

Supplementary Files
for
Multifunctional Biomass-based Ionic Liquids/CuCl Catalyzed CO₂-promoted
Hydration of Propargylic Alcohols: A Green Synthesis of α -Hydroxy Ketones

Ye Yuan,^{a, b} Siqu Zhang,^b Kang Duan,^b Yong Xu,^b Kaixuan Guo,^b Cheng Chen,^{a, b}
Somboon Chaemchuen,^{a, b} Dongfeng Cao,^{a, b, *} Francis Verpoort,^{a, b, c, *}

^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan
University of Technology, Wuhan 430070, PR China

^b School of Material Science and Engineering, Wuhan University of Technology, Wuhan 430070,
PR China

^c National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russia

Corresponding Authors: Dongfeng Cao (D. Cao): cao_dongf@whut.edu.cn; Francis Verpoort (F.
Verpoort): francis@whut.edu.cn

1. Synthesis of the imidazole-based ILs

The imidazole-based ILs was synthesized based on the ion exchange resin methods, as reported in literatures with modifications.¹⁻² Taking [C₂C₁im][Lev] as an example, 20 mmol [C₂C₁im][Br] and 45 mL anhydrous ethanol were added in a 100 mL round-bottomed flask. Upon complete dissolution, 20 mL of anion-exchange resin (D201 OH, supplied by Ningbo Zhengguang resin Co., LTD) was added and the mixture was stirred at room temperature for 6 hours. Subsequently, the resin was separated and washed 3-5 times with total 20 mL anhydrous ethanol in a Bush funnel. The obtained [C₂C₁im][OH] filtrate was concentrated to 50 mL and added with 20 mmol levulinic acid. The mixture continued to stir at room temperature for 12 hours, then the solvents in the mixture were totally removed under vacuum to obtain the final [C₂C₁im][Lev].

2. Calculation of green metrics

“**1a**” in Table 3 (entry 1) was selected as examples to show how AE, E-factor, CE, RME, MI and MP were calculated:

The reaction of **1a** (2.5 mmol, 0.2103 g), H₂O (5 mmol, 0.09 g) and equivalent CO₂ (2.5 mmol, 0.044 g) were carried out with the employment of 1 mol% of CuCl (0.025 mmol, 0.00247 g) and 1 equiv. of [C₂C₁im][Lev] (2.5 mmol, 0.5682 g). **2a** (95%) was obtained.

(1)

$$\begin{aligned} AE (\%) &= \frac{\text{Mole weight of product} \times 100}{\text{Sum of mole weights of reactants}} \\ &= \frac{102.13 \times 100}{84.12 + 18.02} \\ &= 100.0 \end{aligned}$$

(2)

$$MI = \frac{\text{Total mass in process}}{\text{Mass of product}}$$

$$\begin{aligned}
&= \frac{0.2103 + 0.09 + 0.002474 + 0.5682 + 0.11}{0.0025 \times 0.95 \times 102.13} \\
&= 4.04
\end{aligned}$$

(3)

$$\begin{aligned}
CE (\%) &= \frac{\text{Carbon in product} \times 100}{\text{Total carbon in reactants}} \\
&= \frac{5 \times 0.95 \times 2.5}{2.5 \times 5} \times 100 \\
&= 95
\end{aligned}$$

(4)

$$\begin{aligned}
E &= \frac{\text{Total mass of waste}}{\text{Mass of final product}} \\
&= MI - 1 \\
&= 3.04
\end{aligned}$$

(5)

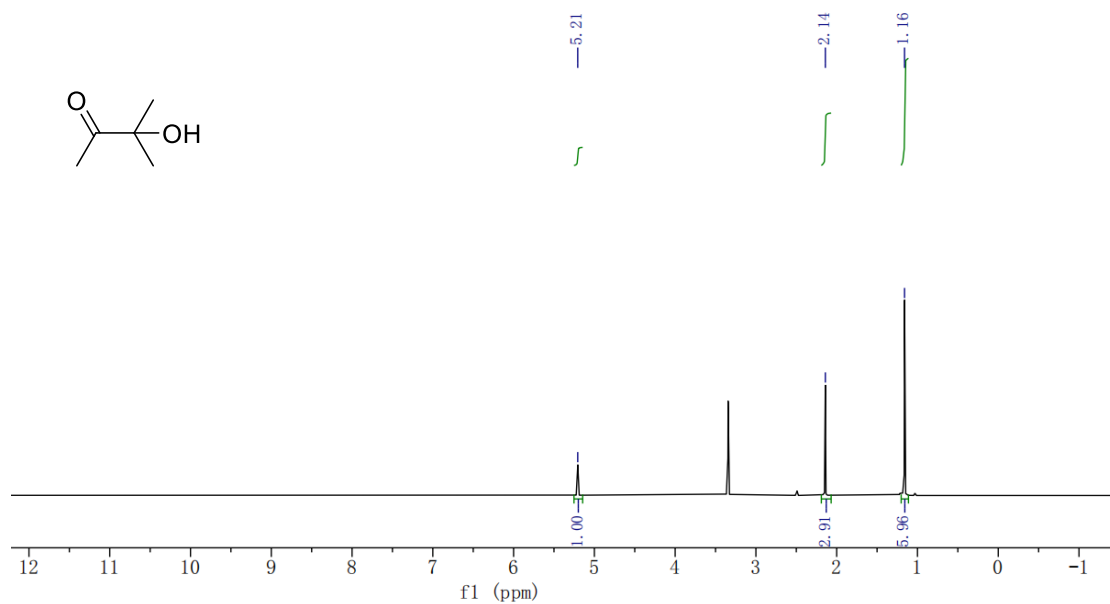
$$\begin{aligned}
ME (\%) &= \frac{\text{Mass of product} \times 100}{\text{Total mass of reactants}} \\
&= \frac{0.0025 \times 0.95 \times 102.13}{0.2103 + 0.09} \times 100 \\
&= 80.8
\end{aligned}$$

(6)

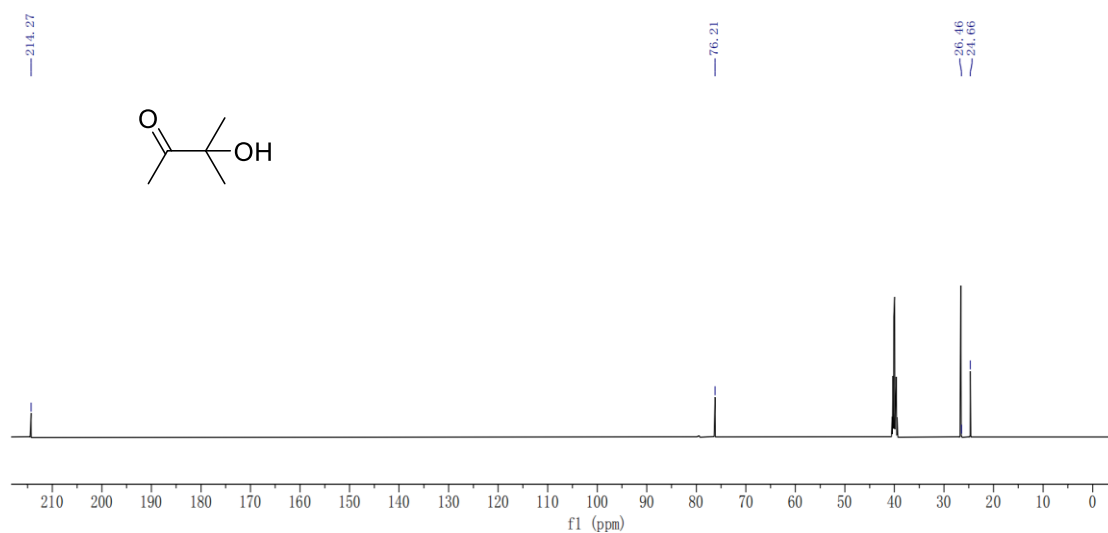
$$\begin{aligned}
MP (\%) &= \frac{\text{Mass of product} \times 100}{\text{Total mass}} \\
&= \frac{1}{MI} \times 100 \\
&= \frac{1}{4.04} \times 100 \\
&= 24.7
\end{aligned}$$

3. NMR spectra of the products and ionic liquids

^1H NMR of **2a**

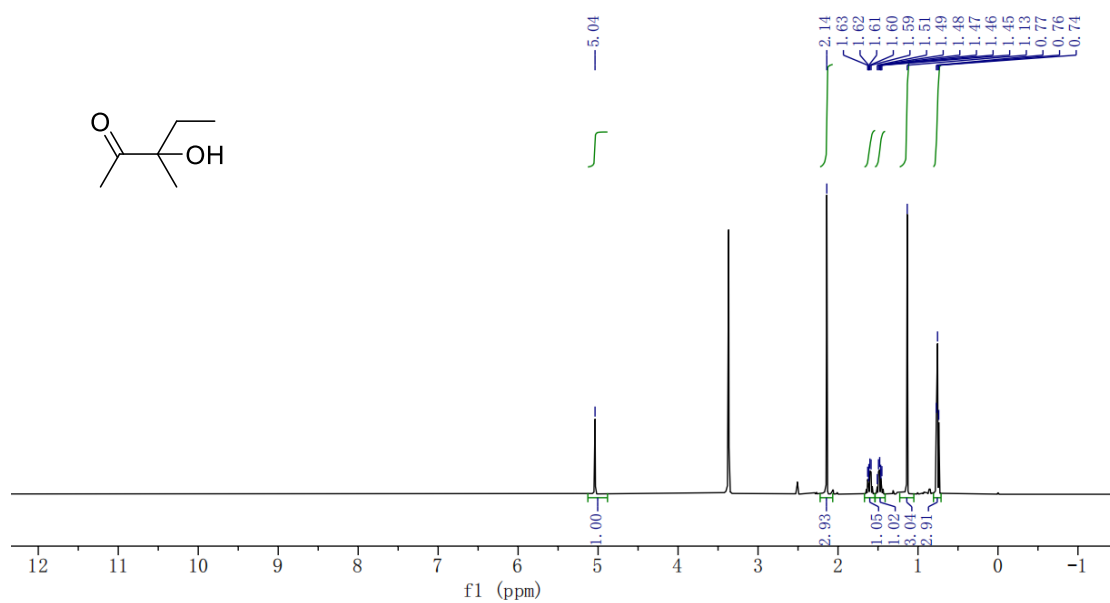


^{13}C NMR of **2a**

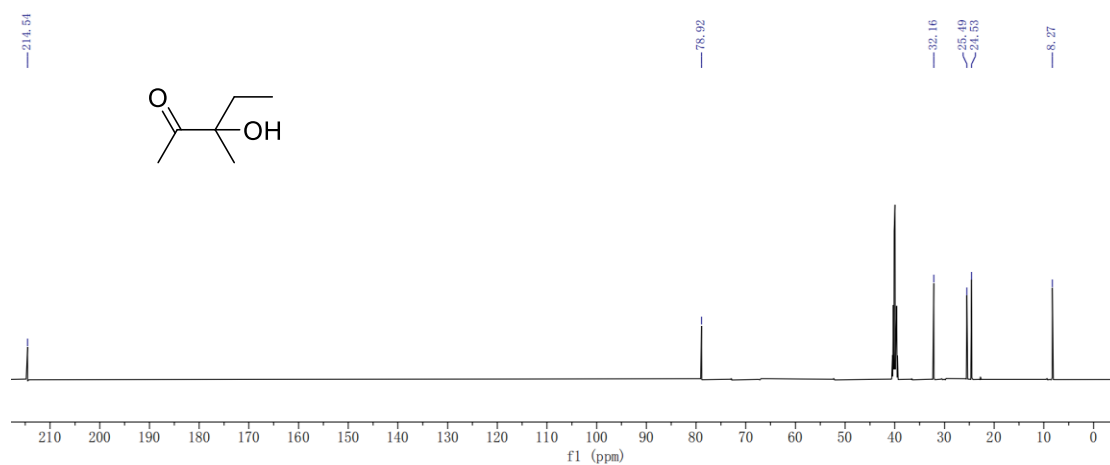


These spectra are matched with the reported publication ³.

^1H NMR of **2b**

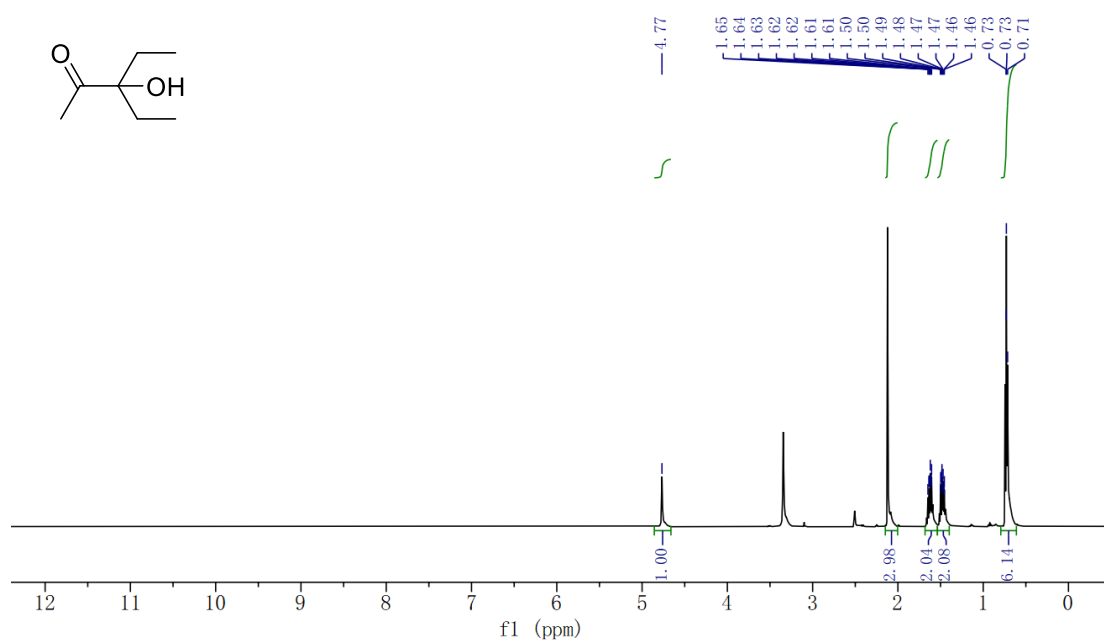


^{13}C NMR of **2b**

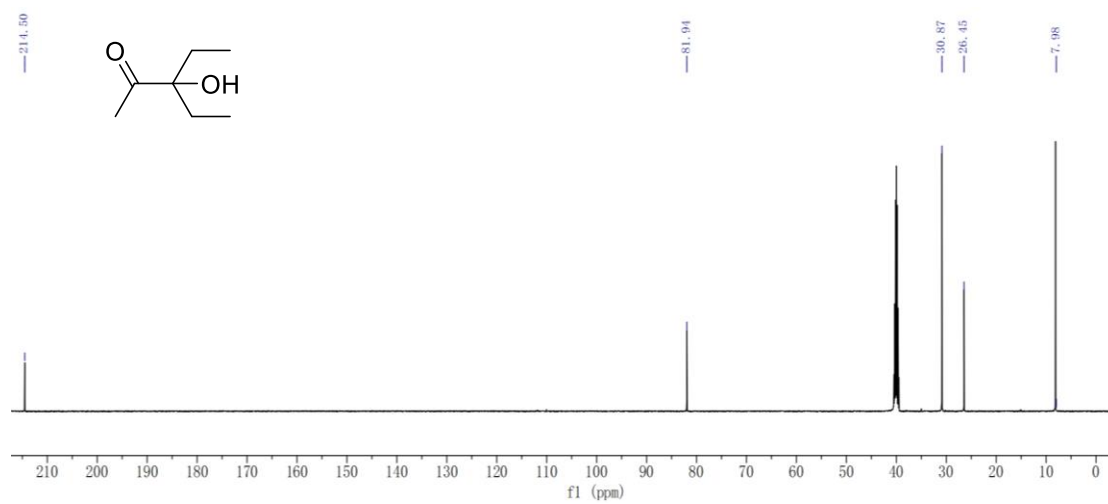


These spectra are matched with the reported publication ³.

^1H NMR of **2c**

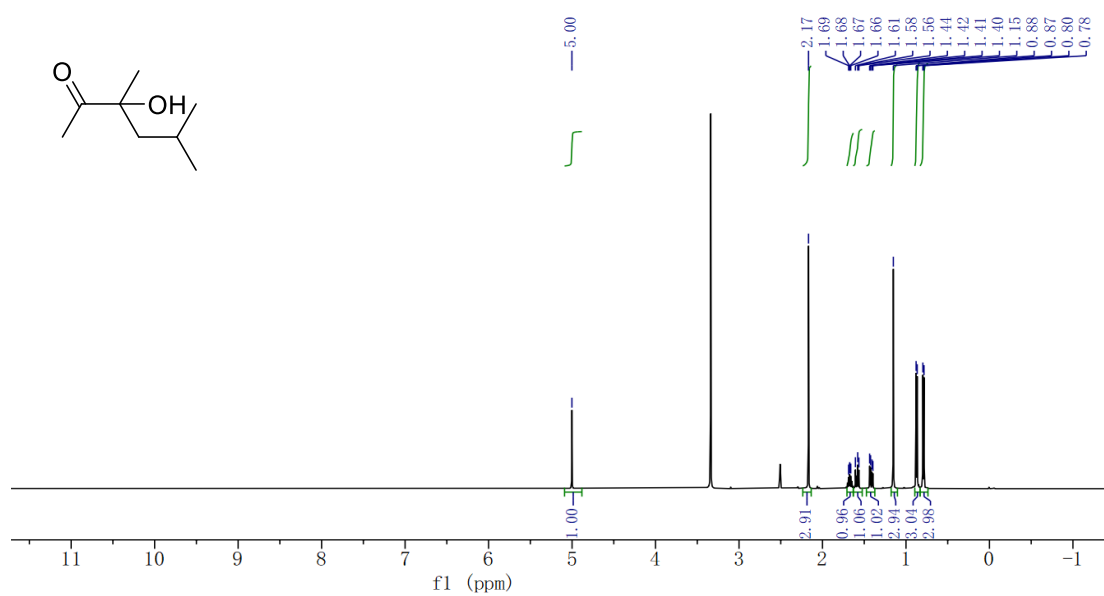


^{13}C NMR of **2c**

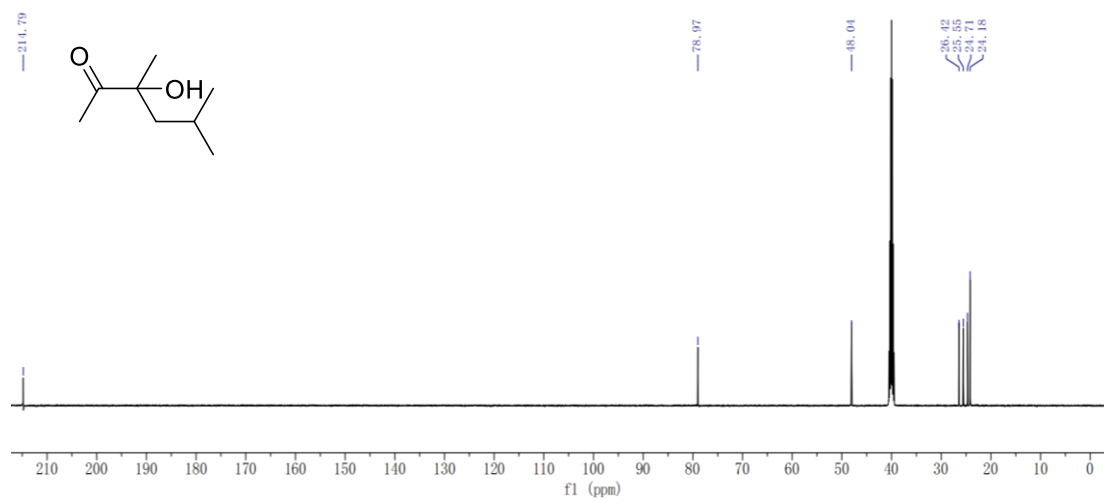


These spectra are matched with the reported publication ³

^1H NMR of **2d**

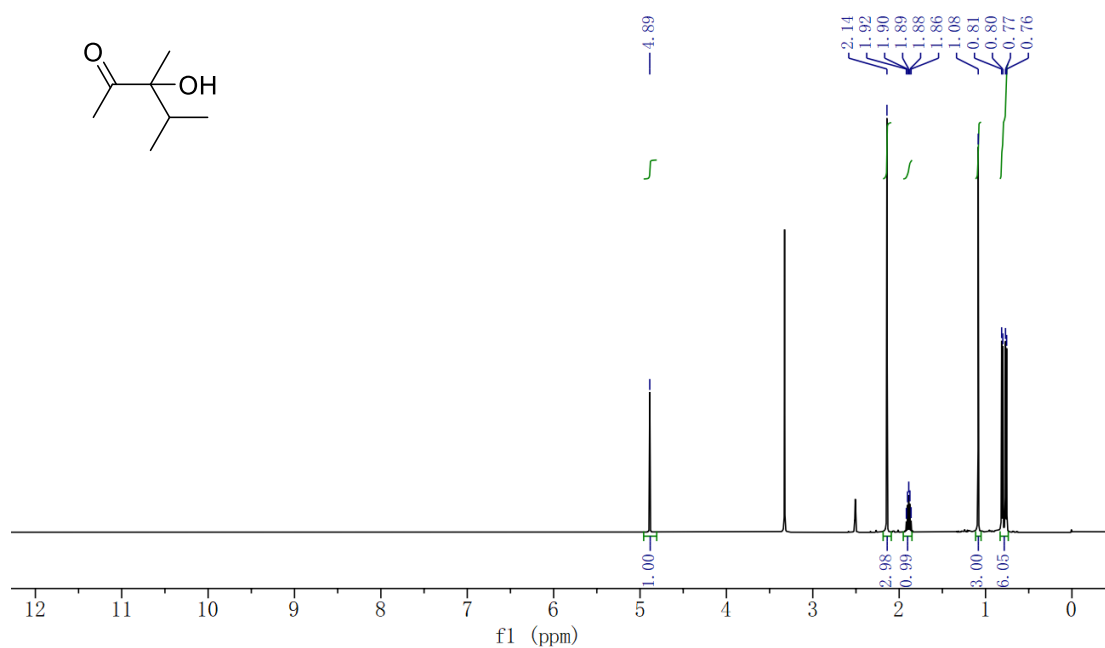


^{13}C NMR of **2d**

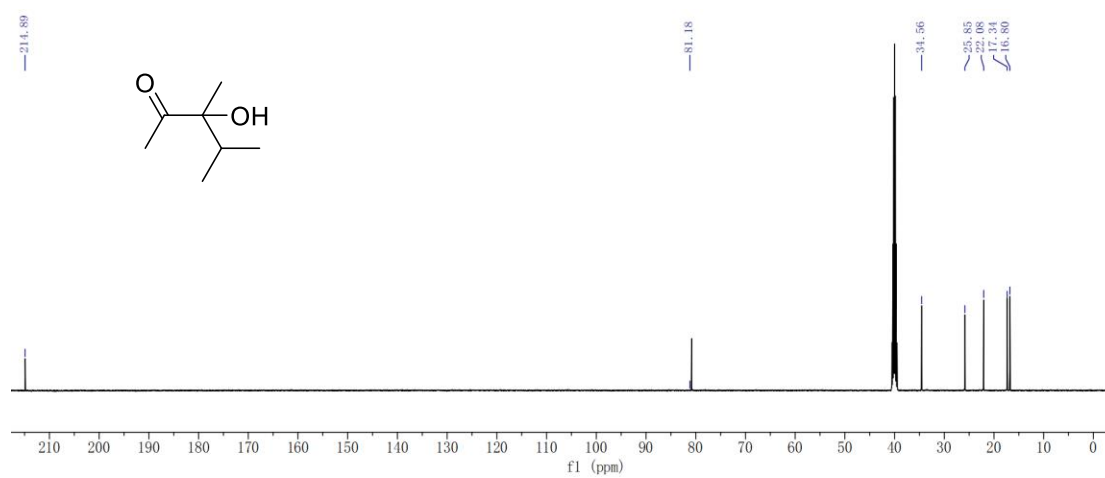


These spectra are matched with the reported publication ³

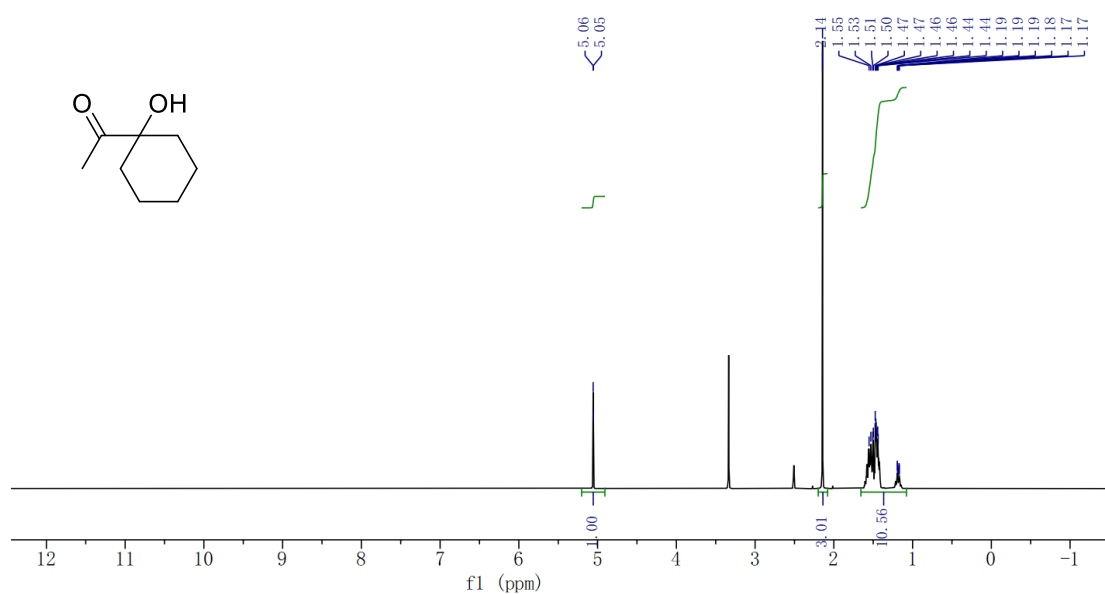
¹H NMR of **2e**



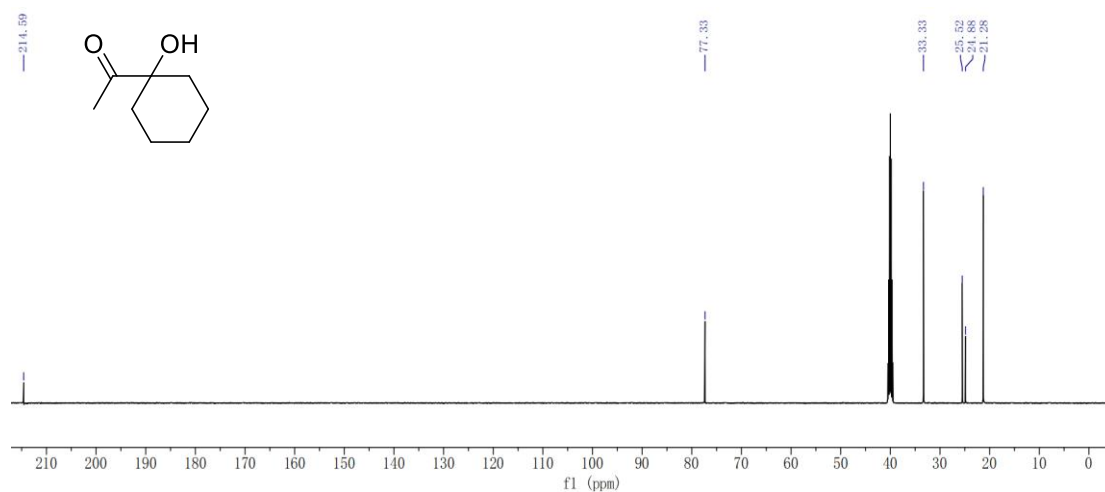
¹³C NMR of **2e**



^1H NMR of **2f**

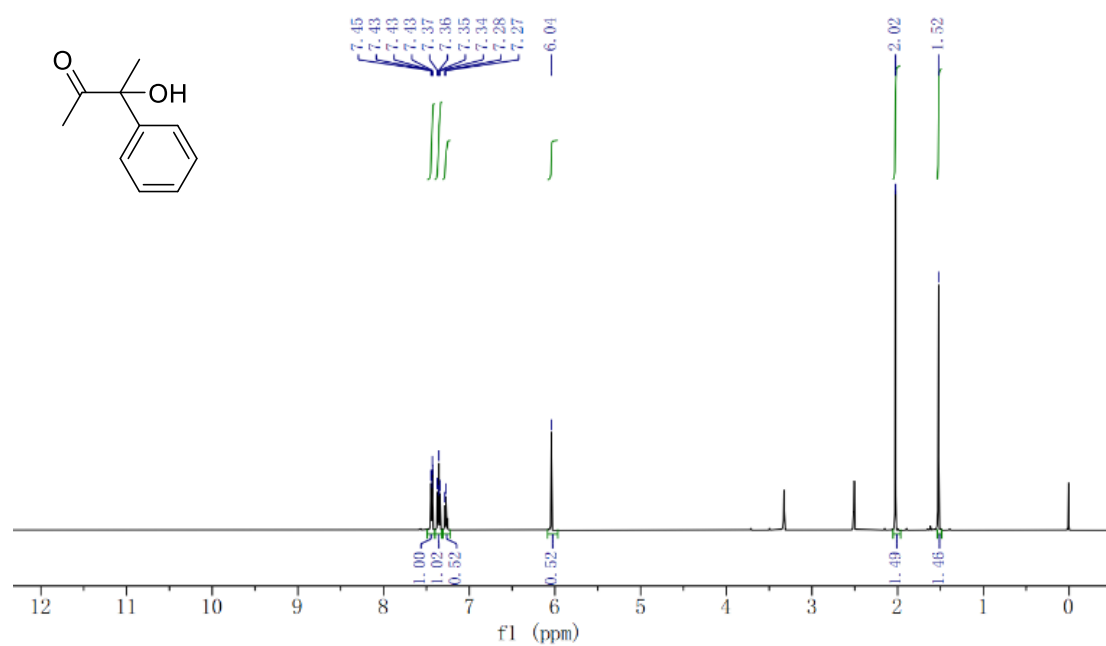


^{13}C NMR of **2f**

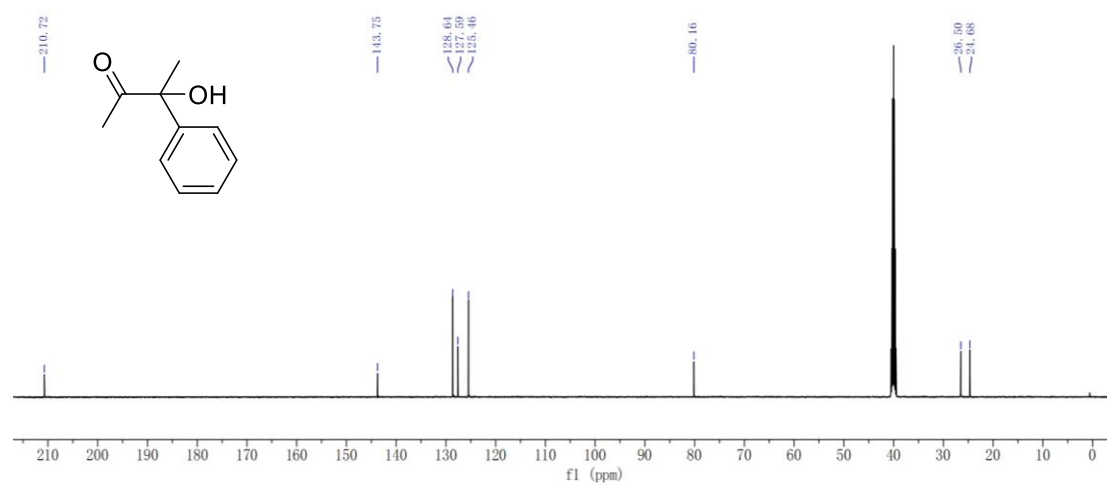


These spectra are matched with the reported publication ³

^1H NMR of **2g**

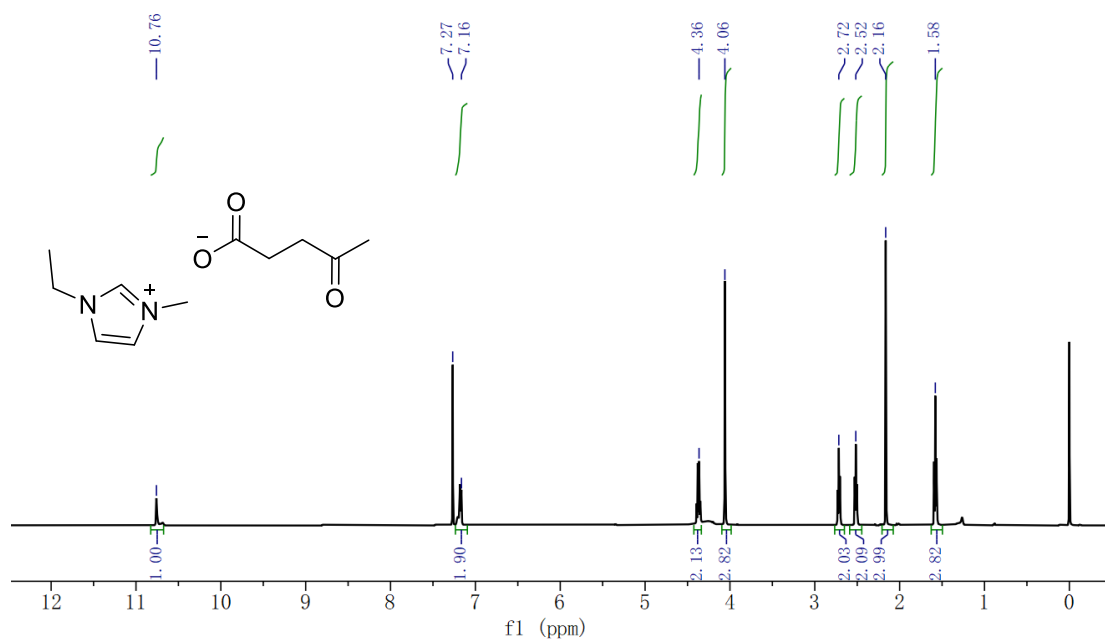


^{13}C NMR of **2g**

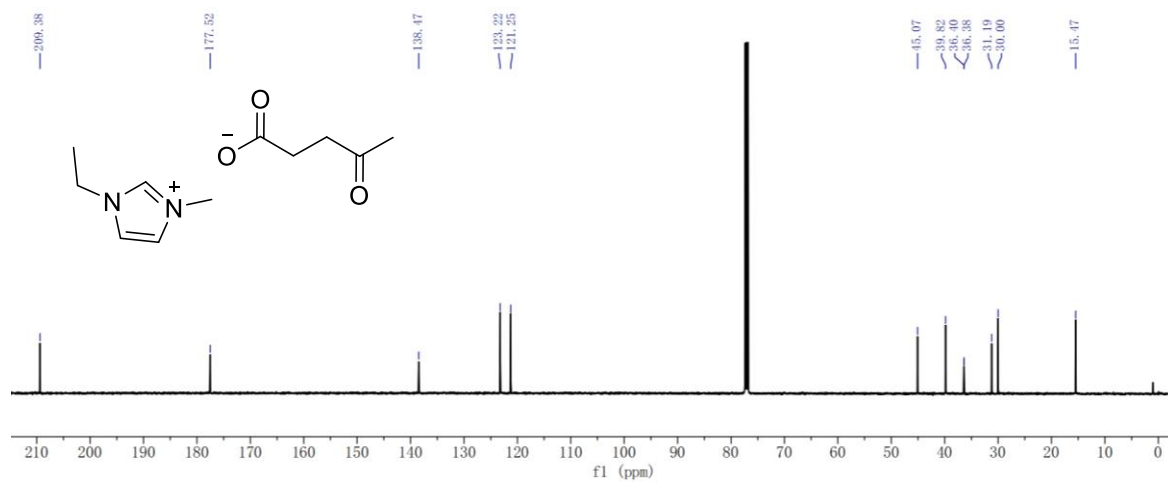


These spectra are matched with the reported publication ³

^1H NMR of $[\text{C}_2\text{C}_1\text{im}][\text{Lev}]$



^{13}C NMR of $[\text{C}_2\text{C}_1\text{im}][\text{Lev}]$



4. References

1. Hu, Y.; Song, J.; Xie, C.; Wu, H.; Jiang, T.; Yang, G.; Han, B., Transformation of CO₂ into α -Alkylidene Cyclic Carbonates at Room Temperature Cocatalyzed by CuI and Ionic Liquid with Biomass-Derived Levulinate Anion. *ACS Sustainable Chem. Eng.* **2019**, 7 (6), 5614-5619.
2. Mezzetta, A.; Becherini, S.; Pretti, C.; Monni, G.; Casu, V.; Chiappe, C.; Guazzelli, L., Insights into the levulinate-based ionic liquid class: synthesis, cellulose dissolution evaluation and ecotoxicity assessment. *New J. Chem.* **2019**, 43 (33), 13010-13019.
3. Zhao, Y.; Yang, Z.; Yu, B.; Zhang, H.; Xu, H.; Hao, L.; Han, B.; Liu, Z., Task-specific ionic liquid and CO₂-cocatalysed efficient hydration of propargylic alcohols to α -hydroxy ketones. *Chem. Sci.* **2015**, 6 (4), 2297-2301.