Electronic Supplementary Material (ESI) for Dalton Transactions.


Supporting Information for:

# Carbonic Anhydrase Mimics for Enhanced $CO_2$ Absorption in an Amine-Based Capture Solvent

Rachael A. Burrows,[b] David A. Miller,[b] Sean R. Parkin,[b] Kun Liu,[a] Joe E. Remias,[a] Yue Yang,[d] Felice C. Lightstone,[d] Kunlei Liu,[a,c] Cameron A. Lippert,[a]* and Susan A. Odom,[b]*

[a]*University of Kentucky, Center for Applied Energy Research, Lexington, KY 40511-8410*

[b]*Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055*

[c]Department of Mechanical Engineering, University of Kentucky, Lexington, KY 40506-0055

[d]Biosciences and Biotechnology Division, Lawrence Livermore National Laboratory, Livermore, CA, 94550-9234

E-mail: Cameron.lippert@uky.edu; kunlei.liu@uky.edu

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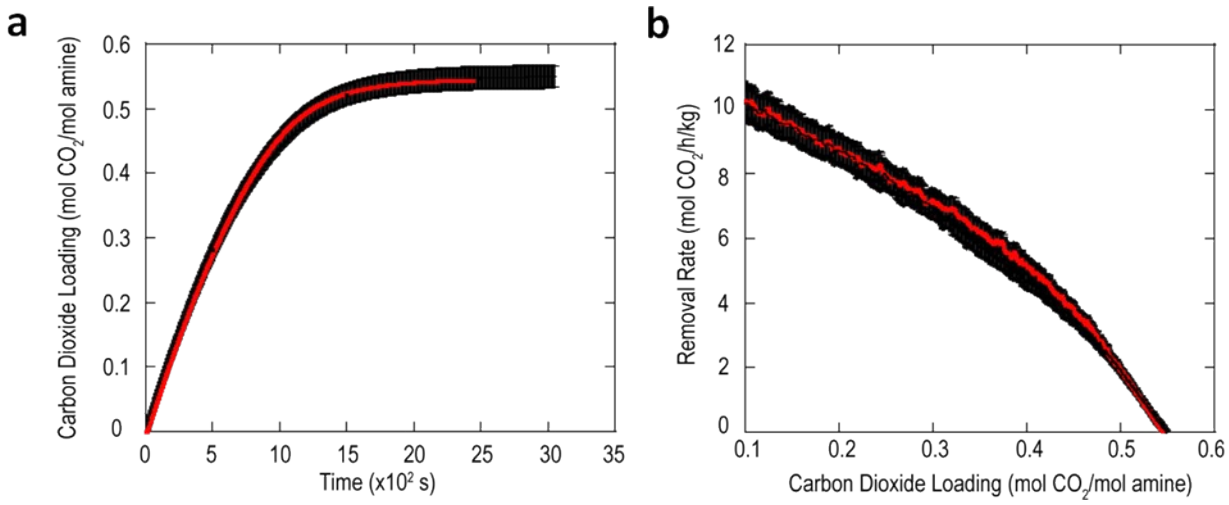



**Figure S1.** Breakthrough data of 30 wt% MEA with standard error of 5% (black) and 30 wt% MEA with 2.3 g/L carbonic anhydrase (red) for (a) increase in carbon loading versus time, and (b) removal rate as a function of carbon loading.

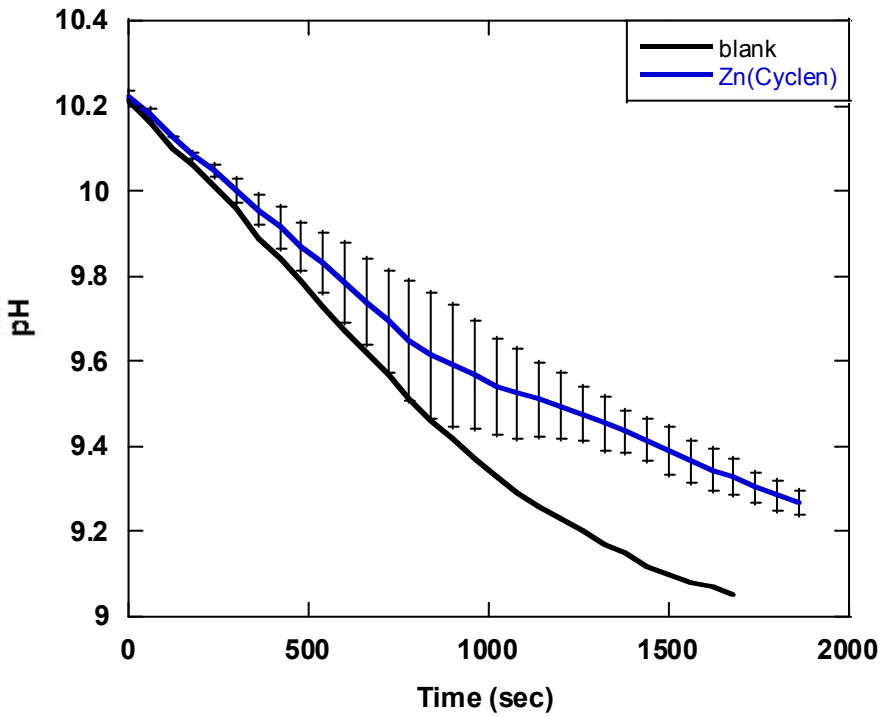



**Figure S2**. $CO_2$ absorption studies of 30 wt% MEA (black line) and Zn-cyclen in 30 wt% MEA (blue line).

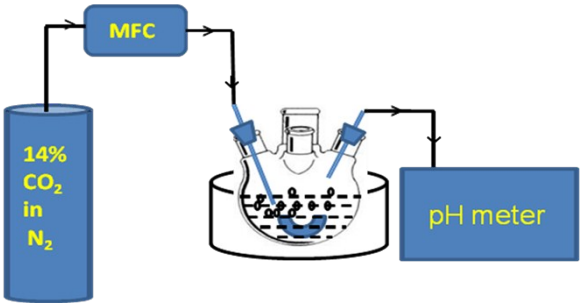



**Figure S3.** Schematic representation of the delta-pH testing method apparatus.

$$\sqrt{\frac{D_{CO2} \cdot k_2 \cdot [amine]}{H_{CO2}}} \quad \text{(S1)}$$

$$k_2[amine] = k_{obs} = k[amine] + k'[cat] \quad \text{(S2)}$$

where k is ~6000 $M^{-1}s^{-1}$ and [amine] is ~5 M; therefore, with a catalyst loading of 0.03 mM, k' needs to be >1 x $10^5$ $M^{-1}s^{-1}$ in order to contribute to the overall $k_{obs}$.

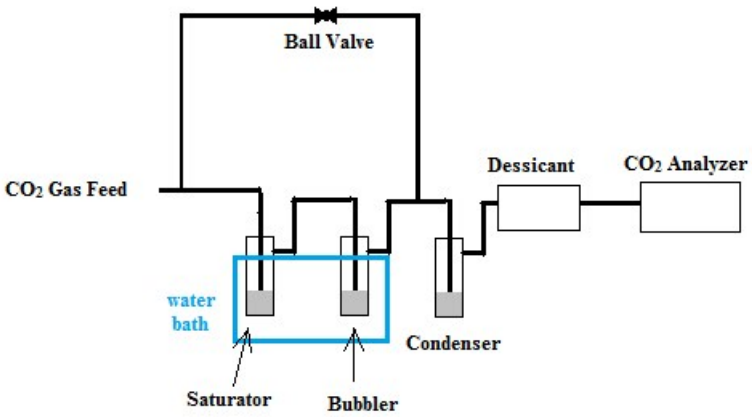



**Figure S4**. Schematic of simple $CO_2$ bubbling apparatus.

**Table S1**. Important bond lengths (Å), angles and dihedrals (deg).

| Complex **1** | | | Complex **2** | | |
|---|---|---|---|---|---|
| bond/angle | exp value | computed value | bond/angle/ | exp value | computed value |
| Zn1-O5 | 1.984 | 1.956 | Zn1-O1 | 1.978 | 1.956 |
| Zn1-O1 | 2.038 | 2.057 | Zn1-N1 | 2.105 | 2.176 |

| | | | | | |
|---|---|---|---|---|---|
| Zn1-O2 | 2.044 | 2.048 | Zn1-O2 | 1.966 | 1.955 |
| Zn1-N2 | 2.095 | 2.180 | Zn1-N2 | 2.140 | 2.182 |
| Zn1-N1 | 2.097 | 2.129 | Zn1-N3 | 2.108 | 2.141 |
| Zn2-O2 | 1.960 | 1.954 | N1-C7 | 1.342 | 1.334 |
| Zn2-O3 | 2.001 | 2.009 | N1-C11 | 1.361 | 1.354 |
| Zn2-O4 | 2.008 | 2.100 | N2-C16 | 1.344 | 1.332 |
| Zn2-N3 | 2.026 | 2.080 | N2-C12 | 1.360 | 1.356 |
| Zn2-N4 | 2.045 | 2.056 | O1-C1 | 1.323 | 2.182 |
| Zn3-O1 | 1.967 | 2.009 | O2-C22 | 1.327 | 1.299 |
| Zn3-O3 | 1.998 | 2.054 | O1-Zn1-O2 | 96.99 | 104.28 |
| Zn3-O4 | 2.008 | 2.048 | O1-Zn1-N1 | 86.42 | 85.34 |
| Zn3-Cl | 2.212 | 2.185 | O2-Zn1-N1 | 155.38 | 157.79 |
| Zn1-O1-Zn3 | 122.35 | 127.37 | O2-Zn1-N2 | 147.59 | 151.71 |
| Zn2-O2-Zn1 | 126.01 | 121.70 | N1-Zn1-N2 | 78.22 | 76.64 |
| Zn3-O3-Zn2 | 93.52 | 92.29 | N2-Zn1-N3 | 109.18 | 102.87 |
| Zn2-O3-Zn3 | 93.15 | 92.45 | C1-C6-C7-N1 | -28.10 | -28.80 |
| | | | N2-C16-C17-C22 | 19.00 | 25.30 |

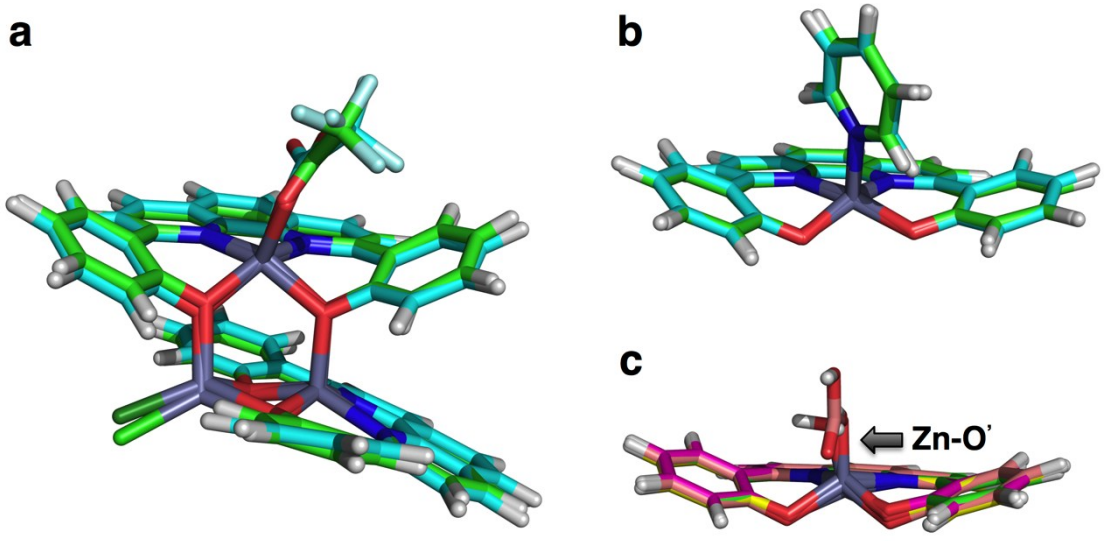
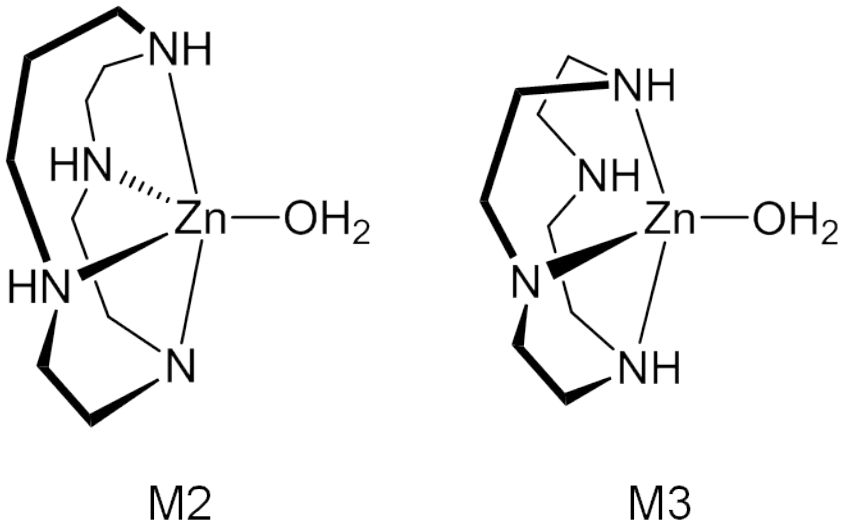



**Figure S5.** Overlay of (a) complex **1** and (b) complex **2** crystal structures (carbon atoms in green) and optimized structures (carbon atoms in cyan). (c) Overlay of complex **2** backbone

(green, from the crystal structure) and its Zn-$H_2O$ (magenta), Zn-$OH^-$ (yellow), and Zn-$HCO_3^-$ (pink) species, with Zn-O' for the latter 3 species labeled.




M2 M3

**Figure S6.** Structures of Zinc(Cyclen) complexes M2 and M3.

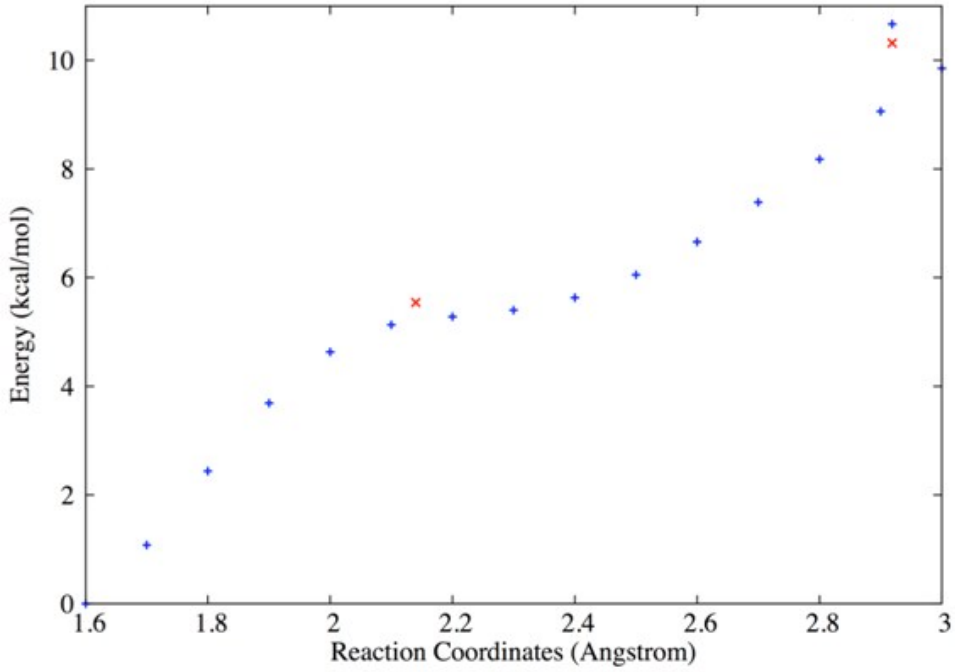



**Figure S7.** Energy profile of $CO_2$ addition step. $CO_2$ approaching (blue) is scanned using a series of restraint optimization, while transition state (red) is obtained using restraint-free saddle point optimization with a single imaginary frequency along RC confirmed.

Atomic Coordinates

**(Optimized) Crystal structure**

Energy: -3209.9007745

| | | | |
|---|---|---|---|
| Zn | 3.88437 | 3.72082 | 15.53830 |
| N | 1.90568 | 4.40580 | 14.94696 |
| N | 4.04879 | 3.92750 | 13.37215 |
| O | 2.99430 | 3.03799 | 17.14065 |
| O | 5.55158 | 2.70352 | 15.44215 |
| C | 2.12370 | 3.71882 | 17.81854 |
| C | 2.14033 | 3.62597 | 19.24363 |
| H | 2.90075 | 2.96266 | 19.67213 |
| C | 1.26389 | 4.33108 | 20.03761 |
| H | 1.32661 | 4.23441 | 21.12949 |
| C | 0.29605 | 5.17873 | 19.46391 |
| H | -0.38816 | 5.75776 | 20.09316 |
| C | 0.22518 | 5.26133 | 18.08822 |
| H | -0.52175 | 5.92769 | 17.63828 |
| C | 1.10286 | 4.54664 | 17.23988 |
| C | 0.88997 | 4.61154 | 15.78760 |
| C | -0.41081 | 4.88326 | 15.25504 |
| H | -1.25447 | 4.99528 | 15.94179 |
| C | -0.60637 | 4.95610 | 13.90315 |
| H | -1.60524 | 5.15529 | 13.49340 |
| C | 0.48015 | 4.74530 | 13.01598 |
| C | 1.71904 | 4.45961 | 13.60669 |
| C | 2.86979 | 4.19972 | 12.76071 |
| C | 2.71376 | 4.23812 | 11.36807 |
| C | 3.86642 | 3.93877 | 10.59923 |
| H | 3.79369 | 3.91397 | 9.50417 |
| C | 5.05025 | 3.66162 | 11.22442 |
| H | 5.92807 | 3.38446 | 10.63519 |
| C | 5.14583 | 3.68528 | 12.65321 |
| C | 6.44205 | 3.43719 | 13.30777 |
| C | 7.62385 | 3.68368 | 12.57081 |
| H | 7.54404 | 4.13722 | 11.57536 |
| C | 8.88358 | 3.41924 | 13.07087 |
| H | 9.77577 | 3.64274 | 12.47530 |
| C | 8.99277 | 2.86365 | 14.35856 |
| H | 9.98223 | 2.62944 | 14.77220 |
| C | 7.86461 | 2.62199 | 15.11225 |
| H | 7.92664 | 2.19196 | 16.11912 |
| C | 6.55095 | 2.92187 | 14.64098 |
| C | 0.35691 | 4.78565 | 11.58632 |
| H | -0.62393 | 5.01150 | 11.15017 |
| C | 1.43369 | 4.54069 | 10.79248 |
| H | 1.34335 | 4.56362 | 9.69950 |
| N | 4.68830 | 5.57044 | 16.25620 |
| C | 4.01967 | 6.72993 | 16.24726 |

| | | | |
|---|---|---|---|
| H | 3.02665 | 6.71212 | 15.77702 |
| C | 4.54038 | 7.89427 | 16.80093 |
| H | 3.95906 | 8.82227 | 16.77191 |
| C | 5.80151 | 7.84377 | 17.39142 |
| H | 6.24137 | 8.74241 | 17.84055 |
| C | 6.49265 | 6.63516 | 17.40647 |
| H | 7.48417 | 6.54879 | 17.86397 |
| C | 5.89991 | 5.51849 | 16.82537 |
| H | 6.38938 | 4.53485 | 16.81018 |

**Zn-$H_2O$**

Energy: -3038.1465466

| | | | |
|---|---|---|---|
| Zn | 3.85055 | 3.66437 | 15.45785 |
| N | 1.89788 | 4.37180 | 14.91258 |
| N | 4.04415 | 3.90226 | 13.33741 |
| O | 3.01804 | 3.03768 | 17.11704 |
| O | 5.60246 | 2.84366 | 15.46822 |
| C | 2.14241 | 3.71863 | 17.79240 |
| C | 2.17881 | 3.65484 | 19.21873 |
| H | 2.94832 | 3.00499 | 19.65181 |
| C | 1.30278 | 4.36506 | 20.01105 |
| H | 1.37597 | 4.28619 | 21.10370 |
| C | 0.32243 | 5.19342 | 19.43352 |
| H | -0.36551 | 5.77236 | 20.05858 |
| C | 0.24185 | 5.25869 | 18.05672 |
| H | -0.50785 | 5.91999 | 17.60355 |
| C | 1.11500 | 4.53642 | 17.21034 |
| C | 0.89012 | 4.59103 | 15.75581 |
| C | -0.40985 | 4.87021 | 15.22961 |
| H | -1.25082 | 4.99055 | 15.91813 |
| C | -0.60911 | 4.94125 | 13.87760 |
| H | -1.60874 | 5.14376 | 13.47162 |
| C | 0.47338 | 4.72817 | 12.98702 |
| C | 1.71202 | 4.43358 | 13.57337 |
| C | 2.86348 | 4.17908 | 12.72734 |
| C | 2.70648 | 4.22877 | 11.33699 |
| C | 3.86021 | 3.93335 | 10.56683 |
| H | 3.78585 | 3.90397 | 9.47191 |
| C | 5.04527 | 3.65904 | 11.18905 |
| H | 5.91863 | 3.38544 | 10.59274 |
| C | 5.14740 | 3.67374 | 12.61963 |
| C | 6.44645 | 3.42879 | 13.26630 |
| C | 7.62304 | 3.62714 | 12.50156 |
| H | 7.53905 | 4.05022 | 11.49375 |
| C | 8.88551 | 3.36297 | 12.98935 |
| H | 9.77005 | 3.55197 | 12.37183 |
| C | 9.01078 | 2.85361 | 14.29562 |
| H | 10.00286 | 2.61377 | 14.69943 |
| C | 7.89504 | 2.67187 | 15.07946 |
| H | 7.96575 | 2.29469 | 16.10603 |
| C | 6.58001 | 2.98961 | 14.62474 |

| | | | |
|---|---|---|---|
| C | 0.34898 | 4.77549 | 11.55791 |
| H | -0.63049 | 5.00890 | 11.12304 |
| C | 1.42566 | 4.53169 | 10.76346 |
| H | 1.33419 | 4.55581 | 9.67058 |
| O | 4.47588 | 5.52865 | 16.35852 |
| H | 5.26727 | 5.27224 | 16.85926 |
| H | 3.80623 | 5.76167 | 17.02306 |

**Zn-OH$^-$**

Energy: -3037.5944552

| | | | |
|---|---|---|---|
| Zn | 4.02646 | 4.05340 | 15.63588 |
| N | 1.90732 | 4.37159 | 14.94898 |
| N | 4.05274 | 3.93118 | 13.36222 |
| O | 3.05512 | 3.06667 | 17.11731 |
| O | 5.49118 | 2.68156 | 15.39359 |
| C | 2.15626 | 3.67540 | 17.80197 |
| C | 2.16009 | 3.55454 | 19.23220 |
| H | 2.94892 | 2.91850 | 19.65156 |
| C | 1.26661 | 4.22469 | 20.03686 |
| H | 1.33957 | 4.12190 | 21.12886 |
| C | 0.27834 | 5.05830 | 19.47689 |
| H | -0.41108 | 5.62465 | 20.11324 |
| C | 0.20777 | 5.15459 | 18.09918 |
| H | -0.54782 | 5.81812 | 17.65812 |
| C | 1.09829 | 4.47669 | 17.24044 |
| C | 0.89246 | 4.56609 | 15.78786 |
| C | -0.41244 | 4.83440 | 15.26019 |
| H | -1.25757 | 4.93094 | 15.94787 |
| C | -0.60967 | 4.92306 | 13.90963 |
| H | -1.60911 | 5.12276 | 13.49956 |
| C | 0.47802 | 4.72632 | 13.02366 |
| C | 1.72017 | 4.44073 | 13.61543 |
| C | 2.87464 | 4.19923 | 12.76067 |
| C | 2.71040 | 4.24923 | 11.36598 |
| C | 3.85757 | 3.95809 | 10.58816 |
| H | 3.77686 | 3.94187 | 9.49251 |
| C | 5.04207 | 3.66746 | 11.20619 |
| H | 5.91606 | 3.38540 | 10.61187 |
| C | 5.14078 | 3.68140 | 12.63622 |
| C | 6.42906 | 3.40014 | 13.28758 |
| C | 7.62060 | 3.61207 | 12.56106 |
| H | 7.55861 | 4.06927 | 11.56444 |
| C | 8.87181 | 3.31715 | 13.06976 |
| H | 9.77556 | 3.52389 | 12.48427 |
| C | 8.95310 | 2.76714 | 14.36455 |
| H | 9.93522 | 2.52528 | 14.79475 |
| C | 7.81549 | 2.55185 | 15.10799 |
| H | 7.86013 | 2.14571 | 16.12559 |
| C | 6.50188 | 2.88075 | 14.62988 |
| C | 0.35249 | 4.78529 | 11.59456 |
| H | -0.62992 | 5.01891 | 11.16400 |

| | | | |
|---|---|---|---|
| C | 1.42789 | 4.55234 | 10.79566 |
| H | 1.33625 | 4.58639 | 9.70224 |
| O | 4.56569 | 5.81286 | 16.02977 |
| H | 5.17444 | 5.83309 | 16.77800 |

**Zn-$HCO_3^-$ (single Zn-O')**

Energy: -3226.1664909

| | | | |
|---|---|---|---|
| C | 6.53499 | 2.73952 | 14.67419 |
| C | 6.47536 | 3.30553 | 13.35277 |
| C | 7.67557 | 3.50787 | 12.63674 |
| C | 8.91375 | 3.13659 | 13.12665 |
| C | 8.97283 | 2.51295 | 14.38773 |
| C | 7.82843 | 2.31914 | 15.12745 |
| C | 5.19604 | 3.64212 | 12.70438 |
| C | 5.11158 | 3.70295 | 11.27564 |
| C | 3.93642 | 4.04003 | 10.66400 |
| C | 2.78774 | 4.31505 | 11.44479 |
| C | 2.93686 | 4.20336 | 12.83516 |
| N | 4.10374 | 3.87155 | 13.42879 |
| C | 1.78585 | 4.44431 | 13.69065 |
| C | 0.55816 | 4.78343 | 13.10307 |
| C | 0.44224 | 4.89592 | 11.67635 |
| C | 1.51771 | 4.67073 | 10.87700 |
| C | -0.52948 | 4.98338 | 13.98732 |
| C | -0.34591 | 4.85232 | 15.33556 |
| C | 0.94459 | 4.52591 | 15.86356 |
| N | 1.95542 | 4.31746 | 15.02382 |
| Zn | 4.01671 | 3.86348 | 15.63123 |
| O | 4.72062 | 5.64548 | 16.11218 |
| C | 4.39048 | 6.65884 | 15.38077 |
| O | 4.95263 | 7.83303 | 15.82604 |
| C | 1.13732 | 4.39697 | 17.31852 |
| C | 2.19448 | 3.59724 | 17.87771 |
| C | 2.18137 | 3.43123 | 19.30124 |
| C | 1.26373 | 4.05989 | 20.11242 |
| C | 0.27601 | 4.89874 | 19.56115 |
| C | 0.22861 | 5.04057 | 18.18652 |
| O | 3.11768 | 3.01596 | 17.19413 |
| O | 5.52236 | 2.56800 | 15.44913 |
| O | 3.67395 | 6.68663 | 14.39186 |
| H | 2.97279 | 2.79194 | 19.71064 |
| H | 1.31607 | 3.91749 | 21.20110 |
| H | -0.43407 | 5.43343 | 20.20227 |
| H | -0.52609 | 5.71254 | 17.75820 |
| H | -1.19302 | 4.96362 | 16.01772 |
| H | -1.51911 | 5.22776 | 13.57773 |
| H | 3.86704 | 4.08448 | 9.56844 |
| H | 5.98778 | 3.44496 | 10.67465 |
| H | 7.63231 | 4.01634 | 11.66535 |
| H | 9.82424 | 3.33187 | 12.54887 |
| H | 9.94202 | 2.19264 | 14.79541 |

| | | | |
|---|---|---|---|
| H | 7.85403 | 1.85723 | 16.12114 |
| H | -0.53207 | 5.16713 | 11.24970 |
| H | 1.43787 | 4.75577 | 9.78529 |
| H | 5.46903 | 7.56729 | 16.60022 |

**Zn-$HCO_3^-$ (double Zn-O')**

Energy: -3226.1577024

| | | | |
|---|---|---|---|
| C | -4.61913 | 0.73110 | -0.21551 |
| C | -3.30518 | 0.50580 | 0.24593 |
| C | -2.64646 | 1.50549 | 1.05306 |
| C | -3.44432 | 2.64634 | 1.40685 |
| C | -4.72763 | 2.82596 | 0.94452 |
| C | -5.33465 | 1.86995 | 0.10343 |
| C | -2.65923 | -0.78655 | -0.00638 |
| C | -3.44408 | -1.96621 | -0.21615 |
| C | -2.83786 | -3.18546 | -0.34142 |
| C | -1.42854 | -3.29148 | -0.23015 |
| C | -0.72399 | -2.09129 | -0.03612 |
| N | -1.33127 | -0.88917 | 0.03399 |
| C | -0.72872 | -4.54341 | -0.27511 |
| C | 0.62021 | -4.58395 | -0.11024 |
| C | 1.36760 | -3.37742 | 0.10292 |
| C | 0.72255 | -2.12924 | 0.13287 |
| N | 1.37026 | -0.95799 | 0.32150 |
| C | 2.69730 | -0.93134 | 0.43474 |
| C | 3.41424 | -2.17393 | 0.49458 |
| C | 2.76508 | -3.36381 | 0.32645 |
| C | 3.43610 | 0.34409 | 0.50284 |
| C | 2.79559 | 1.60752 | 0.76227 |
| C | 3.65715 | 2.74903 | 0.89242 |
| C | 5.01748 | 2.68201 | 0.70873 |
| C | 5.62973 | 1.45573 | 0.38341 |
| C | 4.83513 | 0.32954 | 0.29128 |
| O | 1.53392 | 1.79121 | 0.90511 |
| Zn | -0.01134 | 0.87001 | 0.09266 |
| O | 0.60603 | 0.42339 | -2.02439 |
| C | -0.20991 | 1.32722 | -2.26281 |
| O | -0.46325 | 1.69588 | -3.54449 |
| O | -1.43904 | 1.42000 | 1.47244 |
| O | -0.84476 | 1.93865 | -1.34403 |
| H | -2.95124 | 3.39240 | 2.04168 |
| H | -5.27954 | 3.73503 | 1.22313 |
| H | -6.34522 | 2.02534 | -0.29148 |
| H | -5.08025 | -0.01100 | -0.88176 |
| H | -4.53517 | -1.88795 | -0.22996 |
| H | -3.43458 | -4.09543 | -0.49324 |
| H | 3.31496 | -4.31393 | 0.37042 |
| H | 4.48627 | -2.17279 | 0.70309 |
| H | 5.32119 | -0.60882 | 0.00118 |
| H | 6.70744 | 1.39303 | 0.19427 |
| H | 5.62471 | 3.59341 | 0.80095 |

| | | | |
|---|---|---|---|
| H | 3.15157 | 3.69394 | 1.12468 |
| H | -1.30646 | -5.46301 | -0.43567 |
| H | 1.16321 | -5.53789 | -0.13300 |
| H | -1.12674 | 2.39738 | -3.46632 |

**Zn-OH$^-$□□□$CO_2$ TS**

Energy: -3226.1401996

| | | | |
|---|---|---|---|
| C | 2.73754 | -1.81307 | -0.74538 |
| C | 3.37364 | -0.60041 | -0.29971 |
| C | 4.71055 | -0.64608 | 0.15112 |
| C | 5.46446 | -1.80480 | 0.14586 |
| C | 4.87400 | -2.98260 | -0.35342 |
| C | 3.56735 | -2.98288 | -0.78598 |
| C | 2.68740 | 0.70087 | -0.35772 |
| C | 3.45166 | 1.90788 | -0.46332 |
| C | 2.82667 | 3.12337 | -0.51102 |
| C | 1.41323 | 3.19094 | -0.47553 |
| C | 0.73208 | 1.96554 | -0.40243 |
| N | 1.35805 | 0.77080 | -0.34315 |
| C | -0.72278 | 1.96572 | -0.39751 |
| C | -1.40692 | 3.18957 | -0.45989 |
| C | -0.67724 | 4.42488 | -0.51968 |
| C | 0.68168 | 4.42551 | -0.52932 |
| C | -2.82103 | 3.11984 | -0.47884 |
| C | -3.44374 | 1.90324 | -0.43735 |
| C | -2.67570 | 0.69698 | -0.35278 |
| N | -1.34674 | 0.77086 | -0.34104 |
| Zn | 0.00108 | -0.99241 | -0.15548 |
| O | 1.51273 | -1.90463 | -1.12060 |
| C | -3.35464 | -0.60809 | -0.31755 |
| C | -2.71211 | -1.80413 | -0.79672 |
| C | -3.53145 | -2.97923 | -0.86027 |
| C | -4.83455 | -3.00024 | -0.41749 |
| C | -5.43139 | -1.83949 | 0.11229 |
| C | -4.68790 | -0.67378 | 0.13978 |
| O | -1.48859 | -1.87470 | -1.18368 |
| O | -0.03502 | -1.32132 | 1.72739 |
| C | -0.06492 | 0.24255 | 3.18201 |
| O | -0.05927 | 1.15526 | 2.44154 |
| O | -0.07590 | -0.37696 | 4.17975 |
| H | -3.04259 | -3.87688 | -1.25718 |
| H | -5.40598 | -3.93794 | -0.46379 |
| H | -6.45642 | -1.85721 | 0.49964 |
| H | -5.14403 | 0.22654 | 0.57227 |
| H | -4.53367 | 1.84033 | -0.49994 |
| H | -3.40497 | 4.04782 | -0.54913 |
| H | 3.40888 | 4.05126 | -0.59736 |
| H | 4.54051 | 1.84689 | -0.54378 |
| H | 5.16164 | 0.26849 | 0.55771 |
| H | 6.49273 | -1.80481 | 0.52483 |
| H | 5.45501 | -3.91474 | -0.38361 |

| | | | |
|---|---|---|---|
| H | 3.08674 | -3.89194 | -1.16730 |
| H | -1.24111 | 5.36595 | -0.55439 |
| H | 1.24447 | 5.36731 | -0.57390 |
| H | 0.07427 | -2.21651 | 2.06584 |

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