Supporting Information

Zemplén Transesterification: A Name Reaction Having Been Misleading Us for 90 Years

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Contents

General methods: All commercially available starting materials and solvents were of reagent grade and used without further purification. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates (Macherey-Nagel). Flash column chromatography was performed on silica gel 60 (SDS 0.040-0.063 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded at 298K in $CDCl_3$, D_2O, CD_3OD and d_6-DMSO using the residual signals from $CHCl_3$ (^{1}H: δ = 7.25 ppm; ^{13}C: δ = 77.2 ppm), D_2O (^{1}H: δ = 4.80 ppm), CD_3OD (^{1}H: δ = 3.31 ppm; ^{13}C: δ = 49.1 ppm) and d_6-DMSO (^{1}H: δ = 2.50 ppm; ^{13}C: δ = 39.5 ppm) as internal standard. ^{1}H peak assignments were made by first order analysis of the spectra, supported by standard ^{1}H-^{1}H correlation spectroscopy (COSY).

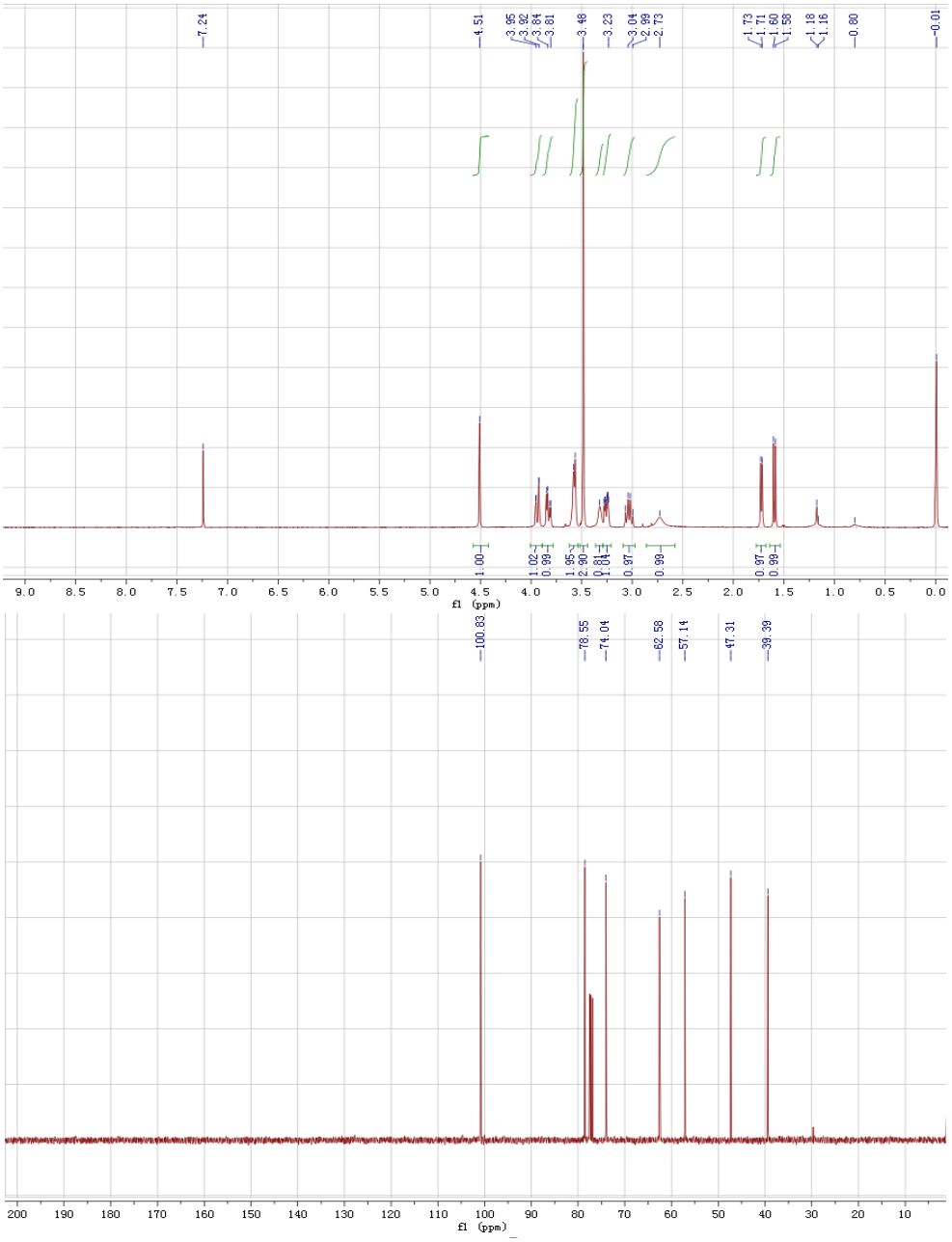
General Deacylation Catalyzed by NaOH or NaOMe: carbohydrate substrates (100 mg) in dry methanol (1 mL) were added NaOH or NaOMe (0.1 eq.). The mixtures were stirred at room temperature for 2 - 12 h, followed by ion exchange with H^+ exchanged resin. After being filtered, the filtrate was concentrated to afford the products. All the products **2**, **4**, **7**, **10**, **11**, **14**, **15**, **17** and **21** are known compounds.

General Deacylation Catalyzed by $^-$OH exchanged resin: carbohydrate substrates (100 mg) in dry methanol (1 mL) were added $^-$OH exchanged resin (85 mg). The mixtures were stirred at room temperature for 2 - 12 h. After being filtered, the filtrate was concentrated to afford the products.

Large Scale: penta-acetyl-glucoside **1** (10g) were deacylated in methanol (100 mL) using 0.1 equiv. of NaOH (105 mg), KOH (144 mg) and hydroxyl anion resin (8.5 g) separately. After stirring at room temperature for 2 hours, the reaction mixtures were treated with H^+ exchanged resin until neutrality (it is not necessary for reaction mixture with hydroxyl anion resin as a catalyst). After being filtered, the filtrate was concentrated and crystallized. The free glucoses **2** were obtained in 92% (4.24 g), 97% (4.48 g) and 89% (4.1 g) yields respectively.

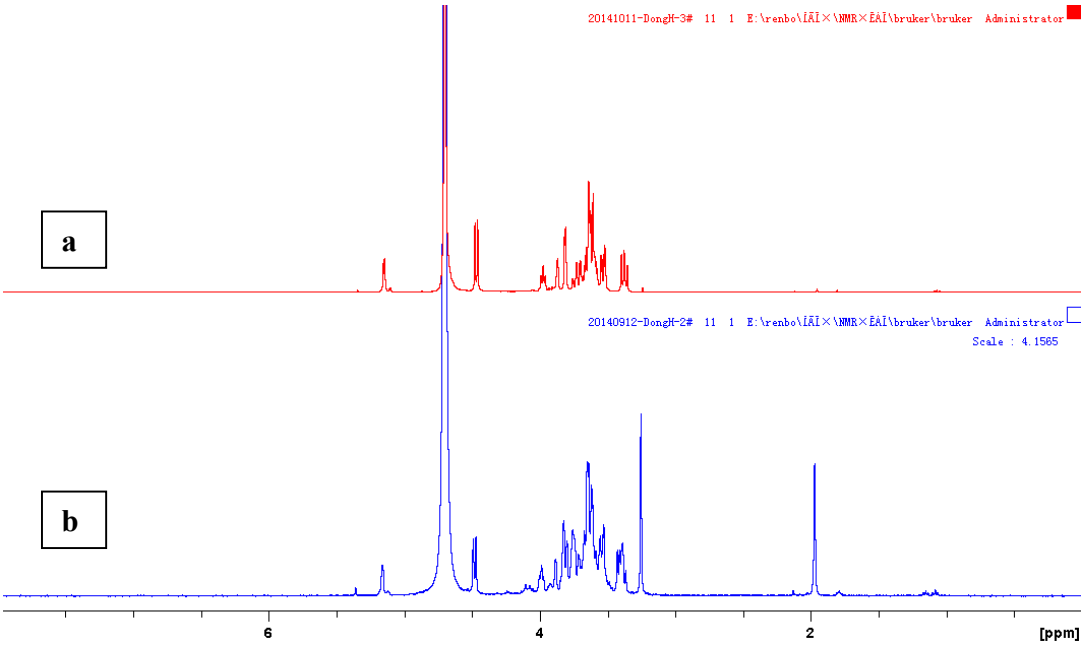
1-Thio-β-D-mannopyranose 21[1]: Compound **20** (101 mg, 0.25 mmol) was dissolved in 3 mL dry MeOH, and sodium hydroxide (11 mg, 0.27 mmol) in methanol (1 mL) was added dropwise. After 40 minutes, the reaction mixture was neutralized with Amberlite IR-120 H^+ ion exchange resin, filtered, concentrated in vacuum, and lyophilized to afford compound **2** (48.5 mg, 99%). ^{1}H NMR (400 MHz, D_2O) δ = 5.05 (d, J = 1.0, 1H, H-1), 4.26 (dd, J=1.0 Hz and 3.1 Hz, 1H, H-2), 4.00 (dd, J=2.2 Hz, 12.4 Hz, 1H, H-3), 3.82 (dd, J = 5.9 Hz, 12.4 Hz, 1H, H-6), 3.74 (dd, J = 3.2 Hz, 9.6 Hz 1H, H-6'), 3.69 (t, J = 9.4 Hz, 1H, H-4), 3.57–3.48 (m, 1H, H-5).

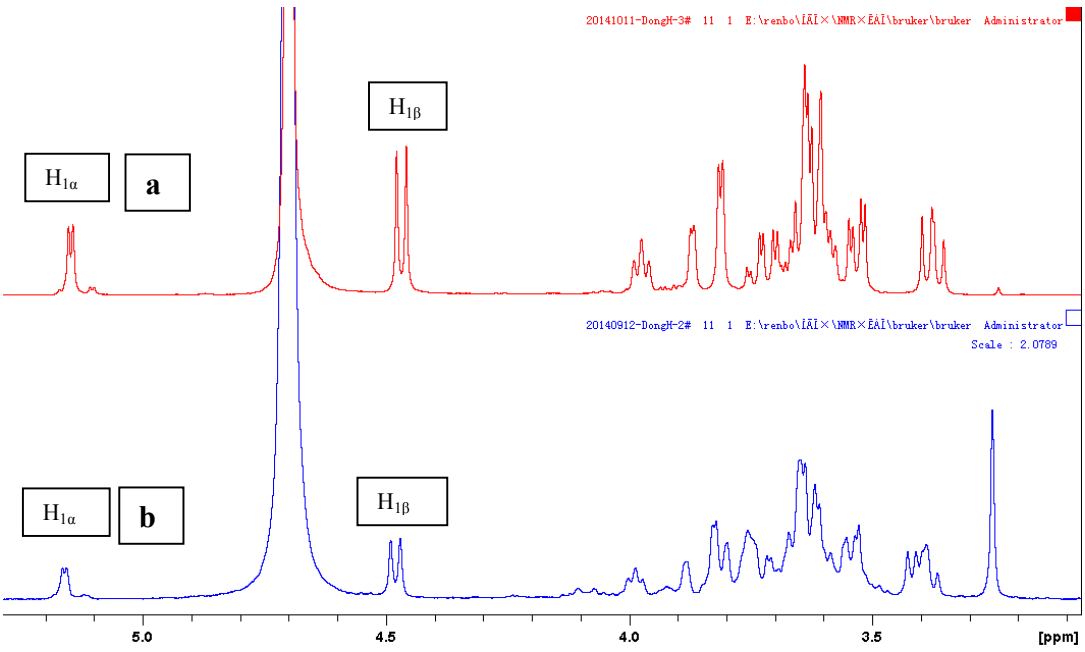
Methyl 2,4-thio-β-D-mannopyranoside 23: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.51 (s, 1H, H-1), 3.94 (dd, *J* = 12.2, 2.1, 1H, H-6), 3.83 (dd, *J* = 4.6 Hz and 12.2 Hz, 1H, H-6'), 3.57 (m, 2H, H-2, H-3), 3.48 (s, 3H, OMe), 3.35 (s, 1H, OH), 3.29–3.21 (m, 1H, H-5), 3.12 – 2.97 (m, 1H, H-4), 2.77 (s, 1H, OH), 1.72 (d, *J* = 6.3 Hz, 1H, SH), 1.59 (d, *J* = 8.2 Hz, 1H, SH). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 100.8, 78.6, 74.0, 62.6, 57.1, 47.3, 39.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_4S_2Na$ 249.0231; found 249.0226.



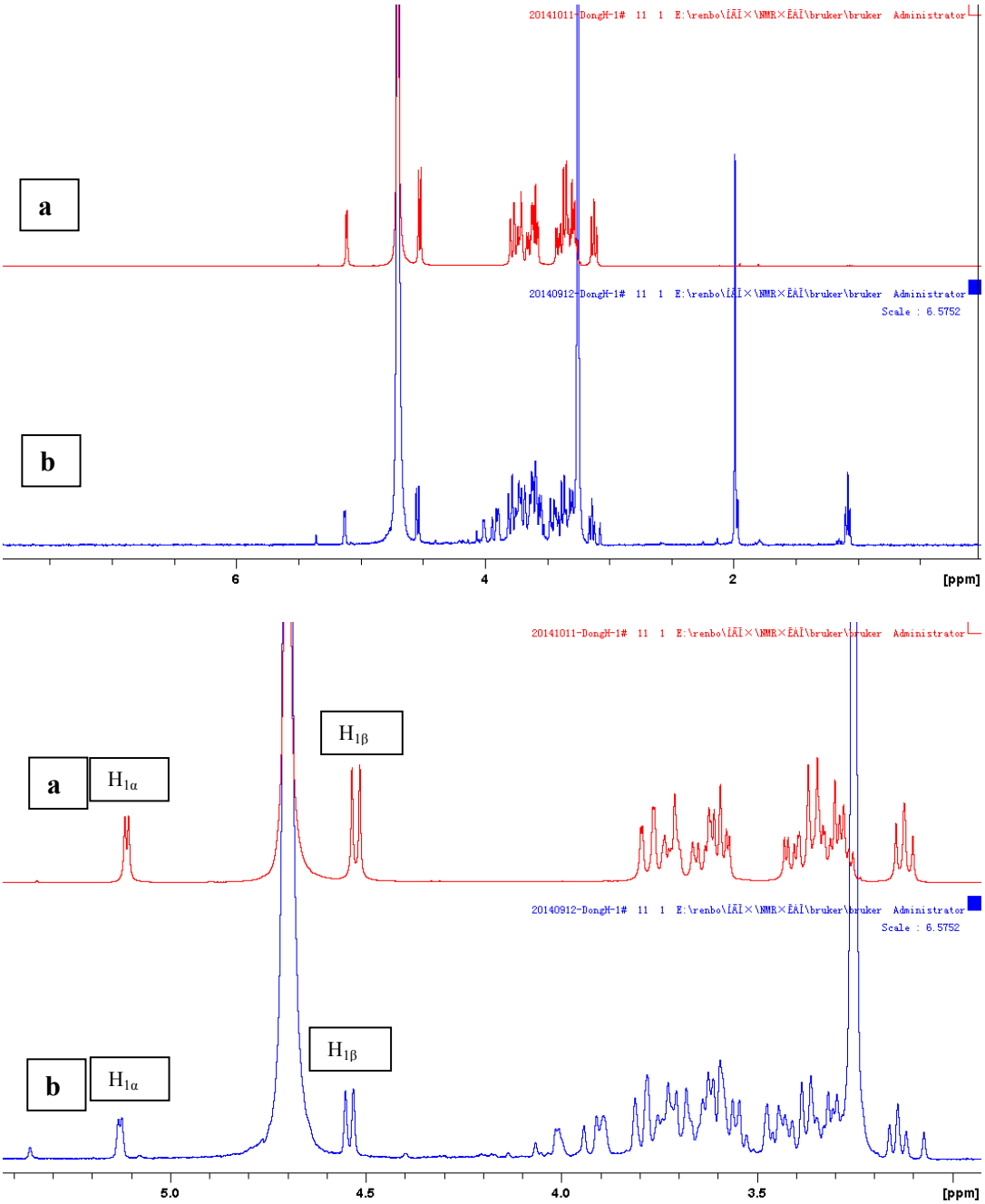
Comparison of ^{1}H NMR spectrum (H_1 peak) of crude product from deacylation with that of reagent grade sample indicating a quantitative NMR yield: carbohydrate substrates (100 mg) in dry methanol (1 mL) were added NaOH (0.1 eq.). The mixtures were stirred at room temperature for 2, followed by ion exchange with H^+ exchanged resin. After being filtered, the filtrate was concentrated and directly tested by NMR instrument.

Deacylation of compound 3 (tested in D_2O): a) reagent grade sample; b) crude product.

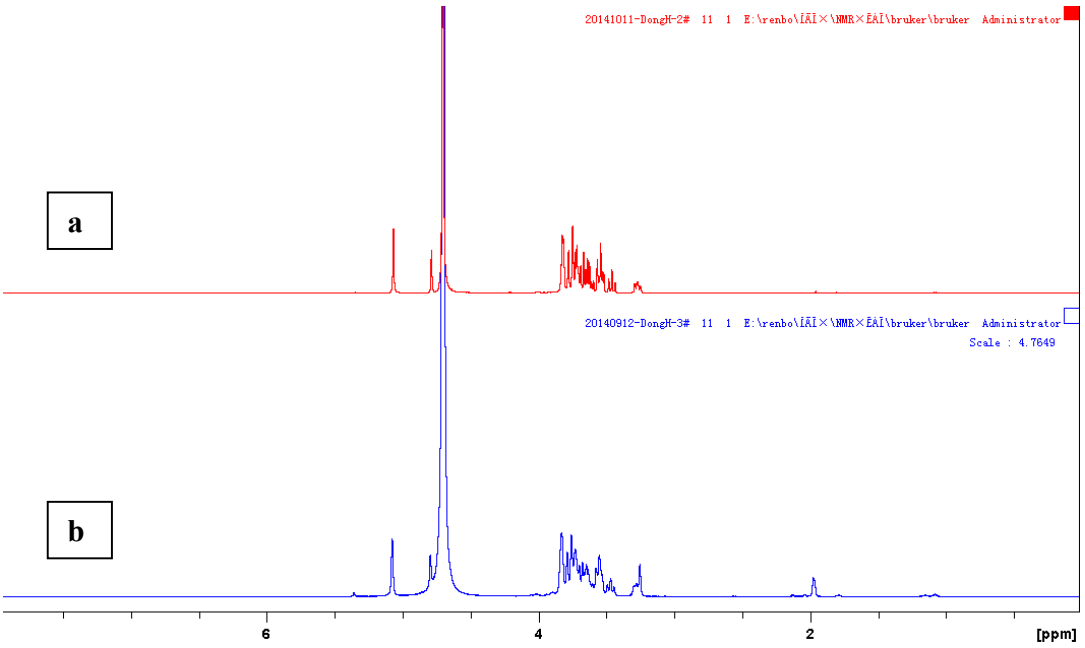


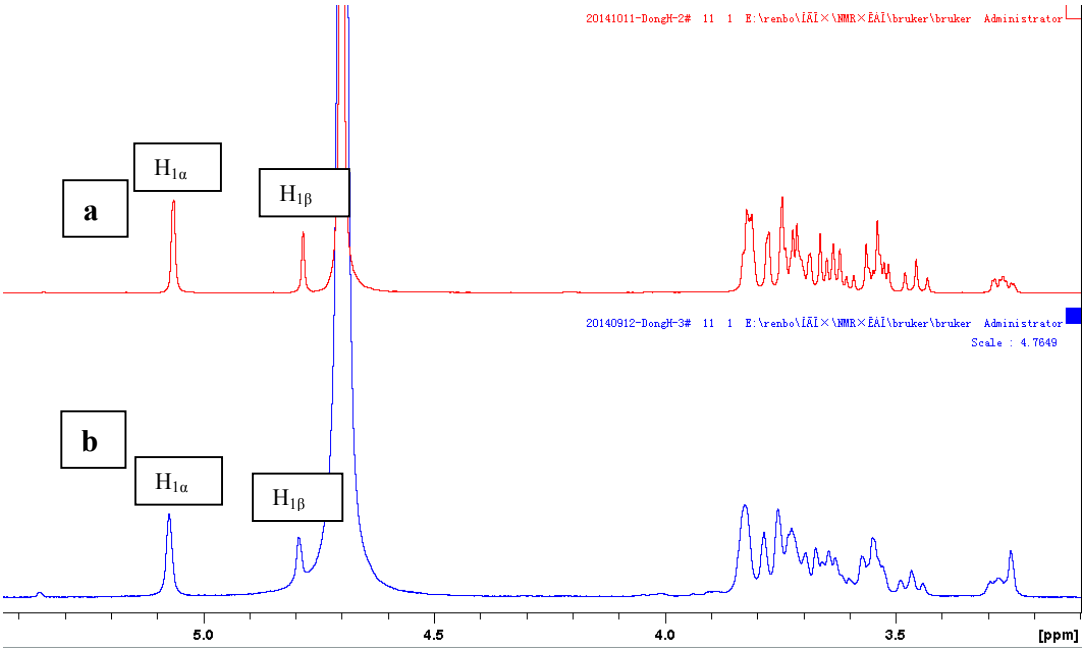


Deacylation of compound 5 (tested in D_2O): a) reagent grade sample; b) crude product.

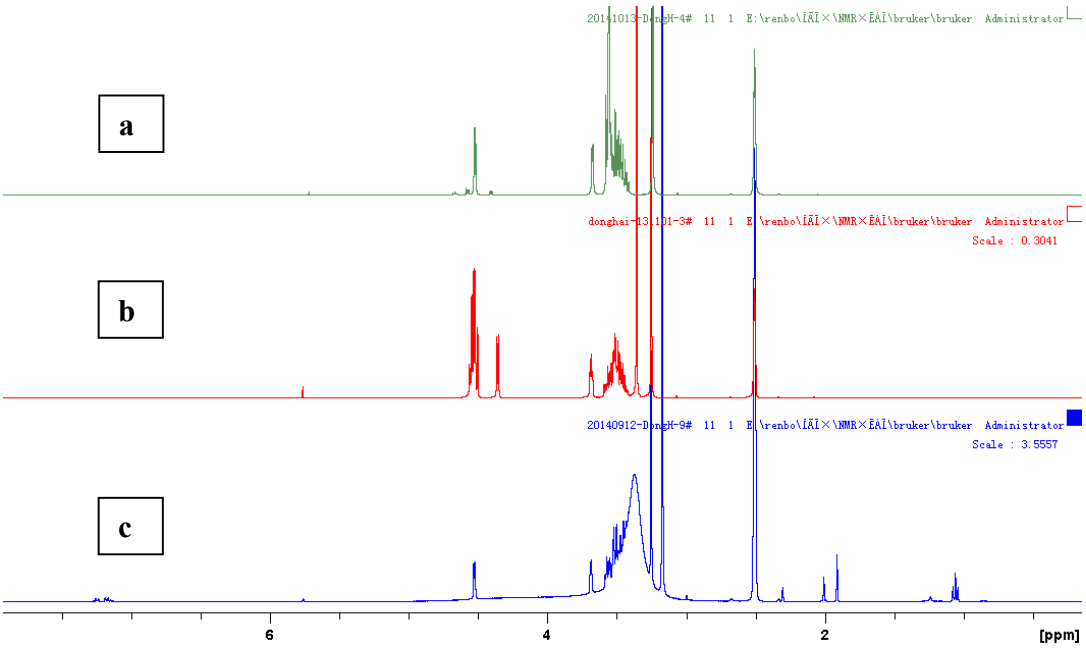


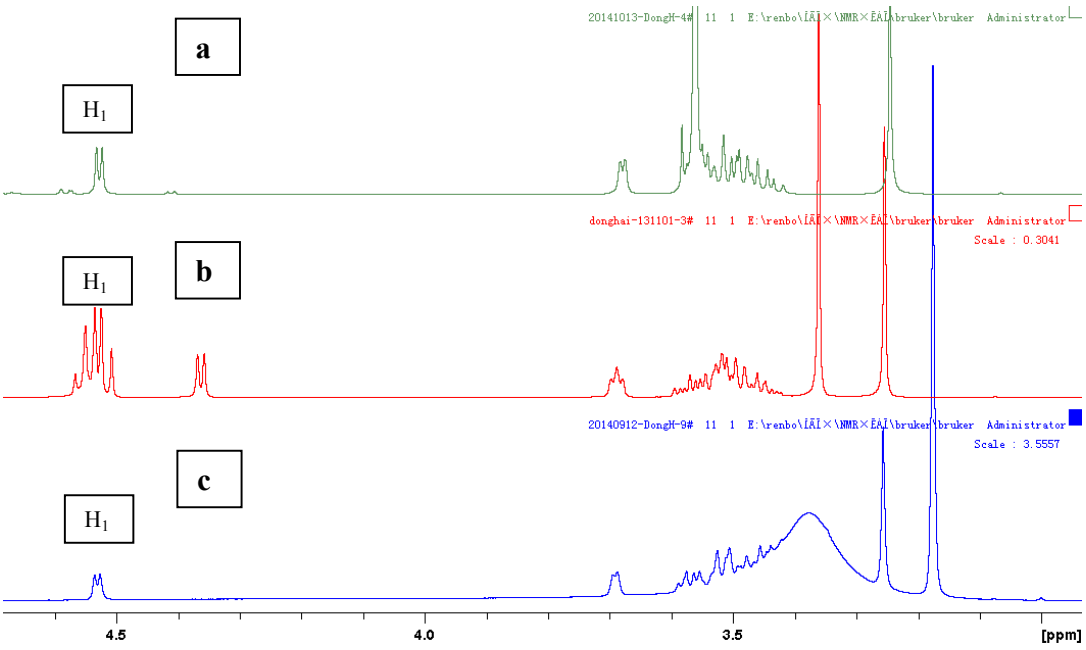
Deacylation of compound 6 (tested in D_2O): a) reagent grade sample; b) crude product.



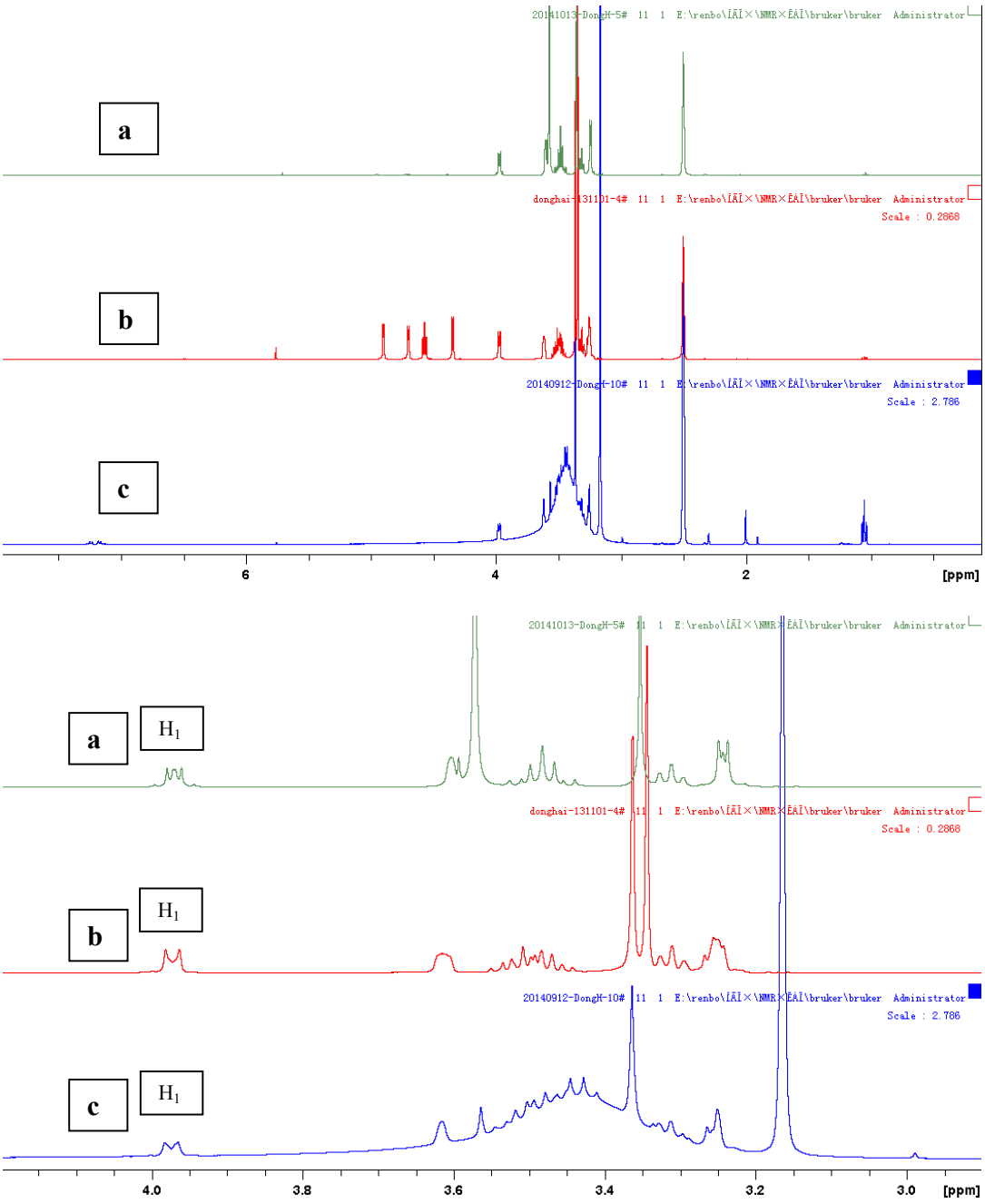


Deacylation of compound 8 (tested in d_6-DMSO): a) reagent grade sample with addition of a drop of D_2O; b) reagent grade sample; c) crude product.

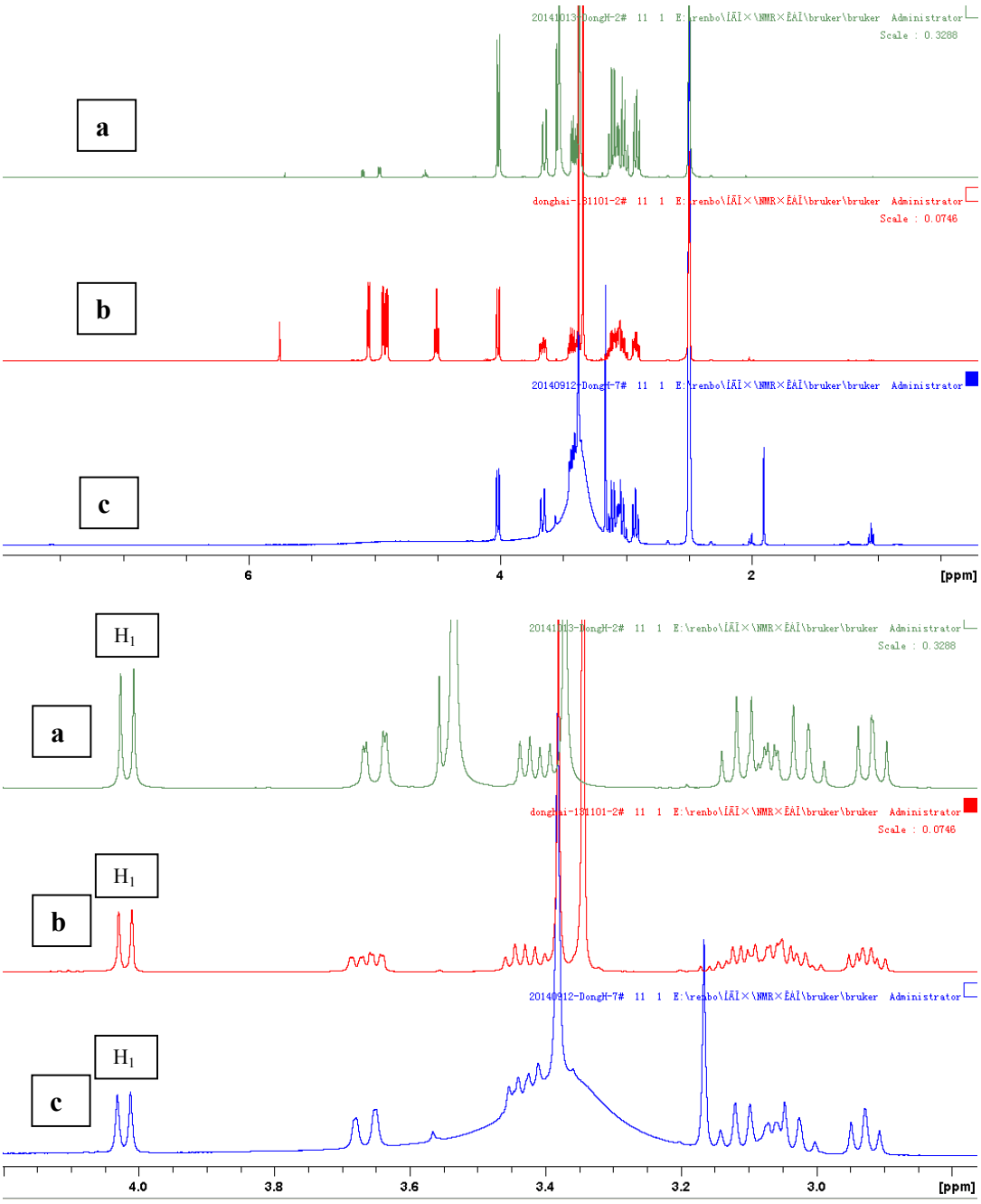




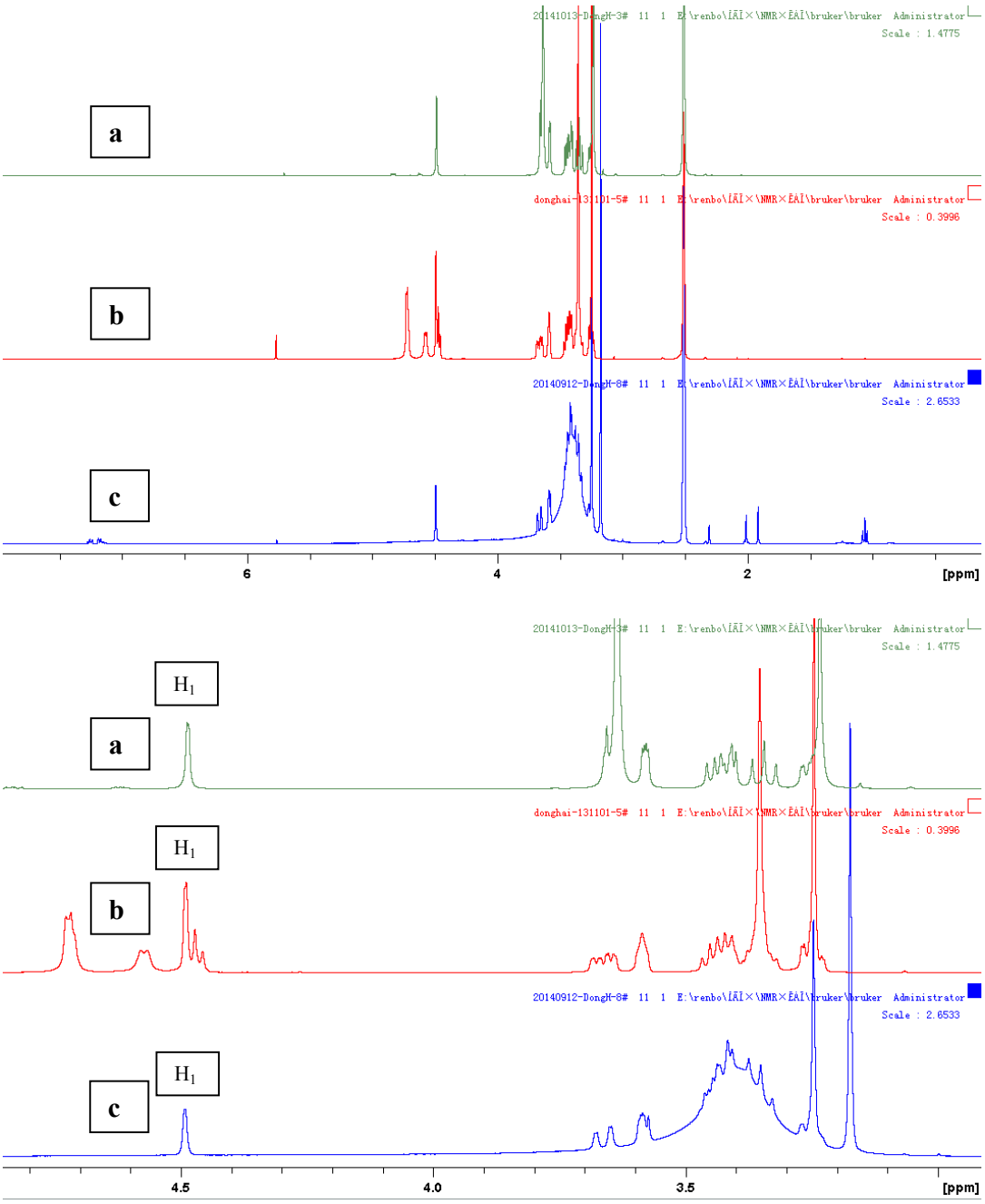
Deacylation of compound 12 (tested in d_6-DMSO): a) reagent grade sample with addition of a drop of D_2O; b) reagent grade sample; c) crude product.



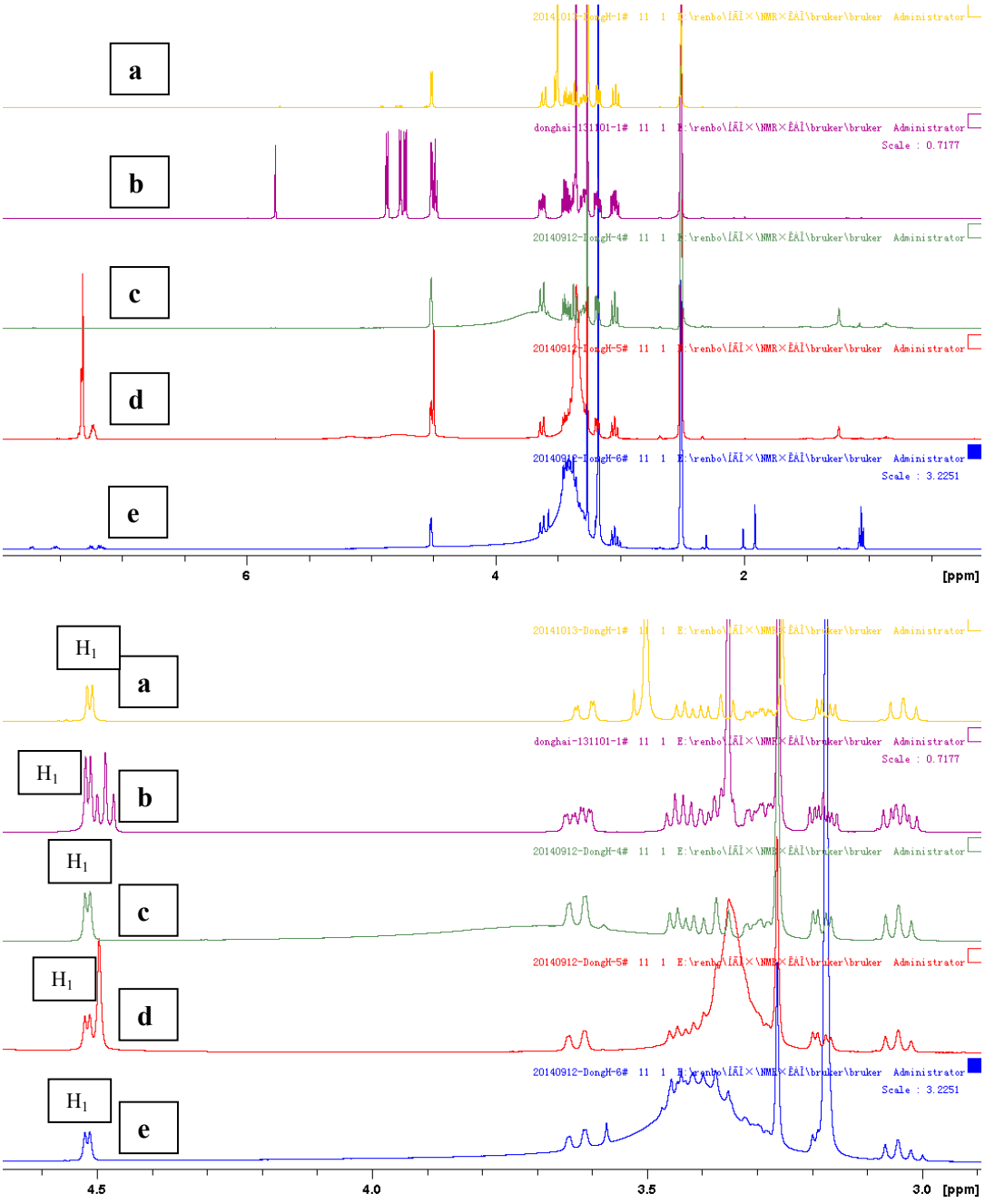
Deacylation of compound 13 (tested in d_6-DMSO): a) reagent grade sample with addition of a drop of D_2O; b) reagent grade sample; c) crude product.



Deacylation of compound 16 (tested in d_6-DMSO): a) reagent grade sample with addition of a drop of D_2O; b) reagent grade sample; c) crude product.



Deacylation of compound 9, 18 and 19 (tested in *d*$_6$-DMSO): a) reagent grade sample with addition of a drop of D_2O; b) reagent grade sample; c) crude product for compound **18**; d) crude product for compound **19**; e) crude product for compound **9**.



General Method for Measuring KIE Value: As step b) is the rate-determining step, the rate constants can be measured using the following equation: ln (B_0/B) = k*A*t, where A stands for the concentration of base catalysts, B stands for the concentration of esters, k stands for the rate constant, and t is the reaction time. The values of B_0/B can be measured over time using 1H NMR tests. In Figure **S1**, A stands for the concentration of the H-bonding complex and X stands for MeO or OH group. As methanol acts as solvent in the reaction, A equals to the concentration of hydroxyl anion or methoxyl anion and is a constant. Therefore, we can get the differential equation (1) which is related to the rate constant k and the concentration of the esters (B). To solve the differential equation (1) gets equation (2). B_0 stands for the initial concentration of the esters in equation (2). Therefore, the value of k can be measured through recording the concentration of the esters (B) with time (t).

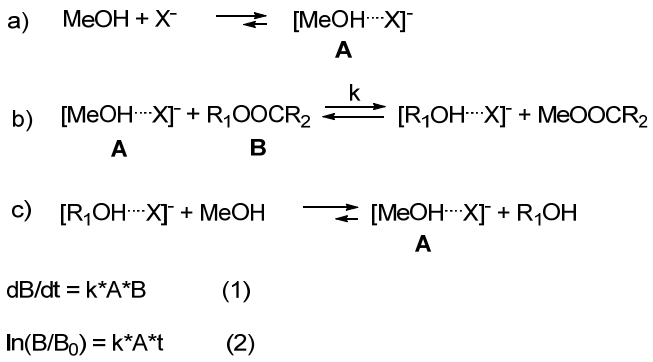


Figure **S1**. The value of k can be measured via recording the concentration of the esters (B) with time (t).

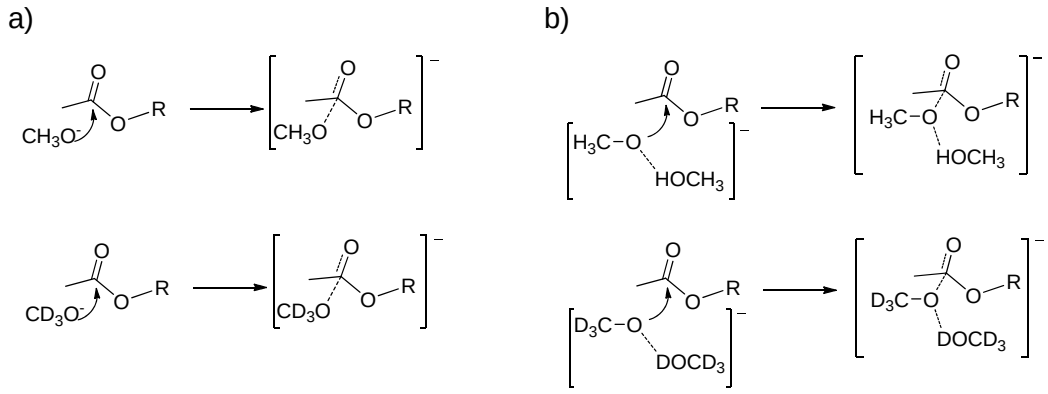
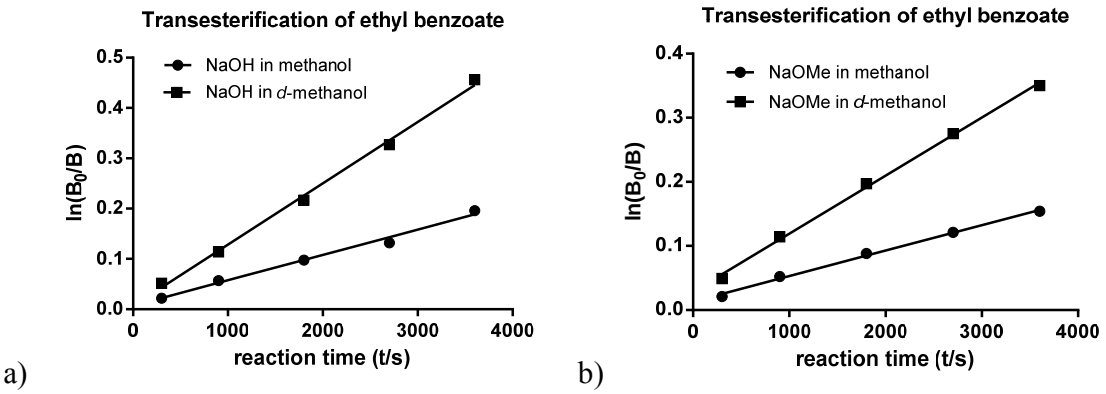
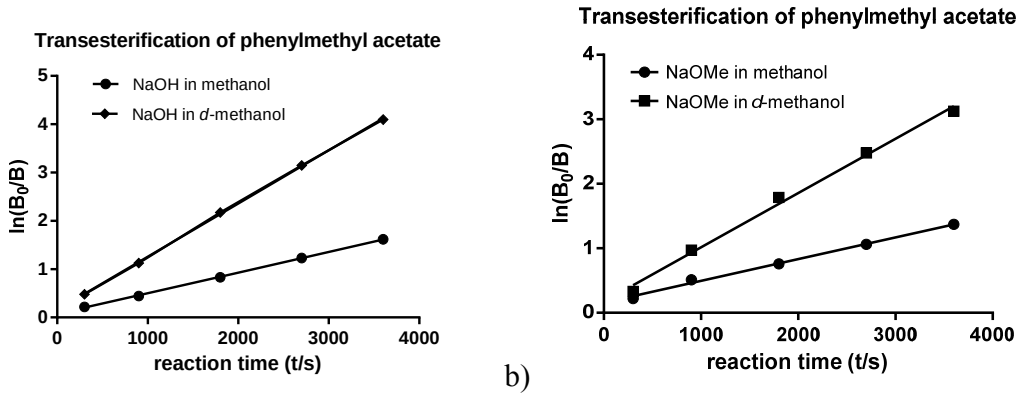


Figure **S2**. Inverse isotope effect supporting H-bond involved transesterification mechanism. a) The traditional base-catalyzed transesterification mechanism should not lead to isotope effect since no hydrogen atom is involved in the reaction. b) The proposed H-bond involved transesterification mechanism should lead to an inverse isotope effect as the case involving conversion of a dicoordinate COH bond to a tricoordinate transition state.



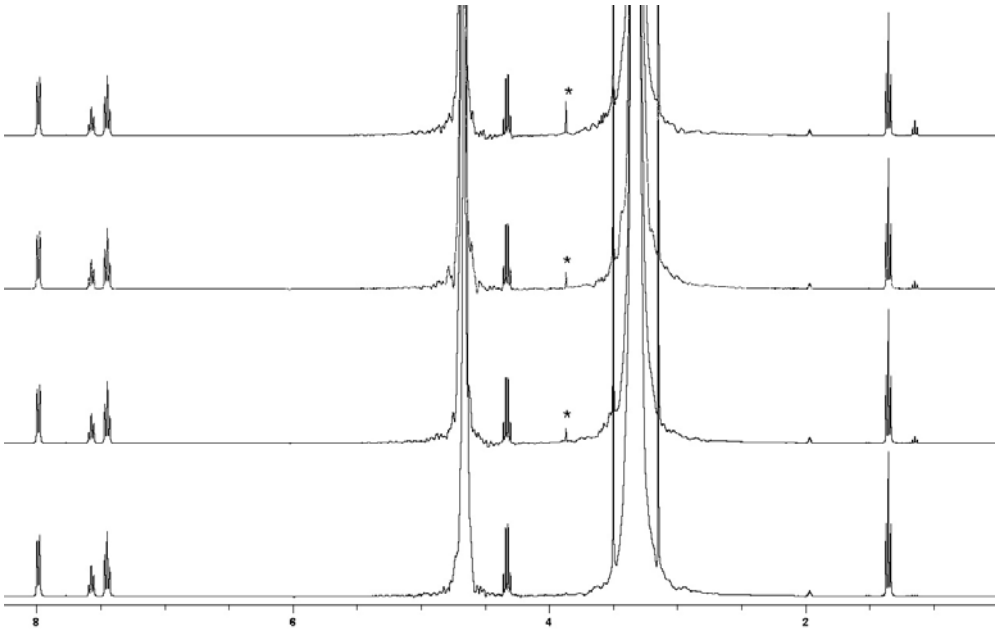
a) b)

Figure **S3**. The values of k were measured for transesterification of ethyl benzoate in methanol. a) NaOH (0.1 eq.) as catalyst, k_H*A = 5.035 x 10^{-5}/s, R^2 = 0.9953, k_D*A = 1.189 x 10^{-4}/s, R^2 = 0.9963, therefore, k_H/k_D = 0.42; b) NaOMe (0.1 eq.) as catalyst, k_H*A = 3.971 x 10^{-5}/s, R^2 = 0.9962, k_D*A = 9.057 x 10^{-5}/s, R^2 = 0.9980, therefore, k_H/k_D = 0.44.

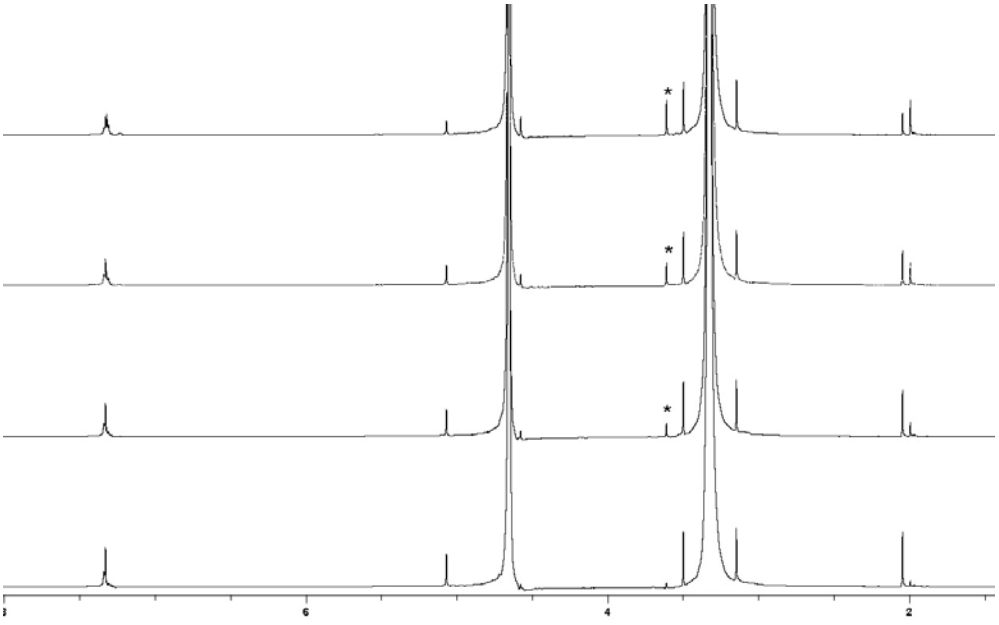


a) b)

Figure **S4**. The values of k were measured for transesterification of phenylmethyl acetate in methanol. a) NaOH (0.02 eq.) as catalyst, k_H*A = 4.277 x 10^{-4}/s, R^2 = 0.9995, k_D*A = 1.102 x 10^{-3}/s, R^2 = 0.9997, therefore, k_H/k_D = 0.39; b) NaOMe (0.02 eq.) as catalyst, k_H*A = 3.371 x 10^{-4}/s, R^2 = 0.9952, k_D*A = 8.406 x 10^{-4}/s, R^2 = 0.9944, therefore, k_H/k_D = 0.40.



Figures **S5**. Recorded transesterification of ethyl benzoate in methanol catalyzed by NaOH with time. * stands for the methyl peak of the formed methyl benzoate.



Figures **S6**. Recorded transesterification of phenylmethyl acetate in methanol catalyzed by NaOH with time. * stands for the methyl peak of the formed methyl acetate.

Computational methods

Molecular geometries of all species were optimized without constraints via DFT calculations using the B3LYP functional.[2] The 6-31+G(d,p) basis set was used for C, H and O atoms. Frequency calculations were carried out at the same level of theory to identify the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency), and to provide the thermal correction to free energies at 298.15 K. Intrinsic reaction coordinates (IRC)[3] were calculated for all transition states to confirm that the structures indeed connect two relevant minima. To take the solvent effect into account, single-point energy calculations were performed at the M06 level[4] using 6-311++G(d,p) basis set for all the atoms with continuum solvent model SMD[5] in methanol. The solvation- and entropy-corrected relative free energies are used to analyze the reaction mechanism. All calculations were performed with the Gaussian 09 software package.[6]

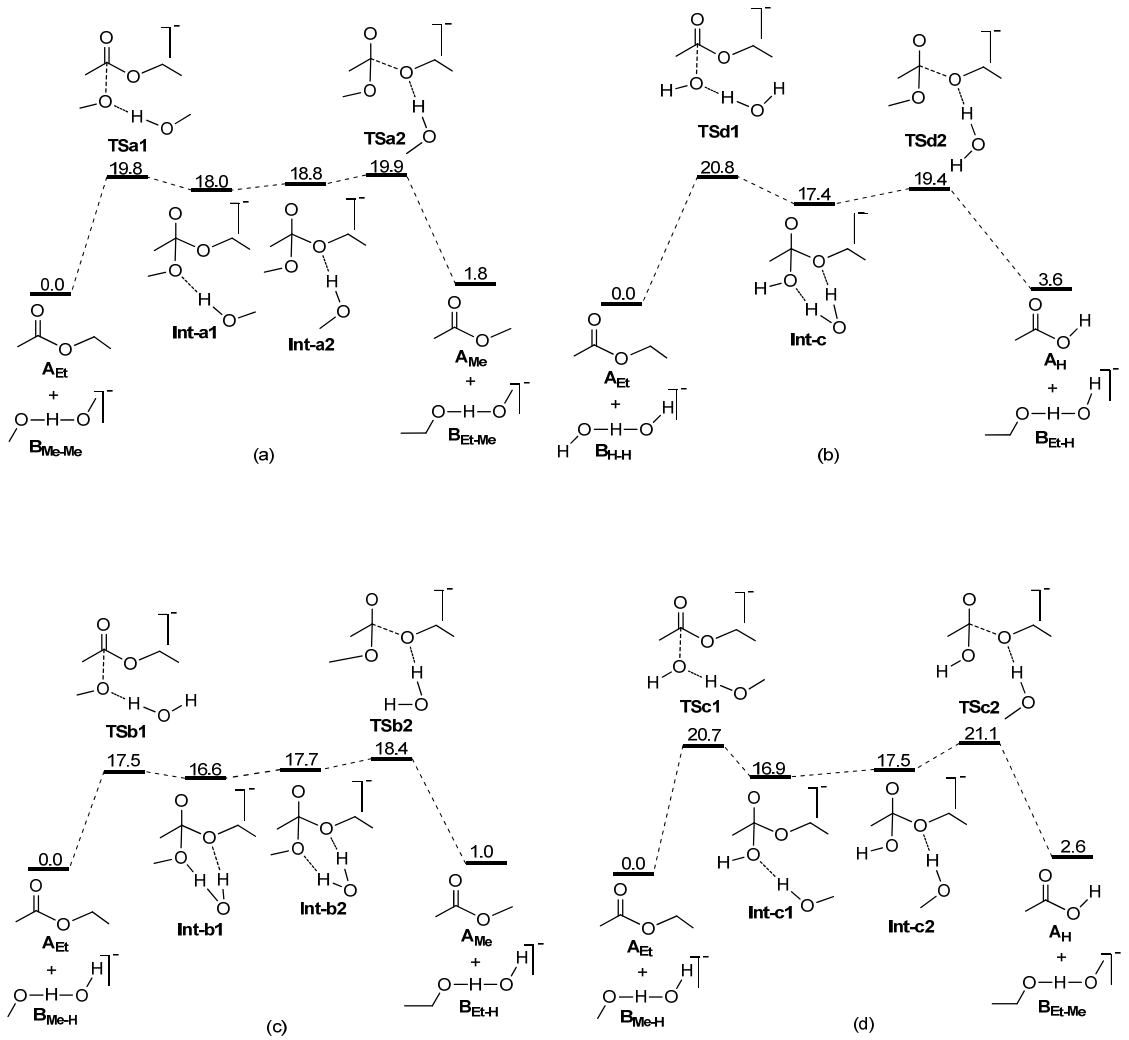


Figure S7. The possible four approaches for transesterification of ethyl acetate in methanol with hydroxide as a catalyst. a) Process through [MeO⋯H⋯OMe]$^-$, b) Process through [HO⋯H⋯OH]$^-$), and (c) and (d) Process through [MeO⋯H⋯OH]$^-$. The energy values are all in kcal/mol.

References

1. Floyd, N.; Vijayakrishnan, B.; Koeppe, J. R.; Davis, B. G. *Angew. Chem. Int. Ed.* **2009**, *48*, 7798-7802.
2. (a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, 157, 200. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
3. (a) Fukui, K. *J. Phys. Chem.* **1970**, 74, 4161. (b) Fukui, K. *Acc. Chem. Res.* **1981**, 14, 363.
4. Zhao, Y.; Truhlar, D. G.; *Theor. Chem. Acc.* **2008**,120,215.
5. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, 113, 6378.
6. Frisch, M. J. In Gaussian 09, revision A.02; Gaussian, Inc., Wallingford, CT, 2009.

Cartesian coordinates and free energies for all calculated species

[MeO····H····OMe]$^-$

```
G = -230.8599036 a.u.
O    -1.89974   2.09015   1.43042
H    -2.46805   3.10467   1.53166
O    -3.08995   4.19558   1.59961
C    -4.44179   4.01880   1.40981
H    -4.73002   2.95125   1.27105
H    -4.83839   4.55716   0.51294
H    -5.05843   4.38645   2.26668
C    -1.45089   1.92551   0.13224
H    -1.66698   2.80574  -0.50815
H    -1.91035   1.04713  -0.37893
H    -0.35002   1.76271   0.07653
```

[MeO····H····OH]$^-$

```
G = -191.6143201 a.u.
O    -2.01494   1.86227   1.46947
H    -1.49473   2.03812   2.26187
H    -2.48158   2.81623   1.26110
O    -3.04463   4.10075   1.07202
C    -4.38326   4.17241   1.33977
H    -5.04614   3.94761   0.45975
H    -4.71164   5.18669   1.68777
H    -4.73121   3.46758   2.14102
```

[EtO····H····OMe]$^-$

```
G = -270.1265687 a.u.
O    -1.70435   2.57110  -2.51352
H    -2.49373   3.61302  -2.04734
O    -3.13405   4.40369  -1.66560
C    -4.28341   3.83298  -1.12849
H    -4.07208   3.08767  -0.33425
H    -4.91612   4.61683  -0.67326
H    -4.90950   3.31317  -1.88369
C    -0.59608   2.31896  -1.75442
H    -0.49593   3.01715  -0.88489
H     0.36012   2.44364  -2.32954
C    -0.56592   0.88184  -1.17568
H     0.34694   0.69362  -0.58400
H    -1.44144   0.71665  -0.53379
H    -0.61101   0.15013  -1.99339
```

[EtO⋯H⋯OH]$^-$

G = -230.8823468 a.u.

O	-1.84705	2.52771	-2.25556
H	-2.61782	3.43202	-1.42103
O	-3.17004	4.15222	-0.86377
C	-0.58155	2.27044	-1.81889
H	-0.23345	2.98624	-1.02745
H	0.18604	2.35759	-2.63569
C	-0.41076	0.84850	-1.22141
H	0.62615	0.65997	-0.89047
H	-1.08321	0.72107	-0.36302
H	-0.68315	0.09446	-1.97224
H	-3.14304	4.93466	-1.42602

MeC(O)OEt

G = -307.5288120 a.u.

C	-1.85776	0.37122	0.16603
O	-1.28541	0.15062	1.21493
C	-3.34453	0.24169	-0.06285
H	-3.53994	-0.47796	-0.86388
H	-3.82588	-0.08679	0.85818
H	-3.76050	1.20350	-0.37868
O	-1.22222	0.77144	-0.95897
C	0.21584	0.93366	-0.86721
H	0.65588	-0.02278	-0.56821
H	0.43499	1.66276	-0.08100
C	0.71294	1.39149	-2.22580
H	1.79944	1.52562	-2.19389
H	0.48046	0.65296	-2.99922
H	0.25723	2.34492	-2.51023

MeC(O)OMe

G = -268.2592136 a.u.

C	-1.88836	0.35269	0.16382
O	-1.25549	0.05545	1.15685
C	-3.38277	0.21972	0.00163
H	-3.61039	-0.45107	-0.83267
H	-3.81374	-0.17322	0.92228
H	-3.82351	1.19369	-0.23214
O	-1.31698	0.85447	-0.95639
C	0.11319	1.02218	-0.91380
H	0.60505	0.06060	-0.74710
H	0.38608	1.43110	-1.88644
H	0.39267	1.71095	-0.11269

MeC(O)OH

G = -229.0124747 a.u.

C	-1.88827	0.38991	0.07352
O	-1.15669	0.04693	0.97827
C	-3.38191	0.20345	0.02129
H	-3.65229	-0.39147	-0.85659
H	-3.71871	-0.29542	0.92942
H	-3.87488	1.17549	-0.07808
O	-1.41856	1.00802	-1.04227
H	-0.45580	1.09300	-0.93669

TSa1

G = -538.3571985 a.u.

C	-1.61986	0.13532	0.05921
O	-1.65068	1.06329	0.89016
C	-2.88511	-0.62032	-0.33192
H	-2.65520	-1.50060	-0.93660
H	-3.40462	-0.92943	0.57789
H	-3.53846	0.05363	-0.90334
O	-0.82287	0.26222	-1.10798
C	0.37868	0.99805	-0.92200
H	0.97802	0.51343	-0.14038
H	0.14563	2.01724	-0.58520
C	1.13199	1.01185	-2.24588
H	2.06293	1.58591	-2.14850
H	1.38692	-0.00776	-2.55272
H	0.52500	1.47074	-3.03605
O	-0.70471	-1.31215	0.80714
O	1.14075	-2.64210	-0.48839
H	0.45121	-2.10641	0.02329
C	-0.52937	-1.19633	2.18216
H	-1.16486	-1.90722	2.75334
H	0.51984	-1.39507	2.47809
H	-0.78415	-0.17555	2.51846
C	0.49297	-3.22378	-1.59133
H	1.24784	-3.71756	-2.22045
H	-0.24605	-3.99072	-1.29428
H	-0.03303	-2.47746	-2.20860

Inta1

G = -538.3600854 a.u.

C	-1.5149	0.03605	0.10718
O	-1.59274	1.05244	0.85051
C	-2.80721	-0.67200	-0.32443
H	-2.60233	-1.56317	-0.92560
H	-3.36530	-0.95987	0.57159
H	-3.41603	0.02831	-0.90940
O	-0.71939	0.14368	-1.10885
C	0.45147	0.92708	-0.96567
H	1.16786	0.41170	-0.30747
H	0.19919	1.88666	-0.49526
C	1.05946	1.13656	-2.34859
H	1.97311	1.74242	-2.27953
H	1.31879	0.17749	-2.81159
H	0.35124	1.65222	-3.00850
O	-0.68217	-1.20876	0.84771
O	1.05075	-2.88115	-0.34324
H	0.42689	-2.24633	0.10590
C	-0.63951	-1.12016	2.24544
H	-1.41417	-1.74948	2.72795
H	0.34251	-1.46221	2.61190
H	-0.79524	-0.07802	2.56063
C	0.49191	-3.21284	-1.59478
H	1.26745	-3.70244	-2.20007
H	-0.35506	-3.91701	-1.50390
H	0.13428	-2.32337	-2.13285

Inta2

G = -538.3588040 a.u.

C	-1.75817	0.16648	-0.13951
O	-1.94113	1.08622	-0.97414
C	-2.88218	-0.81975	0.18377
H	-2.52963	-1.63947	0.81549
H	-3.27296	-1.22605	-0.75236
H	-3.68589	-0.28059	0.70137
O	-1.16680	0.51175	1.13452
C	-0.17382	1.51225	1.04749
H	0.71096	1.14467	0.50608
H	-0.55060	2.40605	0.53388
O	-0.54337	-0.94156	-0.70658
O	0.64255	-2.82746	0.76690
H	0.18554	-2.14345	0.19857
C	-0.10440	-0.71542	-2.01356
H	1.00295	-0.68673	-2.03483
H	-0.46863	0.27073	-2.34416
C	1.14461	-2.17480	1.91115
H	2.06987	-1.60753	1.70108
H	1.38727	-2.93600	2.66611
H	0.41409	-1.47442	2.34065
H	0.11253	1.76494	2.07535
C	-0.59008	-1.79501	-2.99489
H	-1.68560	-1.80116	-3.03817
H	-0.20563	-1.60852	-4.00955
H	-0.25643	-2.79009	-2.67564

TSa2

G = -538.3569332 a.u.

C	-1.91700	0.30623	-0.06522
O	-2.07880	1.20631	-0.91661
C	-3.01838	-0.70656	0.23453
H	-2.65185	-1.52276	0.86165
H	-3.38907	-1.11243	-0.70924
H	-3.84061	-0.19167	0.74931
O	-1.32284	0.64494	1.19316
C	-0.32219	1.63999	1.10477
H	0.54574	1.26966	0.54081
H	-0.69979	2.54558	0.61351
O	-0.64515	-0.84985	-0.64370
O	0.52025	-2.72830	0.81639
H	0.06807	-2.03959	0.24202
C	-0.20644	-0.61916	-1.94483
H	0.90180	-0.56501	-1.97101
H	-0.58786	0.35926	-2.28473
C	1.03881	-2.07408	1.95044
H	1.95992	-1.50464	1.72660
H	1.29477	-2.83280	2.70395
H	0.31457	-1.37403	2.39255
H	-0.01706	1.87096	2.13182
C	-0.66484	-1.70882	-2.93059
H	-1.76008	-1.74078	-2.97602
H	-0.28263	-1.51323	-3.94468
H	-0.30941	-2.69610	-2.61043

TSb1

G = -499.1153172 a.u.

C	-1.73665	0.35501	0.05244
O	-1.74818	0.97348	1.12107
C	-2.96020	-0.33543	-0.51779
H	-2.68841	-1.05023	-1.29558
H	-3.47462	-0.85744	0.29108
H	-3.63604	0.42636	-0.93457
O	-0.89426	0.74063	-0.99346
O	-0.70999	-1.39111	0.42507
H	-0.17492	-2.60107	-2.16566
O	-0.50325	-3.17012	-1.46001
H	-0.60041	-2.52440	-0.67404
C	-0.70029	-1.72629	1.76460
H	-1.39980	-2.55679	2.01962
H	-0.98876	-0.85952	2.39295
C	0.33292	1.33053	-0.57556
H	0.13455	2.25135	-0.01114
H	0.84095	0.62244	0.09004
H	0.30481	-2.05347	2.11386
C	1.16207	1.61711	-1.82025
H	2.11849	2.07889	-1.54264
H	1.37215	0.69134	-2.36697
H	0.63340	2.29999	-2.49624

Intb1

G = -499.1166832 a.u.

C	-1.59163	0.00843	0.16107
O	-1.62289	0.88280	1.07634
C	-2.92307	-0.44987	-0.45939
H	-2.77603	-1.20230	-1.24064
H	-3.55064	-0.87104	0.33321
H	-3.43348	0.42249	-0.88333
O	-0.73672	0.31841	-1.02420
O	-0.89605	-1.35276	0.62263
H	-0.16609	-1.51231	-2.03807
O	0.01031	-2.43279	-1.78145
H	-0.24250	-2.36146	-0.83636
C	-1.01549	-1.61825	1.99490
H	-1.95991	-2.14285	2.24301
H	-0.98170	-0.68374	2.57144
C	0.45997	1.00013	-0.69755
H	0.23719	1.79996	0.02032
H	1.17051	0.30908	-0.21479
H	-0.18110	-2.26750	2.30144
C	1.06441	1.56693	-1.97895
H	1.99447	2.10886	-1.75876
H	1.29806	0.76960	-2.69500
H	0.36473	2.26063	-2.46024

Intb2

G = -499.1148689 a.u.

C	-1.79481	0.01979	-0.10638
O	-1.86051	0.79678	-1.09982
C	-3.06978	-0.30128	0.68408

```
H    -2.88798  -1.03894   1.47179
H    -3.81843  -0.69257  -0.01037
H    -3.44615   0.62467   1.13355
O    -0.80648   0.39173   0.94917
O    -1.28186  -1.47358  -0.50477
H    -0.13990  -1.39668   2.08062
O    -0.05892  -2.33062   1.83023
H    -0.46138  -2.27103   0.93321
C    -0.83471  -1.62788  -1.82650
H    -0.92538  -0.66168  -2.34390
H     0.23363  -1.91792  -1.82898
C    -1.64757  -2.69618  -2.56896
H    -1.26531  -2.84273  -3.59045
H    -1.60292  -3.65830  -2.04329
H    -2.69917  -2.39319  -2.63256
C     0.37818   0.95866   0.43075
H     0.14983   1.75084  -0.29333
H     0.93576   1.37622   1.27862
H     1.00776   0.20153  -0.06475
```

TSb2

```
G = -499.1138356 a.u.
C    -1.85664   0.29893  -0.02215
O    -1.82927   0.94210  -1.07603
C    -3.13726  -0.17821   0.63339
H    -2.93705  -0.96683   1.36047
H    -3.80468  -0.55976  -0.14022
H    -3.61668   0.67356   1.13759
O    -0.89719   0.53355   0.97868
O    -1.24703  -1.59292  -0.48317
H     0.01659  -1.62043   2.09846
O     0.11454  -2.44220   1.60142
H    -0.38192  -2.21220   0.75044
C    -0.84439  -1.72688  -1.79562
H    -0.98156  -0.76843  -2.33777
H     0.24152  -1.97243  -1.87281
C    -1.62641  -2.82337  -2.54818
H    -1.28554  -2.91907  -3.59184
H    -1.50107  -3.79358  -2.05061
H    -2.69735  -2.58413  -2.55261
C     0.35687   0.98858   0.48900
H     0.24183   1.89215  -0.12050
H     0.97197   1.20186   1.36898
H     0.83323   0.20555  -0.11275
```

TSc1

```
G = -499.1102010 a.u.
C    -1.89175   0.38964   0.26604
O    -1.76246   0.88275   1.39546
C    -3.11967  -0.40172  -0.14948
H    -2.93872  -0.95168  -1.07426
H    -3.37155  -1.10256   0.64744
H    -3.95678   0.29710  -0.29444
O    -1.36384   1.02528  -0.85666
C    -0.18041   1.78379  -0.61668
H     0.49004   1.19590   0.01874
```

```
H    -0.43343   2.71090  -0.08226
C     0.46962   2.07310  -1.96241
H     1.36351   2.69583  -1.82463
H     0.77071   1.13421  -2.43705
H    -0.22174   2.60548  -2.62759
O    -0.65597  -1.21607   0.23544
O     1.31376  -1.55128  -1.36225
H     0.54083  -1.38789  -0.69280
H    -0.40409  -1.21101   1.16795
C     0.90518  -2.53909  -2.26542
H     0.00742  -2.24746  -2.84162
H     1.71600  -2.72430  -2.98744
H     0.67321  -3.50193  -1.77223
```

Intc1

```
G = -499.1161756 a.u.
C    -1.56645   0.01738   0.14841
O    -1.63397   1.08916   0.84483
C    -2.88283  -0.62263  -0.32908
H    -2.70946  -1.55185  -0.88351
H    -3.50304  -0.83462   0.54689
H    -3.40535   0.08967  -0.97620
O    -0.75806   0.09854  -1.10514
C     0.40904   0.88454  -0.99090
H     1.20324   0.32315  -0.46803
H     0.18760   1.78084  -0.39594
C     0.88226   1.26376  -2.39210
H     1.80301   1.86167  -2.34255
H     1.08713   0.36964  -2.99343
H     0.11418   1.85022  -2.91029
O    -0.85932  -1.09845   0.95088
O     0.97251  -2.89382   0.00238
H     0.32940  -2.23347   0.36626
H    -0.62426  -0.60439   1.74906
C     0.57458  -3.19169  -1.32038
H     0.25697  -2.29064  -1.86221
H     1.42976  -3.63992  -1.84447
H    -0.25627  -3.91927  -1.35154
```

Intc2

```
G = -499.1153200 a.u.
C    -1.36314  -0.08706  -0.12478
O    -1.28135   0.93092  -0.89120
C    -2.75192  -0.54234   0.35027
H    -2.69847  -1.44153   0.97318
H    -3.37617  -0.74594  -0.52466
H    -3.19902   0.27184   0.93028
O    -0.51802   0.03883   1.08341
O    -0.82880  -1.42146  -0.78869
O    -0.43625  -3.58375   0.83685
H    -0.61022  -2.80510   0.24740
H    -0.04613   0.86038   0.88565
C     0.28264  -1.23156  -1.63544
H     0.23560  -0.21373  -2.04617
H     1.22750  -1.32457  -1.06678
C     0.25896  -2.26840  -2.75885
```

```
H     1.13242  -2.14916  -3.41632
H     0.26995  -3.28732  -2.35392
H    -0.64910  -2.15191  -3.36179
C     0.40026  -3.15439   1.89488
H     0.19179  -3.77323   2.77953
H     1.47061  -3.27754   1.64807
H     0.22686  -2.10036   2.14414
```

TSc2

```
G = -499.1094938 a.u.
C    -1.42885   0.06785   0.10022
O    -0.97817   1.03466  -0.53983
C    -2.82662  -0.48380  -0.13769
H    -2.95224  -1.46071   0.33328
H    -2.99585  -0.57316  -1.21209
H    -3.55865   0.22119   0.28138
O    -1.12533  -0.04281   1.46971
O    -0.47428  -1.51223  -0.47066
O     0.94315  -2.69056   1.39113
H     0.40306  -2.21530   0.67686
H    -0.25011   0.36309   1.55505
C     0.26047  -1.31017  -1.63225
H     0.31599  -0.22751  -1.85548
H     1.30510  -1.66108  -1.50048
C    -0.33766  -2.03947  -2.85107
H     0.27092  -1.87629  -3.75464
H    -0.39647  -3.11908  -2.66216
H    -1.35344  -1.67683  -3.05156
C     0.03828  -3.22911   2.32223
H    -0.55291  -4.06554   1.90435
H     0.60762  -3.62297   3.17719
H    -0.67029  -2.47355   2.69642
```