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Effect of Lewis acid on catalytic dehydration of chitin-derived sugar alcohol

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–Totals– 9 pages, 8 figures, 4 tables

Table of Contents

Figure S1	Synthetic route of isosorbide from D-(+)-glucose	S2
Figure S2	¹ H NMR spectrum of ADIAc	S2
Figure S3	¹³ C NMR spectrum of ADIAc	S3
Figure S4	DEPT spectra of ADIAc	S3
Figure S5	¹³ C- ¹ H HMQC and ¹³ C- ¹ H HMBC of ADIAc	S4
Figure S6	LR-ESI-MS of ADIAc	S5
Figure S7	Relationship between physical properties of rare earth triflate and ADI yield in the dehydration of ADS at 150 °C for 1 h	S6
Figure S8	Energy diagrams for the dehydration of ADS in the presence and absence of Yb(OTf) ₃ (EG) calculated by DFT	S6
Table S1	Orientation, charge and multiplicity for the transition state of 3,6-dehydration with Yb(OTf) ₃ (EG) in a format of Gaussian input	S7
Table S2	Orientation, charge and multiplicity for the transition state of 1,4-dehydration with Yb(OTf) ₃ (EG) in a format of Gaussian input	S8
Table S3	Orientation, charge and multiplicity for the transition state of 3,6-dehydration without Yb(OTf) ₃ (EG) in a format of Gaussian input	S9
Table S4	Orientation, charge and multiplicity for the transition state of 1,4-dehydration without Yb(OTf) ₃ (EG) in a format of Gaussian input	S9

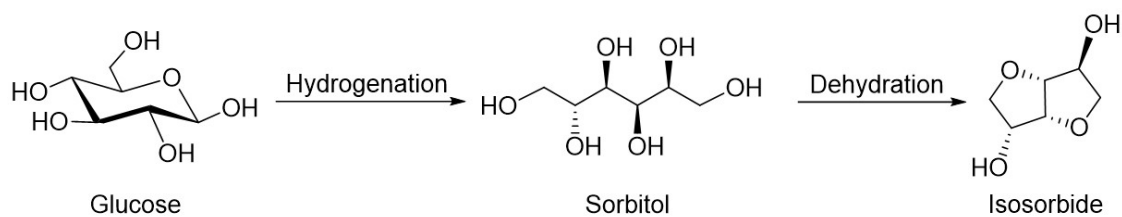


Figure S1. Synthetic route of isosorbide from D-(+)-glucose.

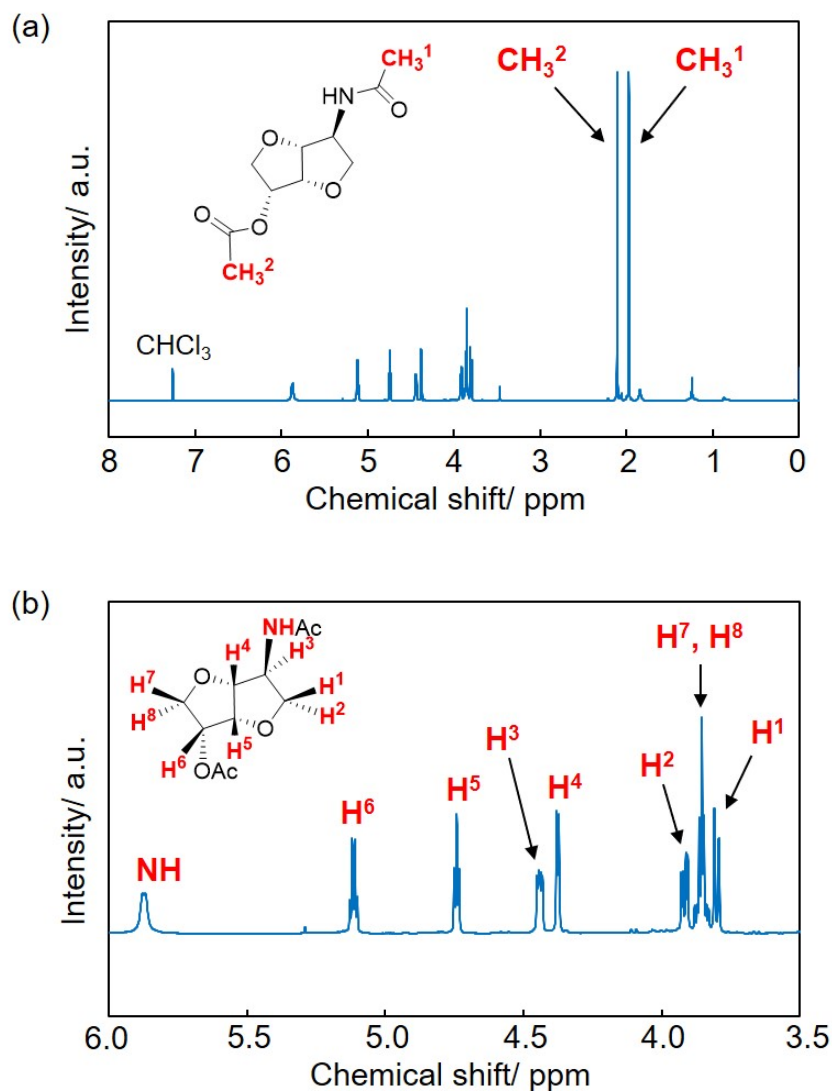


Figure S2. ^1H NMR spectrum of ADIAc. Top: full scale, Bottom: enlarged view.

^1H NMR (600 MHz, CDCl_3): δ = 1.97 (s, 3H, CH_3^1), 2.11 (s, 3H, CH_3^2), 3.82 (d, J = 9.6 Hz, 1H, H^1), 3.84 (dd, J = 4.9, 10.3 Hz, 1H, H^8), 3.88 (dd, J = 5.5, 10.3 Hz, 1H, H^7), 3.92 (dd, J = 4.1, 9.6 Hz, 1H, H^2), 4.38 (d, J = 4.8, 1H, H^4), 4.44 (dd, J = 4.1, 7.5 Hz, 1H, H^3), 4.74 (dd, J = 4.8, 4.8 Hz, 1H, H^5), 5.12 (dd, J = 4.8, 5.5 Hz, 1H, H^6), 5.87 (d, J = 7.5 Hz, 1H, NH).

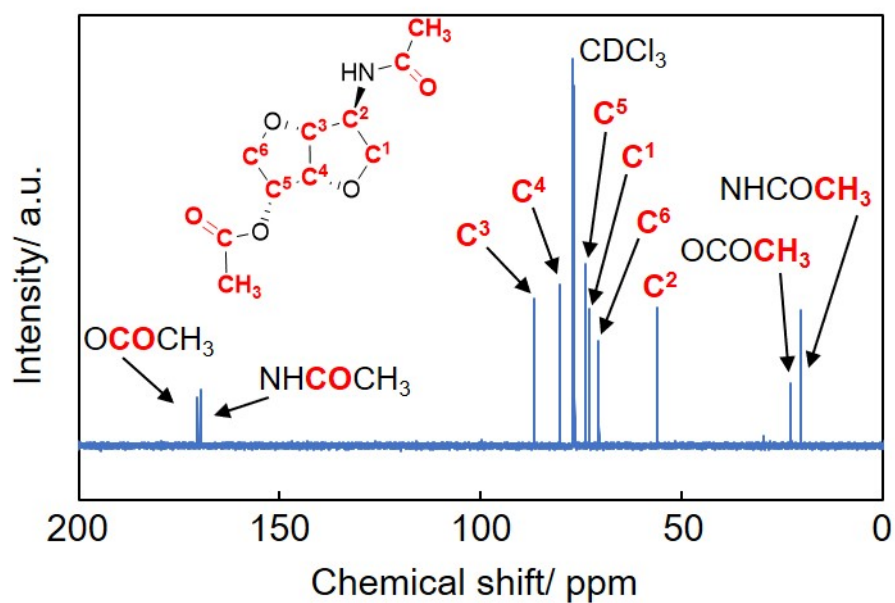


Figure S3. ^{13}C NMR spectrum of ADIAc.

^{13}C NMR (151 MHz, CDCl_3): δ = 20.6 (NHCOCH_3), 23.1 (OCOCH_3), 56.2 (C^2), 70.7 (C^6), 73.0 (C^1), 74.0 (C^5), 80.3 (C^4), 86.6 (C^3), 169.7 (NHCOCH_3), 170.4 (OCOCH_3).

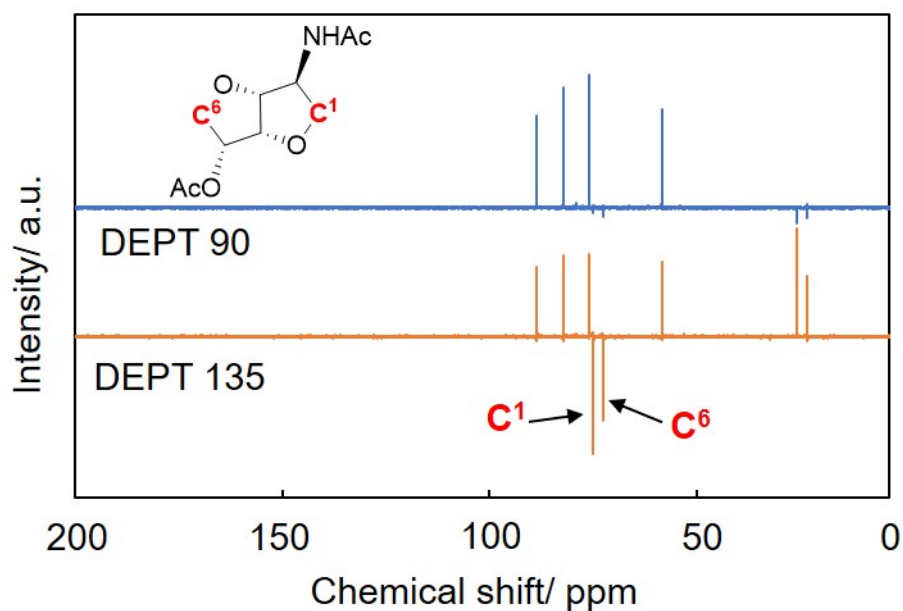


Figure S4. DEPT spectra of ADIAc.

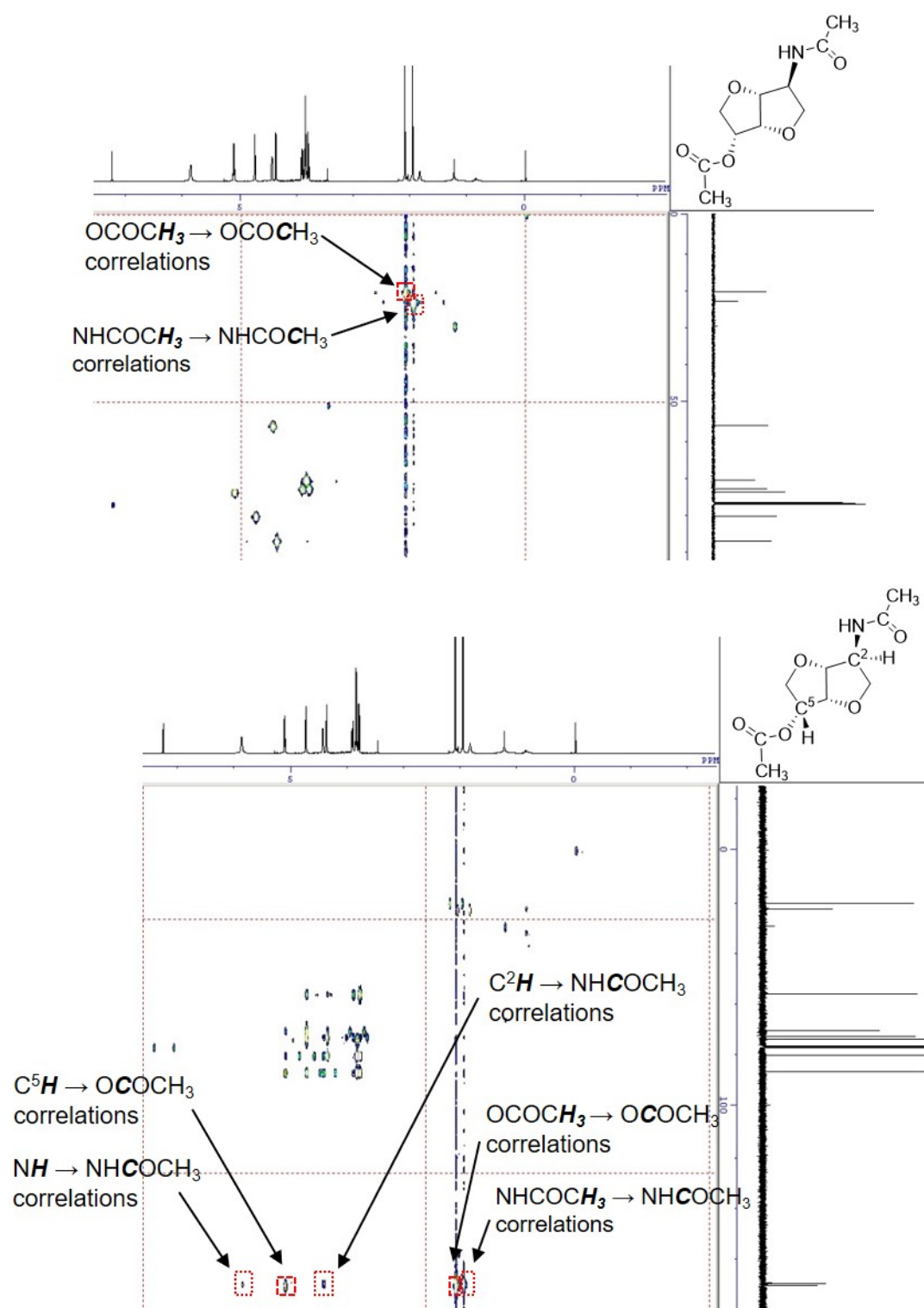


Figure S5. ^{13}C - ^1H HMQC (horizontal axis: ^1H , vertical axis: ^{13}C) (top) and ^{13}C - ^1H HMBC (horizontal axis: ^1H , vertical axis: ^{13}C) (bottom) of ADIAc.

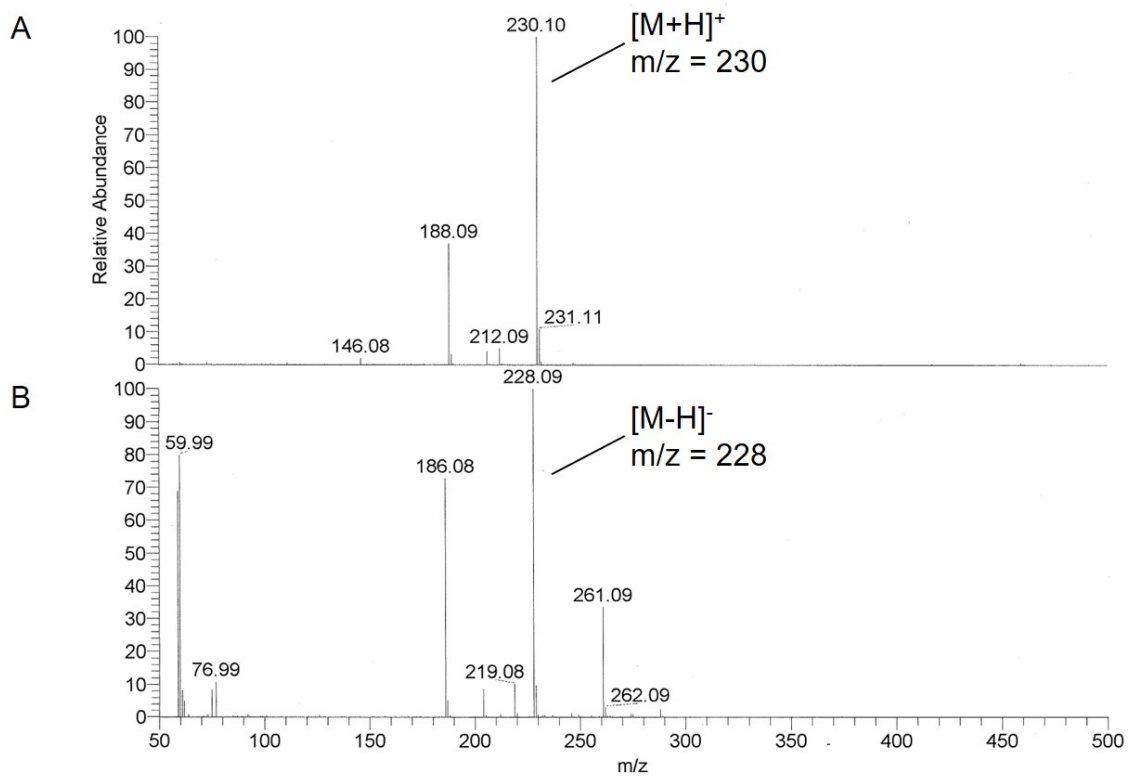


Figure S6. LR-ESI positive (A) and negative (B) mass spectra of ADIAc.

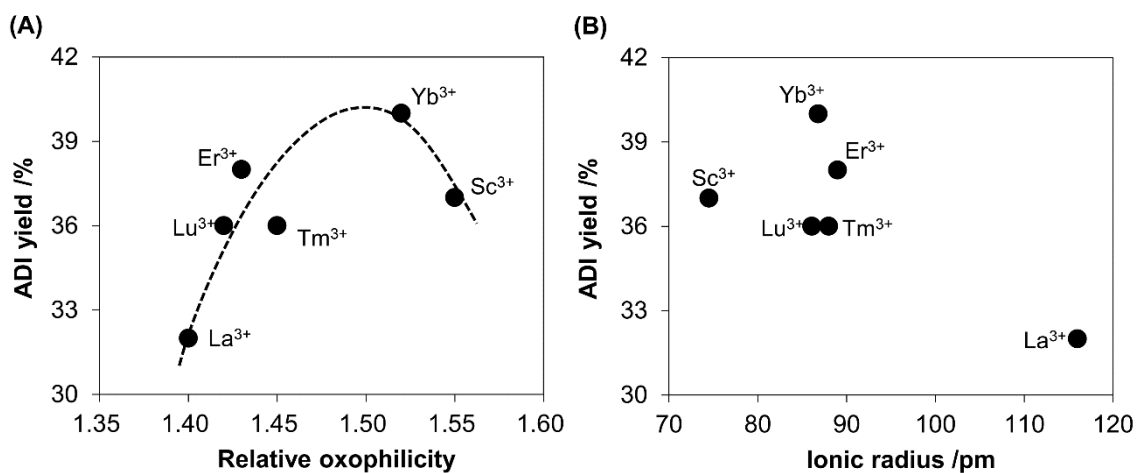


Figure S7. Relationship between physical properties of rare earth triflate and ADI yield in the dehydration of ADS at 150 °C for 1 h. Six coordination is assumed for the ionic radius.

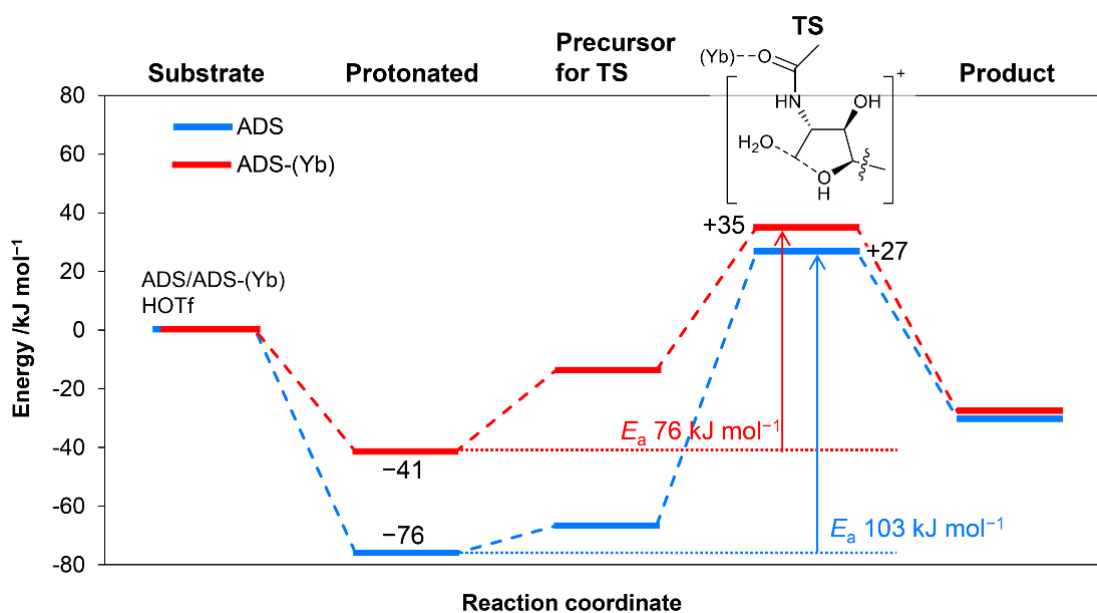


Figure S8. Energy diagrams for the 1,4-dehydration of ADS in the presence and absence of Yb(OTf)₃(EG) calculated by DFT. (Yb) represents Yb(OTf)₃(EG).

Table S1. Orientation, charge and multiplicity for the transition state of 3,6-dehydration with Yb(OTf)₃(EG) in a format of Gaussian input.

1	2				
Yb	-1	0.59807000	-0.39873000	-0.03193900	
O	0	-1.09881600	0.18355900	-1.36084400	
C	0	-1.46443200	0.82491300	-2.38064000	
N	0	-2.43285400	1.74795700	-2.31016500	
C	0	-0.83408200	0.56140400	-3.71702100	
H	0	-2.62644100	2.27697400	-3.15710700	
H	0	-0.85438900	-0.51502100	-3.91552900	
H	0	-1.32571200	1.09696100	-4.53214500	
H	0	0.21673600	0.87127600	-3.66563700	
O	-1	1.84700800	-0.12371000	2.15047200	
O	-1	-0.84295600	0.16456300	1.80164300	
C	-1	1.10081000	0.65158200	3.10983200	
H	-1	1.55800900	0.56393100	4.10236100	
H	-1	1.08793100	1.70397900	2.81473400	
C	-1	-0.29606500	0.08776400	3.14548200	
H	-1	-0.92335100	0.66626700	3.83028000	
H	-1	-0.28479900	-0.96160400	3.46584100	
H	-1	2.64774000	0.40590900	1.90341400	
H	-1	-1.60321300	-0.45702400	1.76002400	
O	-1	2.53358900	-1.31938600	-0.87739000	
O	-1	-0.28249800	-2.50477400	0.37455700	
O	-1	1.74390400	1.66677500	-0.41213000	
S	-1	-1.54319000	-3.14908600	0.90492400	
S	-1	3.62900700	-2.36031700	-0.85255800	
S	-1	2.99809800	2.41509900	-0.03719600	
O	-1	-2.38152800	-2.19917000	1.67513000	
O	-1	-1.31812000	-4.47145000	1.49809000	
O	-1	3.62381400	1.88973300	1.20274800	
O	-1	3.89944000	2.68693100	-1.16412000	
O	-1	4.11313000	-2.69015600	-2.20606600	
O	-1	3.34172400	-3.49210700	0.04721700	
C	-1	5.02082000	-1.44119100	-0.05001300	
C	-1	-2.50756600	-3.45773300	-0.65449000	
C	-1	2.31190100	4.07258500	0.44529000	
F	-1	-3.63617200	-4.10860000	-0.36360600	
F	-1	-2.81304700	-2.29057300	-1.23656400	
F	-1	-1.78343800	-4.19020700	-1.50673100	
F	-1	5.26674300	-0.30493800	-0.71187000	
F	-1	4.70821100	-1.14672400	1.21871100	
F	-1	6.12410000	-2.19680200	-0.05802300	
F	-1	3.29595700	4.85509900	0.89768500	
F	-1	1.74084600	4.65357100	-0.61393400	
F	-1	1.39203800	3.92986800	1.40918100	
C	0	-2.99701100	2.27067100	-1.05799600	
C	0	-4.54276000	2.20352500	-1.12115400	
H	0	-2.63696600	1.62440600	-0.25829200	
C	0	-2.47868400	3.69313000	-0.83312700	
C	0	-5.29930100	2.21439200	0.21887900	
H	0	-4.92449000	2.99910500	-1.77013800	
O	0	-4.99371900	0.94498000	-1.66090000	
H	0	-2.73248400	4.31723700	-1.70268000	
H	0	-2.95861700	4.12337800	0.05114200	
O	0	-1.06622400	3.60276500	-0.66300900	
H	0	-6.36240000	2.33732600	-0.01173000	
C	0	-5.11719800	0.82801200	0.92094800	
O	0	-4.83895300	3.24044900	1.07067500	
H	0	-4.33679700	0.59295100	-2.29721000	
H	0	-0.71840600	4.50671100	-0.59734800	
C	0	-5.15989900	-0.27554700	-0.08517600	
H	0	-5.96306100	0.70721100	1.61131500	
O	0	-3.88797600	0.78234600	1.62438400	
H	0	-5.55853600	3.48771100	1.67720600	
H	0	-4.25728800	-0.77565300	-0.39310800	
H	0	-6.10688100	-0.62296400	-0.46967200	
H	0	-3.76052200	1.68034500	1.99039600	
O	0	-5.24389000	-1.87101400	1.28832200	
H	0	-5.70444000	-1.58082300	2.09731200	
H	0	-4.30899700	-1.99425600	1.56197900	

Table S2. Orientation, charge and multiplicity for the transition state of 1,4-dehydration with Yb(OTf)₃(EG) in a format of Gaussian input.

1	2				
Yb	-1	-0.98601400	0.43254600	0.38568600	
O	0	1.12204400	0.28120300	-0.41380600	
C	0	1.74169600	0.32105600	-1.51076900	
N	0	2.88083000	-0.35934000	-1.67117300	
C	0	1.24043600	1.13576000	-2.66641100	
C	0	3.46046600	-1.21181700	-0.64420700	
H	0	3.34784500	-0.29518700	-2.57038300	
H	0	1.19142300	2.18594600	-2.36066000	
H	0	1.87658900	1.04398000	-3.54968000	
H	0	0.22372700	0.81229500	-2.91434000	
C	0	3.61993200	-2.63028200	-1.12210300	
C	0	4.82448700	-0.68651400	-0.11567800	
H	0	2.78285300	-1.19985400	0.20969800	
H	0	3.46510200	-2.90119600	-2.15606900	
H	0	3.89842300	-3.39582500	-0.41427500	
C	0	5.87967000	-1.01837000	-1.17147900	
H	0	4.74968000	0.40014900	0.02057100	
O	0	5.04535700	-1.34218300	1.12253800	
O	0	5.59029400	-2.40066500	-1.51255800	
H	0	5.72261100	-0.38639200	-2.05146800	
C	0	7.34908200	-0.90461000	-0.73962000	
H	0	6.00092400	-1.56986100	1.17197900	
H	0	5.76010000	-2.55524200	-2.46182700	
C	0	7.75050800	0.51627100	-0.35251600	
H	0	7.97567100	-1.22585200	-1.58072900	
O	0	7.62669600	-1.73451700	0.40257100	
H	0	7.19090500	0.83102100	0.54039200	
H	0	7.51258100	1.20372300	-1.16956800	
O	0	9.15251200	0.60936700	-0.13163200	
H	0	7.64058600	-2.66297100	0.10921600	
H	0	9.36764000	-0.01719400	0.58091000	
H	0	1.51834200	-3.34412200	0.06413000	
O	0	1.64008300	-3.12298900	-0.87869400	
O	-1	-3.04342900	0.07880200	1.81494400	
O	-1	-0.55117900	0.70851800	2.72849700	
C	-1	-2.70817500	-0.22039600	3.18514500	
H	-1	-3.60102700	-0.14513500	3.81666500	
H	-1	-2.30320800	-1.23328400	3.25965200	
C	-1	-1.68935700	0.79828100	3.62643000	
H	-1	-1.36502000	0.59340000	4.65122000	
H	-1	-2.10470100	1.81216300	3.57510700	
H	-1	-3.46660700	-0.72998700	1.43186700	
H	-1	-0.04002500	1.54342800	2.82015200	
O	-1	-2.40890200	0.46350200	-1.42674500	
O	-1	-0.94722700	2.74842500	0.45720300	
O	-1	-1.27055200	-1.93801800	0.21296900	
S	-1	-0.30535900	3.87100800	1.24046000	
S	-1	-3.58276100	1.04229000	-2.18231500	
S	-1	-2.32853100	-3.01193400	0.23931900	
O	-1	0.24133700	3.41194600	2.53996600	
O	-1	-1.09876500	5.10458700	1.24981400	
O	-1	-3.58793000	-2.55313700	0.87822800	
O	-1	-2.46344700	-3.75799900	-1.01845400	
O	-1	-3.39934400	0.96217400	-3.64303900	
O	-1	-4.05382700	2.32852400	-1.63799000	
C	-1	-4.92717700	-0.17099200	-1.79532600	
C	-1	1.19795600	4.25078000	0.21443700	
C	-1	-1.60018000	-4.22260800	1.44516700	
F	-1	1.84574500	5.29515500	0.73561900	
F	-1	2.01652000	3.19051100	0.20071700	
F	-1	0.83870300	4.53674700	-1.04109200	
F	-1	-4.53828400	-1.40990000	-2.11700000	
F	-1	-5.22133000	-0.13269600	-0.48914700	
F	-1	-6.02558200	0.13530600	-2.49384400	
F	-1	-2.46226600	-5.22048200	1.66060000	
F	-1	-0.46252700	-4.72355000	0.95485300	
F	-1	-1.33889400	-3.61471800	2.61041400	
H	0	1.52261100	-3.97567200	-1.34079700	

Table S3. Orientation, charge and multiplicity for the transition state of 3,6-dehydration without Yb(OTf)₃(EG) in a format of Gaussian input.

1	1			
O	-1.72202100	-2.13996000	-0.03999300	
C	-2.56814600	-1.21458700	-0.00393700	
N	-2.21875600	0.07838800	0.11348600	
C	-4.04081600	-1.52680700	-0.07732600	
C	-0.85791400	0.61341300	-0.09823200	
H	-2.96024100	0.76227700	0.00384700	
H	-4.29390200	-2.23763700	0.71621900	
H	-4.67174900	-0.63925200	0.01452500	
H	-4.24667300	-2.01570800	-1.03641800	
C	0.05843000	0.28479300	1.10761300	
H	-0.44237800	0.14896800	-0.99910300	
C	1.49787600	0.82961900	1.13630200	
H	-0.45587700	0.59788300	2.02398700	
O	0.32512500	-1.12655900	1.18726900	
H	1.90089500	0.54926200	2.11652400	
C	2.35072000	0.10133500	0.06265800	
H	-0.40044600	-1.63112000	0.69839800	
C	2.05483100	-1.36410400	0.06291400	
H	3.40525400	0.24064200	0.33668600	
O	2.10058000	0.61654900	-1.23640200	
H	1.42680300	-1.79911100	-0.69956200	
H	2.41688700	-1.98733800	0.86636800	
O	3.65891000	-1.87287300	-1.02242700	
H	2.12871700	1.58823400	-1.15076000	
H	3.53359400	-1.42599000	-1.88228100	
H	3.54097800	-2.82161200	-1.22202200	
O	1.56217400	2.22888800	0.95212600	
H	2.37263000	2.55605600	1.37914700	
C	-1.00968900	2.12176600	-0.33916200	
H	-1.25373300	2.63156800	0.60289500	
H	-0.06582200	2.52195300	-0.71484200	
O	-2.05693300	2.30459900	-1.29409100	
H	-2.25809400	3.25449500	-1.32484600	

Table S4. Orientation, charge and multiplicity for the transition state of 1,4-dehydration without Yb(OTf)₃(EG) in a format of Gaussian input.

1	1			
O	3.84754900	0.20634700	-0.53424400	
C	3.09461600	1.08684000	-0.07396400	
N	1.76681900	0.89291700	0.09732500	
C	3.63526200	2.43934600	0.31637400	
C	1.05313200	-0.28452900	-0.37847200	
H	1.22580200	1.66648800	0.46569700	
H	4.06205200	2.91387800	-0.57442000	
H	2.87668400	3.09960600	0.74398400	
H	4.44714000	2.30208900	1.03809500	
C	1.06090400	-1.44157200	0.59772200	
C	-0.42334300	0.05314500	-0.71822400	
H	1.51144300	-0.61960500	-1.31195800	
H	1.52738500	-1.36133000	1.56750500	
H	0.64948200	-2.39098600	0.29227300	
C	-1.17134900	0.16314900	0.61469500	
H	-0.45641300	1.01287800	-1.25009000	
O	-0.89496000	-0.99715500	-1.54597700	
O	-0.68915600	-0.98455200	1.36690200	
H	-0.87130200	1.08073400	1.13009000	
C	-2.70481500	0.11795700	0.55155600	
H	-1.80708600	-1.22268000	-1.25681600	
H	-0.58122400	-0.75163200	2.30923500	
C	-3.29381800	1.27774400	-0.24792800	
H	-3.09170900	0.16576300	1.57675300	
O	-3.17068400	-1.08817500	-0.07747000	
H	-2.97068500	1.20678900	-1.29671600	
H	-2.93722200	2.22818100	0.15965000	
O	-4.71284800	1.29696100	-0.15467800	
H	-3.02384600	-1.83001800	0.53605800	
H	-5.03006400	0.44820200	-0.50902700	
H	3.40219500	-1.41799100	-0.22738600	
O	2.92580900	-2.25126100	0.04008200	
H	2.75040700	-2.71058200	-0.80167900	