*Supplementary information for*

# $O_2$ activation and external substrate oxidation capability of Co(II)-semiquinonato complex

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## *Experimental details*

**Instruments**. IR measurements were carried out as KBr pellets using JASCO FT/IR-4200 spectrometer. IR spectra of the solution samples were recorded using a Mettler Toledo ReactIR iC10. $^1$H NMR spectra were recorded on JEOL JNM EX-270 spectrometer. Chemical shifts (δ) were reported in ppm downfield from internal $SiMe_4$. UV-vis spectra were recorded on JASCO V-670 spectrometer. Gas chromatographic (GC) analyses were carried out on Shimadzu GC-2010 instrument with a flame ionization detector equipped with RESTEK Rtx-1 or Rtx-1701 (30 m, 0.25 mmID, 0.25 μmdf) capillary columns. GC-MS analyses were carried out on Shimadzu PARVUM2 system equipped with RESTEK Rxi-5MS (30 m, 0.25 mmID, 0.25 μmdf) capillary column.

**Materials and Methods.** Organic solvents used in this study ($CH_2Cl_2$, MeCN, toluene) were purified by Glass Counter System. Other reagents of the highest grade

commercially available were used without further purification. All manipulations were performed under argon by standard Schlenk techniques.

**Synthesis and characterization of a cobalt(II)-DTBSQ complex with $Tp^{Me3}$ (1')**: A hydrotris(3,4,5-trimethylpyrazolyl)borate (= $Tp^{Me3}$) analogue of **1**, $[Co^{II}(DTBSQ)(Tp^{Me3})]$ (**1'**), was synthesized by the procedure similar to that for **1**, i.e., reaction of a hydroxo complex, $[(Co^{II}Tp^{Me3})_2(\mu\text{-}OH)_2]$ (**2'**),[1] with two equiv. of $DTBCH_2$ under $O_2$. Compound **1'** was alternatively synthesized by the reaction of a dinuclear cobalt(III)-bis(μ-oxo) complex, $[(Co^{III}Tp^{Me3})_2(\mu\text{-}O)_2]$ (**3'**),[1] with two equiv. of $DTBCH_2$ under argon (Scheme S1). Spectroscopic data of **1'**: IR (KBr, $\nu/cm^{-1}$); 2520 (BH). UV-vis ($CH_2Cl_2$, r.t., nm, $\varepsilon/M^{-1}cm^{-1}$); 304 (5530), 336 (sh, 4075), 376 (3640), 598 (343), 718 (326). FD-MS (m/z): 618 ($M^+$). $^1H$ NMR ($C_6D_6$, r.t.); $\delta_H$ –62.2 (9H), –3.2 (9H), 0.6 (9H), 5.6 (9H), 40.3 (9H) 71.5 (1H). Dark green crystals of the acetonitrile adduct of **1'** with substrate, **1'(MeCN)**·$DTBCH_2$, were obtained from an MeCN solution of the reaction mixture of **3'** with small excess (2.3 equiv.) $DTBCH_2$, and preliminary X-ray crystallographic analysis was performed. Diffraction measurement was made on a Rigaku AFC-7R automated four-circle diffractometer. A molybdenum X-ray source equipped with a graphite monochrometer (Mo Kα, λ = 0.71069 Å) was used. Data collection was carried out at room temperature (23°C). Crystallographic data and the result of refinement are summarized in Table S1. Structure analysis was performed by using Win-GX program package.[2] The structure of the complexes was solved by the direct methods using SIR-92 program.[3] The structure was refined on $F^2$ with full-matrix least-squares methods using SHELXL-97.[4,5] All non-hydrogen atoms except disordered carbon atoms of one of two *tert*-butyl groups on $DTBCH_2$ were refined anisotropically. All hydrogen atoms attached on non-disordered atoms were added in the riding model with C–H = 0.93 Å (for methyl groups) or 0.96 Å (for aromatic rings) with *U*iso(H) = 1.2*U*iso (attached atom). CCDC 760804 contains the supplementary crystallographic data of **1'(MeCN)**·$DTBCH_2$. The

data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Catalytic oxidation of $DTBCH_2$ by 1' with $O_2$**: In NMR sample tube, 7.0 mg (0.0113 mmol) of **1'** and 12.6 mg (0.0565 mmol; 5 equiv. of 1') of $DTBCH_2$ were dissolved in 0.7 mL of $C_6D_6$. Then $O_2$ gas was bubbled for 10 min and the resulting solution was stored at room temperature. The progress of reaction was monitored by $^1H$ NMR spectroscopy and added $DTBCH_2$ was oxidized to DTBQ completely after 48 h. The structure of **1'** was retained at the end of reaction.

***References for supporting information***

1 S. Hikichi, M. Yoshizawa, Y. Sasakura, H. Komatsuzaki, Y. Moro-oka and M. Akita, *Chem. Eur. J.*, 2001, **7**, 5011–5028.

2 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.

3 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435–436.

4 G. M. Sheldrick, SHELXS-86: program for crystal structure determination, University of Göttingen, Göttingen, Germany, 1986.

5 G. M. Sheldrick, *Acta. Crystallogr.*, 2008, **A64**, 112–122.

**Table S1.** Crystal Data and Data Collection Details of $[Co^{II}(DTBSQ)(Tp^{Me3})(MeCN)]\cdot DTBCH_2$ (**1'(MeCN)**·$DTBCH_2$)

| | |
|---|---|
| Formula | $C_{48}H_{76}N_7O_4BCo$ |
| Formula Weight | 884.92 |
| Space Group | Monoclinic |
| Crystal System | *P* 21/n (#14) |
| *a* / Å | 15.884 (4) |
| *b* / Å | 15.482 (4) |
| *c* / Å | 21.539 (6) |
| b / deg | 94.23 (2) |
| *V* / $Å^3$ | 5283 (2) |
| *Z* | 4 |
| D(calcd) / $g\cdot cm^{-1}$ | 1.112 |
| Data Collection Temp. / °C | 23 |
| Diffractometer | Rigaku AFC7R |
| Radiation | Graphite-monochromated Mo Kα (λ = 0.71069 Å) |
| μ(Mo Kα) / $cm^{-1}$ | 3.70 |
| 2θ range / deg | 6.0 – 50.0 |
| Scan type | ω – 2θ |
| No. of Measured Reflections | 7897 (Unique reflections; 7604) |
| Structure solution | Direct methods (SIR-92) |
| Refinement | Full-matrix least-squares (SHELXL-97) |
| No. of Observed Reflections | 4164 ($I > 2\sigma(I)$) |
| No. of Parameters Refined | 556 |
| R ($I > 2\sigma(I)$) | 0.0930 |
| R (for all data) | 0.1888 |
| wR ($I > 2\sigma(I)$) | 0.2733 |
| wR (for all data) | 0.3647 |
| GOF | 1.060 |

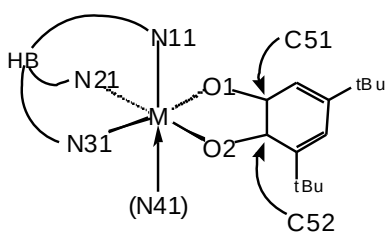
**Table S2.** Selected bond lengths (Å) and angles (°) of $[Co^{II}(DTBSQ)(Tp^{Me3})(MeCN)]\cdot DTBCH_2$ (**1'(MeCN)**·$DTBCH_2$) and the related dioxolene complexes with $Tp^R$

| $Tp^R$ : M | $Tp^{Me3}$ : $Co^{II}$ (**1'**) | $Tp^{iPr2}$ : $Mn^{II}$ (**5**) | $Tp^{iPr2}$ : $Fe^{III}$ (**4**) | $Tp^{tBu,iPr}$ : $Fe^{III}$ |
|---|---|---|---|---|
| dioxolene ligand | DTBSQ (–1) | DTBSQ (–1) | DTBC (–2) | DTBC (–2) |
| additional ligand | MeCN | MeCN | MeCN | — |
| coord. number | 6 | 6 | 6 | 5 |
| Geometry of M | *oh* | *oh* | *oh* | *tbp* |
| Reference (in main text) | This work | 15 | 14 | 14 |
| Bond Lengths (Å) | | | | |
| M-O1 | 2.093(6) [a] | 2.1113(19) | 1.929(3) | 1.94(1) |
| M-O2 | 2.091(6) [a] | 2.1739(16) | 1.969(3) | 1.93(1) |
| M-N11 | 2.140(8) | 2.239(2) | 2.143(4) | 2.20(1) |
| M-N21 | 2.121(8) | 2.2229(19) | 2.163(4) | 2.086(9) |
| M-N31 | 2.118(7) | 2.234(2) | 2.174(4) | 2.086(9) |
| M-N41 | 2.236(10) | 2.420(2) | 2.326(5) | — |
| O1-C51 | 1.298(11) [a] [1.370(13)] [b] | 1.287(3) | 1.334(5) | 1.35(2) |
| O2-C52 | 1.266(11) [a] [1.366(12)] [b] | 1.283(3) | 1.340(5) | 1.38(2) |
| C51-C52 | 1.440(14) [1.376(15)] [b] | 1.471(3) | 1.418(7) | 1.39(2) |
| C52-C53 | 1.462(13) [1.409(14)] [b] | 1.440(3) | 1.405(6) | 1.43(2) |
| C53-C54 | 1.377(14) [1.400(13)] [b] | 1.380(4) | 1.395(6) | 1.40(2) |
| C54-C55 | 1.404(15) [1.390(13)] [b] | 1.437(4) | 1.382(7) | 1.33(2) |
| C55-C56 | 1.378(13) [1.420(14)] [b] | 1.379(4) | 1.379(7) | 1.37(2) |
| C56-C51 | 1.406(13) [1.406(15)] [b] | 1.416(4) | 1.396(6) | 1.40(2) |
| Bond Angles (°) | | | | |
| O1-M-O2 | 77.7(3) [a] | 76.01(6) | 82.5(1) | 83.8(5) |
| O1-M-N11 | 95.2(3) [a] | 103.05(8) | 100.7(2) | 177.0(5) |
| O1-M-N21 | 96.9(3) [a] | 102.43(7) | 96.0(1) | 91.2(3) |
| O1-M-N31 | 173.7(3) [a] | 169.21(7) | 173.2(2) | 91.2(3) |

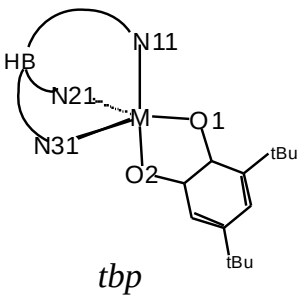
| | | | | |
|---|---|---|---|---|
| O1-M-N41 | 88.2(3) [a] | 85.46(8) | 86.8(2) | — |
| O2-M-N11 | 97.2(3) [a] | 98.82(7) | 98.6(1) | 99.2(5) |
| O2-M-N21 | 173.7(3) [a] | 175.20(8) | 174.7(2) | 130.2(3) |
| O2-M-N31 | 96.8(3) [a] | 94.75(7) | 94.0(1) | 130.2(3) |
| O2-M-N41 | 88.4(3) [a] | 84.01(7) | 85.4(1) | — |
| N11-M-N21 | 86.4(3) | 85.94(7) | 86.7(2) | 86.9(3) |
| N11-M-N31 | 88.5(3) | 83.66(8) | 85.5(2) | 86.9(3) |
| N11-M-N41 | 174.0(3) | 171.44(8) | 171.9(2) | — |
| N21-M-N31 | 88.4(3) | 86.33(7) | 87.0(2) | 99.4(5) |
| N21-M-N41 | 88.2(4) | 91.35(8) | 89.5(2) | — |
| N31-M-N41 | 88.6(3) | 88.07(8) | 87.2(2) | — |
| M-O1-C51 | 112.9(6) [a] | 115.88(16) | 113.9(3) | 111(1) |
| M-O2-C52 | 113.8(6) [a] | 113.88(15) | 112.5(3) | 113(1) |
| C51-C52-C53 | 117.3(9) [120.8(9)] [b] | 118.5(2) | 119.7(5) | 123(2) |
| C52-C53-C54 | 117.3(10) [117.7(9)] [b] | 118.1(2) | 116.7(5) | 113(2) |
| C53-C54-C55 | 124.9(9) [123.3(9)] [b] | 123.5(2) | 124.3(5) | 127(2) |
| C54-C55-C56 | 118.3(9) [117.4(9)] [b] | 119.4(3) | 118.8(5) | 118(2) |
| C55-C56-C51 | 120.5(10) [119.8(10)] [b] | 119.9(3) | 119.5(5) | 121(2) |
| C56-C51-C52 | 121.4(9) [120.7(10)] [b] | 120.5(2) | 121.0(5) | 118(2) |

[a] The oxygen atoms of the DTBSQ ligand of **1'(MeCN)** (i.e. "O1" and "O2") are mentioned as "O51" and "O52" in the corresponding CIF file (CCDC 760804) as well as Fig.S2.

[b] Parameters of the non-coordinated $DTBCH_2$ in the crystal of **1'(MeCN)**·$DTBCH_2$




*oh* (*sp*)

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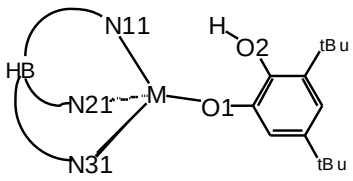


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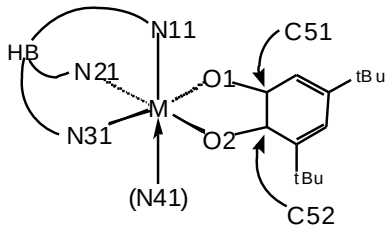
**Table S2.** (continued)

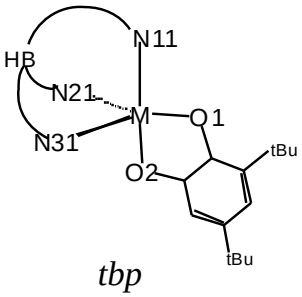
| $Tp^{R}$ : M | $Tp^{tBu,iPr}$ : $Fe^{II}$ | $Tp^{Cum,Me}$ : $Co^{II}$ *c* | $Tp^{Cum,Me}$ : $Co^{II}$ *d* | $Tp^{Cum,Me}$ : $Co^{II}$ |
|---|---|---|---|---|
| dioxolene ligand | DTBCH (–1) | DTBSQ (–1) | DTBSQ (–1) | DTBSQ (–1) |
| additional ligand | — | — | — | — |
| coord. number | 4 | 5 | 5 | 5 |
| geometry of M | *td* | *tbp* | *tbp* | *spy* |
| Reference (in main text) | 14 | 10 | 10 | 10 |
| Bond Lengths (Å) | | | | |
| M-O1 | 1.876(7) | 1.952(3) | 1.970(3) | 1.952(3) |
| M-O2 | — | 2.060(3) | 2.045(2) | 1.971(3) |
| M-N11 | 2.15(1) | 2.198(3) | 2.144(3) | 2.239(4) |
| M-N21 | 2.084(9) | 2.027(3) | 2.038(3) | 1.993(4) |
| M-N31 | 2.118(8) | 2.033(3) | 2.052(3) | 1.982(4) |
| M-N41 | — | — | — | — |
| O1-C51 | 1.35(1) | 1.305(5) | 1.298(4) | 1.279(5) |
| O2-C52 | 1.36(1) | 1.269(4) | 1.274(4) | 1.265(6) |
| C51-C52 | 1.45(1) | 1.471(5) | 1.451(5) | 1.457(7) |
| C52-C53 | 1.39(1) | 1.446(5) | 1.441(5) | 1.409(7) |
| C53-C54 | 1.43(2) | 1.361(5) | 1.356(5) | 1.368(8) |
| C54-C55 | 1.40(2) | 1.449(5) | 1.432(6) | 1.434(8) |
| C55-C56 | 1.40(1) | 1.370(6) | 1.385(5) | 1.346(7) |
| C56-C51 | 1.37(1) | 1.388(5) | 1.404(5) | 1.437(7) |
| Bond Angles (°) | | | | |
| O1-M-O2 | — | 80.94(10) | 80.78(10) | 82.70(14) |
| O1-M-N11 | 116.6(4) | 93.18(11) | 95.31(11) | 115.10(14) |
| O1-M-N21 | 135.2(4) | 137.22(11) | 124.18(11) | 95.63(15) |
| O1-M-N31 | 118.5(3) | 127.49(12) | 141.31(12) | 151.59(15) |
| O1-M-N41 | — | — | — | — |
| O2-M-N11 | — | 173.88(10) | 172.69(11) | 92.37(14) |
| O2-M-N21 | — | 97.44(12) | 97.95(11) | 176.93(15) |
| O2-M-N31 | — | 98.68(12) | 95.24(11) | 93.49(15) |
| O2-M-N41 | — | — | — | — |
| N11-M-N21 | 96.1(3) | 85.72(12) | 89.36(12) | 90.68(15) |
| N11-M-N31 | 91.0(4) | 86.20(12) | 83.94(12) | 93.23(15) |
| N11-M-N41 | — | — | — | — |
| N21-M-N31 | 88.5(4) | 95.16(12) | 94.51(12) | 86.80(15) |

| | | | | |
|---|---|---|---|---|
| N21-M-N41 | — | — | — | — |
| N31-M-N41 | — | — | — | — |
| M-O1-C51 | 142.1(7) | 114.6(2) | 113.4(2) | 111.7(3) |
| M-O2-C52 | — | 112.1(2) | 112.2(2) | 112.1(3) |
| C51-C52-C53 | 120(1) | 117.9(3) | 119.4(3) | 119.2(5) |
| C52-C53-C54 | 117(1) | 116.9(3) | 116.7(4) | 116.9(5) |
| C53-C54-C55 | 123(1) | 125.1(4) | 125.1(3) | 124.2(5) |
| C54-C55-C56 | 118(1) | 118.3(4) | 118.7(4) | 118.8(5) |
| C55-C56-C51 | 122(1) | 119.9(4) | 119.3(4) | 121.3(5) |
| C56-C51-C52 | 120(1) | 121.8(4) | 120.9(3) | 119.4(5) |

[c, d] Two crystallographically independent molecules of [$Co^{II}$(DTBSQ)($Tp^{Cum,Me}$)] (adopted from the CIF files of the supporting information of ref. 10)




*oh* (*sp*)

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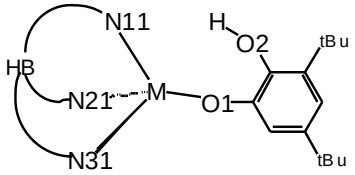


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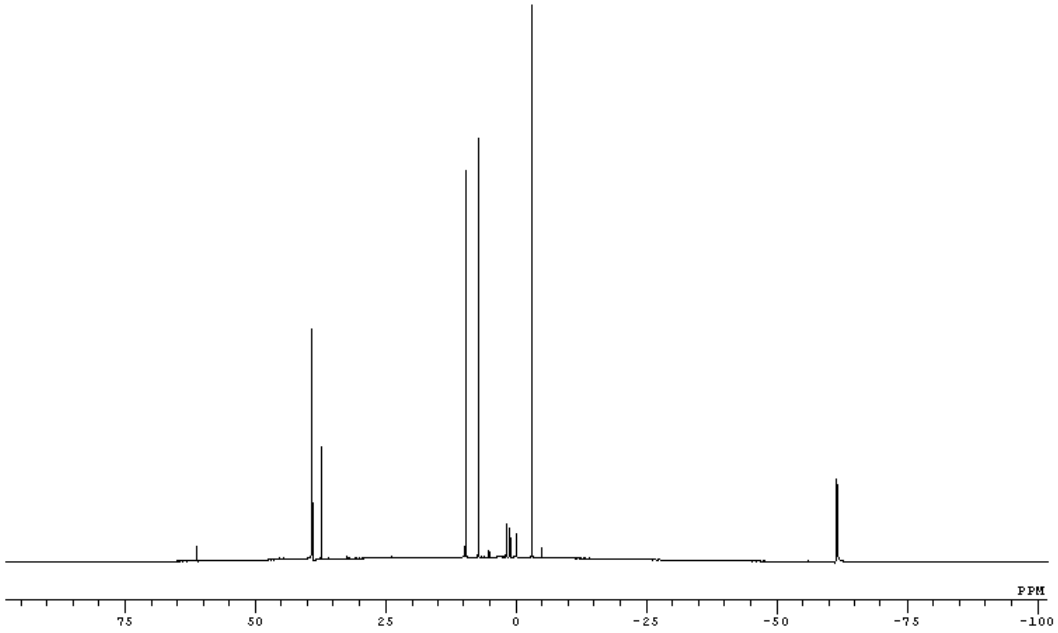



**Fig. S1** $^{1}$H NMR spectrum of **1** (in $CDCl_3$, at room temperature).

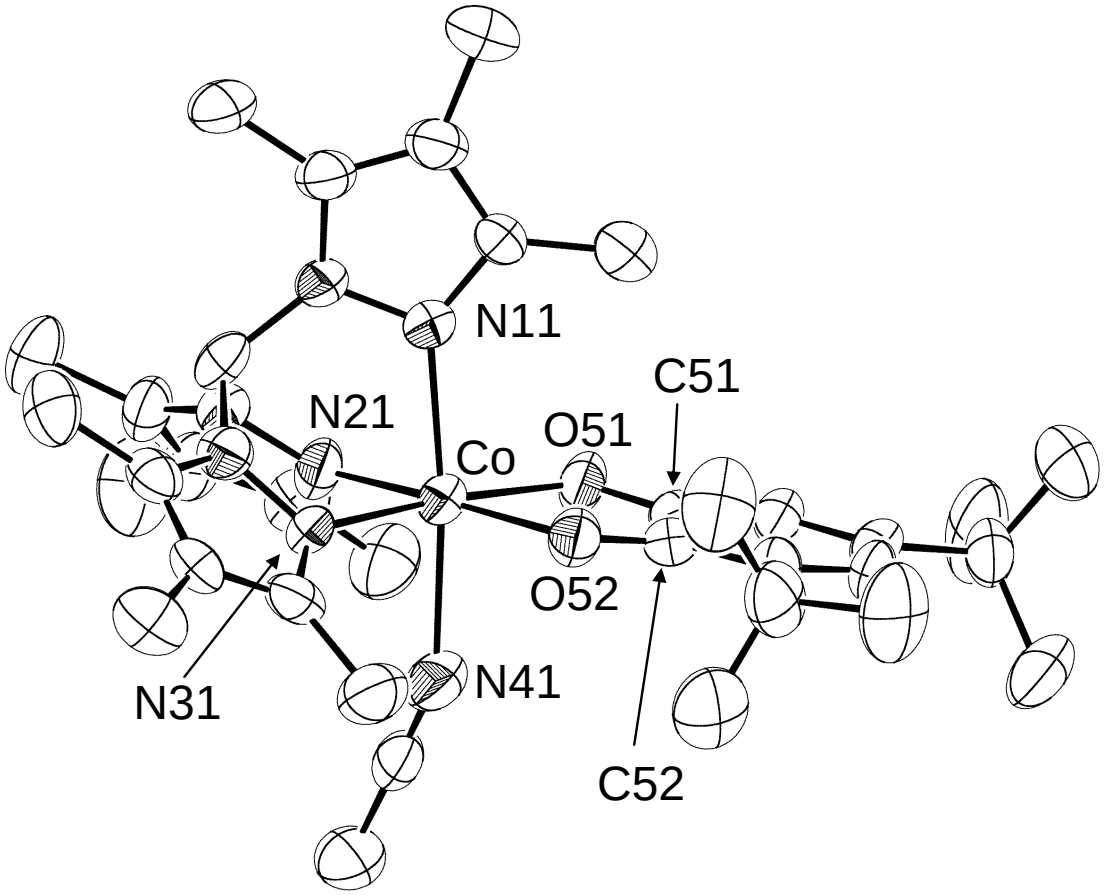



**Fig. S2** Perspective view of [$Co^{II}$(DTBSQ)($Tp^{Me3}$)(MeCN)] (**1'(MeCN)**) showing 50% thermal ellipsoids. The oxygen atoms O51 and O52 correspond to O1 and O2, respectively, in Table S2.

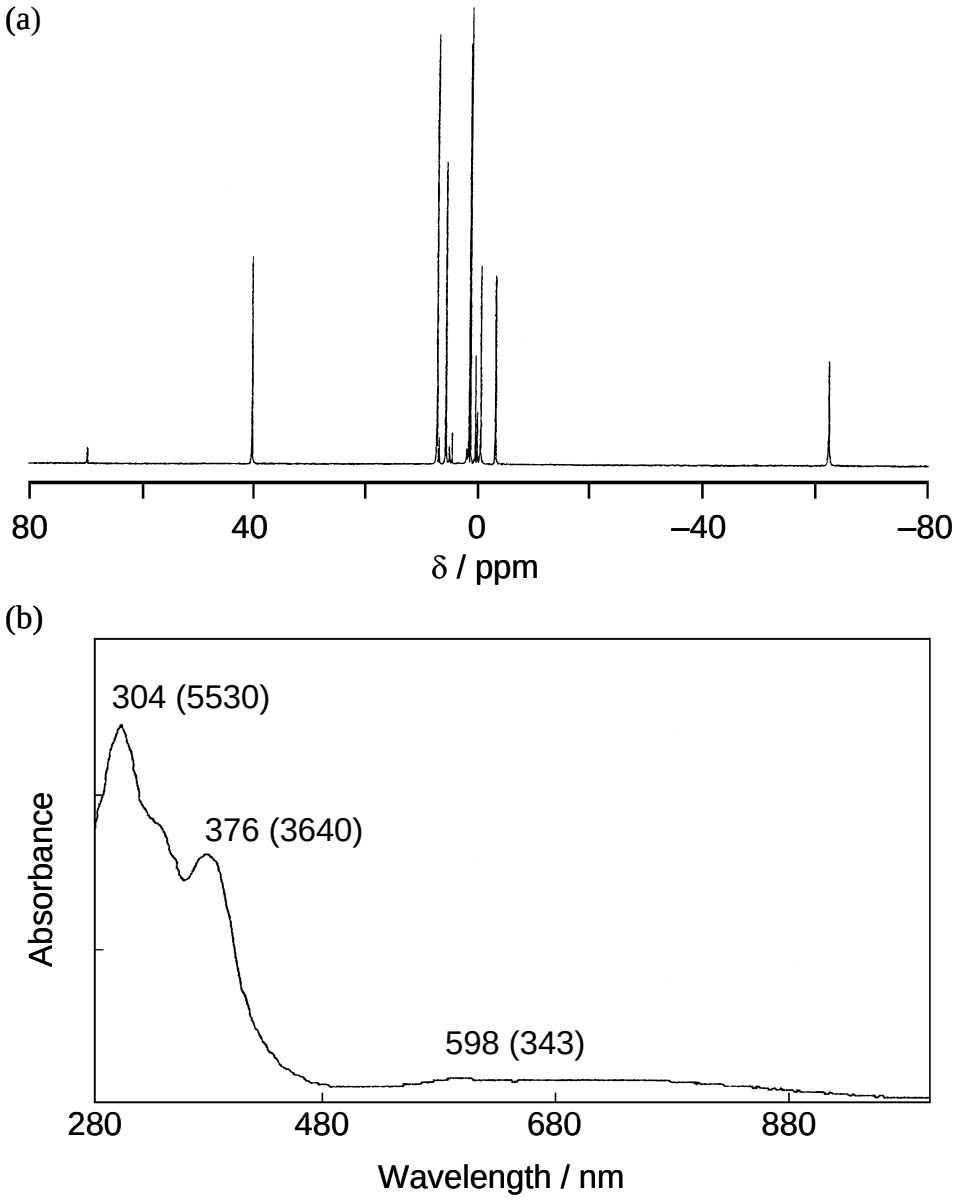



**Fig. S3** $^{1}$H NMR and UV-vis spectra of **1'**. (a) $^{1}$H NMR spectrum (in $C_6D_6$, at room temperature). (b) UV-vis spectrum (in $CH_2Cl_2$, at room temperature, under Ar).

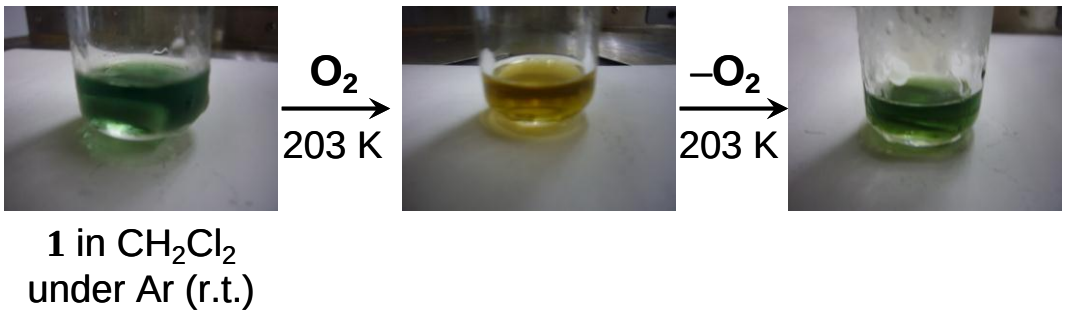



**Fig. S4** Change of the solution colors of **1** by introduction of $O_2$ and following purged solution at low temperature.

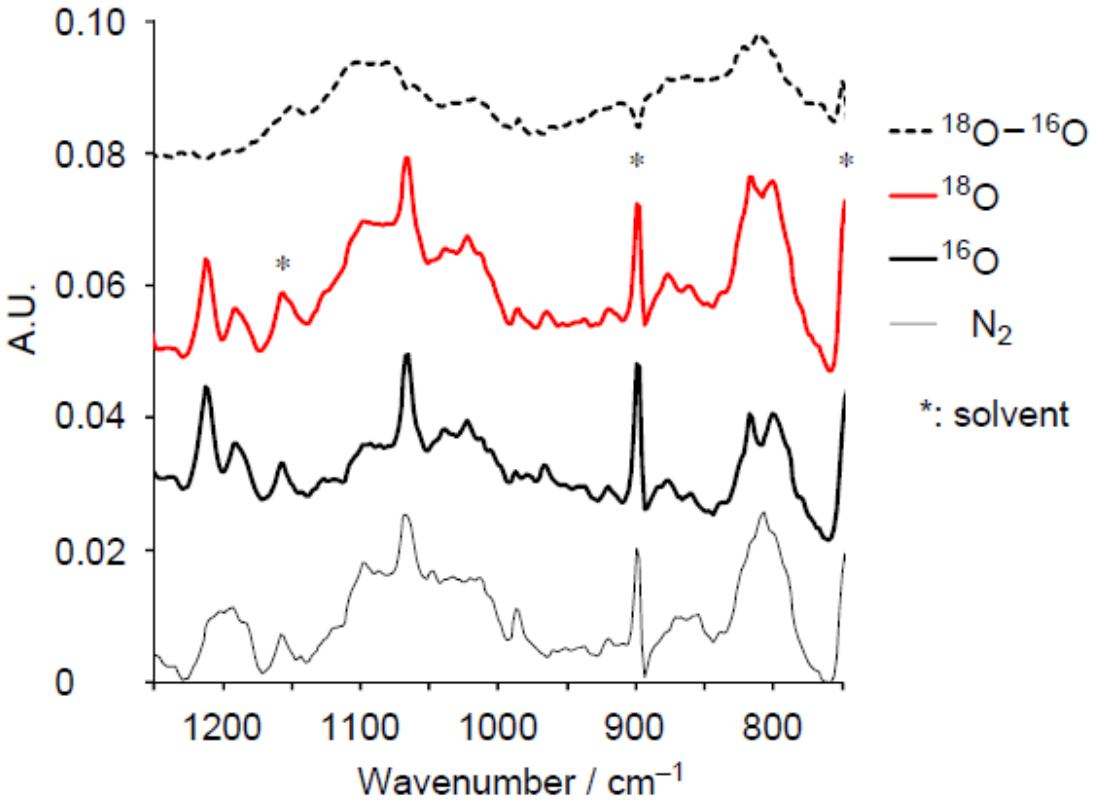



**Fig. S5** IR spectra of the $CH_2Cl_2$ solution of **1** (recorded under Ar) and *in situ* generated **1**•$O_2$ (recorded under $^{16}O_2$ or $^{18}O_2$ atmosphere) at 198 K. Differential spectrum of **1**•$O_2$ which were prepared under $^{18}O_2$ and $^{16}O_2$ is also presented as dashed line.

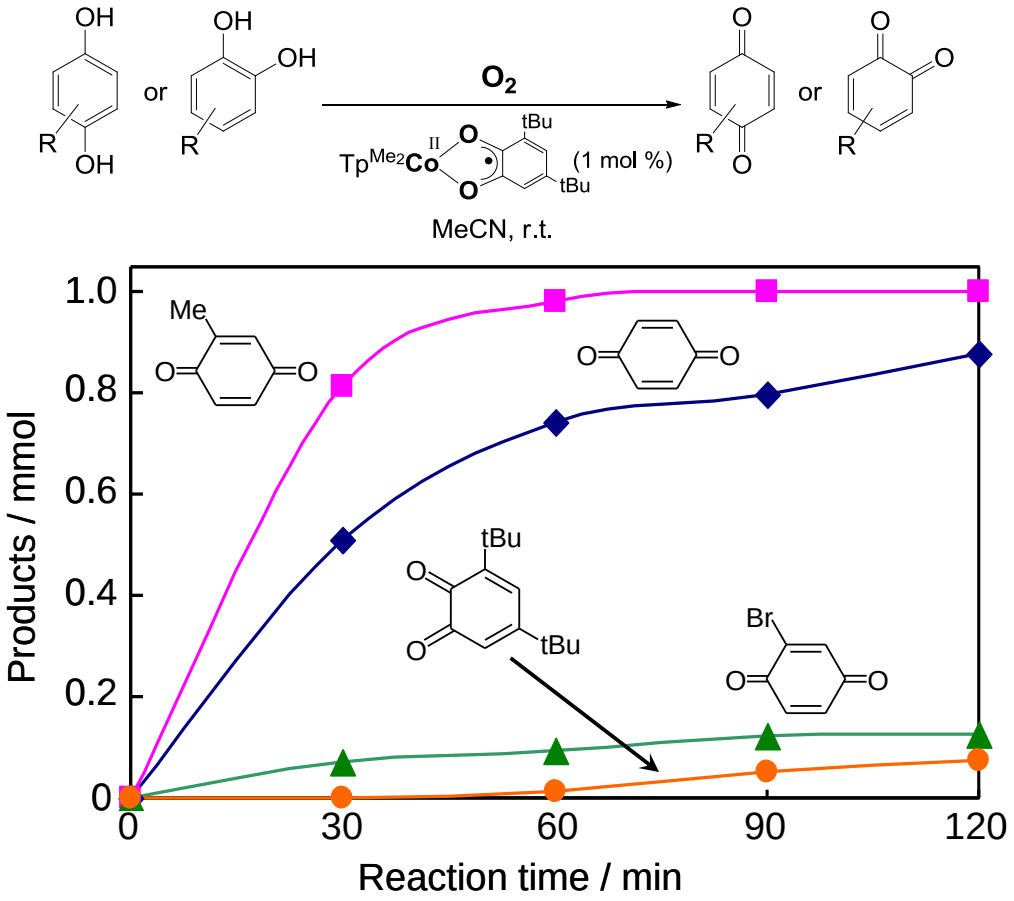
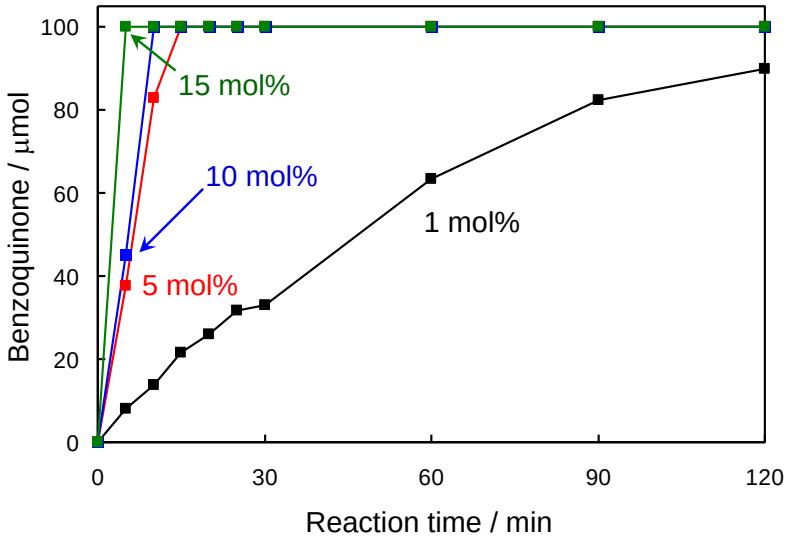



**Fig. S6** $O_2$ oxidation of *para*- and *ortho*-hydroquinones mediated by **1**. Reaction conditions: Catalyst (**1**), 10 μmol; substrate, 1.0 mmol; $O_2$, 1 atm; solvent (MeCN), 4.0 mL, Reaction temperature, 315 K.

(a)




(b)

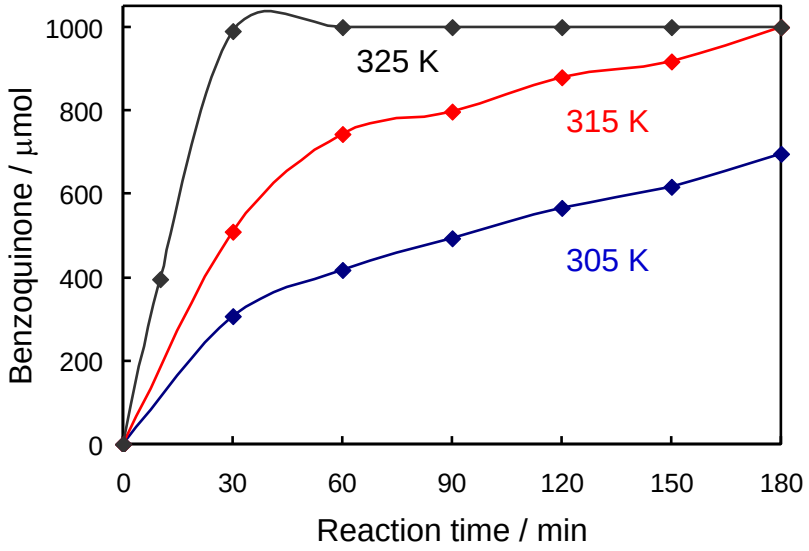



**Fig. S7** $O_2$ oxidation of *para*-hydroquinone mediated by **1**. (a) Effect of catalyst ratio. Reaction conditions: Catalyst (**1**), 10 μmol; substrate, 100 μmol; $O_2$, 1 atm; solvent (1:1 mixture of $CH_2Cl_2$ and MeCN), 4.0 mL, Reaction temperature, 335 K. (b) Effect of temperature. Reaction conditions: Catalyst (**1**), 10 μmol; substrate, 1.0 mmol ; $O_2$, 1 atm; solvent (MeCN), 4.0 mL.

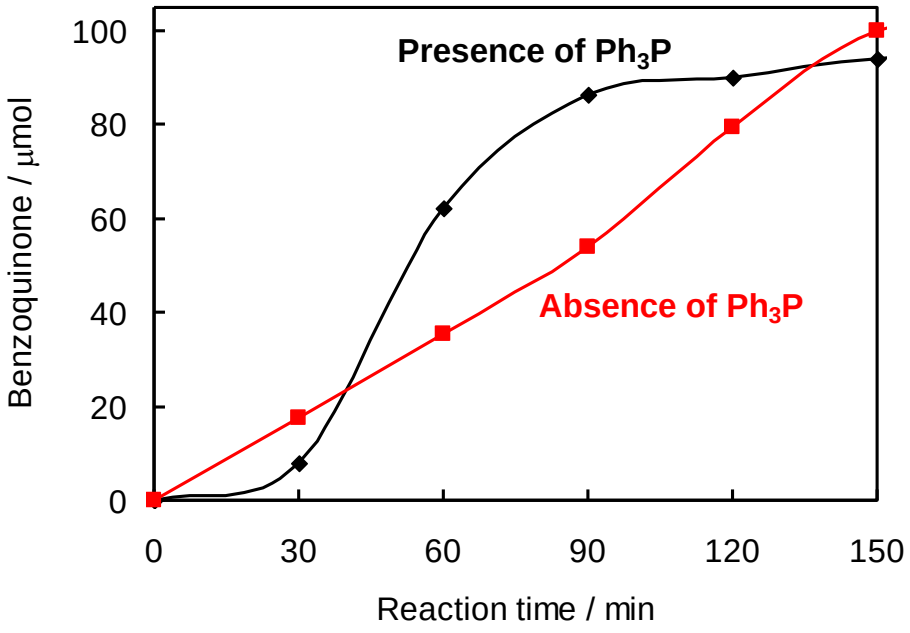



**Fig. S8** Effect of $Ph_3P$ additive for the oxidation of *para*-hydroquinone mediated by **1**. Reaction conditions: Catalyst (**1**), 10 μmol; substrates, 100 μmol; $O_2$, 1 atm; solvent (1:1 mixture of $CH_2Cl_2$ and MeCN), 4.0 mL, Reaction temperature, 305 K.

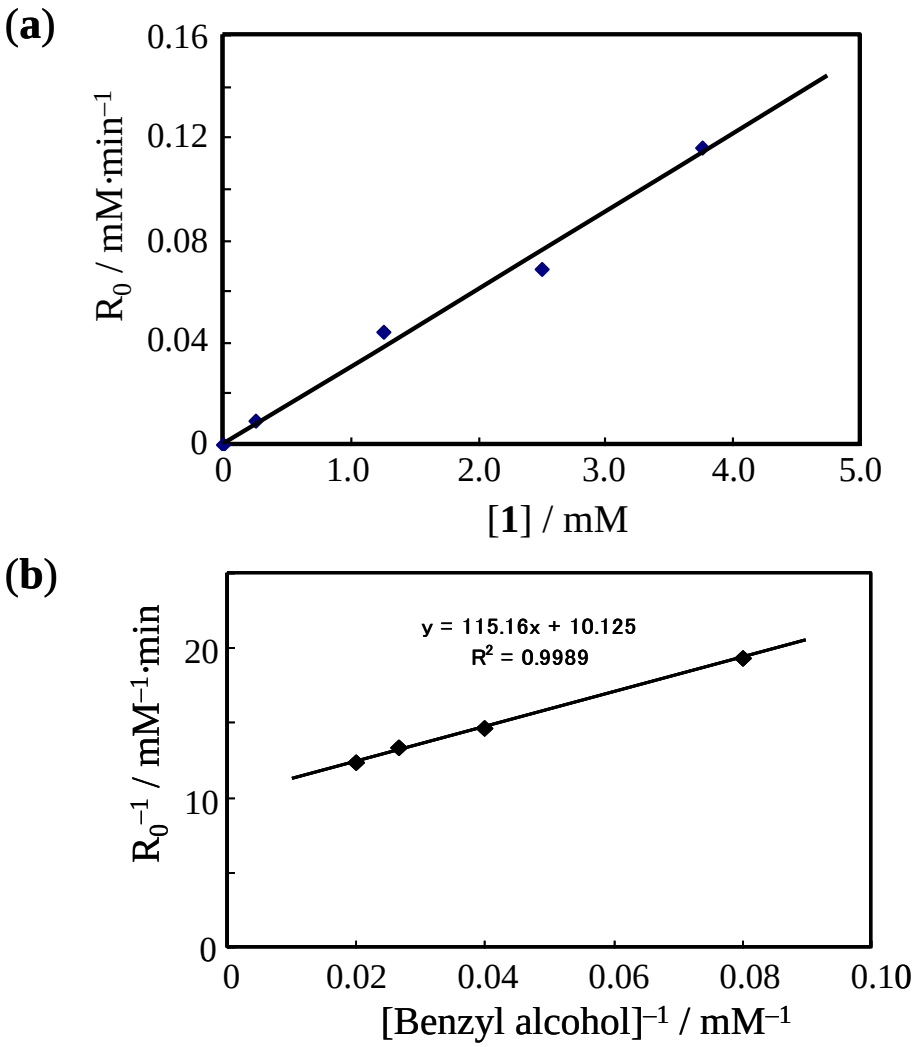



**Fig. S9** Kinetic analyses of aerobic oxidation of benzyl alcohol mediated by **1**. (a) Initial reaction rate ($R_0$) versus concentration of **1**. (b) Lineweaver-Burk plot. Reaction conditions: $O_2$, 1 atm; solvent (MeCN), 4.0 mL, Reaction temperature, 335 K.

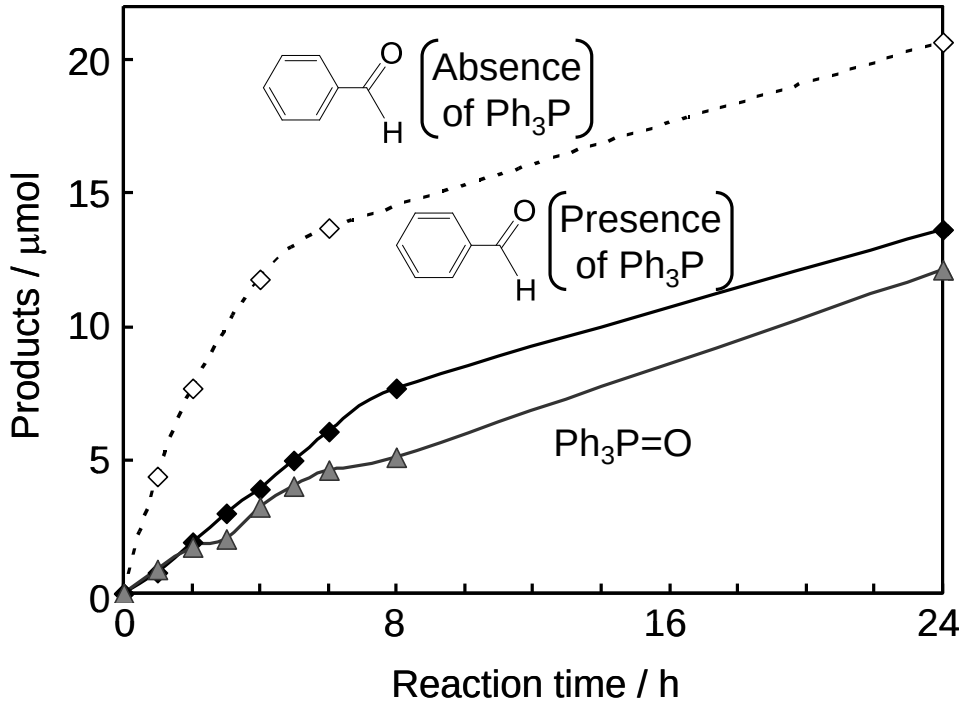



**Fig. S10** Effect of $Ph_3P$ additive for the oxidation of benzylalcohol mediated by **1**. (dashed line) Benzaldehyde derived from the benzylalcohol oxidation in the absence of $Ph_3P$. (solid lines) Products derived from the co-oxidation of benzylalcohol and $Ph_3P$. Reaction conditions: Catalyst (**1**), 10 μmol; substrates, 100 μmol; $O_2$, 1 atm; solvent (1:1 mixture of $CH_2Cl_2$ and MeCN), 4.0 mL, Reaction temperature, 305 K.