**Electronic Supplementary Information (ESI)**

# Kinetic and Mechanistic Investigations of Baylis-Hillman Reaction in Ionic Liquids

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Contents:

**Synthesis of Ionic Liquids**

**Synthesis of $NTf_2$ based ionic liquids:**[1,2] There are two main steps in synthesis 1) quaternization: 1-methylpyrrolidine (14.6 mmol) was added to a stirred solution of slightly excess (10%) of haloalkane (17.5 mmol). The reaction mixture was then refluxed for 12h and the temperature was never allowed to rise above 70°C. The unreacted materials were removed by washing with ethylacetate (3-4 times) and the excess solvent was removed by rotary evaporator. The compound was further dried under reduced pressure, and 2) metathesis: To a stirred solution of Lithium bis(trifluoromethane)sulfonimide (10 mmol) in deionised water, halogenated product (10 mmol) of step 1 was added under inert atmosphere. The mixture was stirred for 12 h. The desired product was obtained by repeated extraction of the reaction mixture in dichloromethane. The collected fraction in dichloromethane was subjected to heating in a rotary evaporator followed by drying under reduced pressure. [Bmim][Br] was synthesized by following similar procedure as explained for the halogenated product of step 1. In quaternization step 1-methylimidazole was refluxed with 1-bromobutane for 12 h. The unreacted material was removed by washing with ethylacetate. The halogenated product was further dried under reduced pressure. Purity of the ionic liquids synthesized in our laboratory was further confirmed by $^1$H NMR spectra and agreed well with the literature values.[2]

**Synthesis of [Pyr][HCOO] based ionic liquids:**[1,3,4]

This ionic liquid was synthesized by mixing equimolar amounts of acid and base. The synthesis was carried out by drop-wise addition of 25.2 mmol of pyrrolidine as a base to a stirred solution of 25.2 mmol of 95% (v/v) formic acid solution under ice cold conditions. After stirring for 8h, the excess water was removed *in vacuo*. The

synthesized ionic liquid was further dried under reduced pressure for 10h. Other protic ionic liquids based on $CH_3COO^-$ and $CF_3COO^-$ anions were synthesized by adding the equimolar amounts of pyrrolidine and acetic acid (99.7% v/v) for [Pyr][$CH_3COO$], and pyrrolidine and trifluoroacetic acid 99%v/v) for [Pyr][$CF_3COO$]. The nitrate based ionic liquid was prepared by adding equimolar amounts of 70% (v/v) nitric acid to a stirred solution of pyrrolidine in a dropwise manner for 2 h. The temperature was never allowed to rise above 20°C. After completion of the reaction, excess water was removed *at vacuo*. Final traces of water were removed under high pressure. Purity of the ionic liquids synthesized was further confirmed by $^1$H NMR spectra and agreed well with the literature reports.[3,4]

**Synthesis of $HSO_4$ based ionic liquids:[1,5]**

To an ice cold solution of 1-octylpyrrolidinium bromide (6mmol, 1 equiv) in 10 ml of acetonitrile, 1 equiv of conc. $H_2SO_4$ was added in a dropwise manner. The mixture was refluxed for 48 h and HBr formed as a byproduct was distilled out of the condenser. The excess solvent was removed by rotary evaporator followed by drying under reduced pressure. Similar procedure was followed for synthesis of other $HSO_4$ based ionic liquids. Purity of the ionic liquids synthesized was further confirmed by a good agreement of $^1$H NMR spectra with the reported values.[5]

**Synthesis of $MeSO_4$ based ionic liquids:** [1,6]

To an ice cold solution of 1-morpholine in 10 ml of toluene, 6 mmol of dimethylsulfate was added in a dropwise manner. The synthesis was carried out in an inert atmosphere. Temperature was never allowed to rise above 40°C. After 4h of stirring, upper organic layer was removed by decantation, the remaining solvent was removed *in vacuo* and was further dried under reduced pressure for 12h. The purity of the ionic liquid synthesized was further confirmed by $^1$H NMR spectra.

1. **Parameters of Gas Chromatography:** The reaction was initiated by the addition of methyl acrylate to a stirred solution of *p*-nitrobenzaldehyde and DABCO in 1ml of ionic liquid. 1 ml of aliquot was withdrawn at appropriate intervals of time and diluted and extracted in ether. Extracted sample was injected into GC (Varian CP 3800). The parameters of gas chromatography are :

| | |
|---|---|
| Column make | CP SIL 5CB |
| Internal diameter | 0.25 mm |
| Column length: | 15m |
| Film thickness | 0.25-micron |
| Injector temperature: | 200 °C |
| Flow rate | 1 ml/min of nitrogen |
| Detector temperature: | 250 °C. |
| Total run time | 18.95 min (hold at 70°C for 5 min ramp at 4°C, then maintain at 100°C for 0 min, ramp at 79°C and then maintain at 180°C for 5 min.) |
| Internal Standard (IS) | Chlorobenzene |

Typical Retention Times of the compounds analyzed:

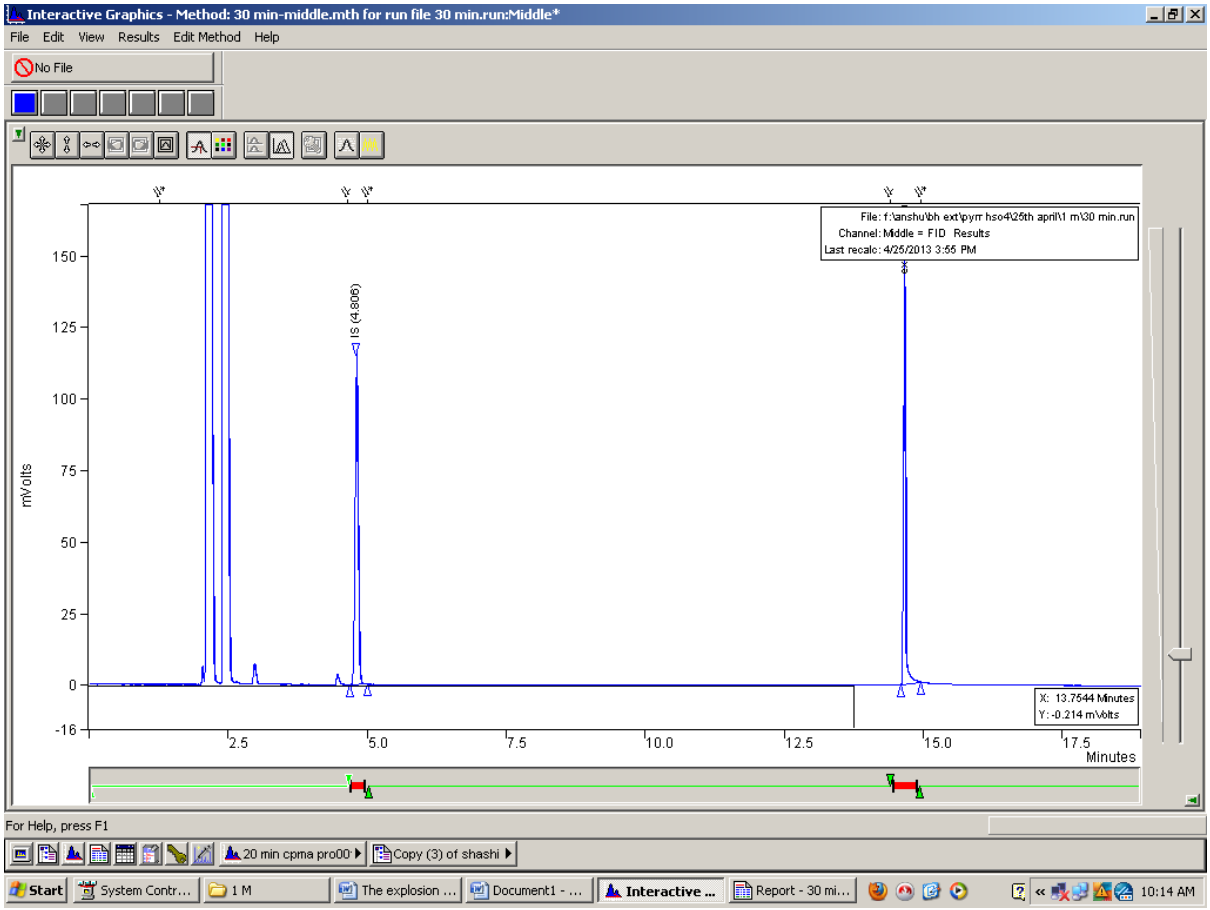
(a) IS = 4.806 min

(b) Product = 14.657 min

The GC method was already calibrated with respect to the product concentrations using pure samples of the Baylis-Hillman product. The amount of product formed as a function of time gave the extent of the reaction (x).

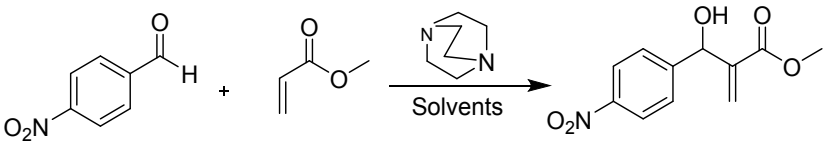
**General procedure of Baylis-Hillman Reaction:** The reaction was initiated by the addition of methyl acrylate 0.9028 ml (1 M) to the stirred solution of *p*-nitrobenzaldehyde and 1 ml of DABCO (1M) in a given solvent. The temperature was maintained by Julabo constant temperature bath maintained at 25 °C with an accuracy of ±0.01K. Upon completion, the reaction mixture was extracted in diethyl ether. Then the combined ethereal fraction was evaporated in vacuo. The crude product was purified by column chromatography (silica gel, ethylacetate: petroleum ether, 1:5-1:3). Desired product was characterized by $^{1}$H NMR.

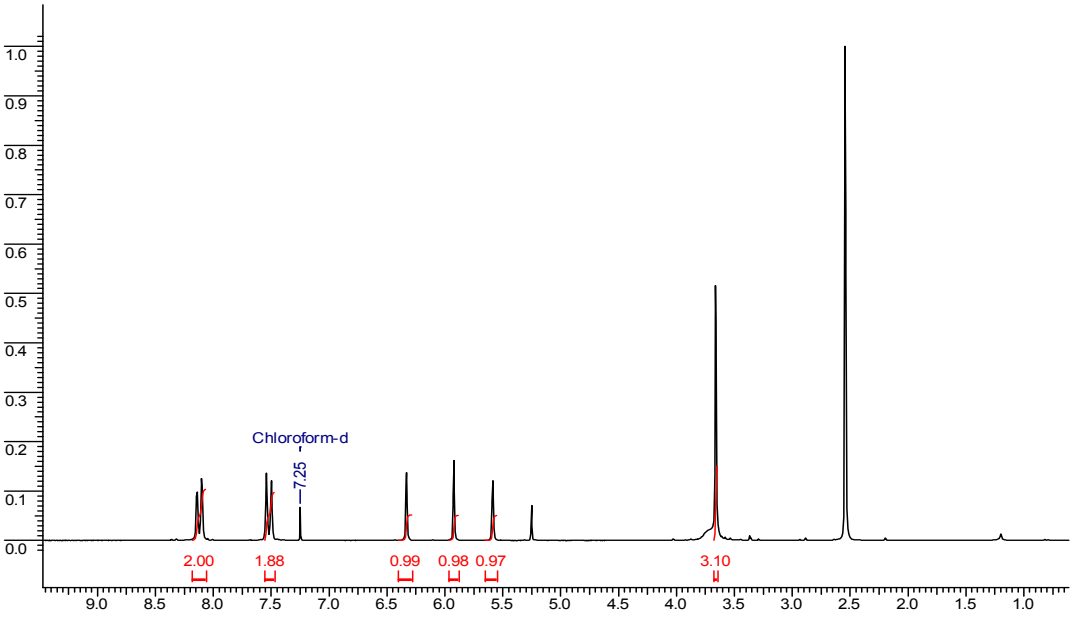
## Typical GC spectra



## 1. [1]H NMR spectra of the product

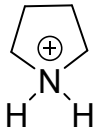
**NMR of product:**



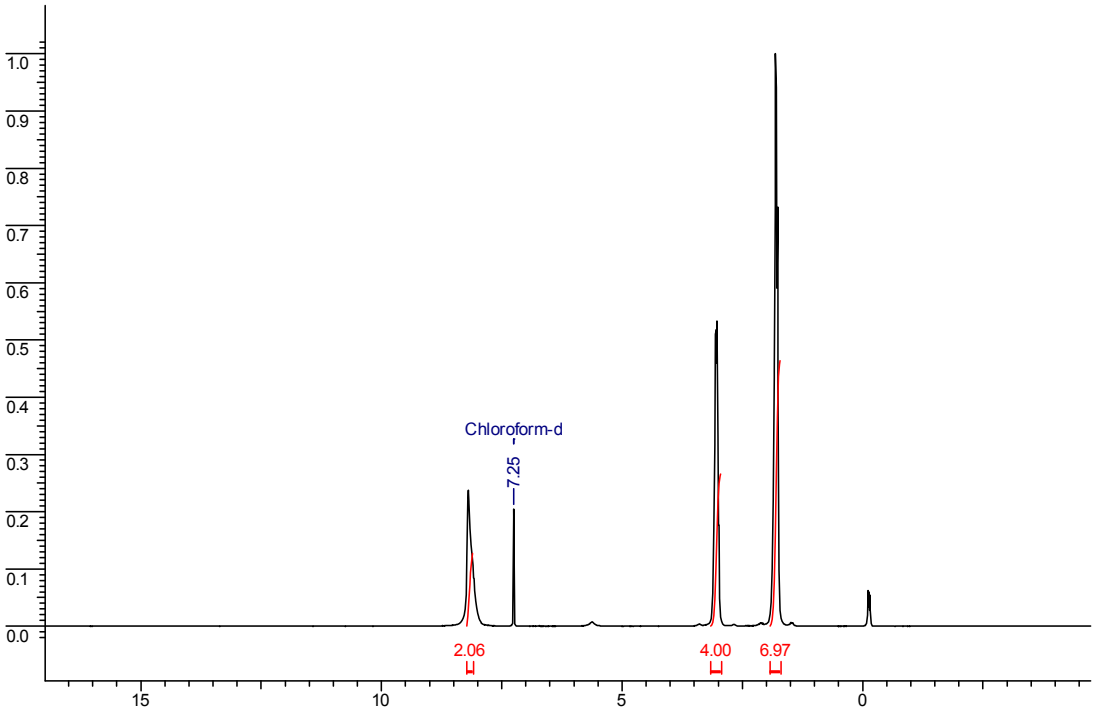




**[1]H NMR, 200 MHz, $CDCl_3$**: 2-[Hydroxy(4-nitrophenyl)methyl]acrylic Acid Methyl Ester: δ 8.18 ( d, *J* = 8.84 Hz, 2H), δ 7.52 (d, *J* = 8.8 Hz, 2H), δ 6.37 (s, 1H), δ 5.89 (s, 1H), δ 5.61 (s, 1H), δ 3.70 (s, 3H)

[Pyr][$CH_3COO$]

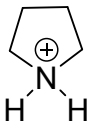



$[CH_3COO]^-$

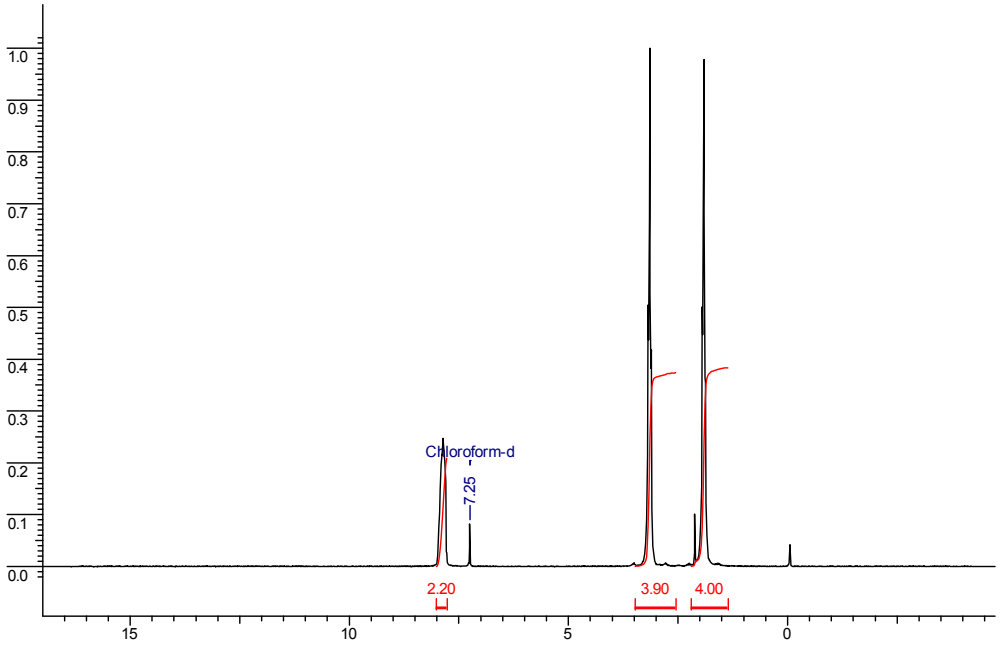



**$^1$H NMR, 200 MHz, $CDCl_3$**: δ 1.93 (m, 7H), δ 3.16 (m, 4H), δ 8.31 (s, 2H)

[Pyr][$CF_3COO$]

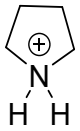


$[CF_3COO]^-$

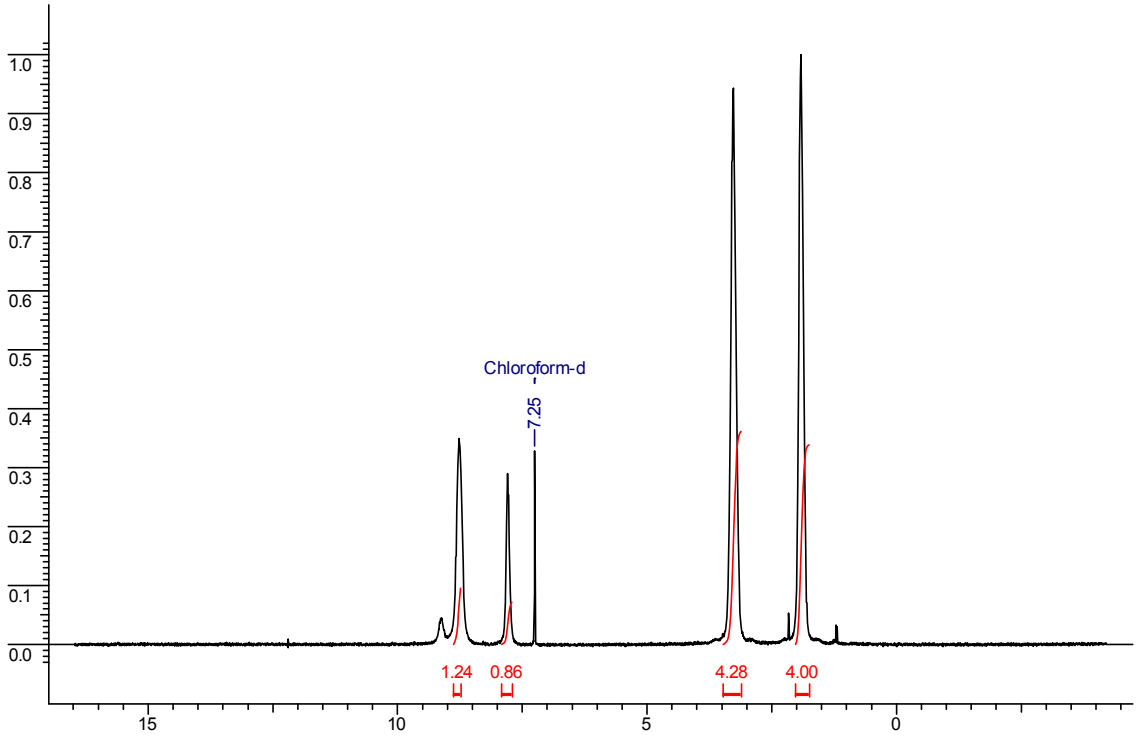



**$^1$H NMR, 200 MHz, $CDCl_3$**: δ 1.91 (m, 4H), δ 3.14 (m, 4H), δ 7.86 (s, 2H)

[Pyr][$HSO_4$]

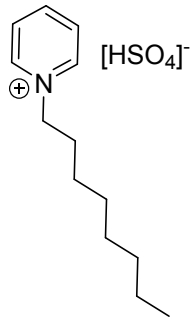


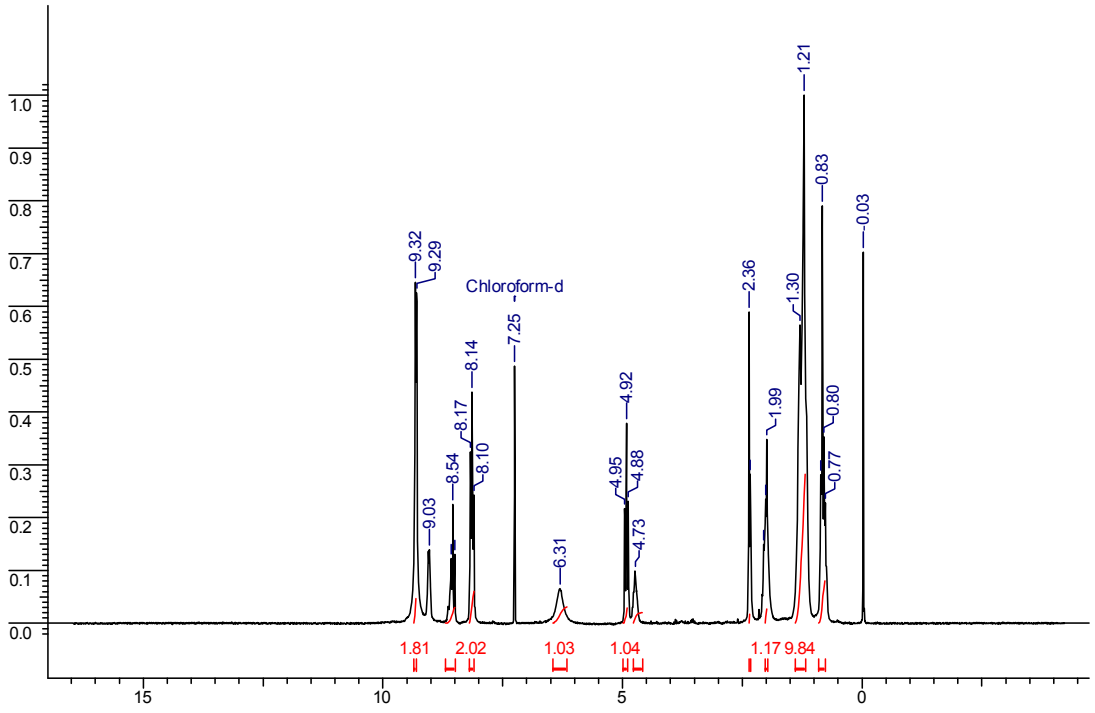

[$HSO_4$]$^-$




**$^1$H NMR, 200 MHz, $CDCl_3$**: δ 1.92 (m, 4H), δ 3.27 (m, 4H), δ 7.80 (s, 1H), δ 8.76 (s, 1H)

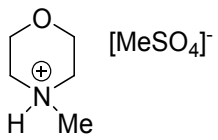
[Opy][$HSO_4$]



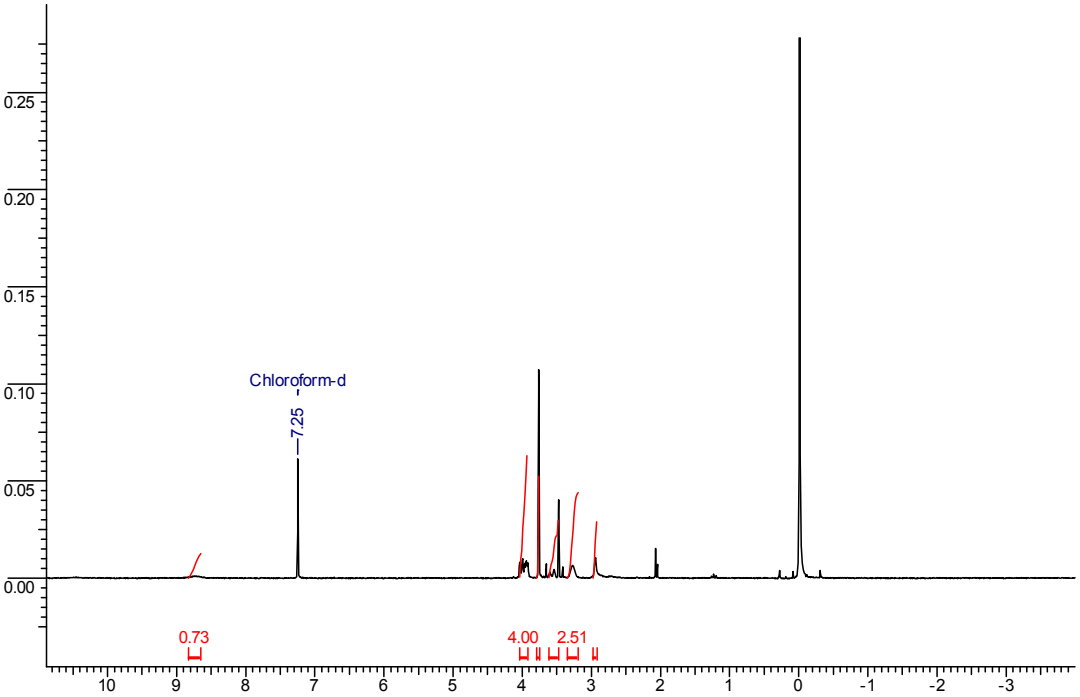




**$^1$H NMR, 200 MHz, $CDCl_3$:** δ 0.83 (t, *J* = 7.5 Hz, 3H), δ 1.21 (m, 10H), δ 1.99 (m, 1H), δ 2.36 (m, 1H), δ 4.73 (t, *J* = 7.3 Hz, 1H), δ 4.92 (t, *J* = 7.3 Hz, 1H), δ 6.31 (broad, 1H), δ 8.14 (m, 2H), δ 8.54 (m,1H), δ 9.32 (m, 2H)

[MeMO][$MeSO_4$]

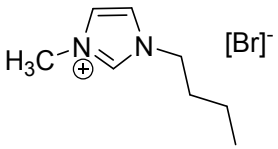


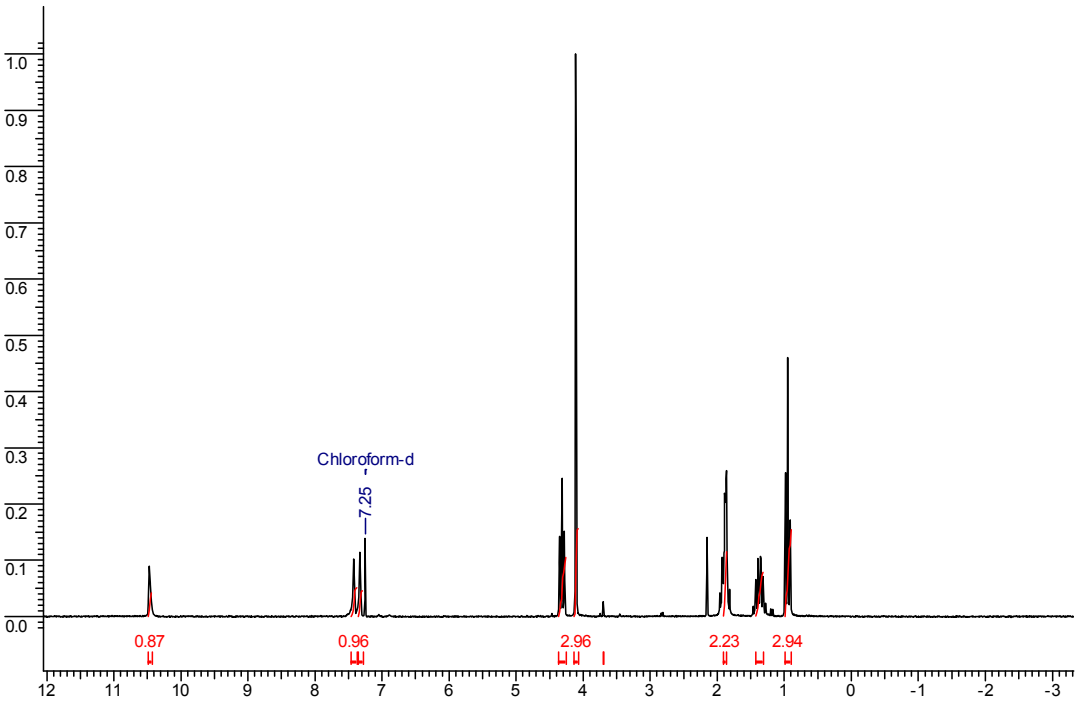

$[MeSO_4]^-$




**$^1$H NMR, 200 MHz, $CDCl_3$:** δ 2.95 (m, 2H), 3.29 (m, 2H), δ 3.49 (s, 3H), δ 3.79 (s, 3H), δ 4.01 (m, 4H), δ 8.8 (s, 1H)

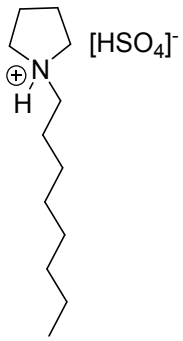
[Bmim][Br]

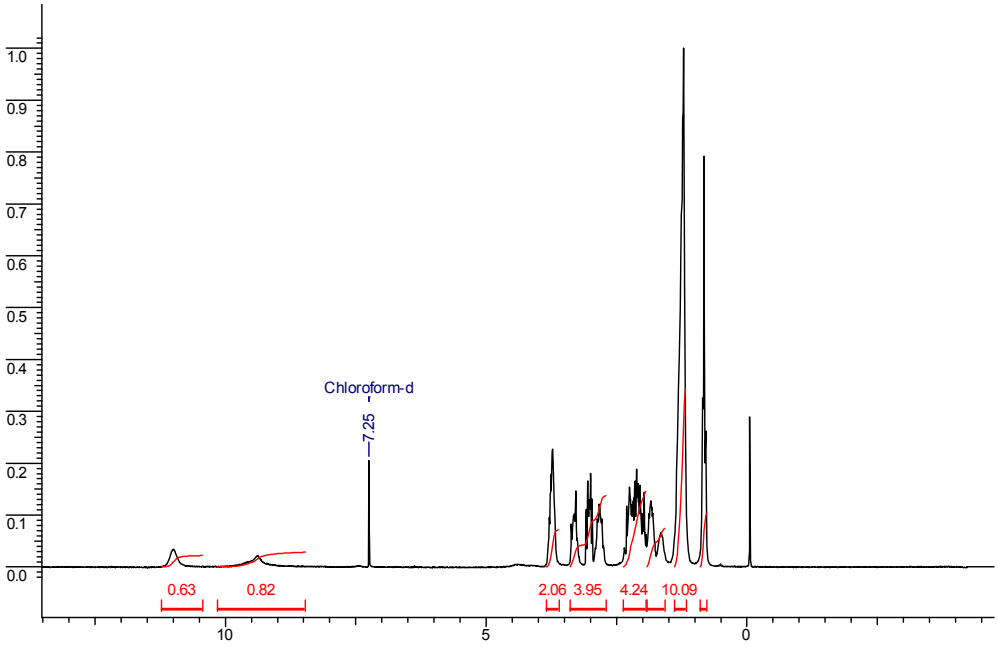



**$^{1}$H NMR, 200 MHz, $CDCl_3$:** δ 0.94 (t, *J* = 7.32 Hz, 3H), δ 1.35 (m, 2H), δ 1.86 (m, 2H), δ 4.11 (s, 3H), δ 4.31 (t, *J* = 7.4 Hz, 2H), δ 7.33 (s, 1H), 7.42 (s, 1H), δ 10.47 (s, 1H)

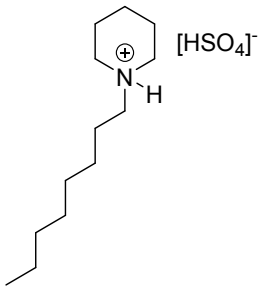
[Opyr][$HSO_4$]

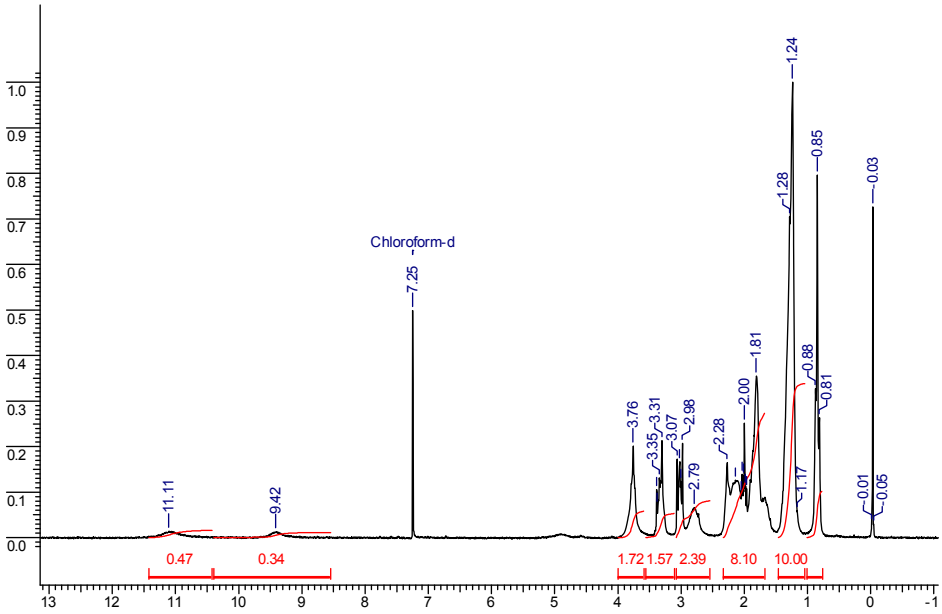



**$^1$H NMR, 200 MHz, $CDCl_3$:** δ 0.83 (t, *J* = 7.3 Hz, 3H), δ 1.22 (m, 10 H), δ 1.66 (m, 2 H), δ 2.12 (m, 4H), δ 3.0 (m, 4H), δ 3.73 (m, 2H), δ 9.39 (b, 1H), δ 10.99 (b, 1H)

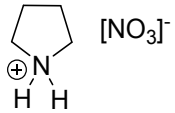
[Opip][$HSO_4$]

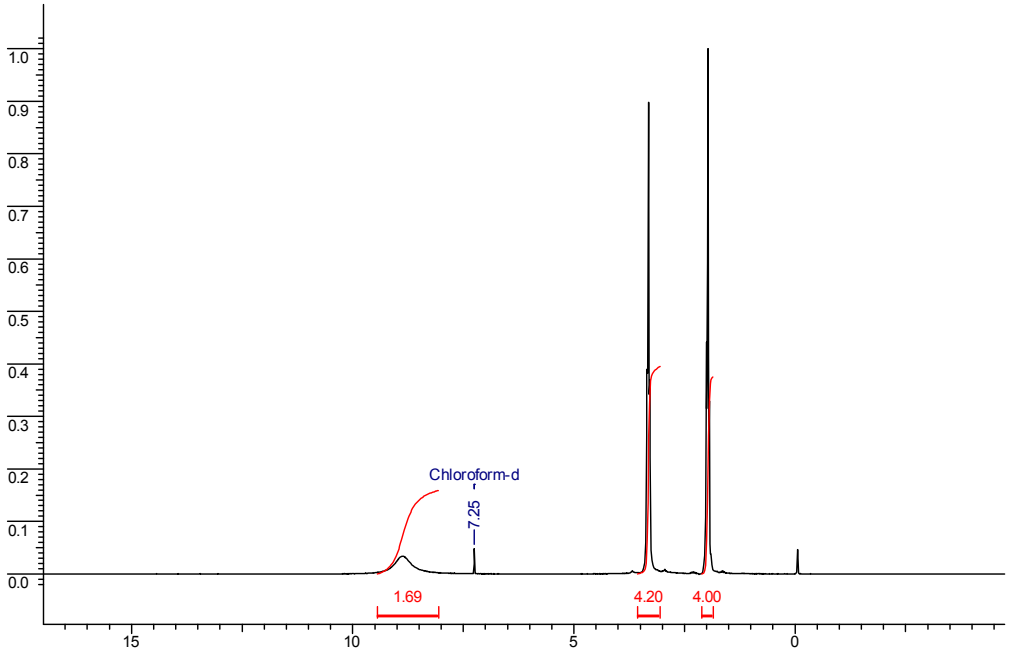



**$^1$H NMR, 200 MHz, $CDCl_3$:** δ 0.85 (t, *J* = 7.0 Hz, 3H), δ 1.24 (m, 10 H), δ 2 (m, 8H), δ 2.98 (m, 2H), δ 3.31 (m, 2H), δ 3.76 (m, 2H), δ 9.42 (b, 1H), δ 11.11 (b, 1 H)

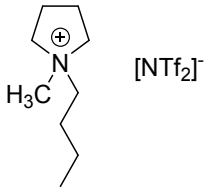
[Pyr][$NO_3$]

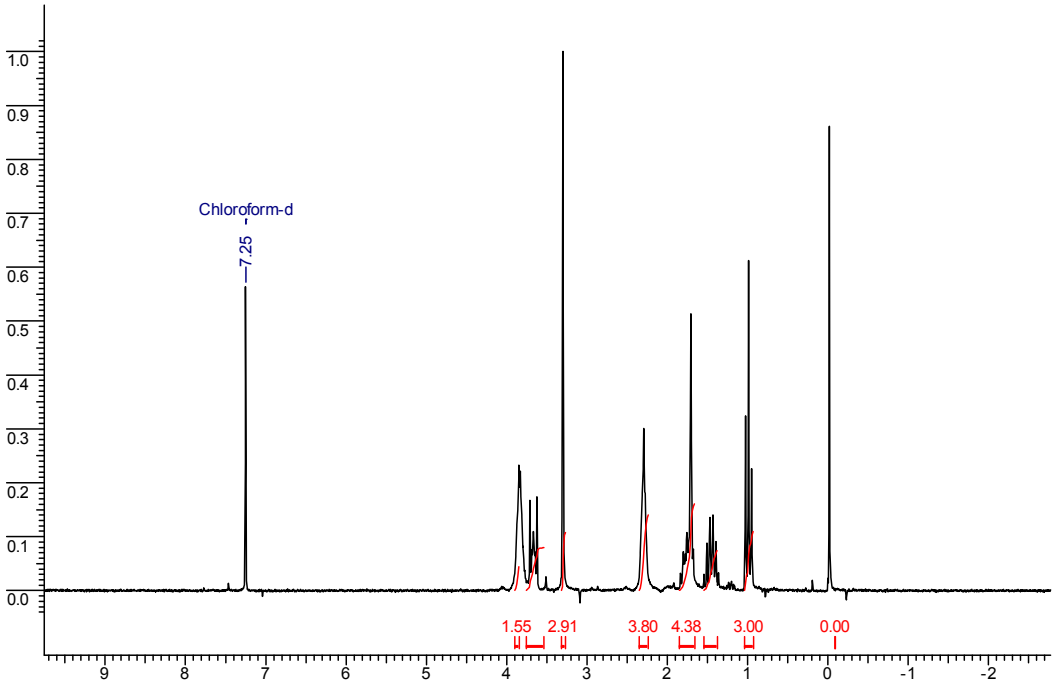



**$^1$H NMR, 200 MHz, $CDCl_3$:** δ 1.97 (m, 4H), δ 3.31 (m, 4H), δ 8.88 (b, 2H)

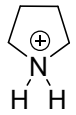
[Mbpyr][$NTf_2$]



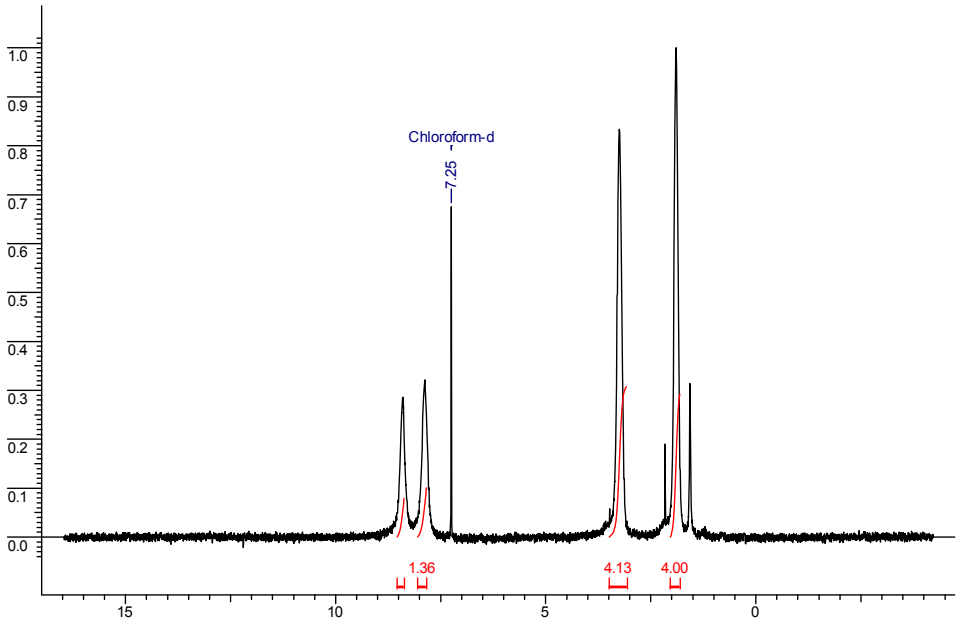




**$^1$H NMR, 200 MHz, $CDCl_3$:** δ 0.99 (t, *J* = 7.2 Hz, 3H), δ 1.43 (m, 2H), δ 1.71 (m, 4H), δ 2.29 (m, 4H), δ 3.30 (s, 3H), δ 3.71 (m, 2H), δ 3.83 (m, 2H)

[Pyr][HCOO]




$[HCOO]^-$




**$^1$H NMR, 200 MHz, $CDCl_3$:** δ 1.90 (m, 4H), δ 3.26 (m, 4H), δ 7.88 (s, 1H), δ 8.40 (s, 1H)

**References :**

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