Supplementary Materials

Polymeric copper(II) complexes with a newly synthesized biphenyldicarboxylic acid Schiff base ligand – synthesis, structural and thermal characterization

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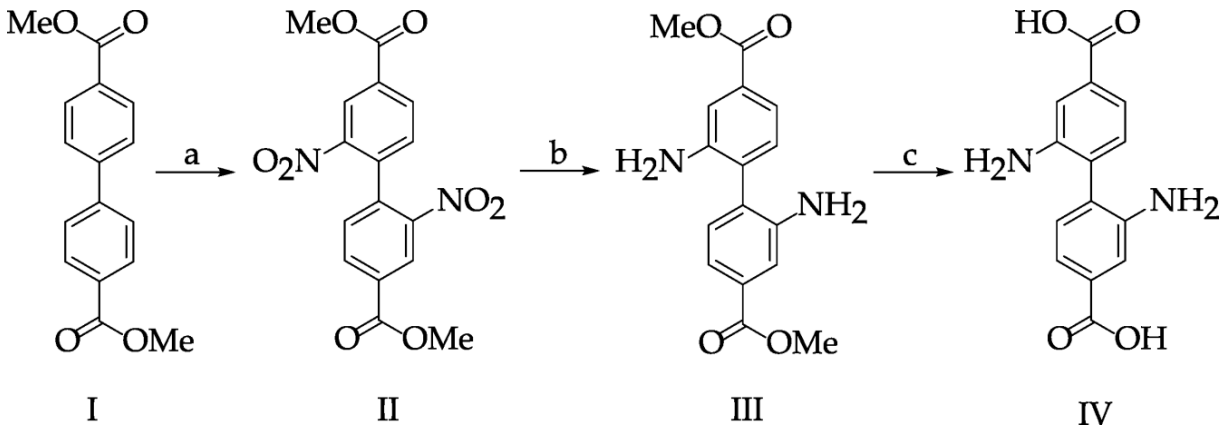
1. Preparation of III and IV

III

Dimethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate (**II**) (0.5 g, 1.39 mmol) dissolved in THF (28 mL) was added to a mixture of 1 % Pd/C catalyst (109.9 mg) in chilled MeOH (14.4 mL). Ammonium formate (799.8 mg, 12.68 mmol) was added portion-wise and the mixture was heated at 60 °C for 2 h. After cooling to room temperature, the Pd/C was removed by filtration and MeOH and THF were removed by rotary evaporation. The resulting precipitate was taken up in EtOAc (25 mL), then washed with H_2O (3 × 25 mL), brine and dried over anhydrous Na_2SO_4. After removing the solvent by rotary evaporation the crude product was recrystallized from EtOH. Yield 358 mg, 86%. ν_{max}/cm^{-1} (ATR): 3449 w, 3358 m, 3232 w, 3065 w, 2999 w, 2949 w, 2846 w, 2100 w, 1784 w, 1696 s, 1614 m, 1564 m, 1515 w, 1495 w, 1436 m, 1418 s, 1373 w, 1297 s, 1280 m, 1233 s, 1195 s, 1158 m, 1112 s, 1045 m, 999 m, 986 m, 893 m, 829 w, 795 m, 762 s, 750 s, 731 s, 669 m, 584 m, 555 s, 523 s, 487 m, 453 s, 425 s, 406 m, 402 m.

IV

A mixture of dimethyl 2,2'-diamino-[1,1'-biphenyl]-4,4′-dicarboxylate (**III**) (350 mg, 1.17 mmol) in THF (11.7 mL) and aq. 1 M KOH (4 mL) was heated for reflux for 16 hours. After cooling to room temperature the THF was removed by rotary evaporation and the solution was acidified with 1M HCl. The resulting yellow precipitate was separated by filtration washed with water then methanol and air-dried. Yield 286 mg, 90%. ^{1}H NMR (400 MHz, DMSO-d_6) 12.68 (br s, 2H, H5), 7.43 (d, J = 1.7 Hz, 2H, H3), 7.23 (dd, J = 9.5 Hz, 2H, H2), 7.06 (d, J = 7.8 Hz, 2H, H1), 4.94 (br s, 4H, H4). ν_{max}/cm^{-1} (ATR): 3421 w, 3359 w, 2798 w, 2527 w, 2285 w, 1687 m, 1615 w, 1547 m, 1506 m, 1412 m, 1389 w, 1302 m, 1281 m, 1264 m, 1228 s, 1139 w, 1113 w, 920 m, 882 m, 837 m, 786 s, 764 s, 754 s, 715 m, 660 s, 610 m, 579 m, 554 s, 458 s, 430 s.



Scheme S1. Synthesis of **IV**. Reagents and conditions: (a) cc H_2SO_4, 65% HNO_3 (2 eq), 15–20 °C, 1 h; (b) Pd/C, MeOH, THF, 60 °C, 2 h (c) 1 M KOH, THF/H_2O, reflux, 16 h, then 1M HCl.

2. FTIR Spectra of IV and desolvated form of 2

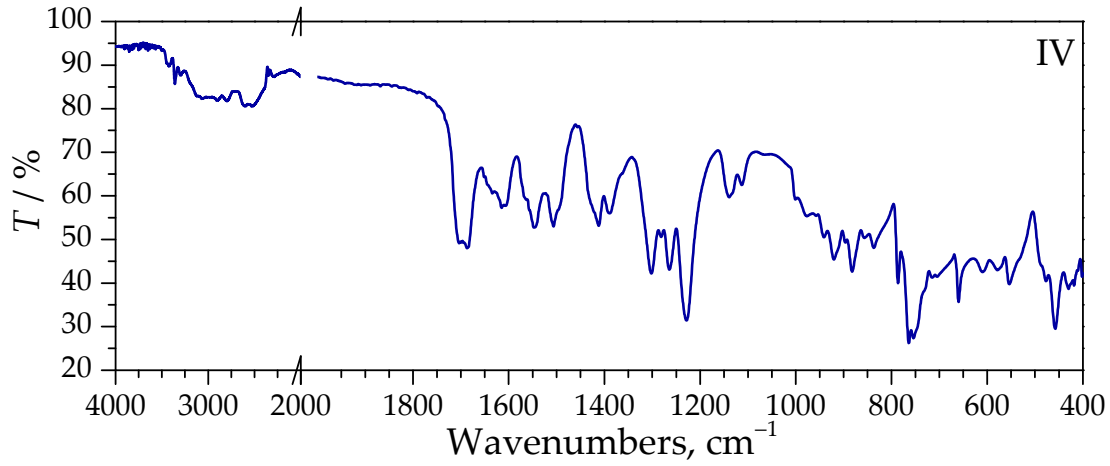


Figure S1. FTIR spectrum of **IV.**

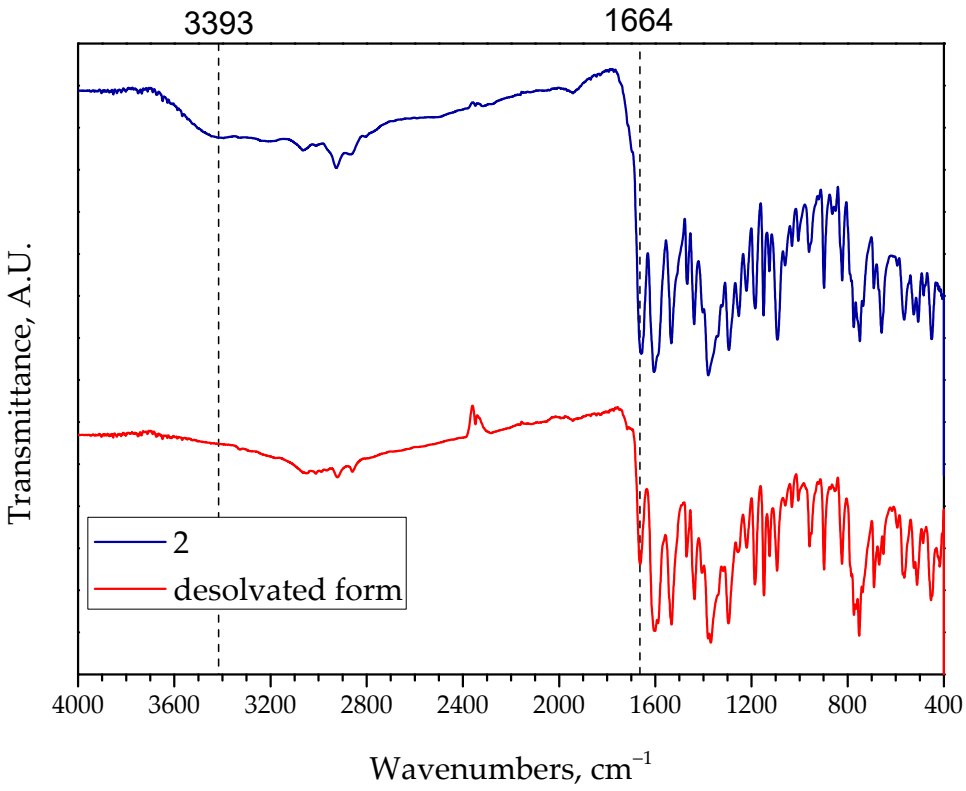


Figure S2. FTIR spectra of **2** and its desolvated form.

3. NMR Spectra of IV and H_4L

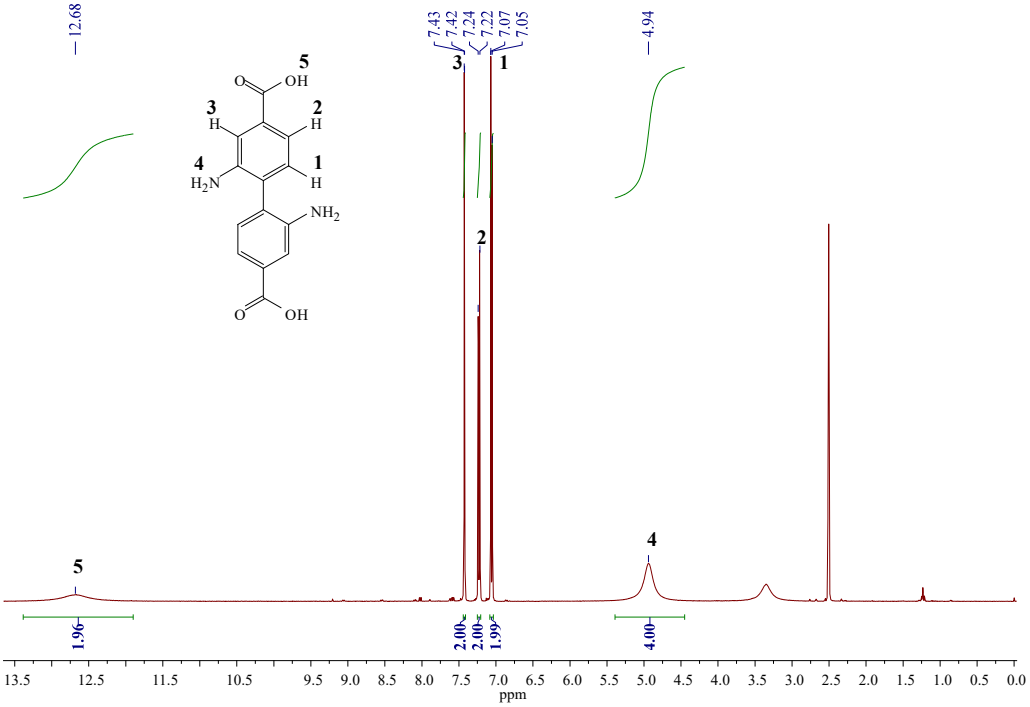


Figure S3. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **IV**

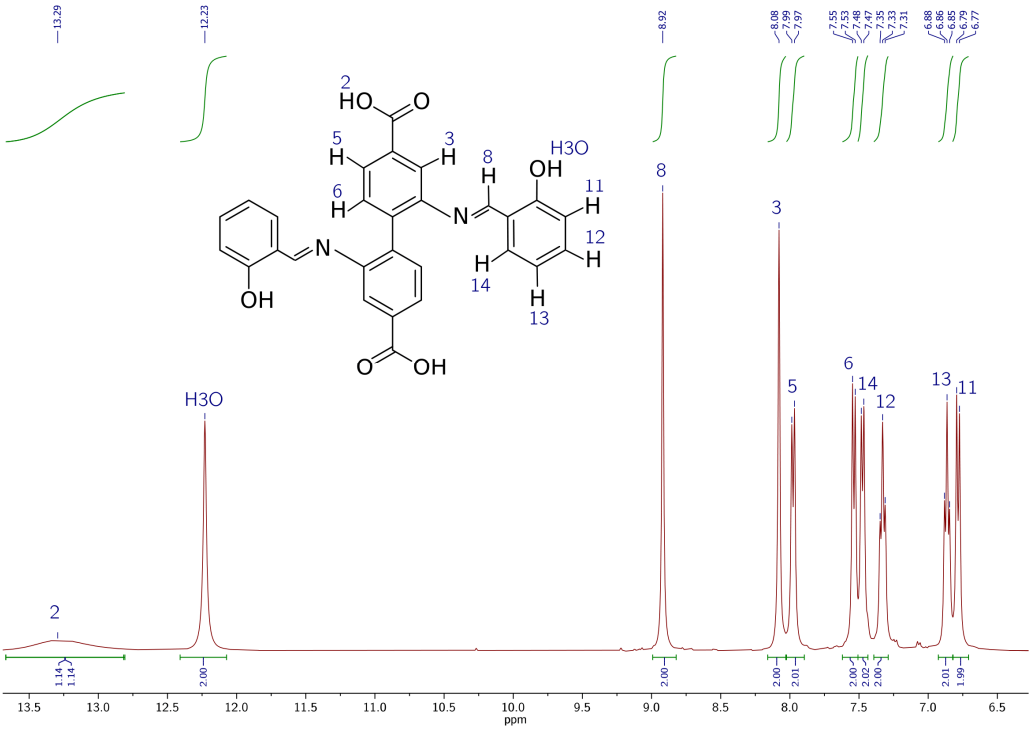


Figure S4. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **H_4L.**

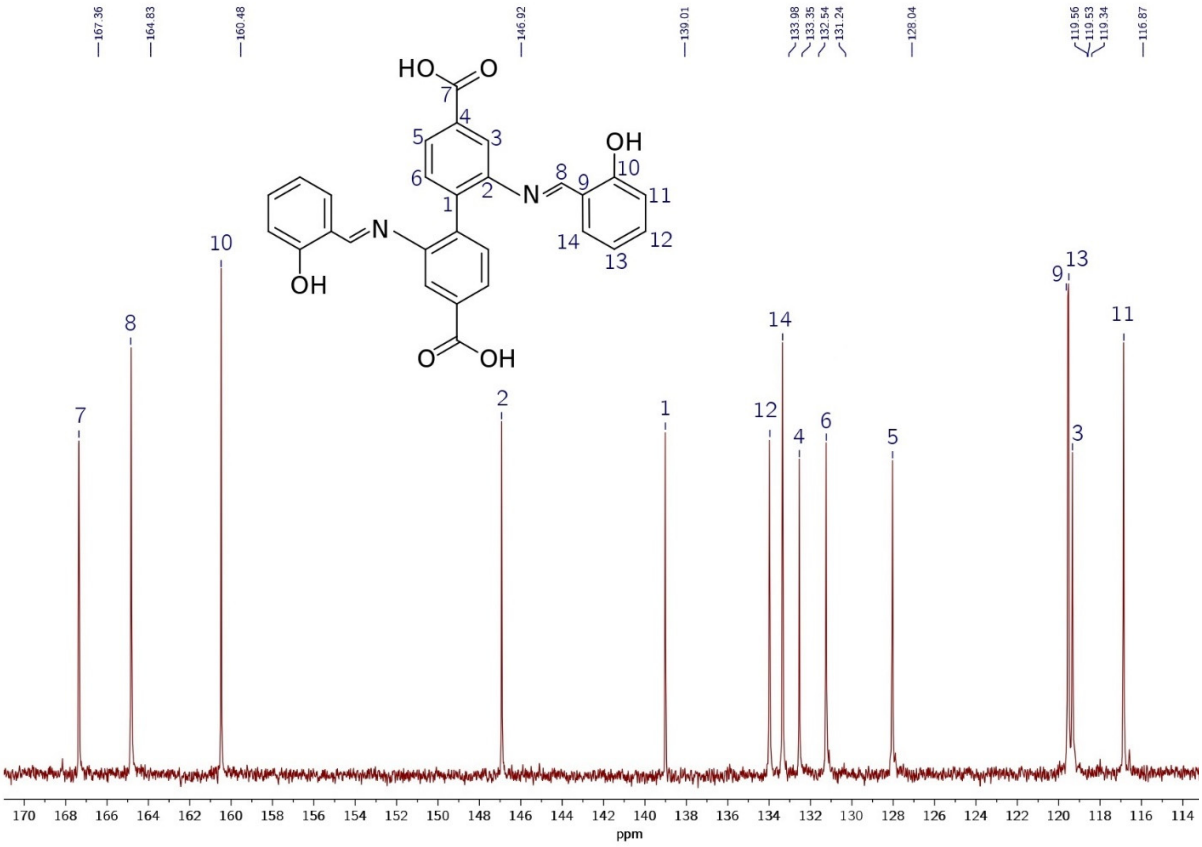


Figure S5. ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of **H$_4$L.**

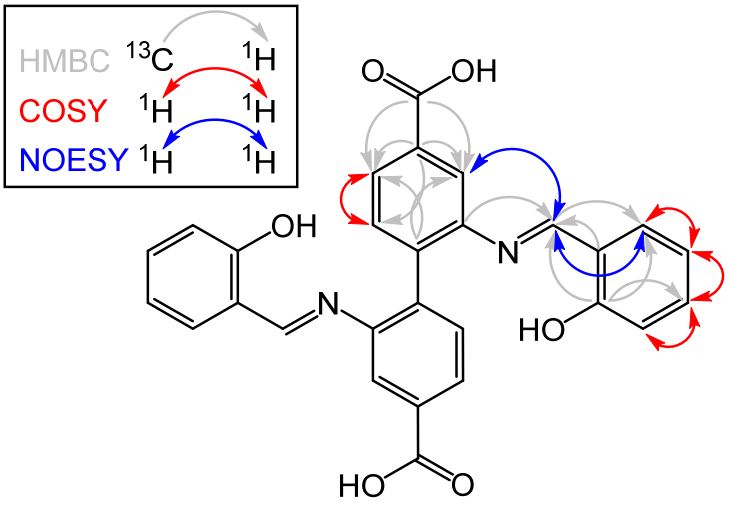


Figure S6. Relevant HMBC (in gray), COSY (in red), and NOESY (in blue) correlations of **H$_4$L**.

4. Single Crystal Data

Table S1. Crystallographic and refinement details.

	H_4L·3DMF	**1**	**2**
Crystal data			
Chemical formula	$C_{28}H_{20}N_2O_6·3(C_3H_7NO)$	$C_{28}H_{18}CuN_2O_6$ [+solvent]	$C_{28}H_{18}CuN_2O_6·C_3H_7NO$
M_r	699.75	541.98	615.08
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*–1	$P2_1/c$	$P2_1/c$
a / Å	10.6732 (2)	9.8123 (16)	15.4534 (5)
b / Å	12.9669 (4)	16.0633 (19)	9.8628 (3)
c / Å	14.7722 (4)	17.156 (3)	19.2122 (8)
α / °	70.686 (3)	90	90
β / °	85.775 (2)	98.827 (16)	109.527 (4)
γ / °	73.868 (2)	90	90
V / Å^3	1853.04 (9)	2672.1 (7)	2759.79 (18)
Z	2	4	4
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ / mm^{-1}	0.75	0.86	0.85
Crystal size, mm	0.94 × 0.55 × 0.28	0.35 × 0.12 × 0.08	0.35 × 0.13 × 0.05
Data collection			
Absorption correction	Analytical	Analytical	Analytical
T_{min}	0.624	0.829	0.946
T_{max}	0.835	0.933	0.991
Measured reflections	40554	17613	27320
Independent reflections	7204	5474	5643
Observed reflections [$I>2\sigma(I)$]	5933	2417	3572
R_{int}	0.029	0.126	0.076
$(\sin\theta/\lambda)_{max}$ / Å^{-1}	0.617	0.628	0.625
Refinement			
R [$F^2 > 2\sigma(F^2)$]	0.074	0.087	0.065
wR [F^2]	0.258	0.242	0.193
S	1.09	1.02	1.03
Reflections	7204	5474	5643
Parameters	470	337	383
H-atom treatment	Mixed	Mixed	Constrained
$\Delta\rho_{max}$ / e Å^{-3}	1.08	0.44	1.86
$\Delta\rho_{min}$ / e Å^{-3}	−0.38	−0.78	−0.47

Table S2. Selected dihedral angles of structures with 2,2'-bis(((*E*)-2-hydroxybenzylidene)amino)-[1,1'-biphenyl] fragment.

CSD refcode	δ(ph1–sal1) / °	δ(ph2–sal2) / °	δ(ph1–ph2) / °
BAMWUI	38,4	38,7	73,7
DUYLOB	24,7	25,2	62,1
EYUROF	19,5	26,6	62,8
EYUROF	38,5	46,7	63,0
KEYGIH	35,2	37,2	56,3
KEYGON	6,8	26,5	71,3
KEYGUT	16,7	16,9	67,7
KEYHAA	35,9	37,6	56,1
LOCTOP	15,0	15,2	79,5
LOCTUV	10,4	10,5	79,3
LOCVAD	13,6	14,3	71,3
LOCVEH	12,2	12,3	70,7
QADDEH	33,9	34,7	89,4
QICPOH	24,8	28,2	73,6
RUVRIM	41,6	41,7	43,7
RUVRUY	14,0	26,7	65,5
TISGIL	34,6	34,7	89,0

Table S3. Hydrogen bonding geometry parameters for complexes **1** and **2**.

Bond		**Distances (Å)**		**Angles (°)**	**Symmetry operation on *A***
D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*	
1					
O2–H2· · · O3	0.82	1.82	2.623(6)	166.9	$-x$, y+1/2, $-z$+1/2
O2′–H2′· · · O3′	0.82	1.87	2.660(6)	159.9	x+1, y, z
2					
O2′–H2′· · · O4	0.82	1.85	2.642(8)	163.3	
O2–H2· · · O3	0.82	1.83	2.620(4)	161.9	x, y−1, z

Table S4. Structural parameters of π···π and C–H···π interactions in the crystal structures of **1** and **2**

Cg(*m*)···Cg(*n*)	***d*(Cg···Cg) / Å**	***α* / °**	***β* / °**	***γ* / °**	**Symmetry operation on Cg(*n*)**
1					
Cg(1)···Cg(1)	3.820(5)	0.0(4)	25.1	25.1	−*x*+1, −*y*, −*z*+1
2					
Cg(2)···Cg(2)	3.889(3)	0.0(3)	27.9	27.9	−*x*, −*y*+1, −*z*+1
C–H···Cg(*n*)	***d*(C···Cg) / Å**	***d*(H···Cg) / Å**	**∠(C–H···Cg) / °**	***δ* / °**	**Symmetry operation on Cg(*n*)**
1					
C8–H8···Cg(1)	3.730(8)	2.86	156	17.89	*x*, −*y*+1/2, *z*−1/2
C13–H13···Cg(3)	3.644(11)	2.96	132	18.00	*x*, −*y*+1/2, *z*−1/2
C13'–H13'···Cg(3)	3.554(11)	2.95	124	10.83	*x*, −*y*+1/2, *z*+1/2
2					
C12'–H12'···Cg(3)	3.514(6)	2.78	137	12.49	*x*, −*y*+1/2, *z*−1/2
C13–H13···Cg(4)	3.788(7)	2.98	146	3.70	−*x*, −*y*+1, −*z*+1
C17–H17A···Cg(2)	3.521(12)	2.72	141	8.10	*x*+1, −*y*+3/2, *z*+1/2

Cg = geometric center of a ring; *α* = dihedral angle between mean planes of rings *m* and *n*; *β* = angle between Cg(*m*)→Cg(*n*) vector and normal to mean plane of ring *m*; *γ* = angle between Cg(*m*)→Cg(*n*) vector and normal to mean plane of ring *n*; *δ* = angle between Cg(*n*)→H vector and normal to mean plane of ring *n*. Ring numbering: (1) C9',C10',C11',C12',C13',C14'; (2) C9,C10,C11,C12,C13,C14; (3) C1,C2,C3,C4,C5,C6; (4) C1',C2',C3',C4',C5',C6'.

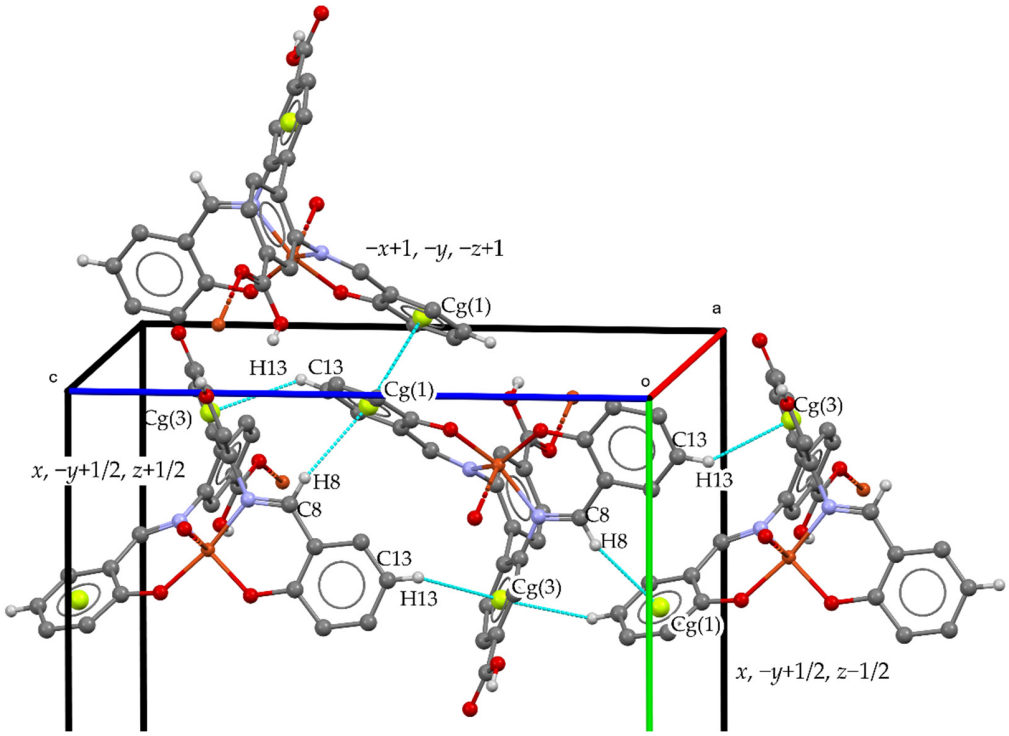


Figure S7. Intermolecular π···π and C–H···π interactions in the crystal structure of **1**. Only relevant hydrogen atoms involved are shown.

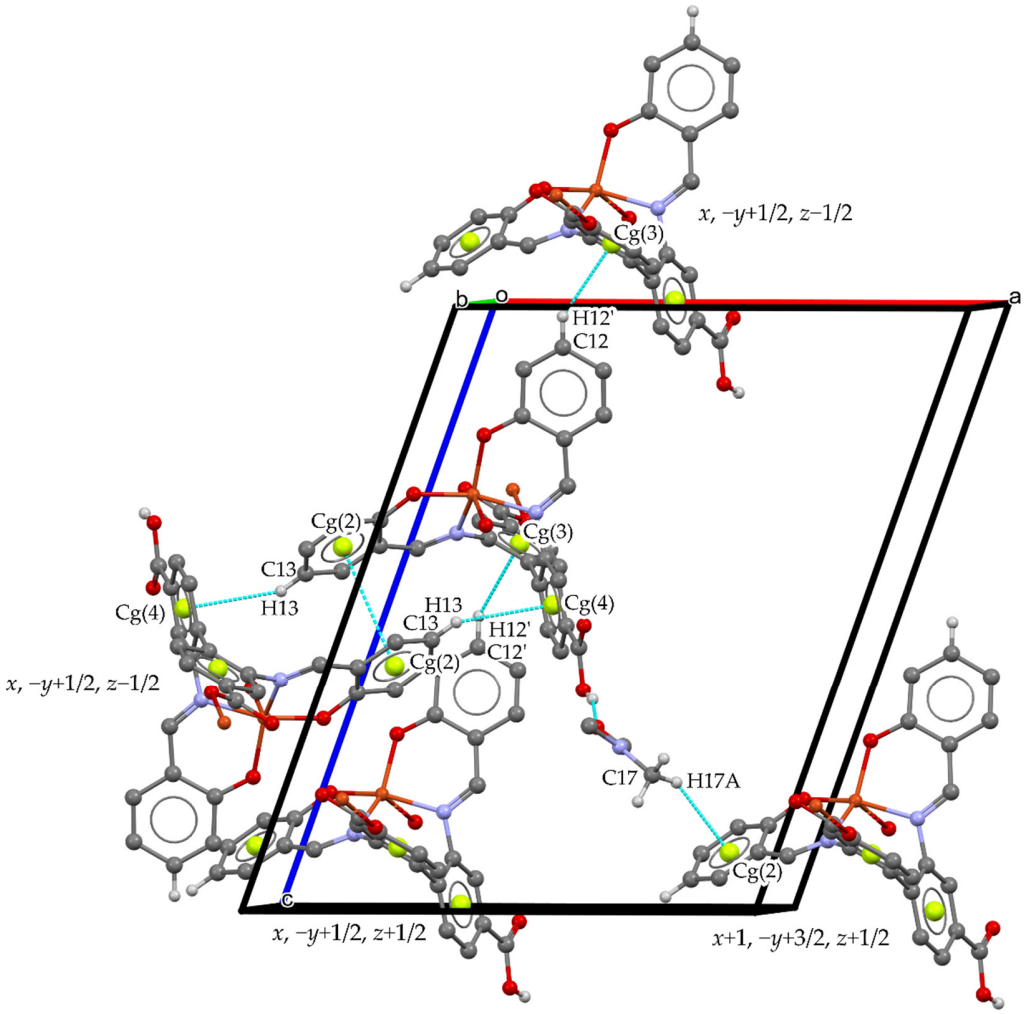


Figure S8. Intermolecular π···π and C–H···π interactions in the crystal structure of **2**. Only relevant hydrogen atoms involved are shown.