Electronic Supplementary Information

Catalytic oxidative C-C bond cleavage route of levulinic acid and methyl levulinate

Fei Xia,[a,b] Zhongtian Du,[c] Junxia Liu,[a] Yangyang Ma,[a,b] and Jie Xu*[a]

[a]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, P. R. China

[b]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

E-mail: xujie@dicp.ac.cn

[c]School of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin 124221 P. R. China.

Figures

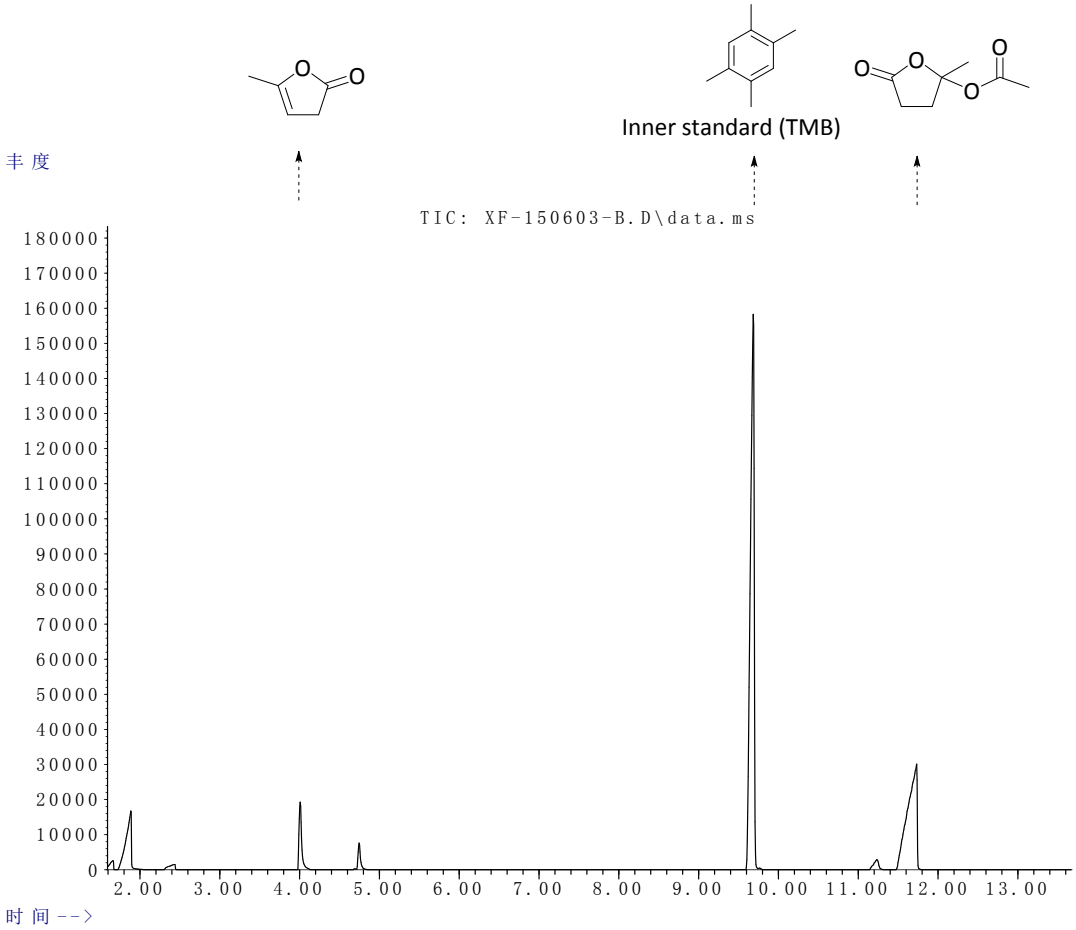

Figure S1. GC-MS trace of oxidation products of levulinic acid monitored at 30 min.

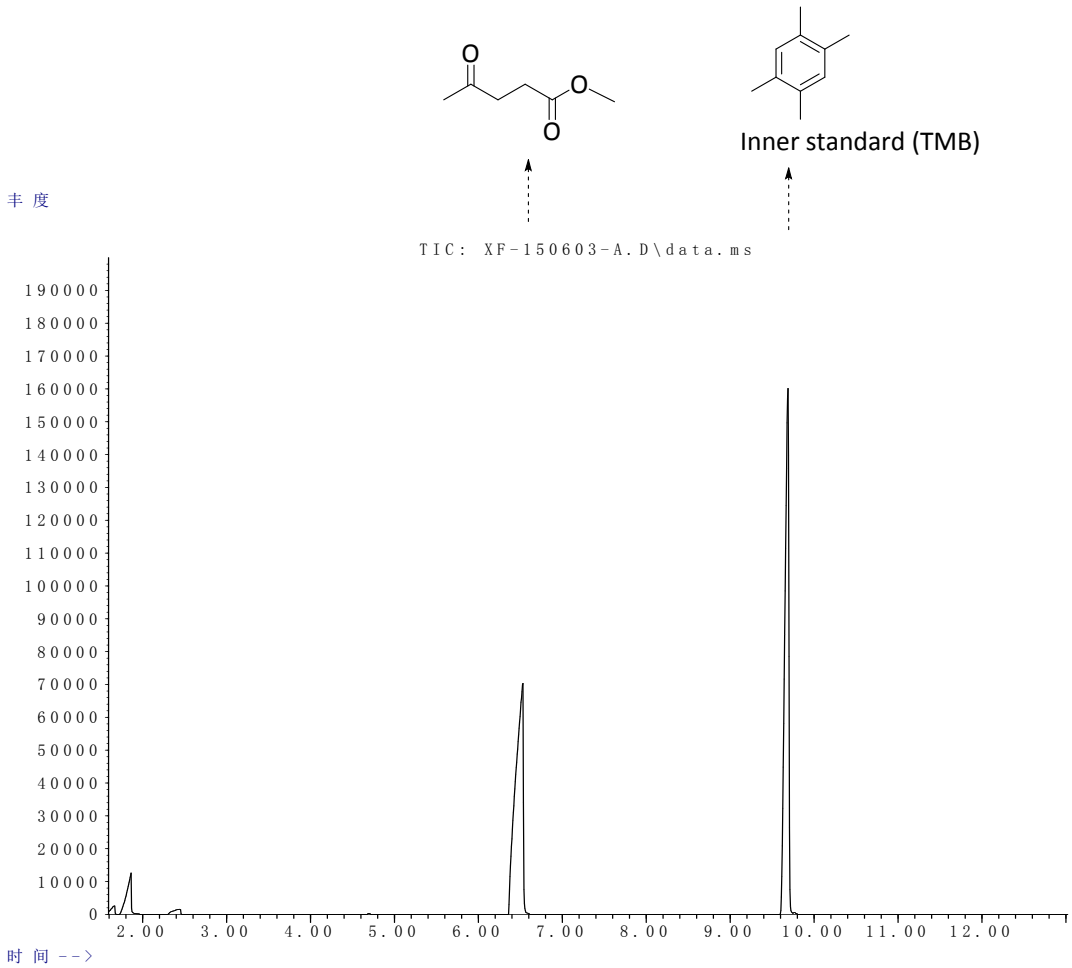

Figure S2. GC-MS trace of oxidation products of methyl levulinate monitored at 30 min.

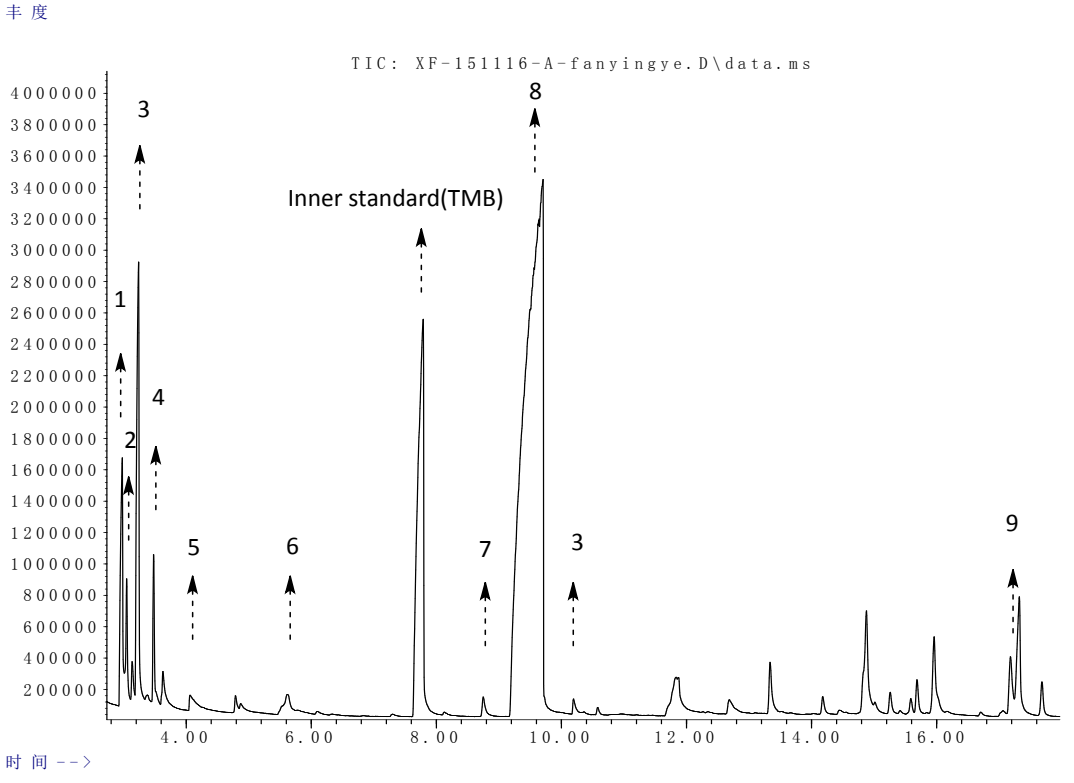

Figure S3. GC-MS Characterization for products of oxidation of levulinic acid catalyzed by $Mn(OAc)_3 \cdot 2H_2O$ in acetic anhydride.

Peaks assignment of some main products, **1**: maleic anhydride, **2**: α-angelica lactone, **3**: acetyloxy acetic acid, **4**: 1,1-ethanediol diacetate, **5**: β-angelica lactone, **6**: succinic anhydride, **7**: 1,1,2-ethanetriol triacetate, **8**: 2-methyl-5-oxotetrahydro-2-furanyl acetate, **9**: 4-hydroxy-2-pentenoic acid.

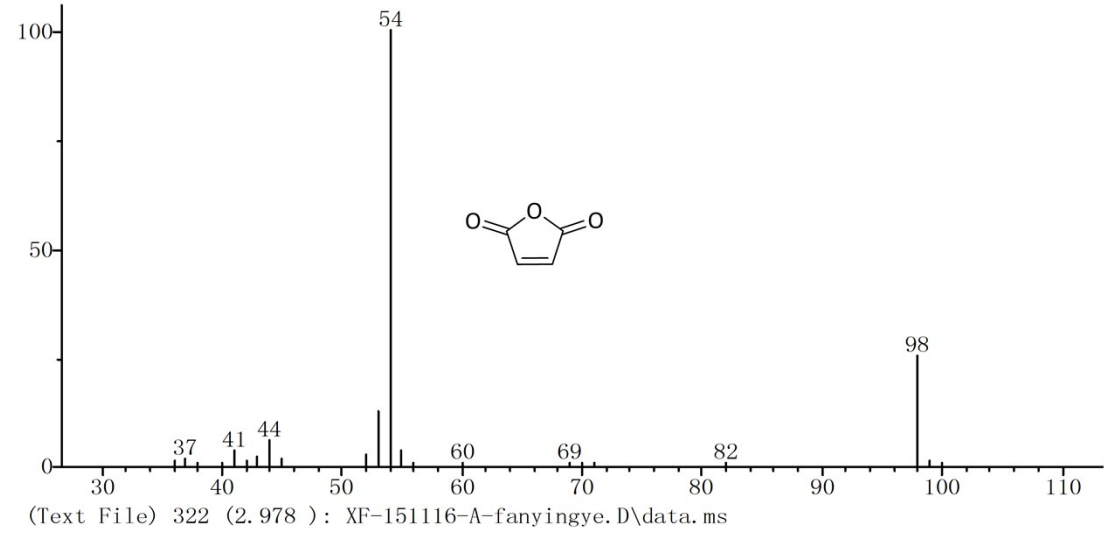

Figure S4. Mass spectrum of maleic anhydride (**1**). MS (70 eV): *m/z* (%), 98 (25) [M+], 85 (1), 69 (1), 60 (1), 55 (4), 54 (100), 53 (13), 44 (6), 41 (4), 36 (1), 32 (1).

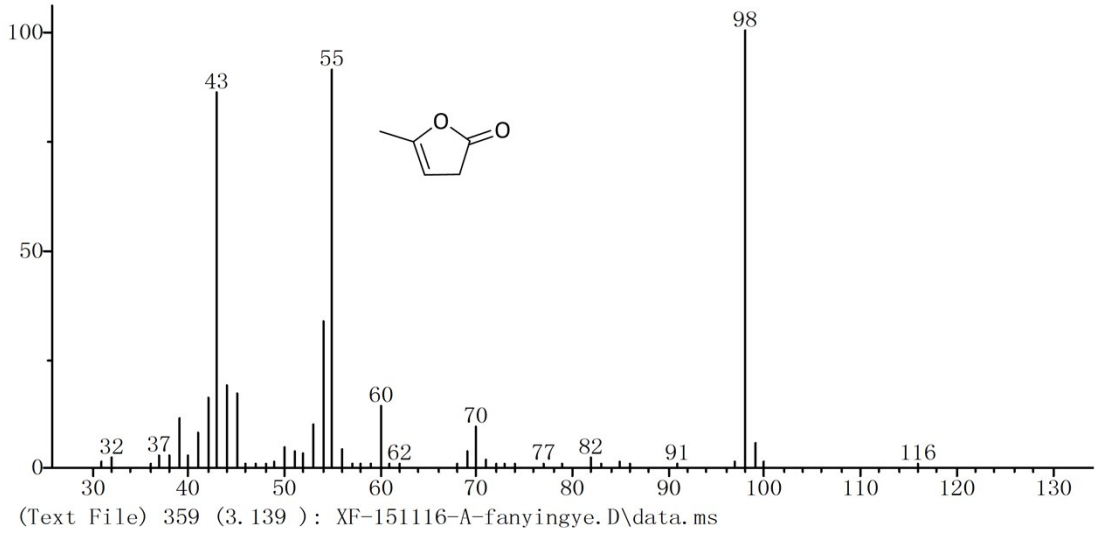

Figure S5. Mass spectrum of α-angelica lactone (**2**). MS (70 eV): *m/z* (%), 98 (100) [M+], 82 (2), 70 (10), 60 (14), 55 (91), 54 (33), 43 (86), 37 (2), 32 (1).

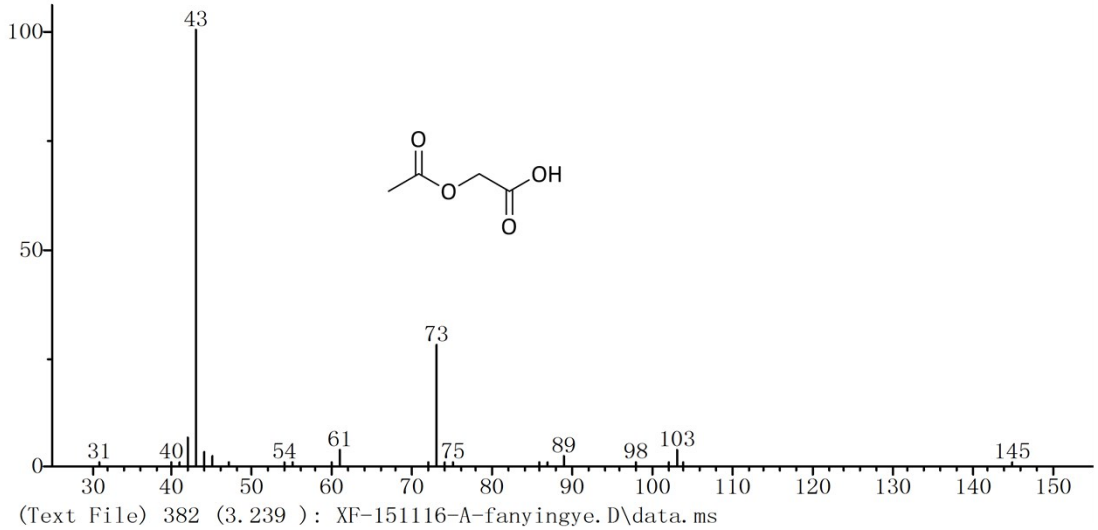

Figure S6. Mass spectrum of acetyloxy acetic acid (**3**). MS (70 eV): *m/z* (%), 118 (0) [M+], 145 (1), 103 (4), 98 (1), 89 (2), 73 (27), 43 (100), 42 (6), 31 (1).

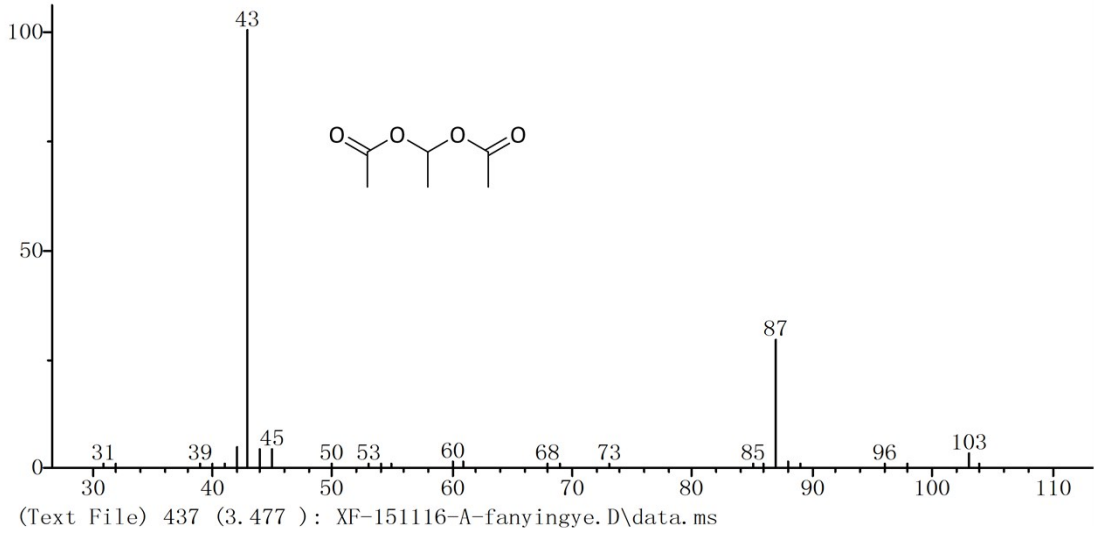

Figure S7. Mass spectrum of 1,1-ethanediol diacetate (**4**). MS (70 eV): *m/z* (%), 146 (0) [M+], 103 (3), 96 (1), 87 (30), 85 (1), 73 (1), 60 (1), 45 (4), 43 (100), 31 (1).

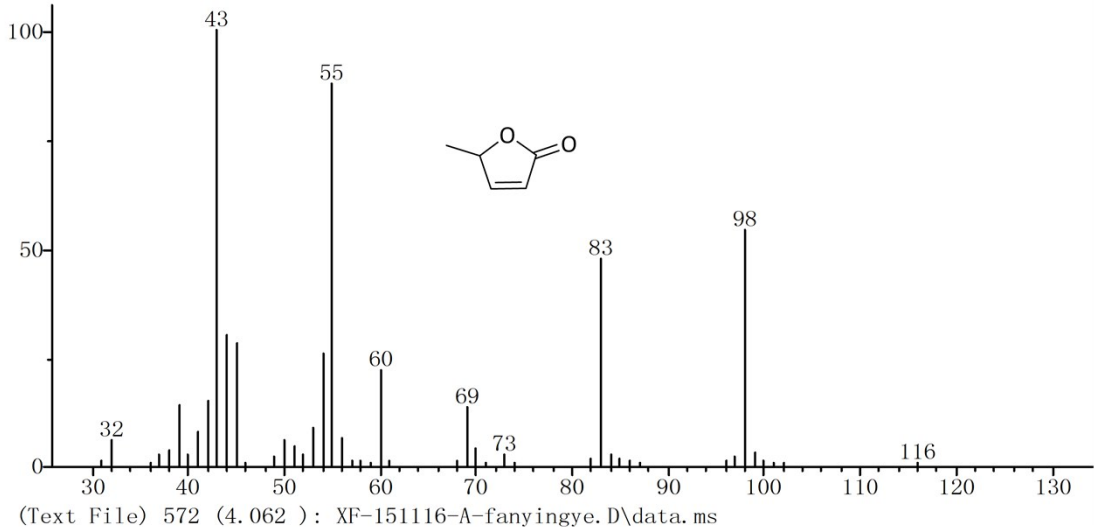

Figure S8. Mass spectrum of β-angelica lactone (**5**). MS (70 eV): *m/z* (%), 98 (54) [M+], 116 (1), 83 (47), 73 (3), 69 (13), 60 (22), 55 (88), 45 (28), 44 (30), 43 (100), 32 (6).

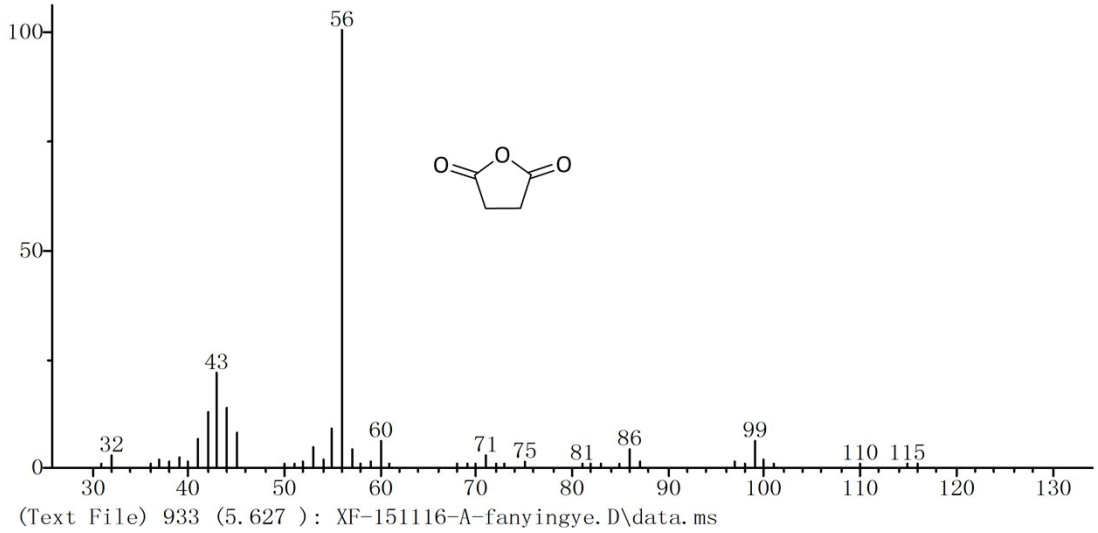

Figure S9. Mass spectrum of succinic anhydride (**6**). MS (70 eV): *m/z* (%), 100 (2) [M+], 116 (1), 99 (6), 86 (4), 75 (2), 71 (3), 60 (6), 56 (100), 55 (9), 43 (21), 32 (3).

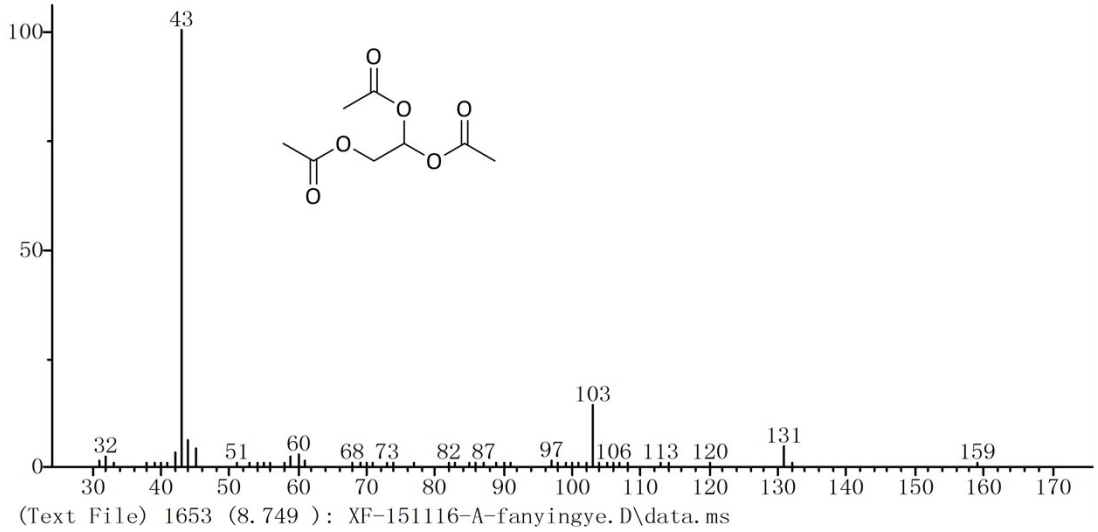

Figure S10. Mass spectrum of 1,1,2-ethanetriol triacetate (**7**). MS (70 eV): *m/z* (%), 204 (0) [M+], 131 (5), 103 (14), 60 (3), 43 (100), 32 (2).

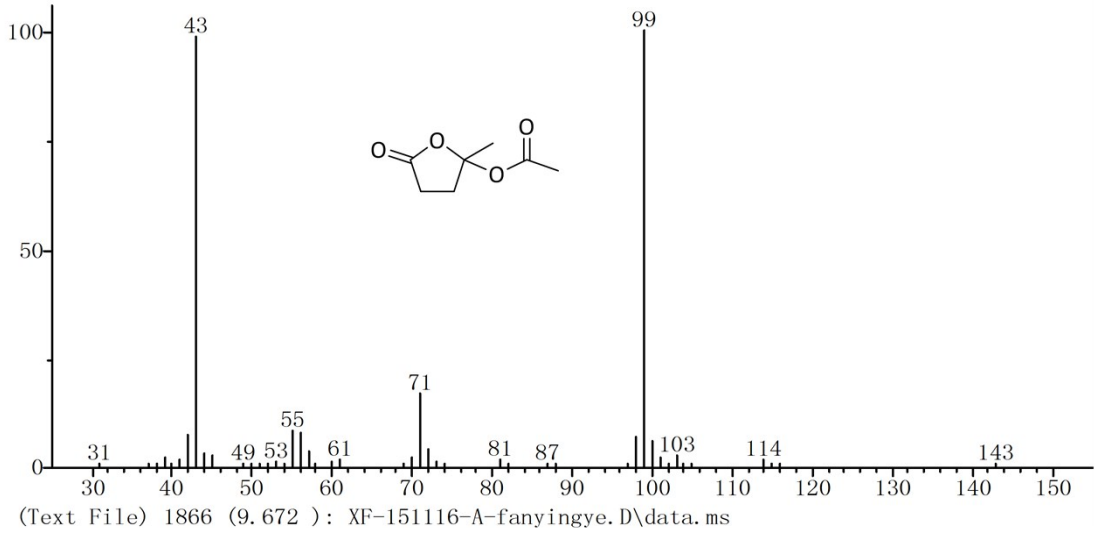

Figure S11. Mass spectrum of 2-methyl-5-oxotetrahydro-2-furanyl acetate (**8**). MS (70 eV): *m/z* (%), 158 (0) [M+], 143 (1), 122 (1), 116 (2), 99 (98), 87 (1), 81 (1), 71 (17), 61 (2), 55 (8), 45 (3), 43 (100), 31 (1).

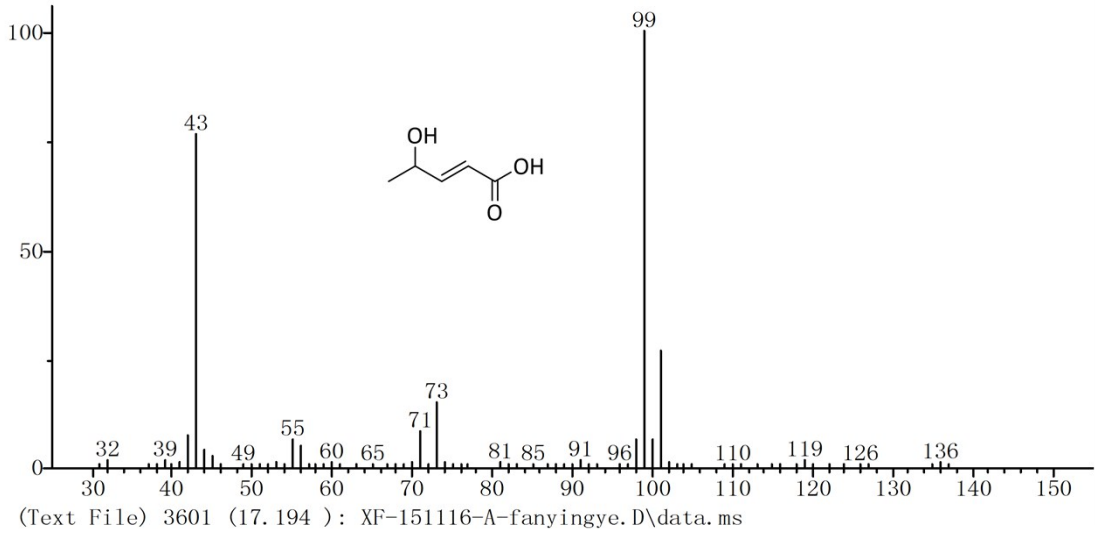

Figure S12. Mass spectrum of 4-hydroxy-2-pentenoic acid (**9**). 116 (1) [M+], 101 (26), 99 (100), 85 (1), 73 (15), 65 (1), 60 (1), 55 (7), 43 (77), 32 (1).

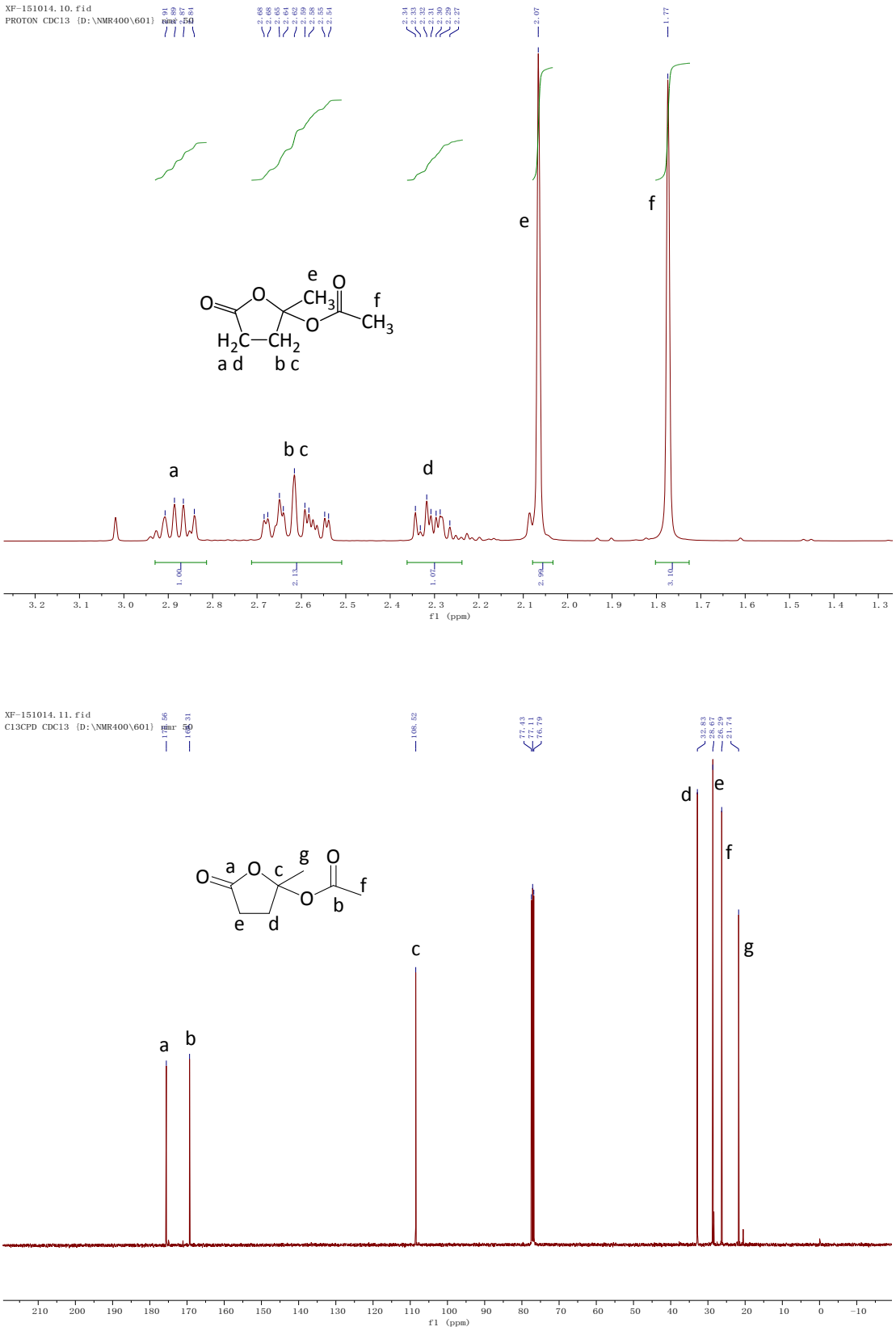

Figure S13. ^{1}H-NMR and ^{13}C-NMR characterization for 2-methyl-5-oxotetrahydro-2-furanyl acetate in $CDCl_3$ at room temperature.

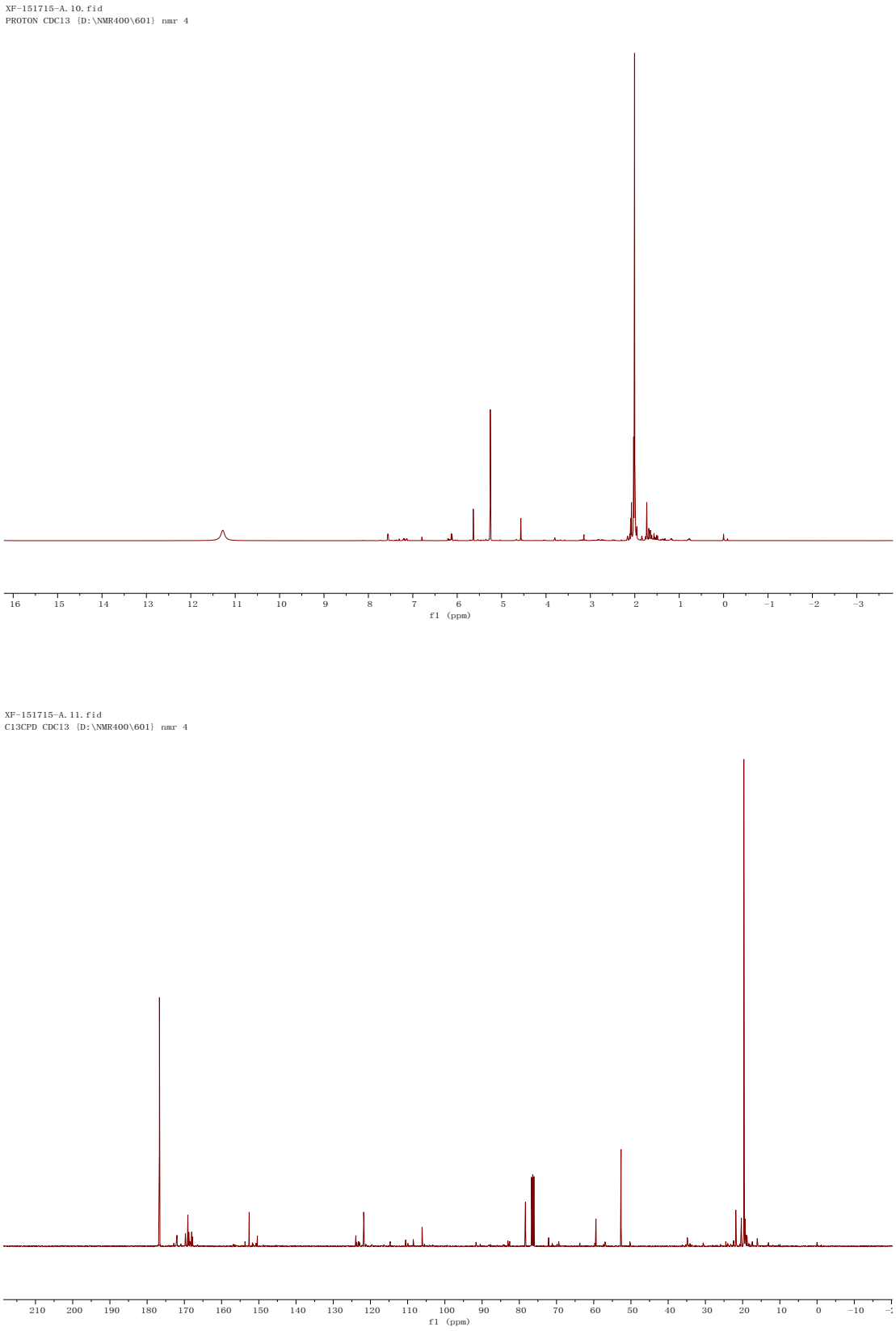

Figure S14. ^{1}H-NMR and ^{13}C-NMR characterization for side-products of oxidation of α-angelica lactone

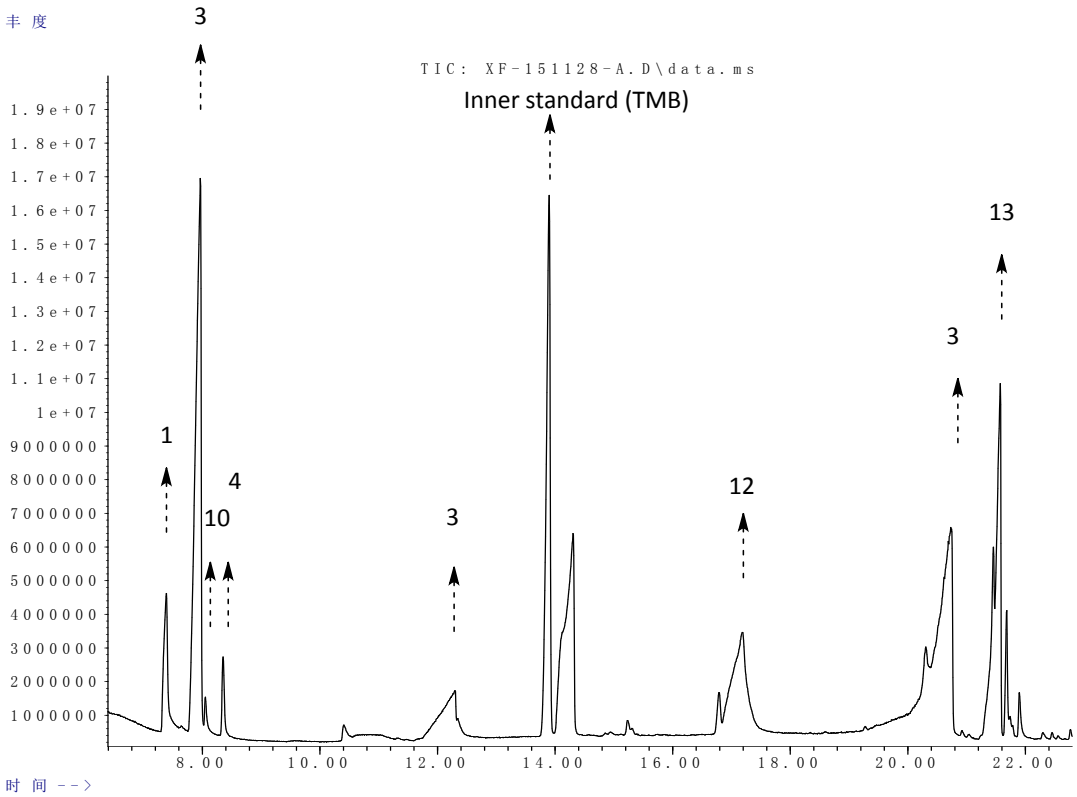

Figure S15. GC-MS Characterization for products of oxidation of α-angelica lactone catalyzed by $Mn(OAc)_3 \cdot 2H_2O$.

Peaks assignment of some main products, **1**: maleic anhydride, **3**：acetyloxy acetic acid, **4**: 1,1-ethanediol diacetate, **10**: 4-cyclopentene-1,3-dione, **12**: ethenyl acetate, **13**: 1,2,3,5-tetra-O-acetylpentofuranose.

Figure S16. Mass spectrum of 4-cyclopentene-1,3-dione (**10**). MS (70 eV): *m/z* (%), 96 (55) [M+], 73 (11), 68 (40), 60 (5), 54 (32), 43 (100), 42 (45), 41 (10), 40 (23), 39 (19), 26 (25), 15 (7).

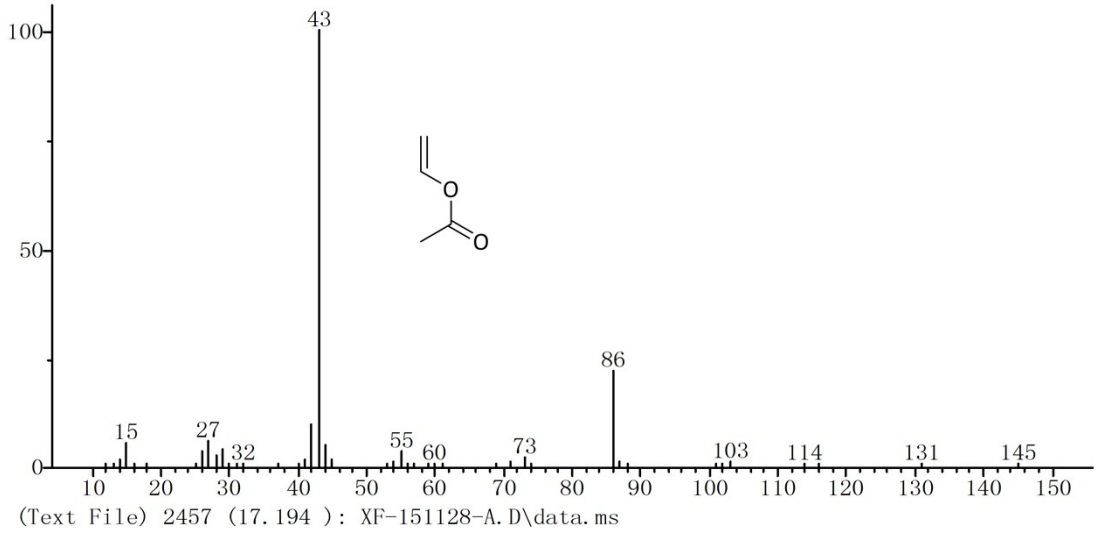

Figure S17. Mass spectrum of ethenyl acetate (**12**). MS (70 eV): *m/z* (%), 86(20) [M+], 73 (0), 55 (3), 43 (100), 27 (10), 15 (10).

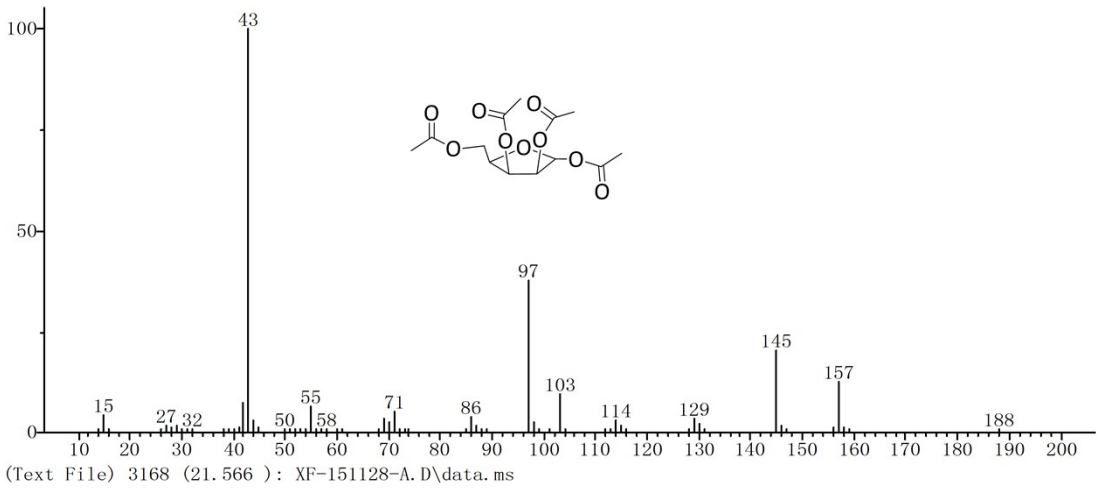

Figure S18. Mass spectrum of 1,2,3,5-tetra-O-acetylpentofuranose (**13**). MS (70 eV): *m/z* (%), 318 (0) [M+], 157 (12), 145 (19), 129 (4), 103 (10), 97 (37), 86 (3), 71 (5), 55 (6), 43 (100), 29 (2), 15 (4).