

*Supporting information for:*

**Heteroleptic cobalt(III) acetylacetonato complexes with N-heterocyclic carbene-donating scorpionate ligands: synthesis, structural characterization and catalysis.**

Toshiki Nishiura, Asako Takabatake, Mariko Okutsu, Jun Nakazawa, Shiro Hikichi\*

Department of Material and Life Chemistry

Faculty of Engineering

Kanagawa University

3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Fax: +81-45-413-9770

\*E-mail: hikichi@kanagawa-u.ac.jp

## EXPERIMENTAL DETAIL

### 1. General

Elemental analysis was performed on a Elementar Vario MICRO Cube. IR spectra were recorded on a JASCO FT/IR 4200 spectrometer for solid samples (as KBr pellet). NMR spectra were recorded on a JEOL ECA-500 spectrometer. ESI-MS spectra were recorded on a JMS-T100LC. spectrometer. GC analysis was performed on a Shimadzu GC2010 gas chromatograph with an Rtx-5 column (Restek, length = 30 m, i.d. = 0.25 mm, thickness = 0.25  $\mu$ m). UV-vis spectra were measured on a V650 spectrometer. All commercial reagents and solvents were used without further purification unless otherwise noted. Preparations of oxygen-sensitive compounds were performed by Schlenk technique under Ar atmosphere.

### 2. Synthesis of the compounds

#### 2.1. [PhB(MeImH)<sub>3</sub>](OTf)<sub>2</sub>

This ligand precursor was prepared by the literature procedure with some modification.<sup>1</sup> 1-methylimidazole (1.9 mL, 24 mmol) was added dropwise to PhBCl<sub>2</sub> (1.0 mL, 8.0 mmol) in toluene (70 mL). After 10 min of stirring, TMSOTf (2.9 mL, 16 mmol) was added to the reactant and the resulting mixture was heated to reflux for one day. The solution layer was removed by decantation under Ar stream, then CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added to the remaining solid. The suspension was heated to reflux for 3 h, and the resulting clear solution was concentrated by evaporation and then cooled at -30°C. Washing with CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O, then drying under reduced pressure of the precipitates yielded the desired ligand precursor as white powder (3.96 g, 6.26

mmol, 78.3%).

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , 25°C):  $\delta$  = 8.55 (s, 3H; Im-*H*), 7.80 (s, 3H; Im-*H*), 7.43 (m, 3H; meta/para-*Ph*), 7.38 (s, 3H; Im-*H*), 7.11 (s, 2H; ortho-*Ph*), 3.84 (s, 9H; Im-*Me*). ESI-MS<sup>+</sup> (MeOH):  $m/z$  = 483 ( $\{[\text{PhB}(\text{MeImH})_3](\text{OTf})\}^+$ ), 401 ( $\{[\text{PhB}(\text{MeImH})_2](\text{OTf})\}^+$ ).

## 2.2. $[\text{Co}^{\text{III}}([\text{PhB}(\text{MeIm})_3])(\text{acac})(\text{MeImH})](\text{OTf})$ (**1**[OTf])

A 2.0 M LDA in THF/heptane/ethylbenzene solution (2.8 mL, 5.60 mmol) was added to a suspension of  $[\text{PhB}(\text{MeImH})_3](\text{OTf})_2$  (1.14 g, 1.79 mmol) in THF (25 mL) under Ar at room temperature and then stirred for 4 h. This suspension was added into a THF (30 mL) solution of  $\text{Co}^{\text{II}}(\text{acac})_2$  (467 mg, 1.82 mmol) under Ar at ambient temperature and then 1-methylimidazole (0.12 mL, 1.51 mmol) was added. The resulting green colored slurry was exposed to  $\text{O}_2$  and stirred overnight. After the removal of the volatiles by evaporation, the residue was re-dissolved in  $\text{CH}_2\text{Cl}_2$ . The solution was then passed through a filter with Celite pad to remove any insoluble components. To this  $\text{CH}_2\text{Cl}_2$  solution, *n*-hexane was added and the desired compound was precipitated as brown powder (580 mg, 0.81 mmol, 45 %). Re-crystallization from the  $\text{CH}_2\text{Cl}_2$ /*n*-hexane solution at room temperature gives a yellow block crystal of **1**[OTf]· $\text{H}_2\text{O}$  suitable for X-ray crystallography and elemental analysis.

FT/IR (KBr):  $\nu$  = 3576 (m), 3498 (m), 3170 (w), 3140 (s), 3085 (w), 3047 (w), 3000 (w), 2957 (m), 1586 (vs,  $\nu_{\text{C=O}}$ ), 1540 (w), 1513 (s,  $\nu_{\text{C=C}}$ ), 1454 (w), 1403 (w), 1384 (w), 1317 (w), 1274 (m), 1190 (w), 1153 (m), 1101 (m), 1030 (vs), 946 (w), 887 (s), 832 (w), 811 (w), 796 (w), 774 (w), 738 (vs), 712 (s), 676 (w), 666 (w), 637  $\text{cm}^{-1}$  (vs). UV-vis ( $\text{CH}_2\text{Cl}_2$ , r.t.):  $\lambda$  = 422 nm ( $\epsilon$  = 615  $\text{M}^{-1} \text{cm}^{-1}$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ , 20°C, TMS):  $\delta$  = 27.55, 30.77, 34.26, 35.95, 36.32, 102.15, 122.72, 123.80, 123.85, 123.96, 125.15, 125.48, 129.15, 135.02, 142.11, 191.54, 191.56. ESI-MS<sup>+</sup> (MeOH):  $m/z$  = 489  $\{[\text{Co}([\text{PhB}(\text{MeIm})_3](\text{acac})]^+ (\mathbf{1} - \text{MeImH})\}$ , 327;  $[\text{Co}([\text{PhB}(\text{MeIm})_2](\text{H}_2\text{O})]^+$ . CSI-MS<sup>+</sup> (acetone):  $m/z$  = 571;  $[\text{Co}([\text{PhB}(\text{MeIm})_3](\text{acac})(\text{MeImH})]^+ (\mathbf{1})$ , 489;  $[\text{Co}([\text{PhB}(\text{MeIm})_3](\text{acac})]^+ (\mathbf{1} - \text{MeImH})$ . Elemental analysis calcd (%) for  $[\text{Co}([\text{PhB}(\text{MeIm})_3](\text{acac})(\text{MeImH})](\text{OTf})\cdot\text{H}_2\text{O}$  ( $\text{C}_{28}\text{H}_{35}\text{BCoF}_3\text{N}_8\text{O}_6\text{S}$ ): Calc. C 45.54, H 4.78, N 15.17; found: C 45.04, H 4.74, N 14.70.

## 2.3. $[\text{Co}^{\text{III}}([\text{PhB}(\text{MeIm})_3])_2](\text{OTf})$ (**2**[OTf])

A 2.0 M LDA in THF/heptane/ethylbenzene solution (2.6 mL, 5.20 mmol) was added into a THF solution (20 mL) of  $[\text{PhB}(\text{MeImH})_3](\text{OTf})_2$  (1.05 g, 1.65 mmol) at room temperature and then stirred for 3 h to generate  $\text{Li}[\text{PhB}(\text{MeIm})_3]$ . A THF solution (20 mL) of  $\text{Co}(\text{acac})_2$  (213 mg, 0.83 mmol) was added to the suspension involving  $\text{Li}[\text{PhB}(\text{MeIm})_3]$  and the resulting reaction mixture was stirred for overnight. The volatiles were evaporated, and the residue was re-dissolved in  $\text{CH}_2\text{Cl}_2$ . The solution was then passed through a filter with Celite pad to remove insoluble components. After evaporation of  $\text{CH}_2\text{Cl}_2$ , the obtained yellow-brown solid was washed with THF to give the entitled complex as pale-yellow powder (41.2 mg, 0.05 mmol, 3.0 %). The obtained pale-yellow compound was applied to elemental analysis. Re-crystallization from the  $\text{CH}_2\text{Cl}_2$ /*n*-hexane solution at room temperature gives colorless block crystals of **2**[OTf]· $2\text{CH}_2\text{Cl}_2$  suitable for X-ray crystallography.

FT/IR (KBr):  $\nu = 3134$  (s), 3083 (w), 3044 (w), 2950 (s), 1559 (w), 1448 (s), 1407 (s), 1360 (s), 1300 (m), 1277 (vs), 1223 (w), 1184 (vs), 1159 (w), 1076 (w), 1031 (vs), 884 (s), 800 (s), 736 (vs), 711 (vs), 638 (vs), 620  $\text{cm}^{-1}$  (w). UV-vis ( $\text{CH}_2\text{Cl}_2$ , r.t.): Not characteristic peaks.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ,  $20^\circ\text{C}$ , TMS):  $\delta = 8.05$  (d, 4H; *ortho-Ph*), 7.63 (t, 4H; *meta-Ph*), 7.56 (t, 2H; *para-Ph*), 7.15 (d, 6H; 4-*Im*), 7.04 (d, 6H; 5-*Im*), 2.13 (s, 18H; *Me-Im*).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ , r.t.)  $\delta_{\text{C}}$ : 34.26, 122.71, 123.40, 128.67, 128.87, 129.04, 135.33, 187.66. ESI-MS<sup>+</sup> (MeOH):  $m/z = 721$ ;  $\text{Co}([\text{PhB}(\text{MeIm})_3]_2)^+$  (**2**). Elemental analysis calcd (%) for  $[\text{Co}([\text{PhB}(\text{MeIm})_3]_2)(\text{OTf})\cdot\text{H}_2\text{O}$  ( $\text{C}_{37}\text{H}_{42}\text{B}_2\text{CoF}_3\text{N}_{12}\text{O}_4\text{S}$ ): Calc. C 50.02, H 4.77, N 18.92; found: C 49.66, H 4.48, N 19.06.

### 3. Crystallographic analysis

Diffraction data for single crystals were collected using a Rigaku Saturn 70 CDD area detector system with graphite monochromated Mo-K $\alpha$  radiation. The block shaped crystals were mounted on a CryoLoop with liquid paraffin and flash cooled to 113 K (for **1** $[\text{OTf}]\cdot\text{H}_2\text{O}$ ) or 173 K (for **2** $[\text{OTf}]\cdot 2\text{CH}_2\text{Cl}_2$ ) by cold  $\text{N}_2$  gas flow on the goniometer. For **1** $[\text{OTf}]\cdot\text{H}_2\text{O}$ , three set of sweeps (at  $\phi = 0, 90, \text{ and } 180^\circ$ ) of data were done using  $\omega$  oscillations from  $-115.0$  to  $65.0^\circ$  in  $0.3^\circ$  steps at  $\chi = 45^\circ$  with the exposure rate = 15.0 [sec/ $^\circ$ ], the detector swing angle =  $-25^\circ$  and the crystal-to-detector distance = 55 mm (total of 1800 oscillation images). For **2** $[\text{OTf}]\cdot 2\text{CH}_2\text{Cl}_2$ , two set of sweeps (at  $\phi = 0$  and  $90^\circ$ ) of data were done using  $\omega$  oscillations from  $-115.0$  to  $65.0^\circ$  in  $0.3^\circ$  steps at  $\chi = 45^\circ$  with the exposure rate = 5 [sec/ $^\circ$ ], the detector swing angle =  $-20^\circ$ , and the crystal-to-detector distance = 55 mm (total of 1800 oscillation images).

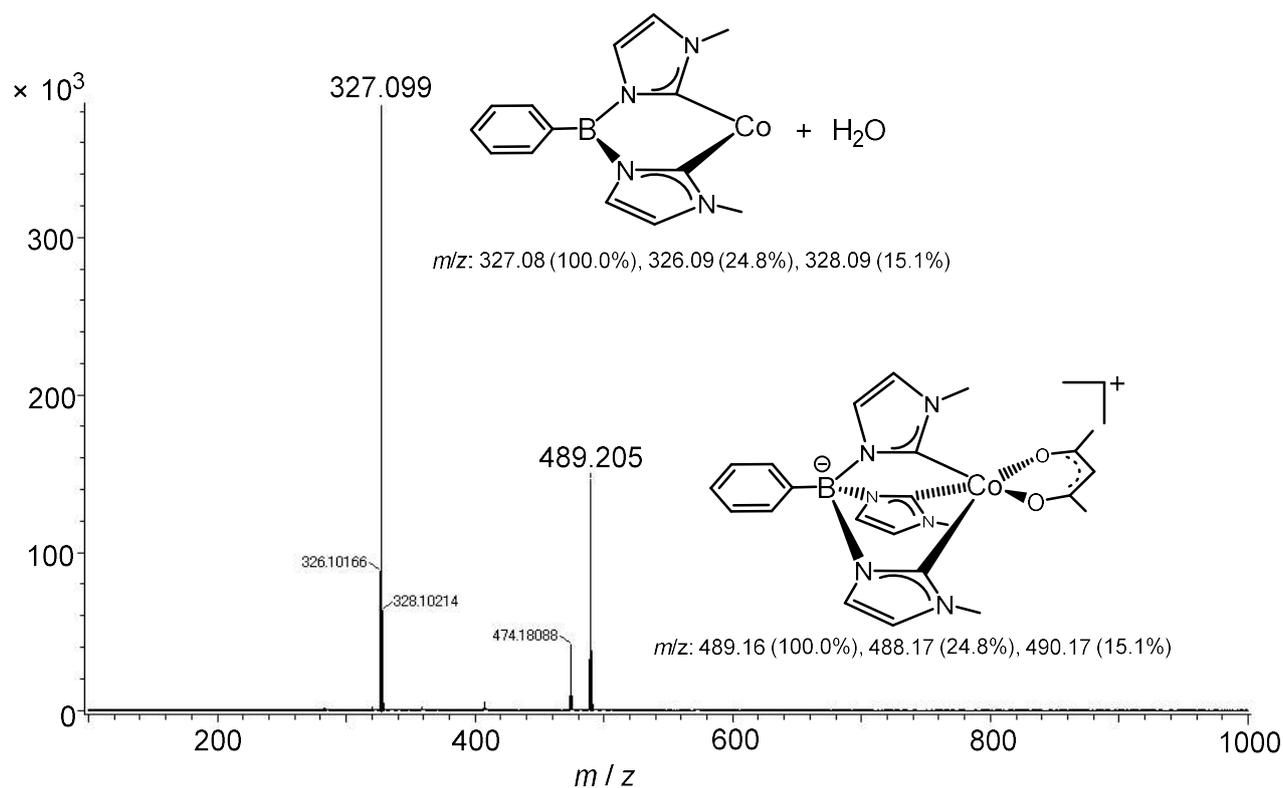
Data collection and processing were performed using Rigaku CrystalClear software.<sup>2</sup> 7487 reflections (**1** $[\text{OTf}]\cdot\text{H}_2\text{O}$ ,  $R_{\text{int}} = 0.019$ ) and 10024 reflections (**2** $[\text{OTf}]\cdot 2\text{CH}_2\text{Cl}_2$ ,  $R_{\text{int}} = 0.015$ ) were collected. Equivalent reflections were merged. The linear absorption coefficient,  $\mu$ , for Mo-K $\alpha$  radiation is  $6.88 \text{ cm}^{-1}$  for **1** $[\text{OTf}]\cdot\text{H}_2\text{O}$  and  $7.15 \text{ cm}^{-1}$  for **2** $[\text{OTf}]\cdot 2\text{CH}_2\text{Cl}_2$ , respectively. A numerical absorption correction was applied which resulted in transmission factors ranging from 0.7551 to 0.9232 for **1** $[\text{OTf}]\cdot\text{H}_2\text{O}$  and from 0.7781 to 0.8463 for **2** $[\text{OTf}]\cdot 2\text{CH}_2\text{Cl}_2$ , respectively. The data were corrected for Lorentz and polarization effects. Structural solution by a direct method (SIR-92)<sup>3</sup> and refinement by full-matrix least squares (SHELXL-2014/7)<sup>4</sup> against  $F^2$  with all reflections were performed on WinGX<sup>5</sup> software. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms adjacent to carbon atoms were placed in calculated positions with C-H = 0.96 Å (for methyl groups) or 0.93 Å (for aromatic rings) with  $\text{Uiso}(\text{H}) = 1.2 \text{ Uiso}(\text{attached atom})$ . The molecular structure was drawn on ORTEP-3 for Windows<sup>6</sup> program. In the crystal lattice of **2** $[\text{OTf}]\cdot 2\text{CH}_2\text{Cl}_2$ , two independent molecules of **2** were involved. The cobalt centers of **2** sat on the inversion centers. Crystal Information Files (CIF) of the complexes reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1866426 (**1** $[\text{OTf}]\cdot\text{H}_2\text{O}$ ) and CCDC-1866427 (**2** $[\text{OTf}]\cdot 2\text{CH}_2\text{Cl}_2$ ). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### 4. Procedure of the catalytic reactions

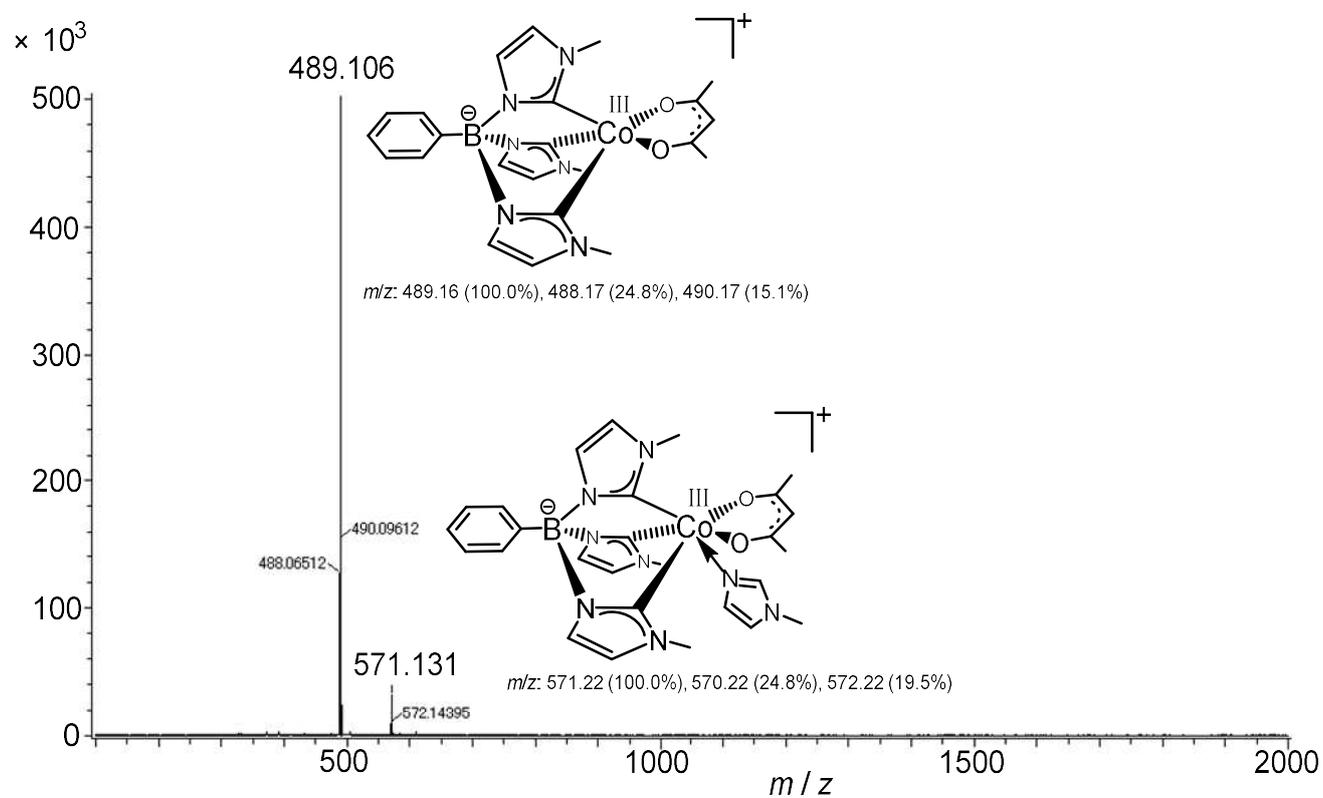
A solution of the cobalt compounds (2.0  $\mu\text{mol}$ ), cyclohexane (15.0 mmol) in MeCN (1 mL), and

CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was placed in a Schlenk tube, and degassed with Ar gas. Next, a CH<sub>2</sub>Cl<sub>2</sub> (2 mL) solution of *m*CPBA (2.0 mmol) was added under Ar atmosphere and stirred at appropriate temperature (25 or 35°C). To monitor product formation, 0.2 mL of the reaction mixture was corrected at certain times (reaction time 0, 10, 30, 60, 120, 180 min) and quenched with a dichloromethane solution (0.5 mL) of triphenylphosphine (10 mg), and then the solution was subjected to GC analysis.

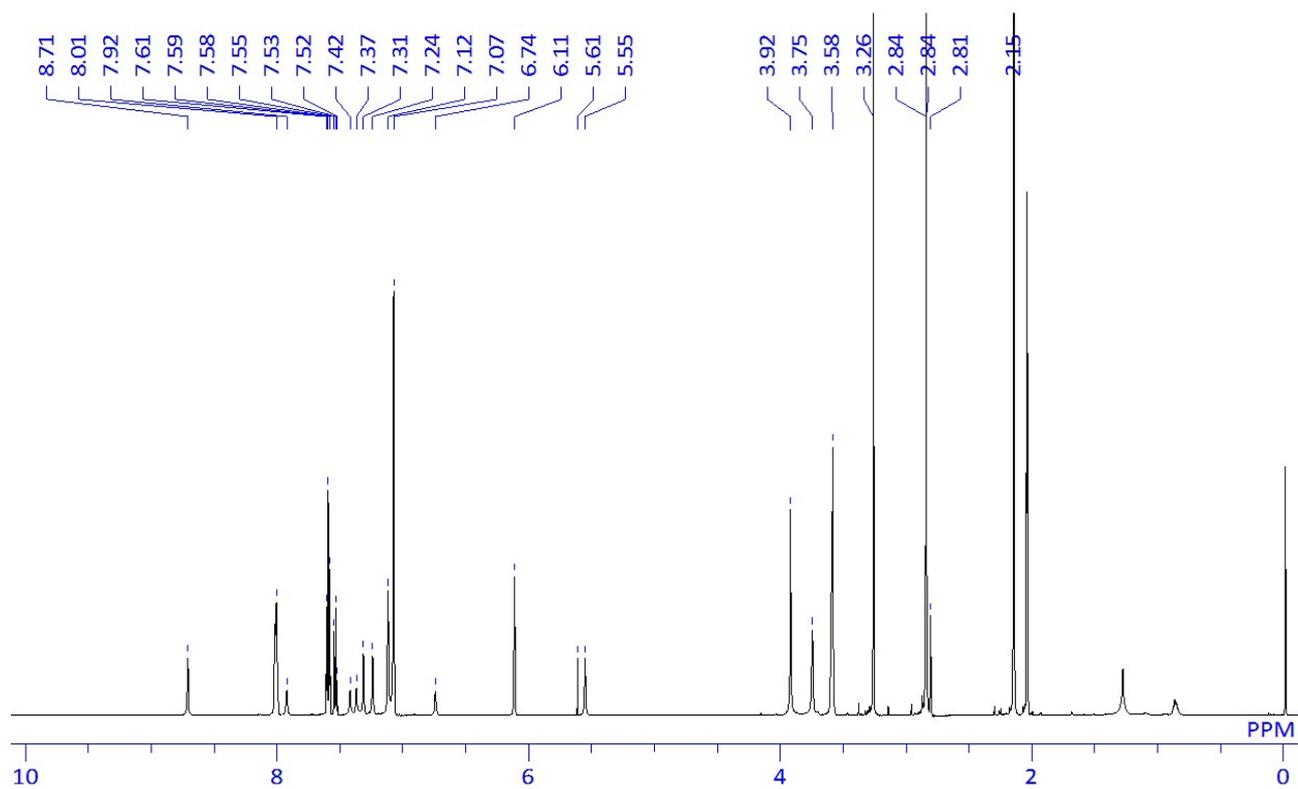
#### 4. Characterization of Co(III) complexes.



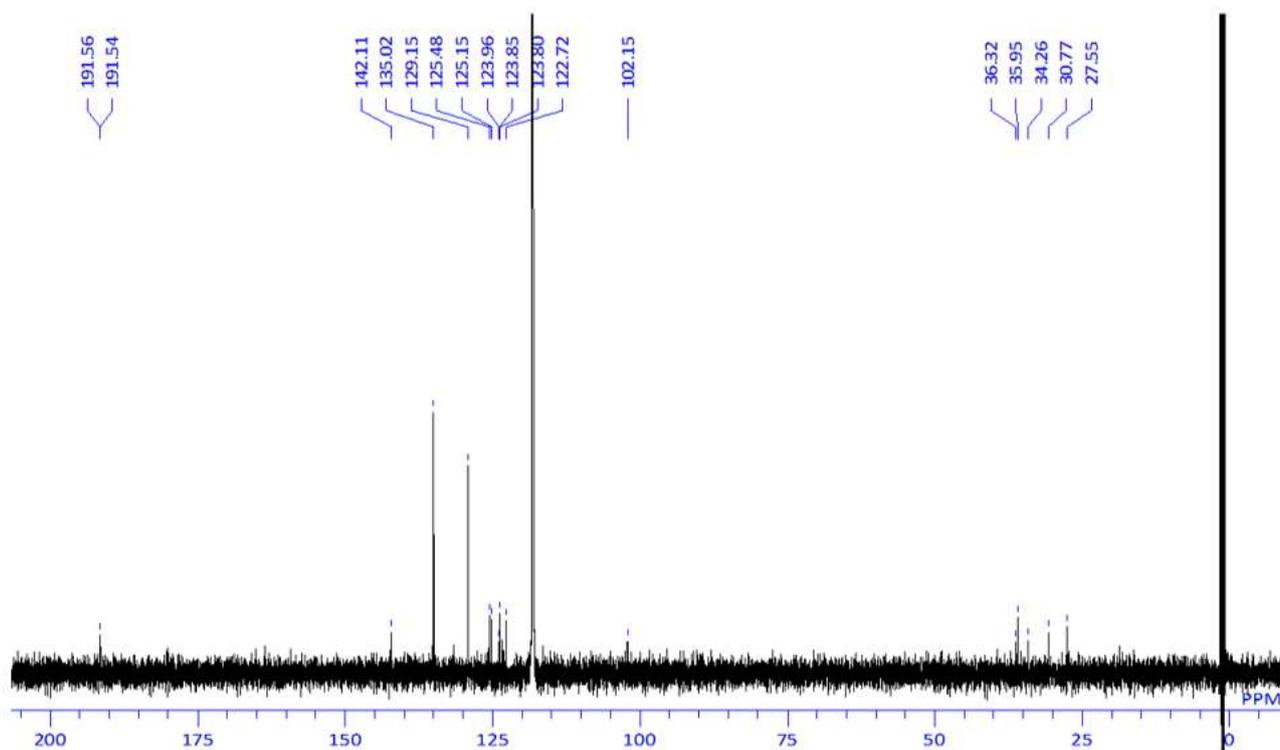
**Fig. S1** ESI-MS(+) spectrum of  $[\text{Co}^{\text{III}}([\text{PhB}(\text{MeIm})_3](\text{acac})(\text{MeImH})](\text{OTf})$  (**1[OTf]**; MeOH solution).



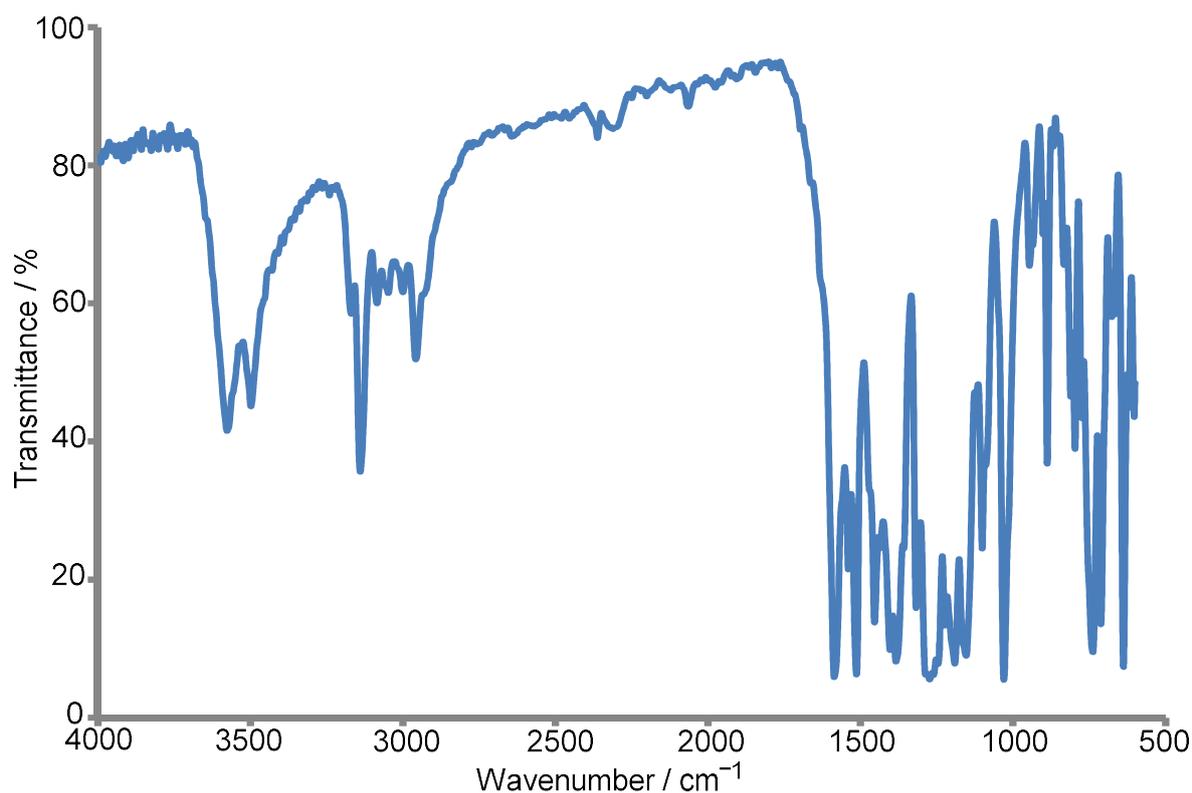
**Fig. S2** CSI-MS(+) spectrum of  $[\text{Co}^{\text{III}}([\text{PhB}(\text{MeIm})_3](\text{acac})(\text{MeImH})](\text{OTf})$  (**1[OTf]**; acetone solution).



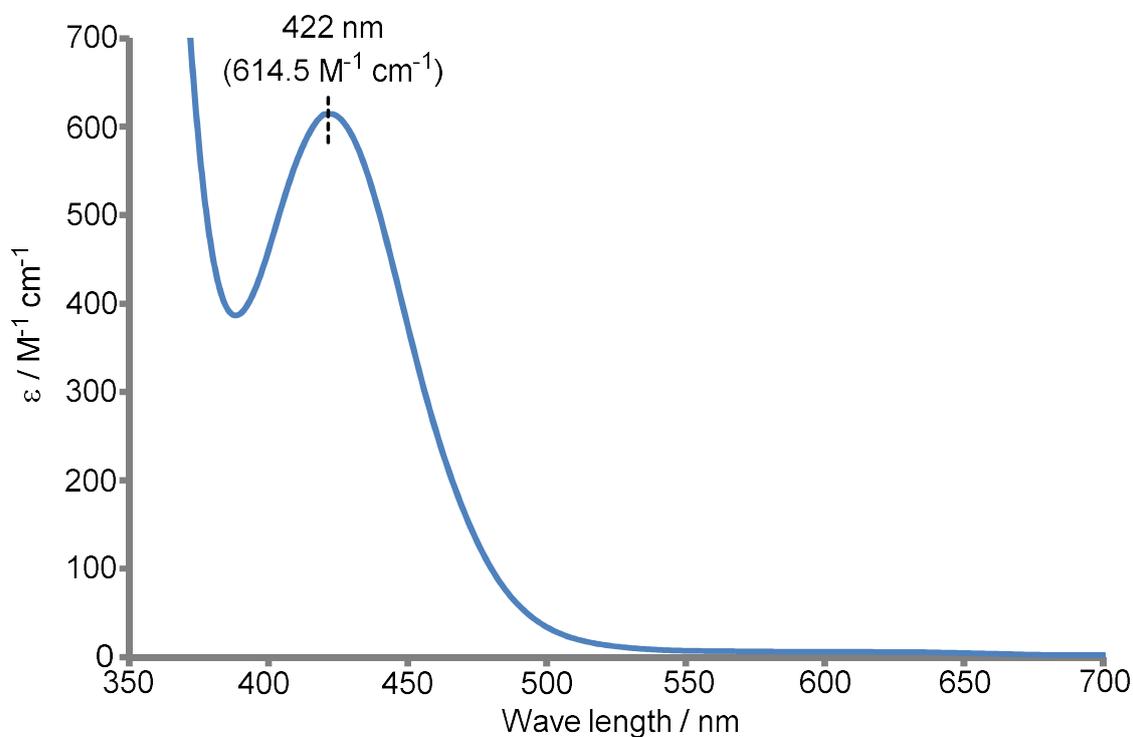
**Fig. S3**  $^1\text{H}$  NMR spectrum of  $[\text{Co}^{\text{III}}([\text{PhB}(\text{MeIm})_3])(\text{acac})(\text{MeImH})](\text{OTf})$  (**1[OTf]**) in acetone- $d_6$  at room temperature (600 MHz).



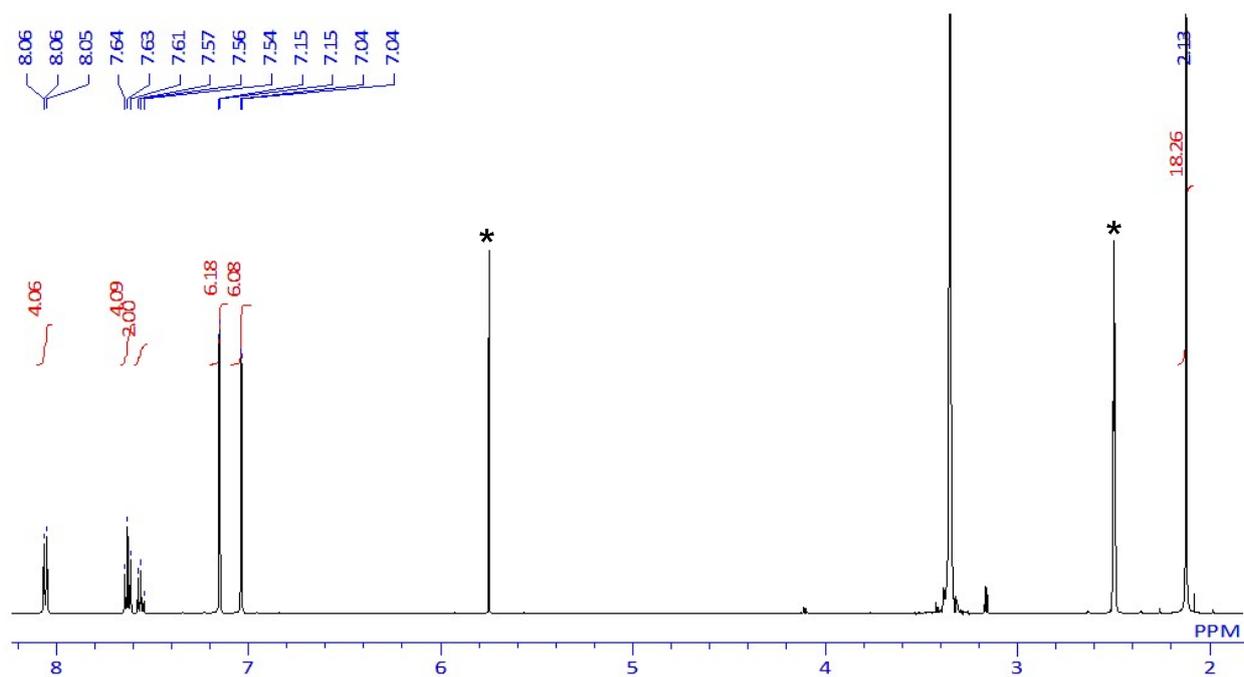
**Fig. S4**  $^{13}\text{C}$  NMR spectrum of  $[\text{Co}^{\text{III}}([\text{PhB}(\text{MeIm})_3])(\text{acac})(\text{MeImH})](\text{OTf})$  (**1[OTf]**) in acetonitrile- $d_3$  at room temperature (125 MHz).



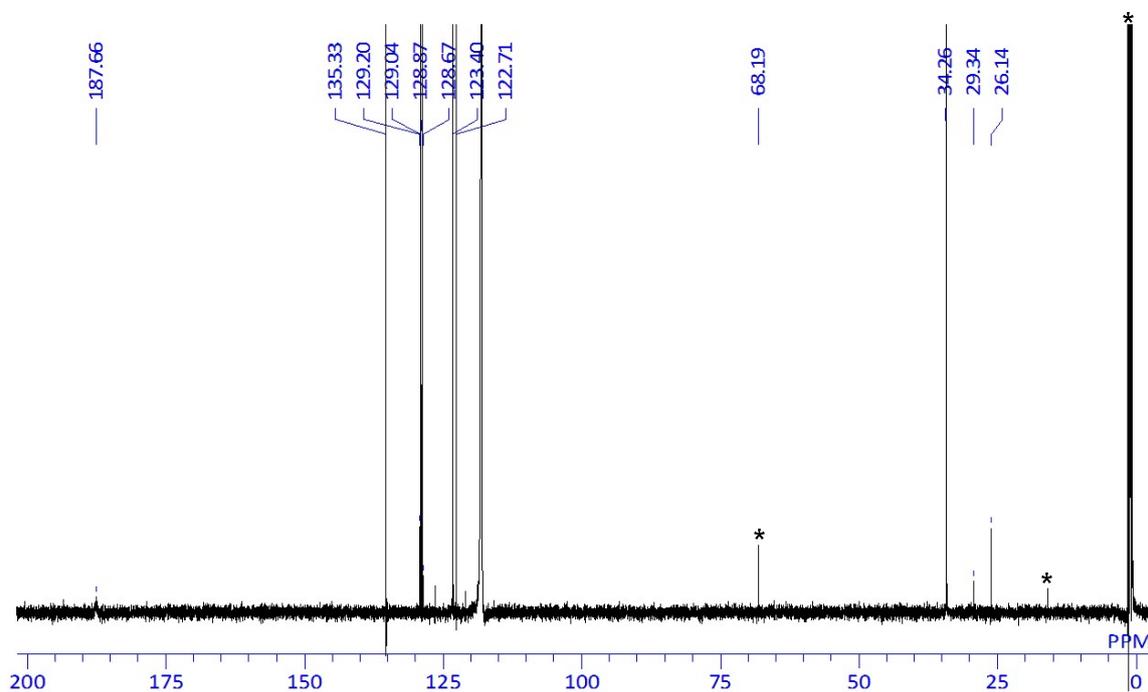
**Fig. S5** FT/IR spectrum of  $[\text{Co}^{\text{III}}(\text{PhB}(\text{MeIm})_3)(\text{acac})(\text{MeImH})](\text{OTf})$  (**1[OTf]**; KBr pellet) at room temperature.



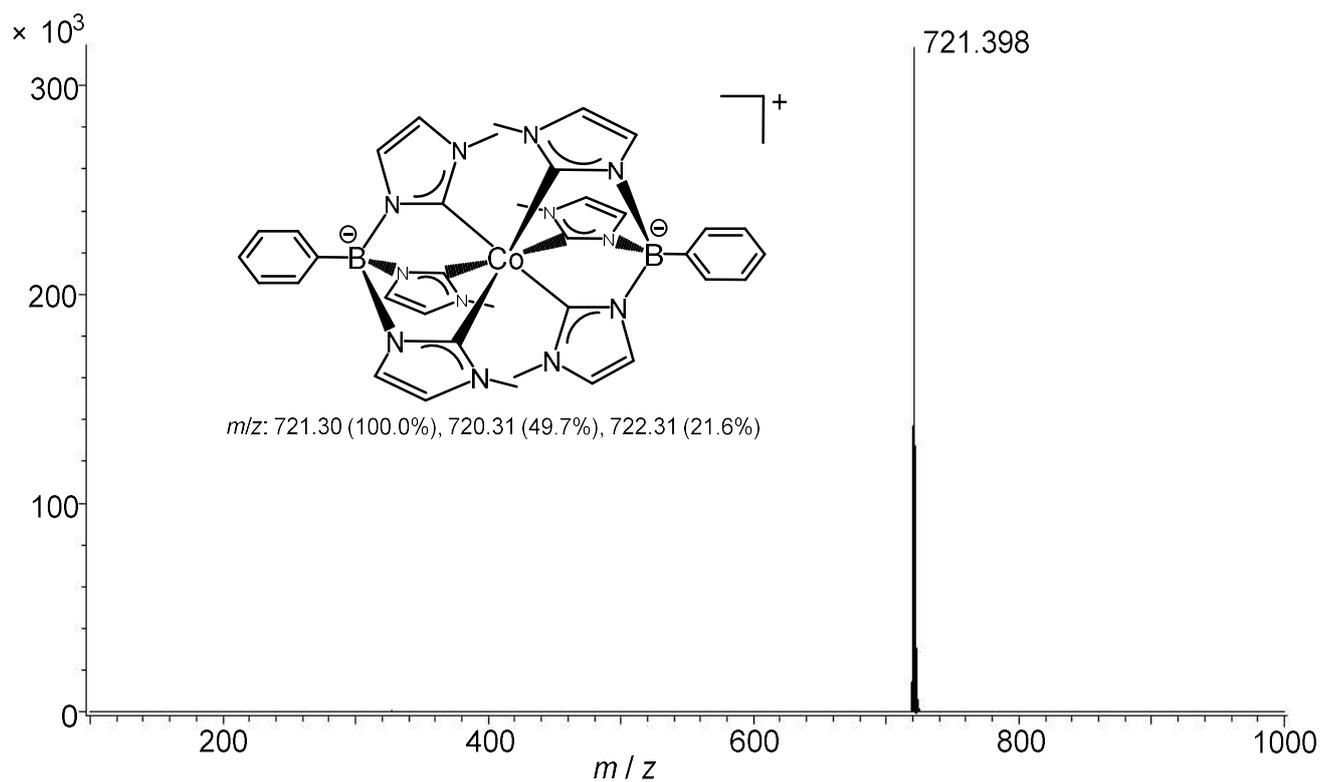
**Fig. S6** UV-vis spectrum of  $[\text{Co}^{\text{III}}(\text{PhB}(\text{MeIm})_3)(\text{acac})(\text{MeImH})](\text{OTf})$  (**1[OTf]**;  $\text{CH}_2\text{Cl}_2$  solution) at room temperature.



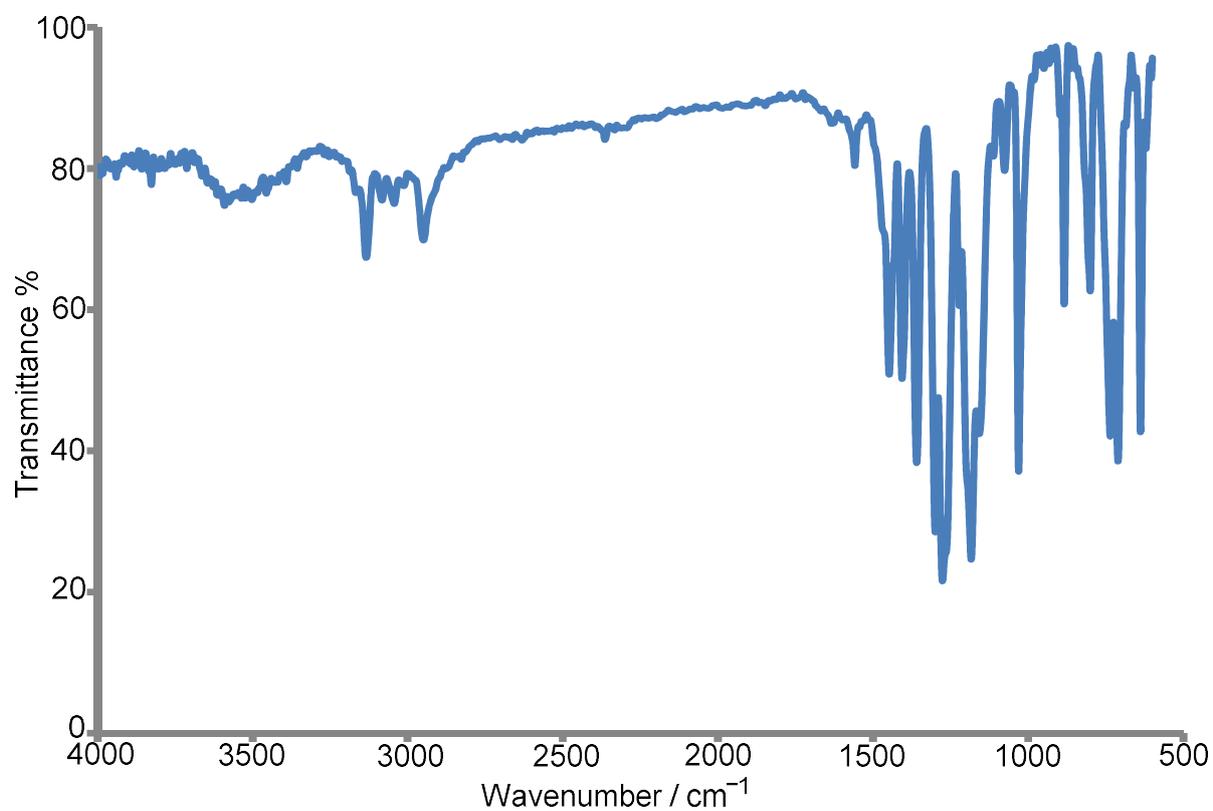
**Fig. S7**  $^1\text{H}$  NMR spectrum of  $[\text{Co}^{\text{III}}(\text{PhB}(\text{MeIm})_3)_2](\text{OTf})$  ( $2[\text{OTf}]$ ) in  $\text{DMSO-}d_6$  at room temperature (500 MHz). Peaks with asterisk are arising from the solvents used for the compound synthesis.



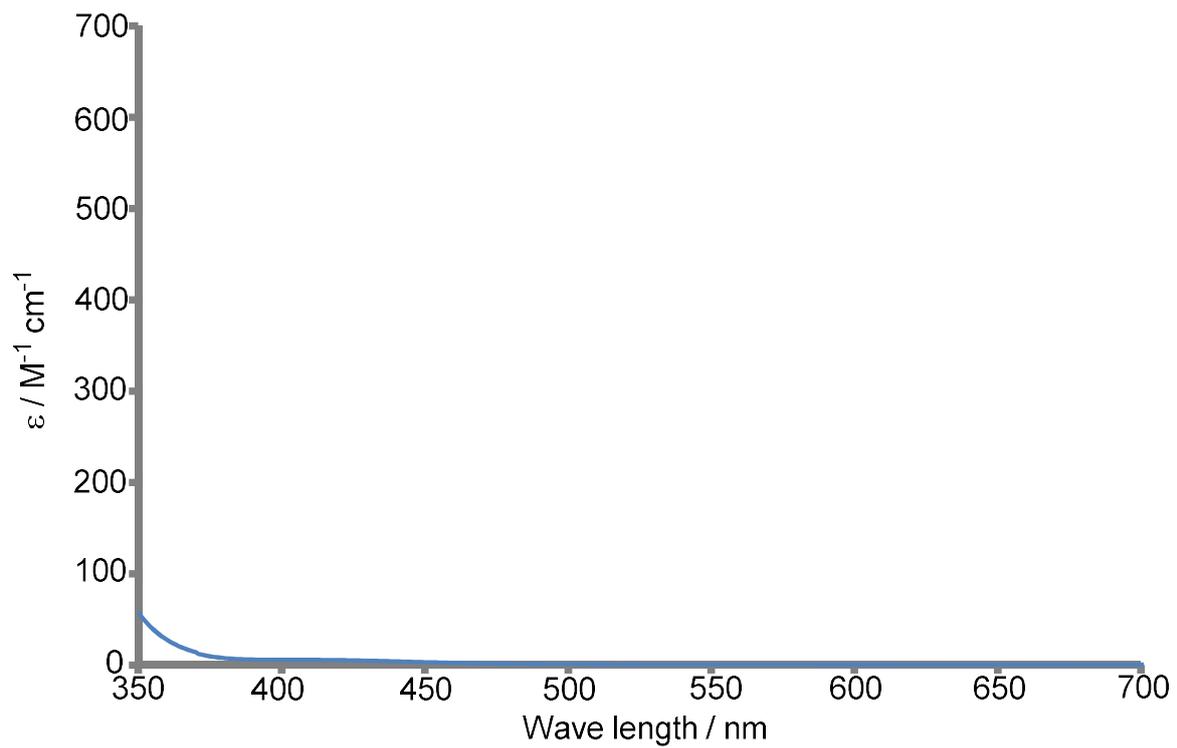
**Fig. S8**  $^{13}\text{C}$  NMR spectrum of  $[\text{Co}^{\text{III}}(\text{PhB}(\text{MeIm})_3)_2](\text{OTf})$  ( $2[\text{OTf}]$ ) in  $\text{MeCN-}d_3$  at room temperature (600 MHz). Peaks with asterisk are arising from the solvents used for the compound synthesis.



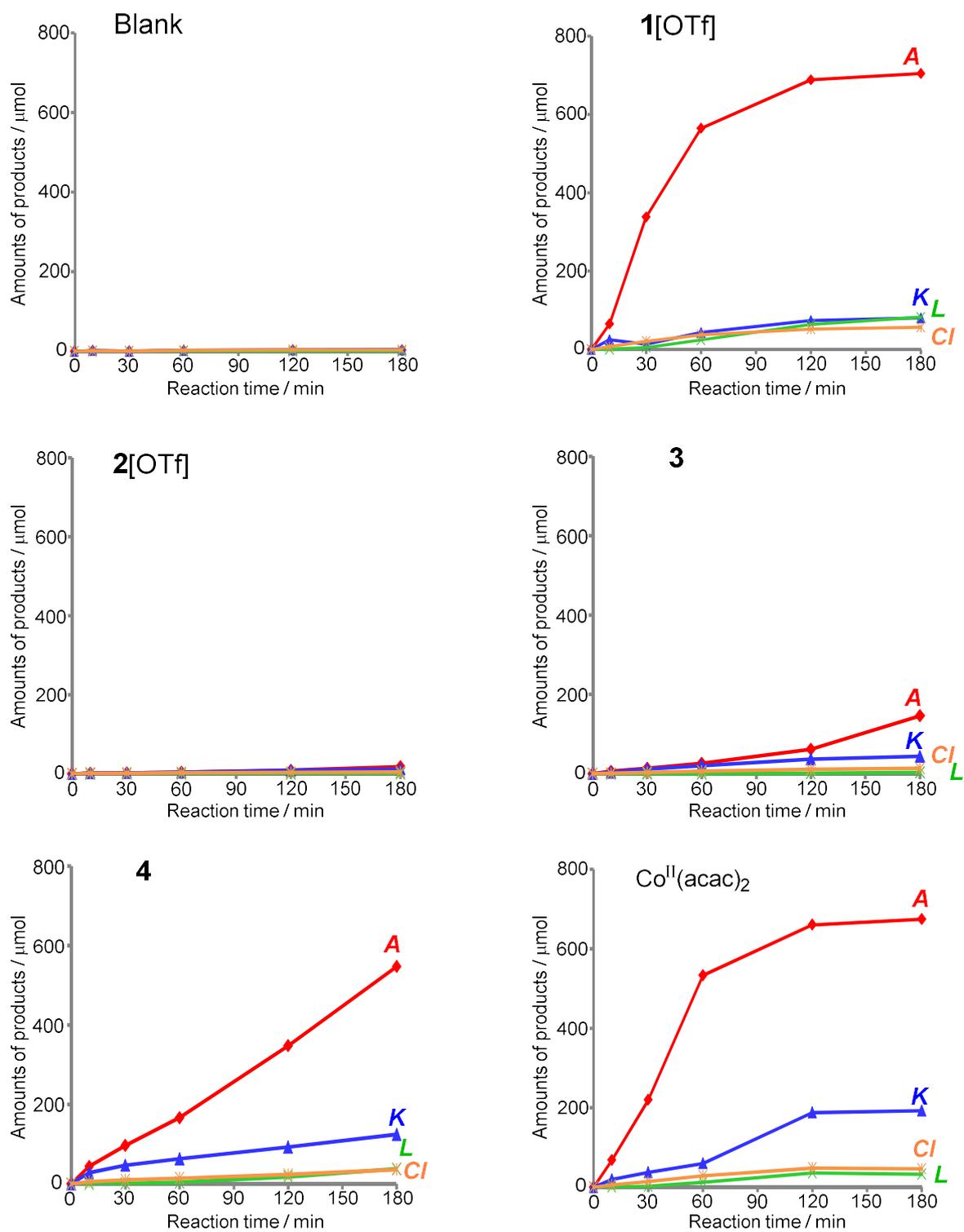
**Fig. S9** ESI-MS(+) spectrum of  $[\text{Co}^{\text{III}}([\text{PhB}(\text{MeIm})_3]_2)(\text{OTf})_2]$  ( $2[\text{OTf}]$ ; MeOH solution).



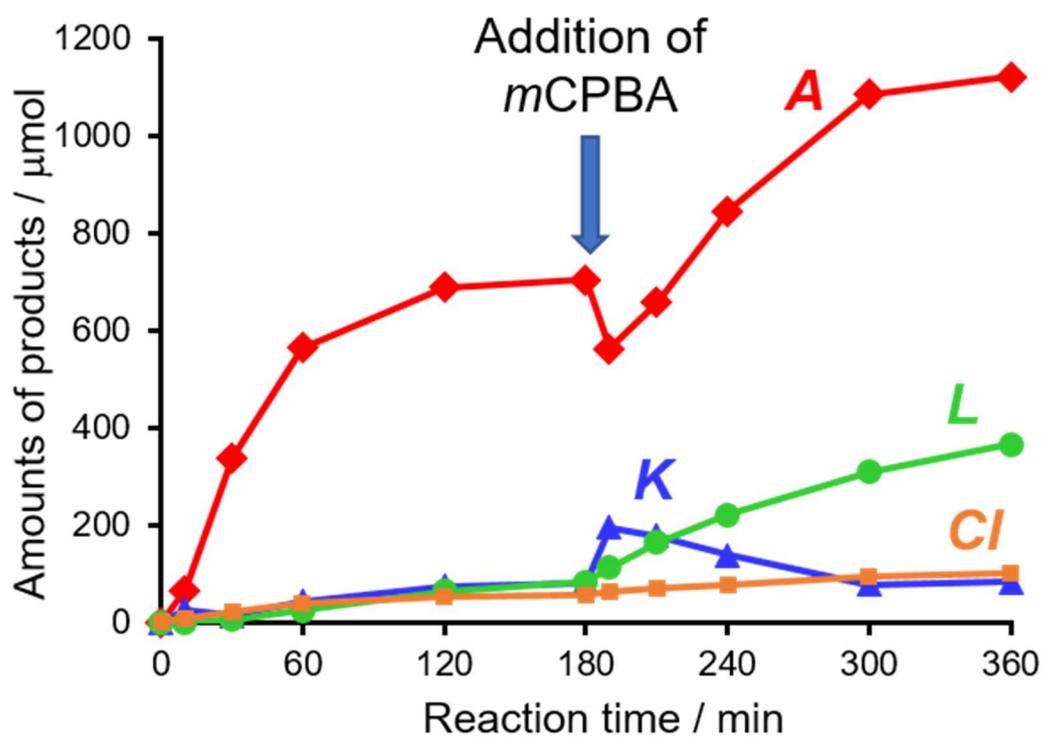
**Fig. S10** FT/IR spectrum of  $[\text{Co}^{\text{III}}([\text{PhB}(\text{MeIm})_3]_2)(\text{OTf})_2]$  ( $2[\text{OTf}]$ ; KBr pellet) at room temperature.



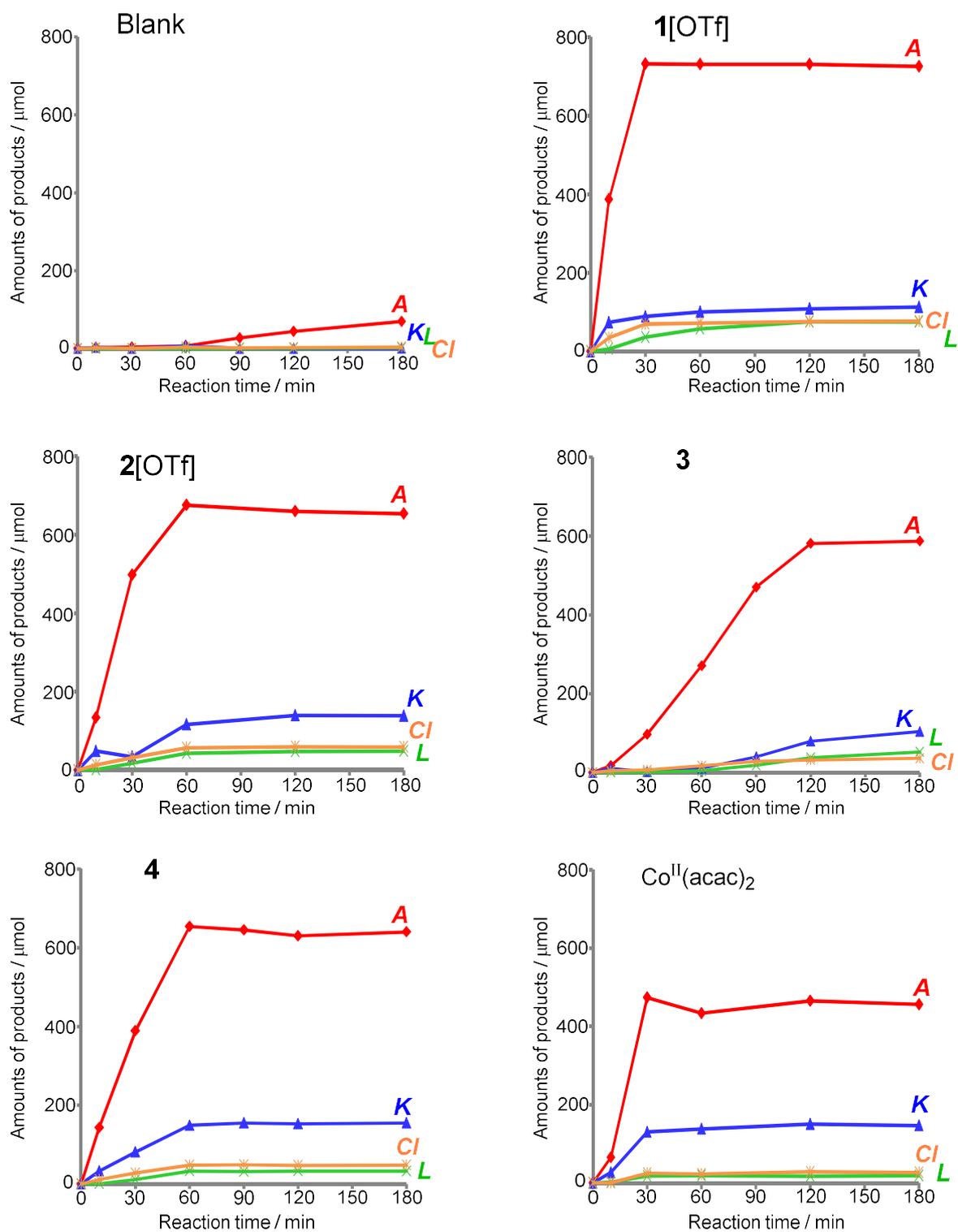
**Fig. S11** UV-vis spectrum of of  $[\text{Co}^{\text{III}}(\text{PhB}(\text{MeIm})_3)_2](\text{OTf})$  ( $2[\text{OTf}]$ ;  $\text{CH}_2\text{Cl}_2$  solution) at room temperature.



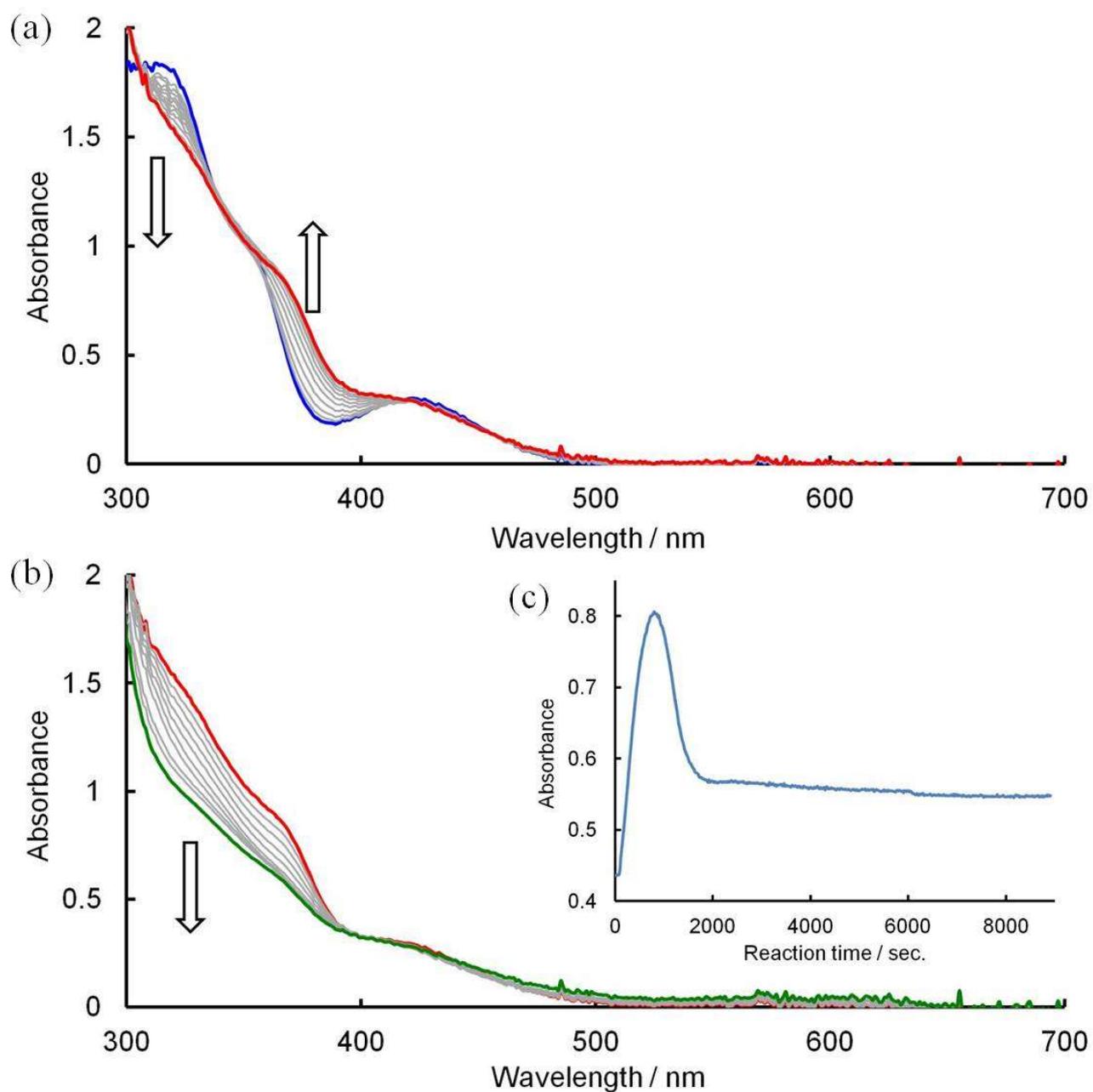
**Fig. S12** Time course of the cyclohexane oxidation with *m*CPBA at 25°C. Abbreviations of the products are as follows: **A** (red) = cyclohexanol, **K** (blue) = cyclohexanone, **L** (green) = ε-caprolactone, **CI** (orange) = chlorocyclohexane.



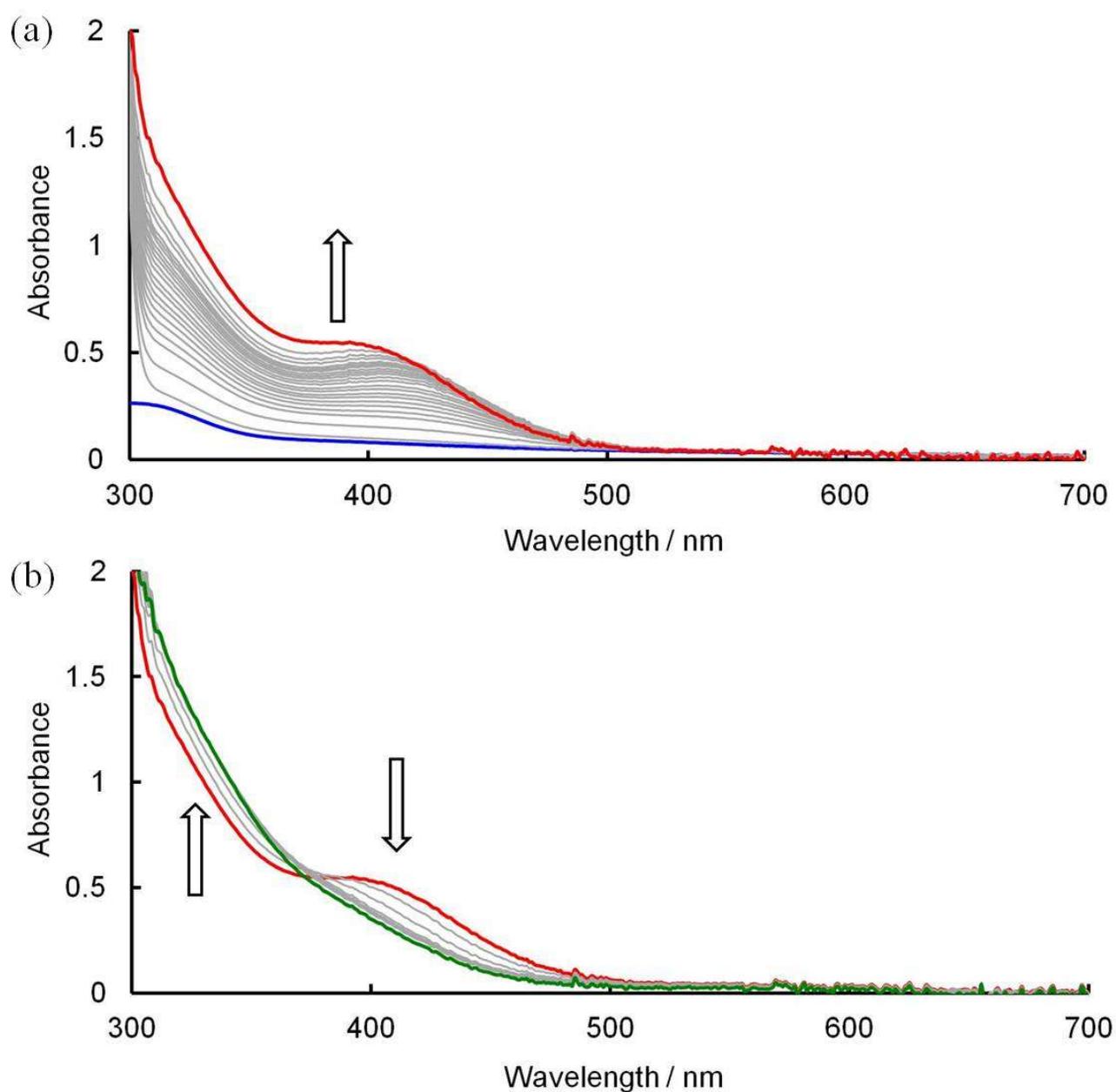
**Fig. S13** Time course of the cyclohexane oxidation with *m*CPBA at 25°C catalyzed by 1[OTf]. When the catalytic reaction reached saturation, additional *m*CPBA (2 mmol) was added. Abbreviations of the products are as follows: *A* (red) = cyclohexanol, *K* (blue) = cyclohexanone, *L* (green) =  $\epsilon$ -caprolactone, *Cl* (orange) = chlorocyclohexane.



**Fig. S14** Time course of the cyclohexane oxidation with *m*CPBA at 35°C. Abbreviations of the products are as follows: **A** (red) = cyclohexanol, **K** (blue) = cyclohexanone, **L** (green) = ε-caprolactone, **Cl** (orange) = chlorocyclohexane.

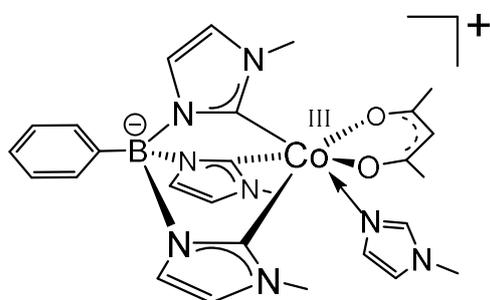


**Fig. S15** Time course of UV-vis spectra of the reaction mixture of **1**[OTf] with excess *m*CPBA at 25°C. (a) Spectra observed from start to 800 seconds. (b) Spectra observed from 820 seconds to 8900 seconds. (c) Time course of absorbance at 370 nm. Conditions are as follows; solvent: mixed CH<sub>2</sub>Cl<sub>2</sub> and MeCN with 3:1 volume ratio, concentration of **1**:  $4.80 \times 10^{-4}$  mol L<sup>-1</sup>, concentration of *m*CPBA:  $4.84 \times 10^{-3}$  mol L<sup>-1</sup>.

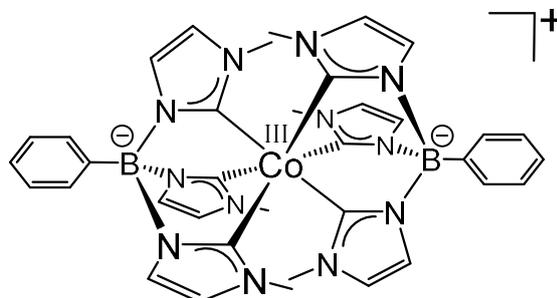


**Fig. S16** Time course of UV-vis spectra of the reaction mixture of **2**[OTf] with excess *m*CPBA. (a) Spectra observed until saturation of spectral change (from start to 2600 seconds) at 25°C. (b) Spectral change by increasing the temperature from 25°C (the maximum absorption state of (a) indicated red line) to 35°C (final spectrum indicated as green line). Conditions are as follows; solvent: mixed CH<sub>2</sub>Cl<sub>2</sub> and MeCN with 3:1 volume ratio, concentration of **1**:  $4.64 \times 10^{-4}$  mol L<sup>-1</sup>, concentration of *m*CPBA:  $4.84 \times 10^{-3}$  mol L<sup>-1</sup>.

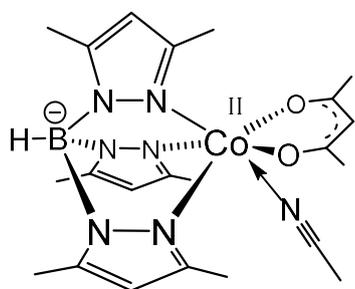
## Scorpionate ligands complexes



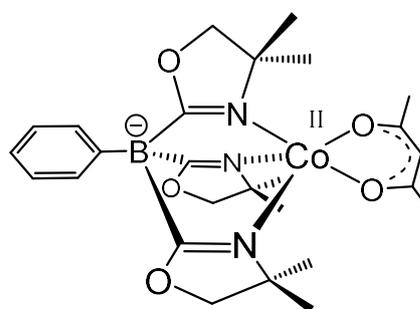
[Co<sup>III</sup>([PhB(MeIm)<sub>3</sub>])(acac)]<sup>+</sup> (1)



[Co<sup>III</sup>([PhB(MeIm)<sub>3</sub>])<sub>2</sub>]<sup>+</sup> (2)

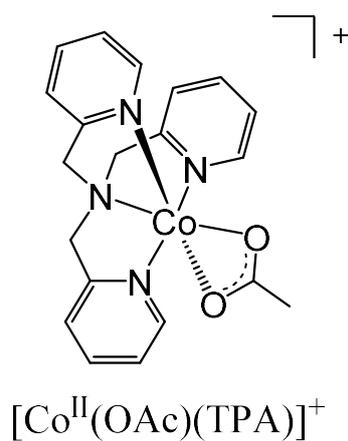


[Co<sup>II</sup>(Tp\*)(acac)(NCMe)] (3)

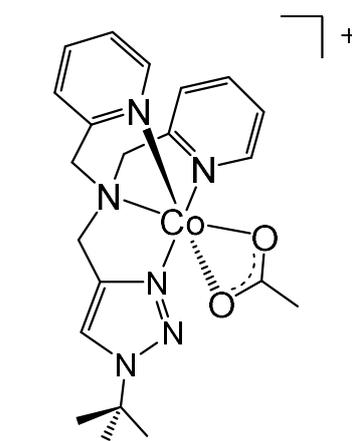


[Co<sup>II</sup>(To<sup>M</sup>)(acac)] (4)

## N4-donating ligands complexes



[Co<sup>II</sup>(OAc)(TPA)]<sup>+</sup>



[Co<sup>II</sup>(OAc)(L<sup>tBu</sup>)]<sup>+</sup>

Fig. S17 Schematic drawings of the cobalt complexes.

**Table S1.** Crystallographic data for **1**[OTf] and **2**[OTf].

	<b>1</b> [OTf]·H <sub>2</sub> O	<b>2</b> [OTf]·2CH <sub>2</sub> Cl <sub>2</sub>
Formula	C <sub>28</sub> H <sub>35</sub> BCoF <sub>3</sub> N <sub>8</sub> O <sub>6</sub> S	C <sub>39</sub> H <sub>44</sub> B <sub>2</sub> Cl <sub>4</sub> CoF <sub>3</sub> N <sub>12</sub> O <sub>3</sub> S
Formula Weight	738.44	1040.27
Space Group	<i>C2/c</i> (No. 15)	<i>P-1</i> (No. 2)
Crystal System	monoclinic	triclinic
<i>a</i> / Å	24.1934(16)	9.9266(4)
<i>b</i> / Å	13.0996(6)	12.0407(7)
<i>c</i> / Å	21.9782(16)	19.3675(8)
$\alpha$ / °	90	89.360(6)
$\beta$ / °	115.652(2)	86.399(5)
$\gamma$ / Å	90	85.143(5)
<i>V</i> / Å <sup>3</sup>	6278.9(7)	2301.96(19)
<i>Z</i>	8	2
<i>F</i> (000)	3056	1068
<i>D</i> (calcd) / g·cm <sup>-3</sup>	1.562	1.501
Temp./K	113(2)	173(2)
$\mu$ (MoK $\alpha$ ) / cm <sup>-1</sup>	6.88	7.15
$2\theta_{\max}$ / °	55.036	54.946
Measured reflections	7487	10024
Observed reflections ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	6734	8867
Parameters	481	625
<i>R</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) / all <sup>(a)</sup>	0.0488 / 0.0513	0.0532 / 0.0579
w <i>R</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) / all <sup>(a)</sup>	0.1388 / 0.1415	0.1525 / 0.1571
Goodness of fit <i>S</i> <sup>(b)</sup>	1.069	1.036
Crystal Color	yellow	colorless
Crystal habit	block	block

(a)  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  $R_w = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ . (b)  $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$ , where *n* is the number of reflections and *p* is the total number of parameters refined.

**Table S2.** Selected bond length (Å) and angles (°) for 1[OTf]·H<sub>2</sub>O.

Bond length (Å)					
Co1–C1	1.943(2)	Co1–C5	1.908(2)	Co1–C9	1.922(2)
Co1–O1	1.9472(16)	Co1–O2	1.9638(15)	Co1–N8	1.9963(18)
Bond angles (°)					
C5–Co1–C9	89.09(9)	C5–Co1–C1	88.10(9)	C9–Co1–C1	85.90(9)
C5–Co1–O1	89.29(8)	C9–Co1–O1	178.15(7)	C1–Co1–O1	93.14(8)
C5–Co1–O2	179.42(8)	C9–Co1–O2	90.34(8)	C1–Co1–O2	91.97(8)
O1–Co1–O2	91.28(6)	C5–Co1–N8	89.03(8)	C9–Co1–N8	89.50(8)
C1–Co1–N8	174.61(8)	O1–Co1–N8	91.38(7)	O2–Co1–N8	90.85(7)

**Table S3.** Selected bond length (Å) and angles (°) for 2[OTf]·2CH<sub>2</sub>Cl<sub>2</sub>.

Bond length (Å)					
Molecule 1					
Co1–C1	1.932(2)	Co1–C5	1.946(2)	Co1–C9	1.952(2)
Molecule 2					
Co2–C19	1.946(2)	Co2–C23	1.931(2)	Co2–C27	1.951(2)
Bond angles (°)					
Molecule 1					
C1–Co1–C1'	180.0	C1–Co1–C5	88.48(9)	C1–Co1–C5'	91.52(9)
C1–Co1–C9	88.36(9)	C1–Co1–C9'	91.64(9)	C5–Co1–C5'	180.00(13)
C5–Co1–C9	87.62(9)	C5–Co1–C9'	92.38(9)	C9–Co1–C9'	180.0
Molecule 2					
C19–Co2–C19'	180.0	C19–Co2–C23	88.16(10)	C19–Co2–C23'	91.84(10)
C19–Co2–C27	87.82(10)	C19–Co2–C27'	92.18(10)	C23–Co2–C23'	180.0
C23–Co2–C27	91.68(10)	C23–Co2–C27'	88.32(10)	C27–Co2–C27'	180.00(8)

## References

1. A. P. Forshaw, R. P. Bontchev and J. M. Smith, *Inorg. Chem.*, 2007, **46**, 3792-3794.
2. Rigaku. CrystalClear. Rigaku Corporation, Tokyo, Japan, 2008.
3. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *SIR92* - a program for automatic solution of crystal structures by direct methods. *J. Appl. Cryst.* **1994**, *27*, 435.
4. G. M. Sheldrick, A short history of SHELX. *Acta Cryst.* **2008**, *A64*, 112–122.
5. L. J. Farrugia, WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Cryst.* **1999**, *32*, 837–838.
6. L. J. Farrugia, WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **2012**, *45*, 849–854.