Electronic Supplementary Material (ESI) for New Journal of Chemistry.

# Supporting Information

# Mechano-catalysis boosts glycolaldehyde conversion into tetroses over a new Zn-COF catalyst

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## 1. Experiments:

### 1.1 Materials preparation

All chemicals were purchased from commercial source. Pyridine, ethanol, tetrahydrofuran (THF), acetone, acetic acid, methanol and triethylamine were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,4-Dioxiane, 1,2-Diaminocyclohexane and *N*,*O*-bis(trimethylsilyl)triflfluoroacetamide (BSTFA) (99%) were bought from Macklin Chemical Reagent. Glycolaldehyde dimer was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. *O*-ethylhydroxylamine hydrochloride (98%), phenyl-β-D-glucopyranoside (>99%) were purchased from Bidepharm or TCI. 5,5',5'',5'''-((methanetetrayltetrakis(benzene-4,1-diyl))tetrakis(ethyne-2,1-diyl))tetrakis(3-(tertbutyl)-2-hydroxybenzaldehyde (THPM) was synthesized according to sonogashira coupling reaction [1].

**1.2 Synthesis of Ligand THPM.** In short, tetrakis (4-ethynylphenyl) Methane (416 mg, 1 mmol), Benzaldehyde, 3-(1, 1-dimethylethyl)-2-hydroxy-5-iodo (1.368 g, 4.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.8 mmol, 144 mg) and CuI (0.2 mmol. 78 mg) in 15 mL $Et_3N$ were added to 25 mL Schlenk flask and degassed under vacuum. The resulting mixture was stirred at 50 °C under $N_2$ atmosphere for 24 h. Upon cooling to room temperature, the mixture was poured into saturated aqueous $NH_4Cl$ and extracted with $CH_2Cl_2$. The obtained organic phase was dried over anhydrous $Na_2SO_4$ and then concentrated to remove the solvent.

**1.3 Synthesis of Zn-COF**. THPM (0.04 mmol, 45.0 mg), 1,2-Diaminocyclohexane (0.08 mmol, 10 μL) and $Zn(OAc)_2 \cdot 2H_2O$ (1 mmol, 21.9 mg) were put into a 20 mL glass vial and 1, 4-dioxane (3.2 mL), EtOH (0.8 mL) and 0.3 mL of aqueous acetic acid (3 M) were added to the mixture. The glass vial was placed in an oven at 80 °C for 3 days. Upon cooling, a brown powder was isolated by filtration and washed with THF and acetone, respectively. The powder was dried at 80 °C under vacuum overnight.

**1.4 Catalytic activity test**.

For glycolaldehyde conversion under mechanical condition, glycolaldehyde dimer (60 mg) and Zn-COF (100 mg) were put into 15 mL stainless steel grinding bowls with twenty stainless steel balls. The reaction mixtures were immediately ground using ball mill (Shanghai Jingxin Industrial Development Co., Ltd) at frequency of 30 Hz for 7200 s.

For glycolaldehyde conversion under heterogeneous condition in THF solution, glycolaldehyde dimer (60 mg) and Zn-COF (100 mg) were added to the 25 mL flask, and then add 10 mL THF to the flask. The solution was stirred at room temperature for a few days.

## 2. Method

Gas chromatography-mass spectrometry (GC-MS) analysis of reaction products followed a published method [2]. In general: About 2 to 5 mg of the sample was dissolved in 200 μL pyridine, mixed with 200 μL of a 40 mg/mL *O*-ethylhydroxylamine hydrochloride solution with 50 mM phenyl-β-D-glucopyranoside as internal standard and heated for 60 min at 70 ℃ on an oven. Then, it was cooled down to room temperature, and 120 μL BSTFA was added into the resulting solution, which was heated again for 60 min at 70 ℃. The derived sugars were separated by GC-MS (GCMS-QP2010 SE). Injections were performed using a split injector in split mode at 250 ℃. Flame ionization detection was co-recorded with MS data and operated under carbon-correction at 250 ℃. A Rtx-5MS column (30 m length, ID 0.250 mm, 0.250 μm film thickness) with 80 kPa helium was used with the following temperature program: ① Beginning and retaining at 50 ℃ for 2 min and ② increasing temperature by 10 K/min to 140 ℃ and then ③ elevating by 5 K/min to

240 °C and keeping the temperature for 2 min.

FID peak areas of respective carbohydrates (C2-C7) were corrected by their effective carbon number to account for different response factors. This number has been calculated for each derivatized sugar and the internal standard from literature values for individual functional groups (Table S4).

## 3. Figures

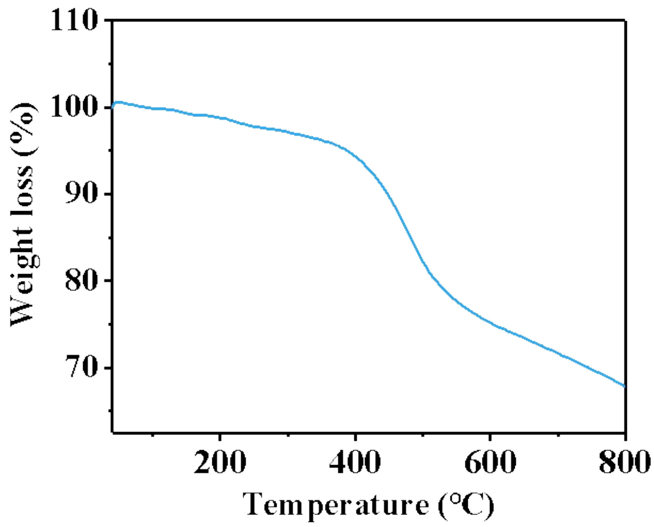


**Figure S1** The thermogravimetric analysis (TGA) isotherms of Zn-COF (Under Ar condition)

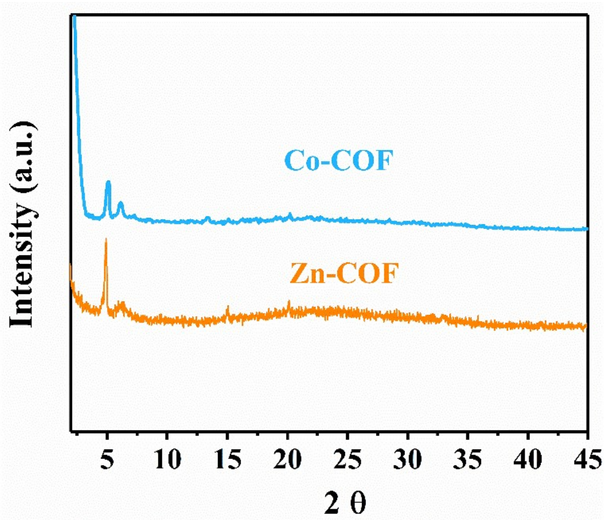


**Figure S2** The XRD profiles of Zn-COF and Co-COF materials

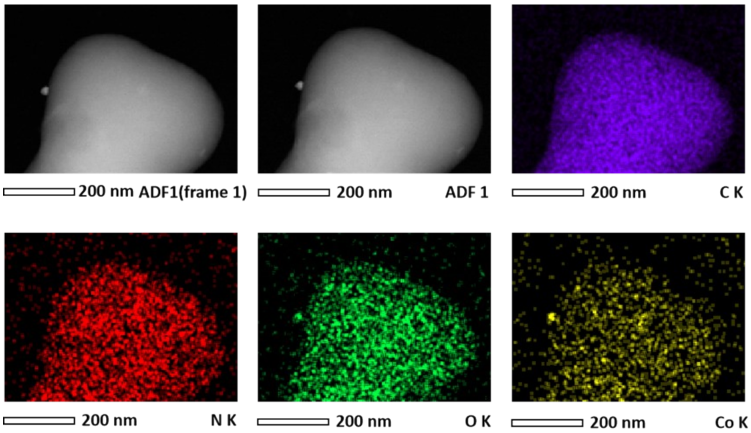


**Figure S3** The elemental mapping results of Co-COF materials

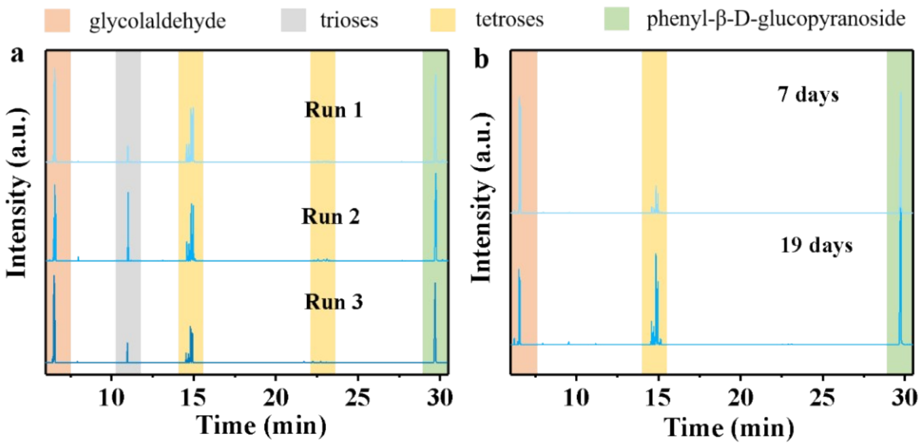


**Figure S4** GC chromatograms for the products. (a) Mechanical reaction condition: 100 mg catalyst, 60 mg glycolaldehyde dimer, Oscillatory ball mill, 30Hz. (b) Heterogeneous liquid reaction condition: 100 mg catalyst, 60 mg glycolaldehyde dimer, Solvent tetrahydrofuran (THF), 30 °C.

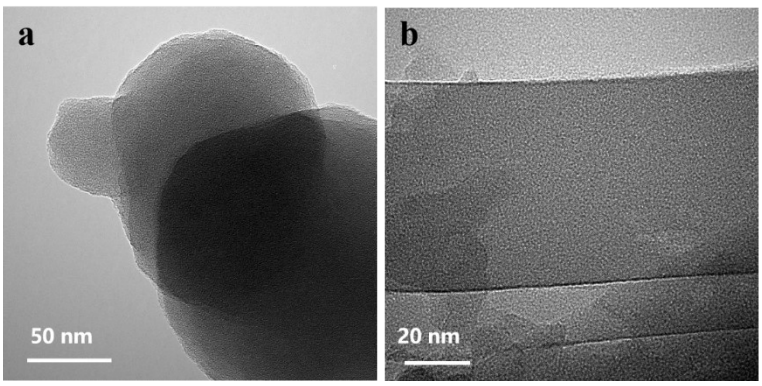


**Figure S5** The TEM images of used (a) Zn-COF and (b) Co-COF materials

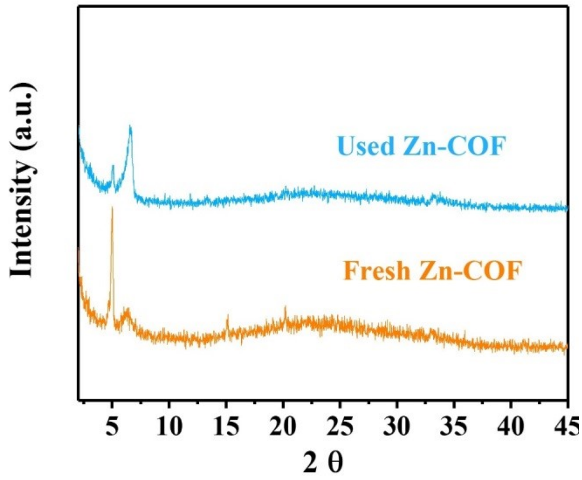


**Figure S6** The XRD profiles of fresh Zn-COF and used Zn-COF materials

## 4. Tables

**Table S1** Fractional atomic coordinates for the unit cell of Zn-COF

Zn-COF
Space group: *P*2
a=20.3239 Å, b=47.6649 Å, c=15.1319 Å
α=90.0000º, β=90.0000º, γ= 90.0000º

| Atom | x (Å) | y (Å) | z (Å) | Atom | x (Å) | y (Å) | z (Å) |
|---|---|---|---|---|---|---|---|
| C1 | 0.3562 | 0.39362 | 0.27996 | C185 | 0.08412 | 0.15534 | 0.72046 |
| C2 | 0.30273 | 0.38428 | 0.32116 | H186 | -0.00828 | 0.16362 | 0.77356 |
| C3 | 0.39778 | 0.37475 | 0.2273 | C187 | 0.16521 | 0.11656 | 0.62658 |
| C4 | 0.28383 | 0.35438 | 0.3178 | C188 | 0.23631 | 0.15379 | 0.55454 |
| H5 | 0.27439 | 0.39876 | 0.36134 | C189 | 0.07128 | 0.12481 | 0.72408 |
| C6 | 0.38436 | 0.34713 | 0.21668 | C190 | 0.11003 | 0.1067 | 0.68163 |
| H7 | 0.44041 | 0.38442 | 0.19795 | H191 | 0.19064 | 0.10048 | 0.58992 |
| C8 | 0.32436 | 0.33532 | 0.26215 | C192 | 0.20965 | 0.17782 | 0.49569 |
| C9 | 0.23274 | 0.34654 | 0.36756 | C193 | 0.29667 | 0.164 | 0.60707 |
| C10 | 0.42989 | 0.32807 | 0.1605 | C194 | 0.26031 | 0.13042 | 0.4909 |
| O11 | 0.31091 | 0.3105 | 0.25186 | H195 | 0.02928 | 0.11701 | 0.76062 |
| N12 | 0.21129 | 0.31821 | 0.37738 | H196 | 0.31662 | 0.21079 | 0.76171 |
| H13 | 0.20669 | 0.36258 | 0.40415 | H197 | 0.38999 | 0.22619 | 0.80476 |
| C14 | 0.45832 | 0.3044 | 0.21865 | H198 | 0.39308 | 0.20588 | 0.70476 |
| C15 | 0.39069 | 0.31564 | 0.08234 | H199 | 0.2732 | 0.23017 | 0.60297 |
| C16 | 0.48987 | 0.34351 | 0.12036 | H200 | 0.35364 | 0.22737 | 0.55866 |
| Zn17 | 0.24244 | 0.2882 | 0.29947 | H201 | 0.31289 | 0.26081 | 0.55922 |
| C18 | 0.14905 | 0.31193 | 0.42249 | H202 | 0.45039 | 0.24577 | 0.62859 |
| O19 | 0.26866 | 0.25894 | 0.22264 | H203 | 0.44818 | 0.26417 | 0.73084 |
| N20 | 0.17286 | 0.2656 | 0.35273 | H204 | 0.41677 | 0.28055 | 0.63097 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C21 | 0.13435 | 0.27968 | 0.42126 | H205 | 0.16385 | 0.17108 | 0.46145 |
| H22 | 0.10882 | 0.32233 | 0.38461 | H206 | 0.24629 | 0.18391 | 0.44479 |
| C23 | 0.24967 | 0.23467 | 0.21562 | H207 | 0.19866 | 0.19705 | 0.53382 |
| C24 | 0.16435 | 0.23647 | 0.33521 | H208 | 0.33633 | 0.17112 | 0.5619 |
| H25 | 0.08123 | 0.27666 | 0.40552 | H209 | 0.3164 | 0.14686 | 0.64933 |
| C26 | 0.27844 | 0.21663 | 0.14348 | H210 | 0.28381 | 0.18177 | 0.65027 |
| C27 | 0.19851 | 0.22233 | 0.27444 | H211 | 0.28571 | 0.11332 | 0.52748 |
| H28 | 0.12672 | 0.22545 | 0.37214 | H212 | 0.29639 | 0.13887 | 0.44264 |
| C29 | 0.25796 | 0.1897 | 0.13753 | H213 | 0.21841 | 0.12154 | 0.45265 |
| C30 | 0.32717 | 0.22902 | 0.07484 | C214 | 0.31408 | 0.33923 | 0.85201 |
| C31 | 0.18048 | 0.19263 | 0.26053 | C215 | 0.09396 | 0.07724 | 0.67967 |
| C32 | 0.20755 | 0.17767 | 0.1959 | C216 | 0.08092 | 0.0527 | 0.67113 |
| H33 | 0.27593 | 0.17578 | 0.08686 | C217 | 0.33815 | 0.36117 | 0.8755 |
| C34 | 0.29251 | 0.25259 | 0.02216 | C218 | 0.36979 | 0.38676 | 0.90357 |
| C35 | 0.38881 | 0.24044 | 0.12253 | C219 | 0.36824 | 0.39482 | 0.99236 |
| C36 | 0.3523 | 0.2074 | 0.00606 | C220 | 0.40799 | 0.402 | 0.84377 |
| H37 | 0.14162 | 0.18327 | 0.29982 | C221 | 0.40682 | 0.41724 | 1.02186 |
| H38 | 0.42012 | 0.2922 | 0.25335 | H222 | 0.33937 | 0.38306 | 1.03963 |
| H39 | 0.49155 | 0.31324 | 0.2701 | C223 | 0.44701 | 0.42429 | 0.87316 |
| H40 | 0.48691 | 0.28959 | 0.1771 | H224 | 0.41054 | 0.39567 | 0.7751 |
| H41 | 0.34912 | 0.30266 | 0.10479 | C225 | 0.44719 | 0.43243 | 0.96298 |
| H42 | 0.4225 | 0.30212 | 0.04058 | H226 | 0.40727 | 0.42207 | 1.09172 |
| H43 | 0.37055 | 0.33268 | 0.04035 | H227 | 0.47974 | 0.43399 | 0.82606 |
| H44 | 0.52086 | 0.32885 | 0.08144 | C228 | 0.06498 | 0.02393 | 0.6516 |
| H45 | 0.52157 | 0.35218 | 0.1736 | C229 | -0.00013 | 0.0148 | 0.65723 |
| H46 | 0.47413 | 0.36067 | 0.07538 | C230 | 0.11207 | 0.00673 | 0.61186 |
| H47 | 0.25002 | 0.24393 | -0.0154 | C231 | -0.01892 | -0.01058 | 0.61859 |
| H48 | 0.32689 | 0.26242 | -0.02575 | H232 | -0.03739 | 0.02809 | 0.68645 |
| H49 | 0.27322 | 0.26938 | 0.06539 | C233 | 0.09324 | -0.01838 | 0.57127 |
| H50 | 0.42513 | 0.24873 | 0.07436 | H234 | 0.16249 | 0.01384 | 0.60564 |
| H51 | 0.41286 | 0.22354 | 0.16156 | C235 | 0.02668 | -0.02707 | 0.57091 |
| H52 | 0.37684 | 0.25772 | 0.16791 | H236 | -0.07066 | -0.01596 | 0.61856 |
| H53 | 0.37786 | 0.18963 | 0.03913 | H237 | 0.13002 | -0.02933 | 0.53312 |
| H54 | 0.38831 | 0.21728 | -0.0394 | C238 | -0.39133 | -0.39297 | 0.81891 |
| H55 | 0.31127 | 0.19921 | -0.03532 | C239 | -0.4306 | -0.37478 | 0.77729 |
| C56 | 0.3774 | 0.42202 | 0.2946 | C240 | -0.33538 | -0.38322 | 0.87322 |
| C57 | 0.18079 | 0.15069 | 0.17364 | C241 | -0.41726 | -0.34427 | 0.78056 |
| C58 | 0.15644 | 0.12896 | 0.14983 | H242 | -0.47328 | -0.38248 | 0.74157 |
| C59 | 0.39586 | 0.44531 | 0.31267 | C243 | -0.31834 | -0.35586 | 0.88019 |
| C60 | 0.4187 | 0.47223 | 0.34219 | H244 | -0.30959 | -0.39935 | 0.90945 |
| C61 | 0.37595 | 0.48999 | 0.3877 | C245 | -0.35492 | -0.33507 | 0.82367 |
| C62 | 0.48559 | 0.47864 | 0.33806 | C246 | -0.46373 | -0.32688 | 0.74988 |
| C63 | 0.40041 | 0.51328 | 0.43312 | C247 | -0.26392 | -0.34609 | 0.94569 |

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|---|---|---|---|---|---|---|---|
| H64 | 0.32425 | 0.48476 | 0.39324 | O248 | -0.33248 | -0.3114 | 0.81505 |
| C65 | 0.51009 | 0.50219 | 0.38178 | N249 | -0.45451 | -0.29726 | 0.74288 |
| H66 | 0.51946 | 0.46469 | 0.30477 | H250 | -0.51022 | -0.33575 | 0.72865 |
| C67 | 0.46839 | 0.51963 | 0.43235 | C251 | -0.28997 | -0.32179 | 1.00371 |
| H68 | 0.36633 | 0.5248 | 0.474 | C252 | -0.20338 | -0.33625 | 0.89341 |
| H69 | 0.5627 | 0.50575 | 0.38127 | C253 | -0.24056 | -0.36941 | 1.01013 |
| C70 | 0.12498 | 0.10421 | 0.11615 | Zn254 | -0.36714 | -0.28021 | 0.75312 |
| C71 | 0.08578 | 0.08774 | 0.17117 | C255 | -0.50611 | -0.27817 | 0.71071 |
| C72 | 0.12784 | 0.09846 | 0.02576 | O256 | -0.28359 | -0.2629 | 0.76184 |
| C73 | 0.04789 | 0.06606 | 0.1355 | N257 | -0.40681 | -0.24799 | 0.69358 |
| H74 | 0.08211 | 0.09247 | 0.24101 | C258 | -0.47866 | -0.24749 | 0.70546 |
| C75 | 0.09039 | 0.07673 | -0.01002 | H259 | -0.54708 | -0.27863 | 0.75878 |
| H76 | 0.15702 | 0.1115 | -0.01776 | C260 | -0.26349 | -0.24026 | 0.73497 |
| C77 | 0.04974 | 0.05996 | 0.04407 | C261 | -0.36978 | -0.22394 | 0.66678 |
| H78 | 1.01458 | 0.05524 | 0.17922 | H262 | -0.48871 | -0.23749 | 0.77036 |
| H79 | 0.09118 | 0.0736 | 0.9191 | C263 | -0.19328 | -0.23215 | 0.75495 |
| C80 | 0.7092 | 0.67765 | 0.30842 | C264 | -0.30567 | -0.22033 | 0.68423 |
| C81 | 0.68213 | 0.69233 | 0.24294 | H265 | -0.39543 | -0.2073 | 0.63226 |
| C82 | 0.75966 | 0.68991 | 0.36667 | C266 | -0.17139 | -0.20704 | 0.72492 |
| C83 | 0.69989 | 0.722 | 0.22827 | C267 | -0.14754 | -0.25227 | 0.80794 |
| H84 | 0.6434 | 0.68277 | 0.2035 | C268 | -0.27538 | -0.19377 | 0.65433 |
| C85 | 0.78037 | 0.71678 | 0.35954 | C269 | -0.21319 | -0.18744 | 0.6742 |
| H86 | 0.77767 | 0.67619 | 0.41801 | H270 | -0.12157 | -0.20009 | 0.73654 |
| C87 | 0.75105 | 0.73462 | 0.28699 | C271 | -0.13775 | -0.27964 | 0.75499 |
| C88 | 0.66547 | 0.73587 | 0.16688 | C272 | -0.1775 | -0.25867 | 0.89954 |
| C89 | 0.82995 | 0.72932 | 0.42726 | C273 | -0.07794 | -0.24026 | 0.82599 |
| O90 | 0.76964 | 0.75893 | 0.27947 | H274 | -0.30449 | -0.17885 | 0.6166 |
| N91 | 0.67346 | 0.76498 | 0.14872 | H275 | -0.29974 | -0.30256 | 0.96498 |
| H92 | 0.628 | 0.72465 | 0.12992 | H276 | -0.33632 | -0.32811 | 1.037 |
| C93 | 0.79571 | 0.75282 | 0.48042 | H277 | -0.25346 | -0.31591 | 1.05536 |
| C94 | 0.89077 | 0.74091 | 0.37858 | H278 | -0.21594 | -0.3185 | 0.84981 |
| C95 | 0.85648 | 0.70777 | 0.49551 | H279 | -0.16348 | -0.32923 | 0.93873 |
| Zn96 | 0.74293 | 0.78788 | 0.20144 | H280 | -0.18415 | -0.35356 | 0.85162 |
| C97 | 0.63522 | 0.77865 | 0.07881 | H281 | -0.20457 | -0.361 | 1.05892 |
| O98 | 0.81126 | 0.81047 | 0.24852 | H282 | -0.28279 | -0.37813 | 1.04771 |
| N99 | 0.71133 | 0.81754 | 0.12219 | H283 | -0.21521 | -0.38663 | 0.9743 |
| C100 | 0.64895 | 0.81095 | 0.07728 | H284 | -0.11116 | -0.27513 | 0.69268 |
| H101 | 0.58201 | 0.77534 | 0.09301 | H285 | -0.10808 | -0.29499 | 0.79348 |
| C102 | 0.82435 | 0.83528 | 0.23754 | H286 | -0.18476 | -0.28982 | 0.73671 |
| C103 | 0.73247 | 0.84595 | 0.13113 | H287 | -0.1444 | -0.27246 | 0.93886 |
| H104 | 0.60869 | 0.82117 | 0.11524 | H288 | -0.18446 | -0.23886 | 0.93707 |
| C105 | 0.88429 | 0.84734 | 0.28297 | H289 | -0.22533 | -0.26957 | 0.89529 |
| C106 | 0.78347 | 0.85408 | 0.18109 | H290 | -0.08043 | -0.22021 | 0.86339 |

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|---|---|---|---|---|---|---|---|
| H107 | 0.70622 | 0.8618 | 0.09373 | H291 | -0.04794 | -0.25517 | 0.86574 |
| C108 | 0.89728 | 0.87496 | 0.27182 | H292 | -0.05137 | -0.23697 | 0.76313 |
| C109 | 0.93025 | 0.8285 | 0.33968 | C293 | -0.40751 | -0.4224 | 0.82097 |
| C110 | 0.80192 | 0.88402 | 0.17711 | C294 | -0.18603 | -0.16089 | 0.64637 |
| C111 | 0.85529 | 0.89359 | 0.21851 | C295 | -0.16213 | -0.13889 | 0.62333 |
| H112 | 0.93985 | 0.8848 | 0.30114 | C296 | -0.42042 | -0.44694 | 0.82964 |
| C113 | 0.9588 | 0.80478 | 0.28211 | C297 | -0.43598 | -0.47573 | 0.84926 |
| C114 | 0.89149 | 0.81614 | 0.41799 | C298 | -0.50092 | -0.48506 | 0.84275 |
| C115 | 0.99016 | 0.84416 | 0.37962 | C299 | -0.38867 | -0.49278 | 0.88964 |
| H116 | 0.77334 | 0.89832 | 0.13637 | C300 | -0.51932 | -0.5105 | 0.88104 |
| H117 | 0.77545 | 0.76949 | 0.43736 | H301 | -0.53835 | -0.47187 | 0.81311 |
| H118 | 0.75395 | 0.74405 | 0.51883 | C302 | -0.40713 | -0.51798 | 0.92979 |
| H119 | 0.83066 | 0.76278 | 0.5276 | H303 | -0.33842 | -0.48549 | 0.89663 |
| H120 | 0.878 | 0.75827 | 0.33385 | C304 | -0.47353 | -0.52688 | 0.92925 |
| H121 | 0.92777 | 0.74917 | 0.42618 | H305 | -0.57098 | -0.51603 | 0.88046 |
| H122 | 0.91437 | 0.72411 | 0.33878 | H306 | -0.37028 | -0.52884 | 0.96843 |
| H123 | 0.89369 | 0.71767 | 0.53944 | C307 | -0.13062 | -0.11326 | 0.5956 |
| H124 | 0.8164 | 0.69969 | 0.53839 | C308 | -0.13204 | -0.10527 | 0.50674 |
| H125 | 0.8811 | 0.6899 | 0.46188 | C309 | -0.09244 | -0.09799 | 0.65572 |
| H126 | 0.99168 | 0.81359 | 0.23053 | C310 | -0.09319 | -0.08295 | 0.47747 |
| H127 | 0.98782 | 0.79018 | 0.32409 | H311 | -0.16098 | -0.11701 | 0.45924 |
| H128 | 0.92067 | 0.79238 | 0.24762 | C312 | -0.0532 | -0.07579 | 0.62657 |
| H129 | 0.92352 | 0.80265 | 0.45982 | H313 | -0.09002 | -0.10427 | 0.72447 |
| H130 | 0.87166 | 0.83322 | 0.45989 | C314 | -0.0528 | -0.06775 | 0.53667 |
| H131 | 0.84971 | 0.80318 | 0.3958 | H315 | -0.09261 | -0.07819 | 0.40758 |
| H132 | 0.97438 | 0.86139 | 0.42418 | H316 | -0.02048 | -0.06607 | 0.67395 |
| H133 | 1.02148 | 0.82966 | 0.41891 | C317 | 1.01211 | 0.27011 | 0.13388 |
| H134 | 1.02153 | 0.85277 | 0.32623 | C318 | 1.0835 | 0.26141 | 0.1198 |
| C135 | 0.68259 | 0.65071 | 0.33111 | C319 | 1.08784 | 0.23117 | 0.0856 |
| C136 | 0.87606 | 0.92201 | 0.20348 | C320 | 1.03298 | 0.21176 | 0.12081 |
| C137 | 0.8944 | 0.9453 | 0.1853 | H321 | 0.98516 | 0.26792 | 0.07051 |
| C138 | 0.65815 | 0.629 | 0.35469 | H322 | 1.0108 | 0.29258 | 0.15343 |
| C139 | 0.62632 | 0.60427 | 0.38752 | H323 | 1.05368 | 0.19028 | 0.12502 |
| C140 | 0.5878 | 0.58777 | 0.33135 | H324 | 0.99162 | 0.21094 | 0.07334 |
| C141 | 0.62803 | 0.59857 | 0.47801 | H325 | 1.13658 | 0.22251 | 0.10383 |
| C142 | 0.54947 | 0.56609 | 0.36588 | H326 | 1.08617 | 0.23142 | 0.01232 |
| H143 | 0.58499 | 0.59247 | 0.26139 | H327 | 1.11073 | 0.26342 | 0.18319 |
| C144 | 0.59015 | 0.57685 | 0.51267 | H328 | 1.10704 | 0.27579 | 0.07148 |
| H145 | 0.65665 | 0.61164 | 0.52237 | C329 | 0.85089 | 0.32438 | 0.48267 |
| C146 | 0.5502 | 0.56004 | 0.45738 | C330 | 0.90444 | 0.31114 | 0.42524 |
| H147 | 0.51674 | 0.55525 | 0.32116 | C331 | 0.89643 | 0.27914 | 0.41664 |
| H148 | 0.59008 | 0.57375 | 0.58357 | C332 | 0.85231 | 0.26623 | 0.48787 |
| C149 | 0.9174 | 0.97218 | 0.15594 | H333 | 0.80215 | 0.32099 | 0.45067 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C150 | 0.87501 | 0.98989 | 0.10923 | H334 | 0.85985 | 0.34735 | 0.48544 |
| C151 | 0.98423 | 0.9786 | 0.16166 | H335 | 0.95322 | 0.31595 | 0.4548 |
| C152 | 0.89983 | 1.01317 | 0.0643 | H336 | 0.90332 | 0.32084 | 0.35843 |
| H153 | 0.82337 | 0.98464 | 0.10246 | H337 | 0.94583 | 0.26916 | 0.41988 |
| C154 | 1.00907 | 1.00214 | 0.11846 | H338 | 0.87482 | 0.2741 | 0.3514 |
| H155 | 1.01785 | 0.96467 | 0.19582 | H339 | 0.86147 | 0.24328 | 0.48919 |
| C156 | 0.96778 | 1.01955 | 0.0668 | H340 | 0.7999 | 0.26941 | 0.46978 |
| H157 | 0.86612 | 1.02466 | 1.0225 | C341 | 0.53358 | 0.71213 | 0.37955 |
| H158 | 0.06166 | 1.00571 | 0.12029 | C342 | 0.58834 | 0.73152 | 0.41563 |
| C159 | 0.28674 | 0.31276 | 0.82359 | C343 | 0.58433 | 0.76171 | 0.38096 |
| C160 | 0.22495 | 0.30622 | 0.84443 | C344 | 0.51301 | 0.77054 | 0.3662 |
| C161 | 0.32803 | 0.29342 | 0.7716 | H345 | 0.49214 | 0.71126 | 0.42651 |
| C162 | 0.19462 | 0.27964 | 0.81448 | H346 | 0.55426 | 0.69066 | 0.37544 |
| H163 | 0.19623 | 0.32096 | 0.88311 | H347 | 0.63717 | 0.7228 | 0.39847 |
| C164 | 0.30614 | 0.26828 | 0.74164 | H348 | 0.58616 | 0.73186 | 0.48888 |
| H165 | 0.37758 | 0.30053 | 0.75933 | H349 | 0.51193 | 0.793 | 0.34628 |
| C166 | 0.23639 | 0.25991 | 0.76276 | H350 | 0.48613 | 0.7685 | 0.42941 |
| C167 | 0.13083 | 0.27582 | 0.8329 | H351 | 0.61155 | 0.76355 | 0.31776 |
| C168 | 0.35171 | 0.24823 | 0.68856 | H352 | 0.60809 | 0.7761 | 0.42927 |
| O169 | 0.21635 | 0.23722 | 0.73615 | C353 | 0.34976 | 0.76513 | 1.01131 |
| N170 | 0.09379 | 0.25175 | 0.80598 | C354 | 0.39374 | 0.77746 | 1.0841 |
| H171 | 0.10542 | 0.29231 | 0.86821 | C355 | 0.40455 | 0.8093 | 1.07548 |
| C172 | 0.36313 | 0.22119 | 0.74272 | C356 | 0.35198 | 0.82331 | 1.01771 |
| C173 | 0.32072 | 0.24123 | 0.5977 | H357 | 0.29729 | 0.76873 | 1.02787 |
| C174 | 0.4206 | 0.2606 | 0.6687 | H358 | 0.35784 | 0.74212 | 1.00967 |
| Zn175 | 0.13331 | 0.21962 | 0.74628 | H359 | 0.44234 | 0.76675 | 1.0828 |
| C176 | 0.02187 | 0.25211 | 0.79437 | H360 | 0.37066 | 0.77283 | 1.1485 |
| O177 | 0.16778 | 0.18846 | 0.68433 | H361 | 0.45364 | 0.8133 | 1.04609 |
| N178 | 0.04641 | 0.20231 | 0.75784 | H362 | 0.40442 | 0.81903 | 1.14226 |
| C179 | -0.00536 | 0.22138 | 0.7892 | H363 | 0.36259 | 0.84616 | 1.01521 |
| H180 | 0.01128 | 0.26211 | 0.72951 | H364 | 0.30304 | 0.82053 | 1.04933 |
| C181 | 0.14576 | 0.16469 | 0.67641 | C365 | 0 | 0.03985 | 0 |
| C182 | 0.03774 | 0.17263 | 0.75159 | C366 | 0.5 | 0.53992 | 0.5 |
| H183 | -0.04624 | 0.22082 | 0.74064 | C367 | 0 | -0.0476 | 0.5 |
| C184 | 0.18213 | 0.14394 | 0.6198 | C368 | -0.5 | 0.45259 | 0 |

**Table S2** ICP values of Zn-COF and Co-COF

| Catalyst | ICP Zn | ICP Co |
|---|---|---|
| Zn-COF | 12.0% | 0 |
| Co-COF | 0.6% | 7.9% |

**Table S3** The catalytic stability of Zn-COF under mechanical conditions

| Circle | Catalyst | Time | Conversion (%) | Selectivity (%) | Yield (%) | Rg ($10^{-4}$mol·h$^{-1}$·g$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | Zn-COF | 2 h | 62.7 | 91.3 | 57.2 | 31.35 |
| 2 | Zn-COF | 2 h | 48.8 | 82.1 | 40.1 | 24.40 |
| 3 | Zn-COF | 2 h | 37.0 | 87.5 | 32.4 | 18.5 |
| 4 | Zn-COF | 2 h | 34.6 | 86.7 | 30.0 | 17.3 |
| 5 | Zn-COF | 2 h | 33.2 | 88.4 | 29.3 | 16.6 |

100 mg catalyst, 60 mg glycolaldehyde dimer, Oscillatory ball mill, 30Hz.

Note: Reaction·rate·per·gram·catalyst (Rg) = moles of converted substrate / (time * grams of catalyst).

## Effective carbon number (ECN)

To account for different response factors, the effective carbon numbers of monosaccharides and the internal standard were calculated from literature values [3].

**Table S4** Calculated ECN values of monosaccharides

| Compound | ECN |
|---|---|
| Glycolaldehyde | 5.29 |
| Trioses | 8.98 |
| Tetroses | 12.67 |
| Pentoses | 16.36 |
| Hexoses | 20.05 |
| phenyl-β-D-glucopyranoside | 20.76 |

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3. Scanlon, J. T.; Willis, D. E., Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept. *Journal of Chromatographic Science* 1985**, 23** (8), 333-340.