Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

An Experimental and Theoretical Study on Stereocontrolled Glycosylations by "One-pot" Procedure

Xuemei Zhong,[a,#] Xiaoya Zhao,[a,#] Jiaming Ao,[a,#] Yan Huang,[a,] Yuhua Liu,[b*] Siai Zhou,[a] Bizhi Li,[a] Akihiro Ishiwata,[c] Qianglin Fang,[d] Chongguang Yang,[d] Hui Cai,*[a] Feiqing Ding*[a]

[a]School of Pharmaceutical Sciences (Shenzhen), Sun Yat-sen University, Shenzhen 518107, China

[b]School of Physics and Electronic Engineering, Guangzhou University, Guangzhou 510006, China

[c]RIKEN Cluster for Pioneering Research, Saitama 351-0198, Japan

[d]School of Public Health (Shenzhen), Shenzhen Campus of Sun Yat-sen University, Shenzhen 518107, China

E-mail: liuyuhua@gzhu.edu.cn, caihui5@mail.sysu.edu.cn, and: dingfq3@mail.sysu.edu.cn

Table of Contents

1 General Information

All reactions sensitive to air and/or moisture were carried out under nitrogen or argon atmosphere with anhydrous solvents. Substrates of glycosylations were dried by a zeotropic removal with toluene. Column chromatography was performed on silica gel, 300–400 mesh. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F254 of 0.2mm thickness, and compounds were detected by examination under UV light and by charring with 10% sulfuric acid in MeOH. Noted that when using toluene–ethyl acetate (CAUTION! STRONG CARCINOGENIC ACTIVITY). 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 (4Å) were activated at 170 °C for 2–3 h under reduced pressure prior to application. All reactions were carried out under an argon atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker spectrometers at 400 MHz or JEOL ECX 400 spectrometer. ^{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 ^{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 native scale. Assignments were made by standard 2D experiments. Optical rotations were measured with 'Insmark IP-digi300/1' polarimeter. HRMS were recorded on Shimadzu (LCMS-IT-TOF). All other reagents were purchased from Adamas-Beta Co., Bidepharm Co. and Macklin Co.

The calculation package used is the Gaussian program.[1] All geometries were optimized at the theory level of B3LYP [2] //BS1 (BS1 = 6-31G(d) [3] for main group elements and Lanl2dz [4] for Sn) in the gas phase. Vibrational frequency calculations were used to confirm that the optimized structures are minima on the potential energy surface. The single point energies for the B3LYP optimized geometries were computed using the SMD [5] solvent model (solvent = DCM) at the M06 [6] //BS2 (BS2=6-311+G** [4] for main group elements and SDD [7] for Sn) level of theory.

2 Cartesian coordinates of all the key structures

TS4

Charge = 0 Multiplicity = 1

H	2.06158	-0.84197	-1.0792
Cl	1.50483	0.52711	-1.41039
Cl	-0.70483	-0.46186	1.40732
Cl	-1.41844	-1.59589	-2.28873
Cl	-0.72329	-3.98442	0.42136
C	2.63535	-2.95346	0.0944
H	2.20053	-3.94917	0.20091
H	3.57032	-3.01827	-0.46561
H	2.81575	-2.512	1.07898
Sn	-0.17903	-1.85347	-0.36417
O	1.74764	-2.11835	-0.68303

Thermal correction to Energy=	0.063922
Thermal correction to Enthalpy=	0.064866
Thermal correction to Gibbs Free Energy=	0.011712
Sum of electronic and zero-point Energies=	-1959.953068
Sum of electronic and thermal Energies=	-1959.941634

Sum of electronic and thermal Enthalpies= -1959.940689

Sum of electronic and thermal Free Energies= -1959.993844

SCF Done: E(RM06) = -1959.97209909

TS7

Charge = 0 Multiplicity = 1

C	1.56299	0.0197	0.17844
H	1.49616	-1.01917	-0.02876
C	0.29809	0.70658	0.62337
H	0.39262	0.83783	1.7153
C	0.19942	2.11257	0.01193
H	0.06428	2.02633	-1.07327
C	1.51076	2.86459	0.29005
H	1.61541	3.00335	1.37836
C	2.71961	2.08653	-0.25551
H	2.67178	2.10492	-1.34785
O	2.69431	0.65879	0.10025
C	-1.18954	-1.02575	1.32443
H	-1.45971	-0.47767	2.24031
C	-2.35009	-1.84261	0.8251
C	-2.14863	-3.13532	0.32813
H	-1.14697	-3.55846	0.32185
C	-3.22451	-3.88534	-0.15077
H	-3.05611	-4.88954	-0.53
C	-4.51212	-3.34626	-0.13947
H	-5.35055	-3.92995	-0.51013
C	-4.72222	-2.05603	0.3547
C	-3.64653	-1.31064	0.83606
O	-0.86284	2.83526	0.59859
C	-2.07722	2.84289	-0.1655
O	1.53277	4.11162	-0.37763
C	1.11636	5.23609	0.4244
C	4.06	2.62601	0.23584
H	4.03288	3.72123	0.14063
H	-5.72359	-1.63408	0.36905
O	1.37381	-0.15046	-1.9174
C	2.06483	-1.22948	-3.90298
O	2.30737	-1.31681	1.74785
C	2.89491	-0.74837	2.89345
H	3.51062	-1.4695	3.44791
H	3.52982	0.12033	2.65805
H	2.08435	-0.41975	3.56229
C	2.11796	-1.05649	-2.32519
N	2.91392	-1.89	-1.64484
H	3.40262	-2.53276	-2.26733

Cl	2.45162	0.36621	-4.63906
Cl	0.38966	-1.71071	-4.32365
Cl	3.2081	-2.45101	-4.5633
O	-0.83361	-0.05902	0.3075
H	-0.32566	-1.66121	1.55414
H	-3.81154	-0.30814	1.22489
H	-1.89019	3.29049	-1.15237
H	-2.40728	1.80833	-0.32331
C	-3.12139	3.63847	0.57912
C	-3.94363	4.5416	-0.10451
C	-3.30722	3.46121	1.95705
C	-4.94135	5.24828	0.5713
H	-3.80509	4.69106	-1.17314
C	-4.29684	4.17254	2.63486
H	-2.66137	2.77418	2.49564
C	-5.11918	5.06627	1.94326
H	-5.57291	5.94491	0.02647
H	-4.42774	4.02934	3.70427
H	-5.89097	5.61902	2.47199
C	1.05968	6.4569	-0.45602
C	2.23842	7.04974	-0.92801
C	-0.17212	7.00883	-0.82536
C	2.18741	8.17166	-1.75392
H	3.20022	6.62765	-0.64573
C	-0.22693	8.13621	-1.64783
H	-1.0922	6.55473	-0.46433
C	0.95251	8.71826	-2.11448
H	3.10852	8.62323	-2.11257
H	-1.18956	8.55849	-1.92341
H	0.91174	9.5959	-2.75404
H	1.84445	5.37617	1.23922
H	0.13848	5.02909	0.86704
O	5.16242	2.07638	-0.44553
H	4.18295	2.36596	1.29325
C	5.47192	2.70859	-1.68295
H	5.54848	3.79846	-1.5198
H	4.669	2.55359	-2.42065
C	6.77507	2.16552	-2.22263
C	7.79187	1.74226	-1.35871
C	6.99364	2.12535	-3.60433
C	9.00712	1.28765	-1.87199
H	7.61715	1.75327	-0.28806
C	8.21299	1.68084	-4.11773
H	6.20443	2.4398	-4.28435

C	9.22338	1.2595	-3.25144
H	9.78538	0.95111	-1.19219
H	8.36822	1.65284	-5.19302
H	10.17023	0.90389	-3.64891
Sn	3.677	-2.57181	0.29343
Cl	5.56905	-1.56402	1.27773
Cl	2.34146	-4.34764	1.09765
Cl	5.02484	-4.0156	-1.07417

Thermal correction to Energy= 0.756009
Thermal correction to Enthalpy= 0.756953
Thermal correction to Gibbs Free Energy= 0.591507
Sum of electronic and zero-point Energies= -4778.552194
Sum of electronic and thermal Energies= -4778.497306
Sum of electronic and thermal Enthalpies= -4778.496362
Sum of electronic and thermal Free Energies= -4778.661808
SCF Done: E(RM06) = -4778.50245395

TS10

Charge = 0 Multiplicity = 1

H	1.49098	-1.31437	-1.51627
Cl	0.4018	-0.68127	-2.30303
Cl	-0.15561	0.5197	1.11142
Cl	-2.37059	-2.14187	-0.62162
Cl	-0.10363	-3.04993	2.03629
Sn	-0.25769	-1.61087	0.19233
N	1.8601	-1.83664	-0.37041
C	2.64292	-3.01721	-0.27137
O	3.61034	-3.10177	0.43577
C	2.2543	-4.17404	-1.24787
Cl	2.97548	-3.73554	-2.83814
Cl	0.45716	-4.30486	-1.42563
Cl	2.90528	-5.71227	-0.66819
H	2.36076	-1.12411	0.17321

Thermal correction to Energy= 0.062329
Thermal correction to Enthalpy= 0.063273
Thermal correction to Gibbs Free Energy= -0.002404
Sum of electronic and zero-point Energies= -3432.160597
Sum of electronic and thermal Energies= -3432.144165
Sum of electronic and thermal Enthalpies= -3432.143221
Sum of electronic and thermal Free Energies= -3432.208898
SCF Done: E(RM06) = -3432.17327234

12

Charge = 0 Multiplicity = 1

C	-0.50447	-0.82175	-0.43832
H	-1.11031	-1.58742	-0.89601

C	-1.12822	0.36755	0.31577
H	-1.03923	0.18117	1.39699
C	-0.3839	1.67588	0.02176
H	-0.86439	1.87401	-0.93957
C	1.10934	1.97111	-0.09013
H	1.60025	1.76426	0.87286
C	1.85048	1.46219	-1.33949
H	1.40536	1.9216	-2.22242
O	1.74563	0.01503	-1.53291
C	-3.44296	-0.37126	0.35139
H	-3.69457	-0.27238	1.42018
C	-4.66322	-0.17016	-0.51734
C	-4.49396	0.12007	-1.87904
H	-3.4841	0.23784	-2.26819
C	-5.61339	0.26655	-2.69835
H	-5.48051	0.49443	-3.75295
C	-6.90102	0.12253	-2.1728
H	-7.76945	0.23818	-2.81634
C	-7.06891	-0.1643	-0.8173
C	-5.95112	-0.30538	0.00862
O	-0.91024	2.49185	1.05918
C	-2.2065	3.03406	0.79296
O	1.35402	3.30834	-0.49671
C	1.5663	4.2474	0.57933
C	3.34099	1.72907	-1.24761
H	3.8439	1.63795	-2.21401
H	3.49537	2.72575	-0.83323
O	3.90368	0.73917	-0.33722
C	5.27276	1.07506	0.09709
H	-8.06702	-0.2693	-0.39982
H	5.86662	1.28335	-0.79741
H	5.63763	0.15744	0.55725
C	5.28184	2.22388	1.06773
C	4.72268	2.07149	2.34566
C	5.87537	3.44463	0.72352
C	4.75135	3.12498	3.25803
H	4.27093	1.12244	2.62329
C	5.91224	4.49869	1.64011
H	6.32161	3.56718	-0.26078
C	5.34709	4.34065	2.90643
H	4.3183	2.99704	4.24607
H	6.383	5.43834	1.36533
H	5.37336	5.15921	3.62005
O	-2.47043	0.5948	-0.02526

H	-3.05157	-1.3887	0.20296
H	-6.08424	-0.51783	1.06774
H	-2.19028	3.59273	-0.15433
H	-2.92665	2.2138	0.67755
C	-2.6051	3.94822	1.92771
C	-3.36244	5.098	1.67131
C	-2.26287	3.64582	3.25243
C	-3.77855	5.92563	2.71635
H	-3.63158	5.34581	0.64658
C	-2.67036	4.47654	4.29661
H	-1.6665	2.76179	3.45464
C	-3.43202	5.61761	4.03289
H	-4.36646	6.81385	2.50013
H	-2.39434	4.2318	5.31924
H	-3.75016	6.26316	4.84721
C	1.68313	5.62647	-0.01578
C	2.90307	6.08	-0.53336
C	0.56436	6.46581	-0.08296
C	3.00405	7.34599	-1.11072
H	3.77933	5.4382	-0.4739
C	0.66195	7.73405	-0.65759
H	-0.38461	6.1245	0.32404
C	1.88179	8.17552	-1.1743
H	3.95677	7.68779	-1.50697
H	-0.21257	8.37783	-0.69994
H	1.95925	9.16351	-1.62048
H	2.48769	3.97586	1.11524
H	0.72788	4.1915	1.27773
O	-0.06268	-1.79203	0.98647
C	-1.06175	-2.49689	1.73464
H	-1.65227	-3.15014	1.0845
H	-0.56943	-3.09826	2.50303
H	-1.70964	-1.76137	2.2197
Sn	3.39312	-1.39256	-1.09613
Cl	5.44068	-2.38906	-0.37046
Cl	4.48507	-1.1924	-3.21265
Cl	2.32576	-3.2996	-2.06362
Cl	2.50882	-2.20783	0.96917

Thermal correction to Energy= 0.718816

Thermal correction to Enthalpy= 0.719761

Thermal correction to Gibbs Free Energy= 0.578992

Sum of electronic and zero-point Energies= -3651.507872

Sum of electronic and thermal Energies= -3651.461030

Sum of electronic and thermal Enthalpies= -3651.460086

Sum of electronic and thermal Free Energies= -3651.600854

SCF Done: E(RM06) = -3651.47710568

13

Charge = 0 Multiplicity = 1

C	2.0692	2.19754	1.76033
O	-0.07362	-0.00849	-0.89147
C	-0.47625	1.31363	-0.99163
C	0.0836	2.12319	0.17316
C	-0.22328	1.45496	1.53524
C	1.13456	1.08816	2.19536
C	4.30355	3.01939	1.95409
C	-0.23311	1.83077	-2.41563
O	1.71605	-0.10959	1.80333
C	1.06478	-1.31353	2.2777
O	-0.89457	2.37818	2.37723
C	-2.29666	2.09026	2.59735
O	1.58283	2.24178	0.17538
C	2.20783	3.23486	-0.70548
O	-0.97742	0.9263	-3.2374
C	-0.85855	1.16412	-4.6609
C	-1.55372	2.44032	-5.0715
C	-0.88466	3.41096	-5.82505
C	-2.89474	2.65475	-4.71784
C	-1.54342	4.57416	-6.2324
C	-3.54949	3.81948	-5.11542
C	-2.87639	4.781	-5.87606
H	1.76323	3.19669	2.09268
H	-1.56768	1.41581	-0.82569
H	-0.30097	3.14781	0.17319
H	-0.80208	0.54419	1.37535
H	0.99215	1.15481	3.28647
H	4.72665	3.22894	0.96916
H	3.82668	3.91491	2.37003
H	-0.61298	2.85029	-2.56283
H	0.82508	1.77379	-2.69869
H	0.30476	-1.6129	1.54946
H	2.44752	4.11697	-0.09995
H	0.20362	1.16979	-4.93237
H	-1.32469	0.28669	-5.11307
H	0.15509	3.25163	-6.10321
H	-3.41654	1.90407	-4.12996
H	-1.01418	5.31685	-6.82371
H	-4.58903	3.97456	-4.83898
H	-3.391	5.68515	-6.19052

O	3.36054	1.93665	1.85303
Cl	-1.98711	-2.10421	-4.17975
Cl	1.2879	-1.37495	-3.31843
Cl	-3.09809	-0.64187	-1.27259
Cl	-0.63451	-3.25178	-0.88417
Sn	-0.8909	-1.28792	-2.20065
H	5.08862	2.67375	2.62756
H	3.06689	2.82459	-1.19395
C	1.66241	3.87483	-1.99566
C	2.30773	3.65084	-3.21215
C	0.52324	4.6783	-1.94809
C	1.8143	4.23077	-4.38067
H	3.20625	3.01797	-3.2492
C	0.02896	5.25769	-3.11702
H	0.01441	4.85481	-0.98941
C	0.67434	5.03418	-4.33319
H	2.32325	4.05477	-5.33946
H	-0.86948	5.89081	-3.07928
H	0.28544	5.49128	-5.25466
C	-3.03725	2.04653	1.24782
C	-3.96649	1.03717	0.9945
C	-2.77914	3.01605	0.27882
C	-4.63693	0.99702	-0.22784
H	-4.16919	0.27253	1.75836
C	-3.45043	2.9766	-0.94357
H	-2.04692	3.81176	0.47838
C	-4.37911	1.96723	-1.19709
H	-5.36892	0.2011	-0.42783
H	-3.24702	3.74139	-1.70724
H	-4.9079	1.93541	-2.16076
H	-2.45943	1.18402	3.14246
H	-2.64634	2.94147	3.1433
C	0.37885	-1.01764	3.62438
C	0.98259	-0.15544	4.54011
C	-0.84604	-1.6115	3.9286
C	0.36185	0.11226	5.76005
H	1.94864	0.31199	4.30029
C	-1.46757	-1.34305	5.14845
H	-1.32211	-2.29093	3.2069
C	-0.8638	-0.48143	6.06421
H	0.83797	0.79136	6.48215
H	-2.43353	-1.8111	5.38787
H	-1.35307	-0.27017	7.02612
H	1.81105	-2.07144	2.39405

Thermal correction to Energy= 0.718444
Thermal correction to Enthalpy= 0.719388
Thermal correction to Gibbs Free Energy= 0.580582
Sum of electronic and zero-point Energies= -3651.461083
Sum of electronic and thermal Energies= -3651.414173
Sum of electronic and thermal Enthalpies= -3651.413229
Sum of electronic and thermal Free Energies= -3651.552036
SCF Done: E(RM06) = -3651.45413091

14

Charge = 1 Multiplicity = 1

C	1.40569	0.00768	-0.94711
H	1.44891	-1.0179	-1.26833
C	0.14467	0.55091	-0.29821
H	0.28767	0.46237	0.78317
C	-0.0409	2.03985	-0.60086
H	-0.3012	2.1845	-1.65754
C	1.2778	2.75399	-0.28881
H	1.53362	2.58538	0.76325
C	2.40822	2.23157	-1.17907
H	2.22352	2.56342	-2.2045
O	2.41023	0.74852	-1.3008
C	-1.54257	-1.04046	0.31768
H	-1.94893	-0.37904	1.09468
C	-2.62978	-1.87568	-0.30234
C	-2.39815	-3.217	-0.62999
H	-1.43003	-3.66052	-0.40981
C	-3.3998	-3.9848	-1.22715
H	-3.21039	-5.02683	-1.47049
C	-4.64305	-3.41451	-1.50741
H	-5.4246	-4.0119	-1.96944
C	-4.8832	-2.07577	-1.18599
C	-3.88178	-1.31277	-0.58564
O	-1.06901	2.52806	0.23995
C	-2.02461	3.36189	-0.40743
O	1.16906	4.14081	-0.56289
C	1.2383	4.98266	0.60875
C	3.81051	2.70334	-0.77796
H	4.55647	2.06902	-1.27417
H	3.9126	3.71861	-1.17424
O	4.03822	2.80154	0.60922
C	4.46988	1.59452	1.27431
H	-5.85186	-1.63024	-1.39659
H	3.71284	0.8054	1.20078
H	4.53133	1.89545	2.32577

C	5.81014	1.0847	0.78837
C	6.90143	1.95532	0.65299
C	5.97951	-0.27393	0.49378
C	8.14134	1.4757	0.2329
H	6.77	3.01173	0.87429
C	7.22547	-0.7557	0.0824
H	5.13223	-0.94883	0.59397
C	8.30681	0.11639	-0.05062
H	8.98058	2.15928	0.13077
H	7.34706	-1.81261	-0.14022
H	9.27447	-0.25834	-0.37447
O	-0.96029	-0.21423	-0.72056
H	-0.76136	-1.66528	0.76438
H	-4.07002	-0.27294	-0.32792
H	-1.5167	4.19101	-0.91798
H	-2.55492	2.77506	-1.17626
C	-3.0111	3.89997	0.60547
C	-3.83565	4.97655	0.25016
C	-3.14441	3.33392	1.87779
C	-4.78248	5.4724	1.14646
H	-3.73621	5.42923	-0.73464
C	-4.08862	3.83482	2.77741
H	-2.49939	2.50988	2.16179
C	-4.91169	4.90183	2.4153
H	-5.4147	6.30751	0.85645
H	-4.17861	3.38856	3.76436
H	-5.64545	5.28986	3.11657
C	1.0817	6.41551	0.172
C	2.16101	7.10287	-0.39895
C	-0.14621	7.07411	0.30793
C	2.01677	8.42184	-0.82766
H	3.11951	6.59961	-0.50299
C	-0.29324	8.39633	-0.11678
H	-0.99018	6.55055	0.75157
C	0.78749	9.07161	-0.68632
H	2.86243	8.94507	-1.26599
H	-1.25	8.89847	-0.00025
H	0.67507	10.10143	-1.01492
H	2.20571	4.82038	1.1018
H	0.43935	4.70015	1.30463

Thermal correction to Energy= 0.654963

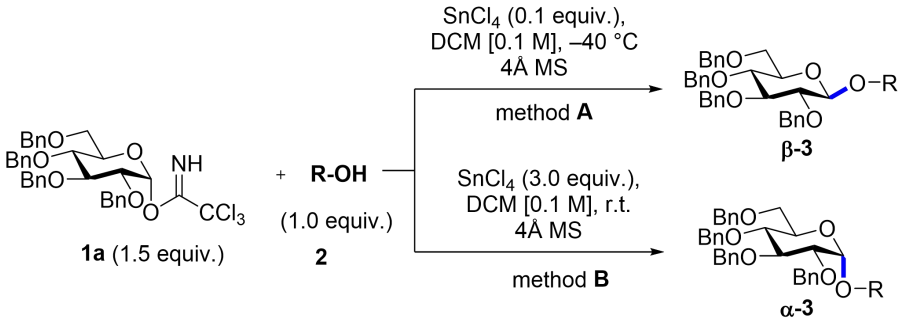
Thermal correction to Enthalpy= 0.655907

Thermal correction to Gibbs Free Energy= 0.541902

Sum of electronic and zero-point Energies= -1691.844062

Sum of electronic and thermal Energies=	-1691.808999
Sum of electronic and thermal Enthalpies=	-1691.808055
Sum of electronic and thermal Free Energies=	-1691.922060
SCF Done: E(RM06) =	-1691.81594352

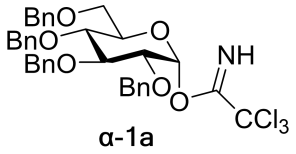
3 General Glycosylation Procedures



General procedure of **Method A**: The trichloroacetimidate donor **1a** and alcohol acceptor **2** were combined in a flask, co-evaporated with toluene (3 × 3 mL) and dissolved in DCM to maintain a concentration of 0.01 M (based on the acceptor). Powdered freshly activated molecular sieves (100 mg/mL solvent) were added, and the mixture was stirred for 30 min under argon at ambient temperature and then cooled to −40 °C. A solution of $SnCl_4$ in DCM (0.10 equiv, 0.1 M solution in DCM) was added dropwise. After stirring for 12 hours at the same temperature, TLC indicated that the reaction was complete and then the reaction was allowed to warm slowly to room temperature. The reaction was quenched by the addition of Et_3N. The suspension was diluted with DCM and filtered through a pad of Celite, and the filtrate washed with saturated $NaHCO_3$ and NaCl aqueous, dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography or simple preparative thin-layer chromatography on silica gel (EtOAc–hexane or EtOAc–toluene or acetone–toluene elution) to afford the β-isomer and a trace amount of N-glucosyl trichloroacetamide.

General procedure of **Method B**: The trichloroacetimidate donor **1a** and alcohol acceptor **2** were combined in a flask, co-evaporated with toluene (3 × 3 mL) and dissolved in DCM to maintain a concentration of 0.01 M (based on acceptor). Powdered freshly activated molecular sieves (100 mg/mL solvent) were added, and the mixture was stirred for 15 min under argon at ambient temperature. Then, a solution of $SnCl_4$ in DCM (3.0 equiv., 0.1 M solution in DCM) was added dropwise at 0 °C. After stirring for 3 hours at ambient temperature, TLC indicated that the reaction was complete, and then the reaction was quenched by the addition of Et_3N. The suspension was diluted with EtOAc and filtered through a pad of Celite, and the filtrate washed with saturated $NaHCO_3$ and NaCl aqueous, dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography or simple preparative thin-layer chromatography on silica gel (EtOAc–hexane or EtOAc–toluene or acetone–toluene elution) to afford pure α-isomer concomitant as major with pure β-isomer as minor.

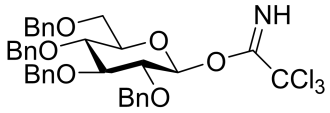
4 NMR data of Compounds



α-1a

2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside trichloroacetimidate **α-1a:**

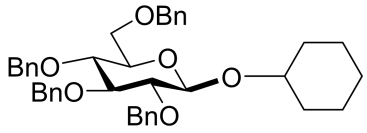
To a magnetically stirred solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (500 mg, 0.9 mmol) and CCl_3CN (0.37 mL, 3.7 mmol, 4 equiv.) in anhydrous CH_2Cl_2 (20 mL), DBU (26 μL, 0.18 mmol, 0.2 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 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, 4:1) to afford compound **α-1a** (600 mg, 97% yield) as a white powder. TLC (hexane–EtOAc, 4:1): R_f = 0.60; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.60 (s, 1H, NH), 7.36–7.16 (m, 20H, ArH), 6.55 (d, 1H, *J* = 3.48Hz, C1^{Glc}-H), 4.98 (d, 1H, *J* = 11.00 Hz, OCH_2Ph), 4.89–4.83 (m, 2H, OCH_2Ph), 4.77 (d, 1H, *J* = 11.56 Hz, OCH_2Ph), 4.70 (d, 1H, *J* = 11.36 Hz, OCH_2Ph), 4.62 (d, 1H, *J* = 12.04 Hz, OCH_2Ph), 4.55 (d, 1H, *J* = 10.72 Hz, OCH_2Ph), 4.49 (d, 1H, *J* = 12.04 Hz, OCH_2Ph), 4.07 (t, 1H, *J* = 9.36 Hz, C3^{Glc}-H), 4.02–4.00 (m, 1H, C5^{Glc}-H), 3.83–3.77 (m, 3H, C4^{Glc}-H, C6^{Glc}-H and C2^{Glc}-H), 3.69 (dd, 1H, *J* = 1.92, 10.76 Hz, C6^{Glc}-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 162.3, 138.3, 137.9, 137.8, 128.6, 128.5, 127.9, 92.5, 77.5, 77.1, 77.0, 76.8, 76.6, 75.6, 73.7, 73.0, 72.0; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{36}H_{36}Cl_3NNaO_6$ 706.1506, found 706.1509.



β-1a

2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside trichloroacetimidate **β-1a:**

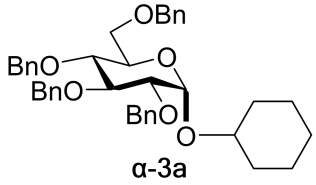
To a magnetically stirred solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (60 mg, 0.12 mmol) and CCl_3CN (0.15 mL, 1.44 mmol, 13.0 equiv.) in anhydrous CH_2Cl_2 (2.0 mL), K_2CO_3 (77.0 mg, 0.55 mmol, 5.0 equiv.) was added at room temperature, and the reaction mixture was stirred at the same temperature for overnight, 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, 5:1) to afford compound **β-1a** (71.3 mg, 87% yield) as a white powder. TLC (hexane–EtOAc, 4:1): R_f = 0.60, $[\alpha]_D^{21}$ = +18.6 (*c* = 0.66, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (s, 1H, NH), 7.33–7.15 (m, 20H, ArH), 5.80 (d, 1H, *J* = 6.80 Hz, C1^{Glc}-H), 4.94 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.91 (d, 1H, *J* = 11.20 Hz, OCH_2Ph), 4.83–4.74 (m, 3H, OCH_2Ph), 4.62 (d, 1H, *J* = 12.40 Hz, OCH_2Ph), 4.57 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.53 (d, 1H, *J* = 12.40 Hz, OCH_2Ph), 3.76–3.61 (m, 6H, C3^{Glc}-H, C5^{Glc}-H, C4^{Glc}-H, C6^{Glc}-H, C6^{Glc}-H and C2^{Glc}-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 161.2, 138.4, 138.1, 138.0, 137.9, 128.4, 128.3, 128.0, 127.9, 128.8, 127.7, 127.6, 100.0, 98.4 (C1^{Glc}), 91.0, 84.6, 80.9, 77.4, 77.3, 77.0, 76.7, 75.9, 75.6, 75.0, 75.9, 73.3, 68.2, 29.7; HRMS (ESI) m/z [M+Na]+ calcd for $C_{36}H_{36}Cl_3NNaO_6$ 706.1506, found 706.1512.



β-3a

Cyclohexanol 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside **β-3a:**

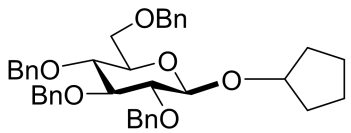
Following the general procedure of Method **A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (4.87 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3a** (24 mg, 80% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +16.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.09 (m, 20H, ArH), 4.92 (d, 1H, *J* = 10.88 Hz, OCH_2Ph), 4.85 (d, 1H, *J* = 10.96 Hz, OCH_2Ph), 4.72 (dd, 2H, *J* = 10.88, 16.24 Hz, OCH_2Ph), 4.64 (d, 1H, *J* = 10.92 Hz, OCH_2Ph), 4.52–4.45 (m, 3H, OCH_2Ph), 4.43 (d, 1H, *J* = 7.8Hz, $C1^{Glc1}$-H) , 3.69–3.61 (m, 2H, $C6^{Glc1}$-H and OCH) , 3.60–3.54 (m, 2H, $C3^{Glc1}$-H and $C6^{Glc1}$-H), 3.50–3.45 (m, 1H, $C4^{Glc1}$-H), 3.40–3.35 (m, 2H, $C2^{Glc1}$-H and $C5^{Glc1}$-H), 1.96–1.16 (m, 10H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.6, 138.3, 138.2, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 101.9 ($C1^{Glc1}$), 84.9, 82.3, 77.4, 77.0, 76.7, 74.8, 73.4, 69.2, 58.4, 33.8, 32.0, 29.7, 25.7, 24.1, 24.0, 18.4; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{40}H_{46}O_6Na$ 645.3192, found 645.3199.



α-3a

Cyclohexanol 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **α-3a:**

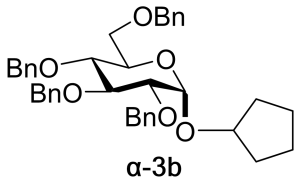
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (4.87 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3a** (23 mg, 76% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +31.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.25 (m, 20H, ArH), 4.99 (d, 1H, *J* = 10.88 Hz, OCH_2Ph), 4.96 (d, 1H, *J* = 3.68 Hz, $C1^{Glc1}$-H), 4.84–4.79 (m, 2H, OCH_2Ph), 4.74 (d, 1H, *J* = 12.08 Hz, OCH_2Ph), 4.65 (d, 1H, *J* = 11.96 Hz, OCH_2Ph), 4.61 (d, 1H, *J* = 12.16 Hz, OCH_2Ph), 4.48 (d, 1H, *J* = 2.40 Hz, OCH_2Ph), 4.45 (d, 1H, *J* = 3.84 Hz, OCH_2Ph), 4.00 (t, 1H, *J* = 9.28 Hz, $C3^{Glc1}$-H), 3.89–3.86(m, 1H, OCH_2), 3.75–3.70 (m, 1H, $C6^{Glc1}$-H), 3.64–3.60 (m, 2H, $C6^{Glc1}$-H and $C5^{Glc1}$-H), 3.57–3.53 (m, 2H, $C4^{Glc1}$-H and $C2^{Glc1}$-H), 1.86–1.33 (m, 10H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.4, 138.3, 138.1, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 94.7 ($C1^{Glc1}$), 82.1, 80.0, 78.0, 77.3, 77.0, 76.7, 75.6, 75.4, 75.1, 74.8, 73.5, 73.0, 70.1, 68.7, 33.4, 31.5, 29.7, 25.6, 24.5, 24.2; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{40}H_{46}O_6Na$ 645.3192, found 645.3199.



β-3b

Cyclopentanol 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside **β-3b:**

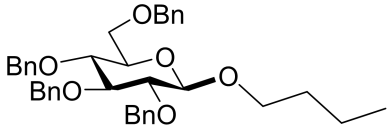
Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **2b** (4.19 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3b** (24 mg, 80% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +28.3 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.26–7.08 (m, 20H, ArH), 4.85 (dd, 1H, *J* = 5.36, 10.92 Hz, O$\underline{CH_2}$Ph), 4.83 (d, 1H, *J* = 9.96 Hz, O$\underline{CH_2}$Ph), 4.74 (d, 1H, *J* = 10.84 Hz, O$\underline{CH_2}$Ph), 4.70 (d, 1H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.62 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.55–4.45 (m, 3H, O$\underline{CH_2}$Ph), 4.35 (d, 1H, *J* = 7.84 Hz, $C1^{Glc1}$-H), 4.31–4.29 (m, 1H, O$\underline{CH_2}$), 3.67 (dd, 1H, *J* = 1.76, 10.76 Hz, $C6^{Glc1}$-H), 3.61–3.54 (m, 2H, $C6^{Glc1}$-H and $C3^{Glc1}$-H), 3.47 (t, 1H, *J* = 9.56 Hz, $C4^{Glc1}$-H), 3.40–3.32 (m, 2H, $C5^{Glc1}$-H and $C2^{Glc1}$-H),1.81–1.45 (m, 8H, $\underline{CH_2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.6, 138.3, 138.2, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 102.1, 84.9, 82.3, 81.0, 78.0, 77.4, 77.0, 76.7, 75.7, 75.0, 74.9, 74.8, 73.5, 69.2, 33.6, 32.1, 29.7, 23.7, 23.4; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{39}H_{44}O_6Na$ 631.3036, found 631.3041.



α-3b

Cyclopentanol 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **α-3b:**

Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **3b** (4.19 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3b** (17mg, 61% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +110.1 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.12 (m, 20H, ArH), 4.99 (d, 1H, *J* =10.88 Hz, O$\underline{CH_2}$Ph), 4.86 (d, 1H, *J* = 3.64 Hz, $C1^{Glc1}$-H), 4.82 (d, 1H, *J* = 9.96 Hz, O$\underline{CH_2}$Ph), 4.77 (d, 1H, *J* = 12.76 Hz, O$\underline{CH_2}$Ph), 4.74 (d, 1H, *J* = 12.04 Hz, O$\underline{CH_2}$Ph), 4.65–4.57 (m, 3H, O$\underline{CH_2}$Ph), 4.47 (d, 1H, *J* = 11.60 Hz, O$\underline{CH_2}$Ph), 4.15–4.14 (m, 1H, O$\underline{CH_2}$), 3.97 (t, 1H, *J* = 9.28 Hz, $C3^{Glc1}$-H), 3.83–3.80 (m, 1H, $C6^{Glc1}$-H), 3.74 (dd, 1H, *J* = 3.60, 10.52 Hz, $C6^{Glc1}$-H), 3.64–3.61 (m, 2H, $C5^{Glc1}$-H and $C4^{Glc1}$-H), 3.54 (dd, 1H, *J* = 3.68, 9.60 Hz, $C2^{Glc1}$-H), 1.74–1.33(m, 8H, $\underline{CH_2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.4, 138.3, 138.1, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 95.6 ($C1^{Glc1}$), 82.1, 80.2, 79.0, 78.0, 77.9, 77.4, 77.0, 76.7, 75.6, 75.1, 75.0, 73.5, 73.0, 70.1, 68.7, 32.9, 31.7, 29.7, 23.5, 23.3; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{39}H_{44}O_6Na$ 631.3036, 631.3041.

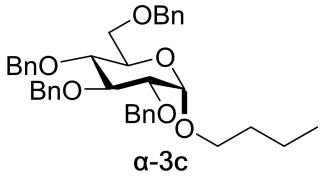


β-3c

n-Butanol 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside **β-3c:**

Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor n-butanol **2c** (3.61 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3c** (20 mg, 69% yield) as a white solid (eluent, Toluene–acetonitrile 15:1). $[\alpha]_D^{21}$ = +23.0 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.08 (m, 20H, ArH), 4.87 (t, 2H, *J* = 9.4 Hz, O$\underline{CH_2}$Ph), 4.74 (d, 1H, *J* = 8.64 Hz, O$\underline{CH_2}$Ph), 4.71(d, 1H, *J* = 8.76Hz, O$\underline{CH_2}$Ph), 4.64 (d, 1H, *J* = 8.79 Hz, O$\underline{CH_2}$Ph), 4.54 (d, 1H, *J* = 9.76 Hz, O$\underline{CH_2}$Ph), 4.50–4.44 (m, 2H, O$\underline{CH_2}$Ph), 4.31 (d, 1H, *J* = 6.24Hz, $C1^{Glc1}$-H), 3.92–3.87 (m, 1H, OCH_2), 3.67 (d, 1H, *J* = 8.44 Hz, $C6^{Glc1}$-H), 3.61–3.55 (m, 2H, $C6^{Glc1}$-H and $C3^{Glc1}$-H), 3.52–3.45(m, 2H, $C5^{Glc1}$-H and OCH_2), 3.40–3.36 (m, 2H, $C4^{Glc1}$-H and

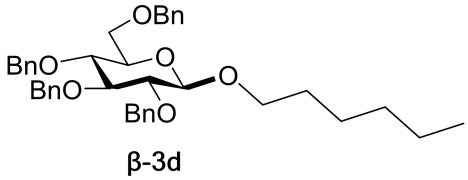
C2^{Glc1}-H), 1.61–1.54 (m, 2H, CH_2), 1.39–1.33 (m, 2H, CH_2), 0.86 (t, 3H, *J* = 5.88 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.5, 138.2, 138.1, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 103.7 (C1^{Glc1}), 84.8, 82.3, 78.0, 77.0, 76.8, 75.7, 75.0, 74.9, 74.8, 73.5, 69.8, 69.1, 33.5, 31.9, 31.8, 29.7, 29.4, 29.3, 29.1, 24.8, 22.7, 19.3, 14.1, 13.9; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{38}H_{44}O_6Na$ 619.3036, found 619.3038.



α-3c

n-Butanol 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **α-3c:**

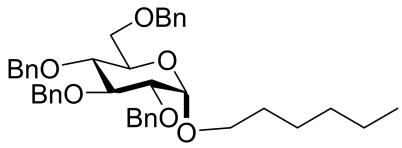
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor n-butanol **2c** (3.61 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3c** (23 mg, 77% yield) as a white solid (eluent, Toluene–acetonitrile 15:1. $[\alpha]_D^{21}$ = +204.2 (*c* = 0.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.13 (m, 20H, ArCH), 4.99 (d, 1H, *J* = 10.88 Hz, O<u>CH$_2$</u>Ph), 4.84–4.79 (m, 3H, O<u>CH$_2$</u>Ph), 4.75 (d, 1H, *J* = 2.44 Hz, C1^{Glc1}-H), 4.62 (dd, 2H, *J* = 12.12, 16.40 Hz, O<u>CH$_2$</u>Ph), 4.48–4.45 (m, 2H, O<u>CH$_2$</u>Ph), 3.98 (t, 1H, *J* = 9.28 Hz, C3^{Glc1}-H), 3.79–3.76 (m, 1H, OCH_2), 3.72 (dd, 1H, *J* = 3.76, 10.56 Hz, C6^{Glc1}-H), 3.66–3.60 (m, 3H, C6^{Glc1}-H, C4^{Glc1}-H and OCH_2), 3.55 (dd, 1H, *J* = 3.64, 9.64 Hz, C2^{Glc1}-H), 3.45–3.39 (m, 1H, C5^{Glc1}-H), 1.63–1.58 (m, 2H, CH_2), 1.42–1.33 (m, 2H, CH_2), 0.91 (t, 3H, *J* = 7.36Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.4, 138.3, 138.0, 128.4, 128.3, 128.2, 128.1, 127.9, 129.0, 127.8, 127.7, 127.5, 96.9 (C1^{Glc1}), 82.1, 80.2, 77.8, 77.4, 77.0, 76.7, 75.7, 75.1, 73.5, 73.1, 70.1, 68.6, 67.9, 31.9, 31.5, 29.7, 29.4, 22.7, 19.4, 14.1, 13.9; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{38}H_{44}O_6Na$ 619.3036, found 619.3038.



β-3d

n-Hexanol 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside **β-3d:**

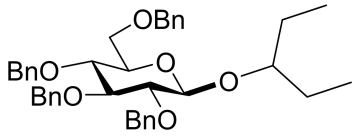
Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **3d** (4.97 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3d** (24 mg, 81% yield) as a white solid (eluent, Toluene–Ethyl acetate 30:1). $[\alpha]_D^{21}$ = –1.2 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.08 (m, 20H, ArH), 4.87 (t, 2H, *J* = 10.92 Hz, O<u>CH$_2$</u>Ph), 4.76–4.70 (m, 2H, O<u>CH$_2$</u>Ph), 4.64 (d, 1H, *J* = 10.96 Hz, O<u>CH$_2$</u>Ph), 4.56–4.41 (m, 3H, O<u>CH$_2$</u>Ph), 4.31 (d, 1H, *J* = 7.80Hz, C1^{Glc1}-H), 3.92–3.86 (m, 1H, OCH_2), 3.68–3.66 (m, 1H, C6^{Glc1}-H) , 3.62–3.43(m, 4H, C6^{Glc1}-H, C3^{Glc1}-H, C5^{Glc1}-H and OCH_2), 3.41–3.35 (m, 2H, C4^{Glc1}-H and C2^{Glc1}-H), 1.62–1.53 (m, 4H, CH_2), 1.35–1.22 (m, 4H, CH_2), 0.81 (t, 3H, *J* = 6.80 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.6, 138.3, 138.2, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 103.7 (C1^{Glc1}), 84.8, 82.3, 78.0, 77.3, 77.0, 76.7, 75.7, 75.0, 74.9, 74.8, 73.5, 70.2, 69.1, 31.7, 29.8, 29.7, 25.9, 22.6, 14.1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{40}H_{48}O_6Na$ 647.3349, found 647.3355.



α-3d

n-Hexanol 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **α-3d:**

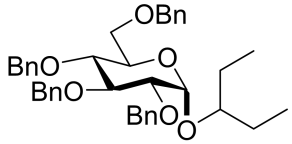
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **3d** (4.97 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3d** (24 mg, 80% yield) as a white solid (eluent, Toluene–Ethyl acetate 30:1). $[\alpha]_D^{21}$ = +27.0 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.12 (m, 20H, ArH), 5.00 (d, 1H, *J* = 10.88 Hz, O$\underline{CH_2}$Ph), 4.84–4.76 (m, 3H, O$\underline{CH_2}$Ph), 4.75 (d, 1H, *J* = 3.72 Hz, $C1^{Glc}$-H), 4.64 (d, 1H, *J* = 12.12 Hz, O$\underline{CH_2}$Ph), 4.60 (d, 1H, *J* = 12.12 Hz, O$\underline{CH_2}$Ph), 4.46 (d, 2H, *J* = 11.52 Hz, O$\underline{CH_2}$Ph), 3.99 (d, 1H, *J* = 9.24Hz, $C3^{Glc}$-H), 3.79–3.76 (m, 1H, OCH_2), 3.72 (dd, 1H, *J* = 3.60, 10.48 Hz, $C6^{Glc}$-H), 3.65–3.59 (m, 3H, OCH_2, $C4^{Glc}$-H and $C6^{Glc}$-H), 3.55 (dd, 1H, *J* = 3.68, 9.68 Hz, $C2^{Glc}$-H), 3.46–3.39 (m, 1H, $C5^{Glc}$-H), 1.65–1.56 (m, 4H, CH_2), 1.35–1.25 (m, 4H, CH_2), 0.88 (t, 3H, *J* = 6.72 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 140.0, 138.7, 138.6, 138.3, 138.2, 138.1, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 103.7, 96.9, 84.8, 82.3, 82.1, 80.2, 80.0, 78.00, 77.8, 77.4, 77.0, 76.7, 75.7, 75.1, 75.0, 74.9, 74.8, 73.5, 73.1, 70.2, 70.1, 69.1, 68.6, 68.3, 31.7, 29.8, 29.4, 25.9, 22.6, 22.5; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{40}H_{48}O_6Na$ 647.3349, found 647.3355.



β-3e

Isoamyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside **β-3e:**

Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **3e** (4.29 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3e** (25 mg, 82% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +24.9 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.26–7.13 (m, 20H, ArH), 4.91 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.85 (d, 1H, *J* = 10.86 Hz, O$\underline{CH_2}$Ph), 4.73 (dd, 2H, *J* = 13.64, 2.76 Hz, O$\underline{CH_2}$Ph), 4.64 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.56–4.48 (m, 3H, O$\underline{CH_2}$Ph), 4.37 (d, 1H, *J* = 7.76 Hz, $C1^{Glc1}$-H), 3.68–3.64 (m, 1H, $C6^{Glc1}$-H), 3.62–3.57 (m, 2H, $C6^{Glc1}$-H and $C3^{Glc1}$-H), 3.54–3.47 (m, 2H, OCH_2 and $C5^{Glc1}$-H) , 3.39–3.35(m, 2H, $C4^{Glc1}$-H and $C2^{Glc1}$-H), 1.59–1.50 (m, 4H, CH_2), 0.91–0.79 (m, 6H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.8, 138.6, 138.5, 138.2, 128.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.5, 102.6 ($C1^{Glc1}$), 85.0, 82.5, 82.0, 78.1, 77.3, 77.0, 76.7, 75.7, 75.0, 74.9, 73.5, 69.2, 29.7, 27.0, 26.0, 9.7, 9.5; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{39}H_{46}O_6Na$ 633.3192, found 633.3199.

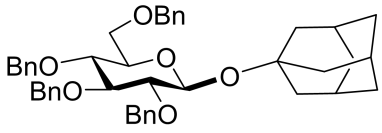


α-3e

Isoamyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **α-3e:**

Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **3e** (4.29 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 4 hours

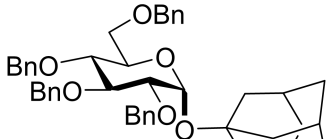
afforded **α-3e** (24 mg, 80% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +19.4 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.06 (m, 20H, ArH), 4.91 (d, 1H, *J* = 10.88 Hz, O$\underline{CH_2}$Ph), 4.89 (d, 1H, *J* = 3.64 Hz, C1^{Glc1}-H), 4.76 (d, 1H, *J* = 7.48 Hz, O$\underline{CH_2}$Ph), 4.73 (d, 1H, *J* = 7.68 Hz, O$\underline{CH_2}$Ph), 4.64–4.62 (m, 2H, O$\underline{CH_2}$Ph), 4.54 (d, 1H, *J* = 12.08 Hz, O$\underline{CH_2}$Ph), 4.42–4.37 (m, 2H, O$\underline{CH_2}$Ph), 3.92 (t, 1H, *J* = 9.32 Hz, C3^{Glc1}-H), 3.84–3.82 (m, 1H, OCH$_2$), 3.66 (dd, 1H, *J* = 3.56, 10.52 Hz, C6^{Glc1}-H), 3.58–3.54 (m, 2H, C6^{Glc1}-H and C4^{Glc1}-H), 3.51–3.47 (m, 1H, C2^{Glc1}-H), 3.44–3.35 (m, 1H, C5^{Glc1}-H), 1.59–1.44 (m, 4H, CH$_2$), 0.91–0.81 (m, 6H, CH$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.4, 138.3, 138.1, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 95.6, 82.1, 80.2, 78.0, 77.3, 77.0, 76.7, 75.1, 73.2,70.4, 68.6, 29.7, 26.6, 26.0, 25.1, 10.2, 9.2; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{39}H_{46}O_6Na$ 633.3192, found 633.3199.



β-3f

Adamantyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside **β-3f:**

Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor 1-admantanol **2f** (7.46 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3f** (29 mg, 88% yield) as a white solid (eluent, Toluene–Ethyl acetate 30:1). $[\alpha]_D^{21}$ = –21.6 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.29–7.11 (m, 20H, ArH), 4.93 (d, 1H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.83 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.74 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.69 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.64 (d, 1H, *J* = 7.32 Hz, C1^{Glc1}-H), 4.61 (d, 1H, *J* = 4.16 Hz, O$\underline{CH_2}$Ph), 4.53–4.45 (m, 3H, O$\underline{CH_2}$Ph), 3.65 (dd, 1H, *J* = 1.56, 10.84 Hz, C6^{Glc1}-H), 3.59–3.52 (m, 2H, C4^{Glc1}-H and C6^{Glc1}-H), 3.46–3.34 (m, 3H, C3^{Glc1}-H, C2^{Glc1}-H and C5^{Glc1}-H), 2.07 (s, 3H, CH$_3$), 1.88–1.75 (m, 6H, CH$_3$), 1.59–1.52 (m, 6H, CH$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.6, 138.4, 138.2, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 96.3 (C1^{Glc1}), 85.2, 82.4, 78.3, 77.4, 77.1, 76.7, 75.7, 75.3, 75.0, 74.6, 73.4, 69.6, 42.8, 36.3, 30.7, 30.7, 29.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{44}H_{50}O_6Na$ 697.3505, found 697.3508.

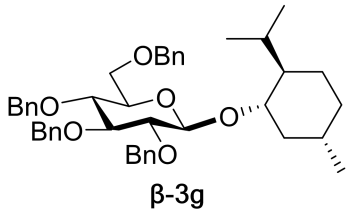


α-3f

Adamantyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **α-3f:**

Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor 1-admantanol **2f** (7.46 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3f** (26 mg, 80% yield) as a white solid (eluent, Toluene–Ethyl acetate 30:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.30 (m, 20H, ArH), 5.29 (d, 1H, *J* = 4.12 Hz, C1^{Glc1}-H), 5.00 (d, 1H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.83 (t, 2H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.69–4.63 (m, 3H, O$\underline{CH_2}$Ph), 4.48–4.44 (m, 2H, O$\underline{CH_2}$Ph), 4.05–4.00 (m, 2H, C3^{Glc1}-H and C5^{Glc1}-H), 3.76 (dd, 1H, *J* = 3.68, 6.88 Hz, C6^{Glc1}-H), 3.69–3.60 (m, 2H, C4^{Glc1}-H and C6^{Glc1}-H), 3.54 (dd, 1H, *J* = 3.68, 10.00 Hz, C2^{Glc1}-H), 2.14 (s, 3H, CH$_3$), 1.88–1.83 (m, 6H, CH$_3$), 1.62–1.59 (m, 6H, CH$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.2, 138.5, 138.4, 128.5, 128.4, 128.0, 89.9 (C1^{Glc1}), 82.2, 80.2, 78.2, 77.5, 77.1, 76.8, 74.7, 69.7,

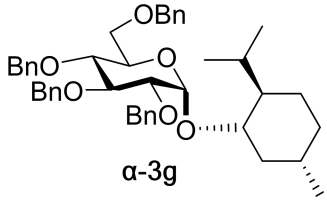
69.7, 68.8, 42.5, 36.4, 30.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{44}H_{50}O_6Na$ 697.3505, found 697.3508.



β-3g

(L)-Menthyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside **β-3g:**

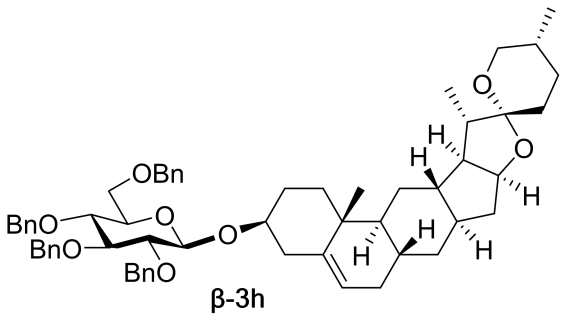
Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor (L)-menthyl **3g** (7.60 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3g** (27 mg, 82% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = –15.5 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.11 (m, 20H, ArH), 4.86 (t, 2H, *J* = 10.68 Hz, O$\underline{CH_2}$Ph), 4.73 (t, 2H, *J* = 11.24 Hz, O$\underline{CH_2}$Ph), 4.61 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.55–4.45 (m, 3H, O$\underline{CH_2}$Ph), 4.40 (d, 1H, *J* = 7.80 Hz, $C1^{Glc1}$-H), 3.63–3.58 (m, 2H, $C5^{Glc1}$-H and $C6^{Glc1}$-H), 3.56–3.50 (m, 2H, $C3^{Glc1}$-H and $C6^{Glc1}$-H), 3.46–3.40 (m, 1H, OCH), 3.56–3.32 (m, 2H, $C2^{Glc1}$-H and $C4^{Glc1}$-H), 2.29–2.26 (m, 1H, CH_2), 2.06 (d, 1H, *J* = 9.00 Hz, CH_2), 1.60–1.57 (m, 3H, CH_2), 0.86–0.74 (m, 13H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 128.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.6, 100.9 ($C1^{Glc1}$), 82.4, 78.1, 77.5, 77.2, 76.8, 75.7, 75.1, 75.0, 73.8, 48.3, 31.6, 29.9, 22.4, 21.2, 16.1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{44}H_{54}O_6Na$ 701.3818, found 701.3826.



α-3g

(L)-Menthyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside **α-3g:**

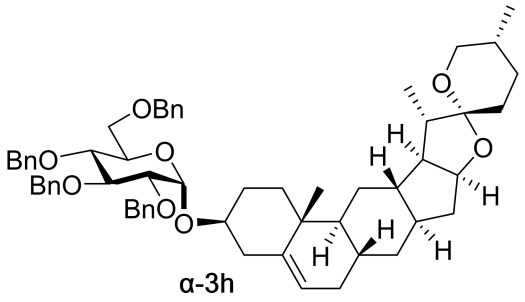
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor (L)-menthyl **3g** (7.60 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3g** (53 mg, 81% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +31.5 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33–7.14 (m, 20H, ArH), 5.02 (d, 1H, *J* = 3.68 Hz, $C1^{Glc1}$-H), 4.98 (d, 1H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.84 (d, 1H, *J* = 5.96 Hz, O$\underline{CH_2}$Ph), 4.82 (d, 1H, *J* = 5.96 Hz, O$\underline{CH_2}$Ph), 4.73–4.63 (m, 3H, O$\underline{CH_2}$Ph), 4.49–4.44 (m, 2H, O$\underline{CH_2}$Ph), 4.04–3.96 (m, 2H, $C3^{Glc1}$-H and $C5^{Glc1}$-H), 3.75 (dd, 1H, *J* = 4.12, 10.56 Hz, $C6^{Glc1}$-H), 3.66–3.61 (m, 2H, $C4^{Glc1}$-H and $C6^{Glc1}$-H), 3.56–3.53 (m, 1H, $C2^{Glc1}$-H), 3.39–3.32 (m, 1H, OCH), 2.45–2.39 (m, 1H, CH_2), 2.12 (d, 1H, *J* = 12.35 Hz, CH_2), 1.63–1.57 (m, 3H, CH_2), 1.38–1.26 (m, 2H, CH_2), 1.08–0.97 (m, 7H, CH_3), 0.72–0.70 (d, 3H, *J* = 6.88 Hz, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.4, 138.1, 128.5, 128.0, 127.7, 98.7 ($C1^{Glc1}$), 82.1, 81.1, 80.6, 78.2, 77.5, 77.1, 76.8, 70.4, 68.7, 48.9, 43.2, 34.4, 31.8, 24.7, 23.0, 22.4, 21.2, 16.2; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{44}H_{54}O_6Na$ 701.3818, found 701.3826.



β-3h

3-*O*-[2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside]diosgenin **β-3h:**

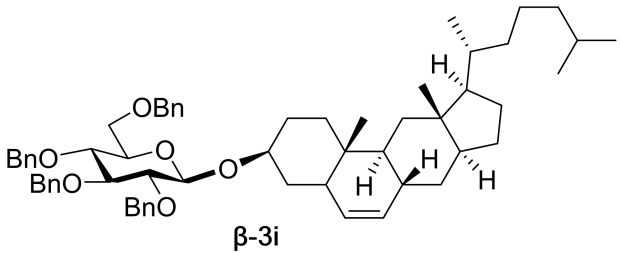
Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor diosgenin **2h** (20.3 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3h** (28 mg, 60% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = –11.2 (*c* = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29–7.09 (m, 20H, ArH), 5.26 (d, 1H, *J* = 4.72 Hz, CH=C<u>H</u>$_2$), 4.90 (d, 1H, *J* = 10.88 Hz, OC<u>H</u>$_2$Ph), 4.85 (d, 1H, *J* = 10.92 Hz, OC<u>H</u>$_2$Ph), 4.75–4.63 (m, 3H, OC<u>H</u>$_2$Ph), 4.52–4.45 (m, 3H, OC<u>H</u>$_2$Ph), 4.42 (d, 1H, *J* = 7.84 Hz, C1^{Glc1}-H), 4.39–4.31 (m, 1H, OCH), 3.67–3.64 (m, 1H, C6^{Glc1}-H), 3.59–3.45 (m, 4H, C6^{Glc1}-H, C3^{Glc1}-H, C5^{Glc1}-H and OCH), 3.41–3.28 (m, 4H, C4^{Glc1}-H, C2^{Glc1}-H, OCH and OCH), 2.36–0.71 (m, 34H, diosgeninyl); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 140.6, 138.7, 138.5, 138.3, 138.1, 128.4, 128.3, 128.0, 127.9, 127.7, 121.6, 109.3, 102.2 (C1^{Glc1}), 84.8, 82.4, 80.8, 79.6, 78.0, 77.3, 77.0, 76.7, 75.7, 75.0, 74.8, 73.4, 69.2, 66.9, 62.1, 56.5, 50.1, 41.6, 40.3, 39.8, 39.1, 37.3, 36.9, 31.5, 31.4, 30.3, 29.7, 28.8, 20.9, 19.5, 17.2, 16.3, 14.5; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{60}H_{74}O_8Na$ 945.5281, found 945.5288.



α-3h

3-*O*-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside]diosgenin **α-3h:**

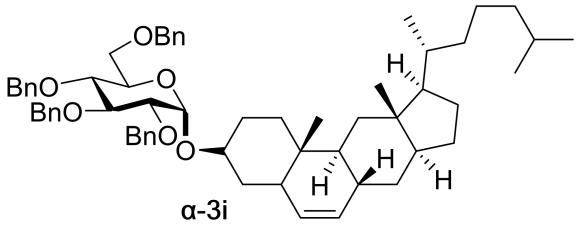
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor diosgenin **2h** (18.8 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3h** (38 mg, 85% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.13 (m, 20H, ArH), 5.28 (d, 1H, *J* = 5.04 Hz, CH=C<u>H</u>$_2$), 5.01 (d, 1H, *J* = 11.00 Hz, OC<u>H</u>$_2$Ph), 4.93 (d, 1H, *J* = 3.68 Hz, C1^{Glc1}-H), 4.85–4.76 (m, 3H, OC<u>H</u>$_2$Ph), 4.63 (dd, 2H, *J* = 3.68, 12.36 Hz, OC<u>H</u>$_2$Ph), 4.48–4.39 (m, 3H, OC<u>H</u>$_2$Ph and OCH), 4.00 (t, 1H, *J* = 9.60 Hz, C3^{Glc1}-H), 3.88 (d, 1H, *J* = 10.08 Hz, C5^{Glc1}-H), 3.74 (dd, 1H, *J* = 3.64, 6.88 Hz, C6^{Glc1}-H), 3.66–3.61 (m, 2H, C6^{Glc1}-H and C4^{Glc1}-H), 3.55 (dd, 1H, *J* = 3.68, 9.64 Hz, C2^{Glc1}-H), 3.50–3.35 (m, 3H, OCH), 2.42–0.75 (m, 34H, diosgeninyl); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 141.0, 139.0, 138.4, 138.0, 128.5, 128.4, 128.0, 121.6,109.4, 94.7 (C1^{Glc1}), 82.2, 80.9, 80.0, 78.0, 77.5, 77.1, 76.8, 76.5, 73.5, 70.1, 66.9, 62.2, 56.6, 50.1, 41.7, 40.4, 39.9, 39.9, 37.0, 32.0, 31.5, 30.4, 28.9, 27.5, 20.9, 19.5, 17.3, 16.4, 14.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{60}H_{74}O_8Na$ 945.5281, found 945.5288.



β-3i

3-*O*-[2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside]cholesterol **β-3i:**

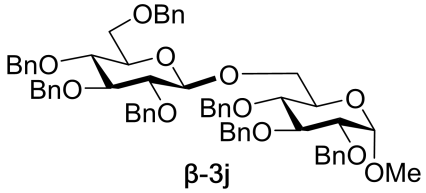
Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor cholesterol **2i** (18.8 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **β-3i** (34 mg, 76% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = –20.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29–7.09 (m, 20H, ArH), 5.28–5.22 (m, 1H, CH=C$\underline{H_2}$), 4.90 (d, 1H, *J* = 10.88 Hz, OC$\underline{H_2}$Ph), 4.85 (d, 1H, *J* = 10.96 Hz, OC$\underline{H_2}$Ph), 4.77–4.63 (m, 3H, OC$\underline{H_2}$Ph), 4.55–4.44 (m, 3H, OC$\underline{H_2}$Ph), 4.40 (d, 1H, *J* = 9.48 Hz, C1^{Glc1}-H), 3.67–3.65 (m, 1H, C6^{Glc1}-H), 3.59–3.45 (m, 4H, C3^{Glc1}-H, C6^{Glc1}-H, C5^{Glc1}-H and OCH), 3.39–3.35 (m, 2H, C4^{Glc1}-H and C2^{Glc1}-H), 2.35-0.79 (m, 43H, cholesteryl); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 140.6, 138.7, 138.6, 138.3, 138.2, 128.4, 128.3, 128.0, 127.9, 127.7, 121.9, 102.3 (C1^{Glc1}), 84.9, 82.4, 79.7, 78.0, 77.4, 77.0, 76.7, 74.7, 75.0, 75.0, 74.8, 73.4, 69.2, 56.8, 56.2, 50.2, 42.4, 39.8, 39.6, 36.8, 35.8, 32.0, 31.9, 30.0, 29.7, 28.3, 28.0, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.8, 11.9; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{61}H_{80}O_6Na$ 931.5853, found 931.5860.



α-3i

3-*O*-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside]cholesterol **α-3i:**

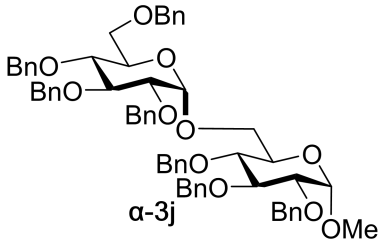
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor cholesterol **2i** (20.3 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3i** (38 mg, 82% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.15 (m, 20H, ArH), 5.29 (d, 1H, *J* = 5.08 Hz, CH=C$\underline{H_2}$), 5.01 (d, 1H, *J* = 11.00 Hz, OC$\underline{H_2}$Ph), 4.94 (d, 1H, *J* = 3.68 Hz, C1^{Glc1}-H), 4.85–4.76 (m, 3H, OC$\underline{H_2}$Ph), 4.64 (dd, 2H, *J* = 12.36, 16.04 Hz, OC$\underline{H_2}$Ph), 4.46 (dd, 2H, *J* = 4.60, 11.00 Hz, OC$\underline{H_2}$Ph), 4.01 (t, 1H, *J* = 9.64 Hz, C3^{Glc1}-H), 3.88 (d, 1H, *J* = 10.08 Hz, C5^{Glc1}-H), 3.74 (dd, 1H, *J* = 3.68, 11.00 Hz, C6^{Glc1}-H), 3.67–3.62 (m, 2H, C6^{Glc1}-H and C4^{Glc1}-H), 3.56 (dd, 1H, *J* = 3.68, 9.64 Hz, C2^{Glc1}-H), 3.51–3.45 (m, 1H, OCH), 2.47–0.68 (m, 43H, cholesteryl); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 140.9, 139.0, 138.4, 138.1, 128.6, 128.5, 128.0, 121.8, 94.7 (C1^{Glc1}), 82.2, 80.0, 78.0, 77.5, 77.1, 76.8, 76.6, 73.5, 73.2, 70.1, 56.9, 56.2, 50.2, 42.4, 40.0, 39.6, 36.9, 35.9, 32.0, 31.9, 28.4, 28.1, 23.9, 23.0, 22.7, 19.5, 18.8, 12.0; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{61}H_{80}O_6Na$ 931.5853, found 931.5860.



β-3j

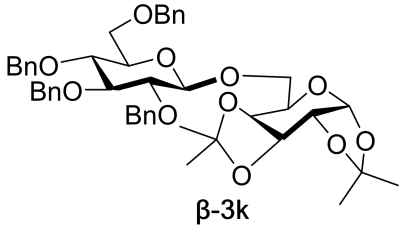
Methyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **β-3j:**

Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **2j** (22.6 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **α-3j** (40 mg, 83% yield) as a white solid (eluent, Toluene–Ethyl acetate 50:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.15 (m, 35H, ArH), 4.97 (d, 1H, *J* = 3.20 Hz, O$\underline{CH_2}$Ph), 4.95 (d, 1H, *J* = 2.76 Hz, O$\underline{CH_2}$Ph), 4.90 (d, 1H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.82–4.49 (m, 12H, O$\underline{CH_2}$Ph and C1^{Glc1}-H), 4.34 (d, 1H, *J* = 7.80 Hz, C1^{Glc2}-H), 4.22–4.16 (m, 1H, C6^{Glc2}-H), 3.99 (t, 1H, *J* = 9.16 Hz, C3^{Glc1}-H), 3.84–3.81 (m, 1H, C6^{Glc1}-H), 3.73–3.48 (m, 8H, C4^{Glc2}-H, C3^{Glc2}-H, C5^{Glc2}-H, C6^{Glc2}-H, C6^{Glc1}-H, C4^{Glc1}-H, C2^{Glc1}-H and C3^{Glc1}-H), 3.44–3.41 (m, 1H, C2^{Glc2}-H), 3.32 (s, 3H, OMe); ^{13}C{^{1}H} ($CDCl_3$, 400 MHz): δ 138.9, 138.6, 138.5, 138.3, 138.2, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 103.9 (C1^{Glc2}), 98.1 (C1^{Glc1}), 84.9, 82.2, 82.1, 79.8, 78.1, 78.0, 77.4, 77.1, 76.8, 75.8, 75.1, 75.0, 73.5, 73.5, 69.9, 69.1, 68.6, 55.3; HRMS (ESI) m/z [M+Na]$^{+}$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.4503, found 1009.4510.



Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside-(1 → 6) -2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **α-3j:**

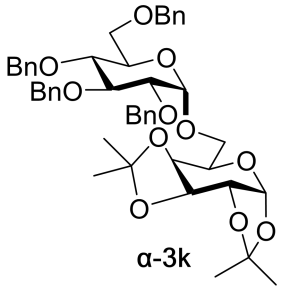
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **2j** (22.6 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3j** (43 mg, 90% yield) as a white solid (eluent, Toluene–Ethyl acetate 50:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29–7.10 (m, 35H, ArH), 4.98 (d, 1H, *J* = 2.28 Hz, C1^{Glc1}-H), 4.95–4.90 (m, 3H, O$\underline{CH_2}$Ph), 4.84–4.78 (m, 3H, O$\underline{CH_2}$Ph), 4.75–4.56 (m, 6H, O$\underline{CH_2}$Ph), 4.55 (d, 1H, *J* = 4.12 Hz, C1^{Glc2}-H), 4.43 (t, 2H, *J* = 11.92 Hz, O$\underline{CH_2}$Ph), 3.99 (d, 1H, *J* = 9.64 Hz, C3^{Glc2}-H), 3.94 (d, 1H, *J* = 9.64 Hz, C3^{Glc1}-H), 3.83–3.60 (m, 7H, C6^{Glc1}-H, C5^{Glc1}-H, C5^{Glc2}-H, C6^{Glc2}-H, C6^{Glc2}-H, C6^{Glc1}-H and C4^{Glc2}-H), 3.56–3.52 (m, 2H, C4^{Glc1}-H and C2^{Glc1}-H), 3.44 (dd, 1H, *J* = 3.68, 10.08 Hz, C2^{Glc2}-H), 3.35 (s, 3H, OMe); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.9, 138.5, 138.3, 138.1, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 127.8, 127.7, 98.0 (C1^{Glc1}), 97.4 (C1^{Glc2}), 82.2, 81.8, 80.2, 80.1, 77.9, 77.7, 77.4, 77.1, 76.8, 75.8, 75.6, 75.1, 75.0, 73.5, 72.5, 70.4, 70.3, 68.5, 66.1, 55.3; HRMS (ESI) m/z [M+Na]$^{+}$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.4503, found 1009.4510.



2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **β-3k:**

Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **2k** (12.7 mg, 0.049 mmol) in DCM (4.90 mL) at –40 °C for 12 hours afforded

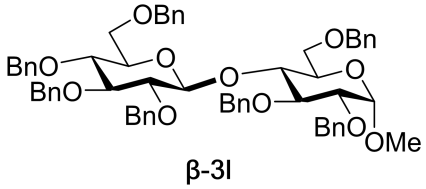
β-3k (30 mg, 79% yield) as a white solid (eluent: Toluene–acetone 15:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.05 (m, 20H, ArH), 5.49 (d, 1H, *J* = 5.00 Hz, C1^{Gal2}-H), 4.98 (d, 1H, *J* = 11.16 Hz, O$\underline{CH_2}$Ph), 4.87 (d, 1H, *J* = 10.96 Hz, O$\underline{CH_2}$Ph), 4.71 (dd, 2H, *J* = 10.08, 14.00 Hz, O$\underline{CH_2}$Ph), 4.64 (d, 1H, *J* = 11.12 Hz, O$\underline{CH_2}$Ph), 4.52–4.42 (m, 4H, C3^{Gal2}-H and O$\underline{CH_2}$Ph) , 4.38 (d, 1H, *J* = 7.76 Hz, C1^{Glc1}-H), 4.24 (dd, 1H, *J* = 2.36, 4.96 Hz, C2^{Gal2}-H), 4.17 (dd, 1H, *J* = 1.64, 7.92 Hz, C4^{Gal2}-H), 4.09–4.04 (m, 2H, C5^{Gal2}-H and C6^{Gal2}-H), 3.68–3.51 (m, 5H, C6^{Glc1}-H, C6^{Glc1}-H, C6^{Gal2}-H, C5^{Glc1}-H and C3^{Glc1}-H), 3.41–3.37 (m, 2H, C4^{Glc1}-H and C2^{Glc1}-H), 1.43 (s, 3H, Me), 1.38 (s, 3H, Me), 1.24 (s, 3H, Me), 1.19 (s, 3H, Me); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.2, 128.6, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 109.4, 104.4 (C1^{Glc1}), 96.4 (C1^{Gal2}), 84.6, 81.7, 77.8, 77.3, 77.0, 76.7, 75.7, 75.0, 74.8, 74.4, 73.5, 71.5, 70.8, 70.5, 69.7, 68.8, 67.4, 29.7, 26.1, 26.0, 25.0, 24.5; HRMS (ESI) m/z [M+Na]$^{+}$ calcd for $C_{46}H_{54}O_{11}Na$ 805.3564, found 805.3567.



α-3k

2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **α-3k:**

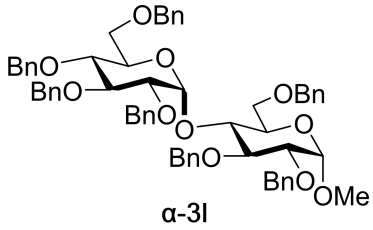
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **3k** (12.7 mg, 0.049 mmol) in DCM (4.90 mL) at at room temperature for 3 hours afforded **α-3k** (26 mg, 68% yield) as a white solid, (eluent: Toluene–acetone 15:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.12 (m, 20H, ArH), 5.52 (d, 1H, *J* = 5.20 Hz, C1^{Gal1}-H), 5.00 (d, 1H, *J* = 3.44 Hz, C1^{Glc2}-H), 4.98 (d, 1H, *J* = 10.76 Hz, O$\underline{CH_2}$Ph), 4.82 (d, 1H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.80 (d, 1H, *J* = 11.44 Hz, O$\underline{CH_2}$Ph), 4.72 (q, 2H, *J* = 11.92 Hz, O$\underline{CH_2}$Ph), 4.63 (d, 1H, *J* = 12.40 Hz, O$\underline{CH_2}$Ph), 4.60 (dd, 1H, *J* = 2.32, 10.08 Hz, C3^{Gal1}-H), 4.48 (d, 1H, *J* = 10.96 Hz, O$\underline{CH_2}$Ph), 4.46 (d, 1H, *J* = 12.36 Hz, O$\underline{CH_2}$Ph), 4.36 (dd, 1H, *J* = 1.84, 7.80 Hz, C4^{Gal1}-H), 4.32 (dd, 1H, *J* = 2.28, 5.04 Hz, C2^{Gal1}-H), 4.06–4.02 (m, 1H, C5^{Gal1}-H), 3.99 (t, 1H, *J* = 9.64 Hz, C3^{Glc2}-H), 3.84–3.79 (m, 1H, C3^{Glc2}-H), 3.78–3.74 (m, 3H, C6^{Glc2}-H, C6^{Gal1}-H and C6^{Gal1}-H), 3.72–3.63 (m, 2H, C6^{Glc2}-H and C4^{Glc2}-H), 3.58 (dd, 1H, *J* = 3.68, 9.60 Hz, C2^{Glc2}-H), 1.53 (s, 3H, Me), 1.45 (s, 3H, Me), 1.33 (s, 3H, Me), 1.32 (s, 3H, Me); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.4, 138.1, 128.5, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 109.3, 108.7, 97.1 (C1^{Glc2}), 96.4 (C1^{Gal1}), 82.1, 79.9, 77.7, 77.4, 75.7, 75.1, 73.6, 72.5, 70.9, 70.8, 70.7, 70.3, 68.4, 66.3, 65.8, 26.3, 26.2, 25.0, 25.0; HRMS (ESI) m/z [M+Na]$^{+}$ calcd for $C_{46}H_{54}O_{11}Na$ 805.3564, found 805.3567.



β-3l

Methyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside-(1 → 4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **β-3l:**

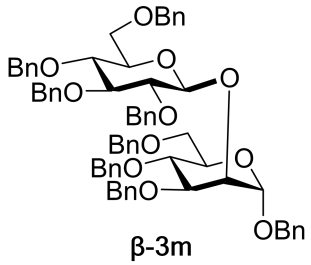
Following the general procedure of **Method A** using trichloroacetimidate **1a** (65 mg, 0.095 mmol, 1.5 equiv.) and acceptor **3l** (29.4 mg, 0.063 mmol) in DCM (6.30 mL) at –40 °C for 12 hours afforded **β-3l** (38 mg, 71% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +79.6 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.26–7.09 (m, 35H, ArH), 4.89 (dd, 2H, *J* = 3.88, 11.04 Hz, O$\underline{CH_2}$Ph), 4.83 (d, 1H, *J* = 10.96 Hz, O$\underline{CH_2}$Ph), 4.74–4.63 (m, 6H, O$\underline{CH_2}$Ph), 4.57 (d, 1H, *J* = 12.12 Hz, O$\underline{CH_2}$Ph), 4.53 (d, 1H, *J* = 3.12 Hz, $C1^{Glc2}$-H), 4.50–4.42 (m, 4H, O$\underline{CH_2}$Ph), 4.27 (d, 1H, *J* = 7.76 Hz, $C1^{Glc1}$-H), 4.11–4.09 (m, 1H, $C6^{Glc2}$-H), 3.92 (t, 1H, *J* = 9.28 Hz, $C3^{Glc2}$-H), 3.77–3.74 (m, 1H, $C3^{Glc1}$-H), 3.86–3.81 (m, 5H, $C6^{Glc1}$-H, $C6^{Glc2}$-H , $C5^{Glc2}$-H, $C4^{Glc1}$-H and $C6^{Glc1}$-H), 3.46–3.39 (m, 3H, $C2^{Glc2}$-H, $C4^{Glc2}$-H and $C2^{Glc1}$-H), 3.37–3.34 (m, 1H, $C5^{Glc1}$-H), 3.25 (s, 3H, OMe); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.9, 138.6, 138.4, 138.3, 138.2, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 103.8 ($C1^{Glc1}$), 98.1 ($C1^{Glc1}$), 84.8, 82.1, 79.8, 78.0, 77.9, 77.3, 77.0, 76.7, 75.7, 75.1, 75.0, 74.9, 73.5, 73.4, 69.9, 55.2, 29.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.4503, found 1009.4509.



α-3l

Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside-(1 → 4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **α-3l:**

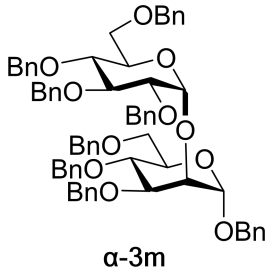
Following the general procedure of **Method B** using trichloroacetimidate **1a** (65 mg, 0.095 mmol, 1.5 equiv.) and acceptor **3l** (29.4 mg, 0.063 mmol) in DCM (6.30 mL) at room temperature for 3 hours afforded **α-3l** (37 mg, 63% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32–7.08 (m, 35H, ArH), 5.69 (d, 1H, *J* = 3.68 Hz, $C1^{Glc2}$-H), 5.03 (d, 1H, *J* = 11.32 Hz, O$\underline{CH_2}$Ph), 4.88 (d, 1H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.82–4.76 (m, 3H, O$\underline{CH_2}$Ph), 4.70 (d, 1H, *J* = 12.36 Hz, O$\underline{CH_2}$Ph), 4.60 (d, 1H, *J* = 3.68 Hz, $C1^{Glc1}$-H), 4.58–4.49 (m, 6H, O$\underline{CH_2}$Ph), 4.42 (d, 1H, *J* = 11.44 Hz, O$\underline{CH_2}$Ph), 4.27 (d, 1H, *J* = 12.84 Hz, O$\underline{CH_2}$Ph), 4.11–4.02 (m, 2H, $C3^{Glc1}$-H and $C4^{Glc1}$-H), 3.90 (t, 1H, *J* = 8.72 Hz, $C3^{Glc2}$-H), 3.86–3.81 (m, 2H, $C5^{Glc1}$-H and $C6^{Glc1}$-H), 3.72–3.62 (m, 3H, $C6^{Glc1}$-H, $C4^{Glc2}$-H and $C5^{Glc2}$-H), 3.59 (dd, 1H, *J* = 3.64, 9.16 Hz, $C2^{Glc1}$-H), 3.51–3.47 (m, 2H, $C2^{Glc2}$-H and $C6^{Glc2}$-H), 3.39 (dd, 1H, *J* = 1.84, 11.00 Hz, $C6^{Glc1}$-H), 3.37 (s, 3H, OMe),; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.1, 138.9, 138.6, 138.3, 138.1, 138.0, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.9, 97.9 ($C1^{Glc1}$), 96.7 ($C1^{Glc1}$), 82.1, 80.3, 79.6, 77.7, 77.4, 75.6, 75.0, 74.5, 73.6, 73.5, 73.3, 73.2, 72.4, 71.1, 69.6, 69.1, 68.3, 55.2; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{62}H_{66}O_{11}Na$ 1009.4503, found 1009.4509.



β-3m

Benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside-(1 → 2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside **β-3m:**

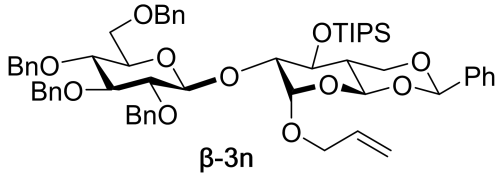
Following the general procedure of **Method A** using trichloroacetimidate **1a** (65 mg, 0.095 mmol, 1.5 equiv.) and acceptor **2m** (34 mg, 0.063 mmol) in DCM (6.30 mL) at –40 °C for 12 hours afforded **β-3m** (17 mg, 55% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +31.0 (*c* = 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.06 (m, 40H, ArH), 5.09 (d, 1H, *J* = 10.16 Hz, O$\underline{CH_2}$Ph), 5.01 (s, 1H, C1^{Glc1}-H), 4.88–4.83 (m, 3H, O$\underline{CH_2}$Ph), 4.74–4.65 (m, 3H, O$\underline{CH_2}$Ph), 4.45–4.41 (m, 5H, O$\underline{CH_2}$Ph), 4.36 (d, 1H, *J* = 2.04 Hz, C1^{Man2}-H), 4.38–4.36 (m, 2H, O$\underline{CH_2}$Ph), 4.33 (d, 2H, *J* = 3.00 Hz, O$\underline{CH_2}$Ph), 4.23–4.22 (m, 1H, C2^{Glc1}-H), 3.98 (t, 1H, *J* = 9.28 Hz, C4^{Glc1}-H), 3.92 (dd, 1H, *J* = 3.20, 9.36 Hz, C3^{Glc1}-H), 3.77–3.74 (m, 1H, C5^{Glc1}-H), 3.67 (dd, 1H, *J* = 4.60, 10.52 Hz, C6^{Glc1}-H), 3.66–3.40 (m, 7H, C6^{Glc1}-H, C6^{Man2}-H, C6^{Man2}-H, C4^{Man2}-H, C5^{Man2}-H, C2^{Man2}-H and C3^{Man2}-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 129.2, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.3, 103.0 (C1^{Glc1}), 97.6 (C1^{Man2}), 84.7, 81.5, 77.3, 77.0, 76.7, 75.0, 73.3, 29.5; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{68}H_{70}O_{11}Na$ 1085.4816, found 1085.4822.



α-3m

Benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside-(1 → 2)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside **α-3m:**

Following the general procedure of **Method B** using trichloroacetimidate **1a** (65 mg, 0.095 mmol, 1.5 equiv.) and acceptor **2m** (34 mg, 0.063 mmol) in DCM (6.30 mL) at room temperature for 3 hours afforded **α-3m** (17 mg, 51% yield) as a white solid (eluent, Toluene–Ethyl acetate 15:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.09 (m, 40H, ArH), 5.44 (d, 1H, *J* = 3.64 Hz, C1^{Glc2}-H), 4.92 (d, 1H, *J* = 1.84 Hz, C1^{Man1}-H), 4.88 (d, 1H, *J* = 11.00 Hz, O$\underline{CH_2}$Ph), 4.82–4.51 (m, 10H, O$\underline{CH_2}$Ph), 4.45–4.40 (m, 4H, O$\underline{CH_2}$Ph), 4.35 (d, 1H, *J* = 11.44 Hz, O$\underline{CH_2}$Ph), 4.21 (t, 1H, *J* = 2.28 Hz, C2^{Man1}-H), 4.07 (t, 1H, *J* = 9.64 Hz, C4^{Man1}-H), 4.01–3.96 (m, 2H, C3^{Man1}-H and C3^{Glc2}-H), 3.83–3.77 (m, 3H, C5^{Man1}-H, C6^{Man1}-H and C6^{Glc2}-H), 3.73–3.69 (m, 1H, C6^{Man1}-H), 3.63 (dd, 1H, *J* = 4.12, 11.00 Hz, C6^{Glc2}-H), 3.59 (t, 1H, *J* = 9.64 Hz, C4^{Glc2}-H), 3.53 (dd, 1H, *J* = 3.64, 10.08 Hz, C2^{Glc2}-H), 3.48 (dd, 1H, *J* = 1.64, 9.16 Hz, C5^{Glc2}-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 139.1, 138.7, 138.6, 138.5, 138.2, 138.0, 137.4, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.3, 98.3 (C1^{Glc2}), 97.3 (C1^{Man1}), 81.6, 80.6, 79.8, 77.3, 77.1, 75.6, 75.2, 75.1, 73.6, 73.5, 73.2, 73.1, 72.8, 71.8, 70.7, 69.5, 69.0, 68.5; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{68}H_{70}O_{11}Na$ 1085.4816, found 1085.4822.

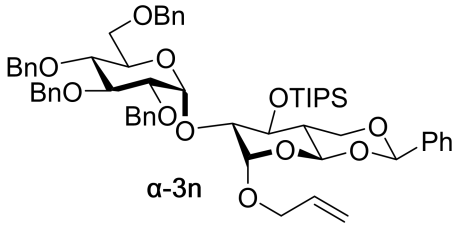


β-3n

Benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1→2)-4,6-*O*-benzylidene-3-*O*-TIBS-α-D-gluco pyranoside **β-3n:**

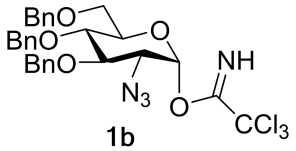
Following the general procedure of **Method A** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **2n** (23 mg, 0.049 mmol) in DCM (4.90 mL) at –40 °C for 12 hours afforded **β-3n** (26 mg, 54% yield) as a white solid (eluent, N-hexane–Ethyl acetate 6:1). $[\alpha]_D^{21}$ = +28.5 (*c* = 1.0,

$CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.48–7.18 (m, 25H, ArH), 6.01–5.91 (m, 1H, $OCH_2\underline{CH}=CH_2$), 5.43 (s, 1H, ArCH), 5.40 (dd, 1H, *J* = 1.40, 17.44 Hz, $OCH_2CH=\underline{CH_2}$), 5.18 (dd, 1H, *J* = 0.88, 11.44 Hz, $OCH_2CH=\underline{CH_2}$), 5.05 (d, 1H, *J* = 10.48 Hz, $O\underline{CH_2}Ph$), 5.04 (d, 1H, *J* = 2.96 Hz, $C1^{Glc1}$-H), 4.94 (d, 1H, *J* = 10.48 Hz, $O\underline{CH_2}Ph$), 4.82 (d, 1H, *J* = 7.56 Hz, $C1^{Glc2}$-H), 4.81–4.75 (m, 3H, $O\underline{CH_2}CH$), 4.64–4.53 (m, 3H, $O\underline{CH_2}CH$), 4.36 (t, 1H, *J* = 9.16Hz, $C3^{Glc1}$-H), 4.30–4.22 (m, 2H, $C5^{Glc2}$-H and $O\underline{CH_2}CH$), 4.09 (dd, 1H, *J* = 5.12, 13.40 Hz, $C6^{Glc2}$-H), 3.98–3.87 (m, 2H, $C2^{Glc1}$-H and $O\underline{CH_2}CH$), 3.77–3.68 (m, 3H, $C6^{Glc2}$-H, $C6^{Glc1}$-H and $C3^{Glc2}$-H), 3.64–3.60 (m, 2H, $C6^{Glc1}$-H and $C4^{Glc2}$-H), 3.50–3.41 (m, 3H, $C5^{Glc1}$-H, $C4^{Glc1}$-H and $C2^{Glc2}$-H), 1.09–0.92 (m, 21H, TIPIS); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ138.2, 134.2, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 126.4, 104.2, 102.3, 98.2, 81.7, 77.9, 77.3, 77.0, 76.7, 75.4, 74.9, 48.2, 18.1, 13.2; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{59}H_{74}NaO_{11}Si$ 1009.4898, found 1009.4905.



Benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (1→2)-4,6-*O*-benzylidene-3-O-TIBS-α-D-gluco pyranoside **α-3n:**

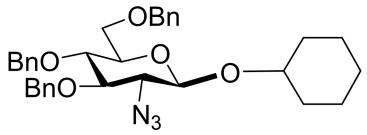
Following the general procedure of **Method B** using trichloroacetimidate **1a** (50 mg, 0.073 mmol, 1.5 equiv.) and acceptor **2n** (23 mg, 0.049 mmol) in DCM (4.90 mL) at room temperature for 3 hours afforded **α-3n** (24 mg, 51% yield) as a white solid (eluent, hexane–Ethyl acetate 6:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47–7.16 (m, 25H, ArH), 5.93–5.84 (m, 1H, $OCH_2\underline{CH}=CH_2$), 5.43 (s, 1H, ArCH), 5.31 (dd, 1H, *J* = 1.40, 17.44 Hz, $OCH_2CH=\underline{CH_2}$), 5.21 (d, 1H, *J* = 3.68 Hz, $C1^{Glc1}$-H), 5.17 (d, 1H, *J* = 3.68 Hz, $C1^{Glc2}$-H), 5.15 (dd, 1H, *J* = 0.88, 11.44 Hz, $OCH_2CH=\underline{CH_2}$), 4.89 (d, 1H, *J* = 11.00 Hz, $O\underline{CH_2}Ph$), 4.87 (d, 1H, *J* = 11.32 Hz, $O\underline{CH_2}Ph$), 4.78 (d, 1H, *J* = 11.92 Hz, $O\underline{CH_2}Ph$), 4.71 (d, 1H, *J* = 11.00 Hz, $O\underline{CH_2}Ph$), 4.61 (d, 1H, *J* = 12.36 Hz, $O\underline{CH_2}Ph$), 4.59 (d, 1H, *J* = 11.92 Hz, $O\underline{CH_2}Ph$), 4.49 (d, 1H, *J* = 11.00 Hz, $O\underline{CH_2}Ph$), 4.46 (d, 1H, *J* = 12.36 Hz, $O\underline{CH_2}Ph$), 4.38 (t, 1H, *J* = 9.16Hz, $C3^{Glc1}$-H), 4.26–4.19 (m, 2H, $C6^{Glc1}$-H and $O\underline{CH_2}CH$), 4.11 (t, 1H, *J* = 9.16Hz, $C3^{Glc2}$-H), 4.02–3.96 (m, 2H, $C6^{Glc2}$-H and $O\underline{CH_2}CH$), 3.90–3.84 (m, 1H, $C5^{Glc1}$-H), 3.74–3.64 (m, 5H, $C4^{Glc2}$-H, $C6^{Glc1}$-H, $C6^{Glc2}$-H $C2^{Glc1}$-H and $C5^{Glc2}$-H), 3.62 (dd, 1H, *J* = 3.68, 9.60 Hz, $C2^{Glc2}$-H), 3.41 (t, 1H, *J* = 9.04Hz, $C4^{Glc1}$-H), 1.15–0.95 (m, 21H, TIPIS); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.9, 138.6, 138.1, 137.3, 133.5, 129.2, 128.4, 128.30, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.3, 127.2, 126.5, 118.4, 102.5, 95.2 ($C1^{Glc1}$), 92.6 ($C1^{Glc2}$), 82.7, 82.0, 79.4, 77.4, 75.8, 74.7, 73.6, 71.7, 71.2, 70.5, 69.2, 68.5, 68.3, 62.5, 18.3, 18.2, 13.3; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{59}H_{74}NaO_{11}Si$ 1009.4898, found 1009.4905.



2-azide-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside trichloroacetimidate **1b:**

To a magnetically stirred solution of 2-azide-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (103.4 mg, 0.22 mmol) and CCl_3CN (0.22 mL, 2.2 mmol, 10.0 equiv.) in anhydrous CH_2Cl_2 (5 mL), DBU (15.3 μL, 0.11 mmol, 0.5 equiv.) was added dropwise at 0 °C, and the reaction mixture was

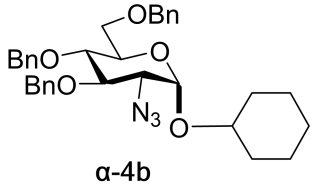
stirred at the same temperature for 3 h, after which complete consumption of starting materials was observed. The reaction mixture was concentrated and purified by flash chromatography on silica gel (preconditioned with Et_3N; eluent: toluene–EtOAc, 12:1) to afford compound **1b** (133 mg, 99% yield) as a white powder. TLC (toluene–EtOAc, 12:1): R_f = 0.60, $[\alpha]_D^{21}$ = +61.4 (*c* = 0.53, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.70 (s, 1H, NH), 7.40–7.14 (m, 15H, ArH), 6.44 (d, 1H, *J* = 3.60Hz, $C1^{Glc}$-H), 4.94 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.89 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.82 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.62 (d, 1H, *J* = 11.60 Hz, OCH_2Ph), 4.57 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.47 (d, 1H, *J* = 11.60 Hz, OCH_2Ph), 4.06–3.97 (m, 2H, $C3^{Glc}$-H and $C5^{Glc}$-H), 3.88 (t, 1H, *J* = 9.20 Hz, $C4^{Glc}$-H), 3.80 (dd, 1H, *J* = 3.20, 11.20 Hz, $C6^{Glc}$-H), 3.71–3.65 (m, 2H, $C6^{Glc}$-H and $C2^{Glc}$-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 160.8, 137.7, 137.6, 128.5, 128.4, 128.0, 127.9, 127.8, 95.0 ($C1^{Glc}$), 90.9, 80.1, 77.8, 77.3, 77.0, 76.7, 75.5, 75.3, 73.6, 67.8, 63.1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{29}H_{29}Cl_3N_4NaO_5$ 641.1101, found 641.1108.



β-4b

Cyclohexanol 2-azide-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside **β-4b:**

Following the general procedure of Method **A** using trichloroacetimidate **1b** (50 mg, 0.081 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (4.87 mg, 0.048 mmol) in DCM (4.80 mL) at –40°C temperature for 12 hours afforded **α/β-4b** (18.7 mg, 70% yield, α/β=9/91) as a white solid (eluent, Toluene–Ethyl acetate 30:1). $[\alpha]_D^{21}$ = +2.12 (*c* = 1.29, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.16 (m, 15H, ArH), 4.88 (d, 1H, *J* = 11.24 Hz, O$\underline{CH_2}$Ph), 4.80 (d, 1H, *J* = 10.36 Hz, O$\underline{CH_2}$Ph), 4.78 (d, 1H, *J* = 10.28 Hz, O$\underline{CH_2}$Ph), 4.62–4.53 (m, 3H, O$\underline{CH_2}$Ph), 4.38 (d, 1H, *J* = 7.72 Hz, $C1^{Glc1}$-H), 3.73–3.64 (m, 3H, $C6^{Glc1}$-H, $C6^{Glc1}$-H and $C4^{Glc1}$-H), 3.57 (t, 1H, *J* = 8.92 Hz, $C3^{Glc1}$-H), 3.44–3.36 (m, 3H, $C5^{Glc1}$-H, $C2^{Glc1}$-H and CHO), 1.98–1.23 (m, 10H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.2, 138.1, 137.9, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 100.6 ($C1^{Glc1}$), 83.2, 78.0, 77.8, 77.4, 77.3, 77.2, 77.1, 77.0, 76.7, 75.5, 75.1, 75.0, 73.5, 68.9, 66.5, 33.6, 31.7, 25.6, 23.9, 23.8; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{33}H_{39}N_3O_5Na$ 580.2787, found 580.2769.

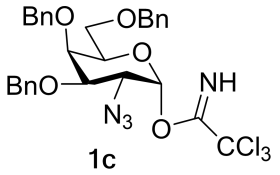


α-4b

Cyclohexanol 2-azide-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside **α-4b:**

Following the general procedure of Method **B** using trichloroacetimidate **1b** (50 mg, 0.081 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (5.39 mg, 0.048 mmol) in DCM (4.80 mL) at room temperature for 3 hours afforded **α-4b** (21.7 mg, 81% yield) as a white solid (eluent, Toluene–Ethyl acetate 30:1); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.39–7.14 (m, 15H, ArH), 5.07 (d, 1H, *J* = 3.64 Hz, $C1^{Glc1}$-H), 4.89 (d, 1H, *J* = 10.68 Hz, OCH_2Ph), 4.86 (d, 1H, *J* = 10.72 Hz, OCH_2Ph), 4.80 (d, 1H, *J* = 10.72 Hz, OCH_2Ph), 4.63 (d, 1H, *J* = 12.04 Hz, OCH_2Ph), 4.52–4.47 (m, 2H, OCH_2Ph), 4.03 (dd, 1H, *J* = 8.76, 10.28 Hz, $C6^{Glc1}$-H), 3.95–3.91 (m, 1H, $C3^{Glc1}$-H), 3.79–3.59 (m, 4H, $C4^{Glc1}$-H, $C5^{Glc1}$-H, $C6^{Glc1}$-H and OCH), 3.28 (dd, 1H, *J* = 3.60, 10.24 Hz,

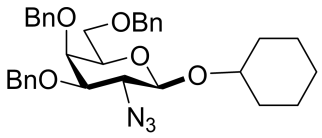
C2^{Glc1}-H), 1.92–1.21 (m, 10H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.1, 138.0, 137.9, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 96.3 (C1^{Glc1}), 80.1, 78.5, 77.3, 77.0, 76.7, 76.4, 75.3, 75.1, 73.5, 70.7, 68.4, 63.29, 33.3, 33.4, 29.7, 25.6, 24.1, 23.8; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{33}H_{39}N_3O_5Na$ 580.2787, found 580.2759.



1c

2-azide-3,4,6-tri-*O*-benzyl-α-D-galactose-pyranoside trichloroacetimidate **1c:**

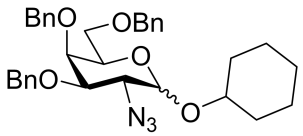
To a magnetically stirred solution of 2-azide-3,4,6-tri-*O*-benzyl-α-D-galactose-pyranoside (117.7 mg, 0.25 mmol) and CCl_3CN (0.25 mL, 2.5 mmol, 10.0 equiv.) in anhydrous CH_2Cl_2 (5 mL), DBU (17.5 µL, 0.12 mmol, 0.5 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same 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, 4:1) to afford compound **1c** (144.3 mg, 97% yield) as a white powder. TLC (hexane–EtOAc, 4:1): R_f = 0.60, $[\alpha]_D^{21}$ = +66.0 (*c* = 0.36, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.65 (s, 1H, NH), 7.43–7.23 (m, 15H, ArH), 6.38 (d, 1H, *J* = 3.60 Hz, C1^{Gal}-H), 4.91 (d, 1H, *J* = 11.20 Hz, OCH_2Ph), 4.79 (d, 1H, *J* = 11.20 Hz, OCH_2Ph), 4.69 (d, 1H, *J* = 11.20 Hz, OCH_2Ph), 4.57 (d, 1H, *J* = 11.20 Hz, OCH_2Ph), 4.48 (d, 1H, *J* = 11.60 Hz, OCH_2Ph), 4.42 (d, 1H, *J* = 11.60 Hz, OCH_2Ph), 4.20–4.13 (m, 3H, C2^{Gal}-H, C6^{Gal}-H and C4^{Gal}-H), 4.03 (dd, 1H, *J* = 2.40, 10.40 Hz, C3^{Gal}-H), 3.68–3.64 (m, 1H, C5^{Gal}-H), 3.58–3.54 (m, 1H, C6^{Gal}-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 160.8, 138.1, 137.7, 137.2, 128.6, 128.4, 128.3, 128.0, 127.9, 127.8, 95.5 (C1^{Gal}), 91.1, 77.3, 77.2, 77.0, 76.7, 75.0, 73.6, 72.8, 72.2, 72.1, 68.0, 59.2, 29.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{29}H_{29}Cl_3N_4NaO_5$ 641.1101, found 641.1120.



β-4c

Cyclohexanol 2-azide-3,4,6-tri-*O*-benzyl-β-D-galactose-pyranoside **β-4c:**

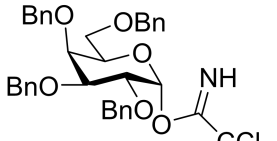
Following the general procedure of Method **A** using trichloroacetimidate **1c** (54.7 mg, 0.088 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (5.89 mg, 0.059 mmol) in DCM (5.90 mL) at –40°C temperature for 12 hours afforded **α/β-4c** (23.7 mg, 72% yield, α/β=10:90) as a white solid (eluent, Toluene–Ethyl acetate 30:1). $[\alpha]_D^{21}$ = –1.33 (*c* = 0.86, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40–7.25 (m, 15H, ArH), 4.88 (d, 1H, *J* = 11.24 Hz, O<u>CH</u>$_2$Ph), 4.67 (s, 2H, O<u>CH</u>$_2$Ph), 4.59 (d, 1H, *J* = 12.00 Hz, O<u>CH</u>$_2$Ph), 4.46–4.40 (m, 2H, O<u>CH</u>$_2$Ph), 4.31 (d, 1H, *J* = 8.00 Hz, C1^{Gal} -H), 3.85–3.78 (m, 2H, C4^{Gal}-H and C2^{Gal}-H), 3.69–3.55 (m, 4H, OCH, C5^{Gal}-H, C6^{Gal}-H and C6^{Gal}-H), 3.26 (dd, 1H, *J* = 2.80, 10.40 Hz, C3^{Gal}-H), 1.92–1.22 (m, 10H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.4, 138.0, 137.8, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 100.7 (C1^{Gal}), 80.7, 77.8, 77.4, 77.1, 76.7. 74.6, 73.6, 72.6, 72.2, 68.8, 63.5, 33.5, 31.6, 25.6, 24.0, 23.9; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{33}H_{39}N_3O_5Na$ 580.2787, found 580.2868.



α/β-4c

Cyclohexanol 2-azide-3,4,6-tri-*O*-benzyl-D-galactose-pyranoside **α/β-4c:**

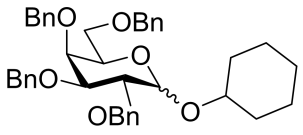
Following the general procedure of Method **B** using trichloroacetimidate **1c** (54.7 mg, 0.088 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (5.89 mg, 0.059 mmol) in DCM (5.90 mL) at room temperature for 3 hours afforded **α/β-4c** (19.7 mg, 60% yield, α/β=50:50) as a white solid (eluent, Toluene–Ethyl acetate 30:1). $[\alpha]_D^{21}$ = +56.47 (*c* = 0.61, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42–7.24 (m, 30H, ArH), 5.05 (d, 1H, *J* = 3.60 Hz, C1^{Gal}-H), 4.90–4.86 (m, 2H, OCH_2Ph), 4.76–4.67 (m, 4H, OCH_2Ph), 4.60–4.40 (m, 6H, OCH_2Ph), 4.31 (d, 1H, *J* = 8.00 Hz, C1^{Gal}-H), 4.08–3.98 (m, 6H), 3.85–3.75 (m, 6H), 3.69–3.45 (m, 6H), 3.26 (dd, 1H, *J* = 3.60, 12.00 Hz), 1.91–1.25 (m, 20H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.4, 138.0, 137.8, 137.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 100.7 (C1^{Gal}), 96.7 (C1^{Gal}), 80.7, 77.3, 77.2, 77.0, 76.7, 76.4, 74.8, 74.6, 73.6, 72.6, 72.2, 69.6, 68.8, 63.5, 59,7, 33.5, 33.3, 31.6, 31.5, 29.7, 25.6, 24.1, 24.0, 23.9; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{33}H_{39}N_3O_5Na$ 580.2787, found 580.2780.



1d

2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranoside trichloroacetimidate **1d**:

To a magnetically stirred solution of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranoside (49.6 mg, 0.09 mmol) and CCl_3CN (0.93 mL, 0.92 mmol, 10.0 equiv.) in anhydrous CH_2Cl_2 (5.0 mL), DBU (7.1 μL, 0.05 mmol, 0.5 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, 5:1) to afford compound **1d** (61 mg, 99% yield) as a white powder. TLC (hexane–EtOAc, 5:1): R_f = 0.60. The ^{1}H NMR is accordance with the literature previously reported[8].

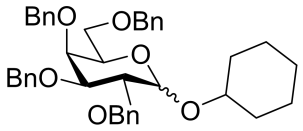


α/β-4d

Cyclohexanol 2,3,4,6-tetra-*O*-benzyl-D-galactose-pyranoside **α/β-4d:**

Following the general procedure of Method **A** using trichloroacetimidate **1d** (50.0 mg, 0.073 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (4.87 mg, 0.049 mmol) in DCM (4.90 mL) at –40°C temperature for 12 hours afforded **α/β-4d** (18.6 mg, 61% yield, α/β=14:86) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +32 (*c* = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.18 (m, 24H, ArH), 4.94-4.84 (m, 2H), 4.79–4.49 (m, 6H), 4.42–4.22 (m, 4H), 3.98–3.87 (m, 1H), 3.80–3.70 (m, 2H), 3.62–3.58 (m, 1H), 3.51–3.41 (m, 5H), 1.86–0.79 (m, 12H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.7, 128.4, 128.3, 128.2, 128.1, 127.9,

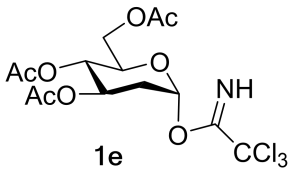
127.8, 127.5, 127.4, 102.2 ($C1^{Gal}$), 82.5, 79.6, 77.3, 77.0, 76.7, 75.2, 75.3, 74.5, 73.7, 73.5, 73.4, 73.2, 69.1, 33.7, 31.9, 29.7, 25.7, 24.1, 24.0; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{40}H_{46}O_6Na$ 645.3192, found 645.3222.



α/β-4d

Cyclohexanol 2,3,4,6-tetra-*O*-benzyl-D-galactose -pyranoside **α/β-4d:**

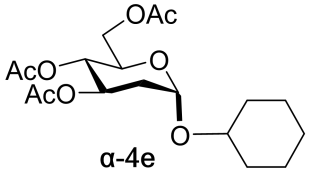
Following the general procedure of Method **B** using trichloroacetimidate **1d** (95.0 mg, 0.139 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (9.26 mg, 0.092 mmol) in DCM (9.20 mL) at room temperature for 3 hours afforded **α/β-4d** (48.7 mg, 85% yield, α/β=67:33) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +1.7 (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.18 (m, 30H, ArH), 4.93 (d, 1H, *J* = 3.65 Hz, $C1^{Gal}$-H), 4.90–4.84 (m, 2H), 4.77 (d, 1H, *J* = 11.64 Hz), 4.72–4.48 (m, 6H), 4.42–4.31 (m, 5H), 4.23 (t, 1H, *J* = 6.72 Hz), 3.99–3.87 (m, 4H), 3.80–3.70 (m, 1H), 3.63–3.41 (m, 6H), 1.84–0.79 (m, 15H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.8, 138.2, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 102.2 ($C1^{Gal}$), 95.5 ($C1^{Gal}$), 82.5, 79.6, 79.2, 77.3, 77.0, 76.7, 76.6, 75.4, 75.3, 74.8, 73.7, 73.5, 73.4, 73.2, 73.0, 69.3, 69.2, 65.6, 33.7, 33.4, 31.6, 29.7, 25.7, 24.5, 24.3, 19.2, 13.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{40}H_{46}O_6Na$ 645.3192, found 645.3222.



1e

3,4,6-tri-*O*-acetyl-2-dexoy-α-D-glucopyranoside trichloroacetimidate **1e**:

To a magnetically stirred solution of 3,4,6-tri-*O*-acetyl-2-dexoy-α-D-glucopyranosid (39.9 mg, 0.14 mmol) and CCl_3CN (0.14 mL, 1.37 mmol, 10.0 equiv.) in anhydrous CH_2Cl_2 (5.0 mL), DBU (2.0 μL, 0.01 mmol, 0.1 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 5 min, after 5 min the ice bath was remove and solution stirred for 1.5 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, 2:1) to afford compound **1e** (60.2 mg, 99% yield) as a white powder. TLC (hexane–EtOAc, 2:1): R_f = 0.50. The ^1H NMR is accordance with the literature previously reported[9].

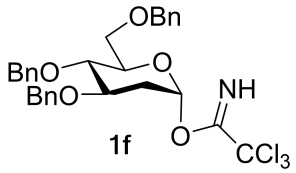


α-4e

Cyclohexanol 3,4,6-tri-*O*-acetyl-2-dexoy-α-D-glucopyranoside **α-4e:**

Following the general procedure of **Method A** using trichloroacetimidate **1e** (41.4 mg, 0.095 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (6.74 mg, 0.064 mmol) in DCM (6.40 mL) at –40°C temperature for 12 hours afforded **α/β-4e** (17.1 mg, 72% yield, α/β=88/12) as a white solid (eluent, Hex–Ethyl acetate 3:1).; ^1H NMR ($CDCl_3$, 400 MHz): δ 5.40–5.34 (m, 1H, $C3^{Glc1}$-H), 5.13 (d, 1H, *J* = 3.16 Hz,

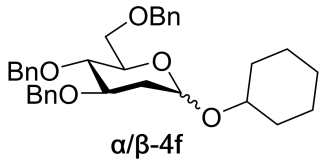
$C4^{Glc1}$-H), 5.00 (t, 1H, *J* = 9.64 Hz, $C1^{Glc1}$-H), 4.30 (dd, 1H, *J* = 5.24, 12.64 Hz, $C6^{Glc1}$-H), 4.10–4.06 (m, 2H, $C5^{Glc1}$-H and $C6^{Glc1}$-H), 3.59–3.52 (m, 1H, OCH), 2.20 (dd, 1H, *J* = 5.04, 12.48 Hz, $C2^{Glc1}$-H), 2.11 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.89–1.23 (m, 11H, $C2^{Glc1}$-H and CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 170.8, 170.3, 170.0, 101.1, 94.9, 77.3, 77.0, 76.7, 75.5, 69.7, 69.3, 67.9, 62.6, 35.6, 33.4, 31.5, 25.6, 24.2, 23.9, 21.0, 20.8, HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{28}O_8Na$ 395.1682, found 395.1673.



1f

3,4,6-tri-*O*-benzyl-2-dexoy-α-D-glucopyranoside trichloroacetimidate **1f**:

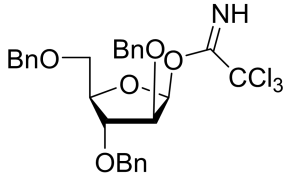
To a magnetically stirred solution of 3,4,6-tri-*O*-benzyl-2-dexoy-α-D-glucopyranosid (50.0 mg, 0.12 mmol) and CCl_3CN (0.12 mL, 1.15 mmol, 10.0 equiv.) in anhydrous CH_2Cl_2 (3.0 mL), DBU (1.7 µL, 0.01 mmol, 0.1 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature for 5 min, after 5 min the ice bath was remove and solution stirred for 1.5 h. Evaporation of solvents afforded **1f**, the product was used without purification for the glycosytion.. The ^1H NMR is accordance with the literature previously reported[9].



α/β-4f

Cyclohexanol 3,4,6-tri-*O*-benzyl-2-dexoy-D-glucopyranoside **α/β-4f:**

Following the general procedure of **Method A** using trichloroacetimidate **1f** (33.3 mg, 0.06 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (3.85 mg, 0.04 mmol) in DCM (4.00 mL) at –40°C temperature for 12 hours afforded **α/β-4f** (18.0 mg, 87% yield, α/β=33/67) as a white solid (eluent, Toluene–Ethyl acetate 15:1).; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.39–7.19 (m, 22.5H), 5.14 (d, 1H, *J* = 2.96 Hz), 4.94–4.90 (m, 1.4H), 4.73–4.51 (m, 7.7H), 4.08–4.02 (m, 1.0H), 3.90–3.78 (m, 2.6H), 3.73–3.42 (m, 5.2H), 2.37–1.24 (m, 22H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.9, 138.6, 138.4, 138.3, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 97.9, 95.1, 78.5, 77.9, 77.3, 77.0, 76.7, 75.0, 74.9, 73.4, 71.8, 70.7, 65.9, 36.0, 33.4, 31.5, 25.7, 24.3, 24.0; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{33}H_{40}O_5Na$ 539.2773, found 539.2764.

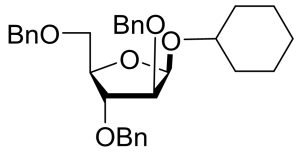


1g

2,3,5-tri-O-benzyl-β-D-Arabinose-furanose trichloroacetimidate **1g:**

To a magnetically stirred solution of 2,3,5-tri-O-benzyl-β-D-Arabinose-furanose (131.7 mg, 0.29 mmol) and CCl_3CN (0.3 mL, 2.94 mmol, 10.0 equiv.) in anhydrous CH_2Cl_2 (10.0 mL), DBU (22 µL, 0.15 mmol, 0.5 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

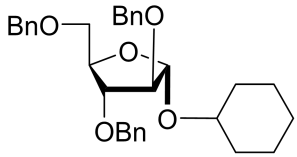
silica gel (preconditioned with Et_3N; eluent: hexane–EtOAc, 3:1) to afford compound **1g** (159 mg, 97% yield) as a white powder. TLC (hexane–EtOAc, 3:1): R_f = 0.50, $[\alpha]_D^{21}$ = +22.9 (*c* = 0.65, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.52 (s, 1H, NH), 7.39–7.24 (m, 15H, ArH), 6.36 (s, 1H, $C1^{Ara}$-H), 4.70 (d, 1H, *J* = 11.60 Hz, OCH_2Ph), 4.57–4.54 (m, 3H, OCH_2Ph), 4.50 (d, 2H, *J* = 2.40 Hz, OCH_2Ph), 4.48–4.43 (m, 1H, $C4^{Ara}$-H), 4.26 (d, 1H, *J* = 2.40 Hz, $C2^{Ara}$-H), 4.06 (dd, 1H, *J* = 2.40, 6.00 Hz, $C3^{Ara}$-H), 3.70–3.65 (m, 2H, $C5^{Ara}$-H and $C5^{Ara}$-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 161.1, 138.0, 137.7, 137.3, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5, 104.4, 86.6, 83.7, 83.5, 77.4, 77.0, 76.7, 73.5, 72.1, 72.0, 69.4, 29.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{28}H_{28}Cl_3NNaO_5$ 586.0931, found 586.0935.



β-4g

Cyclohexanol 2,3,5-tri-*O*-benzyl-β-D-Arabinose-furanose **β-4g:**

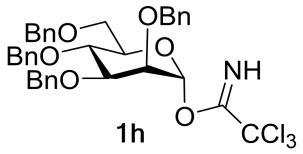
Following the general procedure of **Method A** using trichloroacetimidate **1g** (83.1 mg, 0.15 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (10.01 mg, 0.10 mmol) in DCM (10.00 mL) at –40°C temperature for 12 hours afforded **α/β-4g** (25.1 mg, 50% yield, α/β=25/75) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = +49.68 (*c* = 0.92, $CHCl_3$); 1H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.24 (m, 15H, ArH), 5.10 (d, 1H, *J* = 4.40 Hz, $C1^{Ara}$-H), 4.70–4.50 (m, 6H, $O\underline{CH_2}Ph$), 4.11–4.03 (m, 3H, OCH, $C3^{Ara}$-H and $C2^{Ara}$-H), 3.59–3.52 (m, 3H, $C4^{Ara}$-H, $C5^{Ara}$-H and $C5^{Ara}$-H), 1.90–1.14 (m, 10H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.3, 138.1, 137.8, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 98.7 ($C1^{Ara1}$), 84.0, 83.7, 79.9, 77.3, 77.0, 76.7, 75.9, 73.3, 73.0, 72.3, 72.2, 33.7, 31.8, 25.6, 24.5, 24.3; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{32}H_{38}O_5Na$ 525.2617, found 525.2608.



α-4g

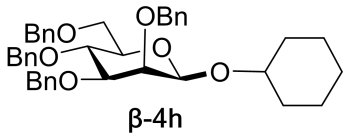
Cyclohexanol 2,3,5-tri-*O*-benzyl-α-D-Arabinose-furanose **α-4g:**

Following the general procedure of **Method B** using trichloroacetimidate **1g** (83.1 mg, 0.15 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (10.01 mg, 0.10 mmol) in DCM (10.00 mL) at room temperature for 3 hours afforded **α/β-4g** (31.1 mg, 62% yield, α/β=86/14) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = –20.4 (*c* = 2.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.34–7.23 (m, 15H, ArH), 5.21 (d, 1H, *J* = 1.60 Hz, $C1^{Ara}$-H), 4.60–4.46 (m, 6H, $O\underline{CH_2}Ph$), 4.22–4.19 (m, 1H, $C4^{Ara}$-H), 4.03–4.01 (dd, 1H, *J* = 1.60, 3.60 Hz, $C2^{Ara}$-H), 3.94–3.91 (q, 1H, *J* = 3.60 Hz, $C3^{Ara}$-H), 3.67–3.57 (m, 3H, $C5^{Ara}$-H, $C5^{Ara}$-H and OCH), 1.91–1.24 (m, 10H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ 138.2, 138.0, 137.7, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 104.1 ($C1^{Ara1}$), 88.8, 83.6, 80.0, 77.3, 77.0, 76.7, 74.9, 73.3, 72.0, 71.9, 70.0, 33.7, 31.7, 25.7, 24.2, 24.1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{32}H_{38}O_5Na$ 525.2617, found 525.2733.



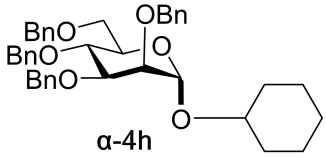
2,3,4,6-tetra-*O*-benzyl-α-D-mannose-pyranoside trichloroacetimidate **1h:**

To a magnetically stirred solution of 2,3,4,6-tetra-*O*-benzyl-α-D-mannose-pyranoside (73.7 mg, 0.14 mmol) and CCl_3CN (0.14 mL, 1.36 mmol, 10.0 equiv.) in anhydrous CH_2Cl_2 (5.0 mL), DBU (9.6 μL, 0.068 mmol, 0.5 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, 4:1) to afford compound **1h** (91.3 mg, 98% yield) as a white powder. TLC (hexane–EtOAc, 4:1): R_f = 0.50, $[\alpha]_D^{21}$ = +26.0 (*c* = 0.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (s, 1H, NH), 7.43–7.19 (m, 20H, ArH), 6.36 (d, 1H, *J* = 2.00 Hz, C1^{Man}-H), 4.89 (d, 1H, *J* = 10.40 Hz, OCH_2Ph), 4.77 (s, 2H, OCH_2Ph), 4.69–4.51 (m, 5H, OCH_2Ph), 4.15 (t, 1H, *J* = 9.60 Hz, C4^{Man}-H), 3.98–3.91 (m, 2H, C6^{Man}-H and C3^{Man}-H), 3.88–3.87 (m, 1H, C2^{Man}-H), 3.82 (dd, 1H, *J* = 4.40, 11.20 Hz, C5^{Man}-H), 3.74–3.71 (m, 1H, C6^{Man}-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 161.0, 138.3, 138.1, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 96.1, 78.9, 77.3, 77.0, 76.7, 75.4, 74.8, 74.2, 73.5, 73.4, 72.7, 72.4, 68.8, 29.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{36}H_{36}Cl_3NNaO_6$ 706.1506, found 706.1510.



Cyclohexanol 2,3,4,6-tetra-*O*-benzyl-β-D-mannose-pyranoside **β-4h:**

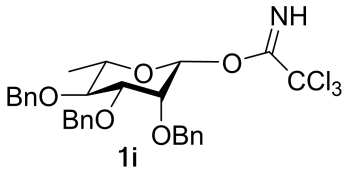
Following the general procedure of Method **A** using trichloroacetimidate **1h** (40.4 mg, 0.059 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (3.90 mg, 0.039 mmol) in DCM (3.90 mL) at –40°C temperature for 12 hours afforded **α/β-4h** (21.1 mg, 87% yield, α/β=25:75) as a white solid (eluent, Toluene–Acetonitrile 15:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.25 (m, 20H, ArH), 4.99 (d, 1H, *J* = 1.60 Hz, C1^{Glc1}-H), 4.87 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.78–4.61 (m, 5H, OCH_2Ph), 4.55–4.49 (m, 2H, OCH_2Ph), 4.00–3.91 (m, 2H, C3^{Glc1}-H and C4^{Glc1}-H), 3.86–3.70 (m, 4H, C2^{Glc1}-H, C5^{Glc1}-H, C6^{Glc1}-H and C6^{Glc1}-H), 3.61–3.54 (m, 1H, OCH), 1.67–1.16 (m, 10H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.5, 138.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 95.7 (C1^{Glc1}), 80.3, 77.4, 77.0, 76.7, 75.4, 75.1, 74.8, 73.3, 72.6, 72.2, 71.8, 69.4, 33.2, 31.3, 25.7, 24.0, 23.8; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{40}H_{46}O_6Na$ 645.3192, found 645.3202.



Cyclohexanol 2,3,4,6-tetra-*O*-benzyl-α-D-mannose-pyranoside **α-4h:**

Following the general procedure of Method **B** using trichloroacetimidate **1h** (46.2 mg, 0.067 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (4.50 mg, 0.045 mmol) in DCM (4.50 mL) at room temperature for 3 hours afforded **α/β-4h** (24.1 mg, 86% yield, α/β=25:75) as a white solid

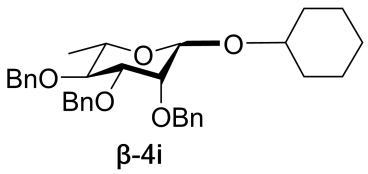
(eluent, Toluene–Acetonitrile 15:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49–7.19 (m, 20H, ArH), 5.02 (d, 1H, *J* = 12.40 Hz, OCH_2Ph), 4.92–4.89 (m, 2H, OCH_2Ph), 4.64–4.42 (m, 6H, $C1^{Glc1}$-H and OCH_2Ph), 3.86–3.81 (m, 3H, $C2^{Glc1}$-H, $C4^{Glc1}$-H and $C6^{Glc1}$-H), 3.74–3.69 (m, 2H, $C6^{Glc1}$-H and OCH), 3.50 (dd, 1H, *J* = 3.20, 9.20 Hz, $C3^{Glc1}$-H), 3.47–3.42 (m, 1H, $C5^{Glc1}$-H), 1.79–1.26 (m, 10H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.9, 138.6, 138.4, 138.3, 128.5, 128.3, 128.1, 127.8, 127.6, 127.5, 127.4, 127.3, 99.5 ($C1^{Glc1}$), 82.6, 77.3, 77.0, 76.7, 75.9, 75.1, 75.0, 74.1, 73.7, 73.4, 71.4, 69.9, 33.5, 31.6, 25.8, 23.9, 23.7; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{40}H_{46}O_6Na$ 645.3192, found 645.3199.



1i

2,3,4,6-tetra-*O*-benzyl-β-D-rhamnose-pyranoside trichloroacetimidate **1i**:

To a magnetically stirred solution of 2,3,4,6-tetra-*O*-benzyl-β-D-rhamnose-pyranoside (60 mg, 0.14 mmol) and CCl_3CN (0.1 mL, 1.11 mmol, 8.0 equiv.) in anhydrous CH_2Cl_2 (3.0 mL), DBU (8.0 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, 4:1) to afford compound **1i** (91.3 mg, 98% yield) as a white powder. TLC (hexane–EtOAc, 4:1): R_f = 0.50, $[\alpha]_D^{21}$ = –29.5 (*c* = 0.36, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (s, 1H, NH), 7.42–7.25 (m, 15H, ArH), 6.24 (d, 1H, *J* = 2.00 Hz, $C1^{Rha}$-H), 4.96 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.78 (s, 2H, OCH_2Ph), 4.67–4.57 (m, 3H, OCH_2Ph), 3.92–3.85 (m, 3H, $C5^{Rha}$-H, $C2^{Rha}$-H and $C3^{Rha}$-H), 3.71 (t, 1H, *J* = 9.20 Hz, $C4^{Rha}$-H), 1.35 (d, 1H, *J* = 6.40 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 160.6, 138.3, 138.1, 137.9, 128.6, 128.5, 128.4, 128.2, 128.0, 127.8, 127.7, 96.0, 79.8, 78.9, 77.3, 77.0, 76.7, 75.6, 73.9, 72.8, 72.3, 71.1, 29.7,18.1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{29}H_{30}Cl_3NNaO_5$ 600.1087, found 600.1089.



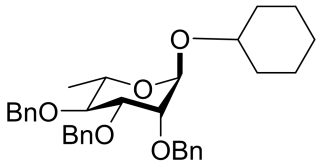
β-4i

Cyclohexanol 2,3,4,6-tetra-*O*-benzyl-β-D-rhamnose-pyranoside **β-4i:**

Following the general procedure of Method **A** using trichloroacetimidate **1i** (36.0 mg, 0.062 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (4.15 mg, 0.041 mmol) in DCM (4.10 mL) at –40°C temperature for 12 hours afforded **α/β-4i** (19.1 mg, 90% yield, α/β=52:48) as a white solid (eluent, Toluene–Ethyl acetate 15:1). $[\alpha]_D^{21}$ = –45.9 (*c* = 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.23 (m, 15H, ArH), 5.02–4.89 (m, 3H, OCH_2Ph), 4.65 (d, 1H, *J* = 10.80 Hz, OCH_2Ph),

4.51–4.40 (m, 3H, $C1^{Glc1}$-H and OCH_2Ph), 3.84 (d, 1H, *J* = 2.80 Hz, $C2^{Glc1}$-H), 3.71–3.65 (m, 1H, OCH), 3.62 (t, 1H, *J* = 9.20 Hz, $C4^{Glc1}$-H), 3.44 (dd, 1H, *J* = 2.80, 9.20 Hz, $C3^{Glc1}$-H), 3.32–3.26 (m, 1H, $C5^{Glc1}$-H), 1.92–1.24 (m, 13H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.9, 138.6, 138.3, 128.5, 128.3, 128.1, 128.0, 127.6, 127.5, 127.4, 127.3, 99.2 ($C1^{Glc1}$), 82.4,

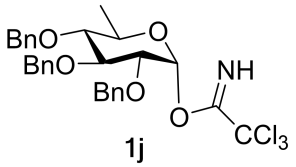
80.2, 77.3, 77.0, 76.7, 76.2, 75.4, 74.3, 73.7, 71.8, 71.3, 33.4, 31.5, 25.8, 23.8, 23.6, 18.1; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{33}H_{40}O_5Na$ 539.2773, found 539.2752.



α-4i

Cyclohexanol 2,3,4,6-tetra-*O*-benzyl-α-D-rhamnose-pyranoside **α-4i:**

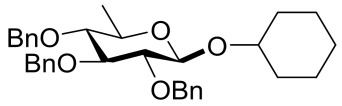
Following the general procedure of Method **B** using trichloroacetimidate **1i** (39.7 mg, 0.069 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (4.58 mg, 0.046 mmol) in DCM (4.60 mL) at room temperature for 3 hours afforded **α/β-4i** (20.7 mg, 87% yield, α/β=91:9) as a white solid (eluent, Toluene–Ethyl acetate 15:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.25 (m, 15H, ArH), 4.94 (d, 1H, *J* = 10.80 Hz, OCH_2Ph), 4.86 (d, 1H, *J* = 1.60 Hz, C1^{Glc1}-H), 4.79–4.61 (m, 5H, OCH_2Ph), 3.88 (dd, 1H, *J* = 3.20, 9.60 Hz), 3.79–3.70 (m, 2H, C5^{Glc1}-H and C2^{Glc1}-H), 3.61 (t, 1H, *J* = 9.20 Hz, C4^{Glc1}-H), 3.55–3.48 (m, 1H, OCH), 1.76–1.15 (m, 13H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.6, 138.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 95.7 (C1^{Glc1}), 80.8, 80.3, 77.4, 77.0, 76.7, 75.6, 75.5, 74.5, 72.8, 72.2, 68.0, 33.3, 31.2, 25.7, 24.0, 23.8, 18.0; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{33}H_{40}O_5Na$ 539.2773, found 539.2764.



1j

2,3,4-tri-*O*-benzyl-6-dexoy-α-D-glucopyranoside trichloroacetimidate **1j:**

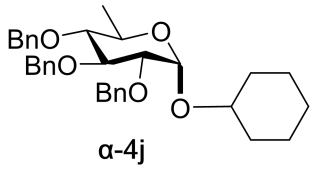
To a magnetically stirred solution of 2,3,4-tri-*O*-benzyl-6-dexoy-α-D-glucopyranoside (60 mg, 0.14 mmol) and CCl_3CN (0.14 mL, 1.38 mmol, 10.0 equiv.) in anhydrous CH_2Cl_2 (5.0 mL), DBU (10.0 μL, 0.07 mmol, 0.5 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at the same temperature 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, 3:1) to afford compound **1j** (79.4 mg, 98% yield) as a white powder. TLC (hexane–EtOAc, 3:1): R_f = 0.50, $[\alpha]_D^{21}$ = +78.3 (*c* = 0.56, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 (s, 1H, NH), 7.31–7.25 (m, 15H, ArH), 6.40 (d, 1H, *J* = 3.56Hz, C1^{Glc}-H), 4.96 (d, 1H, *J* = 10.88 Hz, OCH_2Ph), 4.91 (d, 1H, *J* = 10.92 Hz, OCH_2Ph), 4.82 (d, 1H, *J* = 10.88 Hz, OCH_2Ph), 4.75–4.63 (m, 3H, OCH_2Ph), 4.04–3.93 (m, 2H, C3^{Glc}-H and C5^{Glc}-H), 3.72 (dd, 1H, *J* = 3.36, 9.44 Hz, C2^{Glc}-H), 3.22 (t, 1H, *J* = 9.48 Hz, C4^{Glc}-H), 1.25 (d, 3H, *J* = 3.24 Hz, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 161.5, 138.6, 138.1, 138.0, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 127.6, 94.1 (C1^{Glc}), 91.3, 82.9, 81.2, 79.7, 77.4, 77.0, 76.7, 75.7, 75.6, 72.9, 69.7, 29.7, 18.0; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{29}H_{30}Cl_3NNaO_5$ 600.1087, found 600.1092.



β-4j

Cyclohexanol 2,3,4-tri-*O*-benzyl-6-dexoy-β-D-glucopyranoside **β-4j:**

Following the general procedure of **Method A** using trichloroacetimidate **1j** (46.7 mg, 0.08 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (5.78 mg, 0.05 mmol) in DCM (5.00 mL) at –40°C temperature for 12 hours afforded **α/β-4j** (23.2 mg, 90% yield, α/β=33/67) as a white solid (eluent, Hex–Ethyl acetate 4:1).; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39–7.28 (m, 15H, ArH), 5.02 (d, 1H, *J* = 10.88 Hz, O$\underline{CH_2}$Ph), 4.94 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.88 (d, 1H, *J* = 10.84 Hz, O$\underline{CH_2}$Ph), 4.80 (d, 1H, *J* = 10.92 Hz, O$\underline{CH_2}$Ph), 4.73 (d, 1H, *J* = 10.88 Hz, O$\underline{CH_2}$Ph), 4.64 (d, 1H, *J* = 10.84 Hz, O$\underline{CH_2}$Ph), 4.51 (d, 1H, *J* = 7.84 Hz, C1^{Glc1}-H), 3.74–3.67 (m, 1H, OCH), 3.62 (t, 1H, *J* = 9.12 Hz, C4^{Glc1}-H), 3.47–3.36 (m, 2H, C2^{Glc1}-H and C5^{Glc1}-H), 3.22 (t, 1H, *J* = 9.12 Hz, C3^{Glc1}-H), 2.01–1.24 (m, 13H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 138.7, 138.6, 138.2, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 101.6 (C1^{Glc1}), 84.7, 83.4, 82.6, 77.3, 77.0, 76.7, 75.7, 75.3, 74.9, 71.0, 33.8, 31.9, 25.6, 24.1, 24.0, 18.0; HRMS (ESI) m/z [M+Na]$^+$ calcd for $C_{33}H_{40}O_5Na$ 539.2773, found 539.2762.



α-4j

Cyclohexanol 2,3,4-tri-*O*-benzyl-6-dexoy-α-D-glucopyranoside **α-4j:**

Following the general procedure of **Method B** using trichloroacetimidate **1j** (46.7 mg, 0.08 mmol, 1.5 equiv.) and acceptor cyclohexanol **2a** (5.78 mg, 0.05 mmol) in DCM (5.00 mL) at room temperature for 3 hours afforded **α/β-4j** (24.8 mg, 87% yield, α/β=33/67) as a white solid (eluent, Hex–Ethyl acetate 4:1). $[\alpha]_D^{21}$ = +64.3 (*c* = 0.61, $CHCl_3$), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40–7.28 (m, 15H, ArH), 5.02 (d, 1H, *J* = 10.76 Hz, O$\underline{CH_2}$Ph), 4.92 (d, 1H, *J* = 10.80 Hz, O$\underline{CH_2}$Ph), 4.88 (d, 1H, *J* = 3.68 Hz, C1^{Glc1}-H), 4.83 (d, 1H, *J* = 10.72 Hz, O$\underline{CH_2}$Ph), 4.77 (d, 1H, *J* = 11.92 Hz, O$\underline{CH_2}$Ph), 4.70–4.64 (m, 2H, O$\underline{CH_2}$Ph), 4.00 (t, 1H, *J* = 9.82 Hz, C3^{Glc1}-H), 3.91–3.84 (m, 1H, C5^{Glc1}-H), 3.56–3.52 (m, 2H, C2^{Glc1}-H and CHO), 3.15 (t, 1H, *J* = 9.24 Hz, C4^{Glc1}-H), 1.93–1.20 (m, 13H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ 139.0, 138.4, 128.4, 128.3, 128.0, 94.4 (C1^{Glc1}), 84.1, 80.4, 77.3, 77.0, 76.7, 75.6, 75.4, 75.2, 72.9, 33.4, 31.5, 25.6, 24.5, 24.2; HRMS (ESI) m/z [M+Na]$^+$ calcd for $C_{33}H_{40}O_5Na$ 539.2773, found 539.2806.

5 Reference

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A.Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M.Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A.Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi,J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar,J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox,J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O.Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A.Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

2 A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem.*, 2009, **113**, 6378–6396.

3 (a) P. C. Hariharan, J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chem. Acc.*, 1973, **28**, 213–222. (b) M. J. Frisch, J. A. Pople, J. S. Binkley, Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets, *J. Chem. Phys.*, 1984, **80**, 3265–3269.

4 M. Dolg, U. Wedig, H. Stoll, H. Preuss, Energy-adjusted ab initio pseudopotentials for the first row transition elements, *J. Chem. Phys.*, 1987, **86**, 866–872.

5 A. V. Marenich, C. J. Cramer, D. G Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions, *J. Phys. Chem. B.*, 2009, **113**, 6378–6396.

6 Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

7 P. Fuentealba, H. Preuss, H. Stoll, L.V. Szentpaly, A proper account of core-polarization with pseudopotentials: single valence-electron alkali compounds, *Chem. Phys. Lett.*, 1982, **89**, 418–422.

8 S. Kim, S. Song, T. Lee, S. Jung, D. Kim, Practical Synthesis of KRN7000 from Phytosphingosine, *Synthesis*, 2004, **6**, 847-850

9. C. Bucher, Prof. Dr. Ryan Gilmour, Fluorine-Directed Glycosylation, *Angew. Chew*., 2010, **122**, 8906-8910

6 NMR Spectrums of Compounds

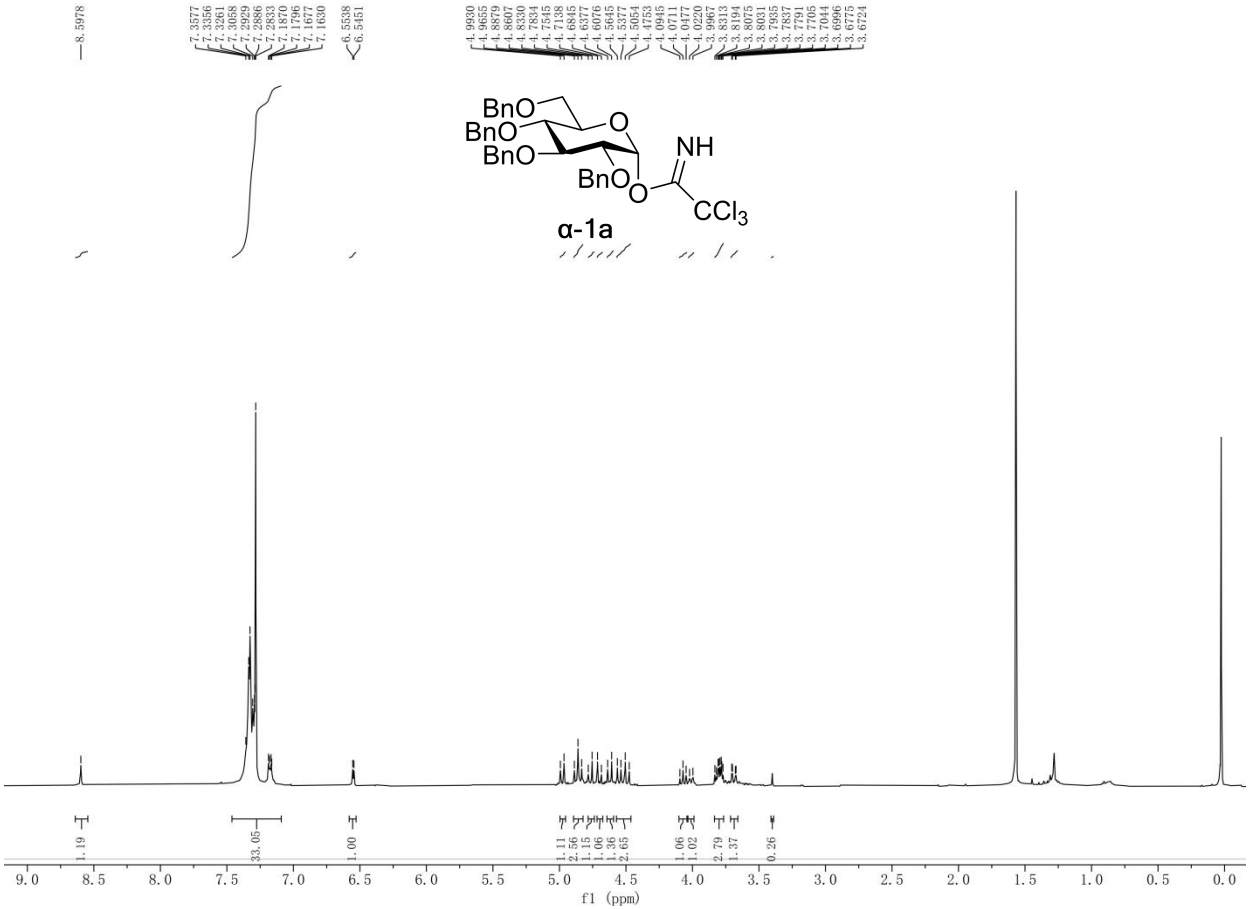


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-1a**

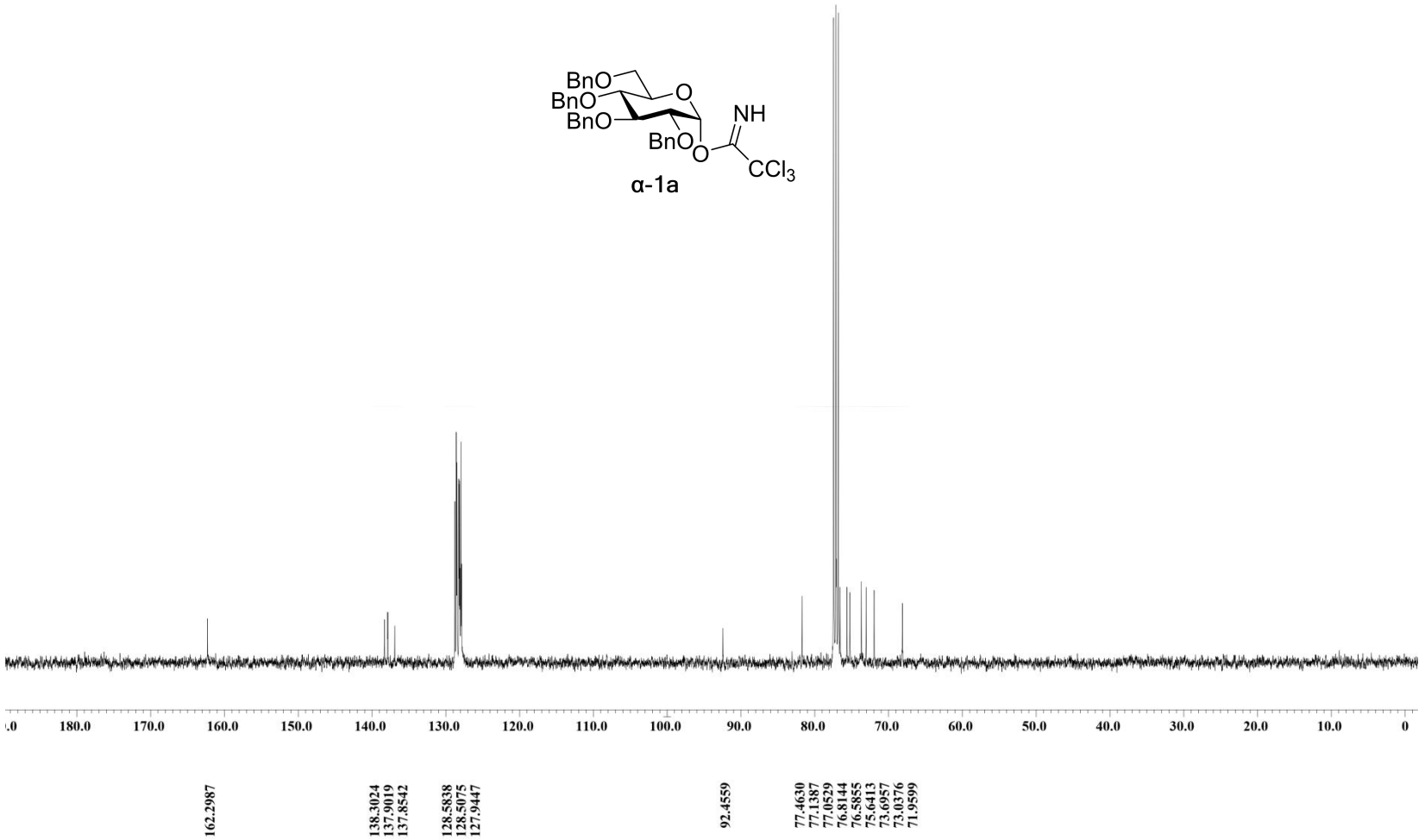


Figure S2. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-1a**

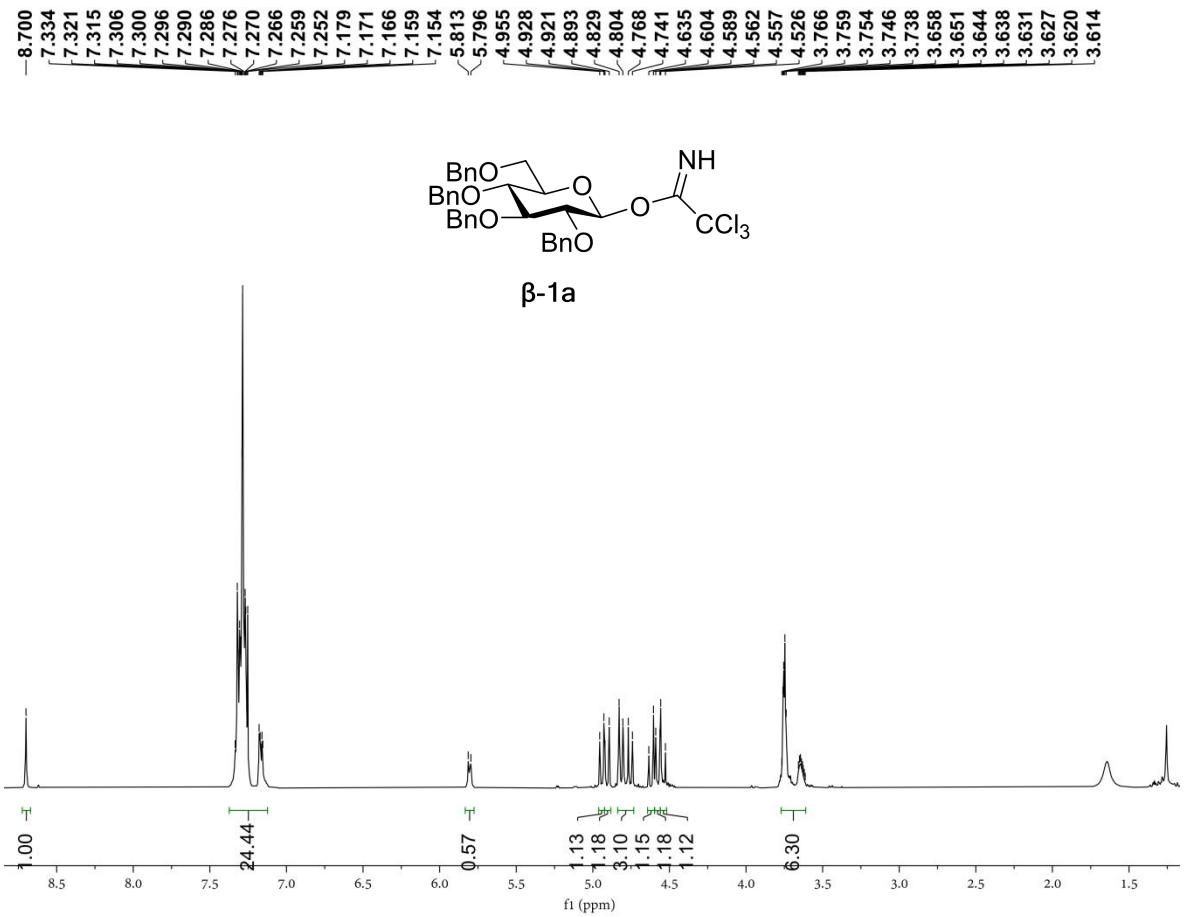


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-1a**

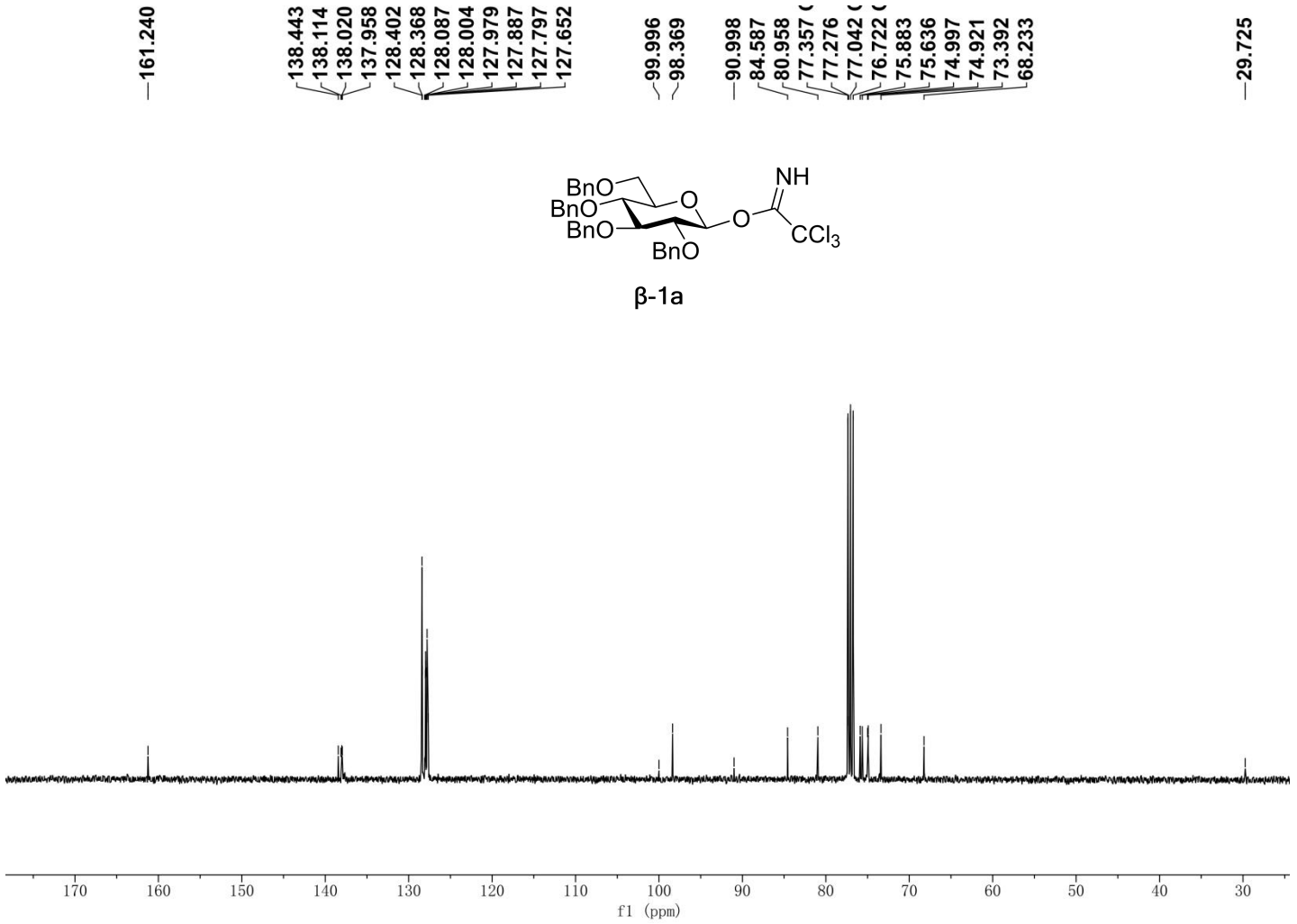


Figure S4. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-1a**

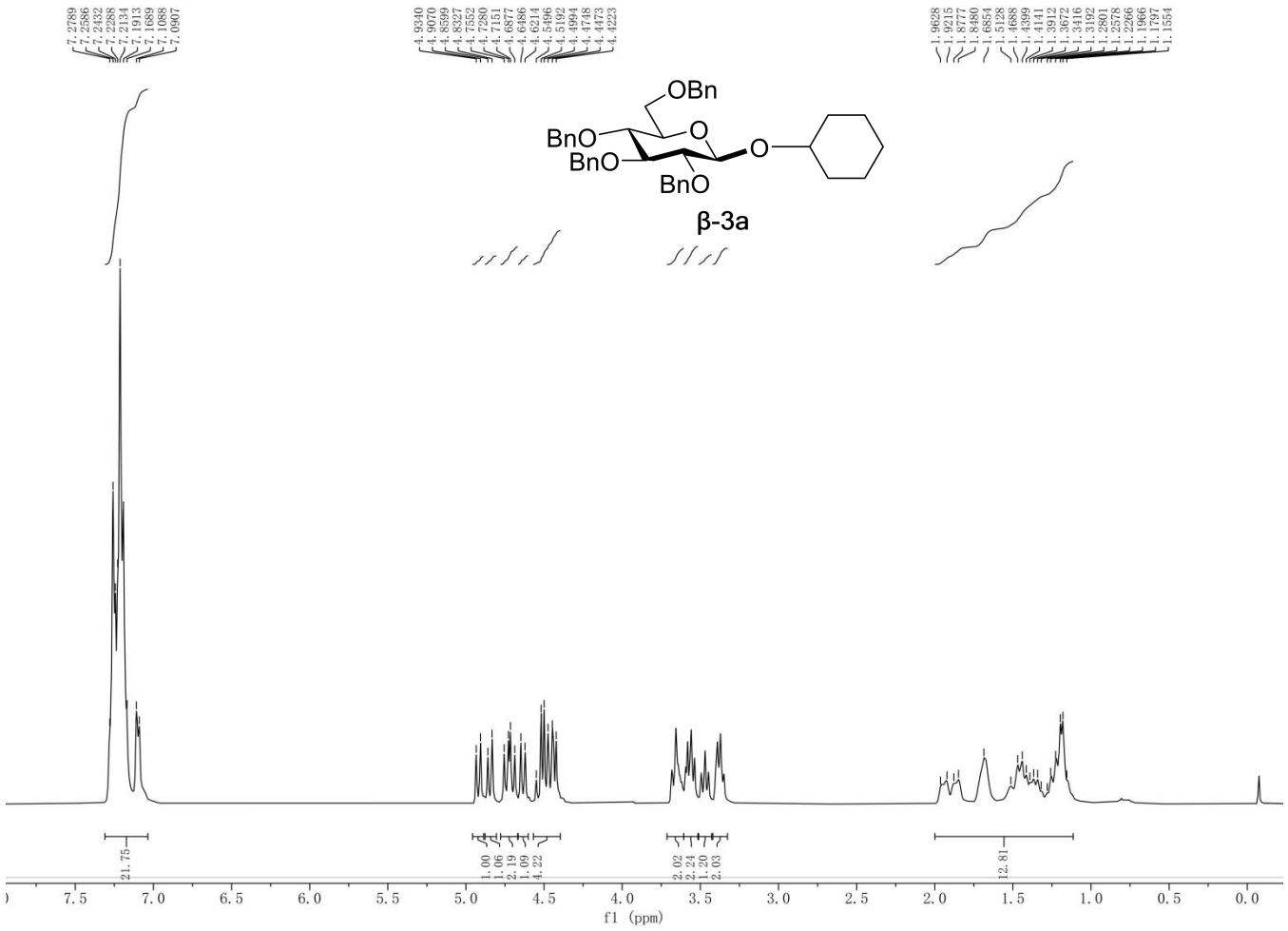


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3a**

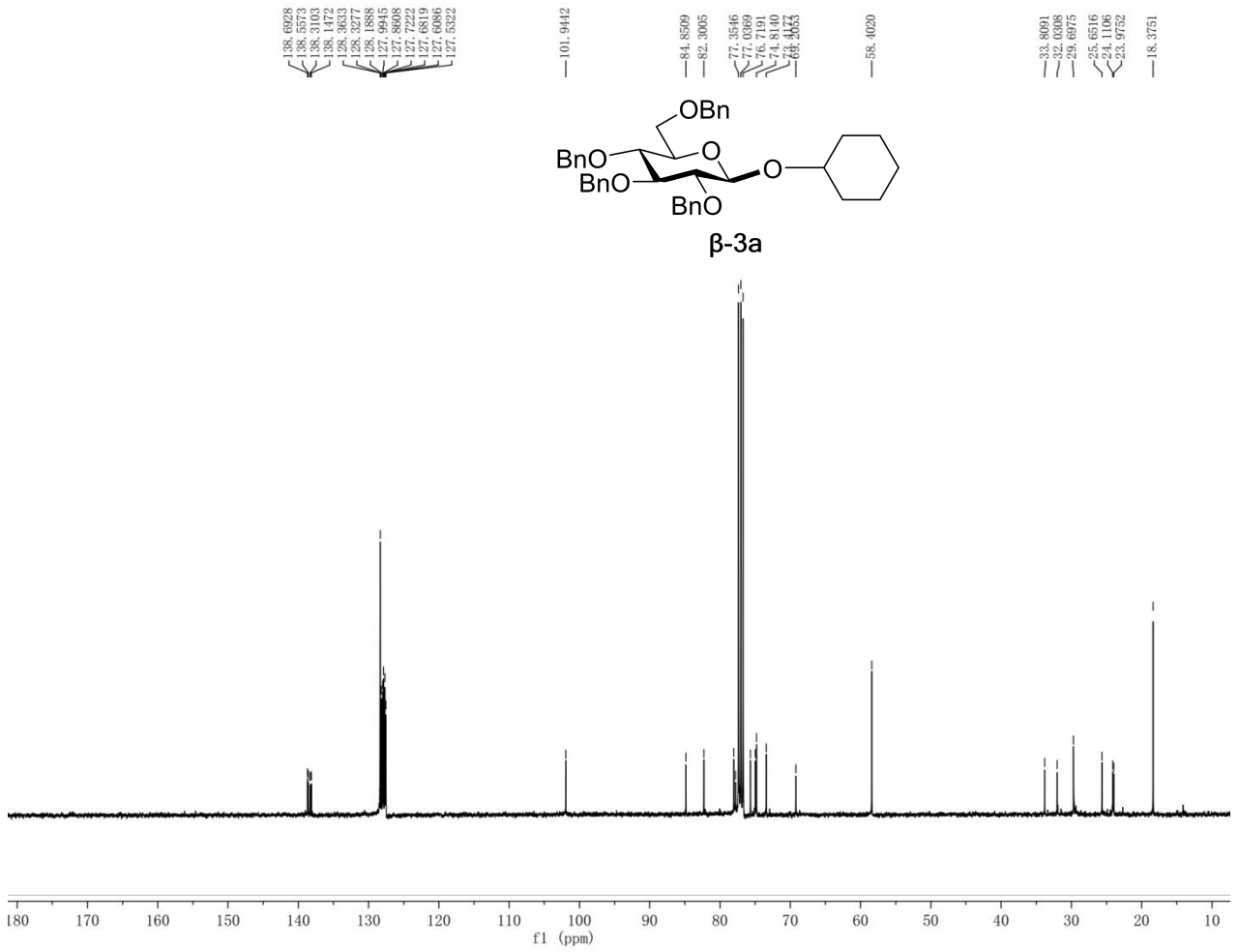


Figure S6. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3a**

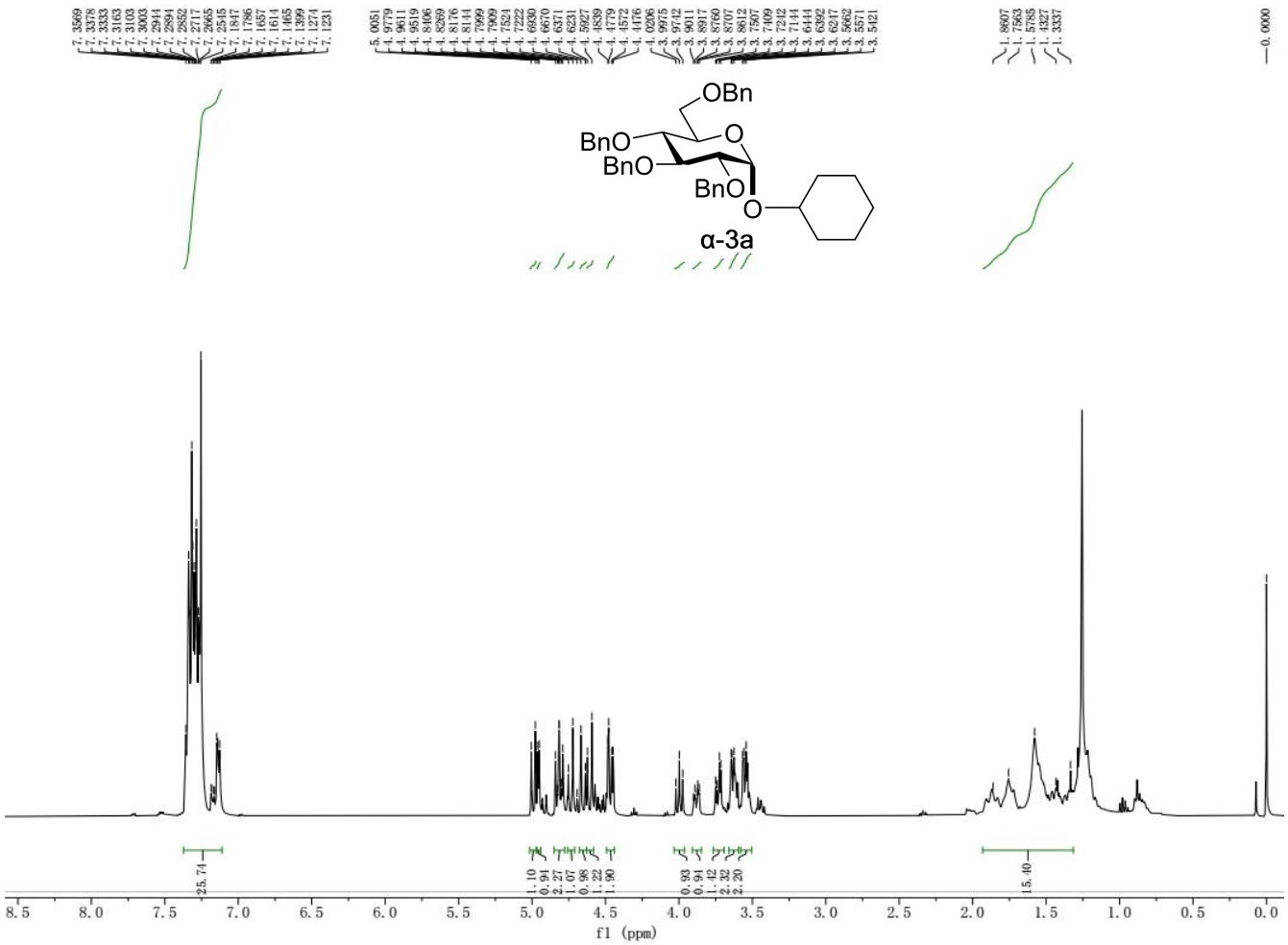


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3a**

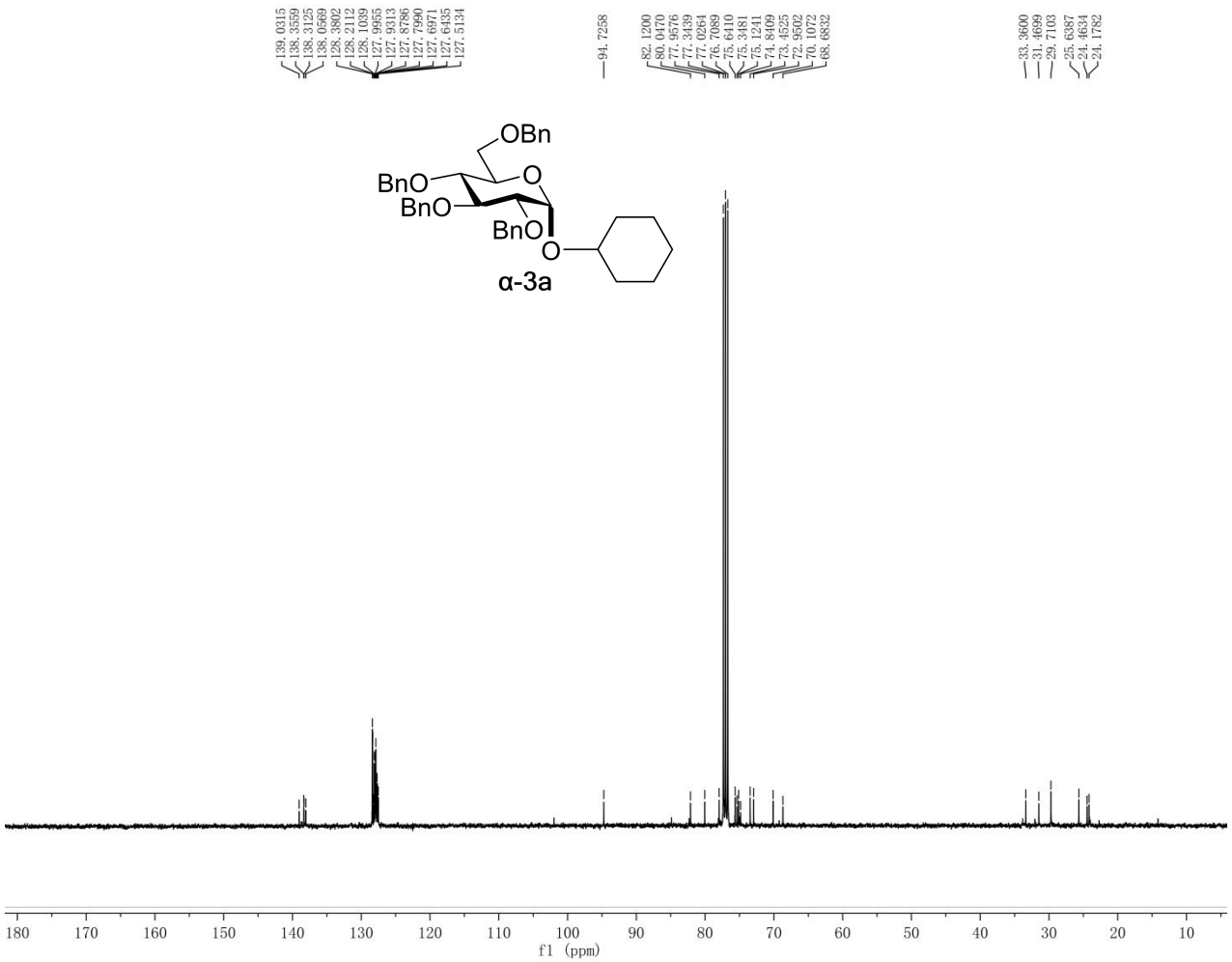


Figure S8. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3a**

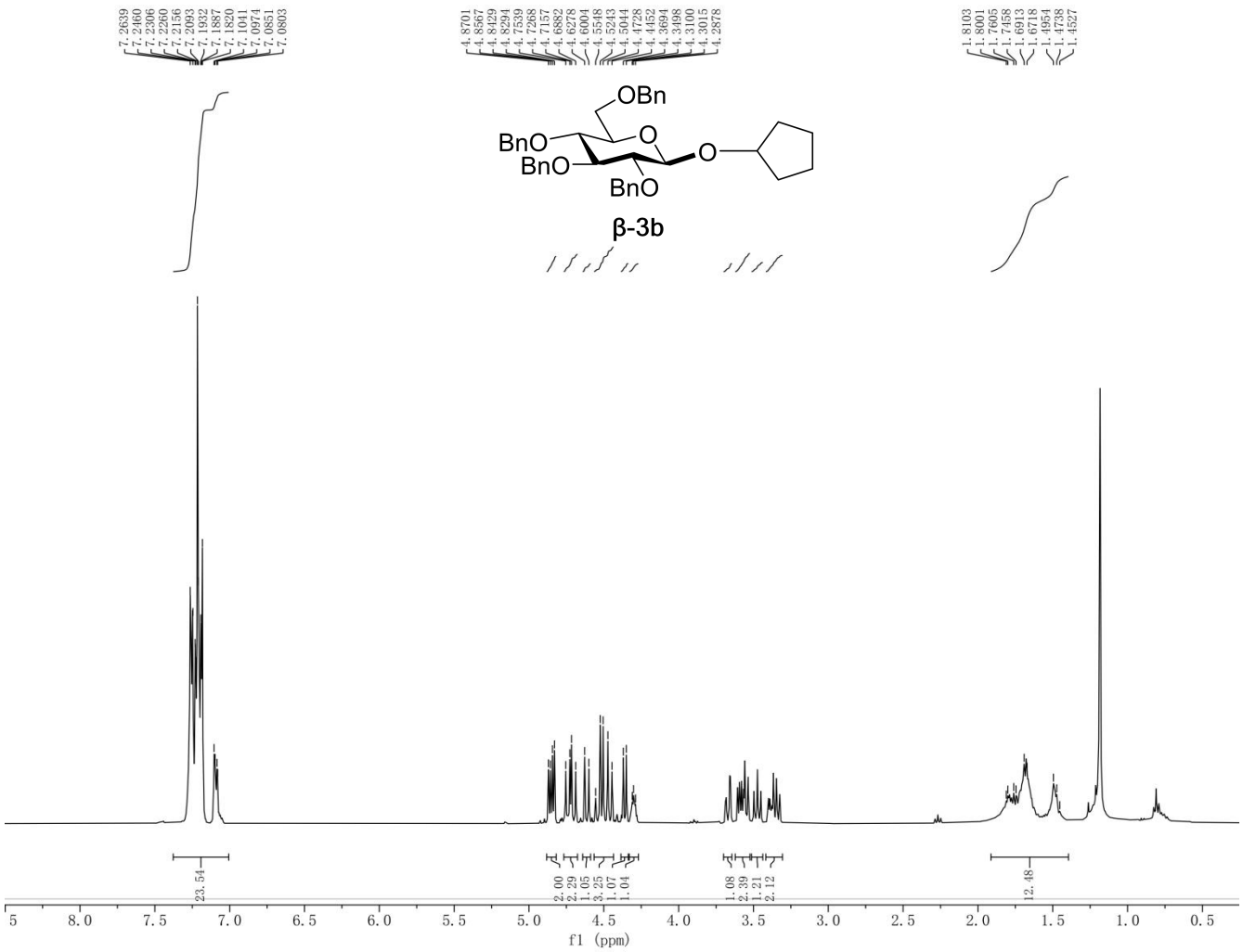


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3b**

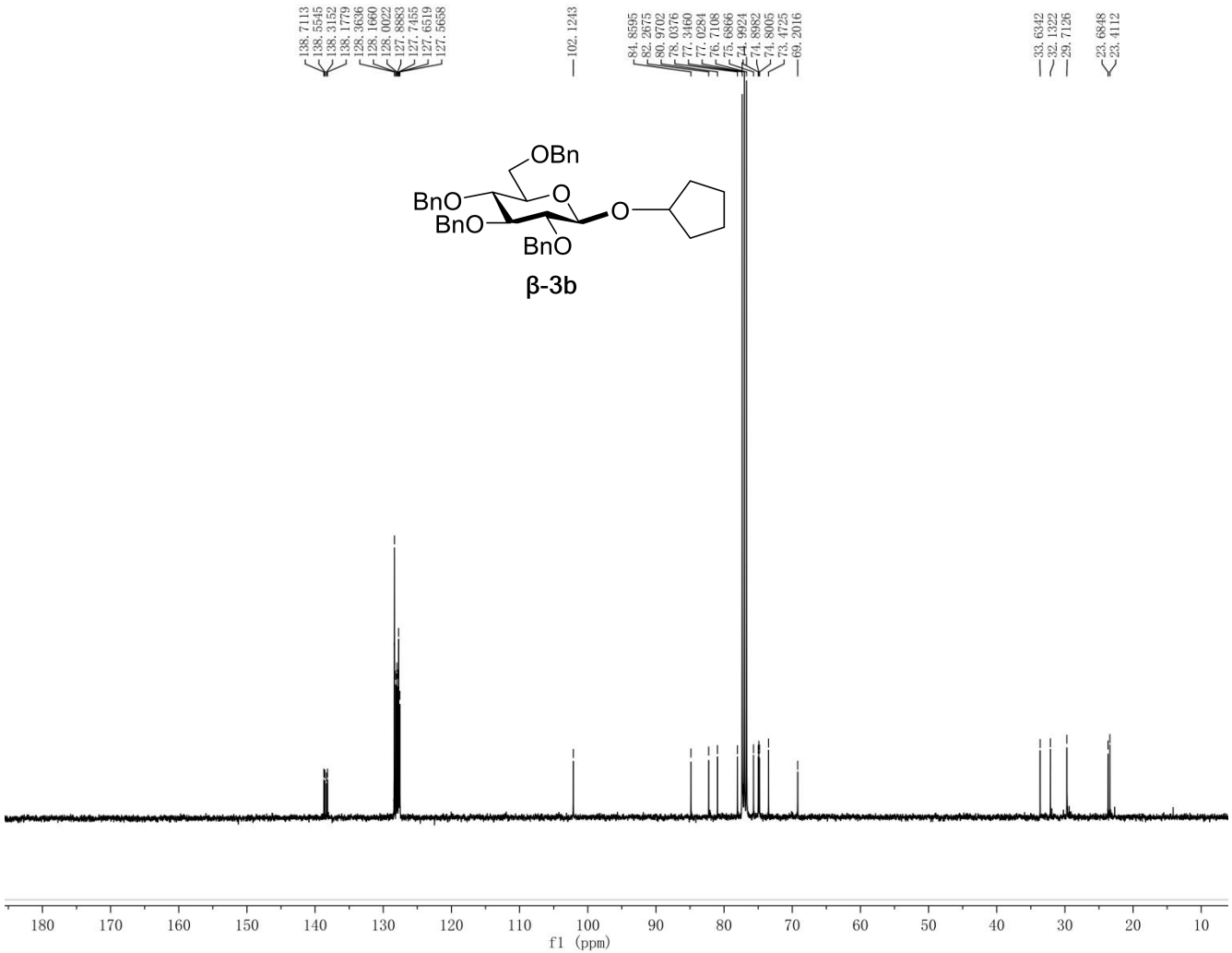


Figure S10. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3b**

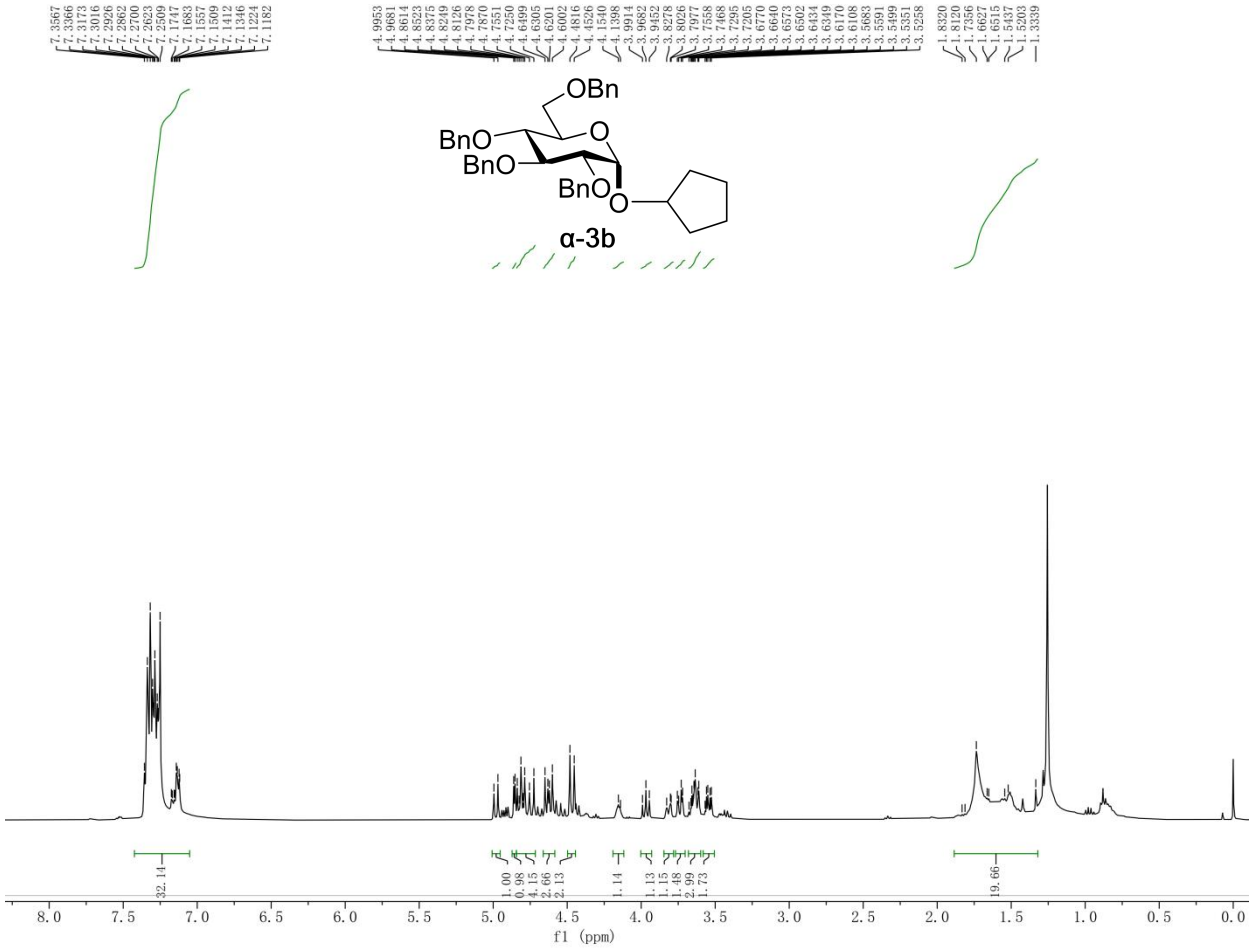


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3b**

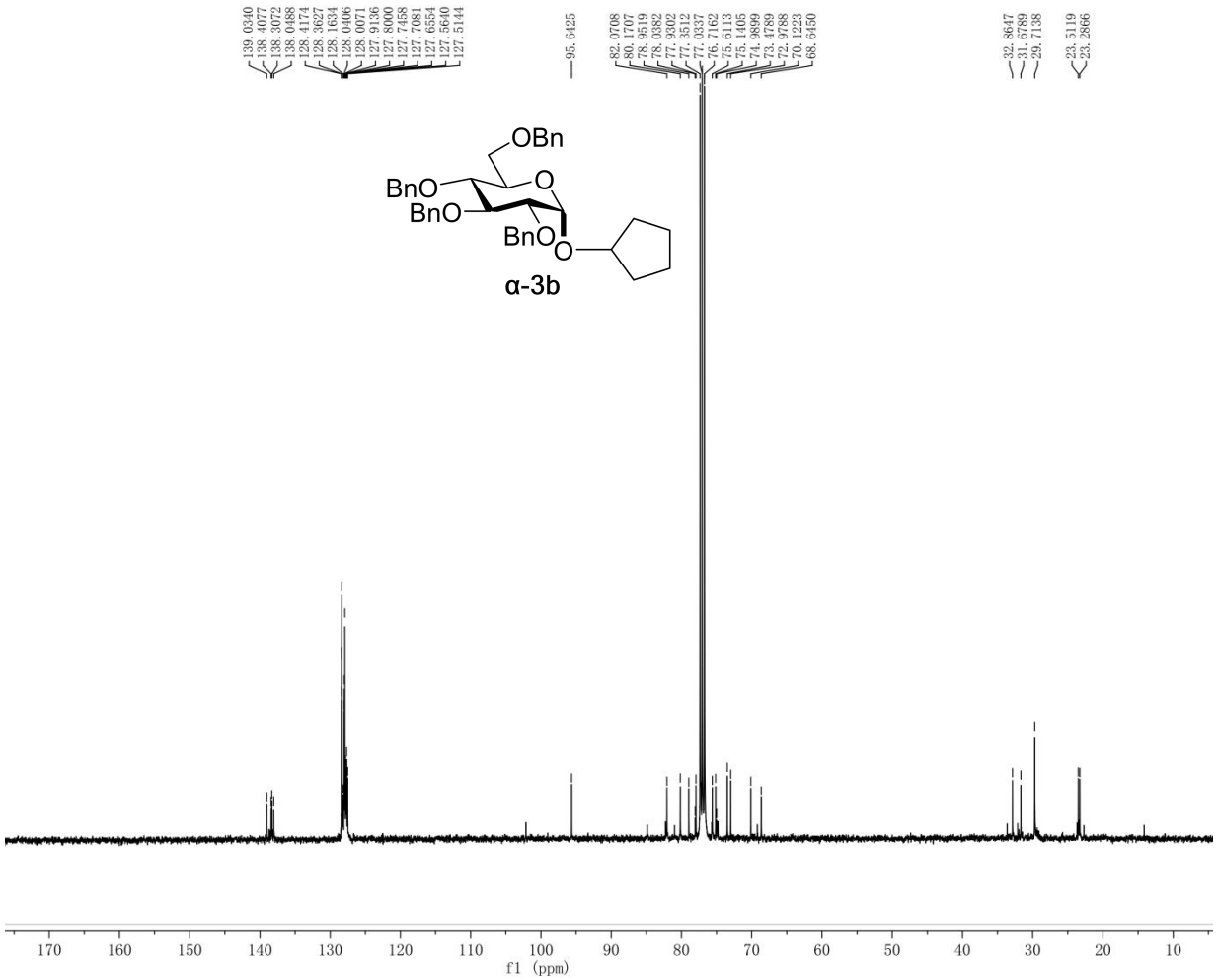


Figure S12. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3b**

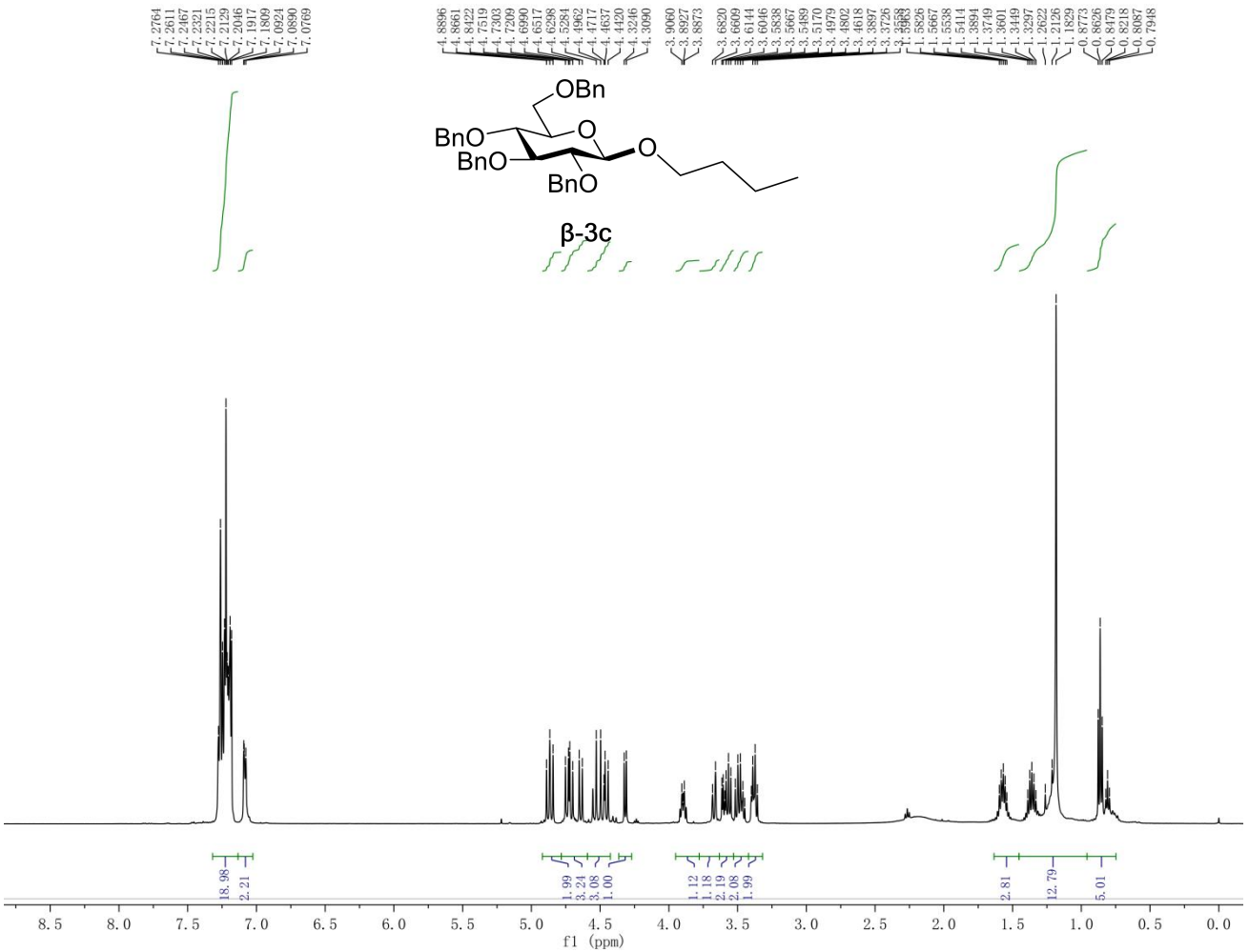


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3c**

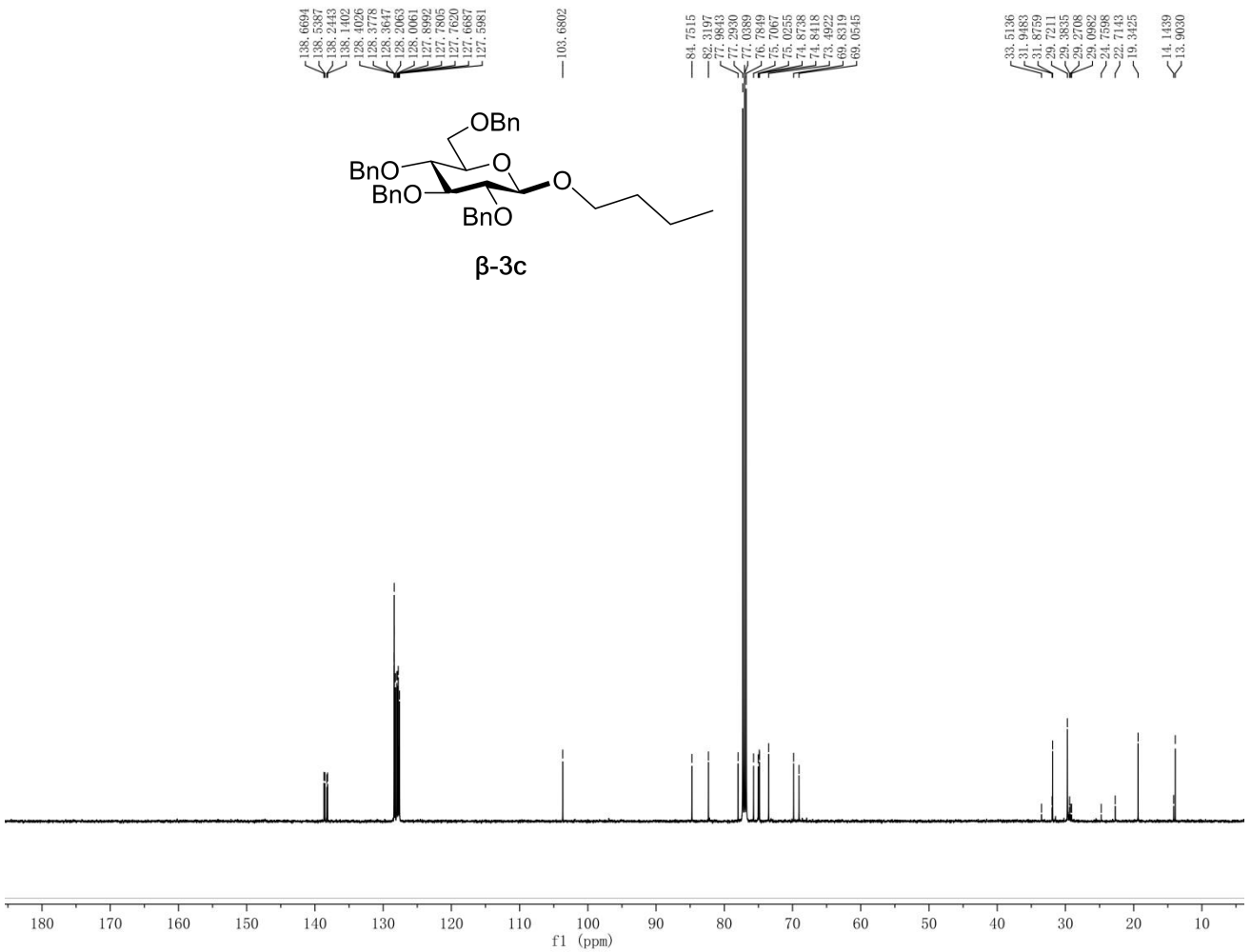


Figure S14. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3c**

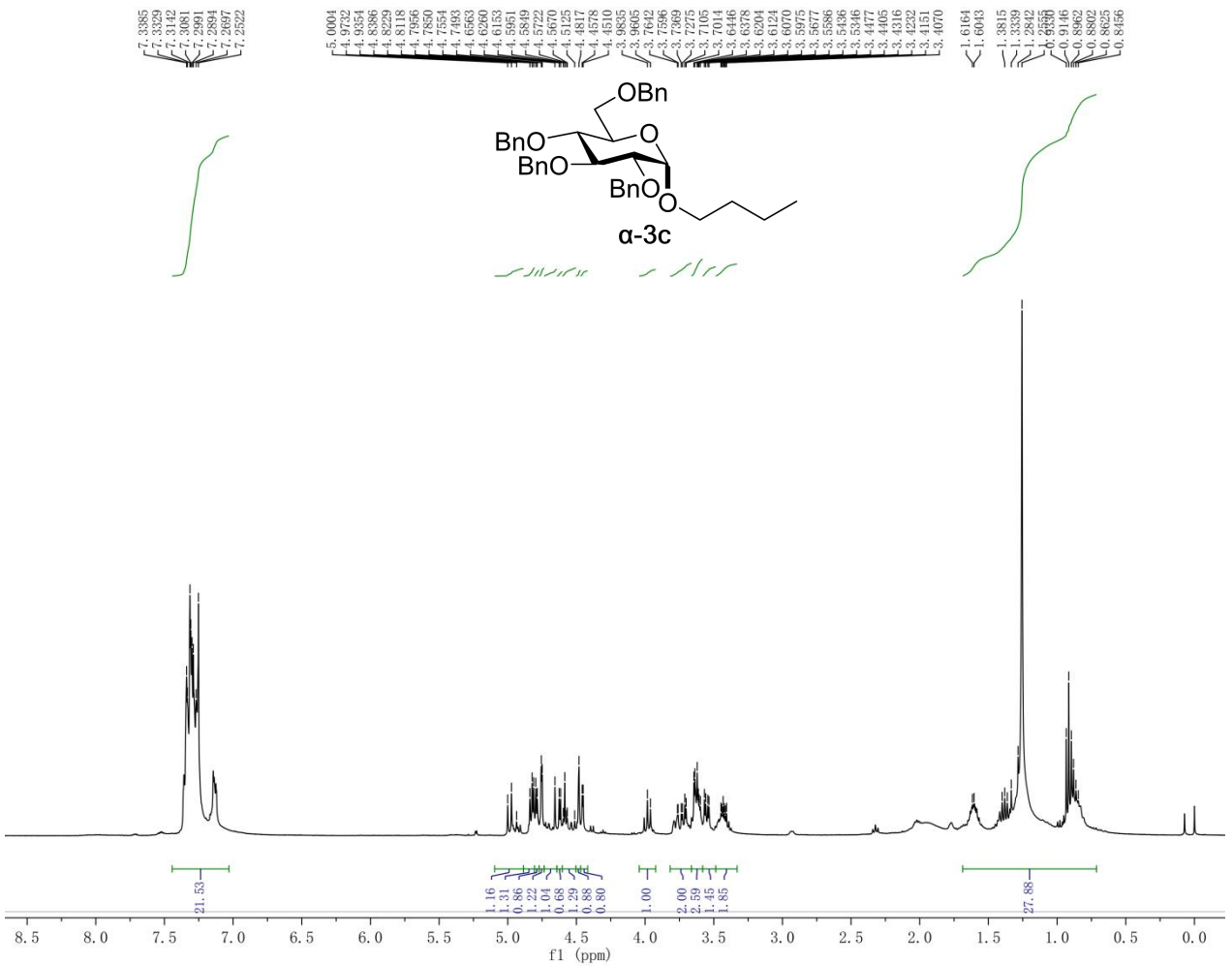


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3c**

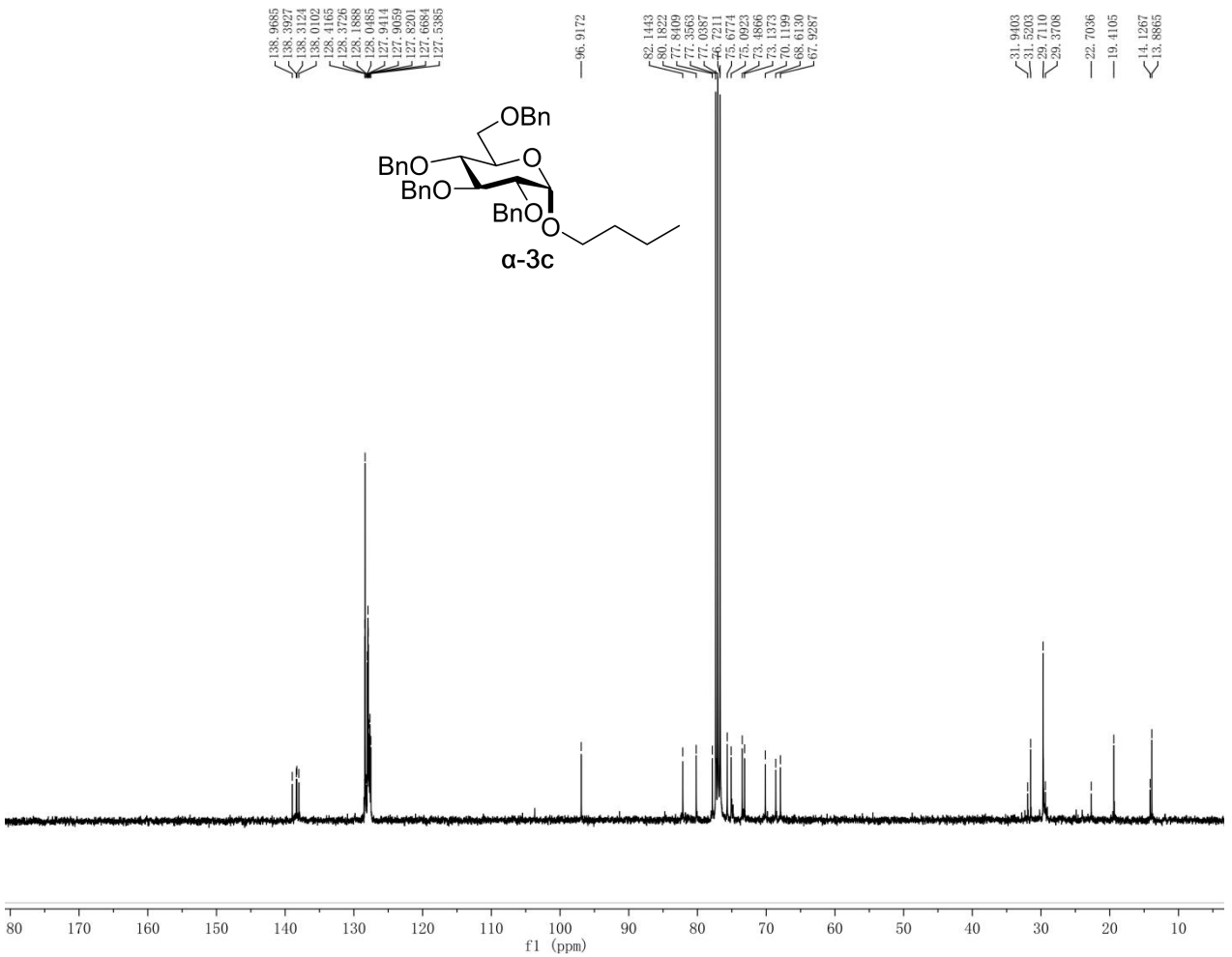


Figure S16. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3c**

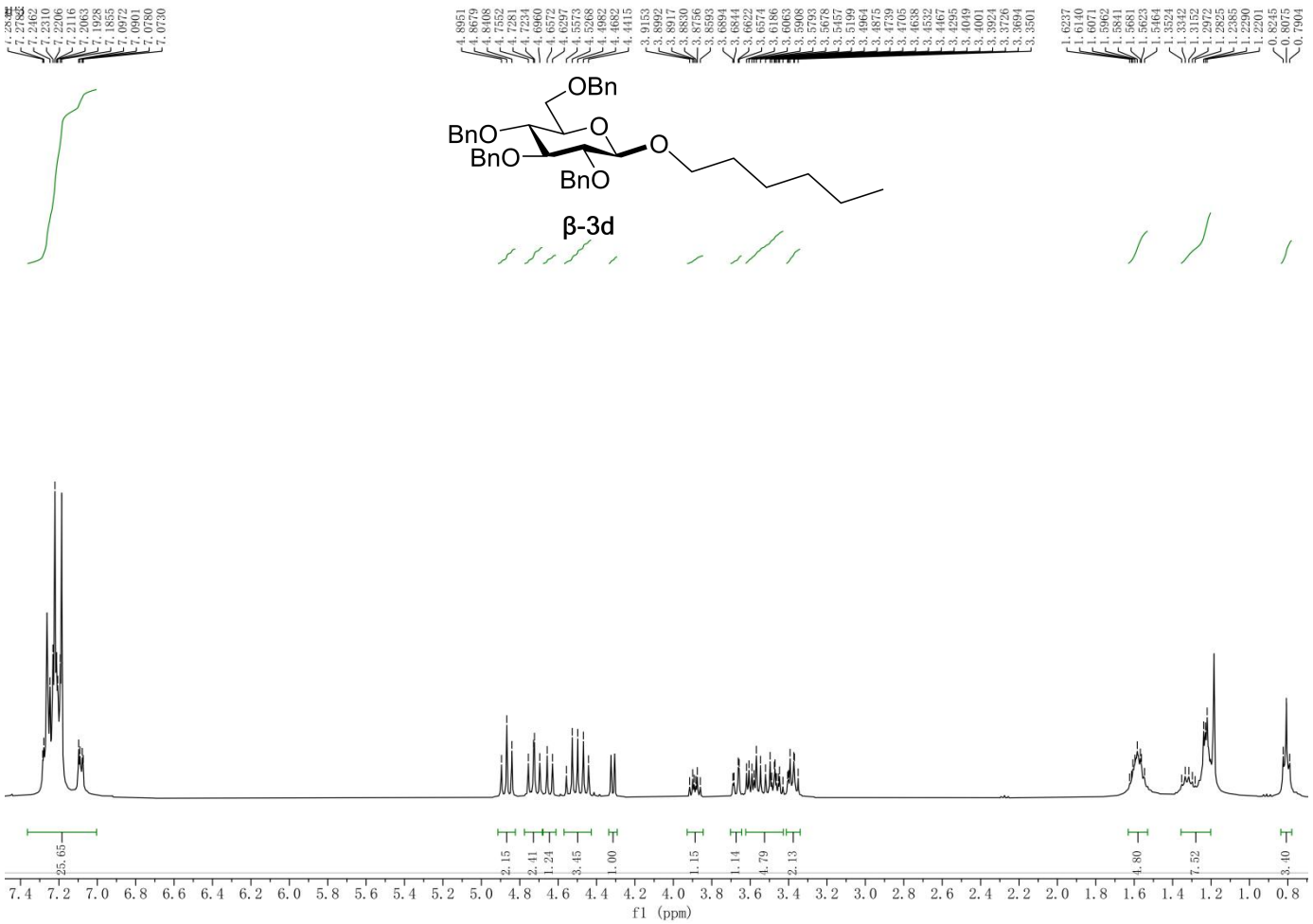


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3d**

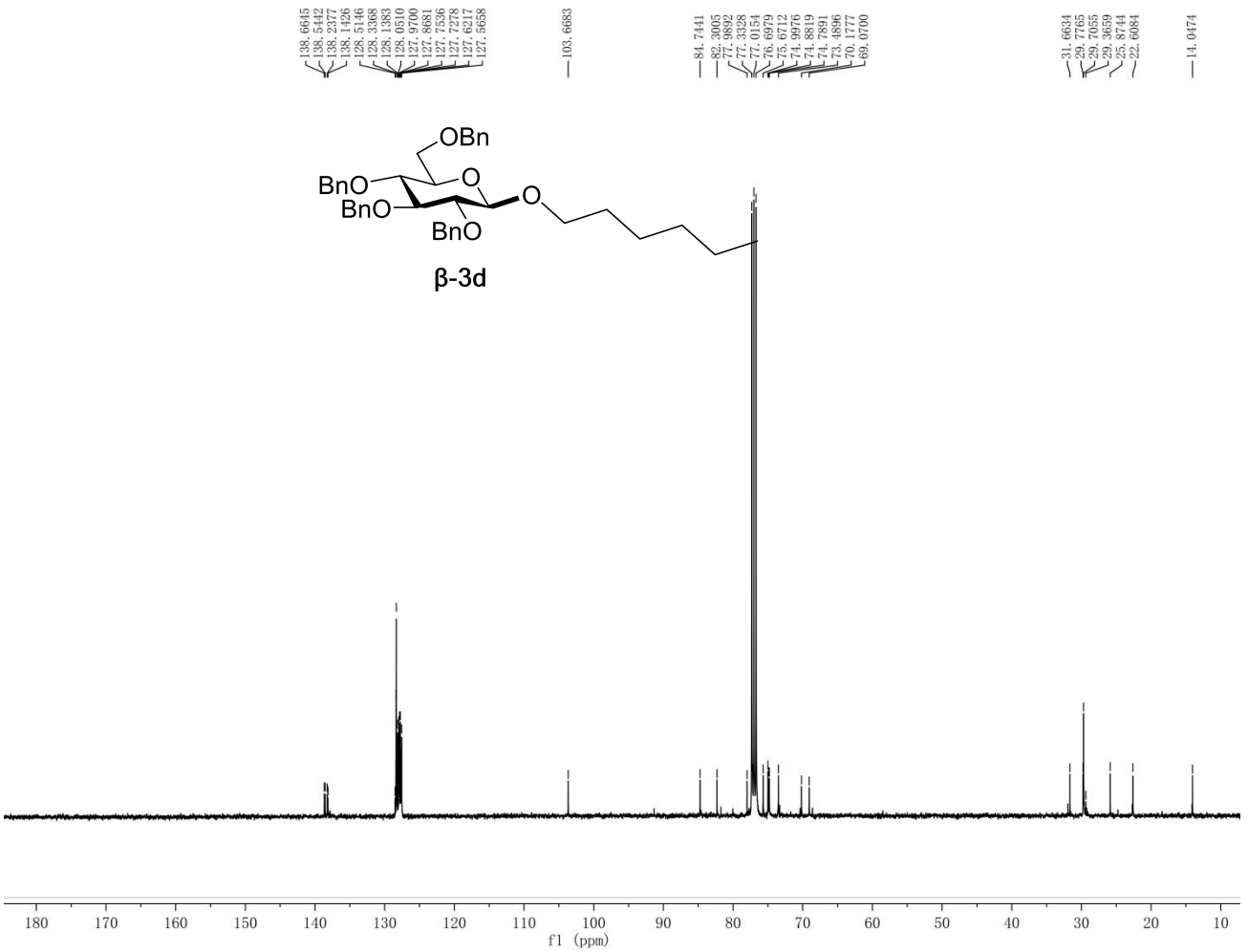


Figure S18. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3d**

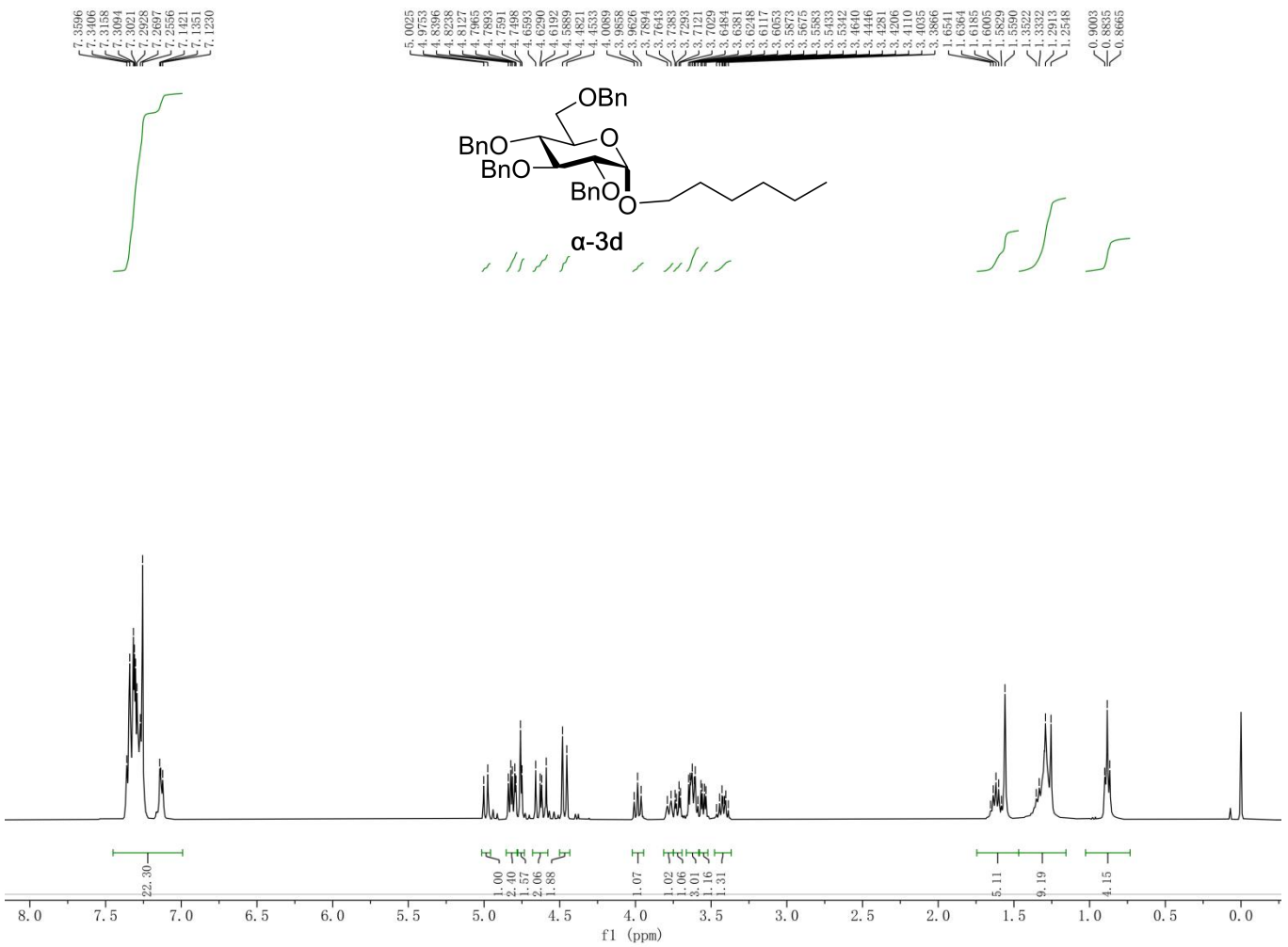


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3d**

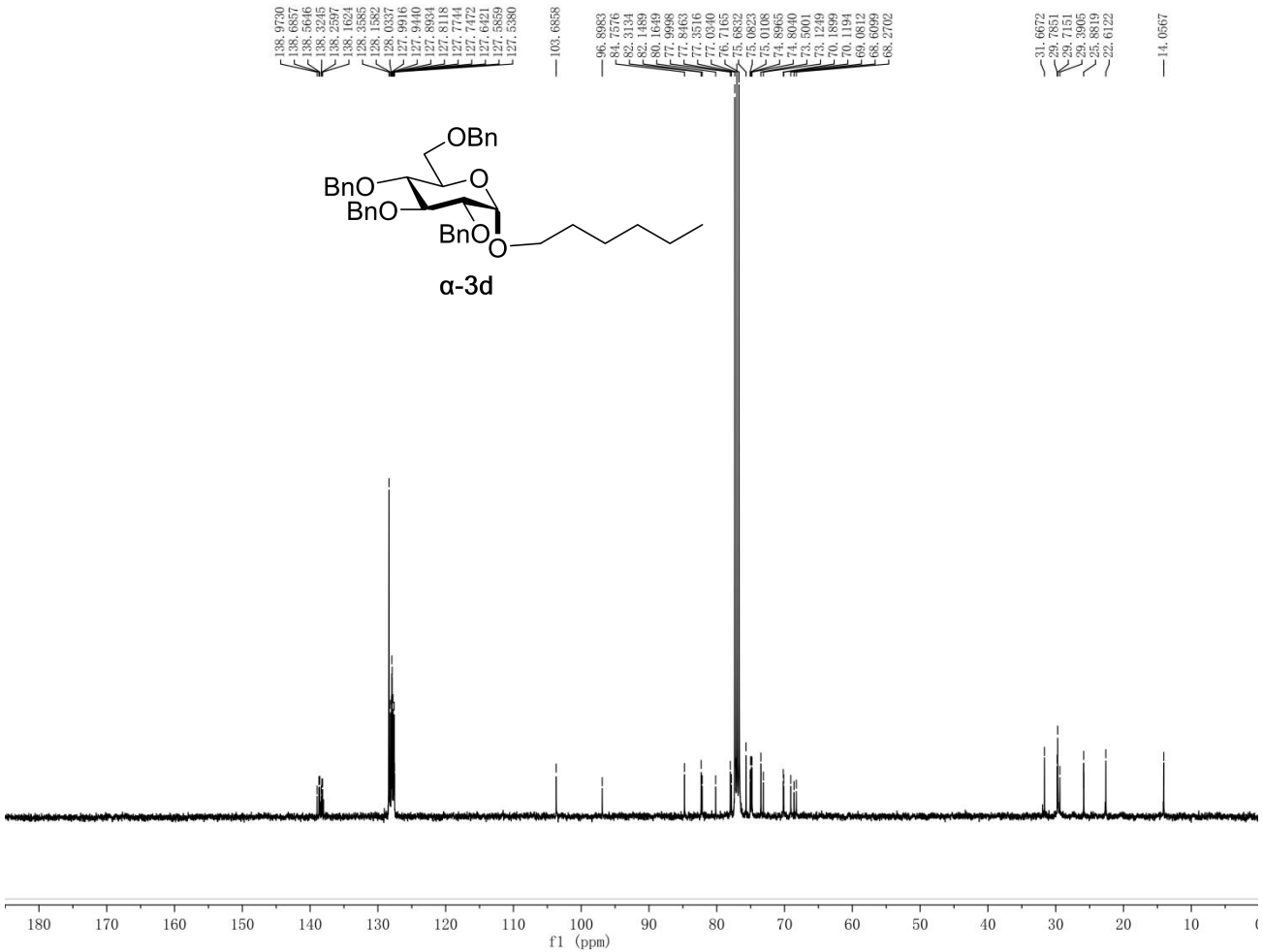


Figure S20. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3d**

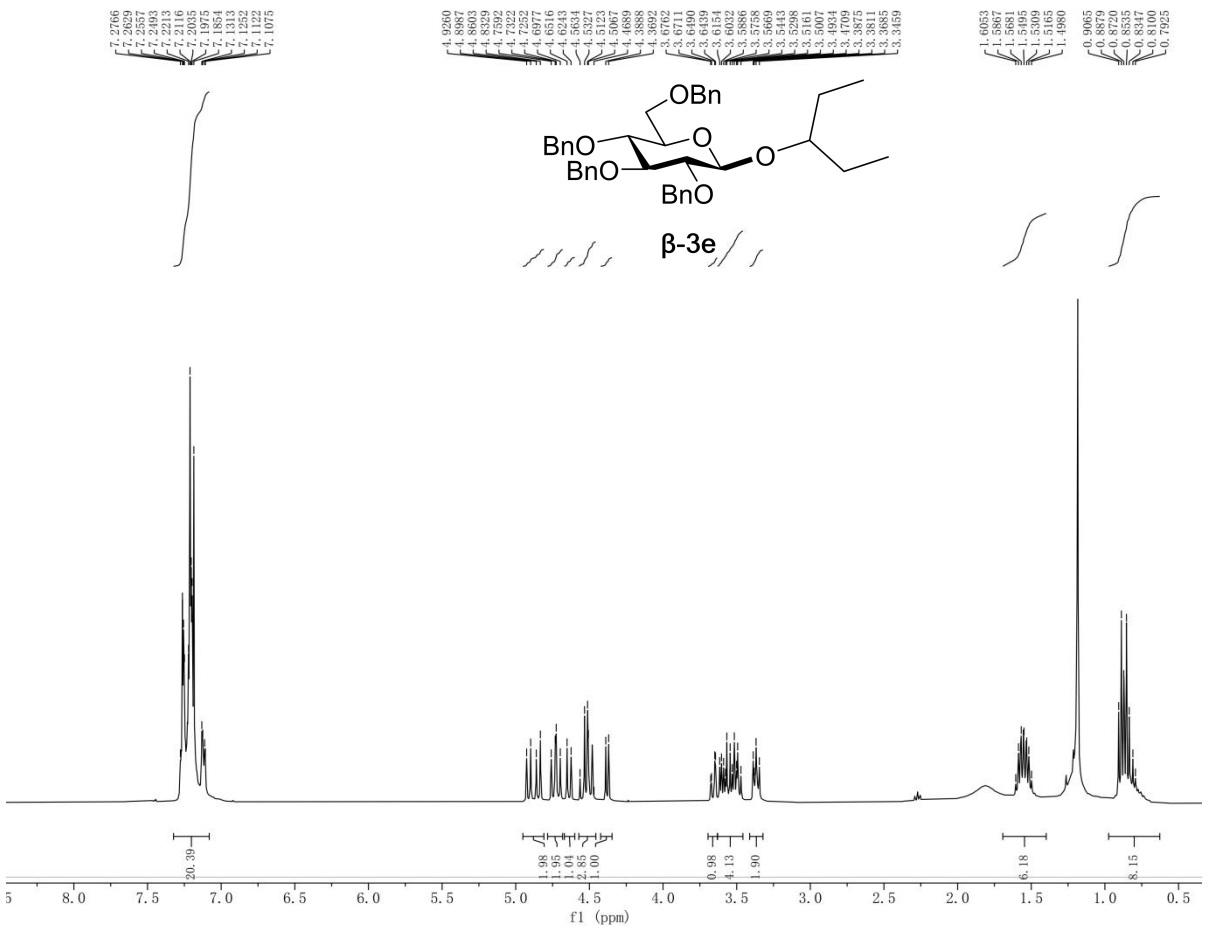


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3e**

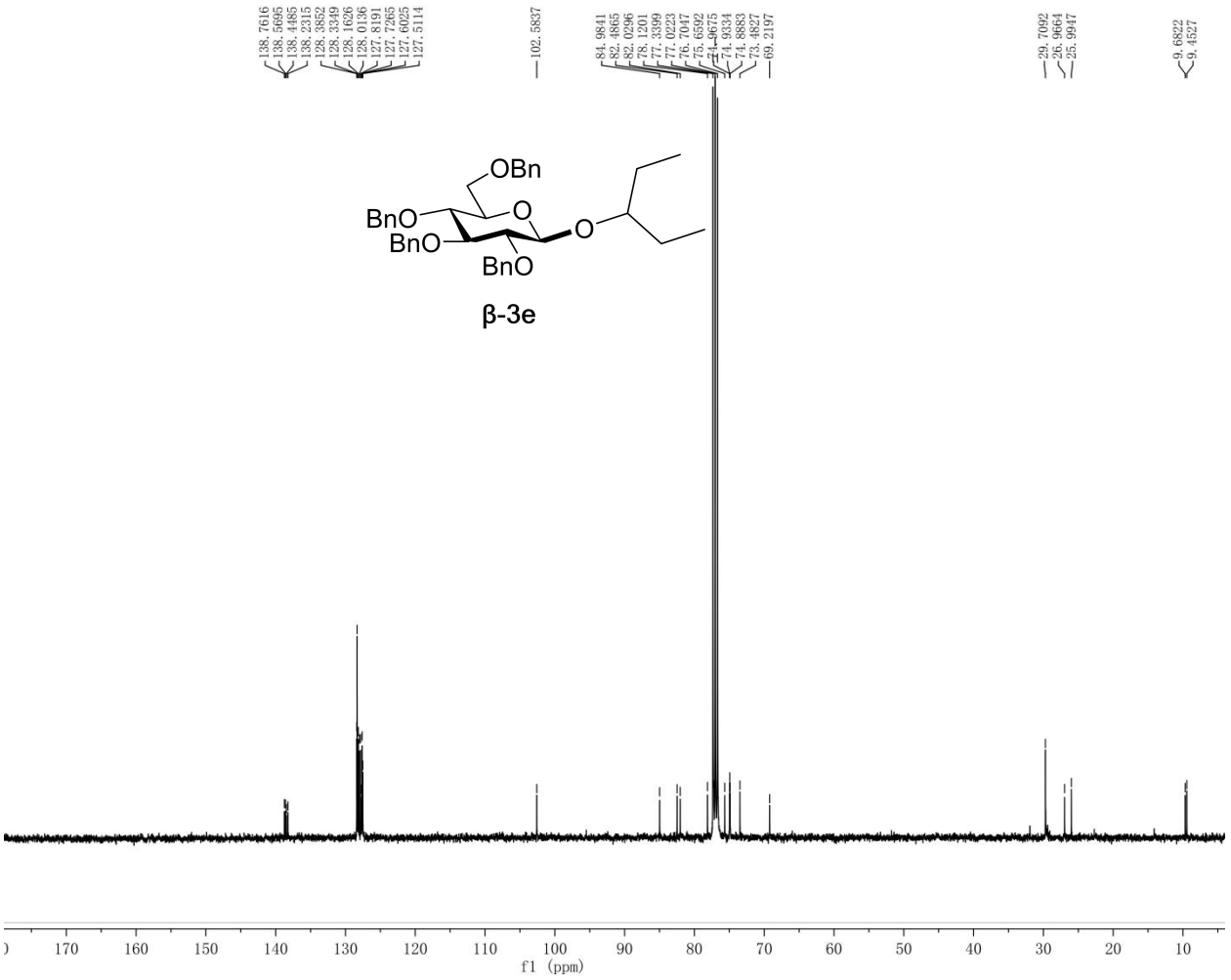


Figure S22. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3e**

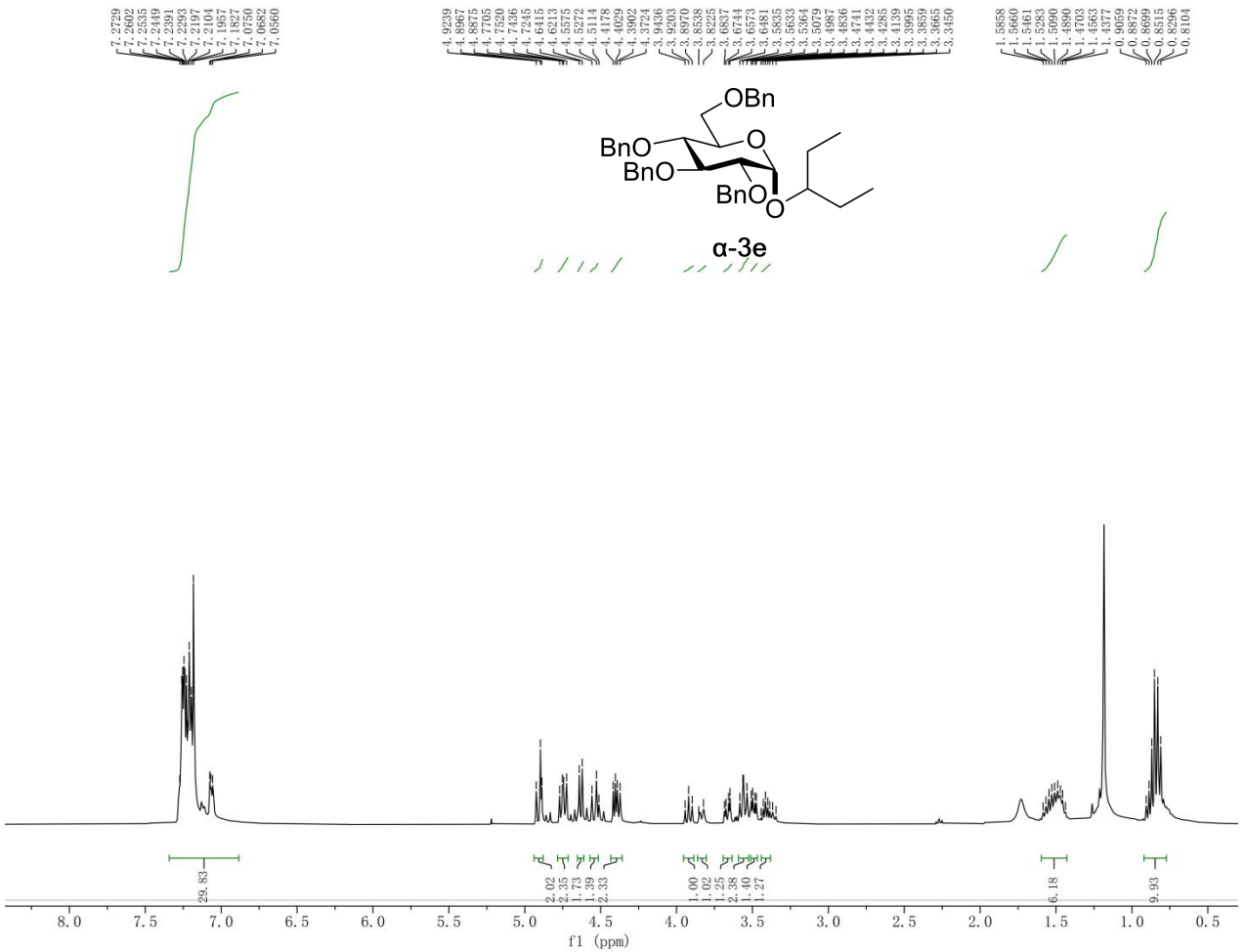


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3e**

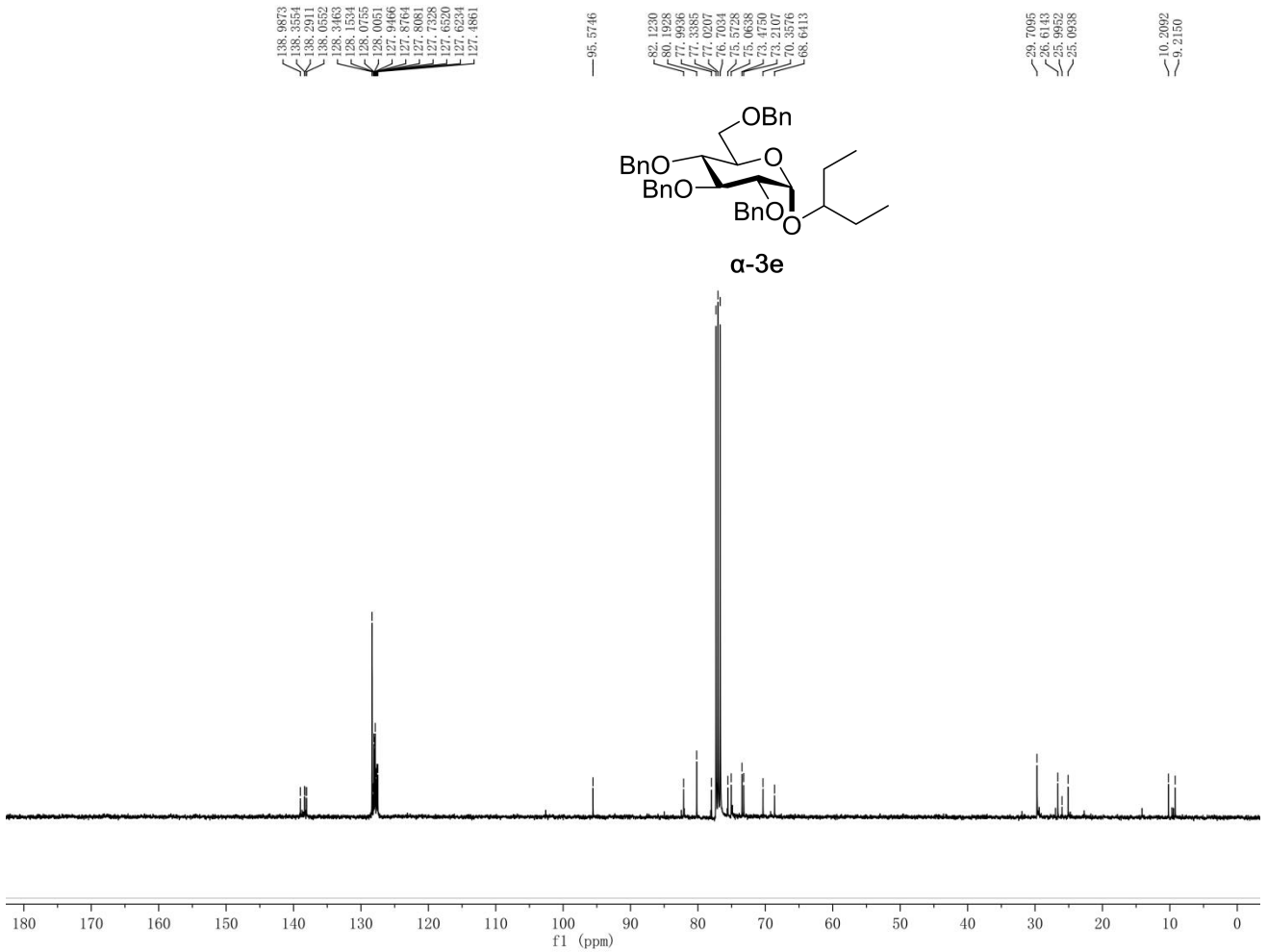


Figure S24. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3e**

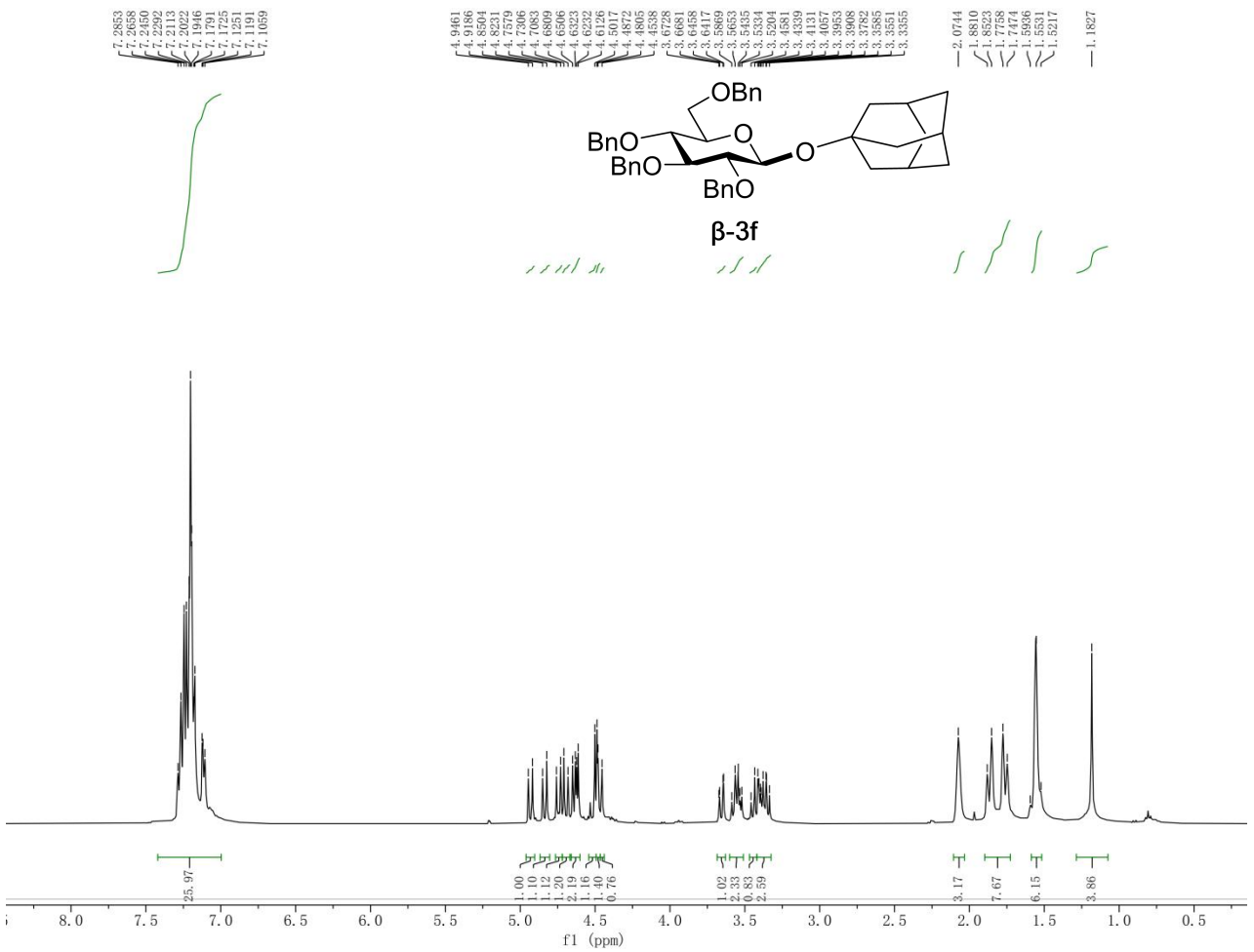


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3f**

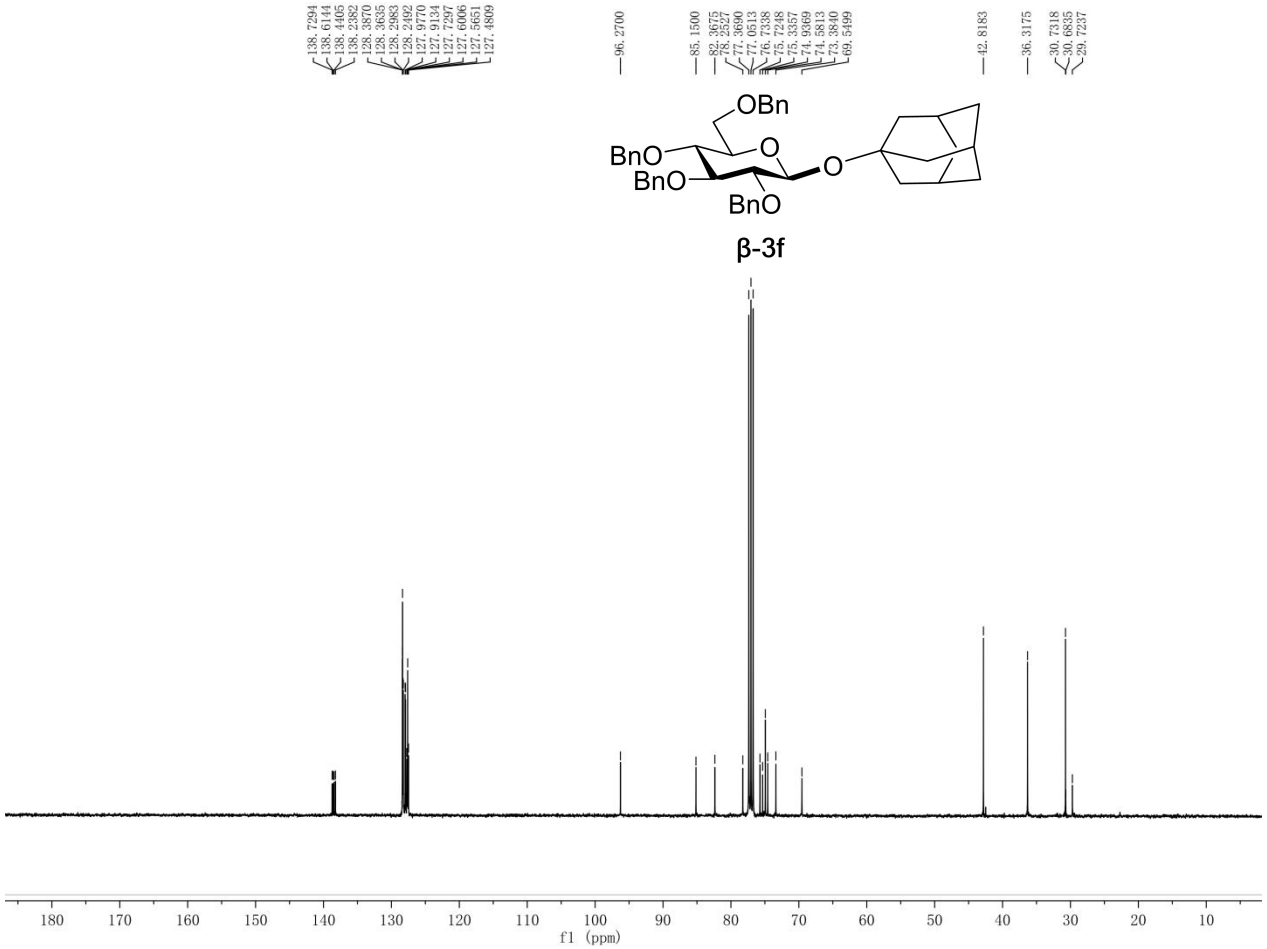


Figure S26. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3f**

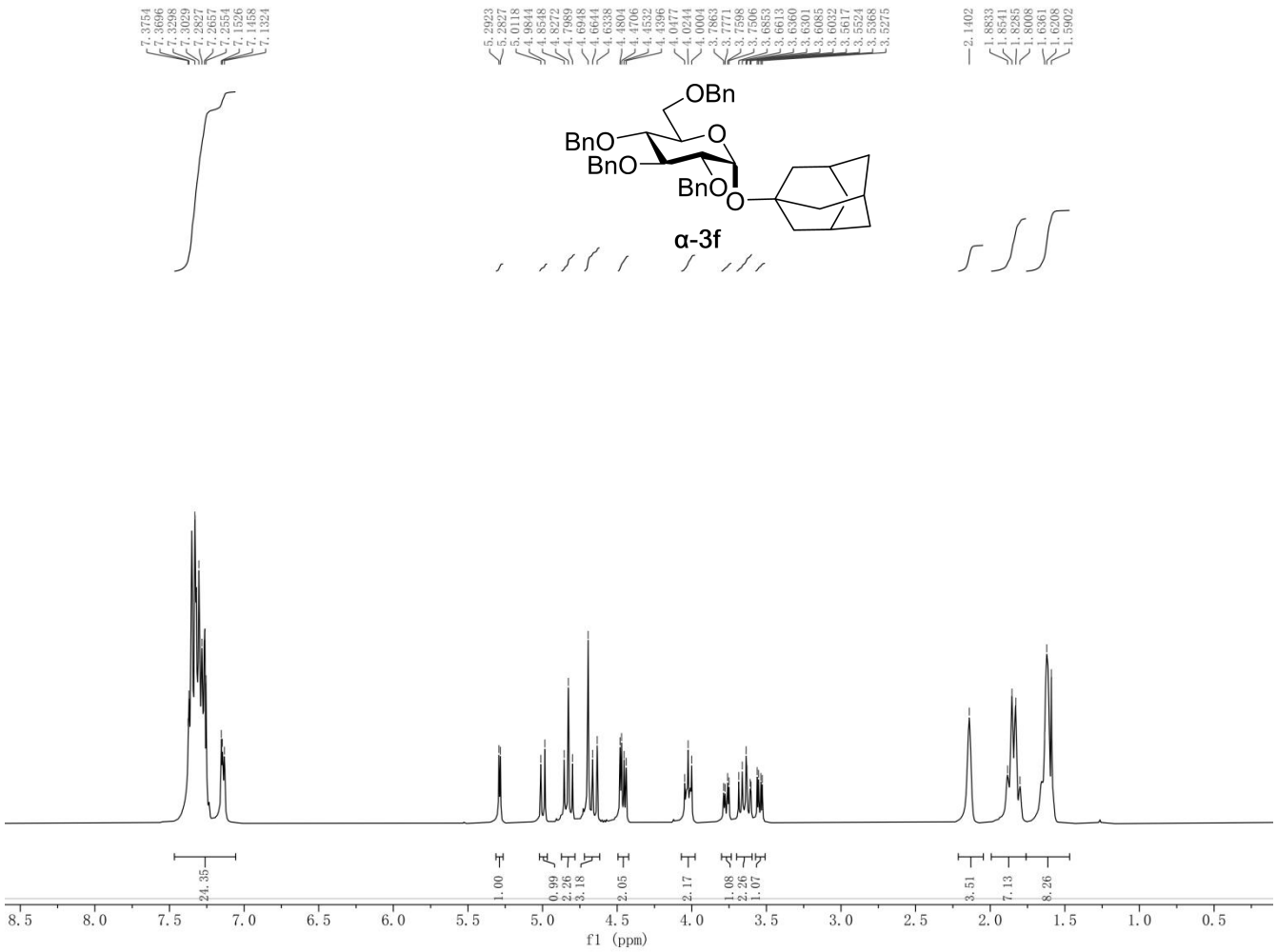


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3f**

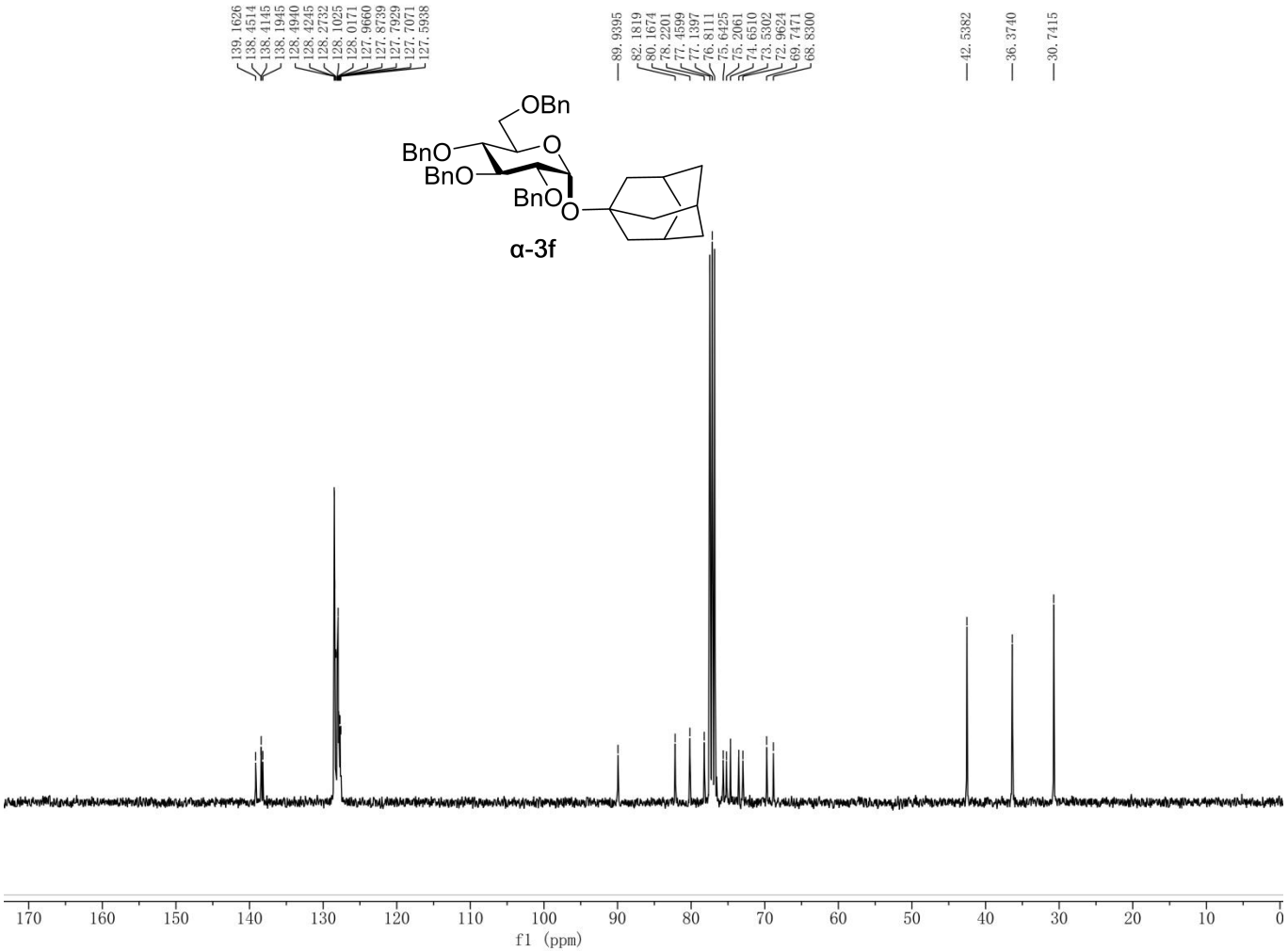


Figure S28. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3f**

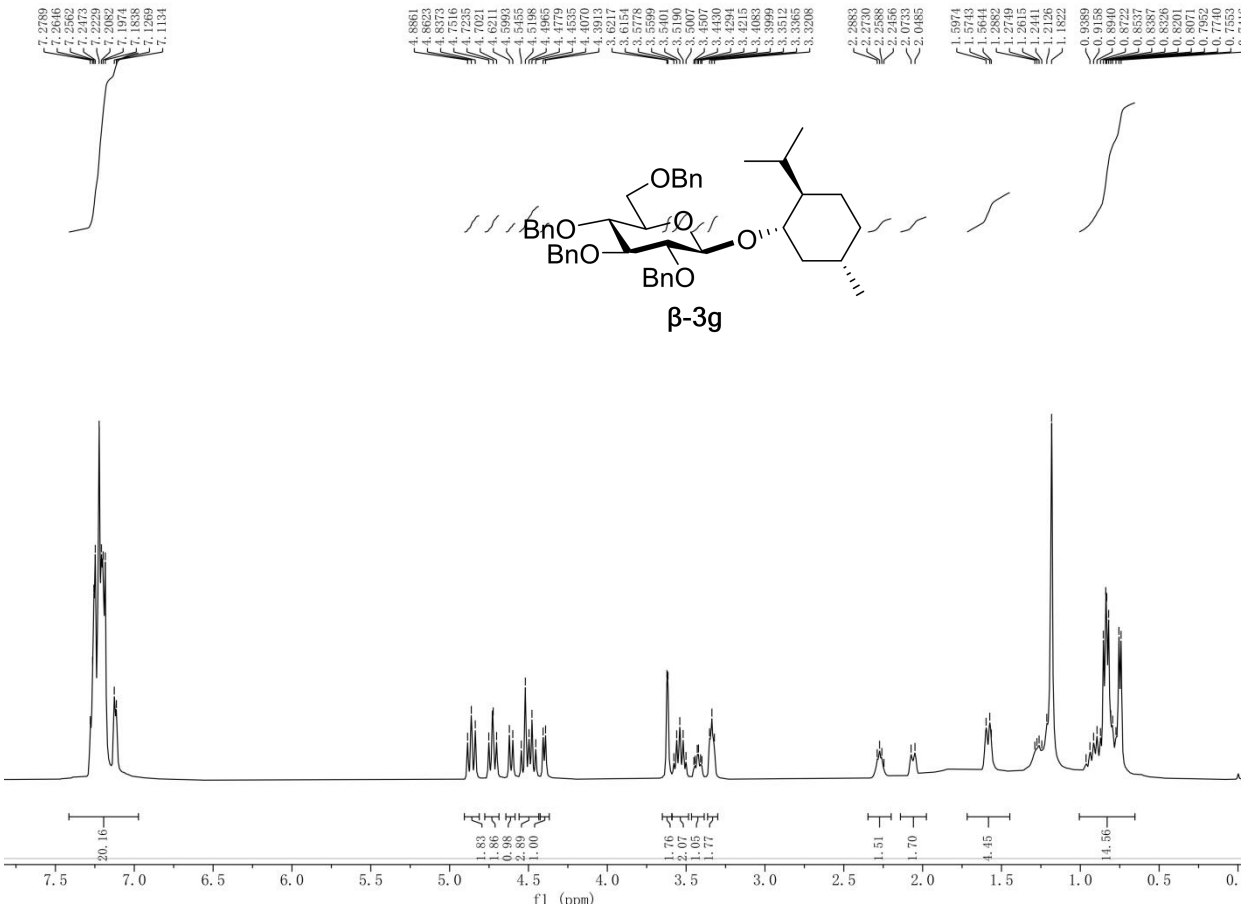


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3g**

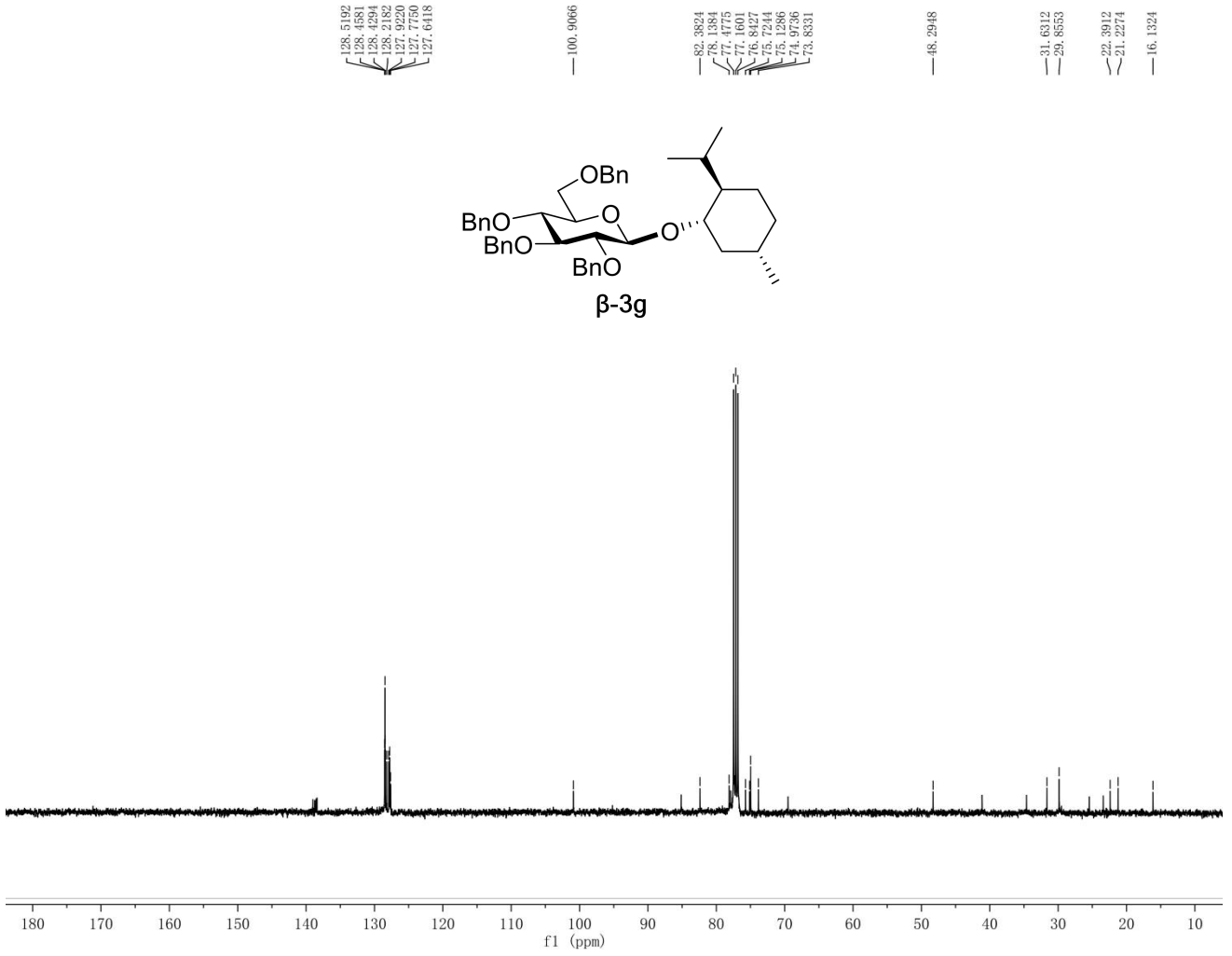


Figure S30. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3g**

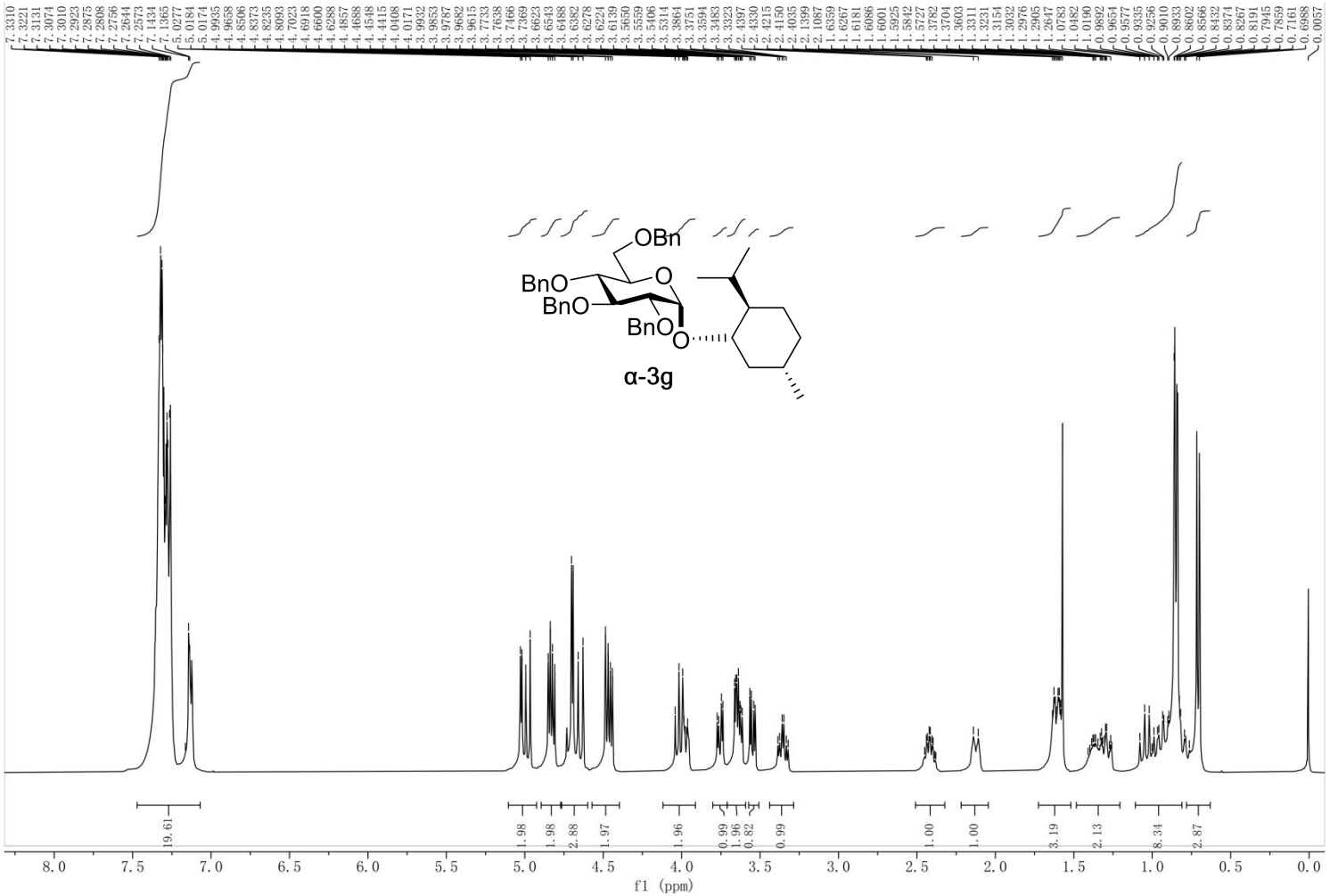


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3g**

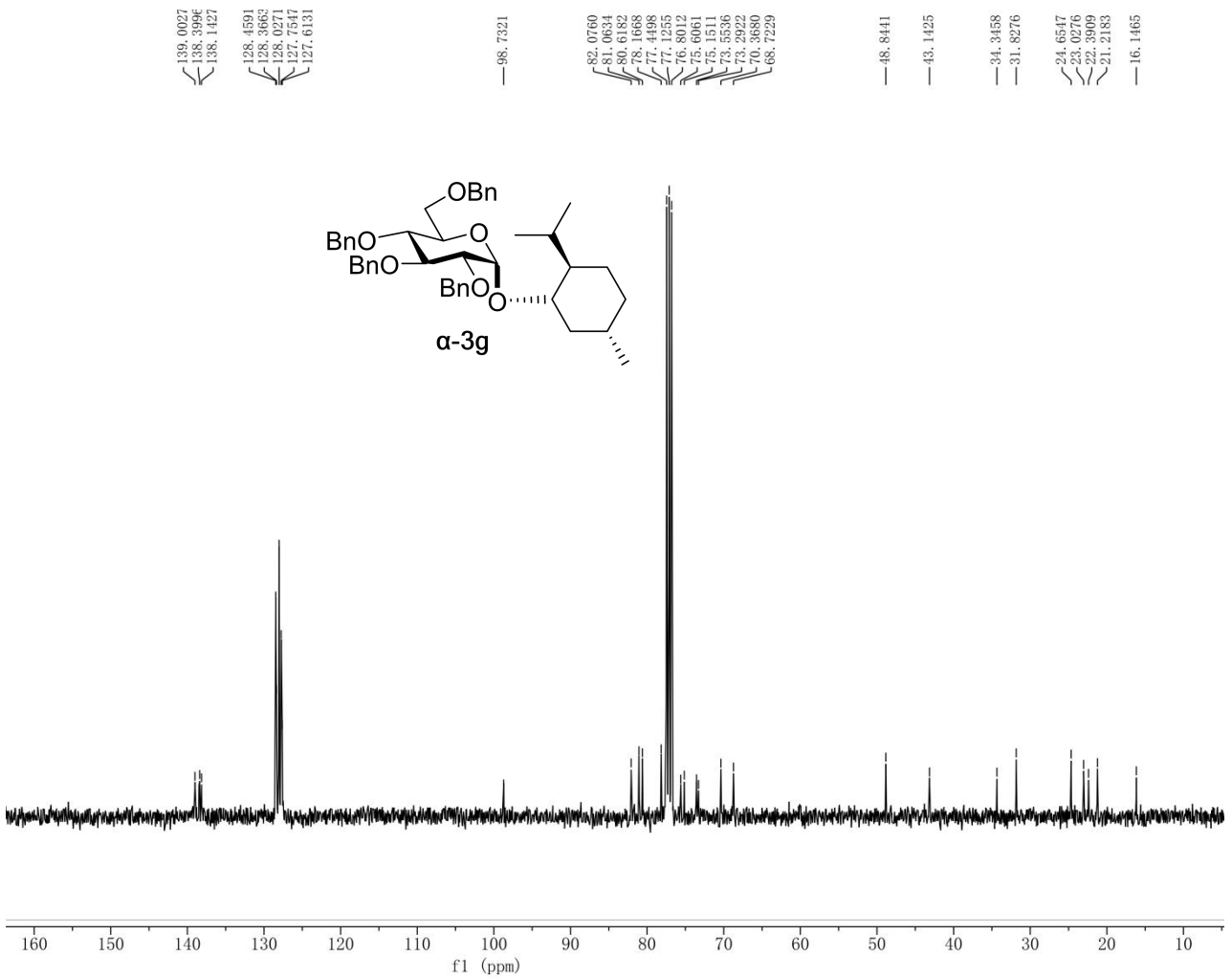


Figure S32. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3g**

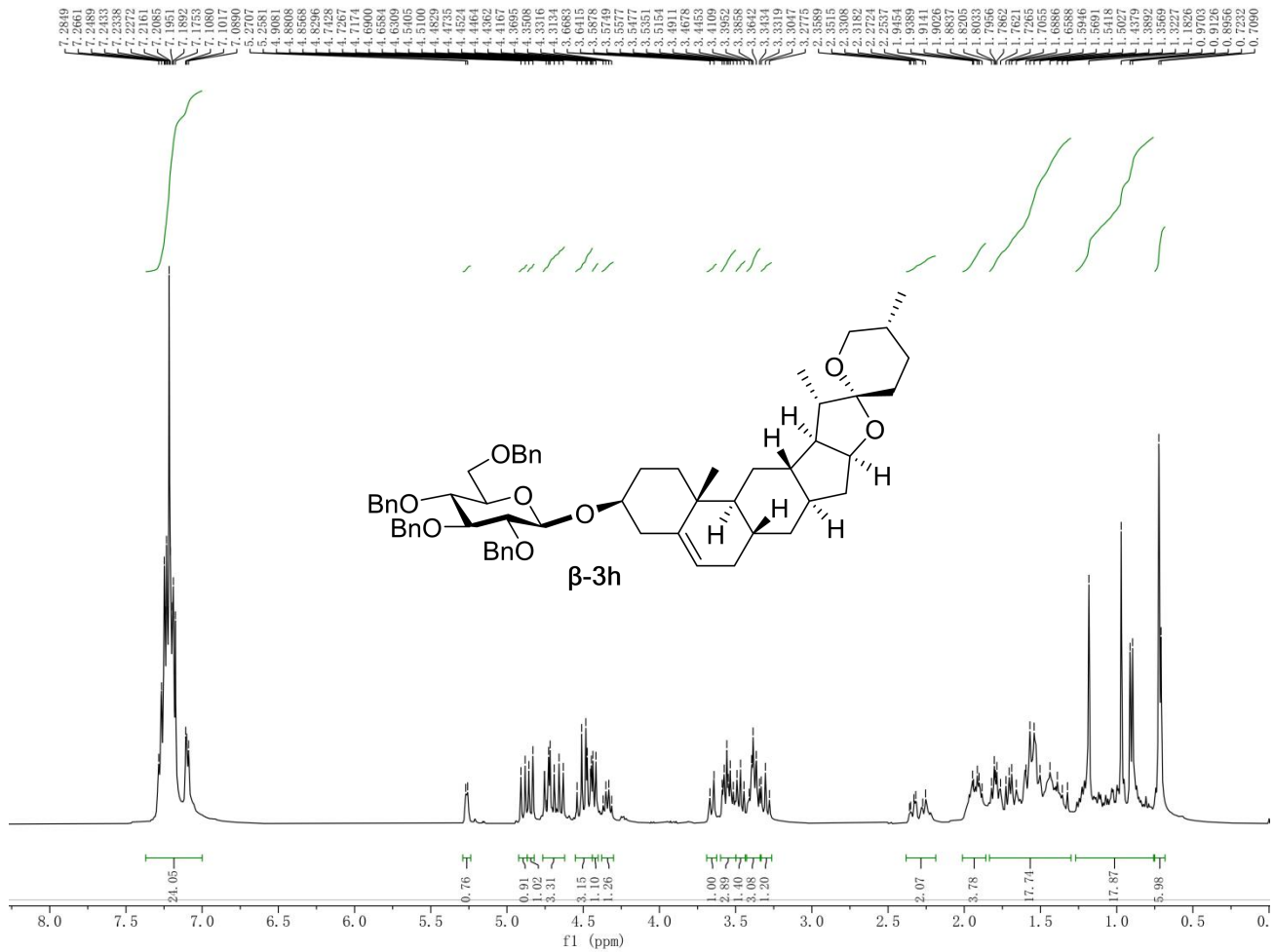


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3h**

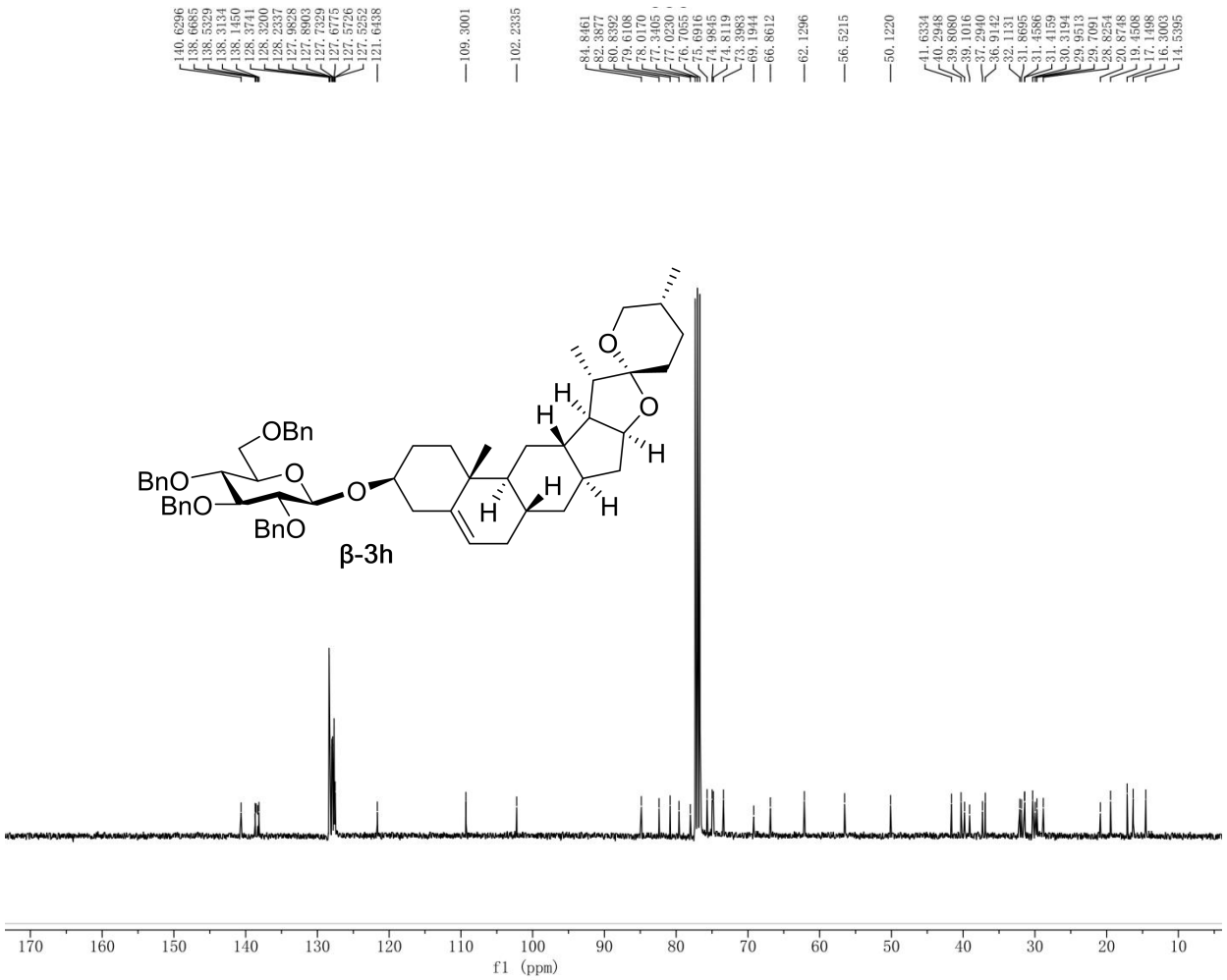


Figure S34. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3h**

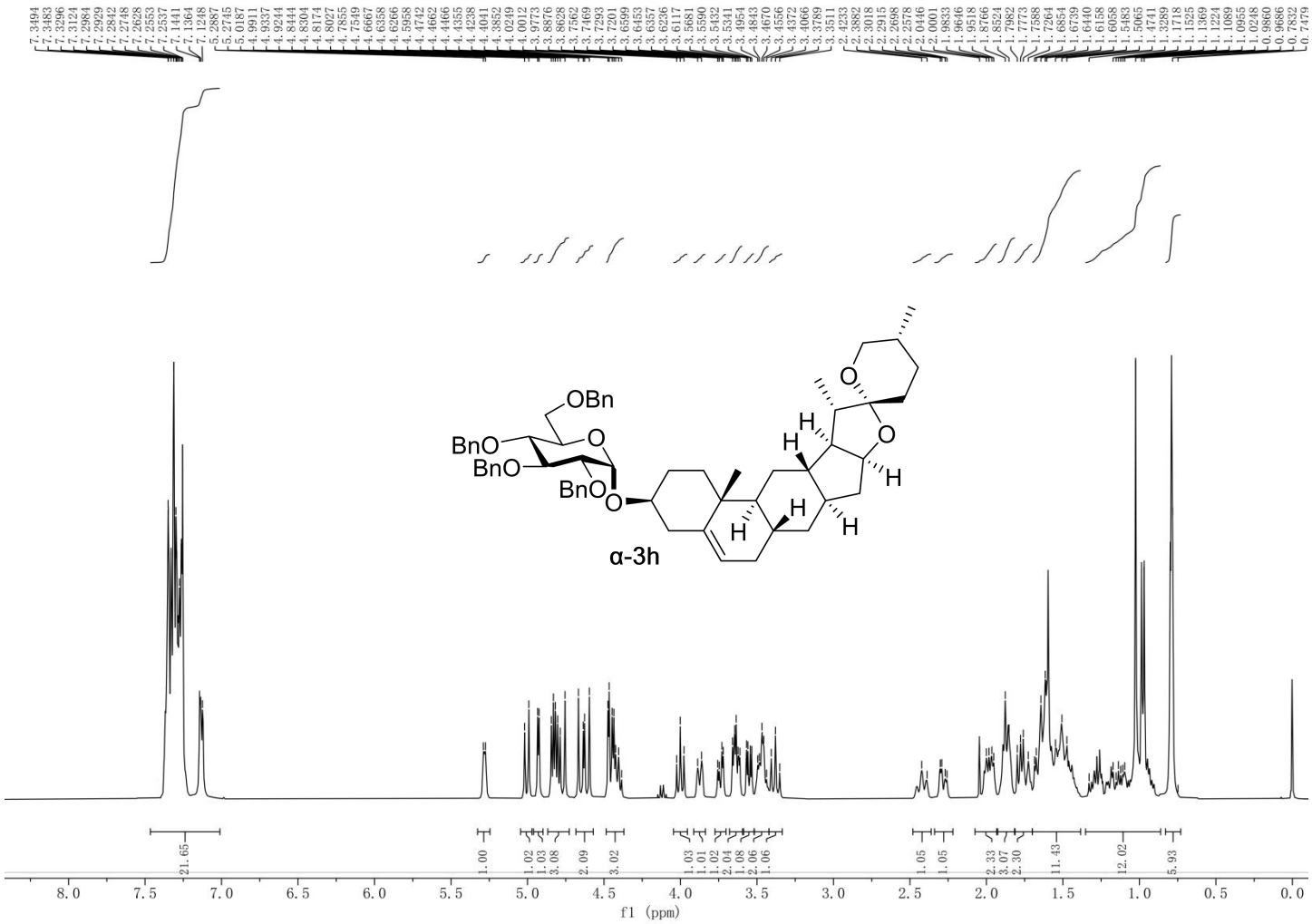


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3h**

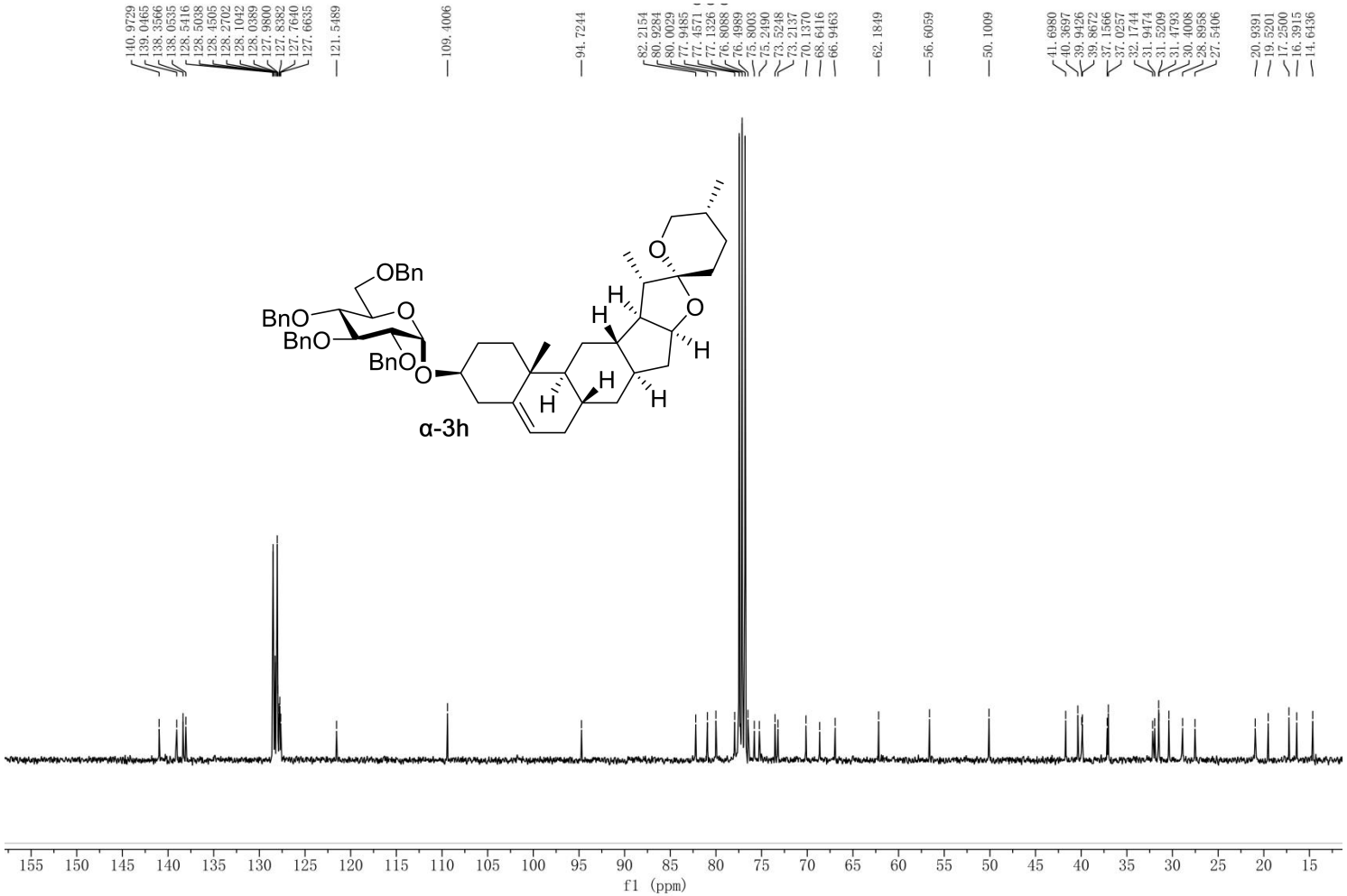


Figure S36. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3h**

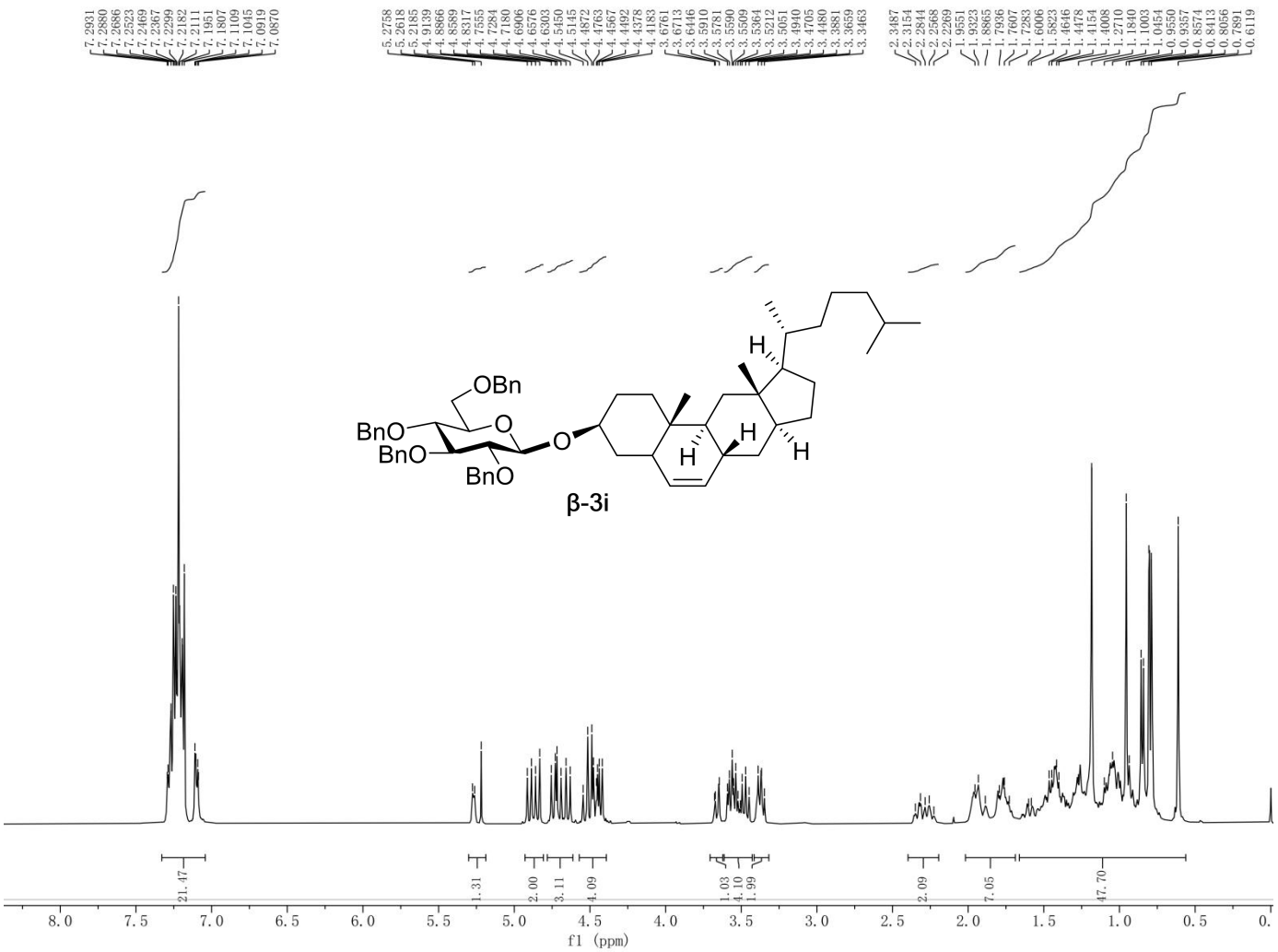


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of

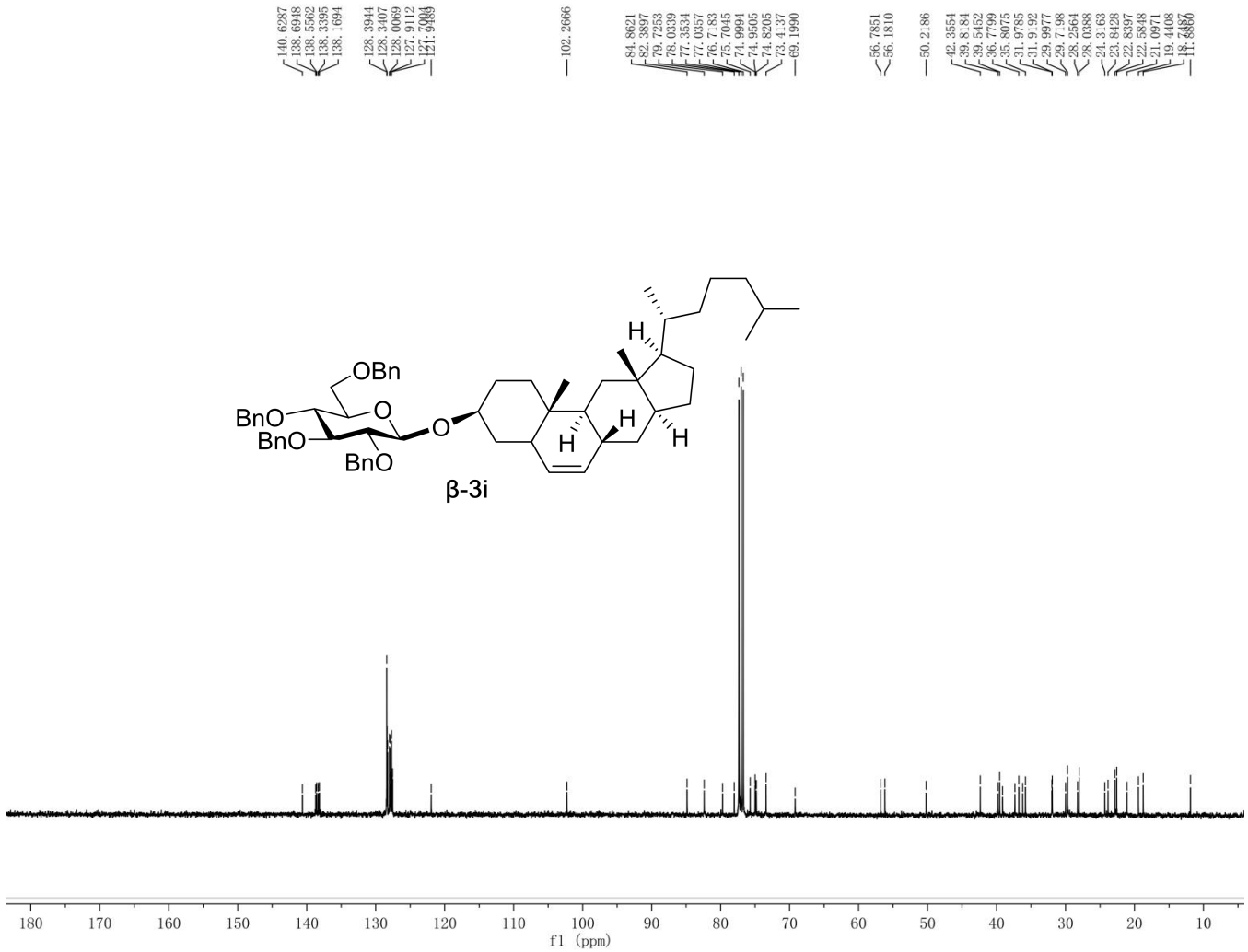


Figure S38. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3i**

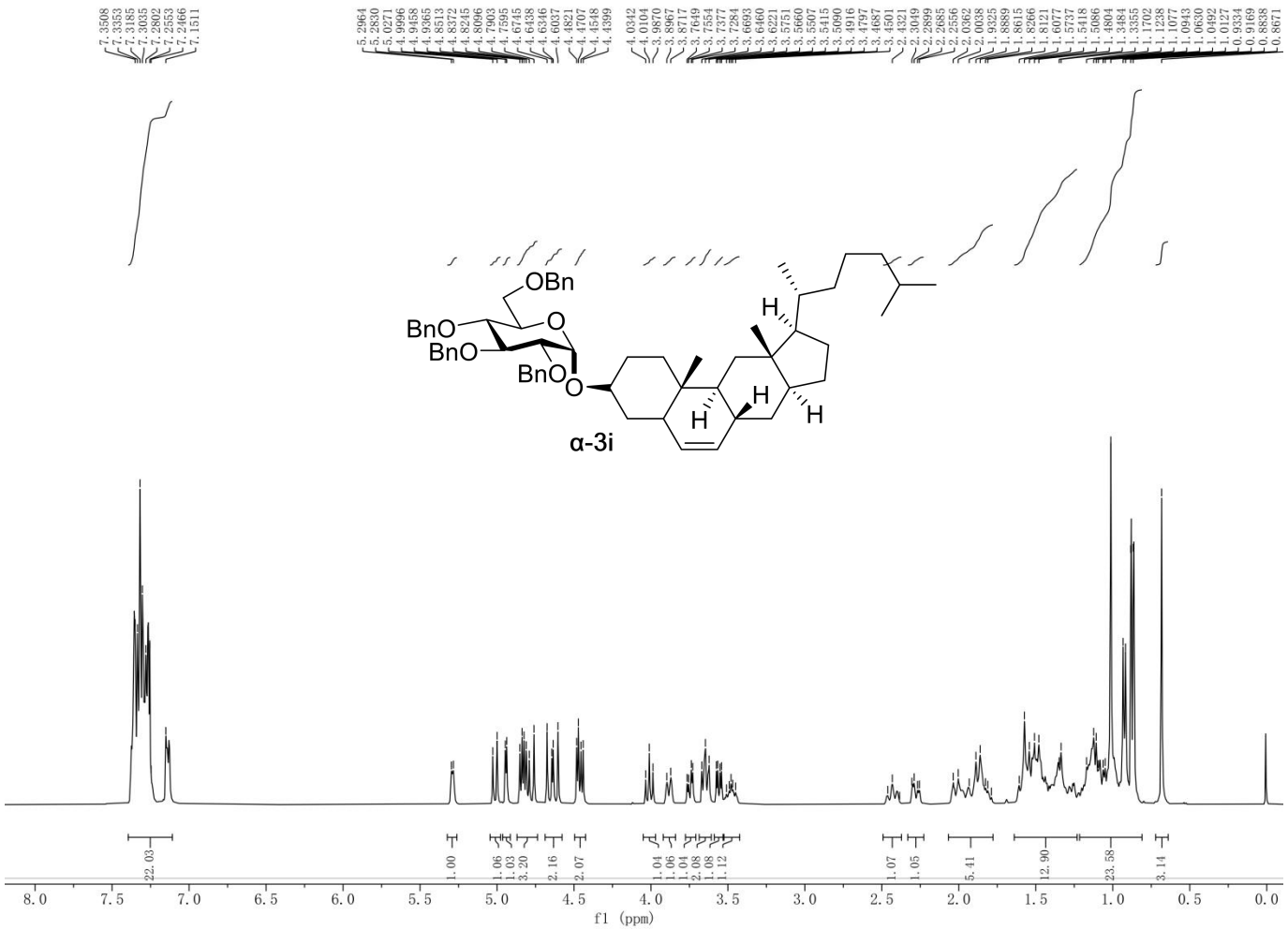


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3i**

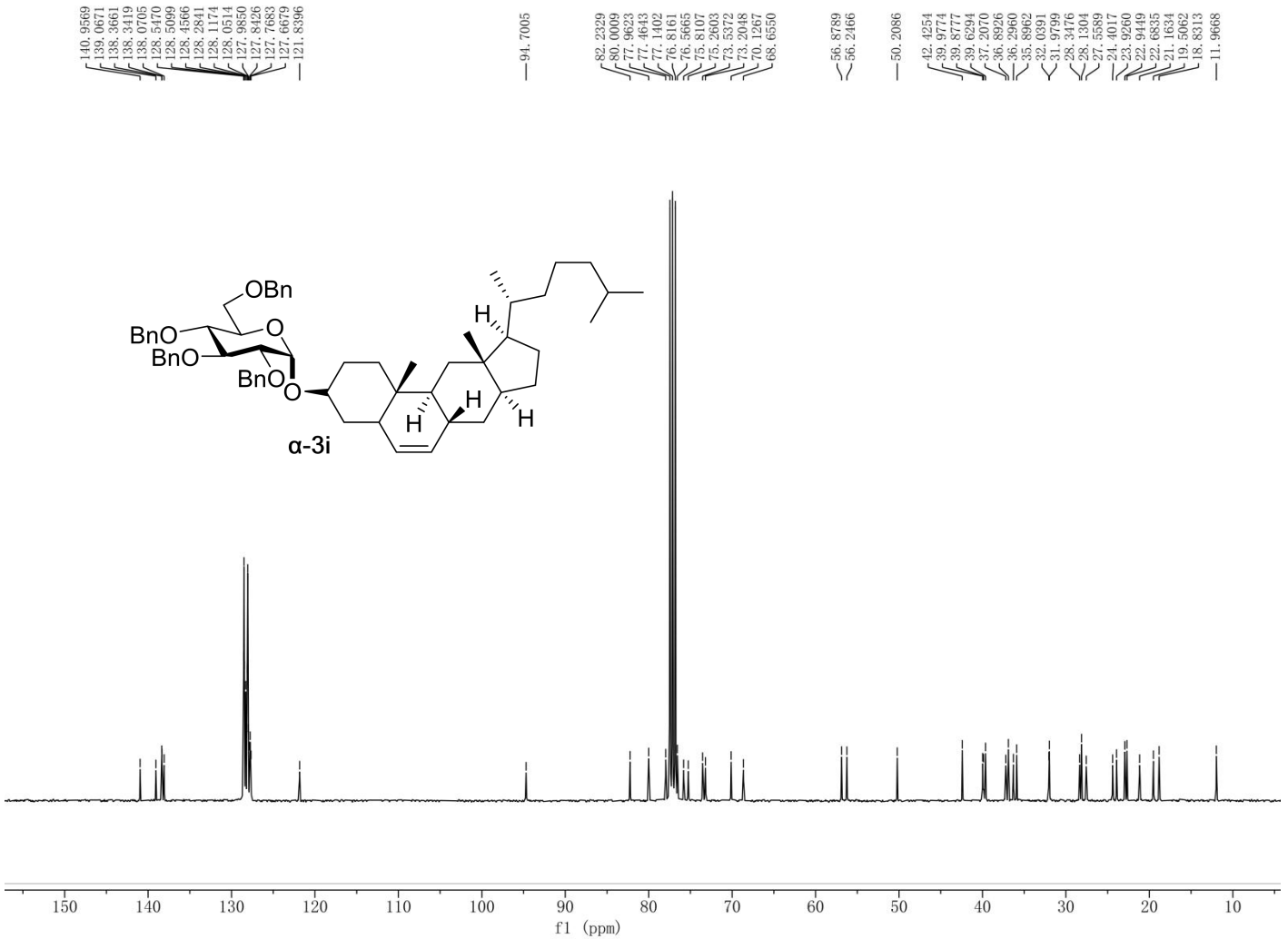


Figure S40. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3i**

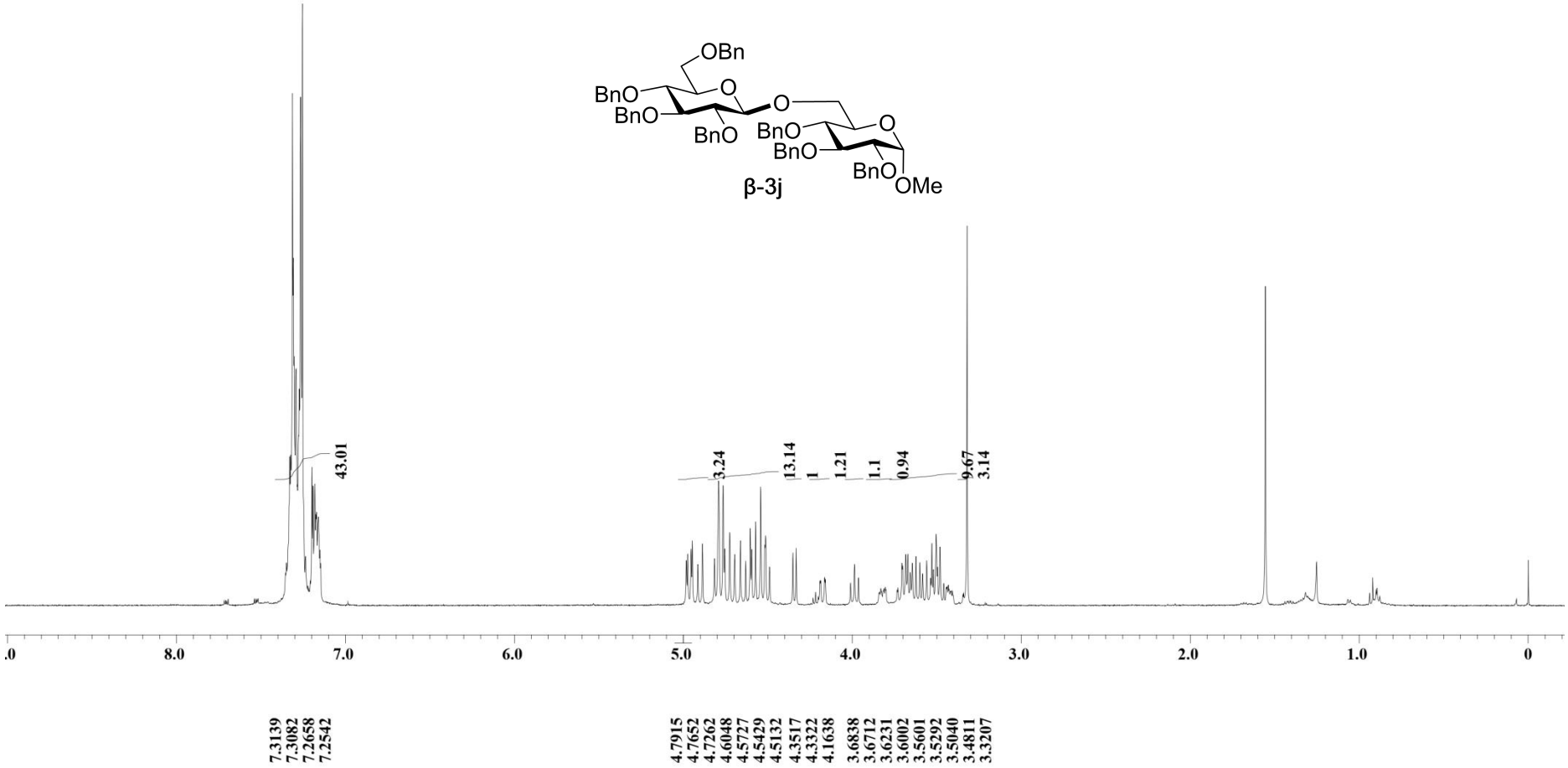


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3j**

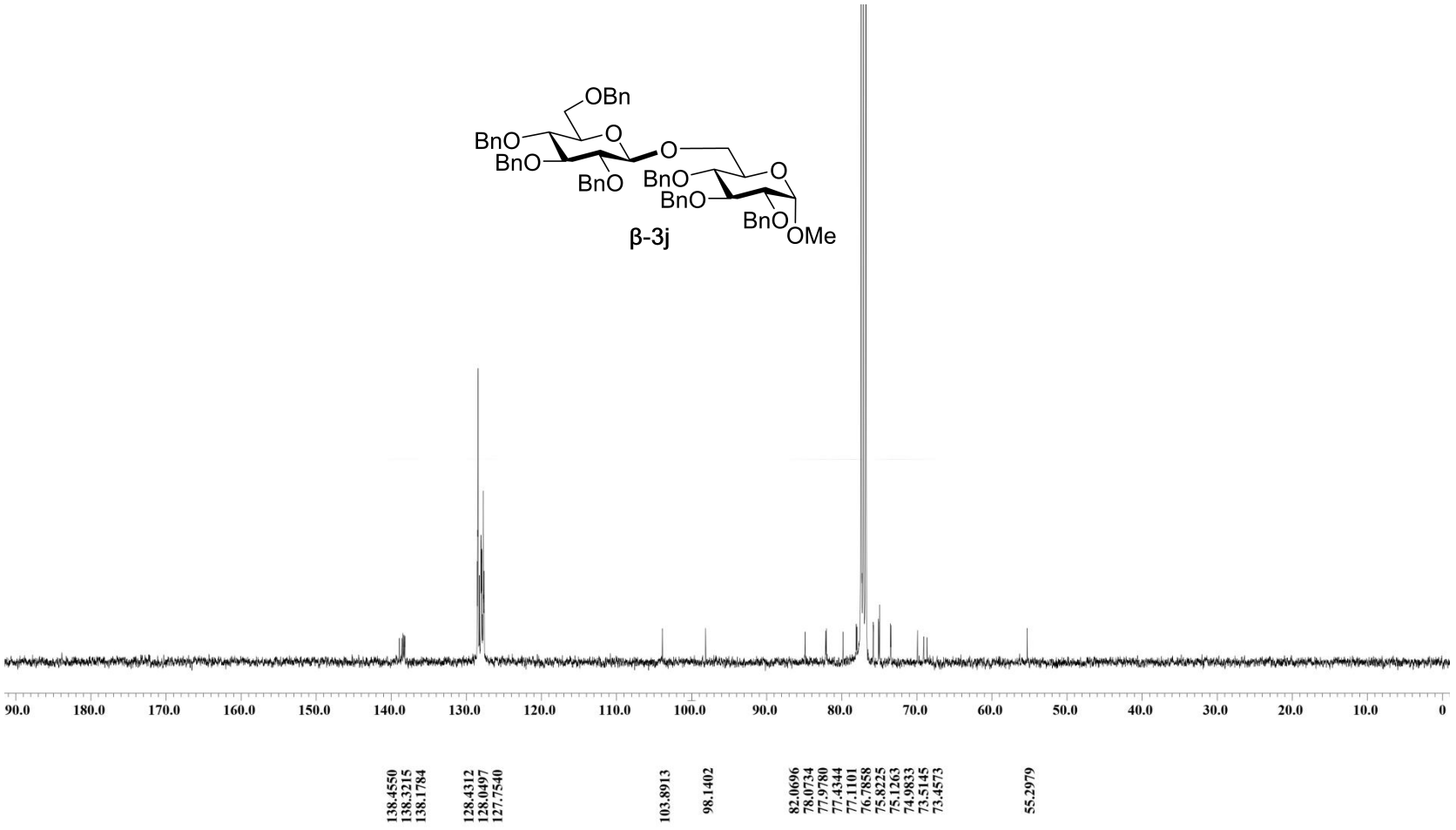


Figure S42. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3j**

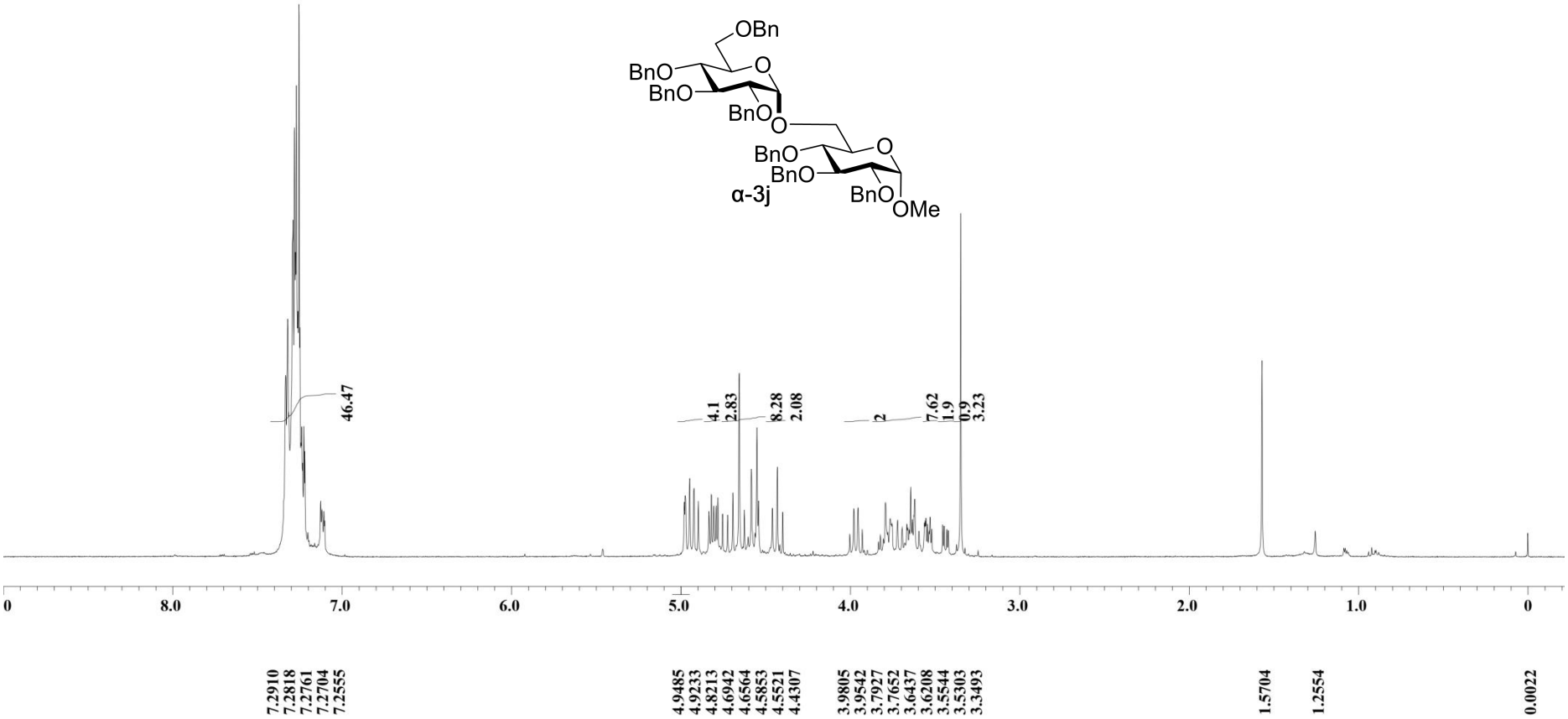


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3j**

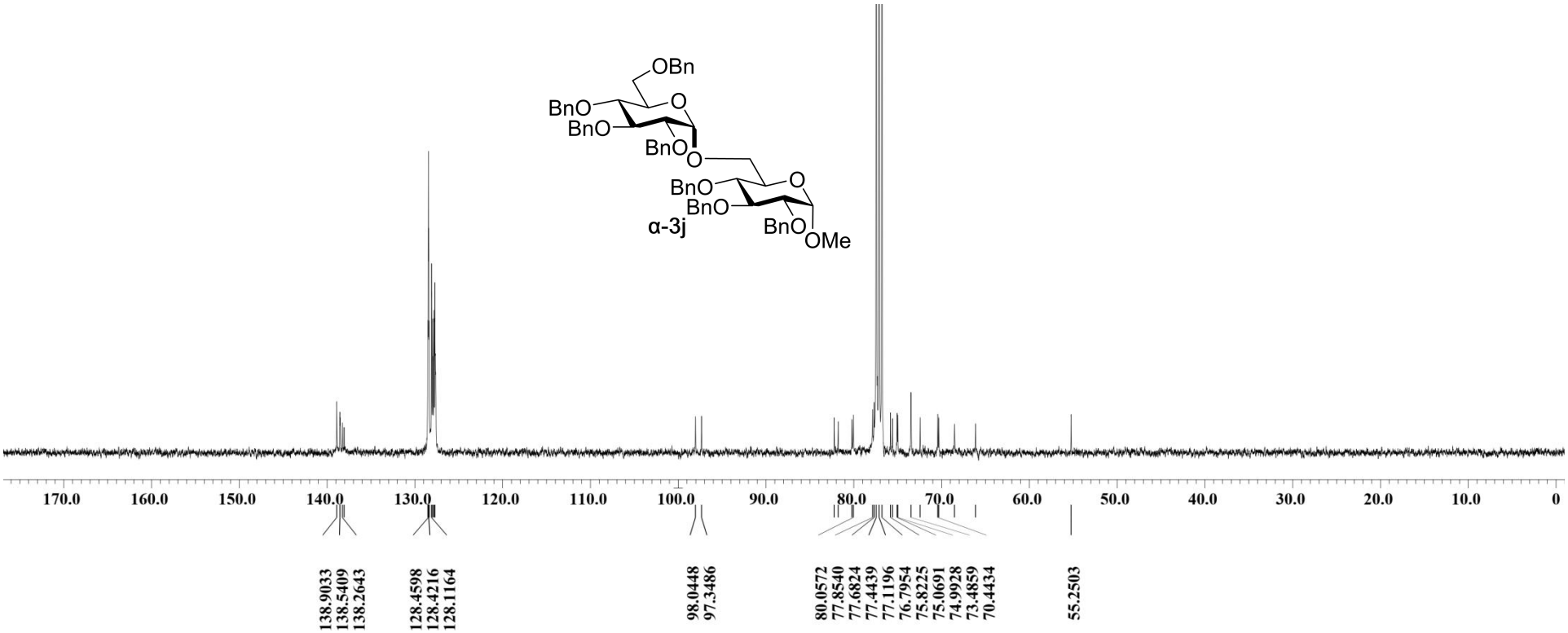


Figure S44. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3j**

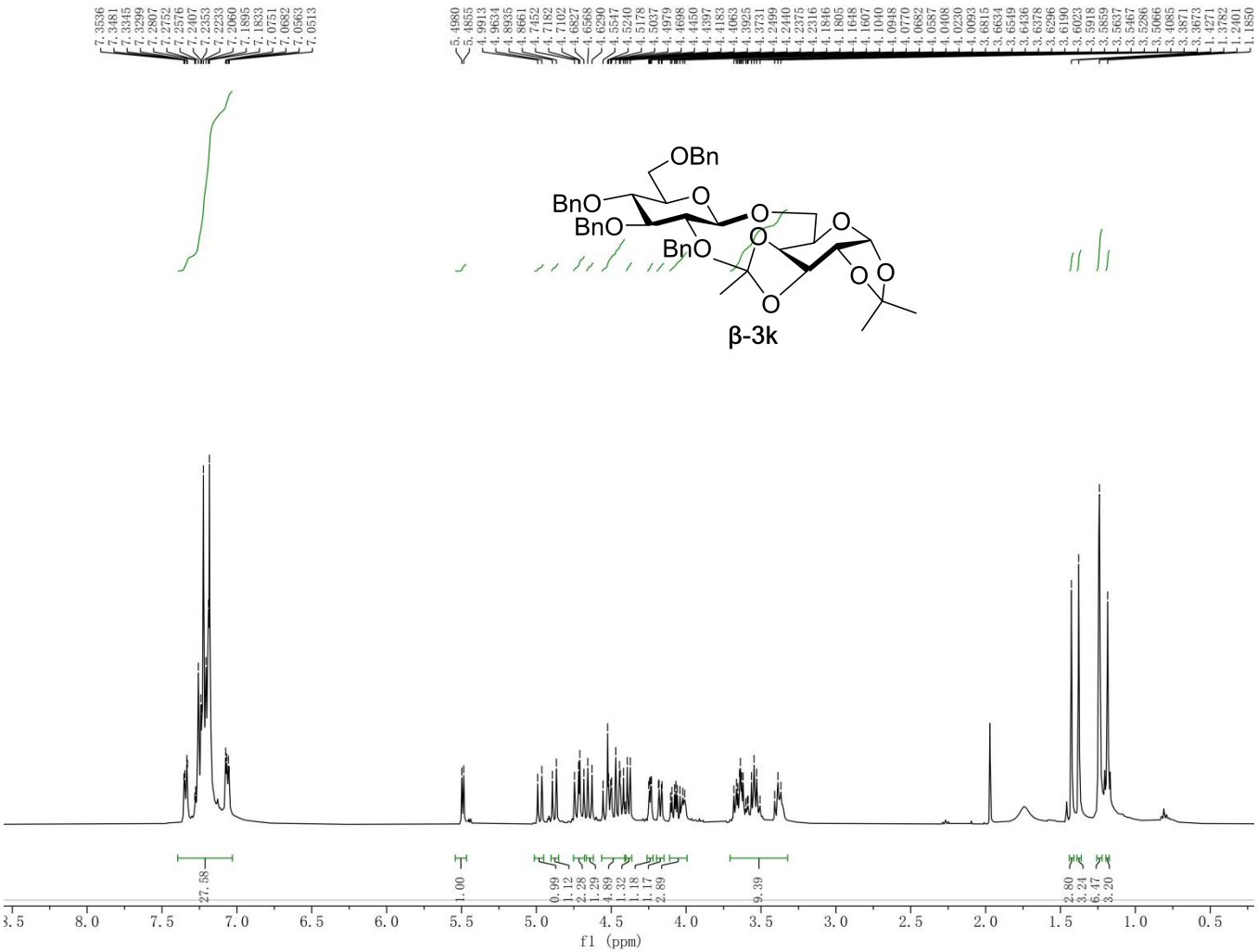


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3k**

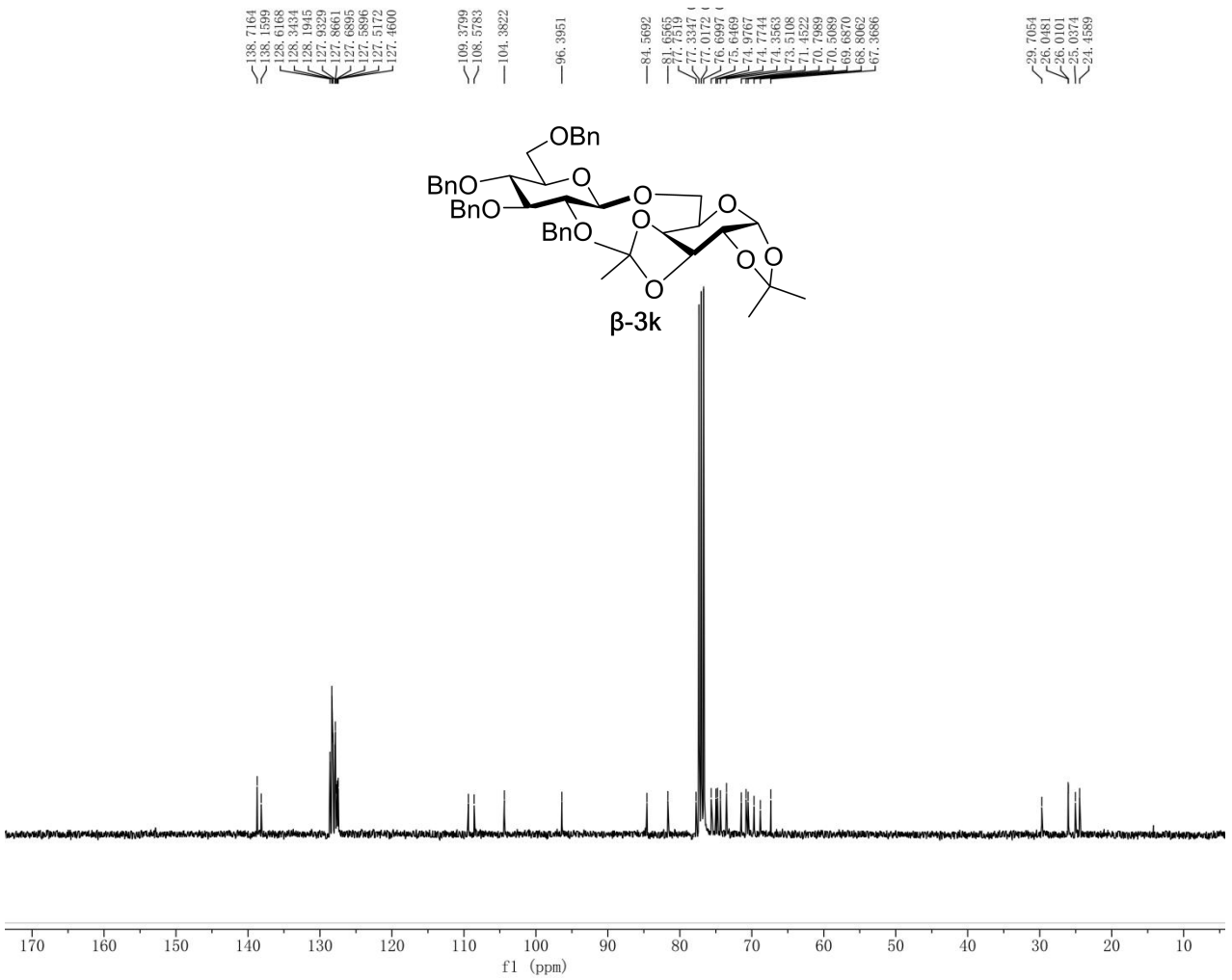


Figure S46. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3k**

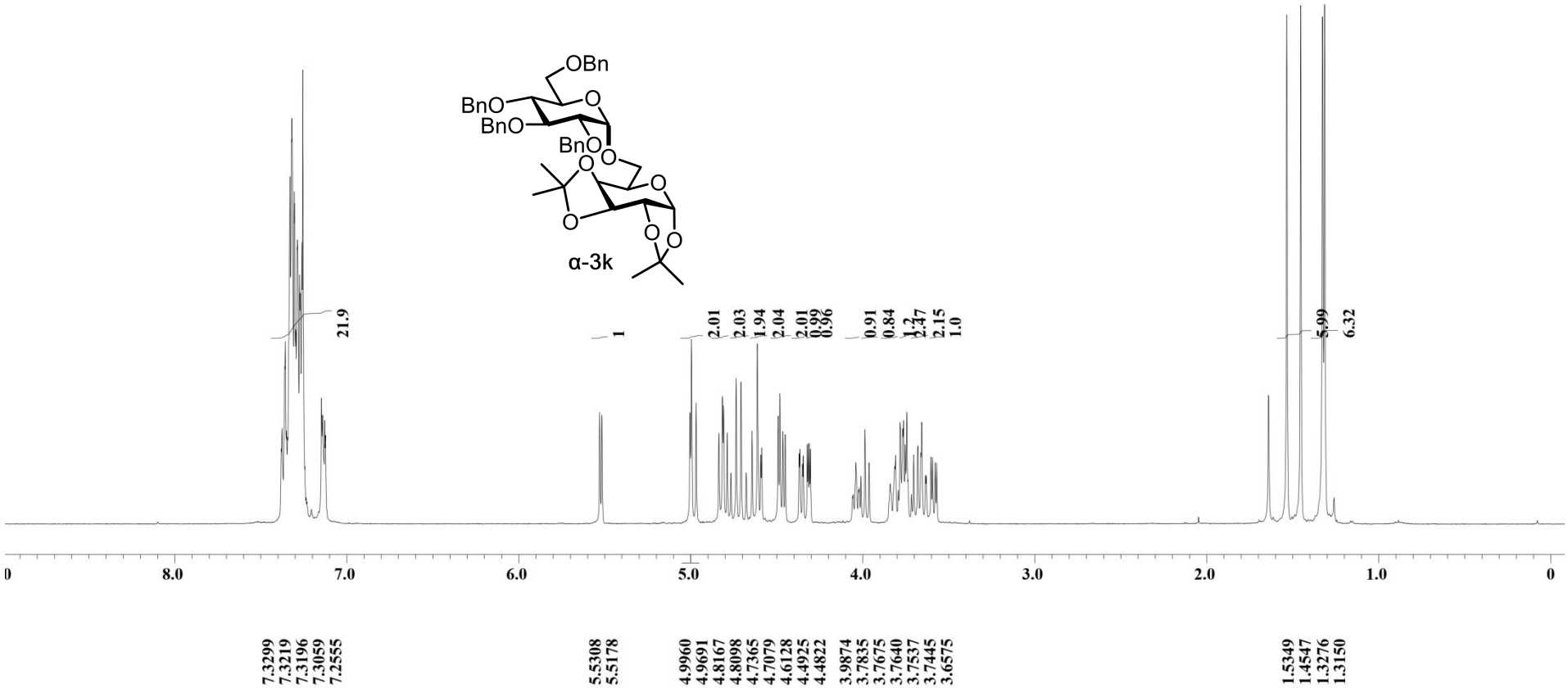


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3k**

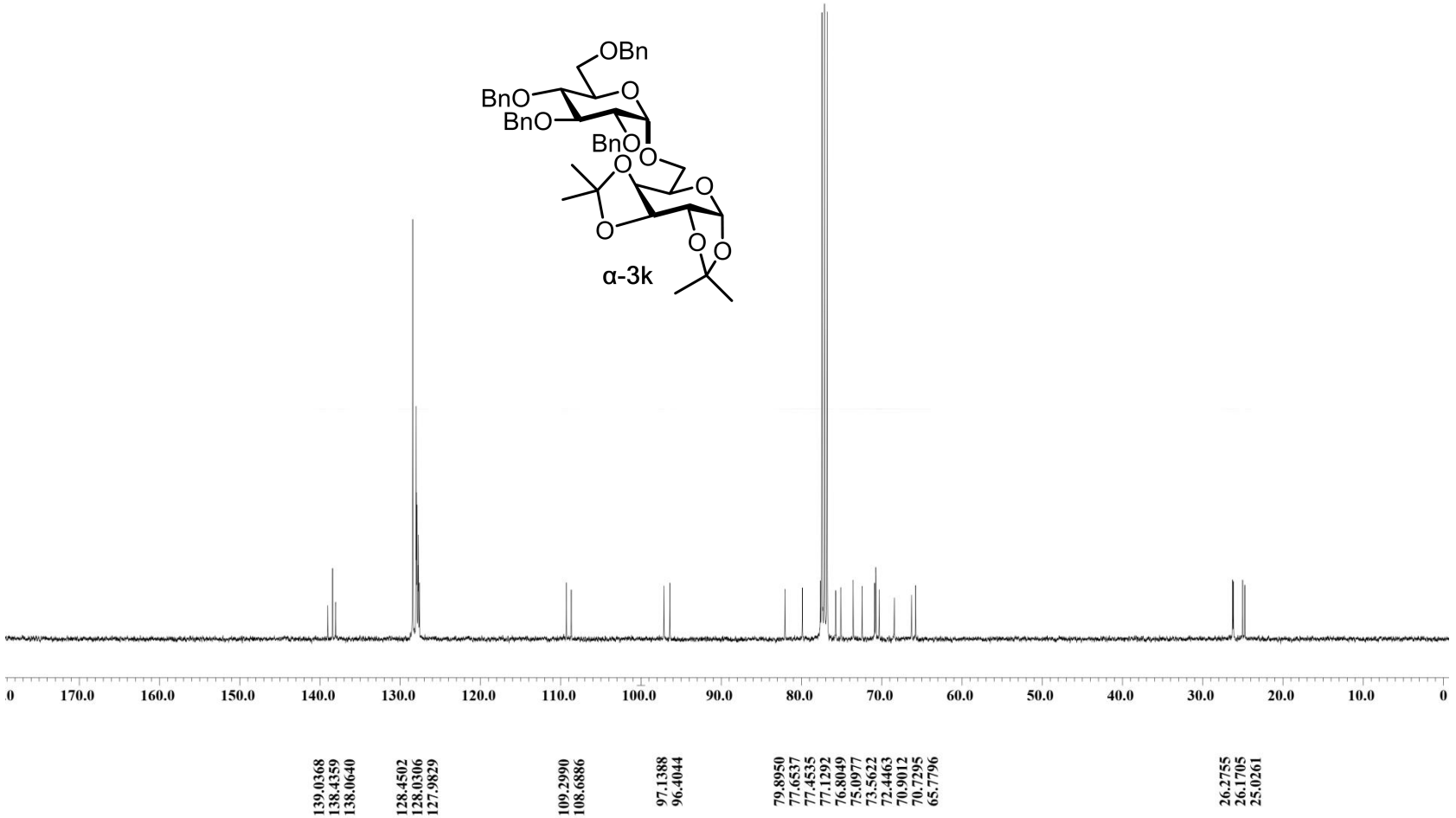


Figure S48. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3k**

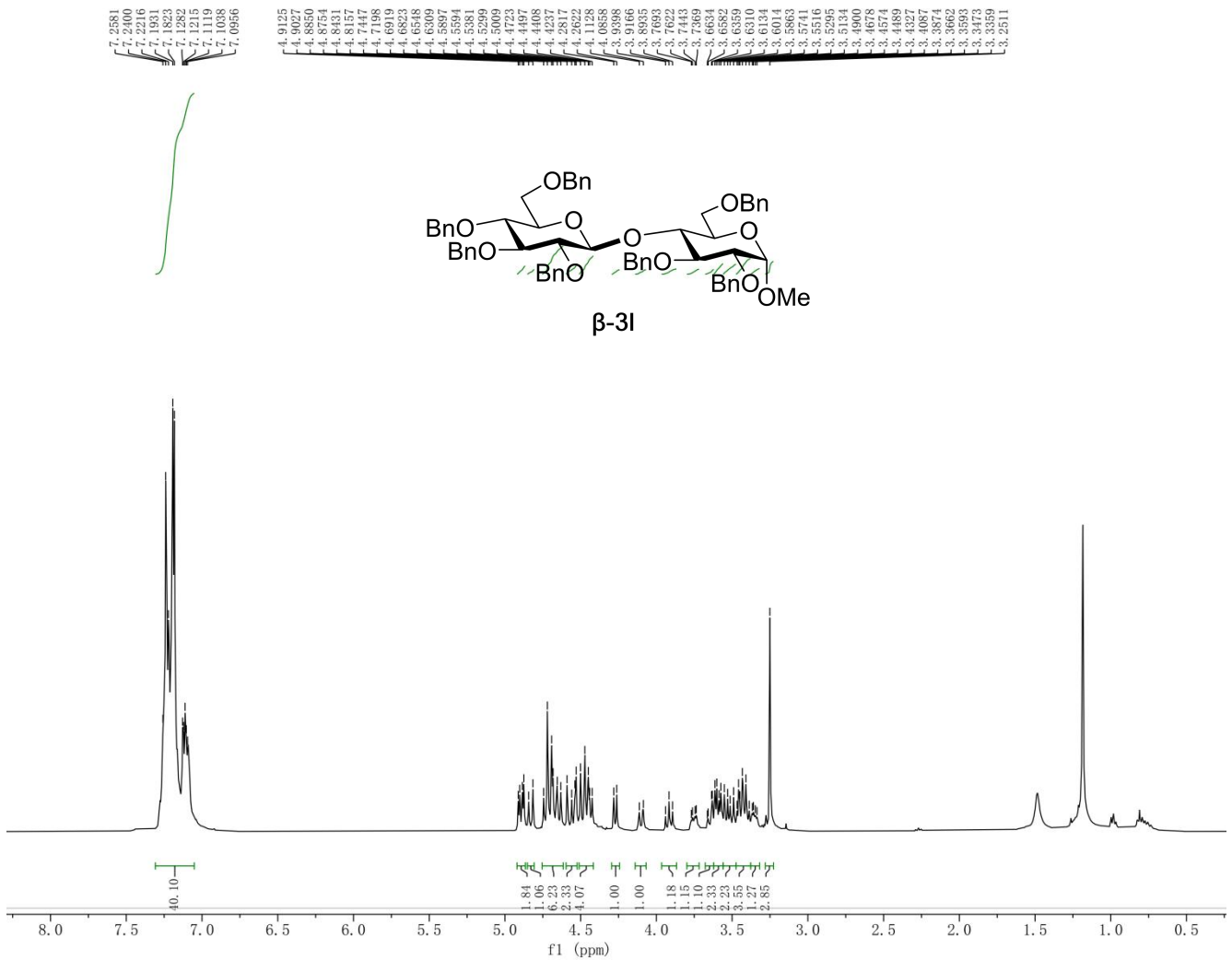


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3l**

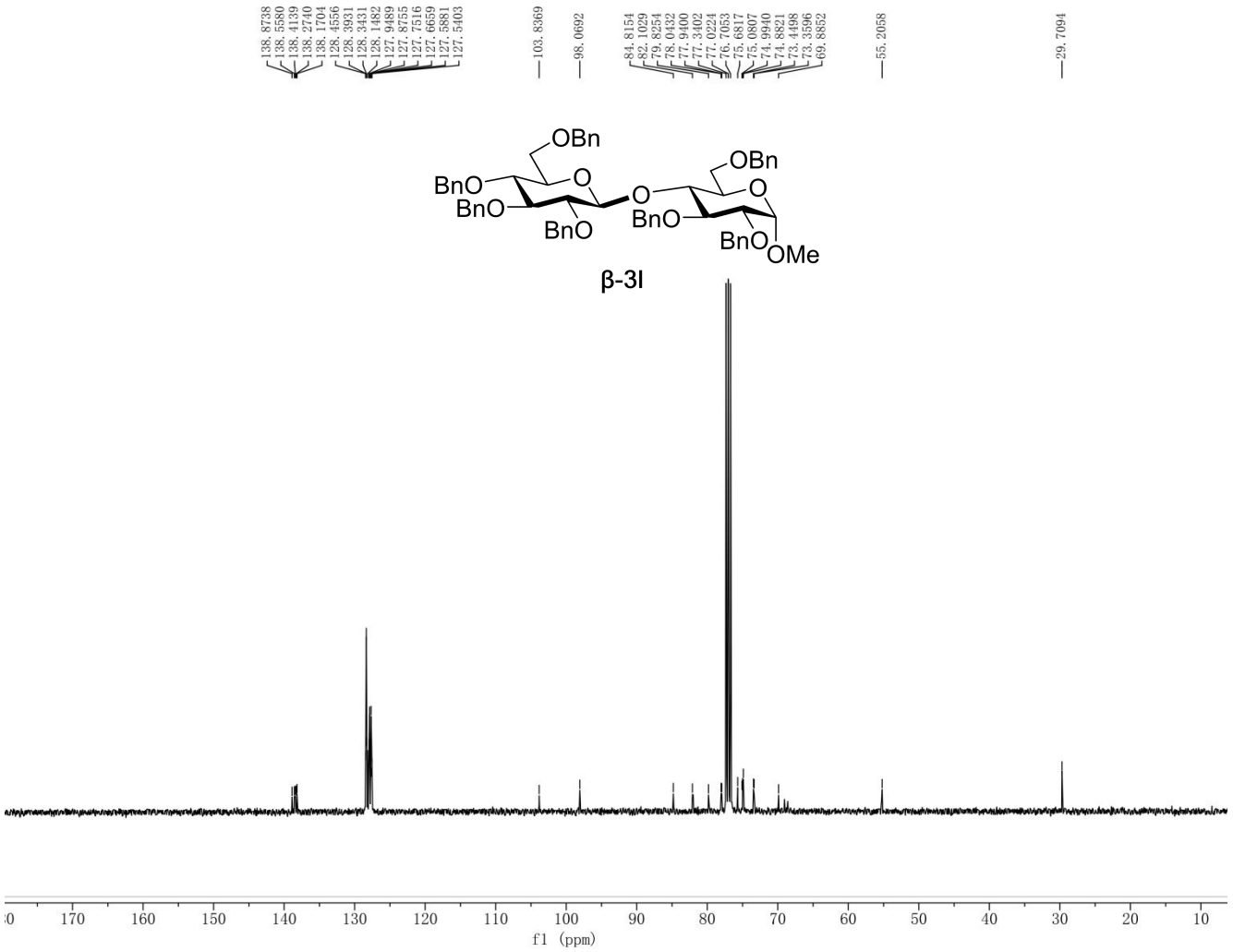


Figure S50. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3l**

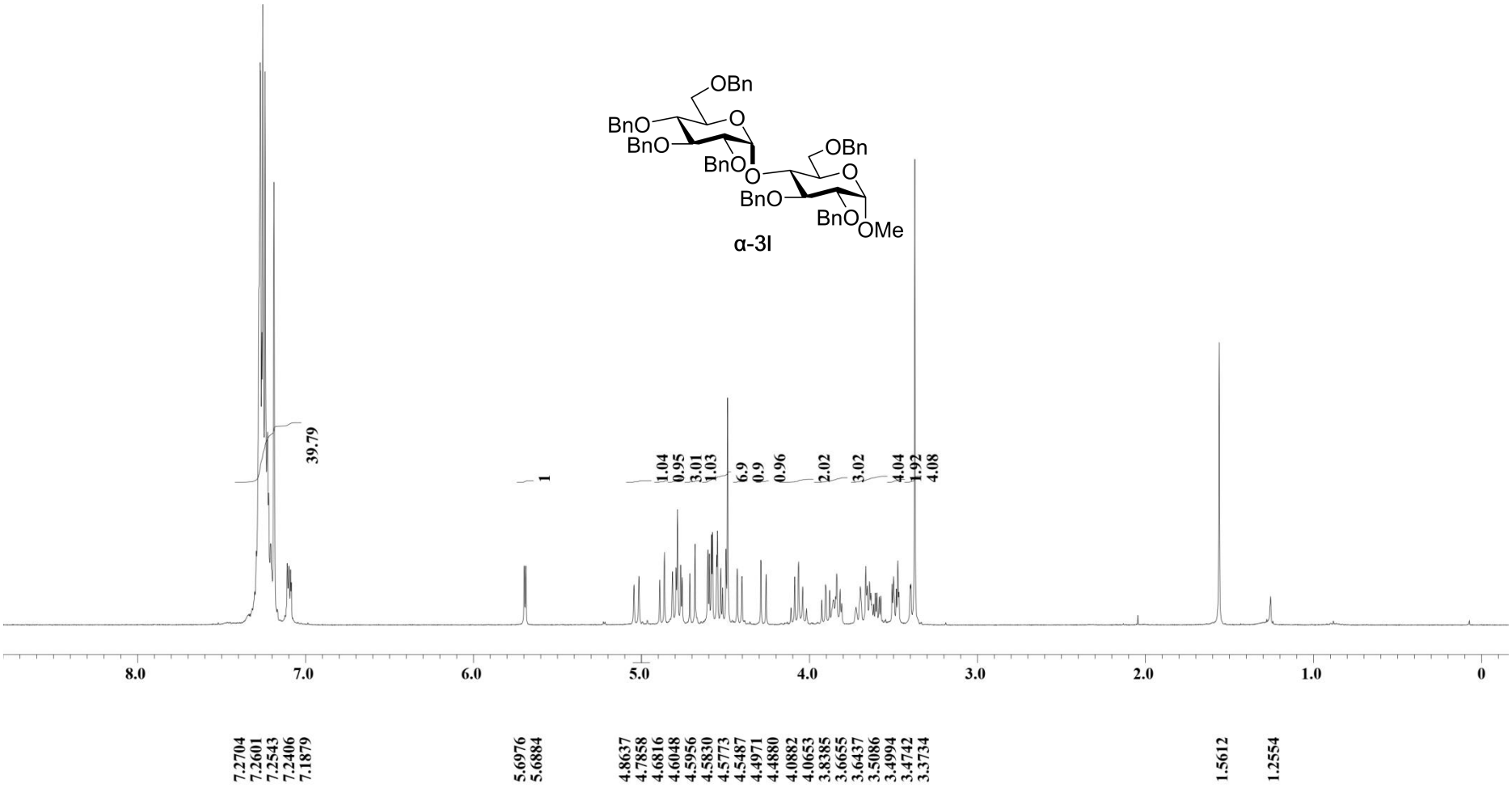


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3l**

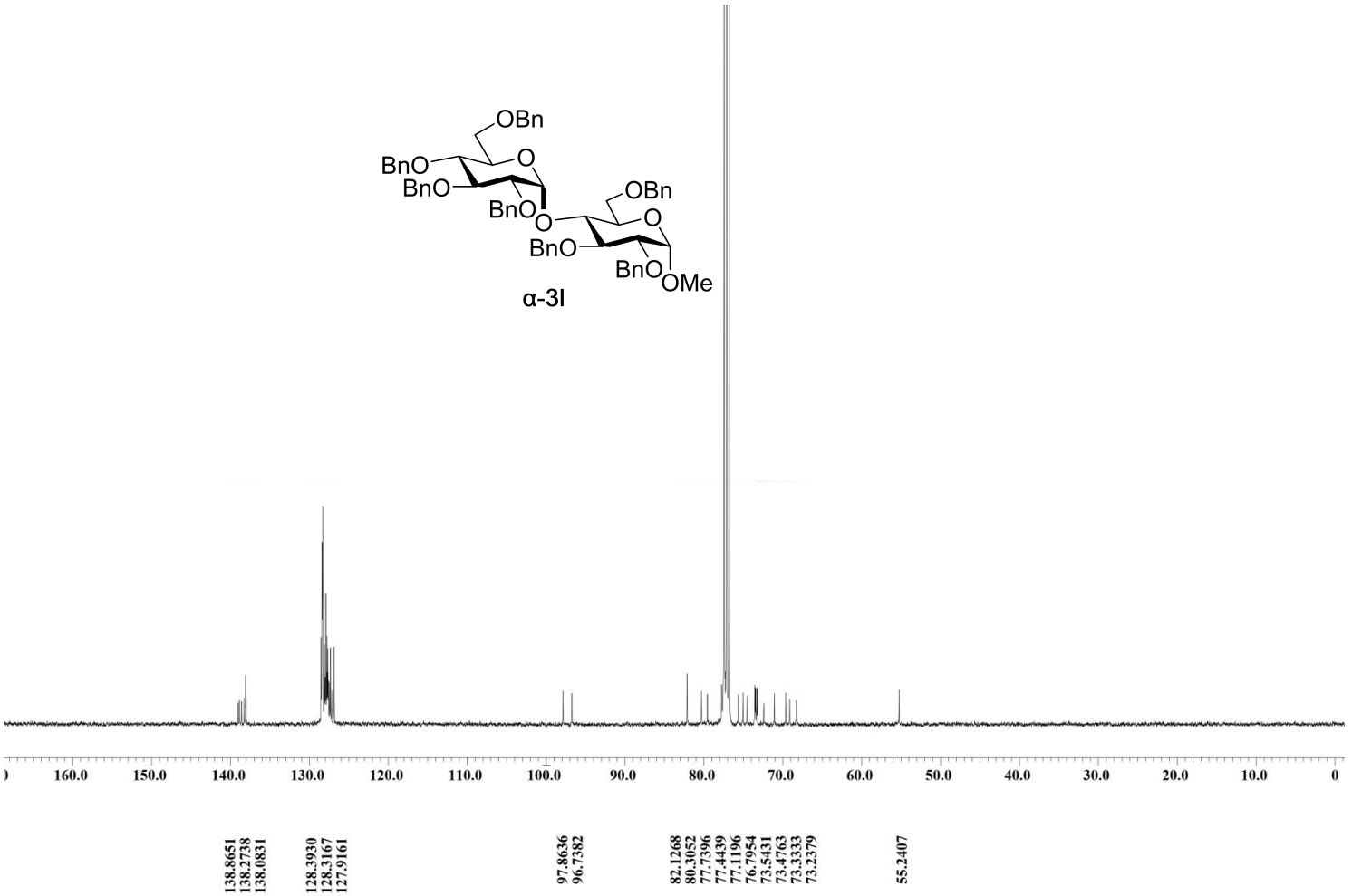


Figure S52. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3l**

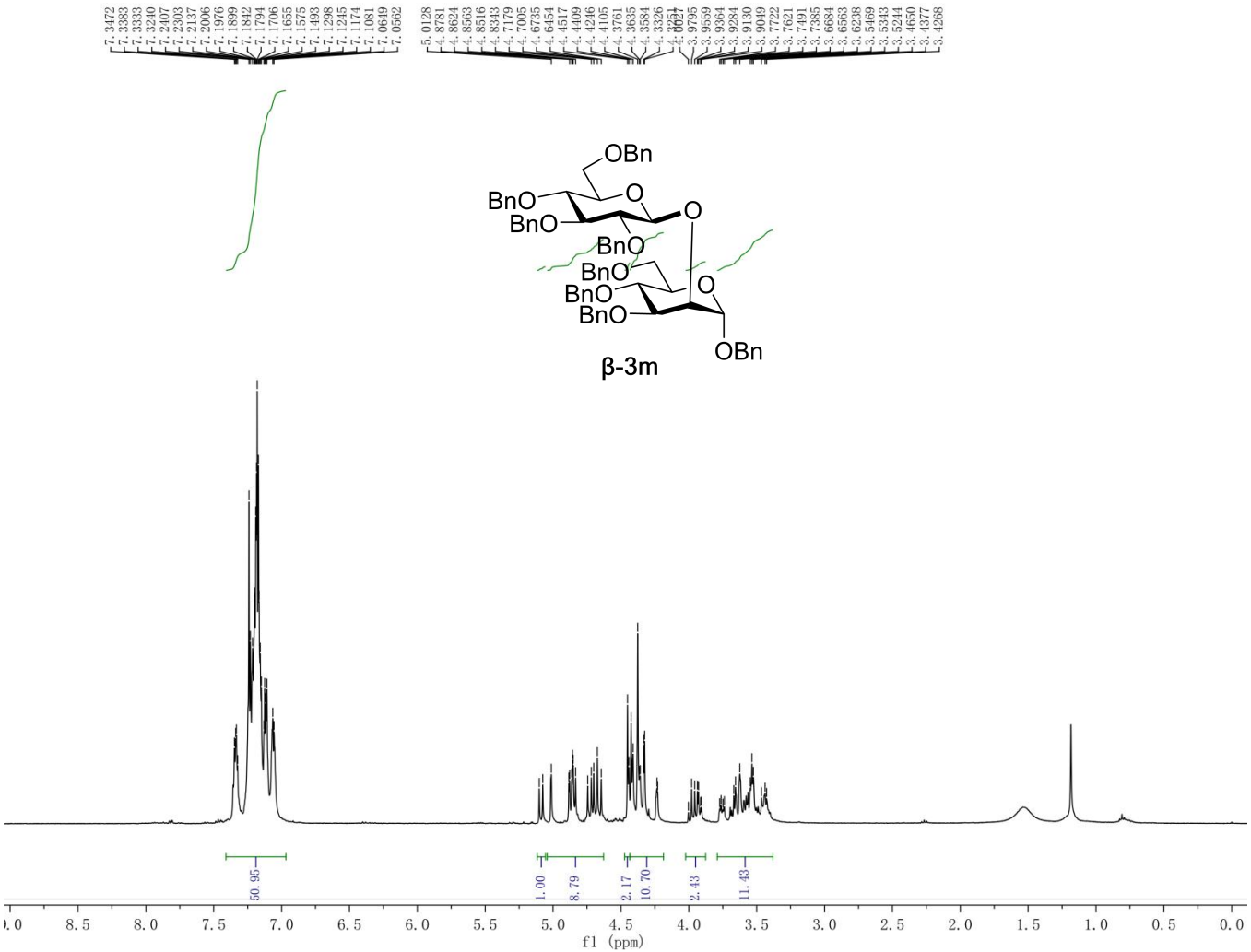


Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3m**

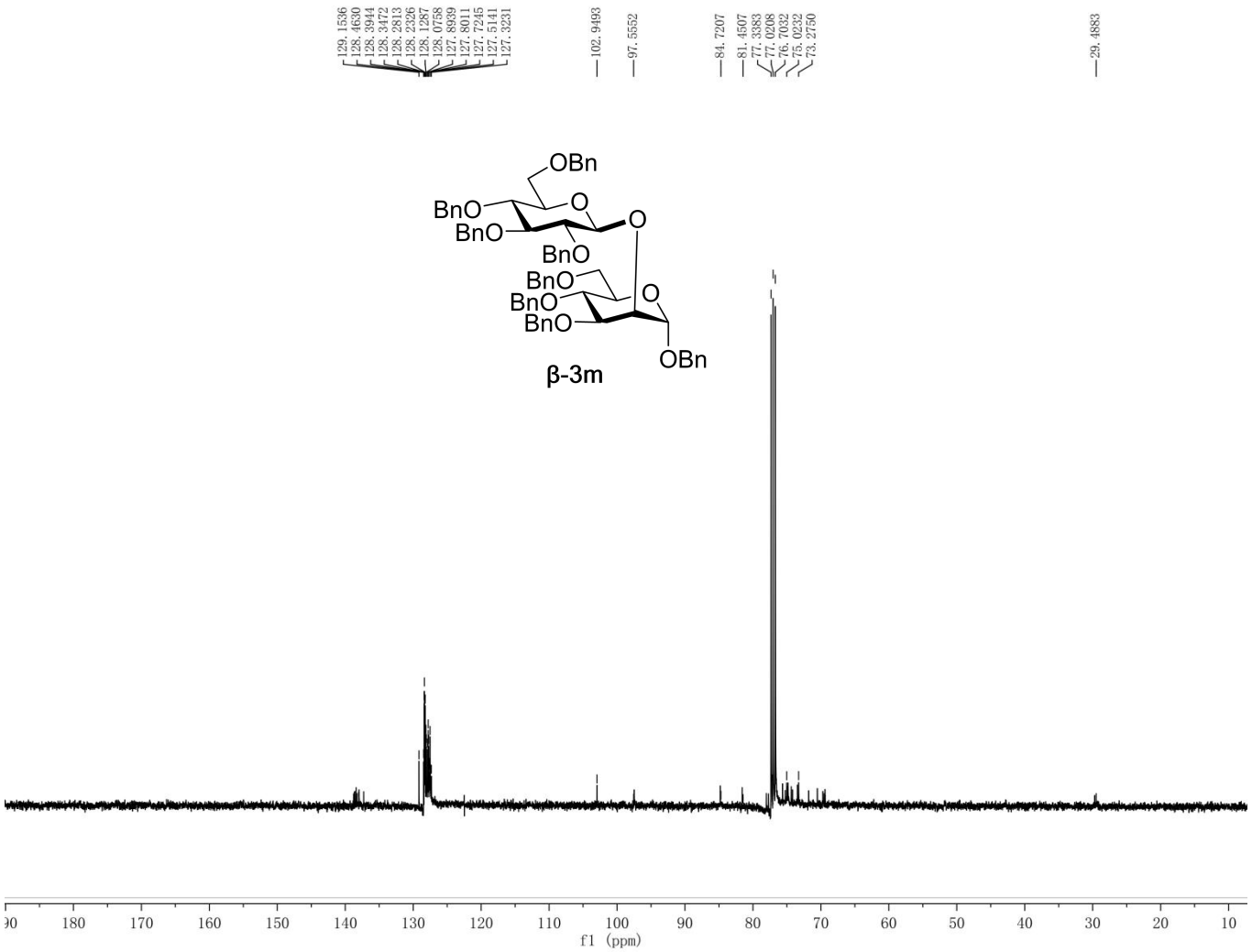


Figure S54. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3m**

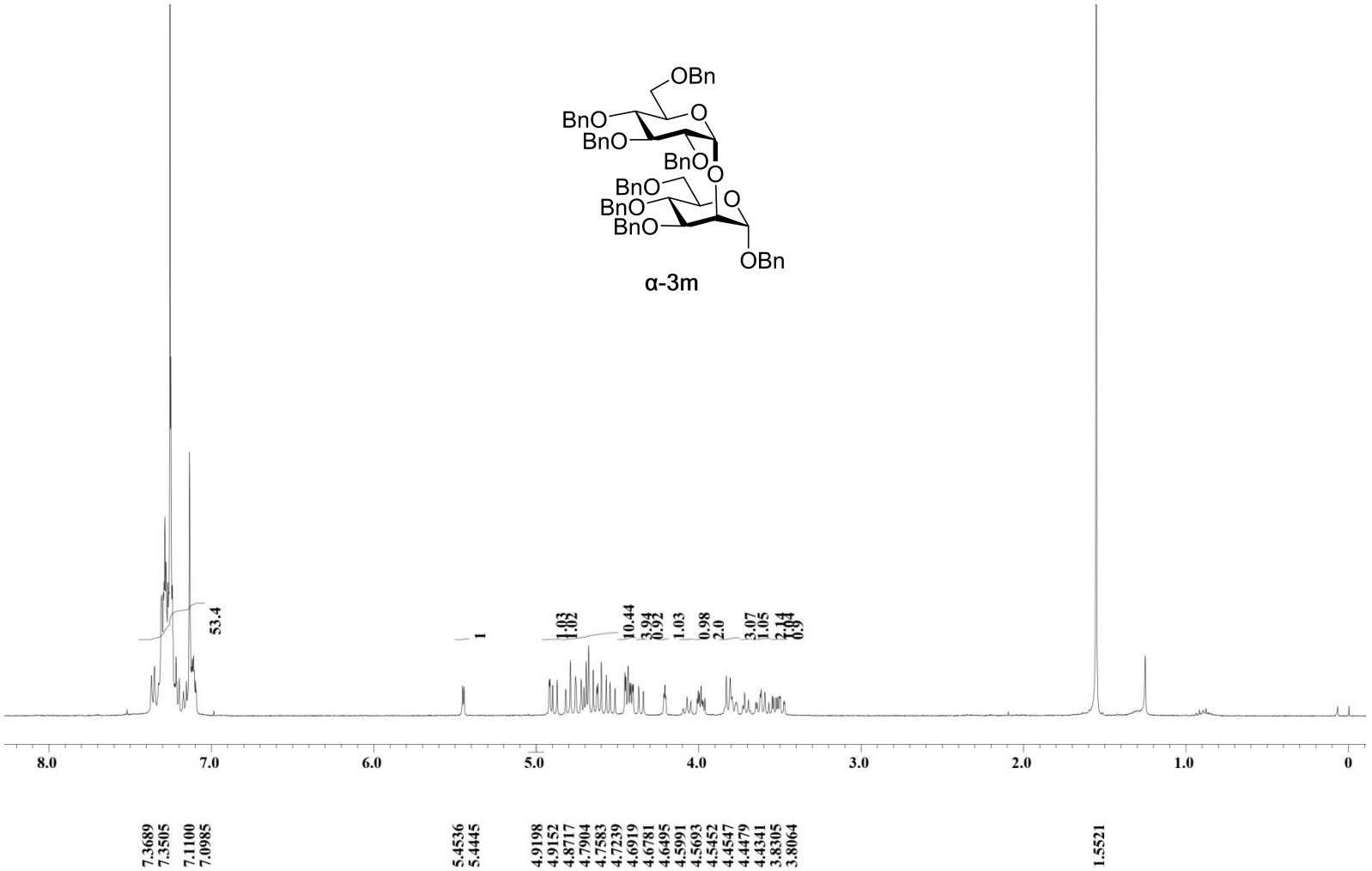


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3m**

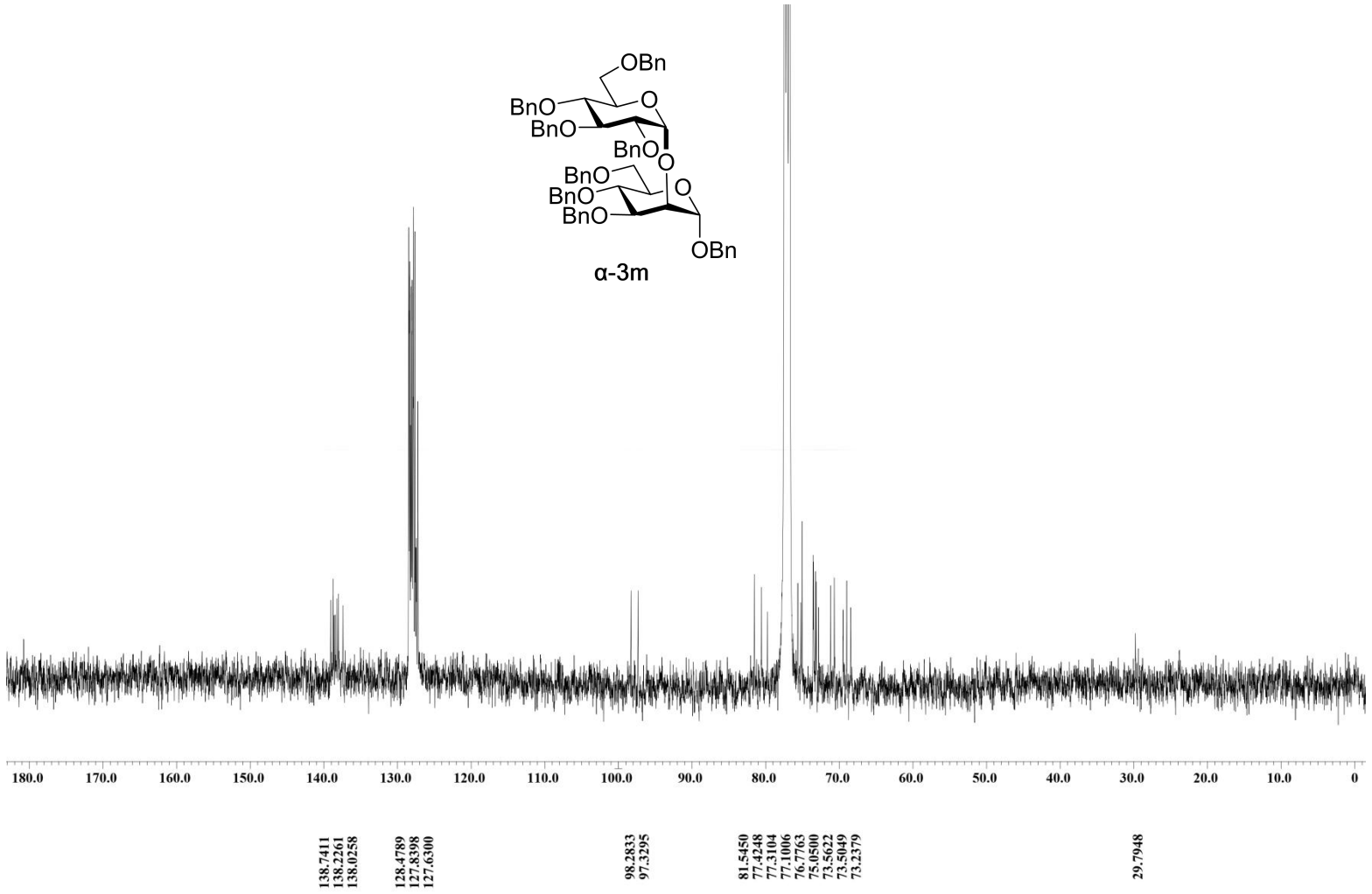


Figure S56. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3m**

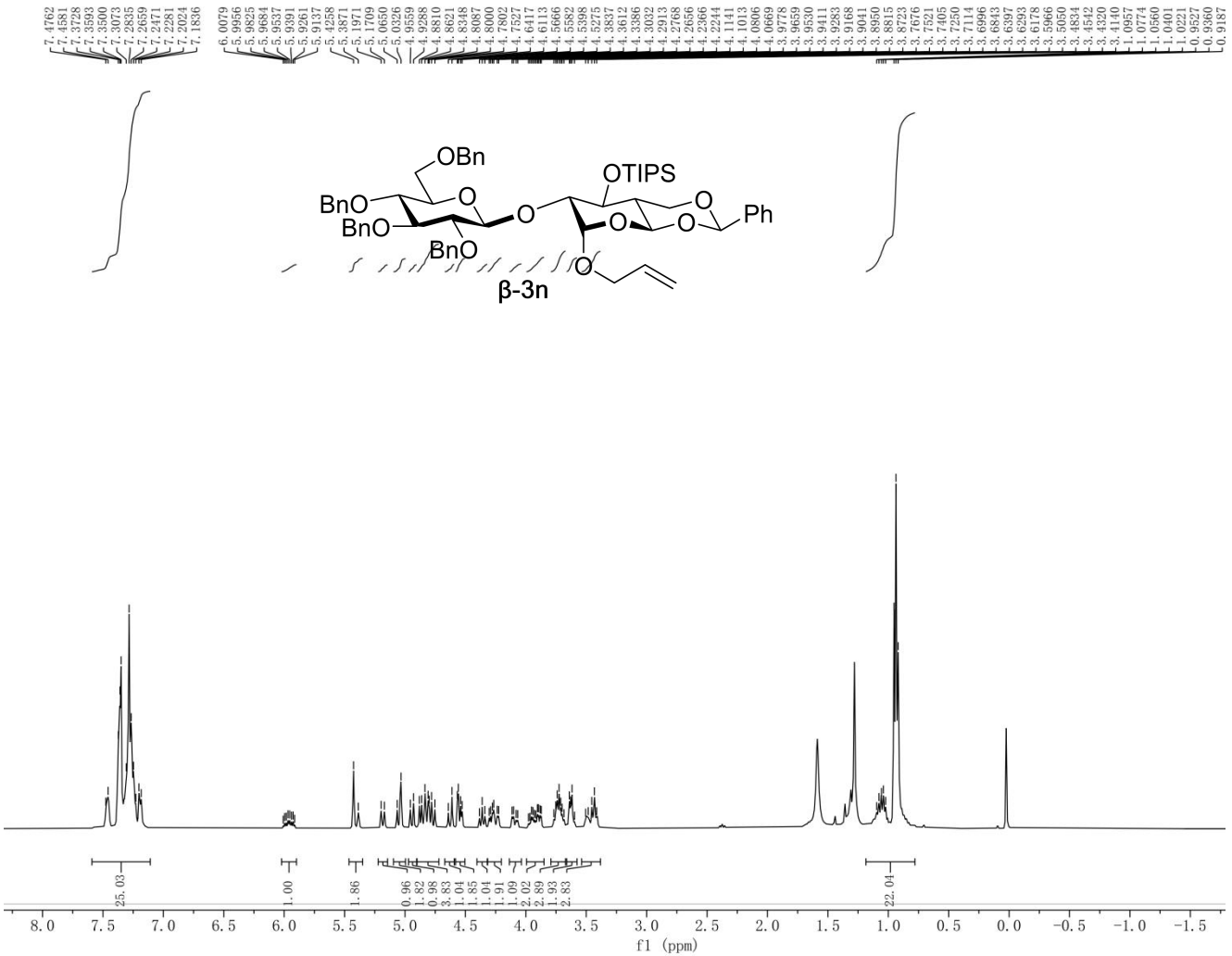


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-3n**

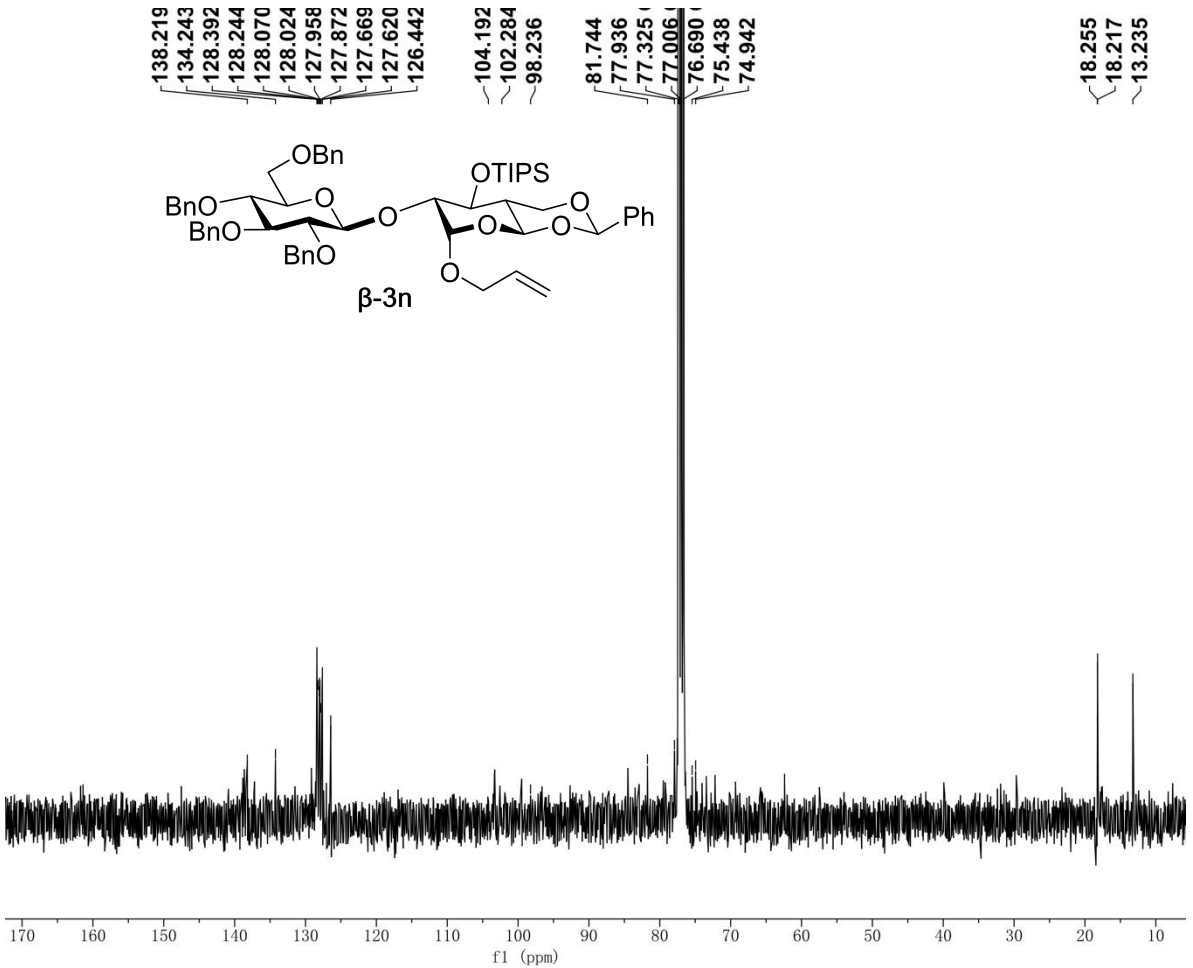


Figure S58. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-3n**

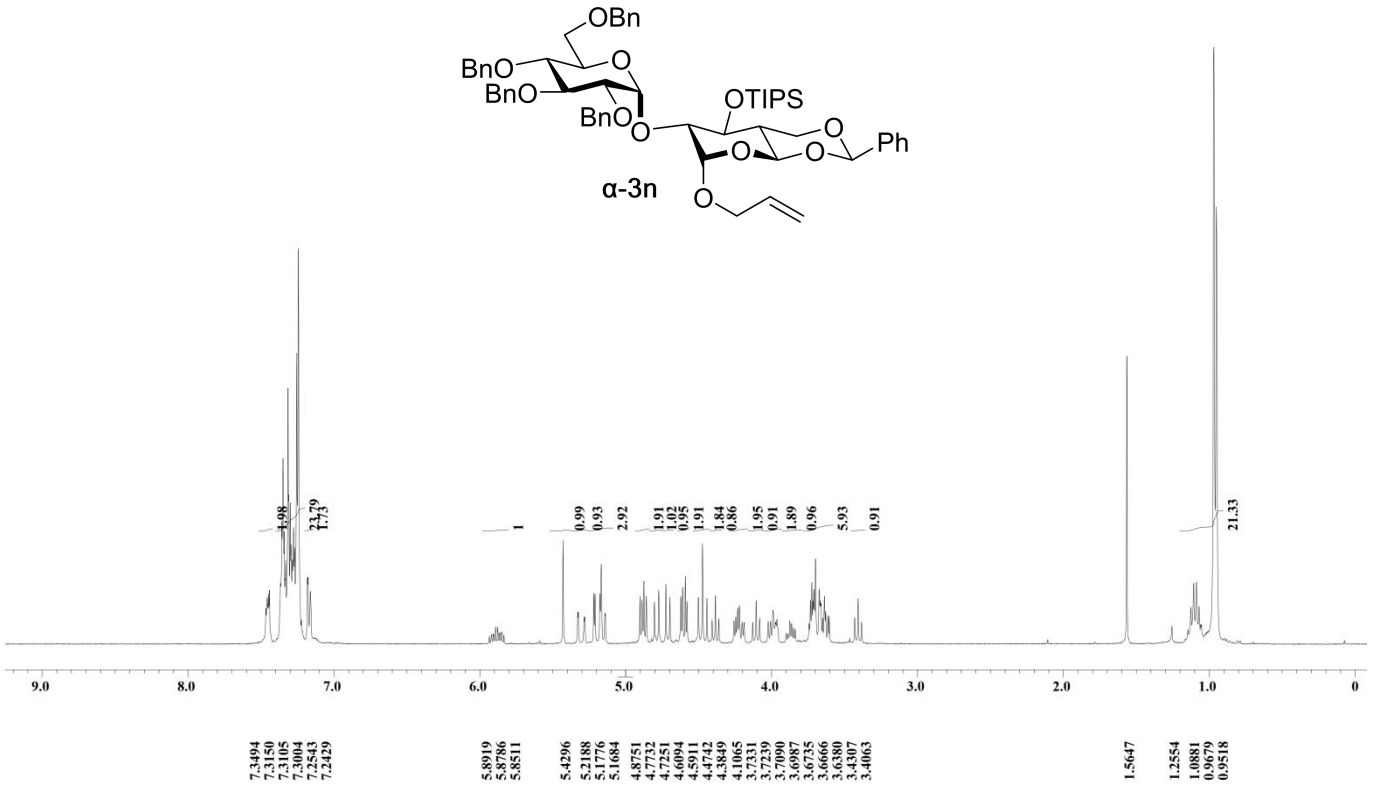


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-3n**

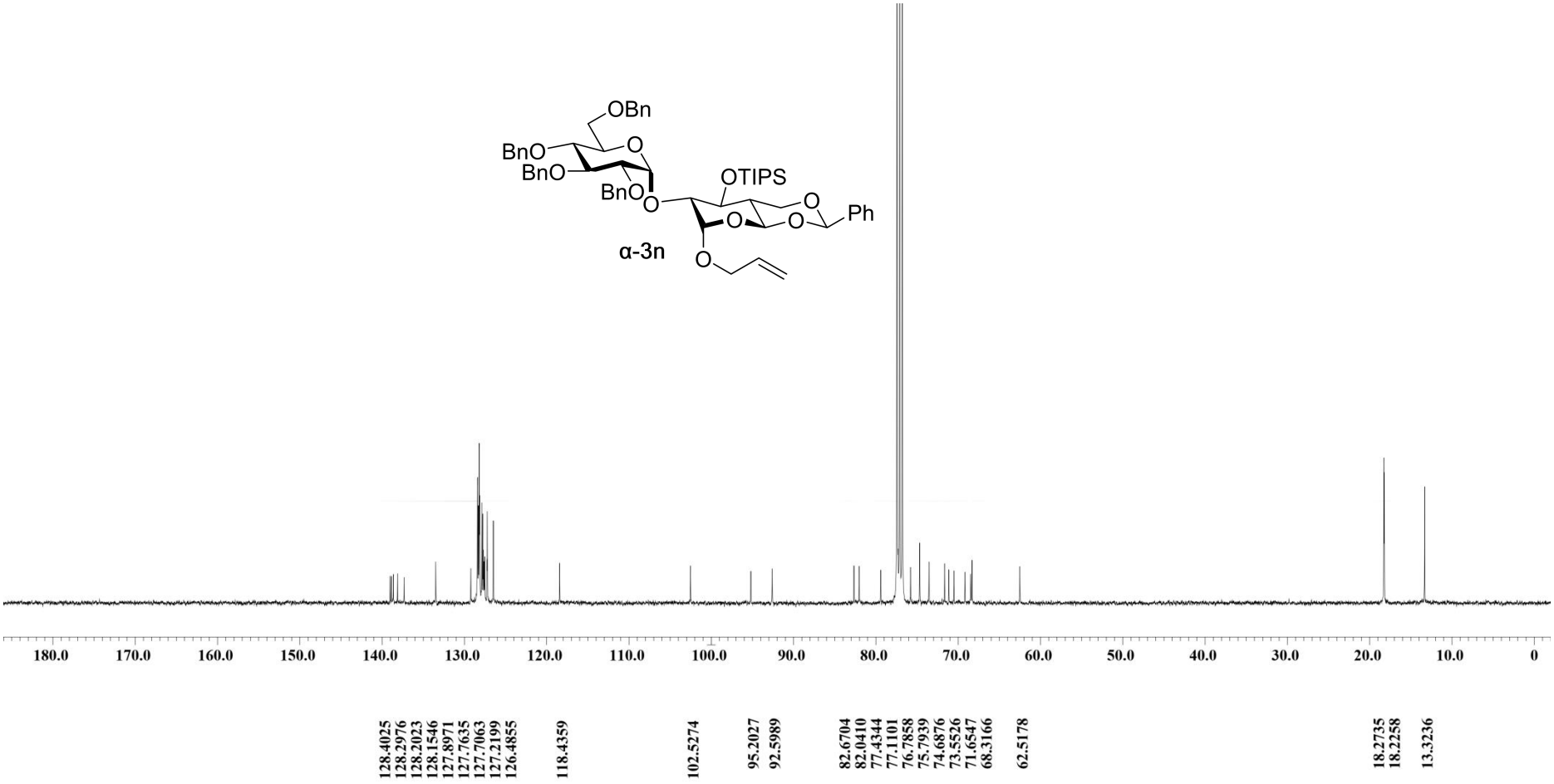


Figure S60. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-3n**

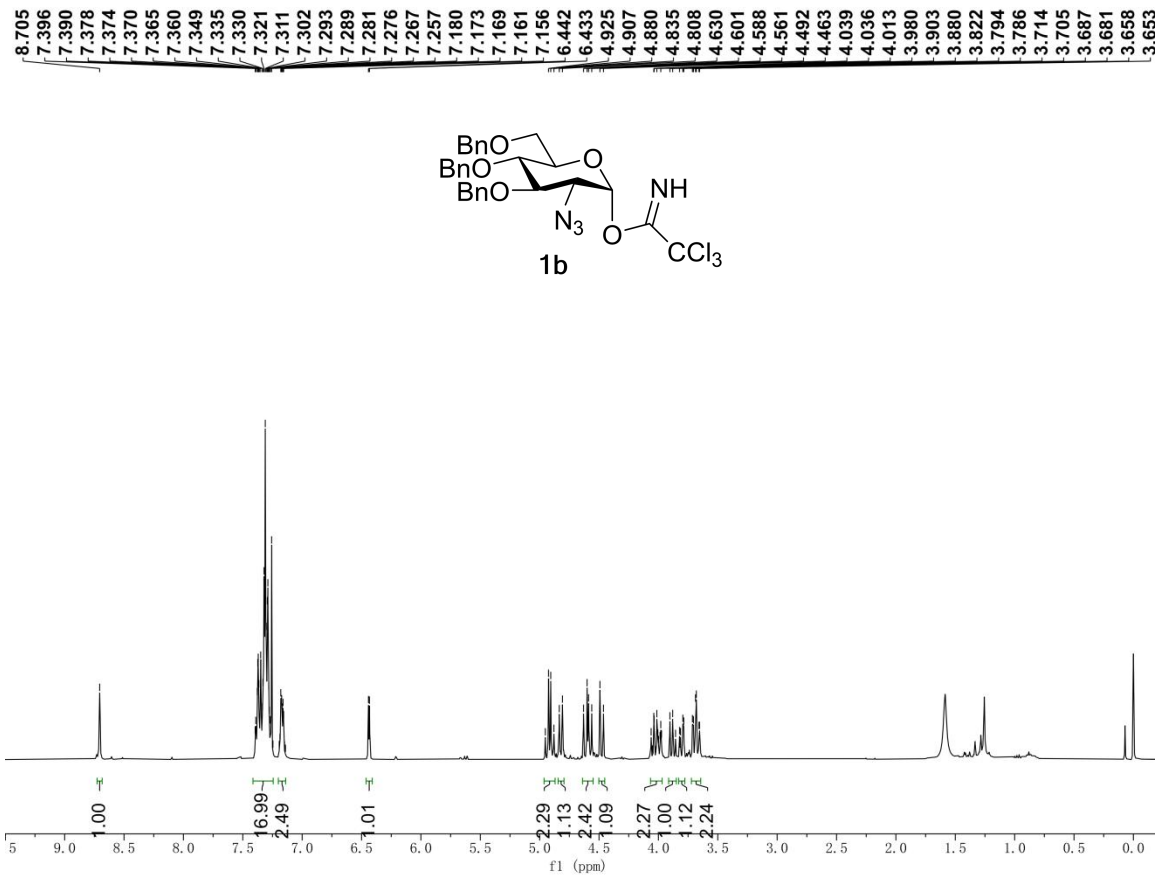


Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1b**

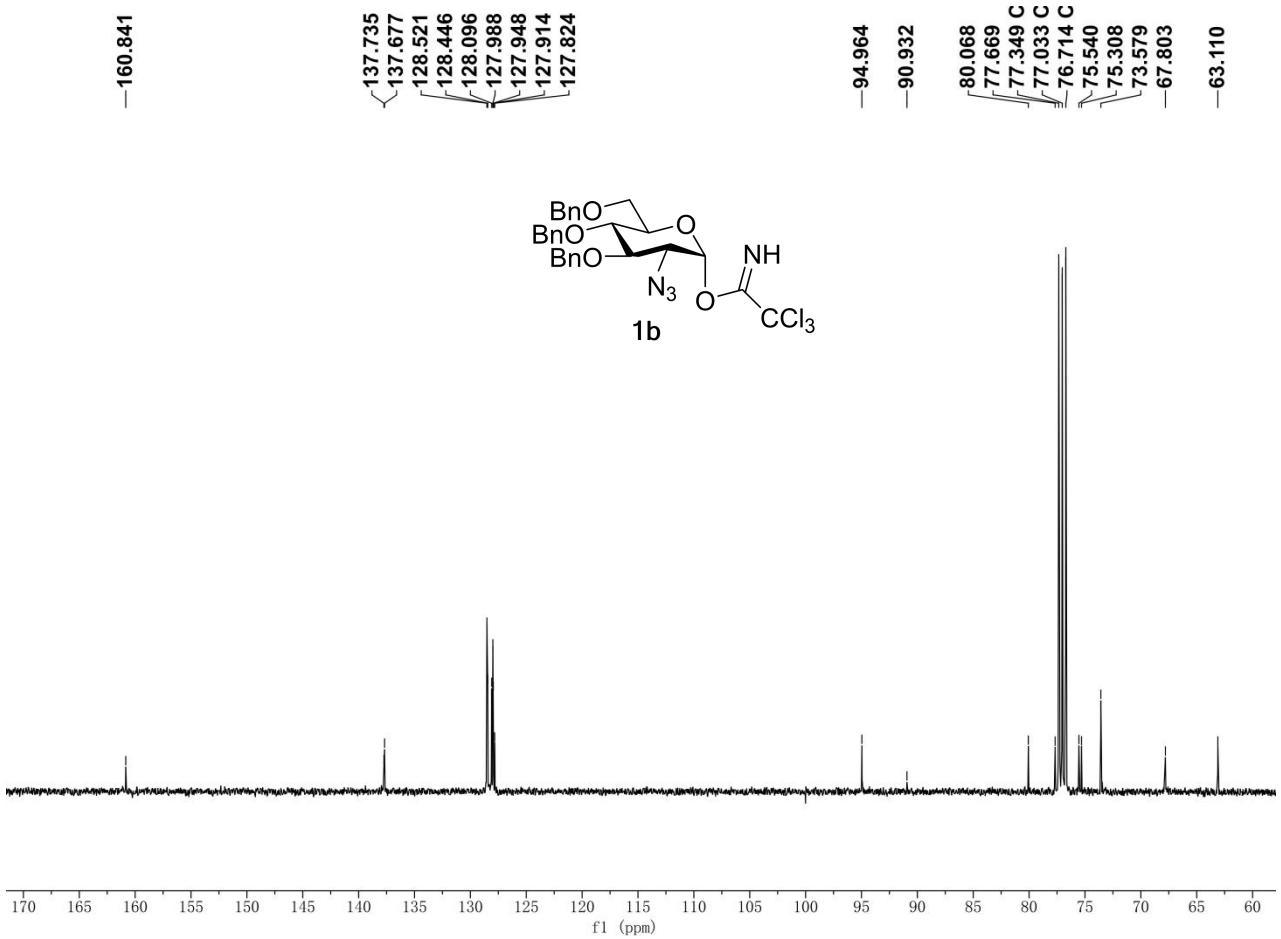


Figure S62. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **1b**

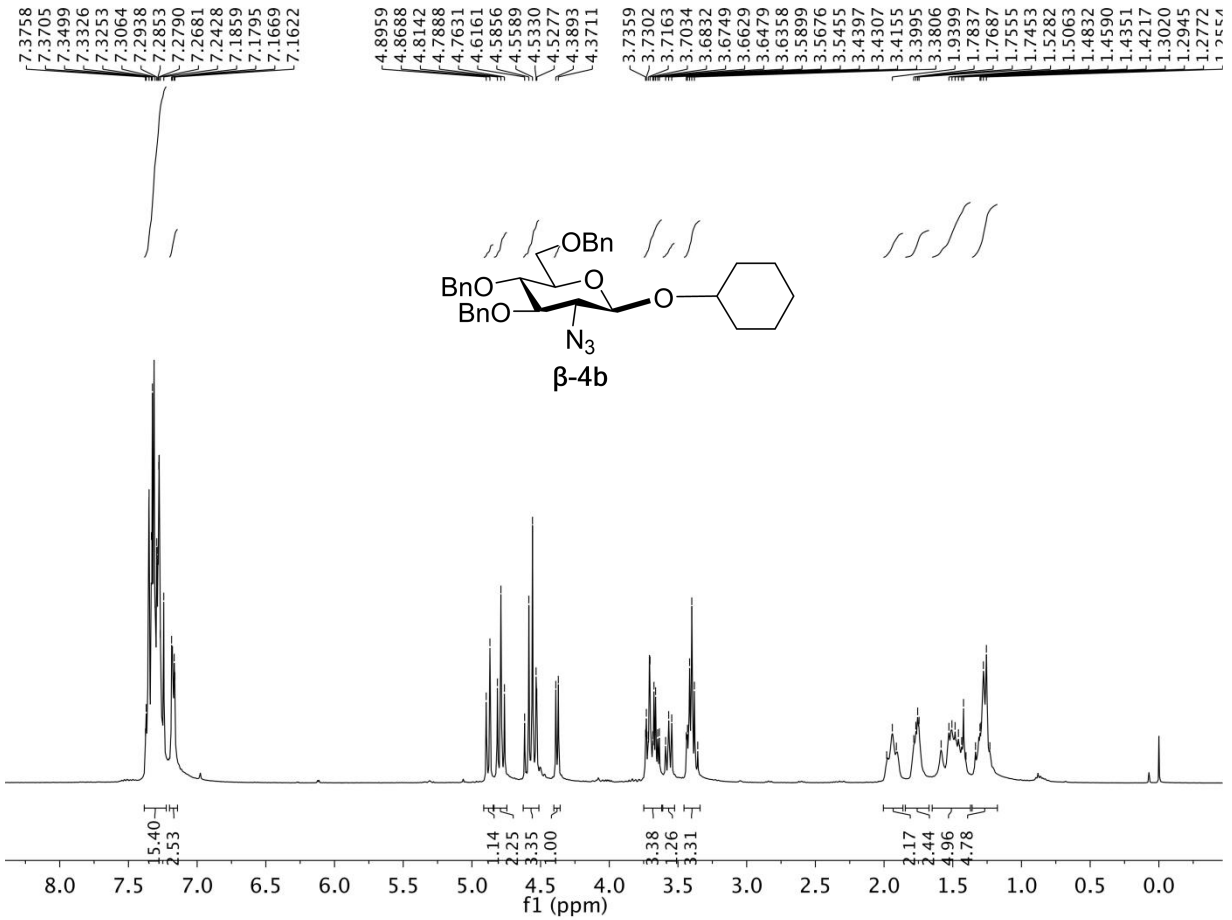


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-4b**

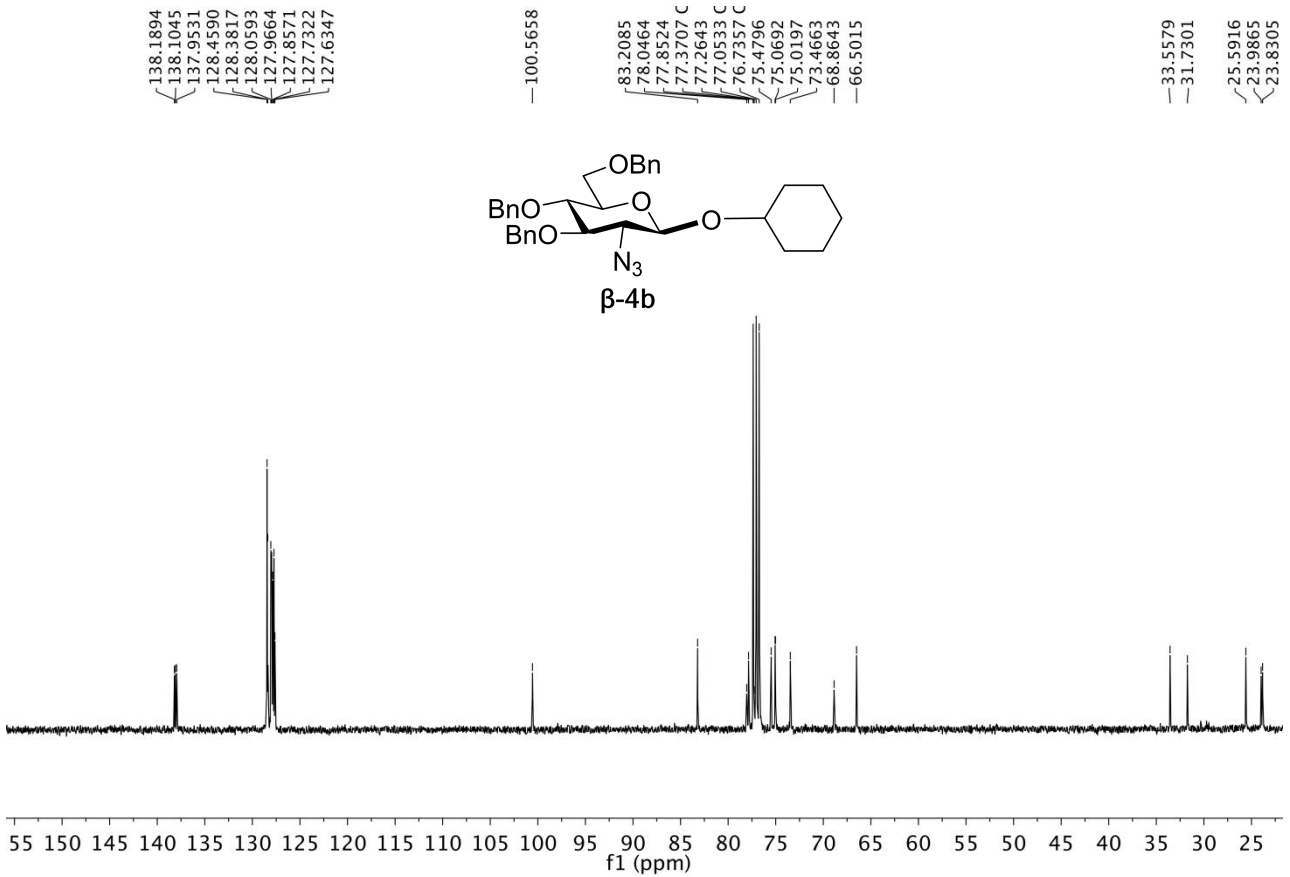


Figure S64. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-4b**

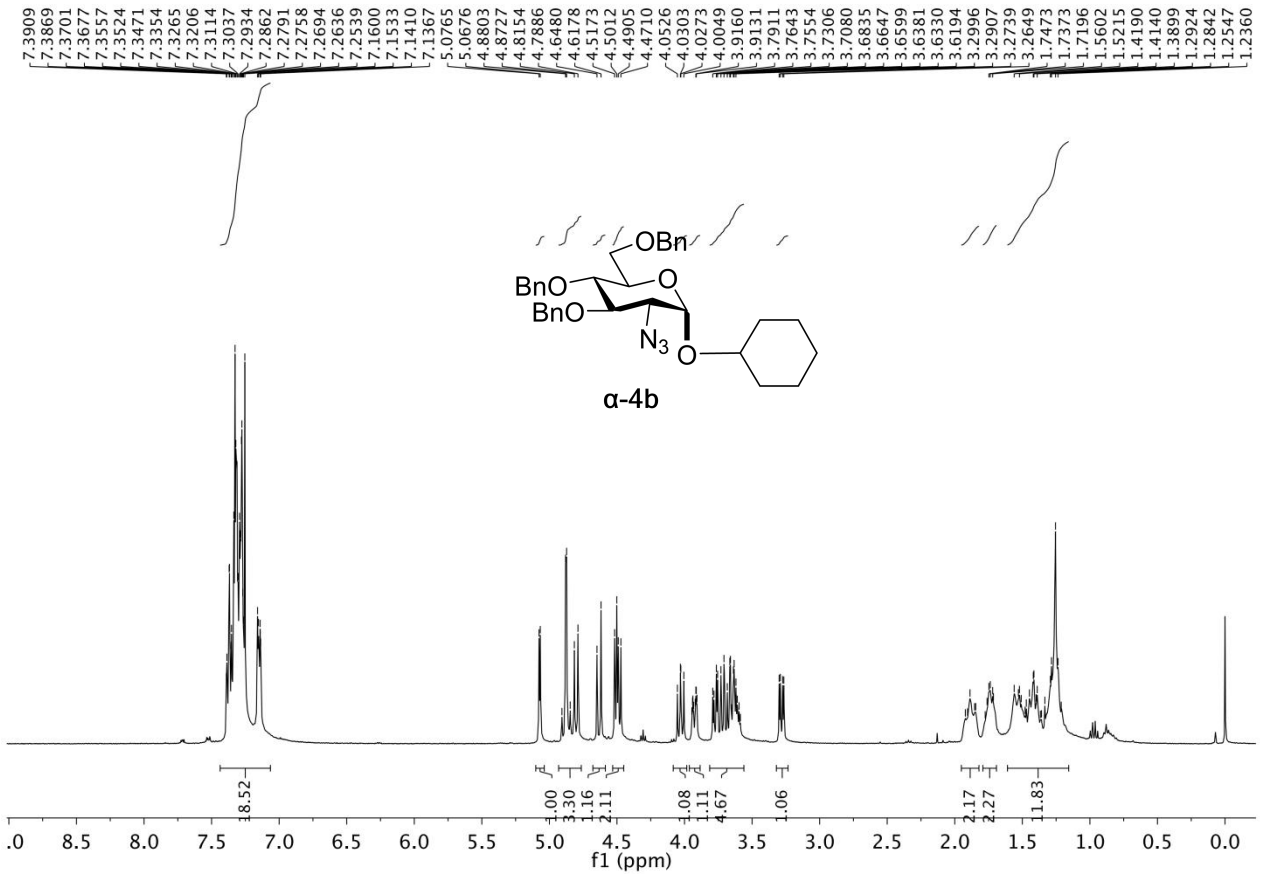


Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-4b**

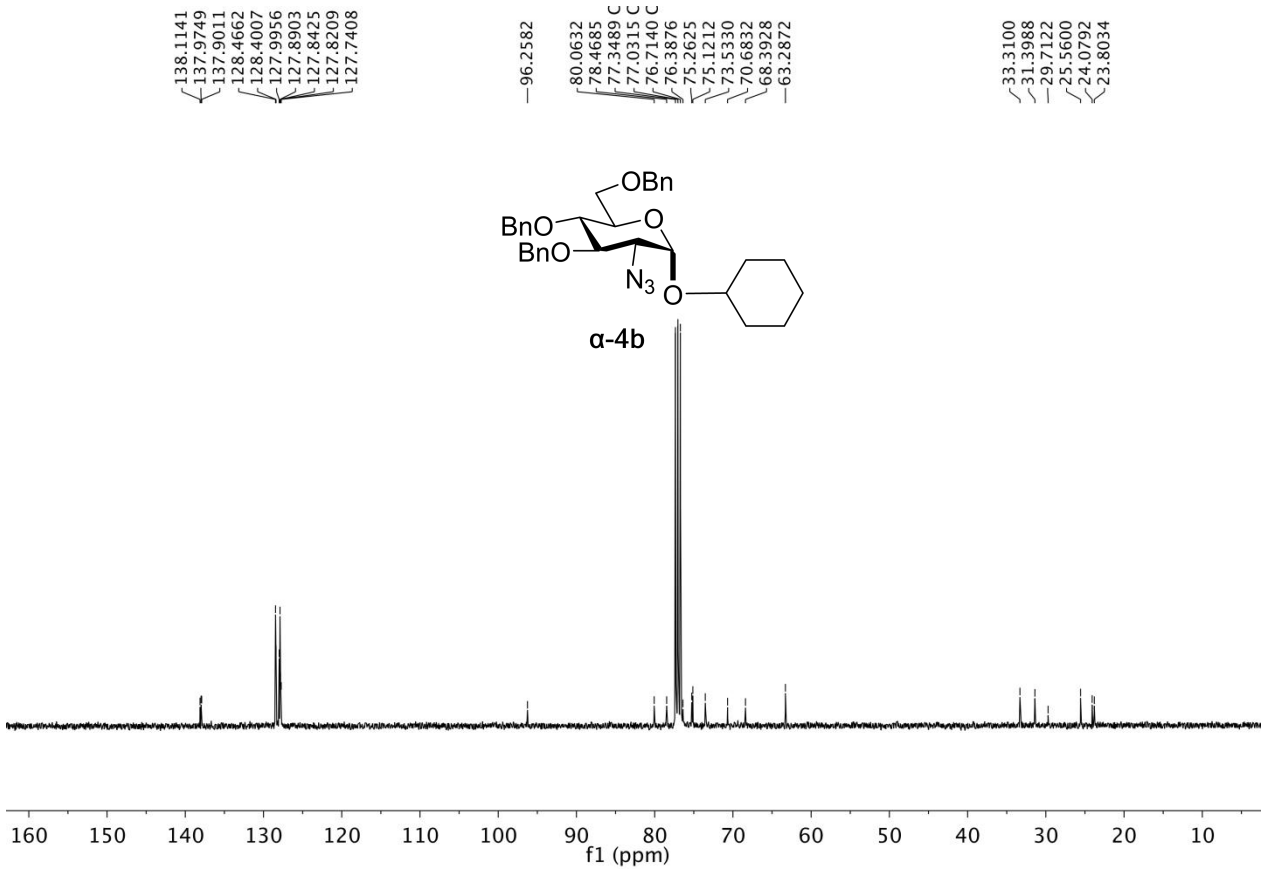


Figure S66. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-4b**

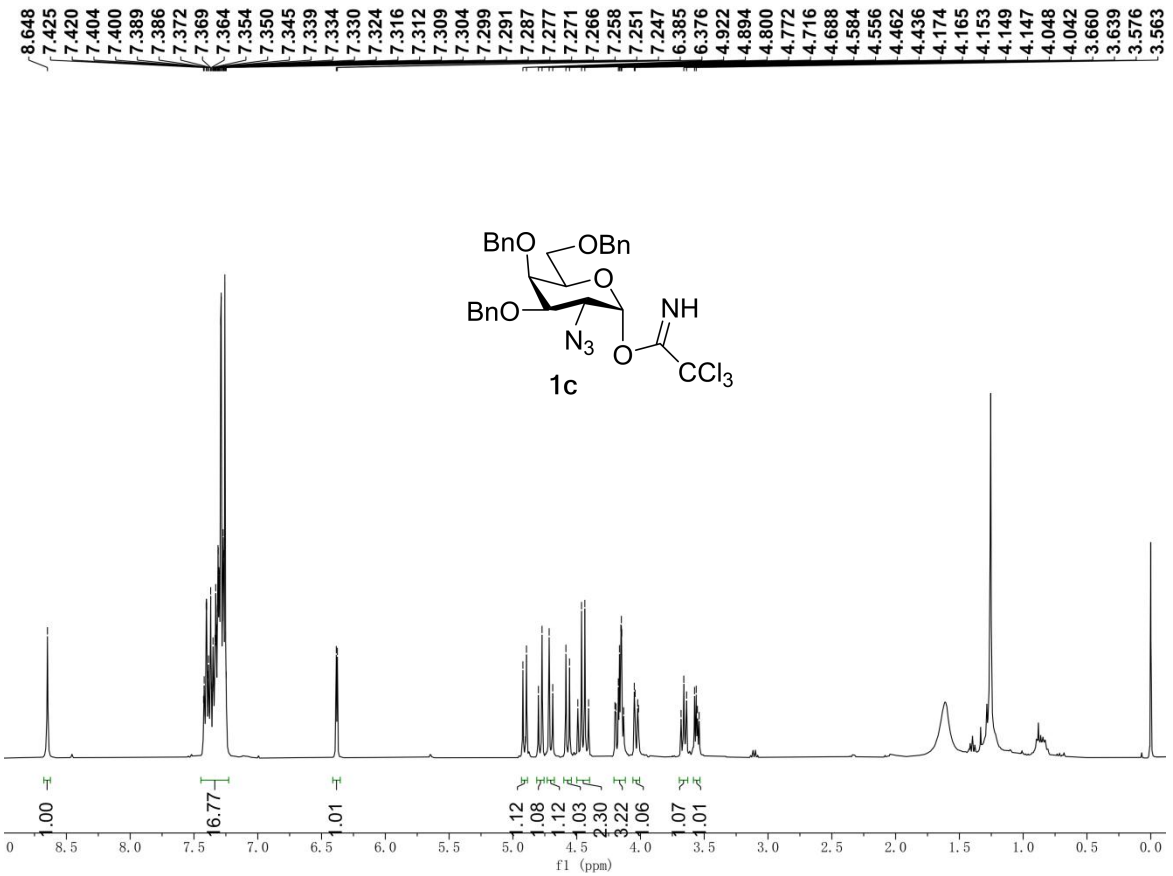


Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1c**

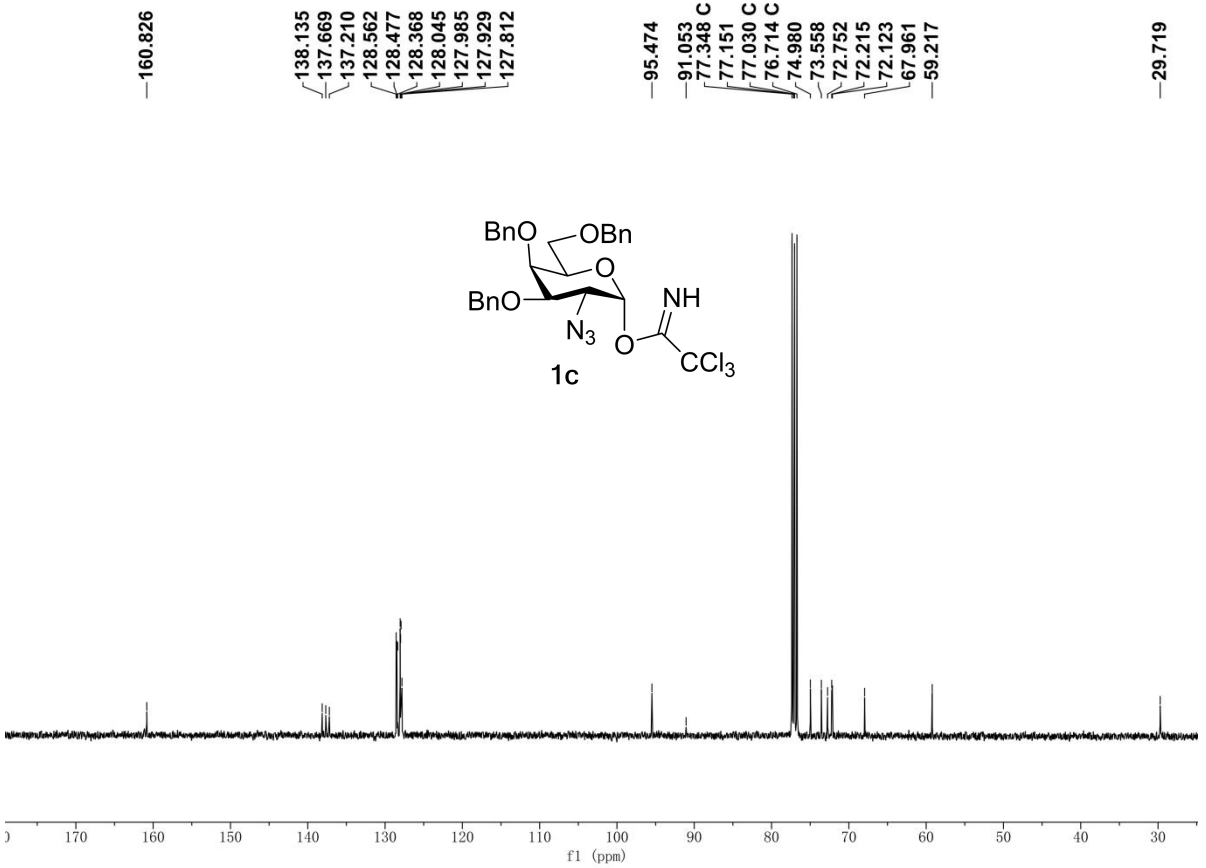


Figure S68. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **1c**

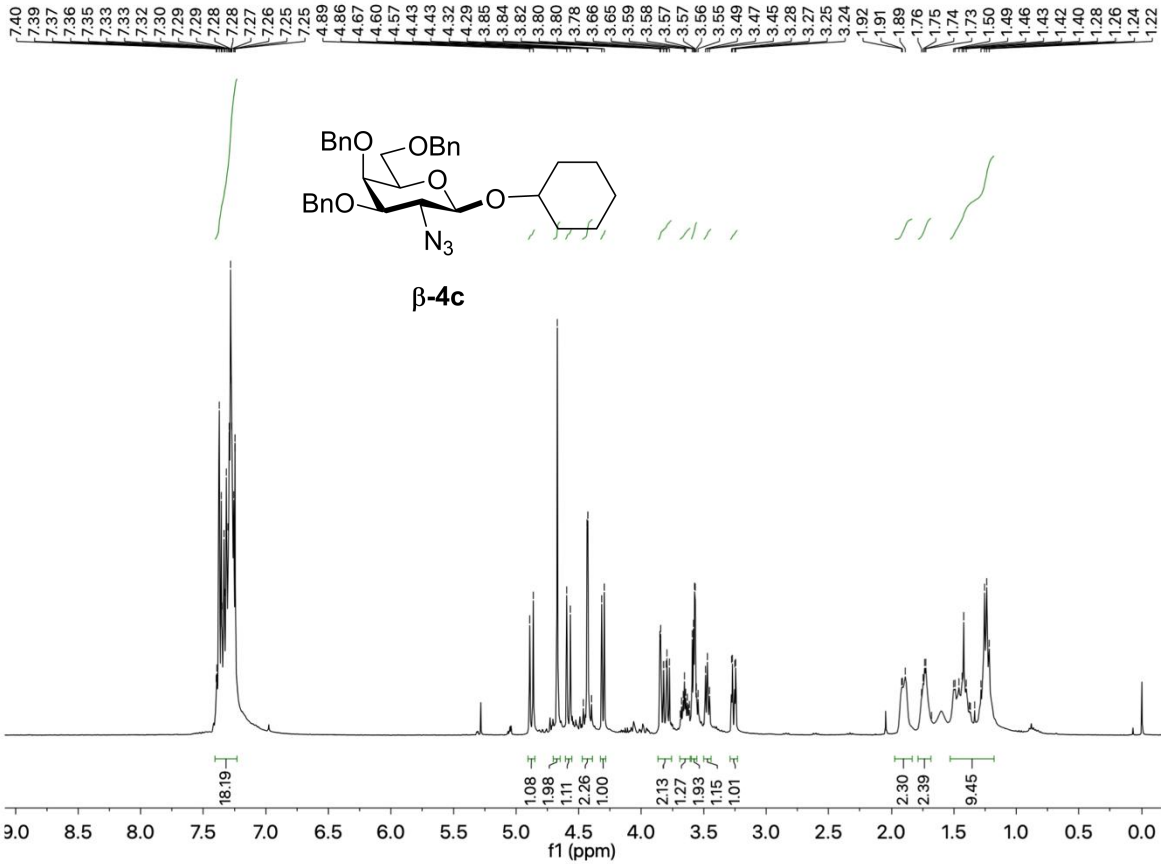


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-4c**

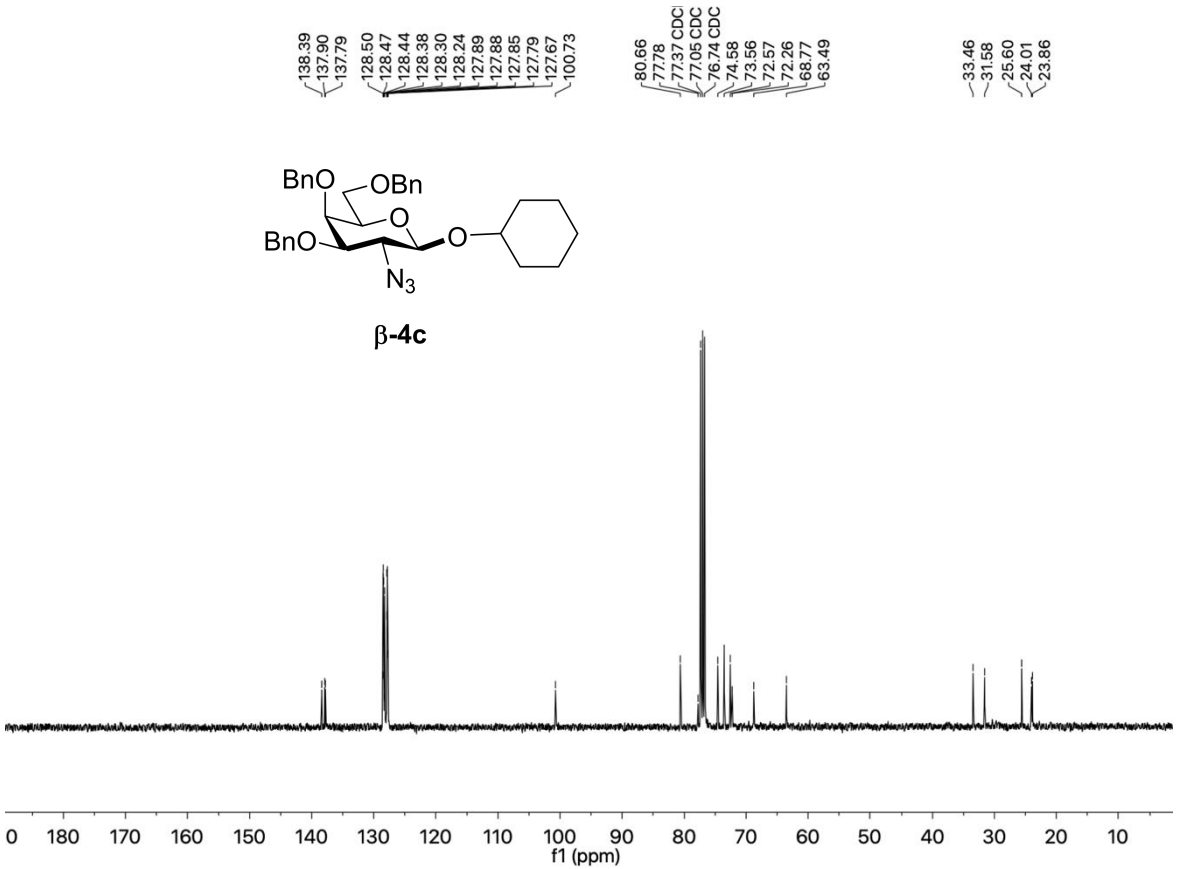


Figure S70. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-4c**

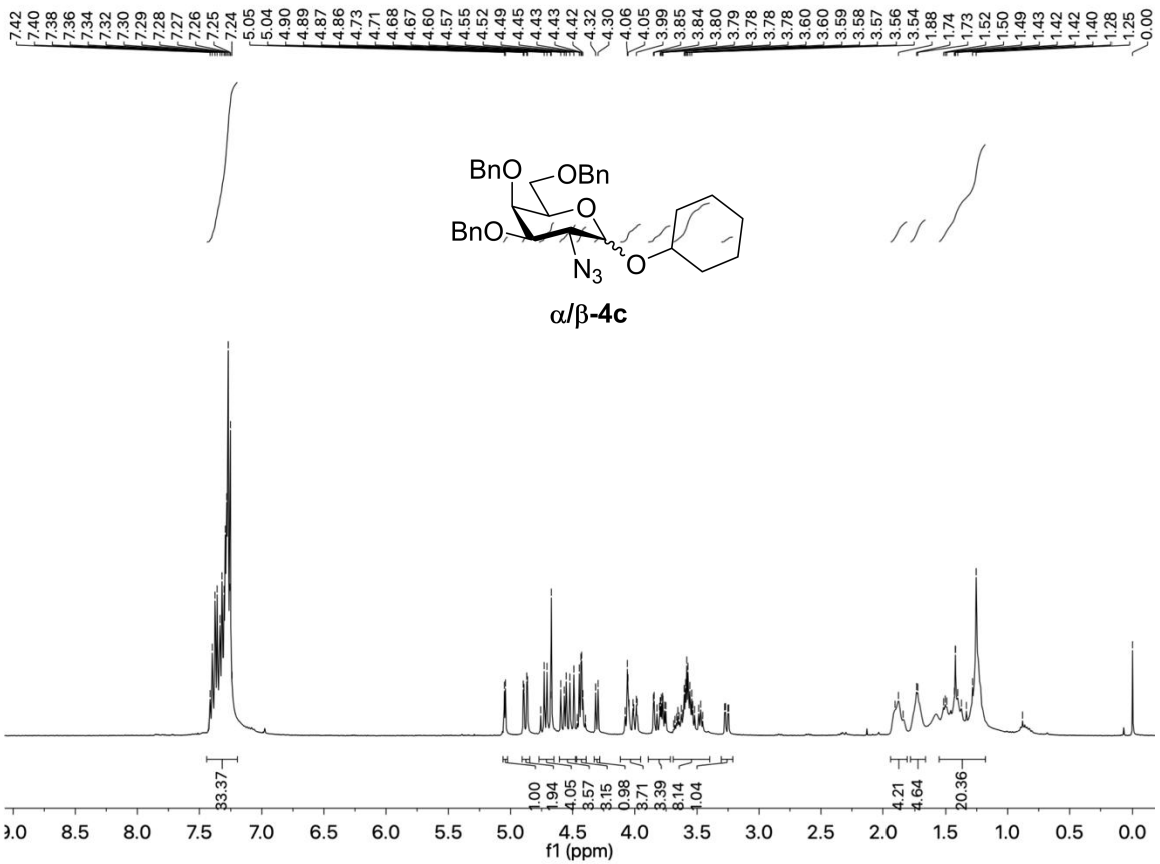


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α/β-4c**

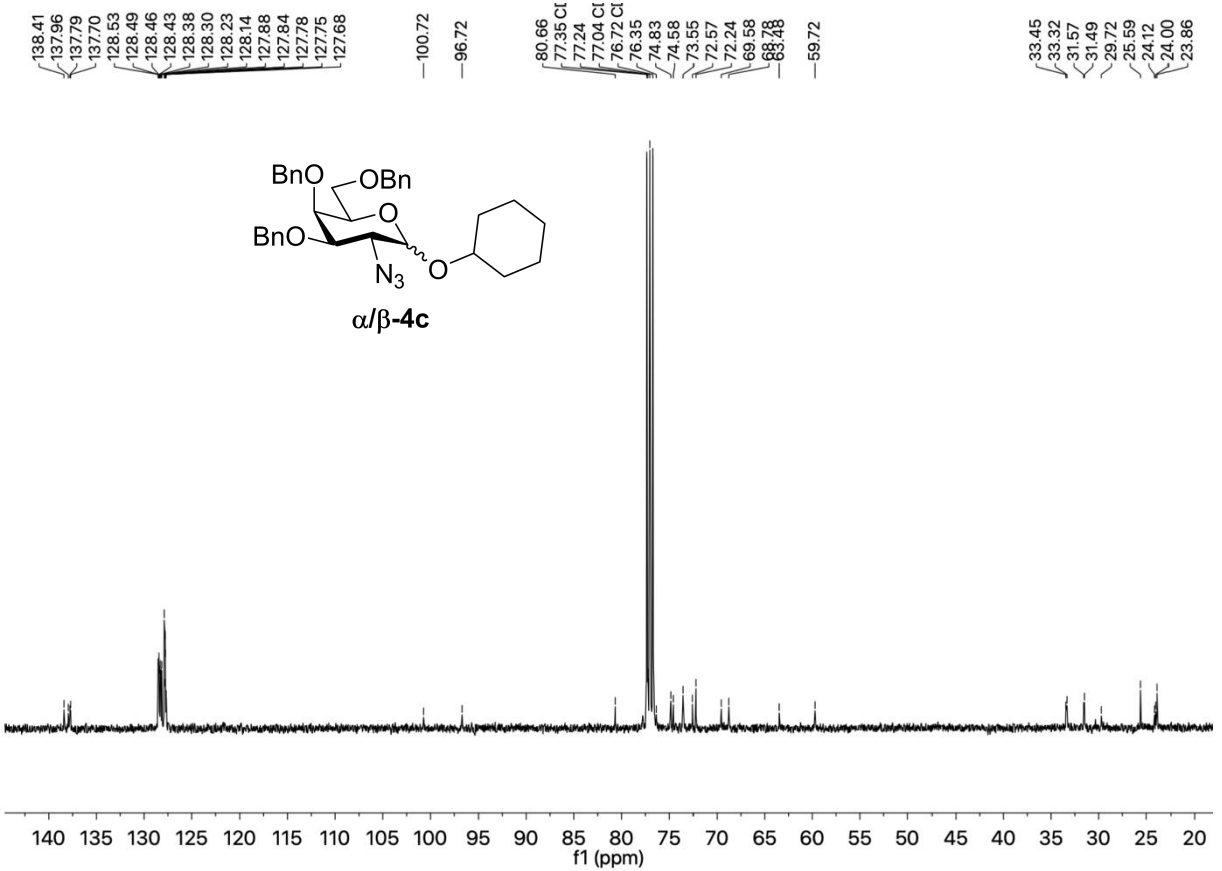


Figure S72. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α/β-4c**

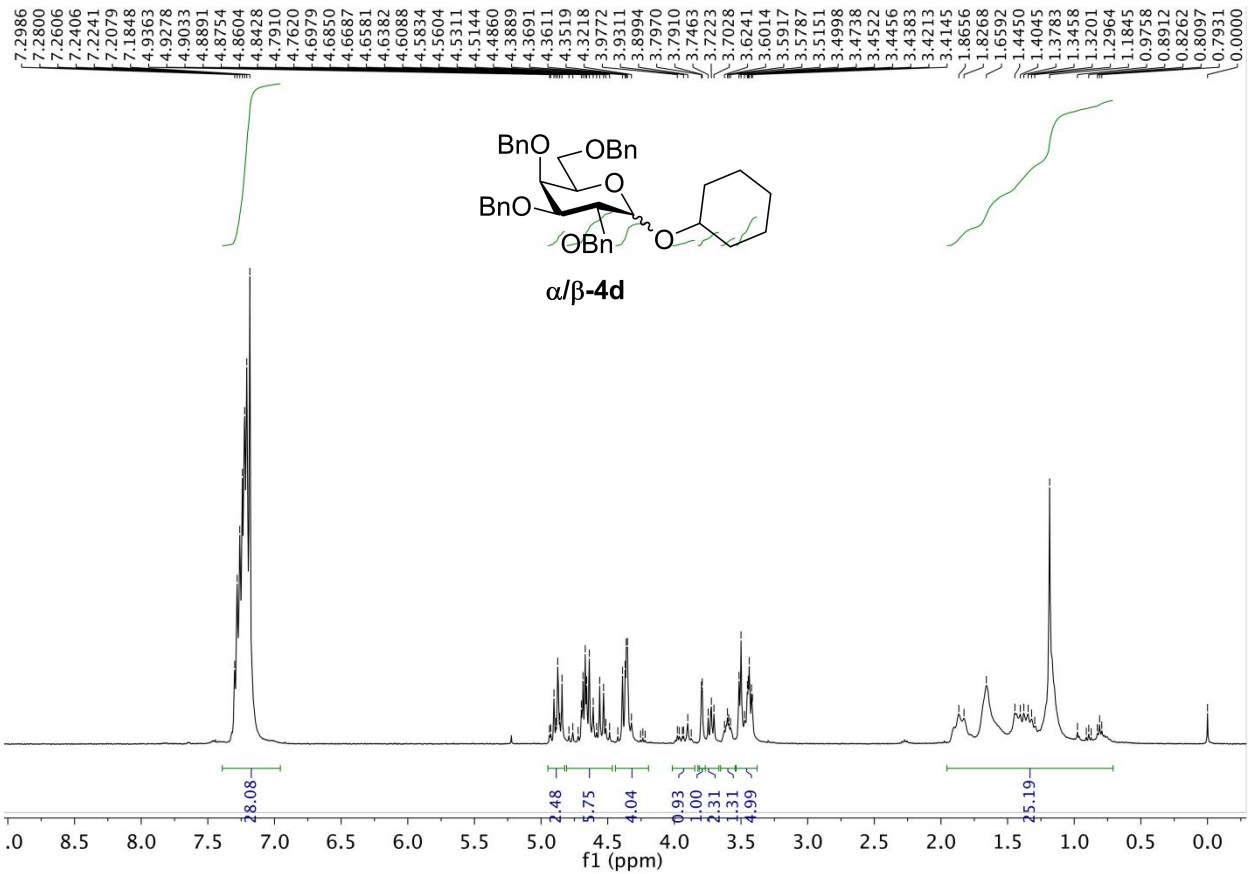


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α/β-4d** (condition A)

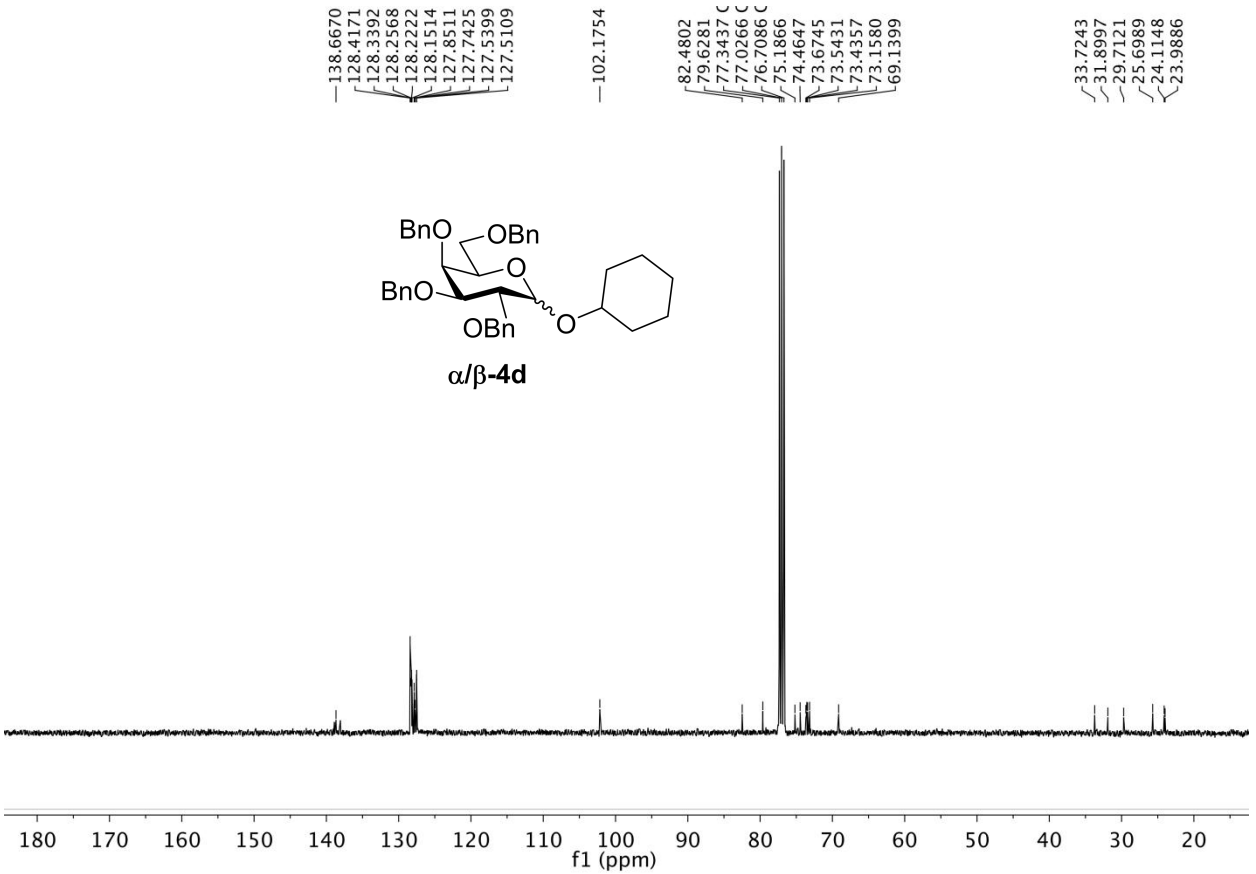


Figure S74. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α/β-4d** (condition A)

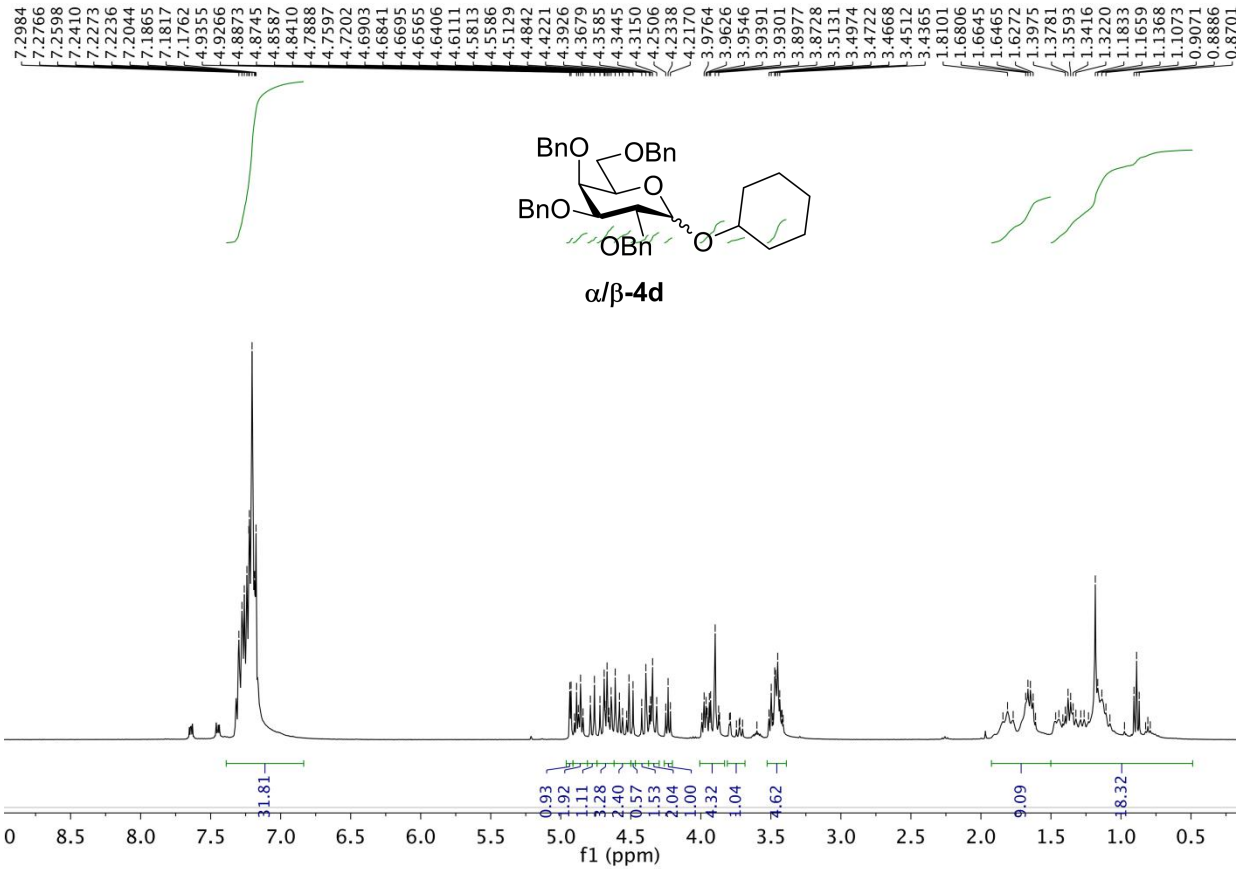


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α/β-4d** (condition B)

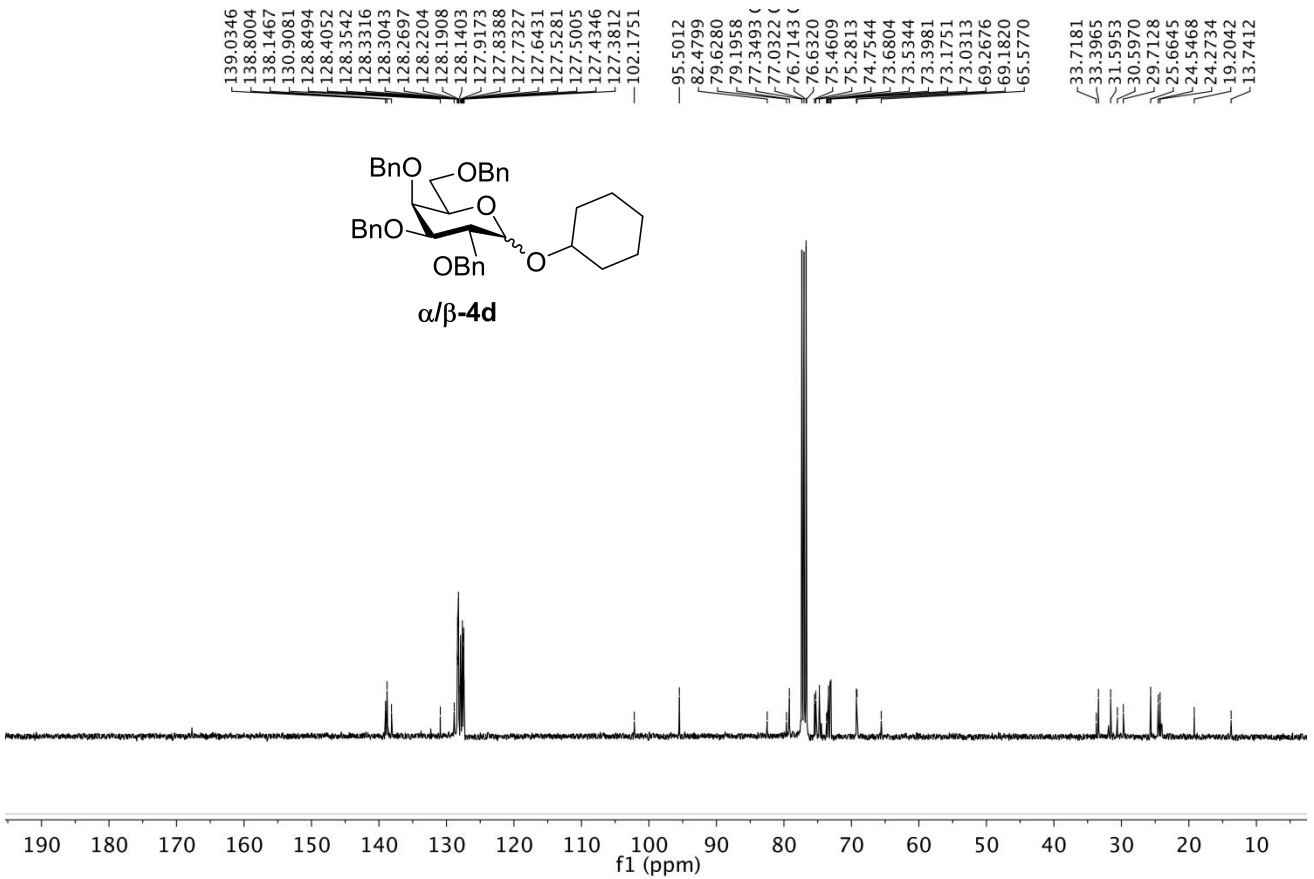


Figure S76. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α/β-4d** (condition B)

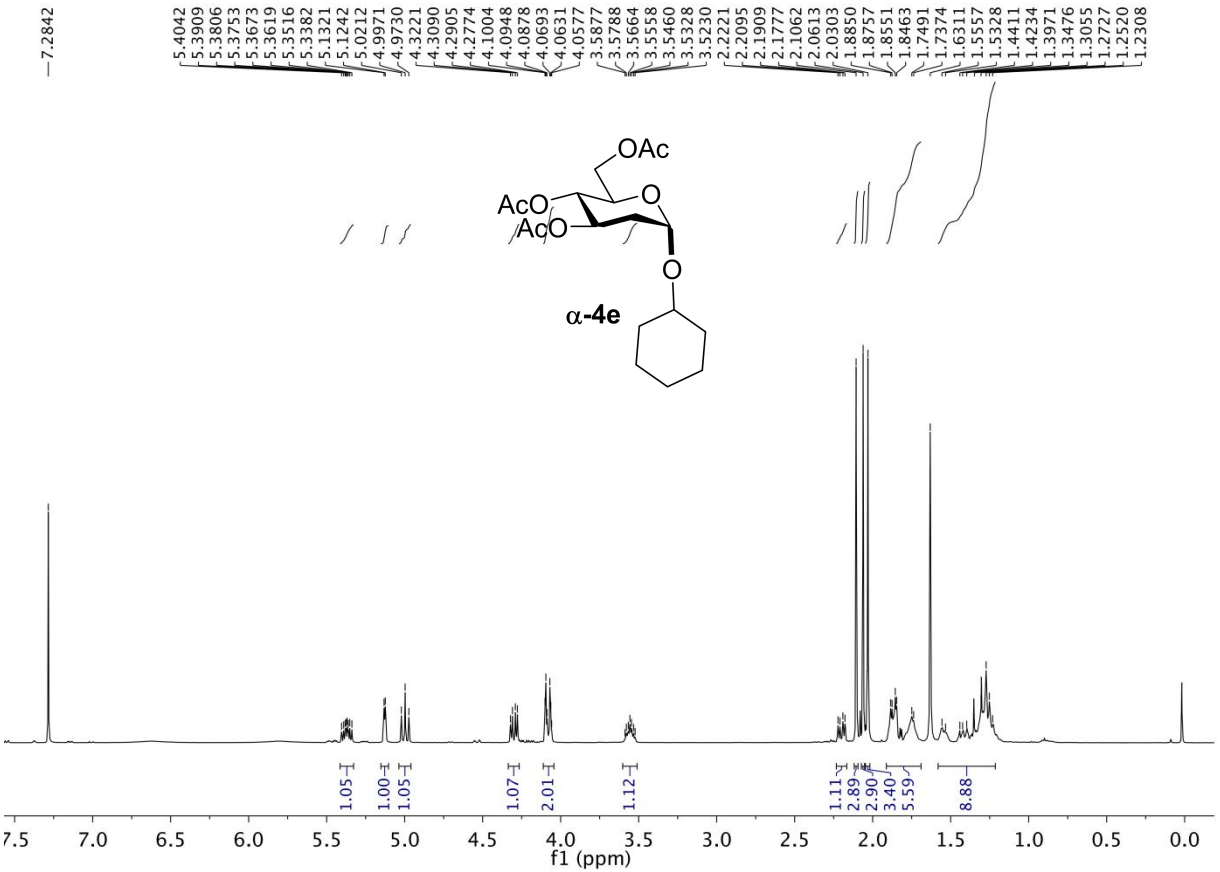


Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-4e**

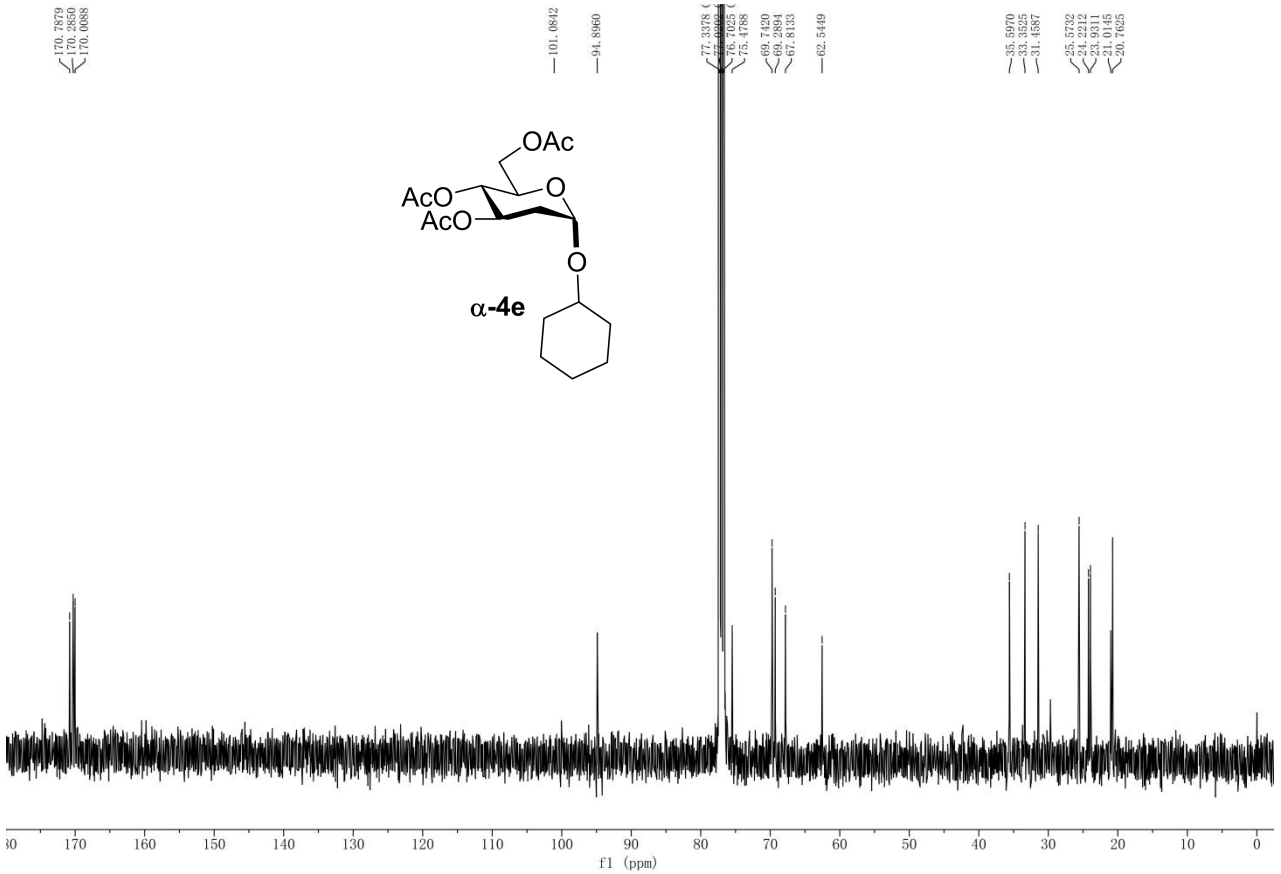


Figure S78. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-4e**

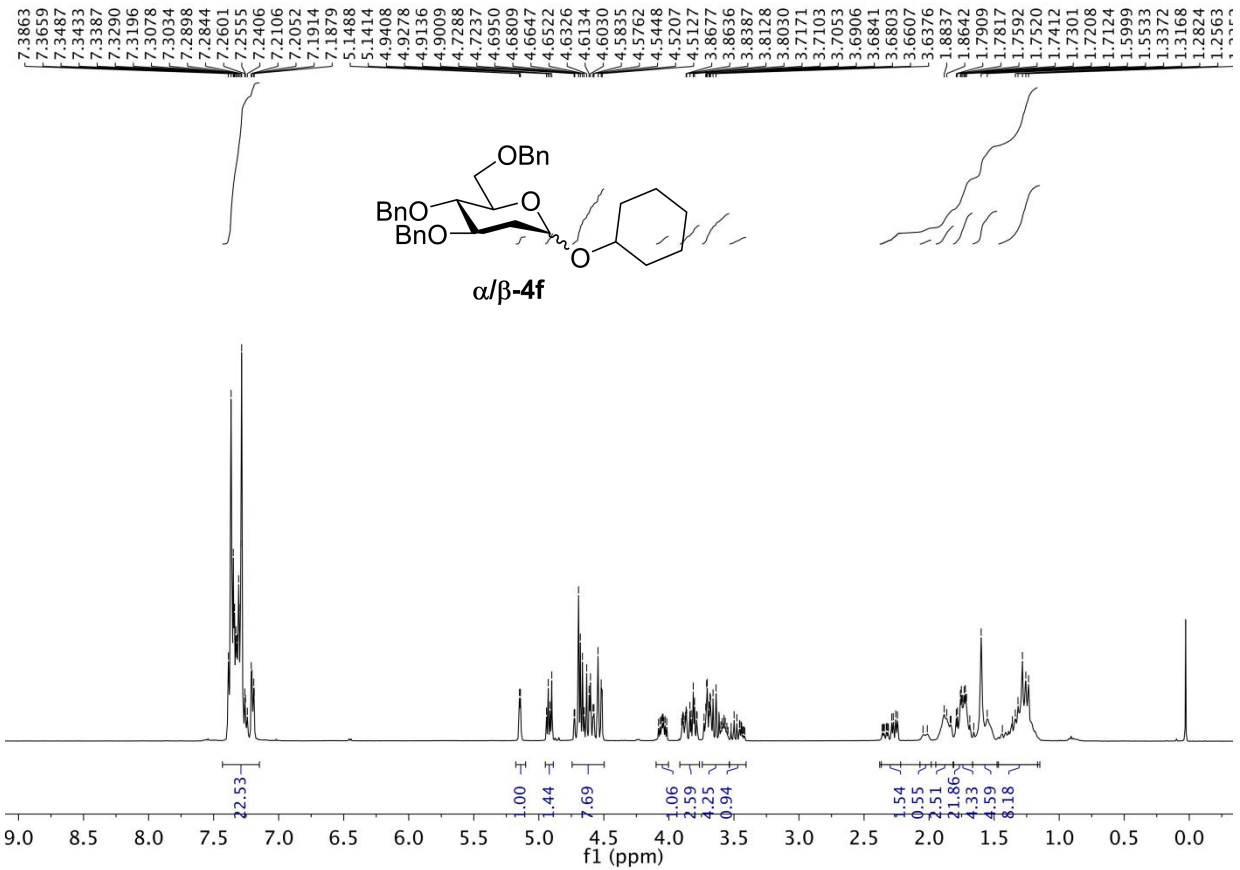


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α/β-4f**

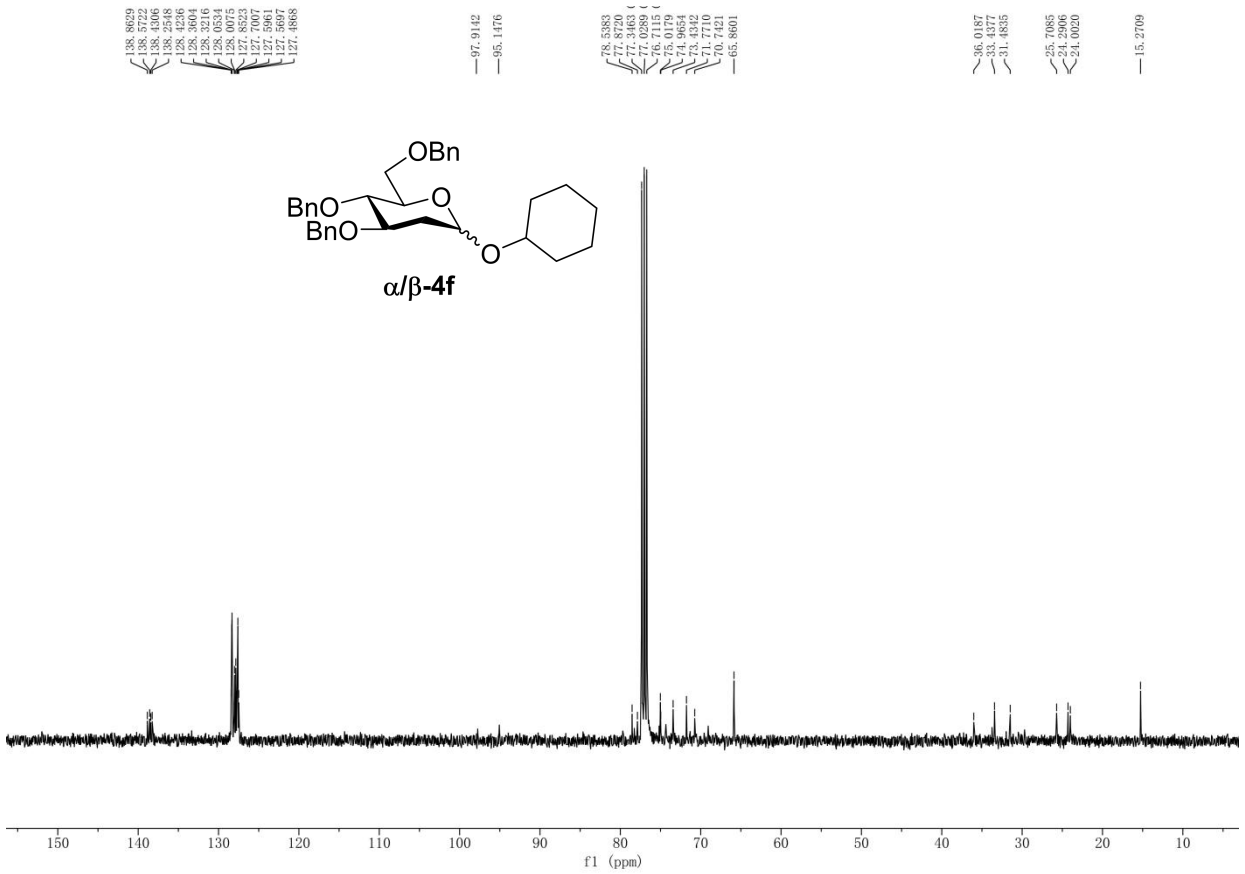


Figure S80. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α/β-4f**

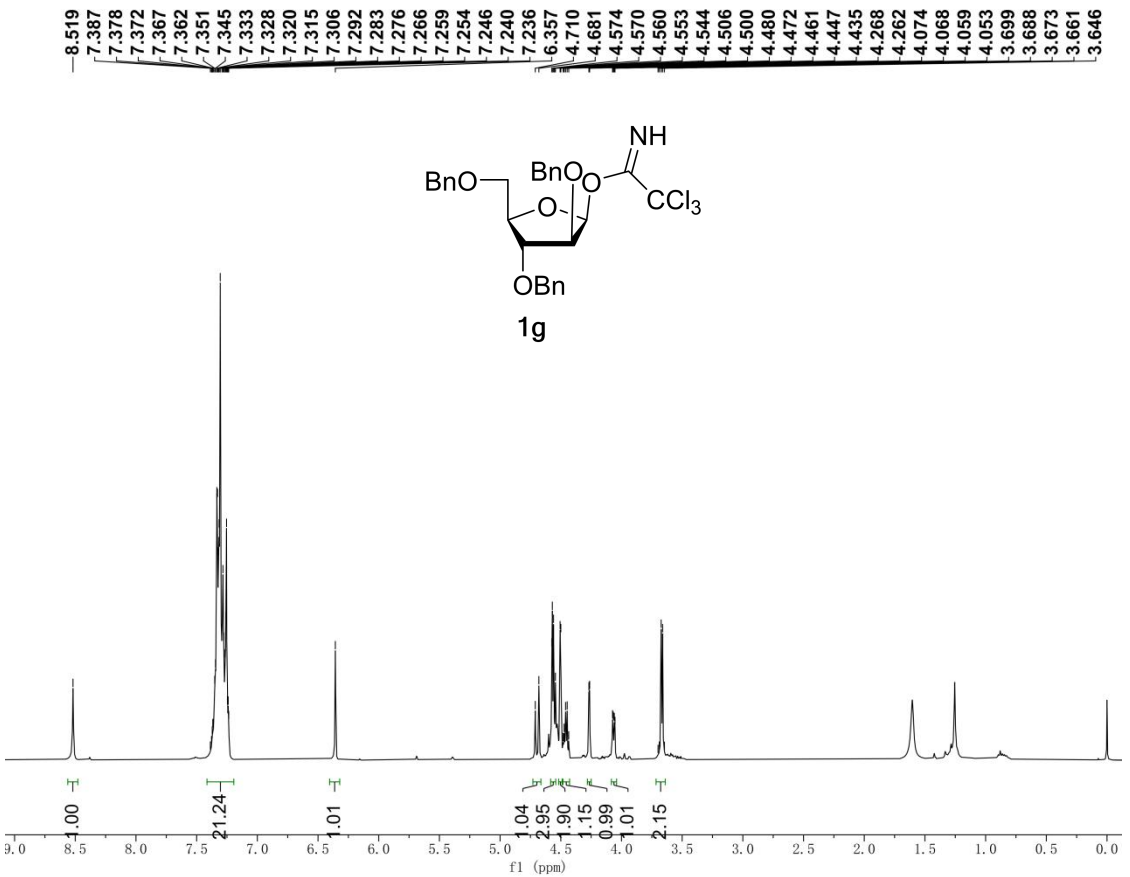


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1g**

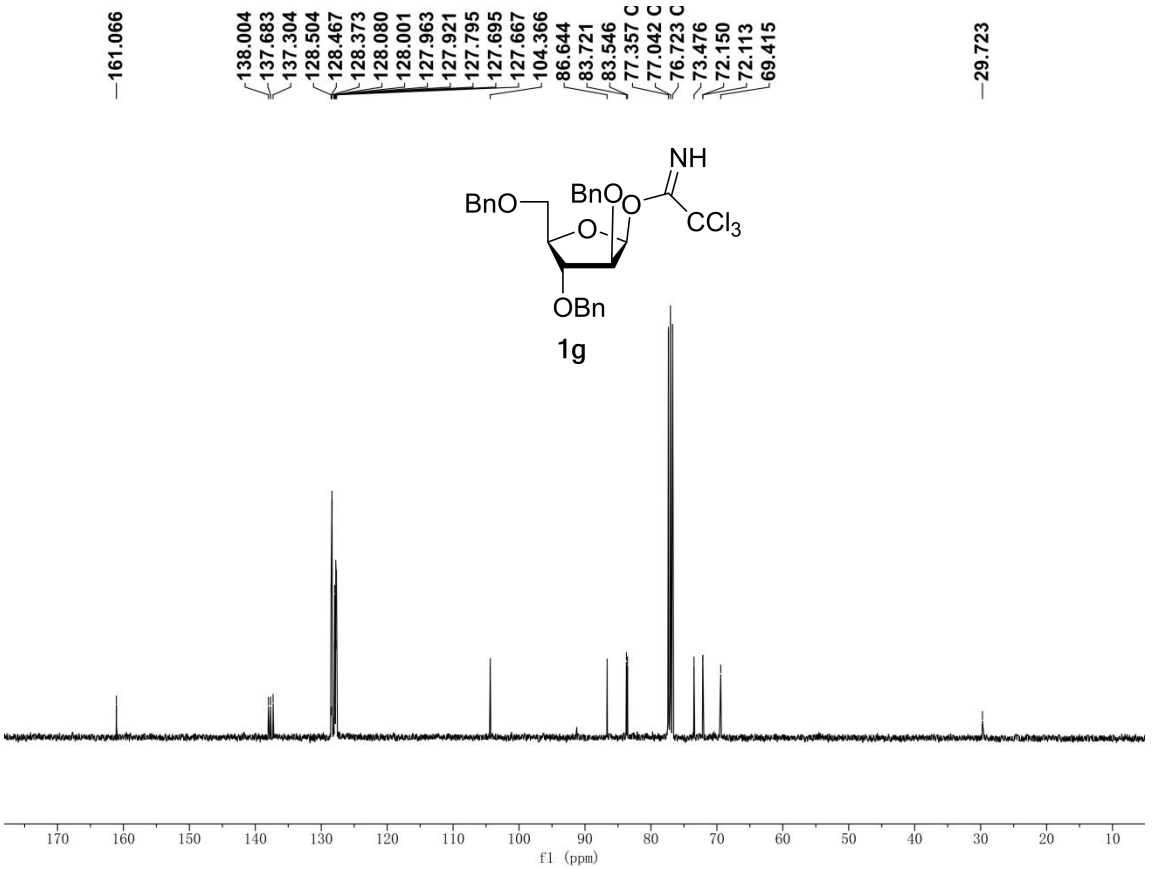


Figure S82. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **1g**

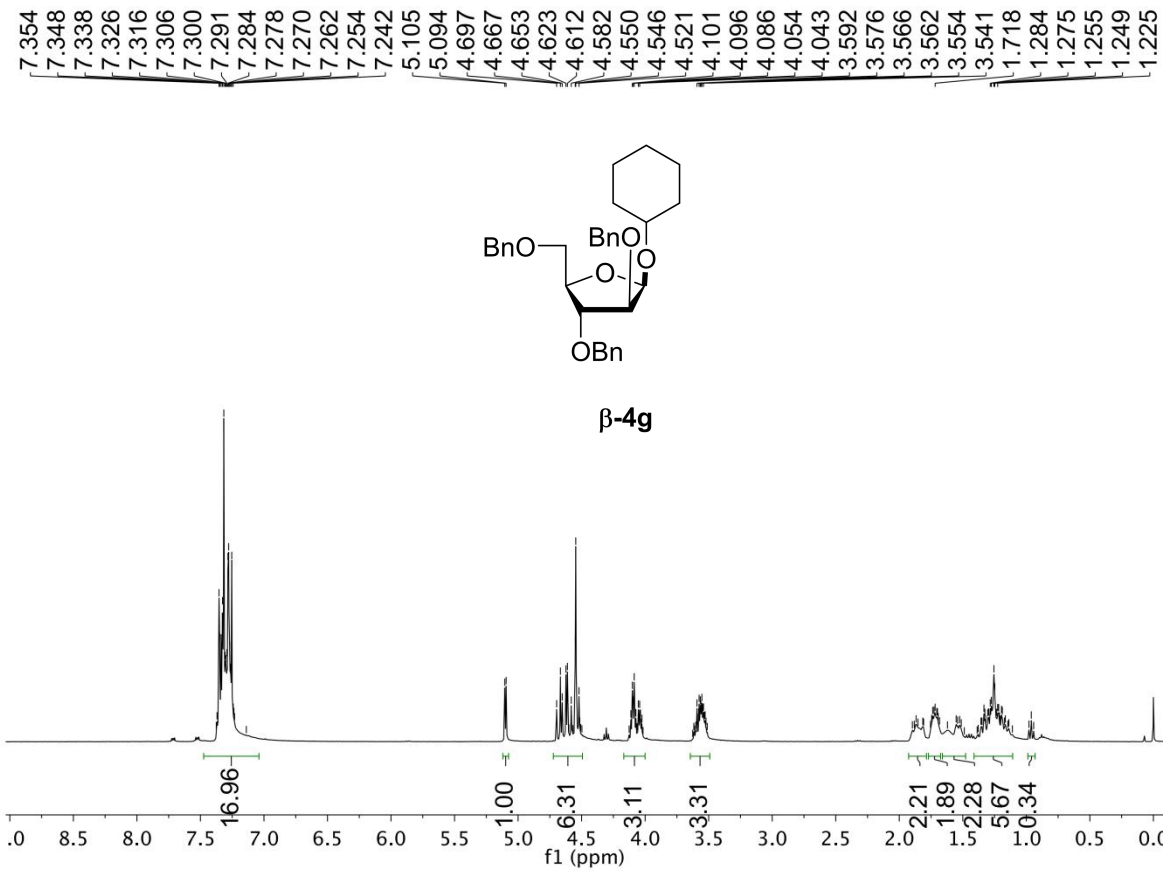


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-4g**

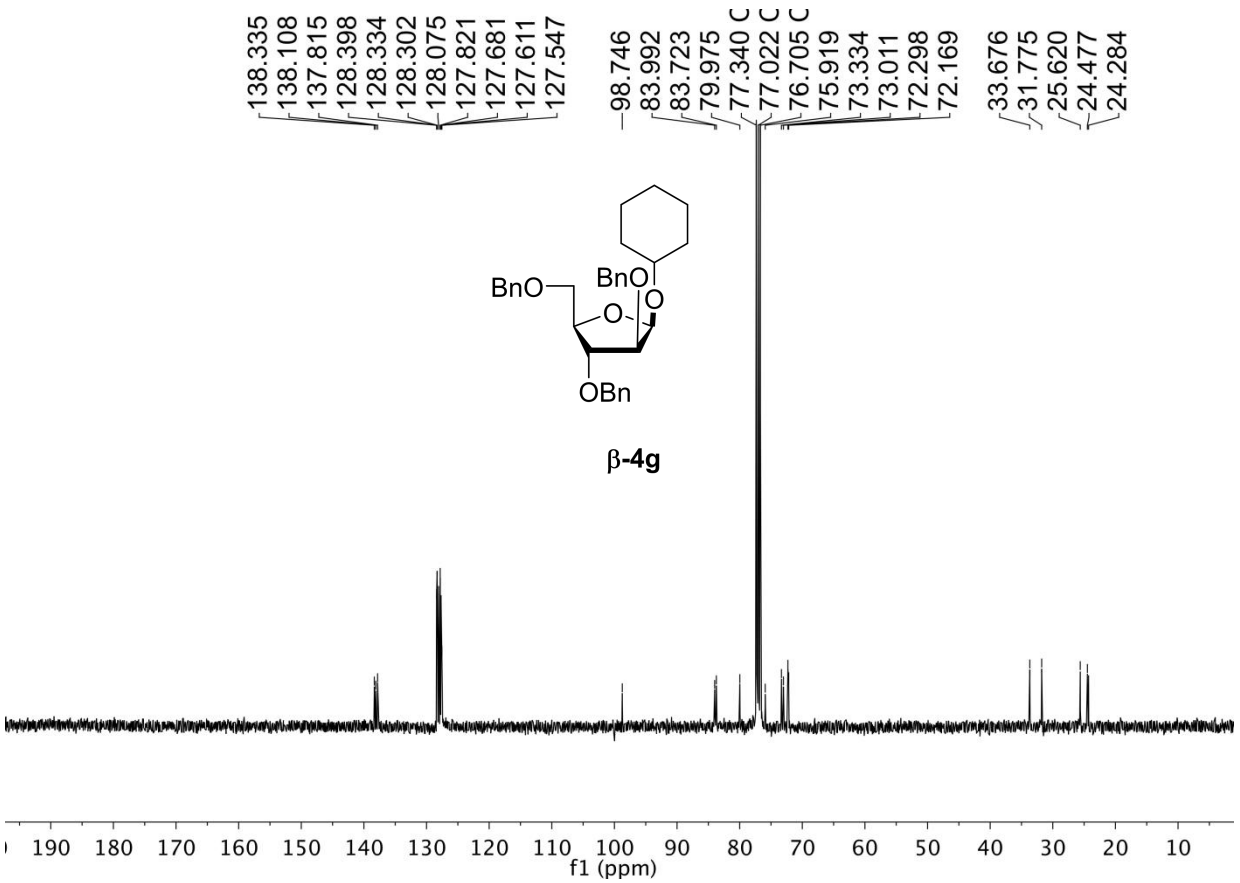


Figure S84. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-4g**

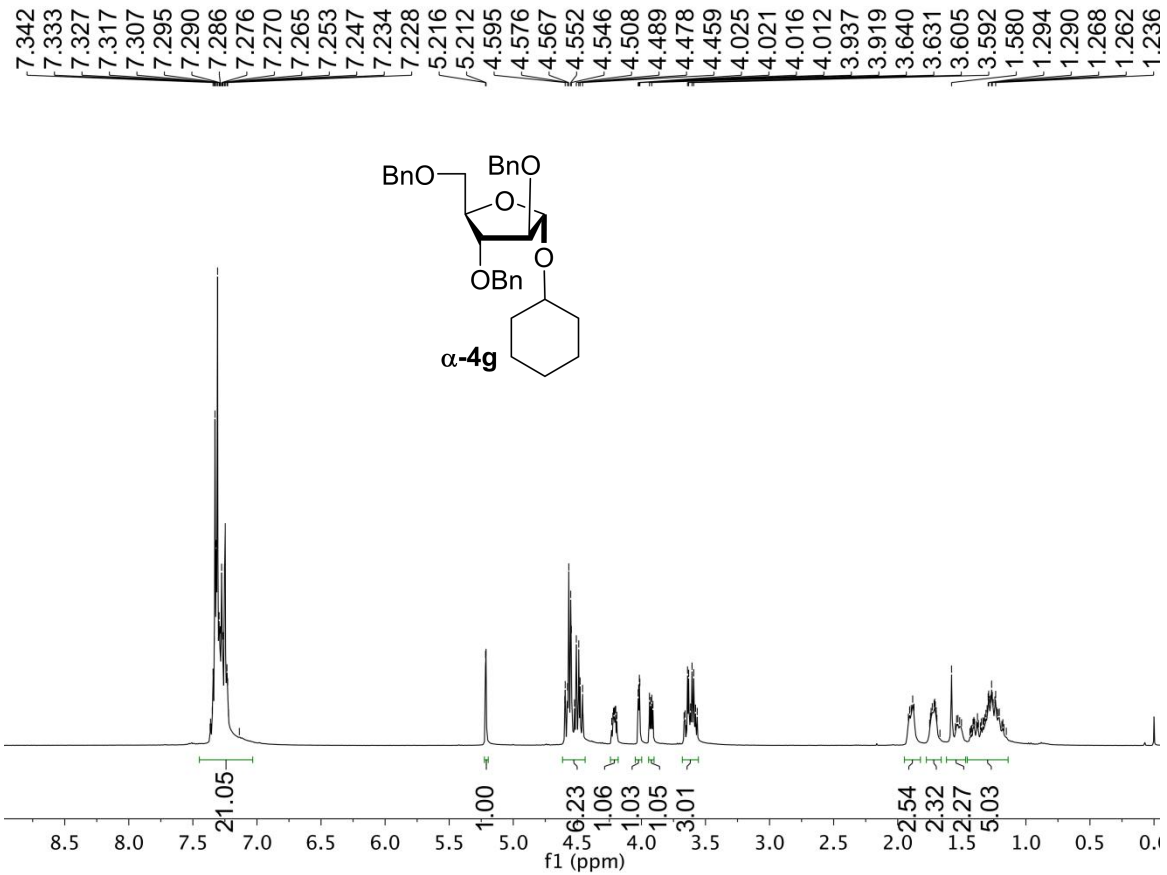


Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-4g**

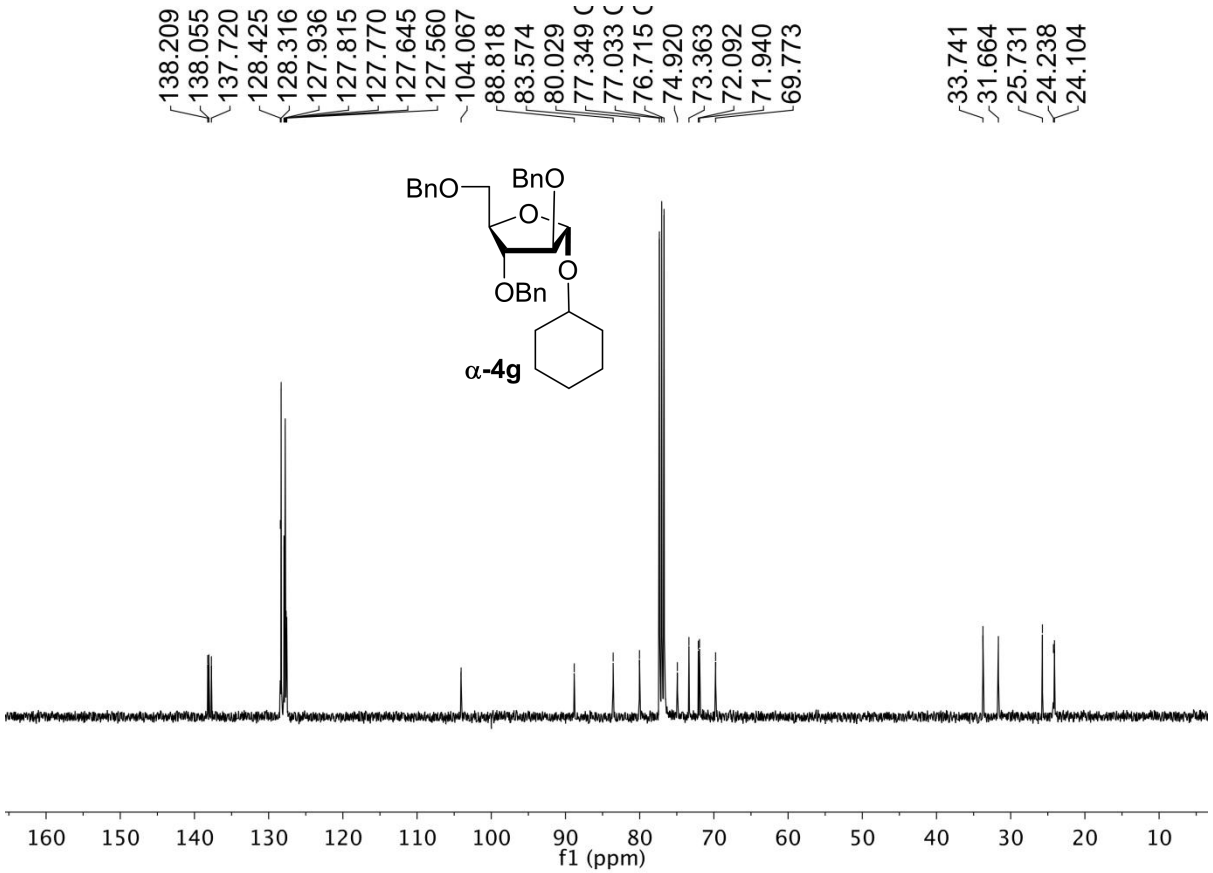


Figure S86. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-4g**

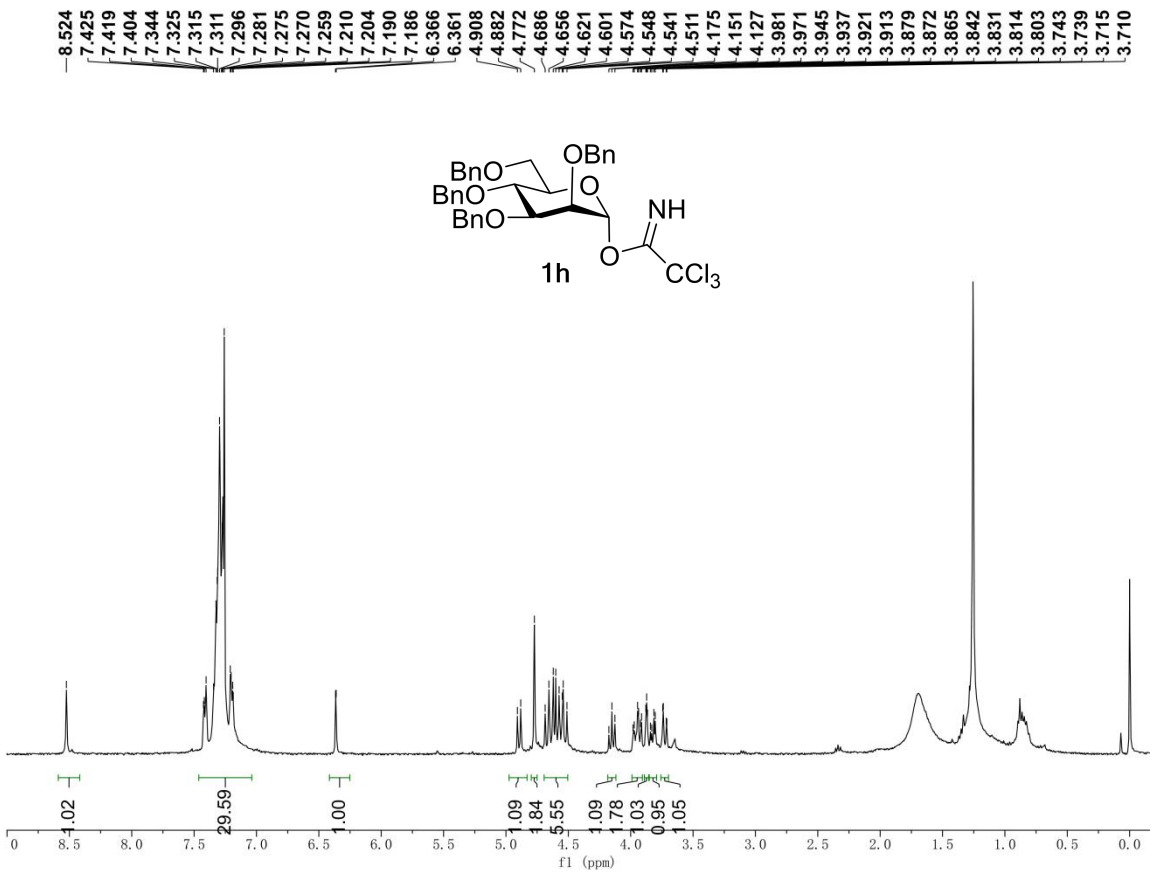


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1h**

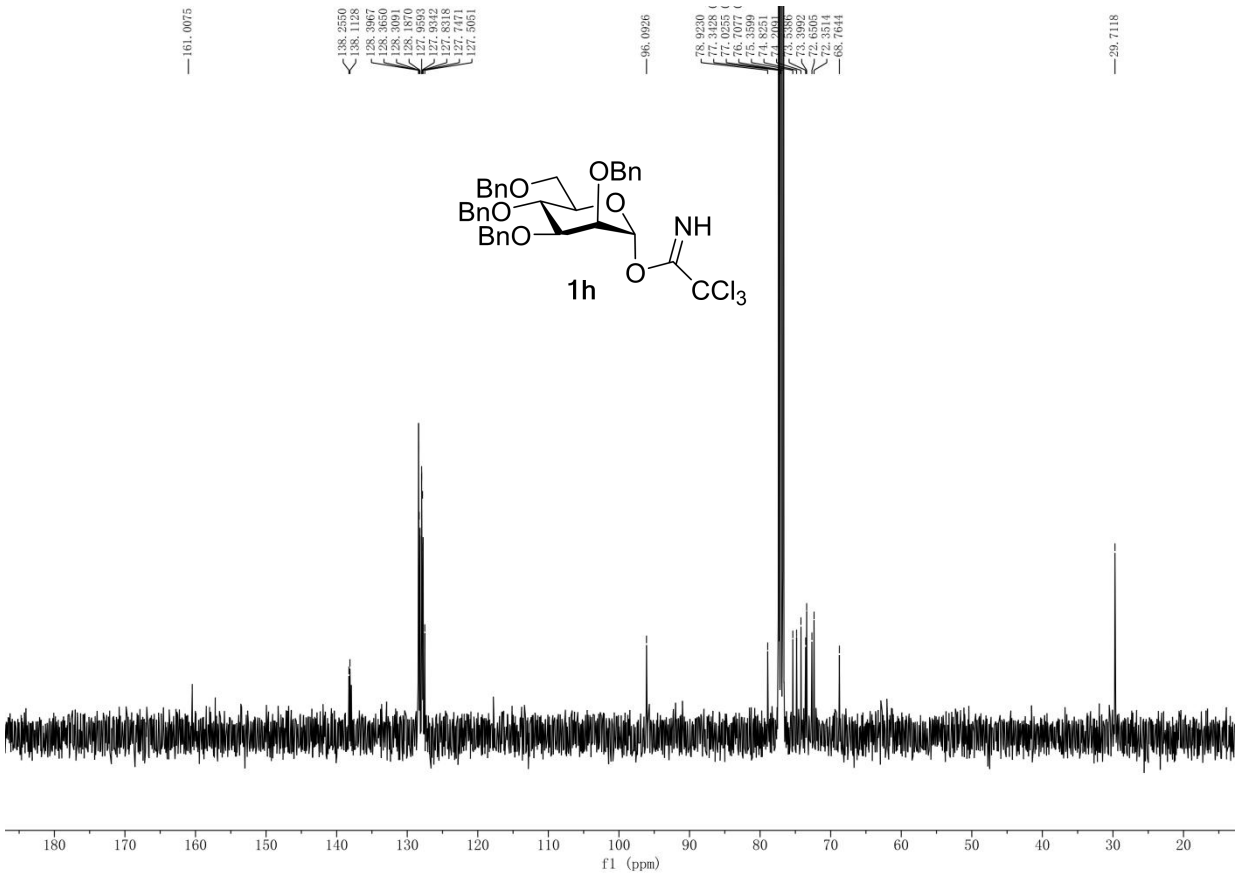


Figure S88. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **1h**

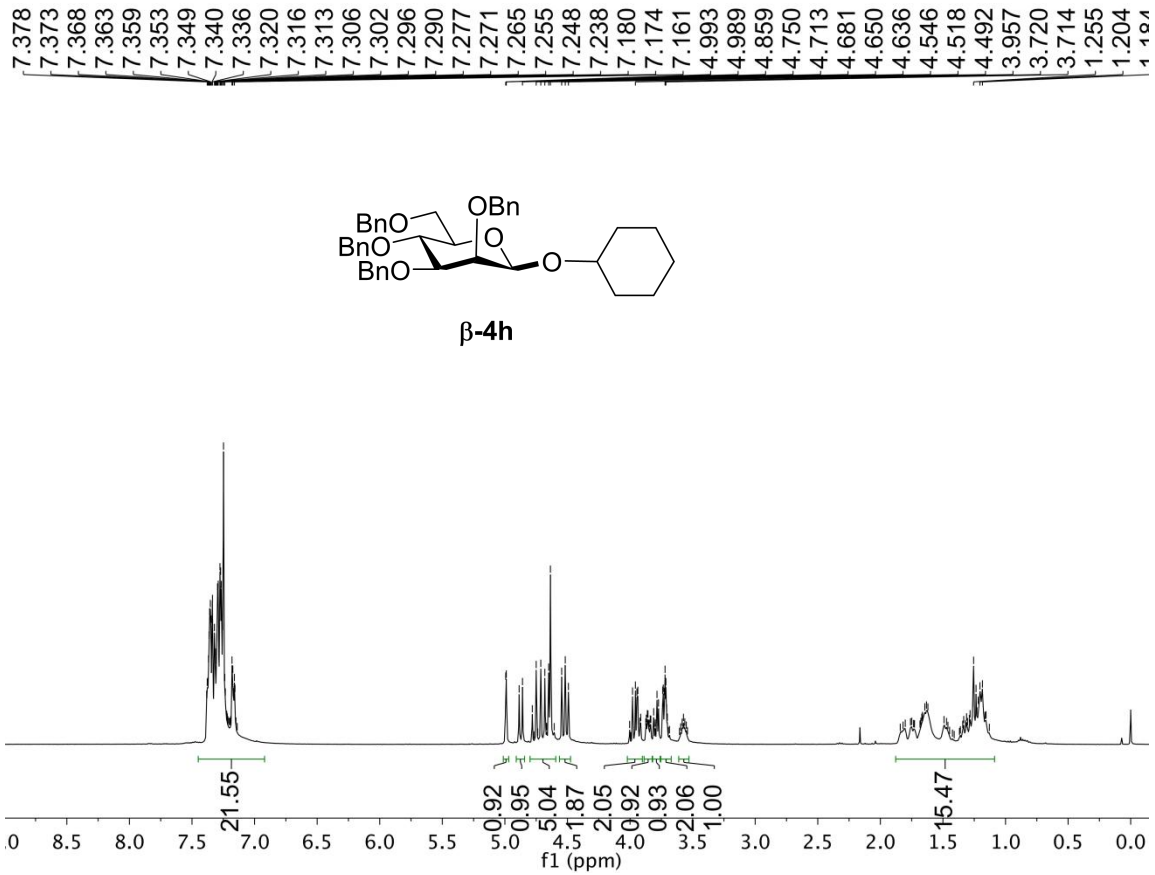


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-4h**

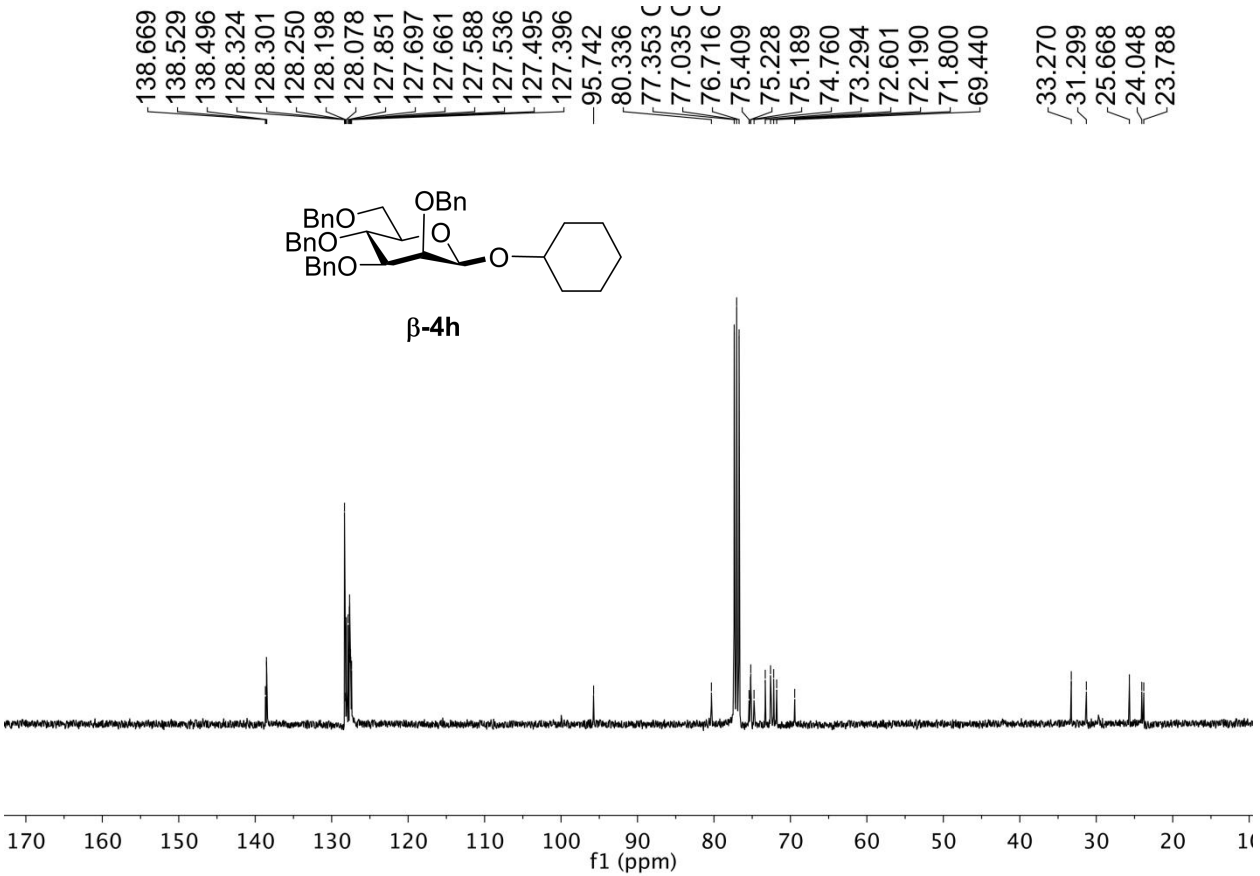


Figure S90. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-4h**

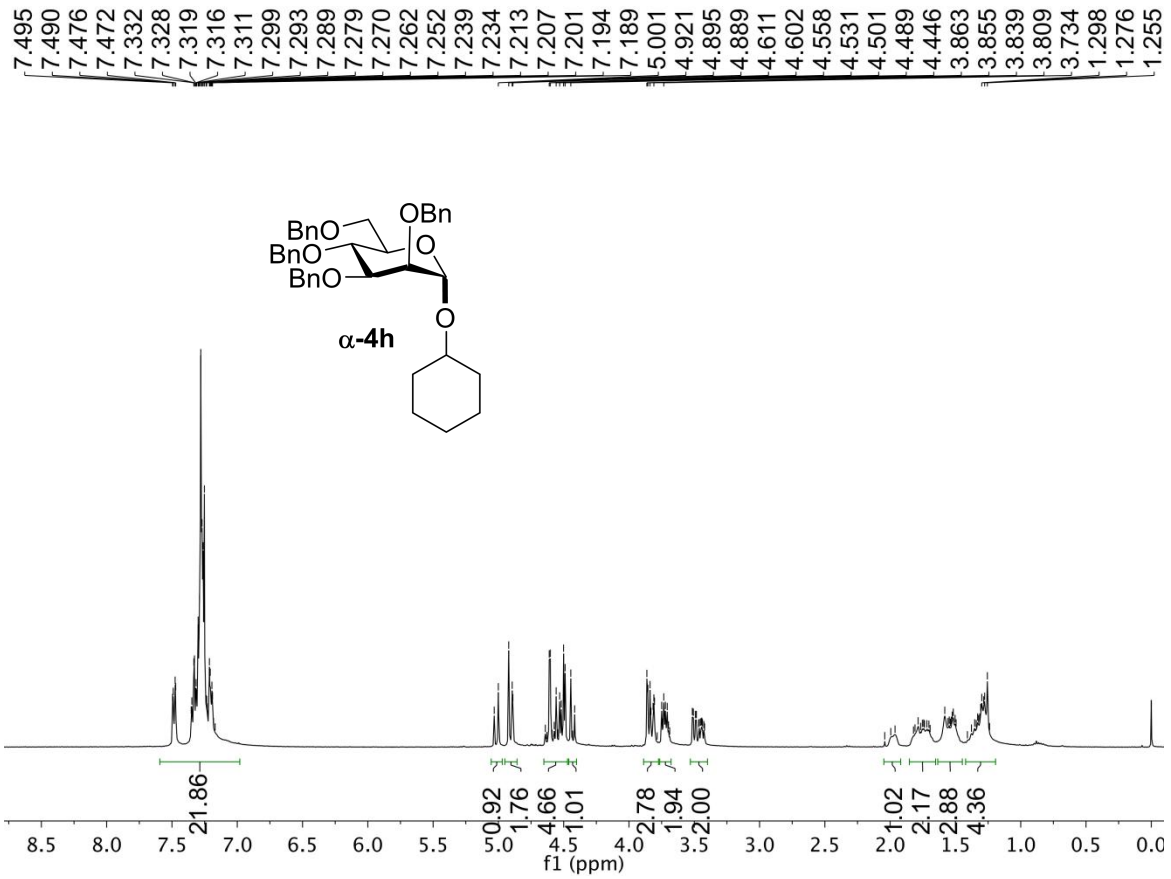


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-4h**

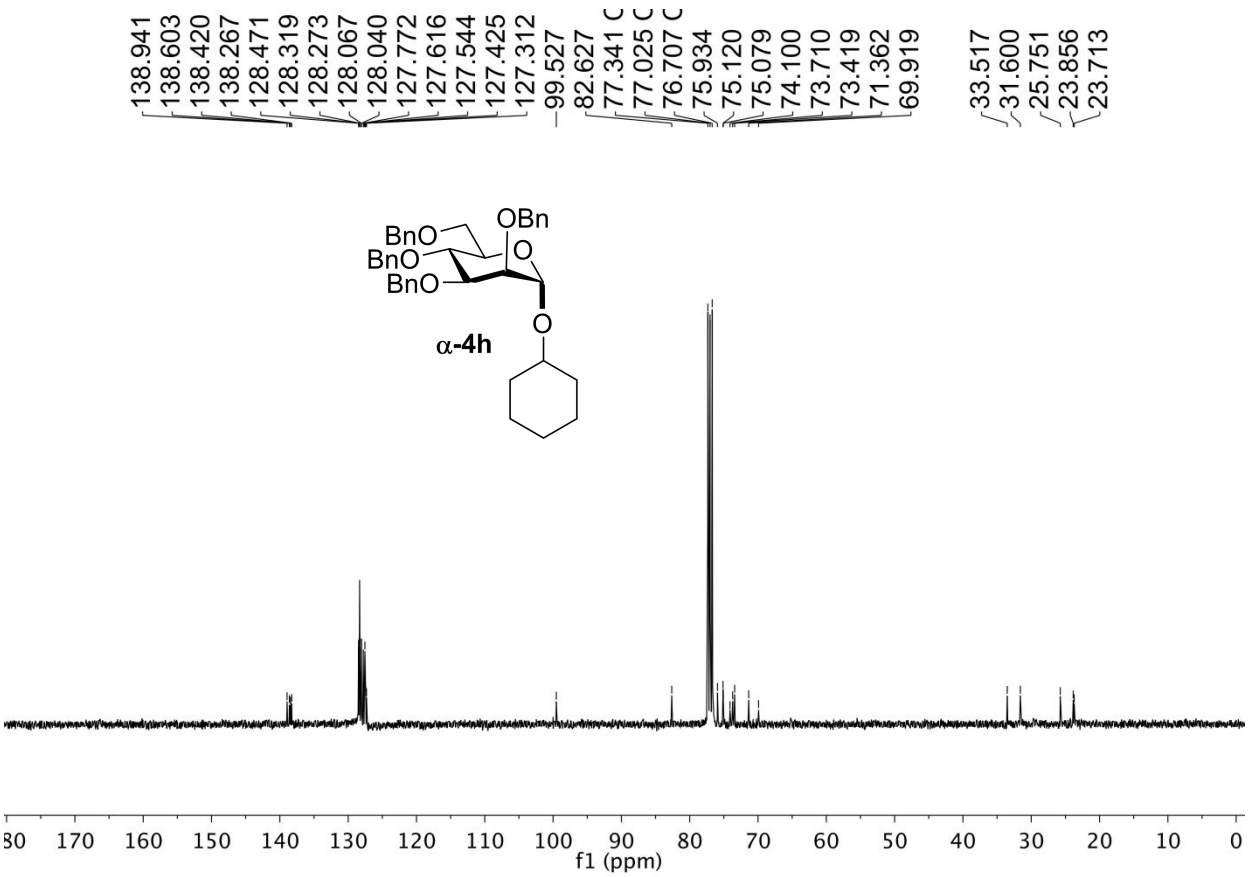


Figure S92. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-4h**

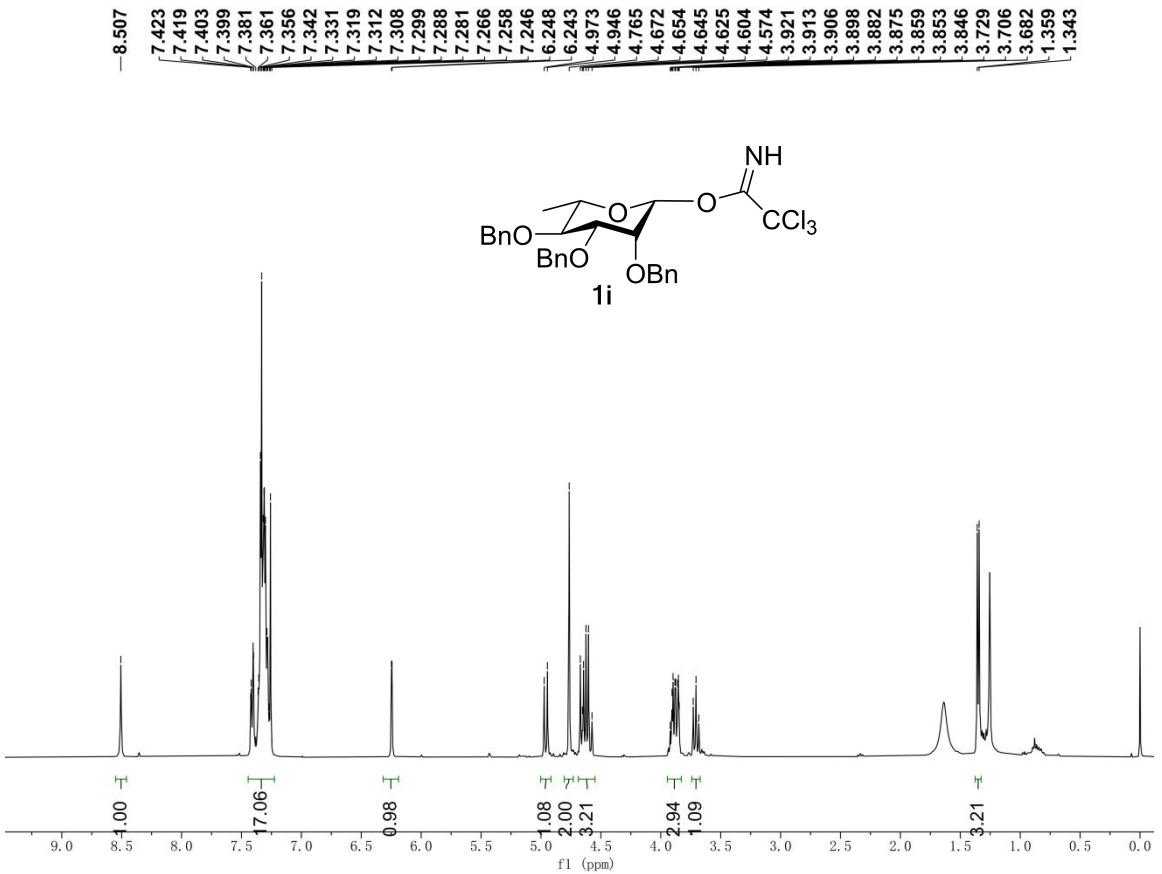


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1i**

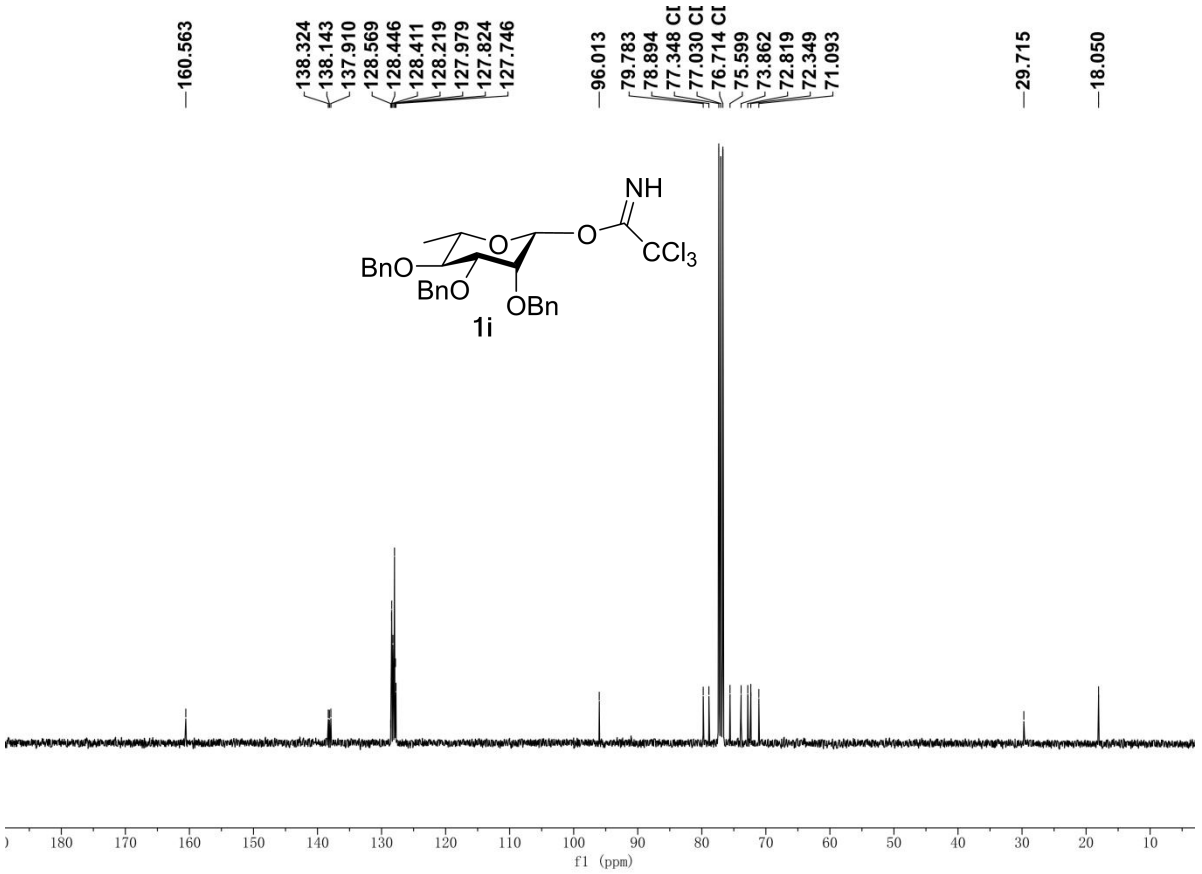


Figure S94. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **1i**

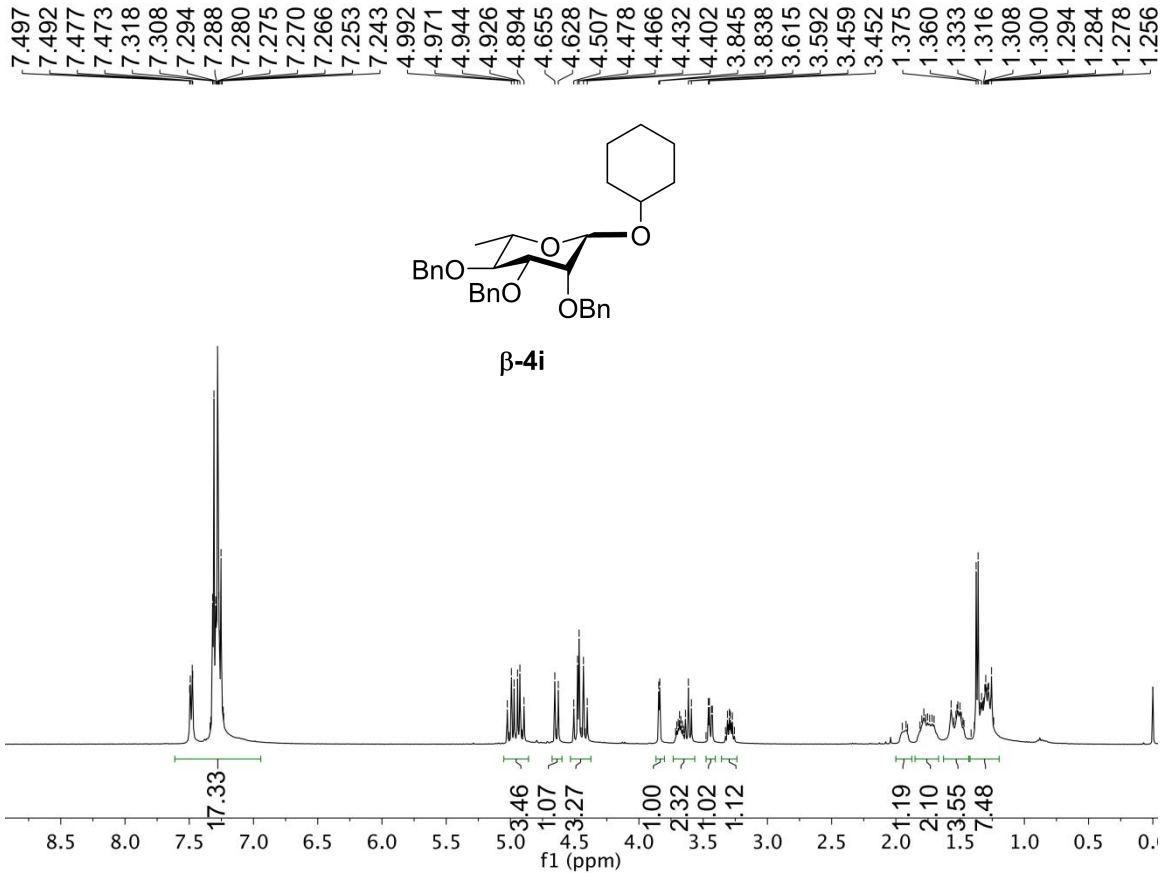


Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-4i**

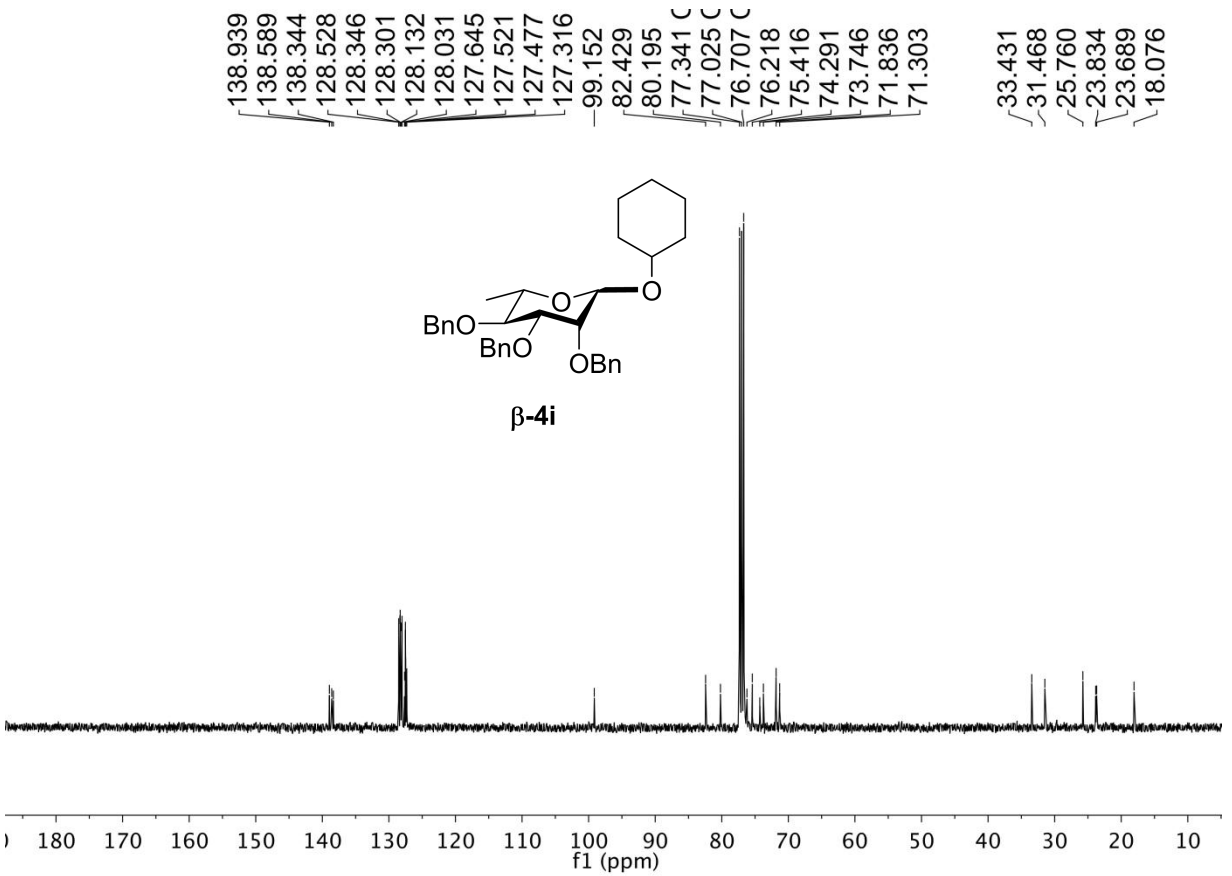


Figure S96. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-4i**

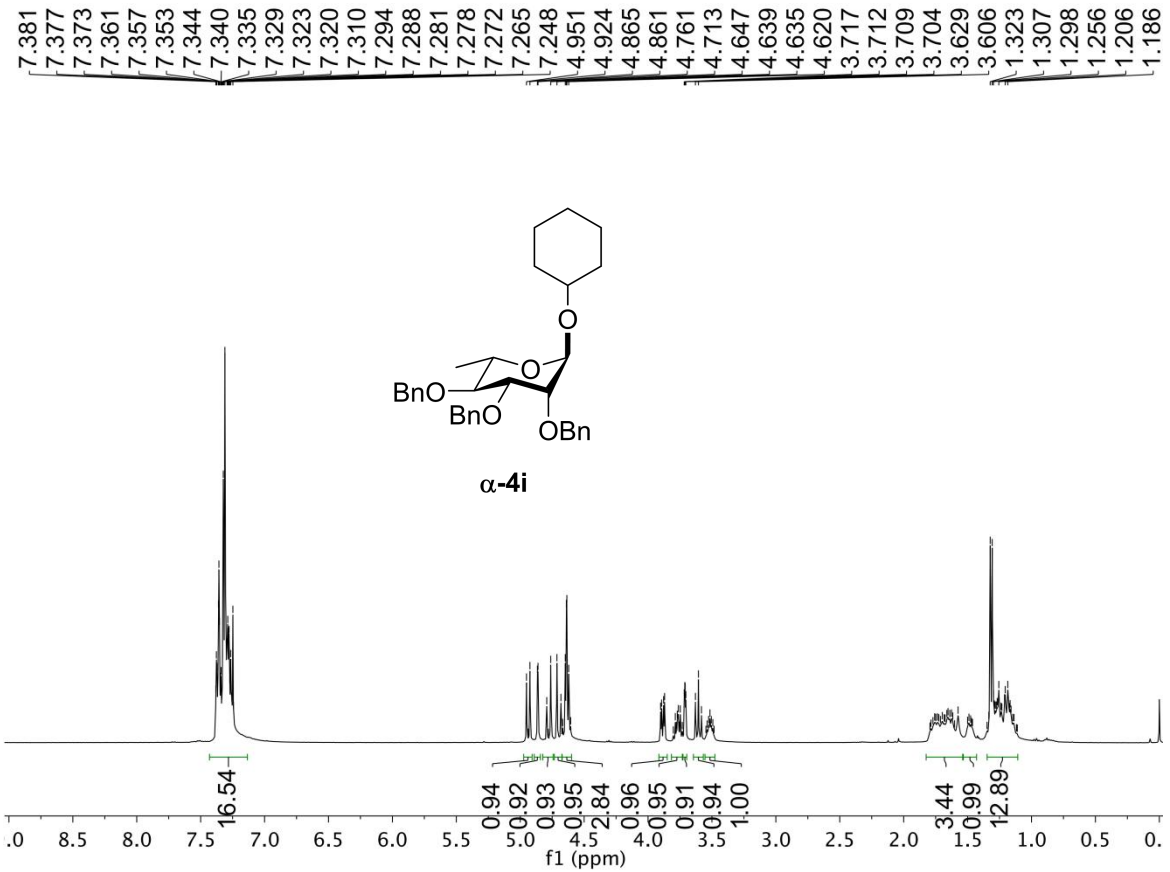


Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-4i**

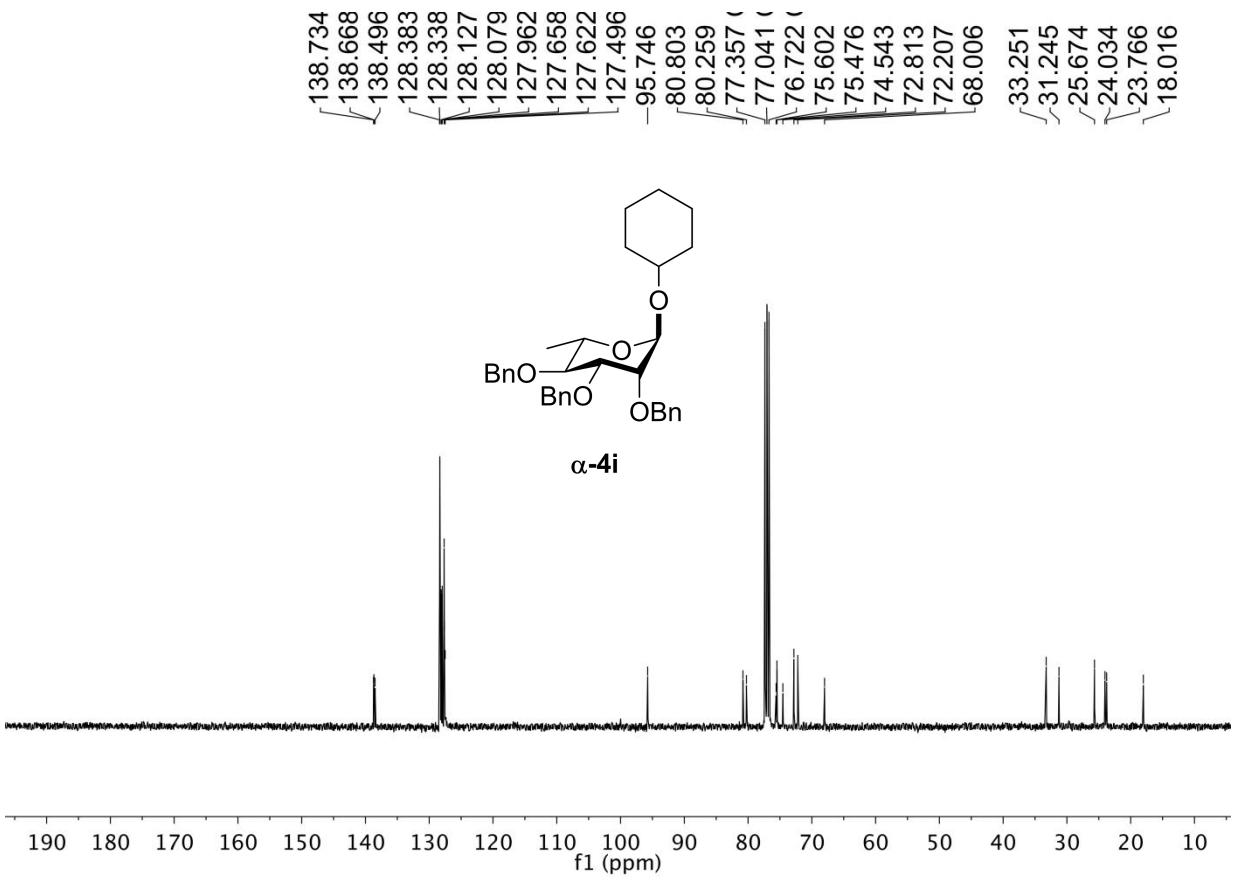


Figure S98. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-4i**

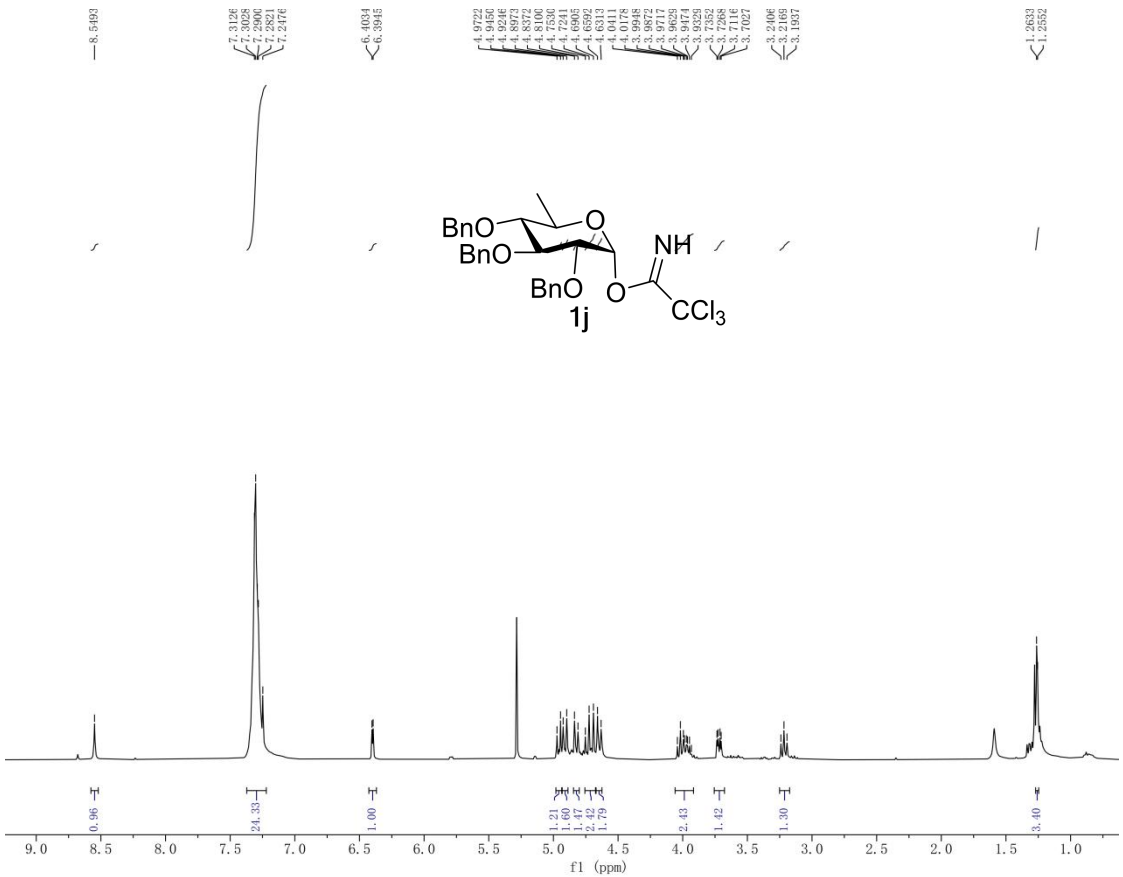


Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1j**

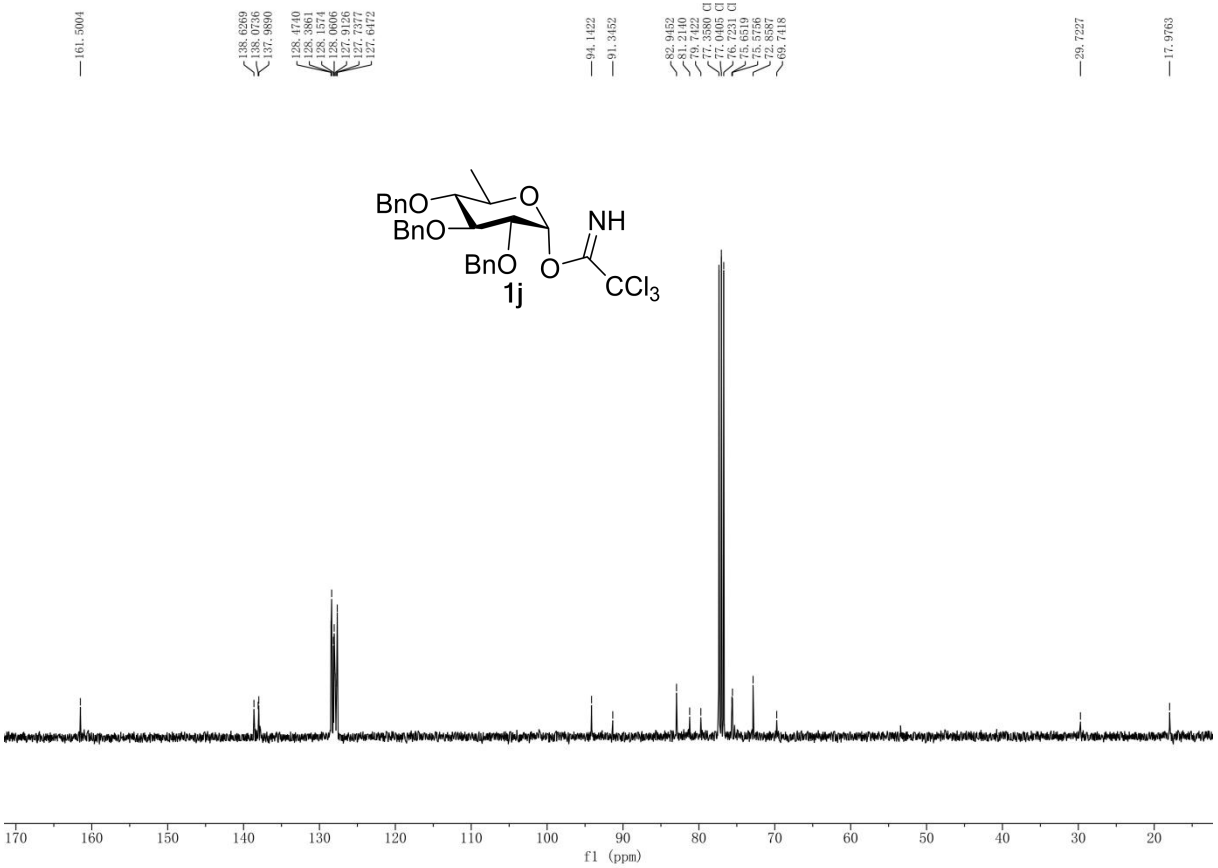


Figure S100. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-4i**

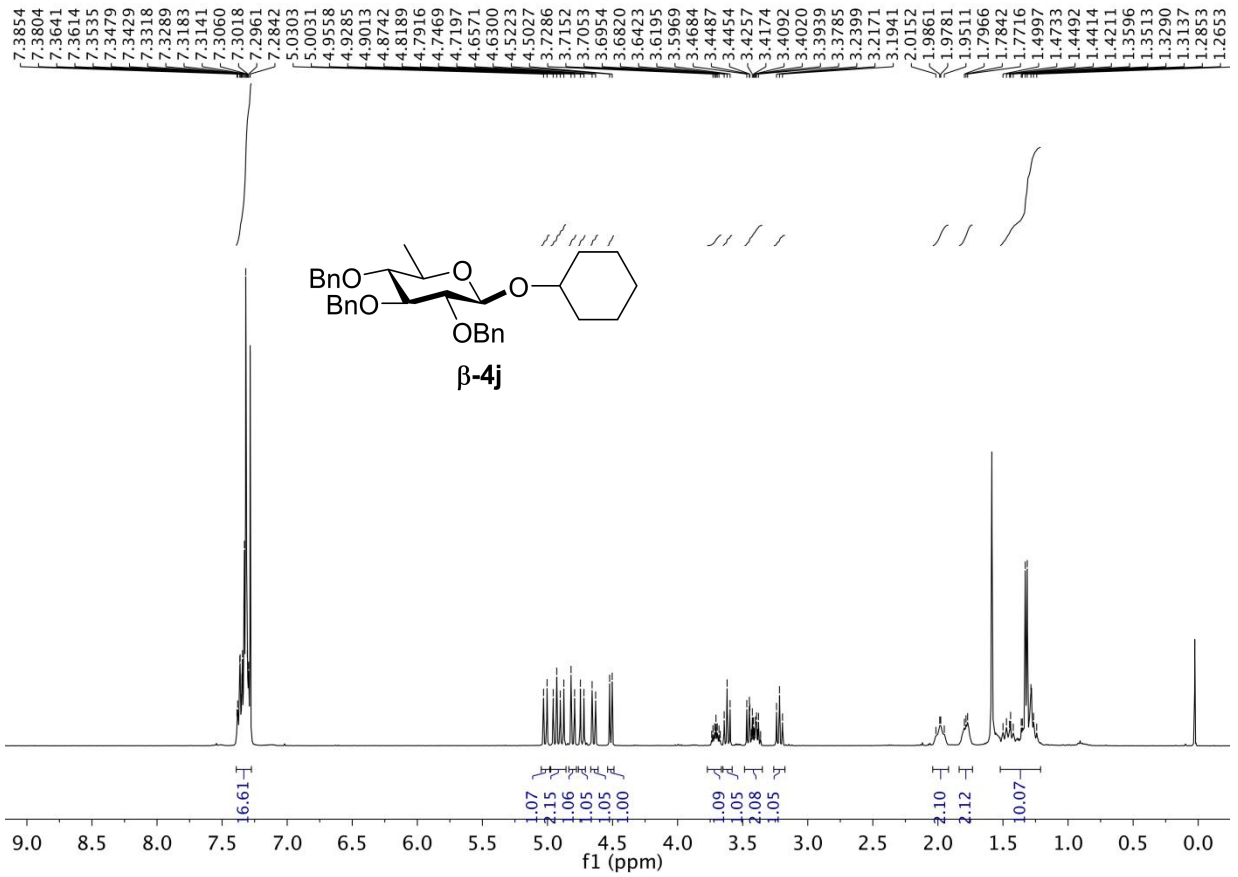


Figure S101. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **β-4j**

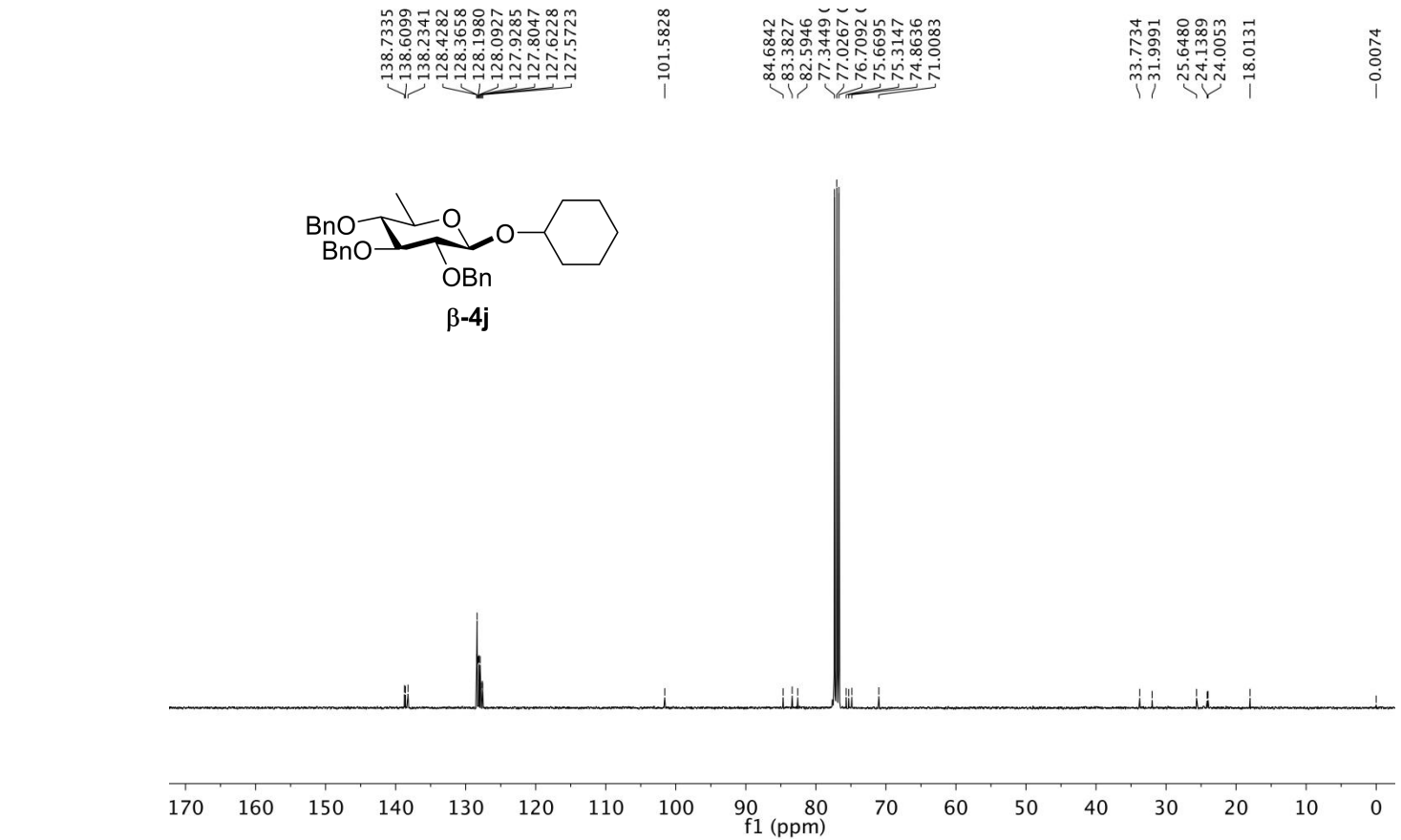


Figure S102. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **β-4j**

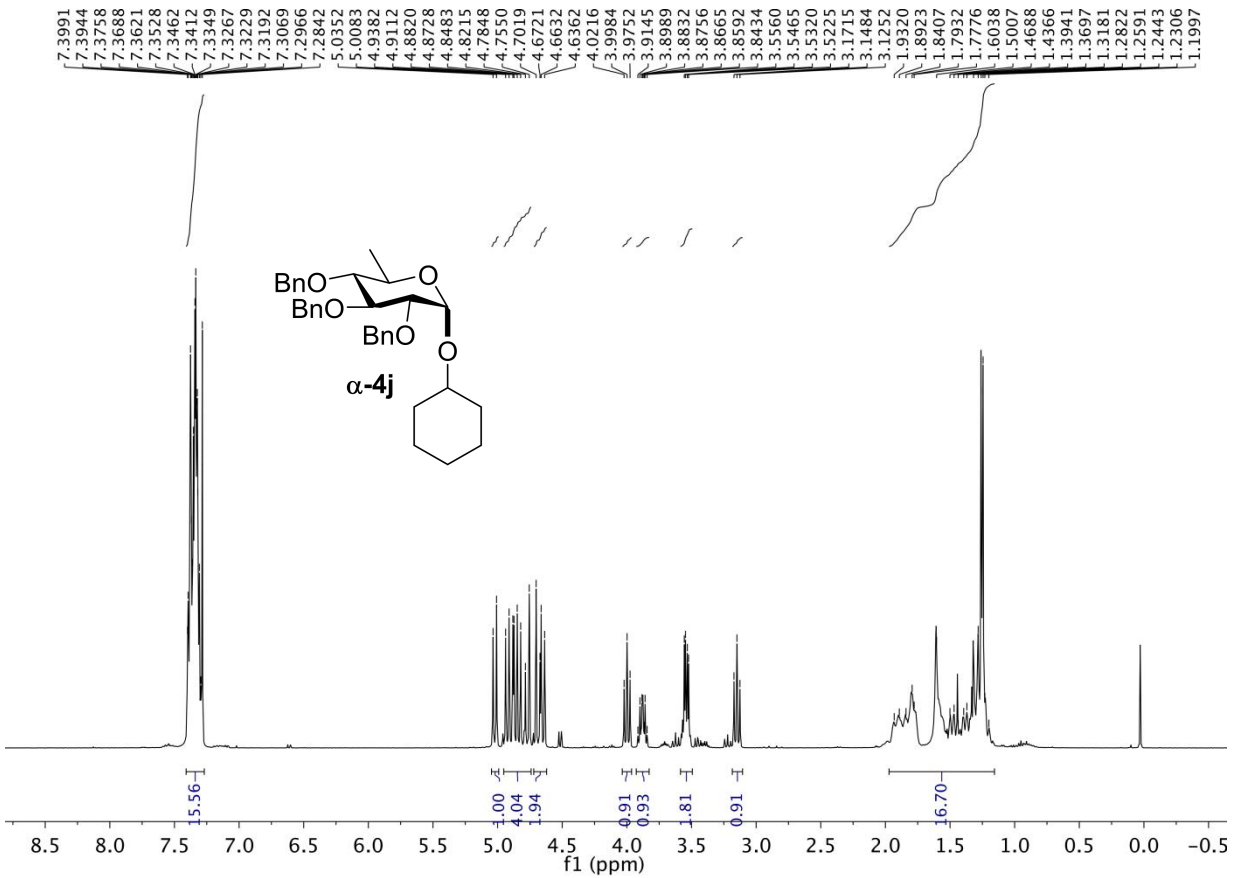


Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **α-4j**

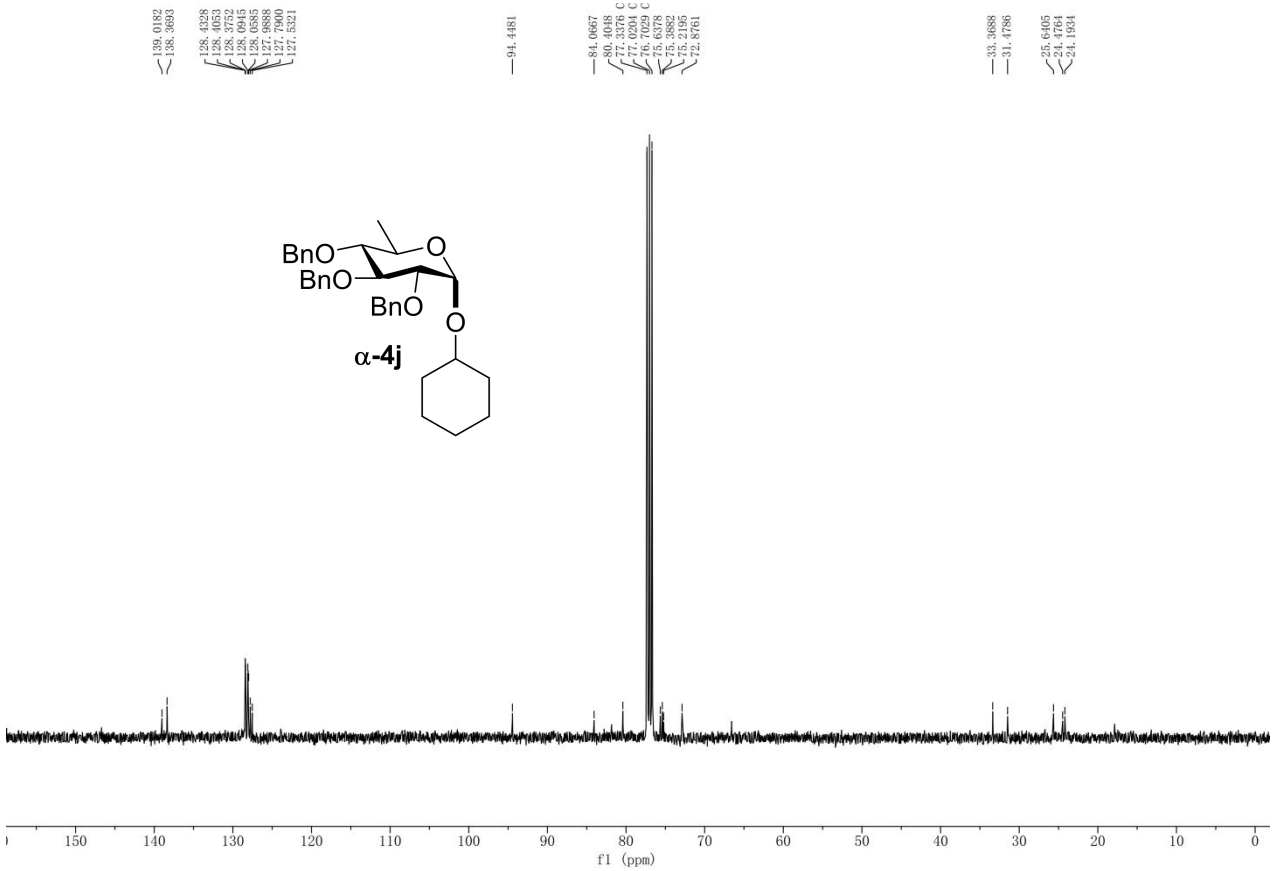


Figure S104. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **α-4j**