Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2018

New Journal of Chemistry

Supporting Information

Insight into the Claisen condensation of methyl acetate and dimethyl carbonate to dimethyl malonate

Sainan Zheng[a], Shiwei Xu[a], Jinghong Zhou[a,*], Rongchun Shen[a], Yang Ji[b], Ming Shen[c], Wei Li[a,#]

[a] *School of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China*

[b] *Shanghai Pujing Chemical Industry Co. Ltd, 1305 Huajing Road, Shanghai 200231, China*

[c] *Shanghai Key Laboratory of Magnetic Resonance, East China Normal University, 3663 Northern Zhongshan Road, Shanghai 200062, China*

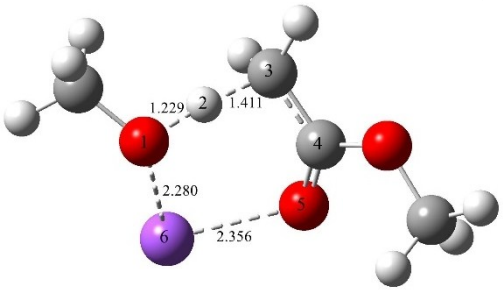
*** Corresponding author.** Tel: +86-21-64252169; Fax: +86-21-64252169; E-mail: jhzhou@ecust.edu.cn

Corresponding author. Tel: +86-21-64253118; Fax: +86-21-64253118; E-mail: liwei@ecust.edu.cn

This work was supported by the National Natural Science Foundation of China (21376076).

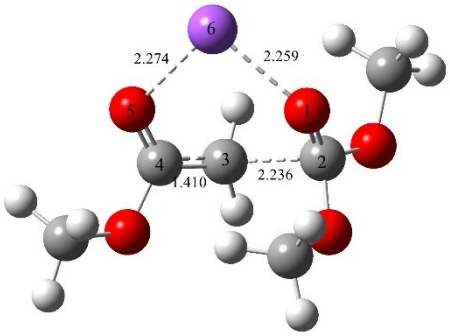
Table of Contents

(A)

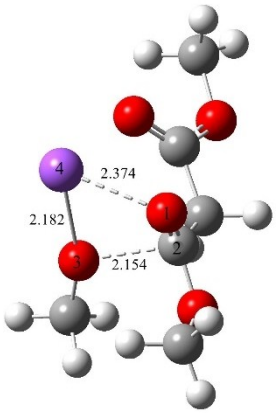

1.229
2
1.411
3
1
4
2.280
5
6
2.356

(

(B)


6
2.274
2.259
5
1
4
3
2
2.236
1.410

(C)


4
2.374
2.182
1
2
3
2.154

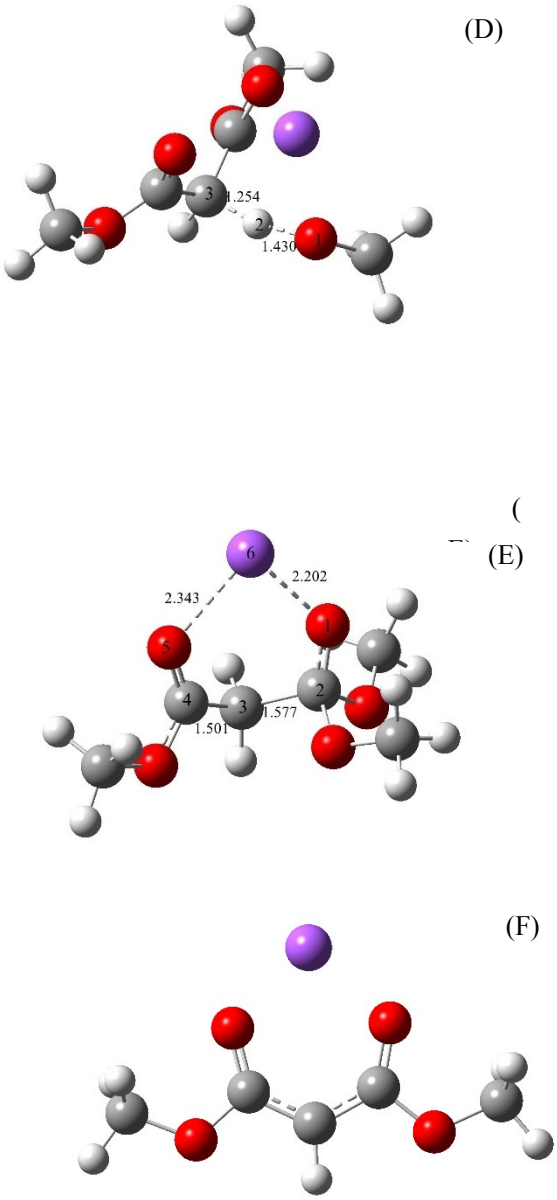


Fig. S1. TS structures for each step catalyzed by CH_3ONa. (A) deprotonation of methyl acetate; (B) addition of deprotonated MA to DMC; (C) elimination of methoxy group; (D) deprotonation of DMM; (E) intermediate of addition; (F) DMNa.

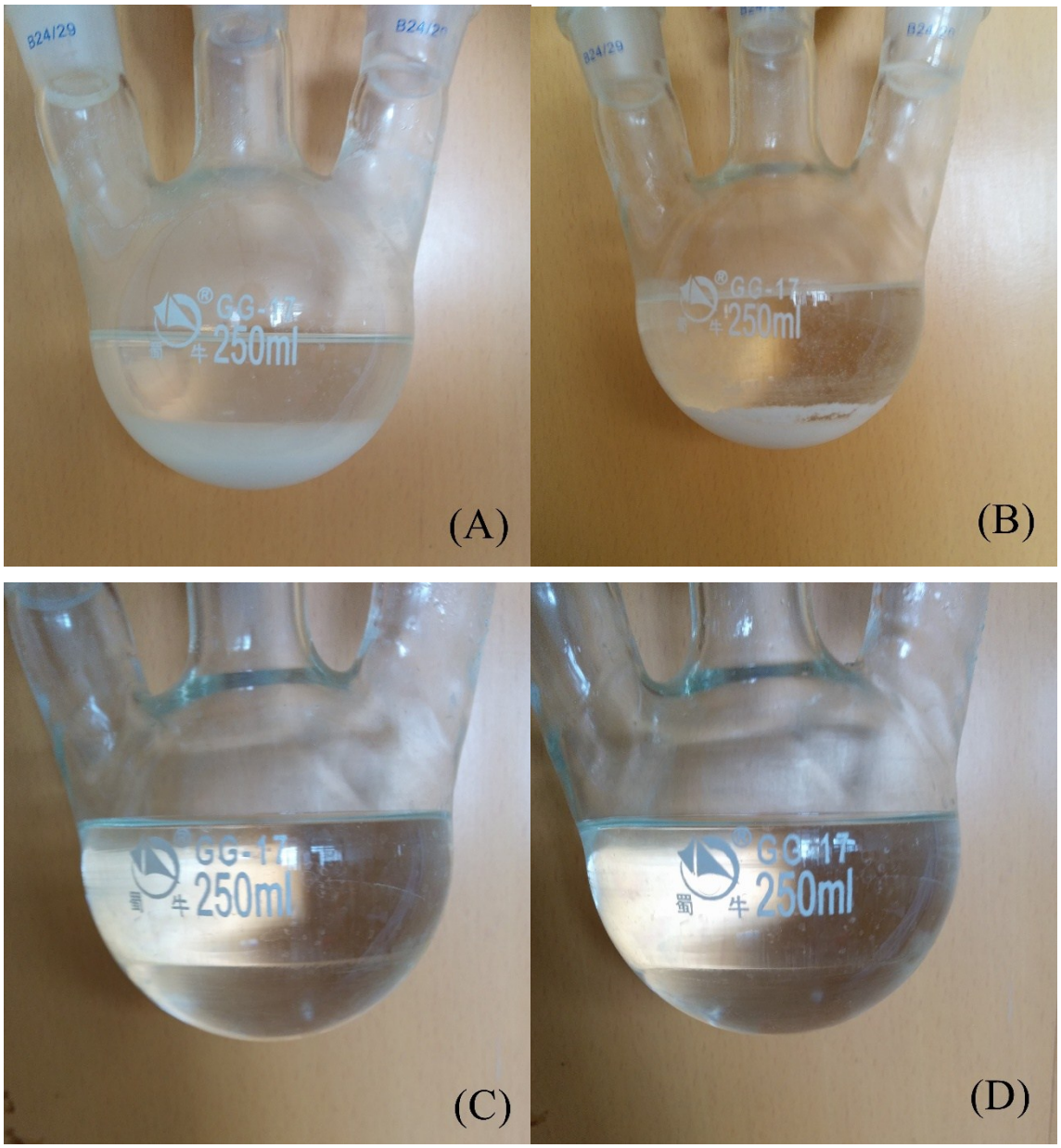


Fig. S2. Optical pictures of the reaction system after standing for 12 h.

Reaction condition: DMC/MA/CH_3ONa= 10/2/1 (mol/mol/mol), T = 341 K, reaction time =12 h, stood still for 12 h .

(A) without proton-donor treatment, (B) post-treated with HAc, (C) post-treated by H_2O, (D) post-treated by HCl.

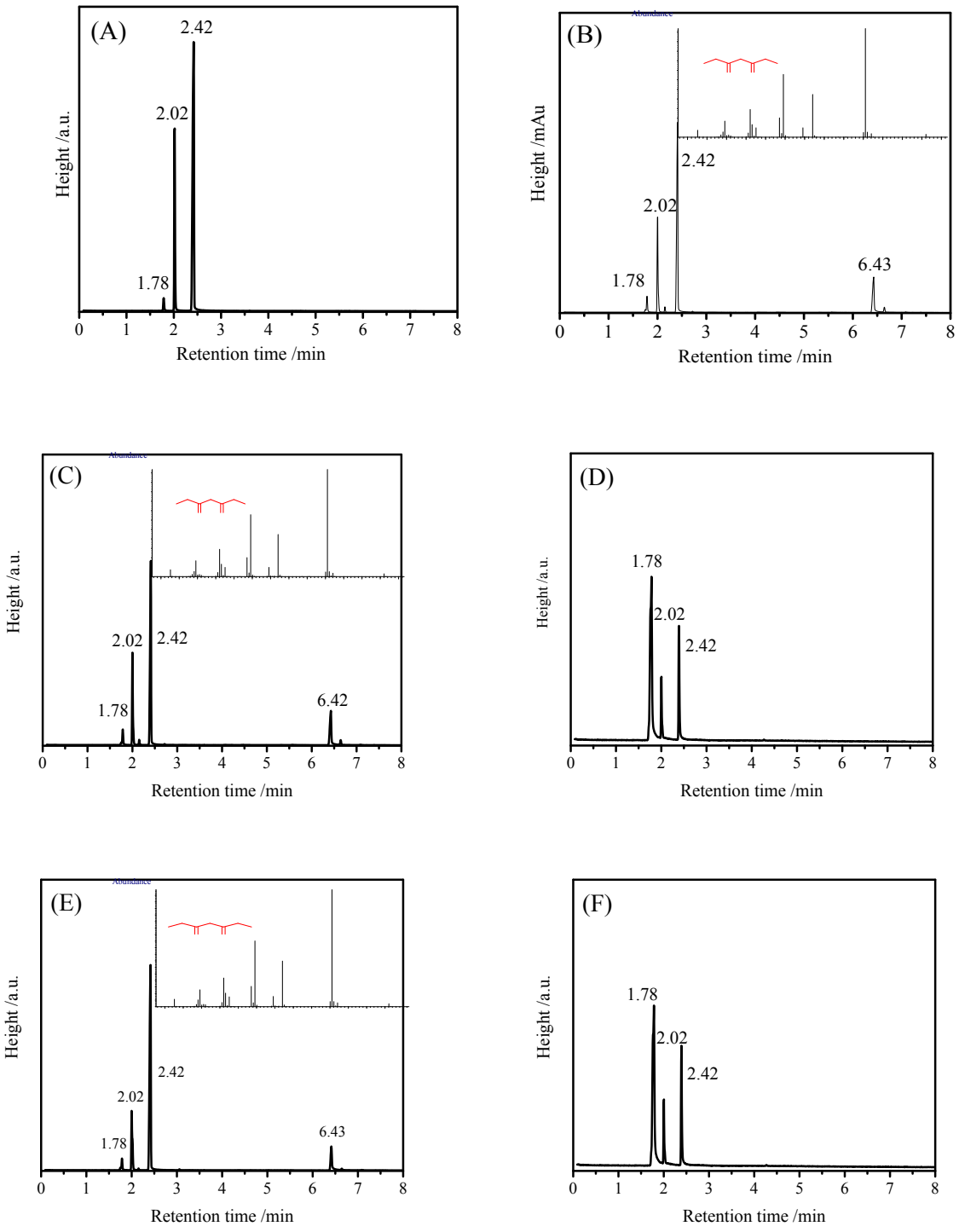
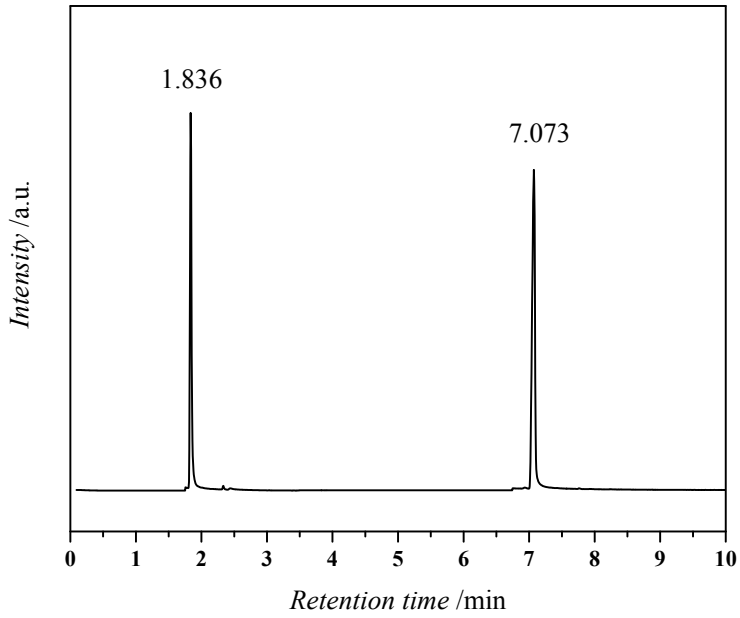


Fig. S3. GC-MS results. (A) Liquid phase after condensation, (B) oil phase after addition of HAc, (C) oil phase after addition of H_2O, (D) aqueous phase after addition of H_2O, (E) oil phase after addition of HCl, (F) aqueous phase after addition of HCl.

Reaction condition: DMC/MA/CH_3ONa= 10/2/1 (mol/mol/mol), T = 341 K, reaction time =12 h.

Retention time: methanol (1.78 min), methyl acetate (2.02 min), dimethyl carbonate (2.42 min), dimethyl malonate (6.43 min).



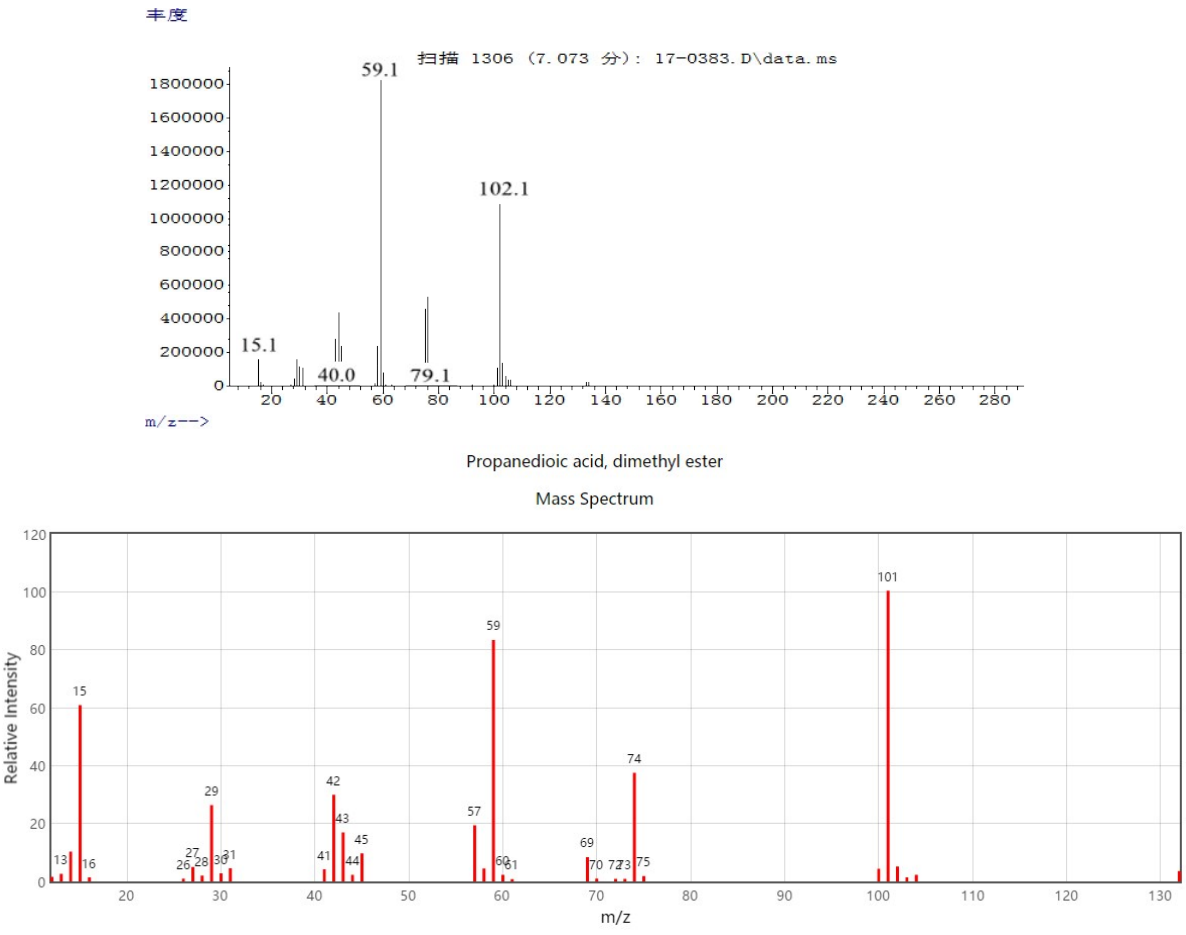


Fig. S4. GC-MS spectrum of D_2O-protonated reacted products

Retention time: CH_3OH (1.836 min), D-substituted DMM (7.073 min)

Standard DMM mass spectrum source: NIST

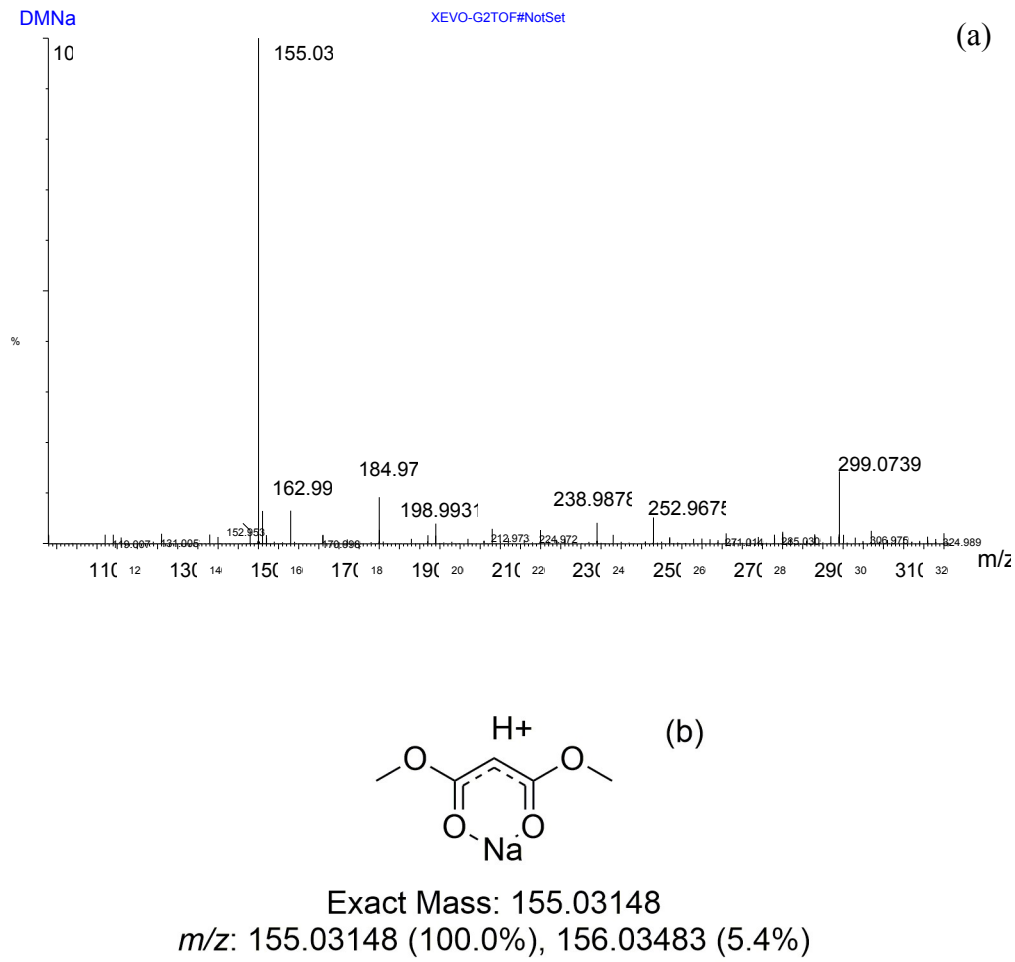


Fig. S5. (a) ESI-high resolution mass spectrum of DMNa in DMSO : Mass spectrum in an *m/z* range of 30-300. (b) Theoretical *m/z* of $[(CH_3OCO]_2CH_2^+Na]^+$ fragment from ChemOffice 2015.

The mass spectrum showed a strong peak at *m/z* of 155.0319 belonging to $[(CH_3OCO]_2CH_2^+Na]^+$ fragment, indicating the cleavage between α-C and α-H bond of DMM and the coordination of the Na ion. This result provides further evidence for the formation of the DMNa species