Electronic Supplementary Information (ESI)

for

Selective Oxygenation of C-H and C=C Bonds with H_2O_2 by High-Spin Cobalt(II)-Carboxylate Complexes

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Table S1. Crystallographic data for **1**, **2'**, **3** and **4**.

	1	**2'**	**3**	**4**
Empirical formula	$C_{208}H_{196}B_4Co_4N_{16}O_8$	$C_{59}H_{55}BCoN_4O_3$	$C_{424.2}H_{399.3}B_8Co_8N_{32}O_{28}$	$C_{54}H_{53}BCoN_4O_3$
Formula weight	3326.76	937.81	6925.72	875.74
Temperature/K	293.15	293(2)	293.15	293(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	P-1	P-1
a/Å	21.6102(19)	16.5064(6)	18.507(5)	11.211(2)
b/Å	9.4202(8)	11.9166(4)	20.425(5)	14.094(3)
c/Å	21.831(2)	27.6323(8)	25.548(7)	14.988(3)
α/°	90	90	102.515(7)	86.897(4)
β/°	94.067(2)	119.470(2)	95.986(7)	88.338(4)
γ/°	90	90	106.785(7)	70.768(4)
Volume/Å^3	4433.1(7)	4732.0(3)	8881(4)	2232.6(8)
Z	1	4	1	2
D_{calc} (g/cm^3)	1.246	1.316	1.300	1.303
μ/mm^{-1}	0.432	0.415	0.437	0.434
F(000)	1748.0	1972.0	3649.0	874.0
Crystal size/mm^3	0.2 × 0.15 × 0.15	0.08 × 0.07 × 0.06	0.2 × 0.2 × 0.15	0.12 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.562 to 54.268	2.834 to 49.994	1.66 to 51.23	2.722 to 57.99
Index ranges	$-27 \le h \le 27$, $-11 \le k \le 12$, $-27 \le l \le 27$	$-19 \le h \le 19$, $-14 \le k \le 13$, $-32 \le l \le 32$	$-22 \le h \le 21$, $-24 \le k \le 24$, $-30 \le l \le 30$	$-14 \le h \le 15$, $-19 \le k \le 19$, $-18 \le l \le 18$
Reflections collected	48560	43892	62486	24996
Independent reflections	9765 [R_{int} = 0.0750, R_{sigma} = 0.0621]	8344 [R_{int} = 0.0398, R_{sigma} = 0.0286]	31871 [R_{int} = 0.1231, R_{sigma} = 0.2160]	10418 [R_{int} = 0.0273, R_{sigma} = 0.0414]
Data/restraints/ parameters	9765/0/544	8344/0/616	31871/6/2262	10418/162/856
Goodness-of-fit on F^2	1.040	1.035	1.081	1.071
Final R indexes [I>2σ (I)]	R_1 = 0.0436, wR_2 = 0.0943	R_1 = 0.0309, wR_2 = 0.0738	R_1 = 0.1287, wR_2 = 0.3226	R_1 = 0.0368, wR_2 = 0.0809

Table S2. Selected bond lengths (Å) and bond angles (°) of **1**.

Distance (Å)/ Angle (°)	**1**
Co1-O1	2.0525(14)
Co1-O2	2.2339(14)
Co1-N2	2.1216(17)
Co1-N3	2.1498(16)
Co1-N1	2.1635(17)
Co1-N4	2.2476(17)
O1-Co1-O2	61.55(5)
O1-Co1-N2	165.91(6)
O1-Co1-N3	111.99(6)
O1-Co1-N1	100.98(6)
O1-Co1-N4	99.32(6)
O2-Co1-N4	89.45(6)
N2-Co1-O2	104.36(6)
N2-Co1-N3	81.99(6)
N2-Co1-N1	77.64(6)
N2-Co1-N4	79.76(6)
N3-Co1-O2	170.05(6)
N3-Co1-N1	99.14(6)
N3-Co1-N4	84.10(6)
N1-Co1-O2	89.80(6)
N1-Co1-N4	156.45(6)

Table S3. Selected bond lengths (Å) and bond angles (°) of **2'**.

Distance (Å)/ Angle (°)	**2'**
Co1-O2	2.0111(11)
Co1-O1	2.1630(11)
Co1-N1	2.2032(14)
Co1-N2	2.1188(14)
Co1-N3	2.1713(14)
Co1-N4	2.2249(14)
O2-Co1-O1	75.78(4)
O2-Co1-N1	98.95(5)
O2-Co1-N2	168.15(5)
O2-Co1-N3	101.71(5)
O2-Co1-N4	109.58(5)
O1-Co1-N1	86.38(5)
O1-Co1-N3	91.85(5)
O1-Co1-N4	168.46(5)
N1-Co1-N4	82.71(5)
N2-Co1-O1	92.38(5)
N2-Co1-N1	79.45(5)
N2-Co1-N3	78.87(5)
N2-Co1-N4	81.97(5)
N3-Co1-N1	158.15(5)
N3-Co1-N4	96.88(5)

Table S4. Selected bond lengths (Å) and bond angles (°) of **3**.

Distance(Å)/ Angle(°)	**3**
Co1-O1	2.004(6)
Co1-O5	2.098(7)
Co1-N4	2.143(8)
Co1-N5	2.105(8)
Co1-N6	2.203(8)
Co1-N1	2.231(9)
O1-Co1-O5	77.1(3)
O1-Co1-N4	108.7(3)
O1-Co1-N5	165.9(3)
O1-Co1-N6	94.3(3)
O1-Co1-N1	109.8(3)
O5-Co1-N4	170.9(3)
O5-Co1-N5	92.1(3)
O5-Co1-N6	92.4(3)
O5-Co1-N1	89.3(3)
N4-Co1-N6	94.1(3)
N4-Co1-N1	82.1(3)
N5-Co1-N4	83.1(3)
N5-Co1-N6	76.9(3)
N5-Co1-N1	78.7(3)
N6-Co1-N1	155.6(3)

Table S5. Selected bond lengths (Å) and bond angles (°) of **4**.

Distance(Å)/ Angle(°)	**4**
Co1-N1	2.1136(14)
Co1-O2	2.097(6)
Co1-O1	2.306(6)
Co1-N3	2.1205(13)
Co1-N2	2.1733(14)
Co1-N4	2.1711(13)
N1-Co1-O1	179.07(12)
N1-Co1-N3	80.59(5)
N1-Co1-N2	99.59(5)
N1-Co1-N4	97.26(5)
O2-Co1-N1	121.02(14)
O2-Co1-O1	59.89(16)
O2-Co1-N3	157.51(14)
O2-Co1-N2	99.67(18)
O2-Co1-N4	93.23(18)
N3-Co1-O1	98.52(13)
N3-Co1-N2	81.06(5)
N3-Co1-N4	76.66(5)
N2-Co1-O1	79.98(19)
N4-Co1-O1	82.8(2)
N4-Co1-N2	149.35(5)

Table S6. Catalytic oxygenation of C-H and C=C bonds complexes **1**, **2** and **3** with hydrogen peroxide (100 equiv) and carboxylic acids (for complexes **2** and **3**).

Substrate (500 equiv)	Product(s)	TON of products		
		Complex **1**	Complex **2** + 15 equiv of sodium benzilate	Complex **3** + 6 equiv of sodium mandelate
9,10-Dihydroanthracene[a]	Anthracene Anthraquinone	1.7 ± 0.1 0.3 ± 0.03	1.2 ± 0.1 0.2 ± 0.02	1.1 ± 0.3 0.2 ± 0.03
Triphenylmethane[a]	Triphenylmethanol	2.5 ± 0.1	1.9 ± 0.5	2.2 ± 0.4
Toluene	Benzyl alcohol Benzaldehyde	1.4 ± 0.3 0.3 ± 0.06	1 ± 0.3 0.3 ± 0.08	1.1 ± 0.2 0.4 ± 0.03
Adamantane[a]	1-Adamantanol 2-Adamantanol	1.6 ± 0.1 0.2 ± 0.01	1.2 ± 0.4 0.2 ± 0.06	1.2 ± 0.2 0.1 ± 0.03
Cyclohexane	Cyclohexanol Cyclohexanone	0.4 ± 0.02 0.06 ± 0.01	0.3 ± 0.03 0.04 ± 0.01	0.3 ± 0.02 0.05 ± 0.01
Methyl cyclohexane	1-Methyl cyclohexanol 2-Methyl cyclohexanone	0.6 ± 0.02 0.07 ± 0.01	0.6 ± 0.03 0.04 ± 0.03	0.5 ± 0.01 0.06 ± 0.01
cis-1,2-Dimethyl cyclohexane	*cis*-1,2-Dimethylcyclohexanol	0.7 ± 0.01	0.5 ± 0.04	0.6 ± 0.02
cis-Decalin	*cis*-4-Decalol	0.9 ± 0.02	0.7 ± 0.01	0.8 ± 0.02
1-Octene	2-Hexyloxirane	3.5 ± 0.3	2.9 ± 0.2	2.8 ± 0.1
Cyclooctene	9-Oxabicyclo[6.1.0]nonane	3.8 ± 0.4	3.0 ± 0.4	3.1 ± 0.4
Styrene	2-Phenyloxirane Benzaldehyde	2.8 ± 0.3 0.7 ± 0.04	2.1 ± 0.5 0.5 ± 0.06	1.9 ± 0.3 0.3 ± 0.08
cis-2-Heptene	*cis*-2-Butyl-3-methyl oxirane *trans*-2-Butyl-3-methyl oxirane	2.9 ± 0.2 0.1 ± 0.04	2.3 ± 0.2 0.1 ± 0.02	2.6 ± 0.2 0.2 ± 0.03

Experimental conditions: 0.01 mmol complex, 100 equiv of H_2O_2 and 100 equiv of substrate in acetonitrile at 25°C. [a]10 equiv of substrate. Reaction time: 20 h. Turnover number TON (S^{Ox}) = mol of product/mol of catalyst.

Table S7. Optimized bond distances (Å) and angles (°) of **I**, **I-O2H** and **Co-O2H** and Mayer bond orders for selected bonds.

Bond distances (Å) / Angles (°)	**I**	**I-O2H**	**I-O2H2**	**Co-O2H**
Co1-N1	2.013	1.997	2.017	2.040
Co1-N2	2.004	1.984	1.957	2.013
Co1-N3	1.996	1.992	1.994	1.981
Co1-N4	1.988	1.931	1.903	1.987
Co1-O1	1.852	1.942	2.053	1.836
Co1-O3	1.919	1.908	2.037	1.911
O1-O2	1.383	1.467	1.463	1.436
Co2-N5	2.052	1.975	1.970	-----
Co2-N6	1.980	1.928	1.920	-----
Co2-N7	2.337	2.036	1.972	-----
Co2-N8	2.061	2.017	2.004	-----
Co2-O4	1.919	1.907	1.950	-----
Co2-O2	1.844	1.860	1.963	-----
Co1-Co2	4.056	4.236	4.420	-----
Mayer Bond Order				
Co1-O1	0.61	0.48	0.35	-----
Co2-O2	0.78	0.68	0.48	-----

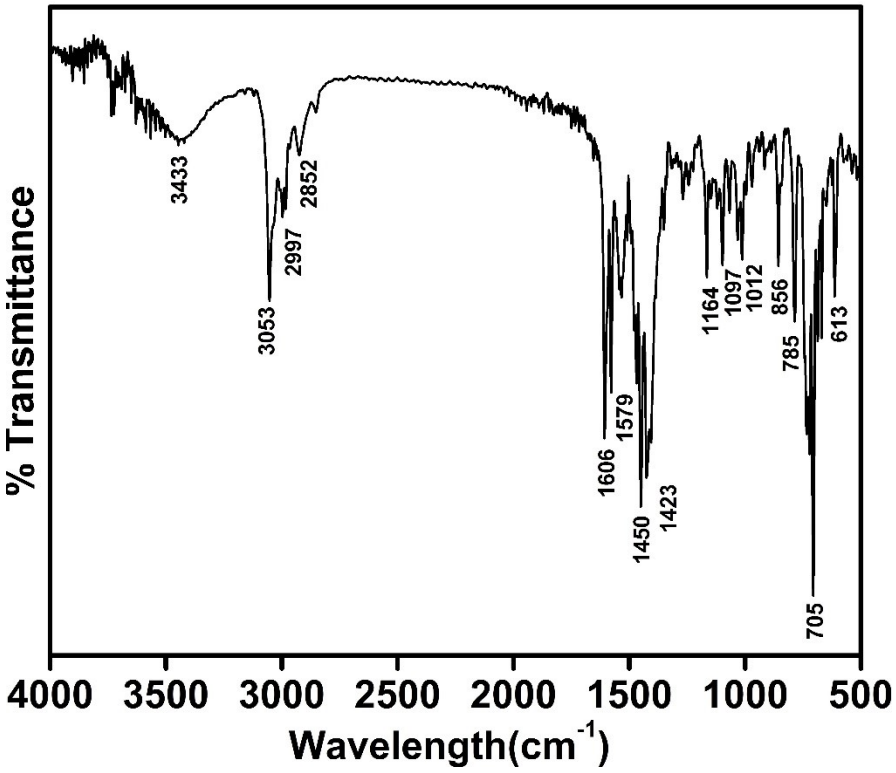

Fig. S1. FT-IR spectrum of [(6-Me_3-TPA)Co^{II}(benzoate)](BPh_4) (**1**).

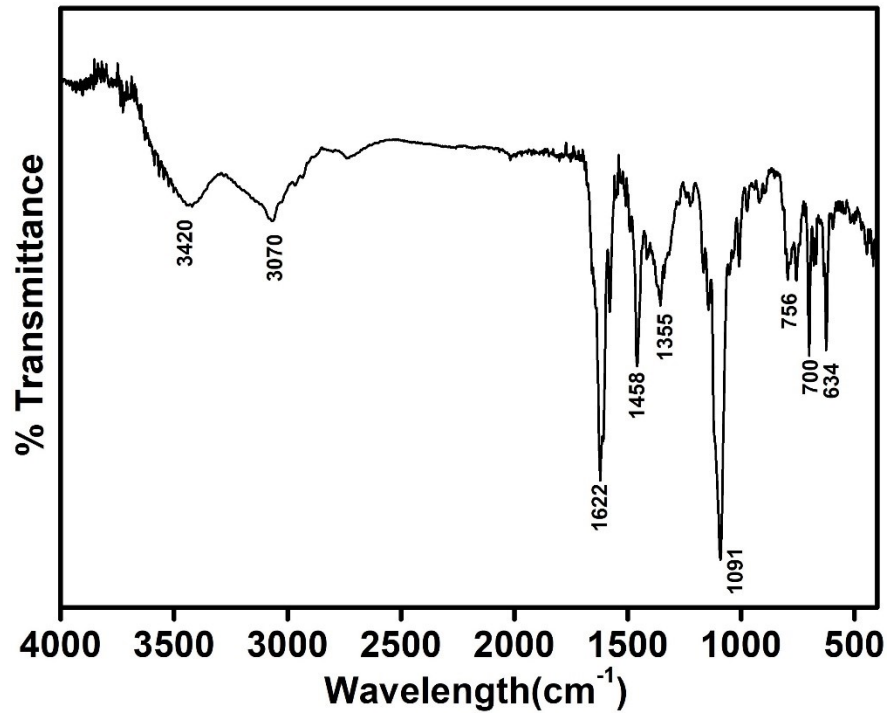

Fig. S2. FT-IR spectrum of [(6-Me_3-TPA)Co^{II}(benzilate)](ClO_4) (**2**).

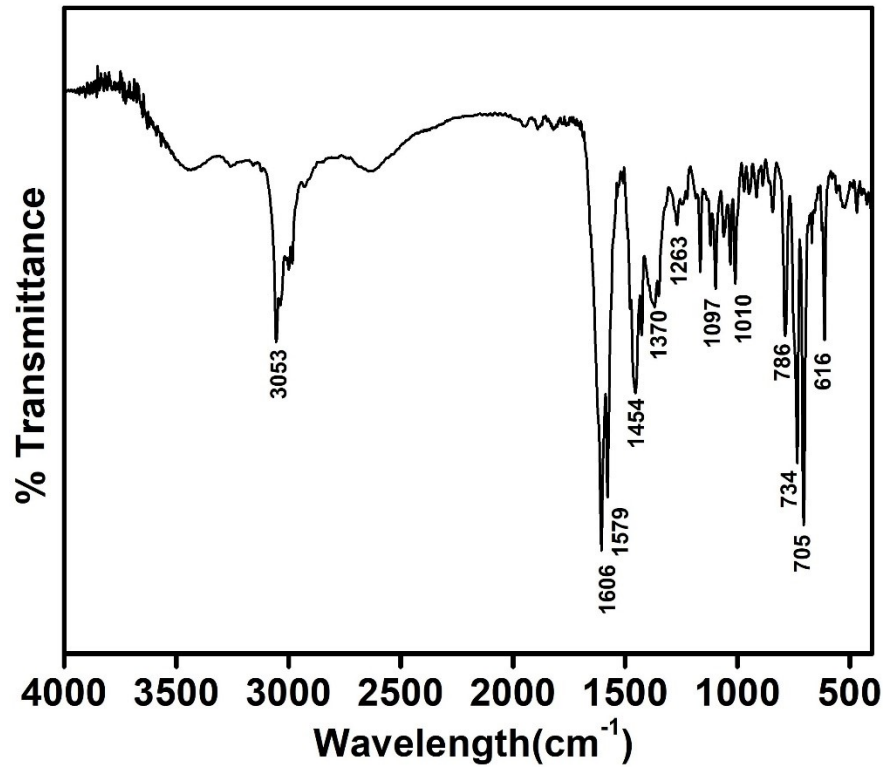

Fig. S3. FT-IR spectrum of [(6-Me_3-TPA)Co^{II}(mandelate)](BPh_4) (**3**).

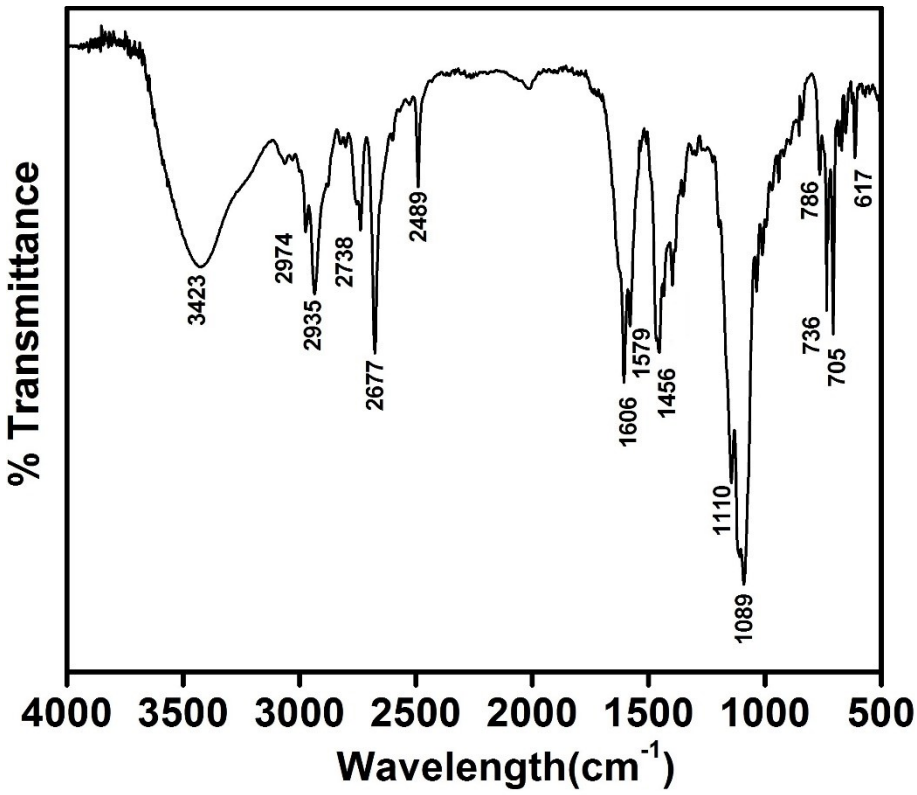

Fig. S4. FT-IR spectrum of [(6-Me_3-TPA)Co^{II}(MPA)](BPh_4) (**4**).

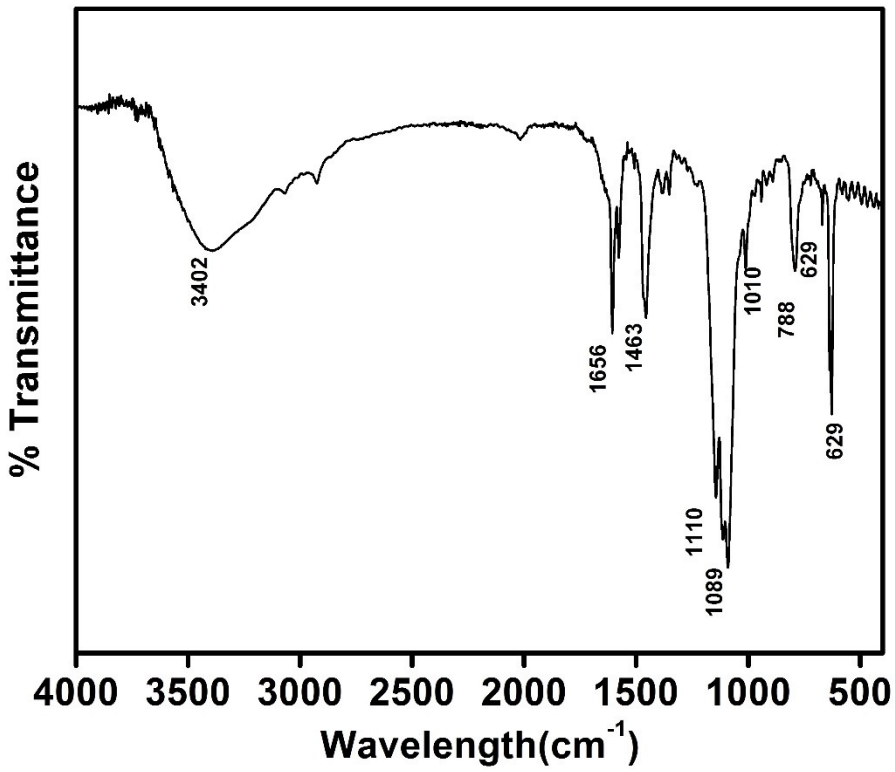

Fig. S5. FT-IR spectrum of $[(6\text{-}Me_3\text{-}TPA)Co^{II}(CH_3CN)_2](ClO_4)_2$ (**5**).

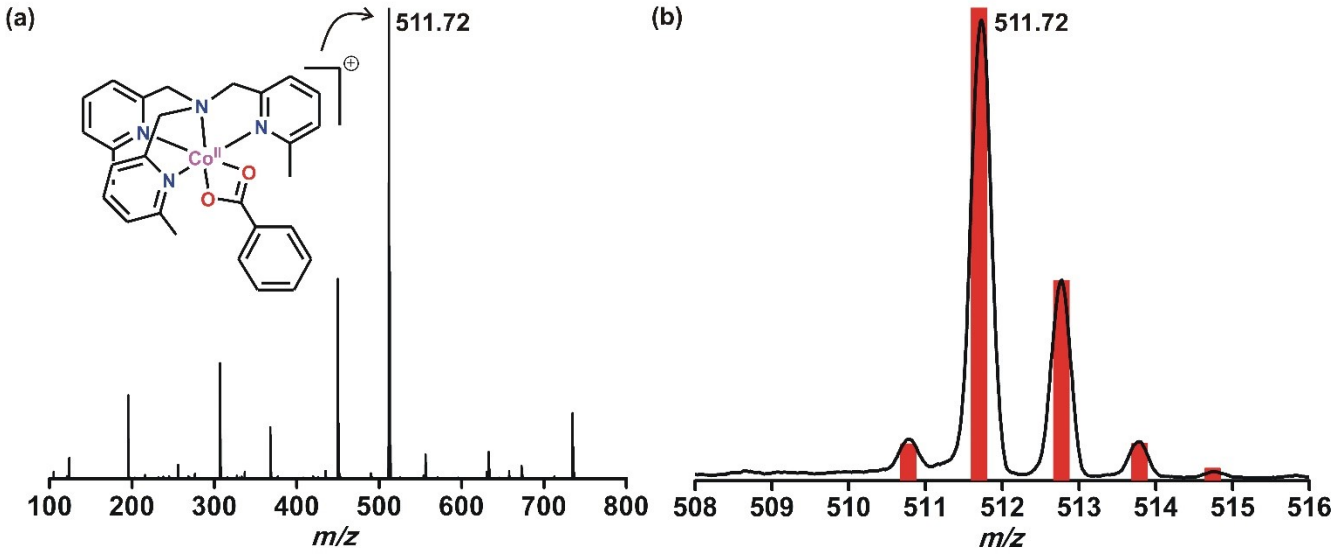

Fig. S6. (a) ESI-mass spectrum of $[(6\text{-}Me_3\text{-}TPA)Co^{II}(benzoate)](BPh_4)$ (**1**). (b) Isotope distribution pattern of the ion peak at *m/z* 511.72. The solid red bars indicate the calculated isotope distribution pattern.

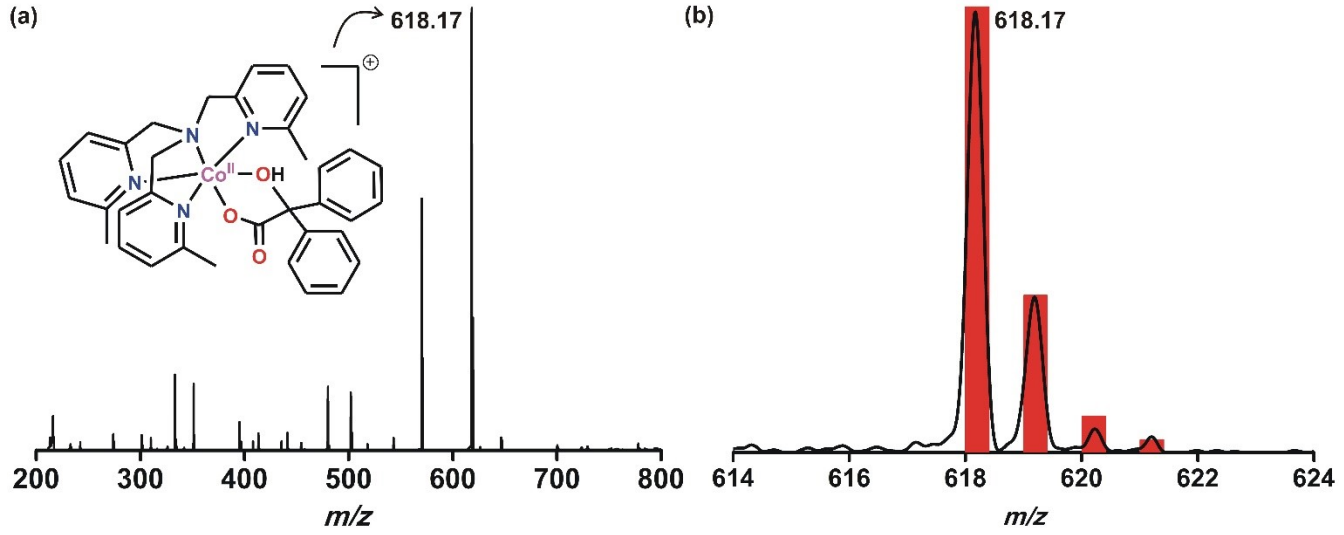

Fig. S7. (a) ESI-mass spectrum of [(6-Me_3-TPA)Co^{II}(benzilate)](ClO_4) (**2**). (b) Isotope distribution pattern of the ion peak at *m/z* 618.17. The solid red bars indicate the calculated isotope distribution pattern.

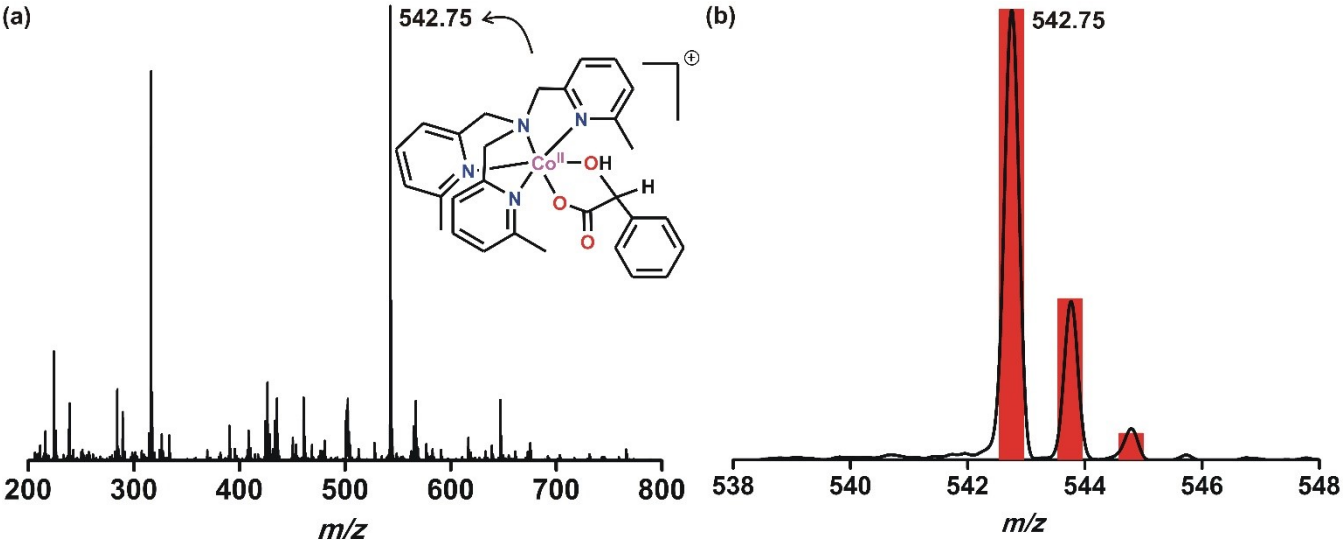

Fig. S8. (a) ESI-mass spectrum of [(6-Me_3-TPA)Co^{II}(mandelate)](BPh_4) (**3**). (b) Isotope distribution pattern of the ion peak at *m/z* 542.75. The solid red bars indicate the calculated isotope distribution pattern.

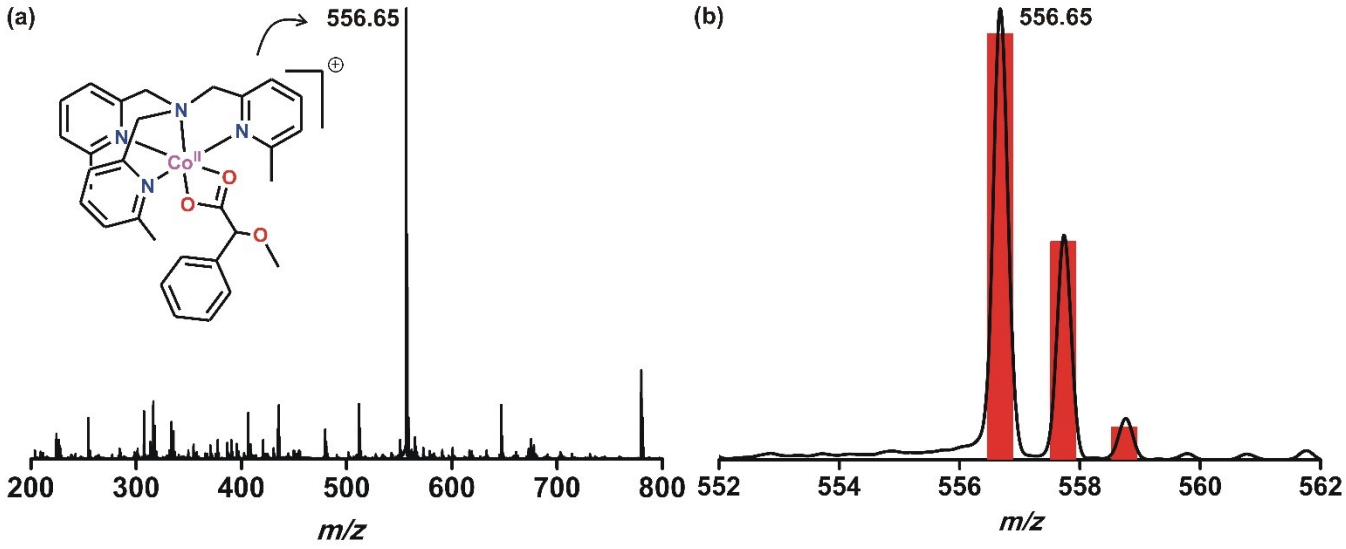

Fig. S9. (a) ESI-mass spectrum of [(6-Me_3-TPA)Co^{II}(MPA)](BPh_4) (**4**). (b) Isotope distribution pattern of the ion peak at *m/z* 556.65. The solid red bars indicate the calculated isotope distribution pattern.

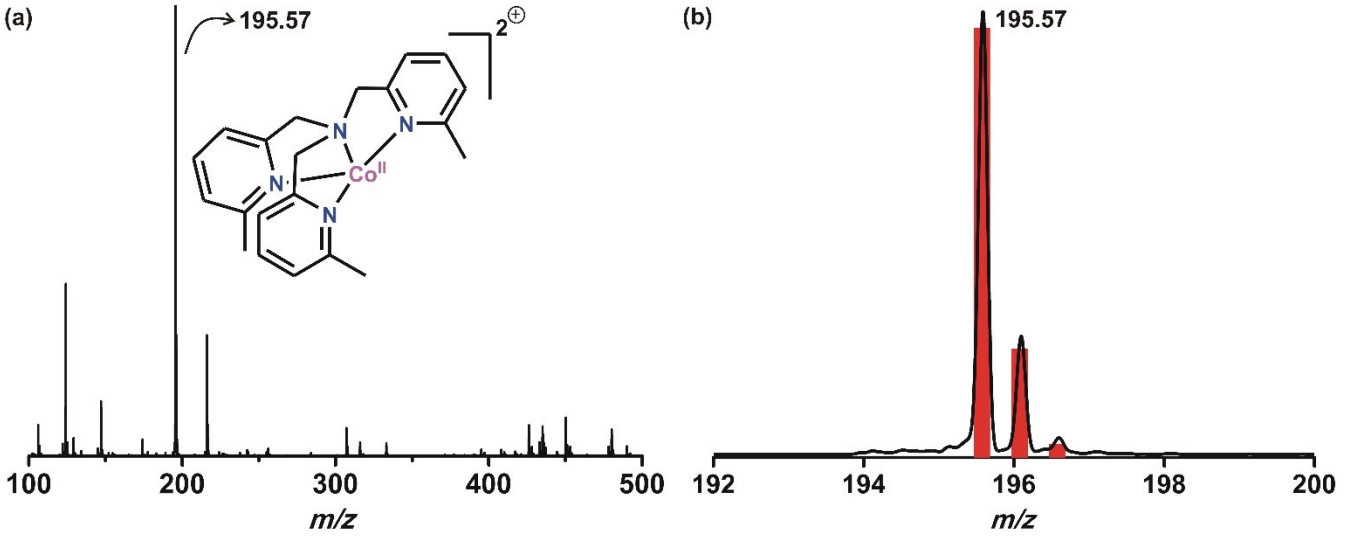

Fig. S10. (a) ESI-mass spectrum of [(6-Me_3-TPA)Co^{II}(CH_3CN)$_2$](ClO_4)$_2$ (**5**). (b) Isotope distribution pattern of the ion peak at *m/z* 195.57. The solid red bars indicate the calculated isotope distribution pattern.

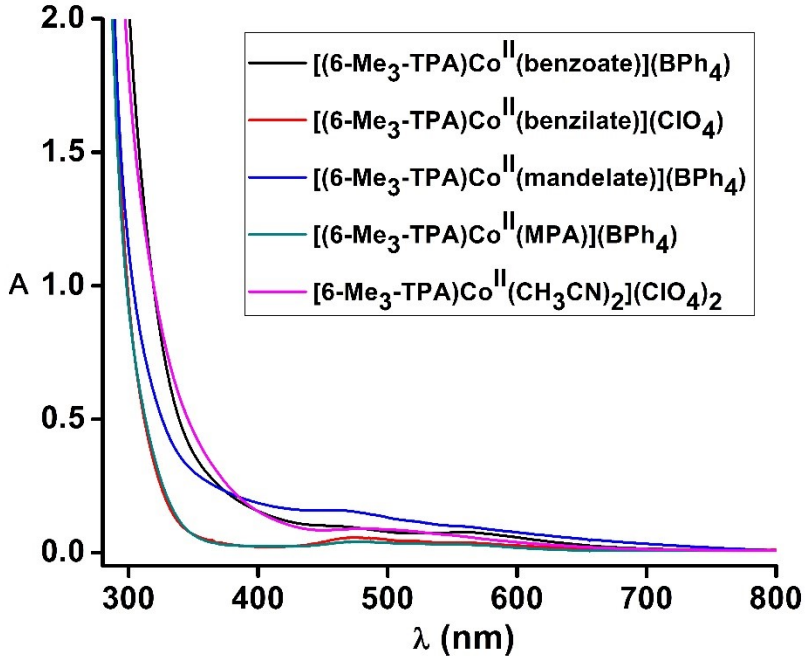

Fig. S11. Optical spectra of the cobalt(II) complexes (1 mM in CH_3CN) at 298 K.

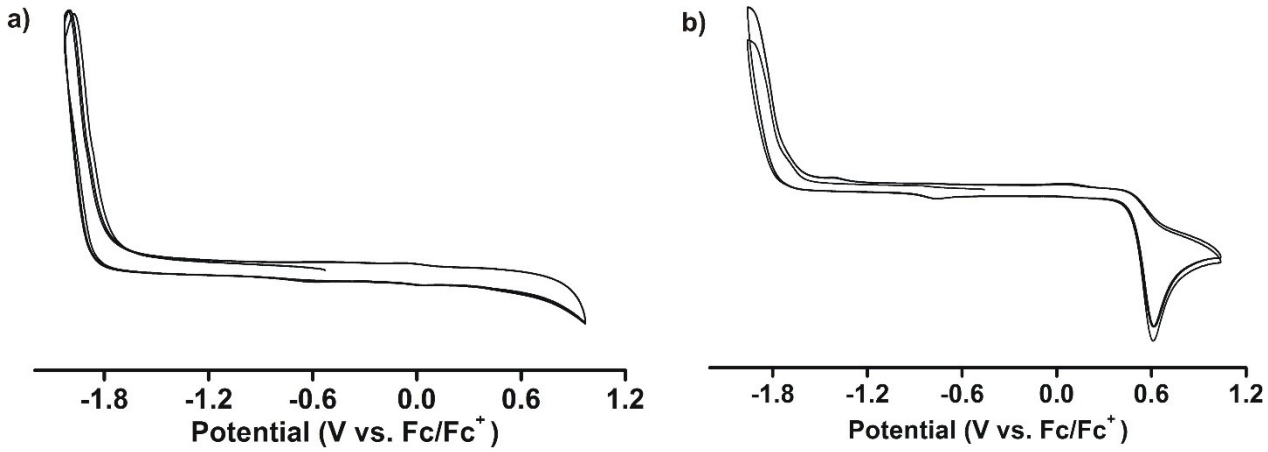

Fig. S12. Cyclic voltammogram (CV) of (a) [(6-Me_3-TPA)Co^{II}(benzoate)](BPh_4) (**1**) and (b) [(TPA)Co^{II}(benzoate)](BPh_4)[1] has been recorded at a glassy carbon working electrode and Ag/AgCl reference electrode in acetonitrile solutions containing 0.1 *M* $^nBu_4NPF_6$ as supporting electrolyte.

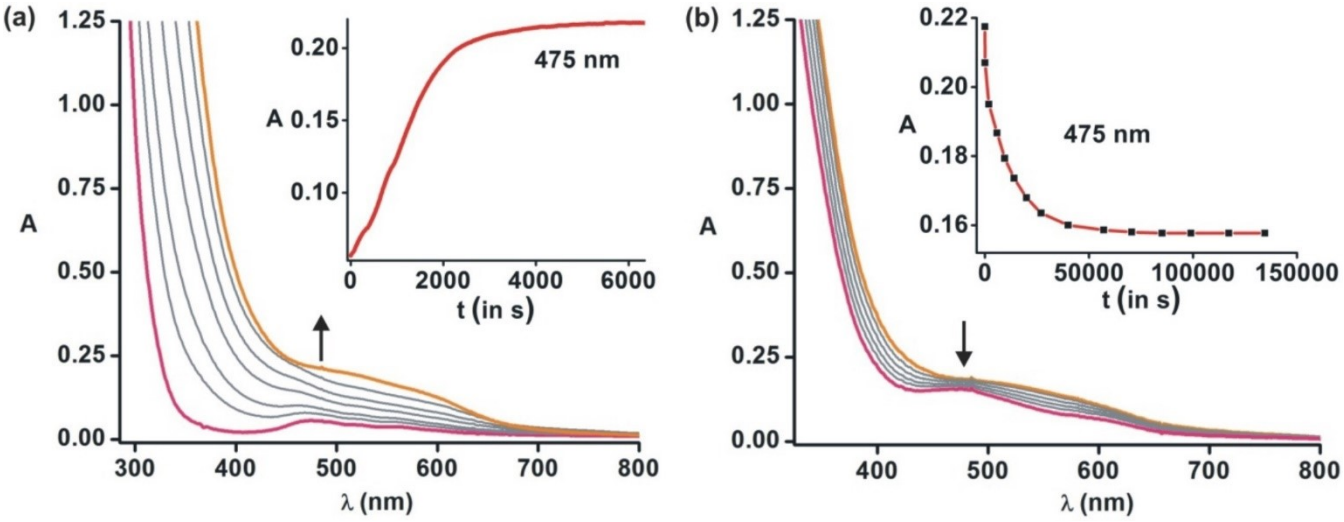

Fig. S13. Time-dependent optical spectra of complex **2** (1 mM in acetonitrile) during the reaction with 10 equiv of aqueous hydrogen peroxide (30%). (a) Formation and (b) decay of the intermediate species. Insets: Absorbance *vs* time plot for the band at 475 nm.

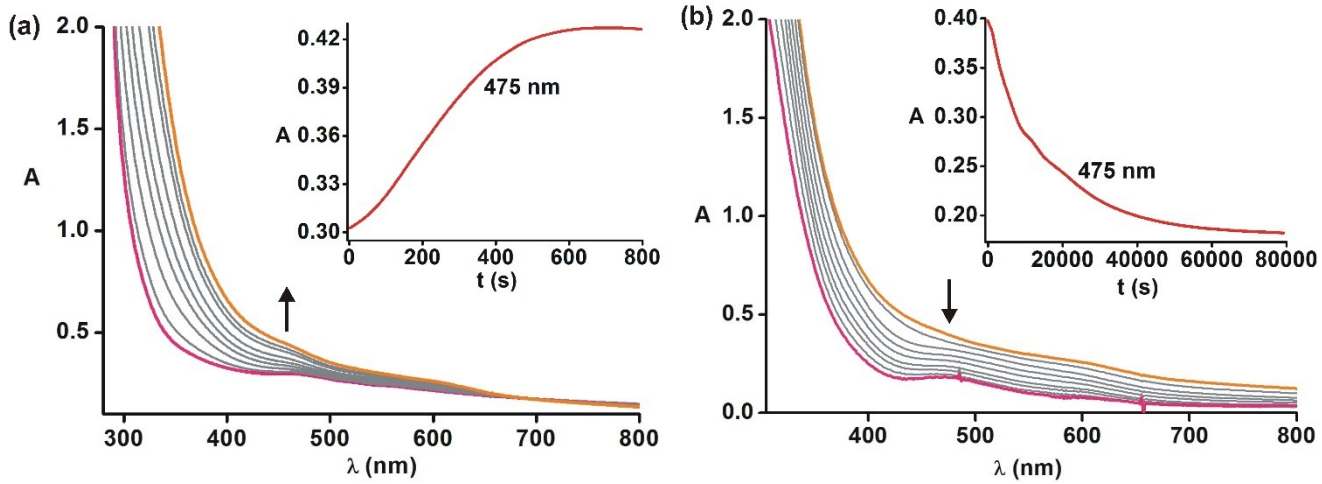

Fig. S14. Time-dependent optical spectra of complex **3** (1 mM in acetonitrile) during the reaction with 10 equiv of aqueous hydrogen peroxide (30%). (a) Formation and (b) decay of the intermediate species. Insets: Absorbance *vs* time plot for the band at 475 nm.

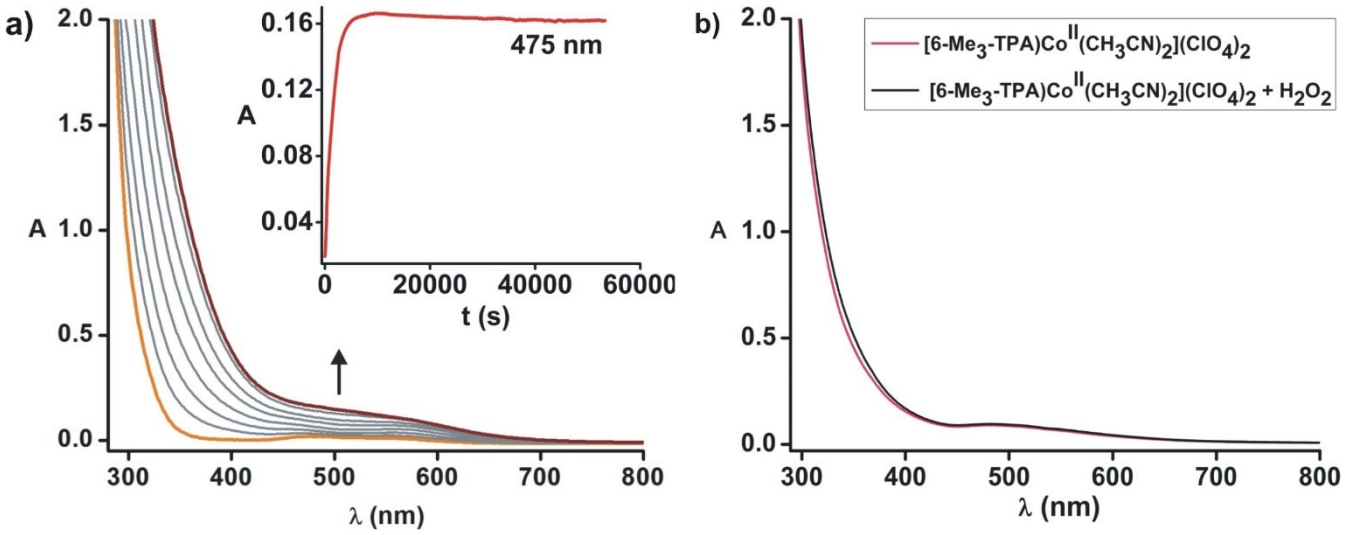

Fig. S15. Change in optical spectra of complexes (a) **4** and (c) **5** (1 mM in acetonitrile) during the reaction with 10 equiv of aqueous hydrogen peroxide (30%).

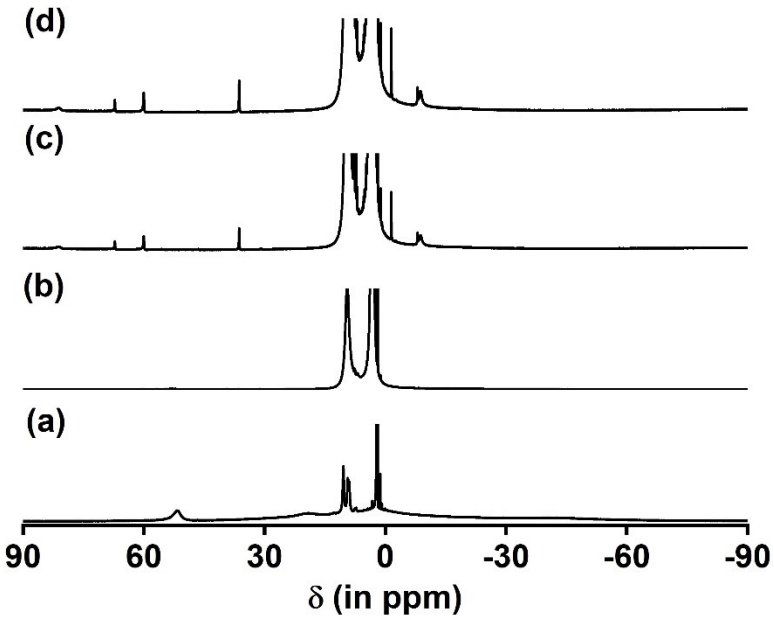

Fig. S16. Time-dependent ^{1}H NMR spectra (400 MHz, at 298 K) during the reaction of complex **2** (in CD_3CN) with 10 equiv H_2O_2 (30% aqueous solution). Spectra were recorded with different time interval; (a) as prepared cobalt(II) complex, (b) immediately after addition of H_2O_2 to the solution, (c) the same solution after 2 h (d) and after 20 h.

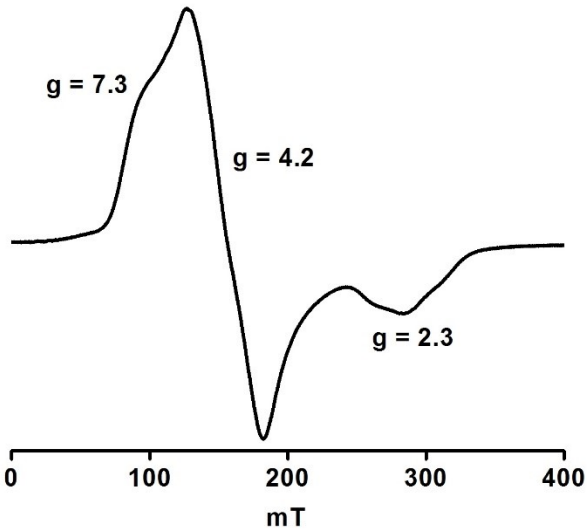

Fig. S17. X-band EPR spectrum of complex **2**. Experimental conditions for EPR: temperature = 12 K, microwave frequency = 9.12 GHz, microwave power = 0.998 mW, modulation amplitude = 100 kHz, modulation width = 1.2 mT, time constant = 0.03 s.

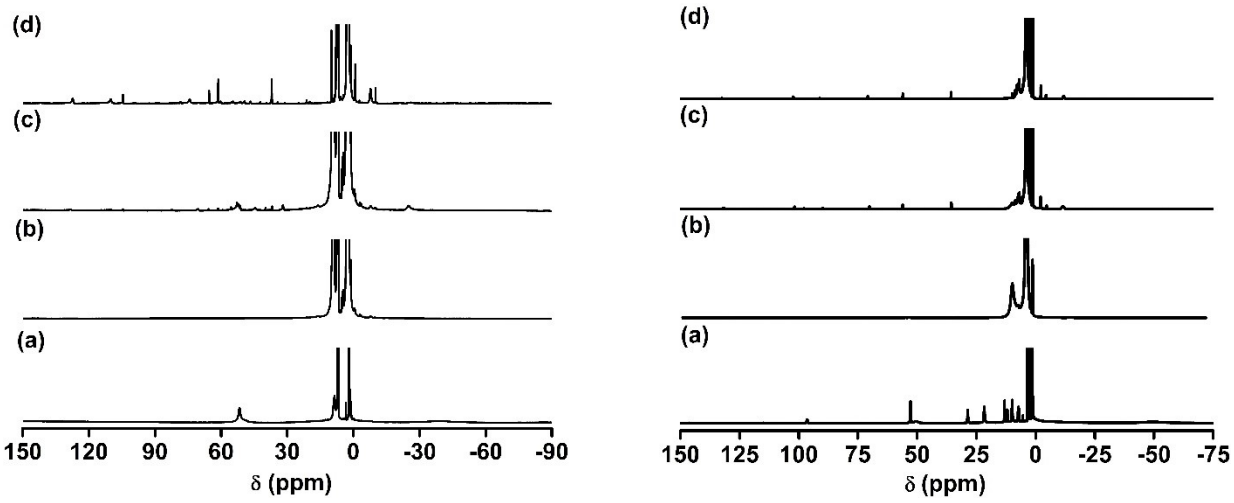

Fig. S18. Time-dependent ^{1}H NMR spectra (400 MHz, at 298 K) during the reaction of complexes **3** (left) and **4** (right) **(**in CD_3CN) with 10 equiv H_2O_2 (30% aqueous solution). Spectra were recorded with different time interval; (a) as prepared cobalt(II) complex, (b) after addition of H_2O_2 to the solution, (c) the same solution after 2 h (d) and after 20 h.

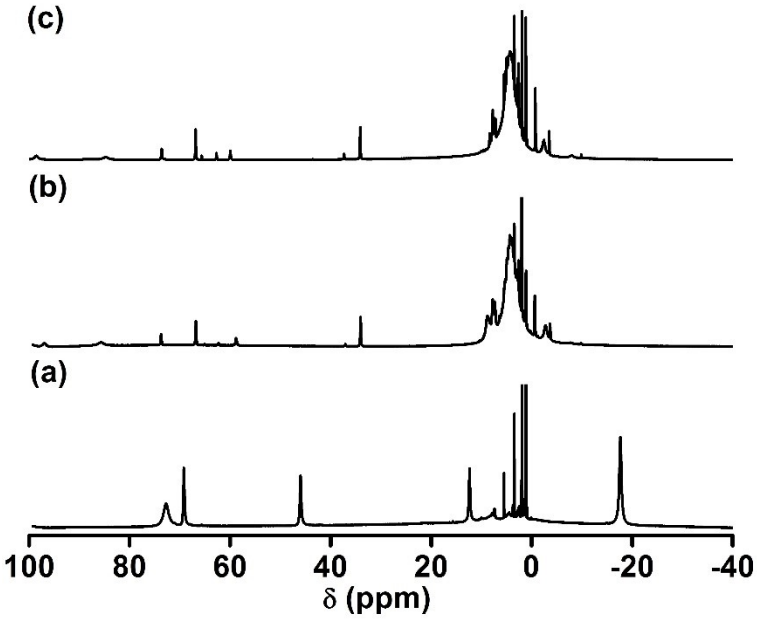

Fig. S19. Time-dependent ^{1}H NMR spectra (400 MHz, at 298 K) during the reaction of complex **5 (**in CD_3CN) with 10 equiv H_2O_2 (30% aqueous solution). Spectra were recorded with different time interval; (a) as prepared cobalt(II) complex, (b) after addition of H_2O_2 to the solution, (c) the same solution after 20 h.

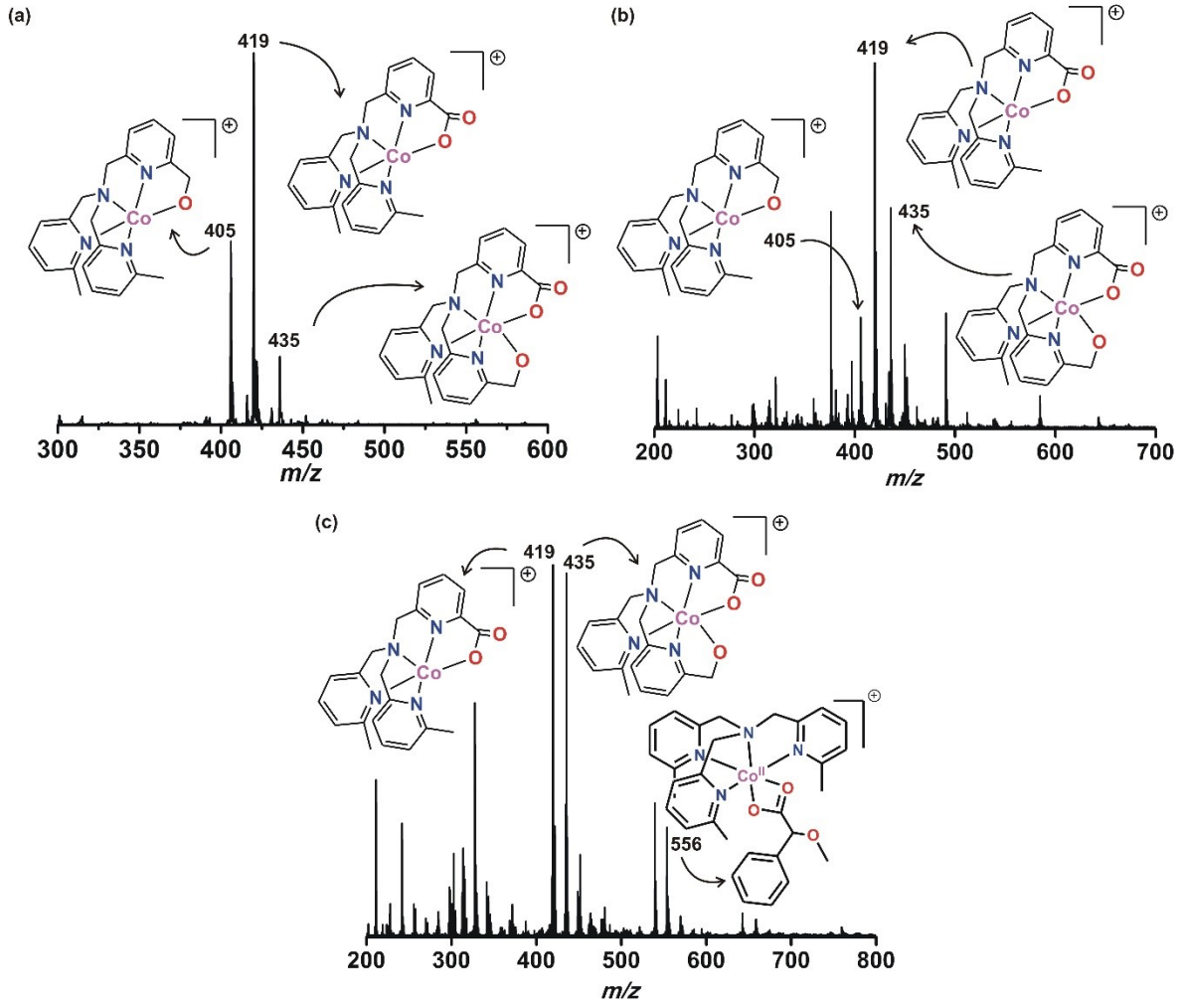

Fig. S20. ESI-mass spectra of the oxidized solutions after the reaction of (a) **2**, (b) **3** and (c) **4** with H_2O_2 for 20 h.

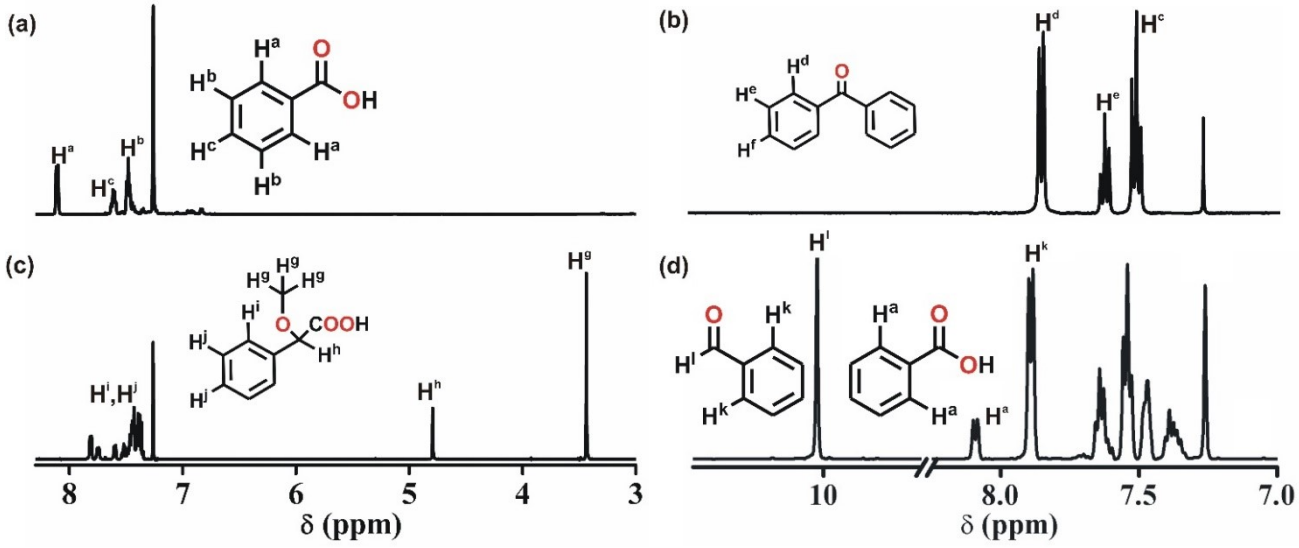

Fig. S21. ^{1}H NMR spectra of organic products obtained from the oxidized solution of (a) **1**, (b) **2**, (c) **4** and (d) **3** after the reaction with 10 equiv of H_2O_2 for 20 h.

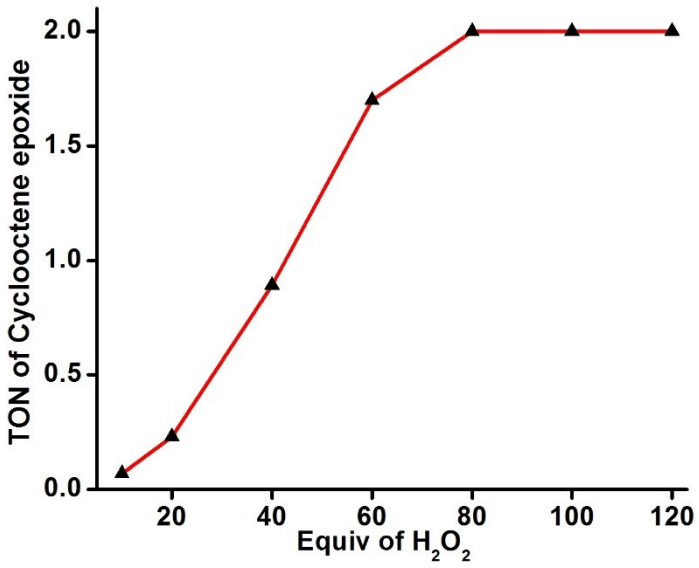

Fig. S22. TON in the oxidation of cyclooctene by complex **2** with different equivalents of H_2O_2. Experimental conditions: 0.01 mmol complex **2**, 100 equiv of substrate in acetonitrile at room temperature. Reaction time: 20 h. Turnover number TON (cyclooctene epoxide) = mol of product/mol of catalyst.

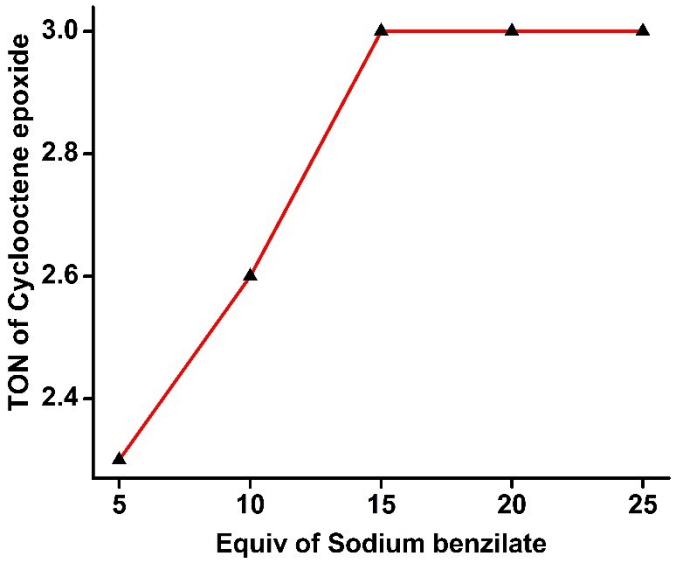

Fig. S23. TON in the oxidation of cyclooctene by complex **2** with different equivalents of sodium benzilate. Experimental conditions: 0.01 mmol complex **2**, 100 equiv of H_2O_2, 100 equiv of substrate in acetonitrile at room temperature. Reaction time: 20 h. Turnover number TON (cyclooctene epoxide) = mol of product/mol of catalyst.

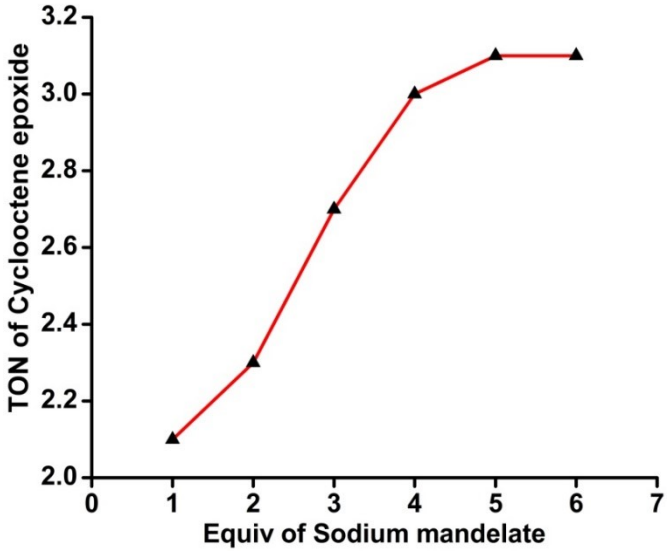

Fig. S24. TON in the oxidation of cyclooctene by complex **3** with different equivalents of sodium mandelate. Experimental conditions: 0.01 mmol complex **3**, 100 equiv of H_2O_2, 100 equiv of substrate in acetonitrile at room temperature. Reaction time: 20 h. Turnover number TON (cyclooctene epoxide) = mol of product/mol of catalyst.

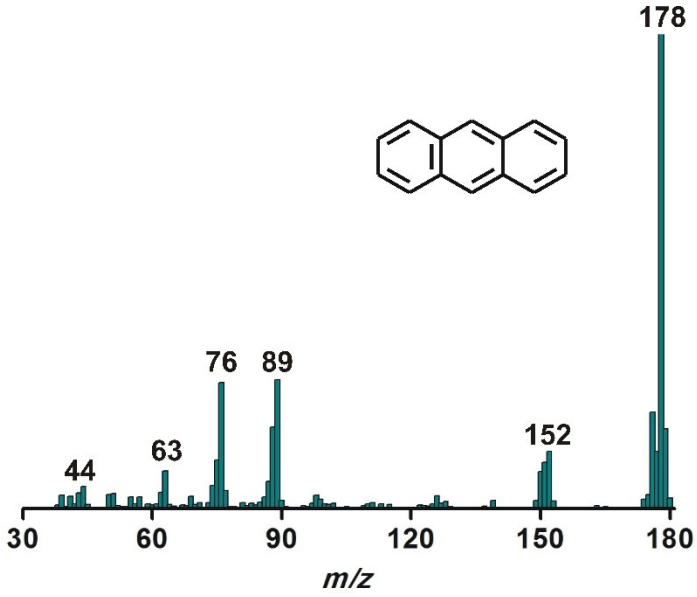

Fig. S25. GC-mass spectrum of anthracene formed from 9,10-dihydroanthracene in the catalytic oxidation by complex **1**.

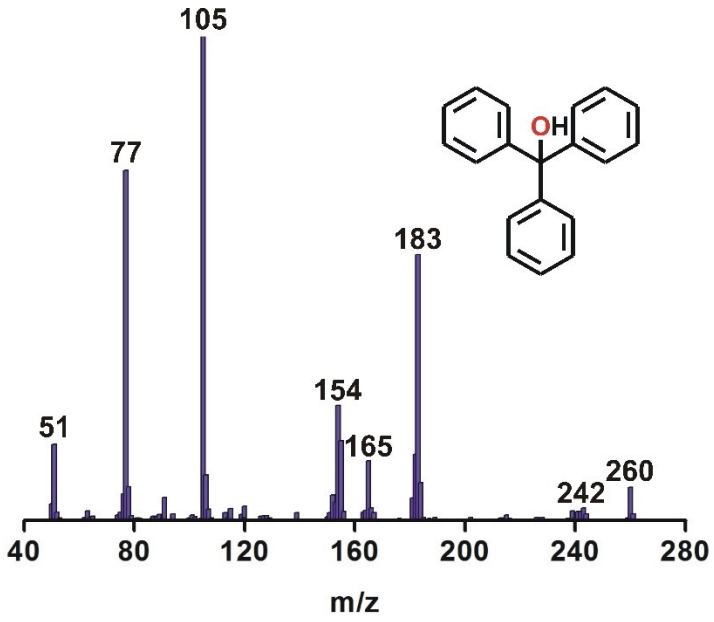

Fig. S26. GC-mass spectrum of triphenylmethanol formed from triphenylmethane in the catalytic oxidation by complex **1**.

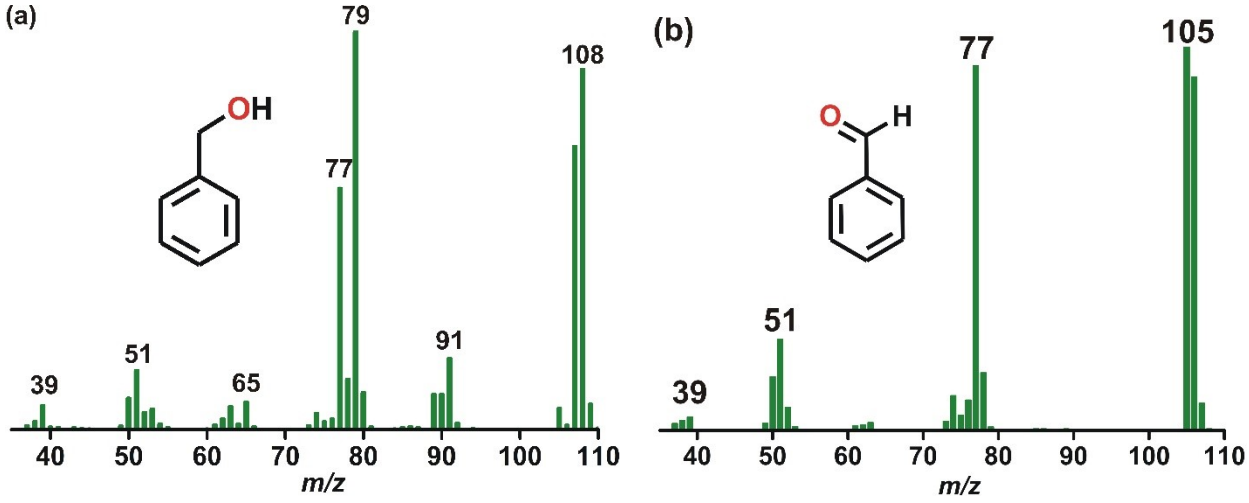

Fig. S27. GC-mass spectra of (a) benzyl alcohol and (b) benzaldehyde formed from toluene in the catalytic oxidation by complex **1**.

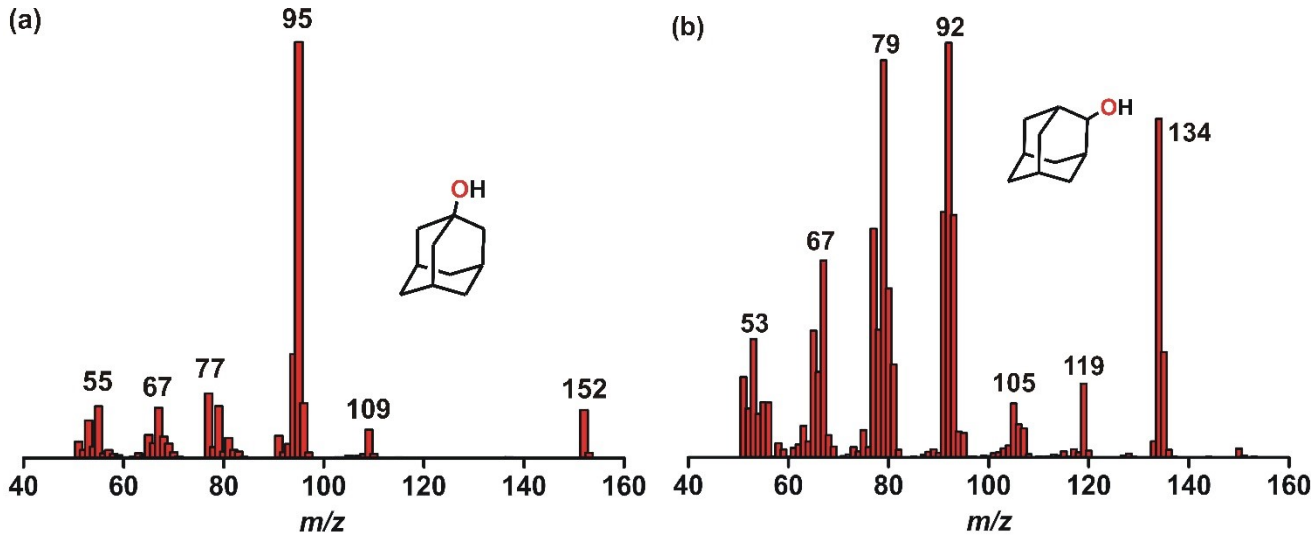

Fig. S28. GC-mass spectra of (a) 1-adamantanol and (b) 2-adamantanol formed from adamantane in the catalytic oxidation by complex **1**.

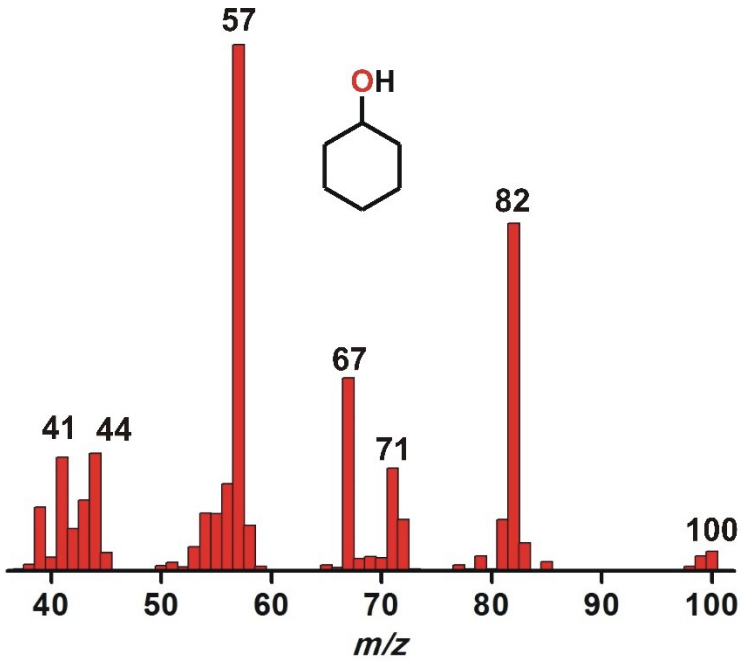

Fig. S29. GC-mass spectrum of cyclohexanol formed from cyclohexane in the catalytic oxidation by complex **1**.

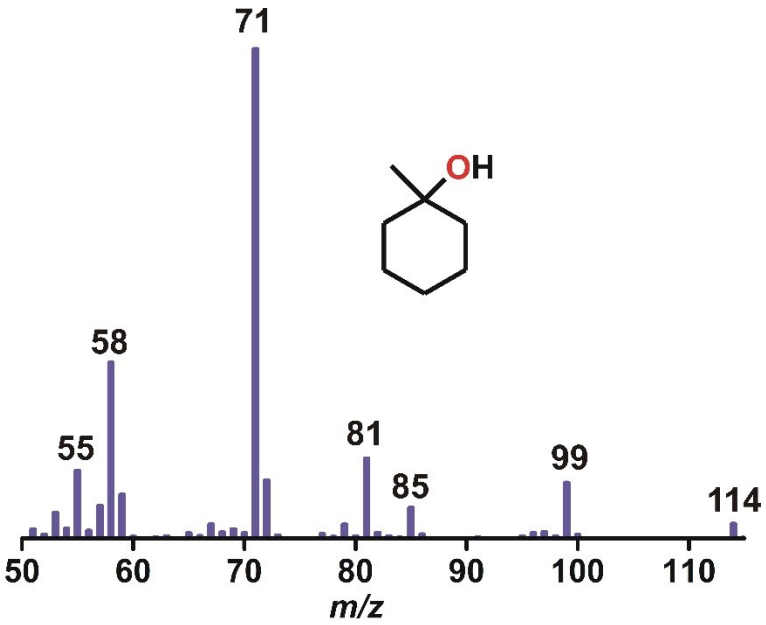

Fig. S30. GC-mass spectrum of 3º methylcyclohexanol formed from methylcyclohexane in the catalytic oxidation by complex **1**.

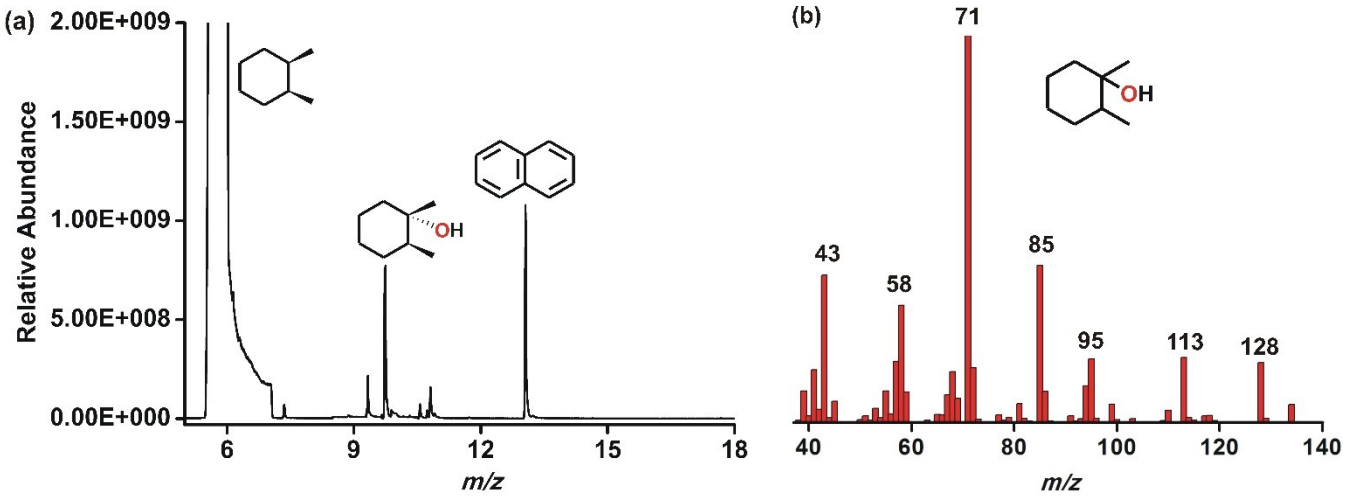

Fig. S31. (a) Chromatogram and (b) GC-mass spectrum of 1,2-dimethylcyclohexanol formed from *cis*-1,2-dimethylcyclohexane in the catalytic oxidation by complex **1**.

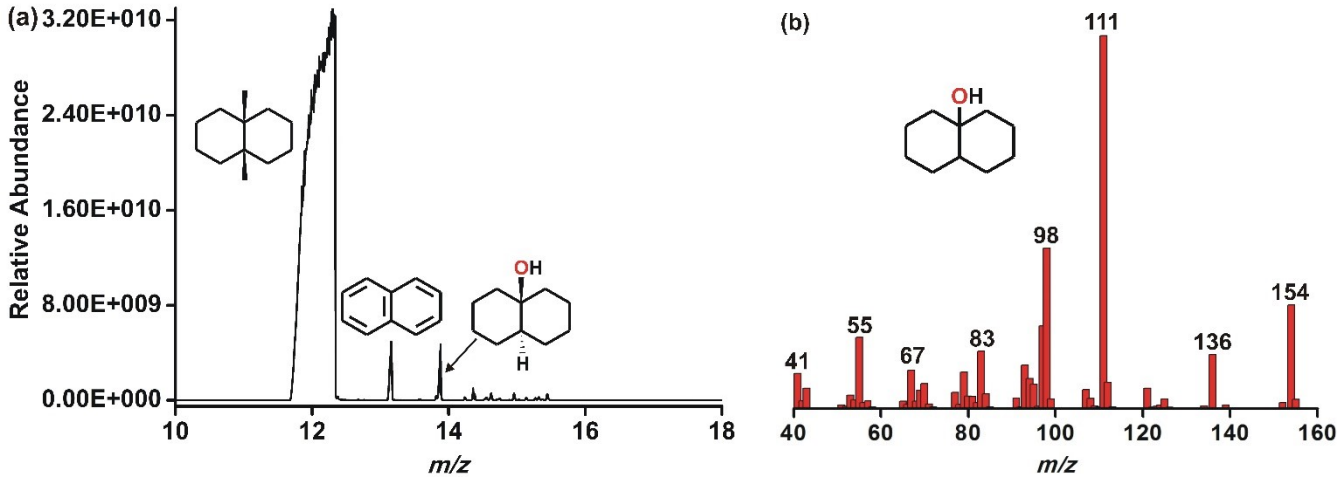

Fig. S32. (a) Chromatogram and (b) GC-mass spectrum of 4-decalol formed from *cis*-decalin in the catalytic oxidation by complex **1**.

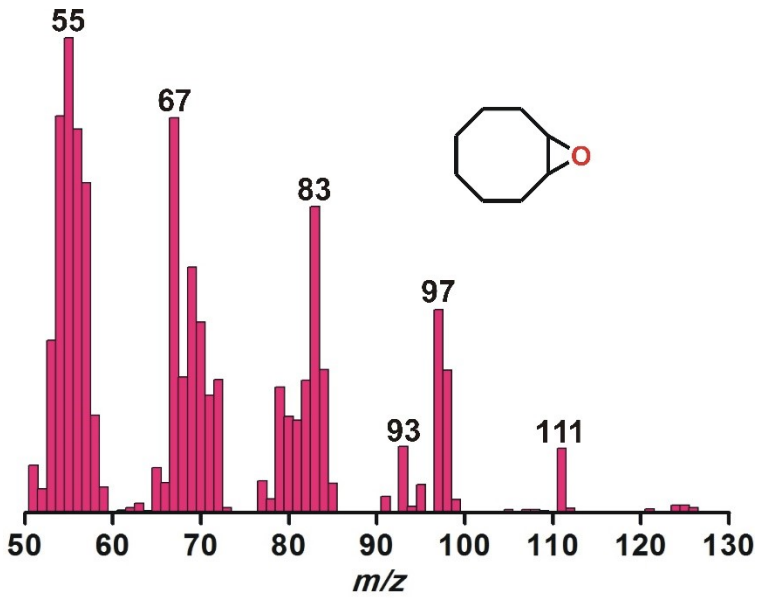

Fig. S33. GC-mass spectrum of cyclooctene epoxide formed from cyclooctene in the catalytic oxidation by complex **1**.

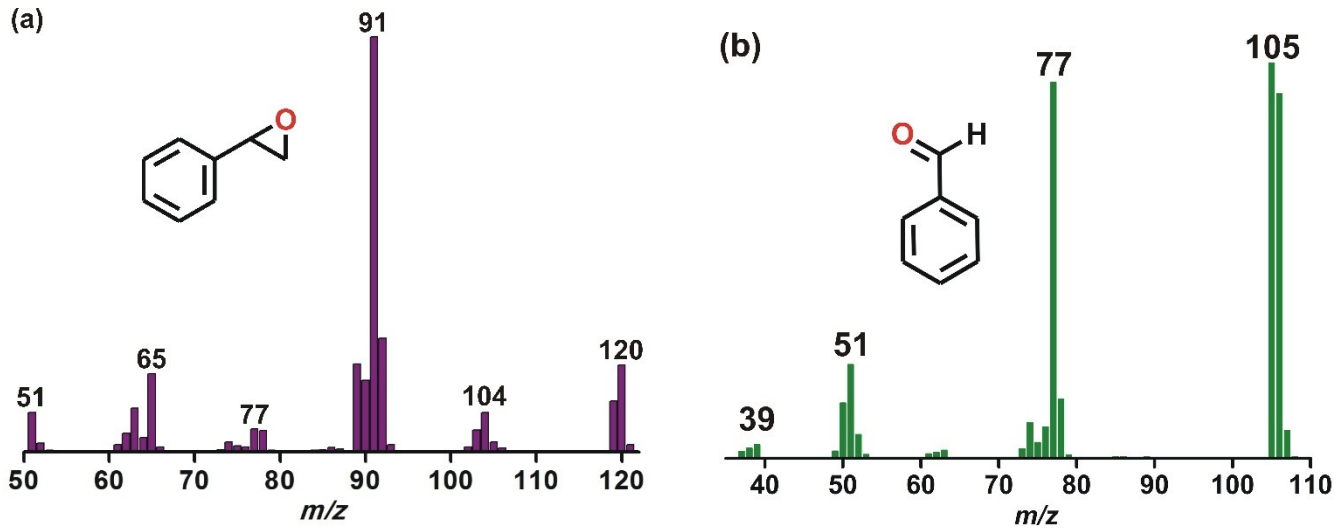

Fig. S34. GC-mass spectra of (a) styrene epoxide and (b) benzaldehyde formed from styrene in the catalytic oxidation by complex **1**.

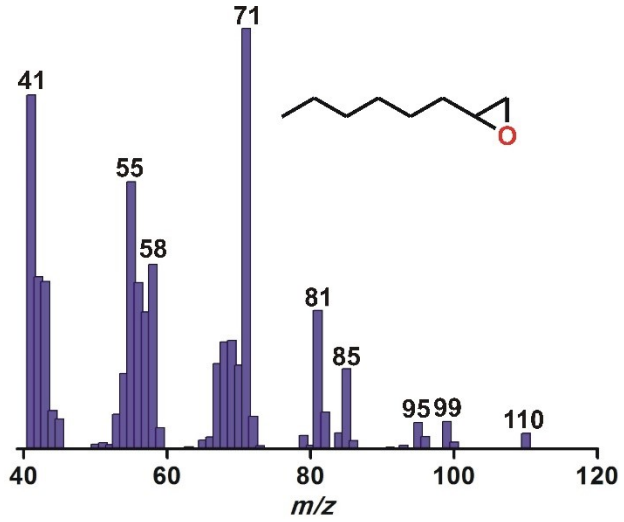

Fig. S35. GC-mass spectrum of 1-octene epoxide formed from 1-octene in the catalytic oxidation by complex **1**.

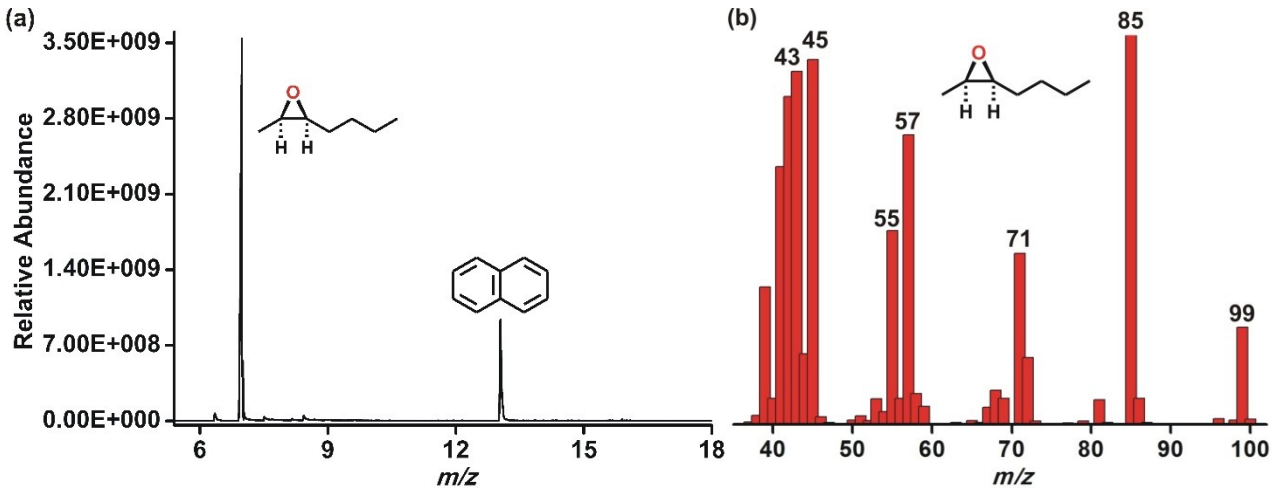

Fig. S36. (a) Chromatogram and (b) GC-mass spectrum of *cis*-2-heptene epoxide formed from *cis*-2-heptene in the catalytic reaction by complex **1**.

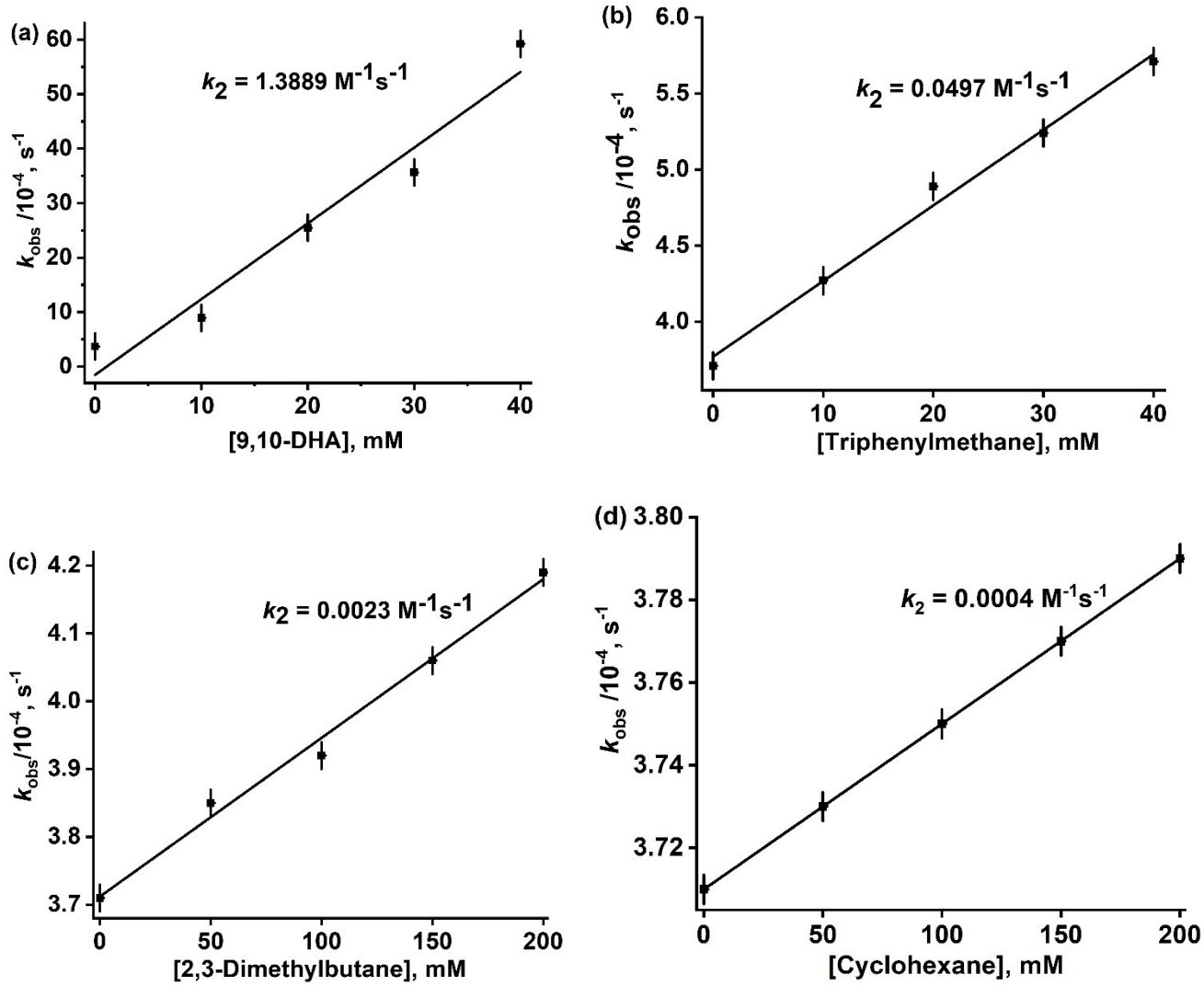

Fig. S37. Plots of k_{obs} *vs* substrate concentration for the reaction of complex **2** with H_2O_2 (10 equiv) in the presence (a) 9,10-dihydroanthracene, (b) triphenylmethane, (c) 2,3-dimethylbutane and (d) cyclohexane at 298 K.

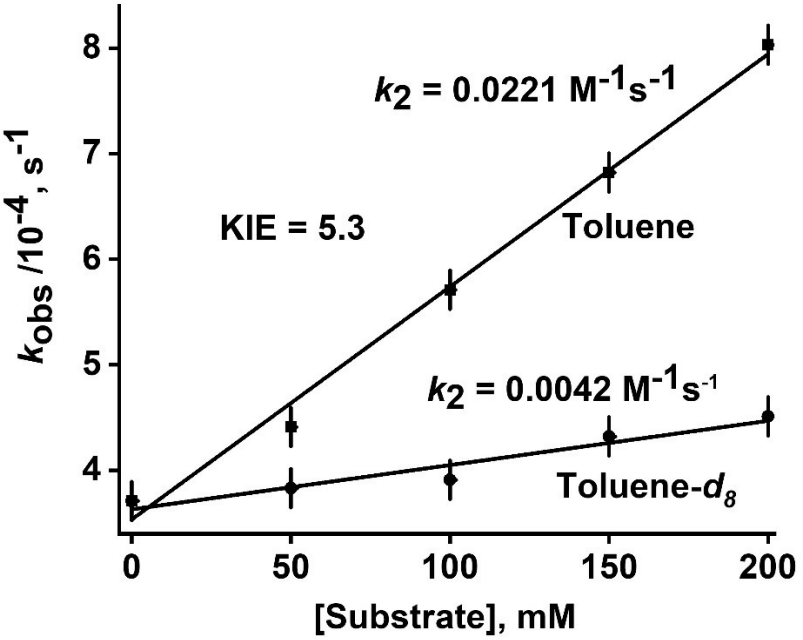

Fig. S38. Kinetic isotope effect value obtained from separate reactions of complex **2** with toluene and toluene-d_8 at 298 K.

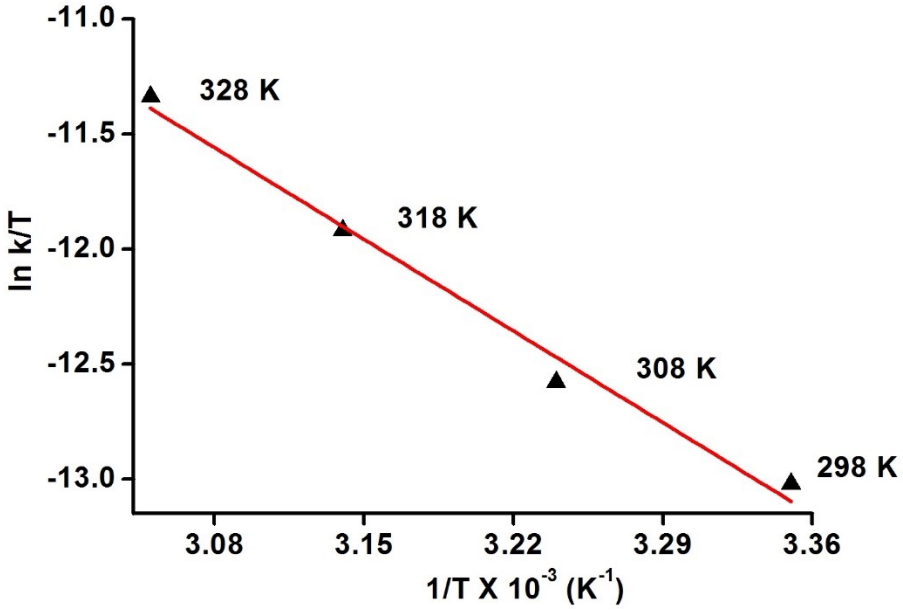

Fig. S39. Eyring plot for the reaction of complex **2** with 10 equiv H_2O_2.

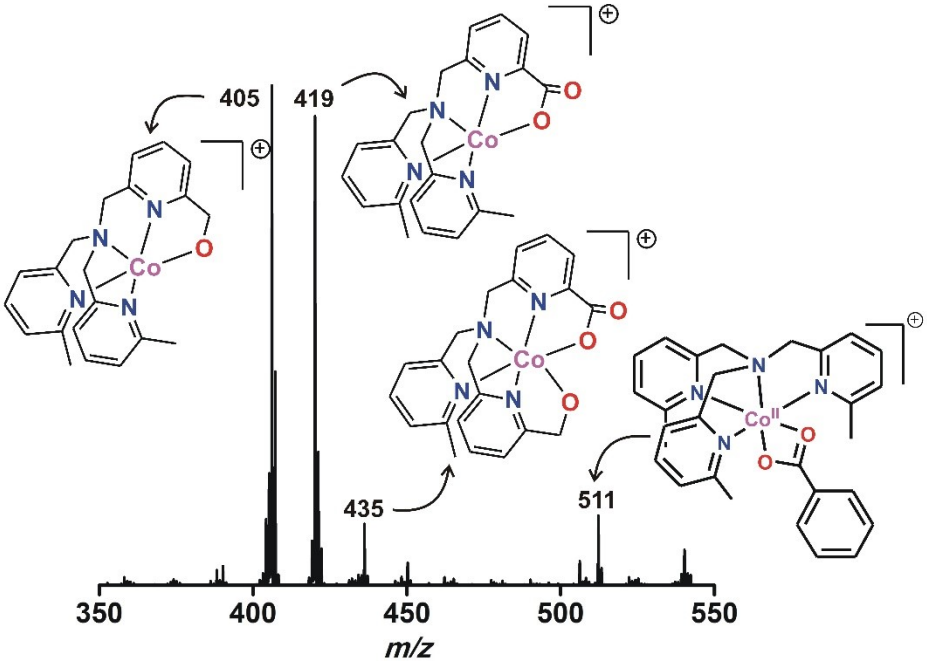

Fig. S40. ESI-mass spectrum of the oxidized solution after the reaction of complex **5** with H_2O_2 in the presence of 1 equiv of sodium benzoate after 20 h.

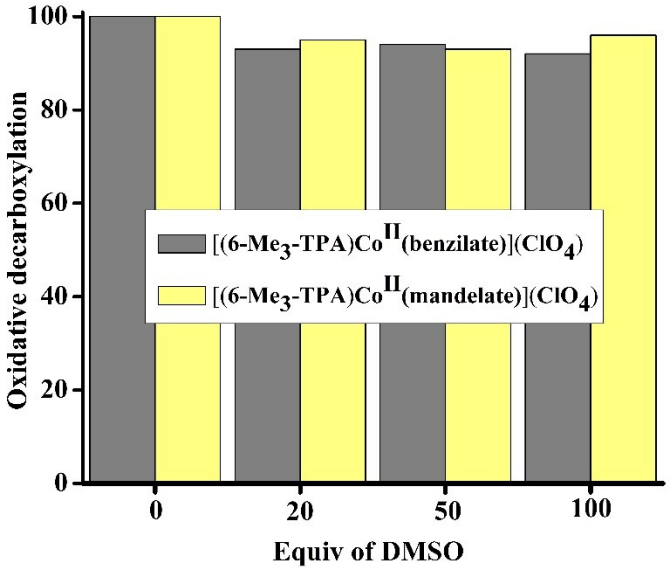

Fig. S41. Oxidative decarboxylation of complexes **2** and **3** in the presence of radical scavenger DMSO.

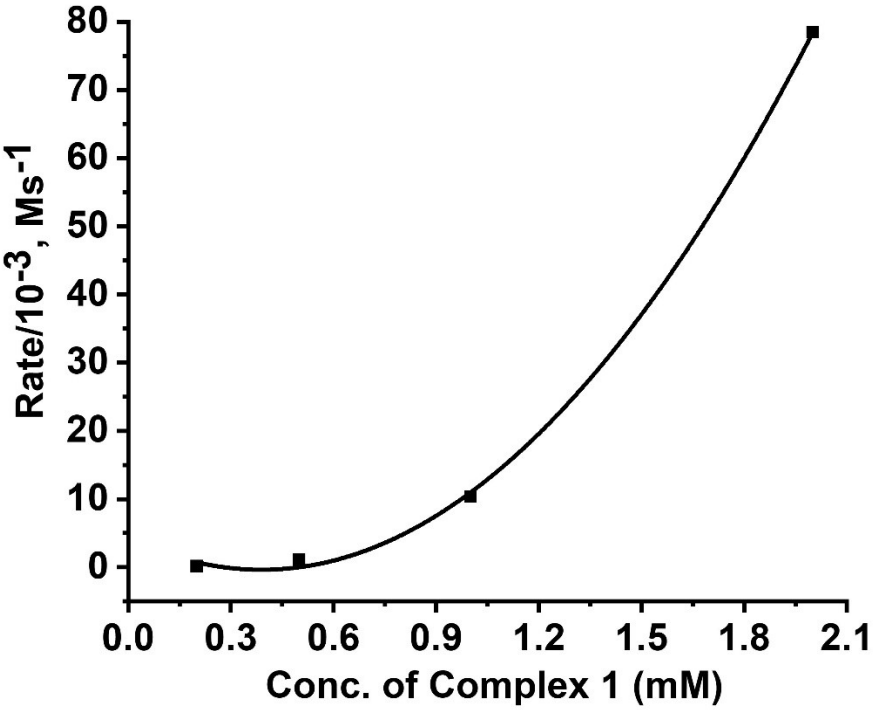

Fig. S42. Concentration dependence of the initial rate for the reaction of complex **1** with H_2O_2.

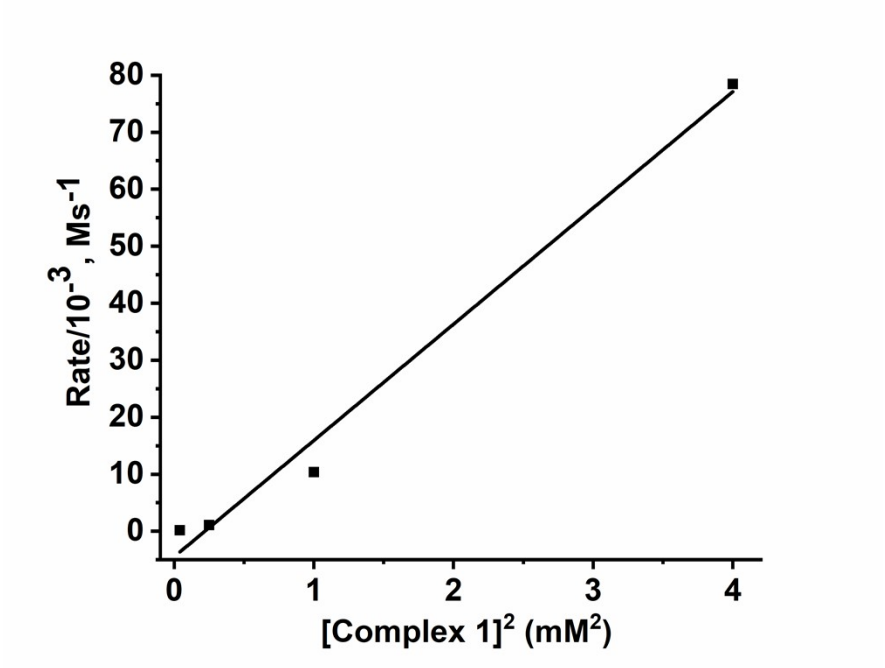

Fig. S43. Second order dependence of rate on the concentration of complex **1** for its reaction with H_2O_2.

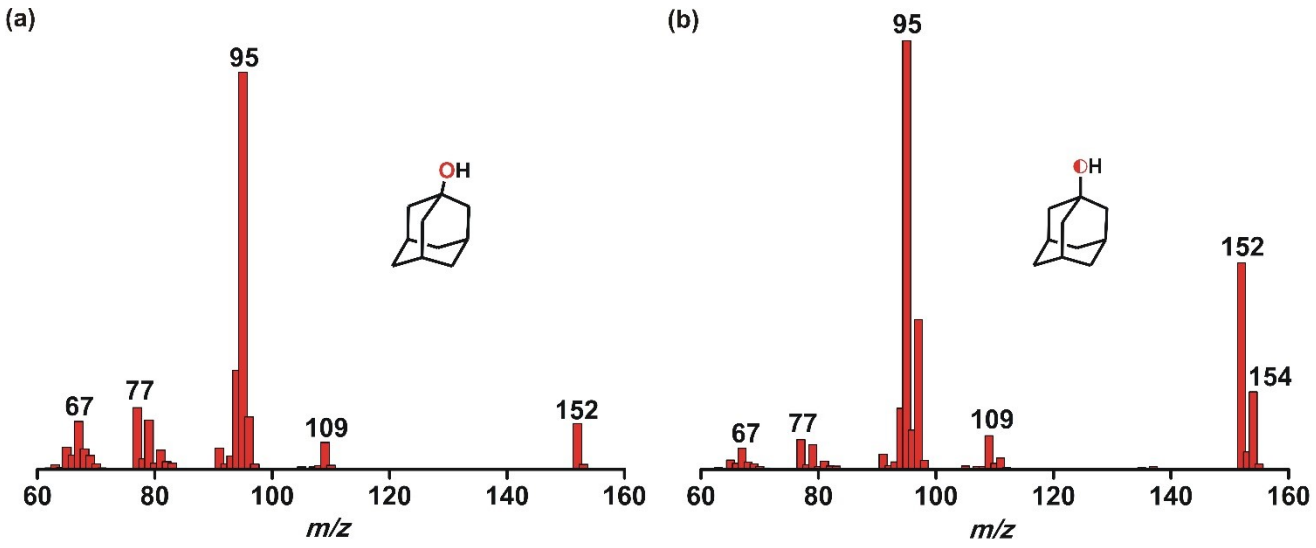

Fig. S44. GC-mass spectra of 1-adamantanol formed in the reaction of complex **1** with adamantane under catalytic conditions (a) in the absence of $H_2{}^{18}O$ (b) in the presence of $H_2{}^{18}O$.

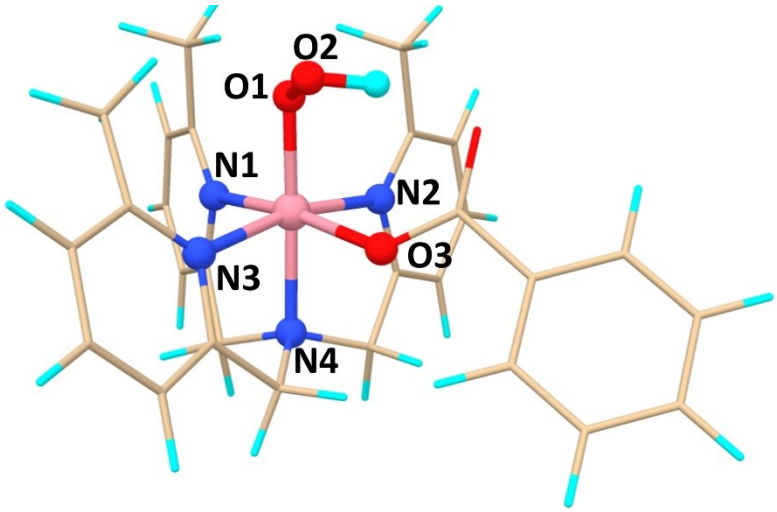

Fig. S45. Optimized structures of the monomeric analogue of the intermediate **Co-O2H.**

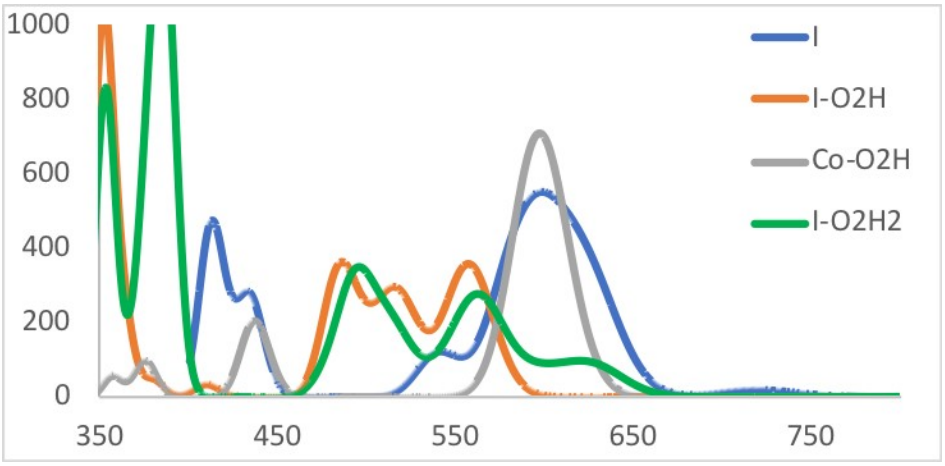

Fig. S46. Absorption spectra of the optimized intermediates simulated through TDDFT.

Cartesian coordinates for the optimized structure of I:

Atom	Coordinates (Angstroms)		
	X	Y	Z
Co	-1.472482000	1.712785000	0.051292000
O	0.162926000	1.114618000	0.681248000
N	-1.423242000	3.561781000	0.823384000
N	-3.302855000	2.136029000	-0.599221000
N	-2.506552000	0.921869000	1.564898000
N	-0.858975000	2.534261000	-1.680976000
C	0.813845000	3.677336000	1.982761000
H	0.939612000	2.627894000	1.731215000
H	0.716649000	3.773021000	3.072059000
H	1.703284000	4.241869000	1.687068000
C	-0.402963000	4.289643000	1.350822000
C	-0.485878000	5.693207000	1.393846000
H	0.361538000	6.238146000	1.801998000

C	-1.609272000	6.364667000	0.935919000
C	-2.684194000	5.600715000	0.478635000
H	-3.612851000	6.056678000	0.146184000
C	-2.559877000	4.219164000	0.453961000
C	-3.735150000	3.360489000	0.116018000
H	-4.197618000	3.049001000	1.060597000
H	-4.488422000	3.907104000	-0.460044000
C	-4.162972000	0.988997000	-0.207334000
H	-4.019666000	0.181918000	-0.928121000
H	-5.220591000	1.279895000	-0.220075000
C	-3.750359000	0.549439000	1.162067000
C	-4.619766000	-0.172130000	1.972562000
H	-5.601639000	-0.441410000	1.592152000
C	-4.208717000	-0.515970000	3.259101000
H	-4.853334000	-1.095022000	3.916042000
C	-2.969859000	-0.059994000	3.696568000
H	-2.627830000	-0.257698000	4.708632000
C	-2.134369000	0.679815000	2.847799000
C	-0.872298000	1.256650000	3.398458000
H	-0.999731000	2.338405000	3.520773000
H	-0.027902000	1.082519000	2.732505000
H	-0.665957000	0.825559000	4.380503000
C	-3.267032000	2.296144000	-2.073289000
H	-3.931701000	3.111794000	-2.380801000
H	-3.650071000	1.378933000	-2.528279000
C	-1.878520000	2.559640000	-2.572612000
C	-1.687912000	2.814508000	-3.929158000

H	-2.546023000	2.815815000	-4.596872000
C	-0.395792000	3.046272000	-4.393915000
H	-0.203206000	3.211618000	-5.451427000
C	0.635027000	3.105430000	-3.461731000
H	1.650539000	3.346050000	-3.765648000
C	0.383469000	2.892058000	-2.099797000
Co	1.227056000	-1.312186000	-0.070210000
O	-0.442417000	-1.742709000	-0.912268000
O	-1.746895000	0.135333000	-1.006749000
N	2.003429000	-3.480060000	0.329184000
N	3.006171000	-0.837820000	0.657841000
N	2.256920000	-1.072865000	-1.828525000
N	0.689696000	-1.499998000	1.910594000
C	0.136357000	-4.890207000	-0.424888000
H	-0.268485000	-3.949095000	-0.798027000
H	0.405322000	-5.515047000	-1.287328000
H	-0.630582000	-5.428166000	0.142089000
C	1.357469000	-4.658011000	0.414720000
C	1.853894000	-5.684037000	1.237639000
H	1.307201000	-6.622068000	1.297442000
C	3.024634000	-5.489486000	1.962736000
C	3.709926000	-4.277770000	1.823945000
H	4.642210000	-4.086935000	2.349116000
C	3.169373000	-3.305938000	0.988719000
C	3.905278000	-2.035066000	0.678831000
H	4.330437000	-2.132304000	-0.326746000
H	4.726615000	-1.859734000	1.380912000

C	3.590176000	0.195112000	-0.245266000
H	3.134401000	1.156828000	-0.004315000
H	4.672386000	0.268895000	-0.086187000
C	3.273278000	-0.186918000	-1.661174000
C	3.993551000	0.329252000	-2.732082000
H	4.802807000	1.030623000	-2.545890000
C	3.657636000	-0.080874000	-4.023032000
H	4.185680000	0.316172000	-4.886986000
C	2.667270000	-1.045882000	-4.178074000
H	2.418421000	-1.437422000	-5.161152000
C	1.985452000	-1.555996000	-3.063405000
C	0.998323000	-2.667003000	-3.246925000
H	0.981951000	-3.317195000	-2.372941000
H	-0.014204000	-2.282363000	-3.405023000
H	1.277097000	-3.250505000	-4.129292000
C	2.775819000	-0.289116000	2.021224000
H	3.707684000	-0.267122000	2.595515000
H	2.416206000	0.738004000	1.897954000
C	1.708756000	-1.081663000	2.706865000
C	1.732477000	-1.301166000	4.078886000
H	2.581661000	-0.954262000	4.661203000
C	0.655909000	-1.963819000	4.668721000
H	0.639777000	-2.161398000	5.737953000
C	-0.401320000	-2.358578000	3.856505000
H	-1.269451000	-2.859481000	4.276028000
C	-0.374679000	-2.119512000	2.473566000
C	-1.400158000	-1.032952000	-1.339490000

O	0.905461000	0.488973000	-0.303014000
C	-2.264436000	-1.672742000	-2.384052000
C	-2.576096000	-0.957413000	-3.552107000
C	-2.741726000	-2.982167000	-2.216020000
H	-2.176530000	0.044218000	-3.692601000
H	-2.502856000	-3.535364000	-1.311475000
C	-3.356401000	-1.550733000	-4.548409000
C	-3.542862000	-3.562097000	-3.204187000
H	-3.579170000	-0.998911000	-5.459562000
H	-3.926342000	-4.570864000	-3.063970000
C	-3.847278000	-2.850620000	-4.372102000
H	-4.462402000	-3.309437000	-5.143898000
H	-1.658828000	7.450903000	0.951823000
C	1.479244000	3.190578000	-1.126922000
H	1.368812000	2.636253000	-0.202221000
H	2.450551000	2.970217000	-1.578462000
H	1.454198000	4.266066000	-0.903328000
H	3.406580000	-6.269176000	2.618122000
C	-1.551154000	-2.532828000	1.645807000
H	-1.267418000	-3.244097000	0.870436000
H	-2.304324000	-2.994280000	2.287948000
H	-1.996138000	-1.664665000	1.153897000

Cartesian coordinates for the optimized structure of I-OOH:

Atom	Coordinates (Angstroms)		
	X	Y	Z

Co	-1.499135000	1.733581000	0.087268000
O	0.159974000	1.009273000	0.789197000
N	-1.465791000	3.586544000	0.795786000
N	-3.258457000	2.096705000	-0.621380000
N	-2.559958000	0.996694000	1.604289000
N	-0.804135000	2.487916000	-1.626152000
C	0.748544000	3.743677000	2.013170000
H	0.904745000	2.688066000	1.821398000
H	0.634146000	3.887462000	3.094988000
H	1.639237000	4.300661000	1.708555000
C	-0.461725000	4.325553000	1.339534000
C	-0.563669000	5.727657000	1.365007000
H	0.265685000	6.286334000	1.790906000
C	-1.681284000	6.381798000	0.869415000
C	-2.737323000	5.604537000	0.390872000
H	-3.660684000	6.047870000	0.028481000
C	-2.599023000	4.225698000	0.385819000
C	-3.747378000	3.342341000	0.033334000
H	-4.247366000	3.053708000	0.965449000
H	-4.480534000	3.844517000	-0.603421000
C	-4.129204000	0.944885000	-0.231833000
H	-3.971577000	0.125869000	-0.934843000
H	-5.181117000	1.249783000	-0.284334000
C	-3.758329000	0.539346000	1.155760000
C	-4.612403000	-0.224241000	1.942358000
H	-5.557927000	-0.563480000	1.527853000
C	-4.227821000	-0.525862000	3.246993000

H	-4.852949000	-1.146864000	3.883760000
C	-3.050758000	0.034831000	3.735375000
H	-2.749788000	-0.114096000	4.768518000
C	-2.238872000	0.829117000	2.916567000
C	-1.091381000	1.567714000	3.532929000
H	-1.307884000	2.641136000	3.509273000
H	-0.132362000	1.403983000	3.040639000
H	-0.981725000	1.260971000	4.575176000
C	-3.179690000	2.199930000	-2.107274000
H	-3.874066000	2.969666000	-2.459924000
H	-3.500098000	1.245188000	-2.532681000
C	-1.789267000	2.505899000	-2.556918000
C	-1.552756000	2.772202000	-3.902106000
H	-2.386314000	2.768648000	-4.599687000
C	-0.246298000	3.016150000	-4.316812000
H	-0.015491000	3.190839000	-5.364904000
C	0.749012000	3.072511000	-3.347330000
H	1.773646000	3.318725000	-3.612339000
C	0.452518000	2.851121000	-1.996305000
Co	1.326188000	-1.421703000	-0.009904000
O	-0.378990000	-1.756608000	-0.796370000
O	-1.703511000	0.113530000	-0.899290000
N	1.939474000	-3.340709000	0.286461000
N	3.059643000	-0.874029000	0.633475000
N	2.201264000	-1.165696000	-1.761455000
N	0.766158000	-1.519852000	1.925436000
C	-0.011221000	-4.724459000	-0.475461000

H	-0.433228000	-3.799820000	-0.855219000
H	0.205466000	-5.381087000	-1.328497000
H	-0.743544000	-5.245755000	0.149933000
C	1.262068000	-4.516960000	0.289556000
C	1.785792000	-5.632088000	0.967402000
H	1.203740000	-6.550138000	0.962155000
C	3.007482000	-5.567395000	1.620709000
C	3.733103000	-4.376861000	1.538900000
H	4.715541000	-4.269525000	1.990202000
C	3.175415000	-3.306385000	0.856881000
C	3.957542000	-2.062352000	0.605032000
H	4.385539000	-2.128006000	-0.402106000
H	4.777994000	-1.930984000	1.316272000
C	3.584005000	0.170232000	-0.291248000
H	3.191730000	1.141539000	0.008561000
H	4.678194000	0.204540000	-0.224935000
C	3.139059000	-0.186479000	-1.675814000
C	3.678889000	0.427689000	-2.799258000
H	4.428146000	1.205319000	-2.676020000
C	3.238813000	0.018071000	-4.056967000
H	3.613112000	0.495083000	-4.959629000
C	2.357209000	-1.057160000	-4.135382000
H	2.053830000	-1.459881000	-5.098025000
C	1.865818000	-1.671160000	-2.976177000
C	1.063711000	-2.928916000	-3.091470000
H	1.468374000	-3.684488000	-2.413708000
H	0.009146000	-2.780190000	-2.853246000

H	1.134582000	-3.303616000	-4.115340000
C	2.874339000	-0.336892000	2.006944000
H	3.820516000	-0.350804000	2.556169000
H	2.550914000	0.705497000	1.915414000
C	1.809037000	-1.111654000	2.708854000
C	1.846177000	-1.313368000	4.080609000
H	2.709232000	-0.973548000	4.646135000
C	0.764659000	-1.945401000	4.694202000
H	0.758015000	-2.123207000	5.766845000
C	-0.308591000	-2.339194000	3.903014000
H	-1.176881000	-2.819966000	4.344514000
C	-0.302823000	-2.130898000	2.516965000
C	-1.322179000	-1.043261000	-1.245178000
O	0.950363000	0.380361000	-0.274480000
C	-2.149511000	-1.663064000	-2.330768000
C	-2.244080000	-1.012557000	-3.572154000
C	-2.805511000	-2.886202000	-2.120333000
H	-1.712727000	-0.077611000	-3.736805000
H	-2.741853000	-3.382069000	-1.154968000
C	-2.983329000	-1.594624000	-4.605513000
C	-3.561649000	-3.450490000	-3.152201000
H	-3.040008000	-1.098822000	-5.572458000
H	-4.082146000	-4.391362000	-2.985408000
C	-3.646750000	-2.810164000	-4.394896000
H	-4.228365000	-3.258028000	-5.198291000
H	-1.741256000	7.467431000	0.872875000
C	1.517088000	3.154838000	-0.993391000

H	1.435573000	2.569259000	-0.085836000
H	2.501826000	2.989134000	-1.437742000
H	1.450230000	4.220102000	-0.735438000
H	3.398310000	-6.425172000	2.162808000
C	-1.505975000	-2.550156000	1.731255000
H	-1.252067000	-3.246650000	0.935183000
H	-2.221363000	-3.029945000	2.401593000
H	-1.995341000	-1.686437000	1.272004000
H	-0.057490000	0.235533000	1.349923000

Cartesian coordinates for the optimized structure of I-O2H2:

Atom	Coordinates (Angstroms)		
	X	Y	Z
Co	-1.459864000	0.154543000	1.833039000
O	0.093928000	-0.876857000	0.973690000
N	-1.662022000	-0.716804000	3.573424000
N	-2.838650000	1.378875000	2.305374000
N	-2.957963000	-0.830797000	0.961782000
N	-0.220895000	1.428074000	2.787895000
C	-0.031328000	-2.664004000	3.461353000
H	0.212304000	-2.398589000	2.439179000
H	-0.514541000	-3.648522000	3.460699000
H	0.900213000	-2.767611000	4.025018000
C	-0.932879000	-1.696784000	4.174243000
C	-1.049830000	-1.887805000	5.561950000

H	-0.449297000	-2.673882000	6.012041000
C	-1.890559000	-1.103636000	6.336878000
C	-2.670929000	-0.143394000	5.692921000
H	-3.378226000	0.481695000	6.231009000
C	-2.543712000	0.005325000	4.321887000
C	-3.473428000	0.887560000	3.566756000
H	-4.347939000	0.289003000	3.284751000
H	-3.820151000	1.736623000	4.161481000
C	-3.850579000	1.395992000	1.211621000
H	-3.523539000	2.090378000	0.437750000
H	-4.804535000	1.765837000	1.605414000
C	-3.976730000	0.019247000	0.665705000
C	-5.075891000	-0.349581000	-0.098709000
H	-5.850171000	0.384862000	-0.302866000
C	-5.142500000	-1.652440000	-0.583783000
H	-5.970212000	-1.974284000	-1.210717000
C	-4.145483000	-2.546559000	-0.204667000
H	-4.189125000	-3.589379000	-0.506249000
C	-3.073407000	-2.138071000	0.597479000
C	-2.134907000	-3.175452000	1.121712000
H	-2.246036000	-3.239913000	2.207805000
H	-1.084107000	-2.998981000	0.886670000
H	-2.392267000	-4.147272000	0.695780000
C	-2.225678000	2.736197000	2.427731000
H	-2.848154000	3.357540000	3.079108000
H	-2.216276000	3.190063000	1.434896000
C	-0.831885000	2.632940000	2.932680000

C	-0.204693000	3.746364000	3.475922000
H	-0.757626000	4.677851000	3.561916000
C	1.121917000	3.633215000	3.883003000
H	1.659018000	4.487653000	4.287276000
C	1.728290000	2.386453000	3.792522000
H	2.746190000	2.235688000	4.141178000
C	1.040703000	1.276974000	3.282516000
Co	1.447436000	-0.011734000	-1.491939000
O	-0.444021000	0.366937000	-1.778678000
O	-1.109547000	1.282672000	0.173765000
N	2.098596000	-0.202744000	-3.343295000
N	3.259356000	-0.232899000	-0.895705000
N	1.898958000	1.894649000	-1.282406000
N	1.317583000	-2.011539000	-1.515891000
C	0.009100000	0.078737000	-4.739063000
H	-0.517274000	0.356757000	-3.833157000
H	0.043734000	0.953701000	-5.401197000
H	-0.547147000	-0.700383000	-5.269669000
C	1.420378000	-0.374814000	-4.508922000
C	2.082918000	-0.928885000	-5.618254000
H	1.506453000	-1.067758000	-6.529132000
C	3.422946000	-1.279590000	-5.563106000
C	4.123558000	-1.014541000	-4.384818000
H	5.185492000	-1.221227000	-4.285623000
C	3.436251000	-0.469485000	-3.313535000
C	4.143486000	-0.030443000	-2.080377000
H	4.344585000	1.043787000	-2.166168000

H	5.094352000	-0.548376000	-1.928707000
C	3.541308000	0.818069000	0.128686000
H	3.238512000	0.457555000	1.111550000
H	4.620241000	1.010725000	0.163090000
C	2.791283000	2.051871000	-0.266360000
C	3.011759000	3.278783000	0.344507000
H	3.725519000	3.350990000	1.160500000
C	2.302683000	4.385834000	-0.118977000
H	2.418968000	5.357335000	0.355057000
C	1.493595000	4.238849000	-1.244124000
H	0.999148000	5.097622000	-1.689870000
C	1.321913000	2.989201000	-1.850313000
C	0.612073000	2.889454000	-3.164143000
H	1.276655000	2.419859000	-3.896161000
H	-0.313859000	2.316435000	-3.120230000
H	0.366146000	3.894291000	-3.513936000
C	3.377821000	-1.601439000	-0.316075000
H	4.423581000	-1.922405000	-0.321072000
H	3.042980000	-1.556589000	0.725433000
C	2.495249000	-2.538456000	-1.067973000
C	2.829605000	-3.875391000	-1.216944000
H	3.789328000	-4.227989000	-0.849687000
C	1.916358000	-4.728259000	-1.836352000
H	2.144402000	-5.781893000	-1.977512000
C	0.704555000	-4.200001000	-2.264722000
H	-0.041974000	-4.833205000	-2.735183000
C	0.409316000	-2.838468000	-2.110646000

C	-1.284267000	1.018791000	-1.100280000
O	0.986047000	0.135915000	0.410224000
C	-2.446193000	1.587814000	-1.800310000
C	-2.802001000	2.929488000	-1.551706000
C	-3.139610000	0.832246000	-2.763766000
H	-2.221370000	3.526678000	-0.851405000
H	-2.861617000	-0.201175000	-2.949074000
C	-3.862419000	3.500628000	-2.254890000
C	-4.218468000	1.404612000	-3.437165000
H	-4.127691000	4.540484000	-2.079157000
H	-4.778015000	0.813458000	-4.158264000
C	-4.578526000	2.735330000	-3.185279000
H	-5.414877000	3.179792000	-3.720787000
H	-1.950330000	-1.244453000	7.413200000
C	1.716580000	-0.052017000	3.403398000
H	1.444586000	-0.768802000	2.637045000
H	2.800355000	0.088607000	3.384607000
H	1.467943000	-0.476271000	4.384645000
H	3.918717000	-1.728198000	-6.420417000
C	-0.930751000	-2.350629000	-2.563937000
H	-0.852072000	-1.562973000	-3.309609000
H	-1.482210000	-3.184256000	-3.002960000
H	-1.521658000	-1.960972000	-1.730923000
H	-0.075910000	-1.457658000	0.200809000
H	0.249559000	0.902719000	0.357522000

Cartesian coordinates for the optimized structure of Co-O2H:

Atom	Coordinates (Angstroms)		
	X	Y	Z
Co	-0.020715000	0.021940000	0.330614000
O	1.275593000	-2.304772000	2.337758000
O	0.104676000	-1.881555000	0.446986000
N	0.082935000	1.996835000	-0.169519000
N	0.013292000	-0.332295000	-1.624089000
N	-1.967896000	-0.187259000	0.033638000
N	1.988079000	0.095900000	0.212487000
C	0.109687000	3.156304000	2.059959000
H	-0.108669000	2.178564000	2.486913000
H	-0.748491000	3.819857000	2.232969000
H	0.970065000	3.611869000	2.562054000
C	0.360036000	3.095034000	0.581059000
C	0.842580000	4.268645000	-0.026128000
H	1.069276000	5.116700000	0.614901000
C	1.023803000	4.346881000	-1.398821000
C	0.668340000	3.237079000	-2.167510000
H	0.752428000	3.238972000	-3.250628000
C	0.196403000	2.102297000	-1.522931000
C	-0.310335000	0.938817000	-2.309992000
H	-1.402471000	1.020126000	-2.363295000
H	0.075735000	0.938290000	-3.334394000
C	-1.043686000	-1.332592000	-1.898481000
H	-0.648033000	-2.322356000	-1.671706000
H	-1.334915000	-1.310200000	-2.955541000

C	-2.214354000	-1.013524000	-1.015414000
C	-3.482579000	-1.510267000	-1.296792000
H	-3.623159000	-2.165741000	-2.152079000
C	-4.544711000	-1.134306000	-0.475528000
H	-5.548073000	-1.514452000	-0.652409000
C	-4.300370000	-0.216602000	0.542038000
H	-5.111687000	0.154969000	1.162210000
C	-3.006809000	0.272498000	0.774490000
C	-2.807954000	1.351205000	1.793069000
H	-2.208463000	2.158843000	1.367757000
H	-2.286856000	0.975798000	2.676133000
H	-3.782742000	1.749625000	2.086993000
C	1.365288000	-0.828292000	-1.950482000
H	1.601361000	-0.674616000	-3.008744000
H	1.375268000	-1.905283000	-1.750854000
C	2.382877000	-0.184194000	-1.058751000
C	3.683917000	0.009364000	-1.509292000
H	3.929446000	-0.215302000	-2.543535000
C	4.640442000	0.481099000	-0.611481000
H	5.666606000	0.655087000	-0.926328000
C	4.250210000	0.703684000	0.703480000
H	4.968869000	1.038761000	1.446334000
C	2.920585000	0.503702000	1.111593000
C	0.826171000	-2.626542000	1.221295000
C	2.591726000	0.706852000	2.558938000
H	1.901900000	1.537445000	2.709987000
H	2.111242000	-0.189124000	2.957523000

H	3.517330000	0.913238000	3.103021000
C	1.101760000	-3.998288000	0.675766000
C	2.216144000	-4.708950000	1.153361000
C	0.274733000	-4.583841000	-0.297629000
H	2.847012000	-4.253244000	1.913310000
H	-0.606815000	-4.050804000	-0.644304000
C	2.511475000	-5.977856000	0.647017000
C	0.559575000	-5.860891000	-0.789674000
H	3.384583000	-6.516543000	1.010612000
H	-0.093684000	-6.312745000	-1.533665000
C	1.683427000	-6.556305000	-0.324313000
H	1.910193000	-7.547268000	-0.713453000
O	-0.142770000	0.311342000	2.139816000
O	-0.810789000	-0.745157000	2.847507000
H	-0.064302000	-1.396765000	2.895446000
H	1.415762000	5.248910000	-1.862404000

References

1. B. Chakraborty, I. Ghosh, R. D. Jana and T. K. Paine, *Dalton Trans.*, 2020, **49**, 3463-3472.

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