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

Takuya Sagawa[a,b], Hirokazu Kobayashi[a,*], Atsushi Fukuoka [a,*]

[a]Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan.

[b]Department of Industrial Chemistry, Faculty of Science, Tokyo University of Science, 12-1 Ichigayafunagawara-machi, Shinjuku-ku, Tokyo, 162-0826, Japan.

*Corresponding authors: kobayashi.hi@cat.hokudai.ac.jp (H.K.); fukuoka@cat.hokudai.ac.jp (A.F.)

Fax: +81-11-706-9139

–Totals– 9 pages, 8 figures, 4 tables

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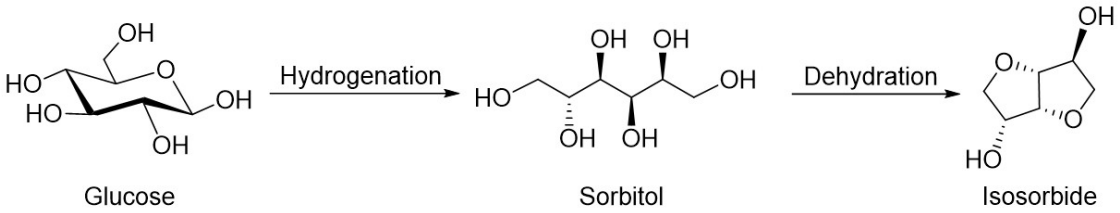

Figure S1. Synthetic route of isosorbide from D-(+)-glucose.

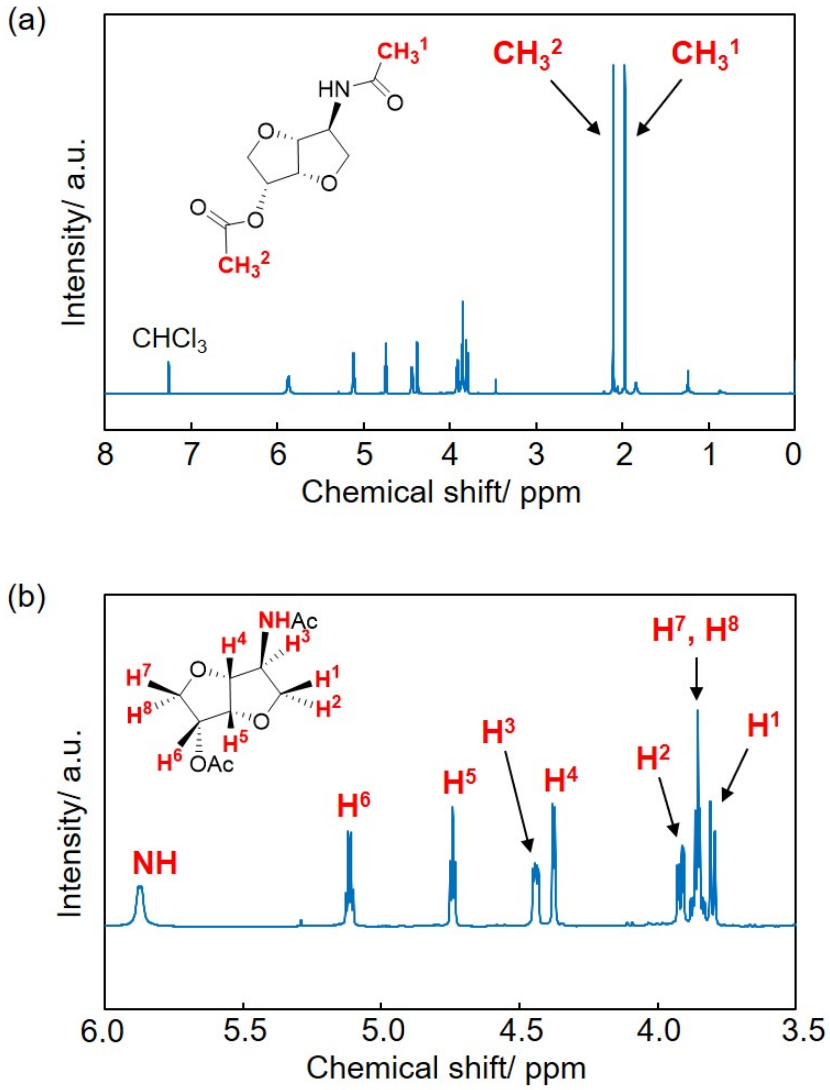

Figure S2. ^{1}H NMR spectrum of ADIAc. Top: full scale, Bottom: enlarged view.

^{1}H 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).

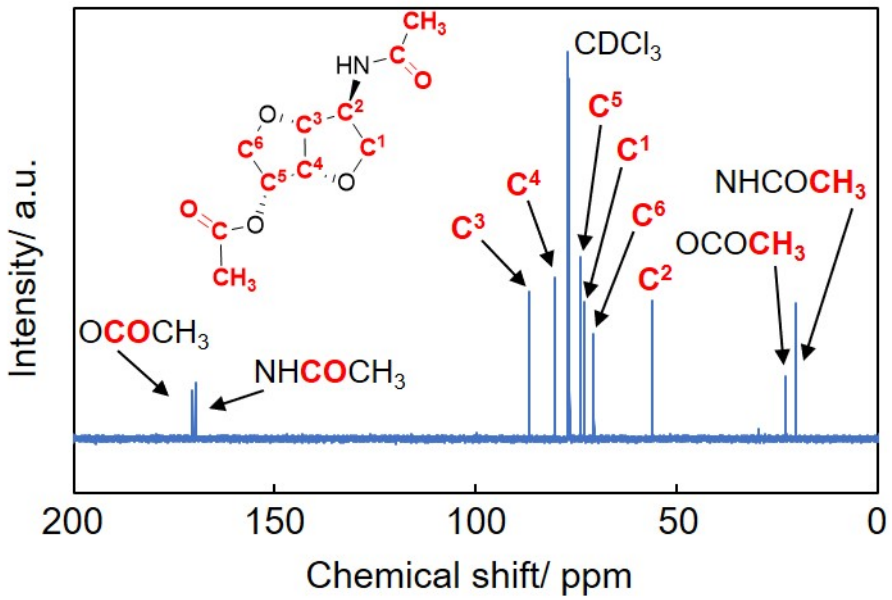

Figure S3. ^{13}C NMR spectrum of ADIAc.

^{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 ($OCOCH_3$).

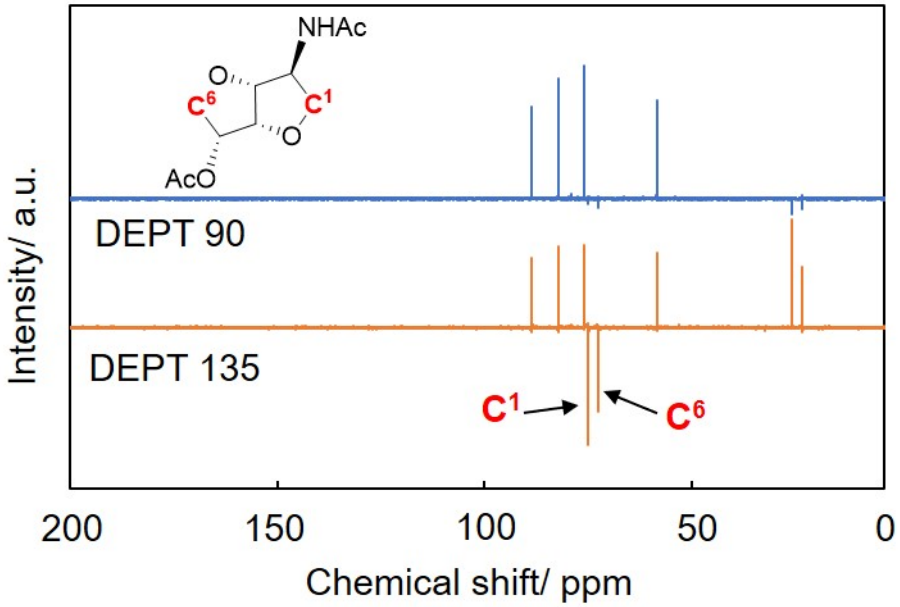

Figure S4. DEPT spectra of ADIAc.

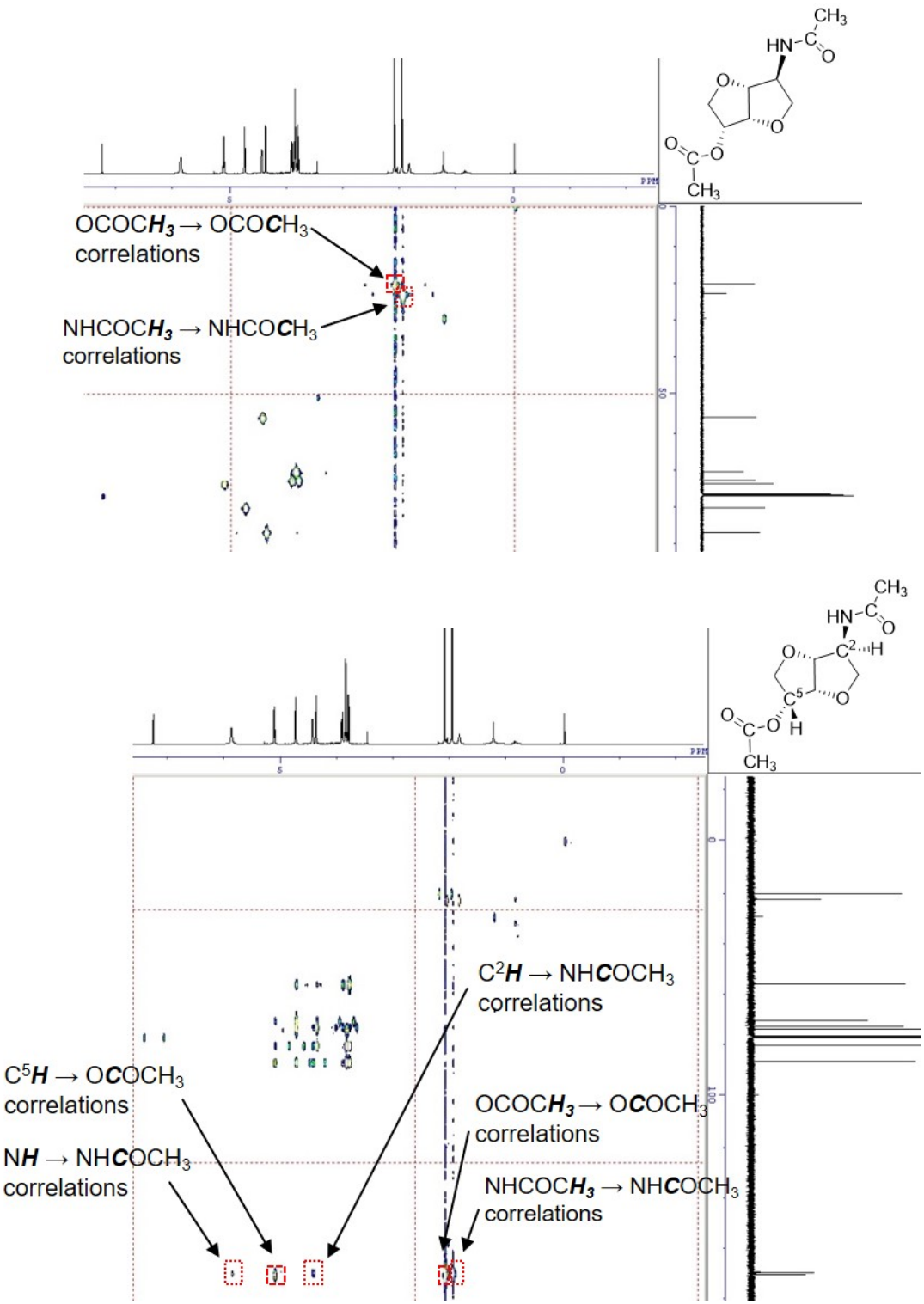

Figure S5. ^{13}C-^{1}H HMQC (horizontal axis: ^{1}H, vertical axis: ^{13}C) (top) and ^{13}C-^{1}H HMBC (horizontal axis: ^{1}H, vertical axis: ^{13}C) (bottom) of ADIAc.

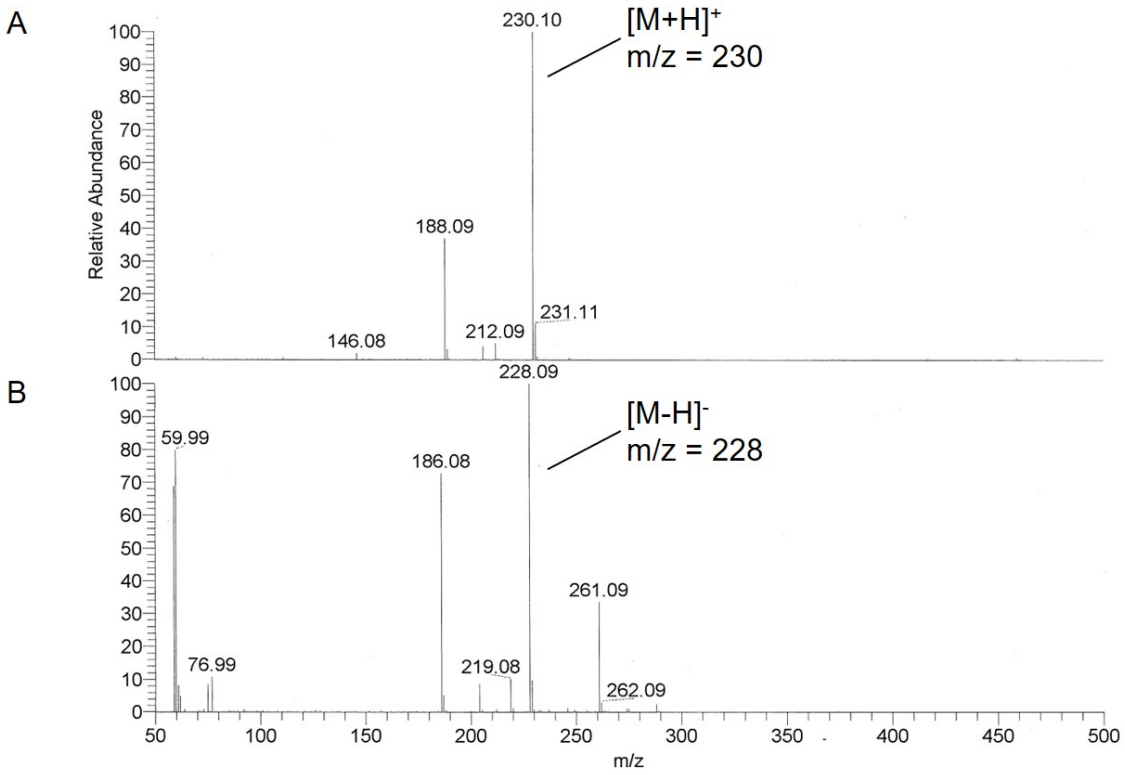

Figure S6. LR-ESI positive (A) and negative (B) mass spectra of ADIAc.

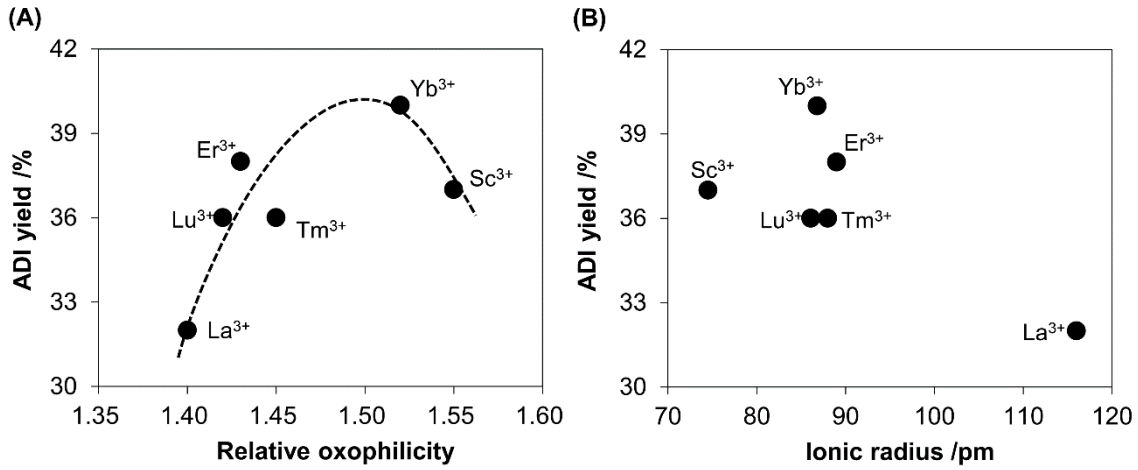

Figure S7. Relationship between physical properties of rare earth triflate and ADI yield in the dehydration of ADS at 150 °C for 1 h. Six coordination is assumed for the ionic radius.

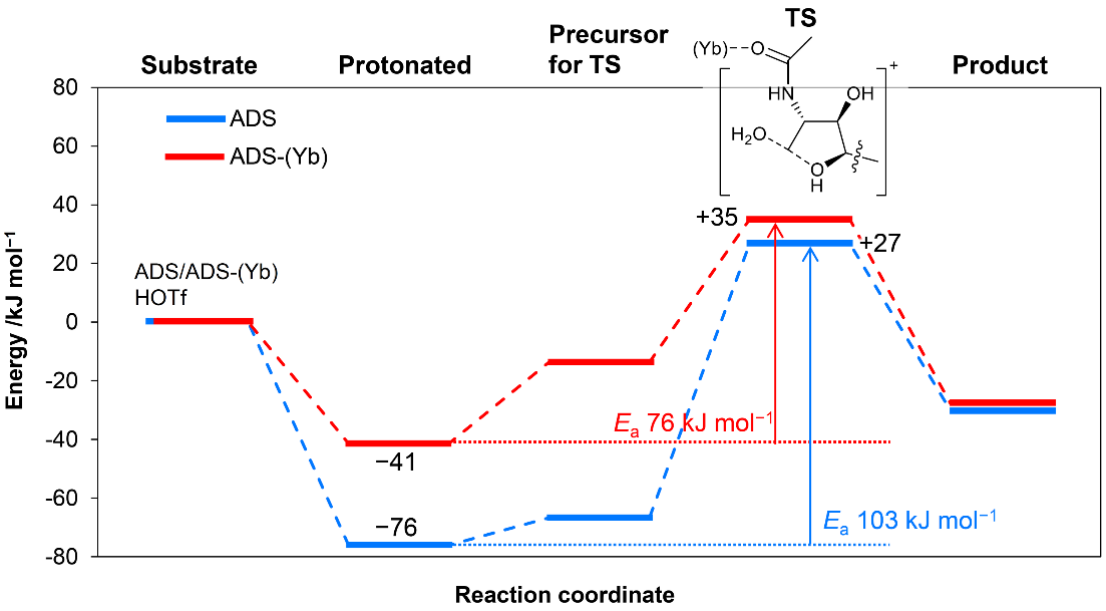

Figure S8. Energy diagrams for the 1,4-dehydration of ADS in the presence and absence of $Yb(OTf)_3(EG)$ calculated by DFT. (Yb) represents $Yb(OTf)_3(EG)$.

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
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 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.

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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
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