

# Clean osmium-catalyzed asymmetric dihydroxylation of olefins in ionic liquids and supercritical CO<sub>2</sub> product recovery

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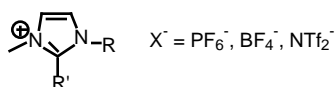
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**General:** The general experimental information has been published elsewhere.<sup>1</sup> For the determination of osmium content by ICP was followed reported procedure. However, in order to achieve a lower detection limit, were prepared different standard solutions (0.10; 0.25; 0.50; 1.00; 5.00; 10.00 and 20.00 ppm) which were used to obtain the calibration curve. After each recycling experiment, the organic phases (after extraction with Et<sub>2</sub>O or scCO<sub>2</sub>) were removed and diluted in 10 mL of distilled water.

Structures of the ionic liquids (ILs) tested:



[C<sub>4</sub>mim] R = *n*-butyl, R' = H

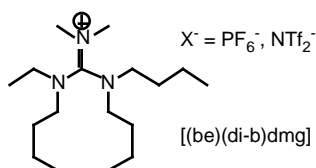
[C<sub>8</sub>mim] R = *n*-octyl, R' = H

[C<sub>10</sub>mim] R = *n*-decyl, R' = H

[C<sub>5</sub>O<sub>2</sub>mim] R = (CH<sub>2</sub>)<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>OMe, R' = H

[C<sub>2</sub>OHmim] R = (CH<sub>2</sub>)<sub>2</sub>OH R' = H

[bdmim] R = *n*-butyl, R' = Me



All ILs tested in the asymmetric dihydroxylation (AD) reaction were prepared in this laboratory. The ILs based on the [C<sub>4</sub>mim], [C<sub>8</sub>mim], [bdmim] and [C<sub>10</sub>mim] cations were prepared according to reported procedures<sup>2</sup> and the ILs containing the [C<sub>5</sub>O<sub>2</sub>mim] and [C<sub>2</sub>OHmim] and the tetra-alkyl-dimethylguanidinium [dmg] cations were reported previously from this laboratory.<sup>3</sup>

**General procedure used for the AD reaction presented in Table SI.1 using K<sub>3</sub>Fe(CN)<sub>6</sub> as co-oxidant (Table SI.1):** A 5 mL flask was charged with K<sub>3</sub>[Fe(CN)<sub>6</sub>] (495 mg; 1.5 mmol); K<sub>2</sub>CO<sub>3</sub> (210 mg; 1.5 mmol); ionic liquid (1.0 mL), and under stirring were added the ligand (DHQD)<sub>2</sub>PHAL (1.0 mol%) and the catalyst K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (0.5 mol%). The olefin (1-hexene or styrene, 0.5 mmol) was then added to the heterogeneous mixture and the reaction mixture

stirred at room temperature during 24 h. The obtained mixture was dissolved in a small amount of dichloromethane (2 mL) and purified by flash chromatography to give (R)-1,2-hexanediol or (R)-1-phenyl-1,2-ethanediol.<sup>1</sup>

**Table SI.1.** Screening of different ionic liquids for the AD reaction using 1-hexene and styrene as substrates, (DHQD)<sub>2</sub>PHAL, K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub>.

Ionic Liquid	1-Hexene		Styrene	
	Yield [%]	e.e. [%]	Yield [%]	e.e. [%]
[C <sub>4</sub> mim]PF <sub>6</sub>	59	60	69	86
[C <sub>4</sub> mim]BF <sub>4</sub>	41	63	20	68
[C <sub>4</sub> mim]NTf <sub>2</sub>	99	92	77	94
[C <sub>8</sub> mim]PF <sub>6</sub>	74	98	62	97
[C <sub>8</sub> mim]BF <sub>4</sub>	81	87	55	82
[C <sub>10</sub> mim]BF <sub>4</sub>	93	94	33	88
[C <sub>5</sub> O <sub>2</sub> mim]PF <sub>6</sub>	63	83	60	89
[C <sub>2</sub> OHmim]PF <sub>6</sub>	54	75	38	79
[bdmim]PF <sub>6</sub>	84	85	77	94
[bdmim]BF <sub>4</sub>	81	75	76	75
[bdmim]NTf <sub>2</sub>	86	74	74	91
[(be)(di-b)dmg]PF <sub>6</sub>	90	67	91	71
[(be)(di-b)dmg]NTf <sub>2</sub>	89	72	96	85

**General procedure used for the AD reaction presented in Tables SI.2 and SI.3 using NMO as co-oxidant:** A 5 mL flask was charged with NMO (100 mg; 0.5 mmol); ionic liquid (1.0 mL), and under stirring were added the ligand [(DHQD)<sub>2</sub>PHAL; (DHQD)<sub>2</sub>PYR; (DHQD)<sub>2</sub>AQN or (DHQ)<sub>2</sub>PHAL] (1.0 mol%) and the catalyst K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (0.5 mol%). Then, different olefins (0.5 mmol) were added to the mixture (formation of a second phase for liquid olefins for some ILs which disappears during the reaction), which was stirred at room temperature during 24 h. The obtained mixture was dissolved in a small amount of dichloromethane (2 mL) and purified by flash chromatography to give the corresponding diol.<sup>1</sup>

**Table SI.2.** Screening of different ionic liquids for the AD reaction using 1-hexene and styrene as substrates, (DHQD)<sub>2</sub>PHAL, K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> and NMO

Ionic Liquid	1-Hexene		Styrene	
	Yield [%] <sup>a</sup>	e.e.[%] <sup>a</sup>	Yield [%] <sup>a</sup>	e.e.[%] <sup>a</sup>
[C <sub>4</sub> mim]PF <sub>6</sub>	82 (83)	67 (99)	87 (84)	60 (60)
[C <sub>4</sub> mim]BF <sub>4</sub>	77 (81)	66 (95)	98 (92)	91 (99)
[C <sub>4</sub> mim]NTf <sub>2</sub>	96	97	92	93
[C <sub>8</sub> mim]PF <sub>6</sub>	85 (89)	63 (97)	81 (83)	63 (95)
[C <sub>8</sub> mim]BF <sub>4</sub>	87	95	92	93
[C <sub>10</sub> mim]BF <sub>4</sub>	96	97	82	93
[C <sub>5</sub> O <sub>2</sub> mim]PF <sub>6</sub>	63(68)	83(85)	82(87)	67 (74)
[C <sub>2</sub> OHmim]PF <sub>6</sub>	37	86	88	93
[bdmim]PF <sub>6</sub>	98	90	90	99
[bdmim]BF <sub>4</sub>	91	90	89	95
[bdmim]NTf <sub>2</sub>	93	95	92	98
[(be)(di-b)dmg]PF <sub>6</sub>	96	74	96	90
[(be)(di-b)dmg]NTf <sub>2</sub>	91	77	88	96

<sup>a</sup>In brackets are presented the experiments performed by slow addition of olefin (12 h).

**Table SI.3.** Asymmetric dihydroxylation of olefins in ionic liquids using NMO as co-oxidant.

olefin	Ionic Liquid	Ligand	Yield [%]	e.e. [%]	
1-hexene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQD) <sub>2</sub>	97	94	
	[C <sub>8</sub> mim]BF <sub>4</sub>		67	92	
	[bdmim]PF <sub>6</sub>		91	90	
	[bdmim]BF <sub>4</sub>		PYR	94	98
	[bdmim]NTf <sub>2</sub>		96	99	
1-hexene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQD) <sub>2</sub>	93	92	
	[C <sub>8</sub> mim]BF <sub>4</sub>		88	92	
	[bdmim]PF <sub>6</sub>		56	87	
	[bdmim]BF <sub>4</sub>		AQN	93	99
	[bdmim]NTf <sub>2</sub>		97	99	
1-hexene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQ) <sub>2</sub>	99	94	
	[C <sub>8</sub> mim]BF <sub>4</sub>		81	98	
	[bdmim]PF <sub>6</sub>		55	78	
	[bdmim]BF <sub>4</sub>		PHAL	82	93
	[bdmim]NTf <sub>2</sub>		96	99	
styrene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQD) <sub>2</sub>	93	97	
	[C <sub>8</sub> mim]BF <sub>4</sub>		40	90	
	[bdmim]PF <sub>6</sub>		63	74	
	[bdmim]BF <sub>4</sub>		PYR	91	88
	[bdmim]NTf <sub>2</sub>		80	97	
styrene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQD) <sub>2</sub>	95	99	
	[C <sub>8</sub> mim]BF <sub>4</sub>		91	98	
	[bdmim]PF <sub>6</sub>		80	89	
	[bdmim]BF <sub>4</sub>		AQN	87	99
	[bdmim]NTf <sub>2</sub>		96	99	
styrene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQ) <sub>2</sub>	92	98	
	[C <sub>8</sub> mim]BF <sub>4</sub>		90	86	
	[bdmim]PF <sub>6</sub>		74	93	
	[bdmim]BF <sub>4</sub>		PHAL	88	99
	[bdmim]NTf <sub>2</sub>		98	99	
-methyl-styrene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQD) <sub>2</sub>	92	89	
	[C <sub>8</sub> mim]BF <sub>4</sub>		60	74	
	[bdmim]PF <sub>6</sub>		86	88	
	[bdmim]BF <sub>4</sub>		PHAL	91	78
	[bdmim]NTf <sub>2</sub>		94	89	
trans-stilbene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQD) <sub>2</sub>	97	67	
	[C <sub>8</sub> mim]BF <sub>4</sub>		81	66	
	[bdmim]PF <sub>6</sub>		75	60	
	[bdmim]BF <sub>4</sub>		PHAL	96	82
	[bdmim]NTf <sub>2</sub>		94	85	
1-methyl-cyclohexene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQD) <sub>2</sub>	99	98	
	[C <sub>8</sub> mim]BF <sub>4</sub>		53	68	
	[bdmim]PF <sub>6</sub>		67	92	
	[bdmim]BF <sub>4</sub>		PHAL	87	71
	[bdmim]NTf <sub>2</sub>		92	93	
trans-5-decene	[C <sub>4</sub> mim]NTf <sub>2</sub>	(DHQD) <sub>2</sub>	94	99	
	[C <sub>8</sub> mim]BF <sub>4</sub>		74	65	
	[bdmim]PF <sub>6</sub>		75	75	
	[bdmim]BF <sub>4</sub>		PHAL	93	83
	[bdmim]NTf <sub>2</sub>		89	98	

**General procedure for the reuse of the K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub>/(DHQD)<sub>2</sub>PHAL/IL system using NMO as co-oxidant and extraction with Et<sub>2</sub>O (Table SI.4):** A 10 mL flask was charged with NMO (100 mg; 0.5 mmol); 1-*n*-butyl-3-methylimidazolium (bis-trifluoromethanesulfonyl)imide [C<sub>4</sub>mim]NTf<sub>2</sub> or 1-*n*-butyl-2,3-dimethylimidazolium (bis-trifluoromethanesulfonyl)imide [bdmim]NTf<sub>2</sub> (3 mL), and under stirring were added the ligand

[(DHQD)<sub>2</sub>PHAL] (4 mg; 1 mol%) and the catalyst K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (1.0 ± 0.1 mg; 0.5 mol%). 1-Hexene (63 µL) was then added to the resulting mixture that was stirred for 24 h at room temperature. The ionic liquid was extracted with diethyl ether (1x10 mL) and the ethereal layer was dried (MgSO<sub>4</sub>), evaporated in *vacuo* and purified by flash chromatography using diethyl ether. Then, more 1-hexene (63 µL) and NMO (100 mg; 0.5 mmol) were added to the recycled ionic liquid and the cycle repeated. In case of entries 15 a new portion of catalyst (0.5 mol%) and ligand (1.0 mol%) was added into the ionic reaction mixture. The other parallel experiment was performed as described before and used for the determination of the osmium content (in relation to initial amount) in the ethereal phase.

**Table SI.4.** Reuse of the catalyst for the AD reaction of 1-hexene in [C<sub>4</sub>mim]NTf<sub>2</sub> and [bdmim]NTf<sub>2</sub>, using NMO as co-oxidant and extraction with Et<sub>2</sub>O.

	[C <sub>4</sub> mim]NTf <sub>2</sub>			[bdmim]NTf <sub>2</sub>		
	Yield [%]	e.e. [%]	Os <sup>a</sup> [%]	Yield [%]	e.e. [%]	Os <sup>a</sup> [%]
1	98	96	1.57	94	93	1.15
2	97	98	1.32	92	96	1.05
3	99	96	1.17	95	95	1.56
4	95	97	1.84	93	95	1.98
5	96	94	1.62	93	92	1.32
6	95	97	1.37	94	90	1.43
7	96	96	1.22	91	93	1.48
8	94	93	1.56	92	93	1.80
9	97	95	1.70	90	90	1.57
10	93	96	1.28	90	91	1.31
11	94	94	1.68	92	89	1.25
12	92	92	1.45	90	90	1.60
13	95	93	1.40	93	92	1.12
14	92	92	1.31	88	87	1.28
15	99 <sup>b</sup>	98 <sup>b</sup>	1.05	95 <sup>b</sup>	96 <sup>b</sup>	1.76
16	97	97	1.28	94	94	1.78

<sup>a</sup>Osmium content in the extracted ethereal phases determined by ICP.

<sup>b</sup>New addition of K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (0.5 mol%) and (DHQD)<sub>2</sub>PHAL (1.0 mol%)

**AD reaction in [bdmim]BF<sub>4</sub>, using K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub>/(DHQD)<sub>2</sub>PHAL system and NMO as a co-oxidant, followed by *sc*CO<sub>2</sub> extraction at different pressures (Table SI.5):** A 5 mL glass vial was charged with NMO (400 mg; 0.5 mmol); 1-*n*-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim]BF<sub>4</sub> (2 mL), and under stirring were added the ligand [(DHQD)<sub>2</sub>PHAL] (16 mg; 1 mol%) and the catalyst K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (4.0 ± 0.1 mg; 0.5 mol%). 1-Hexene (252 µL) was then added to the resulting mixture that was stirred for 24 h at room temperature.

When completed, 1 mL of the reaction mixture was transferred to the high-pressure cell, placed inside a constant temperature water bath (Figure SI.1.). Vigorous mixing was achieved with a magnetic plate.

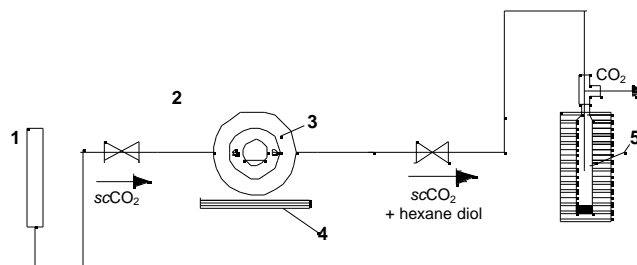
CO<sub>2</sub> was introduced to the cell by a screw injector pump, at a constant temperature of 40 °C, and four different pressures (100, 120, 140 and 200 bar). When the system equilibrated, *sc*CO<sub>2</sub> extraction was performed at constant pressure. The extraction was considered finished, when two volumes of screw injector pump (120 cm<sup>3</sup>; 1.72 mol of CO<sub>2</sub>) were passed through the system. The product was collected in a cold trap, that was cooled by (liquid nitrogen + ethanol) mixture. After washing the cold trap with ethanol, the sample thus obtained was divided in two equal parts. One was used for the determination

of the osmium content by ICP<sup>1</sup>, while the other one was used for the isolation of the 1,2-(*R*)-hexanediol and for the e.e. determination.<sup>1</sup>

The results of these experiments are given in the Table SI.5.

**Table SI.5. Yield and osmium content for *sc*CO<sub>2</sub> extractions performed at 40 °C and different pressures from ionic liquid [bdmim]BF<sub>4</sub>.**

Pressure [bar]	100	120	140	200
Yield [%]	90	96	76	79
Os content [%]	0.34	1.64	2.00	24.22



**Figure SI.1** Schematic diagram of the apparatus used in *sc*CO<sub>2</sub> extraction experiments: 1-CO<sub>2</sub> screw injector pump; 2-constant temperature water bath; 3-high-pressure cell; 4-magnetic stirrer; 5-cold trap.

**AD reaction in ionic liquids [bdmim][BF<sub>4</sub>], [C<sub>8</sub>mim]BF<sub>4</sub>, [C<sub>10</sub>mim]BF<sub>4</sub>, [bdmim]NTf<sub>2</sub>, and [C<sub>4</sub>mim]NTf<sub>2</sub>, using K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub>/(DHQD)<sub>2</sub>PHAL system and NMO as a co-oxidant, followed by *sc*CO<sub>2</sub> extraction at 100 bar (Table SI.6.):** The AD reaction was carried out as described before in ionic liquids (2 mL) [bdmim]BF<sub>4</sub>, [C<sub>8</sub>mim]BF<sub>4</sub>, [C<sub>10</sub>mim]BF<sub>4</sub>, [bdmim]NTf<sub>2</sub>, and [C<sub>4</sub>mim]NTf<sub>2</sub>, at room temperature for 24 hours. When completed, 1 mL of a reaction mixture was transferred to the high-pressure cell, and *sc*CO<sub>2</sub> extraction with 2 volumes of screw injector pump (120 cm<sup>3</sup>; 1.72 mol of CO<sub>2</sub>) was performed at a constant pressure of 100 bar.

The results of these experiments are presented in Table SI.6.

**Table SI.6.** Yield, enantiomeric excess and osmium content for AD reaction performed in [bdmim]BF<sub>4</sub>, [C<sub>8</sub>mim]BF<sub>4</sub>, [C<sub>10</sub>mim]BF<sub>4</sub>, [bdmim]NTf<sub>2</sub>, and [C<sub>4</sub>mim]NTf<sub>2</sub>, followed by *sc*CO<sub>2</sub> extraction.

Ionic liquid	Yield [%]	e.e. [%]	Os content [%]
[bdmim]BF <sub>4</sub>	86 <sup>a</sup>	88 <sup>a</sup>	0.38 <sup>a</sup>
[C <sub>8</sub> mim]BF <sub>4</sub>	90 <sup>a</sup>	94 <sup>a</sup>	0.47 <sup>a</sup>
[C <sub>10</sub> mim]BF <sub>4</sub>	90	96	0.56
[bdmim]NTf <sub>2</sub>	33 <sup>a</sup>	88 <sup>a</sup>	0.24 <sup>a</sup>
[C <sub>4</sub> mim]NTf <sub>2</sub>	91 <sup>b</sup>	96 <sup>b</sup>	0.51 <sup>b</sup>

<sup>a</sup>Average of two independent CO<sub>2</sub> extraction procedures

<sup>b</sup>Average of three independent CO<sub>2</sub> extraction procedures

**General procedure for reuse of the K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub>/(DHQD)<sub>2</sub>PHAL/IL system using NMO as a co-oxidant, followed by *sc*CO<sub>2</sub> extraction at 100 bar (Table SI.7. and Table 2):** In a 5 mL glass vial, ionic liquids [C<sub>10</sub>mim]BF<sub>4</sub> or [C<sub>4</sub>mim]NTf<sub>2</sub> (2 mL), (DHQD)<sub>2</sub>PHAL ligand (16 mg; 1 mol%), K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (4.0 ± 0.1 mg; 0.5 mol%), NMO (400 mg; 0.5 mmol) and substrate 1-hexene (280 µL) were added. The reaction was carried out for 24 hours at room temperature. When completed, the reaction

mixture was transferred to the high-pressure cell, and *sc*CO<sub>2</sub> extraction was performed at a constant pressure of 100 bar. After 120 cm<sup>3</sup> of CO<sub>2</sub> were passed through the system, the samples were collected. Fresh quantity of NMO co-oxidant (400 mg) and substrate (280 μL) were added to the ionic liquid phase that remains in the cell after the extraction. The cell was pressurized up to 100 bar, and a new *sc*CO<sub>2</sub> extraction was carried out. The results of [C<sub>10</sub>mim]BF<sub>4</sub> recycling experiments are given in Table SI.7.

In case of [C<sub>4</sub>mim]NTf<sub>2</sub>, for some runs (runs 1, 2, 3, 4 and 8 in Table 2), the sample was not only collected at the end of extraction, but also at the point when the first 60 cm<sup>3</sup> of CO<sub>2</sub> were passed through the system, in order to determine how much of the product is extracted with this quantity of *sc*CO<sub>2</sub>. The results suggest that most of the product is extracted with the first 60 cm<sup>3</sup> of CO<sub>2</sub> (CO<sub>2</sub>/product molar ratio ~ 400).

This high CO<sub>2</sub>/product ratio is the consequence of low extraction pressure, that was chosen in order to obtain CO<sub>2</sub>

higher selectivity towards the desired diol product. On lowering the pressure, CO<sub>2</sub> density and solvent power decrease, so it is necessary to use higher amount of CO<sub>2</sub> to fully recover the product.

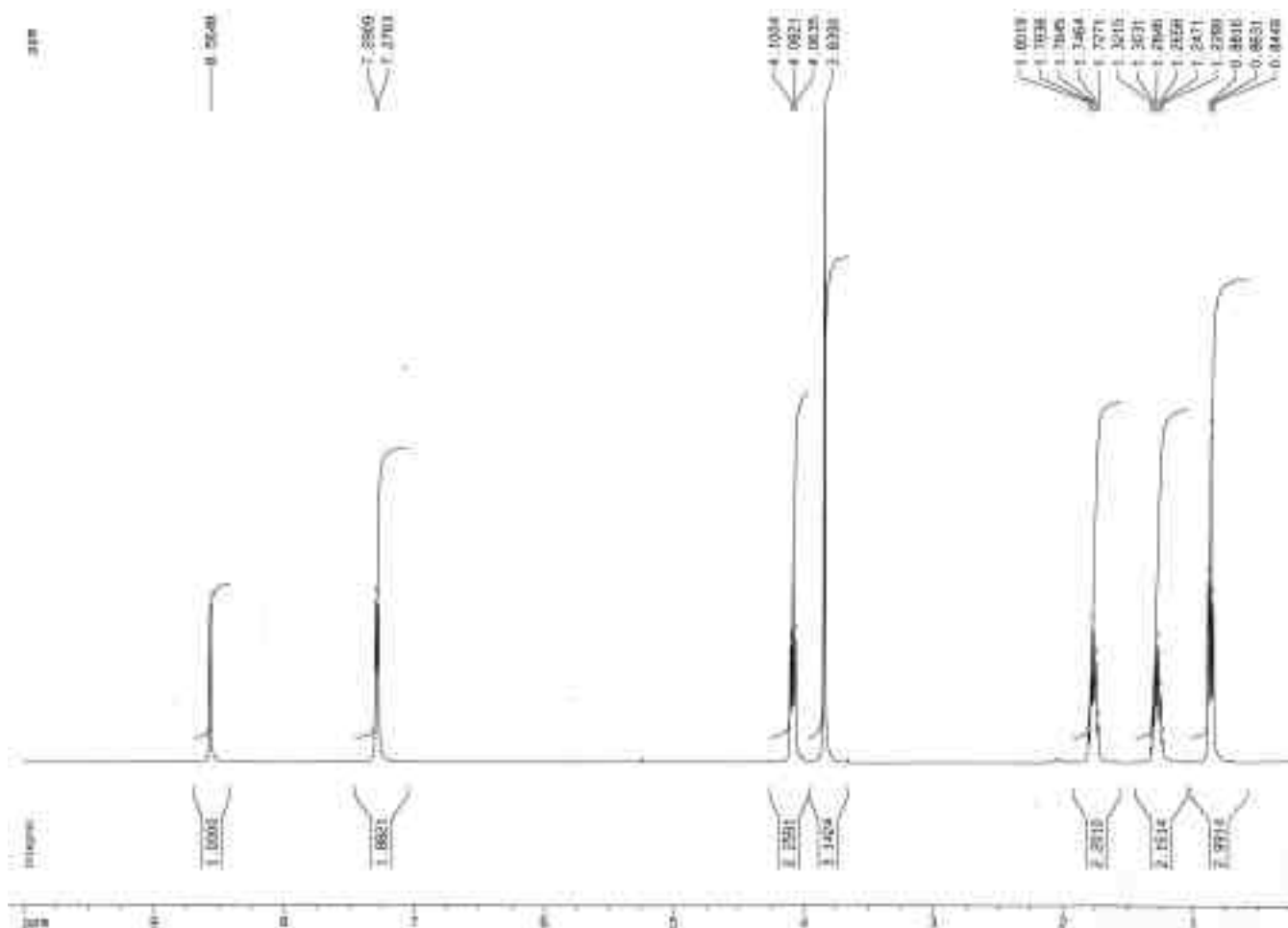
**Table SI.7.** Yield, enantiomeric excess and osmium content for recycling experiments of osmium catalyst, immobilized in ionic liquid [C<sub>10</sub>mim]BF<sub>4</sub>.

Run	Yield [%]	e.e.[%]	Os content [%] <sup>a</sup>
1	90	96	0.56
2	86	94	0.48
3	94	97	0.32
4	85	91	0.30
5	75	88	0.32

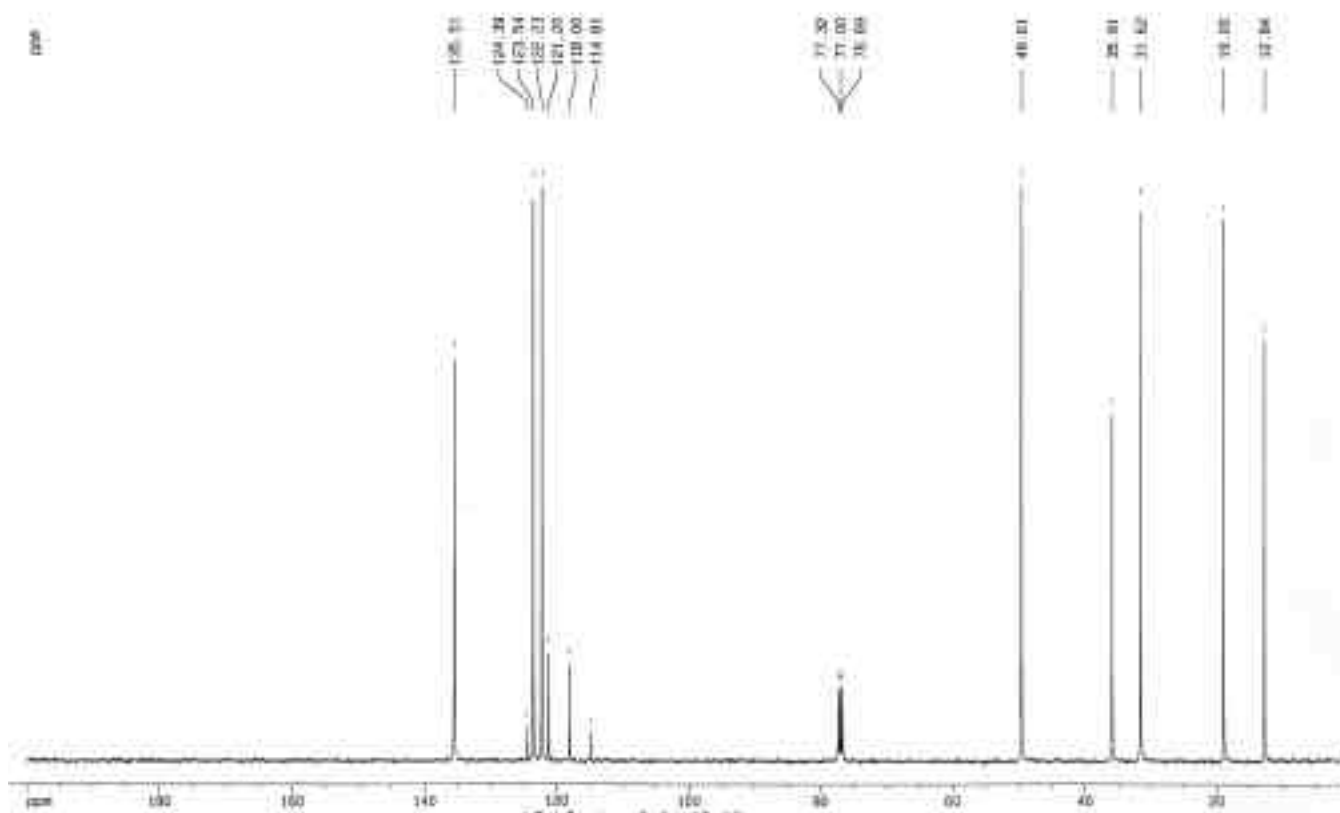
<sup>a</sup>The osmium content in the extracted *sc*CO<sub>2</sub> phase for all runs are in the range of the detection limit of the method used (by ICP)

### Comparison of Spectral Data (1H and 13C NMR) of the Ionic Liquid Between the Initial and Final Recycled Sample

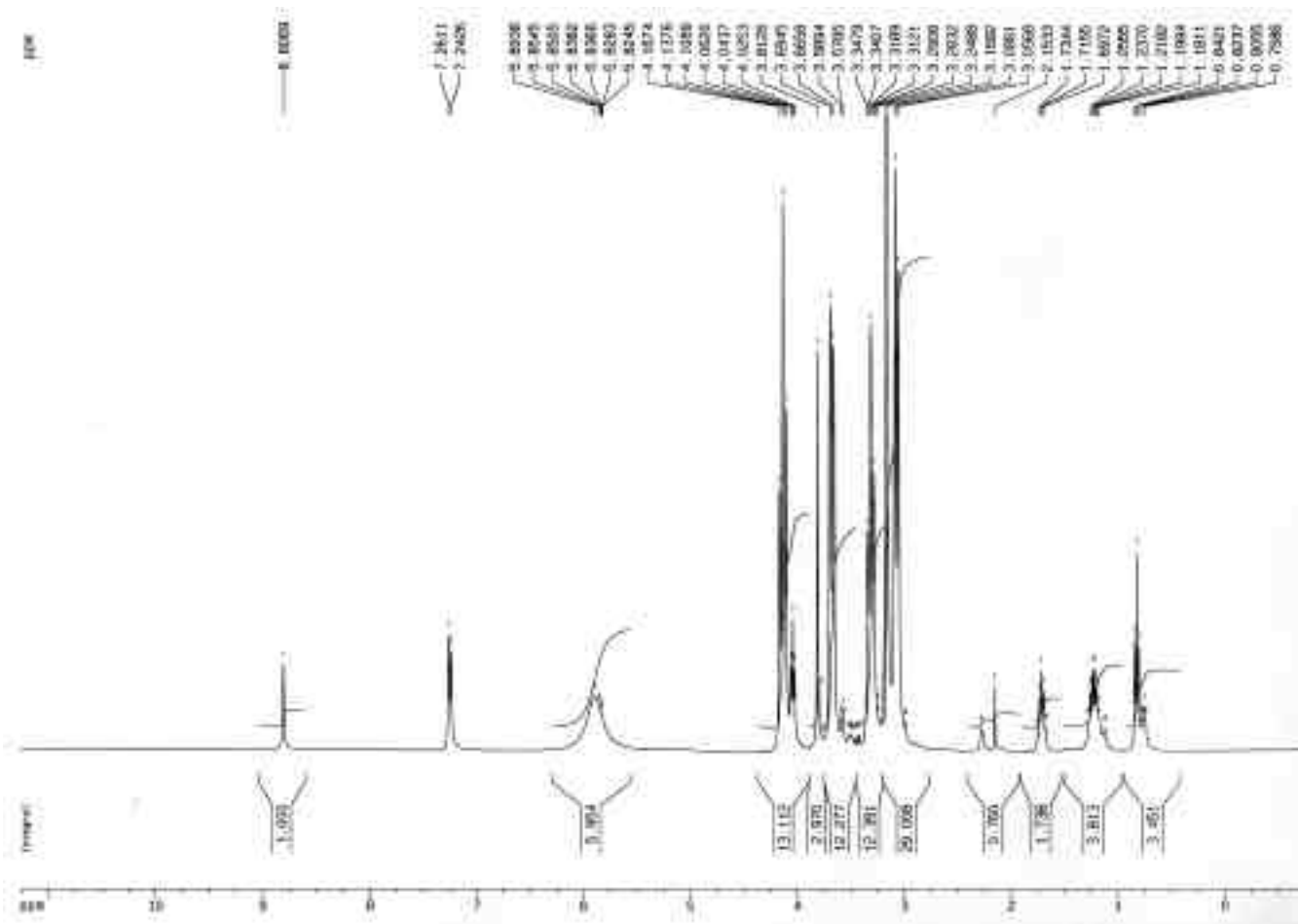
**Figure SI.2.** <sup>1</sup>H NMR spectra (in CDCl<sub>3</sub>) of initial [C<sub>4</sub>mim]NTf<sub>2</sub>.



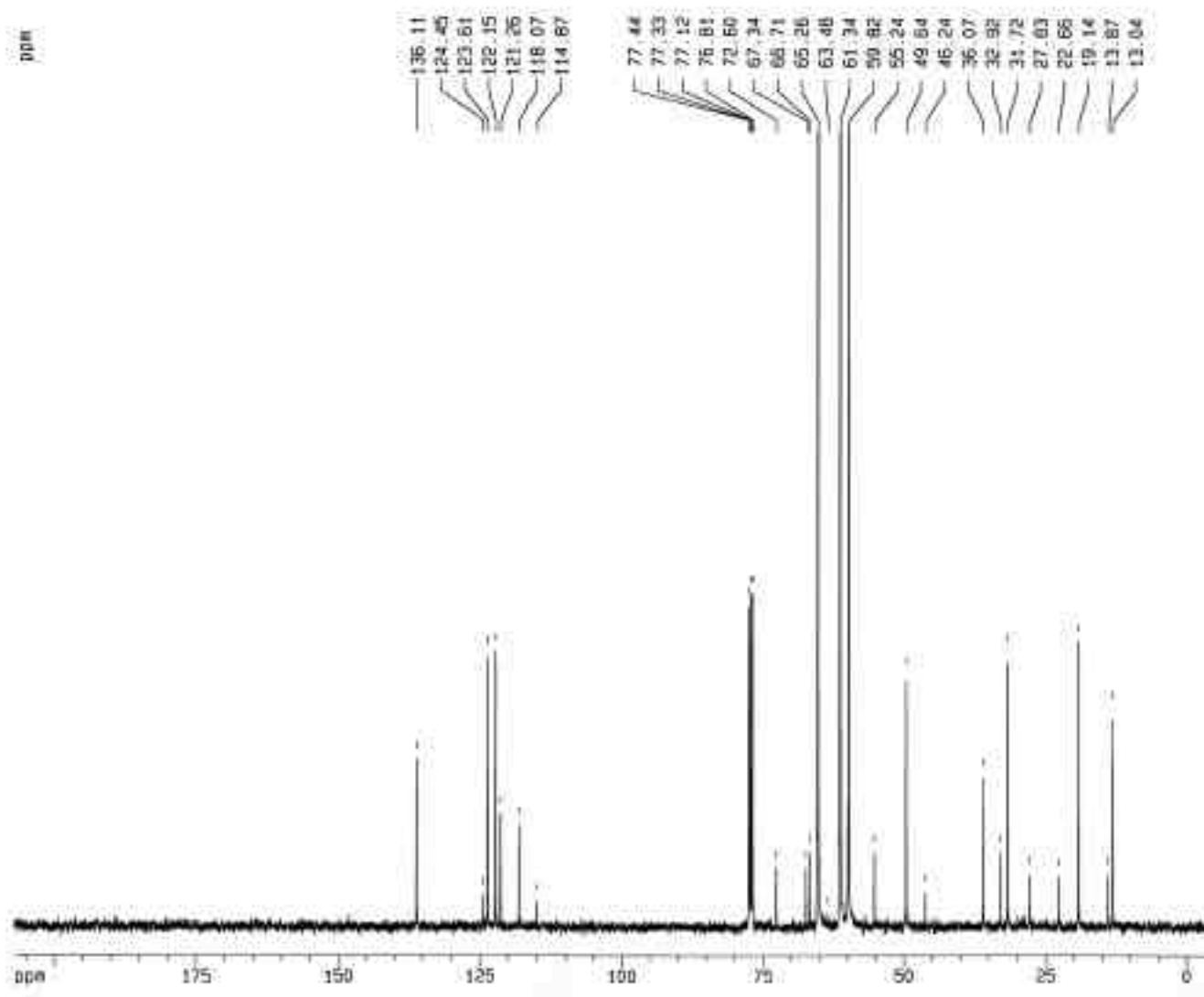
**Figure SI.3.**  $^{13}\text{C}$  NMR spectra (in  $\text{CDCl}_3$ ) of initial  $[\text{C}_4\text{mim}]\text{NTf}_2$ .



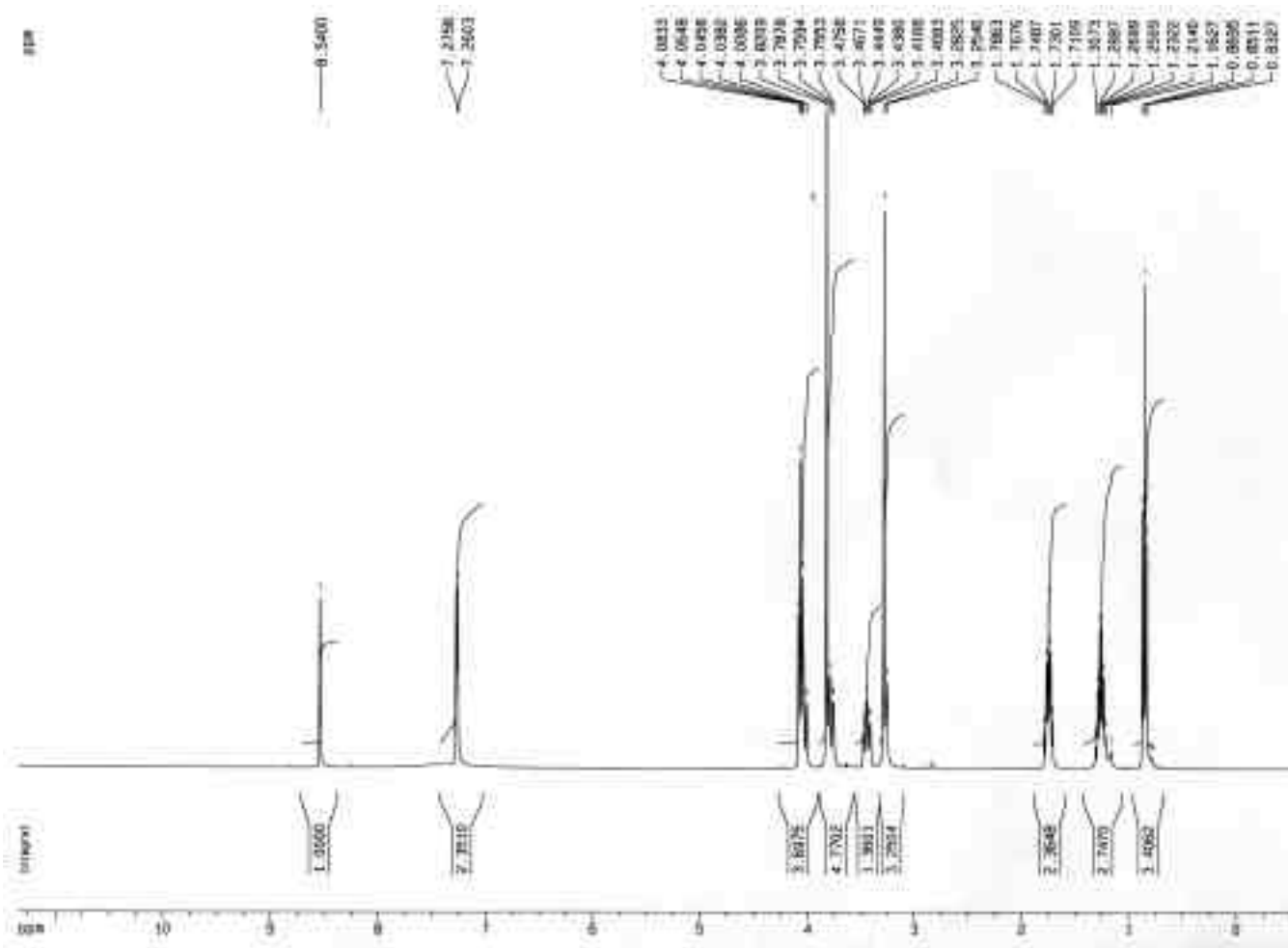
**Figure SI.4.**  $^1\text{H}$  NMR spectra (in  $\text{CDCl}_3$ ) of  $[\text{C}_4\text{mim}]\text{NTf}_2$  after run 9 of the experiment presented in Table 2 (extraction with  $\text{scCO}_2$ ).



**Figure SI.5.**  $^{13}\text{C}$  NMR spectra (in  $\text{CDCl}_3$ ) of  $[\text{C}_4\text{mim}]\text{NTf}_2$  after run 9 of the experiment presented in Table 2 (extraction with  $\text{scCO}_2$ ). Other compounds present in the ionic liquid: (*R*)-1,2-hexanediol; 72.60, 66.71, 32.92, 27.83, 22.66, 13.87; NMO; 65.26, 61.34, 59.82; *N*-Methyl-morpholine; 67.34, 55.24, 46.24.

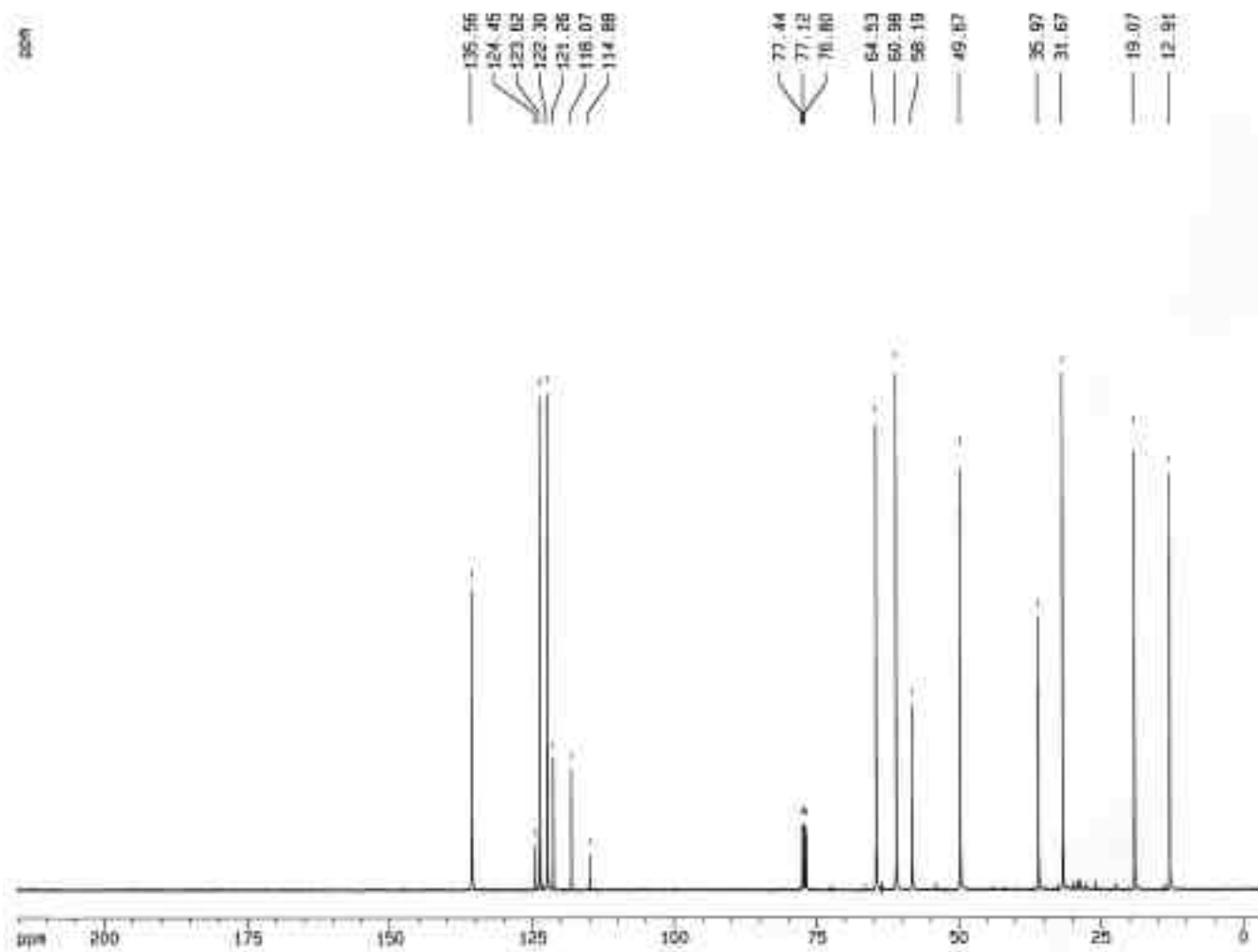


**Figure SI.6.**  $^1\text{H}$  NMR spectra (in  $\text{CDCl}_3$ ) of  $[\text{C}_4\text{mim}]\text{NTf}_2$  after run 9 of the experiment presented in Table 2 (extraction with  $\text{scCO}_2$ ) and further purification by washing with water and diethyl ether.





**Figure SI.7.**  $^{13}\text{C}$  NMR spectra (in  $\text{CDCl}_3$ ) of  $[\text{C}_4\text{mim}]\text{NTf}_2$  after run 9 of the experiment presented in Table 2 (extraction with  $s\text{cCO}_2$ ) and further purification by washing with water and diethyl ether..



## References

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