Electronic supporting information

Ionic Liquids as Bifunctional Cosolvent Enhanced CO_2 Conversion Catalysed by NADH-dependent Formate Dehydrogenase

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Supporting Information

1 General information

Enzyme reagent were all purchased from sigma-aldrich. Reagent (+98%) were commercially available unless otherwise stated. UV-Visible spectra were acquired with a Shimadzu UV-2550 UV–Visible spectrophotometer. NMR spectra were recorded on a Bruker ASCEND spectrometer (^{1}H, 600 MHz). ^{1}H NMR chemical shift δ is given relative to TMS and referenced to the solvent signal. The enzymatic reaction was conducted in a stainless-steel reactor (25 ml) equipped with two valves and a pressure gage. In such a reactor,

a buffer solution of FDH (3 μL) and NADH (1 mM) was bubbled with CO_2 for 5 min to remove the residual air, of which the pressure was adjusted to 1 bar afterwards. It was positioned in water bath at 37 °C for 3h. A sample was then taken out from reactor and prepared accordingly for analysis.

2 Analytical methods

2.1 N Methods for standard calibration curve

0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mM NADH solution were prepared with 100mM phosphate buffer, and measured at 340nm by UV-vis spectrometer. Standard calibration curve is presented in Figure S1.

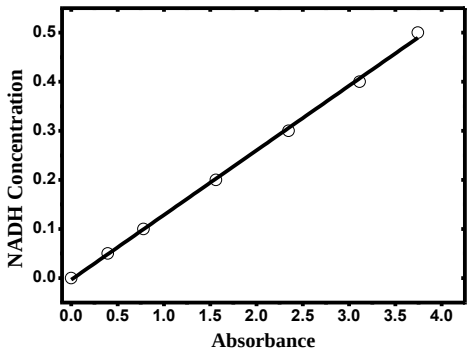


Figure S1. Standard calibration curve for NADH method.

Standard equation: $y = -0.00329+0.13173x$； $R^2=0.9988$

2.2 C Method for standard calibration curve

In case of formate in buffer, samples (0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mM formate solution) were prepared with 100mM phosphate buffer. Similarly, In case of formate in ILs, samples (0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mM formate solution) were prepared with accordingly contained-IL phosphate buffer. In a 10mL vial, 3.5 mL of 100% acetic anhydride, 50 μL of 30% (w/v) sodium acetate, and 1 mL of 2-propanol solution containing 0.5% (w/v) citric acid and 10% (w/v) acetamide were added. Assasy solution was added 0.5 mL of sample with 90min of incubation time at 25 °C. Using a UV–visible spectrophotometer, the absorbance was determined at 515 nm. The formate standard calibration curve is presented in Figure S2, S3, S4.

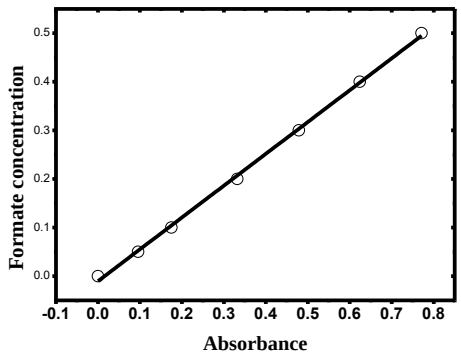


Figure S2. Standard calibration of formate for colorimetric method in buffer

Standard equation: $y=-0.01046+0.65532x$； $R^2=0.9987$

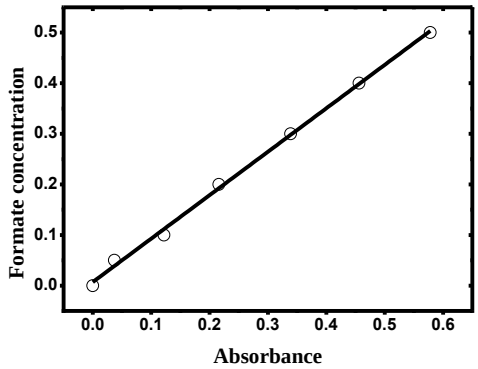


Figure S3. Standard calibration curve of formate for colorimetric method in $BmimBF_4$.
Standard equation: y=-0.00702+0.85863*x;* R^2=0.9978

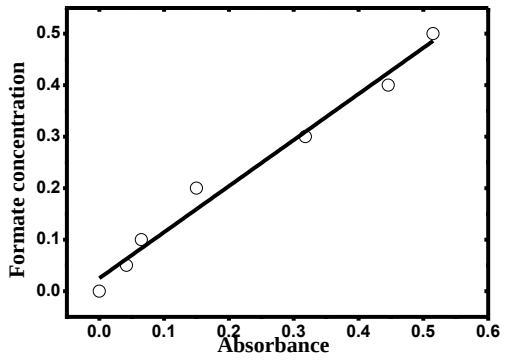


Figure S4. Standard calibration curve of formate for colorimetric method in BmimDCA.
Standard equation: y=-0.02502+0.89511*x;* R^2=0.9794

3 Results for degradation of NADH research.

3.1 Kinectic degradation of NADH.

The aqueous reaction of NADH with $BmimBF_4$ (5.0 equiv.) was conducted within a temperature range from 10 to 80 °C and Temperature-course plot (time interval: 10 min), which was monitored by an in-situ UV-vis spectrum.

To obtain the relation between NADH degradation kinetic rate (*k*) and temperature (T), data for NADH degradation is correlated by Arrhenius equation. According to kinetic law, the degradation of NADH follows the expressions:

r (rate) = d*x*/dt = *k* c(NADH) c($BmimBF_4$) (1)

Since degradation of NADH follows first-order kinetic.[1] Therefore,

r (rate) = d*x*/dt = k c(NADH) (2);

$$k = \frac{1}{t} ln \frac{1}{1-y} \quad (3)$$

According to Arrhenius equation:

$$lnk = lnA - \frac{Ea}{RT} \quad (4)$$

r, reaction rate; dx, changing in concentration; t, min; *k*, rate constant; c, subtract concentration; *A*, pre-exponential factor; *Ea*, activation energy; *R*, constant; *T*, temperature; *y*, conversion ratio.

Data for degradation of NADH in $BmimBF_4$ is correlated by Arrhenius equation, as follows:

$y = 18.0 - 7157.1x$, $R^2 = 0.989$ (5)

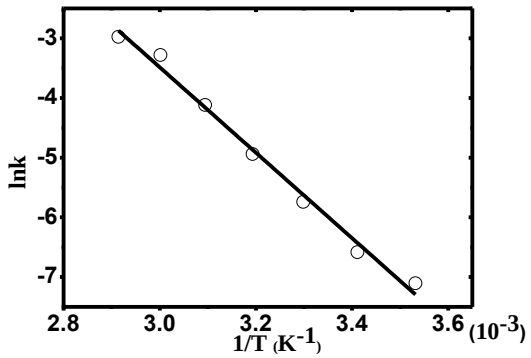


Figure S5. Arrhenius plots for degradation of NADH in $BmimBF_4$ as temperature increases.
Arrhenius equation: $y = 18.0 - 7157.1x$, $R^2 = 0.989$

3.2 Stability of NADH in ILs

pH solutions (from 7.0 to 4.5) were prepared by progressively adding phosphoric acid in phosphate solution (pH=7), which is monitored by pH meter in the whole process (Figure S6). A buffer solution (2 mL) of $BmimBF_4$ (V_{IL}/V_{buffer} = 20%) and NADH (2 μmol) was prepared, which was incubation at 37 °C for 3h, an apparent decrease of the absorption intensity at 340 nm accompanied with an increase of that at 260 nm was observed (Figure S7). The aqueous reaction of NADH with ILs (5.0 equiv.) was incubation at 37 °C for 3h, which was monitored by an in-situ UV-vis spectrum (Figure S8).

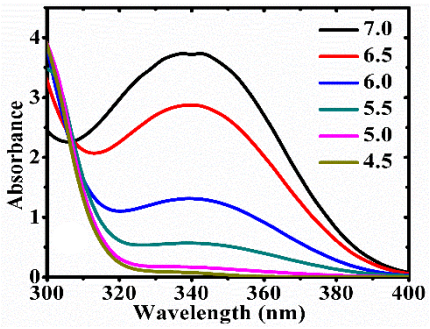


Figure S6. NADH degrades in phosphate buffer whose pH in range from 7.0 to 4.5.

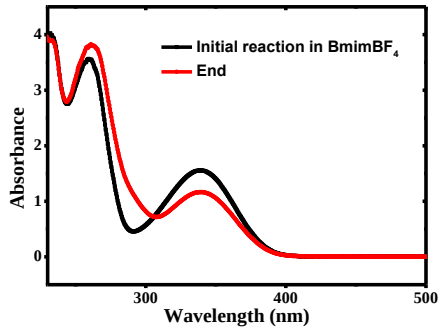


Figure S7. NADH degrades in contained-$BmimBF_4$ reaction.

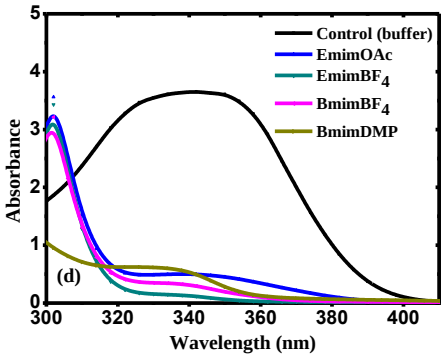


Figure S8. NADH degrades in ILs.

3.3 DFT calculation.

All the DFT calculations throughout this work were carried out with the Gaussian09 software package.[2] The structures in pH calculations were computed with a polarized continuum model (PCM)[3,4] in water using the B3LYP method in conjunction with the 6-311+g(d,p) basis set,[5,6] that were ensured by the absence of imaginary vibrational frequency.

3.3.1 Mechanism for NADH degradation.

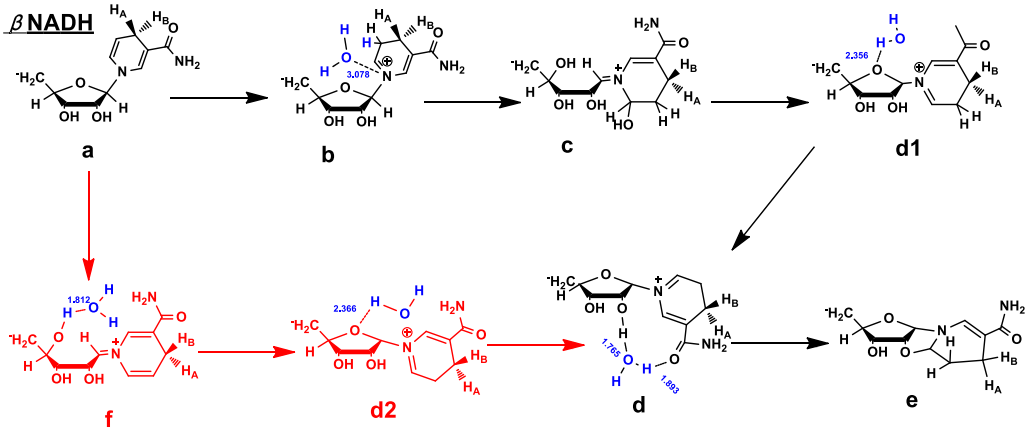
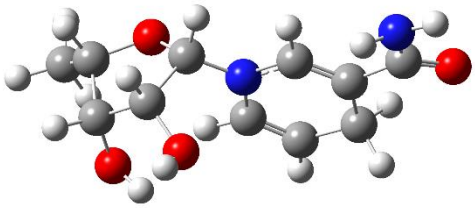
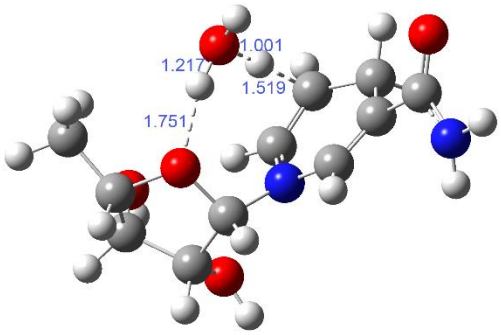
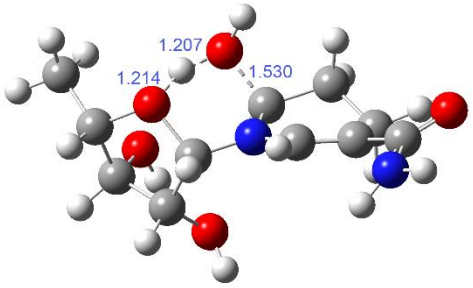


Figure S9. Two possible pathway (red and black) for NADH degradation mechanism proposed by the Norman and co-worker.[7]

Table S1 Structure for the NADH and its derivatives

Model compound of β-NADH				
	C	0.963703	-0.78851	-0.62697
	O	1.906224	-0.06235	-1.39935
	C	3.252122	-0.27039	-0.91575
	C	3.096605	-0.56894	0.579843
	C	1.778773	-1.3689	0.585705
	H	0.561513	-1.62238	-1.21657
	H	3.660812	-1.17397	-1.39852
	C	4.102919	0.931383	-1.28258
	H	5.143686	0.759576	-0.98847
	H	4.070596	1.092465	-2.3637
	H	3.740155	1.827805	-0.77606
	C	-0.00629	1.351867	0.202965
	C	-1.4497	-0.45099	-0.41364
	C	-1.04948	2.110236	0.563758
	H	1.017845	1.695201	0.247071
	C	-2.56254	0.234248	-0.05353
	H	-1.51402	-1.43874	-0.85875
	H	-0.84767	3.116076	0.919807
	H	-3.07633	2.323396	-0.16014
	N	-0.16937	0.047684	-0.3036
	C	-2.48645	1.653871	0.481807
	C	-3.9149	-0.32808	-0.24608
	O	-4.9157	0.390476	-0.2614
	N	-4.03324	-1.70061	-0.44235
	H	-3.37759	-2.31594	0.016885
	H	-4.99146	-2.02464	-0.44983
	H	-2.97335	1.715599	1.46714
	O	2.972558	0.624023	1.332713
	H	2.318057	0.459059	2.031408
	O	1.050857	-1.24287	1.799831
	H	1.287392	-1.96421	2.39656
	H	3.943332	-1.16446	0.951989
	H	1.995152	-2.42348	0.375208
TS-ab				
	C	0.933265	-0.72805	-0.90153
	O	1.342165	0.651373	-1.0319
	C	2.806347	0.717435	-1.12816
	C	3.272331	-0.41444	-0.21402
	C	2.228641	-1.52148	-0.4926
	H	0.569391	-1.0749	-1.87289
	H	3.074046	0.46593	-2.16355
	C	3.277771	2.117158	-0.79292
	H	4.36277	2.175694	-0.92037
	H	2.824242	2.843998	-1.47293
	H	3.045133	2.379617	0.241047
	C	-0.01151	-0.37261	1.300265
	C	-1.49518	-0.6719	-0.55037
	C	-1.01883	0.217527	2.031229
	H	1.017205	-0.36045	1.645178
	C	-2.56513	-0.27138	0.155007

	H	-1.54329	-0.87756	-1.61359
	H	-0.79383	0.468388	3.06538
	H	-3.04744	0.975792	1.828549
	N	-0.1947	-0.79955	0.014145
	C	-2.47443	0.064574	1.630025
	C	-3.87299	0.020432	-0.52711
	O	-4.48897	1.039046	-0.23225
	N	-4.27829	-0.84724	-1.4995
	H	-3.93582	-1.79604	-1.52931
	H	-5.17627	-0.66385	-1.92919
	H	-2.95105	-0.72563	2.228756
	H	-0.50467	1.416624	1.253909
	O	-0.13198	2.320283	0.528372
	H	0.429495	1.872383	-0.16954
	H	-0.8519	2.823444	0.111275
	O	3.202465	0.015857	1.135174
	H	3.510908	-0.70586	1.702522
	O	2.084541	-2.34216	0.646897
	H	1.902313	-3.25629	0.394611
	H	4.286006	-0.74351	-0.47063
	H	2.546351	-2.10912	-1.36096
b				
	C	-1.15013	0.074113	1.010679
	O	-2.22593	0.889708	0.707569
	C	-3.39777	0.102873	0.269319
	C	-2.80836	-1.24756	-0.13046
	C	-1.66364	-1.38604	0.894197
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	H	-4.02551	-0.0365	1.158035
	C	-4.16054	0.874818	-0.78695
	H	-5.08807	0.346815	-1.0286
	H	-4.42379	1.86529	-0.40674
	H	-3.58098	0.977272	-1.7064
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	C	1.298414	-0.10736	0.455021
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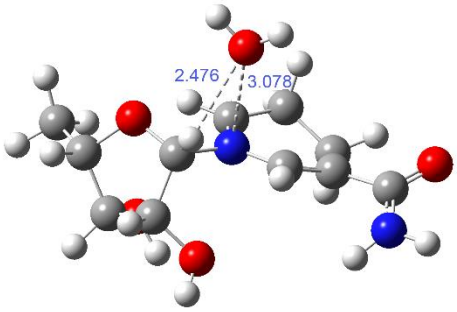
	H	1.351262	-0.45951	1.475459
	H	0.657083	1.689521	-2.85135
	H	3.087678	0.945724	-2.11207
	N	0.006181	0.364181	0.062093
	C	2.151551	0.483578	-1.79067
	C	3.72196	-0.47126	0.019972
	O	4.682188	0.165937	-0.391
	N	3.822494	-1.51627	0.89152

	H	3.076325	-2.18766	0.993483
	H	4.757003	-1.81521	1.139929
	H	1.955989	-0.34916	-2.48088
	H	1.333281	2.482236	-1.44144
	O	0.477842	2.467189	2.258978
	H	-0.17283	3.125581	2.538566
	H	1.309867	2.748282	2.663323
	O	-2.29174	-1.17082	-1.44896
	H	-1.79224	-1.98043	-1.62985
	O	-0.64057	-2.2842	0.50422
	H	-0.78947	-3.14896	0.909325
	H	-3.55073	-2.05074	-0.03709
	H	-2.07851	-1.65748	1.872772
TS-bc				
	C	0.854297	-0.98083	-0.38796
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	C	3.192518	-0.56202	-0.93495
	C	3.129582	-0.71422	0.581694
	C	1.773398	-1.42371	0.815753
	H	0.526766	-1.84959	-0.96167
	H	3.367847	-1.53896	-1.39856
	C	4.131308	0.481831	-1.50038
	H	5.161809	0.181433	-1.28828
	H	4.018009	0.551085	-2.5853
	H	3.965803	1.458964	-1.04257
	C	-0.04925	1.173969	0.359078
	C	-1.57809	-0.61054	-0.45013
	C	-1.32428	1.984806	0.568768
	H	0.625886	1.174781	1.212288
	C	-2.66828	-0.05336	0.10152
	H	-1.61391	-1.40904	-1.18482
	H	-1.11182	2.804765	1.259075
	H	-3.40395	1.692562	1.086198
	N	-0.27603	-0.16393	-0.11453
	C	-2.48373	1.105462	1.052417
	C	-4.06461	-0.40579	-0.31838
	O	-4.94442	0.447232	-0.30699
	N	-4.28313	-1.68675	-0.75605
	H	-3.69991	-2.44753	-0.44167
	H	-5.24082	-1.91637	-0.98905
	H	-2.29295	0.736395	2.069852
	H	-1.62339	2.431695	-0.38906
	O	0.819529	1.873578	-0.68819
	H	1.455727	0.937362	-1.1076
	H	0.260618	2.275893	-1.37671
	O	3.119538	0.577226	1.154624

	H	2.993899	0.488264	2.11129
	O	1.261389	-1.05293	2.077699
	H	0.822888	-1.79785	2.50786
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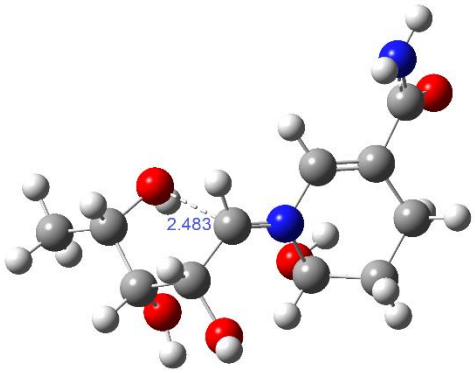	C	0.76704	-0.14284	1.123088
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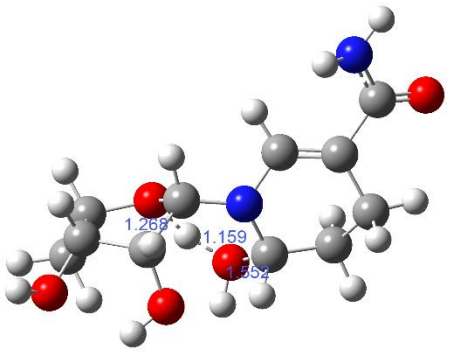
	C	3.184652	0.119487	0.284299
	C	2.096009	0.553802	1.324202
	H	0.652837	-1.0817	1.657325
	H	3.304072	-1.89116	1.04128
	C	4.277391	-1.87532	-0.88094
	H	5.267372	-1.63733	-0.47876
	H	4.209561	-2.95861	-1.00581
	H	4.183099	-1.39575	-1.85918
	C	-0.348	1.456844	-0.4665
	C	-1.49163	-0.52117	0.562193
	C	-1.64759	2.211727	-0.21703
	H	0.525349	2.058497	-0.24238
	C	-2.67905	-0.06285	0.133949
	H	-1.34258	-1.53315	0.923082
	H	-1.62403	2.599025	0.807592
	H	-3.16009	1.221966	-1.47993
	N	-0.3036	0.274381	0.512567
	C	-2.87987	1.320568	-0.42273
	C	-3.85944	-1.00132	0.019548
	O	-4.52129	-0.98805	-1.00891
	N	-4.08739	-1.84627	1.062822
	H	-3.70087	-1.67678	1.979232
	H	-4.89856	-2.44875	1.00002
	H	-3.75835	1.778298	0.045856
	H	-1.67347	3.076516	-0.88624
	O	-0.19202	0.945126	-1.7516
	H	1.746016	-1.43879	-1.27678
	H	-1.04383	0.700905	-2.1429
	O	2.922981	0.726637	-0.95997
	H	3.133083	1.669579	-0.92014
	O	1.999853	1.972643	1.280427
	H	2.050322	2.344505	2.170867
	H	4.149628	0.446577	0.695057
	H	2.444679	0.221601	2.310448
TS-cd				
	C	-0.79296	-0.76485	-0.06971
	O	-1.51039	-0.27069	1.155577

	C	-2.92197	-0.71816	1.113676
	C	-3.13576	-1.2064	-0.3572
	C	-1.89264	-0.69489	-1.1301
	H	-0.53836	-1.81205	0.11116
	H	-2.96405	-1.56541	1.803494
	C	-3.8289	0.397123	1.595824
	H	-4.8581	0.033998	1.644048
	H	-3.53369	0.711376	2.600982
	H	-3.81746	1.255268	0.918992
	C	0.368133	1.403784	-0.34636
	C	1.64828	-0.67563	0.079173
	C	1.703272	2.093129	-0.10402
	H	-0.13167	1.694578	-1.26813
	C	2.833427	-0.10958	-0.1925
	H	1.547213	-1.65891	0.525569
	H	1.647771	3.110339	-0.50175
	H	3.815391	1.766003	-0.42638
	N	0.414977	-0.02586	-0.20297
	C	2.867654	1.305073	-0.71418
	C	4.137171	-0.75783	0.168583
	O	5.097133	-0.07209	0.498704
	N	4.176091	-2.12975	0.159178
	H	3.563	-2.65538	-0.4459
	H	5.078816	-2.54357	0.354852
	H	2.825342	1.31201	-1.81253
	H	1.853411	2.163857	0.978154
	O	-0.60304	1.896318	0.759861
	H	-1.20177	0.957121	1.078863
	H	-1.18949	2.585343	0.403116
	O	-4.30993	-0.6548	-0.93053
	H	-4.85665	-1.34269	-1.33131
	O	-2.10605	0.647906	-1.5281
	H	-3.02029	0.702483	-1.85763
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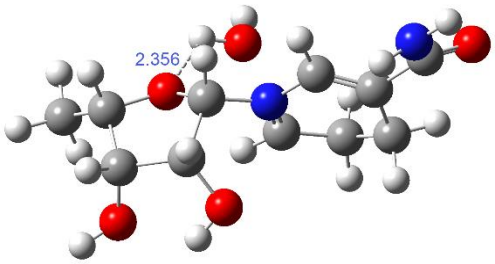
	H	-1.64298	-1.32858	-1.9906
d1				
	C	0.92133	-0.38466	-0.77534
	O	1.908286	0.612259	-0.80902
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	C	3.079167	-1.30833	-0.06589
	C	1.534993	-1.59243	0.025638
	H	0.637102	-0.689	-1.79114
	H	3.201051	-0.44001	-2.03607
	C	4.316979	0.883942	-0.74879
	H	5.273129	0.379319	-0.91976
	H	4.258131	1.725323	-1.44395

	H	4.298255	1.258728	0.27645
	C	-0.2091	0.93468	0.894707
	C	-1.56244	-0.28933	-0.64348
	C	-1.43087	1.44088	1.57068
	H	0.784897	1.240034	1.195388
	C	-2.675	-0.15467	0.090981
	H	-1.53029	-0.68589	-1.65013
	H	-1.19395	1.684184	2.609874
	H	-3.55668	0.99423	1.649259
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	C	-2.61613	0.47126	1.461546
	C	-4.03656	-0.51159	-0.45701
	O	-4.98839	0.212925	-0.20418
	N	-4.10993	-1.61178	-1.25971
	H	-3.41078	-2.33837	-1.22361
	H	-5.02957	-1.86926	-1.59552
	H	-2.53868	-0.3275	2.212107
	H	-1.64999	2.400372	1.074191
	O	0.417131	3.201945	-0.51794
	H	1.190169	2.849161	-0.98086
	H	0.385444	4.147428	-0.7144
	O	3.537621	-1.03244	1.254103
	H	4.385545	-1.46221	1.422574
	O	1.075499	-1.60721	1.349881
	H	1.859362	-1.50256	1.923285
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	H	1.26688	-2.53334	-0.46707
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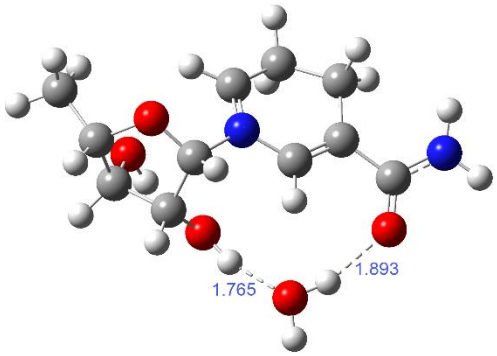	C	-1.19445	0.314358	-1.08075
	O	-2.32466	-0.43667	-1.33071
	C	-3.48345	0.087582	-0.57743
	C	-2.85341	0.834325	0.591566
	C	-1.57799	1.4313	-0.03869
	H	-0.76281	0.706924	-2.00782
	H	-3.97847	0.813812	-1.2343
	C	-4.4286	-1.05154	-0.25926
	H	-5.33402	-0.65442	0.209677
	H	-4.71931	-1.56402	-1.1799
	H	-3.97693	-1.76719	0.430672
	C	-0.35524	-1.71553	0.039734
	C	1.204121	-0.01299	-0.50926
	C	0.708438	-2.48941	0.736374
	H	-1.39187	-2.03612	0.02755
	C	2.277779	-0.70928	-0.11592
	H	1.260137	1.007948	-0.85692
	H	0.581943	-2.23308	1.802617

	H	2.398072	-2.79034	-0.60751
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	C	3.58451	0.042206	-0.12278
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	N	4.715907	-0.69803	-0.09395
	H	4.726405	-1.70371	-0.16581
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	H	2.840673	-2.4362	1.059145
	H	0.490062	-3.55865	0.665325
	O	1.479339	3.141418	0.040481
	H	1.680693	4.083231	0.107969
	H	2.328784	2.65507	0.078246
	O	-2.50231	-0.08788	1.614377
	H	-1.95795	0.392331	2.257372
	O	-0.62656	1.673402	0.9585
	H	0.045183	2.341703	0.688204
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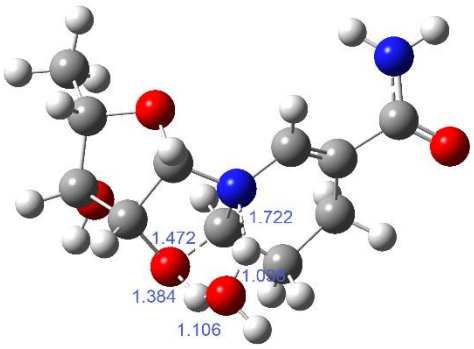	C	-1.21123	0.33302	-1.16138
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	H	-3.50112	-0.97474	-1.5587
	C	-3.12277	-2.58307	-0.17421
	H	-4.17742	-2.71382	0.085257
	H	-2.87414	-3.29611	-0.96418
	H	-2.52195	-2.79444	0.711605
	C	-0.19573	0.872918	0.914876
	C	1.257358	-0.29696	-0.7279
	C	1.008432	1.474688	1.596088
	H	-0.4512	-0.11241	1.318615
	C	2.201194	-0.34474	0.218819
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	H	1.265135	2.42638	1.118626
	H	2.130275	-0.24791	2.336166
	N	0.139154	0.64079	-0.55368
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	C	3.452557	-1.17129	-0.00352
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	H	4.106468	-2.97624	-0.67857

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	H	1.68226	3.154416	-2.364
	H	0.424709	1.563945	-0.95535
	O	-2.76451	-0.45971	1.637515
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	O	-1.33424	1.686081	0.812664
	H	0.540503	3.934378	-1.66602
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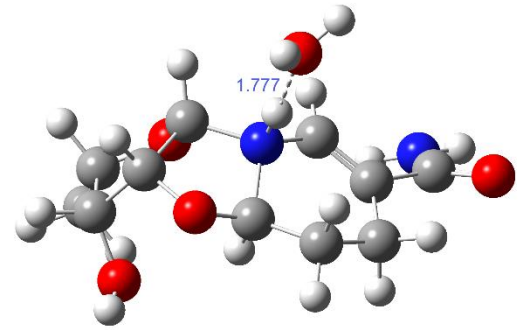	C	-1.0907	-0.10757	-1.20735
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	C	-3.0935	-0.09215	0.249723
	C	-2.1368	0.852264	-0.54339
	H	-1.10041	-0.09983	-2.30459
	H	-3.33613	-1.51153	-1.35388
	C	-3.0688	-2.69009	0.431191
	H	-4.13963	-2.75653	0.645323
	H	-2.7745	-3.58471	-0.1229
	H	-2.52715	-2.65565	1.377647
	C	-0.15005	0.926103	0.644721
	C	1.387749	-0.33116	-0.77797
	C	1.008243	1.662919	1.274877
	H	-0.49908	0.112004	1.284923
	C	2.333607	-0.22338	0.169159
	H	1.503051	-0.92134	-1.68024
	H	1.30843	2.52498	0.667766
	H	2.063745	0.037317	2.276902
	N	0.182436	0.435892	-0.70766
	C	2.185923	0.666521	1.385981
	C	3.674797	-0.89094	0.008619
	O	4.690215	-0.32229	0.391953
	N	3.689066	-2.10708	-0.6143
	H	2.865476	-2.68912	-0.64739
	H	4.5866	-2.56912	-0.68386
	H	3.124942	1.208211	1.529904
	H	0.723682	2.03778	2.261441
	O	-0.23516	2.87985	-1.4866
	H	0.349673	3.656067	-1.46155
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	O	-2.7823	-0.13576	1.62765
	H	-3.23613	0.578022	2.094419
	O	-1.33674	1.735418	0.322041

	H	-0.82005	2.654091	-0.57528
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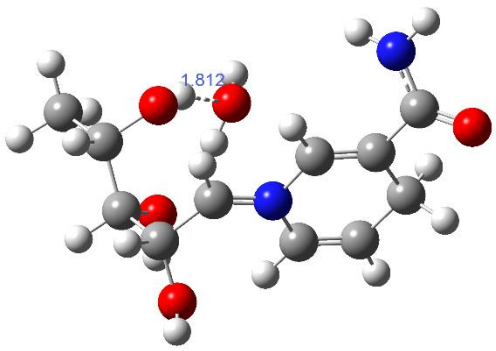	C	-0.60436	0.461962	-1.22202
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	C	-2.99726	0.39635	-0.32481
	C	-1.9514	1.146041	-1.21296
	H	-0.47224	-0.30191	-1.97735
	H	-3.28867	-1.20336	-1.69962
	C	-4.11654	-1.84627	0.173037
	H	-5.11038	-1.43536	-0.03149
	H	-4.11837	-2.90195	-0.10859
	H	-3.93112	-1.76857	1.247409
	C	0.510928	1.648575	0.585745
	C	1.619918	-0.10791	-0.71529
	C	1.623935	1.807481	1.30825
	H	-0.39107	2.220638	0.720997
	C	2.738391	0.018069	0.009064
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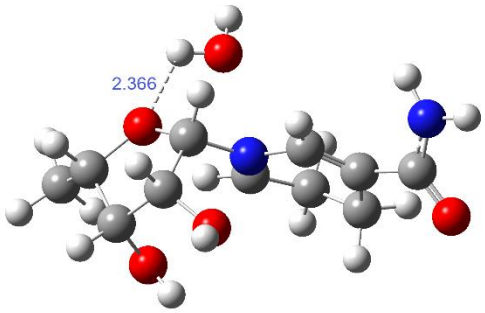
	H	1.606723	2.557867	2.09277
	H	3.160659	0.51915	2.047514
	N	0.449056	0.687993	-0.47732
	C	2.876342	1.022807	1.111408
	C	3.985468	-0.75839	-0.34746
	O	5.069896	-0.19719	-0.28364
	N	3.814198	-2.04369	-0.76698
	H	2.975581	-2.56387	-0.55539
	H	4.652542	-2.57351	-0.97004
	H	3.728147	1.680599	0.886668
	H	-1.61126	-0.69766	2.308439
	O	-1.03689	-1.46866	2.173362
	H	-1.53749	-1.8012	0.464381
	H	-1.14392	-2.0485	2.938327
	O	-2.68741	0.602846	1.050154
	H	-2.93989	1.504016	1.29472
	O	-1.93096	2.493897	-0.76278
	H	-1.78869	3.10114	-1.50161
	H	-3.96861	0.850357	-0.56037
	H	-2.31801	1.089136	-2.24625
d2				
	C	1.061894	-0.24656	-1.08996
	O	2.192444	0.539155	-0.91869
	C	3.319313	-0.25016	-0.36899
	C	2.641738	-1.46031	0.267083



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C	4.163599	0.631784	0.52653
H	5.048887	0.077941	0.853506
H	4.503149	1.512422	-0.02522
H	3.613779	0.94588	1.415661
C	0.128461	1.099984	0.738693
C	-1.40213	-0.10184	-0.62908
C	-1.00412	1.685155	1.501582
H	1.156568	1.372323	0.936784
C	-2.45234	0.143847	0.16708
H	-1.45643	-0.64629	-1.56182
H	-0.66869	1.939838	2.510605
H	-3.13087	1.358368	1.806397
N	-0.07865	0.276542	-0.23818
C	-2.24764	0.784333	1.517306
C	-3.82397	-0.39499	-0.14296
O	-4.50846	-0.8286	0.773486
N	-4.20404	-0.41681	-1.45382
H	-3.77705	0.19391	-2.13447
H	-5.14351	-0.74003	-1.64807
H	-2.15311	-0.01354	2.265617
H	-1.21092	2.645317	0.998888
O	0.769879	3.148379	-1.07766
H	1.628143	2.795557	-1.35318
H	0.742025	4.063989	-1.38527
O	2.158669	-1.113	1.553488
H	1.59387	-1.83337	1.871224
O	0.388954	-2.40386	-0.12194
H	0.368755	-3.31803	-0.43396
H	3.32235	-2.32014	0.31222
H	1.830113	-2.1927	-1.61206

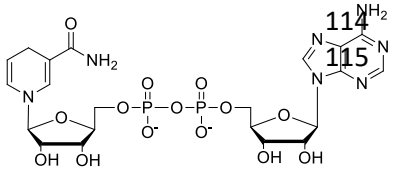
4 Chemicals Characterization

Table S2. Summary of chemicals NMR data

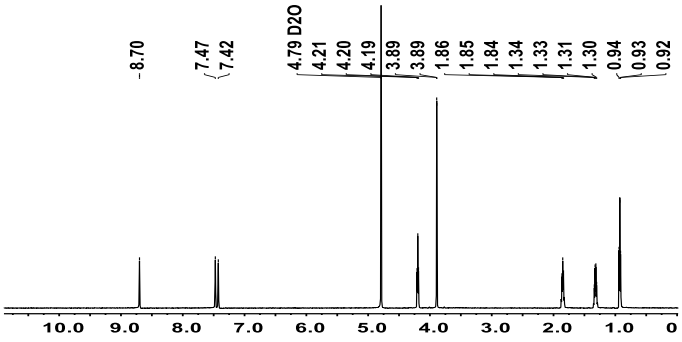
Compound	NMR results ^{1}H NMR (600 MHz, D_2O, 298K)
$BmimBF_4$	δ = 8.70 (s, 1H), 7.47 (s, 1H), 7.42 (s, 1H), 4.20 (t, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 2.03 – 1.58 (m, 2H), 1.32 (q, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).
NADH	δ = 8.49 (s, 1H), 8.25 (s, 1H), 6.95 (s, 1H), 6.14 (d, J = 5.7 Hz, 1H), 6.00 (d, J = 8.4 Hz, 1H), 4.72 (t, J = 5.2 Hz, 1H), 4.52 (s, 1H), 4.39 (s, 1H), 4.30 – 4.17 (m, 2H), 4.09 (d, J = 7.0 Hz, 2H), 3.65 (s, 1H), 2.81 (d, J = 18.1 Hz, 1H), 2.69 (d, J = 15.8 Hz, 1H), 1.18 (s, 1H)
NAD^+	δ = 9.43 (s, 1H), 9.27 (d, J = 6.2 Hz, 1H), 8.94 (d, J = 7.6 Hz, 1H), 8.60 (s, 1H), 8.39 (s, 1H), 8.29 (t, J = 7.0 Hz, 1H), 6.17 (d, J = 5.5 Hz, 1H), 6.15 (d, J = 5.6 Hz, 1H), 4.60 (s, 1H), 4.57 (t, J = 5.3 Hz, 1H), 4.53 (t, J = 4.2

	Hz, 1H), 4.48 (s, 1H), 4.40 (s, 2H), 4.26 (d, J = 12.2 Hz, 2H), 4.22 (d, J = 11.2 Hz, 1H), 2.23 (s, 1H)
NADH+BmimBF$_4$	δ = 9.43 (s, 1H), 9.27 (d, J = 6.2 Hz, 1H), 8.94 (d, J = 7.6 Hz, 1H), 8.60 (s, 1H), 8.39 (s, 1H), 8.29 (t, J = 7.0 Hz, 1H), 6.17 (d, J = 5.5 Hz, 1H), 6.15 (d, J = 5.6 Hz, 1H), 4.60 (s, 1H), 4.57 (t, J = 5.3 Hz, 1H), 4.53 (t, J = 4.2 Hz, 1H), 4.48 (s, 1H), 4.40 (s, 2H), 4.26 (d, J = 12.2 Hz, 2H), 4.22 (d, J = 11.2 Hz, 1H), 2.23 (s, 1H)

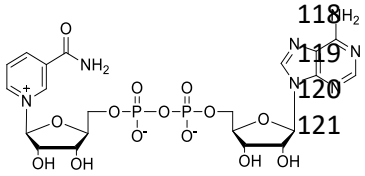
4.1 NMR of 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF$_4$)



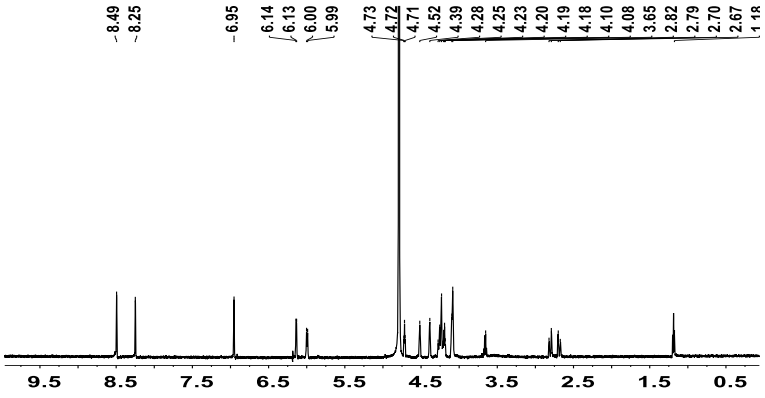
^{1}H NMR (600 MHz, D_2O, 298K): δ = 8.70 (s, 1H), 7.47 (s, 1H), 7.42 (s, 1H), 4.20 (t, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 2.03 – 1.58 (m, 2H), 1.32 (q, *J* = 7.5 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).



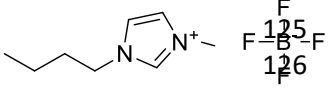
4.2 NMR of Nicotinamide adenine dinucleotide (NADH)



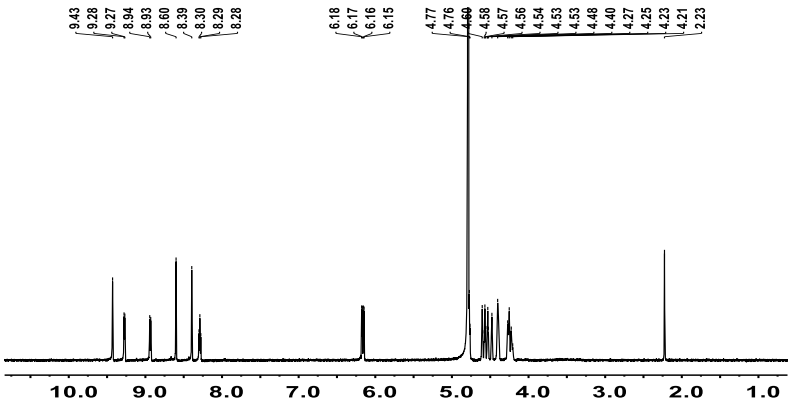
NADH ^{1}H NMR (600 MHz, D_2O, 298K)：δ = 8.49 (s, 1H), 8.25 (s, 1H), 6.95 (s, 1H), 6.14 (d, J = 5.7 Hz, 1H), 6.00 (d, J = 8.4 Hz, 1H), 4.72 (t, J = 5.2 Hz, 1H), 4.52 (s, 1H), 4.39 (s, 1H), 4.30 – 4.17 (m, 2H), 4.09 (d, J = 7.0 Hz, 2H), 3.65 (s, 1H), 2.81 (d, J = 18.1 Hz, 1H), 2.69 (d, J = 15.8 Hz, 1H), 1.18 (s, 1H).



4.3 NMR of nicotinamide adenine dinucleotide (NAD$^+$)

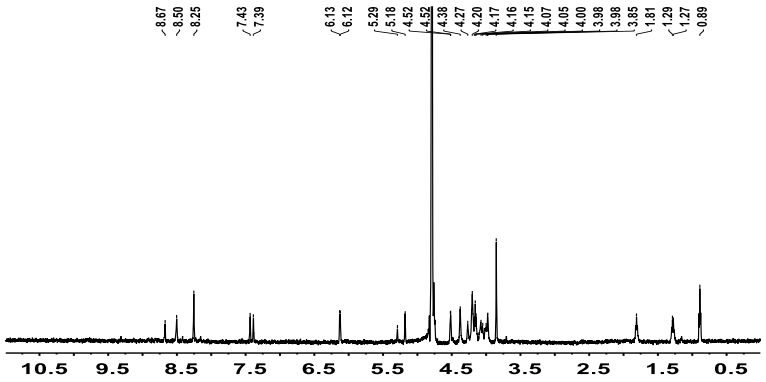


NAD$^+$ ^{1}H NMR (600 MHz, D_2O, 298K)：δ = 9.43 (s, 1H), 9.27 (d, J = 6.2 Hz, 1H), 8.94 (d, J = 7.6 Hz, 1H), 8.60 (s, 1H), 8.39 (s, 1H), 8.29 (t, J = 7.0 Hz, 1H), 6.17 (d, J = 5.5 Hz, 1H), 6.15 (d, J = 5.6 Hz, 1H), 4.60 (s, 1H), 4.57 (t, J = 5.3 Hz, 1H), 4.53 (t, J = 4.2 Hz, 1H), 4.48 (s, 1H), 4.40 (s, 2H), 4.26 (d, J = 12.2 Hz, 2H), 4.22 (d, J = 11.2 Hz, 1H), 2.23 (s, 1H).



4.4 NMR of Mixture of NADH and BmimBF$_4$.

NADH + BmimBF$_4$ ^{1}H NMR (600 MHz, D_2O, 298K)：δ = 1H NMR (600 MHz, Deuterium Oxide) δ 8.67 (s, 1H), 8.50 (s, 3H), 8.25 (s, 4H), 7.43 (s, 3H), 6.13 (d, J = 6.1 Hz, 3H), 5.29 (s, 1H), 5.18 (s, 2H), 4.78 – 4.73 (m, 8H), 4.54 – 4.50 (m, 4H), 4.38 (s, 2H), 4.22 – 4.13 (m, 7H), 4.06 (d, J = 15.1 Hz, 1H), 4.02 – 3.96 (m, 2H), 3.85 (s, 7H), 1.81 (s, 1H), 1.28 (d, J = 8.5 Hz, 2H), 0.89 (s, 4H).



4.5 NMR for degradation of NADH.

A mixture of NADH (1.4 mg) and BmimBF$_4$ (0.452 mg) (molar ratio = 1:1) was incubated for 3h at 60℃. Then samples are separately identified by NMR (Figure S8). NADH (1.4mg) was dissvoled in deuteroxide (0.5 mL), and then solution (0.25mM NADH) is gradually added by deuterosulfuric acid to adjust pH (3, 1), which is monitored by pH meter. After that, the samples are incubated for three hours at 37 ℃ and measured.

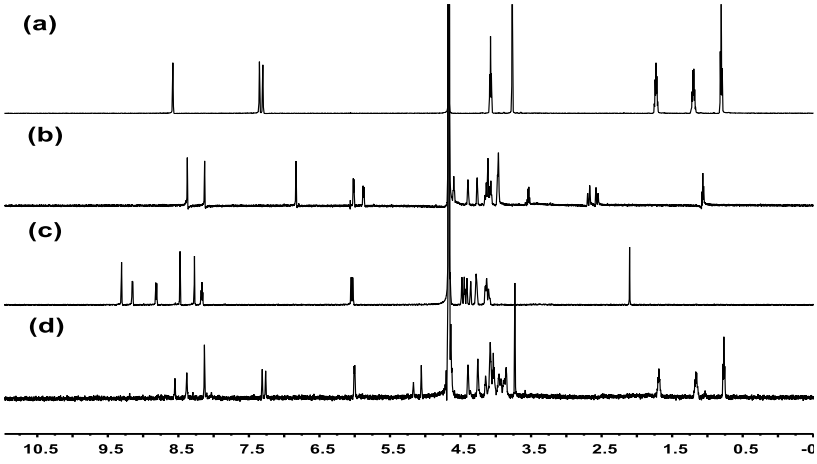


Figure S10. ^{1}H NMR (600 MHz, D_2O, 298K) (δ: ppm). (a) $BmimBF_4$; (b) NADH; (c), NAD^+; (d) a mixture of NADH and $BmimBF_4$ (molar ratio = 1:1); D_2O was used as the solvent.

Abbreviation:

DBULat: 1,8-Diazabicyclo[5.4.0]undec-7-ene lactate
$BmimBF_4$: 1-butyl-3-methylimidazolium tetrafluoroborate
BmimDCA: 1-butyl-3-methylimidazolium dicyanamide
BmimDMP: 1-butyl-3-methylimidazolium dimethylphosphate
$EmimBF_4$: 1-ethyl-3-methylimidazolium tetrafluoroborate
EmimOAc: 1-ethyl-3-methylimidazolium acetate
NADH: reduced nicotinamide adenine dinucleotide
NAD^+: nicotinamide adenine dinucleotide

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