Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

The effect of an electron-withdrawing group in the imidazolium cation: the case of nitro-functionalized imidazolium salts as acidic catalysts for the acetylation of glycerol

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1. Theoretical calculations

The conceptual density functional theory (CDFT) provides several descriptors that can give information about the reactivity of a system, based only in ab initio calculations using a chemical structure.[1] These descriptors can be employed as quantitative and semi-quantitative indices of reactivity, and can help to rationalize chemical interactions in reactional systems. They are mathematically derived coefficients from the DFT formulism that comprehend physical and chemical meanings explored by the theories of Mulliken, Fukui and Pearson.[2] The rationalization of the effects relevant to a chemical reaction used in the CDFT works with descriptors of electron transfer tendencies, polarizability and energy variation in function of the electron density changes. The reaction descriptors originate from the total differential equation of electronic energy (dE) in function to the variation of the number of electrons (dN) and the external electrostatic potential (dv), as represented in Equation 1, where "r" is a three-dimensional space variable.

Eq. 1 $\mathrm{dE} = \mu \mathrm{dN} + \int \rho\,(\mathrm{r})\mathrm{dv}(\mathrm{r})\mathrm{dr}$

For this work, the following descriptors were calculated:[3] I) The chemical hardness, which is the second derivative of the energy in respect to the change in the number of electrons (Eq. 2), represent the electron escape resistance and resistance to change the polarizations of electronic density. II) The electrophilicity, which is the stabilization energy of a system that has received electron density (Eq. 3). III) The electronegativity, which describes the tendency to receive electron density (Eq. 4). IV) Another descriptor was calculated using the previously described descriptors, the net electron transfer from one chemical system to another (Eq. 5).

Eq. 2 $\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_v \approx \frac{E_{LUMO} - E_{HOMO}}{2}$

Eq. 3 $\omega = \frac{\chi^2}{2\eta}$

Eq. 4 $\chi = -\frac{E_{HOMO} + E_{LUMO}}{2}$

Eq. 5 $\Delta N = \frac{\chi_a - \chi_b}{2(\eta_a + \eta_b)}$

The counterpoise correction[4] was used to correct basis set sobreposition errors (BSSE). A simple step by step description of this method can be found in the ORCA Manual.[5]

2. Computational data

Three-dimensional structures optimized at the B3LYP-D3/6-31+G* level used in this study and their energies.

Glycerol

C	-1.303759	0.343324	-0.238812
C	-0.026507	-0.359196	-0.718530
H	-0.045193	-0.425931	-1.815574
O	0.020619	-1.692360	-0.204686
H	-2.182769	-0.123717	-0.693412
H	-1.285221	1.403683	-0.531052
O	-1.469685	0.195642	1.171399
C	1.245096	0.388561	-0.306615
H	2.125804	-0.123053	-0.716287
O	1.357106	0.502904	1.119969
H	1.228660	1.414112	-0.690423
H	-0.565063	-1.709993	0.574530
H	1.569020	-0.381364	1.461928
H	-0.668109	0.567383	1.587565

Energy = -344.622247867358 E_h

Acetic Acid

C	0.158490	0.277732	-0.026273
O	1.365734	0.260636	-0.143452
O	-0.576526	-0.862053	0.078418
C	-0.712822	1.505482	0.022861
H	0.049435	-1.610307	0.038085
H	-0.091739	2.398009	-0.061746
H	-1.274836	1.527402	0.963181
H	-1.443001	1.477930	-0.793880

Energy = -228.980808056332 E_h

Acetic anhydride

C	-0.486919	3.618103	-0.595721
C	0.766148	4.435202	-0.749487
H	-1.291189	4.247684	-0.211607
H	-0.310773	2.771633	0.076147
H	-0.772347	3.208823	-1.572066
O	1.850335	3.602152	-1.037026
O	0.878179	5.622254	-0.608213
C	2.935697	4.070156	-1.781960
C	4.187451	3.334720	-1.390341
O	2.825711	4.907414	-2.635556
H	4.470621	3.621937	-0.370597
H	4.993254	3.587783	-2.081396
H	4.010812	2.253773	-1.389286

Energy = -381.553988633430 E_h

[Hmim]Cl

N	1.089881	1.126065	0.122072
C	1.465612	-0.129930	-0.060408
N	0.382815	-0.939290	-0.016543
C	-0.729978	-0.142779	0.205573
C	-0.272715	1.147120	0.290702
H	-1.721507	-0.562902	0.282386
H	2.480700	-0.462114	-0.222838
H	1.849514	2.067678	0.142630
C	0.382600	-2.389427	-0.181422
H	1.412754	-2.731452	-0.295550
H	-0.056035	-2.865711	0.699908
H	-0.188538	-2.667160	-1.072033
Cl	2.908524	3.300626	0.191492
H	-0.804308	2.071374	0.459932

Energy = -726.135021234702 E_h

[Hmim][TsO]

N	-0.476881	-2.721664	-0.541314
C	0.816285	-2.951317	-0.746350
N	0.946898	-4.102326	-1.433980
C	-0.321196	-4.617450	-1.669944
C	-1.208362	-3.742988	-1.102956
H	-0.469288	-5.542690	-2.204948
H	1.596207	-2.289023	-0.388537

H	-0.819467	-1.837501	0.027664
C	2.210392	-4.702185	-1.854365
H	2.311229	-5.700166	-1.420114
H	2.248134	-4.768168	-2.945310
H	3.029140	-4.072775	-1.502065
C	-0.349632	5.984311	0.746720
C	-0.220833	4.487747	0.909444
C	-0.052637	3.920616	2.181037
C	-0.273516	3.630529	-0.199891
C	0.059708	2.539148	2.346969
C	0.002970	1.708697	1.227691
C	-0.162488	2.248103	-0.048332
H	-1.268503	6.357205	1.218339
H	0.490505	6.510458	1.217353
H	-0.376801	6.270972	-0.309852
H	-0.403102	4.051445	-1.194719
H	-0.007920	4.568255	3.054531
H	0.189575	2.096313	3.328973
H	-0.203444	1.592274	-0.912726
S	0.173987	-0.067164	1.432888
O	0.286603	-0.327665	2.879515
O	1.353431	-0.480638	0.608427
O	-1.105655	-0.637512	0.814495
H	-2.286469	-3.768031	-1.053118

Energy = -1160.490999921606 E_h

[NO_2Hmim]Cl

N	0.940591	1.180510	0.037876
C	1.367608	-0.064022	-0.019842
N	0.325607	-0.955918	-0.050256
C	-0.835482	-0.226125	-0.009602
C	-0.420174	1.086198	0.043816
N	-1.277853	2.244139	0.101370
H	-1.818841	-0.669328	-0.021124
H	2.404212	-0.371563	-0.041979
H	2.208193	2.519017	0.009959
O	-2.495691	2.022657	0.101163
O	-0.751341	3.351618	0.146158
C	0.429814	-2.410790	-0.114174
H	1.486529	-2.683674	-0.129631
H	-0.043576	-2.861207	0.762753
H	-0.049843	-2.783346	-1.023633
Cl	3.347709	3.191631	-0.042350

Energy = -930.557571821164 E_h

[NO_2Hmim][TsO]

N	-0.527349	-2.677778	-0.749790
C	0.739124	-2.930668	-1.020618
N	0.916471	-4.237872	-1.391580
C	-0.311906	-4.849904	-1.354766
C	-1.180301	-3.858930	-0.954156
N	-2.600937	-3.995801	-0.763742
H	-0.470408	-5.887568	-1.601806
H	1.537452	-2.202824	-0.954302
H	-0.998011	-1.113691	-0.110436
O	-3.232464	-3.003993	-0.407192
O	-3.080467	-5.116309	-0.978657
C	2.185252	-4.864478	-1.751103
H	2.149364	-5.226657	-2.782251
H	2.977061	-4.118299	-1.660139
H	2.397746	-5.696663	-1.074667
C	-0.439419	6.260542	1.221268
C	-0.215200	4.771943	1.108370
C	-0.134283	3.963372	2.249255
C	-0.086289	4.167737	-0.154567
C	0.064845	2.584606	2.145801
C	0.186346	2.017226	0.879577
C	0.113691	2.796029	-0.278755
H	-1.401595	6.547857	0.777964
H	-0.440561	6.586792	2.265928
H	0.340903	6.820494	0.691509
H	-0.142727	4.782394	-1.050164
H	-0.227994	4.415008	3.233733
H	0.129820	1.956335	3.027827
H	0.220086	2.332064	-1.254072
S	0.441536	0.261601	0.736073
O	0.738776	-0.296196	2.058417
O	1.386939	-0.013345	-0.363169
O	-1.035502	-0.173024	0.260205

Energy = -1364.915772313801 E_h

[HSO_3-pmim][BF_4]

N	-0.948864	-0.003213	1.525815
C	-0.465644	-1.131195	0.988768
N	-1.320786	-2.125842	1.247173
C	-2.386345	-1.623997	1.977404
C	-2.153218	-0.291285	2.152591
H	-2.732629	0.470368	2.650879
H	-3.208340	-2.247900	2.292485
H	0.420892	-1.248411	0.378905

C	-0.345977	1.340382	1.391424
C	-1.172386	-3.493236	0.733194
H	-2.064324	-3.755132	0.159450
H	-1.038272	-4.187804	1.566026
H	-0.304646	-3.514347	0.072046
H	-1.179176	2.039733	1.272929
C	0.591727	1.404794	0.186766
H	0.173991	1.579928	2.325853
H	0.068564	1.006609	-0.686723
H	1.476825	0.782210	0.357261
C	1.045451	2.832716	-0.099061
S	2.282008	2.857436	-1.433329
H	1.549480	3.299458	0.754587
H	0.226617	3.479196	-0.427873
O	2.543859	4.253624	-1.762252
O	1.448628	2.238524	-2.668122
O	3.361291	1.945019	-1.049594
H	1.494445	1.241723	-2.691721
B	0.519092	-1.446545	-2.271995
F	0.254865	-2.394462	-3.234065
F	1.353469	-0.406480	-2.779344
F	1.189879	-2.040672	-1.152483
F	-0.680474	-0.861196	-1.776986

Energy = -1431.858508884429 E_h

[HSO_3-pmim][H_2PO_4]

N	2.699344	1.116987	-0.354960
C	1.893086	0.353405	0.391706
N	1.079661	1.155256	1.093048
C	1.370924	2.473572	0.781018
C	2.393738	2.449021	-0.123504
H	2.921563	3.248751	-0.619012
H	0.830062	3.297731	1.219167
H	1.806839	-0.727933	0.383421
C	3.666100	0.585969	-1.324873
C	-0.082165	0.667171	1.859609
H	0.147320	-0.357031	2.156959
C	-1.332574	0.687399	0.976220
H	-0.180281	1.293191	2.751642
H	-1.603663	1.712772	0.704818
C	-2.509589	0.006584	1.671059
H	-1.092625	0.154207	0.054834
S	-3.859182	-0.333114	0.496368
H	-2.958599	0.627197	2.453394
H	-2.237640	-0.964320	2.094408
O	-5.065456	-0.631182	1.261595

O	-3.402919	-1.728753	-0.169122
O	-3.854227	0.730224	-0.515965
H	-2.621688	-1.614301	-0.784570
H	4.576566	0.269017	-0.809330
H	3.903855	1.376870	-2.038037
H	3.185330	-0.253319	-1.837110
P	0.281450	-2.073112	-1.267836
O	-1.216059	-1.452694	-1.717159
O	1.350035	-1.369912	-2.076649
O	0.260635	-1.994853	0.236077
O	0.162001	-3.629317	-1.765823
H	0.771045	-3.778057	-2.507406
H	-1.282889	-1.297433	-2.673988

Energy = -1650.921557836709 E_h

[HSO_3-pmim][TsO]

N	-1.902178	1.066475	-1.453341
C	-2.105449	1.254335	-0.143784
N	-3.330223	0.799187	0.162268
C	-3.914674	0.289833	-0.988082
C	-3.015659	0.454915	-1.999605
H	-3.063159	0.184711	-3.042967
H	-4.905435	-0.136314	-0.980230
H	-1.342305	1.627243	0.531013
C	-0.640513	1.325915	-2.154113
H	-0.838312	1.947547	-3.030708
H	-0.195064	0.372684	-2.445305
H	0.037311	1.828250	-1.463990
C	-4.002168	0.868776	1.477765
H	-4.566847	1.807010	1.513274
C	-3.048667	0.779831	2.665221
H	-4.718063	0.041158	1.493557
H	-2.330928	1.607365	2.653990
C	-2.296043	-0.549042	2.740748
H	-3.657387	0.918804	3.566484
S	-1.237806	-0.559819	4.222465
H	-1.650353	-0.714445	1.873310
H	-2.969878	-1.404720	2.847257
O	-2.027497	-1.073906	5.342377
O	-0.603466	0.758664	4.313933
O	-0.156392	-1.682490	3.860308
H	0.486027	-1.329656	3.154985
C	2.222594	-0.420229	-0.510325
C	2.101968	-1.372696	-1.519676
C	3.146082	-1.537343	-2.435720
C	4.312108	-0.766363	-2.350710

C	4.409356	0.184359	-1.319924
C	3.376834	0.361070	-0.402009
H	3.053263	-2.282742	-3.223271
C	5.448880	-0.956642	-3.326977
H	5.308729	0.791367	-1.236272
H	3.456207	1.099265	0.390634
H	1.202661	-1.978375	-1.576206
S	0.901395	-0.189569	0.682072
H	6.334281	-1.367817	-2.824755
H	5.748629	-0.004415	-3.781529
H	5.173507	-1.645077	-4.132806
O	-0.291429	-0.913387	0.137243
O	0.674232	1.288886	0.752760
O	1.415827	-0.772599	1.960634

Energy = -1902.033855472011 E_h

[HSO_3-pmim][HSO_4]

N	-0.012488	-0.075755	-1.749860
C	0.579736	1.015589	-1.250834
N	1.837880	1.066183	-1.697676
C	2.074477	-0.052678	-2.480966
C	0.914301	-0.769511	-2.515122
H	0.665507	-1.691847	-3.015701
H	3.032984	-0.231753	-2.942166
H	0.145318	1.706397	-0.539822
C	2.848271	1.999150	-1.185932
H	3.604323	2.160383	-1.956446
H	3.289498	1.582263	-0.276726
H	2.363740	2.944666	-0.939848
S	1.193443	0.957728	2.088158
O	0.525666	0.400173	3.313921
O	0.105885	2.093030	1.522043
O	1.282113	-0.060386	1.001872
O	2.412992	1.730856	2.313975
H	-0.796492	1.709332	1.646316
C	-1.319607	-0.574089	-1.293798
H	-1.886163	-0.900738	-2.171567
H	-1.836141	0.273398	-0.841238
C	-1.142776	-1.703977	-0.263771
H	-0.289825	-1.460380	0.378074
H	-0.906276	-2.643038	-0.779222
C	-2.399136	-1.917142	0.585099
S	-2.534814	-0.740636	1.963760
H	-2.406136	-2.902129	1.058786
H	-3.330218	-1.804316	0.018210
O	-1.375274	-1.231828	2.918933

O	-3.833996	-0.946973	2.594037
O	-2.210661	0.609623	1.432543
H	-0.596132	-0.541598	3.064964

Energy = -1707.013701122237 E_h

3. Spectral data

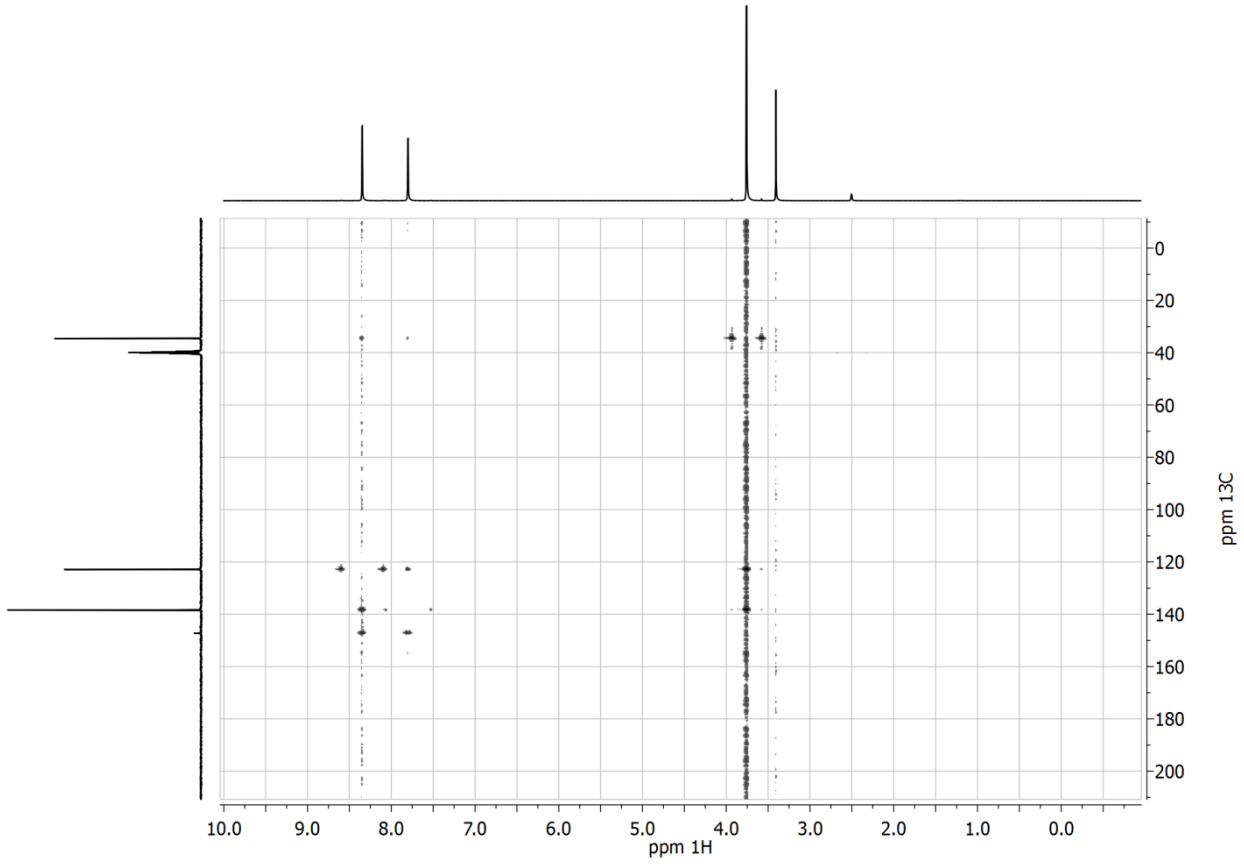

Fig. S1 HMBC analysis of 1-methyl-4-nitroimidazole in DMSO-d_6.

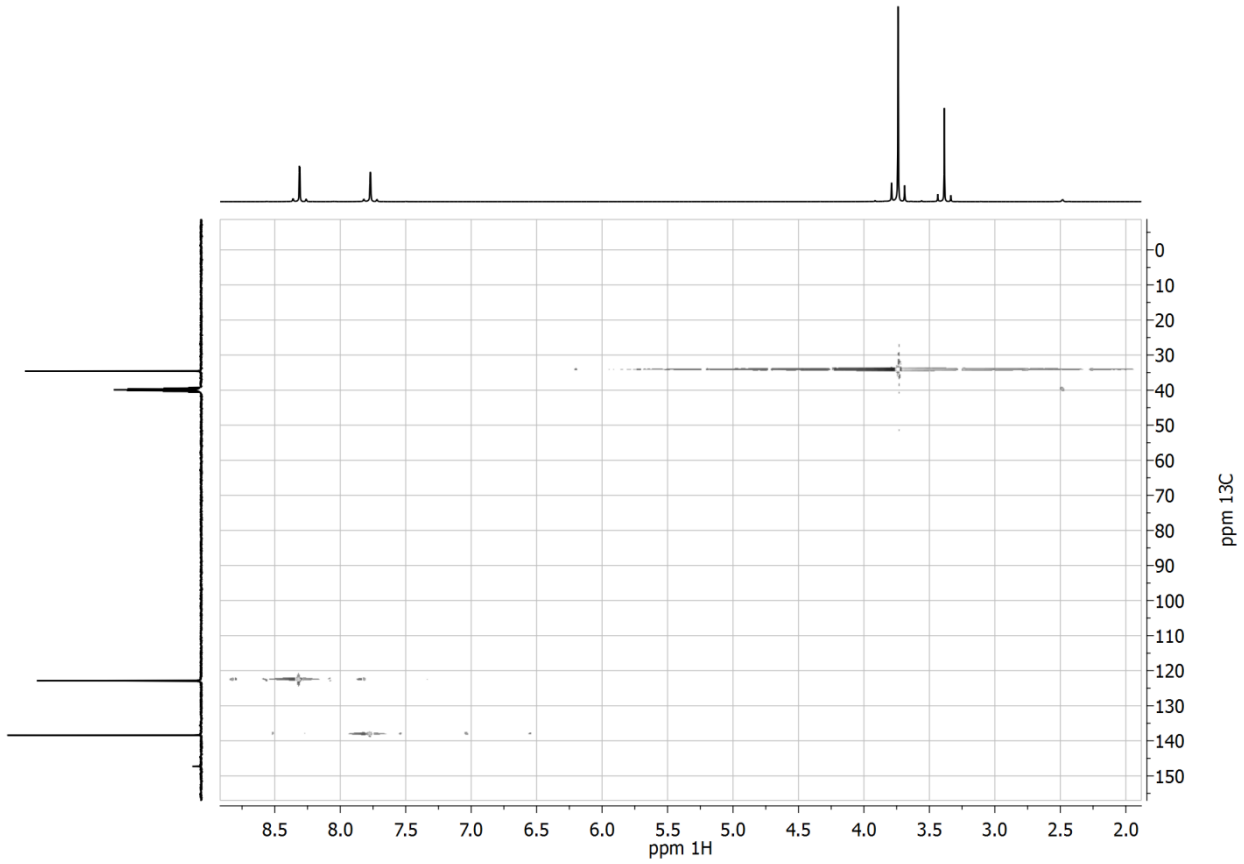

Fig. S2 HSQC analysis of 1-methyl-4-nitroimidazole in DMSO-d_6.

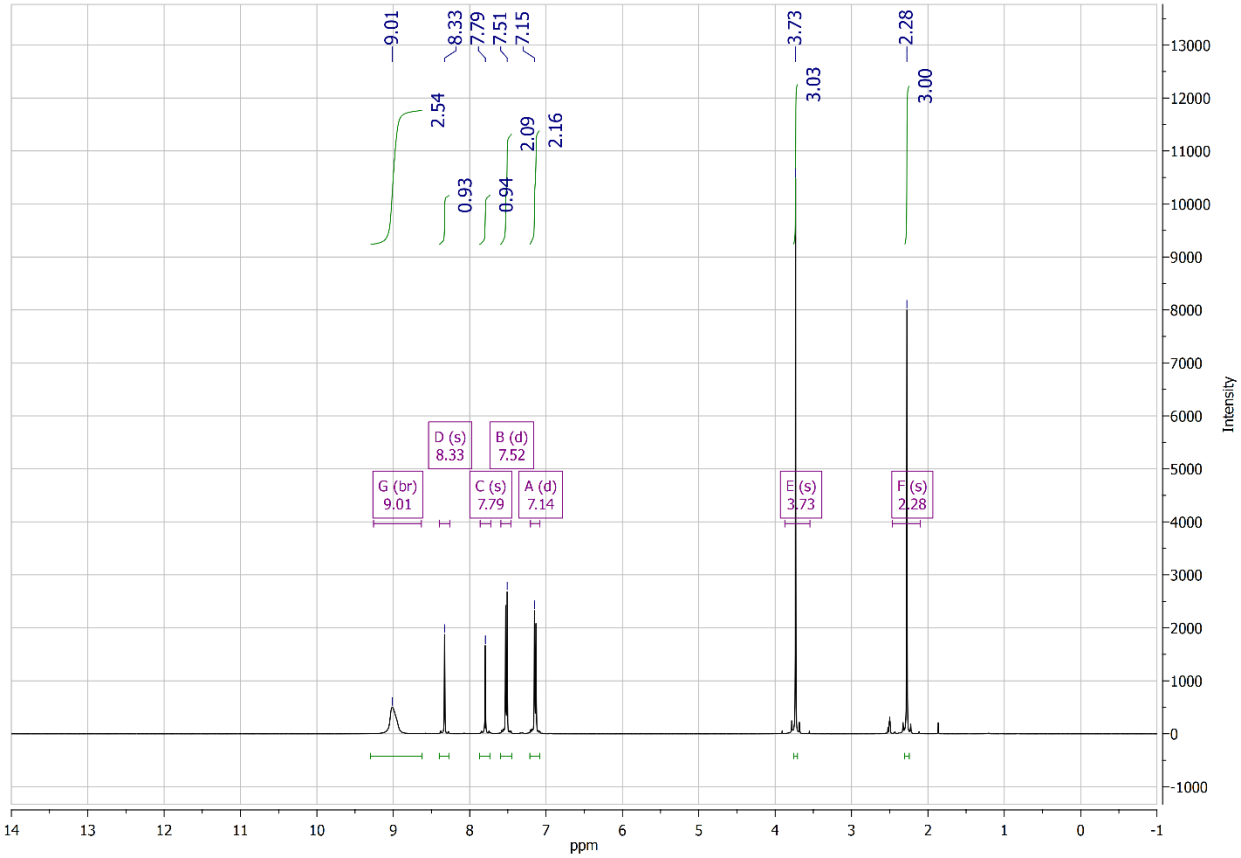

Fig. S3 ^{1}H NMR analysis of [NO_2Hmim][TsO]. δ_H (400 MHz, DMSO-d_6): 8.33 (1 H, s), 7.80 (1 H, s), 7.52 (2 H, d, *J* = 7.9 Hz), 7.14 (2 H, d, *J* = 7.8 Hz), 3.73 (3 H, s), 2.28 (3 H, s).

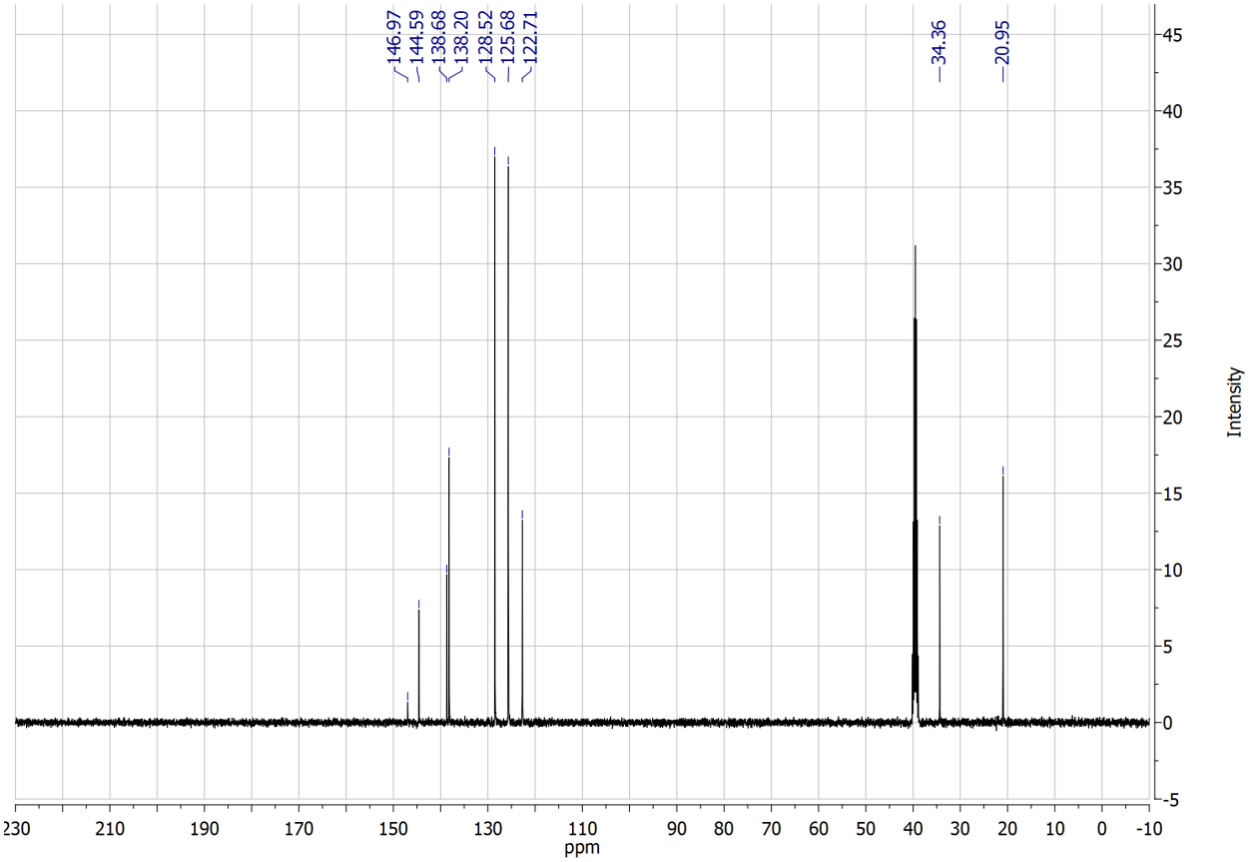

Fig. S4 ^{13}C NMR analysis of [NO_2Hmim][TsO]. δ_C (101 MHz, DMSO-d_6): 147.0, 144.6, 138.7, 138.2, 128.5, 125.7, 122.7, 34.4, 21.0.

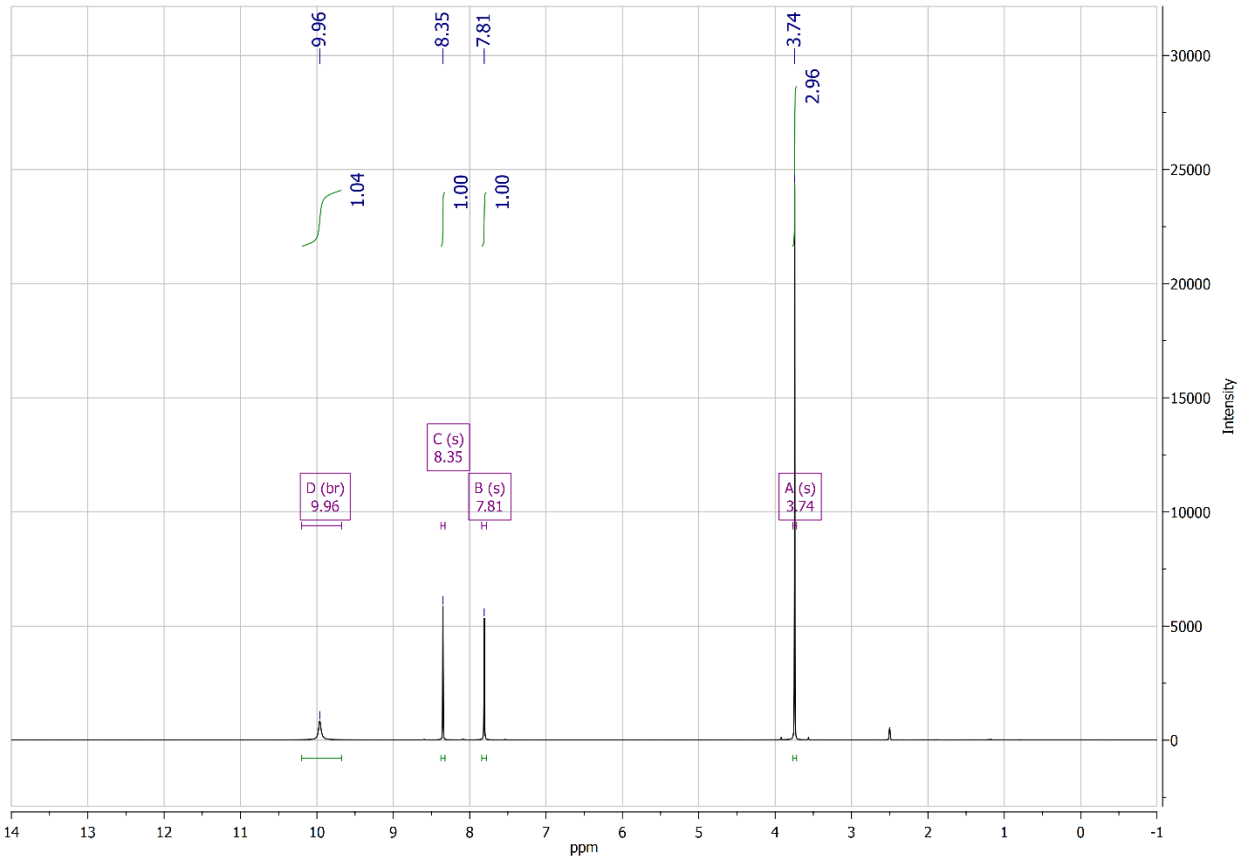

Fig. S5 ^{1}H NMR analysis of [NO_2Hmim]Cl. δ_H (400 MHz, DMSO-d_6): 9.96 (1 H, br), 8.35 (1 H, s), 7.81 (1 H, s), 3.74 (3 H, s).

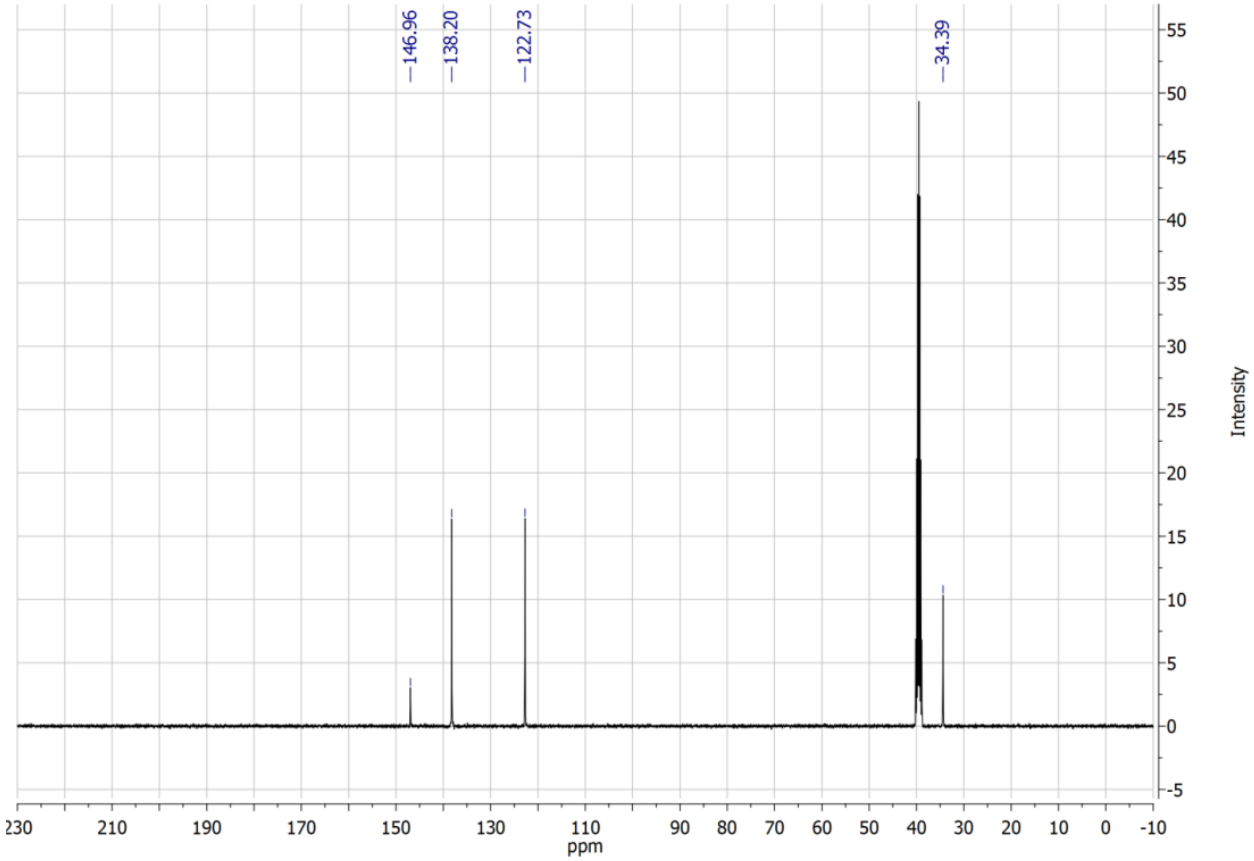

Fig. S6 ^{13}C NMR analysis of [NO_2Hmim]Cl. δ_C (101 MHz, DMSO-d_6): 147.0, 138.2, 122.7, 34.4.

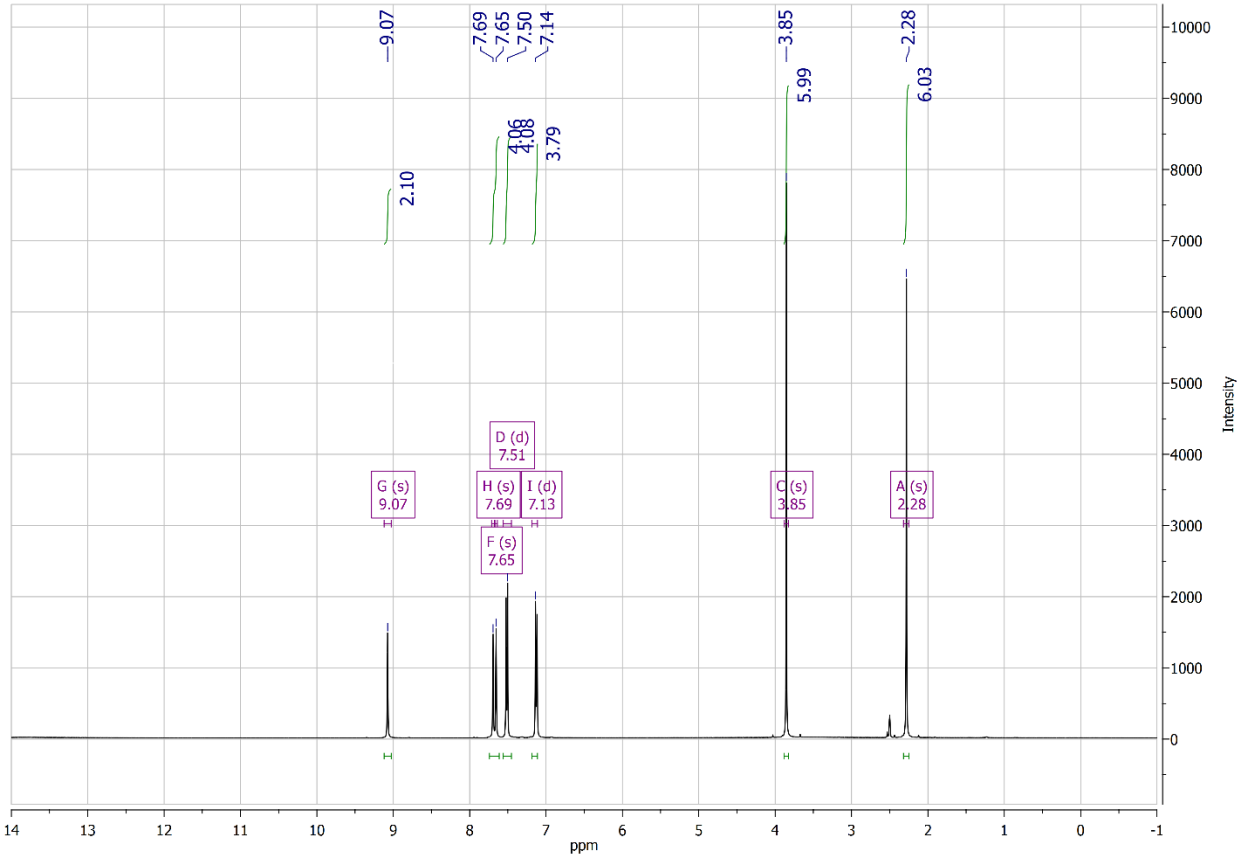

Fig. S7 ^{1}H NMR analysis of [Hmim][TsO]. δ_H (400 MHz, DMSO-d_6): 9.07 (1 H, s), 7.69 (1H, s), 7.65(1H, s), 7.50 (2 H, d, J = 8.0 Hz), 7.14 (2 H, d, J = 7.9 Hz), 3.85 (3 H, s), 2.28 (3 H, s).

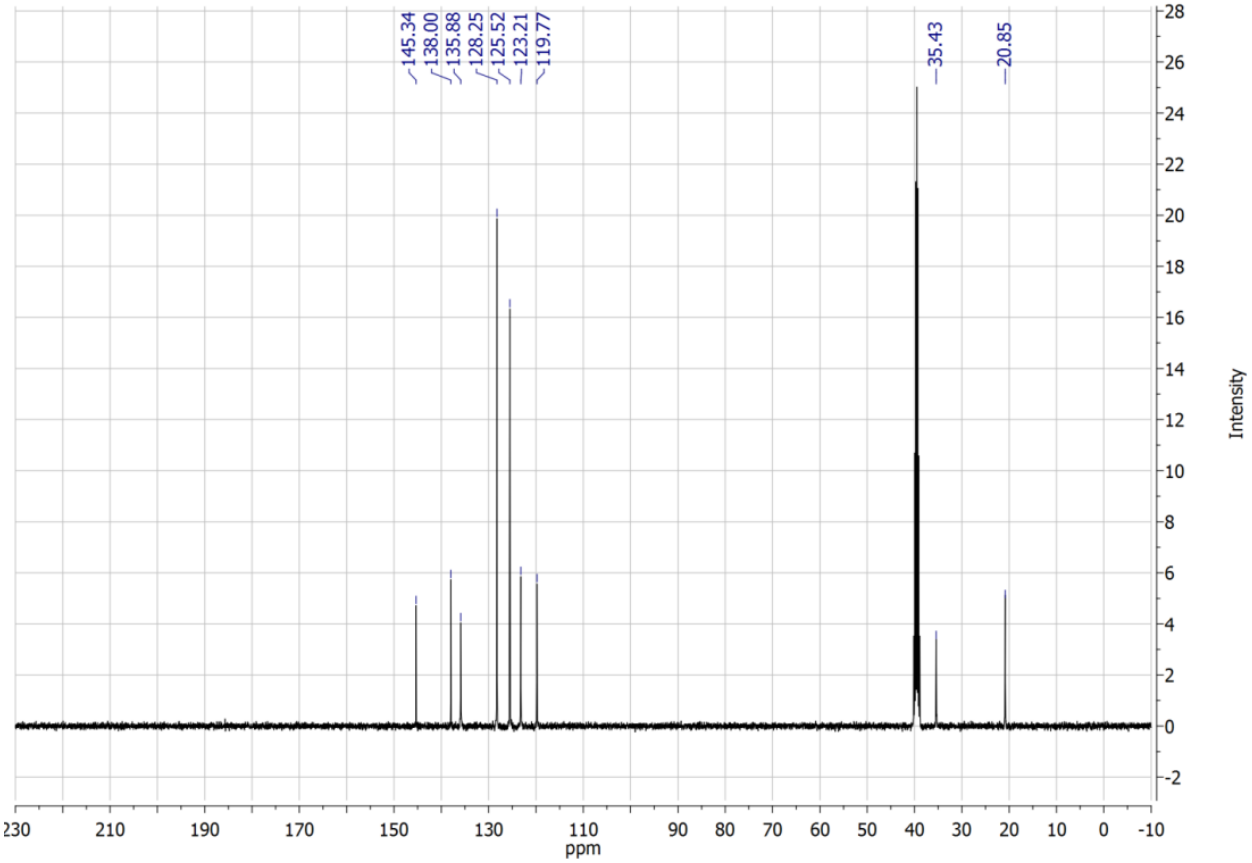

Fig. S8 ^{13}C NMR analysis of [Hmim][TsO]. δ_C (101 MHz, DMSO-d_6): 145.3, 138.0, 135.9, 128.3, 125.5, 123.2, 119.8, 35.4, 20.9.

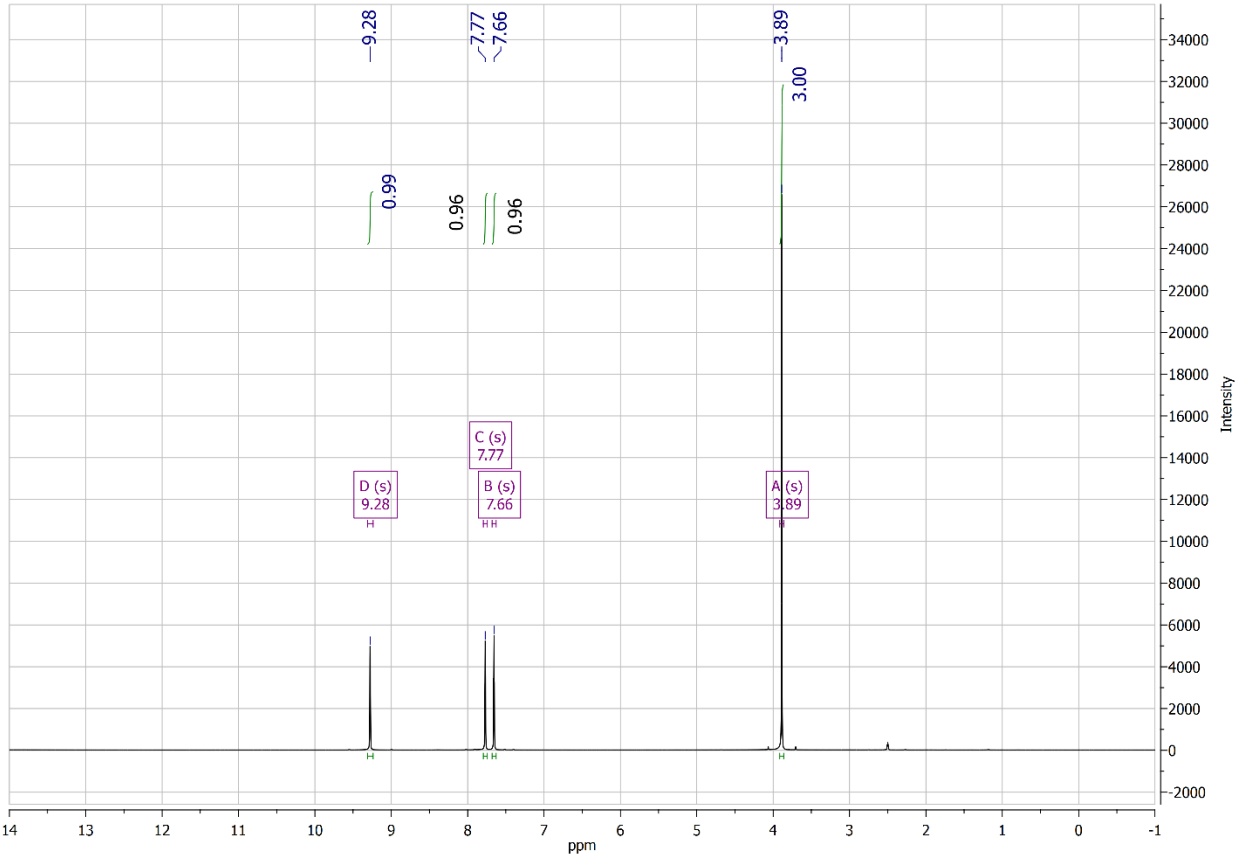

Fig. S9 ^{1}H NMR analysis of [Hmim]Cl. δ_H (400 MHz, DMSO-d_6): 9.28 (1 H, s), 7.77 (1 H, s), 7.66 (1 H, s), 3.89 (3 H, s).

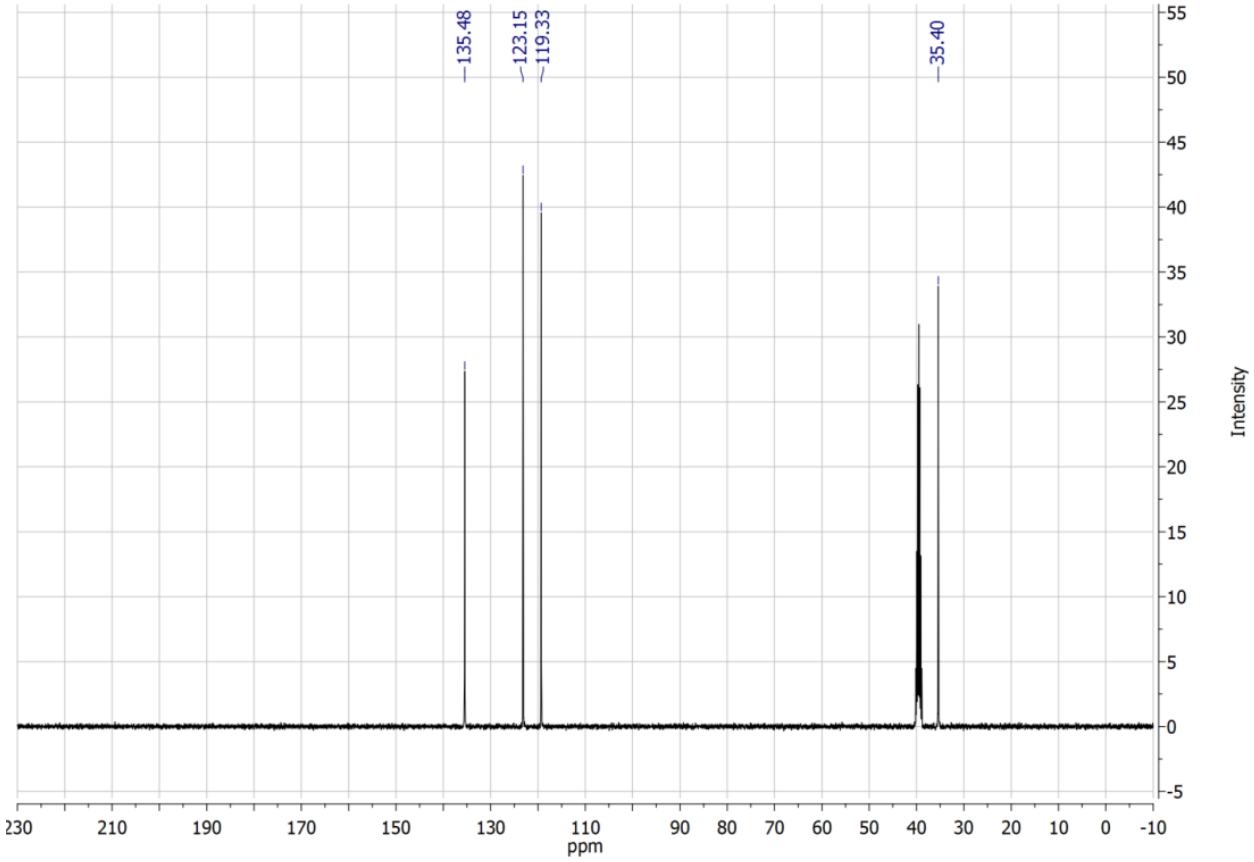

Fig. S10 ^{13}C NMR analysis of [Hmim]Cl. δ_C (101 MHz, DMSO-d_6): 135.5, 123.2, 119.3, 35.4.

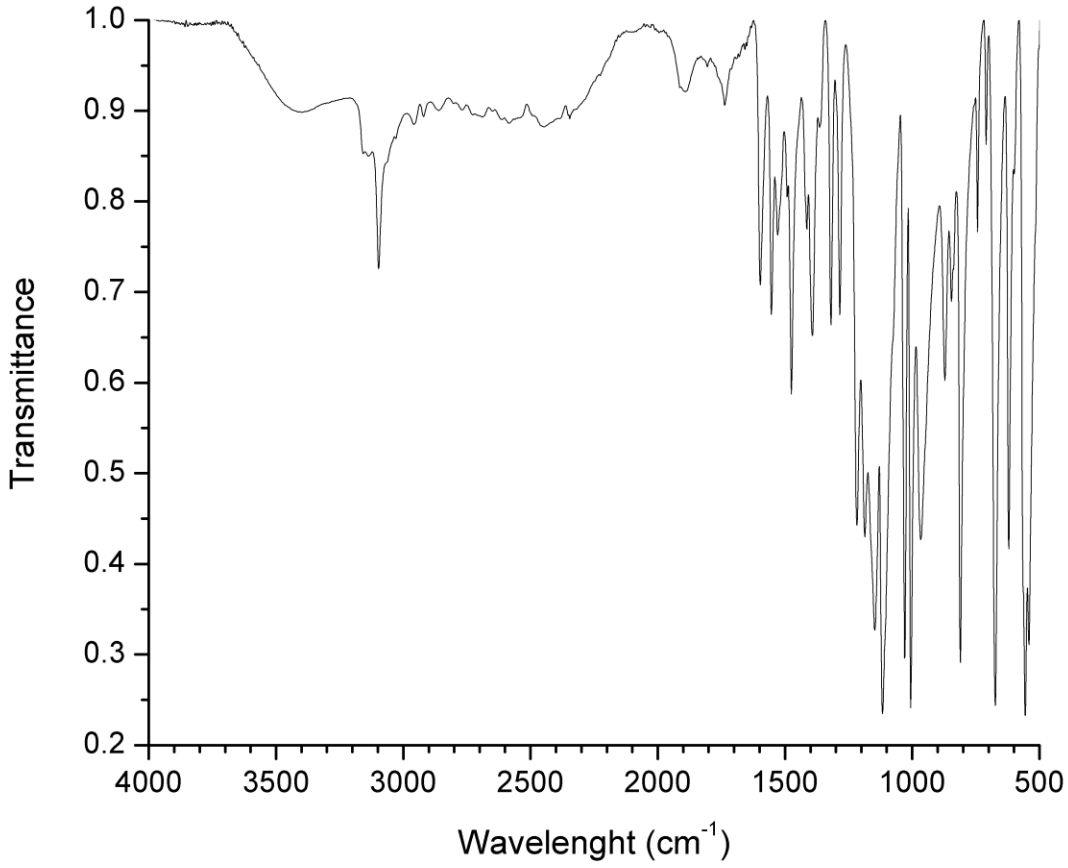

Fig. S11 ATR-FTIR analysis of [NO_2Hmim][TsO].

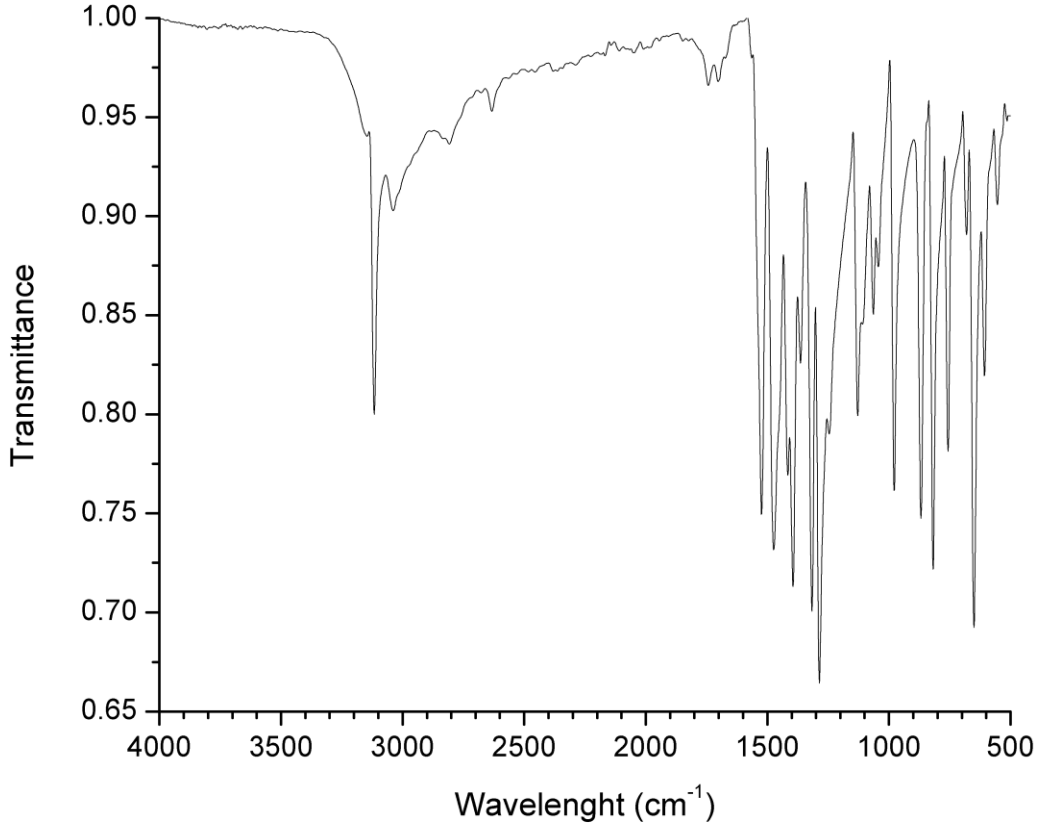

Fig. S12 ATR-FTIR analysis of [NO_2Hmim]Cl.

4. References

1. P. Geerlings, F. De Proft and W. Langenaeker, *Chem. Rev.*, 2003, **103**, 1793-1873.
2. L. R. Domingo, M. Ríos-Gutiérrez and P. Pérez, *Molecules*, 2016, **21**, 748.
3. P. K. Chattaraj, S. Giri and S. Duley, *Chem. Rev.*, 2011, **111**, PR43-PR75.
4. S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553-566.
5. F. Neese, in *Orca Manual 4.0*, https://orcaforum.cec.mpg.de/OrcaManual.pdf, 2017.