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

Supplementary Information

Single component, metal-free, solvent-free HO-functionalized 1,2,3-triazole-based ionic liquid catalysts for efficient CO_2 conversion

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Summary

1. Experimental section

1.1. Synthesis of triazole ionic liquids

Synthesis of 4b. To a round-bottom flask were added 1.3 mmol of **3a**, 52.4 mmol of NaBr, 2.5 mL of water and 7.5 mL of ethanol. The mixture was stirred at room temperature for 1 hour. Then, the ethanol was evaporated under reduced pressure and the residue was extracted with CH_2Cl_2 and water. The organics were dried with anhydrous Na_2SO_4, filtered and the solvent was removed to yield the product as a brown gelatinous solid.

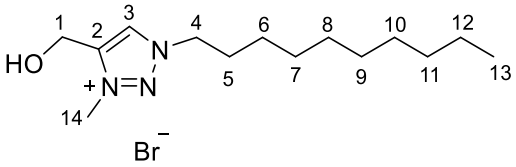

Figure S1. Compound **4b**.

Yield: 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm), *J* (Hz): 0.88 (t, *J* = 6.9, 3H, H-13); 1.24 – 1.40 (m, 14H, H-6 a H-12); 2.03 (p, *J* = 7.5, 2H, H-5); 4.39 (s, 3H, H-14); 4.63 (t, *J* = 7.5, 2H, H-4); 5.04(s, 2H, H-1); 8.97 (s, 1H, H-3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 14.0 (C-13); 22.6 (C-12); 26.1 (C-11); 28.8; 29.1; 29.2; 29.3; 29.4 (C-6 a C-10); 31.7 (C-5); 39.4 (C-14); 52.7 (C-4); 54.3 (C-1); 129.8 (C-3); 143.7 (C-2). MALDI-TOF-MS: m/z calculated for $C_{14}H_{28}N_3O$: $[M]^+$ = 254.2227, found 254.2230. MP (°C): 66-68.

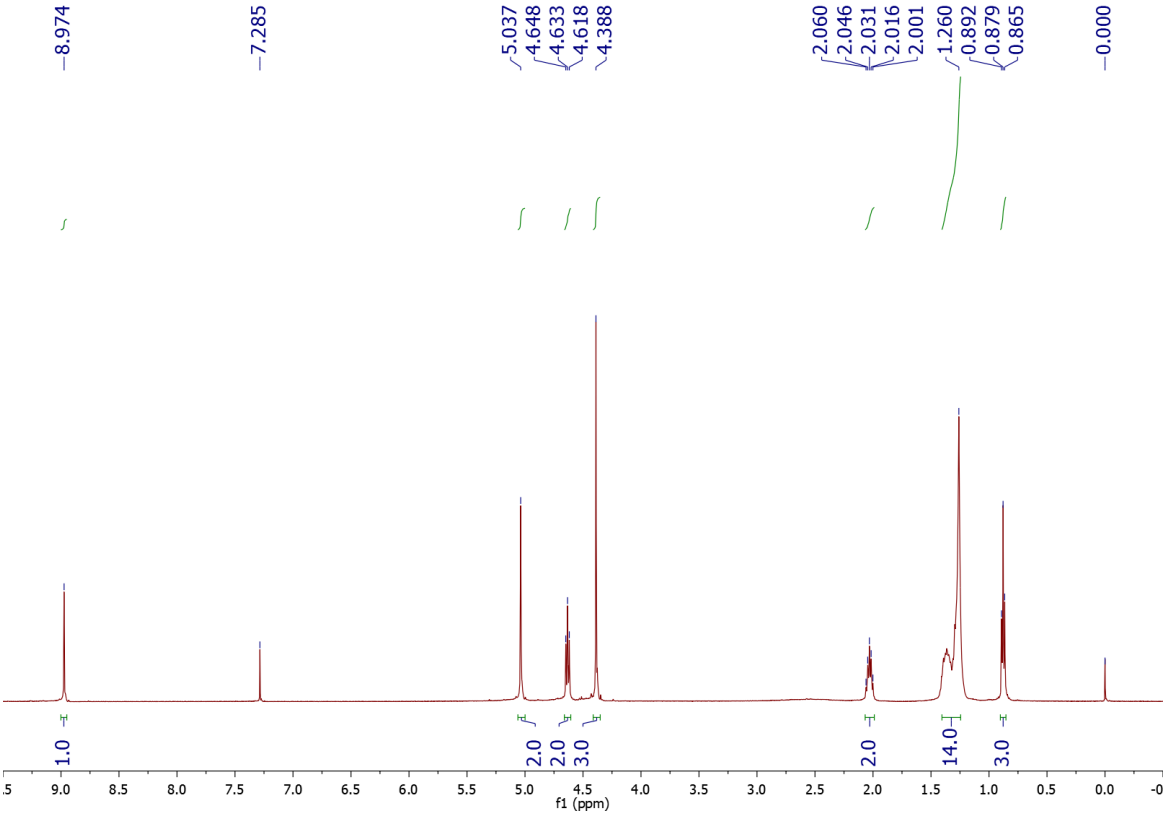

Figure S2. ^{1}H NMR spectra of **4b** (500 MHz, $CDCl_3$).

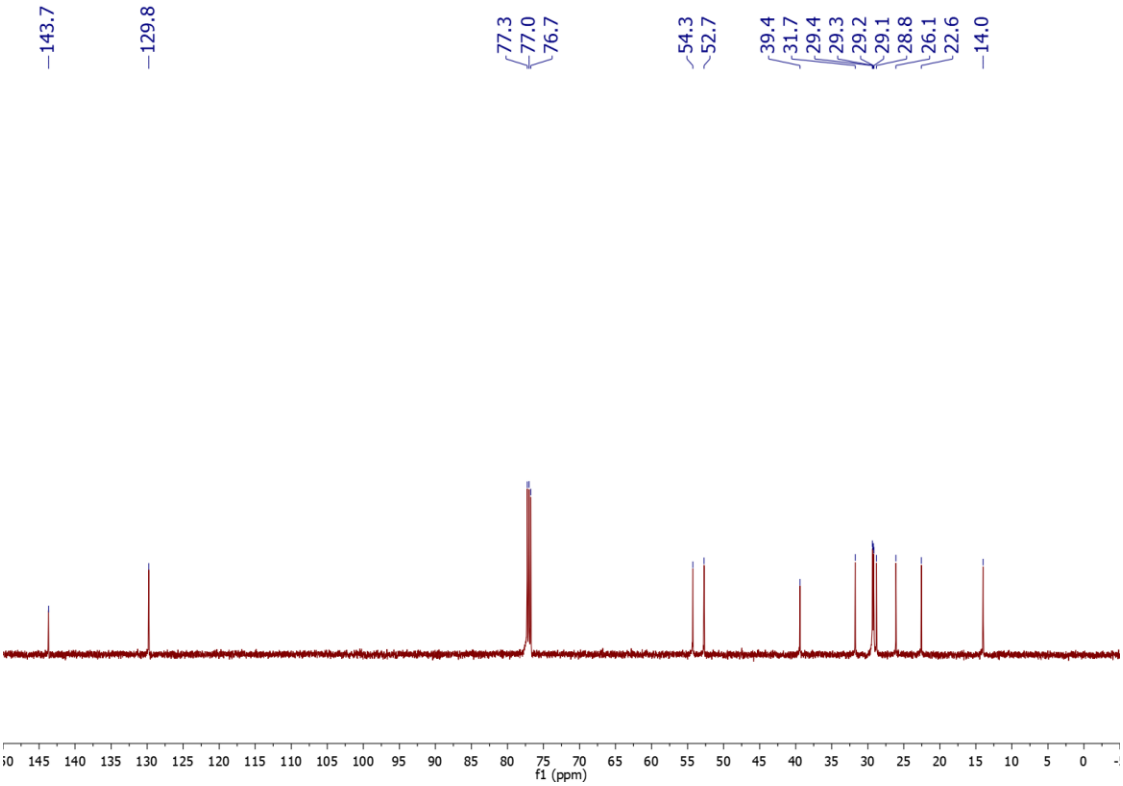

Figure S3. ^{13}C NMR spectra of **4b** (126 MHz, $CDCl_3$).

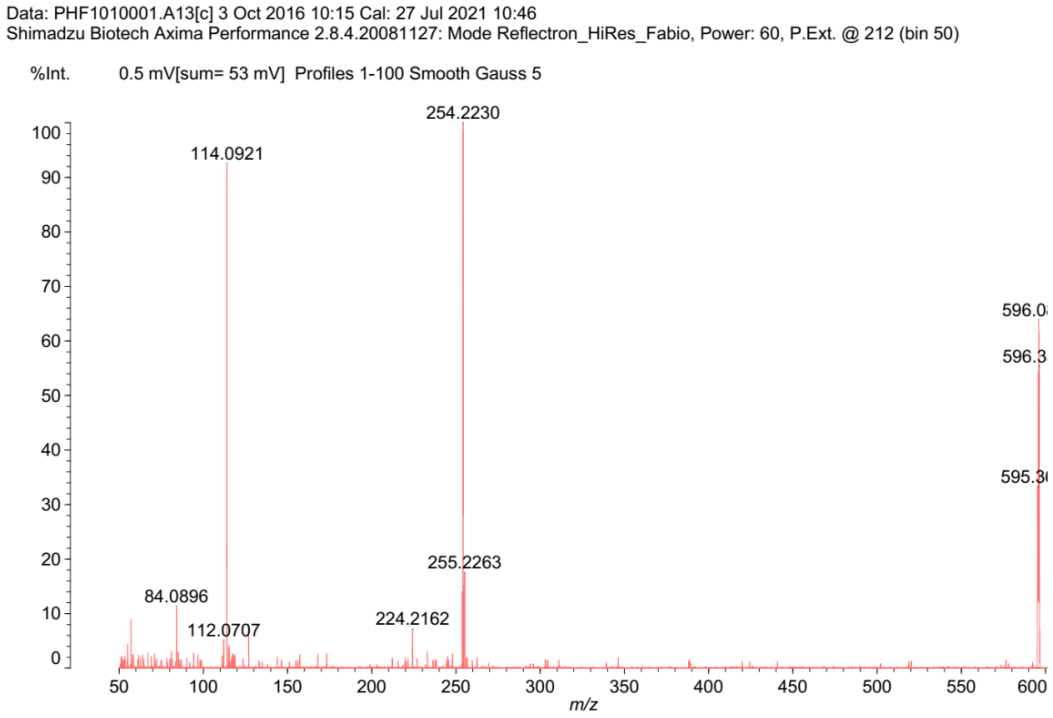

Figure S4. MALDI-TOF-MS spectra of **4b**.

Synthesis of 8b and 9b. An ion exchange column filled with Amberlite® IRA-400 resin was activated with a NaOH solution of 1M in deionized water. Then, 1.0 mmol of **3a** was slowly passed through the column using a mixture of ethanol and deionized water (7:3) as mobile phase. After the ion exchange, the mobile phase was added dropwise to 0.5 mmol of H_2SO_4 (**8b**) or 1.0 mmol of TfOH (**9b**) in ethanol. Finally, the solvents were evaporated in reduced pressure and the products was obtained in the form of a brown gelatinous solid (**8b**) or a brown oil (**9b**).

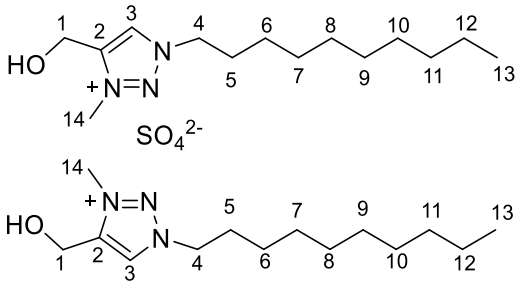

Figure S5. Compound **8b**.

Yield: 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm), *J* (Hz): 0.87 (t, *J* = 6.9, 3H, H-13); 1.22 – 1.36 (m, 14H, H-6 a H-12); 1.96 (p, *J* = 6.9, 2H, H-5); 4.28 (s, 3H, H-14); 4.55 (t, *J* = 7.4, 2H, H-4); 4.91 (s, 2H, H-1); 8.62 (s, 1H, H-3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 14.1 (C-13); 22.7 (C-12); 26.3 (C-11); 29.1; 29.2; 29.4; 29.5; 29.6 (C-6 a C-10); 31.9 (C-5); 38.3 (C-14); 52.5 (C-4); 53.8 (C-1); 129.3 (C-3); 143.6 (C-2). FT-ICR-MS: m/z calculated for $C_{14}H_{28}N_3O$: $[M]^+$ = 254.22269, found 254.22469. MP (°C): 81-83.

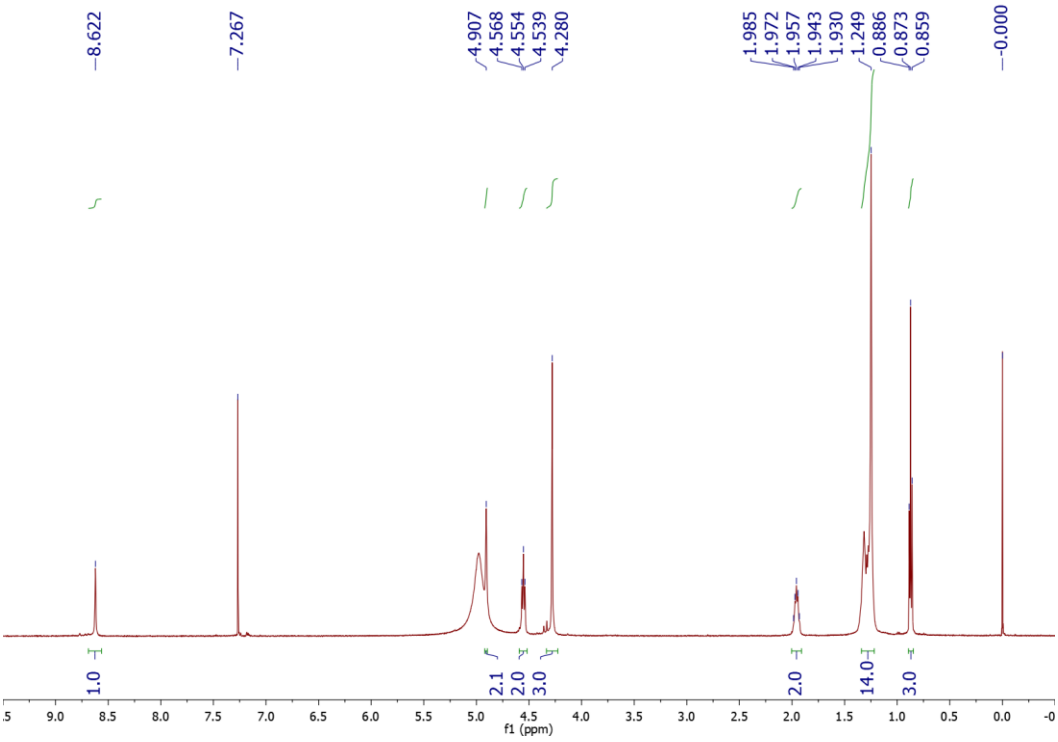

Figure S6. ^{1}H NMR spectra of **8b** (500 MHz, $CDCl_3$).

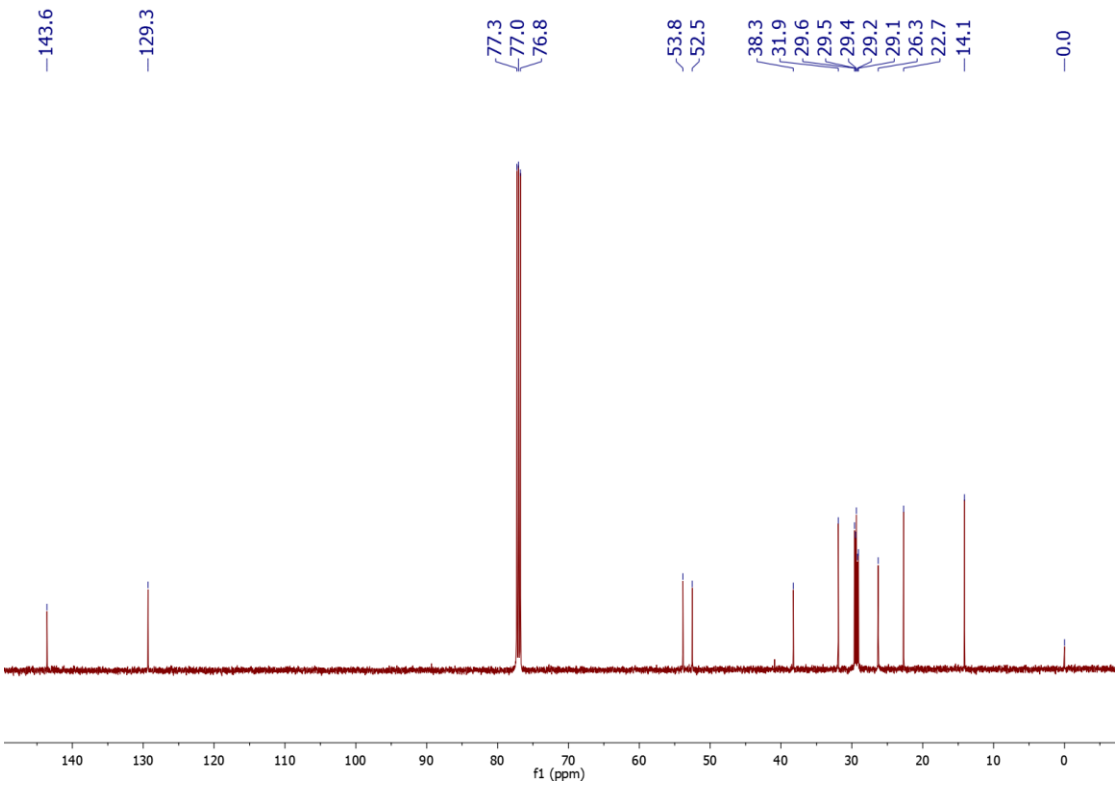

Figure S7. ^{13}C NMR spectra od **8b** (126 MHz, $CDCl_3$).

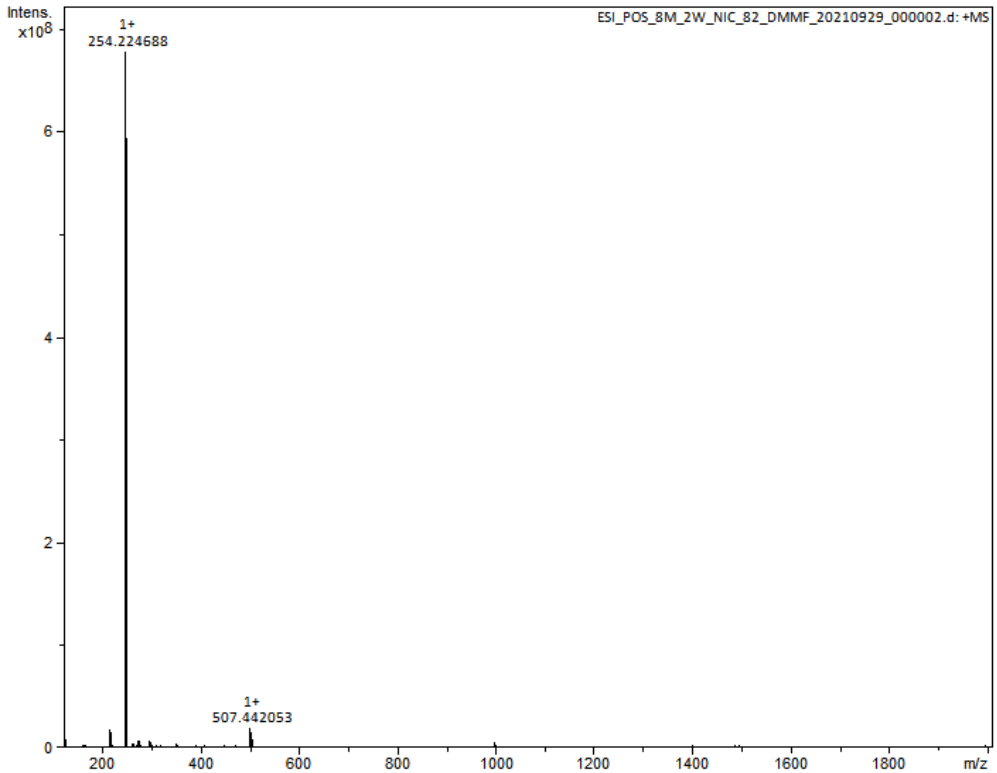

Figure S8. FT-ICR-MS spectra of **8b**.

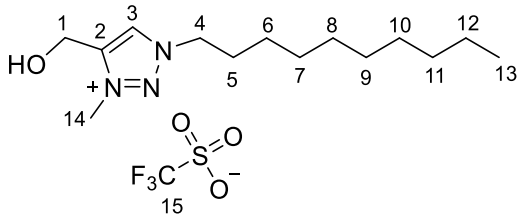

Figure S9. Compound **9b**.

Yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm), *J* (Hz): 0.88 (t, *J* = 6.9, 3H, H-13); 1.23 – 1.38 (m, 14H, H-6 a H-12); 1.98 (p, *J* = 7.6, 2H, H-5); 3.79 (s, 1H, OH); 4.28 (s, 3H, H-14); 4.50 (t, *J* = 7.5, 2H, H-4); 4.87 (s, 2H, H-1); 8.52 (s, 1H, H-3). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm), *J* (Hz): 14.1 (C-13); 22.7 (C-12); 26.1 (C-11); 28.8; 29.2; 29.2; 29.3; 29.5 (C-6 a C-10); 31.8 (C-5); 38.2 (C-14); 52.7 (C-4); 54.0 (C-1); 120.3 (q, *J* = 319.7, C-15); 129.0 (C-3); 143.9 (C-2). MALDI-TOF-MS: m/z calculated for $C_{14}H_{28}N_3O$: $[M]^+$ = 254.2227, found 254.2224.

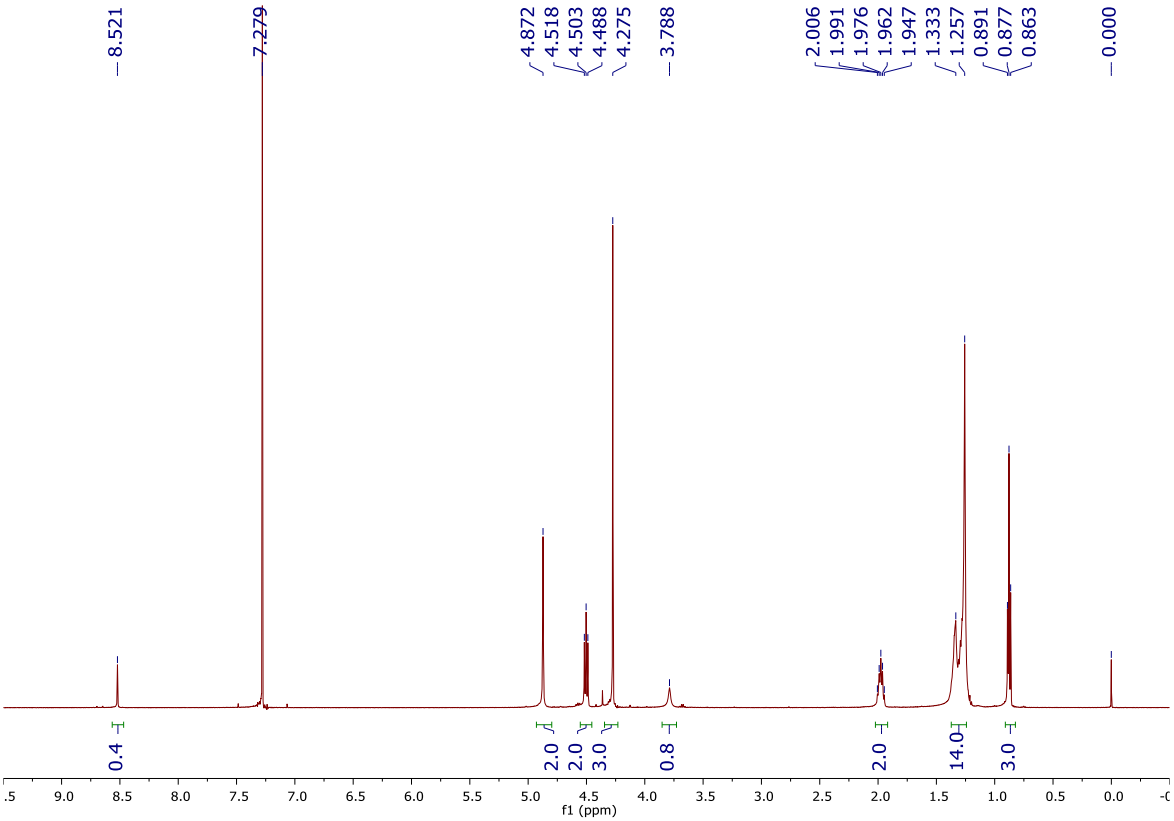

Figure S10. ^{1}H NMR spectra of **9b** (500 MHz, $CDCl_3$).

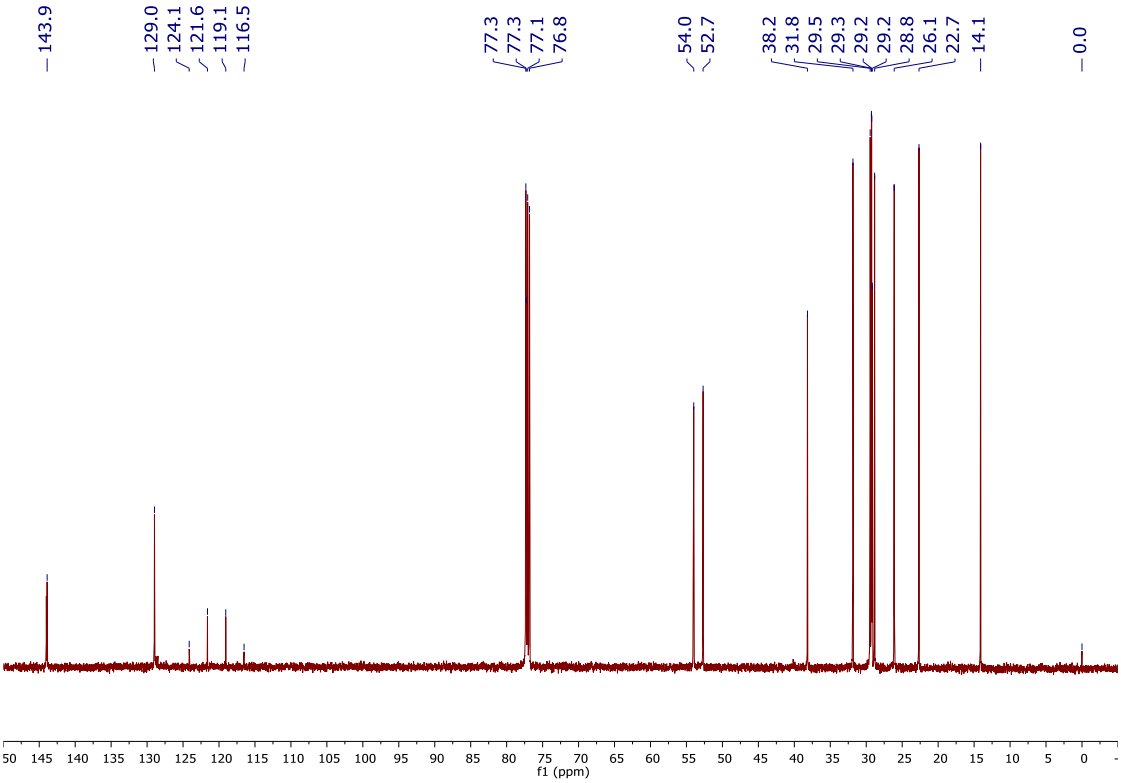

Figure S11. ^{13}C NMR spectra of **9b** (126 MHz, $CDCl_3$)

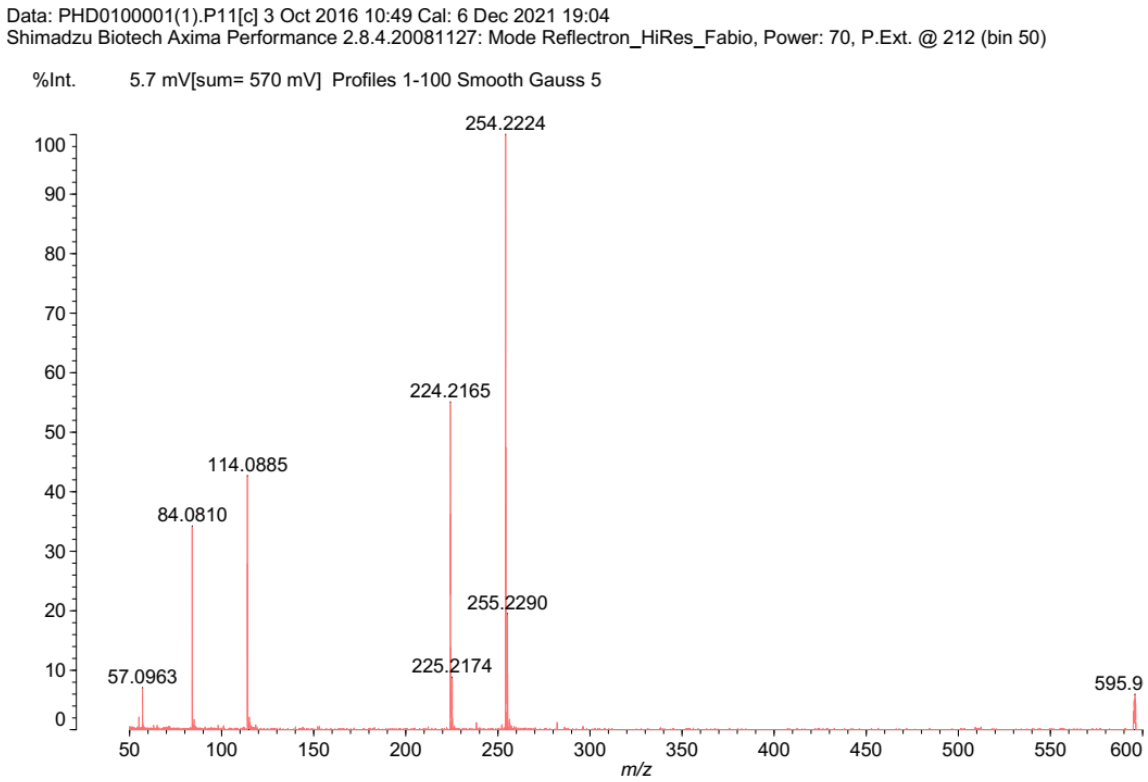

Figure S12. MALDI-TOF-MS spectra of **9b**.

Compound **3c** was synthesized according literature[1]

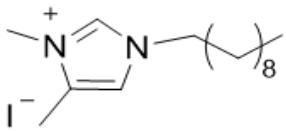

Figure S13. Compound **3c**, imidazole-IL derivative.

1.2. Thermogravimetric analysis

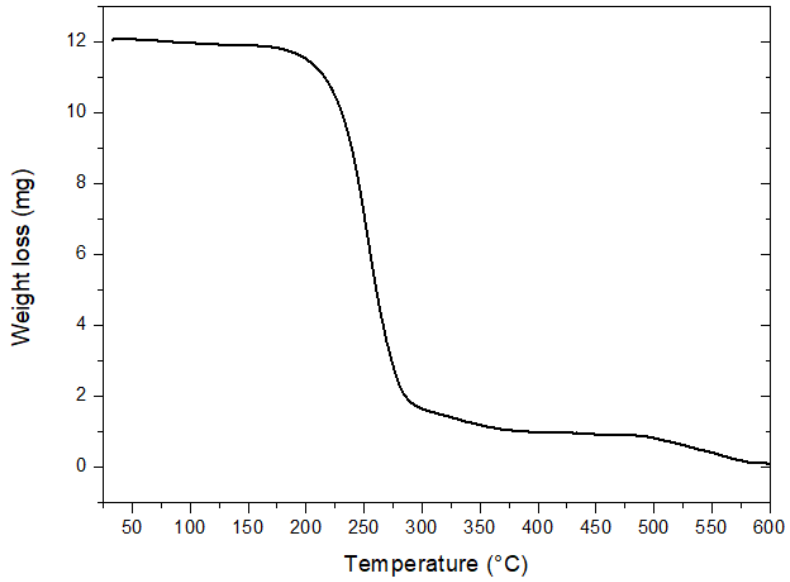

Figure S14. TG curves of **1b**.

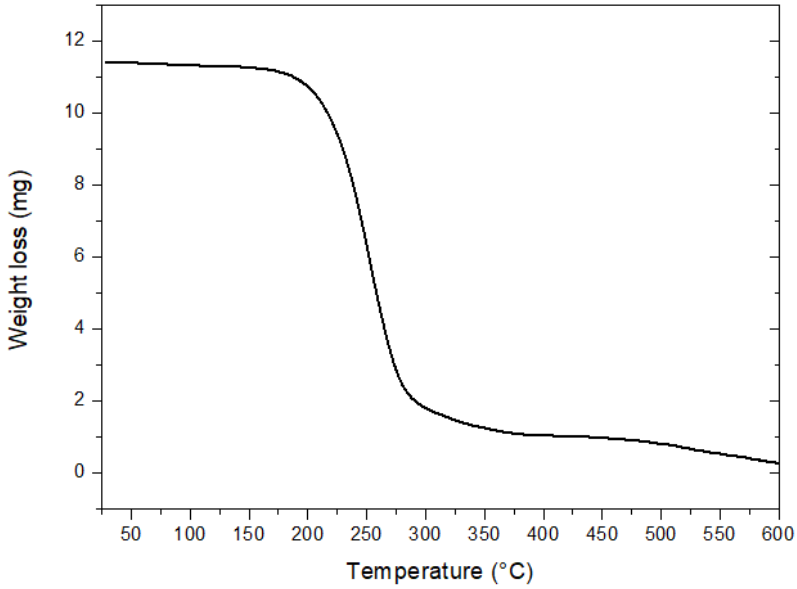

Figure S15. TG curves of **2b**.

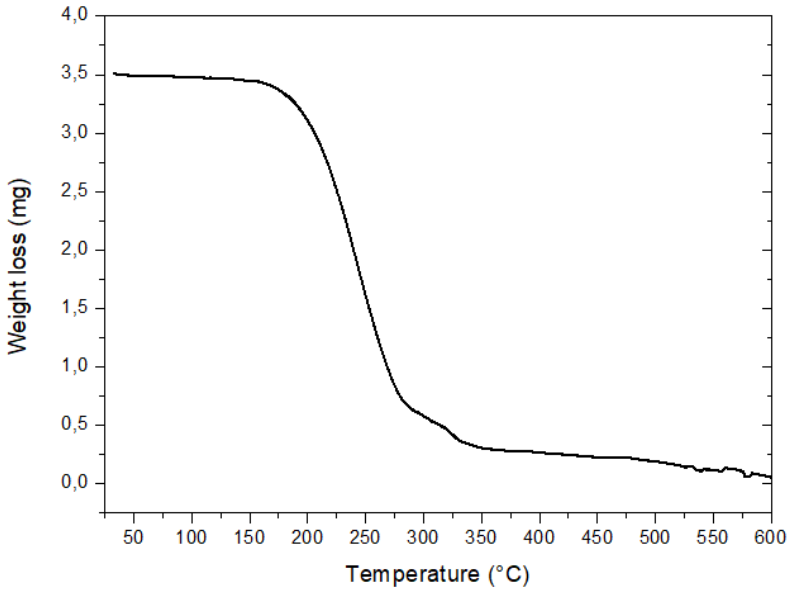

Figure S16. TG curves of **3b**.

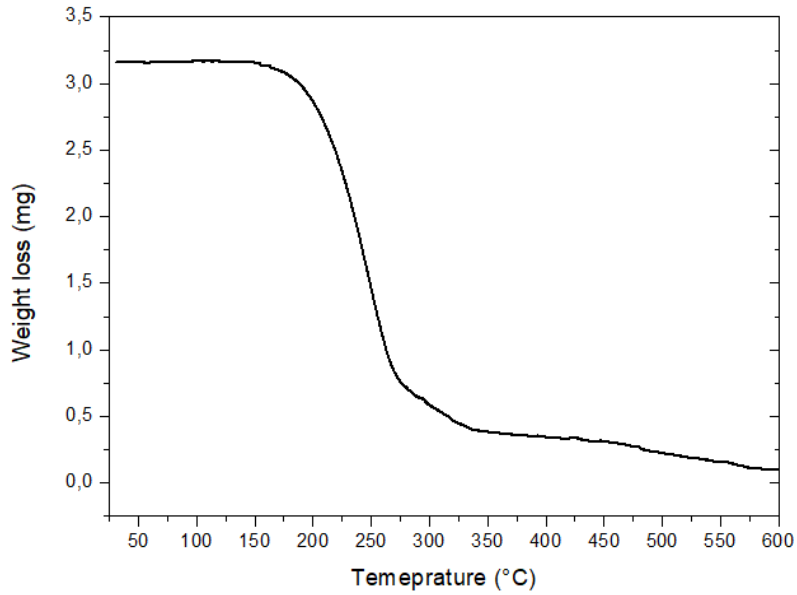

Figure S17. TG curves of **4b**.

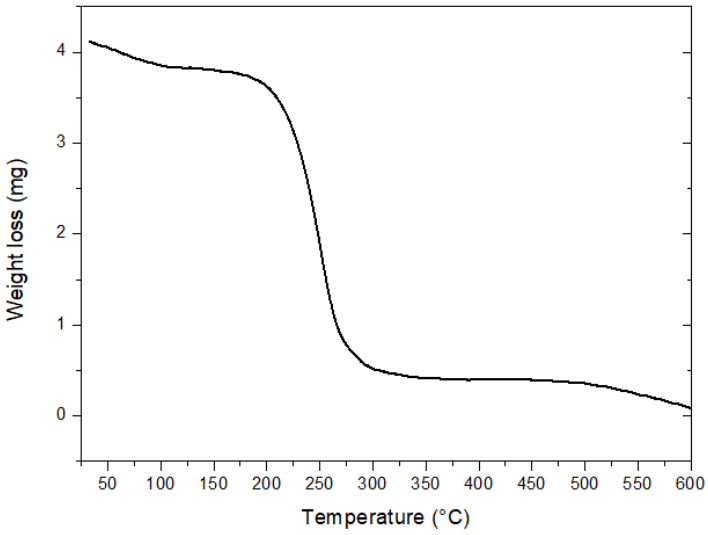

Figure S18. TG curves of **5b**.

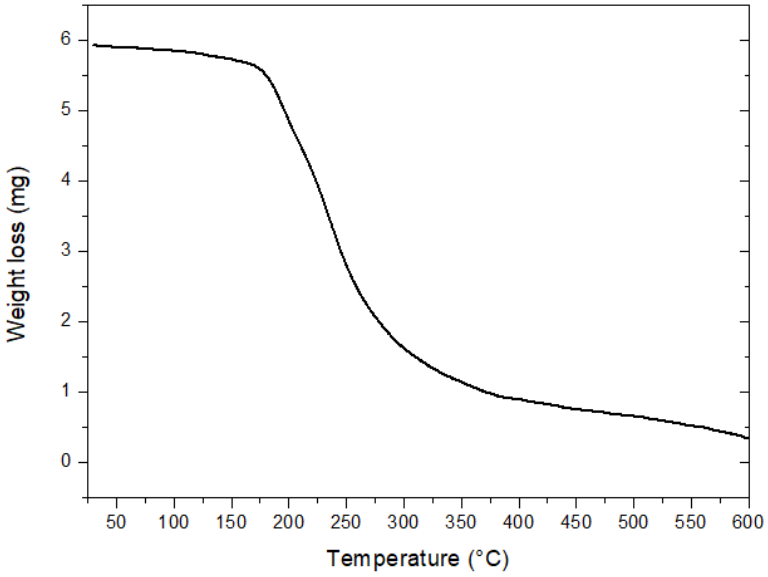

Figure S19. TG curves of **6b**.

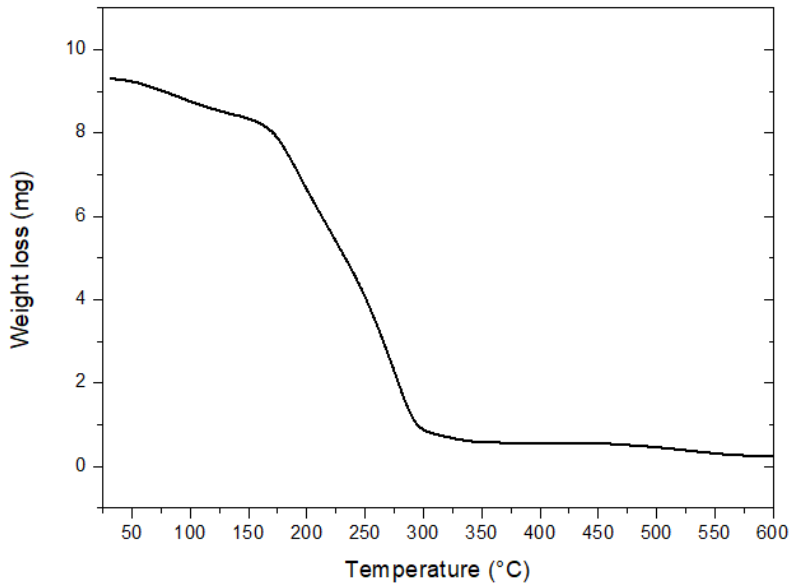

Figure S20. TG curves of **7b**.

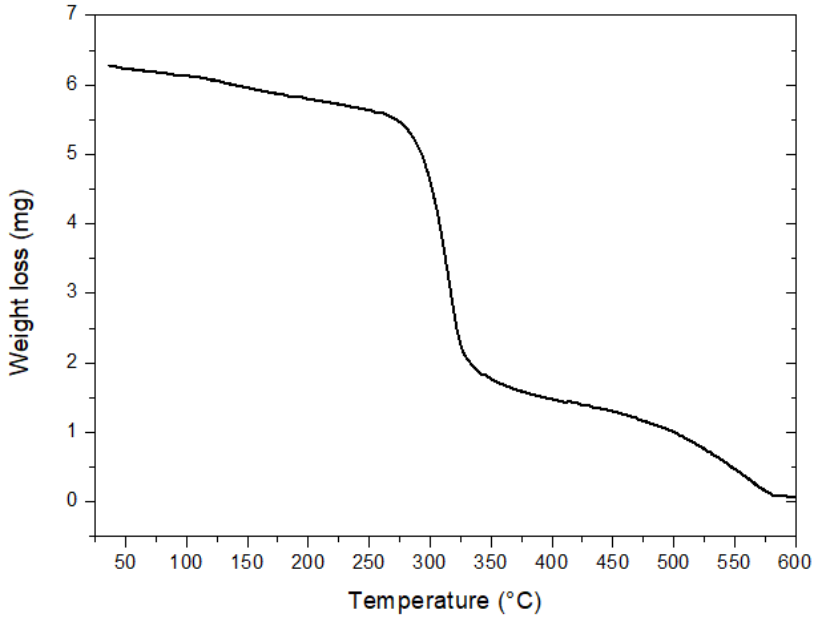

Figure S21. TG curves of **8b**.

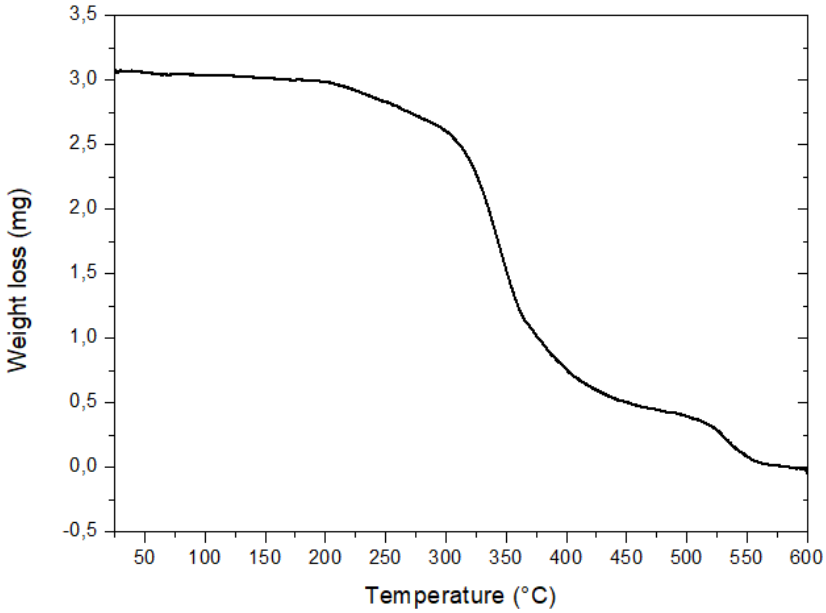

Figure S22. TG curves of **9b**.

1.3. Single crystal X-ray diffraction of 3b

Room temperature (298(2) K) single-crystal X-ray diffraction data were acquired on a Bruker-AXS Kappa Duo X-ray diffractometer with a Photon II CMOS detector and a MoKα microfocus source. Cell indexing and intensity dataset acquiring strategy and treatment were performed with Bruker software SAINT and SADABS.[1] Structure solution and refinements were achieved with SHELXS and SHELXL,[2] respectively. ORTEP-3[3] was used to prepare the crystal structure projection. Non-hydrogen and hydrogen atoms were treated as anisotropic and isotropic ($1.2U_{iso}$ = C; $1.5U_{iso}$ = C_{methyl} or O) in the refinements, respectively. For hydrogen positions, riding model was employed, with fixed valence bond lengths and angles since hydrogen coordinates oscillated as their bonded carbon or oxygen. The entire X-ray diffraction dataset, loading all structure factors, was deposited in CCDC under deposit code shown below in Table S1. In this table, a briefing of the crystal data acquisition, raw data treatment and the refinement figures-of-merit are also displayed.

References:

1 APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. C,* 2015, **71**, 3–8.

3 L. J. Farrugia, *J. Appl. Crystallogr.,* 2012, **45**, 849–854.

Table S1. Crystal data and refinement statistics for the compound elucidated in this study.

		3b
Structural formula		$C_{14}H_{28}IN_3O$
Molar weight (g/mol)		381.29
Crystal system		triclinic
Space group		*P*-1
Z		10
□ (Å)		0.71073
T (K)		298(2)
Unit cell dimensions	*a* (Å)	11.2155(12)
	b (Å)	18.933(2)
	c (Å)	22.600(3)
	□(°)	104.219(4)
	□(°)	99.501(4)
	□(°)	92.327(4)
V (Å^3)		4571.5(9)
Calculated Density (Mg/M^3)		1.385
Absorption coefficient (Mm^{-1})		1.750
θ-range for data collection (°)		0.945 –
Index ranges		-13 to 13
		-22 to 22
		-26 to 26
Data collected		309582
Unique reflections		16321
Unique reflections with *I*>2□(*I*)		9815
Symmetry factor (R_{int})		0.1110
Completeness to □=25°		99.7
F (000)		1940
Parameters refined		860
Goodness-of-fit on F^2		1.035
Final R_1factor for *I*>2□(*I*)		0.0458
wR2 factor for all data		0.1274
Largest diff. peak / hole (*e*/Å^3)		0.872/-0.595
CCDC deposit number		2129558

1.4. Cycloaddition reactions

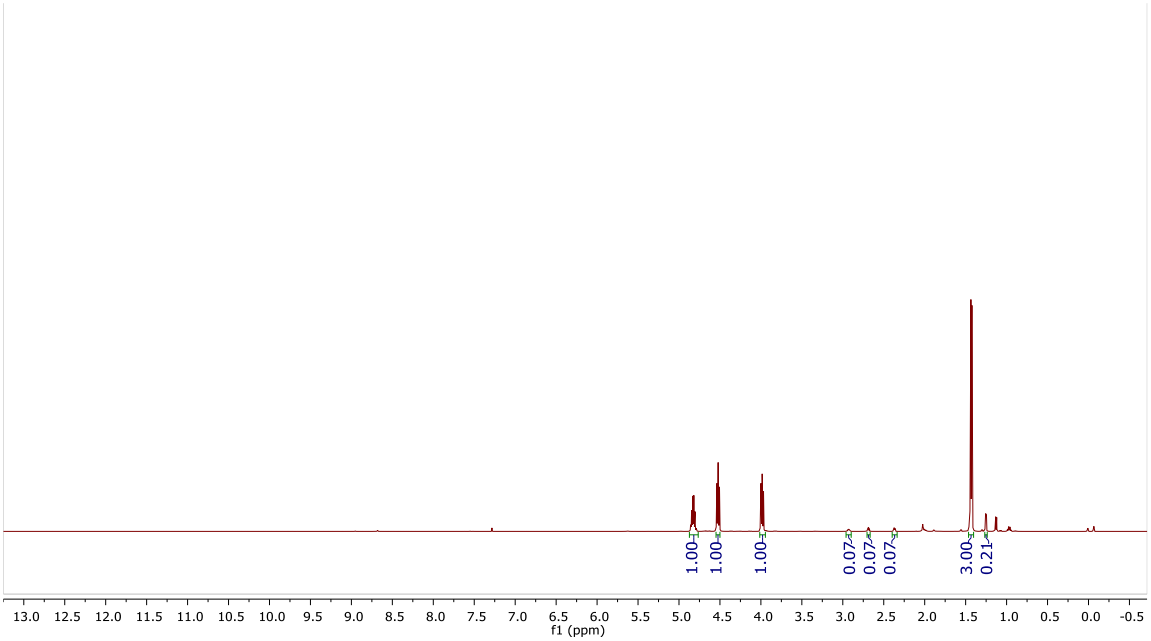

Figure S23. ^{1}H NMR of crude mixture of reaction using propylene oxide and its respective carbonate, entry 1, Table 3.

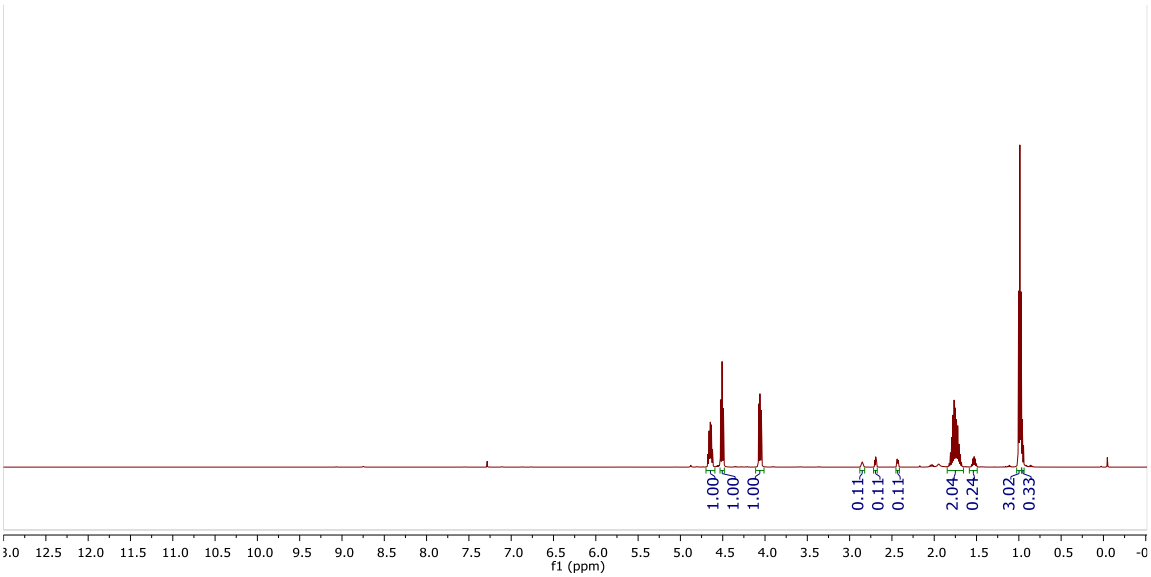

Figure S24. ^{1}H NMR of crude mixture of reaction using 2-butyloxirane and its respective carbonate, entry 2, Table 3.

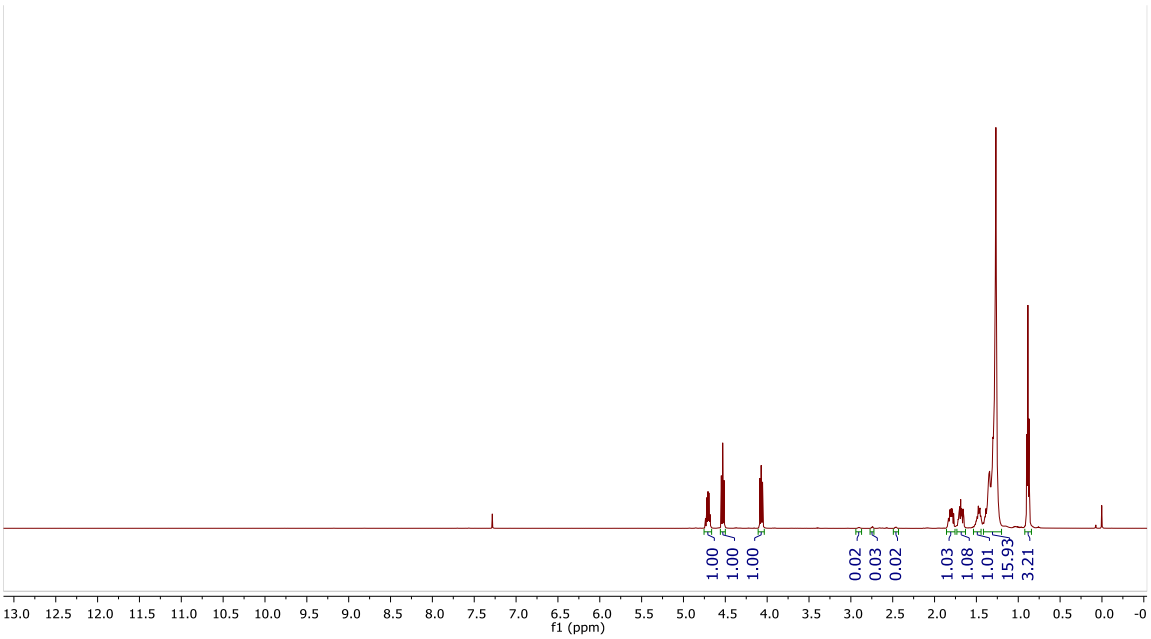

Figure S25. ^{1}H NMR of crude mixture of reaction using 2-decyloxirane and its respective carbonate, entry 3, Table 3.

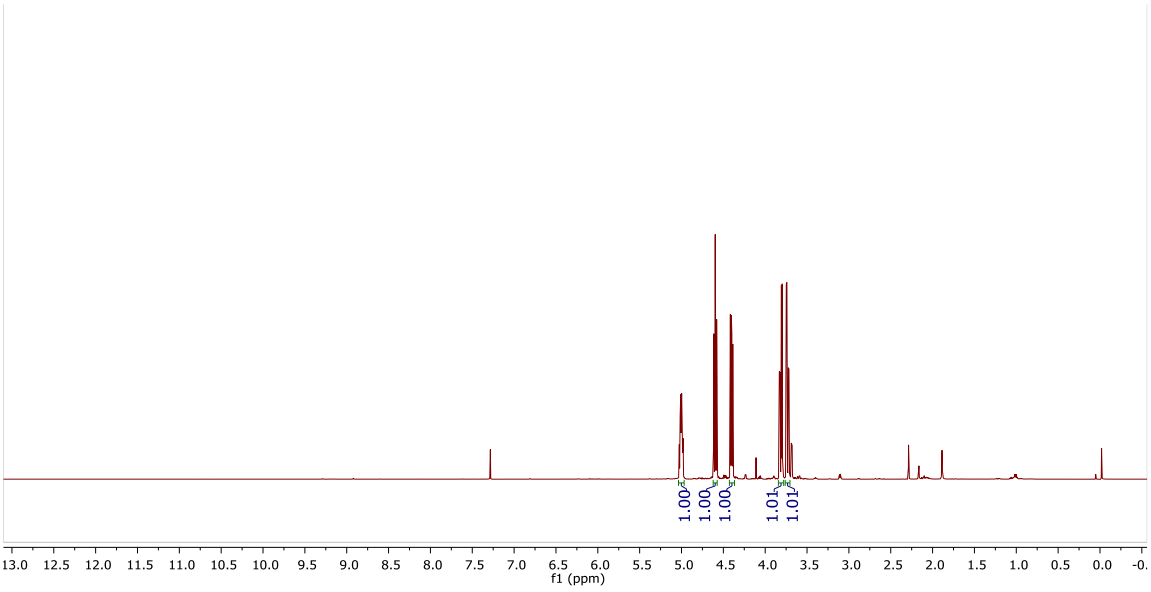

Figure S26. ^{1}H NMR of crude mixture of reaction using epichloridrine and its respective carbonate, entry 4, Table 3.

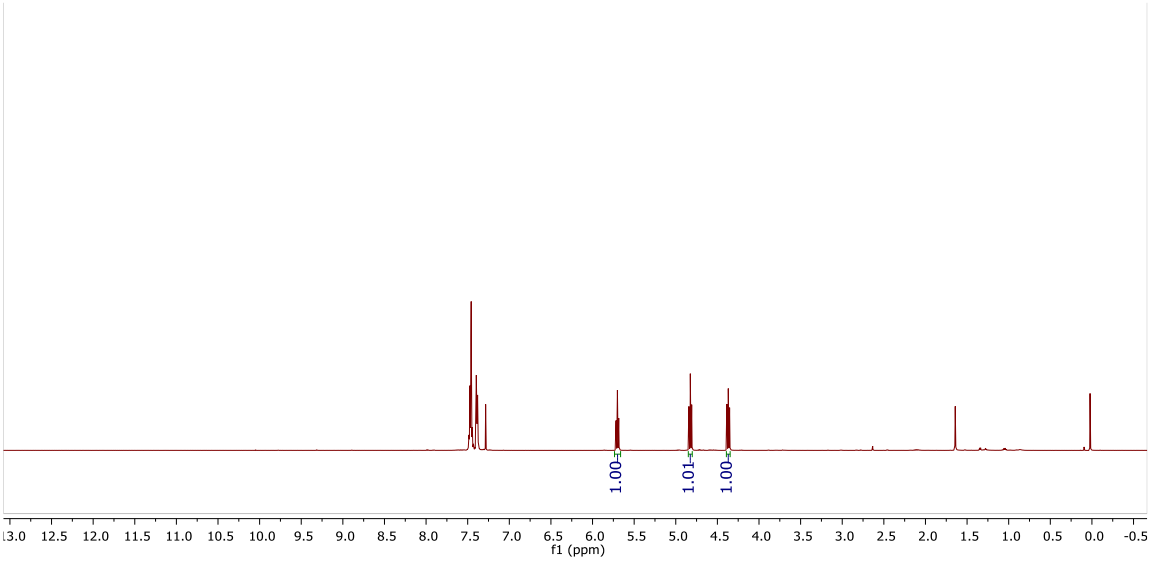

Figure 27. ^{1}H NMR of crude mixture of reaction using styrene oxide and its respective carbonate, entry 5, Table 3.

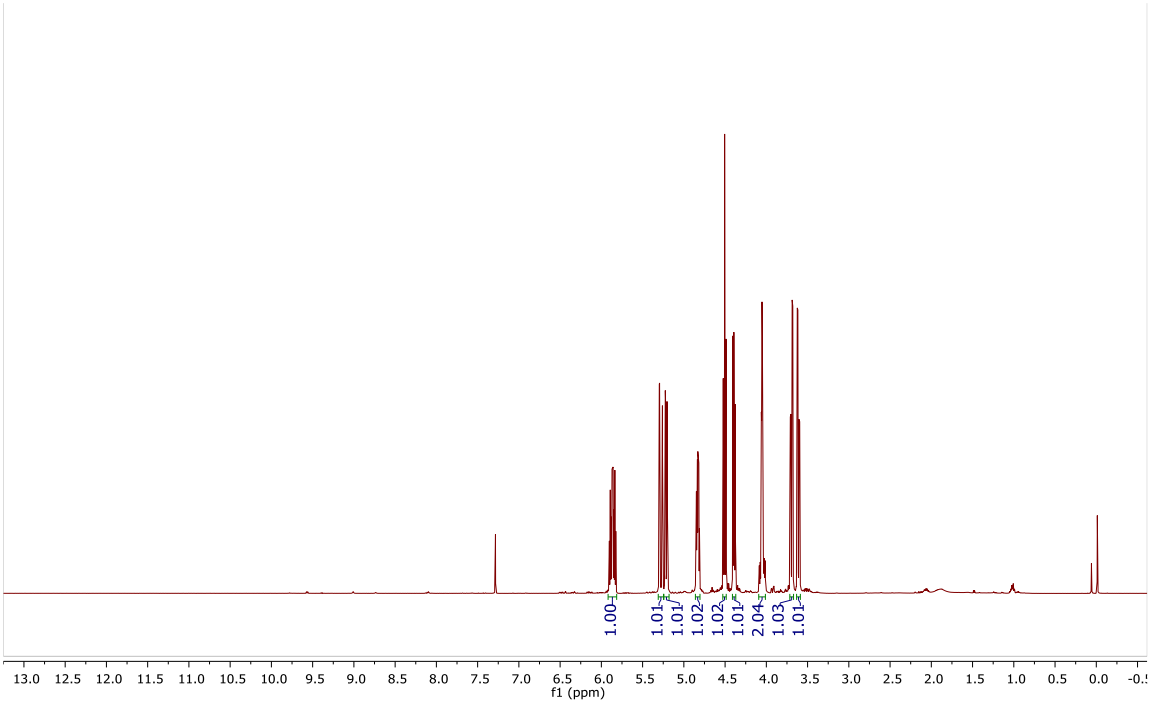

Figure 28. ^{1}H NMR of crude mixture of reaction using allyl glycidyl ether and its respective carbonate, entry 6, Table 3.

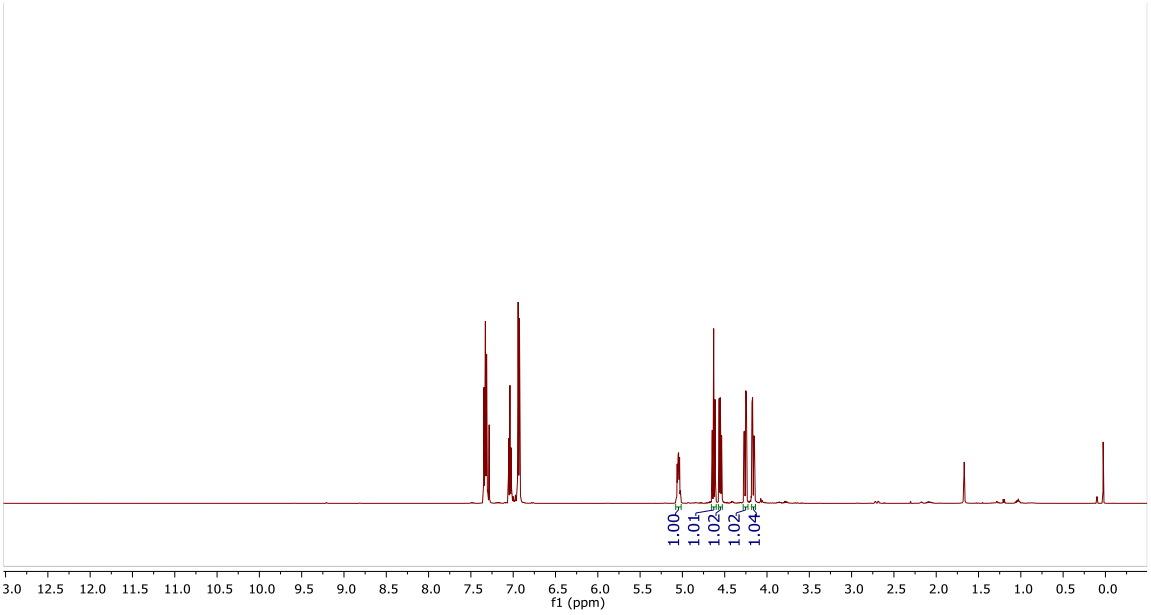

Figure S29. ^{1}H NMR of crude mixture of reaction using 2-(phenoxymethyl)oxirane and its respective carbonate, entry 7, Table 3.

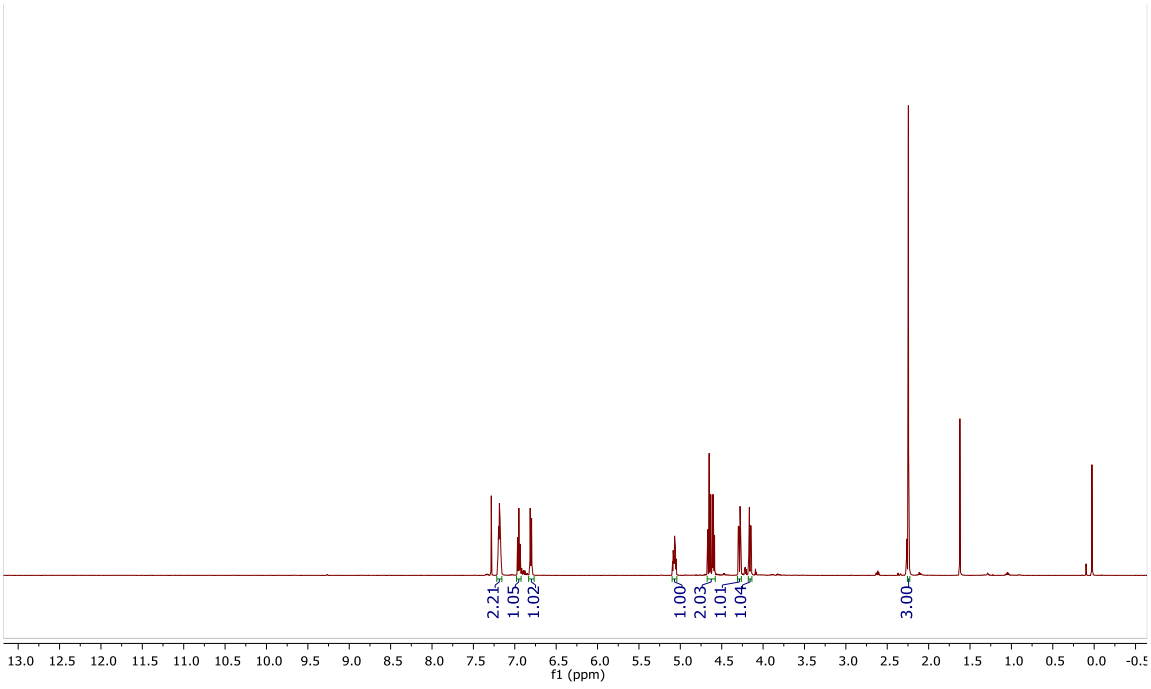

Figure S30. ^{1}H NMR of crude mixture of reaction using glycidyl 2-methylphenyl ether and its respective carbonate, entry 8, Table 3.

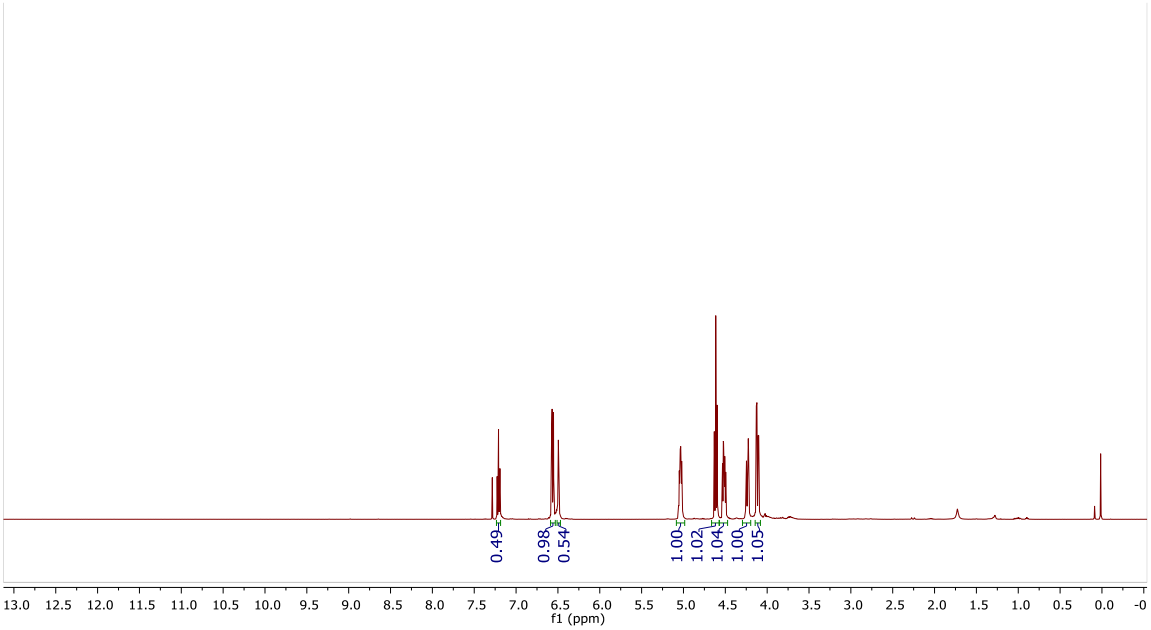

Figure S31. ^{1}H NMR of crude mixture of reaction using resorcinol diglycidyl ether and its respective carbonate, entry 9, Table 3.

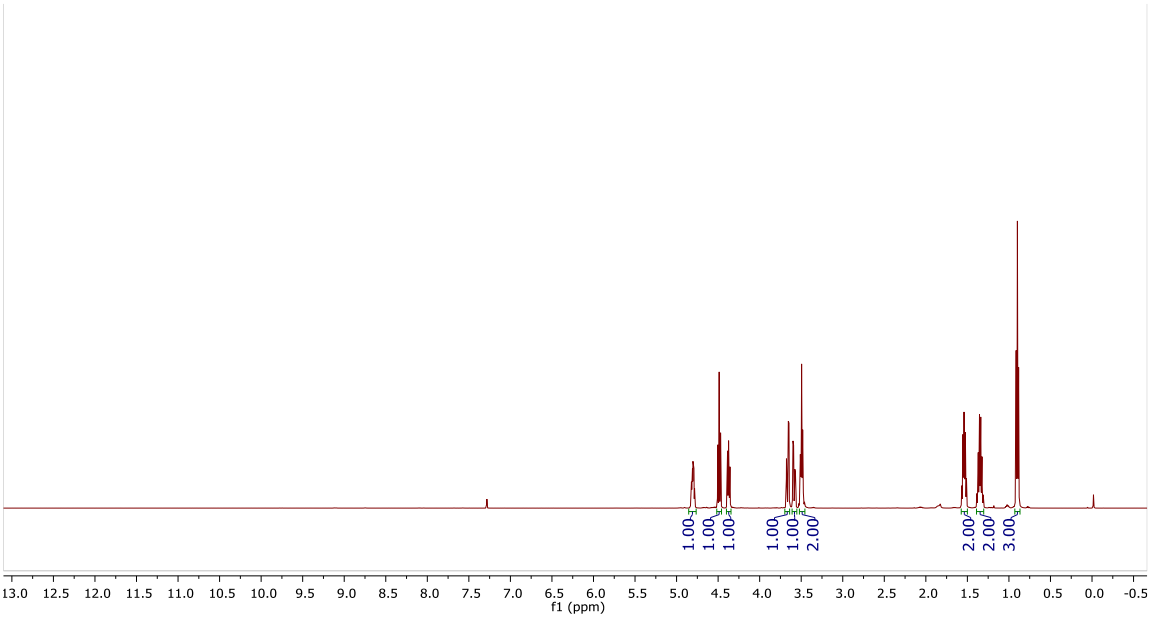

Figure S32. ^{1}H NMR of crude mixture of reaction using butyl glycidyl ether and its respective carbonate, entry 10, Table 3.

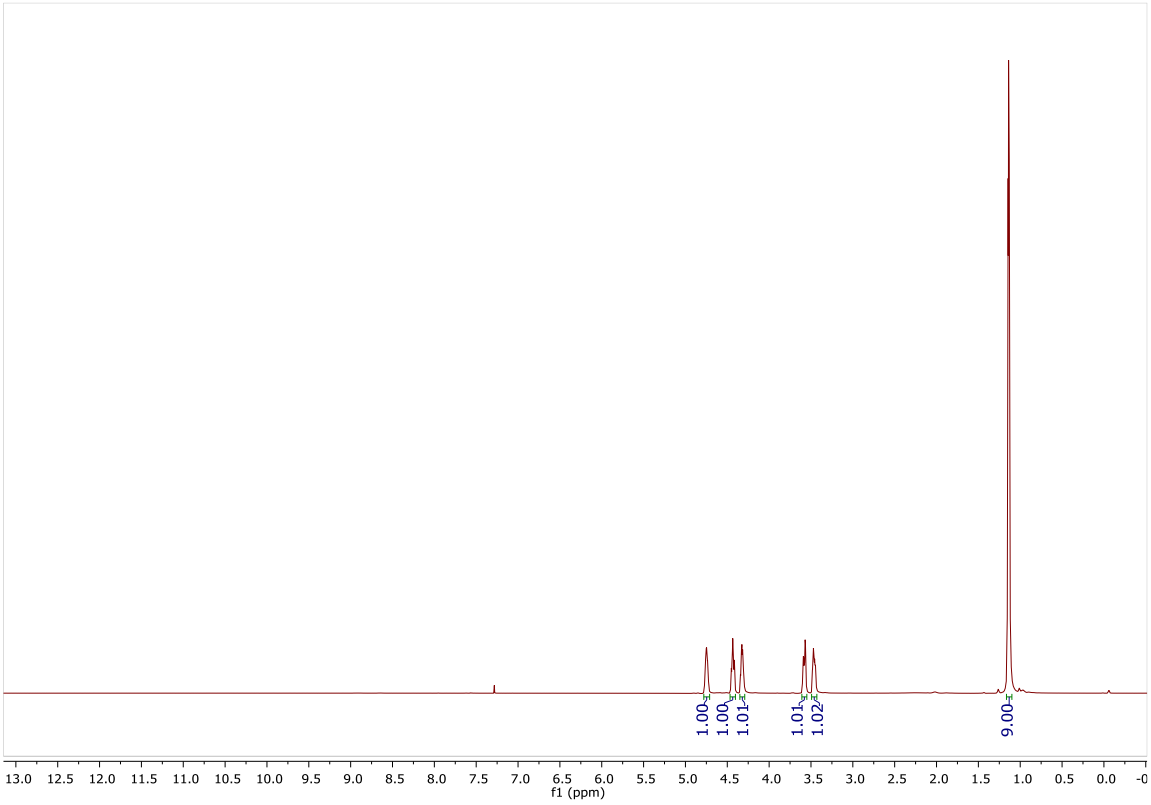

Figure S33. ^{1}H NMR of crude mixture of reaction using tert-butyl glycidyl ether and its respective carbonate, entry 11, Table 3.

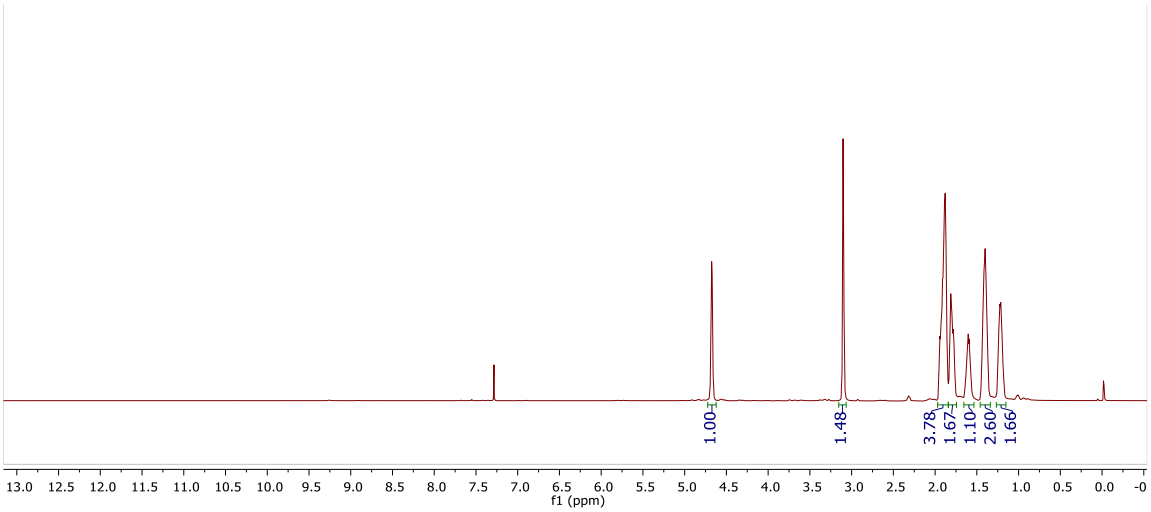

Figure S34. ^{1}H NMR of crude mixture of reaction using cyclohexane oxide (1 hours) and its respective carbonate, entry 12, Table 3.

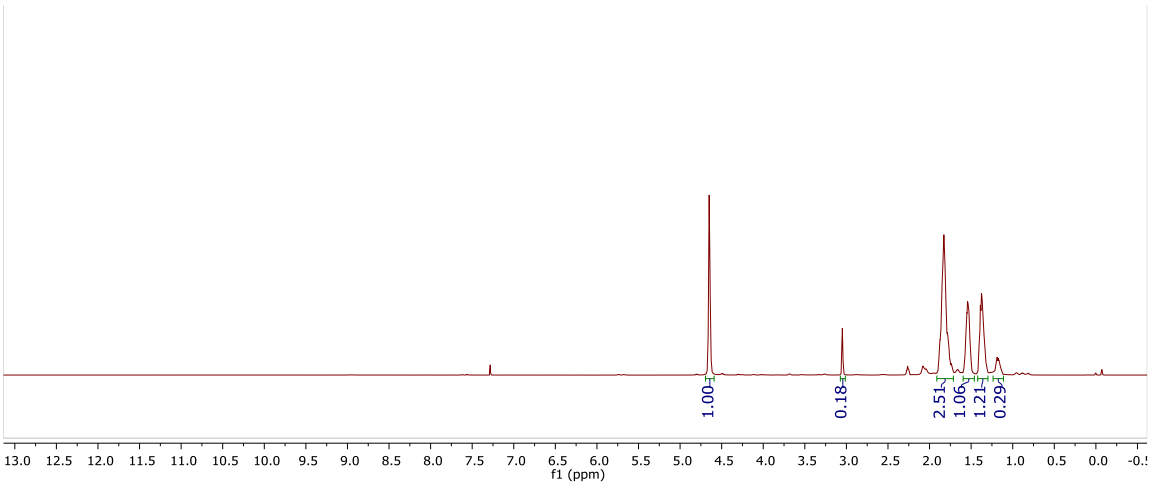

Figure S35. ^{1}H NMR of crude mixture of reaction using cyclohexane oxide (6 hours) and its respective carbonate, entry 13, Table 3.

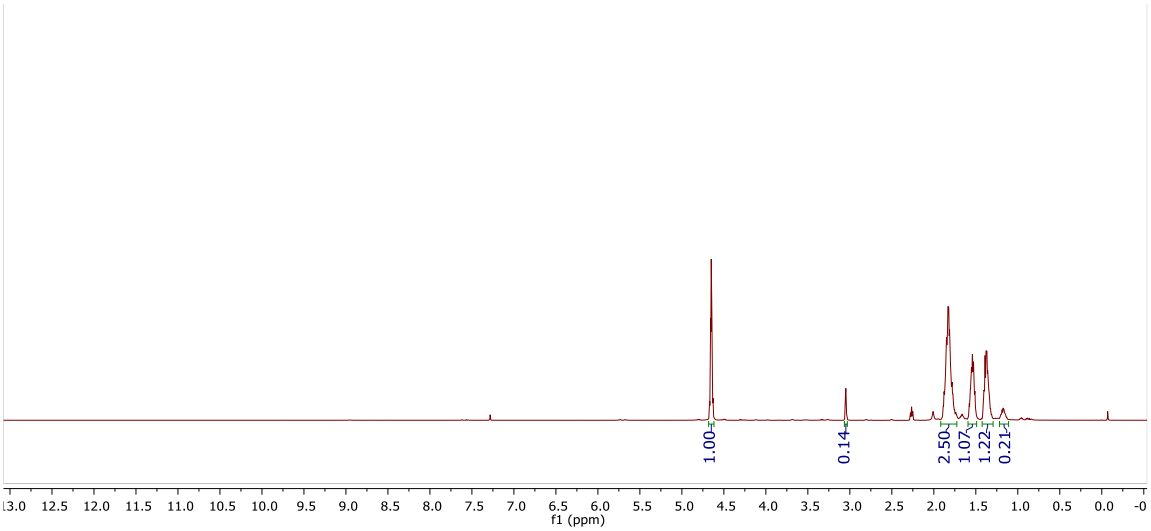

Figure S36. ^{1}H NMR of crude mixture of reaction using cyclohexane oxide (10 hours) and its respective carbonate, entry 14, Table 3.

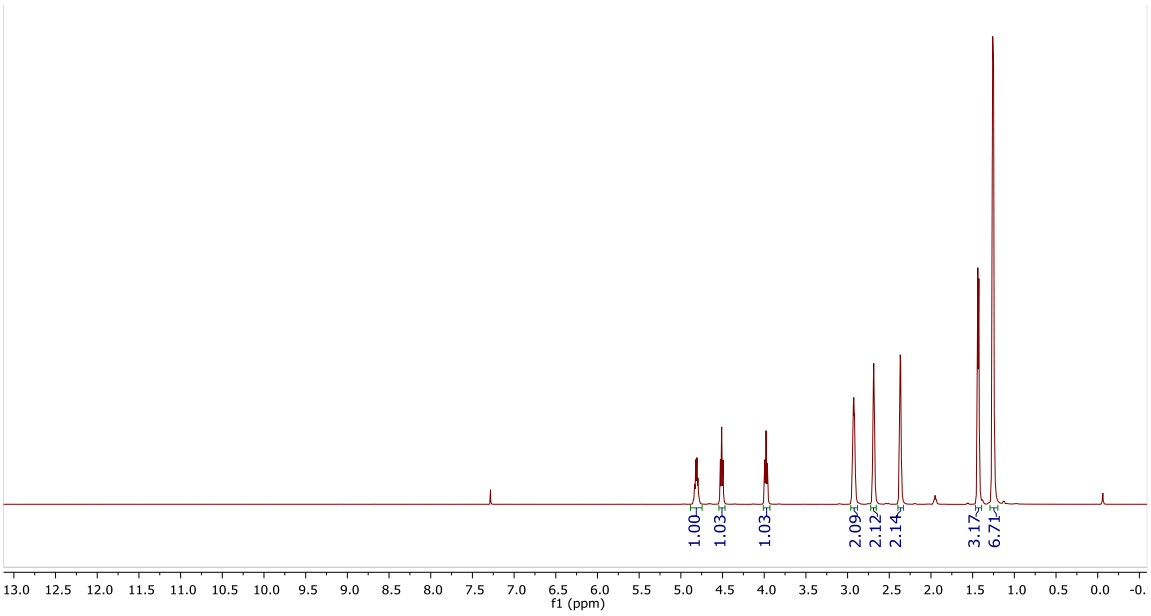

Figure S37. ^{1}H NMR of crude mixture of reaction using propylene oxide (500 mmol, 1 hour) and its respective carbonate, entry 1, Table 4.

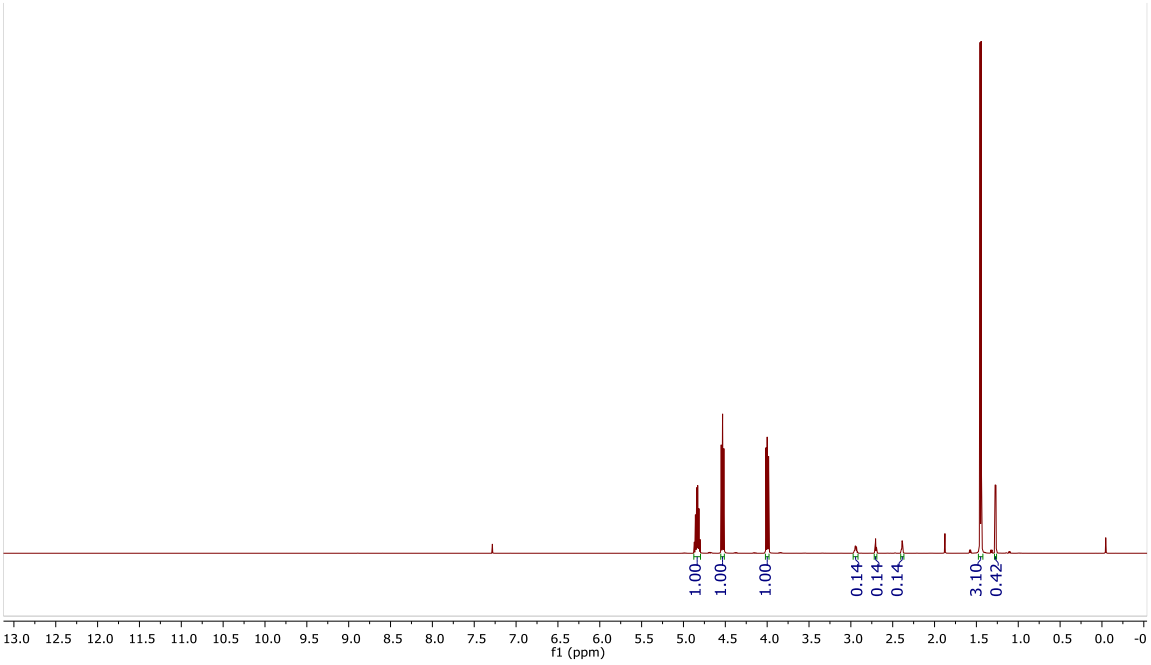

Figure S38. ^{1}H NMR of crude mixture of reaction using propylene oxide (500 mmol, 10 hours) and its respective carbonate, entry 2, Table 4.

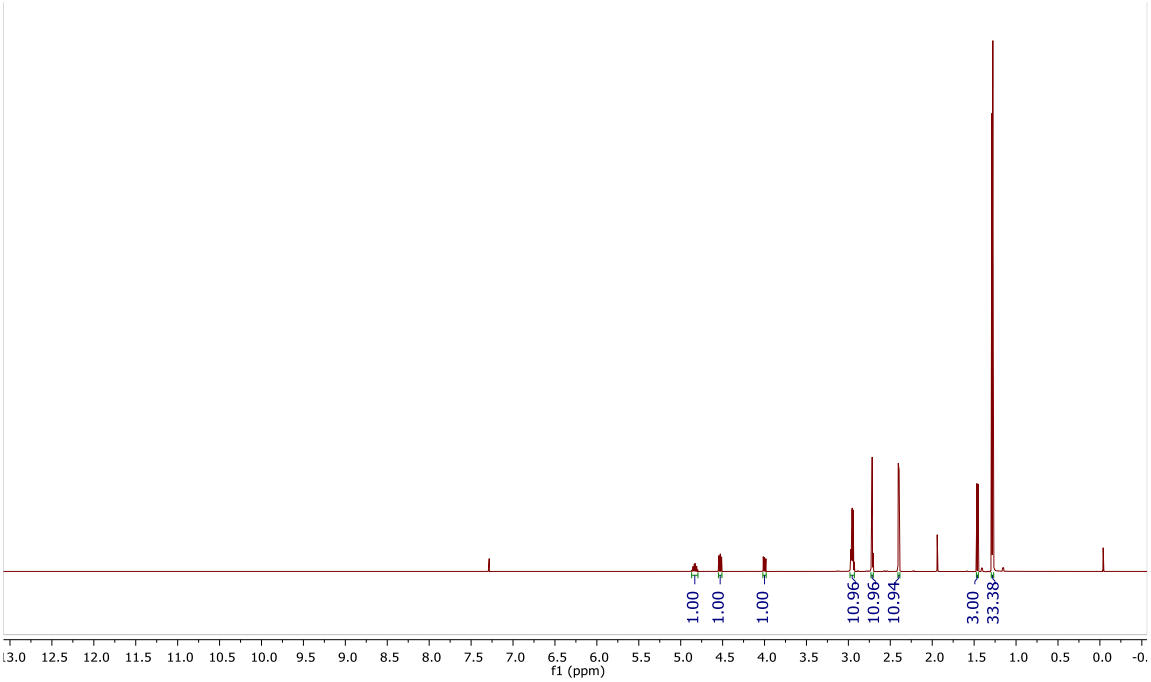

Figure S39. ^{1}H NMR of crude mixture of reaction using propylene oxide (1 mol, 1 hour) and its respective carbonate, entry 3, Table 4.

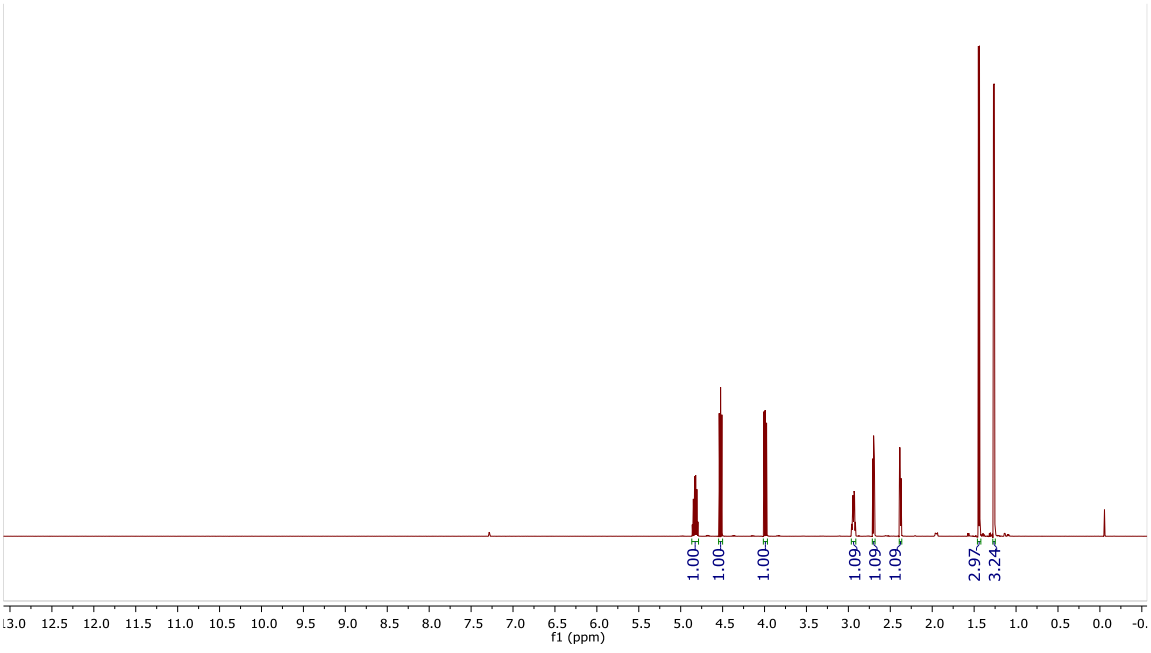

Figure S40. ^{1}H NMR of crude mixture of reaction using propylene oxide (1 mol, 24 hours) and its respective carbonate, entry 4, Table 4.

1.5. Reuse experiment

In order to test the reusability of our catalyst, it was performed experiments using 1.5 mol% of catalyst, 25 mmol of PO, 140 °C, 30 bar at 1 hour. The results showed in Figure S35 suggest the IL degradation into respective neutral 1,2,3-triazole which present very low activity (see entry 1, Table 1).

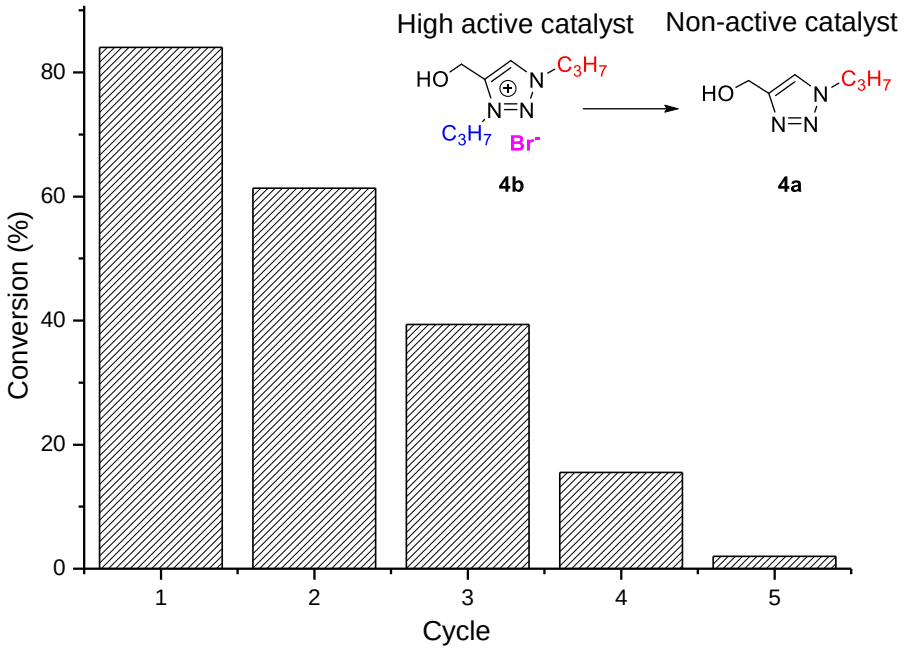

Figure S41. Catalyst reuse experiment.

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[1] Seung-Hwan Jeon, A.R. Sathiya Priya, Eun-Ji Kang, Kang-Jin Kim Synthesis of a novel alkylimidazolium iodide containing an amide group for electrolyte of dye-sensitized solar cells **2010**, 55, 5652-5658.