Supporting Information

Novel 2-Alkyl-1-Ethylpyridinium Ionic Liquids: Synthesis, Dissociation Energies and Volatility

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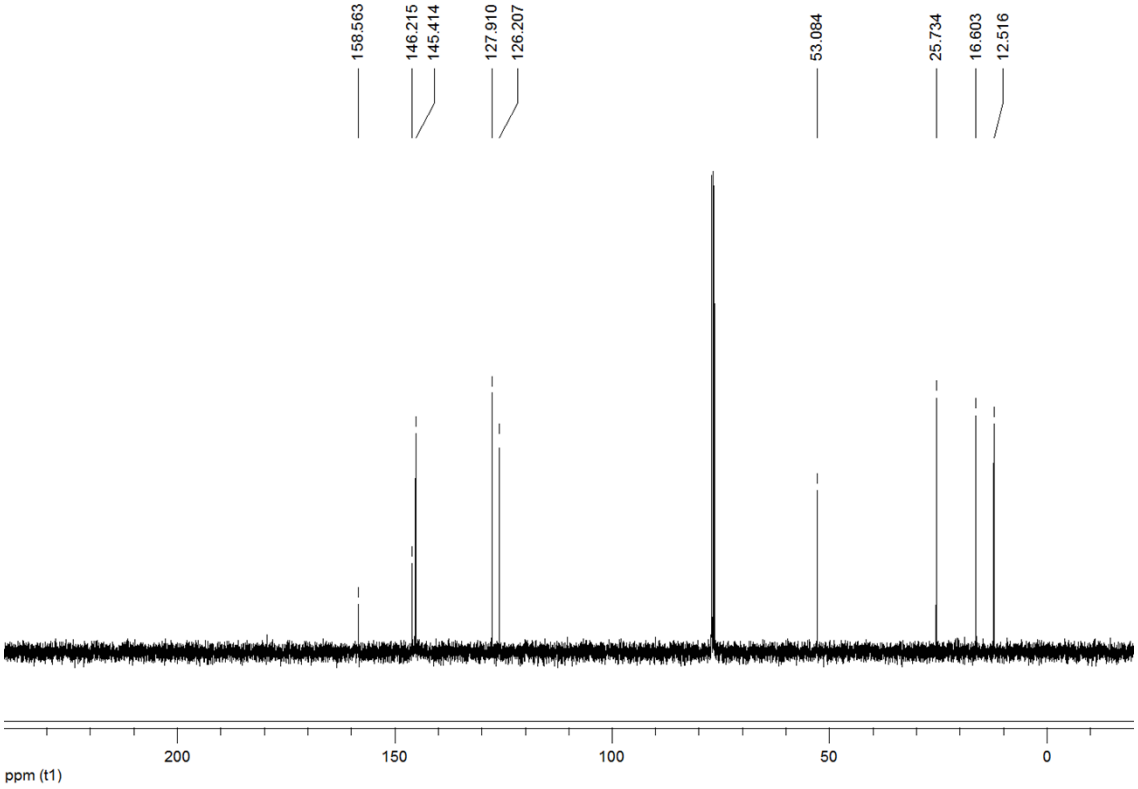
Supporting Information

Characterization of the 1-alkyl-2-ethylpyridinium ionic liquids (^{13}C NMR spectra)

1,2-Diethylpyridinium bromide (9).



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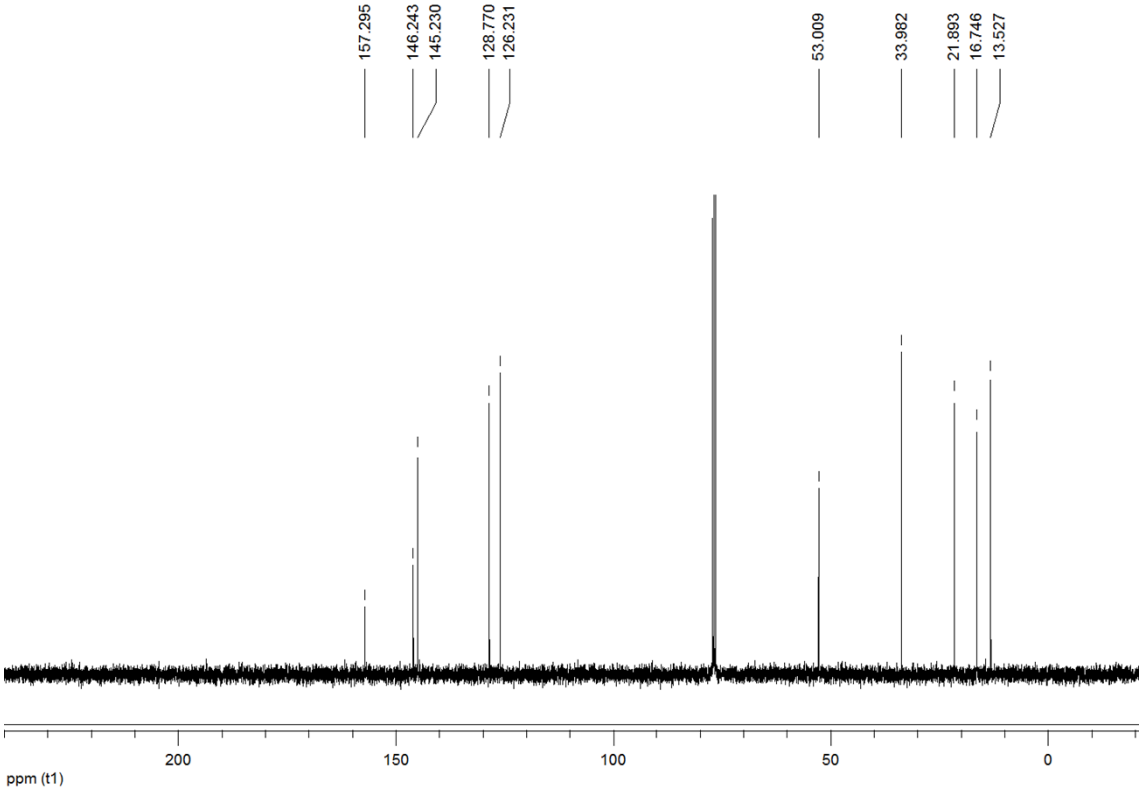

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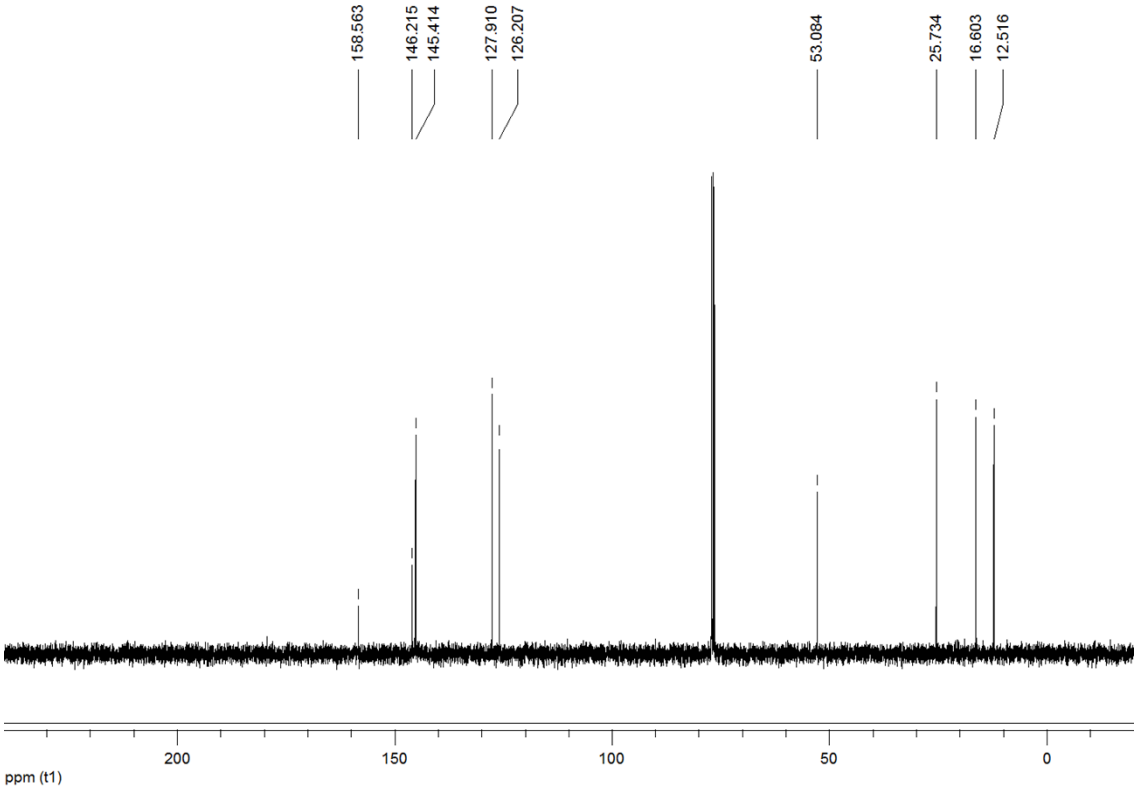

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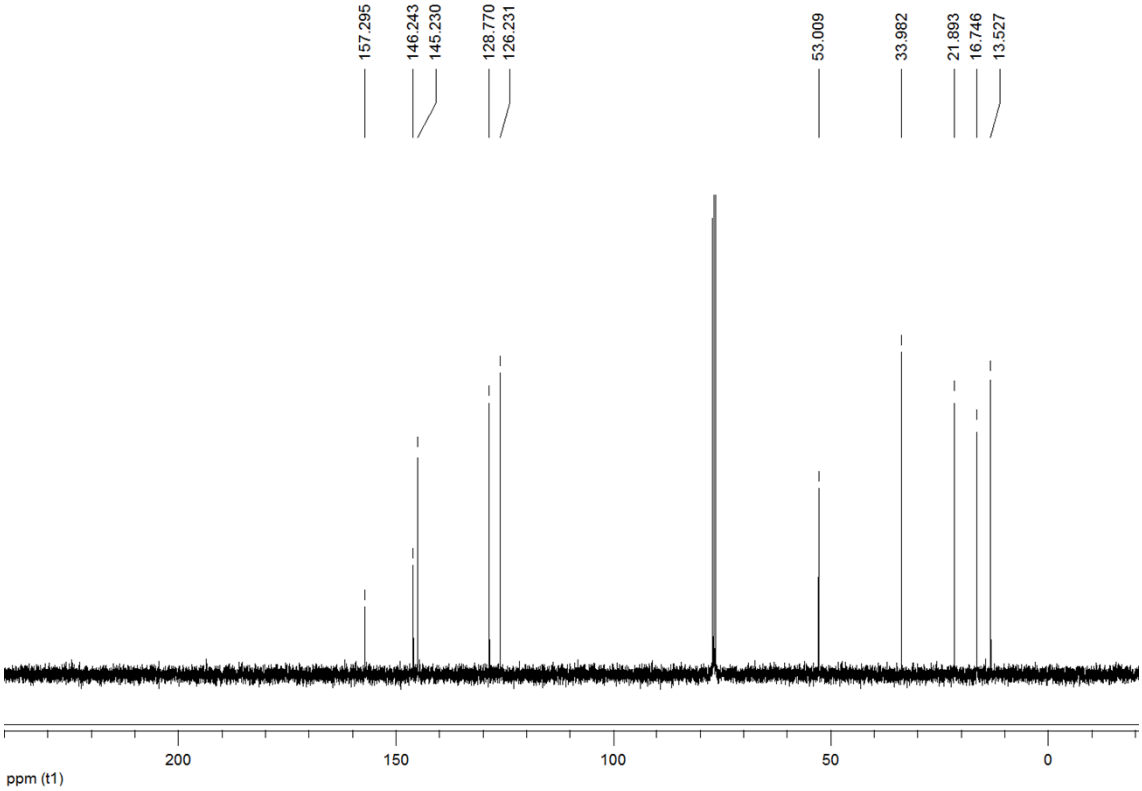

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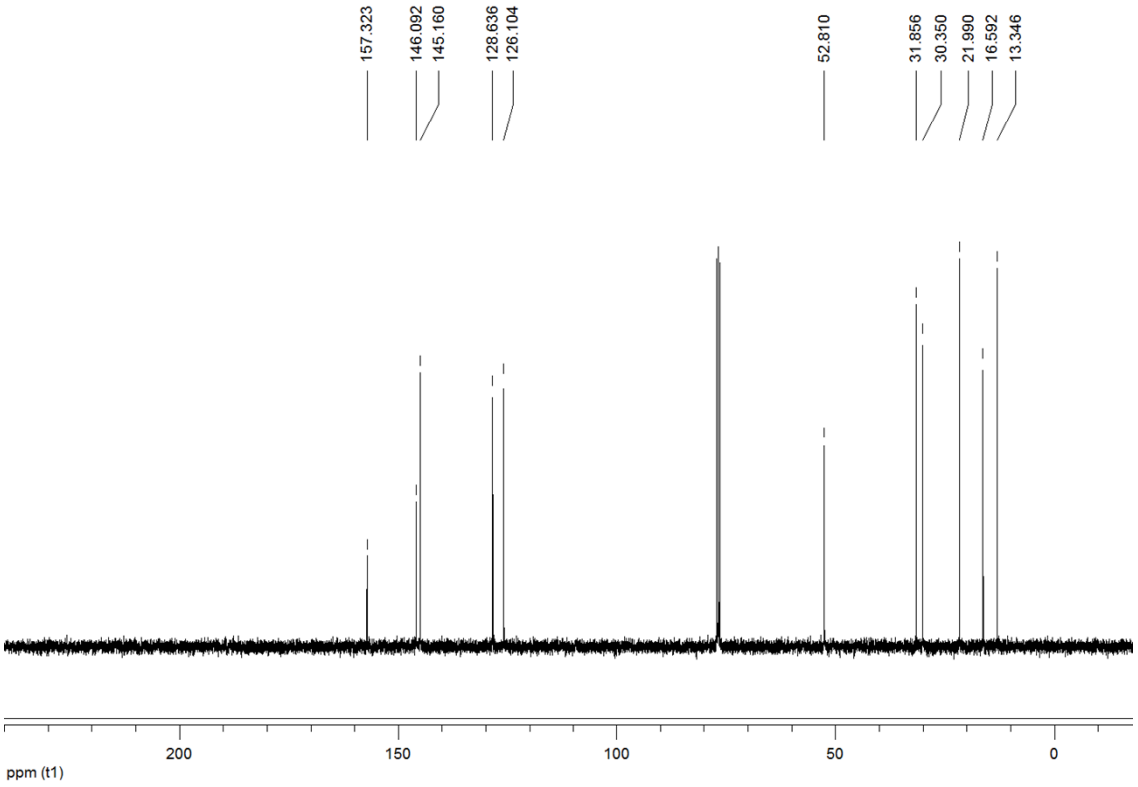

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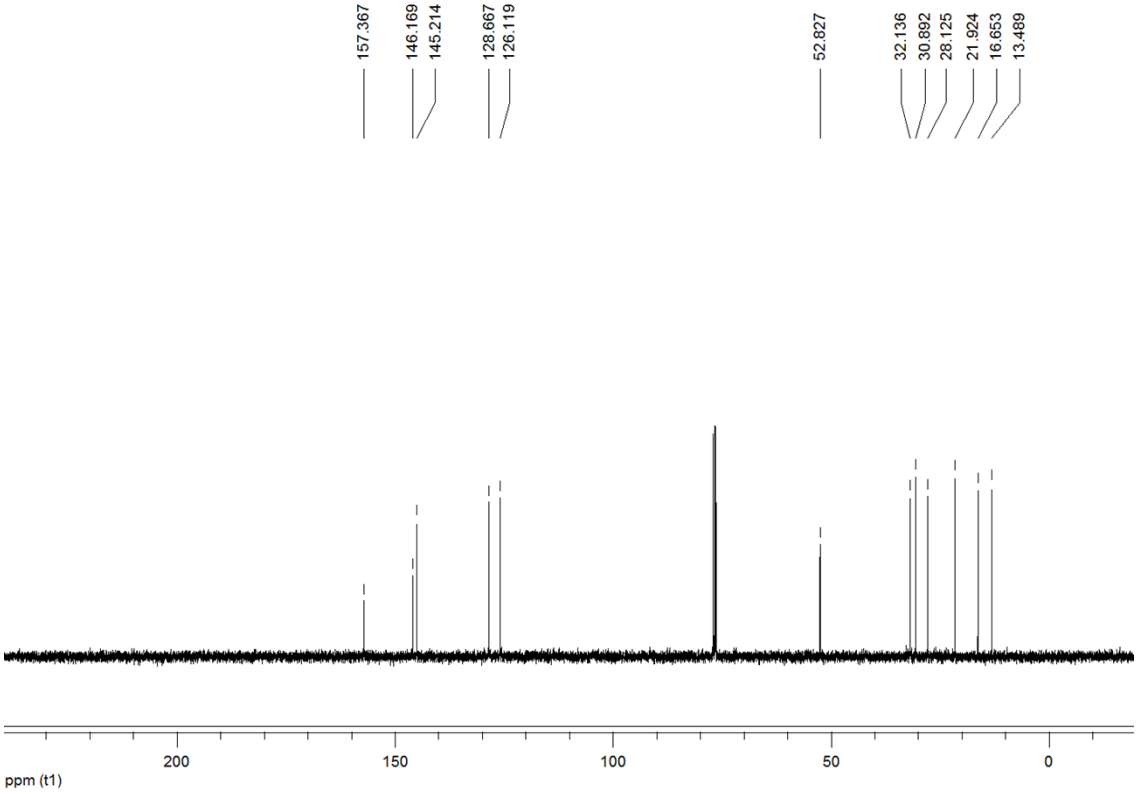

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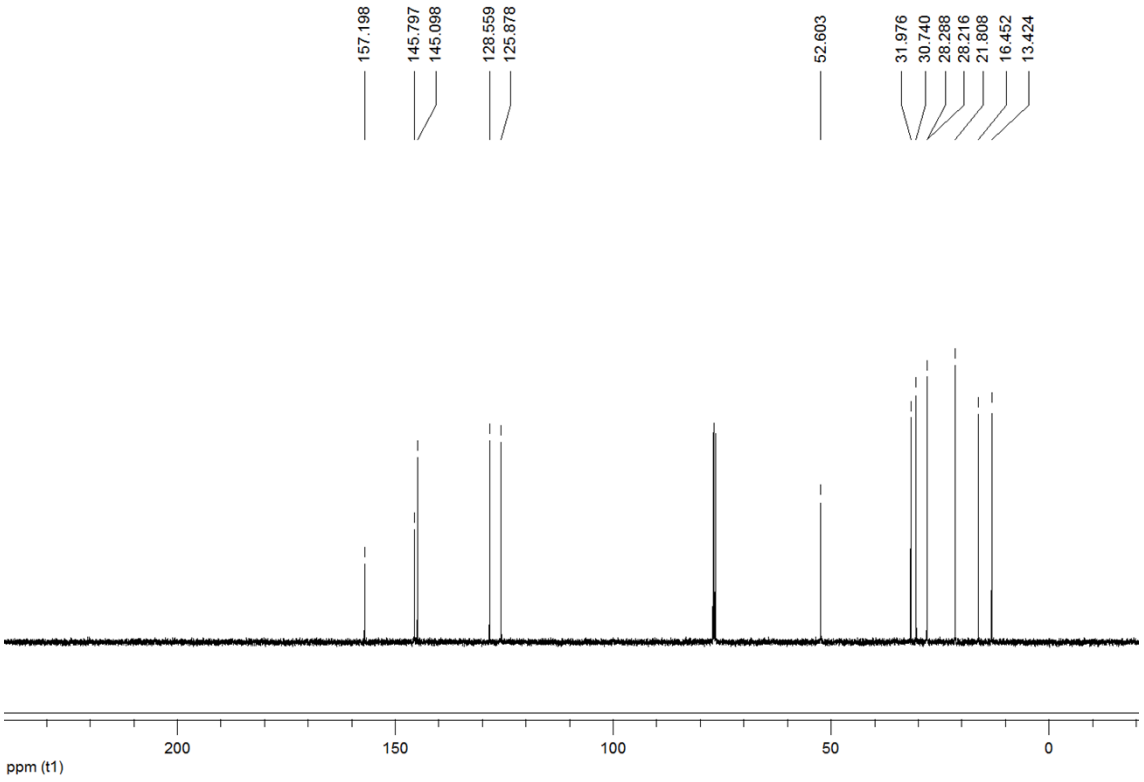

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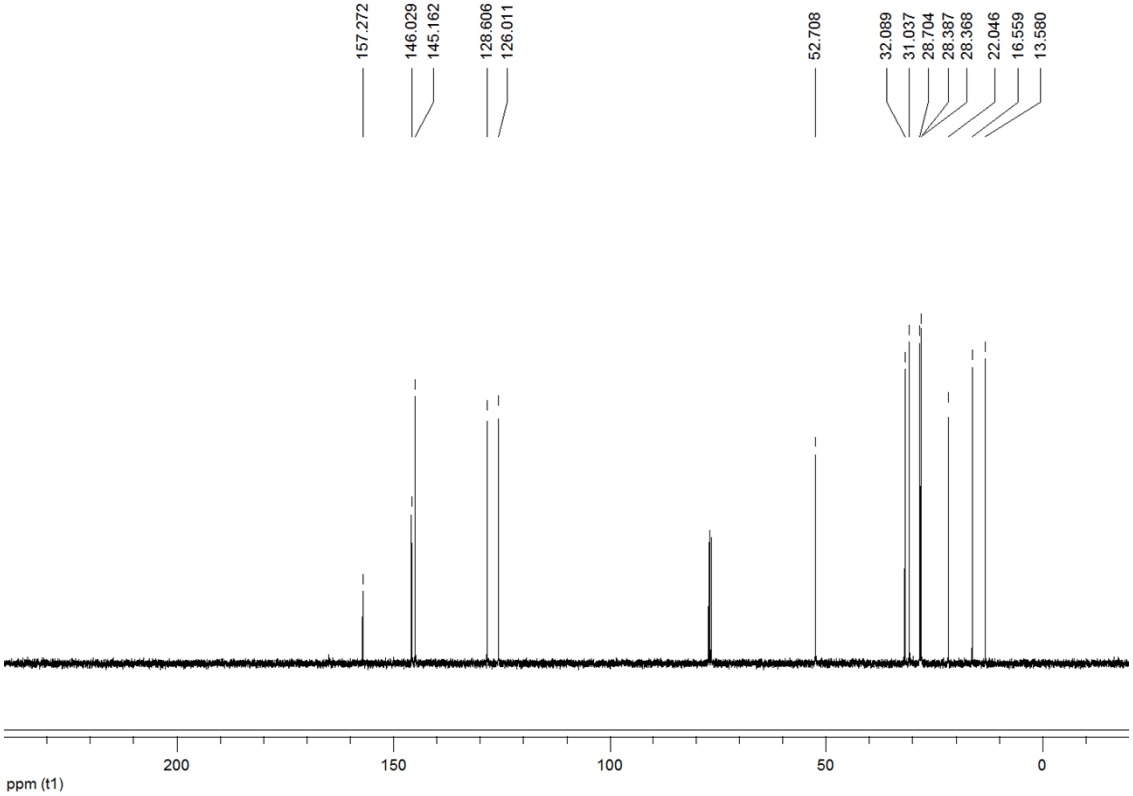

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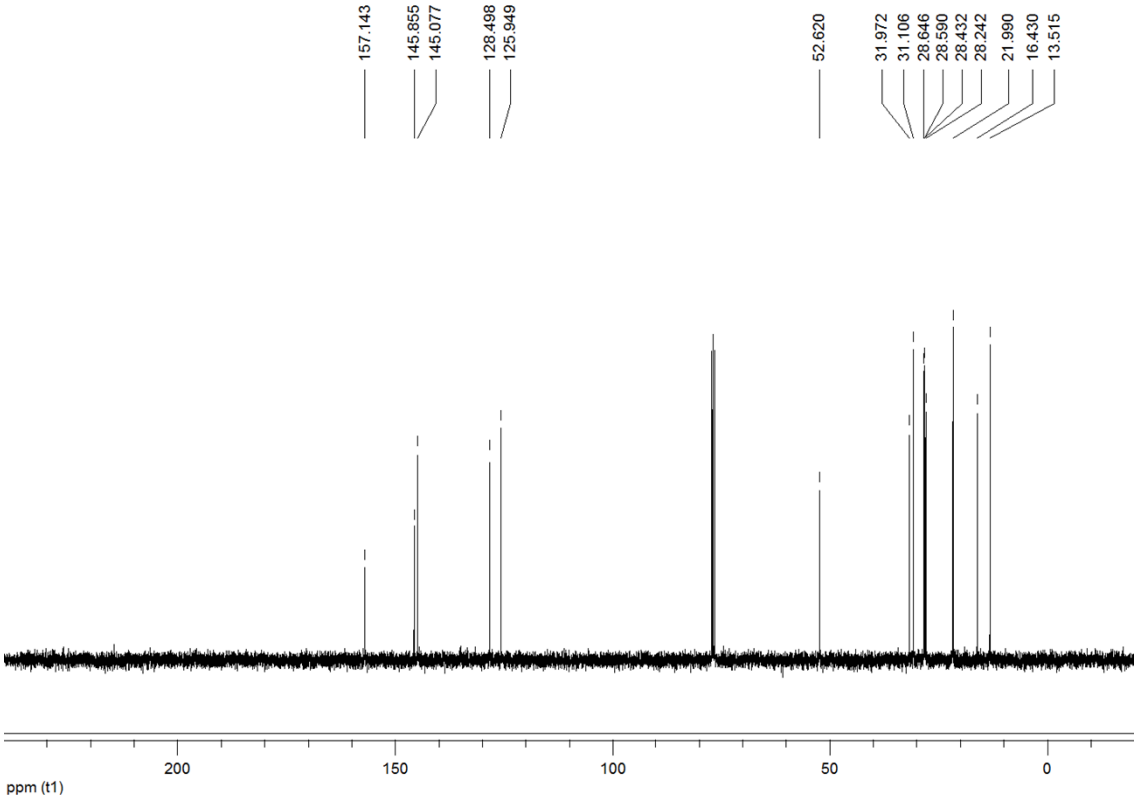

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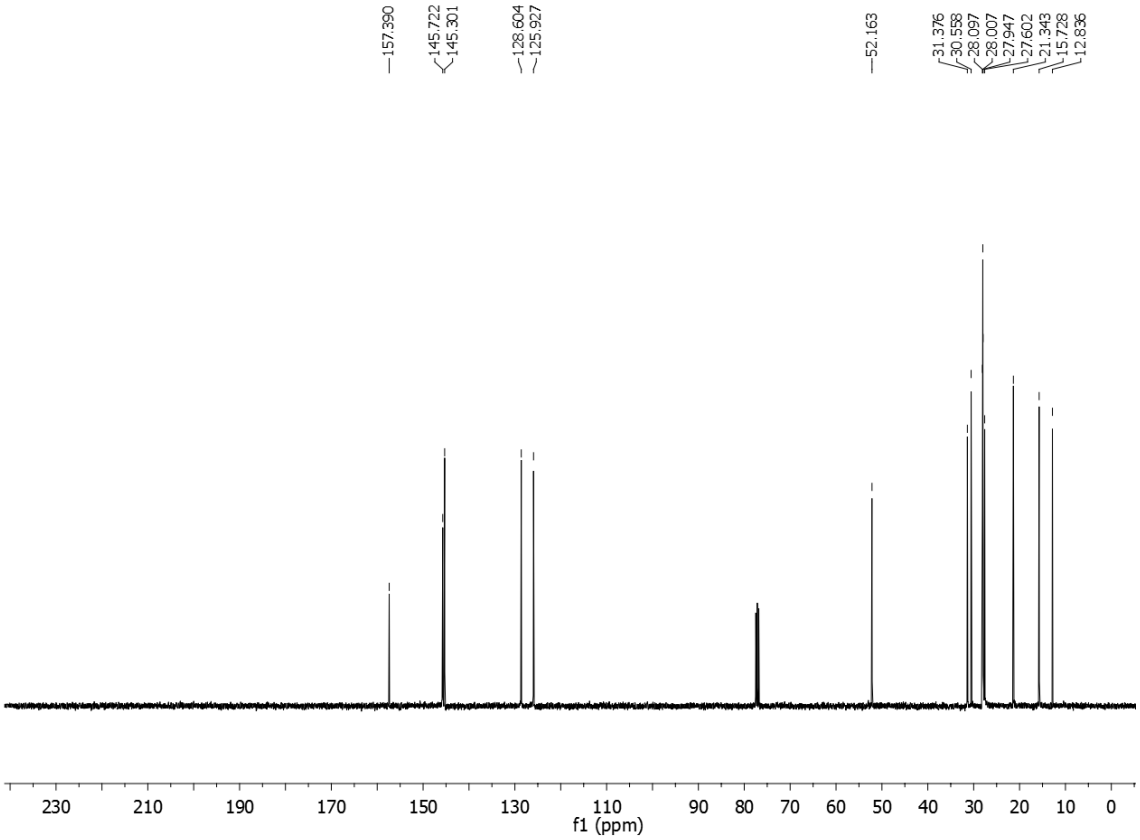

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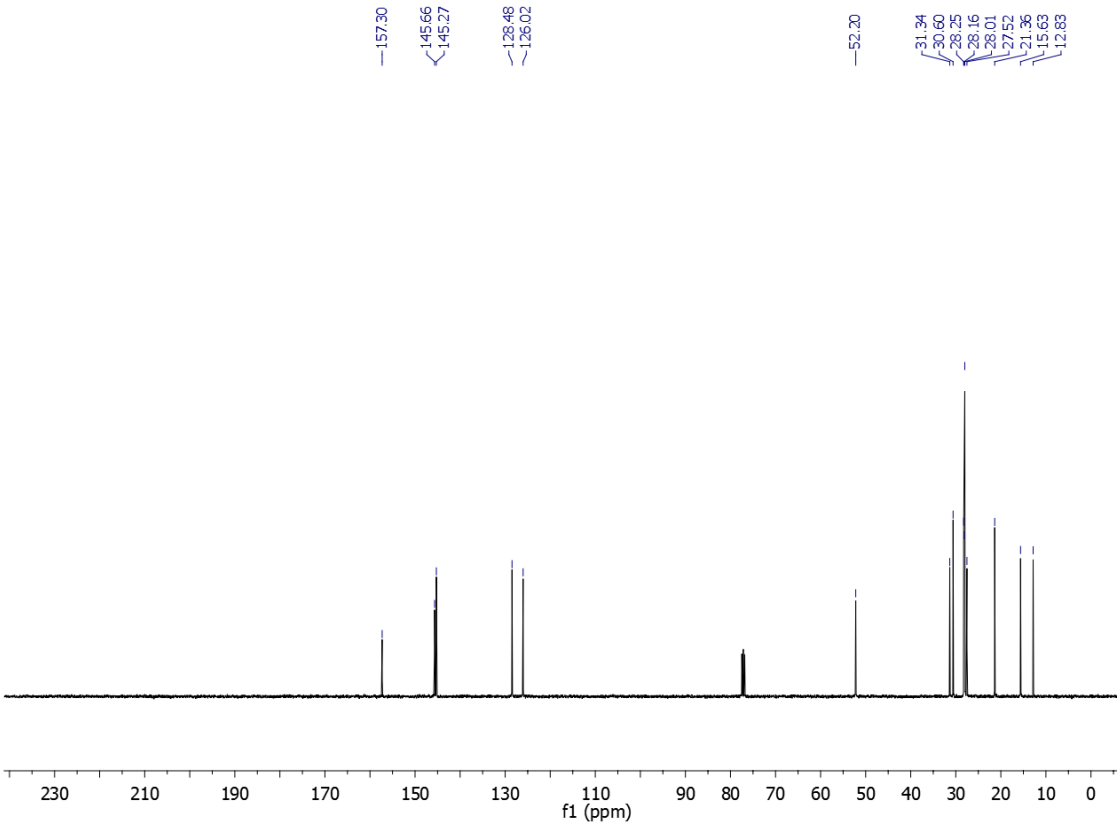
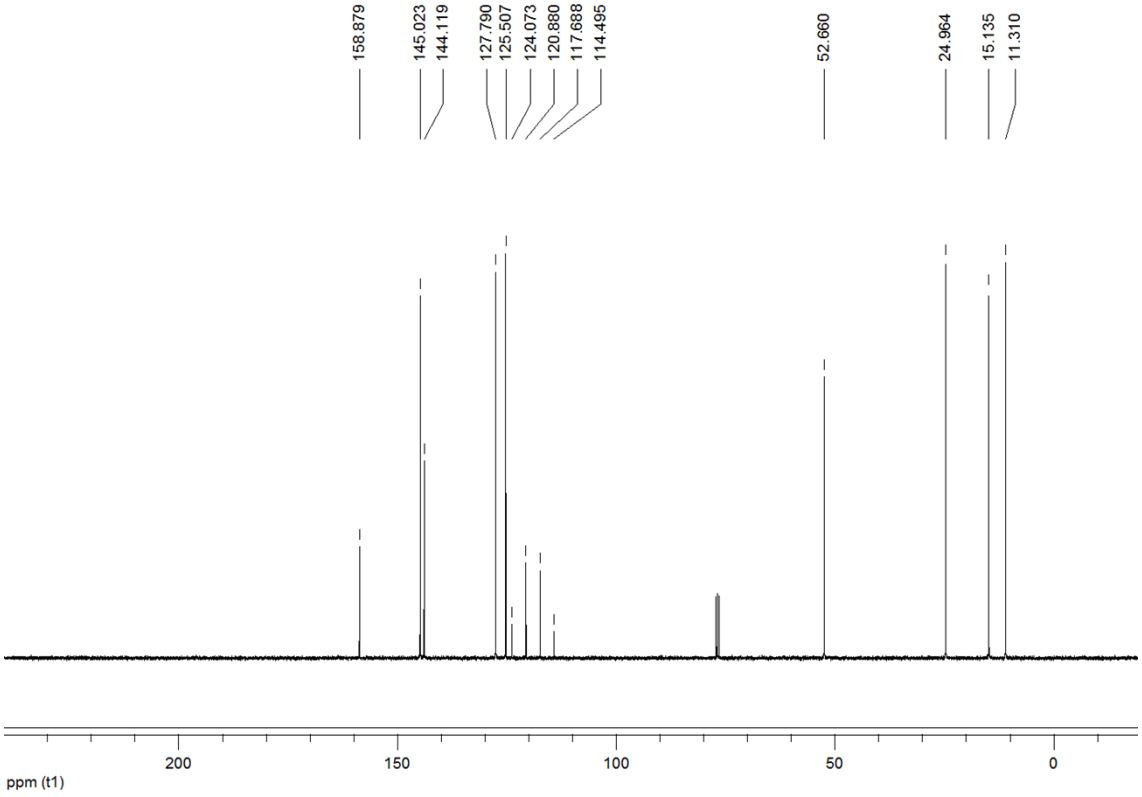


1,2-Diethylpyridinium bis(trifluoromethanesulfonyl)imide (20).



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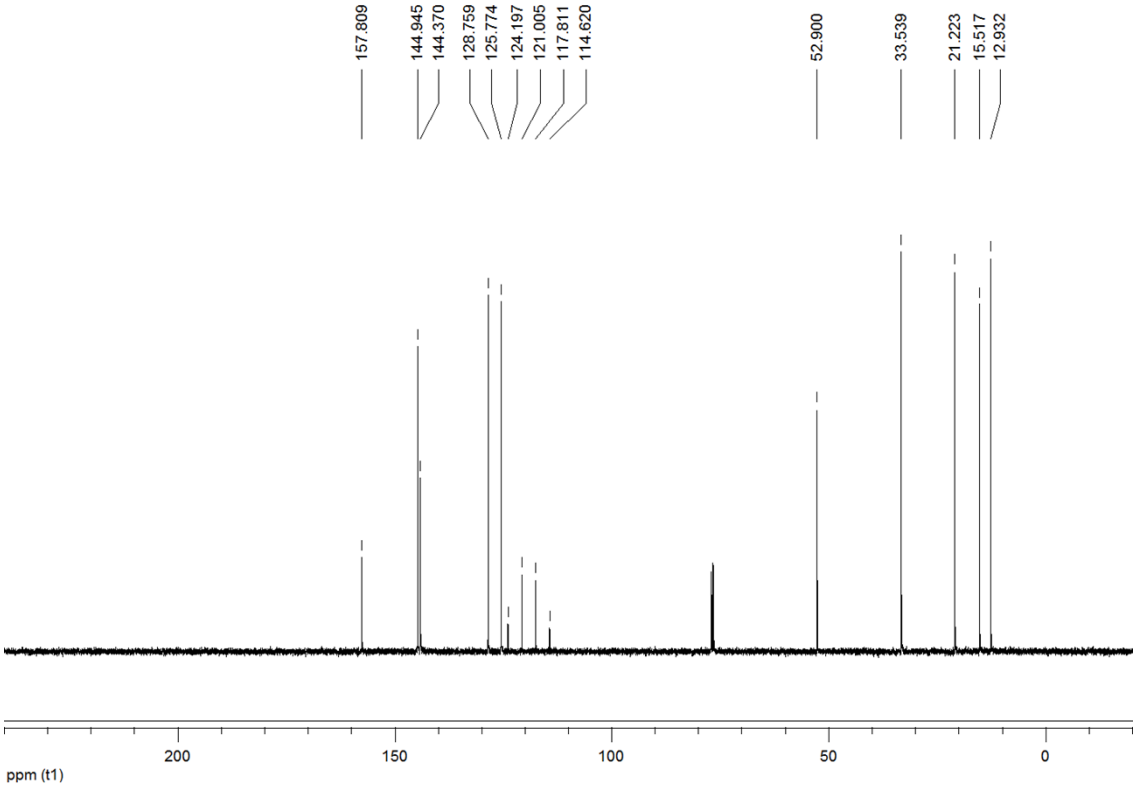
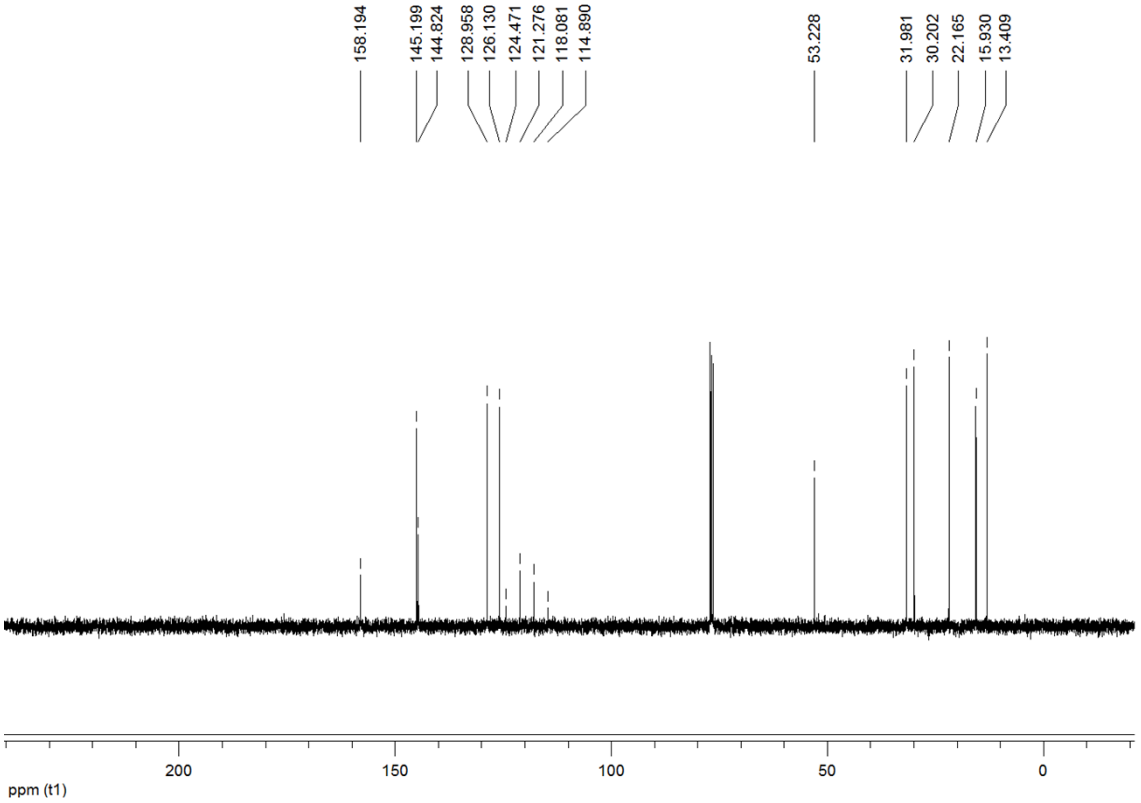


2-Butyl-1-ethylpyridinium bis(trifluoromethanesulfonyl)imide (22).



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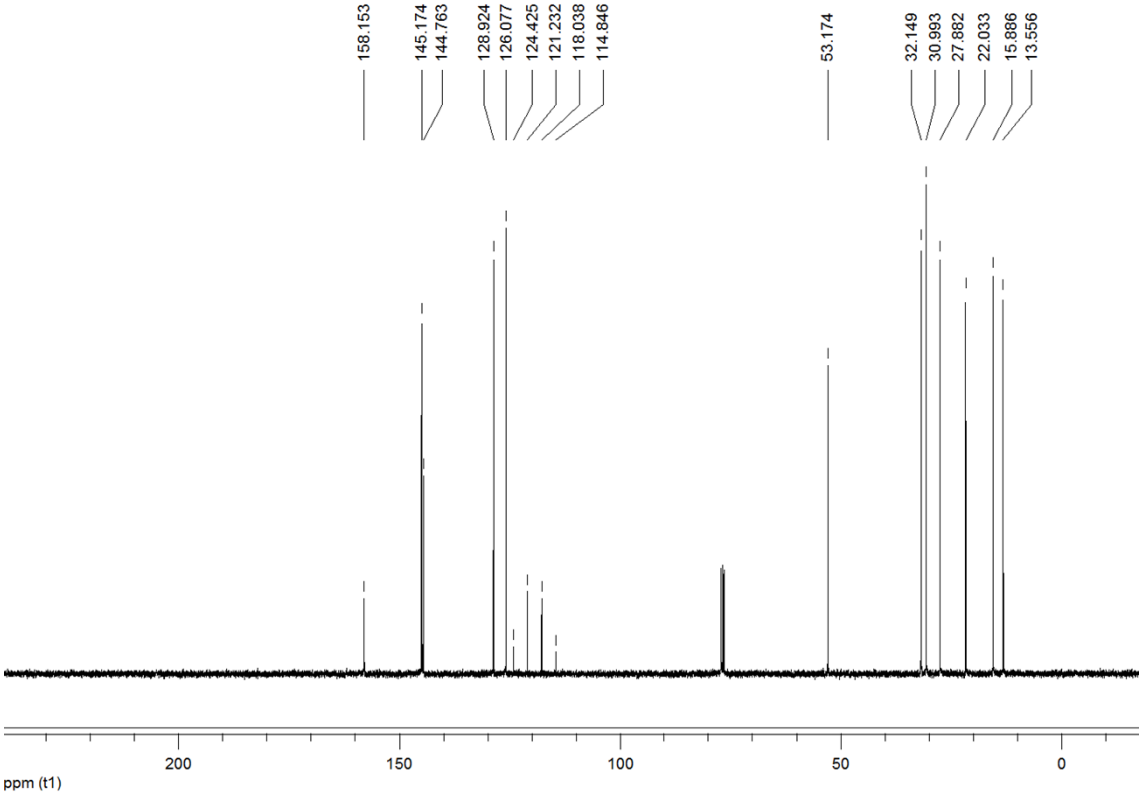

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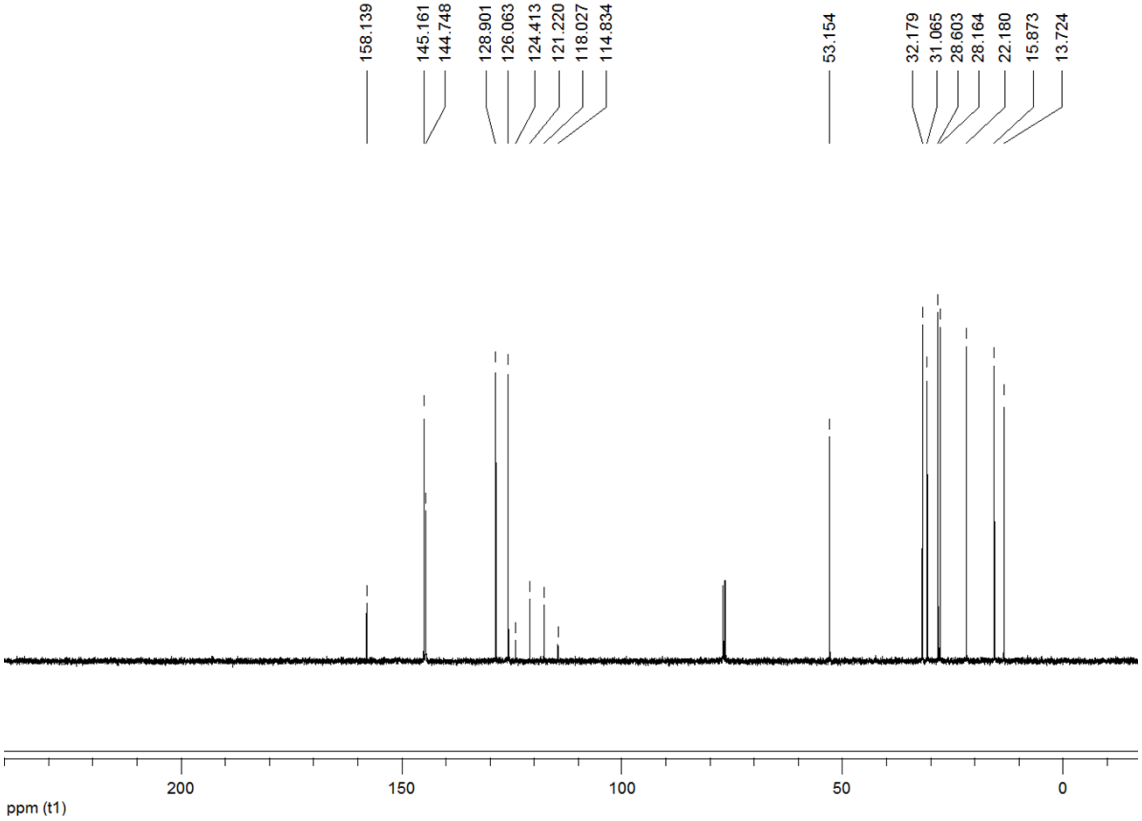

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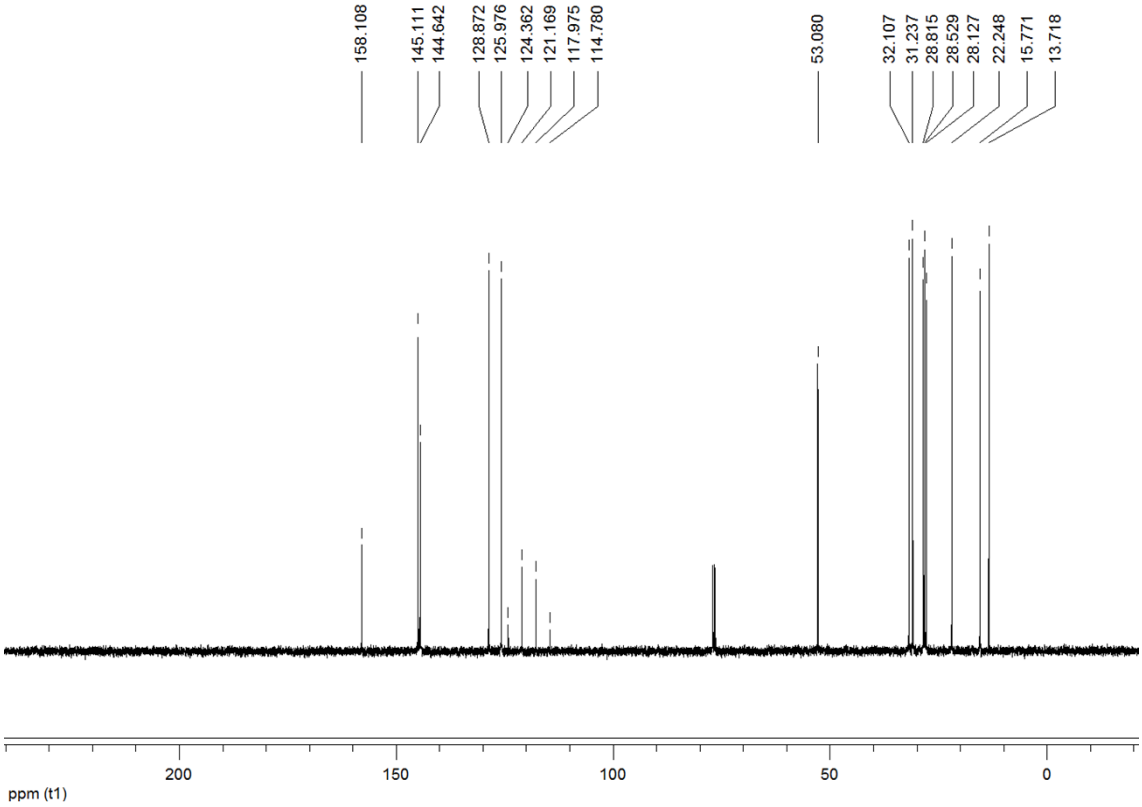
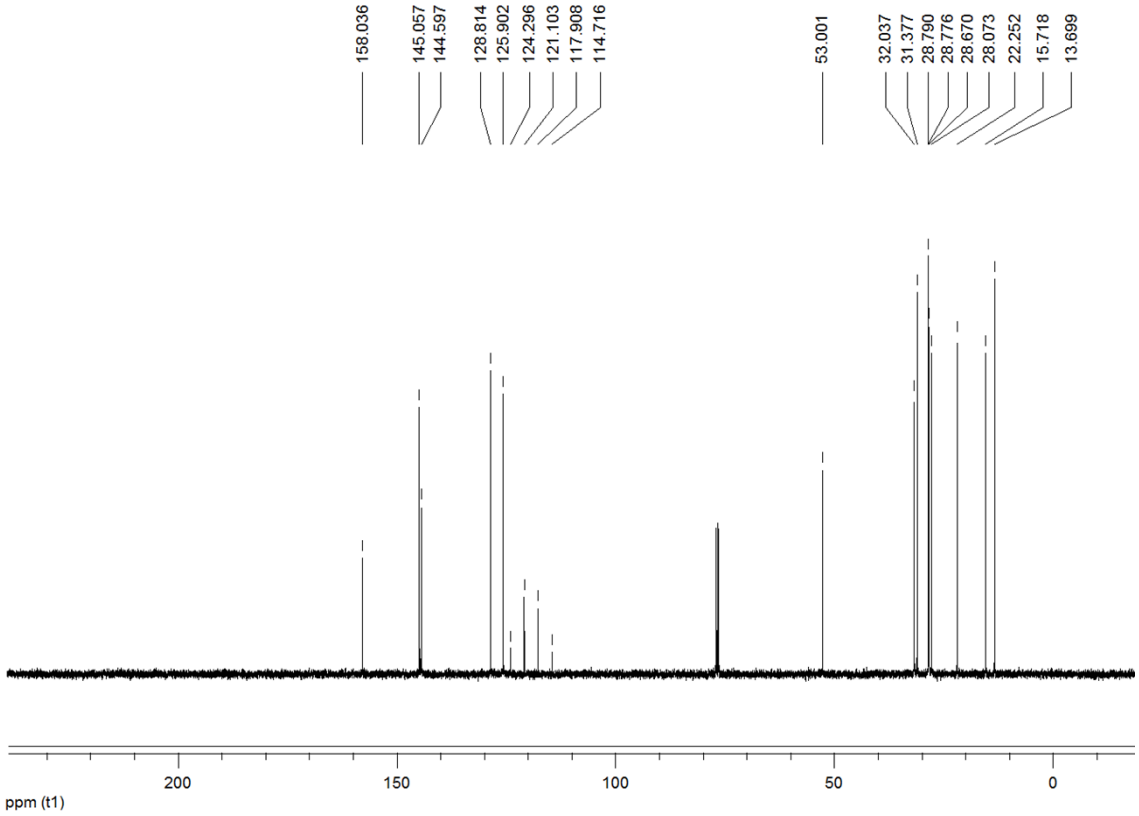


1-Ethyl-2-octylpyridinium bis(trifluoromethanesulfonyl)imide (26).



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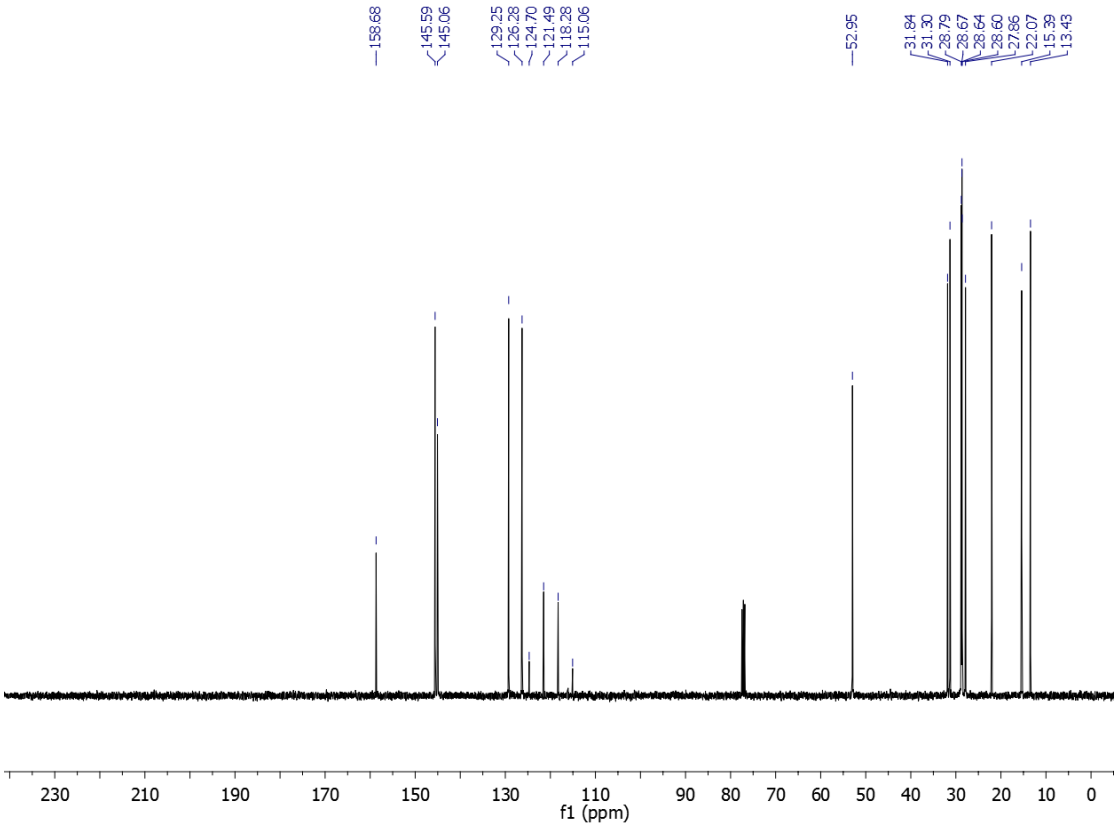
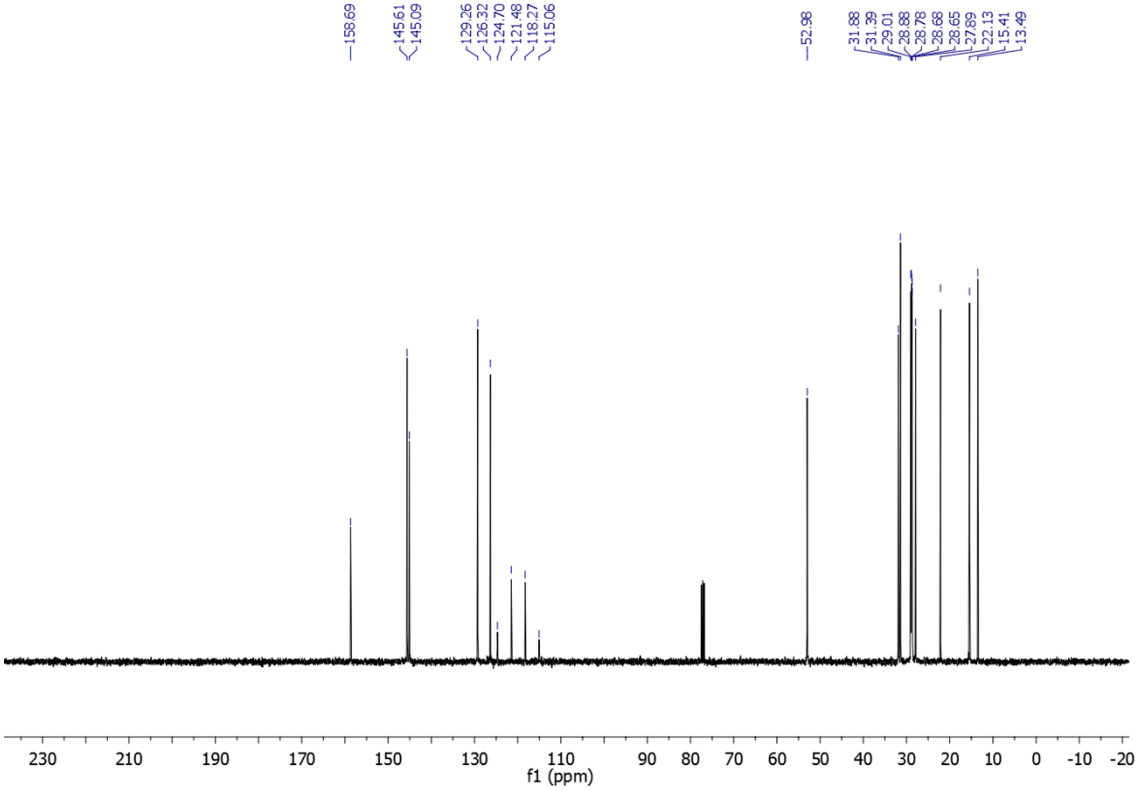


2-Decyl-1-ethylpyridinium bis(trifluoromethanesulfonyl)imide (28)



Volatility of new 1-alkyl-2-ethylpyridinium ionic liquids

Table S1. Experimental vapor pressures for the nine pyridinium based ILs, obtained by the quartz crystal microbalance Knudsen effusion apparatus.

T / K	p / Pa	Δp / Pa	T / K	p / Pa	Δp / Pa
		$[^2C_2{}^1C_2Py][NTf_2]$			
493.11	0.0414	-0.0083	513.10	0.1348	-0.0003
498.41	0.0560	0.0159	518.10	0.1784	-0.0006
503.11	0.0759	-0.0058	523.10	0.2343	0.0005
508.10	0.1013	-0.0014			
		$[^2C_3{}^1C_2Py][NTf_2]$			
498.10	0.0584	0.0003	513.08	0.1369	0.0045
503.09	0.0781	0.0017	518.08	0.1806	-0.0001
508.09	0.1047	-0.0057	523.08	0.2358	-0.0006
		$[^2C_4{}^1C_2Py][NTf_2]$			
493.14	0.0461	-0.0016	508.13	0.1111	0.0003
498.14	0.0622	0.0000	513.10	0.1471	-0.0018
503.14	0.0832	0.0031			
		$[^2C_5{}^1C_2Py][NTf_2]$			
498.13	0.0623	-0.0034	513.13	0.1531	-0.0002
503.16	0.0846	0.0002	518.15	0.2020	0.0102
508.14	0.1139	0.0022	523.13	0.2723	-0.0090
		$[^2C_6{}^1C_2Py][NTf_2]$			
493.15	0.0453	-0.0021	508.15	0.1145	-0.0023
498.16	0.0620	0.0009	513.16	0.1530	0.0025
503.17	0.0843	0.0030	518.14	0.2048	-0.0021
		$[^2C_7{}^1C_2Py][NTf_2]$			
498.29	0.0505	-0.0093	513.24	0.1255	0.0058
503.25	0.0682	0.0046	518.24	0.1714	-0.0102
508.25	0.0925	0.0090			
		$[^2C_8{}^1C_2Py][NTf_2]$			
493.42	0.0288	-0.0076	508.06	0.0752	0.0089
498.43	0.0400	0.0056	513.03	0.1037	0.0041
503.07	0.0549	-0.0018	518.03	0.1434	-0.0091
		$[^2C_9{}^1C_2Py][NTf_2]$			
508.06	0.0720	-0.0050	528.02	0.2488	0.0088
513.06	0.0988	0.0026	533.00	0.3353	0.0056
518.04	0.1362	-0.0019	537.99	0.4556	-0.0107
523.03	0.1853	0.0004			

		$[^2C_{10}{}^1C_2Py][NTf_2]$			
508.01	0.0608	-0.0103	523.00	0.1606	0.0024
513.01	0.0836	0.0068	528.00	0.2204	-0.0009
518.01	0.1162	0.0054	533.00	0.3006	-0.0048

$\Delta p = p - p_{calc}$, where p_{calc} is calculated from the Clarke and Glew equation (eq. 1) with the parameters given in Table 1.

Thermodynamic properties of vaporization

The graphic representations of the standard molar enthalpies, entropies and Gibbs energies of vaporization at reference temperature, T = 298.15K, as a function of the total number of carbon atoms in the two alkyl side chains of the cation, N, are presented in figures S1 − S6.

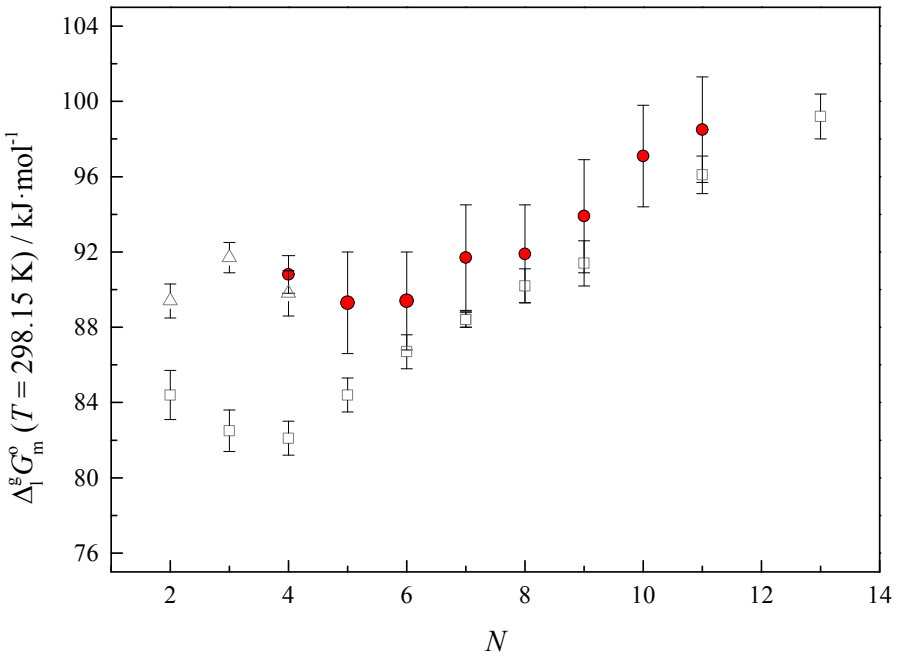


Figure S1. Standard (p^o=10^5 Pa) molar Gibbs energy of vaporization $\Delta_l^g G_m^o$ (T = 298.15K) as a function of the total number of carbons in the alkyl side chains of the cation, N. ⭘ - $[C_{N-1}C_1im][NTf_2]$ [1,2] (N = 2 - 9, 11, 13); ❐ - $[C_NPy][NTf_2]$[3] (N = 2 - 4); ∞ - $[^2C_{N-2}{}^1C_2Py][NTf_2]$ (N = 4 - 10).

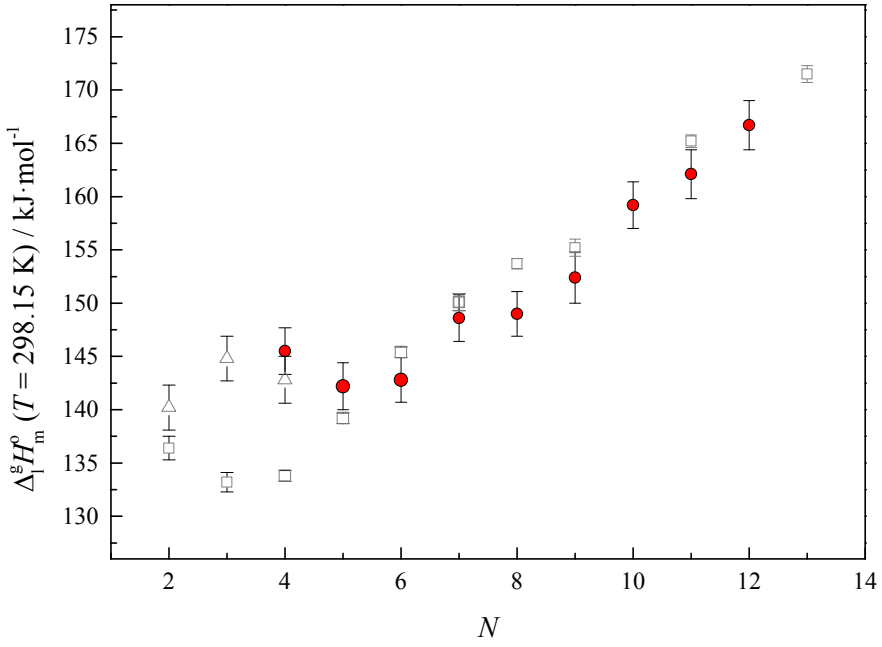


Figure S2. Standard (p^o=10^5 Pa) molar enthalpies of vaporization $\Delta_l^g H_m^o$ (T = 298.15 K) as a function of the total number of carbons in the alkyl side chains of the cation, *N*. ⭘ - $[C_{N-1}C_1im][NTf_2]$[1,2] (N = 2 - 9, 11, 13); ❒ - $[C_NPy][NTf_2]$[3] (N = 2 - 4); ᔓ - $[^2C_{N-2}{}^1C_2Py][NTf_2]$ (N = 4 - 10).

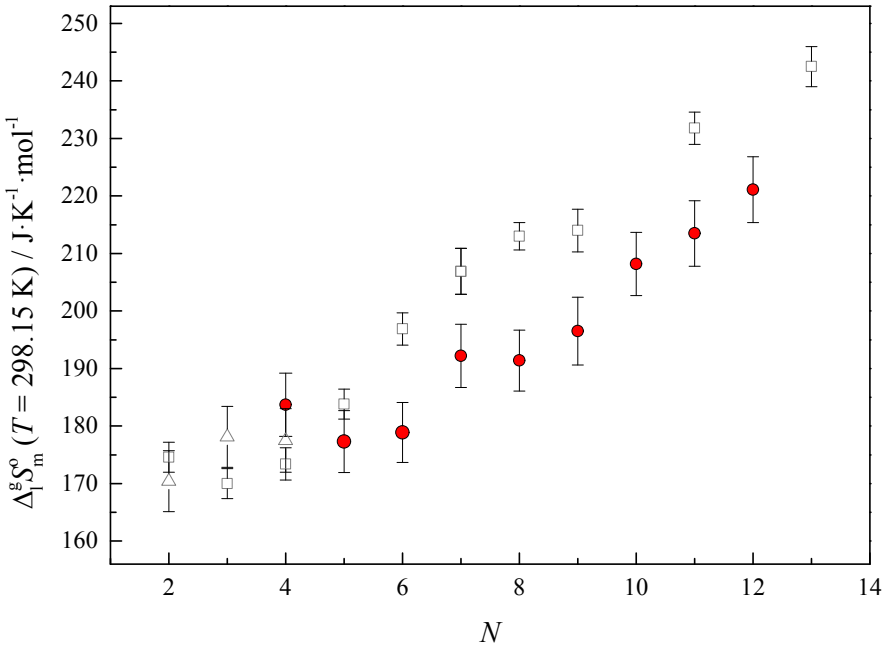


Figure S3. Standard (p^o=10^5 Pa) molar entropies of vaporization $\Delta_l^g S_m^o$ (T = 298.15 K) as a function of the total number of carbons in the alkyl side chains of the cation, *N*. ⭘ - $[C_{N-1}C_1im][NTf_2]$[1,2] (N = 2 - 9, 11, 13); ❒ - $[C_NPy][NTf_2]$[3] (N = 2 - 4); ᔓ - $[^2C_{N-2}{}^1C_2Py][NTf_2]$ (N = 4 - 10).

References

[1] M. A. A. Rocha, C. F. R. A. C. Lima, L. R. Gomes, B. Schröder, J. A. P. Coutinho, I. M. Marrucho, J. M. S. S. Esperança, L. P. N. Rebelo, K. Shimizu, J. N. Canongia Lopes, L. M. N. B. F. Santos, *J. Phys. Chem. B* **2011**, 115, 10919.

[2] M. A. A. Rocha, F. M. S. Ribeiro, B. Schröder, J. A. P. Coutinho, L. M. N. B. F. Santos, *J. Chem. Thermodyn.* **2013**, 68, 317.

[3] M. A. A. Rocha, L. M. N. B. F. Santos, *Chem. Phys. Lett.* **2013**, 585, 59.