Rhenium complex with non-innocent dioxolene ligand: combined experimental and ab initio study of [(3,5-*tert*-Bu$_2$C$_6$H$_2$O$_2$)ReCl$_3$(OPPh$_3$)]

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1. Results of the CASSCF(4,6)/ANO-RCC-VDZ and SOC-CASSCF(4,6)/ANO-RCC-VDZ calculations for the room temperature XRD structure of complex 1

At first, we performed CASSCF calculations with minimal active space consisting of 4 electrons and 6 molecular orbitals composed by five rhenium 5d-orbitals and LUMO of o-quinone ligand (Fig. S1). The room temperature XRD structure of complex **1** (Fig. S3) was used in the calculations. One of the d orbitals interacts with the ligand LUMO yielding bonding and untibonding (π and π^*) MOs (Fig. S1). The contribution of the LUMO to other MOs is minor.

According to the state specific CASSCF(4,6)/ANO-RCC-VDZ calculations, the triplet state is a ground state of **1**. The quintet state is a first excited state being 0.38 eV (3060 cm^{-1}) higher in energy. The second excited state is a singlet state with the energy 1.36 eV (10940 cm^{-1}) relative to the ground state.

The quintet state wavefunction consists almost exclusively of one configuration with bonding and untibonding (π and π^*) MOs and two d-orbitals (Fig. S2b) each occupied by one electron. In the framework of localized orbitals, this is equivalent to three unpaired electrons on rhenium cation (R^{IV}) and one on the ligand (QS). The Mulliken spin densities are equal to 2.735 and 1.065 for rhenium and dioxolene ligand, respectively (Fig. S2) In turn, Mulliken charges are equal to q_{Re} = 1.12 and q_{lig} = -0.21. More balanced LoProp population analysis [L. Gagliardi, R. Lindh, G. Karlstrom, J. Chem. Phys. 2004, 121, 4494] leads to q_{Re} = 1.79 and q_{lig} = -0.37.

The ground triplet state has more complicated wavefunction: the main configuration corresponds to doubly occupied π MO and two singly occupied d-orbitals; the next configuration corresponds to doubly occupied π^* and singly occupied d-orbitals. There is also a contribution of configurations with singly occupied π, π^* and two d-orbitals with three α spins and one β spin. In the ground state, the Mulliken spin densities are equal to 2.22 and -0.37 for rhenium and dioxolene ligand, respectively (Fig. S5). Mulliken charges are equal to q_{Re} = 1.12 and q_{lig} = -0.22. The LoProp population analysis [L. Gagliardi, R. Lindh, G. Karlstrom, J. Chem. Phys. 2004, 121, 4494] predicts q_{Re} = 1.78 and q_{lig} = -0.38, the values similar to those of quintet state.

To estimate zero-field splitting (ZFS) of the ground triplet state, we employed state averaged CASSCF(4,6)/ANO-RCC-VDZ procedure followed by SO-RASSI/SINGLE-ANISO calculations; 15 quintet, 105 triplet and 105 singlet states were involved in these calculations. As in the state specific calculations, the triplet state was found to be the ground state and quintet

state is a first excited state. Account of the SO (spin-orbit) coupling leads to the splitting of the ground triplet state into three components with the energy of 0, 304 and 351 cm^{-1}. Note, that splitting of the first quintet state is much smaller (0, 4, 81, 124, 140 cm^{-1}). The ZFS parameters for the ground state with the pseudo-spin S = 1 were extracted using SINGLE-ANIZO module of the MOLCAS 7.6 program package [F. Aquilante, L. De Vico, N. Ferre, G. Ghigo, P.-A. Malmqvist, P. Neogrady, T.B. Pedersen, M. Pitoňak, M. Reiher, B.O. Roos, L. Serrano-Andres, M. Urban, V. Veryazov, R. Lindh, J. Comput. Chem., 2010, 31, 224-247] and were found to be D = 327 cm^{-1} and E/D = 0.07.
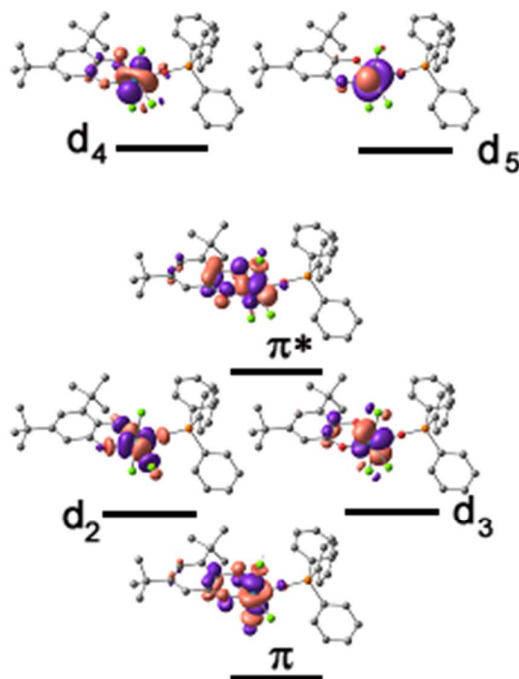
Figures S1. Molecular orbitals involved in the active space for the CASSCF(4,6)/ANO-RCC-VDZ calculations. Geometry corresponds to the XRD structure of rhenium complex **1** at room temperature.

Ground state, S = 1   First excited state, S = 2

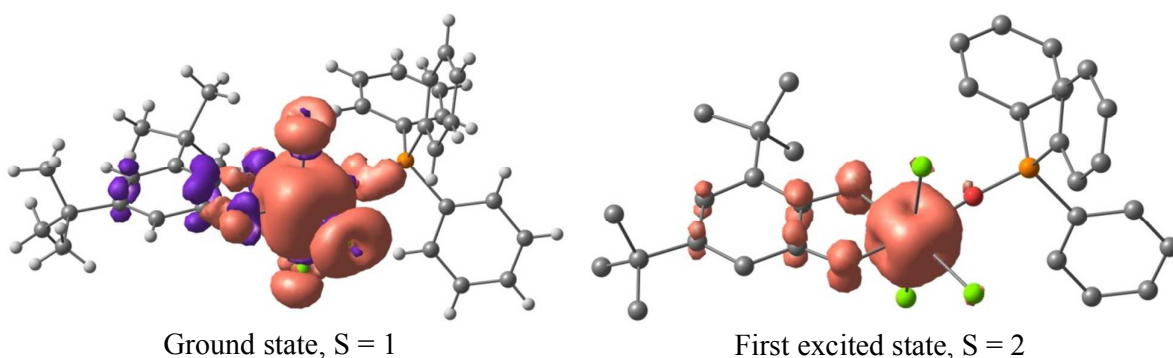**Figure S2.** Spin distribution in the ground triplet state (Mulliken spin densities: ρ_{Re} = 2.22, ρ_{SQ} = -0.37) and first excited quintet state (Malliken spin density: ρ_{Re} = 2.74, ρ_{SQ} = 1.07).

2. Results of representative CASSCF(6,9)/NEVPT2/TZV-DKH2 and SOC-CASSCF(6,9)/NEVPT2/TZV-DKH2 calculations for the reduced structure of complex 1 with phenyl groups replaced by methyl ones and tr-Bu groups replaced by hydrogen atoms.
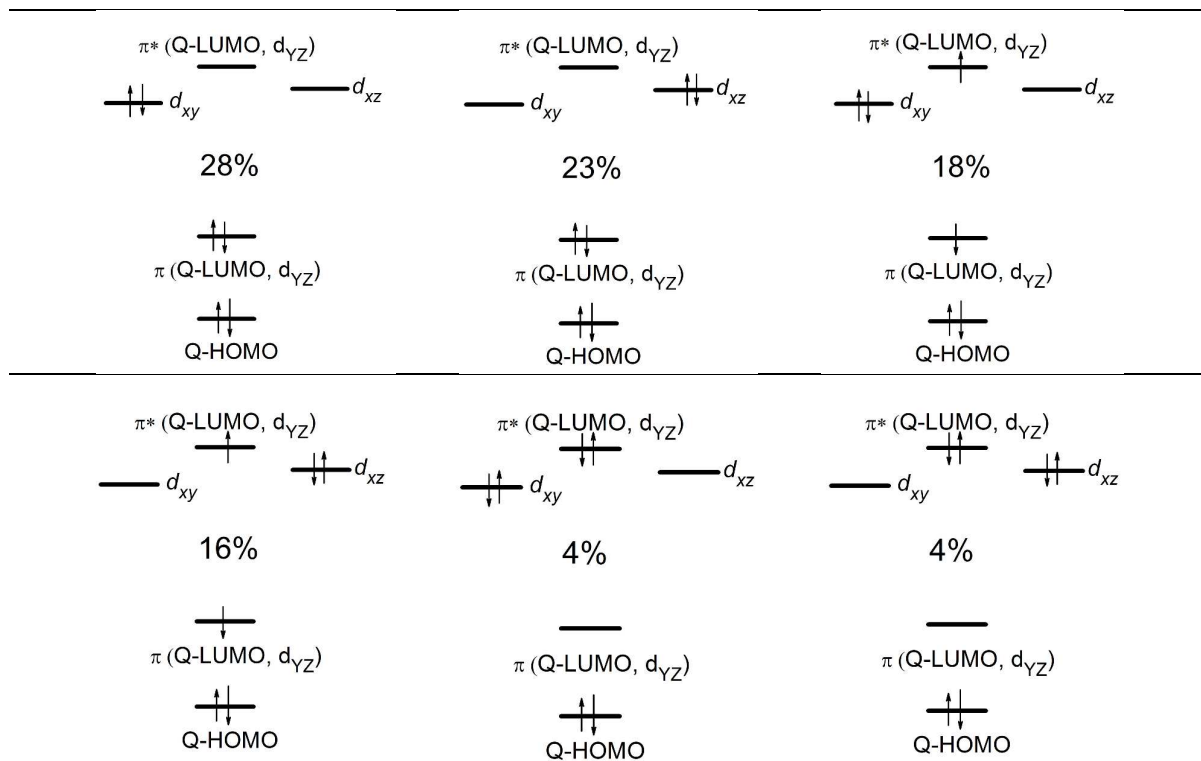

Figure S3. Occupations of the active orbitals in the configurations contributing mainly to wavefunction of the lowest excited singlet state.
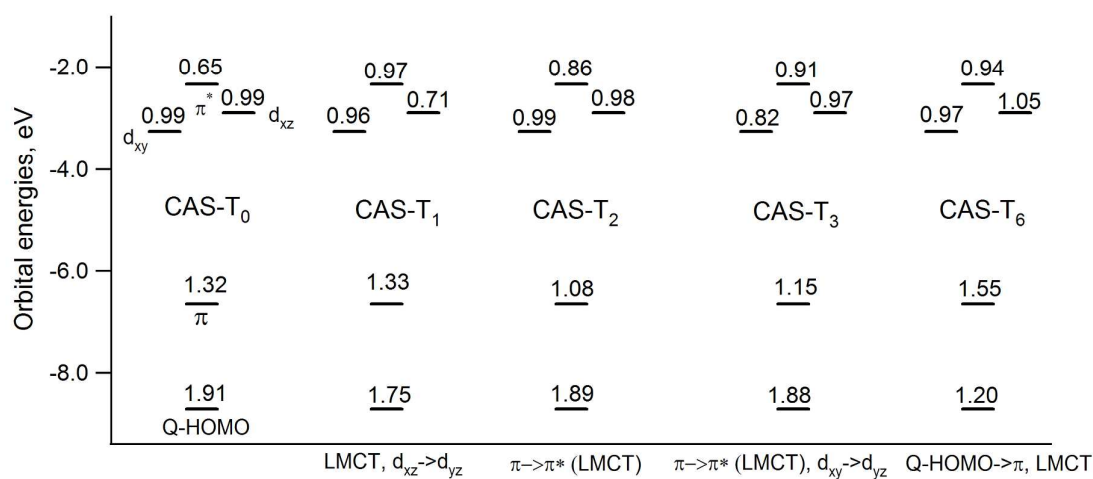

Figure S4. Occupation numbers of the active orbitals for the ground and excited triplet states calculated at the CASSSF(6,9)/def2- TZVP-DKH2 level.

Table S1. Results of CASSCF(6,9)/NEVPT2 calculations for modified complex **1** (with phenyl groups replaced by methyl ones and tr-Bu groups replaced by hydrogen): energies of spin multiplets, E; occupation of active orbitals for most important configurations and their contributions; contribution of different spin states to the calculated value of D parameter for ground state with pseudo-spin 1; the wavelengths (λ) and oscillator strengths (f) for the electronic transitions in the electronic absorption spectrum of modified complex **1**, calculated at NEVPT2 level without account of SO coupling.

#	2S +1	E, cm^{-1}	Contrib. to D, cm^{-1}	f	λ, nm	% cont.	HOMO	π: LUMO, d_{yz}	d_{xy}	d_{xz}	π^*: LUMO, d_{yz}	d_{z2}	d_{x2-y2}
0	3	0	0			46	2	1	1	1	1		
						40	2	2	1	1	0		
0	5	5746	0			93	2	1	1	1	1		
0	1	8403	2			28	2	2	2	0	0		
						23	2	2	0	2	0		
						18	2	1	2	0	1		
						16	2	1	0	2	1		
1	1	8749	0			51	2	2	1	1	0		
						33	2	1	1	1	1		
1	3	12208	3	0.0010	819	28	2	2	1	0	1		
						25	2	1	1	2	0		
						23	2	1	1	0	2		
3	3	14087	5	0.0001	710	34	2	1	2	1	0		
						29	2	1	0	1	2		
						20	2	2	0	1	1		
2	3	14143	-5	0.0016	707	75	2	1	1	1	1		
5	1	14483	677			26	2	2	0	2	0		
						24	2	2	2	0	0		
						18	2	1	0	2	1		
						14	2	1	2	0	1		
2	1	14495	2										
3	1	16236	0										
4	1	16570	-1										
4	3	16886	0	0.0000	592								
5	3	17014	0	0.0001	588								
6	3	17270	1	0.0060	579	61	1	2	1	1	1		
						14	2	1	1	2	0		
1	5	17274	0										
8	3	18934	45	0.0000	528	47	2	1	2	1	0		
						20	2	2	0	1	1		
						17	2	1	0	1	2		
7	3	19072	50	0.0005	524	45	2	1	1	2	0		
						20	2	1	1	0	2		
						16	2	2	1	0	1		
6	1	19493	-143			46	2	1	1	2	0		

						20	2	1	1	0	2		
						18	2	2	1	0	1		
7	1	21361	-99			44	2	1	2	1	0		
						25	2	1	0	1	2		
						17	2	2	0	1	1		
9	3	23278	-54	0.0000	430	46	2	1	0	2	1		
						43	2	1	2	0	1		
10	3	26779	0	0.0012	373								
8	1	27012	-5										
9	1	27305	0										
11	3	27780	0	0.0000	360								
11	1	27907	3										
13	3	27970	1	0.0006	358	74	1	2	1	1	1		
12	3	28060	0	0.0001	356								
10	1	28261	1										
12	1	28710	1										
14	3	28828	0	0.0000	347								
17	3	32622	1	0.0000	307								
18	3	33132	1	0.0032	302	56	1	2	1	0	2		
14	1	33279	1										
13	1	33899	0										
15	3	33920	-161	0.0000	295	42	2	1	1	0	1	1	0
						38	2	2	1	0	0	1	0
15	1	34346	0										
20	3	35493	0	0.0000	282								
16	1	35750	0										
21	3	36188	0	0.0000	276								
19	3	37088	101	0.0003	270	45	2	1	0	1	1	0	1
						39	2	2	0	1	0	0	1
2	5	37191	0										
16	3	37548	63	0.0004	266	74	2	1	1	1	0	1	0
4	5	37723	0										
3	5	39426	0										
17	1	41468	95			42	2	2	1	0	0	1	0
						35	2	1	1	0	1	1	0
22	1	43770	-9										
20	1	44554	-3										
123	1	45500	-40			23	2	2	0	1	0	0	1
						18	2	1	0	1	1	0	1
19	1	46069	-58			73	2	1	1	1	0	1	0
21	1	46094	-12										
18	1	46176	-9										
24	1	48856	1										

Table S2. Composition of the wavefunctions corresponding to the lowest states arising from the ground triplet multiplet due to account of SOC.

	Weight	Real	Image	: Block	Root	Spin	Ms
STATE 0:	0.0000						
	0.471839	-0.465067	-0.505522 :	1	0	1	1
	0.471839	-0.465067	0.505522 :	1	0	1	-1
	0.028614	0.169156	0.000000 :	2	5	0	0
STATE 1:	334.1279 cm^{-1}						
	0.059803	-0.198655	0.142615 :	1	0	1	1
	0.844780	-0.000000	0.919119 :	1	0	1	0
	0.059803	-0.198655	-0.142615 :	1	0	1	-1
	0.011767	0.108476	0.000000 :	2	6	0	0
STATE 2:	347.3525 cm^{-1}						
	0.424209	-0.471654	0.449168 :	1	0	1	1
	0.117479	-0.000000	-0.342753 :	1	0	1	0
	0.424209	-0.471654	-0.449168 :	1	0	1	-1

Table S3. X-ray experimental details.

For all structures: $C_{32}H_{35}Cl_3O_3PRe$, M_r = 791.12, orthorhombic, $P2_12_12_1$, Z = 4. Experiments were carried out with Mo $K\alpha$ radiation. Absorption was corrected for by multi-scan methods, *SADABS* (Bruker-AXS, 2004). Refinement was on 358 parameters. H-atom parameters were constrained.

Crystal data		
Temperature (K)	150	296
a, b, c (Å)	9.5060 (3), 17.3013 (7), 19.4327 (7)	9.5060 (3), 17.3013 (7), 19.4327 (7)
V (Å^3)	3196.0 (2)	3196.0 (2)
μ (mm^{-1})	4.13	4.13
Crystal size (mm)	0.32 × 0.15 × 0.08	0.32 × 0.15 × 0.08
Data collection		
Diffractometer	Bruker Apex Duo	Bruker Nonius X8Apex CCD
T_{min}, T_{max}	0.351, 0.733	0.351, 0.733
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23260, 7076, 6151	14247, 7220, 6220
R_{int}	0.033	0.028
θ values (°)	θ_{max} = 27.7, θ_{min} = 2.1	θ_{max} = 27.7, θ_{min} = 1.6
Range of h, k, l	h = -12→10, k = -22→22, l = -25→25	h = -12→12, k = -21→22, l = -24→23
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.080, 1.04	0.037, 0.081, 1.02
No. of reflections	7076	7220
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	2.49, -1.02	1.79, -1.13
Absolute structure	Flack x determined using 2443 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons and Flack (2004), Acta Cryst. A60, s61).	Flack x determined using 2369 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons and Flack (2004), Acta Cryst. A60, s61).
Absolute structure parameter	-0.011 (4)	0.020 (6)

Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS2013*, *SHELXL2013*, Diamond 3.1, CIFTAB-97 (Sheldrick, 1998).

Figure S5. XRD structure of complex **1** (thermal ellipsoids 50% probability) measured at 293 K, disordering of one ^tBu group is not presented for clarity.
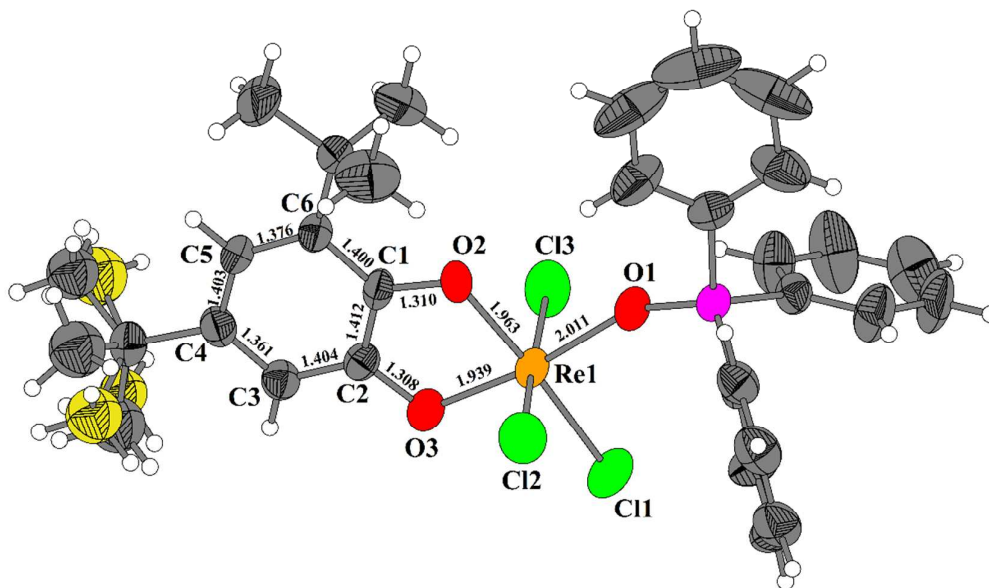

Figure S6. XRD structure of complex **1** (thermal ellipsoids 50% probability) measured at 150 K, disordering of one ^tBu group is not presented for clarity.
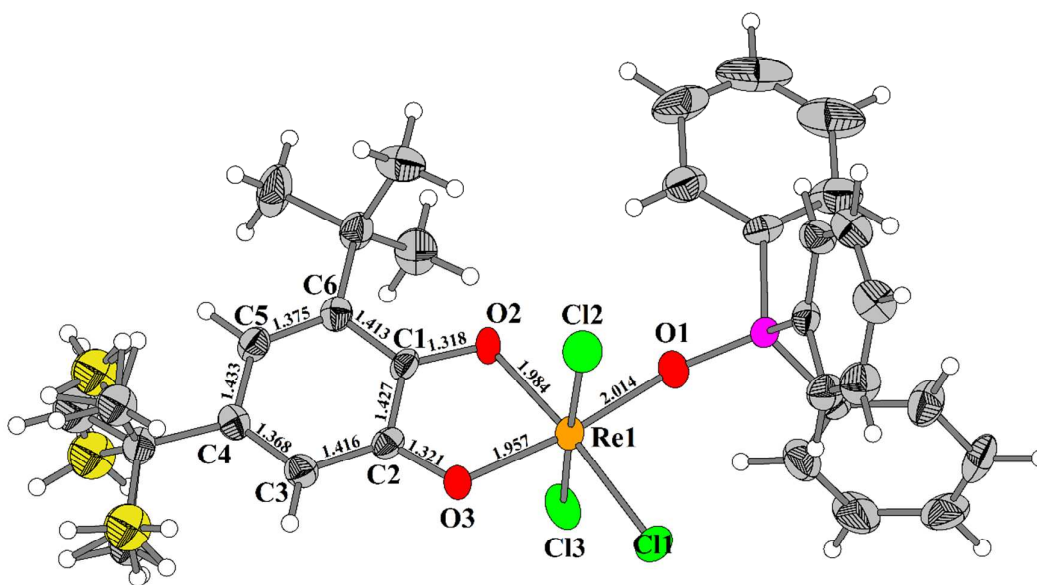
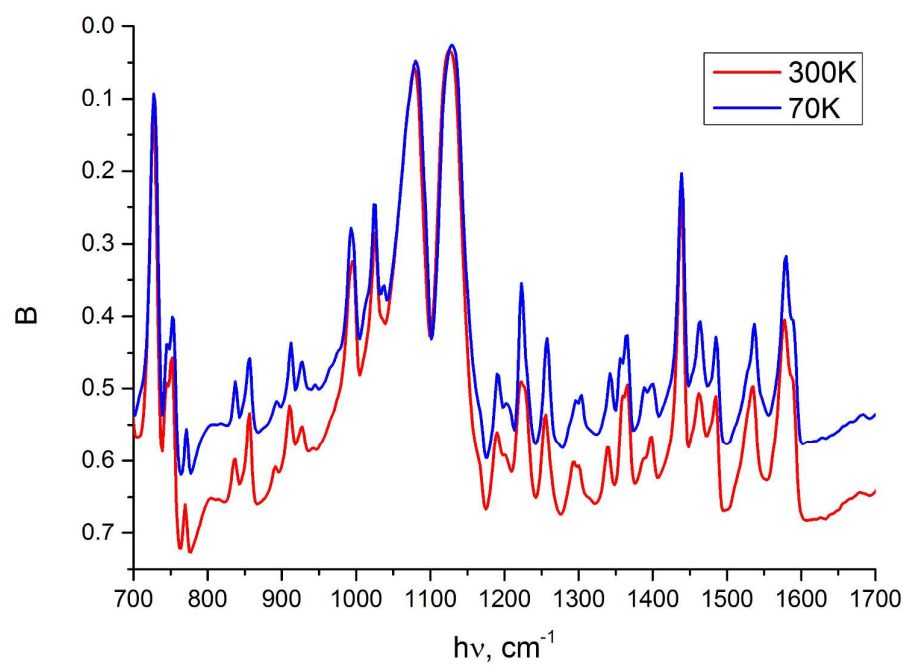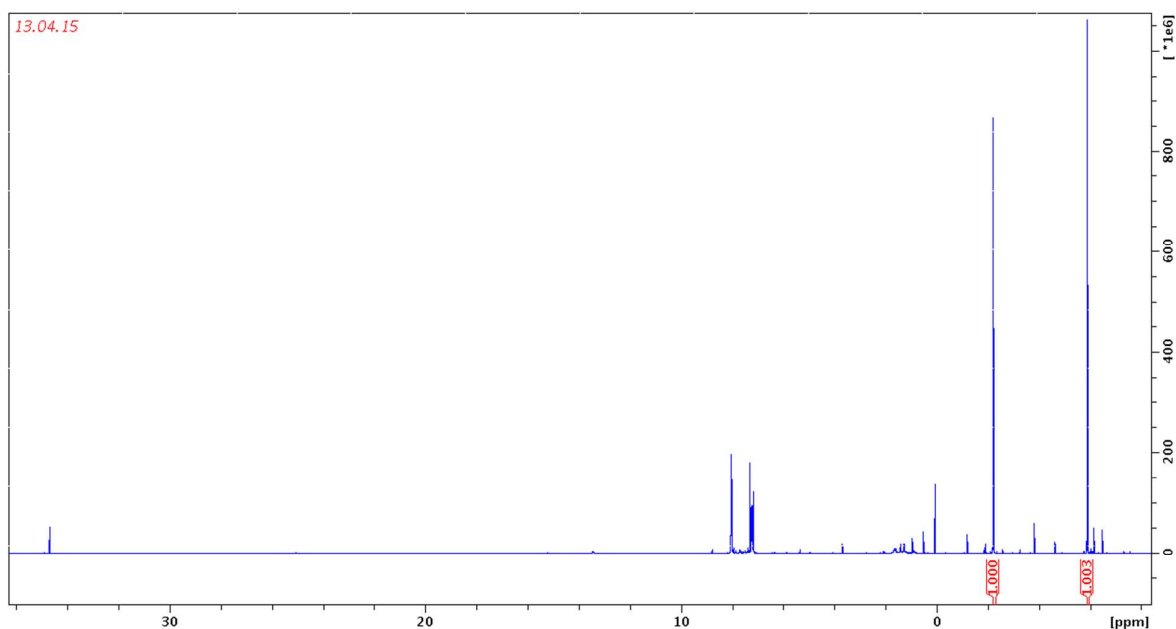**Figure S7**. FT-IR spectra of **1** measured at 300 and 77 K.

Figure S8. 1H NMR spectrum at 293 K

The data from AIST database (http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi):

Ph3PO: 7,64-7,27 (m), 7,71 (m)
C14H20O2 (3,5-DTBQ): 6,946 (d), 6,211(d), 1,274 (s), 1,235 (s)

In the case of **1** all signals have strong paramagnetic shifts: singlets from tBu groups shifted to -2.2 and -5.9 ppm, doublets from the ligand shifted to 34.7 and -3.83 ppm. Signals from OPPh₃ are not shifted.

Table S4. Details of CV experiment.

υ, V	lg υ, V s^{-1}	υ$^{1/2}$,	-E$_c$, V	E$_a$, V	-I$_c$, μA	I$_a$, μA
0.05	-1.3	0.224	0.016	0.272	4.22	1.45
0.10	-1.0	0.316	0.032	0.300	5.15	2.64
0.15	-0.82	0.378	0.041	0.333	5.81	3.33
0.20	-0.70	0.447	0.051	0.334	6.6	3.85
0.25	-0.60	0.5	0.058	0.344	7.13	4.36

$E_p^a = 0.102 \log υ + 0.402$, $R^2 = 0.9914$.
$I_p^a = 10.03 υ^{1/2} - 0.66$, $R^2 = 0.9909$.
$I_p^a = 13.76 υ - 1.030$, $R^2 = 0.9618$.

$E_p^c = -0.059 \log υ$, $R^2 = 0.9979$
$I_p^c = -10.46 υ^{1/2} - 1.87$, $R^2 = 0.9965$.
$I_p^c = -14.54 υ - 3.61$, $R^2 = 0.9923$.