1H, NH), 7.45–6.32 (m, 8H, ArH), 6.30 (d, 1H, *J* = 2.0 Hz, C1^{Rha}-H), 4.84 (d, 1H, *J* = 11.4 Hz, O$\underline{CH_2}$Ph), 4.79 (d, 1H, *J* = 12.9 Hz, O$\underline{CH_2}$Ph), 4.45 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.43 (s, 1H, O$\underline{CH_2}$Ph), 4.42 (s, 1H, O$\underline{CH_2}$Ph), 4.38 (d, 1H, *J* = 13.0 Hz, O$\underline{CH_2}$Ph), 4.01–3.93 (m, 1H, C5^{Rha}-H), 3.90 (dd, 1H, *J* = 3.0, 9.1 Hz, C3^{Rha}-H), 3.71 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.65 (t, 1H, *J* = 2.5 Hz, C2^{Rha}-H), 1.12 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 159.2, 141.1, 135.5, 134.8, 132.7, 132.7, 132.4, 132.3, 131.4, 131.3, 127.5, 127.3, 127.1, 126.9, 126.6, 126.4, 125.7, 125.5, 125.3, 125.2, 125.1, 124.9, 123.5, 116.3, 110.5, 95.6 (C1^{Rha}), 90.4, 79.2, 78.6, 75.1, 74.6, 71.9, 70.7, 70.3, 17.2; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{24}H_{23}Cl_3N_2O_5Na$, 547.0570; found, 547.0573.

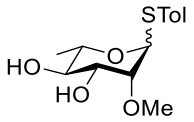
Tolyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-2-*O*-methyl-1-thio-α-L-rhamnopyranoside (S27):



To a magnetically stirred solution of **S11α,β** (240 mg, 0.62 mmol) in anhydrous DMF (3.1 mL) was added sodium hydride (60% dispersion in oil, 50 mg, 1.25 mmol, 2.0 equiv.) in small portions at 0 °C. After 15 min, iodomethane (48 μL, 0.94 mmol, 1.5 equiv.) was added and stirred at room temperature. Complete consumption of starting materials was observed after 3 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 20 mL), washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash

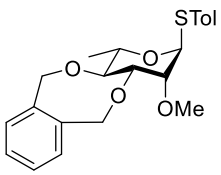
chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S27** (207.0 mg, 83% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.45; $[\alpha]_D^{21}$ = –34.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, 2H, *J* = 8.1 Hz, ArH), 7.11 (d, 2H, *J* = 8.0 Hz, ArH), 5.48 (d, 1H, *J* = 1.4 Hz, C1^{Rha}-H), 4.26–4.22 (m, 1H, C5^{Rha}-H), 3.97 (dd, 1H, *J* = 3.0, 10.0 Hz, C3^{Rha}-H), 3.77 (t, 1H, *J* = 9.8 Hz, C4^{Rha}-H), 3.72 (dd, 1H, *J* = 1.4, 3.8 Hz, C2^{Rha}-H), 3.47 (s, 3H, OMe), 3.31 (s, 3H, OMe), 3.26 (s, 3H, OMe), 2.33 (s, 3H, Me of Tol), 1.34 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.28 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.5, 131.8, 131.0, 129.8, 100.0, 99.6, 85.9 (C1^{Rha}), 80.4, 77.4, 77.1, 76.7, 68.9, 68.8, 67.9, 58.4, 48.0, 47.7, 21.1, 17.9, 17.8, 16.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{30}O_6SNa$, 421.1661; found, 421.1655.

Tolyl 2-*O*-methyl-1-thio-α/β-L-rhamnopyranoside (S28α,β):



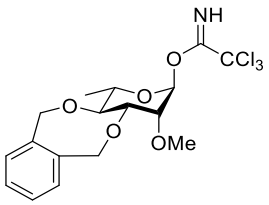
To a magnetically stirred solution of **S27** (207.0 mg, 0.52 mmol) in CH_2Cl_2 (1.2 mL) were added trifluoroacetic acid / water (265 μL, 10:1, v/v) at room temperature and reaction mixture was stirred for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried over $MgSO_4$, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 2:1) afforded the title compound **S28α,β** (156.3 mg, 88% yield) as a white powder. TLC (hexane–EtOAc, 2:1): R_f = 0.30; (**α**) $[\alpha]_D^{21}$ = –164.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (d, 2H, *J* = 8.1 Hz, ArH), 7.12 (d, 2H, *J* = 7.9 Hz, ArH), 5.53 (s, 1H, C1^{Rha}-H), 4.17–4.10 (m, 1H, C5^{Rha}-H), 3.78–3.74 (m, 2H, C3^{Rha}-H and C2^{Rha}-H), 3.47 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.44 (s, 3H, OMe), 3.12 (s, 1H, OH), 2.94 (d, 1H, *J* = 11.2 Hz, OH), 2.33 (s, 3H, Me of Tol), 1.32 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 132.0, 130.6, 129.9, 84.5 (C1^{Rha}), 81.8, 77.4, 77.1, 76.8, 74.1, 72.0, 69.0, 58.1, 21.1, 17.5; (**β**) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (d, 2H, *J* = 8.2 Hz, ArH), 7.12 (d, 2H, *J* = 7.8 Hz, ArH), 4.72 (d, 1H, *J* = 1.1 Hz, C1^{Rha}-H), 3.79 (dd, 1H, *J* = 1.2, 3.5 Hz, C2^{Rha}-H), 3.74 (s, 3H, OMe), 3.49–3.44 (m, 2H, C3^{Rha}-H and C4^{Rha}-H), 3.28–3.21 (m, 1H, C5^{Rha}-H), 2.34 (s, 3H, Me of Tol), 1.37 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 131.8, 129.7, 87.8 (C1^{Rha}), 82.5, 77.3, 77.0, 76.7, 76.1, 75.5, 73.8, 62.9, 21.1, 17.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{14}H_{20}O_4SNa$, 307.0980; found, 307.0995.

Tolyl 3,4-*O*-(o-xylylene)-2-*O*-methyl-1-thio-α-L-rhamnopyranoside (S29):



To a magnetically stirred solution of **S28α,β** (127 mg, 0.45 mmol) in anhydrous DMF (8.9 mL) was added sodium hydride (60% dispersion in oil, 89 mg, 2.23 mmol, 5.0 equiv.) in small portions at 0 °C. After 30 min, 1,2-bis(bromomethyl)benzene (235 mg, 0.89 mmol, 2.0 equiv.) was added and stirred at room temperature. Complete consumption of starting materials was observed after 2 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 30 mL), washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 100:1) afforded the title compound **S29** (133 mg, 77% yield) as a coloreless oil. TLC (hexane–EtOAc, 10:1): R_f = 0.45; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83–7.05 (m, 8H, ArH), 5.48 (d, 1H, *J* = 1.6 Hz, C1^{Rha}-H), 5.14 (d, 1H, *J* = 11.2 Hz, OCH$_2$Ph), 4.89 (s, 2H, OCH$_2$Ph), 4.83 (d, 1H, *J* = 11.1 Hz, OCH$_2$Ph), 4.23–4.19 (m, 1H, C5^{Rha}-H), 3.94 (dd, 1H, *J* = 3.1, 9.4 Hz, C3^{Rha}-H), 3.77 (dd, 1H, *J* = 1.8, 3.2 Hz, C2^{Rha}-H), 3.68 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.47 (s, 3H, OMe), 2.29 (s, 3H, Me of Tol), 1.36 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.6, 136.1, 135.7, 133.4, 133.1, 131.8, 129.9, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 126.9, 126.6, 126.2, 126.1, 126.1, 126.0, 125.9, 85.3 (C1^{Rha}), 80.7, 80.1, 79.8, 77.5, 77.2, 76.8, 75.6, 72.5, 69.2, 58.5, 21.2, 18.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{26}O_4SNa$, 409.1449; found, 409.1458.

3,4-*O*-(o-xylylene)-2-*O*-methyl-α-L-rhamnopyranosyltrichloroacetimidate (2j):



To a magnetically stirred solution of **S29** (137 mg, 0.35 mmol) in acetone–H_2O (20:1, 6.5 mL) was added NBS (189 mg, 1.06 mmol, 3 equiv.) in small portions at 0 °C. Starting materials were consumed at the same temperature after 2 h. The reaction mixture was dissolved in CH_2Cl_2 (30 mL), washed with saturated aq. $Na_2S_2O_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated in vacuo. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 5:1) afforded the mixture of isomers **S30** (70 mg, 70% yield) as a white solid. TLC (hexane–EtOAc, 4:1): R_f = 0.30. To a magnetically stirred solution of **S30** (70 mg, 0.25 mmol) and CCl_3CN (201 μL, 1.99 mmol, 8 equiv.) in anhydrous CH_2Cl_2 (5.0 mL), DBU (15 μL, 0.10 mmol, 0.4 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (preconditioned with Et_3N; eluent: hexane–EtOAc, 50:1) to afford compound **2i** (98 mg, 93% yield) as a coloreless oil. TLC (hexane–EtOAc, 5:1): R_f = 0.75; $[\alpha]_D^{21}$ = –2.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 8.12 (s, 1H, NH), 7.44–6.86 (m, 4H, ArH), 6.30 (d, 1H, *J* = 2.0 Hz, C1^{Rha}-H), 4.85 (d, 1H, *J* = 11.4 Hz, O$\underline{CH_2}$Ph), 4.44 (d, 1H, *J* = 10.5 Hz, O$\underline{CH_2}$Ph), 4.43 (s, 2H, O$\underline{CH_2}$Ph), 3.99–3.91 (m, 1H, C5^{Rha}-H), 3.87 (dd, 1H, *J* = 3.0, 9.4 Hz, C3^{Rha}-H), 3.69 (t, 1H, *J* = 9.5 Hz, C4^{Rha}-H), 3.39 (dd, 1H, *J* = 2.1, 3.1 Hz, C2^{Rha}-H), 3.04 (s, 3H, OMe), 1.11 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 160.3, 136.4, 136.0, 133.6, 133.5, 133.22, 133.16, 128.2, 127.9, 127.7, 127.5, 126.8, 126.5, 126.3, 126.10, 126.05, 126.01, 125.96, 125.9, 125.9, 125.83, 125.67, 125.5, 96.0 (C1^{Rha}), 80.0, 79.3, 76.8, 76.7, 75.4, 72.2, 71.5, 71.4, 58.8, 18.1, 18.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{20}Cl_3NO_5Na$, 446.0305; found, 446.0314.

Preparation of a ZnI_2 solution (1.0 M in Et_2O).[10] In the flame-dried, argon-flushed schlenk flask with a rubber septum, the desired mass of ZnI_2 (e.g., 310 mg, 1 mmol) was added, capped with argon balloon, and added with a desired amount of dry Et_2O (1 mL) to make a 1.0 M solution.

General Glycosylation Procedure (Method A). The glycosyl donor **2** (1.5 equiv.) and alcohol acceptor **3** (1.0 equiv.) were combined in a flask, coevaporated with toluene (3 × 3 mL), and dissolved in Et_2O to maintain a concentration of 0.01 M (based on the donor). Powdered freshly activated molecular sieves (100 mg/mL solvent) were added, and the mixture was stirred for 30 min at ambient temperature. A solution of ZnI_2 in Et_2O (0.50 equiv., 0.1 M solution in Et_2O) was added to the mixture, and stirring was continued until TLC indicated disappearance of the glycosyl donor (12–48 h). The reaction was quenched by the addition of Et_3N and diluted with EtOAc, then filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure to give a residue, following purified by flash chromatography or simple preparative thin-layer chromatography on silica gel (EtOAc–hexane or EtOAc–toluene or acetone–toluene or acetonitrile-toluene elution) to the desired products.

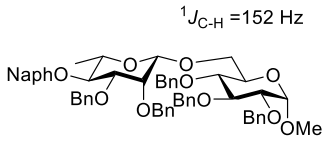
General Method B of Deprotection of TBS. To a solution of starting material (1 mmol) in anhydrous THF (5 mL/ 0.1mmol), TBAF (1M in THF, 4 equiv.) was added at the same temperature. The reaction mixture was stirred at room temperature for 3 h. The mixtue was diluted with EtOAc (5 mL), washed with saturated aqueous $NaHCO_3$ and brine, dried with Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel afforded the desired product.

General Method C of Reductive Ring-Opening Reaction of the 4,6-*O*-Acetal with $BH_3 \cdot Et_2O$.[11] To a solution of $BH_3 \cdot Et_2O$ (8 equiv.) in anhydrous DCM (8 mL/mmol) was added starting material (1 mmol) and Et_3SiH (10 equiv.) in anhydrous DCM (10 mL/mmol) at 0 °C and the reaction mixture was stirred at room temperature for 15-20 minutes. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$, extracted with ethyl acetate (3 ×), washed with brine, dried with Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel afforded the desired product.

General Method D of global deprotection. To a magnetically stirred solution of fully protected oligasaccaride (20 mg) in EtOH (2 mL) was added Pd/C (10 wt%, 20 mg), and then the mixture was stirred under H_2 at room temperature for 48 h, after which complete consumption of starting materials was observed. The reaction mixture was filtered through a short Celite® pad, washed with methanol, and evaporated in vacuo, followed by flash chromatography on silica gel (eluent: 1:2 MeOH–$CHCl_3$, 1:2) to give the desired product.

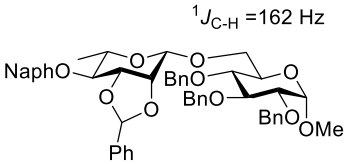
General Procedure E of NAP Group Removal. DDQ (1.5 mmol) was added slowly to a stirring solution of the NAP protected compound (1.0 mmol) in a mixture of CH_2Cl_2 (5 mL/mmol) and distilled water (5 mL/mmol) and the resulting reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with EtOAc, washed with saturated aqueous $Na_2S_2O_3$, H_2O and brine, dried with Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel afforded the desired product.

Methyl 2,3-di-*O*-benzyl-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-benzyl-α-D-glucopyranoside (4a):



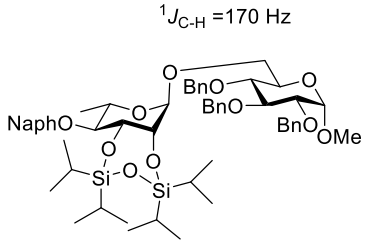
Following the general procedure of method A using trichloroacetimidate **2a** (42 mg, 0.068 mmol) and methyl 2,3,4-*tri*-*O*-benzyl-α-D-glucopyranoside **3a** (21 mg, 0.045 mmol) in Et_2O (5.0 mL) at room temperature for 12 h afforded **4a** (16.8 mg, 40% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:15; R_f = 0.30). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.75–7.14 (m, 32H, ArH), 5.02 (d, 1H, *J* = 11.0 Hz, OC$\underline{H_2}$Ph), 4.90 (d, 1H, *J* = 12.3 Hz, OC$\underline{H_2}$Ph), 4.89 (d, 1H, *J* = 10.8 Hz, OC$\underline{H_2}$Ph), 4.80 (d, 1H, *J* = 12.4 Hz, OC$\underline{H_2}$Ph), 4.79 (d, 1H, *J* = 10.8 Hz, OC$\underline{H_2}$Ph), 4.73 (d, 1H, *J* = 11.1 Hz, OC$\underline{H_2}$Ph), 4.71 (d, 1H, *J* = 10.1 Hz, OC$\underline{H_2}$Ph), 4.69 (d, 1H, *J* = 14.7 Hz, OC$\underline{H_2}$Ph), 4.68 (d, 1H, *J* = 10.7 Hz, OC$\underline{H_2}$Ph), 4.59 (d, 1H, *J* = 12.2 Hz, OC$\underline{H_2}$Ph), 4.54 (s, 1H, C1^{Glc}-H), 4.68 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.40 (d, 1H, *J* = 12.1 Hz, OC$\underline{H_2}$Ph), 4.37 (s, 1H, C1^{Rha}-H), 4.20 (d, 1H, *J* = 10.7 Hz, C6^{Glc}-H), 3.91 (t, 2H, *J* = 8.6 Hz, C3^{Glc}-H and C3^{Rha}-H), 3.67 (d, 1H, *J* = 10.0 Hz, C5^{Glc}-H), 3.60–3.55 (m, 3H, C4^{Rha}-H, C4^{Glc}-H, and C6^{Glc}-H), 3.41 (d, 2H, *J* = 9.3 Hz, C2^{Glc}-H and C2^{Rha}-H), 3.28 (s, 3H, OMe), 3.28–3.26 (m, 1H, C5^{Rha}-H), 1.29 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.9, 138.8, 138.4, 138.2, 138.2, 133.3, 133.0, 128.5, 128.4, 128.3, 128.2, 128.13, 128.07, 127.9, 127.7, 127.7, 127.62, 127.57, 127.4, 126.7, 126.1, 126.0, 125.8, 101.4 (C1^{Rha}), 98.3 (C1^{Glc}), 82.0, 81.9, 80.3, 79.9, 77.8, 77.3, 77.0, 76.8, 75.7, 75.5, 75.2, 74.3, 74.1, 73.5, 72.0, 71.3, 70.0, 67.3, 55.2, 29.7, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{59}H_{62}O_{10}Na$, 953.4241; found, 953.4253.

Methyl 2,3-*O*-benzylidene-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-benzyl-α-D-glucopyranoside (4b):



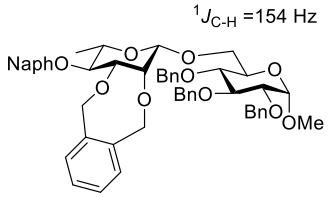
Following the general procedure of method A using trichloroacetimidate **2b** (50 mg, 0.10 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **3a** (30 mg, 0.06 mmol) in Et_2O (6.0 mL) at room temperature for 12 h afforded **4b** (40.0 mg, 75% yield of mixture isomers) as a colourless oil (eluent: DCM–Et_2O, 100:1; R_f = 0.45). $[\alpha]_D^{21}$ = +0.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz): δ 7.74 (s, 1H, ArH), 7.65–7.05 (m, 26H, ArH), 6.33 (s, 1H, Ar$\underline{CH}$), 5.08 (d, 1H, *J* = 12.1 Hz, OC$\underline{H_2}$Ph), 5.00 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.99 (d, 1H, *J* = 11.4 Hz, OC$\underline{H_2}$Ph), 4.82 (d, 1H, *J* = 12.1 Hz, OC$\underline{H_2}$Ph), 4.80 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.79 (d, 1H, *J* = 12.6 Hz, OC$\underline{H_2}$Ph), 4.76 (d, 1H, *J* = 2.8 Hz, C1^{Rha}-H), 4.58 (d, 1H, *J* = 3.4 Hz, C1^{Glc}-H), 4.45 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.38–4.33 (m, 2H, C3^{Rha}-H and C4^{Glc}-H), 4.24 (d, 1H, *J* = 9.2 Hz, OC$\underline{H_2}$Ph), 4.22–4.17 (m, 2H, C2^{Rha}-H and C6^{Glc}-H), 3.93–3.85 (m, 2H, C4^{Rha}-H and C3^{Glc}-H), 3.81 (d, 1H, *J* = 8.9 Hz, C5^{Glc}-H), 3.78–3.74 (m, 1H, C6^{Glc}-H), 3.52–3.48 (m, 2H, C2^{Glc}-H and C5^{Rha}-H), 3.14 (s, 3H, OMe), 1.45 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR (C_6D_6, 100 MHz): δ 139.5, 139.1, 138.91, 138.88, 136.1, 133.5, 133.2, 129.0, 128.3, 128.24, 128.21, 128.19, 128.17, 128.13, 128.10, 128.07, 128.05, 128.0, 127.9, 127.82, 127.76, 127.70, 127.6, 127.53, 127.46, 127.4, 127.3, 127.1, 126.8, 126.7, 126.0, 125.8, 104.6, 98.8 (C1^{Rha}), 98.1 (C1^{Glc}), 81.9, 80.9, 80.5, 78.8, 78.1, 75.2, 74.8, 72.6, 72.3, 70.5, 70.2, 67.3, 54.6, 29.9, 19.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{52}H_{54}O_{10}Na$, 861.3615; found, 861.3628.

Methyl 2,3-*O*-[1,1,3,3-tetrakis(1-methylethyl)-1,3-disiloxanediyl]-4-*O*-(2-naphthylmethyl)-α-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-benzyl-α-D-glucopyranoside (4c):



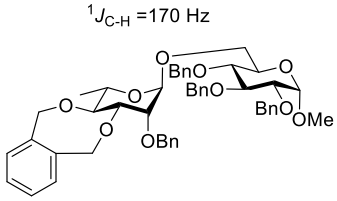
Following the general procedure of method A using trichloroacetimidate **2c** (22 mg, 0.03 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **3a** (10 mg, 0.02 mmol) in Et_2O (2.0 mL) at room temperature for 12 h afforded **4c** (18.9 mg, 90% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:15; R_f = 0.25). $[\alpha]_D^{21}$ = –29.2 (*c* = 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76–7.70 (m, 4H, ArH), 7.43–7.38 (m, 3H, ArH), 7.29–7.15 (m, 15H, ArH), 5.05 (d, 1H, *J* = 13.9 Hz, OC$\underline{H_2}$Ph), 4.89 (d, 1H, *J* = 13.6 Hz, OC$\underline{H_2}$Ph), 4.78 (d, 1H, *J* = 13.6 Hz, OC$\underline{H_2}$Ph), 4.72 (d, 1H, *J* = 13.7 Hz, OC$\underline{H_2}$Ph), 4.71 (d, 1H, *J* = 15.1 Hz, OC$\underline{H_2}$Ph), 4.69 (d, 1H, *J* = 14.1 Hz, OC$\underline{H_2}$Ph), 4.67 (d, 1H, *J* = 1.9 Hz, C1^{Rha}-H), 4.57 (d, 1H, *J* = 15.1 Hz, OC$\underline{H_2}$Ph), 4.45 (d, 1H, *J* = 4.5 Hz, C1^{Glc}-H), 4.44 (d, 1H, *J* = 13.9 Hz, OC$\underline{H_2}$Ph), 4.25 (dd, 1H, *J* = 4.0, 11.4 Hz, C3^{Rha}-H), 4.20–4.19 (m, 1H, C2^{Rha}-H), 3.89 (t, 1H, *J* = 11.6 Hz, C3^{Glc}-H), 3.80 (d, 1H, *J* = 12.0 Hz, C6^{Glc}-H), 3.70–3.65 (m, 2H, C5^{Rha}-H and C5^{Glc}-H), 3.43–3.39 (m, 2H, C2^{Glc}-H and C6^{Glc}-H), 3.37 (t, 1H, *J* = 11.7 Hz, C4^{Rha}-H), 3.28 (t, 1H, *J* = 11.5 Hz, C4^{Glc}-H), 3.26 (s, 3H, OMe), 1.19 (d, 3H, *J* = 7.8 Hz, C6^{Rha}-H), 1.18 (s, 3H, CH_3), 1.05–1.00 (m, 21H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.7, 138.14, 138.09, 136.3, 133.3, 133.0, 128.47, 128.45, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.69, 127.67, 126.7, 126.2, 126.0, 125.8, 100.3 (C1^{Rha}), 97.8 (C1^{Glc}), 82.1, 81.5, 80.1, 78.3, 77.3, 77.0, 76.7, 75.8, 75.6, 75.4, 75.1, 73.4, 72.7, 70.1, 67.6, 66.2, 54.9, 29.7, 18.1, 17.7, 17.6, 17.5, 17.4, 17.2, 17.1, 14.5, 13.7, 13.1, 12.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{57}H_{76}O_{11}Si_2Na$, 1015.4824; found, 1015.4813.

Methyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-benzyl-α-D-glucopyranoside (4d):



Following the general procedure of method A using trichloroacetimidate **2d** (24 mg, 0.05 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **3a** (14 mg, 0.03 mmol) in Et_2O (3.0 mL) at room temperature for 12 h afforded **4d** (26.2 mg, 95% yield of mixture isomers) as a colourless oil (eluent: EtOAc–hexane, 1:4; R_f = 0.28). $[\alpha]_D^{21}$ = +26.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78–6.99 (m, 26H, ArH), 5.53 (d, 1H, *J* = 12.8 Hz, OC$\underline{H_2}$Ph), 5.34 (d, 1H, *J* = 14.5 Hz, OC$\underline{H_2}$Ph), 5.05 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.89 (d, 1H, *J* = 10.8 Hz, OC$\underline{H_2}$Ph), 4.80 (d, 1H, *J* = 10.4 Hz, OC$\underline{H_2}$Ph), 4.79 (d, 1H, *J* = 9.7 Hz, OC$\underline{H_2}$Ph), 4.76 (d, 1H, *J* = 11.0 Hz, OC$\underline{H_2}$Ph), 4.73 (d, 1H, *J* = 9.7 Hz, OC$\underline{H_2}$Ph), 4.71 (d, 1H, *J* = 12.1 Hz, OC$\underline{H_2}$Ph), 4.70 (d, 1H, *J* = 14.2 Hz, OC$\underline{H_2}$Ph), 4.57 (d, 1H, *J* = 12.1 Hz, OC$\underline{H_2}$Ph), 4.47 (d, 1H, *J* = 3.5 Hz, C1^{Glc}-H), 4.41 (s, 1H, C1^{Rha}-H), 4.34 (d, 1H, *J* = 12.8 Hz, OC$\underline{H_2}$Ph), 4.13 (dd, 1H, *J* = 4.0, 12.1 Hz, C6^{Glc}-H), 3.90 (t, 2H, *J* = 9.0 Hz, C3^{Glc}-H and C2^{Rha}-H), 3.71 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.65–3.61 (m, 3H, C6^{Glc}-H, C5^{Glc}-H and C3^{Rha}-H), 3.53 (t, 1H, *J* = 9.2 Hz, C4^{Glc}-H), 3.40 (dd, 1H, *J* = 3.6, 9.6 Hz, C2^{Glc}-H), 3.33–3.27 (m, 1H, C5^{Rha}-H), 3.26 (s, 3H, OMe), 1.33 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.8, 138.4, 138.2, 137.7, 136.7, 135.9, 133.3, 133.1, 131.5, 128.48, 128.46, 128.4, 128.32, 128.25, 128.2, 128.1, 128.0, 127.93, 127.89, 127.8, 127.7, 126.9, 126.3, 126.1, 125.9, 100.3 (C1^{Rha}), 98.1 (C1^{Glc}), 82.0, 80.1, 79.1, 77.8, 77.4, 77.0, 76.7, 76.0, 75.3, 74.9, 73.5, 73.5, 71.8, 70.2, 67.1, 67.1, 55.2, 29.7, 18.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{53}H_{56}O_{10}Na$, 875.3771; found, 875.3760.

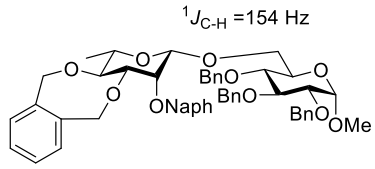
Methyl 3,4-*O*-(o-xylylene)-2-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-benzyl-α-D-glucopyranoside (4e):



Following the general procedure of method A using trichloroacetimidate **2e** (38 mg, 0.08 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **3a** (23.5 mg, 0.05 mmol) in Et_2O (5.1 mL) at room temperature for 12 h afforded **4e** (24.6 mg, 60% yield of mixture isomers) as a colourless oil (eluent: EtOAc–hexane, 1:3; R_f = 0.40). $[\alpha]_D^{21}$ = +47.4 (*c* = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.04 (m, 24H, ArH), 4.99 (d, 1H, *J* = 13.6 Hz, OC$\underline{H_2}$Ph), 4.97 (d, 1H, *J* = 11.3 Hz, OC$\underline{H_2}$Ph), 4.96 (d, 1H, *J* = 13.6 Hz, OC$\underline{H_2}$Ph), 4.89 (d, 1H, *J* = 10.8

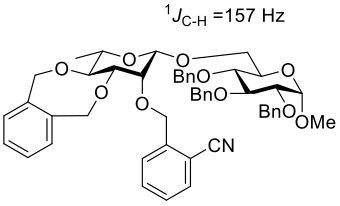
Hz, OCH$_2$Ph), 4.86 (d, 1H, *J* = 13.6 Hz, OCH$_2$Ph), 4.74 (d, 1H, *J* = 10.9 Hz, OCH$_2$Ph), 4.71 (d, 1H, *J* = 10.8 Hz, OCH$_2$Ph), 4.70 (d, 1H, *J* = 12.1 Hz, OCH$_2$Ph), 4.65 (d, 1H, *J* = 12.2 Hz, OCH$_2$Ph), 4.60 (d, 1H, *J* = 1.7 Hz, C1^{Rha}-H), 4.58 (d, 1H, *J* = 12.1 Hz, OCH$_2$Ph), 4.53 (d, 1H, *J* = 12.2 Hz, OCH$_2$Ph), 4.46 (d, 1H, *J* = 3.5 Hz, C1^{Glc}-H), 4.35 (d, 1H, *J* = 11.0 Hz, OCH$_2$Ph), 3.88 (t, 1H, *J* = 9.0 Hz, C3^{Glc}-H), 3.74 (dd, 1H, *J* = 1.9, 10.9 Hz, C6^{Glc}-H), 3.70 (dd, 1H, *J* = 3.2, 8.8 Hz, C4^{Rha}-H), 3.67–3.65 (m, 1H, C2^{Rha}-H), 3.62–3.59 (m, 1H, C5^{Glc}-H), 3.57–3.50 (m, 2H, C5^{Rha}-H and C3^{Rha}-H), 3.42–3.36 (m, 2H, C2^{Glc}-H and C6^{Glc}-H), 3.29 (t, 1H, *J* = 8.8 Hz, C4^{Glc}-H), 3.18 (s, 3H, OMe), 1.24 (d, 3H, *J* = 5.9 Hz, C6^{Rha}-H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 138.7, 138.5, 138.1, 137.2, 137.0, 130.2, 129.2, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.72, 127.67, 127.4, 98.8 (C1^{Rha}), 97.8 (C1^{Glc}), 82.0, 81.0, 80.0, 79.4, 77.9, 77.3, 77.2, 77.0, 76.7, 75.8, 75.0, 73.5, 73.4, 73.4, 72.6, 70.0, 67.7, 66.0, 55.0, 29.7, 17.6; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for C$_{49}$H$_{54}$O$_{10}$Na, 825.3615; found, 825.3603.

Methyl 3,4-*O*-(o-xylylene)-2-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-benzyl-α-D-glucopyranoside (4h):



Following the general procedure of method A using trichloroacetimidate **2h** (27.8 mg, 0.05 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **3a** (15.6 mg, 0.03 mmol) in Et$_2$O (3.4 mL) at room temperature for 12 h afforded **4h** (21.0 mg, 73% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:10; R$_f$ = 0.50). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.74–7.11 (m, 26H, ArH), 5.06 (d, 1H, *J* = 10.3 Hz, OCH$_2$Ph), 5.01 (d, 1H, *J* = 14.8 Hz, OCH$_2$Ph), 4.98 (d, 2H, *J* = 12.6 Hz, OCH$_2$Ph), 4.97 (d, 2H, *J* = 13.8 Hz, OCH$_2$Ph), 4.92 (d, 1H, *J* = 11.7 Hz, OCH$_2$Ph), 4.85 (d, 1H, *J* = 10.9 Hz, OCH$_2$Ph), 4.79 (d, 1H, *J* = 10.1 Hz, OCH$_2$Ph), 4.76 (d, 1H, *J* = 11.6 Hz, OCH$_2$Ph), 4.75 (d, 1H, *J* = 10.4 Hz, OCH$_2$Ph), 4.61 (d, 1H, *J* = 12.0 Hz, OCH$_2$Ph), 4.56 (d, 1H, *J* = 3.3 Hz, C1^{Glc}-H), 4.47 (s, 1H, C1^{Rha}-H), 4.25 (dd, 1H, *J* = 3.0, 11.32 Hz, C6^{Glc}-H), 4.00–3.95 (m, 2H, C3^{Glc}-H and C2^{Rha}-H), 3.74–3.65 (m, 3H, C5^{Glc}-H, C4^{Glc}-H and C6^{Glc}-H), 3.58 (t, 1H, *J* = 9.2 Hz, C4^{Rha}-H), 3.49–3.43 (m, 2H, C3^{Rha}-H and C2^{Glc}-H), 3.33 (s, 3H, OMe), 3.30–3.25 (m, 1H, C5^{Rha}-H), 1.37 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 138.9, 138.4, 138.2, 137.1, 137.0, 136.5, 133.2, 132.9, 130.2, 129.5, 128.5, 128.44, 128.40, 128.37, 128.3, 128.2, 128.2, 128.11, 128.07, 128.01, 127.96, 127.94, 127.9, 127.69, 127.65, 127.62, 127.57, 126.4, 126.3, 125.7, 125.5, 101.2 (C1^{Rha}), 98.3 (C1^{Glc}), 81.9, 81.4, 80.2, 80.0, 77.8, 77.4, 77.3, 77.0, 76.8, 76.7, 75.8, 75.2, 74.6, 73.5, 73.2, 72.1, 71.9, 70.2, 67.1, 55.2, 29.7, 17.7, 0.0; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for C$_{53}$H$_{56}$O$_{10}$Na, 875.3771; found, 875.3785.

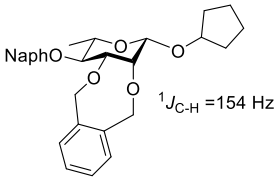
Methyl 3,4-*O*-(o-xylylene)-2-*O*-(2-cyanobenzyl)-β-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-benzyl-α-D-glucopyranoside (4i):



Following the general procedure of method A using trichloroacetimidate **2i** (34 mg, 0.06 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **3a** (20 mg, 0.04 mmol) in Et$_2$O (4.3 mL) at room temperature for 12 h afforded **4i** (20.1 mg, 56% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:10; R$_f$ = 0.40). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.66 (d, 1H, *J* = 7.8 Hz, ArH), 7.46–7.11 (m, 22H, ArH), 5.12 (d, 1H, *J* = 14.0 Hz, OCH$_2$Ph), 5.08 (d, 1H, *J* = 13.7 Hz, OCH$_2$Ph), 5.03 (d, 1H, *J* = 14.0 Hz, OCH$_2$Ph), 4.98 (d, 2H, *J* = 14.2 Hz, OCH$_2$Ph), 4.94 (d, 1H, *J* = 10.7 Hz, OCH$_2$Ph), 4.91 (d, 1H, *J* = 13.3 Hz, OCH$_2$Ph), 4.80 (d, 1H, *J* = 11.0 Hz, OCH$_2$Ph), 4.78 (d, 1H, *J* = 12.1 Hz, OCH$_2$Ph), 4.67 (d, 1H, *J* = 12.1 Hz, OCH$_2$Ph), 4.64 (d, 1H, *J* = 10.1 Hz, OCH$_2$Ph), 4.63 (d, 1H, *J* = 10.1 Hz, OCH$_2$Ph), 4.62 (d, 1H, *J* = 2.3 Hz, C1^{Glc}-H), 4.50 (s, 1H, C1^{Rha}-H), 4.23 (dd, 1H, *J* = 3.1, 11.0 Hz, C6^{Glc}-H), 3.97 (d, 1H, *J* = 2.6 Hz, C2^{Rha}-H), 3.93 (t, 1H, *J* = 9.3 Hz, C3^{Glc}-H), 3.72–3.69 (m, 1H, C5^{Glc}-H), 3.65 (dd, 1H, *J* = 2.0, 11.0 Hz, C6^{Glc}-H), 3.58–3.51 (m, 4H, C4^{Glc}-H, C3^{Rha}-H, C4^{Rha}-H and C2^{Glc}-H), 3.33 (s, 3H, OMe), 3.33–3.26 (m, 1H, C5^{Rha}-H), 1.37 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 143.3, 139.2, 138.5, 138.4, 137.0, 136.8, 132.6, 132.1, 130.4, 129.5, 128.4, 128.3, 128.3, 128.17, 128.15, 128.0, 127.9, 127.8, 127.6, 127.5, 127.2, 117.3, 110.0, 100.6 (C1^{Rha}), 98.2 (C1^{Glc}), 81.8, 81.1,

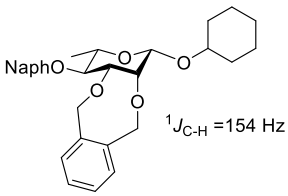
80.04, 79.99, 78.5, 77.6, 77.4, 77.2, 77.0, 76.7, 75.6, 75.0, 73.4, 73.1, 72.1, 72.0, 71.8, 70.0, 67.0, 55.2, 29.7, 17.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{50}H_{53}NO_{10}Na$, 850.3567; found, 850.3554.

Cyclopentyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5b):



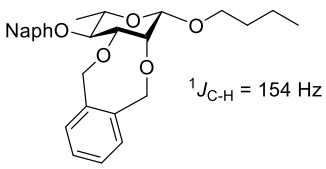
Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and cyclopentanol **3b** (3.3 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 °C for 24 h afforded **5b** (17.6 mg, 96% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:15; R_f = 0.55). $[\alpha]_D^{21}$ = +48.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.10 (m, 11H, ArH), 5.63 (d, 1H, *J* = 12.7 Hz, O$\underline{CH_2}$Ph), 5.44 (d, 1H, *J* = 14.6 Hz, O$\underline{CH_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.84 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.75 (d, 1H, *J* = 14.6 Hz, O$\underline{CH_2}$Ph), 4.42 (s, 1H, C1^{Rha}-H), 4.41 (d, 1H, *J* = 12.7 Hz, O$\underline{CH_2}$Ph), 4.31–4.27 (m, 1H, C1-H of cyclopentyl), 3.85 (d, 1H, *J* = 2.7 Hz, C2^{Rha}-H), 3.80 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.70 (dd, 1H, *J* = 2.7, 9.6 Hz, C3^{Rha}-H), 3.39–3.32 (m, 1H, C5^{Rha}-H), 1.84–1.48 (m, 8H, cyclopentyl), 1.41 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 136.9, 135.9, 133.3, 133.0, 131.4, 128.4, 128.1, 127.9, 127.7, 127.6, 126.9, 126.3, 126.0, 125.8, 98.8 (C1^{Rha}), 80.2, 79.1, 77.6, 77.3, 77.2, 77.0, 76.7, 74.9, 73.4, 71.6, 67.1, 33.3, 32.0, 23.4, 23.3, 18.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{34}O_5Na$, 497.2304; found, 497.2316.

Cyclohexyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5c):



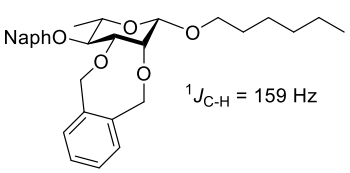
Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and cyclohexanol **3c** (3.9 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 °C for 24 h afforded **5c** (17.0 mg, 90% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:15; R_f = 0.55). $[\alpha]_D^{21}$ = +92.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.11 (m, 11H, ArH), 5.64 (d, 1H, *J* = 12.7 Hz, O$\underline{CH_2}$Ph), 5.46 (d, 1H, *J* = 14.6 Hz, O$\underline{CH_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.84 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.79 (d, 1H, *J* = 14.7 Hz, O$\underline{CH_2}$Ph), 4.50 (s, 1H, C1^{Rha}-H), 4.42 (d, 1H, *J* = 12.7 Hz, O$\underline{CH_2}$Ph), 3.87 (d, 1H, *J* = 2.6 Hz, C2^{Rha}-H), 3.81 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.70 (dd, 1H, *J* = 2.7, 9.6 Hz, C3^{Rha}-H), 3.67–3.62 (m, 1H, C1-H of cyclohexyl), 3.38–3.31 (m, 1H, C5^{Rha}-H), 1.94–1.44 (m, 8H, cyclohexyl), 1.40 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H), 1.31–1.22 (m, 2H, cyclohexyl); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 137.0, 135.9, 133.3, 133.0, 131.4, 128.3, 128.1, 127.9, 127.7, 127.6, 126.9, 126.3, 126.0, 125.8, 98.0 (C1^{Rha}), 79.1, 77.8, 77.3, 77.1, 77.0, 76.7, 76.2, 74.9, 73.4, 71.5, 67.1, 33.3, 31.6, 25.6, 23.9, 23.8, 18.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{36}O_5Na$, 511.2460; found, 511.2472.

***n*-Butyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5d):**



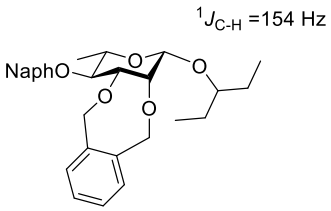
Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and *n*-butanol **3d** (2.9 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 °C for 24 h afforded **5d** (9.3 mg, 52% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:15; R_f = 0.55). $[\alpha]_D^{21}$ = –74.4 (*c* = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.12 (m, 11H, ArH), 5.63 (d, 1H, *J* = 12.8 Hz, O$\underline{CH_2}$Ph), 5.49 (d, 1H, *J* = 14.4 Hz, O$\underline{CH_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.85 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.77 (d, 1H, *J* = 14.4 Hz, O$\underline{CH_2}$Ph), 4.45 (d, 1H, *J* = 12.9 Hz, O$\underline{CH_2}$Ph), 4.37 (s, 1H, C1^{Rha}-H), 3.92 (d, 1H, *J* = 2.8 Hz, C2^{Rha}-H), 3.90–3.86 (m, 1H, O$\underline{CH_2}$ of butyl), 3.80 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 3.70 (dd, 1H, *J* = 2.7, 9.6 Hz, C3^{Rha}-H), 3.49–3.42 (m, 1H, O$\underline{CH_2}$ of butyl), 3.40–3.34 (m, 1H, C5^{Rha}-H), 1.63–1.56 (m, 2H, $CH_2\underline{CH_2}CH_2$ of butyl), 1.41 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H), 1.40–1.36 (m, 2H, $\underline{CH_2}CH_3$ of butyl), 0.92 (t, 3H, *J* = 7.4 Hz, $CH_2\underline{CH_3}$ of butyl); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 136.5, 135.9, 133.3, 133.0, 131.0, 128.7, 128.1, 128.0, 127.9, 127.8, 127.6, 126.8, 126.3, 126.0, 125.8, 100.2 (C1^{Rha}), 79.5, 77.4, 77.3, 77.2, 77.0, 76.7, 76.6, 74.9, 73.3, 71.6, 69.3, 67.4, 31.6, 29.6, 19.2, 18.1, 13.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{29}H_{34}O_5Na$, 485.2304; found, 485.2321.

_n_-Hexyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5e):



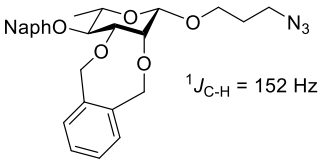
Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and *n*-hexanol **3e** (3.9 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 °C for 24 h afforded **5e** (15.6 mg, 82% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:15; R_f = 0.55). $[\alpha]_D^{21}$ = +63.9 (*c* = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.11 (m, 11H, ArH), 5.62 (d, 1H, *J* = 12.9 Hz, OC$\underline{H_2}$Ph), 5.49 (d, 1H, *J* = 14.4 Hz, OC$\underline{H_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.85 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.77 (d, 1H, *J* = 14.4 Hz, OC$\underline{H_2}$Ph), 4.45 (d, 1H, *J* = 13.0 Hz, OC$\underline{H_2}$Ph), 4.37 (s, 1H, C1^{Rha}-H), 3.91 (d, 1H, *J* = 2.6 Hz, C2^{Rha}-H), 3.90–3.85 (m, 1H, OC$\underline{H_2}$ of hexyl), 3.80 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 3.70 (dd, 1H, *J* = 2.7, 9.6 Hz, C3^{Rha}-H), 3.45–3.41 (m, 1H, OC$\underline{H_2}$ of hexyl), 3.39–3.33 (m, 1H, C5^{Rha}-H), 1.64–1.57 (m, 2H, CH_2 of hexyl), 1.41 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H), 1.36–1.26 (m, 6H, CH_2 of hexyl), 0.88 (t, 3H, *J* = 6.3 Hz, $CH_2\underline{CH_3}$ of hexyl); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 136.5, 135.9, 133.3, 133.0, 131.0, 128.7, 128.08, 128.06, 127.9, 127.8, 127.6, 126.8, 126.3, 126.0, 125.8, 100.2 (C1^{Rha}), 79.6, 77.4, 77.3, 77.2, 77.0, 76.7, 74.9, 73.3, 71.6, 69.7, 67.4, 31.6, 29.7, 29.5, 25.6, 22.5, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{38}O_5Na$, 513.2617; found, 513.2625.

3-Pentyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5f):



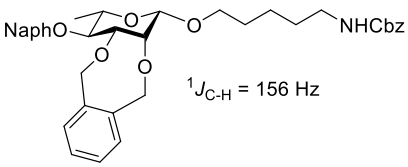
Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and 3-pentanol **3f** (3.4 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 °C for 24 h afforded **5f** (14.9 mg, 82% yield of mixture isomers) as a colourless oil (eluent: EtOAc–hexane, 1:4; R_f = 0.60). $[\alpha]_D^{21}$ = +48.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.10 (m, 11H, ArH), 5.64 (d, 1H, *J* = 12.6 Hz, OC$\underline{H_2}$Ph), 5.45 (d, 1H, *J* = 14.7 Hz, OC$\underline{H_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.85 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.79 (d, 1H, *J* = 14.8 Hz, OC$\underline{H_2}$Ph), 4.42 (s, 1H, C1^{Rha}-H), 4.40 (d, 1H, *J* = 11.3 Hz, OC$\underline{H_2}$Ph), 3.89 (d, 1H, *J* = 2.7 Hz, C2^{Rha}-H), 3.82 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.68 (dd, 1H, *J* = 2.8, 9.7 Hz, C3^{Rha}-H), 3.53–3.47 (m, 1H, $\underline{CH}CH_2$), 3.37–3.30 (m, 1H, C5^{Rha}-H), 1.66–1.25 (m, 4H, $CH\underline{CH_2}CH_3$), 1.40 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H), 0.92 (t, 3H, *J* = 7.4 Hz, $CHCH_2\underline{CH_3}$), 0.84 (t, 3H, *J* = 7.4 Hz, $CHCH_2\underline{CH_3}$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 137.0, 135.9, 133.3, 133.0, 131.6, 128.2, 128.1, 128.1, 127.9, 127.7, 127.6, 126.9, 126.3, 126.0, 125.8, 99.5 (C1^{Rha}), 81.6, 79.1, 77.8, 77.3, 77.2, 77.0, 76.7, 74.83, 73.5, 71.5, 67.0, 29.7, 26.9, 25.5, 18.2, 9.5, 9.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{36}O_5Na$, 499.2460; found, 499.2481.

3-Azidopropyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5g):



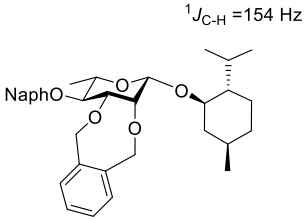
Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and 3-azidopropanol **3g** (3.9 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 °C for 24 h afforded **5g** (13.1 mg, 70% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:15; R_f = 0.55). $[\alpha]_D^{21}$ = –7.3 (*c* = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.13 (m, 11H, ArH), 5.60 (d, 1H, *J* = 13.2 Hz, OC$\underline{H_2}$Ph), 5.52 (d, 1H, *J* = 14.2 Hz, OC$\underline{H_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.85 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.75 (d, 1H, *J* = 14.2 Hz, OC$\underline{H_2}$Ph), 4.47 (d, 1H, *J* = 13.2 Hz, OC$\underline{H_2}$Ph), 4.38 (s, 1H, C1^{Rha}-H), 3.98–3.95 (m, 1H, OC$\underline{H_2}$), 3.93 (d, 1H, *J* = 2.5 Hz, C2^{Rha}-H), 3.79 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.71 (dd, 1H, *J* = 2.7, 9.6 Hz, C3^{Rha}-H), 3.57–3.53 (m, 1H, OC$\underline{H_2}$), 3.43–3.35 (m, 3H, $OCH_2\underline{CH_2}$ and C5^{Rha}-H), 1.97–1.83 (m, 2H, $\underline{CH_2}N_3$), 1.41 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 136.1, 135.8, 133.2, 133.0, 130.7, 128.9, 128.1, 127.9, 127.9, 127.6, 126.9, 126.3, 126.0, 125.9, 100.4 (C1^{Rha}), 79.8, 77.4, 77.29, 77.26, 77.0, 76.7, 76.2, 75.0, 73.2, 71.7, 67.6, 66.3, 48.4, 29.6, 29.1, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{31}N_3O_5Na$, 512.2161; found, 512.2144.

5-(*N*-Benzyloxycarbonylamino) pentyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5h):



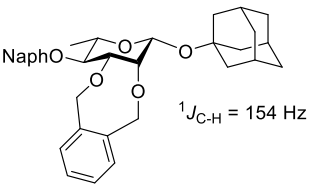
Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and 5-(*N*-benzyloxycarbonylamino) pentanol **3h** (9.3 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 ℃ for 24 h afforded **5h** (14.8 mg, 60% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:15; R_f = 0.55). $[\alpha]_D^{21}$ = +118.6 (*c* = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.11 (m, 16H, ArH), 5.60 (d, 1H, *J* = 13.6 Hz, OCH_2Ph), 5.49 (d, 1H, *J* = 14.4 Hz, OCH_2Ph), 5.13 (d, 1H, *J* = 11.1 Hz, OCH_2Ph), 5.10 (d, 2H, *J* = 10.8 Hz, OCH_2Ph), 4.84 (d, 1H, *J* = 10.0 Hz, OCH_2Ph), 4.76 (s, 1H, NH), 4.74 (d, 2H, *J* = 14.4 Hz, OCH_2Ph), 4.45 (d, 1H, *J* = 13.1 Hz, OCH_2Ph), 4.35 (s, 1H, $C1^{Rha}$-H), 3.91 (t, 1H, *J* = 2.7 Hz, $C2^{Rha}$-H), 3.90–3.84 (m, 1H, OCH_2), 3.79 (t, 1H, *J* = 9.3 Hz, $C4^{Rha}$-H), 3.69 (dd, 1H, *J* = 2.7, 9.4 Hz, $C3^{Rha}$-H), 3.45–3.32 (m, 2H, OCH_2 and $C5^{Rha}$-H), 3.22–3.17 (m, 2H, CH_2), 1.66–1.49 (m, 6H, CH_2), 1.40 (d, 3H, *J* = 6.1 Hz, $C6^{Rha}$-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 136.6, 136.3, 135.8, 133.3, 130.8, 128.8, 128.5, 128.1, 128.1, 127.9, 127.8, 127.6, 126.8, 126.3, 126.0, 125.8, 100.2 ($C1^{Rha}$), 79.7, 77.4, 77.3, 77.2, 77.0, 76.9, 76.7, 76.4, 75.0, 73.2, 71.6, 69.2, 67.5, 66.5, 29.6, 29.1, 23.2, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{38}H_{43}NO_7Na$, 648.2937; found, 648.2926.

(L)-Menthyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5i):



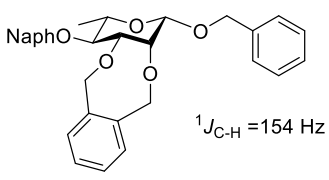
Following the general procedure of method A using trichloroacetimidate **2d** (30 mg, 0.05 mmol) and (L)-menthol **3i** (5.7 mg, 0.04 mmol) in Et_2O (3.6 mL) at –5 ℃ for 24 h afforded **5i** (14.6 mg, 73% yield of mixture isomers) as a colourless oil (eluent: EtOAc–hexane, 1:6; R_f = 0.70). $[\alpha]_D^{21}$ = +5.8 (*c* = 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.09 (m, 11H, ArH), 5.63 (d, 1H, *J* = 12.7 Hz, O$\underline{CH_2}$Ph), 5.45 (d, 1H, *J* = 14.6 Hz, O$\underline{CH_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.84 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.77 (d, 1H, *J* = 14.7 Hz, O$\underline{CH_2}$Ph), 4.43 (d, 1H, *J* = 12.7 Hz, O$\underline{CH_2}$Ph), 4.40 (s, 1H, $C1^{Rha}$-H), 3.90 (d, 1H, *J* = 2.7 Hz, $C2^{Rha}$-H), 3.81 (t, 1H, *J* = 9.4 Hz, $C4^{Rha}$-H), 3.68 (dd, 1H, *J* = 2.7, 9.7 Hz, $C3^{Rha}$-H), 3.39–3.24 (m, 2H, $C5^{Rha}$-H and C1-H of menthyl), 2.21–1.57 (m, 7H, menthyl), 1.41 (d, 3H, *J* = 6.1 Hz, $C6^{Rha}$-H), 1.35–0.68 (m, 11H, menthyl); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 137.0, 136.0, 133.3, 133.1, 131.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 126.9, 126.3, 126.1, 125.9, 101.6 ($C1^{Rha}$), 81.6, 79.3, 74.9, 73.5, 71.5, 67.2, 48.3, 43.0, 34.4, 31.7, 29.7, 25.9, 23.3, 22.2, 21.0, 18.4, 16.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{44}O_5Na$, 567.3086; found, 567.3090.

Admantyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5j):



Following the general procedure of method A using trichloroacetimidate **2d** (30 mg, 0.05 mmol) and 1-admantanol **3j** (7.6 mg, 0.04 mmol) in Et_2O (3.6 mL) at –5 ℃ for 24 h afforded **5j** (11.8 mg, 60% yield of mixture isomers) as a colourless oil (eluent: acetonitrile–toluene, 1:15; R_f = 0.35). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.10 (m, 11H, ArH), 5.66 (d, 1H, *J* = 12.5 Hz, O$\underline{CH_2}$Ph), 5.42 (d, 1H, *J* = 14.9 Hz, O$\underline{CH_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.84 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.80 (d, 1H, *J* = 15.1 Hz, O$\underline{CH_2}$Ph), 4.68 (s, 1H, $C1^{Rha}$-H), 4.39 (d, 1H, *J* = 12.5 Hz, O$\underline{CH_2}$Ph), 3.79 (t, 1H, *J* = 9.3 Hz, $C4^{Rha}$-H), 3.76 (d, 1H, *J* = 2.8 Hz, $C2^{Rha}$-H), 3.70 (dd, 1H, *J* = 2.7, 9.6 Hz, $C3^{Rha}$-H), 3.37–3.30 (m, 1H, $C5^{Rha}$-H), 2.14–1.24 (m, 15H, adamantyl), 1.38 (d, 3H, *J* = 6.1 Hz, $C6^{Rha}$-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.5, 136.0, 133.3, 133.1, 131.9, 128.2, 128.1, 128.0, 127.9, 127.7, 126.8, 126.3, 126.0, 125.9, 93.1 ($C1^{Rha}$), 78.8, 77.3, 77.2, 77.0, 76.7, 74.8, 74.5, 71.2, 66.8, 42.5, 36.3, 30.7, 29.7, 18.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{40}O_5Na$, 563.2773; found, 563.2782.

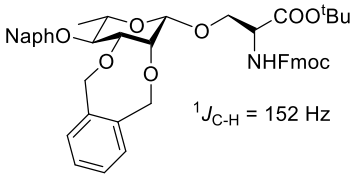
Benzyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranoside (5k):



Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and benzyl alcohol **3k** (4.2 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 ℃ for 24 h afforded **5k** (18.6 mg, 97% yield of mixture isomers) as a colourless oil (eluent: EtOAc–

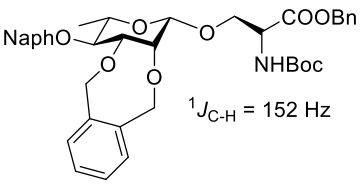
toluene, 1:15; R_f = 0.55). $[\alpha]_D^{21}$ = +100.8 (*c* = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.13 (m, 16H, ArH), 5.60 (d, 1H, *J* = 13.1 Hz, O$\underline{CH_2}$Ph), 5.54 (d, 1H, *J* = 14.2 Hz, O$\underline{CH_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.93 (d, 1H, *J* = 11.1 Hz, O$\underline{CH_2}$Ph), 4.85 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.80 (d, 1H, *J* = 14.3 Hz, O$\underline{CH_2}$Ph), 4.60 (d, 1H, *J* = 12.2 Hz, O$\underline{CH_2}$Ph), 4.46 (d, 1H, *J* = 13.2 Hz, O$\underline{CH_2}$Ph), 4.40 (s, 1H, C1^{Rha}-H), 3.93 (d, 1H, *J* = 2.7 Hz, C2^{Rha}-H), 3.81 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 3.67 (dd, 1H, *J* = 2.8, 9.6 Hz, C3^{Rha}-H), 3.37–3.33 (m, 1H, C5^{Rha}-H), 1.45 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 137.3, 136.1, 135.9, 133.3, 133.0, 130.6, 129.0, 128.3, 128.1, 128.03, 128.0, 127.9, 127.9, 127.7, 127.6, 126.8, 126.2, 126.0, 125.8, 98.5 (C1^{Rha}), 80.0, 77.5, 77.3, 77.2, 77.0, 76.7, 76.3, 75.0, 73.2, 71.7, 70.2, 67.7, 29.7, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{32}H_{32}O_5Na$, 519.2147; found, 519.2141.

_N_-9-Fluorenylmethyloxycarbonyl-_O_-[2,3-_O_-(o-xylylene)-4-_O_-(2-naphthylmethyl)-β-L-rhamnopyranosyl]-L-serine tert-Butyl Ester (5l):



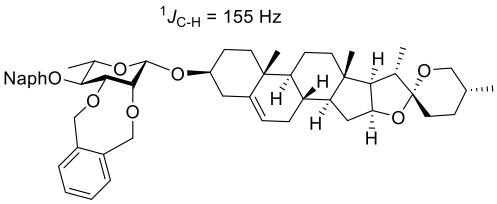
Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and *N*-Fmoc-L-serine tert-butyl ester **3l** (15 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 ℃ for 24 h afforded **5l** (10.5 mg, 35% yield of mixture isomers) as a colourless oil (eluent: acetonitrile–toluene, 1:15; R_f = 0.40). $[\alpha]_D^{21}$ = –21.5 (*c* = 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87–7.26 (m, 19H, ArH), 5.91 (d, 1H, *J* = 8.9 Hz, NH), 5.61 (d, 1H, *J* = 12.9 Hz, OCH_2Ph), 5.47 (d, 1H, *J* = 14.4 Hz, O$\underline{CH_2}$Ph), 5.13 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.85 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.72 (d, 1H, *J* = 14.5 Hz, O$\underline{CH_2}$Ph), 4.43 (d, 1H, *J* = 12.9 Hz, O$\underline{CH_2}$Ph), 4.43–4.38 (m, 2H, CH_2), 4.37 (s, 1H, C1^{Rha}-H), 4.24 (t, 1H, *J* = 14.4 Hz, CH_2), 4.11 (dd, 1H, *J* = 2.5, 10.0 Hz, CH_2), 3.99 (dd, 1H, *J* = 3.3, 9.9 Hz, CH_2), 3.87 (d, 1H, *J* = 2.7 Hz, C2^{Rha}-H), 3.80 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.79–3.68 (m, 2H, CH_2 and C3^{Rha}-H), 3.39–3.35 (m, 1H, C5^{Rha}-H), 1.43 (s, 9H, CH_3), 1.40 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.0, 144.0, 141.3, 137.7, 136.3, 135.7, 133.1, 131.2, 128.6, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.1, 127.0, 126.3, 126.1, 126.0, 125.3, 120.0, 100.6 (C1^{Rha}), 82.2, 79.2, 77.3, 77.2, 77.0, 77.0, 76.7, 76.5, 75.03, 73.4, 71.9, 70.7, 68.0, 67.5, 67.2, 54.9, 47.2, 31.6, 29.7, 28.1, 25.6, 22.7, 18.1, 14.1, 0.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{47}H_{49}NO_9Na$, 794.3305; found, 794.3313.

_N_-tert-Butoxycarbonyl-_O_-[2,3-_O_-(o-xylylene)-4-_O_-(2-naphthylmethyl)-β-L-rhamnopyranosyl]-L-serine Benzyl Ester (5m):



Following the general procedure of method A using trichloroacetimidate **2d** (33 mg, 0.06 mmol) and *N*-Boc-L-serine benzyl ester **3m** (11.8 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 ℃ for 24 h afforded **5m** (13.6 mg, 50% yield of mixture isomers) as a colourless oil (eluent: acetonitrile–toluene, 1:12; R_f = 0.55). $[\alpha]_D^{21}$ = +32.0 (*c* = 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.05 (m, 16H, ArH), 5.64 (d, 1H, *J* = 9.2 Hz, NH), 5.55 (d, 1H, *J* = 12.6 Hz, O$\underline{CH_2}$Ph), 5.35 (d, 1H, *J* = 12.1 Hz, O$\underline{CH_2}$Ph), 5.33 (d, 2H, *J* = 14.7 Hz, O$\underline{CH_2}$Ph), 5.10 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.96 (d, 2H, *J* = 12.1 Hz, O$\underline{CH_2}$Ph), 4.82 (d, 1H, *J* = 11.2 Hz, O$\underline{CH_2}$Ph), 4.56–4.51 (m, 2H, O$\underline{CH_2}$Ph and CH), 4.13–4.08 (m, 1H, CH_2), 4.06 (s, 1H, C1^{Rha}-H), 3.92 (dd, 1H, *J* = 3.0, 9.9 Hz, CH_2), 3.72 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.47 (dd, 1H, *J* = 2.8, 9.7 Hz, C3^{Rha}-H), 3.35 (t, 1H, *J* = 2.7 Hz, C2^{Rha}-H), 3.29–3.23 (m, 1H, C5^{Rha}-H), 1.45 (s, 9H, CH_3), 1.38 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 155.5, 137.5, 136.8, 135.7, 133.3, 133.1, 131.8, 128.5, 128.4, 128.3, 128.2, 127.9, 127.9, 127.7, 127.0, 126.3, 126.1, 126.0, 100.8 (C1^{Rha}), 79.9, 78.5, 77.3, 77.2, 77.0, 76.8, 76.7, 76.6, 75.0, 73.5, 71.8, 70.8, 67.0, 66.9, 54.0, 29.7, 28.4, 18.0, 0.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{40}H_{45}NO_9Na$, 706.2992; found, 706.2994.

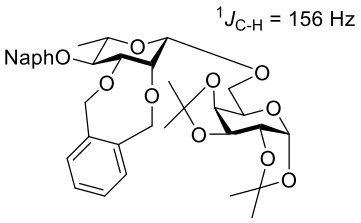
3-_O_-[2,3-_O_-(o-xylylene)-4-_O_-(2-naphthylmethyl)-β-L-rhamnopyranosyl]diosgenin (5n):



Following the general procedure of method A using trichloroacetimidate **2d** (32 mg, 0.06 mmol) and diosgenin **3n** (16.0 mg, 0.04 mmol) in Et_2O (4.0 mL)

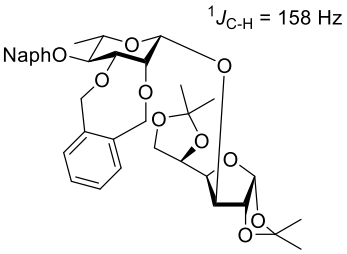
at –5 °C for 24 h afforded **5n** (16.8 mg, 54% yield of mixture isomers) as a colourless oil (eluent: acetonitrile–toluene, 1:50; R_f = 0.65). $[\alpha]_D^{21}$ = –105.6 (*c* = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.12 (m, 11H, ArH), 5.63 (d, 1H, *J* = 12.9 Hz, OCH_2Ph), 5.49 (d, 1H, *J* = 14.5 Hz, OCH_2Ph), 5.34 (d, 1H, *J* = 5.4 Hz, C1-H of diosgenin), 5.13 (d, 2H, *J* = 11.2 Hz, OCH_2Ph), 4.84 (d, 1H, *J* = 11.2 Hz, OCH_2Ph), 4.79 (d, 1H, *J* = 14.6 Hz, OCH_2Ph), 4.50 (s, 1H, C1^{Rha}-H), 4.44 (d, 2H, *J* = 12.9 Hz, OCH_2Ph), 4.43–4.37 (m, 1H, diosgenin), 3.87 (t, 1H, *J* = 2.6 Hz, C2^{Rha}-H), 3.80 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 3.69 (dd, 1H, *J* = 2.6, 9.6 Hz, C3^{Rha}-H), 3.56–3.31 (m, 4H, diosgenin and C5^{Rha}-H), 2.04–0.96 (m, 39H, diosgenin and C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 137.8, 136.7, 135.9, 133.2, 133.0, 131.1, 128.6, 128.1, 128.0, 127.9, 127.7, 127.6, 126.9, 126.3, 126.0, 125.8, 121.4, 109.2, 98.2 (C1^{Rha}), 80.8, 79.5, 78.0, 77.3, 77.0, 76.7, 74.9, 73.3, 71.5, 67.3, 66.8, 62.1, 56.5, 50.0, 41.6, 40.2, 40.0, 39.7, 37.0, 36.8, 32.0, 31.8, 31.4, 31.3, 30.3, 28.8, 28.0, 20.8, 19.4, 18.2, 17.1, 16.2, 14.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{52}H_{66}O_7Na$, 825.4706; found, 825.4715.

2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5o):



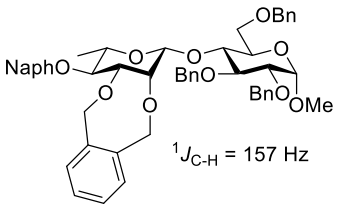
Following the general procedure of method A using trichloroacetimidate **2d** (34 mg, 0.06 mmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **3o** (10.7 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 °C for 24 h afforded **5o** (23.2 mg, 87% yield of mixture isomers) as a colourless oil (eluent: EtOAc–hexane, 1:3; R_f = 0.40). $[\alpha]_D^{21}$ = –74.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.11 (m, 11H, ArH), 5.60 (d, 1H, *J* = 13.1 Hz, OCH_2Ph), 5.51 (d, 1H, *J* = 12.5 Hz, OCH_2Ph), 5.49 (d, 1H, *J* = 1.8 Hz, C1^{Gal1}-H), 5.13 (d, 2H, *J* = 11.2 Hz, OCH_2Ph), 4.85 (d, 1H, *J* = 11.2 Hz, OCH_2Ph), 4.78 (d, 2H, *J* = 14.4 Hz, OCH_2Ph), 4.60 (dd, 1H, *J* = 2.4, 8.0 Hz, C3^{Gal}-H), 4.46 (d, 1H, *J* = 13.0 Hz, OCH_2Ph), 4.45 (s, 1H, C1^{Rha}-H), 4.34–4.29 (m, 2H, C4^{Gal}-H and C2^{Gal}-H), 4.15–4.05 (m, 1H, C5^{Gal}-H), 3.98 (d, 1H, *J* = 2.7 Hz, C2^{Rha}-H), 3.92–3.88 (m, 1H, C6^{Gal}-H), 3.81–3.75 (m, 2H, C4^{Rha}-H and C6^{Gal}-H), 3.70 (dd, 1H, *J* = 2.7, 9.6 Hz, C3^{Rha}-H), 3.41–3.34 (m, 1H, C5^{Rha}-H), 1.52 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.40 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H), 1.33 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 136.3, 135.8, 133.3, 133.1, 130.9, 128.9, 128.2, 128.1, 128.0, 127.9, 127.7, 127.0, 126.3, 126.1, 125.9, 109.1, 108.6, 100.6 (C1^{Rha}), 96.3 (C1^{Gal}), 79.8, 77.4, 77.1, 76.7, 76.3, 75.1, 73.3, 71.8, 70.8, 70.6, 70.5, 67.6, 67.5, 65.5, 60.4, 29.7, 26.2, 26.0, 24.9, 24.4, 21.1, 18.2, 14.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{44}O_{10}Na$, 671.2832; found, 671.2838.

2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (5p):



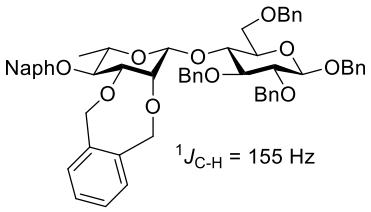
Following the general procedure of method A using trichloroacetimidate **2d** (33 mg, 0.06 mmol) and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **3p** (10.4 mg, 0.04 mmol) in Et_2O (4.0 mL) at –5 °C for 24 h afforded **5p** (9.8 mg, 38% yield of mixture isomers) as a colourless oil (eluent: acetonitrile–toluene, 1:12; R_f = 0.50). $[\alpha]_D^{21}$ = +32.0 (*c* = 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.11 (m, 11H, ArH), 5.93 (d, 1H, *J* = 3.6 Hz, C1^{Glc}-H), 5.59 (d, 1H, *J* = 13.1 Hz, OCH_2Ph), 5.50 (d, 1H, *J* = 14.2 Hz, OCH_2Ph), 5.13 (d, 2H, *J* = 11.2 Hz, OCH_2Ph), 4.86 (d, 1H, *J* = 11.2 Hz, OCH_2Ph), 4.83 (d, 1H, *J* = 3.6 Hz, C2^{Glc}-H), 4.73 (d, 1H, *J* = 14.3 Hz, OCH_2Ph), 4.56 (s, 1H, C1^{Rha}-H), 4.45 (d, 1H, *J* = 13.1 Hz, OCH_2Ph), 4.18 (d, 1H, *J* = 2.7 Hz, C3^{Glc}-H), 4.13–4.04 (m, 3H, C5^{Glc}-H, C6^{Glc}-H and C4^{Glc}-H), 3.98–3.94 (m, 2H, C6^{Glc}-H and C2^{Rha}-H), 3.79 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 3.70 (dd, 1H, *J* = 2.7, 9.6 Hz, C3^{Rha}-H), 3.42–3.39 (m, 1H, C5^{Rha}-H), 1.49 (s, 3H, CH_3), 1.43 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H), 1.37 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.18 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.9, 136.0, 135.1, 133.3, 133.1, 130. 9, 128. 8, 128.3, 128.2, 128.1, 127.9, 127.7, 127.0, 126.3, 126.1, 126.0, 111.8, 109.1, 105.5 (C1^{Glc}), 101.8 (C1^{Rha}), 84.1, 83.0, 81.1, 79.6, 77.3, 77.2, 77.0, 76.7, 76.4, 75.0, 73.5, 72.7, 71.9, 67.6, 29.7, 26.8, 26.2, 25.3, 18.2, 0.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{44}O_{10}Na$, 671.2832; found, 671.2835.

Methyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→4)-2,3,6-*tri*-*O*-benzyl-α-D-glucopyranoside (5q):



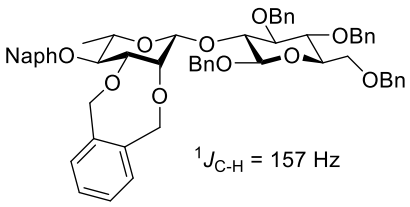
Following the general procedure of method A using trichloroacetimidate **2d** (33 mg, 0.06 mmol) and methyl 2,3,6-*tri*-*O*-benzyl-α-D-glucopyranoside **3q** (18.6 mg, 0.04 mmol) in Et_2O (5.0 mL) at –5 °C for 24 h afforded **5q** (16.6 mg, 48% yield of mixture isomers) as a colourless oil (eluent: acetone–toluene, 1:12; R_f = 0.55). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84–6.97 (m, 26H, ArH), 5.47 (d, 1H, *J* = 13.8 Hz, OC$\underline{H_2}$Ph), 5.45 (d, 1H, *J* = 13.4 Hz, OC$\underline{H_2}$Ph), 5.07 (d, 1H, *J* = 11.3 Hz, OC$\underline{H_2}$Ph), 4.91 (d, 1H, *J* = 11.4 Hz, OC$\underline{H_2}$Ph), 4.79 (d, 1H, *J* = 11.3 Hz, OC$\underline{H_2}$Ph), 4.71 (d, 1H, *J* = 12.1 Hz, OC$\underline{H_2}$Ph), 4.65 (d, 1H, *J* = 14.2 Hz, OC$\underline{H_2}$Ph), 4.64 (d, 1H, *J* = 3.4 Hz, C1^{Glc}-H), 4.62 (d, 1H, *J* = 12.2 Hz, OC$\underline{H_2}$Ph), 4.61 (d, 1H, *J* = 11.8 Hz, OC$\underline{H_2}$Ph), 4.60 (s, 1H, C1^{Rha}-H), 4.53 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.30 (d, 1H, *J* = 13.5 Hz, OC$\underline{H_2}$Ph), 4.29 (d, 1H, *J* = 11.4 Hz, OC$\underline{H_2}$Ph), 3.88–3.62 (m, 6H, C3^{Glc}-H, C6^{Glc}-H, C5^{Glc}-H, C6^{Glc}-H C4^{Glc}-H and C4^{Rha}-H), 3.53–3.49 (m, 2H, C2^{Glc}-H and C2^{Rha}-H), 3.40 (s, 3H, OMe), 3.35 (dd, 1H, *J* = 2.7, 9.6 Hz, C3^{Rha}-H), 3.25–3.18 (m, 1H, C5^{Rha}-H), 1.28 (d, 3H, *J* = 6.0 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.7, 138.39, 138.37, 138.0, 135.88, 135.86, 133.3, 133.1, 130.3, 129.3, 128.5, 128.4, 128.2, 128.14, 128.09, 128.00, 127.95, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127.0, 126.4, 126.1, 125.9, 101.6 (C1^{Rha}), 98.0 (C1^{Glc}), 81.8, 80.6, 80.1, 77.5, 77.4, 77.0, 76.7, 75.7, 75.5, 75.0, 73.3, 73.1, 73.0, 71.6, 69.6, 69.0, 67.9, 55.3, 18.1; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{53}H_{56}O_{10}Na$, 875.3771; found, 875.3785.

Benzyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (5r):



Following the general procedure of method A using trichloroacetimidate **2d** (51 mg, 0.09 mmol) and benzyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside **3r** (33 mg, 0.06 mmol) in Et_2O (6.0 mL) at –5 °C for 24 h afforded **5r** (16.8 mg, 30% yield of mixture isomers) as a colourless oil (eluent: acetone–toluene, 1:20; R_f = 0.60). $[\alpha]_D^{21}$ = +27.8 (*c* = 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–6.95 (m, 31H, ArH), 5.46 (d, 1H, *J* = 13.8 Hz, OC$\underline{H_2}$Ph), 5.44 (d, 1H, *J* = 13.4 Hz, OC$\underline{H_2}$Ph), 5.07 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.98–4.91 (m, 2H, OC$\underline{H_2}$Ph), 4.83 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.80 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.72 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.68 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.66 (d, 1H, *J* = 12.4 Hz, OC$\underline{H_2}$Ph), 4.62 (d, 1H, *J* = 13.4 Hz, OC$\underline{H_2}$Ph), 4.59 (d, 1H, *J* = 11.1 Hz, OC$\underline{H_2}$Ph), 4.54 (s, 1H, C1^{Rha}-H), 4.49 (d, 1H, *J* = 7.4 Hz, C1^{Glc}-H), 4.31 (d, 1H, *J* = 13.0 Hz, OC$\underline{H_2}$Ph), 4.28 (d, 1H, *J* = 11.0 Hz, OC$\underline{H_2}$Ph), 3.04 (dd, 1H, *J* = 1.72, 11.0 Hz, C4^{Glc}-H), 3.79–3.43 (m, 7H, C3^{Glc}-H, C4^{Rha}-H, C6^{Glc}-H, C5^{Glc}-H, C2^{Rha}-H and C2^{Glc}-H), 3.34 (dd, 1H, *J* = 2.7, 9.60 Hz, C3^{Rha}-H), 3.23–3.19 (m, 1H, C5^{Rha}-H), 1.30 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.9, 138.4, 137.4, 135.8, 135.7, 133.3, 128.6, 128.4, 128.39, 128.36, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.5, 127.5, 127.4, 127.0, 126.4, 126.1, 125.9, 102.1 (C1^{Glc}), 101.3 (C1^{Rha}), 84.4, 84.1, 82.3, 81.8, 80.6, 77.4, 77.2, 77.0, 76.7, 75.5, 75.0, 74.7, 74.5, 73.7, 73.3, 72.9, 71.6, 71.2, 71.0, 70.3, 69.8, 68.0, 18.1, 0.0; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{59}H_{60}O_{10}Na$, 951.4084; found, 951.4088.

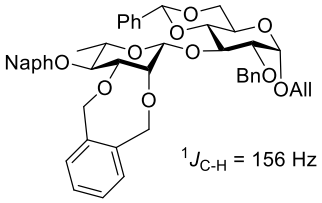
Benzyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (5s):



Following the general procedure of method A using trichloroacetimidate **2d** (51 mg, 0.09 mmol) and benzyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside **3s** (33 mg, 0.06 mmol) in Et_2O (6.0 mL) at –5 °C for 24 h afforded **5s** (31.4 mg, 55% yield of mixture isomers) as a colourless oil (eluent: acetone–toluene, 1:20; R_f = 0.55). $[\alpha]_D^{21}$ = –3.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86–7.12 (m, 31H, ArH), 5.54 (d, 1H, *J* = 13.1 Hz, OC$\underline{H_2}$Ph), 5.40 (d, 1H, *J* = 14.2 Hz, OC$\underline{H_2}$Ph), 5.29 (d, 1H, *J* = 10.3 Hz,

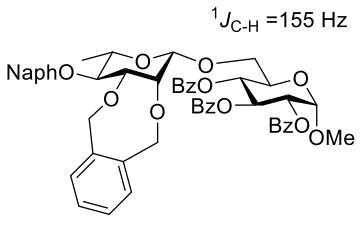
OCH$_2$Ph), 5.12 (d, 1H, *J* = 11.2 Hz, OCH$_2$Ph), 4.86 (d, 1H, *J* = 11.4 Hz, OCH$_2$Ph), 4.83 (d, 2H, *J* = 11.8 Hz, OCH$_2$Ph), 4.77 (d, 1H, *J* = 0.8 Hz, C1^{Rha}-H), 4.69 (d, 1H, *J* = 10.3 Hz, OCH$_2$Ph), 4.67 (d, 1H, *J* = 14.3 Hz, OCH$_2$Ph), 4.60 (d, 1H, *J* = 12.2 Hz, OCH$_2$Ph), 4.53 (d, 1H, *J* = 12.3 Hz, OCH$_2$Ph), 4.49 (d, 1H, *J* = 10.9 Hz, OCH$_2$Ph), 4.38 (d, 1H, *J* = 12.1 Hz, OCH$_2$Ph), 4.36 (d, 1H, *J* = 7.9 Hz, C1^{Glc}-H), 3.81–3.64 (m, 6H, C2^{Glc}-H, C6^{Glc}-H, C2^{Rha}-H, C4^{Rha}-H, C3^{Glc}-H and C6^{Glc}-H), 3.59–3.53 (m, 2H, C5^{Glc}-H and C3^{Rha}-H), 3.49–3.37 (m, 1H, C4^{Glc}-H), 3.33–3.29 (m, 1H, C5^{Rha}-H), 1.39 (d, 3H, *J* = 6.0 Hz, C6^{Rha}-H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 139.0, 138.4, 138.3, 138.2, 137.0, 136.6, 136.1, 133.4, 133.1, 130.9, 128.9, 128.8, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 126.8, 126.3, 126.1, 125.9, 102.1 (C1^{Glc}), 100.5 (C1^{Rha}), 83.5, 80.8, 80.0, 77.7, 77.4, 77.0, 76.7, 75.2, 75.1, 75.0, 75.0, 73.5, 73.1, 71.7, 71.3, 69.2, 67.5, 18.3; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{59}H_{60}O_{10}Na$, 951.4084; found, 951.4093.

Allyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-benzyl-α-D-glucopyranoside (5t):



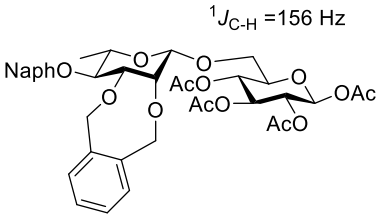
Following the general procedure of method A using trichloroacetimidate **2d** (34 mg, 0.06 mmol) and Allyl 4,6-*O*-benzylidene-3-*O*-benzyl-β-D-glucopyranoside **3t** (16.3 mg, 0.04 mmol) in Et$_2$O (4.0 mL) at –5 °C for 24 h afforded **5t** (21 mg, 65% yield of mixture isomers) as a colourless oil (eluent: acetone–toluene, 1:12; R_f = 0.50). $[\alpha]_D^{21}$ = +53.8 (*c* = 0.5, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.85–7.07 (m, 20H, ArH), 6.49 (d, 1H, *J* = 7.6 Hz, ArCH), 5.93–5.84 (m, 1H, CH=CH$_2$), 5.58 (d, 1H, *J* = 12.8 Hz, OCH$_2$Ph), 5.40 (s, 1H, ArCH), 5.34 (d, 1H, *J* = 14.6 Hz, OCH$_2$Ph), 5.28 (dd, 1H, *J* = 1.7, 17.2 Hz, CH$_2$CH=CH$_2$), 5.20 (dd, 1H, *J* = 1.6, 10.2 Hz, CH$_2$CH=CH$_2$), 5.10 (d, 1H, *J* = 11.2 Hz, OCH$_2$Ph), 4.98 (d, 1H, *J* = 12.3 Hz, OCH$_2$Ph), 4.82 (d, 1H, *J* = 11.2 Hz, OCH$_2$Ph), 4.79 (s, 1H, C1^{Rha}-H), 4.75 (d, 1H, *J* = 14.6 Hz, OCH$_2$Ph), 4.74 (d, 1H, *J* = 12.3 Hz, OCH$_2$Ph), 4.63 (d, 1H, *J* = 3.8 Hz, C1^{Glc}-H), 4.33 (d, 1H, *J* = 12.8 Hz, OCH$_2$Ph), 4.24–4.19 (m, 1H, C6^{Glc}-H), 4.15 (t, 1H, *J* = 6.9 Hz, C3^{Glc}-H), 4.14–4.09 (m, 1H, CH=CH$_2$), 4.00–3.97 (m, 1H, CH=CH$_2$), 3.94 (d, 1H, *J* =2.9 Hz, C2^{Rha}-H), 3.87–3.82 (m, 1H, C5^{Glc}-H), 3.77 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.65 (t, 1H, *J* = 10.3 Hz, C6^{Glc}-H), 3.61–3.57 (m, 2H, C2^{Glc}-H and C4^{Glc}-H), 3.53 (t, 1H, *J* = 9.4 Hz, C3^{Rha}-H), 3.33–3.30 (m, 1H, C5^{Rha}-H), 1.39 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 138.7, 137.7, 137.1, 136.8, 135.9, 133.6, 133.3, 133.1, 131.3, 129.2, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 127.8, 127.7, 127.6, 126.9, 126.3, 126.2, 126.0, 125.9, 118.5, 101.9, 101.8 (C1^{Rha}), 97.1 (C1^{Glc}), 81.3, 79.1, 78.9, 78.4, 77.4, 77.24, 77.15, 77.1, 77.0, 76.7, 74.9, 74.0, 73.4, 71.8, 69.1, 68.6, 67.1, 62.1, 29.7, 18.3, 0.0; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{48}H_{50}O_{10}Na$, 809.3302; found, 809.3311.

Methyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-benzoyl-α-D-glucopyranoside (5u):



Following the general procedure of method A using trichloroacetimidate **2d** (68.9 mg, 0.13 mmol) and methyl 2,3,4-*tri*-*O*-benzoyl-α-D-glucopyranoside **3u** (42.3 mg, 0.08 mmol) in Et$_2$O (8.3 mL) at –5 °C for 24 h afforded **5u** (55.7 mg, 82% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:10; R_f = 0.45). $[\alpha]_D^{21}$ = +84.5 (*c* = 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.98–6.99 (m, 26H, ArH), 6.14 (t, 1H, *J* = 9.8 Hz, C3^{Glc}-H), 5.56–5.52 (m, 2H, C4^{Glc}-H and C6^{Glc}-H), 5.33 (d, 1H, *J* = 14.6 Hz, OCH$_2$Ph), 5.23–5.19 (m, 2H, C2^{Glc}-H and C1^{Glc}-H), 5.10 (d, 1H, *J* = 11.2 Hz, OCH$_2$Ph), 4.81 (d, 1H, *J* = 11.2 Hz, OCH$_2$Ph), 4.65 (d, 1H, *J* = 14.7 Hz, OCH$_2$Ph), 4.42 (s, 1H, C1^{Rha}-H), 4.35 (d, 1H, *J* = 12.7 Hz, C5^{Glc}-H), 4.25–4.21 (m, 1H, C6^{Glc}-H), 4.12 (dd, 1H, *J* = 4.7, 11.5 Hz, C3^{Rha}-H), 3.79–3.73 (m, 2H, C4^{Rha}-H and C2^{Rha}-H), 3.47 (s, 3H, OMe), 3.33 (t, 1H, *J* = 7.4 Hz, C5^{Rha}-H), 1.35 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR (CDCl$_3$, 151 MHz): δ 165.8, 165.3, 137.4, 136.9, 135.9, 133.34, 133.28, 133.1, 133.0, 131.5, 129.9, 129.7, 129.3, 129.11, 129.08, 128.43, 128.41, 128.36, 128.3, 128.2, 128.1, 127.9, 127.69, 127.67, 126.9, 126.3, 126.1, 125.9, 100.3 (C1^{Rha}), 96.9 (C1^{Glc}), 78.7, 77.3, 77.1, 77.0, 76.8, 74.9, 73.5, 72.2, 71.7, 70.5, 68.5, 68.3, 67.0, 55.6, 29.7, 18.0; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{53}H_{50}O_{13}Na$, 917.3149; found, 917.3164.

Acetyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→6)-2,3,4-*tri*-*O*-acetyl-β-D-glucopyranoside (5v):

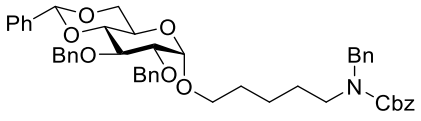


Following the general procedure of method A using trichloroacetimidate **2d** (69.0 mg, 0.13 mmol) and acetyl 2,3,4-*tri*-*O*-acetyl-β-D-glucopyranoside **3v** (29.4 mg, 0.08 mmol) in Et_2O (8 mL) at –5 °C for 24 h afforded **5v** (43.8 mg, 78% yield of mixture isomers) as a colourless oil (eluent: EtOAc–hexane, 1:2; R_f = 0.30). $[\alpha]_D^{21}$ = +54.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–7.20 (m, 11H, ArH), 5.67 (d, 1H, *J* = 8.2 Hz, C1^{Glc}-H), 5.61 (d, 1H, *J* = 13.0 Hz, OC$\underline{H_2}$Ph), 5.47 (d, 1H, *J* = 14.4 Hz, OC$\underline{H_2}$Ph), 5.23 (t, 1H, *J* = 9.4 Hz, C3^{Glc}-H), 5.16–5.05 (m, 3H, C4^{Glc}-H, OC$\underline{H_2}$Ph and C2^{Glc}-H), 4.83 (d, 1H, *J* = 11.1 Hz, OC$\underline{H_2}$Ph), 4.79 (d, 1H, *J* = 14.6 Hz, OC$\underline{H_2}$Ph), 4.46 (d, 1H, *J* = 13.1 Hz, OC$\underline{H_2}$Ph), 4.40 (s, 1H, C1^{Rha}-H), 3.97 (dd, 1H, *J* = 3.7, 11.9 Hz, C6^{Glc}-H), 3.94 (d, 1H, *J* = 2.6 Hz, C2^{Rha}-H), 3.80–3.68 (m, 4H, C5^{Glc}-H, C4^{Rha}-H, C3^{Rha}-H and C6^{Glc}-H), 3.36–3.32 (m, 1H, C5^{Rha}-H), 2.07 (s, 3H, Me), 2.02 (s, 3H, Me), 2.01 (s, 3H, Me), 1.94 (s, 3H, Me), 1.39 (d, 3H, *J* = 6.1 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 169.3, 169.0, 137.8, 136.4, 135.9, 133.3, 133.1, 130.9, 129.1, 128.2, 128.2, 127.9, 127.9, 127.7, 126.9, 126.3, 126.1, 125.9, 100.3 (C1^{Rha}), 91.8 (C1^{Glc}), 79.6, 77.4, 77.2, 77.0, 76.7, 76.0, 75.0, 73.7, 73.2, 73.0, 71.8, 70.4, 68.6, 67.5, 66.9, 20.8, 20.6, 20.6, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{39}H_{44}O_{14}Na$, 759.2629; found, 759.2645.

4-Methoxyphenyl 2,3-*O*-(o-xylylene)-4-*O*-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (5w):

Following the general procedure of method A using trichloroacetimidate **2d** (51 mg, 0.09 mmol) and 4-methoxyphenyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside **3w** (25.5 mg, 0.03 mmol) in Et_2O (3.0 mL) at –5 °C for 24 h afforded **5w** (39.0 mg, 70% yield of mixture isomers) as a colourless oil (eluent: acetone–toluene, 1:15; R_f = 0.45). $[\alpha]_D^{21}$ = +19.7 (*c* = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85–6.80 (m, 45H, ArH), 5.60 (d, 1H, *J* = 12.6 Hz, OC$\underline{H_2}$Ph), 5.36 (d, 1H, *J* = 15.0 Hz, OC$\underline{H_2}$Ph), 5.11 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 5.03 (d, 1H, *J* = 11.0 Hz, OC$\underline{H_2}$Ph), 4.97 (d, 1H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.93 (d, 1H, *J* = 10.9 Hz, OC$\underline{H_2}$Ph), 4.90 (d, 1H, *J* = 13.1 Hz, OC$\underline{H_2}$Ph), 4.83 (d, 1H, *J* = 10.9 Hz, OC$\underline{H_2}$Ph), 4.82 (d, 1H, *J* = 5.3 Hz, C1^{Glc}-H), 4.78 (d, 1H, *J* = 11.0 Hz, OC$\underline{H_2}$Ph), 4.76 (d, 1H, *J* = 11.0 Hz, OC$\underline{H_2}$Ph), 4.75 (d, 1H, *J* = 11.3 Hz, OC$\underline{H_2}$Ph), 4.62 (d, 1H, *J* = 15.0 Hz, OC$\underline{H_2}$Ph), 4.54 (d, 1H, *J* = 13.1 Hz, OC$\underline{H_2}$Ph), 4.42 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.38 (d, 1H, *J* = 5.0 Hz, C1^{Gal}-H), 4.35 (s, 1H, C1^{Rha}-H), 4.33 (d, 1H, *J* = 12.5 Hz, OC$\underline{H_2}$Ph), 4.32 (d, 1H, *J* = 11.8 Hz, OC$\underline{H_2}$Ph), 4.28 (d, 1H, *J* = 11.9 Hz, OC$\underline{H_2}$Ph), 4.19 (d, 1H, *J* = 11.8 Hz, OC$\underline{H_2}$Ph), 4.12 (d, 1H, *J* = 3.1 Hz, C4^{Gal}-H), 3.93–3.88 (m, 1H, C3^{Glc}-H), 3.83 (t, 1H, *J* = 9.3 Hz, C4^{Rha}-H), 3.79–3.70 (m, 8H, C5^{Glc}-H, C6^{Glc}-H, C2^{Gal}-H, $\underline{Me}$ of OMP and C2^{Rha}-H), 3.64–3.62 (m, 1H, C2^{Glc}-H), 3.53 (dd, 1H, *J* = 2.8 Hz, 9.6 Hz, C3^{Rha}-H), 3.46–3.42 (m, 1H, C4^{Glc}-H), 3.33–3.22 (m, 5H, C6^{Gal}-H, C5^{Gal}-H, C3^{Glc}-H and C5^{Rha}-H), 1.38 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.3, 151.7, 139.1, 138.9, 138.8, 138.5, 138.4, 137.4, 137.3, 136.8, 135.9, 133.3, 133.1, 131.7, 128.6, 128.3, 128.18, 128.15, 128.12, 128.07, 127.9, 127.8, 127.8, 127.74, 127.69, 127.6, 127.4, 127.3, 126.9, 126.3, 126.1, 125.9, 118.5, 114.5, 103.2 (C1^{Rha}), 102.7 (C1^{Glc}), 101.0 (C1^{Gal}), 82.8, 81.4, 79.7, 78.9, 77.8, 77.34, 77.27, 77.02, 76.98, 76.7, 75.3, 75.2, 74.8, 73.5, 73.0, 72.2, 71.8, 70.5, 67.4, 67.0, 55.7, 29.7, 18.1, 0.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{86}H_{88}O_{16}Na$, 1399.5970; found, 1399.5983.

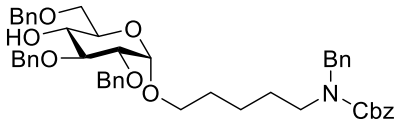
***N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (8):**



Following the general procedure of method A using trichloroacetimidate **6** (1.32 g, 2.23 mmol) and acceptor **7** (487 mg, 1.49 mmol) in Et_2O (150.0 mL) at room temperature for 48 h afforded **8** (977 mg, 87% yield) as a colourless oil (eluent: EtOAc–hexane, 1:15; R_f = 0.30).^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.14 (m, 25H, ArH), 5.55 (s, 1H, Ar$\underline{CH}$), 5.16 (d, 2H, *J*

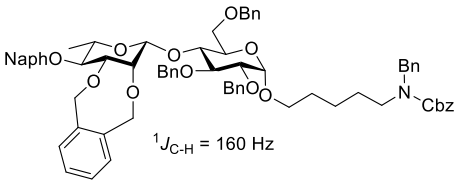
= 3.6 Hz, OCH$_2$Ph), 4.91 (d, 1H, *J* = 11.2 Hz, OCH$_2$Ph), 4.82 (d, 1H, *J* = 11.3 Hz, OCH$_2$Ph), 4.81 (d, 1H, *J* = 12.2 Hz, OCH$_2$Ph), 4.69 (s, 1H, C1^{Glc}-H), 4.65 (d, 1H, *J* = 12.3 Hz, OCH$_2$Ph), 4.48 (d, 2H, *J* = 5.4 Hz, OCH$_2$Ph), 4.25–4.22 (m, 1H, C6^{Glc}-H), 4.03 (t, 1H, *J* = 9.2 Hz, C3^{Glc}-H), 3.83–3.80 (m, 1H, C5^{Glc}-H), 3.69 (t, 1H, *J* = 10.3 Hz, C6^{Glc}-H), 3.60 (t, 1H, *J* = 9.4 Hz, C4^{Glc}-H), 3.54 (dd, 1H, *J* = 3.8, 9.3 Hz, C2^{Glc}-H), 3.36 (s, 1H, CH$_2$), 3.25 (s, 1H, CH$_2$), 3.20 (s, 1H, CH$_2$), 1.57–1.24 (m, 7H, CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 138.9, 138.3, 137.9, 137.4, 128.9, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 127.87, 127.85, 127.6, 127.3, 126.0, 101.2 (ArCH), 98.1 (C1^{Glc}), 82.3, 79.5, 78.6, 77.3, 77.0, 76.7, 75.3, 73.5, 69.1, 67.2, 62.5, 29.2, 23.4; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{47}H_{51}NO_8Na$, 780.3512; found, 780.3524.

_N_-Benzyl-_N_-benzyloxycarbonyl-5-aminopentyl-2,3,6-tri-_O_-benzyl-α-D-glucopyranoside (9):



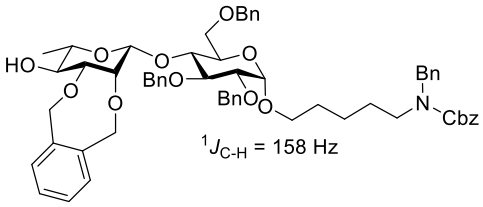
Following the general procedure of method C of reductive ring-opening reaction of 4,6-*O*-acetal with BH$_3$ • Et$_2$O: To a solution of BH$_3$ • Et$_2$O (1.3 mL, 10.56 mmol) in anhydrous DCM (10.5 mL) was added compound **8** (1.0 g, 1.32 mmol) and Et$_3$SiH (2.1 mL, 13.19 mmol) in anhydrous DCM (13.2 mL) at 0 °C and the reaction mixture was stirred at room temperature for 15 minutes. The reaction was quenched by the addition of saturated aqueous NaHCO$_3$, extracted with ethyl acetate (3 ×50 mL), washed with brine, dried with Na$_2$SO$_4$, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 5:1) afforded the title compound **9** (529 mg, 53% yield) as a coloreless oil. TLC (hexane–EtOAc, 4:1): R_f = 0.30. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.37–7.15 (m, 25H, ArH), 5.16 (d, 2H, *J* = 11.6 Hz, OCH$_2$Ph), 4.99 (d, 1H, *J* = 11.4 Hz, OCH$_2$Ph), 4.75–4.71 (m, 3H, OCH$_2$Ph and C1^{Glc}-H), 4.61 (d, 1H, *J* = 12.0 Hz, OCH$_2$Ph), 4.57 (d, 1H, *J* = 12.2 Hz, OCH$_2$Ph), 4.52 (d, 1H, *J* = 12.2 Hz, OCH$_2$Ph), 4.48 (d, 2H, *J* = 6.5 Hz, OCH$_2$Ph), 3.78 (t, 1H, *J* = 9.1 Hz, C3^{Glc}-H), 3.74–3.57 (m, 4H, C5^{Glc}-H, C6^{Glc}-H and C4^{Glc}-H), 3.51 (dd, 1H, *J* = 3.6, 9.5 Hz, C2^{Glc}-H), 3.35–3.19 (m, 3H, CH$_2$), 1.63–1.22 (m, 7H, CH$_2$); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 139.0, 138.3, 138.1, 137.9, 128.6, 128.53, 128.47, 128.44, 128.41, 128.36, 128.0, 127.9, 127.91, 127.85, 127.8, 127.64, 127.61, 127.56, 127.3, 97.0 (C1^{Glc}), 81.6, 79.8, 77.4, 77.3, 77.1, 76.7, 75.4, 73.6, 72.9, 71.0, 70.1, 69.6, 68.0, 67.2, 31.5, 30.2, 29.7, 29.1; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{47}H_{53}NO_8Na$, 782.3669; found, 782.3661.

_N_-Benzyl-_N_-benzyloxycarbonyl-5-aminopentyl 2,3-_O_-(o-xylylene)-4-_O_-(2-naphthylmethyl)-β-L-rhamnopyranosyl-(1→4)-2,3,6-tri-_O_-benzyl-α-D-glucopyranoside (10):



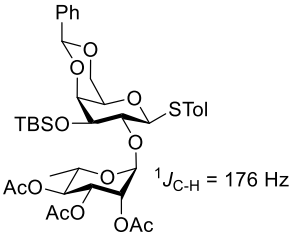
Following the general procedure of method A using trichloroacetimidate **2d** (229 mg, 0.42 mmol) and compound **9** (210 mg, 0.28 mmol) in Et$_2$O (27.7 mL) at –5 °C for 48 h afforded **10** (160 mg, 50% yield of mixture isomers) as a colourless oil (eluent: EtOAc–toluene, 1:4; R_f = 0.45). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.80 (s, 1H, ArH), 7.68–6.80 (m, 36H, ArH), 5.44 (d, 1H, *J* = 13.6 Hz, OCH$_2$Ph), 5.34 (d, 1H, *J* = 13.5 Hz, OCH$_2$Ph), 5.23–5.16 (m, 2H, OCH$_2$Ph), 5.13 (d, 1H, *J* = 11.6 Hz, OCH$_2$Ph), 4.94 (d, 1H, *J* = 11.7 Hz, OCH$_2$Ph), 4.85 (s, 1H, C1^{Glc}-H), 4.75 (s, 1H, C1^{Rha}-H), 4.72 (d, 1H, *J* = 11.6 Hz, OCH$_2$Ph), 4.66 (d, 2H, *J* = 11.3 Hz, OCH$_2$Ph), 4.58 (d, 1H, *J* = 12.2 Hz, OCH$_2$Ph), 4.49–4.40 (m, 3H, OCH$_2$Ph), 4.38 (d, 1H, *J* = 11.7 Hz, OCH$_2$Ph), 4.30 (d, 1H, *J* = 10.7 Hz, OCH$_2$Ph), 4.23 (d, 1H, *J* = 13.6 Hz, OCH$_2$Ph), 4.21–4.16 (m, 3H, C5^{Glc}-H, C3^{Glc}-H and C6^{Glc}-H), 4.01–3.97 (m, 1H, C6^{Glc}-H), 3.90–3.85 (m, 1H, C4^{Glc}-H), 3.77 (t, 1H, *J* = 9.2 Hz, C4^{Rha}-H), 3.71–3.70 (m, 1H, CH$_2$), 3.59 (d, 1H, *J* = 2.8 Hz, C2^{Rha}-H), 3.55 (dd, 1H, *J* = 3.5, 9.6 Hz, C2^{Glc}-H), 3.47 (dd, 1H, *J* = 2.7, 9.4 Hz, C3^{Rha}-H), 3.24–3.17 (m, 3H, C5^{Rha}-H and CH$_2$), 3.04 (s, 1H, CH$_2$), 1.49–1.09 (m, 9H, CH$_2$ and C6^{Rha}-H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 139.5, 139.1, 138.9, 138.7, 138.5, 136.8, 133.6, 133.2, 128.4, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 126.5, 126.3, 125.9, 125.6, 101.1 (C1^{Rha}), 96.5 (C1^{Glc}), 82.2, 81.0, 78.1, 75.3, 74.7, 73.1, 72.8, 72.2, 71.6, 70.7, 70.0, 67.8, 29.1, 23.4, 18.2; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{72}H_{77}NO_{12}Na$, 1170.5343; found, 1170.5351.

_N_-Benzyl-_N_-benzyloxycarbonyl-5-aminopentyl 2,3-_O_-(o-xylylene)-β-L-rhamnopyranosyl-(1→4)-2,3,6-tri-_O_-benzyl-α-D-glucopyranoside (11):



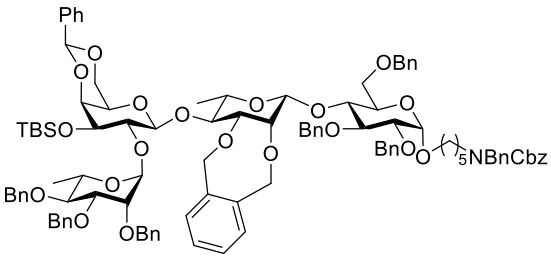
Following the general procedure of method E of NAP group removal: To a magnetically stirred solution of DDQ (52 mg, 1.5 mmol) was added slowly to a stirring solution of the NAP protected compound **10** (174 mg, 1.0 mmol) in a mixture of CH_2Cl_2 (0.55 mL) and distilled water (55 μL) and the resulting reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with EtOAc (20 mL), washed with saturated aqueous $Na_2S_2O_3$, H_2O and brine, dried with Na_2SO_4 and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 2:1) afforded the title compound **11** (55 mg, 55% yield) as a coloreless oil. TLC (hexane–EtOAc, 2:1): R_f = 0.45. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–6.93 (m, 29H, ArH), 5.43 (d, 1H, *J* = 13.7 Hz, OC$\underline{H_2}$Ph), 5.37 (d, 1H, *J* = 13.6 Hz, OC$\underline{H_2}$Ph), 5.18 (d, 2H, *J* = 11.2 Hz, OC$\underline{H_2}$Ph), 4.94 (d, 1H, *J* = 15.4 Hz, OC$\underline{H_2}$Ph), 4.75 (s, 1H, C1^{Glc}-H), 4.67–4.48 (m, 8H, OC$\underline{H_2}$Ph and C1^{Rha}-H), 4.29 (d, 1H, *J* = 13.8 Hz, OC$\underline{H_2}$Ph), 4.26 (d, 1H, *J* = 12.9 Hz, OC$\underline{H_2}$Ph), 3.85–3.77 (m, 4H, C6^{Glc}-H, C3^{Glc}-H and C4^{Glc}-H), 3.74–3.69 (m, 1H, C5^{Glc}-H), 3.69 (t, 1H, *J* = 9.4 Hz, C4^{Rha}-H), 3.60 (s, 1H, CH_2), 3.56 (t, 1H, *J* = 1.3 Hz, C2^{Rha}-H), 3.50 (dd, 1H, *J* = 3.6, 9.5 Hz, C2^{Glc}-H), 3.35–3.19 (m, 3H, CH_2), 3.17–3.12 (m, 1H, C5^{Rha}-H), 3.03 (dd, 1H, *J* = 2.9, 9.7 Hz, C3^{Rha}-H), 2.29 (s, 1H, OH), 1.58–1.25 (m, 9H, CH_2 and C6^{Rha}-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.7, 138.5, 138.1, 138.0, 129.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.5, 127.44, 127.35, 127.3, 101.9 (C1^{Rha}), 96.4 (C1^{Glc}), 81.9, 80.2, 77.4, 77.1, 76.7, 75.4, 73.3, 72.8, 72.1, 69.9, 69.5, 68.9, 68.0, 67.2, 29.7, 29.1, 25.6, 23.4, 20.9, 20.7, 17.7, 0.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{61}H_{69}NO_{12}Na$, 1030.4717; found, 1030.4710.

Tolyl 2,3,4-tri-_O_-benzyl-α-L-rhamnopyranosyl-(1→2)-3-_O_-tert-butyldimethylsilyl-4,6-_O_-(phenylmethylene)-β-D-galacopyranoside (14):



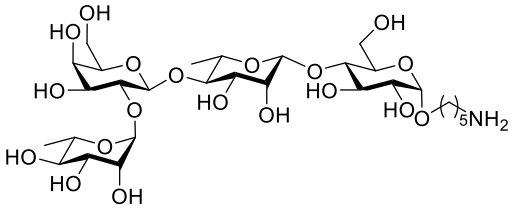
Compound **12**[12] (570 mg, 1.17 mmol) and compound **13**[13] (1.1657 g, 2.68 mmol) were combined in a flask, coevaporated with toluene (3 × 3 mL), and dissolved in anhydrous CH_2Cl_2 to maintain a concentration of 0.01 M (based on the donor). Powdered freshly activated molecular sieves (100 mg/mL solvent) were added, and the mixture was stirred for 30 min at –40 °C. A solution of TMSOTf in anhydrous CH_2Cl_2 was added to the mixture and stirred at –40 °C for 2 h. The reaction was quenched by the addition of Et_3N and diluted with EtOAc, then filtered through a pad of Celite® and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 2:1) afforded the title compound **14** (696 mg, 78% yield with uncertain by-product) as a coloreless oil. TLC (hexane–EtOAc, 4:1): R_f = 0.30; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47–6.95 (m, 9H, ArH), 5.35 (s, 1H, Ar$\underline{CH}$), 5.30 (dd, 1H, *J* = 1.8, 3.2 Hz, C2^{Rha}-H), 5.18 (d, 1H, *J* = 1.7 Hz, C1^{Rha}-H), 5.17 (dd, 1H, *J* = 3.5, 10.2 Hz, C3^{Rha}-H), 5.00 (t, 1H, *J* = 10.0 Hz, C4^{Rha}-H), 4.60–4.54 (m, 1H, C5^{Rha}-H), 4.51 (d, 1H, *J* = 9.5 Hz, C1^{Gal}-H), 4.24 (dd, 1H, *J* = 1.6, 12.4 Hz, C6^{Gal}-H), 4.00 (t, 1H, *J* = 9.0 Hz, C4^{Gal}-H), 3.98 (d, 1H, *J* = 3.4 Hz, C2^{Gal}-H), 3.90 (dd, 1H, *J* = 1.7, 12.4 Hz, C6^{Gal}-H), 3.84 (dd, 1H, *J* = 3.4, 8.8 Hz, C3^{Gal}-H), 3.36 (s, 1H, C5^{Gal}-H), 2.23 (s, 3H, $\underline{Me}$ of Tol), 2.02 (s, 3H, $\underline{Me}$ of OAc), 1.99 (s, 3H, $\underline{Me}$ of OAc), 1.90 (s, 3H, $\underline{Me}$ of OAc), 1.12 (d, 3H, *J* = 6.2 Hz, C6^{Rha}-H), 0.76 (s, 9H, $\underline{Me}$ of TBS), 0.00 (s, 6H, $\underline{Me}$ of TBS); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.9, 132.7, 129.9, 129.7, 129.5, 129.2, 128.9, 128.1, 126.2, 100.8 (ArCH), 98.8 (C1^{Rha}), 86.2 (C1^{Gal}), 76.7, 76.4, 74.8, 70.8, 69.73, 69.71, 69.5, 69.3, 67.4, 25.7, 21.2, 21.1, 20.9, 20.9, 20.8, 20.7, 20.6, 18.1, 17.7, 17.2, -3.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{38}H_{52}O_{12}SSiNa$, 783.2846; found, 783.2838.

_N_-Benzyl-_N_-benzyloxycarbonyl-5-aminopentyl 2,3,4-tri-_O_-benzyl-α-L-rhamnopyranosyl-(1→2)-3-_O_-_t_-butyldimethylsilyl-4,6-_O_-(phenylmethylene)-β-D-galacopyranosyl-(1→4)-2,3-_O_-(o-xylylene)-β-L-rhamnopyranosyl-(1→4)-2,3,6-tri-_O_-benzyl-α-D-glucopyranoside (16):



Compound **14** (17.4 mg, 0.023 mmol) and compound **11** (15.4 mg, 0.015 mmol) were dissolved in anhydrous MeCN/CH_2Cl_2 (3:1, 1.3 mL). Powdered freshly activated molecular sieves (100 mg/mL solvent) were added, and the mixture was stirred for 1 h at –40 ℃. NIS (3.4 mg, 0.015 mmol) was added to the mixture and stirred for 30 min at –40 ℃. Then a solution of TfOH (0.4 μL, 0.005 mmol) in anhydrous CH_2Cl_2 was added to the mixture and stirred at –40 ℃ for 16 h. The reaction was diluted with EtOAc, then filtered through a pad of Celite® and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: hexane–EtOAc, 1:1) afforded the title compound **15** (17.5 mg, 70% yield) as a coloreless oil. TLC (toluene–acetonitrile, 6:1): R_f = 0.50; To a magnetically stirred solution of NaOMe (0.22 mg, 0.004 mmol) was added to compound **15** (34 mg, 0.02 mmol) in anhydrous MeOH (0.55 mL) at 0 ℃ and stirred at room temperature for 30 min. After complete consumption of starting material, the reaction mixture was neutralized with Amberlite 120 H^+ resin, filtered and concentrated under vacuum to afforded the intermediate. To a magnetically stirred solution of the intermediate in anhydrous DMF (1 mL) was added sodium hydride (60% dispersion in oil, 3 mg, 0.12 mmol, 6.0 equiv.) in small portions at 0 °C. After 15 min, benzyl bromide (10 μL, 0.08 mmol, 4.0 equiv.) was added dropwise for 30 s and stirred at room temperature. Complete consumption of starting materials was observed after 2 h, followed by dropwise addition of MeOH and ice-water to quench excess reagents. The reaction mixture was extracted with DCM (2 × 10 mL), washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: toluene–acetonitrile, 6:1) afforded the title compound **16** (22.8 mg, 62% yield) as a coloreless oil; R_f = 0.45; ^{1}H NMR (C_6D_6, 600 MHz): δ 7.61–6.96 (m, 49H, ArH), 5.67 (d, 1H, _J_ = 12.6 Hz, OC<u>H</u>$_2$Ph), 5.56 (d, 1H, _J_ = 1.7 Hz, C1^{Glc1}-H), 5.37 (d, 1H, _J_ = 14.6 Hz, OC<u>H</u>$_2$Ph), 5.22 (s, 1H, ArC<u>H</u>), 5.17–5.11 (m, 3H, OC<u>H</u>$_2$Ph), 5.01 (d, 1H, _J_ = 11.6 Hz, OC<u>H</u>$_2$Ph), 4.90 (d, 1H, _J_ = 11.2 Hz, OC<u>H</u>$_2$Ph), 4.85 (d, 1H, _J_ = 7.7 Hz, C1^{Gal3}-H), 4.80 (d, 1H, _J_ = 2.9 Hz, C1^{Rha4}-H), 4.79 (d, 1H, _J_ = 11.6 Hz, OC<u>H</u>$_2$Ph), 4.76 (s, 1H, C1^{Rha2}-H), 4.75 (d, 1H, _J_ = 11.8 Hz, OC<u>H</u>$_2$Ph), 4.73 (s, 2H, OC<u>H</u>$_2$Ph), 4.61–4.56 (m, 4H, C5^{Rha2}-H and OC<u>H</u>$_2$Ph), 4.50 (d, 1H, _J_ = 12.1 Hz, OC<u>H</u>$_2$Ph), 4.49 (d, 1H, _J_ = 11.2 Hz, OC<u>H</u>$_2$Ph), 4.43 (s, 1H, C<u>H</u>$_2$), 4.38–4.35 (m, 3H, OC<u>H</u>$_2$Ph), 4.31 (dd, 1H, _J_ = 2.8, 9.4 Hz, C3^{Glc1}-H), 4.29 (d, 1H, _J_ = 10.3 Hz, OC<u>H</u>$_2$Ph), 4.26–4.21 (m, 3H, C4^{Gal3}-H, C4^{Rha4}-H and C2^{Glc1}-H), 4.12–4.10 (m, 3H, C3^{Rha2}-H, C5^{Gal3}-H and C5^{Glc1}-H), 3.93–3.84 (m, 4H, C4^{Rha2}-H, C6-H and C4^{Glc1}-H), 3.75 (dd, 1H, _J_ = 2.8, 10.3 Hz, C3^{Gal3}-H), 3.73 (dd, 1H, _J_ = 1.6, 7.3 Hz, C3^{Rha4}-H), 3.63–3.62 (m, 3H, C2^{Gal3}-H, C6-H and C2^{Rha4}-H), 3.48 (dd, 1H, _J_ = 3.5, 9.6 Hz, C2^{Rha2}-H), 3.38–3.34 (m, 1H, C5^{Rha4}-H), 3.12–2.95 (m, 4H, C6-H and C<u>H</u>$_2$), 1.59 (d, 3H, _J_ = 6.1 Hz, C6^{Rha4}-H), 1.41–1.12 (m, 9H, C<u>H</u>$_2$ and C6^{Rha2}-H), 0.88 (s, 9H, C<u>H</u>$_3$ of TBS), 0.08 (s, 3H, C<u>H</u>$_3$ of TBS), 0.00 (s, 3H, C<u>H</u>$_3$ of TBS); ^{13}C NMR (C_6D_6, 151 MHz): δ 139.5, 139.4, 139.3, 139.2, 139.1, 138.8, 138.6, 138.4, 128.6, 128.4, 128.4, 128.3, 128.21, 128.17, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.4, 127.4, 127.31, 127.29, 127.23, 127.17, 127.0, 126.4, 101.9 (C1^{Gal3}), 101.2 (Ar<u>C</u>H), 100.7 (C1^{Rha4}), 99.4 (C1^{Glc1}), 96.5 (C1^{Rha2}), 81.6, 81.5, 81.0, 81.0, 77.2, 76.5, 75.9, 75.6, 75.1, 74.7, 73.4, 73.1, 72.4, 72.2, 72.1, 71.7, 70.7, 70.3, 68.9, 68.1, 67.7, 66.9, 65.8, 29.8, 29.8, 29.1, 25.8, 23.3, 18.5, 18.1, 18.0, -4.2, -4.2; HRMS (ESI-TOF) _m/z_: [M + Na]$^+$ calcd for $C_{107}H_{125}NO_{21}SiNa$, 1810.8411; found, 1810.8418.

5-aminopentyl α-L-rhamnopyranosyl-(1→2)-β-D-galacopyranosyl-(1→4)-β-L-rhamnopyranosyl-(1→4)-α-D-glucopyranoside (1b):



Following the general procedure of method B of deprotection of TBS: To a solution of starting material **16** (15.8 mg, 0.004 mmol) in anhydrous THF (1 mL), TBAF (35 μL, 0.035 mmol, 1M in THF, 4 equiv.) was added at the same temperature. The reaction mixture was stirred at room temperature for

3 h. The mixtue was diluted with EtOAc (5 mL), washed with saturated aqueous $NaHCO_3$ and brine, dried with Na_2SO_4, and concentrated under vacuum. The following purification by flash chromatography on silica gel (eluent: acetonitrile–toluene, 1:6) afforded the intermediate **17** (11.3 mg, 76% yield) as a coloreless oil; R_f = 0.50. Following the general procedure of Method D of global deprotection: To a magnetically stirred solution of fully protected compound **17** (11.3 mg) in EtOH (2 mL) was added Pd/C (10 wt%, 20 mg), and then the mixture was stirred under H_2 at room temperature for 48 h, after which complete consumption of starting materials was observed. The reaction mixture was filtered through a short Celite® pad, washed with methanol, and evaporated in vacuo, followed by flash chromatography on silica gel (eluent: H_2O–acetonitrile, 1:3) to afforded the desired product **1b** (3.6 mg, 75% yield) as a white soild. TLC (acetonitrile–H_2O, 3:1): R_f = 0.40. ^{1}H NMR (CD_3OD, 400 MHz): δ 5.60 (d, 1H, *J* = 8.6 Hz, C1-H), 5.16 (s, 1H, C1-H), 4.96–4.62 (m, 4H, C1-H and C1-H), 4.33–4.08 (m, 6H), 3.99–3.40 (m, 27H), 3.09–2.83 (m, 5H), 2.42 (d, 2H, *J* = 2.8 Hz), 2.11–2.01 (m, 3H), 1.79–1.70 (m, 2H), 1.54–1.44 (m, 3H), 1.28–1.24 (m, 2H), 0.96–0.90 (m, 2H); ^{13}C NMR (CD_3OD, 100 MHz): δ 101.9, 101.7, 101.1, 98.7, 78.6, 78.4, 76.8, 73.6, 72.2, 72.0, 71.8, 71.2, 70.9, 67.2, 66.6, 66.4, 61.8, 60.1, 42.1, 39.2, 31.7, 29.3, 28.4, 26.8, 25.1, 22.8, 22.3, 21.6, 16.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{29}H_{53}NO_{19}Na$, 719.3212; found, 719.3267.

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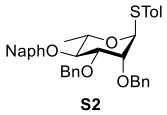
NMR spectra of all new compounds



S2

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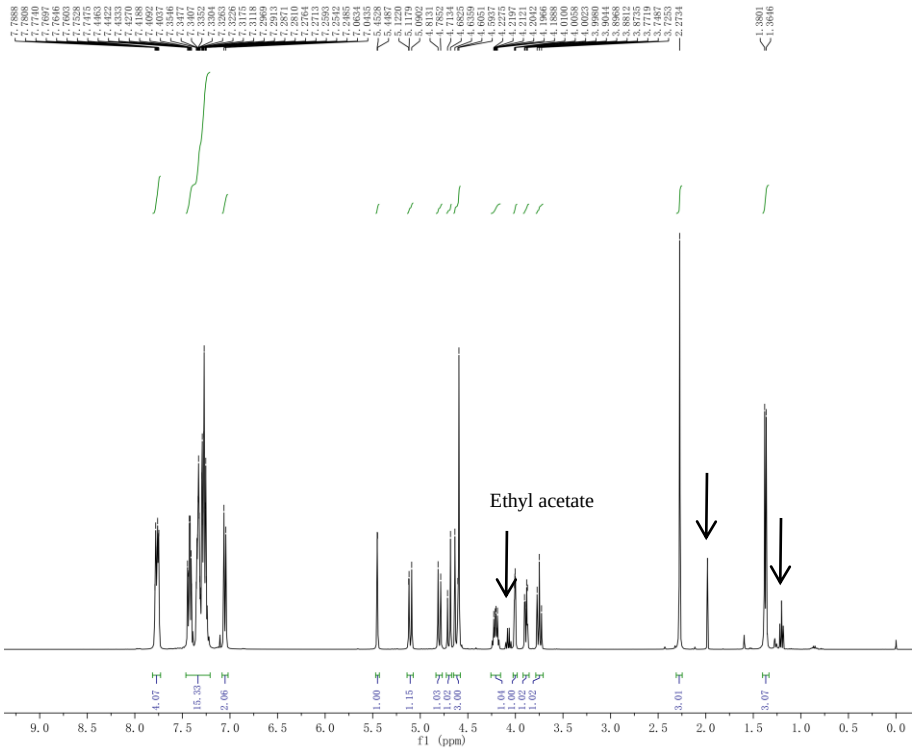

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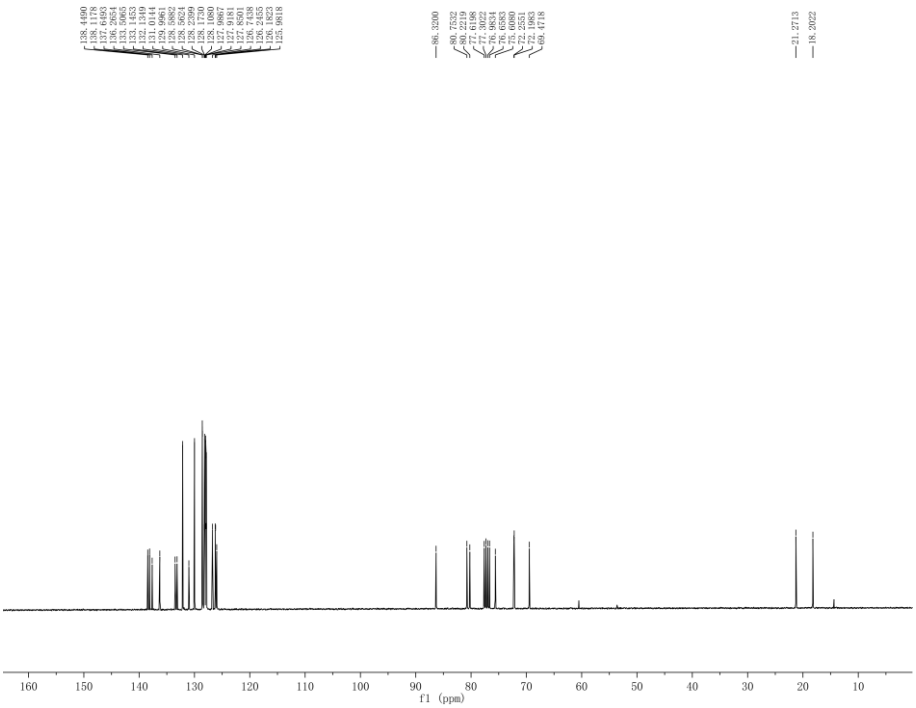

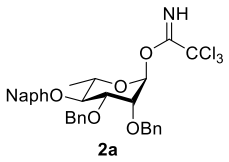

2a

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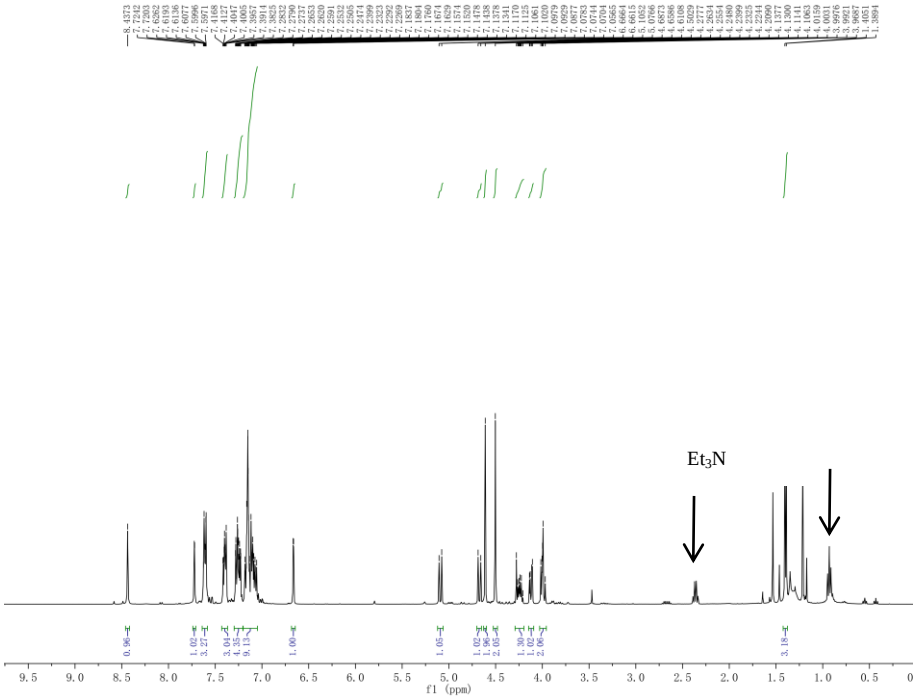

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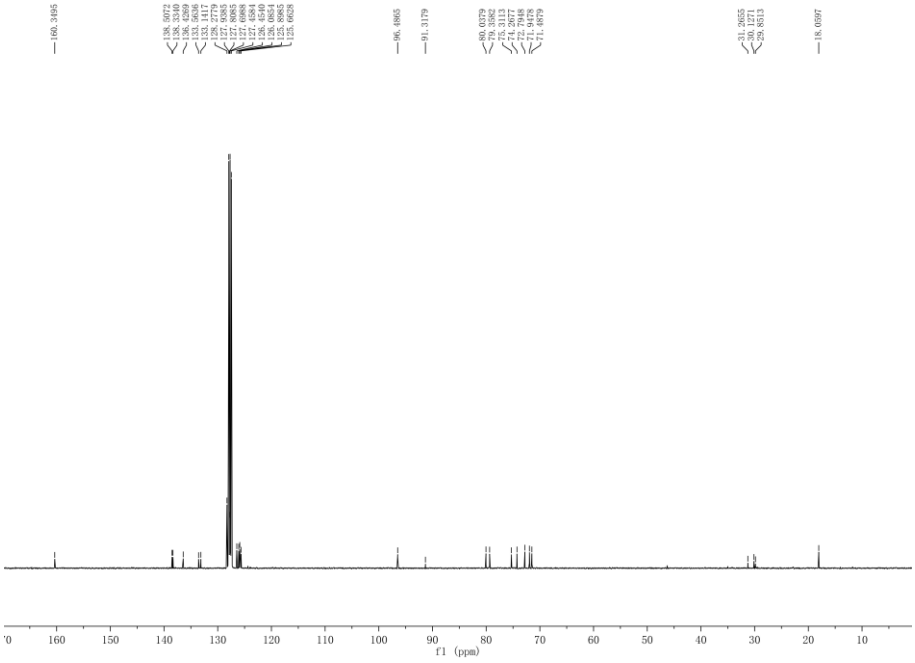

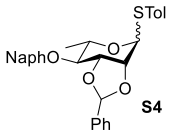

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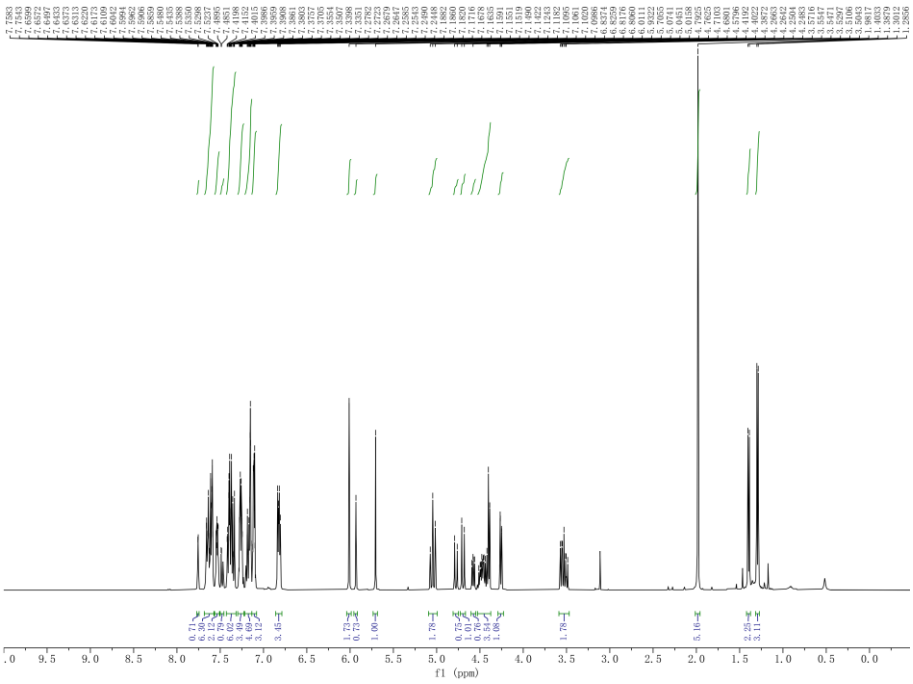

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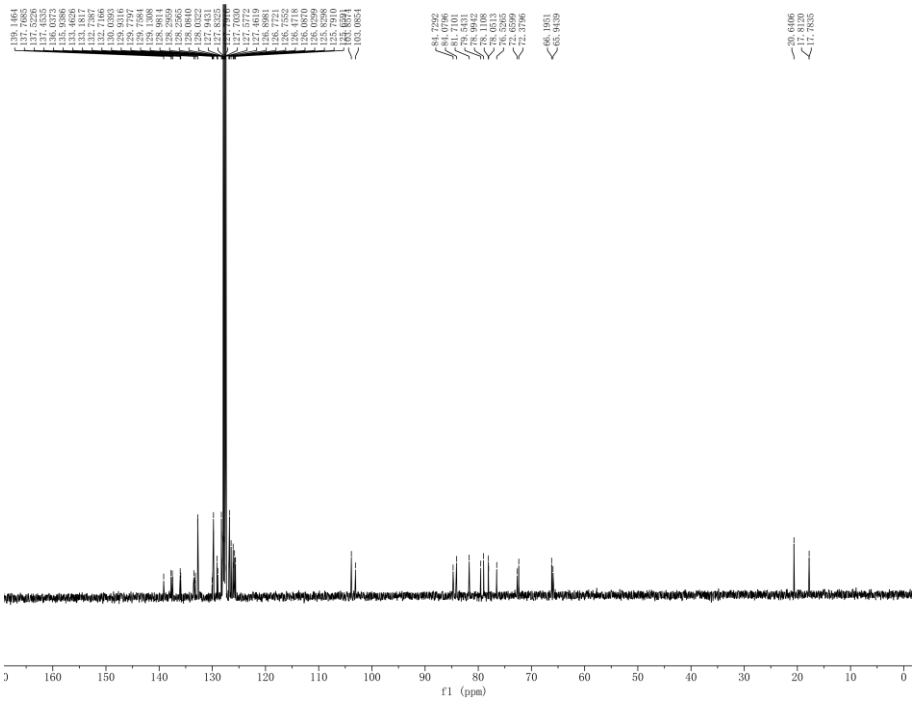

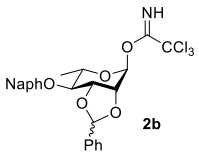

2b

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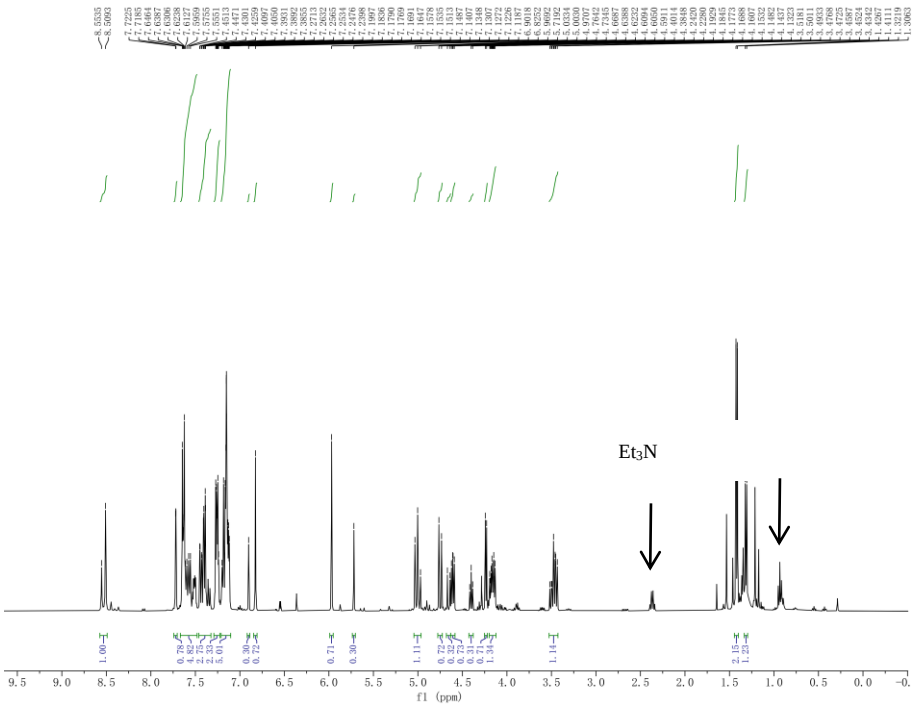

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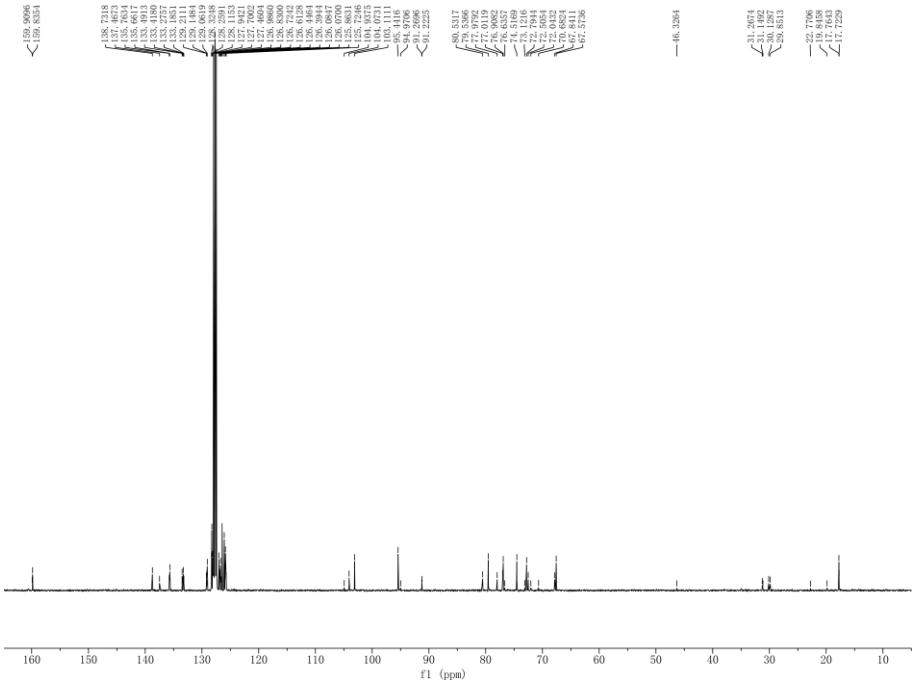

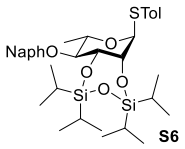

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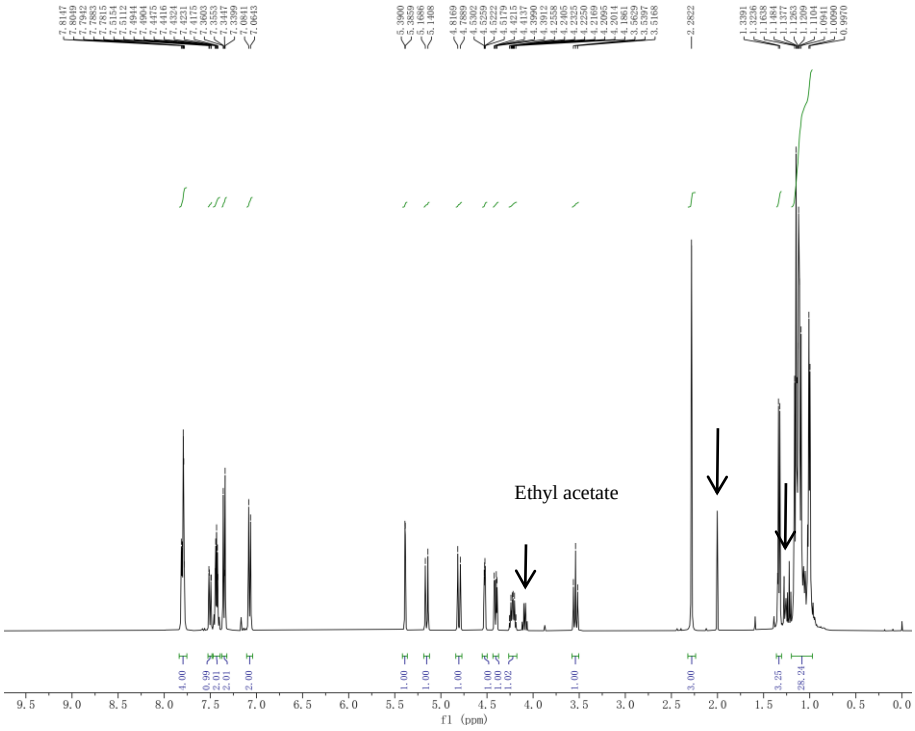

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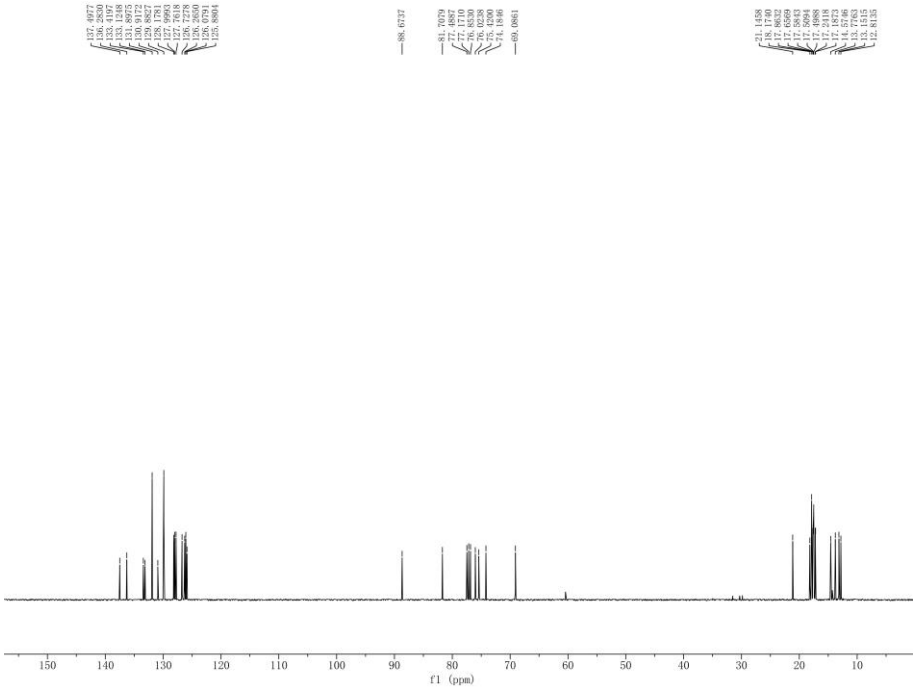

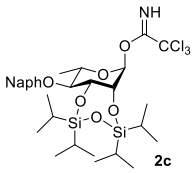

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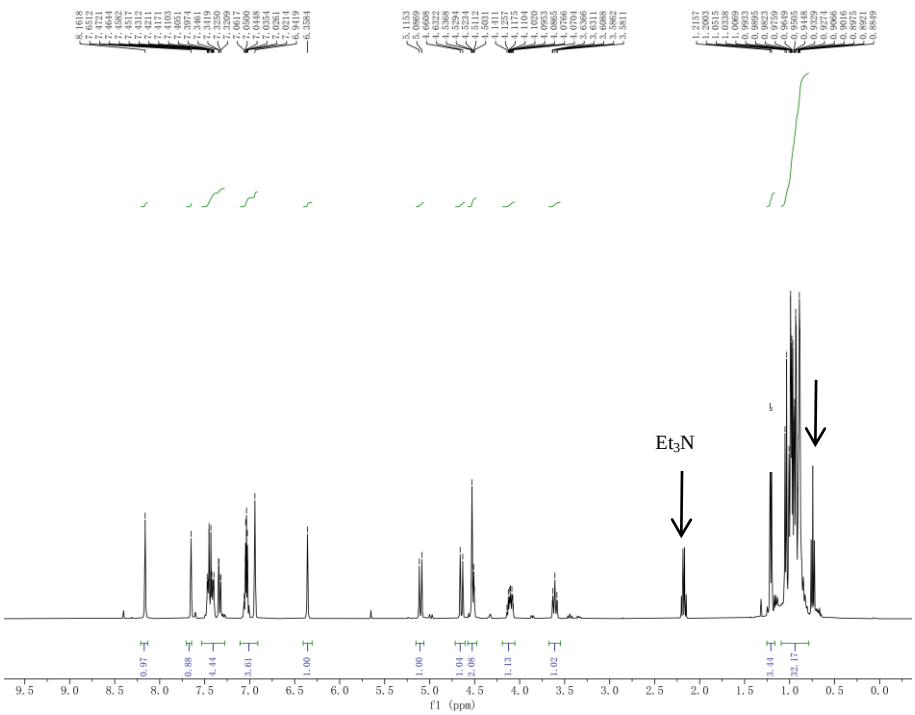

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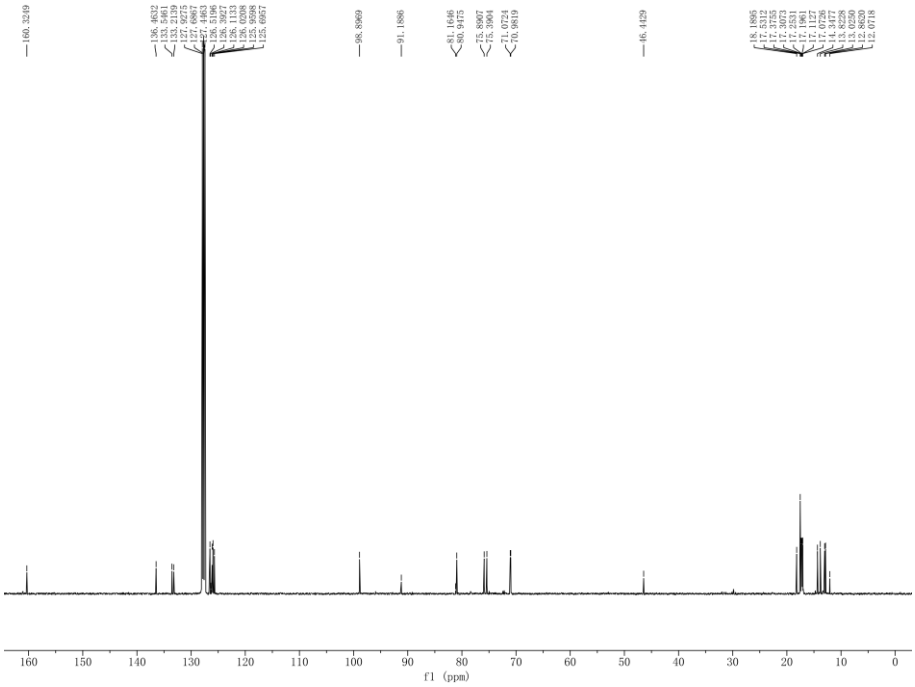

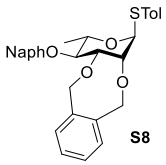

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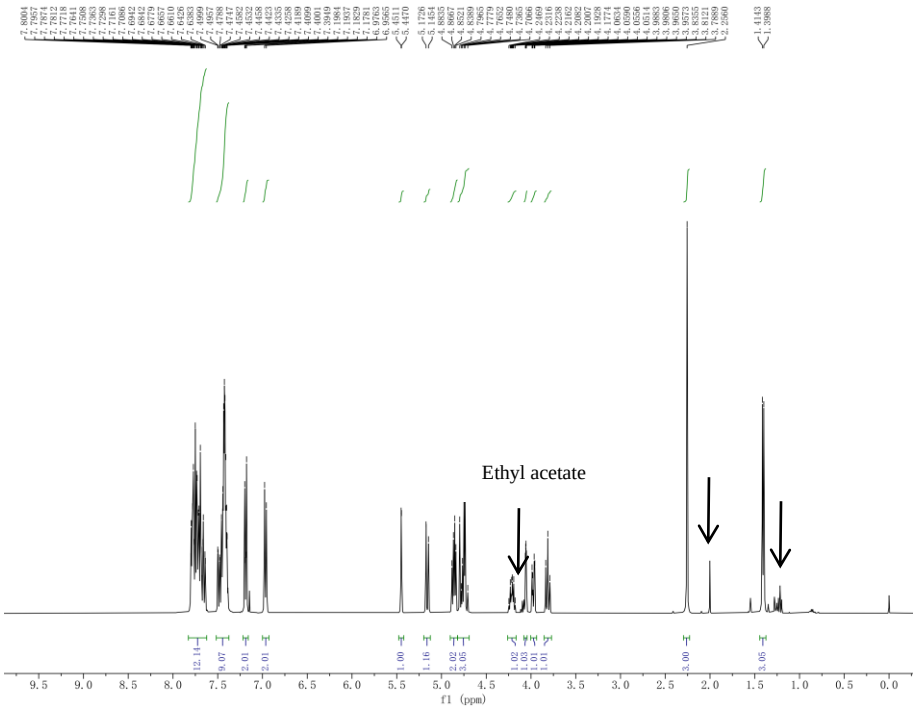

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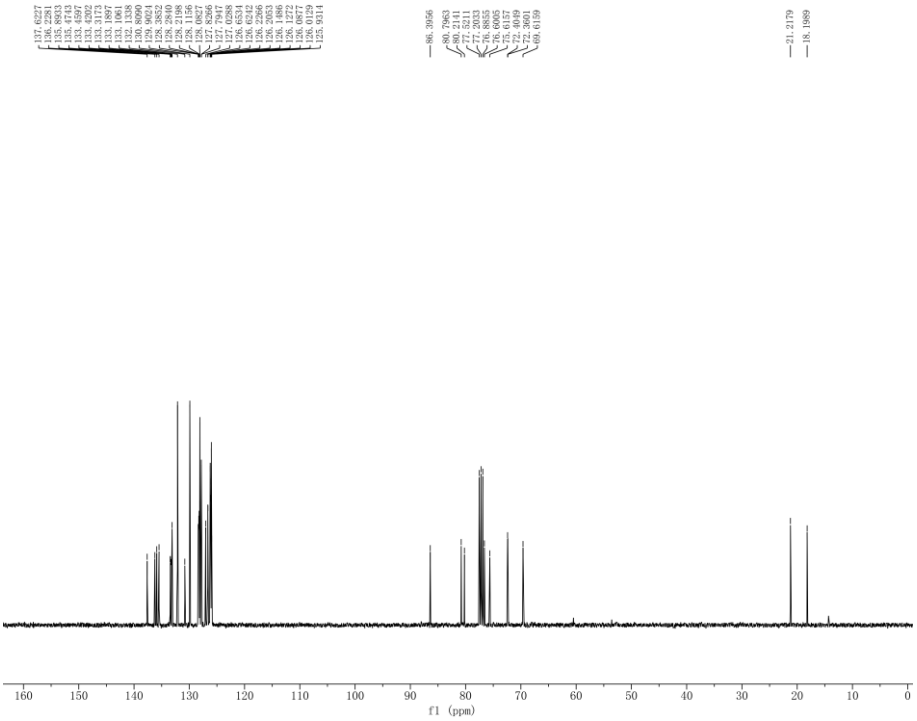

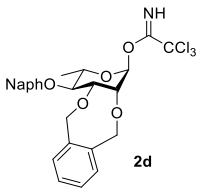

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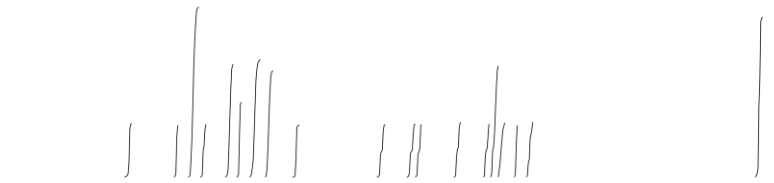

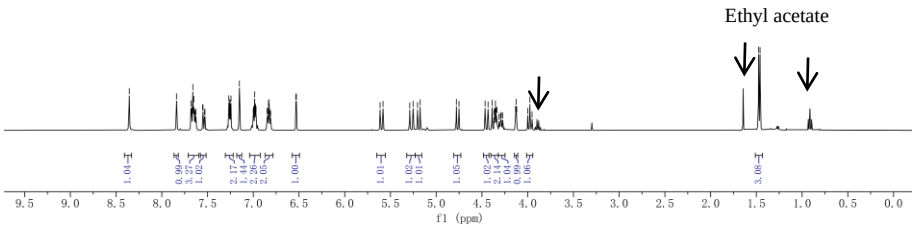

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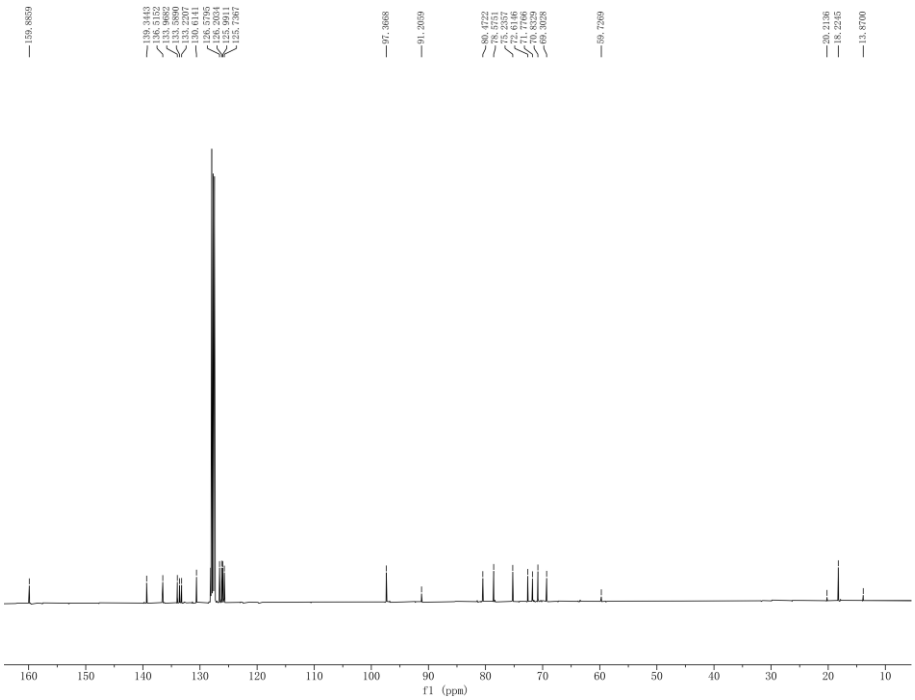

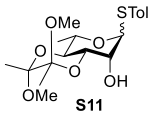

S11

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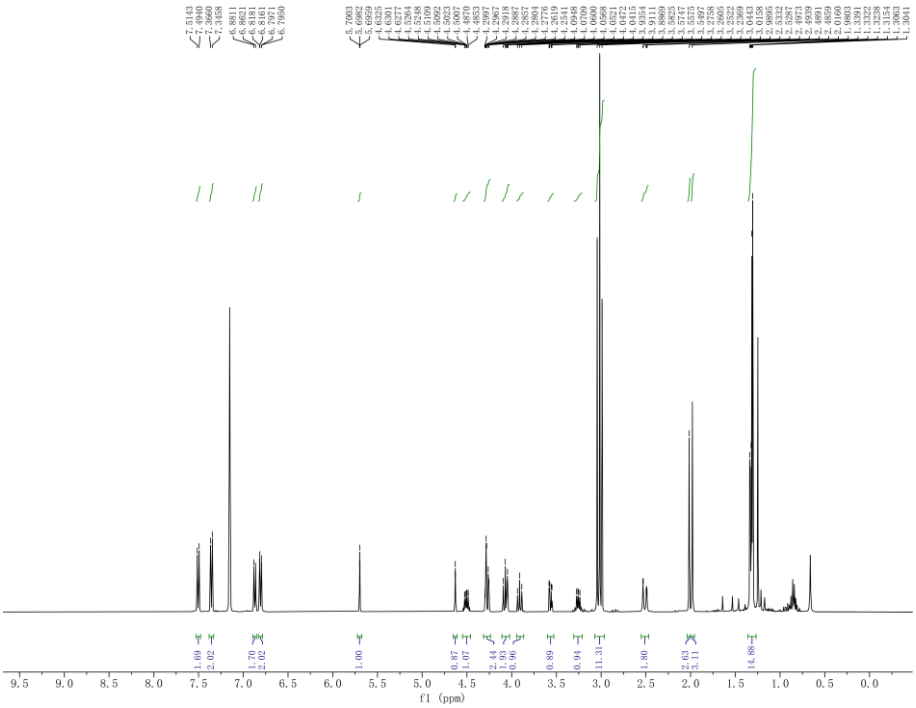
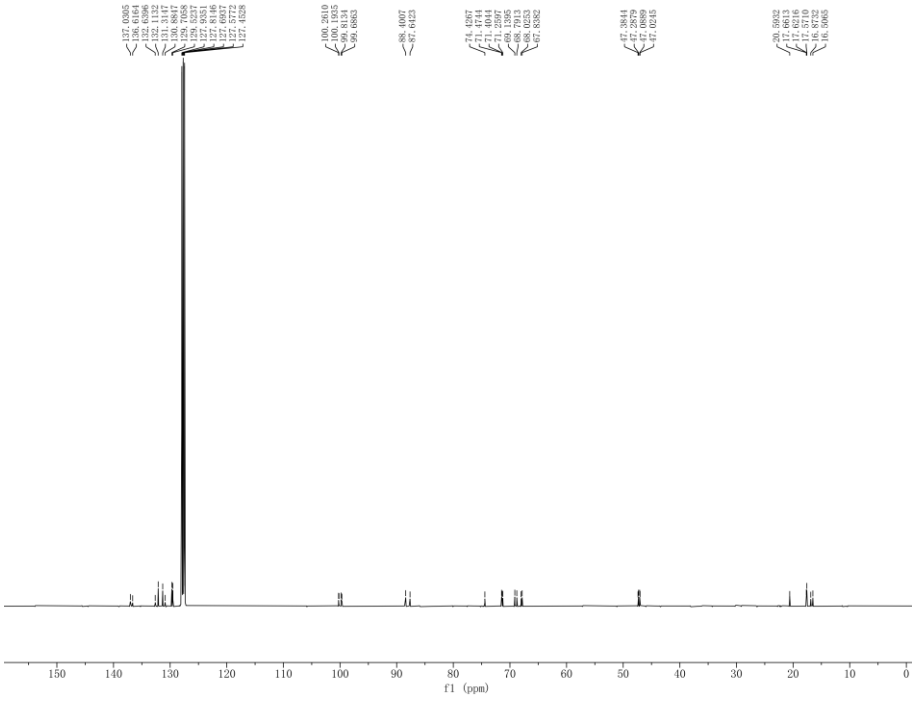
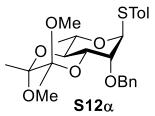


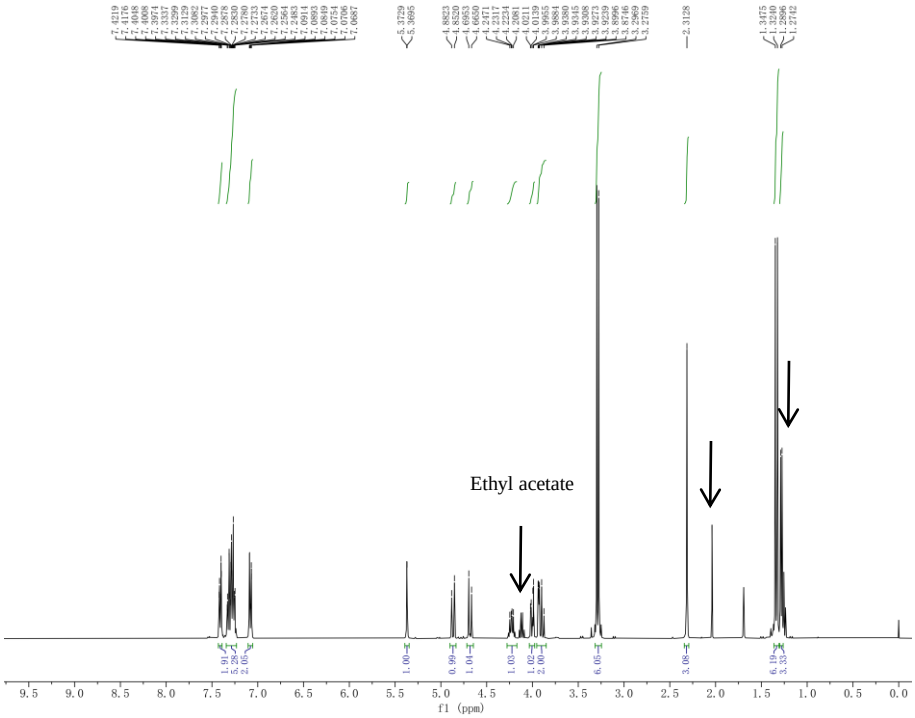
^{13}C NMR, 100 MHz, C_6D_6



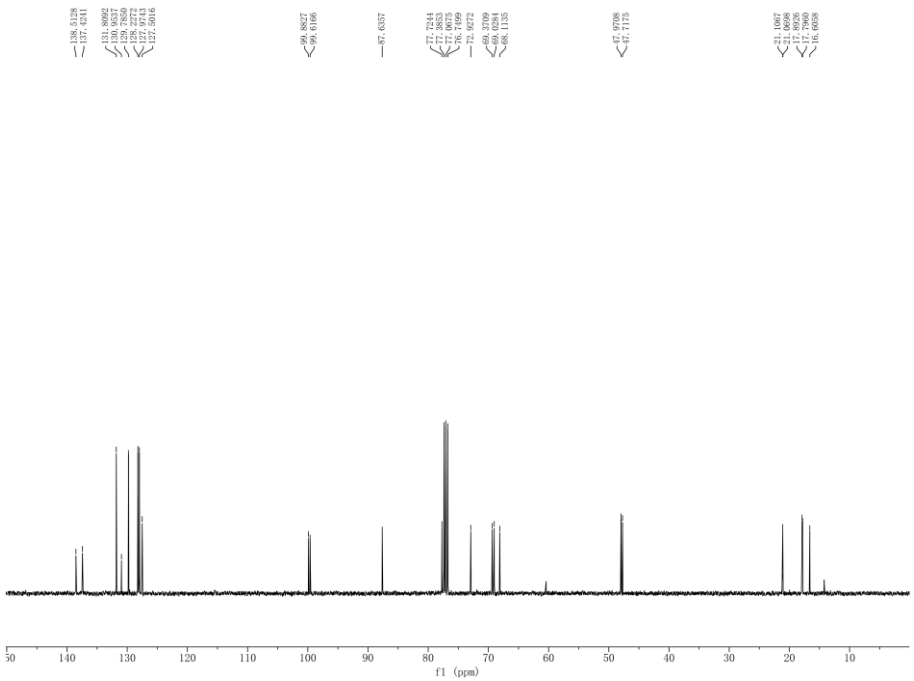


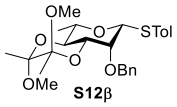
S12α

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



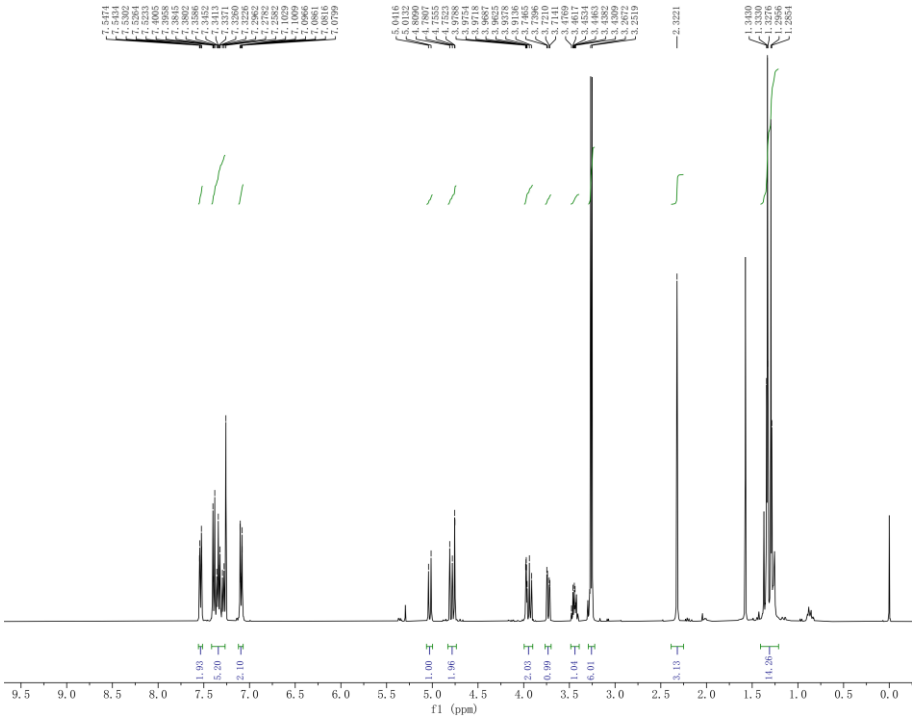
^{13}C NMR, 100 MHz, $CDCl_3$



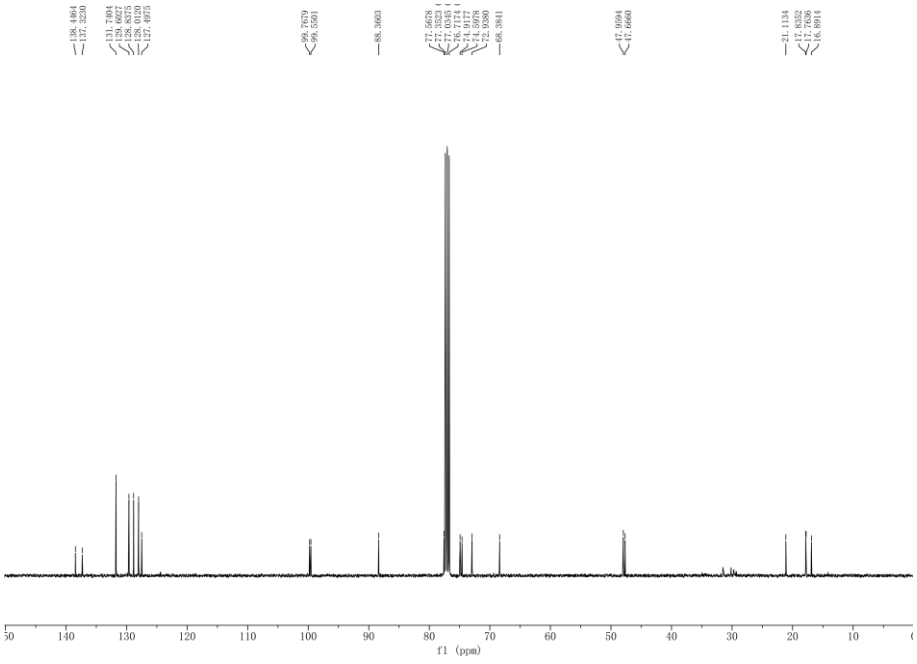


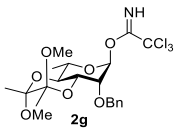
S12β

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

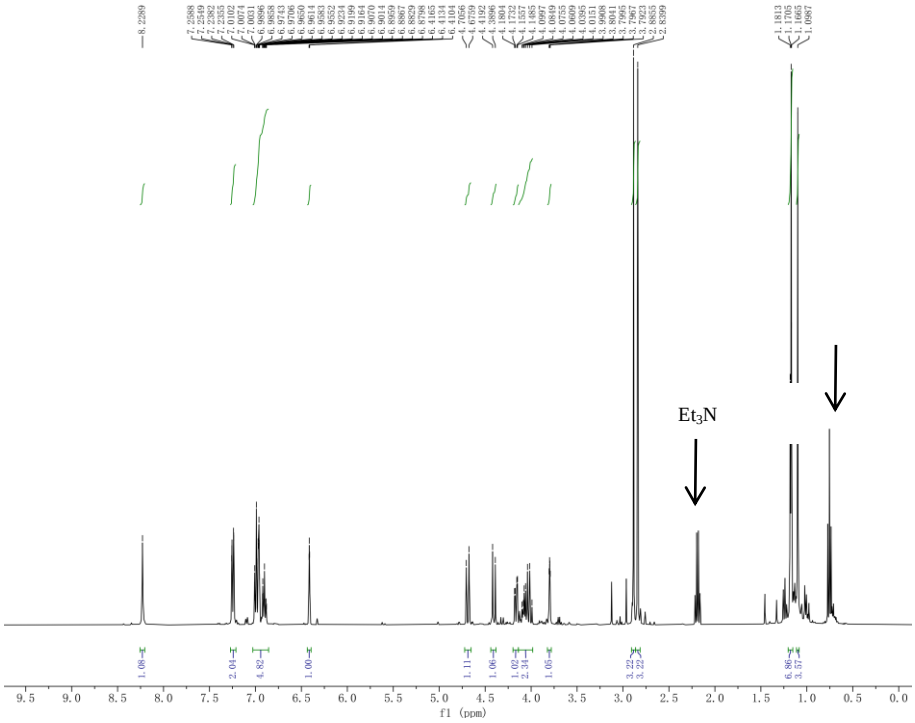


^{13}C NMR, 100 MHz, $CDCl_3$

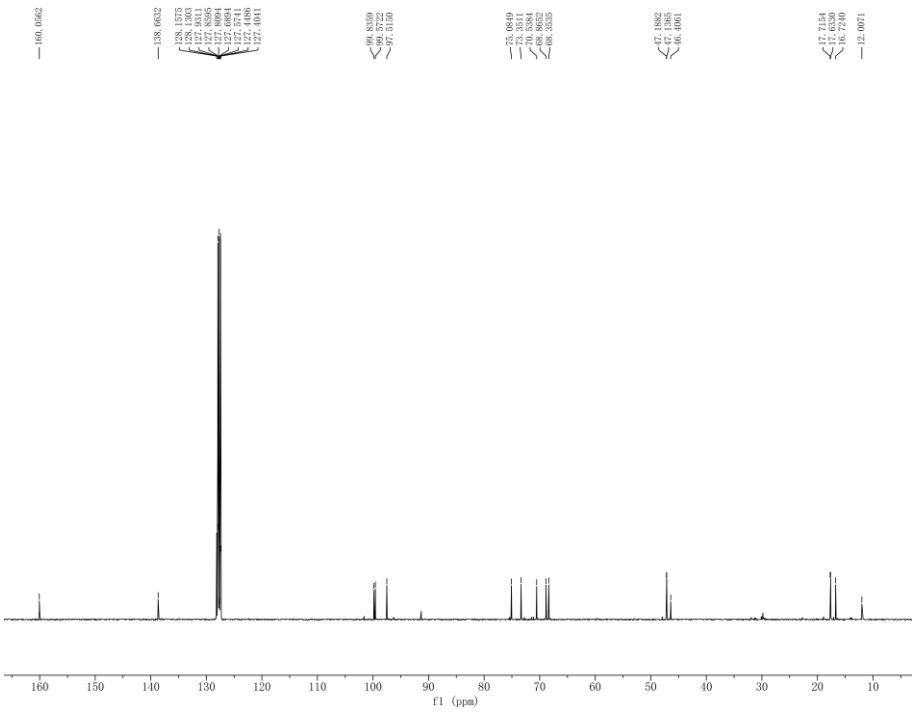


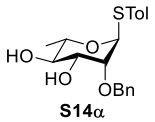


^{1}H NMR, 400 MHz, C_6D_6



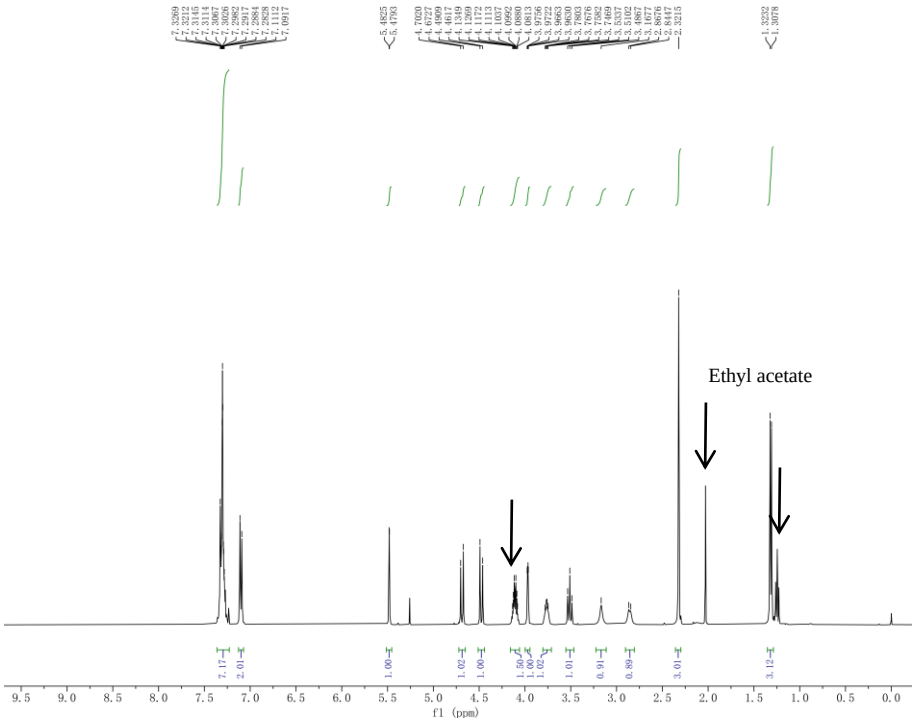
^{13}C NMR, 100 MHz, C_6D_6



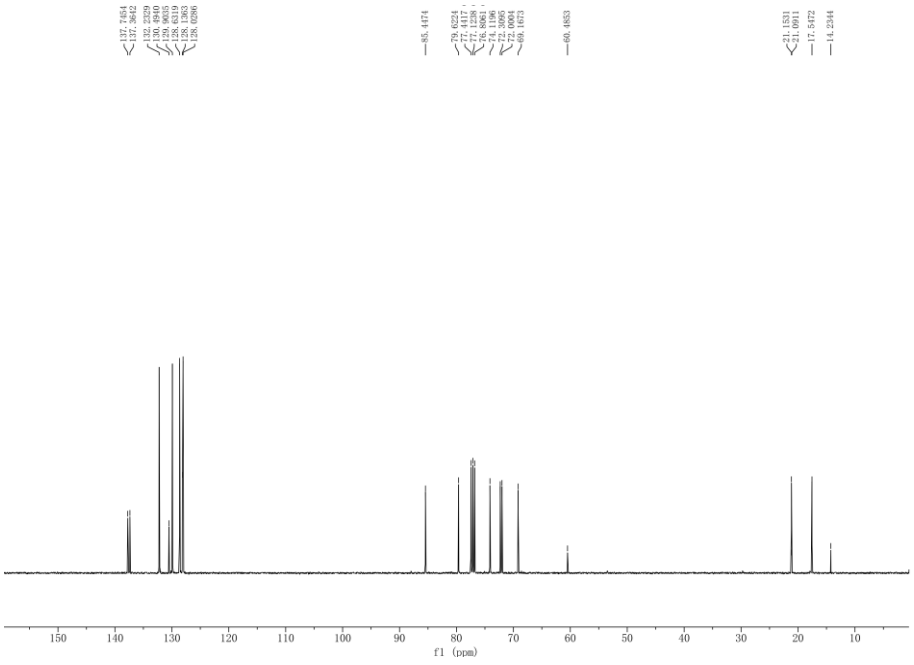


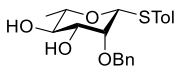
S14α

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



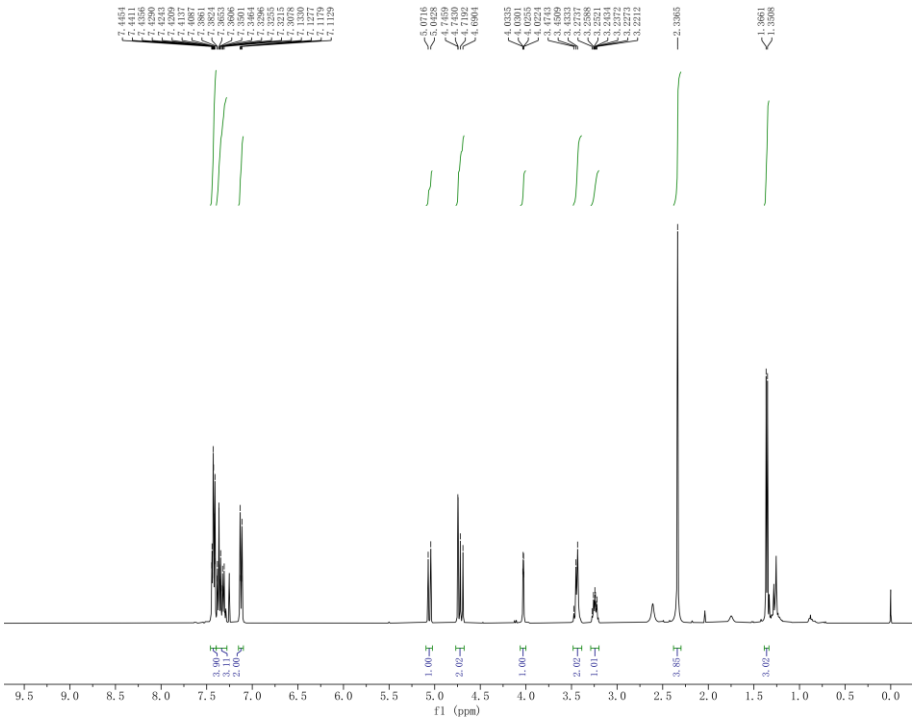
^{13}C NMR, 100 MHz, $CDCl_3$



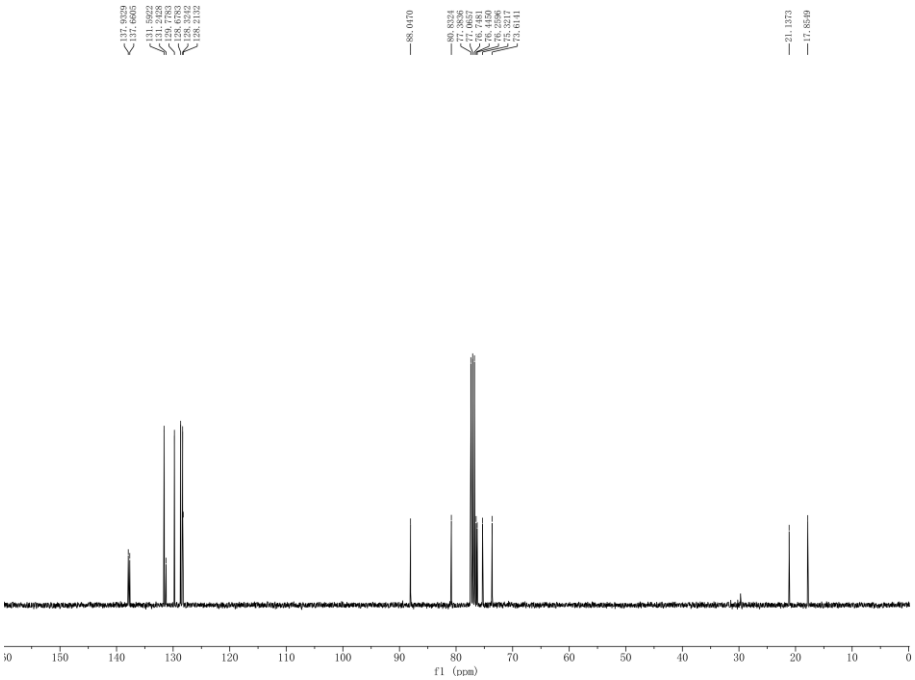


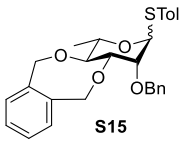
S14β

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



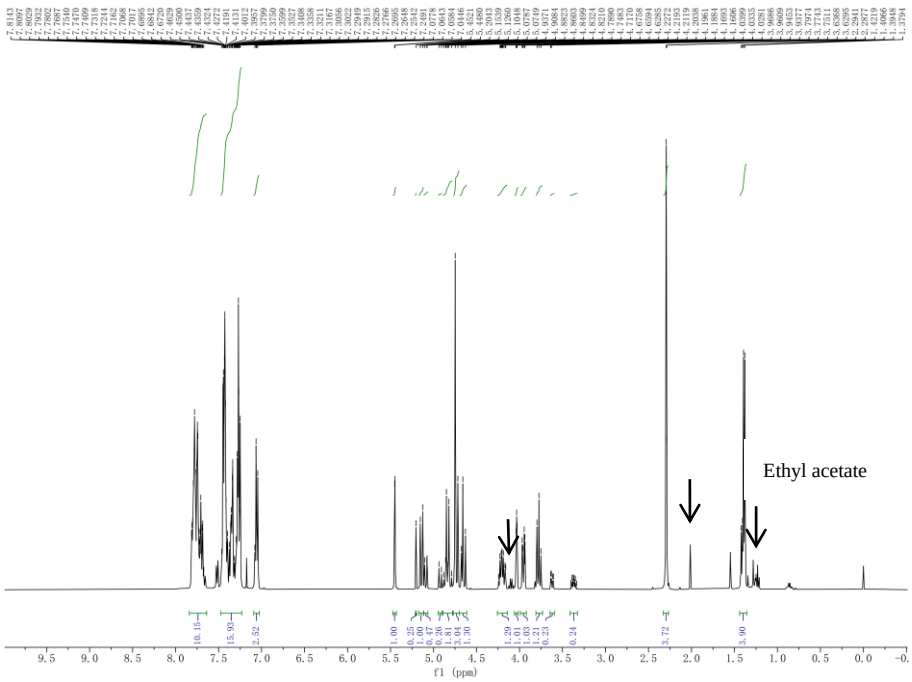
^{13}C NMR, 100 MHz, $CDCl_3$



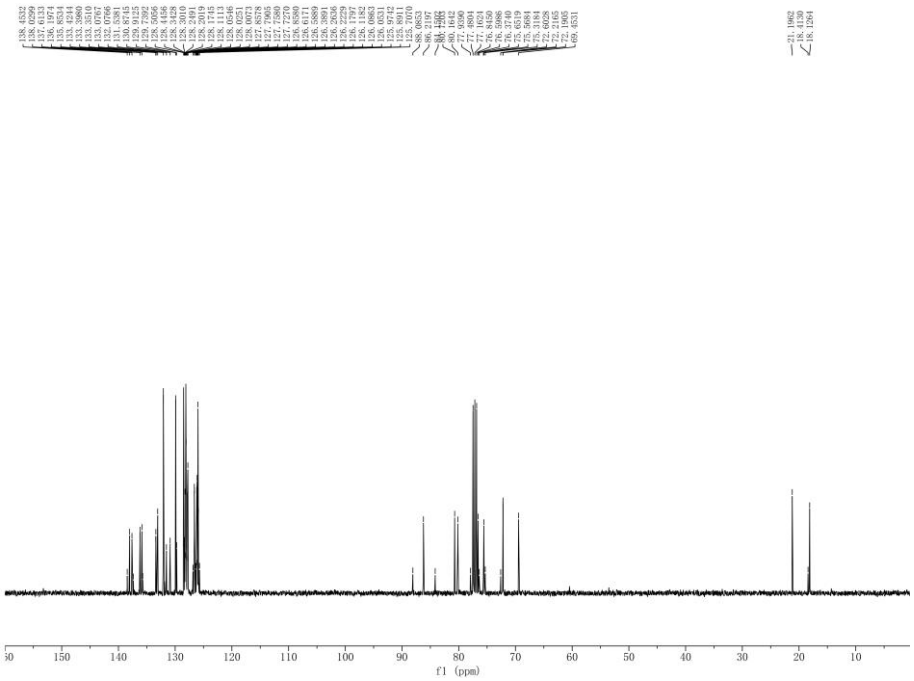


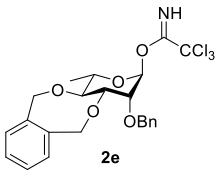
S15

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



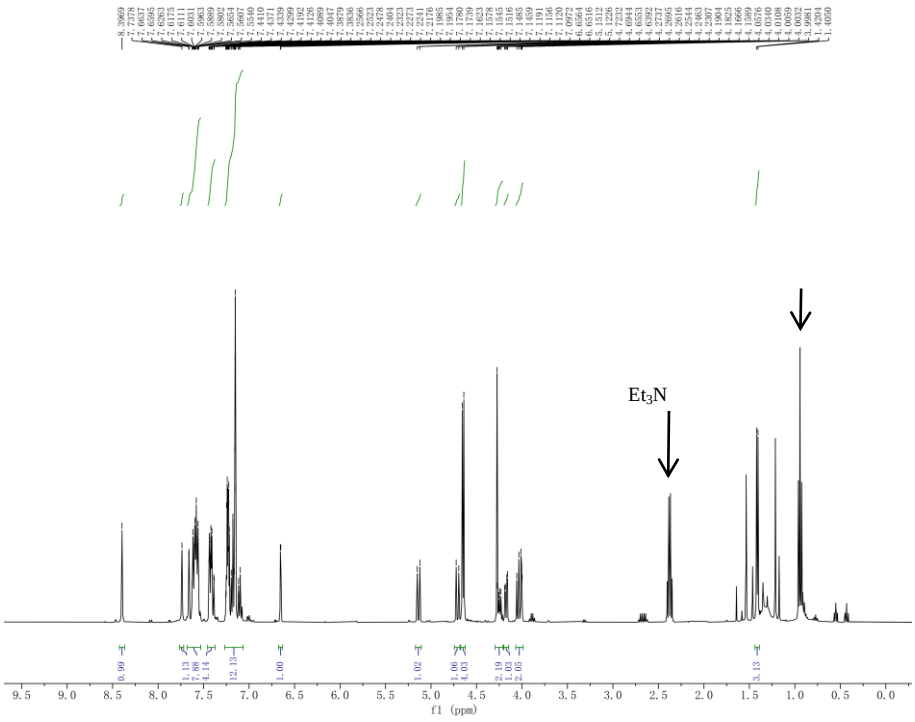
^{13}C NMR, 100 MHz, $CDCl_3$



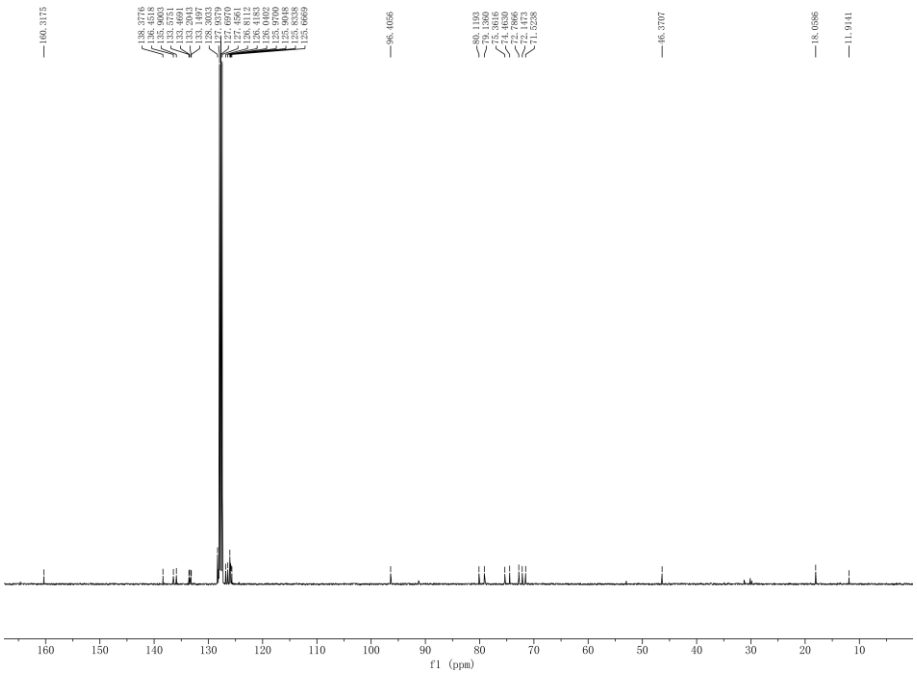


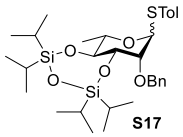
2e

^{1}H NMR, 400 MHz, C_6D_6



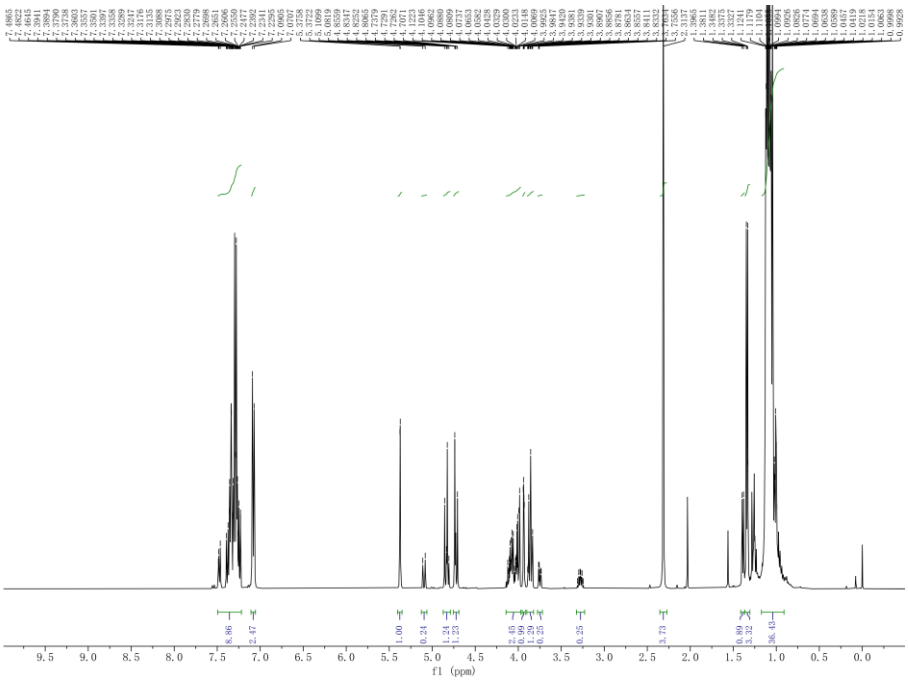
^{13}C NMR, 100 MHz, C_6D_6



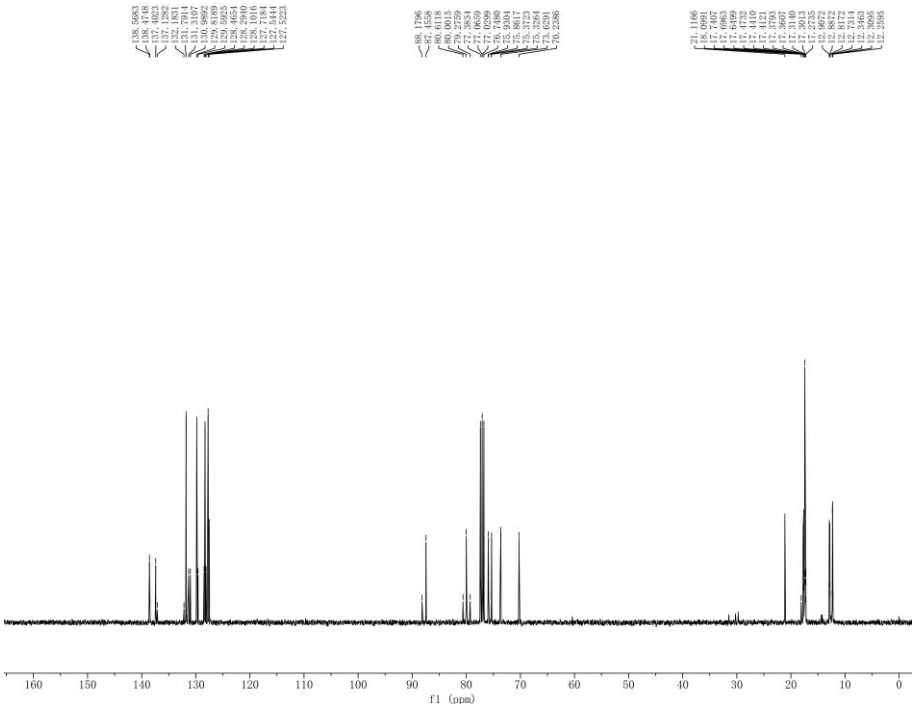


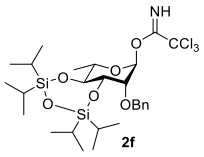
S17

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

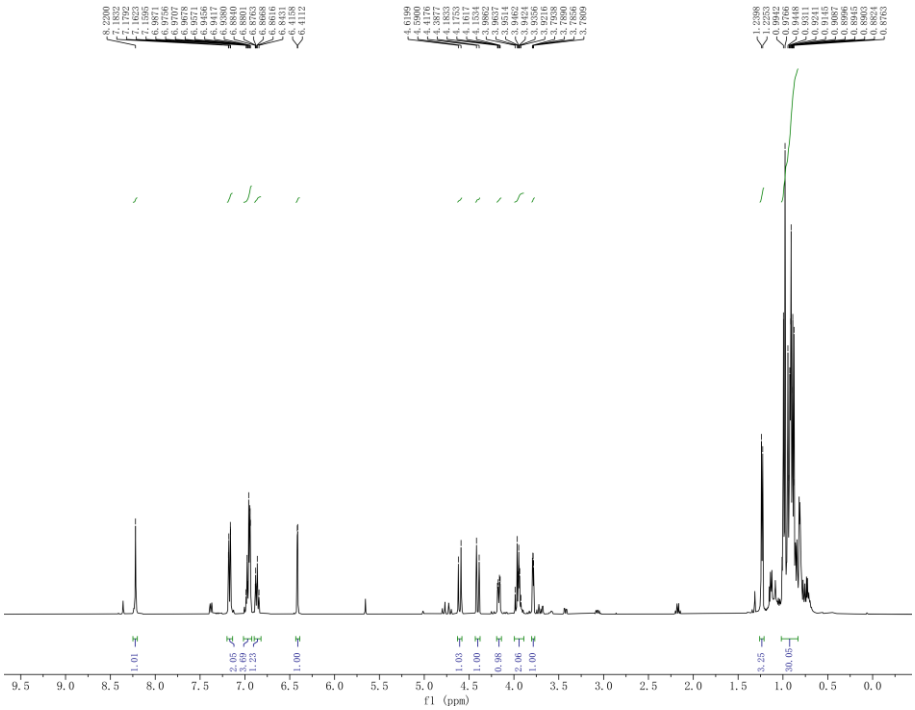


^{13}C NMR, 100 MHz, $CDCl_3$

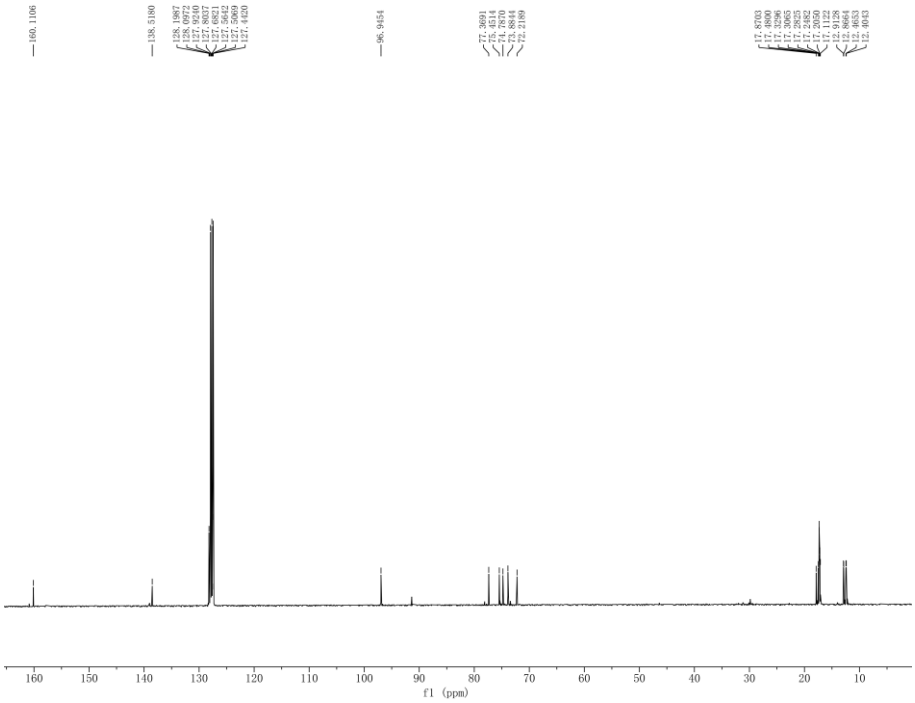


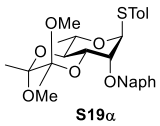


^{1}H NMR, 400 MHz, C_6D_6



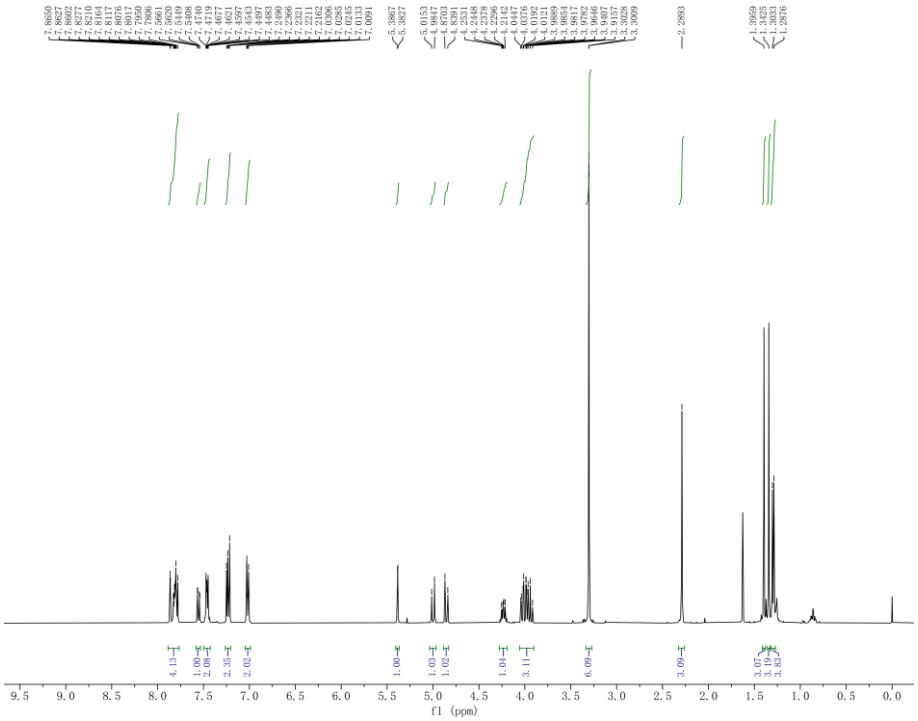
^{13}C NMR, 100 MHz, C_6D_6



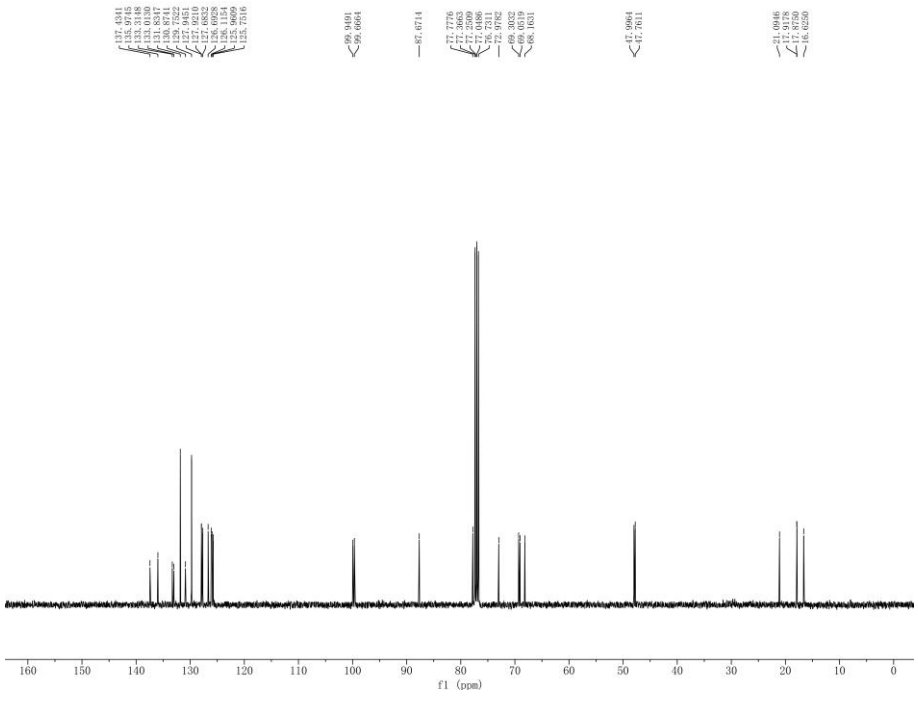


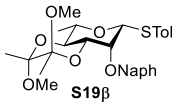
S19α

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



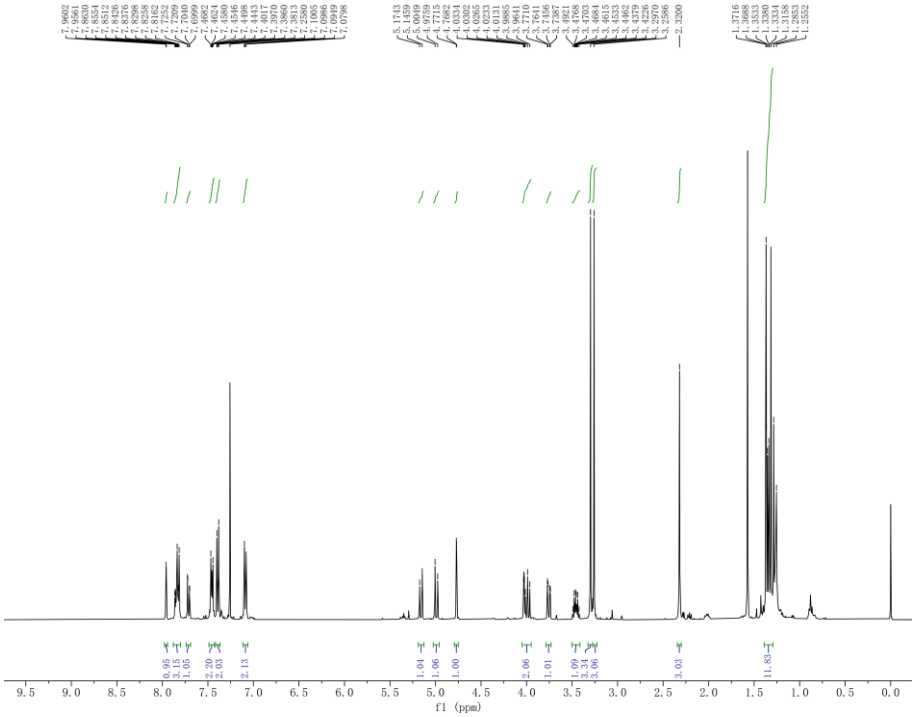
^{13}C NMR, 100 MHz, $CDCl_3$



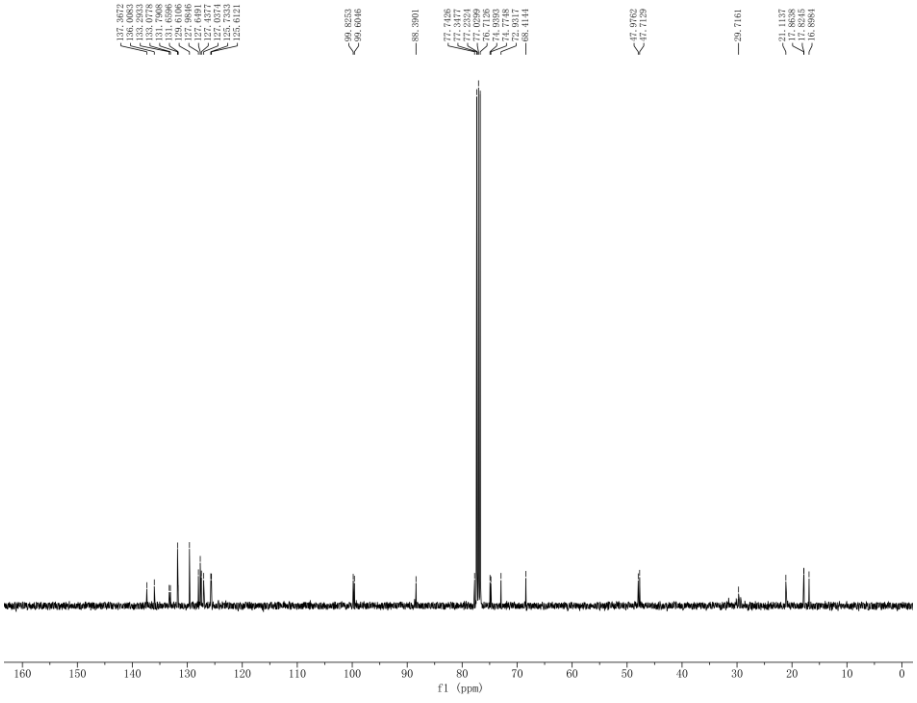


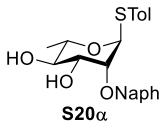
S19β

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



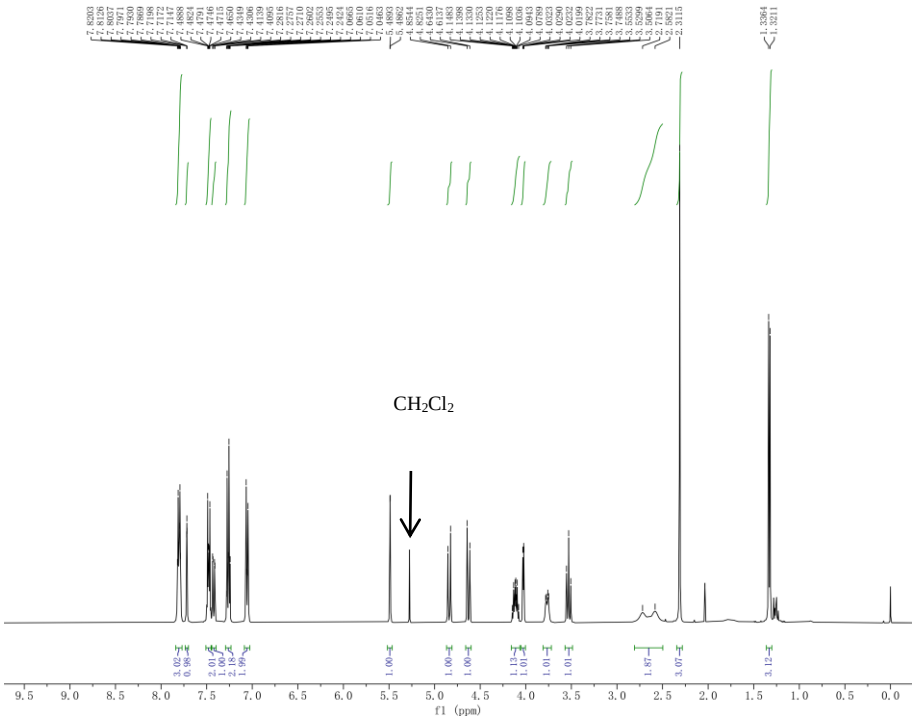
^{13}C NMR, 100 MHz, $CDCl_3$



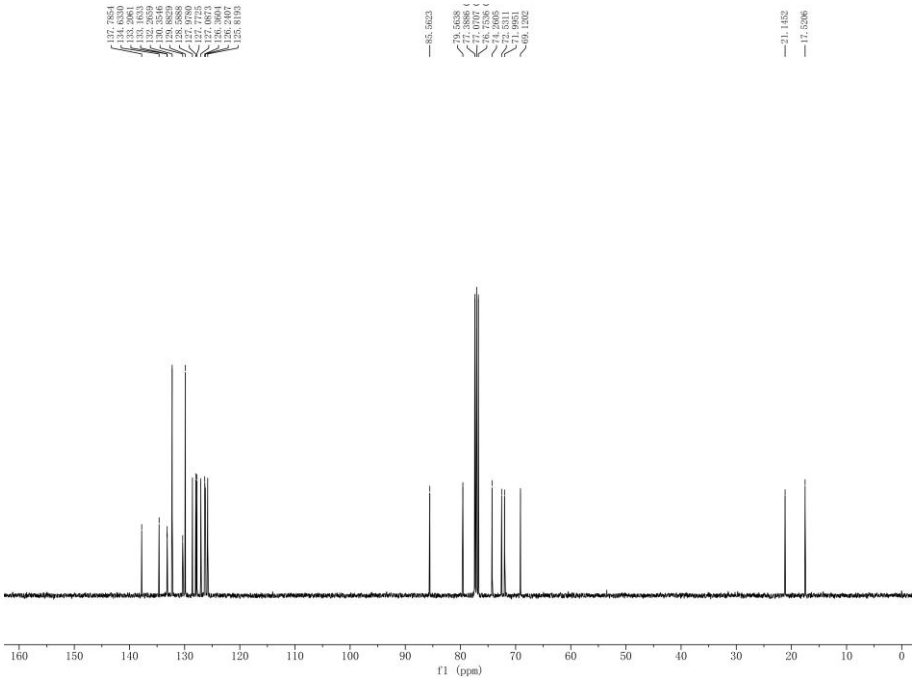


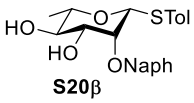
S20α

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



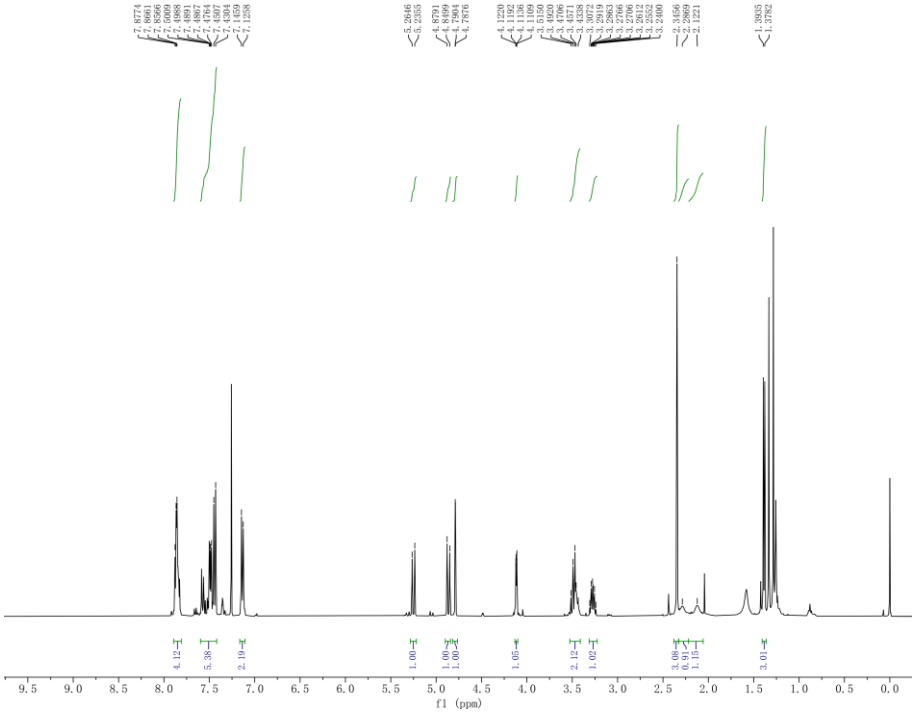
^{13}C NMR, 100 MHz, $CDCl_3$



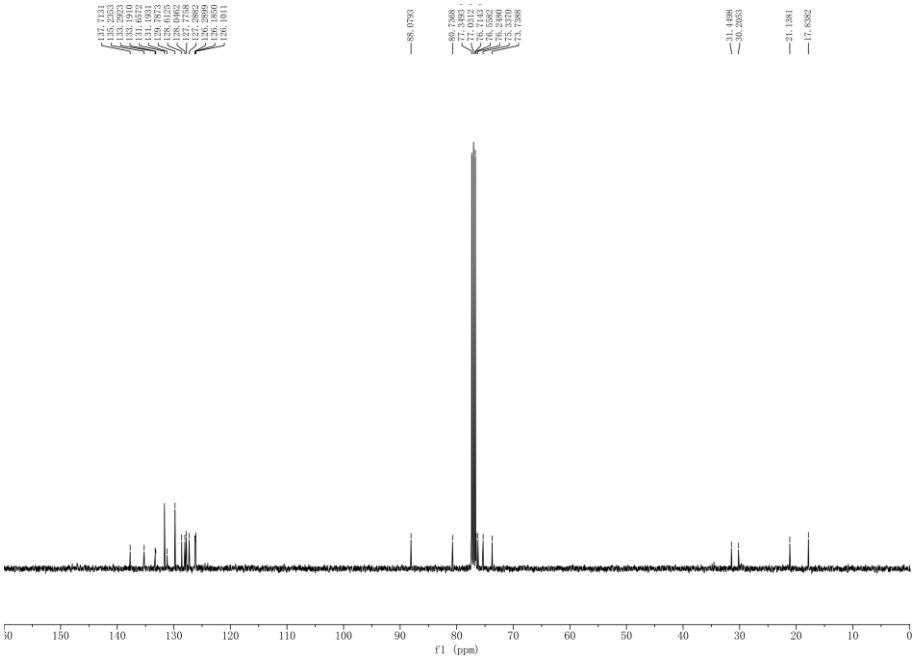


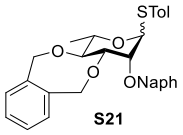
S20β

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



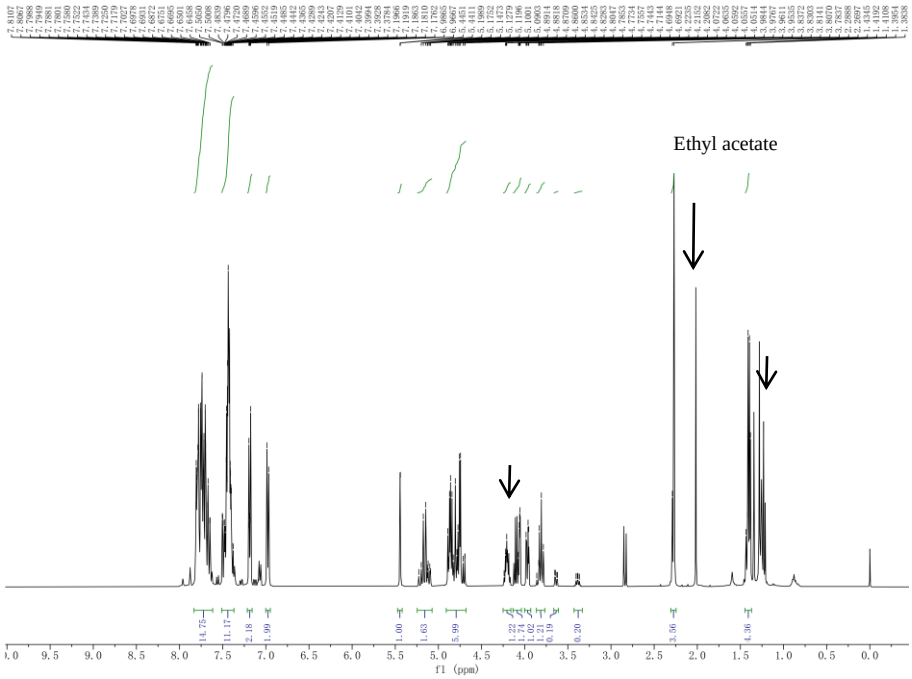
^{13}C NMR, 100 MHz, $CDCl_3$



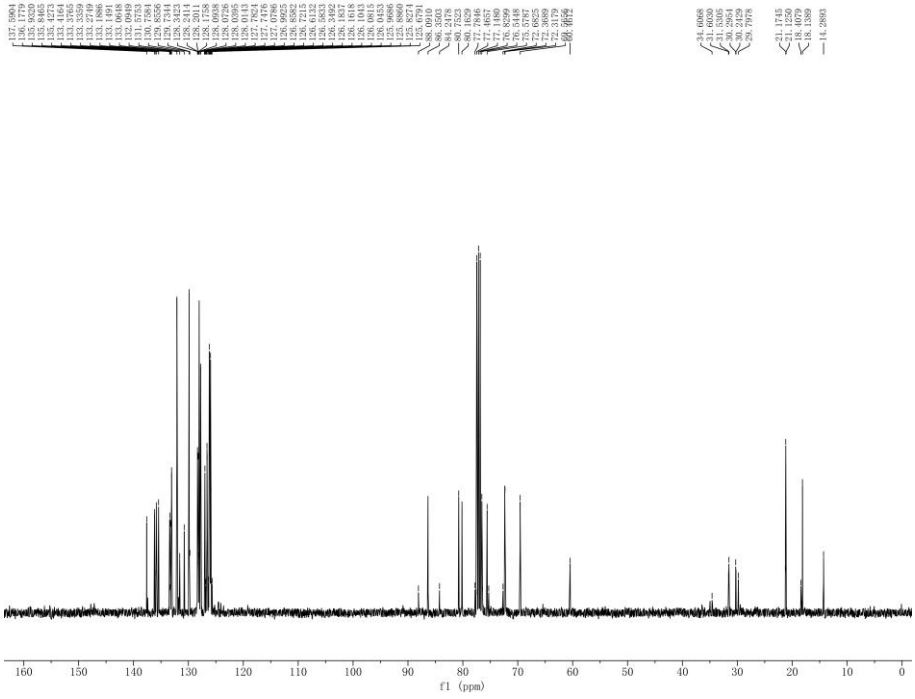


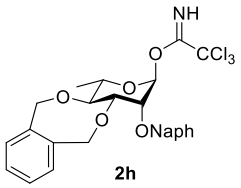
S21

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



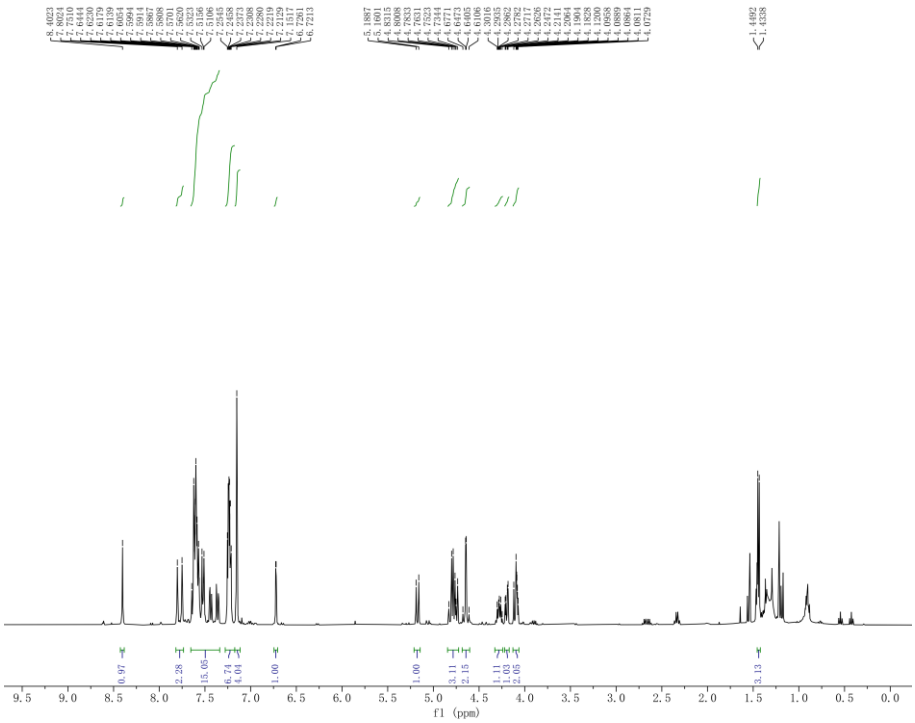
^{13}C NMR, 100 MHz, $CDCl_3$



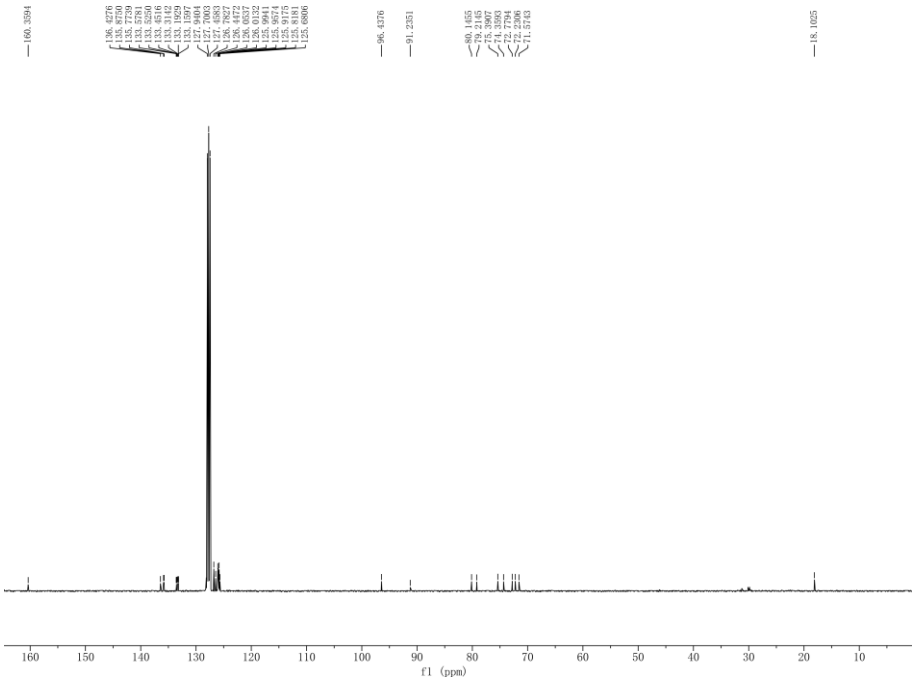


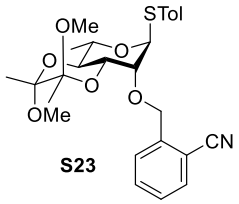
2h

^{1}H NMR, 400 MHz, C_6D_6



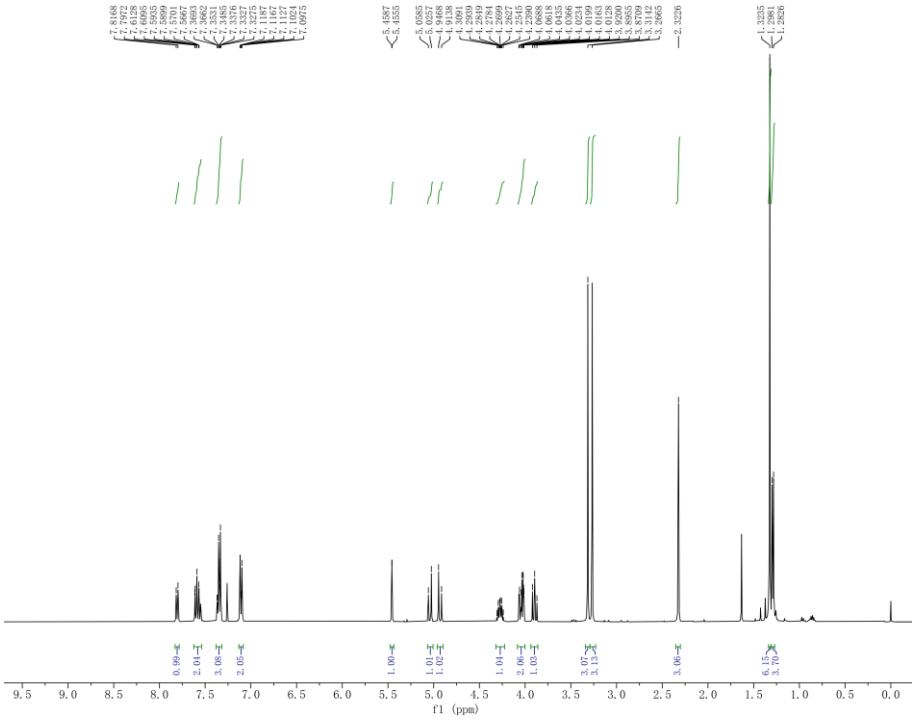
^{13}C NMR, 100 MHz, C_6D_6



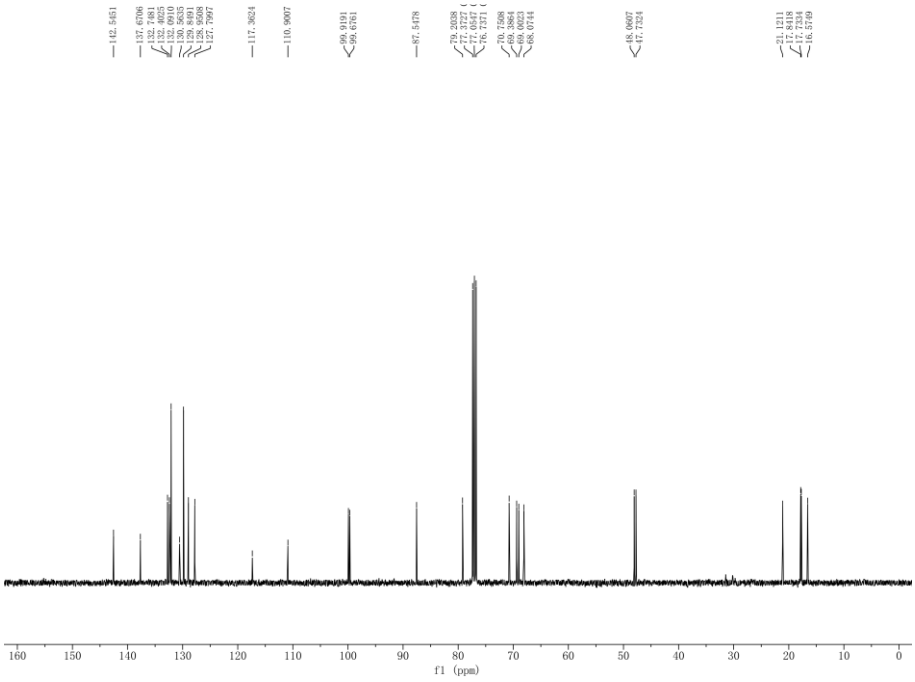


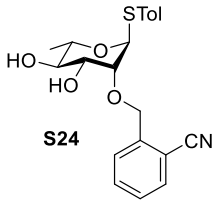
S23

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



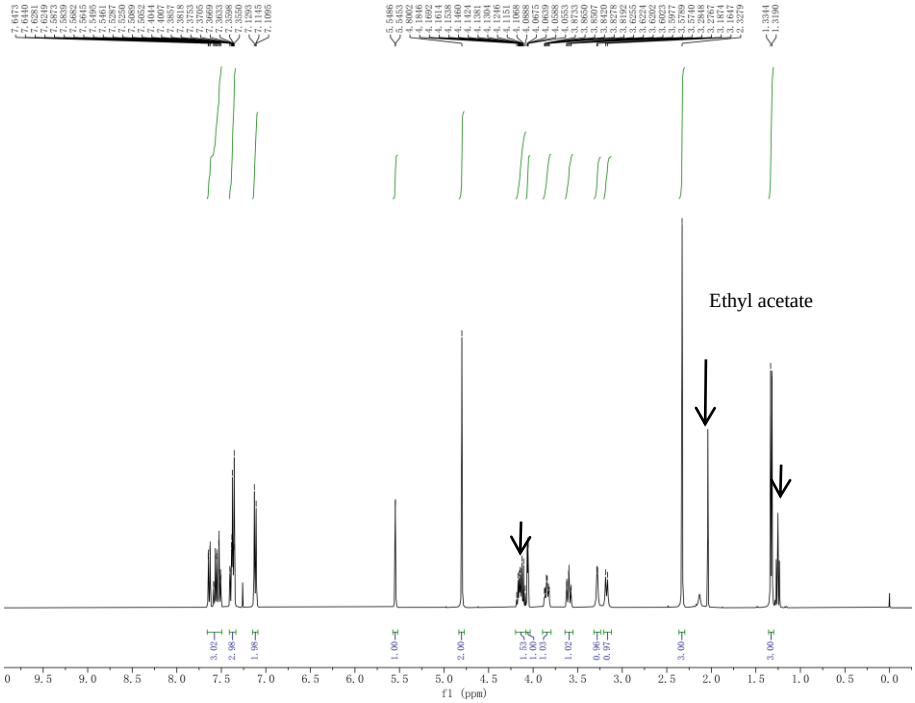
^{13}C NMR, 100 MHz, $CDCl_3$



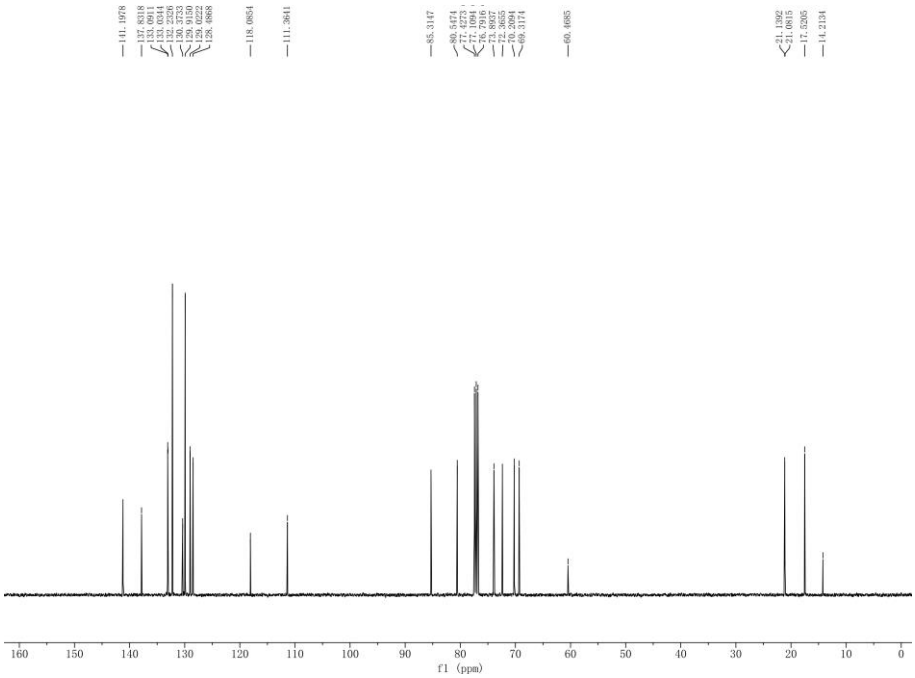


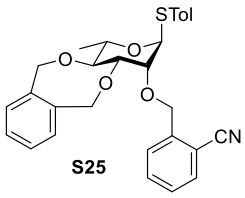
S24

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



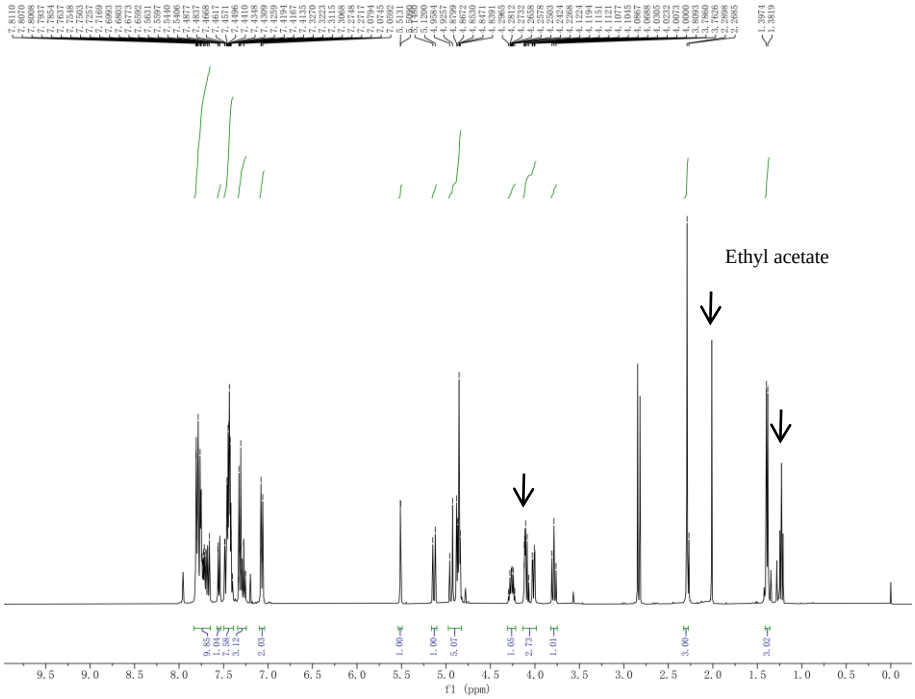
^{13}C NMR, 100 MHz, $CDCl_3$



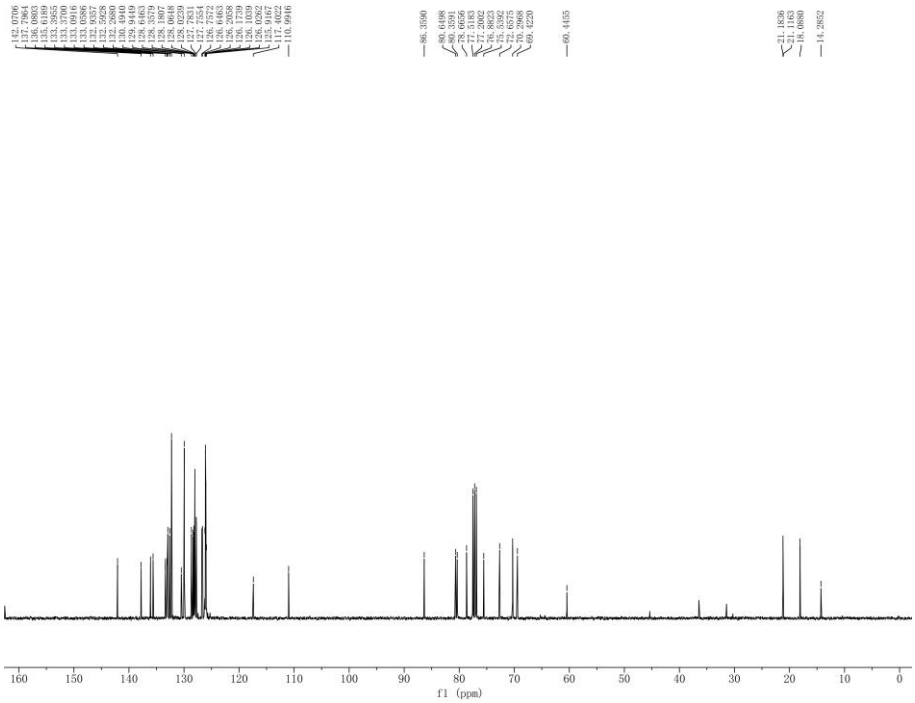


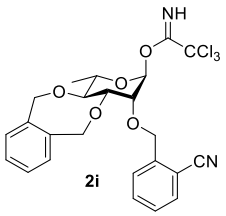
S25

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



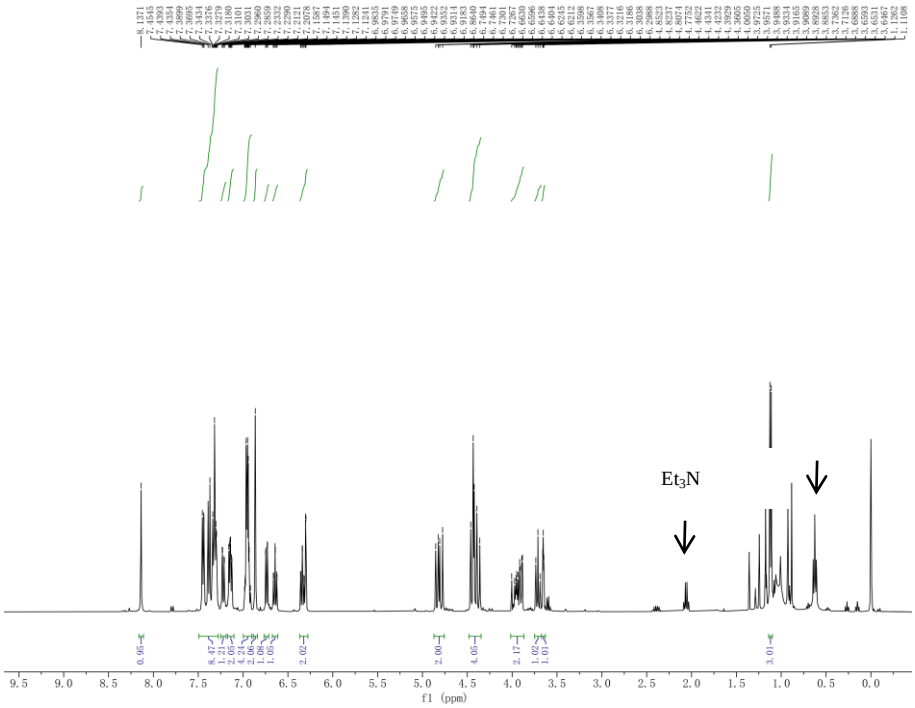
^{13}C NMR, 100 MHz, $CDCl_3$



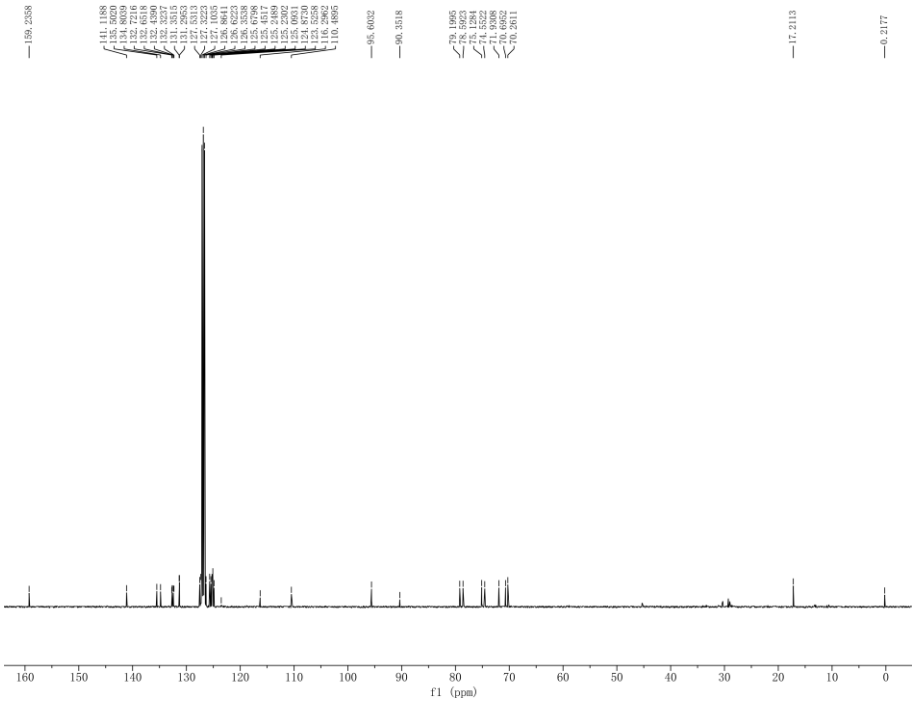


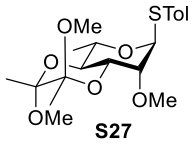
2i

^{1}H NMR, 400 MHz, C_6D_6



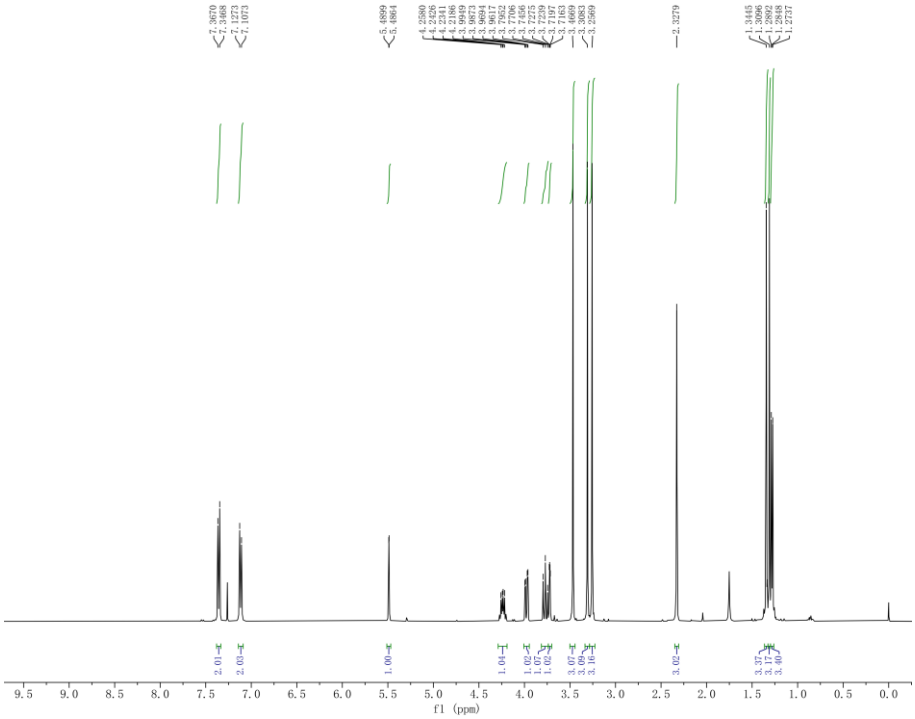
^{13}C NMR, 100 MHz, C_6D_6



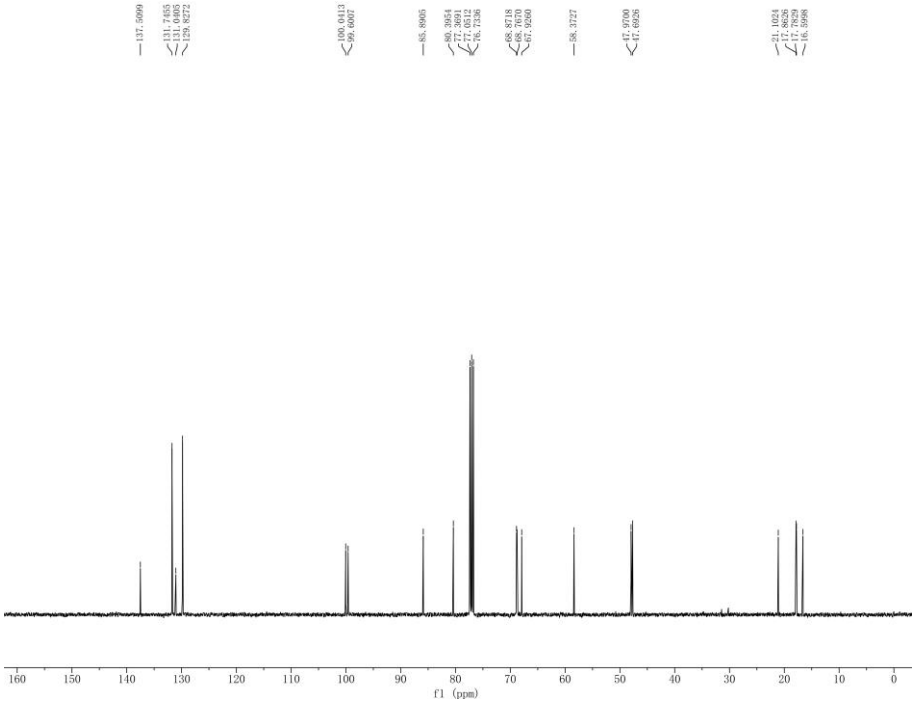


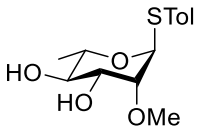
S27

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



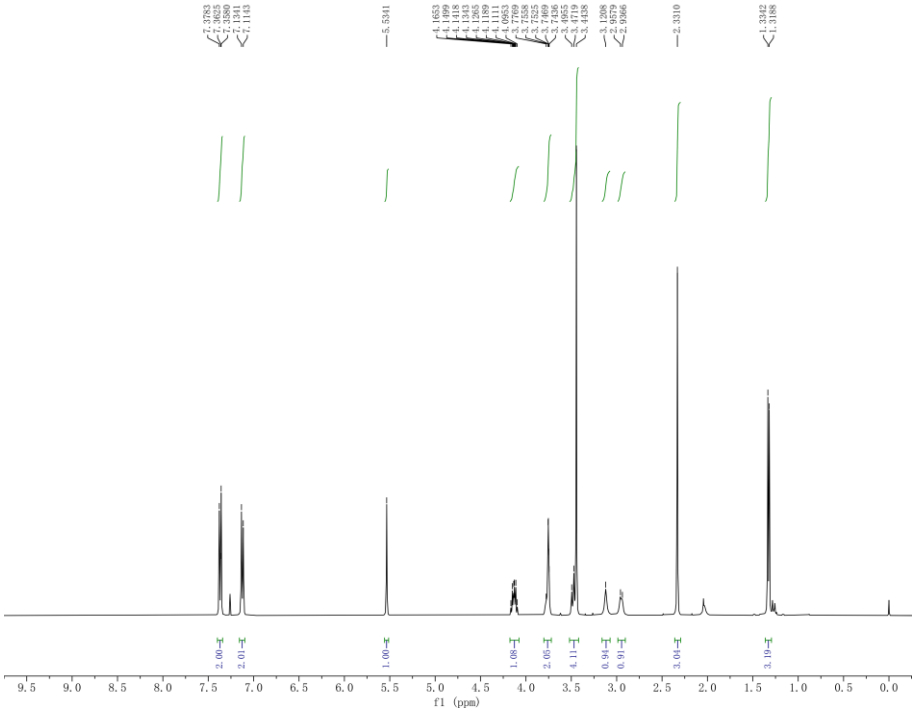
^{13}C NMR, 100 MHz, $CDCl_3$



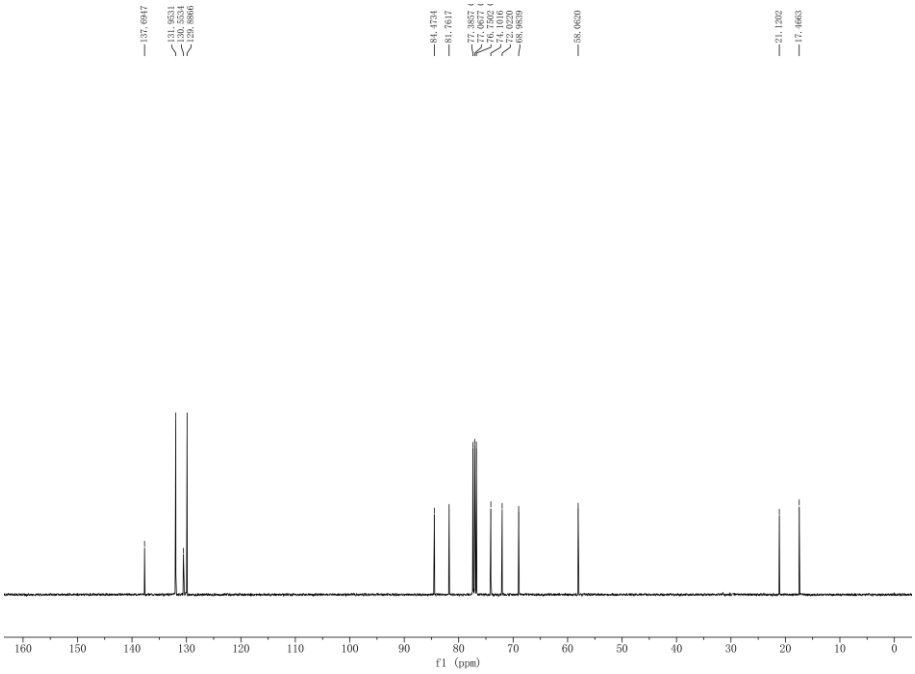


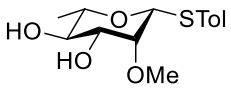
S28α

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



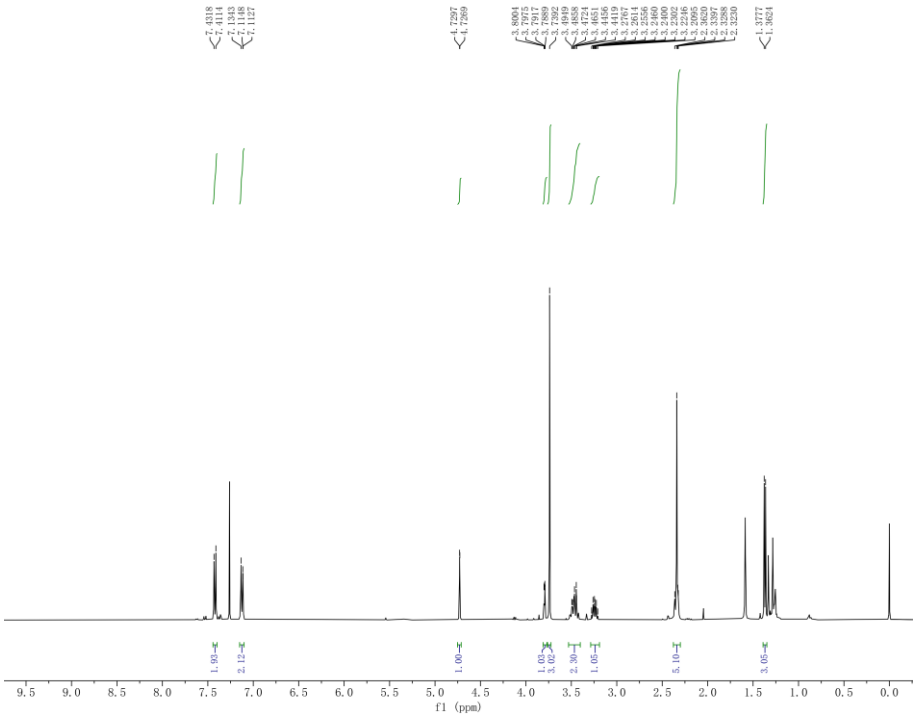
^{13}C NMR, 100 MHz, $CDCl_3$



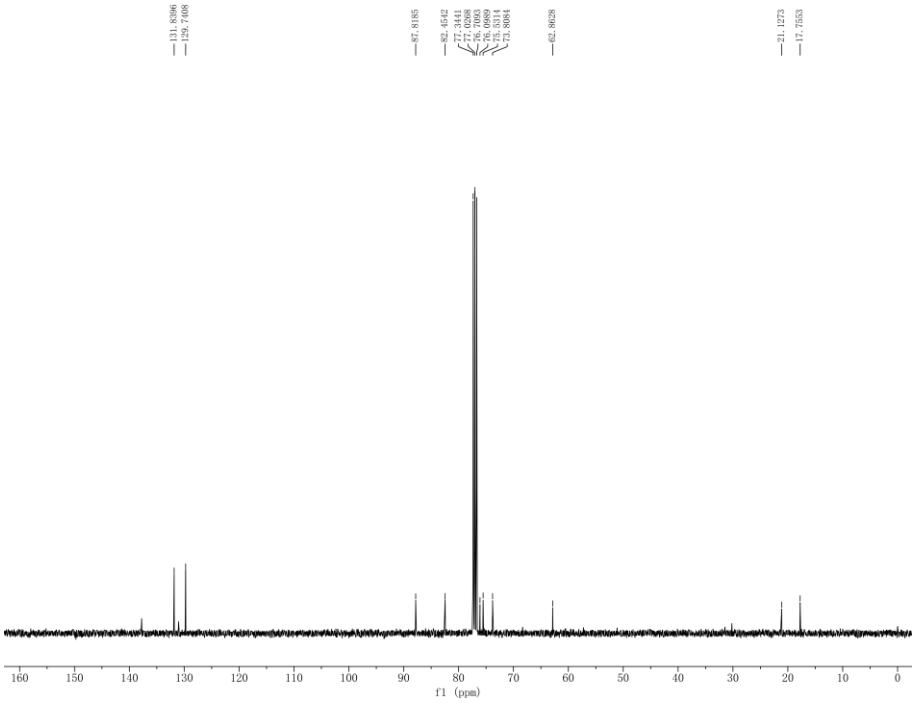


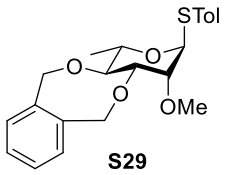
S28β

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



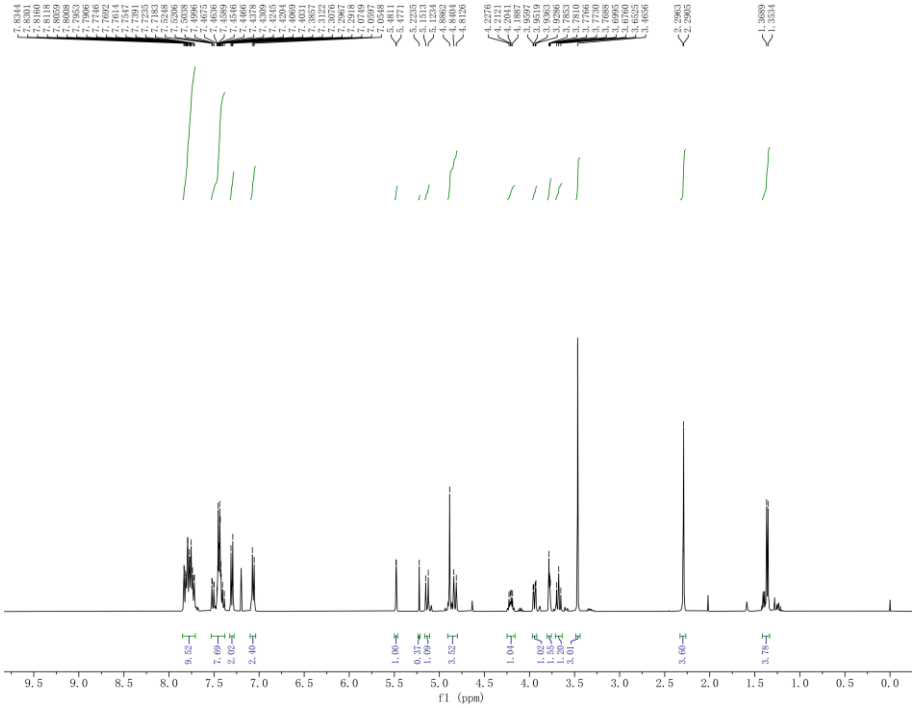
^{13}C NMR, 100 MHz, $CDCl_3$



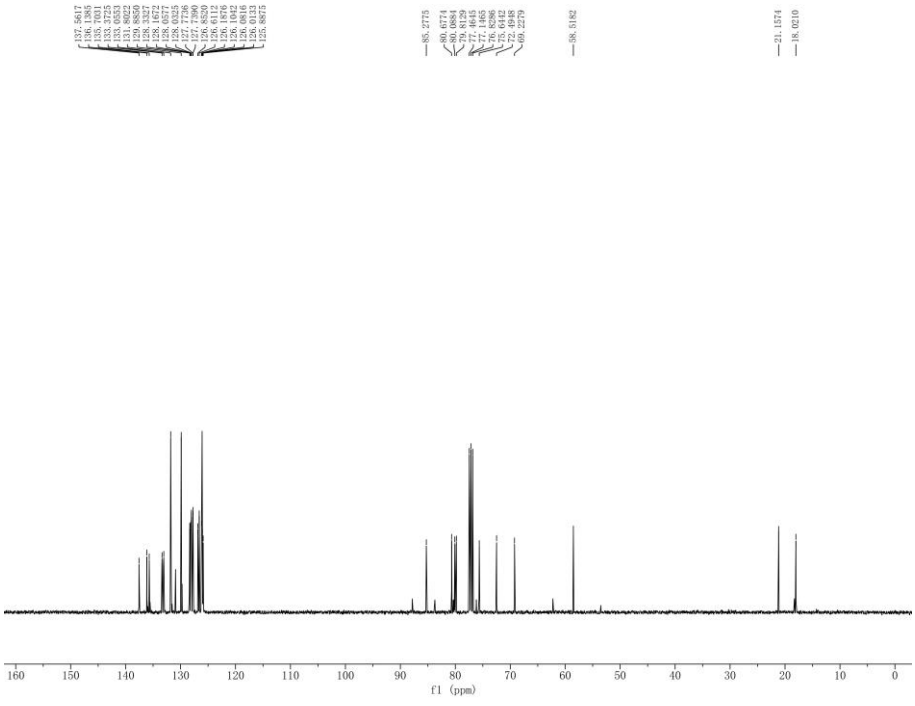


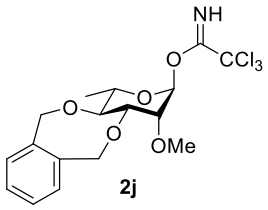
S29

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



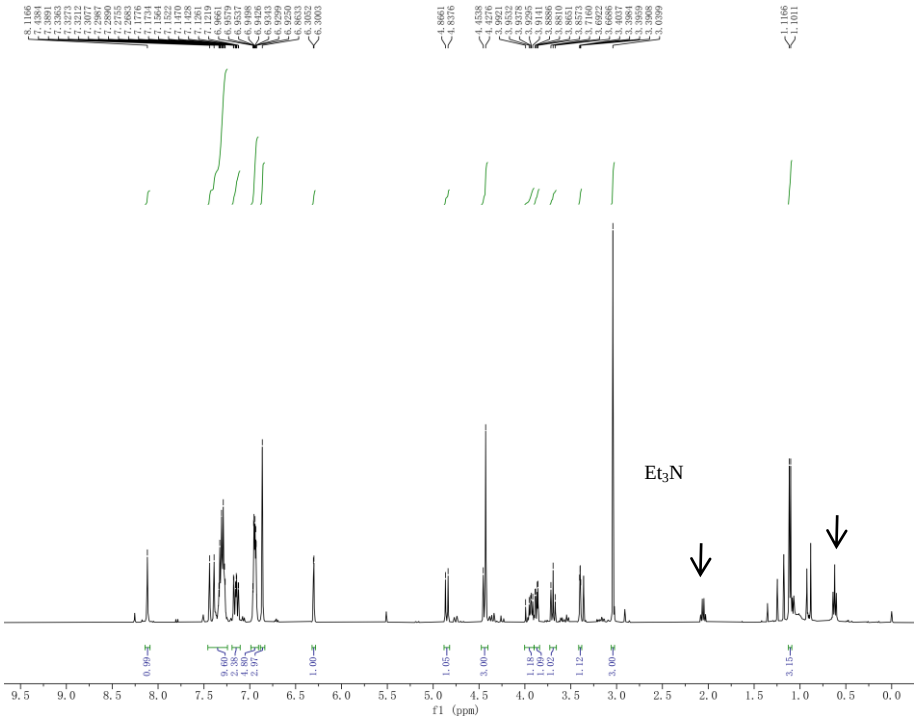
^{13}C NMR, 100 MHz, CDCl3



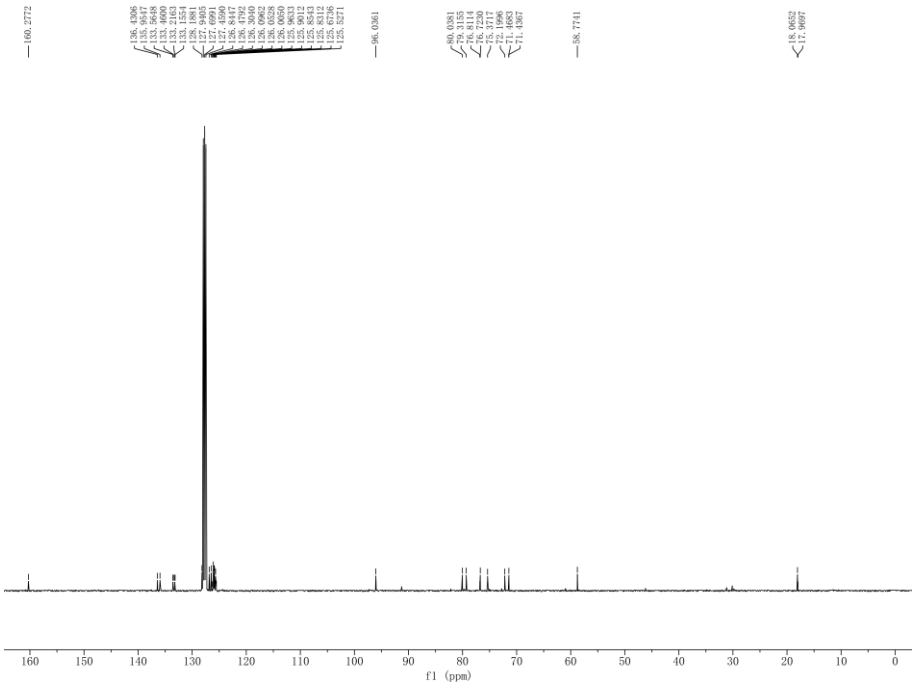


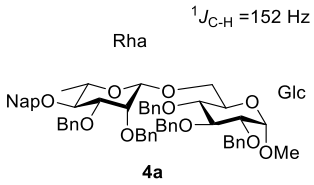
2j

^{1}H NMR, 400 MHz, C_6D_6



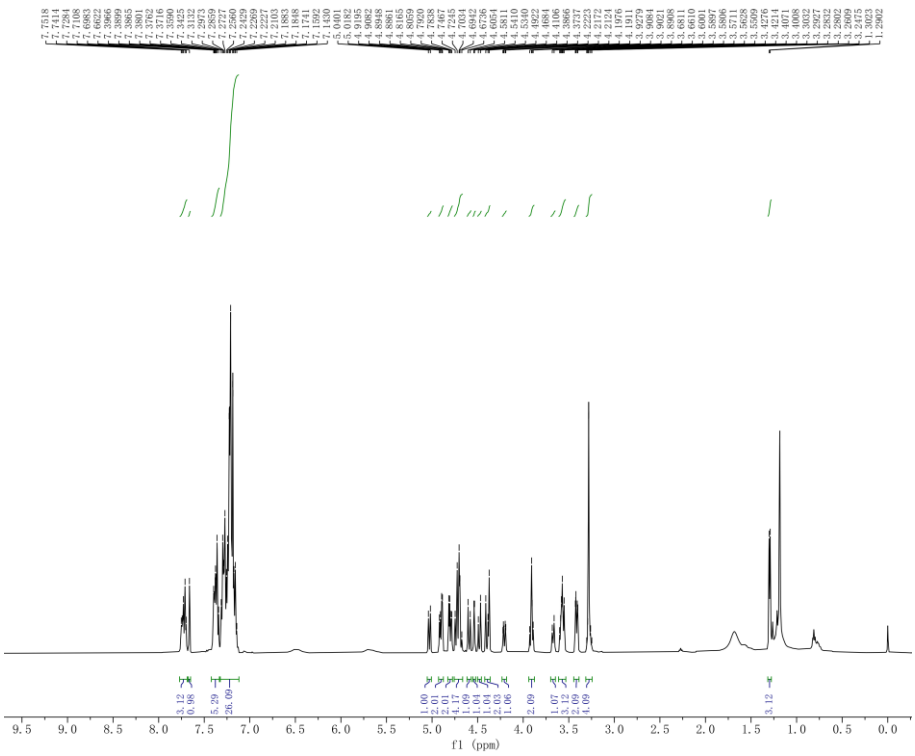
^{13}C NMR, 100 MHz, C_6D_6



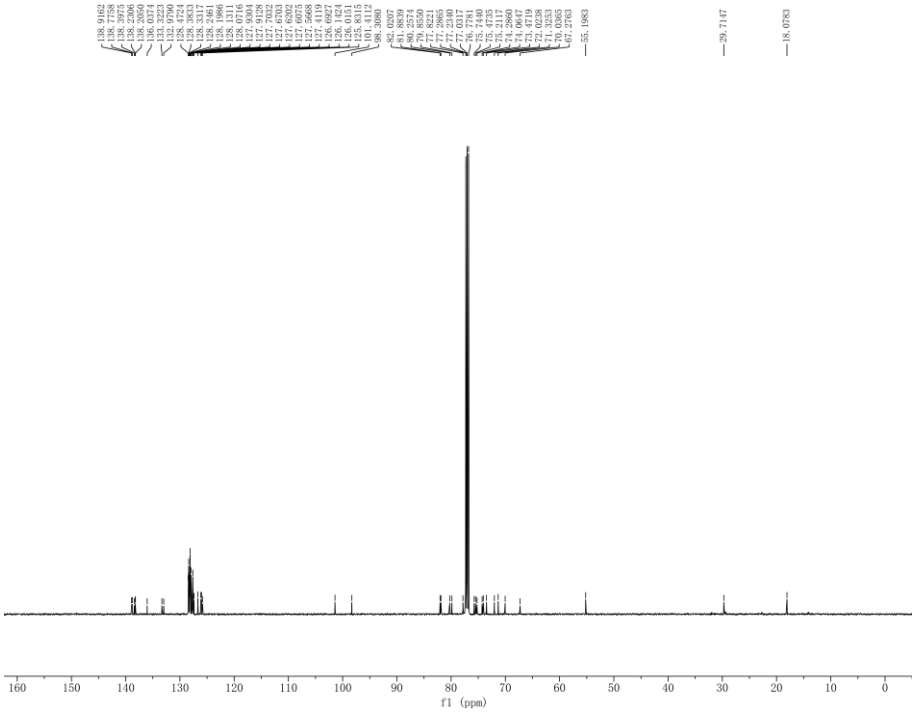


4a

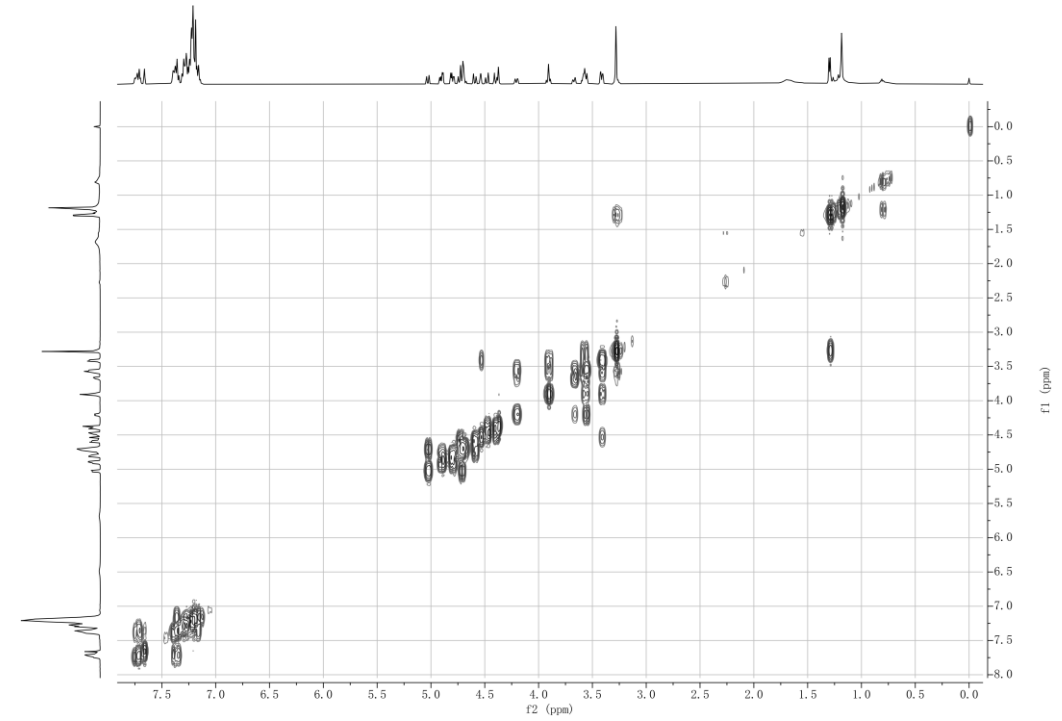
^{1}H NMR, 500 MHz, $CDCl_3$



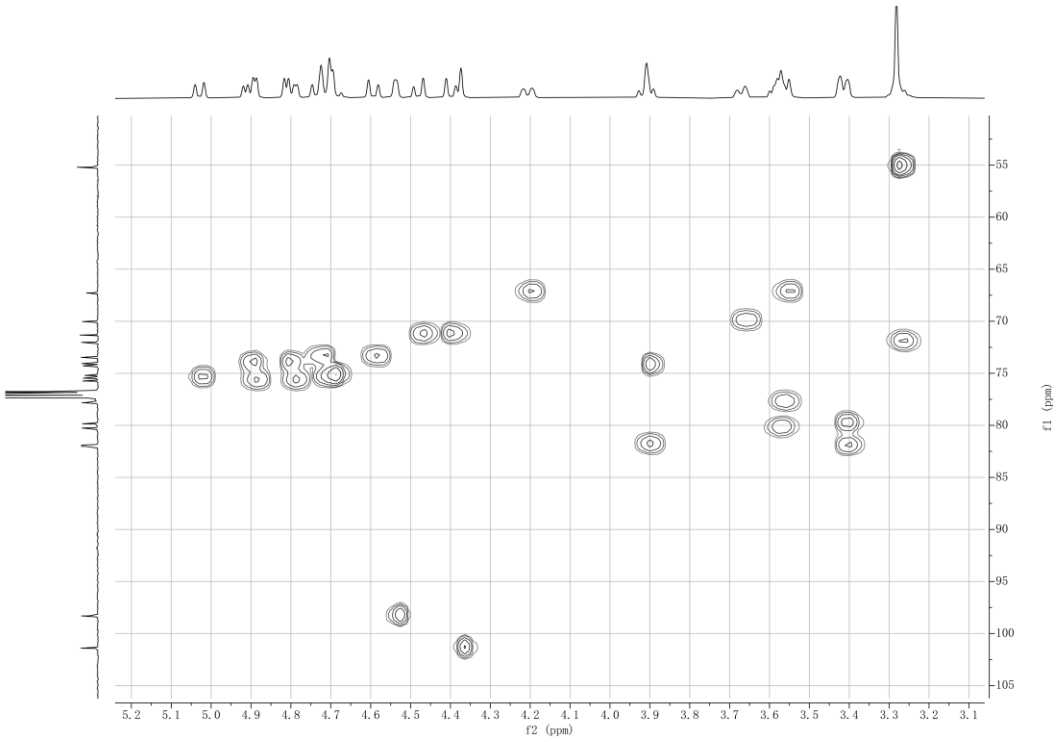
^{13}C NMR, 125 MHz, $CDCl_3$

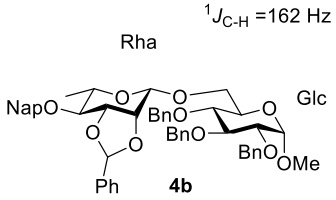


COSY, 500 MHz, $CDCl_3$

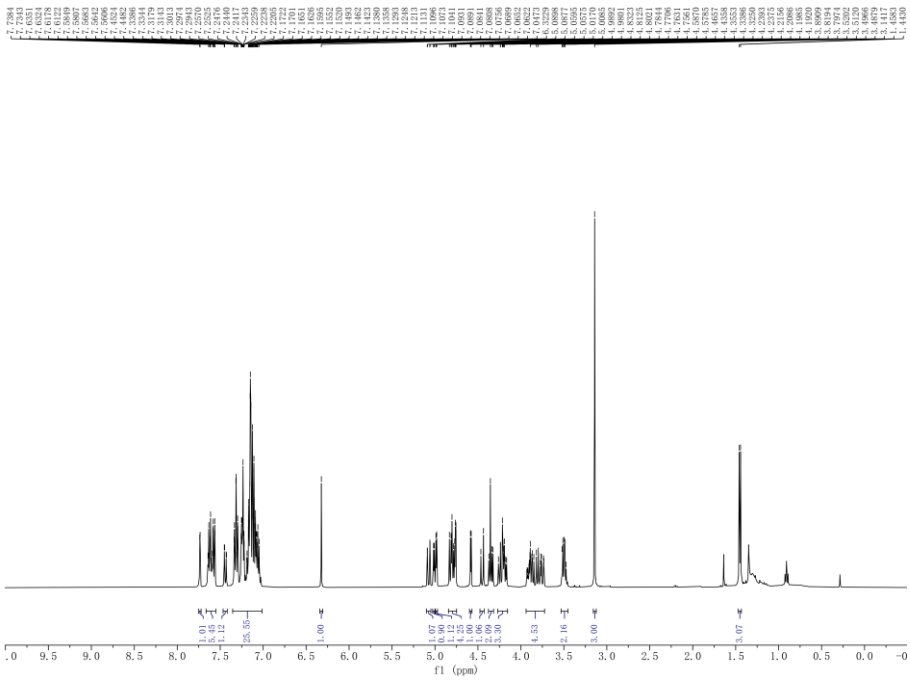


HSQC, 500 MHz, $CDCl_3$

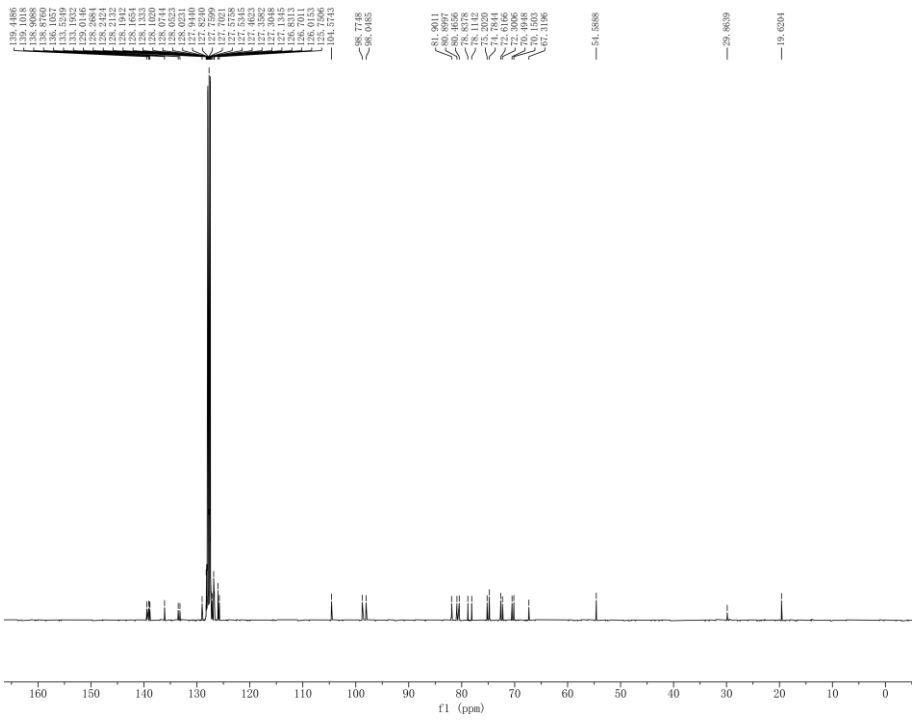




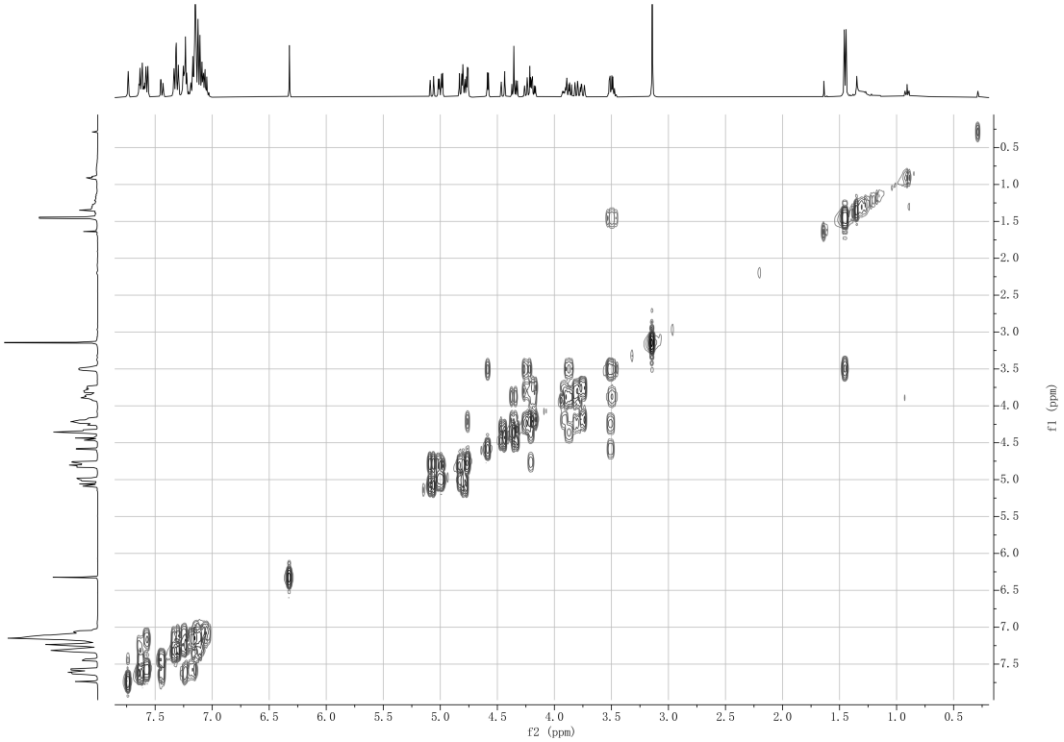
^{1}H NMR, 400 MHz, C_6D_6



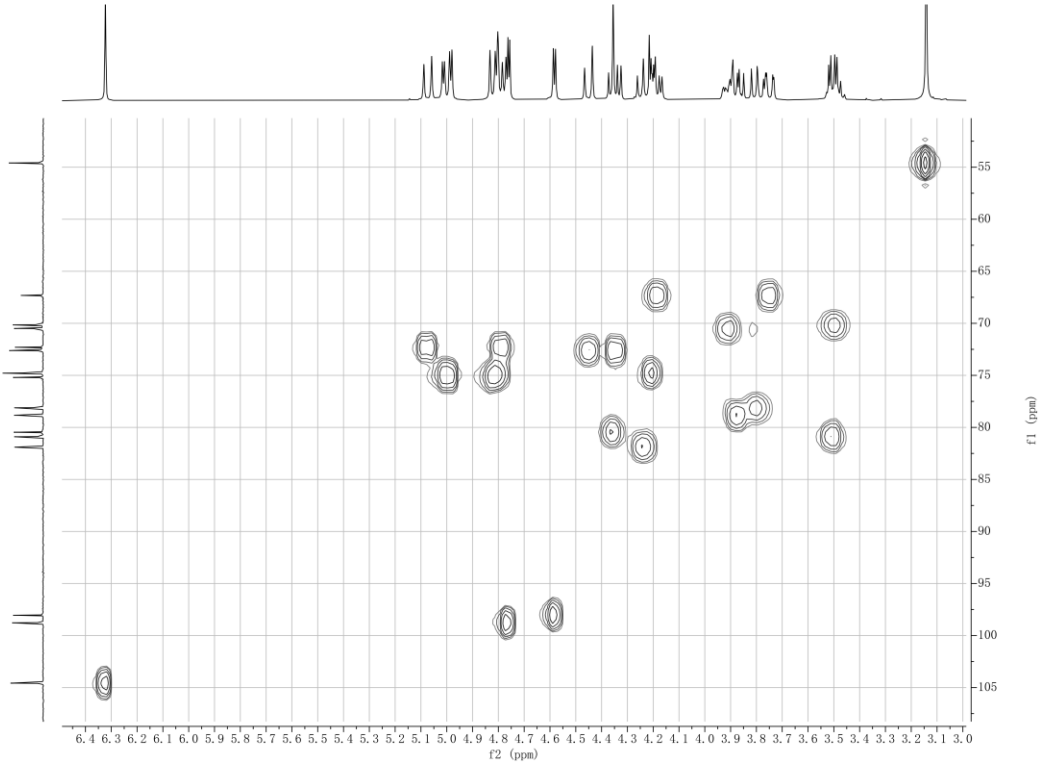
^{13}C NMR, 100 MHz, C_6D_6

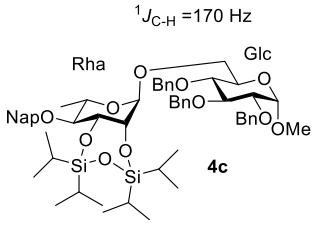


COSY, 400 MHz, C_6D_6

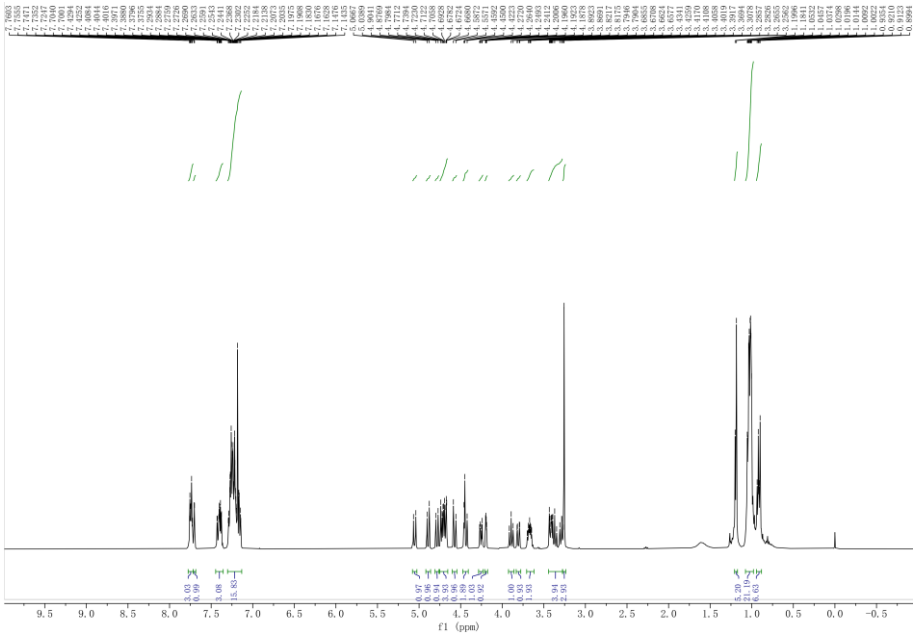


HSQC 400 MHz, C_6D_6

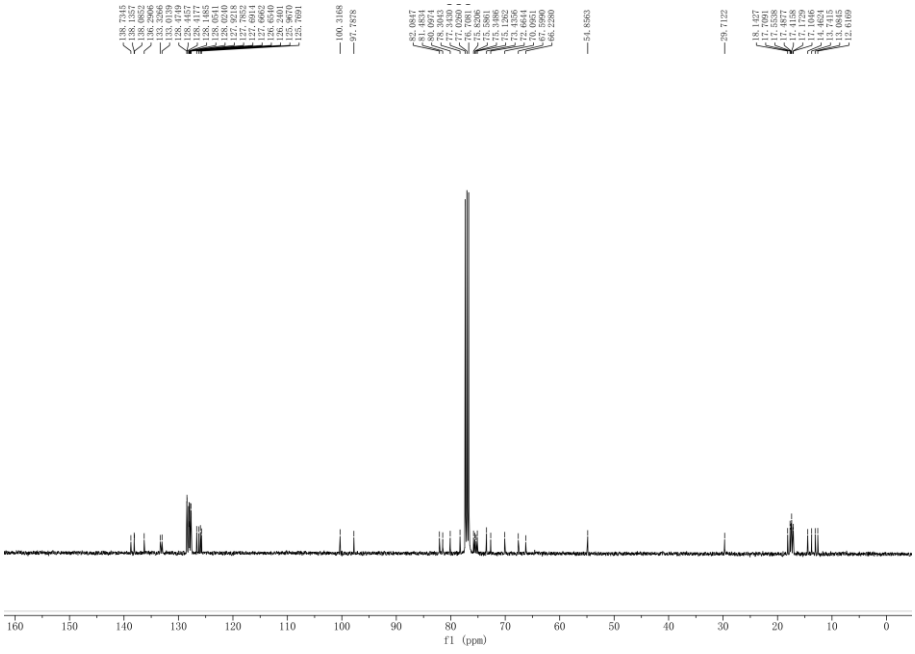




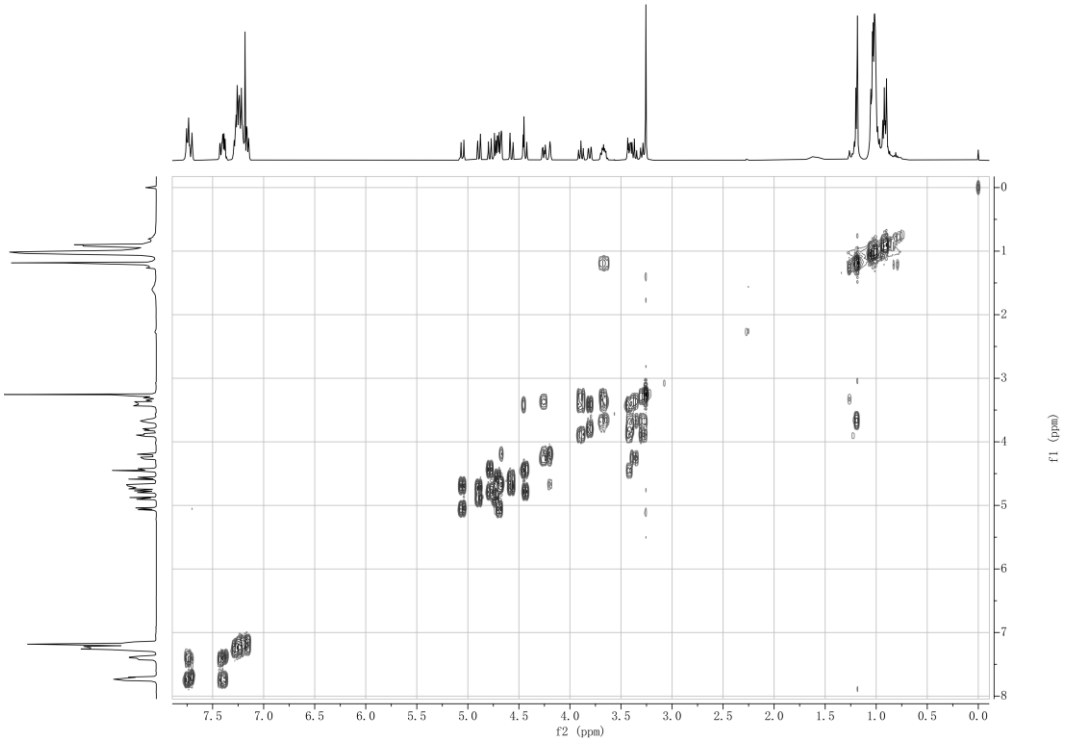
^{1}H NMR, 500 MHz, $CDCl_3$



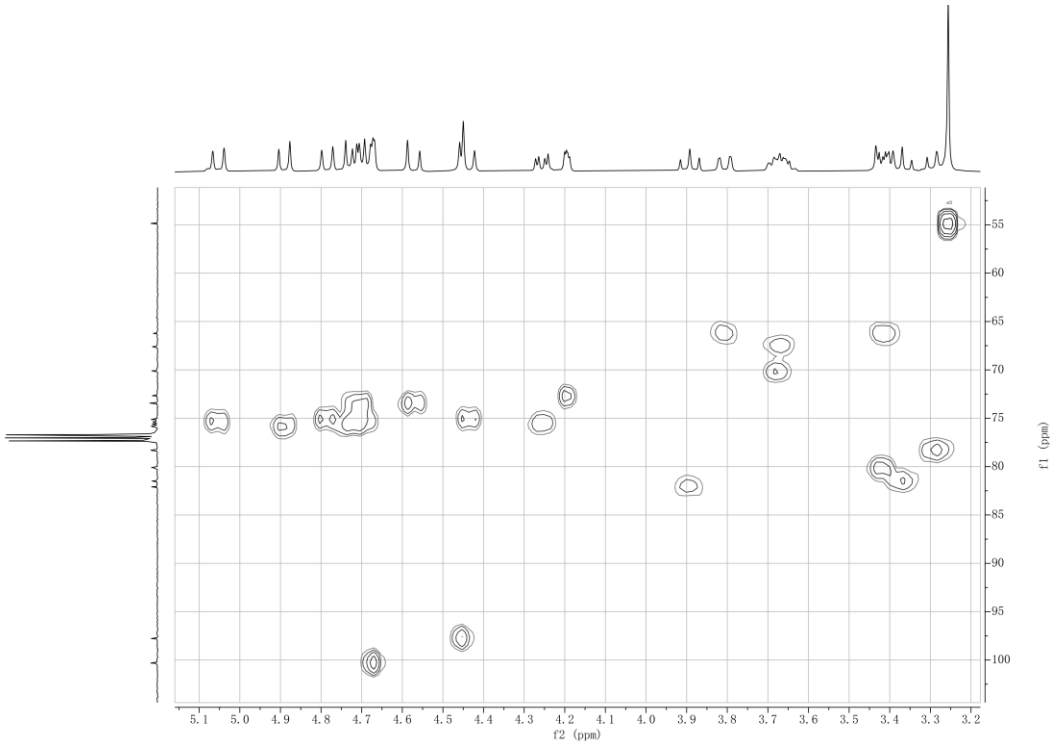
^{13}C NMR, 125 MHz, $CDCl_3$

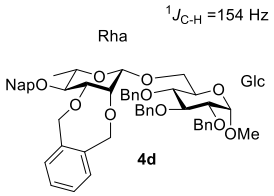


COSY, 500 MHz, $CDCl_3$

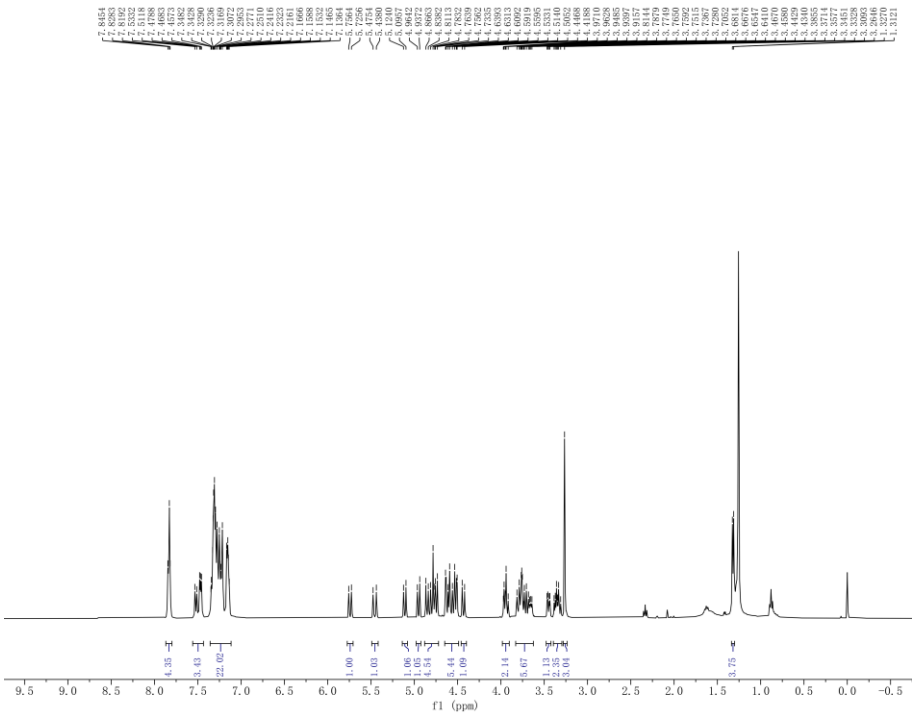


HSQC, 500 MHz, $CDCl_3$

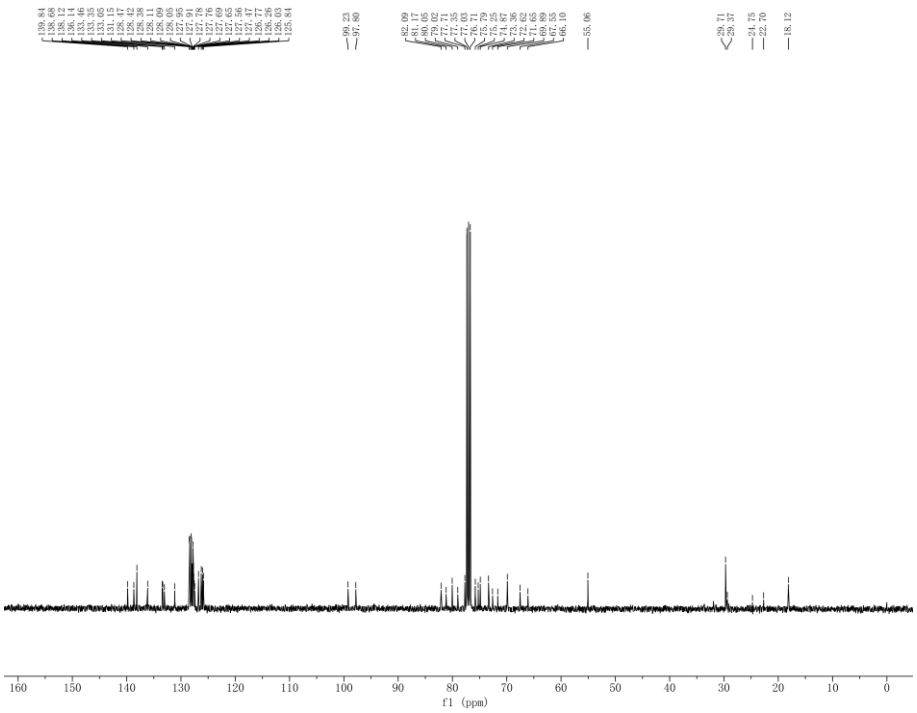




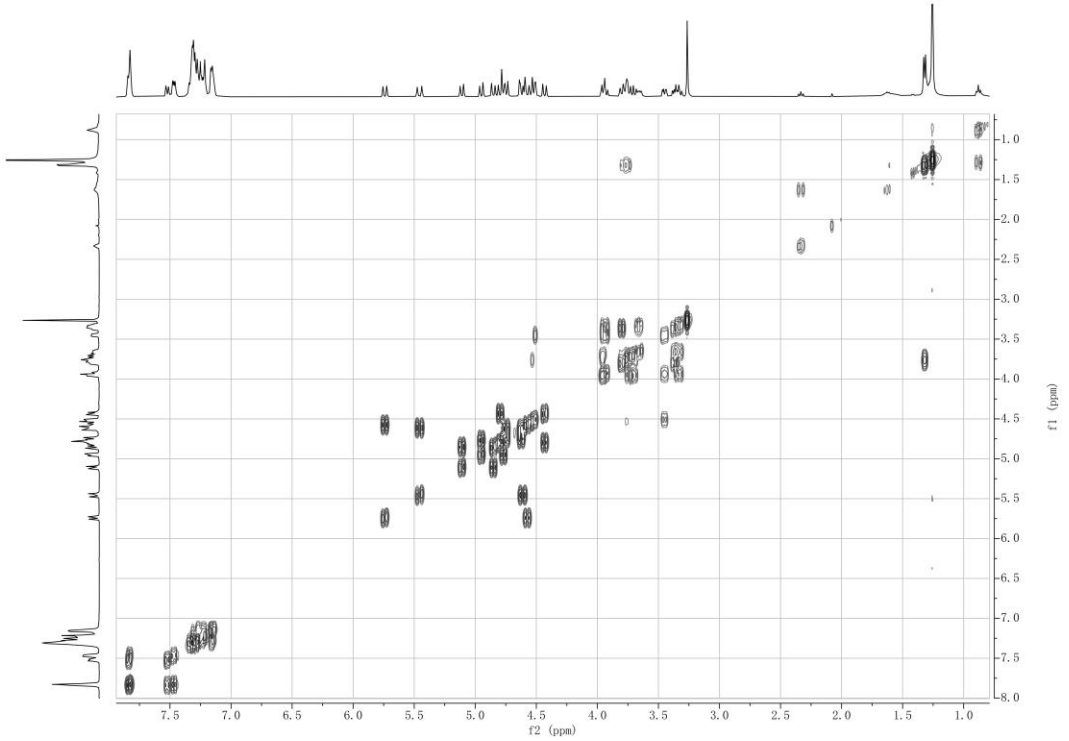
^{1}H NMR, 400 MHz, $CDCl_3$



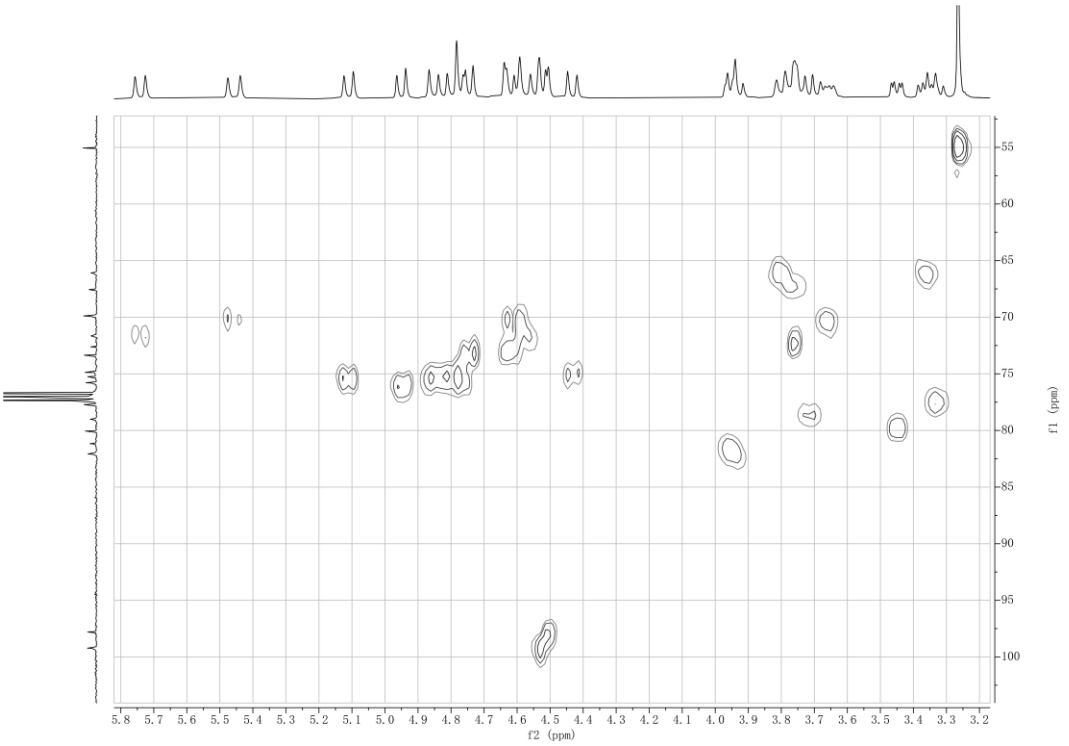
^{13}C NMR, 100 MHz, $CDCl_3$

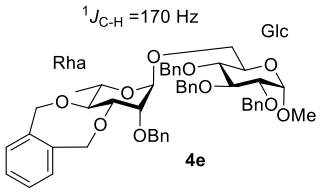


COSY, 400 MHz, $CDCl_3$

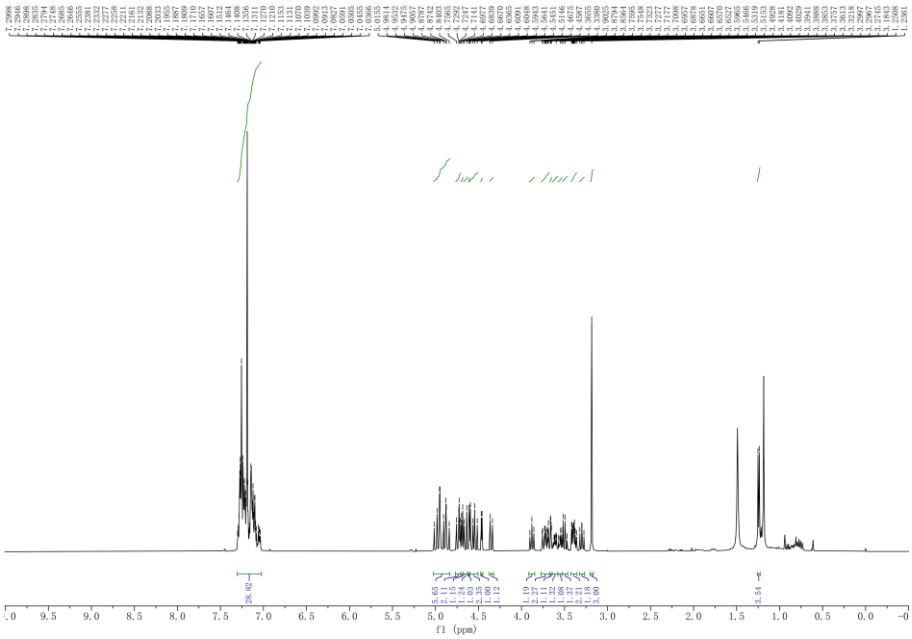


HSQC, 400 MHz, $CDCl_3$

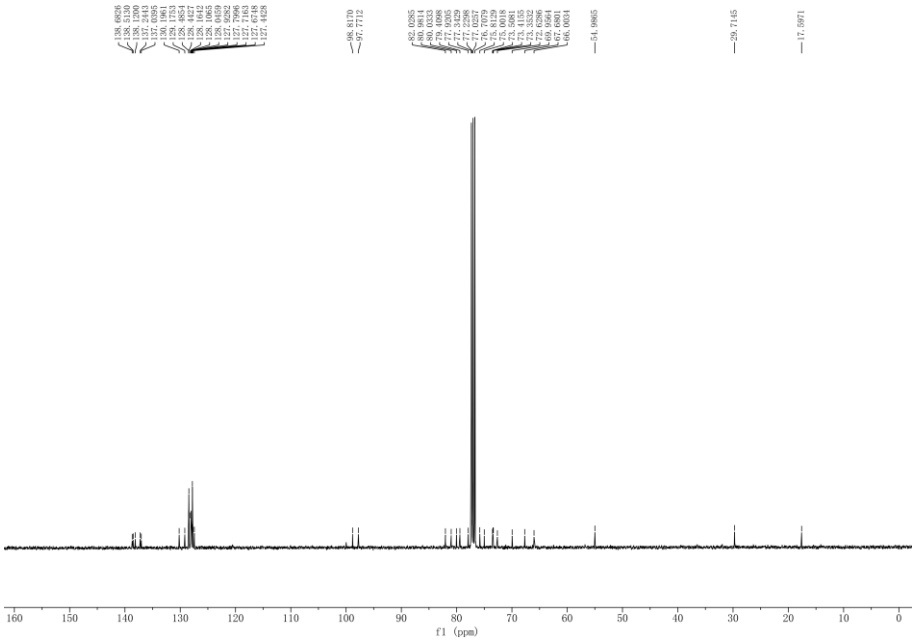




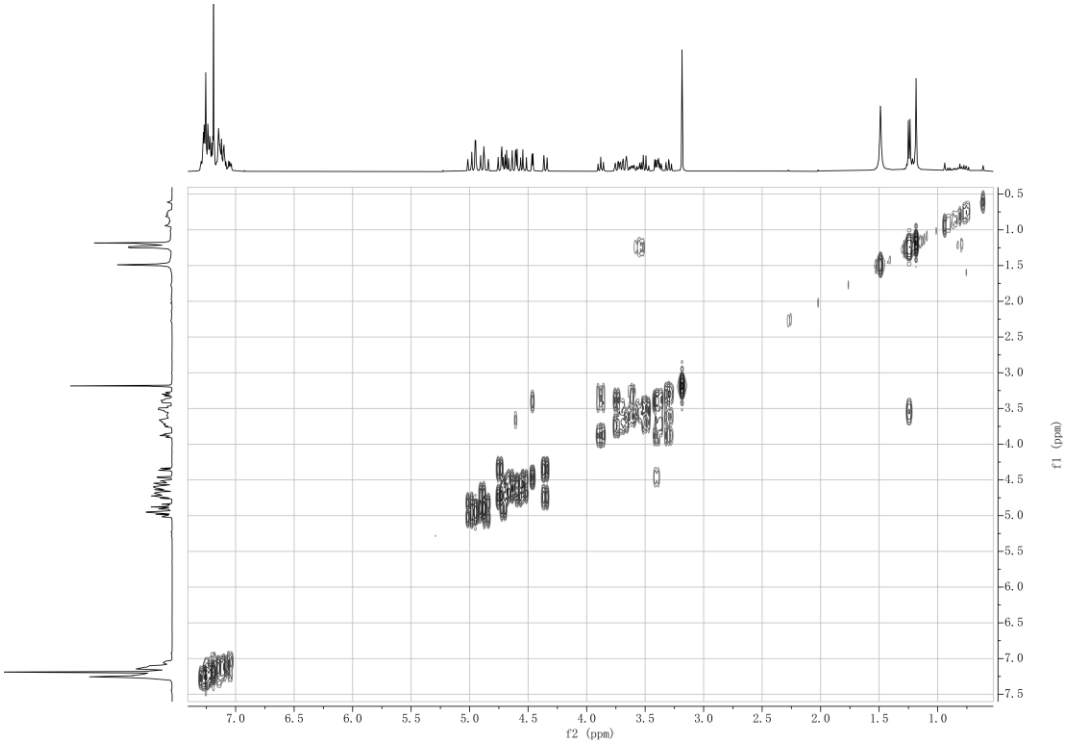
^{1}H NMR, 400 MHz, $CDCl_3$



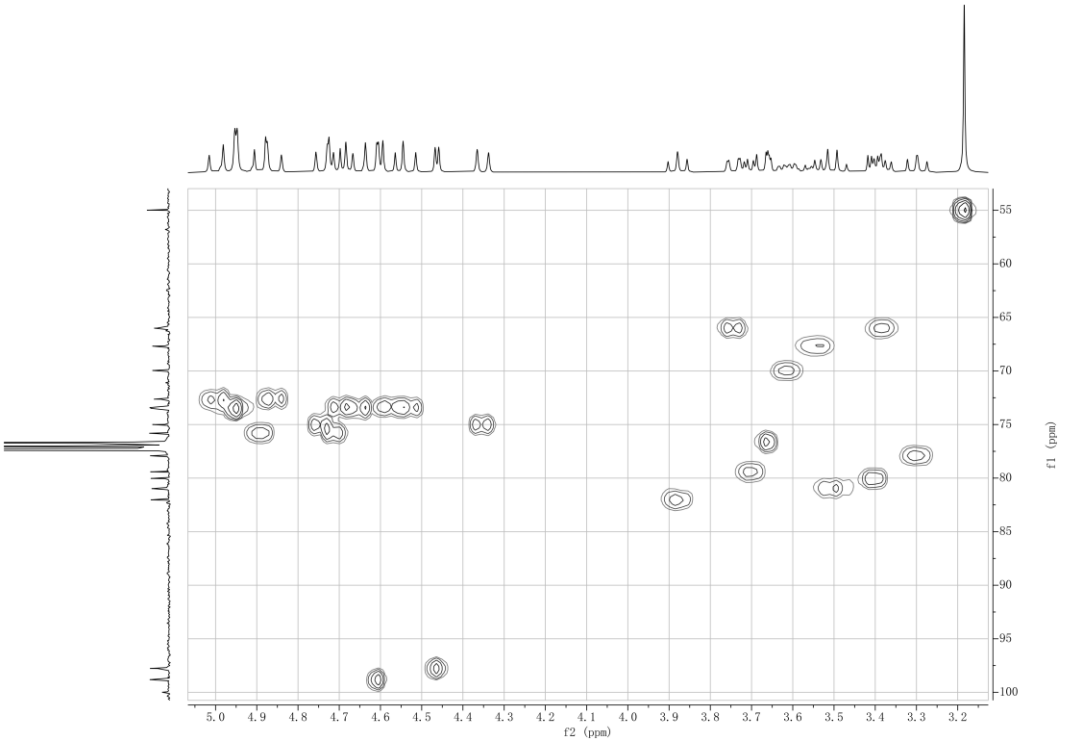
^{13}C NMR, 100 MHz, $CDCl_3$

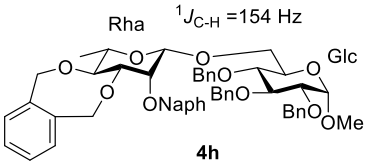


COSY, 400 MHz, $CDCl_3$



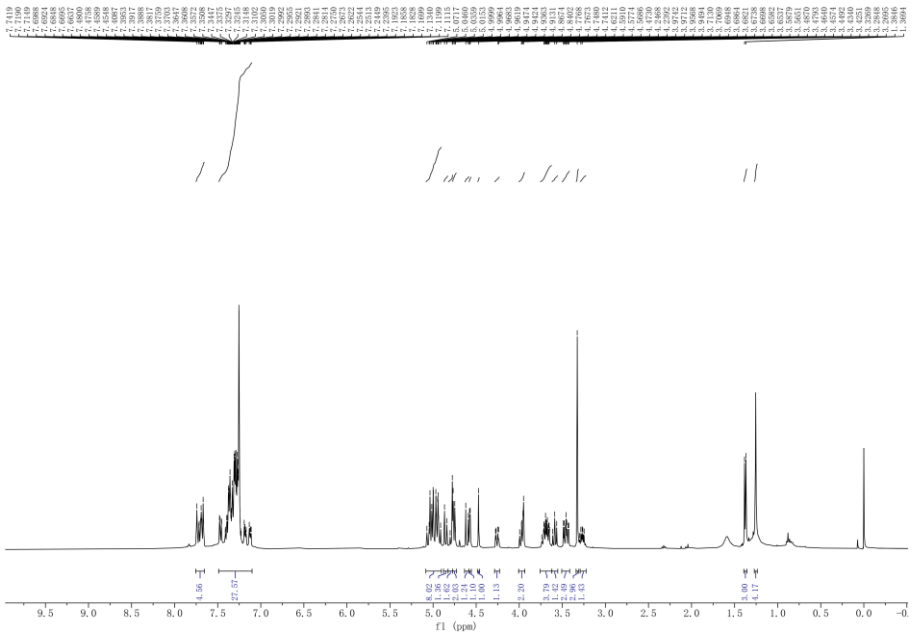
HSQC, 400 MHz, $CDCl_3$



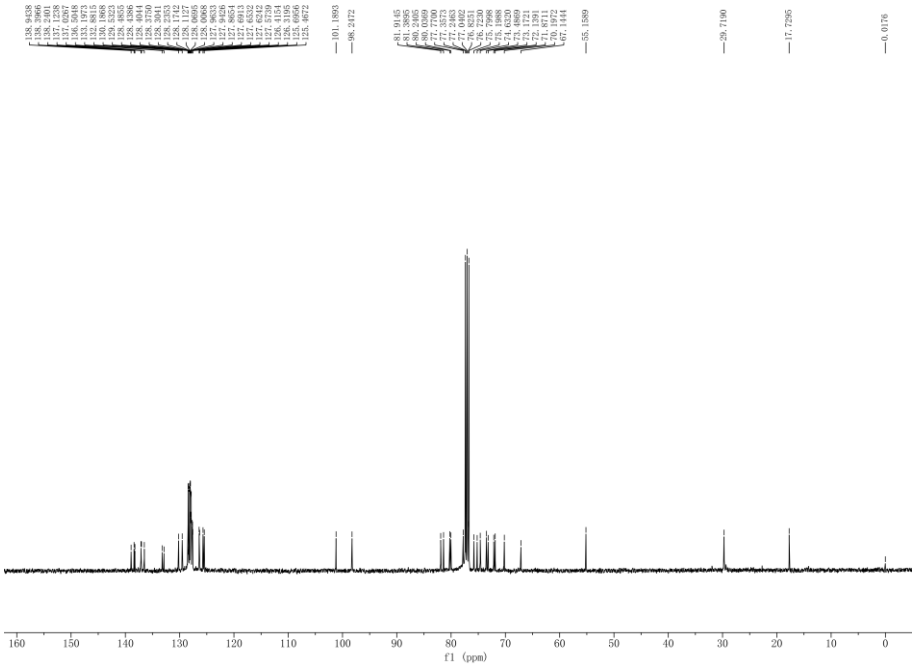


4h

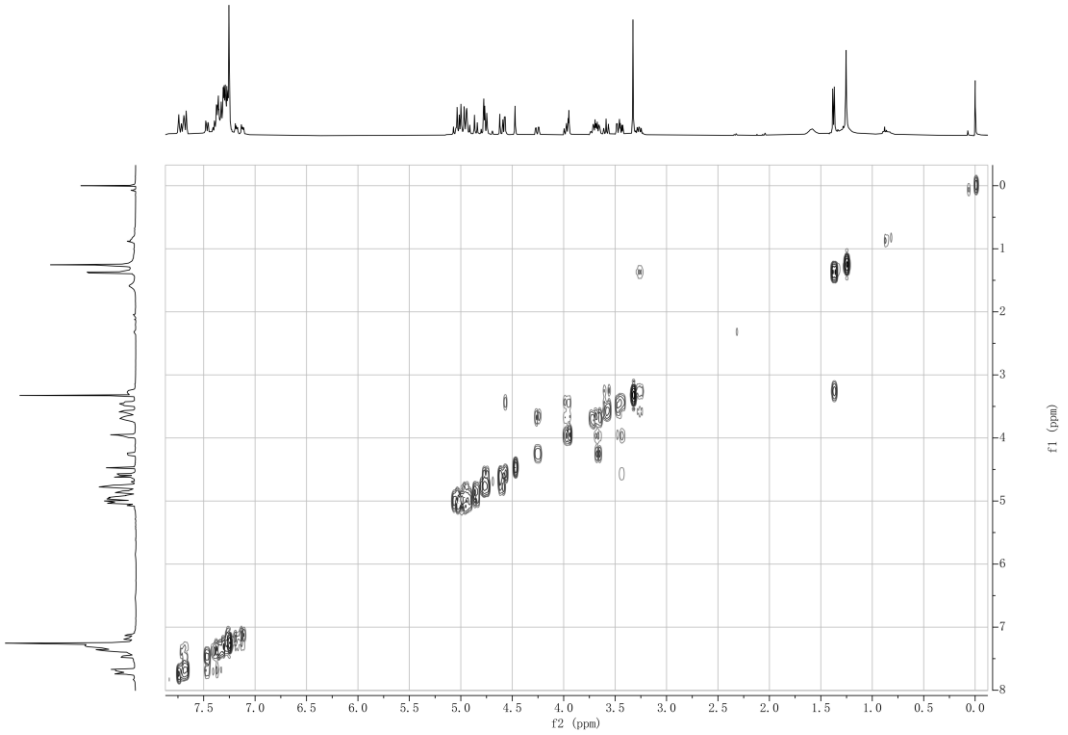
^{1}H NMR, 400 MHz, $CDCl_3$



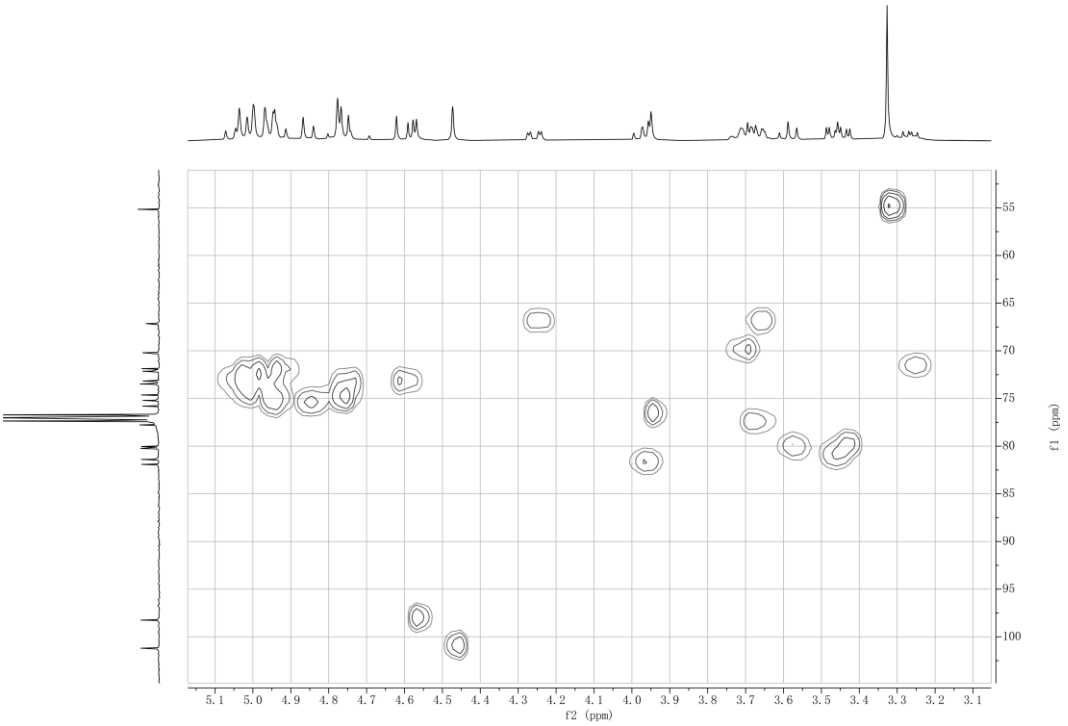
^{13}C NMR, 100 MHz, $CDCl_3$

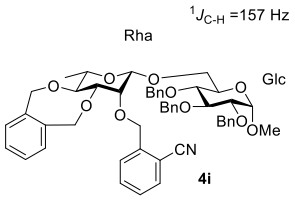


COSY, 400 MHz, $CDCl_3$

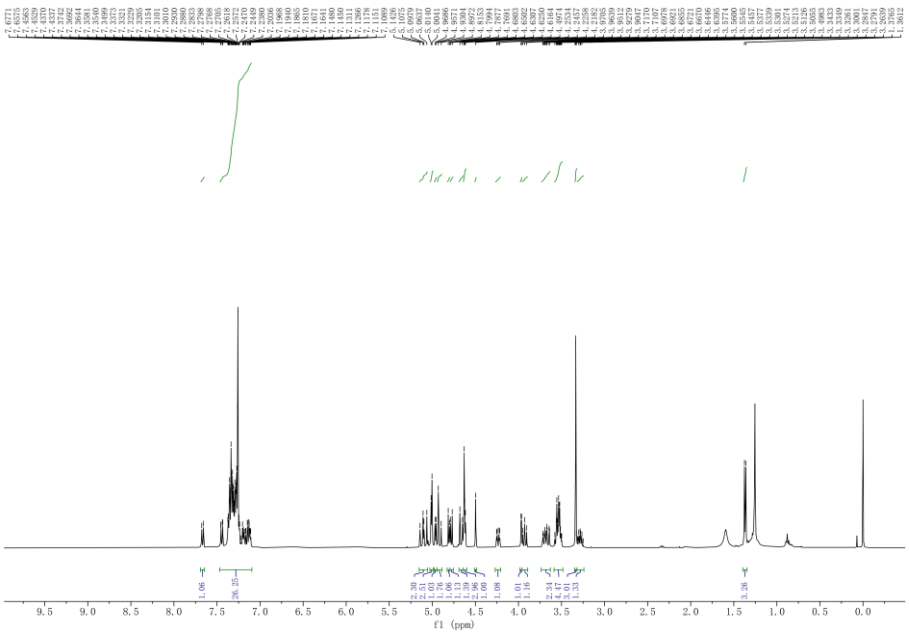


HSQC, 400 MHz, $CDCl_3$

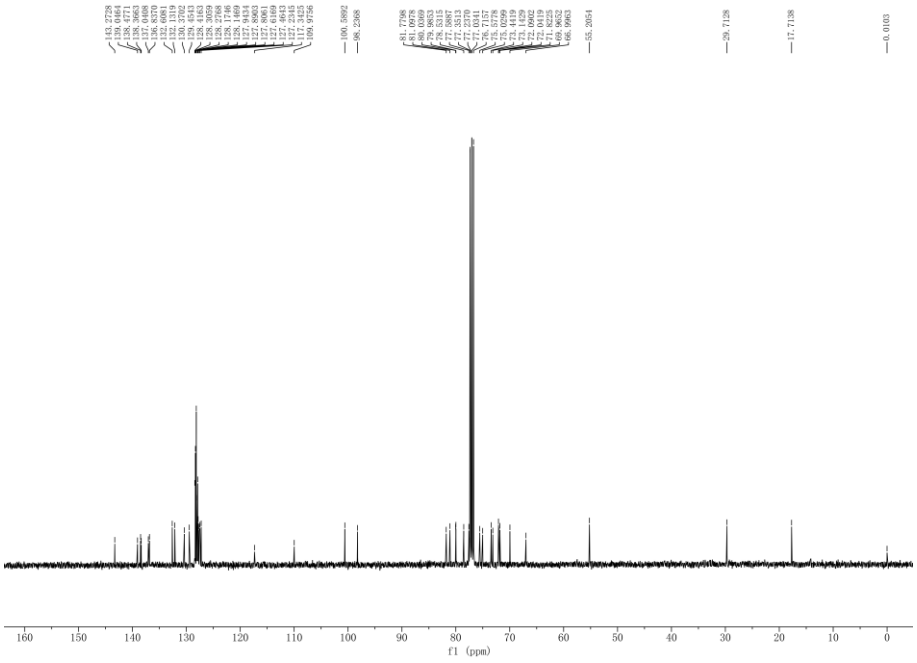




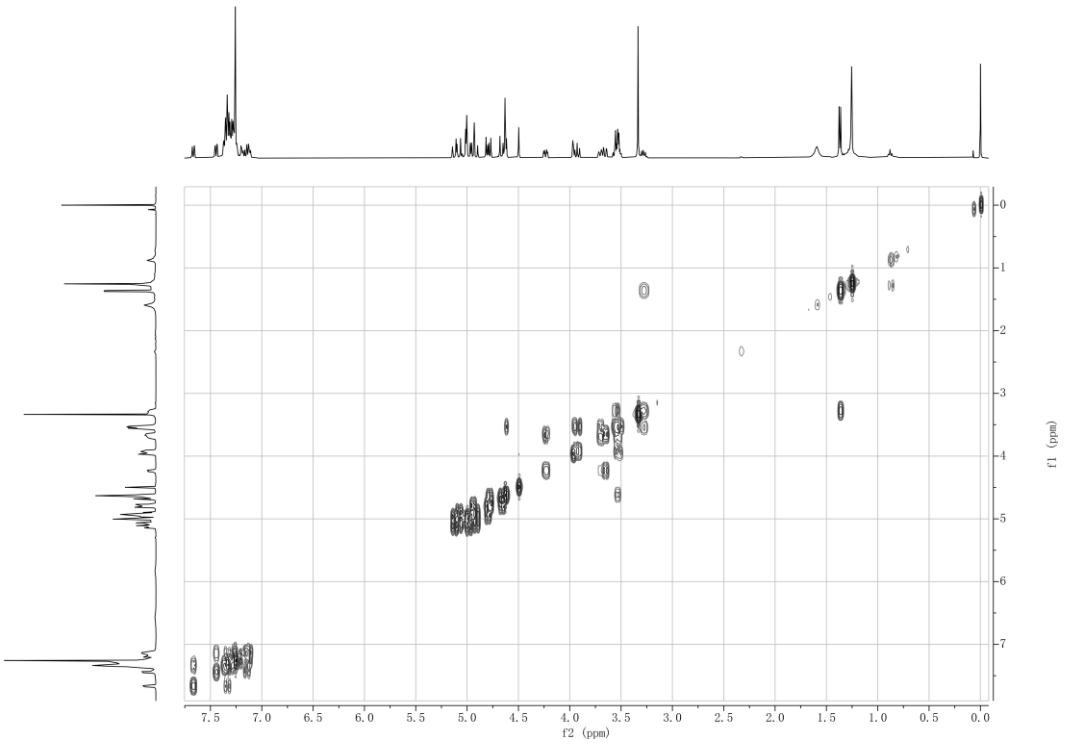
^{1}H NMR, 400 MHz, $CDCl_3$



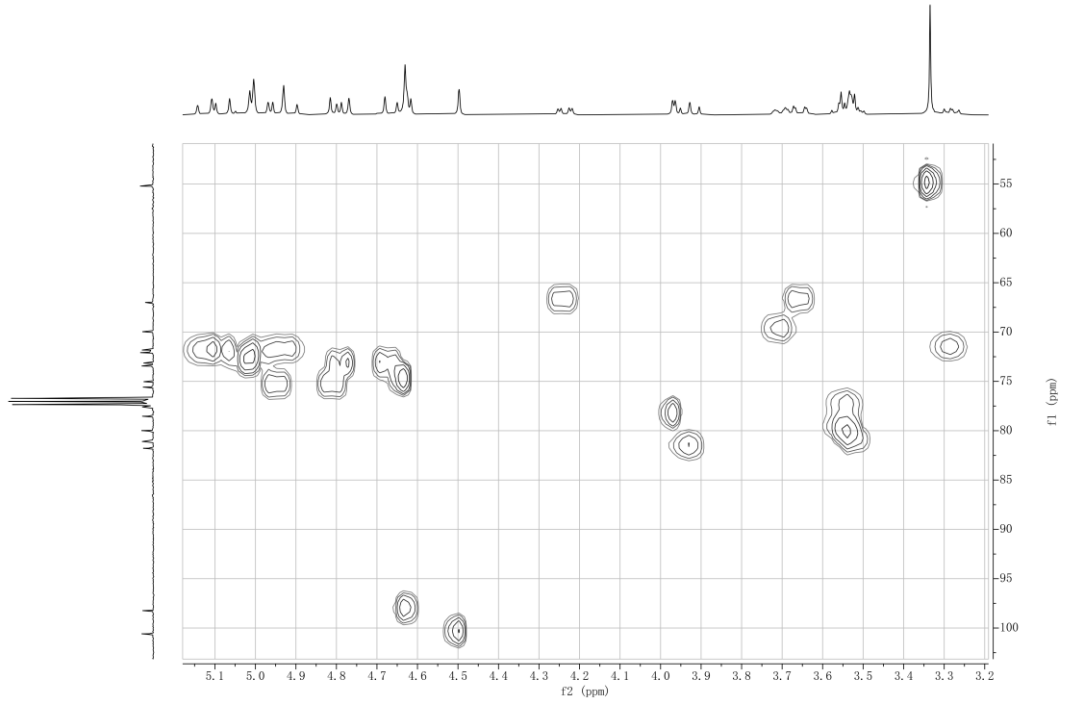
^{13}C NMR, 100 MHz, $CDCl_3$

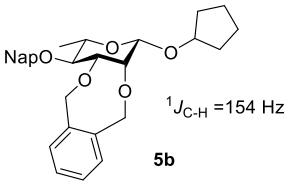


COSY, 400 MHz, $CDCl_3$



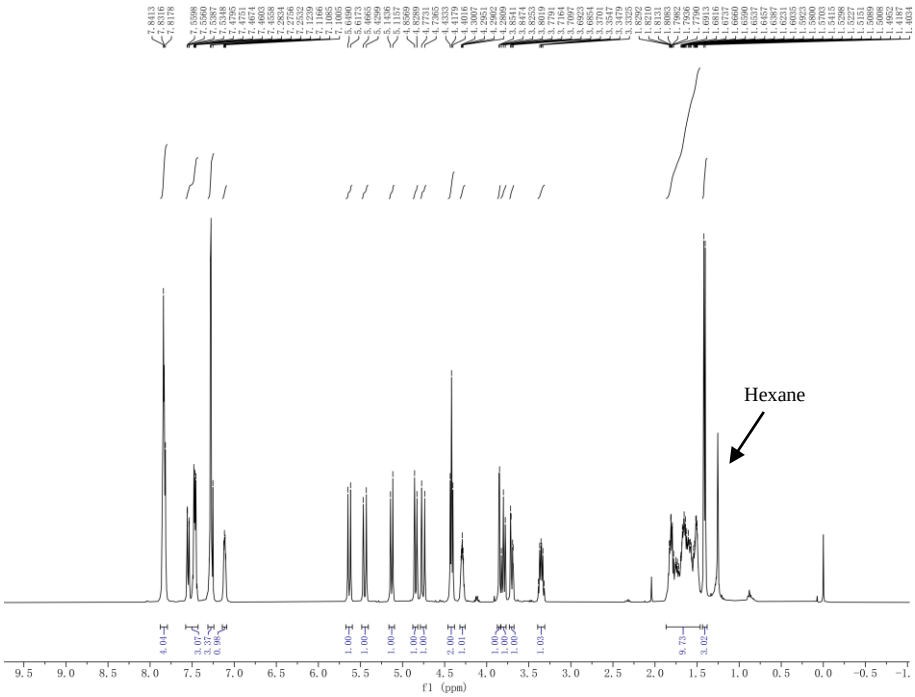
HSQC, 400 MHz, $CDCl_3$



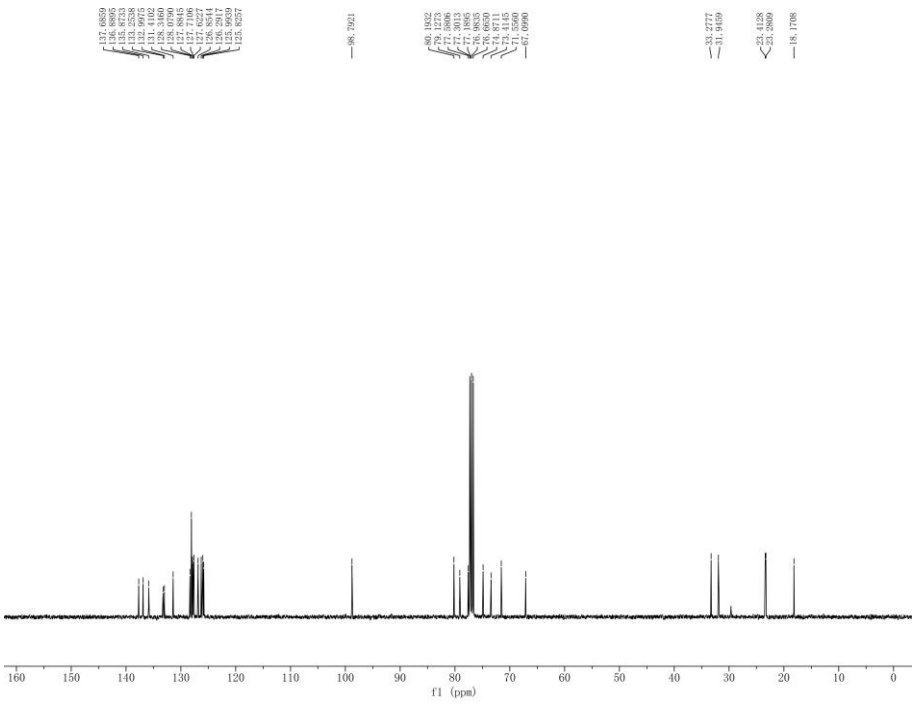


5b

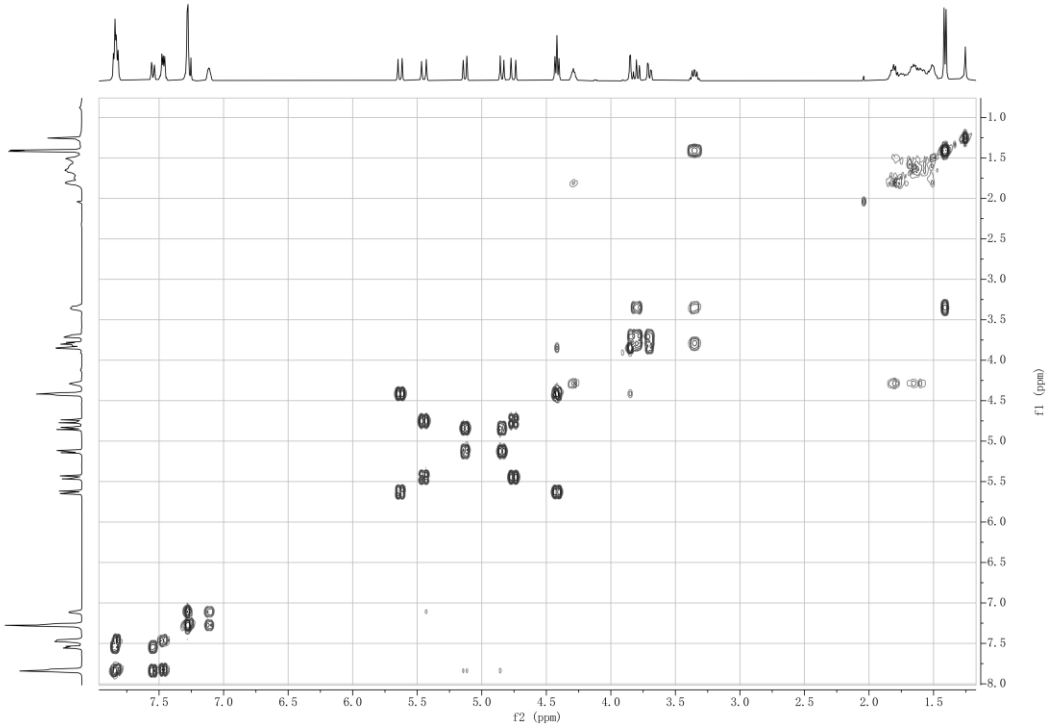
^{1}H NMR, 400 MHz, $CDCl_3$



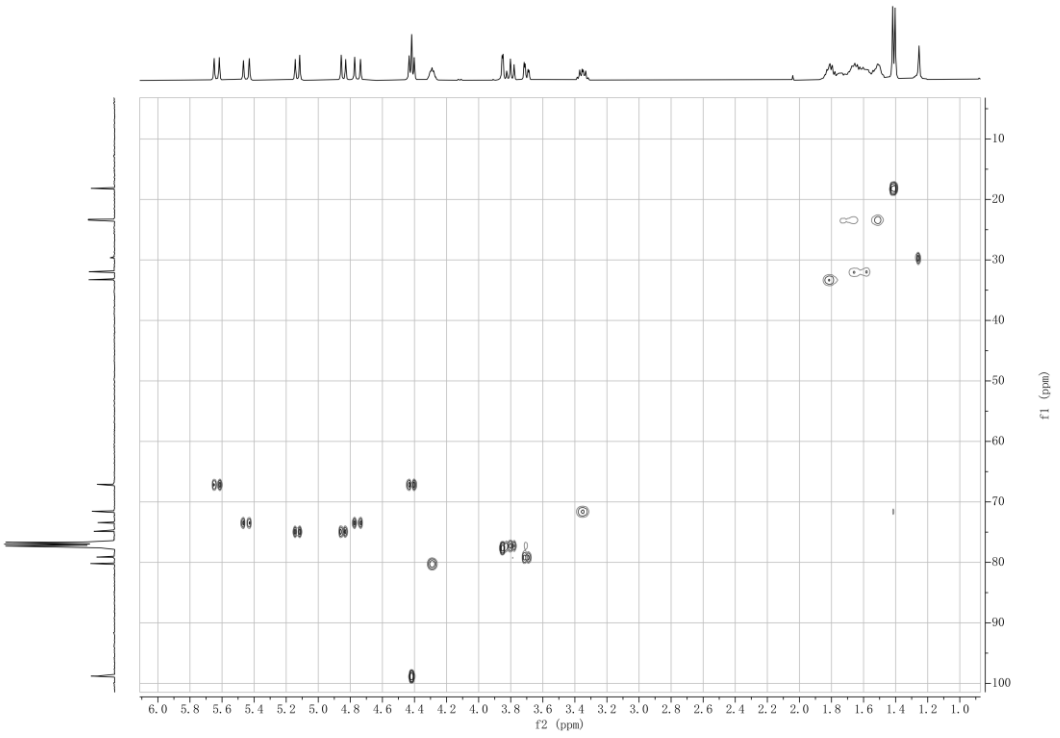
^{13}C NMR, 100 MHz, $CDCl_3$

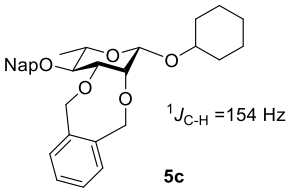


COSY, 400 MHz, $CDCl_3$



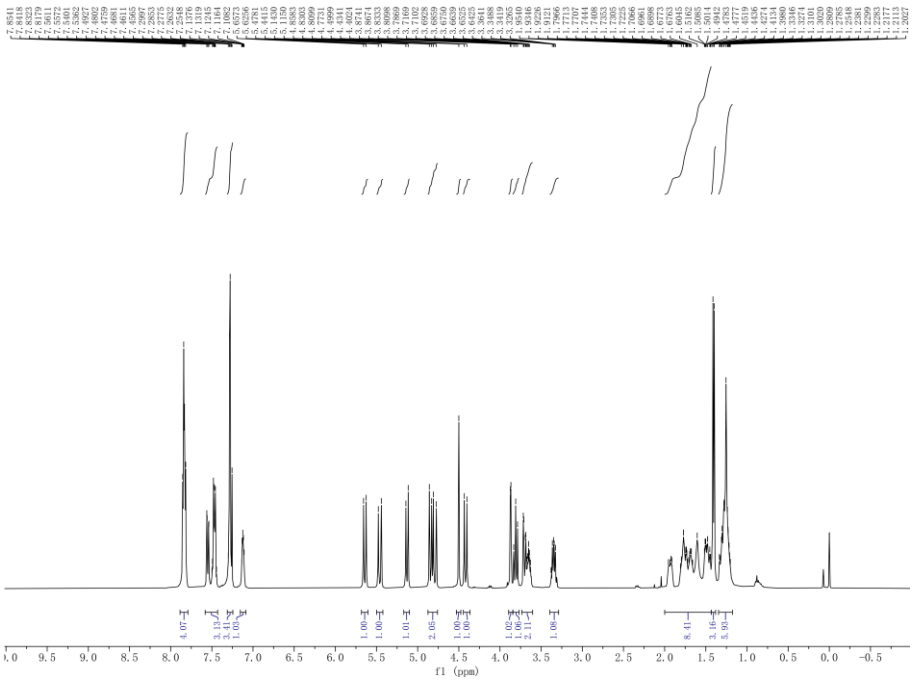
HSQC, 400 MHz, $CDCl_3$



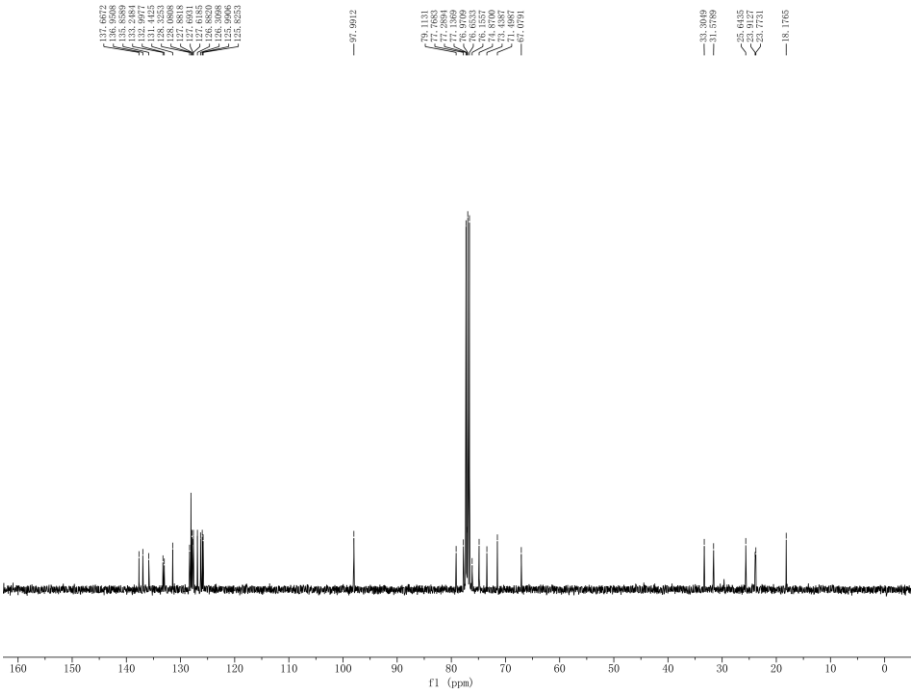


5c

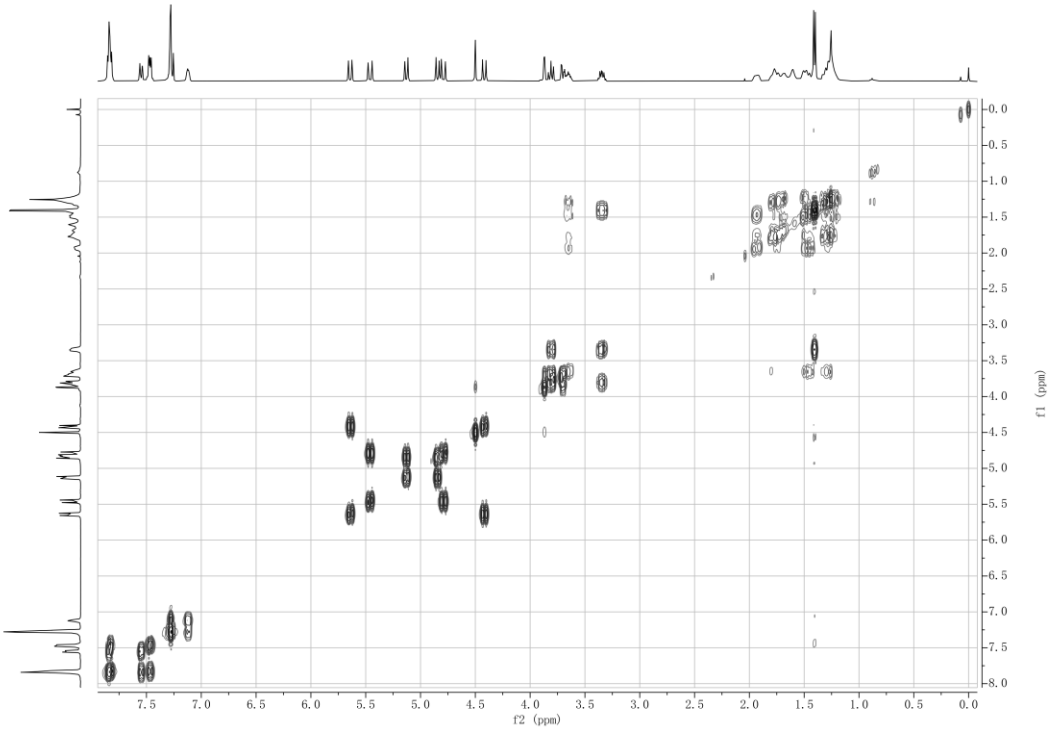
^{1}H NMR, 400 MHz, $CDCl_3$



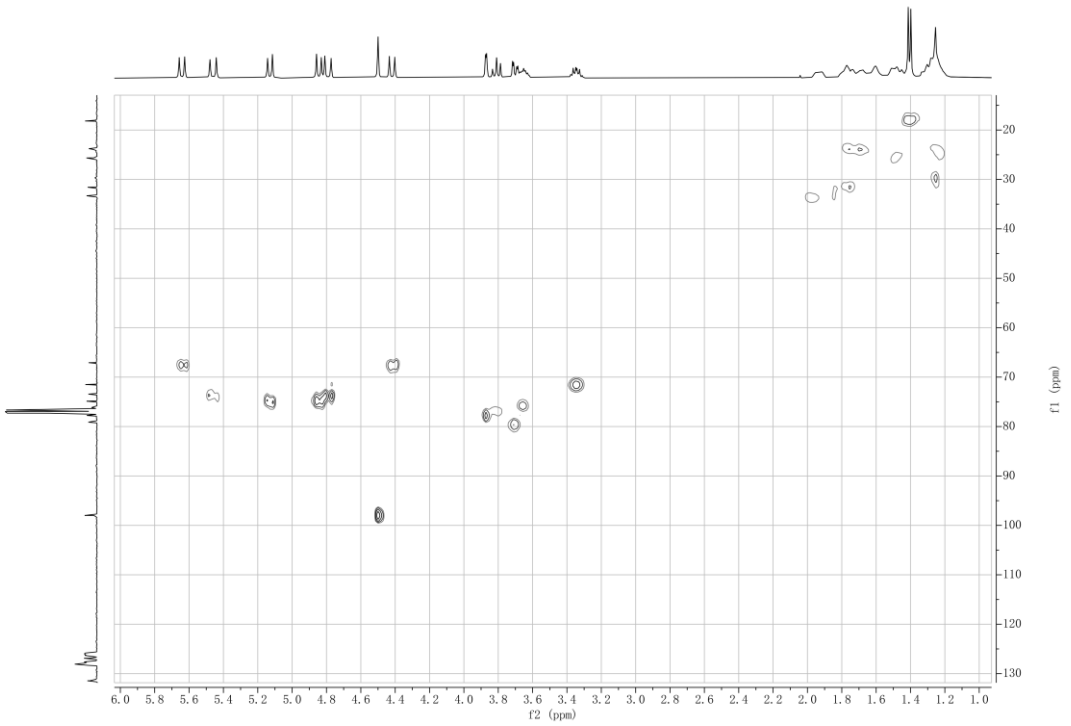
^{13}C NMR, 100 MHz, $CDCl_3$

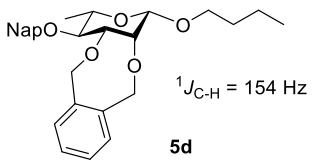


COSY, 400 MHz, $CDCl_3$



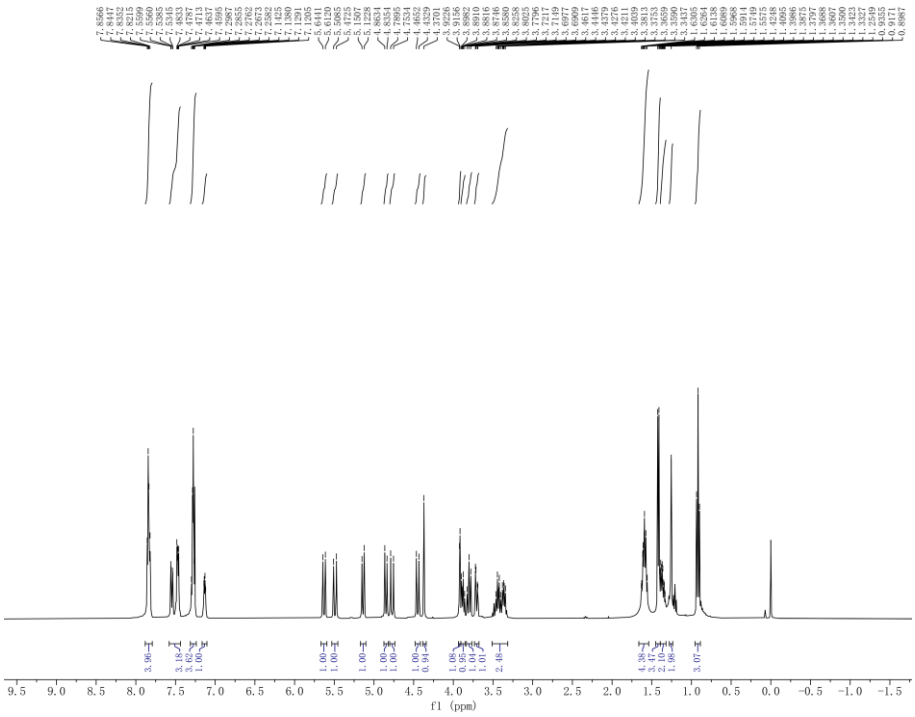
HSQC, 400 MHz, $CDCl_3$



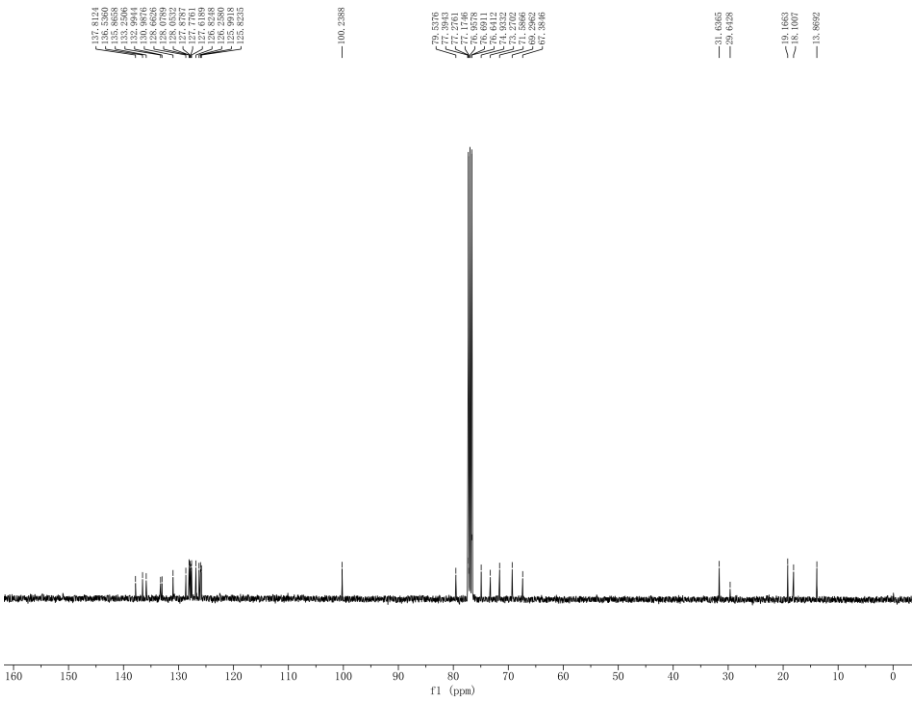


5d

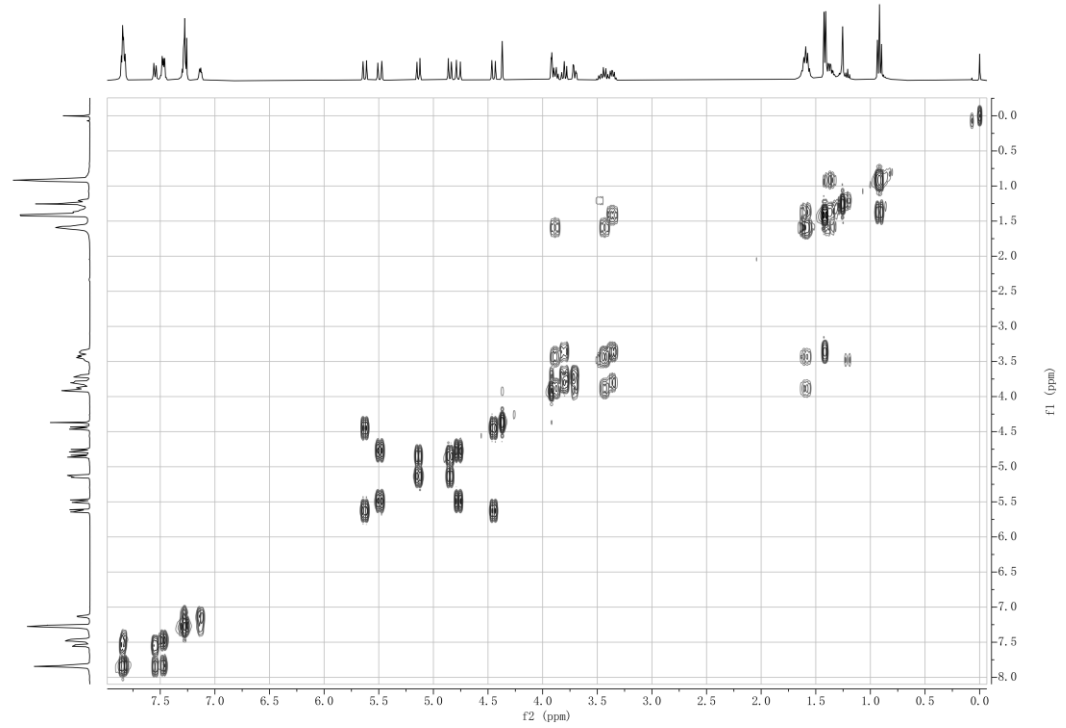
^{1}H NMR, 400 MHz, $CDCl_3$



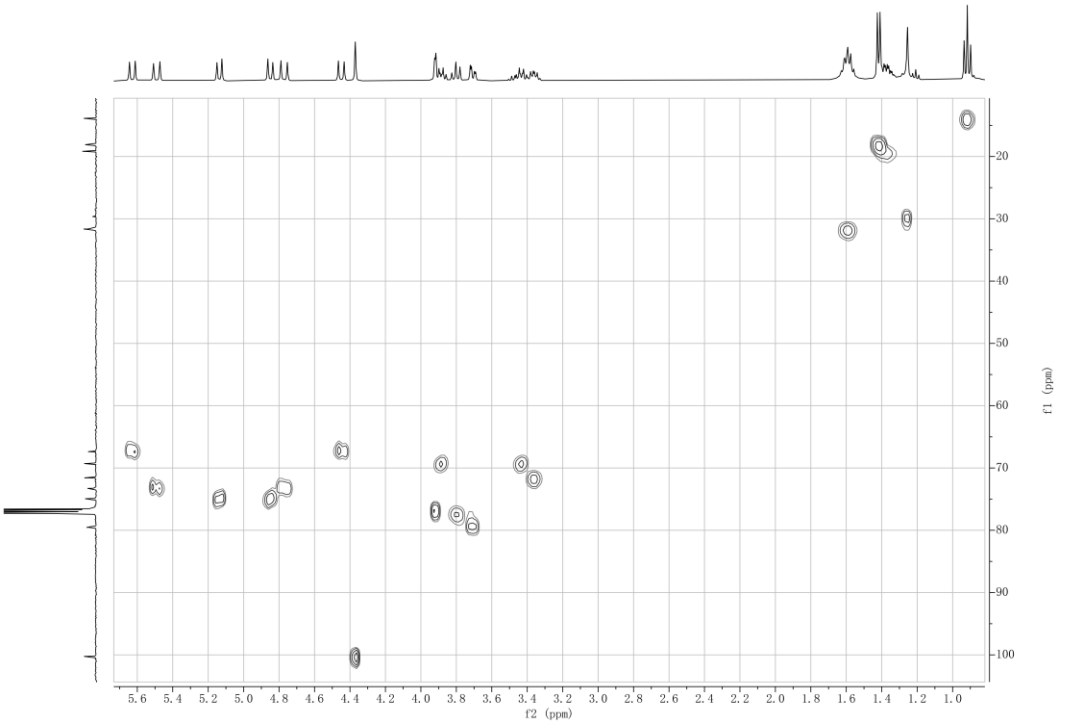
^{13}C NMR, 100 MHz, $CDCl_3$

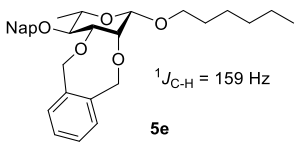


COSY, 400 MHz, $CDCl_3$

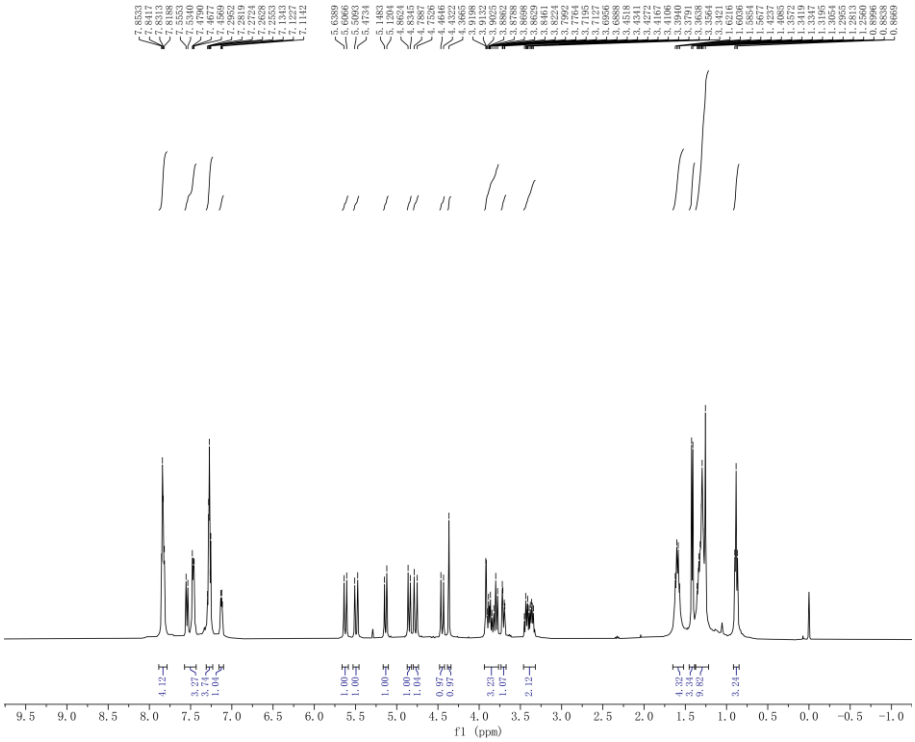


HSQC, 400 MHz, $CDCl_3$

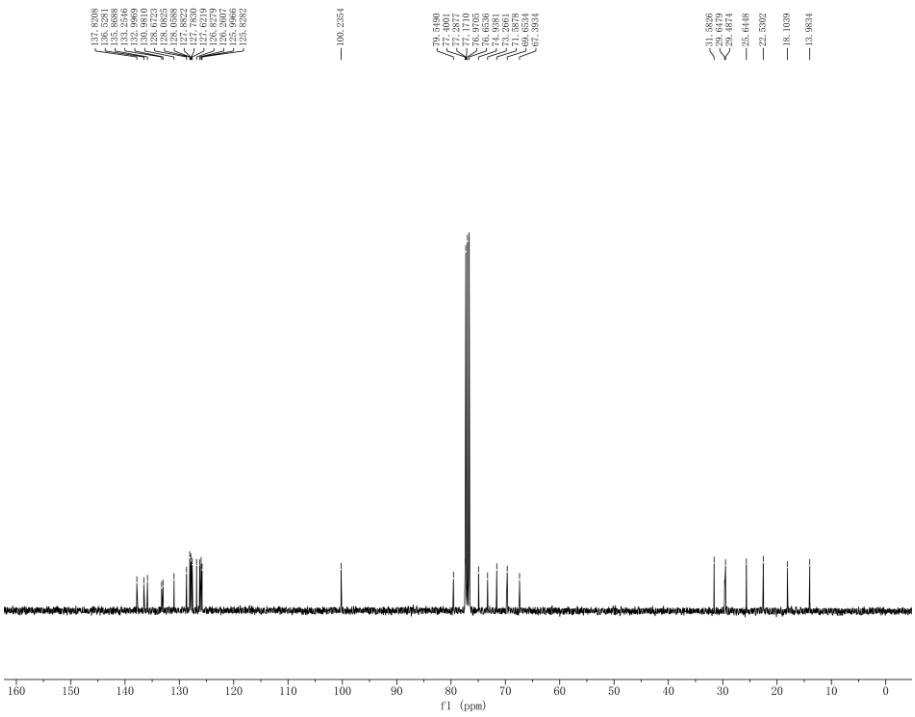




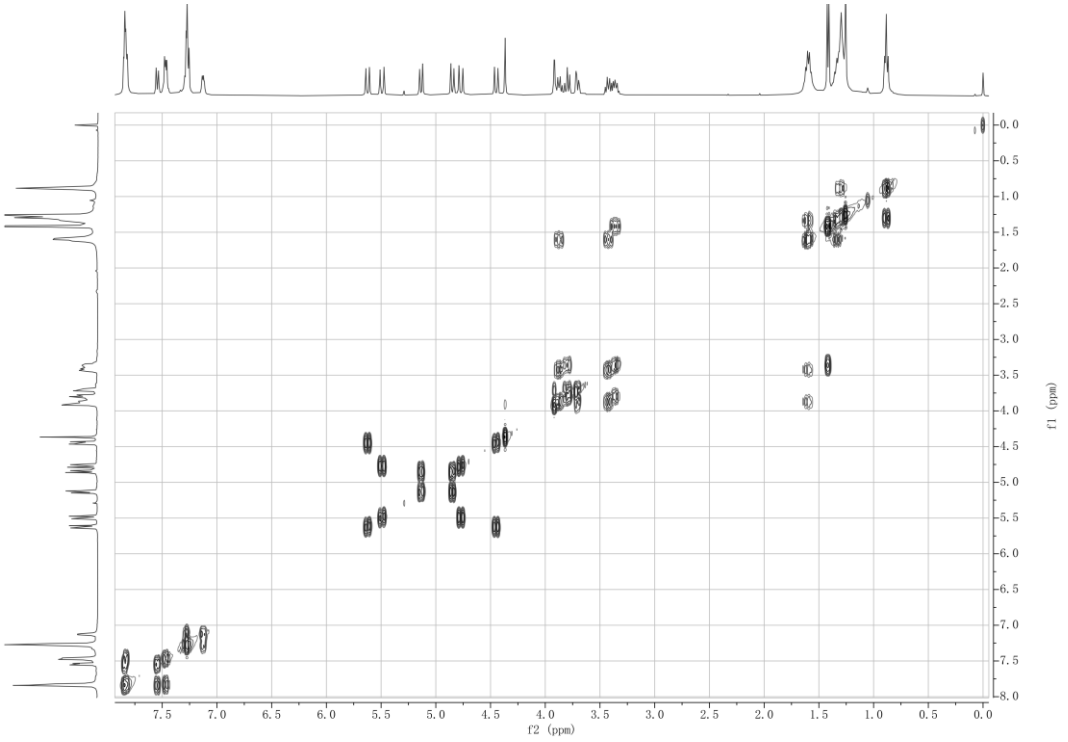
^{1}H NMR, 400 MHz, $CDCl_3$



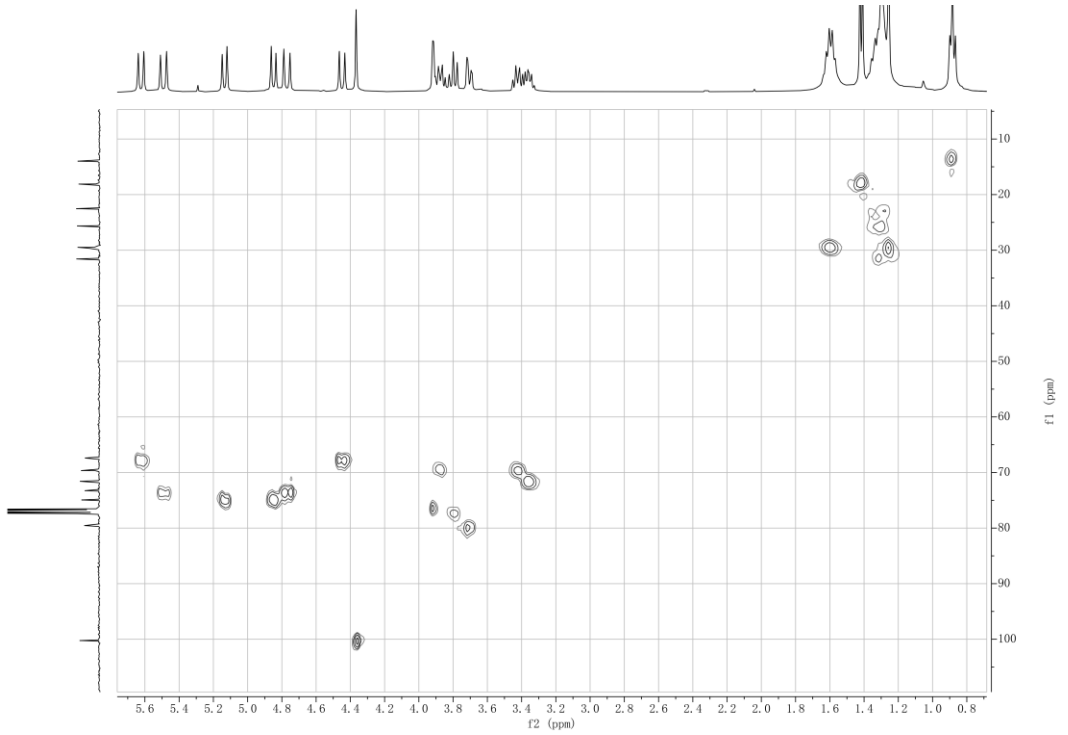
^{13}C NMR, 100 MHz, $CDCl_3$

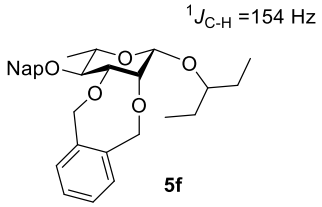


COSY, 400 MHz, $CDCl_3$

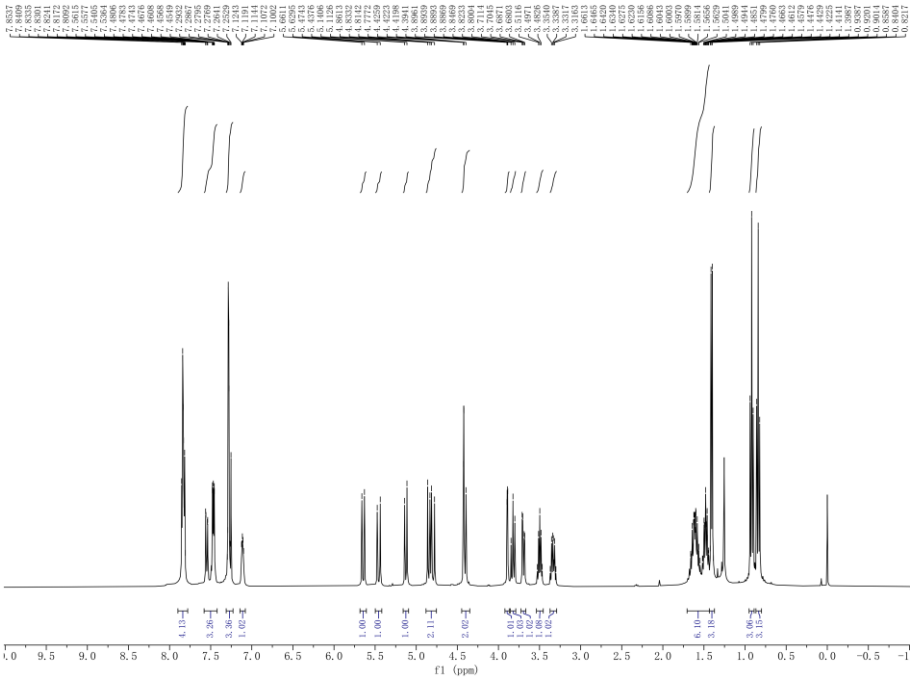


HSQC, 400 MHz, $CDCl_3$

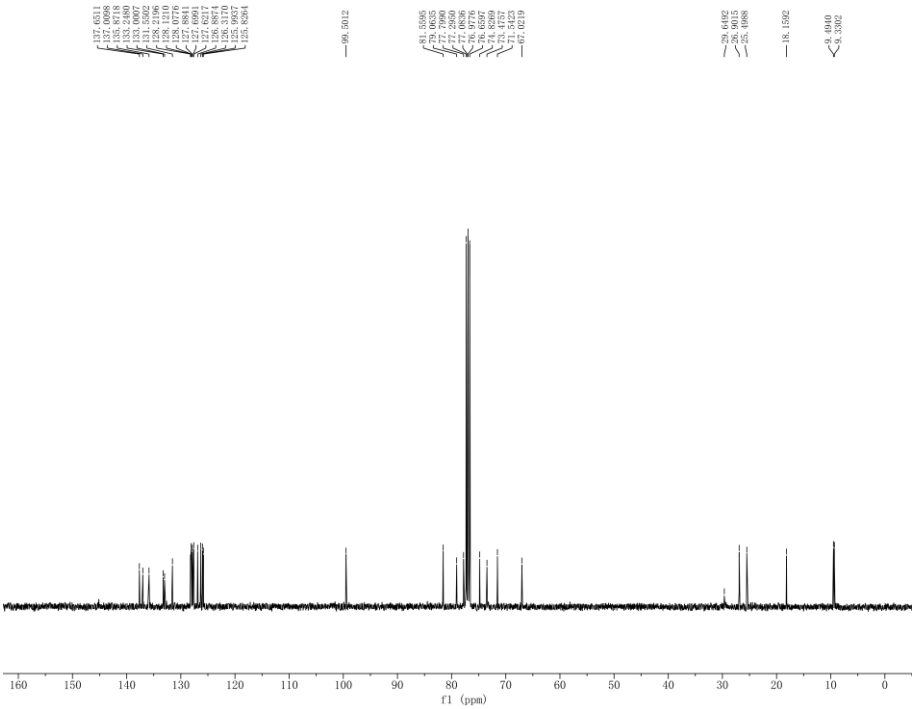




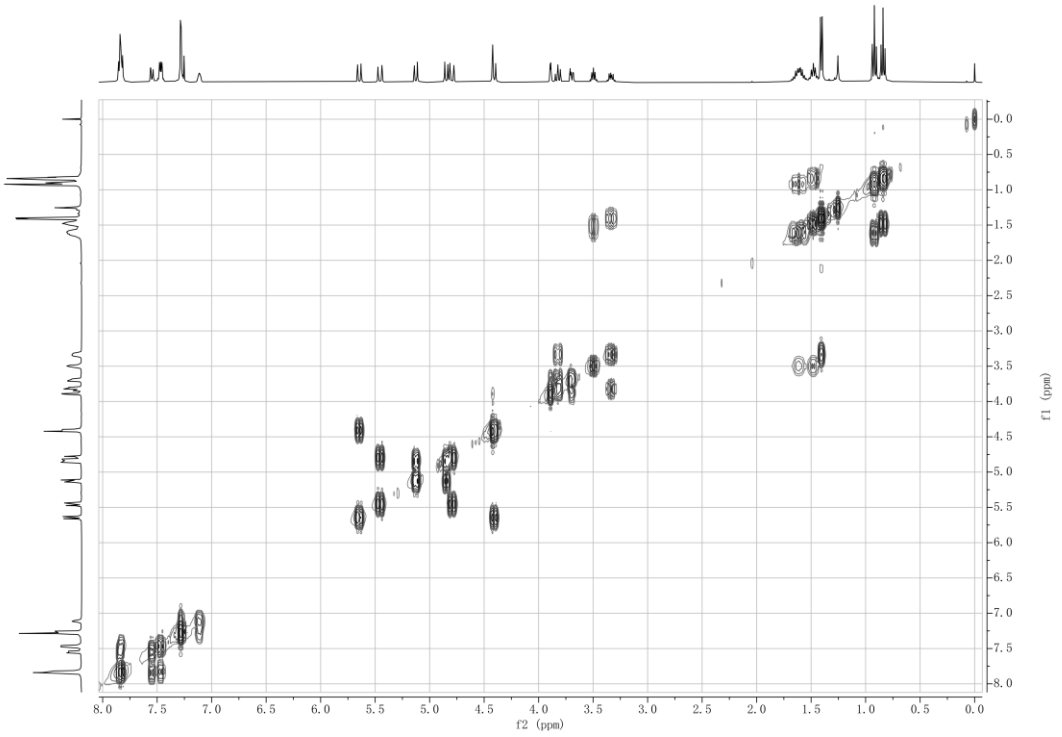
^{1}H NMR, 400 MHz, $CDCl_3$



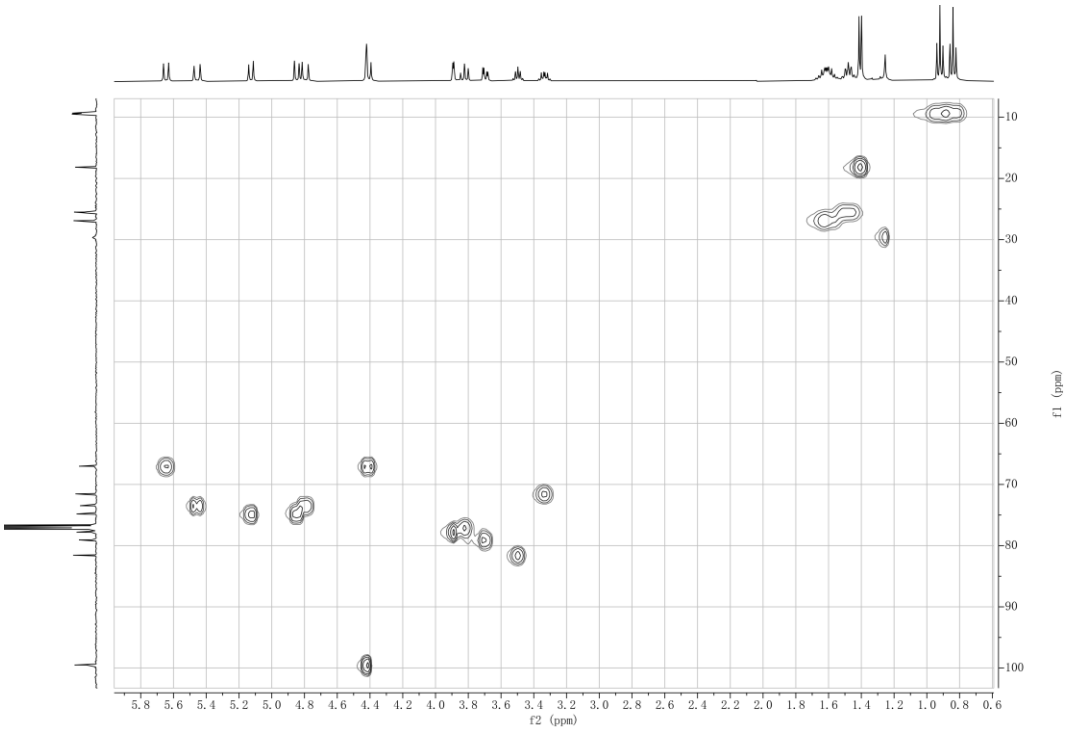
^{13}C NMR, 100 MHz, $CDCl_3$

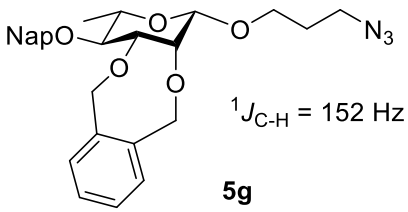


COSY, 400 MHz, $CDCl_3$



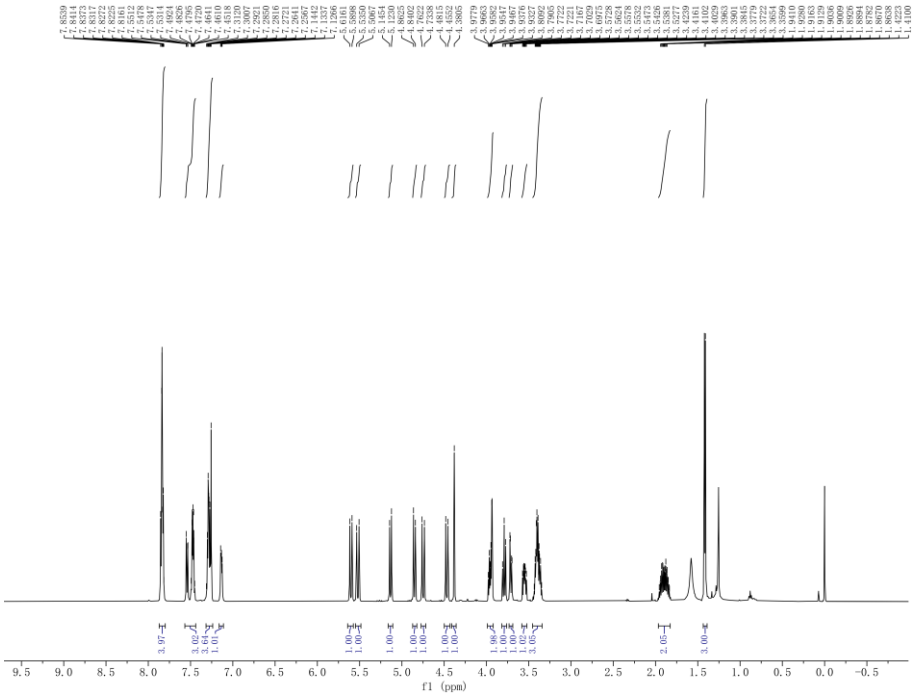
HSQC, 400 MHz, $CDCl_3$



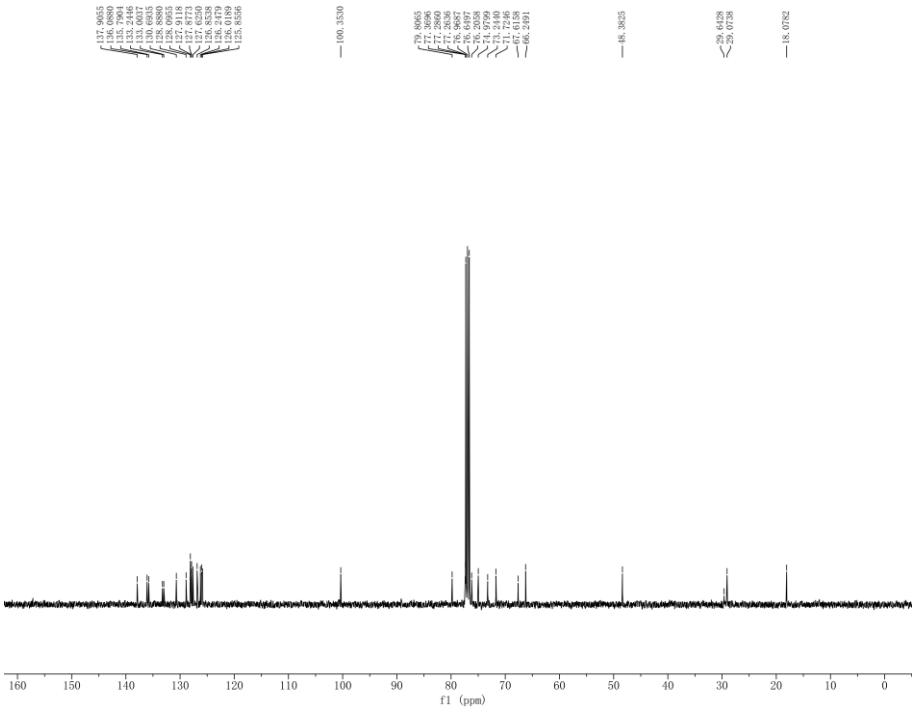


5g

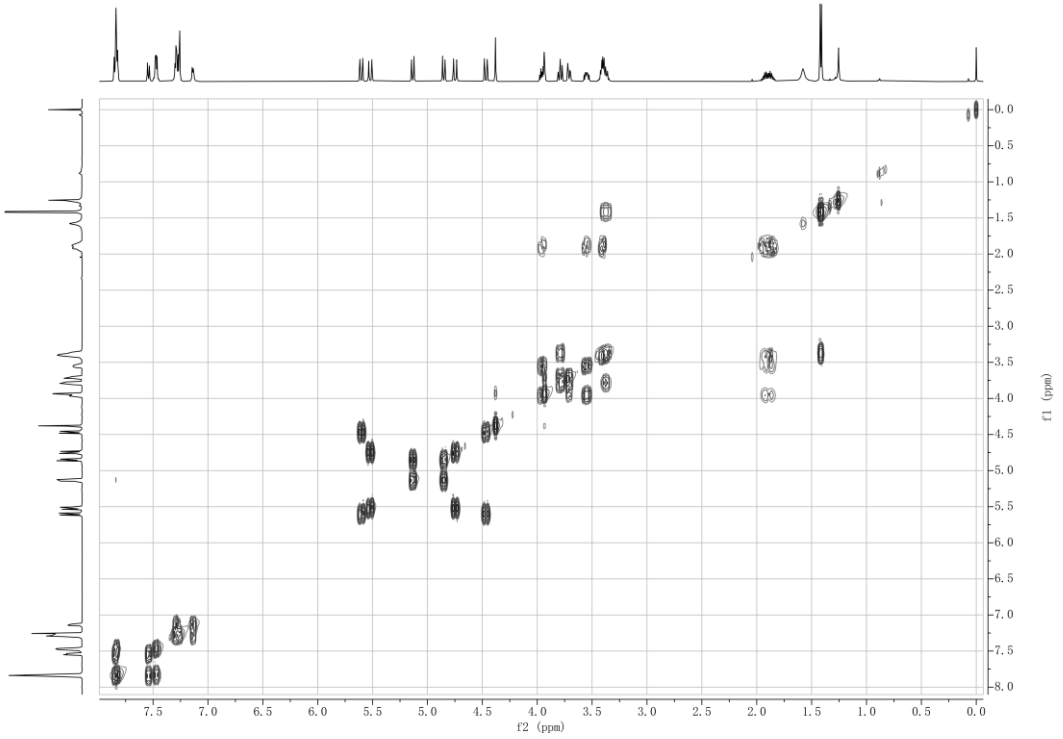
^{1}H NMR, 500 MHz, $CDCl_3$



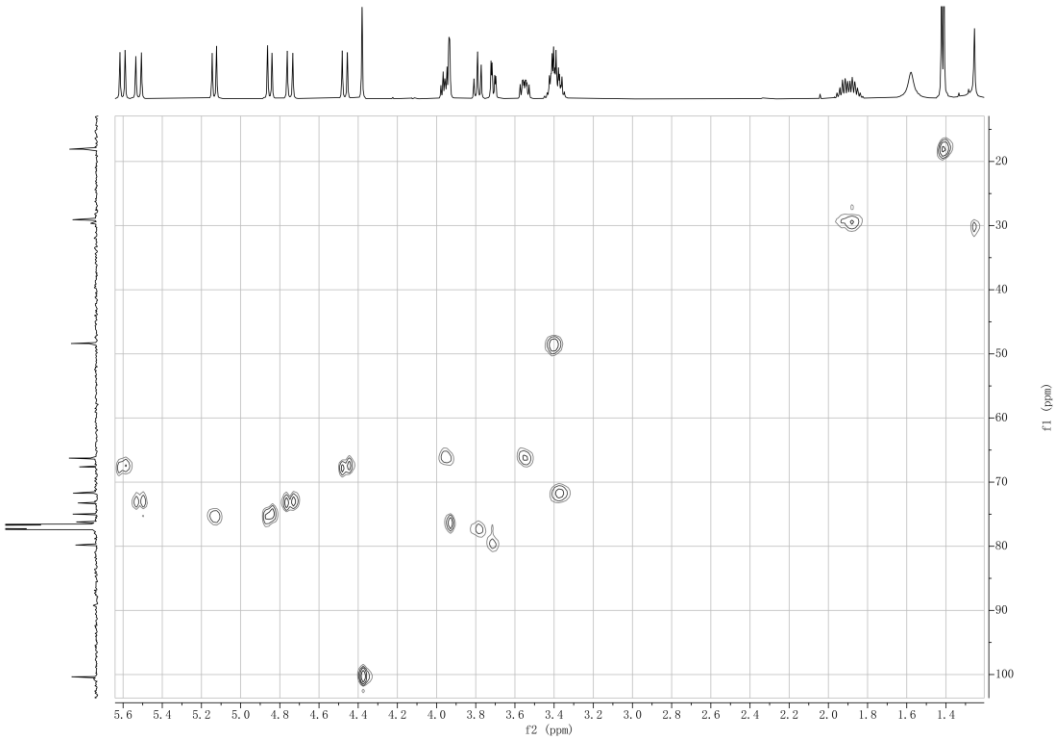
^{13}C NMR, 125MHz, $CDCl_3$

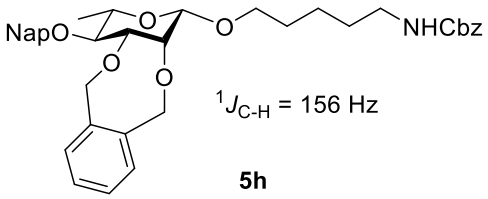


COSY, 500 MHz, $CDCl_3$



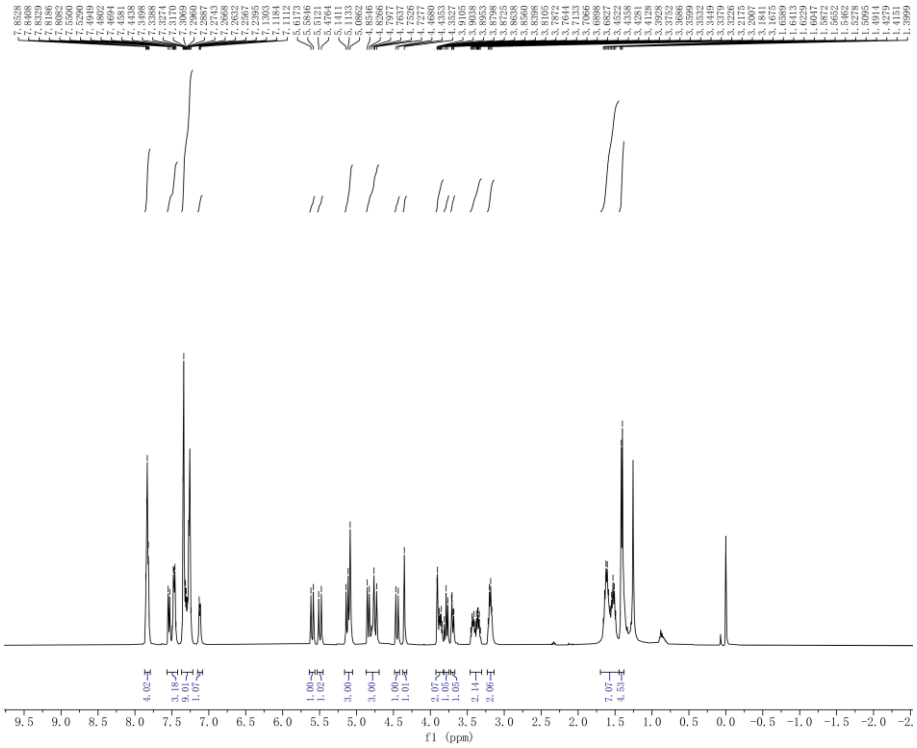
HSQC, 500 MHz, $CDCl_3$



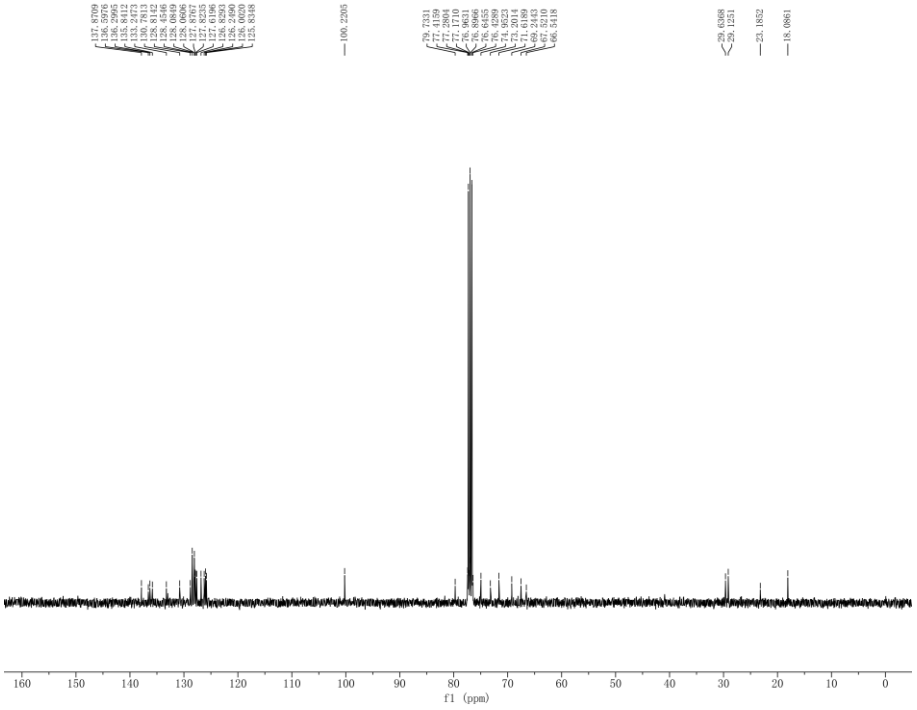


5h

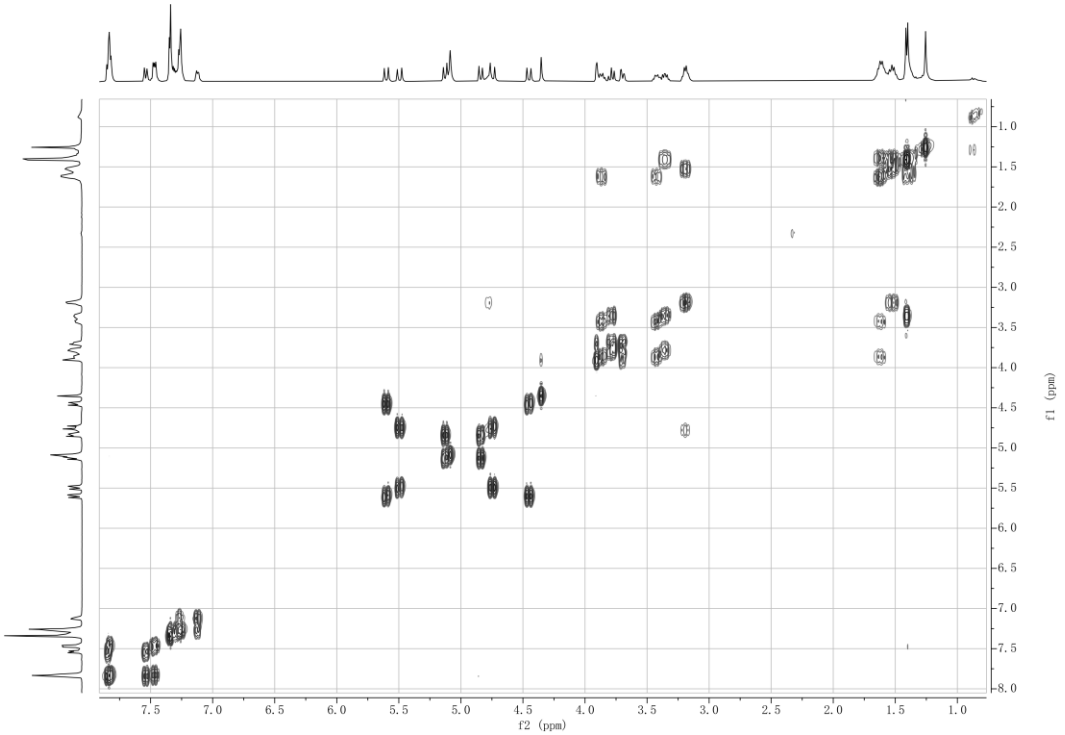
^{1}H NMR, 400 MHz, $CDCl_3$



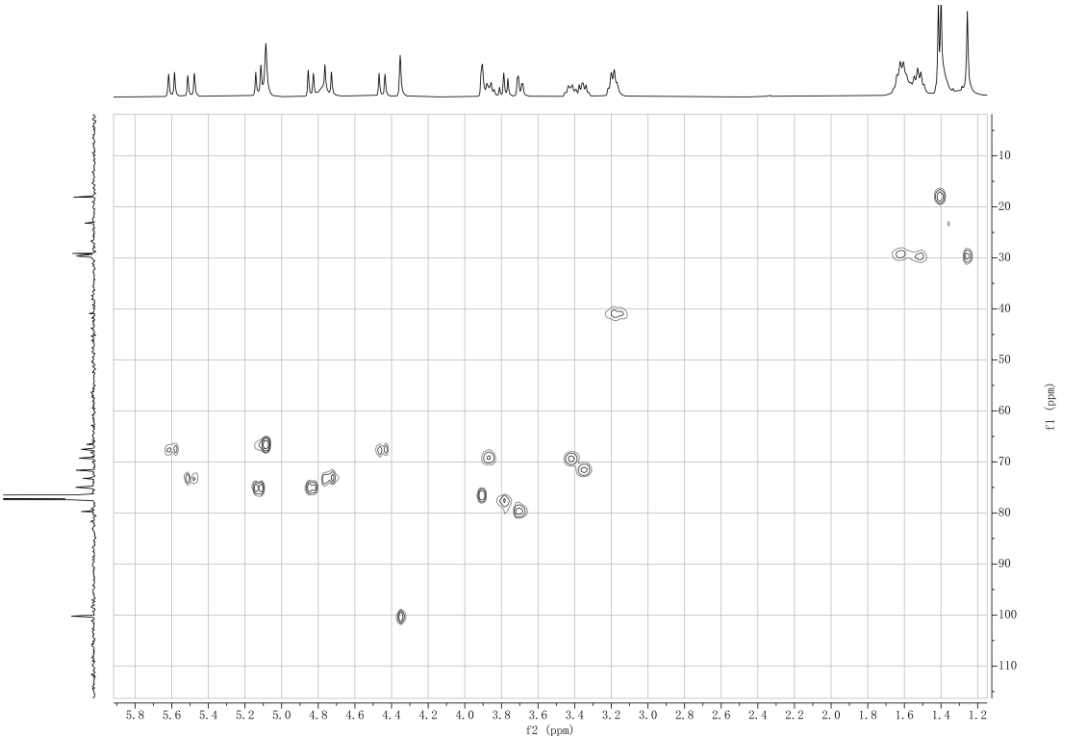
^{13}C NMR, 100 MHz, $CDCl_3$

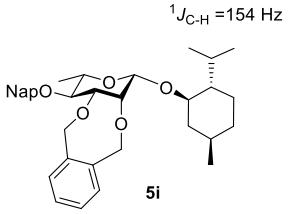


COSY, 400 MHz, $CDCl_3$

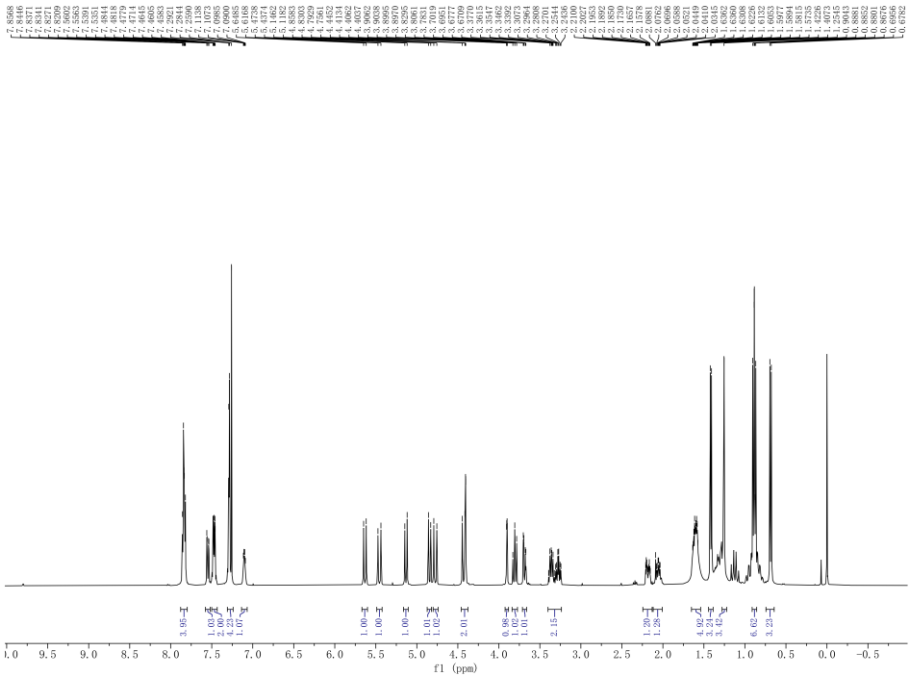


HSQC, 400 MHz, $CDCl_3$

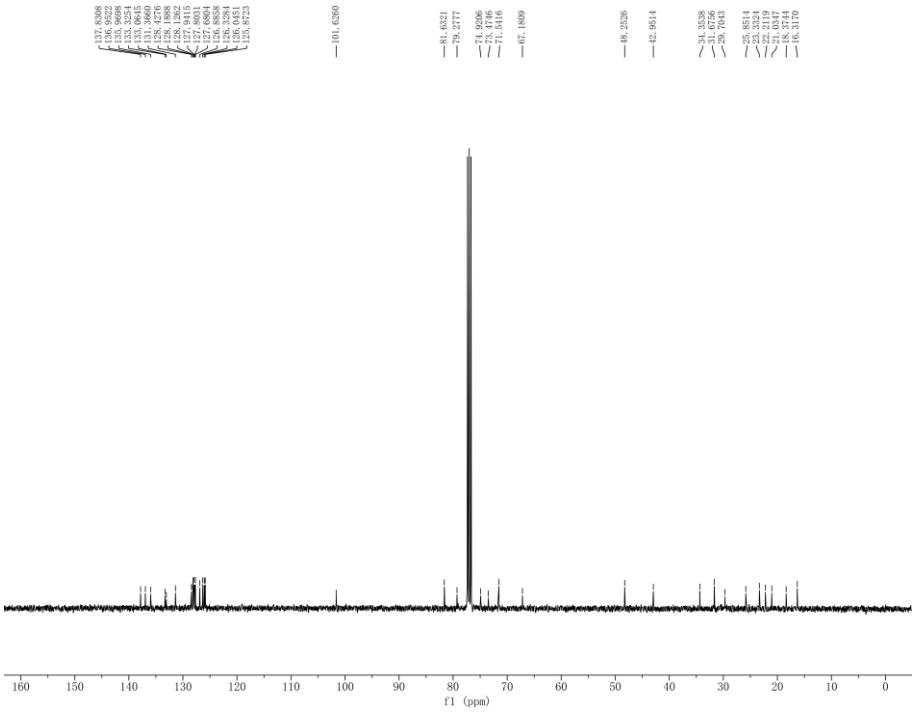




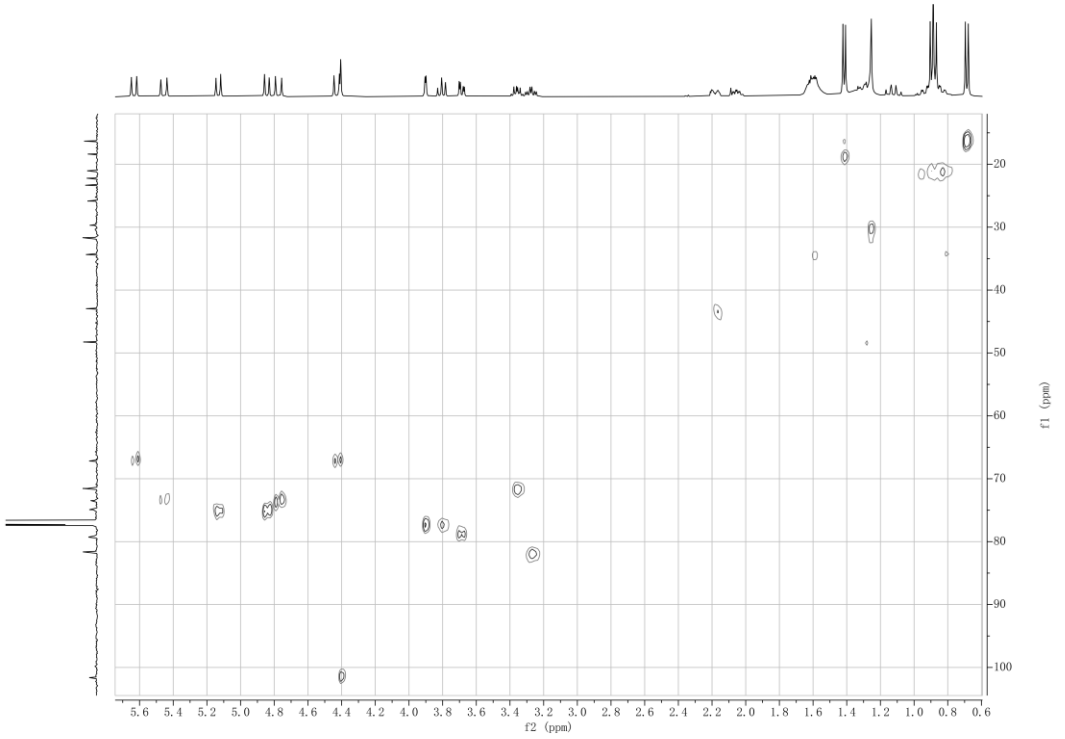
^{1}H NMR, 400 MHz, $CDCl_3$



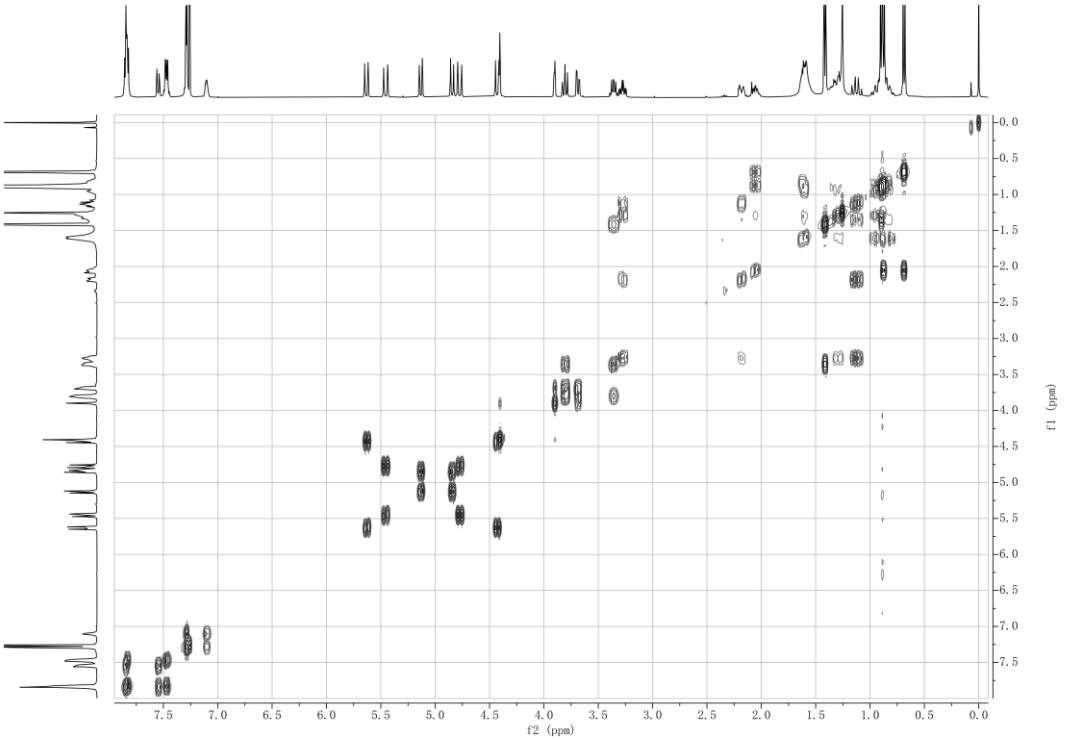
^{13}C NMR, 100 MHz, $CDCl_3$

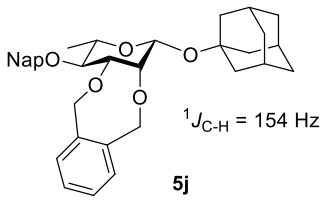


COSY, 400 MHz, $CDCl_3$



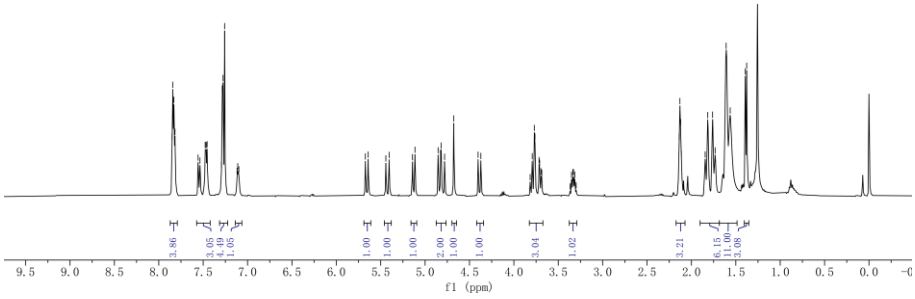
HSQC, 400 MHz, $CDCl_3$



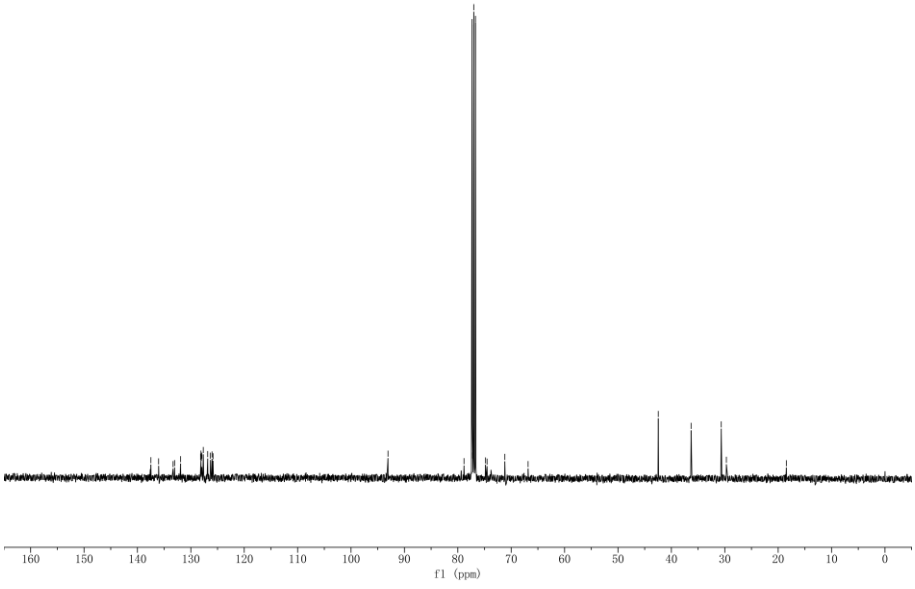


5j

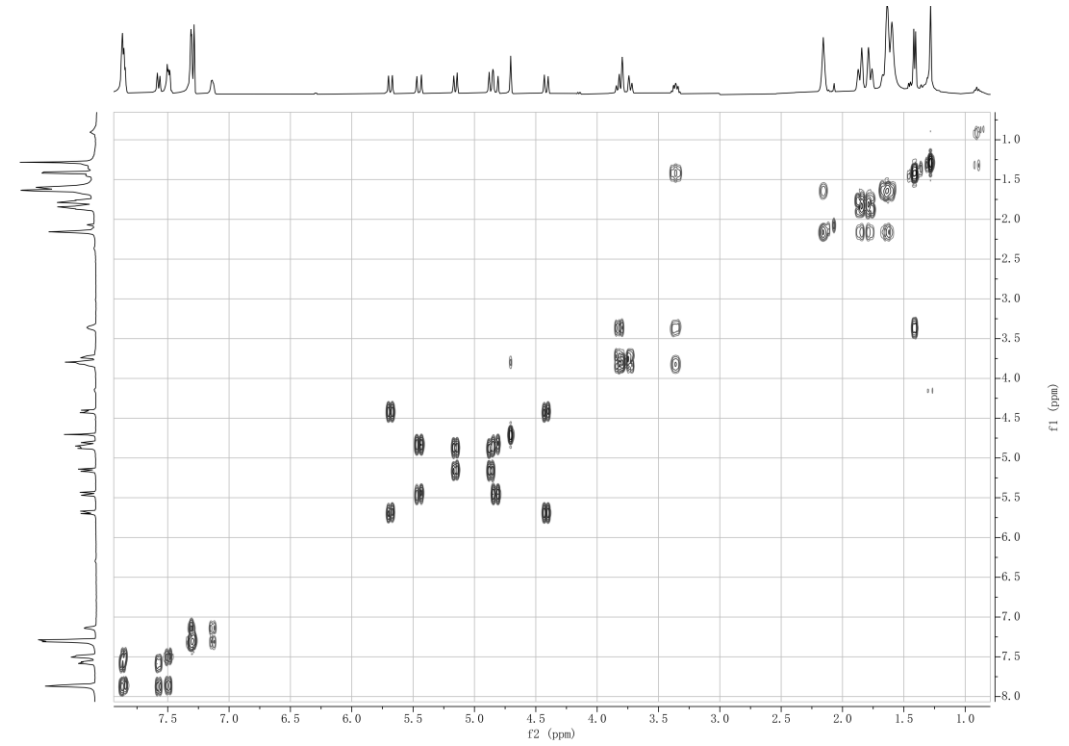
^{1}H NMR, 400 MHz, $CDCl_3$



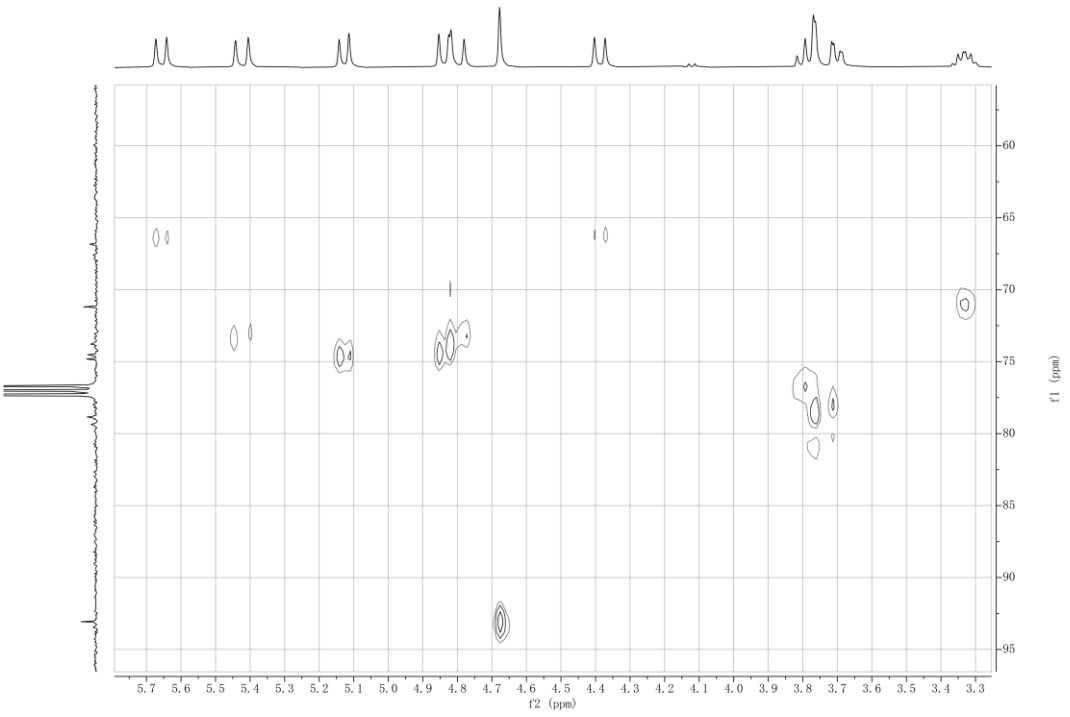
^{13}C NMR, 100 MHz, $CDCl_3$

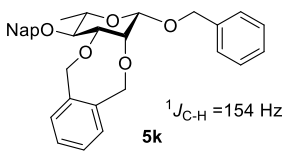


COSY, 400 MHz, $CDCl_3$

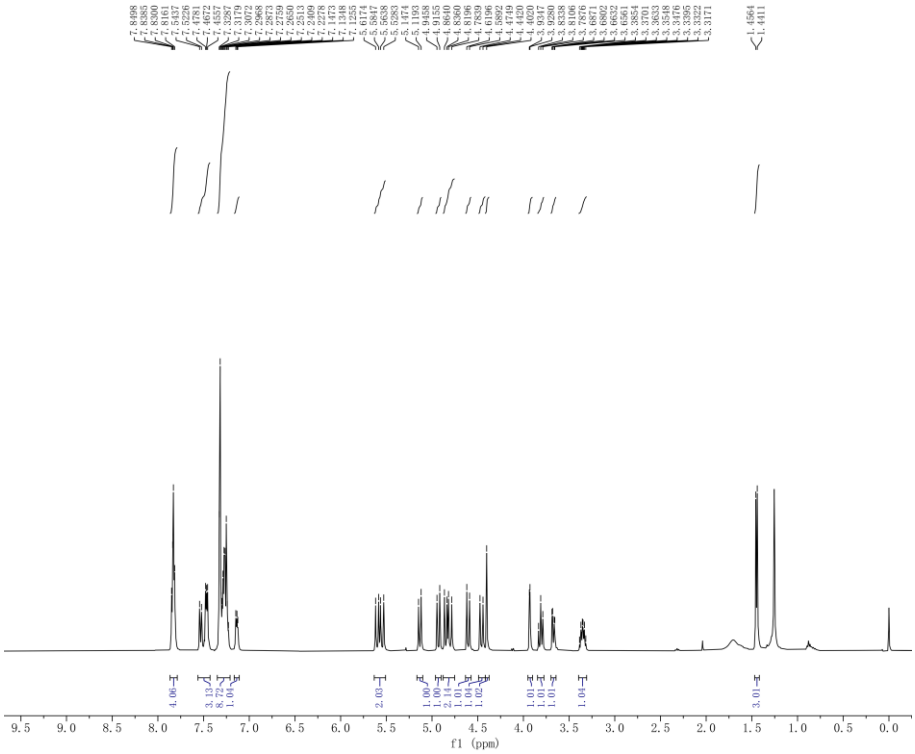


HSQC, 400 MHz, $CDCl_3$

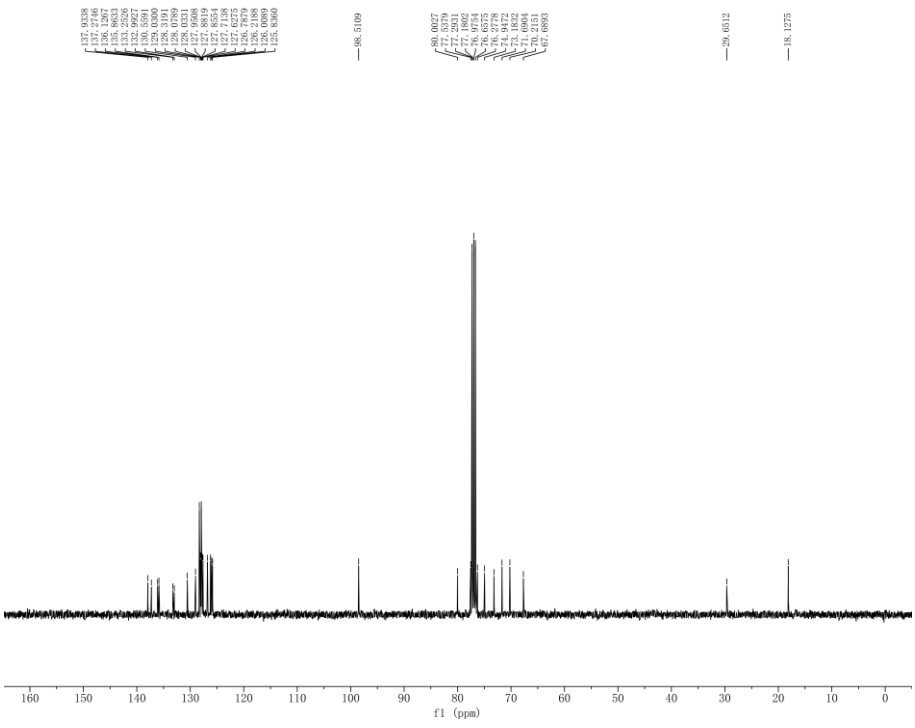




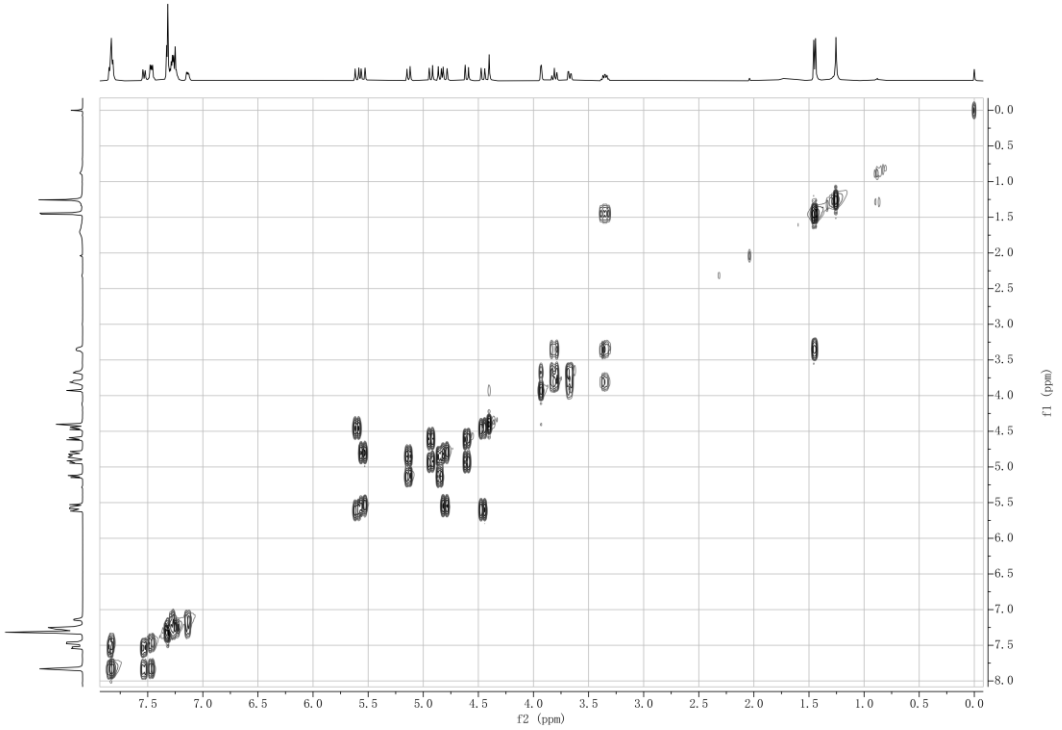
^{1}H NMR, 400 MHz, $CDCl_3$



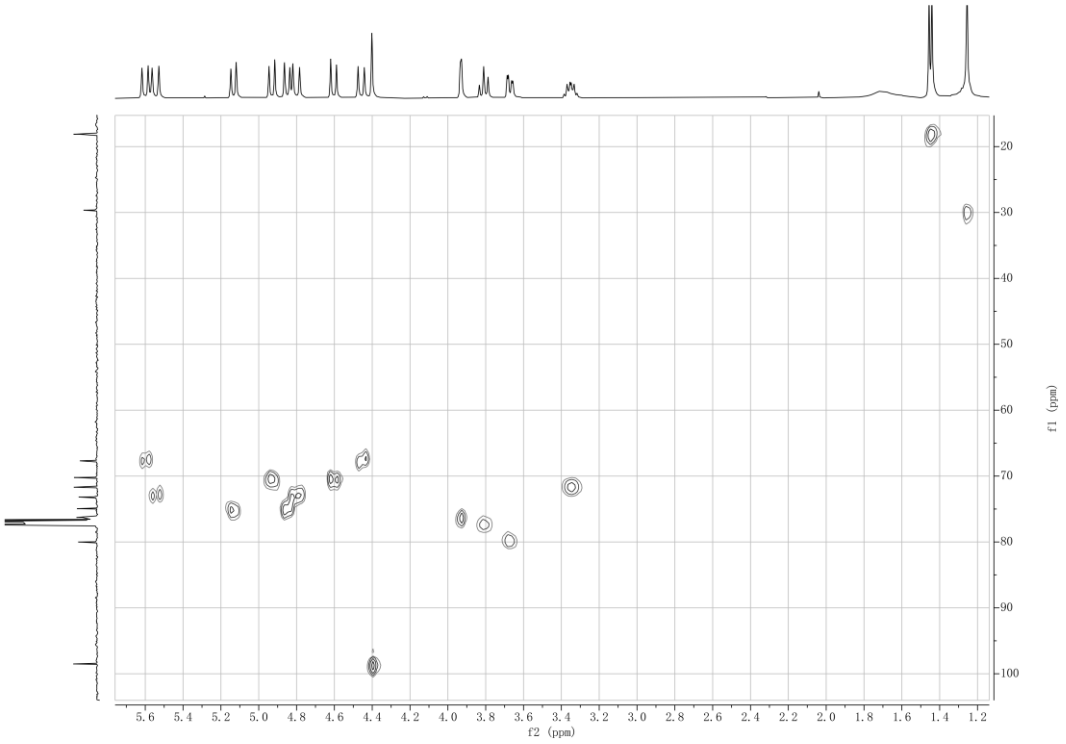
^{13}C NMR, 100 MHz, $CDCl_3$

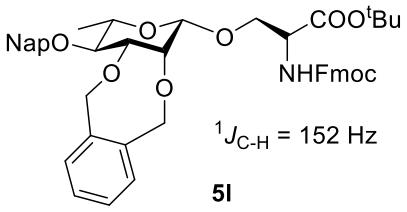


COSY, 400 MHz, $CDCl_3$



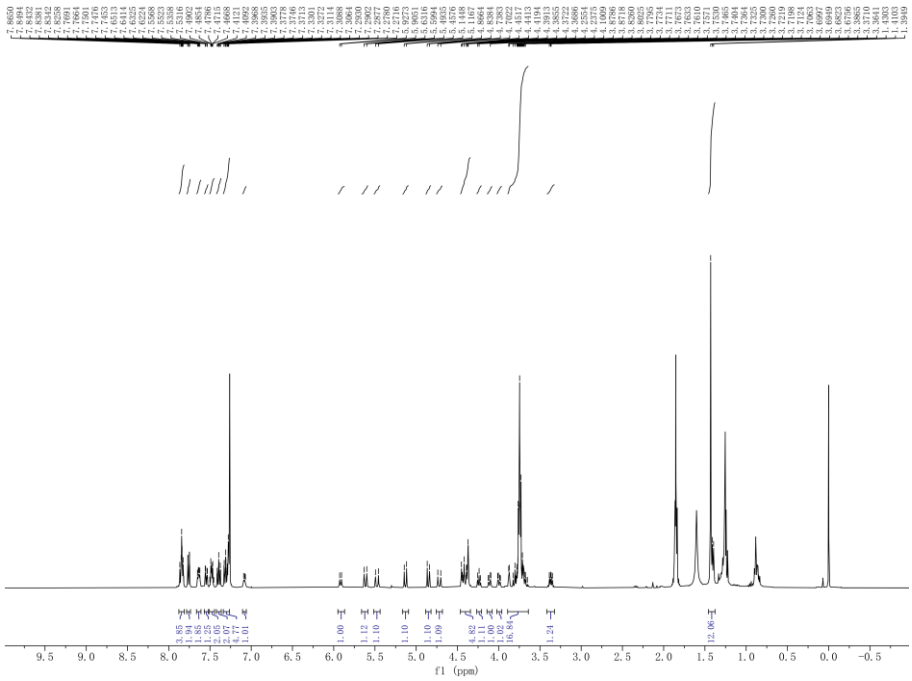
HSQC, 400 MHz, $CDCl_3$



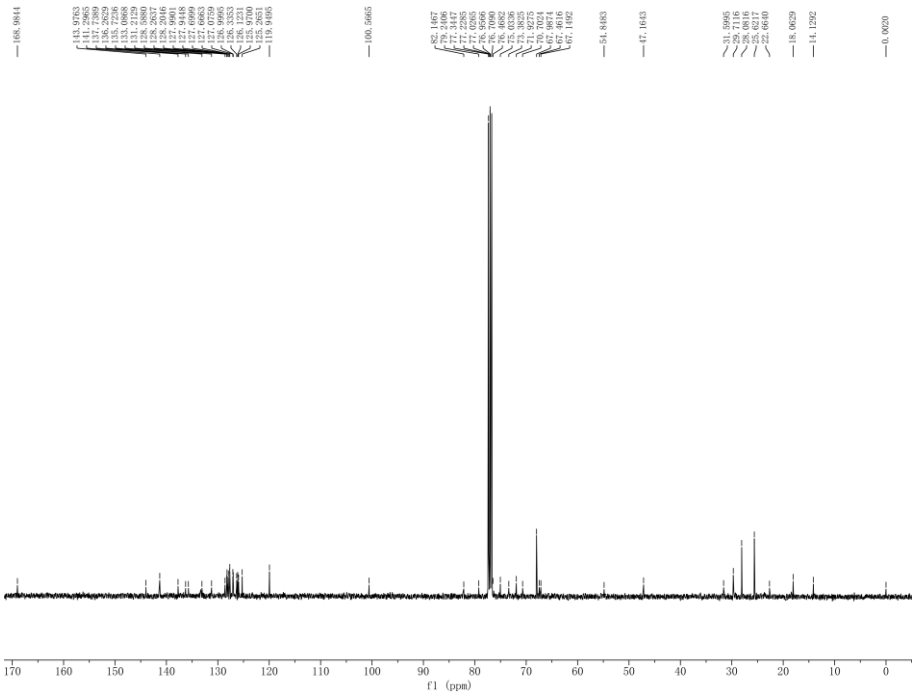


5l

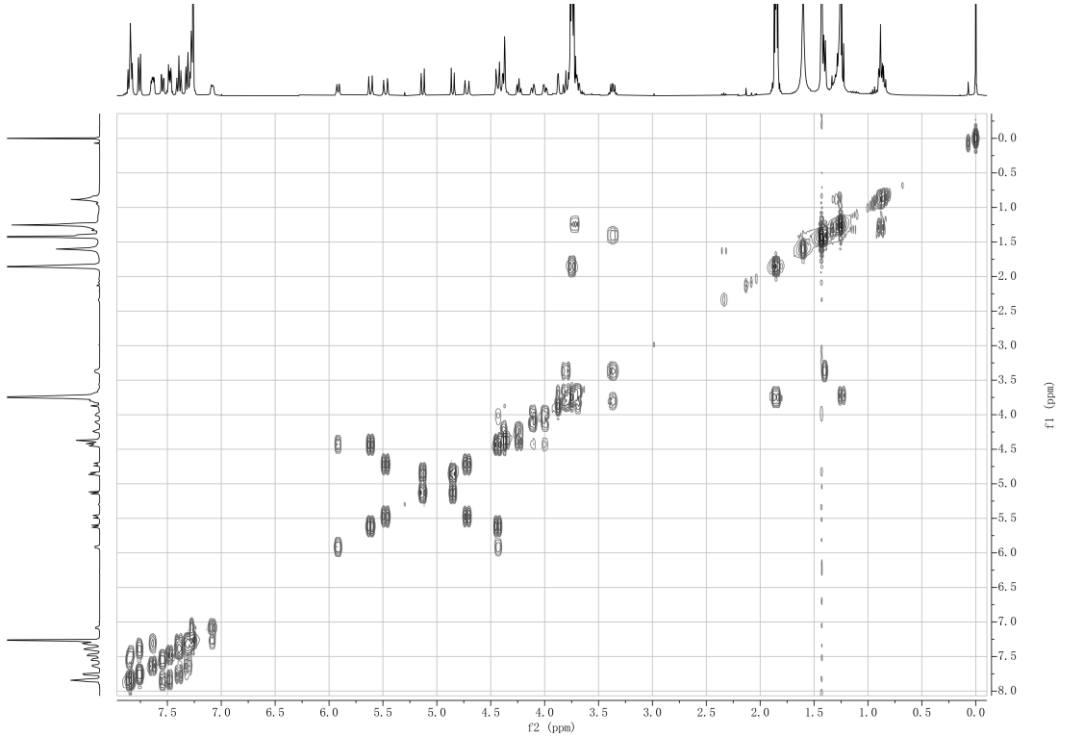
^{1}H NMR, 400 MHz, $CDCl_3$



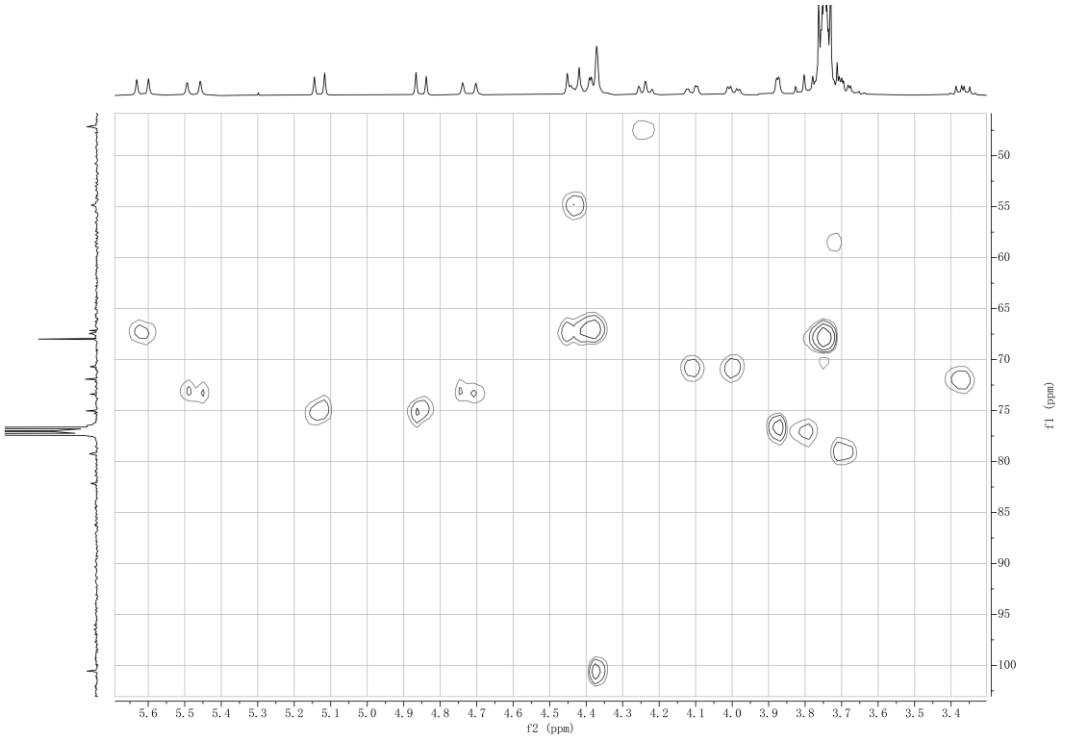
^{13}C NMR, 100 MHz, $CDCl_3$

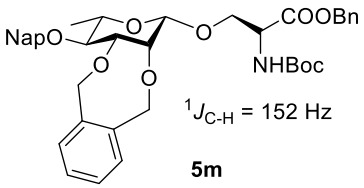


COSY, 400 MHz, $CDCl_3$



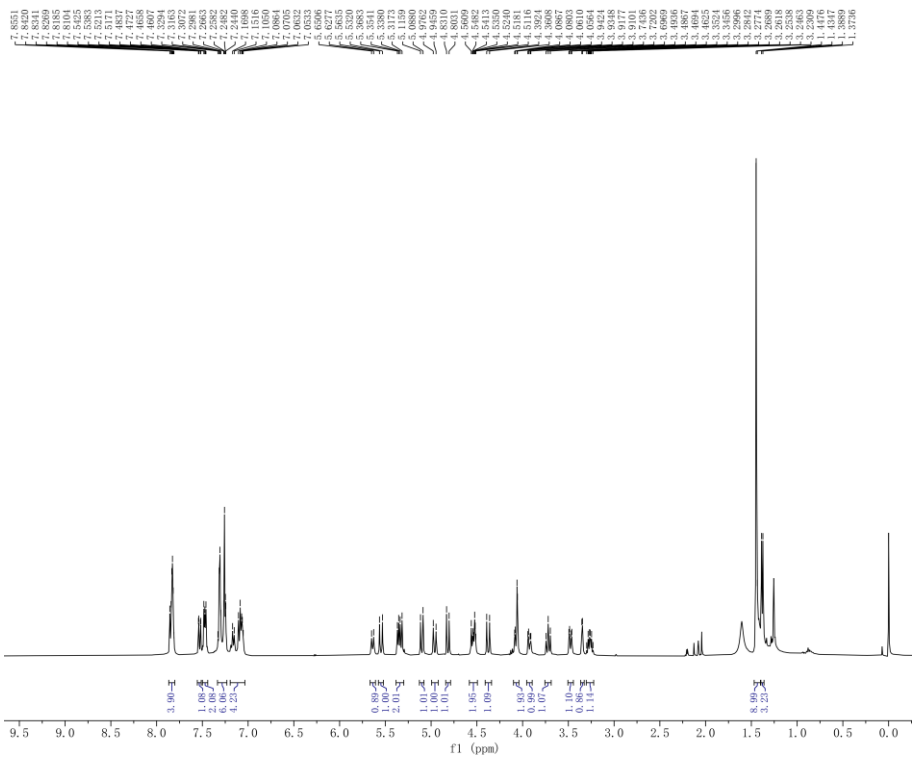
HSQC, 400 MHz, $CDCl_3$



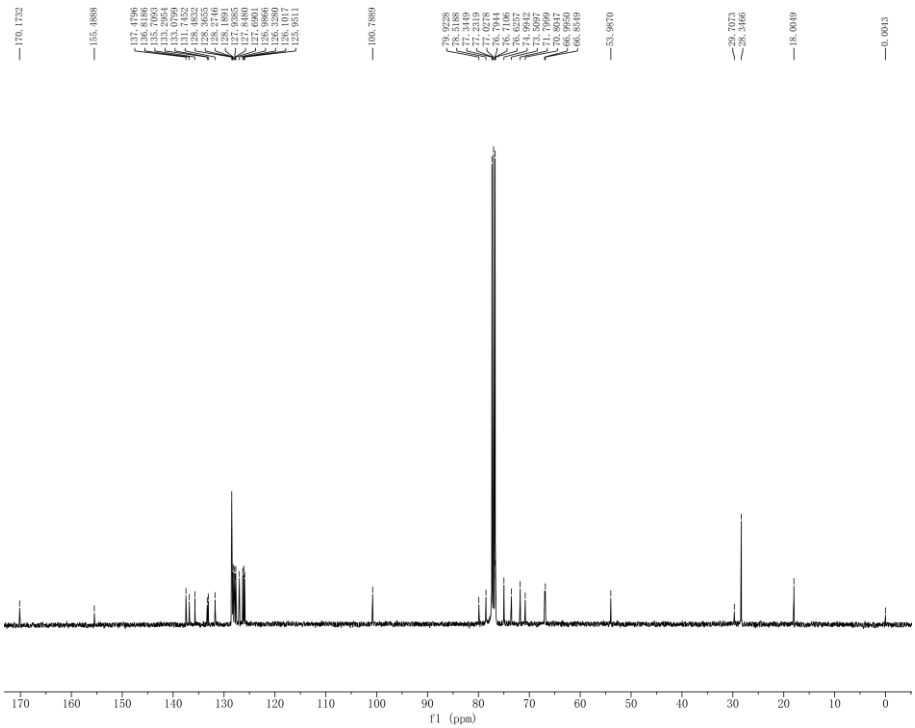


5m

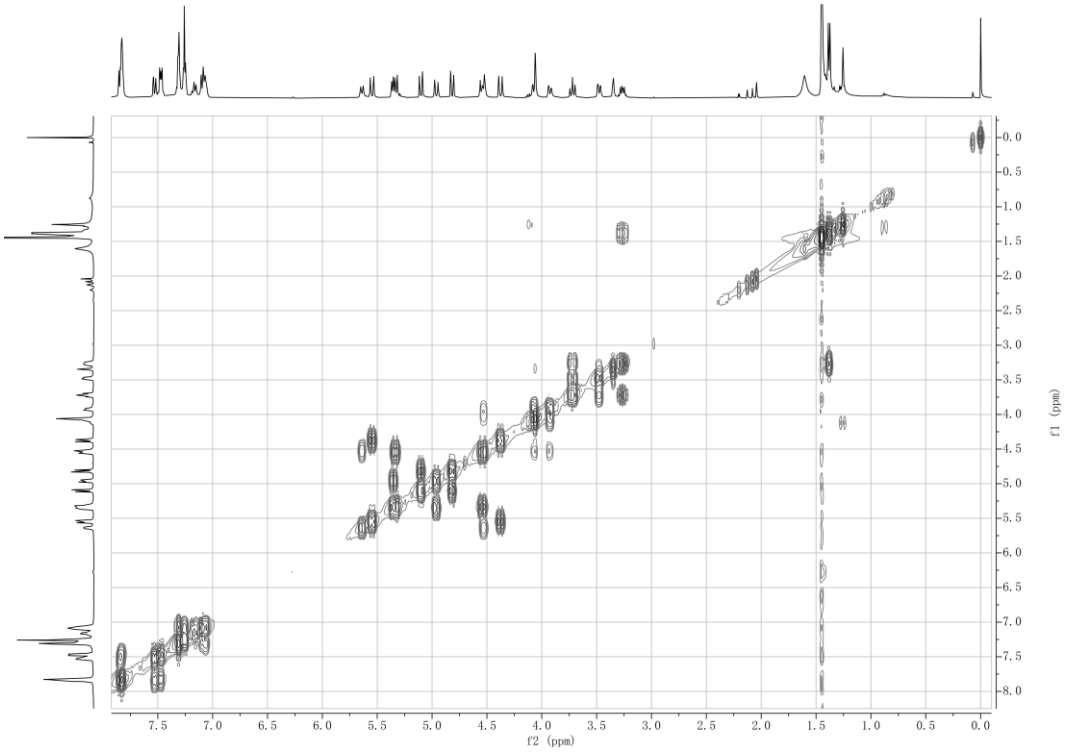
^{1}H NMR, 400 MHz, $CDCl_3$



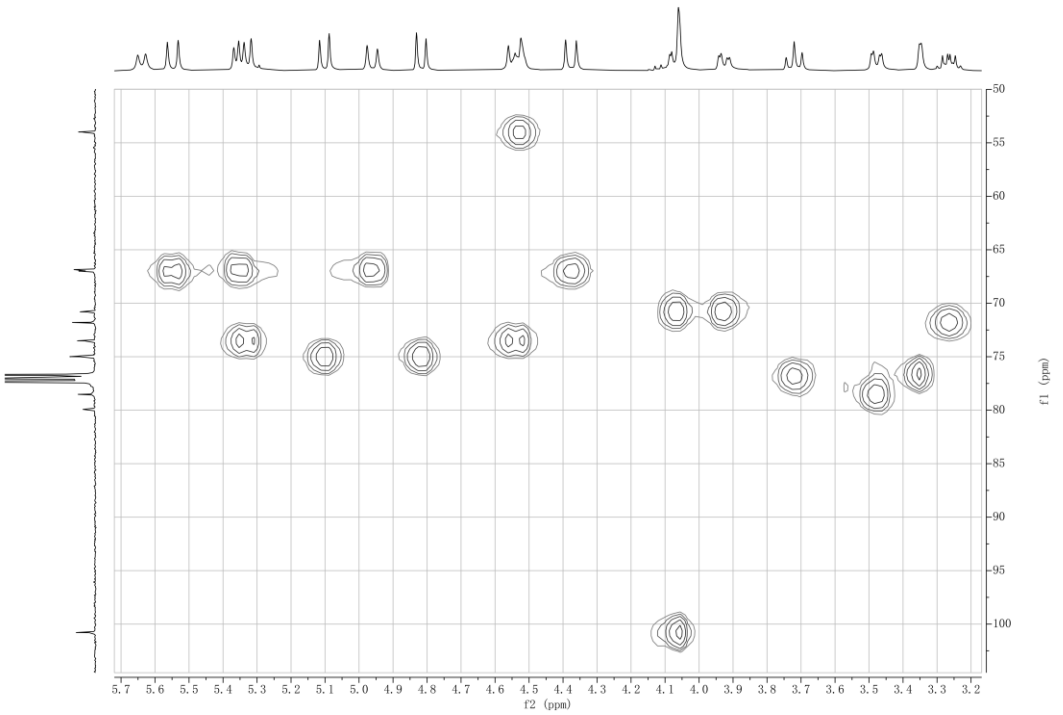
^{13}C NMR, 100 MHz, $CDCl_3$

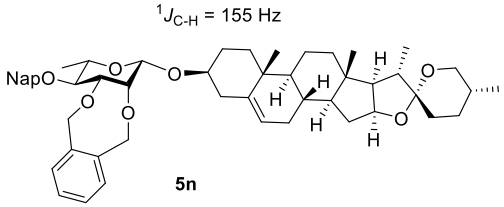


COSY, 400 MHz, $CDCl_3$



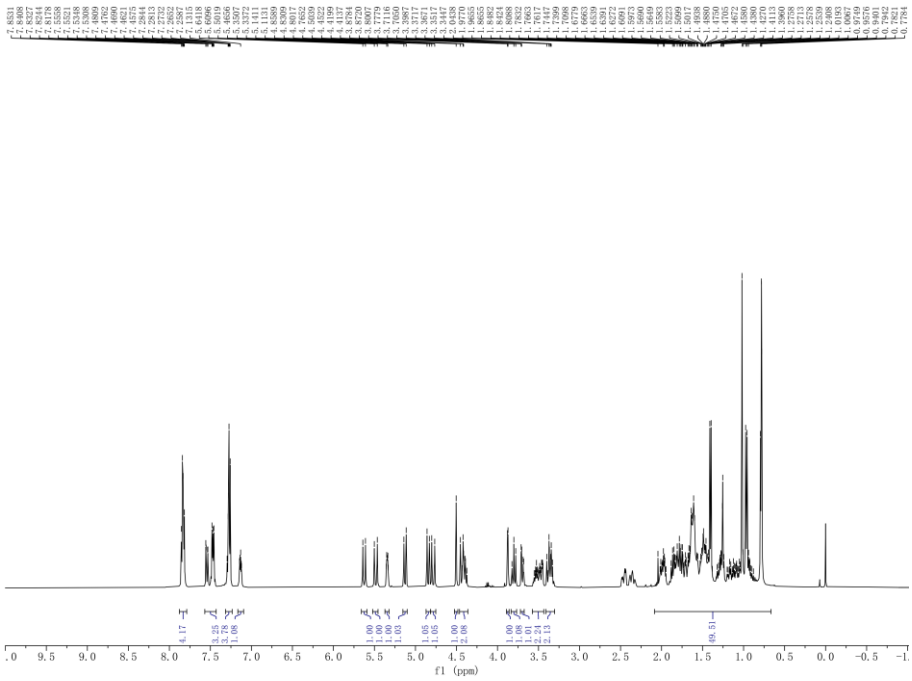
HSQC, 400 MHz, $CDCl_3$



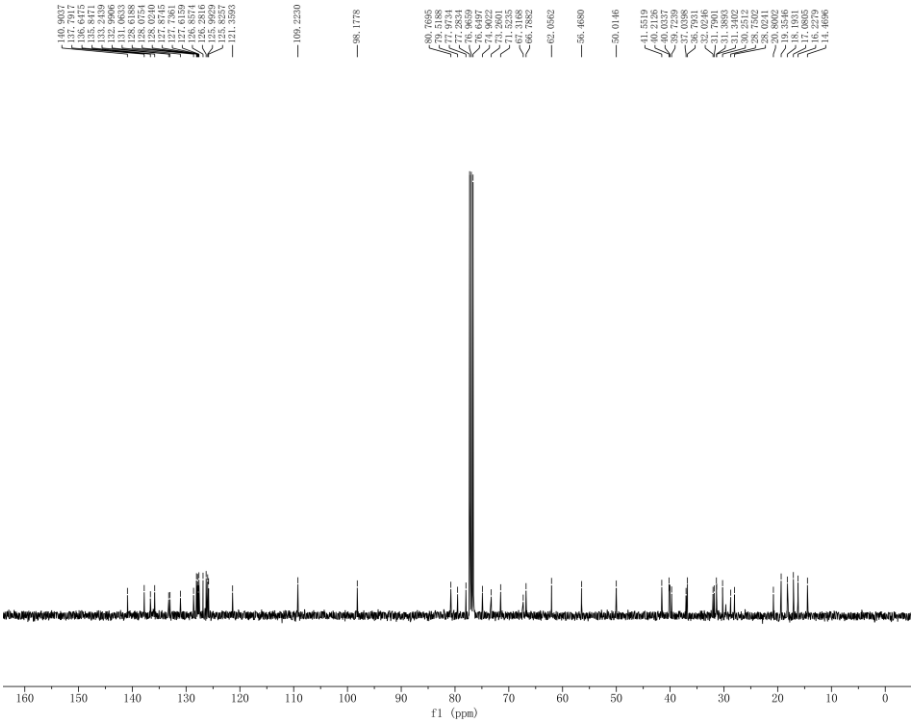


5n

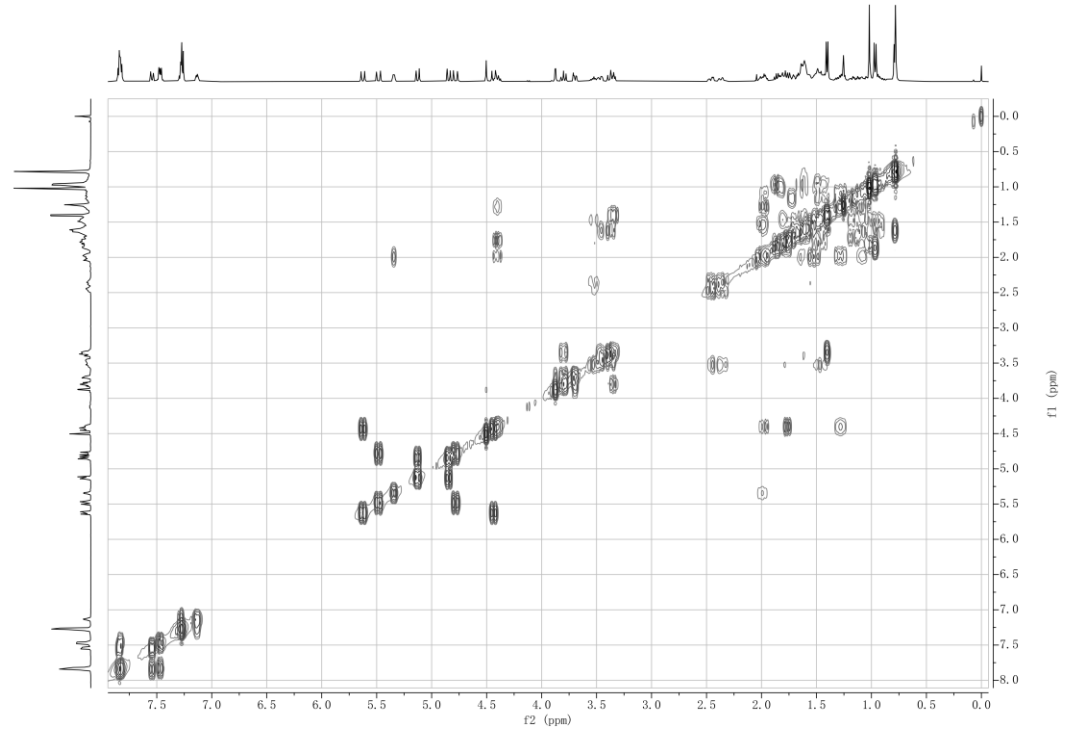
^{1}H NMR, 400 MHz, $CDCl_3$



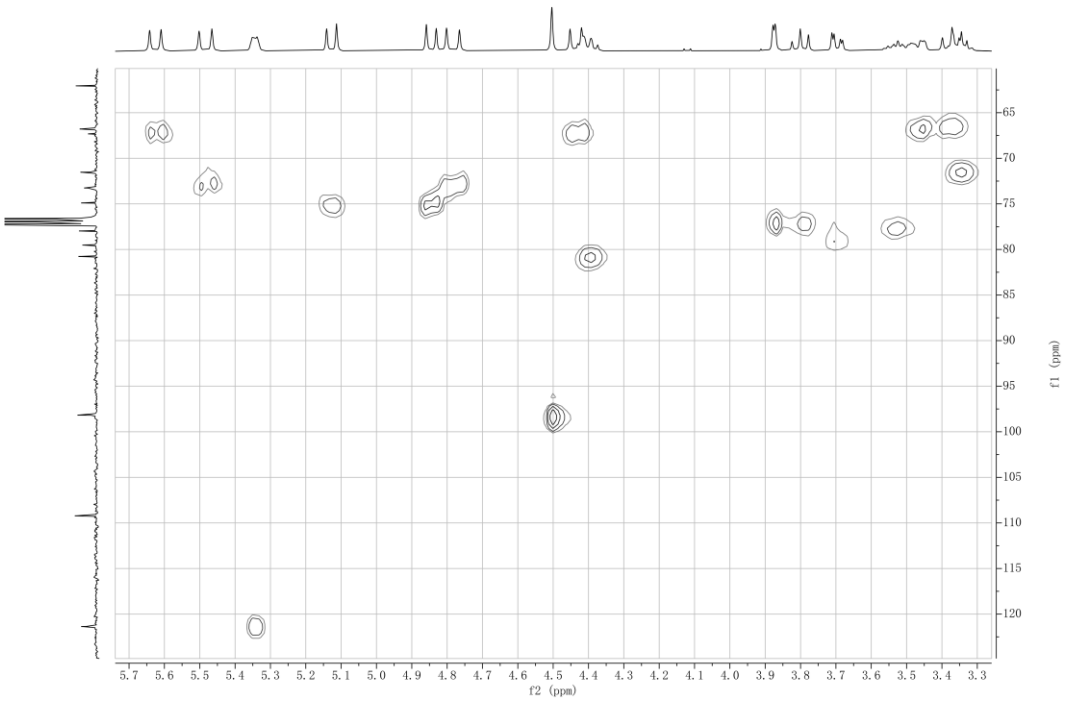
^{13}C NMR, 100 MHz, $CDCl_3$

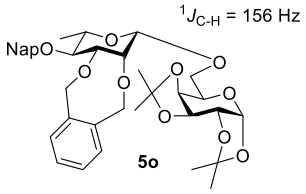


COSY, 400 MHz, $CDCl_3$

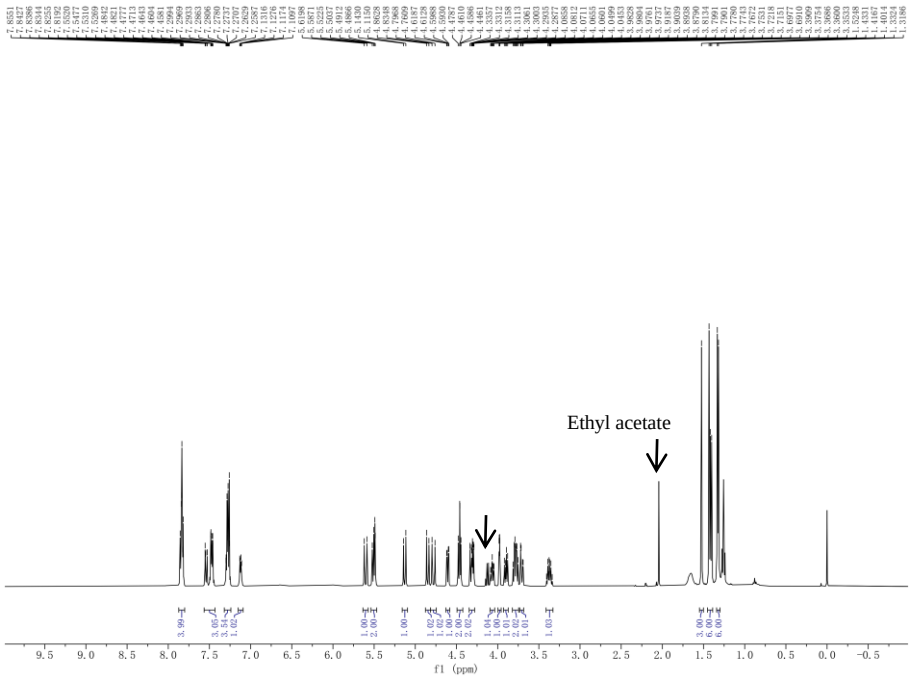


HSQC, 400 MHz, $CDCl_3$

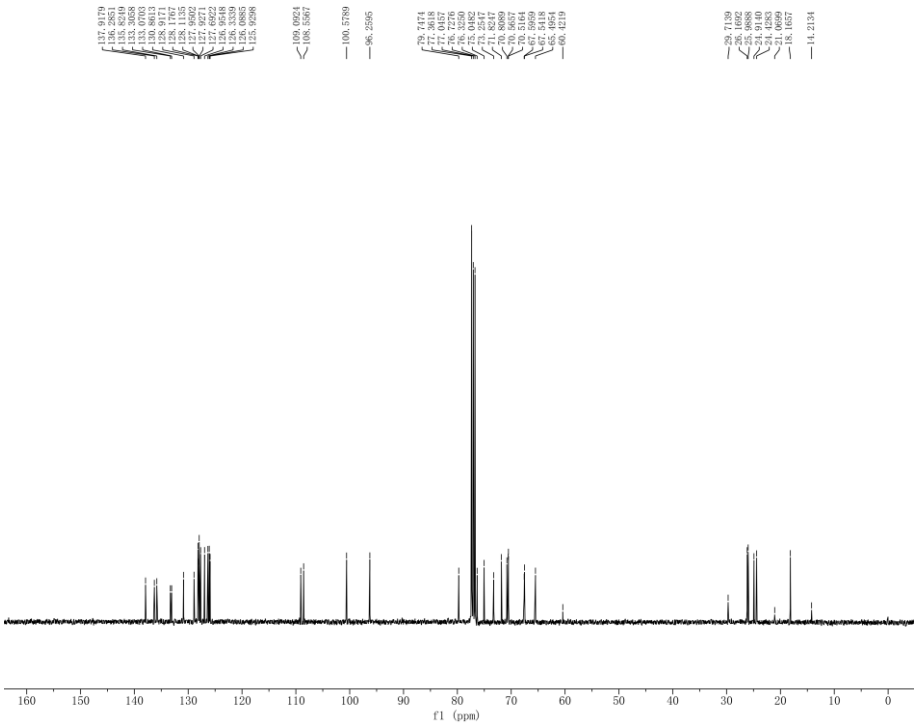




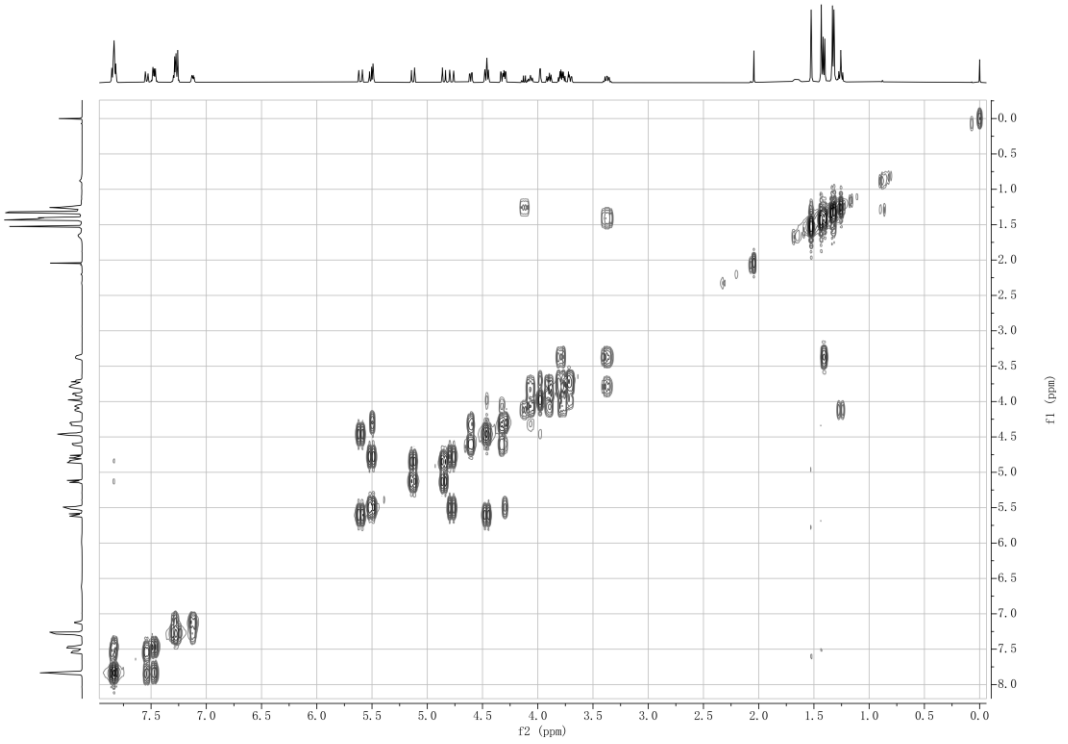
^{1}H NMR, 400 MHz, $CDCl_3$



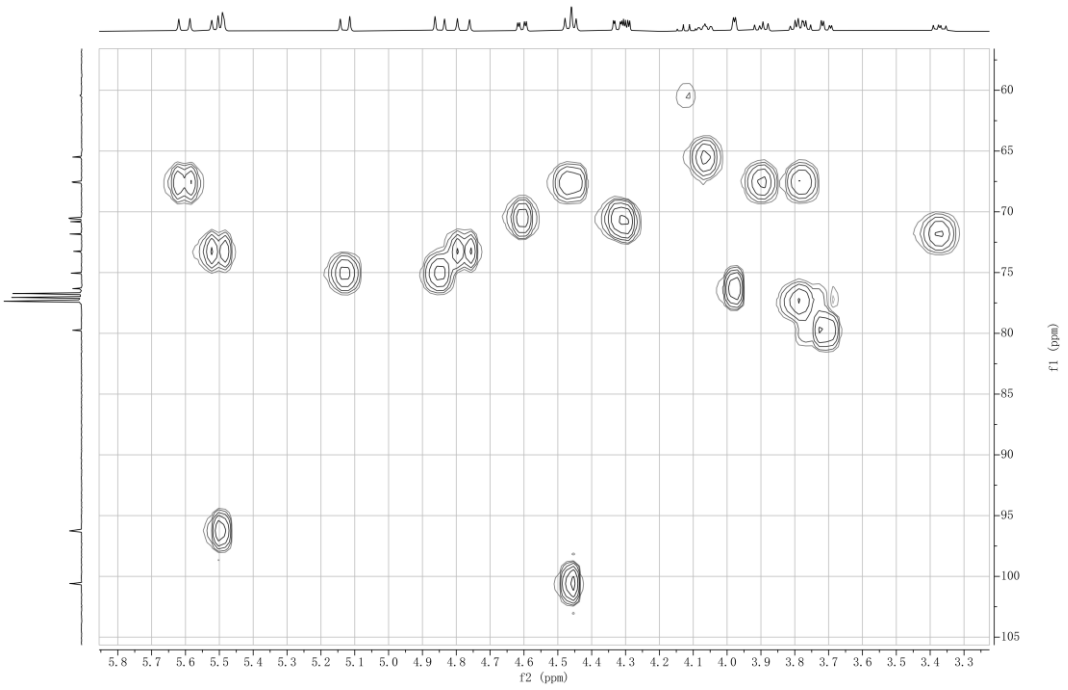
^{13}C NMR, 100 MHz, $CDCl_3$

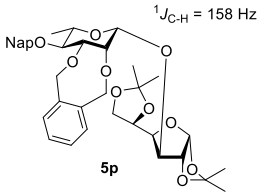


COSY, 400 MHz, $CDCl_3$

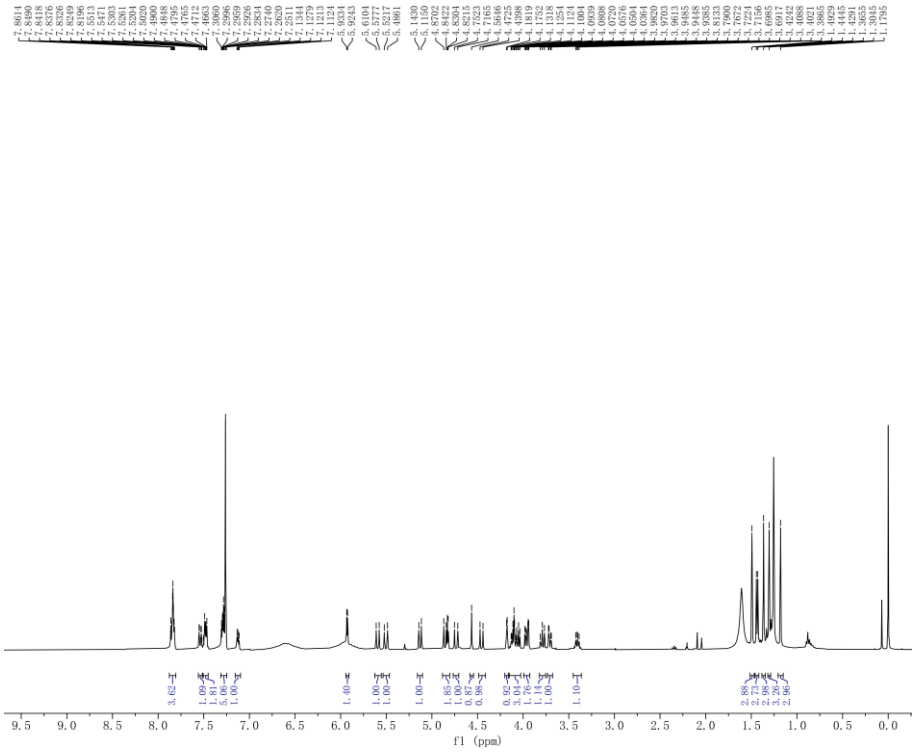


HSQC, 400 MHz, $CDCl_3$

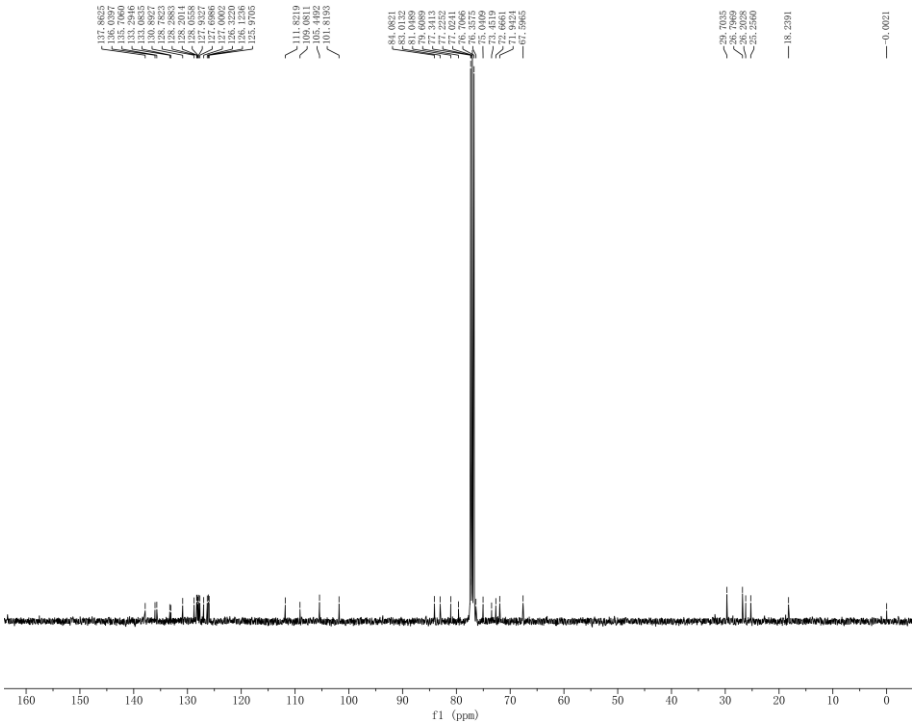




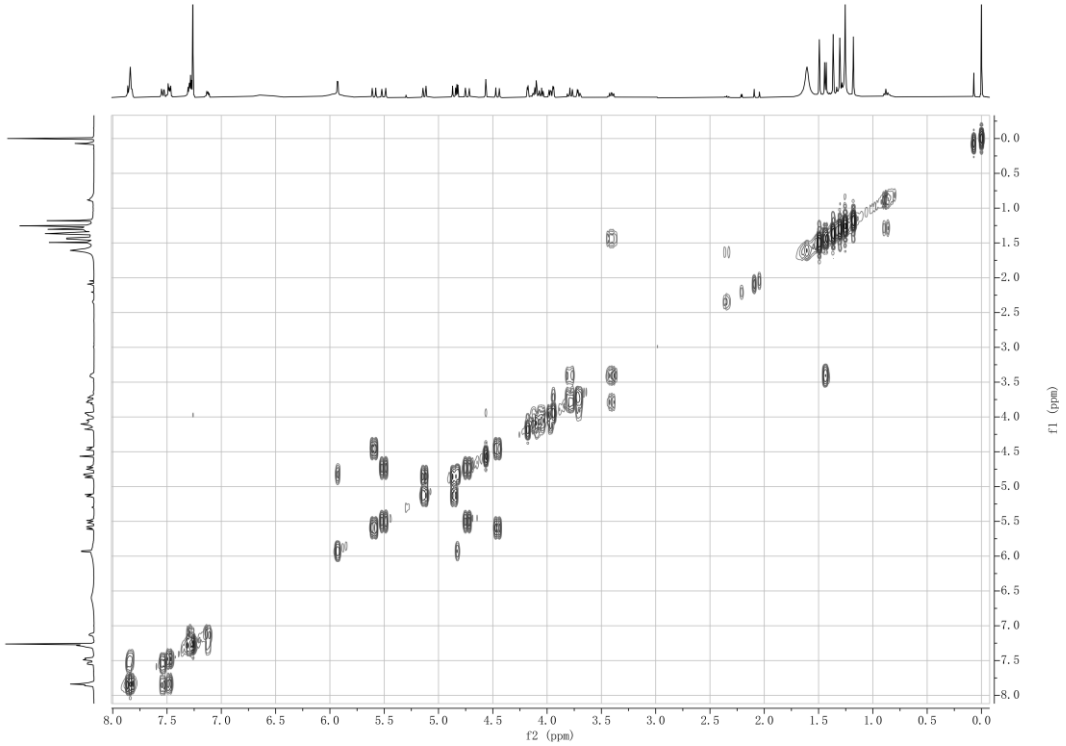
^{1}H NMR, 400 MHz, $CDCl_3$



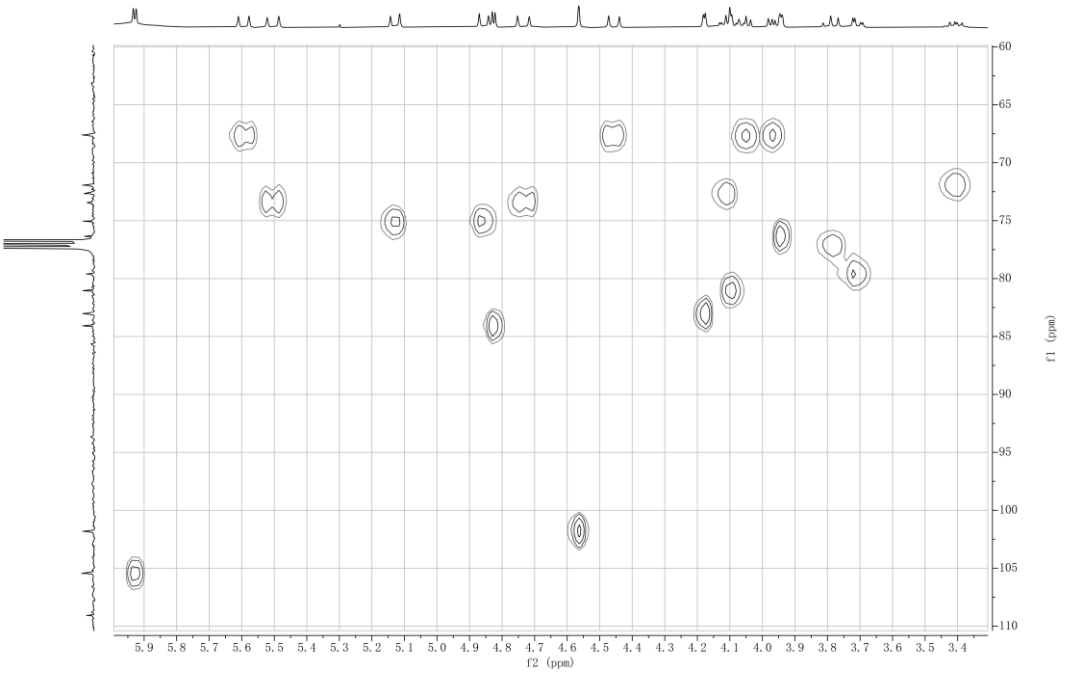
^{13}C NMR, 100 MHz, $CDCl_3$

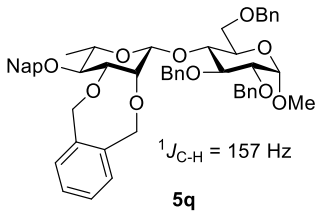


COSY, 400 MHz, $CDCl_3$



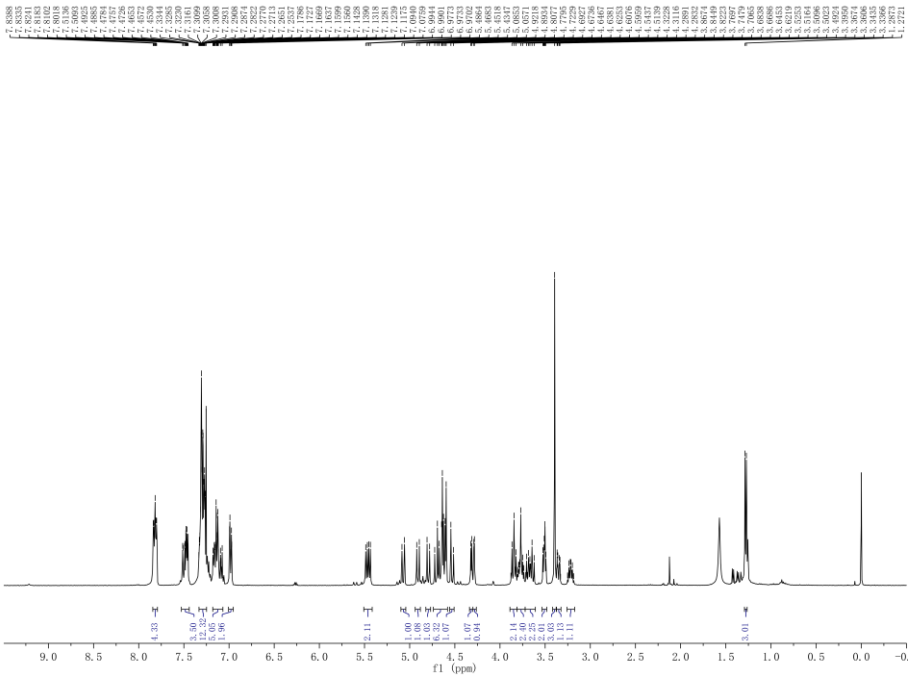
HSQC, 400 MHz, $CDCl_3$



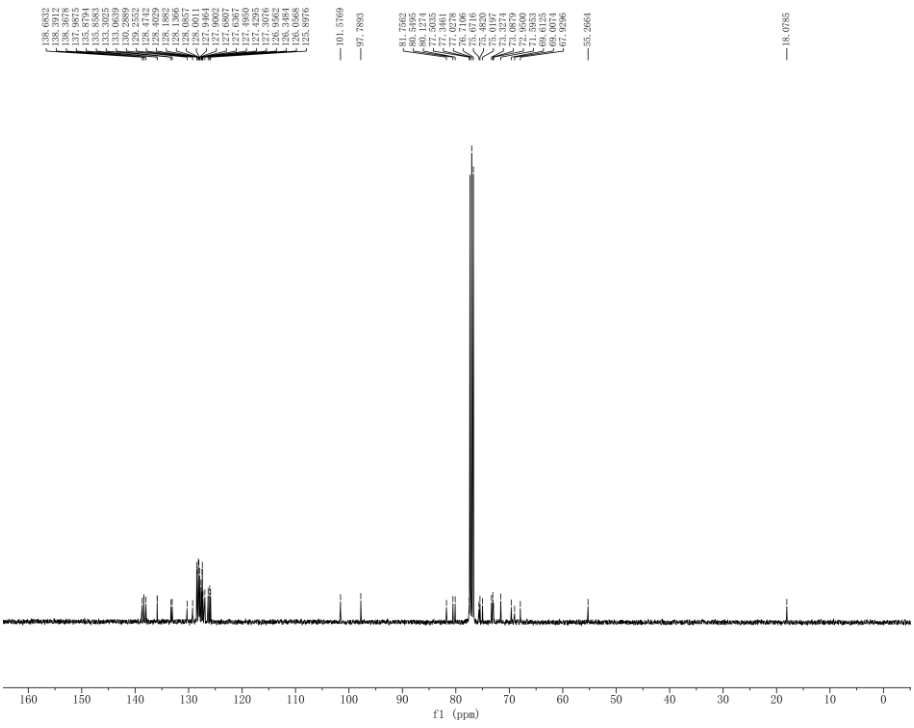


5q

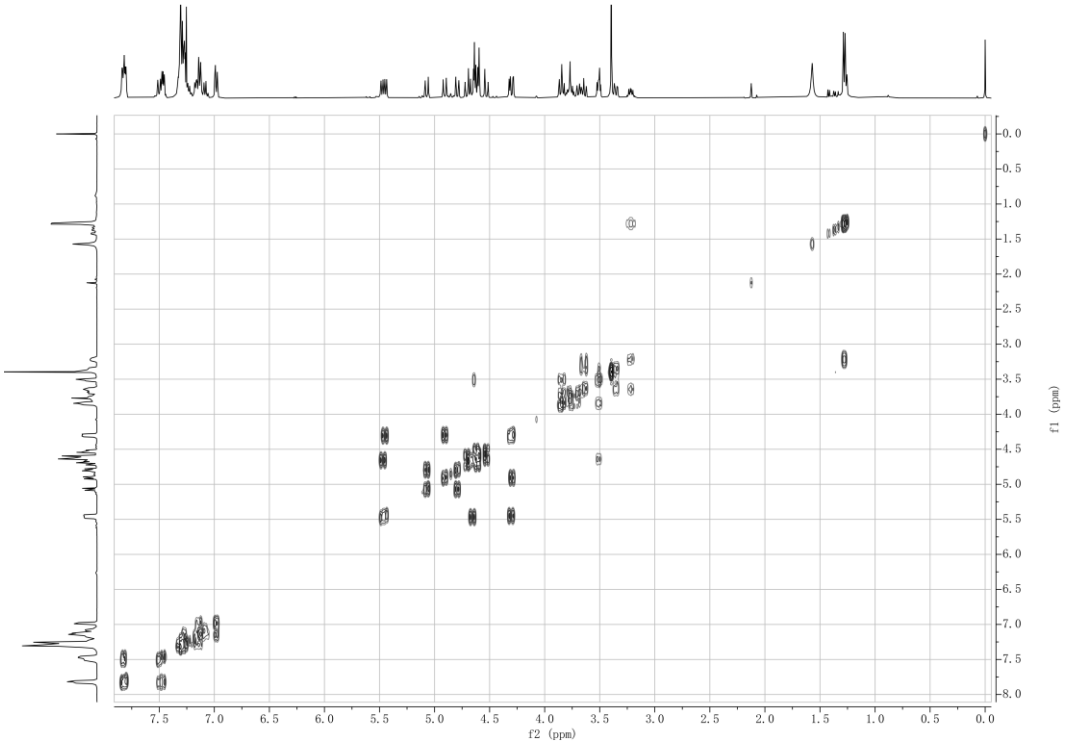
^{1}H NMR, 400 MHz, $CDCl_3$



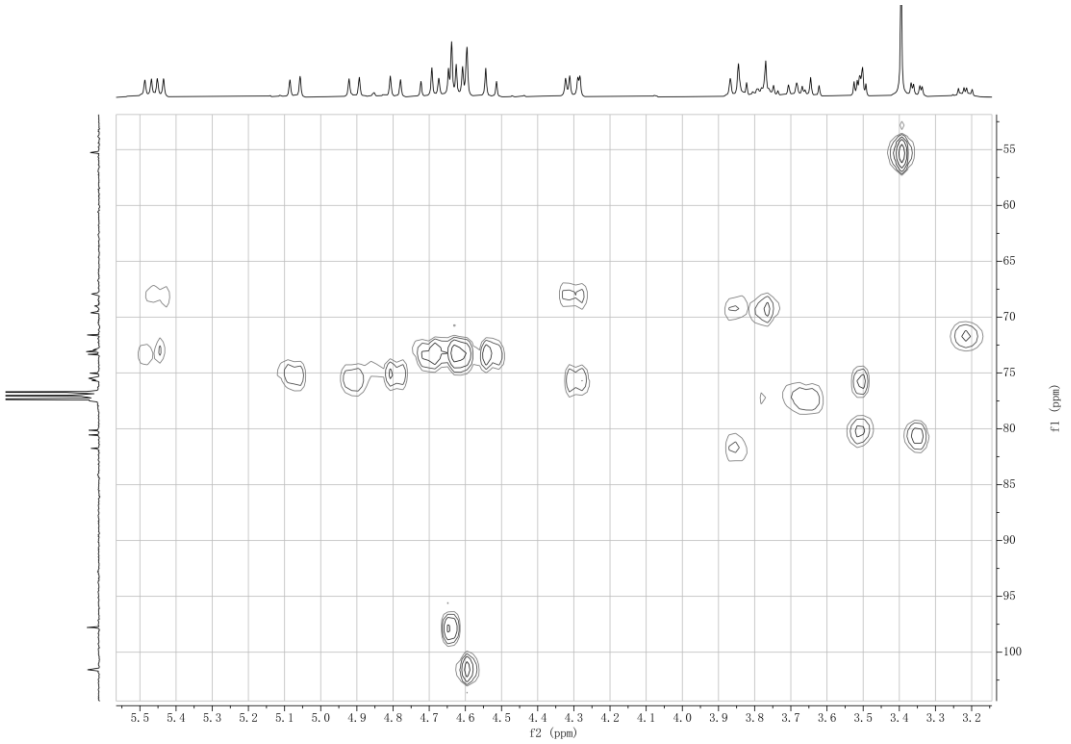
^{13}C NMR, 100 MHz, $CDCl_3$

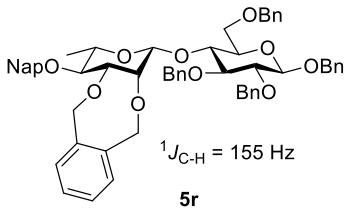


COSY, 400 MHz, $CDCl_3$



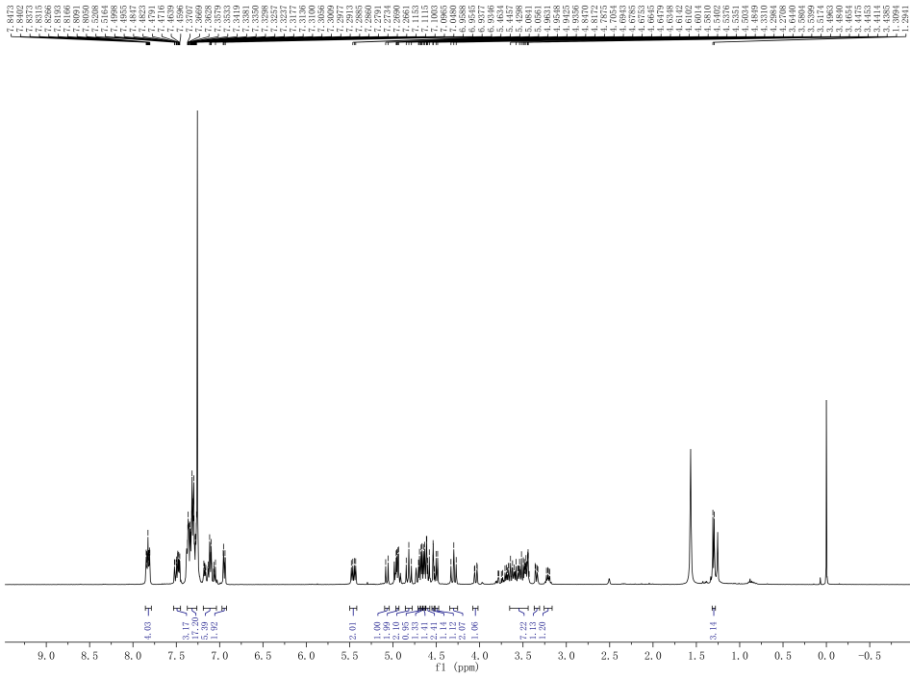
HSQC, 400 MHz, $CDCl_3$



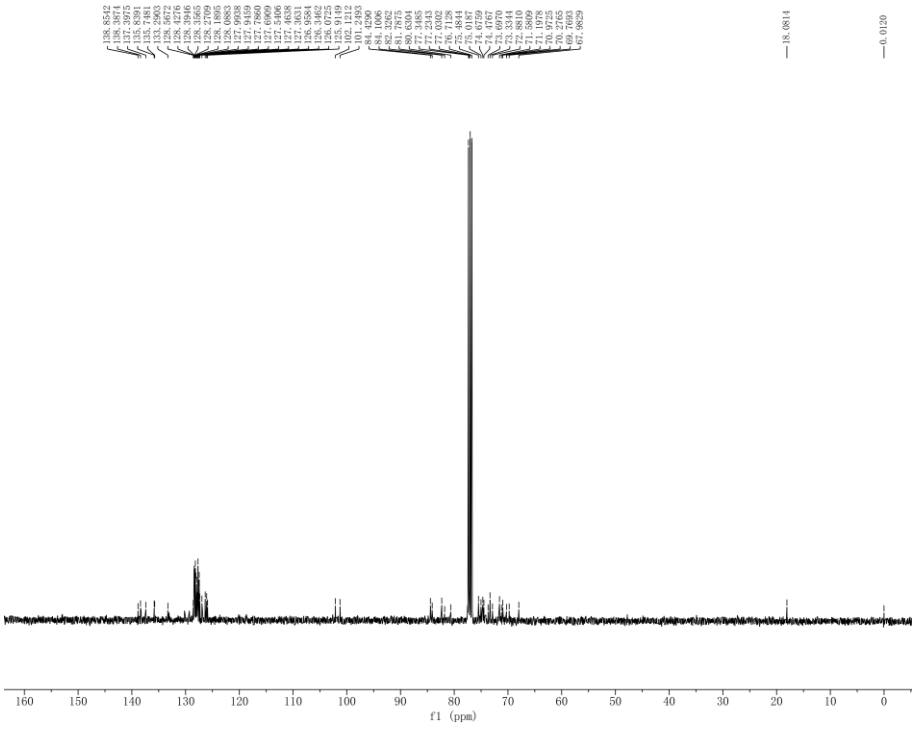


5r

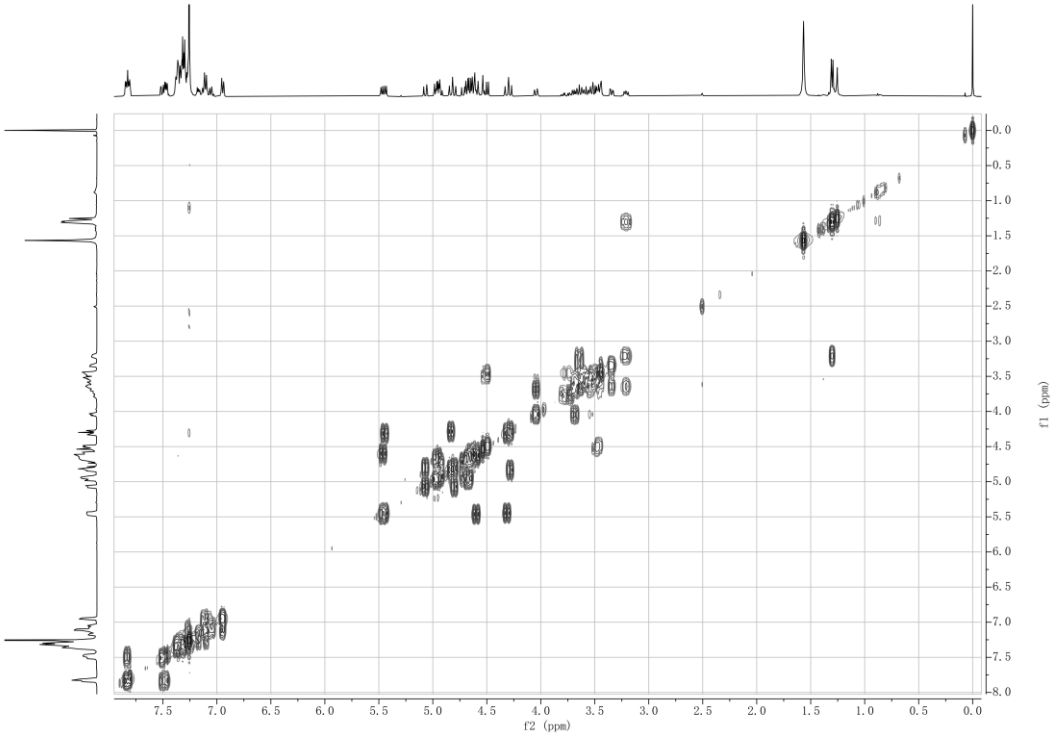
^{1}H NMR, 400 MHz, $CDCl_3$



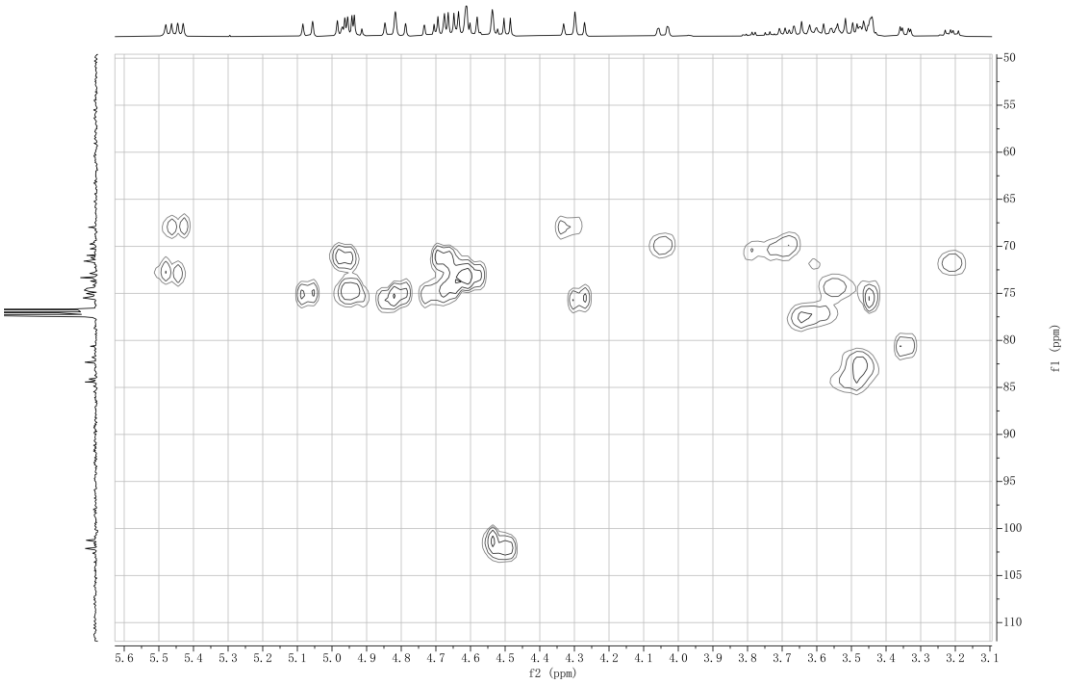
^{13}C NMR, 100 MHz, $CDCl_3$

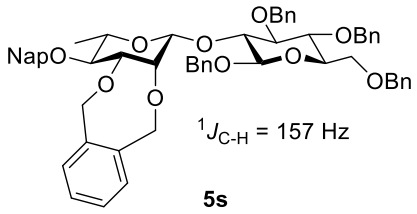


COSY, 400 MHz, $CDCl_3$



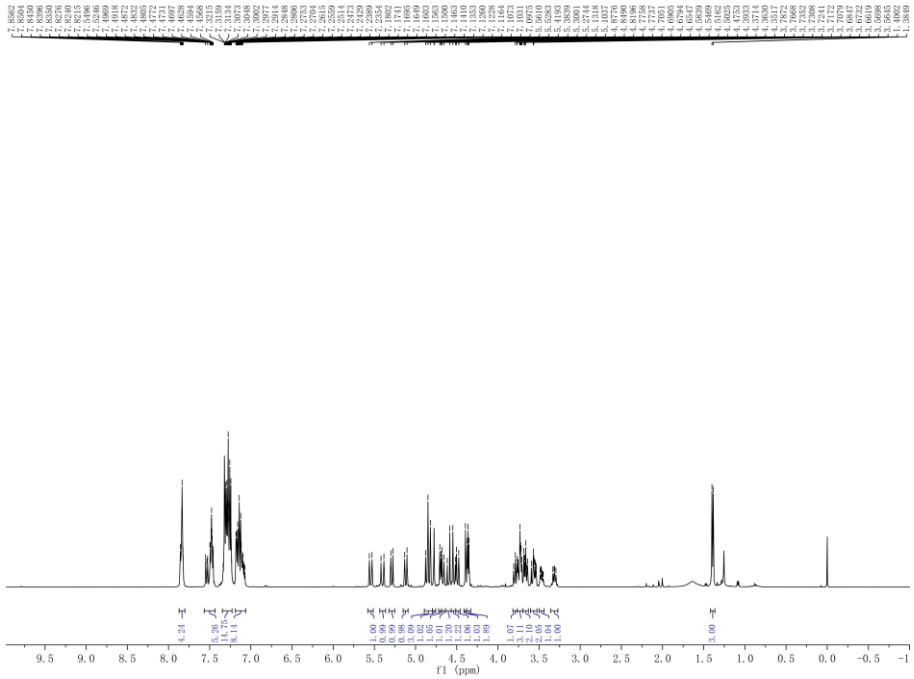
HSQC, 400 MHz, $CDCl_3$



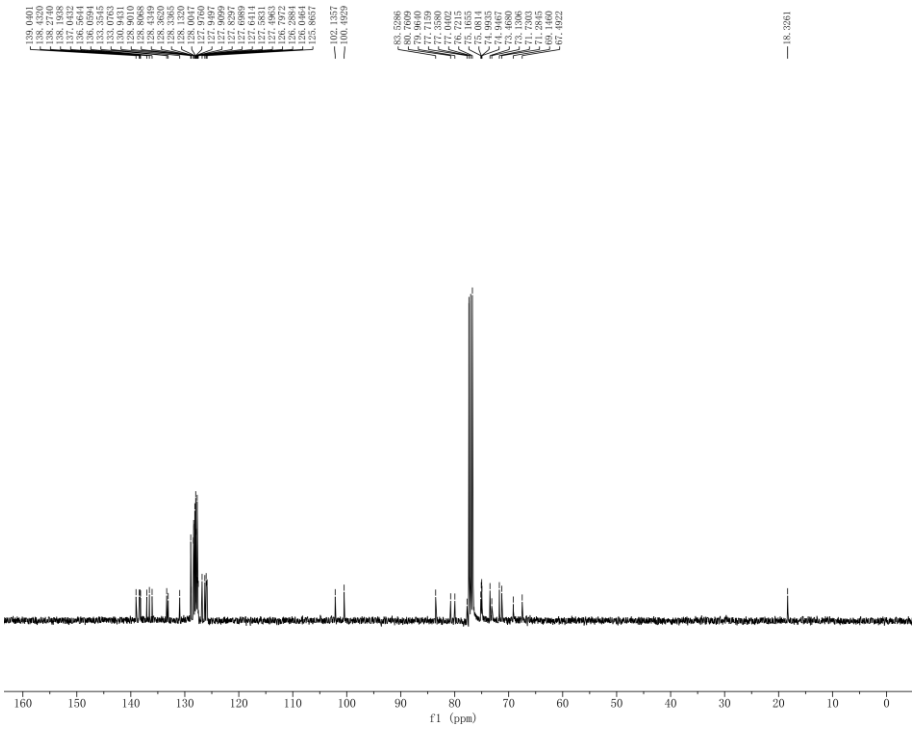


5s

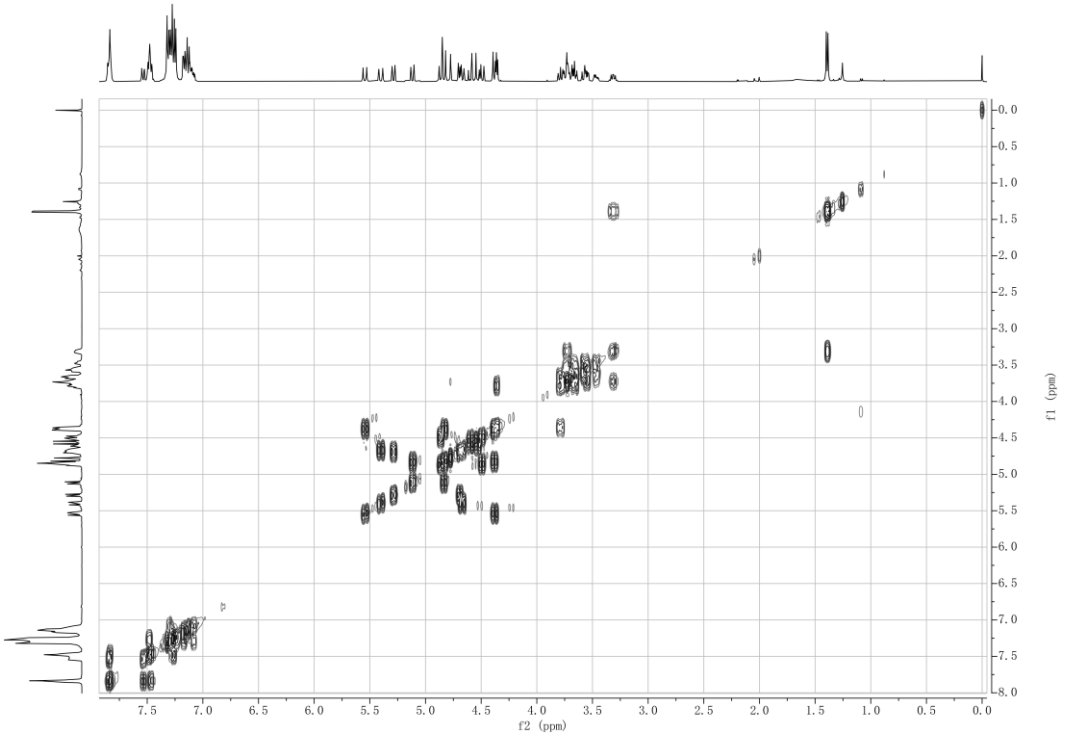
^{1}H NMR, 400 MHz, $CDCl_3$



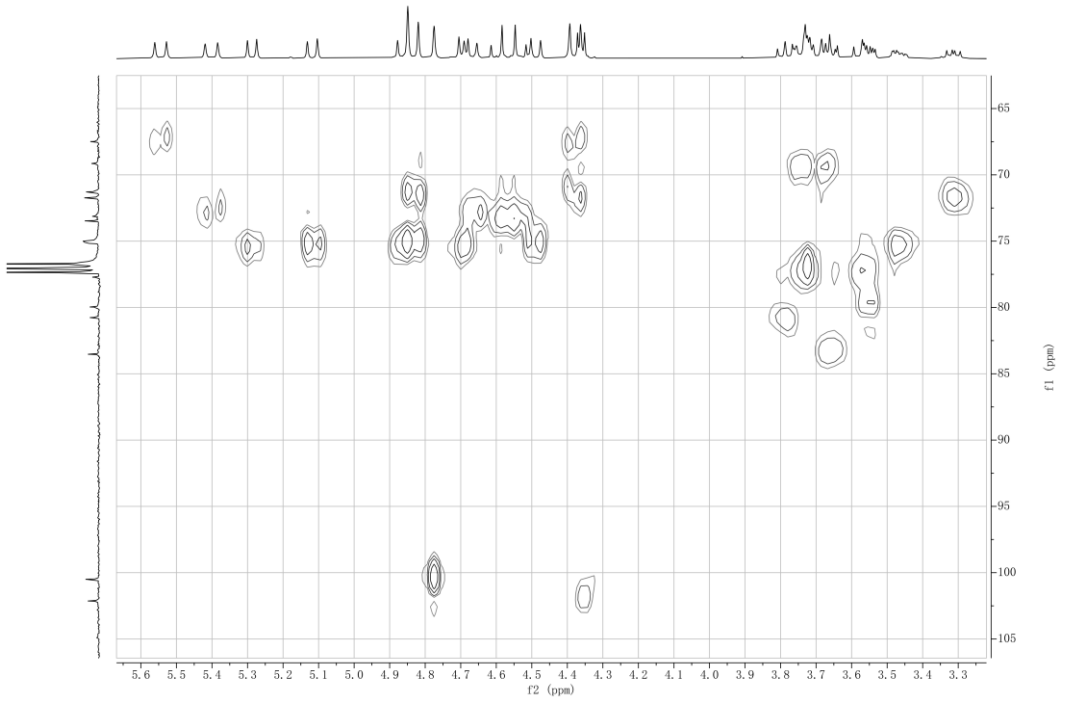
^{13}C NMR, 100 MHz, $CDCl_3$

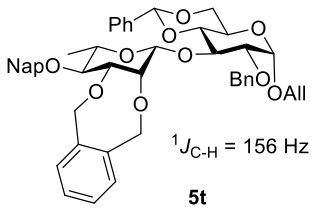


COSY, 400 MHz, $CDCl_3$



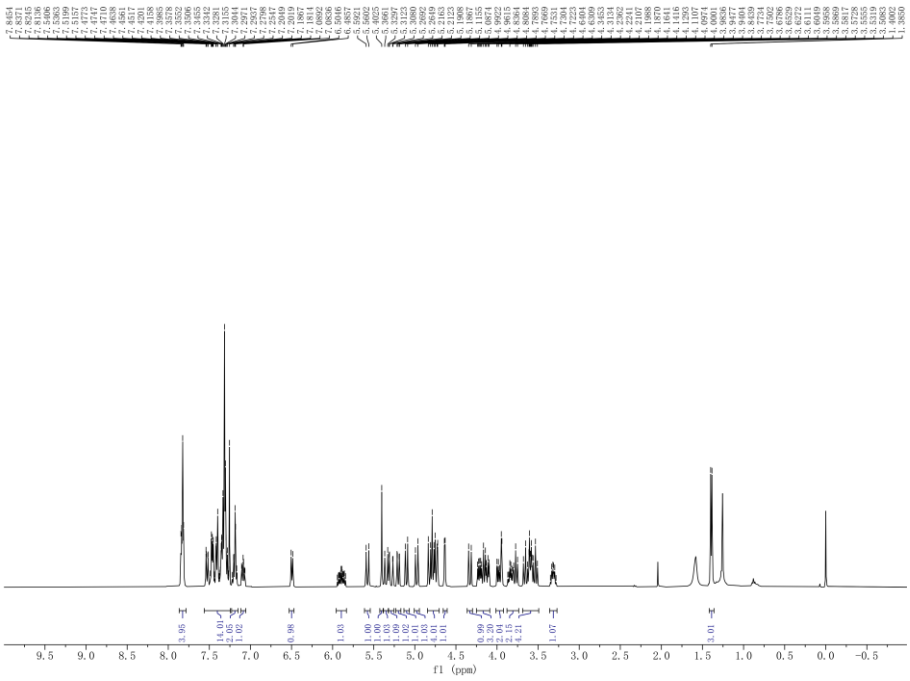
HSQC, 400 MHz, $CDCl_3$



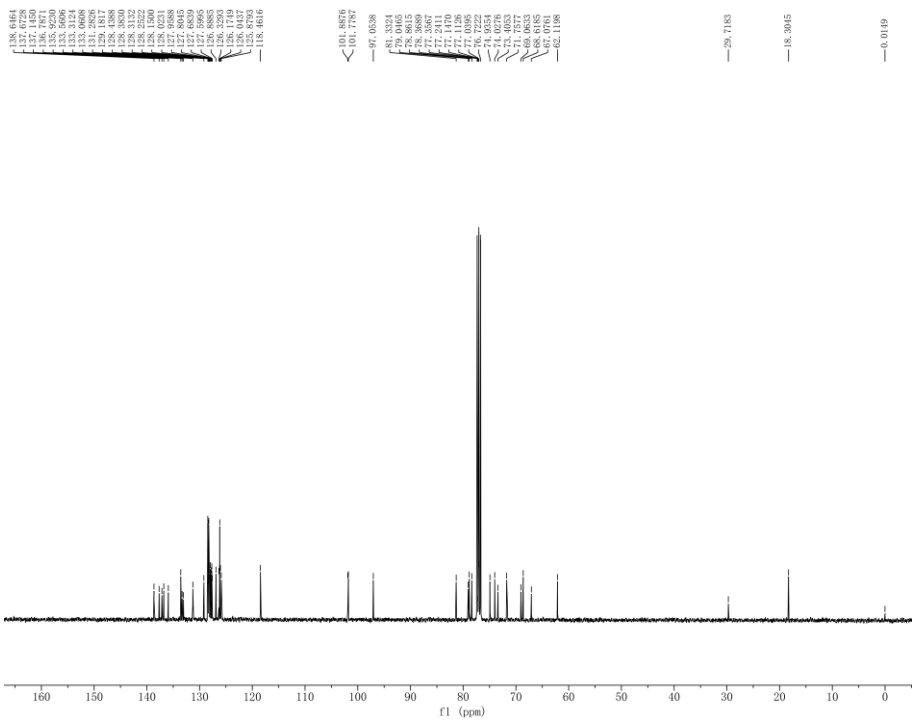


5t

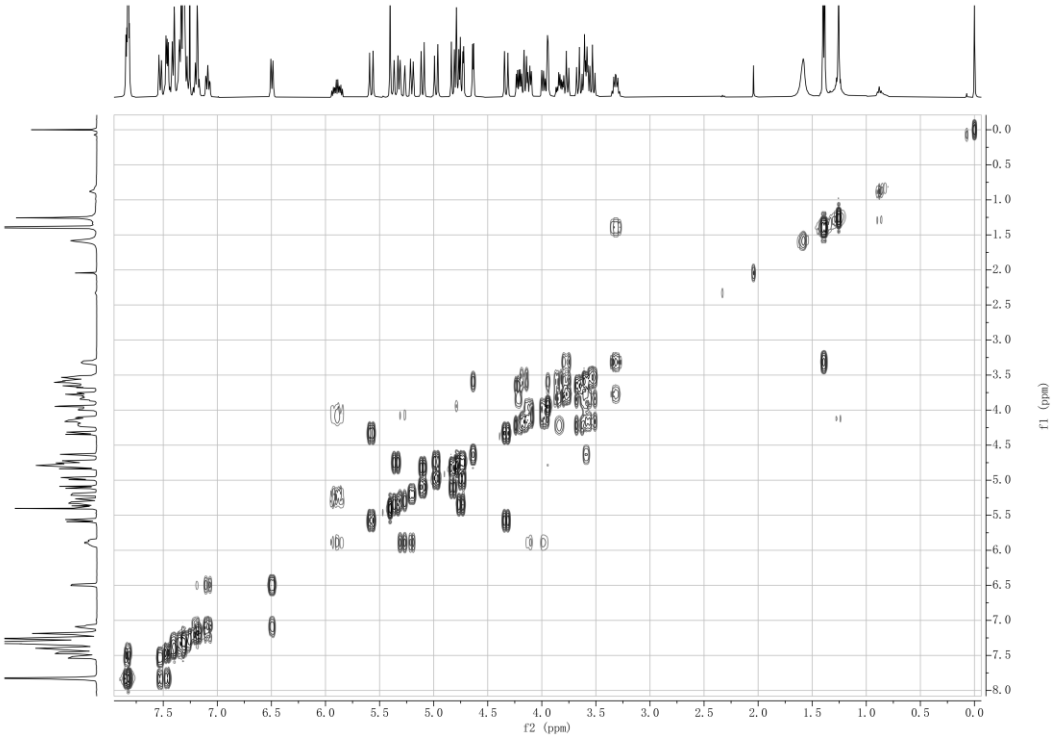
^{1}H NMR, 400 MHz, $CDCl_3$



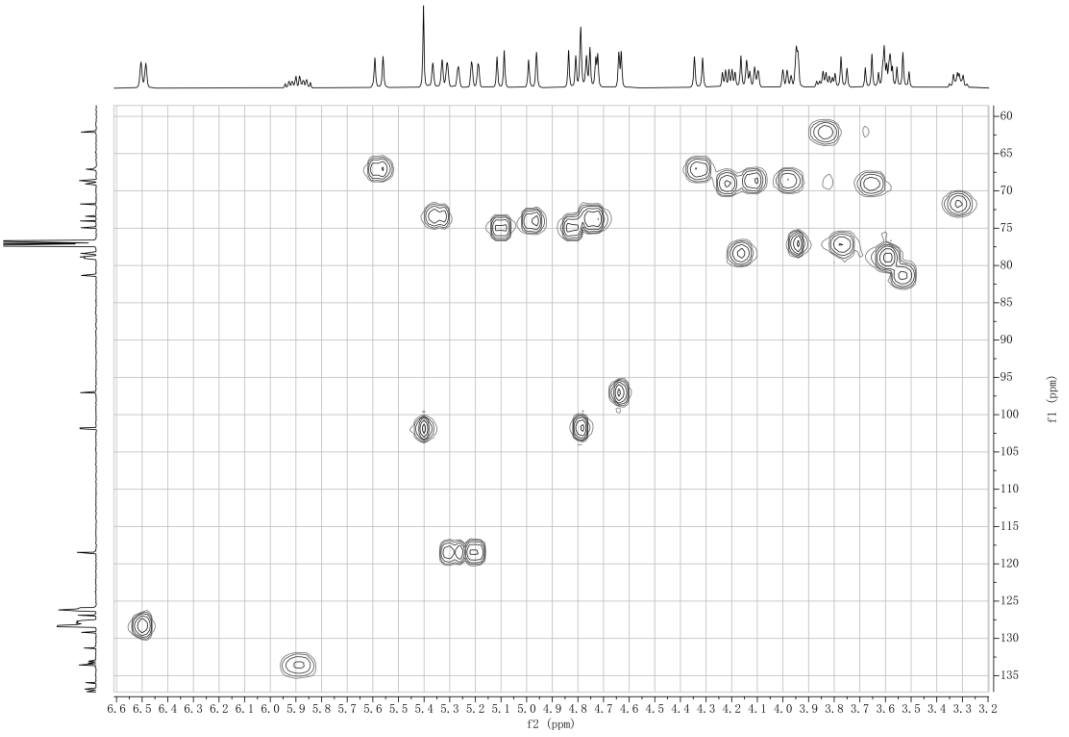
^{13}C NMR, 100 MHz, $CDCl_3$

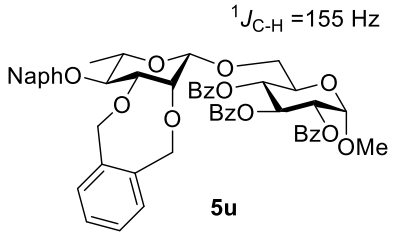


COSY, 400 MHz, $CDCl_3$



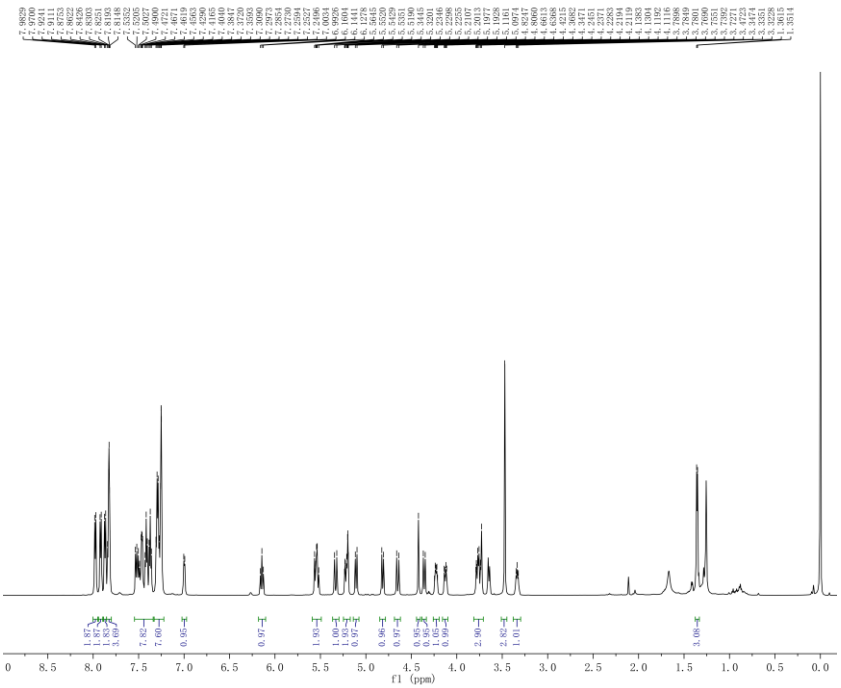
HSQC, 400 MHz, $CDCl_3$



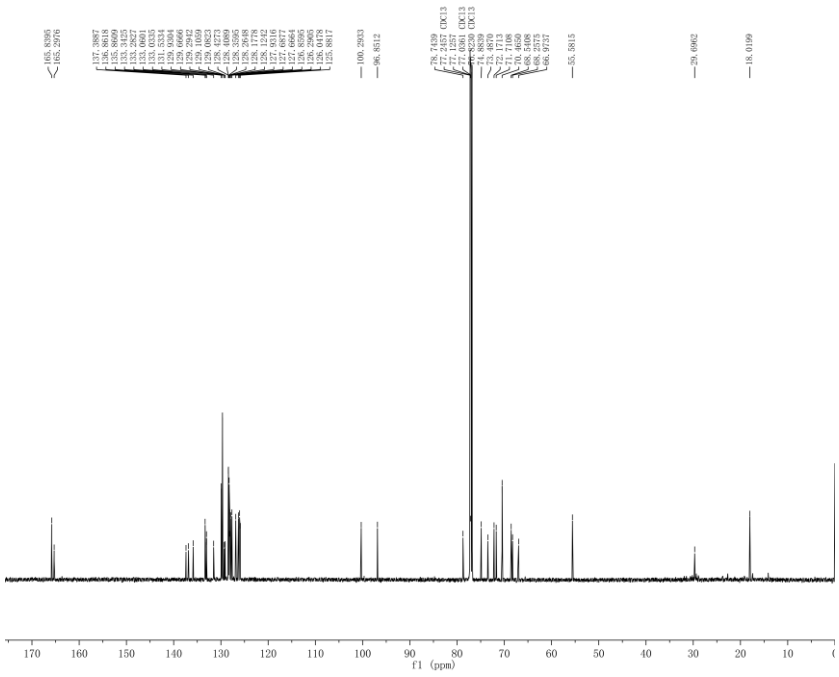


5u

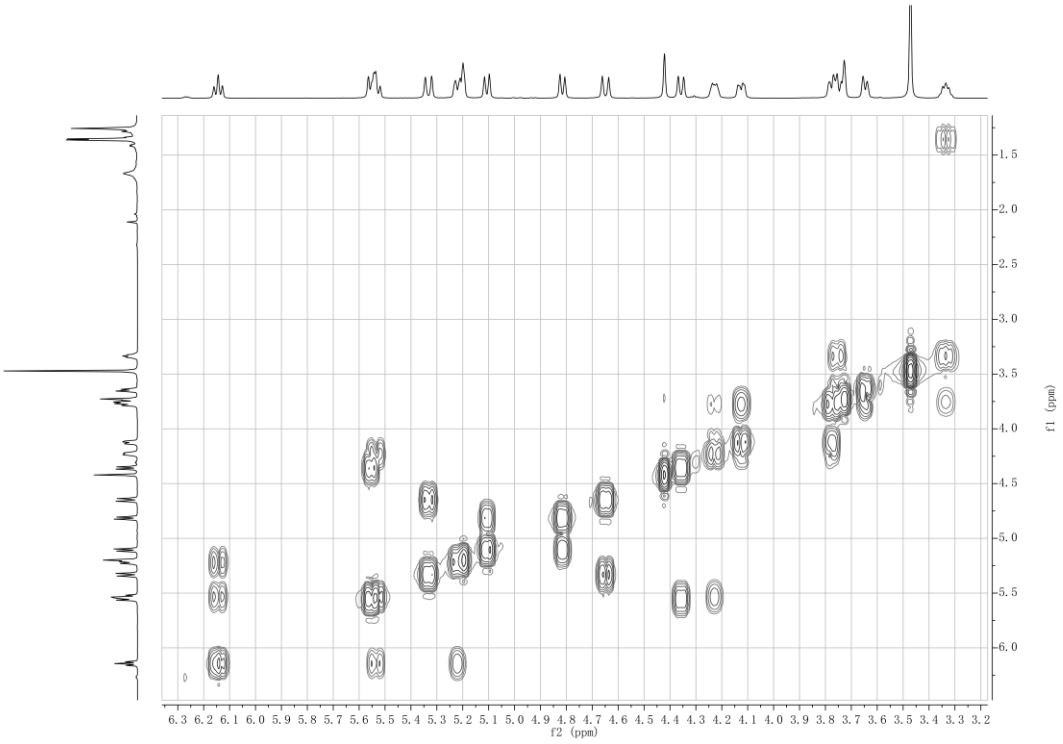
^{1}H NMR, 600 MHz, $CDCl_3$



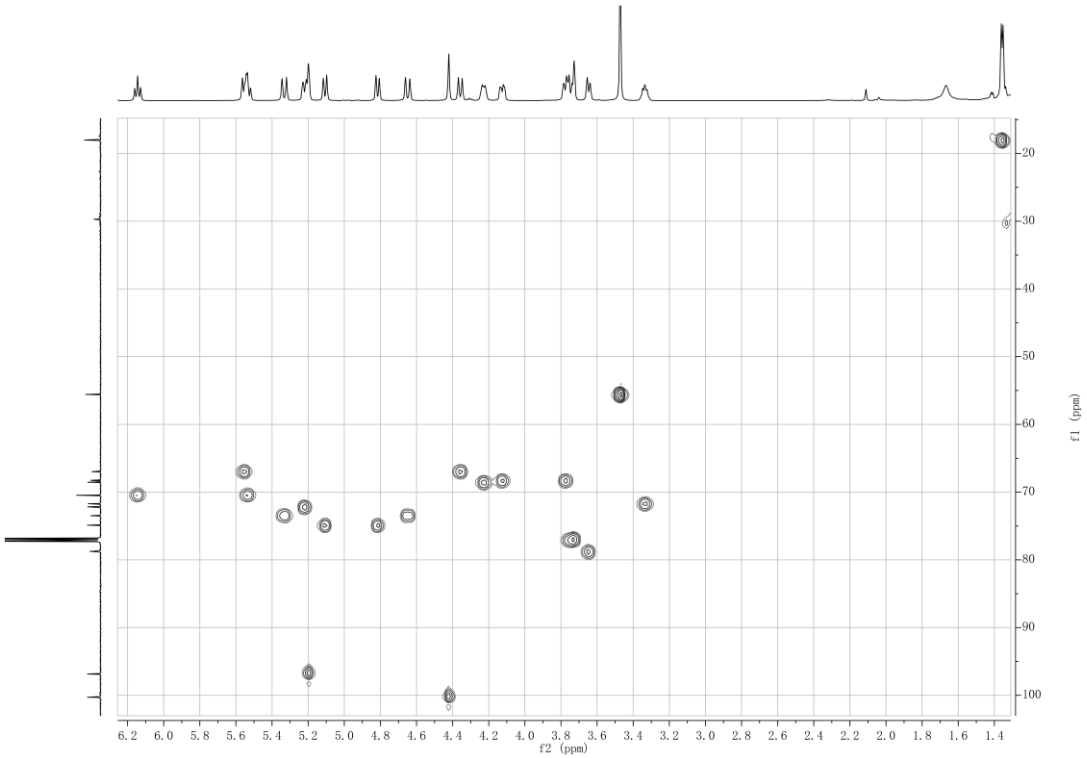
^{13}C NMR, 151 MHz, $CDCl_3$

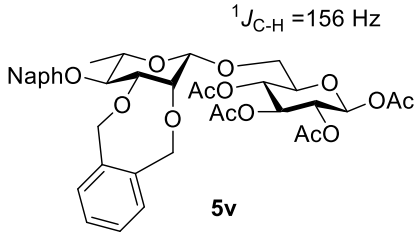


COSY, 600 MHz, $CDCl_3$



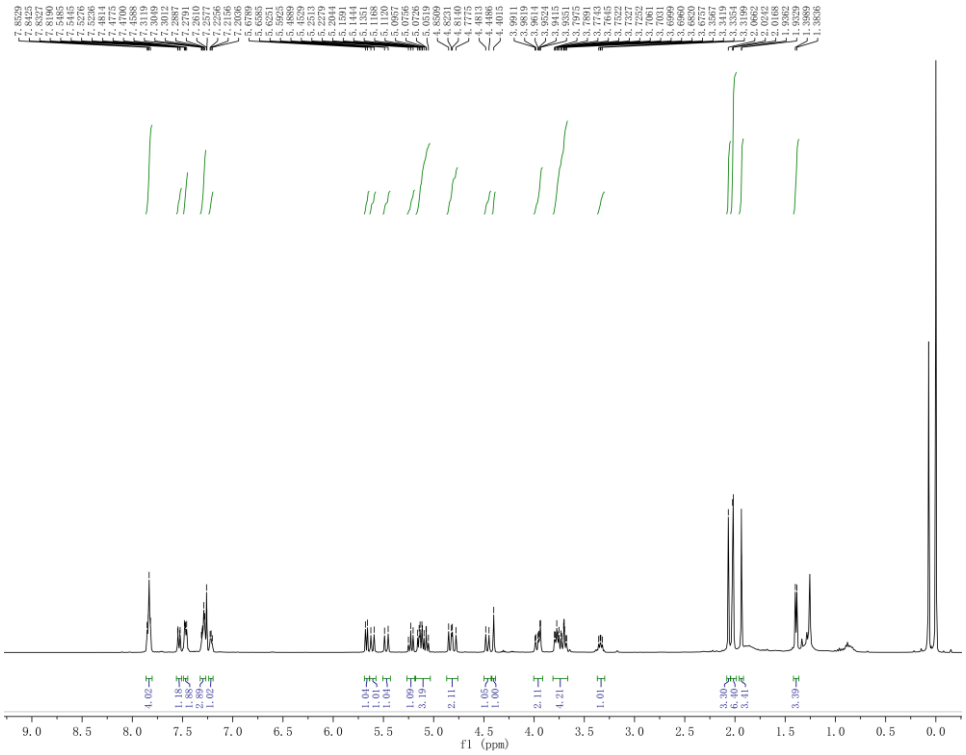
HSQC, 600 MHz, $CDCl_3$



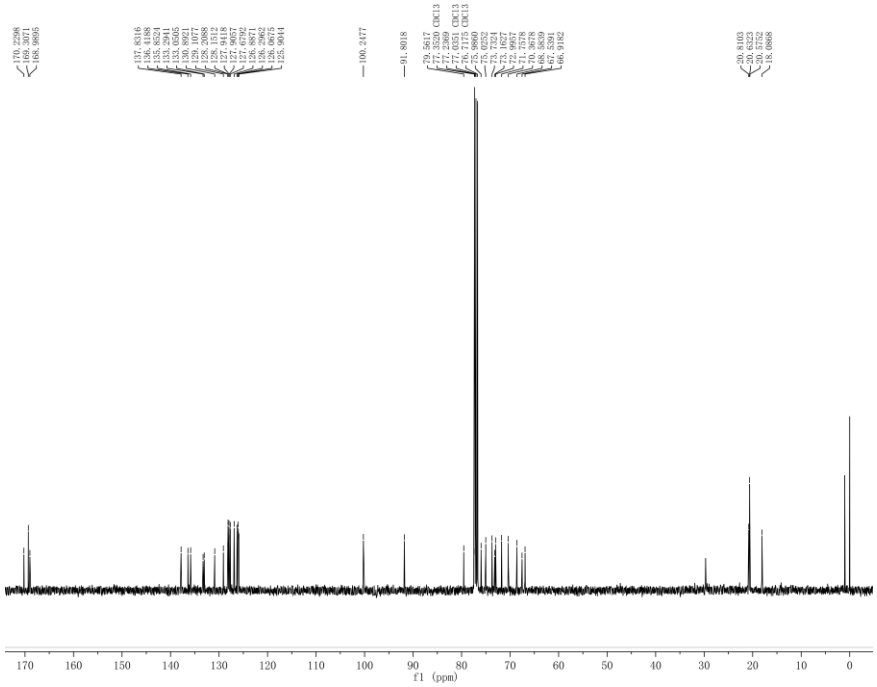


5v

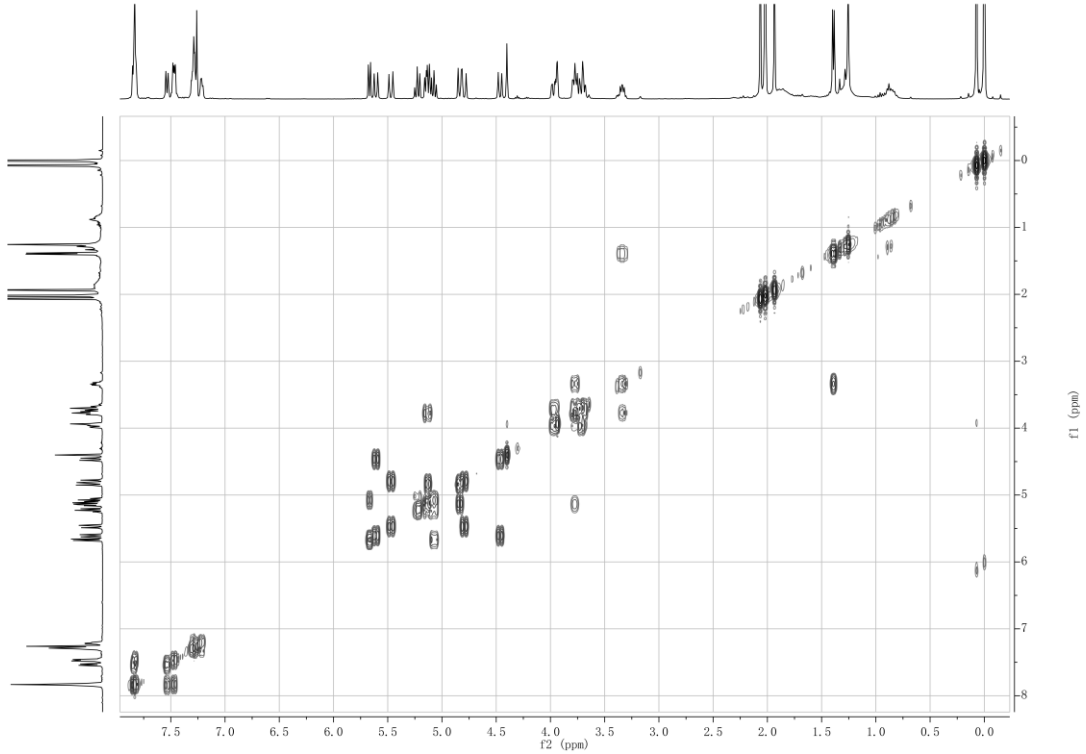
^{1}H NMR, 400 MHz, $CDCl_3$



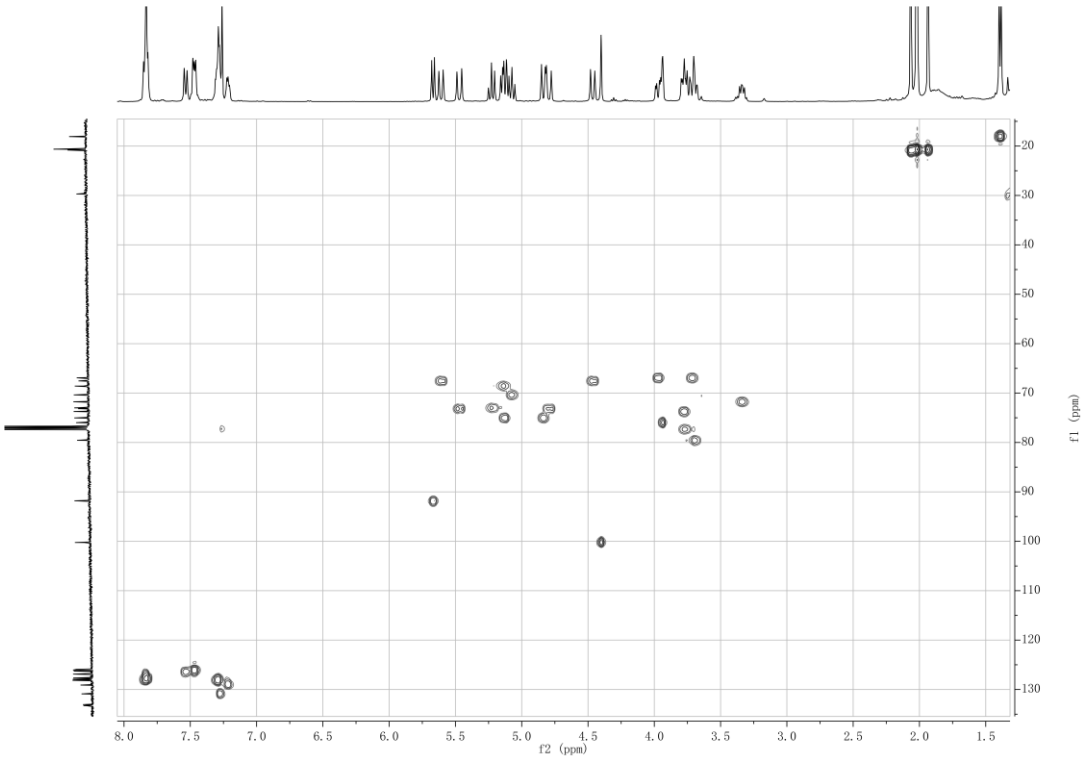
^{13}C NMR, 100 MHz, $CDCl_3$

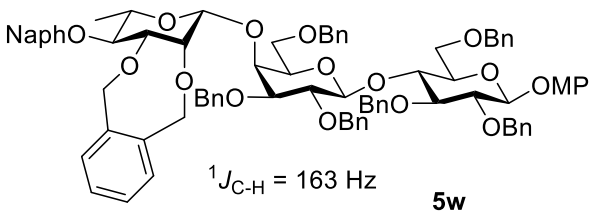


COSY, 400 MHz, $CDCl_3$



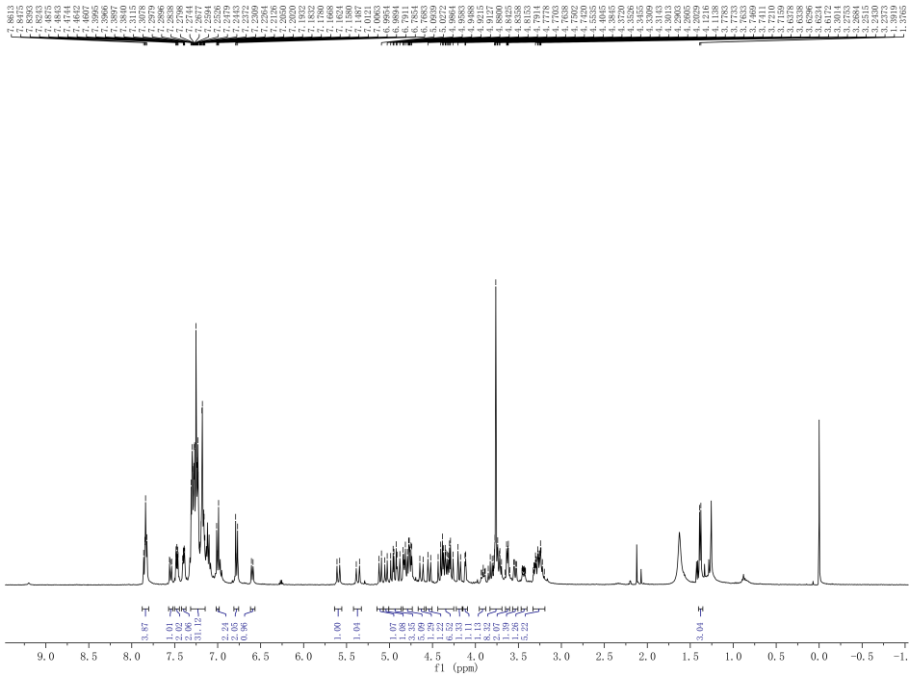
HSQC, 400 MHz, $CDCl_3$



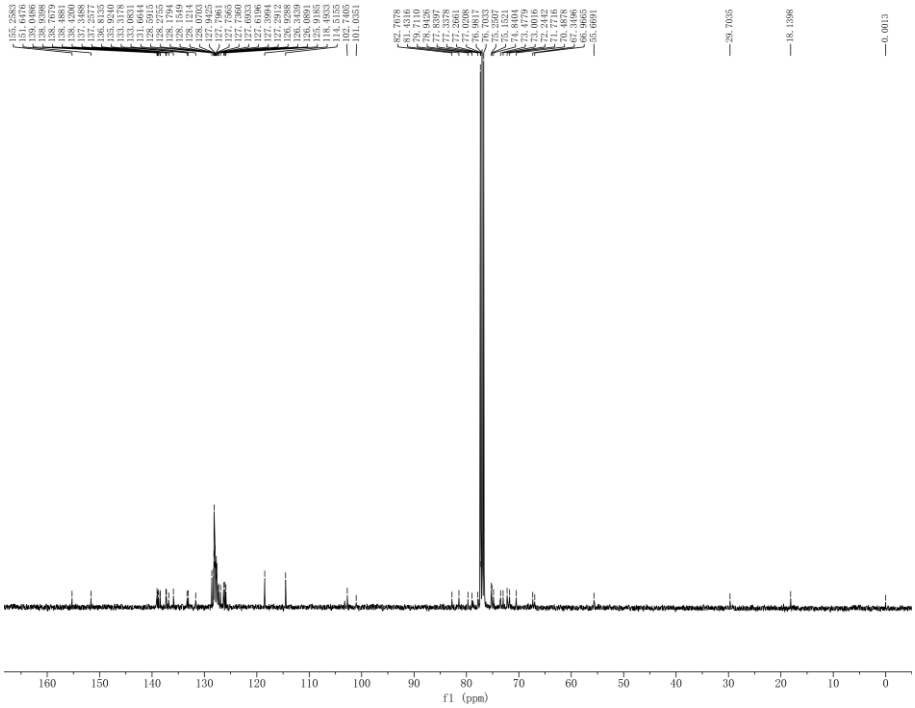


5w

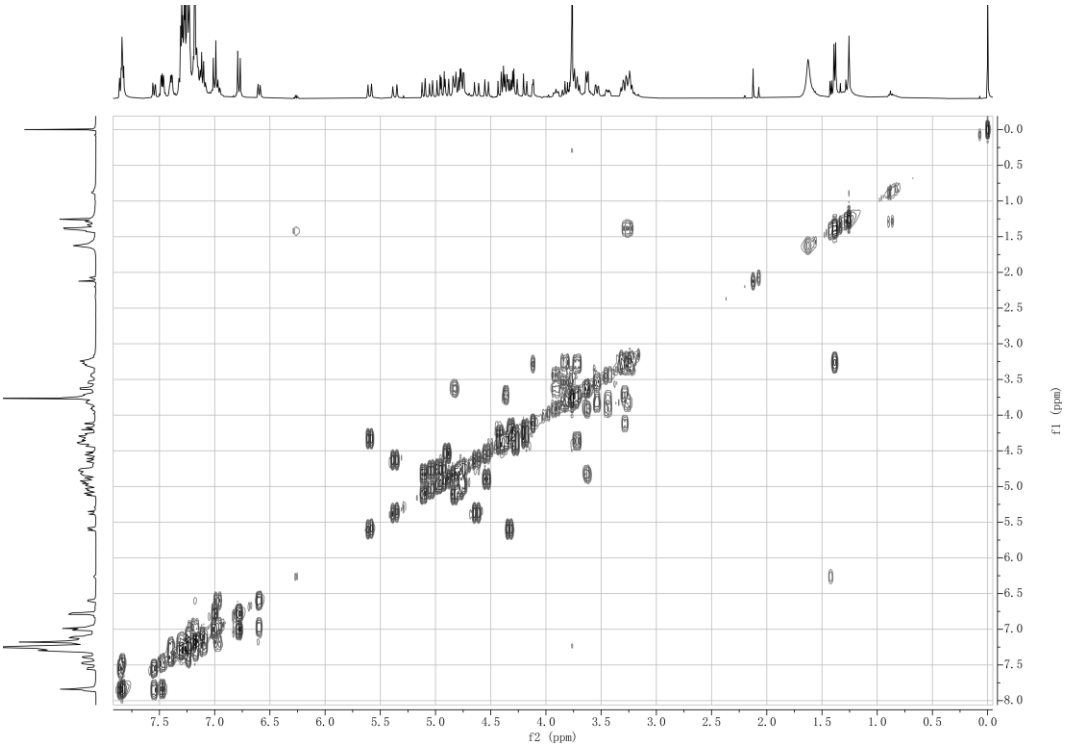
^{1}H NMR, 400 MHz, $CDCl_3$



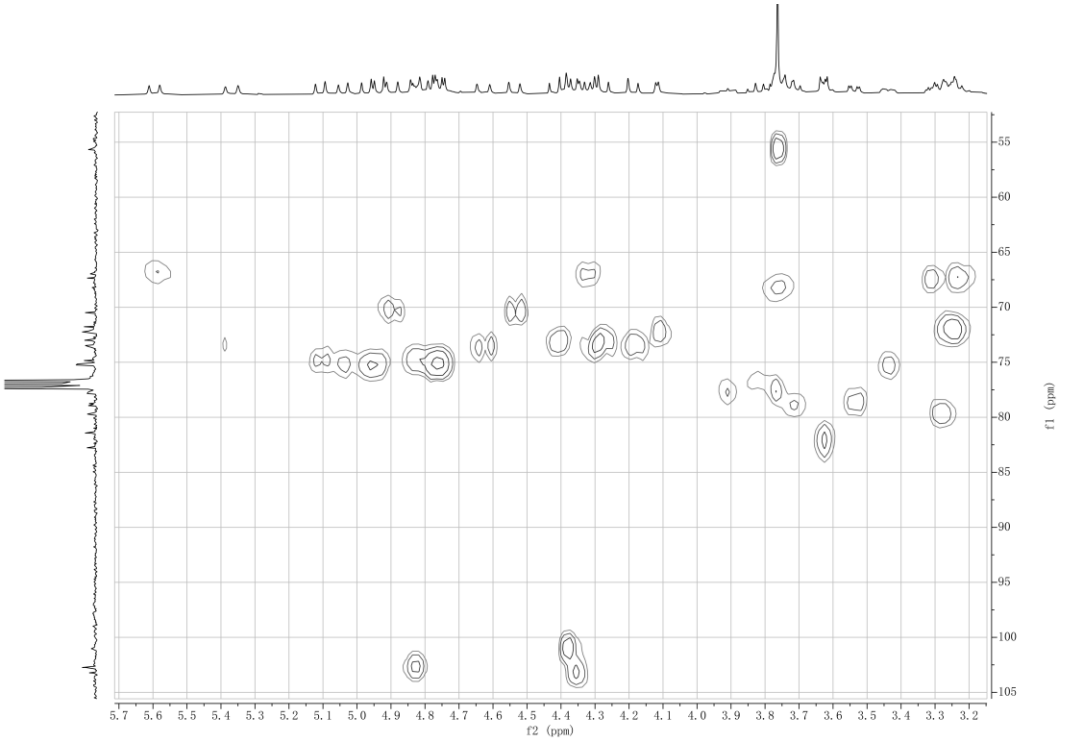
^{13}C NMR, 100 MHz, $CDCl_3$

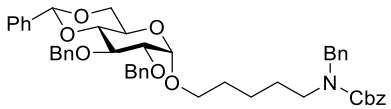


COSY, 400 MHz, $CDCl_3$



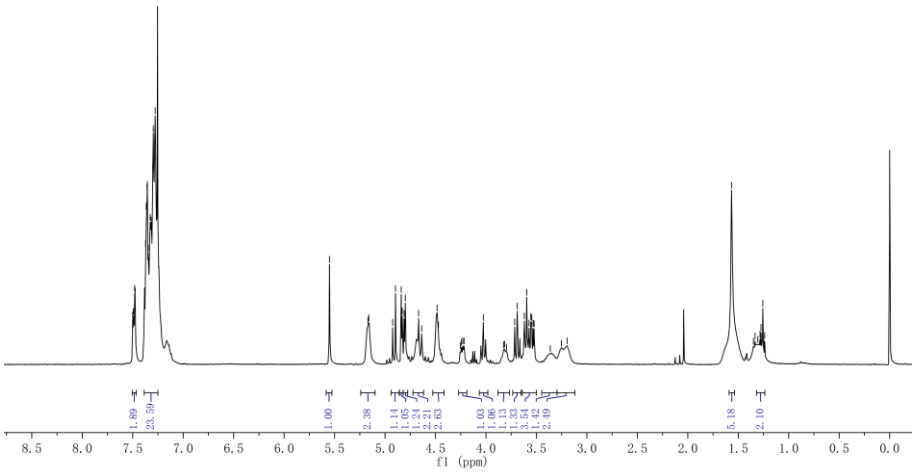
HSQC, 400 MHz, $CDCl_3$



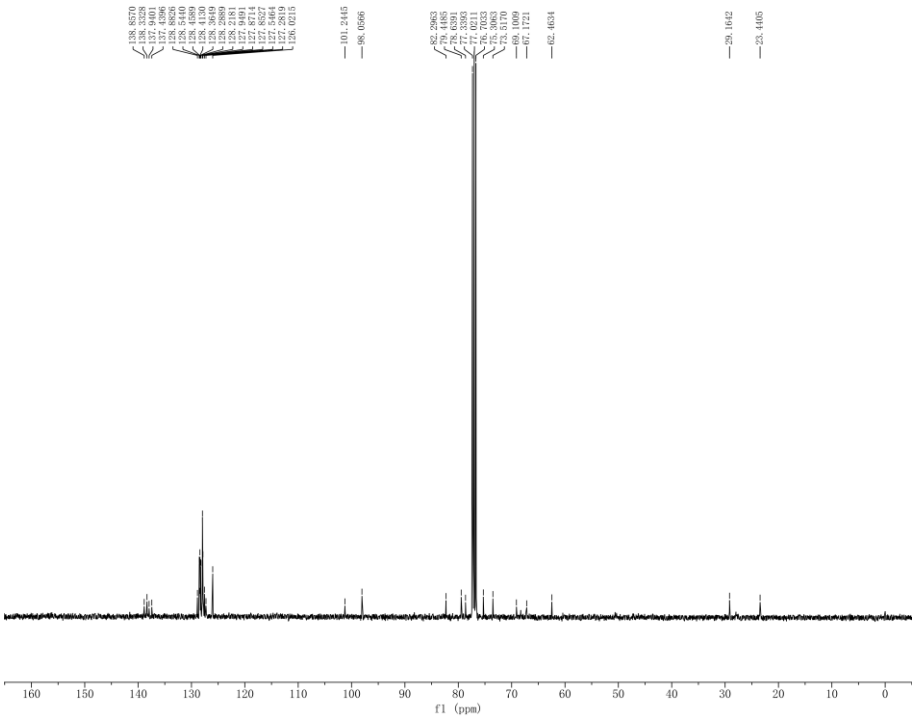


8

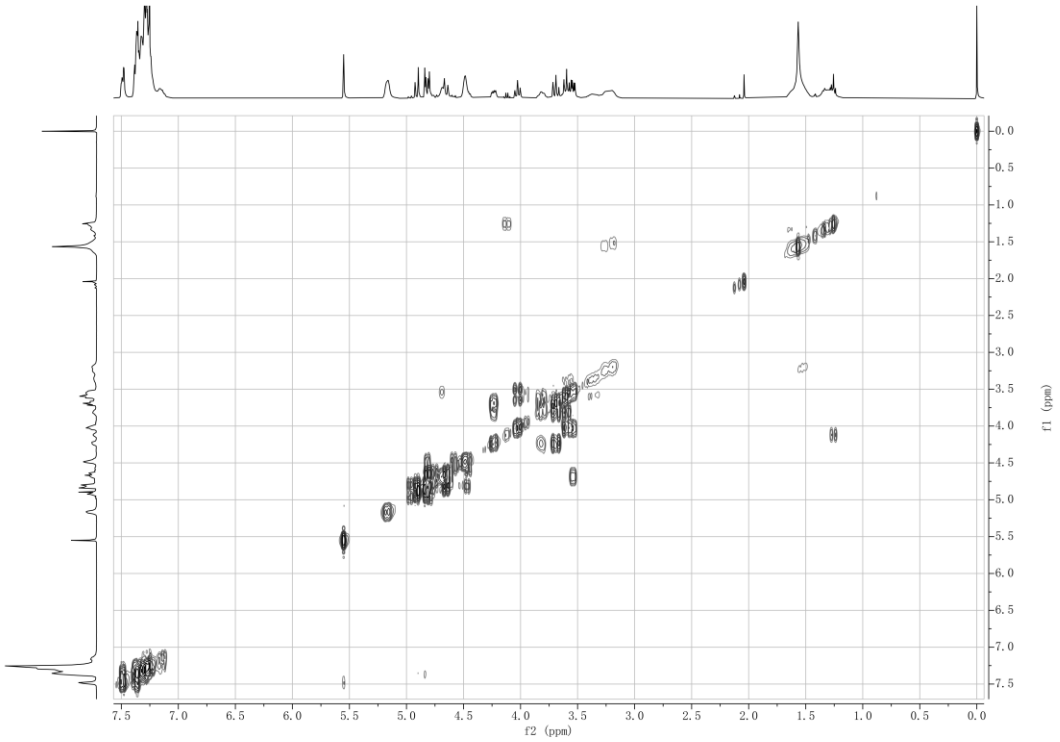
^{1}H NMR, 400 MHz, $CDCl_3$



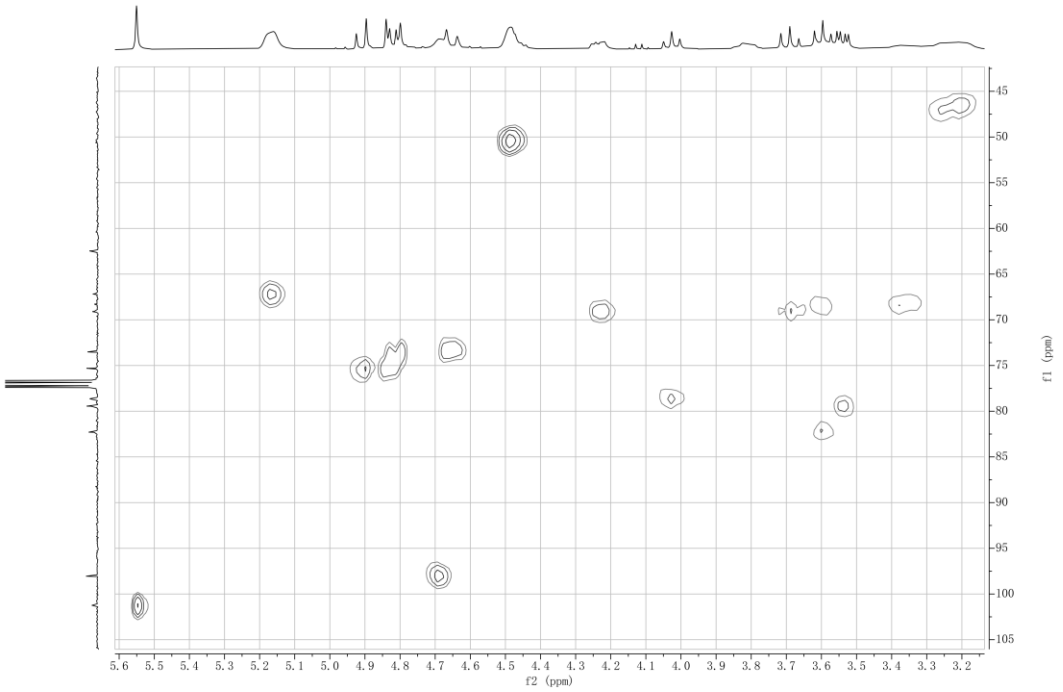
^{13}C NMR, 100 MHz, $CDCl_3$

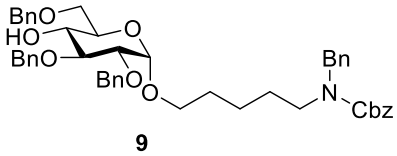


COSY, 400 MHz, $CDCl_3$



HSQC, 400 MHz, $CDCl_3$





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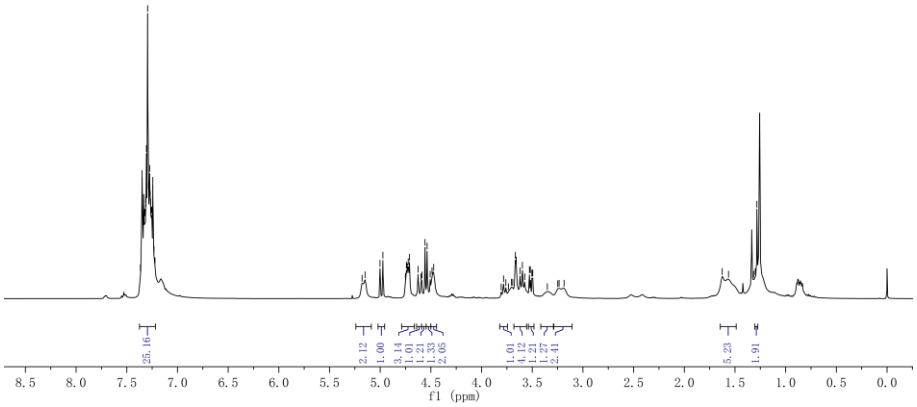
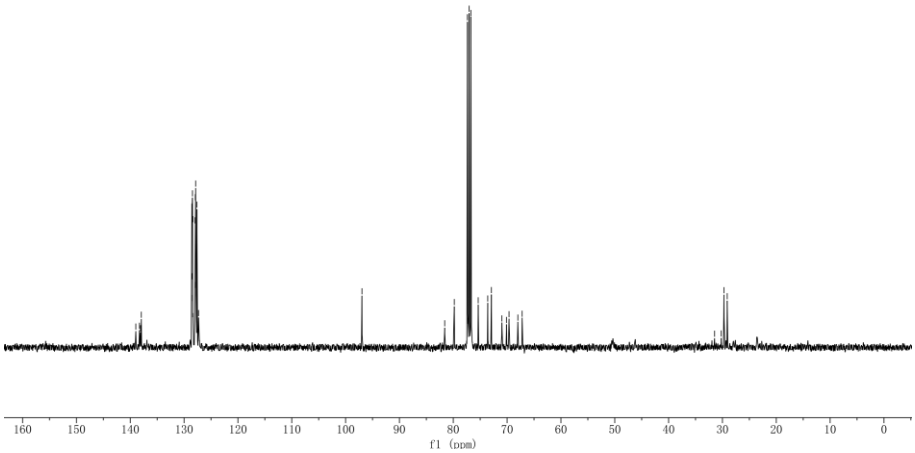
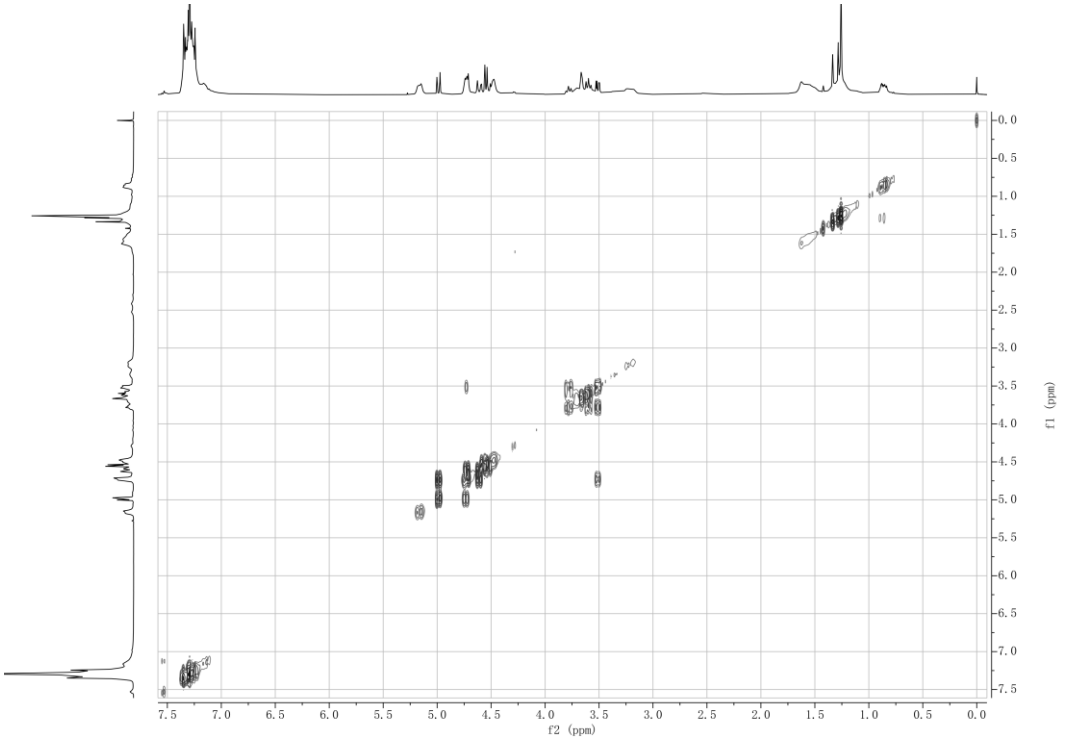
^{1}H NMR, 400 MHz, $CDCl_3$



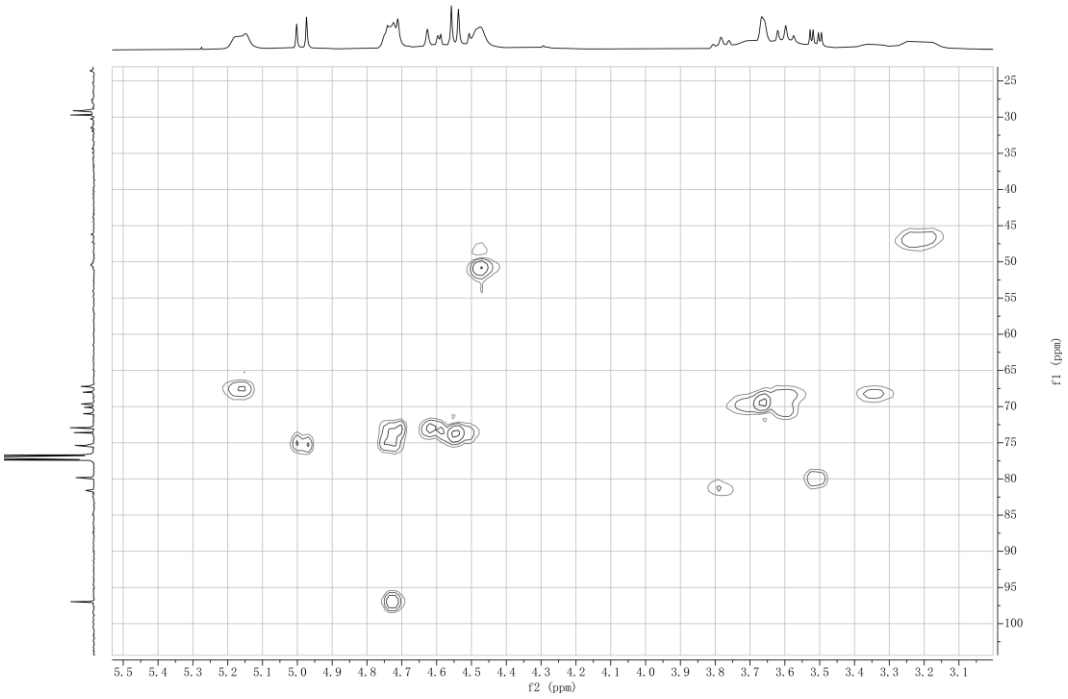
^{13}C NMR, 100 MHz, $CDCl_3$

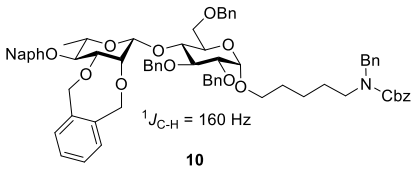


COSY, 400 MHz, $CDCl_3$



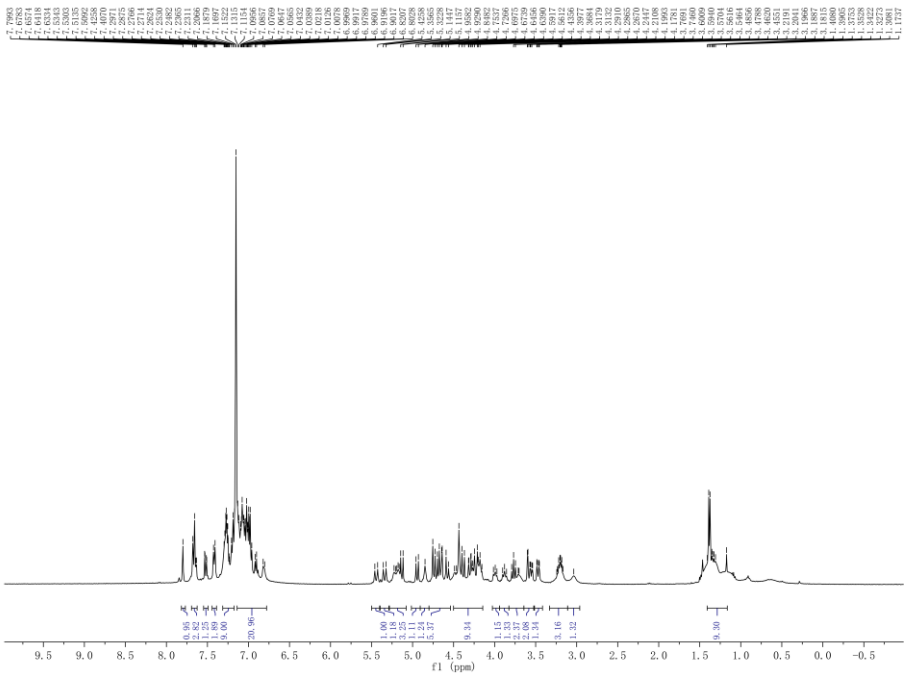
HSQC, 400 MHz, $CDCl_3$



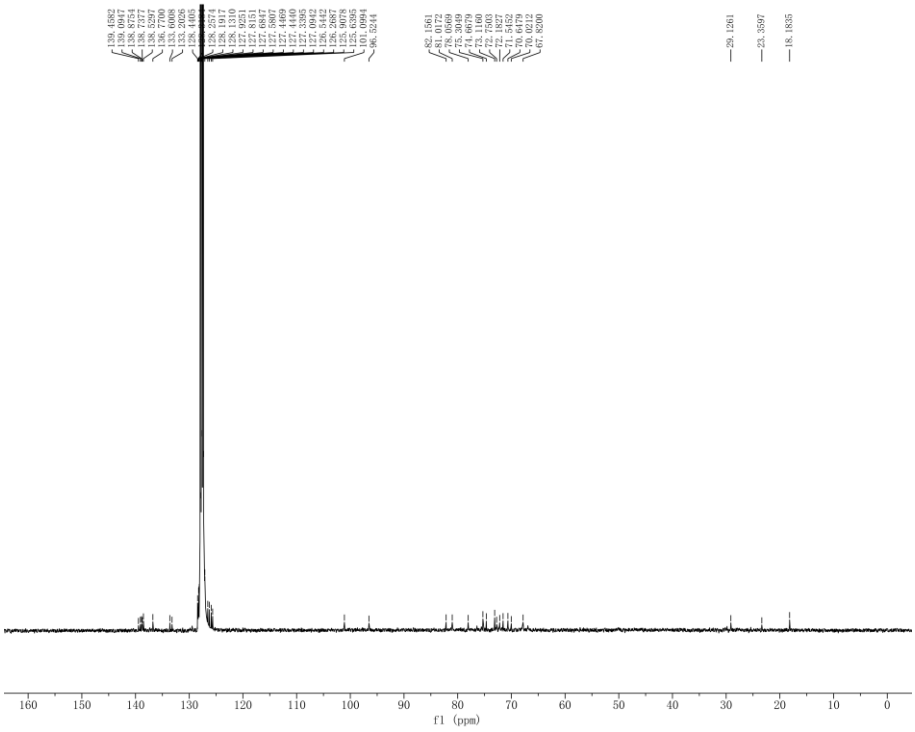


10

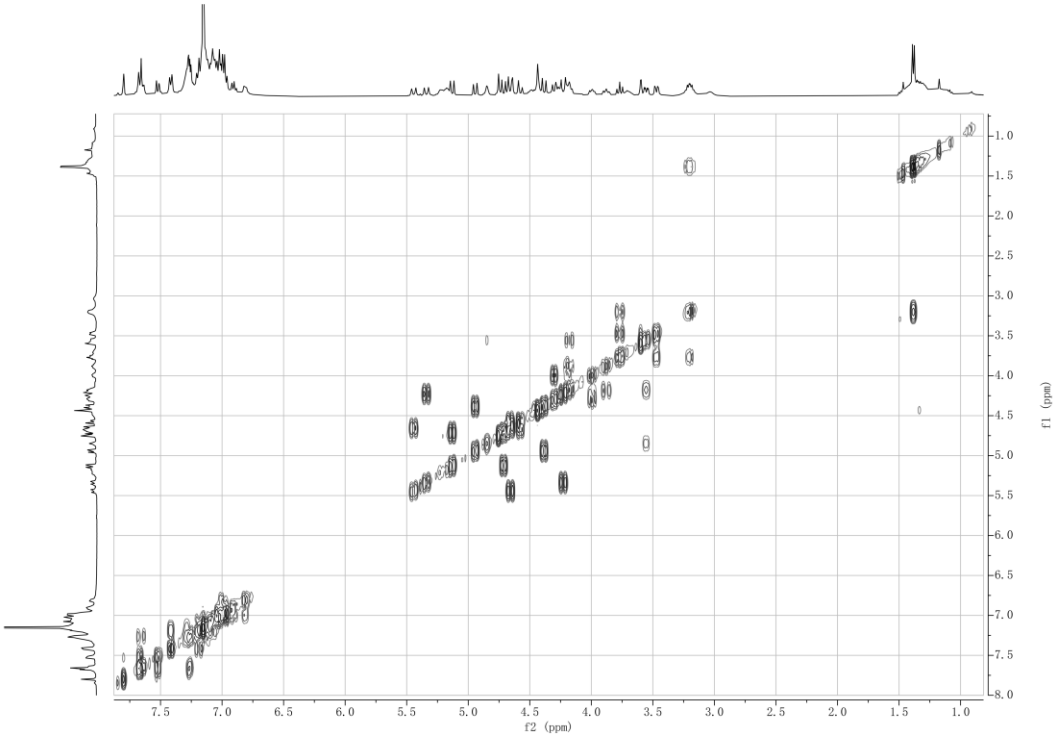
^{1}H NMR, 400 MHz, $CDCl_3$



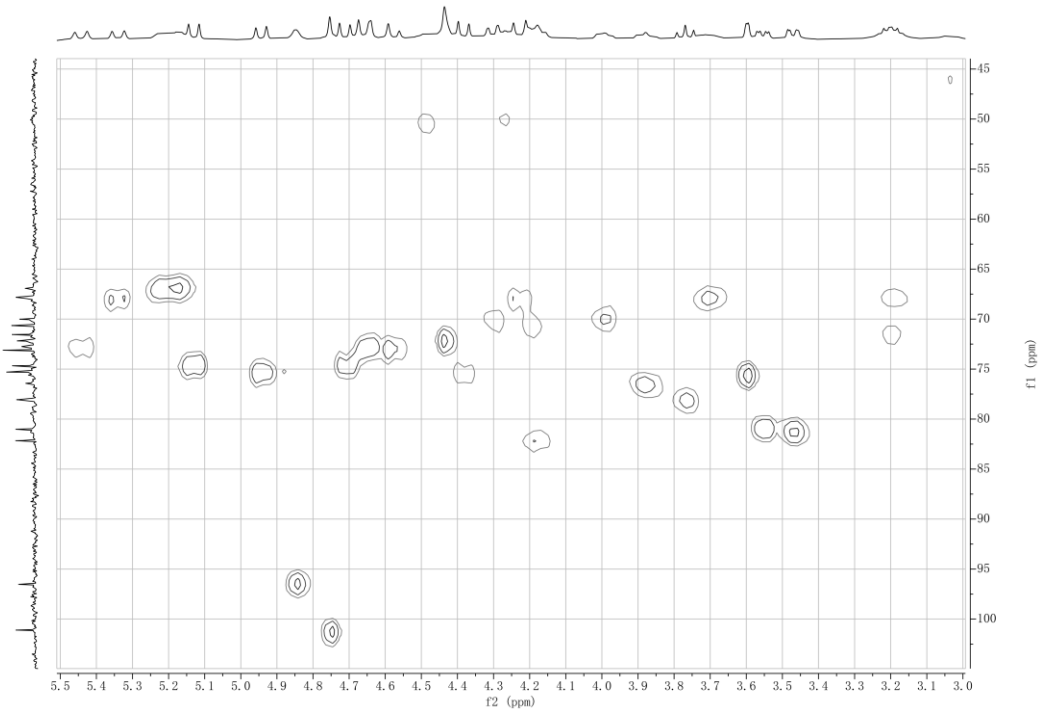
^{13}C NMR, 100 MHz, $CDCl_3$

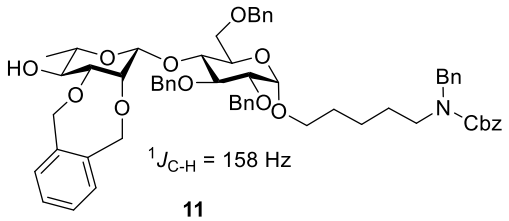


COSY, 400 MHz, $CDCl_3$



HSQC, 400 MHz, $CDCl_3$





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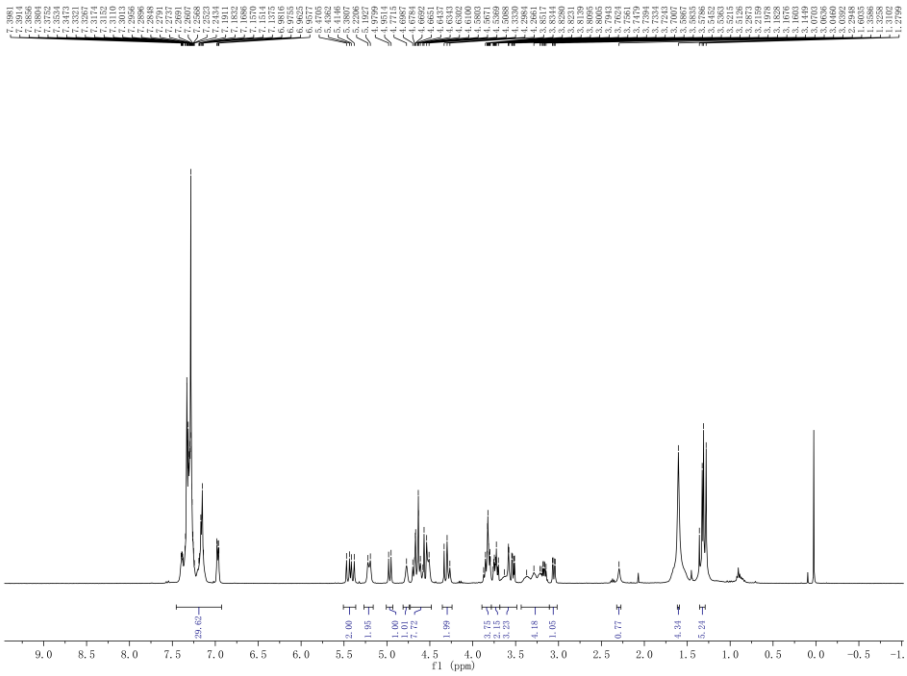
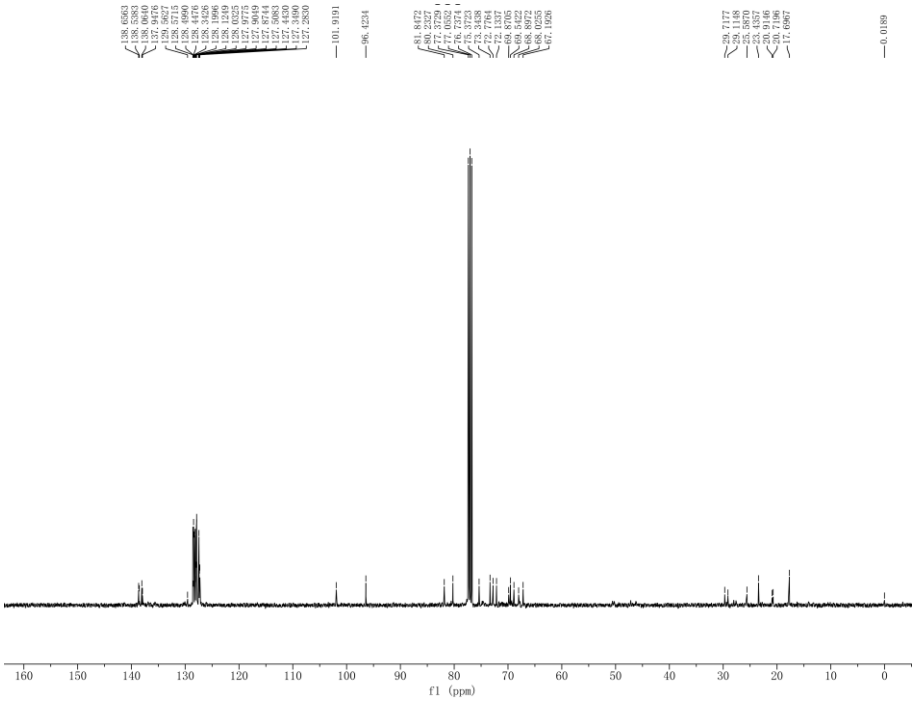
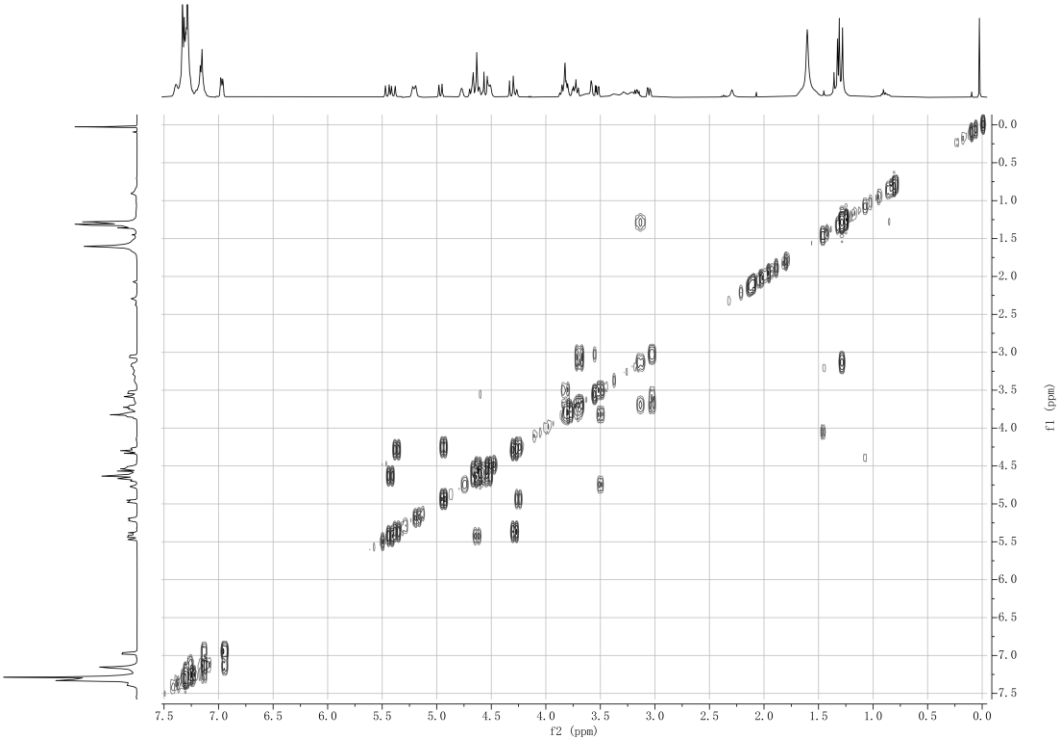
^{1}H NMR, 400 MHz, $CDCl_3$



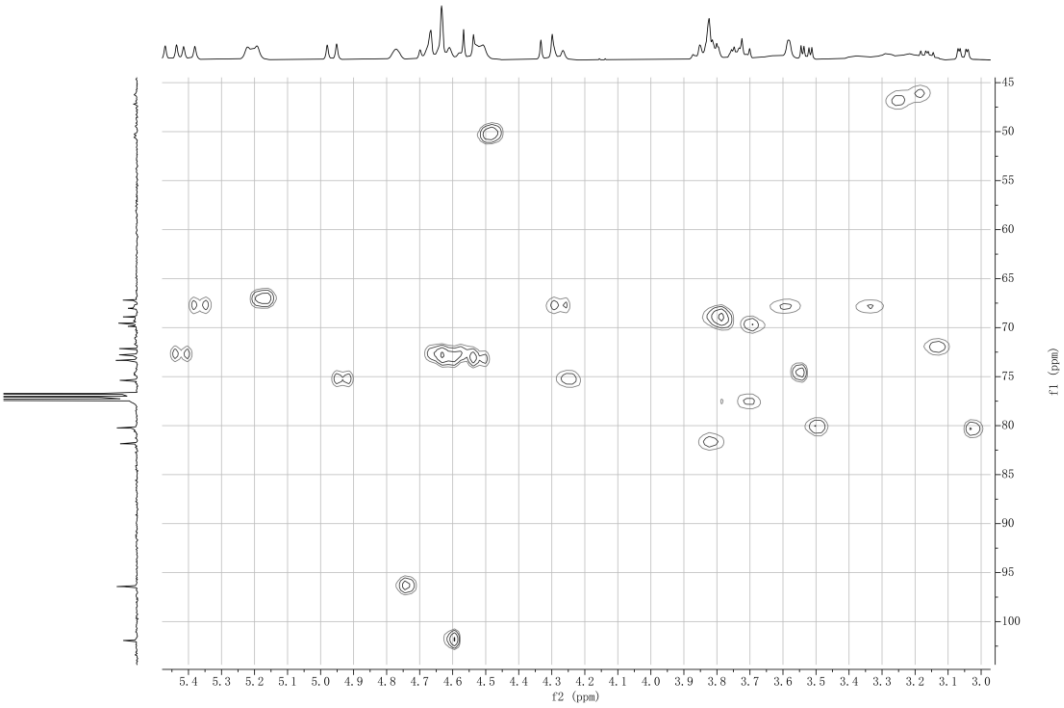
^{13}C NMR, 100 MHz, $CDCl_3$

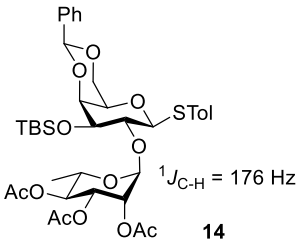


COSY, 400 MHz, $CDCl_3$



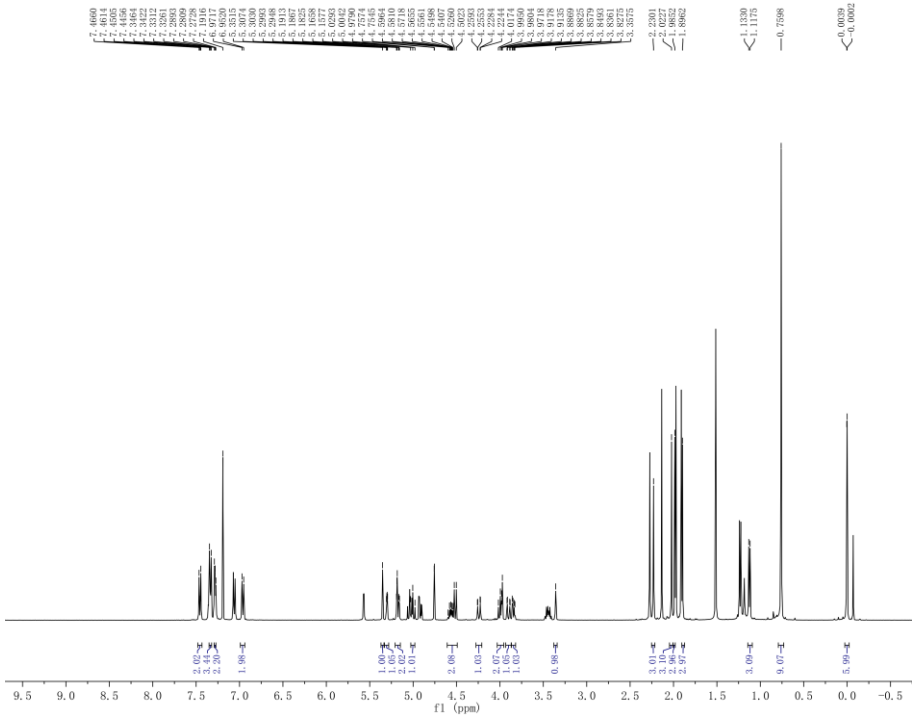
HSQC, 400 MHz, $CDCl_3$



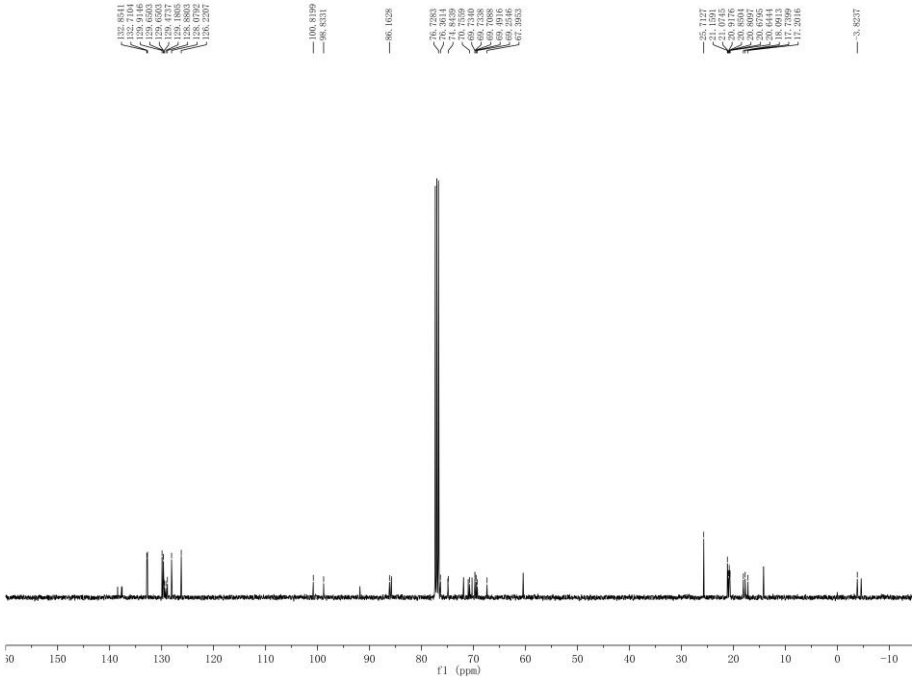


14

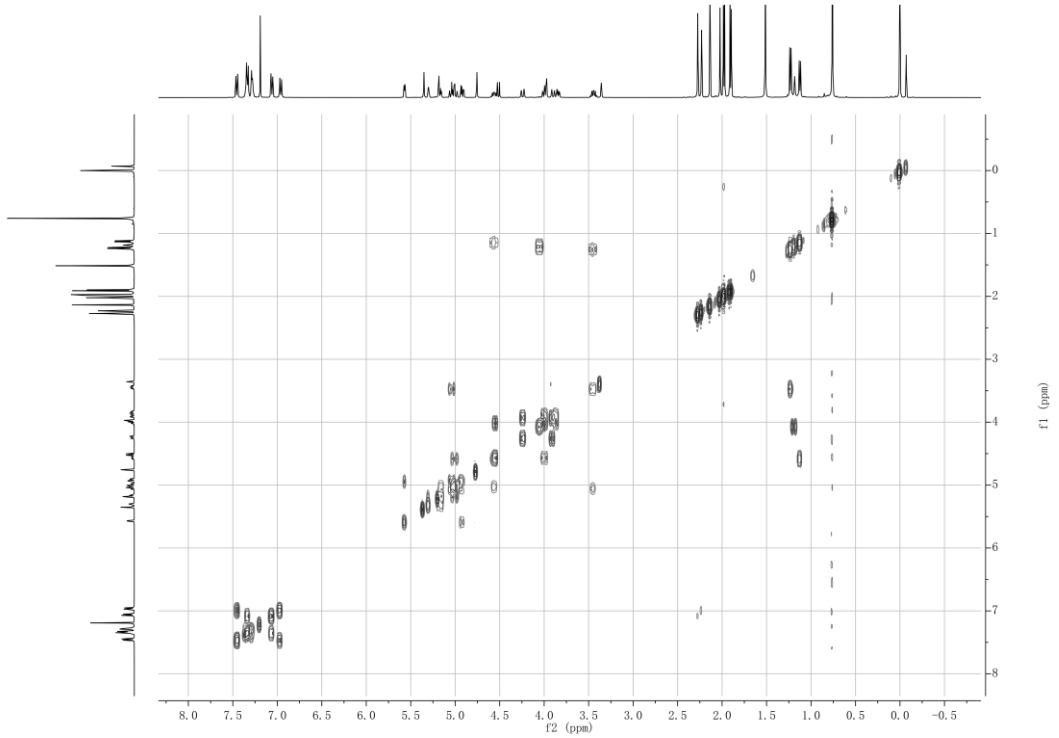
^{1}H NMR, 400 MHz, $CDCl_3$



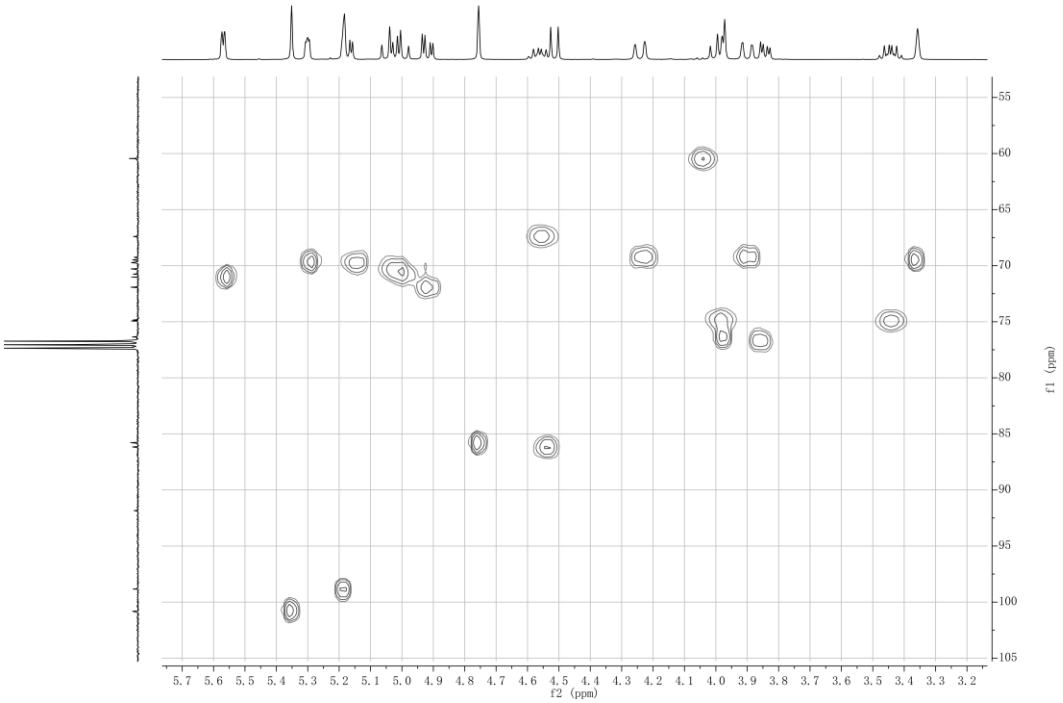
^{13}C NMR, 100 MHz, $CDCl_3$

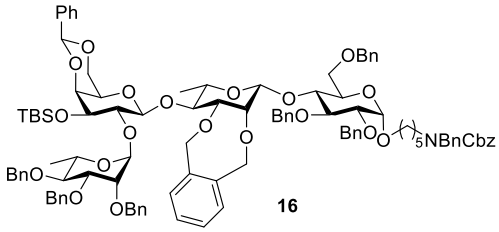


COSY, 400 MHz, $CDCl_3$

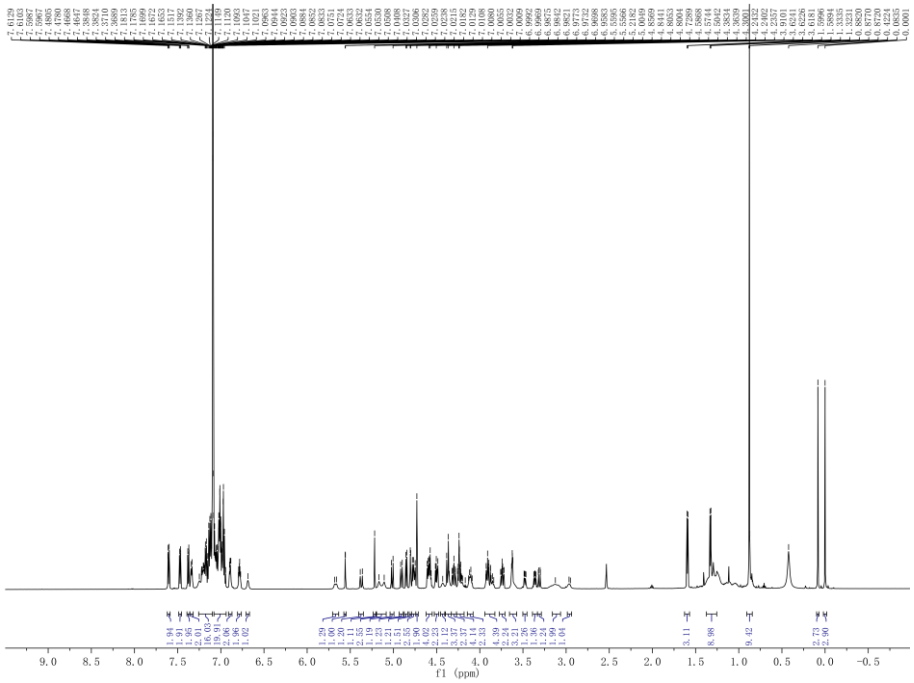


HSQC, 400 MHz, $CDCl_3$

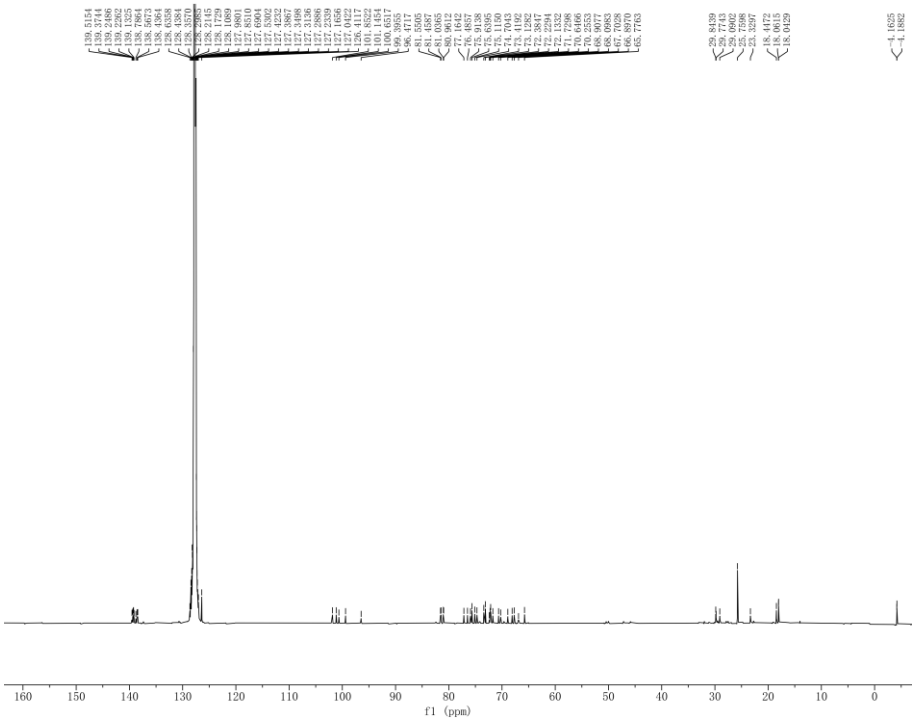




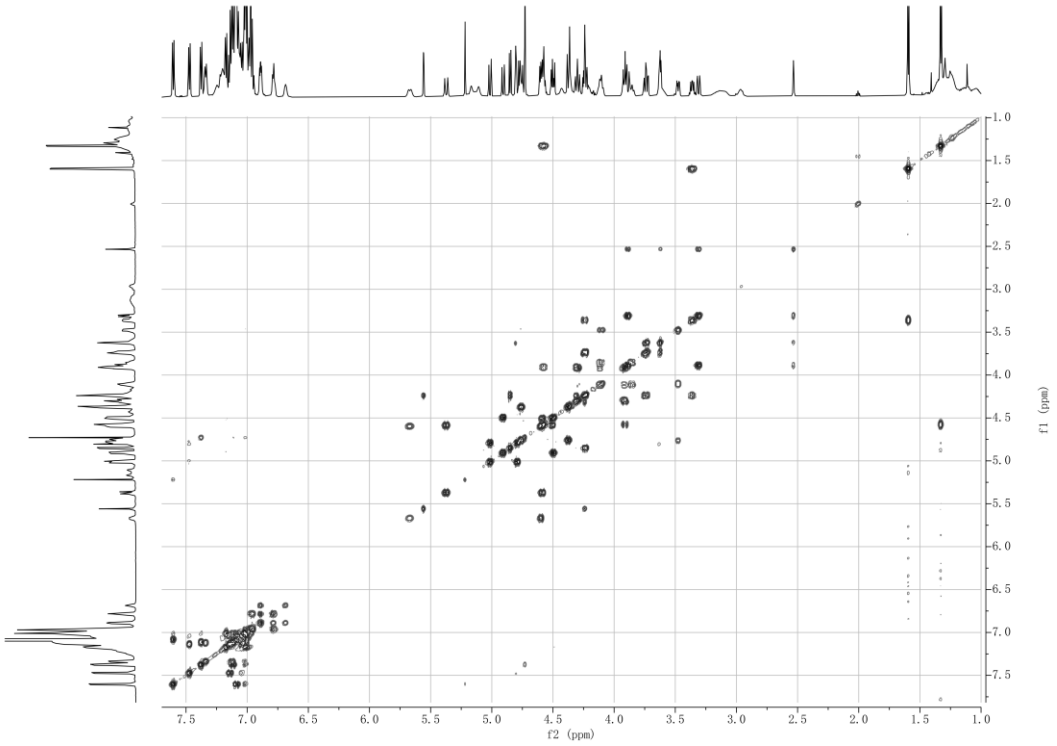
^{1}H NMR, 600 MHz, C_6D_6



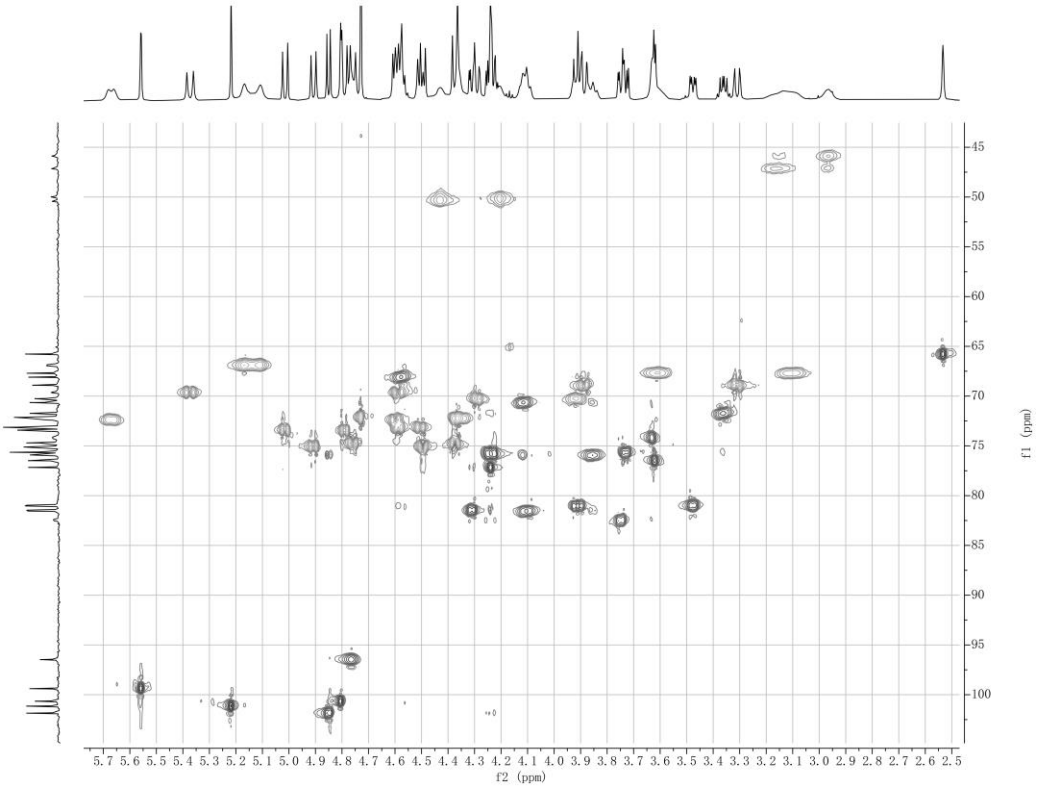
^{13}C NMR, 151 MHz, C_6D_6

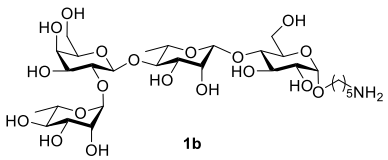


COSY, 600 MHz, C_6D_6



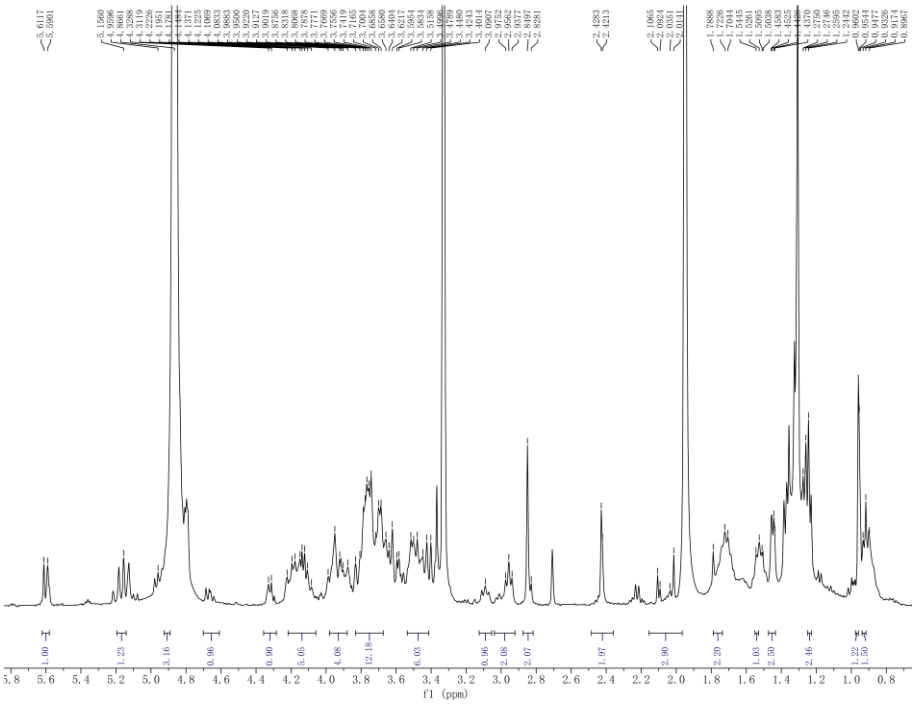
HSQC, 600 MHz, C_6D_6





1b

^{1}H NMR, 400 MHz, CD_3OD



^{13}C NMR, 100 MHz, CD_3OD