Supporting information for:
Multiscale Modelling of Lytic Polysaccharide Monoxygenases

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1 Coordinates for optimised structures

Coordinates for structures of 1, 2 and 3 (all with protein "free") are given below.

Cu rest state (1) TPSS-D3/def2-SV(P); Energy=-3169.58248468946
N 1.8469642 -12.3296119 -2.7479741
H 1.4433474 -11.5072242 -2.2679424
H 1.2081462 -12.5401947 -3.5381929
C 3.1279736 -11.9299209 -3.3706337
H 3.7279360 -11.4201661 -2.6056435
C 3.8985958 -13.1821511 -3.8317212
H 3.2045756 -13.9120662 -4.2895438
H 4.6446384 -12.9083600 -4.5918828
C 4.5926935 -13.7141658 -2.6177426
N 3.9130962 -13.8275617 -1.4100055
C 4.8223496 -14.0849295 -0.4664342
H 4.6261972 -14.2355491 0.5929180

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Cu rest state (1) TPSS-D3/def2-TZVPD; Energy = -3171.43914365641

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| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | 3.5397849 | -7.7122130 | -4.7994223 |
| H    | -4.4115477 | -13.4202406 | -1.8576020 |
| C    | -3.5298457 | -12.8863723 | -2.2651870 |
| H    | -3.7278479 | -12.6750830 | -3.3180825 |
| H    | -3.4348200 | -11.9428032 | -1.7350808 |
| C    | -2.2402838 | -13.6271047 | -2.0747593 |
| N    | -1.9746034 | -14.9548602 | -2.4042364 |
| H    | -2.6205902 | -15.6559061 | -2.7717990 |
| C    | -0.6640027 | -15.2102413 | -2.1666118 |
| H    | -0.2014138 | -16.1671415 | -2.3489107 |
| N    | -0.0703144 | -14.1230453 | -1.6857673 |
| C    | -1.0386164 | -13.1352624 | -1.6240432 |
| H    | -0.8116526 | -12.1361592 | -1.2845273 |
| H    | 1.4196020  | -5.9053769  | 0.9033237  |
| C    | 1.1417294  | -6.5118846  | -0.0058788 |
| H    | 0.1054458  | -6.2635473  | -0.2511592 |
| H    | 1.7731817  | -6.1774304  | -0.8323069 |
| C    | 1.2855600  | -8.0140251  | 0.1755153  |
| C    | 0.3402002  | -8.7725301  | 0.8840737  |
| H    | -0.5113290 | -8.2845081  | 1.3455951  |
| C    | 0.4196911  | -10.1637775 | 0.9632179  |
| H    | -0.3464294 | -10.7142412 | 1.4956716  |
| C    | 1.4807684  | -10.8358299 | 0.3556425  |
| O    | 1.6279153  | -12.2203035 | 0.3945516  |
| H    | 1.1195877  | -12.6548768 | 1.1230476  |
| C    | 2.4307878  | -10.1013723 | -0.3559634 |
| H    | 3.2707353  | -10.6052489 | -0.8184196 |
| C    | 2.3191578  | -8.7130299  | -0.4582072 |
| H    | 3.0480482  | -8.1769360  | -1.0568928 |
| Cu   | 1.9152197  | -13.8962450 | -1.4073737 |
| O    | 2.4797948  | -16.3747144 | -2.9947568 |
| H    | 3.3941213  | -16.5420302 | -3.3080374 |
| H    | 1.9018336  | -16.8368215 | -3.6320671 |
| O    | 1.8902399  | -15.7454698 | -0.5052800 |
| H    | 2.1693894  | -16.2444192 | -1.3286972 |
| H    | 2.6075549  | -15.9133161 | 0.1402913 |

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Cu rest state (1) B3LYP-D3/def2-TZVPD; Energy = -3170.35495089520
N 1.8234746  -12.3680849  -2.7053875
H 1.4087166  -11.5644343  -2.2349587
H 1.2043436  -12.5775863  -3.4917734
C 3.0977993  -11.4276987  -2.5558952
H 3.6781574  -11.4276987  -2.5558952
C 3.8935888  -13.1601377  -3.7839340
H 3.2313922  -13.8824588  -4.2658601
H 4.6317288  -12.8616038  -4.5229521
C 4.5803384  -13.7039209  -2.5827502
C 4.8041015  -14.1141165  -0.4508695
H 4.6119145  -14.2937292  0.5896720
N 6.0314115  -14.1446885  -0.9889370
C 7.2769116  -14.3876677  -0.2726159
H 7.9392572  -13.5359139  -0.4009389
H 7.0574278  -14.5229168  0.7821083
C 7.7546348  -15.2839108  -0.6629191
C 5.9052103  -13.8985079  -2.3382237
H 6.7471909  -13.8728898  -3.0006672
C 2.7359193  -10.9483579  -4.4081344
C 3.1836697  -8.6880521  -5.2243104
H 3.7023026  -8.9093471  -6.1625815
H 2.1231145  -8.6188811  -5.4752433
H 3.5373125  -7.7452027  -4.8144256
H -4.4097318  -13.4249342  -1.8511046
C -3.5272382  -12.8939265  -2.2540128
H -3.7217190  -12.6842307  -3.3054196
H -3.4379947  -11.9502077  -1.7289709
C -2.2418922  -13.6322273  -2.0571928
N -1.9756011  -14.9529227  -2.3904517
H -2.6172636  -15.6479136  -2.7682172
C -0.6721308  -15.2087712  -2.1451511
H -0.2064807  -16.1617327  -2.3288996
N -0.0865295  -14.1312187  -1.6546129
C -1.0499694  -13.1445088  -1.5934430
H -0.8277856  -12.1496481  -1.2474813
H 1.4244622  -5.9062597  0.8997087
C 1.1492561 -6.5129236 -0.0086527
H 0.1178430 -6.2616782 -0.2589042
H 1.7812312 -6.1759923 -0.8296865
C 1.2907657 -8.0115876 0.1715992
C 0.3512792 -8.7642207 0.8847637
H -0.4953735 -8.2745762 1.3469410
C 0.4301581 -10.1509471 0.9667343
H -0.3321488 -10.6981209 1.5019631
C 1.4789524 -10.8258698 0.3523398
O 1.6084813 -12.2043201 0.3898805
H 1.1221771 -12.6362298 1.1285689
C 2.4230344 -10.0969255 -0.3621991
H 3.2522167 -10.6015832 -0.8342172
C 2.3157347 -8.7127414 -0.4634828
H 3.0410642 -8.1816046 -1.0654270
H 0.4301581 -11.8932447 -1.3863176
O 2.4054677 -16.3517470 -2.9653515
H 3.3213719 -16.5055427 -3.2704687
H 1.8414047 -16.8075971 -3.6148119
O 1.8907283 -15.7193701 -0.4180382
H 2.1277444 -16.2662146 -1.2071619
H 2.5963092 -15.8968140 0.2318445

Cu rest state reduced (2) TPSS-D3/def2-SV(P); Energy = -3169.55536959113
N 1.4328883 -12.7082474 -3.2515454
H 0.7319083 -12.0205958 -2.9336259
H 1.1515812 -12.9094947 -4.2297969
C 2.7261940 -11.9986101 -3.3844216
H 2.9549400 -11.5370357 -2.4139662
C 3.8459487 -13.0157944 -3.7181182
H 3.4380151 -13.7867688 -4.4009217
H 4.6588032 -12.5038450 -4.2562420
C 4.3952496 -13.6199268 -2.4626829
N 3.5685632 -14.1250680 -1.4665036
C 4.3453630 -14.4464923 -0.4343682
H 3.9868220 -14.8872121 0.4956464
N 5.6492993 -14.1735563 -0.7159515
C 6.8150436 -14.4349450 0.1260011

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| Element | X    | Y    | Z    |
|---------|------|------|------|
| H       | 2.9766328 | -7.8540871 | -1.1463688 |
| Cu      | 1.6549335  | -14.2350920 | -1.8584410  |
| O       | 2.0446641  | -16.2925320 | -2.7686810  |
| H       | 3.0079258  | -16.4153668 | -2.9675865  |
| H       | 1.5734948  | -16.6330198 | -3.5701773  |
| O       | 1.6762460  | -15.9390215 | 0.6340391   |
| H       | 2.0740836  | -16.7185720 | 0.1791626   |
| H       | 1.6389558  | -15.2448171 | -0.0812378  |

Cu rest state reduced (2) TPSS-D3/def2-TZVPD; Energy = -3171.41970542255

| Element | X    | Y    | Z    |
|---------|------|------|------|
| N       | 1.4518795  | -12.5569806 | -2.3969150 |
| H       | 0.8607263  | -11.8274967 | -2.5896404 |
| H       | 1.0422381  | -12.7242411 | -3.9250836 |
| C       | 2.7726429  | -11.9500008 | -3.2866179 |
| H       | 3.1374917  | -11.4840643 | -2.3717127 |
| C       | 3.7731071  | -13.0516406 | -3.6960948 |
| H       | 3.2593557  | -13.7876408 | -4.3248501 |
| H       | 4.5738377  | -12.6124055 | -4.2927782 |
| C       | 4.3576620  | -13.663061 | -2.4701628 |
| N       | 3.5646664  | -14.1310903 | -1.4247010 |
| C       | 4.3834155  | -14.4374027 | -0.4220919 |
| H       | 4.0799152  | -14.8472948 | 0.5269126 |
| N       | 5.6699471  | -14.1966834 | -0.7712198 |
| C       | 6.8679691  | -14.4587173 | 0.0256963 |
| H       | 7.6246017  | -13.7172847 | -0.2351302 |
| H       | 6.6262530  | -14.3792375 | 1.3856859 |
| H       | 7.2484562  | -15.4600022 | -0.1878463 |
| C       | 5.6634839  | -13.7215611 | -2.0696781 |
| H       | 6.5709013  | -13.4459098 | -2.5731564 |
| C       | 2.5638067  | -10.9016727 | -4.3638365 |
| O       | 1.7223518  | -11.1477620 | -5.2550700 |
| N       | 3.2500574  | -9.7721754  | -4.2148003 |
| H       | 3.9654622  | -9.7312474  | -3.4875188 |
| C       | 3.1819819  | -8.6787669  | -5.1650009 |
| H       | 3.7657196  | -8.9556661  | -6.0552791 |
| H       | 2.1416995  | -8.5958663  | -5.5010710 |
| H       | 3.5281885  | -7.7220326  | -4.7742921 |
| H       | -4.5747623 | -13.7484169 | -1.6633652 |
Cu rest state reduced (2) TPSS-D3/def2-TZVPD; Energy = -3170.34397636151

C -3.6406902 -13.2497299 -1.9974077
H -3.7611716 -13.0137305 -3.0591930
H -3.5312648 -12.3083662 -1.4607505
C -2.4013138 -14.0500459 -1.7412383
N -2.1649674 -15.3727630 -2.1039470
H -2.8318568 -16.0464690 -2.4862243
C -0.8469450 -15.6459971 -1.9067516
H -0.3915412 -16.6055572 -2.0972774
N -0.2166899 -14.5669401 -1.4438190
C -1.1793540 -13.5812843 -1.3154943
H -0.9215834 -12.5864646 -0.9885996
H 1.3568830 -5.6369782 0.9889980
C 1.0243375 -6.2080773 0.0763648
H -0.0303502 -5.9677253 -0.0893382
H 1.5980606 -5.8317480 -0.7739382
C 1.2295656 -7.7013632 0.2003825
C 0.3695917 -8.5288237 0.9351793
H -0.4844098 -8.1052159 1.4562099
C 0.5498539 -9.9129543 0.9756184
H -0.1527960 -10.5348601 1.5206410
C 1.6138802 -10.5008618 0.2819418
O 1.8648273 -11.8489014 0.2621185
H 1.3427628 -12.3508604 0.9421264
C 2.4756091 -9.6849037 -0.4548784
H 3.3083998 -10.1236831 -0.9893340
C 2.2774881 -8.3104105 -0.4985934
H 2.9415331 -7.7073426 -1.1104894
Cu 1.6578409 -14.1794392 -1.6988879
O 2.1370433 -16.2630640 -3.0642606
H 3.0776232 -16.4187776 -3.2909918
H 1.6326875 -16.6454516 -3.8079749
O 1.5269784 -16.1658296 0.5911254
H 1.9566883 -16.9961598 0.3109866
H 1.6589284 -15.5422320 -0.1688133

Cu rest state reduced (2) TPSS-D3/def2-TZVPD; Energy = -3170.34397636151
N 1.4708637 -12.4326396 -2.8815355
H 0.9456715 -11.6711615 -2.4585312

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H  1.5945670 -5.8526749 -0.7742669
C  1.2259325 -7.7177255  0.2018967
C  0.3607101 -8.5346011  0.9333392
H  -0.4913716 -8.1044462  1.4441411
C  0.5346669 -9.9146355  0.9854436
H  -0.1693378 -10.5271767  1.5318353
C  1.5968619 -10.5105193  0.3066924
O  1.8391345 -11.8521401  0.3049413
H  1.3271570 -12.3503024  0.9850050
C  2.4628765 -9.7052672 -0.4273166
H  3.2946912 -10.1496269 -0.9502676
C  2.2719703 -8.3343070 -0.4831205
H  2.9414129 -7.7417936 -1.0930135
Cu 1.6655518 -14.0703809 -1.5564497
O  2.1274421 -16.3191042 -3.0521886
H  3.0660733 -16.4608818 -0.4831205
H  1.6361888 -16.7084277 -3.7936244
O  1.5312333 -16.1941692  0.6161967
H  1.7124455 -15.5711483 -0.1129353

Cu-O2 equatorial (3eq, triplet) TPSS-D3/def2-SV(P); Energy = -3396.13661038825
N  1.7007705 -12.6433672 -2.8683847
H  1.1836240 -11.8938933 -2.3839948
H  1.1492279 -12.8485644 -3.7207687
C  2.9786489 -12.0763589 -3.3605922
H  3.4827434 -11.5848783 -2.5162722
C  3.8875948 -13.2282612 -3.8415739
H  3.2785008 -13.9765587 -4.3821671
H  4.6552776 -12.8383695 -4.5271160
C  4.5605421 -13.8167130 -2.6413828
N  3.8524187 -14.1444962 -1.4924969
C  4.7436810 -14.4521915 -0.5556645
H  4.4936948 -14.7891798  0.4496232
N  6.0069615 -14.3432953 -1.0443662
C  7.2420927 -14.5951785 -0.3084346
H  6.9882058 -14.8239505  0.7382713
H  7.7795591 -15.4520205 -0.7525853

Cu-02 equatorial (3eq, triplet) TPSS-D3/def2-SV(P); Energy = -3396.13661038825
N  1.7007705 -12.6433672 -2.8683847
H  1.1836240 -11.8938933 -2.3839948
H  1.1492279 -12.8485644 -3.7207687
C  2.9786489 -12.0763589 -3.3605922
H  3.4827434 -11.5848783 -2.5162722
C  3.8875948 -13.2282612 -3.8415739
H  3.2785008 -13.9765587 -4.3821671
H  4.6552776 -12.8383695 -4.5271160
C  4.5605421 -13.8167130 -2.6413828
N  3.8524187 -14.1444962 -1.4924969
C  4.7436810 -14.4521915 -0.5556645
H  4.4936948 -14.7891798  0.4496232
N  6.0069615 -14.3432953 -1.0443662
C  7.2420927 -14.5951785 -0.3084346
H  6.9882058 -14.8239505  0.7382713
H  7.7795591 -15.4520205 -0.7525853
Cu-O2 equatorial (3eq, singlet) TPSS-D3/def2-SV(P); Energy = -3396.1313136967

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Cu-O2 axial (3ax, triplet) TPSS-D3/def2-SV(P); Energy = -3396.11491775603
N 1.6940975 -12.6065113 -2.8633083
H 1.1433963 -11.8724424 -2.3912019
H 1.1627909 -12.8442186 -3.7227335
C 2.9642751 -12.0059055 -3.3428779
H 3.449897 -11.5050762 -2.4926902
C 3.9144503 -13.1128415 -3.8357588
H 3.3452455 -13.8703848 -4.4069523
H 4.6684192 -12.6785908 -4.5099061
C 4.6004313 -13.6947074 -2.6399849
N 3.9119219 -13.9340145 -1.4576591
C 4.8183611 -14.2843842 -0.5455871
H 4.6187964 -14.5622216 0.4881816
N 6.0655892 -14.2770140 -1.0816113
C 7.3130373 -14.5723320 -0.3818129
H 7.9977716 -13.7131638 -0.4733905
H 7.0866257 -14.7503389 0.6801217
H 7.7830222 -15.4703691 -0.8191733
C 5.9381326 -13.9176093 -2.4118843
H 6.7886781 -13.8398074 -3.0796141
C 2.6105148 -10.9675085 -4.4089352
O 1.7443589 -11.2463614 -5.2596437
N 3.2526410 -9.8001379 -4.2650603
C 3.1191919 -8.7006339 -5.2030646
H 3.6650849 -8.9639123 -6.1345399
H 2.0515764 -8.6172916 -5.4867402
H 3.4899073 -7.7368223 -4.8084877
H -4.5880530 -13.6353380 -1.7251188
C -3.6533466 -13.1272413 -2.0783920
H -3.7945290 -12.8923559 -3.1508462
H -3.5500183 -12.1720387 -1.5418968
C -2.3911869 -13.9033221 -1.8428769
N -2.1235701 -15.2153752 -2.2300753
H -2.7814160 -15.9039600 -2.6253846
C  -0.8027703  -15.4714383  -2.0172289
H   -0.3229865  -16.4139872  -2.2986043
N   -1.1763799  -13.4267024  -1.3756615
C   -0.9404838  -12.4263324  -1.0052743
H    1.4034838   -5.9465617   0.8785721
C    0.1012789   -6.5543855  -0.0331333
H    0.0467651   -6.3011655  -0.2557348
H    0.7169025   -6.2090998  -0.8841852
C    1.2581994  -10.3073834  -0.345126
C    0.3309661  -18.8304687  -0.8732219
N    2.3400146  -18.3461375  -1.3555877
C    0.4256032  -10.2300045  -0.9434469
H   -0.3399526  -10.7984553  -1.4814311
C    0.4828540  -10.9006094  -0.3023898
O    1.6343530  -12.2693742   0.2975456
H    1.1194223  -12.7307350  -0.0198805
C    2.4219864  -10.1397806  -0.4143513
H    3.2557135  -10.6449766  -0.9057627
C    2.2981041  -10.9006094  -0.3023898
O    0.8304687  -18.4856567  -0.5087086
H    0.3230385  -8.201534  -1.1208334
Cu   1.8899788  -14.1936669  -1.6214545
O    1.9570701  -15.5232190  -3.4813754
O    2.6195348  -16.6118015  -3.1664838
O    2.0067773  -16.9247207  -0.7524669
H    2.3502612  -16.5171439  -1.5954371
H    2.7171422  -16.1704336  -0.0767886
O    5.2015759  -16.8746941  -4.1290623
H    4.2143237  -16.8101716  -4.1500715
H    5.5599016  -16.0494176  -4.5410154
O    0.2951099  -17.7450436  -4.4717737
H    0.6637319  -16.8493840  -4.6308094
H    1.0808333  -18.3268346  -4.6823068

Cu-O2 axial (3ax, singlet) TPSS-D3/def2-SV(P); Energy = -3396.11317807983
N   1.7024507  -12.5829958  -2.8427256
H   1.1707988  -11.8401055  -2.3627180
H   1.1509227  -12.8233869  -3.6882976
2 Molecular orbital plots
Figure S1: Selected molecular orbitals for \( 3_{\text{eq}} \). Orbitals marked with “(L)” are mainly centered on the ligands and are not shown.
Figure S2: Selected molecular orbitals for $3_{\text{ax}}$. Orbitals marked with “(L)” are mainly centered on the ligands and are not shown.