Supporting information

Ammonia borane enabled upgrading of biomass derivatives at room temperature

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General information

All air-sensitive operations were conducted in an inert atmosphere of nitrogen using a Young Schlenk tube in a glovebox. Unless noted otherwise, all chemicals were purchased from commercial suppliers and used without further purification. NMR spectra for quantification and qualitative research were recorded on a Bruker Avance 400 MHz instrument. *In situ* ^{13}C NMR and ^{1}H-^{13}C HSQC studies were carried out on a Bruker Avance III 800 MHz spectrometer equipped with an 18.7 T magnet (Oxford instruments) and a TCI cryoprobe. *In situ* ^{11}B NMR studies were recorded on a Bruker Avance 400 MHz instrument equipped with a BBFO SmartProbe. MS data were acquired using GC-MS (Agilent 6890N-5973 system) with EI detection. The reactions were quantified by NMR using DMF as an internal standard in aquoues solvent, and mesitylene as internal standard in methanol solvent.

Synthesis of deuterated ammonia borane[S1,S2]: NH_3BD_3 (AB(D)) was synthesized as follows: 260 mg $NaBD_3$, 660 mg $(NH_4)_2CO_3$, and 10 mL dry THF were added into a Young

Schlenk bottle. Then, the mixture was heated under stirring at 40 °C for 24 h. The crude AB(D) was obtained by filtering the resulting mixture upon dilution with an extra 20 mL dry THF, and then evaporating the filtrate. Finally, the prepared crude AB(D) was purified by sublimation at 60 °C under vacuum. The ND_3BH_3 isotopologue was prepared by dissolving NH_3BH_3 (AB) in D_2O followed by the removal of the solvent at room temperature under vacuum. This procedure was repeated 3 times. ND_3BD_3 (A(D)B(D)) was prepared from AB(D) using the same method.

Preparation of ammonia methanol solvent: Pure ammonia was bubbled through 20 mL methanol in an ice-bath for 4 h, resulting in the solvent containing 16 wt.% ammonia content, as determined gravimetrically. Methanol with different content of ammonia was prepared by diluting the above solution with methanol.

Production of γ-valerolactone (GVL): The reactions were carried out in 15 mL ACE pressure tubes. In a typical reaction procedure, 1 mmol EL, 2 mL deionized water, and 1 mmol AB were successively added into the ACE tube, which was regularly stirred under room temperature for a specific time. The produced GVL could be isolated by extracting three times with ethyl acetate. For the production of GVL from EL in methanol, 1 mmol EL, 2 mL methanol, and 1 mmol AB were successively added into the ACE tube, which was heated with stirring and incubated at 140 °C for 8 h. For the production of GVL from LA, 1 mmol LA, 2 mL methanol, and 1 mmol AB were successively added into the ACE tube, which was heated under stirring and incubated at 140 °C for 8 h.

Production of alcohols: The reactions employing various carbonyl-containing compounds as substrates were conducted in ACE tubes. In a typical reaction procedure, 1 mmol substrate, 2 mL methanol, and 1 mmol AB were succesively added into the tube, which was stirred at room temperature for 30 min.

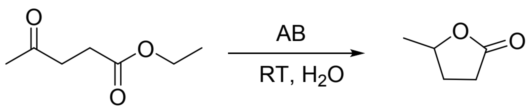
Production of 4-aminopentanoic acid (APA): In a typical reaction procedure, 1 mmol LA, 4 mL methanol (16 wt.% ammonia) and 1 mmol AB were successively added into 15 mL ACE tube and the mixture stirred at room temperature for 2 h.

Production of 5-methyl pyrrolidinone (MPD): In a typical reaction procedure, 1 mmol LA, 4 mL methanol (16 wt.% ammonia), 1 mmol AB were successively added into 15 mL stainless steel autoclave, which was placed in a preheated oil bath with stirring at 120 °C for a specified time.

Production of GVL from carbohydrates: The reactions using biomass-derived sugars as feedstocks were conducted by two-steps in one-pot. 1 mmol fructose, sucrose, or inulin, 100 mg Amberlyst-15, and 5 mL methanol were loaded into a 25 mL stainless steel autoclave. The autoclave was placed into a preheated oil bath (160 °C) with stirring for 5 h. After the autoclave was cooled down to room temperature, 1 mmol AB and 5 mL water were directly added into the resulting crude mixture (without previous filtration) and the reaction mixture continued to stir for 8 h at room temperature. For glucose, cellobiose, or mannose as the substrates, Lewis acid catalyst Sn-beta(125) was added into the system to promote the isomerization of carbohydrate into fructose.

In situ ^{13}C NMR: Selected reactions were followed on an 800 MHz NMR instrument. In a typical reaction procedure, 0.5 mmol EL, 1 mL water, and 0.5 mmol ammonia borane were mixed, 0.6 mL were immediately transferred into a 5 mm NMR tube with a pierced cap for releasing gas, and put into the NMR spectrometer at room temperature for recording *in situ* NMR spectra of the ongoing reaction for up to 4 h. All NMR spectra were processed with ample zero filling in Bruker Topspin 3.6 software. The designed in situ ^{13}C NMR experiments were as follow:

1.



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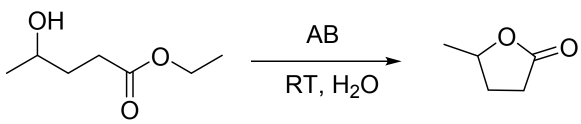

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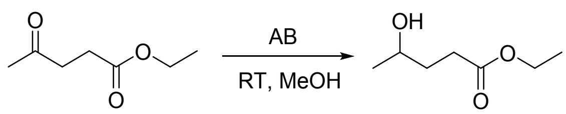

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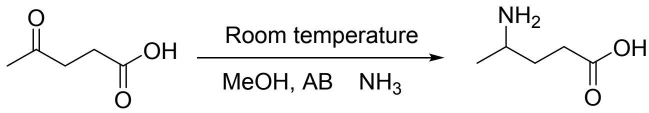

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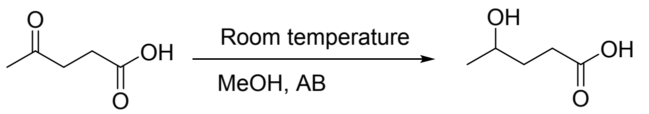
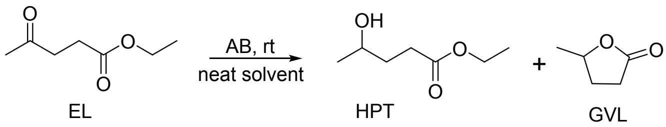


***In situ* ^{11}B NMR**: In a typical reaction procedure, 0.5 mmol EL, 1 mL D_2O, and 0.5 mmol AB were mixed, 0.6 mL of this mixture were transferred into an NMR tube with a pierced cap for releasing gas and were immediately placed into the NMR spectrometer equilibrated to 25 ºC for recording in situ NMR spectra for 2 h. All NMR spectra were processed with ample zero filling in Bruker Topspin 3.6 software.

Computational Details: All structure optimizations and energy calculations were carried out at B3LYP level theory applying density functional theory (DFT) in the Gaussian 09 program package. The electron basis set 6-31G(d,p) was utilized for all calculations.[S3,S4]

Table S1. Solvent screening for the conversion of EL[a]



Entry	Solvent	C(EL,%)	Y(GVL,%)	Y(HPT,%)
1	THF	14	0	14
2	DMSO	100	0	>99
3	CH_3CN	90	0	90
4	Heptane	100	0	>99
5	MeOH	100	6	94
6[b]	MeOH	100	0	>99
7	H_2O	100	95	0

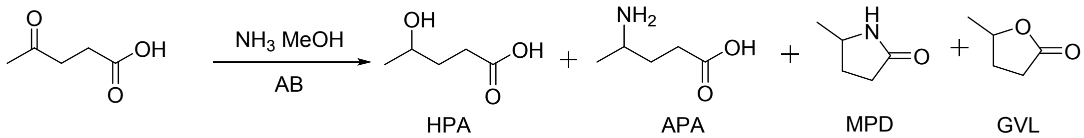
[a] Reaction conditions: 1 mmol EL, 1 mmol AB, 2 mL solvent, room temperature and 4 h. [b] Reaction time was 15 min. Quantified by ^{1}H NMR spectroscopy with DMF as an internal standard.

Table S2. Production of GVL using methanol as solvent [a]

Entry	T (ºC)	t (h)	Y(GVL,%)	Y(HPA,%)	C(EL,%)
1	100	8	72	27	99
2	120	8	74	23	96
3	120	12	85	11	96
4	140	2	67	30	97
5	140	5	80	18	98
6	140	8	93	5	98

[a] Reaction conditions: 1 mmol EL, 1 mmol AB, 2.0 mL MeOH, quantified by ^{1}H NMR spectroscopy with mesitylene as internal standard.

Table S3. Reductive amination of LA introducing extra ammonia source [a]



Entry	Ammonia source	T(ºC)	t(h)	Y(%)				C(LA,%)
				GVL	MPD	APA	HPA	
1[b]	$(NH_4)_2CO_3$	140	8	36	50	8	5	>99
2[b]	CH_3COONH_4	140	8	25	70	3	2	>99
3[b]	NH_4Cl	140	8	55	25	5	12	>99
4[c]	NH_3•H_2O	140	8	0	17	6	77	>99
5[d]	NH_3	140	8	18	74	4	2	>99
6[d]	NH_3	120	8	6	83	9	2	>99
7	NH_3	120	8	1	84	11	1	>99
8	NH_3	120	2	1	79	17	3	>99
9	NH_3	120	4	1	82	13	1	>99
10	NH_3	120	12	1	92	6	0	>99
11	NH_3	120	20	1	90	8	0	>99
12	NH_3	100	2	1	17	66	12	>99
13	NH_3	RT	2	0	0	82	14	99

[a] Reaction conditions: 1 mmol LA, 1 mmol AB, 4 mL methanol (containing 16 wt.% ammonia, 26 mmol ammonia. [b] 13 mmol ammonia from the corresponding salt. [c] 13 mmol ammonia from NH_3•H_2O in 4 mL water. [d] 4 mL methanol containing 13 mmol ammonia.

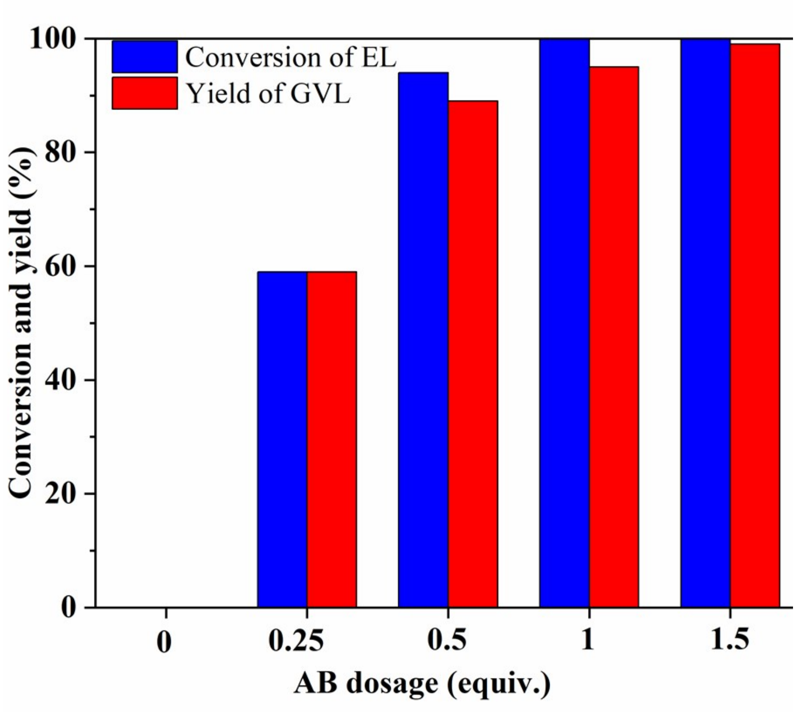


Figure S1. Effect of AB dosage on GVL production from EL.

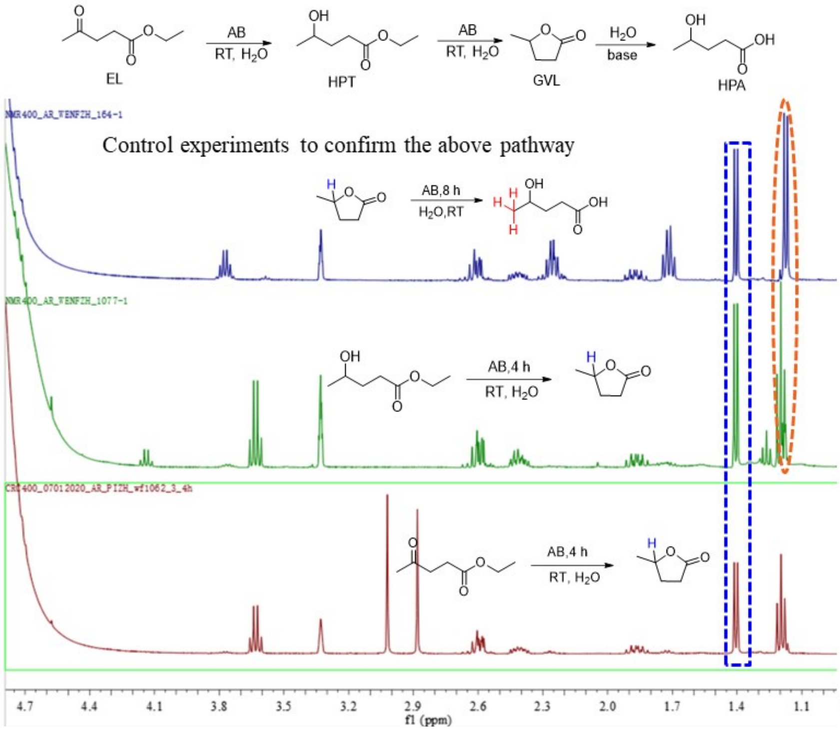


Figure S2. Control experiments for confirming conversion of EL into GVL in water.

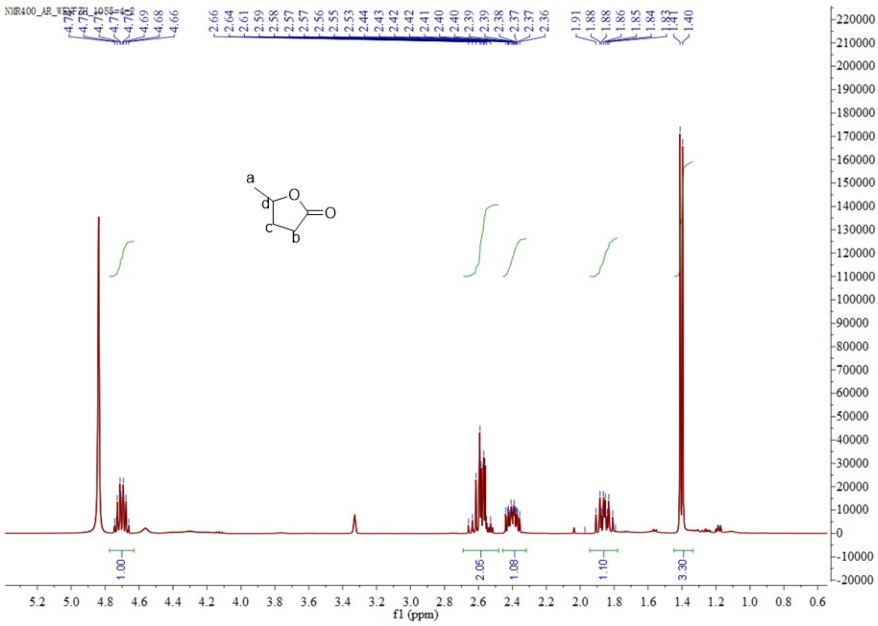


Figure S3. [1]H NMR spectra of GVL isolated with ethyl acetate extraction.

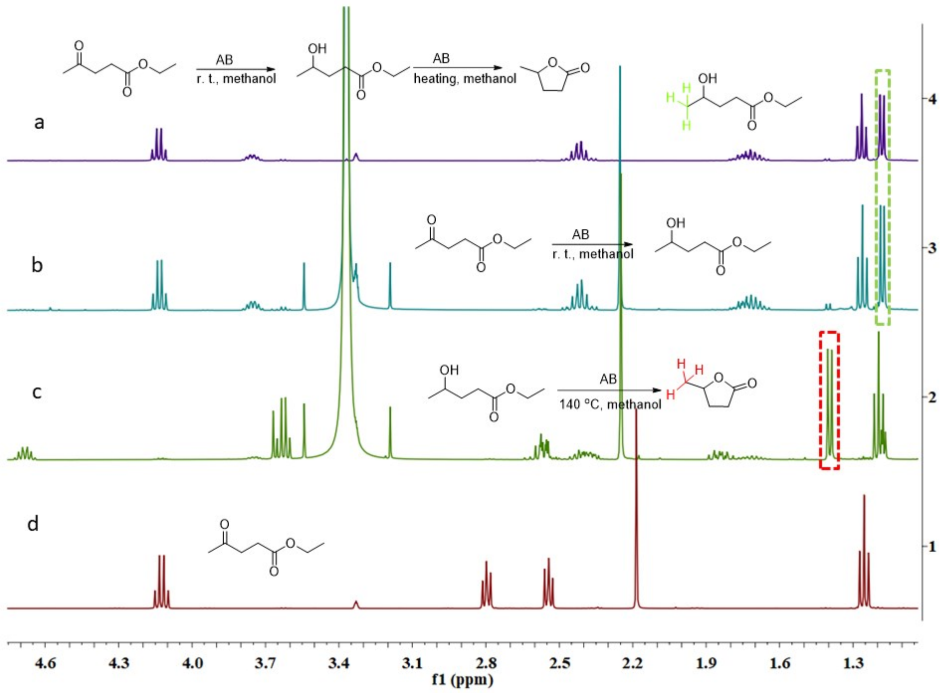


Figure S4. [1]H NMR spectra of EL conversion to HPT and GVL in methanol. a) pure HPT; b) HPT formed from EL at room temparature; c) post-reaction of b) at 140 ºC, showing near-quantitative conversion to GVL; d) pure EL.

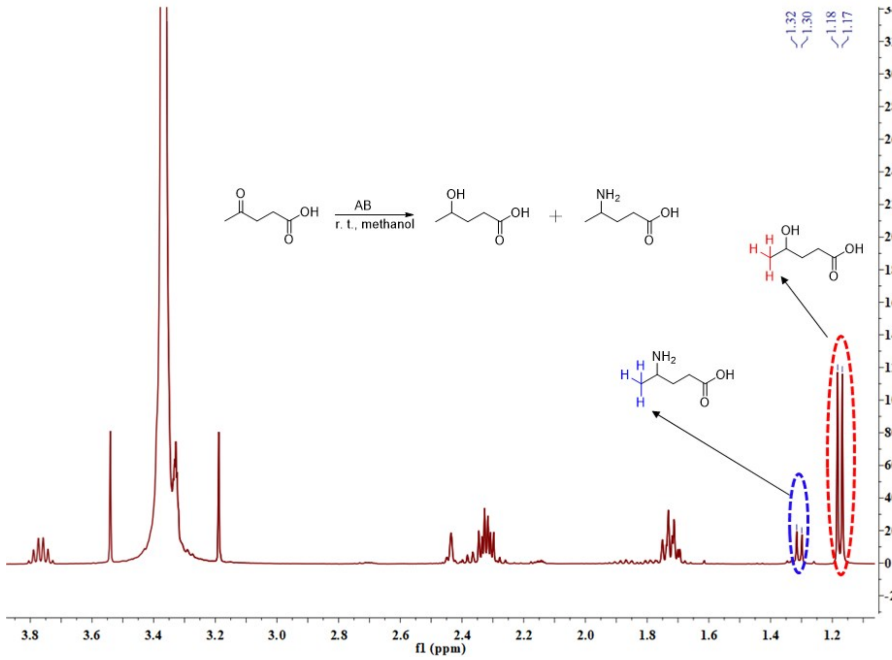


Figure S5. The ^{1}H NMR spectra of the reaction mixture for the conversion of LA in neat methanol (reaction conditions: 1 mmol LA, 1 mmol AB, 2 mL MeOH, rt, and 0.5 h).

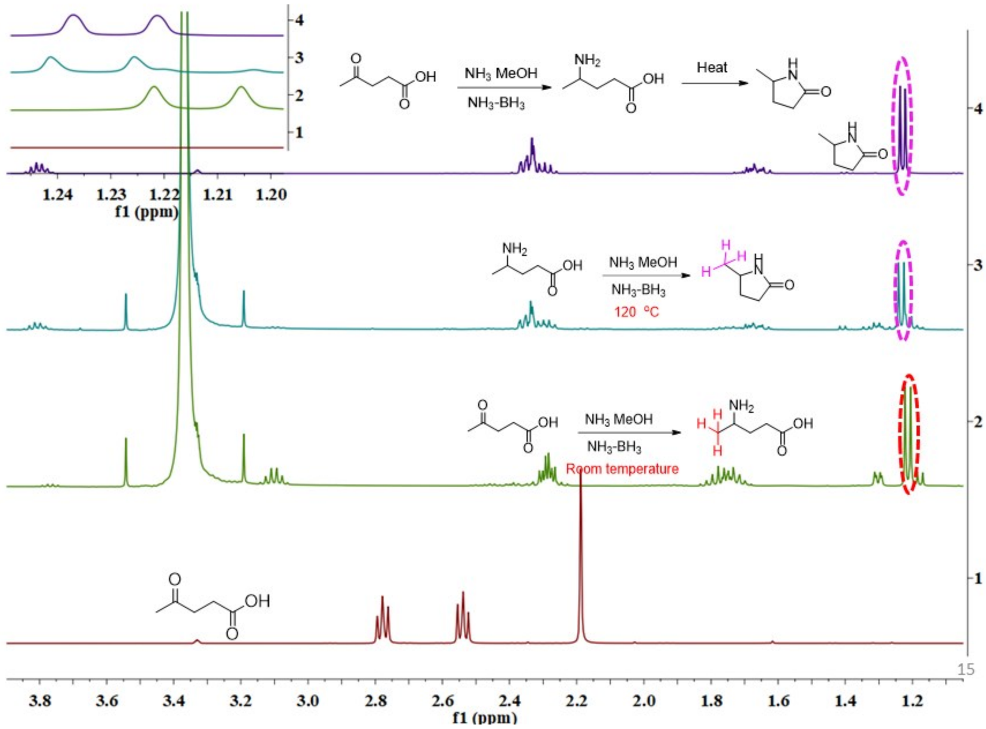


Figure S6. Control experiments for the conversion of LA into MPD and APA.

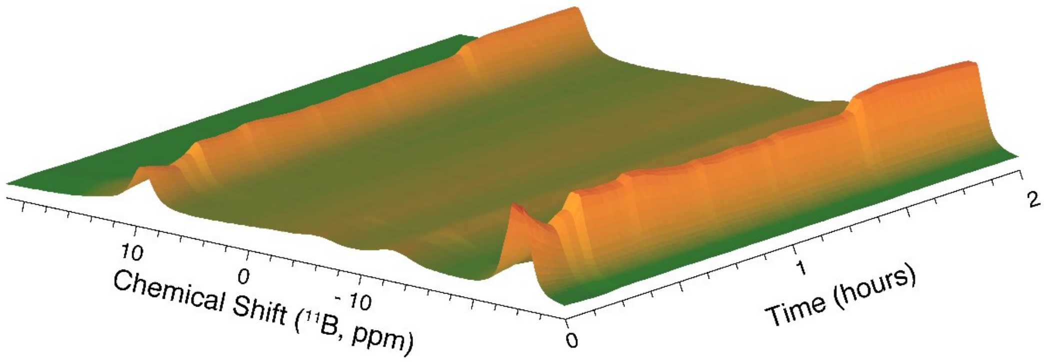


Figure S7. The *in situ* ^{11}B NMR of GVL production from EL in water (0.5 mmol EL, 1 mL water, 0.5 mmol ammonia borane, and rt).

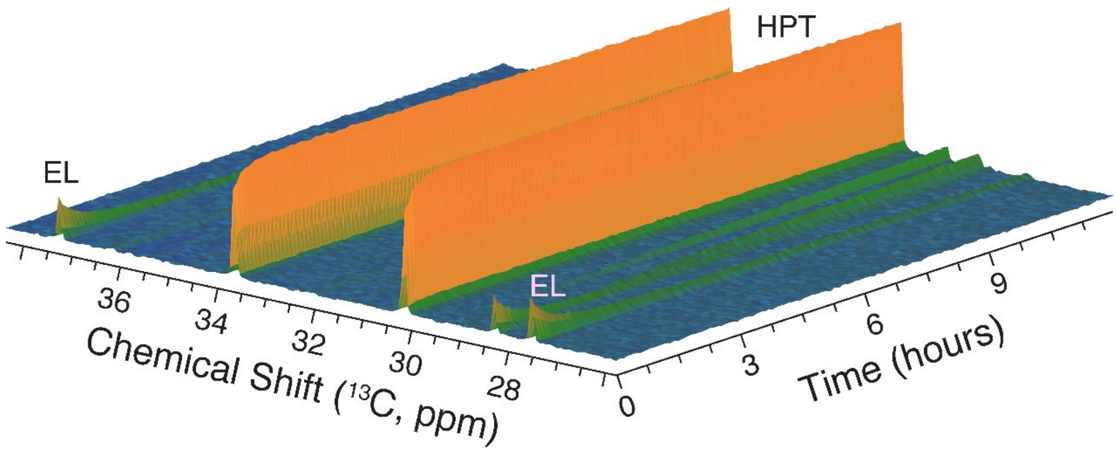


Figure S8. The *in situ* ^{13}C NMR of GVL production from EL in methanol (0.5 mmol EL, 1 mL water, 0.5 mmol ammonia borane, and rt).

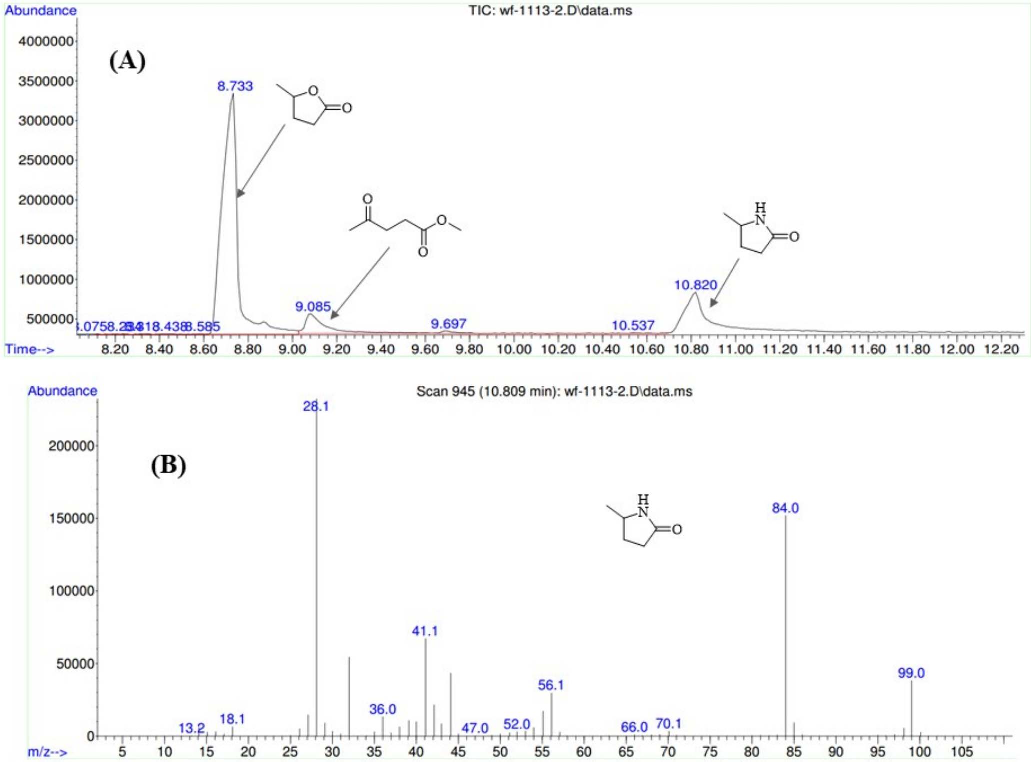
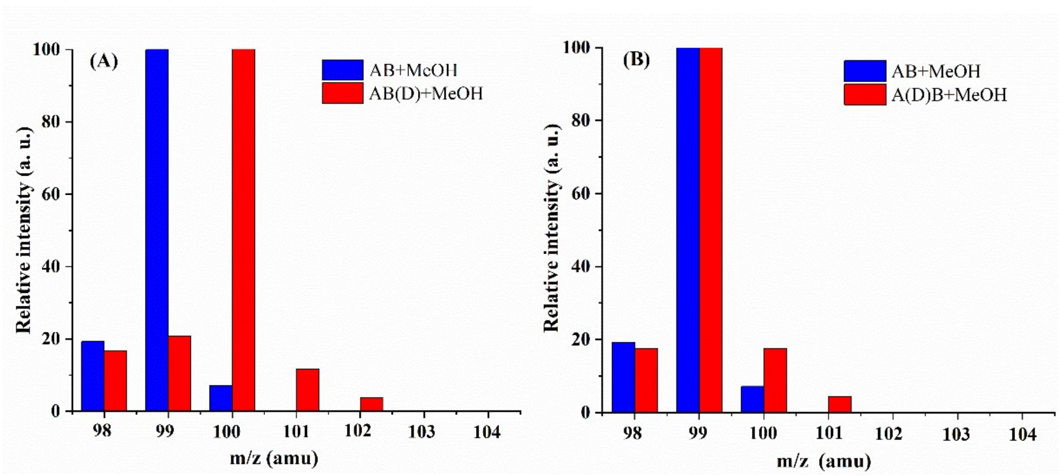


Figure S9. (a) GC-MS spectrum of the reaction mixture achieved from the conversion of LA in the absence of ammonia additive (reaction conditions: 1 mmol LA, 1 mmol AB, 2 mL methanol, 120 °C and 2 h). b) MS spectrum of MPD obtained from the above mixture.



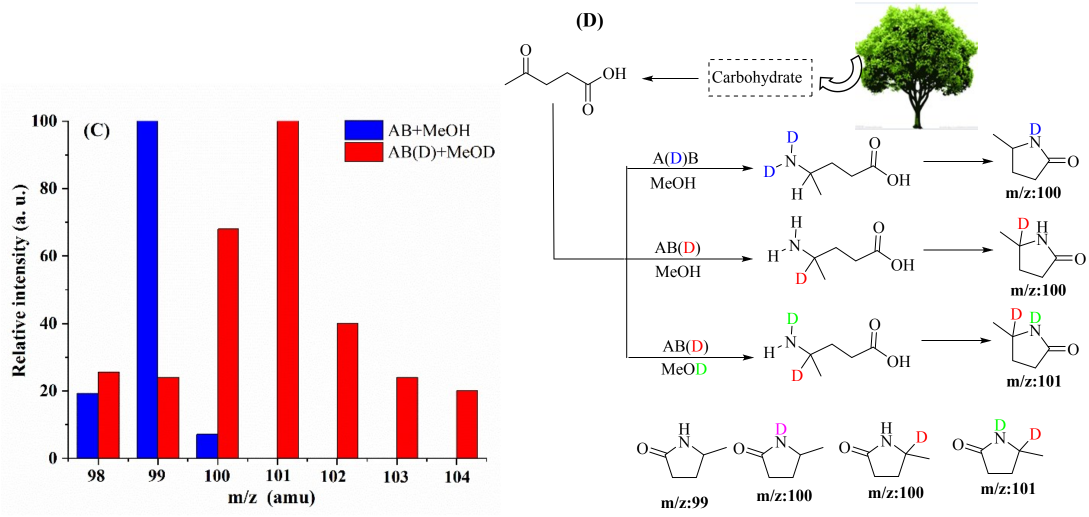


Figure S10. Mass fragmentation analyses (all intensities scaled to 100%) of MPD formed from LA by using (A) NH_3BD_3 (AB(D)) and (B) ND_3BH_3 (A(D)B) in normal methanol, and (C) (A(D)B) in deuterated methanol.

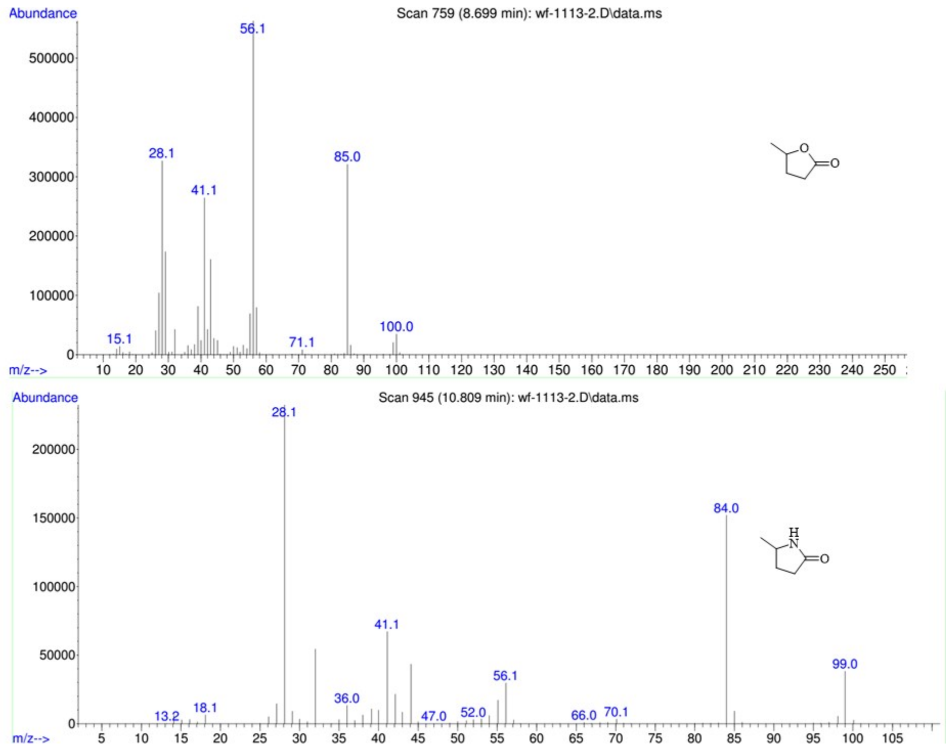


Figure S11. Selected MS spectra of GVL and MPD obtained after reaction of LA with AB in methanol.

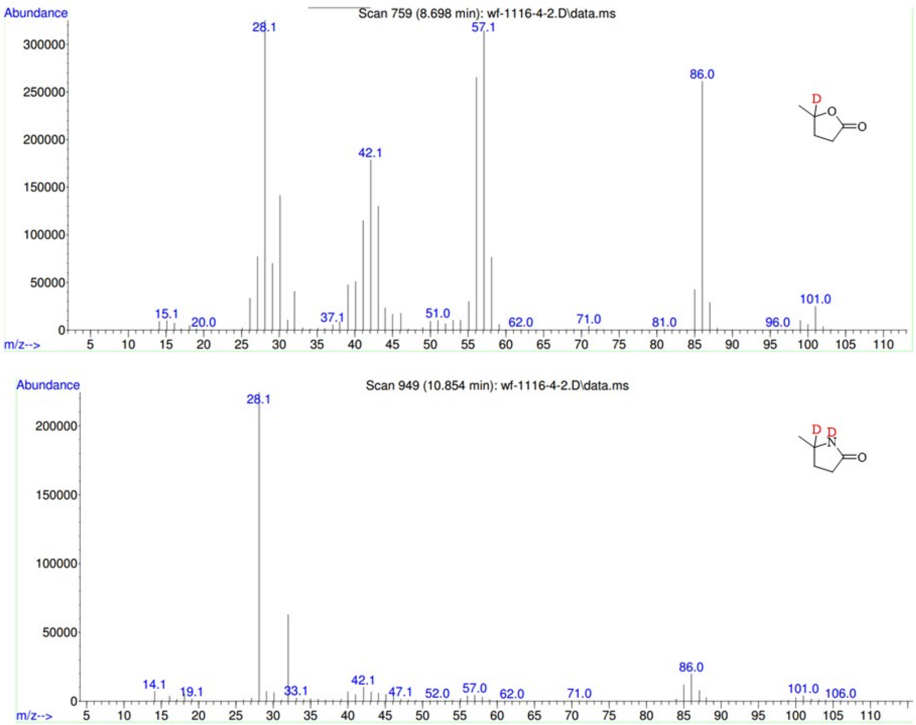


Figure S12. Selected MS spectra of GVL and MPD obtained from LA with AB(D) in methanol.

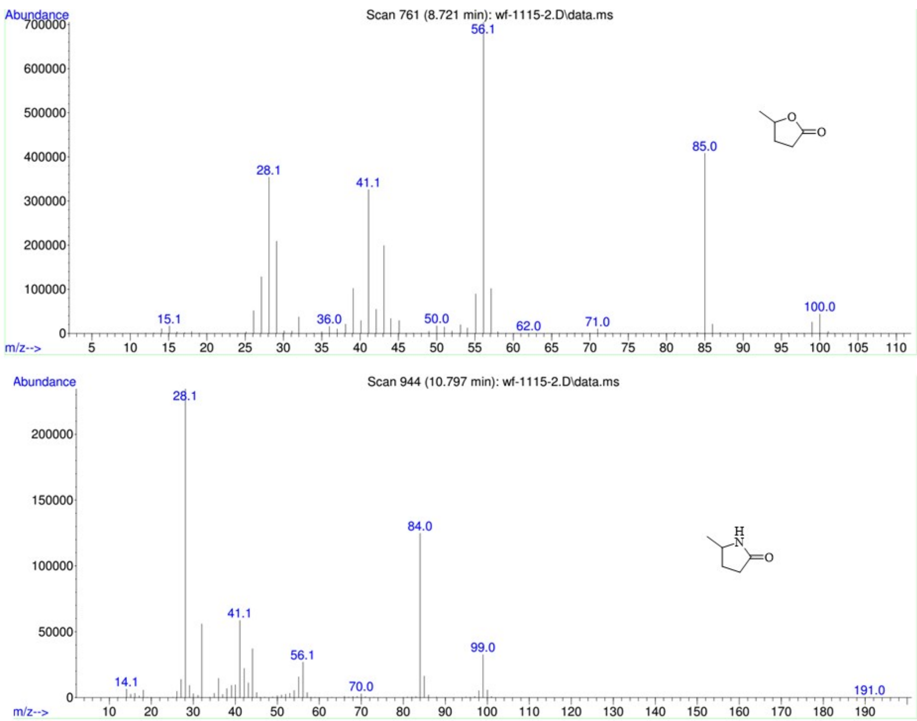


Figure S13. Selected MS spectra of GVL and MPD obtained from LA with A(D)B in methanol.

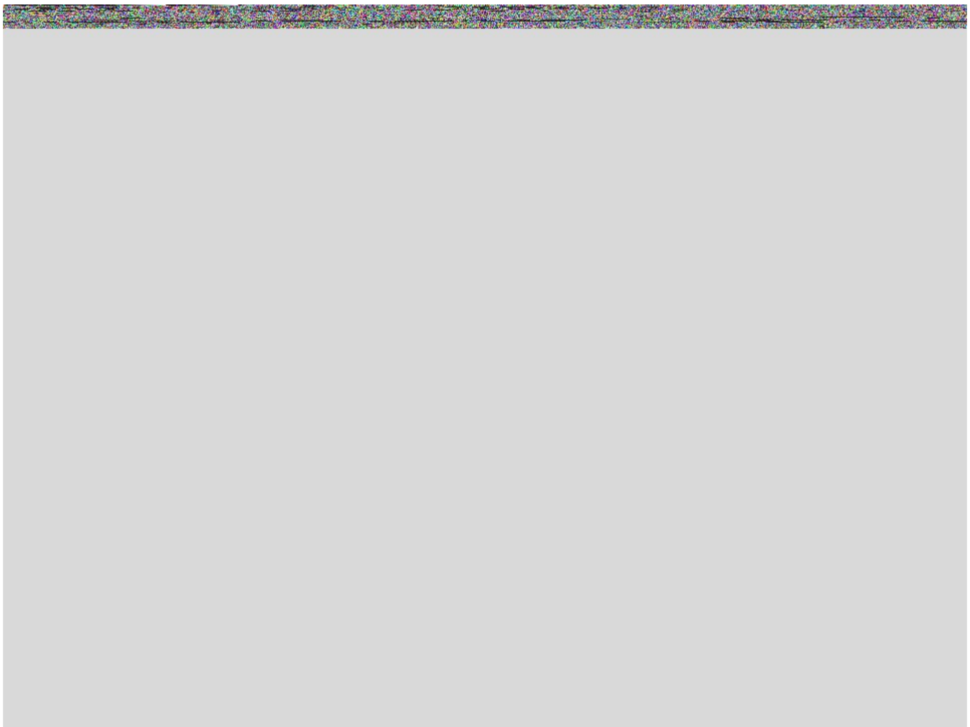


Figure S14. Selected MS spectra of GVL and MPD obtained from LA with AB in deuterated methanol.

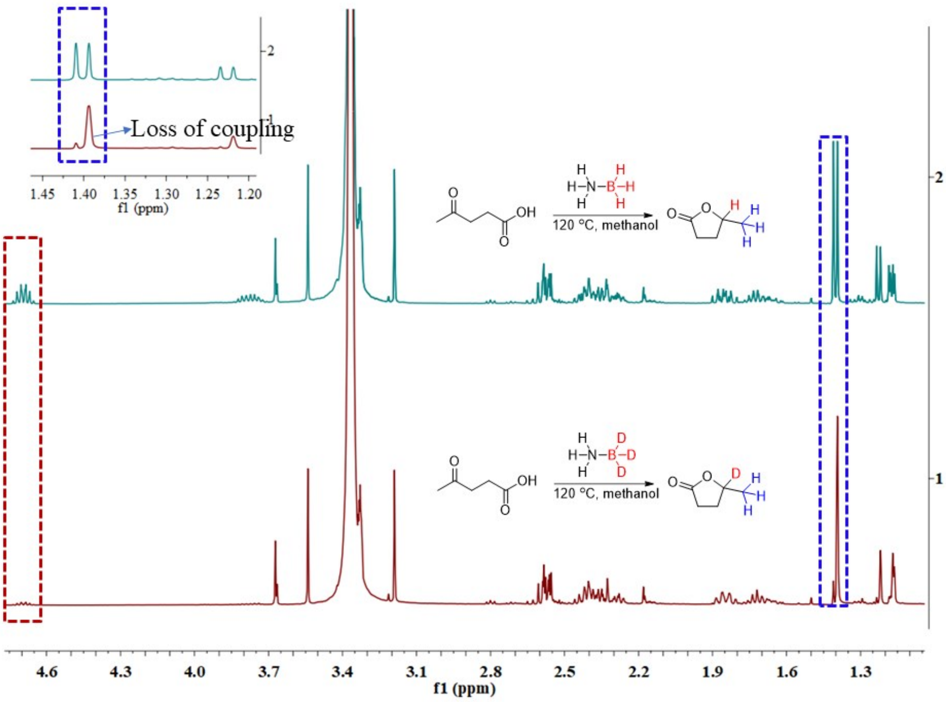
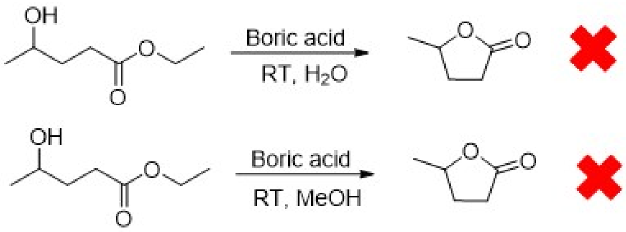


Figure S15. AB(D) as hydrogen donor for production of GVL

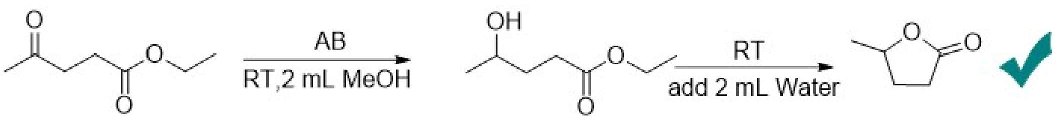
$$NH_3\text{-}BH_3 + H_2O \xrightarrow{\text{fast}} BH_3 + NH_4^+ + OH^- \xrightarrow[H_2O]{\text{fast}} H_3BO_3 + 3H_2 + NH_4^+ + OH^-$$

$$NH_3BH_3 + MeOH \longrightarrow [MeOHBH_3NH_3] \longrightarrow (MeO)_3B + H_2$$

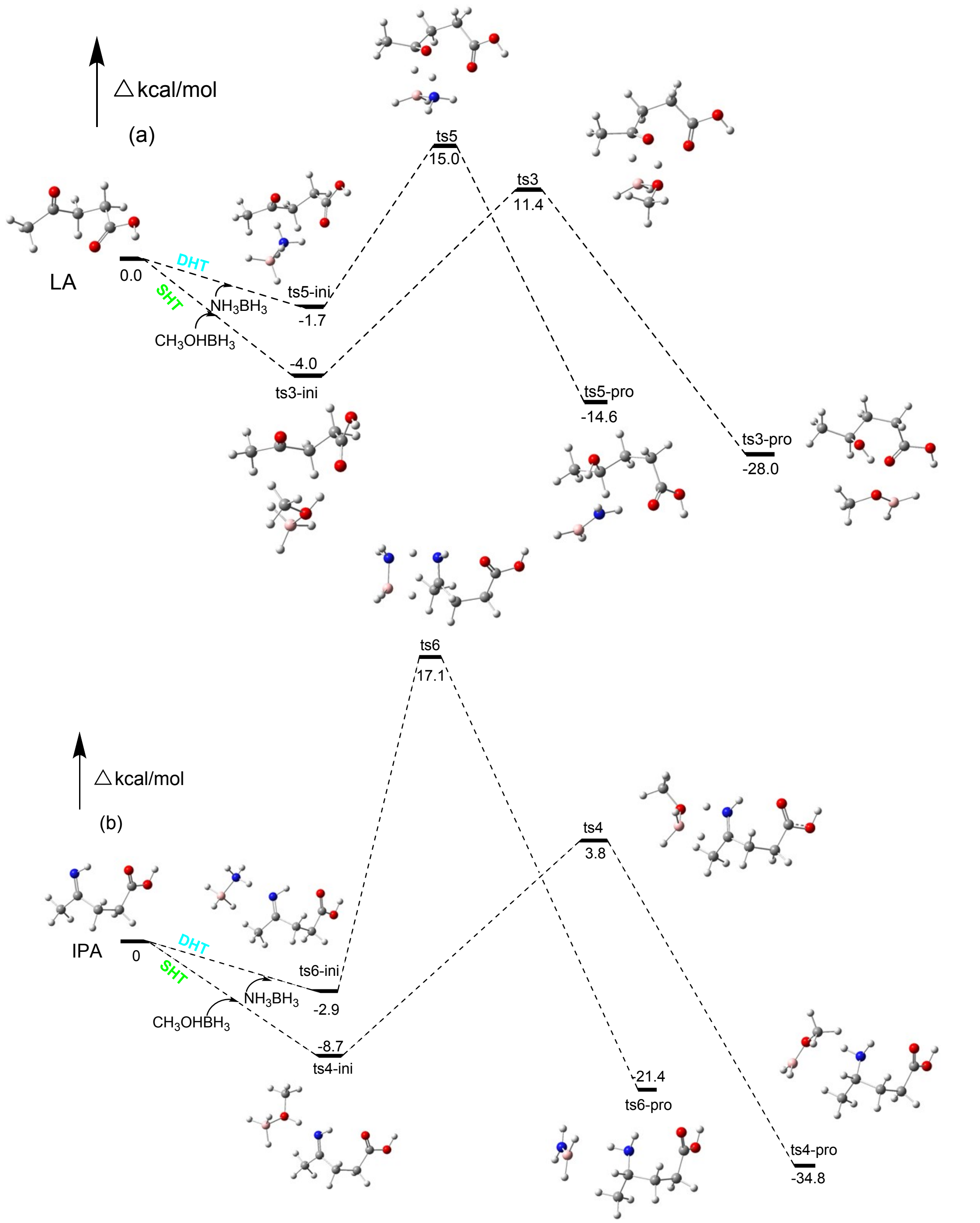
Scheme S1. AB hydrolysis and alcoholysis reactions in water and methanol, respectively.



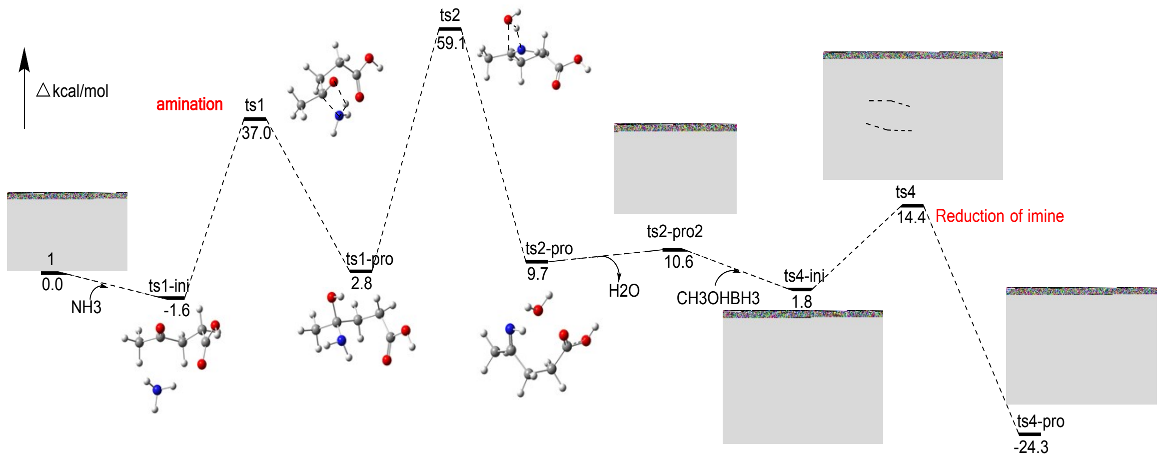
Scheme S2. Reaction of HPT with boric acid in water or in methanol at room temperature did not result in GVL formation.



Scheme S3. Two-step reaction at room temperature of EL with AB in methanol followed by HPT hydrolysis in water enabled GVL formation in 80% yield.

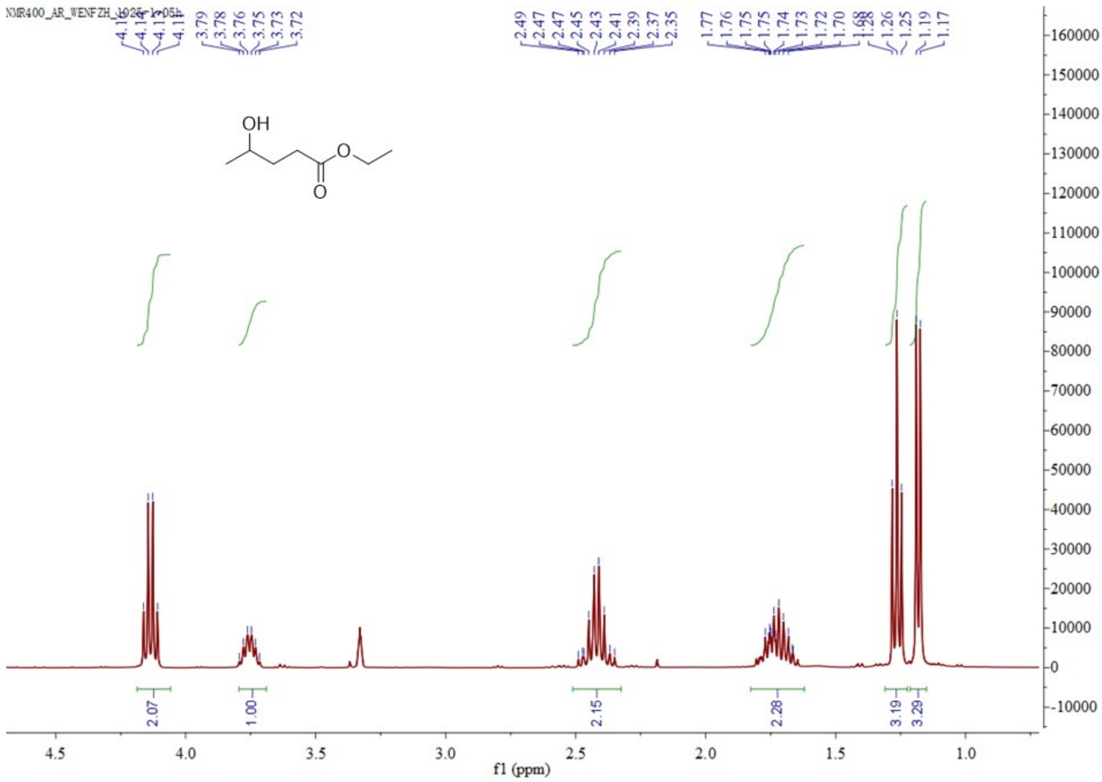


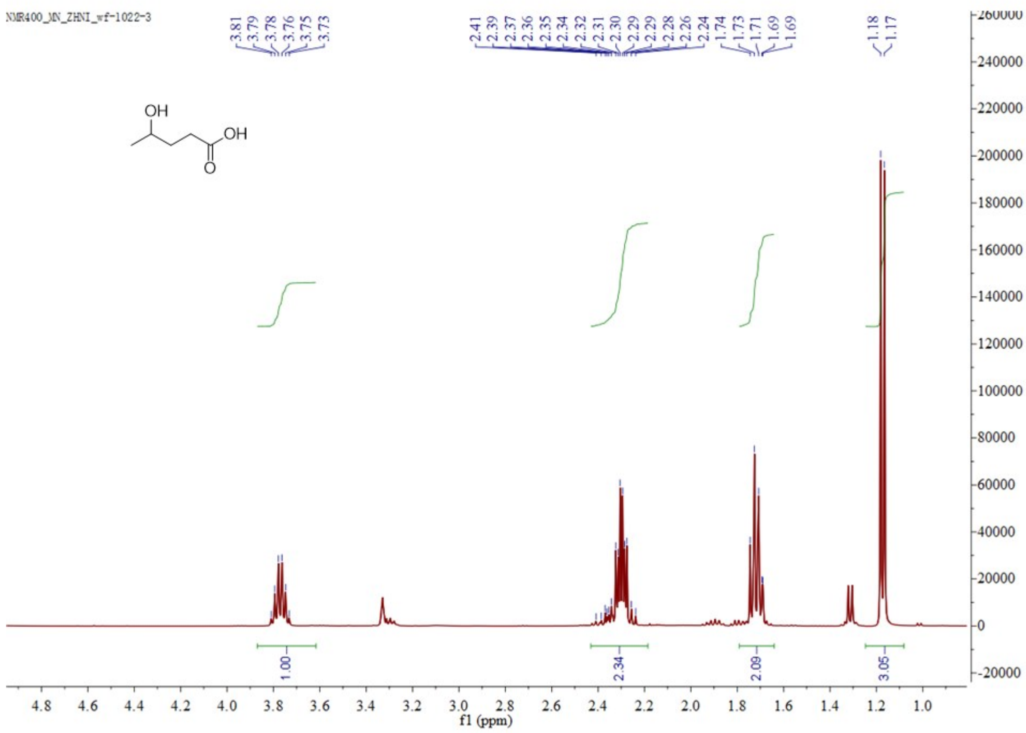
Scheme S4. a) The reaction energy profiles (in kcal/mol) for the synthesis of HPA from LA with different AB forms as the reductant. b) The reaction energy profiles (in kcal/mol) for the synthesis of APA from 4-iminopentanoic acid with different AB forms as the reductant.



Scheme S5. The reaction energy profiles (in kcal/mol) for the synthesis of APA from ammonia and LA.

[1]H NMR spectra





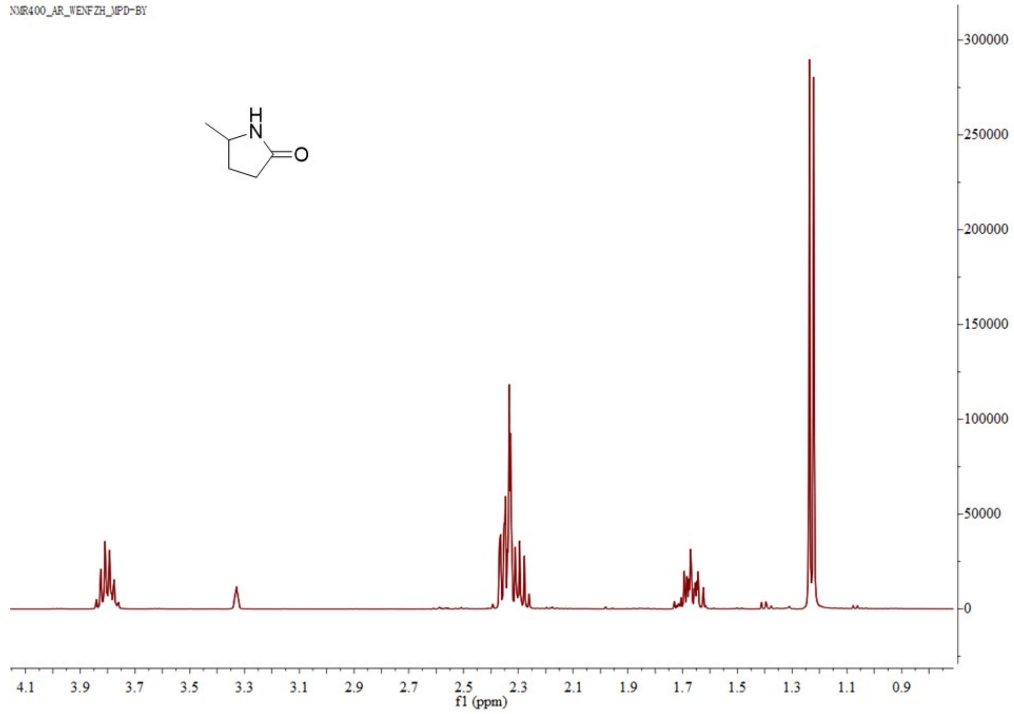

NMR400_AR_WENFZH_MPD-BY
H
N
O
300000
250000
200000
150000
100000
50000
0
4.1 3.9 3.7 3.5 3.3 3.1 2.9 2.7 2.5 2.3 2.1 1.9 1.7 1.5 1.3 1.1 0.9
f1 (ppm)

Table S4. Cartesian coordinates (in Å) of the calculated structures.

Levulinic acid (1a)

atom	x (Å)	y (Å)	z (Å)
C	1.18896	-0.71152	0.27469
O	0.62199	-0.49894	1.32617
C	2.68883	-0.80953	0.16273
H	3.0298	-0.047	-0.54183
H	3.14086	-0.64039	1.13998
H	2.97679	-1.79588	-0.21444
C	0.39352	-0.88428	-1.00872
H	0.55161	0.02947	-1.59362
H	0.80263	-1.71683	-1.58996
C	-1.08395	-1.09542	-0.71736
H	-1.24121	-1.93664	-0.03956
H	-1.63306	-1.30679	-1.64166
C	-1.71711	0.12951	-0.10653
O	-1.38608	1.27306	-0.31906

MeOH●BH_3 (2a)

atom	x (Å)	y (Å)	z (Å)
C	2.71092	-1.57201	-0.68734
H	3.37978	-2.15269	-0.05783
H	3.19004	-0.63963	-0.98148
H	2.41889	-2.1505	-1.56483
O	1.53937	-1.30779	0.08307
H	0.99216	-0.88784	-0.41107
B	1.7457	-0.4287	1.39259
H	2.92456	-0.11021	1.3904
H	1.39468	-1.10447	2.33587
H	1.11911	0.4407	1.32032

ts1 (3a)

atom	x (Å)	y (Å)	z (Å)
C	2.71092	-1.57201	-0.68734
H	3.37978	-2.15269	-0.05783
H	3.19004	-0.63963	-0.98148
H	2.41889	-2.1505	-1.56483
O	1.53937	-1.30779	0.08307
H	0.99216	-0.88784	-0.41107
B	1.7457	-0.4287	1.39259
H	2.92456	-0.11021	1.3904
H	1.39468	-1.10447	2.33587
H	1.11911	0.4407	1.32032

ts1-int(4a)

atom	x (Å)	y (Å)	z (Å)
C	-2.64472	1.4773	-0.11723
O	-2.204	2.46001	-0.76809
C	-4.18472	1.4773	-0.11723
H	-4.54139	0.4685	-0.11528
H	-4.54139	1.9834	0.75544
H	-4.54139	1.98001	-0.99186
C	-1.87736	0.1421	-0.11464
H	-2.13697	-0.41677	0.76009
H	-2.13696	-0.42016	-0.98721
C	-0.36274	0.42051	-0.11518
H	-0.10313	0.98277	0.75738
H	-0.10313	0.97938	-0.98992
C	0.40462	-0.91469	-0.1126
O	-0.22242	-2.00574	-0.11048
O	1.83462	-0.91469	-0.1126
H	2.15462	-1.81979	-0.11084
N	-2.27021	1.87977	1.50979

ts1-pro (5a)

atom	x (Å)	y (Å)	z (Å)
C	1.46777	-0.09439	0.05021
O	1.48085	-0.36171	1.39785
C	2.82679	-0.22693	-0.62695
H	2.79159	0.06558	-1.67799
H	3.55886	0.38367	-0.09518
H	3.1549	-1.26963	-0.56197
C	0.3721	-0.85193	-0.73214
H	0.18133	-0.36077	-1.68973
H	0.78068	-1.84601	-0.95228
C	-0.91075	-1.04302	0.07521
H	-0.61849	-1.07542	1.13337
H	-1.41256	-1.98554	-0.1548
C	-1.91248	0.06164	-0.08695
O	-1.67269	1.2052	-0.42481
O	-3.16077	-0.32634	0.20292
H	-3.72739	0.45497	0.10849
N	1.11772	1.4065	0.19512
H	0.1695	1.64133	-0.10575
H	1.79415	2.05616	-0.19633
H	1.28857	0.74121	1.39824

ts2(6a)

atom	x (Å)	y (Å)	z (Å)
C	1.40461	-0.00377	0.08548
O	1.85497	-1.47428	0.94702
C	2.68091	0.66057	-0.42254
H	2.45249	1.61795	-0.89831
H	3.36159	0.82928	0.41628
H	3.18675	0.0168	-1.1468
C	0.44582	-0.27625	-1.08509
H	0.23876	0.65645	-1.62062
H	0.9671	-0.95016	-1.77002
C	-0.87302	-0.90653	-0.65474
H	-0.72473	-1.68061	0.10304
H	-1.36182	-1.40115	-1.50236
C	-1.86556	0.10281	-0.13225
O	-1.83572	1.29435	-0.333
O	-2.85797	-0.48182	0.55935
H	-3.46137	0.2275	0.82878
N	0.63385	0.43393	1.24121
H	-0.03381	1.1563	0.98471

H	1.17887	-0.67676	1.7625
H	1.44622	-2.16917	0.41547

ts2-pro

atom	x (Å)	y (Å)	z (Å)
C	1.57314	-0.33349	-0.26726
C	2.51023	0.26687	0.74628
H	3.20386	-0.49053	1.12514
H	3.07237	1.08238	0.29161
H	1.94251	0.65799	1.59693
C	0.68934	-1.46413	0.22638
H	0.38444	-2.09139	-0.61603
H	1.24531	-2.08616	0.93445
C	-0.56225	-0.91716	0.92241
H	-0.32248	-0.13708	1.64994
H	-1.08938	-1.71252	1.46047
C	-1.53722	-0.31977	-0.06039
O	-1.45186	-0.37008	-1.26467
O	-2.58511	0.24841	0.55954
H	-3.17551	0.56852	-0.13906
N	1.51196	0.17218	-1.43449
H	0.79615	-0.31373	-1.98209

ts3

atom	x (Å)	y (Å)	z (Å)
C	1.18896	-0.71152	0.27469
O	0.74422	-1.10661	1.33222
C	2.68883	-0.80953	0.16273
H	3.0298	-0.047	-0.54183
H	3.14086	-0.64039	1.13998
H	2.97679	-1.79588	-0.21444
C	0.39352	-0.88428	-1.00872
H	0.55161	0.02947	-1.59362
H	0.80263	-1.71683	-1.58996
C	-1.08395	-1.09542	-0.71736
H	-1.24121	-1.93664	-0.03956
H	-1.63306	-1.30679	-1.64166
C	-1.71711	0.12951	-0.10653
O	-1.38608	1.27306	-0.31906
O	-2.76786	-0.17707	0.66721
H	-3.12228	0.66248	0.99782
C	1.06176	1.70078	3.15825

H	1.48181	2.67183	3.318
H	1.82291	0.95858	3.27945
H	0.27994	1.52915	3.86831
O	0.52802	1.62432	1.83379
H	0.29039	0.25732	1.83891
B	1.21273	1.67613	0.18139
H	2.17822	2.35452	0.17678
H	0.41334	2.12461	-0.56174
H	1.2843	0.51947	0.19585

ts3-pro

atom	x (Å)	y (Å)	z (Å)
C	0.45368	1.23107	-0.08317
O	0.45208	0.38526	-1.09251
C	1.45866	2.37484	-0.16686
H	1.51252	2.91297	0.78695
H	2.44597	1.97649	-0.41041
H	1.15545	3.07241	-0.95174
C	-0.9351	1.6401	0.46752
H	-0.95077	1.50619	1.55577
H	-1.08297	2.70893	0.26951
C	-2.07448	0.85741	-0.1713
H	-2.07476	0.97354	-1.25755
H	-3.04156	1.21709	0.19558
C	-1.99292	-0.61729	0.12782
O	-1.22198	-1.13783	0.89442
O	-2.91639	-1.31667	-0.55803
H	-2.79757	-2.2447	-0.30285
C	2.74077	-1.60292	-0.65817
H	3.41733	-2.199	-0.04407
H	3.24299	-0.67825	-0.96771
H	2.43334	-2.17372	-1.53566
O	1.56153	-1.3002	0.10454
H	0.9236	-0.5777	-0.59249
B	1.75246	-0.47501	1.31396
H	2.84661	0.01287	1.39647
H	1.17813	-0.87359	2.29574
H	0.94992	0.62348	0.91047

ts4

atom	x (Å)	y (Å)	z (Å)
C	-1.55641	0.25623	0.02804
C	-2.59917	-0.59696	-0.64743
H	-3.34402	-0.93193	0.08243
H	-3.09338	-0.02465	-1.43165
H	-2.14922	-1.49779	-1.0799
C	-0.67577	-0.4576	1.04286
H	-0.35245	0.24583	1.81494
H	-1.24292	-1.259	1.52591
C	0.56265	-1.05691	0.37188
H	0.3109	-1.62278	-0.53077
H	1.07664	-1.75789	1.03931
C	1.56748	0.0078	-0.00056
O	1.555	1.15162	0.38357
O	2.52891	-0.47536	-0.80465
H	3.13976	0.25673	-0.98115
N	-1.25411	1.33998	-0.56106
H	-0.2713	1.31571	-0.849
C	-3.59595	3.75908	0.08125
H	-4.27923	4.20848	0.80007
H	-4.15078	3.11417	-0.60477
H	-3.06739	4.53689	-0.47166
O	-2.62676	2.99652	0.80875
H	-1.99447	2.54202	0.08045
B	-3.16248	1.81101	1.61659
H	-4.33231	1.64729	1.37252
H	-2.80407	1.86339	2.75572
H	-2.53556	0.82625	1.07853

ts4-ini

atom	x (Å)	y (Å)	z (Å)
C	0.16723	0.61265	-0.13515
C	0.7648	1.67686	-1.01272
H	0.96123	2.59352	-0.4583
H	1.68632	1.32221	-1.47399
H	0.03164	1.88899	-1.8031
C	-0.89029	1.0204	0.85569
H	-0.85394	0.35951	1.72421
H	-0.70113	2.03862	1.18985
C	-2.2719	0.93325	0.20145
H	-2.2908	1.38549	-0.79551
H	-3.02178	1.47356	0.79002

C	-2.756	-0.49576	0.08005
O	-2.20176	-1.46768	0.54061
O	-3.91076	-0.56693	-0.58788
H	-4.17104	-1.50102	-0.61024
N	0.49065	-0.61293	-0.349
H	-0.01376	-1.26852	0.24631
C	3.92547	-1.27566	-0.27088
H	3.9622	-1.88128	0.64094
H	4.86154	-0.71529	-0.35281
H	3.81503	-1.92413	-1.14963
O	2.84756	-0.36297	-0.22581
H	1.77636	-0.65188	-0.40795
B	2.90361	0.61193	0.99779
H	3.62641	1.54271	0.68567
H	3.33416	-0.0278	1.94798
H	1.80469	0.99839	1.25864

ts4-pro

atom	x (Å)	y (Å)	z (Å)
C	0.26863	0.65165	-0.04155
C	0.7648	1.67686	-1.02052
H	0.94563	2.62472	-0.5129
H	1.69412	1.33001	-1.47399
H	0.00824	1.81879	-1.8031
C	-0.88249	1.0204	0.87129
H	-0.86954	0.36731	1.74761
H	-0.71673	2.04642	1.21325
C	-2.2563	0.92545	0.19365
H	-2.2674	1.37769	-0.80331
H	-2.99838	1.47356	0.78222
C	-2.7482	-0.49576	0.08005
O	-2.20176	-1.46768	0.54061
O	-3.91076	-0.56693	-0.58788
H	-4.17104	-1.50102	-0.61024
N	0.41265	-0.62853	-0.3802
H	-0.02156	-1.30752	0.23851
C	3.94887	-1.26786	-0.25528
H	3.9778	-1.88128	0.65654
H	4.92394	-0.76989	-0.35281
H	3.81503	-1.92413	-1.11843
O	2.90216	-0.33957	-0.21801
H	1.33956	-0.83128	-0.65755
B	2.84901	0.57293	0.93539

H	3.39241	1.65191	0.73247
H	3.11576	0.03461	1.99478
H	1.54729	0.90479	1.00904

ts5

atom	x (Å)	y (Å)	z (Å)
C	0.42038	1.27177	-0.15717
O	0.44098	0.41486	-1.09251
C	1.46236	2.37114	-0.15946
H	1.50512	2.88707	0.80175
H	2.44227	1.95799	-0.39931
H	1.18135	3.09091	-0.93694
C	-0.9351	1.6364	0.46382
H	-0.91007	1.48029	1.54467
H	-1.09037	2.70893	0.29541
C	-2.07818	0.85741	-0.1676
H	-2.08586	0.97724	-1.25385
H	-3.04526	1.21339	0.20298
C	-1.99292	-0.61729	0.12782
O	-1.22198	-1.13783	0.89442
O	-2.91639	-1.31667	-0.55803
H	-2.80127	-2.2447	-0.30285
H	0.93363	-0.61774	-0.59354
B	1.76726	-0.47131	1.36206
H	2.90211	-0.06483	1.40387
H	1.30023	-1.00309	2.32534
H	1.02392	0.54578	1.10657
N	1.56263	-1.34944	0.06459
H	2.45236	-1.65363	-0.27578
H	1.0005	-2.14615	0.28654

ts5-ini

atom	x (Å)	y (Å)	z (Å)
C	-1.09545	-0.77379	-0.22394
O	-0.63302	-0.23102	-1.20807
C	-2.4923	-1.3619	-0.26766
H	-2.89396	-1.59157	0.71936
H	-3.16653	-0.69702	-0.80294
H	-2.39175	-2.29755	-0.83718
C	-0.13492	-1.43235	0.79322
H	-0.19319	-0.96682	1.77728
H	-0.45062	-2.47488	0.89846

C	1.28695	-1.3888	0.24849
H	1.3431	-1.82654	-0.74773
H	1.96836	-1.95242	0.89166
C	1.8215	0.01237	0.1547
O	1.38491	0.98415	0.73055
O	2.91777	0.07792	-0.61813
H	3.22849	0.99691	-0.59239
H	-0.72311	1.47723	-0.94353
B	-1.78579	1.58258	0.85864
H	-2.95386	1.80543	0.61121
H	-1.38631	2.05939	1.91618
H	-1.59526	0.4605	0.8784
N	-0.89533	2.17157	-0.351
H	-1.36241	2.91579	-0.8665
H	0.00527	2.49535	-0.00525

ts5-pro

atom	x (Å)	y (Å)	z (Å)
C	-1.14645	-0.66329	-0.09644
O	-0.62452	-0.14602	-1.21657
C	-2.4838	-1.3874	-0.28466
H	-2.91946	-1.65107	0.68536
H	-3.17503	-0.73102	-0.81994
H	-2.34075	-2.29755	-0.87118
C	-0.13492	-1.44085	0.79322
H	-0.15069	-1.03482	1.81128
H	-0.44212	-2.49188	0.86446
C	1.27845	-1.3888	0.23999
H	1.3261	-1.81804	-0.76473
H	1.96836	-1.96092	0.87466
C	1.8215	0.01237	0.1547
O	1.38491	0.98415	0.73055
O	2.91777	0.07792	-0.61813
H	3.21999	0.99691	-0.59239
H	-0.68911	0.99273	-0.95203
B	-1.74329	1.61658	0.79914
H	-2.92836	1.60993	0.61971
H	-1.28431	1.69389	1.90768
H	-1.45926	0.1715	0.5894
N	-0.91233	2.10357	-0.351
H	-1.37941	2.74579	-0.9855
H	-0.00323	2.46135	-0.06475

ts6

atom	x (Å)	y (Å)	z (Å)
C	0.21923	0.63265	-0.08715
C	0.7648	1.67686	-1.01672
H	0.95323	2.60952	-0.4863
H	1.69032	1.32621	-1.47399
H	0.01964	1.85299	-1.8031
C	-0.88629	1.0204	0.86369
H	-0.86194	0.36351	1.73621
H	-0.70913	2.04262	1.20185
C	-2.2639	0.92925	0.19745
H	-2.2788	1.38149	-0.79951
H	-3.00978	1.47356	0.78602
C	-2.752	-0.49576	0.08005
O	-2.20176	-1.46768	0.54061
O	-3.91076	-0.56693	-0.58788
H	-4.17104	-1.50102	-0.61024
N	0.45065	-0.62093	-0.365
H	-0.01776	-1.28852	0.24231
H	1.59278	-0.73182	-0.53553
B	2.87561	0.59193	0.96579
H	3.50641	1.59871	0.70967
H	3.22216	0.00421	1.97198
H	1.5955	0.93017	0.90815
N	2.87556	-0.39052	-0.27162
H	3.55522	-0.08608	-0.93898
H	3.10157	-1.31465	0.03646

ts6-ini

atom	x (Å)	y (Å)	z (Å)
C	0.296779027	0.920663602	0.429108712
C	1.141938496	1.770274454	-0.47657474
H	1.358022757	2.724130138	0.01705964
H	2.081167099	1.277007064	-0.731333764
H	0.593872181	2.008347237	-1.394963344
C	-1.117479401	1.412604054	0.681345168
H	-1.451000465	1.102920137	1.675360421
H	-1.135466469	2.505159779	0.638314819
C	-2.086520491	0.854289096	-0.364533578
H	-1.701817196	0.963023933	-1.383907156
H	-3.042993906	1.387599266	-0.341453414
C	-2.390512494	-0.605991296	-0.127596591
O	-2.063547886	-1.243901189	0.844552982

O	-3.10978174	-1.13043585	-1.130413822
H	-3.280123267	-2.057482916	-0.903523112
N	0.761967911	-0.158853146	0.919214511
H	0.056997667	-0.627510562	1.493254836
H	2.474380762	-0.862823255	0.500481168
B	4.182191089	-0.343515915	-0.857014302
H	3.445099325	-0.334729349	-1.820861202
H	5.236010832	-0.896873369	-1.074134255
H	4.319906662	0.752241821	-0.355038099
N	3.411273887	-1.247978465	0.271384325
H	3.287795018	-2.200904721	-0.06084704
H	3.955907151	-1.291047495	1.128863061

ts6-pro

atom	x (Å)	y (Å)	z (Å)
C	0.296779027	0.920663602	0.429108712
C	1.141938496	1.770274454	-0.47657474
H	1.358022757	2.724130138	0.01705964
H	2.081167099	1.277007064	-0.731333764
H	0.593872181	2.008347237	-1.394963344
C	-1.117479401	1.412604054	0.681345168
H	-1.451000465	1.102920137	1.675360421
H	-1.135466469	2.505159779	0.638314819
C	-2.086520491	0.854289096	-0.364533578
H	-1.701817196	0.963023933	-1.383907156
H	-3.042993906	1.387599266	-0.341453414
C	-2.390512494	-0.605991296	-0.127596591
O	-2.063547886	-1.243901189	0.844552982
O	-3.10978174	-1.13043585	-1.130413822
H	-3.280123267	-2.057482916	-0.903523112
N	0.761967911	-0.158853146	0.919214511
H	0.056997667	-0.627510562	1.493254836
H	2.474380762	-0.862823255	0.500481168
B	4.182191089	-0.343515915	-0.857014302
H	3.445099325	-0.334729349	-1.820861202
H	5.236010832	-0.896873369	-1.074134255
H	4.319906662	0.752241821	-0.355038099
N	3.411273887	-1.247978465	0.271384325
H	3.287795018	-2.200904721	-0.06084704
H	3.955907151	-1.291047495	1.128863061

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