

Supplementary Information

Solid ionic liquids liquid with macro-microporous structure for efficient heterogeneous macromolecular catalysis

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Experimental

Reagents: All chemicals were obtained from commercial sources and used without further purification. 4-Carboxyphenylboronic acid ($C_7H_7BO_4$, Energy Chemical Company, 98%), 4-bromo-3-methylbenzoic acid ($C_8H_7BrO_2$, Energy Chemical Company, 98%) Zirconium tetrachloride (Cl_4Zr , Energy Chemical Company, 99%), Imidazole ($C_3H_4N_2$, TCI Shanghai, 98%), 1,3-propanesultone ($C_3H_6O_3S$, J&K Scientific Ltd., 99%), Methanesulfonic acid (CH_3SO_3H , Energy Chemical Company, 99%) and ethanol (C_2H_5OH , Sinopharm Chemical Reagent Beijing Co. Ltd., >99.8%) all were used as received.

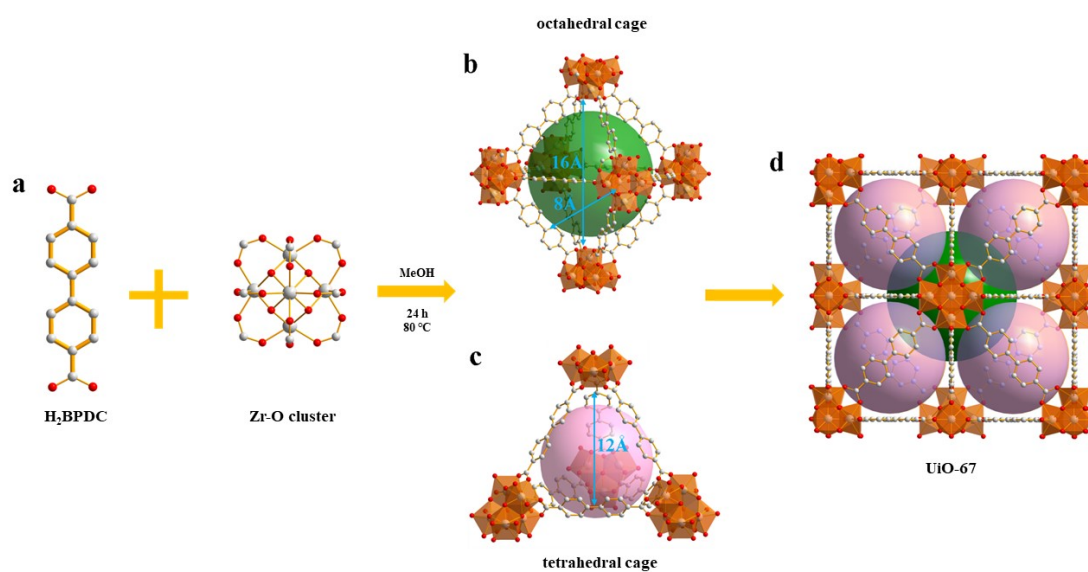


Figure S1. Schematic synthesis of micro structure of UiO-67. (a) H₂BPDC ligand. (b) octahedral cage, (c) tetrahedral cage and (d) UiO-67. Red ball is oxygen, grey ball is carbon.

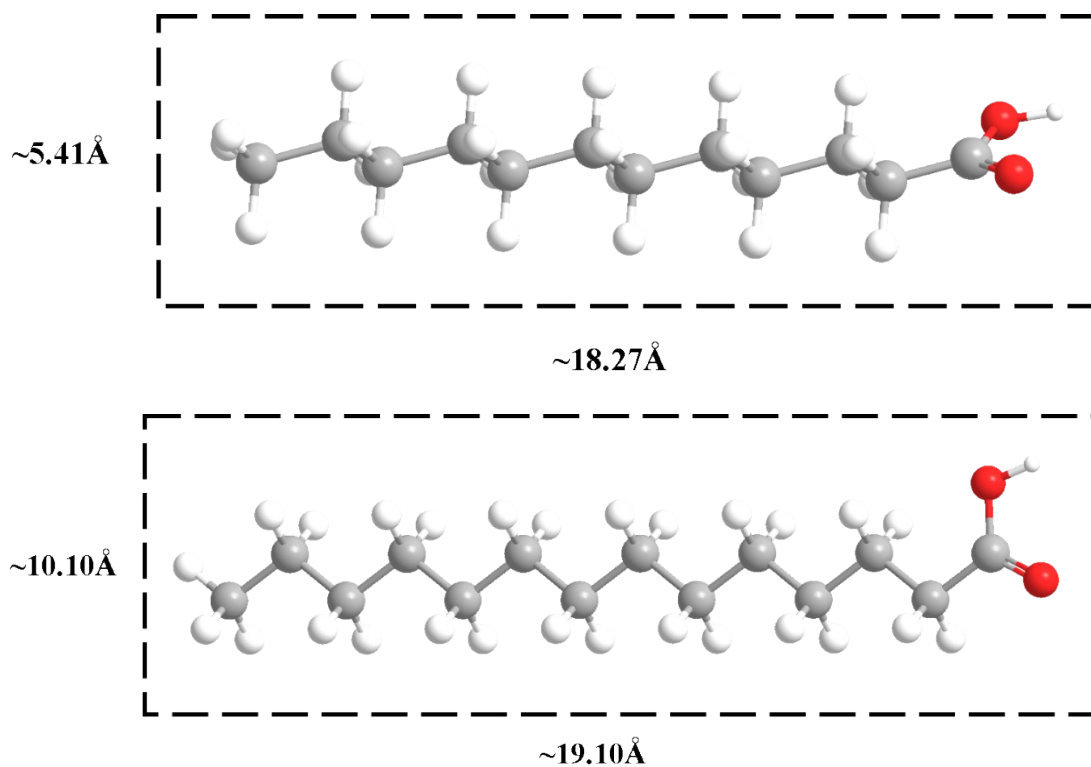


Figure S2. Molecular size data of dodecanoic acid (top) and myristic acid (bottom).

Table S1. BET, pore volume, pore size of UiO-67-MIMS, Macro-UiO-67-MIMS and Macro-UiO-67-ILs

Material	N ₂ adsorption data		
	BET (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)
UiO-67-MIMS	320.22	0.423	~6/~12
Macro-UiO-67-MIMS	364.3191	0.4449	~12
Macro-UiO-67-ILs	101.3936	0.3351	~12

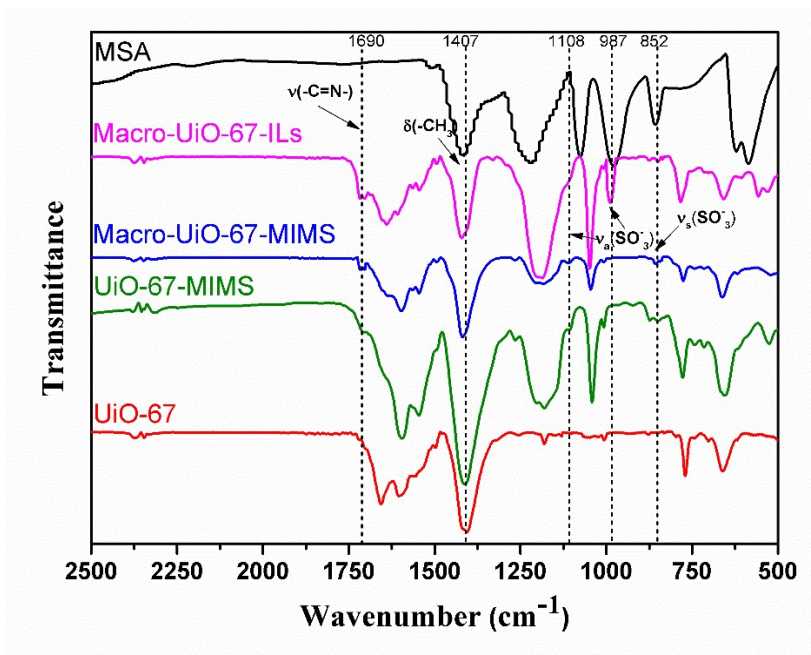


Figure S3. FT-IR of UiO-67, UiO-67-MIMS, Macro-UiO-67-MIMS, Macro-UiO-67-ILs and MSA.

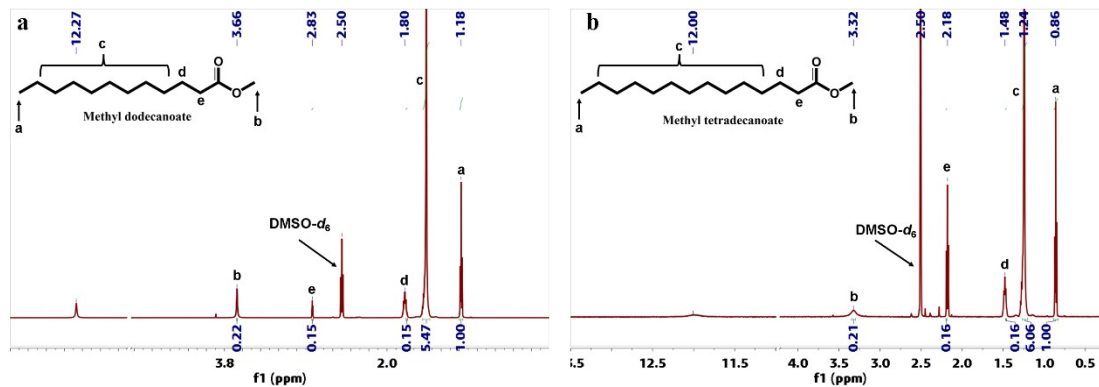


Figure S4. The catalytic process of (a) methyl dodecanoate and (b) methyl tetradecanoate without catalyst digested by $\text{DMSO}-d_6$.

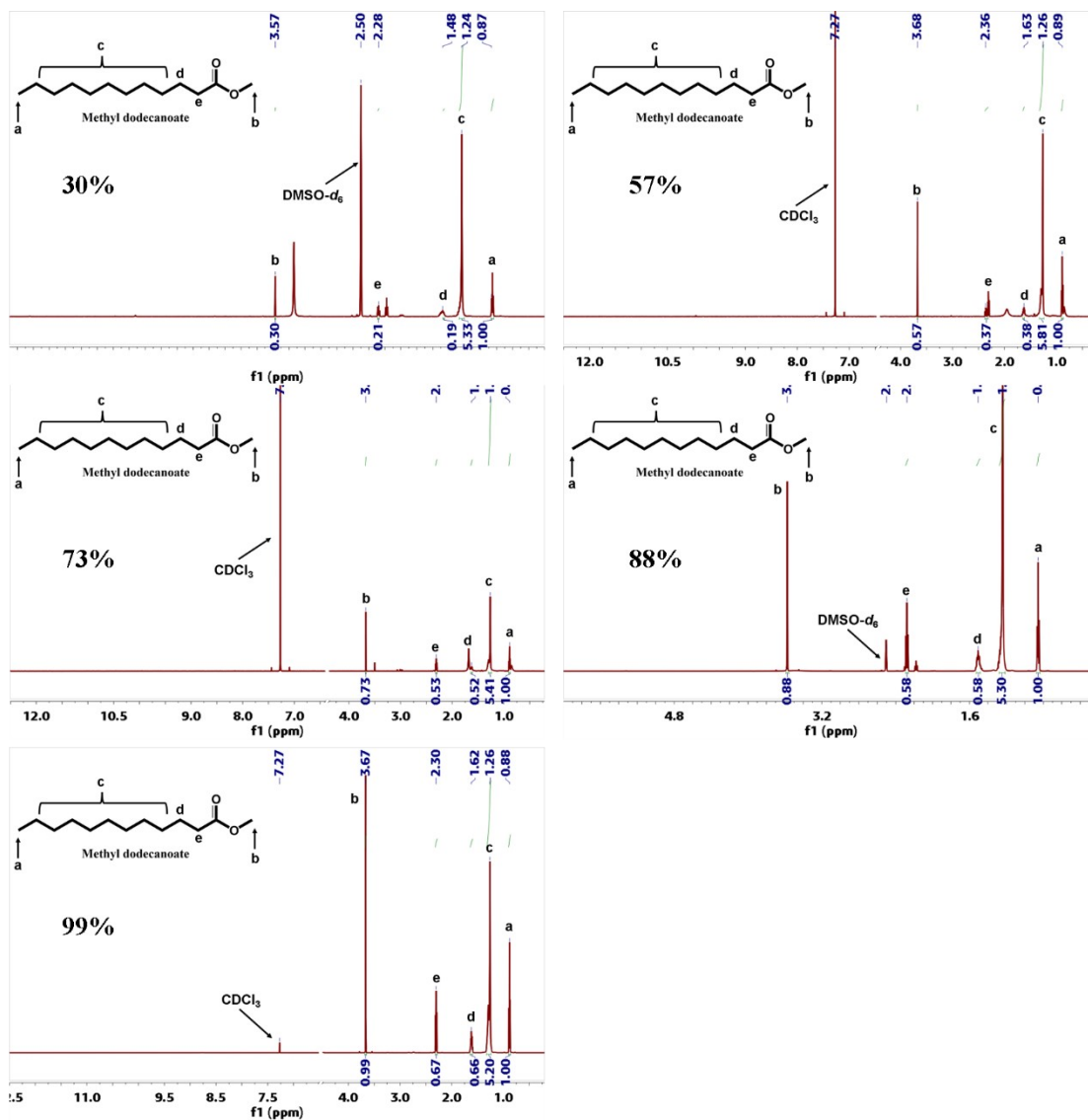


Figure S5. The catalytic process of methyl dodecanoate of **Macro-UiO-67-ILs** digested by DMSO-*d*₆ and CDCl₃.

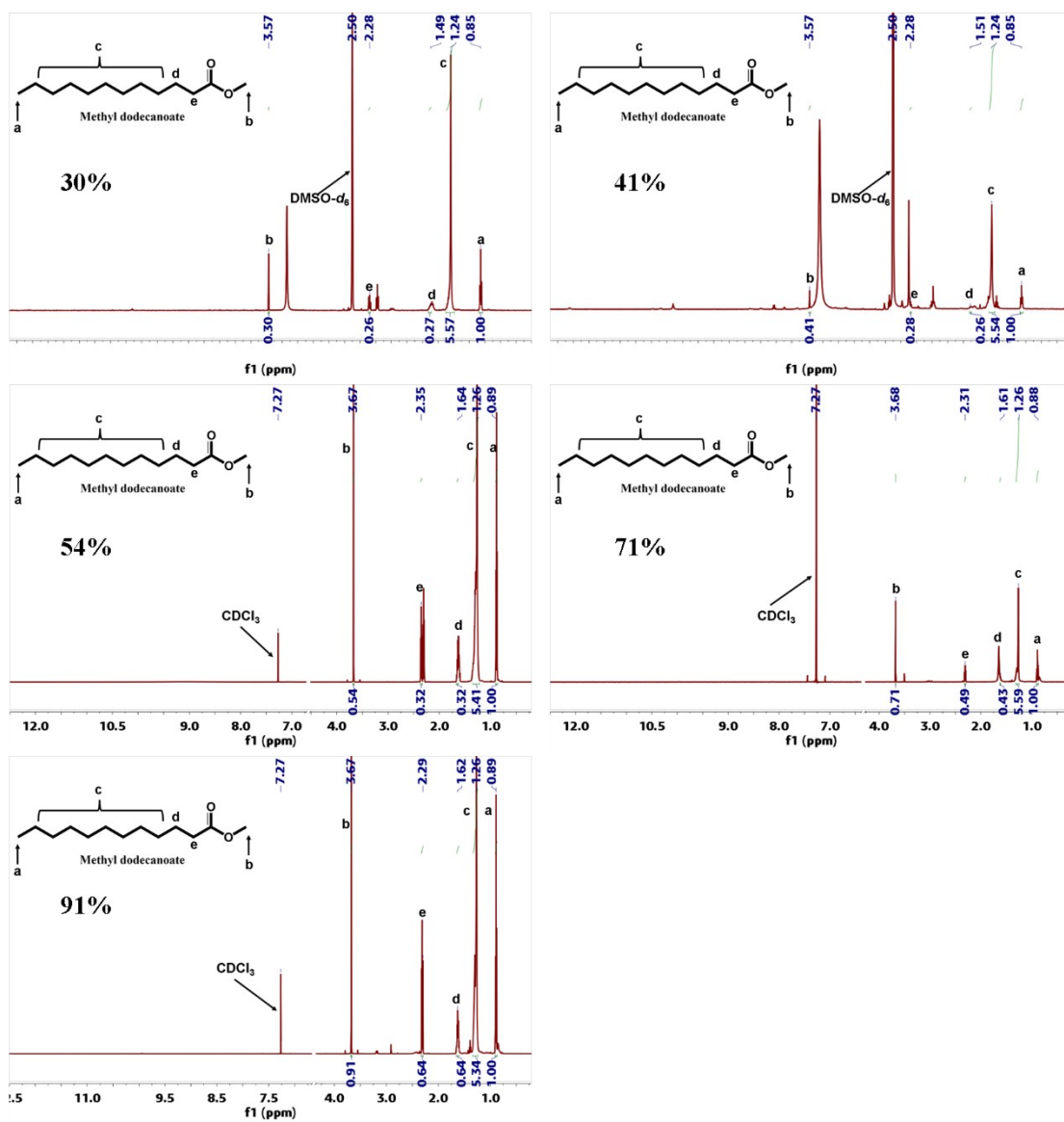


Figure S6. The catalytic process of methyl dodecanoate of MSA digested by DMSO-d₆ and CDCl₃.

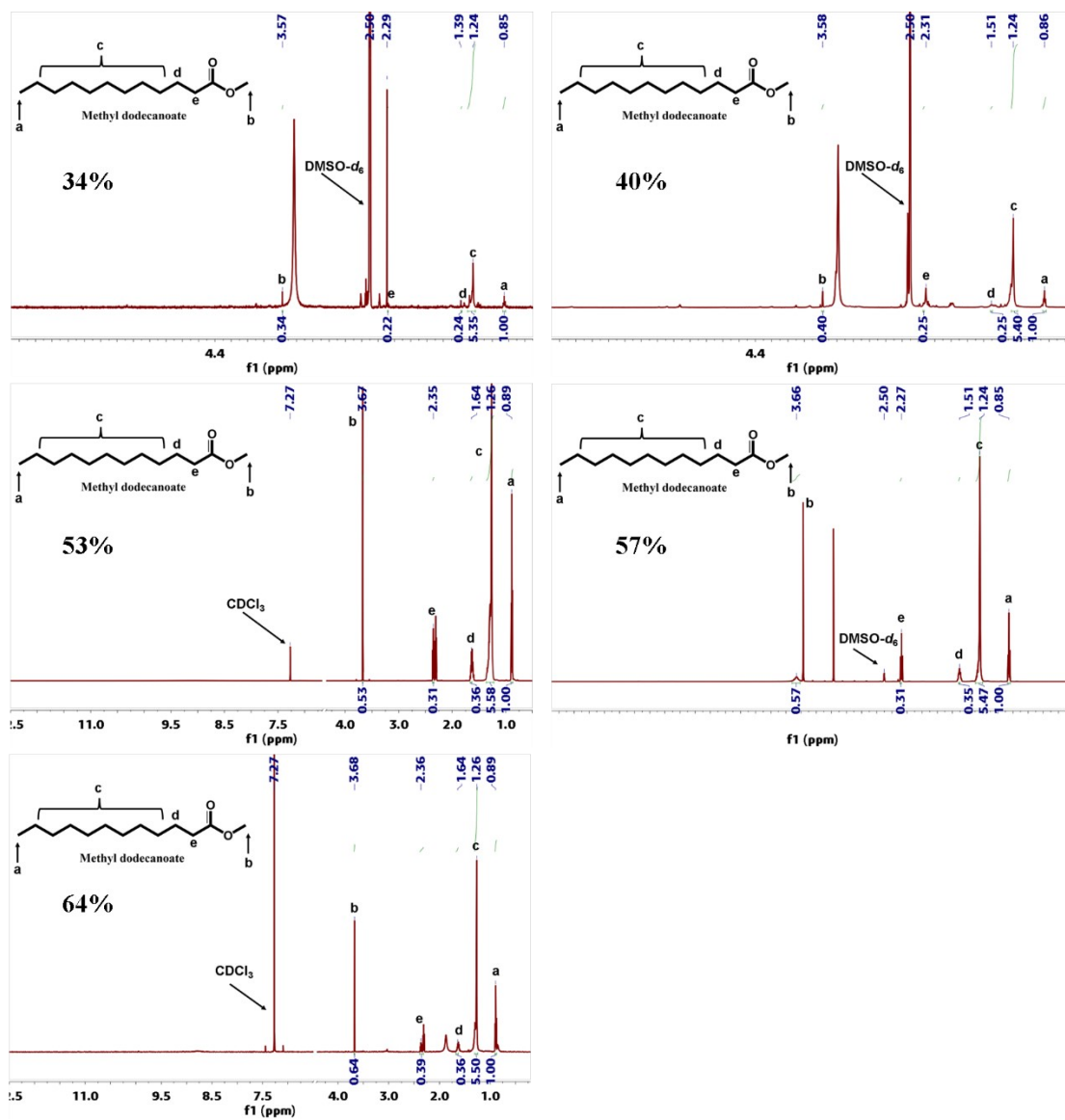


Figure S7. The catalytic process of methyl dodecanoate of **UiO-67-ILs** digested by DMSO-d_6 and CDCl_3 .

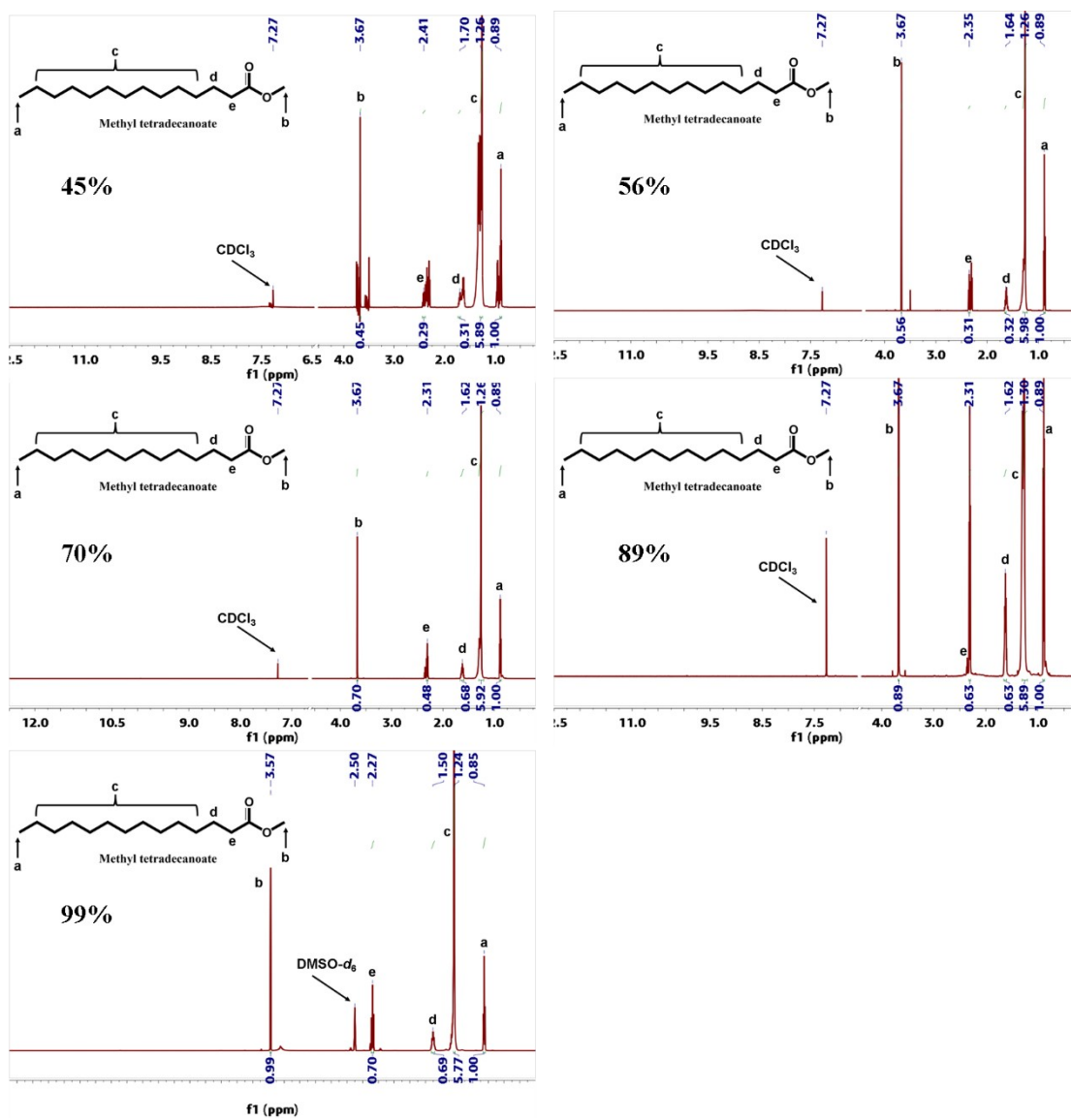


Figure S8. The catalytic process of methyl tetradecanoate of macro-UiO-67-ILs digested by DMSO-d₆ and CDCl₃.

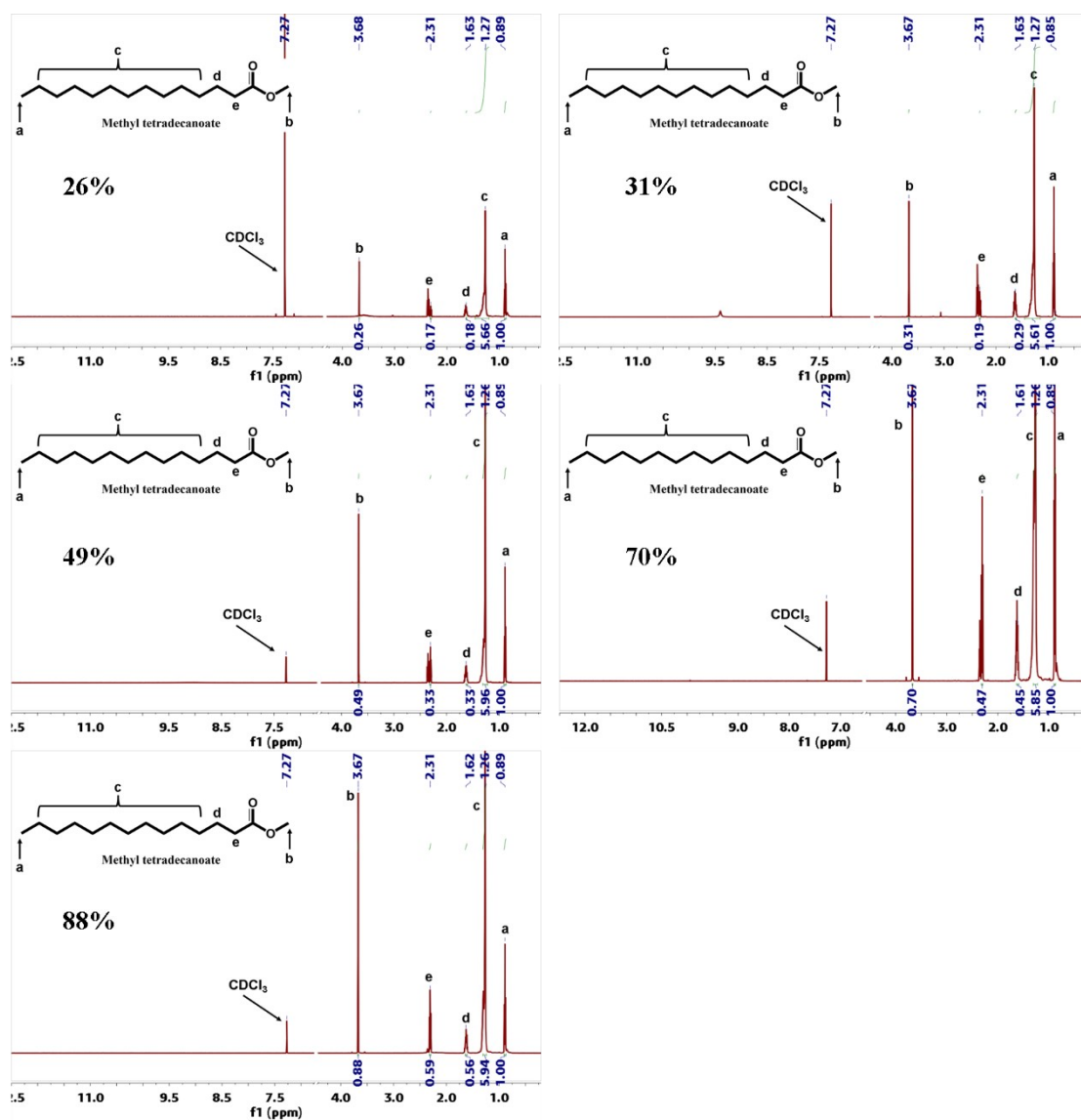


Figure S9. The catalytic process of methyl tetradecanoate of MSA digested by DMSO-d₆ and CDCl₃.

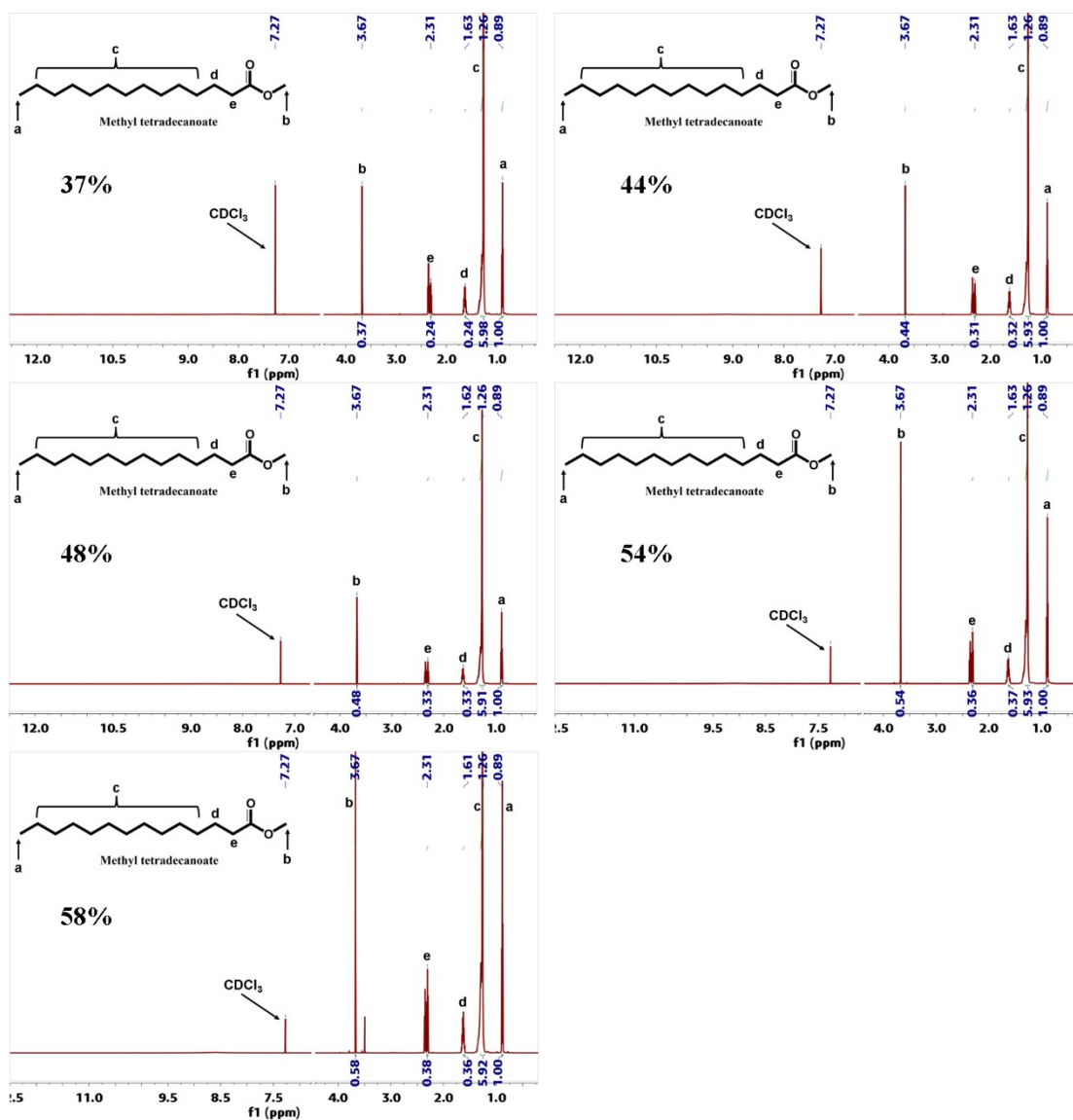


Figure S10. The catalytic process of methyl tetradecanoate of UiO-67-ILs digested by DMSO-d_6 and CDCl_3 .

In the course of the reaction, take 200 μl of the mixed liquid every 5 minutes last 30 minutes, dry it in a vacuum oven, and dissolve it in the deuterated reagent. The ratio of the methyl peak at b to the area of the methyl peak at a is used to determine the degree of reaction.