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

Organotin-Bridged-Ionic Liquid as a Solvent-free, Leaching-resistive Catalyst for Ring Opening Polymerization of ε-caprolactone

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Supporting Information available

1. General Procedures

All the reagents were purchased from commercial sources (Sigma-Aldrich, Accros, and Alfa Aeser). Acetonitrile and isopropanol were distilled over CaH_2 and stored under 3Å molecular sieve. CH_2Cl_2, diethyl ether and toluene were dried thanks to a MBraun MB-SPS apparatus with less than 30 ppm of water. ε-Caprolactone (Sigma-Aldrich, 99%) was purified by distillation under reduced pressure over CaH_2 and $SnCl_4$ was distillated prior to be used.

^{1}H (300 MHz), ^{13}C (75.5 MHZ), ^{19}F (282 MHz) and ^{31}P (121.5 MHz) nuclear magnetic resonance (NMR) spectra were acquired using a Bruker avance 300 MHz at 293°K, and were referenced with $CHCl_3$ (7.27 and 77.00 ppm for ^{1}H and ^{13}C, respectively) or DMSO (2.54 and 40.45 ppm for ^{1}H and ^{13}C, respectively). ^{1}H NMR coupling constants were reported in Hertz. Data were reported as follows: chemical shift (units is parts per million (ppm)), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), the coupling constants (J) were reported in Hz. IR spectra were performed on a Perkin-Elmer spectrum 100 FT-IR spectrometer. ESI-MS

data were acquired using a HCT Ultra Ion Trap mass spectrometer (BrukerDaltonics, Bremen, Germany) or using a LCT Premier XE (Waters, Manchester, UK). HRMS (Accurate mass measurements) were realized using a Synapt G2 HDMS (Waters, Manchester, UK) equipped with a lock spray electrospray (ESI) source. Experiments were achieved in positive or negative ion mode using protonated or deprotonated molecule of bombesine as internal reference (m/z 1619.8229 and 1617.8073 respectively). Elementary analyses were performed by the Service of Microanalyses of Institut de Recherche en Chimie Organique Fine of Mont-Saint-Aignan. The molecular weights and dispersity indices were determined by a liquid chromatography method using a GPC-PL (gel permeation chromatography) 50 Plus. THF was used as eluent with a flow rate of 1 mL/min at 35ºC. The molecular weights were intended with calibration relative to PMMA standards, and the error was estimated at 10%.

2. Experimental Procedures for the synthesis of catalyst 6

2.1. Synthesis of (4-chlorobutyl)tricyclohexylstannane 2

In a three-necked flask under nitrogen, a solution of 1-bromo-4-chlorobutane (0.860 mL, 7.43 mmol) in 5 mL of diethyl ether (Et_2O) was slowly added at room temperature to magnesium (196 mg, 8.17 mmol) in diethyl ether (10 mL). The mixture was heated at reflux for 30 minutes and cooled at room temperature, and a solution of triclohexyltin chloride (2 g, 4.95 mmol) in Et_2O (30 mL) was added. The resulting mixture was refluxed for 2 hours and hydrolyzed with a saturated solution of NH_4Cl, extracted with ether (100 mL), and dried with $MgSO_4$. Afterward the solvents were evaporated and the recrystallization from methanol gave the product **2**: 75% yield; mp 98 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (t, *J* = 6.5 Hz, 1H, $\underline{CH_2}$-Cl); 1.85 – 1.26 (m, 37H, 33H, Cy-Sn and 4H, Sn-CH_2 -$\underline{CH_2}$-$\underline{CH_2}$-); 0.72 – 0.67 (m, 2H, Sn-$\underline{CH_2}$-). ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.7 (C1); 37.7 (C2); 32.5 (C6), 29.4 (C7); 27.4 (C8); 26.1 (C3); 24.6 (C5); 5.8 (C4). IR (ATR-D) υmax (cm^{-1}): 2916-2845 (-CH_2); 1444 (C-H-alkyl); 800 (CH_2-Cl). Elemental analysis: Anal. Calcd for $C_{22}H_{41}ClSn$: C, 57.4; H, 8.9; N, 0. Found: C, 56.65; H, 8.91; N, 0.

2.2. Synthesis of tricyclohexyl-4-iodobutylstannane 3

To a solution of a 4-chlorobutyltricyclohexylstannane **2** (2 g, 4.35 mmol) in THF (10 mL), sodium iodide (1.95 g, 13.05 mmol) was added. The reaction mixture was stirred at 65°C for 72 hours. The solvent was removed under reduced pressure and

dichloromethane was added, the organic phase was washed twice with water, dried over $MgSO_4$, filtrated and concentrated under reduced pressure to give a tricyclohexyl-4-iodobutylstannane **3**: 73% yield; mp 98.6°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.23 (t, *J* = 6.5 Hz, 1H, $\underline{CH_2}$-Cl); 1.85 – 1.26 (m, 37H, 33H Cy-Sn and 4H Sn-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-); 0.77 – 0.71 (m, 2H, Sn-$\underline{CH_2}$-). IR (ATR-D) υmax (cm^{-1}): 2916-2845 (-CH_2); 1440 (C-H-alkyl); 550 (CH_2-I).

2.3 Synthesis of 1- methyl-(4-(tricyclohexylstannyl)butyl)-1H-imidazol-3-ium iodide 4

Tricyclohexyl-4-iodobutylstannane **3** (360 mg, 0.653 mmol) was added to a solution of 1-methyl-1H-imidazole (5 mL) then the reaction mixture was stirred at 100°C for 96 hours. Dichloromethane (10 mL) was added and the organic layer was washed twice with acidified water (0.1 N), dried over $MgSO_4$ and the solvent was evaporated under reduced pressure to give the desired compound **4**: 85% yield; mp: 89-90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.58 (s, 1H, H2); 7.40 (s, 1H, H4); 7.24 (s, 1H, H3); 4.27 (t, 2H, H5); 4.13 (s, 3H, H1); 1.85-1.13 (m, 37H, H6-7-9-10-11-12); 0.80-0.66 (m, 2H, H8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3 (C2); 123.3 (C3); 121.5 (C4); 49.7 (C5); 36.9 (C1); 35.5 (C6); 32.6 (C10); 32.4 (C11); 29.3 (C12); 26.2 (C7); 24.3 (C9), 6.0 (C8). IR (ATR-D) υmax (cm^{-1}): 3010 (NH^+ salt); 2916-2845 (CH_2); 1575 (C-N-H conjugated systems); 1444 (C-H-alkyl). HR-MS (m/z): calculated 507.2756 [M + Na]; found, 507.2760 [$M+I^-$].

2.4 Synthesis of 3-methyl-1-(4-(tricyclohexylstannyl)butyl)-1H-imidazol-3-ium hexafluorophosphate 5

To a solution of 3-methyl-1-(4-tricyclohexylstannyl)- butyl)-1H-imidazol-3-ium iodide **4** (212 mg, 0.334 mmol) in acetonitrile (6 mL), potassium hexafluorophos-phate (123 mg, 0.669 mmol) was added. The resulting mixture was stirred at 100°C for 24 hours. The solvent was evaporated under reduced pressure and the residue was dissolved in dichloromethane (10 mL) then washed twice with water. The organic phase was dried over anhydrous $MgSO_4$ and after filtration, the solvent was removed under vacuum and the ionic liquid was triturated five times with Et_2O to give the desired product **5**: 99% yield; mp: 110-120 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 1H, H2); 7.29 (s, 1H, H4); 7.23 (s, 1H, H3); 4.15 (t, *J* = 7.6 Hz, 2H, H5); 3.93 (s, 3H, H1); 2.02-1.09 (m, 37H, H6-7-9-10-11-12); 0.89-0.49 (m, 2H, H8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7 (C2); 123.7 (C3); 122 (C4); 49.7 (C5); 36.5 (C1); 35.1 (C6); 32.4 (C10); 29.4 (C11);

27.3 (C12); 26.2 (C7); 24.2 (C9); 5.9 (C8). ^{19}F NMR (282 MHz, $CDCl_3$) δ -72.4 (d, *J* = 710 Hz). ^{31}P (121 MHz, $CDCl_3$) δ -144.4 (hept, *J* = 709 Hz). IR (ATR-D) υmax (cm^{-1}): 3010 (-NH + salt); 2916-2845 ($-CH_2$); 1575 (C-N-H conjugated systems); 1444 (C-H-alkyl). LRMS (ESI-MS+): m/z 507.27 [M + Na]+. Anal. Calcd for $C_{26}H_{47}F_2N_2PSn$: C, 47.94; H, 7.27; N, 4.30. Found: C, 47.35; H, 7.23; N, 4.14. HR-MS (m/z): calculated 507.2756 [M + Na]+; found, 507.2766 [$M+PF_6^-$].

2.5 Synthesis of 3-methyl-1-(4-(trichlorostannyl)butyl)-1H-imidazol-3-ium hexafluorophosphate 6

Tin tetrachloride (90.63 mg, 0.347 mmol) was slowly added, under nitrogen, to a solution of ionic liquid tricyclohexyltin **5** (206 mg, 0.316 mmol) in 100 mL of dichloromethane/acetonitrile (5/5, v/v). After 3 hours of reaction at 35°C, the solvent was removed under reduced pressure and 100 mL of acetonitrile and 100 mL of pentane were added and the mixture was stirred for 18 hours at room temperature. The mixture was decanted and the acetonitrile solution was extracted three time with pentane (3 x 20 mL). Evaporation of acetonitrile gave the trichloride derivative **6** as yellow oil: 74% yield. ^{1}H NMR (300 MHz, CD_3CN) δ 9.08 (s, 1H, H2); 7.73 (d, *J* = 14 Hz, 2H, H3-4); 4.44 (t, *J* = 6.8 Hz, 2H, H5); 4.07 (s, 3H, H1); 2.28 (t, 2H, H8); 2.09 (t, 2H, H7); 1.93 (t, 2H, H6). ^{13}C NMR (75 MHz, CD_3CN) δ 136.9 (C2); 124.6 (C3); 123.3 (C4); 49.8 (C5); 36.9 (C8); 32.6 (C1); 30.8 (C6); 22.6 (C7). ^{19}F NMR (282 MHz, CD_3CN) δ -72.8 (d, *J* = 705 Hz). ^{31}P NMR (121 MHz, CD_3CN) δ -144.3 (hept, *J* = 704 Hz).

3. Polymerization Conditions

All experiments were carried out under argon atmosphere with standard Schlenk techniques. The monomer ε-caprolactone was weighted into a schlenk tube contain-ing a magnetic bar, and three vacuum-argon cycles were performed to remove moisture. In other schlenk the 3-methyl-1-(4-(trichlorostannyl)butyl)-1H-imidazol-3-ium hexafluorophosphate **6** was mixed in toluene with 3 equivalents of isopropanol which was used as coinitiator of the polymerization reaction. After the mixture was stirred for 30 minutes at room temperature it was added to the ε-caprolactone. The polymerization started by immersion of the schlenk into an oil bath preheated at 100°C. At the given time points, control samples (0,5 mL) were withdrawn with a long needle through a septum. The samples were then treated with technical-grade chloroform to quench the polymerization. After the treatment, all solvents were removed in vacuo, and the obtained mixture of monomer and polymer

was analyzed by ^{1}H NMR to determine the conversion. The polymer was then purified by precipitation from dichloromethane/methanol solution (1:3) and was analyzed with GPC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (t, *J* = 6.6 Hz, 2H, H1); 2.27 (t, *J* = 7.5 Hz, 2H, H5); 1.75-1.48 (m, 4H, H2-4); 1.44-1.25 (m, 2H, H3); 1.19 (d, *J* = 6.3 Hz, H8 *i*soPr). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7 (C6); 64.3 (C1); 34.3 (C5); 28.5 (C2); 25.7 (C3); 24.7 (C4); 22.0 (C8).

4. Antibacterial Study Conditions

4.1. Diffusion method

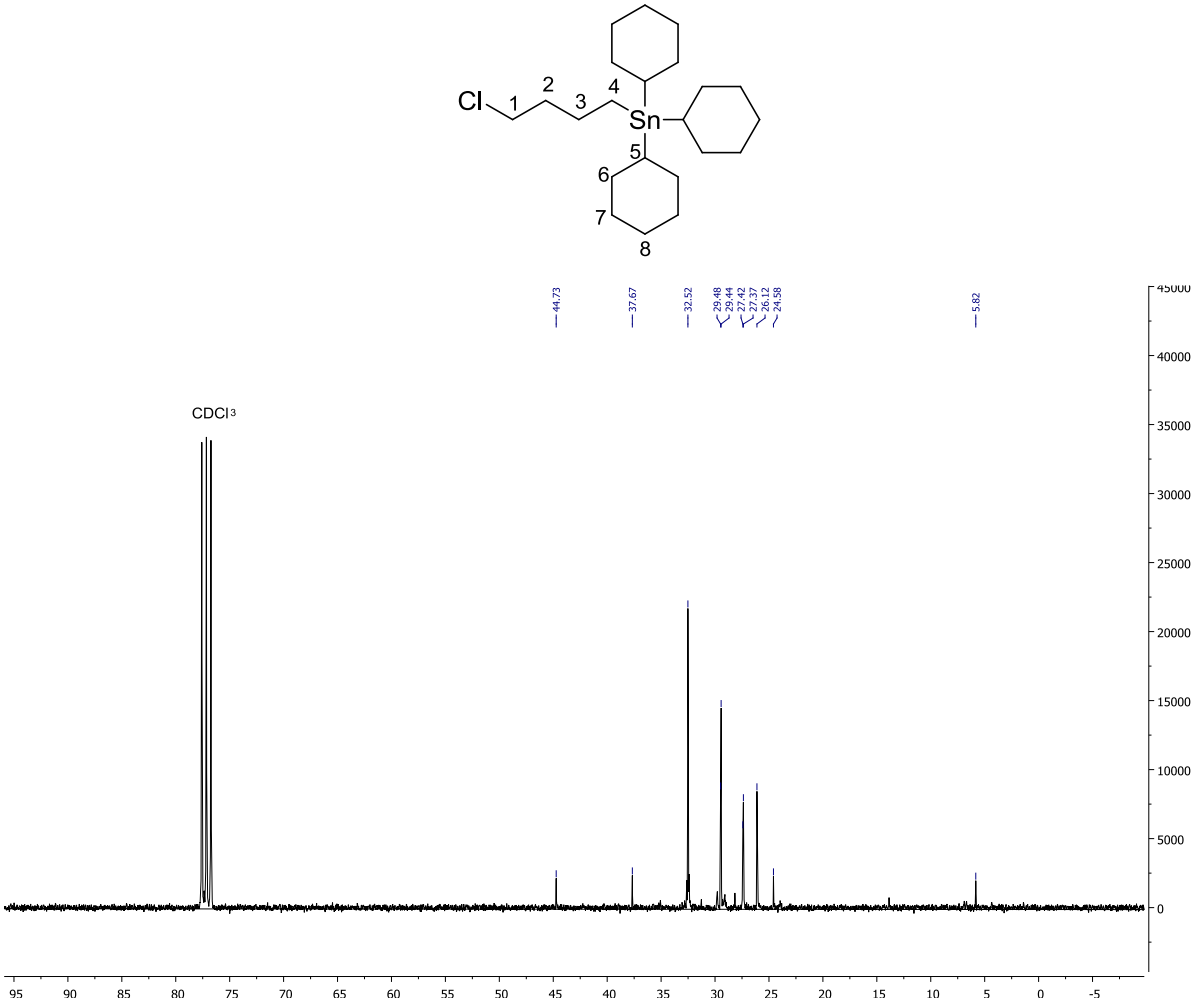
The diffusion method consists of preparing a solution of BHI-Agar (Brain Heart Infusion-Agar, 12 $g.l^{-1}$ agar) inoculated with bacterial pre-culture to obtain a final concentration of bacteria of the order of 10^6 Colony Forming Unit (CFU)/ml. The solution is then poured into petri dishes and allowed to gel at room temperature and then the polymer films / pellets are put to the center of each box. After a first incubation at 5°C for 2 hours to allow pre-diffusion, the petri dishes are incubated at 37°C for 24 hours. For each test, the diameter of the inhibition zone is measured.

4.2. Antibacterial activity in solution

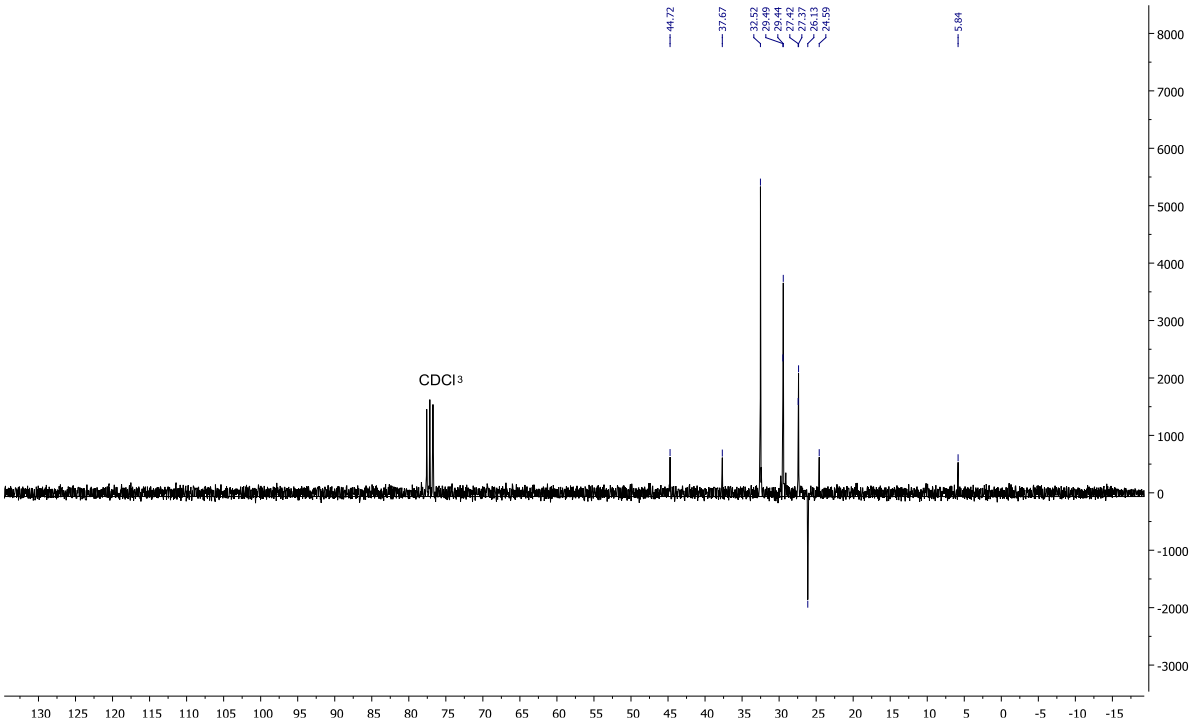
After preculture for 18 hours at 37°C in Brain Heart Infusion (BHI) broth, bacteria were harvested by centrifugation (2,683 x g for 15 minutes) and resuspended in a PBS solution (pH 7.4) to reach an optical density (OD) of about 1 corresponding to a bacterial concentration of 10^7 CFU/ml. The two catalysts were then placed in a solution containing BHI and the bacterial suspension (for a final bacterial concentration of approximately 10^5 CFU/ml, OD of 0.01). Two concentrations were studied (10^{-3} and 10^{-8}M). After 24 hours of incubation at 37°C, the bacterial growth was visualized by the broth turbidity for each solution.

5. Routine NMR analysis

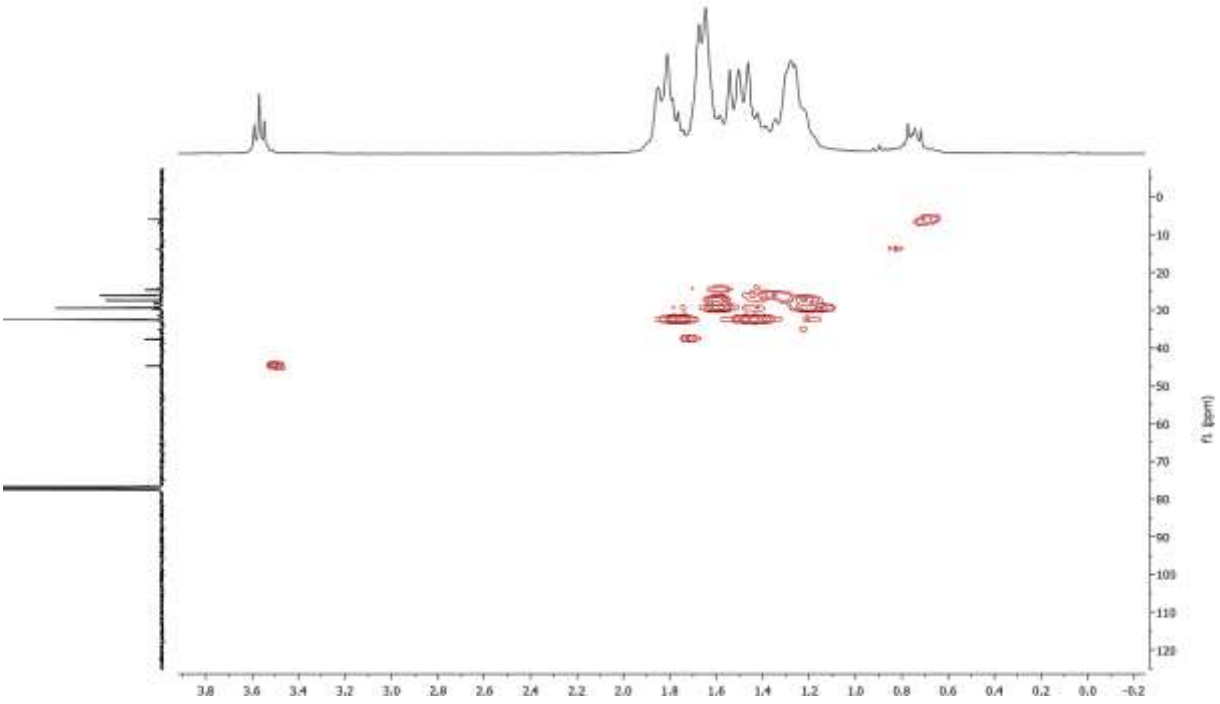
5.1. NMR Spectra of (4-chlorobutyl)tricyclohexylstannane 2



^{13}C NMR spectrum (in d_6-$CDCl_3$) of **2**

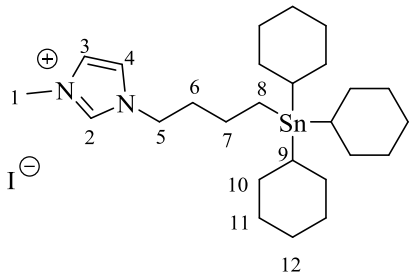


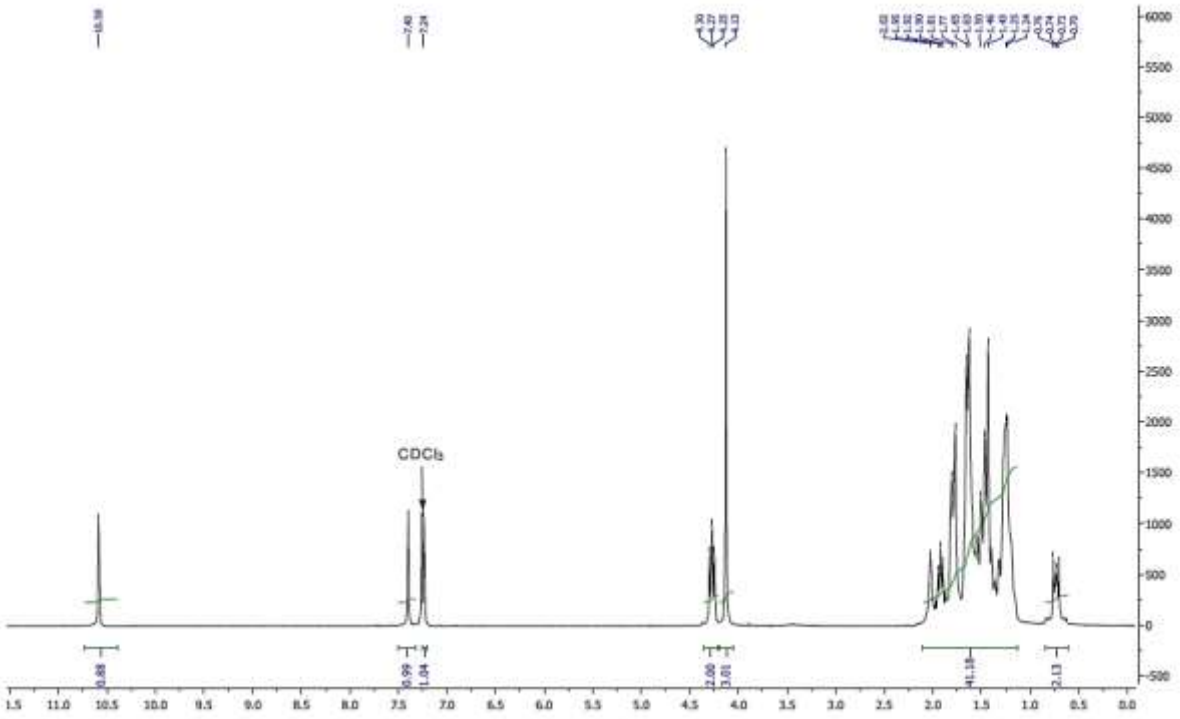
^{13}C NMR spectrum (in d_6-$CDCl_3$) of **2**



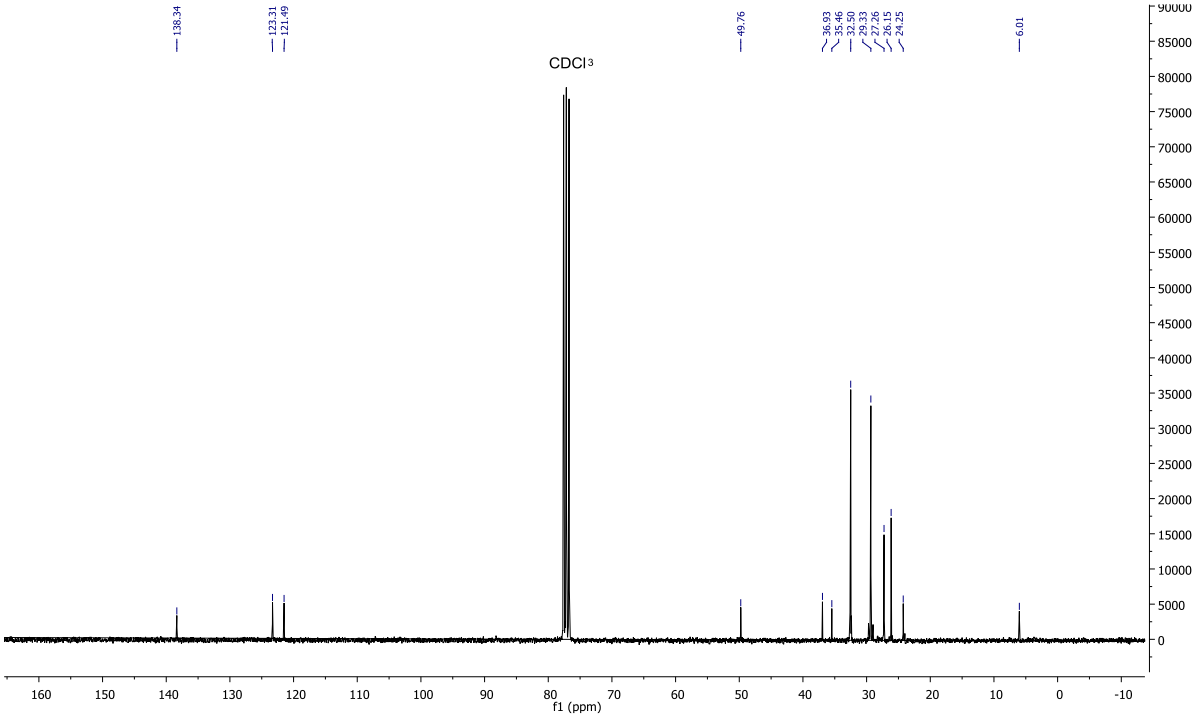
^{1}H-^{13}C HSQC NMR spectrum (in d_6-$CDCl_3$) of **2**

5.2. NMR Spectra of 3-methyl-1-(4-(tricyclohexylstannyl)butyl)-1H-imidazol-3-ium iodide 4

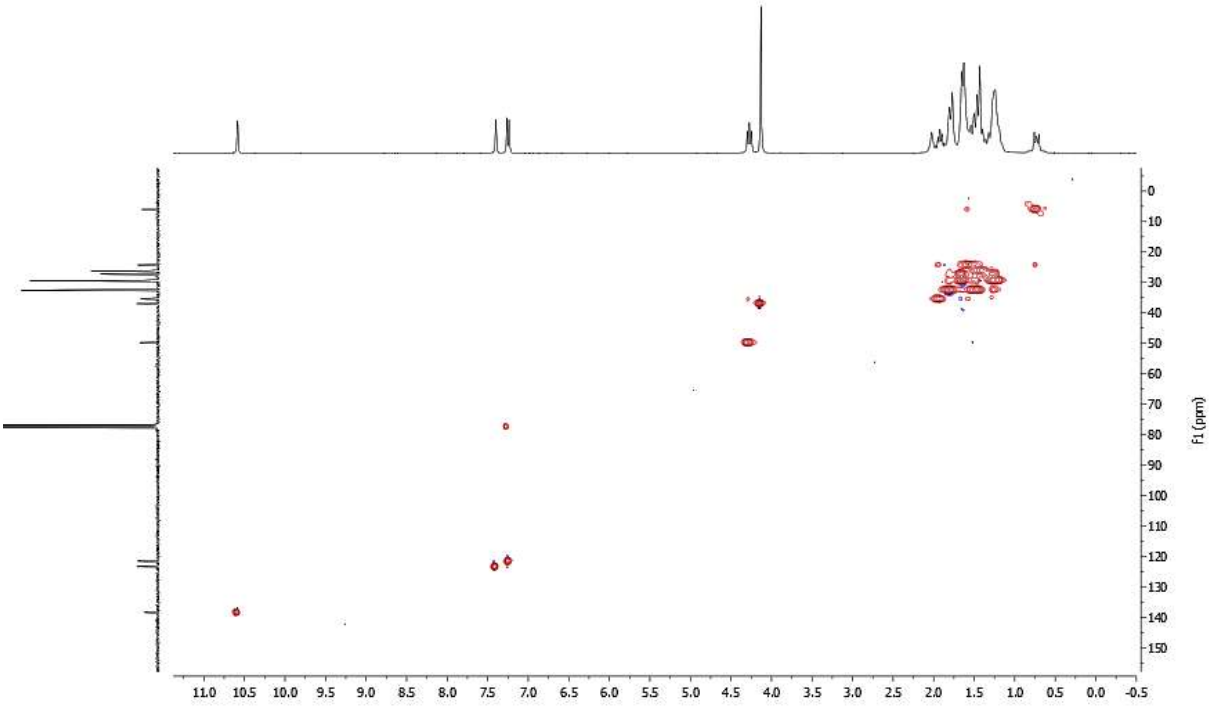




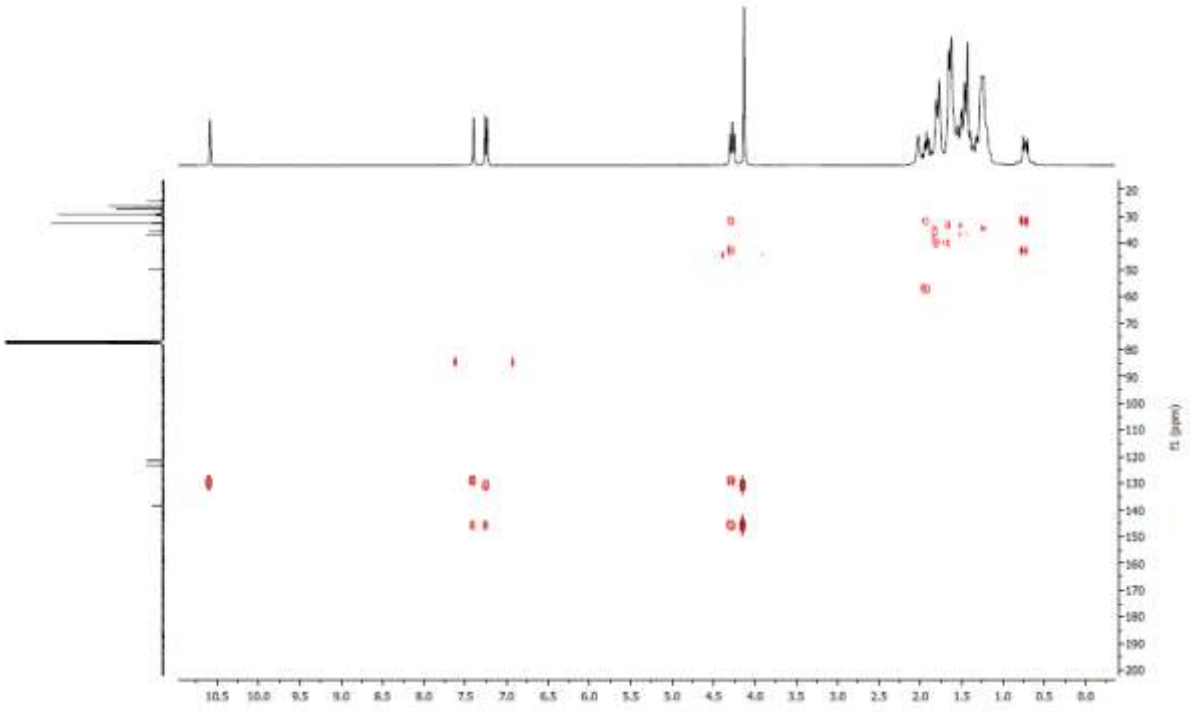
^{1}H NMR spectrum (in d_6-$CDCl_3$) of **4**



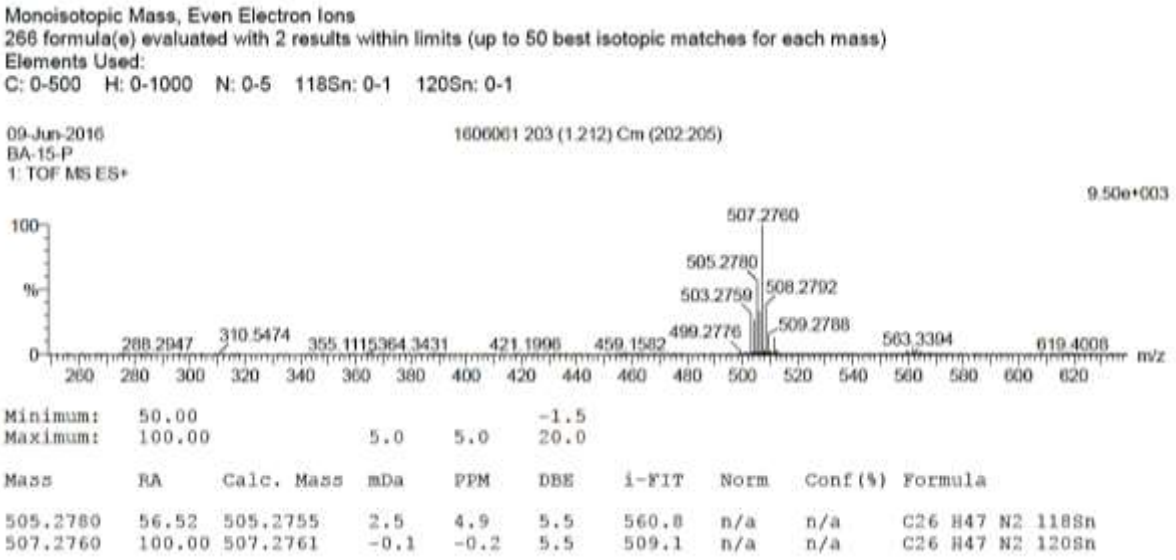
^{13}C NMR spectrum (in d_6-$CDCl_3$) of **4**



^{1}H- ^{13}C HSQC NMR spectrum (in d_6-$CDCl_3$) of **4**

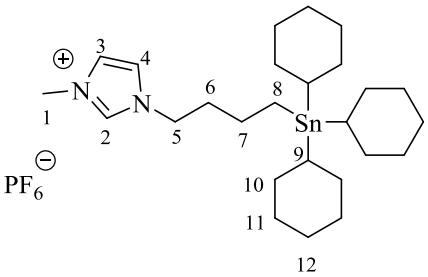


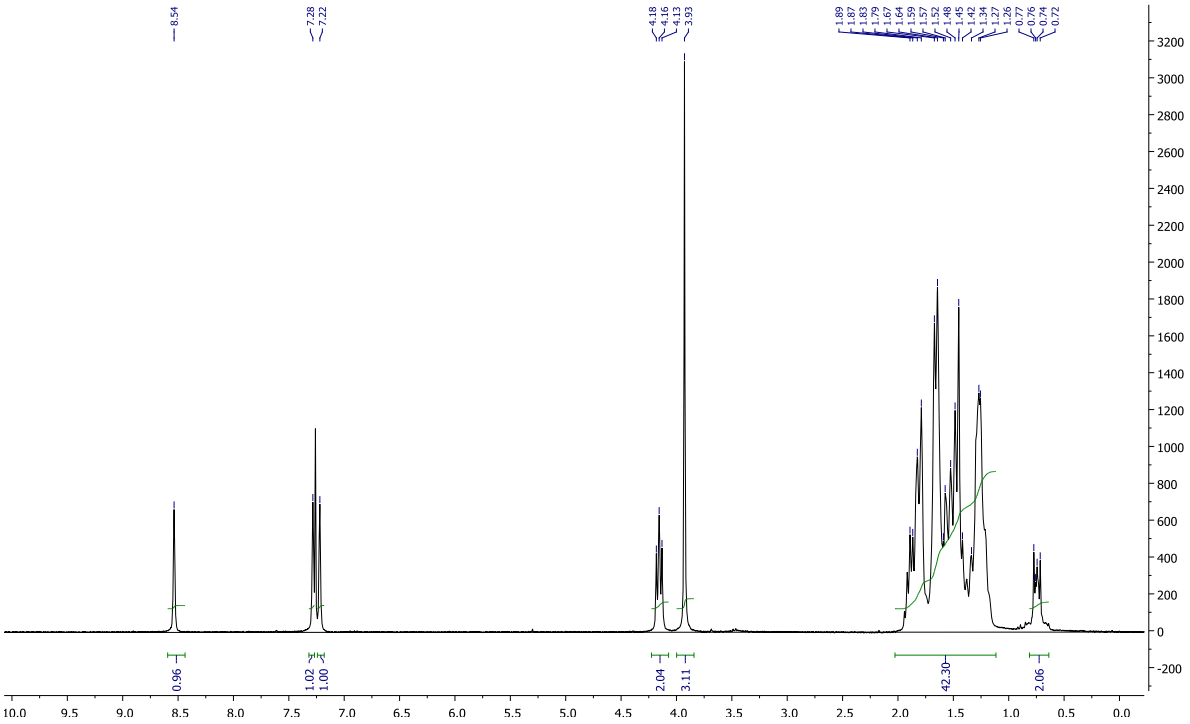
^{1}H-^{13}C HMBC NMR spectrum (in d_6-$CDCl_3$) of **4**



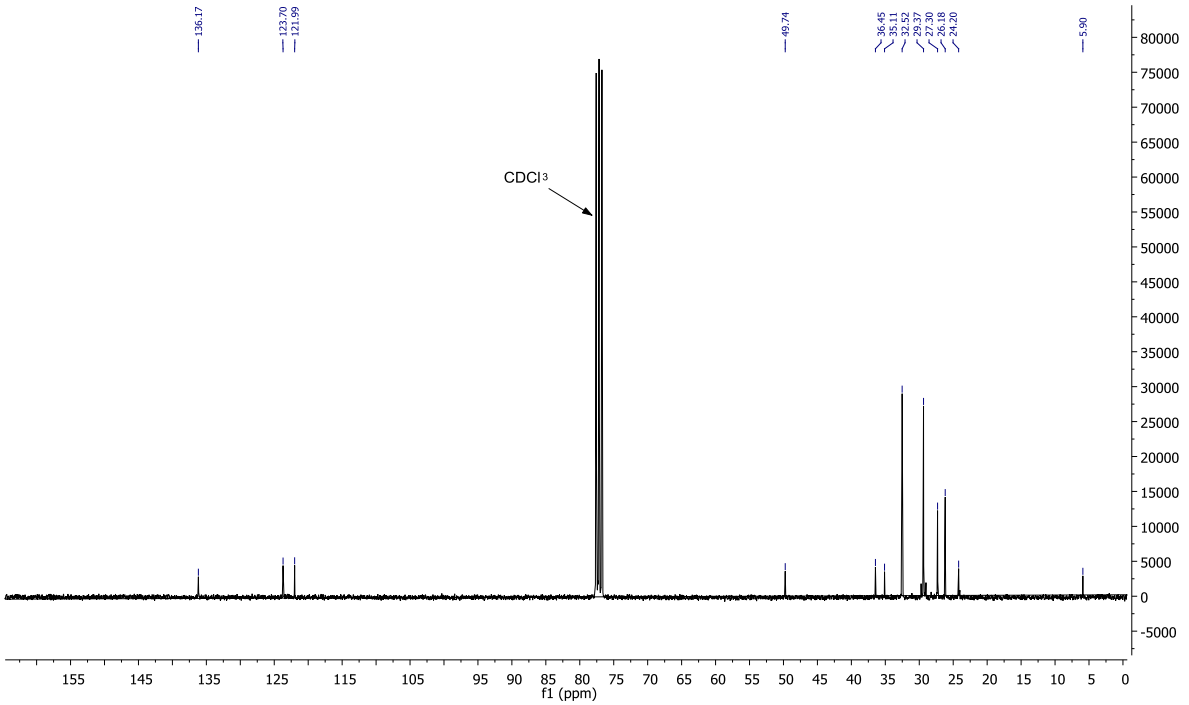
Mass Spectrometry Analysis of **4**

5.3. NMR Spectra of 3-methyl-1-(4-(tricyclohexylstannyl)butyl)-1H-imidazol-3-ium hexafluorophosphate 5

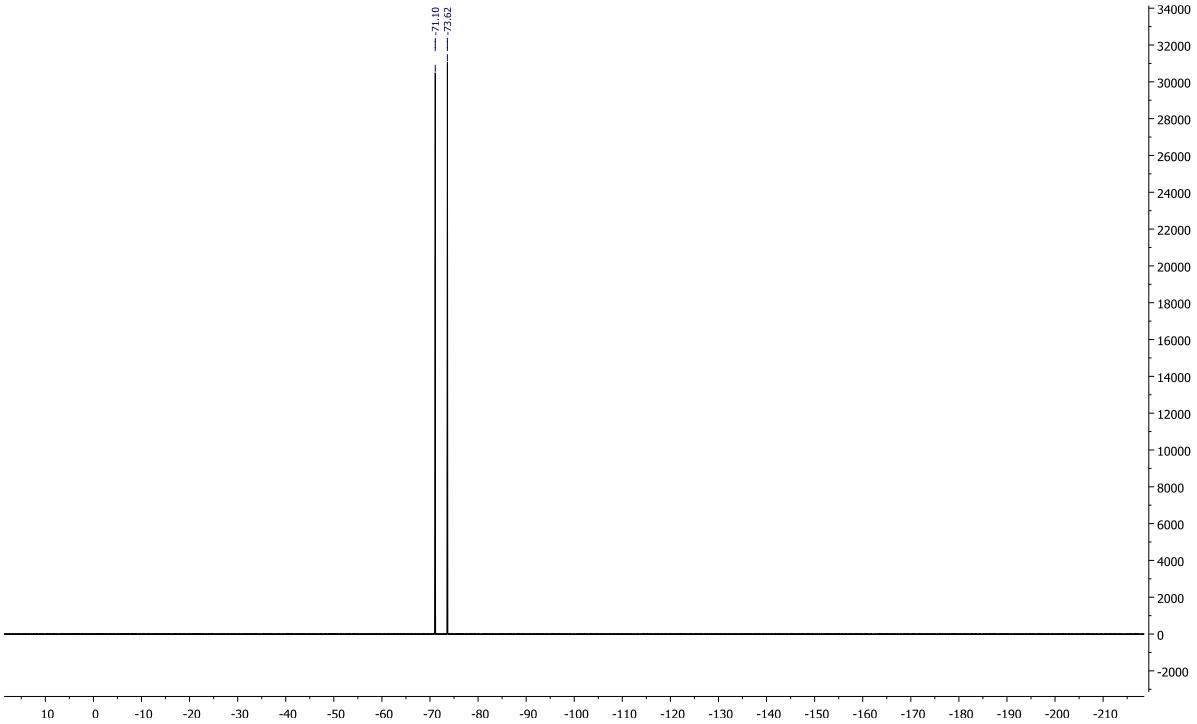




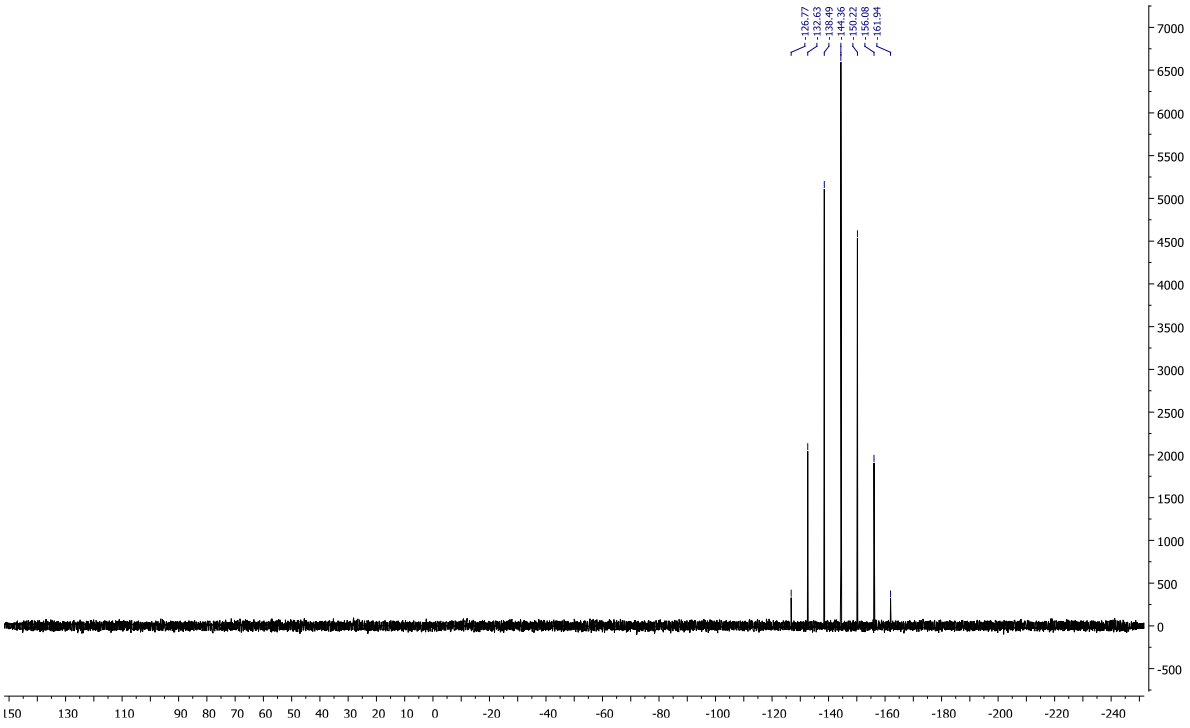
^{1}H NMR spectrum (in d_6-$CDCl_3$) of **5**



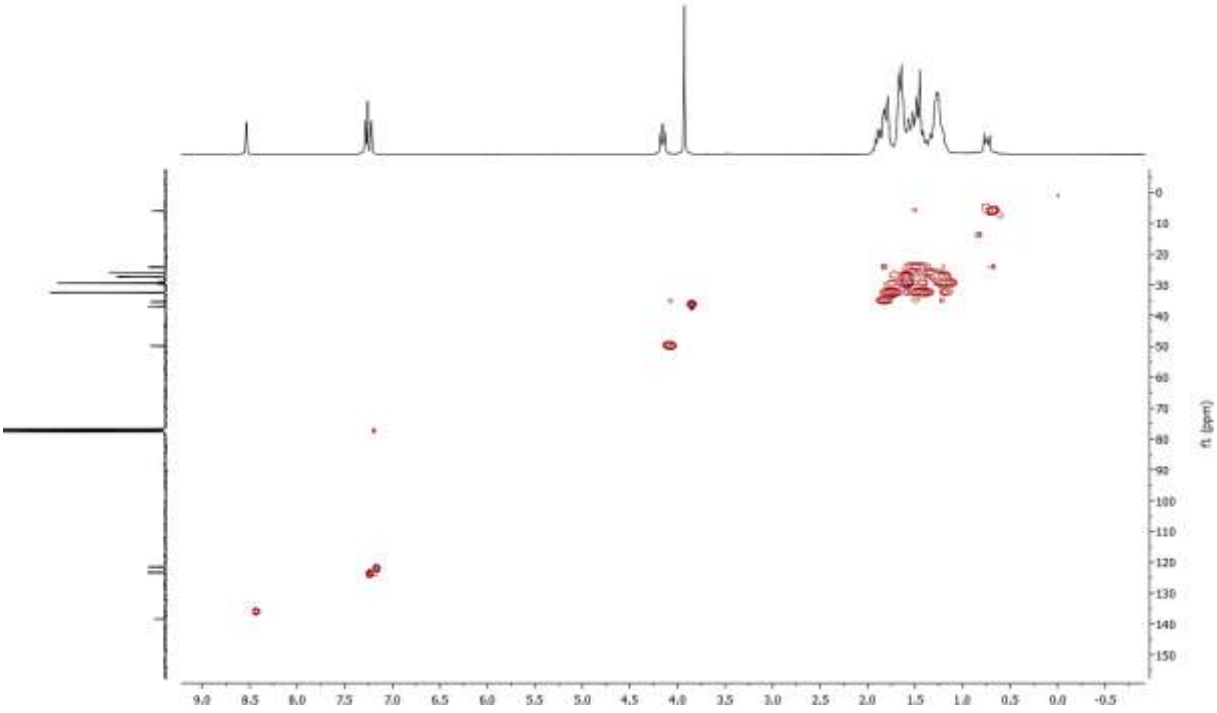
^{13}C NMR spectrum (in d_6-$CDCl_3$) of **5**



^{19}F NMR spectrum (in d_6-$CDCl_3$) of **5**

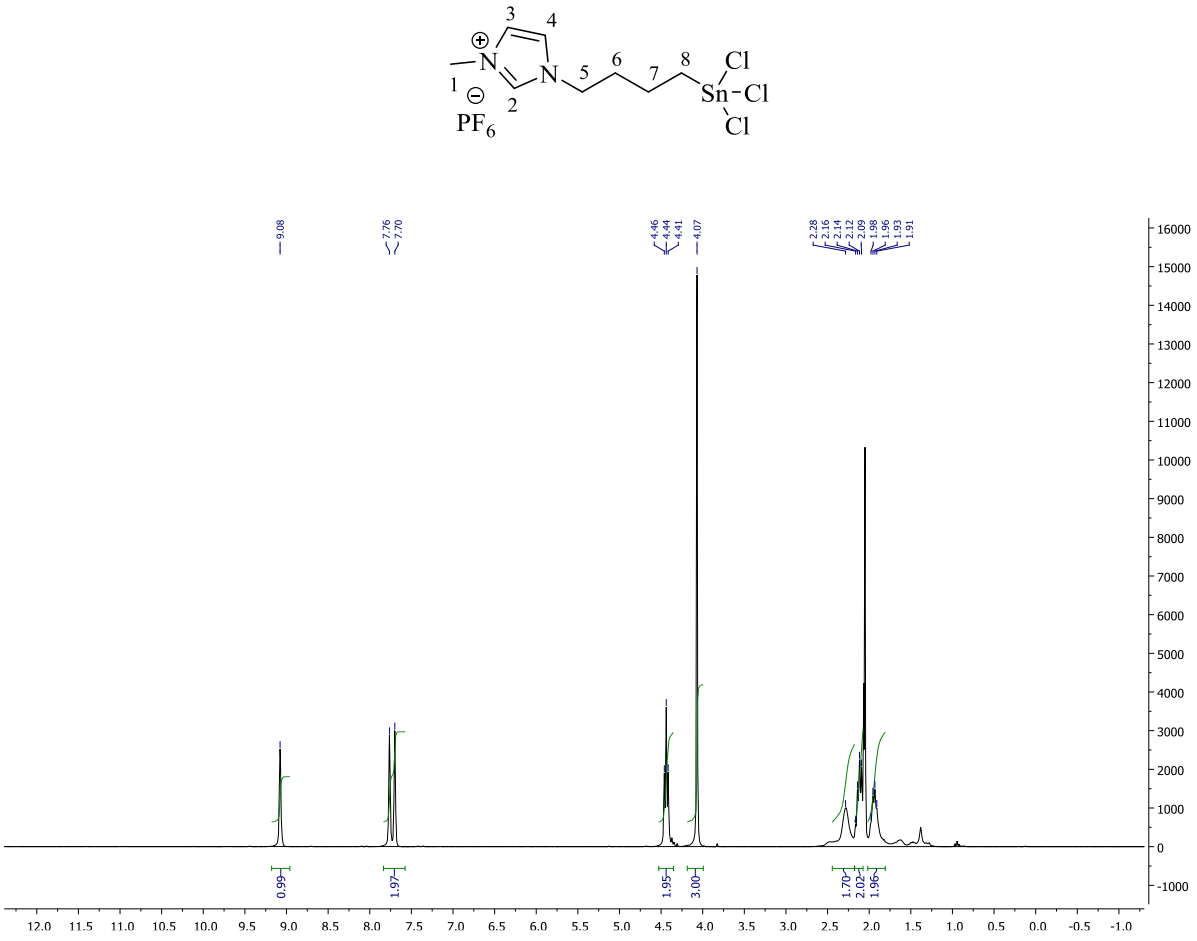


^{31}P NMR spectrum (in d_6-$CDCl_3$) of **5**

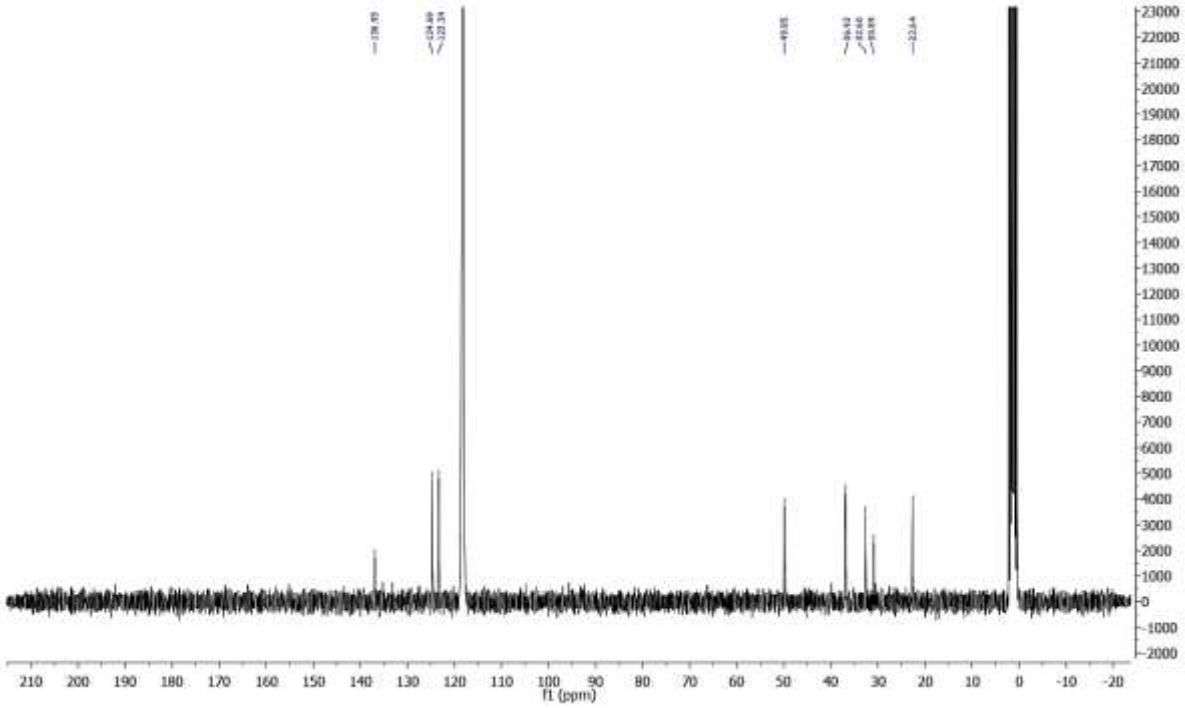


^{1}H-^{13}C HSQC NMR spectrum (in d_6-$CDCl_3$) of **5**

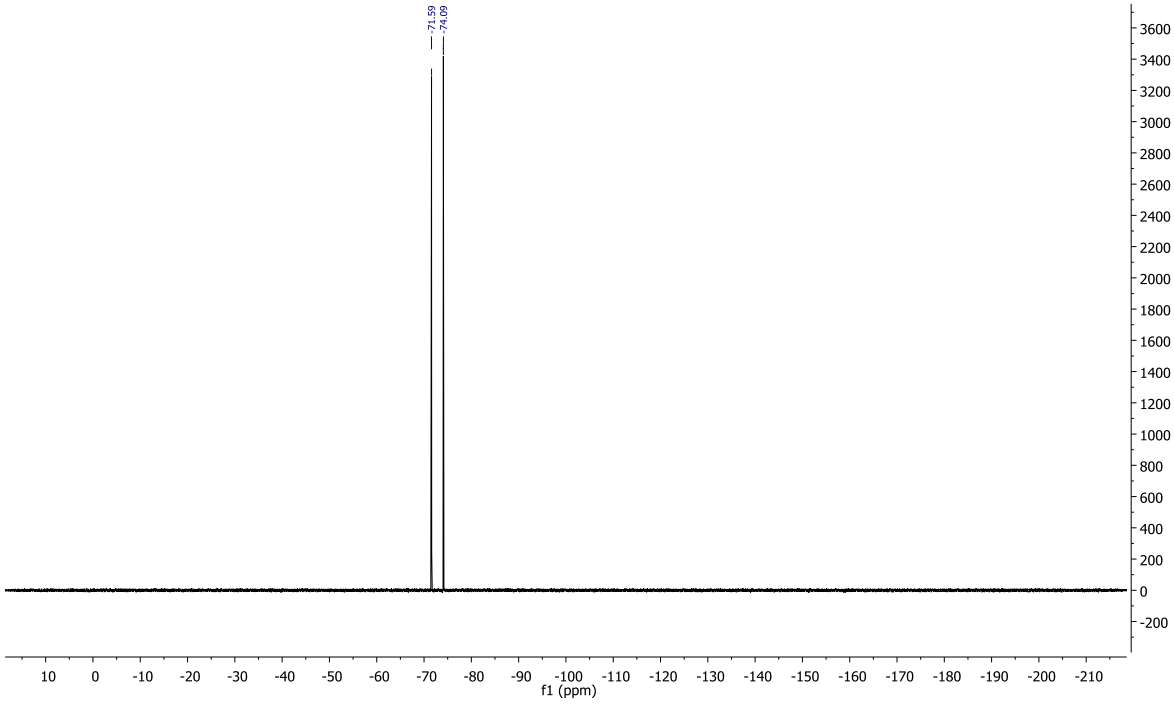
5.4. NMR Spectra of 3-methyl-1-(4-(trichlorostannyl)butyl)-1H-imidazol-3-ium hexafluorophosphate 6



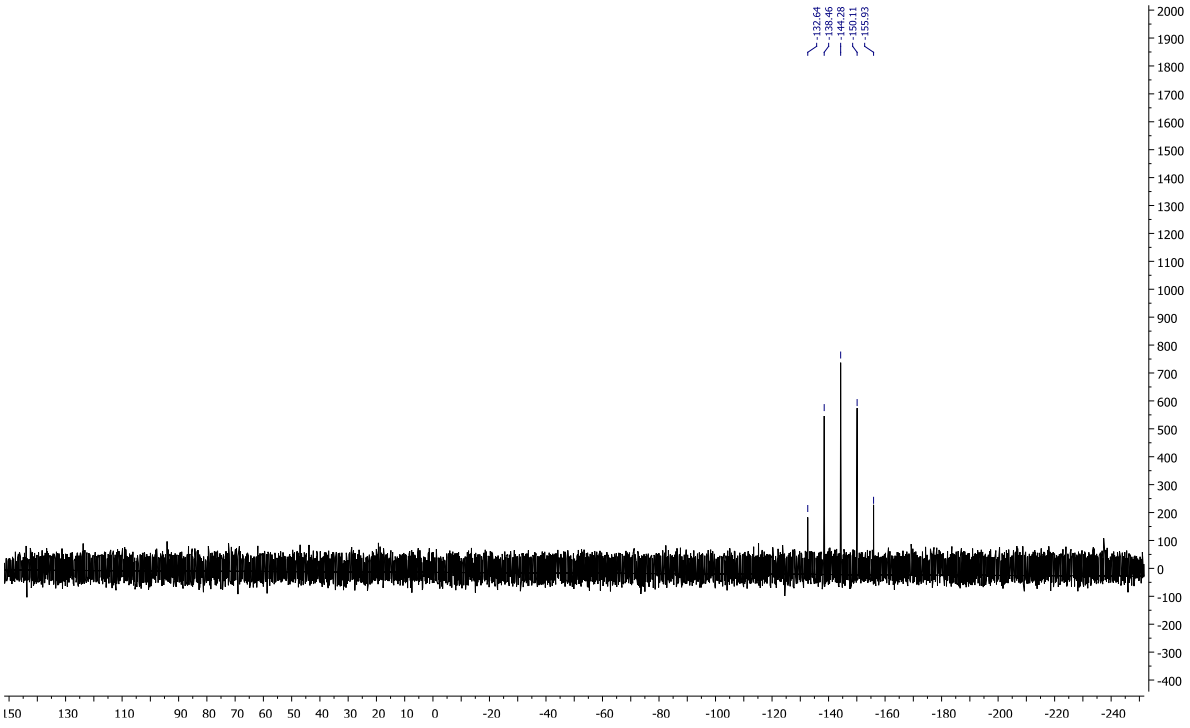
^{1}H NMR spectrum (in d_6-CD_3CN) of **6**



^{13}C NMR spectrum (in d_6-CD_3CN) of **6**

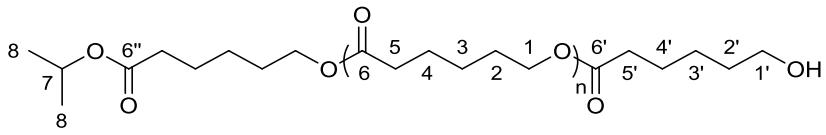


^{19}F NMR spectrum (in d_6-CD_3CN) of **6**

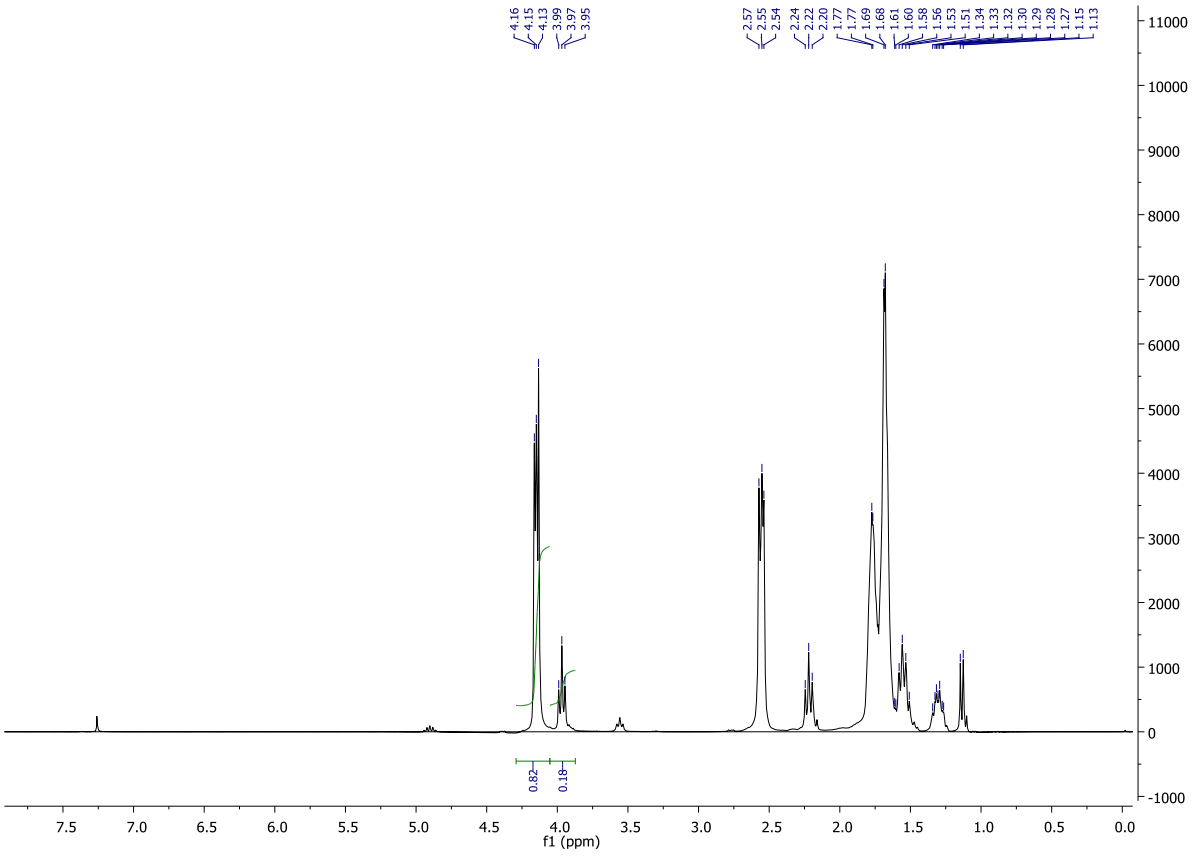


^{31}P NMR spectrum (in d_6-CD_3CN) of **6**

5.5 NMR Spectra of ^{1}H NMR spectra of poly(ε-caprolactone)



^{1}H NMR spectrum (in d_6-$CDCl_3$) of poly(**ε**-caprolactone)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4.15
4.13
3.99
3.97
3.95
2.57
2.55
2.54
2.24
2.22
2.20
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1.77
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1.68
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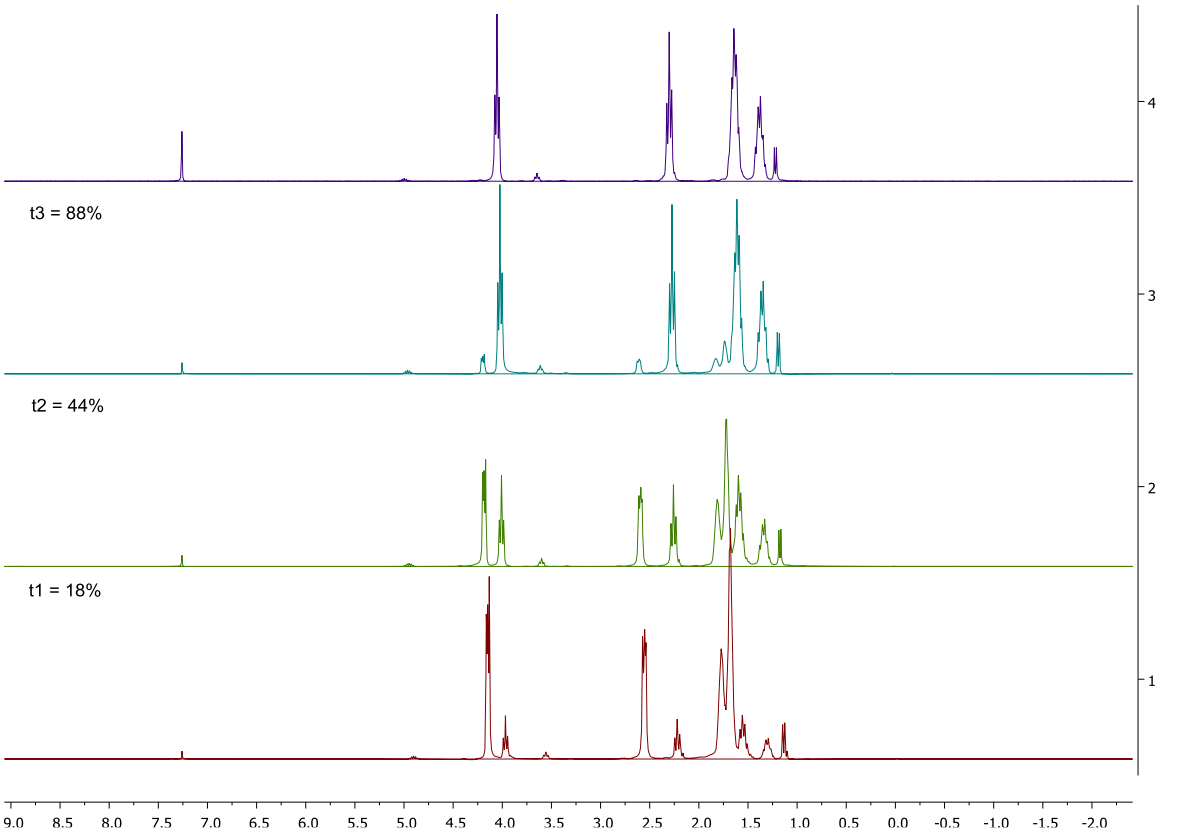
1.60
1.58
1.56
1.53
1.51
1.34
1.33
1.32
1.30
1.29
1.28
1.27
1.15
1.13
0.82
0.18
f1 (ppm)


t3 = 88%
t2 = 44%
t1 = 18%