

## Supporting Information

C–H Bond Activations by HO•/(Salophen<sup>*t-Bu*</sup>)Co(II) Radical Pair  
Generated via Homolysis of a Terminal Co(III)–OH Bond

Jia Zhang,<sup>a</sup> Songyi Li<sup>a</sup> and Huayi Fang<sup>\*a</sup>

<sup>a</sup>School of Materials Science and Engineering, Tianjin Key Lab for Rare Earth Materials and Applications,  
Nankai University, Tianjin 300350, China

## Table of Contents

General information and experimental details	S3-
<b>S5</b>	
NMR spectra of complexes <b>1-7</b>	<b>S6-S13</b>
Powder XRD measurement of complex <b>7</b>	<b>S14</b>
FTIR spectrum of complex <b>7</b>	<b>S15</b>
Solid state structure of complex <b>4</b> and <b>6</b>	<b>S16-S17</b>
XPS measurements of complexes <b>3-7</b>	<b>S18-S22</b>
MS spectrum of DMPO-OH generated in hydrous methanol solution of <b>1</b>	<b>S23</b>
Fluorescence spectrum of hydroxyl radical trapping by disodium terephthalate	<b>S24</b>
GC and HRMS analysis of the <sup>18</sup> O-phenol produced in isotope labelling studies	<b>S25-</b>
<b>S26</b>	
EPR spectrum of DMPO-OH trapped in the reaction of complex <b>6</b> with OH <sup>-</sup>	<b>S27</b>
MS spectrum of DMPO-OH generated by complex <b>6</b> with NaOH/15-crown-5	
<b>S28</b>	
MS spectrum of methanol solution of complex <b>1</b> with OH <sup>-</sup>	
<b>S29</b>	
Scheme for the formation of <b>1, 2, 7, 8</b> and diphenyl and phenol	<b>S30-S32</b>
Selected bond lengths (Å) and angles (deg) for <b>3-7</b>	<b>S33</b>
Optimized structures of <b>1</b> , (Salophen <sup><i>t-Bu</i></sup> )(CH <sub>3</sub> OH)Co(III)(OH), [(Salophen <sup><i>t-Bu</i></sup> )(CH <sub>3</sub> OH)Co(III)(OH <sub>2</sub> )] <sup>+</sup>	
and <b>T5</b>	<b>S34-S37</b>

Relaxed energy surface scans for recombination of OMe and OH radical with Co(II) center **S38-**

**S39**

References

**S40**

**General information.** All operations on air-sensitive materials were performed under N<sub>2</sub> atmosphere using standard Schlenk techniques or in gloveboxes. CD<sub>3</sub>OD, D<sub>2</sub>O, d<sub>6</sub>-DMSO and CD<sub>2</sub>Cl<sub>2</sub> were purchased from Cambridge Isotope Laboratory Inc. All chemicals were purchased from Sigma-Aldrich, Alfa Aesar, or J&K Scientific Ltd. and used without further treatment unless otherwise noted. Solvents were purified and dried before use through standard procedures. <sup>1</sup>H NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer at room temperature, and the chemical shifts were referenced to solvent residual signals. The single crystal X-ray diffraction measurements were performed on Rigaku Smart Lab instrument with Cu K $\alpha$  radiation. The UV/Vis measurements were conducted on a Shimadzu 2600 spectrometer. The infrared spectra were recorded using a Bruker Tensor 37 spectrometer. The XPS spectra were recorded on an ESCALAB 250 instrument. The X-band CW-EPR measurements were recorded on a Bruker EMX plus spectrometer at room temperature. EPR spectral simulations were performed using EasySpin.<sup>1</sup> The elemental analysis results were obtained by a Vario EL cube analyzer. Thermal analysis was carried out on Netzsch TG209 thermobalance under a nitrogen atmosphere. Mass spectra were obtained by an Agilent 6230 mass spectrometer equipped with an electrospray ionization source and time-of-flight mass analyzer, or a Dionex Ultimate 3000 series liquid chromatography combined with a Q Exactive hybrid Quadrupole-Orbitrap mass spectrometer. The GC measurements were performed on Shimadzu GC-2010 Pro instrument equipped with a flame ionization detector and a WondaCap Wax capillary column (30 m  $\times$  0.25 mm).

**Synthesis of (Salophen<sup>*t*-Bu</sup>)Co(CH<sub>2</sub>COCH<sub>3</sub>) (3).** (Salophen<sup>*t*-Bu</sup>)(MeOH)Co(III)(OMe) (**1**) was synthesized based on previously reported method. 20.3 mg of complex **1** and 40  $\mu$ L deionized water were added into a 10 mL round-bottom flask with 5 mL of acetone as the solvent under the N<sub>2</sub> atmosphere. The solution was stirred for 2 h at room temperature until the color of the solution turned to reddish black and then evaporated to dryness under reduced pressure. Redissolving the powder with little amount of acetone and addition of 50 mL deionized water to the solution quickly resulted in the precipitation of the product compound. The precipitate was filtered under reduced pressure and identified as (Salophen<sup>*t*-Bu</sup>)Co(CH<sub>2</sub>COCH<sub>3</sub>) in 74% yield. Crystals suitable for single crystal X-ray diffraction were obtained over one day by dissolving the red powder in acetone and layering with H<sub>2</sub>O. UV/Vis (acetone):  $\lambda_{\text{max}}$ ( $\epsilon$ ) = 389 (12001), 530 (3338), 568 nm (2931 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); elemental analysis calcd (%) for C<sub>31</sub>H<sub>35</sub>CoN<sub>3</sub>O<sub>3</sub> (F.W. = 542.56): C 68.63; H 6.50, N 5.16; found: C 68.18, H 6.76, N 5.25; <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$  (ppm): 8.77 (s, 2H), 8.24 (q,  $J$  = 9.7 Hz, 2H), 7.41 (dd,  $J_1$  = 7.9,  $J_2$  = 1.5 Hz, 2H), 7.34 (q,  $J$  = 9.5 Hz, 2H), 7.22 (dd,  $J_1$  = 7.2,  $J_2$  = 1.6 Hz, 2H), 6.53 (t,  $J$  = 15.0 Hz, 2H), 3.30 (s, 2H), 1.58 (s, 18H), 1.14 (s, 3H). IR (solid):  $\nu$ (C=O) = 1655 cm<sup>-1</sup>.

**Synthesis of (Salophen<sup>*t*-Bu</sup>)Co(CH<sub>2</sub>CH<sub>2</sub>COCH<sub>3</sub>) (4a) and (Salophen<sup>*t*-Bu</sup>)Co(CH<sub>2</sub>COCH<sub>2</sub>CH<sub>3</sub>) (4b)** 100.0 mg of complex **1** and 200  $\mu$ L of deionized water were added into a 25 mL Schlenk flask with 5 mL of CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub> as the solvent under the N<sub>2</sub> atmosphere. The solution was stirred for 6 h at room temperature until the color of the solution turned to reddish black and then a large amount of water was added for recrystallization, the resulting red powder was then filtrated under reduced pressure and identified as the mixture of (Salophen<sup>*t*-Bu</sup>)Co(CH<sub>2</sub>CH<sub>2</sub>COCH<sub>3</sub>) and (Salophen<sup>*t*-Bu</sup>)Co(CH<sub>2</sub>COCH<sub>2</sub>CH<sub>3</sub>) in total 69% yield. Crystals suitable for single crystal X-ray diffraction were obtained over one day by dissolving the red powder in DCM and layering with Et<sub>2</sub>O. elemental analysis calcd (%) for C<sub>32</sub>H<sub>37</sub>CoN<sub>2</sub>O<sub>3</sub> (F.W. = 556.59): C 69.05; H 6.70, N 5.03; found: C 68.88, H 6.80, N 4.98; <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$  (ppm): 8.75 (br, 2H), 8.26 (br, 2H), 7.41 (d,  $J$  = 8.0 Hz, 2H), 7.31 (s, 2H), 7.23 (d,  $J$  = 8 Hz, 2H), 6.54 (m, 2H), 1.65 (s, 3H), 1.65 (s, 18H), 1.50 (m, 2H), 0.26 (t,  $J$  =

16 Hz, 2H). IR (solid):  $\nu(\text{C}=\text{O}) = 1655 \text{ cm}^{-1}$ .

**Synthesis of (Salophen<sup>t-Bu</sup>)Co(CH<sub>2</sub>CN) (5)** 100.0 mg of complex **1** and 40 mg of NaOH were added into a 25 mL Schlenk flask with 5 mL of MeCN as the solvent under the N<sub>2</sub> atmosphere. The solution was stirred for 6 h at room temperature until the color of the solution turned to reddish black and filtrated under reduced pressure. The filtrate was then evaporated to dryness under reduced pressure. Redissolving the red powder with little amount of ethyl acetate and addition of 50 mL *n*-pentane to the solution resulted in the precipitation of the product compound. The precipitate was filtered under reduced pressure and identified as (Salophen<sup>t-Bu</sup>)Co(CH<sub>2</sub>CN) in 56% yield. Crystals suitable for single crystal X-ray diffraction were obtained over one day by dissolving the red powder in DCM and layering with Et<sub>2</sub>O. UV/Vis (DCM):  $\lambda_{\text{max}}(\epsilon) = 342 (18087), 386 (13980), 467 (8087), 559 \text{ nm} (3560 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$ ; elemental analysis calcd (%) for C<sub>30</sub>H<sub>32</sub>CoN<sub>3</sub>O<sub>2</sub> (F.W. = 525.54): C 68.56; H 6.14, N 8.00; found: C 68.42, H 6.56, N 7.96; <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$  (ppm): 8.83 (s, 2H), 8.31 (m, 2H), 7.43 (d,  $J = 7.6 \text{ Hz}$ , 2H), 7.38 (m, 2H), 7.24 (d,  $J = 6.3 \text{ Hz}$ , 2H), 6.54(t,  $J = 14.9 \text{ Hz}$ , 2H), 2.45 (s, 2H), 1.53 (s, 18H). Free DCM and Et<sub>2</sub>O were observed at  $\delta = 5.76$  (CH<sub>2</sub> in DCM), 3.41(CH<sub>2</sub> in Et<sub>2</sub>O) and 1.11 (CH<sub>3</sub> in Et<sub>2</sub>O). <sup>13</sup>C NMR (400MHz, d<sub>6</sub>-DMSO)  $\delta$  (ppm): 153.73, 143.70, 130.54, 129.86, 119.30, 117.98, 113.13, 105.31, 102.12, 101.56, 21.99, 15.82. IR (solid):  $\nu(\text{C}\equiv\text{N}) = 2206 \text{ cm}^{-1}$ .

**Synthesis of [(Salophen<sup>t-Bu</sup>)(Py)<sub>2</sub>Co(III)](BPh<sub>4</sub>) (6).** (Salophen<sup>t-Bu</sup>)Co(II) (**2**) was synthesized based on previously reported method and isolated as a brown crystalline solid.<sup>2</sup> 97.1 mg of complex **2**, 102.7 mg of NaBPh<sub>4</sub>, and 0.15 mL of pyridine were added into a 10 mL Schlenk flask with 5 mL of toluene as the solvent. After three freeze-pump-thaw cycles, 1 atm of O<sub>2</sub> was inflated into the Schlenk flask. The solution was stirred for one day at room temperature. The crude material was filtered and washed with *n*-pentane, the dark powder was identified as **6** in 76% yield. The crystal suitable for single crystal X-ray diffraction of **6** was collected by slow diffusion of *n*-pentane into the CH<sub>2</sub>Cl<sub>2</sub> solution of **6** at room temperature over one day. UV/Vis (benzene):  $\lambda_{\text{max}}(\epsilon) = 410 (11920), 479 \text{ nm} (11261 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$ ; elemental analysis calcd (%) for C<sub>62</sub>H<sub>60</sub>BCoN<sub>4</sub>O<sub>2</sub>·H<sub>2</sub>O (F.W. = 980.95): C 75.91, H 6.37, N 5.71; found: C 75.91, H 6.26, N 5.79; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 8.45 (s, 2H), 7.93 (q,  $J = 9.5 \text{ Hz}$ , 2H), 7.83 (d,  $J = 5.4 \text{ Hz}$ , 4H), 7.64 (t,  $J = 15.2 \text{ Hz}$ , 2H), 7.49 (dd,  $J = 7.4, 1.6 \text{ Hz}$ , 2H), 7.48 (q,  $J = 9.5 \text{ Hz}$ , 2H), 7.30 (s, 8H), 7.23 (dd,  $J_1 = 8.0, J_2 = 1.4 \text{ Hz}$ , 2H), 7.06 (t,  $J = 14.1 \text{ Hz}$ , 4H), 7.00 (t,  $J = 14.6 \text{ Hz}$ , 8H), 6.85 (t,  $J = 14.2 \text{ Hz}$ , 4H), 6.69 (t,  $J = 15.3 \text{ Hz}$ , 2H), 1.51 (s, 18H).

**Synthesis of [(Salophen<sup>t-Bu</sup>)(H<sub>2</sub>O)Co(III)](μ-OH)Co(III)(Salophen<sup>t-Bu</sup>)(H<sub>2</sub>O)][OTs] (7).** (Salophen<sup>t-Bu</sup>)Co(OTs) (**8**) was synthesized based on previously reported method.<sup>3</sup> 97.1 mg of **2** and 38.0 mg 4-methylbenzenesulfonic acid hydrate were added into a 10 mL round-bottom flask with 5 mL of dichloromethane as the solvent. The solution was stirred for 3 h at room temperature and filtered. The precipitate was filtered under reduced pressure and identified as (Salophen<sup>t-Bu</sup>)Co(OTs) (**8**). By dissolving the **8** with a small amount of ethanol and then layering with H<sub>2</sub>O, dark red crystals were obtained in 2 days with a yield of 17%. UV/Vis (ethanol):  $\lambda_{\text{max}}(\epsilon) = 395 (23785), 449 \text{ nm} (18694 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$ ; elemental analysis calcd (%) for C<sub>63</sub>H<sub>76</sub>Co<sub>2</sub>N<sub>4</sub>O<sub>12</sub>S (F.W. = 1231.24): C 62.37, H 6.15, N 4.62, S 2.64; found: C 62.69, H 6.19, N 4.59, S 2.31; IR (BrK):  $\nu(\mu\text{-O-H stretching}) = 3548 \text{ (s) cm}^{-1}$ .

**Isotope (<sup>18</sup>O) labelling experiment.** 19.4 mg (1 eq) of **2**, 72 μL (100 eq) of H<sub>2</sub><sup>18</sup>O and 15.2 mg (9.5 eq) of NaOH were added into a 10 mL Schlenk flask with 5 mL of anhydrous methanol and 1 mL of anhydrous benzene. After three freeze-pump-thaw cycles, 1 atm of <sup>16</sup>O<sub>2</sub> dried by passing

through P<sub>2</sub>O<sub>5</sub> powder was inflated. After stirring the reaction mixture for one day at room temperature, 1 mL of reaction solution was filtered through a nylon membrane filter (0.25 μm pore size) and used for GC and MS analysis.

**DFT calculations.** All calculations were performed on the ORCA quantum chemistry program package (version 5.0.3).<sup>4</sup> The BP functional was used in geometry optimizations and relaxed energy surface scans without any constraint except for the spin multiplicity, and the hybrid B3LYP functional was applied for single-point calculations.<sup>5-9</sup> The all-electron ZORA-Def2-SVP basis set was applied for all elements in geometry optimizations and relaxed energy surface scans. The ZORA-Def2-TZVPP basis set was used for single-point calculations. The ZORA-Def2-TZVP basis set was used in the calculations for NBO analysis.<sup>10</sup> The RIJCOSX plus chain of spheres approximation was used to accelerate the calculations.<sup>11</sup> The general-purpose Coulomb-fitting auxiliary basis sets SARC/J were used. The relativistic effect was taken into account based on the 0<sup>th</sup>-order regular approximation (ZORA).<sup>12, 13</sup> Atom-pairwise dispersion correction to the DFT energy with Becke-Johnson damping (D3BJ) was involved.<sup>14-16</sup> The solvation effect was considered using the conductor-like polarizable continuum model (C-PCM).<sup>17</sup> For the calculation of the energy profile for the C-H bond activation of acetone, acetone ( $\epsilon = 20.7$ ) was used as the solvent. For the calculation of the energy profile for the C-H bond activation of acetonitrile, acetonitrile ( $\epsilon = 36.6$ ) was used as the solvent. For the calculation of the energy profile for the C-H bond activation of 2-butanone, 2-butanone ( $\epsilon = 18.5$ ) was used as the solvent. For other calculations, methanol ( $\epsilon = 32.63$ ) was used as the solvent. The natural bond orbital analysis was performed using the NBO 7.0 program package.<sup>18</sup>

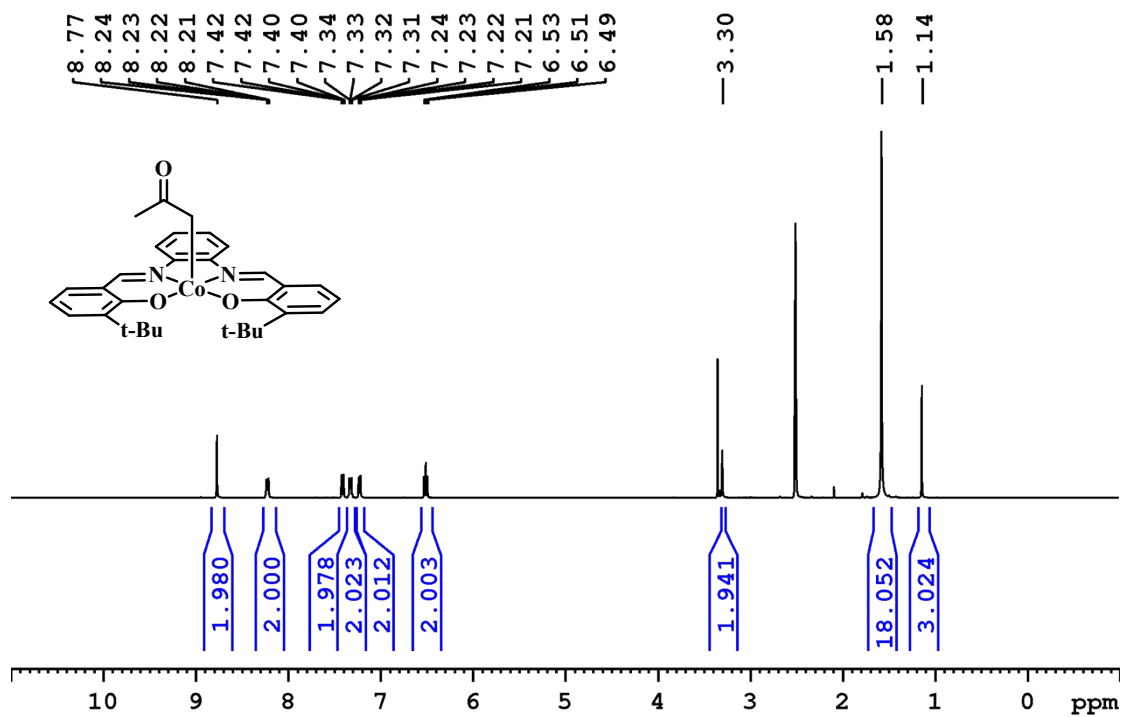
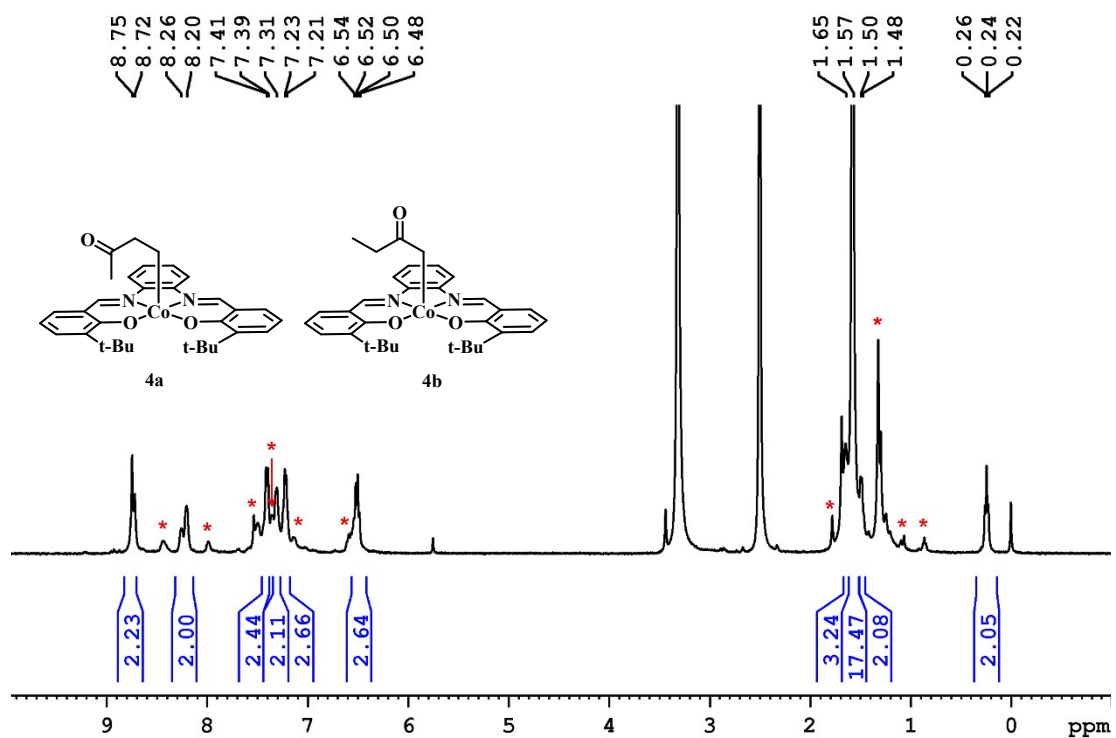


Figure S1  $^1\text{H}$  NMR spectrum of **3** in  $d_6$ -DMSO.



**Figure S2**  $^1\text{H}$  NMR spectrum of **4a** and **4b** in  $d_6$ -DMSO (\*: resonances assigned to **4b**).



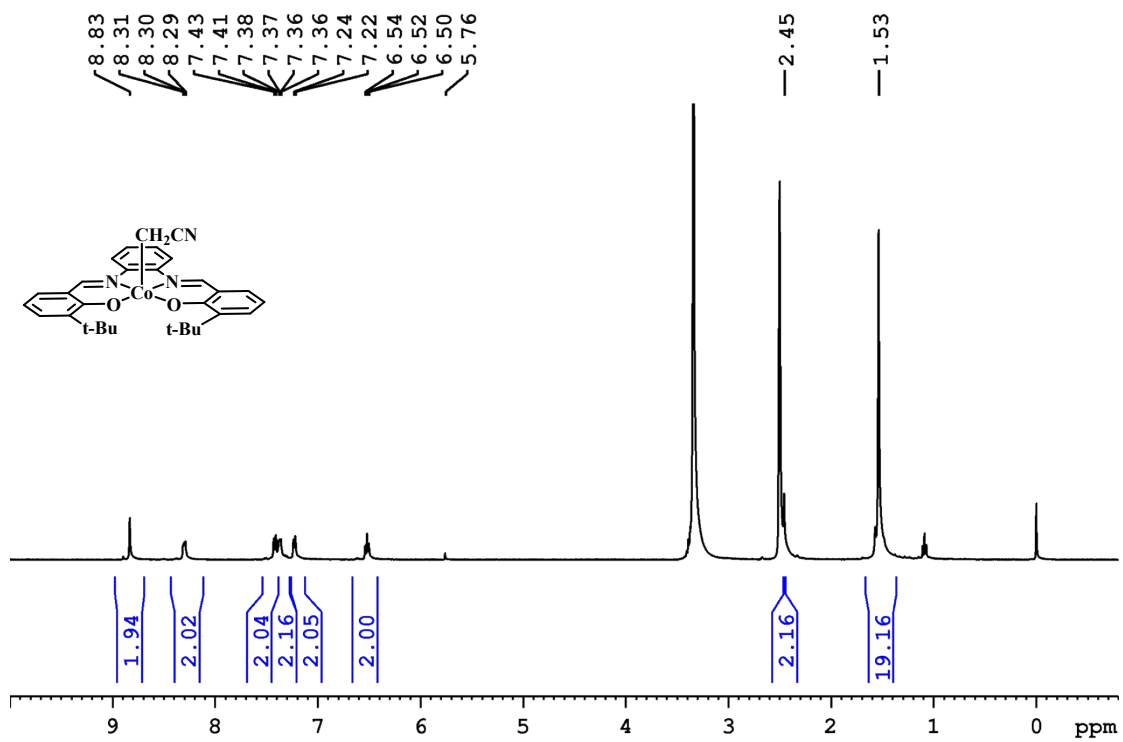


Figure S3 <sup>1</sup>H NMR spectrum of 5 in d<sub>6</sub>-DMSO.

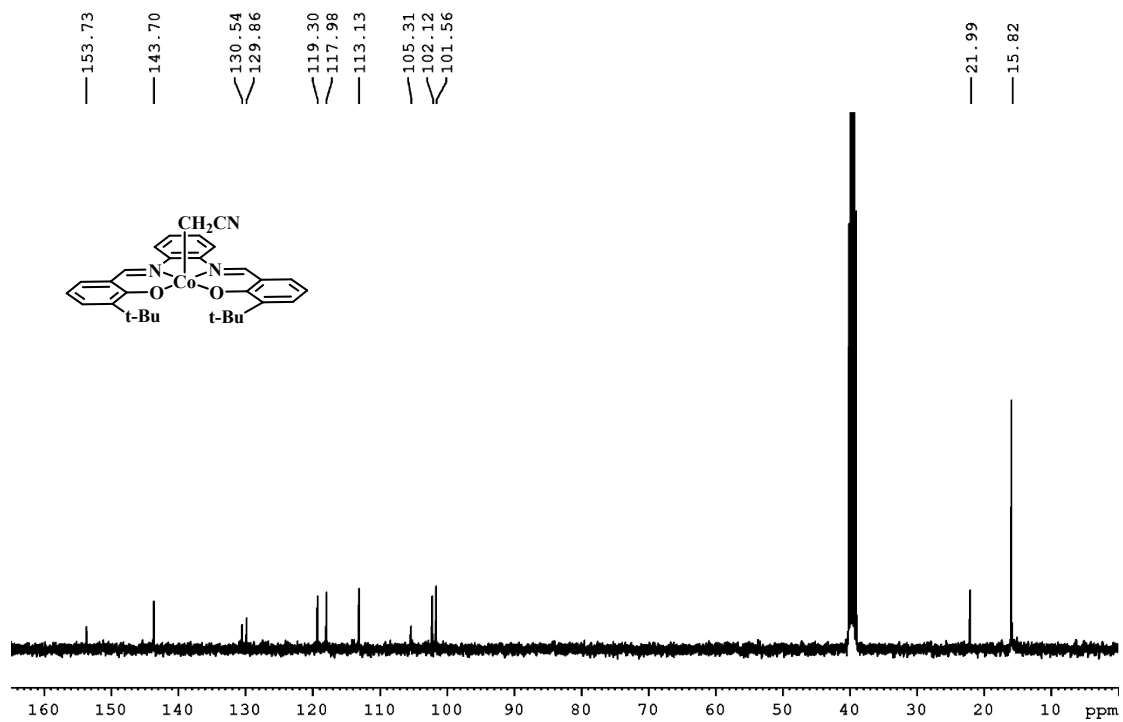


Figure S4  $^{13}\text{C}$  NMR spectrum of 5 in  $d_6$ -DMSO.

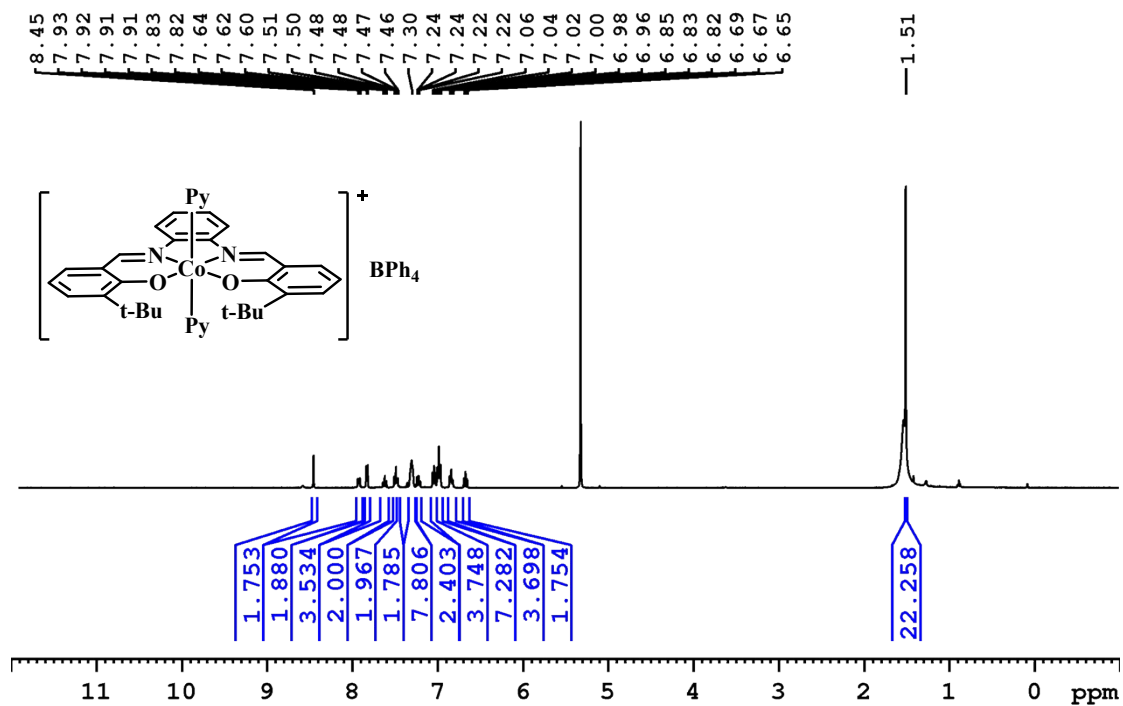


Figure S5  $^1\text{H}$  NMR spectrum of complex 6 in  $\text{CD}_2\text{Cl}_2$ .

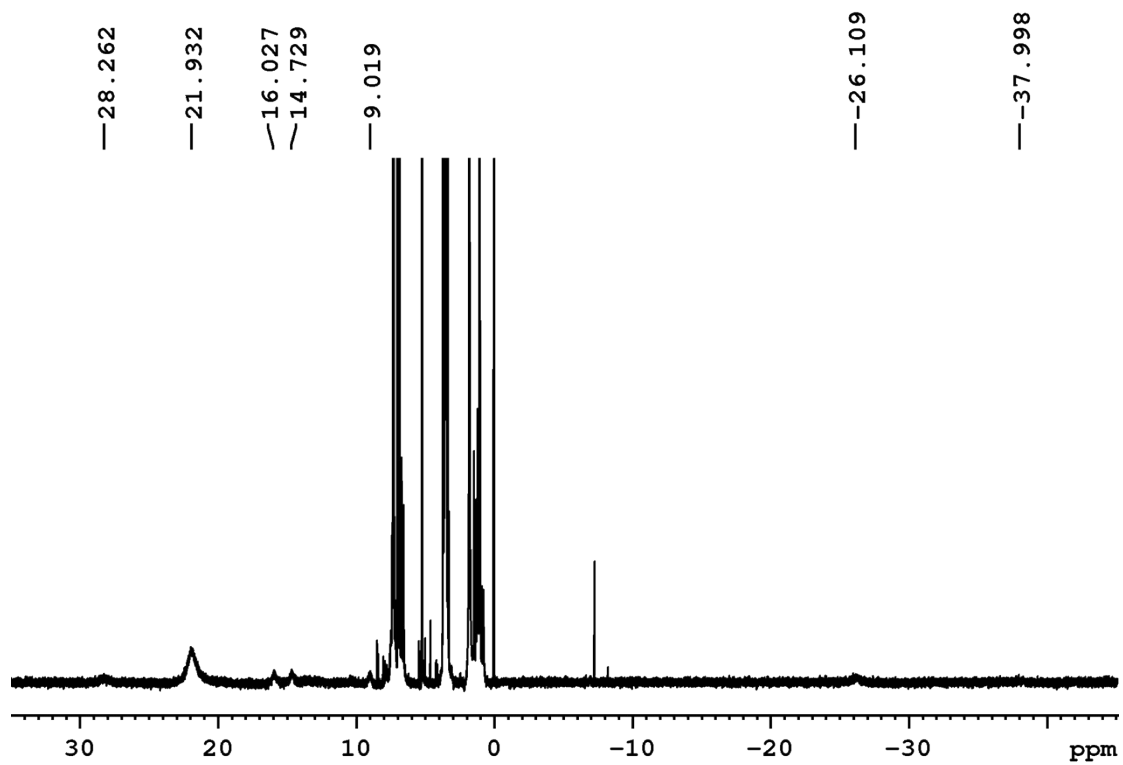


Figure S6  $^1\text{H}$  NMR spectrum of **6** after adding excess amounts of NaOH/15-crown-5 in  $\text{CD}_2\text{Cl}_2$ .

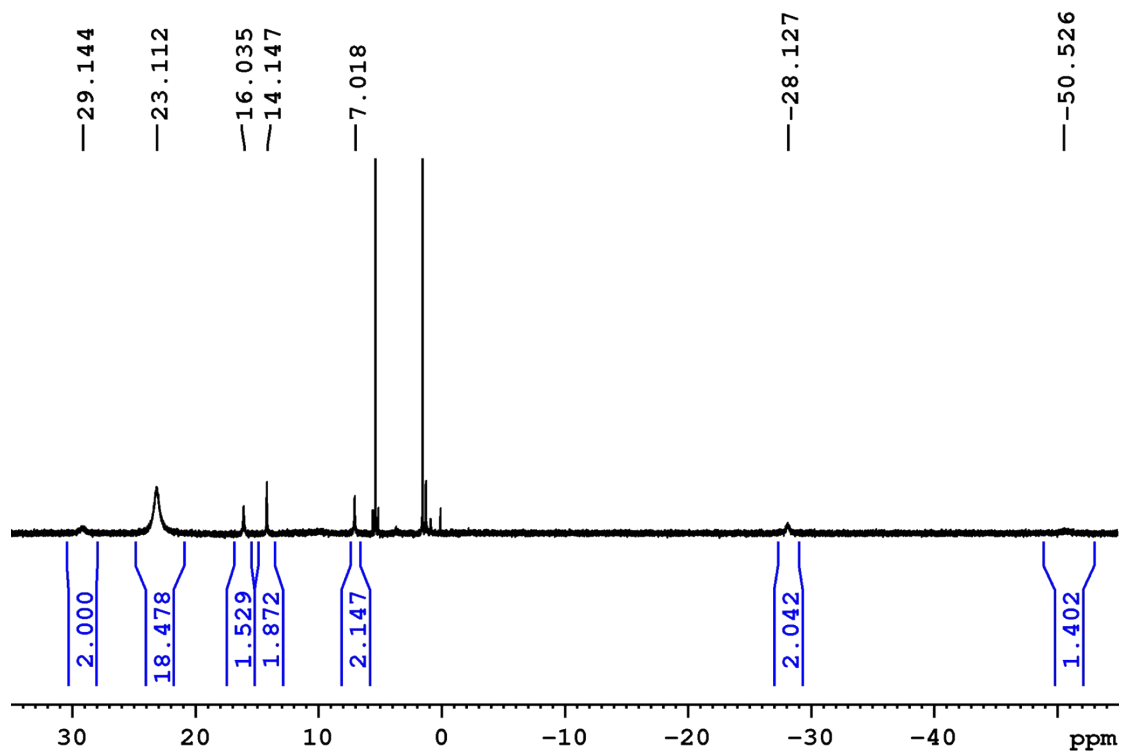


Figure S7  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_2\text{Cl}_2$ .

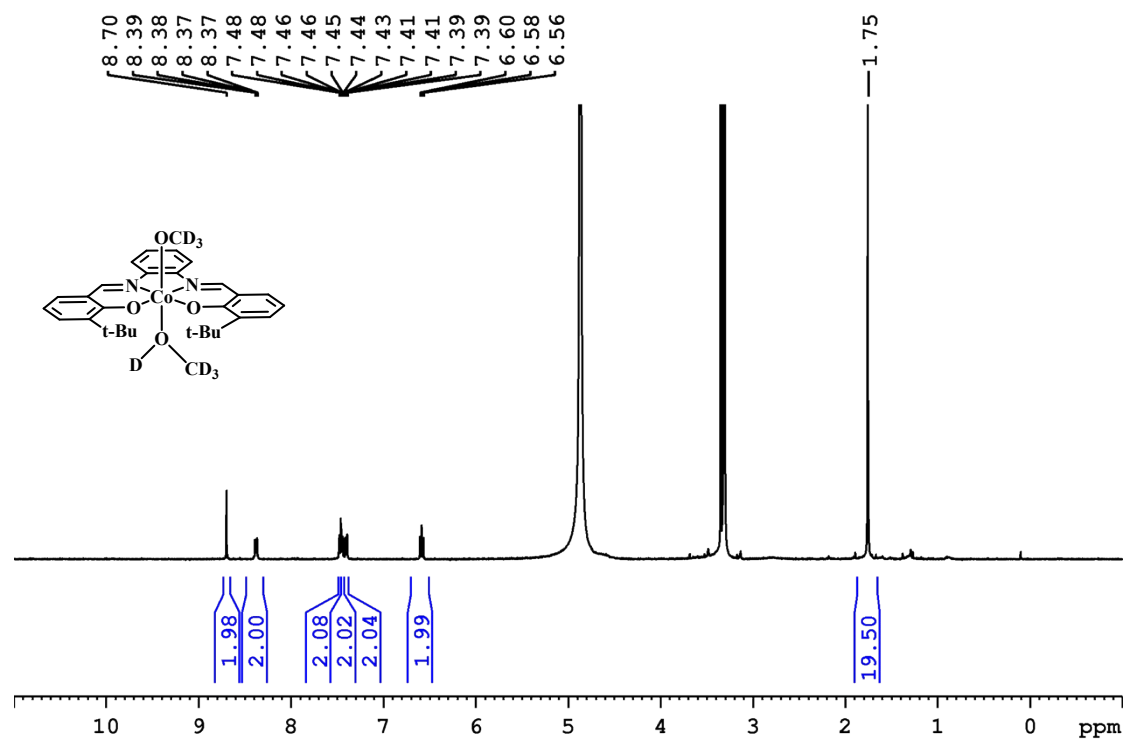
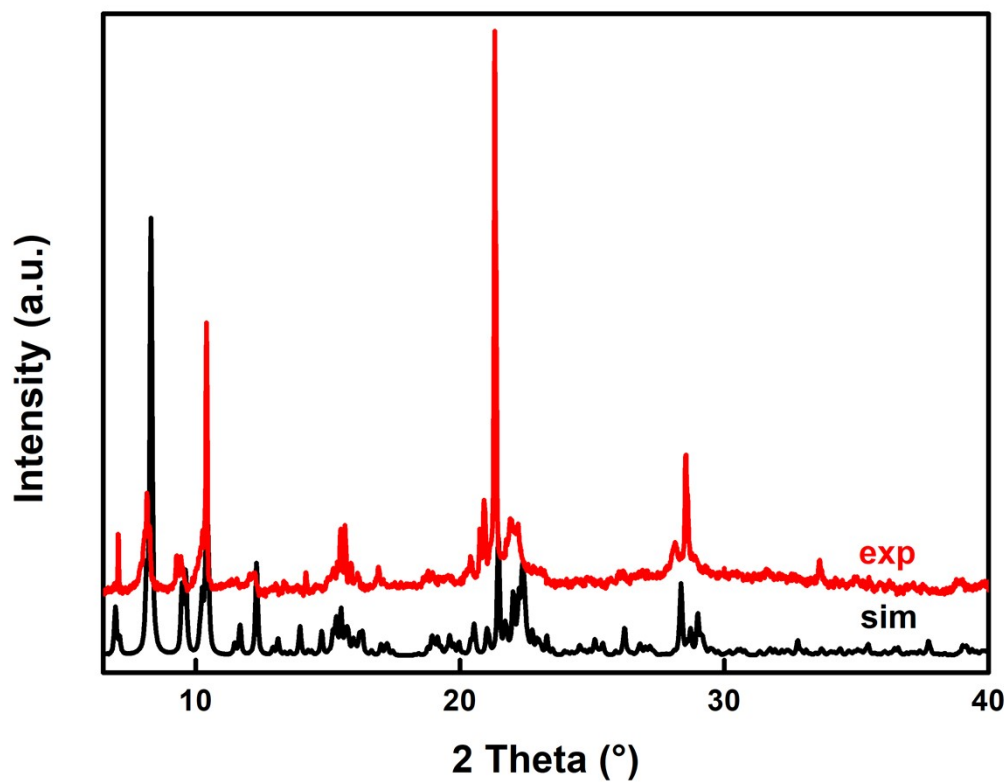


Figure S8  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_3\text{OD}$ .



**Figure S9** Powder X-ray diffraction (PXRD) spectrum of **7** (red: experimental spectrum; black: simulated spectrum).

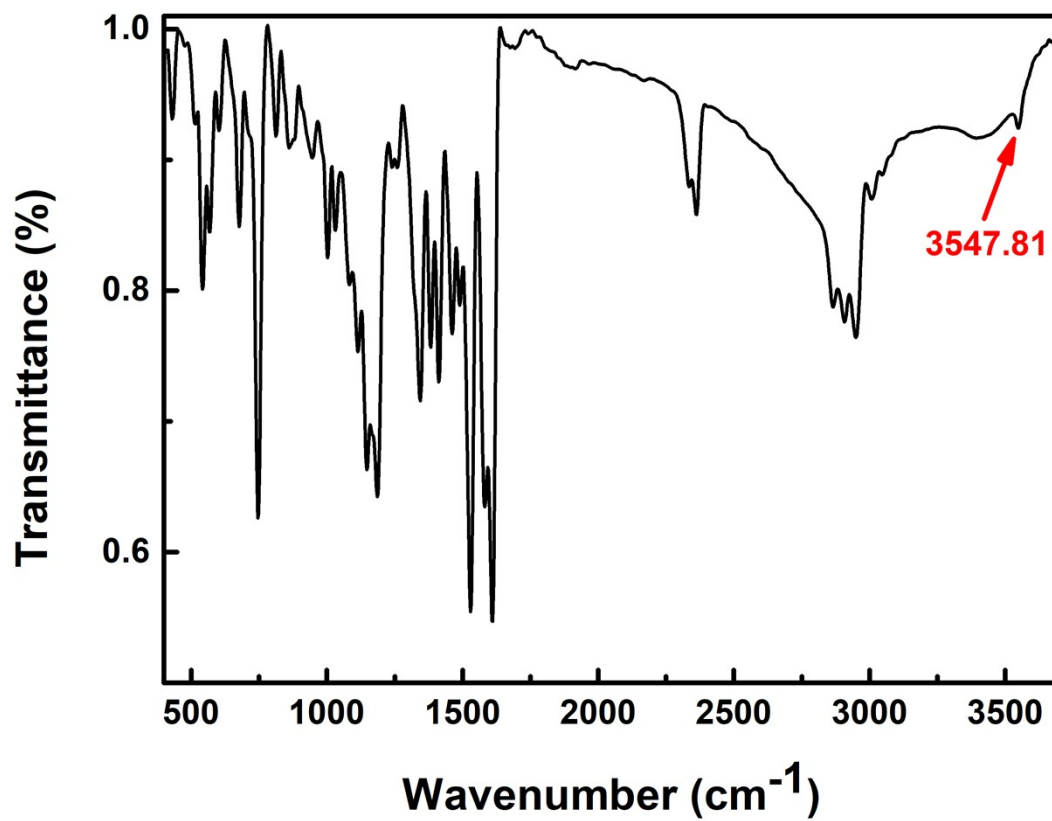
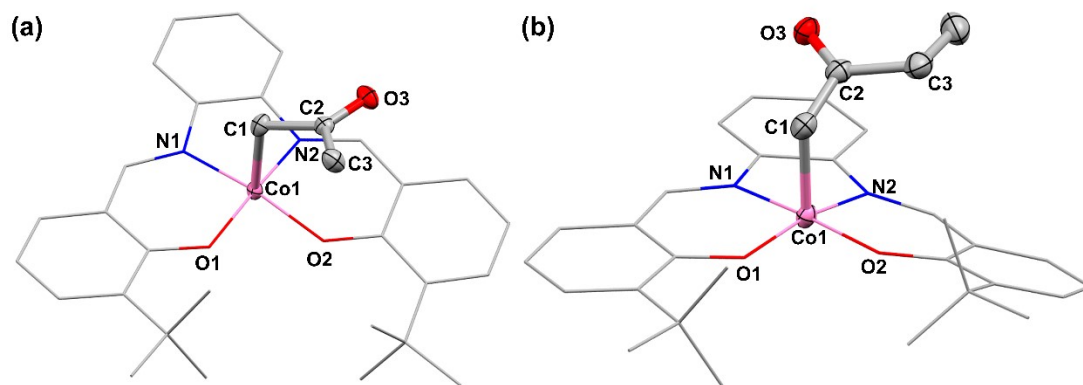
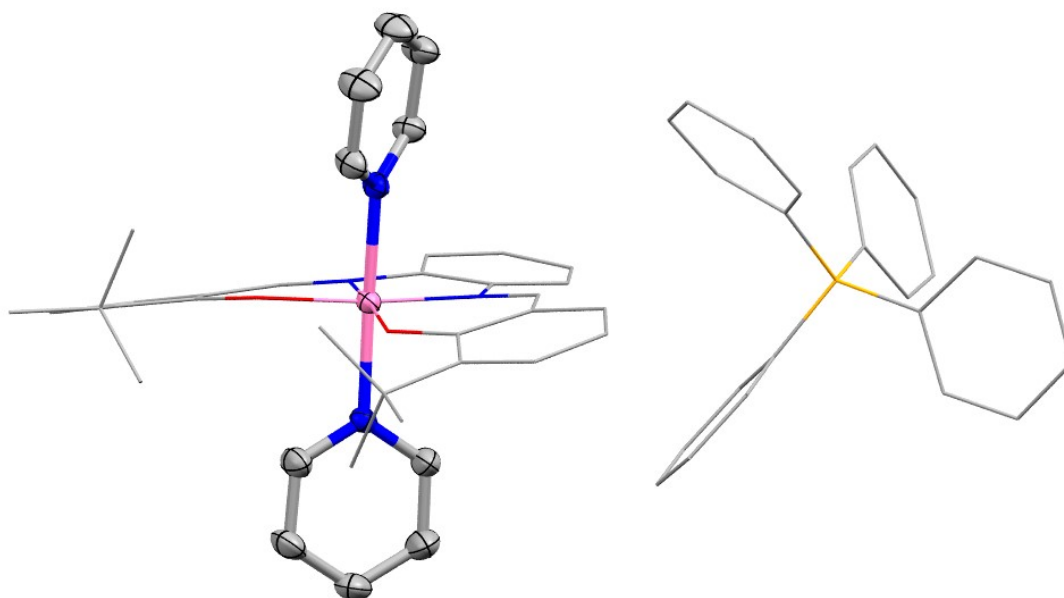


Figure S10 FTIR spectrum of complex 7.





**Figure S11** Solid state structure of complex **4a** and **4b**. Thermal ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity.



**Figure S12** Solid state structure of complex **6**. Thermal ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity.

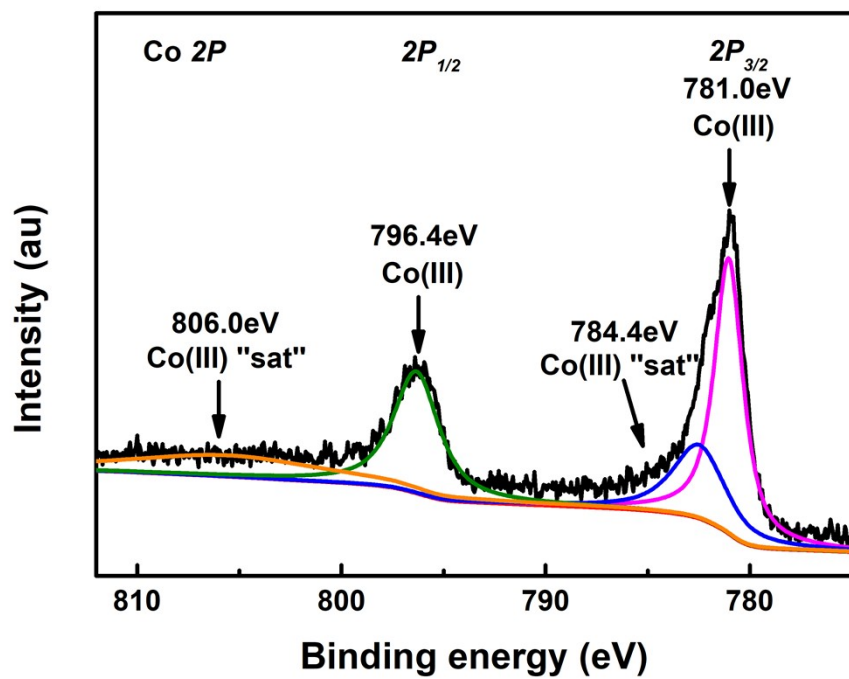


Figure S13 XPS analysis of complex 3.

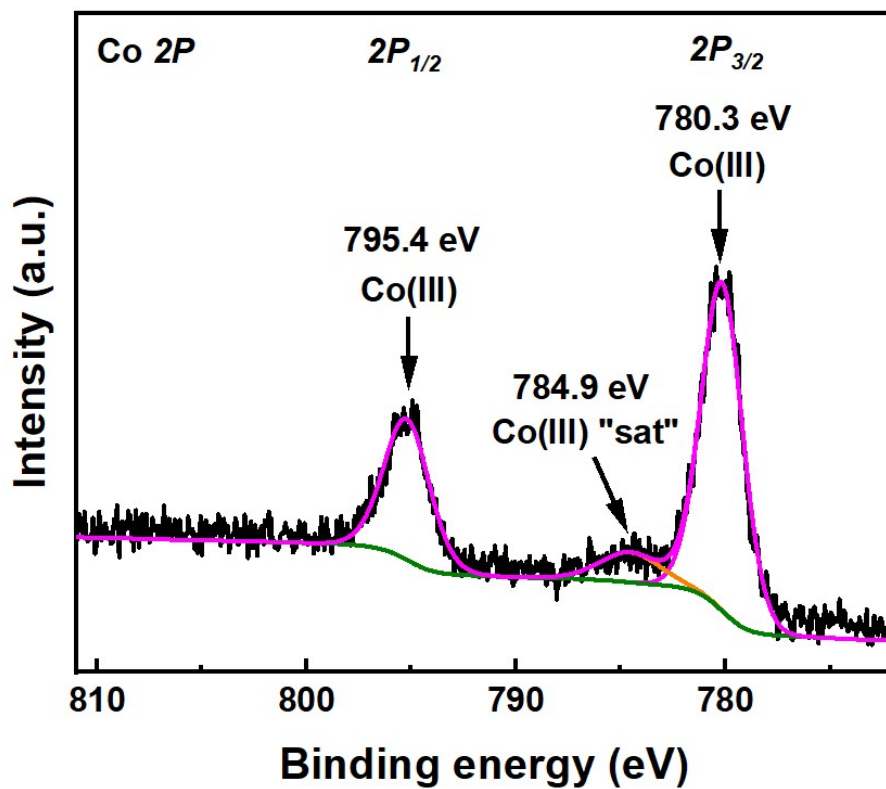


Figure S14 XPS analysis of complex 4a and 4b.

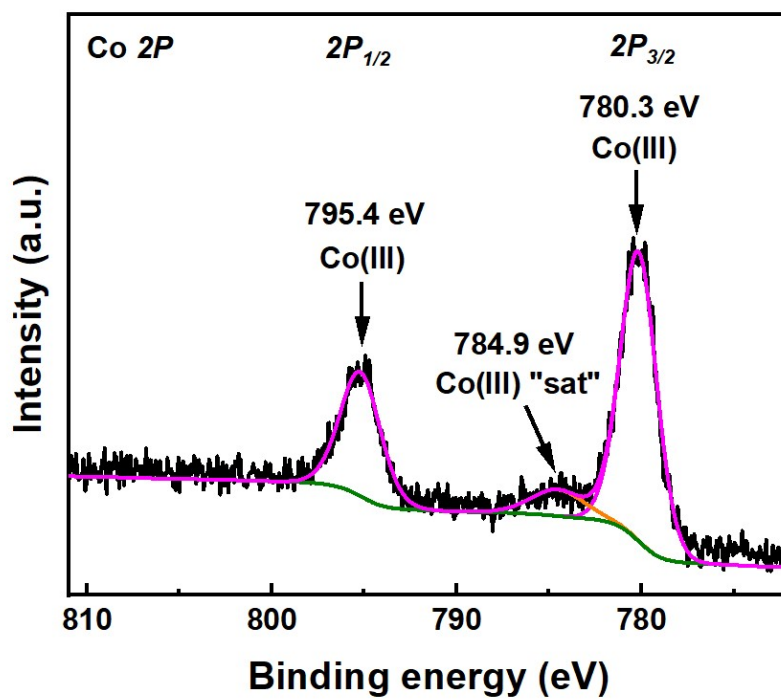


Figure S15 XPS analysis of complex 5.

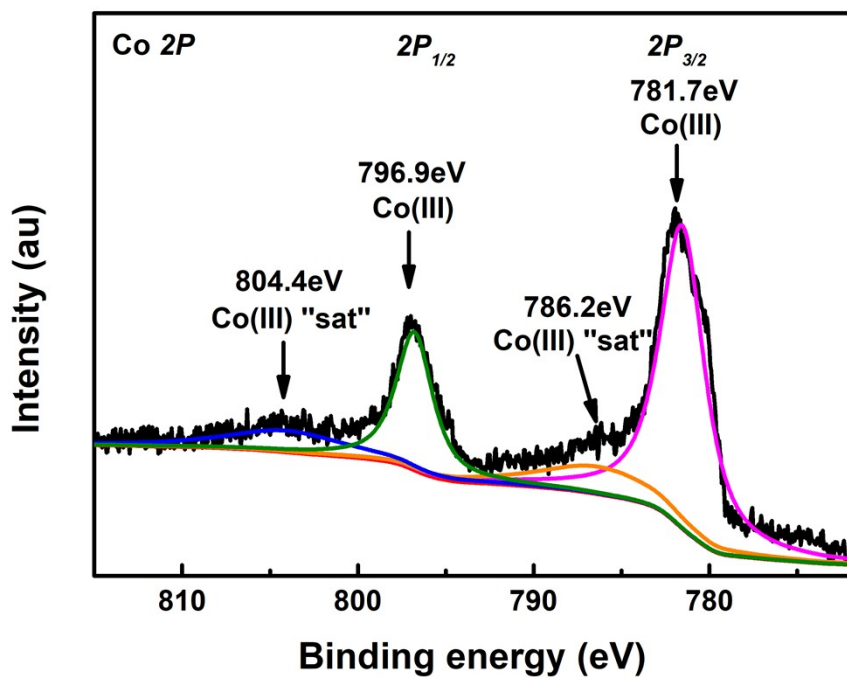


Figure S16 XPS analysis of complex 6.

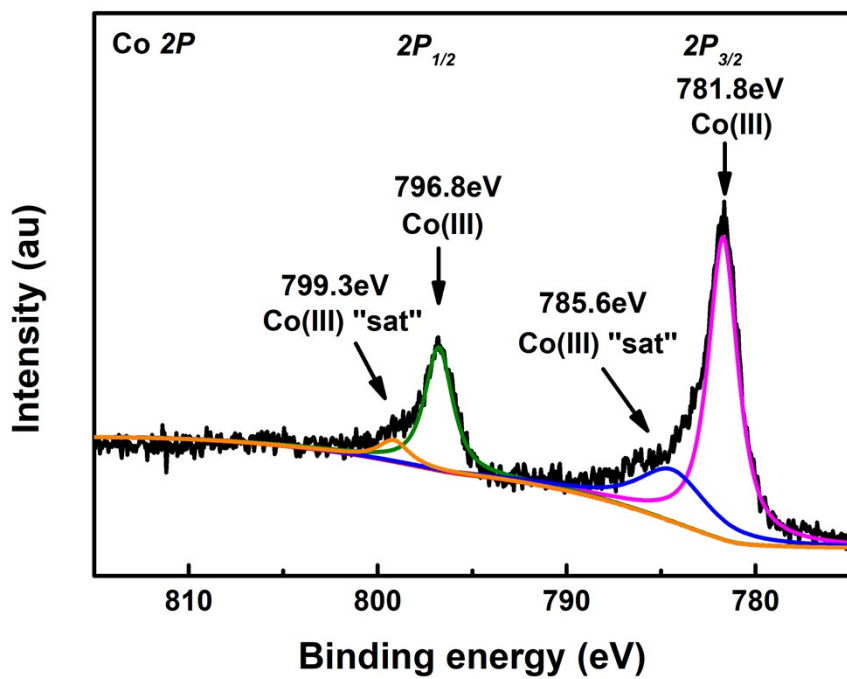


Figure S17 XPS analysis of complex 7.

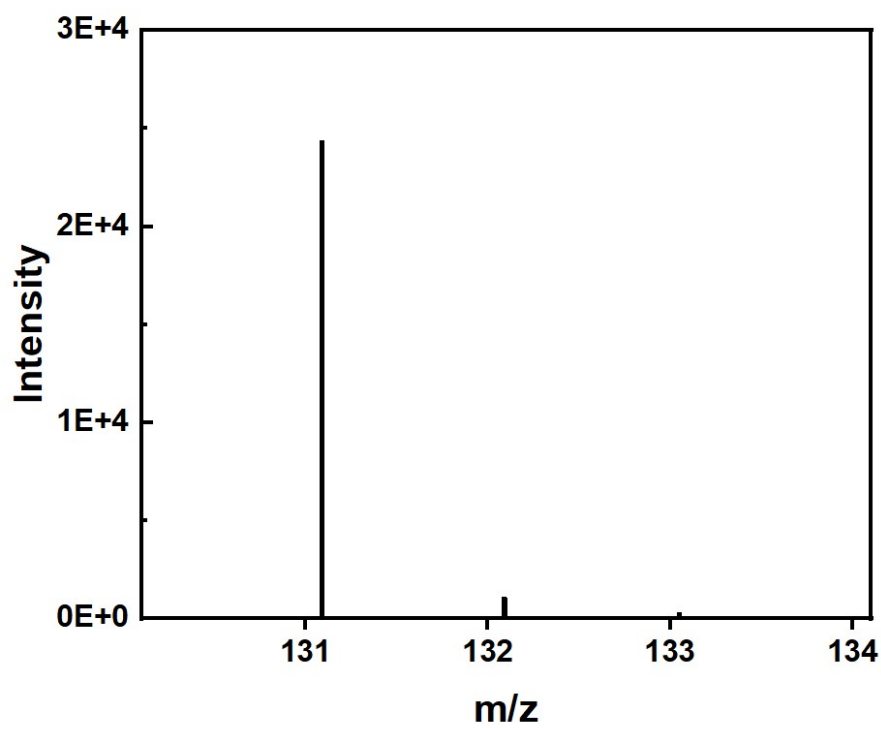
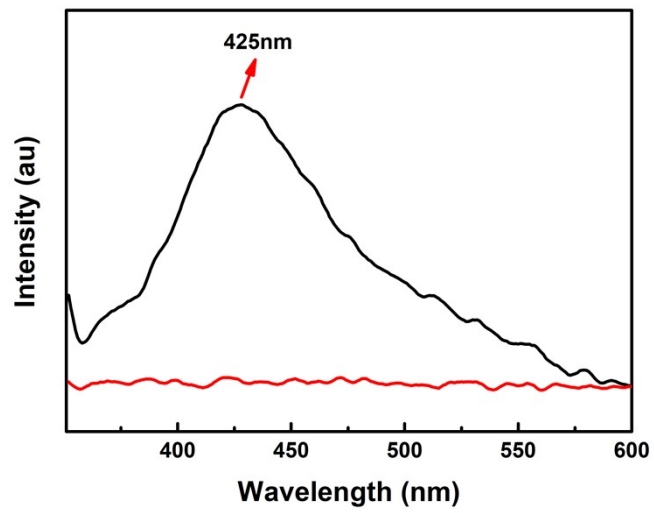


Figure S18 MS spectrum of DMPO-OH adduct generated in the hydrous methanol solution of **1**.





**Figure S19** The fluorescence spectrum of hydroxyl radical trapping by disodium terephthalate in water.

The  $^{18}\text{O}$ -phenol peak was assigned according to the fractionation factor derived based on the diffusion effect (eq S1) and the individual isotopologue selectivity (eq S2),<sup>19, 20</sup>

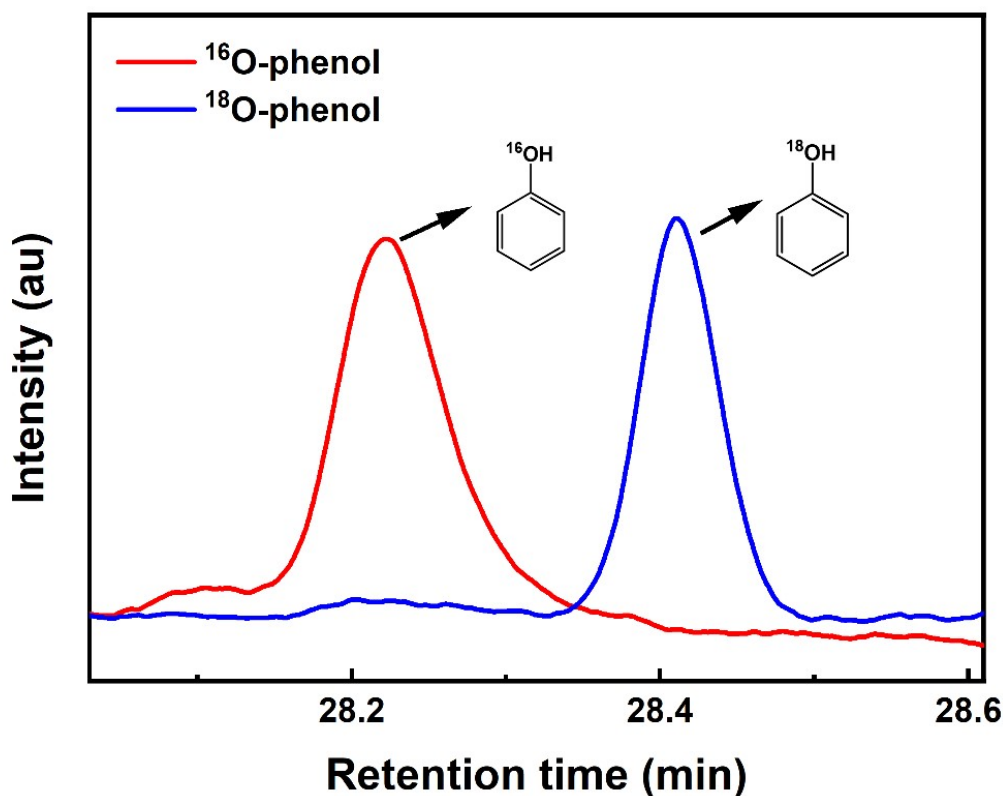
$$\alpha_{\text{diff-N}_2} = \frac{M_{16\text{O}}(M_{18\text{O}} + M_{\text{N}_2})}{M_{18\text{O}}(M_{16\text{O}} + M_{\text{N}_2})} \quad (\text{eq S1})$$

S1)

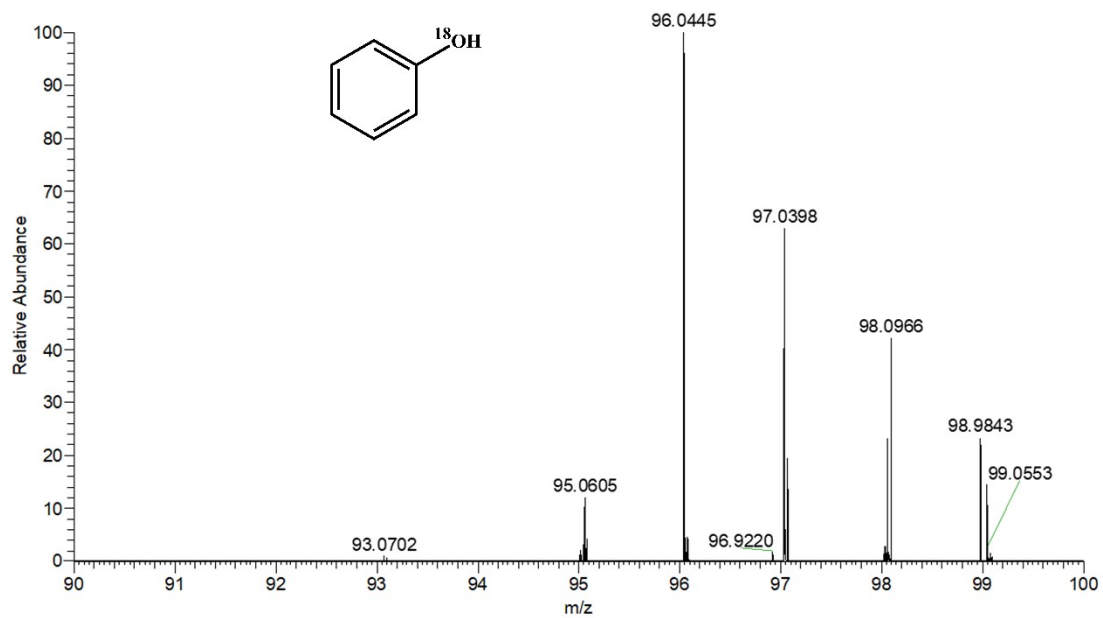
$$\alpha_{\text{exp}} = \frac{t_{\text{R}}(^{18}\text{O}) - t_0}{t_{\text{R}}(^{16}\text{O}) - t_0} \quad (\text{eq S2})$$

S2)

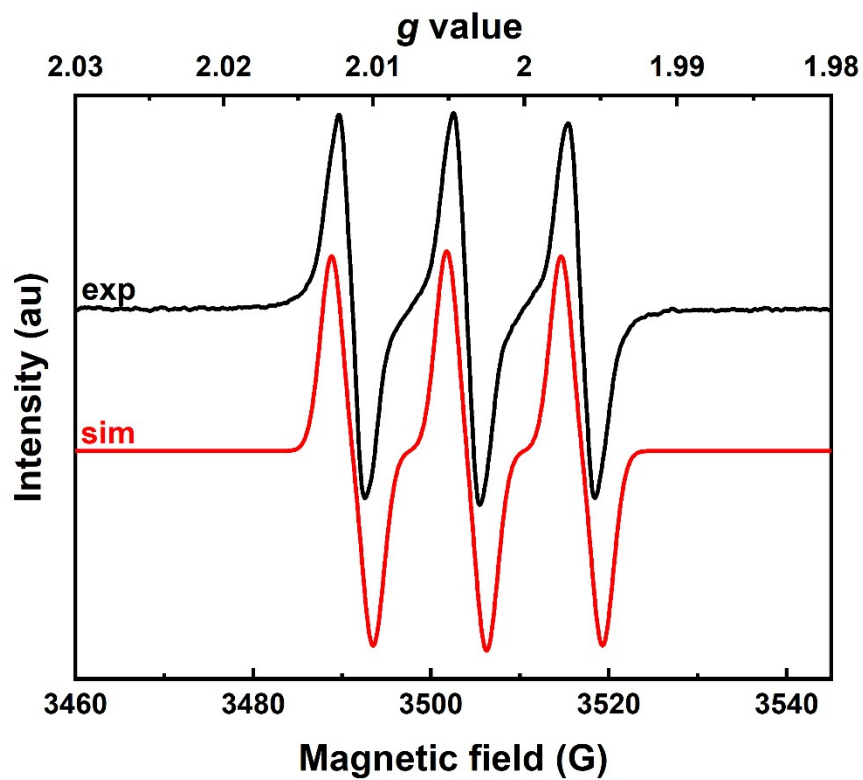
where  $M_{16\text{O}}$  and  $M_{18\text{O}}$  are the molecular weights of the  $^{16}\text{O}$ - and  $^{18}\text{O}$ -phenol,  $M_{\text{N}_2}$  is the molecular weight of  $\text{N}_2$  carrier gas used in GC measurement, and  $t_{\text{R}}(^{16}\text{O})$  and  $t_{\text{R}}(^{18}\text{O})$  are retention times of  $^{16}\text{O}$ - and  $^{18}\text{O}$ -phenol, respectively.  $t_0$  was the deadtime for the column, which was measured to be 1.971 minutes in this study.  $\alpha_{\text{exp}}$  was thus determined to be 0.9929, which was in reasonable consistency with the theoretical value ( $\alpha_{\text{diff-N}_2}$ , 0.9976).



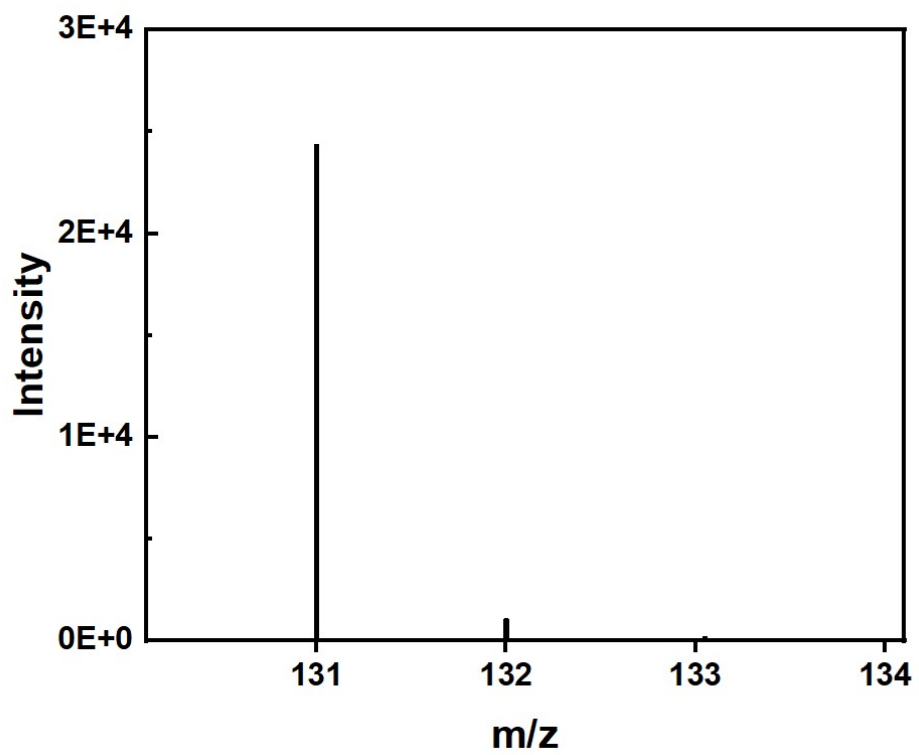
**Figure S20** Gas chromatograms of  $^{16}\text{O}$ -phenol (red, standard solution) and  $^{18}\text{O}$ -phenol (blue, reaction solution from isotope labelling studies).



**Figure S21** HRMS analysis of  $^{18}\text{O}$ -phenol formed in isotope labelling studies.



**Figure S22** Hydroxyl radical tripping using DMPO in the reaction of complex **6** with  $\text{OH}^-$  (complex **6**: 0.2 mM, NaOH: 2 mM, 15-crown-5: 10 mM, DMPO: 1 mM, 298 K, under  $\text{N}_2$  atmosphere, m.w. Frequency: 9.837268 GHz, m.w. power: 47 mW). Experimental spectrum is shown as black line and simulated spectrum is shown as red line.



**Figure S23** MS spectrum of DMPO-OH adduct generated in benzene solution of **6** with NaOH/15-crown-5.

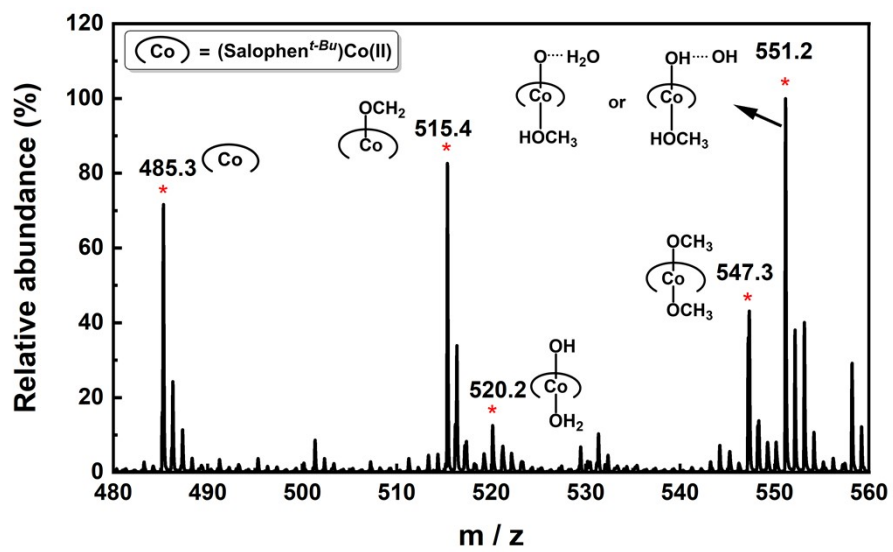
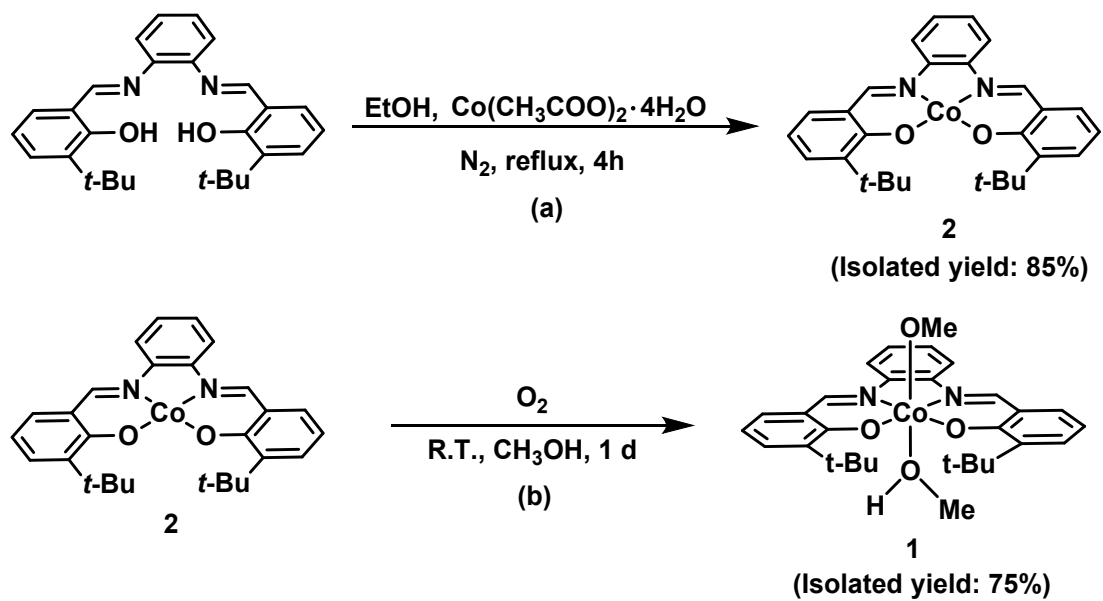
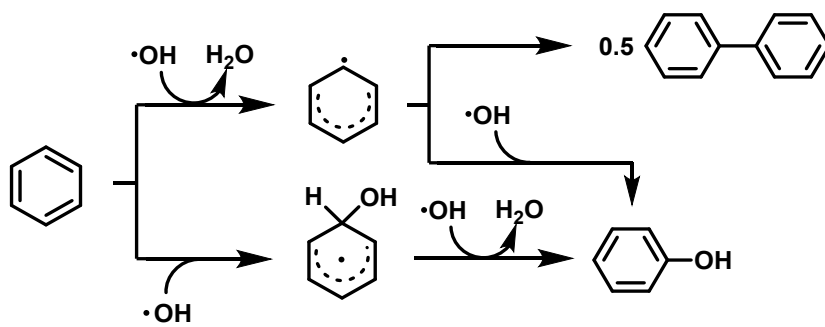


Figure S24 MS analysis of the methanol solution of complex 1 with the presence of NaOH.

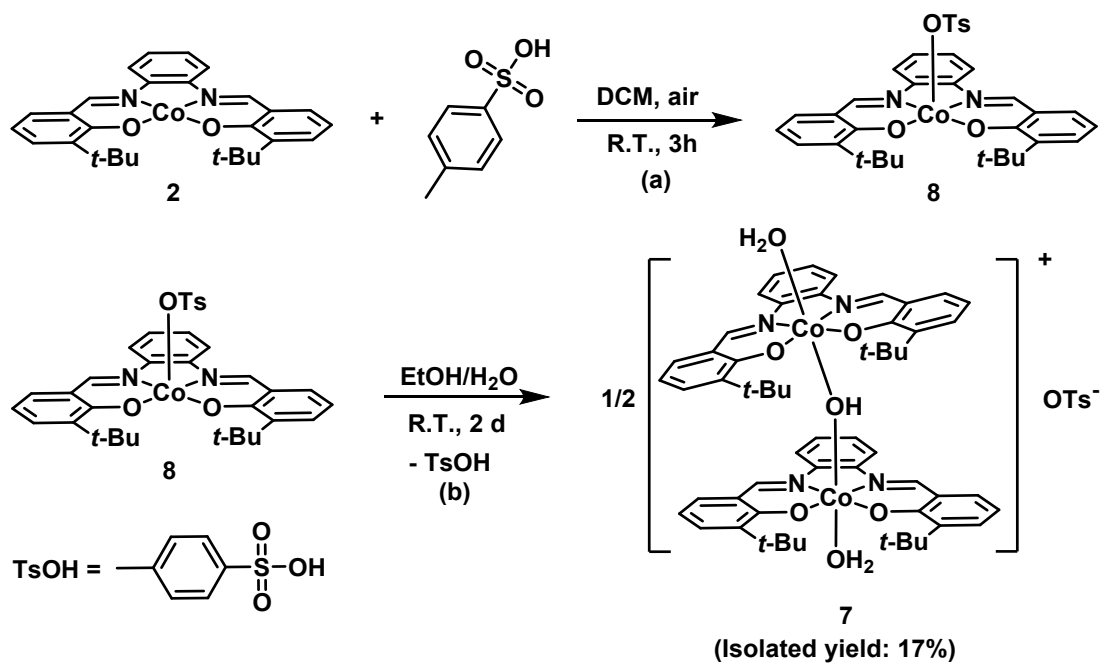


**Scheme S1** The synthesis of **2** (a) and **1** (b).



**Scheme S2** Hydroxyl radical initiated formation of diphenyl and phenol.

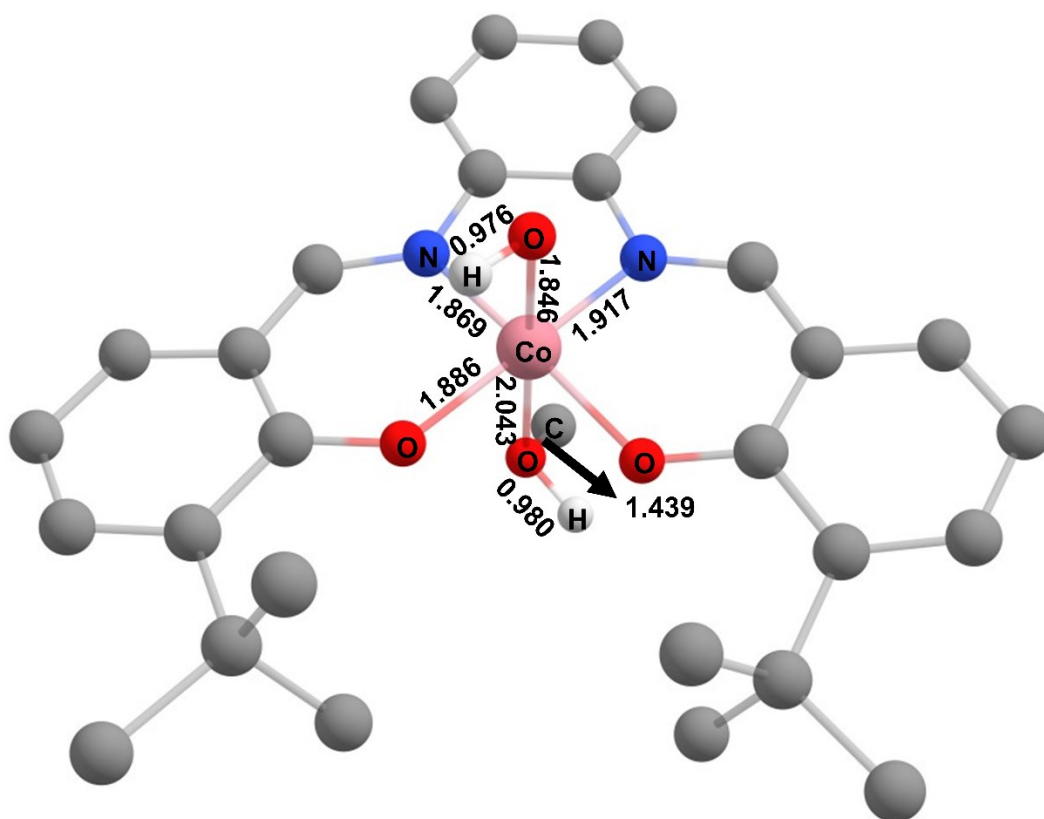




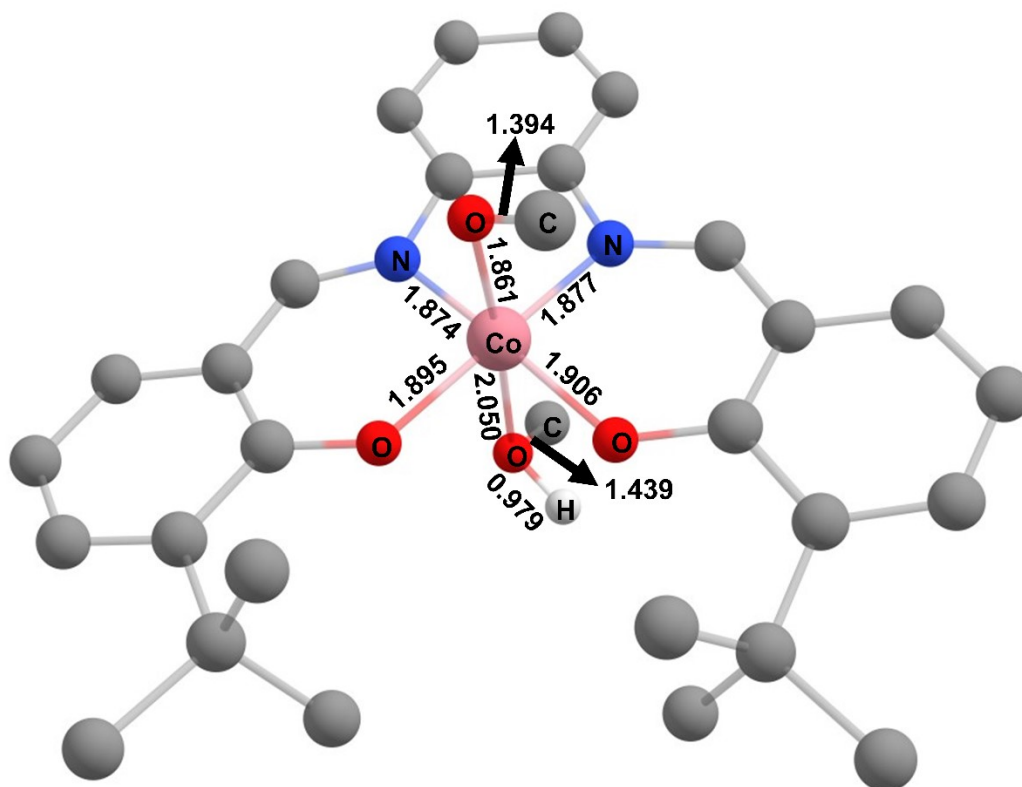
**Scheme S3** The synthesis of **8** (a) and **7** (b).

**Table S1** Selected bond lengths (Å) and angles (deg) for **3 ~ 7**.

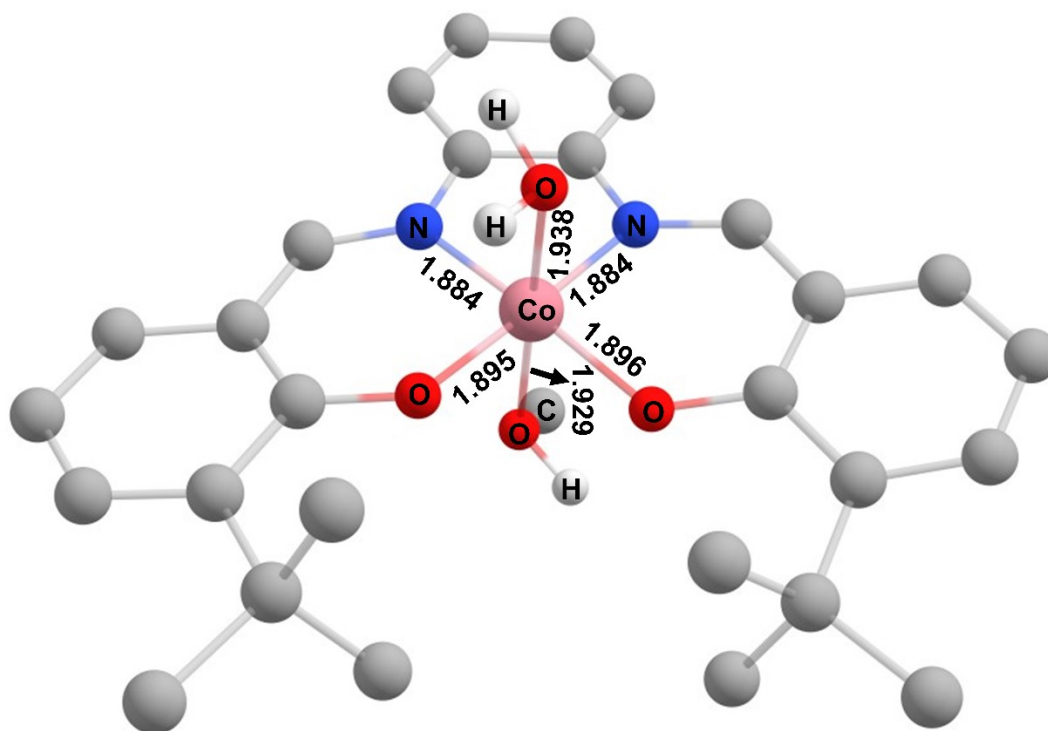
	<b>3</b>	<b>4b</b>	<b>5</b>	<b>6</b>	<b>7</b>
Co(1)–N(1)	1.8750(13)	1.8776(16)	1.878(2)	1.8969(13)	1.8952(10)
Co(1)–N(2)	1.8770(12)	1.8794(16)	1.874(2)	1.8923(13)	1.897(2)
Co(1)–N(3)				1.9807(13)	
Co(1)–N(4)				1.9951(13)	
Co(2)–N(3)					1.889(2)
Co(2)–N(4)					1.882(2)
Co(1)–O(1)	1.8736(10)	1.8682(13)	1.8707(15)	1.9019(11)	1.891(2)
Co(1)–O(2)	1.8663(10)	1.8841(13)	1.8742(16)	1.8889(11)	1.901(2)
Co(1)–O(3)					1.904(2)
Co(1)–O(6)					1.936(2)
Co(2)–O(3)					1.905(2)
Co(2)–O(4)					1.890(2)
Co(2)–O(5)					1.890(2)
Co(2)–O(7)					1.943(2)
Co(1)–C(1)	1.9840(17)	1.9859(19)	1.949(2)		
O(1)–Co(1)–N(2)	173.95(5)	167.80(6)	171.41(8)	175.27(5)	176.77(10)
O(2)–Co(1)–N(1)	167.97(5)	175.82(6)	175.45(8)	175.58(5)	178.63(10)
O(4)–Co(2)–N(4)					178.56(10)
O(5)–Co(2)–N(3)					176.63(10)
O(6)–Co(1)–O(3)					176.13(10)
O(3)–Co(2)–O(7)					176.29(10)
Co(1)–O(3)–Co(2)					152.34(13)
N(3)–Co(1)–N(4)				176.84(5)	



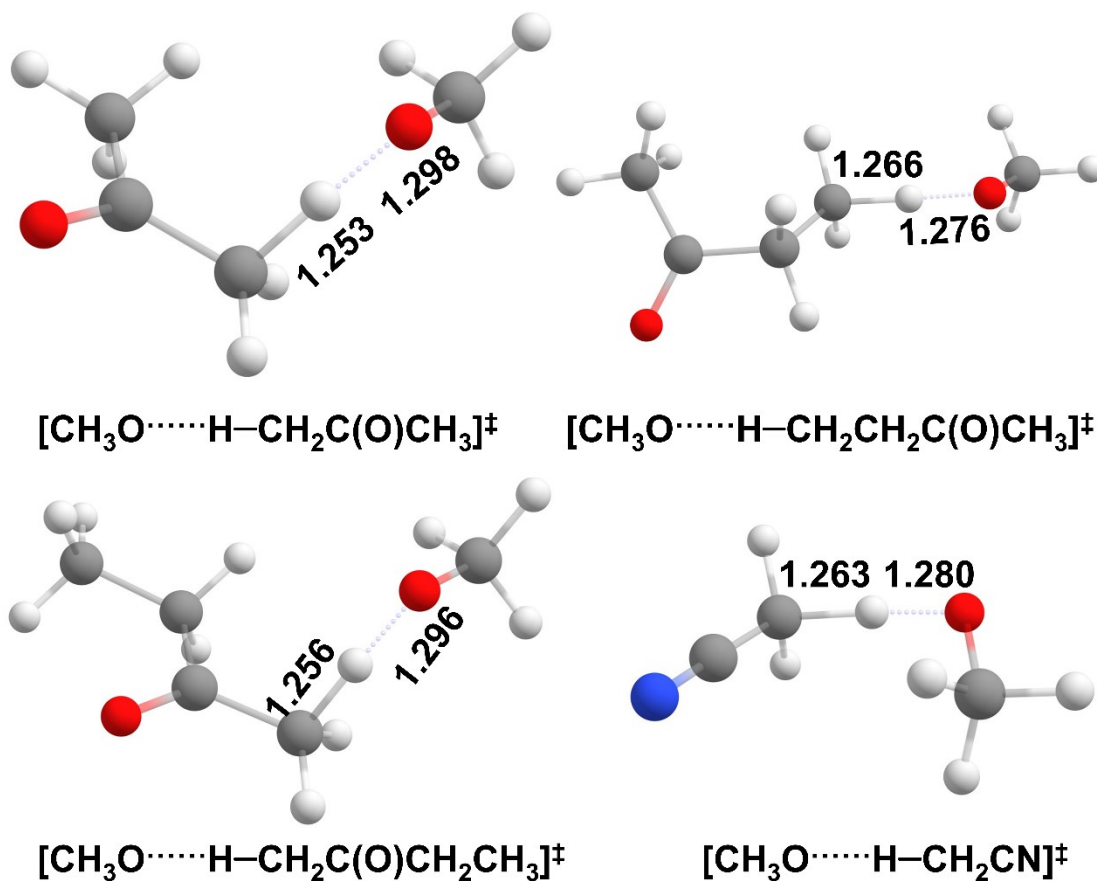
**Figure S25** The optimized structure of (Salophen<sup>t-Bu</sup>)(CH<sub>3</sub>OH)Co(III)(OH). Selected interatomic distances are provided in Å.



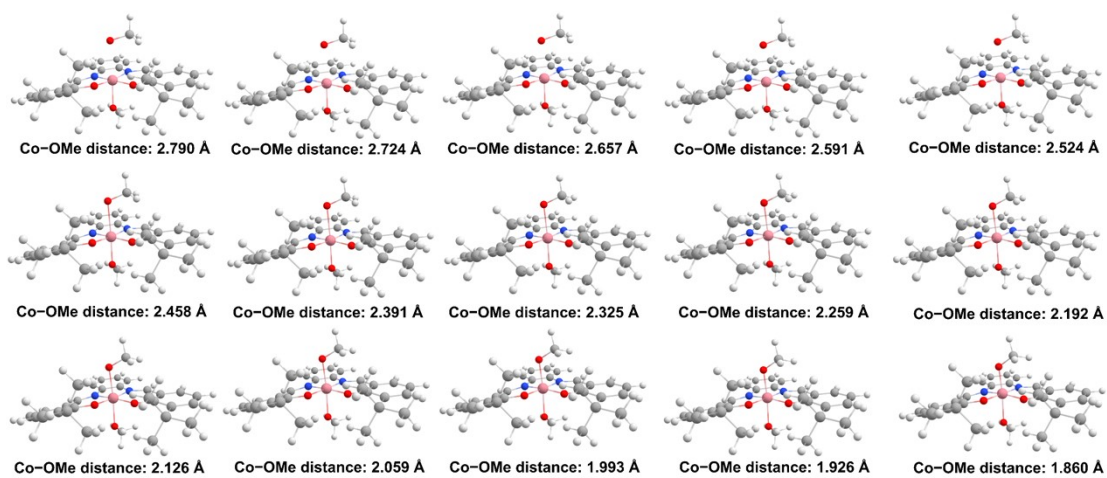
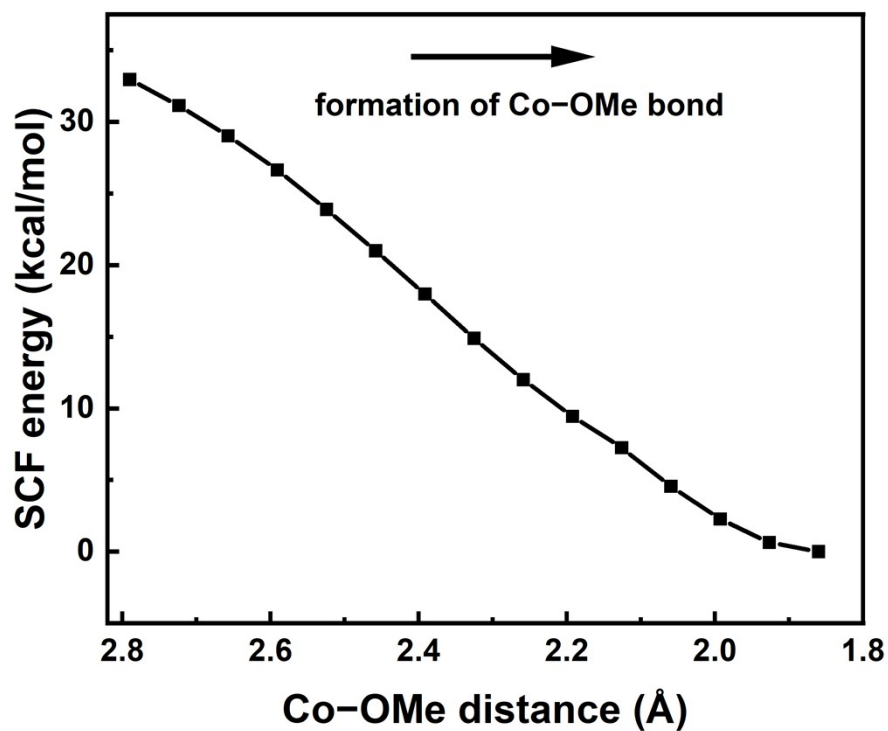
**Figure S26** The optimized structure of (Salophen<sup>t-Bu</sup>)(CH<sub>3</sub>OH)Co(III)(OMe). Selected interatomic distances are provided in Å.



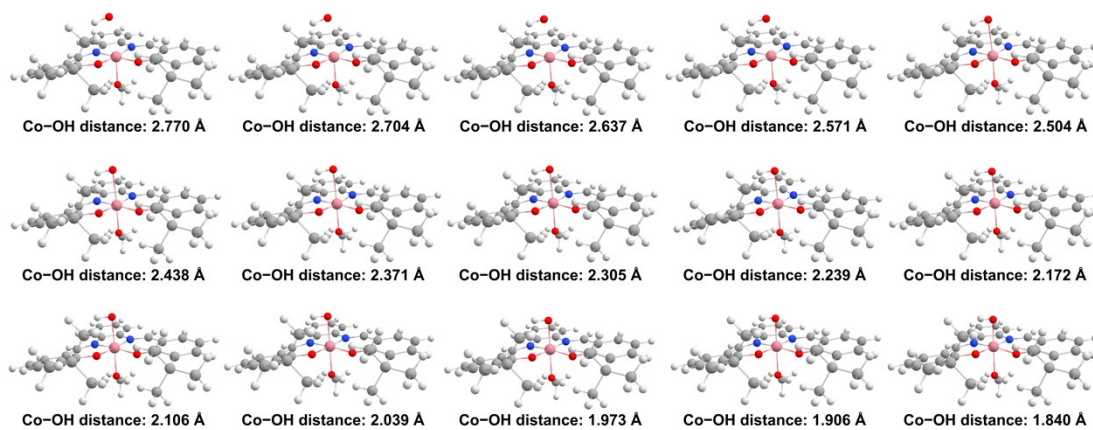
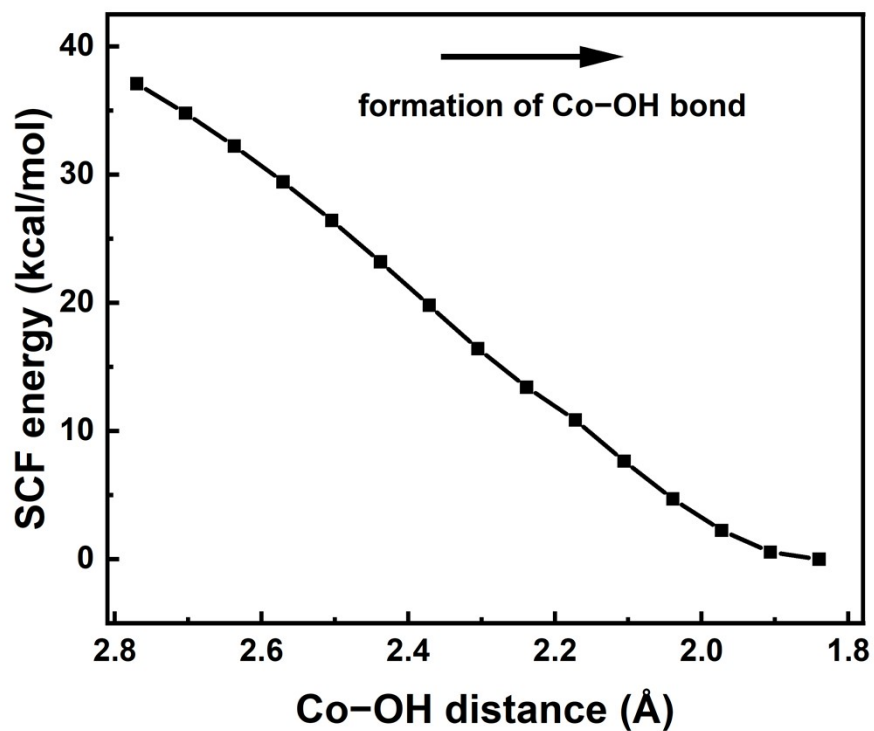
**Figure S27** The optimized structure of  $[(\text{Salophen}^{t\text{-Bu}})(\text{CH}_3\text{OH})\text{Co}(\text{III})(\text{OH}_2)]^+$ . Selected interatomic distances are provided in Å.



**Figure S28** The optimized structures of *TS* for hydrogen atom abstraction of C–H bonds in different substrates by methoxyl radicals. Selected interatomic distances are provided in Å.



**Figure S29** Relaxed energy surface scan for recombination of methoxyl radical with (Salophen<sup>t-Bu</sup>)(MeOH)Co(II) (Co-OMe distance: 2.790 ~ 1.860 Å).



**Figure S30** Relaxed energy surface scan for recombination of hydroxyl radical with (Salophen<sup>t-Bu</sup>)(MeOH)Co(II) (Co-OH distance: 2.770 ~ 1.840 Å).



## Reference

1. S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 14.
2. K. L. Peretti, H. Ajiro, C. T. Cohen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 11566-11567.
3. L. P. Nielsen, S. J. Zuend, D. D. Ford and E. N. Jacobsen, *J. Org. Chem.*, 2012, **77**, 2486-2495.
4. F. Neese, *WIREs Comput Mol Sci.*, 2022, **12**, e1606.
5. A. D. Becke, *Phys. Rev. A.*, 1988, **38**, 3098-3100.
6. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
7. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785-789.
8. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Chem. Phys.*, 1994, **98**, 11623-11627.
9. S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200-1211.
10. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
11. F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.*, 2009, **356**, 98-109.
12. E. v. Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597-4610.
13. C. v. Wüllen, *J. Chem. Phys.*, 1998, **109**, 392-399.
14. A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2005, **123**, 154101-154109.
15. E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2005, **123**, No. 024101.
16. E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2006, **124**, No. 174104.
17. V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001.
18. NBO 7.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI (2018).
19. A. Valleix, S. Carrat, C. Caussignac, E. Léonce and A. Tchaplal, *J. Chromatogr. A.*, 2006, **1116**, 109-126.
20. C. Tang, J. Tan, S. Xiong, J. Liu, Y. Fan and X. Peng, *J. Chromatogr. A.*, 2017, **1514**, 103-109.