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Zinc complex as a source of highly labile non-shielded *o*-iminoquinone

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Experimental Section

Commercially available $ZnCl_2$, $Ni(CO)_4$ and 2,6-diisopropylaniline were used as received. 4,5-Bis(diphenylmethyl)cyclohexa-3,5-diene-1,2-dione was synthesized according to the reported procedure [S1]. The solvents were purified and dehydrated using standard procedures.

The procedures for the syntheses of the neutral zinc complex were carried out in the air. All the procedures of synthesis and isolation of the nickel complex were carried out in inert atmosphere. The C, H, N elemental analyses were performed on an Elementar Vario EL cube. Infrared spectra were recorded on FSN-1201 spectrophotometer in a Nujol and reported in cm^{-1}. NMR spectra were recorded on a Bruker Avance Neo 300 MHz spectrometer operating at 300 MHz (^1H) and 75 MHz (^{13}C) and a Bruker Avance III 400 spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C and DEPT). The X-ray diffraction data were collected on an Oxford Xcalibur Eos diffractometer (Mo-K_α radiation, ω-scan technique, $\lambda = 0.71073$ Å). CCDC **2407494** (**2**) and **2407495** (**3**) contain the supplementary crystallographic data. These data can also be obtained free of charge at ccdc.cam.ac.uk/getstructures from the Cambridge Crystallographic Data Centre.

Synthesis of complex 2

A solution of 2,6-diisopropylaniline (0.39g, 2.2 mmol) in 10 ml of diethyl ether was added to a suspension of $ZnCl_2$ (0.3 g, 2.2 mmol) in diethyl ether (30 ml) with vigorous stirring. After the suspension of the zinc chloride complex with aniline was formed, 4,5-bis(diphenylmethyl)cyclohexa-3,5-diene-1,2-dione (0.88 g, 2 mmol) was added, and the mixture was stirred at room temperature for 8 h until a light brown precipitate formed. Complex **2** was isolated with a yield of 1.28 g (87%) after the product was filtered, washed and dried. Brown crystals of the complex suitable for X-ray diffraction were obtained after recrystallization from toluene.

Elemental Analysis: Calculated (%) for $C_{44}H_{41}Cl_2NOZn$: C, 71.80; H, 5.61; N, 1.90, found (%): C, 71.92; H, 5.65; N, 1.93. IR (Nujol, cm^{-1}): 1645 s, 1616 m, 1599 m, 1554 s, 1493 s, 1455 s, 1353 s, 1263 m, 1222 m, 1173 w, 1157 w, 1129 w, 1078 m, 1057 w, 1002 w, 937 w, 928 w, 917 w, 893 m, 870 w, 828 w, 812 w, 785 m, 748 s, 729 w, 701 s, 658 m, 638 w, 590 w, 575 w, 562 w, 547 w, 520 w, 493 w, 477 w. ^1H NMR (300 MHz, $CDCl_3$, d/ppm, *J*/Hz): 0.79 (d, 6H, CH_3 iPr, *J*=6.6); 1.21 (d, 6H, CH_3 iPr, *J*=6.6); 2.64 (sept, 2H, CH iPr, *J*=6.6), 5.14 (s, 1H, $C\underline{H}Ph_2$), 5.21 (s, 1H, $C\underline{H}Ph_2$), 5.58 (s, 1H, H_{ring}), 6.28 (s, 1H, H_{ring}), 6.64-6.73 (m, $4H_{arom}$); 6.87-6.96 (m, $4H_{arom}$); 6.98-7.06 (m, $2H_{arom}$); 7.11-7.17 (m, $1H_{arom}$); 7.17-7.24 (m, 6H, H_{arom}); 7.31-7.44 (m, $6H_{arom}$).^{13}C NMR, DEPT (75 MHz, $CDCl_3$, d/ppm): 23.9 (CH); 24.6 (CH); 28.6 (CH); 53.2 (CH); 54.2 (CH); 123.7 (CH); 124.1 (CH); 128.0 (CH); 128.4 (CH); 128.5 (CH); 128.7 (CH); 128.9 (CH); 129.03 (CH); 129.3 (CH); 129.5 (CH); 138.5 (C); 138.7 (C); 139.0 (C); 139.1 (C); 156.5 (C); 156.8 (C); 167.8 (C); 183.4 (C).

Synthesis of complex 3

Nickel tetracarbonyl (30 mg, 0.17 mmol) was distilled into the ampoule containing frozen solution of complex **2** (260 mg, 0.35 mmol) in 25 ml THF. The reaction mixture was slowly heated to room temperature for 20 minutes. The reaction is accompanied by a change in the color of the solution and the release of gas. The evolved carbon monoxide was removed by periodic solution degassing operations. After the vigorous bubbling of gas had finished, the mixture was warmed to 70 °C for an hour, after which it was left at -18 °C overnight. The precipitated product was isolated by filtration and dried under vacuum. Green crystals were obtained, yield: 107 mg (49%). Elemental Analysis: Calculated (%) for $C_{88}H_{82}N_2NiO_2$: C, 84.00; H, 6.57; N, 2.23, found (%):C, 83.81; H, 6.55; N, 2.20. IR (Nujol, cm^{-1}): 1600m, 1508m, 1493s, 1450s, 1360m, 1330m, 1305m, 1285m, 1235s, 1220s, 1178s, 1070m, 1030m, 1001w, 983w, 966w, 938w, 912w, 890w, 859w, 846w, 830w, 798w, 758m, 748s, 733s, 717m, 700s, 672w, 660w, 637m, 623w, 588w, 569w, 510w, 499w, 480w, 466w. ^{1}H NMR (400 MHz,CDCl$_3$, d/ppm, *J*/Hz): 0.84 (d, 6H, CH$_3$ iPr, *J*=6.8); 1.24 (d, 6H, CH$_3$ iPr, *J*=6.8); 3.35 (sept, 2H, CH iPr, *J*=6.8), 5.10 (s, 2H), 5.15 (br s, 2H), 5.50 (s, 2H), 6.13 (s, 2H), 6.60-6.67 (m, 8H$_{arom}$); 6.76-6.83 (m, 8H$_{arom}$); 6.98-7.01 (m, 4H$_{arom}$); 7.04-7.10 (m, 12H$_{arom}$); 7.16-7.22 (m, 12H, H$_{arom}$). ^{13}C NMR, DEPT (100 MHz, CDCl$_3$, d/ppm): 23.6 (CH); 24.2 (CH); 28.8 (CH); 52.2 (CH); 53.0 (CH); 120.8 (CH); 121.4 (CH); 122.6 (CH); 126.2 (CH); 126.4 (CH); 126.8 (CH); 128.1 (CH); 128.3 (CH); 129.0 (CH); 129.3 (CH); 137.9 (C); 142.2 (C); 142.6 (C); 142.8 (C); 143.9 (C); 146.2 (C); 155.0 (C); 172.3 (C).

X-ray diffraction data

Data collection, cell refinement, data reduction and absorption corrections were carried out using CrysAlisPro [S2]. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The both compounds were solved by dual method [S3] and were refined on F_{hkl}^2 using SHELXTL package [S4]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except water H-atoms in **3** were placed in calculated positions and were refined using a riding model (U_{iso}(H) = 1.5U_{eq}(C) for CH$_3$-groups and U_{iso}(H) = 1.2U_{eq}(C) for other groups). In turn, the hydrogen atoms of water molecule were located from difference Fourier maps and were refiniment with geometrical (DFIX) and displacement parameter [U_{iso}(H) = 1.2U_{eq}(O)] constraints. The main crystallographic data and structure refinement details for complexes **2** and **3** are presented in Tables S1 and S2.

Table S1. The selected bond lengths [Å] and angles [°] in the complexes **2** and **3**.

Bond	**2**, Å	Bond	**3**, Å	Bond	**3**, Å
Zn(1)-O(1)	2.0783(16)	Ni(1)-O(1)	1.8441(18)	Ni(1)-O(2)	1.8416(18)
Zn(1)-N(1)	2.095(2)	Ni(1)-N(1)	1.833(2)	Ni(1)-N(2)	1.837(2)
O(1)-C(1)	1.232(3)	O(1)-C(1)	1.315(3)	O(2)-C(45)	1.313(3)
N(1)-C(2)	1.295(3)	N(1)-C(2)	1.356(3)	N(2)-C(46)	1.355(3)
C(1)-C(2)	1.512(3)	C(1)-C(2)	1.413(4)	C(45)-C(46)	1.413(4)
C(2)-C(3)	1.440(3)	C(2)-C(3)	1.415(4)	C(46)-C(47)	1.415(4)
C(3)-C(4)	1.340(3)	C(3)-C(4)	1.376(4)	C(47)-C(48)	1.376(4)
C(4)-C(5)	1.489(3)	C(4)-C(5)	1.438(4)	C(48)-C(49)	1.439(4)
C(5)-C(6)	1.344(3)	C(5)-C(6)	1.387(4)	C(49)-C(50)	1.387(4)
C(1)-C(6)	1.439(3)	C(1)-C(6)	1.404(4)	C(45)-C(50)	1.408(4)
Zn(1)-Cl(1)	2.1740(7)				
Zn(1)-Cl(2)	2.1845(7)				
Angle	**2**, deg	Angle	**3**, deg	Angle	**3**, deg
O(1)-Zn(1)-N(1)	79.27(7)	O(1)-Ni(1)-O(2)	178.43(10)	N(1)-Ni(1)-N(2)	179.57(9)
O(1)-Zn(1)-Cl(1)	106.43(5)	O(1)-Ni(1)-N(1)	86.26(9)	O(2)-Ni(1)-N(2)	86.47(9)
N(1)-Zn(1)-Cl(1)	115.40(5)	O(1)-Ni(1)-N(2)	93.93(9)	N(1)-Ni(1)-O(2)	93.34(9)
O(1)-Zn(1)-Cl(2)	109.76(5)				
N(1)-Zn(1)-Cl(2)	111.28(5)				
Cl(1)-Zn(1)-Cl(2)	124.78(3)				

The aromatic substituents at the N(1) and N(2) atoms, as well as one of the phenyl substituents, are disordered over two positions in complex **3**. Identical anisotropic displacement parameters for pairs of disordered atoms were received with EADP instruction. SADI, DFIX and ISOR instructions were used to refine disordered fragments of molecule. In crystal **2**, there are one solvate toluene molecule and 0.125 water molecules per each molecule of the complex, while in crystal **3** there are two THF molecules, one of which is disordered. EADP, DFIX, ISOR and SUMP instructions were used to refine the disordered solvent molecule.

Table S2. Details of crystallographic, collection and refinement data for complexes **2** and **3.**

Complex	**2**	**3**
Empirical formula	$C_{44}H_{41}Cl_2NOZn$, C_7H_8, 0.125(H_2O)	$C_{88}H_{82}N_2NiO_2$, 2(C_4H_8O)
Formula weight	830.43	1402.47
Temperature [K]	100(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	*P–1*	*P2₁/c*
Unit cell dimensions		
a[Å]	10.4603(3)	17.3354(3)
b[Å]	13.2962(4)	35.4135(7)
c[Å]	17.2575(6)	13.4218(3)
α[°]	67.710(3)	90
β[°]	84.999(3)	104.993(2)
γ[°]	89.898(3)	90
Volume [Å^3]	2211.12(14)	7959.2(3)
Z	2	4
Calculated density [Mg/m^3]	1.247	1.170
Absorption coefficient[mm^{-1}]	0.714	0.297
F(000)	870	2992
Crystal size [mm^3]	0.23×0.21×0.15	0.75×0.46×0.22
θ [°]	1.955 – 26.019	2.111 – 26.372
Reflections collected/ unique	27803 / 8700	163579 / 16278
R(int)	0.0485	0.0776
Final R indices [I>2sigma(I)]	R_1=0.0419, wR_2=0.0787	R_1=0.0699, wR_2=0.1488
R indices (all data)	R_1=0.0679, wR_2=0.0870	R_1=0.0923, wR_2=0.1596
S	1.049	1.123
Largest diff. peak and hole [e/Å^3]	0.360/-0.340	0.797/-0.522

IR spectra

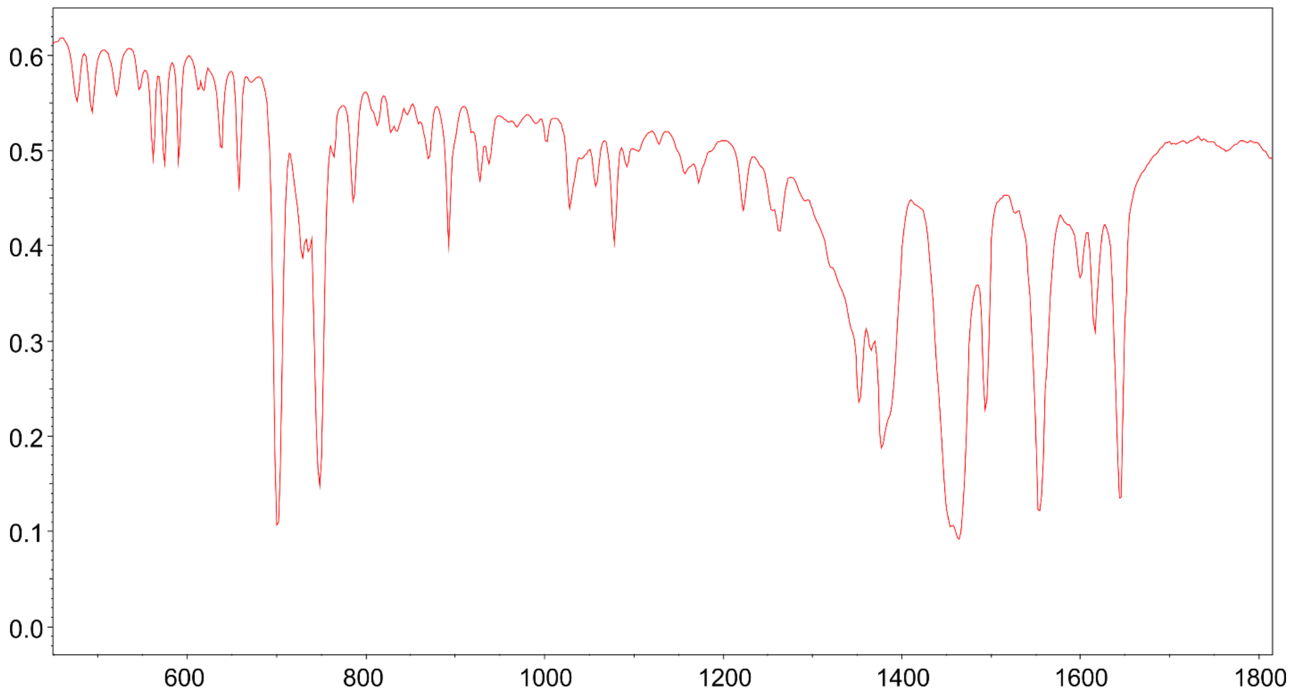

Figure S1. IR spectrum of **2** in nujol.

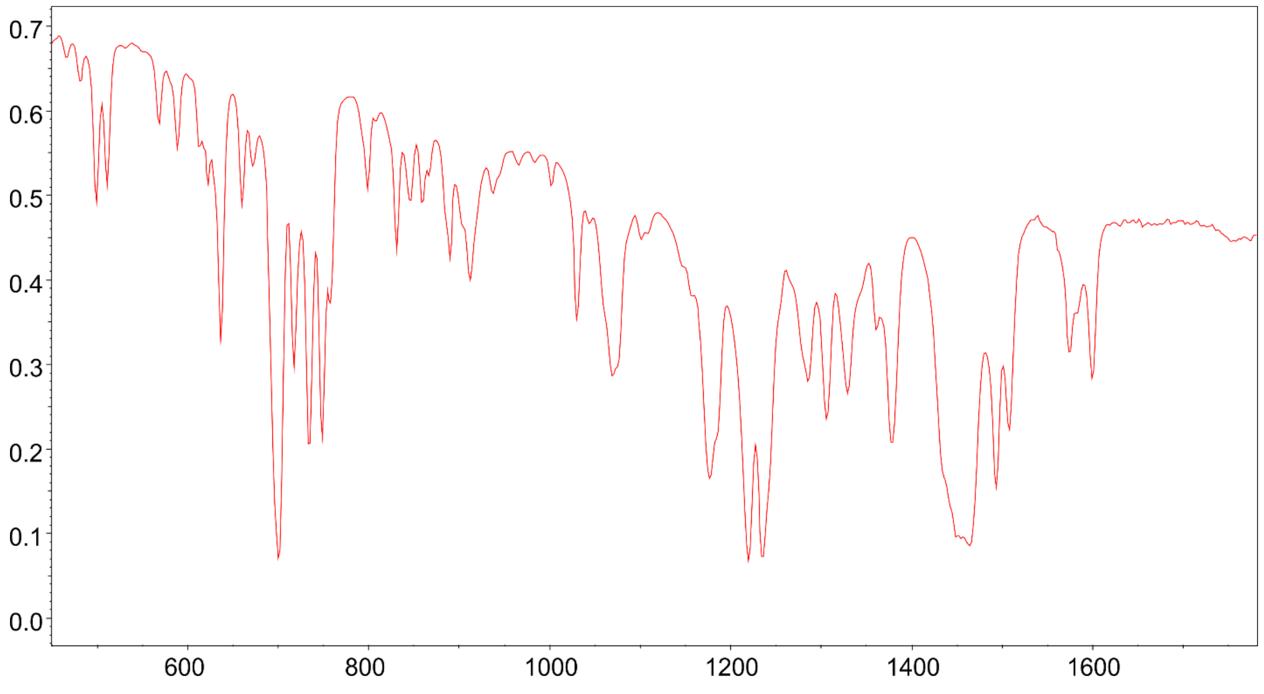

Figure S2. IR spectrum of **3** in nujol.

NMR spectra

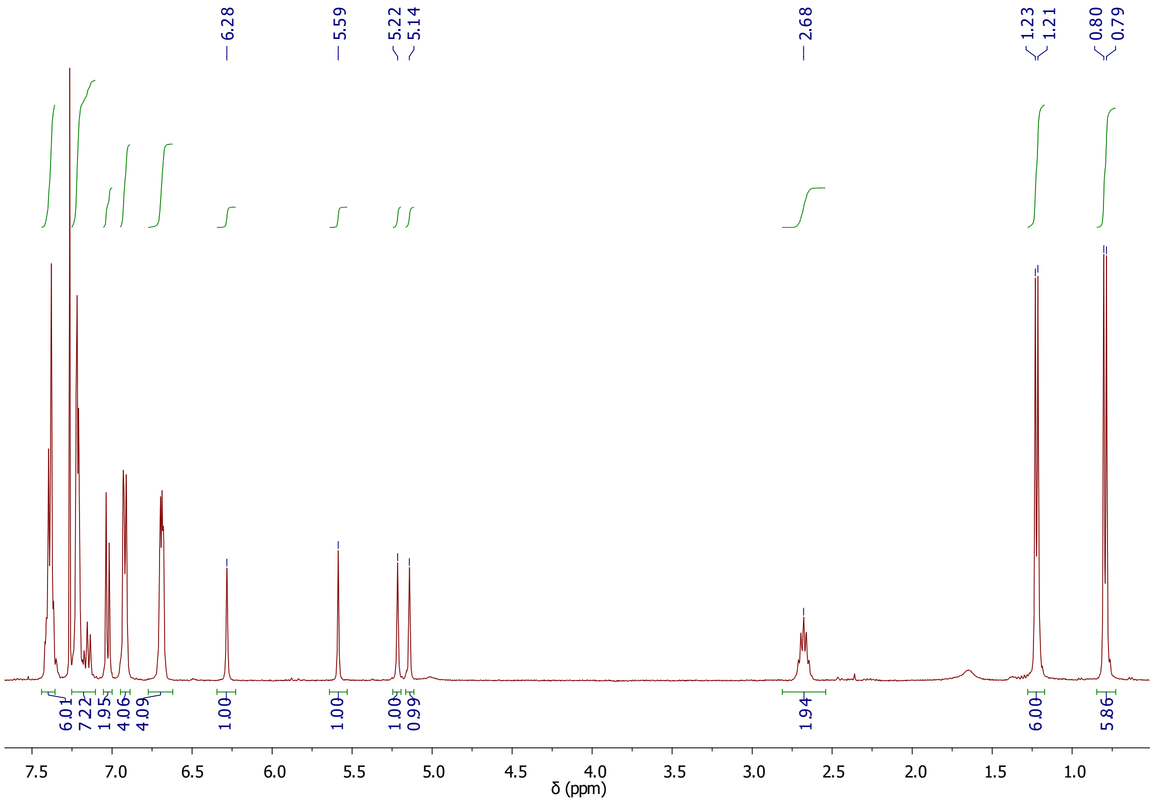

Figure S3.^{1}H-NMR spectrum of **2** $(CDCl_3)$

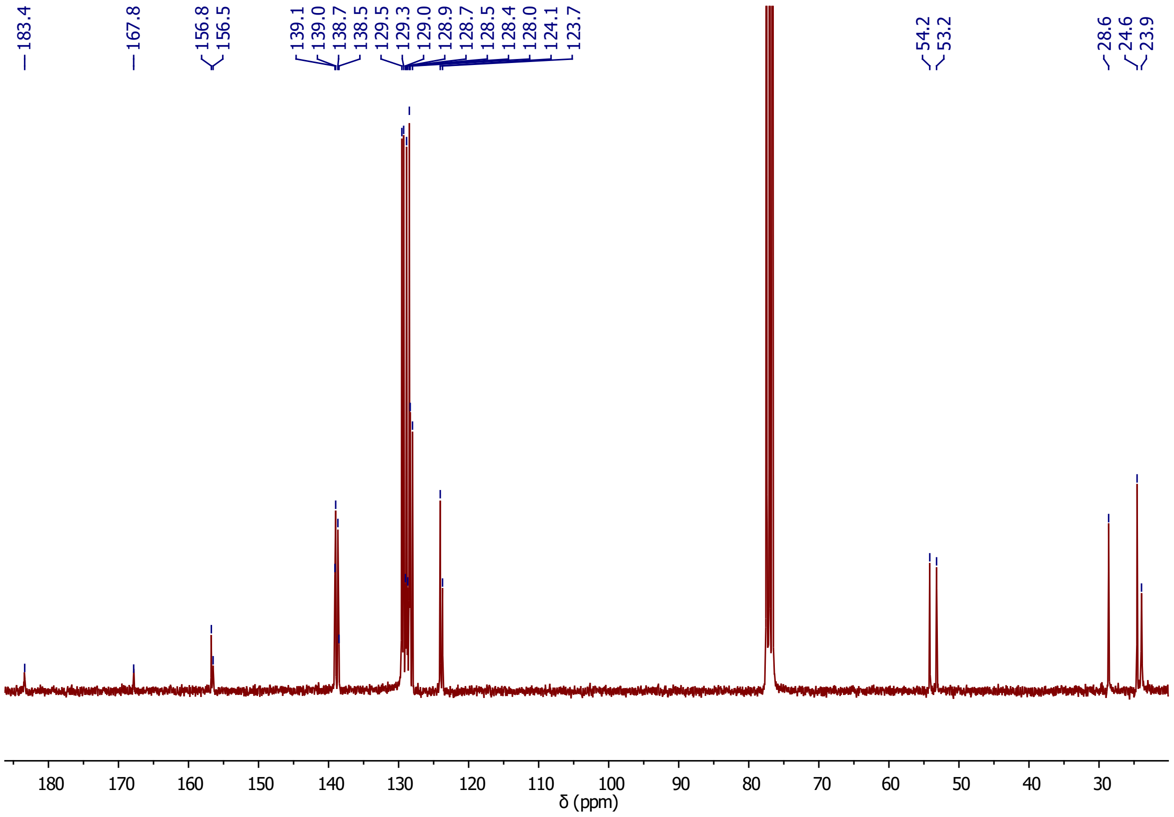

Figure S4.^{13}C-NMR spectrum of **2** $(CDCl_3)$

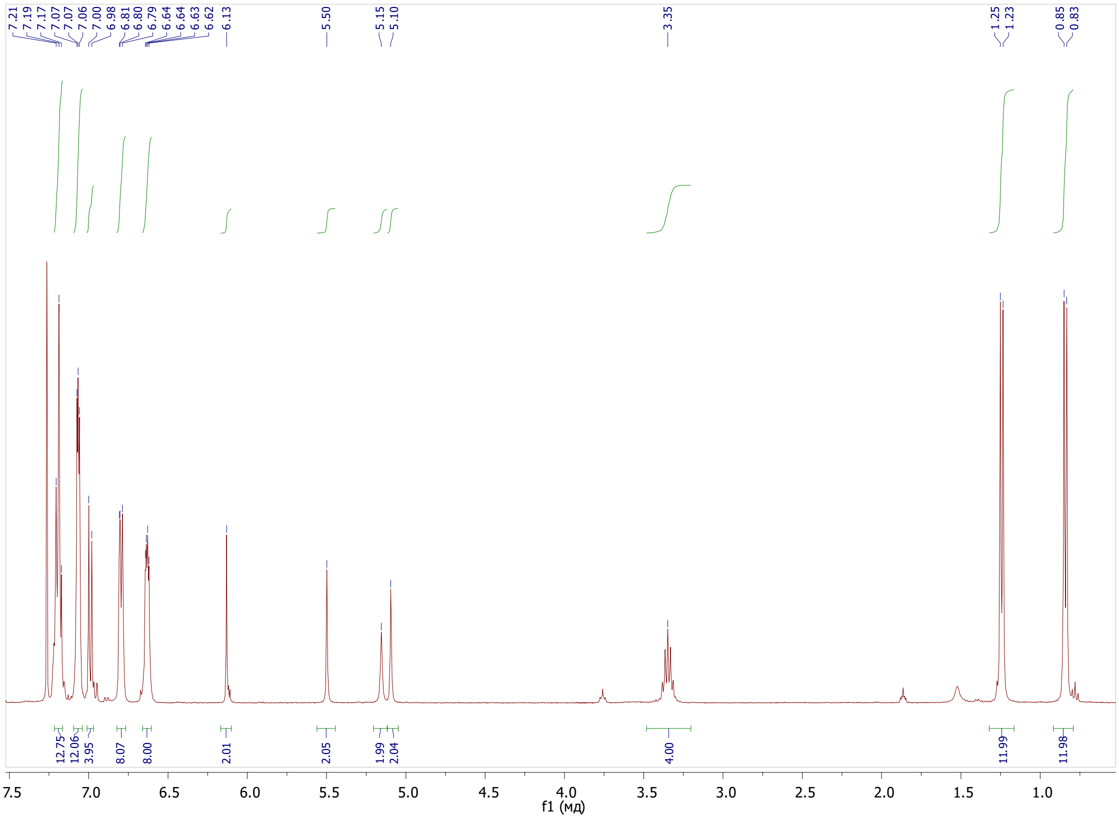

Figure S5. ^{1}H-NMR spectrum of **3** ($CDCl_3$)

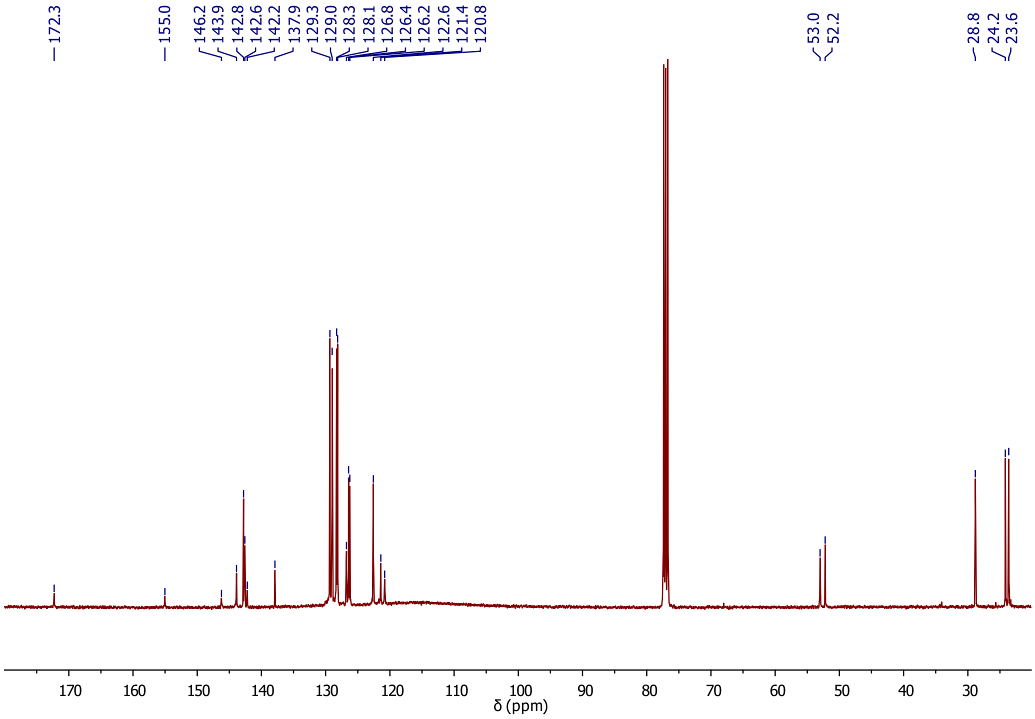

Figure S6.^{13}C-NMR spectrum of **3** ($CDCl_3$)

References

S1. V. K. Cherkasov, G. A. Abakumov, A. S. Shavyrin, V. V. Kuz'michev, E. V. Baranov, I. V. Smolyaninov and V. A. Kuropatov, Asian J. Org. Chem., 2015, 4, 446; https://doi.org/10.1002/ajoc.201500005.

S2. CrysAlisPro, Software System, version 1.171.43.93a, Rigaku Oxford Diffraction, Wroclaw, Rigaku Oxford Diffraction, 2020.

S3. G. M. Sheldrick, Acta Crystallogr., 2015, A71, 3; https://doi.org/10.1107/S2053273314026370.

S4. G. M. Sheldrick, Acta Crystallogr., 2015, C71, 3; https://doi.org/10.1107/S2053229614024218.