Electronic Supplementary Information

Unveiling protic amino acid ionic liquids for efficient capture of carbon dioxide

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1. Materials

Proline (Pro, 98 wt%), β-Alanine (β-Ala, 98 wt%) and Lysine (Gly, 98 wt%) were obtained from Aladdin Reagents (Shanghai) Co., Ltd. Glycine (Gly, 99 wt%) was purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd. 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU, 99 wt%), 1,1,3,3-Tetramethylguanidine (TMG, 99 wt%) and 1,5-Diazabicyclo[4,3,0]non-5-ene (DBN, 99 wt%) were purchased Energy Chemical Reagents (Shanghai) Co., Ltd. N-methyl-2-pyrrolidinone (NMP, 99 wt%) and Valine (Val, 98 wt%) were purchased from Shanghai Adamas Reagents Co., Ltd. Caprolactam (CPL, 99 wt%), pyrrolidin-2-one (2-Pyr, 99 wt%), potassium hydroxide (KOH, 95 wt%) were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. Acetonitrile (99 wt%) and N-Hexane (97 wt%) was obtained from Nanjing Chemical Reagent Co., Ltd. CO_2 (99.99 %) were provided by Taizhou Yaowen Chemical Co., Ltd. HCl (99.99%) were supplied from Nanjing Special Gas Co. Ltd., China.

2. Preparation of PAAILs

The preparation of PAAILs is carried out by ion exchange between organic base chlorine salt and amino acid potassium salt in methanol. Taking the synthesis of [DBUH][Cl] as an example in the process of preparing organic base chlorine salt, pass HCl into a 20 ml screw bottle with 1 g DBU until a solid is produced. Then the unreacted DBU is removed. The solid was dried in an air-dry oven at 100 °C for 12 h. [DBNH][Cl] and [TMGH][Cl] can also be synthesized using DBN or TMG to take the place of DBU as the raw material. Taking the synthesis of K[Maba] as an example in the process of preparing amino acid potassium salt, KOH (5.6 g, 1.0 mol), N-methyl-2-pyrrolidinone

(14.9 g, 1.5 mol), and water (about 20 g) are added into a 250 ml, three-necked, PTFE round-bottom flask. The mixture is placed in the oil bath, stirred and heated at 363.2 K for 24 h, respectively. After the reaction, the water is removed at 363.2 K under reduced pressure. Subsequently, the product is extracted three times with acetonitrile to removed residual N-methyl-2-pyrrolidinone. Finally, acetonitrile was evaporated under reduced pressure to obtain pure K[Maba]. The synthetic procedures of K[Eaca] and K[Gaba] were as the same as that of K[Maba] except that NMP were replaced by CPL and 2-Pyr, respectively. In addition, K[Gly] can also be synthesized using KOH with equimolar glycine.

Subsequently, the preparation of PAAILs is carried out by ion exchange between organic base chlorine salt and amino acid potassium salt in methanol. The water is removed at 363.2 K under reduced pressure.

3. Characterization Methods

The density is measured using an Anton Paar DMA 5000 densitometer with a precision of 0.00001 $g \cdot cm^{-3}$. Distilled water is used to calibrate the densitometer. Viscosity is determined on a Brookfield DV2TLV viscometer equipped with a spindle CPA–41Z (viscosity ranges from 0.58 to 11510 mPa·s). The rotational speed (N) of the spindle ranges from 0.1 to 200 rpm and the shear rate of the spindle is 2.0 $N \cdot s^{-1}$. The uncertainty of the viscometer is ±1% in relation to the full scale. Thermal gravity (TG) traces are recorded on a STA449F3 from room temperature to 873.2 K with a scanning rate of 10 $K \cdot min^{-1}$ under N_2 atmosphere. Fourier transform infrared spectra (FTIR) are determined on a Tensor 27 infrared spectrometer. Nuclear Magnetic Resonance (NMR)

is performed on a Bruker DPX 400 MHz spectrometer with D_2O or Methanol-d_4 as the solvent. Electrospray ionization mass spectra (ESI–MS) are obtained from a Q Exactive (Thermo Fisher) high resolution mass spectrometer. The water contents were obtained using coulometric Karl Fisher titration.

4. Measurement of CO_2 solubility in PAAILs

The solubility of CO_2 in six PAAILs is measured at pressures of 1 bar and temperatures of 313.2 K. The same methodology is followed as presented in our previous work. The whole absorption equipment consists of a water bath, a pressure recording system, and two 316L stainless steel chambers whose volumes are 190.217 cm^3 (V_1) and 42.077 cm^3 (V_2), respectively. The big chamber, named as gas reservoir, is used to isolate CO_2 before it contacts with the IL sample in the small chamber, which is equipped with a magnetic stirrer and used as equilibrium cell. The temperature (T) of both chambers is controlled by the water bath with an accuracy of ±0.1 K. The pressures in the two chambers are monitored online using two pressure transducers (Wideplus Precision Instruments) which are linked to a Numeric Instrument (WP-D821-200-1212—N-2P). The uncertainty of the pressure recording system is ±0.2% in relation to the full scale. In a typical run, a known mass (w) of IL sample was placed into the equilibrium cell. Then the air in the two chambers was evacuated (< 0.005 bar). While the two chambers were separated using a needle valve, CO_2 was fed into the gas reservoir from gas cylinder to a pressure of P_1 and the equilibrium cell was recorded to be P_0. The needle valve between the two chambers was turned on to let CO_2 be introduced to equilibrium cell. Absorption equilibrium was thought to be

obtained when the pressures of the two chambers remained constant for at least 1 h. The equilibrium pressures were denoted as P_2 for the equilibrium cell and P_1' for the gas reservoir. The CO_2 partial pressure in the equilibrium cell was $P_S = P_2 - P_0$. The CO_2 uptake, $n(P_S)$, can thus be calculated using the following equation

$$n(P_S) = \rho_g(P_1, T)V_1 - \rho_g(P_1', T)V_1 - \rho_g(P_S, T)(V_2 - \omega / \rho_{ILs}) \quad \text{(S1)}$$

where ρ_g (Pi, T) represents the density of gas in mol/cm^3 at Pi (i = 1, S) and ρ_{ILs} is the density of the ionic liquid sample in g/cm^3 at temperature. V_1 and V_2 represent the volumes in cm^3 of the two chambers. Subsequent determination of solubility data at elevated pressures were performed by introducing more CO_2 into the equilibrium cell to reach new equilibrium. Duplicate experiments for each sample were preformed to obtain the averaged values of gas solubility. The solubility of N_2 in PAAILs was tested in the pressure range of 0–3 bar at 313.2 K, which used the same approach as the measurement of CO_2 solubility.

5. Supplementary data

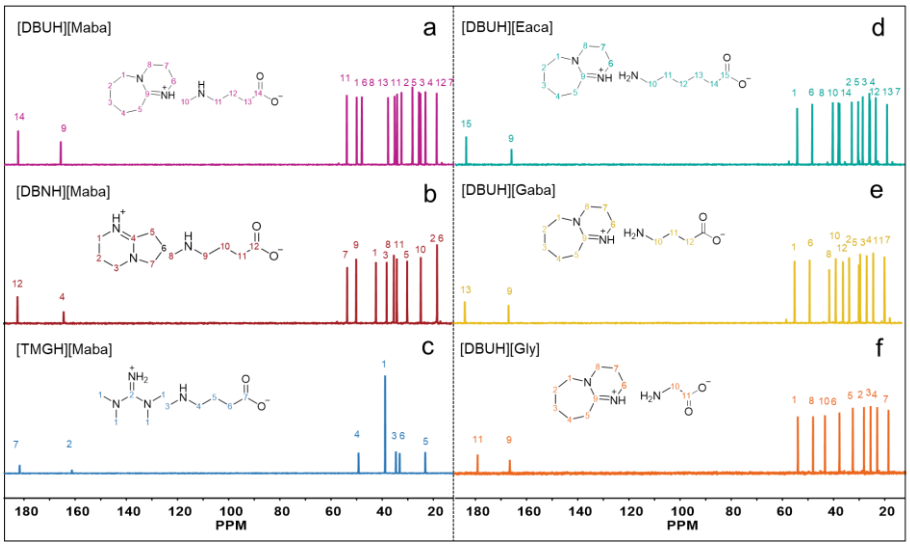
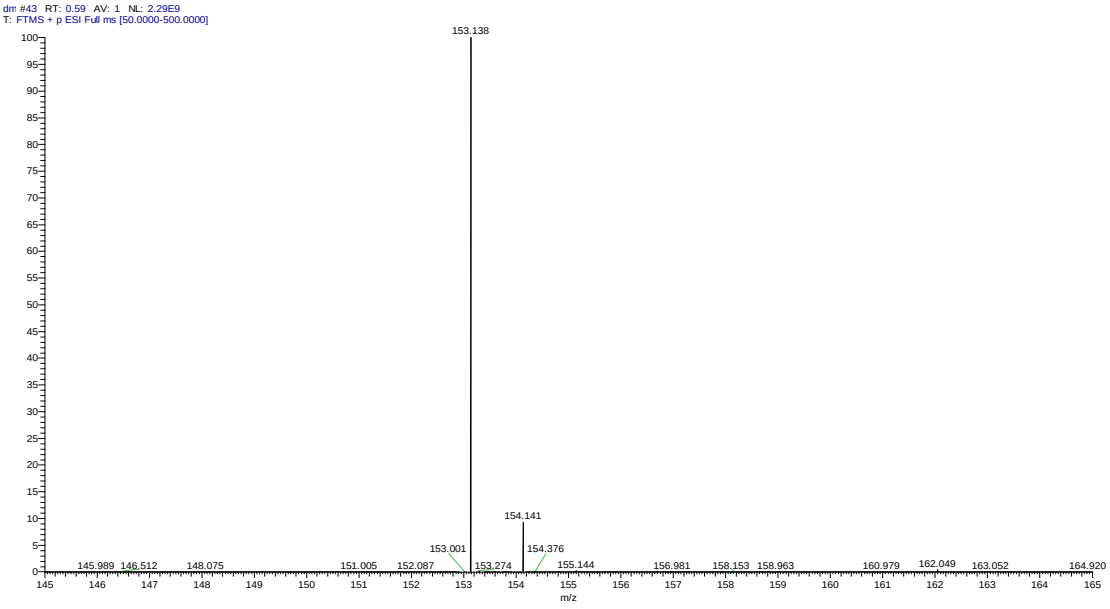


Figure S1. ^{13}C NMR of PAAIL.

a



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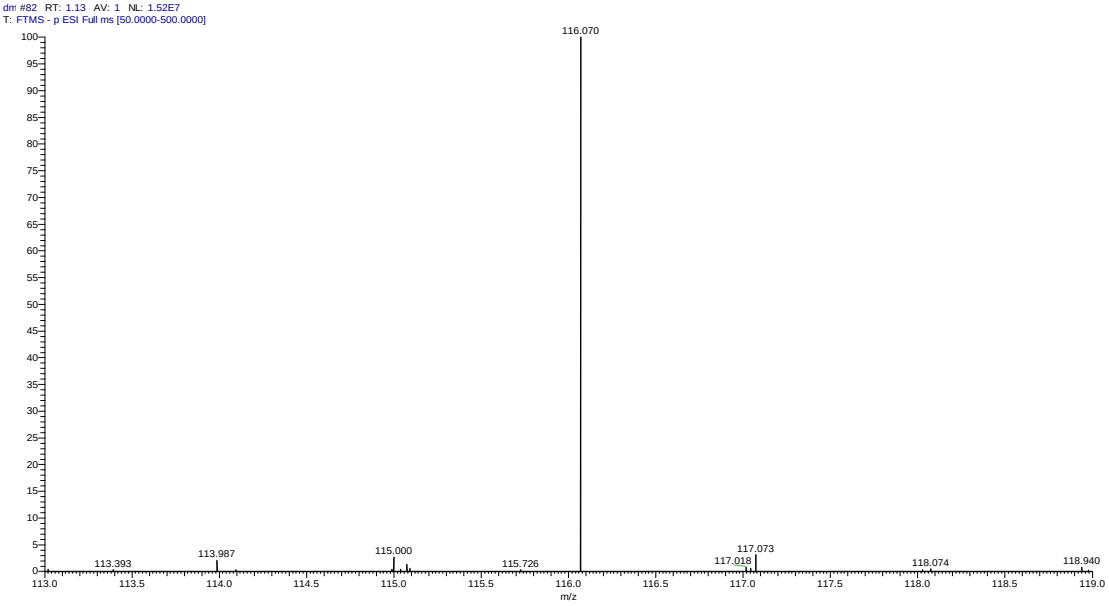
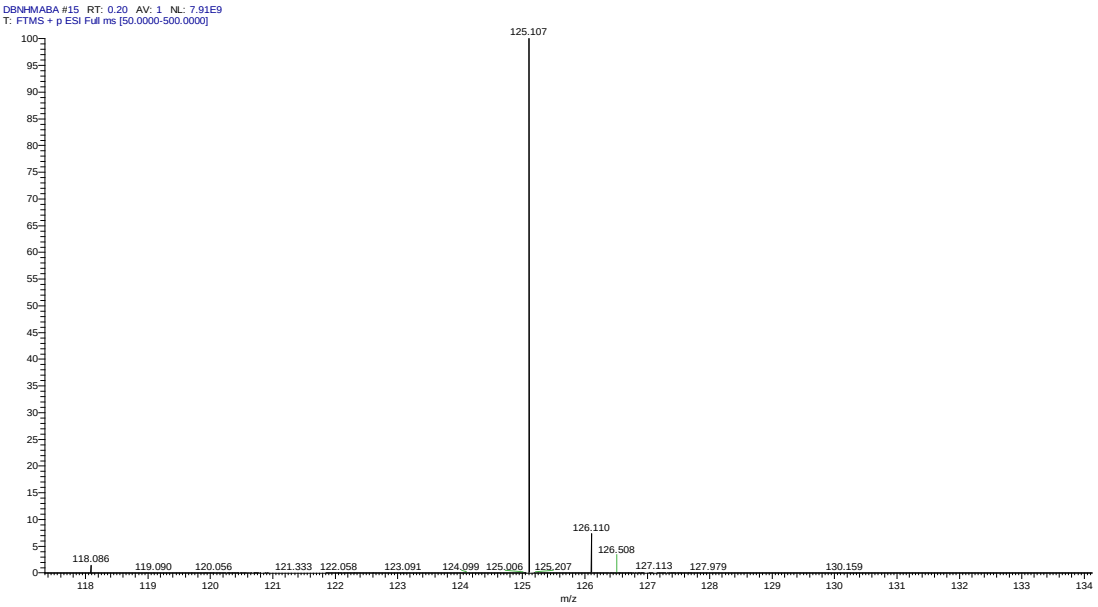


Figure S2. ESI-MS of [DBUH] (a) and [Maba] (b).

a



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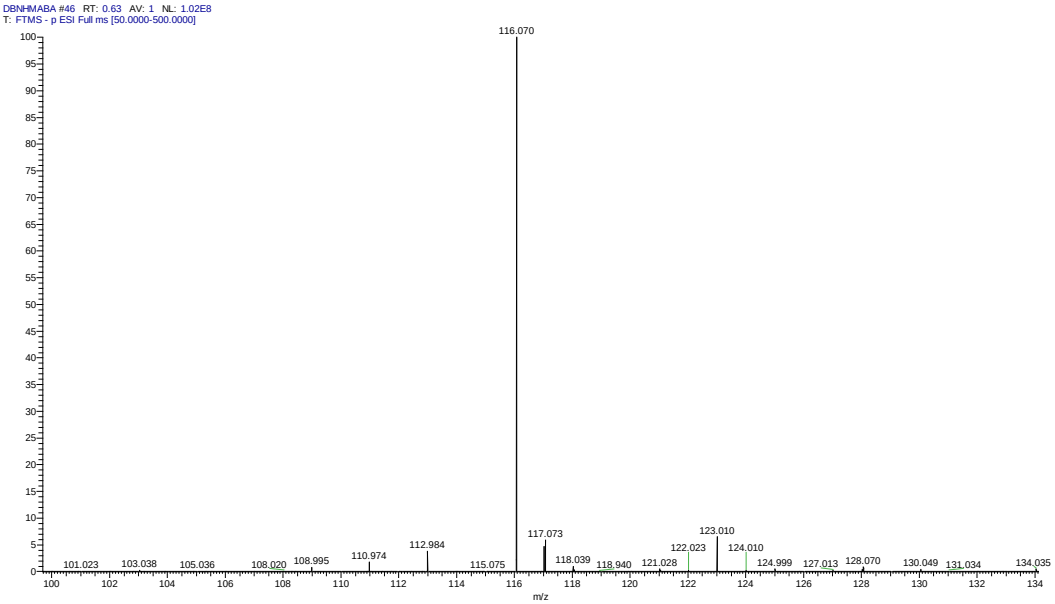
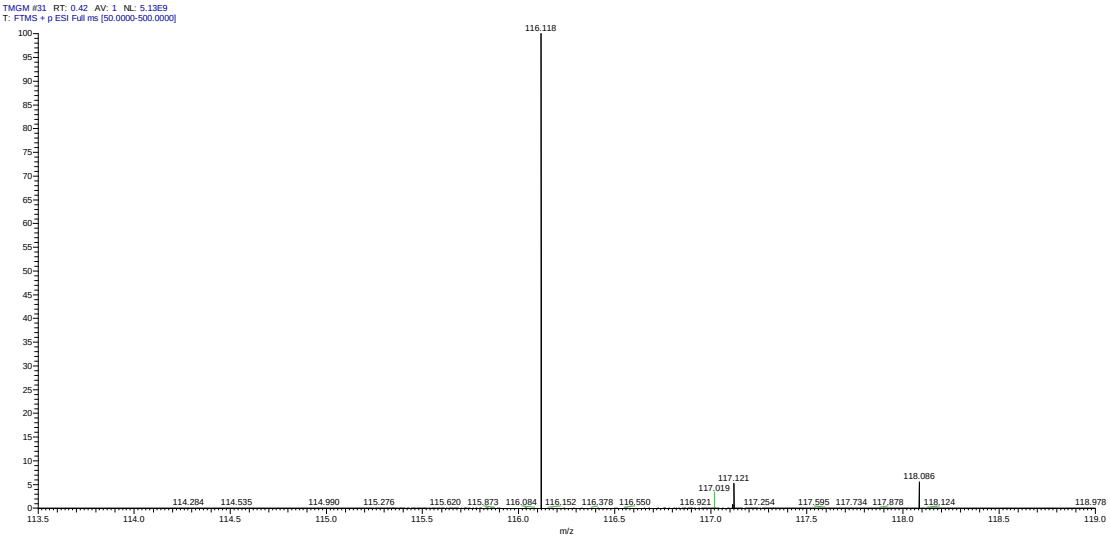


Figure S3. ESI-MS of [DBNH] (a) and [Maba] (b).

a



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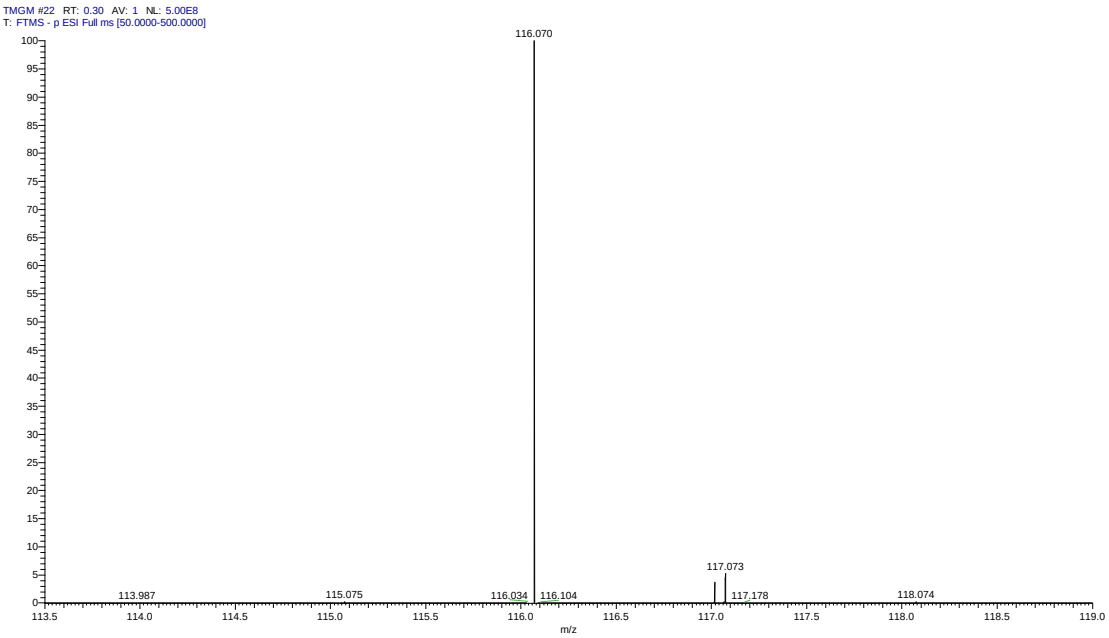

Figure S4. ESI-MS of [TMGH] (a) and [Maba] (b).

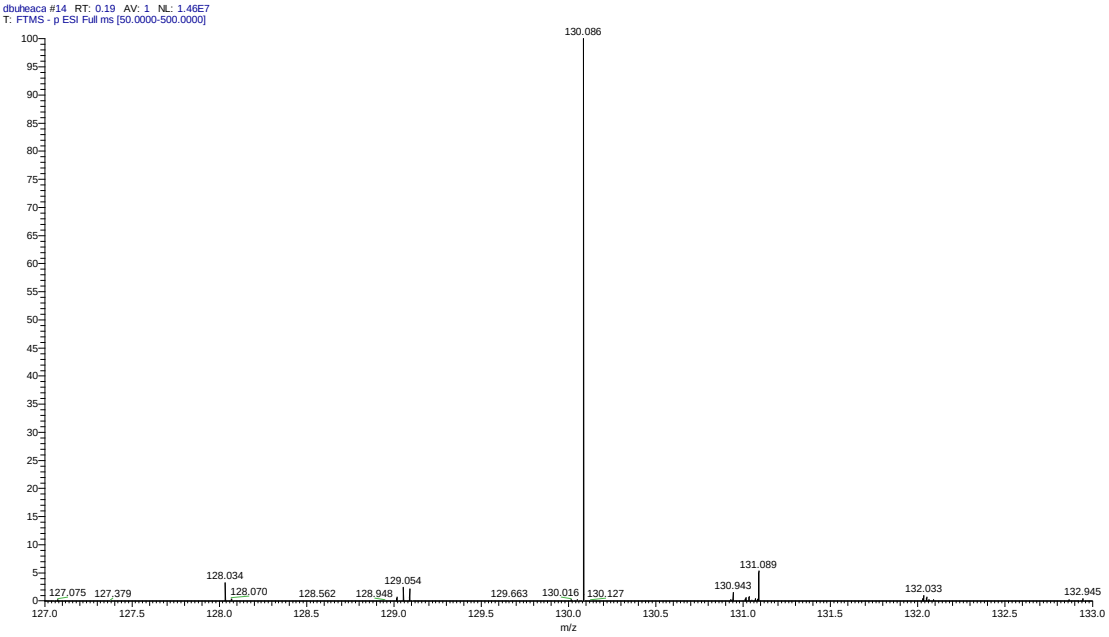

Figure S5. ESI-MS of [Eaca].

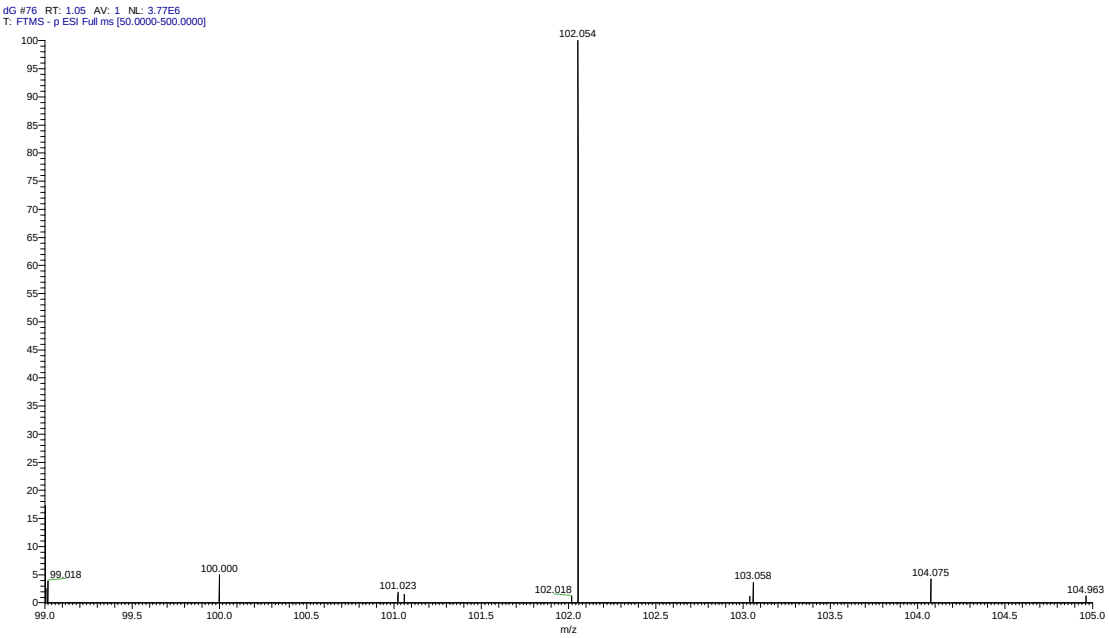

Figure S6. ESI-MS of [Gaba].

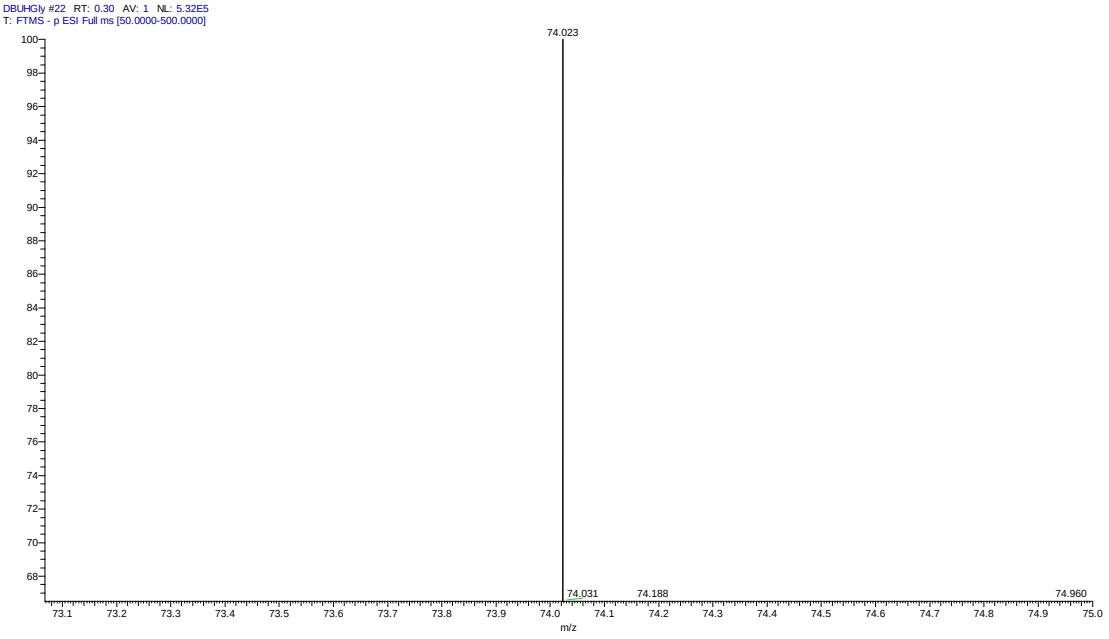

Figure S7. ESI-MS of [Gly].

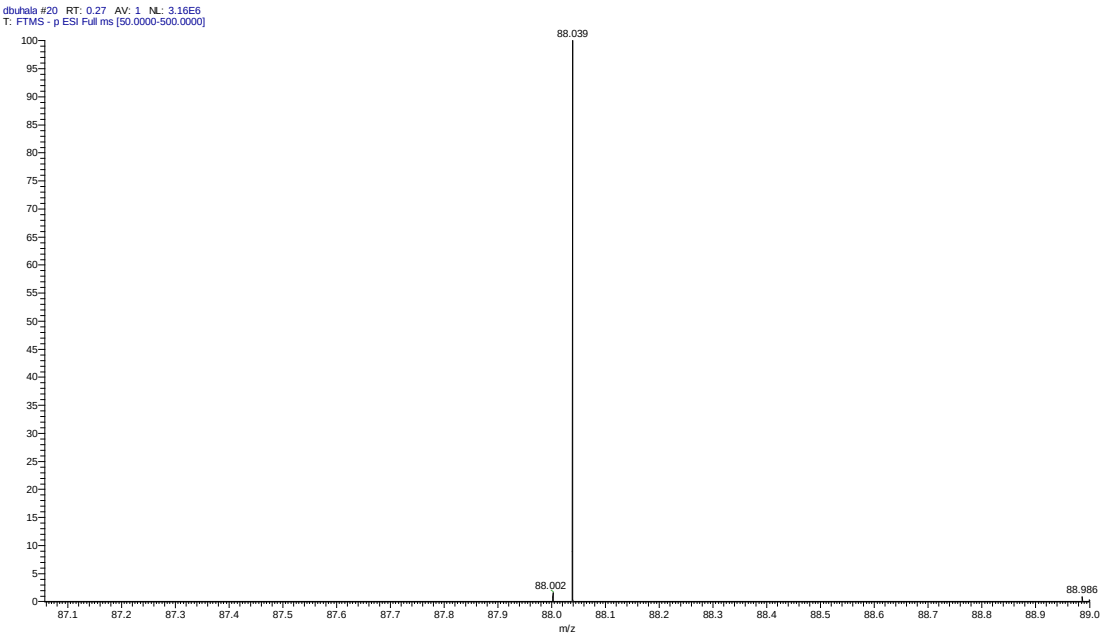

Figure S8. ESI-MS of [β-Ala].

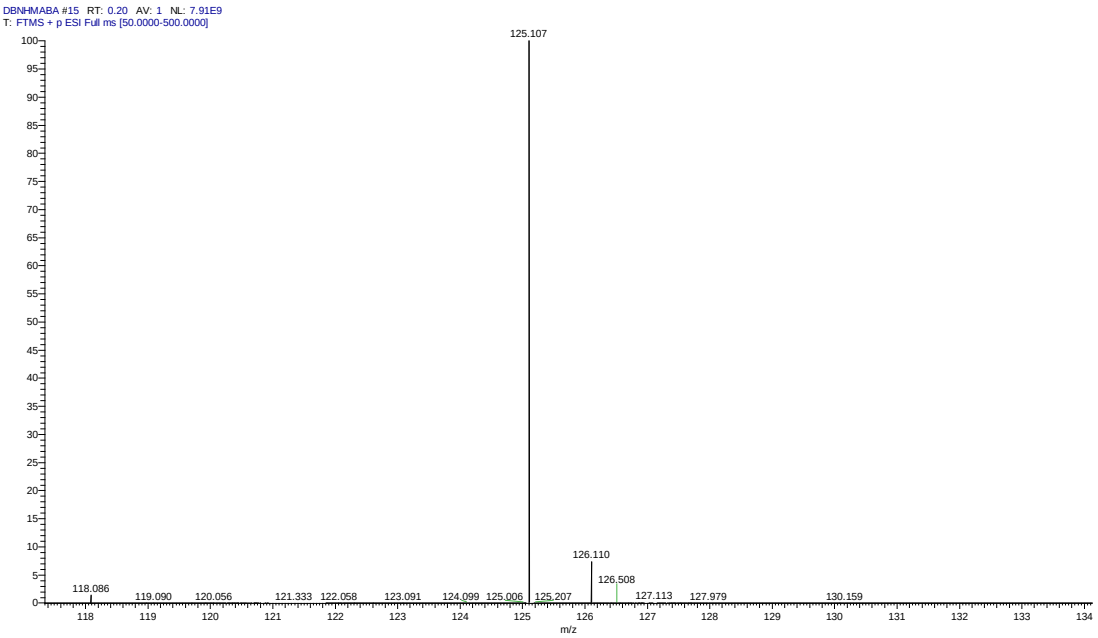

Figure S9. ESI-MS of [Val].

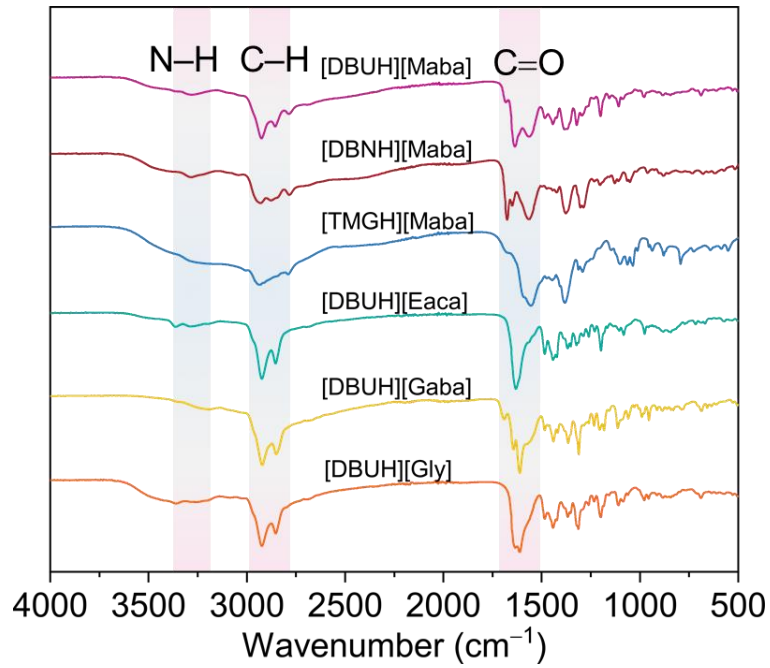

Figure S10. FTIR of PAAIL

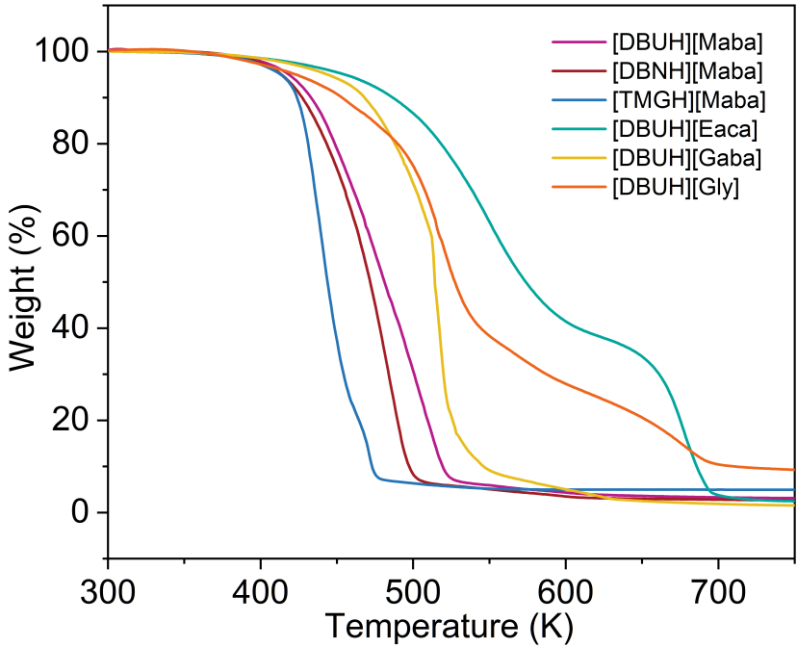

Figure S11. TG of PAAIL.

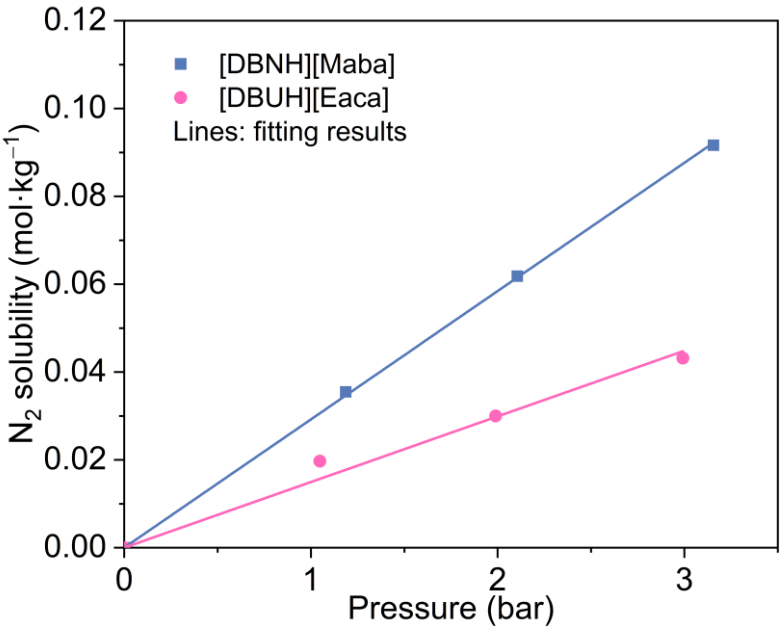

Figure S12. Solubility of N_2 in PAAILs.

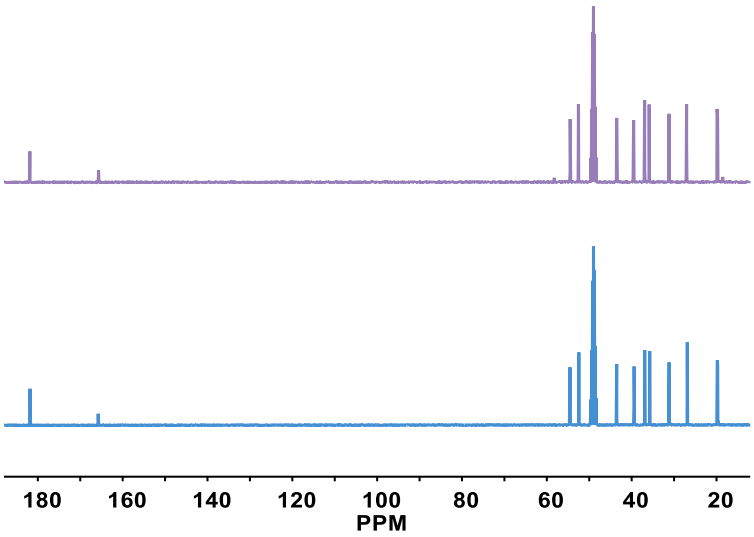

Figure S13. ^{13}C NMR of the fresh (up) and reused (below) [DBNH][Maba].

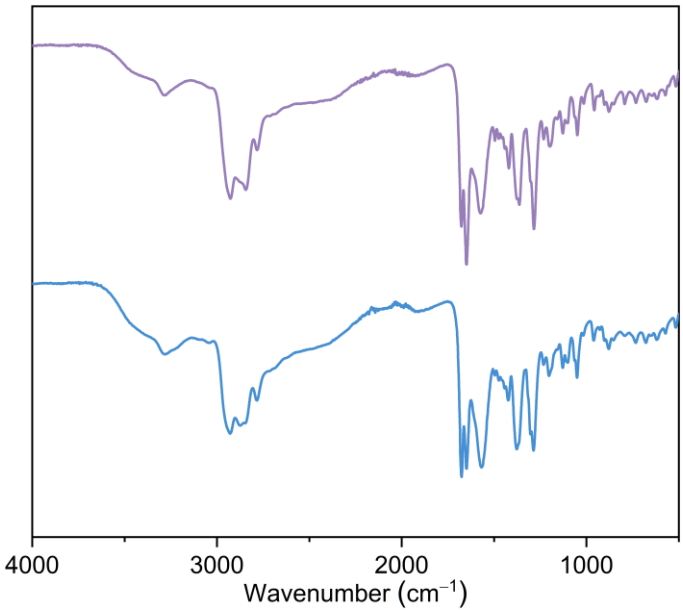

Figure S14. FTIR of the fresh (up) and reused (below) [DBNH][Maba].

Table S1. The Cartesian coordinates of optimized structure ([DBNH][Maba]).

# opt freq b3lyp/6-311+g(d) scrf = (solvent = ethanol, read, pcm) scf = direct test			
C	-4.5517	-2.98801	0.92025
N	-3.43425	-2.15202	0.483483
C	-3.77745	-0.72777	0.432472
C	-2.58543	0.131891	0.013682
C	-2.93217	1.619175	-0.03738
C	-1.80877	2.589321	-0.45891
O	-2.12789	3.798944	-0.54899
O	-0.64839	2.125025	-0.68373
H	-4.22353	-4.02608	1.009254
H	-4.98259	-2.67775	1.88649
H	-5.35053	-2.95282	0.17408
H	-2.65925	-2.27739	1.129172
H	-4.59256	-0.60791	-0.29118
H	-4.16994	-0.37013	1.40186
H	-1.75898	-0.02919	0.715875
H	-2.23111	-0.20522	-0.96555
H	-3.77196	1.787094	-0.72201
H	-3.29032	1.956735	0.942962
C	0.88971	-1.19746	-1.42249
C	2.247587	-1.7534	-1.84943
C	3.172455	-1.92456	-0.64253
N	3.142279	-0.70931	0.175423
C	2.156638	0.177018	0.115244

N	1.0725	0.008886	-0.60492
C	4.26183	-0.26645	1.02245
C	3.651968	0.897764	1.82207
C	2.473825	1.384546	0.95224
H	0.288811	-0.92478	-2.29009
H	0.326291	-1.9394	-0.84831
H	2.11377	-2.71567	-2.34619
H	2.709565	-1.07244	-2.5697
H	4.202554	-2.09232	-0.96258
H	2.87369	-2.77712	-0.025
H	0.343548	0.750092	-0.60592
H	4.600094	-1.0914	1.651329
H	5.096301	0.045739	0.386282
H	4.378988	1.684605	2.018348
H	3.280976	0.534558	2.78224
H	1.609687	1.722484	1.523463
H	2.761988	2.201311	0.283079

Table S2. The Cartesian coordinates of optimized structure ([DBNH][Maba]-0.5CO_2).

# opt freq b3lyp/6-311+g(d) scrf = (solvent = ethanol, read, pcm) scf = direct test			
C	-0.61706	-1.87675	-2.933528
N	-0.80629	-1.67535	-1.506399
C	-1.69723	-0.58722	-1.114202
C	-3.18062	-0.9793	-1.070178
C	-4.0744	0.212897	-0.732722
C	-5.58605	-0.06611	-0.6449
O	-6.31723	0.970075	-0.500814
O	-6.00789	-1.24196	-0.705242
C	0.023046	-2.29057	-0.574242
O	-0.12072	-2.02845	0.647487
O	0.894681	-3.11765	-1.039047
H	-0.17084	-2.85046	-3.115223
H	-1.58102	-1.83322	-3.447589
H	0.034304	-1.10847	-3.375416
H	-1.38124	-0.23188	-0.133386
H	-1.55644	0.24271	-1.820389
H	-3.48169	-1.40314	-2.034411
H	-3.31762	-1.77309	-0.329916
H	-3.77477	0.647664	0.229915
H	-3.93184	1.016633	-1.464695
C	1.298369	-5.01662	1.713558
N	2.264634	-4.2011	0.931278

C	2.945454	-3.13667	1.735502
C	4.036835	-2.43965	0.930763
C	4.693224	-1.32438	1.744645
C	5.822092	-0.55621	1.031028
O	6.282831	0.438917	1.679324
O	6.21594	-0.93972	-0.092209
H	0.859466	-5.76604	1.057083
H	1.80762	-5.50391	2.543802
H	0.519001	-4.35342	2.081425
H	1.720208	-3.73599	0.108224
H	2.967008	-4.81351	0.518128
H	3.352749	-3.60694	2.633718
H	2.159035	-2.44141	2.030305
H	3.608477	-2.02723	0.012829
H	4.795497	-3.16707	0.624716
H	5.115095	-1.72853	2.673055
H	3.943976	-0.59063	2.060865
C	-9.67966	-0.58117	-0.651868
C	-10.9441	-0.78582	0.182067
C	-11.8236	0.466062	0.157846
N	-10.9998	1.650712	0.411839
C	-9.68099	1.661546	0.246889
N	-9.00185	0.65652	-0.248003
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C	9.377127	4.185158	0.61706
C	10.18051	3.719694	-0.599449
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C	9.219467	1.522514	-0.074922
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N	-0.80629	-1.67535	-1.506399
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C	-5.58605	-0.06611	-0.6449
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C	0.023046	-2.29057	-0.574242
O	-0.12072	-2.02845	0.647487
O	0.894681	-3.11765	-1.039047
H	-0.17084	-2.85046	-3.115223
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H	-1.55644	0.24271	-1.820389
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H	-3.31762	-1.77309	-0.329916
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H	-3.93184	1.016633	-1.464695
C	1.298369	-5.01662	1.713558
N	2.264634	-4.2011	0.931278
C	2.945454	-3.13667	1.735502
C	4.036835	-2.43965	0.930763
C	4.693224	-1.32438	1.744645

C	5.822092	-0.55621	1.031028
O	6.282831	0.438917	1.679324
O	6.21594	-0.93972	-0.092209
H	0.859466	-5.76604	1.057083
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H	0.519001	-4.35342	2.081425
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H	3.608477	-2.02723	0.012829
H	4.795497	-3.16707	0.624716
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H	3.943976	-0.59063	2.060865
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N	-10.9998	1.650712	0.411839
C	-9.68099	1.661546	0.246889
N	-9.00185	0.65652	-0.248003
C	-11.5126	2.887753	1.021047
C	-10.338	3.867981	0.8565
C	-9.09683	2.960142	0.730744
H	-8.97278	-1.39936	-0.515633
H	-9.9213	-0.5268	-1.718494
H	-11.5096	-1.63612	-0.202815
H	-10.6658	-1.01662	1.214321
H	-12.5934	0.415537	0.930623
H	-12.3289	0.582724	-0.805791
H	-7.95609	0.734209	-0.351725
H	-12.4176	3.210114	0.503443
H	-11.7648	2.700077	2.069869
H	-10.265	4.563242	1.691785
H	-10.467	4.451009	-0.057266
H	-8.33472	3.342111	0.051901
H	-8.61456	2.782592	1.697198
C	8.021412	3.48147	0.679564
C	9.377127	4.185158	0.61706
C	10.18051	3.719694	-0.599449
N	10.1452	2.257712	-0.680856
C	9.219467	1.522514	-0.074922
N	8.201999	2.028357	0.579414
C	11.1922	1.444261	-1.319716

C	10.56183	0.040561	-1.360103
C	9.516705	0.057923	-0.22537
H	7.514442	3.692141	1.62174
H	7.368212	3.820708	-0.130915
H	9.232385	5.265643	0.56712
H	9.940258	3.971171	1.529982
H	11.22389	4.031253	-0.517942
H	9.780973	4.139146	-1.527925
H	7.475561	1.382449	0.977542
H	11.41987	1.843102	-2.309666
H	12.10456	1.483485	-0.71536
H	11.30544	-0.74555	-1.234222
H	10.06642	-0.11492	-2.320542
H	8.607763	-0.51164	-0.423841
H	9.933307	-0.30442	0.7206

Table S3. The Cartesian coordinates of optimized structure ([DBNH][Maba]-1CO_2).

# opt freq b3lyp/6-311+g(d) scrf = (solvent = ethanol, read, pcm) scf = direct test			
C	0.205407	-3.28004	1.441429
N	0.332846	-2.74025	0.088938
C	1.656012	-2.25976	-0.33241
C	1.876803	-0.80387	0.074439
C	3.225029	-0.24073	-0.35394
C	3.458335	1.248562	-0.02023
O	4.613511	1.689054	-0.216
O	2.479464	1.936312	0.412202
H	-0.72203	-3.83692	1.536621
H	1.042692	-3.95357	1.627183
H	0.221453	-2.48682	2.195882
H	2.399321	-2.9179	0.12202
H	1.730717	-2.36711	-1.415
H	1.081005	-0.21872	-0.38078
H	1.764816	-0.71001	1.158546
H	4.046085	-0.81001	0.093236
H	3.347159	-0.34236	-1.43908
C	-0.62329	1.154657	2.211676
C	-2.12592	1.397443	2.336178
C	-2.87569	0.781492	1.154397
N	-2.2069	1.15402	-0.09276
C	-0.94456	1.55113	-0.14484
N	-0.15278	1.606969	0.89944
C	-2.88311	1.221929	-1.3971

C	-1.7107	1.345848	-2.38531
C	-0.56576	1.943588	-1.54247
H	-0.073	1.703532	2.975342
H	-0.39293	0.091031	2.330258
H	-2.49463	0.965761	3.267019
H	-2.31716	2.473146	2.367229
H	-3.9027	1.147477	1.111698
H	-2.90682	-0.30955	1.224465
H	0.872341	1.745128	0.73433
H	-3.47898	0.321908	-1.55136
H	-3.55093	2.08881	-1.41418
H	-1.96334	1.963765	-3.24495
H	-1.42458	0.35267	-2.72891
H	0.423488	1.572777	-1.80842
H	-0.53446	3.036063	-1.59346
C	-0.73318	-2.3819	-0.65596
O	-0.68375	-1.82723	-1.74854
O	-1.92498	-2.706	-0.07738
H	-2.60999	-2.46157	-0.71437
C	0.205407	-3.28004	1.441429
N	0.332846	-2.74025	0.088938
C	1.656012	-2.25976	-0.33241
C	1.876803	-0.80387	0.074439
C	3.225029	-0.24073	-0.35394
C	3.458335	1.248562	-0.02023
O	4.613511	1.689054	-0.216
O	2.479464	1.936312	0.412202
H	-0.72203	-3.83692	1.536621
H	1.042692	-3.95357	1.627183
H	0.221453	-2.48682	2.195882
H	2.399321	-2.9179	0.12202
H	1.730717	-2.36711	-1.415
H	1.081005	-0.21872	-0.38078
H	1.764816	-0.71001	1.158546
H	4.046085	-0.81001	0.093236
H	3.347159	-0.34236	-1.43908
C	-0.62329	1.154657	2.211676
C	-2.12592	1.397443	2.336178
C	-2.87569	0.781492	1.154397
N	-2.2069	1.15402	-0.09276
C	-0.94456	1.55113	-0.14484
N	-0.15278	1.606969	0.89944
C	-2.88311	1.221929	-1.3971

C	-1.7107	1.345848	-2.38531
C	-0.56576	1.943588	-1.54247
H	-0.073	1.703532	2.975342
H	-0.39293	0.091031	2.330258
H	-2.49463	0.965761	3.267019
H	-2.31716	2.473146	2.367229
H	-3.9027	1.147477	1.111698
H	-2.90682	-0.30955	1.224465
H	0.872341	1.745128	0.73433
H	-3.47898	0.321908	-1.55136
H	-3.55093	2.08881	-1.41418
H	-1.96334	1.963765	-3.24495
H	-1.42458	0.35267	-2.72891
H	0.423488	1.572777	-1.80842
H	-0.53446	3.036063	-1.59346
C	-0.73318	-2.3819	-0.65596
O	-0.68375	-1.82723	-1.74854
O	-1.92498	-2.706	-0.07738
H	-2.60999	-2.46157	-0.71437