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SUPPLEMENTARY MATERIAL

Nitrogen Containing Ionic Liquids: Biodegradation Studies and Utility in Base Mediated Reactions

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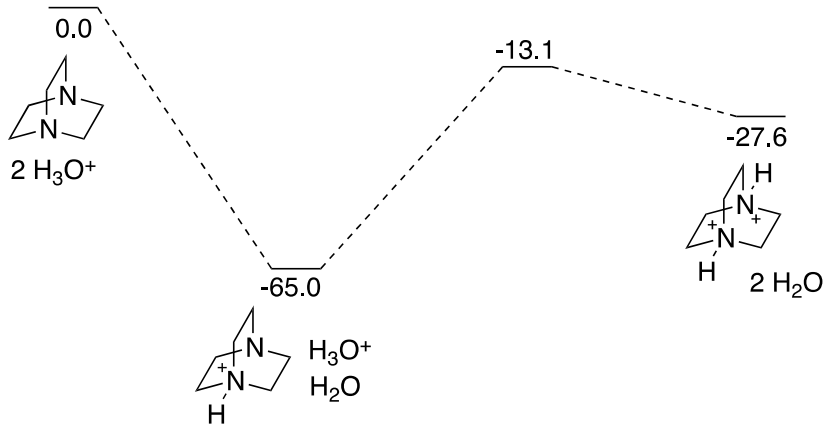
Computational Methods

All computations were conducted with the Spartan'10 and Gaussian 09 (Revision C.01) computational software packages.[1] Initial stationary point searches were carried out with the semiempirical AM1 method.[2] The lowest energy conformers of **16**, **16-H**$^+$, **17**, and **17-H**$^+$ were located via an AM1 conformational search. These AM1 optimized structures were then used as starting points for geometry optimization at the B3LYP[3]/6-31G* level. These DFT optimized structures were then used as starting points for further geometry optimization at the B3LYP/6-311G* level, followed by the B3LYP/6-311++G** level. Vibrational analyses were carried out to confirm the nature of all stationary points and to calculate the thermal corrections (enthalpy and entropy) for 298 K, 1 atm, gas phase. An archive of atomic coordinates in the .pdb file format is provided as Supporting Information.

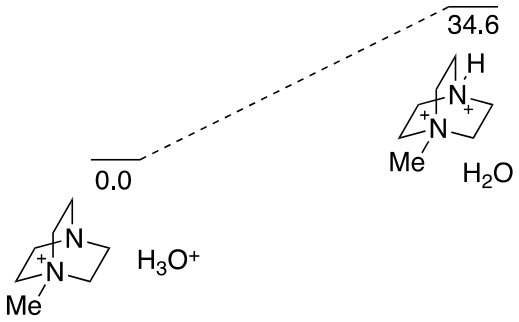
Computational Details



Computations for the production of $DABCOH_2^{2+}$ from the reaction of DABCO and H_3O^+ were performed at the B3LYP/6-311++G** level. The H°, zero-point energy (ZPE), S°, and G° values are collected in Table S1. Energies in the reaction coordinate are reported as Gibbs energy in kcal/mol.

Table S1: Thermodynamic data for Figure S1.

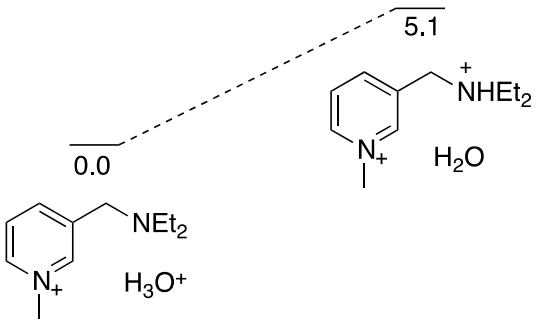
	H° (Hartree)	ZPE (Hartree)	S° (cal/mol•K)	G° (Hartree)
DABCO	-345.231570	0.182497	79.327	-345.269261
$DABCOH^+$	-345.597421	0.198084	80.549	-345.635692
$DABCOH^+$ TS	-422.221395	0.233764	96.847	-422.267410
$DABCOH_2^{2+}$	-345.797422	0.212717	80.213	-345.835534
H_3O^+	-76.693059	0.034307	48.436	-76.716072
H_2O	-76.433469	0.021282	45.088	-76.454892



Computations for the production of **15-H**$^+$ from the reaction of **15** and H_3O^+ were performed at the B3LYP/6-311++G** level. The H°, zero-point energy (ZPE), S°, and G° values are collected in Table S2. Energies in the reaction coordinate are reported as Gibbs energy in kcal/mol.

Table S2: Thermodynamic data for Figure S2.

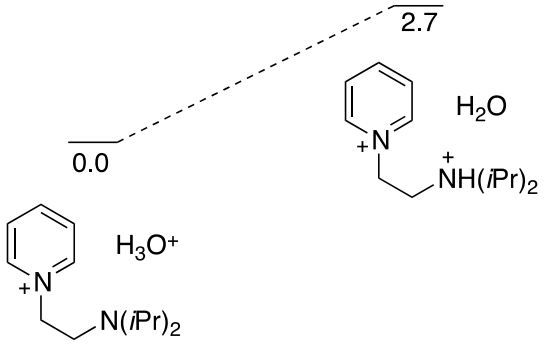
	H° (Hartree)	ZPE (Hartree)	S° (cal/mol•K)	G° (Hartree)
15	-384.891784	0.225330	87.317	-384.933271
15-H$^+$	-385.098765	0.240147	85.286	-385.139287
H_3O^+	-76.693059	0.034307	48.436	-76.716072
H_2O	-76.433469	0.021282	45.088	-76.454892



The ΔG° for protonation of **16** with H_3O^+ was calculated at the B3LYP/6-311++G** level. The protonation transition state was not optimized. The H°, zero-point energy (ZPE), S°, and G° values are collected in Table S3. Energies in the reaction coordinate are reported as Gibbs energy in kcal/mol.

Table S3: Thermodynamic data.

	H° (Hartree)	ZPE (Hartree)	S° (cal/mol•K)	G° (Hartree)
16	-539.722391	0.286867	122.449	-539.780571
16-H$^+$	-539.975342	0.301612	122.752	-540.033665
H_3O^+	-76.693059	0.034307	48.436	-76.716072
H_2O	-76.433469	0.021282	45.088	-76.454892



The ΔG° for protonation of **17** with H_3O^+ was calculated at the B3LYP/6-311++G** level. The protonation transition state was not optimized. The H°, zero-point energy (ZPE), S°, and G° values are collected in Table S4. Energies in the reaction coordinate are reported as Gibbs energy in kcal/mol.

Table S4: Thermodynamic data.

	H° (Hartree)	ZPE (Hartree)	S° (cal/mol•K)	G° (Hartree)
17	-618.311560	0.344198	127.782	-618.372273
17-H$^+$	-618.566220	0.358198	132.363	-618.629110
H_3O^+	-76.693059	0.034307	48.436	-76.716072
H_2O	-76.433469	0.021282	45.088	-76.454892

NMR Spectra

Figure 1A. ^{1}H NMR of IL **1.**

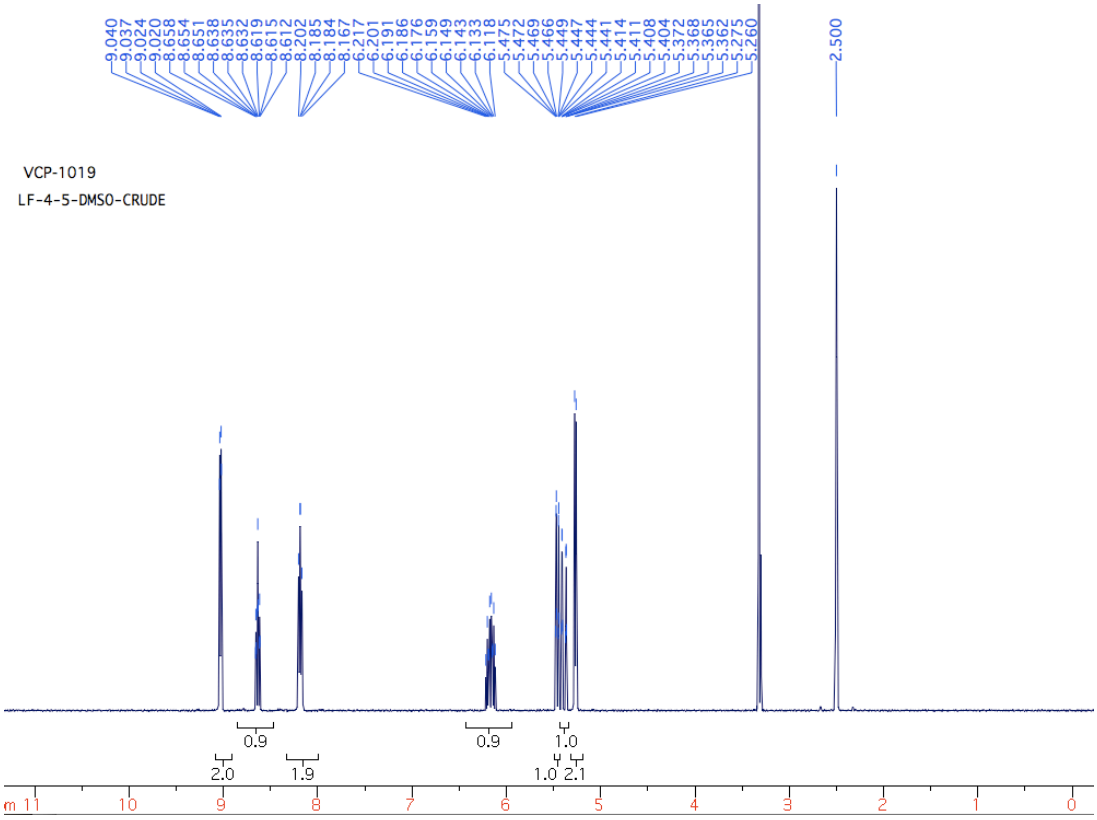


Figure 1B. ^{13}C NMR of IL **1.**

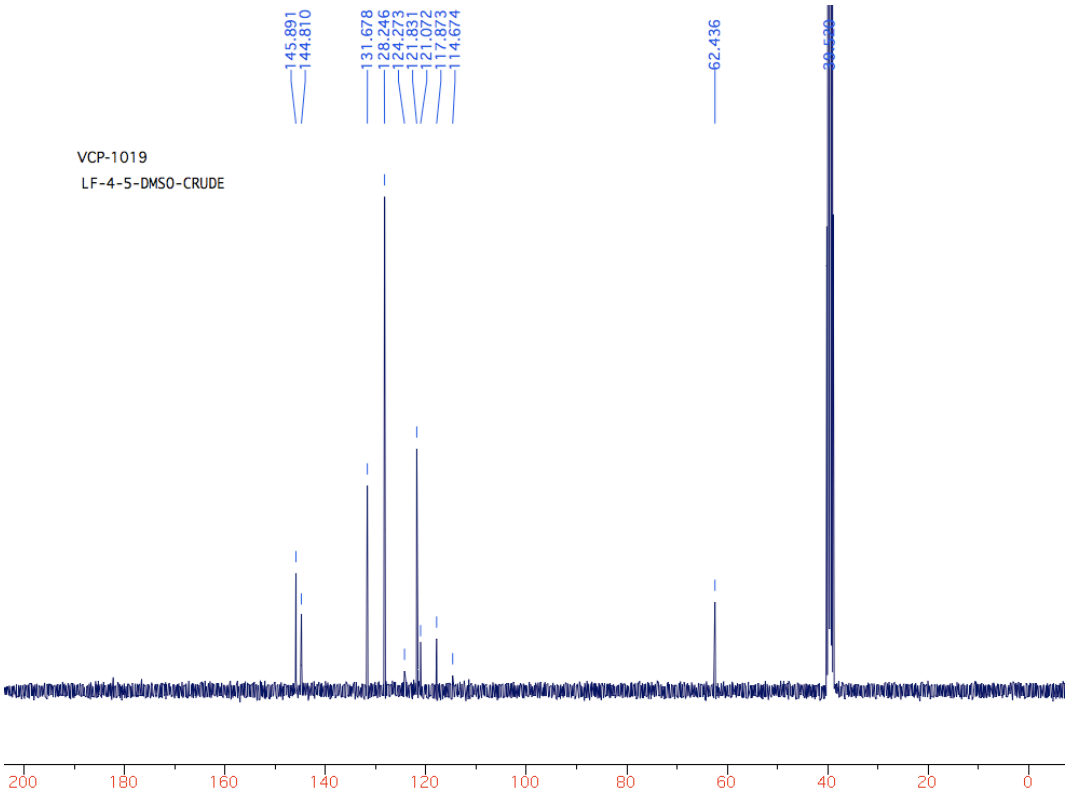


Figure 2A. ^{1}H NMR of IL **2.**

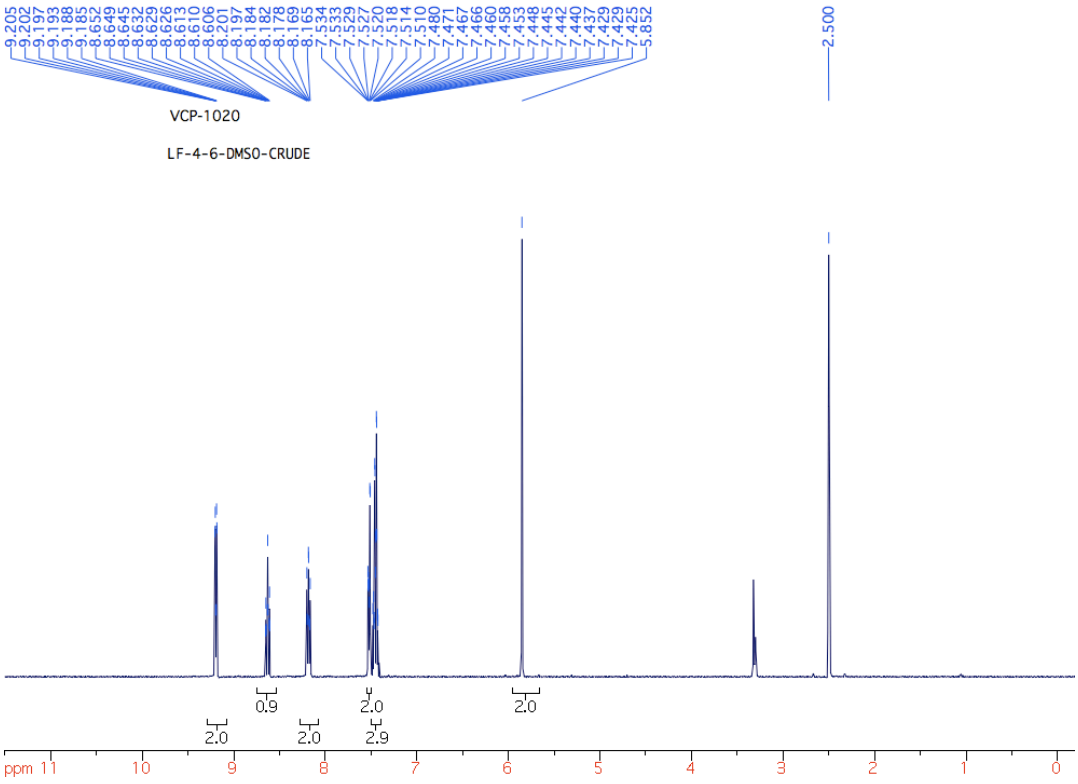


Figure 2B. ^{13}C NMR of IL **2.**

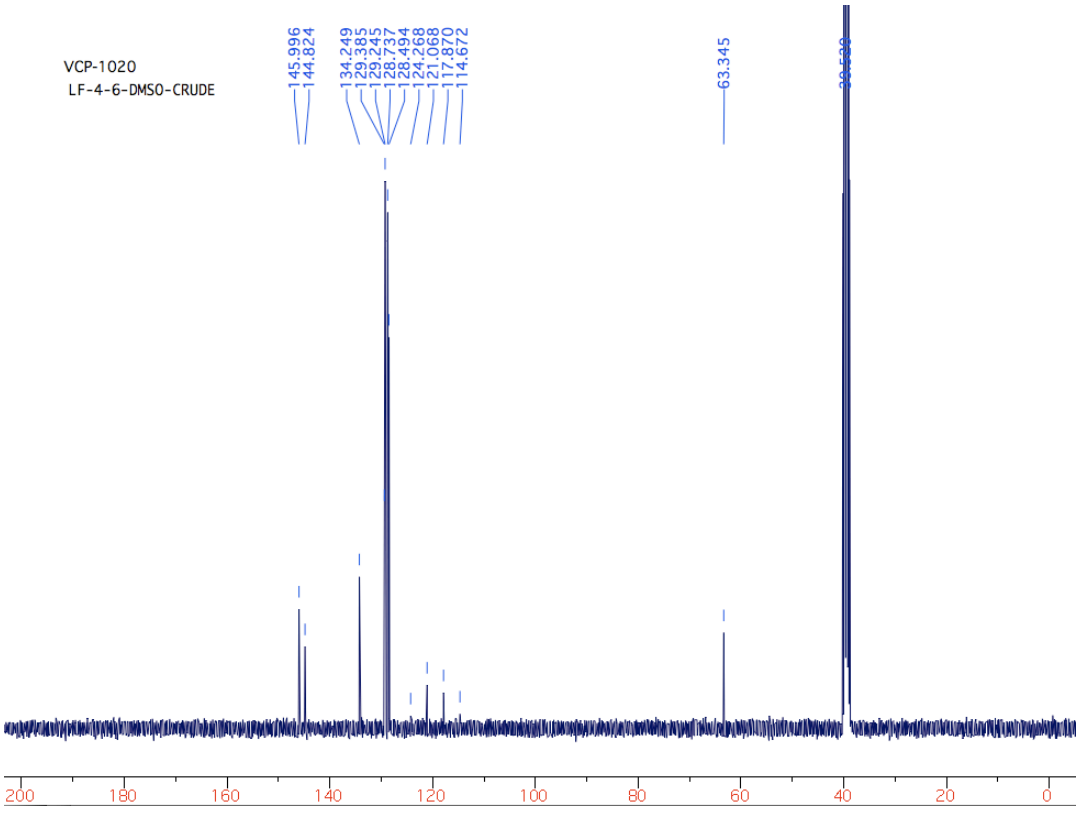


Figure 3A. ^{1}H NMR of IL **3.**

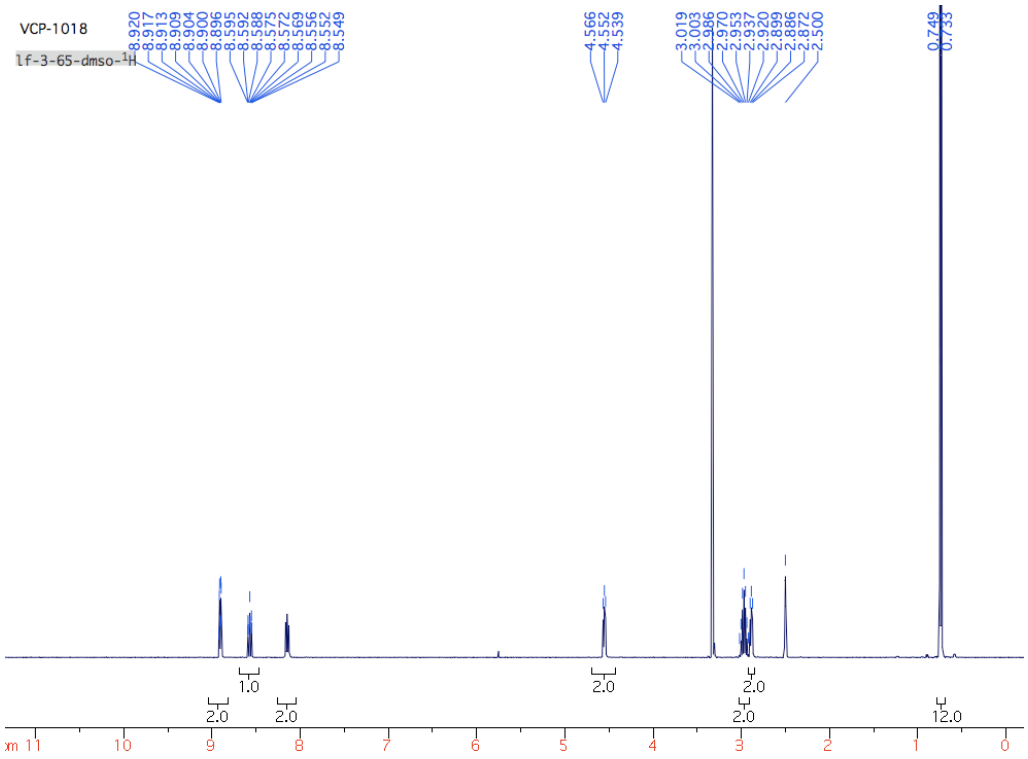


Figure 3B. ^{13}C NMR of IL **3.**

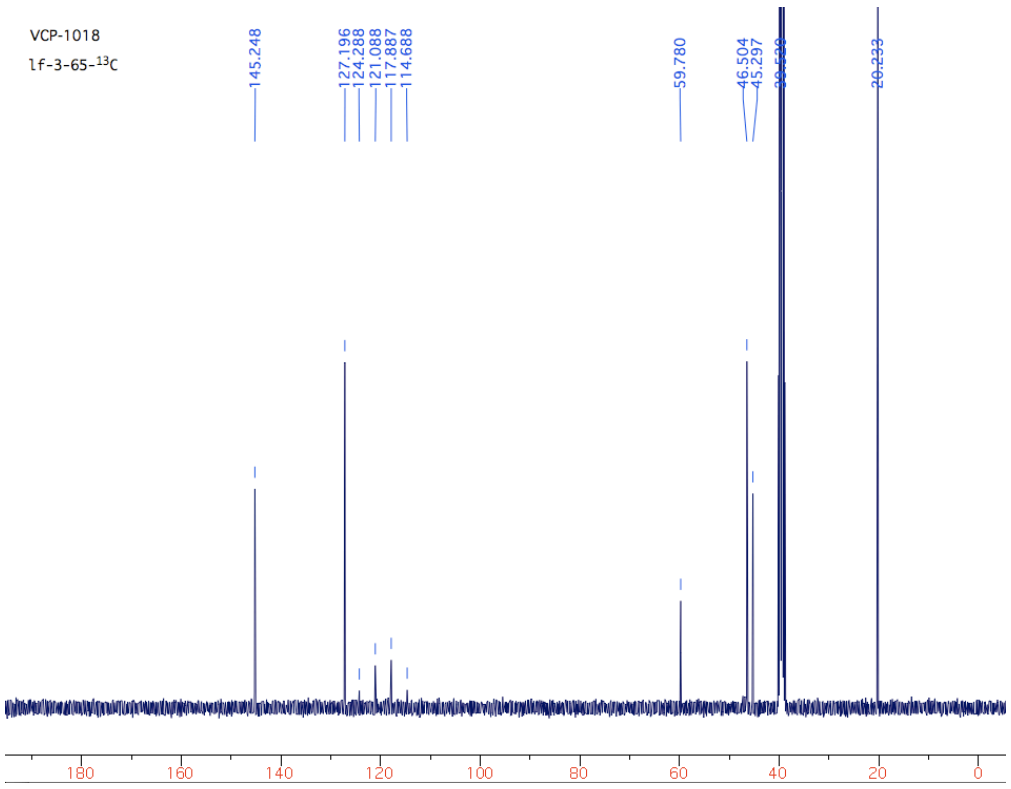


Figure 4A. ^{1}H NMR of IL **4.**

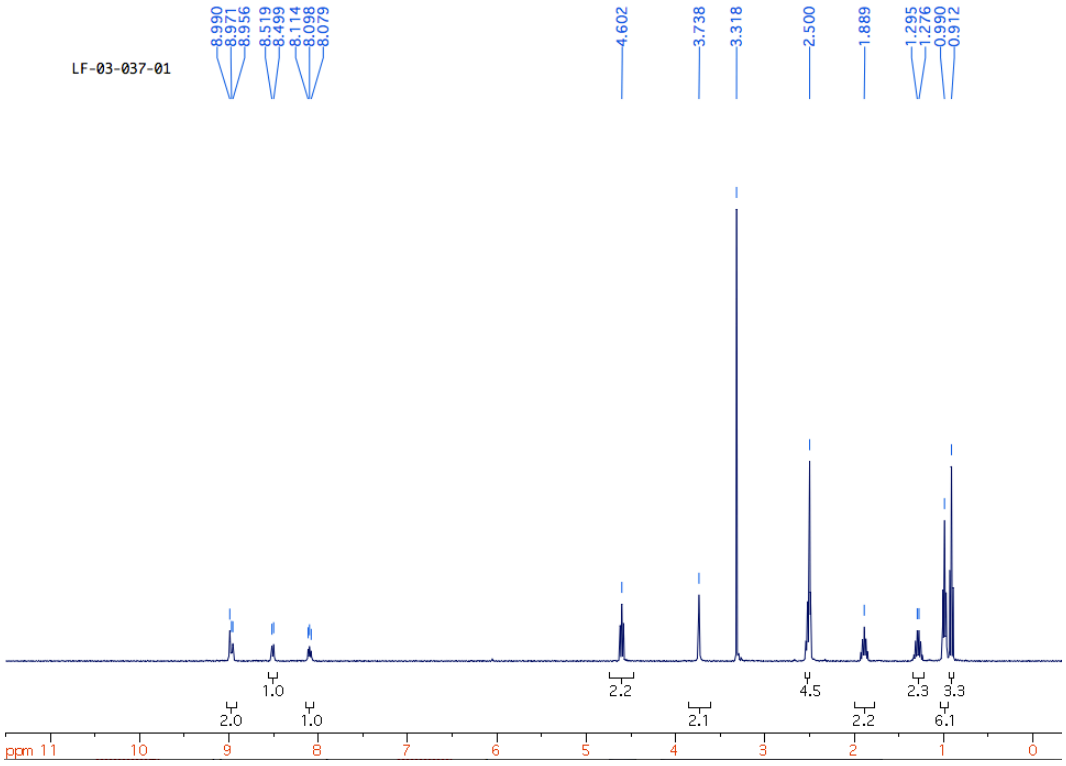


Figure 4B. ^{13}C NMR of IL **4.**

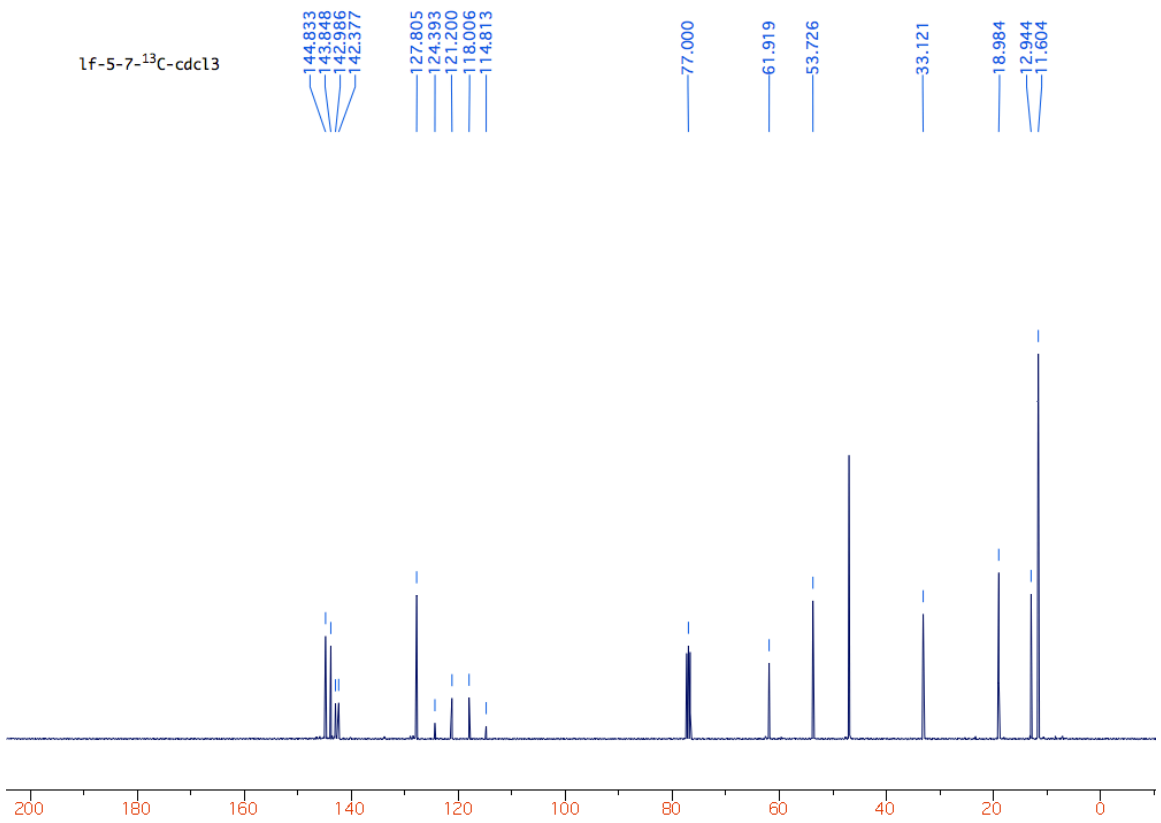


Figure 5A. ^{1}H NMR of IL **5.**

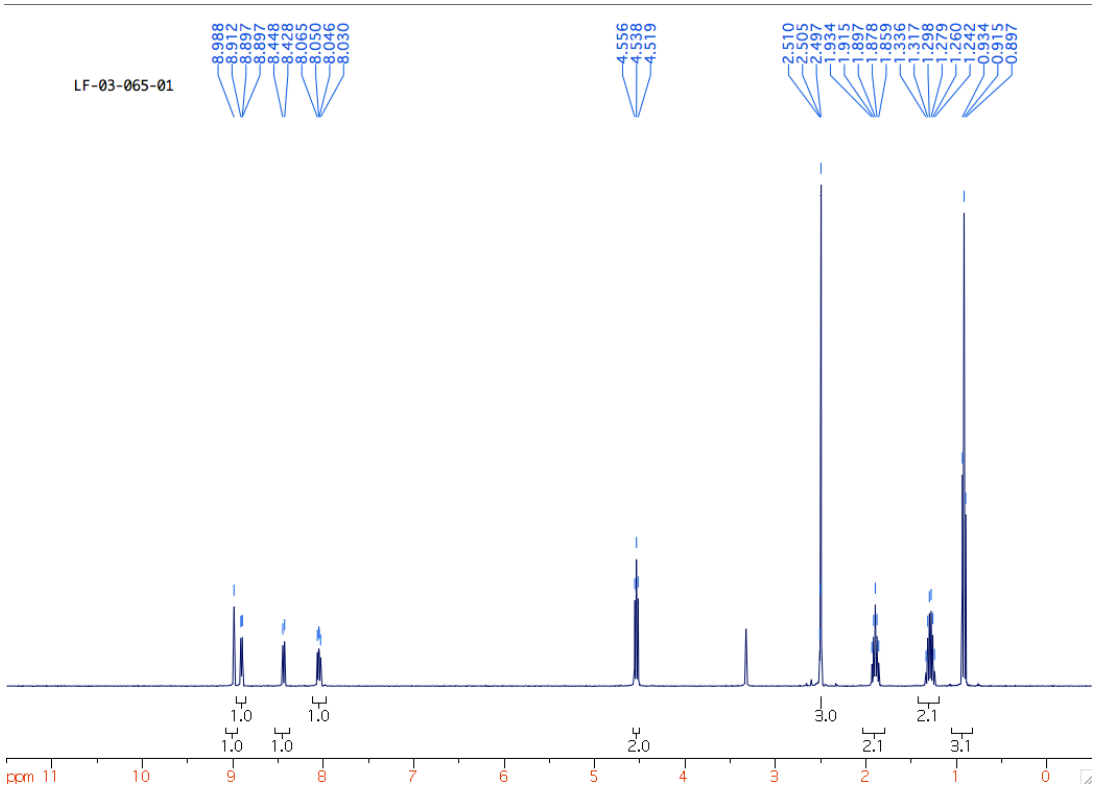


Figure 5B. ^{13}C NMR of IL **5.**

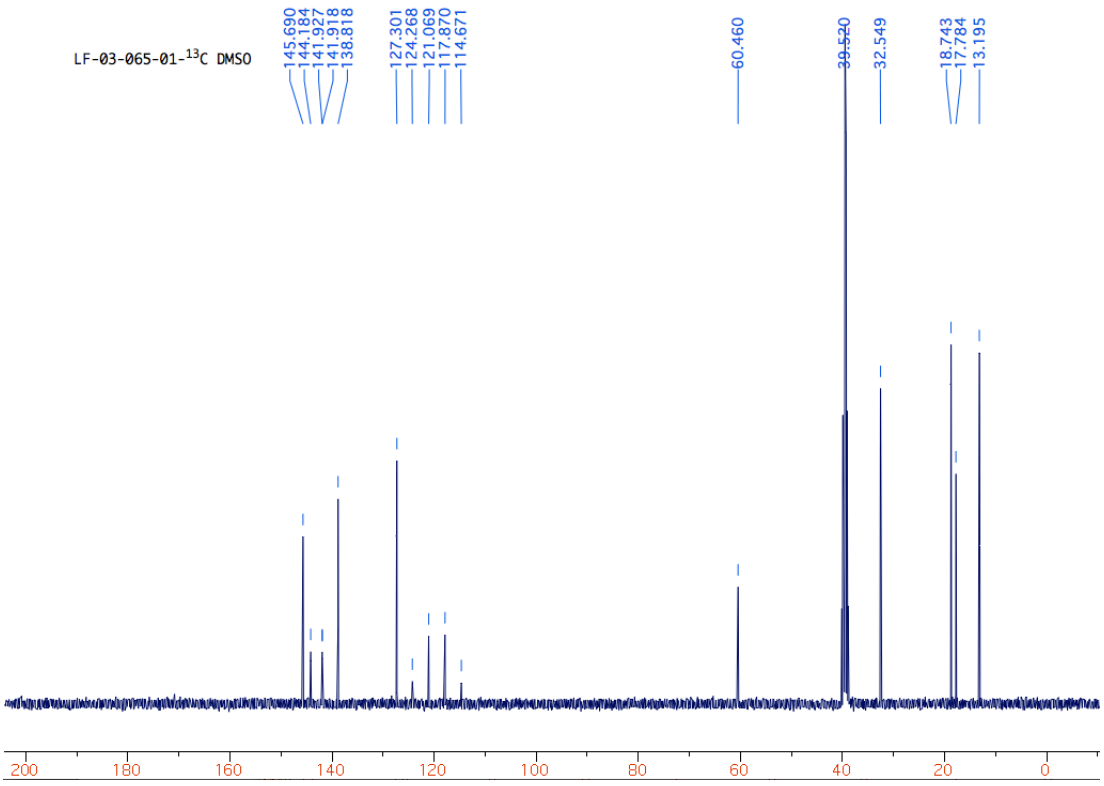


Figure 6A. ^{1}H NMR of IL **6.**

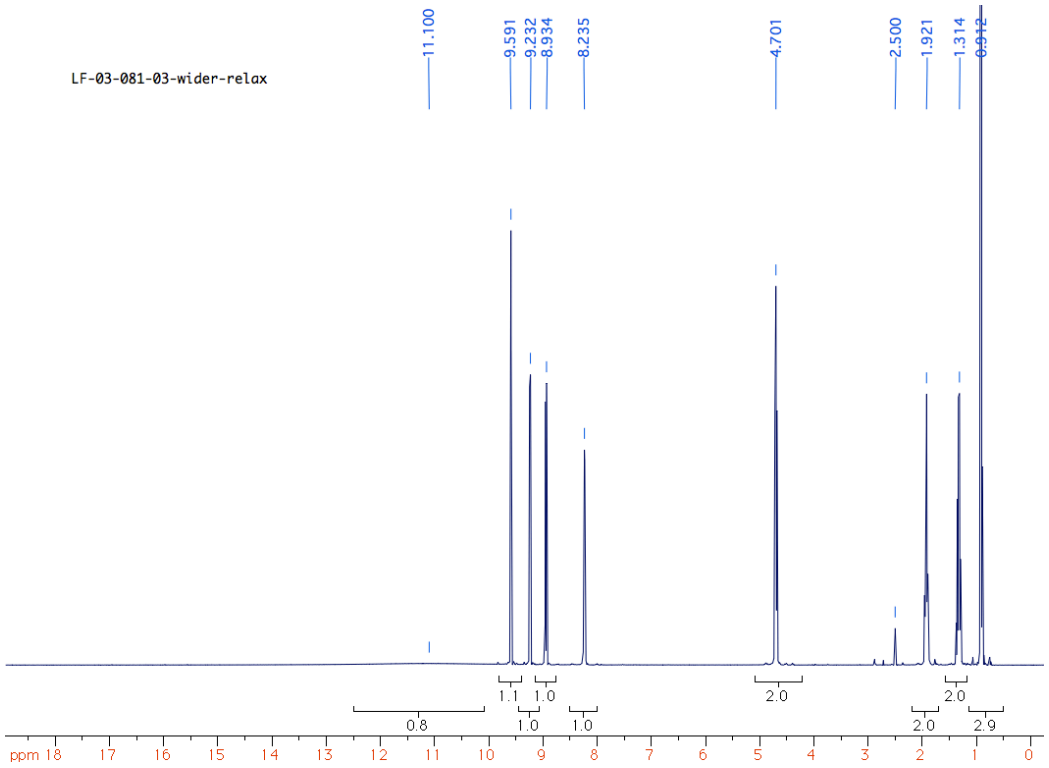


Figure 6B. ^{13}C NMR of IL **6.**

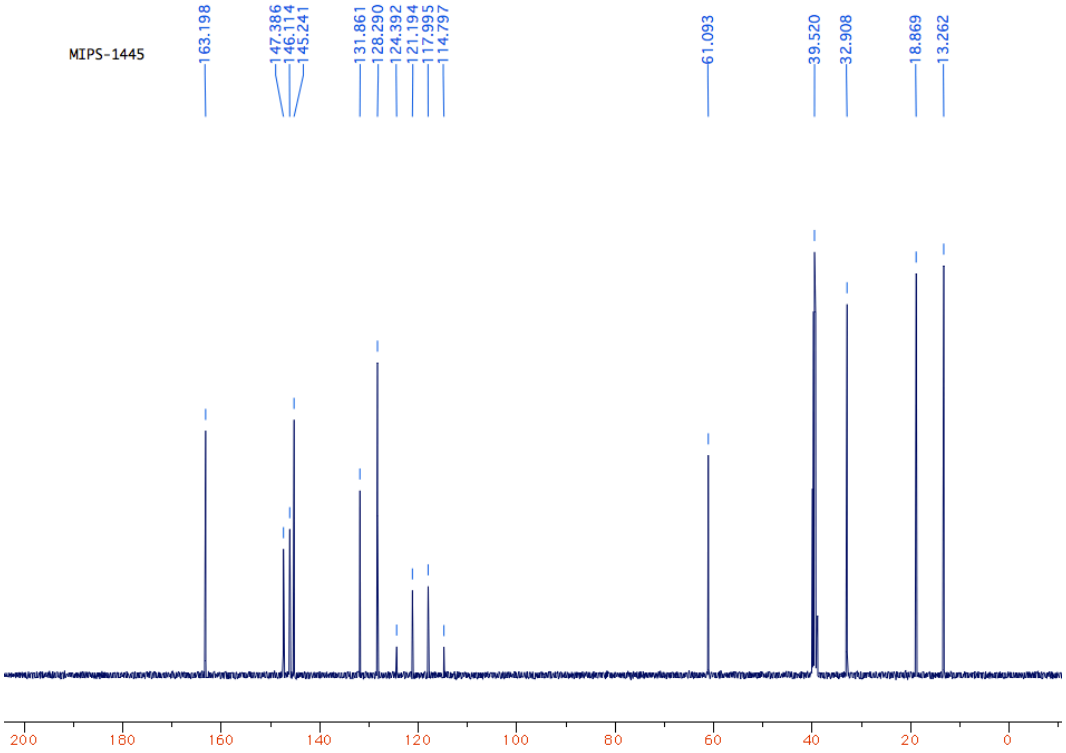


Figure 7A. ^{1}H NMR of IL **7.**

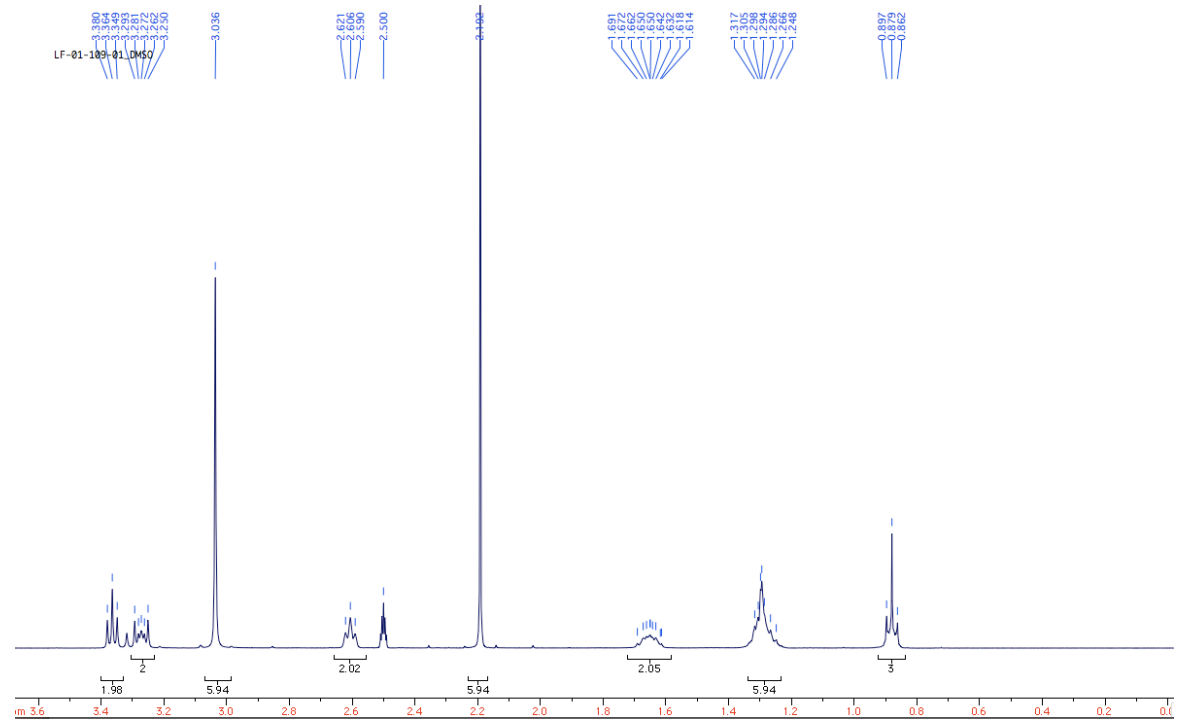


Figure 7B. ^{13}C NMR of IL **7.**

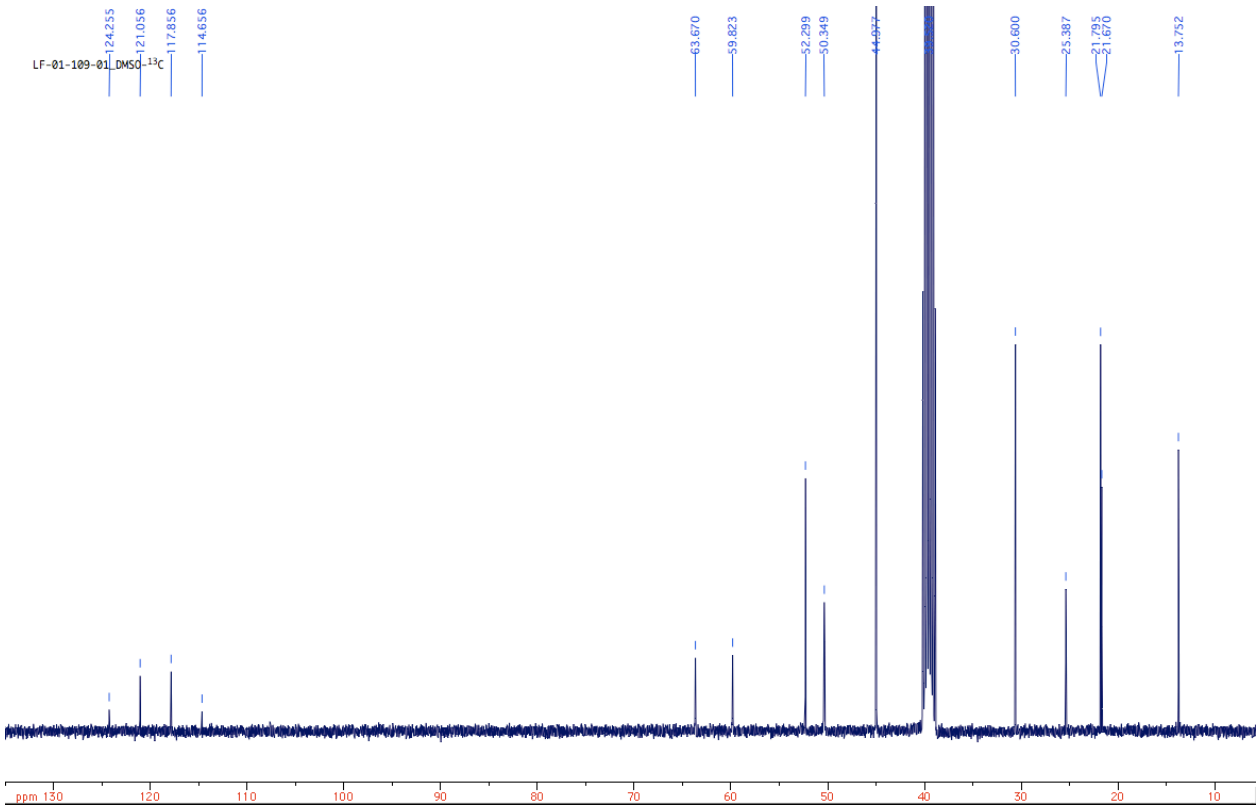


Figure 8A. ^{1}H NMR of IL **8.**

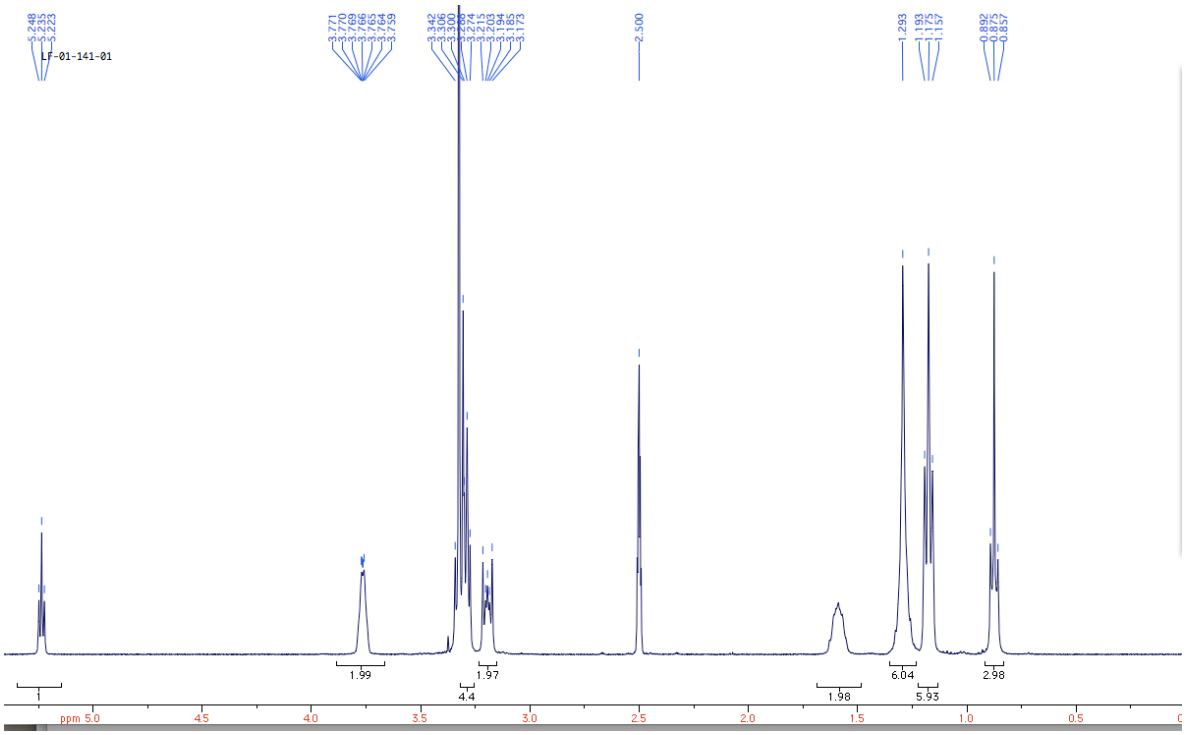


Figure 8B. ^{13}C NMR of IL **8.**

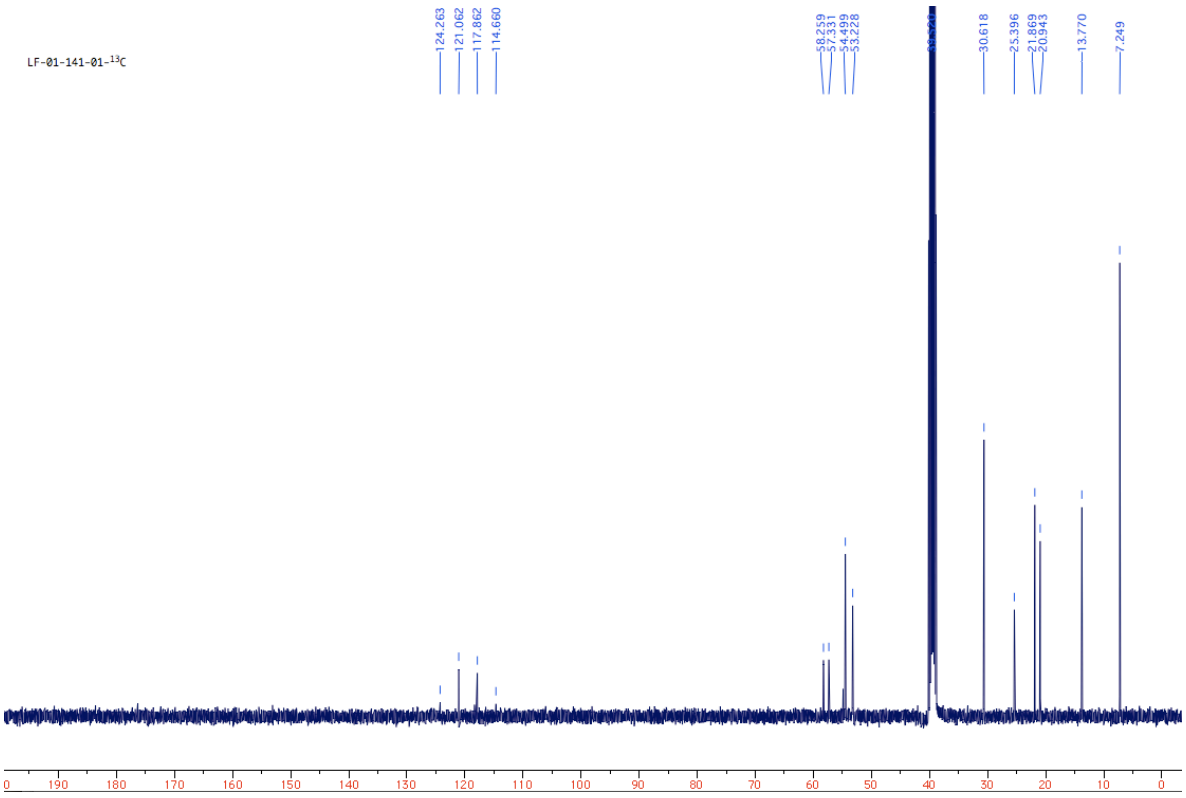


Figure 9A. ^{1}H NMR of IL **9.**

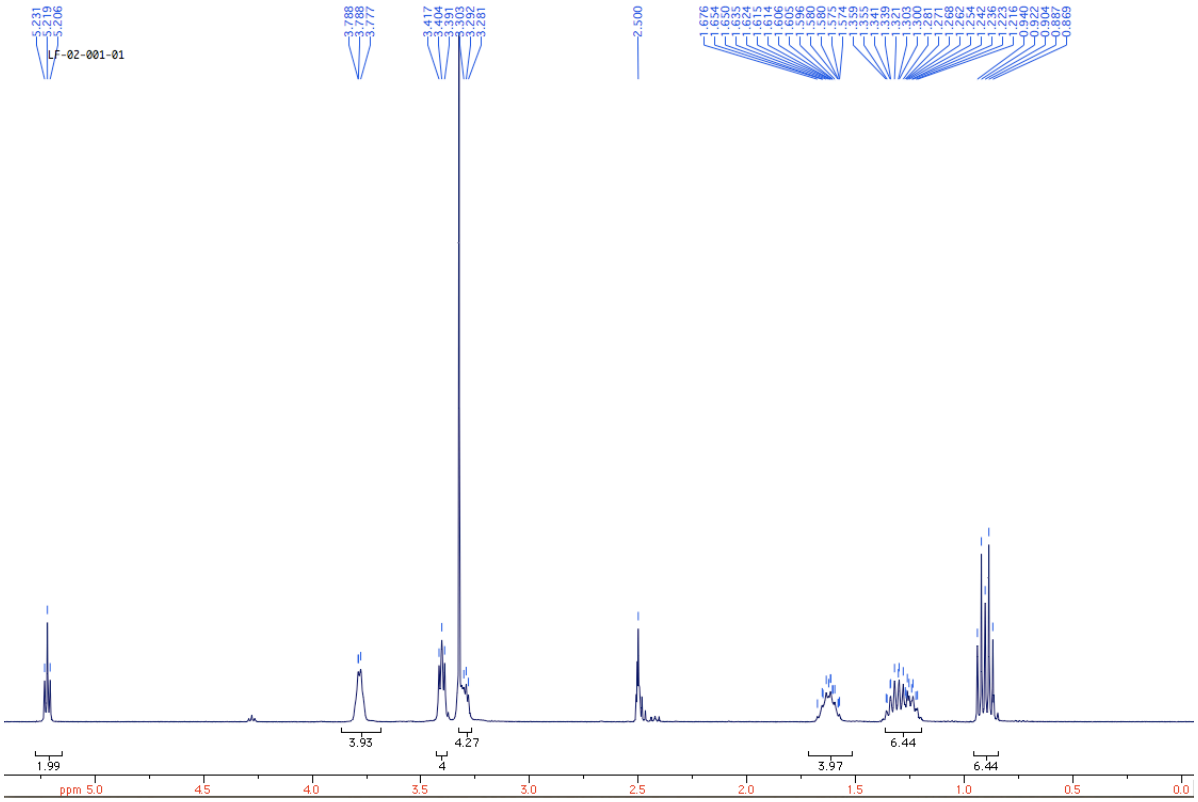


Figure 9B. ^{13}C NMR of IL **9.**

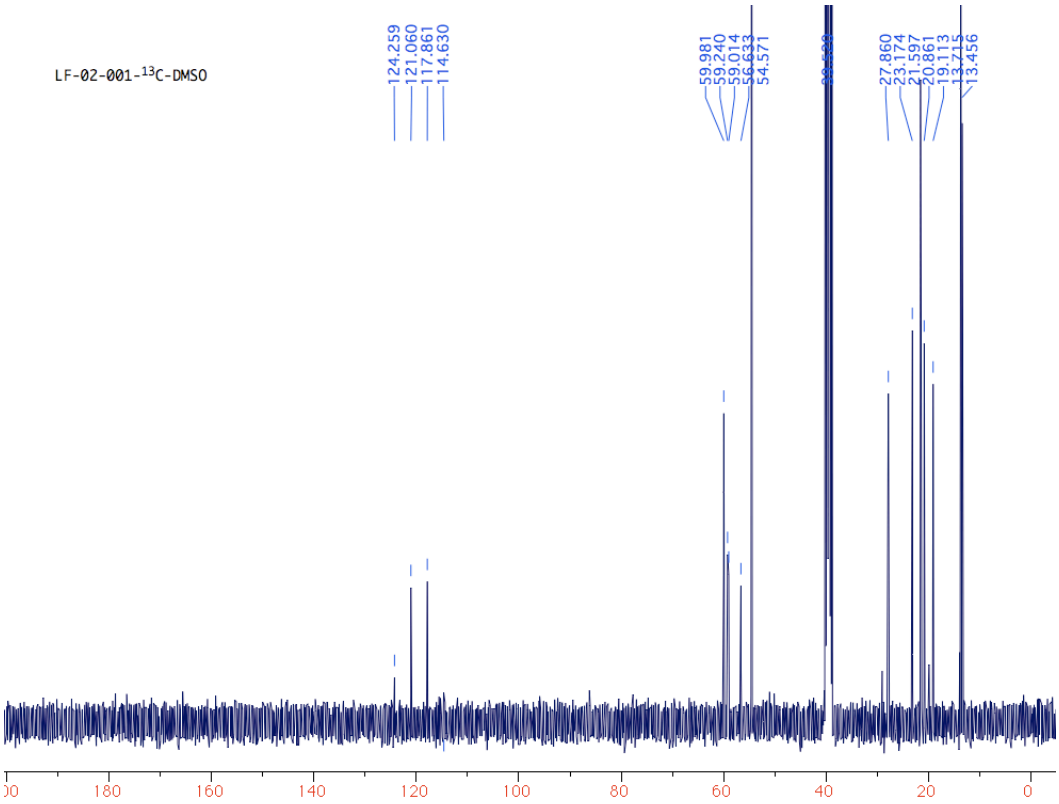


Figure 10A. ^{1}H NMR of IL **10.**

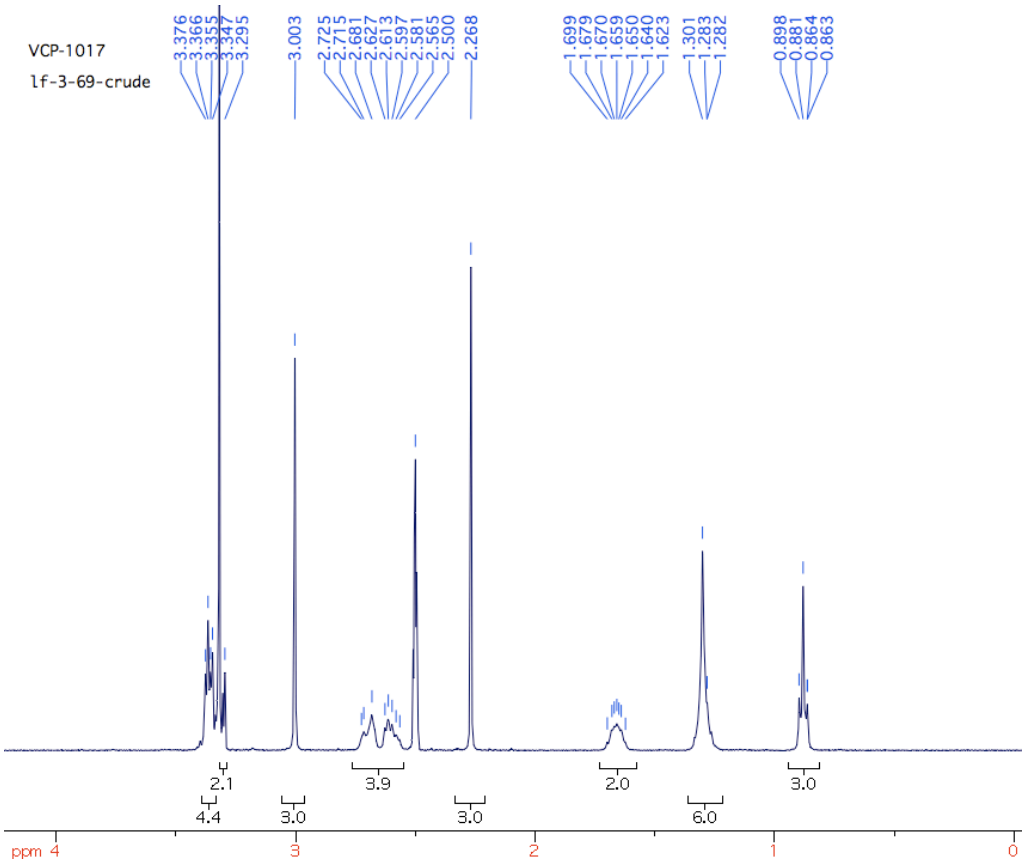


Figure 10B. ^{13}C NMR of IL **10.**

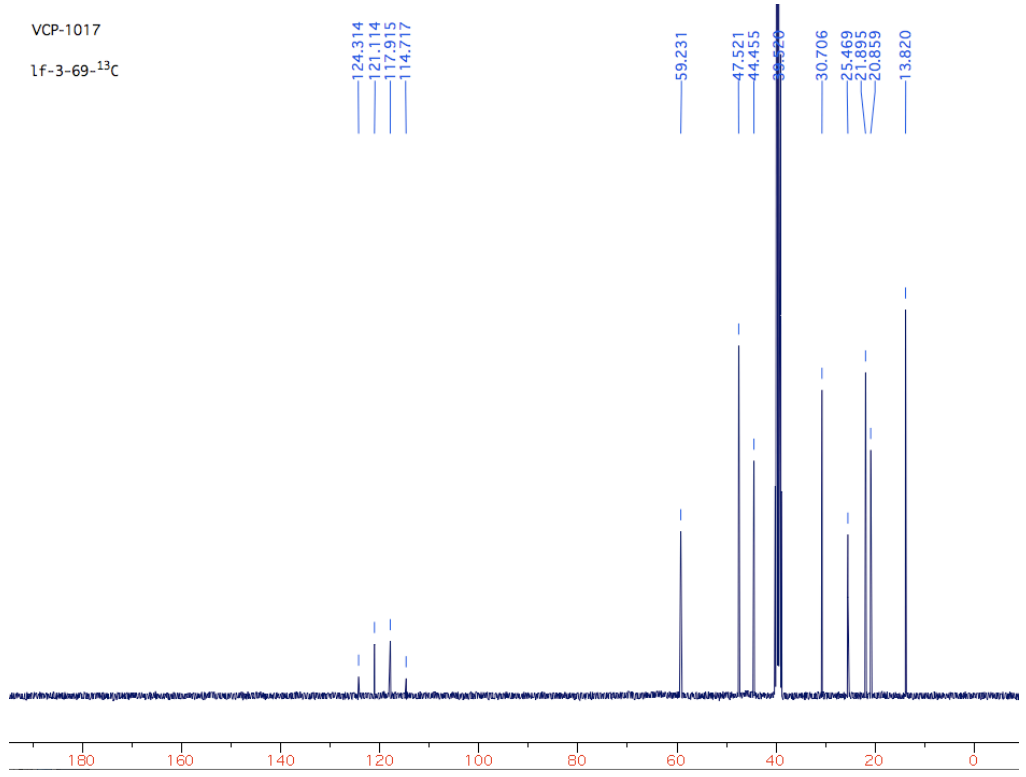


Figure 11A. ^{1}H NMR of IL **11.**

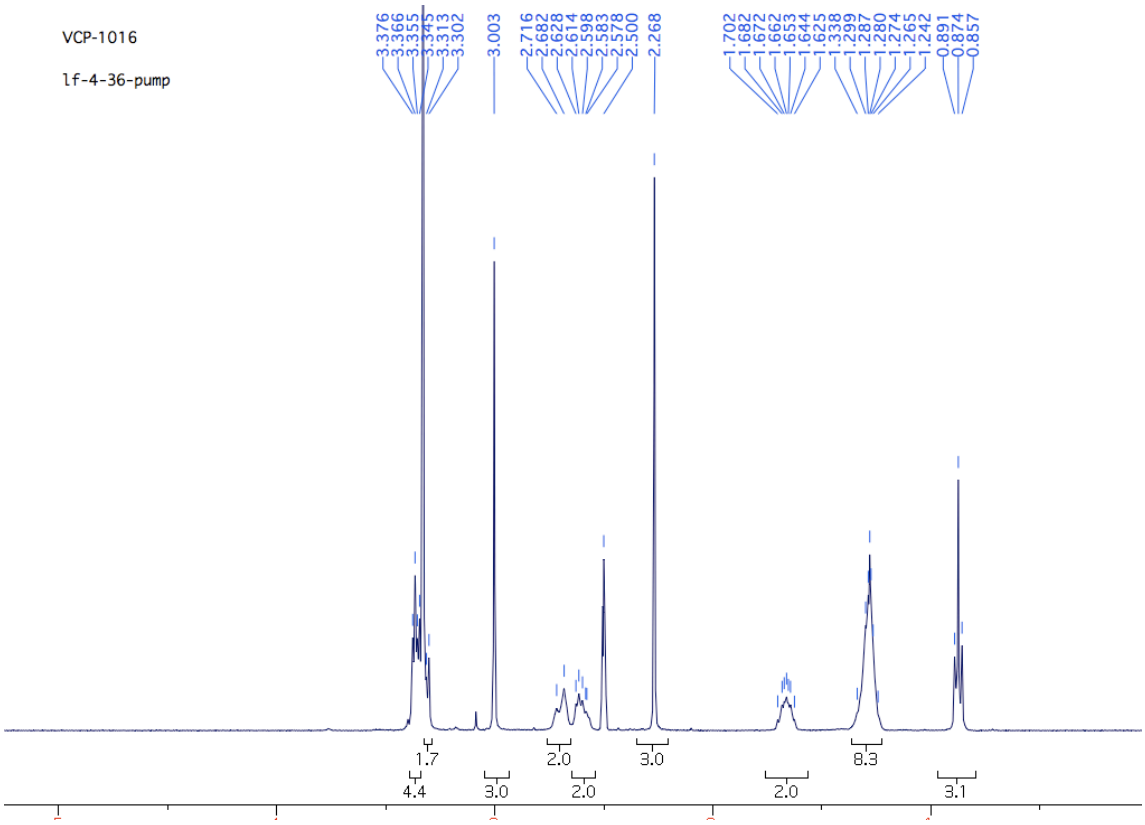


Figure 11B. ^{13}C NMR of IL **11.**

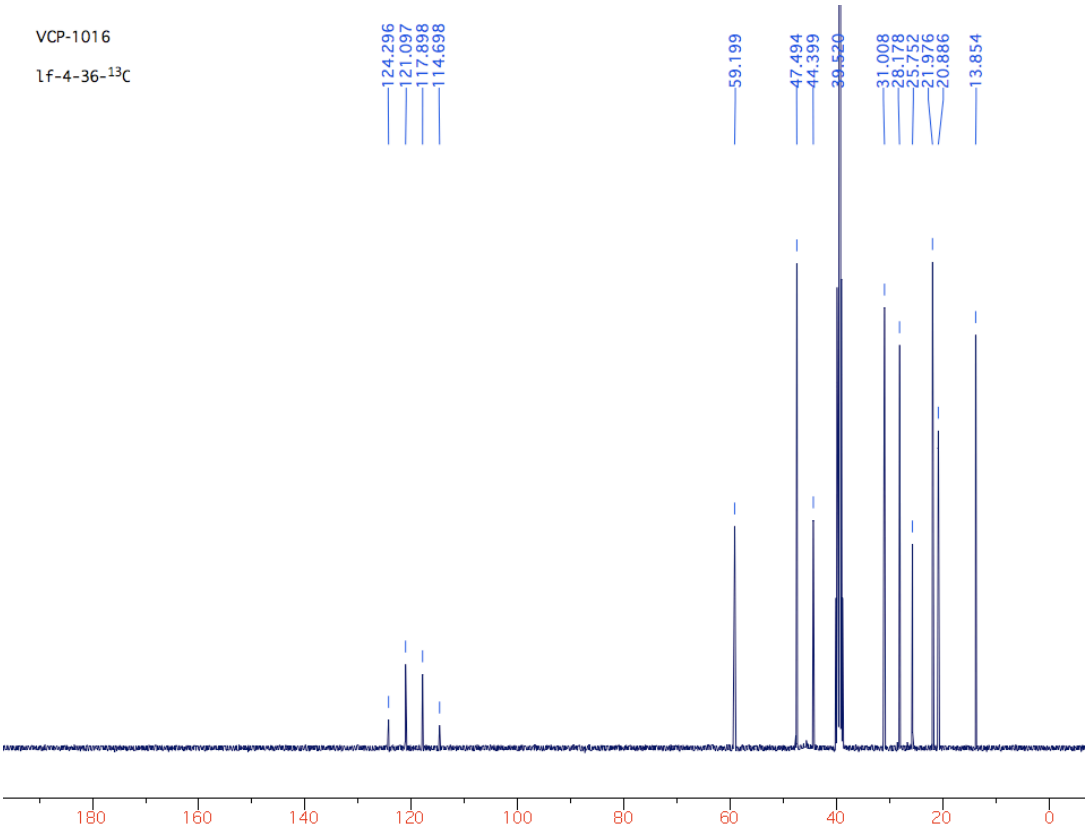


Figure 12A. ^{1}H NMR of IL **12.**

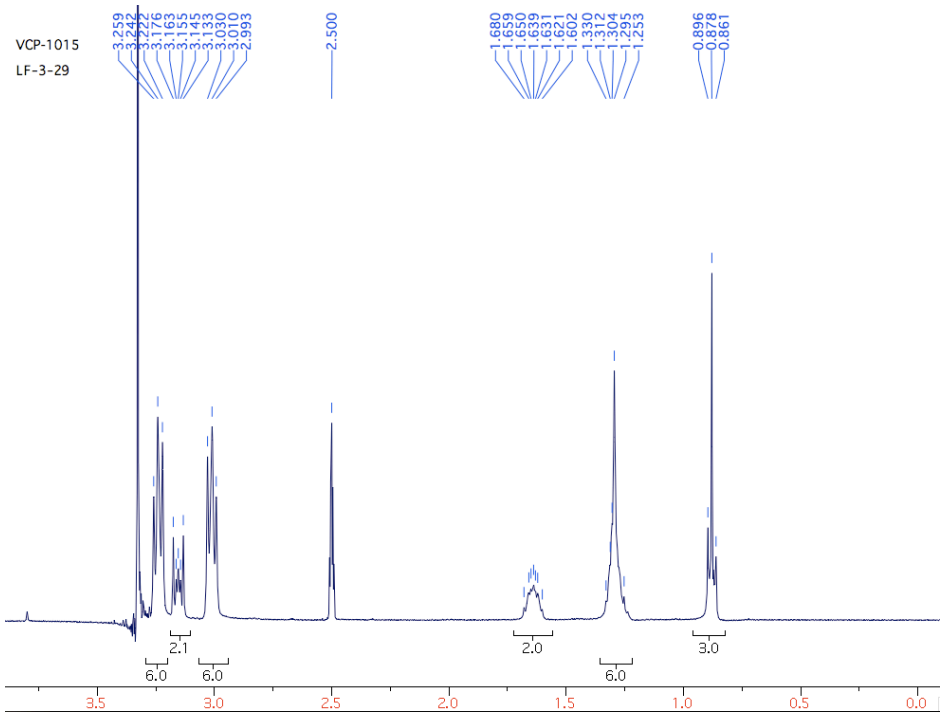


Figure 12B. ^{13}C NMR of IL **12.**

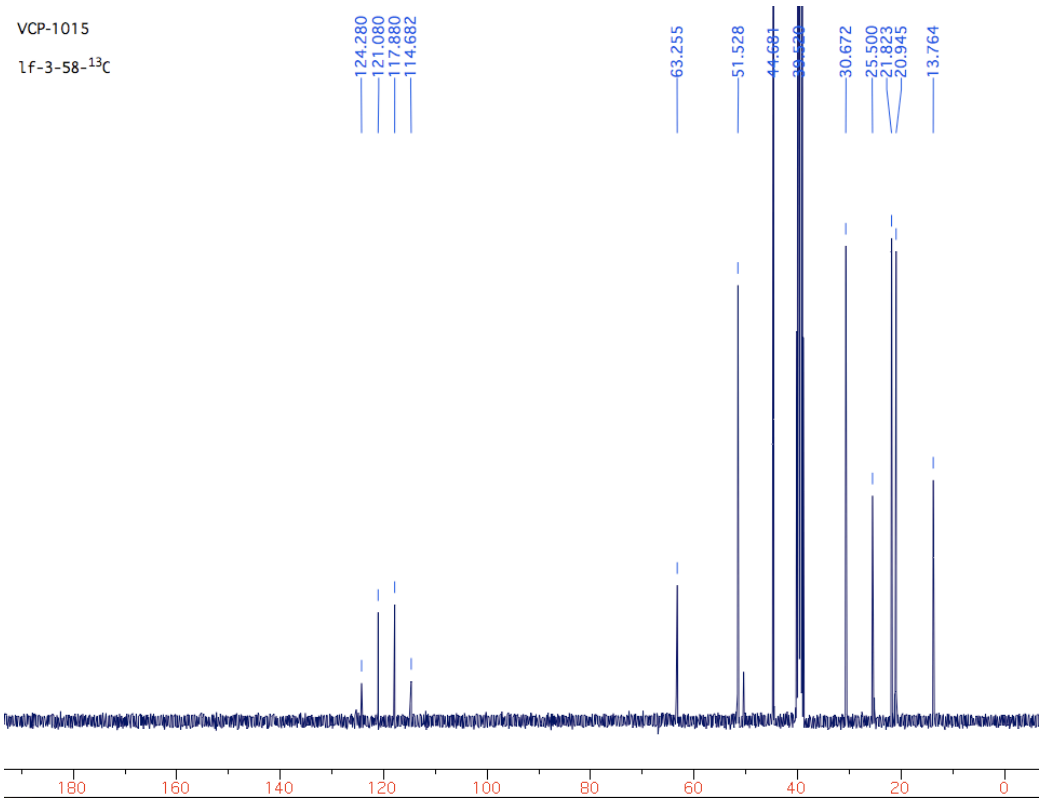


Figure 13A. ^{1}H NMR of IL **13.**

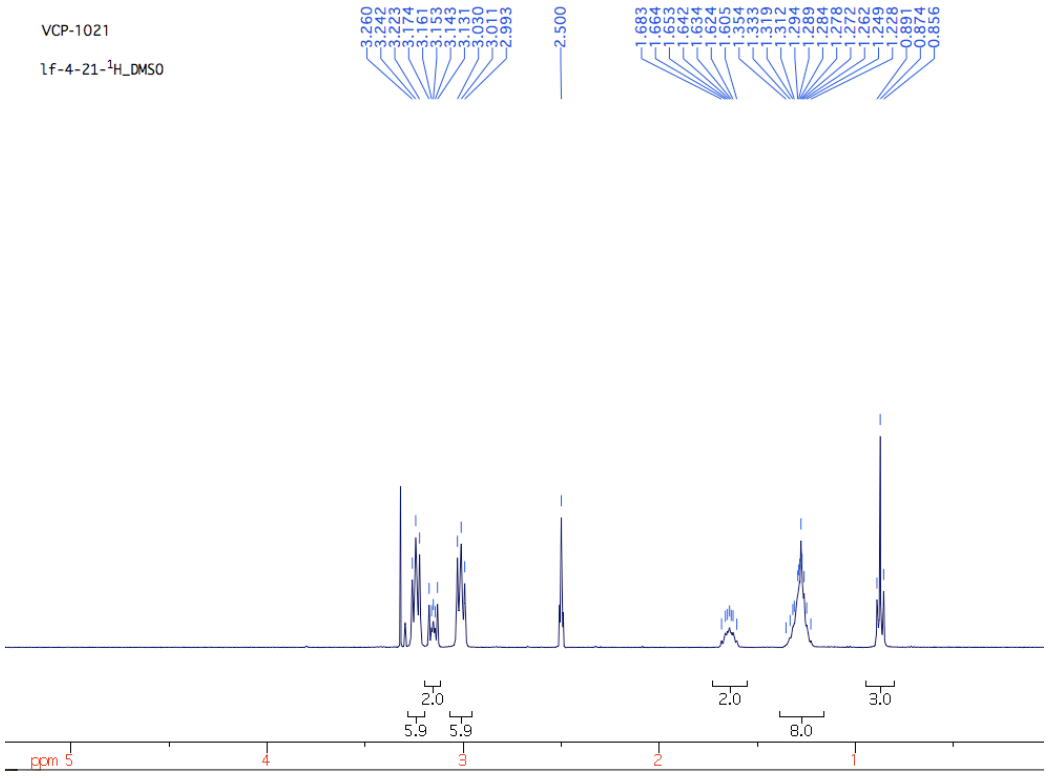


Figure 13B. ^{13}C NMR of IL **13.**

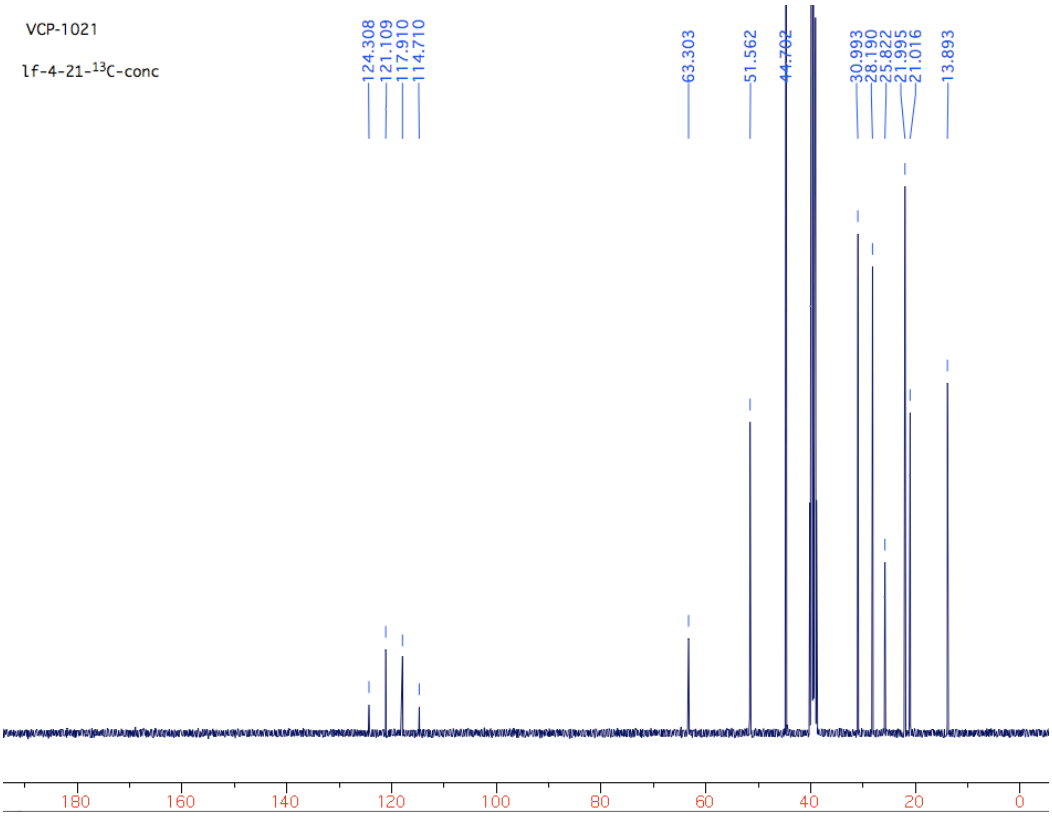


Figure 14A. ^{1}H NMR of IL **14.**

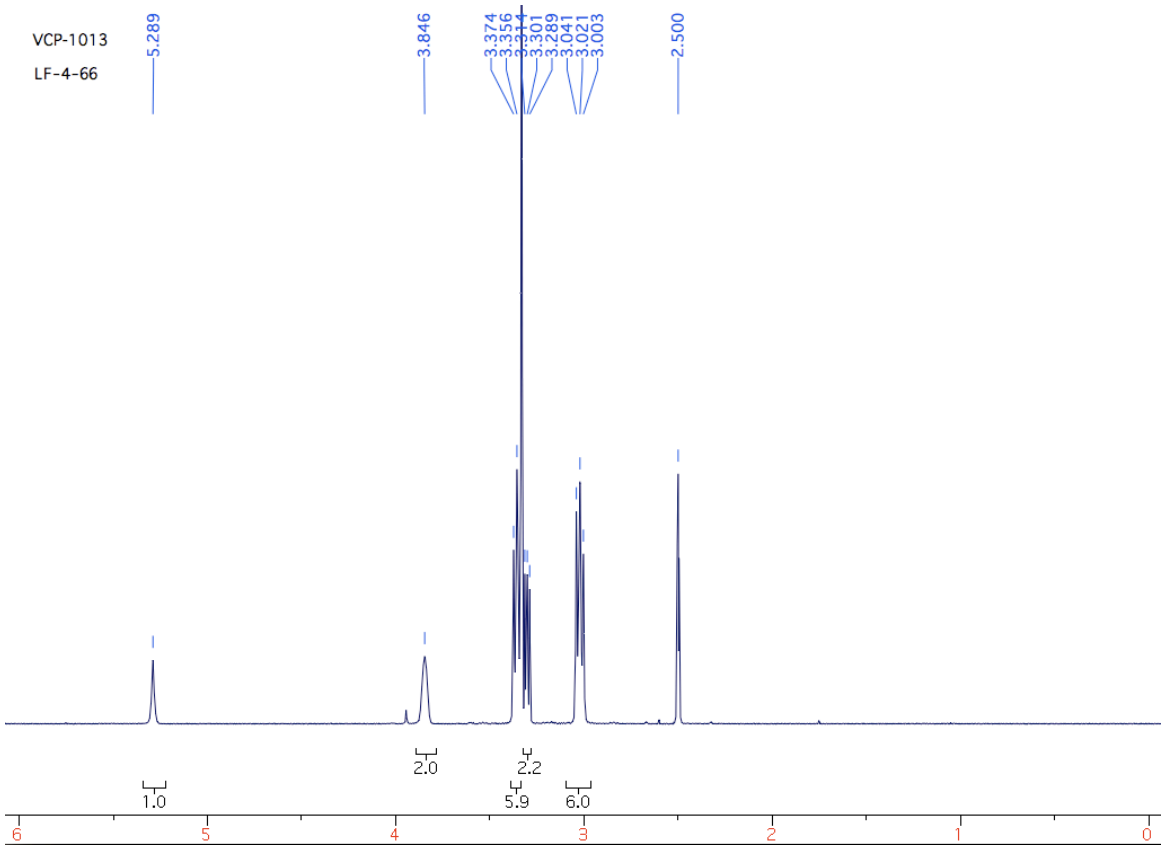
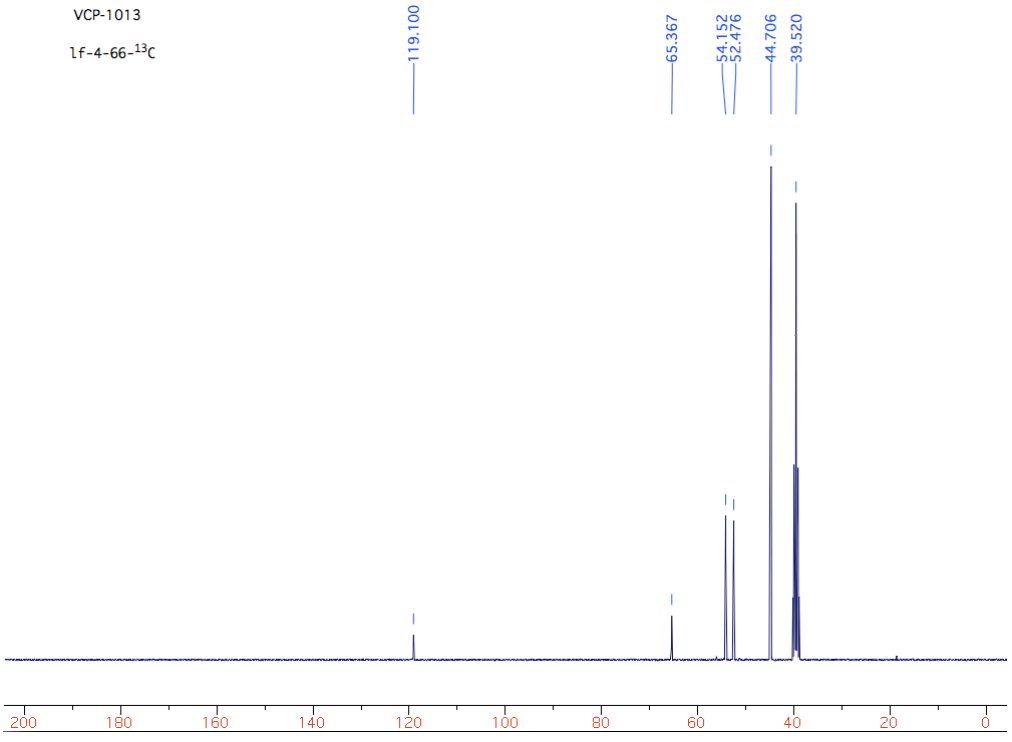


Figure 14B. ^{13}C NMR of IL **14.**



Biodegradation Data

Table S5. Inhibition Tests of ILs.

Compound	Concentration (mg C/L)	Inhibition (%)
14+SDS	20+20	0-10
12+SDS	20+20	0-10
13+SDS	20+20	0-10
11+SDS	20+20	0-10
10+SDS	20+20	0-5
3+SDS	20+20	0-5
1+SDS	20+20	0-5
2+SDS	20+20	0-5
8+SDS	20+20	0-5
7+SDS	20+20	0-5
9+SDS	20+20	0-5
4+SDS	20+20	0-5
5+SDS	20+20	0-5
6+SDS	20+20	0-5

Table S6. Biodegradation Tests of ILs.

Time (days)	% Biodegradation (IL initial concentration= 20 mg C/l)					
	SDS	**1**	**2**	**3**	**4**	**5**
0	0	0	0	0	0	0
7	74	0	0	1	1	0
14	83	0	3	1	5	0
21	89	1	1	0	4	1
28	89	0	1	0	3	3

Time (days)	% Biodegradation (IL initial concentration= 20 mg C/l)					
	SDS	**6**	**7**	**8**	**9**	**10**
0	0	0	0	0	0	0
7	74	0	1	2	1	1
14	83	0	3	5	3	2
21	89	53	5	5	5	1
28	89	60	4	6	3	1

Time (days)	% Biodegradation (IL initial concentration= 20 mg C/l)					
	SDS	**11**	**12**	**13**	**14**	
0	0	0	0	0	0	
7	74	0	0	0	0	
14	83	1	0	0	0	
21	89	0	0	0	0	
28	89	1	0	0	0	

Characterisation of Reaction Products

Methyl 4'-methoxybiphenyl-4-carboxylate[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.09 (m, 2H), 7.56-7.63 (m, 4H), 6.98-7.02 (m, 2H), 3.93 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 159.8, 145.2, 132.4, 130.1, 128.33, 128.20, 126.4, 114.3, 55.4, 52.1.

4-Methoxybiphenyl

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.56 (m, 4H), 7.29-7.43 (m, 3H), 6.96-6.99 (m, 2H), 3.83 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 140.8, 133.7, 128.6, 128.1, 126.7, 126.6, 114.2, 55.3.

3,5-Dimethyl-p-terphenyl

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 4H), 7.64 (d, J = 7.7 Hz, 2H), 7.45 (t, J= 7.7 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.26 (s, 2H), 7.00 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 141.0, 140.7, 140.2, 138.6 (2C), 129.3, 129.1 (2C), 127.8 (2C), 127.7 (2C), 127.5, 127.3 (2C), 125.3 (2C), 21.5 (2C).

1-(4-(2-Phenylethynyl)phenyl)ethanone

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.30 Hz, 2H), 7.61 (d, *J* = 8.40 Hz, 2H), 7.57-7.53 (m, 2H), 7.38-7.36 (m, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 136.1, 131.7, 131.6, 128.7, 128.4, 128.2, 122.6, 92.6, 88.5, 29.6.

1,2-Diphenylethyne

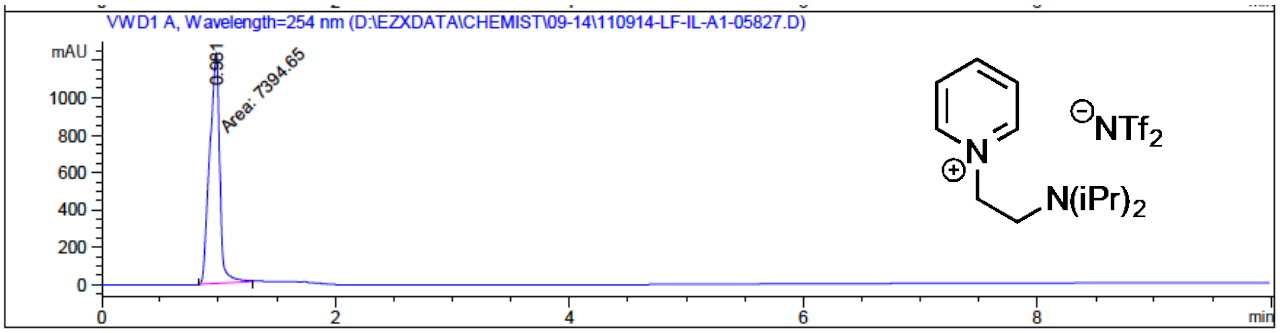
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 4H), 7.36-7.33 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 128.4, 128.2, 123.2, 89.3.

Methyl α-cyanocinnamate

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.00-8.01 (m, 2H), 7.48-7.58 (m, 3H), 4.39 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H). δ 163.1, 155.5, 133.6, 131.5, 131.3, 129.4, 115.6, 102.7, 53.6.

3-Hydroxy-2-methylene-3-phenylpropanoic acid methyl ester

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.40 (m, 5H), 6.35 (dd, J = 1.2, 0.8 Hz, 1H), 5.85 (t, J = 1.2 Hz, 1H), 5.58 (s, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 141.8, 141.2, 128.4, 127.8, 126.5, 1261, 73.1, 51.9.



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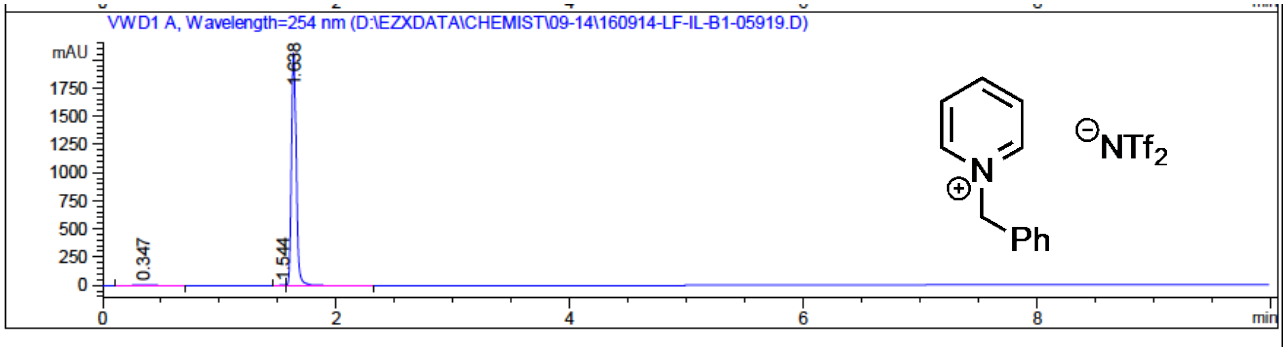
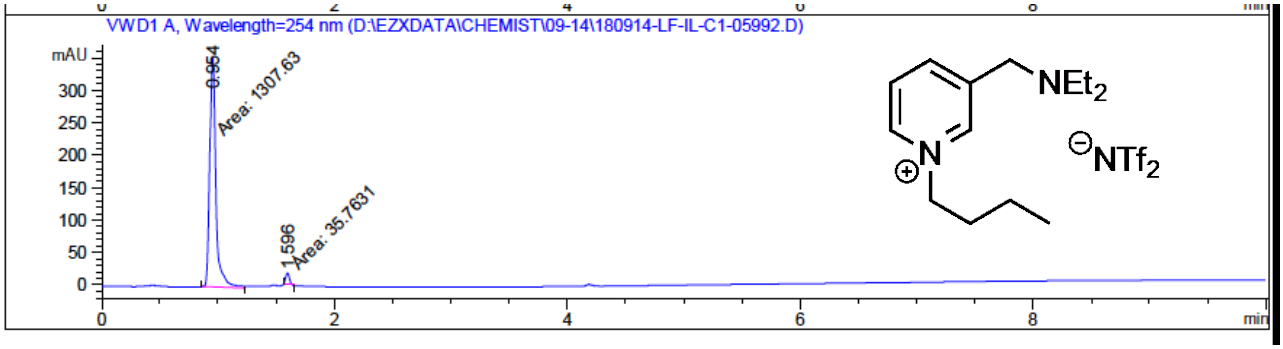
1	0.981	MM	0.1003	7394.64746	1228.36072	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	0.347	BB	0.1886	58.70990	4.50009	0.9843
2	1.544	BV	0.0558	11.95656	3.38119	0.2005
3	1.638	VB	0.0449	5894.07617	2065.32910	98.8153



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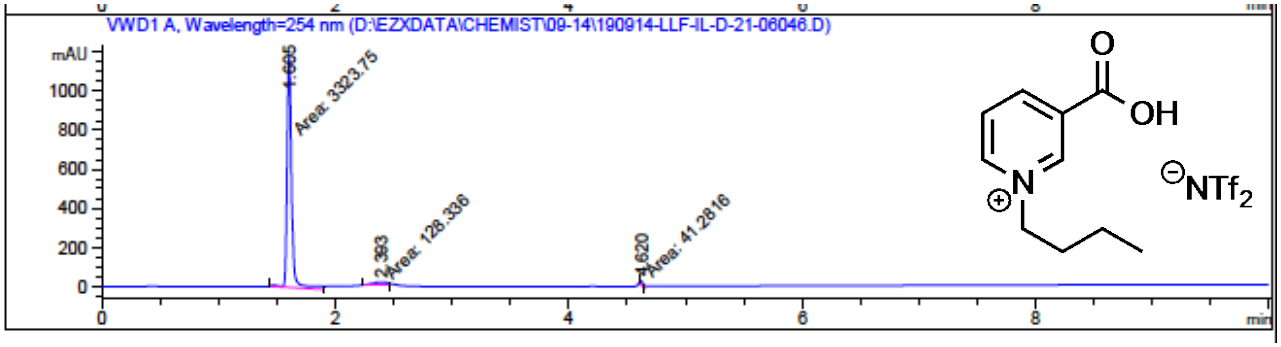
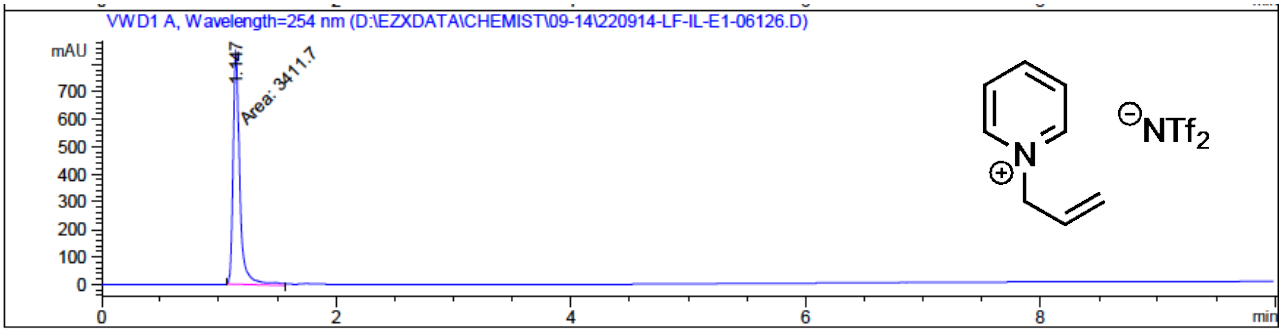
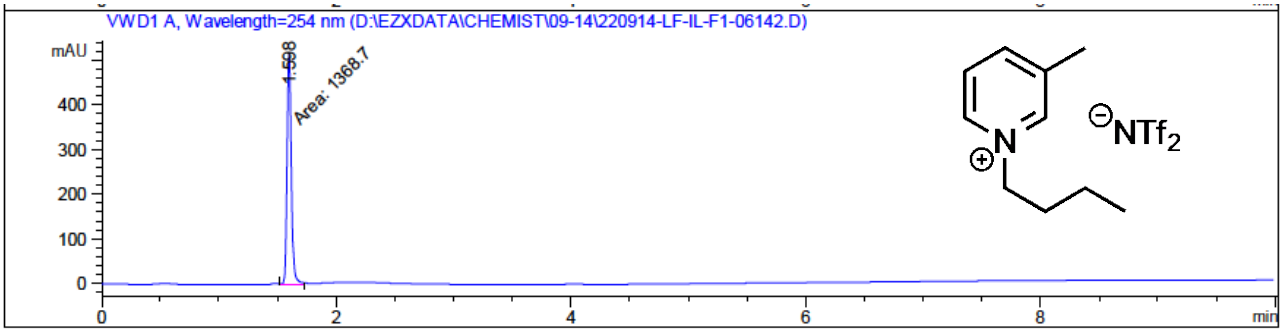
1	0.954	MM	0.0610	1307.62964	357.13321	97.3379
2	1.596	MM	0.0361	35.76311	16.51894	2.6621



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.605	MM	0.0464	3323.75122	1193.91992	95.1446
2	2.393	MM	0.1541	128.33592	13.87587	3.6737
3	4.620	MM	0.0354	41.28158	19.43226	1.1817



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.147	MM	0.0674	3411.70166	844.01617	100.0000



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1	1.598	MM	0.0437	1368.69775	521.44641	100.0000

General Procedures for reactions in IL solvent

Note- All yields unless otherwise indicated are isolated yields, the complete extraction of organics into 4:1 hexanes:Et_2O is confirmed by both 1H NMR of the IL solvent in addition to LC/MS.

Suzuki-Miyuara reaction
Method A – (aq. base)
To ionic liquid (2 mmol), (previously heated overnight at 65^{o}C under vacuum [1 mBar]) was added aryl iodide (0.5mmol), followed by boronic acid (0.55mmol). This mixture was degassed via successive purges with vacuum and nitrogen (x3), $Pd(PPh_3)_2Cl_2$ (0.05mmol) was added and the degassing was repeated. To this mixture was added 2M aq. Na_2CO_3 (1 mL) which had been degassed via sonication under nitrogen gas. The resulting mixture was heated directly at 90 ^{o}C for 1.5h, monitoring by tlc. (10:1 Pet. Sp. : EtOAc – as appropriate). Upon completion of the reaction 5mL CH_2Cl_2 was added and the organic layer collected, the aq. layer was washed with a further 2 x 5mL CH_2Cl_2 the combined organic portions were combined, dried (Na_2SO_4) concentrated in vacuo to give crude material which was extracted with 4 : 1 Pet. Sp. : Et_2O or 4 : 1 toluene : Et_2O {as appropriate} (3 x 25 mL), this solution was concentrated in vacuo and the crude material subjected to flash chromatography (loading with toluene).

Method B – (no aq. base)
To ionic liquid (2 mmol), (previously heated overnight at 65^{o}C under vacuum [1 mBar]) was added aryl iodide (0.5mmol), followed by boronic acid (0.55mmol). This mixture was degassed via successive purges with vacuum and nitrogen (x3), $Pd(PPh_3)_2Cl_2$ (0.05mmol) was added and the degassing was repeated. The resulting mixture was heated directly at 90 ^{o}C for 1.5h, monitoring by tlc. (10:1 Pet. Sp. : EtOAc – as appropriate).

Sonogashira reaction
Method A – (Et_3N)
To ionic liquid (4 mmol), (previously heated overnight at 65^{o}C under vacuum [1 mBar]) was added aryl iodide (1.5 mmol), alkyne (1.65 mmol), triethylamine (2.25 mmol) and $PdCl_2$ (2 mol%). The resulting solution was degassed by bubbling nitrogen for 10 minutes. The reaction mixture was stirred for 5h with occasional sonication. The IL was extracted with 4:1 Pet. Sp : EtOAc (3 x 25mL) this solution was concentrated in vacuo and the crude material subjected to flash chromatography (loading with toluene).

Method B – as above without triethylamine

Knoevenagel reaction
To ionic liquid (0.5 mmol), (previously heated overnight at 65^{o}C under vacuum [1 mBar]) was added benaldehyde (4 mmol) followed by ethyl cyanoacetate (4 mmol), the resulting solution was stirred overnight (16h) at room temperature, monitoring by tlc. The IL was extracted with 4:1 Pet. Sp : EtOAc (3 x 25mL) this solution was concentrated in vacuo and the crude material subjected to flash chromatography (loading with toluene).

Baylis-Hillman reaction
To ionic liquid (2 mmol), (previously heated overnight at 65^{o}C under vacuum [1 mBar]) was added a mixture of methyl acrylate (2 mmol) and benzaldehyde (2 mmol), the resulting solution was stirred overnight (26h) at room temperature, the reaction was monitored by tlc and LCMS.

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