

Electronic Supplementary Information for

Task Specific Ionic Liquids and Ultrasounds Irradiation: A Successful Strategy to Drive the Alcoholysis of Polycarbonate

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Task specific ionic Liquids Characterization

Page S4-S6

Table S1. Conversion and Yields values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of tetramethylguanidinium-based TSILs ($n_c/n_{RU} = 1/12$).

Page S6

Table S2. Conversion and Yields values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, for 120 minutes, in the presence of imidazolate-based TSILs ($n_c/n_{RU} = 1/12$; $m_{2-MeTHF}/m_{MeOH} = 3$).

Page S7

Table S3. Conversion and Yields values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, for 120 minutes, in the presence of [TMG⁺]-, [C₁C₂OHPyrr⁺]- and [C₁C₂OHMor⁺]-based TSILs ($n_c/n_{RU} = 1/12$; $m_{2-MeTHF}/m_{MeOH} = 3$).

Page S7

Table S4. Hammett basicity function (H) determined for TSILs, using *p*-nitrophenol as probe.

Page S8

Table S5. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [TMG][Im] and [C₁C₂OHMor][Im] ($n_c/n_{RU} = 1/12$; $m_{2-MeTHF}/m_{MeOH} = 3$), at different reaction times.

Page S8

Table S6. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [C₁C₂OHMor][Im] ($m_{2-MeTHF}/m_{MeOH} = 3$), at different n_c/n_{RU} ratios.

Page S8

Table S7. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W;

Page S9

250 kHz), at 30 °C, in the presence of [C₁C₂OHMor][Im] (n_c/n_{RU} = 1/12;), at different m_{2-MeTHF}/m_{MeOH} ratios.

Page S9

Table S8. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [C₁C₂OHMor][Im] (n_c/n_{RU} = 1/12; m_{2-MeTHF}/m_{MeOH} = 3), at different temperatures.

Page S9

Table S9. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of different catalysts (n_c/n_{RU} = 1/12; m_{2-MeTHF}/m_{MeOH} = 3).

Page S10

Table S10. Chemical shift values of imidazolate anion in [C₁C₂OHPIP][Im] and [C₁C₂OHMor][Im] and corresponding mixture in the presence of MeOH (n_{MeOH}/n_c = 4.2).

Page S10

Table S11. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of different nucleophiles (n_c/n_{RU} = 1/12; m_{2-MeTHF}/m_{MeOH} = 3).

Page S11

Table S12. Evaluation of methanolysis of BPA-PC, according to the holistic approach to Green Chemistry, performed using different catalysts, under under US irradiation (50 W; 250 kHz), at 30 °C, (n_c/n_{RU} = 1/12; m_{2-MeTHF}/m_{MeOH} = 3). Colors account for: red:< 70%; yellow: 70-89%; green: > 89%.

Page S11

Table S13. IC₅₀ values obtained after 48h of treatment with [TMG][Im], [C₁C₂OHMor][Im] and [C₂₂₂C₂OH][Im] in HB2 and hTERT RPE-1epithelial normal cell lines.

Page S11

Table S14. Conversion and yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [C₁C₂OHMor][Im] (n_c/n_{RU} = 1/12; m_{2-MeTHF}/m_{MeOH} = 3), as a function of sample nature.

Page S12-S13

Figure S1. ¹H NMR spectra of: a) [C₁C₂OHPIP][Im]; b) [C₁C₂OHPIP][Im] in the presence of methanol (n_{MeOH}/n_c = 4.2); c) [C₁C₂OHMor][Im]; d) [C₁C₂OHPIP][Im] in the presence of methanol (n_{MeOH}/n_c = 4.2).

Page S14

Figure S2. ¹H NMR spectra of [C₁C₂OHMor][Im] after sonication (top) and after reaction (bottom).

Figure S3. ^1H NMR, ^{13}C NMR and IR spectra of BPA obtained from methanolysis of PC from CD.

Page S15-S16

Figure S4. ^1H NMR, ^{13}C NMR spectra of catalysts.

Page S16-S34

Experimental Section

Task specific ionic Liquids Characterization

Tetramethylguanidinium imidazolate [TMG][Im]

Yellow oil. Yield: 90%. ¹H NMR, (300 MHz, CDCl₃) δ = 2.76 (s, 12H); 7.08 (s, 1H); 7.28 (s, 1H); 7.67 (s, 1H) ppm. ¹³C NMR, (300 MHz, CDCl₃) δ = 39.3, 121.9, 135.2, 167.5 ppm.

Tetramethylguanidinium succinimide [TMG][Succ]

Yellow oil. Yield: 92%. ¹H NMR (300 MHz, D₂O) δ = 2.51 (s, 4 H); 2.84 (s, 12 H) ppm. ¹³C NMR (300 MHz, D₂O) δ = 29.4, 30.1, 31.4, 32.6, 39.0, 161.2, 178.9, 181.0 ppm.

Tetramethylguanidinium Lysinate [TMG][Lys]

Yellow solid. Yield: 87%. ¹H NMR, (300 MHz, D₂O) δ = 1.27 (m, 2H), 1.51 (m, 4H), 2.80 (s, 1H), 2.84 (s, 12 H), 3.19 (t, 1H, J=6Hz) ppm. ¹³C NMR, (300 MHz, D₂O) δ = 21.89, 27.49, 33.26, 38.82, 39.42, 55.51, 161.63, 182.16 ppm.

Tetramethylguanidinium Glycinate [TMG][Gly]

Yellow solid. Yield: 73%. ¹H NMR (300 MHz, D₂O) δ = 2.80 (s, 12H); 2.90 (s, 2H); 3.22 (s, 2H); 3.67 (s, 2H) ppm.

N-methyl-N-(2-hydroxyethyl)pyrrolidinium Bromide

Colorless oil. Yield: 78%. ¹H NMR (300 MHz, DMSO) δ = 2.07 (s, 4H), 3.04 (s, 3H), 3.44 (t, 2H, J=3 Hz), 3.52 (m, 4H), 3.82 (s, 2H), 5.29 (m, 1H) ppm.

N-methyl-N-(2-hydroxyethyl)piperidinium Bromide

Colorless oil. Yields: 82%. ¹H NMR (300 MHz, D₂O) δ = 1.50 (s, 2H), 1.72 (s, 4H), 2.98 (s, 3H), 3.26 (m, 4H), 3.37 (m, 2H) 3.90 (s, 2H) ppm.

N,N,N-triethyl-(2-hydroxyethyl)ammonium Bromide

White solid. Yield: 61%. ¹H NMR, (300 MHz, DMSO) δ = 1.20 (m, 9H), 3.31 (m, 8H), 3.77 (m, 2H), 5.26 (t, 1H, J=6Hz) ppm.

N-methyl-N-(2-hydroxyethyl)morpholinium Bromide

Colorless oil. Yield: 83%. ¹H NMR, (300 MHz, D₂O) δ = 3.24 (s, 3H), 3.35 (s, 1H), 3.49 (m, 3H), 3.62 (m, 2H), 3.86 (m, 2H), 3.93 (m, 3H), 5.32 (t, 1H, J=6Hz) ppm.

N-methyl-N-(2-hydroxyethyl)imidazolium Bromide

Orange solid. Yield: 94%. ¹H NMR, (300 MHz, DMSO) δ= 3.71(s, 2H), 3.87 (s, 3H), 4.23 (s, 2H), 5.17 (s, 1H), 7.74 (d, 2H), 9.18 (s, 1H) ppm.

N,N-bis(2-hydroxyethyl)1,4-diazabicyclo[2.2.2]octane Bromide

White solid. Yield: 84% ¹H NMR, (300 MHz, DMSO) δ= 3.66 (m, 4H), 3.89 (s, 4H), 4.02 (s, 12H) ppm.

N-methyl-N-ethylmorpholinium Iodide

Colorless solid. Yield: 85% ¹H NMR, (300 MHz, DMSO) δ= 1.25 (t, 3H, J= 6 Hz), 3.10 (s, 3H), 3.39 (m, 4H), 3.50 (m, 2H), 3.91 (m, 4H) ppm. ¹³C (400 MHz, DMSO) δ= 7.2, 46.0, 58.9, 59.8, 60.3 ppm.

N-methyl-N-(2-hydroxy)ethylpyrrolidinium Imidazolate [C₁C₂OHPyrr][Im]

Yellow oil. Yield: 72% ¹H NMR, (300 MHz, DMSO) δ= 2.06 (s, 3H), 3.04 (s, 2H), 3.40 (t, 2H, J=6Hz), 3.51 (d, 3H, J=6Hz), 3.84 (s, 2H), 5.16 (s, 3H), 6.74 (s, 2H), 7.21 (s, 1H) ppm. ¹³C NMR, (300 MHz, DMSO) δ = 21.3, 48.3, 55.4, 64.6, 65.5, 124.1, 140.7 ppm.

N-methyl-N-(2-hydroxy)ethylpyrrolidinium Succinimide [C₁C₂OHPyrr][Im]

Yellow oil. Quantitative yield. ¹H NMR, (300 MHz, D₂O) δ= 2.17 (s, 4H), 2.41 (s, 1H), 2.67 (s, 3H), 2.90 (s, 1H), 3.00 (s, 3H), 3.50 (m, 5H) 3.98 (s, 2H) ppm. ¹³C NMR, (300 MHz, D₂O) δ = 21.3, 30.4, 48.28, 55.7, 64.5, 65.1, 175.9, 182.1 ppm.

N-methyl-N-(2-hydroxyethyl)-piperidinium Imidazolate [C₁C₂OHPIP][Im]

Yellow oil. Quantitative yield. ¹H NMR, (300 MHz, DMSO) δ= 1.52 (m, 2H), 1.78 (m, 4H), 3.09 (s, 3H), 3.35 (quint., 2H), 3.41 (m, 4H) 3.85 (s, 2H), 6.76 (s, 2H) 7.24 (s, 1H) ppm. ¹³C NMR (300 MHz, DMSO) δ=19.8, 21.0, 49.12, 54.35, 61.24, 64.89, 124.16, 140.7 ppm.

N-methyl-N-(2-hydroxyethyl)-morpholinium Imidazolate [C₁C₂OHMor][Im]

Yellow oil. Quantitative yield. ¹H NMR, (300 MHz, DMSO) δ=3.22 (s, 3H), 3.46 (m, 2H), 3.57 (m, 4H), 3.91 (s, 6H), 5.93 (s, 1H), 6.80 (s, 2H), 7.31 (s, 1H) ppm. ¹³C NMR, (300 MHz, DMSO) δ = 48.3, 54.5, 60.2, 60.3, 65.3, 124.5, 140.7 ppm.

N-methyl-N-(2-hydroxyethyl)-morpholinium succinimide [C₁C₂OHMor][Succ]

Colorless oil. Quantitative yield. ¹H NMR, (300 MHz, CD₃OD) δ= 1.69 (s, 2H), 1.93 (s, 1H), 2.56 (s, 3H), 2.78 (m, 2H), 2.92 (m, 3H), 3.28 (m, 5H), 4.13 (s, 3H). ¹³C NMR, (300 MHz, DMSO) δ= 30.1, 33.4, 34.5, 48.2, 54.9, 60.3, 176.3, 180.9 ppm.

N-methyl-N-(2-hydroxyethyl)-morpholinium phosphate [C_1C_2OHMor]₃[PO_4]

Colorless oil. Quantitative yield. ¹H NMR, (300 MHz, CD₃OD) δ = 3.18 (s, 9H), 3.40 (m, 6H), 3.53 (m, 12H), 3.86 (s, 18H) ppm. ¹³C NMR, (300 MHz, DMSO) δ = 47.8, 54.6, 59.9, 60.3, 65.5 ppm.

Triethyl-(2-hydroxyethyl)-ammonium imidazolate [$C_{22}C_2OHN$][Im]

Yellow oil. Quantitative yield. ¹H NMR, (300 MHz, CD₃OD) δ = 1.33 (t, 9H, J₁=7 Hz), 3.44 (m, 5H), 3.96 (m, 2H), 5.02 (s, 3H), 7.06 (s, 2H), 7.69 (s, 1H) ppm. ¹³C NMR, (300 MHz, DMSO) δ = 12.5, 57.9, 59.2, 63.6, 128.5, 144.7 ppm.

N-methyl-N-ethylmorpholinium imidazolate [C_1C_2Mor][Im]

Orange oil. Quantitative yield. ¹H NMR, (300 MHz, DMSO) δ = 1.22 (s, 3H), 3.09 (s, 3H), 3.38 (s, 4H), 3.50 (q, 2H), 3.88 (s, 4H), 6.45 (s, 1H), 6.82 (s, 1H), 7.34 (s, 1H) ppm. ¹³C NMR, (300 MHz, DMSO) δ = 7.3, 45.2, 58.8, 59.7, 60.2, 123.6, 139.4 ppm.

1-ethyl-3-methylimidazolium chloride [C_1C_2Im][Cl]

Colorless oil. Yield: 99% ¹H NMR, (300 MHz, DMSO) δ = 1.40 (t, 3H, J=7 Hz), 3.87 (s, 3H), 4.21 (m, 2H), 7.79 (s, 1H), 7.89 (s, 1H), 9.51 (s, 1H) ppm. ¹³C NMR, (300 MHz, DMSO) δ = 20.4, 40.9, 49.3, 127.2, 128.8, 141.6 ppm.

1-methyl-3-(2-hydroxyethyl)imidazolium chloride [C_1C_2OHIm][Cl]

Yellow oil. Yield: 88%. ¹H NMR, (300 MHz, DMSO) δ = 3.71 (t, 2H, J₁=5 Hz), 3.88 (s, 3H), 4.25 (t, 2H, J₁=5 Hz), 7.74 (s, 1H), 7.78 (s, 1H), 9.32 (s, 1H exch.) ppm. ¹³C NMR, (300 MHz, DMSO) δ = 36.1, 52.0, 59.7, 123.1, 123.7, 137.4 ppm.

Table S1. Conversion and Yields values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of tetramethylguanidinium-based TSILs ($n_c/n_{RU} = 1/12$). Conversion and yield values were reproducible within ± 3%.

TSIL	m2-MeTHF/mMeOH	Reaction Time (min)	Conversion (%)	Yield (%)
[TMG][Im]	3	105	72	57
	3	120	85	81
	3	135	84	78

Table S2. Conversion and Yields values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, for 120 minutes, in the presence of imidazolate-based TSILs ($n_c/n_{RU} = 1/12$; $m_{2-MeTHF}/m_{MeOH} = 3$). Conversion and yield values were reproducible within $\pm 3\%$.

TSIL	Conversion (%)	Yield (%)
[TMG][Im]	85	81
[C ₁ C ₂ OH _{Pip}][Im]	75	67
[C ₁ C ₂ OH _{Pyrr}][Im]	74	71
[C ₁ C ₂ OH _{Mor}][Im]	86	82
[C ₂₂₂ C ₂ OH _N][Im]	79	77
[(C ₂ OH) ₂ DABCO][Im] ₂	59	52
[Ch][Im]	83	78

Table S3. Conversion and Yields values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, for 120 minutes, in the presence of [TMG⁺]-, [C₁C₂OH_{Pyrr}⁺]- and [C₁C₂OH_{Mor}⁺]-based TSILs ($n_c/n_{RU} = 1/12$; $m_{2-MeTHF}/m_{MeOH} = 3$). Conversion and yield values were reproducible within $\pm 3\%$.

TSIL	Conversion (%)	Yield (%)
[TMG][Im]	85	81
[TMG][Succ]	38	38
[TMG][Lys]	8	8
[TMG][Gly]	0	0
[C ₁ C ₂ OH _{Pyrr}][Im]	74	71
[C ₁ C ₂ OH _{Pyrr}][Succ]	59	44
[C ₁ C ₂ OH _{Mor}][Im]	86	82
[C ₁ C ₂ OH _{Mor}][Succ]	40	32
[C ₁ C ₂ OH _{Mor}] ₃ [PO ₄]	67	67

Table S4. Hammett basicity function (H -) determined for TSILs, using *p*-nitrophenol as probe.

TSIL	H -
[TMG][Gly]	10.53
[TMG][Lys]	10.76
[TMG][Succ]	11.44
[TMG][Im]	10.85
[C1C2OHPyrr][Succ]	10.51
[C1C2OHPyrr][Im]	11.51
[C1C2OHMor][Succ]	10.33
[C1C2OHMor] ₃ [PO ₄]	10.60
[C1C2OHMor][Im]	10.76

Table S5. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [TMG][Im] and [C₁C₂OHMor][Im] ($n_c/n_{ru} = 1/12$; $m_{2-MeTHF}/m_{MeOH} = 3$), at different reaction times. Conversion and yield values were reproducible within $\pm 3\%$.

Reaction Time (min)	[TMG][Im]		[C ₁ C ₂ OHMor][Im]	
	Conversion (%)	Yield (%)	Conversion (%)	Yield (%)
80			68	68
90			88	82
105	72	57	85	84
120	85	81	86	82
135	84	78		

Table S6. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [C₁C₂OHMor][Im] ($m_{2-MeTHF}/m_{MeOH} = 3$), at different n_c/n_{ru} ratios. Conversion and yield values were reproducible within $\pm 3\%$.

n_c/n_{ru}	Conversion (%)	Yield (%)
1/6	88	87
1/12	86	82
1/18	74	74

Table S7. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [C₁C₂OHMor][Im] (n_c/n_{RU} = 1/12;), at different m₂-MeTHF/m_{MeOH} ratios. Conversion and yield values were reproducible within ± 3%.

m ₂ -MeTHF/m _{MeOH}	Conversion (%)	Yield (%)
5/3	69	63
6/2	88	82
7/1	62	62

Table S8. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [C₁C₂OHMor][Im] (n_c/n_{RU} = 1/12; m₂-MeTHF/m_{MeOH} = 3), at different temperatures. Conversion and yield values were reproducible within ± 3%.

T (°C)	Conversion (%)	Yield (%)
20	78	78
30	88	82
40	78	72

Table S9. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of different catalysts (n_c/n_{RU} = 1/12; m₂-MeTHF/m_{MeOH} = 3). Conversion and yield values were reproducible within ± 3%.

Catalyst	Conversion (%)	Yield (%)
[C ₁ C ₂ OHIm]Cl	63	63
[C ₁ C ₂ Im]Cl	0	0
[C ₁ C ₂ OHMor][Im]	88	82
[C ₁ C ₂ Mor][Im]	83	77
[C ₁ C ₂ OHpip][Im]	82	66

Table S10. Chemical shift values of imidazolate anion in [C₁C₂OHPIP][Im] and [C₁C₂OHMor][Im] and corresponding mixture in the presence of MeOH ($n_{\text{MeOH}}/n_c = 4.2$).

	[C ₁ C ₂ OHPIP][Im]	[C ₁ C ₂ OHPIP][Im] + MeOH	MeOH
δ (ppm)	7.24	7.46	
Imidazolate anion	6.76	6.89	
δ (ppm) MeOH		4.14	4.01
	[C ₁ C ₂ OHMor][Im]	[C ₁ C ₂ OHMor][Im] + MeOH	MeOH
δ (ppm)	7.31	7.41	
Imidazolate anion	6.80	6.86	
δ (ppm) MeOH		4.10	4.01

Table S11. Conversion and Yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of different nucleophiles ($n_c/n_{\text{RU}} = 1/12$; $m_{2\text{-MeTHF}}/m_{\text{MeOH}} = 3$). Conversion and yield values were reproducible within $\pm 3\%$.

Nucleophile	Conversion (%)	Yield (%)
MeOH	88	82
EtOH	52	52
PrOH	75	73
<i>i</i> -PrOH	48	38
BuOH	43	43
EG	42	33

Table S12. Evaluation of methanolysis of BPA-PC, according to the holistic approach to Green Chemistry, performed using different catalysts, under under US irradiation (50 W; 250 kHz), at 30 °C, ($n_c/n_{RU} = 1/12$; $m_{2-MeTHF}/m_{MeOH} = 3$). Colors account for: red: < 70%; yellow: 70-89%; green: > 89%.

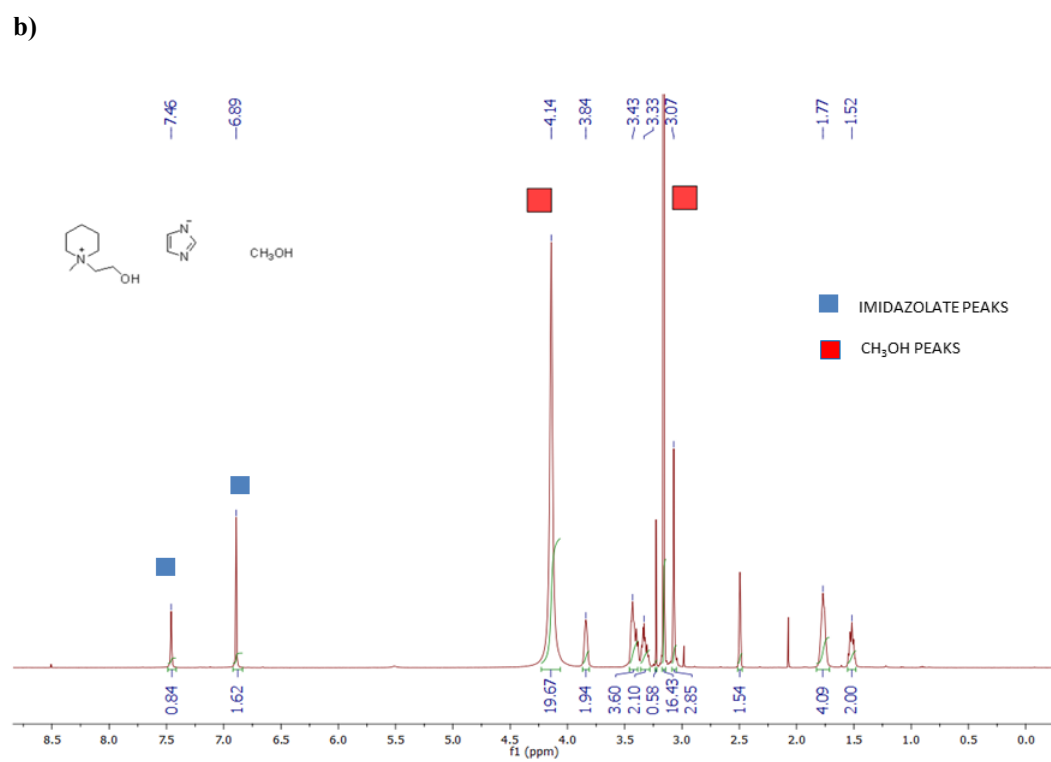
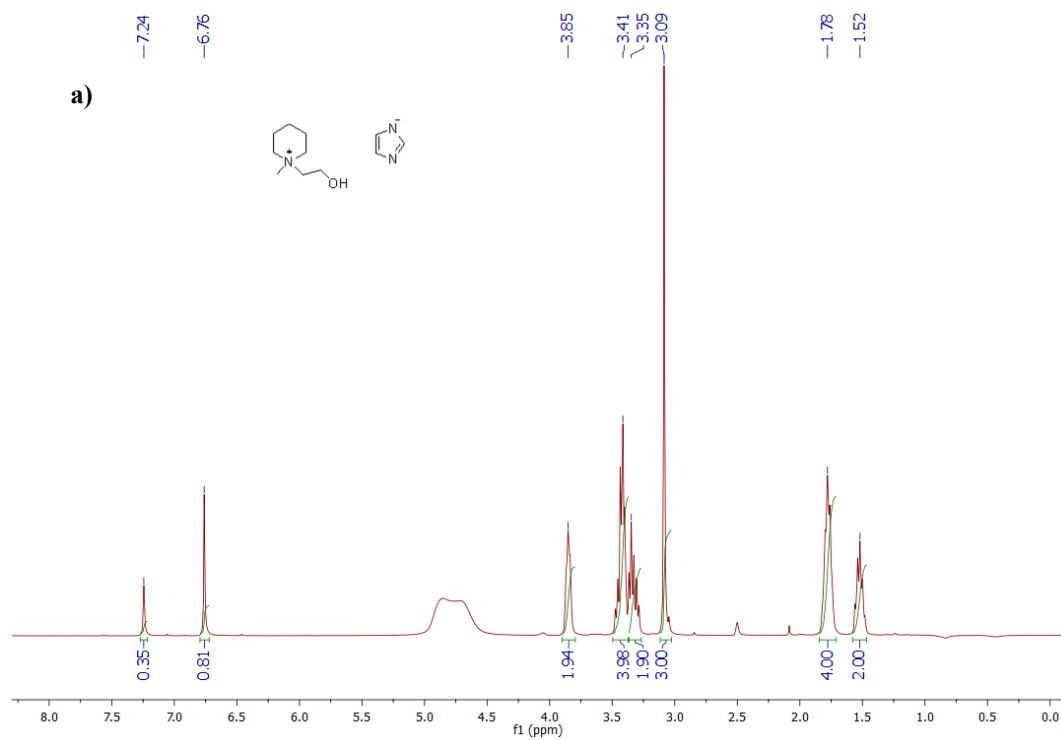
Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
[TMG][Im]			
[TMG][Succ]			
[C ₁ C ₂ OHPyr][Im]			
[C ₁ C ₂ OHPyr][Succ]			
[C ₁ C ₂ OHPip][Im]			
[(C ₂ OH) ₂ DABCO][Im] ₂			
[C ₂₂₂ C ₂ OHN][Im]			
[C ₁ C ₂ OHMor][Im]			
[C ₁ C ₂ OHMor][Succ]			
[C ₁ C ₂ OHMor] ₃ [PO ₄]			

Table S13. IC₅₀ values obtained after 48h of treatment with [TMG][Im], [C₁C₂OHMor][Im] and [C₂₂₂C₂OH][Im] in HB2 and hTERT RPE-1 epithelial normal cell lines.

Catalyst	HB2 (mM)	hTERT-RPE-1 (mM)
[TMG][Im]	2.83 ± 0.19	2.52 ± 0.27
[C ₁ C ₂ OHMor][Im]	0.97 ± 0.14	0.84 ± 0.04
[C ₂₂₂ C ₂ OHN][Im]	1.15 ± 0.07	0.90 ± 0.03

Table S14. Conversion and yield values for the methanolysis of BPA-PC, under US irradiation (50 W; 250 kHz), at 30 °C, in the presence of [C₁C₂OHMor][Im] ($n_c/n_{RU} = 1/12$; $m_{2-MeTHF}/m_{MeOH} = 3$), as a function of sample nature. Conversion and yield values were reproducible within ± 3%.

Sample	Conversion (%)	Yield (%)
Digital CD	90	70
BPA-PC sheet	94	83
BPA-PC grains	86	82



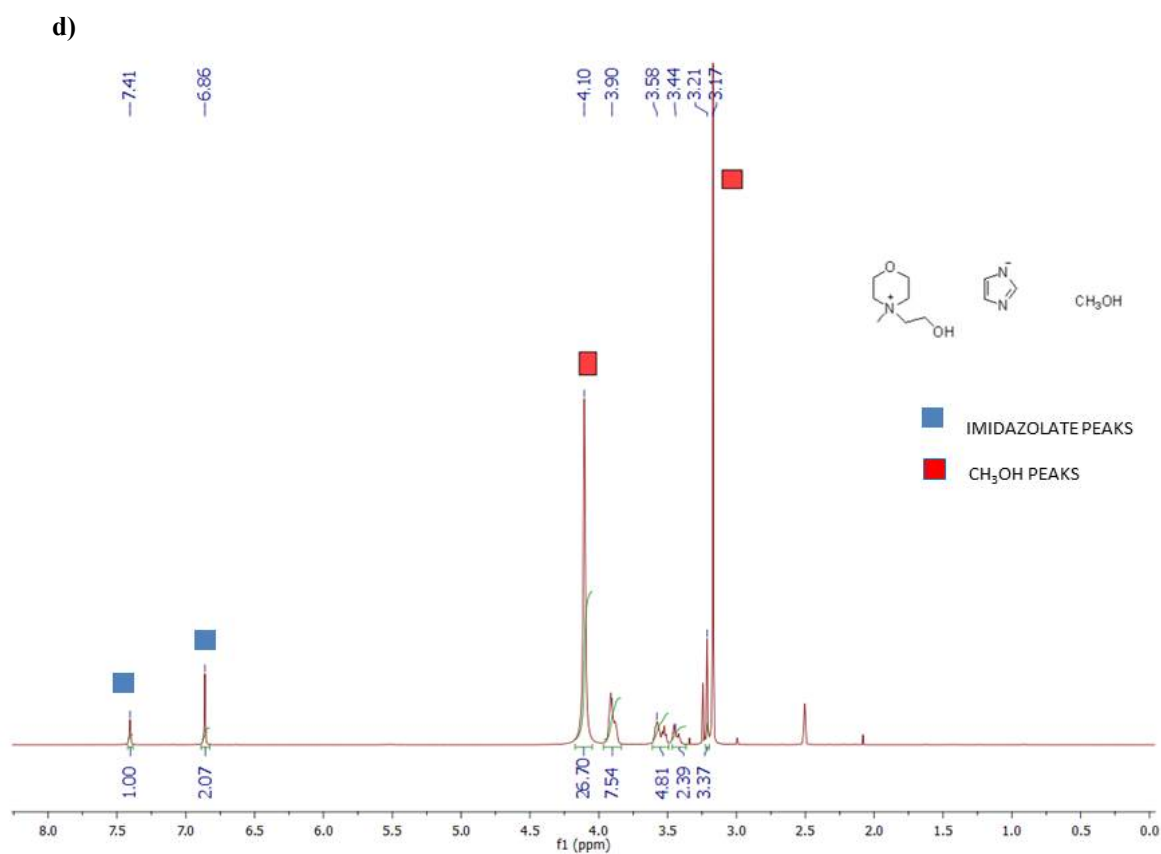
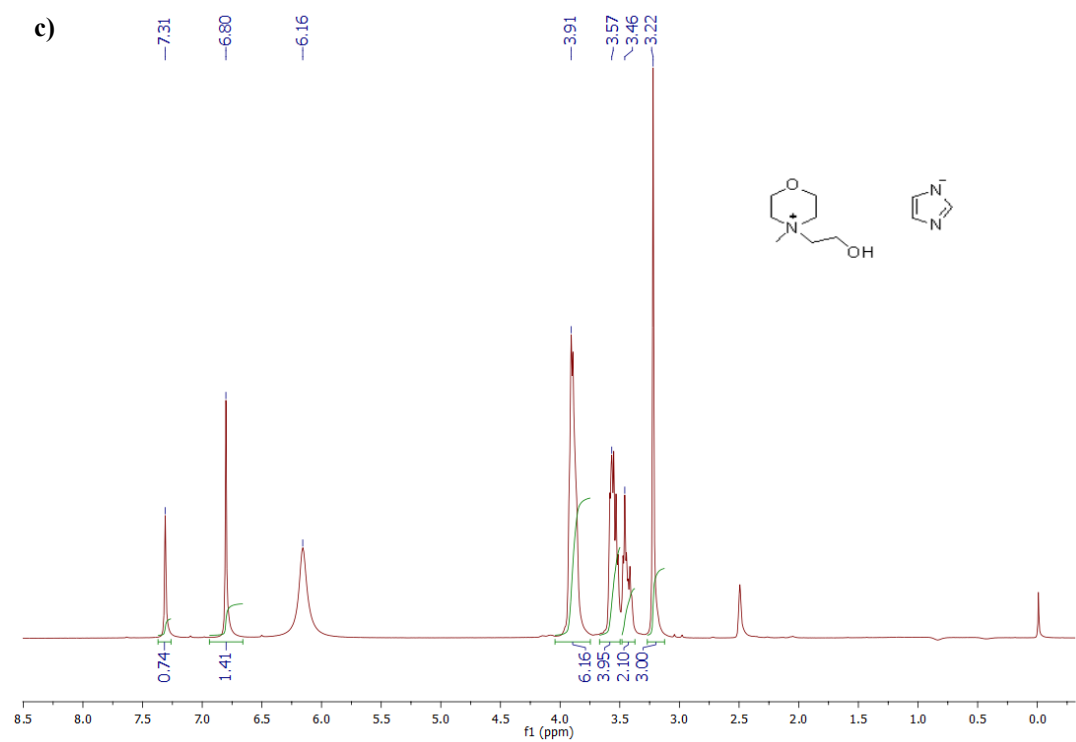
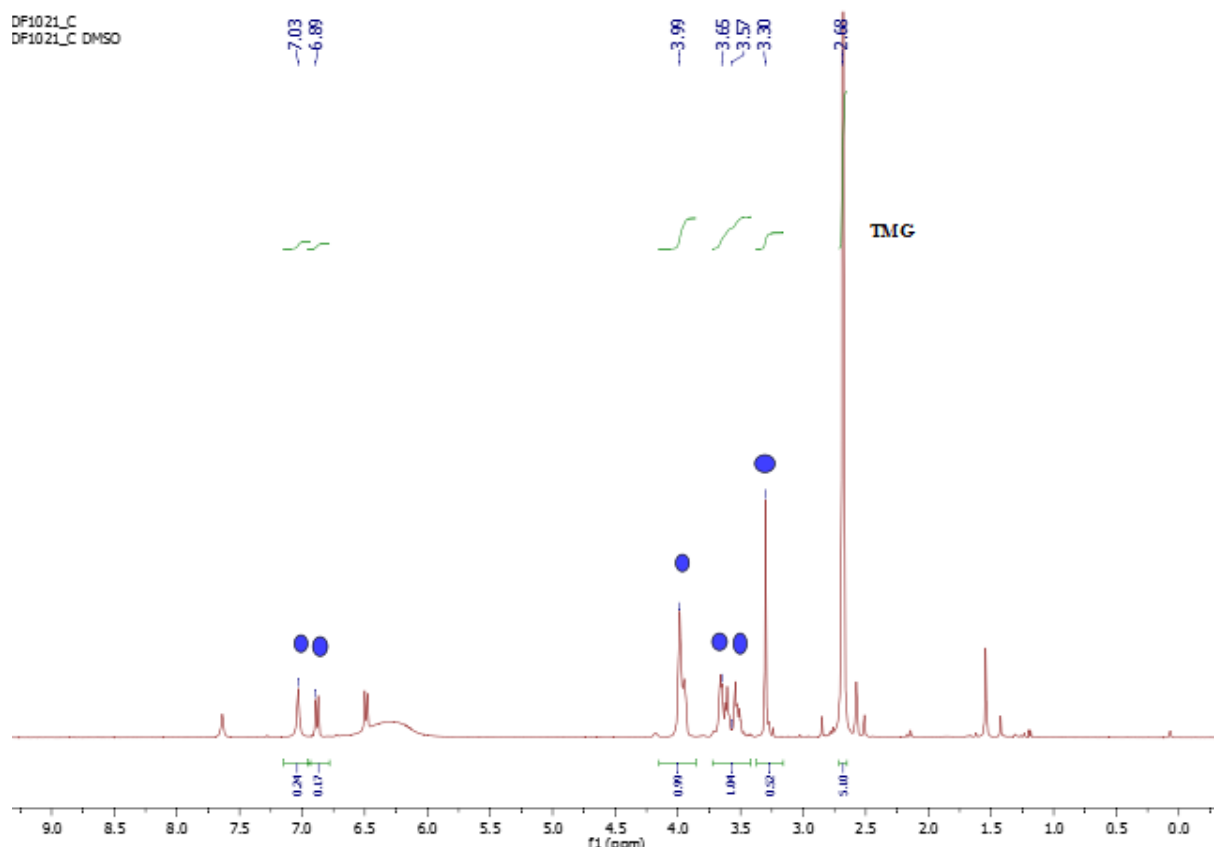


Figure S1. ¹H NMR spectra of: a) [C₁C₂OHPip][Im]; b) [C₁C₂OHPip][Im] in the presence of methanol ($n_{\text{MeOH}}/n_{\text{C}} = 4.2$); c) [C₁C₂OHPip][Im]; d) [C₁C₂OHPip][Im] in the presence of methanol ($n_{\text{MeOH}}/n_{\text{C}} = 4.2$).

DF1021_C
DF1021_C DMSO



DF1130B.1.1.1r
DF1130B DMSO

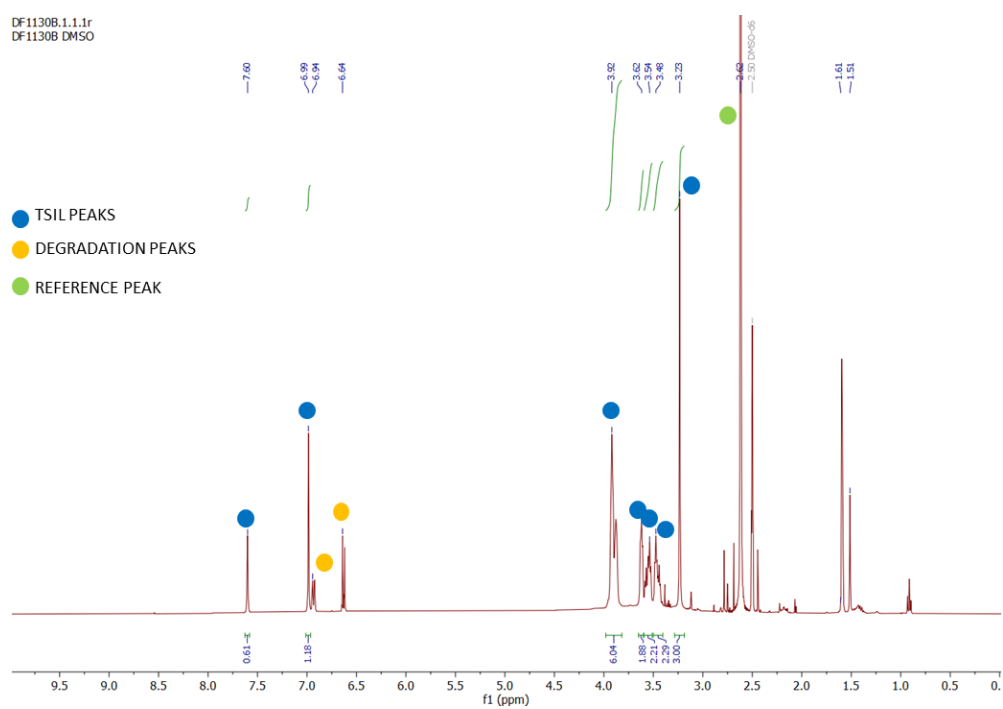
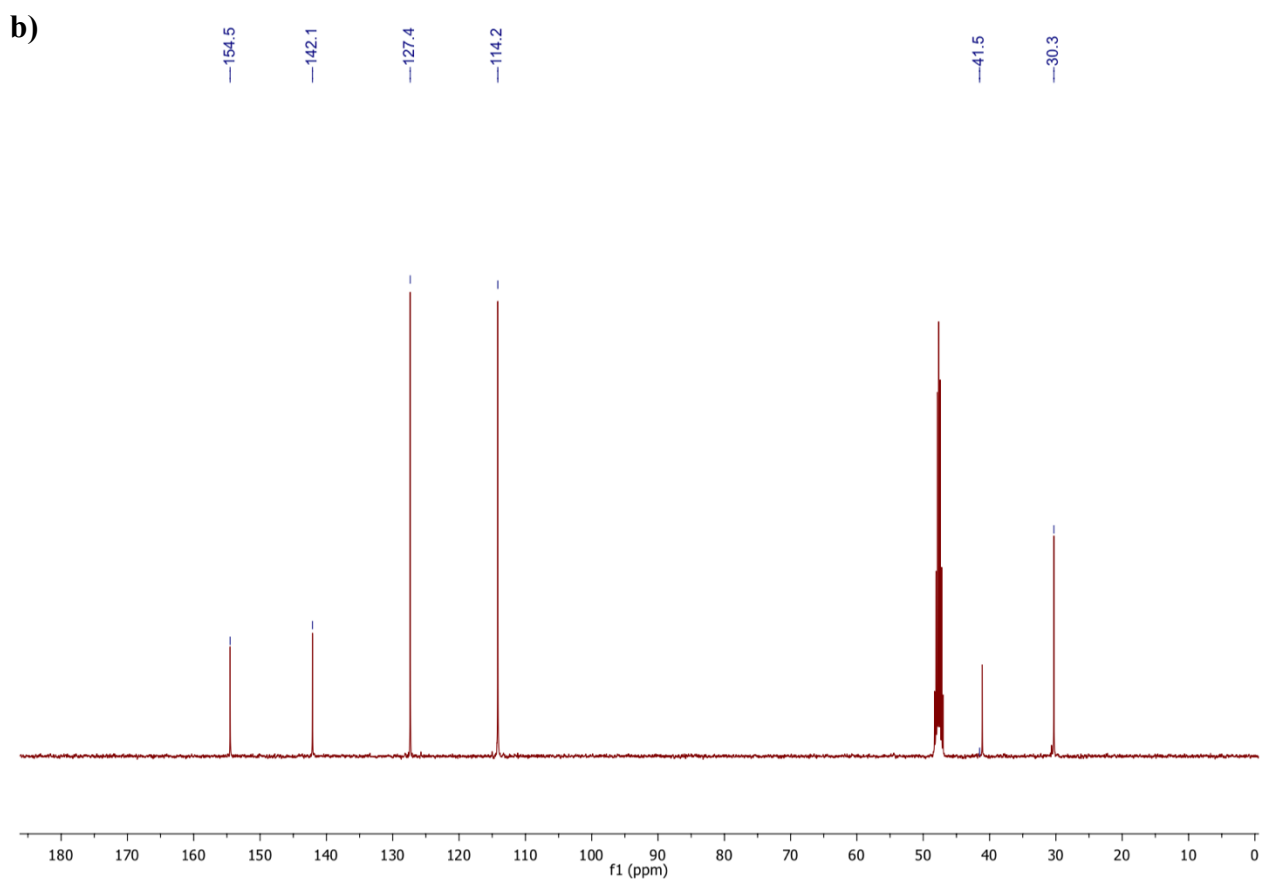
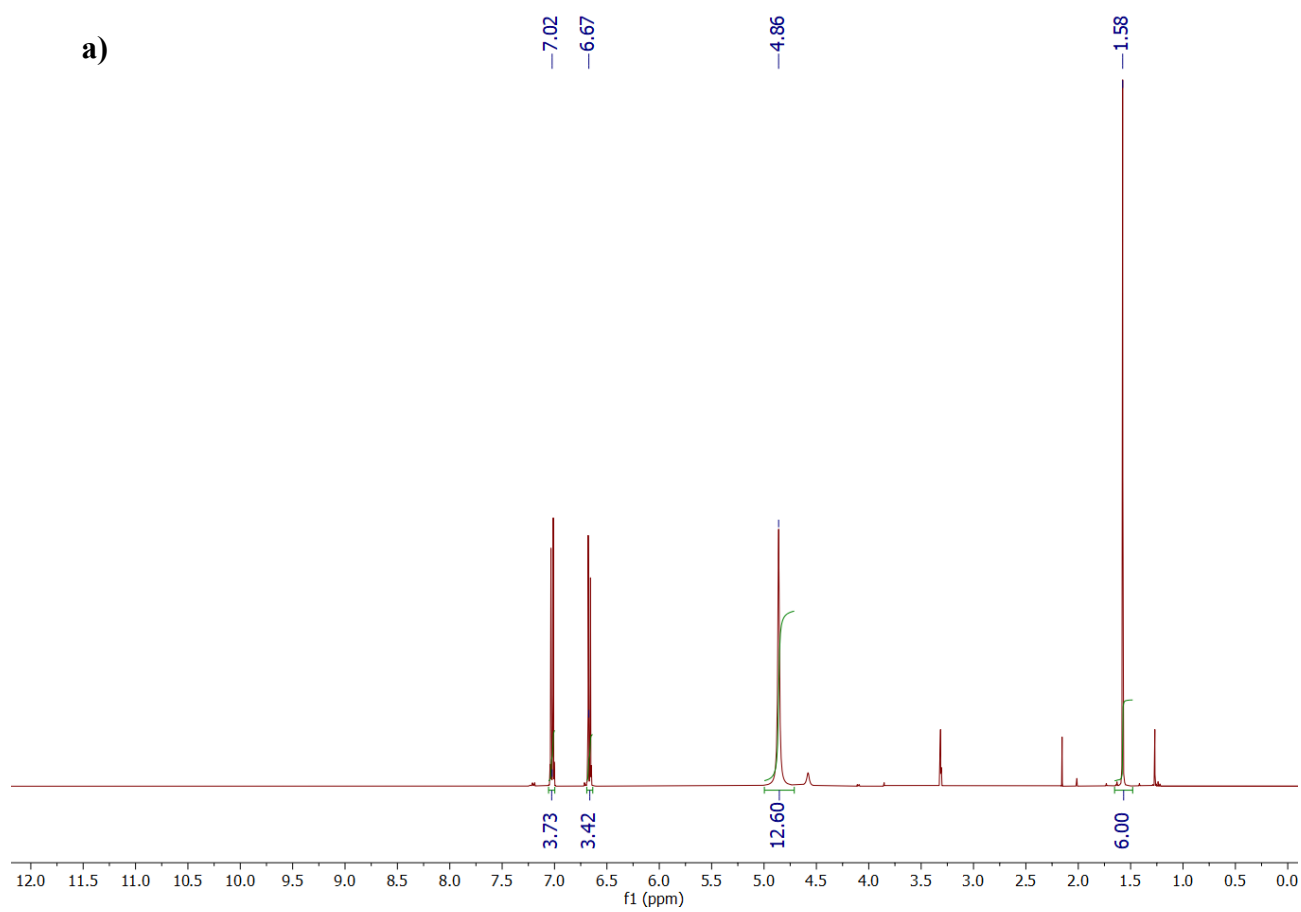


Figure S2. ^1H NMR spectra of $[\text{C}_1\text{C}_2\text{OHMor}][\text{Im}]$ after sonication (top) and after reaction (bottom).



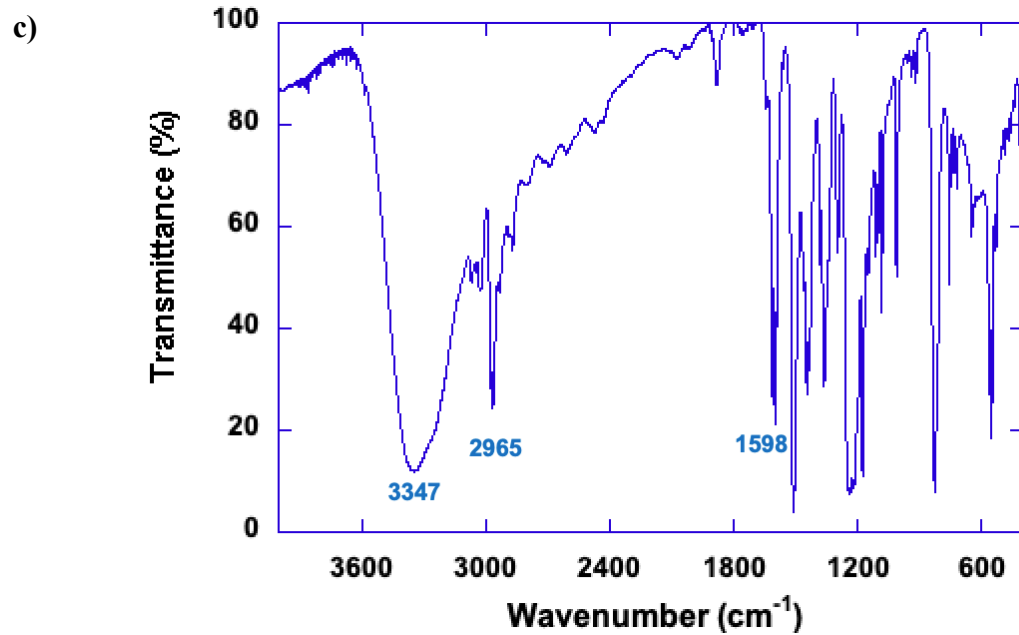
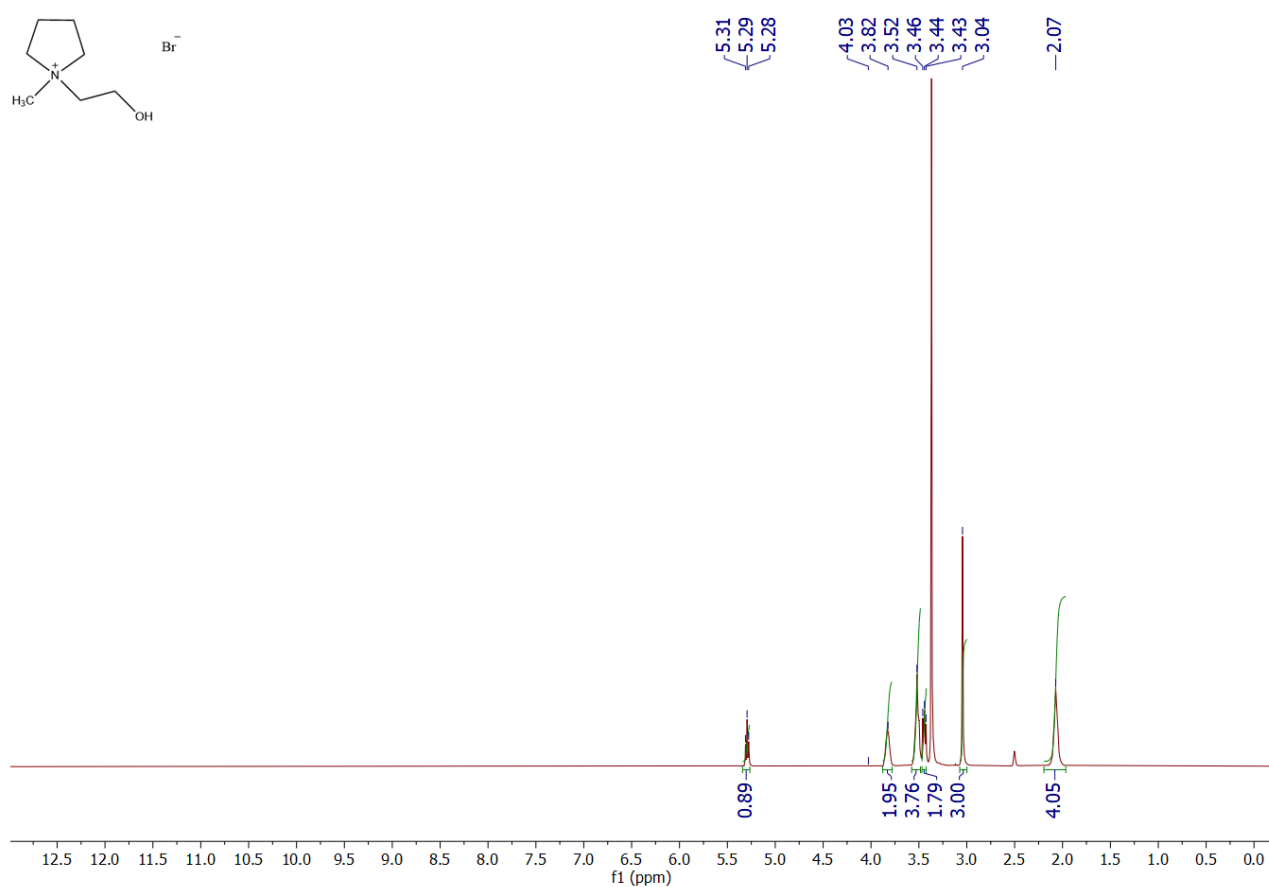
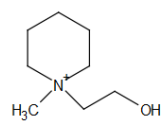
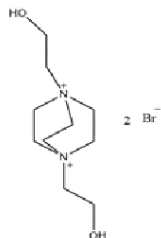
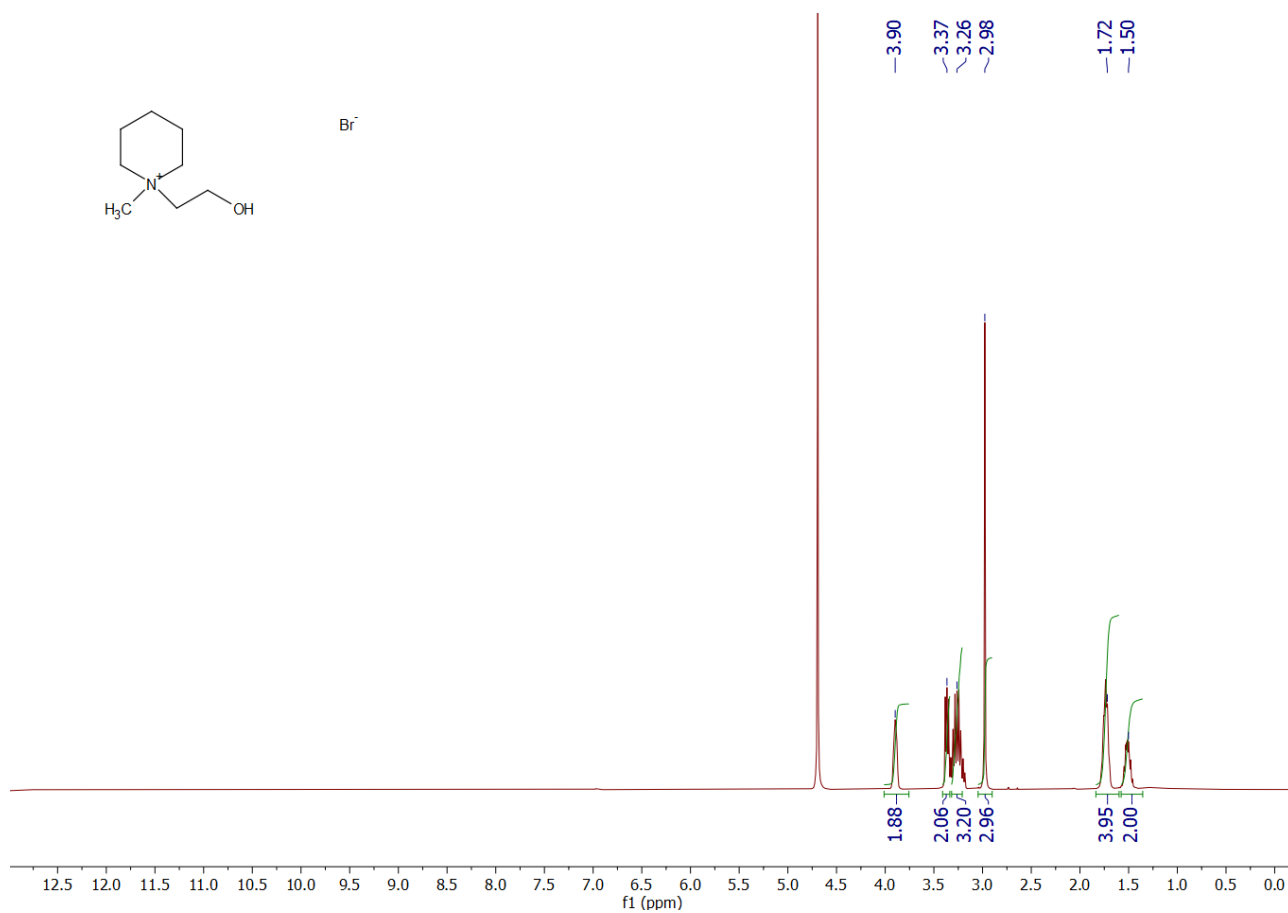


Figure S3. ^1H NMR (a), ^{13}C NMR (b) and IR (c) spectra of BPA obtained from methanolysis of PC from CD.

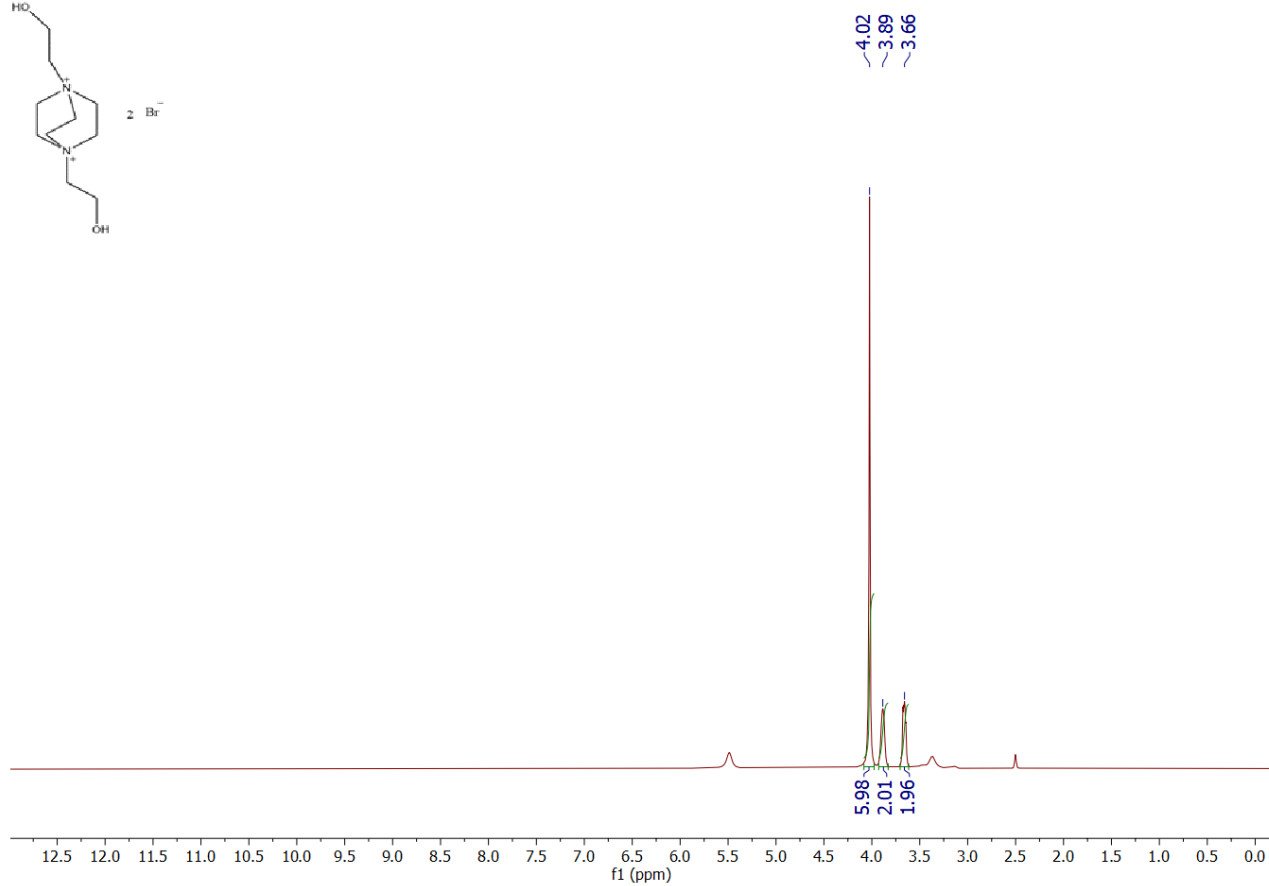


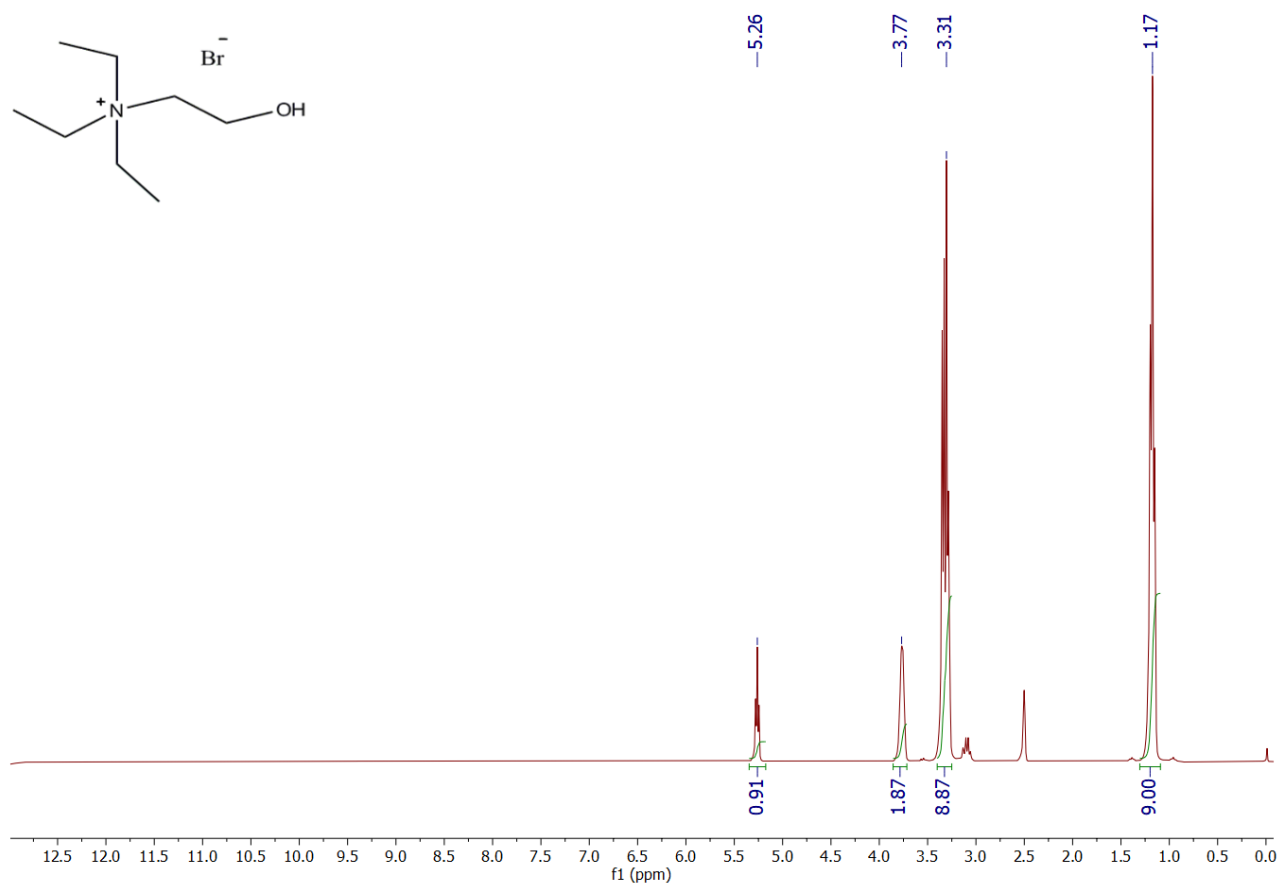
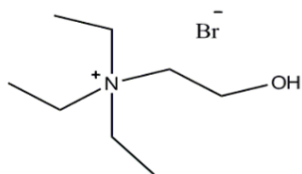
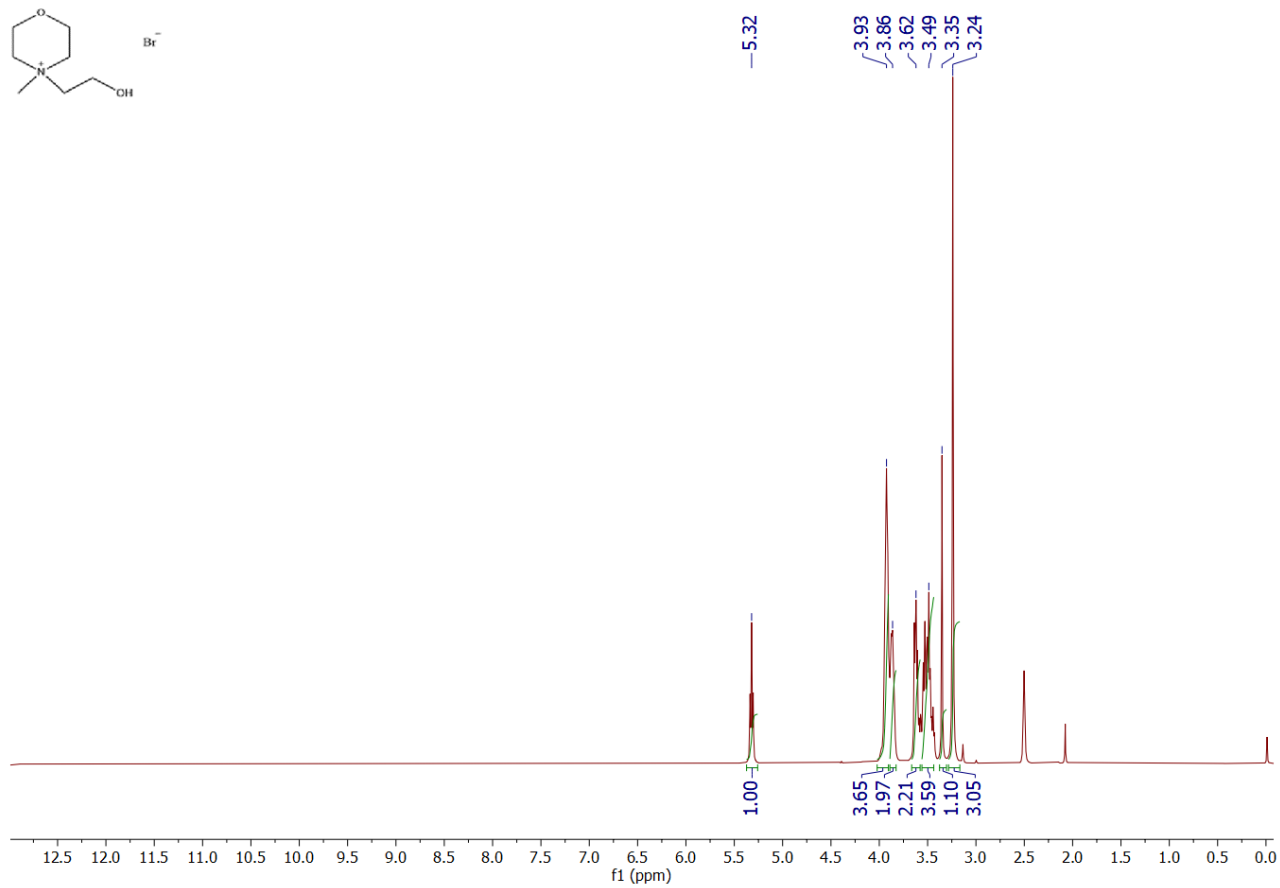
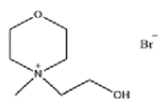


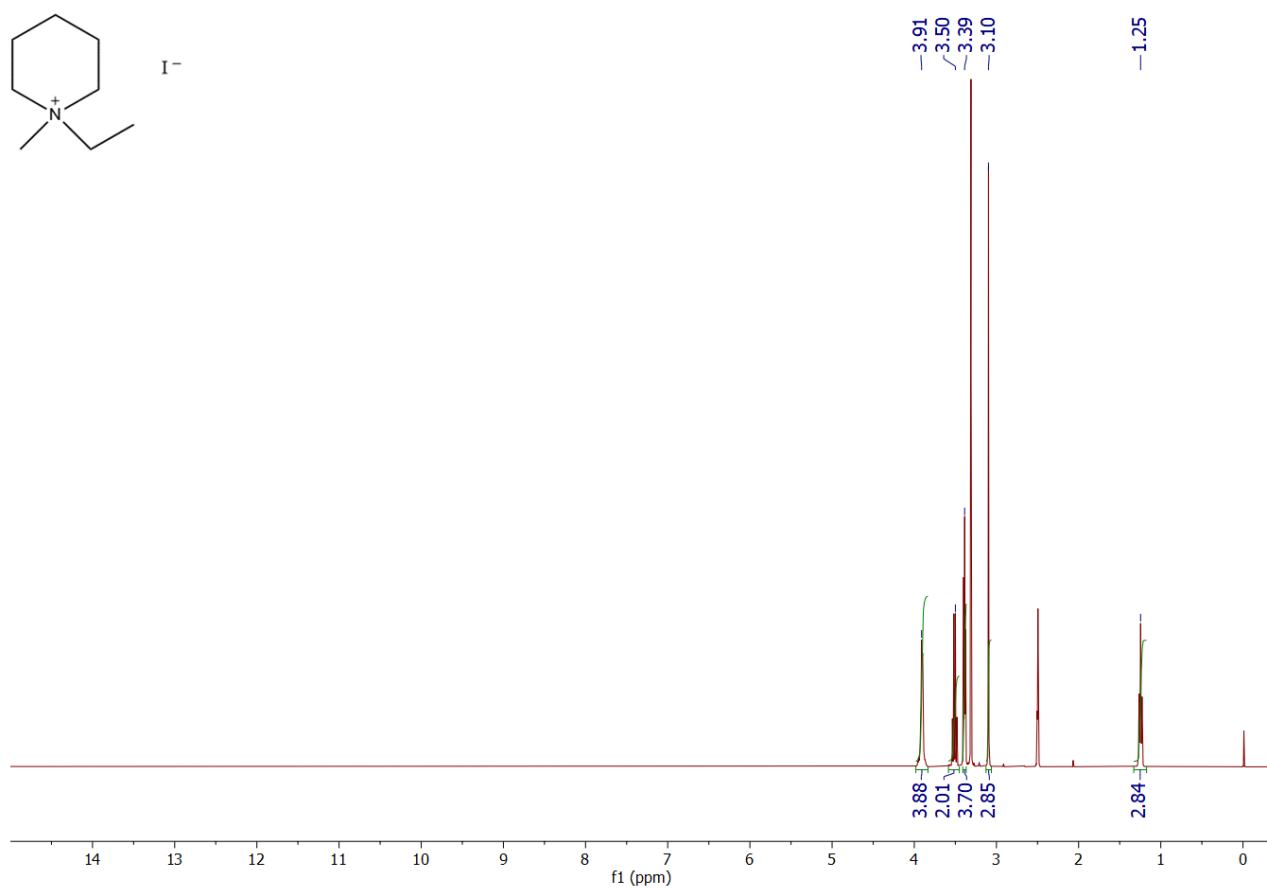
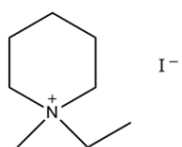
Br⁻



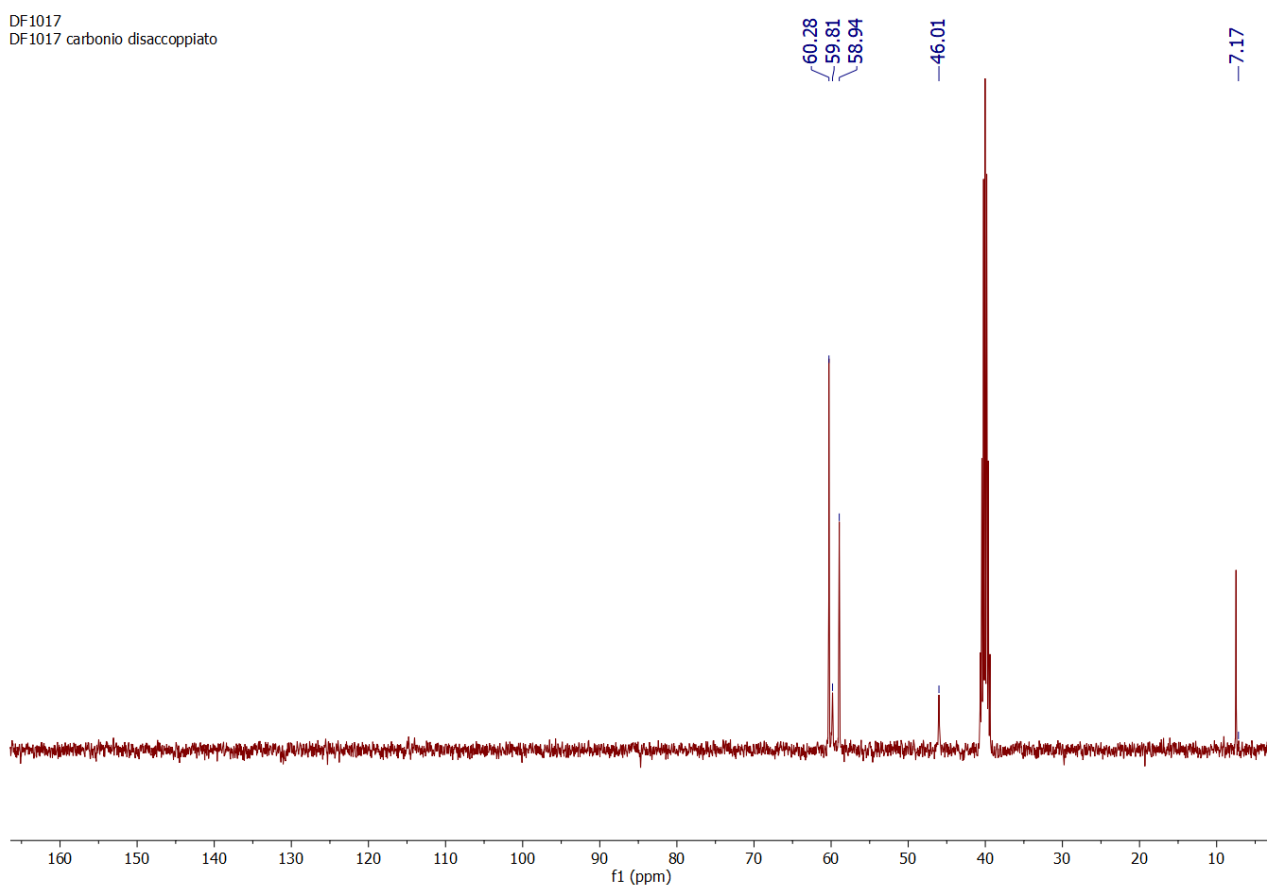
2 Br⁻

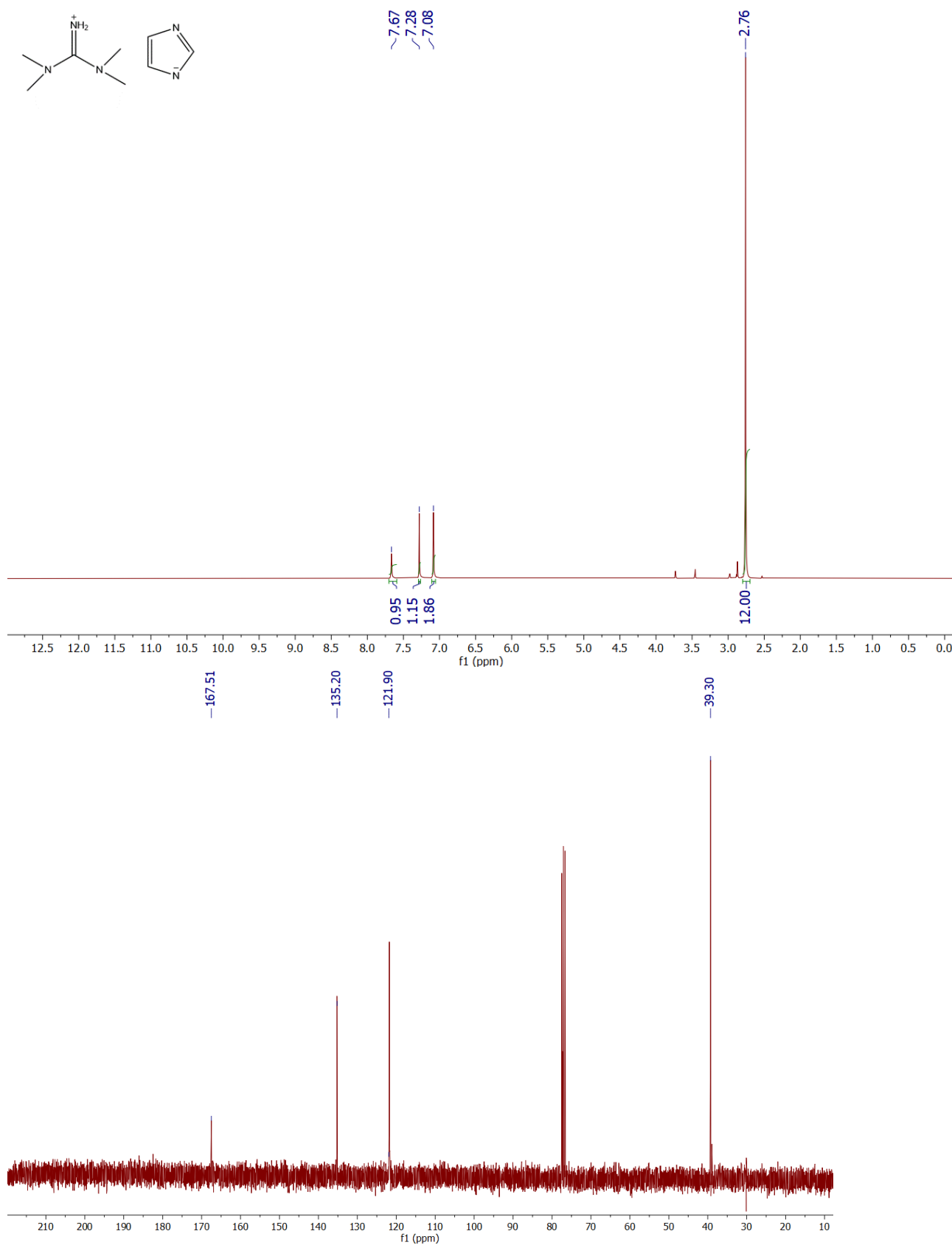
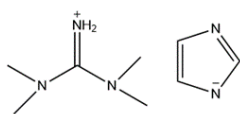


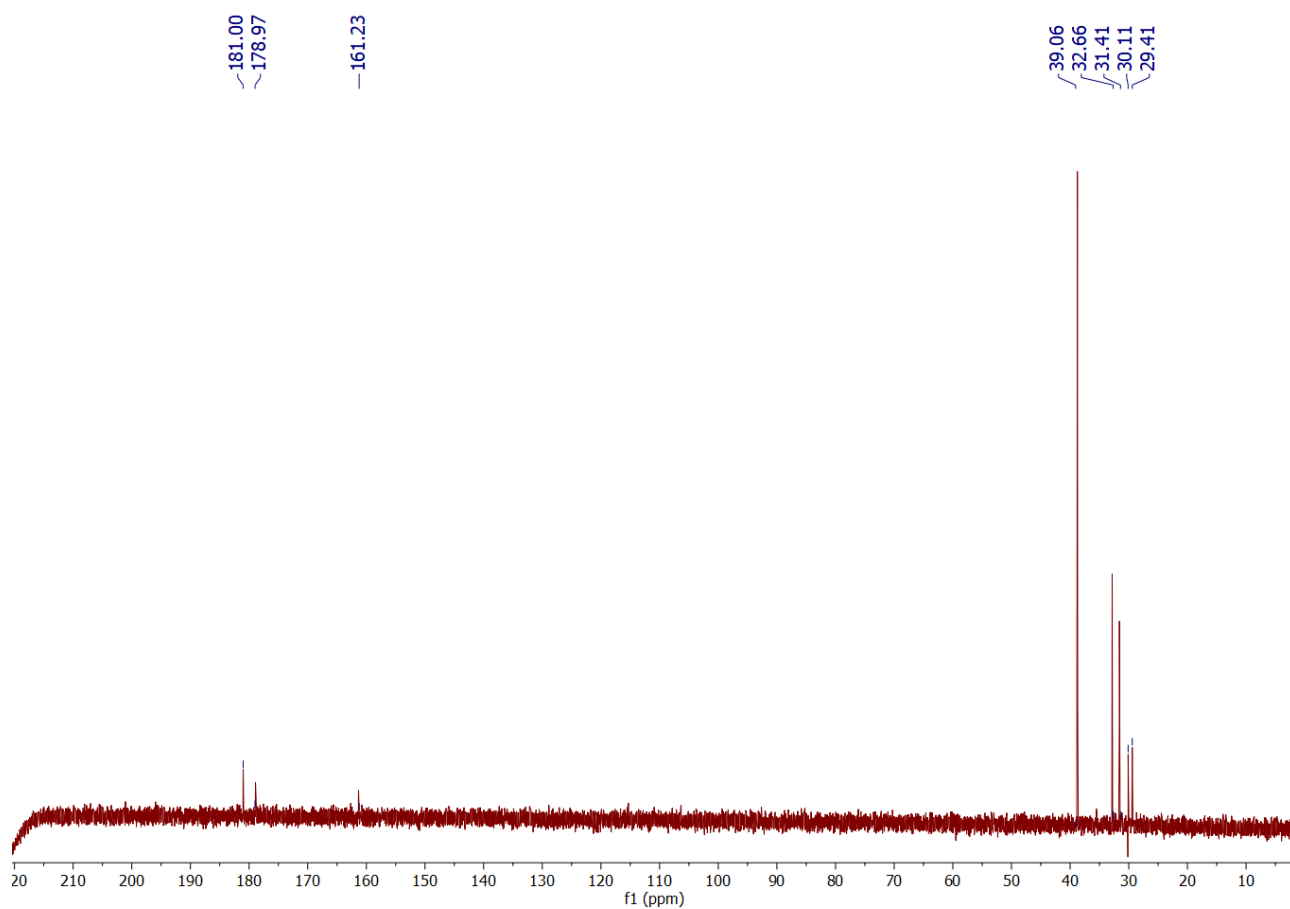
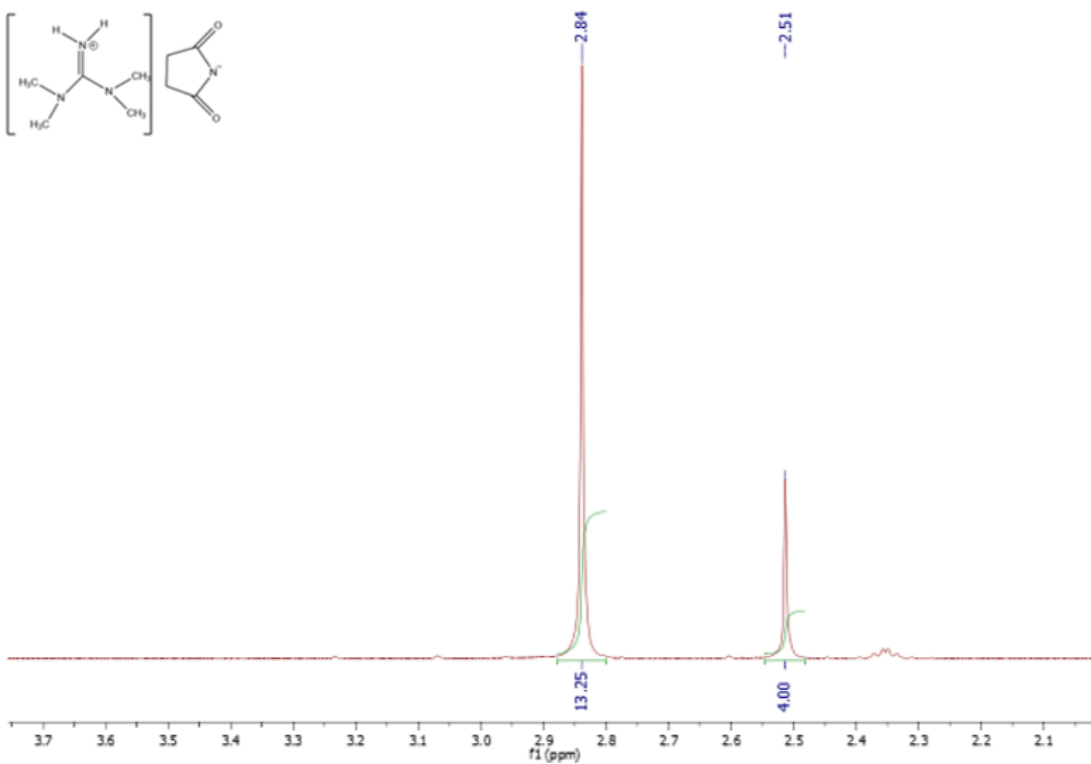
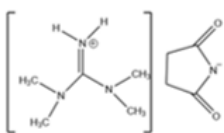


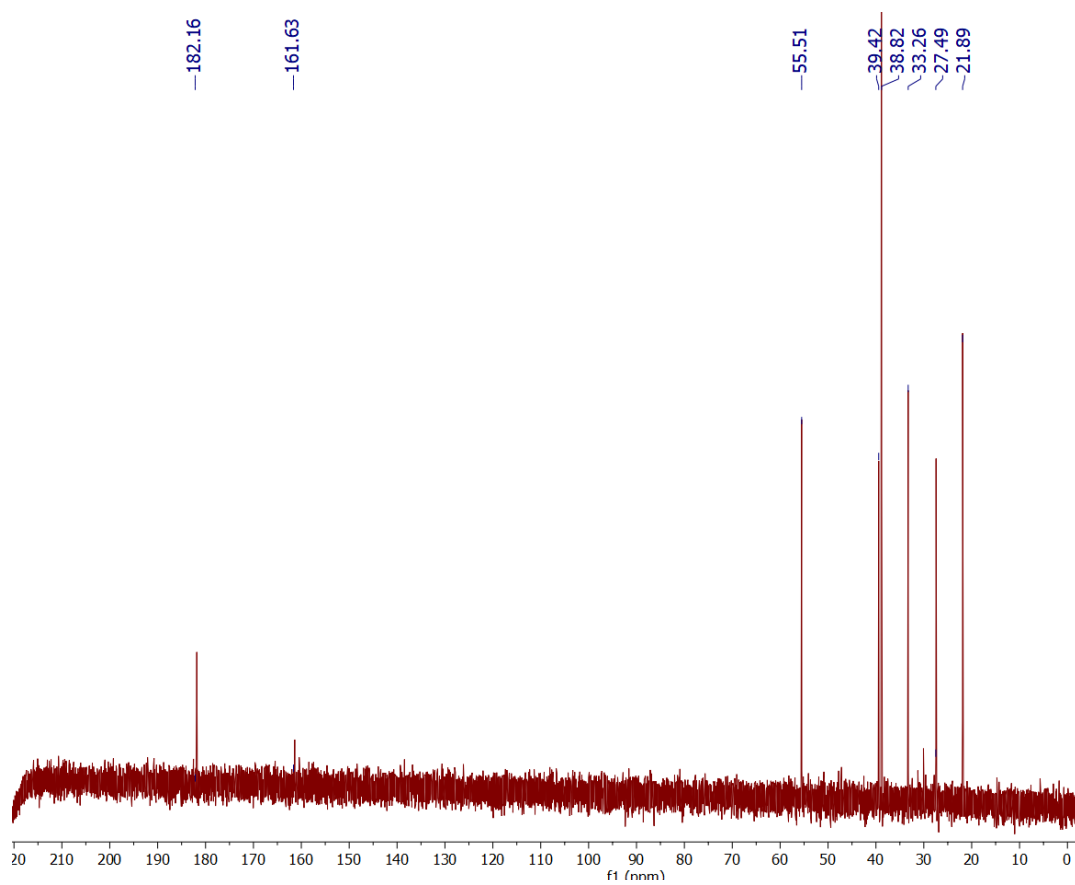
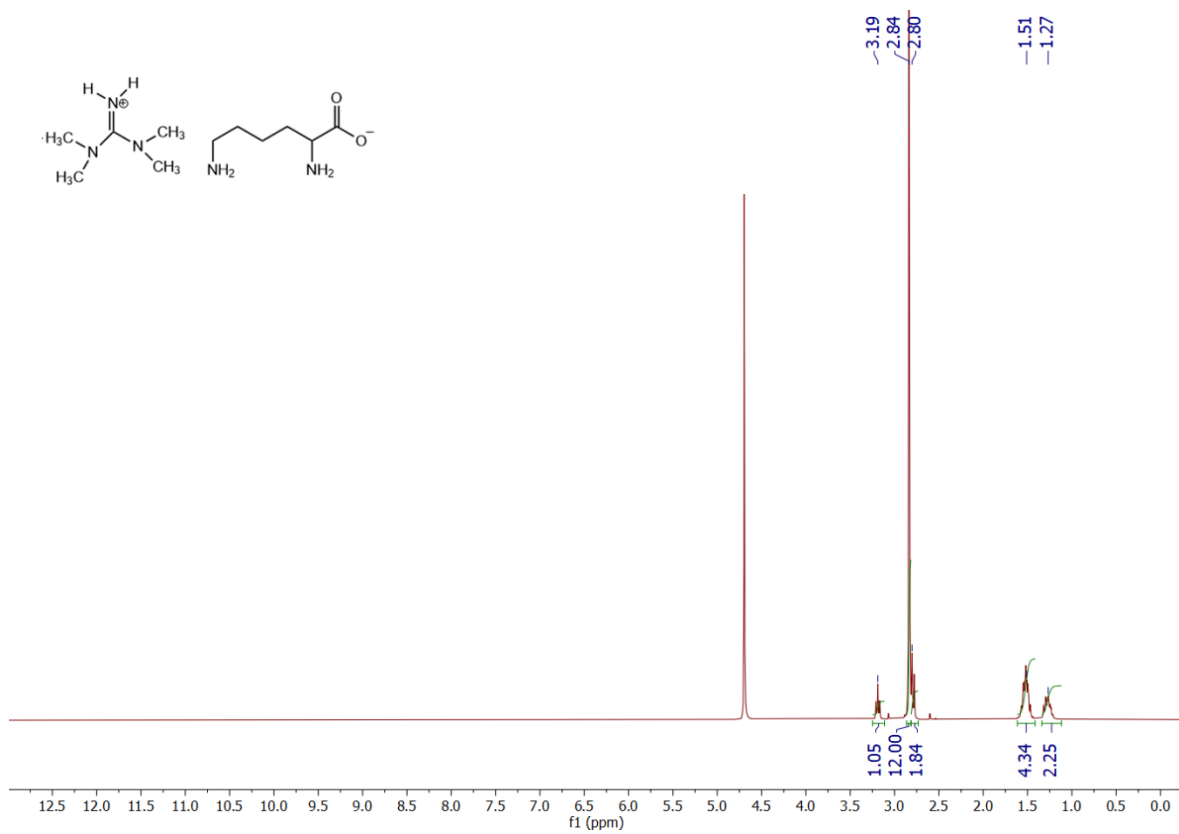


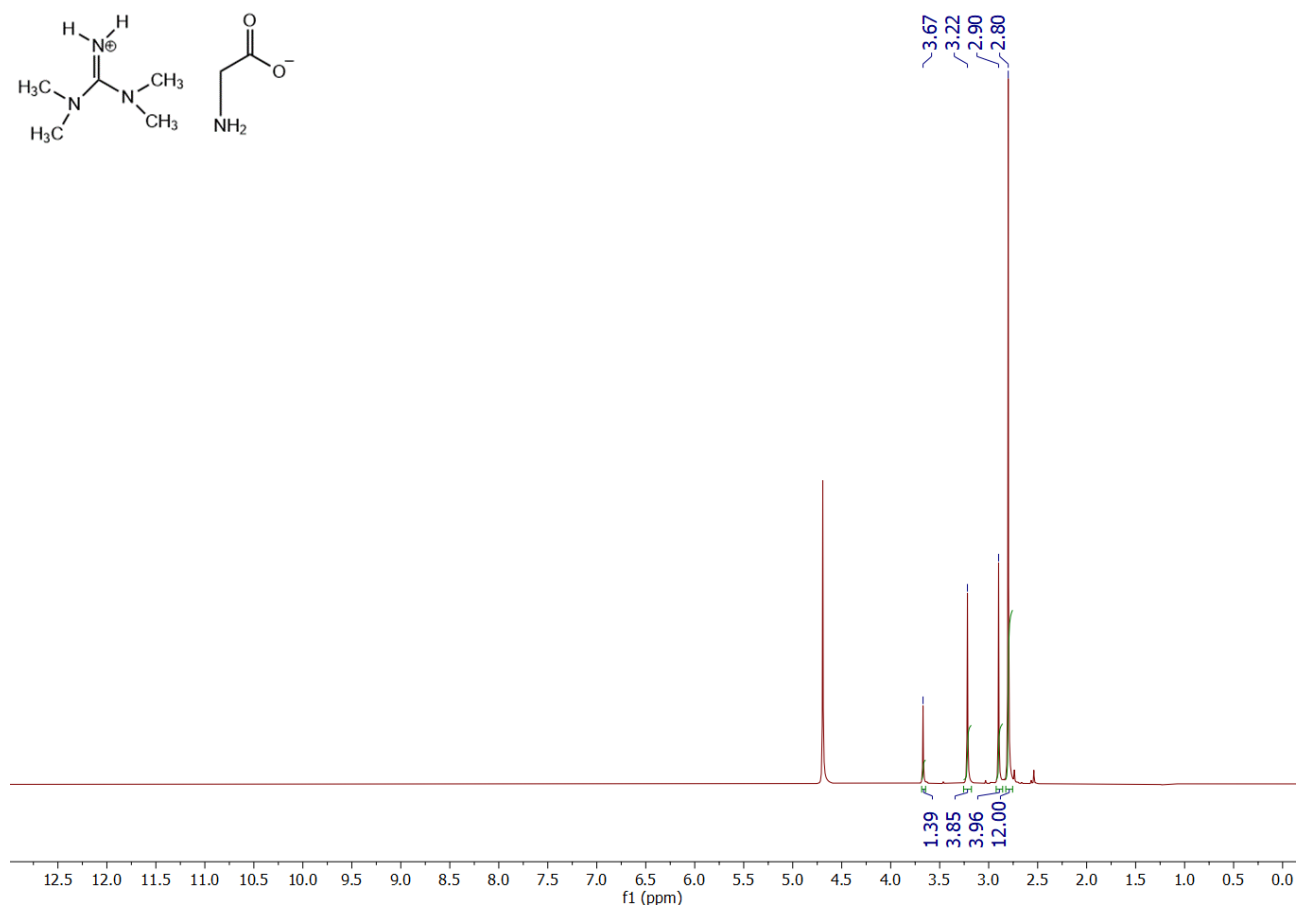
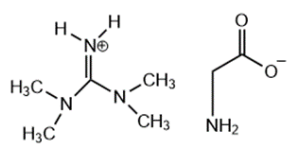
DF1017
DF1017 carbonio disaccoppiato

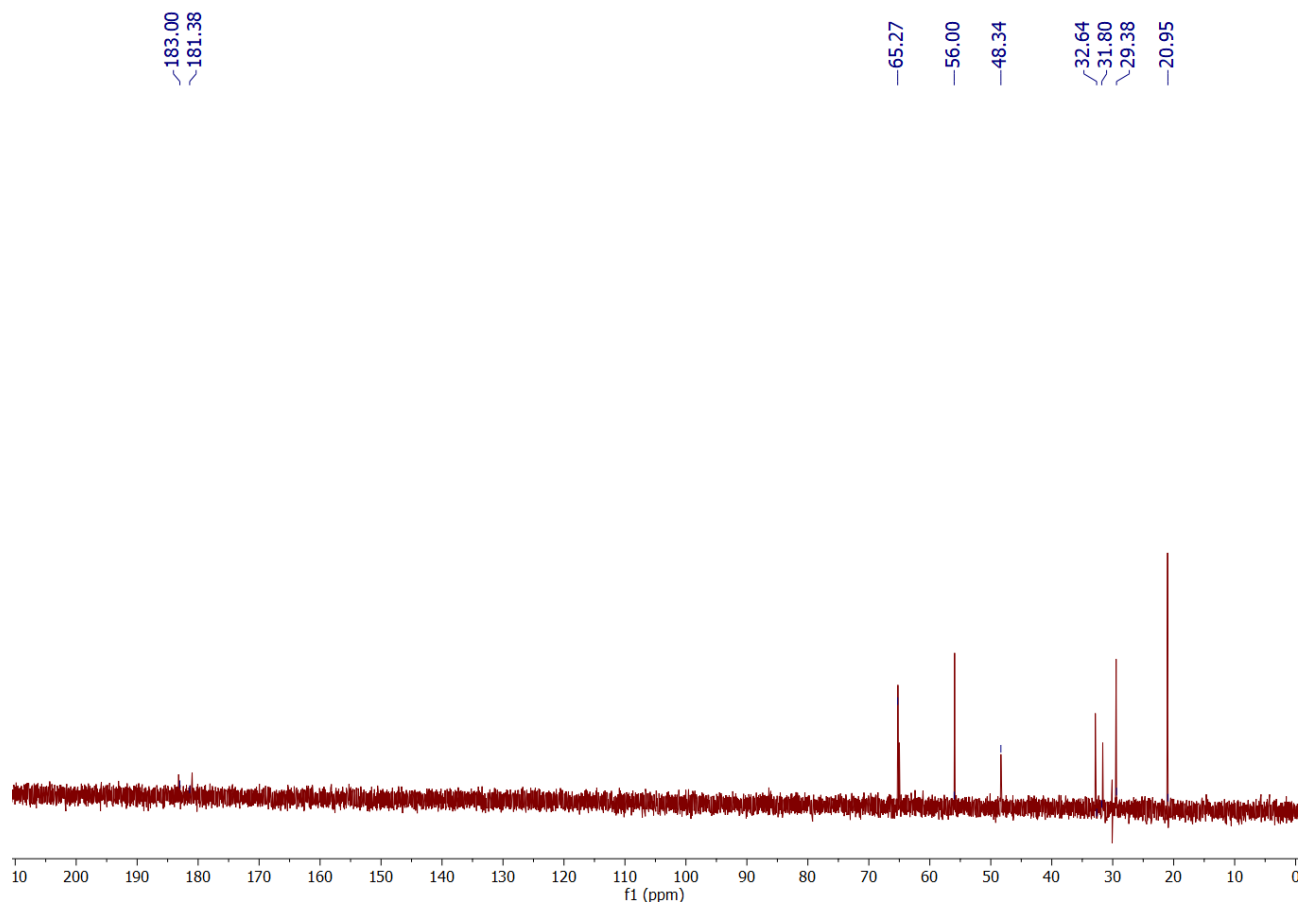
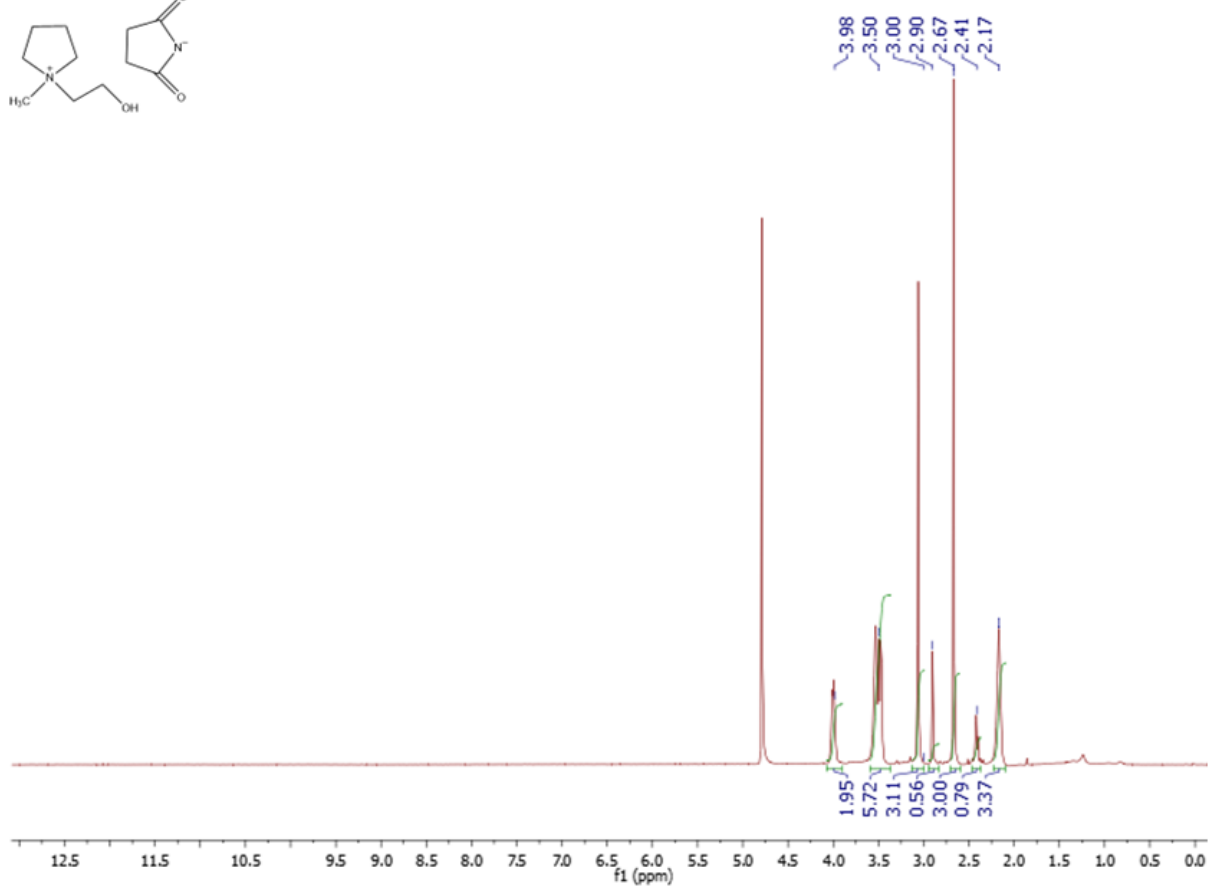
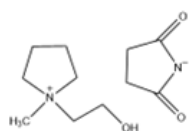


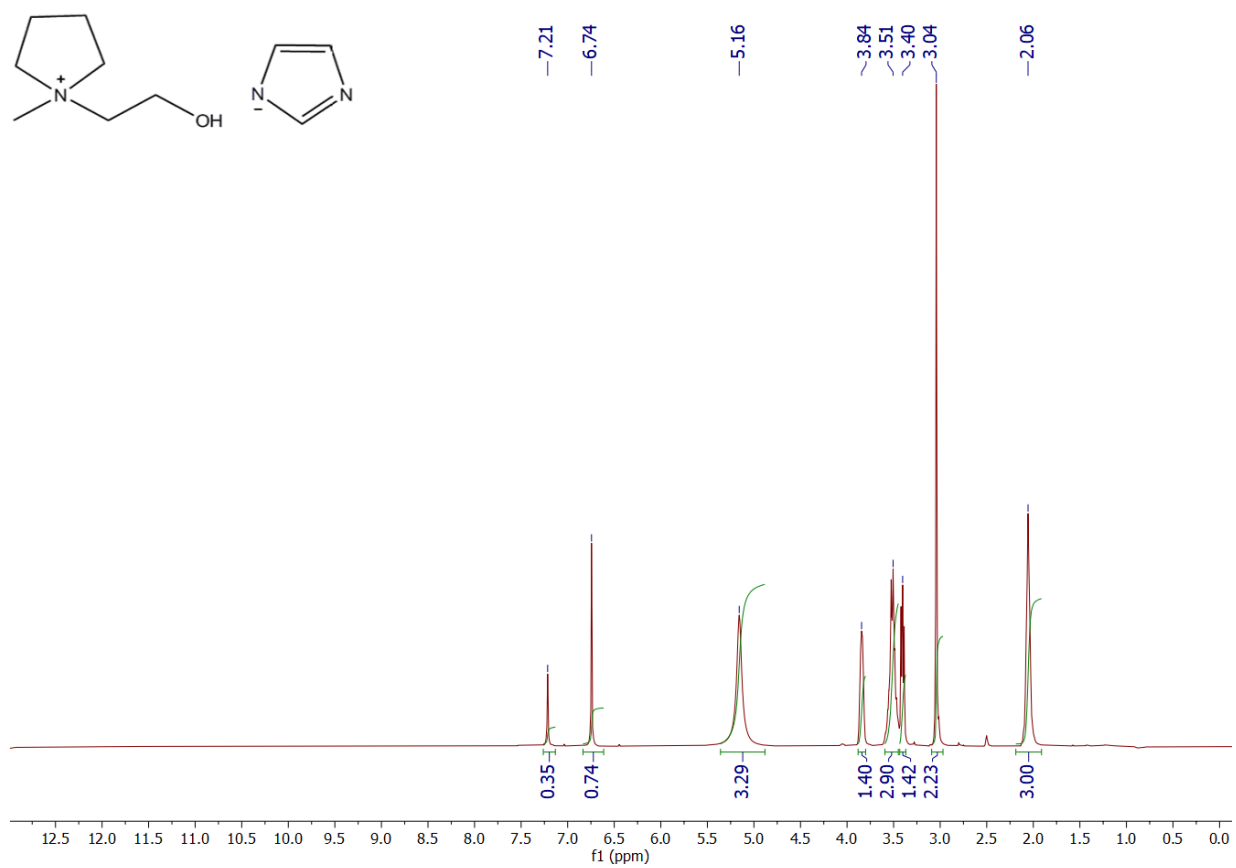


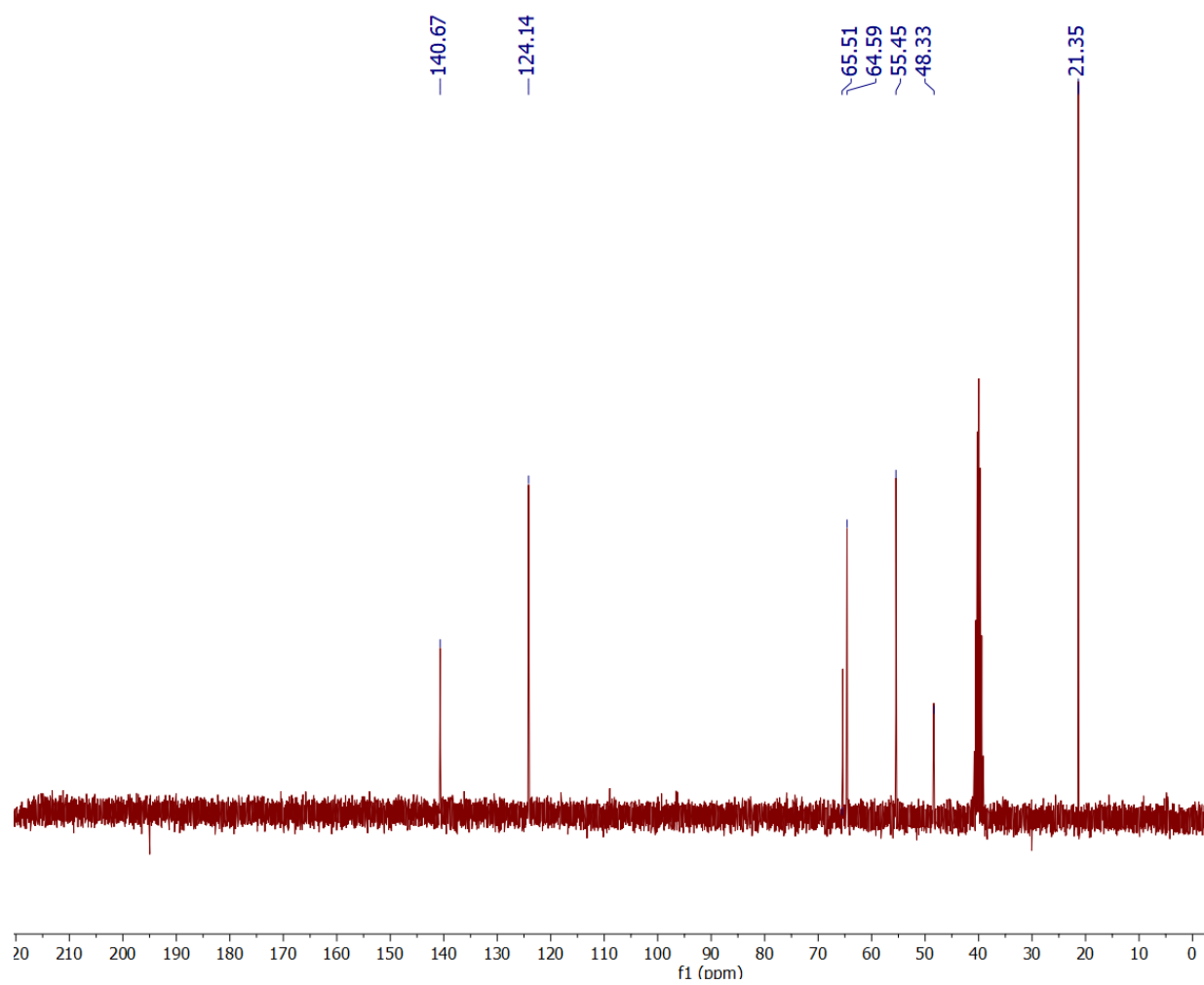


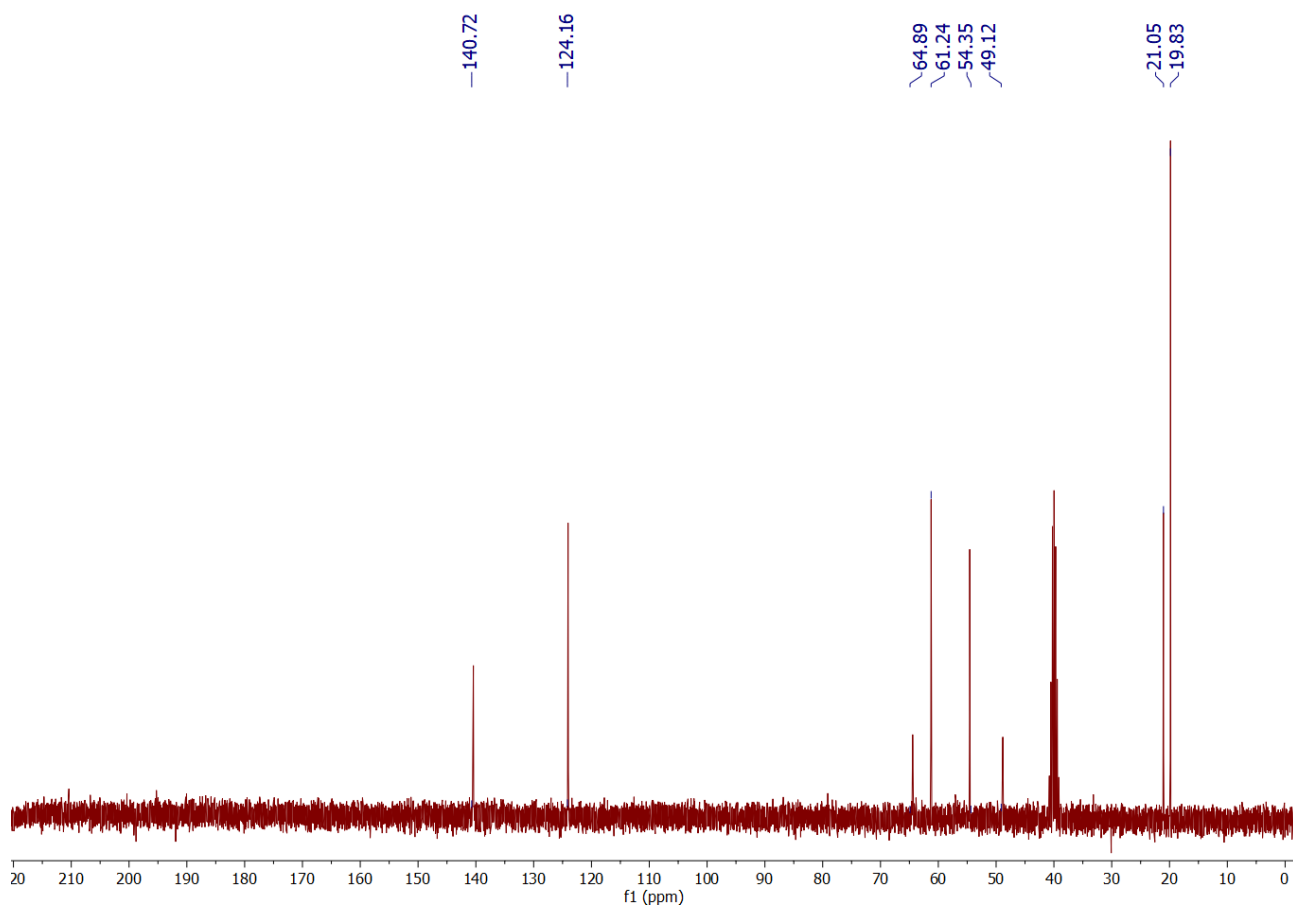
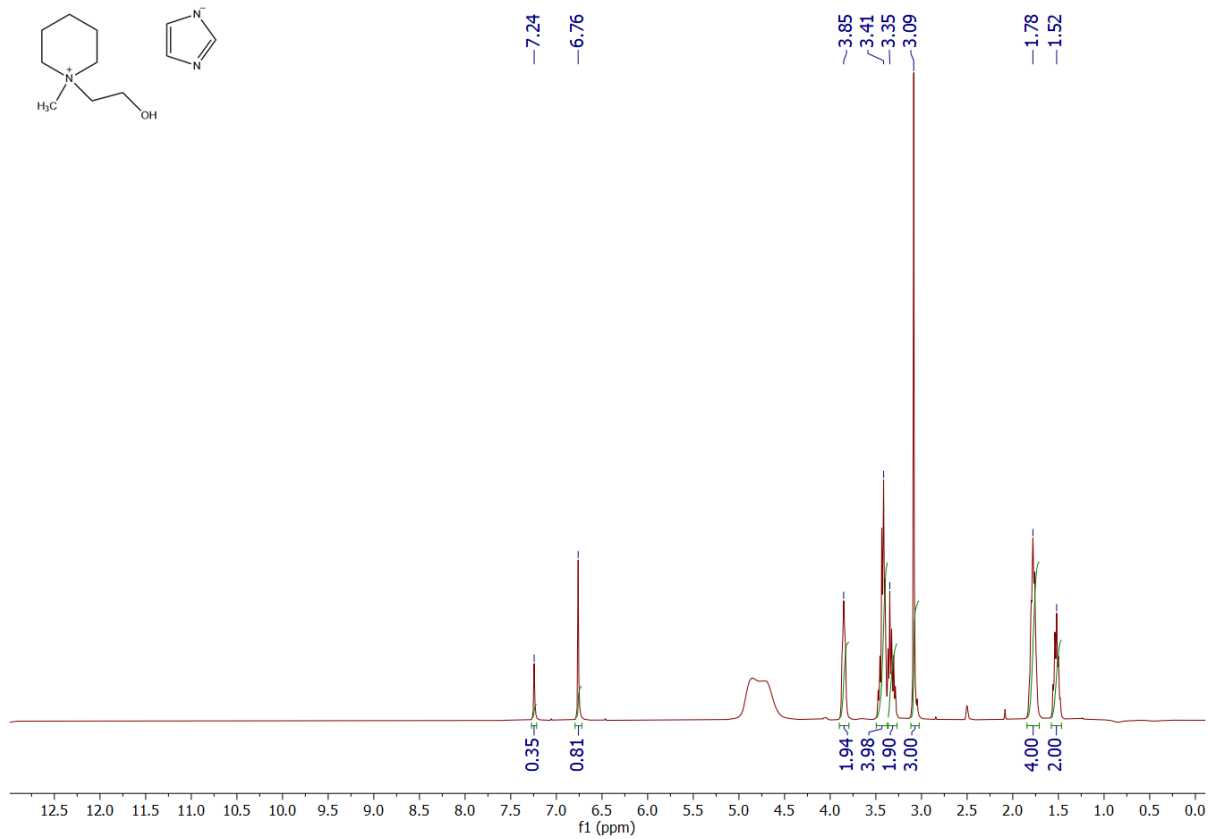
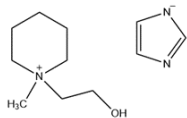


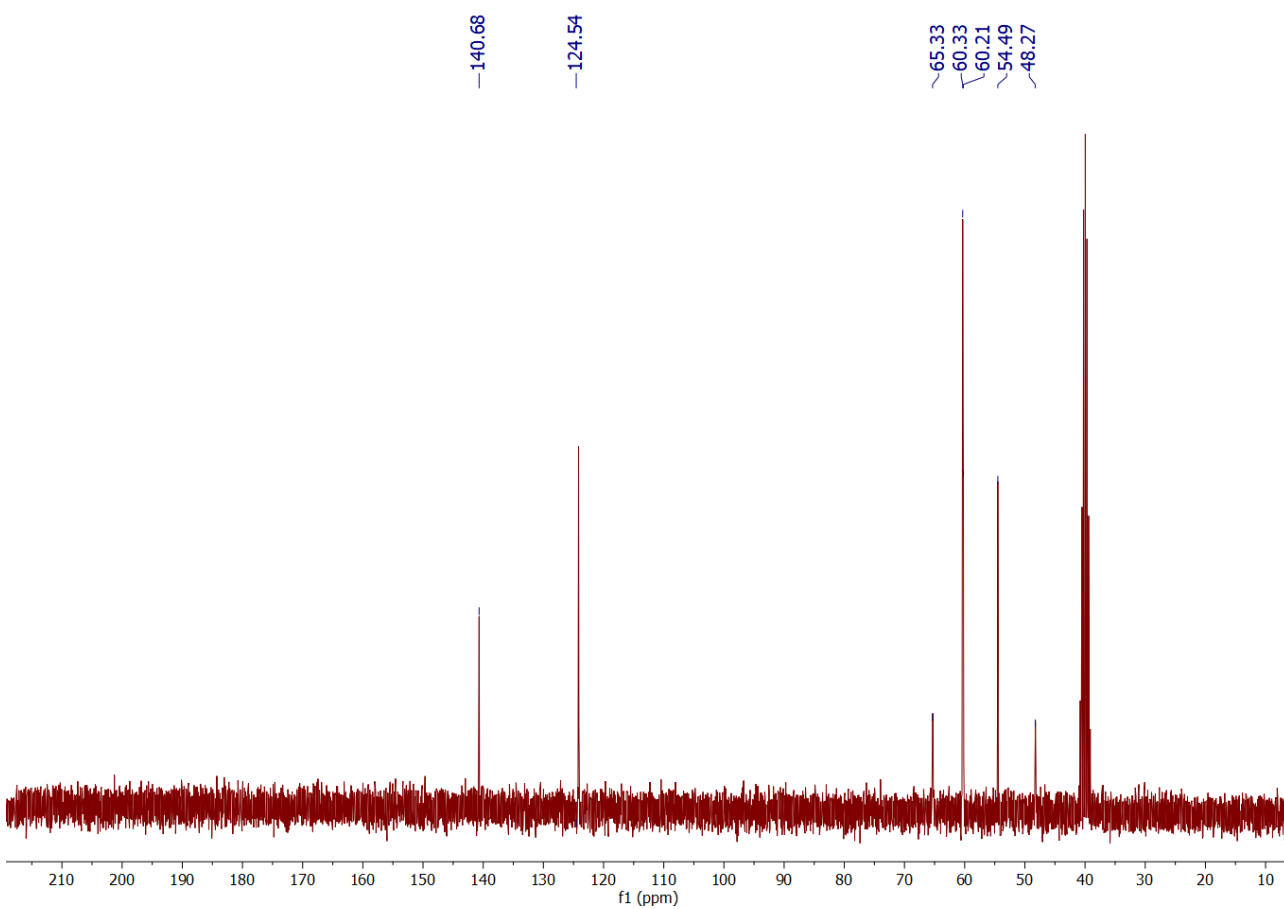
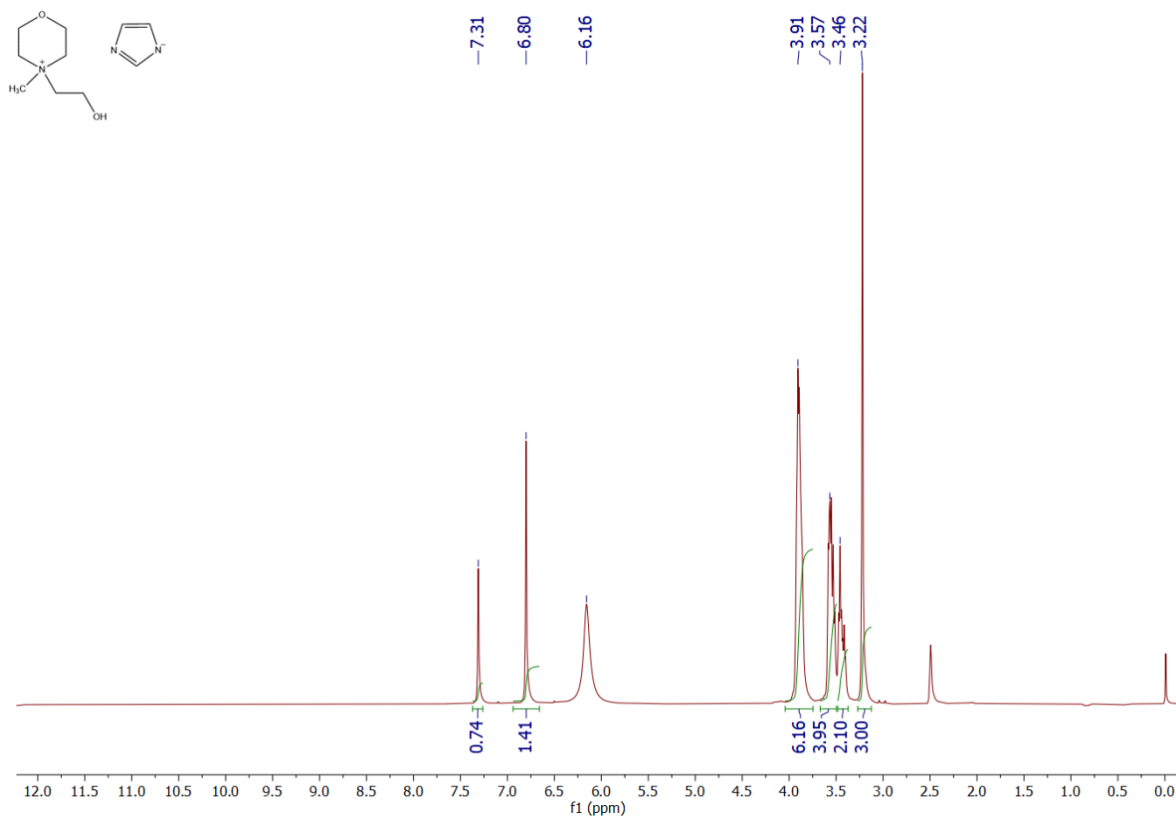
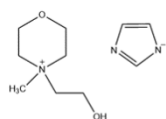


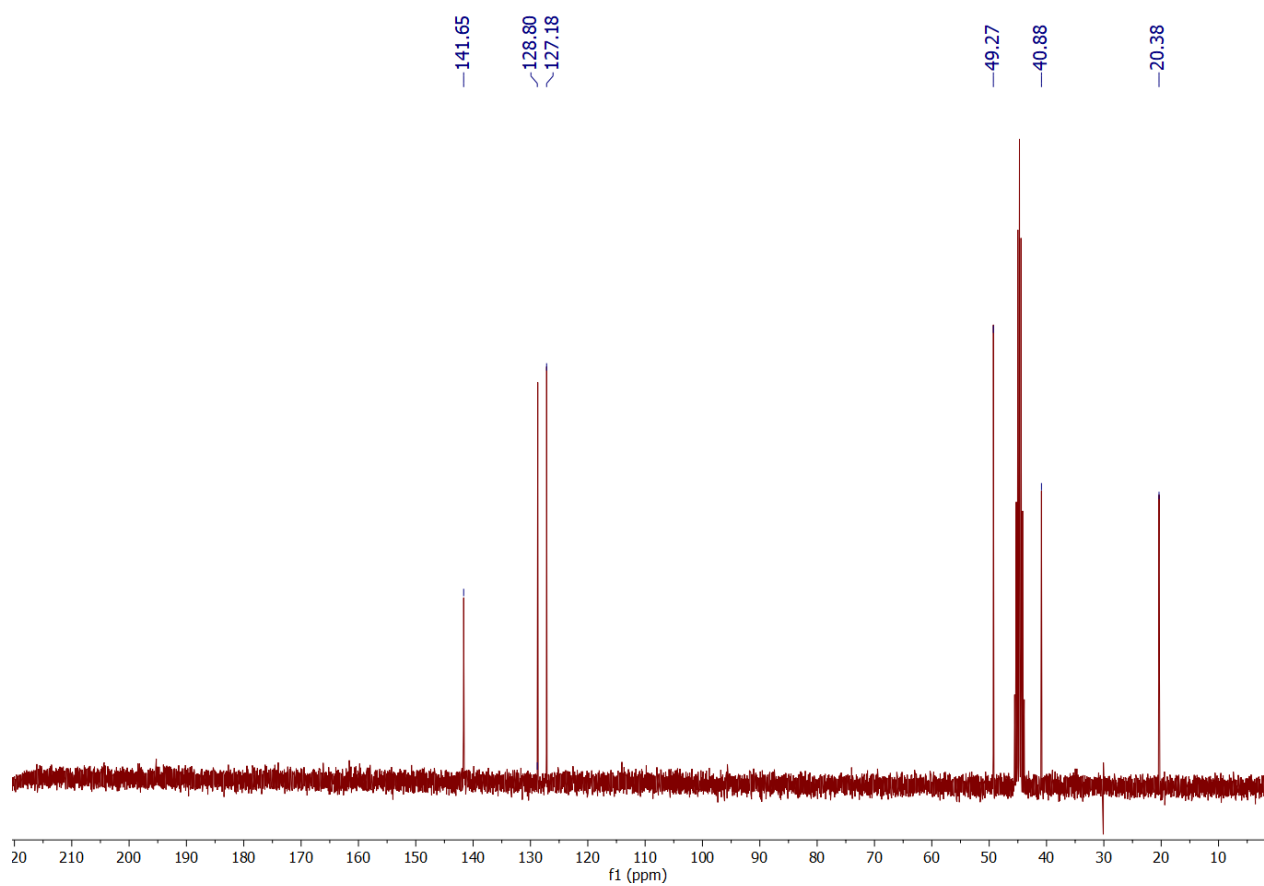
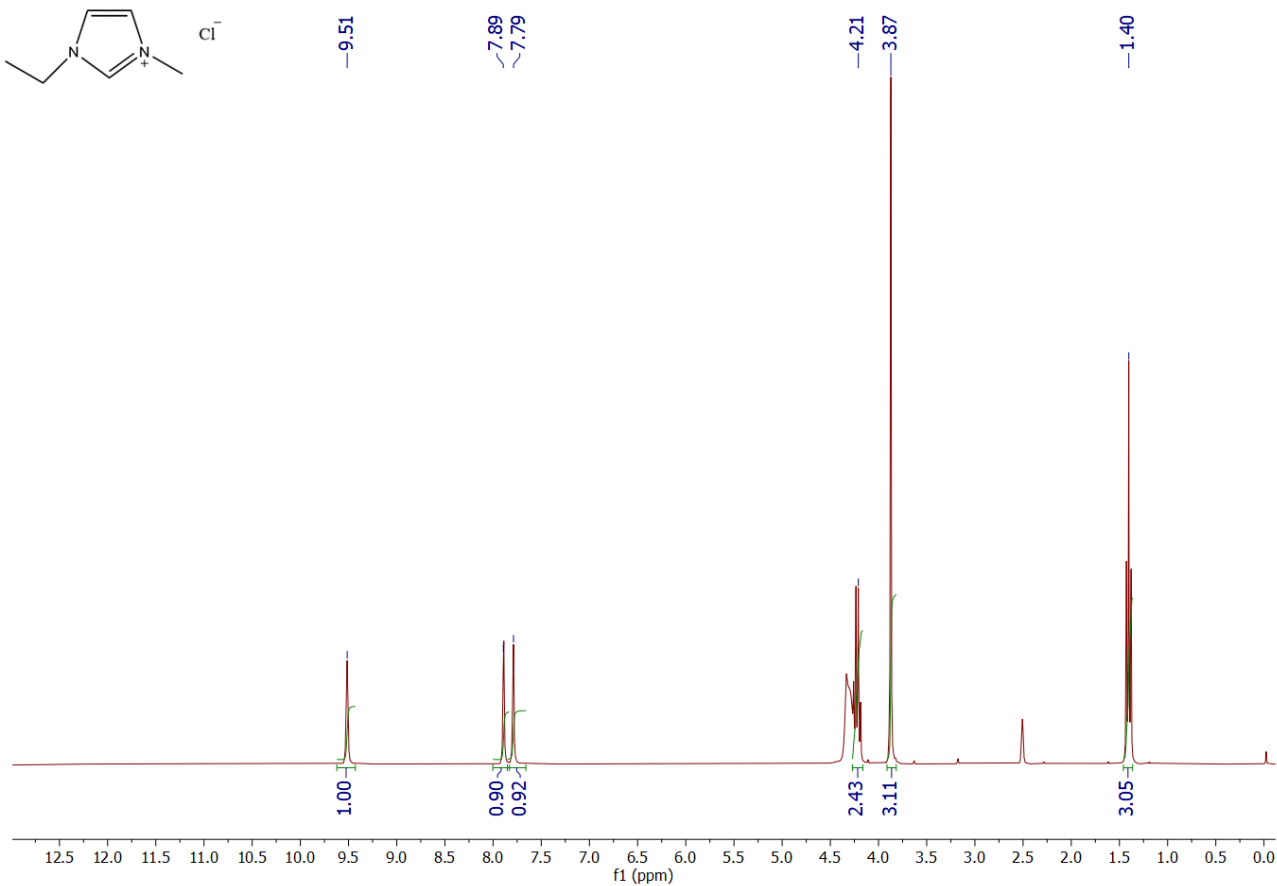
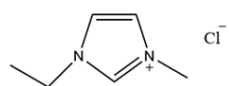


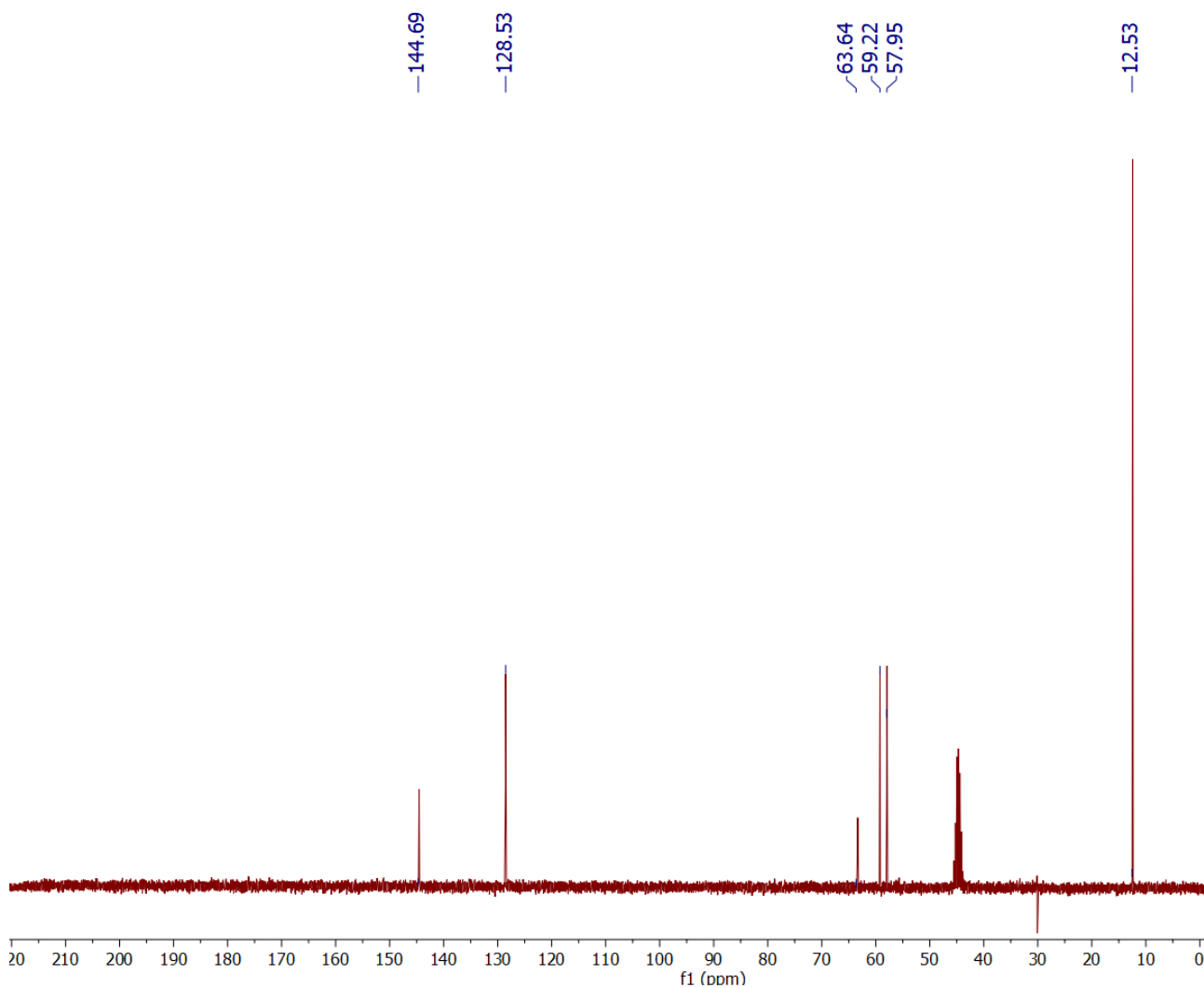
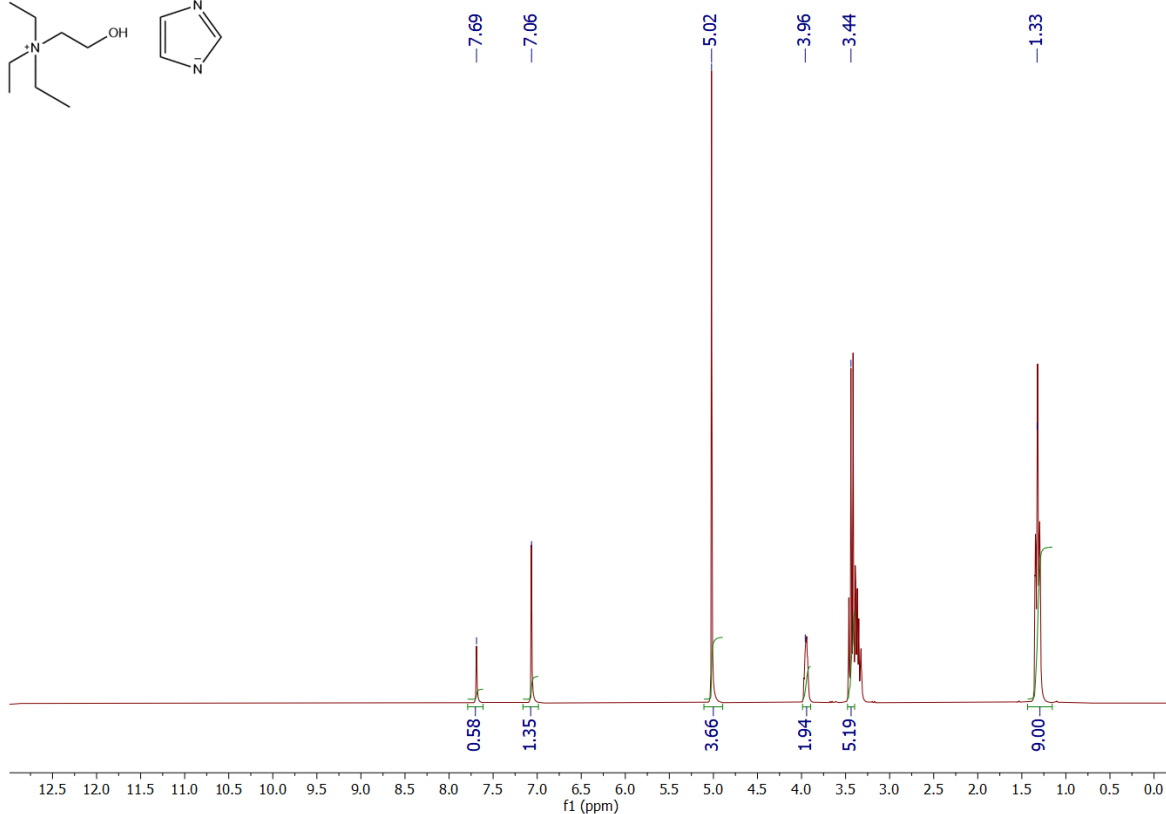
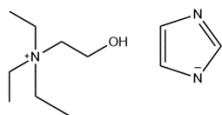


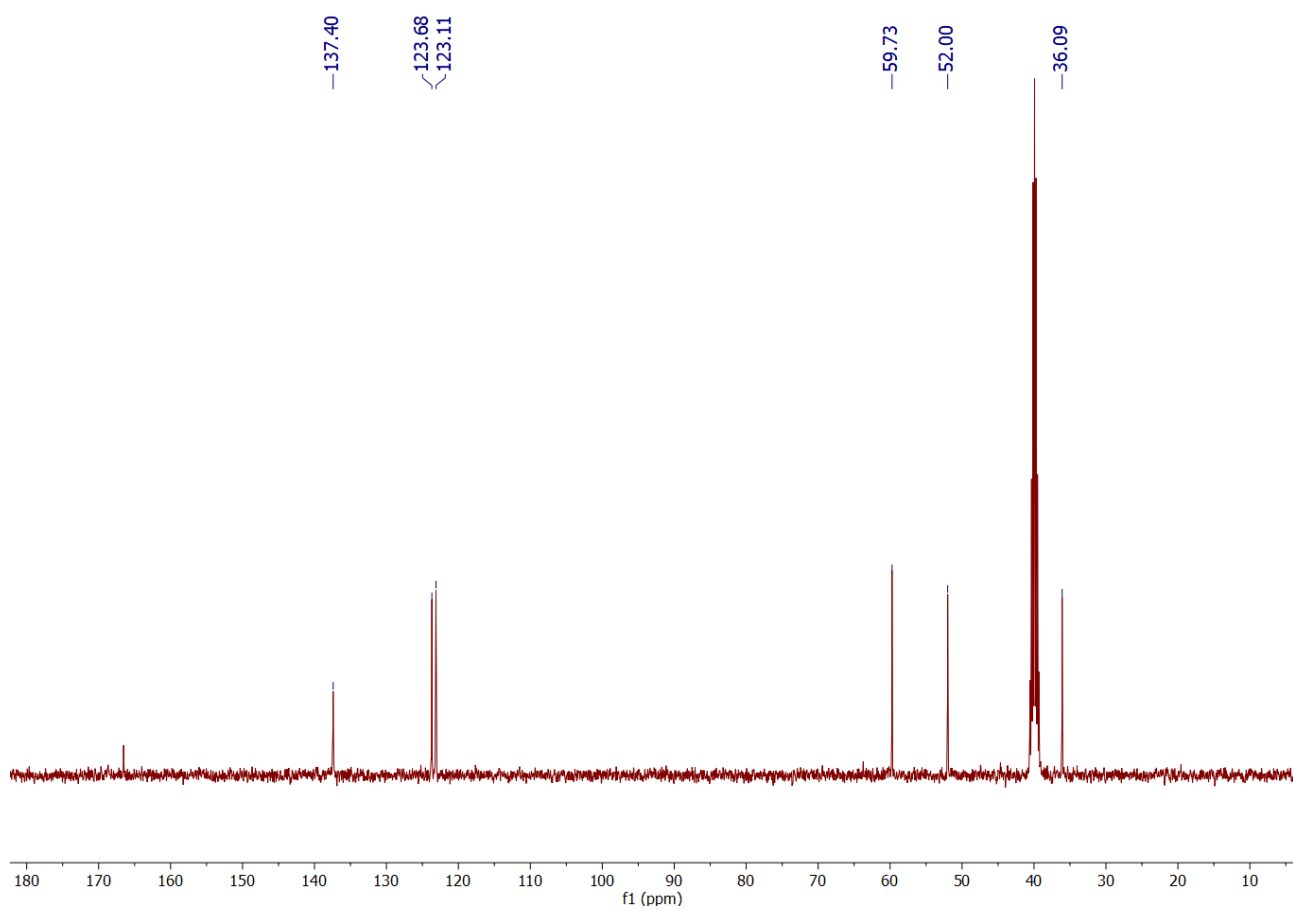
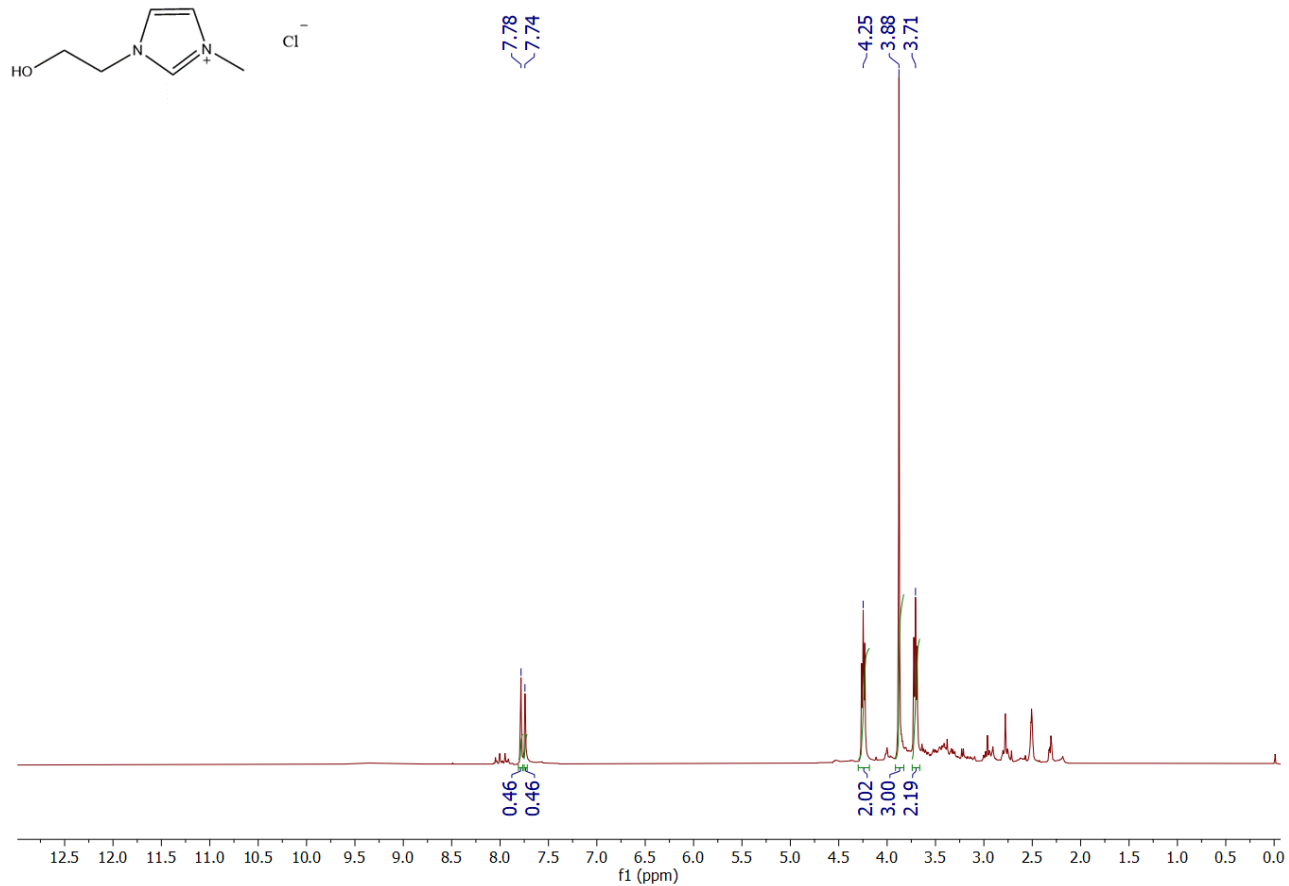
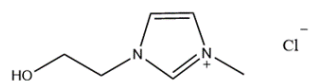


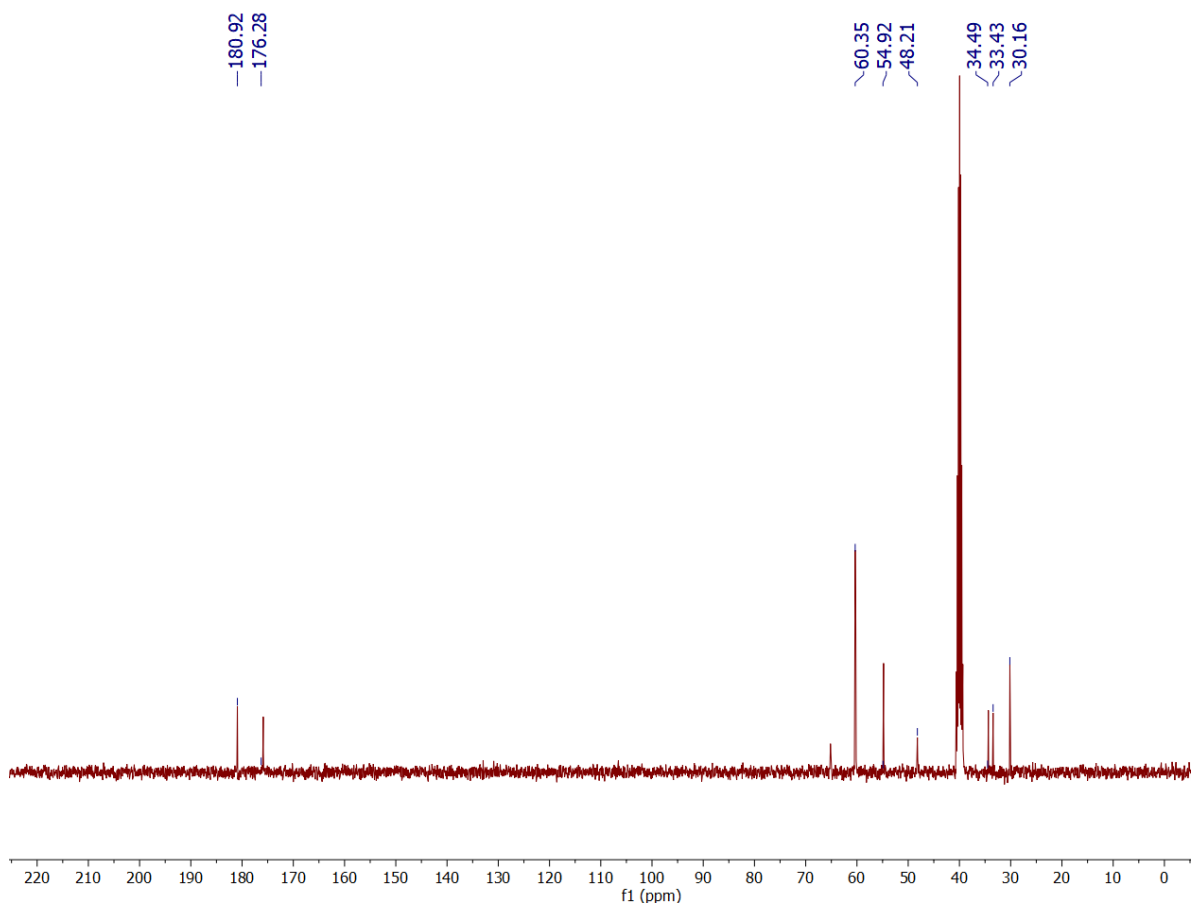
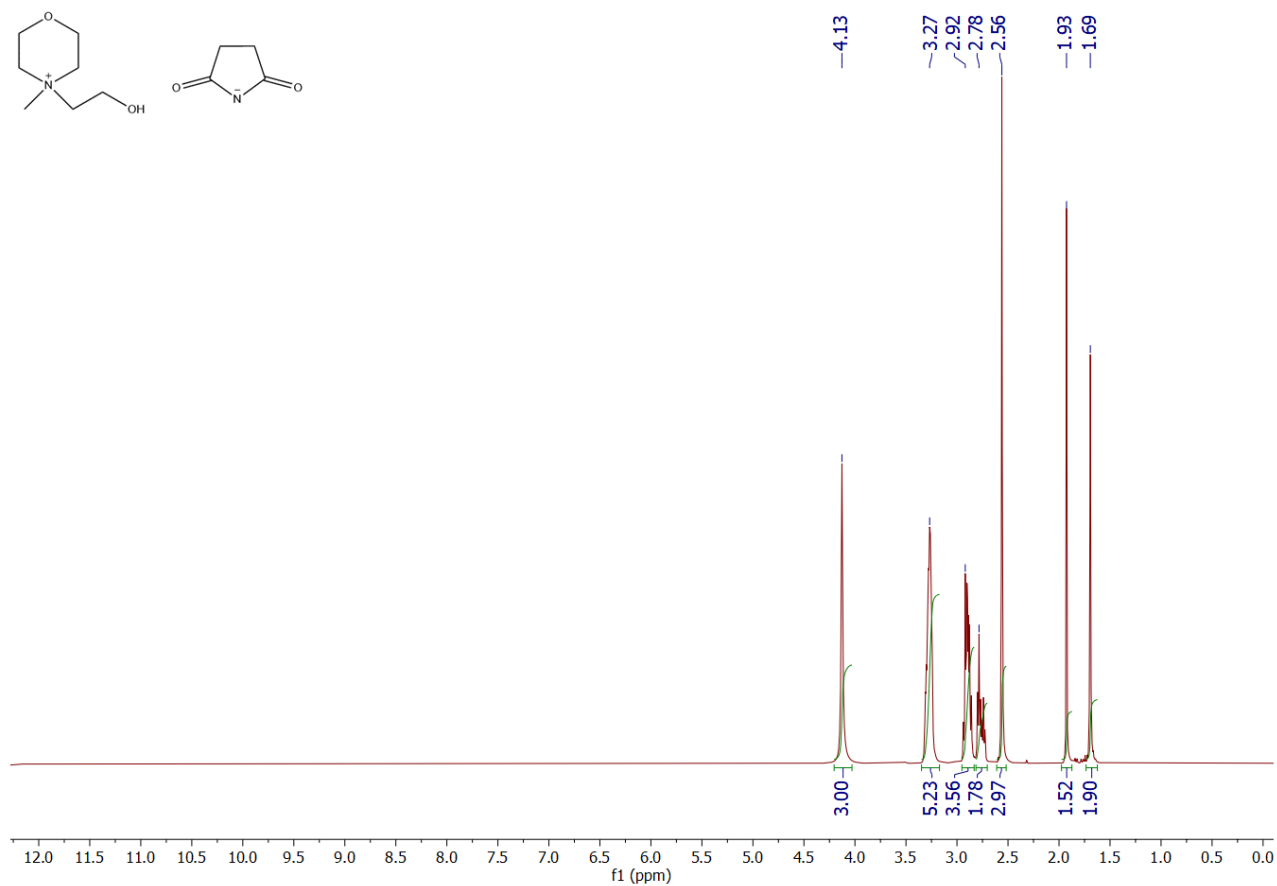
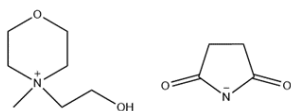


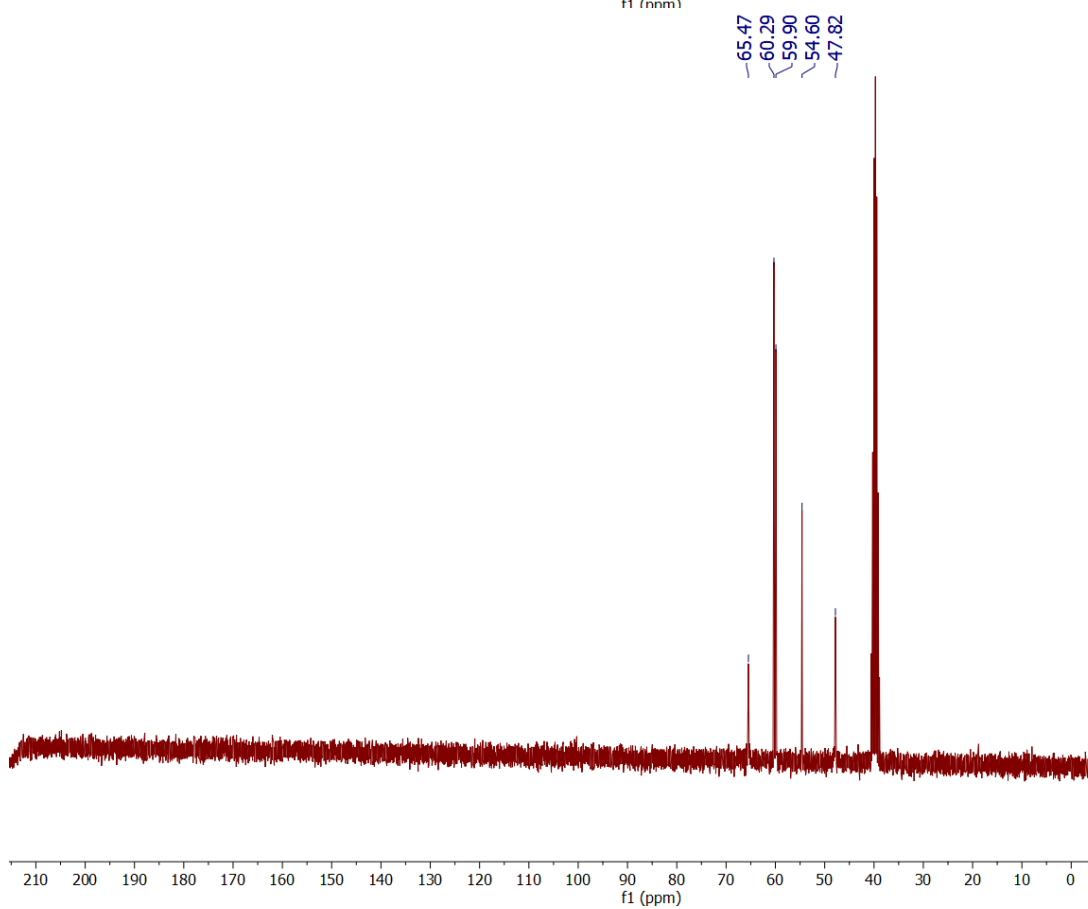
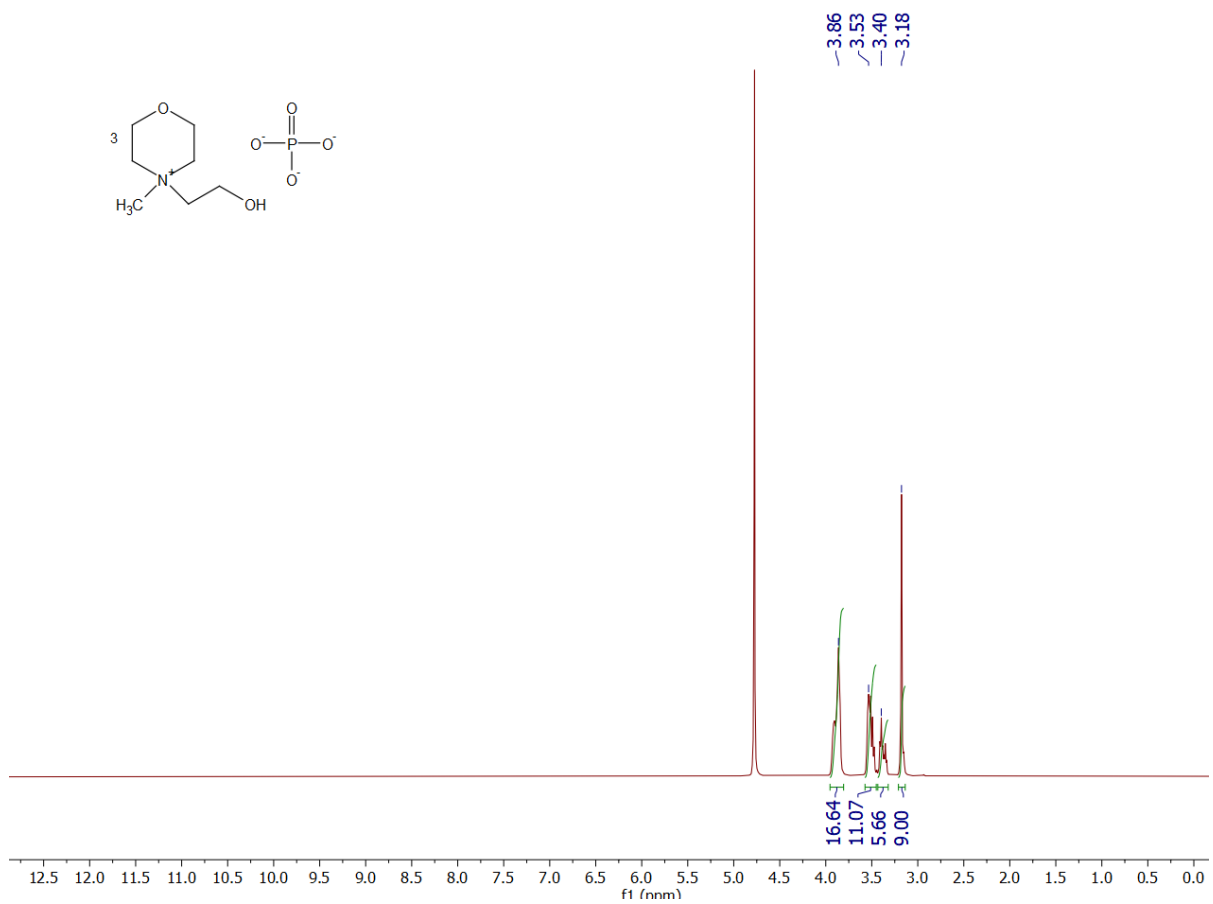












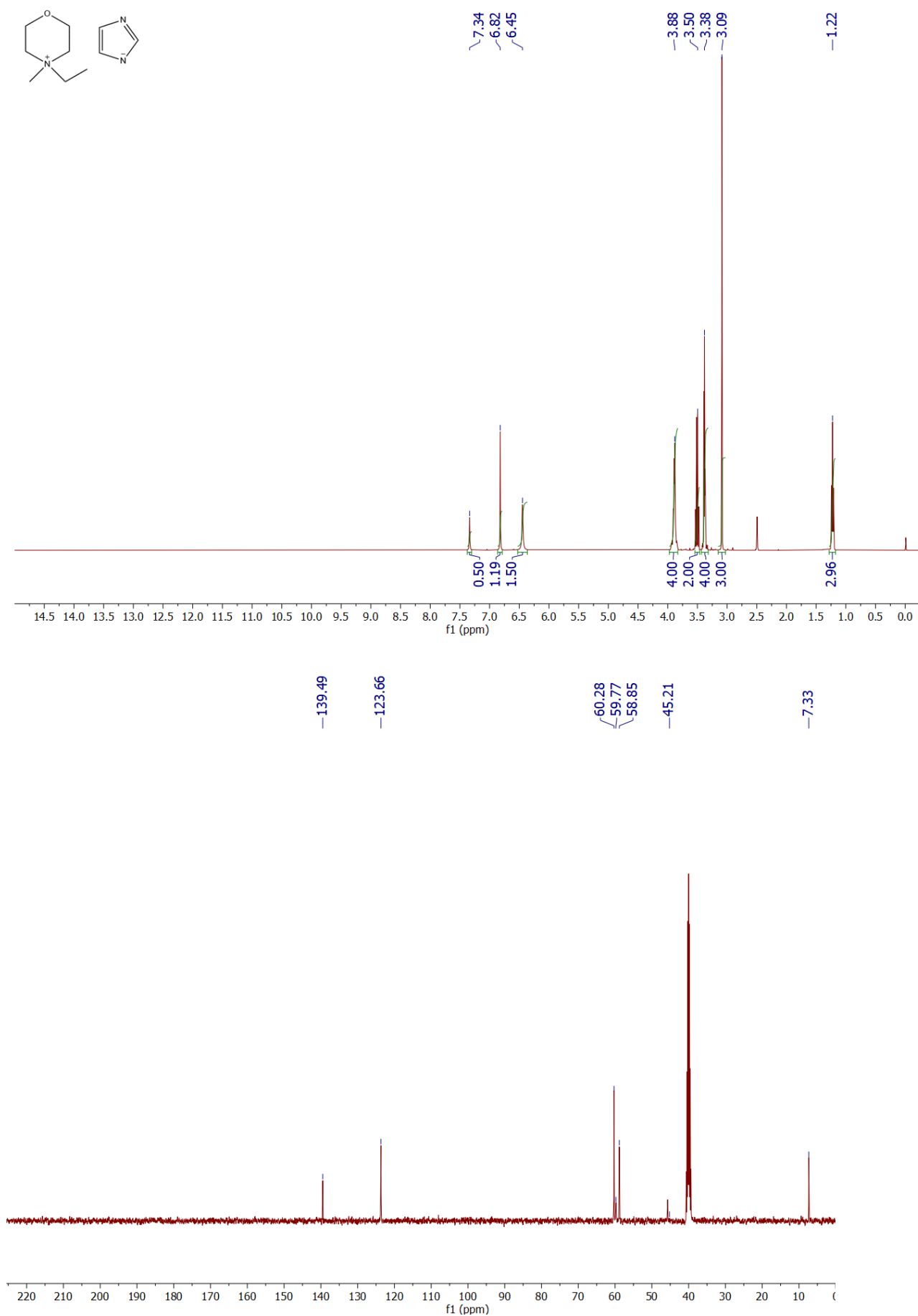


Figure S4. ^1H NMR, ^{13}C NMR spectra of catalysts.