Electronic Supplementary Information

Intermolecular *Head-to-Head* Interaction of Carbonyl Groups in a Bicyclic Hydrogen-Bonded Synthon based on β-Hydroxy Ketones

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General information

All solvents were purified, dried and distilled by standard procedures. NMR spectra were measured on a Bruker Avance III 500 spectrometer at 500.1 MHz (^{1}H) and 125.8 MHz (^{13}C) at 30 °C in DMSO-d_6 using residual protonated solvent signals as an internal standard. Melting points were determined on a hot-stage apparatus Stuart using capillary technique. Elemental analysis was carried out on a EuroVector-3000 analyzer (C, H, N) and by pyrolysis of the weighted sample under an oxygen flow with following titration (total content of halogens).

FTIR spectroscopy. The infrared spectra of the polycrystalline samples in potassium bromide pellets were recorded on a Bruker Tensor 27 FTIR spectrometer with an optical resolution of 4 cm^{-1} equipped with a heating device. The spectra contain groups of frequencies that can be assigned to the O–H stretching vibrations (3600–3200 cm^{-1}), C–H (3130–2760 cm^{-1}), C=O (1850–1680 cm^{-1}), aryl fragments and nitro group (1700–1480 cm^{-1}), C–NO_2 (1305–1260 cm^{-1}), C–O(H) (1080–1050 cm^{-1}) and O–H deformation vibrations (1460–1430 cm^{-1}, 680–650 cm^{-1}). The out-of-plane C–H deformation vibrations, C–Br stretching vibrations, and C–NO_2 deformation vibrations are in the range of 860–700 cm^{-1}. A distinctive feature of the spectrum of compound **2** is the intense band with a frequency of 1091 cm^{-1}, which may correspond to the skeletal vibrations of disubstituted halobenzenes.

Single crystal X-ray diffraction details

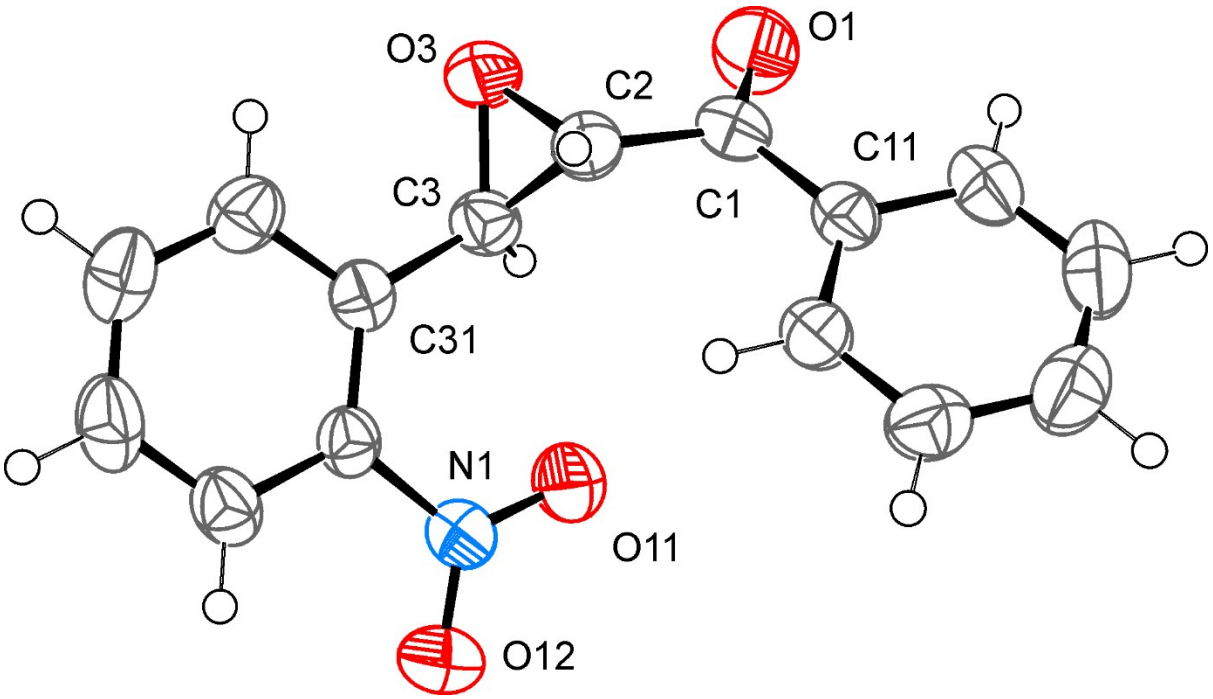


Figure S1. ORTEP diagram of (2*RS*,3*SR*)-3-(2-nitrophenyl)-1-phenyl-2,3-epoxypropan-1-one for non-hydrogen atoms at 50% probability level according to SC-XRD.

Table S1. Selected experimental dihedral angles of compounds **1**-**3**.

Dihedral angle, deg.		**1**	**2**	**3**
$C^1–C^2–C^3–O^3$	φ_1	59.5(5)	62.0(5)	58.7(3)
$O^1–C^1–C^2–C^3$	φ_2	16.8(6)	17.8(6)	42.0(4)
$C^2–C^1–C^{11}–C^{16}$	φ_3	6.7(6)	8.0(7)	18.5(5)
$C^1–C^2–C^3–C^{31}$	φ_4	176.9(4)	–179.4(4)	176.7(2)
$O^{11}–N^1–C^{32}–C^{31}$	φ_5	–50.8(6)	–40.4(8)	–125.6(4)
$O^1–C^1\cdots C^3–O^3$	φ_6	71.0(4)	73.3(3)	90.7(2)
$(C^{11\text{-}16}, C^{31\text{-}36})^a$	ω	4.07(16)	2.90(17)	23.60(14)

a – angle between a normal to plane $C^{11\text{-}16}$ and a normal to plane $C^{31\text{-}36}$.

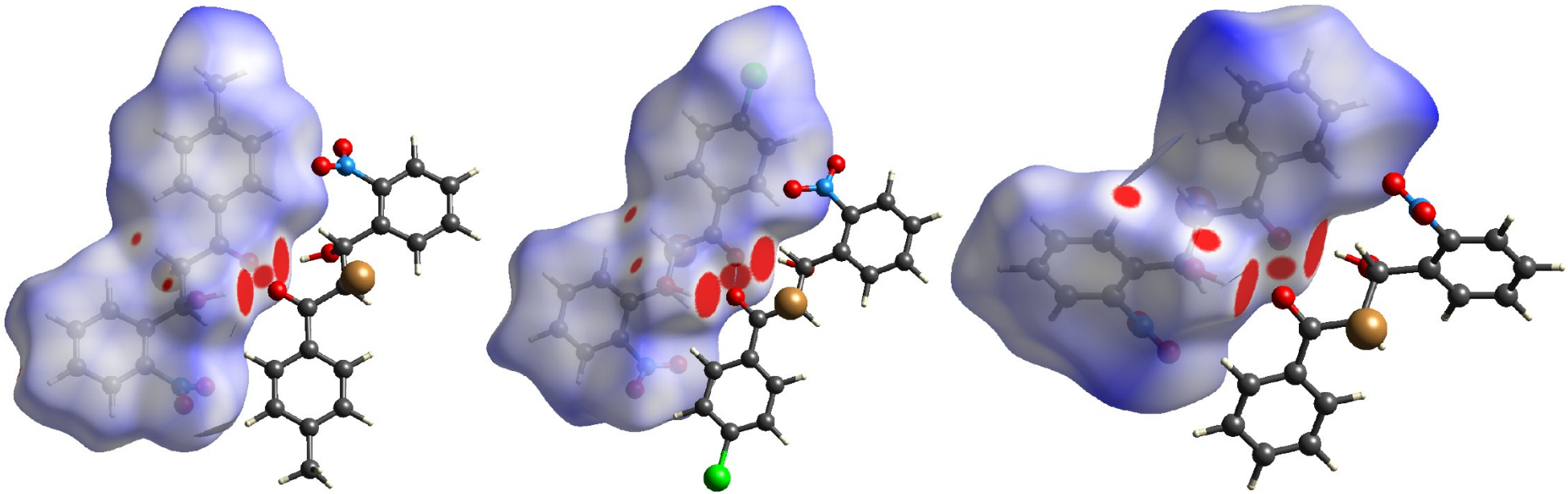
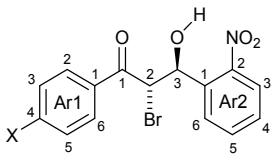


Figure S2. Hiershfeld surfaces for compounds **1**-**3** with the partner dimer-forming molecule. Color range for surface property d_{norm} scaled from blue (1.8176) to red (–0.040).

Synthesis and sample characterization

Synthesis of 1-aryl-3-(2-nitrophenyl)-2,3-epoxypropan-1-ones. The reaction was carried out according to the known procedure.[1] A solution of MeONa obtained by reacting Na (0.73 g, 0.032 mol) with MeOH (20 mL) was added to a stirred solution of 2-nitrobenzaldehide (4.08 g, 0.027 mol) and corresponding 1-aryl-2-chloroethan-1-one (0.027 mol) in MeOH (70 mL) at room temperature. After 0.5 h the resulting white precipitate was filtered off, washed with water (2 × 25 mL) and dried at room temperature. The characteristic data for the obtained compounds were in accordance with our previous results. Single crystals of (2*RS*,3*SR*)-3-(2-nitrophenyl)-1-phenyl-2,3-epoxypropan-1-one appropriate for SC-XRD were obtained by slow evaporation of an ethanol solution at ambient temperature; melting point 115 °C.

Synthesis of 1-aryl-2-bromo-3-hydroxy-(2-nitrophenyl)-propan-1-ones (1-3). To a solution of corresponding 1-aryl-3-(2-nitrophenyl)-2,3-epoxypropan-1-one (1 mmol) in dioxane (20 mL), 47 % hydrobromic acid (10 mL) was slowly added. The reaction mixture was stirred at room temperature and then stored for 3 h. After this period, water was added (40 mL) and a formed precipitate was filtered, washed with water (2×15 mL) and dried. Then the powder was washed with diethyl ether (10 mL) and the pure samples was obtained.



X = CH_3 (**1**), Cl (**2**), H (**3**)

*(2RS,3RS)-2-Bromo-3-hydroxy-1-(4-methylphenyl)-3-(2-nitrophenyl)-propan-1-one (**1**)*

Yield 0.29 g (81 %), the brown solid, mp 100-101 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.41 (s, 3H, Me), 5.70 (d, J = 9.7 Hz, 1H, H2), 5.83 (d, J = 9.6 Hz, 1H, H3), 7.40 (d, J = 8.1 Hz, 2H, H3 and H5-Ar1), 7.58 (dd, J = 7.4 Hz, J = 7.4 Hz, 1H, H4-Ar2), 7.77 (dd, J = 7.7 Hz, J = 7.5 Hz, 1H, H5-Ar2), 7.89 (dd, J = 7.5 Hz, J = 1.0 Hz, 1H, H3-Ar2), 8.03 (d, 1H, J = 7.9 Hz, H6-Ar2), 8.04 (d, J = 8.2 Hz, 2H, H2 and H6-Ar1). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 192.3 (C1), 149.4 (C2-Ar2), 144.8 (C4-Ar1), 135.4 (C1-Ar2), 132.8 (C5-Ar2), 132.1 (C1-Ar1), 130.0 (C6-Ar2), 129.5 (C2 and C6-Ar1), 129.1 (C4-Ar2), 129.0 (C3 and C5-Ar1), 123.5 (C3-Ar2), 67.3 (C3), 47.8 (C2), 21.2 (Me). Anal. Calc. for $C_{16}H_{14}BrNO_4$ (**3**): C, 52.77; H, 3.87; Br, 21.94; N, 3.85. Found: C, 52.98; H, 3.64; Br, 21.78; N, 3.58%.

*(2RS,3RS)-2-Bromo-1-(4-chlorophenyl)-3-hydroxy-3-(2-nitrophenyl)-propan-1-one (**2**)*

Yield 0.24 g (62 %), the tan solid, mp 125 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.74 (d, J = 9.5 Hz, 1H, H2), 5.82 (d, J = 9.5 Hz, 1H, H3), 7.59 (ddd, J = 8.0 Hz, J = 7.8 Hz, J = 1 Hz, 1H, H4-Ar2), 7.67 (d, J = 8.2 Hz, 2H, H3 and H5-Ar1), 7.78 (ddd, J = 7.8 Hz, J = 7.7 Hz, J = 1 Hz, 1H, H5-Ar2), 7.90 (dd, J = 8.1 Hz, J = 1.0 Hz, 1H, H3-Ar2), 8.04 (dd, J = 7.7 Hz, J = 1.0 Hz, 1H, H6-Ar2), 8.17 (d, J = 8.3 Hz, 2H, H2 and H6-Ar1). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 191.9 (C1), 149.3 (C2-Ar2), 139.2 (C4-Ar1), 135.2 (C1-Ar2), 133.3 (C1-Ar1), 132.8 (C5-Ar2), 130.7 (C2 and C6-Ar1), 130.0 (C6-Ar2), 129.3 (C4-Ar2), 129.1 (C3 and C5-Ar1), 123.5 (C3-Ar2), 67.3 (C3), 47.8 (C2). Anal. Calc. for $C_{15}H_{11}BrClNO_4$ (**2**): C, 46.84; H, 2.88; Br+Cl, 30.00; N, 3.64. Found: C, 46.71; H, 2.73; Br+Cl, 30.64; N, 3.37%.

*(2RS,3RS)-2-Bromo-3-hydroxy-3-(2-nitrophenyl)-1-phenylpropan-1-one (**3**)*

Yield 0.28 g (79 %), the brown solid, mp 100-102 °C (lit.[2] 103-104 °C). ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.74 (d, J = 9.6 Hz, 1H, H2), 5.85 (d, J = 9.6 Hz, 1H, H3), 7.58 (dd, J = 7.9 Hz, J = 7.6 Hz, 1H, H4-Ar2), 7.60 (dd, J = 7.6 Hz, J = 7.4 Hz, 2H, H3 and H5-Ar1), 7.72 (dd, J =7.6 Hz, J =7.6 Hz, 1H, H4-Ar1), 7.78 (ddd, J = 7.6 Hz, J = 7.4 Hz, J = 1.0 Hz, 1H, H5-Ar2), 7.90 (dd, J = 8.0 Hz, J = 1.0 Hz, 1H, H3-Ar2), 8.04 (dd, J = 7.4 Hz, J = 1.0 Hz, 1H, H6-Ar2), 8.15 (dd, J = 7.4 Hz, J = 1.1 Hz, 2H, H2 and H6-Ar1). ^{13}C{^{1}H} NMR (DMSO-d_6, 126 MHz): δ 192.8 (C1), 149.4 (C2-Ar2), 135.3 (C1-Ar2), 134.6 (C1-Ar1), 134.1 (C4-Ar1), 132.8 (C5-Ar2), 130.0 (C6-Ar2), 129.2 (C4-Ar2), 129.0 (C3 and C5-Ar1), 128.8 (C2 and C6-Ar1), 123.5 (C3-Ar2), 67.4 (C3), 47.7 (C2). Anal. Calc. for $C_{15}H_{12}BrNO_4$ (**1**): C, 51.45; H, 3.45; Br, 22.82; N, 4.00. Found: C, 51.79; H, 3.28; Br, 22.56; N, 4.17%.

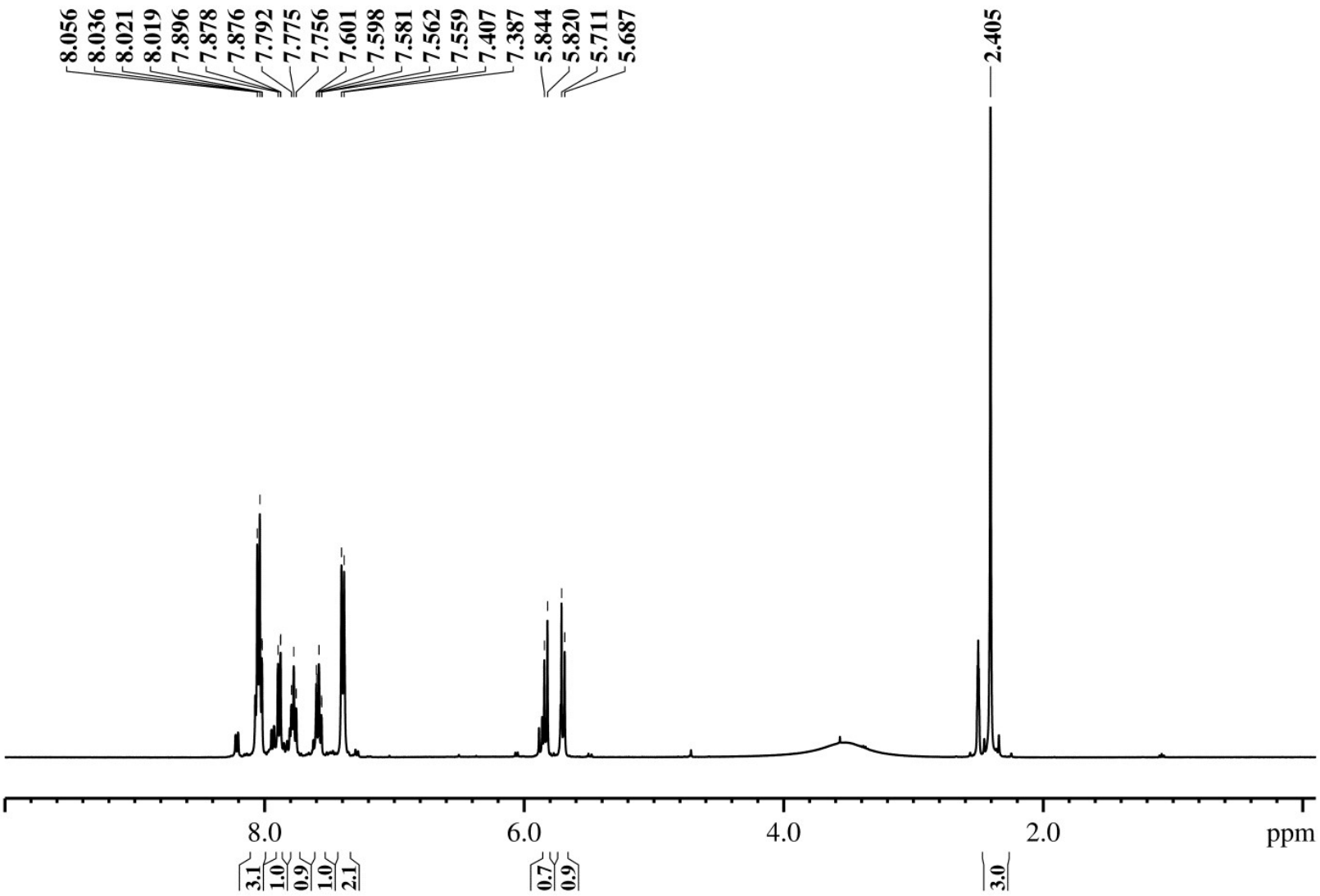


Figure S3. ^{1}H NMR spectrum of **1** in DMSO-d_6.

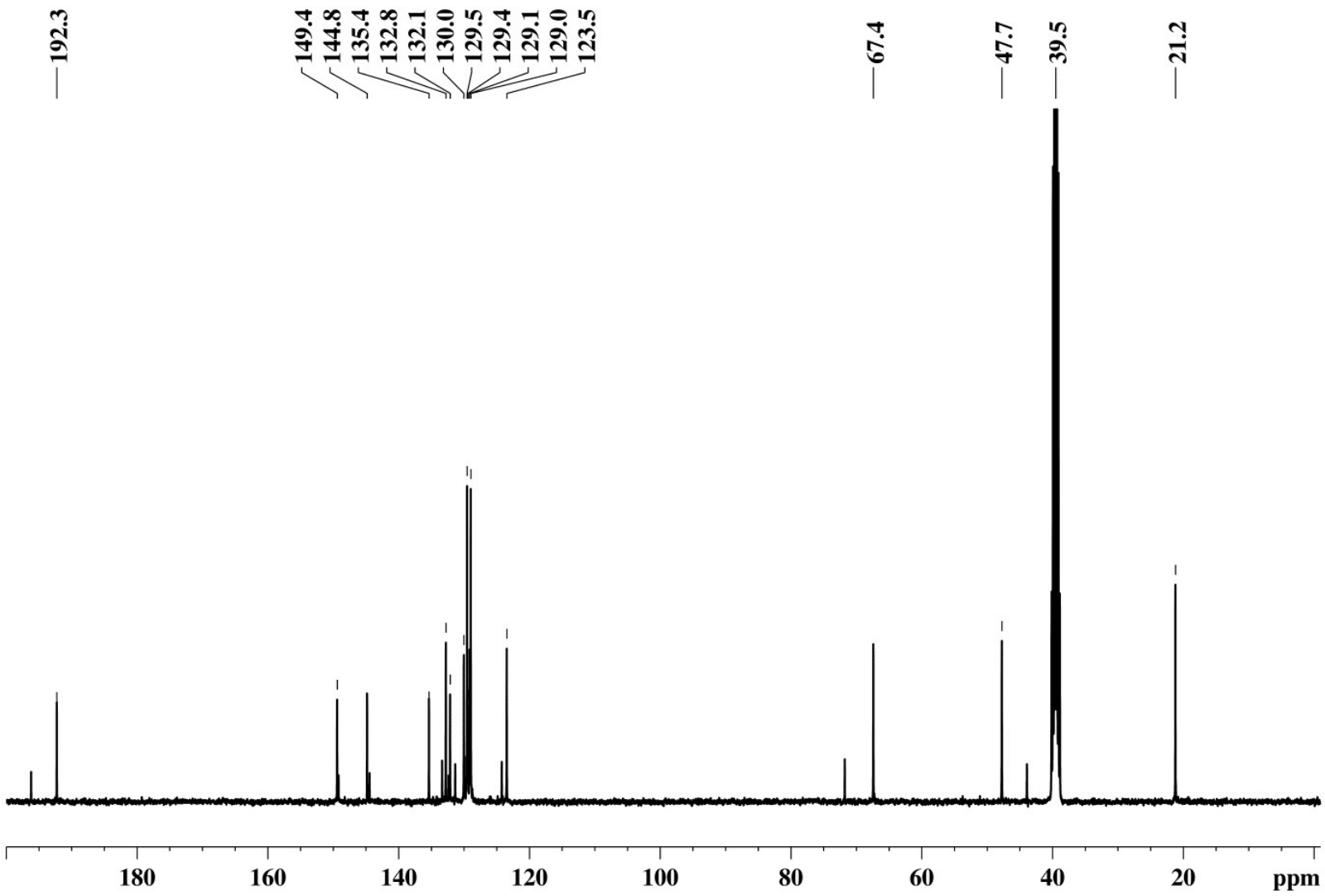


Figure S4. ^{13}C NMR spectrum of **1** in DMSO-d_6.

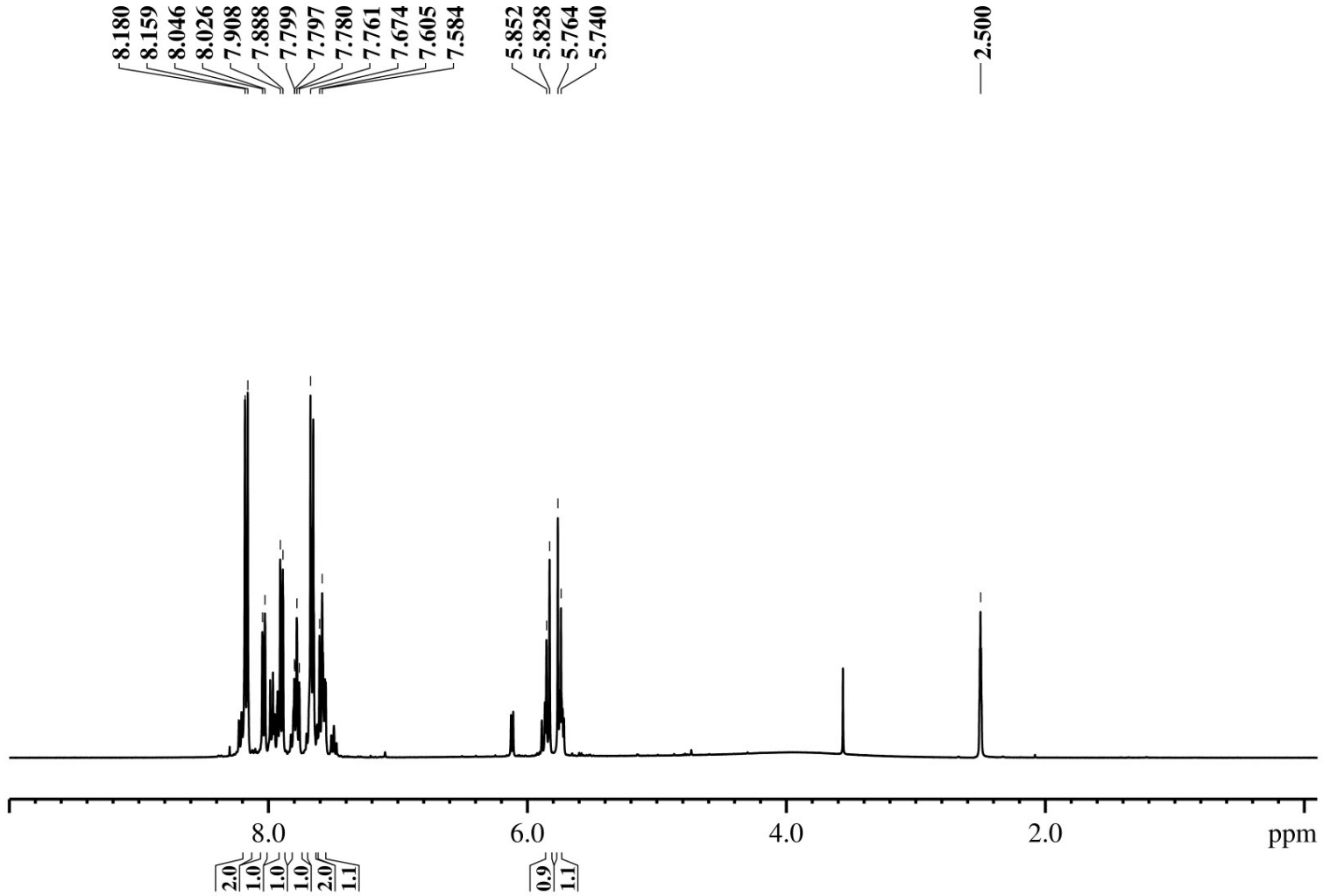


Figure S5. ^{1}H NMR spectrum of **2** in DMSO-d_6.

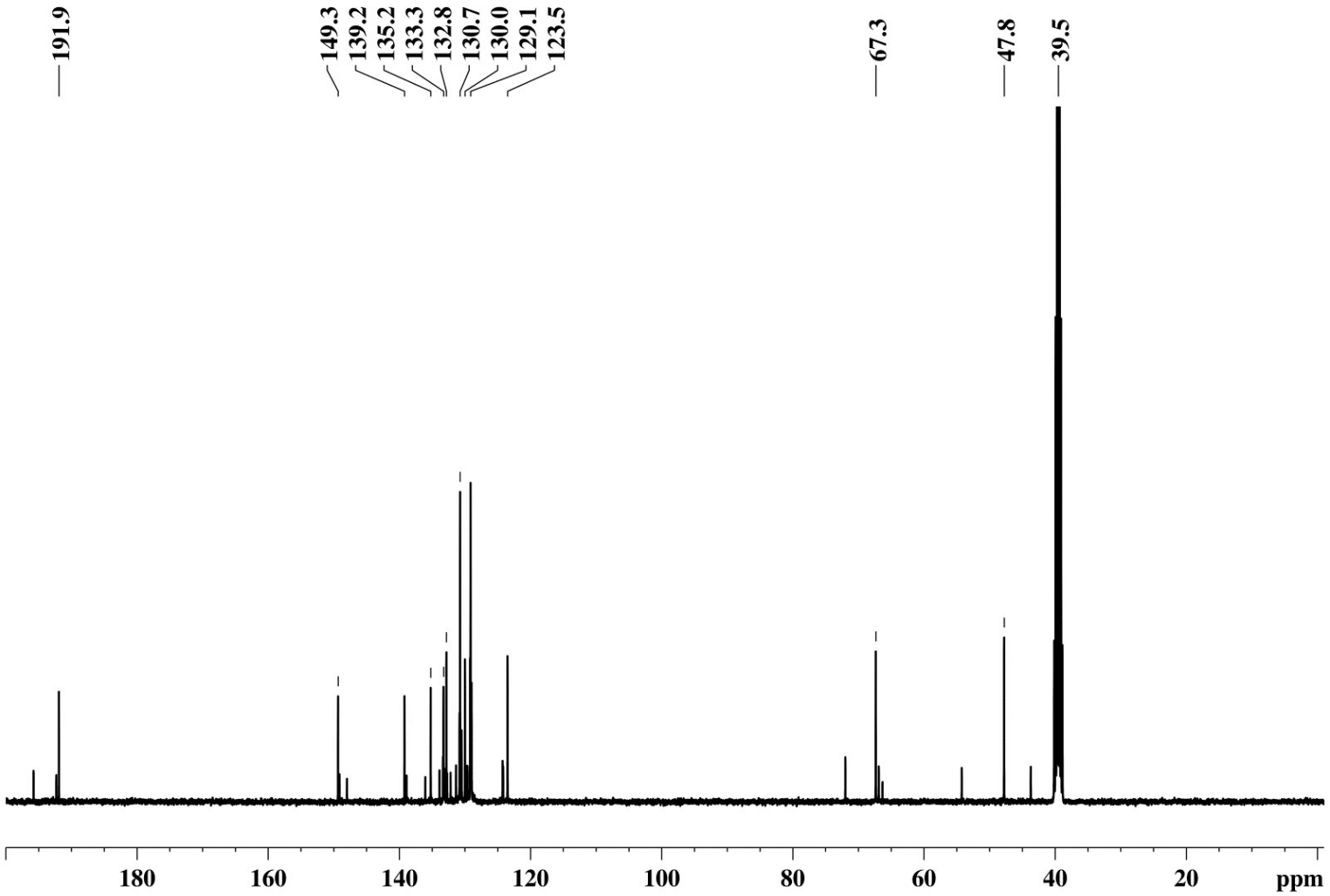


Figure S6. ^{13}C NMR spectrum of **2** in DMSO-d_6.

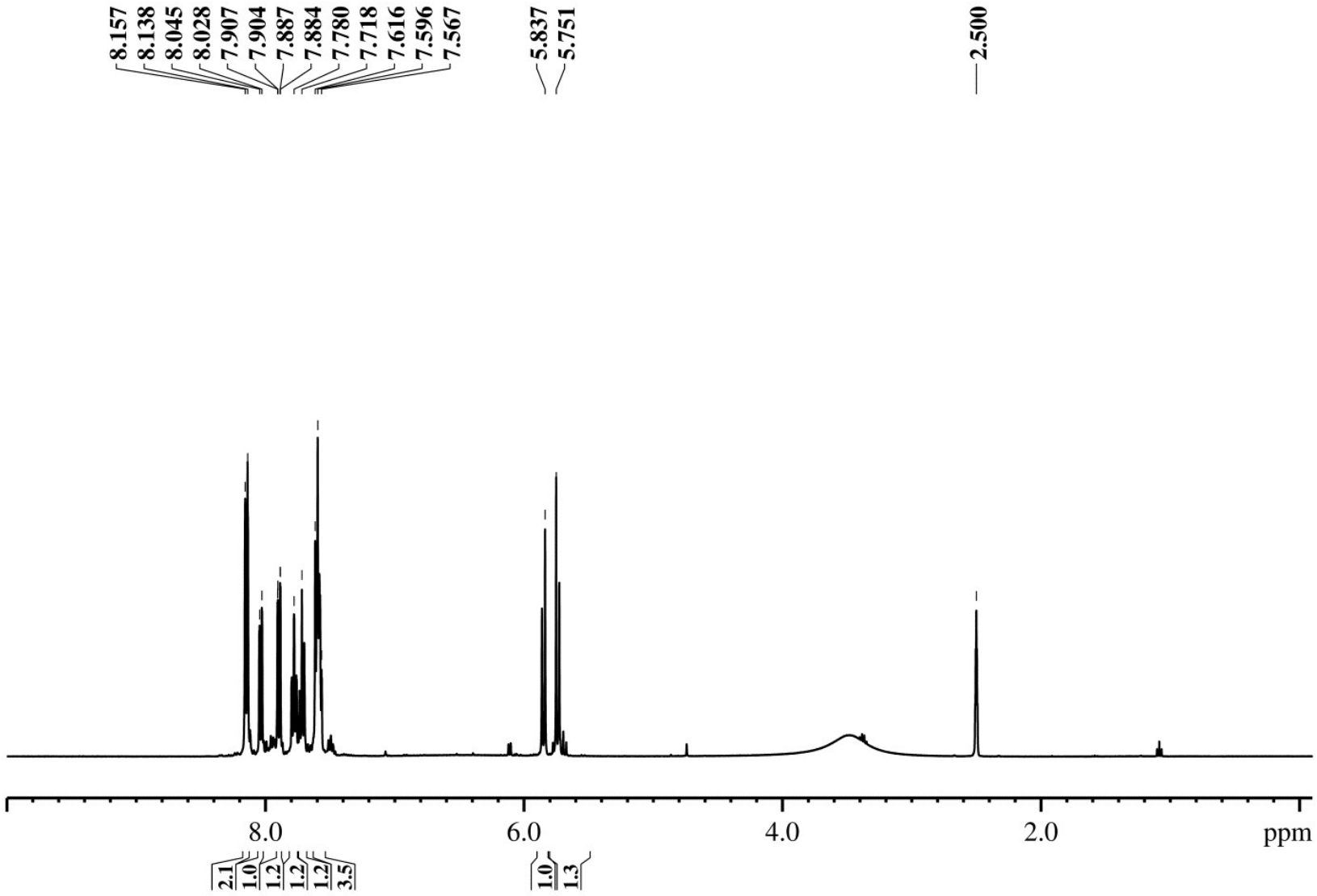


Figure S7. ^{1}H NMR spectrum of **3** in DMSO-d_6.

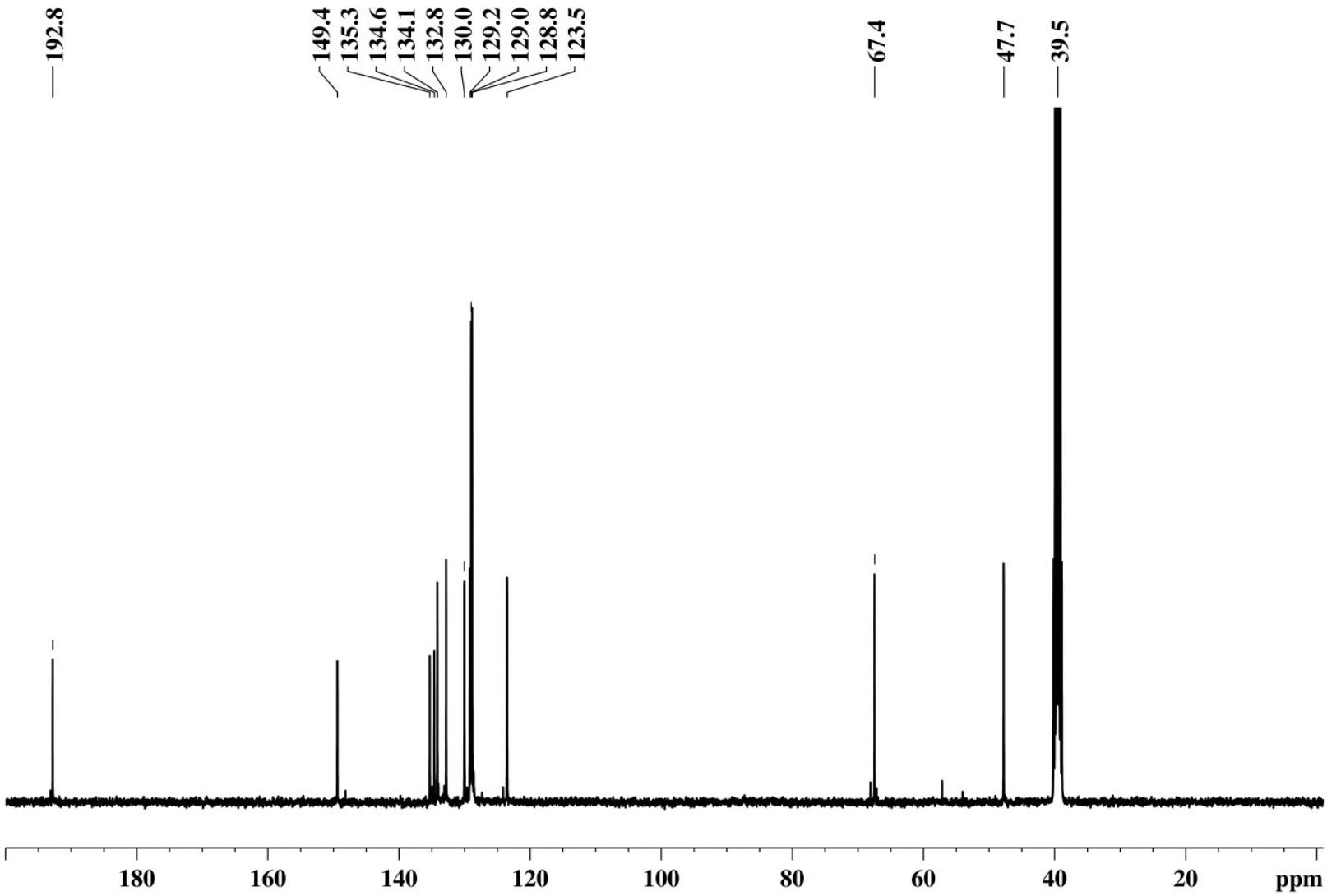


Figure S8. ^{13}C NMR spectrum of **3** in DMSO-d_6.

Computational part

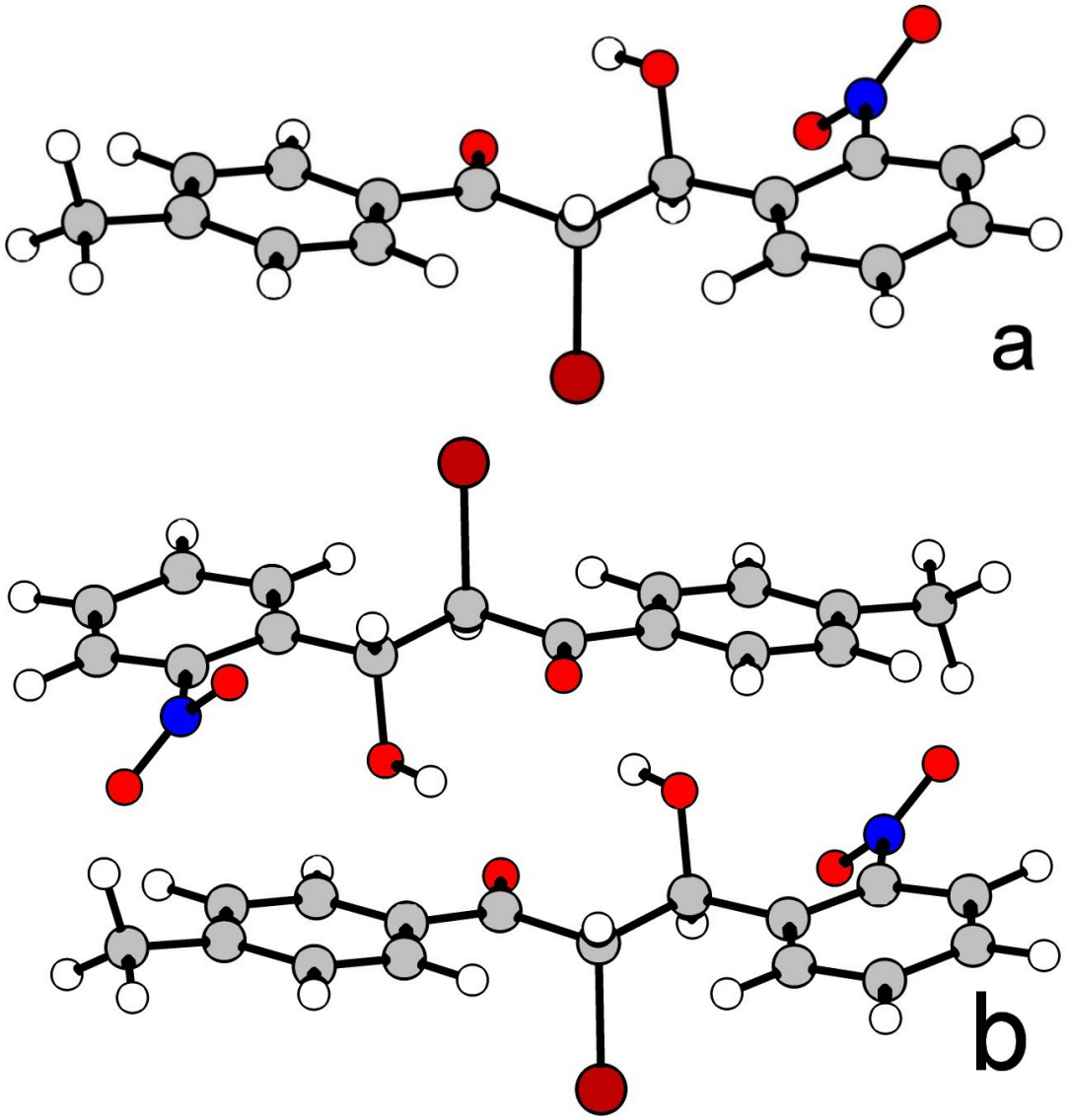


Figure S9. Optimized geometry for compound **1** (a) and its dimer (b).

Table S2. Topological parameters for intramolecular $H^2...H^{16}$ contacts according to the solid-state calculations.

Compound	$d(H^2…H^{16})$	$\rho(\mathbf{r})\ 10^2$	$\nabla^2\rho(\mathbf{r})\ 10^2$	$-V(\mathbf{r})\ 10^3$	$H(\mathbf{r})\ 10^3$
1	2.029	1.3519	5.3971	9.4706	2.0110
2	2.002	1.2888	5.0056	8.5187	1.9976
3	1.971	1.3499	5.0207	8.4218	2.0649

Table S3. Coordinates of all the atoms for the "gas-phase" optimized dimer of compound **1**, PBE0.

Br	3.707478000000	2.471245000000	1.611840000000
O	0.572379000000	1.172268000000	0.693468000000
O	2.267864000000	-0.375761000000	-1.034929000000
O	3.325835000000	-2.464360000000	1.034744000000
O	4.042060000000	-3.634187000000	-0.621246000000
N	4.007199000000	-2.619917000000	0.045110000000
C	1.323092000000	2.024596000000	0.261937000000
C	2.795392000000	1.681217000000	0.064919000000
H	3.188125000000	2.184051000000	-0.814949000000
C	3.049019000000	0.179180000000	0.000409000000
H	2.777115000000	-0.247389000000	0.966801000000
C	0.861538000000	3.386974000000	-0.077145000000
C	-0.472816000000	3.712488000000	0.169814000000
H	-1.120164000000	2.968937000000	0.614644000000
C	-0.964774000000	4.961650000000	-0.145844000000
H	-2.009222000000	5.177563000000	0.044568000000
C	-0.141818000000	5.931421000000	-0.716904000000
C	1.192256000000	5.609266000000	-0.953763000000
H	1.851522000000	6.352276000000	-1.388307000000
C	1.689791000000	4.357966000000	-0.641243000000
H	2.735988000000	4.156317000000	-0.829607000000
C	-0.689200000000	7.273940000000	-1.087257000000
H	-1.400316000000	7.631240000000	-0.340810000000
H	-1.224038000000	7.219387000000	-2.040286000000
H	0.103199000000	8.015055000000	-1.195047000000
C	4.486518000000	-0.193016000000	-0.324964000000
C	4.898071000000	-1.527283000000	-0.360139000000
C	6.160114000000	-1.919800000000	-0.768559000000
H	6.397324000000	-2.974434000000	-0.791335000000
C	7.086484000000	-0.960689000000	-1.134483000000
H	8.082333000000	-1.256071000000	-1.438922000000
C	6.717006000000	0.372252000000	-1.112896000000
H	7.423844000000	1.138982000000	-1.405302000000
C	5.435852000000	0.739167000000	-0.727811000000
H	5.184345000000	1.789981000000	-0.735841000000
H	1.356270000000	-0.487485000000	-0.726650000000

Br	-3.700752000000	-2.472778000000	-1.620624000000
O	-0.572871000000	-1.173140000000	-0.690863000000
O	-2.274027000000	0.373512000000	1.034184000000
O	-3.319373000000	2.468221000000	-1.027640000000
O	-4.038295000000	3.629789000000	0.632886000000
N	-4.003678000000	2.619596000000	-0.039426000000
C	-1.323924000000	-2.025172000000	-0.259147000000
C	-2.797196000000	-1.682390000000	-0.068775000000
H	-3.195014000000	-2.185263000000	0.808678000000
C	-3.051054000000	-0.180367000000	-0.004849000000
H	-2.775318000000	0.246740000000	-0.969971000000
C	-0.862273000000	-3.385994000000	0.085694000000
C	0.472579000000	-3.712061000000	-0.158123000000
H	1.120305000000	-2.969860000000	-0.604795000000
C	0.964300000000	-4.959910000000	0.162961000000
H	2.009093000000	-5.176380000000	-0.024848000000
C	0.140725000000	-5.927740000000	0.736521000000
C	-1.193703000000	-5.605053000000	0.970297000000
H	-1.853370000000	-6.346504000000	1.406879000000
C	-1.691069000000	-4.355045000000	0.652262000000
H	-2.737489000000	-4.152892000000	0.838757000000
C	0.688045000000	-7.268716000000	1.112520000000
H	1.396862000000	-7.630491000000	0.366015000000
H	1.225612000000	-7.209529000000	2.063719000000
H	-0.104602000000	-8.008654000000	1.226321000000
C	-4.489813000000	0.191871000000	0.314842000000
C	-4.898961000000	1.526747000000	0.355407000000
C	-6.162341000000	1.919550000000	0.759018000000
H	-6.397536000000	2.974539000000	0.786877000000
C	-7.092786000000	0.960072000000	1.113818000000
H	-8.089734000000	1.255673000000	1.414435000000
C	-6.726048000000	-0.373451000000	1.085944000000
H	-7.436256000000	-1.140474000000	1.369280000000
C	-5.443358000000	-0.740822000000	0.706144000000
H	-5.194185000000	-1.792236000000	0.708951000000
H	-1.361212000000	0.487021000000	0.729913000000

Table S4. Fractional coordinates of all the atoms in the unit cell for the optimized crystal structure of compound **1**. Cell parameters were not optimized and are shown above in the XRD part.

Atom				X/A	Y/B	Z/C
1	T	35	BR	4.269797565014E-01	-1.981771866916E-01	3.627626788314E-01
2	F	35	BR	-4.269797565014E-01	1.981771866916E-01	-3.627626788314E-01
3	T	8	O	5.352626471698E-02	-4.297156115952E-01	4.039130741542E-01
4	F	8	O	-5.352626471698E-02	4.297156115952E-01	-4.039130741542E-01
5	T	8	O	3.046877366594E-01	-4.387447274803E-01	-3.802664694654E-01
6	F	8	O	-3.046877366594E-01	4.387447274803E-01	3.802664694654E-01
7	T	8	O	2.820677166372E-01	-1.277743296848E-01	-1.919298696759E-01
8	F	8	O	-2.820677166372E-01	1.277743296848E-01	1.919298696759E-01
9	T	8	O	4.231243612690E-01	-1.610491661243E-01	-1.674143085447E-02
10	F	8	O	-4.231243612690E-01	1.610491661243E-01	1.674143085447E-02
11	T	7	N	4.122155237675E-01	-1.542689881150E-01	-1.348862336111E-01
12	F	7	N	-4.122155237675E-01	1.542689881150E-01	1.348862336111E-01
13	T	6	C	1.807088946330E-01	-4.413228922628E-01	3.457135675762E-01
14	F	6	C	-1.807088946330E-01	4.413228922628E-01	-3.457135675762E-01
15	T	6	C	3.607948405091E-01	-3.658260527841E-01	4.240640971339E-01
16	F	6	C	-3.607948405091E-01	3.658260527841E-01	-4.240640971339E-01
17	T	6	C	3.608874290023E-01	-3.175347639108E-01	-4.243608466676E-01
18	F	6	C	-3.608874290023E-01	3.175347639108E-01	4.243608466676E-01
19	T	6	C	1.651457686901E-01	4.763367360074E-01	2.038079744032E-01
20	F	6	C	-1.651457686901E-01	-4.763367360074E-01	-2.038079744032E-01
21	T	6	C	-9.519785858700E-04	4.121194584736E-01	1.311418213459E-01
22	F	6	C	9.519785858700E-04	-4.121194584736E-01	-1.311418213459E-01
23	T	6	C	-2.081457183269E-02	3.297568532399E-01	-8.168796411764E-04
24	F	6	C	2.081457183269E-02	-3.297568532399E-01	8.168796411764E-04
25	T	6	C	1.237511607554E-01	3.095193734247E-01	-6.492253857033E-02
26	F	6	C	-1.237511607554E-01	-3.095193734247E-01	6.492253857033E-02
27	T	6	C	2.888923832703E-01	3.767196700660E-01	6.519021734243E-03
28	F	6	C	-2.888923832703E-01	-3.767196700660E-01	-6.519021734243E-03
29	T	6	C	3.101311820010E-01	4.583310681660E-01	1.394000640738E-01
30	F	6	C	-3.101311820010E-01	-4.583310681660E-01	-1.394000640738E-01
31	T	6	C	1.002155528960E-01	2.181205030278E-01	-2.078117268621E-01
32	F	6	C	-1.002155528960E-01	-2.181205030278E-01	2.078117268621E-01
33	T	6	C	-4.613297709361E-01	-2.428368458401E-01	-3.432982193181E-01
34	F	6	C	4.613297709361E-01	2.428368458401E-01	3.432982193181E-01
35	T	6	C	-4.406233977703E-01	-1.734570399015E-01	-2.051560362570E-01
36	F	6	C	4.406233977703E-01	1.734570399015E-01	2.051560362570E-01
37	T	6	C	-2.795904741168E-01	-1.207206741267E-01	-1.252197481853E-01
38	F	6	C	2.795904741168E-01	1.207206741267E-01	1.252197481853E-01
39	T	6	C	-1.308802383830E-01	-1.340427412056E-01	-1.831549716733E-01

40	F	6	C	1.308802383830E-01	1.340427412056E-01	1.831549716733E-01
41	T	6	C	-1.465179776128E-01	-2.007560117603E-01	-3.196221581036E-01
42	F	6	C	1.465179776128E-01	2.007560117603E-01	3.196221581036E-01
43	T	6	C	-3.092487713698E-01	-2.553783155816E-01	-3.975105200500E-01
44	F	6	C	3.092487713698E-01	2.553783155816E-01	3.975105200500E-01
45	T	1	H	4.548567056261E-01	-4.312879320342E-01	3.963347844850E-01
46	F	1	H	-4.548567056261E-01	4.312879320342E-01	-3.963347844850E-01
47	T	1	H	2.710291158735E-01	-2.471679792567E-01	-4.039862033874E-01
48	F	1	H	-2.710291158735E-01	2.471679792567E-01	4.039862033874E-01
49	T	1	H	-1.146733939753E-01	4.283979077464E-01	1.791305986035E-01
50	F	1	H	1.146733939753E-01	-4.283979077464E-01	-1.791305986035E-01
51	T	1	H	-1.508826180098E-01	2.809950006526E-01	-5.569002145230E-02
52	F	1	H	1.508826180098E-01	-2.809950006526E-01	5.569002145230E-02
53	T	1	H	4.032116226071E-01	3.621176410595E-01	-4.149453234323E-02
54	F	1	H	-4.032116226071E-01	-3.621176410595E-01	4.149453234323E-02
55	T	1	H	4.411864192773E-01	-4.934485844724E-01	1.923396054209E-01
56	F	1	H	-4.411864192773E-01	4.934485844724E-01	-1.923396054209E-01
57	T	1	H	4.536901183982E-02	2.695922695537E-01	-2.757192302166E-01
58	F	1	H	-4.536901183982E-02	-2.695922695537E-01	2.757192302166E-01
59	T	1	H	9.569552372698E-03	1.167050037702E-01	-2.225240567672E-01
60	F	1	H	-9.569552372698E-03	-1.167050037702E-01	2.225240567672E-01
61	T	1	H	2.234106801332E-01	1.969307813609E-01	-2.382130642226E-01
62	F	1	H	-2.234106801332E-01	-1.969307813609E-01	2.382130642226E-01
63	T	1	H	-2.741399346811E-01	-7.021058066496E-02	-1.863129873192E-02
64	F	1	H	2.741399346811E-01	7.021058066496E-02	1.863129873192E-02
65	T	1	H	-3.679582408943E-03	-9.617285494579E-02	-1.222385412645E-01
66	F	1	H	3.679582408943E-03	9.617285494579E-02	1.222385412645E-01
67	T	1	H	-3.117423888405E-02	-2.133948829430E-01	-3.665854665670E-01
68	F	1	H	3.117423888405E-02	2.133948829430E-01	3.665854665670E-01
69	T	1	H	-3.158521698978E-01	-3.097943256938E-01	4.966451651490E-01
70	F	1	H	3.158521698978E-01	3.097943256938E-01	-4.966451651490E-01
71	T	1	H	1.780888632697E-01	-4.702610800040E-01	-3.984817028369E-01
72	F	1	H	-1.780888632697E-01	4.702610800040E-01	3.984817028369E-01

Table S5. Fractional coordinates of all the atoms in the unit cell for the optimized crystal structure of compound **2**. Cell parameters were not optimized and are shown above in the XRD part.

Atom				X/A	Y/B	Z/C
1	T	35	BR	-2.562564007773E-01	3.682859396100E-01	2.241886325265E-01
2	F	35	BR	-2.437435992227E-01	-1.317140603900E-01	2.758113674735E-01
3	F	35	BR	2.562564007773E-01	-3.682859396100E-01	-2.241886325265E-01
4	F	35	BR	2.437435992227E-01	1.317140603900E-01	-2.758113674735E-01
5	T	17	CL	4.437531326618E-01	2.870393365195E-01	4.642133982171E-01
6	F	17	CL	5.624686733816E-02	-2.129606634805E-01	3.578660178288E-02

7	F	17	CL	-4.437531326618E-01	-2.870393365195E-01	-4.642133982171E-01
8	F	17	CL	-5.624686733816E-02	2.129606634805E-01	-3.578660178288E-02
9	T	8	O	-4.342226131310E-01	4.692563363558E-02	1.066718720392E-01
10	F	8	O	-6.577738686904E-02	-4.530743663644E-01	3.933281279608E-01
11	F	8	O	4.342226131310E-01	-4.692563363558E-02	-1.066718720392E-01
12	F	8	O	6.577738686904E-02	4.530743663644E-01	-3.933281279608E-01
13	T	8	O	-4.842635685696E-01	2.775009447947E-01	-6.985354984437E-02
14	F	8	O	-1.573643143036E-02	-2.224990552053E-01	-4.301464501556E-01
15	F	8	O	4.842635685696E-01	-2.775009447947E-01	6.985354984437E-02
16	F	8	O	1.573643143036E-02	2.224990552053E-01	4.301464501556E-01
17	T	8	O	-3.108254529334E-01	9.290712652232E-02	-9.710124480119E-02
18	F	8	O	-1.891745470666E-01	-4.070928734777E-01	-4.028987551988E-01
19	F	8	O	3.108254529334E-01	-9.290712652232E-02	9.710124480119E-02
20	F	8	O	1.891745470666E-01	4.070928734777E-01	4.028987551988E-01
21	T	8	O	-3.339958678469E-01	2.252545189151E-01	-2.351683805921E-01
22	F	8	O	-1.660041321531E-01	-2.747454810849E-01	-2.648316194079E-01
23	F	8	O	3.339958678469E-01	-2.252545189151E-01	2.351683805921E-01
24	F	8	O	1.660041321531E-01	2.747454810849E-01	2.648316194079E-01
25	T	7	N	-3.157885311941E-01	2.252297095400E-01	-1.443022151812E-01
26	F	7	N	-1.842114688059E-01	-2.747702904600E-01	-3.556977848188E-01
27	F	7	N	3.157885311941E-01	-2.252297095400E-01	1.443022151812E-01
28	F	7	N	1.842114688059E-01	2.747702904600E-01	3.556977848188E-01
29	T	6	C	-4.335233145147E-01	1.871906678829E-01	1.404431473126E-01
30	F	6	C	-6.647668548532E-02	-3.128093321171E-01	3.595568526874E-01
31	F	6	C	4.335233145147E-01	-1.871906678829E-01	-1.404431473126E-01
32	F	6	C	6.647668548532E-02	3.128093321171E-01	-3.595568526874E-01
33	T	6	C	-3.907423163457E-01	3.334383551593E-01	1.067473176402E-01
34	F	6	C	-1.092576836543E-01	-1.665616448407E-01	3.932526823598E-01
35	F	6	C	3.907423163457E-01	-3.334383551593E-01	-1.067473176402E-01
36	F	6	C	1.092576836543E-01	1.665616448407E-01	-3.932526823598E-01
37	T	6	C	-3.826834661832E-01	2.914412434247E-01	1.155178802533E-02
38	F	6	C	-1.173165338168E-01	-2.085587565753E-01	4.884482119747E-01
39	F	6	C	3.826834661832E-01	-2.914412434247E-01	-1.155178802533E-02
40	F	6	C	1.173165338168E-01	2.085587565753E-01	-4.884482119747E-01
41	T	6	C	-4.662564661534E-01	2.163753162566E-01	2.179883040620E-01
42	F	6	C	-3.374353384661E-02	-2.836246837434E-01	2.820116959380E-01
43	F	6	C	4.662564661534E-01	-2.163753162566E-01	-2.179883040620E-01
44	F	6	C	3.374353384661E-02	2.836246837434E-01	-2.820116959380E-01
45	T	6	C	-4.719036643027E-01	7.844684066736E-02	2.724444040915E-01
46	F	6	C	-2.809633569729E-02	-4.215531593326E-01	2.275555959085E-01
47	F	6	C	4.719036643027E-01	-7.844684066736E-02	-2.724444040915E-01
48	F	6	C	2.809633569729E-02	4.215531593326E-01	-2.275555959085E-01
49	T	6	C	-4.984761888210E-01	9.883779661413E-02	3.484181705966E-01
50	F	6	C	-1.523811179027E-03	-4.011622033859E-01	1.515818294034E-01
51	F	6	C	4.984761888210E-01	-9.883779661413E-02	-3.484181705966E-01
52	F	6	C	1.523811179027E-03	4.011622033859E-01	-1.515818294034E-01
53	T	6	C	4.789365352832E-01	2.588996524833E-01	3.672568099834E-01
54	F	6	C	2.106346471675E-02	-2.411003475167E-01	1.327431900166E-01
55	F	6	C	-4.789365352832E-01	-2.588996524833E-01	-3.672568099834E-01
56	F	6	C	-2.106346471675E-02	2.411003475167E-01	-1.327431900166E-01
57	T	6	C	4.830546759213E-01	3.983494751905E-01	3.145116487824E-01
58	F	6	C	1.694532407872E-02	-1.016505248095E-01	1.854883512176E-01

59	F	6	C	-4.830546759213E-01	-3.983494751905E-01	-3.145116487824E-01
60	F	6	C	-1.694532407872E-02	1.016505248095E-01	-1.854883512176E-01
61	T	6	C	-4.878998906001E-01	3.764969359803E-01	2.402915131973E-01
62	F	6	C	-1.210010939991E-02	-1.235030640197E-01	2.597084868027E-01
63	F	6	C	4.878998906001E-01	-3.764969359803E-01	-2.402915131973E-01
64	F	6	C	1.210010939991E-02	1.235030640197E-01	-2.597084868027E-01
65	T	6	C	-3.275210922705E-01	4.199421281802E-01	-1.928728176872E-02
66	F	6	C	-1.724789077295E-01	-8.005787181983E-02	-4.807127182313E-01
67	F	6	C	3.275210922705E-01	-4.199421281802E-01	1.928728176872E-02
68	F	6	C	1.724789077295E-01	8.005787181983E-02	4.807127182313E-01
69	T	6	C	-2.981959883790E-01	3.865657530342E-01	-9.376404475441E-02
70	F	6	C	-2.018040116210E-01	-1.134342469658E-01	-4.062359552456E-01
71	F	6	C	2.981959883790E-01	-3.865657530342E-01	9.376404475441E-02
72	F	6	C	2.018040116210E-01	1.134342469658E-01	4.062359552456E-01
73	T	6	C	-2.516541918837E-01	-4.942914440667E-01	-1.256830151440E-01
74	F	6	C	-2.483458081163E-01	5.708555933315E-03	-3.743169848560E-01
75	F	6	C	2.516541918837E-01	4.942914440667E-01	1.256830151440E-01
76	F	6	C	2.483458081163E-01	-5.708555933315E-03	3.743169848560E-01
77	T	6	C	-2.308050614978E-01	-3.369171406499E-01	-8.166347527318E-02
78	F	6	C	-2.691949385022E-01	1.630828593501E-01	-4.183365247268E-01
79	F	6	C	2.308050614978E-01	3.369171406499E-01	8.166347527318E-02
80	F	6	C	2.691949385022E-01	-1.630828593501E-01	4.183365247268E-01
81	T	6	C	-2.607819065190E-01	-2.988901891674E-01	-9.734301597713E-03
82	F	6	C	-2.392180934810E-01	2.011098108326E-01	-4.902656984023E-01
83	F	6	C	2.607819065190E-01	2.988901891674E-01	9.734301597713E-03
84	F	6	C	2.392180934810E-01	-2.011098108326E-01	4.902656984023E-01
85	T	6	C	-3.105606747048E-01	-4.176337122907E-01	1.869550730291E-02
86	F	6	C	-1.894393252952E-01	8.236628770931E-02	4.813044926971E-01
87	F	6	C	3.105606747048E-01	4.176337122907E-01	-1.869550730291E-02
88	F	6	C	1.894393252952E-01	-8.236628770931E-02	-4.813044926971E-01
89	T	1	H	-4.332175664414E-01	4.492607480341E-01	9.803743901420E-02
90	F	1	H	-6.678243355858E-02	-5.073925196590E-02	4.019625609858E-01
91	F	1	H	4.332175664414E-01	-4.492607480341E-01	-9.803743901420E-02
92	F	1	H	6.678243355858E-02	5.073925196590E-02	-4.019625609858E-01
93	T	1	H	-3.440626300932E-01	1.709920115893E-01	2.413655110689E-02
94	F	1	H	-1.559373699068E-01	-3.290079884107E-01	4.758634488931E-01
95	F	1	H	3.440626300932E-01	-1.709920115893E-01	-2.413655110689E-02
96	F	1	H	1.559373699068E-01	3.290079884107E-01	-4.758634488931E-01
97	T	1	H	-4.536503490207E-01	-4.543766561472E-02	2.556524823661E-01
98	F	1	H	-4.634965097932E-02	4.545623343853E-01	2.443475176339E-01
99	F	1	H	4.536503490207E-01	4.543766561472E-02	-2.556524823661E-01
100	F	1	H	4.634965097932E-02	-4.545623343853E-01	-2.443475176339E-01
101	T	1	H	4.987415444765E-01	-6.819244308002E-03	3.926376539228E-01
102	F	1	H	1.258455523518E-03	4.931807556920E-01	1.073623460772E-01
103	F	1	H	-4.987415444765E-01	6.819244308002E-03	-3.926376539228E-01
104	F	1	H	-1.258455523518E-03	-4.931807556920E-01	-1.073623460772E-01
105	T	1	H	4.645865182600E-01	-4.784525505979E-01	3.319615314405E-01
106	F	1	H	3.541348174002E-02	2.154744940210E-02	1.680384685595E-01
107	F	1	H	-4.645865182600E-01	4.784525505979E-01	-3.319615314405E-01
108	F	1	H	-3.541348174002E-02	-2.154744940210E-02	-1.680384685595E-01
109	T	1	H	-4.829660992033E-01	4.863453627907E-01	1.999753534444E-01
110	F	1	H	-1.703390079670E-02	-1.365463720932E-02	3.000246465556E-01

111	F	1	H	4.829660992033E-01	-4.863453627907E-01	-1.999753534444E-01
112	F	1	H	1.703390079670E-02	1.365463720932E-02	-3.000246465556E-01
113	T	1	H	-2.300350176593E-01	4.725944383671E-01	-1.830411780313E-01
114	F	1	H	-2.699649823407E-01	-2.740556163289E-02	-3.169588219687E-01
115	F	1	H	2.300350176593E-01	-4.725944383671E-01	1.830411780313E-01
116	F	1	H	2.699649823407E-01	2.740556163289E-02	3.169588219687E-01
117	T	1	H	-1.919078002652E-01	-2.448046429138E-01	-1.043383404043E-01
118	F	1	H	-3.080921997348E-01	2.551953570862E-01	-3.956616595957E-01
119	F	1	H	1.919078002652E-01	2.448046429138E-01	1.043383404043E-01
120	F	1	H	3.080921997348E-01	-2.551953570862E-01	3.956616595957E-01
121	T	1	H	-2.454399035487E-01	-1.752503394368E-01	2.484169486697E-02
122	F	1	H	-2.545600964513E-01	3.247496605632E-01	4.751583051330E-01
123	F	1	H	2.454399035487E-01	1.752503394368E-01	-2.484169486697E-02
124	F	1	H	2.545600964513E-01	-3.247496605632E-01	-4.751583051330E-01
125	T	1	H	-3.351437426601E-01	-3.820505125750E-01	7.355467570711E-02
126	F	1	H	-1.648562573399E-01	1.179494874250E-01	4.264453242929E-01
127	F	1	H	3.351437426601E-01	3.820505125750E-01	-7.355467570711E-02
128	F	1	H	1.648562573399E-01	-1.179494874250E-01	-4.264453242929E-01
129	T	1	H	4.932924547068E-01	1.606653370805E-01	-7.805560065820E-02
130	F	1	H	6.707545293250E-03	-3.393346629195E-01	-4.219443993418E-01
131	F	1	H	-4.932924547068E-01	-1.606653370805E-01	7.805560065820E-02
132	F	1	H	-6.707545293250E-03	3.393346629195E-01	4.219443993418E-01

Table S6. Fractional coordinates of all the atoms in the unit cell for the optimized crystal structure of compound **3**. Cell parameters were not optimized and are shown above in the XRD part.

Atom				X/A	Y/B	Z/C
1	T	35	BR	-2.233815033083E-01	-4.947843514734E-01	-4.544496513677E-01
2	F	35	BR	2.233815033083E-01	4.947843514734E-01	4.544496513677E-01
3	T	8	O	4.904557392255E-01	1.777905312546E-01	4.661581588464E-01
4	F	8	O	-4.904557392255E-01	-1.777905312546E-01	-4.661581588464E-01
5	T	8	O	-1.673168663006E-01	-6.241435018931E-03	-4.127391319303E-01
6	F	8	O	1.673168663006E-01	6.241435018931E-03	4.127391319303E-01
7	T	8	O	-2.544105231144E-01	2.420297312894E-01	-1.666149863625E-01
8	F	8	O	2.544105231144E-01	-2.420297312894E-01	1.666149863625E-01
9	T	8	O	-1.485387092028E-01	-4.921983964542E-01	-1.200552010979E-01
10	F	8	O	1.485387092028E-01	4.921983964542E-01	1.200552010979E-01
11	T	7	N	-1.401270064641E-01	3.639435486433E-01	-1.634472911432E-01
12	F	7	N	1.401270064641E-01	-3.639435486433E-01	1.634472911432E-01
13	T	6	C	-3.781464587866E-01	2.087778683738E-01	4.295691446476E-01
14	F	6	C	3.781464587866E-01	-2.087778683738E-01	-4.295691446476E-01
15	T	6	C	-2.041607118262E-01	2.644374657581E-01	-4.880536956512E-01
16	F	6	C	2.041607118262E-01	-2.644374657581E-01	4.880536956512E-01
17	T	6	C	-1.768774648579E-01	1.674214767321E-01	-3.827095414908E-01
18	F	6	C	1.768774648579E-01	-1.674214767321E-01	3.827095414908E-01
19	T	6	C	-3.867906654553E-01	1.990217442444E-01	3.106430045542E-01
20	F	6	C	3.867906654553E-01	-1.990217442444E-01	-3.106430045542E-01
21	T	6	C	4.471901605690E-01	2.005901114465E-01	2.377660976275E-01
22	F	6	C	-4.471901605690E-01	-2.005901114465E-01	-2.377660976275E-01
23	T	6	C	4.321762263821E-01	1.889500610837E-01	1.255661811148E-01

24	F	6	C	-4.321762263821E-01	-1.889500610837E-01	-1.255661811148E-01
25	T	6	C	-4.177765549454E-01	1.736593873856E-01	8.472889241876E-02
26	F	6	C	4.177765549454E-01	-1.736593873856E-01	-8.472889241876E-02
27	T	6	C	-2.533176020607E-01	1.691366140091E-01	1.564697578334E-01
28	F	6	C	2.533176020607E-01	-1.691366140091E-01	-1.564697578334E-01
29	T	6	C	-2.366730709081E-01	1.839965143316E-01	2.689600896873E-01
30	F	6	C	2.366730709081E-01	-1.839965143316E-01	-2.689600896873E-01
31	T	6	C	-4.255137845684E-03	2.343702699517E-01	-3.044604790467E-01
32	F	6	C	4.255137845684E-03	-2.343702699517E-01	3.044604790467E-01
33	T	6	C	1.144199486135E-02	3.360771301987E-01	-2.083833439005E-01
34	F	6	C	-1.144199486135E-02	-3.360771301987E-01	2.083833439005E-01
35	T	6	C	1.724832746835E-01	4.137398667181E-01	-1.483585299382E-01
36	F	6	C	-1.724832746835E-01	-4.137398667181E-01	1.483585299382E-01
37	T	6	C	3.251465926204E-01	3.856248898720E-01	-1.824407813577E-01
38	F	6	C	-3.251465926204E-01	-3.856248898720E-01	1.824407813577E-01
39	T	6	C	3.145996842693E-01	2.800321700723E-01	-2.750547766898E-01
40	F	6	C	-3.145996842693E-01	-2.800321700723E-01	2.750547766898E-01
41	T	6	C	1.519532978071E-01	2.075307499624E-01	-3.355908849092E-01
42	F	6	C	-1.519532978071E-01	-2.075307499624E-01	3.355908849092E-01
43	T	1	H	-2.860530446256E-01	-6.594761922435E-02	-4.267184364916E-01
44	F	1	H	2.860530446256E-01	6.594761922435E-02	4.267184364916E-01
45	T	1	H	-8.878022345429E-02	2.612551191173E-01	4.769808430501E-01
46	F	1	H	8.878022345429E-02	-2.612551191173E-01	-4.769808430501E-01
47	T	1	H	-2.893726015094E-01	1.816962908082E-01	-3.460997529314E-01
48	F	1	H	2.893726015094E-01	-1.816962908082E-01	3.460997529314E-01
49	T	1	H	3.307037173671E-01	2.139858379483E-01	2.701570331734E-01
50	F	1	H	-3.307037173671E-01	-2.139858379483E-01	-2.701570331734E-01
51	T	1	H	3.036876095142E-01	1.936700695816E-01	6.908044892946E-02
52	F	1	H	-3.036876095142E-01	-1.936700695816E-01	-6.908044892946E-02
53	T	1	H	-4.302312312720E-01	1.640783832136E-01	-3.666291944305E-03
54	F	1	H	4.302312312720E-01	-1.640783832136E-01	3.666291944305E-03
55	T	1	H	-1.361676949276E-01	1.553770877381E-01	1.247033088848E-01
56	F	1	H	1.361676949276E-01	-1.553770877381E-01	-1.247033088848E-01
57	T	1	H	-1.063592369378E-01	1.788896102371E-01	3.231015586236E-01
58	F	1	H	1.063592369378E-01	-1.788896102371E-01	-3.231015586236E-01
59	T	1	H	1.756054526089E-01	4.920481244637E-01	-7.473838238459E-02
60	F	1	H	-1.756054526089E-01	-4.920481244637E-01	7.473838238459E-02
61	T	1	H	4.519690518155E-01	4.465469708737E-01	-1.370208333986E-01
62	F	1	H	-4.519690518155E-01	-4.465469708737E-01	1.370208333986E-01
63	T	1	H	4.338772584772E-01	2.568371782507E-01	-3.022103342764E-01
64	F	1	H	-4.338772584772E-01	-2.568371782507E-01	3.022103342764E-01
65	T	1	H	1.446665339362E-01	1.289961651360E-01	-4.100008219114E-01
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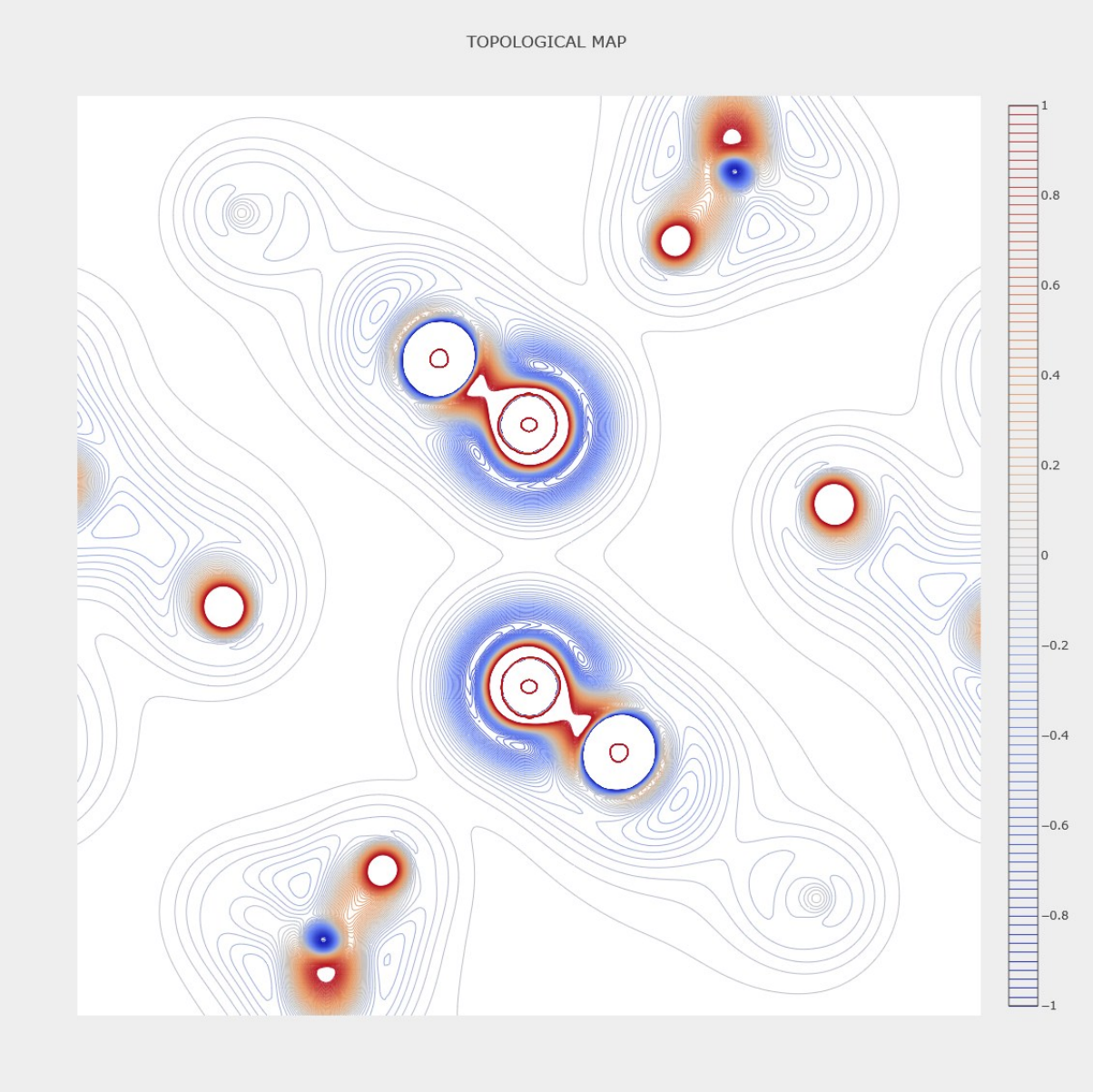

Figure S10. Contour map of the negative Laplacian function of the calculated crystal electron density $-\nabla^2\rho(\mathbf{r})$ for **1** in the plane of C^1, O^1 and $O^{1(a)}$ atoms. Relative scale is chosen from –1 to 1 with the step value of 0.02.

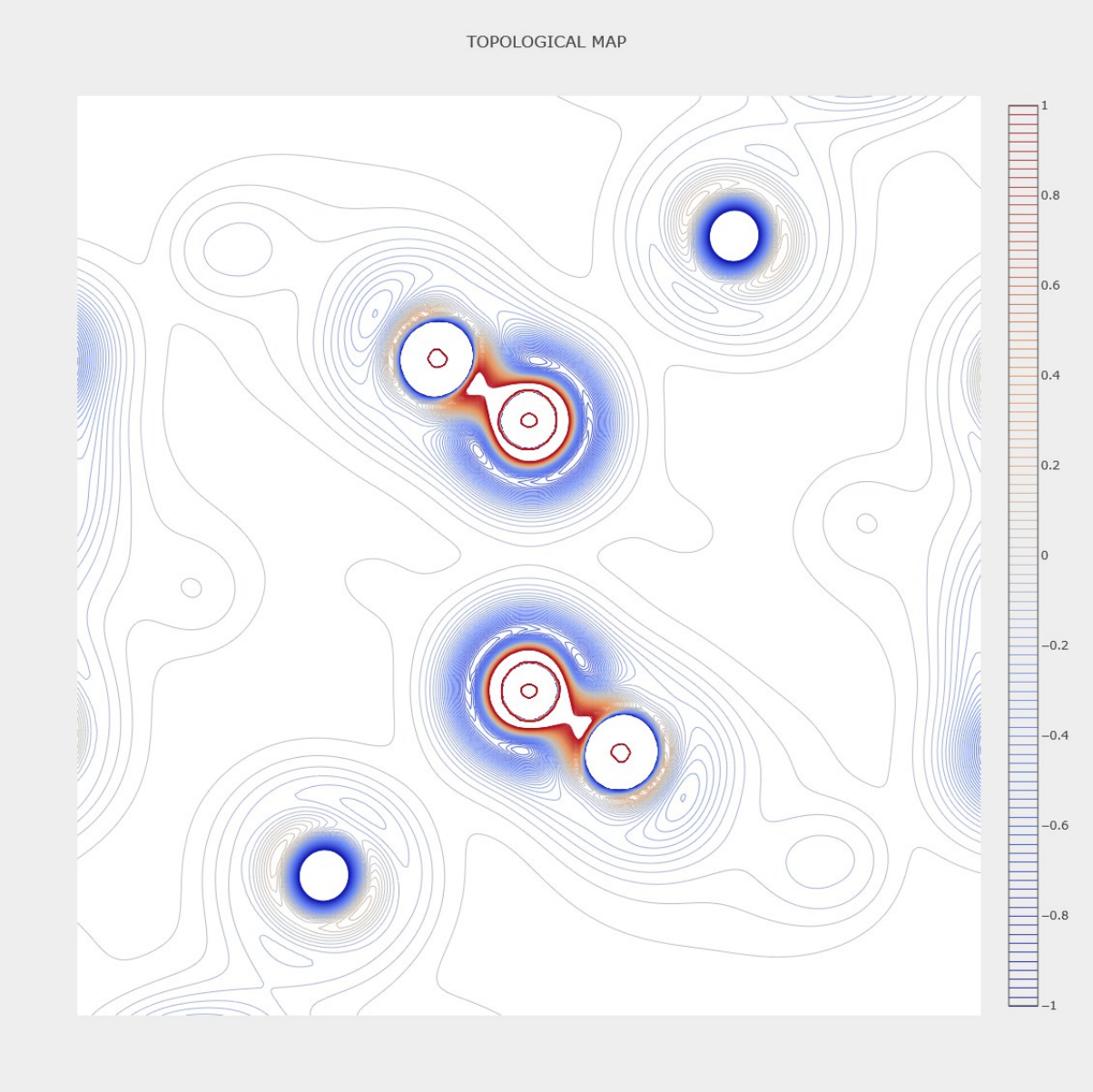

Figure S11. Contour map of the negative Laplacian function of the calculated crystal electron density $-\nabla^2\rho(\mathbf{r})$ for **2** in the plane of C^1, O^1 and $O^{1(e)}$ atoms. Relative scale is chosen from –1 to 1 with the step value of 0.02.

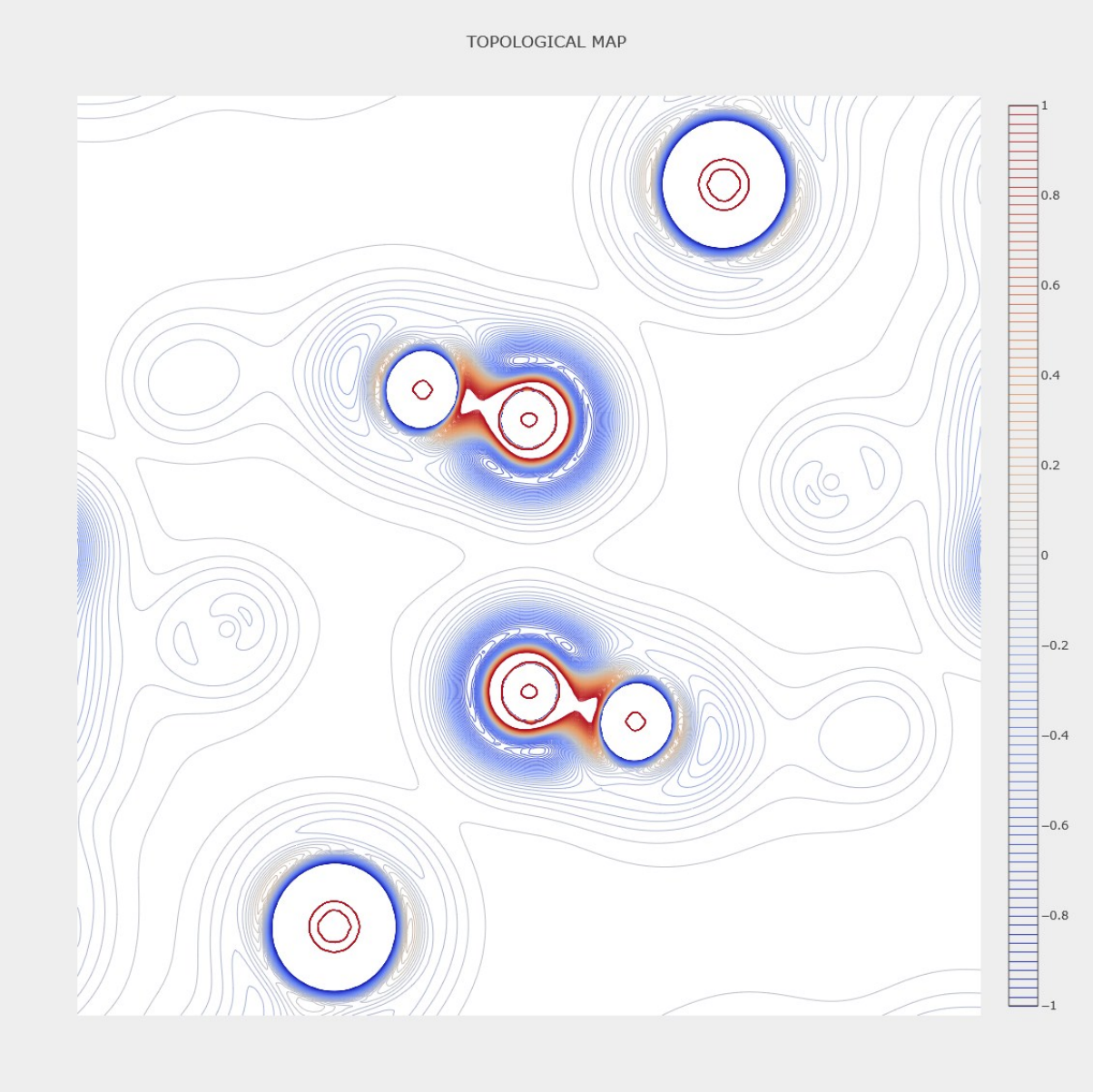

Figure S12. Contour map of the negative Laplacian function of the calculated crystal electron density $-\nabla^2\rho(\mathbf{r})$ for **3** in the plane of C^1, O^1 and $O^{1(h)}$ atoms. Relative scale is chosen from –1 to 1 with the step value of 0.02.

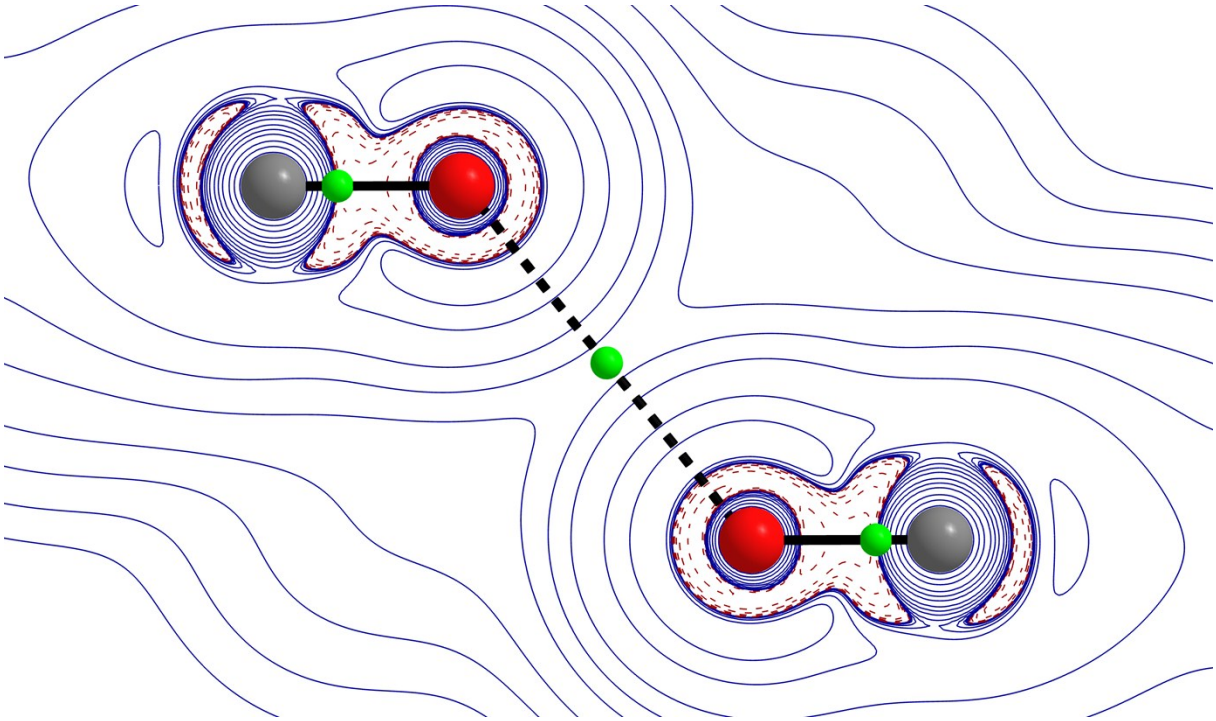

Figure S13. Contour map of the Laplacian function of the calculated electron density $\nabla^2\rho(\mathbf{r})$ for "gas-phase" dimer **1** in the plane of C^1, O^1 and O^{1a} atoms. Only the region of interest is presented. Minimum and maximum electron density values are 0.0001 and $1.0 \cdot 10^{38}$ a.u. respectively, resolution is set to 0.1 a.u. Dashed lines represent local increase of electron density ($\nabla^2\rho(\mathbf{r}) < 0$), while solid lines represent local decrease.

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