nanomaterials

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Supplementary Materials

The Al-Containing Silicates Modified with Organic Ligands and SnO_2 Nanoparticles for Catalytic Baeyer-Villiger Oxidation and Aerobic Carboxylation of Carbonyl Compounds

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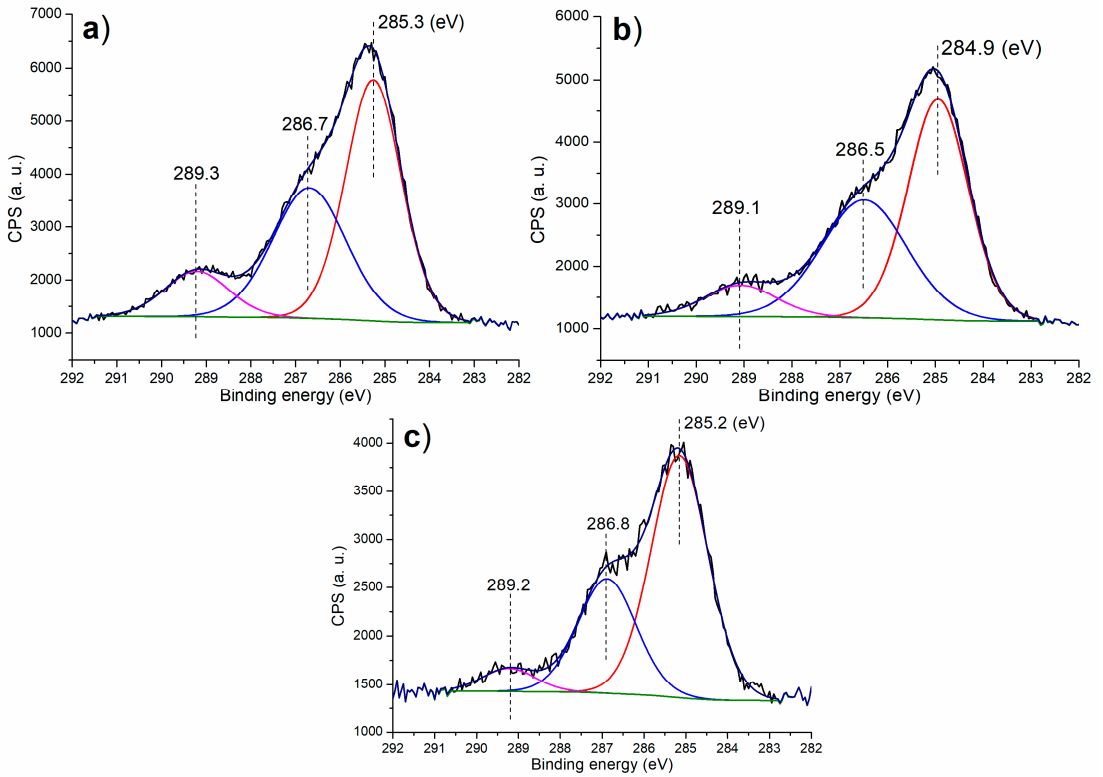


Figure S1. XPS measurement of C 1s region for the synthesized catalyst: (**a**) C1, (**b**) C2, (**c**) C3.

S2. FT-IR spectra of the synthesized catalyst

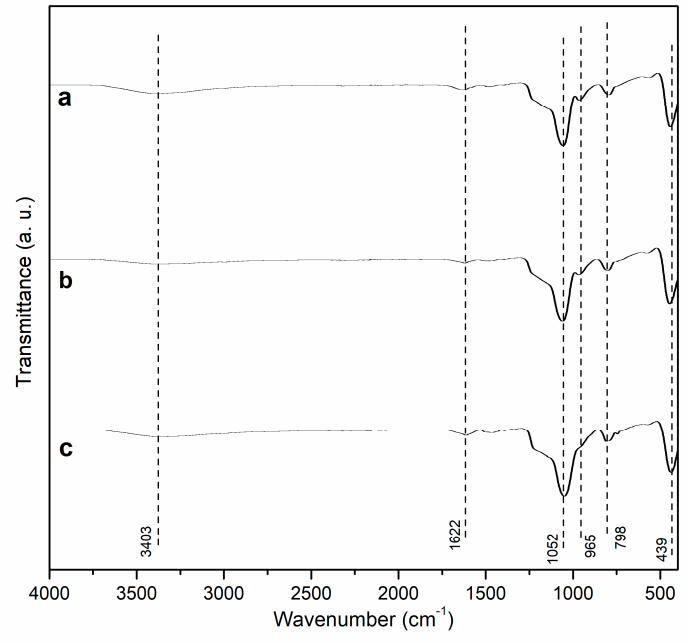


Figure S2. FT-IR spectra of the synthesized catalyst: (**a**) C1, (**b**) C2, (**c**) C3.

S3. GC-MS examples for Table 4

Entry 1, Table 4

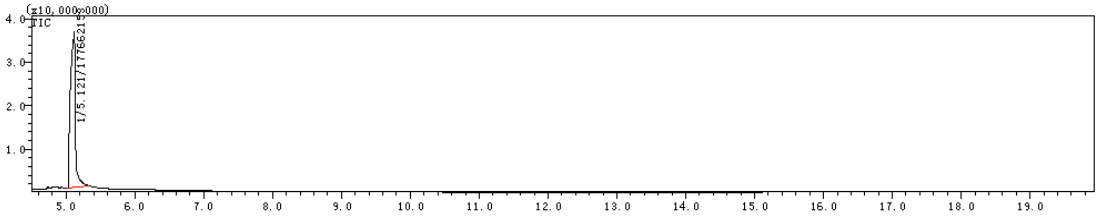
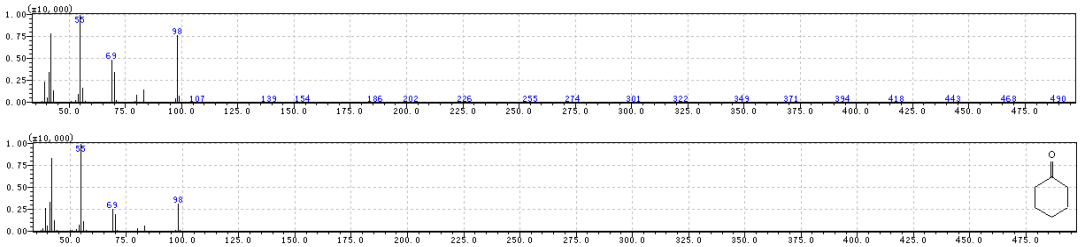


Figure S3. GC part of GC-MS for Entry 1, Table 4.

1) The peak for t_R = 5.121 min is:



GC-MS: calcd. for $C_6H_{10}O$ 98, found 98 ($C_6H_{10}O$). Table 4.

2) Entry 2, Table 4

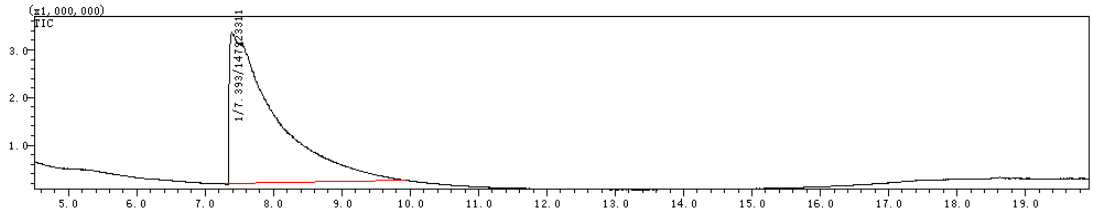
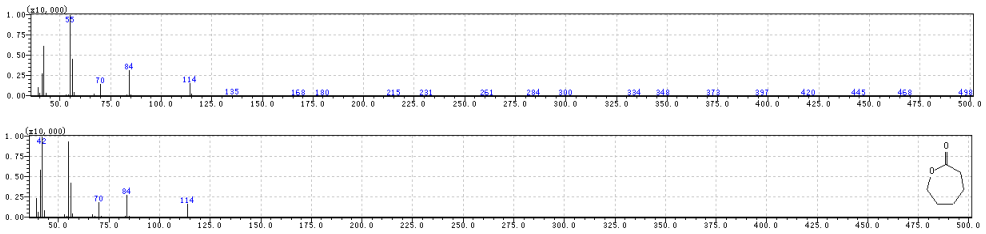


Figure S4. GC part of GC-MS for Entry 2, Table 4.

In this image, data format is peak number / retention time (min) / integral area.
The peak for t_R = 7.393 min is:



GC-MS: calcd. for $C_6H_{10}O_2$ 114, found 114 ($C_6H_{10}O_2$). Table 4.

Note: the upper MS image is experimental result, the lower is reference image from GC-MS library.

3) Entry 3, Table 4

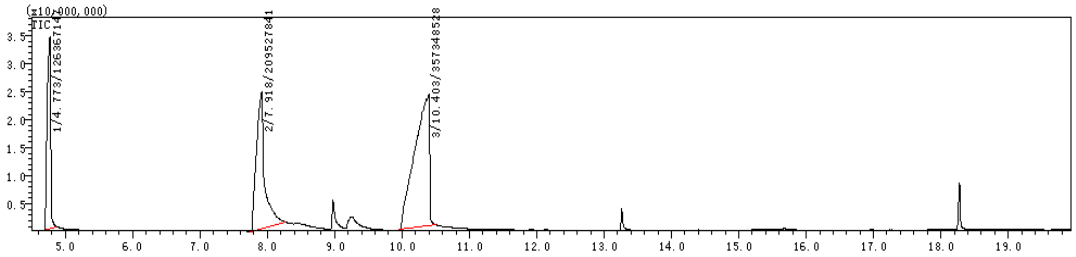
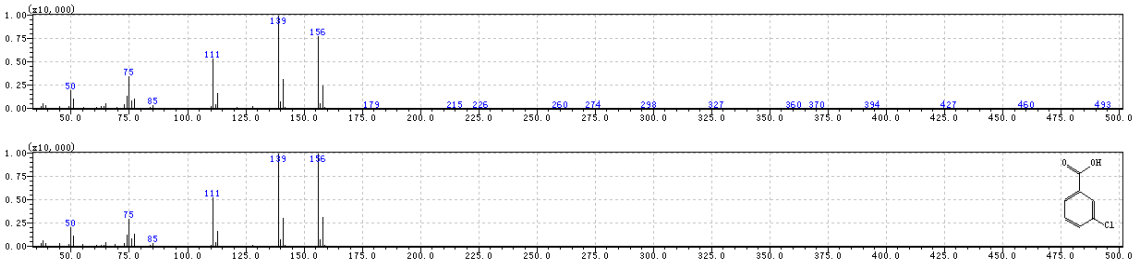


Figure S5. GC part of GC-MS for Entry 3, Table 4.

The peak for t_R = 4.773 min is unreacted substrate (cyclohexanone), the peak for t_R = 7.918 min is Product (oxepan-2-one), Table 4.

The peak for t_R = 10.403 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid), Table 4:



GC-MS: calcd. for $C_7H_5ClO_2$ 156, found 156 ($C_7H_5ClO_2$). Table 4.

4) Entry 4, Table 4

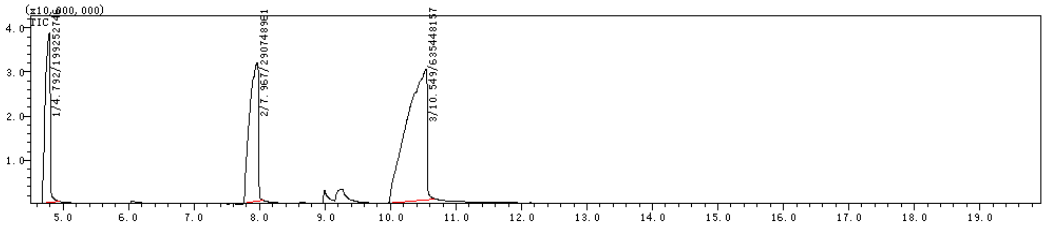


Figure S6. GC part of GC-MS for Entry 4, Table 4.

The peak for t_R = 4.792 min is unreacted substrate (cyclohexanone), the peak for t_R = 7.967 min is Product (oxepan-2-one), Table 4. The peak for t_R = 10.549 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid), Table 4.

5) Entry 5, Table 4

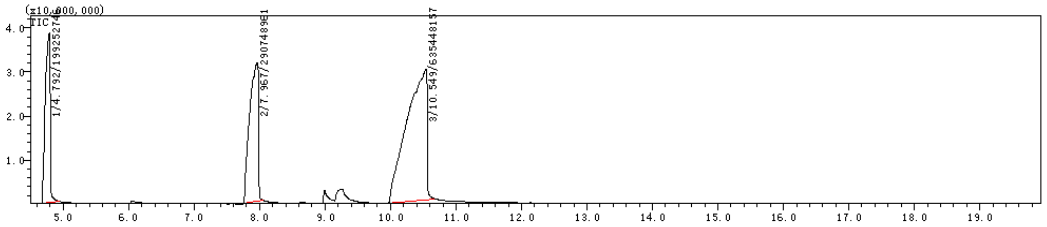


Figure S7. GC part of GC-MS for Entry 5, Table 4.

The peak for t_R = 4.792 min is unreacted substrate (cyclohexanone), the peak for t_R = 7.967 min is Product (oxepan-2-one), Table 4. The peak for t_R = 10.549 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid), Table 4.

S4. GC-MS examples for Table 5

6) Entry 1, Table 5

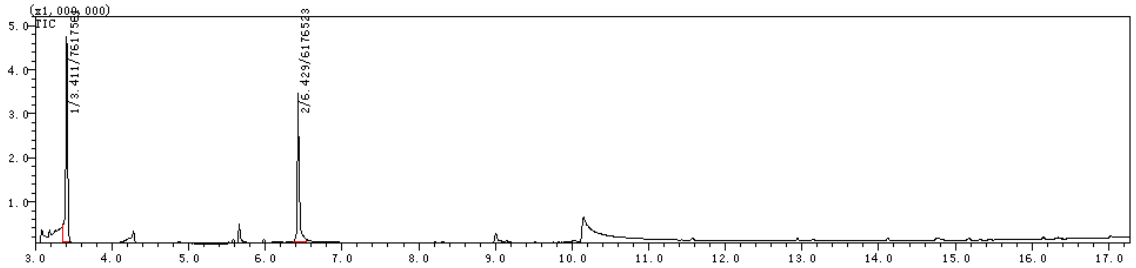
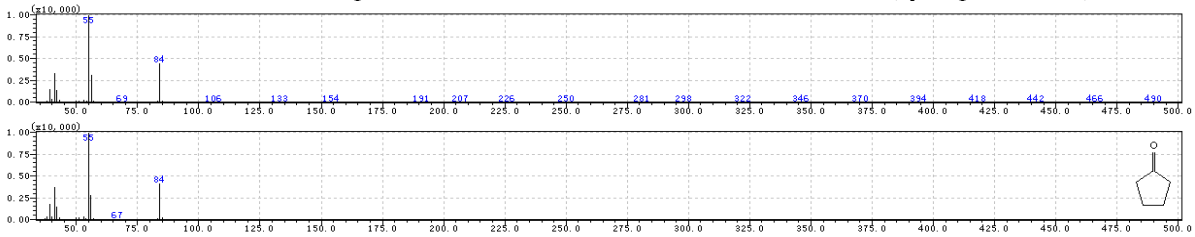


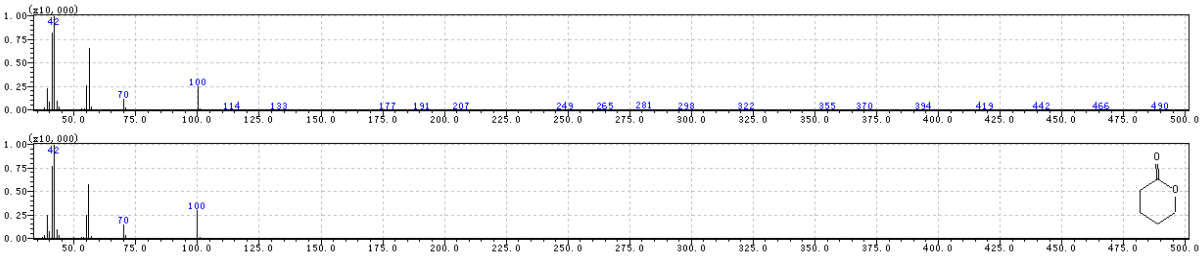
Figure S8. GC part of GC-MS for Entry 1, Table 5.

The peak for t_R = 3.411 min is unreacted substrate (cyclopentanone):



GC-MS: calcd. for C_5H_8O 84, found 84 (C_5H_8O). Table 5.

The peak for t_R = 6.429 min is Product (tetrahydropyran-2-one), Table 5:



GC-MS: calcd. for $C_5H_8O_2$ 100, found 100 ($C_5H_8O_2$). Table 5.

The unmarked peak for t_R = 10.00-11.00 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid).

7) Entry 3, Table 5

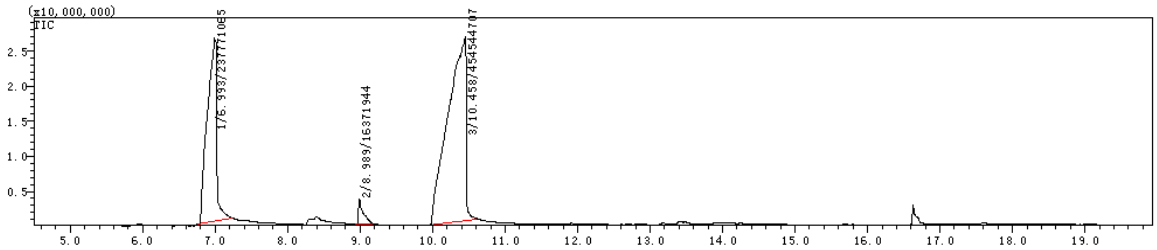
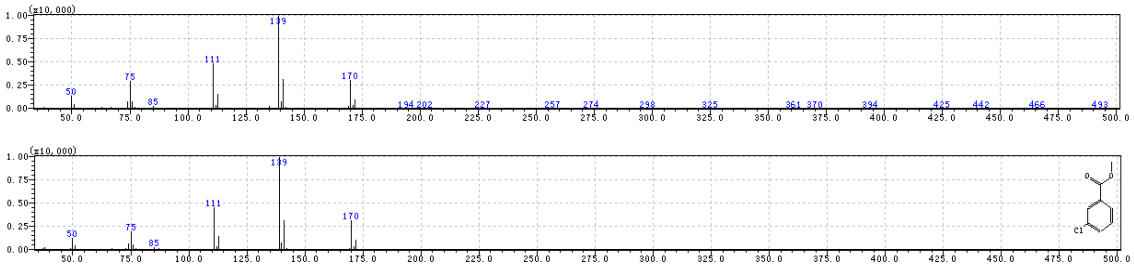


Figure S9. GC part of GC-MS for Entry 3, Table 5.

The peak for t_R = 6.993 min is Product (tetrahydropyran-2-one), Table 5, the peak for t_R = 10.458 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid).

The peak for t_R = 8.989 min is an esterification product of *m*-chlorobenzoic acid:



This by-product is derived from *m*-CPBA-induced oxidation, probably due to radical reaction with some impurities of solvent or reagents.

8) Entry 4, Table 5

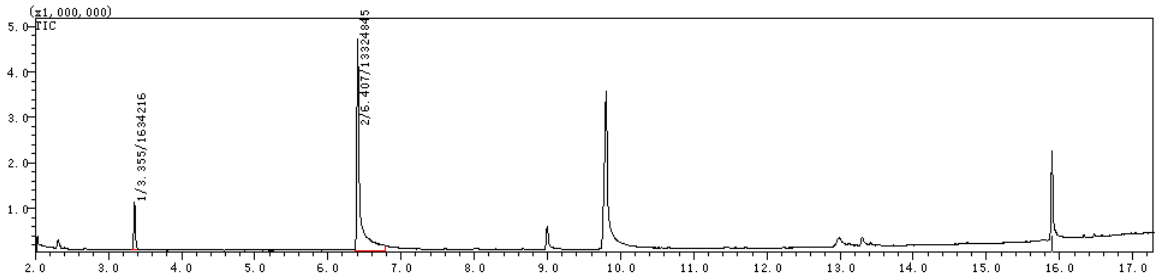


Figure S10. GC part of GC-MS for Entry 4, Table 5.

The peak for t_R = 3.355 min is unreacted substrate (cyclopentanone), the peak for t_R = 6.407 min is Product (tetrahydropyran-2-one), Table 5, the unmarked peak for t_R = 9.8-10.0 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid).

S5. GC-MS examples for Table 6

9) Entry 2, Table 6

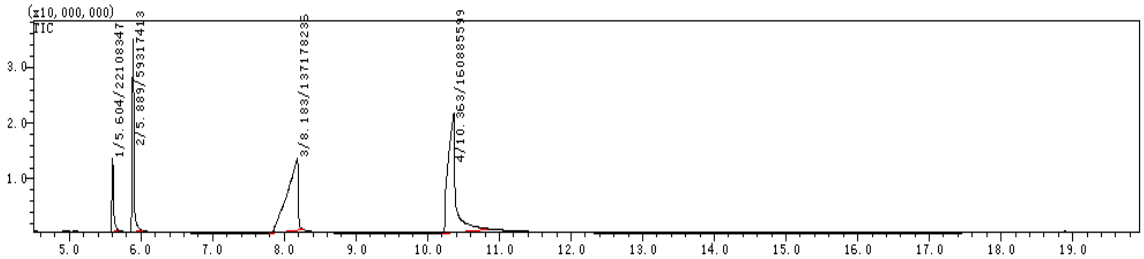
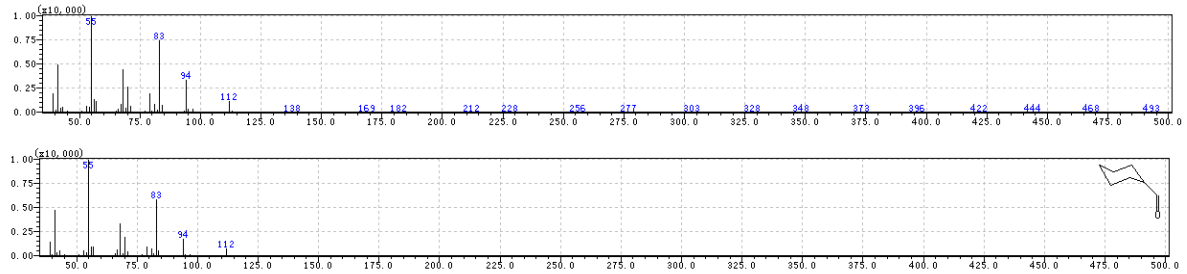


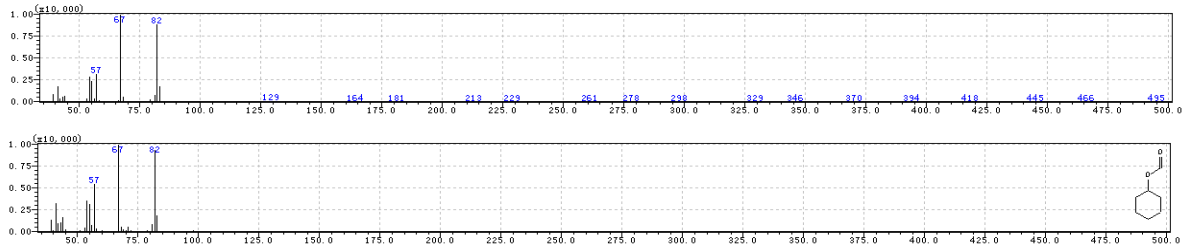
Figure S11. GC part of GC-MS for Entry 2, Table 6.

The peak for t_R = 5.604 min is unreacted substrate (cyclohexanecarbaldehyde):



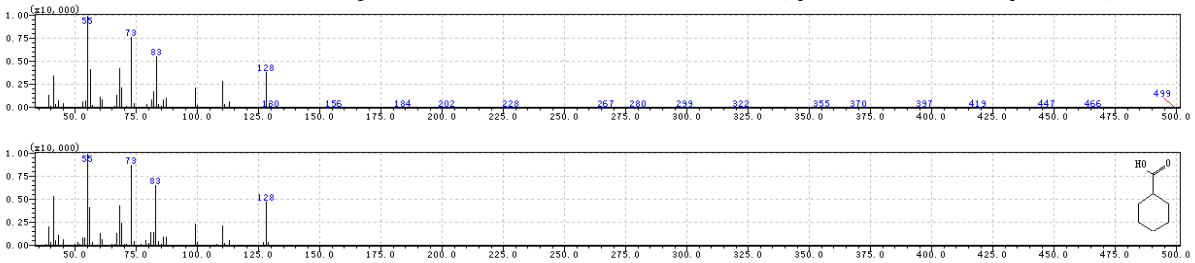
GC-MS: calcd. for $C_7H_{12}O$ 112, found 112 ($C_7H_{12}O$). Table 6.

The peak for t_R = 5.889 min is Product A (cyclohexylformate):



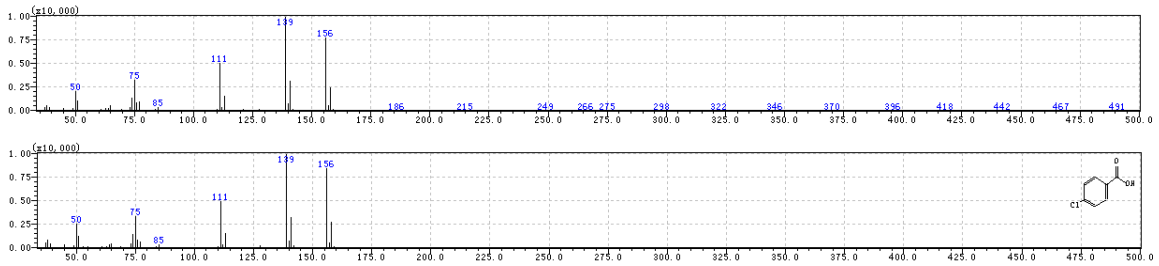
GC-MS: calcd. for $C_7H_{12}O_2$ 128, found 129 ($C_7H_{12}O_2$ + H). Table 6.

The peak for t_R = 8.183 min is Product B (cyclohexanecarboxylic acid), Table 6:



GC-MS: calcd. for $C_7H_{12}O_2$ 128, found 128 ($C_7H_{12}O_2$). Table 6.

The peak for t_R = 10.363 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid), Table 6:



GC-MS: calcd. for $C_7H_5ClO_2$ 156, found 156 ($C_7H_5ClO_2$). Table 6.

10) Entry 4, Table 6

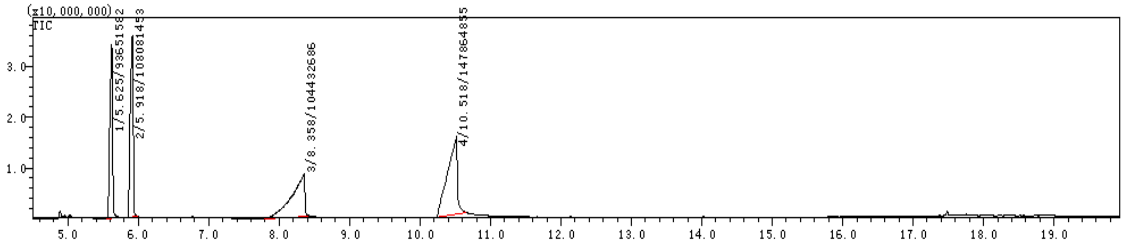


Figure S12. GC part of GC-MS for Entry 4, Table 6.

The peak for t_R = 5.625 min is unreacted substrate (cyclohexanecarbaldehyde), the peak for t_R = 5.918 min is Product A (cyclohexylformate), the peak for t_R = 8.358 min is Product B (cyclohexanecarboxylic acid), Table 6. The peak for t_R = 10.518 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid), Table 6.

S6. GC-MS examples for Table 7

11) Entry 2, Table 7

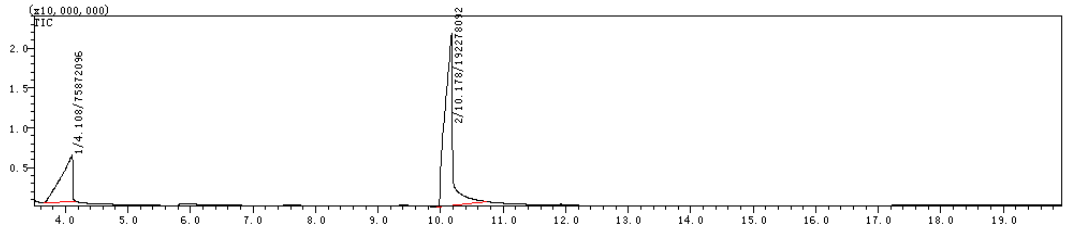
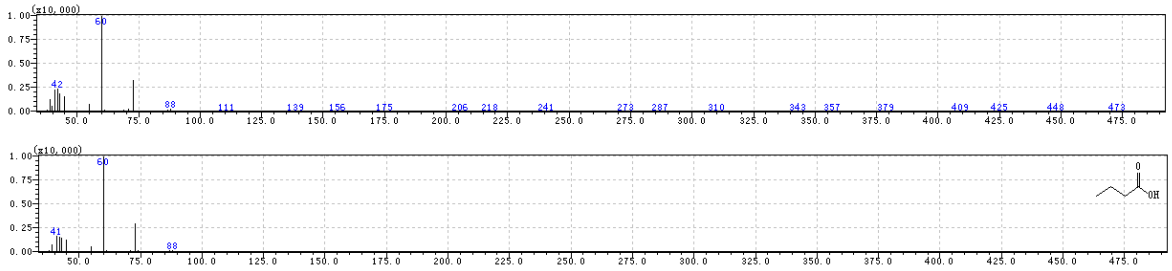


Figure S13. GC part of GC-MS for Entry 2, Table 7.

The peak for t_R = 4.108 min is *n*-butyric acid (Product, Table 7):



GC-MS: calcd. for $C_4H_8O_2$ 88, found 88 ($C_4H_8O_2$). Table 7.
The peak for t_R = 10.178 min is by-product of *m*-CPBA (*m*-chlorobenzoic acid), Table 7.

12) Entry 9, Table 7

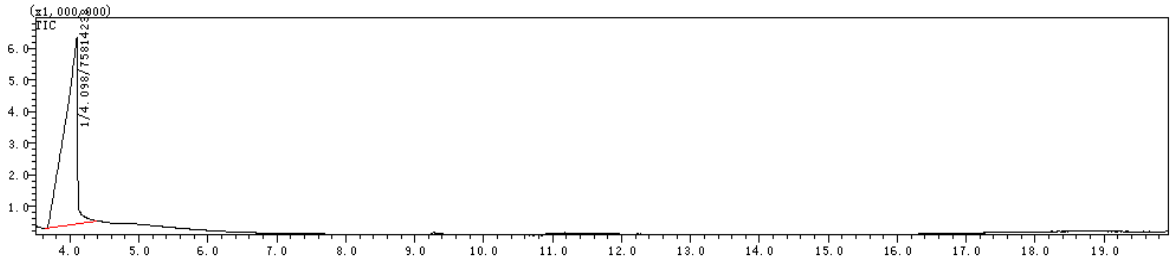


Figure S14. GC part of GC-MS for Entry 9, Table 7.

The peak for t_R = 4.098 min is *n*-butyric acid (Product, Table 7).

S7. GC-MS examples for Table 8
13) Entry 4, Table 8

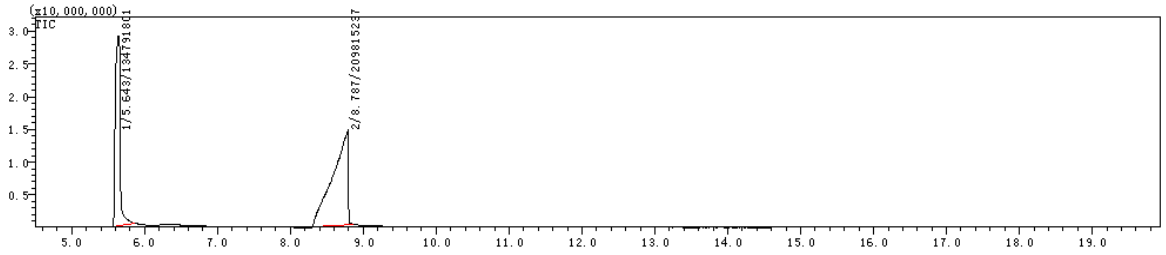
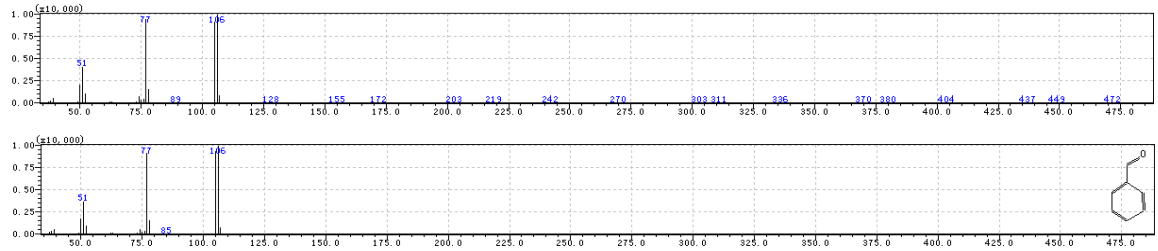
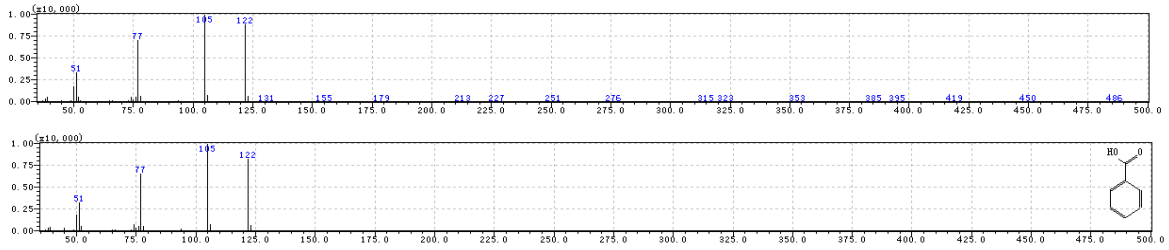


Figure S15. GC part of GC-MS for Entry 4, Table 8.

The peak for t_R = 5.643 min is benzaldehyde (unreacted substrate, Table 8):



GC-MS: calcd. for C_7H_6O 106, found 106 (C_7H_6O). Table 8.
The peak for t_R = 8.787 min is benzoic acid (Product, Table 8):



GC-MS: calcd. for $C_7H_6O_2$ 122, found 122 ($C_7H_6O_2$). Table 8.

14) Entry 5, Table 8

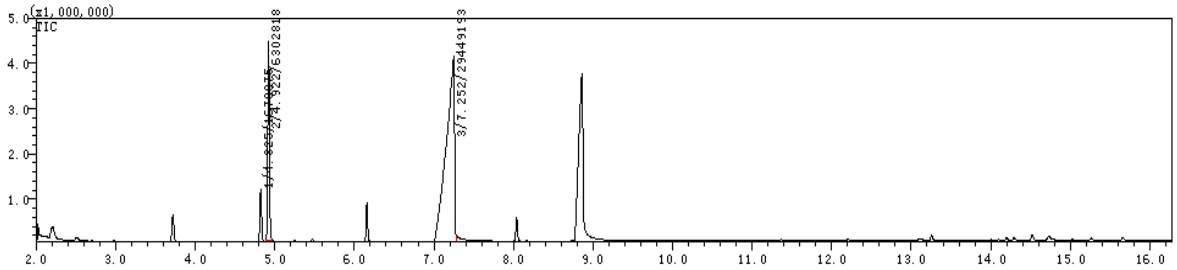
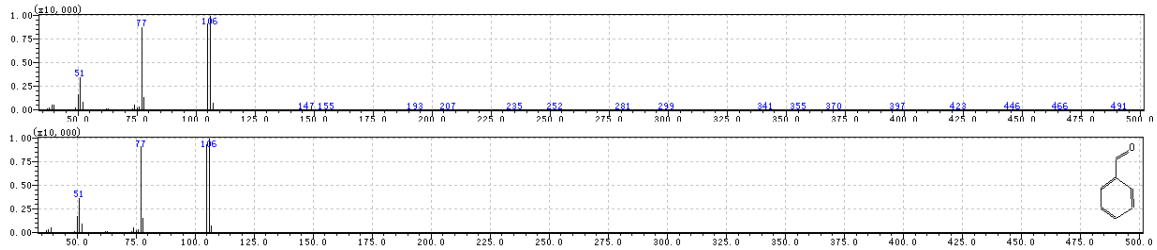


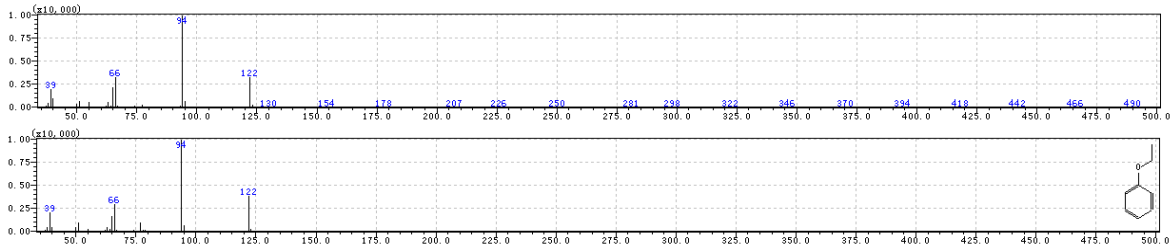
Figure S16. GC part of GC-MS for Entry 5, Table 8.

The peak for t_R = 4.886 min is benzaldehyde (unreacted substrate, Table 8):



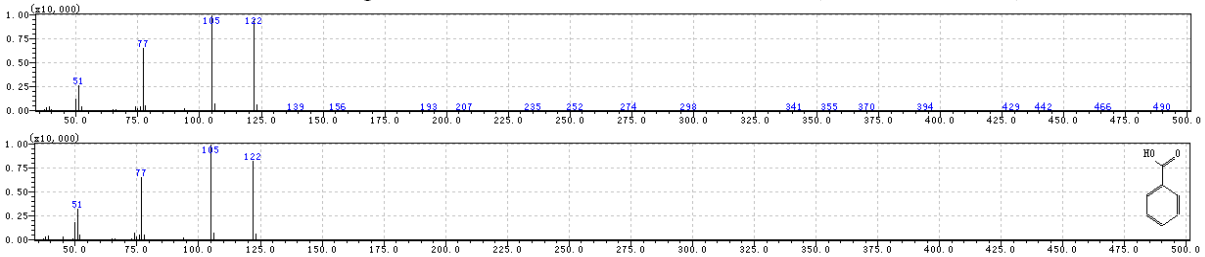
GC-MS: calcd. for C_7H_6O 106, found 106 (C_7H_6O). Table 8.

The peak for t_R = 4.922 min is phenethyl ether (by-product, Table 8):



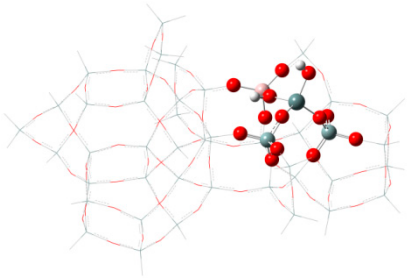
GC-MS: calcd. for $C_8H_{10}O$ 122, found 122 ($C_8H_{10}O$). Table 8.

The peak for t_R = 7.252 min is benzoic acid (Product, Table 8):

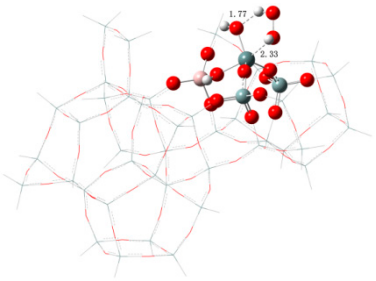


GC-MS: calcd. for $C_7H_6O_2$ 122, found 122 ($C_7H_6O_2$). Table 8.

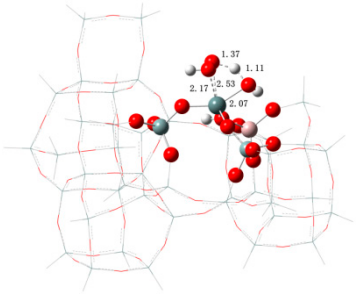
S8. Optimized structures (distance in Å) for the oxidation of cyclopentanone under H_2O_2 catalyzed by C3 and Sn-beta zeolite model



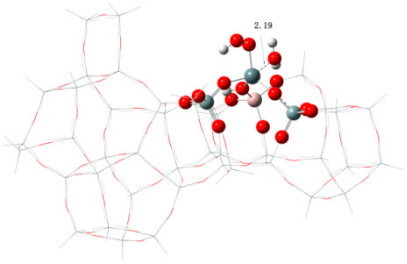
Al-Cat



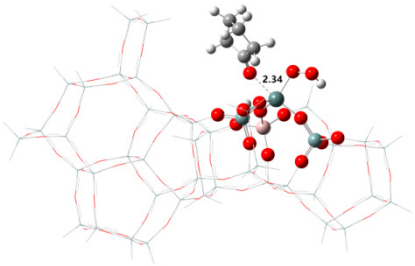
Al-Int-1



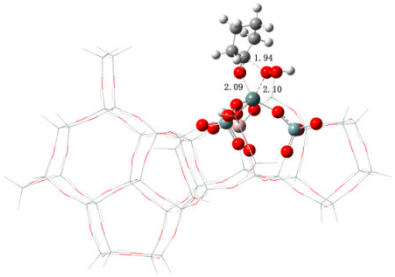
Al-TS-1



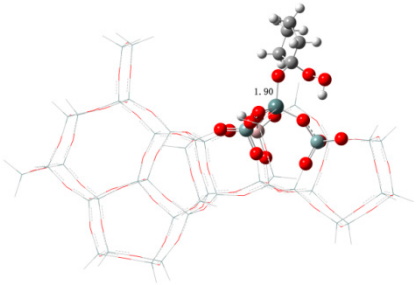
Al-Int-2



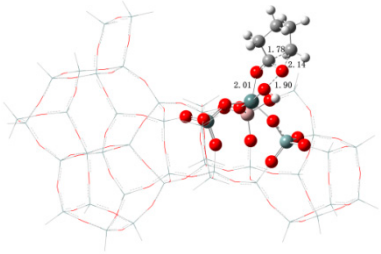
Al-Int-3



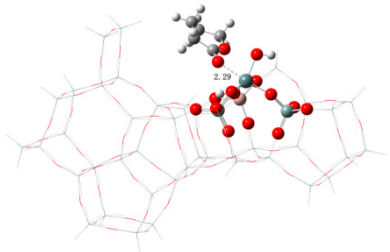
Al-TS-2



Al-Int-4

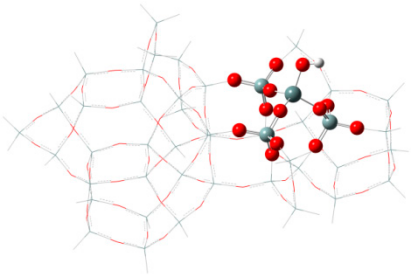


Al-TS-3

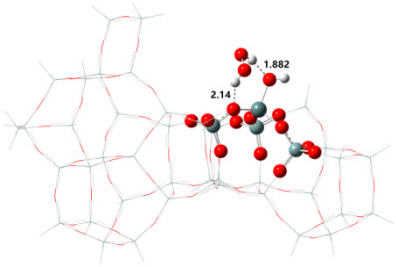


Al-Int-5

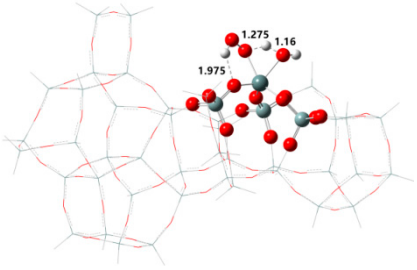
Figure S17. Optimized structures (distance in Å) for the oxidation of cyclopentanone with H_2O_2 catalyzed by C3.



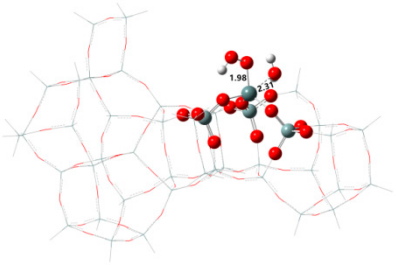
Si-Cat



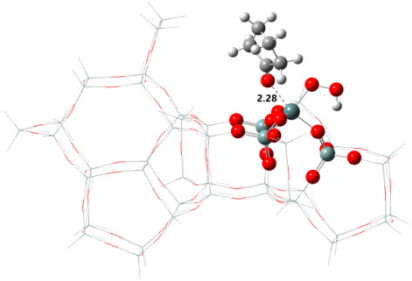
Si-Int-1



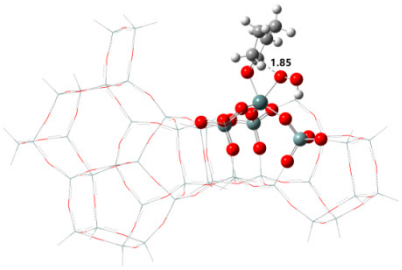
Si-TS-1



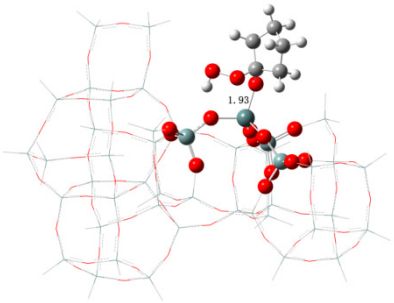
Si-Int-2



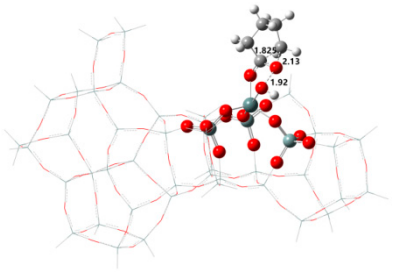
Si-Int-3



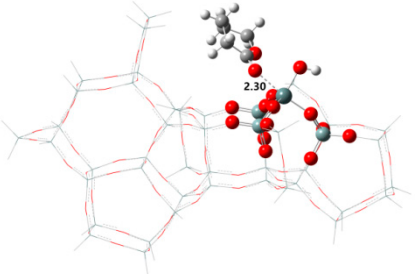
Si-TS-2



Si-Int-4



Si-TS-3



Si-Int-5

Figure S18. Optimized structures (distance in Å) for the oxidation of cyclopentanone with H_2O_2 catalyzed by Sn-beta zeolite model.