Electronic Supplementary Information

Cycloaliphatic Epoxidized Ionic Liquids as New Versatile Monomers for the Development of Shape memory PIL Networks by 3D printing?

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I. General experimental and analytical data

a. Materials

All reagents were purchased from Sigma Aldrich or TCI and were used without further purification. Solvents (including anhydrous) were purchased from Carlo Erba and used as received. Sylanto-7MS was kindly provided by Synthos S.A.

b. Characterization and purification methods

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance III 400 MHz or 500 MHz spectrometer. Samples were dissolved in an appropriate deuterated solvent ($CDCl_3$, CD_3CN or DMSO-d6). The chemical shifts (δ) are expressed in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C nuclei, and coupling constants are indicated in Hz. Abbreviations for signal coupling are as follows: s=singlet; d=doublet; dd=doublet of doublets; t=triplet; q=quartet; quin=quintet; m=multiplet; br=broad signal. To assign the signals to the different proton and carbon atoms, as well as the relative stereochemistry of the cycloadducts, additional 2D NMR experiments (COSY, HSQC, HMBC) were performed.

^{13}C HR-MAS NMR spectroscopy analysis was done using a Bruker Advance II spectrometer (400 MHz), equipped with a 4 mm rotor 1H-13C HR-MAS probe with z-gradient coil at 5 kHz rotation speed and 298 K.

High resolution mass spectra HRMS were obtained by Electrospray Ionization (ESI) on a Micromass-Waters Q-TOF Ultima Global.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet Magna 550 spectrometer at room temperature (25 °C) with Golden Gate (ATR). The spectra were collected in 32 scans with a spectral resolution of 4 cm^{-1} from 4000 to 525 cm^{-1}.

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

Flash chromatography was performed on silica gel column (Merck silica gel, 40-63 mm) using air pressure.

Thermogravimetric analyses (TGA) of the neat ionic liquid epoxy monomer and the resulting epoxy network were performed on a Q500 thermogravimetric analyzer (TA instruments). The samples were heated from 30 to 700 °C at a rate of 10 K min^{-1} under nitrogen flow.

Differential scanning calorimetry analyses (DSC) of ionic liquid epoxy monomer reactive systems and networks were performed on a Q10 (TA instruments) in a dynamic mode at a rate of 10 K min^{-1} under nitrogen flow of 50 mL min^{-1} from -70 to 300 °C.

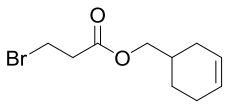
Surface energy of epoxy network was determined with the sessile drop method using a GBX goniometer. From contact angle measurements performed with water and diiodomethane as probe liquids on the samples, polar and dispersive components of surface energy were determined using Owens-Wendt theory[1].

Dynamic mechanical analysis (DMA) were performed on rectangular samples with dimensions of 30 x 4 x 1.5 mm^3 using an ARES-G2 rheometer with torsional fixture (TA Instruments). The material response was measured with a heating rate of 3 °C min^{-1}. All tests were performed within the linear viscoelastic region of each material at a frequency of 1 Hz. Storage modulus G′, loss modulus G″ and loss factor tan δ were measured during temperature ramps from -120 up to 200 °C.

Shape memory tests were performed similarly to the previously reported procedure[2]. The sample was placed in the water bath at 90 °C for 10 min. After that the sample was bended to U-shape and cooled down to room temperature. The sample was fixed in a clamp and put in the bath. The process was filmed and remaining deformation at different times was determined by formula: $D_t = (180 - \alpha_t) / 180$, where D_t is remaining deformation at time t and α_t is the angle between sample ends at time t.

II. Procedure for the synthesis of CEIL-1

Cyclohex-3-en-1-ylmethyl 3-bromopropanoate (1)

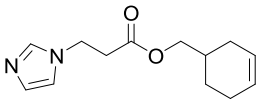


5 g (33 mmol) of 3-bromopropionic acid were dissolved in 8 ml (110.4 mmol) of $SOCl_2$ and stirred overnight at 65 °C. The thionyl chloride was removed under reduced pressure and 1.72 g (10.0 mmol) of obtained 3-bromopropanoyl chloride were added dropwise to a solution containing cyclohex-3-en-1-ylmethanol (0.76 ml, 6.6 mmol), pyridine (0.53 ml, 6.6 mmol) and CH_2Cl_2 (10 ml) at 0 °C. The mixture was stirred for 40 min at room temperature and then 10 ml of HCl (1M) were added, the mixture was transferred in separative funnel and washed one time with 1M HCl. Organic phase was dried with $MgSO_4$, filtered and concentrated in vacuum. The crude product was purified by column chromatography (hexane / ethyl acetate : 90 / 10) (1.3 g, 82 %).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.77–5.53 (m, 2H), 4.04 (d, *J* = 6.5 Hz, 2H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 2.20–1.87 (m, 4H), 1.87–1.69 (m, 2H), 1.40–1.19 (m, 1H). ^{13}C NMR (101

MHz, Chloroform-*d*) δ 170.7, 127.2, 125.5, 69.4, 37.9, 33.1, 28.2, 26.1, 25.4, 24.5. IR (neat) cm^{-1}: 3023, 2915, 2838, 1733, 1231, 1170, 1130. HRMS m/z (ESI): calcd. for $C_{10}H_{15}O_2BrNa$ $[M+Na]^+$: 269.0148, found: 269.0145.

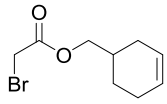
Cyclohex-3-en-1-ylmethyl 3-(1*H*-imidazol-1-yl)propanoate (2)



Imidazole (0.15 g, 2.2 mmol) and **1** (0.5 g, 2.0 mmol) were dissolved in 4 ml of DMF in presence of K_2CO_3 (0.39 g, 2.8 mmol). The mixture was stirred overnight at 85 °C, cooled down to room temperature and then 3 ml of H_2O were added. The mixture was extracted 3 times with Et_2O, the extracts were washed by saturated NaCl solution, dried over $MgSO_4$, filtered and concentrated in vacuum. The crude product was purified by column chromatography in ethyl acetate (0.42 g, 90 %).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (s, 1H), 7.02 (s, 1H), 6.91 (t, *J* = 1.3 Hz, 1H), 5.69–5.57 (m, 2H), 4.25 (t, *J* = 6.6 Hz, 2H), 3.98 (d, *J* = 6.6 Hz, 2H), 2.77 (t, *J* = 6.6 Hz, 2H), 2.09–1.98 (m, 3H), 1.97 – 1.83 (m, 1H), 1.76–1.64 (m, 2H), 1.32–1.19 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 137.3, 129.8, 127.1, 125.4, 118.9, 69.5, 42.4, 36.1, 33.0, 28.1, 25.3, 24.4. IR (neat) cm^{-1}: 3023, 2916, 2839, 1733, 1506, 1166, 1078. HRMS m/z (ESI): calcd. for $C_{13}H_{19}N_2O_2$ $[M+H]^+$: 235.1441, found: 235.1440.

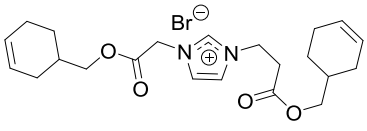
Cyclohex-3-en-1-ylmethyl 2-bromoacetate (5)



Cyclohex-3-en-1-ylmethanol (20.8 ml, 180 mmol) and triethylamine (50.0 ml, 360 mmol) were dissolved in 180 ml of CH_2Cl_2 under N_2 atmosphere. The solution was cooled down to -30 °C and 2-bromoacetyl bromide (23.6 ml, 270 mmol) was added dropwise during 10 min. The mixture was stirred for 2 h and then 200 ml of H_2O were introduced. The product was extracted 2 times by CH_2Cl_2, organic extracts were washed by $NaHCO_3$ saturated solution in water, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (hexane / ethyl acetate : 90 / 10) (31.1 g, 74 %).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.79–5.56 (m, 2H), 4.08 (d, *J* = 6.7 Hz, 2H), 3.84 (s, 2H), 2.23–1.90 (m, 4H), 1.87–1.67 (m, 2H), 1.43–1.27 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 127.2, 125.4, 70.5, 33.0, 28.1, 26.0, 25.2, 24.4. IR (neat) cm^{-1}: 3024, 2915, 2839, 1733, 1650, 1281, 1160, 1109, 996. HRMS m/z (ESI): calcd. for $C_9H_{13}O_2BrNa$ $[M+Na]^+$: 254.9991, found: 254.9991.

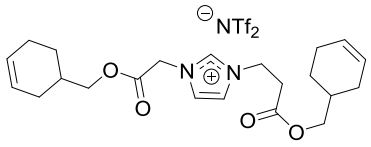
1-(2-(Cyclohex-3-en-1-ylmethoxycarbonyl)ethyl)-3-(1-(cyclohex-3-en-1-ylmethoxycarbonyl)methyl)-1H-imidazol-3-ium bromide (6)



2 (83.5 mg, 0.36 mmol) was dissolved in 0.6 ml of CH_3CN and **5** (91.0 mg, 0.39 mmol) was added. The mixture was stirred overnight at 75 °C, cooled down and precipitated in 20 ml of Et_2O. The product was washed 2 times by Et_2O and dried in vacuum (0.11 g, 90 %).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.47 (s, 1H), 7.60 (s, 1H), 7.49 (s, 1H), 5.72–5.58 (m, 4H), 5.43 (s, 2H), 4.66 (t, *J* = 6.0 Hz, 2H), 4.11 (d, *J* = 6.7 Hz, 2H), 3.99 (d, *J* = 6.7 Hz, 2H), 3.07 (t, *J* = 5.7 Hz, 2H), 2.20–1.84 (m, 8H), 1.81–1.65 (m, 4H), 1.38–1.20 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 166.1, 139.1, 127.2, 127.1, 125.3, 125.2, 123.2, 122.8, 71.2, 69.9, 50.4, 45.8, 34.9, 33.0, 32.9, 28.2, 28.1, 25.3, 25.2, 24.4, 24.3. IR (neat) cm^{-1}: 3023, 2916, 2839, 2192, 1730, 1166, 920. HRMS m/z (ESI): calcd. for $C_{22}H_{31}N_2O_4$ $[M]^+$: 387.2278, found: 387.2282.

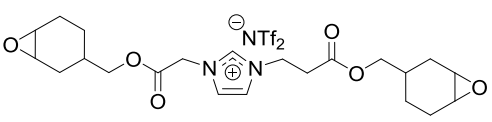
1-(2-(Cyclohex-3-en-1-ylmethoxycarbonyl)ethyl)-3-(1-(cyclohex-3-en-1-ylmethoxycarbonyl)methyl)-1H-imidazol-3-ium bistrifluoromethanesulfonimidate (6a)



6 (0.11 g, 0.23 mmol) was dissolved in 4 ml of H_2O at 80°C, the solution of $LiNTf_2$ (9.12 g, 31.8 mmol) in 5 ml of H_2O was added and the mixture was left overnight at room temperature. The mixture was extracted 3 times by CH_2Cl_2 (3x10ml). Organic extracts were combined and washed twice with water, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure (0.10 g, 67 %).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.00 (t, *J* = 1.8 Hz, 1H), 7.50 (t, *J* = 1.8 Hz, 1H), 7.33 (t, *J* = 1.8 Hz, 1H), 5.73–5.60 (m, 4H), 5.06 (s, 2H), 4.54 (t, *J* = 5.8 Hz, 2H), 4.13 (d, *J* = 6.7 Hz, 2H), 4.02 (d, *J* = 6.7 Hz, 2H), 2.97 (t, *J* = 5.8 Hz, 2H), 2.18–1.87 (m, 8H), 1.84–1.65 (m, 4H), 1.40–1.20 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 165.8, 138.0, 127.3, 127.2, 125.3, 125.2, 123.5, 123.1, 119.9 (q, *J* = 321.2 Hz), 71.4, 70.1, 50.2, 45.9, 34.4, 33.0, 32.9, 28.1, 28.0, 25.3, 25.2, 24.4, 24.3. IR (neat) cm^{-1}: 3054, 2918, 2847, 1732, 1347, 1180, 1133, 1054. HRMS m/z (ESI): calcd. for $C_{22}H_{31}N_2O_4$ $[M]^+$: 387.2278, found: 387.2276.

1-(2-((7-Oxabicyclo[4.1.0]heptan-3-yl)methoxycarbonyl)ethyl)-3-(1-((7-oxabicyclo[4.1.0]heptan-3-yl)methoxycarbonyl)methyl)-1H-imidazol-3-ium bistrifluoromethanesulfonimidate (CEIL-1)



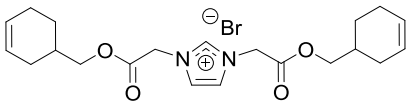
6a (88 mg, 0.13 mmol) was dissolved in 2 ml of CH_3CN and mixed with 0.122 g (0.53 mmol) of mCPBA. The mixture was stirred overnight at 40 °C. Then the solvent was evaporated under reduced pressure and the residue was washed 3 times with Et_2O, dissolved in 1 ml of CH_2Cl_2 and precipitated in Et_2O (25 ml), the solvent was removed by decantation and the product was dried in vacuum (53 mg, 59 %).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.94 (s, 1H), 7.48 (t, *J* = 1.8 Hz, 1H), 7.36 (t, *J* = 1.8 Hz, 1H), 5.05 (s, 2H), 4.52 (t, *J* = 5.8 Hz, 2H), 4.11–3.85 (m, 4H), 3.25–3.09 (m, 4H), 2.95 (t, *J* = 5.8 Hz, 2H), 2.20–0.90 (m, 14H).

^{13}C NMR (101 MHz, Chloroform-*d*) mixture of stereoisomers[3] δ 170.6, 170.5, 165.8, 165.7, 137.8, 123.7, 123.0, 119.9 (q, *J* = 321.2 Hz), 71.0, 69.8, 69.7, 52.6, 52.6, 52.5, 52.5, 51.7, 51.7, 51.1, 51.0, 50.1, 50.1, 45.8, 34.3, 32.0, 32.0, 29.5, 28.2, 28.1, 27.07, 27.0, 24.4, 24.3, 23.8, 23.7, 23.0, 23.0, 21.1, 21.0. IR (neat) cm^{-1}: 3154, 2962, 1732, 1347, 1180, 1133, 1053. HRMS m/z (ESI): calcd. for $C_{22}H_{31}N_2O_6$ $[M]^+$: 419.2177, found: 419.2181.

III. Procedure for the synthesis of CEIL-2

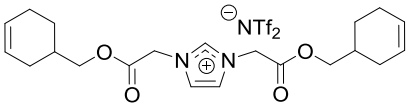
1,3-Bis(1-(cyclohex-3-en-1-ylmethoxycarbonyl)methyl)-1H-imidazol-3-ium bromide (7)



Solution of imidazole (4.08 g, 60 mmol) in 20 ml of anhydrous THF was added dropwise to the mixture of NaH (2.4 g (60 % in mineral oil), 60mmol) and anhydrous THF (20 ml) at 0 °C during 30 min. The mixture was stirred for 2 h at room temperature and then **5** (29 g, 124 mmol) was added dropwise at 0 °C during 30 min. The reaction was left overnight at 75 °C. The mixture was cooled down to room temperature and diluted with 700 ml of CH_2Cl_2, washed with ~5 % $NaHCO_3$ in water and with H_2O, dried

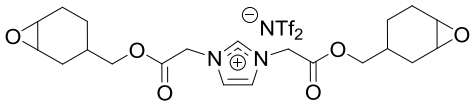
by $MgSO_4$, filtered and concentrated under reduced pressure. Solid product was washed 3 times by Et_2O (3x200 ml) and dried in vacuum (23.2 g, 86 %). M_p: 118 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.13 (t, *J* = 1.6 Hz 1H), 7.67 (d, *J* = 1.6 Hz, 2H), 5.77–5.53 (m, 4H), 5.42 (s, 4H), 4.08 (d, *J* = 6.6 Hz, 4H), 2.19–1.84 (m, 8H), 1.84–1.60 (m, 4H), 1.39–1.17 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 139.1, 127.1, 125.2, 123.5, 71.1, 50.5, 32.8, 28.0, 25.2, 24.3. IR (KBr) cm^{-1}: 3381, 3024, 2923, 2838, 1751, 1231, 1182. HRMS m/z (ESI): calcd. for $C_{21}H_{29}N_2O_4$ $[M]^+$: 373.2122, found: 373.2126.

1,3-Bis(1-(cyclohex-3-en-1-ylmethoxycarbonyl)methyl)-1H-imidazol-3-ium bistrifluoromethanesulfonimidate (7a)



7 (12 g, 26.5 mmol) was dissolved in 440 ml of H_2O at 80 °C, the solution of $LiNTf_2$ (9.1 g, 31.8 mmol) in 54 ml of H_2O was added and the mixture was left overnight at room temperature. The mixture was extracted two times by CH_2Cl_2 (2x200ml), water layer was concentrated under reduced pressure to ~100 ml and extracted twice with CH_2Cl_2. All organic extracts were combined and washed twice with water, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure. (16.9 g, 98 %).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (t, *J* = 1.6 Hz, 1H), 7.41 (d, *J* = 1.6 Hz, 2H), 5.65 (m, 4H), 5.05 (s, 4H), 4.12 (d, *J* = 6.6 Hz, 4H), 2.15–1.91 (m, 8H), 1.83–1.69 (m, 4H), 1.39–1.17 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 138.6, 127.2, 125.2, 123.6, 119.8 (q, *J* = 321.1 Hz), 71.3, 50.2, 32.8, 27.9, 25.1, 24.3. IR (neat) cm^{-1}: 3157, 2918, 1748, 1347, 1178, 1133, 1054. HRMS m/z (ESI): calcd. for $C_{21}H_{29}N_2O_4$ $[M]^+$: 373.2122, found: 373.2122.

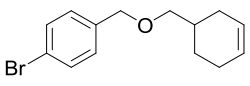
1,3-Bis(1-((7-oxabicyclo[4.1.0]heptan-3-yl)methoxycarbonyl)methyl)-1H-imidazol-3-ium bistrifluoromethanesulfonimidate (CEIL-2)



64.3 g (291 mmol) of mCPBA were added to the solution of **7a** (31.5 g, 48.1 mmol) in CH_3CN (1 L). The mixture was stirred overnight at 40 °C, filtered through a glass filter and concentrated under reduced pressure. The residue was washed 4 times with Et_2O and dried in vacuum (25.7 g, 78 %).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (s, 1H), 7.45 (s, 2H), 5.05 (s, 4H), 4.16–3.92 (m, 4H), 3.27–3.03 (m, 4H), 2.27–1.11 (m, 13H), 1.12–0.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) mixture of stereoisomers[3] δ 165.7, 138.5, 123.7, 119.8 (q, *J* = 321.2 Hz), 70.8, 52.6, 52.5, 51.7, 51.1, 50.1, 31.8, 29.4, 27.9, 26.8, 24.3, 23.5, 22.9, 20.9. IR (neat) cm^{-1}: 3157, 2936, 1750, 1347, 1177, 1133, 1053. HRMS m/z (ESI): calcd. for $C_{21}H_{29}N_2O_4$ $[M]^+$: 405.2020, found: 405.2020.

IV. Procedure for the synthesis of CEIL-3

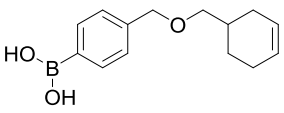
4-Bromobenzyl (cyclohex-3-en-1-ylmethyl) ether (8).



Under Ar atmosphere, cyclohexen-4-ylmethanol (1.0 ml, 9.29 mmol) was added dropwise to a stirred suspension of NaH (0.54 g (60 % in mineral oil), 13.4 mmol) in anhydrous THF (37 ml) at 0 °C. After the addition, the mixture was stirred at room temperature for 20 min. A solution of 4-bromobenzylbromide (2.68 g, 10.7 mmol) in THF (anhydr.) (16.0 ml) was added dropwise to the mixture at 0 °C, and stirring continued for 30 min at room temperature. The mixture was stirred under reflux for 22 h. Then, it was cooled to 0 °C and it was quenched with 3 ml of H_2O. Et_2O (150 ml) was added and the mixture was washed 3 times with water. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The residue was

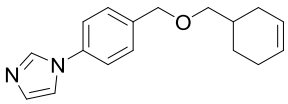
purified by column chromatography on silica gel (eluting with cyclohexane / ethyl acetate : 95 / 5) and then by Kugelrohr distillation to provide colorless liquid (1.16 g, 45 %)
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.75–5.60 (m, 2H), 4.46 (s, 2H), 3.40–3.29 (m, 2H), 2.16–2.08 (m, 1H), 2.08–2.02 (m, 2H), 1.98–1.89 (m, 1H), 1.87–1.79 (m, 1H), 1.79 – 1.69 (m, 1H), 1.35 – 1.20 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.8, 131.5, 129.2, 127.1, 126.0, 121.3, 75.5, 72.3, 34.0, 28.6, 25.7, 24.6. IR (neat) cm^{-1}: 2913, 2852, 1487,1088, 1069, 1011, 801.

(4-((Cyclohex-3-en-1-ylmethoxy)methyl)phenyl)boronic acid (9).



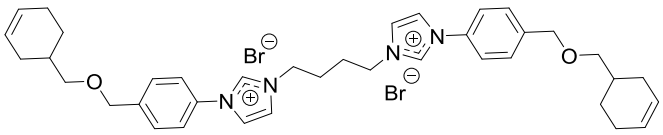
Under Ar atmosphere, the compound **8** (1.5 g, 5.35 mmol) was dissolved in dry THF (14.0 ml) and n-BuLi 2.5 M in hexanes (2.57 ml, 6.4 mmol) was added dropwise at -78 °C. The mixture was stirred at this temperature for 60 min and then 1.8 ml (8.0 mmol) of triisopropyl borate were added dropwise. The mixture was left overnight to worm up to room temperature, afterwards it was cooled down to 0 °C and 3.7 ml of H_2O were added dropwise followed by 9.2 ml of HCl (1M). The aqueous layer was extracted by Et_2O and organic solutions were combined, dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluting cyclohexane / ethyl acetate : 7 / 3) to obtain white solid (0.74 g, 57 %).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 5.85–5.45 (m, 2H), 4.62 (s, 2H), 3.51–3.32 (m, 2H), 2.22–2.12 (m, 1H), 2.11–2.03 (m, 2H), 2.03–1.93 (m, 1H), 1.92–1.83 (m, 1H), 1.83–1.74 (m, 1H), 1.37–1.28 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.6, 135.8, 133.6, 127.1, 126.9, 126.0, 75.6, 72.9, 34.0, 28.6, 25.7, 24.7. HRMS m/z (ESI): calcd. for $C_{14}H_{18}BO_3$ [M - H]$^{-}$: 245.1354, found: 245.1351.

1-(4-((Cyclohex-3-en-1-ylmethoxy)methyl)phenyl)-1*H*-imidazole (10) (Method 1).



Boronic acid **9** (0.74 g, 3.0 mmol), imidazole (0.24 g, 3.6 mmol) and copper (I) iodide (22 mg, 0.11 mmol) were mixed in methanol (11 ml). The mixture was stirred for 5 h under reflux and bubbling air. The solvent was evaporated and the residue was extracted by Et_2O. The solution was filtered through Celite® and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluting cyclohexane / ethyl acetate, cyclohexane from 30 % to 0 %) to obtain colorless liquid (0.63 g, 78 %).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 7.21 (s, 1H), 5.73–5.60 (m, 2H), 4.55 (s, 2H), 3.53–3.24 (m, 2H), 2.19–2.11 (m, 1H), 2.09–2.03 (m, 2H), 2.01–1.92 (m, 1H), 1.88–1.82 (m, 1H), 1.81–1.72 (m, 1H), 1.36–1.28 (m, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.4, 136.6, 135.6, 130.4, 128.9, 127.1, 126.0, 121.5, 118.3, 75.6, 72.2, 34.0, 28.6, 25.7, 24.6. IR (neat) cm^{-1}: 2910, 2853, 1521, 1302, 1055, 813, 656. HRMS m/z (ESI): calcd. for $C_{17}H_{21}N_2O$ [MH]$^{+}$: 269.1648, found: 269.1653.

3,3'-(Butane-1,4-diyl)bis(1-(4-((cyclohex-3-en-1-ylmethoxy)methyl)phenyl)-1*H*-imidazol-3-ium) bromide (11).

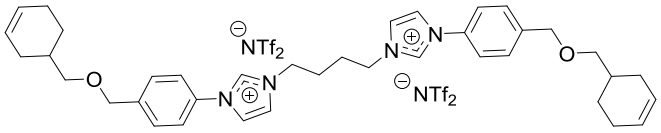


1,4-dibromobutane (102 mg, 0.47 mmol) was added to a solution of the compound **10** (0.3 g, 1.1 mmol) in CH_3CN (1.5 ml). The reaction mixture was stirred at 80 °C for 21 h. The

precipitate was filtered and washed several times with cold CH_3CN. The product was obtained as a white solid (0.25 g, 73 %).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.79 (t, *J* = 1.8 Hz, 2H), 8.43 (t, *J* = 1.8 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 4H), 7.61 (t, *J* = 1.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 4H), 5.72–5.57 (m, 4H), 4.81 (t, *J* = 6.3 Hz, 4H), 4.53 (s, 4H), 3.42–3.30 (m, 4H), 2.36 (t, *J* = 6.3 Hz, 4H), 2.15–2.07 (m, 2H), 2.07–2.00 (m, 4H), 1.97–1.86 (m, 2H), 1.85–1.78 (m, 2H), 1.78–1.68 (m, 2H), 1.33–1.22 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.6, 135.4, 133.6, 129.2, 127.1, 125.9, 124.6, 121.9, 120.4, 75.8, 71.8, 49.2, 34.0, 28.5, 26.7, 25.7, 24.6. IR (neat) cm^{-1}: 3430, 2917, 1566, 1201, 846, 627, 532. HRMS m/z (ESI): calcd. for $C_{38}H_{48}N_4O_2$ $[M]^{2+}$: 296.1883, found: 296.1879

3,3'-(Butane-1,4-diyl)bis(1-(4-((cyclohex-3-en-1-ylmethoxy)methyl)phenyl)-1*H*-imidazol-3-ium) bistrifluoromethanesulfonimidate (11a).

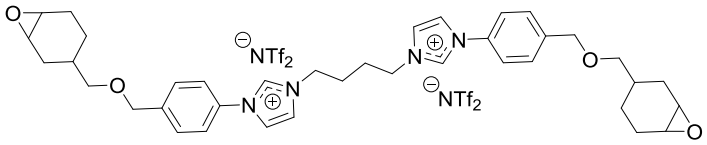


The compound **11** (215 mg, 0.29 mmol) was dissolved in 6.3 ml of H_2O at 88 °C. A solution of $LiNTf_2$ (0.18 g, 0.63 mmol) in 0.5 ml of H_2O was added and the mixture was left to cool down to room temperature overnight. Afterwards, 5 ml of CH_2Cl_2 was added and the organic layer was washed 3 times with H_2O, dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The product was obtained as colorless viscous liquid (0.32 g, 96 %).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.06 (t, *J* = 1.9 Hz, 2H), 7.72 (t, *J* = 1.9 Hz, 2H), 7.60–7.47 (m, 10H), 5.77–5.58 (m, 4H), 4.57 (s, 4H), 4.46–4.39 (m, 4H), 3.46–3.30 (m, 4H), 2.22–2.09 (m, 6H), 2.09–2.01 (m, 4H), 2.01–1.90 (m, 2H), 1.88–1.71 (m, 4H), 1.36–1.25 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.1, 133.9, 133.4, 129.2, 127.1, 125.9, 123.8, 122.1, 121.7, 119.7 (q, *J* = 321.1 Hz), 75.8, 71.8, 49.7, 34.0, 28.5, 26.8, 25.6, 24.6. IR (neat) cm^{-1}: 3141, 2863, 1350, 1176, 1055, 607, 569. HRMS m/z (ESI): calcd. for $C_{38}H_{48}N_4O_2$ $[M]^{2+}$: 296.1883, found: 296.1875.

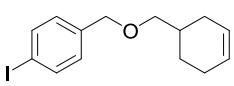
3,3'-(Butane-1,4-diyl)bis(1-(4-(((7-oxabicyclo[4.1.0]heptan-3-yl)methoxy)methyl)phenyl)-1H-imidazol-3-ium) bistrifluoromethanesulfonimidate (CEIL-3).



The compound **11a** (1.30 g, 1.13 mmol) was dissolved in 7 ml of CH_2Cl_2 and the solution of mCPBA (0.66 g, 2.86 mmol) in CH_2Cl_2 (7 ml) was added dropwise at 0 °C. The reaction was stirred at 0 °C for 3 h and then poured into 250 ml of Et_2O. The mixture was left overnight for sedimentation. Insoluble part was separated by decantation and washed two times by Et_2O. The product was dried in vacuum (0.94 g, 71 %).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.92–8.86 (m, 2H), 7.83–7.79 (m, 2H), 7.66–7.57 (m, 10H), 4.61–4.55 (m, 4H), 4.35–4.27 (m, 4H), 3.42–3.28 (m, 4H), 3.18–3.08 (m, 4H), 2.22–1.99 (m, 7H), 1.86–1.37 (m, 9H), 1.21–0.99 (m, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) mixture of stereoisomers[3] δ 142.9, 142.8, 135.6, 134.9, 134.8, 130.1, 130.0, 124.2, 123.5, 123.4, 123.0, 120.9 (q, J = 320.8 Hz), 76.3, 76.1, 72.4, 72.3, 53.2, 53.0, 52.3, 51.8, 50.3, 33.9, 31.3, 29.2, 28.2, 27.1, 25.5, 24.7, 23.9, 22.2. IR (neat) cm^{-1}: 3144, 2928, 1347, 1178, 1133, 1051. HRMS m/z (ESI): calcd. for $C_{38}H_{48}N_4O_4$ $[M]^{2+}$: 312.1832, found: 312.1832.

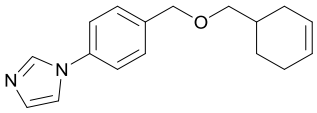
4-Iodobenzyl (cyclohex-3-en-1-ylmethyl) ether (12).



Under Ar atmosphere, methanesulfonyl chloride (1.08 ml, 14 mmol) was added dropwise to a solution of 4-iodobenzyl alcohol (3.0 g, 12.8 mmol) and triethylamine (2.67 ml 19.2 mmol) in CH_2Cl_2 (60 ml) at -15 °C. The mixture was stirred at this temperature for 140 min and then 40 ml of H_2O were added dropwise. The organic layer was quickly washed with 33 ml of HCl (1M) solution, 33 ml of saturated $NaHCO_3$ solution then 33 ml of saturated NaCl solution. The organic phase was dried over anhydrous $MgSO_4$ and then concentrated in vacuo resulting in 3.91 g of crude 4-iodobenzyl methanesulfonate. In a second reactor under Ar atmosphere, cyclohexen-4-ylmethanol (1.46 ml, 12.5 mmol) was added dropwise to a stirred suspension of NaH (0.75 g (60 % in mineral oil), 18.8 mmol) in anhydrous THF (62 ml) at 0 °C. After the addition, the mixture was stirred at room temperature for 30 min. A solution of synthesized crude 4-iodobenzyl methanesulfonate (3.91 g, 12.5 mmol) in THF (25 ml) was added dropwise to the mixture at 0 °C, and stirring continued for 30 min at room temperature. The mixture was stirred under reflux for 7 h, after that it was cooled to 0 °C and 2 ml of H_2O were added. Et_2O (~150 ml) was added and the mixture was washed 3 times with water. The organic layer was dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with cyclohexane / ethyl acetate : 95 / 5). The product was obtained as colorless liquid (3.51 g, 84 %).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 5.72–5.58 (m, 2H), 4.44 (s, 2H), 3.38–3.28 (m, 2H), 2.18–2.00 (m, 3H), 1.98–1.88 (m, 1H), 1.87–1.78 (m, 1H), 1.78–1.68 (m, 1H), 1.34–1.23 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.6, 137.5, 129.5, 127.2, 126.1, 93.0, 75.6, 72.4, 34.1, 28.7, 25.8, 24.7. IR (neat) cm^{-1}: 2914, 2851, 1483, 1087, 1006, 797, 654. HRMS m/z (ESI): calcd. for $C_{14}H_{18}IO$ $[MH]^+$: 329.0397, found: 329.0402.

1-(4-((Cyclohex-3-en-1-ylmethoxy)methyl)phenyl)-1*H*-imidazole (10) (Method 2).



Under Ar atmosphere, a solution of **12** (3.41 g, 10.4 mmol) in DMF (5 ml) was added to a mixture of copper (I) iodide (0.40 g 2.1 mmol), K_3PO_4 (4.41 g, 20.8 mmol), imidazole (0.99 g, 14.5 mmol), N,N'-dimethylethylenediamine (0.23 ml, 2.2 mmol) and 14 ml of DMF in a sealed tube. The mixture was stirred at 40 °C for 40 h then it was filtered on Celite® and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluting with ethyl acetate). The product was obtained as colorless liquid (0.97 g, 35 %).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.50–7.42 (m, 2H), 7.40–7.34 (m, 2H), 7.28 (s, 1H), 7.21 (s, 1H), 5.73–5.60 (m, 2H), 4.55 (s, 2H), 3.53–3.24 (m, 2H), 2.19–2.11 (m, 1H), 2.09–2.03 (m, 2H), 2.01–1.92 (m, 1H), 1.88–1.82 (m, 1H), 1.81–1.72 (m, 1H), 1.36–1.28 (m, 1H).

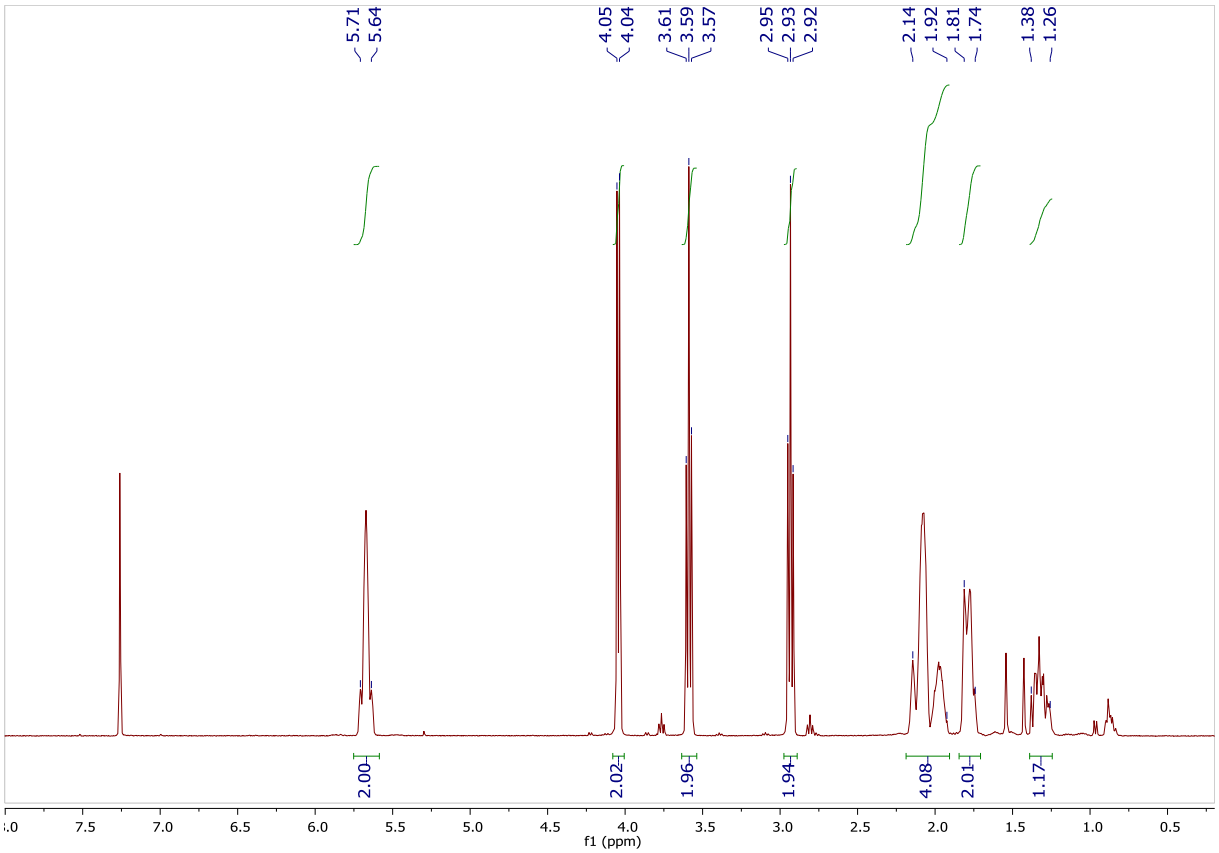
^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.4, 136.6, 135.6, 130.4, 128.9, 127.2, 125.9, 121.5, 118.3, 75.6, 72.2, 34.0, 28.6, 25.7, 24.6. IR (neat) cm^{-1}: 2910, 2853, 1521, 1302, 1055, 813, 656. HRMS m/z (ESI): calcd. for $C_{17}H_{21}N_2O$ $[MH]^+$: 269.1648, found: 269.1653.

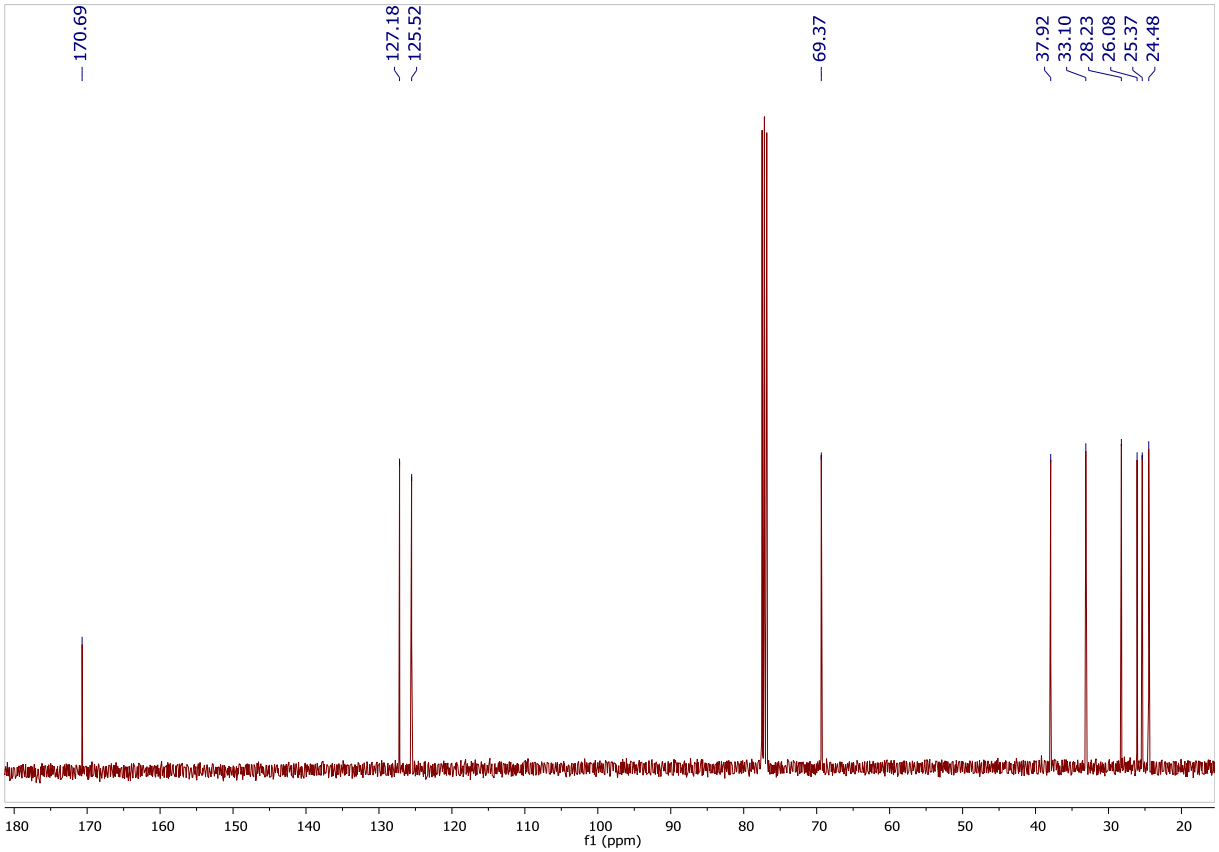
V. Epoxy network preparation

To prepare epoxy networks, CEIL-2 (with or without Sylanto-7MS as mentioned) was dissolved in dichloromethane under stirring at room temperature. The obtained mixture was poured into silicone molds and the solvent was then slowly removed under vacuum. Finally, the mold was placed in the oven at 100 °C for 1 h to liquidize the resin and better fill the molds, then the oven was heated up to 150 °C and the samples were kept for 5 h at this temperature for crosslinking followed by 1 h at 240 °C to finish the reaction.

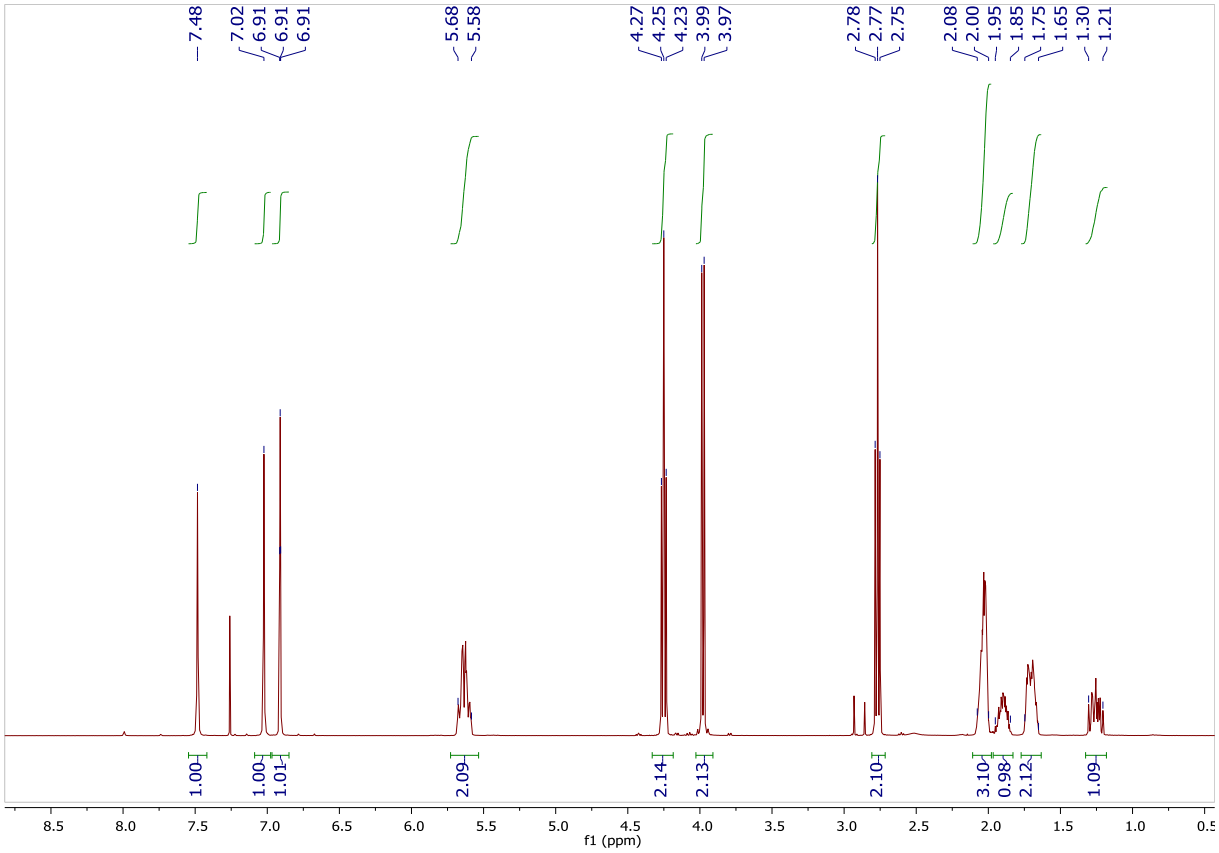
VI. NMR spectra

Compound **1**





Compound **2**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7.02
6.91
6.91
6.91
5.68
5.58
4.27
4.25
4.23
3.99
3.97
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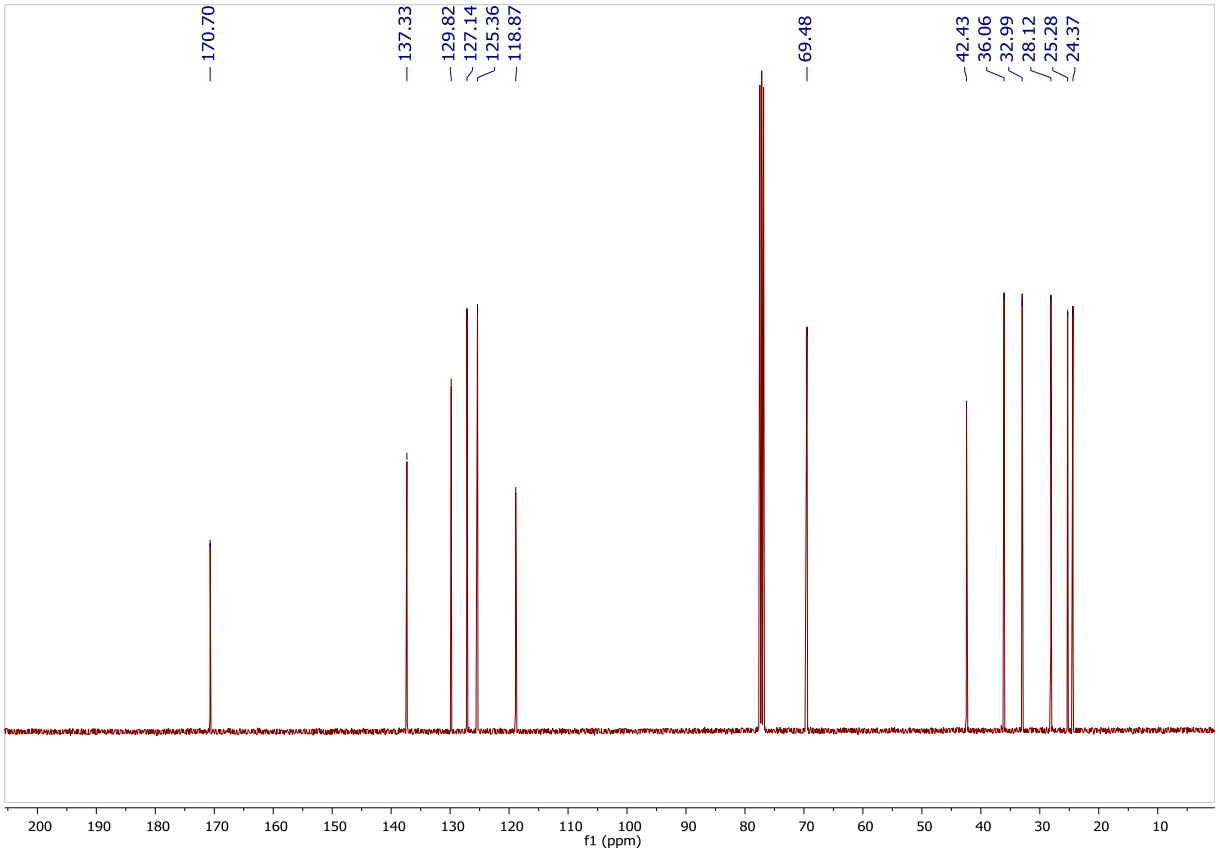
2.77
2.75
2.08
2.00
1.95
1.85
1.75
1.65
1.30
1.21
1.00
1.00
1.01
2.09
2.14
2.13
2.10
3.10
0.98
2.12
1.09
f1 (ppm)


170.70
137.33
129.82
127.14
125.36
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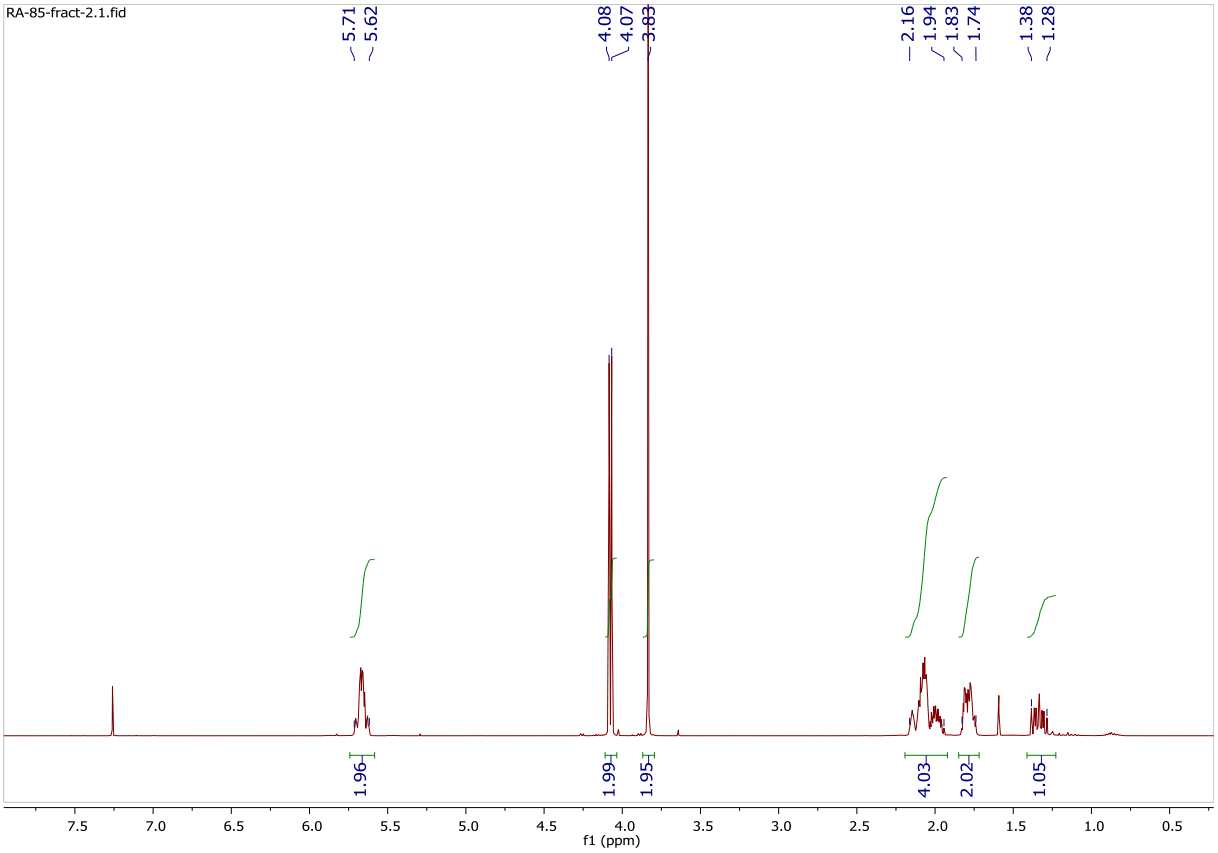
69.48
42.43
36.06
32.99
28.12
25.28
24.37
f1 (ppm)

Compound **5**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4.07
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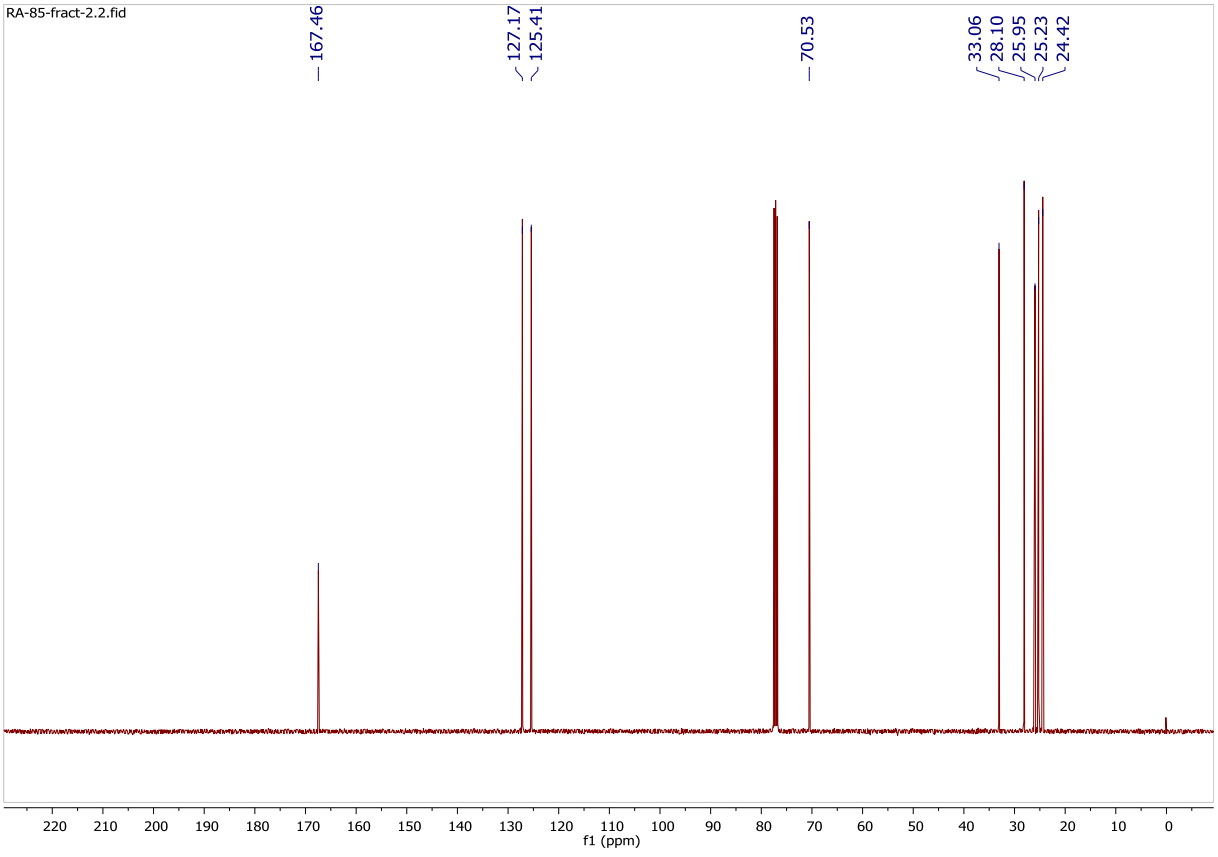
4.03
2.02
1.05
f1 (ppm)


RA-85-fract-2.2.fid
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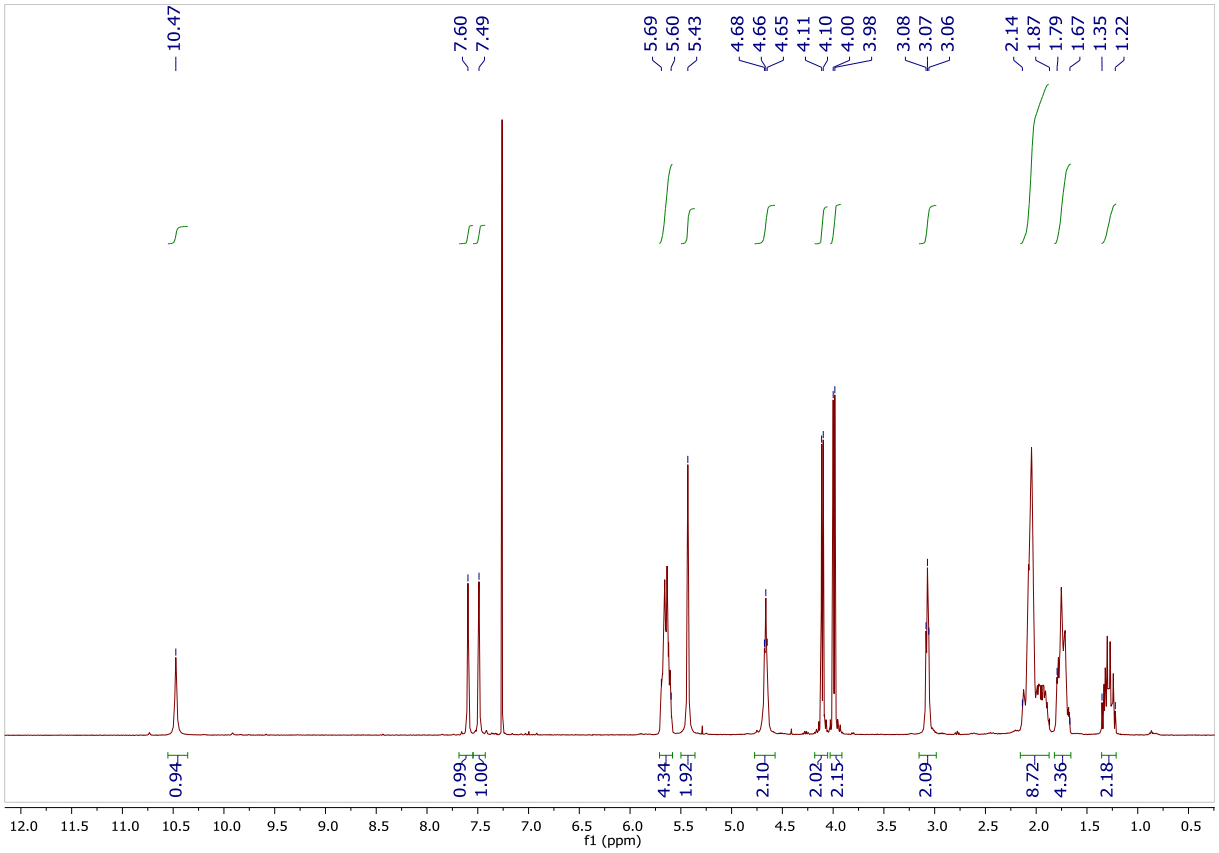
125.41
70.53
33.06
28.10
25.95
25.23
24.42
f1 (ppm)

Compound **6**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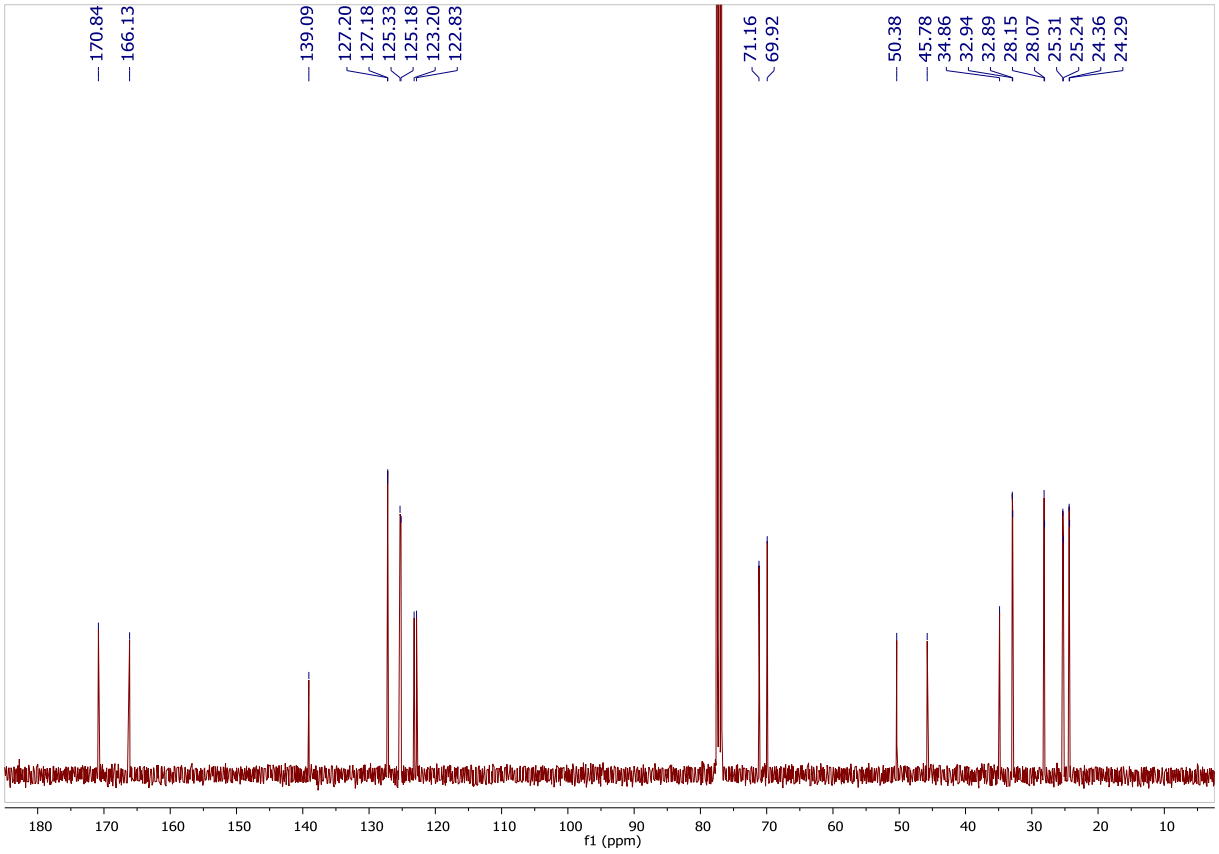
7.60
7.49
5.69
5.60
5.43
4.68
4.66
4.65
4.11
4.10
4.00
3.98
3.08
3.07
3.06
2.14
1.87
1.79
1.67
1.35
1.22
0.94
0.99
1.00
4.34
1.92
2.10
2.02
2.15
2.09
8.72
4.36
2.18
f1 (ppm)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127.20
127.18
125.33
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123.20
122.83
71.16
69.92
50.38
45.78
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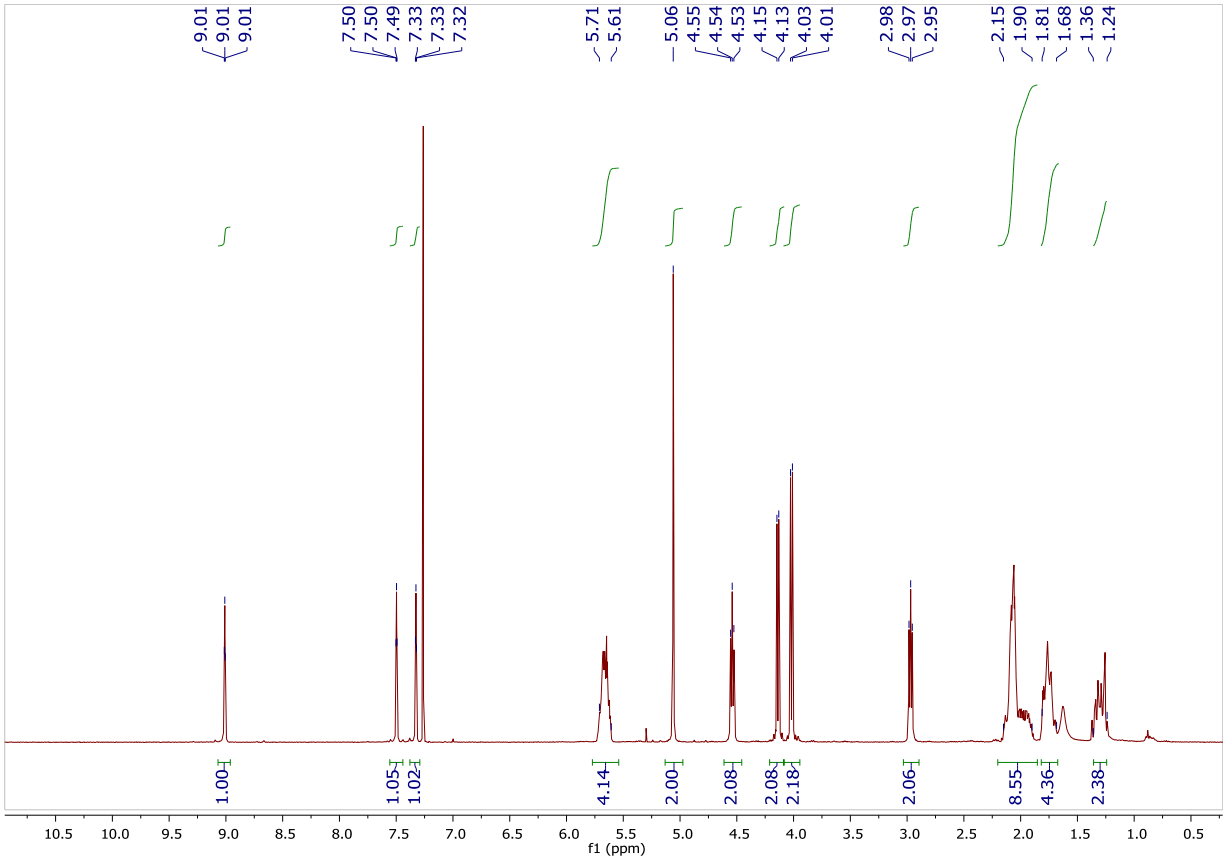
32.94
32.89
28.15
28.07
25.31
25.24
24.36
24.29
f1 (ppm)

Compound **6a**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9.01
9.01
7.50
7.50
7.49
7.33
7.33
7.32
5.71
5.61
5.06
4.55
4.54
4.53
4.15
4.13
4.03
4.01
2.98
2.97
2.95
2.15
1.90
1.81
1.68
1.36
1.24
1.00
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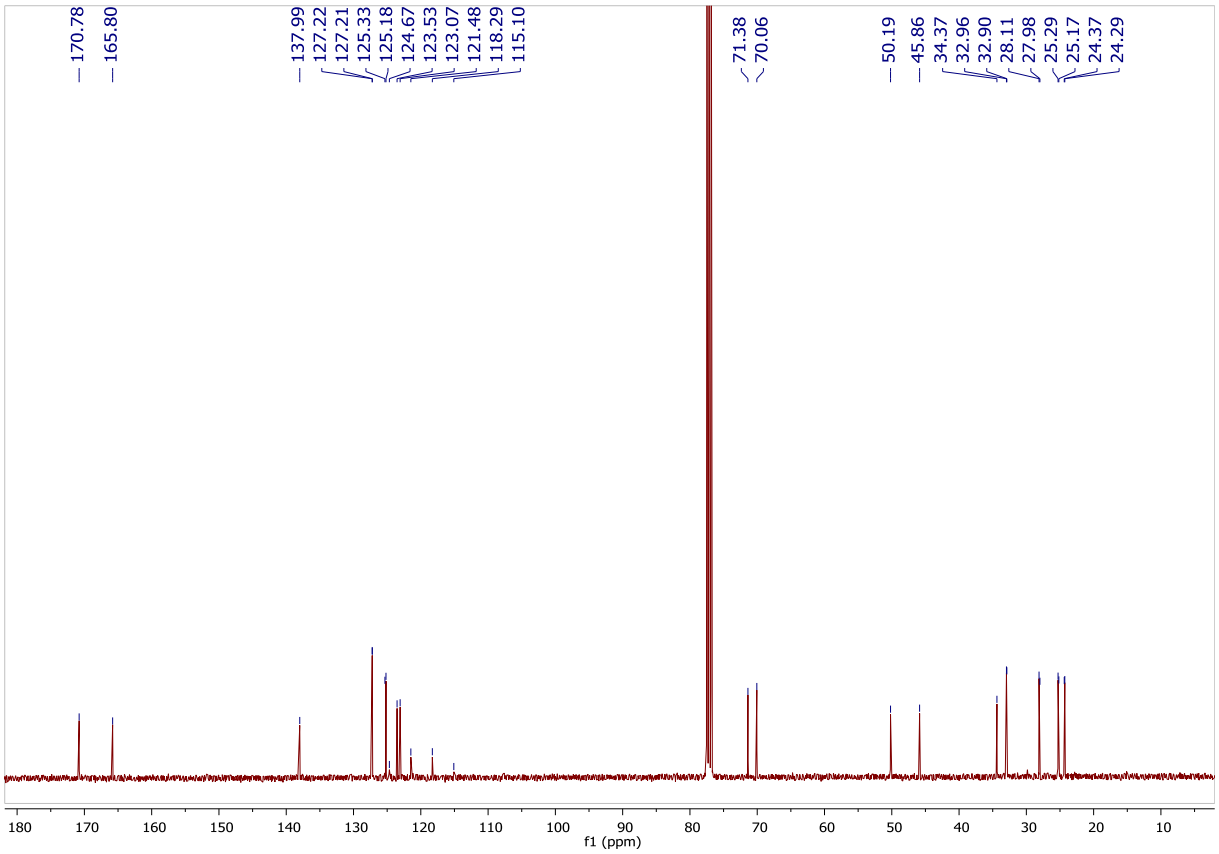
2.06
8.55
4.36
2.38
f1 (ppm)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121.48
118.29
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71.38
70.06
50.19
45.86
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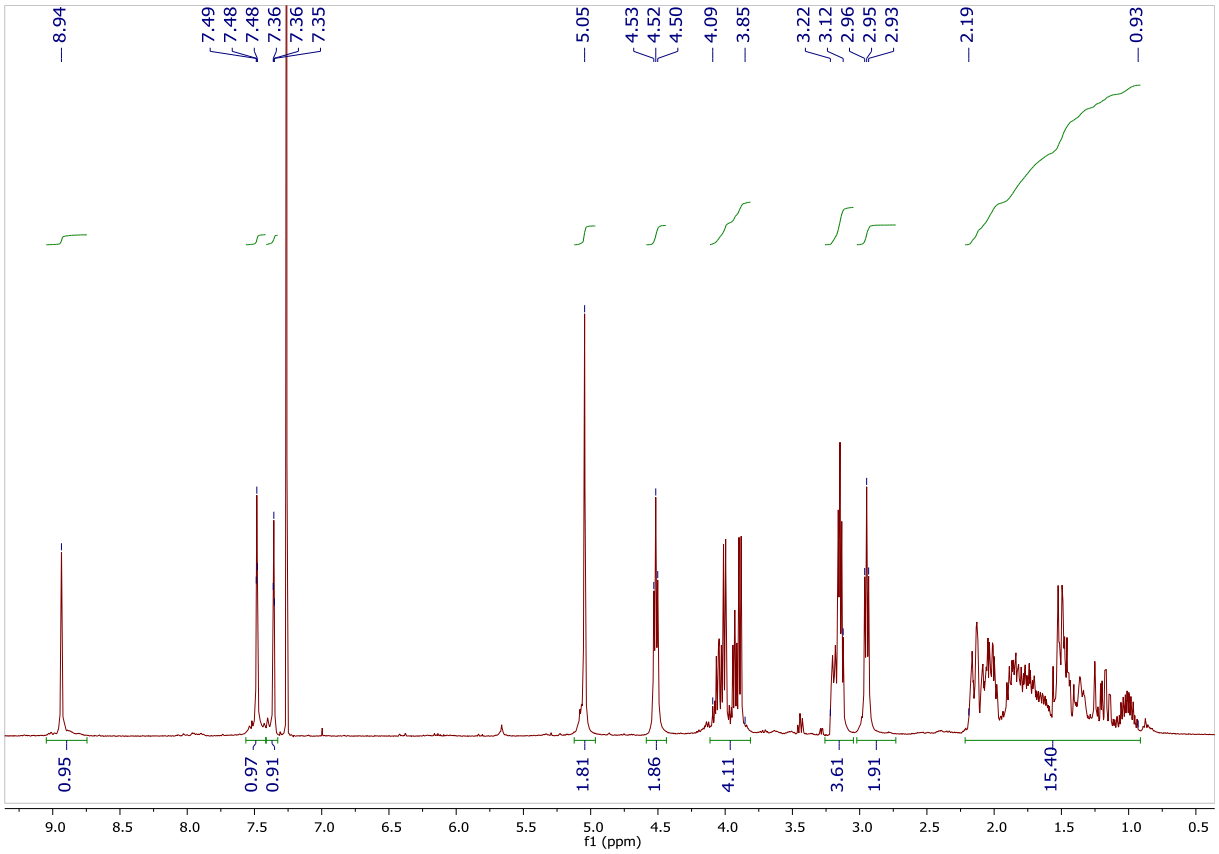
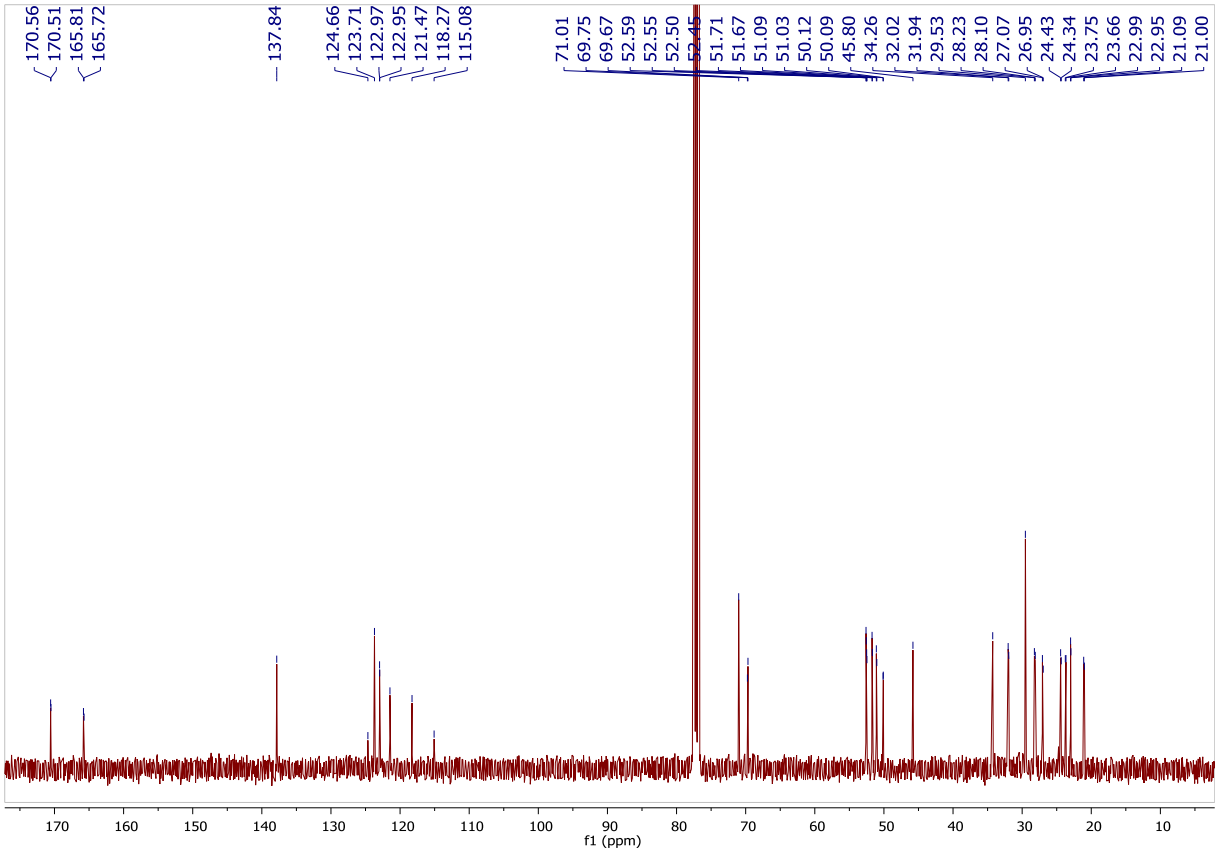
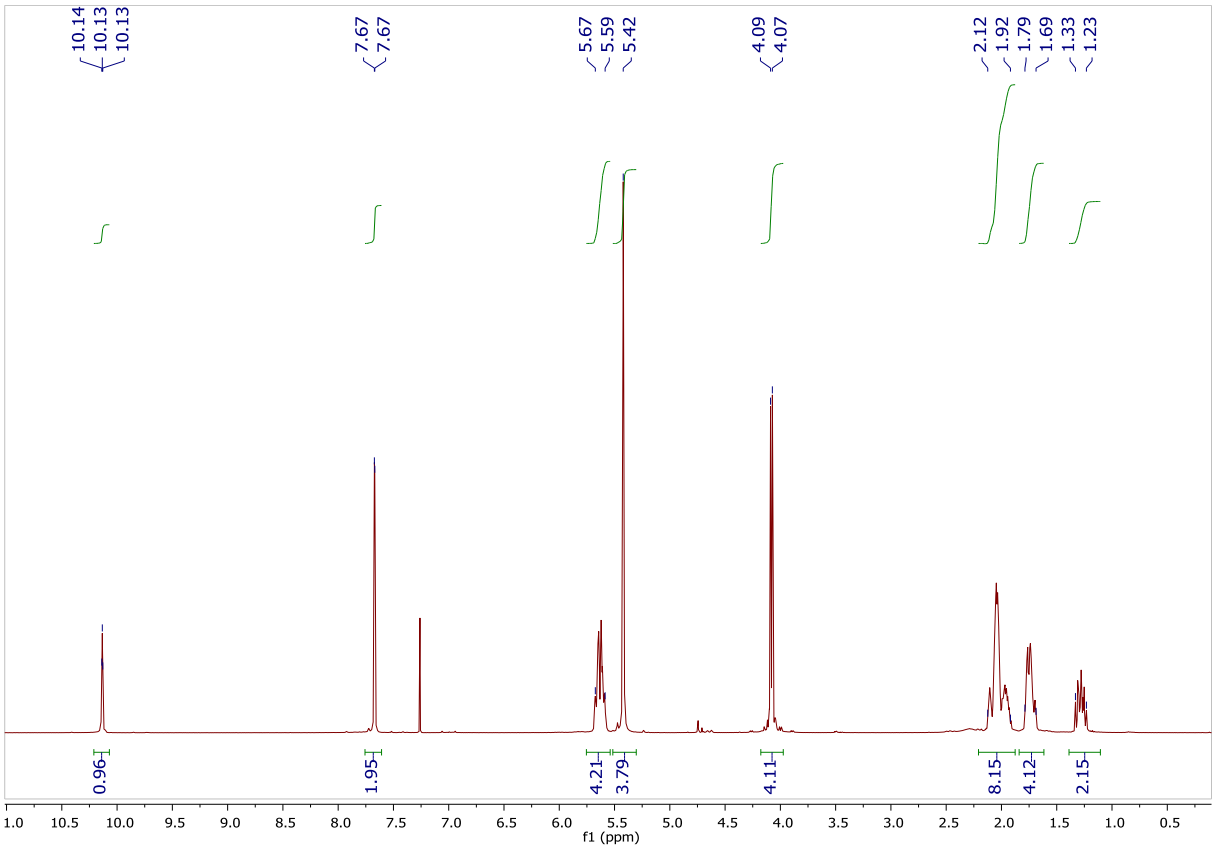
32.96
32.90
28.11
27.98
25.29
25.17
24.37
24.29
f1 (ppm)

Compound **CEIL-1**





Compound **7**


10.14
10.13
10.13
7.67
7.67
5.67
5.59
5.42
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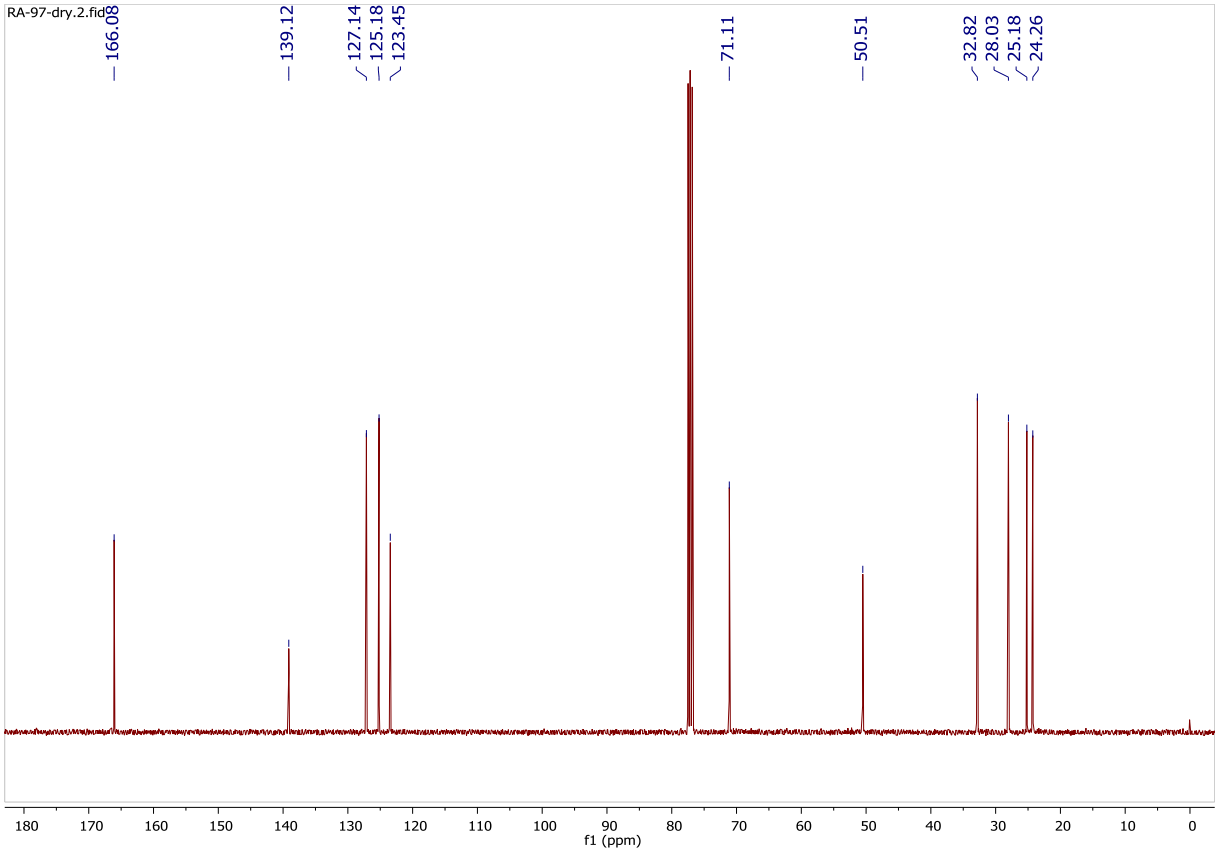
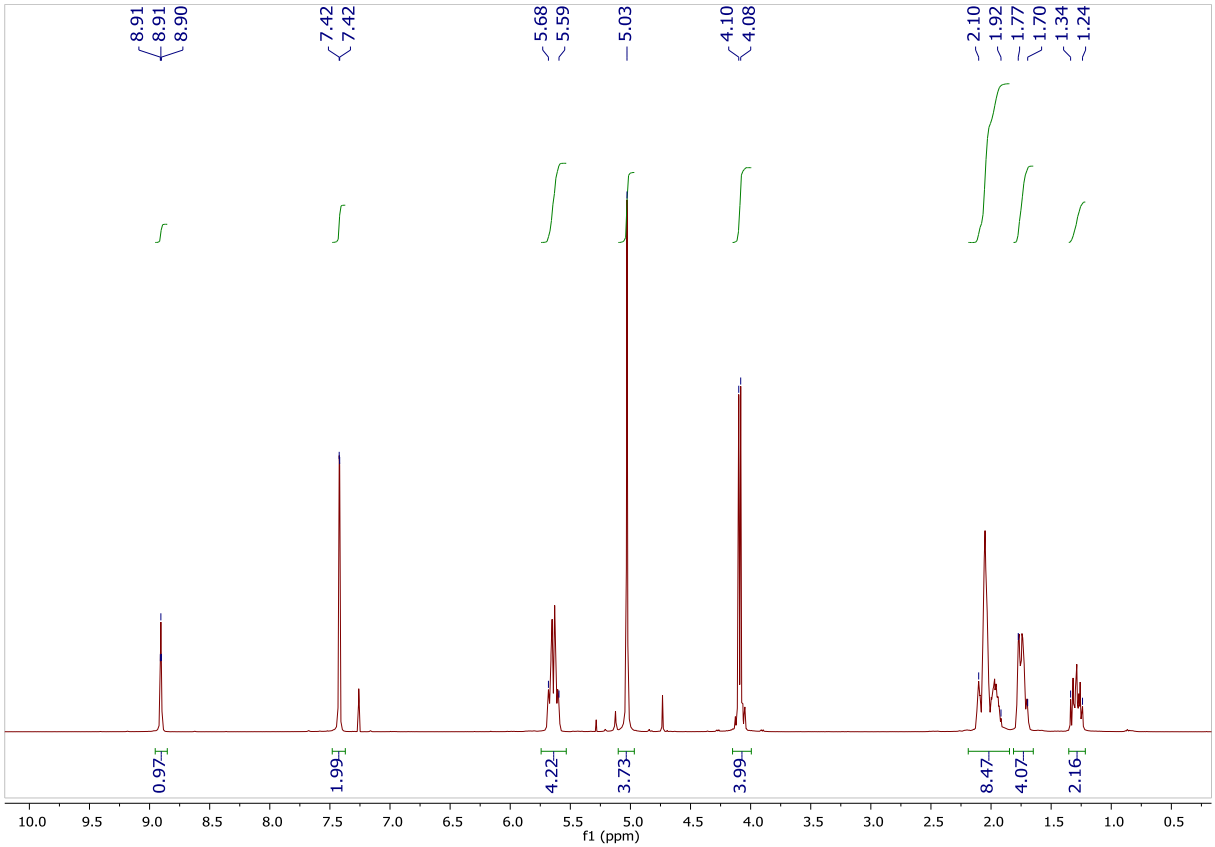
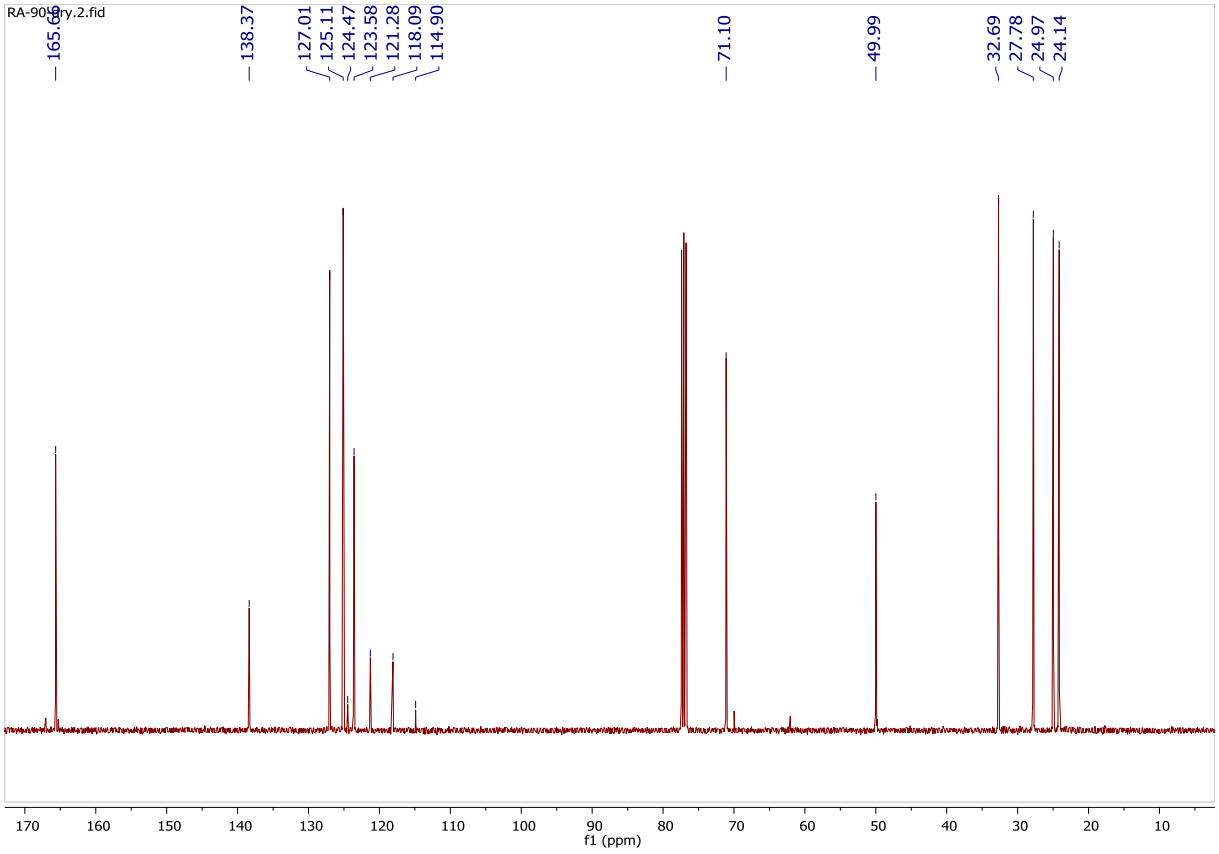
4.07
2.12
1.92
1.79
1.69
1.33
1.23
0.96
1.95
4.21
3.79
4.11
8.15
4.12
2.15
f1 (ppm)

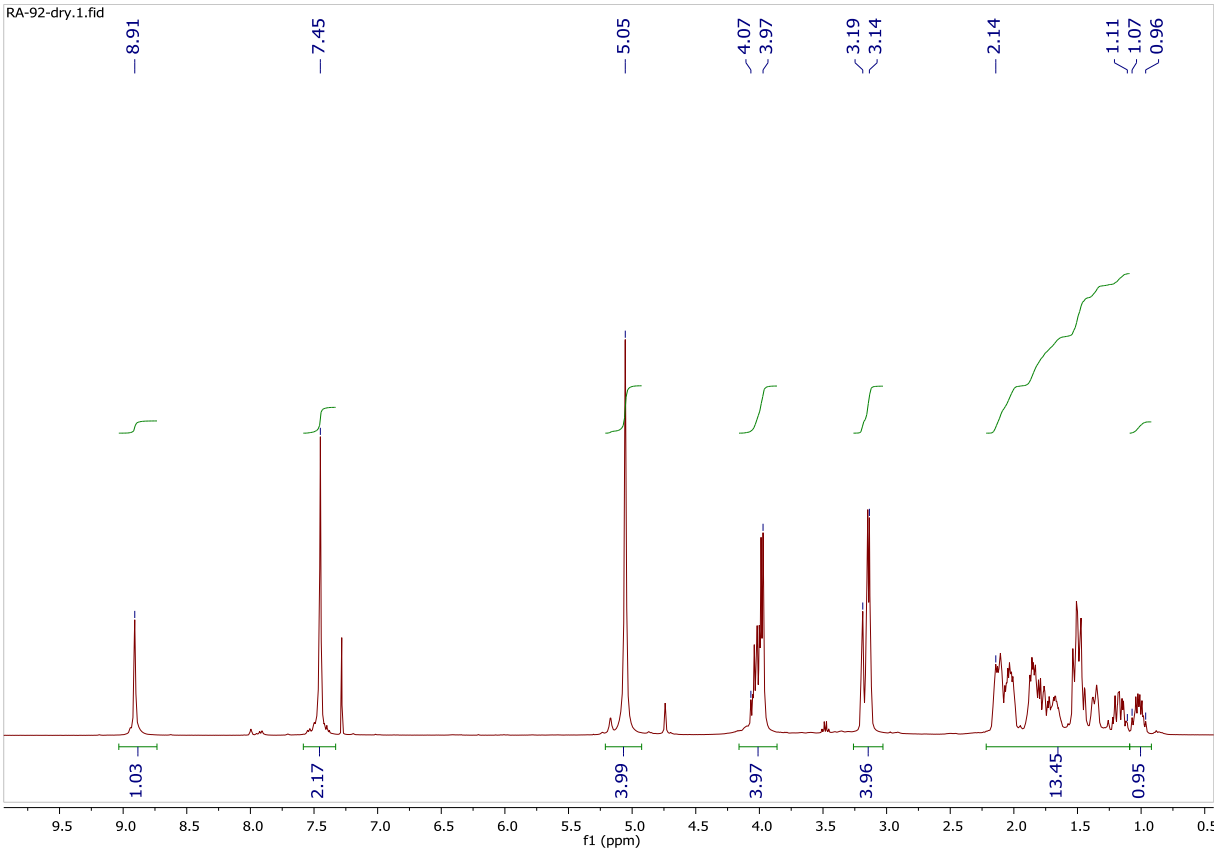

RA-97-dry.2.fid
166.08
139.12
127.14
125.18
123.45
71.11
50.51
32.82
28.03
25.18
24.26
f1 (ppm)

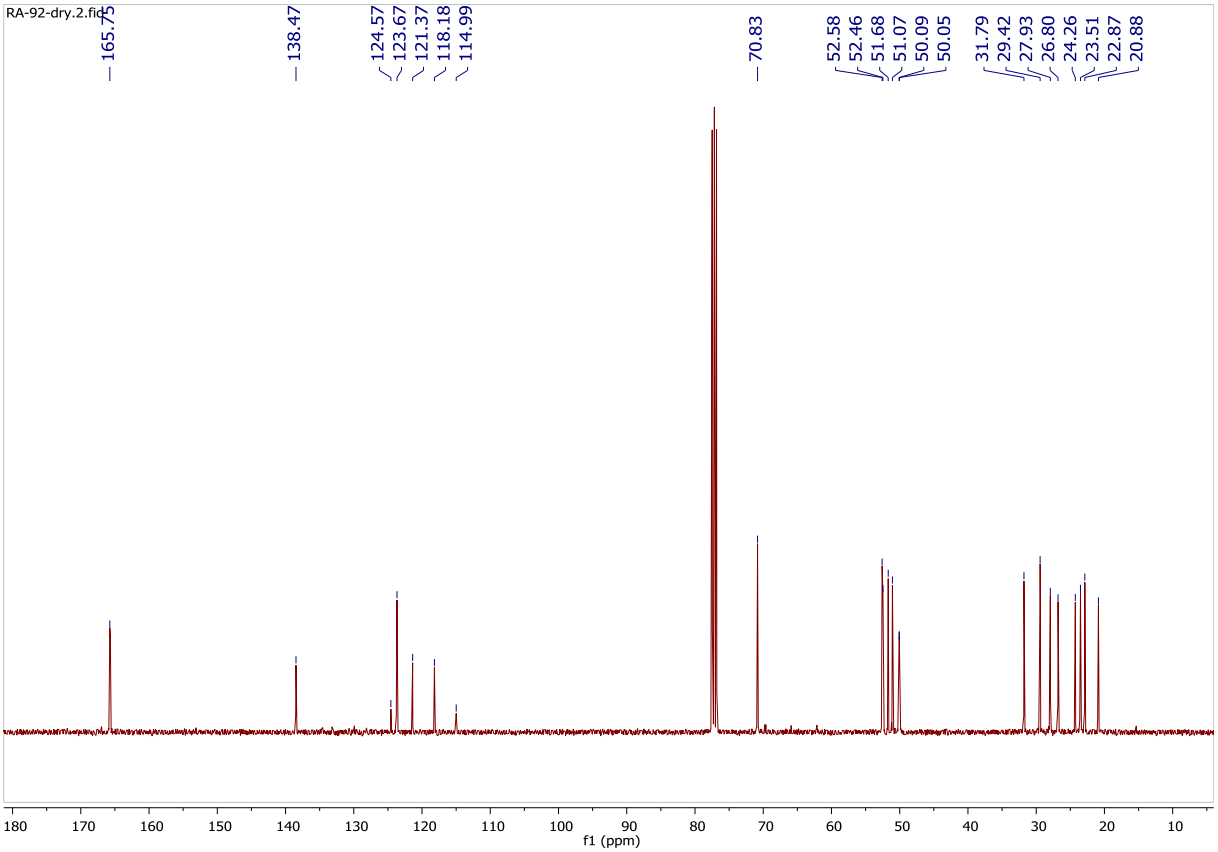
Compound **7a**


8.91
8.91
8.90
7.42
7.42
5.68
5.59
5.03
4.10
4.08
2.10
1.92
1.77
1.70
1.34
1.24
0.97
1.99
4.22
3.73
3.99
8.47
4.07
2.16
f1 (ppm)

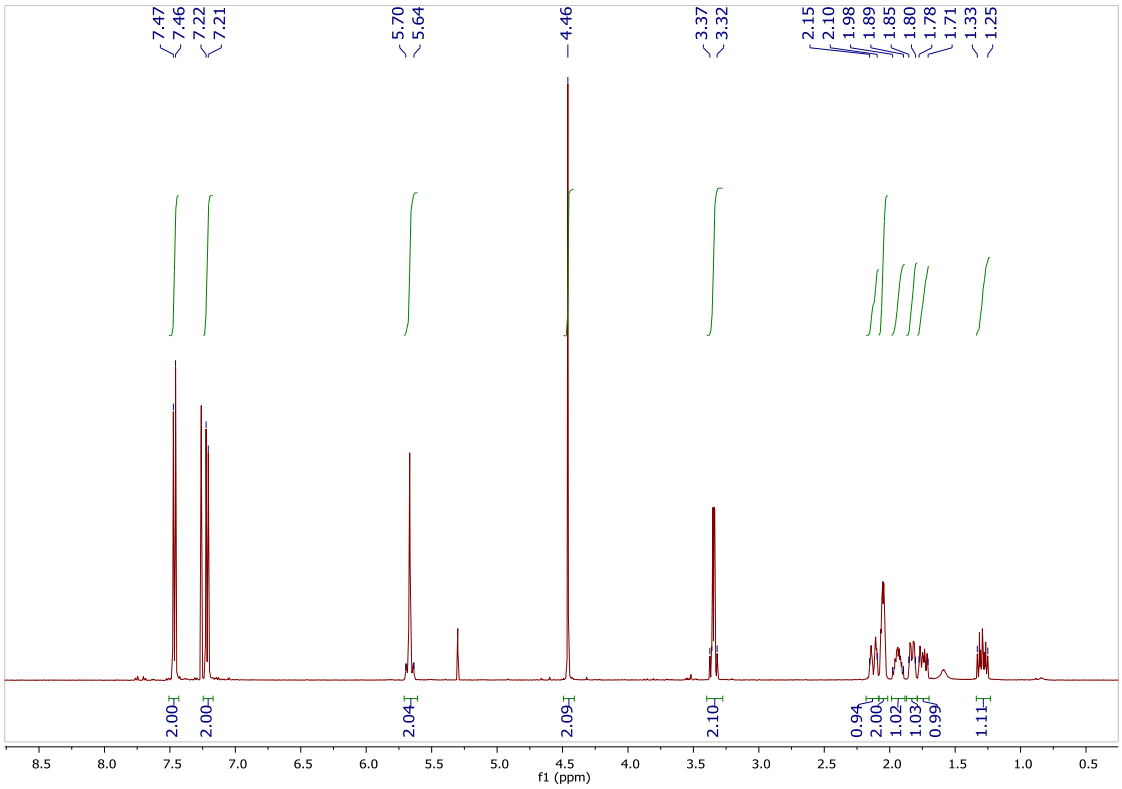

RA-90
165.69
138.37
127.01
125.11
124.47
123.58
121.28
118.09
114.90
71.10
49.99
32.69
27.78
24.97
24.14
f1 (ppm)

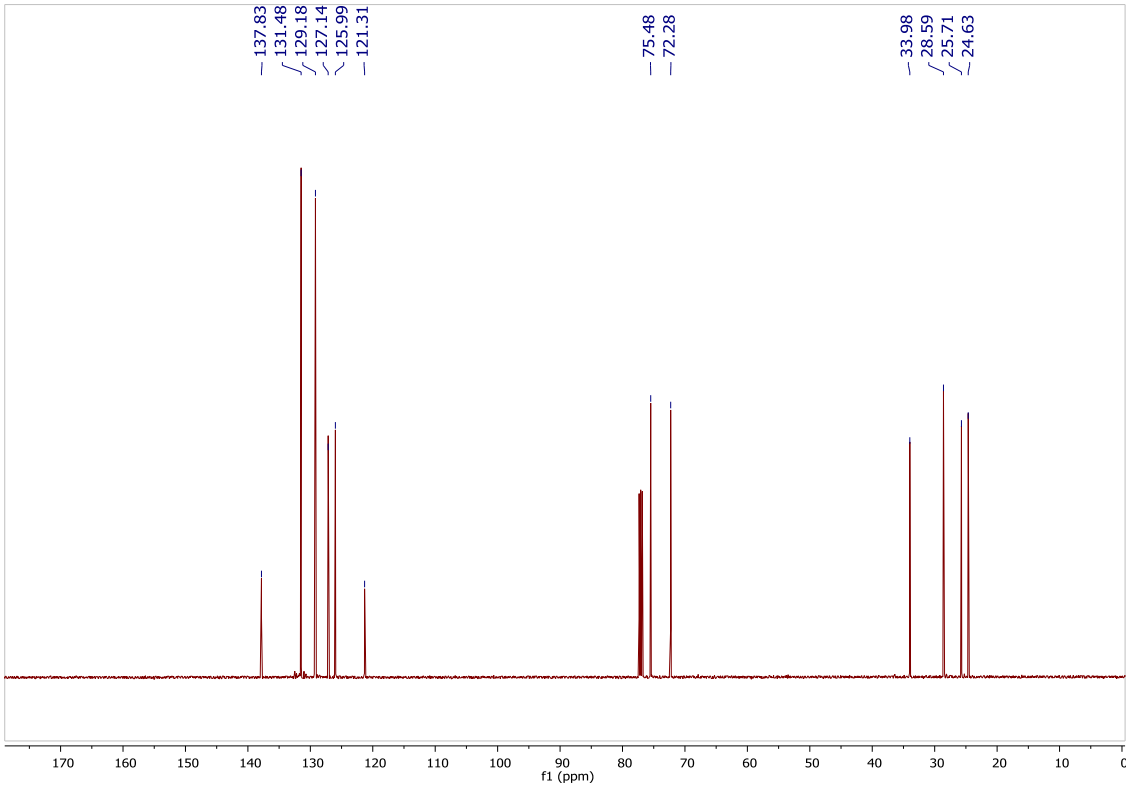
Compound **CEIL-2**



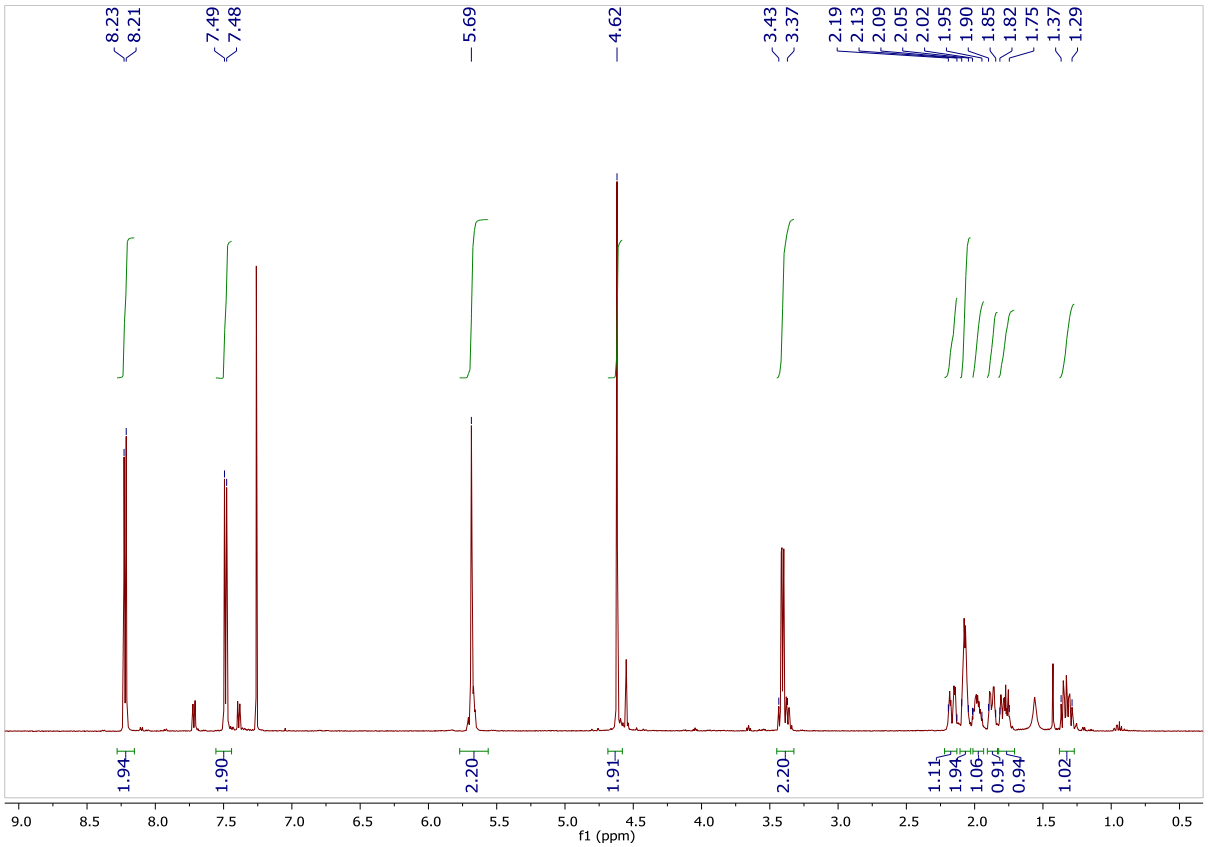


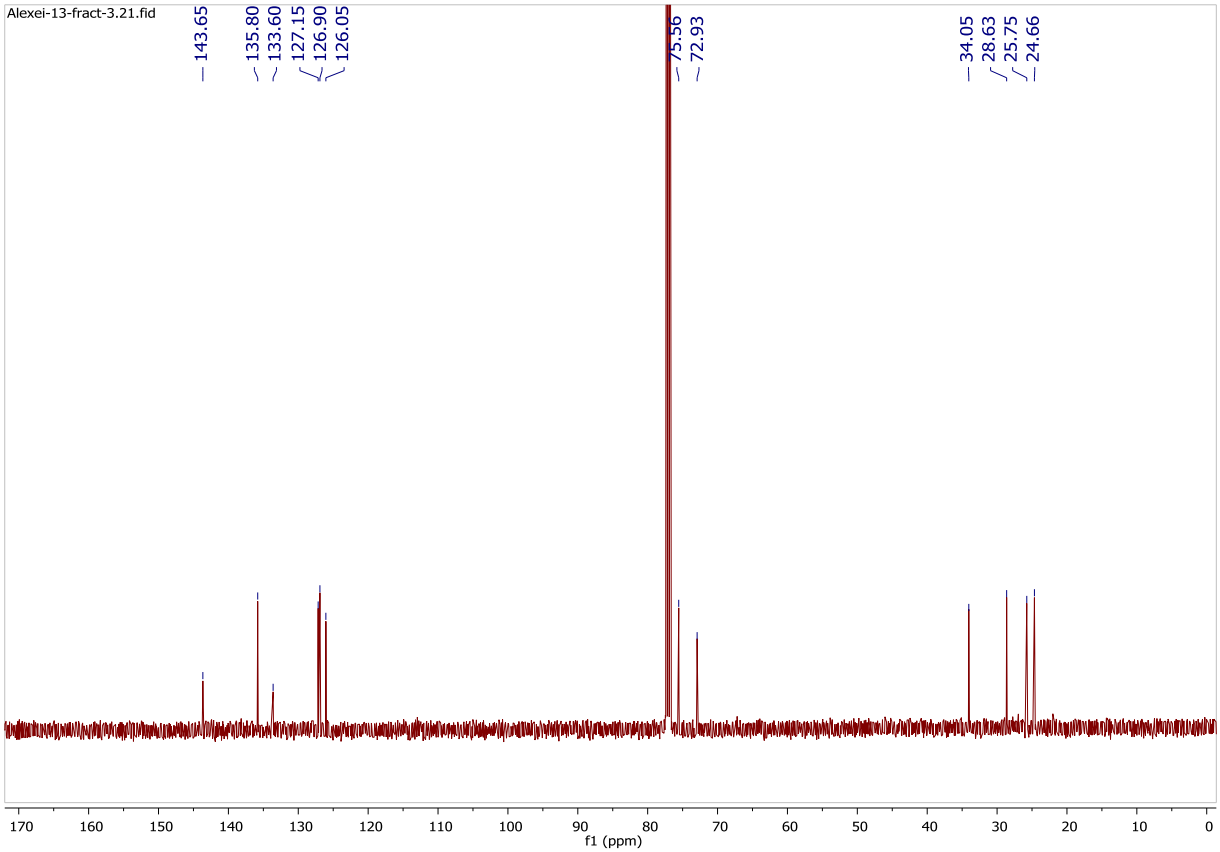
Compound **8**


7.47
7.46
7.22
7.21
5.70
5.64
4.46
3.37
3.32
2.15
2.10
1.98
1.89
1.85
1.80
1.78
1.71
1.33
1.25
2.00
2.00
2.04
2.09
2.10
0.94
2.00
1.02
1.03
0.99
1.11
f1 (ppm)

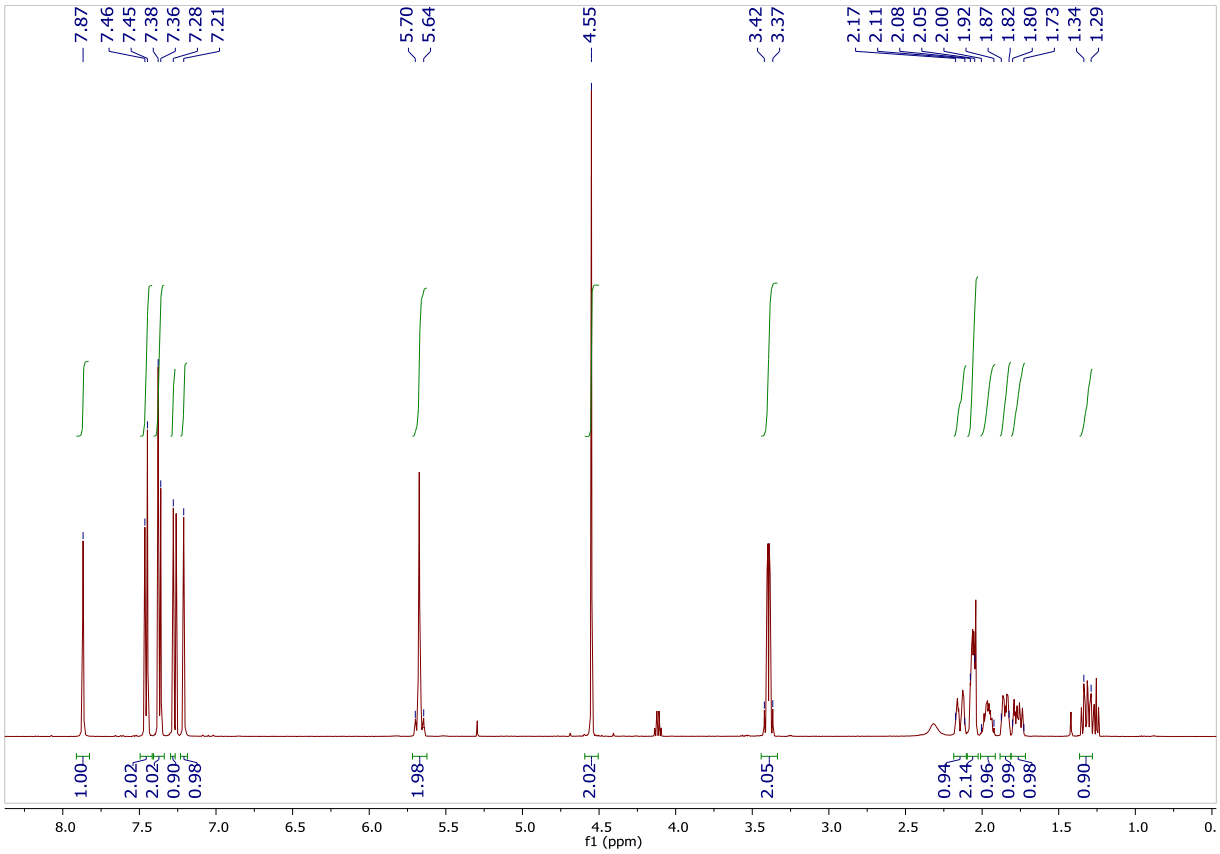

137.83
131.48
129.18
127.14
125.99
121.31
75.48
72.28
33.98
28.59
25.71
24.63
f1 (ppm)

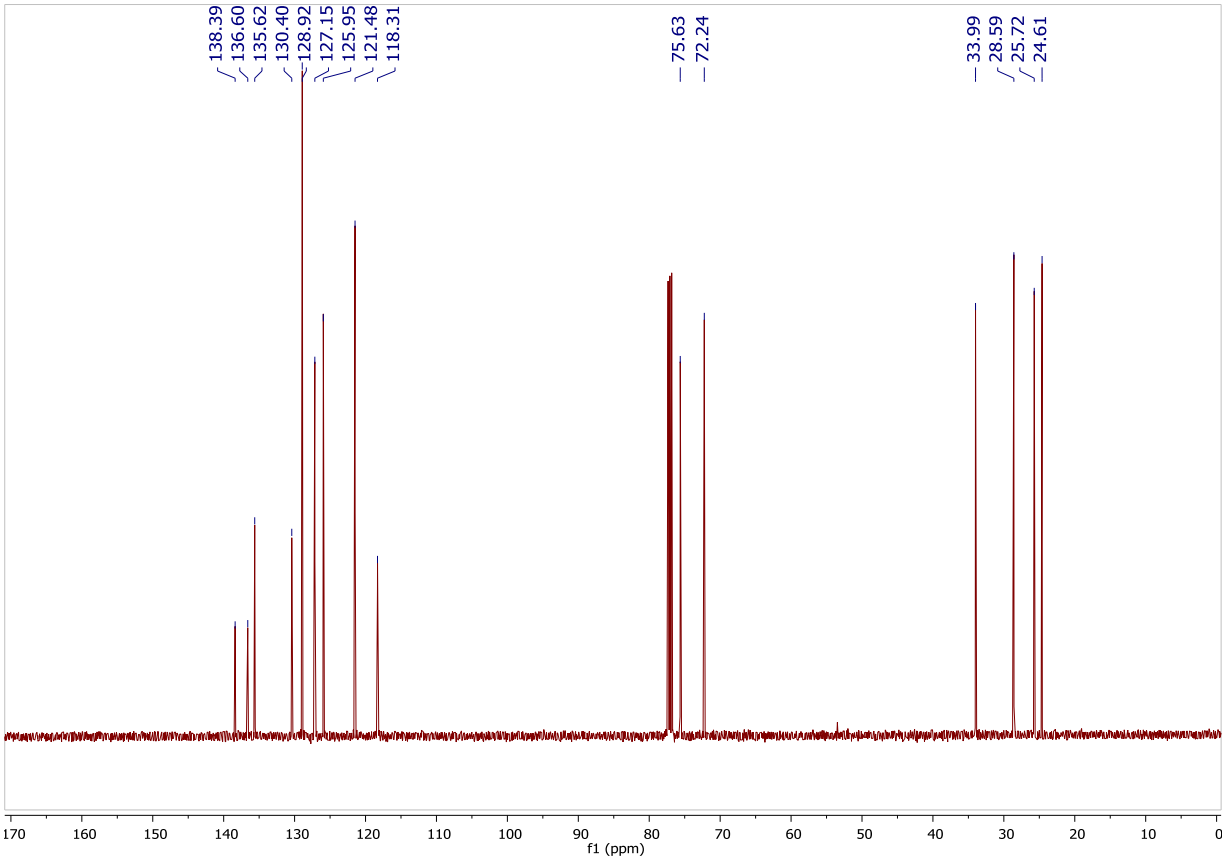
Compound **9**


8.23
8.21
7.49
7.48
5.69
4.62
3.43
3.37
2.19
2.13
2.09
2.05
2.02
1.95
1.90
1.85
1.82
1.75
1.37
1.29
1.94
1.90
2.20
1.91
2.20
1.11
1.94
1.06
0.91
0.94
1.02
f1 (ppm)

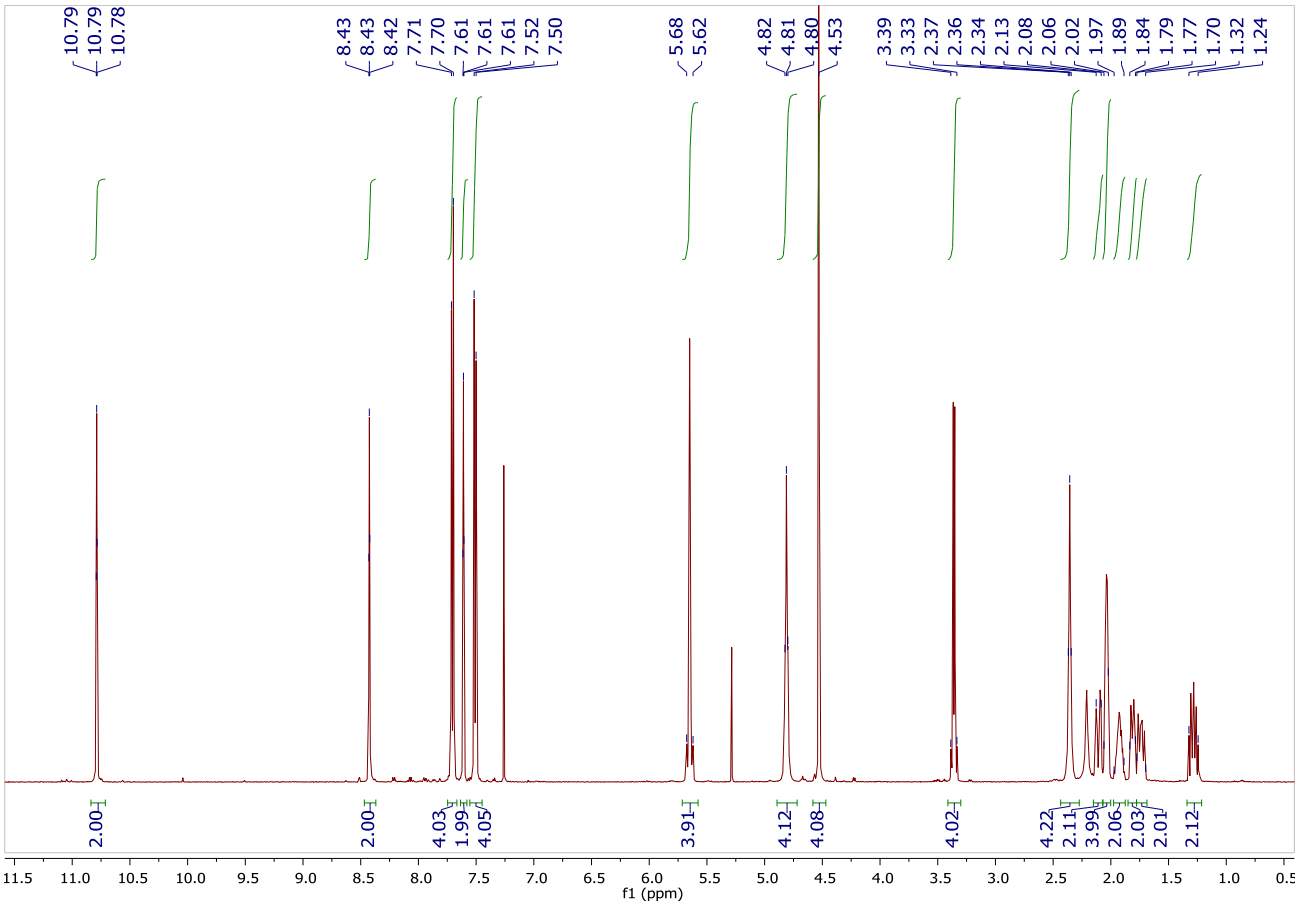

Alexei-13-fract-3.21.fid
143.65
135.80
133.60
127.15
126.90
126.05
75.56
72.93
34.05
28.63
25.75
24.66
f1 (ppm)

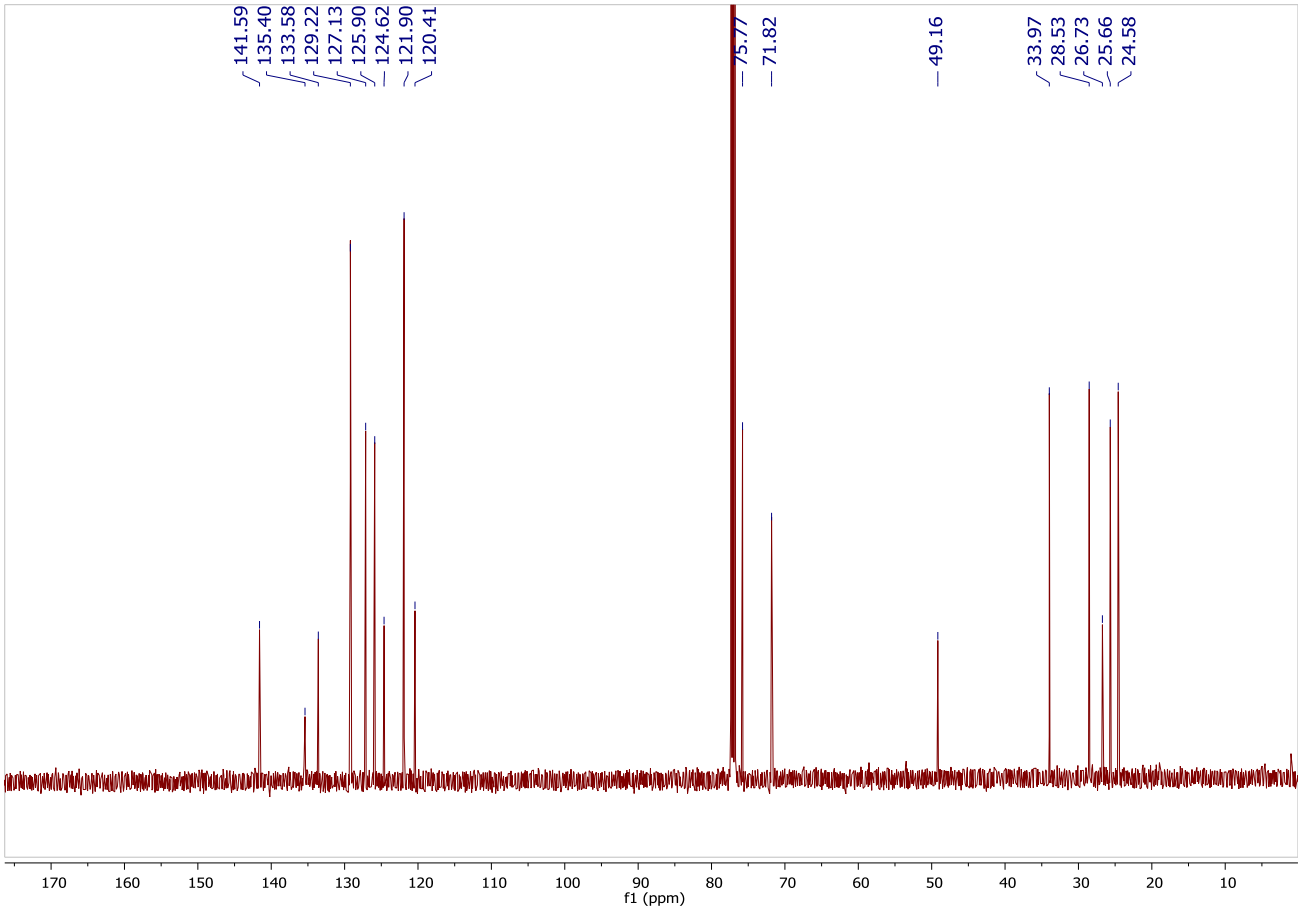
Compound **10**


7.87
7.46
7.45
7.38
7.36
7.28
7.21
5.70
5.64
4.55
3.42
3.37
2.17
2.11
2.08
2.05
2.00
1.92
1.87
1.82
1.80
1.73
1.34
1.29
1.00
2.02
2.02
0.90
0.98
1.98
2.02
2.05
0.94
2.14
0.96
0.99
0.98
0.90
f1 (ppm)

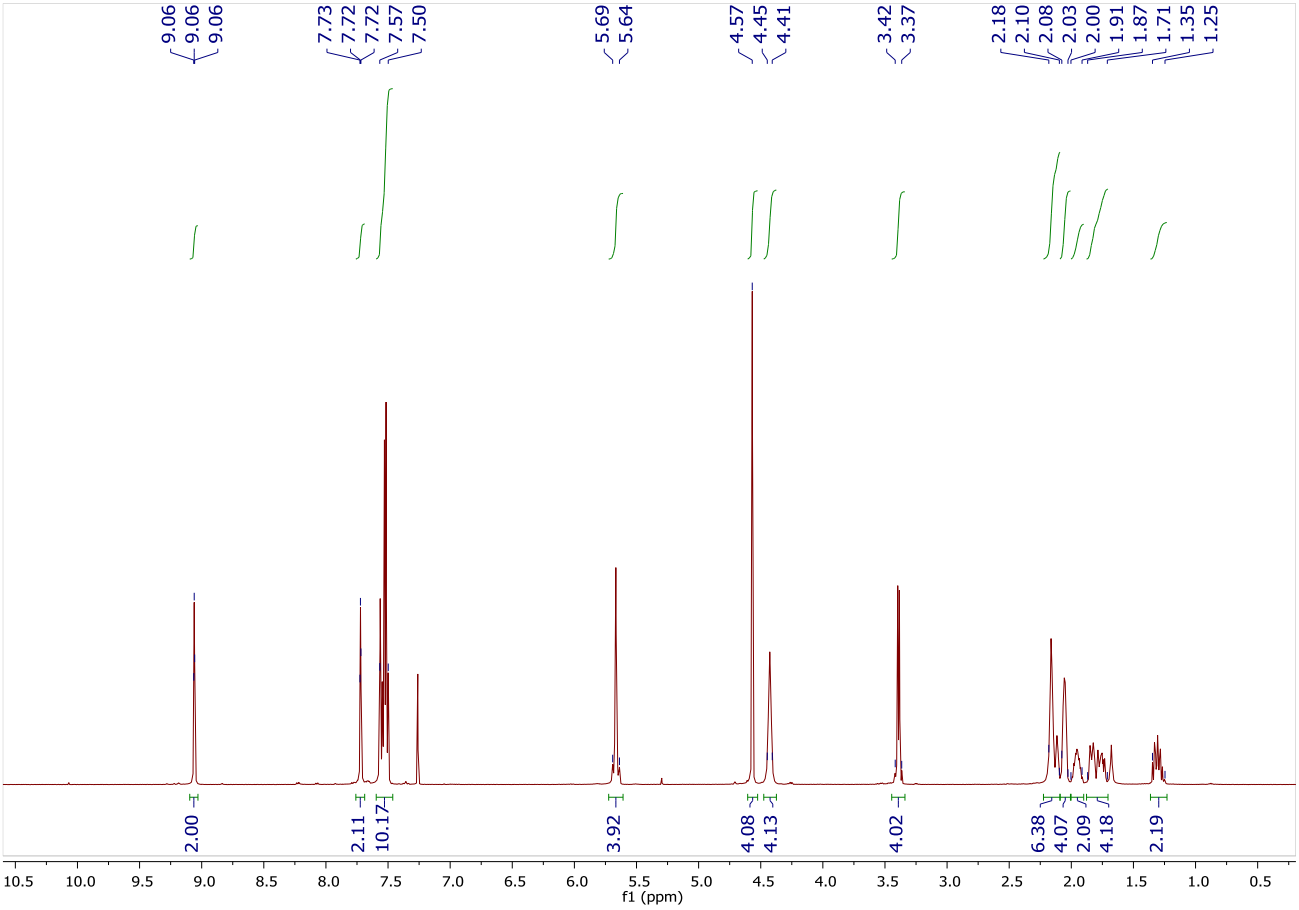

138.39
136.60
135.62
130.40
128.92
127.15
125.95
121.48
118.31
75.63
72.24
33.99
28.59
25.72
24.61
f1 (ppm)

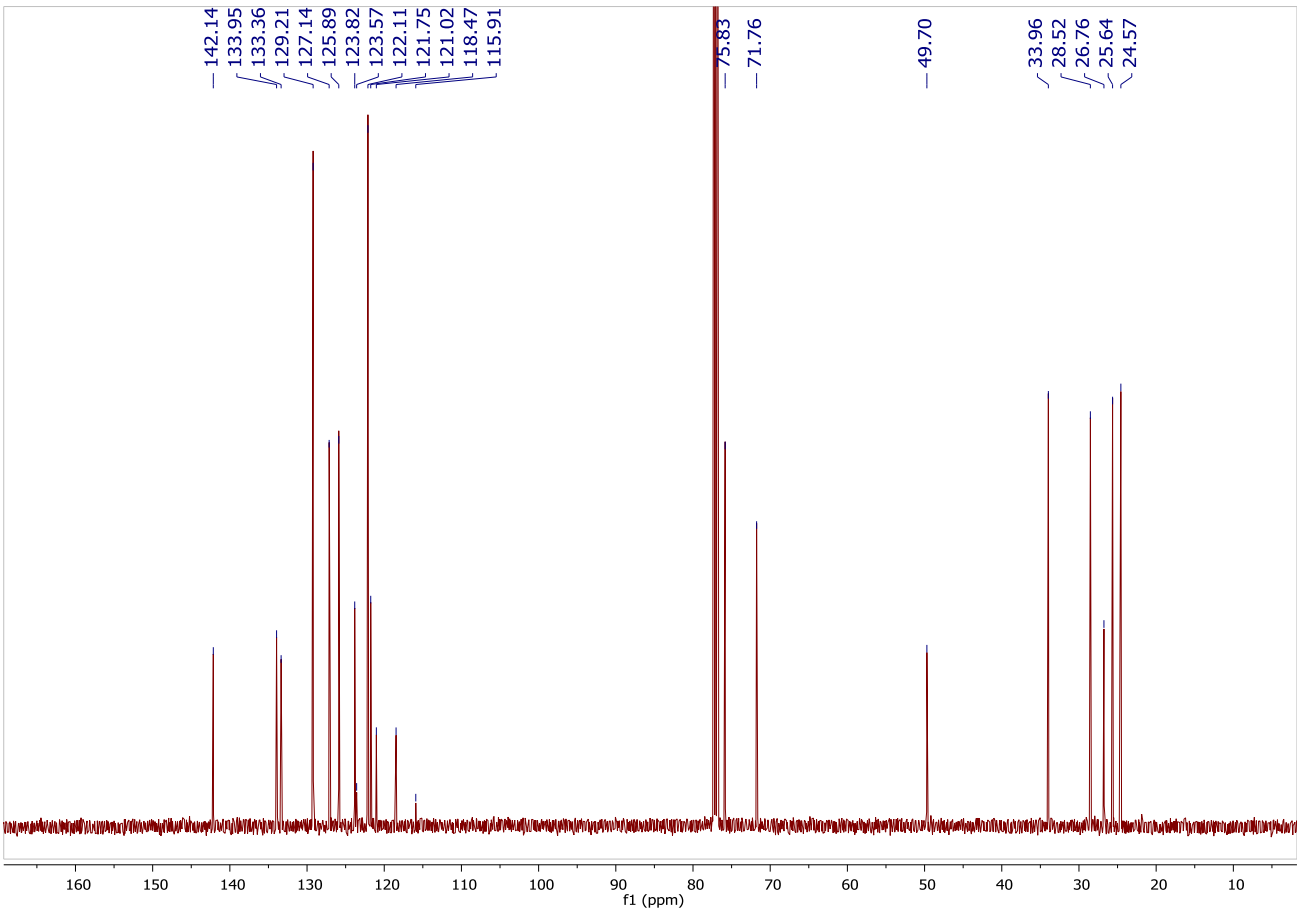
Compound **11**


10.79
10.79
10.78
8.43
8.43
8.42
7.71
7.70
7.61
7.61
7.61
7.52
7.50
5.68
5.62
4.82
4.81
4.80
4.53
3.39
3.33
2.37
2.36
2.34
2.13
2.08
2.06
2.02
1.97
1.89
1.84
1.79
1.77
1.70
1.32
1.24
2.00
2.00
4.03
1.99
4.05
3.91
4.12
4.08
4.02
4.22
2.11
3.99
2.06
2.03
2.01
2.12
f1 (ppm)

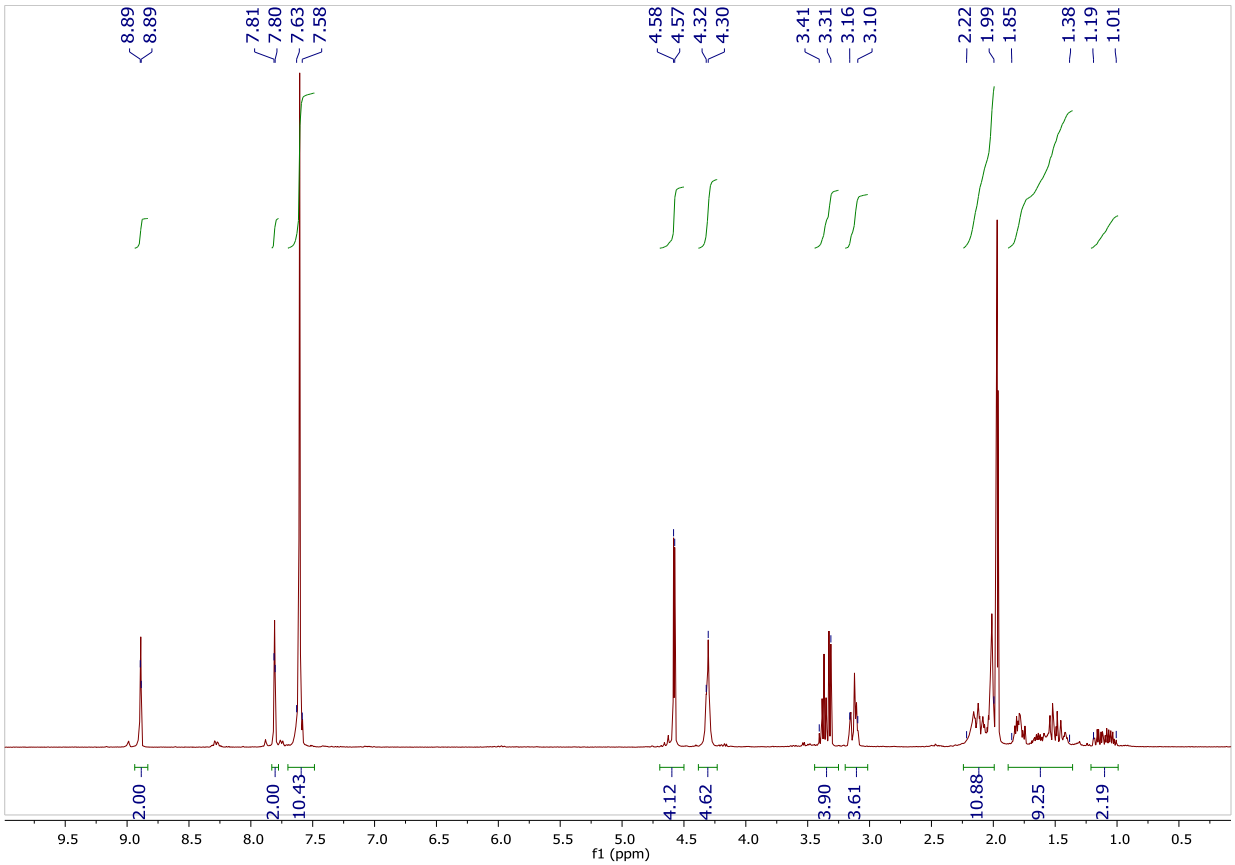

141.59
135.40
133.58
129.22
127.13
125.90
124.62
121.90
120.41
75.77
71.82
49.16
33.97
28.53
26.73
25.66
24.58
f1 (ppm)

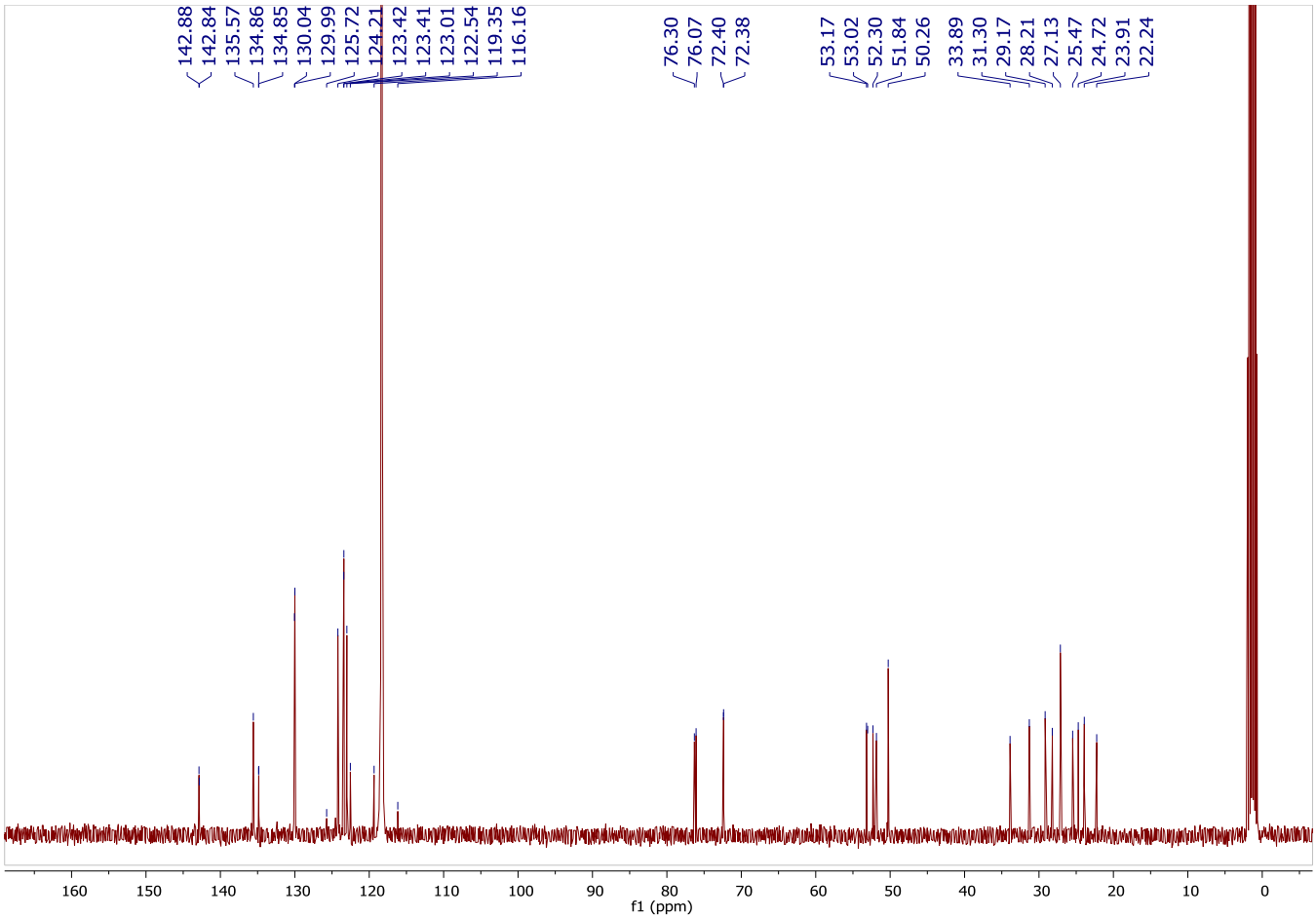
Compound **11a**



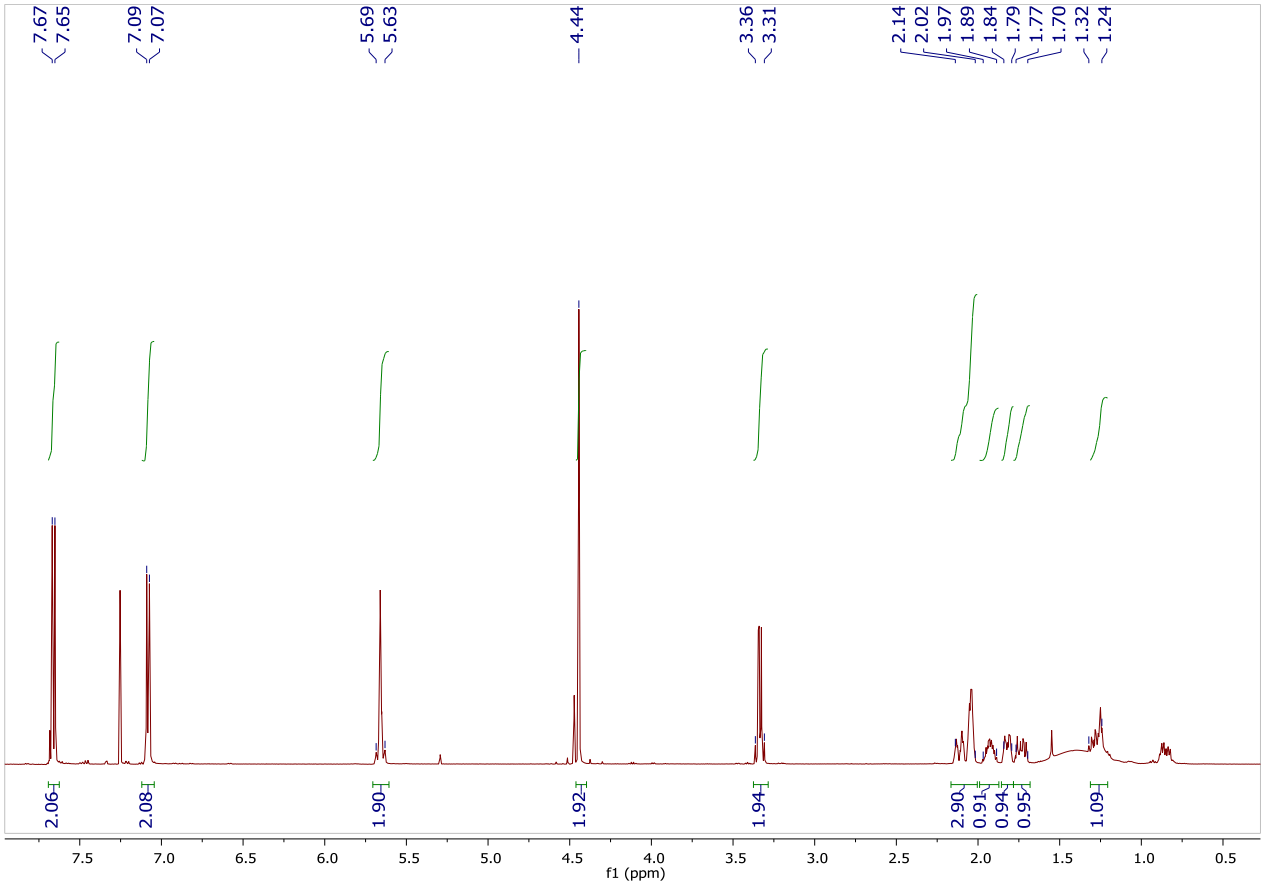


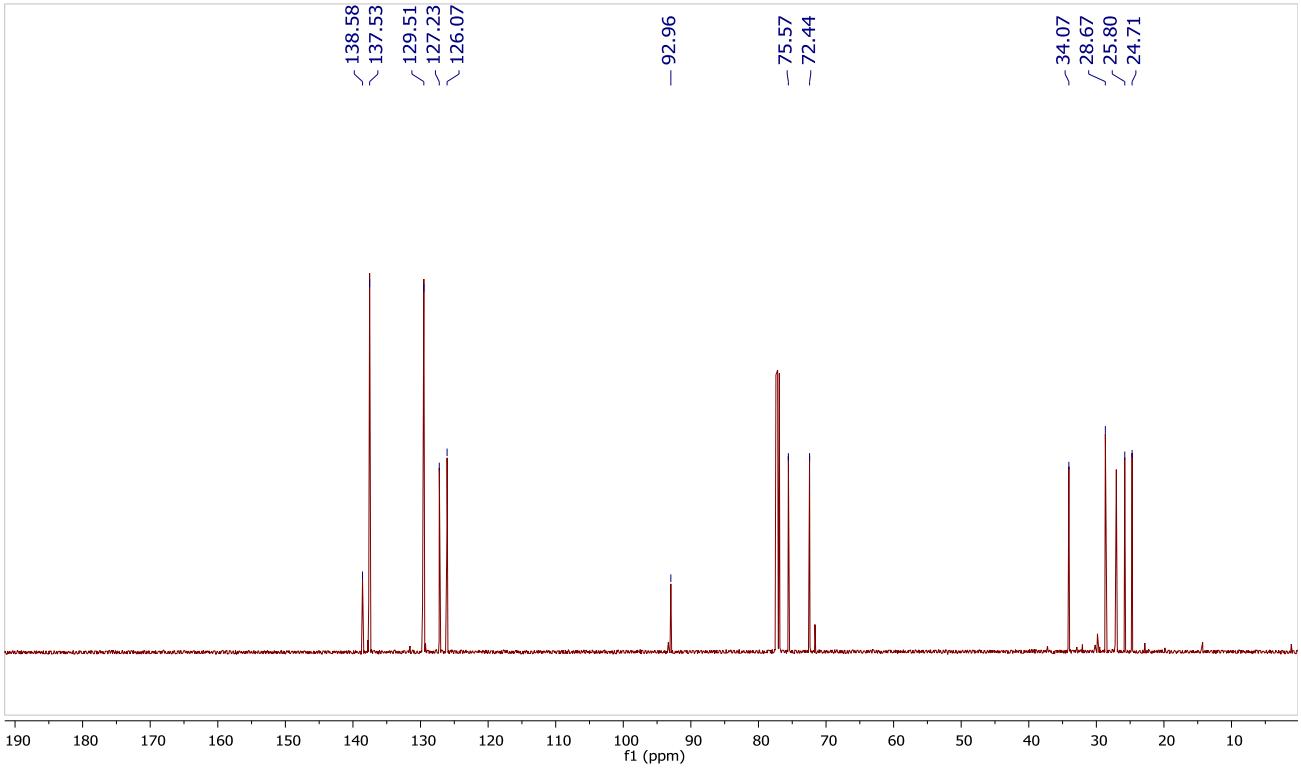
Compound **CEIL-3**





Compound **12**





VII. References

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2. Zhang, Y.; Li, L.; Nie, K.; Zheng, S. Thermomechanical, surface and shape memory properties of thermosetting blends of epoxy with Poly (ethylene oxide): An impact of POSS microdomain formation. *Materials Chemistry and Physics* **2020**, *240*, 122183.
3. Kostoryz, E. L.; Smith, R. E.; Glaros, A. G.; Chappelow, C. C.; Eick, J. D. In vitro mutagenicity and metabolism of the cycloaliphatic epoxy Cyracure™ UVR 6105. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis* **2004**, *563*, 25–34.