

New Sterically-hindered o-Quinones Annelated with Metal-dithiolate: Regiospecificity in Oxidative Addition Reactions of Bifacial Ligand to the Pd and Pt Complexes

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X-ray crystallography

The X-ray diffraction data were collected on a Bruker D8 Quest (for **2a**, **2b**) and Agilent Xcalibur E (for **3**) diffractometers (Mo K α radiation, ω -scan technique, $\lambda = 0.71073$ Å). The intensity data were integrated by SAINT^[1] (for **2a**, **2b**) and CrysAlisPro^[2] (for **3**) programs. SADABS^[3] for **2a**, **2b** and SCALE3 ABSPACK^[4] for **3** were used to perform area-detector scaling and absorption corrections. The structures were solved by dual-space^[5] method and were refined on F² using all reflections with the SHELXTL package^[6]. All non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and refined in the “riding model”. The details of crystallographic, collection and refinement data for **2a**, **2b** and **3** are presented in Table SI1. CCDC-1446632 (**2a**), 1446633 (**2b**), 1446634 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

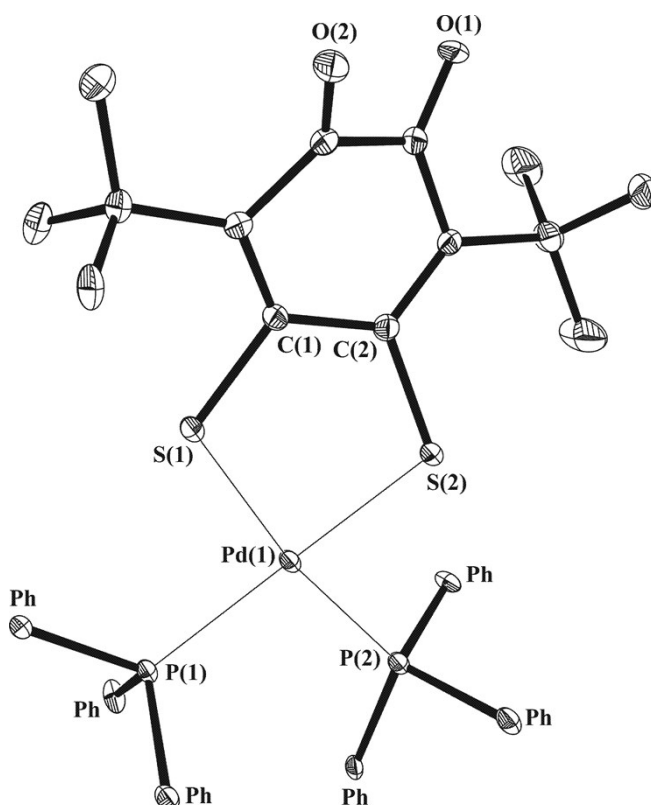


Figure SI1. An ORTEP plot of **2b**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted and phenyl rings are marked “Ph” for clarity.

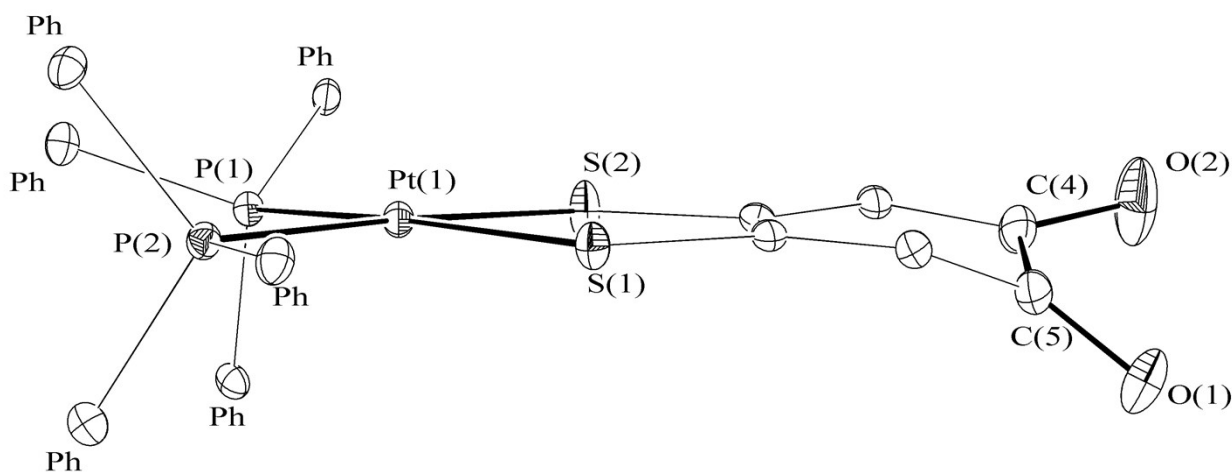


Figure SI2. An ORTEP plot of **3**, illustrating slightly distorted square planar surrounding of metal center and strong distortion in quinone ring. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms, *t*Bu groups are omitted and phenyl rings are marked “Ph” for clarity.

Table SI1. Selected bond lengths, angles and torsions for **2** (M=Pd) and **3** (M=Pt)

	2a	2b	3
M(1) – P(1), Å	2.3411(5)	2.307(1)	2.3190(7)
M(1) – P(2), Å	2.3230(5)	2.322(1)	2.3078(7)
M(1) – S(1), Å	2.2707(5)	2.271(1)	2.2953(7)
M(1) – S(2), Å	2.2707(6)	2.287(1) [S(2)], 2.30(1) [S(2')] *	2.2971(7)
S(1) – M(1) – S(2), °	85.03(2)	85.58(4) [S(2)], 82.3(3) [S(2')] *	85.58(2)
P(1) – M(1) – P(2), °	98.71(2)	97.17(4)	97.93(2)
O(1)-C(5), Å	1.229(3) [O(1)], 1.289(8) [O(1')] *	1.229(5)	1.228(4)
O(2)-C(4), Å	1.224(3)	1.233(5)	1.231(4)
C(1)-C(6), Å	1.379(3)	1.368(6)	1.384(4)
C(1)-C(2), Å	1.493(3)	1.496(5)	1.512(4)
C(2)-C(3), Å	1.370(3)	1.370(5)	1.384(4)
C(3)-C(4), Å	1.453(3)	1.459(6)	1.455(4)
C(4)-C(5), Å	1.504(3)	1.527(6)	1.518(4)
C(5)-C(6), Å	1.454(3)	1.455(5)	1.467(4)
φ[O(1)-C(5)-C(4)-O(2)], °	39.6(3) [O(1)], 14.0(8) [O(1')] *	29.9(5)	37.3(4)

* Two values are given owing to structural disordering on oxygen (**2a**) and sulfur (**2b**) atom

Table SI2. Crystallographic data and refinement parameters for **2** and **3**.

	2a	2b	3
Formula	C ₅₀ H ₄₈ O ₂ P ₂ PdS ₂	C ₅₂ H ₅₂ O _{2.5} P ₂ PdS ₂	C ₅₀ H ₄₈ O ₂ P ₂ PtS ₂
MW	913.34	949.39	1002.03
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /c	P-1	P2 ₁ /c
a, Å	9.7933(8)	10.760(2)	9.82880(10)
b, Å	27.530(2)	12.877(3)	27.6805(3)
c, Å	15.9433(13)	17.948(4)	16.0758(2)
α, °	90	95.401(3)	90
β, °	97.8730(10)	99.297(3)	98.0410(10)
γ, °	90	104.257(3)	90
V, Å ³	4258.0(6)	2355.1(9)	4330.68(8)
Z,	4	2	4
ρ _{calcd.} , g·cm ⁻³	1.425	1.339	1.537
μ, mm ⁻¹	0.650	0.591	3.450
F(000)	1888	984	2016
Crystal dimension, mm	0.280 · 0.260 · 0.050	0.520 · 0.170 · 0.110	0.250 · 0.200 · 0.100
2θ range, °	2.424 – 26.000	3.031 – 27.000	3.042 – 25.999
Reflections measured	39437	18756	65836
Reflections with I ≥ 2σ(I)	7448	7872	7896
R ₁ (all data)	0.0334	0.0785	0.0263
R ₁ with I ≥ 2σ(I)	0.0280	0.0563	0.0233
wR ₂ (all data)	0.0663	0.1448	0.0519
wR ₂ with I ≥ 2σ(I)	0.0646	0.1361	0.0510
Goodness-of-fit on F ²	1.061	1.050	1.121
Highest residue, e·Å ⁻³	0.534	1.525	1.104
Lowest residue, e·Å ⁻³	-0.332	-1.078	-1.152

UV/Vis spectra

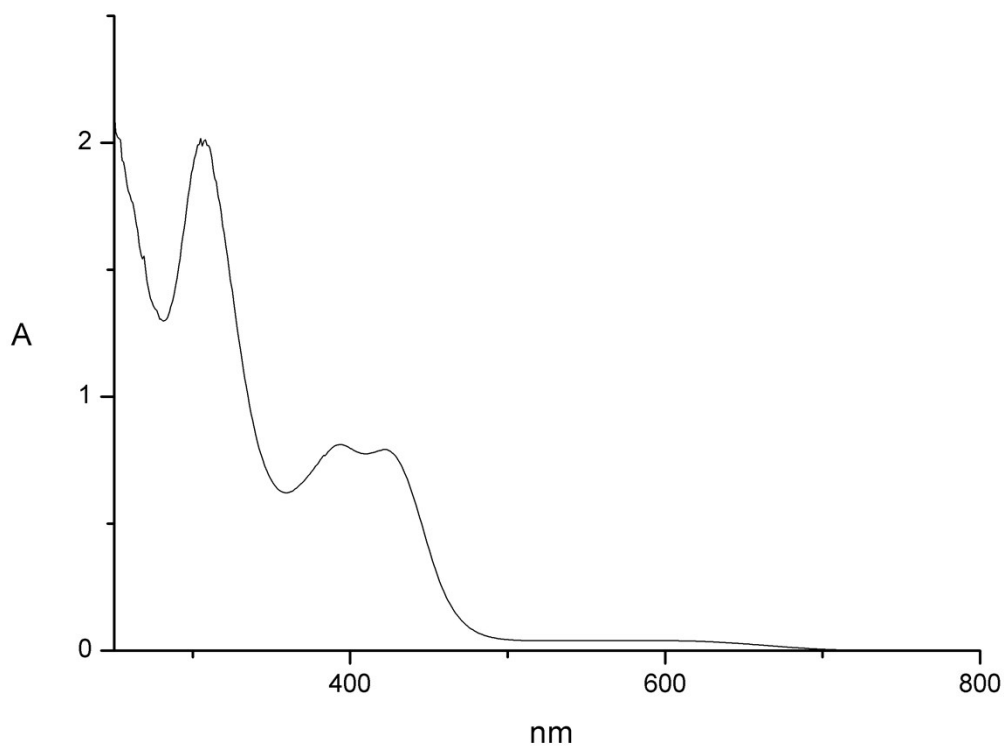


Figure SI3. UV/Vis spectrum of **2** in THF, $c = 4.11 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, 1.0 cm quartz cell; $\epsilon = 520 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 588 \text{ nm}$), $\epsilon = 19800 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 422 \text{ nm}$), $\epsilon = 20200 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 398 \text{ nm}$)

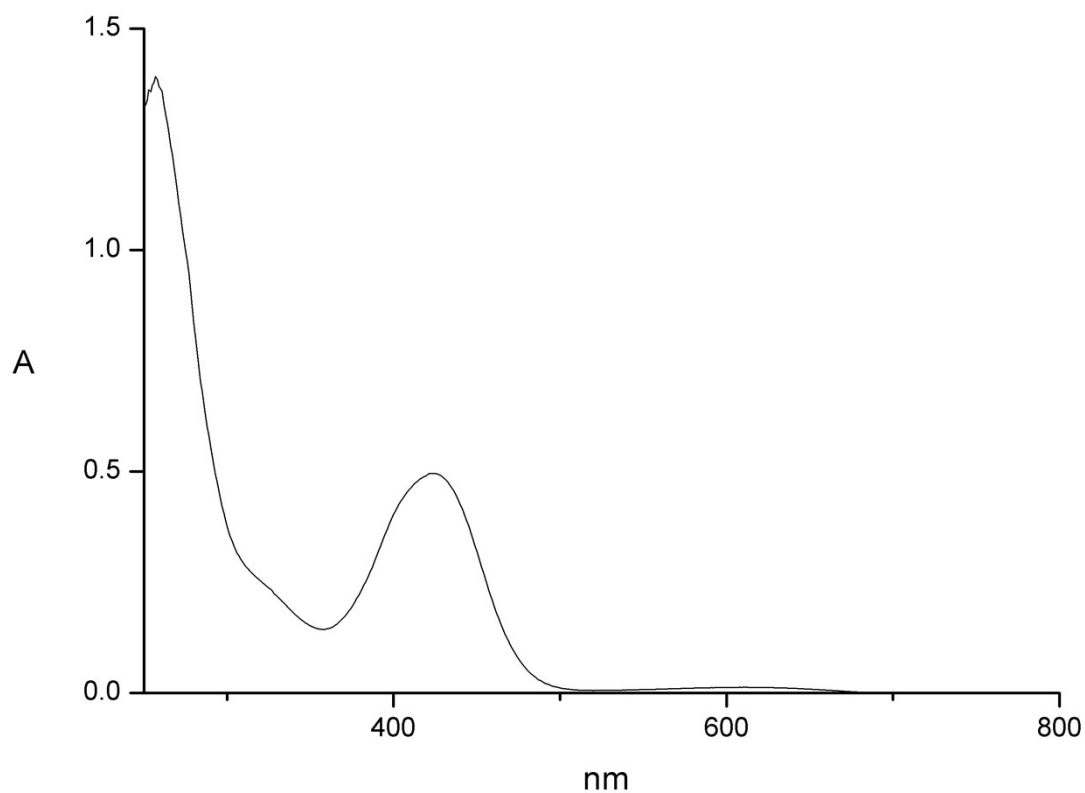


Figure SI4. UV/Vis spectrum of **3** in THF, $c = 2.5 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, 1.0 cm quartz cell; $\epsilon = 580 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 611 \text{ nm}$), $\epsilon = 19900 \text{ M}^{-1}\text{cm}^{-1}$ ($\lambda_{\text{max}} = 424 \text{ nm}$)

¹H-NMR spectra

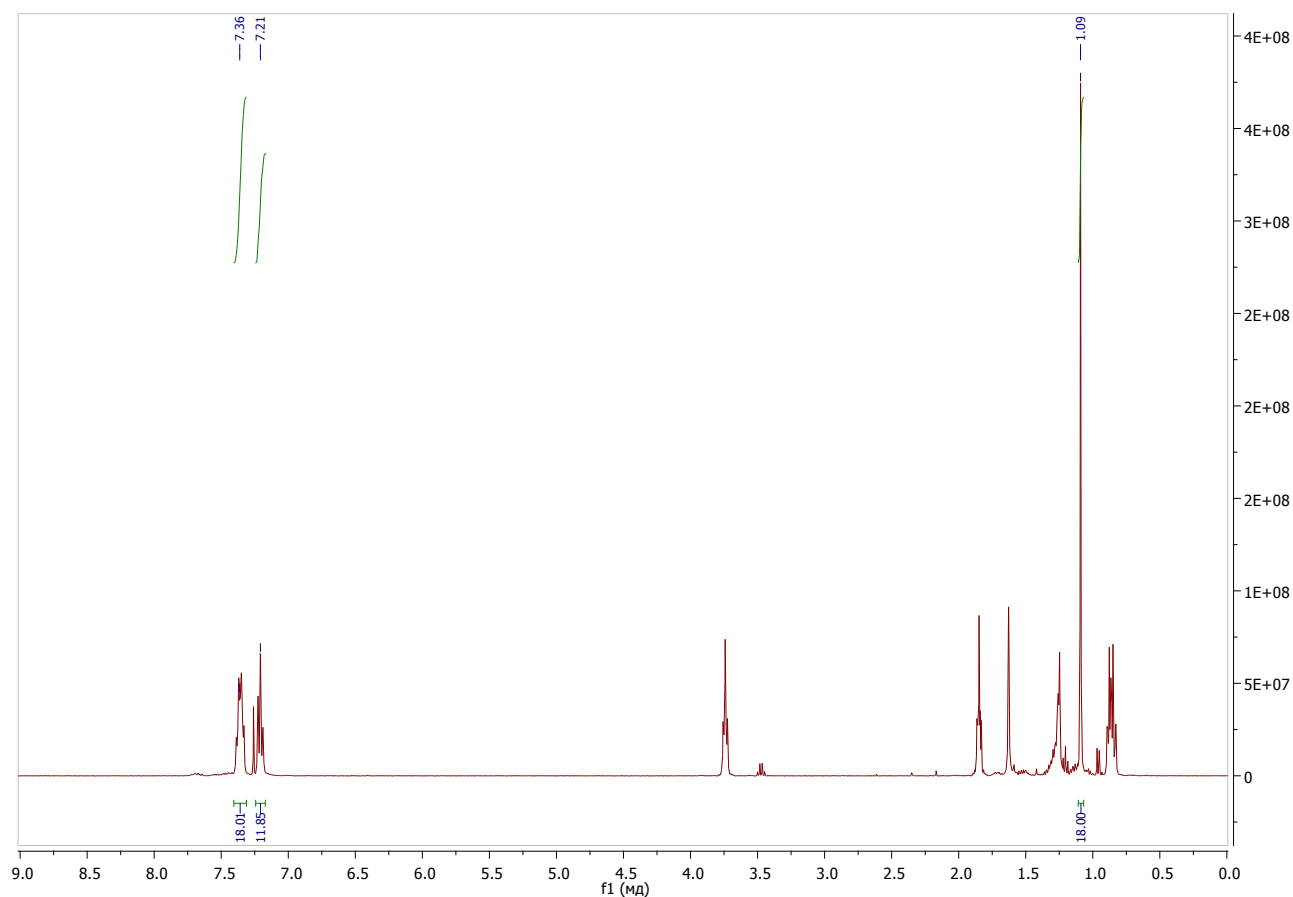


Figure SI5. ¹H NMR spectrum of **2** (400 MHz, CDCl₃, 25°C)

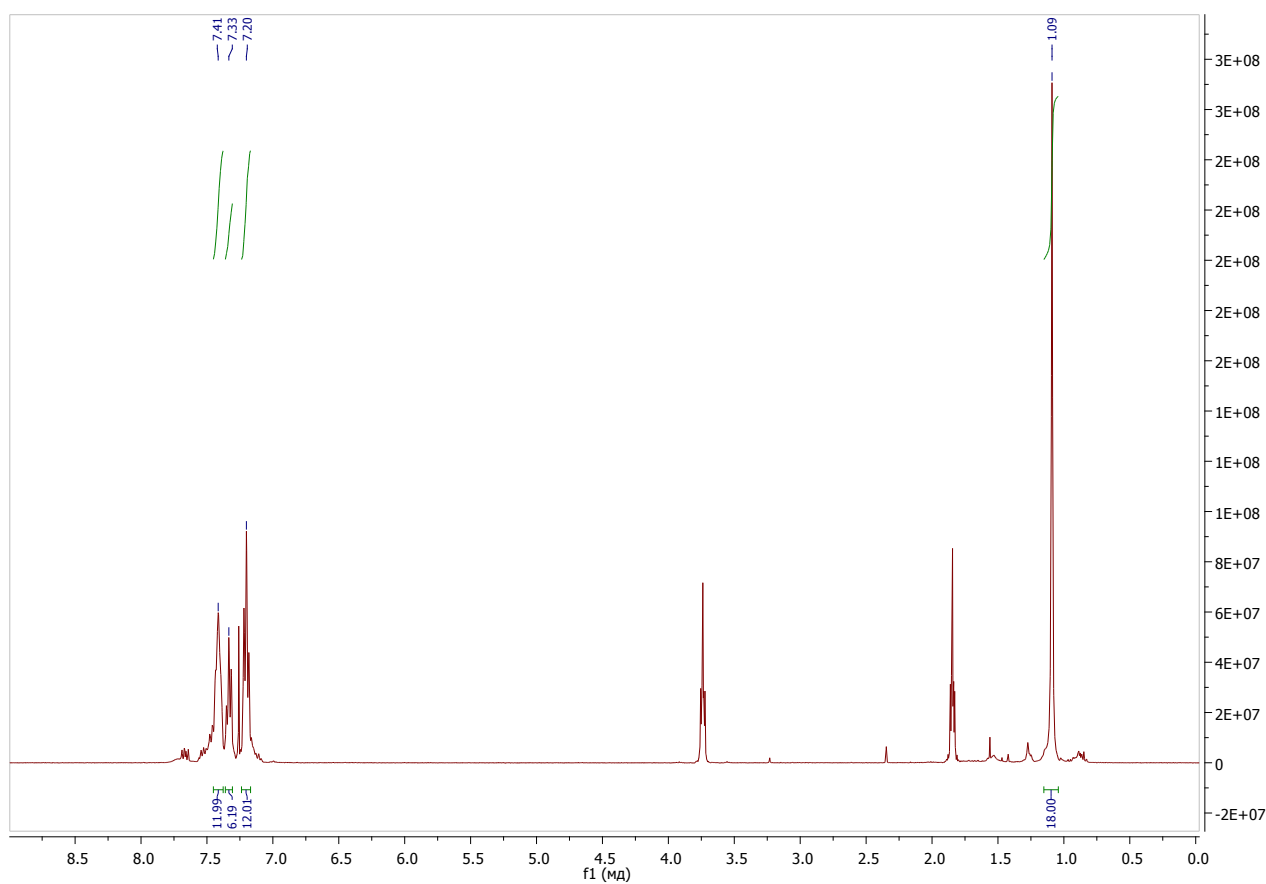


Figure SI6. ¹H NMR spectrum of **3** (400 MHz, CDCl₃, 25°C)

^{13}C -NMR spectra

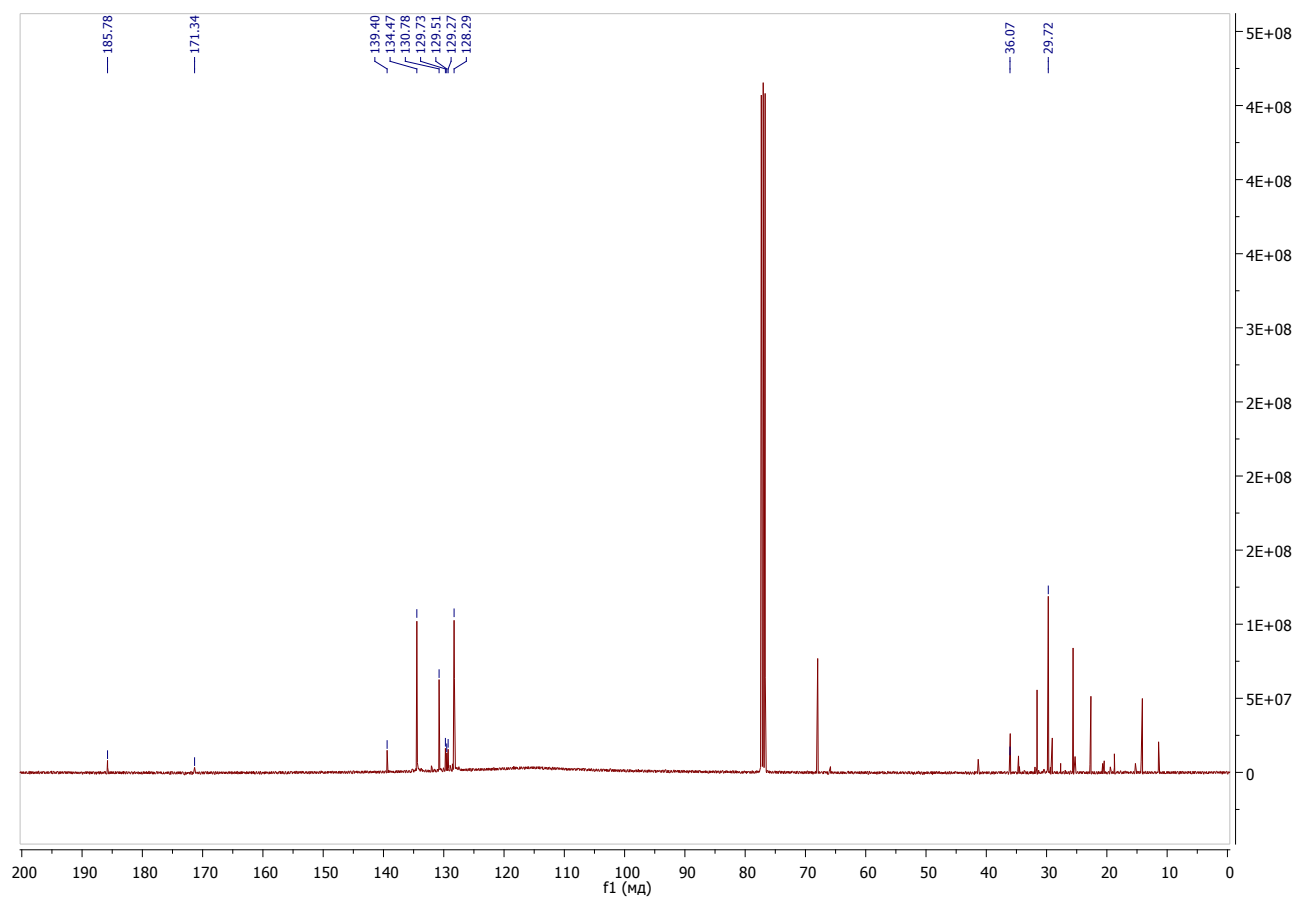


Figure SI7. ^{13}C NMR spectrum of **2** (100 MHz, CDCl_3 , 25°C)

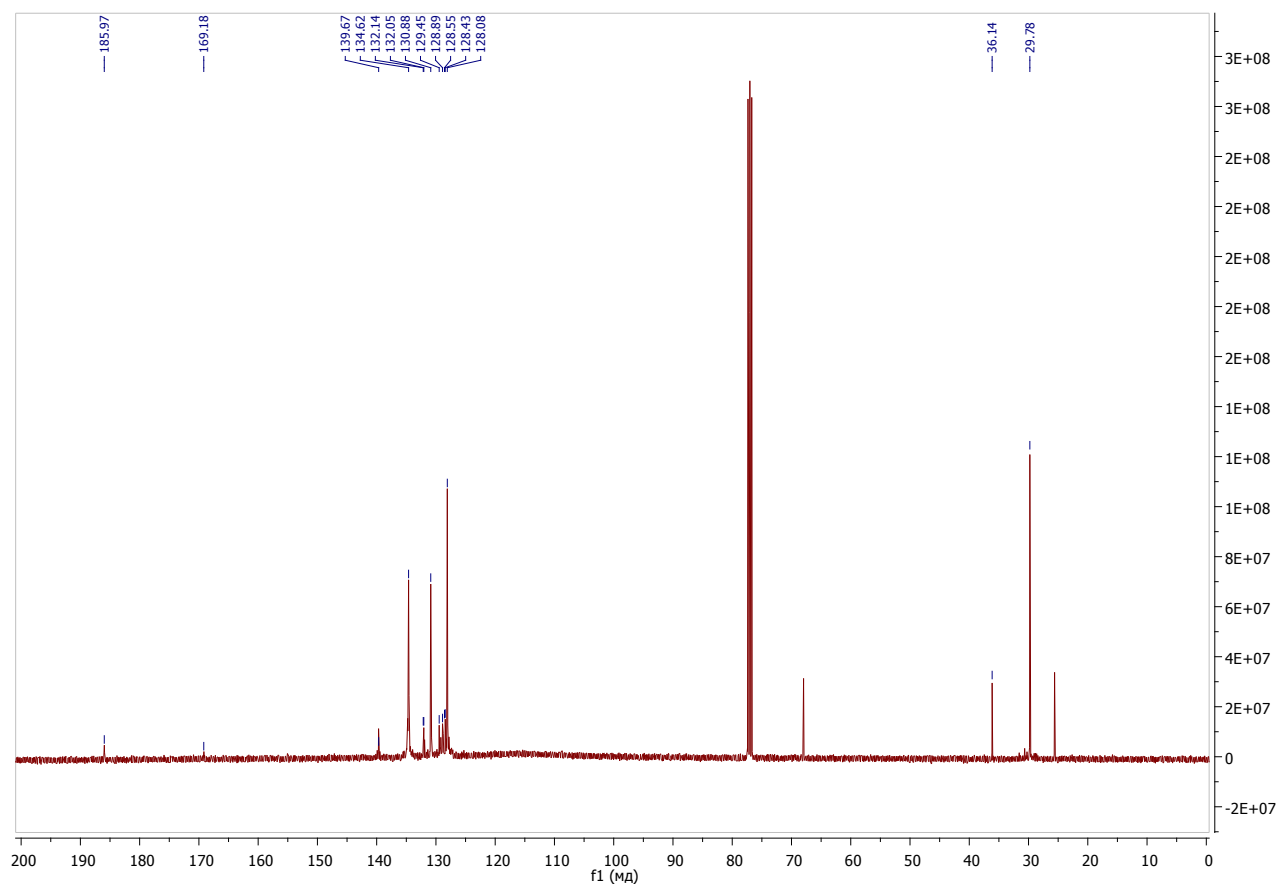


Figure SI8. ^{13}C NMR spectrum of **3** (100 MHz, CDCl_3 , 25°C)

^{31}P -NMR spectra

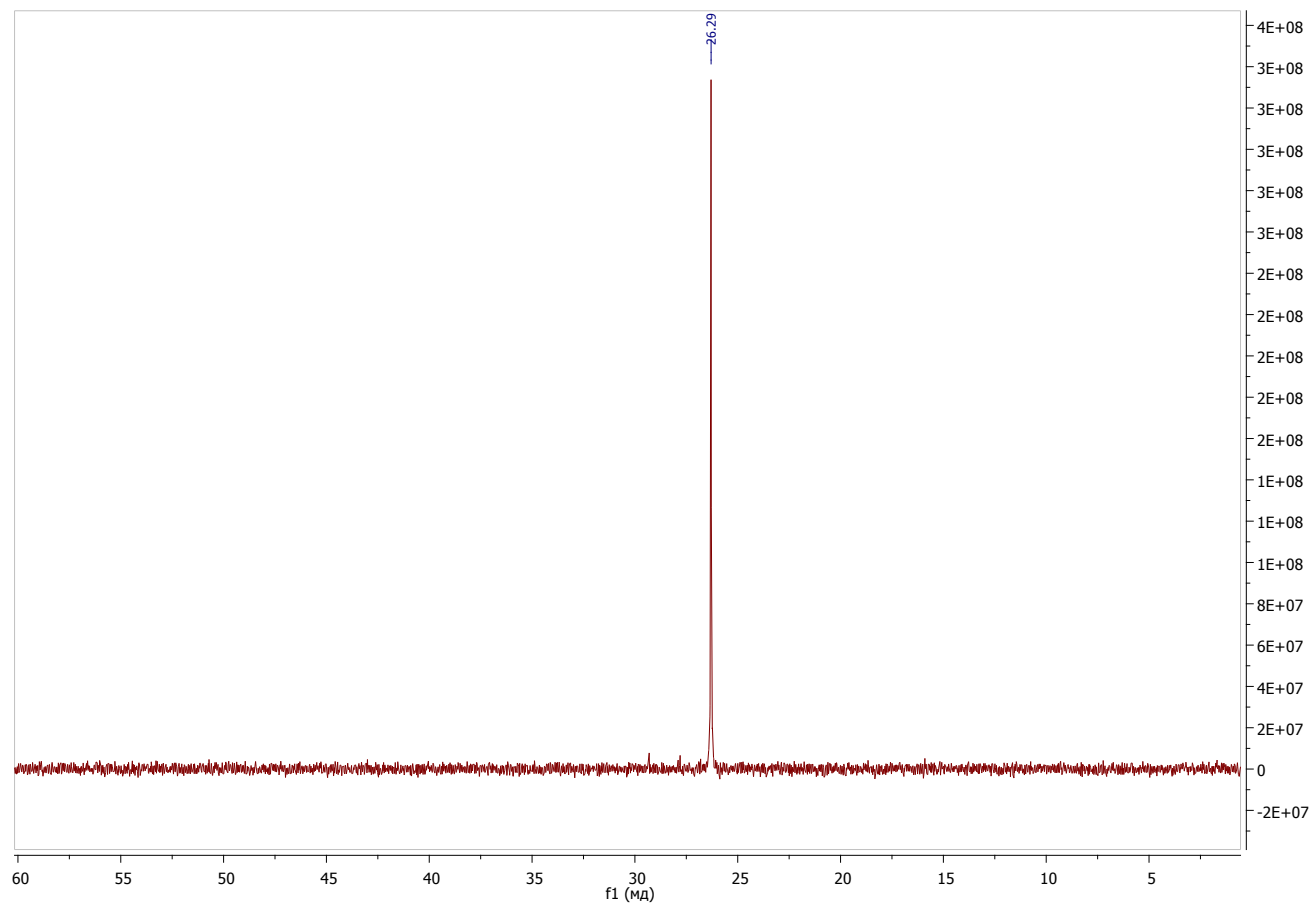


Figure SI9. ^{31}P NMR spectrum of **2** (161.97 MHz, CDCl_3 , 25°C)

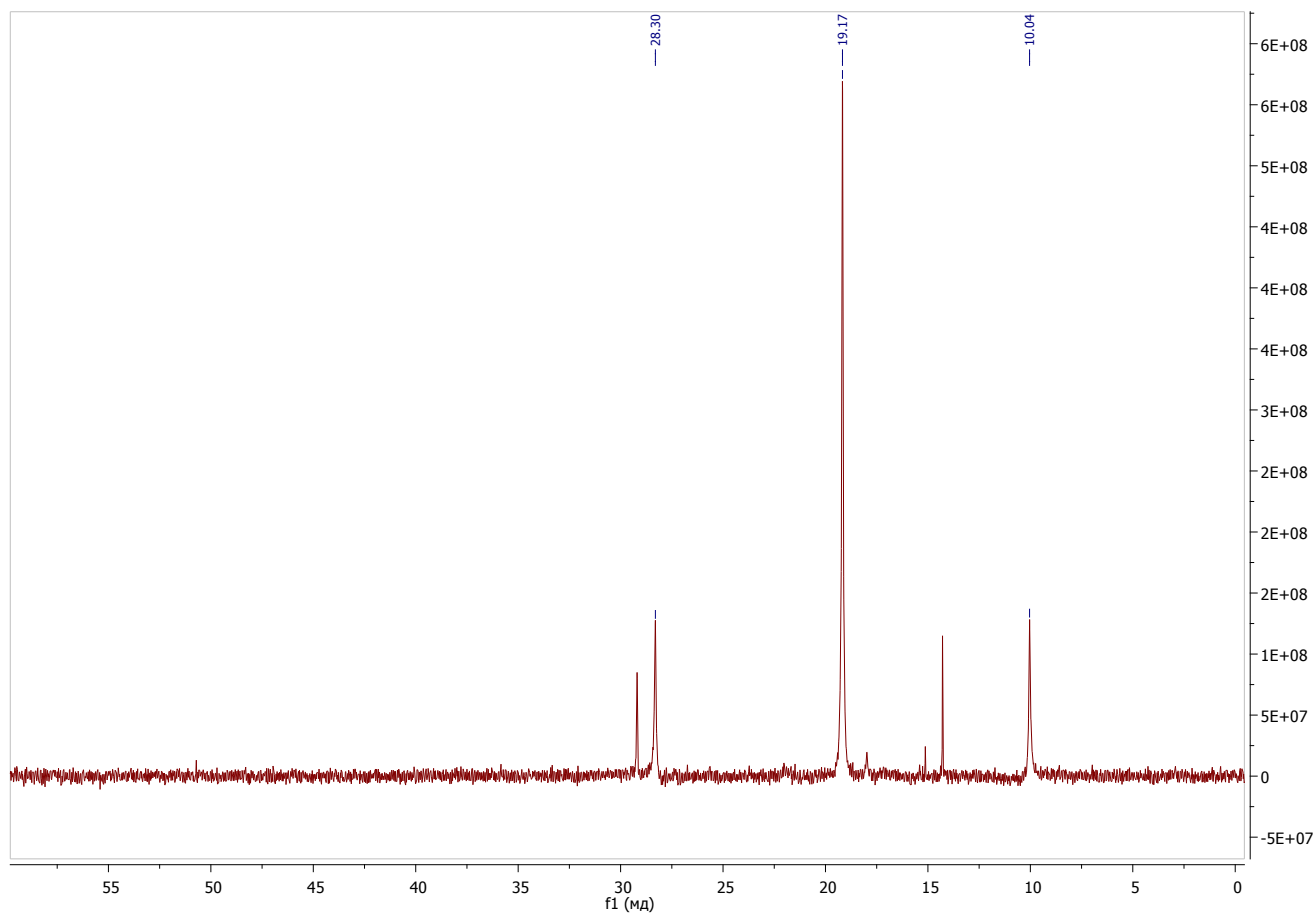


Figure SI10. ^{31}P NMR spectrum of **3** (161.97 MHz, CDCl_3 , 25°C)

Cyclic voltammograms

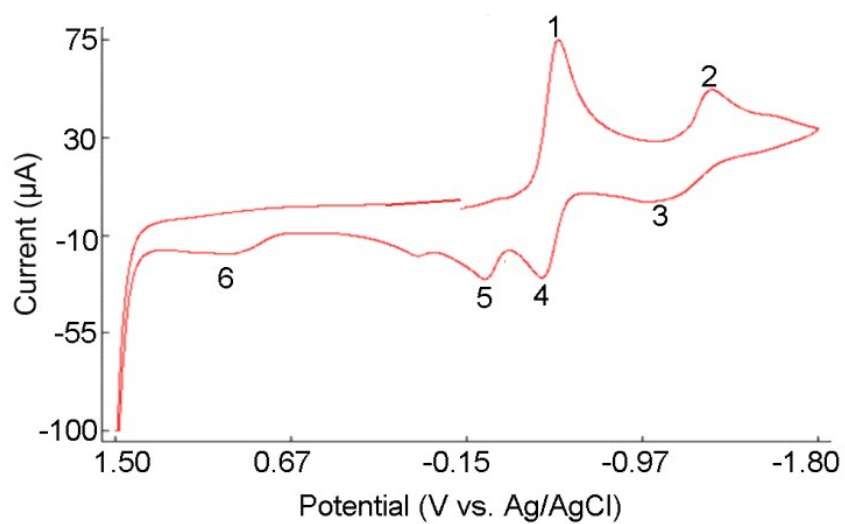


Figure SI11. Cyclic voltammogram of parent *o*-quinone **1** (DMF, vs Ag/AgCl)

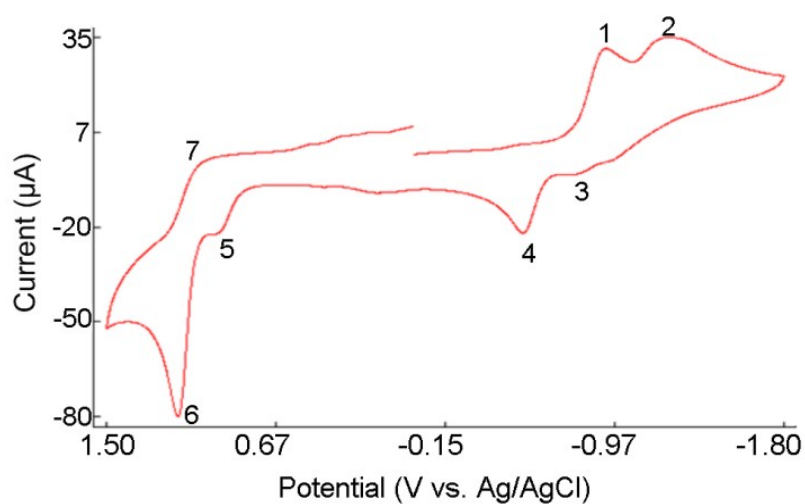


Figure SI12. Cyclic voltammogram of complex **2** (DMF, vs Ag/AgCl)

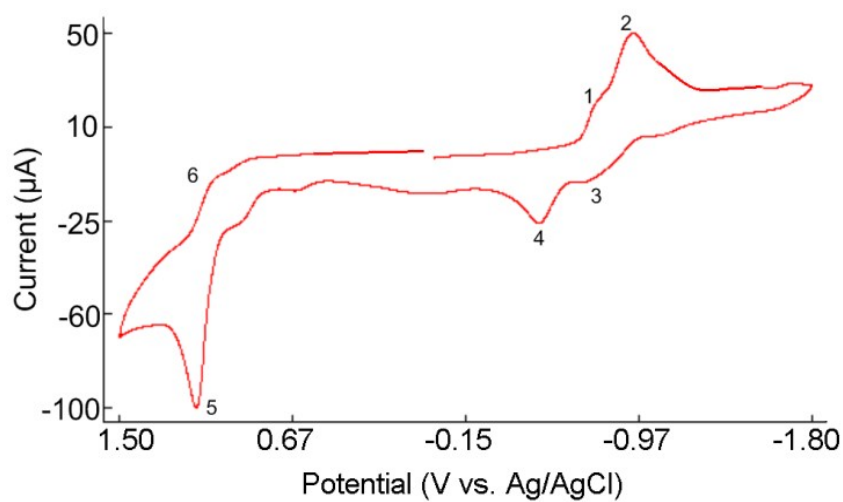


Figure SI13. Cyclic voltammogram of complex **3** (DMF, vs Ag/AgCl)

IR spectra

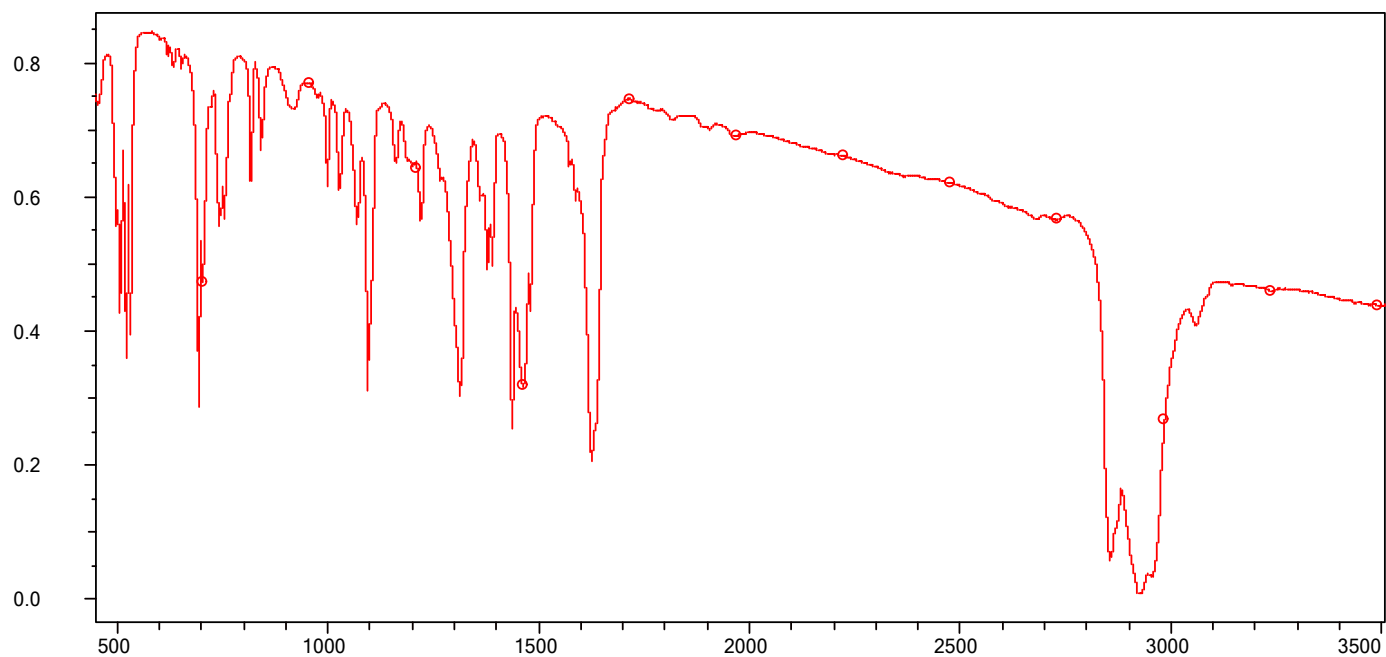


Figure SI14. IR spectrum of **2** in nujol
 $\nu = 1624s$ (C=O), 1435, 1307, 1216, 1189, 1159, 1091, 1026, 997, 914, 840, 813, 754, 692 cm⁻¹

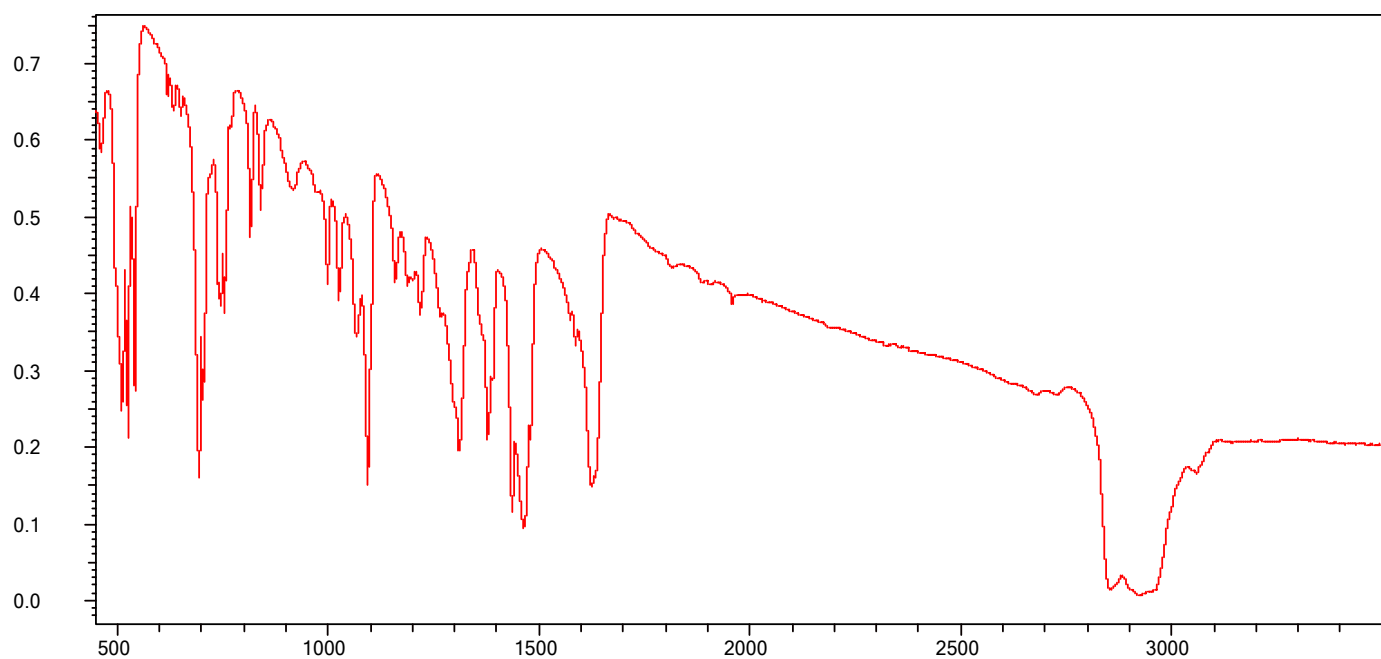
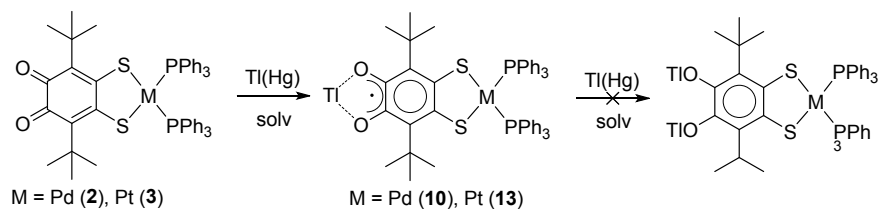


Figure SI15. IR spectrum of **3** in nujol
 $\nu = 1624s$ (C=O), 1438, 1313, 1217, 1163, 1096, 1067, 1029, 996, 912, 841, 816, 754, 741, 691 cm⁻¹

X-band EPR spectra



Scheme SI1. Synthesis of dithiolate complexes **10** and **13** from **2** and **3**

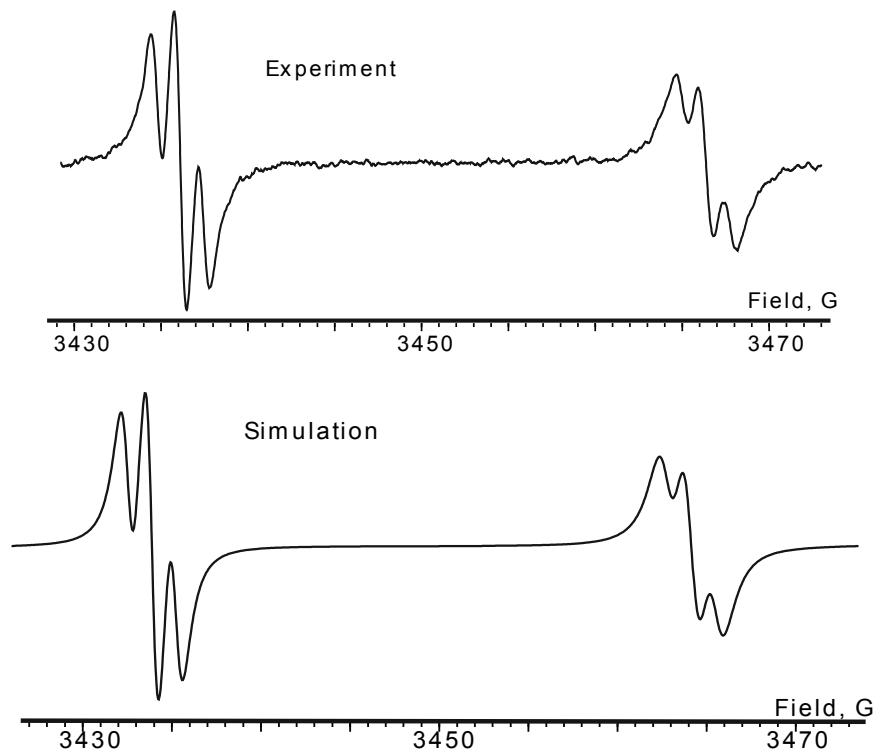


Figure SI16. Experimental (top) and simulated (bottom) X-band EPR spectra of **10** in THF, 298K.

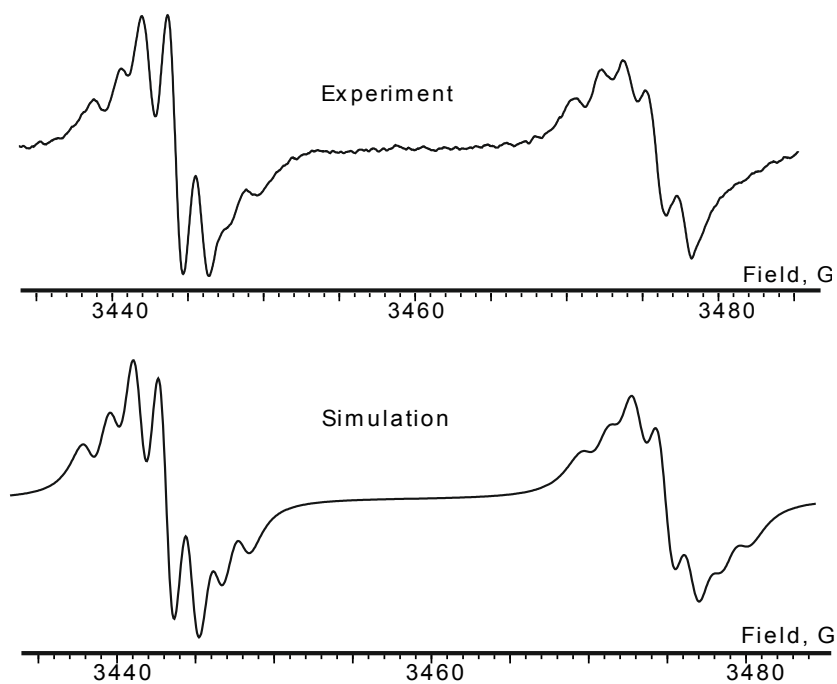


Figure SI17. Experimental (top) and simulated (bottom) X-band EPR spectra of **13** in THF, 298K.

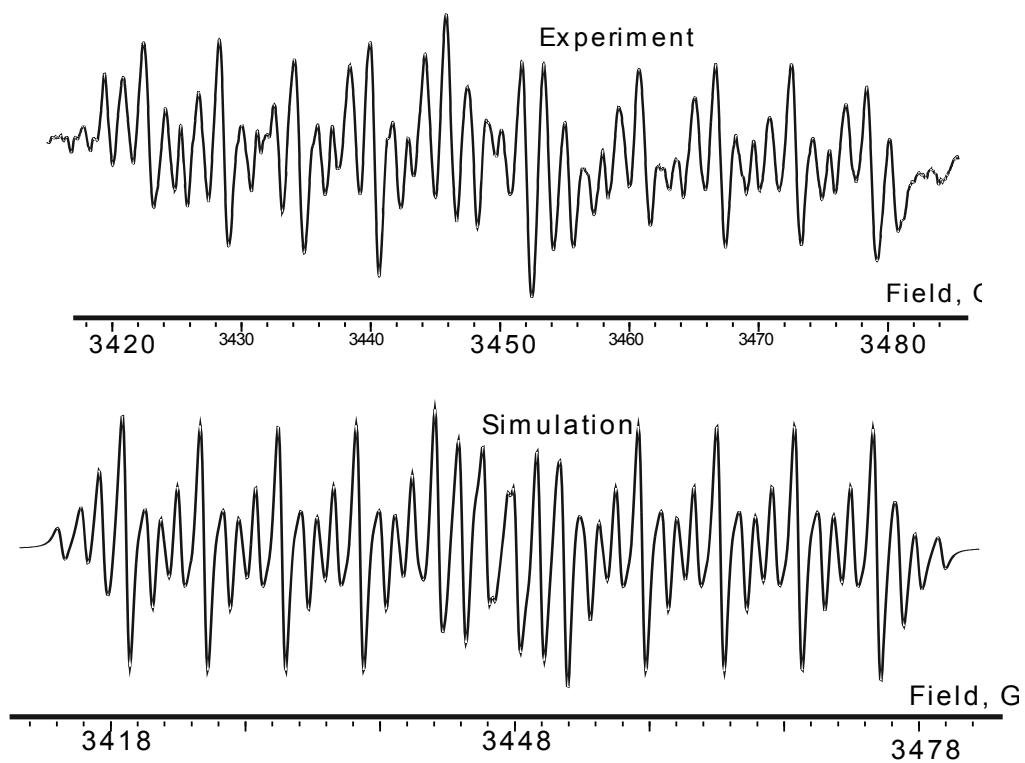


Figure SI18. Experimental (top) and simulated (bottom) X-band EPR spectra of **15** in THF, 298K.

Literature

- [1] SAINT. Data Reduction and Correction Program. Version 8.27B. Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
- [2] Data Collection. Reduction and Correction Program. CrysalisPro – Software Package Agilent Technologies, 2012.
- [3] G.M. Sheldrick, SADABS-2012/1. Bruker/Siemens Area Detector Absorption Correction Program. Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
- [4] SCALE3 ABSPACK: Empirical absorption correction, CrysalisPro – Software Package Agilent Technologies, 2012.
- [5] G.M. Sheldrick, Acta Cryst. 2015, A71, 3-8.
- [6] G.M. Sheldrick, SHELXTL v. 6.14, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2003.