*Supporting information*

# Using Imidazolium-Based Ionic Liquids as Dual Solvent-Catalysts for Sustainable Synthesis of Vitamin Esters: Inspiration from Bio- and Organo-Catalysis

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**Contents**

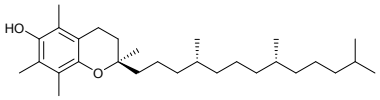
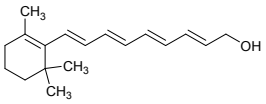
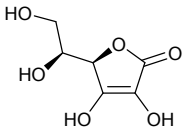
**Table S1** Effects of organic solvents on the esterification of vitamin E with succinic anhydride using *Candida sp.* Lipase as catalysts

| Solvents | Yields/% |
|---|---|
| Hexane | 0 |
| *tert*-Amyl alcohol | 0.5 |
| *Tert*-Butanol | 1.6 |
| Acetonitrile | 0.8 |
| Dichloromethane | 3.2±0.2 |
| DMSO | 72.6±1.8 |
| DMF | 54.5±0.9 |

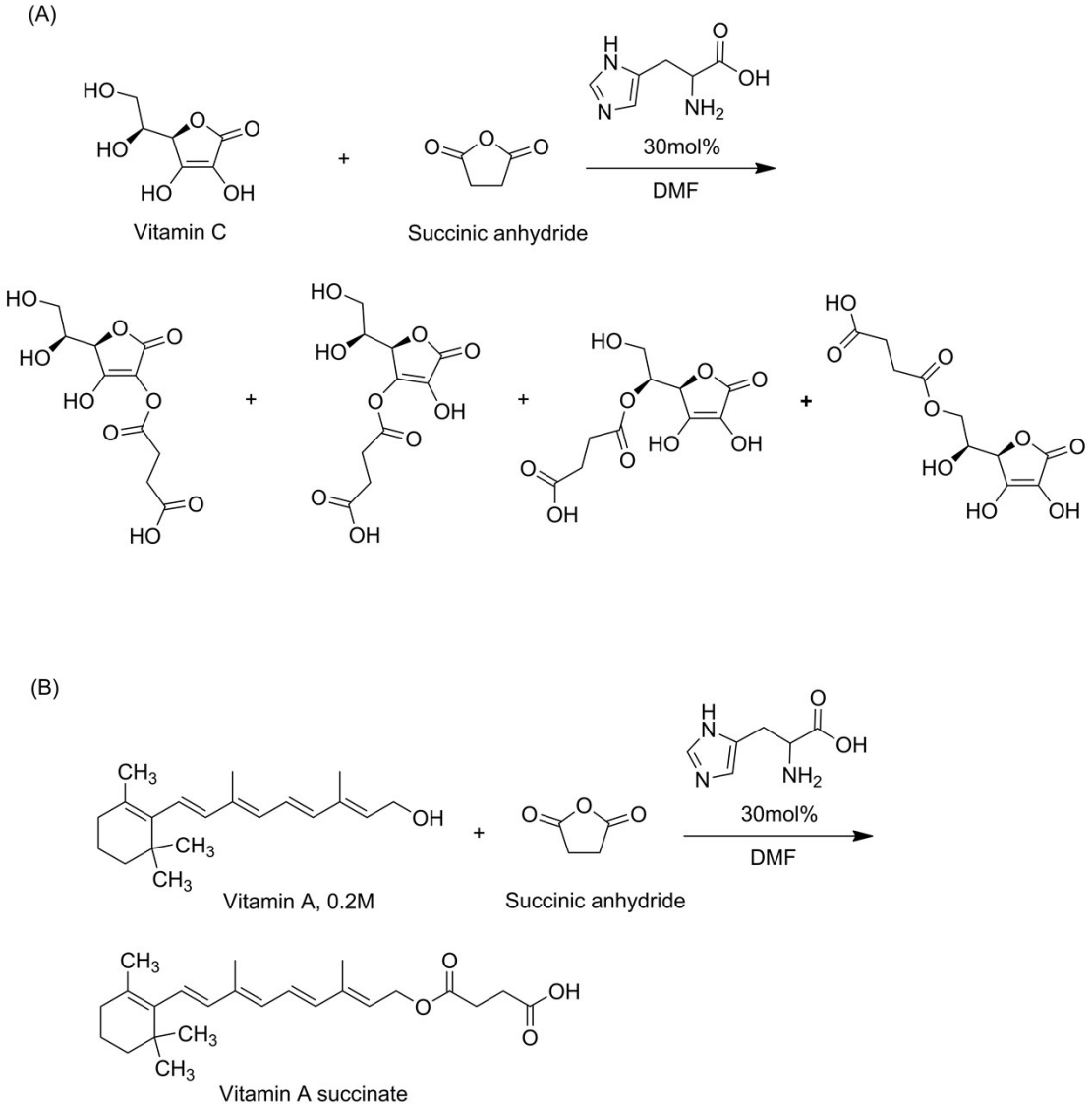
**Table S2** Effects of molar ratio among substrates and ionic liquids on the initial rate and yield when using $[C_5C_1Im][NO_3^-]$ as catalyst for the esterification of vitamin E with succinic anhydride

| Entry | Molar Ratio (α-tocopherol: Succinic Anhydride: ILs) | Initial rate ($10^{-2}$/min) | Yield after 1.5 h (%) |
|---|---|---|---|
| **S1** | 0.5: 1: 4 | 0.70 ±0.01 | 96.2 ±1.2 |
| **S2** | 1.0: 2: 4 | 1.51 ±0.08 | 97.2 ±1.4 |
| **S3** | 1.5: 3: 4 | 2.22 ±0.07 | 96.5 ±1.2 |
| **S4** | 2.0: 4: 4 | 2.69 ±0.09 | 95.2 ±0.8 |
| **S5** | 4.0: 8: 4 | 2.86 ±0.12 | 76.4 ±2.1 |
| **S6** | 0.5: 0.55: 4 | 0.42 ±0.04 | 76.8 ±2.4 |
| **S7** | 0.5: 0.75: 4 | 0.61 ±0.05 | 89.1 ±2.2 |
| **S8** | 0.5: 1.00: 4 | 0.69 ±0.03 | 96.2 ±1.8 |
| **S9** | 0.5: 1.50: 4 | 0.88 ±0.06 | 98.9 ±1.6 |
| **S10** | 0.5: 2.00: 4 | 1.01 ±0.09 | 99.5 ±1.3 |

**Table S3** Synthesis of vitamin esters using [C5C1Im][NO– 3] ionic liquid as dual solvent catalysts

| Vitamins / Acyl donor | Vitamin E  | Vitamin A  | Vitamin C  |
|---|---|---|---|
| Acetic anhydride | + | + | + |
| Succinate | — | — | — |
| Butyric anhydride | + | + | + |
| Succinic anhydride | + | + | + |
| Ketoglutarate | — | — | — |
| Pentyl anhydride | + | + | + |
| Glutaric anhydride | + | + | + |

Conditions: A standard mixture containing 0.5 mmol vitamin, 1 mmol acyl donor and 4 mM ionic liquids was used and the reactions were carried out at 50 °C for 3 h under dark and nitrogen atmosphere.




**Scheme S1** Histidine-catalyzed esterification of (A) vitamin C and (B) vitamin A with succinic anhydride. The products were characterized by LC-MS.

**HRMS spectra of vitamin C and A succinate**

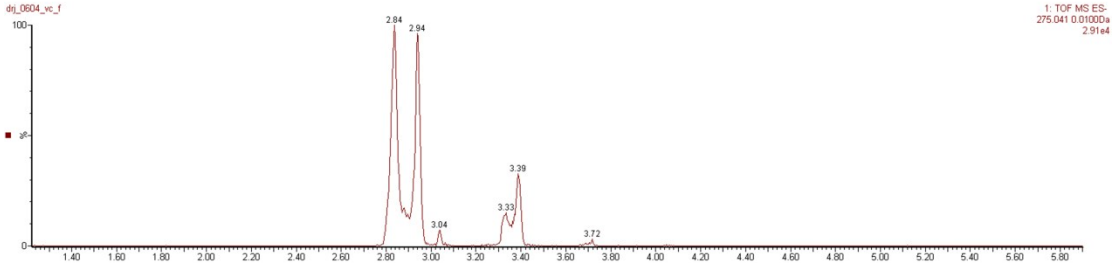



**Fig. S1** LC-MS spectrum of esterification between vitamin C and succinic anhydride. m/z of four peaks (retention time: 2.84 min, 2.94 min, 3.33 min and 3.39 min) were found 277.0559 $[M]^+$, indicating four hydroxyl group of vitamin C can be esterified with succinic anhydride.

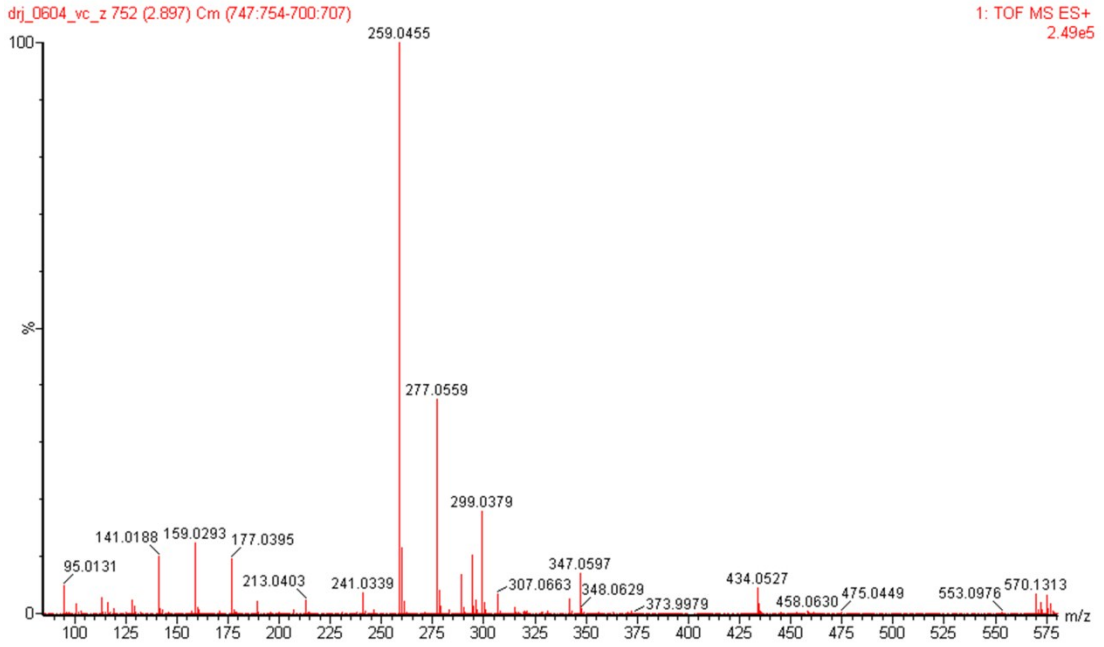



**Fig. S2** HRMS spectrum of vitamin C succinate (EI, m/z: found 277.0559 $[M]^+$; calculated 276.05 for $C_{10}H_{12}O_9$)

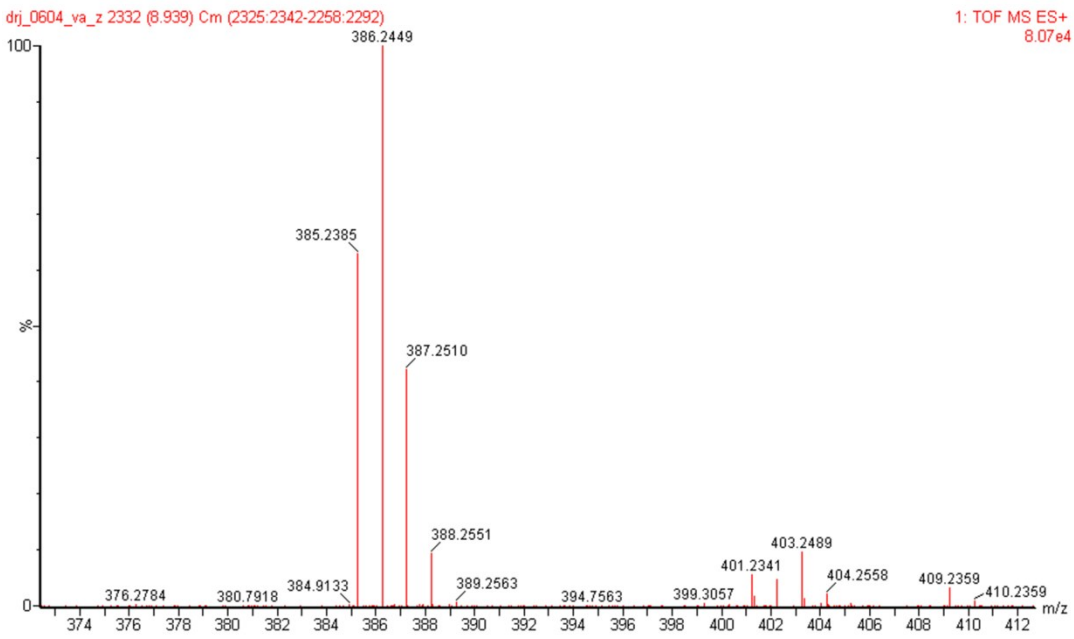
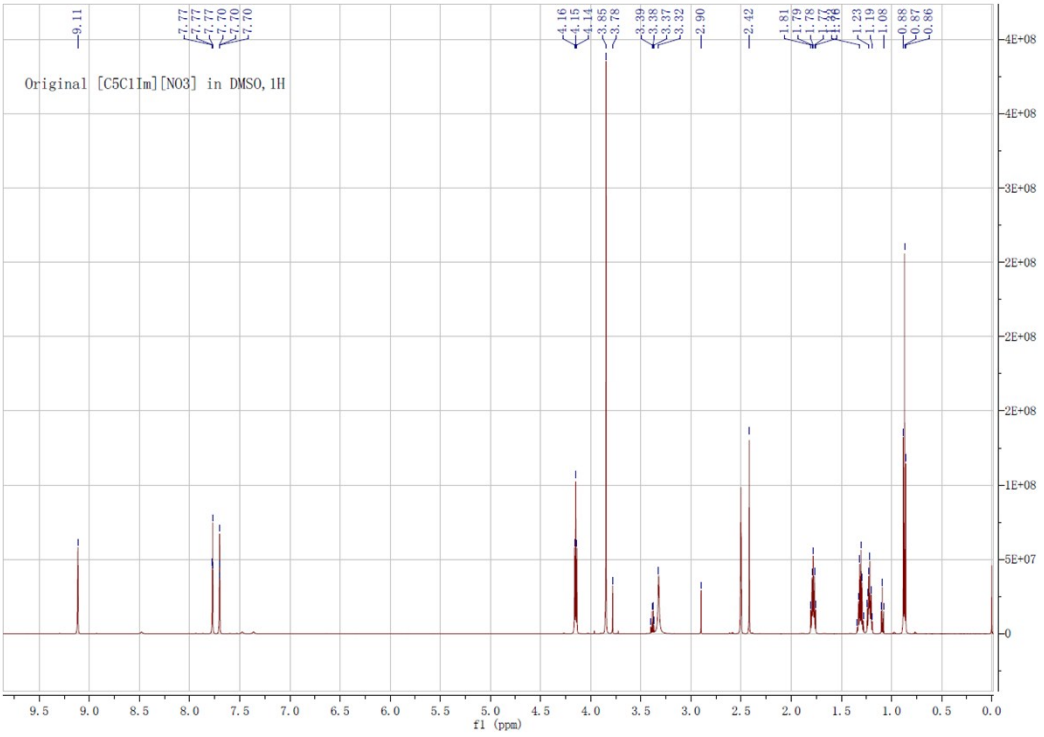
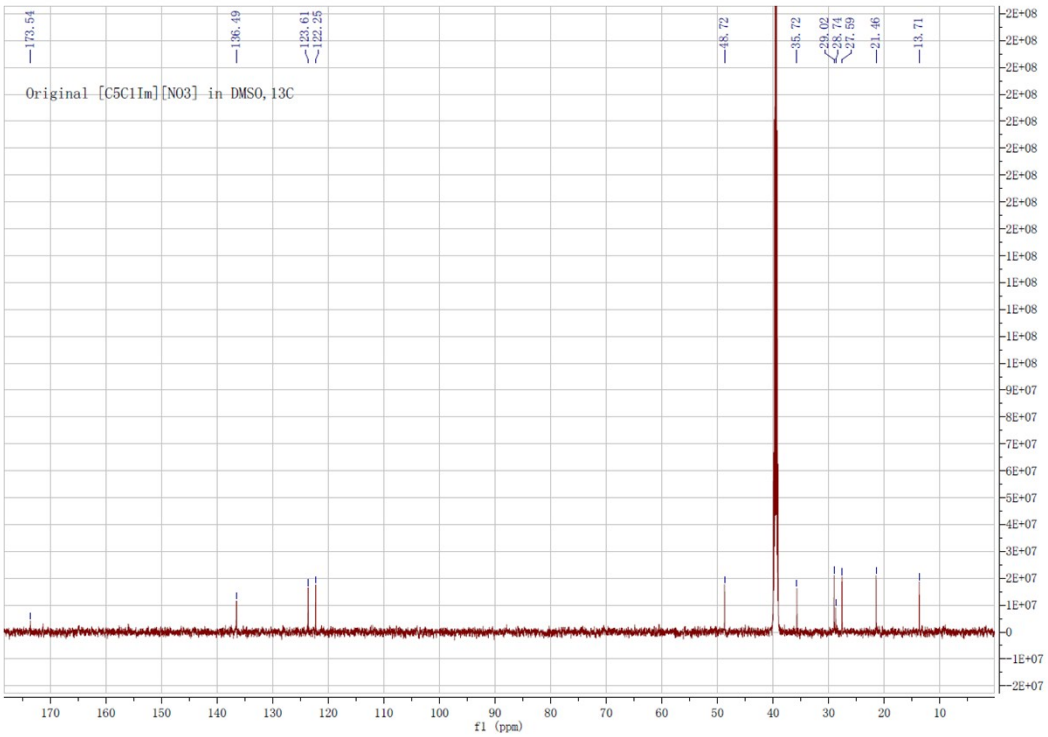


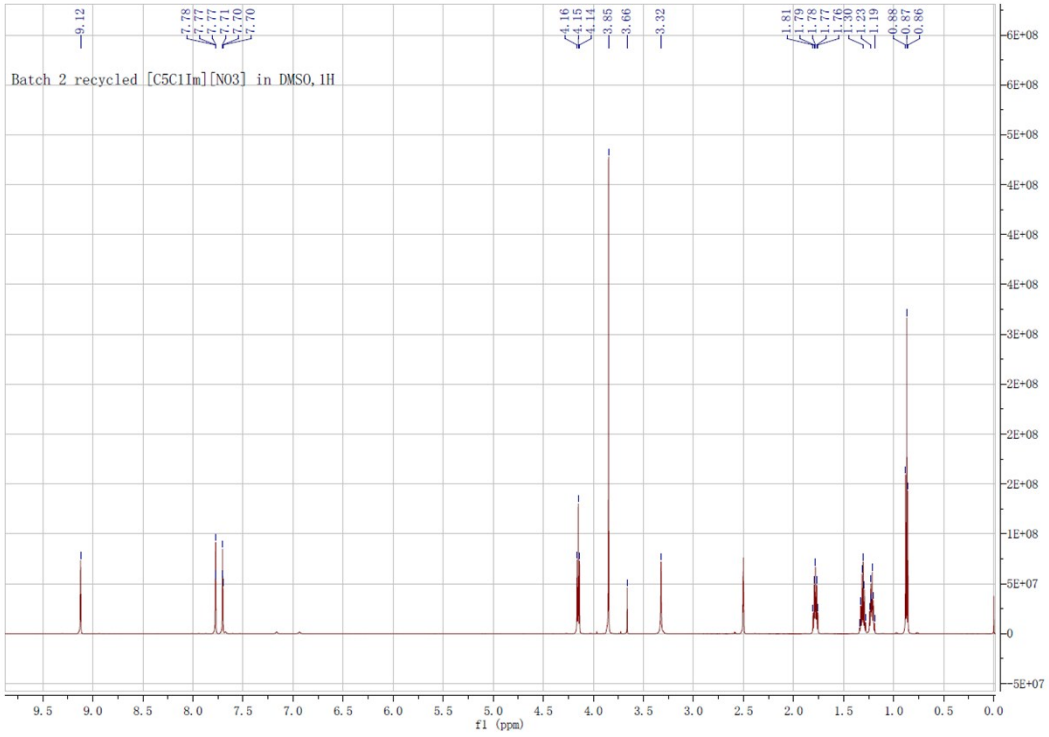

**Fig. S3** HRMS spectrum of vitamin A succinate (EI, m/z: found 386.2449 $[M]^+$; calculated 386.25 for $C_{24}H_{34}O_4$)



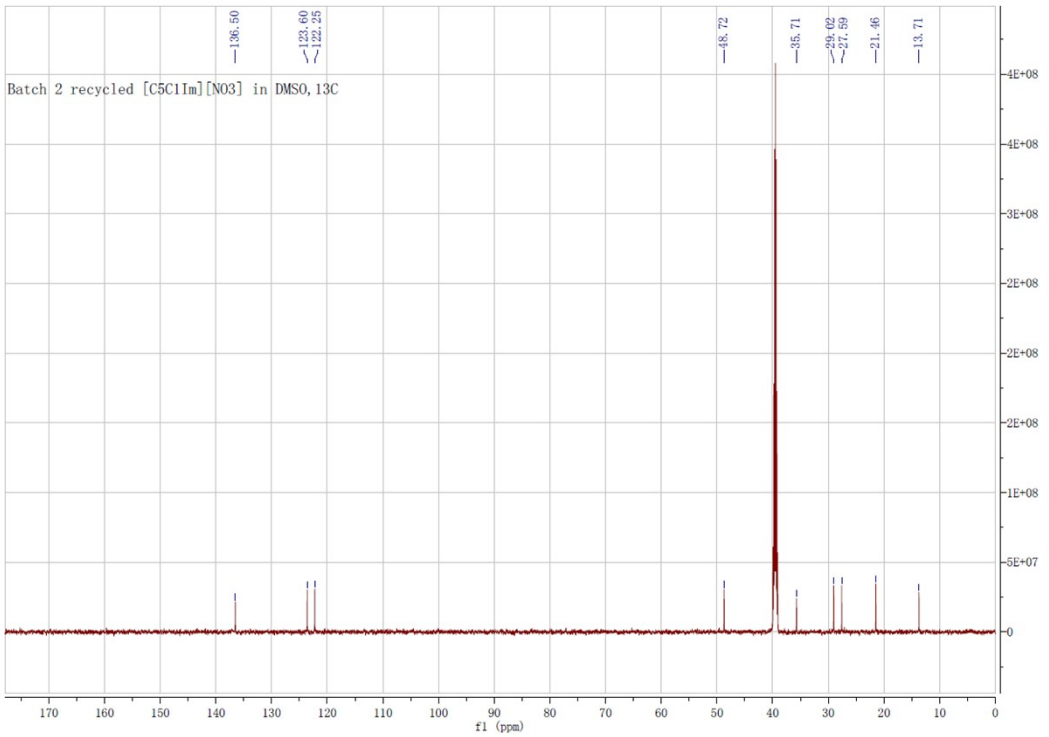

(a) 1H NMR of original $[C_5C_1Im][NO_3^-]$




(b) 13C NMR of original $[C_5C_1Im][NO_3^-]$




(c) 1H NMR of batch 2 recycled [$C_5C_1Im$][NO– 3]




(d) 13C NMR of batch 2 recycled [$C_5C_1Im$][NO– 3]

**Fig. S4** Structural comparison between the recovered and original [$C_5C_1Im$][NO– 3] ionic liquid by the test of 1H and 13C NMR (600 HZ, in DMSO-*d6*)

**HRMS, 1H- and 13C-NMR spectra of vitamin E succinate**

**Purification of vitamin E succinate:** (a) 1 mL of the reaction medium was added to 2 mL diethyl ether and incubated overnight under –18 °C; (b) after centrifugation at 8000 × g for 2 min, the organic phase was removed and added to 1.5 mL deionized water, and then mixed by vortex for 1 min; (c) after centrifugation at 8000 × g for 2 min, the organic phase was carefully transferred into a new tube and then dried with $Na_2SO_4$; (d) after the removal of solvent in a reduced-pressure rotary evaporator, 400 μL *n*-hexane were added to dissolve the unreacted VE further purification of the final isolated ester because α-tocopherol succinate is not soluble in *n*-hexane; (e) Centrifuging at 8000 × g for 2 min again, the liquid was discarded and after dried by nitrogen, white powder was obtained for further characterization. The isolated yield was about 80%, and the purity of final product vitamin E succinate was 97%; the melting point of final product was 75.2-76.5 °C.

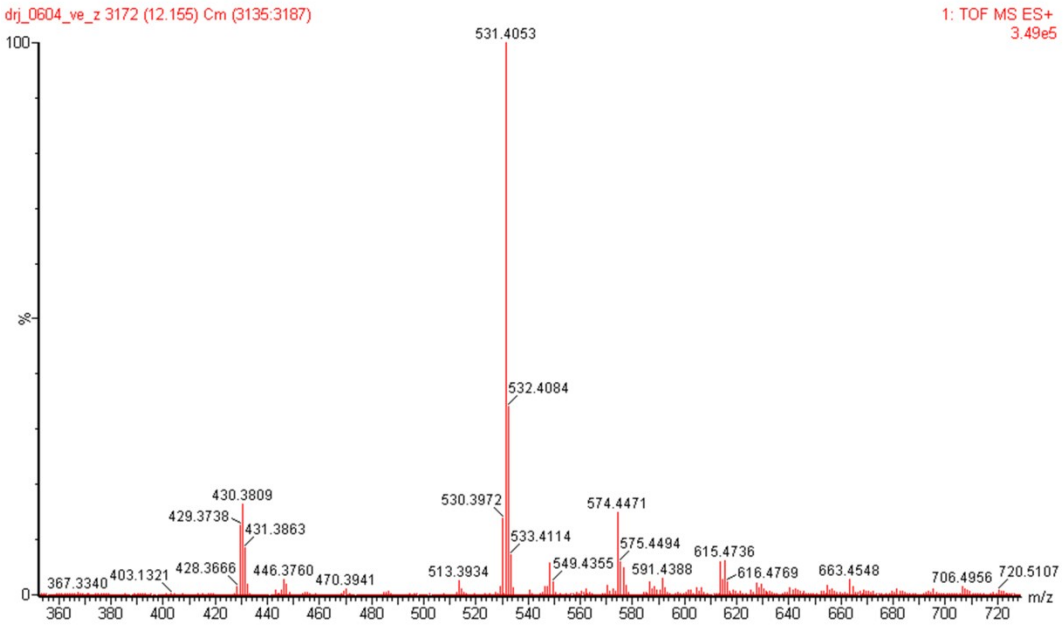



**Fig. S5** HRMS spectrum of vitamin E succinate (EI, m/z: found 531.4053 $[M]^+$; calculated 530.40 for $C_{33}H_{54}O_5$).

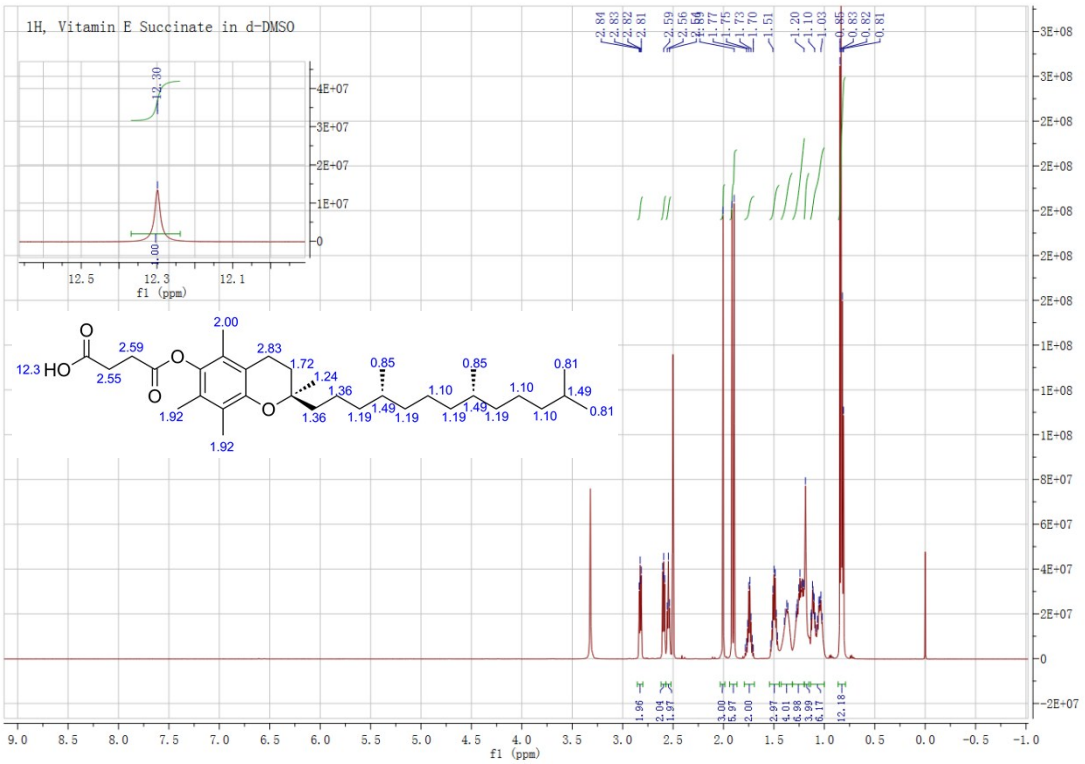



**Fig. S6** 1H-NMR spectrum of vitamin E succinate (600HZ, d6-DMSO)

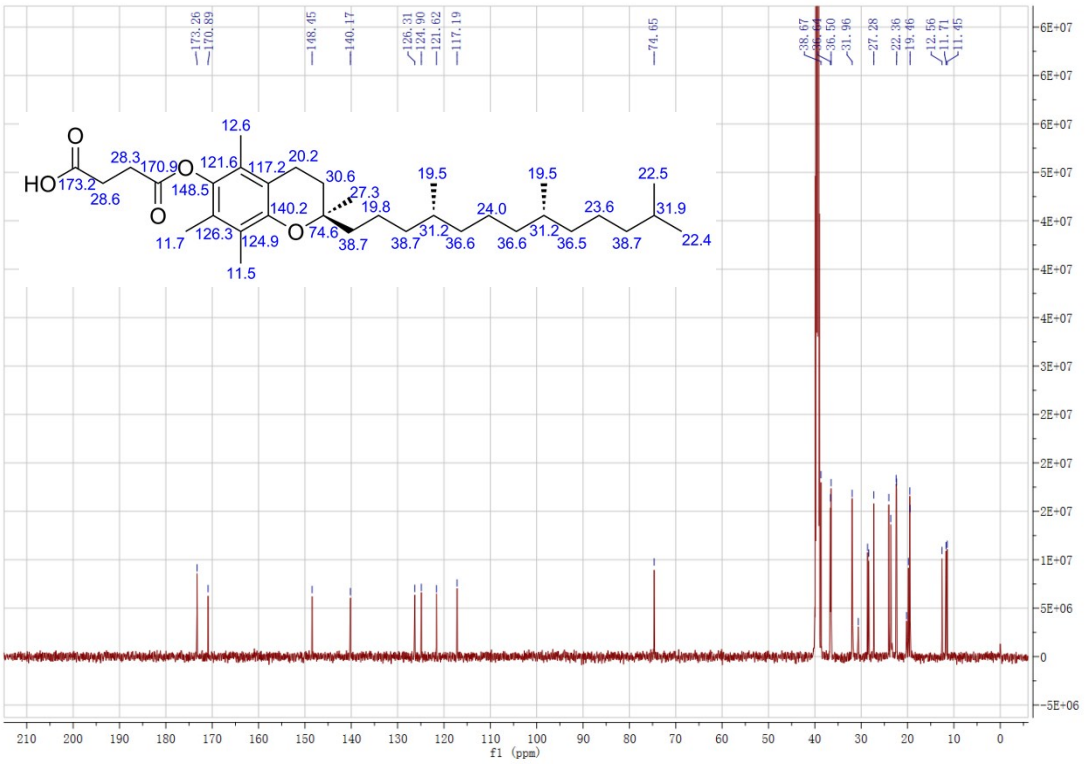



**Fig. S7** 13C-NMR spectrum of vitamin E succinate (600HZ, d6-DMSO)

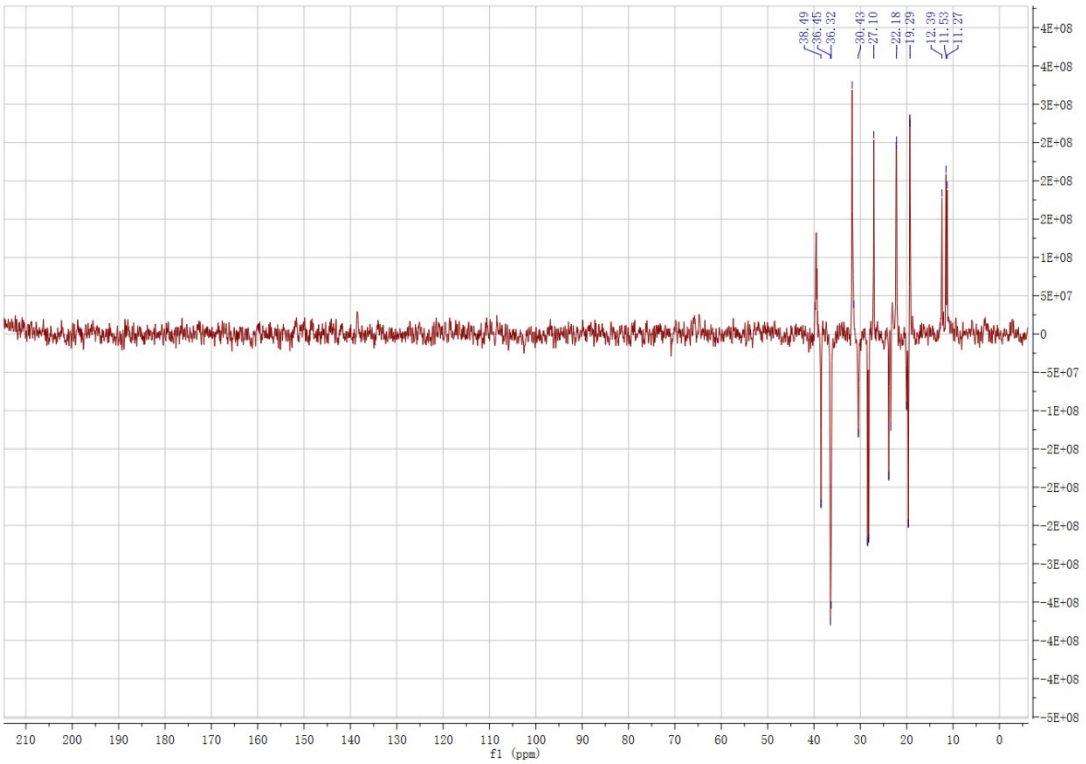



**Fig. S8** 13C-Dept (θ135°)-NMR spectrum of vitamin E succinate (600HZ, d6-DMSO)