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Number of pages: 17

Number of Figures: 19

Number of Table: 5

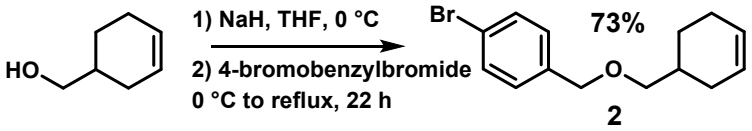
General Methodology

Characterization and Purification Methods

^{1}H and ^{13}C spectra were recorded on a Bruker Avance III spectrometer operating at 400 MHz or 500 MHz. Spectra were obtained using solutions of *ca.* 10 mg in appropriate deuterated solvents. The chemical shifts (δ) are expressed in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C nuclei. The coupling constants were automatically obtained by TopSpin© and expressed in Hz. Abbreviations for signal coupling are indicated as: s = singlet; d=doublet; dd=doublet of doublets; t=triplet; q=quartet; quin=quintet; m=multiplet; br=broad signal. To accurate determine the molecular structure of the monomer CEIL and its intermediates additional 2D NMR experiments (COSY, HSQC, HMBC) were performed.

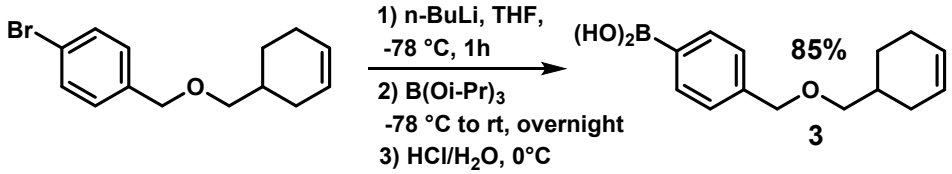
High Resolution Mass Spectra HRMS was carried out on by a Micromass-Waters Q-TOF Ultima Global by the technique of Electrospray Ionization (ESI).

Thin Layer Chromatography (TLC) was run using different eluent mixtures on pre-coated aluminum plates of silica gel 60 F-254 (Merck).



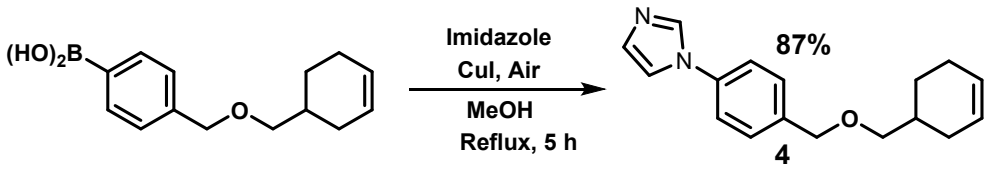
4-Bromobenzyl (cyclohex-3-en-1-ylmethyl) ether (2).

Under Argon atmosphere, cyclohexen-4-ylmethanol (12.5 mL, 0.11 mol) was added dropwise to a stirred suspension of NaH (5.6 g (60 % in mineral oil), 0.14 mol) in anhydrous THF (200 mL) at 0 °C. After the addition, the mixture was left to stir for 30 min at 0 °C. Then, more 200 mL of anhydrous THF was added followed by the addition of 4-bromobenzylbromide (26.75 g, 0.12 mol). The reactional mixture was stirred for 30 min at 27 °C. Finally, the reactional mixture was heated for 22 h under reflux and Argon atmosphere. The reaction was cooled to 0 °C and it was quenched by adding 50 g of ice cubes. The reactional mixture was stirred for 1 h to ensure the complete quenching. The reaction was filtered using paper filter and extracted five times with dichloromethane and dd-water. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The product was further purified by column chromatography using silica gel and hexane: ethyl acetate (solvent mixture gradient from 100:0 until 95:5) as eluent. Compound **2** was obtained as a colorless and transparent oil with 73% of yield. **^{1}H NMR (500 MHz, Chloroform-d) δ**: 7.45 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 5.76–5.61 (m, 2H), 4.47 (s, 2H), 3.41–3.30 (m, 2H), 2.17–2.09 (m, 1H), 2.09–2.03 (m, 2H), 1.99–1.90 (m, 1H), 1.88– 1.80 (m, 1H), 1.80 – 1.70 (m, 1H), 1.34 – 1.21 (m, 1H). **^{13}C NMR (126 MHz, Chloroform-d) δ**: 138.8, 132.5, 129.3, 127.2, 126.7, 122.3, 74.5, 73.3, 33.5, 27.6, 24.9, 25.6.



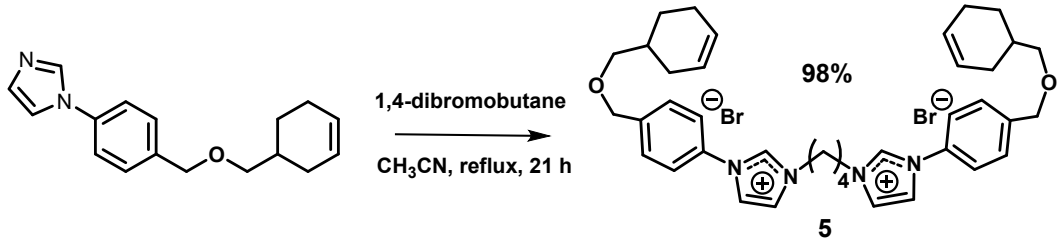
4-((Cyclohex-3-en-1-ylmethoxy)methyl)phenyl)boronic acid (3).

Under Argon atmosphere, the compound **2** (13.85 g, 49.2 mmol) was dissolved in anhydrous THF (129 mL) and mixture was cooled to -78 °C and, subsequently n-BuLi 2.5 M in hexane (23.6 mL, 49.2 mmol) was added dropwise. The mixture was kept stirring at -78 °C for 60 min and then 17 ml (50.5 mmol) of triisopropyl borate was slowly added. The mixture was stirred overnight from -78 °C to room temperature. The reaction was cooled to 0 °C and quenched by adding 50 g of ice cubes followed by the slowly addition of 137 mL of hydrochloric acid (1 M). The yielding mixture was stirred for 30 min. The aqueous layer was extracted by dichloromethane, dried over anhydrous $MgSO_4$ and concentrated in vacuo. Compound **3** was employed in the next step without further purification since the product degrades in the column. The product was obtained as a off-white crystal compound. **^{1}H NMR (500 MHz, Chloroform-d) δ**: 8.21 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 7.7 Hz, 2H), 5.88–5.46 (m, 2H), 4.61 (s, 2H), 3.52–3.32 (m, 2H), 2.28–2.12 (m, 1H), 2.12–2.08 (m, 2H), 2.05–1.95 (m, 1H), 1.95– 1.85 (m, 1H), 1.83–1.72 (m, 1H), 1.35–1.26 (m, 1H). **^{13}C NMR (126 MHz, Chloroform-d) δ**: 143.7, 135.9, 133.5, 127.4, 126.4, 126.7, 75.9, 72.8, 34.1, 28.3, 25.5, 24.4.



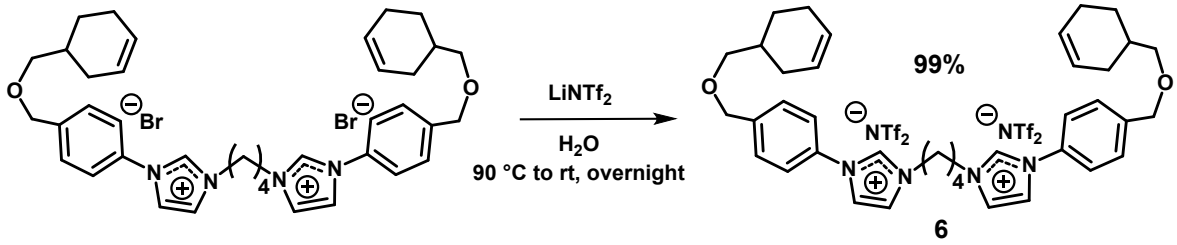
1-(4-((Cyclohex-3-en-1-ylmethoxy)methyl)phenyl)-1H-imidazole (4).

Initially, imidazole (2.5 g, 37.2 mmol) and copper (I) iodide (236 mg, 1.4 mmol) was stirred for 5 min in 114 ml of methanol. Subsequently, the boranic acid derivative **3** was added and stirred overnight under reflux and bubbling air in the reactional mixture. The solution was cooled to room temperature and filtered using a Celite® pellet and concentrated under reduced pressure. The product was further purified by column chromatography using silica gel and hexane: ethyl acetate (solvent mixture gradient from 70:30 until 0:100) as eluent. Compound **4** was obtained as white crystalline powder. **^{1}H NMR (400 MHz, Chloroform-d) δ:** 7.89 (s, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.27 (s, 1H), 7.22 (s, 1H), 5.72–5.61 (m, 2H), 4.54 (s, 2H), 3.54–3.22 (m, 2H), 2.18–2.12 (m, 1H), 2.08–2.04 (m, 2H), 2.02–1.94 (m, 1H), 1.89–1.83 (m, 1H), 1.82–1.73 (m, 1H), 1.37–1.29 (m, 1H). **^{13}C NMR (400 MHz, Chloroform-d) δ:** 138.5, 136.7, 135.6, 130.5, 128.5, 127.2, 126.2, 121.5, 118.9, 75.6, 72.2, 34.5, 28.4, 25.7, 24.3.



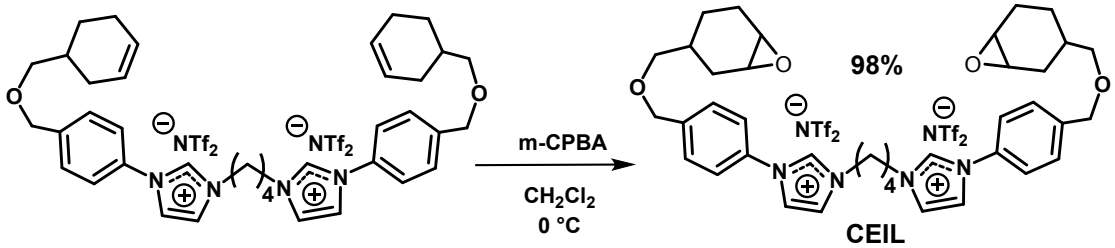
3,3'-(Butane-1,4-diyl)bis(1-(4-((cyclohex-3-en-1-ylmethoxy)methyl)phenyl)-1H-imidazol-3-ium) bromide (5).

Compound **4** (6.37 g, 23.7 mmol) was solubilized in 33 mL of acetonitrile and 1,4-dibromobutane (2.6 g, 11.87 mmol) was slowly added using a syringe and needle. The reaction was stirred for 21 h at 80 °C. The reaction yielded an off-white precipitate that was washed several times with cold acetonitrile. The product was filtered and dried under vacuum resulting in a white powder. **^{1}H NMR (400 MHz, Chloroform-d) δ:** 10.78 (t, J = 1.7 Hz, 2H), 8.44 (t, J = 1.3 Hz, 2H), 7.74 (d, J = 8.5 Hz, 4H), 7.62 (t, J = 1.9 Hz, 2H), 7.52 (d, J = 8.4 Hz, 4H), 5.73–5.54 (m, 4H), 4.82 (t, J = 6.3 Hz, 4H), 4.54 (s, 4H), 3.41–3.35 (m, 4H), 2.37 (t, J = 6.3 Hz, 4H), 2.16–2.08 (m, 2H), 2.08–2.00 (m, 4H), 1.98– 1.87 (m, 2H), 1.86–1.77 (m, 2H), 1.79–1.69 (m, 2H), 1.34–1.23 (m, 2H). **^{13}C NMR (400 MHz, Chloroform-d) δ:** 141.7, 135.5, 133.7, 129.3, 127.2, 125.8, 124.7, 121.8, 120.2, 75.7, 71.9, 49.3, 34.1, 28.5, 26.6, 25.6, 24.5.



3,3'-(Butane-1,4-diyl)bis(1-(4-((cyclohex-3-en-1-ylmethoxy)methyl)phenyl)-1H-imidazol-3-ium) bistrifluoromethanesulfonimidate (6).

The compound 5 (21.22 g, 28.28 mmol) was added in 400 ml of dd-water and heated to 85 °C until complete solubilization of the material. Subsequently, a $LiNTf_2$ (13.52 g, 43 mmol) solution was prepared using 1 mL of dd-water, and it was added to the previous solution. The mixture became cloudy, and this reactional mixture was left to stir for 3h at room temperature. The aqueous layer was extracted by dichloromethane five times, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The compound 6 was obtained as a colorless oil (32.28 g, 27.99 mmol). **^{1}H NMR (400 MHz, Chloroform-d) δ:** 9.07 (t, J = 1.8 Hz, 2H), 7.72 (t, J = 1.8 Hz, 2H), 7.61–7.49 (m, 10H), 5.76–5.57 (m, 4H), 4.59 (s, 4H), 4.44–4.38 (m, 4H), 3.47–3.32 (m, 4H), 2.23–2.12 (m, 6H), 2.10– 2.03 (m, 4H), 2.05–1.93 (m, 2H), 1.90–1.88 (m, 4H), 1.38–1.27 (m, 2H). **^{13}C NMR (400 MHz, Chloroform-d) δ:** 142.2, 133.8, 133.5, 129.3, 127.2, 125.8, 123.9, 122.5, 121.8, 119.5 (q, J = 321.1 Hz), 75.0, 71.2, 49.3, 34.5, 28.5, 26.5, 24.6, 25.6.



3,3'-(Butane-1,4-diyl)bis(1-(4-(((7-oxabicyclo[4.1.0]heptan-3-yl)methoxy)methyl)phenyl)-1Himidazol-3-ium) bistrifluoromethanesulfonimidate (CEIL).

To obtain the final product CEIL, an adaptation of the classical Prilezhaev epoxidation reaction[1] was employed. Compound 6 (9.54 g, 8.31 mmol) was solubilized in anhydrous dichloromethane (54.41 mL) at 0 °C. Next, m-CPBA (5.97 g, 20.8 mmol) was slowly added. The reaction was stirred at 0 °C for 3 h, and a white precipitate was formed. The reaction mixture was concentrated under reduced pressure and filtered to eliminate the excess of m-CPBA and its derivatives. The solution obtained from the filtration was poured in diethyl ether (300 mL). The insoluble part was isolated by decantation and washed three times by diethyl ether. The product was dried under vacuum and resulted in a transparent and colorless viscous oil (9.98 g, 98%). **^{1}H NMR (400 MHz, Acetonitrile-d3) δ:** 8.92–8.86 (m, 2H), 7.84–7.78 (m, 2H), 7.67–7.58 (m, 10H), 4.62– 4.54 (m, 4H), 4.35–4.57 (m, 4H), 3.41–3.29 (m, 4H), 3.19–3.09 (m, 4H), 2.21–1.98 (m, 7H), 1.87–1.38 (m, 9H), 1.21–0.99 (m, 2H). **^{13}C NMR (101 MHz, Acetonitrile-d3) mixture of stereoisomers3 δ:** 143.9, 142.9, 135.7,

134.8, 134.9, 130.2, 130.1, 124.3, 123.6, 123.6, 123.1, 120.8 (q, J = 320.8 Hz), 76.7, 76.2, 72.3, 72.2, 53.1, 53.3, 52.2, 51.7, 50.6, 33.10, 31.3, 29.3, 28.2, 27.2, 25.4, 24.8, 23.7, 22.3.

NMR Spectra

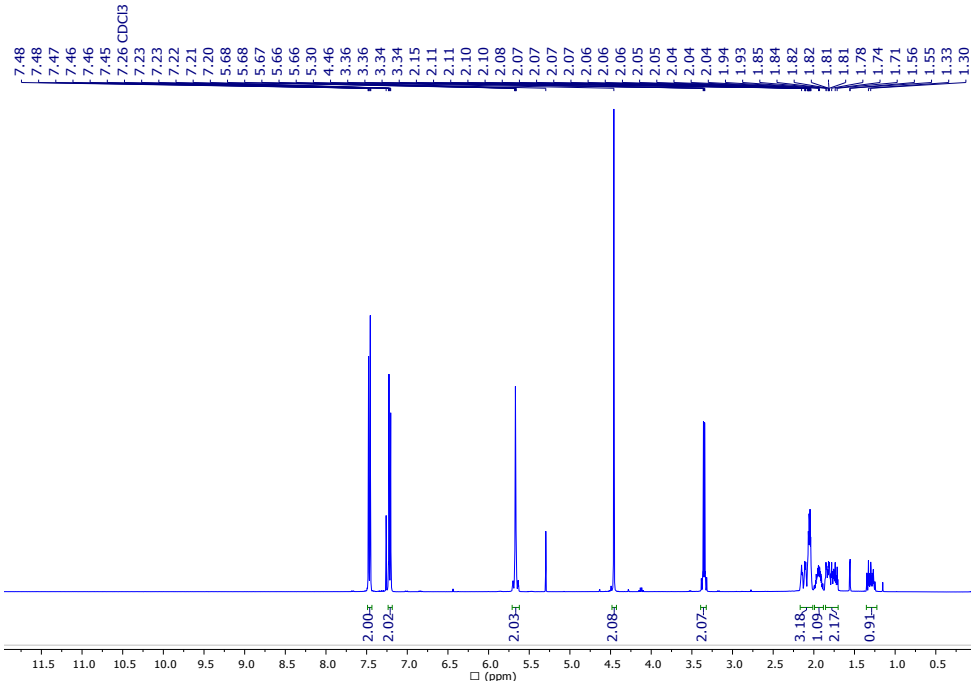


Figure S1 - ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$, 25 ºC).

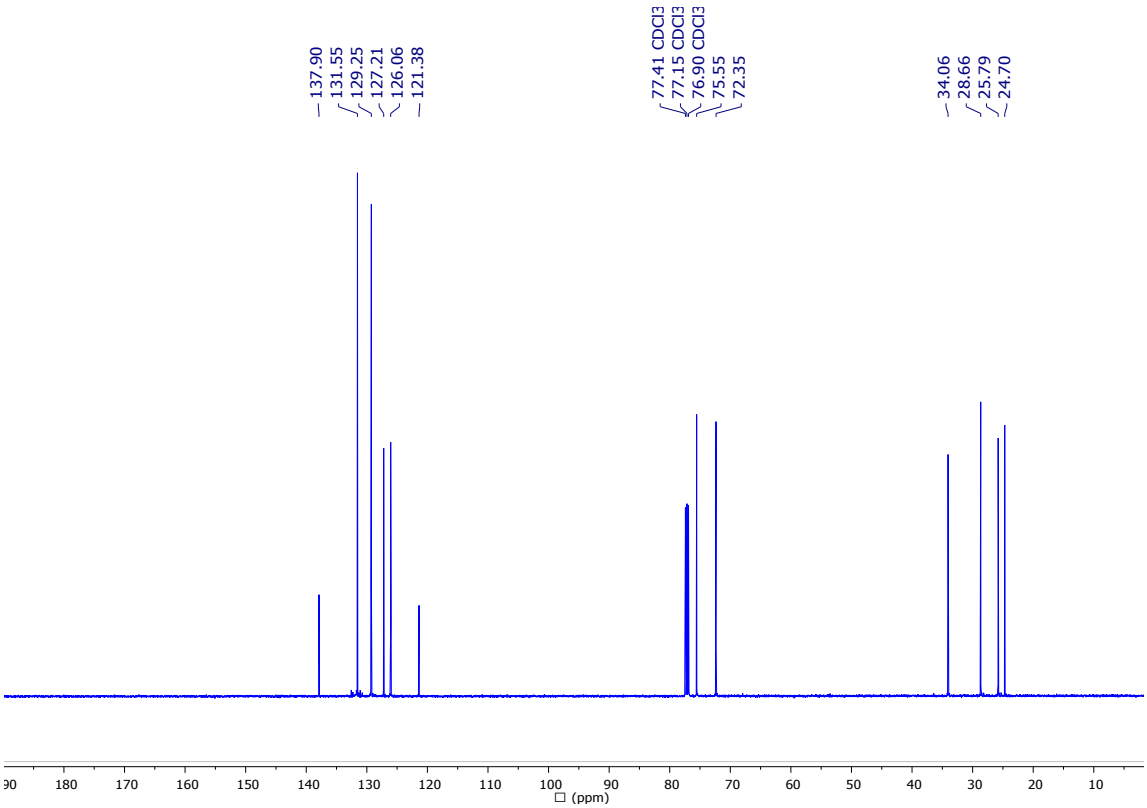


Figure S2 – ^{13}C NMR spectrum of compound **2** (400 MHz, $CDCl_3$, 25 ºC).

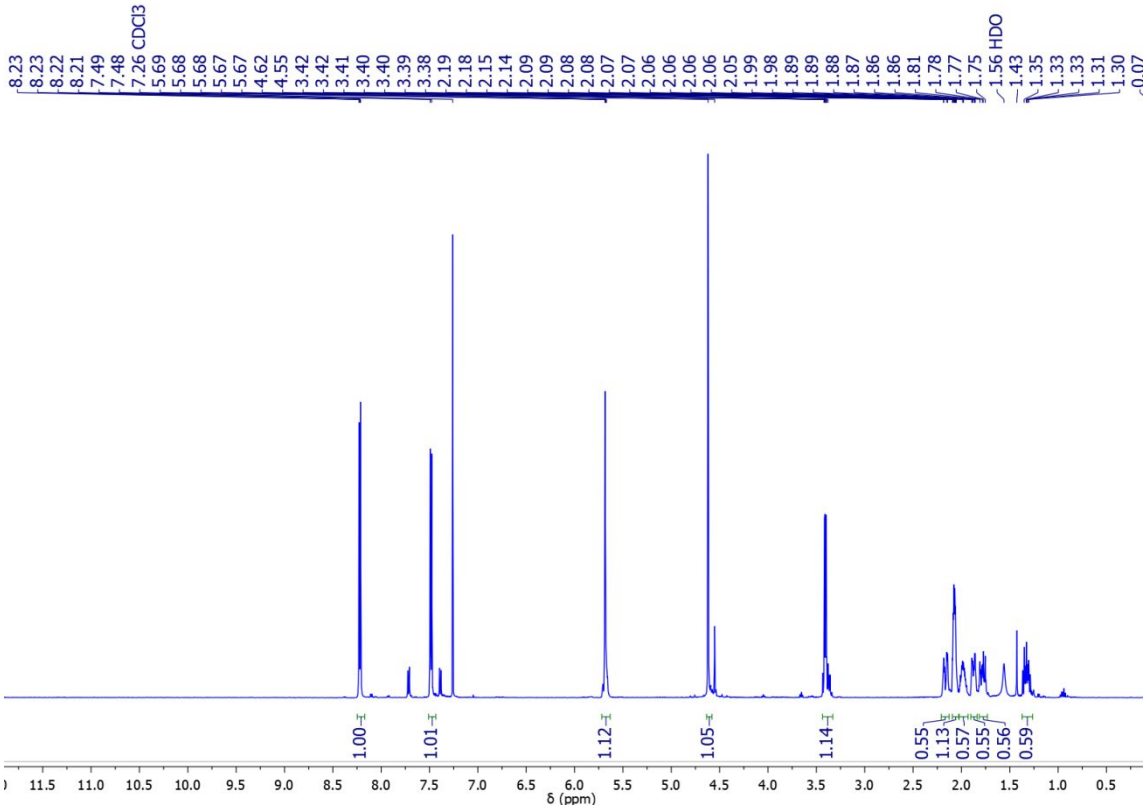


Figure S3 – ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$, 25 ºC).

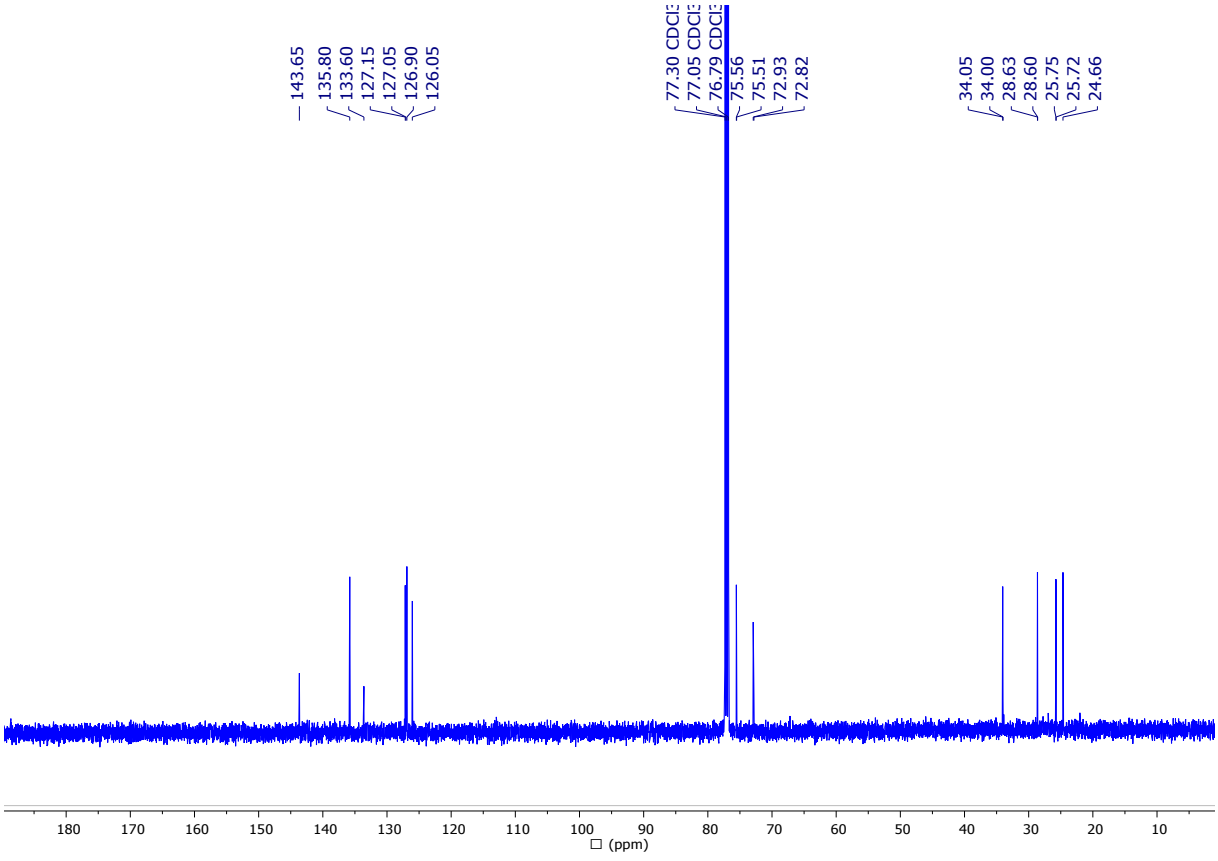


Figure S4 – ^{13}C NMR spectrum of compound **3** (400 MHz, $CDCl_3$, 25 ºC).

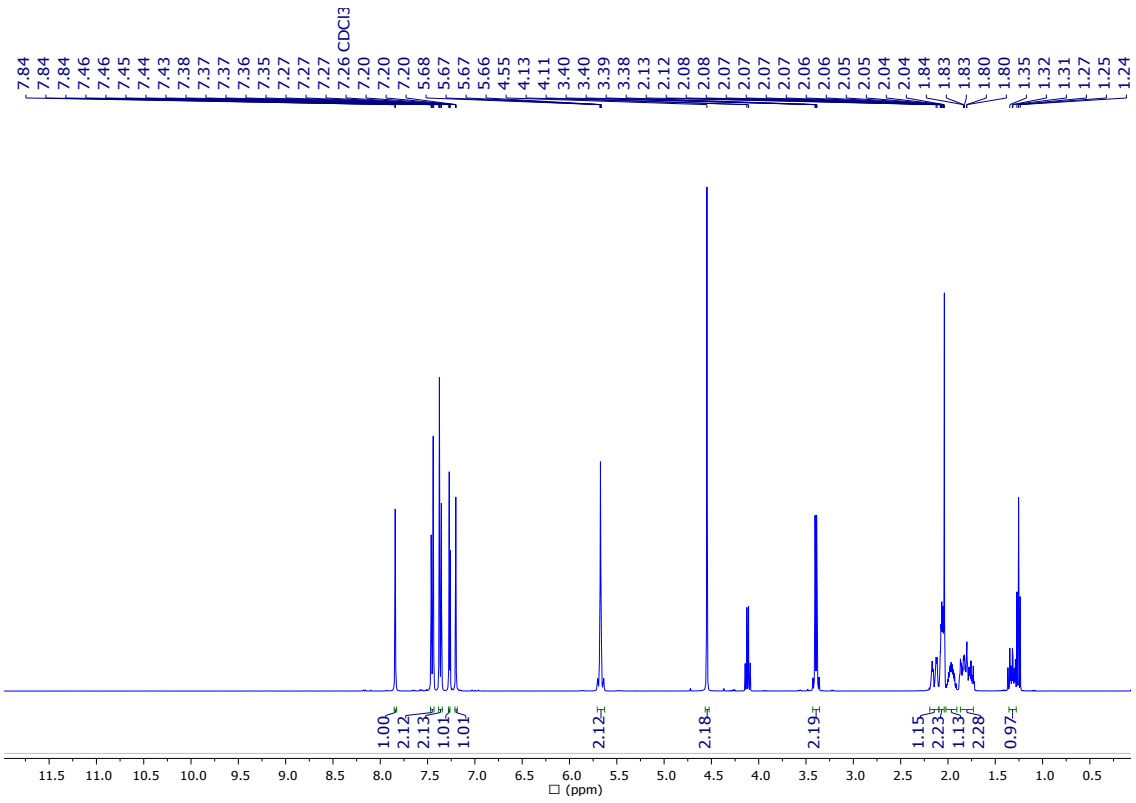


Figure S5 – ^{1}H NMR spectrum of compound **4** (400 MHz, $CDCl_3$, 25 ºC).

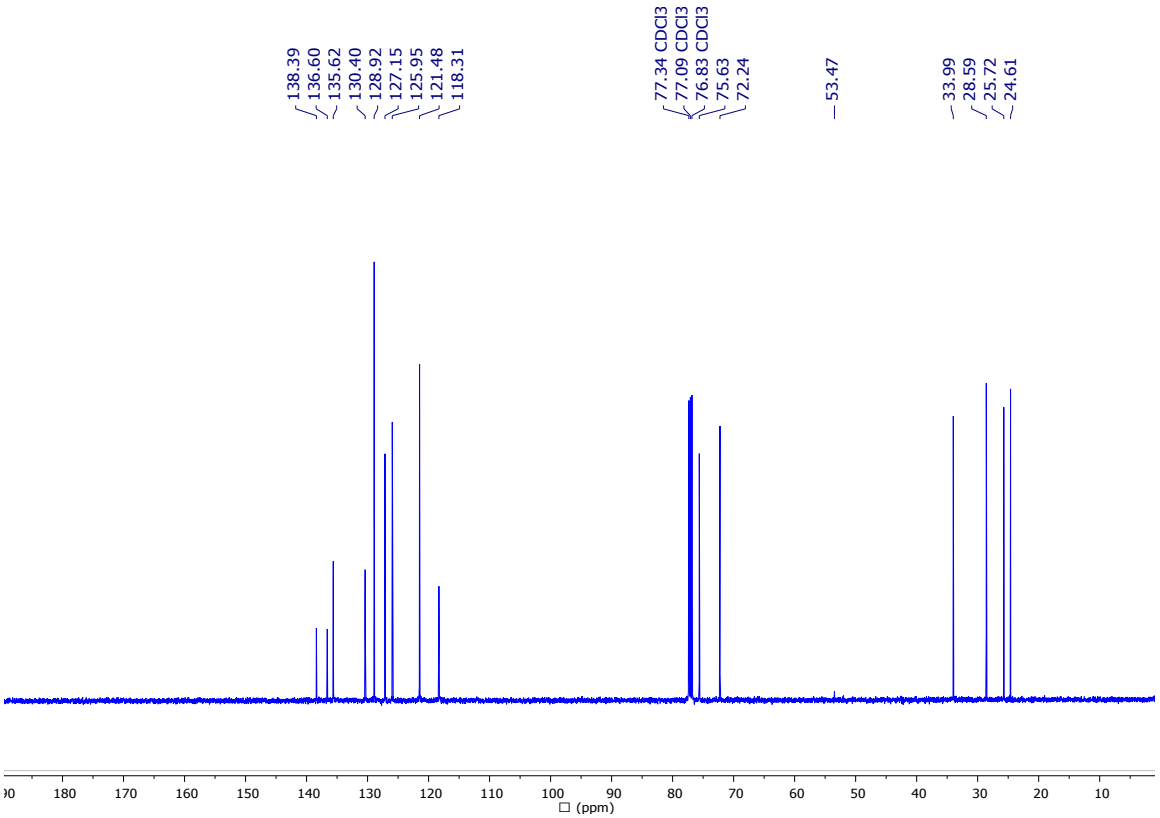


Figure S6 – ^{13}C NMR spectrum of compound **4** (400 MHz, $CDCl_3$, 25 ºC).

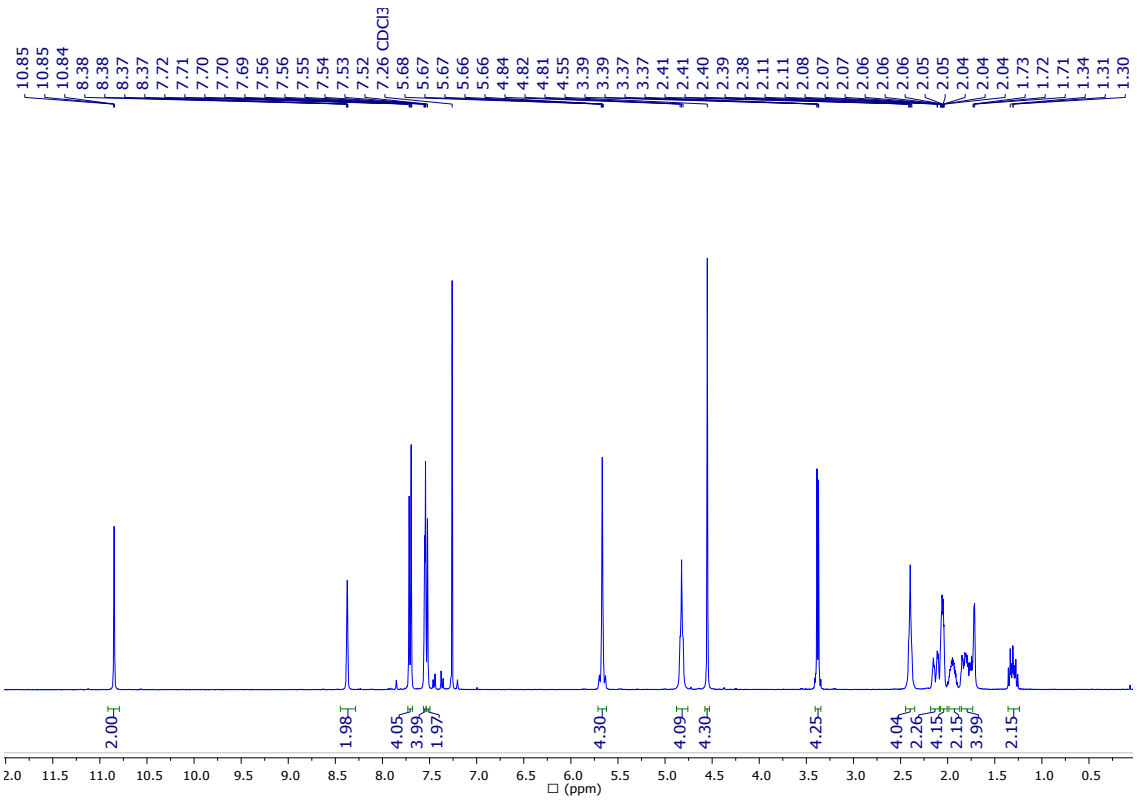


Figure S7 – ^{1}H NMR spectrum of compound **5** (400 MHz, $CDCl_3$, 25 ºC).

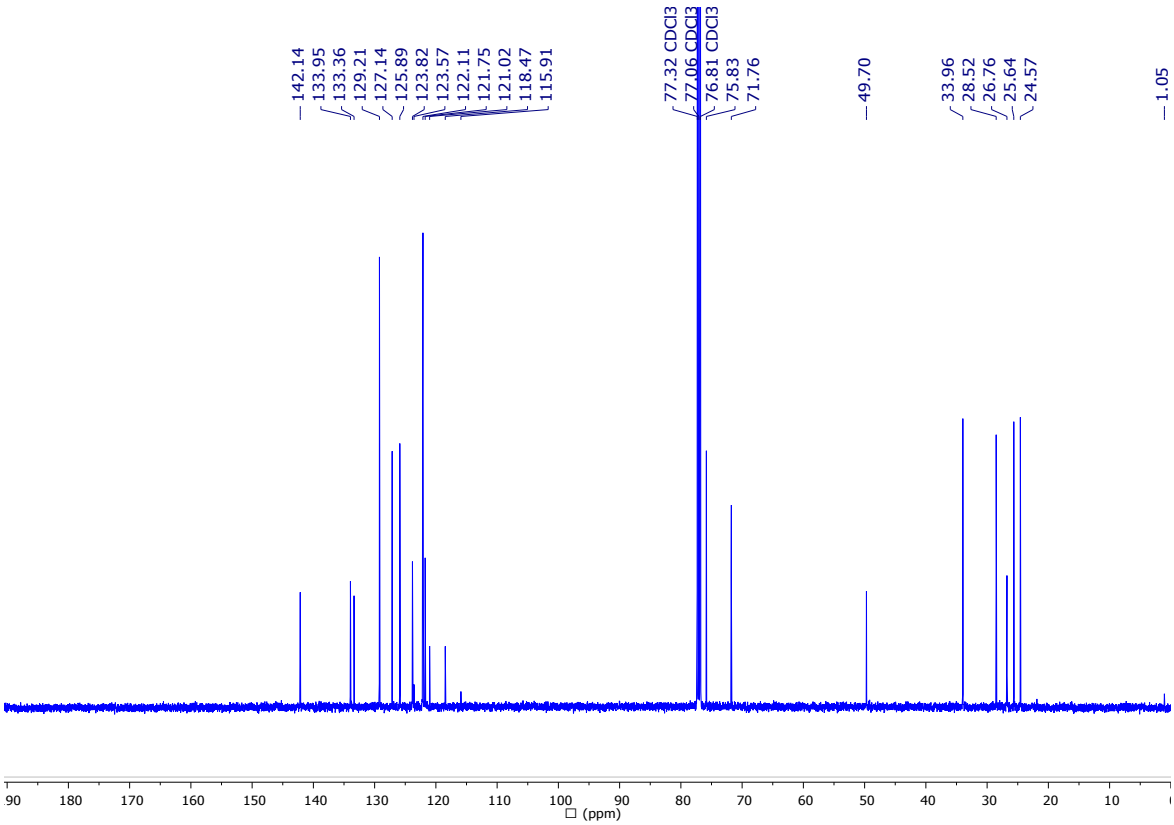


Figure S8 – ^{13}C NMR spectrum of compound **5** (400 MHz, $CDCl_3$, 25 ºC).

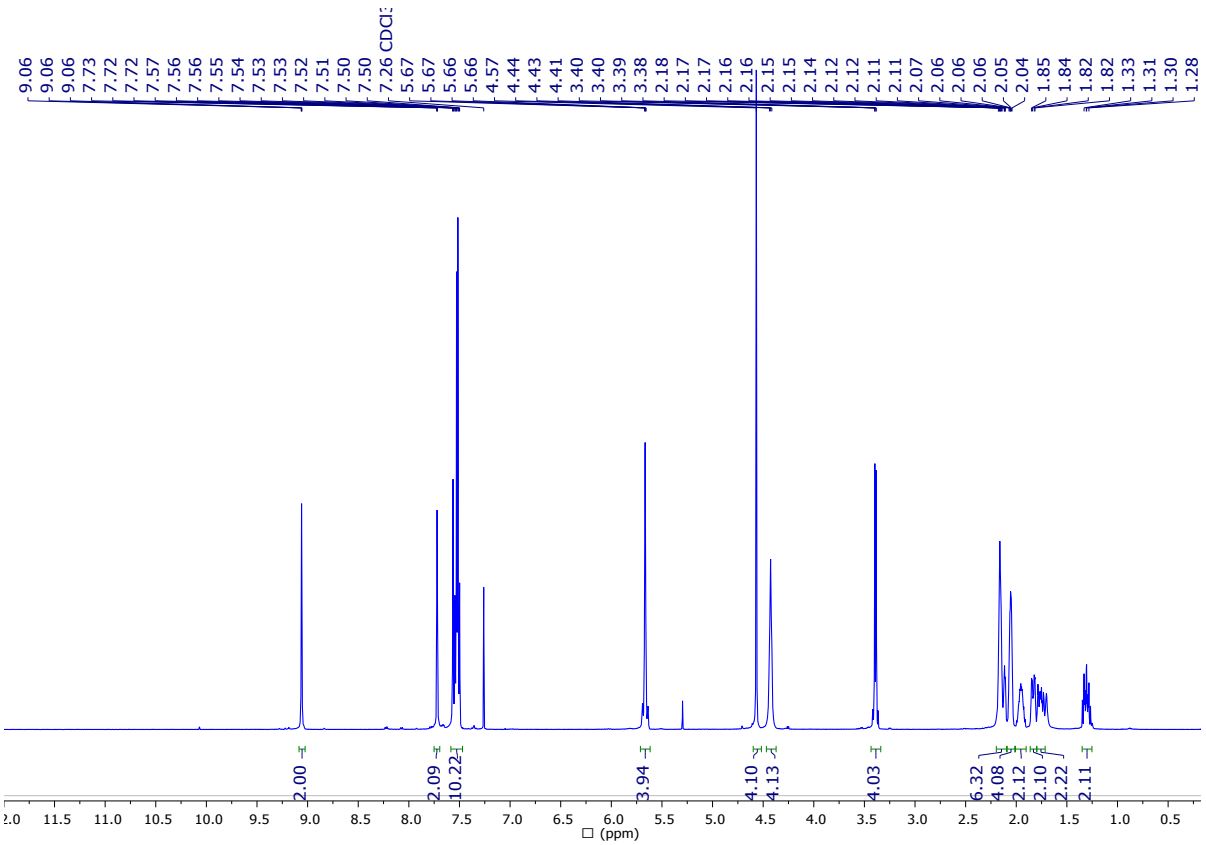


Figure S9 – ^{1}H NMR spectrum of compound **6** (400 MHz, $CDCl_3$, 25 ºC).

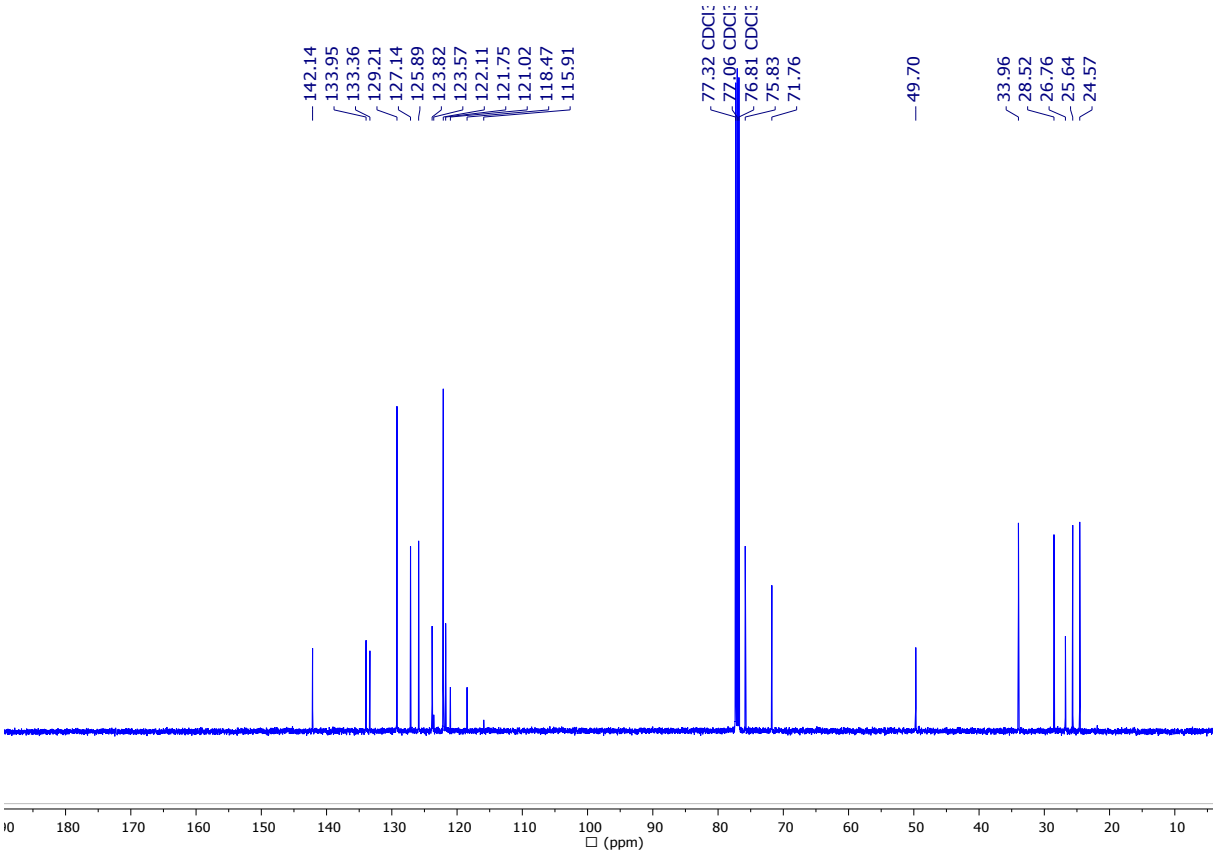


Figure S10 – ^{13}C NMR spectrum of compound **6** (400 MHz, $CDCl_3$, 25 ºC).

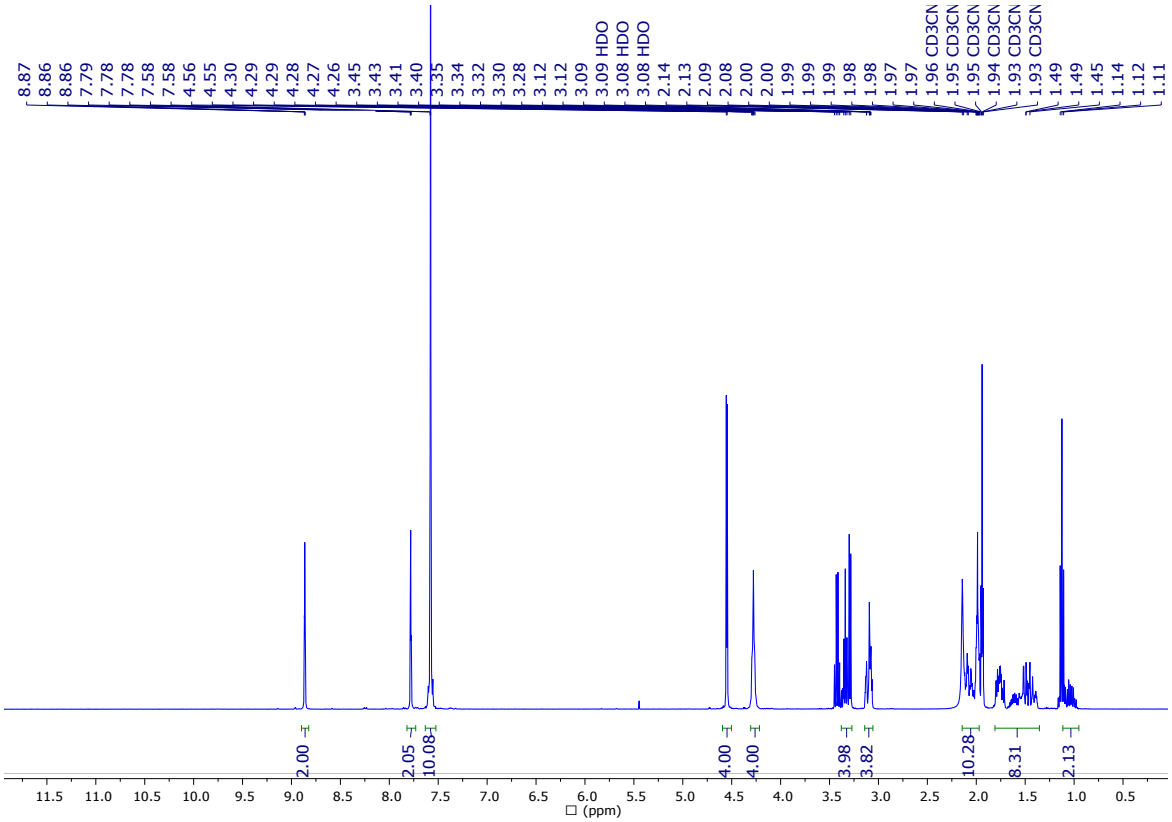


Figure S11 – ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$, 25 ºC).

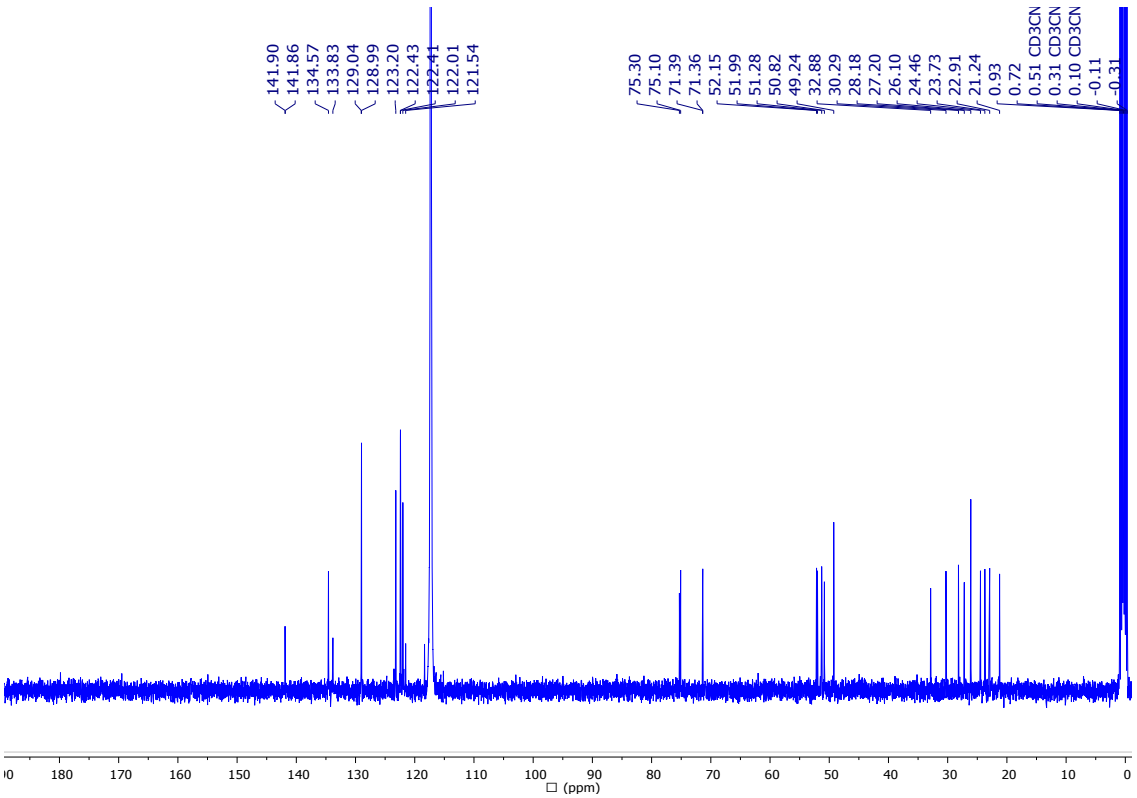


Figure S12 – ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$, 25 ºC).

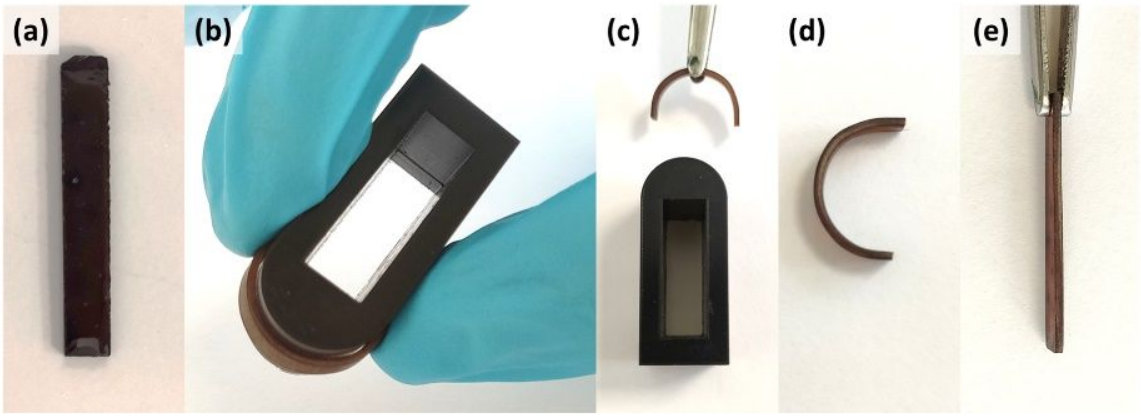


Figure S13 – Fold-deploy experiment showing the different steps. In **(a)** p-CEIL initial shape, **(b)** bending process using a mold, **(c-d)** folded shape and **(e)** the initial shape after the heating process.

Table S1 - Number of ions/monomers used for each system.

System	CEIL	ECC	TFSI	Total Number of Atoms
p-CEIL-ECC	240	560	480	54240
p-ECC	-	1200	-	50400
p-CEIL	400	-	800	51200

Table S2 - Computed thermo-mechanical properties of each system.

	p-CEIL-ECC	p-ECC	p-CEIL
Density / g cm^{-1}	1.25	1.08	1.31
Density, std	0.01	0.01	0.00
T_g / ^{o}C	166.0	215.2	103.0
T_g, std	44.5	18.4	11.6
CVTE, below / K^{-1}	1.99	0.60	4.16
CVTE, below, std	0.14	0.06	0.06
CVTE, above	2.84	1.43	6.45
CVTE, above, std	0.36	0.13	0.14

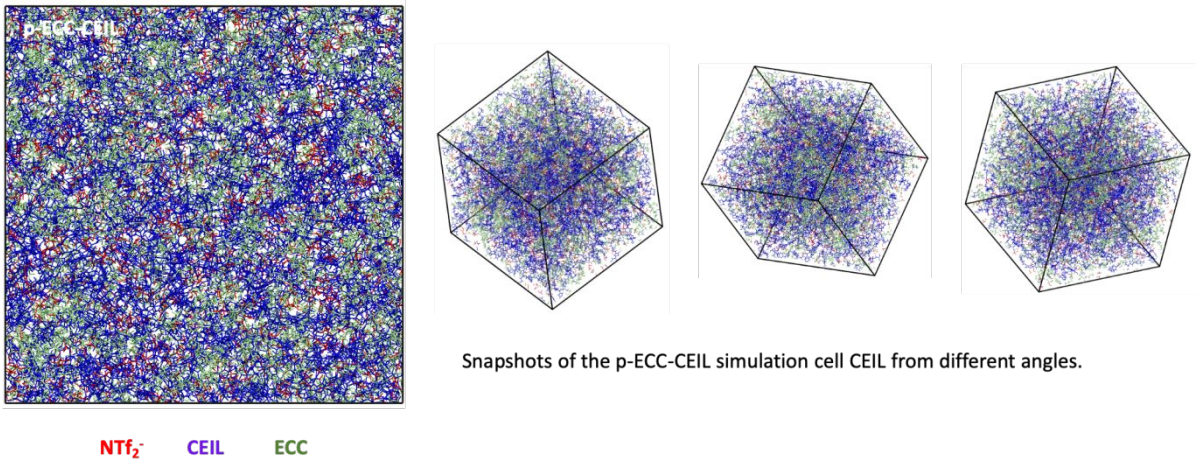


Figure S14 - Snapshots taken from the p-ECC-CEIL system from different angles.

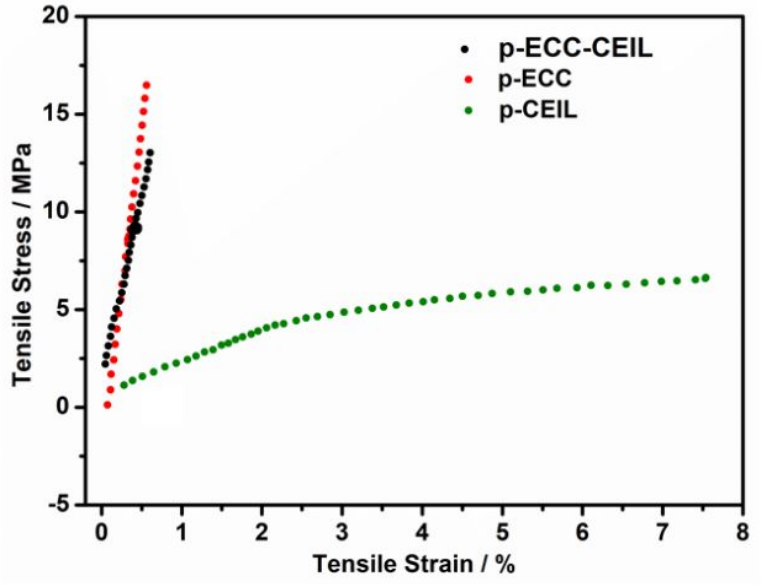


Figure S15 – Stress-strain curves for the three networks prepared by adding 2 wt% of S7MS.

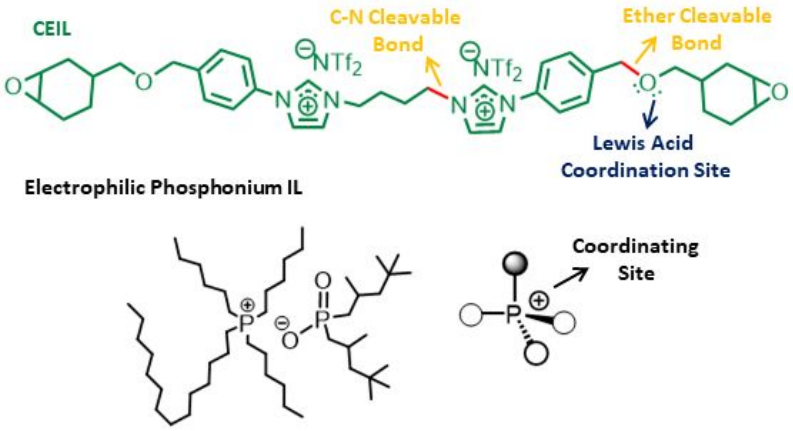


Figure S16 – The CEIL and phosphonium IL104 structures.

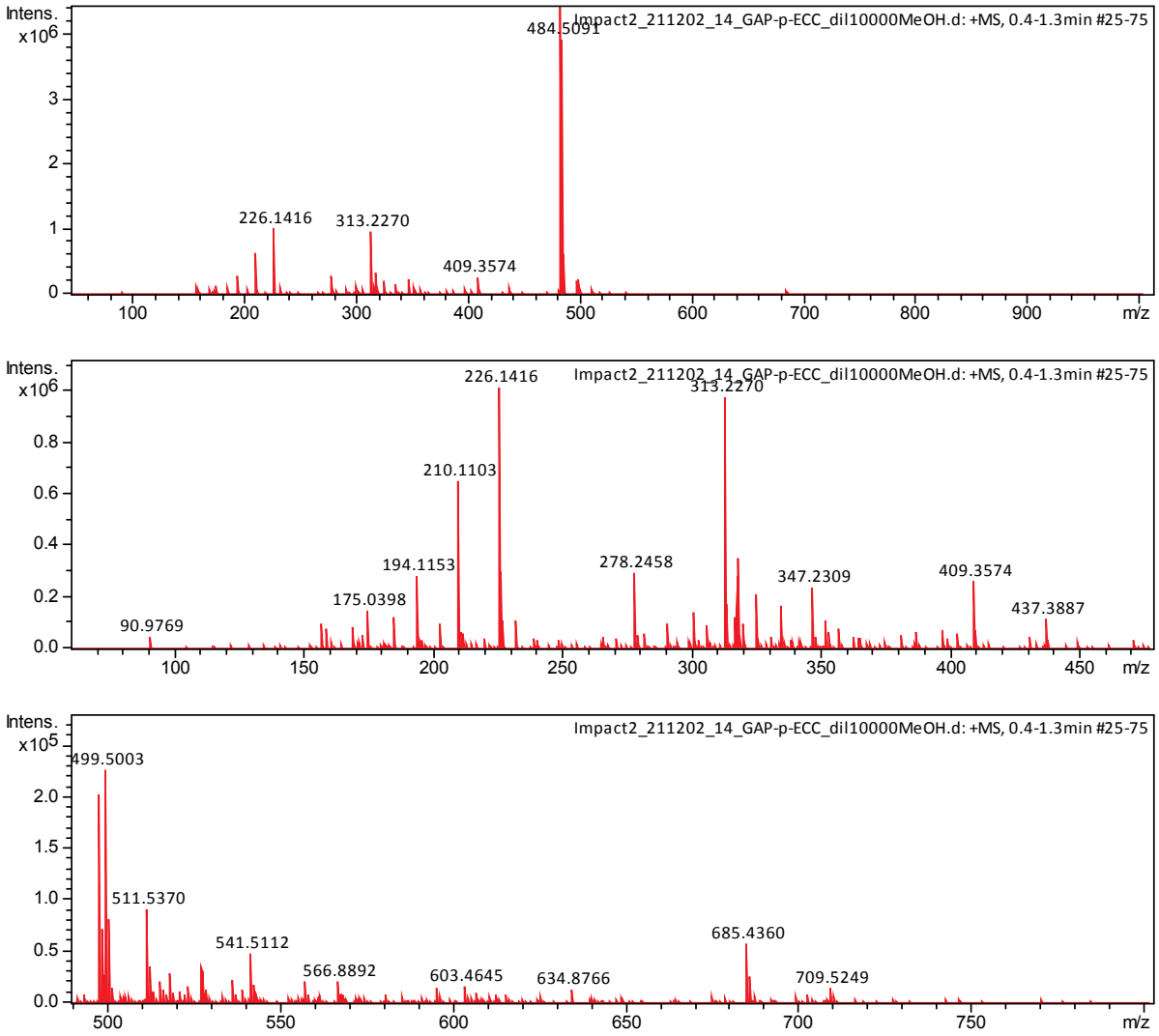


Figure S17 – ESI(+)-QTOF mass spectrum of degradation products of p-ECC.

Table S3 - Molecular ions obtained from ESI(+)-QTOF spectrometry of the degradation products of p-ECC

Meas. m/z	Ion Formula	Sum Formula	m/z	err [ppm]	mSigma	Adduct	z
210.1103	$C_7H_{12}N_7O$	$C_7H_{11}N_7O$	210.1098	-2.4	4.5	M+H	1+
313.227	$C_{20}H_{29}N_2O$	$C_{20}H_{28}N_2O$	313.2274	1.3	29	M+H	1+
409.3574	$C_{28}H_{45}N_2$	$C_{28}H_{45}N_2$	409.3577	0.8	34.6	M	1+
	$C_{28}H_{45}N_2$	$C_{28}H_{44}N_2$	409.3577	0.8	34.6	M+H	1+

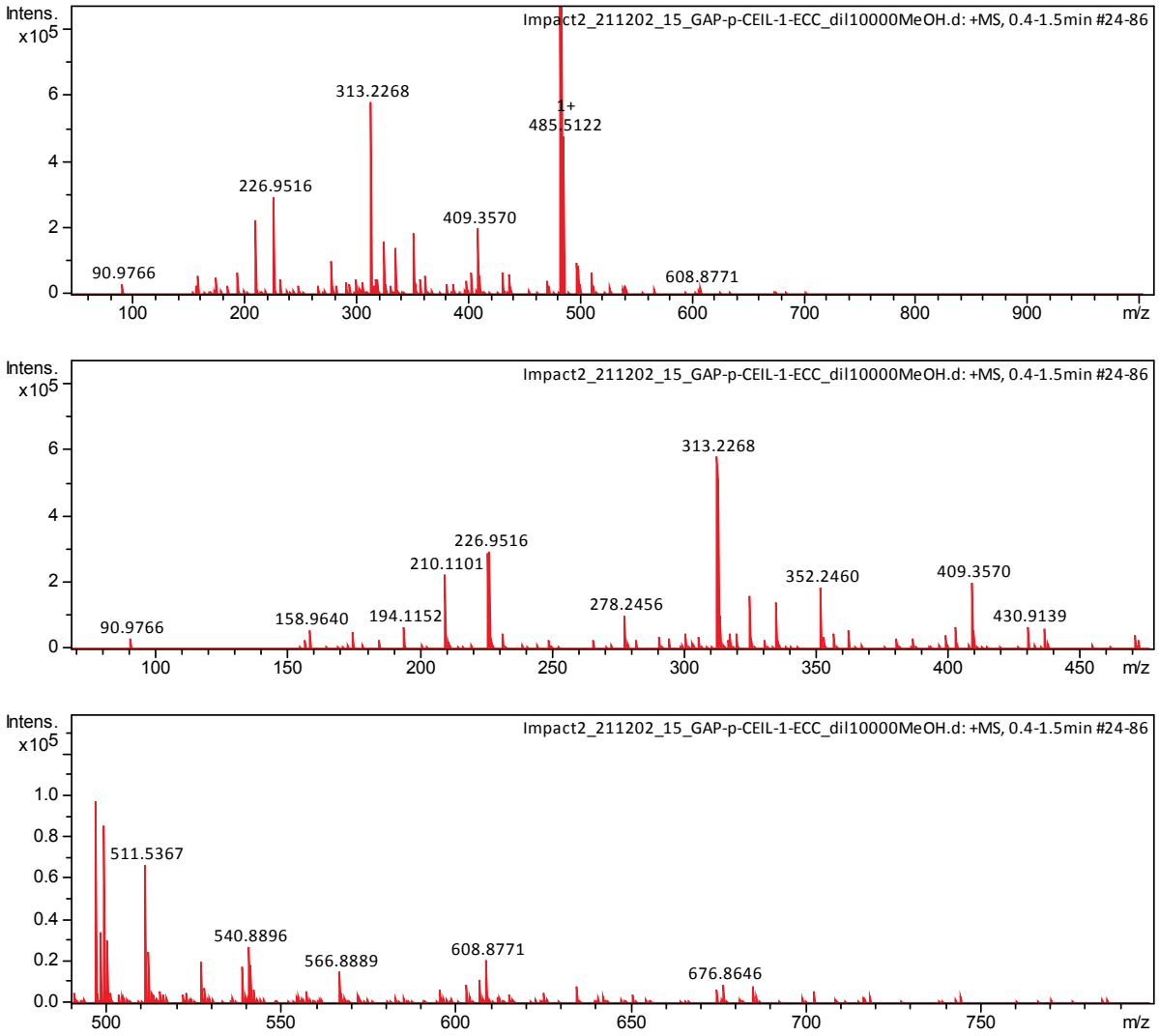


Figure S18 – ESI(+)-QTOF mass spectrum of degradation products of p-ECC-CEIL.

Table S4 - Molecular ions obtained from ESI(+)-QTOF spectrometry of the degradation products of p-ECC-CEIL

Meas. m/z	Ion Formula	Sum Formula	m/z	err [ppm]	mSigma	Adduct	z
210.1101	$C_7H_{12}N_7O$	$C_7H_{11}N_7O$	210.1098	-1.6	4.1	M+H	1+
249.1826	$C_{12}H_{21}N_6$	$C_{12}H_{20}N_6$	249.1822	-1.4	n.a.	M+H	1+
313.2268	$C20H_{29}N_2O$	$C_{20}H_{28}N_2O$	313.2274	2	29	M+H	1+
409.357	$C_{28}H_{45}N_2$	$C_{28}H_{45}N_2$	409.3577	1.7	35.3	M	1+
	$C_{28}H_{45}N_2$	$C_{28}H_{44}N_2$	409.3577	1.7	35.3	M+H	1+

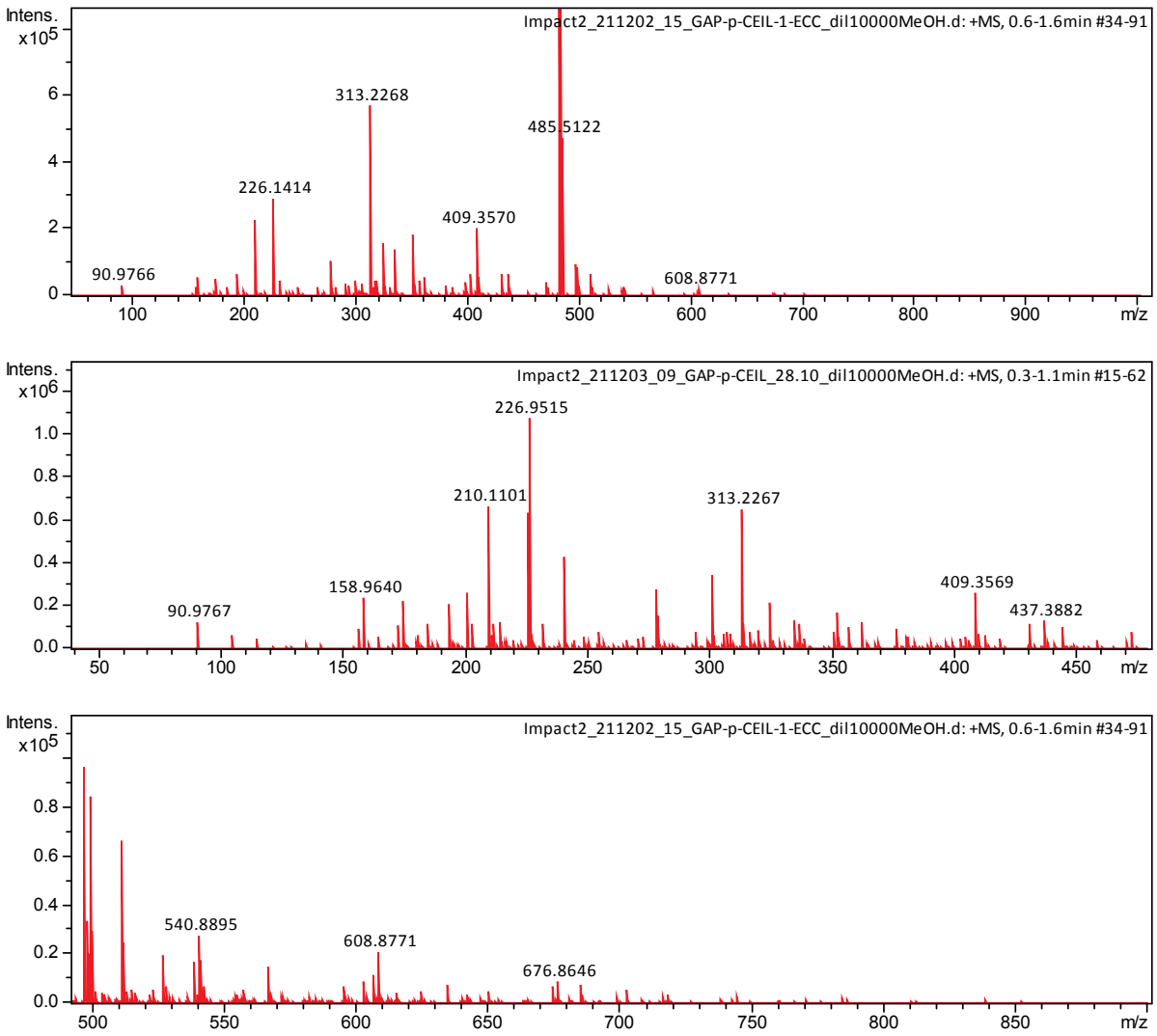


Figure S19 – ESI(+)-QTOF mass spectrum of degradation products of p-CEIL.

Table S5 - Molecular ions obtained from ESI(+)-QTOF spectrometry of the degradation products of p-CEIL

Meas. m/z	Ion Formula	Sum Formula	m/z	err [ppm]	mSigma	Adduct	z
226.1414	$C_8H_{16}N_7O$	$C_8H_{16}N_7O$	226.1411	-1.6	4.9	M	1+
	$C_8H_{16}N_7O$	$C_8H_{15}N_7O$	226.1411	-1.6	4.9	M+H	1+
313.2268	$C_{20}H_{29}N_2O$	$C_{20}H_{29}N_2O$	313.2274	2.1	28.8	M	1+
	$C_{20}H_{29}N_2O$	$C_{20}H_{28}N_2O$	313.2274	2.1	28.8	M+H	1+
409.357	$C_{28}H_{45}N_2$	$C_{28}H_{45}N_2$	409.3577	1.8	34.9	M	1+
	$C_{28}H_{45}N_2$	$C_{28}H_{44}N_2$	409.3577	1.8	34.9	M+H	1+
527.4952	$C_{35}H_{63}N_2O$	$C_{35}H_{62}N_2O$	527.4935	-3.3	n.a.	M+H	1+
539.1711	$C_{33}H_{23}N_4O_4$	$C_{33}H_{22}N_4O_4$	539.1714	0.5	n.a.	M+H	1+
	$C_{17}H_{23}N_{12}O_9$	$C_{17}H_{22}N_{12}O_9$	539.1705	-1.1	n.a.	M+H	1+
	$C_{18}H_{19}N_{16}O_5$	$C_{18}H_{18}N_{16}O_5$	539.1719	1.4	n.a.	M+H	1+
	$C_{20}H_{31}N_2O_{15}$	$C_{20}H_{30}N_2O_{15}$	539.1719	1.4	n.a.	M+H	1+
	$C_{32}H_{27}O_8$	$C_{32}H_{26}O_8$	539.17	-2	n.a.	M+H	1+
	$C_{34}H_{19}N_8$	$C_{34}H_{18}N_8$	539.1727	3	n.a.	M+H	1+
	$C_{16}H_{27}N_8O_{13}$	$C_{16}H_{26}N_8O_{13}$	539.1692	-3.6	n.a.	M+H	1+
	$C_{14}H_{15}N_{22}O_3$	$C_{14}H_{14}N_{22}O_3$	539.1692	-3.6	n.a.	M+H	1+
	$C_{19}H_{15}N_{20}O$	$C_{19}H_{14}N_{20}O$	539.1732	3.9	n.a.	M+H	1+
	$C_{21}H_{27}N_6O_{11}$	$C_{21}H_{26}N_6O_{11}$	539.1732	3.9	n.a.	M+H	1+
	$C_{29}H_{19}N_{10}O_2$	$C_{29}H_{18}N_{10}O_2$	539.1687	-4.5	n.a.	M+H	1+
	$C_4H_{11}N_{32}O_2$	$C_4H_{10}N_{32}O_2$	539.1737	4.8	n.a.	M+H	1+
540.8895	$C_2HN_6O_{27}$	$C_2N_6O_{27}$	540.8884	-2.1	n.a.	M+H	1+
	$C_6H_5O_{29}$	$C_6H_4O_{29}$	540.8911	2.9	n.a.	M+H	1+
566.8889	$C_4H_7O_{32}$	$C_4H_6O_{32}$	566.8915	4.6	n.a.	M+H	1+

References

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