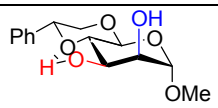
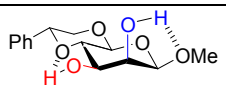
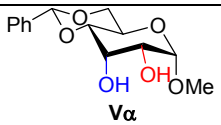
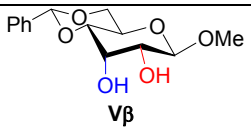
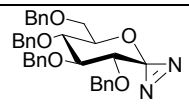
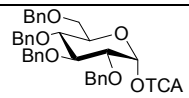
Supplementary material.

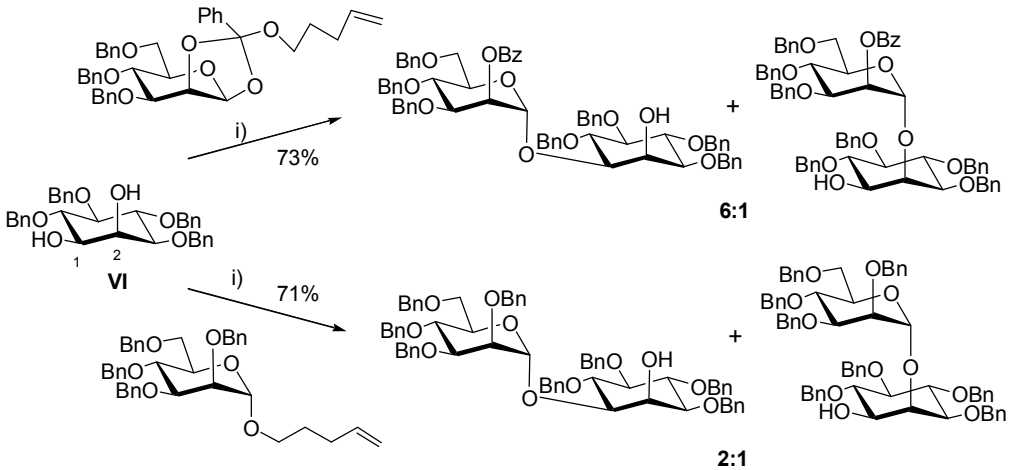
- Conditions and results of glycosylation reactions of acceptors **IV** and **V** with glucosyl donors related to Figure 6.

Acceptors / **Donors**	 **IVα**	 **IVβ**	 **Vα**	 **Vβ**
 0.04 equiv. donor 0.75 equiv. acceptor $ClCH_2CH_2Cl$, 23 ºC, 5h,	Yield = 96% a/e= 36:61	Yield = 85% a/e= 48:52	Yield = 73% a/e= 68:32	Yield = 69% a/e= 46:54
 0.04 equiv. donor 0.9 equiv. acceptor CH_2Cl_2, -30 ºC, $BF_3{\cdot}Et_2O$, 0.5h,	Yield = 93% a/e= 12:88	Yield = 91% a/e= 46:54	Yield = 94% a/e= 72:28	Yield = 90% a/e= 54:46

a) P. R. Muddasani, E. Bozó, B. Bernet, A. Vasella *Helv. Chem. Act*. **1994**, *77*, 257.

b) P. R. Muddasani, B. Bernet, A. Vasella *Helv. Chem. Act*. **1994**, *77*, 334.

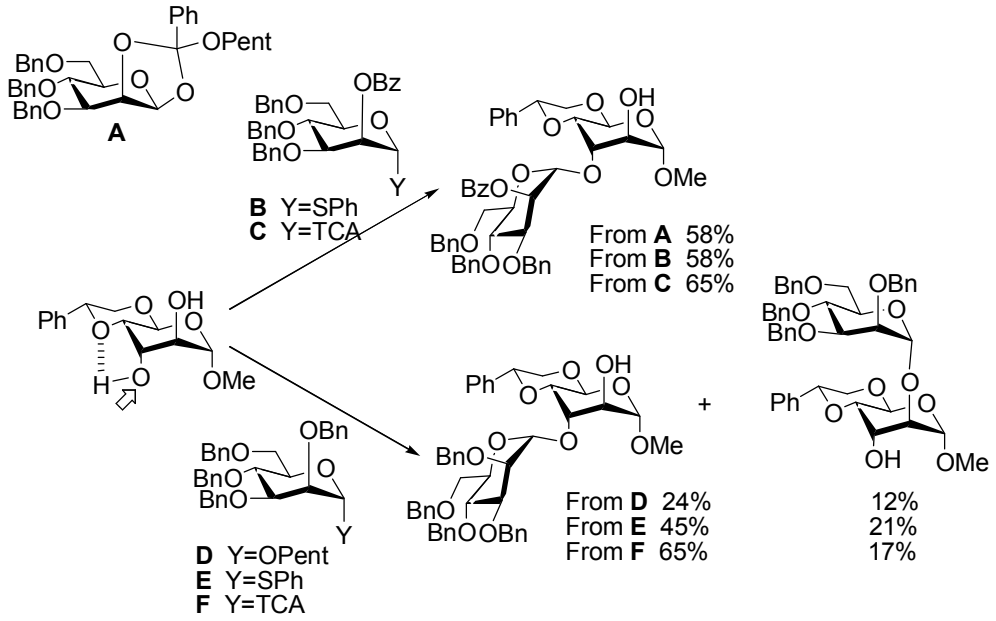
- Conditions and results of glycosylation reactions of acceptor **VI** related to Figure 7.



i) 1.3 equiv. Donor, 1.0 equiv. Acceptor, 1.3 equiv. NIS, CH_2Cl_2, 0.3 equiv. TBDPSOTf.

B. Fraser-Reid, J.C. López, A. M. Gómez, C. Uriel *Eur. J. Org. Chem.* **2004**, 1387 and references therein

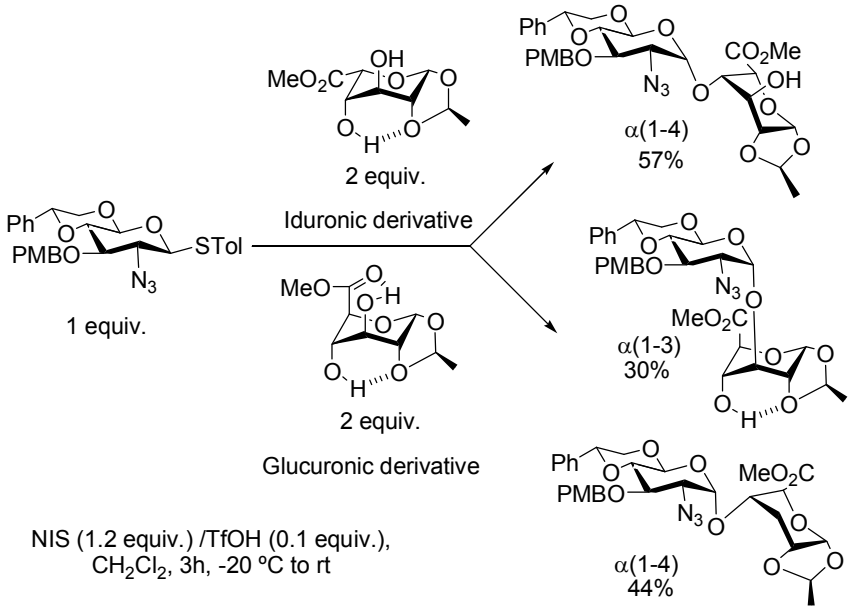
- Results of glycosylation reactions related to altrose acceptor (Figure 8).



B. Fraser-Reid, G. N. Anikumar, L. G. Nair, K. V. Radhakrishnan, J.C. López, A. M. Gómez, C. Uriel *Aus. J. Chem.* **2002**, *55*, 123.

B. Fraser-Reid, J.C. López, A. M. Gómez, C. Uriel *Eur. J. Org. Chem.* **2004**, 1387

- Results of glycosylation reactions related to iduronic and glucuronic acceptors (Figure 8).

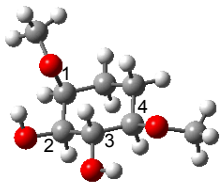


H. N. Yu, J. Furukawa, T. Ikeda, C. Wong *Org. Lett*. **2004**, *6*, 723.

Full citation for reference 18:

(18) Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Cartesian coordinates (Å) of all the optimized structures, electronic energies and ZPVEs (hartrees).

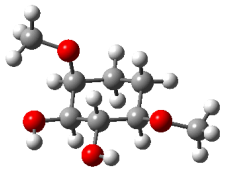


Model structure **A**

SCF Done: E(RB+HF-LYP) = -615.395277517
Sum of electronic and zero-point Energies= -615.151195
Number of imaginary frequencies: 0

6	0.573378	-1.531242	0.153836
6	-0.683102	-1.415846	1.030189
6	-1.555256	-0.221593	0.620166
6	-0.761492	1.098487	0.600064
6	0.522336	0.974932	-0.237258
6	1.370704	-0.224804	0.206490
8	-2.093473	-0.376568	-0.701718
8	-1.590175	2.163069	0.164252
8	1.262385	2.180161	-0.095165
8	2.512592	-0.226188	-0.657044
6	-3.255775	-1.186616	-0.784269
1	0.291213	-1.730982	-0.886132
1	1.189455	-2.371620	0.492326
1	-0.397354	-1.284681	2.083177
1	-1.267954	-2.341337	0.986420
1	-2.391199	-0.100160	1.325546
1	-0.471244	1.350683	1.626954
1	0.245314	0.822271	-1.292149
1	1.713126	-0.036141	1.239023

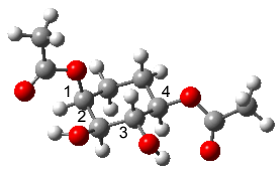
1	-2.010318	1.866661	-0.657532
1	2.102875	2.038444	-0.554736
1	-4.054284	-0.800197	-0.134269
1	-3.591276	-1.153559	-1.823229
1	-3.051025	-2.231608	-0.513877
6	3.641052	-0.930590	-0.162169
1	3.955808	-0.539622	0.816760
1	4.447691	-0.780493	-0.883243
1	3.447469	-2.007812	-0.069936



Model structure **A′**

SCF Done: E(RB+HF-LYP) = -615.398275221
Sum of electronic and zero-point Energies= -615.154045
Number of imaginary frequencies: 0

6	0.819896	-1.552976	0.120846
6	-0.446656	-1.660498	0.990185
6	-1.497528	-0.606969	0.606894
6	-0.871343	0.793029	0.713520
6	0.367702	0.906243	-0.174465
6	1.415541	-0.141459	0.202685
8	-1.940396	-0.910368	-0.714015
8	-1.834356	1.786034	0.377281
8	0.871554	2.234745	-0.007983
8	2.512825	0.072041	-0.691226
6	-3.280135	-0.531505	-1.017917
1	0.570997	-1.770218	-0.923506
1	1.554729	-2.297857	0.445665
1	-0.186943	-1.533136	2.049693
1	-0.893043	-2.654027	0.884710
1	-2.351028	-0.660174	1.299694
1	-0.553515	0.935838	1.760467
1	0.072009	0.748023	-1.220419
1	1.758300	0.064899	1.231782
1	-1.354097	2.621616	0.277564
1	1.685790	2.296573	-0.527498
1	-3.407812	0.554718	-0.999261
1	-3.486826	-0.914211	-2.020422
1	-3.985777	-0.991783	-0.309640
6	3.739416	-0.517589	-0.287930
1	4.029638	-0.182278	0.719076
1	4.496588	-0.192625	-1.005001
1	3.692609	-1.614628	-0.298277

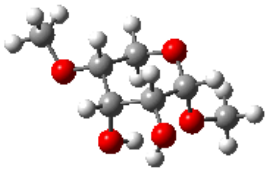


Model structure **D**

SCF Done: E(RB+HF-LYP) = -842.127630982
Sum of electronic and zero-point Energies= -841.864526

Number of imaginary frequencies: 0

6	-0.494027	-1.670452	-0.699339
6	0.707066	-1.340038	-1.596663
6	1.562640	-0.210123	-1.025620
6	0.725751	1.041845	-0.691288
6	-0.494635	0.709737	0.192474
6	-1.322406	-0.412690	-0.454282
8	2.200942	-0.721039	0.179587
8	1.482967	2.031691	-0.018325
8	-1.275290	1.860548	0.469745
8	-2.425190	-0.771162	0.415974
6	3.433497	-0.255305	0.488327
8	4.033633	0.564336	-0.182845
6	3.947323	-0.865538	1.765827
6	-3.605921	-0.133611	0.237663
8	-3.797699	0.709239	-0.619598
6	-4.631068	-0.593466	1.240763
1	-0.150934	-2.073233	0.259945
1	-1.121958	-2.434969	-1.168554
1	0.357881	-1.029479	-2.590179
1	1.333500	-2.225373	-1.744051
1	2.356807	0.063342	-1.726465
1	0.354356	1.436287	-1.654438
1	-0.122791	0.365836	1.164255
1	-1.749272	-0.052733	-1.398080
1	2.382012	2.047031	-0.379613
1	-1.933196	1.985659	-0.230739
1	5.025763	-0.719793	1.828895
1	3.694831	-1.926567	1.826125
1	3.470811	-0.358401	2.612059
1	-4.597711	-1.678381	1.365878
1	-5.622060	-0.271641	0.920812
1	-4.402260	-0.138635	2.210674

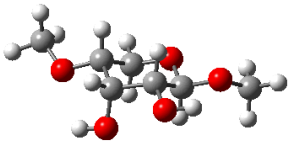


Model structure for **Vα**

SCF Done: E(UB+HF-LYP) = -651.292524038
Sum of electronic and zero-point Energies= -651.071830
Number of imaginary frequencies: 0

6	-0.70135	-1.31384	-0.21844
8	0.47277	-1.31155	-1.04689
6	1.41044	-0.30009	-0.71811
6	0.77127	1.10007	-0.82953
6	-0.48776	1.19429	0.05577
6	-1.43357	0.03407	-0.30362
8	1.69674	2.12955	-0.54533
1	-1.00225	2.1395	-0.14384
8	-2.56594	0.07435	0.54737
1	-0.44303	-1.53516	0.82461
1	-1.3187	-2.13006	-0.59834
1	0.48136	1.2242	-1.87858
1	-1.74543	0.18952	-1.35028
1	1.74628	2.21023	0.4199

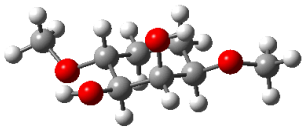
6	-3.73901	-0.5124	0.00295
1	-4.02436	-0.02904	-0.94342
1	-4.53395	-0.35732	0.73541
1	-3.62671	-1.59186	-0.17084
8	-0.13006	1.25513	1.43324
1	0.45726	0.5081	1.63432
8	1.91521	-0.45252	0.59608
6	2.78586	-1.57242	0.7705
1	3.11821	-1.55152	1.80974
1	2.26652	-2.51485	0.56585
1	3.65697	-1.48453	0.10835
1	2.22287	-0.41497	-1.44564



Model structure for **vβ**

SCF Done: E(RB+HF-LYP) = -651.291637582
Sum of electronic and zero-point Energies= -651.071633
Number of imaginary frequencies: 0

6	-0.72154	-1.32267	0.31245
8	0.62308	-1.39008	-0.16305
6	1.36809	-0.20608	0.12972
6	0.73344	0.98766	-0.5918
6	-0.72037	1.15816	-0.15094
6	-1.47231	-0.1666	-0.3737
1	1.38548	-0.04437	1.2203
8	1.44302	2.19045	-0.36327
1	-1.18778	1.94736	-0.75736
8	-2.77751	0.0153	0.17119
1	-0.74693	-1.17501	1.401
1	-1.17006	-2.29052	0.07725
1	0.7317	0.73511	-1.66427
1	-1.54041	-0.3648	-1.45438
1	2.37149	2.01492	-0.573
6	-3.77087	-0.87515	-0.31988
1	-3.85454	-0.80862	-1.41404
1	-4.71729	-0.56822	0.13001
1	-3.56738	-1.91717	-0.03986
8	-0.75157	1.51678	1.22548
1	-1.68137	1.51424	1.49551
8	2.66071	-0.35191	-0.36956
6	3.47074	-1.29338	0.33584
1	3.53131	-1.03185	1.40125
1	3.07449	-2.30809	0.22942
1	4.46618	-1.23884	-0.10825



Model structure for **VI**

SCF Done: E(RB+HF-LYP) = -615.394836382
Sum of electronic and zero-point Energies= -615.150869
Number of imaginary frequencies: 0

6		-0.89218	-1.37147	0.29854
6		0.57455	-1.54573	-0.13685
6		1.38813	-0.26719	0.10879
6		0.72833	0.9199	-0.60076
6		-0.70361	1.12818	-0.10951
6		-1.53317	-0.14288	-0.36734
1		1.44377	-0.04392	1.18373
8		1.46616	2.11748	-0.43162
1		-1.14802	1.96267	-0.67053
8		-2.83742	0.14354	0.14364
1		-0.94803	-1.23635	1.38443
1		-1.45757	-2.27694	0.05314
1		0.63047	-1.78634	-1.20723
1		1.01879	-2.39083	0.40023
1		0.6698	0.6705	-1.67494
1		-1.60307	-0.3003	-1.45723
1		2.39232	1.89064	-0.60236
6		-3.867	-0.73228	-0.28698
1		-3.91912	-0.7727	-1.38532
1		-4.8057	-0.32821	0.0984
1		-3.73538	-1.75127	0.10089
8		-0.68395	1.43452	1.28107
1		-1.60683	1.49396	1.56698
8		2.716	-0.34919	-0.42354
6		3.64795	-1.03412	0.39988
1		3.70748	-0.57604	1.39781
1		3.39571	-2.09754	0.51097
1		4.62108	-0.95457	-0.09002
