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공학석사학위논문

Deoxydehydration Reactions of
Galactaric Acid Using
Imidazolium-based Ionic Liquids:
Screening Study

이미다졸륨 계열의 이온성 액체를 이용한
갈락타릭산의 탈산소탈수 반응: 선별 연구

2017年 2月

서울대학교 대학원

화학생물공학부

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ABSTRACT

Deoxydehydration Reactions of
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Screening Study

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With worldwide caution for the depletion of petroleum resources, research for commodity chemicals derived from biomass has attracted many scientist and industries. In this regard, deoxydehydration(DODH) reaction, especially rhenium catalyzed DODH reaction, has been intensively studied due to its high efficiency of reducing oxygen contents from biomass to provide hydrocarbon chemicals. Although oxo–rhenium catalysts are known to be the most

efficient in removing diol group to afford olefin, the high price of the rare metal catalyst causes hardship in industrialization of biomass-derived chemicals.

In this thesis, as a novel method to provide economical and efficient process for DODH reaction, ionic liquid has been introduced as a reaction media to recycle commercial oxo-rhenium catalyst. The ionic liquid should successfully produce muconate from galactarate while being easily separated selectively dissolving rhenium catalyst. Various imidazolium-based ionic liquids have been screened to find the most appropriate ionic liquid. Among them, [C₄MIm][TfO] showed the best efficiency affording 98% of the desired muconate, and the recovered ionic liquid showed moderate catalytic activity during reusability test.

Keywords: Biomass conversion, Ionic Liquid, Deoxydehydration (DODH) reaction, Catalyst recycle

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LIST OF ABBREVIATIONS

DODH	Deoxydehydration
[C ₂ MIm]	1-ethyl-3-methylimidazolium
[C ₄ MIm]	1-butyl-3-methylimidazolium
[C ₆ MIm]	1-hexyl-3-methylimidazolium
[C ₈ MIm]	3-methyl-1-octylimidazolium
[mesy]	mesylate, methanesulfonate
[OAc]	acetate
[TfO]	triflate, trifluoromethanesulfonate
[TFSI]	bis(trifluoromethane) sulfonimide
DMSO	dimethyl sulfoxide
EtOAc	ethyl acetate
IL	Ionic liquid
MTO	methyltrioxorhenium
NMR	Nuclear magnetic resonance
TLC	Thin layer chromatography
TMS	tetramethylsilane

1. Introduction

1.1. Deoxydehydration(DODH) reaction

Deoxydehydration reaction is one of the promising chemical conversion of biomass to produce hydrocarbon chemicals. It has received much attention from researchers and industries because it can efficiently produce long chain hydrocarbon chemicals by removing vicinal diols from various sugar compounds. Many groups have studied DODH reaction by applying various substrates, reducing agents, and catalysts along with its mechanistic studies (Figure 1) [1].

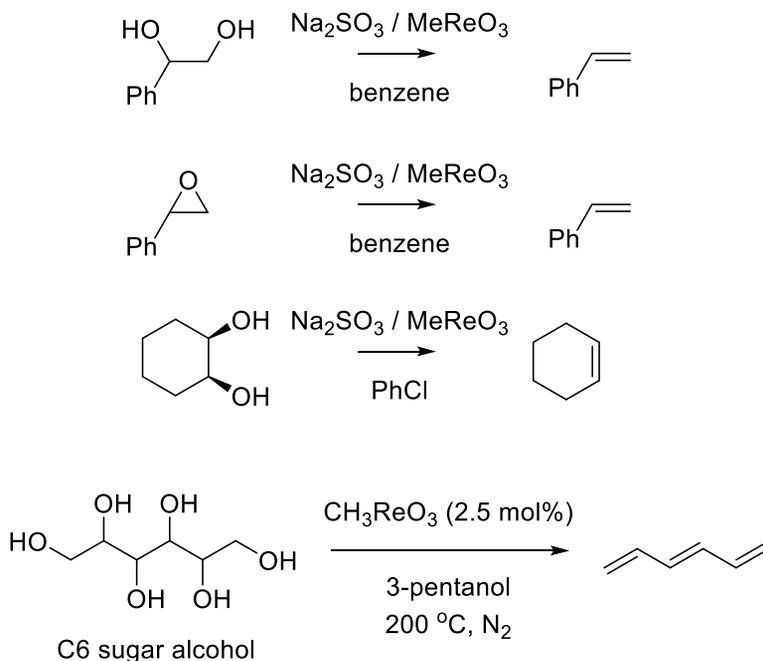


Figure 1. Previously reported DODH reactions using rhenium catalyst [1].

Later, Zhang group proposed DFT studies of reaction mechanisms of DODH reaction using methyltrioxorhenium(MTO) catalyst (Figure 2) [2]. In the proposed mechanism, the Re(VII) is reduced to Re(V) by alcohol reductant. Then, the olefin product is produced as two cycles of deoxydehydration of vicinal diols are conducted.

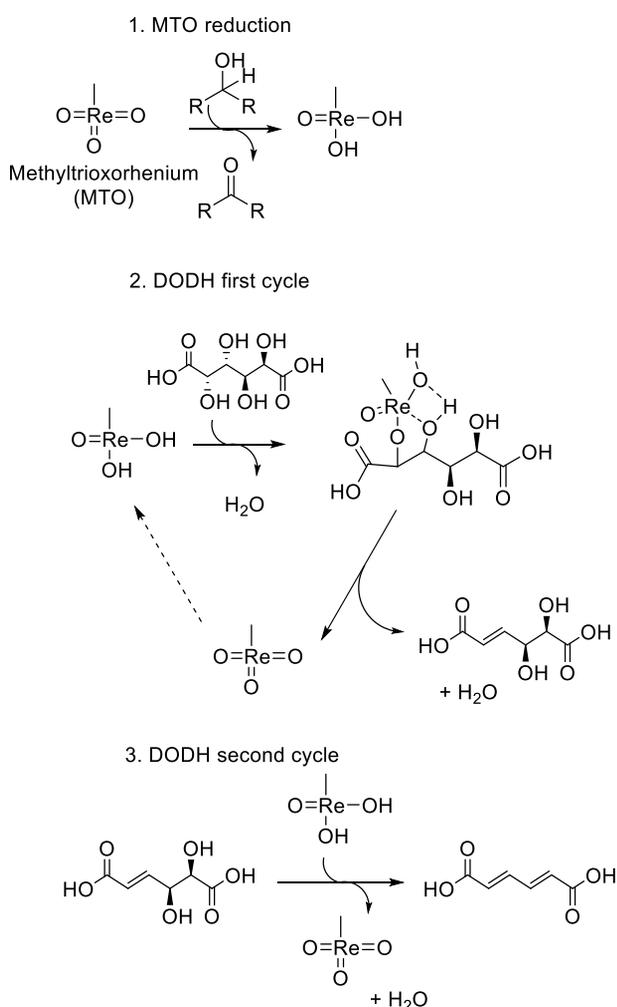
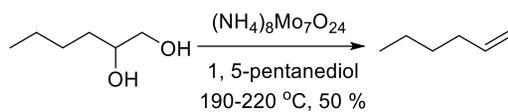


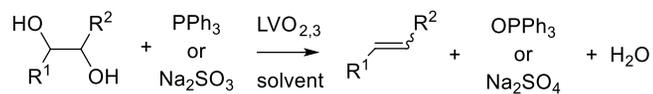
Figure 2. Proposed mechanism of DODH reaction of galactaric acid using MTO catalyst [2].

Despite the recent studies, one of the most significant challenge of industrial production of bio-based chemicals from sugars comes from relatively rare and expensive oxo-rhenium catalyst. In this aspect, other transition metal catalysts, such as molybdenum (Mo) [3,4] and vanadium (V) [5] were suggested as cheap and abundant alternatives of rhenium catalyst. Moreover, heterogeneous supported rhenium catalysts have been developed for easy separation and recycling[6], and polymer supported rhenium catalyst also have been applied to the DODH reaction of tartaric acid[7] (Figure 3). However, these catalysts show low efficiency for removing hydroxyl groups, and additional process for the catalyst preparation is required.

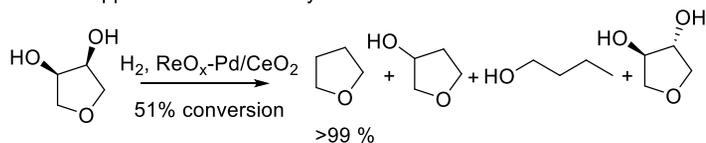
Molybdenum catalyzed DODH reaction



Vanadium catalyzed DODH reaction



Pd/Ce supported rhenium catalyzed DODH reaction



Polymer supported rhenium catalyzed DODH reaction

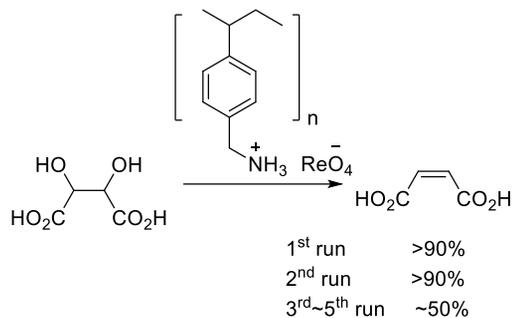


Figure 3. Various alternative catalysts for economical DODH reaction.

1.2. Ionic Liquids: General Description

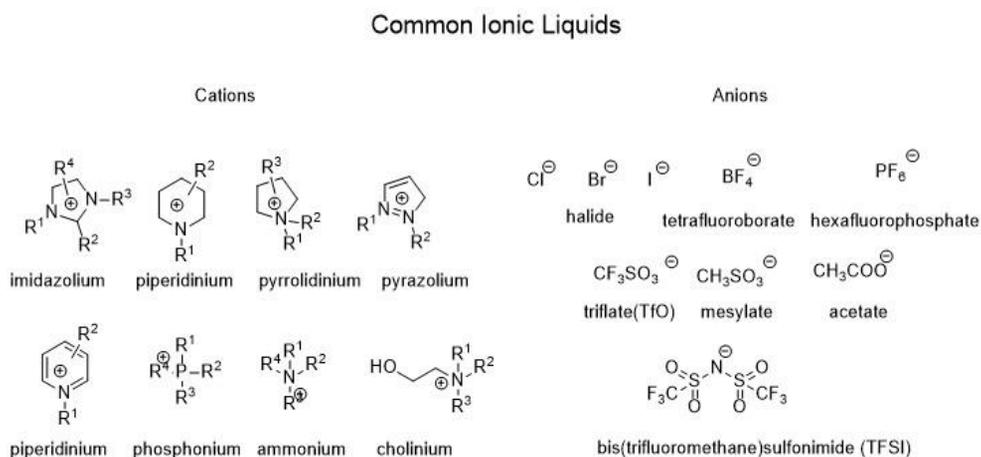


Figure 4. General cations and anions for ionic liquids

Ionic liquid is an organic salt completely composed of cations and anions in liquid state which generally has boiling point lower than 100 °C. It is considered as green solvent due to its extremely low vapor pressure and thermal stability. Depending on the structure and the combination of cations and anions (Figure 4), the physical properties (i.e. melting point, viscosity, polarity, and solubility) and chemical properties (i.e. pH and coordination property) of ionic liquid can be controlled, and from this, ionic liquid is also known as ‘Designer solvent[8].’ Moreover, ionic liquids are suggested to have various applications including electrolyte, solvent for chemical reactions, and gas storage. [9]

1.3. Ionic Liquid for Recyclable Reaction Media

From the special solubility, ionic liquid has been suggested as a recyclable reaction media for various reactions. Especially, the benefits of using ionic liquid as a reaction media is enhanced when it dissolves catalysts and the reactants well while showing poor solubility to the reaction product. In this case, the catalyst can be immobilized or dissolved in ionic liquid phase when the products with or without the unreacted species can be extracted in the organic phase. Then, separated ionic liquid phase having the catalyst can be reused as a “working solution.”

The solubility of ionic liquid has been studied by several groups and it is assumed to be affected by several factors of its cation and anions. Generally, imidazolium cations are more soluble in water, and the solubility decreases as the alkyl side chain on the cation becomes longer. The water solubility of ionic liquids is found to depend mainly on the type of the anion. It follows the ranking less polar borates (e.g. PF_6), fluoroalkylsulfonyl–amide, –imide, –methane < polar borates < fluoroalkyl–sulfonate < halogen. [10]

One example using ionic liquid for the transition metal catalysis includes $[\text{C}_4\text{MIm}][\text{BF}_4]$ –mediated Suzuki coupling. [11]

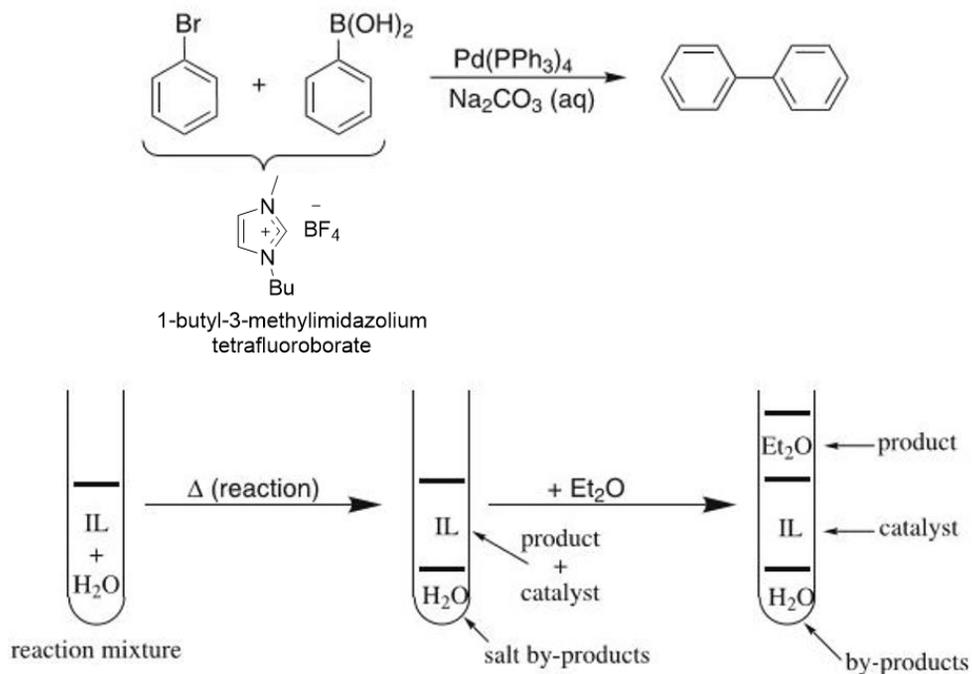


Figure 5. $[\text{C}_4\text{MIm}][\text{BF}_4]$ -mediated Suzuki Coupling reaction [11]

As described in figure 5, the ionic liquid, $[\text{C}_4\text{MIm}][\text{BF}_4]$, forms separable phase with diethyl ether and water while dissolving the catalyst. Therefore, the catalyst, product, and by-products was easily isolated by phase separation behavior of solvents.

In other case, methyl imidazolium chloride was applied to the synthesis of 5-(hydroxymethyl)furfural (HMF) from fructose to work as both recyclable solvent and acid catalyst [12]. The synthesized HMF was extracted from ionic liquid by diethyl ether. Then, the ionic liquid bearing the acidic proton was recovered and reused five more times (Figure 6).

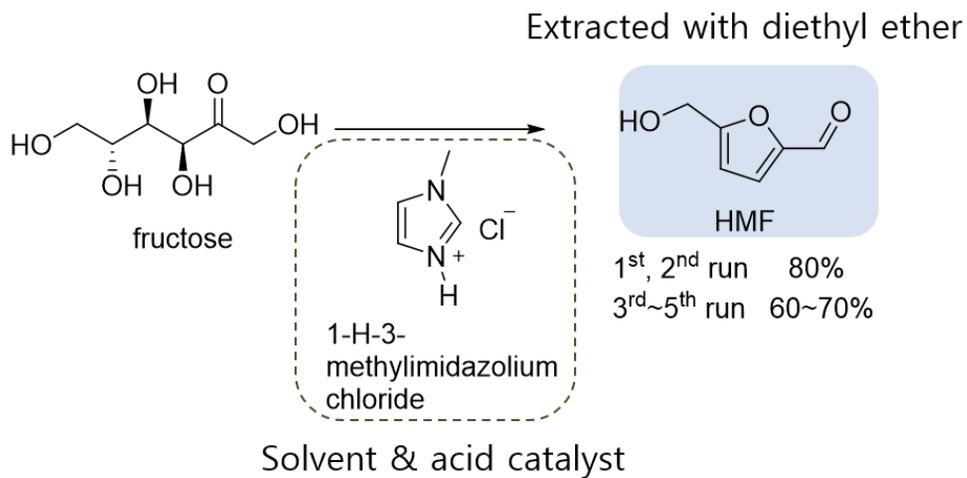


Figure 6. Ionic liquid-mediated HMF synthesis from fructose [12]

2. Results and discussion

2.1. Preparation of Imidazolium-based ILs.

The imidazolium based ionic liquids for DODH reaction was synthesized by the scheme in figure 7. First, 1-methylimidazole reacted with various alkyl halides to form 1-alkyl-3-methylimidazolium halide. Fortunately, the desired alkyl halides were synthesized under mild condition, and the conversion was easily detected by H NMR spectra.

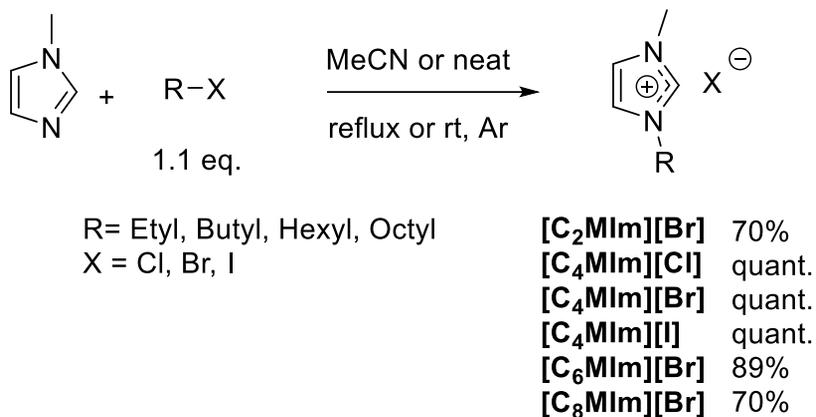


Figure 7. Synthesis of 1-alkyl-3-methylimidazolium halides.

Then, other types of anions were introduced by anion exchange of the synthesized halide ionic liquids (Figure 8, 9).

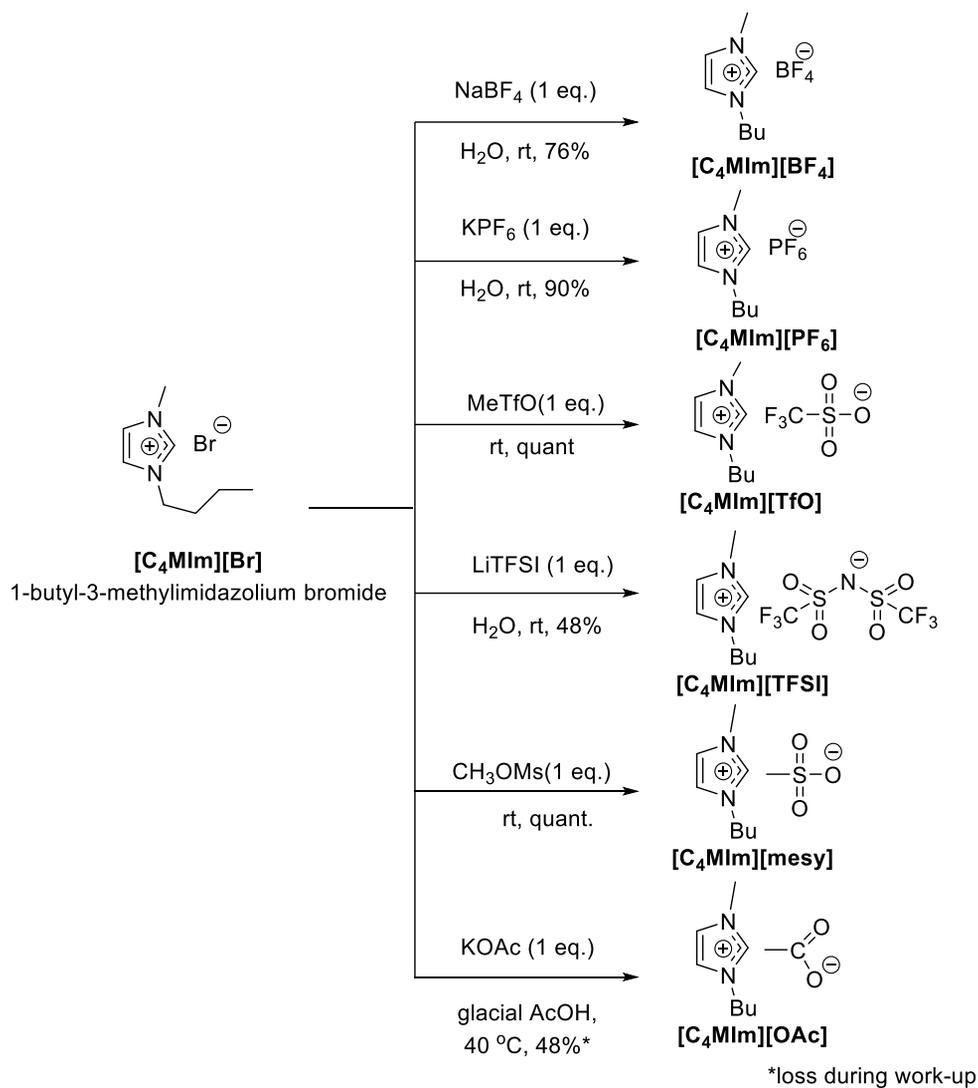


Figure 8. Anion exchange of $[C_4Mim][Br]$

However, because it was difficult to see the difference in H NMR spectra of $[C_4Mim][Br]$ and anion exchanged product, additional silver nitrate test was conducted to check the removal of halide anions. Also, the ionic liquids having $[TfO]$ anion was easily synthesized in quantitative yield (Figure 9) due to volatile side product, methyl bromide, instantly being removed.

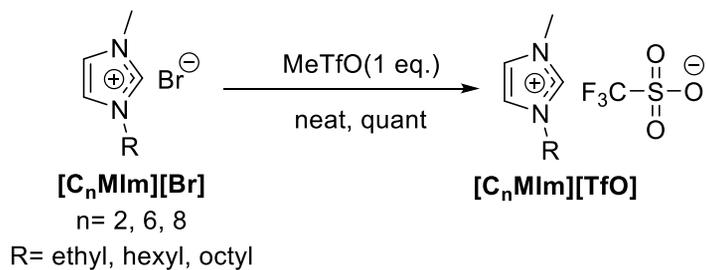


Figure 9. Anion exchange of [C_nMIm] [Br] to [C_nMIm] [TfO]

2.2. Ionic Liquid mediated DODH reaction; Basic concept

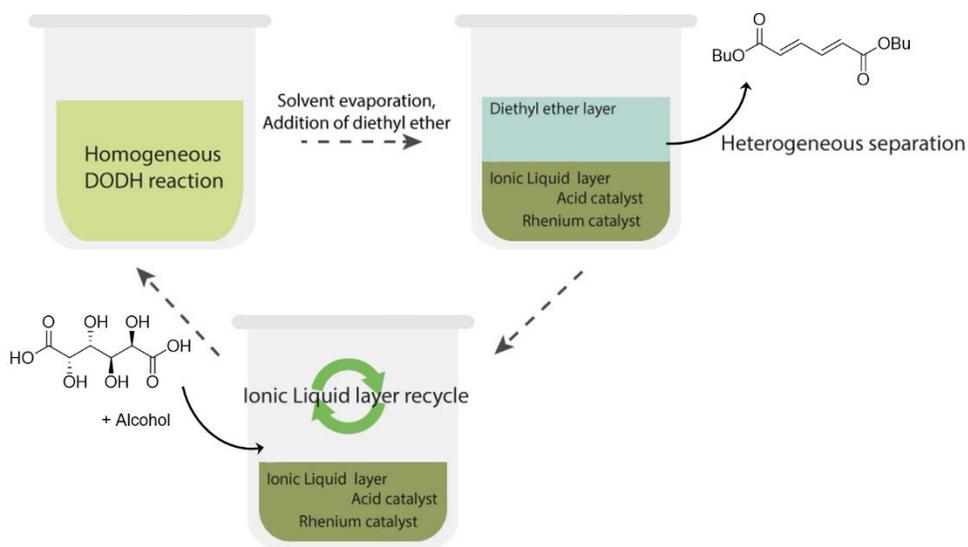


Figure 10. General description of ionic liquid-mediated DODH reaction

The concept of ionic liquid-mediated DODH reaction is

described in figure 6. First, the DODH reaction proceeds homogeneously with galactaric acid as a starting material. Then, after the reaction, solvent is removed and other organic solvent, which can selectively dissolve the muconate product, such as diethyl ether or n-hexane, separates the ionic liquid layer with catalyst and the organic layer with product. These layers are isolated by decantation and the ionic liquid layer is reused again for the next cycle of DODH reaction. Thus, the ionic liquid allows benefits of homogeneous and heterogeneous catalysis at the same time.

For the ionic liquid-mediated DODH reaction, the ionic liquid must be inert or positively affect the reaction. Also, its solubility should be adjusted so it can dissolve rhenium catalyst while being separable with the organic solvent added to selectively remove the non-polar muconate product.

2.3. IL-mediated DODH reaction using various imidazolium bromides

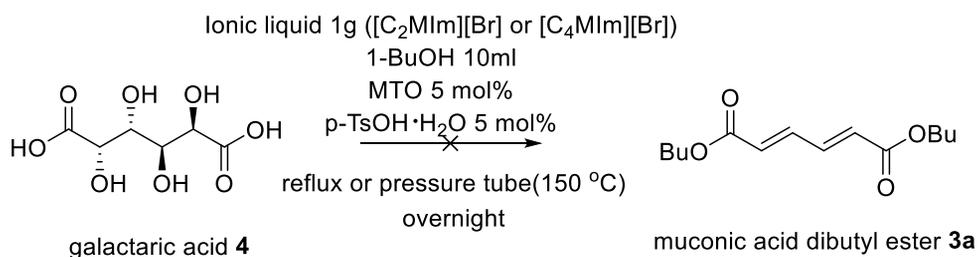


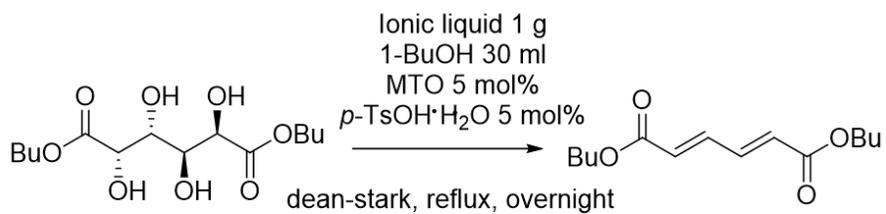
Figure 11. DODH reactions of galactaric acid with $[C_2MIm][Br]$ and

[C₄MIm] [Br]

I first have tried applying [C₂MIm] [Br] and [C₄MIm] [Br], two common types of ionic liquid, and compared the result with general DODH reaction condition. (Figure 7) However, the reaction did not proceed under reflux condition and under higher temperature (150 °C) using pressure tube. This result was rather disappointing because the same condition without the ionic liquid successfully produces the desired muconate product **3a** over 80% yield. [13] It was assumed that the low solubility of the starting material might affect the reaction efficiency [13]. Therefore, the starting material was switched from galactaric acid to its diester form **4a**, and the DODH reaction with several imidazolium bromides were conducted (Table 1).

2.4. IL-mediated DODH reaction : Anion Screening

Then, various types of anions were introduced to ionic liquid with 1-butyl-3-methylimidazolium ($[C_4MIm]$) cation (Table 2). As described in Table 2, halide anions as well as BF_4 , PF_6 anions produced only a small amount of the desired muconate (entry 1~5) whereas larger anions, $[TfO]$ and $[TFSI]$, showed great effect on DODH reaction (entry 6~9). $[C_4MIm][mesy]$, though its anion is structurally similar with $[TfO]$ anion, did not show the good result as $[C_4MIm][TfO]$. Even Re_2O_7 , the cheaper rhenium catalyst, produced the desired product in quantitative yield in $[C_4MIm][TfO]$.



galactaric acid dibutyl ester **4a**

dibutyl muconate **3a**

Entry	Ionic Liquid		Product (%)
	Abbreviation	Structure	
1	[C ₄ MIm] [Cl]		20
2	[C ₄ MIm] [Br]		33
3	[C ₄ MIm] [I]		16
4	[C ₄ MIm] [BF ₄]		5
5	[C ₄ MIm] [PF ₆]		16
6	[C ₄ MIm] [OAc]		No rxn
7	[C ₄ MIm] [mesy]		47*
8	[C ₄ MIm] [TfO]		80 (98*)
9	[C ₄ MIm] [TFSi]		93

* Re₂O₇ was used instead of MTO

Table 2. IL-mediated DODH reactions : anion screening

2.5. Effect of length of alkyl side chain on the imidazolium cation of ILs with [TfO] anion

From the previous anion screening, ILs with [TfO] anion was chosen as the most effective reaction media for DODH reaction of galactaric acid dibutyl ester **4a**. In order to clearly see the effect of cation of the ionic liquid on DODH reaction, the length of the alkyl side chain of [C₄Mim][TfO] was varied (Table 3). But, again, the length of alkyl chain on the cation did not greatly affect the DODH reaction. Besides, isolation of ionic liquid layer became more difficult as the longer alkyl chain on the cation resulted in the lower viscosity of ionic liquid.

2.6. Reusability test of Rhenium catalyst with [C₄MIm] [TfO]

The recycling of the rhenium catalyst by the use of ionic liquid media was conducted with [C₄MIm] [TfO] which showed the highest reactivity during the previous screening test. Although [C₄MIm] [TFSI] also produced high yield of muconic acid dibutyl ester, it was not appropriate for the recycling because the loss of ionic liquid during decantation resulted from higher solubility to non polar organic solvent. So after the decantation using diethyl ether, the recovered ionic liquid was used for the next cycle of DODH reaction by just adding the starting material and 1-butanol. The catalytic activity of reused ionic liquid was detected until 5 cycles for both of MTO and Re₂O₇ catalyst (Figure 12). Further optimization of recycling test showed high reactivity of recovered ionic liquid for more than 10 cycles[13].

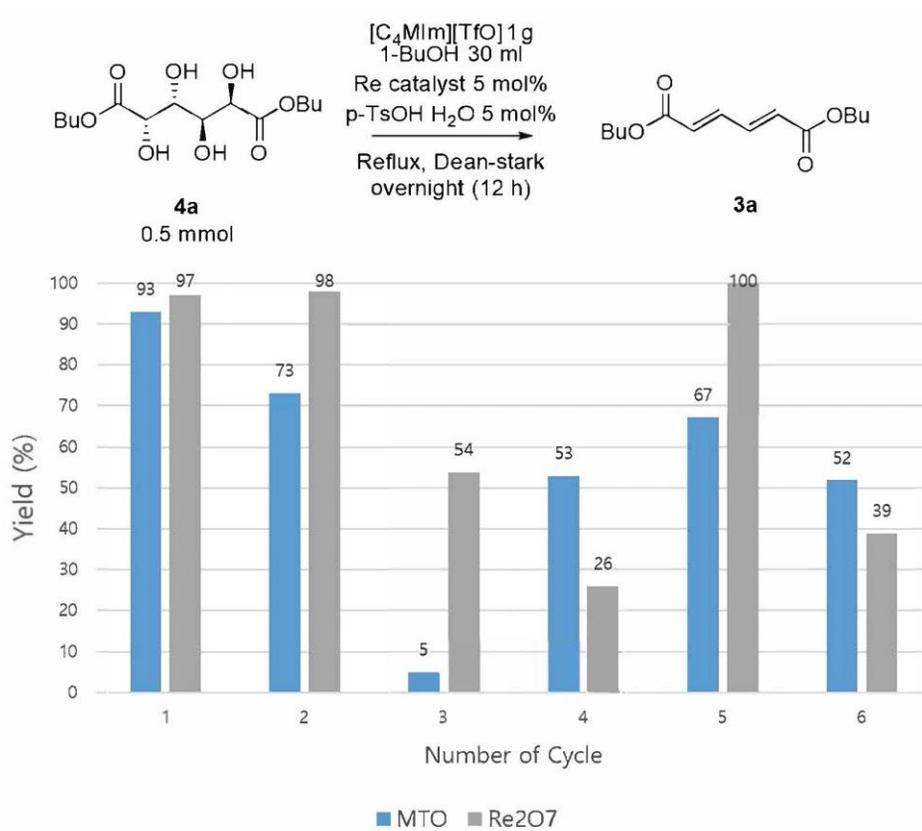


Figure 12. Reusability test of [C₄MIm][TfO]

3. Conclusion

In conclusion, the novel method to provide economical and efficient process for DODH reaction has been developed. Ionic liquid has been introduced to general DODH reaction system to recycle the expensive oxo-rhenium catalyst. In addition, to increase the reaction efficiency for ionic liquid mediated DODH reaction, dibutyl galactarate **4a** was used as a starting material. Commercial oxo-rhenium catalysts well dissolved in several ionic liquids and they were easily separated from the reaction mixture by decantation. Among various ionic liquids, [C₄MIm][TfO] showed the best efficiency for both the isolation of the ionic liquid layer and DODH reaction. The dibutyl muconate **3a** was obtained in moderate yield during 6 consecutive reactions using recovered [C₄MIm][TfO] layer dissolving rhenium catalyst.

Thus, the synthesis of bio-based bulk chemicals has become more economical by recycling the expensive rhenium catalyst used in DODH reaction, the key step for reducing oxygen contents. Further research is expected to realize bulk chemical industry independent of fossil fuels.

4. Experimental Details

4.1. General remarks

Unless otherwise noted, materials were obtained from commercial supplier and were used without further purification. galactaric acid 4 and Re_2O_7 were purchased from Alfa Aesar Co. Ltd., and MeReO_3 and $[\text{C}_4\text{MIm}][\text{TfO}]$ were purchased from Sigma aldrich Co. Another ionic liquid were prepared by modified known procedures [14]. Analytical thin layer chromatography (TLC) was performed by using Merck 60 F254 glass plates pre-coated with a 0.25 mm thickness of silica gel and monitored under UV light (254 nm) . The crude products were column chromatographed on Merck Kieselgel 60 (70–230 mesh) silica gel using solvent mixtures of hexane and ethyl acetate as eluents. Melting points were determined with an open capillary melting point apparatus (Electrothermal IA9100). Low and high resolution mass spectra were measured by the EI or FAB ionization method (JEOL, JMS–600W, JMS–700, 6890 Series). Rhenium contents in ionic liquids were determined by Varian 820–MS. NMR spectra were measured on a Bruker AVIII400 instrument as solutions with TMS as an internal standard (^1H at 400

MHz and ^{13}C at 100 MHz) unless otherwise stated and data were reported as follows in ppm (δ) from TMS: chemical shift (multiplicity, coupling constant in Hz, integration). The percentage yields of each product were calculated by dividing the amount of the desired product obtained after purification by the theoretical yields.

4.2. General procedure for the preparation of imidazolium halide

To pre-distilled 1-methylimidazole, requisite aliphatic halide was added (R-X, 1.1 eq.) dropwise at 0 °C. The reaction mixture was stirred for 24–48 h at 30 °C under Ar. Removal of the residual reactant by washing with diethyl ether and ethyl acetate and drying under reduced pressure afforded crude 1-R-3-methylimidazolium halide. **Butyl-3-methylimidazolium chloride** [C_4MIm] [Cl] ^1H NMR (dmsO) δ 9.12 (s, 1H), 7.77(m, 1H) 7.70 (s, 1H), 4.17–4.14 (t, J=6, 2H) 3.84(s, 3H), 1.79–1.72 (m, 2H), 1.28–1.21(m, 2H) 0.92–0.88 (m, 3H) **1-Butyl-3-methylimidazolium bromide** [C_4MIm] [Br] ^1H NMR (dmsO) δ 9.10 (s, 1H), 7.77–7.76 (t, J=1.8, 1H), 7.70–7.69 (t, J=1.6, 1H), 4.17–4.13 (t, J=7.2, 2H) 3.84(s, 3H), 1.79–1.72 (m, 2H), 1.28–1.22(m, 2H) 0.92–0.88 (m, 3H) **1-Butyl-3-**

methylimidazolium iodide [C₄MIm] [I] ¹H NMR (dmsO) δ 9.11 (s, 1H), 7.76 (s, 1H), 7.69(s, 1H), 4.16–4.13(t, J=6, 2H), 3.84(s, 3H), 1.79–1.72 (m, 2H), 1.28–1.22(m, 2H) 0.92–0.88 (m, 3H) **1-ethyl-3-methylimidazolium bromide [C₂MIm] [Br]** ¹H NMR (dmsO) δ 9.24–9.13 (m, 1H), 7.78 (m, 1H), 7.7 (m, 1H), 4.21–4.16 (m, 2H), 3.84 (s, 3H), 1.42–1.39 (m, 3H) **1-hexyl-3-methylimidazolium bromide [C₆MIm] [Br]** ¹H NMR (dmsO) δ 9.16 (s, 1H), 7.79–7.78 (m, 1H), 7.72–7.71 (m, 1H), 4.17–4.13 (m, 2H), 3.85 (s, 3H), 1.98–1.73(m, 2H), 1.27–1.16 (m, 6H), 0.87–0.83 (m, 3H) **3-methyl-1-octylimidazolium bromide [C₈MIm] [Br]** ¹H NMR (dmsO) δ 9.2 (s, 1H), 7.81–7.80 (m, 1H), 7.74–7.73(m, 1H), 4.18–4.14 (t, J= 7.2 2H), 3.86 (s, 3H), 1.81–1.74 (m, 2H), 1.29–1.24 (m, 10H), 0.87–0.84 (m, 3H)

4.3. General procedure for anion exchange of ILs.

The anion exchange of [C₄MIm] [Br] was conducted under normal pressure and room temperature according to following procedures on Figure 8. In most cases, anion exchange was difficult to clarify by NMR spectra, so, if the case, removal of halide anion was checked with silver nitrate test.

Synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate
[C₄MIm][BF₄] [14f] ¹H NMR (dmsO) δ 9.09 (s, 1H), 7.76–7.75 (m,
1H), 7.70–7.69 (m, 1H), 4.17–4.13 (t, 2H), 3.84 (s, 3H), 1.79–1.72
(m, 2H), 1.30–1.21 (m, 2H), 0.92–0.88 (t, *J*= 3H)

Synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate
[C₄MIm][PF₆] [14e] ¹H NMR (dmsO) δ 9.09 (s, 1H), 7.76–7.75 (t,
1H), 7.69–7.68 (t, 1H), 4.17–4.13 (t, 2H), 3.84 (s, 3H), 1.79–1.72
(m, 2H), 1.30–1.21 (m, 2H), 0.92–0.88 (t, *J*=7.4, 3H)

Synthesis of 1-butyl-3-methylimidazolium acetate [C₄MIm][OAc]
[14i] ¹H NMR (dmsO) δ 9.22 (s, 1H), 7.81–7.73 (m, 1H), 7.71–7.70
(m, 1H), 4.18–4.14 (t, *J*= 7.2, 2H), 3.85 (s, 3H), 1.78–1.72 (m, 5H),
1.28–1.22 (m, 2H), 0.92–0.88 (t, *J*= 7.4, 3H)

Synthesis of 1-butyl-3-methylimidazolium methanesulfonate
[C₄MIm][mesy] [modified procedure in 14g] ¹H NMR (dmsO) δ
9.16 (s, 1H), 7.77 (m, 1H) 7.7 (m, 1H), 4.17–4.14 (t, *J*= 7, 2H),
3.84 (s, 3H), 2.37–2.36 (m, 3H), 1.78–1.71 (m, 2H), 1.28–1.19 (m,
2H), 0.89–0.85 (t, *J*= 7.4 3H)

1-butyl-3-methylimidazolium

bis(trifluoromethane)sulfonimide [C₄MIm][TFSI] [14h] ¹H NMR

(dmsO) δ 9.10 (s, 1H), 7.76–7.75 (m, 1H), 7.69–7.68 (m, 1H), 4.18–4.14 (t, $J=8$, 2H), 3.85 (s, 3H), 1.81–1.73 (m, 2H), 1.31–1.22 (m, 2H) 0.92–0.89 (m, 3H)

4.4. Synthesis of dibutyl galactarate 4a

18 g of galactaric acid 4 and 5 mol% of pTsOH·H₂O is added to 360 ml of n-butanol degassed with Ar, and heated under dean-stark condition for 6 h. The product can be obtained as white crystal after the removal of 1-butanol through rotary evaporator. The product is further purified by filtration, washed with ethyl acetate.

¹H NMR (DMSO) δ 4.87–4.85 (d, 2H) 4.78–4.76 (m, 2H), 4.3–4.28 (d, 2H), 4.08–4.04 (m, 4H), 3.79–3.77 (m, 2H), 1.58–1.54 (m, 4H), 1.36–1.3 (m, 4H), 0.91–0.87 (t, 6H).

4.5. General procedure for DODH reaction with ionic liquids

To a solution of dibutyl galactarate 4a (0.161 g, 0.5 mmol) in mixed solution of IL (1 g) and 1-butanol (30 ml) was added Re₂O₇ (14 mg, 0.03 mmol) or MeReO₃ (7 mg, 0.03 mmol) and pTsOH·H₂O

(6 mg, 0.03 mmol) at room temperature. The resulting mixture was stirred vigorously at reflux condition for 12 h with dean–stark trap. After completion of reaction, the mixture was cooled to room temperature then the volatile components were removed under reduced pressure. The dark brown syrup mixture were diluted with diethyl ether (3 X 30 ml) and stirred for additional 30 min. The diethyl ether layers were decanted and combined organic layers were concentrated *in vacuo*, resulting dark brown liquid. Purification by column chromatography on silica gel (hexane/EtOAc=16:1) afforded desired *trans, trans*-dibutyl muconate 3a as a colorless needle like crystal. mp 39~40 °C (lit. 34~35 °C) [33]; ¹H NMR (CDCl₃) δ 7.32–7.28 (m, 2H), 6.21–6.17 (m, 2H), 4.18 (t, J = 6.6 Hz, 4H), 1.68–1.64 (m, 4H), 1.43–1.38 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H); ¹³C NMR (CDCl₃) δ 166.0, 140.7, 128.4, 64.7, 30.6, 19.1, 13.67; Anal. calcd for C₁₂H₂₂O₄: C, 66.12 H, 8.72; Found: C, 66.51 H, 8.78

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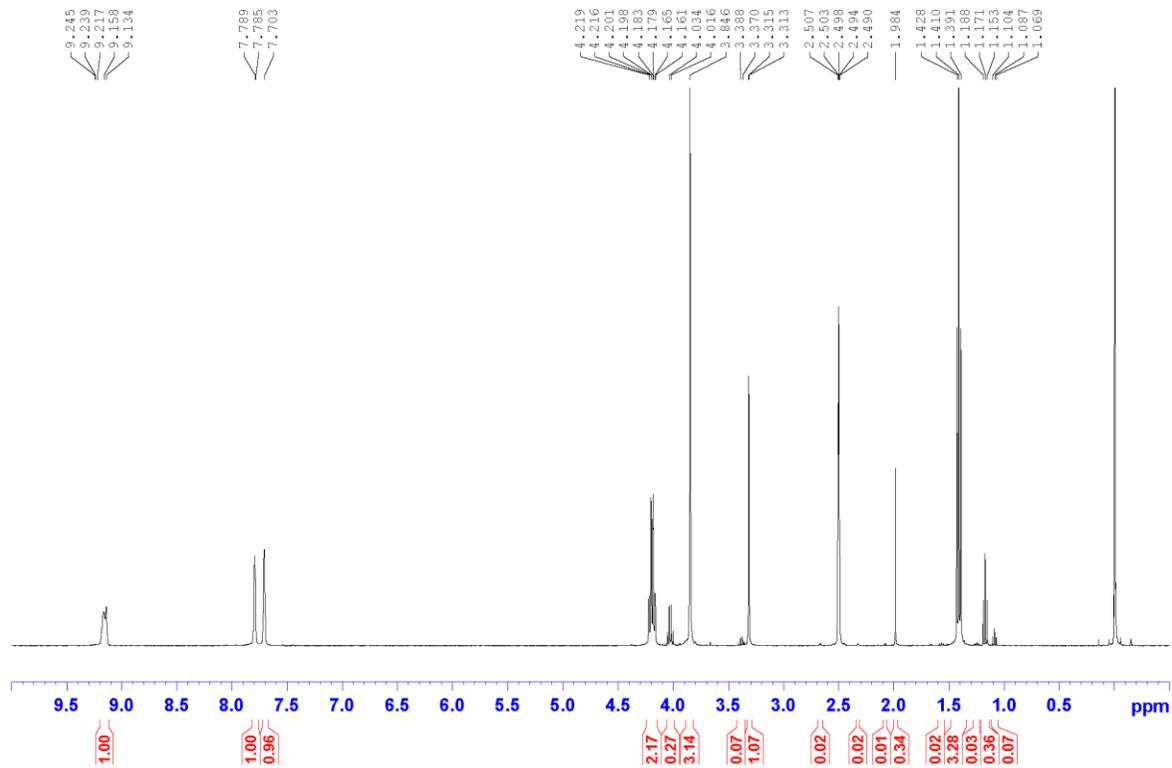
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APPENDICES

List of ^1H NMR Spectra of Selected Compounds

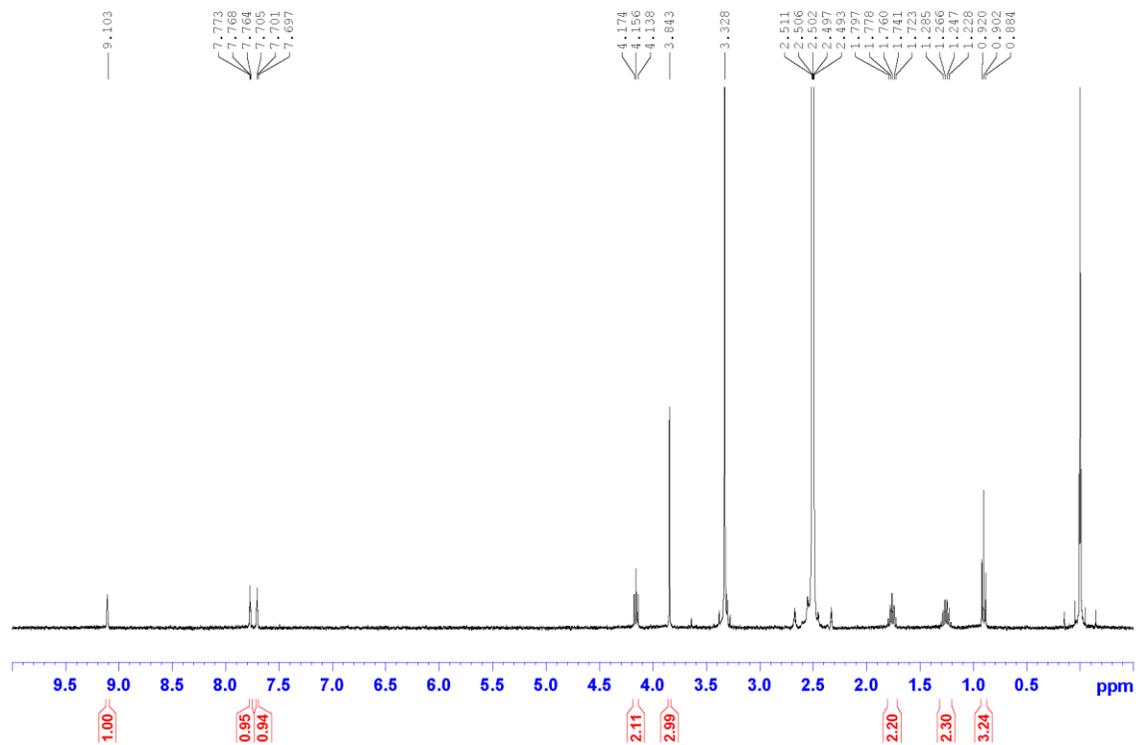
1 .	4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f [C ₂ MIm] [Br]	33
2 .	4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f [C ₄ MIm] [Br]	34
3 .	4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f [C ₆ MIm] [Br]	35
4 .	4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f [C ₈ MIm] [Br]	36
5 .	4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f [C ₄ MIm] [TFSI]	37
6 .	4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f 4 a	38
7 .	4 0 0 M H z ^1H N M R S p e c t r u m (C D C l ₃) o f 3 a	39

SH-EMIM-Br-dmsO



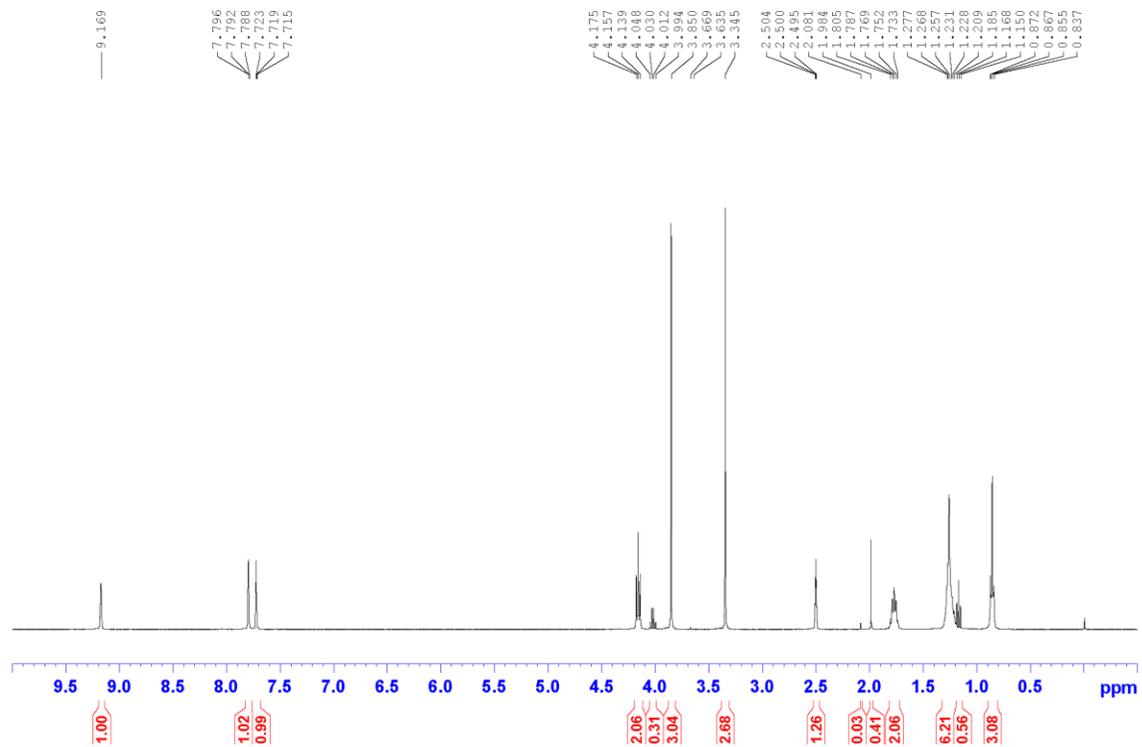
400 MHz ^1H NMR Spectrum (DMSO) of $[\text{C}_2\text{MIm}]\text{Br}$

SH-107-3-solid-dms0

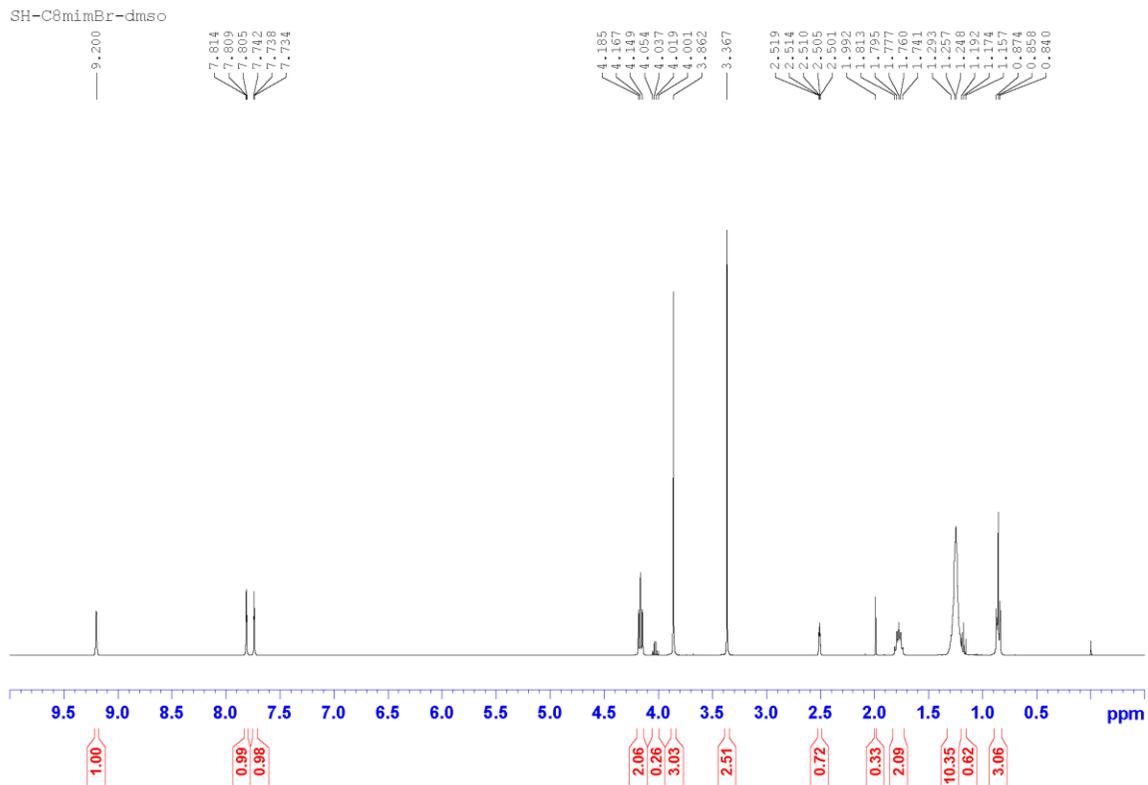


400 MHz ^1H NMR Spectrum (DMSO) of $[\text{C}_4\text{MIm}][\text{Br}]$

SH-[C6mim]Br-dmsO

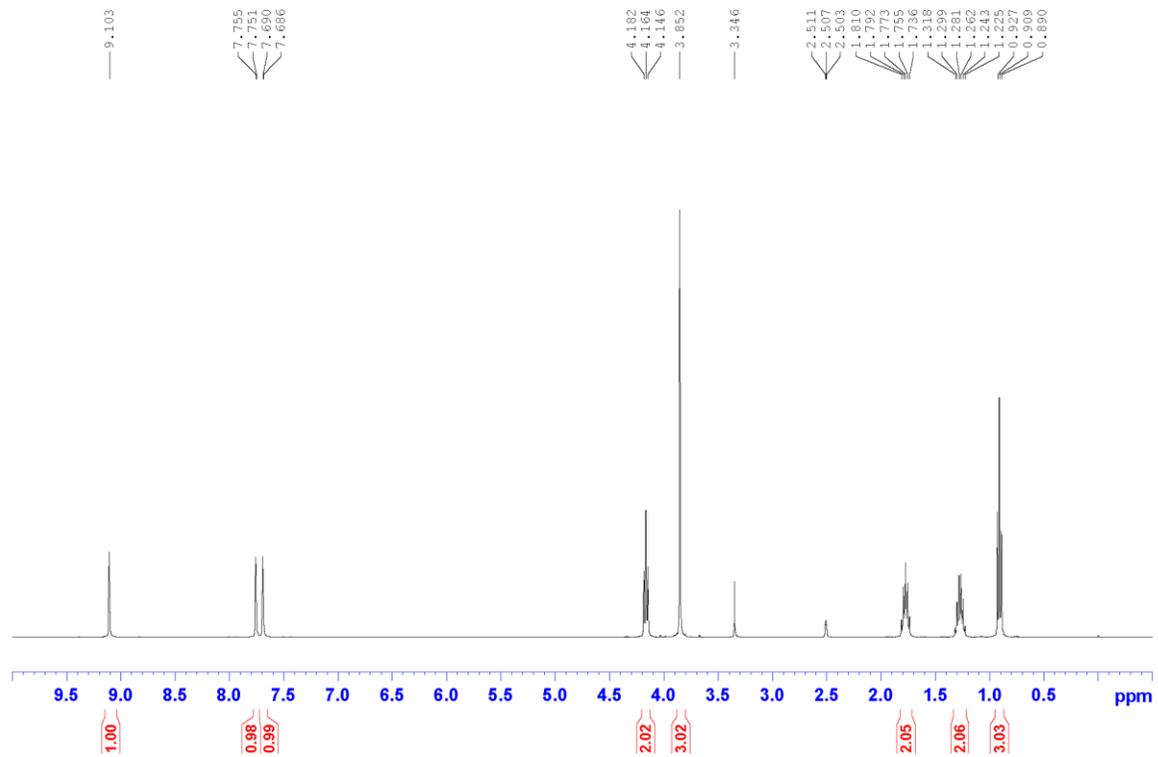


4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f [C₆MIm] [Br]

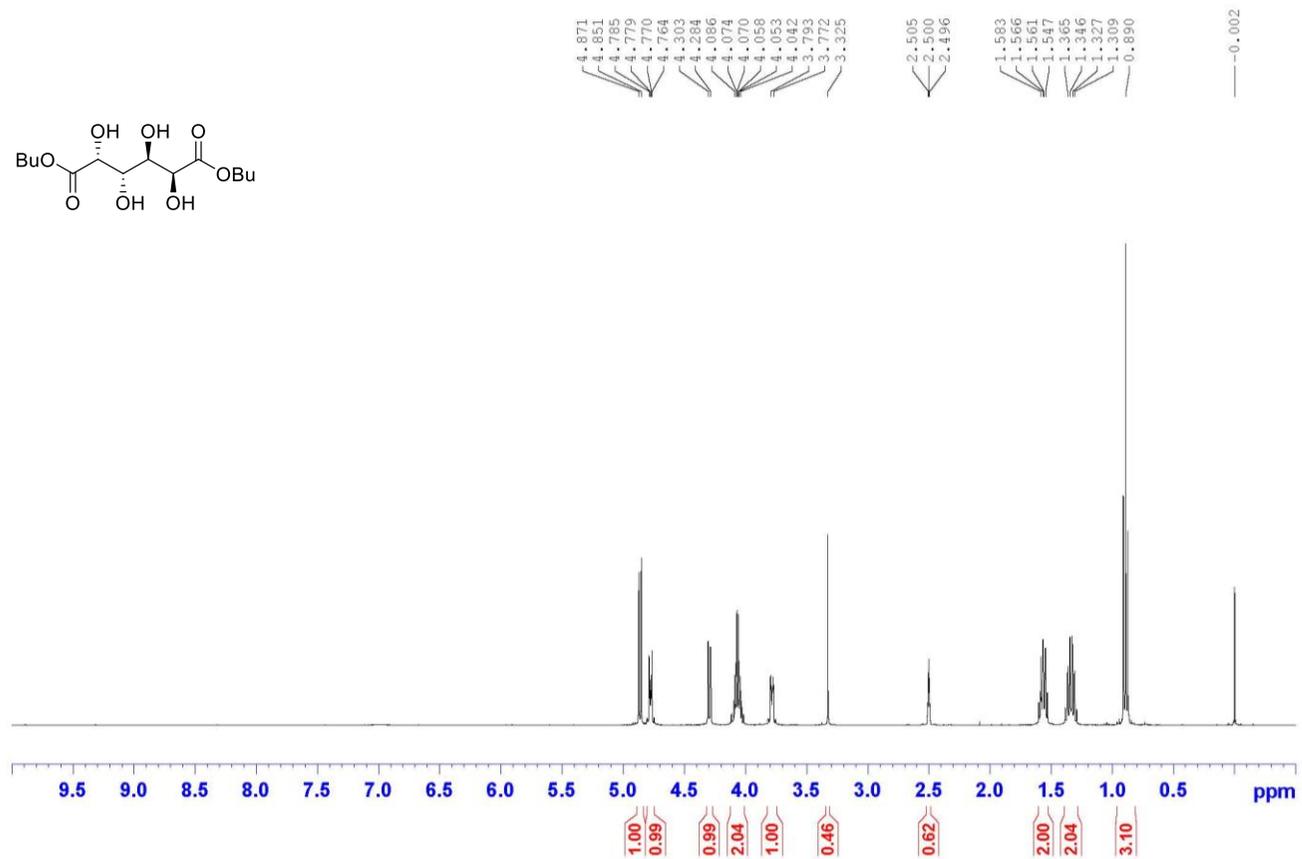
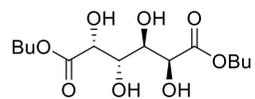


4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f $[\text{C}_8\text{MIm}][\text{Br}]$

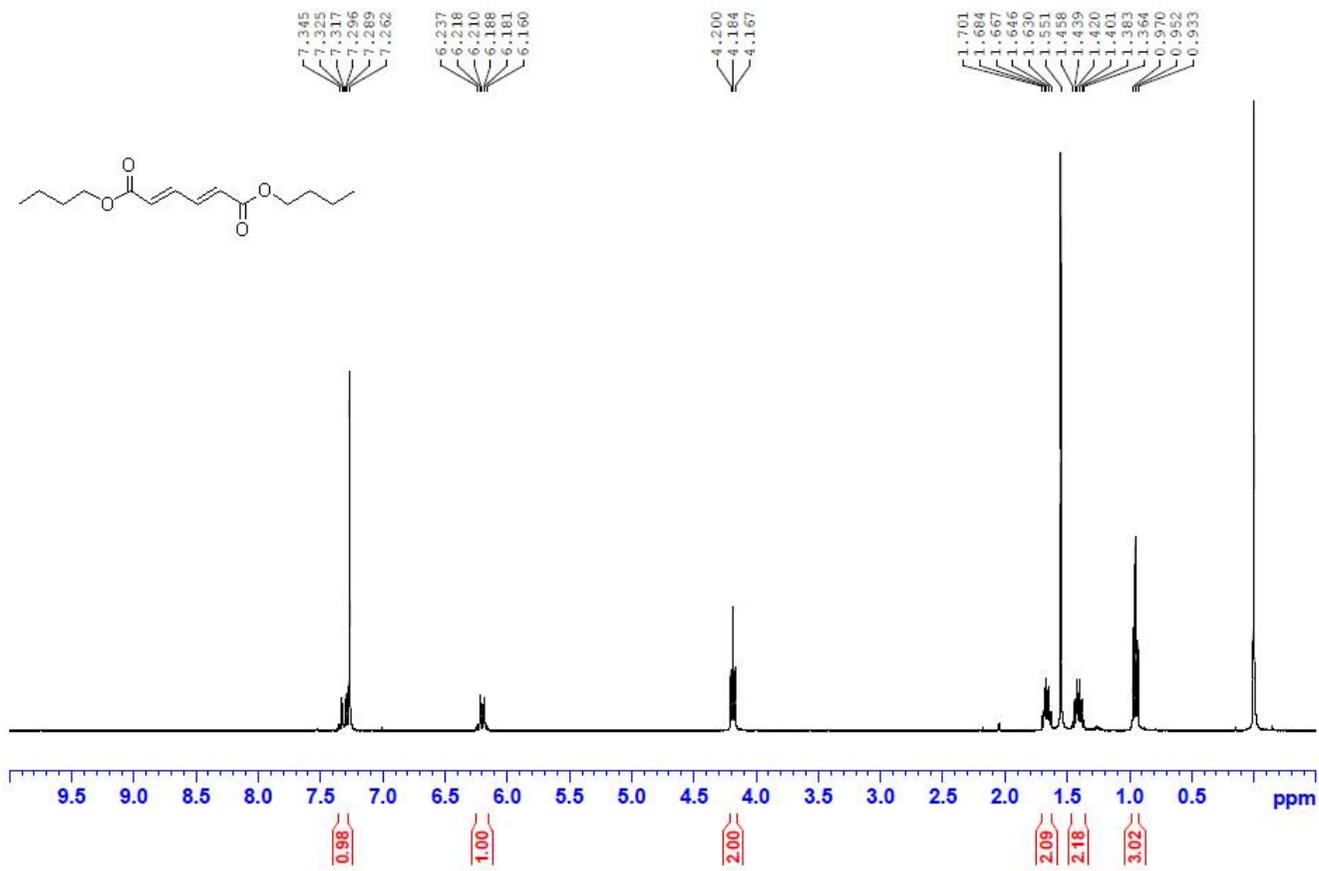
SH-153-bmimTFSi-dmsO



4 0 0 M H z ^1H N M R S p e c t r u m (D M S O) o f $[\text{C}_4\text{MIm}][\text{TFSI}]$



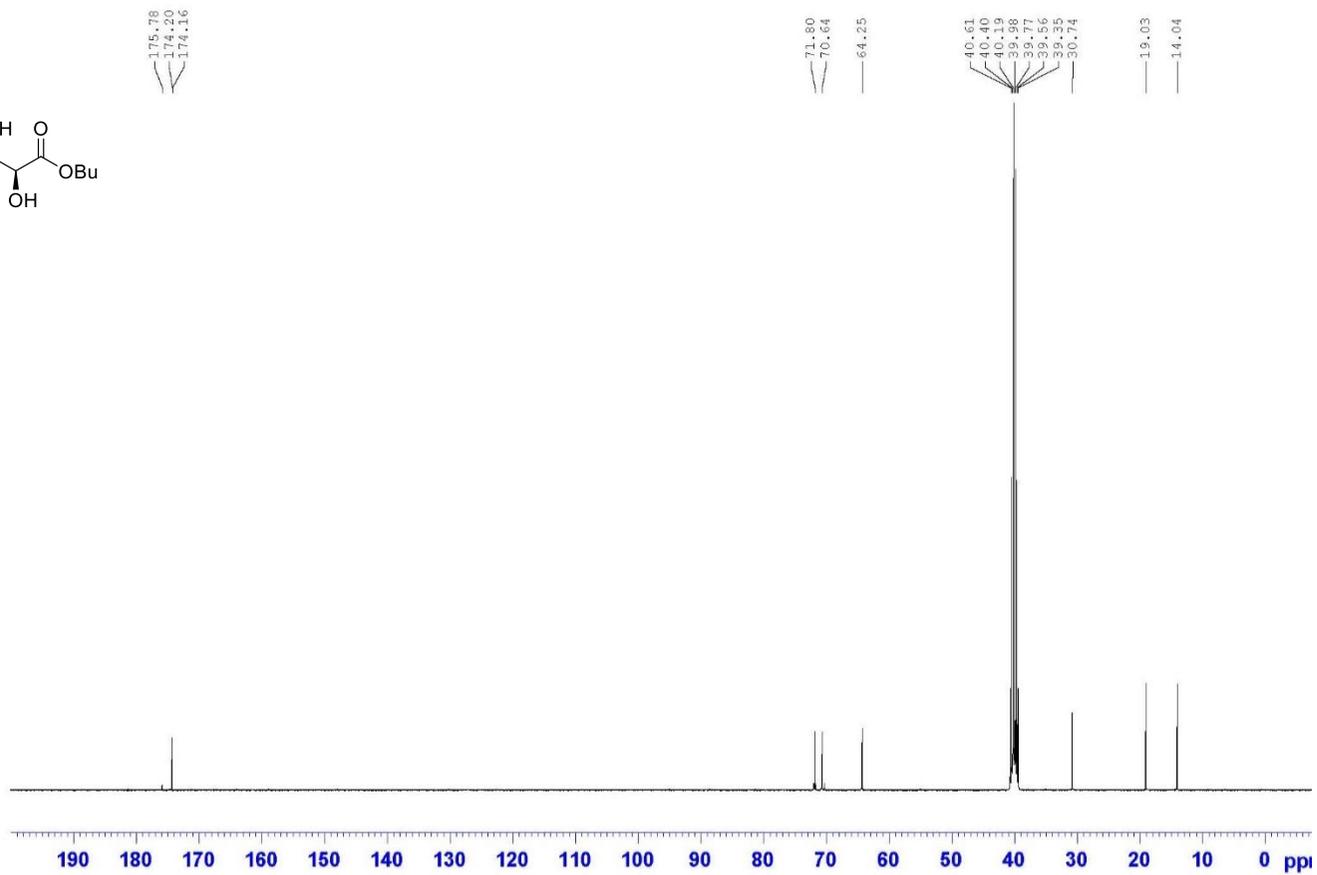
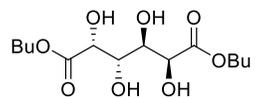
400 MHz ^1H NMR Spectrum (DMSO) of 4a



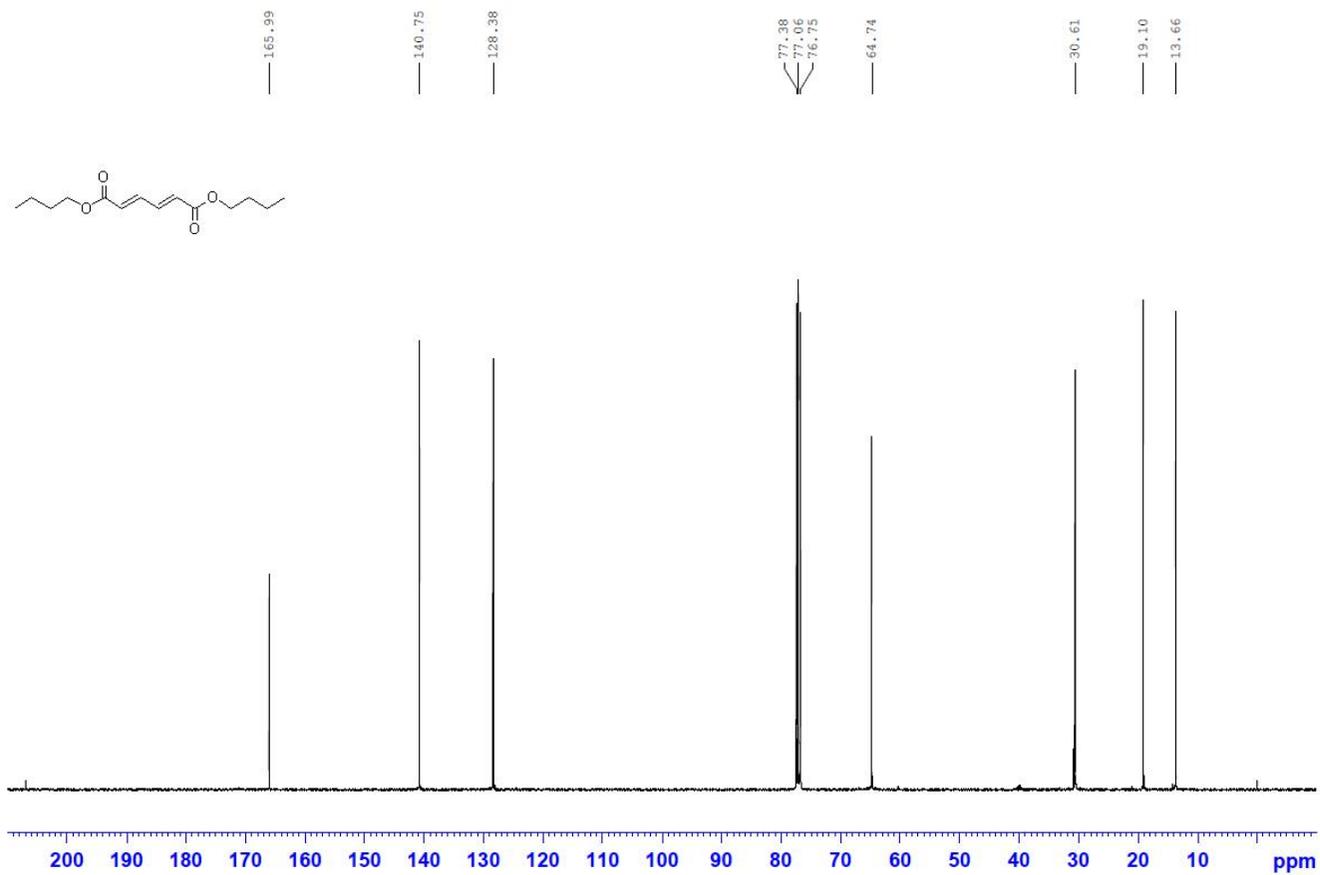
400 MHz ¹H NMR Spectrum (CDCl₃) of 3a

List of ^{13}C NMR Spectra of Selected Compounds

- 1 . 1 0 0 M H z ^{13}C N M R S p e c t r u m (D M S O)
o f 4 a 41
- 2 . 1 0 0 M H z ^{13}C N M R S p e c t r u m (C D C l ₃)
o f 3 a 42



100 MHz ^{13}C NMR Spectrum (DMSO) of 4a



100 MHz ^{13}C NMR Spectrum (CDCl_3) of 3a

ABSTRACT IN KOREAN

석유자원 고갈에 대한 우려와 지속가능 개발에 대한 범 지구적 관심이 높아지면서, 석유 자원으로부터 생산되는 다양한 범용 케미칼을 바이오 원료로부터 얻고자 하는 연구가 활발히 진행되고 있다. 그 중 디옥시디하이드레이션(DODH) 반응, 특히 레늄 촉매를 사용하는 디옥시디하이드레이션 반응은 높은 효율로 바이오매스의 산소 원자의 비율을 줄여 탄화수소 기반의 케미칼을 얻을 수 있게 한다는 점에서 연구가 활발히 진행되어왔다. 하지만 고가의 레늄 촉매로 인해 현재까지 바이오 유래 범용 케미칼의 산업적 적용이 어려운 실정이다.

이에 따라 본 연구에서는, 경제적이면서도 효율적인 탈산소탈수 반응의 새로운 방법으로 이온성 액체를 반응 매개로 도입하여 상용화된 레늄 촉매를 재사용하는 방안을 개발하였다. 이 때 사용되는 이온성 액체는 레늄 촉매를 선택적으로 녹이고 반응산물을 녹이는 유기용매와는 섞이지 않아 용이하게 분리가 가능해야 하며, 본래의 탈산소탈수 반응을 방해하지 않는 성질을 가져야 한다. 탈산소탈수 반응의 반응 매개로 재사용할 수 있는 이온성 액체를 찾기 위해 다양한 종류의 이미다졸류 계열의 이온성 액체를 합성하여 선별 연구를 진행하였다. 그 결과 1-부틸-3-메틸이미다졸륨 트리플루오로메탄설포네이트([C₄MIm][TfO])를 사용한 경우 가장 높은 수율인 98%의 수율로 DODH 반응 산물로 얻어졌으며, 회수된 이온성 액체를 재사용하여도 촉매 활성을 갖는 것을 확인하였다.

주요어 : 바이오매스의 화학적 전환, 이온성 액체,
디옥시디하이드레이션 (D O D H) 반응, 촉매 재사용,

학번 : 2 0 1 5 - 2 1 0 3 9 .