# Electronic Supplementary Information (ESI)

## Mild C–H Functionalization of Alkanes Catalyzed by Bioinspired Copper(II) Cores

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†Electronic Supplementary Information (ESI) contains: detailed description of catalytic experiments, additional structural representations (Figs. S1−S3) and catalysis data (Figs. S4 and S5), H-bonding details (Table S1) and bonding parameters (Tables S2−S4) for **1**−**3**; gas chromatograms (Figs. S6−S52), crystallographic data in CIF format (CCDC 1936224-1936226).

**Experimental details for catalytic oxidation reactions.** The oxidation reactions of alkanes were performed in air atmosphere in thermostated glass reactors equipped with a condenser under vigorous stirring at 50 °C and using MeCN as solvent (up to 2.5 or 5 mL total volume). In a typical experiment, catalyst (10 μmol) and gas chromatography (GC) internal standard ($MeNO_2$, 50 μL) were introduced into MeCN solution, followed by the addition of an acid promoter (typically 0.1 mmol, optional) used as a stock solution in MeCN. An alkane substrate (typically 2 mmol) was then introduced, and the reaction started upon addition of hydrogen peroxide (50% in $H_2O$, 10 mmol) in one portion. The oxidation reactions were monitored by withdrawing small aliquots after different periods of time, which were usually treated with $PPh_3$ (following the Shul'pin's method[3,26]) for the reduction of remaining $H_2O_2$ and alkyl hydroperoxides that are typically formed as primary products in alkane oxidations. The samples were analyzed by GC using nitromethane as an internal standard. Some samples were analyzed twice by GC before and after the reduction with $PPh_3$ in order to confirm the formation of alkyl hydroperoxides. Attribution of peaks was made by comparison with chromatograms of authentic samples. Blank tests confirmed that alkane oxidations do not proceed in the absence of copper catalyst.

**Experimental details for catalytic carboxylation reactions.** In a typical experiment, the reaction mixtures were prepared as follows: to 0.01 mmol of the Cu catalyst contained in a 20.0 mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar, were added 1.50 mmol of $K_2S_2O_8$, 2.0 mL of $H_2O$, 4.0 mL of MeCN (total solvent volume was 6.0 mL), and 1.00 mmol of alkane. Then the autoclave was closed and flushed with CO three times to remove the air, and finally pressurized with 20 atm of CO. *CAUTION: Due to the toxicity of CO, all operations should be carried out in a well-ventilated hood!* The reaction mixture was typically stirred for 4 h at 60 °C using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened and transferred to a flask. Diethyl ether (9.0 mL) and 45 μL of cycloheptanone (typical GC internal standard) were added. In the case of cycloheptane hydrocarboxylation, cyclohexanone (45 μL) was used as a GC standard. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analyzed by gas chromatography (internal standard method), revealing the formation of the corresponding monocarboxylic acids as major products Attribution of peaks was made by comparison with chromatograms of authentic samples. In the reactions with cycloalkane substrates, cyclic ketones and alcohols were also formed as by-products of partial alkane oxidation, whereas in the transformations of linear alkanes the generation of the corresponding oxygenates was negligible (their overall yields did not exceed 1.0%).

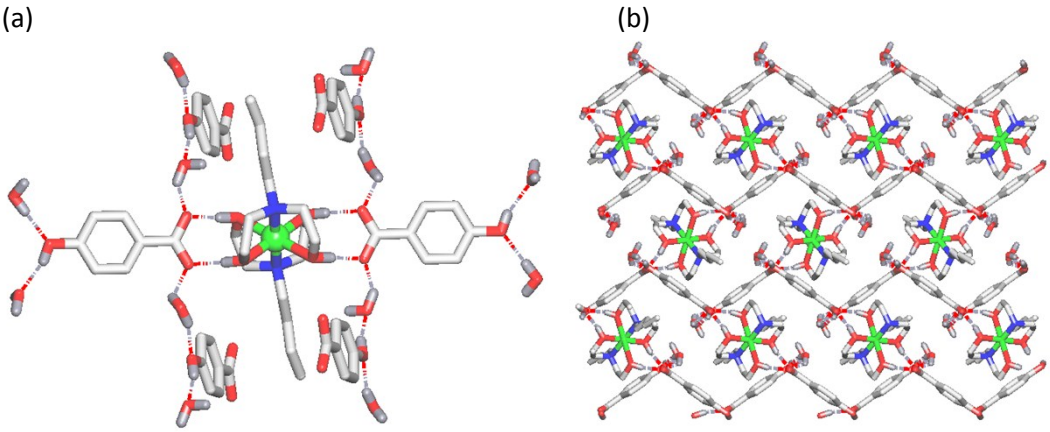


**Fig. S1.** Structural fragments of **1**. (a) H-bonding pattern between the $[Cu(H_{1.5}bdea)_2]^+$ cations, $hba^-$·anions, and crystallization water molecules arranged into $(H_2O)_2$ dimers. (b) 3D H-bonded framework (view along the *a* axis). CH hydrogen atoms are omitted; H bonds are shown as dotted lines. Colors: Cu, green balls; N, blue; O, red; C, gray; H, dark gray.

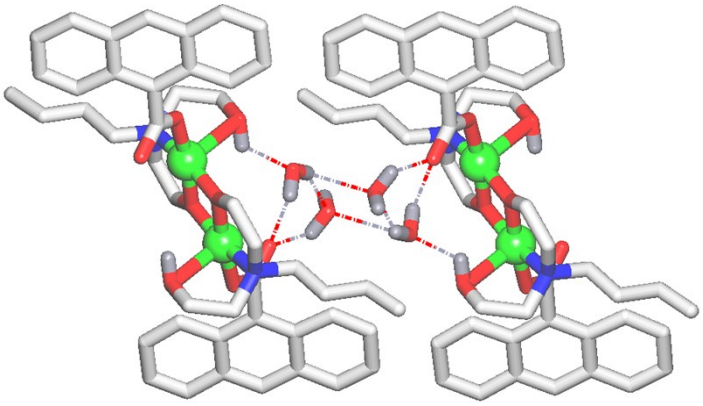

**Fig. S2.** H-bonding pattern in **2** showing the interlinkage of two $[Cu_2(\mu\text{-}Hbdea)_2(aca)_2]$ molecular units with cyclic $(H_2O)_4$ clusters. CH hydrogen atoms are omitted; H bonds are shown as dotted lines. Colors: Cu, green balls; N, blue; O, red; C, gray; H, dark gray.

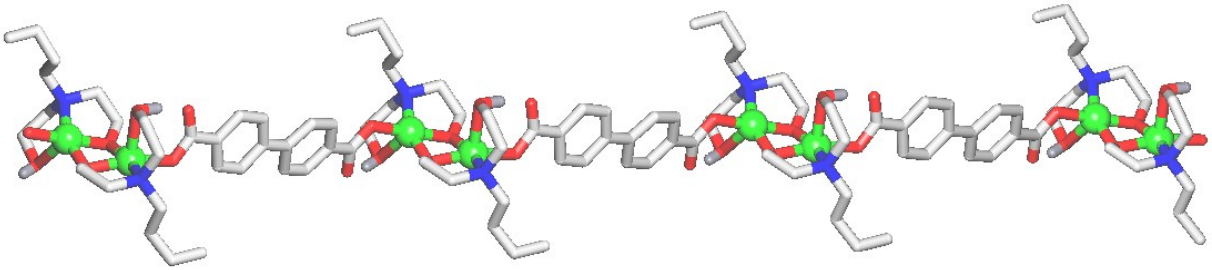

**Fig. S3.** 1D coordination polymer structure of **3**. CH hydrogen atoms are omitted. Colors: Cu, green balls; N, blue; O, red; C, gray; H, dark gray.

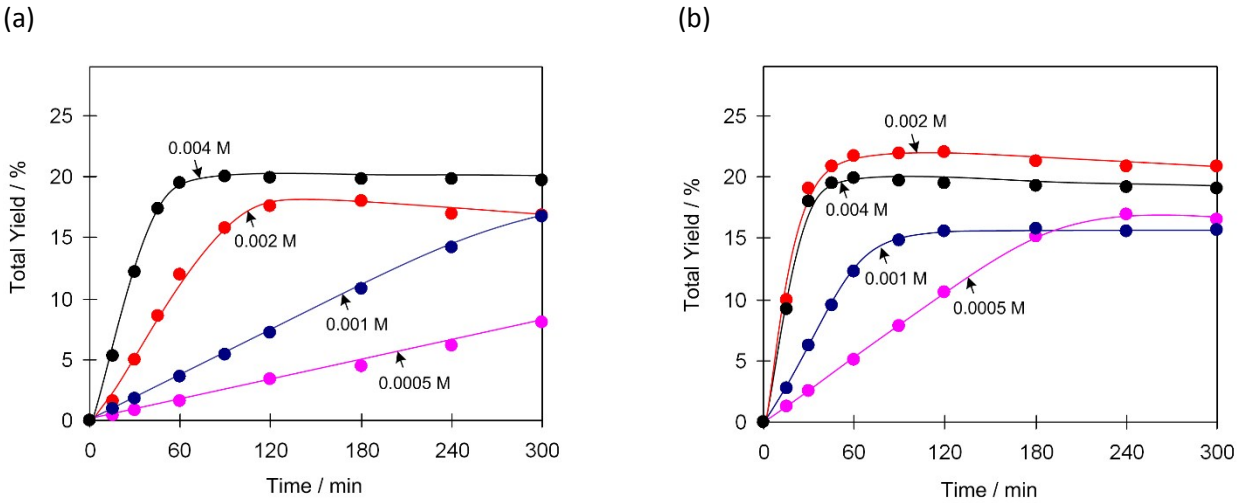


**Fig. S4.** Effect of catalyst amount on the total product yield in the cyclohexane oxidation with $H_2O_2$ catalyzed by **1** (a) and **2** (b). Reaction conditions: catalyst (0.0025–0.02 mmol), TFA (0.1 mmol), $C_6H_{12}$ (2.0 mmol), $H_2O_2$ (10.0 mmol; 50% in $H_2O$), $CH_3CN$ (up to 5.0 mL total volume), 50 °C.

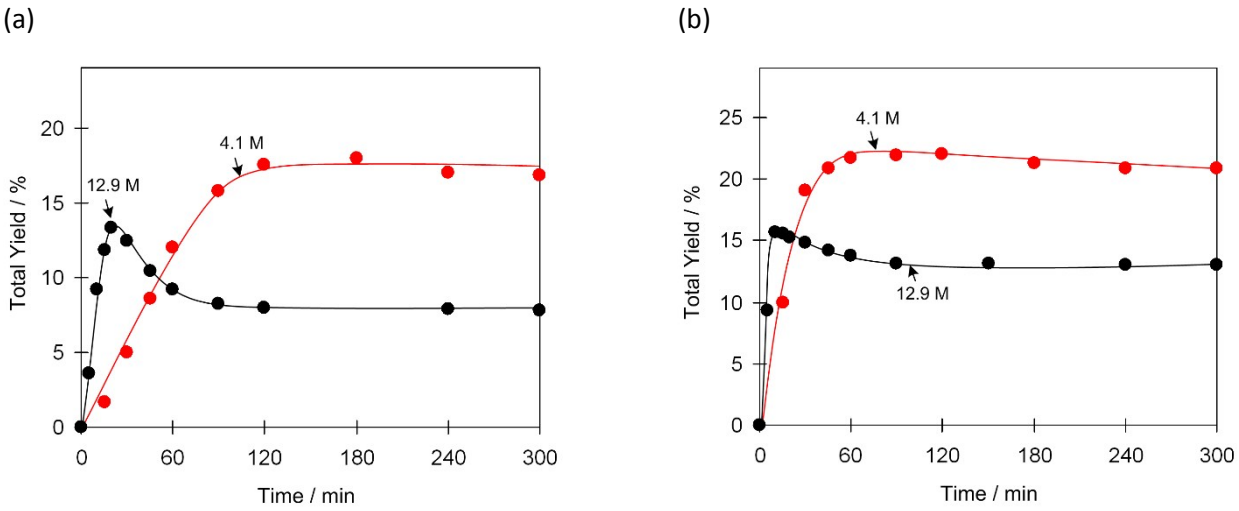


**Fig. S5.** Effect of total $H_2O$ amount in the system (4.1 M and 12.9 M) on the total product yield in the cyclohexane oxidation with $H_2O_2$ catalyzed by **2** (a) and **1** (b). Reaction conditions: catalyst (0.01 mmol), TFA (0.10 mmol), $C_6H_{12}$ (2.0 mmol), $H_2O_2$ (10.0 mmol; 50% in $H_2O$), added $H_2O$ (up to 0.8 mL), $CH_3CN$ (up to 5.0 mL total volume), 50 °C.

**Table S1**. Hydrogen bonding details for compounds **1**–**3**.

| | Sym. Op. | D–H···A | *d* (D–H) (Å) | *d* (H···A) (Å) | *d* (D···A) (Å) | D$\widehat{H}$A (°) |
|---|---|---|---|---|---|---|
| **1** | x, y, z | $O_{1w}$–$H_{1w}$···$O_3$ | 0.86 | 1.89 | 2.722(7) | 163 |
| | -½+x, ½-y, -½+z | $O_{1w}$–$H_{2w}$···$O_1$ | 0.86 | 2.11 | 2.774(7) | 133 |
| | x, y, z | $O_3$–$H_{3O}$···$O_{2w}$ | 0.82 | 1.89 | 2.676(7) | 160 |
| | -½+x, ½-y, ½+z | $O_{2w}$–$H_{3w}$···$O_2$ | 0.86 | 2.24 | 2.734(7) | 116 |
| | x, y, z | $O_4$–$H_{4O}$···$O_2$ | 0.89(3) | 1.77(2) | 2.649(4) | 168(5) |
| | -x, 1-y, -z | $O_{2w}$–$H_{4w}$···$O_{1w}$ | 0.87 | 2.38 | 2.741(9) | 106 |
| | 2-x, -y, -z | $O_5$–$H_{5O}$···$O_1$ | 0.91(4) | 1.71(5) | 2.606(5) | 170(5) |
| **2** | x, y, z | $O_{1w}$–$H_{1w}$···$O_2$ | 0.86 | 2.28 | 2.774(8) | 117 |
| | 2-x, -y, 2-z | $O_{2w}$–$H_{3w}$···$O_2$ | 0.87 | 2.23 | 2.775(9) | 120 |
| | 1+x, y, 1+z | $O_{2w}$–$H_{4w}$···$O_{1w}$ | 0.86 | 2.47 | 2.766(11) | 101 |
| | 2-x, -y, 2-z | $O_{2w}$–$H_{4w}$···$O_{1w}$ | 0.86 | 2.41 | 3.192(11) | 152 |
| **3** | x, y, z | $O_3$–$H_{3O}$···$O_1$ | 0.90(3) | 1.75(4) | 2.611(7) | 158(7) |
| | x, y, z z | $O_6$–$H_{6O}$···$O_8$ | 0.82 | 1.85 | 2.615(6) | 154 |

**Table S2**. Bond lengths [Å] for compound **1**.

| | |
|---|---|
| Cu(1)-O(5) | 2.037(3) |
| Cu(1)-O(5)#1 | 2.037(3) |
| Cu(1)-N(1) | 2.050(4) |
| Cu(1)-N(1)#1 | 2.050(4) |
| Cu(1)-O(4)#1 | 2.324(4) |
| Cu(1)-O(4) | 2.324(4) |
| O(1)-C(1) | 1.266(5) |
| O(2)-C(1) | 1.255(5) |
| N(1)-C(10) | 1.481(6) |
| N(1)-C(9) | 1.493(5) |
| N(1)-C(12) | 1.505(6) |
| O(4)-C(11) | 1.440(6) |
| O(4)-H(4O) | 0.886(19) |
| O(3)-C(5) | 1.372(5) |
| O(3)-H(3O) | 0.8200 |
| O(5)-C(8) | 1.435(6) |
| O(5)-H(5O) | 0.900(19) |
| C(8)-C(9) | 1.511(7) |
| C(8)-H(8B) | 0.9700 |
| C(8)-H(8A) | 0.9700 |
| C(9)-H(9B) | 0.9700 |
| C(9)-H(9A) | 0.9700 |
| C(12)-C(13) | 1.528(7) |
| C(12)-H(12B) | 0.9700 |
| C(12)-H(12A) | 0.9700 |
| C(13)-C(14) | 1.521(7) |
| C(13)-H(13A) | 0.9700 |
| C(13)-H(13B) | 0.9700 |
| C(14)-C(15) | 1.524(9) |
| C(14)-H(14B) | 0.9700 |
| C(14)-H(14A) | 0.9700 |

| | |
|---|---|
| C(15)-H(15C) | 0.9600 |
| C(15)-H(15A) | 0.9600 |
| C(15)-H(15B) | 0.9600 |
| C(10)-C(11) | 1.508(7) |
| C(10)-H(10B) | 0.9700 |
| C(10)-H(10A) | 0.9700 |
| C(11)-H(11B) | 0.9700 |
| C(11)-H(11A) | 0.9700 |
| C(5)-C(4) | 1.376(7) |
| C(5)-C(6) | 1.391(6) |
| C(6)-C(7) | 1.382(6) |
| C(6)-H(6) | 0.9300 |
| C(7)-C(2) | 1.391(6) |
| C(7)-H(7) | 0.9300 |
| C(2)-C(3) | 1.402(6) |
| C(2)-C(1) | 1.505(6) |
| C(4)-C(3) | 1.384(7) |
| C(4)-H(4) | 0.9300 |
| C(3)-H(3) | 0.9300 |
| O(1W)-H(1W) | 0.859(6) |
| O(1W)-H(2W) | 0.863(6) |
| O(2W)-H(3W) | 0.861(5) |
| O(2W)-H(4W) | 0.869(7) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z

**Table S3.** Bond lengths [Å] for compound **2**.

| | |
|---|---|
| Cu(1)-O(4) | 1.917(7) |
| Cu(1)-O(4)#1 | 1.921(6) |
| Cu(1)-O(1) | 1.940(5) |
| Cu(1)-N(1) | 2.031(7) |
| Cu(1)-O(3) | 2.303(9) |
| Cu(1)-Cu(1)#1 | 2.922(2) |
| O(2)-C(1) | 1.252(8) |
| C(10)-C(9) | 1.387(11) |
| C(10)-C(11) | 1.416(10) |
| C(10)-C(15) | 1.440(8) |
| C(3)-C(2) | 1.404(11) |
| C(3)-C(4) | 1.433(10) |
| C(3)-C(8) | 1.444(9) |
| C(15)-C(2) | 1.402(10) |
| C(15)-C(14) | 1.422(10) |
| N(1)-C(17) | 1.466(9) |
| N(1)-C(20) | 1.473(13) |
| N(1)-C(18) | 1.491(8) |
| N(1)-C(20A) | 1.637(19) |
| C(9)-C(8) | 1.394(11) |
| C(9)-H(9) | 0.9500 |
| C(2)-C(1) | 1.509(9) |
| O(3)-C(16) | 1.419(10) |
| O(3)-H(3O) | 0.86(2) |
| O(1)-C(1) | 1.264(8) |
| C(14)-C(13) | 1.364(10) |
| C(14)-H(14) | 0.9500 |

| | |
|---|---|
| C(11)-C(12) | 1.341(12) |
| C(11)-H(11) | 0.9500 |
| C(13)-C(12) | 1.436(10) |
| C(13)-H(13) | 0.9500 |
| C(8)-C(7) | 1.409(11) |
| C(12)-H(12) | 0.9500 |
| C(18)-C(19) | 1.459(13) |
| C(18)-H(18A) | 0.9900 |
| C(18)-H(18B) | 0.9900 |
| C(4)-C(5) | 1.348(11) |
| C(4)-H(4) | 0.9500 |
| C(17)-C(16) | 1.473(11) |
| C(17)-H(17A) | 0.9900 |
| C(17)-H(17B) | 0.9900 |
| C(7)-C(6) | 1.365(12) |
| C(7)-H(7) | 0.9500 |
| C(6)-C(5) | 1.434(12) |
| C(6)-H(6) | 0.9500 |
| O(4)-C(19)#1 | 1.249(10) |
| O(4)-Cu(1)#1 | 1.921(6) |
| C(5)-H(5) | 0.9500 |
| C(19)-O(4)#1 | 1.249(10) |
| C(19)-H(19A) | 0.9900 |
| C(19)-H(19B) | 0.9900 |
| C(16)-H(14A) | 0.9900 |
| C(16)-H(16B) | 0.9900 |
| O(1W)-H(1W) | 0.862(6) |
| O(1W)-H(2W) | 0.859(6) |
| C(23)-C(22) | 1.413(14) |
| C(23)-C(22A) | 1.69(2) |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| O(2W)-H(3W) | 0.868(10) |
| O(2W)-H(4W) | 0.856(8) |
| C(20)-C(21) | 1.481(15) |
| C(20)-H(20A) | 0.9900 |
| C(20)-H(20B) | 0.9900 |
| C(21)-C(22) | 1.514(15) |
| C(21)-H(21A) | 0.9900 |
| C(21)-H(21B) | 0.9900 |
| C(22)-H(22A) | 0.9900 |
| C(22)-H(22B) | 0.9900 |
| C(20A)-C(21A) | 1.53(3) |
| C(20A)-H(20C) | 0.9900 |
| C(20A)-H(20D) | 0.9900 |
| C(21A)-C(22A) | 1.59(3) |
| C(21A)-H(21C) | 0.9900 |
| C(21A)-H(21D) | 0.9900 |
| C(22A)-H(22C) | 0.9900 |
| C(22A)-H(22D) | 0.9900 |

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+2

**Table S4.** Bond lengths [Å] for compound **3**.

| | |
|---|---|
| C(1)-O(1) | 1.239(7) |
| C(1)-O(2) | 1.278(7) |
| C(1)-C(2) | 1.481(7) |
| C(2)-C(7) | 1.371(7) |
| C(2)-C(3) | 1.378(8) |
| C(3)-C(4) | 1.389(8) |
| C(7)-C(6) | 1.391(7) |
| C(13)-C(14) | 1.467(10) |
| C(13)-C(12) | 1.508(9) |
| C(14)-C(15) | 1.412(11) |
| C(19)-O(6) | 1.428(7) |
| C(19)-C(18) | 1.460(9) |
| C(22)-C(23) | 1.296(11) |
| C(22)-C(21) | 1.482(11) |
| C(4)-C(5) | 1.397(8) |
| C(5)-C(6) | 1.383(8) |
| C(5)-C(28)#1 | 1.482(7) |
| C(8)-O(3) | 1.420(8) |
| C(8)-C(9) | 1.496(9) |
| C(9)-N(1) | 1.495(8) |
| C(10)-O(4) | 1.413(7) |
| C(10)-C(11) | 1.506(8) |
| C(11)-N(1) | 1.494(8) |
| C(12)-N(1) | 1.484(7) |
| C(16)-O(5) | 1.398(7) |
| C(16)-C(17) | 1.505(10) |
| C(17)-N(2) | 1.491(8) |
| C(18)-N(2) | 1.498(7) |
| C(20)-C(21) | 1.484(11) |
| C(20)-N(2) | 1.491(8) |
| C(24)-O(8) | 1.252(8) |
| C(24)-O(7) | 1.289(7) |
| C(24)-C(25) | 1.491(8) |
| C(25)-C(26) | 1.381(8) |
| C(25)-C(30) | 1.396(8) |
| C(26)-C(27) | 1.372(8) |
| C(27)-C(28) | 1.396(7) |
| C(28)-C(29) | 1.403(8) |
| C(28)-C(5)#2 | 1.482(7) |
| C(29)-C(30) | 1.356(7) |
| N(1)-Cu(1) | 2.048(4) |
| N(2)-Cu(2) | 2.064(5) |
| O(2)-Cu(1) | 1.922(3) |
| O(3)-Cu(1) | 2.408(5) |
| O(4)-Cu(1) | 1.916(3) |
| O(4)-Cu(2) | 1.949(3) |
| O(5)-Cu(2) | 1.910(3) |
| O(5)-Cu(1) | 1.912(4) |
| O(7)-Cu(2) | 1.925(4) |
| Cu(1)-Cu(2) | 2.8908(9) |

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z-1 #2 x,y,z+1.

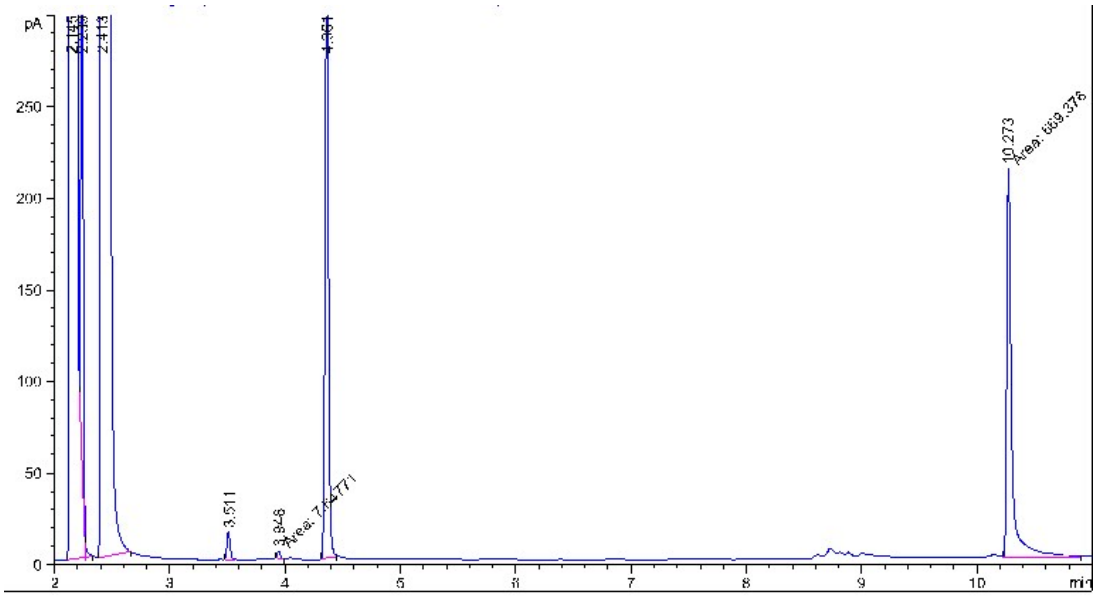


**Fig. S6.** GC plot of the reaction mixture in cyclohexane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.145 (ether), 2.413 ($CH_3CN$), 3.511 (cyclohexanone), 3.946 (cyclohexanol), 4.361 (cycloheptanone, CG standard), 10.273 (cyclohexanecarboxylic acid).

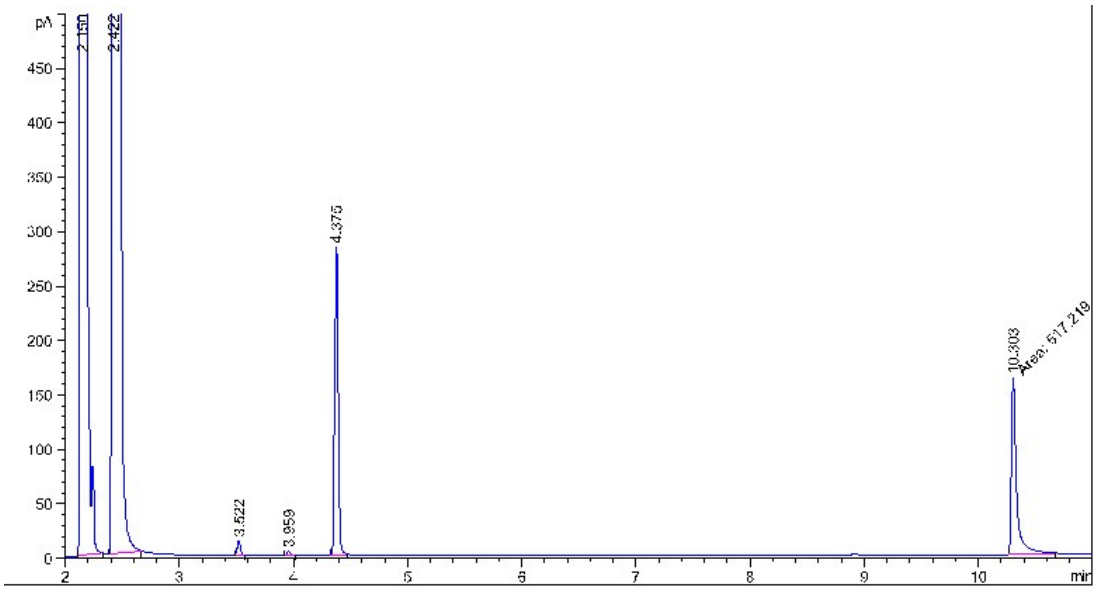


**Fig. S7.** GC plot of the reaction mixture in cyclohexane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.150 (ether), 2.422 ($CH_3CN$), 3.522 (cyclohexanone), 3.969 (cyclohexanol), 4.375 (cycloheptanone, CG standard), 10.303 (cyclohexanecarboxylic acid).

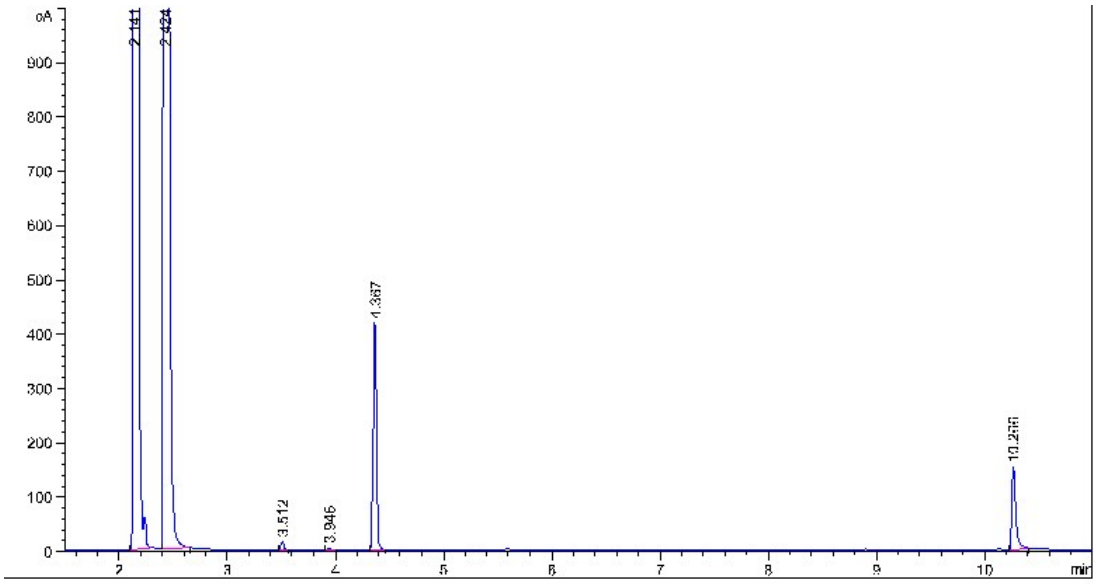


**Fig. S8.** GC plot of the reaction mixture in cyclohexane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.141 (ether), 2.424 ($CH_3CN$), 3.512 (cyclohexanone), 3.946 (cyclohexanol), 4.367 (cycloheptanone, CG standard), 10.266 (cyclohexanecarboxylic acid).

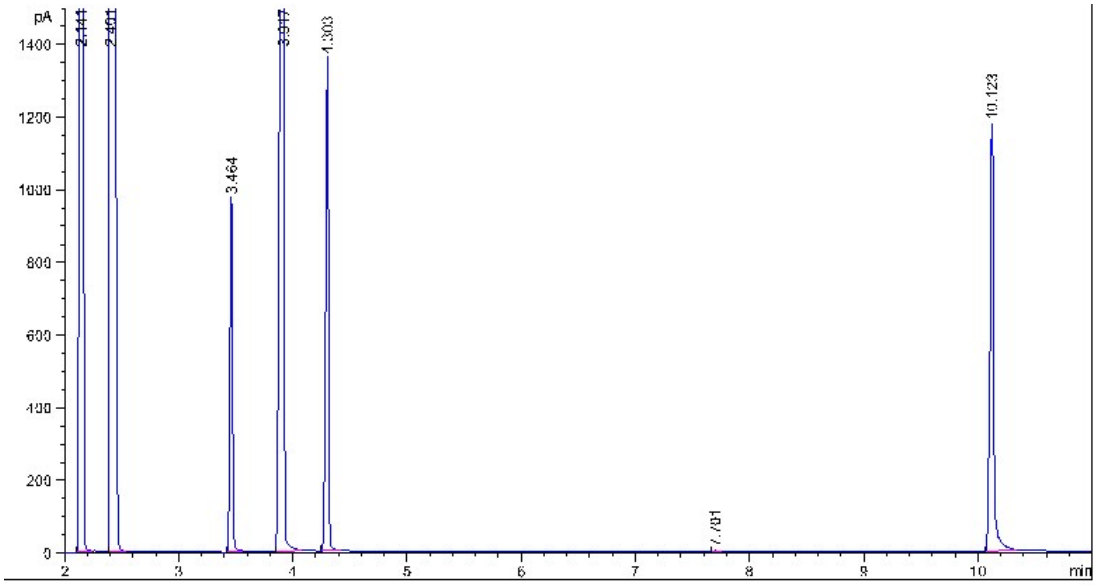


**Fig. S9.** GC plot of authentic samples of cyclohexane carboxylation products. Peak retention time, min (assignment): 2.141 (ether), 2.401 ($CH_3CN$), 3.464 (cyclohexanone), 3.917 (cyclohexanol), 4.303 (cycloheptanone, CG standard), 10.123 (cyclohexanecarboxylic acid).

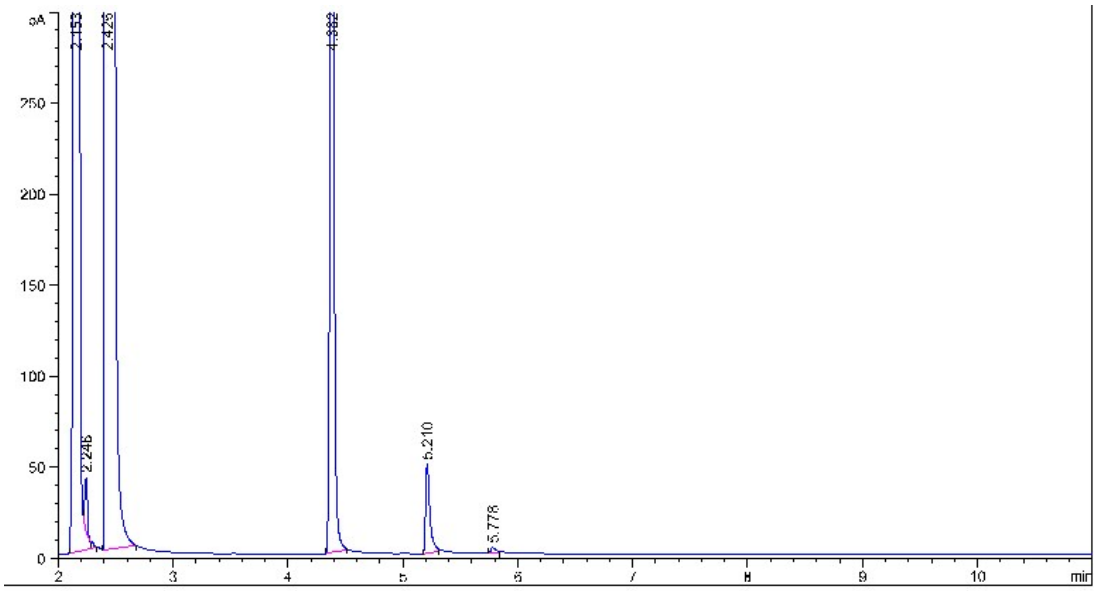


**Fig. S10.** GC plot of the reaction mixture in propane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.153 (ether), 2.426 ($CH_3CN$), 4.382 (cycloheptanone, CG standard), 5.210 (*iso*-butyric acid), 5.778 (*n*-butyric acid).

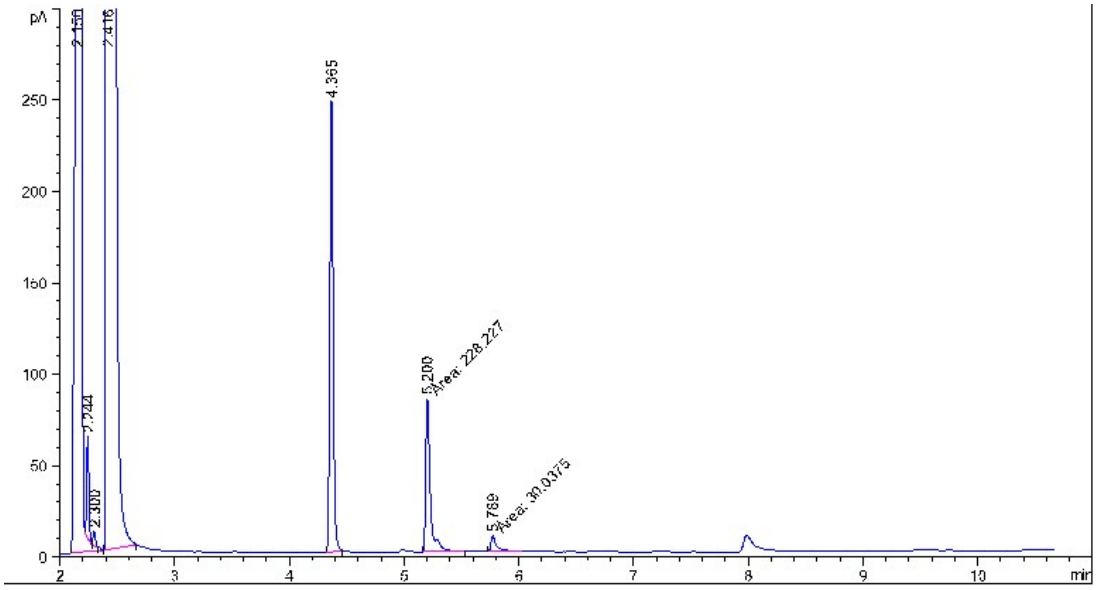


**Fig. S11.** GC plot of the reaction mixture in propane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.150 (ether), 2.416 ($CH_3CN$), 4.365 (cycloheptanone, CG standard), 5.200 (*iso*-butyric acid), 5.769 (*n*-butyric acid).

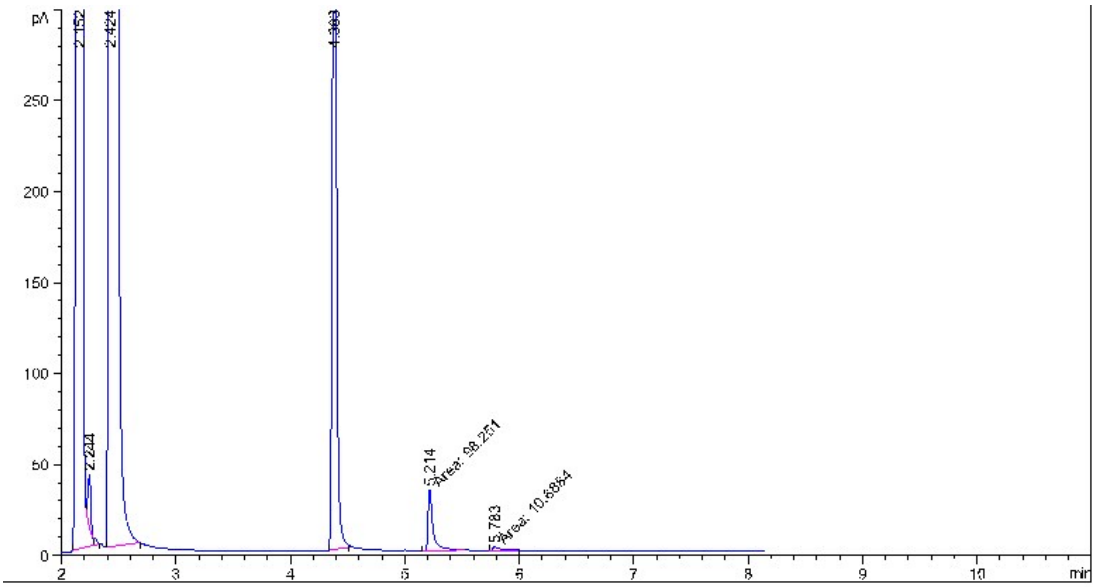


**Fig. S12.** GC plot of the reaction mixture in propane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.152 (ether), 2.424($CH_3CN$), 4.363 (cycloheptanone, CG standard), 5.214 (*iso*-butyric acid), 5.783 (*n*-butyric acid).

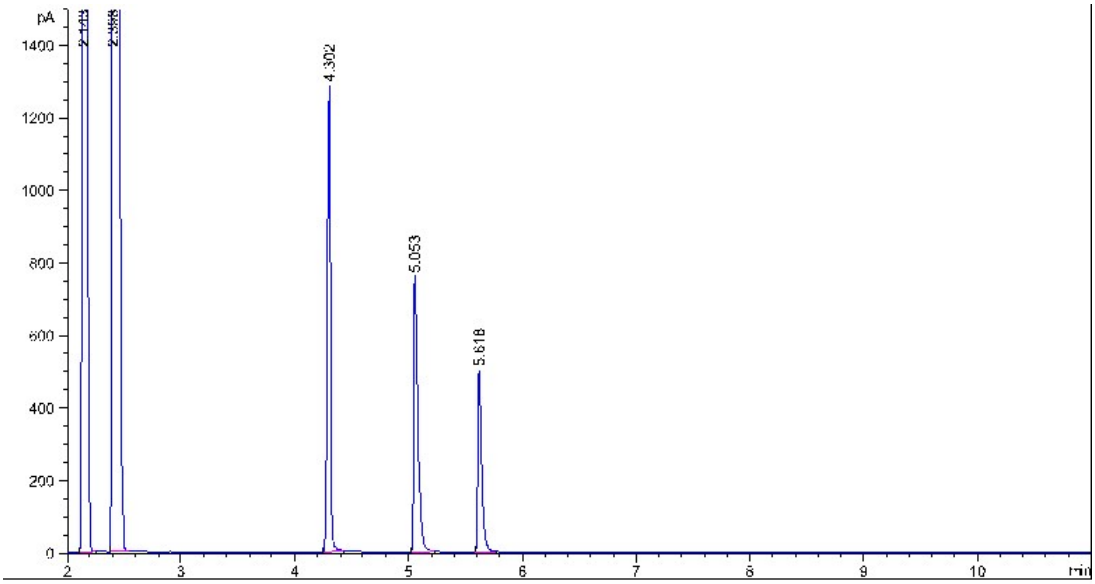


**Fig. S13.** GC plot of authentic samples of propane carboxylation products. Peak retention time, min (assignment): 2.143 (ether), 2.398 ($CH_3CN$), 4.302 (cycloheptanone, CG standard), 5.053 (*iso*-butyric acid), 5.618 (*n*-butyric acid).

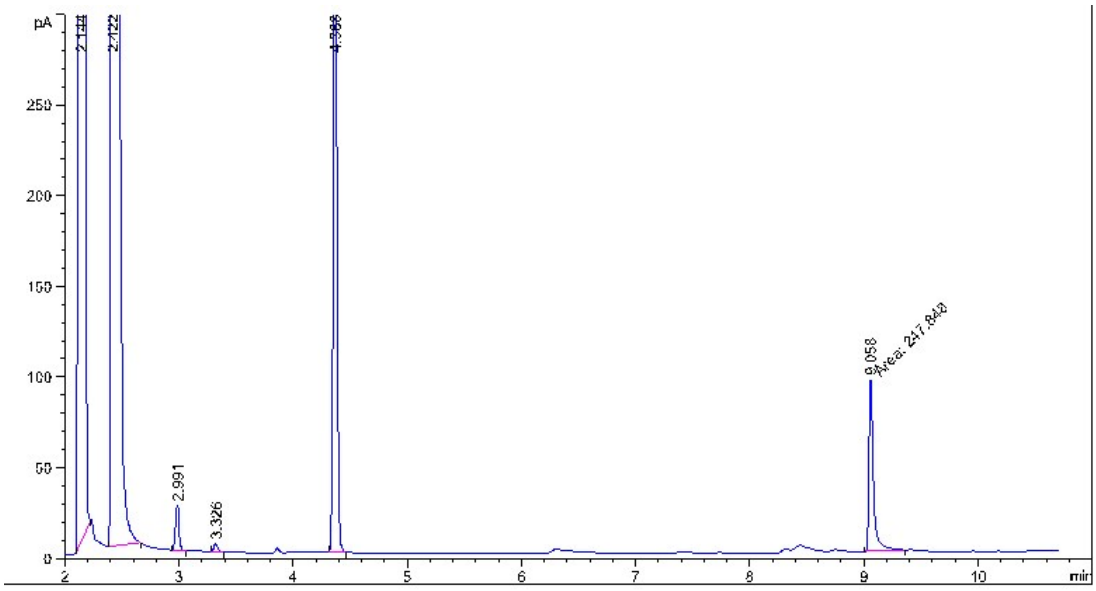


**Fig. S14.** GC plot of the reaction mixture in cyclopentane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.144 (ether), 2.422 ($CH_3CN$), 2.991 (cyclopentanone), 3.326 (cyclopentanol), 4.368 (cycloheptanone, CG standard), 9.058 (cyclopentanecarboxylic acid).

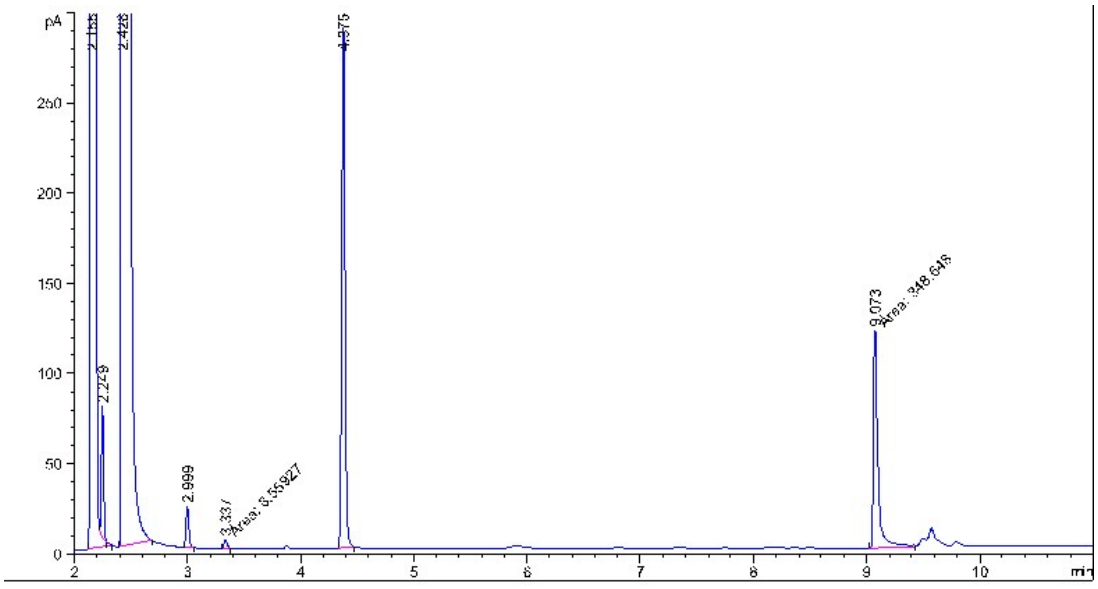


**Fig. S15.** GC plot of the reaction mixture in cyclopentane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.155 (ether), 2.426 ($CH_3CN$), 2.999 (cyclopentanone), 3.337 (cyclopentanol), 4.375 (cycloheptanone, CG standard), 9.073 (cyclopentanecarboxylic acid).

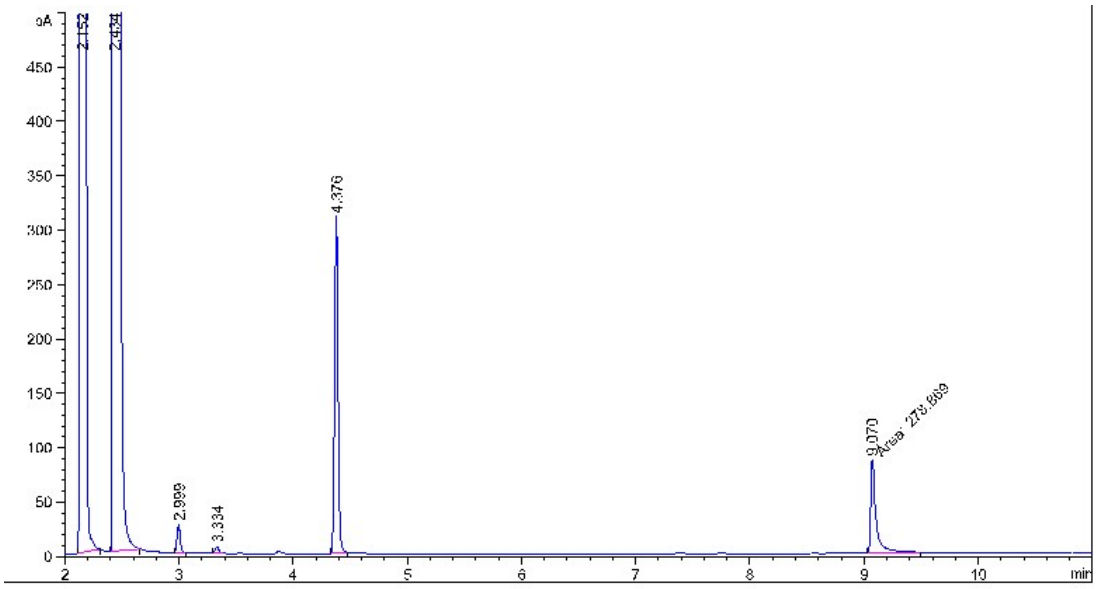


**Fig. S16.** GC plot of the reaction mixture in cyclopentane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.152 (ether), 2.434 ($CH_3CN$), 2.999 (cyclopentanone), 3.334 (cyclopentanol), 4.374 (cycloheptanone, CG standard), 9.070 (cyclopentanecarboxylic acid).

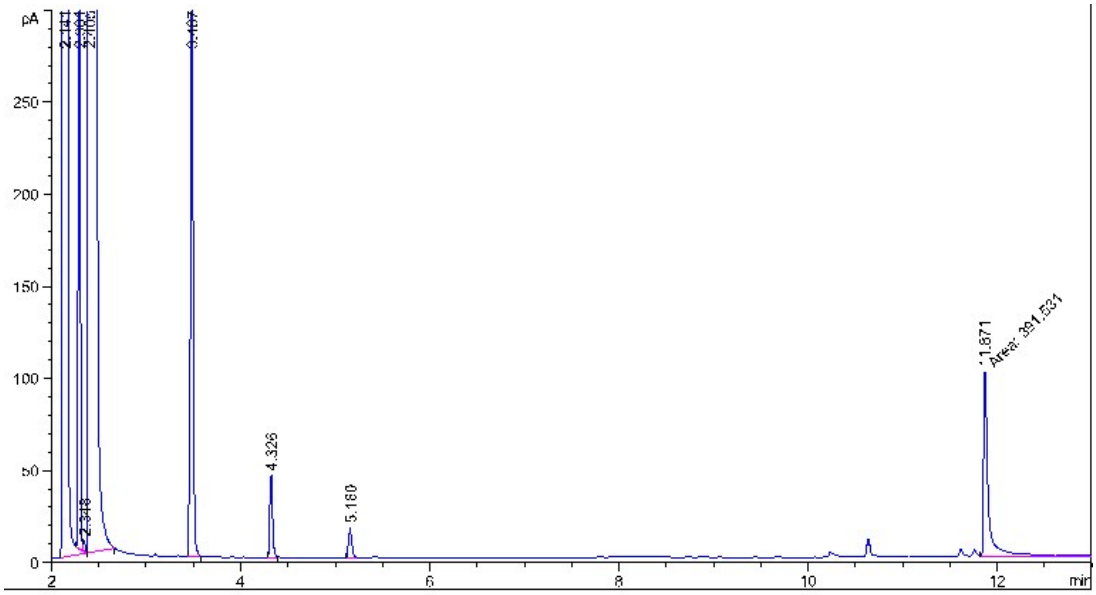


**Fig. S17.** GC plot of the reaction mixture in cycloheptane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.141 (ether), 2.405 ($CH_3CN$), 3.487 (cyclohexanone, CG standard), 4.326 (cycloheptanone), 5.160 (cycloheptanol), 11.871 (cycloheptanecarboxylic acid).

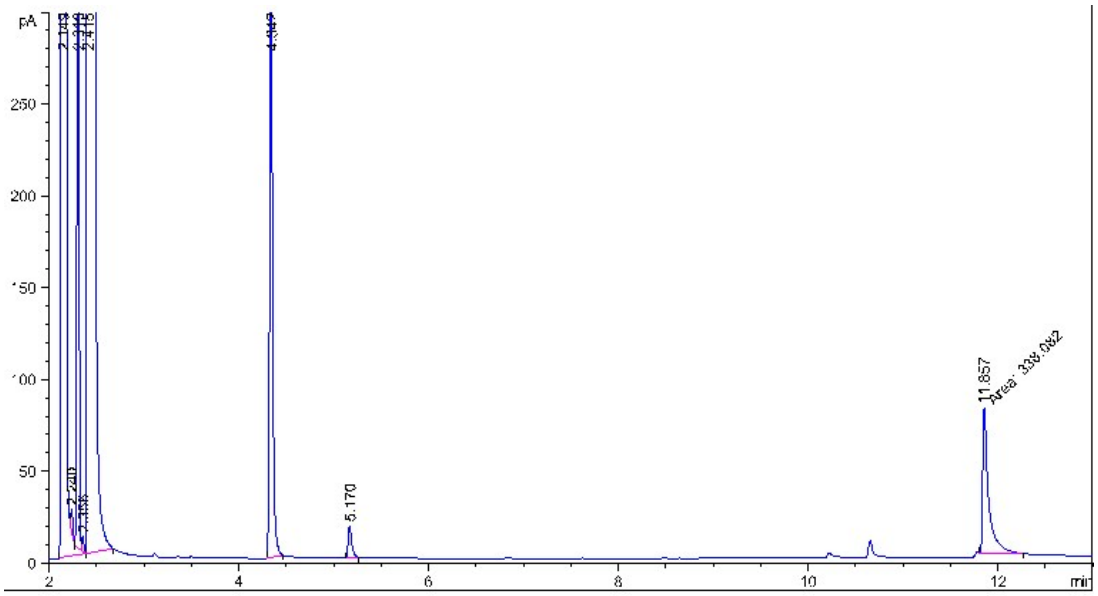


**Fig. S18.** GC plot of the reaction mixture in cycloheptane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.149 (ether), 2.415 ($CH_3CN$), 4.342 (cycloheptanone, product and GC standart), 5.170 (cycloheptanol), 11.857 (cycloheptanecarboxylic acid).

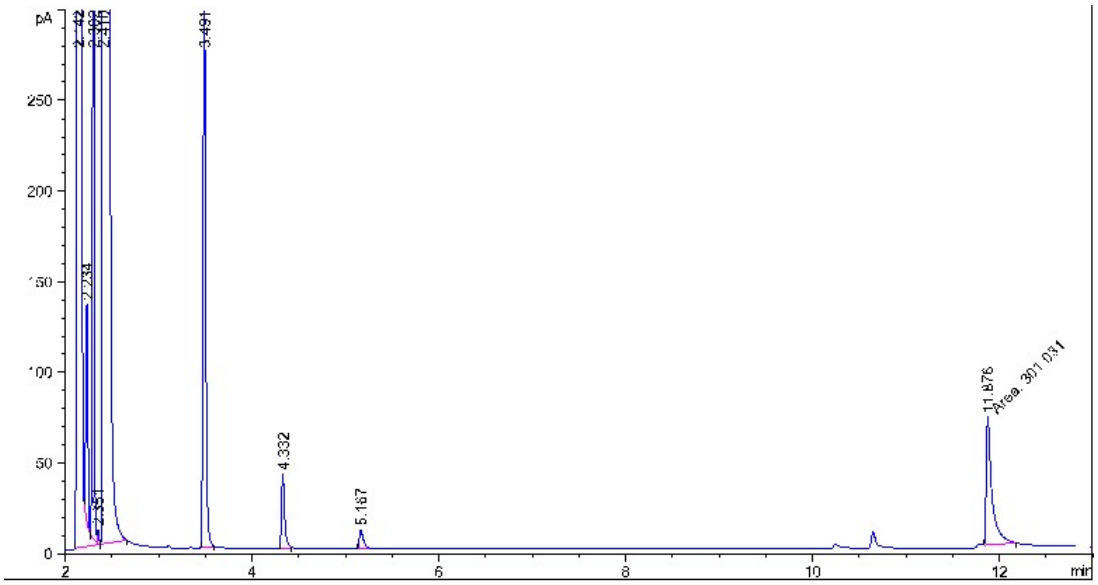


**Fig. S19.** GC plot of the reaction mixture in cycloheptane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.142 (ether), 2.410 ($CH_3CN$), 3.491 (cyclohexanone, CG standard), 4.332 (cycloheptanone), 5.167 (cycloheptanol), 11.876 (cycloheptanecarboxylic acid).

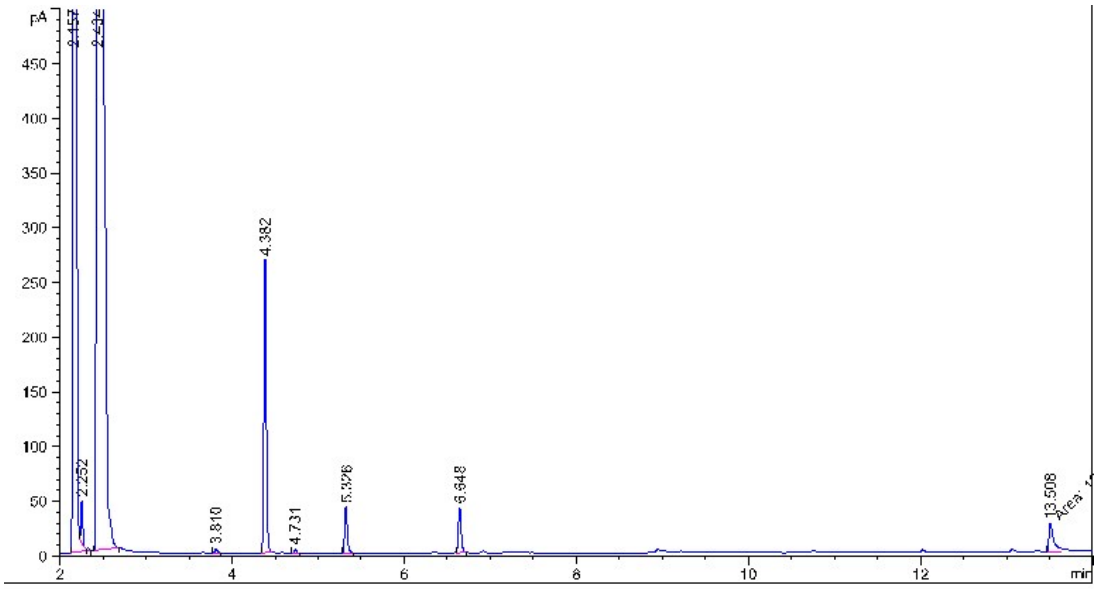


**Fig. S20.** GC plot of the reaction mixture in cyclooctane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.157 (ether), 2.434 ($CH_3CN$), 4.382 (cycloheptanone, CG standard), 5.326 (cyclooctanone), 6.648 (cyclooctanol), 13.508 (cyclooctanecarboxylic acid).

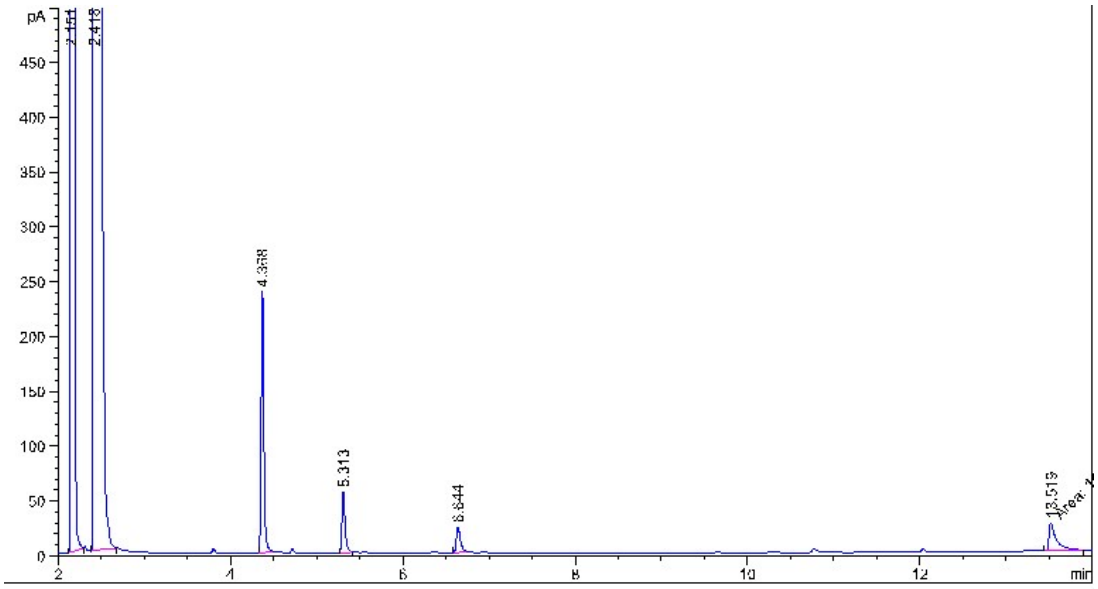


**Fig. S21.** GC plot of the reaction mixture in cyclooctane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.151 (ether), 2.418 ($CH_3CN$), 4.368 (cycloheptanone, CG standard), 5.313 (cyclooctanone), 6.664 (cyclooctanol), 13.519 (cyclooctanecarboxylic acid).

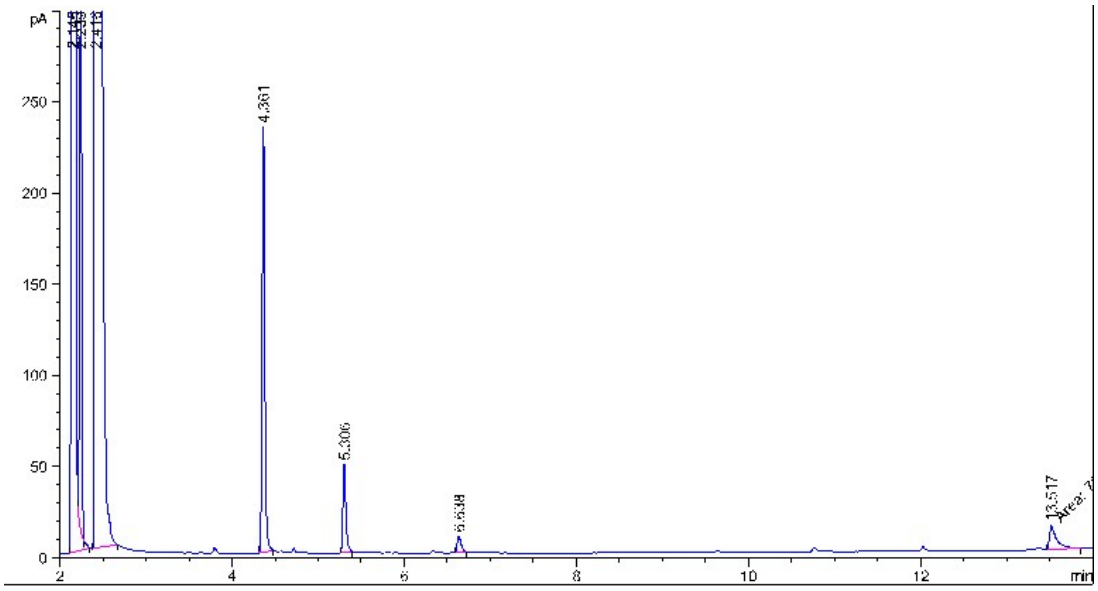


**Fig. S22.** GC plot of the reaction mixture in cyclooctane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.146 (ether), 2.416 ($CH_3CN$), 4.361 (cycloheptanone, CG standard), 5.306 (cyclooctanone), 6.638 (cyclooctanol), 13.517 (cyclooctanecarboxylic acid).

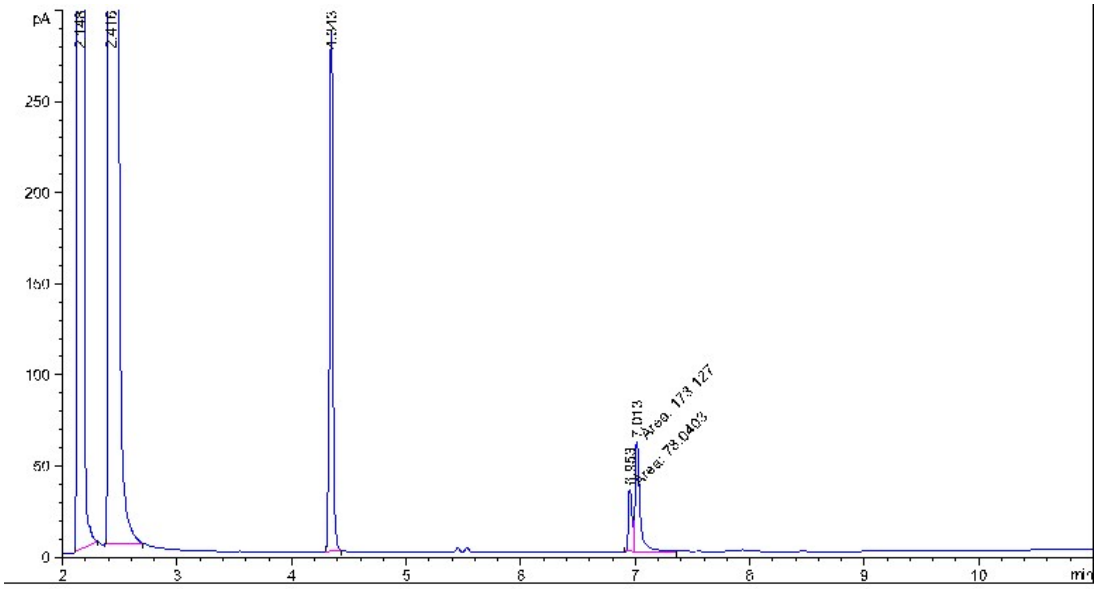


**Fig. S23.** GC plot of the reaction mixture in *n*-pentane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.148 (ether), 2.416 ($CH_3CN$), 4.343 (cycloheptanone, CG standard), 6.953 ($C_2H_5CH(COOH)C_2H_5$), 7.013 ($C_3H_7CH(COOH)CH_3$).

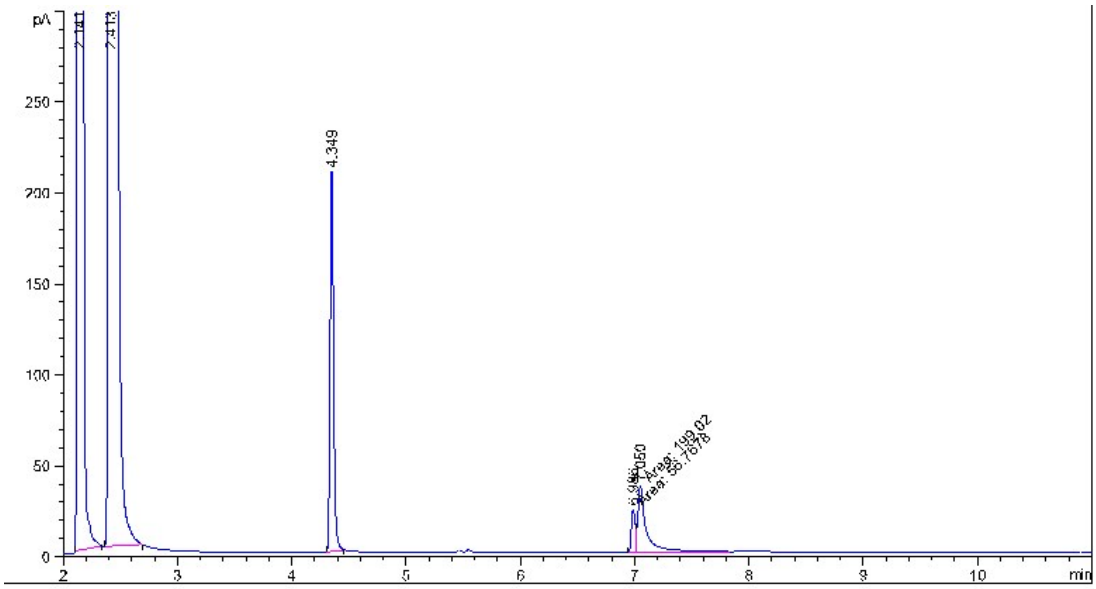


**Fig. S24.** GC plot of the reaction mixture in *n*-pentane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.141 (ether), 2.413 ($CH_3CN$), 4.349 (cycloheptanone, CG standard), 6.986 ($C_2H_5CH(COOH)C_2H_5$), 7.050 ($C_3H_7CH(COOH)CH_3$).

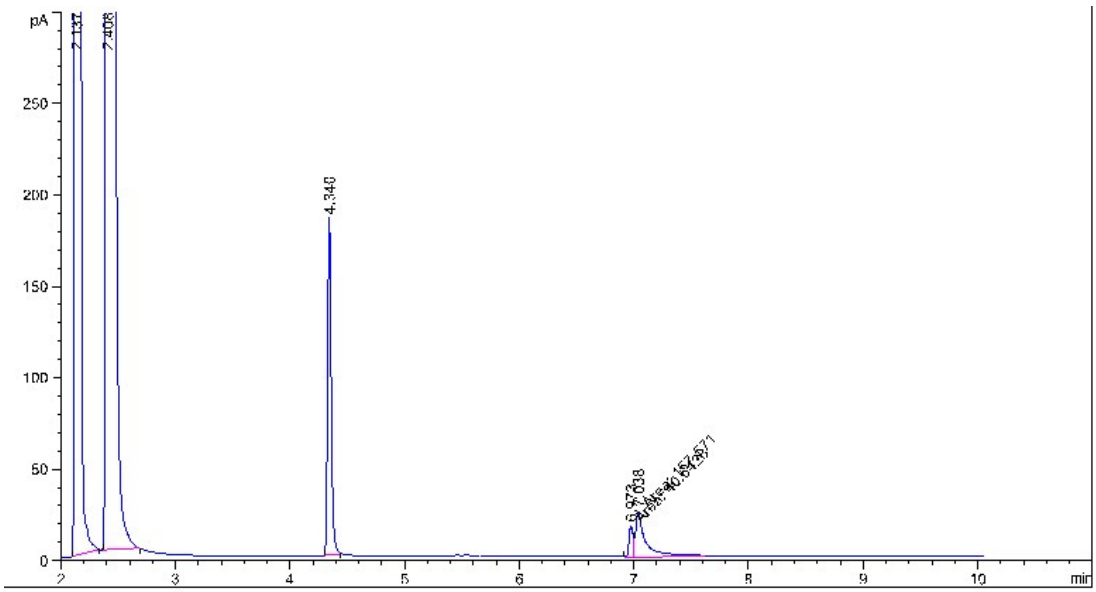


**Fig. S25.** GC plot of the reaction mixture in *n*-pentane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.137 (ether), 2.408 ($CH_3CN$), 4.340 (cycloheptanone, CG standard), 6.973 ($C_2H_5CH(COOH)C_2H_5$), 7.038 ($C_3H_7CH(COOH)CH_3$).

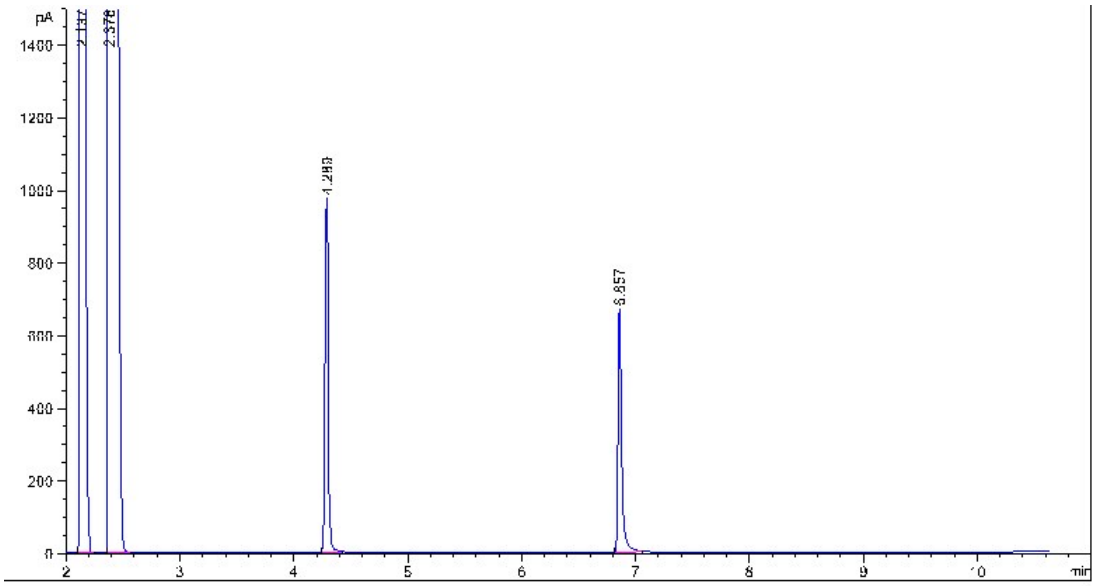


**Fig. S26.** GC plot of authentic sample of 2-Ethyl-Butyric acid ($C_2H_5CH(COOH)C_2H_5$). Peak retention time, min (assignment): 2.137 (ether), 2.378 ($CH_3CN$), 4.289 (cycloheptanone, CG standard), 6.857 ($C_2H_5CH(COOH)C_2H_5$).

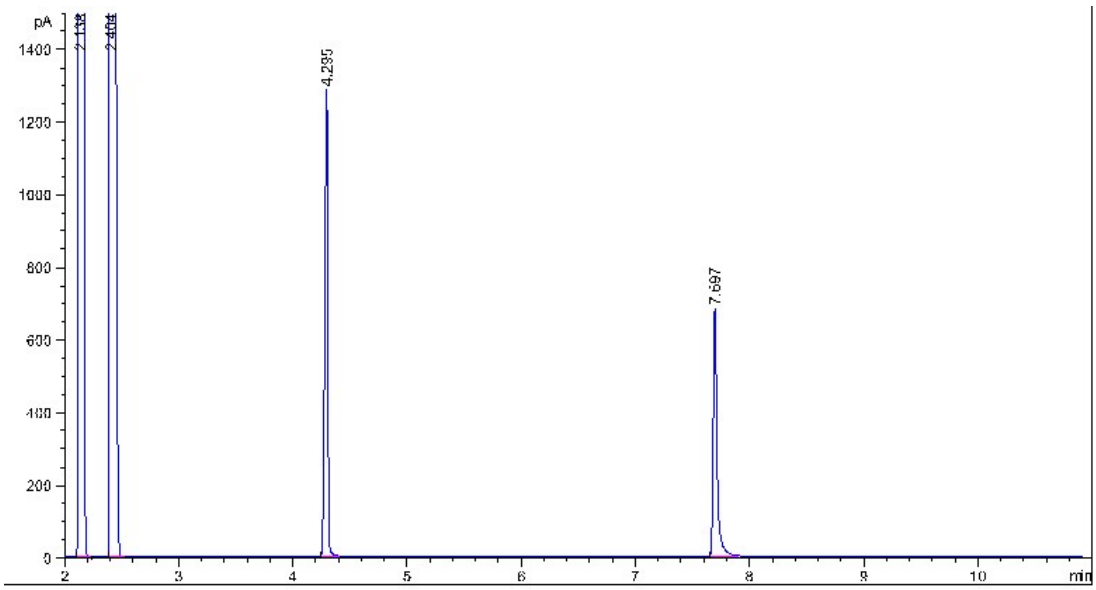


**Fig. S27.** GC plot of authentic sample of hexanoic acid. Peak retention time, min (assignment): 2.138 (ether), 2.404 ($CH_3CN$), 4.295 (cycloheptanone, CG standard), 7.698 (hexanoic acid).

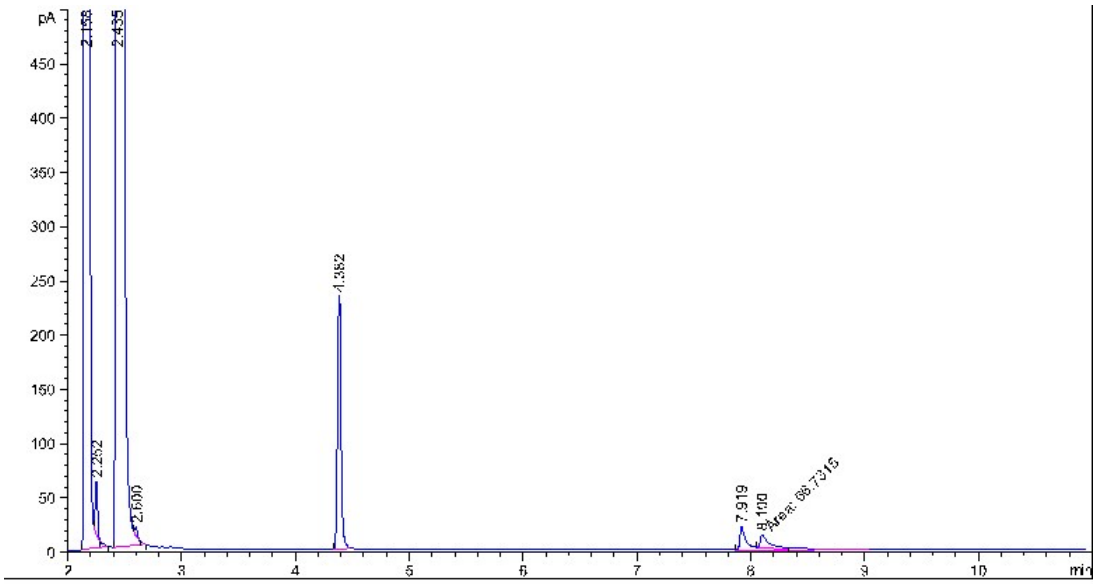


**Fig. S28.** GC plot of the reaction mixture in *n*-hexane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.158 (ether), 2.435 ($CH_3CN$), 4.382 (cycloheptanone, CG standard), 7.919 ($C_2H_5CH(COOH)C_3H_7$), 8.100 ($C_4H_9CH(COOH)CH_3$).

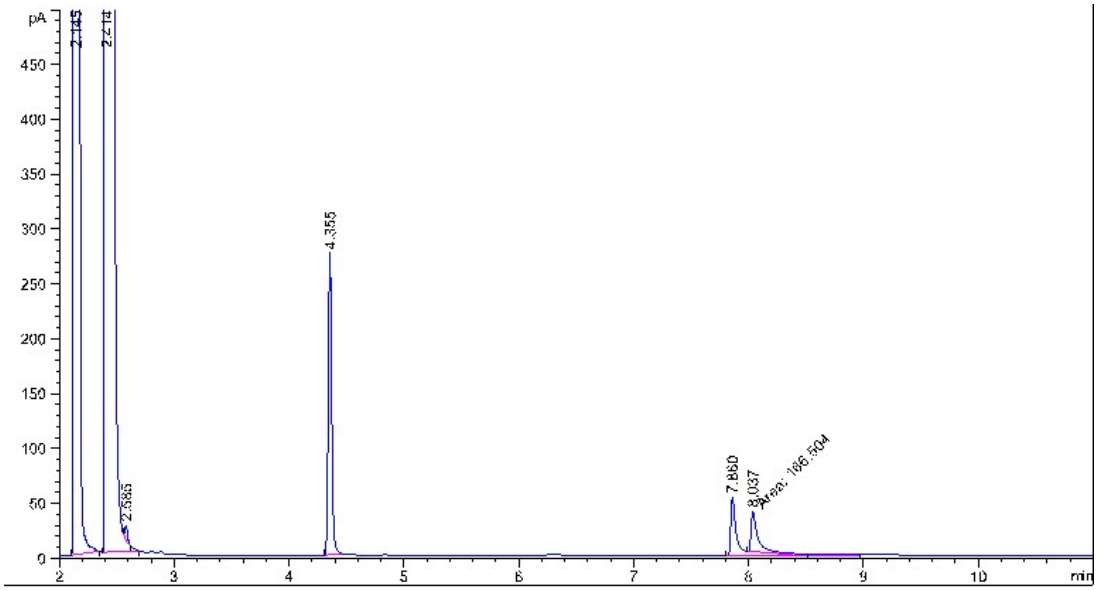


**Fig. S29.** GC plot of the reaction mixture in *n*-hexane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.145 (ether), 2.414 ($CH_3CN$), 4.355 (cycloheptanone, CG standard), 7.860 ($C_2H_5CH(COOH)C_3H_7$), 8.037 ($C_4H_9CH(COOH)CH_3$).

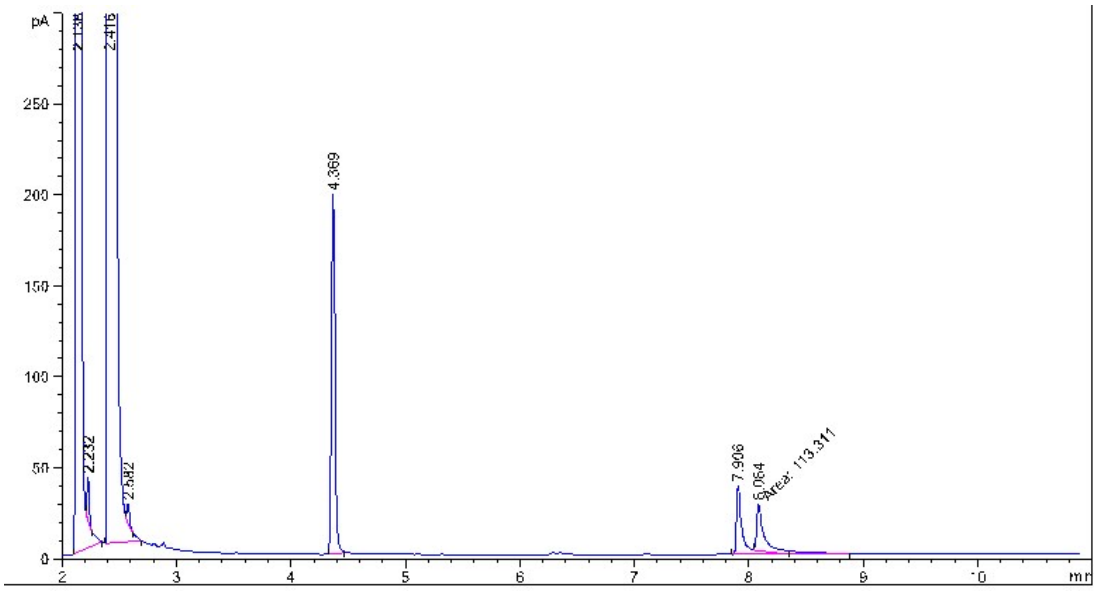


**Fig. S30.** GC plot of the reaction mixture in *n*-hexane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.138 (ether), 2.416 ($CH_3CN$), 4.369 (cycloheptanone, CG standard), 7.906 ($C_2H_5CH(COOH)C_3H_7$), 8.084 ($C_4H_9CH(COOH)CH_3$).

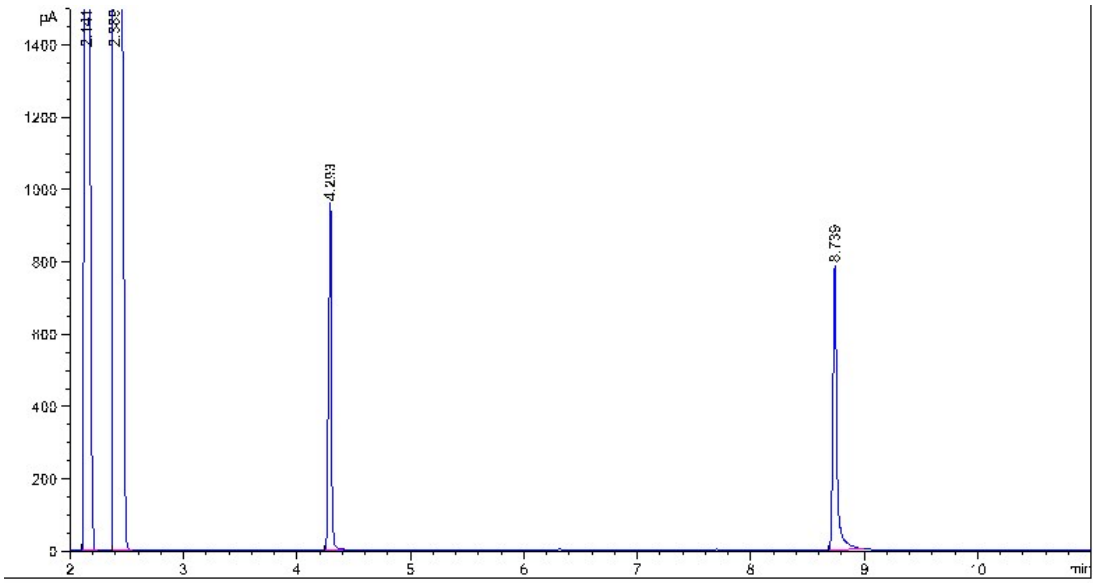


**Fig. S31.** GC plot of authentic sample of heptanoic acid. Peak retention time, min (assignment): 2.141 (ether), 2.389 ($CH_3CN$), 4.293 (cycloheptanone, CG standard), 8.739 (heptanoic acid).

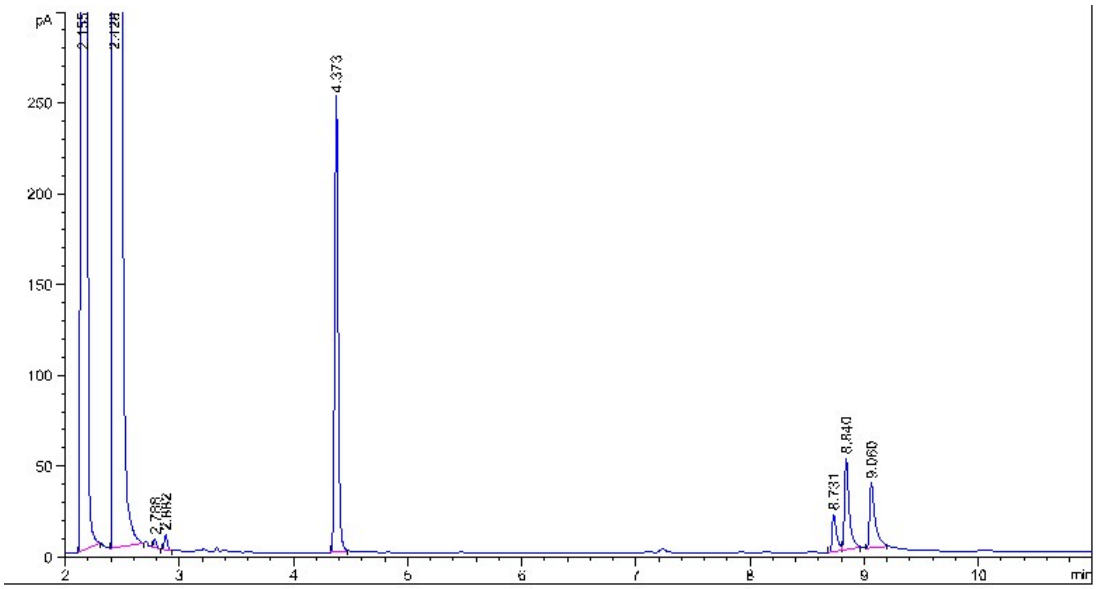


**Fig. S32.** GC plot of the reaction mixture in *n*-heptane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.155 (ether), 2.428 ($CH_3CN$), 4.373 (cycloheptanone, CG standard), 8.731 ($C_3H_7CH(COOH)C_3H_7$), 8.840 ($C_4H_9CH(COOH)C_2H_5$), 9.060 ($C_5H_{11}CH(COOH)CH_3$).

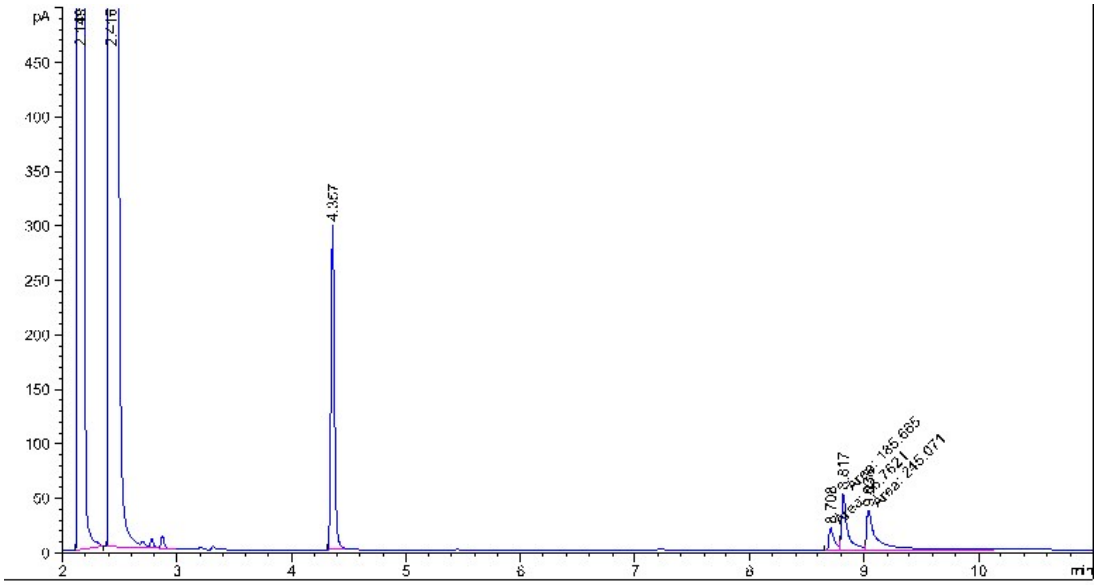


**Fig. S33.** GC plot of the reaction mixture in *n*-heptane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.149 (ether), 2.416 ($CH_3CN$), 4.357 (cycloheptanone, CG standard), 8.708 ($C_3H_7CH(COOH)C_3H_7$), 8.817 ($C_4H_9CH(COOH)C_2H_5$), 9.038 ($C_5H_{11}CH(COOH)CH_3$).

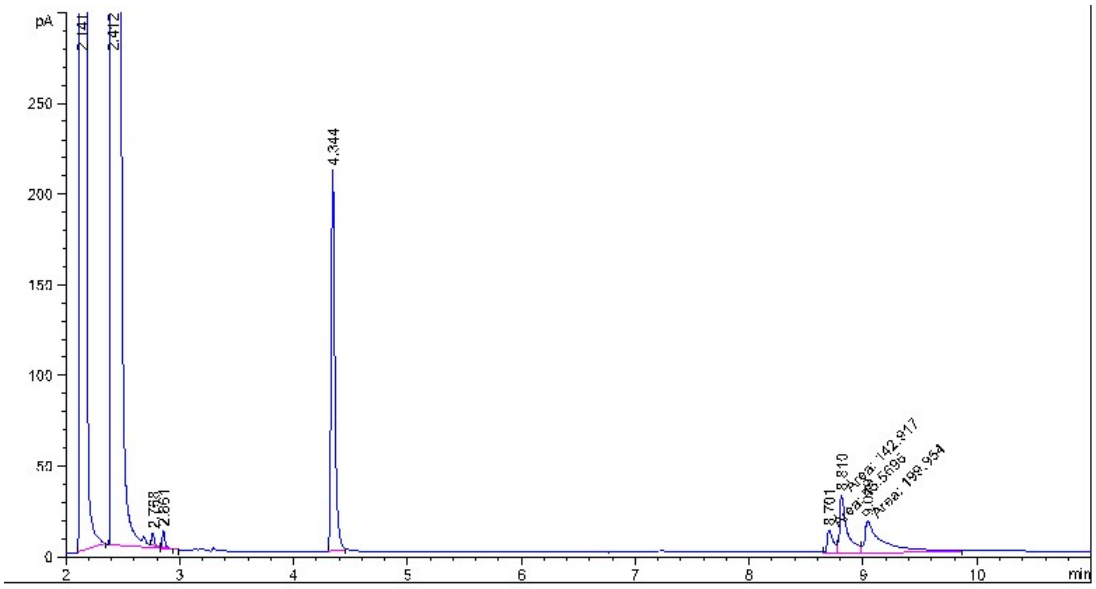


**Fig. S34.** GC plot of the reaction mixture in *n*-heptane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.141 (ether), 2.412 ($CH_3CN$), 4.344 (cycloheptanone, CG standard), 8.701 ($C_3H_7CH(COOH)C_3H_7$), 8.810 ($C_4H_9CH(COOH)C_2H_5$), 9.039 ($C_5H_{11}CH(COOH)CH_3$).

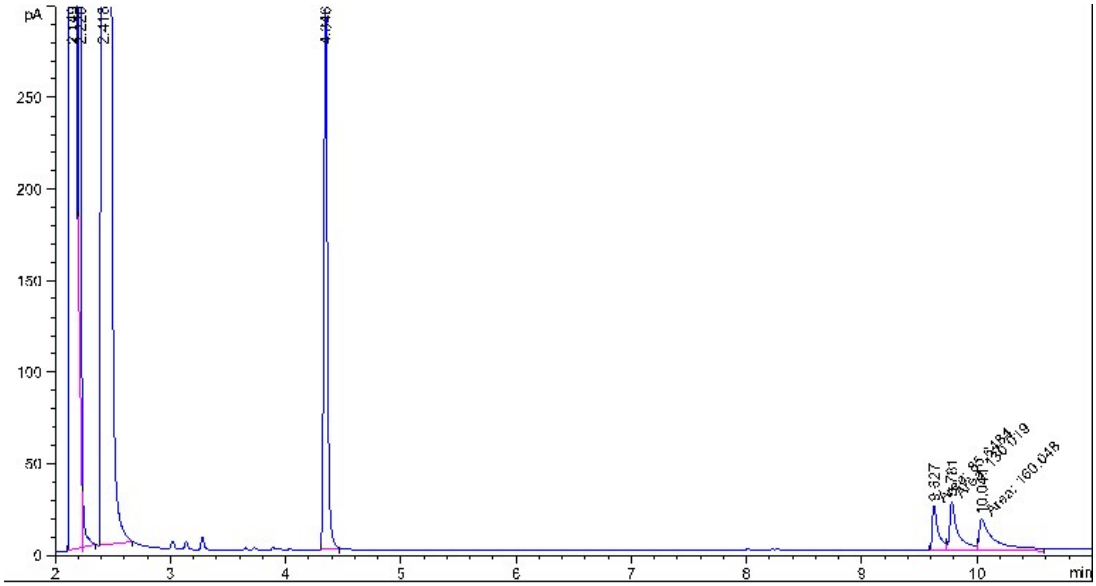


**Fig. S35.** GC plot of the reaction mixture in *n*-octane carboxylation catalyzed by **1**. Peak retention time, min (assignment): 2.149 (ether), 2.418 ($CH_3CN$), 4.346 (cycloheptanone, CG standard), 9.627 ($C_3H_7CH(COOH)C_4H_9$), 9.781 ($C_5H_{11}CH(COOH)C_2H_5$), 10.041 ($C_6H_{13}CH(COOH)CH_3$).

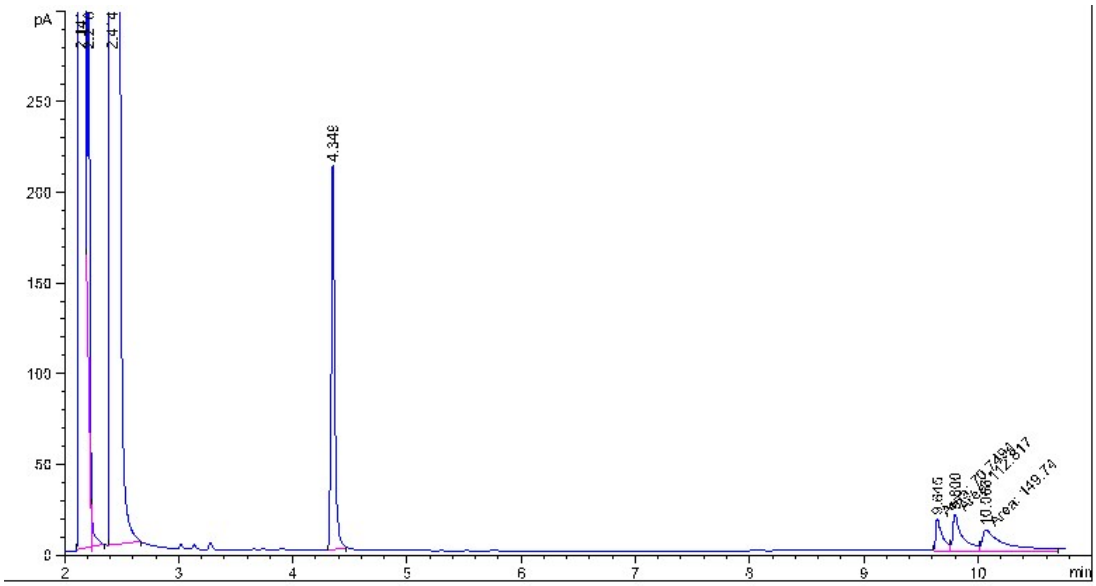


**Fig. S36.** GC plot of the reaction mixture in *n*-octane carboxylation catalyzed by **2**. Peak retention time, min (assignment): 2.141 (ether), 2.414 ($CH_3CN$), 4.349 (cycloheptanone, CG standard), 9.645 ($C_3H_7CH(COOH)C_4H_9$), 9.800 ($C_5H_{11}CH(COOH)C_2H_5$), 10.066 ($C_6H_{13}CH(COOH)CH_3$).

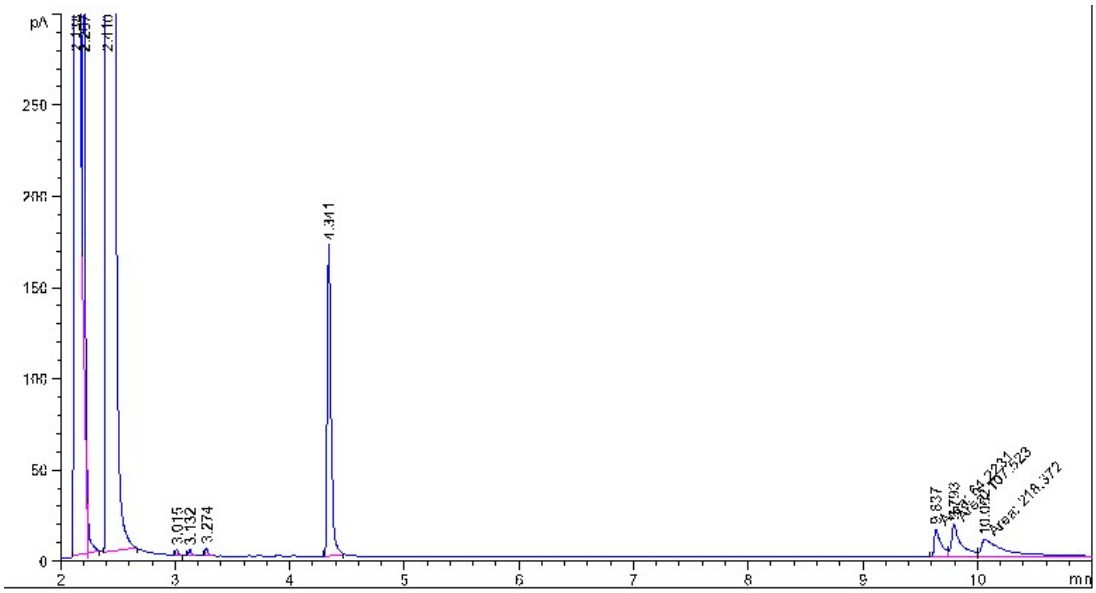


**Fig. S37.** GC plot of the reaction mixture in *n*-octane carboxylation catalyzed by **3**. Peak retention time, min (assignment): 2.138 (ether), 2.410 ($CH_3CN$), 4.341 (cycloheptanone, CG standard), 9.637 ($C_3H_7CH(COOH)C_4H_9$), 9.793 ($C_5H_{11}CH(COOH)C_2H_5$), 10.062 ($C_6H_{13}CH(COOH)CH_3$).

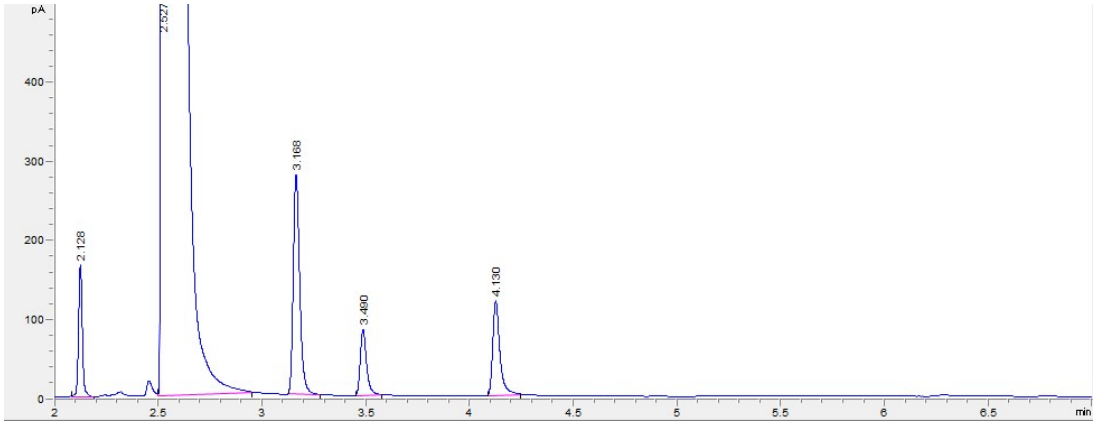


**Fig. S38.** GC plot of the reaction mixture in cyclopentane oxidation catalyzed by **1**. Peak retention time, min (assignment): 2.128 (ether), 2.527 ($CH_3CN$), 3.168 (nitromethane, CG standard), 3.490 ($C_5H_8O$), 4.130 ($C_5H_9OH$).

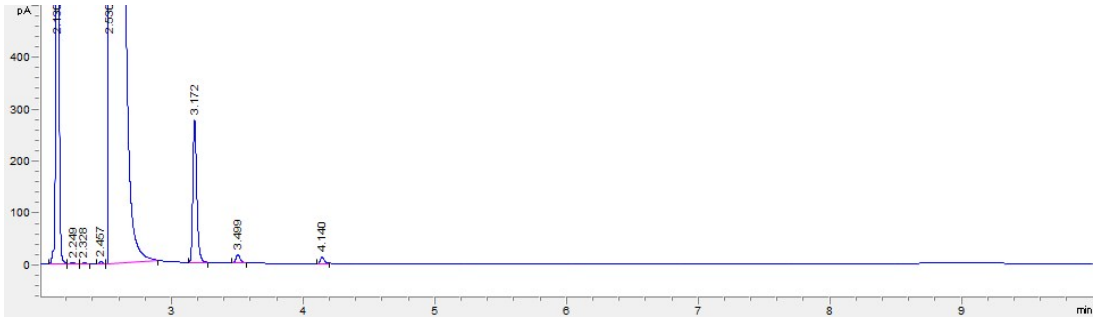


**Fig. S39.** GC plot of the reaction mixture in cyclopentane oxidation catalyzed by **2**. Peak retention time, min (assignment): 2.130 (ether), 2.530 ($CH_3CN$), 3.172 (nitromethane, CG standard), 3.499 ($C_5H_8O$), 4.140 ($C_5H_9OH$).

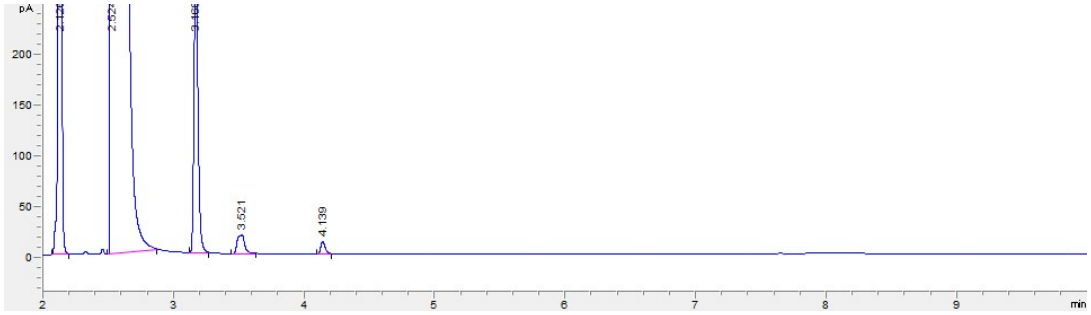


**Fig. S40.** GC plot of the reaction mixture in cyclopentane oxidation catalyzed by **3**. Peak retention time, min (assignment): 2.126 (ether), 2.524 ($CH_3CN$), 3.166 (nitromethane, CG standard), 3.521 ($C_5H_8O$), 4.139 ($C_5H_9OH$).

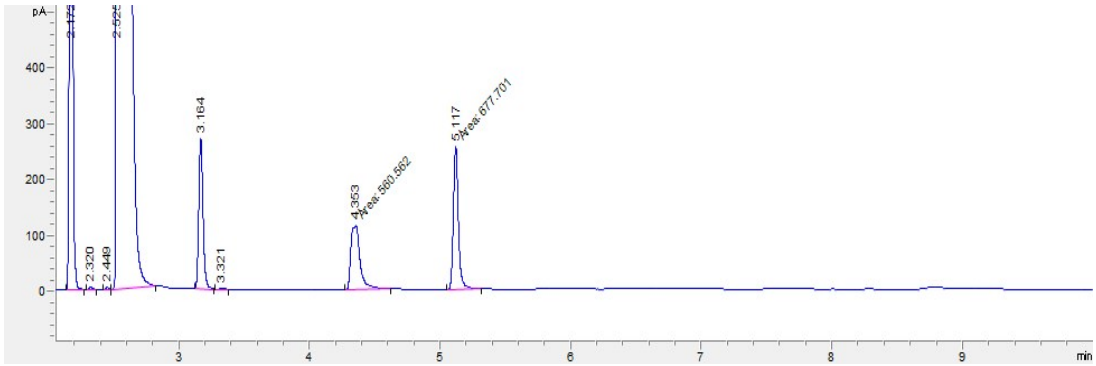


**Fig. S41.** GC plot of the reaction mixture in cyclohexane oxidation catalyzed by **1**. Peak retention time, min (assignment): 2.173 (ether), 2.525 ($CH_3CN$), 3.164 (nitromethane, CG standard), 4.353 ($C_6H_{10}O$), 5.117 ($C_6H_{11}OH$).

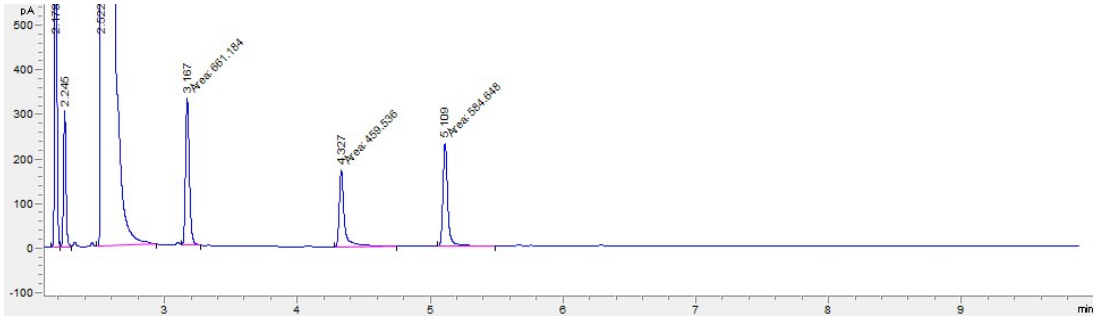


**Fig. S42.** GC plot of the reaction mixture in cyclohexane oxidation catalyzed by **2**. Peak retention time, min (assignment): 2.178 (ether), 2.245 ($C_6H_{12}$), 2.522 ($CH_3CN$), 3.167 (nitromethane, CG standard), 4.327 ($C_6H_{10}O$), 5.109 ($C_6H_{11}OH$).

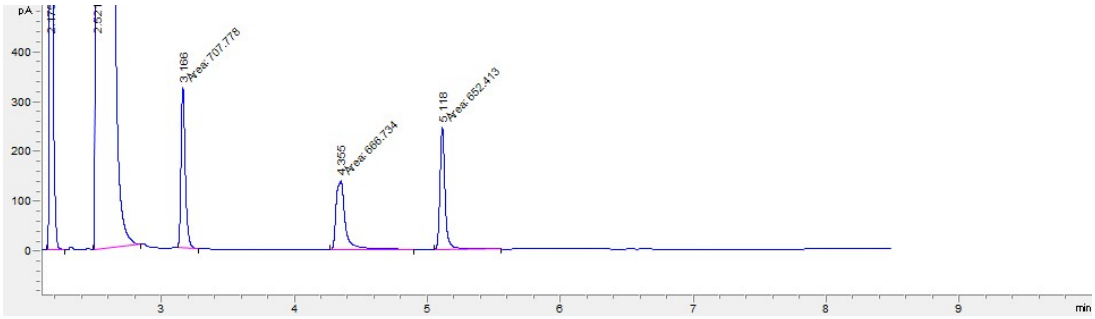


**Fig. S43.** GC plot of the reaction mixture in cyclohexane oxidation catalyzed by **3**. Peak retention time, min (assignment): 2.175 (ether), 2.521 ($CH_3CN$), 3.166 (nitromethane, CG standard), 4.355 ($C_6H_{10}O$), 5.118 ($C_6H_{11}OH$).

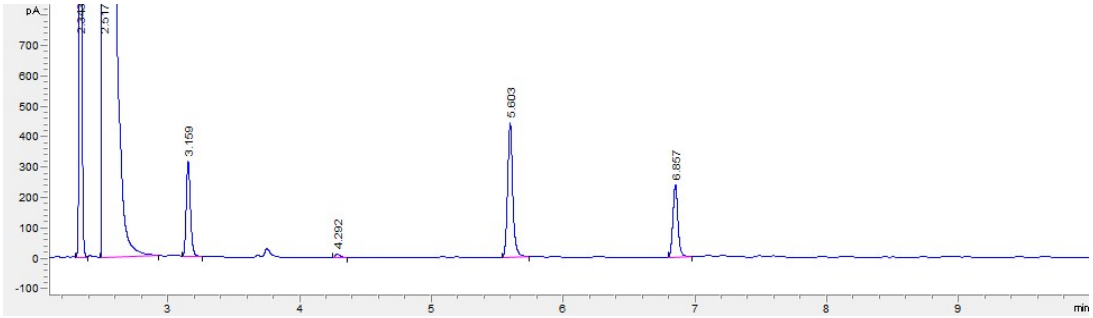


**Fig. S44.** GC plot of the reaction mixture in cycloheptane oxidation catalyzed by **1**. Peak retention time, min (assignment): 2.343 ($C_7H_{14}$), 2.517 ($CH_3CN$), 3.159 (nitromethane, CG standard), 5.603 ($C_7H_{12}O$), 6.857 ($C_7H_{13}OH$).

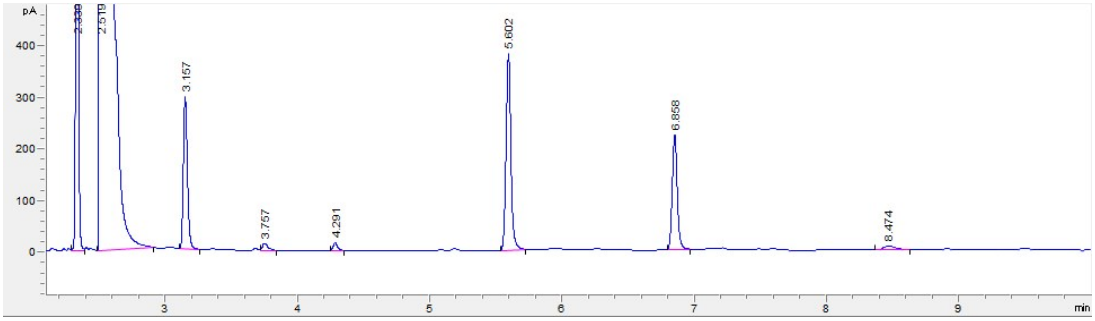


**Fig. S45.** GC plot of the reaction mixture in cycloheptane oxidation catalyzed by **2**. Peak retention time, min (assignment): 2.339 ($C_7H_{14}$), 2.519 ($CH_3CN$), 3.157 (nitromethane, CG standard), 5.602 ($C_7H_{12}O$), 6.858 ($C_7H_{13}OH$).

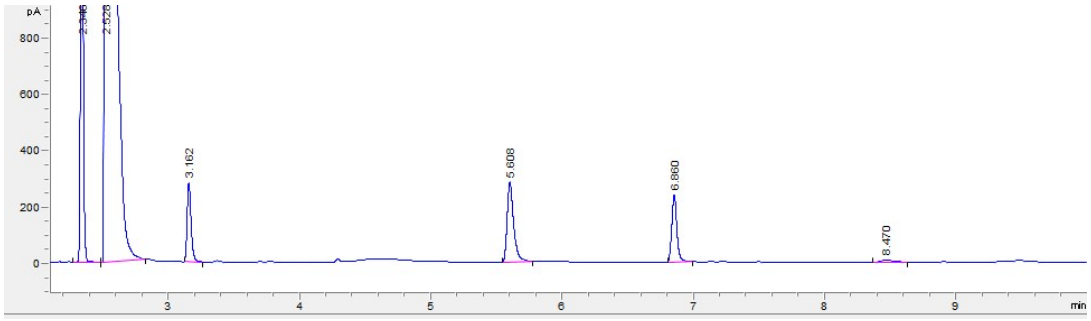


**Fig. S46.** GC plot of the reaction mixture in cycloheptane oxidation catalyzed by **3**. Peak retention time, min (assignment): 2.346 ($C_7H_{14}$), 2.528 ($CH_3CN$), 3.162 (nitromethane, CG standard), 5.608 ($C_7H_{12}O$), 6.860 ($C_7H_{13}OH$).

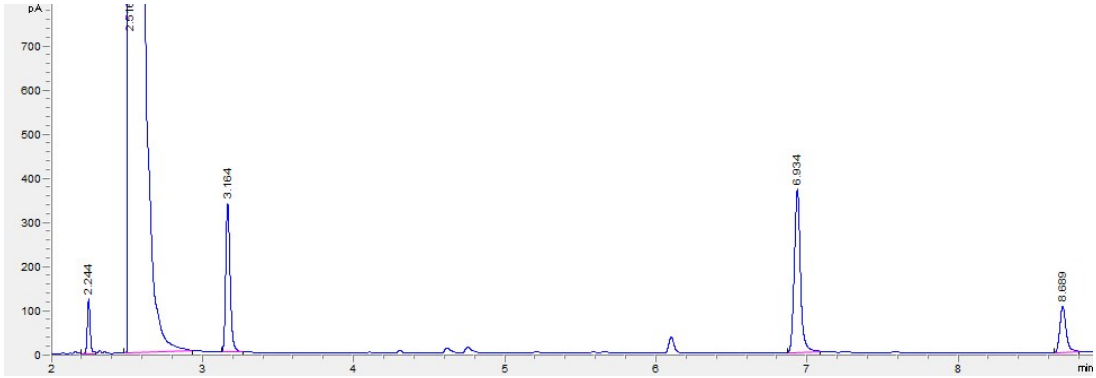


**Fig. S47.** GC plot of the reaction mixture in cyclooctane oxidation catalyzed by **1**. Peak retention time, min (assignment): 2.244 ($C_8H_{16}$), 2.516 ($CH_3CN$), 3.164 (nitromethane, CG standard), 6.934 ($C_8H_{14}O$), 8.689 ($C_8H_{15}OH$).

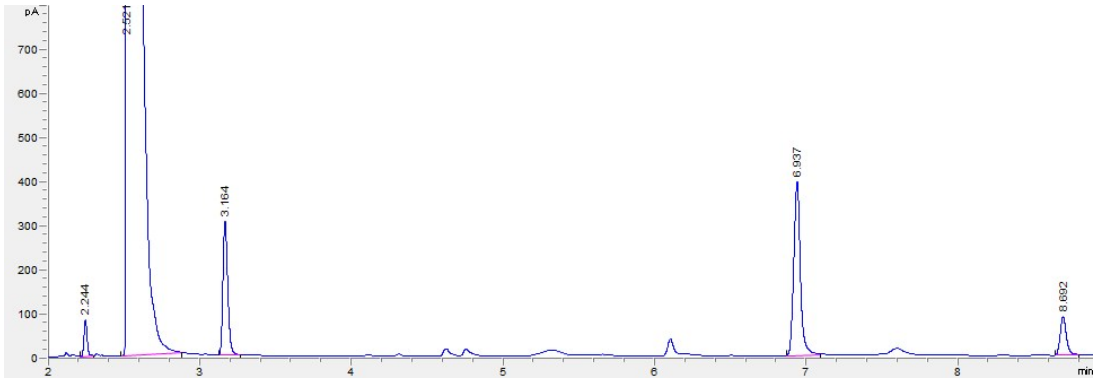


**Fig. S48.** GC plot of the reaction mixture in cyclooctane oxidation catalyzed by **2**. Peak retention time, min (assignment): 2.244 ($C_8H_{16}$), 2.521 ($CH_3CN$), 3.164 (nitromethane, CG standard), 6.937 ($C_8H_{14}O$), 8.682 ($C_8H_{15}OH$).

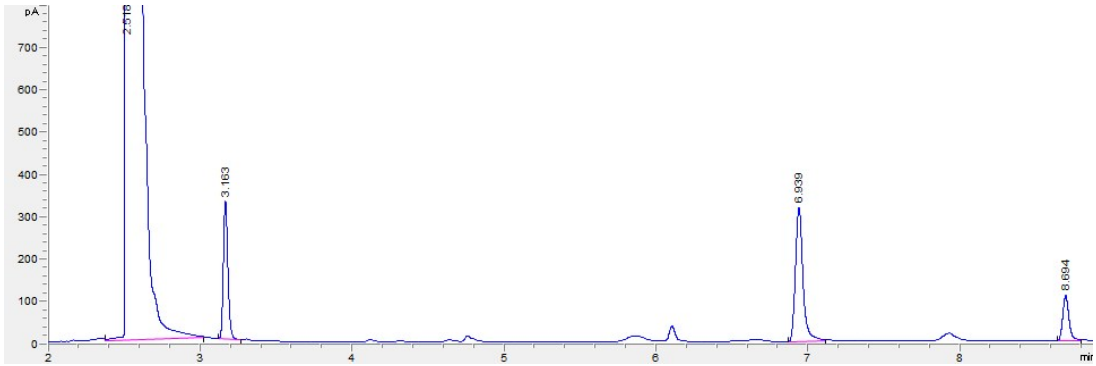


**Fig. S49.** GC plot of the reaction mixture in cyclooctane oxidation catalyzed by **3**. Peak retention time, min (assignment): 2.518 ($CH_3CN$), 3.163 (nitromethane, CG standard), 6.939 ($C_8H_{14}O$), 8.694 ($C_8H_{15}OH$).

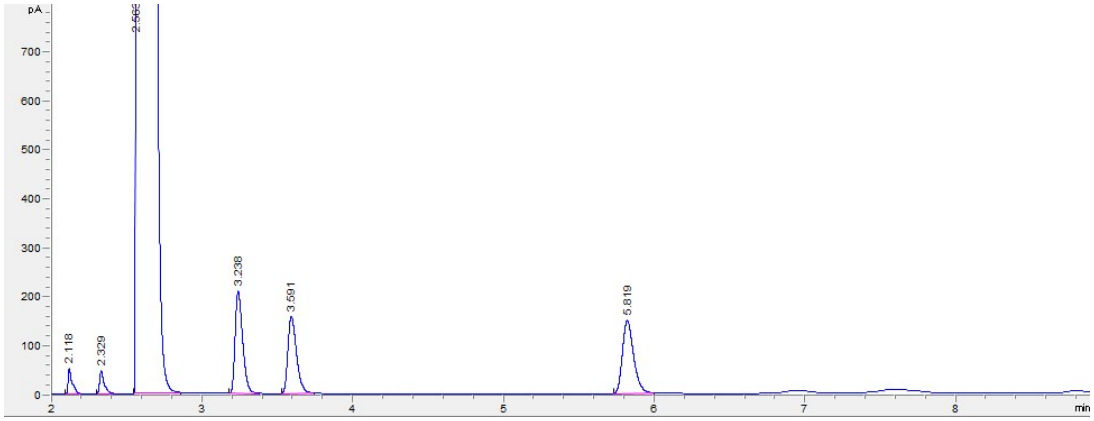


**Fig. S50.** GC plot of authentic sample of cyclopentanone and cycloheptanone. Peak retention time, min (assignment): 2.118 (ether), 2.563 ($CH_3CN$), 3.238 (nitromethane, CG standard), 3.591 ($C_5H_8O$), 5.819 ($C_7H_{12}O$).

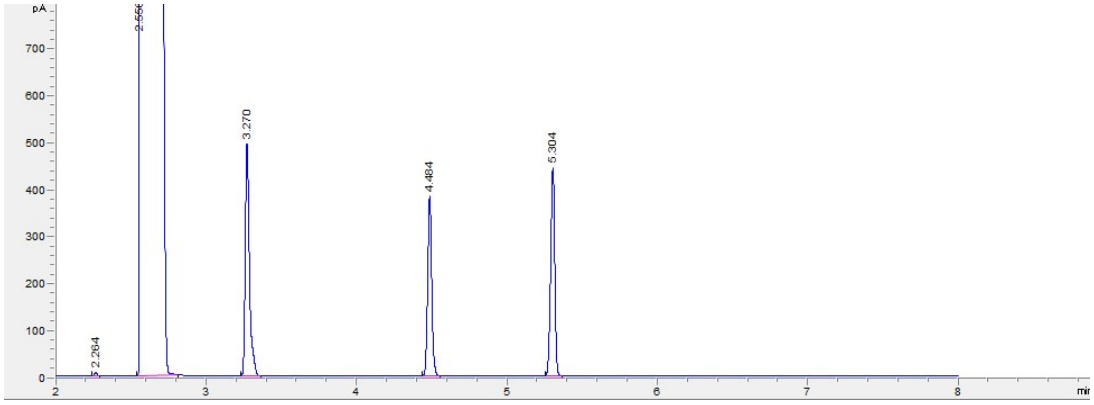


**Fig. S51.** GC plot of authentic sample of cyclohexanone and cyclohexanol. Peak retention time, min (assignment): 2.556 ($CH_3CN$), 3.270 (nitromethane, CG standard), 4.484 ($C_6H_{10}O$), 5.304 ($C_6H_{11}OH$).

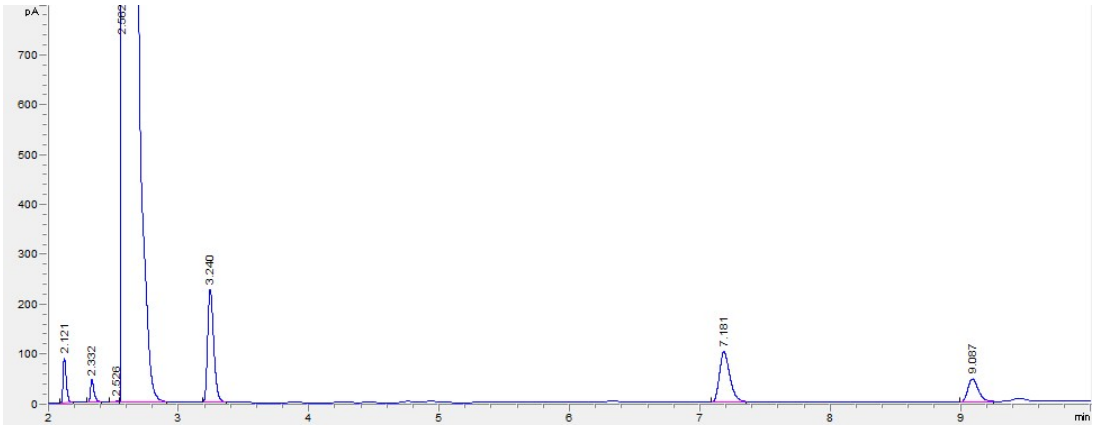


**Fig. S52.** GC plot of authentic sample of cyclooctanone and cyclooctanol. Peak retention time, min (assignment): 2.121 (ether), 2.562 ($CH_3CN$), 3.270 (nitromethane, CG standard), 7.181 ($C_8H_{14}O$), 9.087 ($C_8H_{15}OH$).