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

Supporting Information

A complex of cobalamin with an organic peroxide

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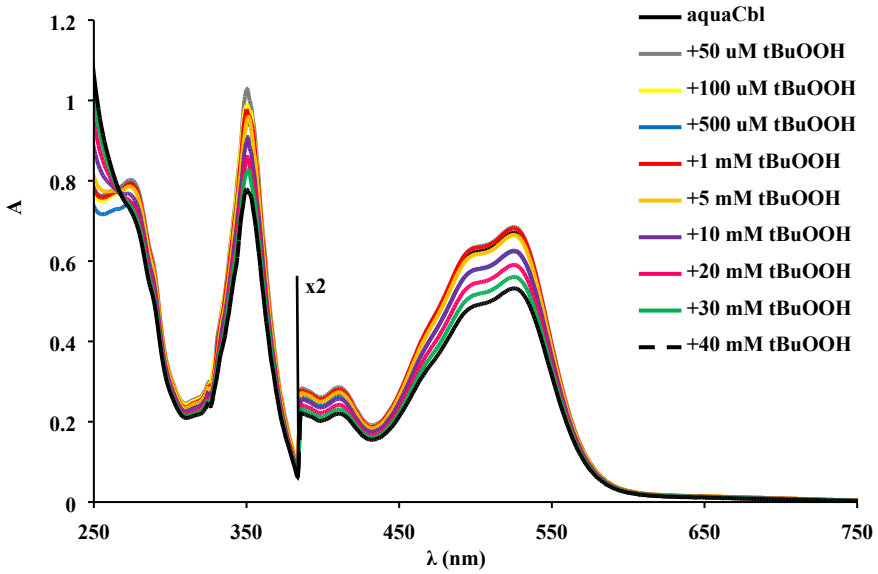


Figure S1. UV-vis spectra of 50 µM aquaCbl treated with at tBuOOH at pH 7, room temperature.

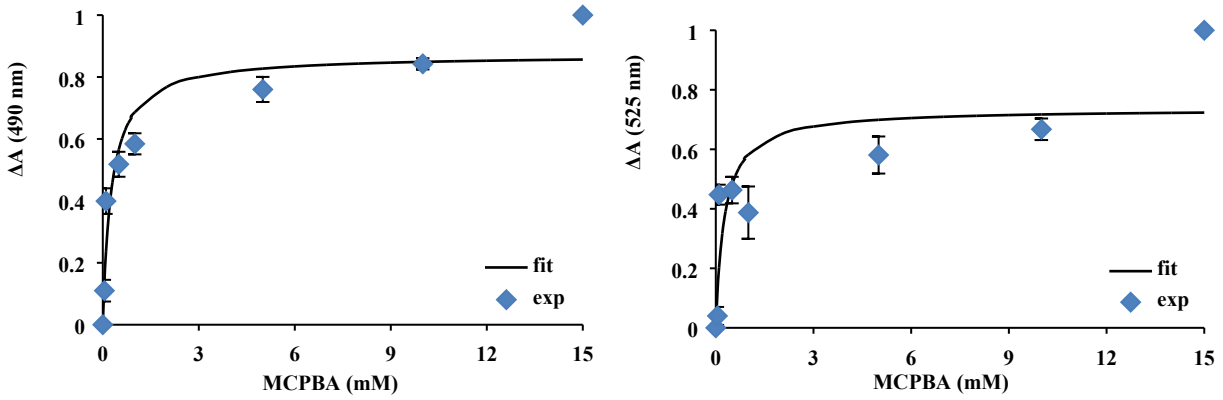


Figure S2. Titration curves for aquaCbl reacting with MCPBA at pH 7, monitored at 490 nm and 525 nm.

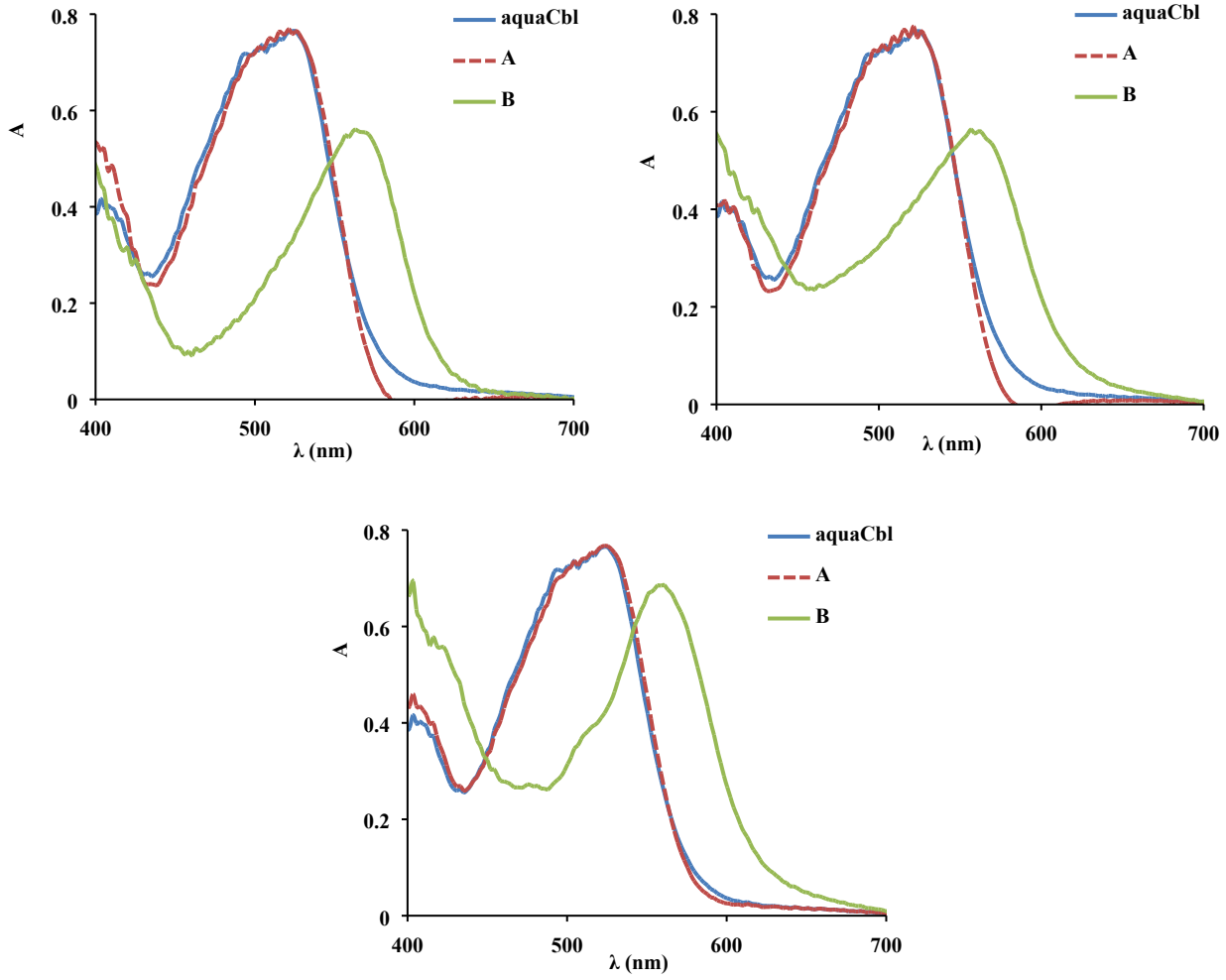


Figure S3. Representative spectra of species A and B at pH 7, room temperature, resulted from fitting of the stopped-flow data upon reaction of 0.3 mM aquaCbl with 25 mM MCPBA (upper left), 75 mM MCPBA (upper right) and 100 mM MCPBA (bottom).

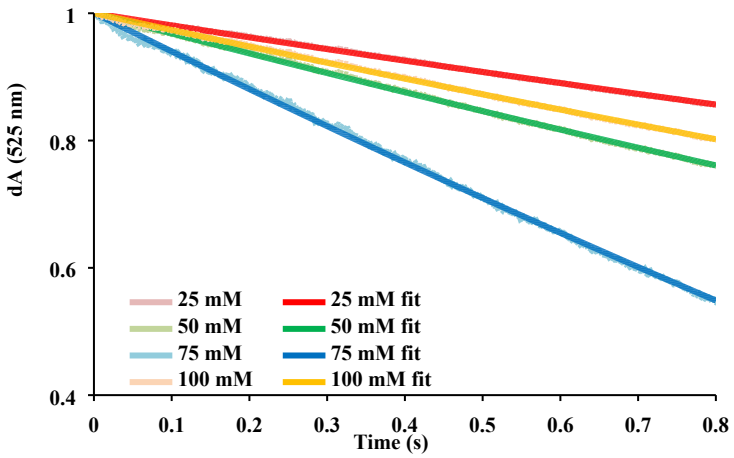


Figure S4. Absorbance time course from stopped-flow UV-vis experiments at varying MCPBA concentrations monitored at 525 nm.

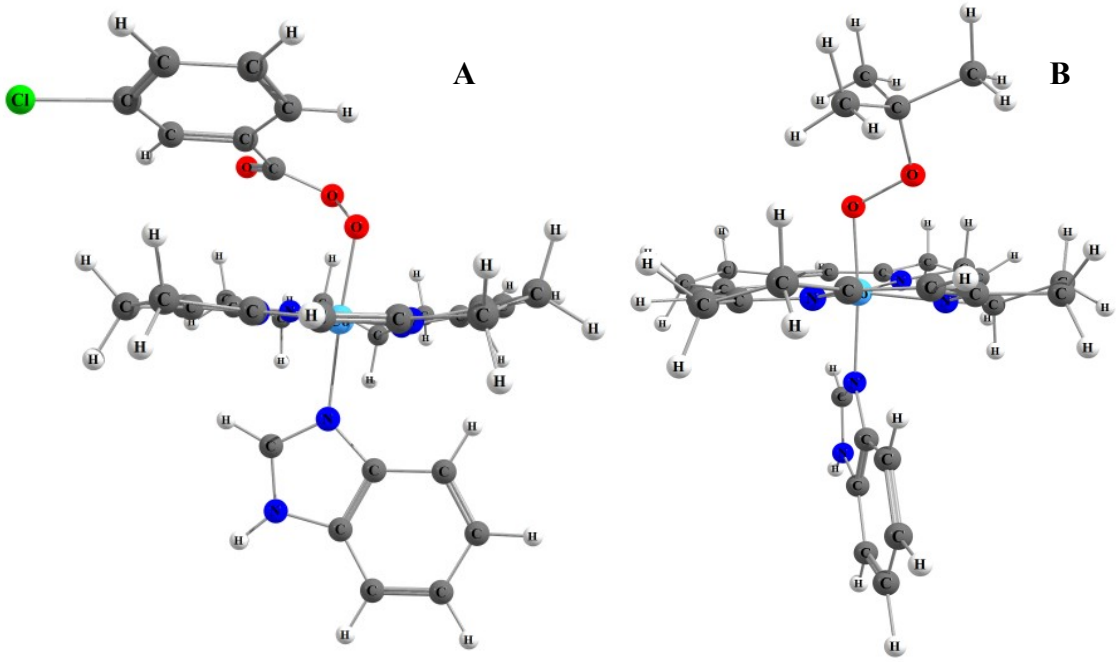


Figure S5. DFT-optimized geometries for Cbl-MCPBA (A) and Cbl-tBuOOH (B) complexes.

Table S1. DFT-derived data (key bond lengths in Å, and relative energies in kcal/mol, where applicable) of Cbl-MCPBA and Cbl-tBuOOH models.

ligand	**dE**	**Co-L**	**O-O**	**O-C**	**Co-DMBZ**
MCPBA, bound via Cl	1.4	3.19	1.45	1.38	1.91
MCPBA, bound via O	0.0	2.07	1.46	1.38	1.92
$MCPBA^-$		1.91	1.44	1.35	2.00
tBuOOH		2.01	1.48	1.47	1.94
$tBuOO^-$		1.88	1.47	1.44	2.02

Table S2. TD-DFT-derived wavelengths (nm) and oscillator strengths (OS) for $Cbl\text{-}MCPBA^-$ and $Cbl\text{-}tBuOO^-$ models; the two most intense bands above 300 nm are reported.

MCPBA		tBuOOH	
nm	OS	nm	OS
312	0.2217	311	0.2573
439	0.1247	444	0.1091

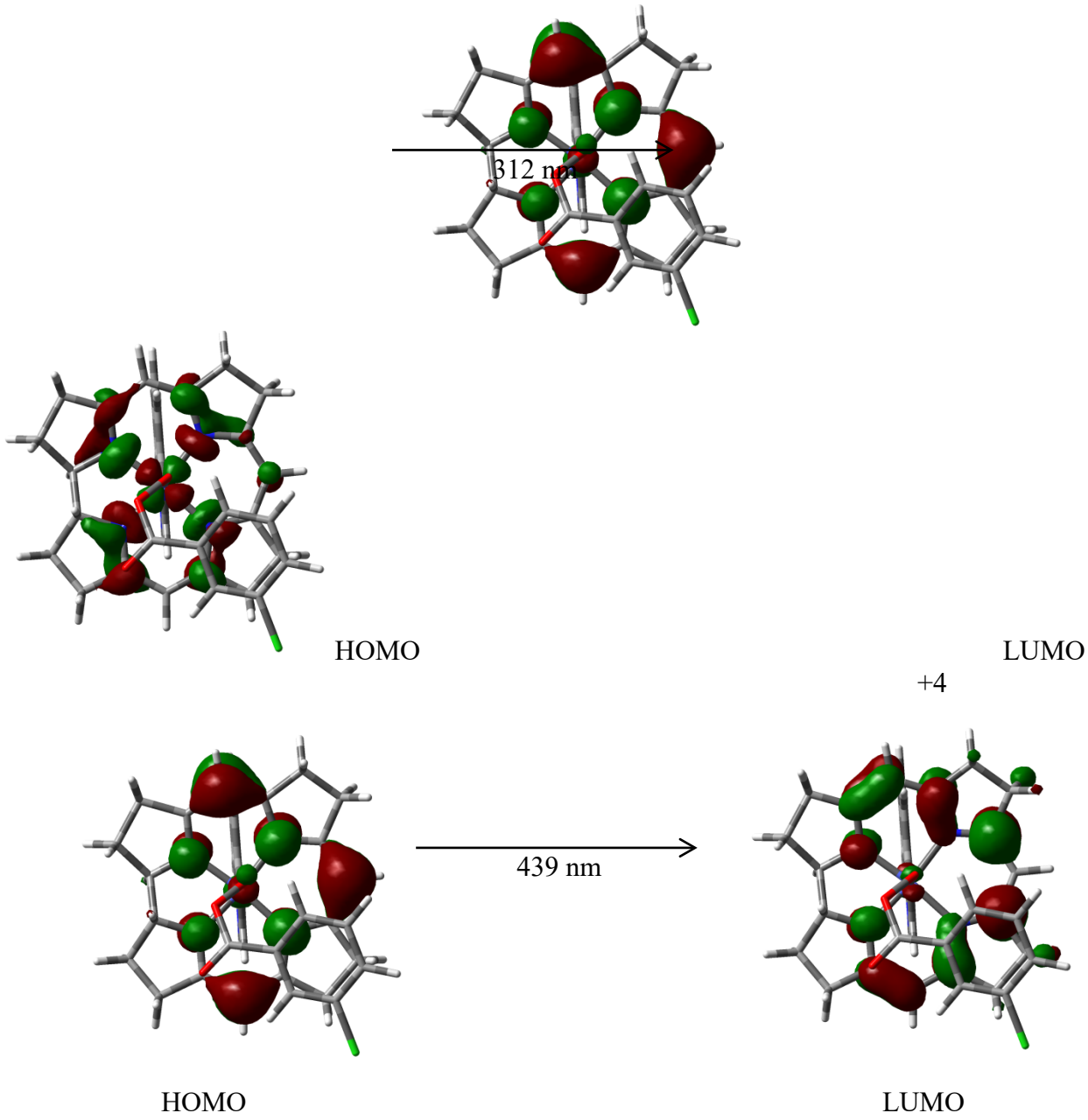


Figure S6. The main orbitals responsible for the main contributors to the two main bands in the TD-DFT spectra in MCPBA cf. B3PW91 calculations.

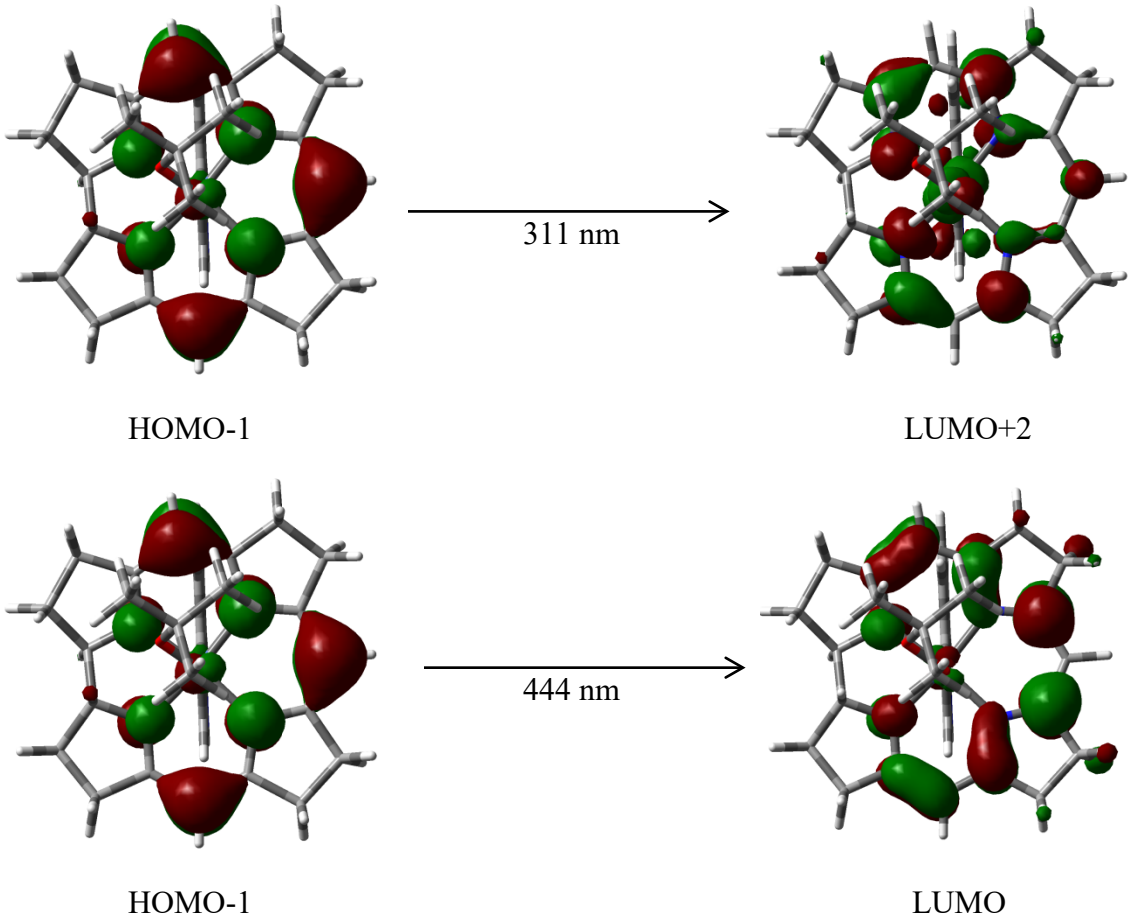
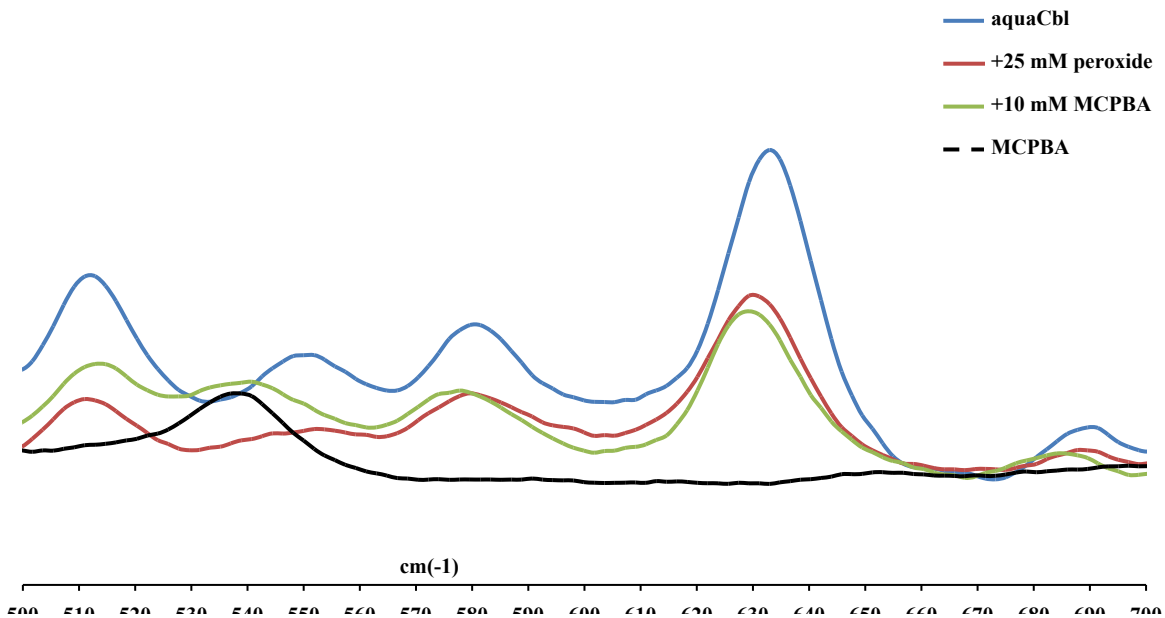
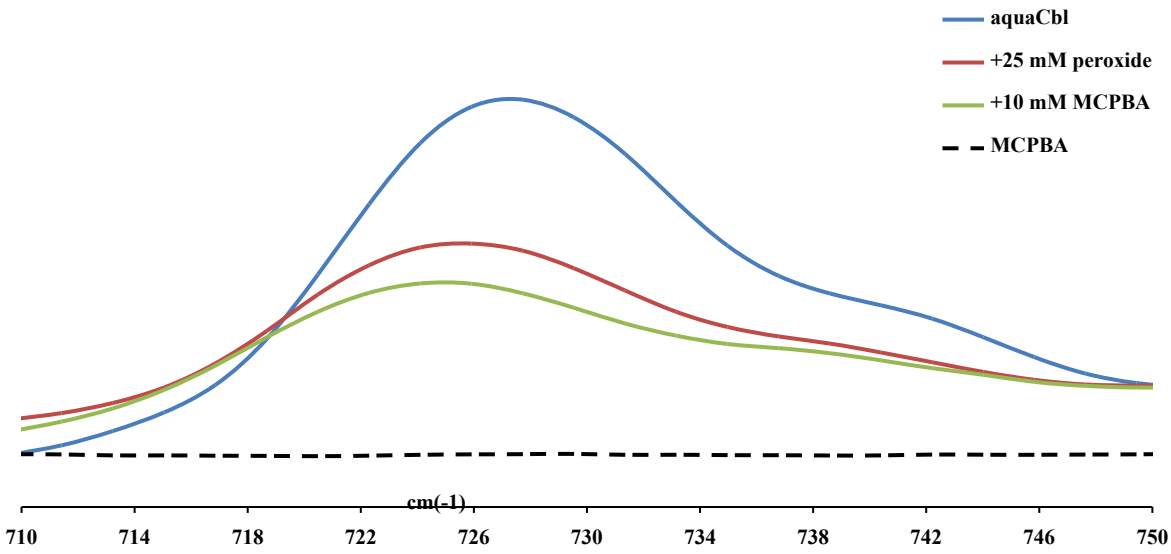


Figure S7. The main orbitals responsible for the main contributors to the two main bands in the TD-DFT spectra in tBuOOH cf. B3PW91 calculations.


aquaCbl
+25 mM peroxide
+10 mM MCPBA
MCPBA
cm(-1)


aquaCbl
+25 mM peroxide
+10 mM MCPBA
MCPBA
cm(-1)
710
714
718
722
726
730
734
738
742
746
750

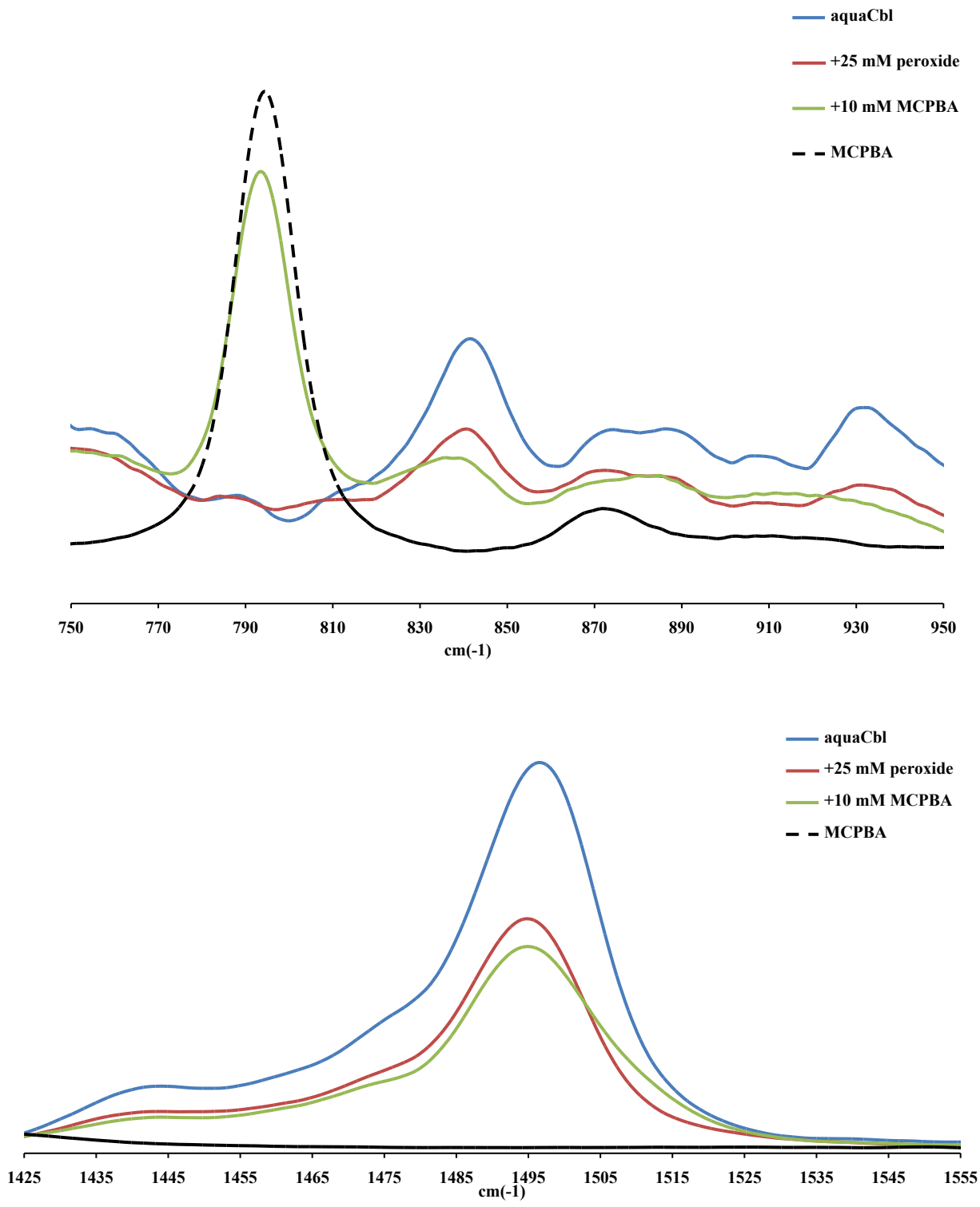


Figure S8. Details of resonance Raman spectra of Cbl in the presence or absence of hydrogen peroxide or MCPBA. Conditions: 1 mM aquaCbl, 25 mM H_2O_2, 10 mM MCPBA, 50 mM phosphate pH 7, 22°C.

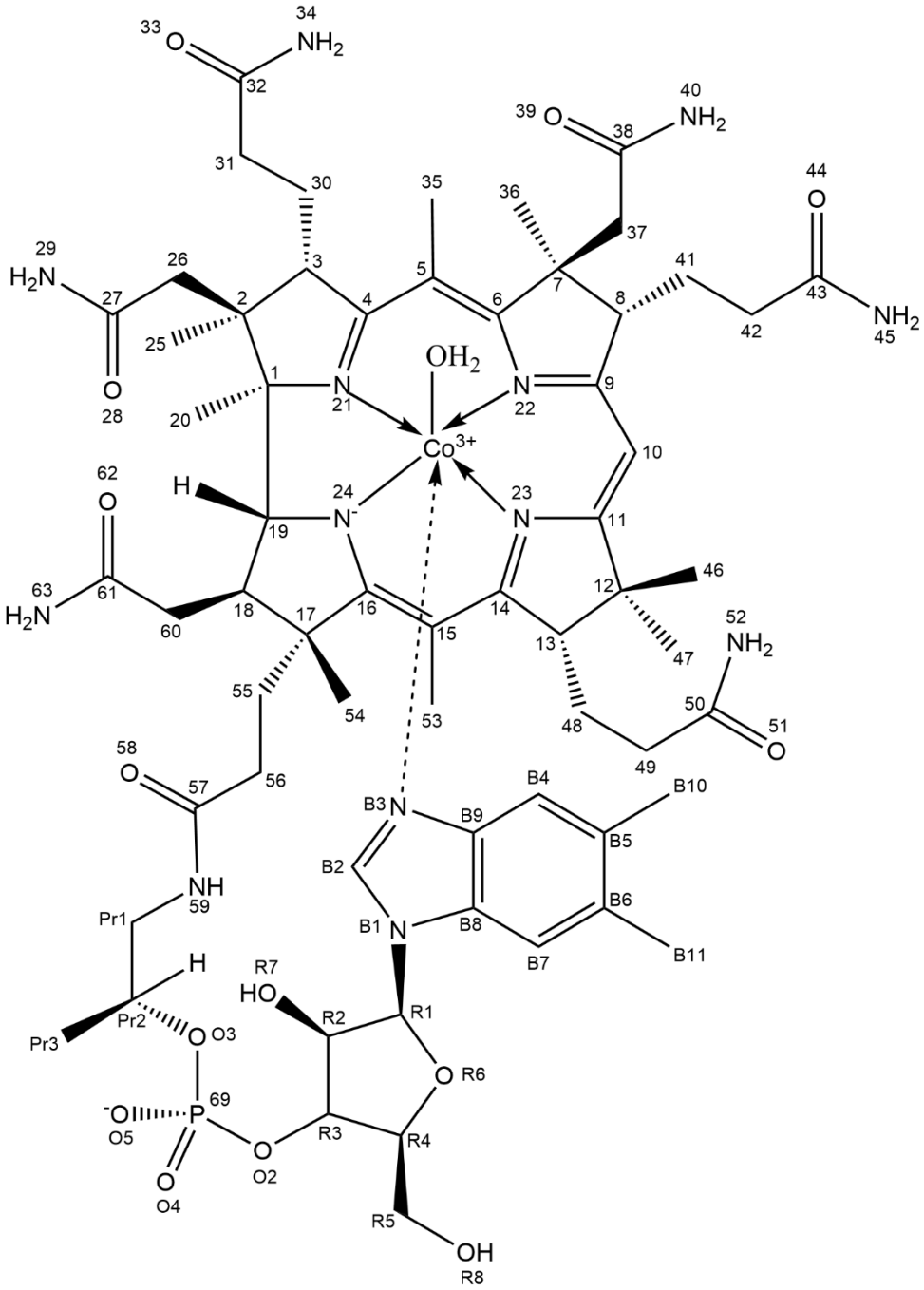


Figure S9. Cbl structure with atom numbering/labeling employed for ^{1}H-NMR assignments. Standard labels are used, including "B" for the dimethylimidazole atoms, "R" for the ribose atoms, and "Pr" for the side-chain propyl group; for all other atoms, the label includes the chemical symbol be default (e.g., B2, R1, C10). Protons are referred to by the name of the atoms to which they are connected to. Hydrogen atoms bound to carbon are not shown explicitly, except for cases where their stereochemistry needs to be emphasized.

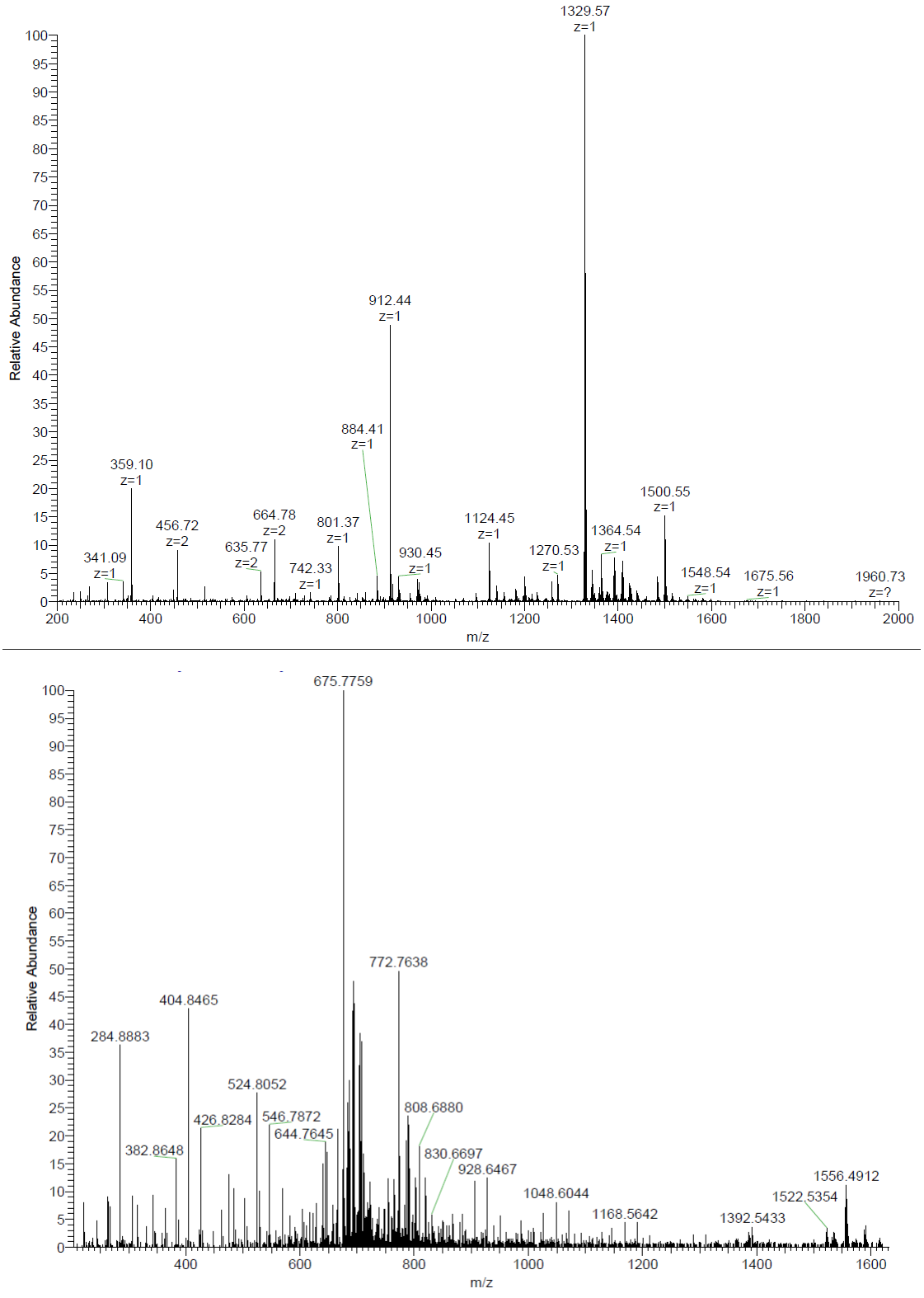


Figure S10. ESI(+)-HRMS (*m/z)* for the Cbl-MCPBA adduct after 4 minutes (upper panel) and 30 minutes (lower panel) from mixing. Conditions: 1 mM H_2OCbl^+, 10 mM MCPBA, 50 mM

phosphate pH 7. Samples were prepared at room temperature; vaporizer temperature 50 °C, capillary temperature 275 °C, analyzer temperature 26 °C.

Cbl-MCPBA, bound via O

```
HETATM    1 Co        0      0.584   0.122   0.217              Co
HETATM    2  N        0      1.927   1.066   1.167              N
HETATM    3  N        0      1.016  -1.536   1.138              N
HETATM    4  N        0     -0.839  -0.654  -0.885              N
HETATM    5  N        0      0.186   1.855  -0.442              N
HETATM    6  C        0      2.198   2.443   0.724              C
HETATM    7  C        0      2.852   3.098   1.956              C
HETATM    8  C        0      3.394   1.894   2.762              C
HETATM    9  C        0      2.543   0.748   2.263              C
HETATM   10  C        0      2.456  -0.550   2.856              C
HETATM   11  C        0      1.746  -1.587   2.308              C
HETATM   12  C        0      1.635  -2.967   2.921              C
HETATM   13  C        0      0.922  -3.782   1.831              C
HETATM   14  C        0      0.420  -2.713   0.888              C
HETATM   15  C        0     -0.564  -2.937  -0.076              C
HETATM   16  C        0     -1.173  -1.957  -0.859              C
HETATM   17  C        0     -2.345  -2.240  -1.768              C
HETATM   18  C        0     -2.543  -0.914  -2.516              C
HETATM   19  C        0     -1.618   0.038  -1.787              C
HETATM   20  C        0     -1.547   1.388  -2.032              C
HETATM   21  C        0     -0.668   2.269  -1.328              C
HETATM   22  C        0     -0.626   3.777  -1.443              C
HETATM   23  C        0      0.720   4.118  -0.762              C
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HETATM 24 N 0 2.650 -0.214 -3.399 N

HETATM 25 C 0 3.691 -0.710 -2.631 C

HETATM 26 C 0 1.616 0.065 -2.570 C

HETATM 27 N 0 1.897 -0.215 -1.310 N

HETATM 28 C 0 3.205 -0.707 -1.301 C

HETATM 29 C 0 4.034 -1.153 -0.260 C

HETATM 30 C 0 5.314 -1.587 -0.590 C

HETATM 31 C 0 5.782 -1.587 -1.923 C

HETATM 32 C 0 4.976 -1.147 -2.969 C

HETATM 33 H 0 3.323 2.017 3.853 H

HETATM 34 H 0 0.104 -4.415 2.204 H

HETATM 35 H 0 -3.582 -0.556 -2.504 H

HETATM 36 H 0 1.543 4.068 -1.495 H

HETATM 37 H 0 6.794 -1.937 -2.136 H

HETATM 38 H 0 5.978 -1.939 0.203 H

HETATM 39 H 0 0.729 5.113 -0.296 H

HETATM 40 H 0 2.893 2.394 -0.137 H

HETATM 41 H 0 4.452 1.676 2.531 H

HETATM 42 H 0 1.618 -4.442 1.284 H

HETATM 43 H 0 -2.239 -0.984 -3.573 H

HETATM 44 H 0 3.692 -1.159 0.770 H

HETATM 45 H 0 5.330 -1.142 -4.002 H

HETATM 46 H 0 0.673 0.477 -2.920 H

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HETATM 48 H 0 2.987 -0.724 3.792 H

HETATM 49 H 0 -2.225 1.817 -2.770 H

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HETATM 56 H 0 2.083 3.622 2.543 H

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HETATM 58 H 0 -1.480 4.170 -0.864 H

HETATM 59 C 0 -2.397 1.684 1.318 C

HETATM 60 O 0 -2.719 2.800 0.984 O

HETATM 61 C 0 -3.280 0.487 1.155 C

HETATM 62 C 0 -4.242 0.555 0.138 C

HETATM 63 C 0 -3.224 -0.635 1.997 C

HETATM 64 C 0 -5.106 -0.521 -0.063 C

HETATM 65 H 0 -4.295 1.440 -0.495 H

HETATM 66 C 0 -4.124 -1.685 1.807 C

HETATM 67 H 0 -2.478 -0.679 2.788 H

HETATM 68 C 0 -5.063 -1.644 0.771 C

HETATM 69 H 0 -4.096 -2.552 2.471 H

HETATM 70 H 0 -5.758 -2.469 0.606 H

HETATM 71 Cl 0 -6.231 -0.478 -1.402 Cl

HETATM 72 O 0 -0.588 0.238 1.699 O

HETATM 73 O 0 -1.173 1.528 1.889 O

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HETATM   75  H         0      0.237   3.192   1.144                H
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CONECT   19   18    4   20
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CONECT   21   20    5   22
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CONECT 26 24 27 46

CONECT 27 26 28

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CONECT 31 30 32 37

CONECT 32 31 25 45

CONECT 33 8

CONECT 34 13

CONECT 35 18

CONECT 36 23

CONECT 37 31

CONECT 38 30

CONECT 39 23

CONECT 40 6

CONECT 41 8

CONECT 42 13

CONECT 43 18

CONECT 44 29

CONECT 45 32

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CONECT 64 62 68 71

CONECT 65 62

CONECT 66 63 68 69

CONECT 67 63

CONECT 68 66 64 70

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CONECT 70 68

CONECT 71 64

CONECT 72 1

CONECT 73 59

CONECT 74 5 6 23 75

CONECT 75 74

Cbl-tBuOOH

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HETATM 2 N 0 0.184 -1.061 -1.261 N

HETATM 3 N 0 -0.083 -1.013 1.478 N

HETATM 4 N 0 0.032 1.851 1.254 N

HETATM 5 N 0 0.505 1.421 -1.420 N

HETATM 6 C 0 0.242 -0.609 -2.661 C

HETATM 7 C 0 0.899 -1.790 -3.401 C

HETATM 8 C 0 0.638 -2.993 -2.466 C

HETATM 9 C 0 0.416 -2.328 -1.127 C

HETATM 10 C 0 0.423 -2.993 0.138 C

HETATM 11 C 0 0.182 -2.358 1.328 C

HETATM 12 C 0 0.184 -3.037 2.679 C

HETATM 13 C 0 -0.373 -1.954 3.617 C

HETATM 14 C 0 -0.306 -0.708 2.765 C

HETATM 15 C 0 -0.439 0.583 3.280 C

HETATM 16 C 0 -0.230 1.763 2.569 C

HETATM 17 C 0 -0.278 3.132 3.211 C

HETATM 18 C 0 0.178 4.068 2.081 C

HETATM 19 C 0 0.244 3.157 0.872 C

HETATM 20 C 0 0.478 3.593 -0.410 C

HETATM 21 C 0 0.654 2.705 -1.518 C

HETATM 22 C 0 1.111 3.085 -2.913 C

HETATM 23 C 0 0.861 1.781 -3.709 C

HETATM 24 C 0 0.996 0.719 -2.612 C

HETATM 25 N 0 -3.812 1.549 -0.669 N

HETATM 26 C 0 -4.154 0.211 -0.547 C

HETATM 27 C 0 -2.473 1.654 -0.483 C

HETATM 28 N 0 -1.908 0.485 -0.244 N

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HETATM 30 C 0 -2.933 -1.853 -0.110 C

HETATM 31 C 0 -4.151 -2.520 -0.208 C

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HETATM 33 C 0 -5.380 -0.454 -0.645 C

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HETATM 36 H 0 1.180 4.486 2.271 H

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HETATM 38 H 0 2.057 0.481 -2.414 H

HETATM 39 H 0 -6.290 -2.399 -0.538 H

HETATM 40 H 0 -4.175 -3.605 -0.081 H

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HETATM 63 C 0 3.903 -0.936 0.327 C

HETATM 64 C 0 3.545 -1.667 1.626 C

HETATM 65 H 0 2.912 -1.022 2.251 H

HETATM 66 H 0 2.995 -2.592 1.401 H

HETATM 67 H 0 4.454 -1.928 2.187 H

HETATM 68 C 0 4.753 0.308 0.606 C

HETATM 69 H 0 5.710 0.031 1.074 H

HETATM 70 H 0 4.964 0.839 -0.335 H

HETATM 71 H 0 4.215 0.993 1.275 H

HETATM 72 C 0 4.600 -1.875 -0.659 C

HETATM 73 H 0 4.820 -1.351 -1.602 H

HETATM 74 H 0 5.547 -2.241 -0.235 H

HETATM 75 H 0 3.960 -2.743 -0.883 H

END

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CONECT 5 1 21 24

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CONECT 42 6

CONECT 43 8

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CONECT 46 30

CONECT 47 33

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