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Supporting Information

69451 Weinheim, Germany

The Confined Cavity of a Self-Assembled Cage Suppresses the Photochemical Cleavage of α-Diketones to Give Kinetically Unfavorable Cyclization Products

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Contents

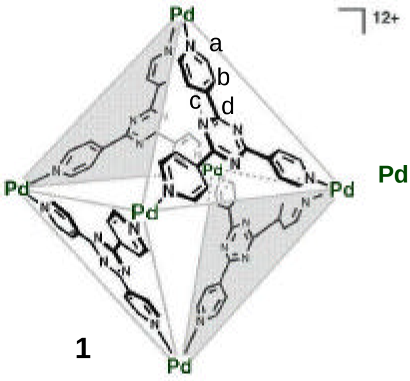
General

NMR spectra were recorded on Bruker DRX-500 (500 MHz) and AV-500 (500 MHz) spectrometers. All NMR spectral data were collected at 300 K. TMS (in $CDCl_3$ solution) in a capillary served as internal standard ($\delta = 0$ ppm). GC-MS spectra were obtained on an Agilent 5973 inert Mass selective Detector equipped with a 6890N Network GC system and an EI source. FAB-MS spectra were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with a FAB source. IR measurements were carried out as KBr pellets using a Varian Scimitar FTS-2000 instrument. The X-ray diffraction data were measured on a Bruker APEX-II CCD diffractometer equipped with a micro-focused rotating anode system combined with an X-ray focusing mirror (MoKa radiation, $\lambda = 0.71073$ Å) with a cryostat system equipped with a N_2 generator (XR-HR 10K, Japan Thermal Eng. Co., Ltd.). The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) using the SHELX-TL program package. Photoirradiation was carried out with a SEN LIGHTS CORP. HL400JH-3 400W high-pressure mercury lamp. GPC was performed on JAIGEL-2H and JAIGEL-1H columns in a series connection purchased from Japan Analytical Industry Co., Ltd. Solvents and reagents were purchased from TCI Co., Ltd. All the chemicals were used without any further purification.

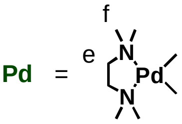
Procedure

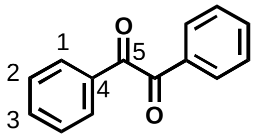
1. Encapsulation of diphenylethanedione (**2**) within the cage **1**.

Excess amount of diphenylethanedione (**2**) (5.4 equiv., 2.6 µmol, 5.4 mg) was suspended in a solution of **1** (0.481 µmol, 16.0 mg) in 0.6 mL of D_2O and stirred at 100 °C for 1 h. Insoluble **2** was filtrated to give the solution of **1**⊃(**2**)$_2$.



1





2

2. Physical data of **1**⊃(**2**)$_2$.

^{1}H NMR (500 MHz, D_2O, TMS): d (ppm) = 2.77 (s, 72H, f), 3.19 (s, 24H, e), 4.12 (br, 4H, 3), 5.37 (br, 8H, 2), 5.41 (br, 8H, 1), 8.69 (br, 24H, b), 9.43 (br, 24H, a). ^{13}C NMR (125 MHz, D_2O, TMS): d (ppm) = 50.48 (f), 62.91 (e), 126.36 (b), 127.62 (1), 128.37 (2), 130.28 (4), 133.00 (3), 145.20 (c), 152.25 (a), 168.72 (d), 193.35 (5). IR (KBr): ν (cm^{-1}) = 3097, 2924, 1668, 1618, 1595, 1575, 1519, 1373, 1354, 1211, 1174, 1061, 1007, 955, 810, 673, 642. Anal. Calcd for $C_{136}H_{222}N_{48}O_{69}Pd_6$ (**1**·(**2**)$_2$·(H_2O)$_{29}$): C, 38.24; H, 5.24; N, 15.74. Found: C, 38.55; H, 5.61; N, 15.98. m.p.: >200 °C (decomposed).

3. Photoreaction of **2** within the cage **1**.

A solution of **1**$\supset$(**2**)$_2$ in H_2O (0.919 g, 8 mM) was thoroughly degassed and sealed in a glass tube. Then the solution was irradiated by a high pressure mercury lamp for 6 h. Crude solution was obtained by extraction with $CDCl_3$, and analyzed by ^1H NMR with CH_2Br_2 as an internal standard, The yields of 2-phenyl-3-benzo[b]furanone (**3**), 2-hydroperoxy-2-phenyl-3-benzo[b]furanone (**4**), and *o*-hydroxylbenzil (**5**) were calculated as 31%, 7%, and 14%, respectively. The products were purified by GPC, silica gel chromatography, and recrystallization to give **3**, **4** and **5**.

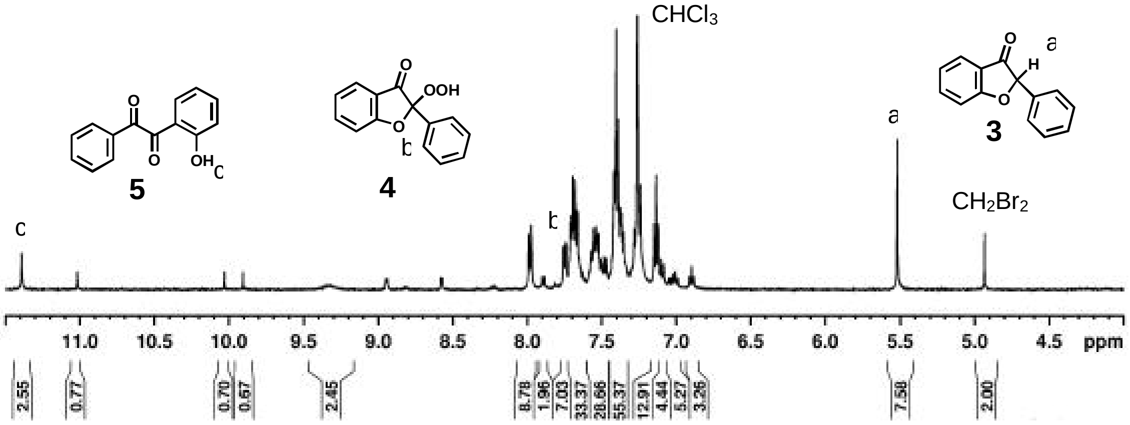


Figure S1. ^1H NMR spectrum (500 MHz, $CDCl_3$, 300 K) of crude solution.

f

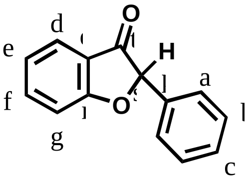
4. Physical data of **3**, **4**, and **5**.

Physical data of 2-phenyl-3-benzo[b]furanone (**3**).

Compound **3** was previously reported in the references (K. Hanaya, T. Muramatsu, E. Hasegawa, *Chem. & Ind.* **1990**, *23*, 802; M. N. Kanvinde, R. M. Kelkar, M. V. Paradkar, *Synth. Commun.* **1993**, *23*, 961; Z. M. Wang, X. T. Liang, S. F. Chen, *Chin. Chem. Lett.* **1996**, *7*, 419; S. Ghosh, I. Banerjee, S. Baul, *Tetrahedron* **1999**, *55*, 11537.) However, all references cite the reference (J. N. Chatterjea, C. Bhakta, *Ind. J. Chem.* **1976**, *53*, 293) for identification of **3** that is wrong. The correct physical data of **3** we definitely determined is as follows:

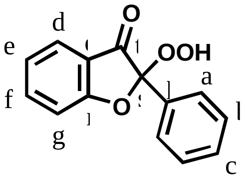
^1H NMR (500 MHz, C_6D_6, TMS): d (ppm) = 5.02 (s, 1H, p), 6.52 (dd, J_1 = 7.7 Hz, J_2 = 7.3 Hz, 1H, e), 6.79 (d, J_1 = 8.4 Hz, 1H, g), 6.97 (dd, J_1 = 7.3 Hz, J_2 = 8.4 Hz, 1H, f), 7.00 (t, J_1 = 7.2 Hz, 1H, c), 7.02 (dd, J_1 = 6.9 Hz, J_2 = 7.2 Hz, 2H, b), 7.28 (d, J_1 = 6.9 Hz, 2H, a), 7.46 (d, J_1 = 7.7 Hz, 1H, d). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): d (ppm) = 85.52 (s), 112.98 (g), 120.52 (q), 121.92 (e), 124.63 (d), 125.92 (a), 118.33 (c), 128.56

(b), 134.32 (p), 137.32 (f), 172.62 (r), 197.77 (t). IR (KBr): ν (cm^{-1}) = 1704, 1608, 1476, 1462, 1324, 1310, 1214, 1193, 1145, 1104, 970, 860, 764, 700, 612, 501. GC-MS (EI): *m/z*: 210 [M^+]. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.77; H, 4.88. m.p.: 80 °C (decomposed).



Physical data of 2-hydroperoxy-2-phenyl-3-benzo[b]furanone (**4**).

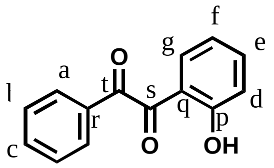
^{1}H NMR (500 MHz, $CDCl_3$, TMS): d (ppm) = 7.13 (dd, J_1 = 7.5 Hz, J_2 = 7.8 Hz, 1H, f), 7.26 (d, J_1 = 7.5 Hz, 1H, d), 7.39 (dd, J_1 = 7.8 Hz, J_2 = 7.9 Hz, 2H, b), 7.41 (t, J_1 = 7.8 Hz, 1H, c), 7.66 (d, J_1 = 7.7 Hz, 1H, g), 7.70 (dd, J_1 = 7.7 Hz, J_2 = 7.8 Hz, 1H, e), 7.42 (d, J_1 = 7.9 Hz, 2H, a), 8.79 (br, 1H, -OO*H*). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): d (ppm) = 109.29 (s), 113.00 (d), 119.36 (q), 122.93 (f), 125.35 (g), 126.64 (a), 128.70 (b), 130.92 (c), 131.33 (p), 139.11 (e), 170.70 (r), 194.55 (t). IR (KBr): ν (cm^{-1}) = 3293, 1719, 1614, 1481, 1463, 1406, 1325, 1247, 1153, 987, 956, 860, 761, 692, 642, 611, 511. FAB-MS *m/z*: 243.1 [$M+H^+$] (matrix: grycerol, calc. 243.1). Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.21; H, 4.30. m.p.: 96.6-97.3 °C.



Physical data of *o*-hydroxylbenzil (**5**).

Compound **5** was identified by NMR, IR, GC-MS, and E.A. (C. E. Spivak, F. L. Harris, *J. Org. Chem.* **1972**, *37*, 2494).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): d (ppm) = 6.88 (dd, J_1 = 7.4 Hz, J_2 = 8.1 Hz, 1H, f), 7.09 (d, J = 8.5 Hz, 1H, d), 7.47 (d, J = 8.1 Hz, 1H, g), 7.54 (dd, J_1 = 7.4 Hz, J_2 = 7.7 Hz, 2H, b) , 7.54 (dd, J_1 = 8.5 Hz, J_2 = 7.4 Hz, 1H, e), 7.68 (t, J_1 = 7.4 Hz, 1H, c), 7.98 (d, J_1 = 7.7 Hz, 1H, a), 11.39 (s, 1H, -O*H*). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): d (ppm) = 117.01 (q), 118.87 (d), 119.88 (f), 129.31 (b), 130.20 (a), 132.58 (g), 132.85 (r),135.36 (c), 138.26 (e), 163.55 (p), 192.16 (t), 199.47 (s). IR (KBr): ν (cm^{-1}) = 1682, 1631, 1595, 1572, 1485, 1451, 1309, 1229, 1199, 1155, 1029, 894, 831, 772, 646, 526. GC-MS (EI) *m/z*: 226 [M^+] Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.10; H, 4.60.   m.p.: 71.9-72.4 °C.



5. **Control experiments**: Photoreaction of **2** in cyclohexane and in H_2O-MeOH solvent.

5.1. Photoreaction of **2** in cyclohexane.

Diphenylethanedione **2** (16.8 mg, 0.0800 mmol, 16 mM) was dissolved in dry cyclohexane (5 mL). The solution was degassed and irradiated by a high pressure mercury lamp for 3 h. After irradiation, the solvent was evaporated, and residue was dissolved in $CDCl_3$. After addition of CH_2Br_2 as an internal standard, ^{1}H NMR spectrum was recorded. By integral ratio, the yields of benzaldehyde, cyclohexyl phenyl ketone, and benzoic acid were calculated as 5%, 10%, and 10%, respectively. The formation of the three products was confirmed by comparison of ^{1}H NMR spectra of authentic samples recorded in the same conditions.

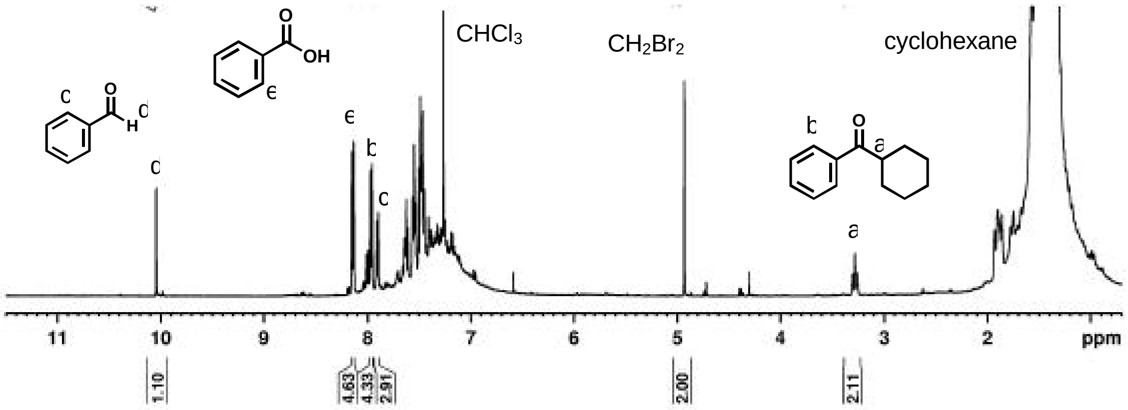


Figure S2. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 300 K) of crude solution.

5.2. Photoreaction of **2** in aqueous conditions (H_2O : MeOH = 6 : 4).

Diphenylethanedione **2** (2.59 mg, 12.3 μmol, 4 mM) was dissolved in an aqueous solvent (H_2O : methanol = 6 : 4, 3 mL). The solution was degassed and irradiated by a high pressure mercury lamp for 30 min. After evaporation of methanol, extraction by $CDCl_3$, and addition of CH_2Br_2 as an internal standard, ^1H NMR spectrum was recorded. By integral ratio, the yield of **3** was calculated as 0.86%.

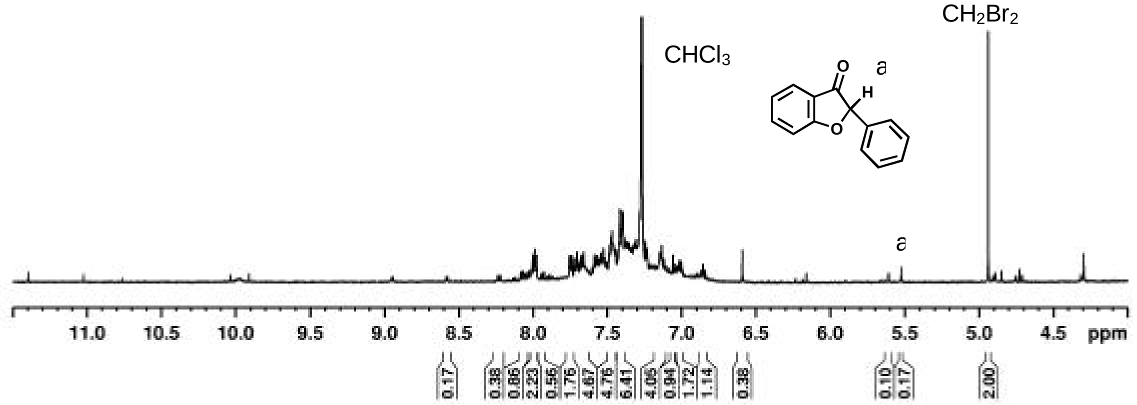


Figure S3. ^1H NMR spectrum (500 MHz, $CDCl_3$, 300 K) of crude solution.

NMR spectra

· ^{1}H NMR/^{13}C NMR/HH COSY/HSQC spectra of $\mathbf{1}\supset(\mathbf{2})_2$.

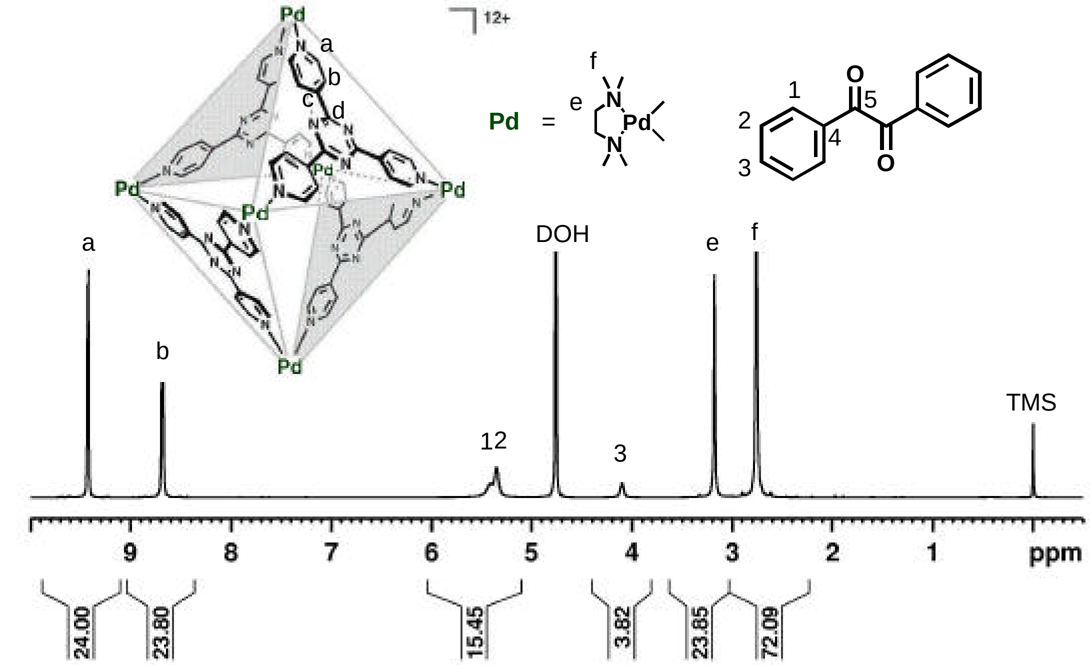


Figure S4. ^{1}H NMR spectrum (500 MHz, D_2O, 300 K) of $\mathbf{1}\cdot(\mathbf{2})_2$.

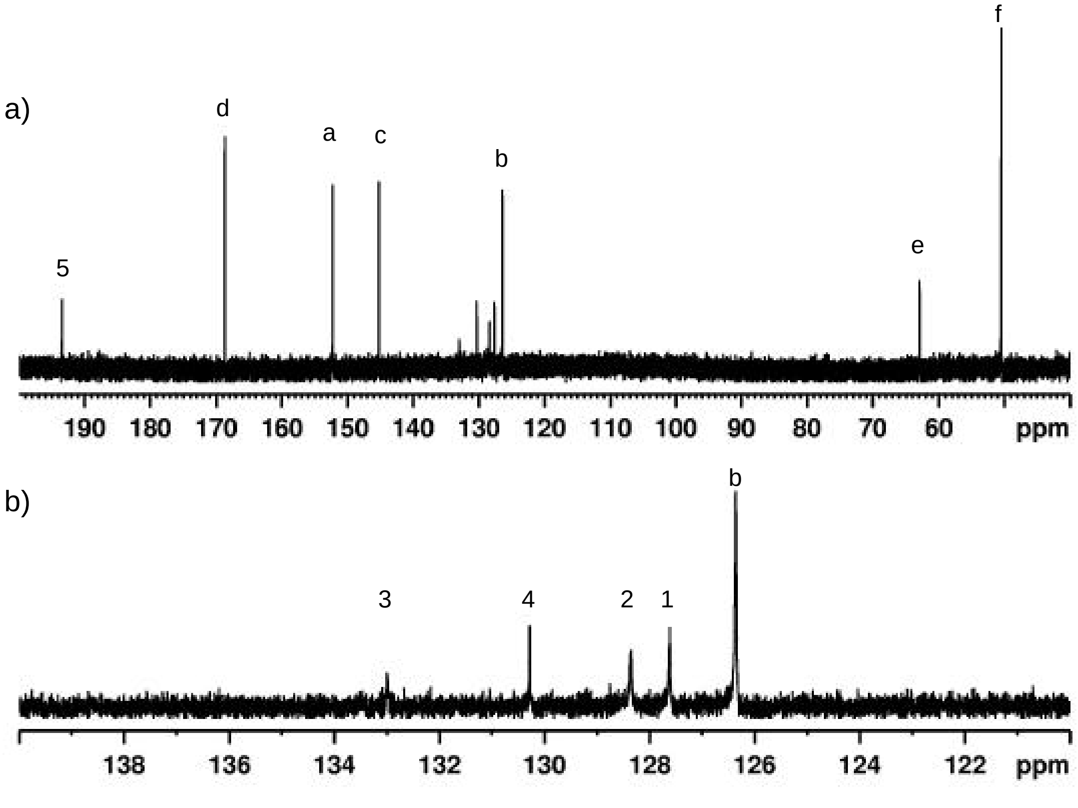


Figure S5. ^{13}C{1H} NMR spectra (125 MHz, D_2O, 300 K) of $\mathbf{1}\cdot(\mathbf{2})_2$: a) whole spectrum and b) enlarged spectrum from 140 ppm to 120 ppm.

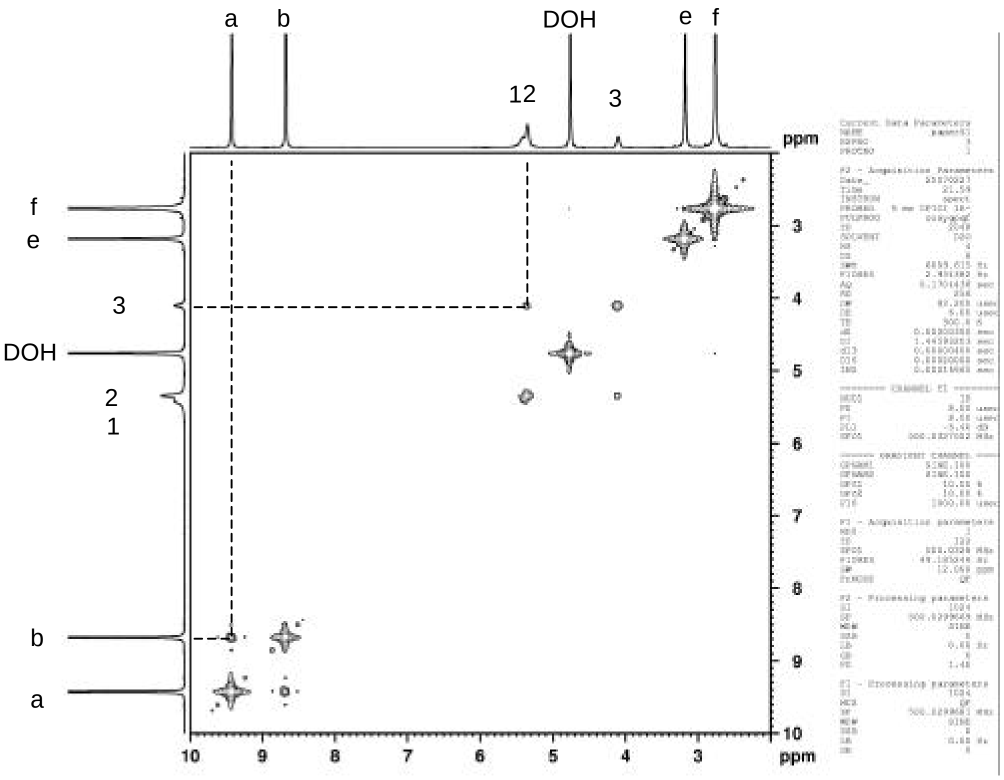


Figure S6. HH COSY spectrum (500 MHz, D_2O, 300 K) of **1**·(**2**)$_2$.

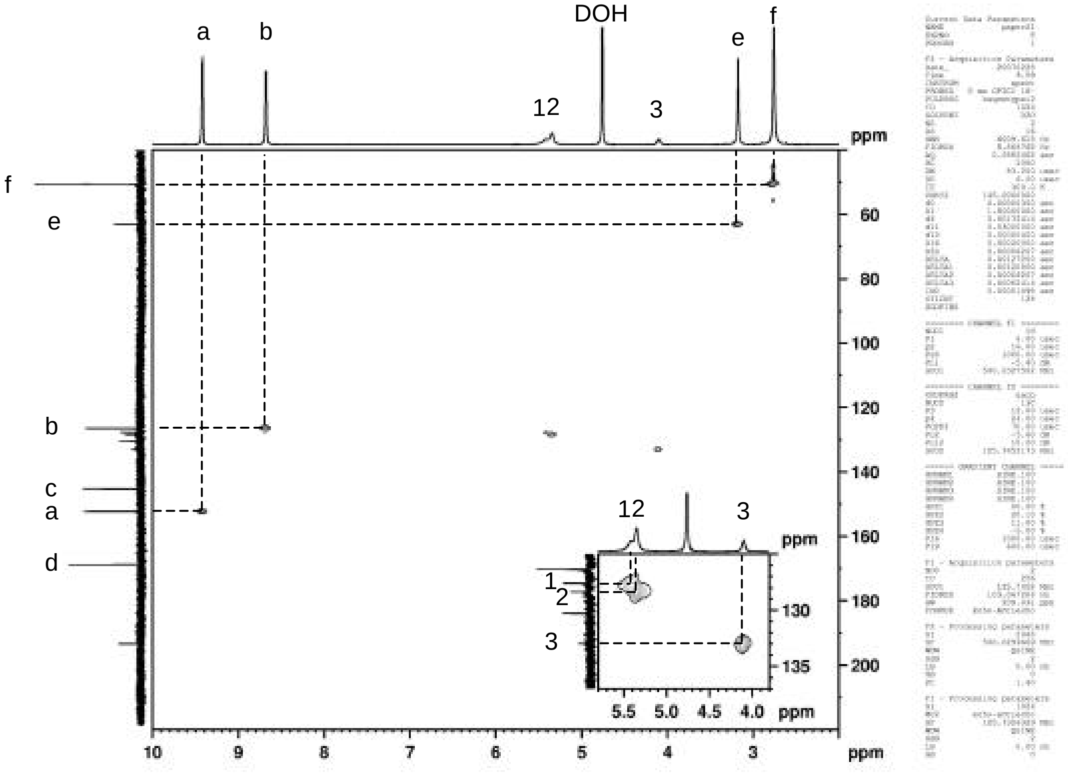


Figure S7. HSQC spectrum (500 MHz, D_2O, 300 K) of **1**·(**2**)$_2$.

· ^{1}H NMR/^{13}C NMR/HH COSY/HSQC/HMBC spectra of **3**.

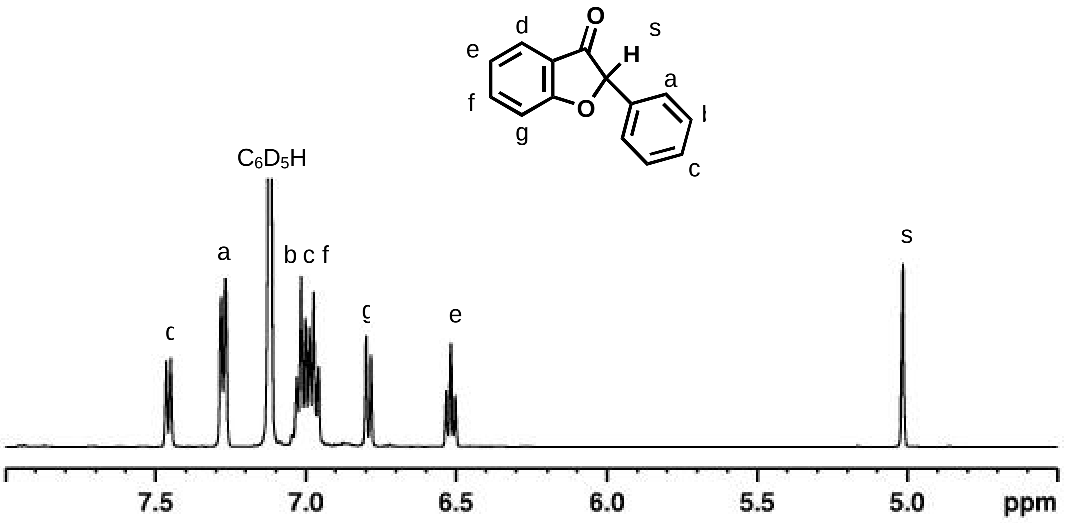


Figure S8. ^{1}H NMR spectrum (500 MHz, C_6D_6, 300 K) of **3**.

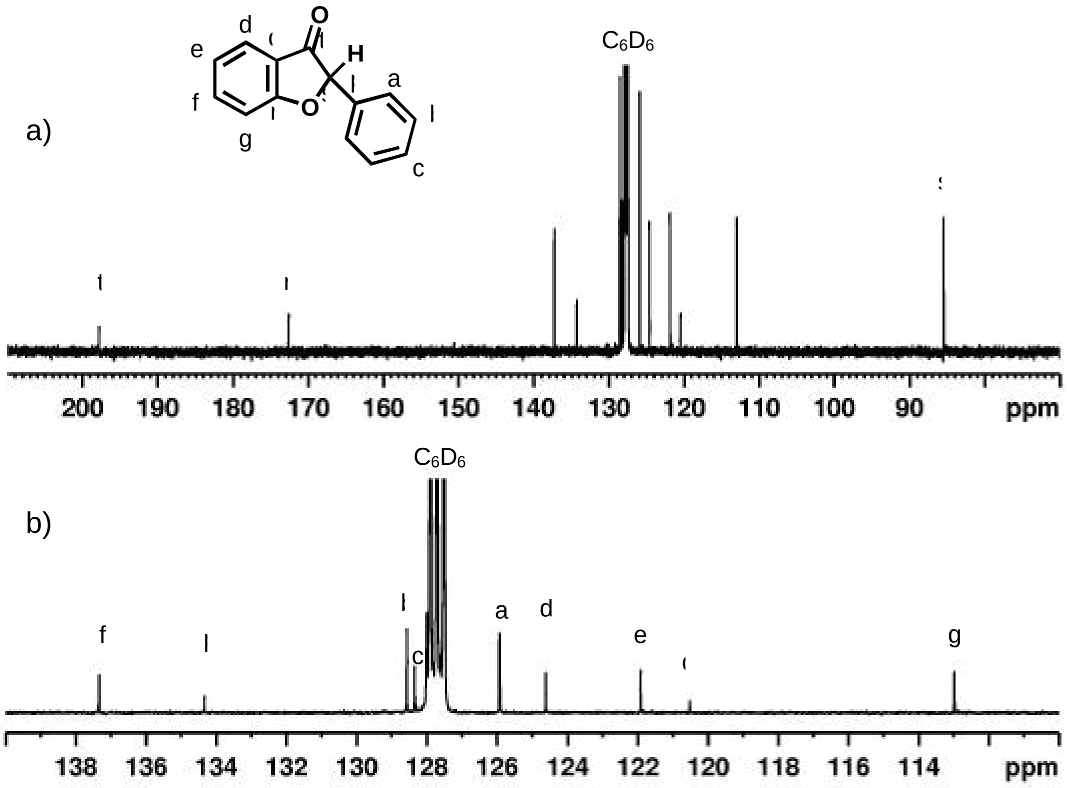


Figure S9. ^{13}C NMR spectra (125 MHz, C_6D_6, 300 K) of **3**: a) whole spectrum and b) enlarged spectrum from 140 ppm to 110 ppm.

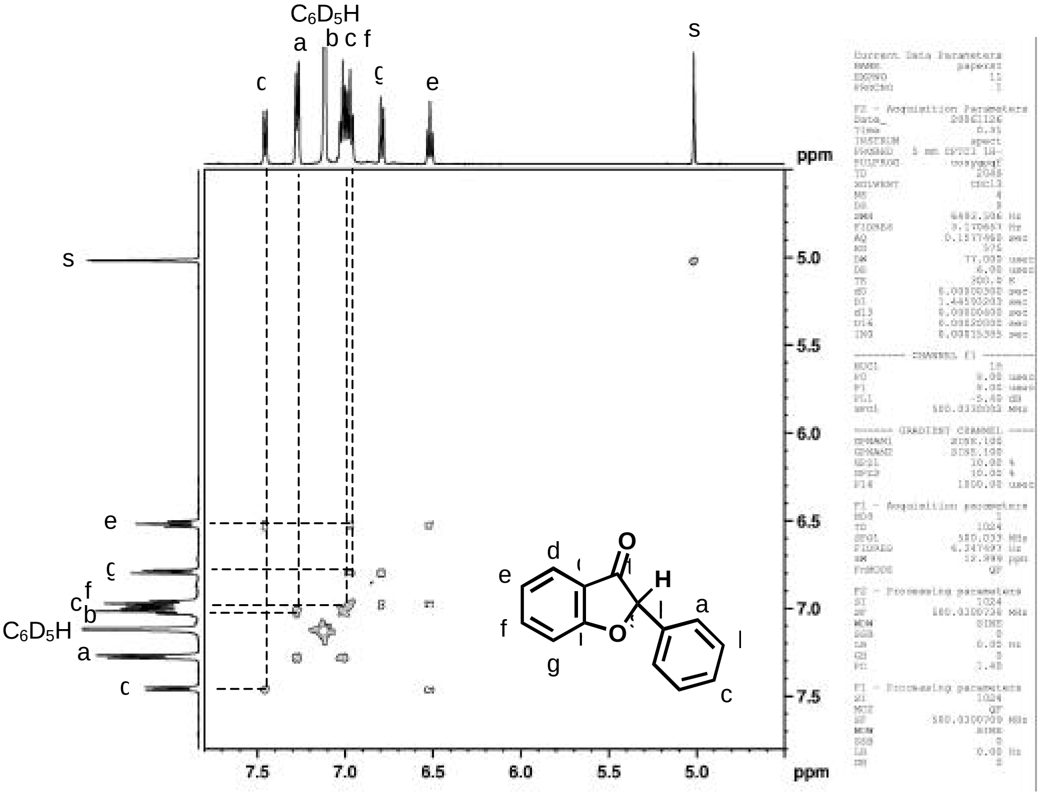


Figure S10. HH COSY spectrum (500 MHz, C_6D_6, 300 K) of **3**.

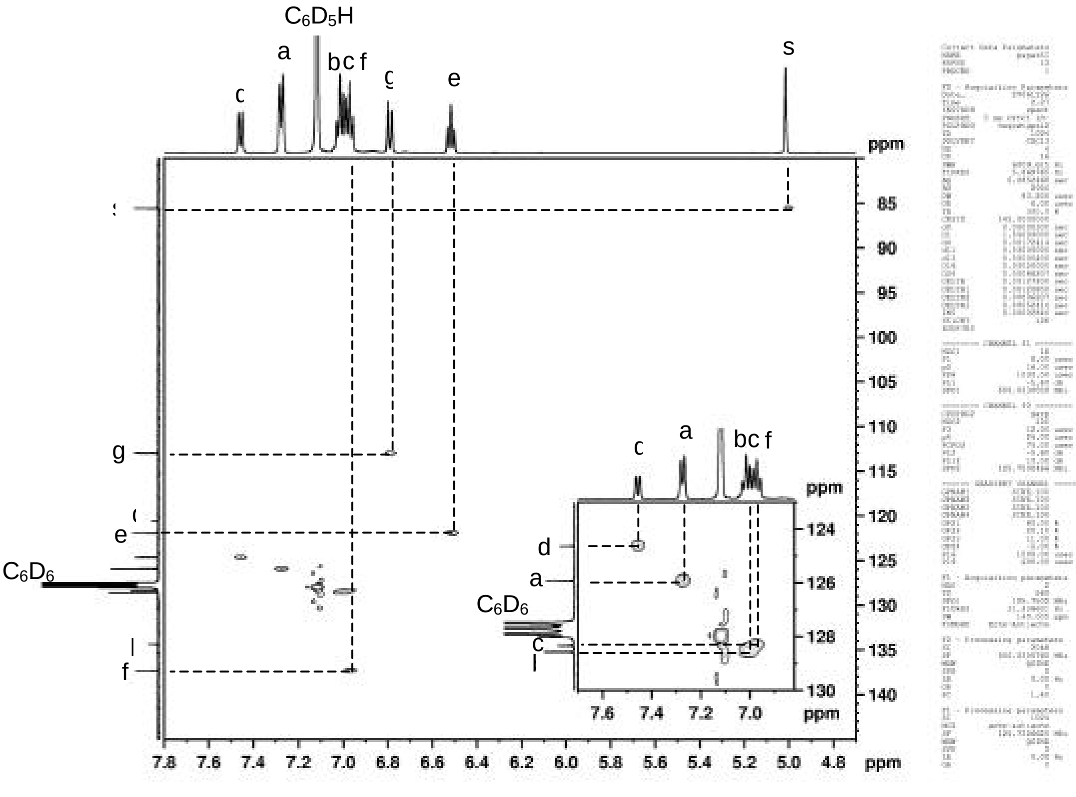


Figure S11. HSQC spectrum (500 MHz, C_6D_6, 300 K) of **3**.

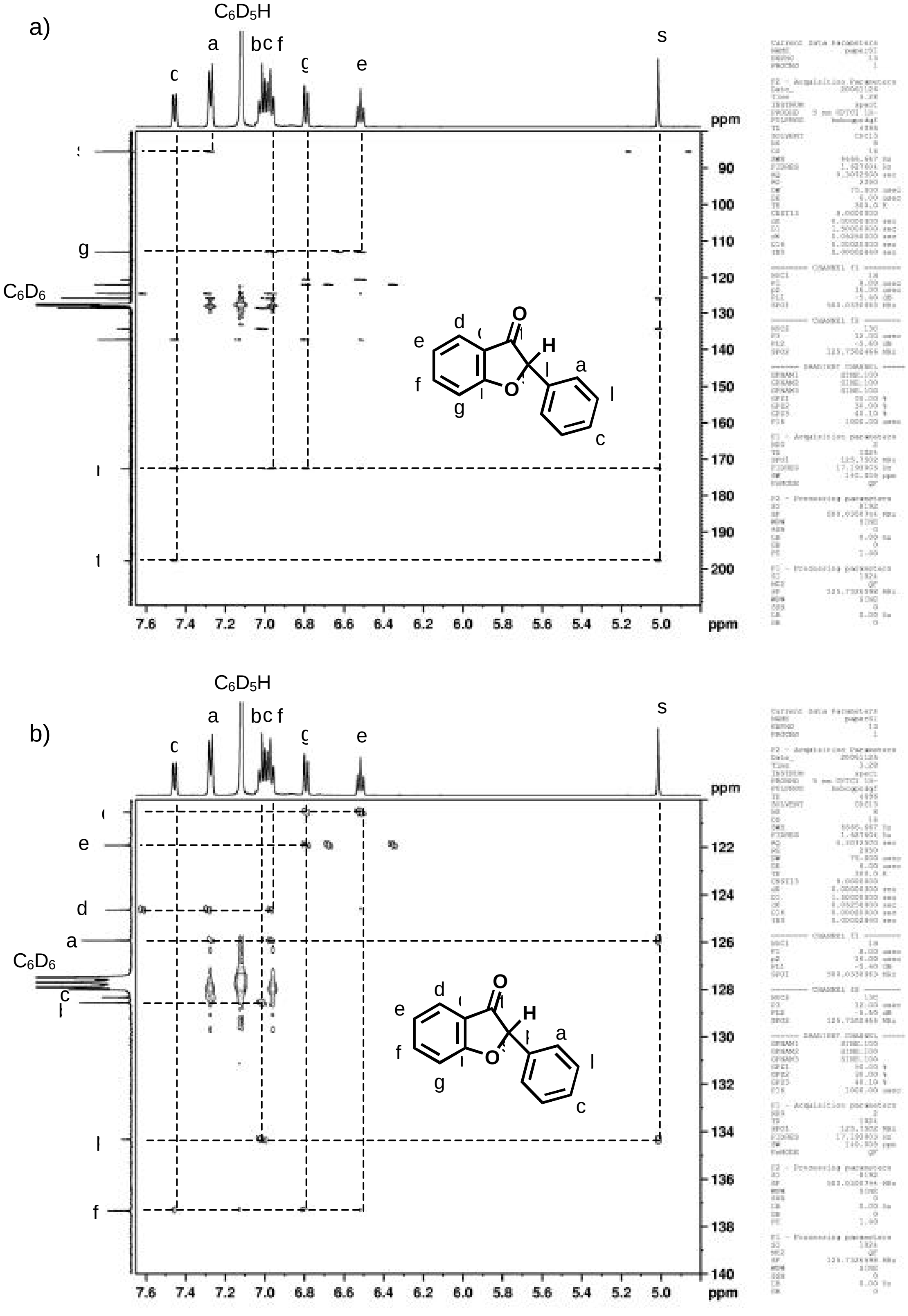


Figure S12. HMBC spectra (500 MHz, C_6D_6, 300 K) of **3**: a) whole spectrum and b) enlarged spectrum.

· ^{1}H NMR/^{13}C NMR/HH COSY/HSQC/HMBC spectra of **4**.

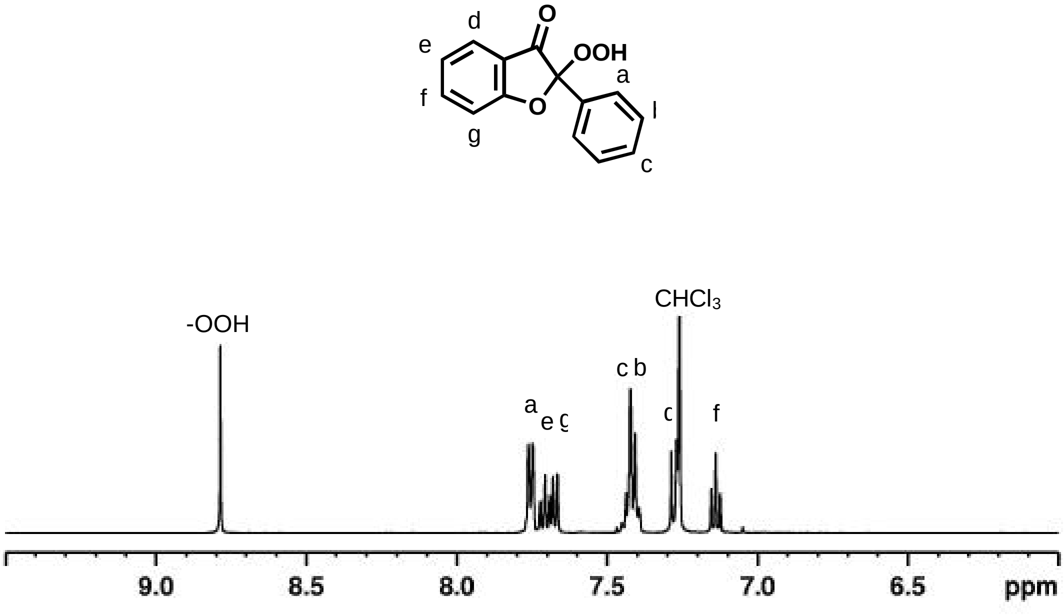


Figure S13. ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 300 K) of **4**.

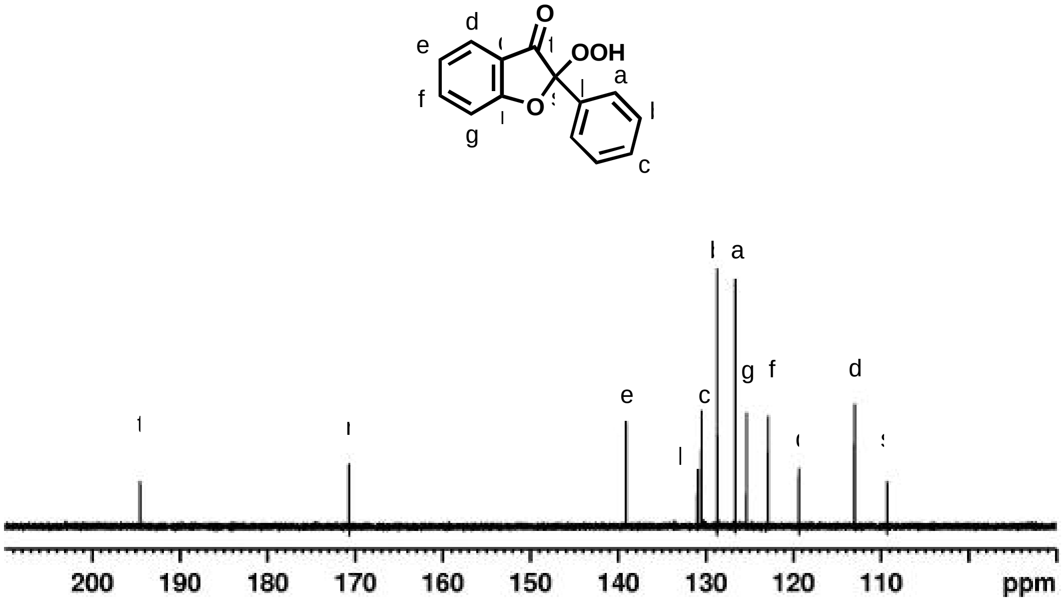


Figure S14. ^{13}C NMR spectrum (125 MHz, CDCl$_3$, 300 K) of **4**.

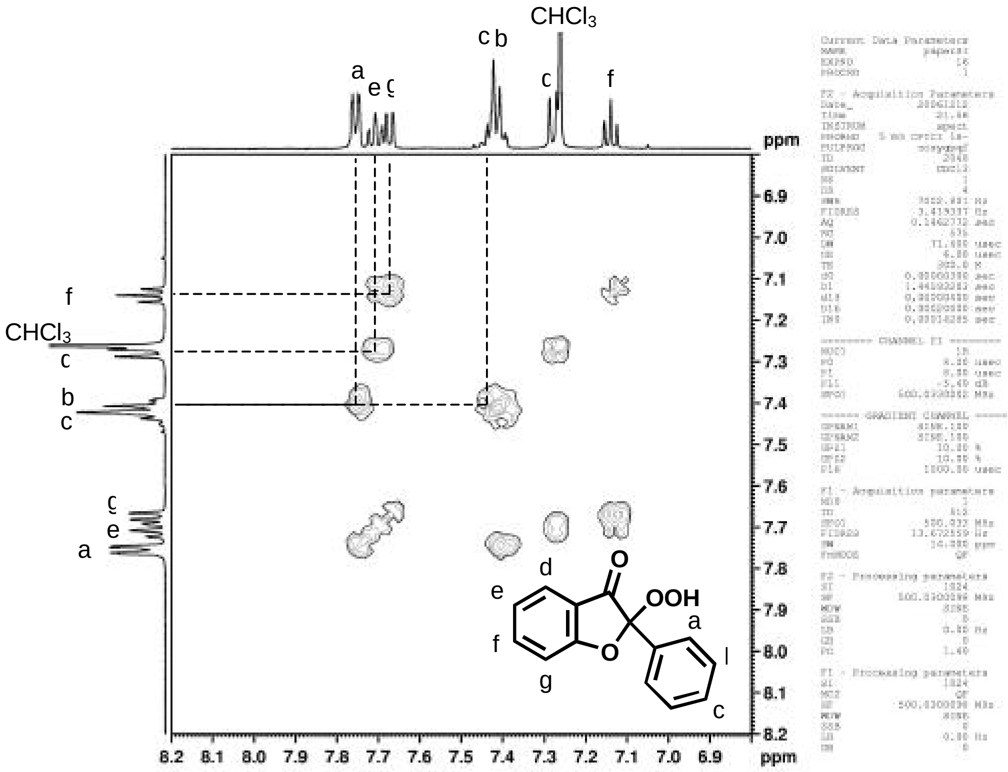


Figure S15. HH COSY spectrum (500 MHz, $CDCl_3$, 300 K) of **4**.

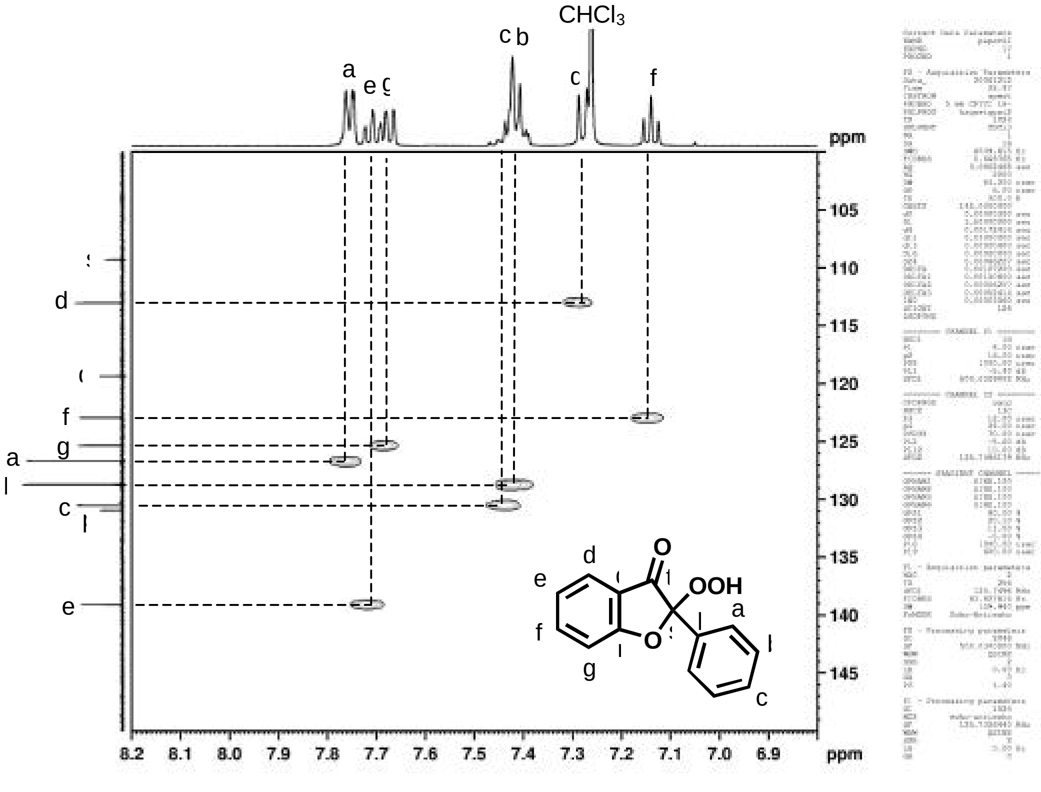


Figure S16. HSQC spectrum (500 MHz, $CDCl_3$, 300 K) of **4**.

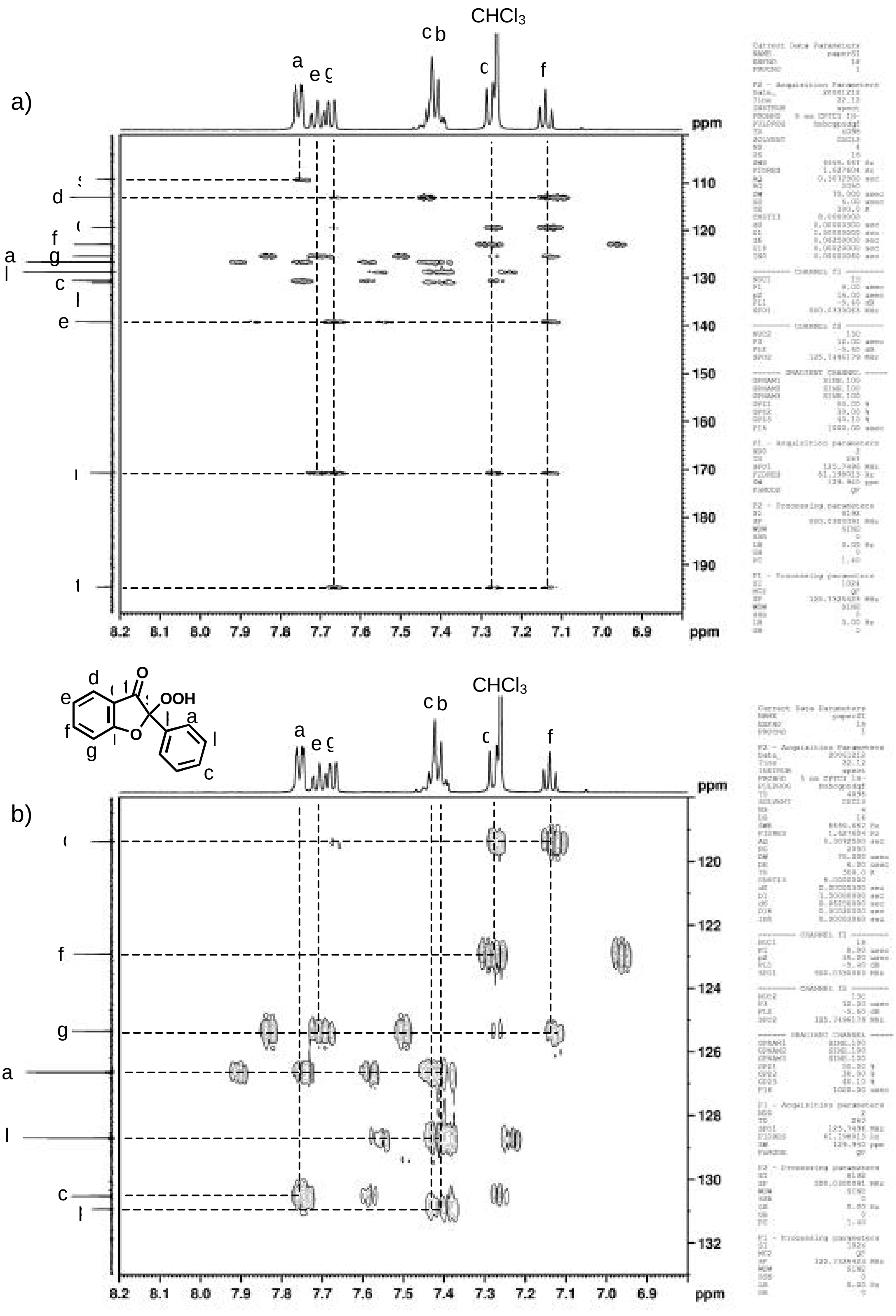


Figure S17. HMBC spectra (500 MHz, $CDCl_3$, 300 K) of **4**: a) whole spectrum and b) enlarged spectrum

· ^{1}H NMR/^{13}C NMR/HH COSY/HSQC/HMBC spectra of **5**.

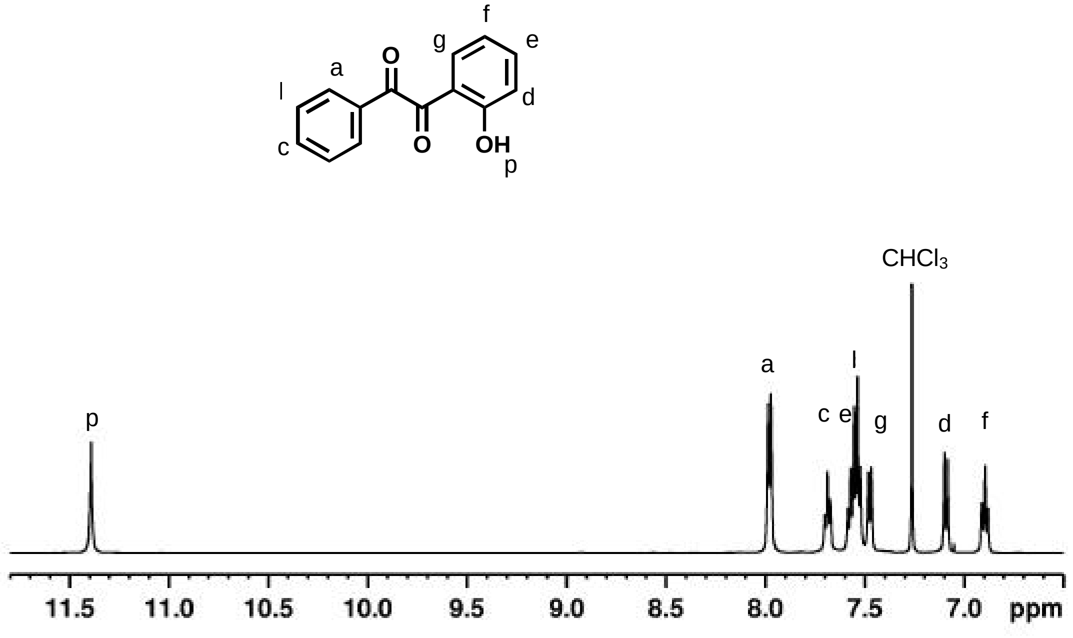


Figure S18. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 300 K) of **5**.

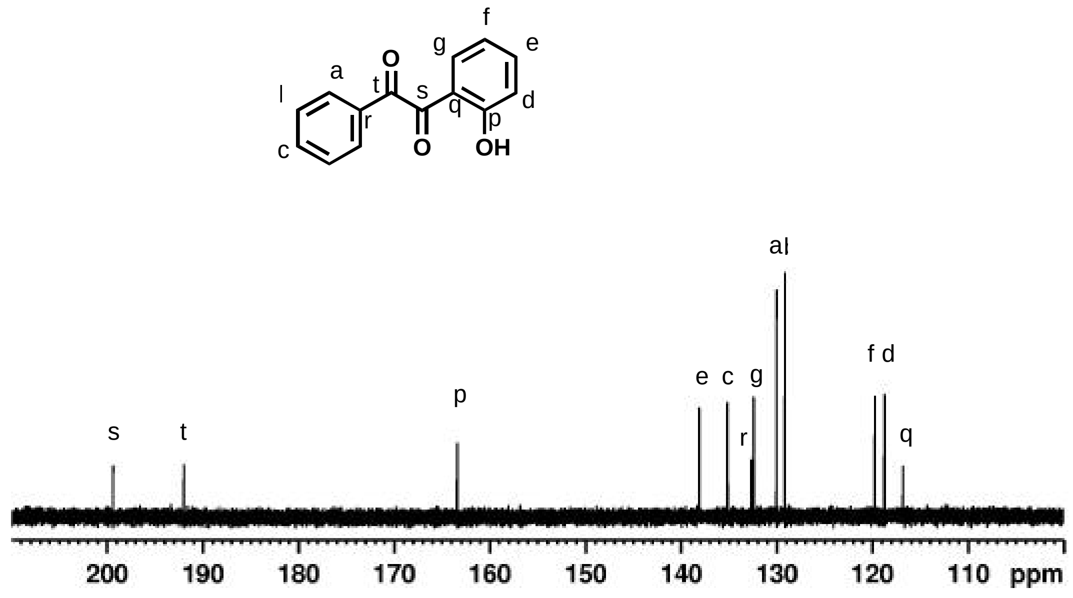


Figure S19. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 300 K) of **5**.

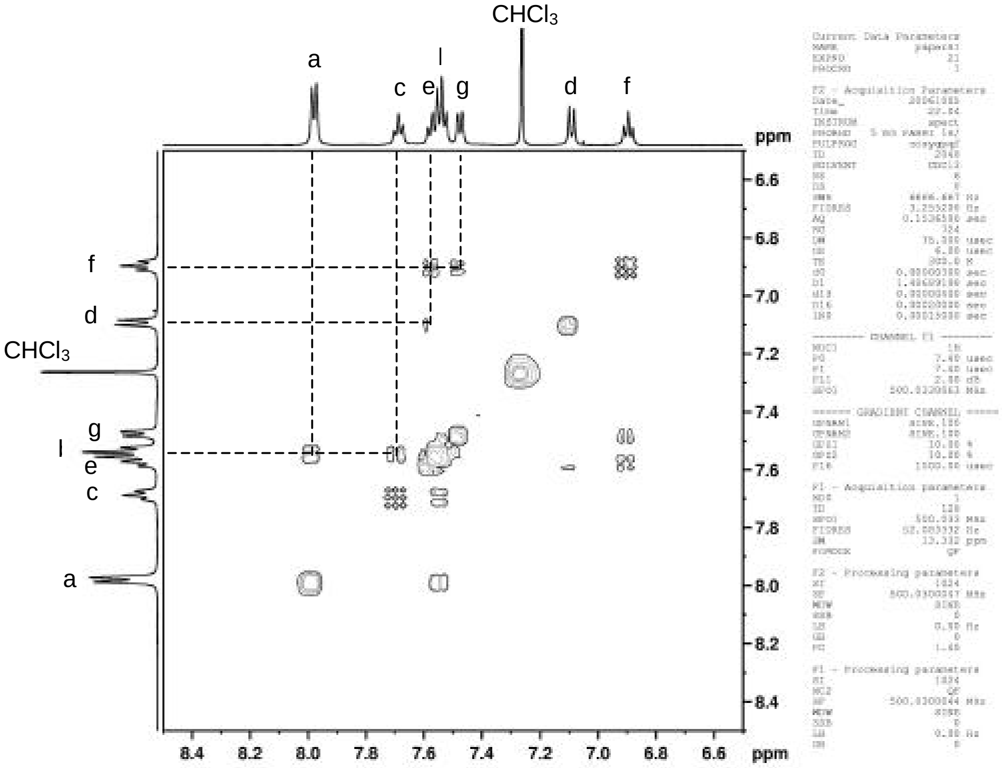


Figure S20. HH COSY spectrum (500 MHz, $CDCl_3$, 300 K) of **5**.

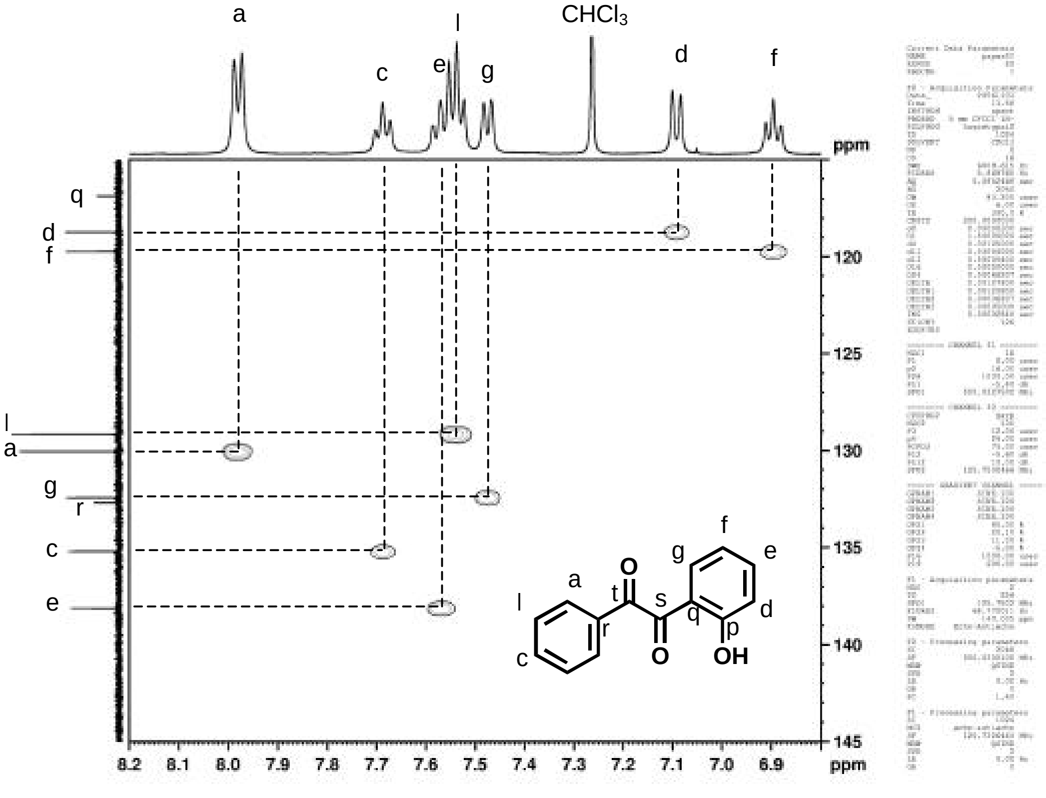


Figure S21. HSQC spectrum (500 MHz, $CDCl_3$, 300 K) of **5**.

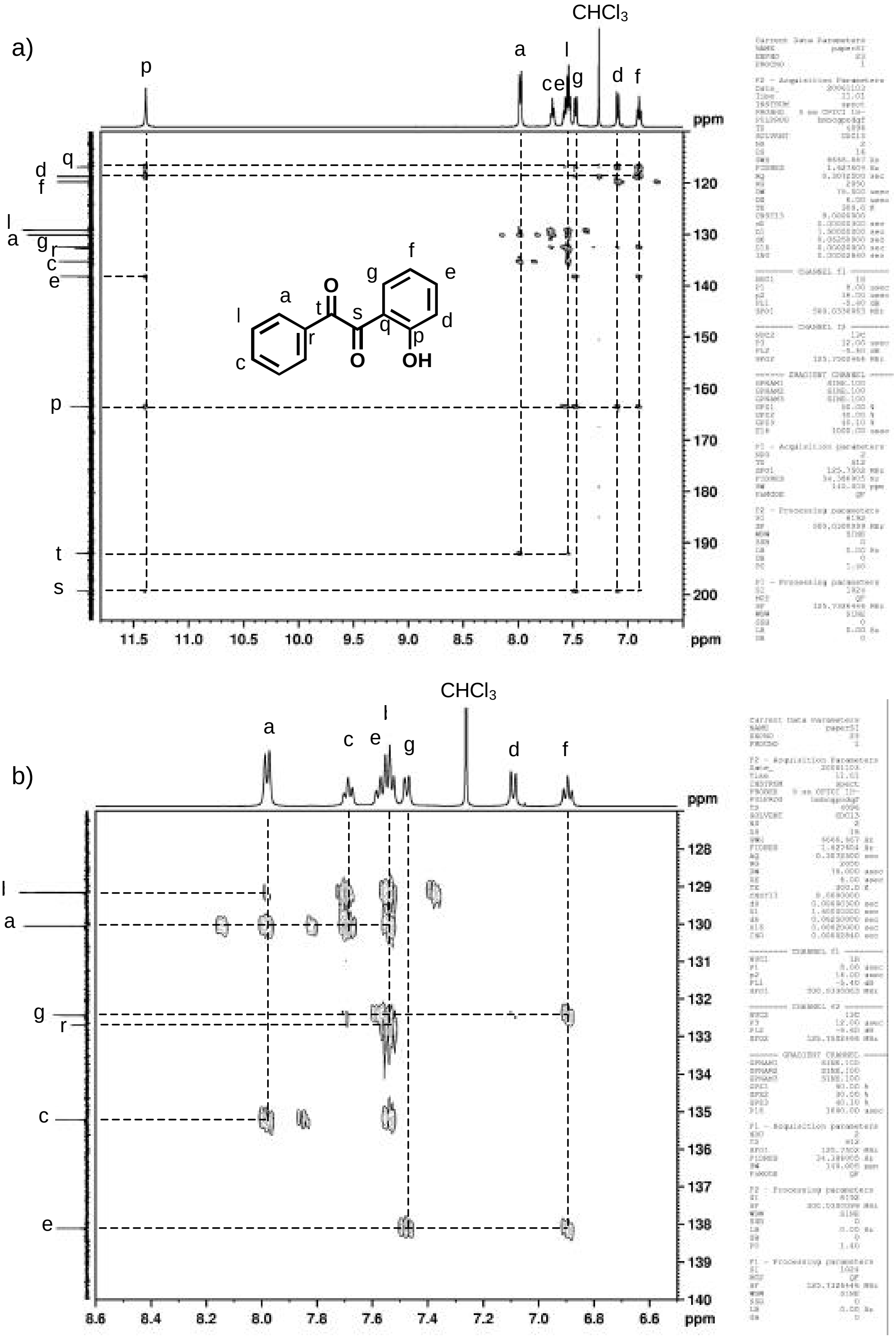


Figure S22. HMBC spectra (500 MHz, CDCl$_3$, 300 K) of **5**. : a) whole spectrum and b) enlarged spectrum

X-ray crystal data

Crystals of **3** were obtained by slow evaporation of a diethyleter solution of **3** overnight. Crystals of **4** were obtained by evaporation of a toluene solution of **4** for an hour. Crystals of **5** were obtained by slow evaporation of a hexane and chloroform (20 : 1) solution of **4** overnight.

· X-ray crystal data and structure of **1**·(**2**)$_2$.

Table S1. Crystal data and structure refinement for **1**·(**2**)$_2$.

Identification code	complex **1**·(**2**)$_2$	
Empirical formula	C136 H164 N48 O122.25 Pd6	
Formula weight	5065.55	
Temperature	80 (2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$I4_1/a$	
Unit cell dimensions	a = 26.3040 (15) Å	a = 90°.
	b = 26.3040 (15) Å	b = 90°.
	c = 31.582 (4) Å	g = 90°.
Volume	21852 (3) Å^3	
Z	4	
Density (calculated)	1.540 Mg/m^3	
Absorption coefficient	0.599 mm^{-1}	
F(000)	10280	
Crystal size	0.15 × 0.14 × 0.07 mm^3	
Theta range for data collection	1.55 to 28.88°.	
Index ranges	-35 <= h <= 35, -33 <= k <=35, -40 <= l <= 41	
Reflections collected	125283	
Independent reflections	13699 [R(int) = 0.0350]	
Completeness to theta = 28.88°	95.3 %	
Max. and min. transmission	0.9593 and 0.9155	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	13699 / 209 / 785
Goodness-of-fit on F^2	1.146
Final R indices [I>2sigma(I)]	R_1 = 0.0789, wR_2 = 0.1859
R indices (all data)	R_1 = 0.1102, wR_2 = 0.2118
Largest diff. peak and hole	1.068 and -1.140 e·Å^{-3}

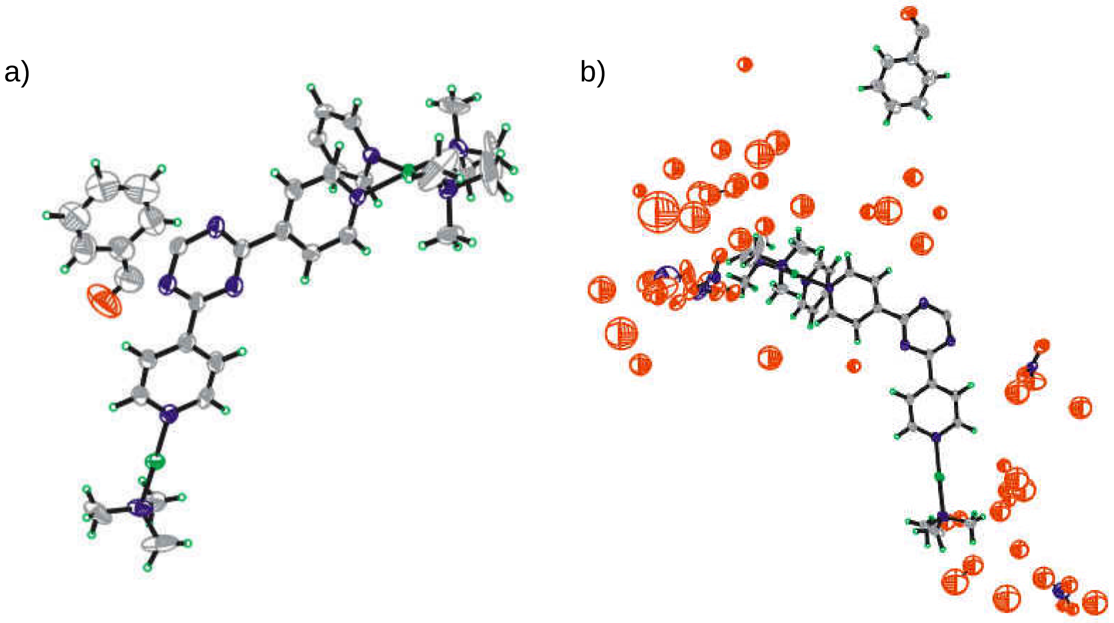


Figure S23. ORTEP diagram of **1**·(**2**)$_2$: a) the host and guest molecules (50% probability level), and b) independent molecular structure of **1** ⊃(**2**)$_2$ (30% probability level). Water molecules and nitrate anions were severely disordered.

· X-ray crystal data and structure of **3**.

Table S2. Crystal data and structure refinement for **3**.

Identification code	Compound **3**
Empirical formula	C14 H10 O2
Formula weight	210.22
Temperature	80 (2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	*a* = 8.3758 (14) Å	*a* = 90°.
	b = 5.7112 (10) Å	*b* = 90.428 (3)°.
	c = 10.6985(18) Å	*g* = 90°.
Volume	511.76 (15) Å^3	
Z	2	
Density (calculated)	1.364 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	220	
Crystal size	1.20 × 1.10 × 0.35 mm^3	
Theta range for data collection	1.90 to 28.49°.	
Index ranges	-10 <= *h* <= 10, -6 <= *k* <= 6, -13 <= *l* <= 13	
Reflections collected	5993	
Independent reflections	2473 [R(int) = 0.0193]	
Completeness to theta = 28.49°	95.0 %	
Max. and min. transmission	0.9689 and 0.8989	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2473 / 1 / 185	
Goodness-of-fit on F^2	0.707	
Final R indices [I>2sigma(I)]	R_1 = 0.0337, wR_2 = 0.0808	
R indices (all data)	R_1 = 0.0361, wR_2 = 0.0836	
Absolute structure parameter	1 (2)	
Largest diff. peak and hole	0.222 and -0.152 e·Å^{-3}	

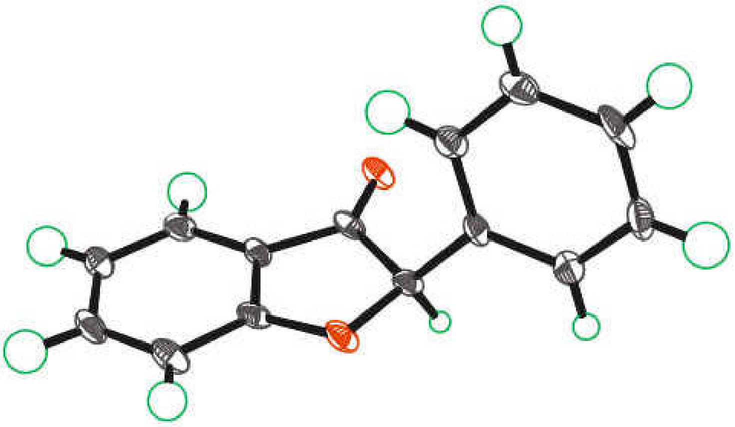


Figure S24. ORTEP diagram of **3** (50% probability level).

· X-ray crystal data and structure of **4**.

Table S3. Crystal data and structure refinement for **4**.

Identification code	Compound **4**	
Empirical formula	C28 H20 O8	
Formula weight	484.44	
Temperature	80 (2) K	
Wavelength	0.71073 Å	
Crystal system	Trinoclinic	
Space group	*P-1*	
Unit cell dimensions	a = 8.6649 (9) Å	a = 66.4870 (10)°.
	b = 11.3077 (12) Å	b = 78.8760 (10)°.
	c = 13.0501 (14) Å	g = 71.0020 (10)°.
Volume	1105.7 (2) Å^3	
Z	2	
Density (calculated)	1.455 Mg/m^3	
Absorption coefficient	0.108 mm^{-1}	
F(000)	504	
Crystal size	0.21 × 0.15 × 0.12 mm^3	
Theta range for data collection	1.71 to 28.91°.	
Index ranges	-11 <= h <= 11, -14 <= k <= 15, -16 <= l <= 17	
Reflections collected	12978	
Independent reflections	5292 [R(int) = 0.0208]	
Completeness to theta = 28.91°	90.6 %	
Max. and min. transmission	0.9872 and 0.9778	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5292 / 0 / 405	

Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R_1 = 0.0386, wR_2 = 0.1077
R indices (all data)	R_1 = 0.0460, wR_2 = 0.1146
Largest diff. peak and hole	0.409 and -0.332 e·Å^{-3}

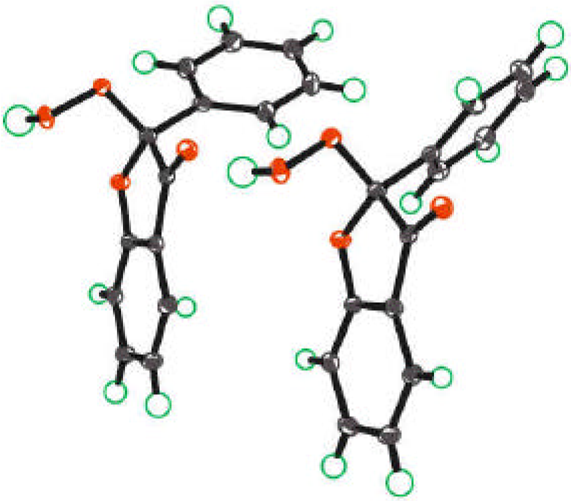


Figure S25. ORTEP diagram of **4** (50% probability level).

- X-ray crystal data and structure of **5**.

Table S4. Crystal data and structure refinement for **5**.

Identification code	2-hydroxybenzil	
Empirical formula	C14 H10 O3	
Formula weight	226.22	
Temperature	80 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	*a* = 15.402 (2) Å	*a* = 90°.
	b = 7.5023 (11) Å	*b* = 125.0350 (10)°.
	c = 11.205 (3) Å	*g* = 90°.

Volume	1060.2 (4) Å^3
Z	4
Density (calculated)	1.417 Mg/m^3
Absorption coefficient	0.100 mm^{-1}
F(000)	472
Crystal size	0.20 × 0.14 × 0.07 mm^3
Theta range for data collection	3.16 to 28.78°.
Index ranges	$-20 <= h <= 20$, $-10 <= k <= 9$, $-14 <= l <=14$
Reflections collected	5818
Independent reflections	1303 [R(int) = 0.0148]
Completeness to theta = 28.78°	94.1 %
Max. and min. transmission	0.9930 and 0.9803
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1303 / 0 / 94
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	$R_1 = 0.0402$, $wR_2 = 0.1165$
R indices (all data)	$R_1 = 0.0465$, $wR_2 = 0.1231$
Largest diff. peak and hole	0.474 and -0.212 e·Å^{-3}

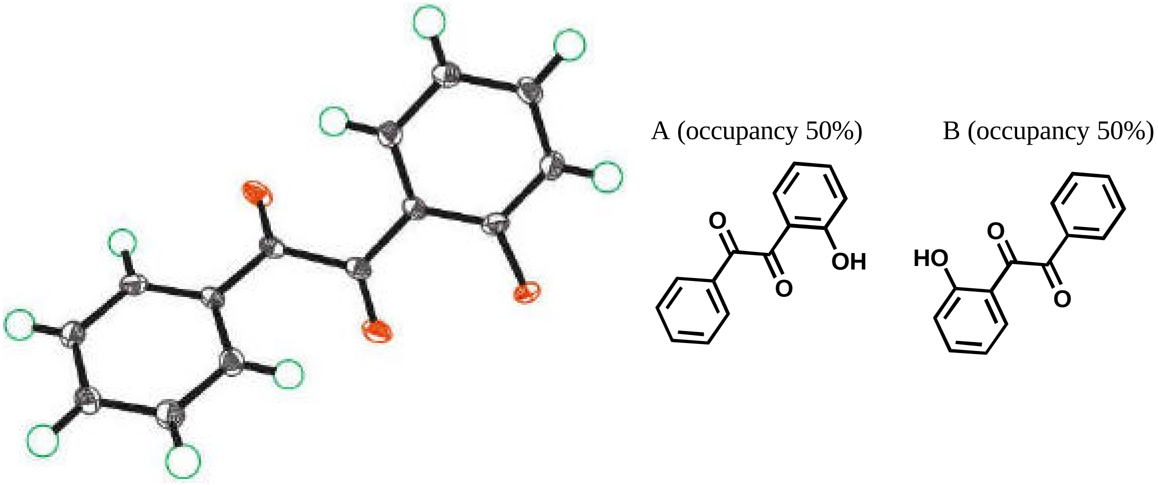


Figure S26. ORTEP diagram of **5** (50% probability level). A hydroxyl group was disordered at two positions with the occupancy of 50%, respectively.