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Glycosyl cations in glycosylation reactions

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Glycosyl Cations in Glycosylation Reactions

PROEFSCHRIFT

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Thomas Hansen
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The cover depicts the conformational energy landscape of the elusive glycosyl cation, which is one of the key reactive intermediates in glycosylation reactions.

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List of abbreviations |

Ac	acetyl	DPS	diphenylsulfoxide
AIBN	2,2'-azobis(2-methyl-propionitrile)	dq	double quartet
All	allyl	dt	double triplet
APT	attached proton test	dtd	doublet of triple doublets
aq.	aqueous	DTBMP	2,6-di- <i>tert</i> -butyl-4-methylpyridine
Ar	aryl	DTBS	di- <i>tert</i> -butylsilylidene
Ara	arabinose	E	energy
Arom	aromatic	<i>E</i>	envelope
ASM	activation strain model	EDA	energy decomposition analysis
<i>B</i>	boat	eq.	molar equivalent
B3LYP	Becke, 3-parameter, Lee-Yang-Parr	Et	ethyl
BAIB	(diacetoxyiodo)benzene	E-X	electrophilic activator system
Bn	benzyl	Fuc	fucose
bs	broad singlet	FT	Fourier transform
BSP	1-benzenesulfinylpiperidine	<i>gg</i>	<i>gauche-gauche</i>
Bu	butyl	<i>gt</i>	<i>gauche-trans</i>
Bz	benzoyl	GATED	proton decoupling applied only during relaxation
<i>C</i>	chair	Gal	galactose
cal	calorie	Glc	glucose
calcd	calculated	GlcA	glucuronic acid
Car	caryophyllose	GlcN ₃	2-azido-2-deoxy glucose
cat.	catalytic	h	hour(s)
CBz	carboxybenzyl	<i>H</i>	half-chair
CDI	carbonyldiimidazole	HATU	1-[bis(dimethylamino)methylene]-1- <i>H</i> -1,2,3-triazolo[4,5- <i>b</i>]pyridinium 3-oxide hexafluorophosphate
CEL	conformational energy landscape	HFIP	hexafluoro- <i>iso</i> -propanol
CID	collision induced dissociation	HMBC	heteronuclear multiple-bond correlation spectroscopy
CIP	contact ion pair	HOMO	highest occupied molecular orbital
COSY	correlation spectroscopy	HPLC	high performance liquid chromatography
C _q	quaternary carbon atom	HRMS	high-resolution mass spectroscopy
CSA	camphor-10-sulfonic acid	HSQC	heteronuclear single quantum coherence
Cy	cyclohexyl	IDCP	iodonium dicollidine perchlorate
δ	chemical shift	IR	infrared
d	doublet	IRIS	infrared ion spectroscopy
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene	IRC	intrinsic reaction coordinate
DCE	1,2-dichloroethane	<i>J</i>	coupling constant
DCM	dichloromethane	KIE	kinetic isotope effect
dd	double doublet	KS-MO	Kohn-Sham molecular orbital theory
ddd	doublet of double doublets	LC-MS	liquid chromatography mass spectrometry
dddd	double doublet of double doublets	LG	leaving group
ddt	doublet of double triplets	LOS	lipooligosaccharides
DEAD	diethyl azocarboxylate	LTQ	linear trap quadropole
DFE	difluoroethanol	LUMO	lowest unoccupied molecular orbital
DFT	density function theory		
DiPEA	diisopropylethylamine		
DMAP	4-dimethylaminopyridine		
DMF	dimethylformamide		
DMNPA	2,2-dimethyl-2-(<i>ortho</i> -nitrophenyl)		
DMP	Dess-Martin periodinane		
DMSO	dimethylsulfoxide		

LRP	long-range participation	TBDPS	<i>tert</i> -butyldiphenylsilyl
Lyx	lyxose	TES	triethylsilyl
M	molar	TEMPO	2,2,6,6-tetramethylpiperidine 1-oxyl
m	multiplet	TFA	trifluoroacetic acid
<i>M.</i>	<i>Mycobacterium</i>	TFE	trifluoroethanol
m.s.	molecular sieves	Tf	triflyl; trifluoromethanesulfonyl
MS ²	tandem-mass spectrometric	THF	tetrahydrofuran
m/z	mass over charge ratio	TIPS	tri- <i>iso</i> -propylsilyl
min	minute(s)	TLC	thin layer chromatography
Man	mannose	TMEDA	tetramethylethylenediamine
ManA	mannuronic acid	TMS	trimethylsilyl
Me	methyl	TOCSY	total correlation spectroscopy
MFE	monofluoroethanol	Tol	tolyl; 4-methylphenyl
MM	molecular mechanics	TPP	triphenylphosphine
M.S.	molecular sieves	TPPO	triphenylphosphine oxide
Nap	2-methylnaphthyl	Trt	trityl; triphenylmethyl
NBS	<i>N</i> -bromosuccinimide	Ts	tosyl; 4-methylbenzene-1-sulfonyl
NIS	<i>N</i> -iodosuccinimide	TS	transition state
NGP	neighboring group participation	td	triple doublet
NMR	nuclear magnetic resonance	tt	triple triplet
NOESY	nuclear Overhauser effect spectroscopy	TPAP	tetrapropylammonium perruthenate
Nuc	nucleophile	TTBP	2,4,6-tri- <i>tert</i> -butylpyrimidine
<i>p</i>	<i>para</i>	UDP	uridine diphosphate
P	protection group	UV	ultraviolet
PC	product complex	VT	variable temperature
PCM	polarizable continuum model	Xyl	xylose
Ph	phenyl	YerA	yersinirose A
PMB	4-methoxybenzyl	ZORA	zeroth order regular approximated
ppm	parts per million	ZPE	zero-point energy
q	quartet		
qd	quartet of doublets		
QM	quantum mechanics		
RC	reaction complex		
R _f	retention factor		
Rib	ribose		
RRV	relative reactivity value		
rxn	reaction		
s	singlet		
<i>S</i>	skew boat		
sat.	saturated		
SCF	self-consistent field		
S _N 1	uni-molecular nucleophilic substitution		
S _N 2	bi-molecular nucleophilic substitution		
SSIP	solvent-separated ion pair		
SAR	structure-activity-relationships		
t	triplet		
<i>t</i>	<i>tert</i>		
<i>T</i>	twist		
<i>tg</i>	<i>trans-gauge</i>		
TBAF	tetrabutylammonium fluoride		
TBAI	tetrabutylammonium iodide		
TBS	<i>tert</i> -butyldimethylsilyl		
TBDMS	<i>tert</i> -butyldimethylsilyl		

