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Supporting information for article:

The X-ray constrained wavefunction of the [Mn(CO)4{(C6H5)2P−S−C(Br2)−P(C6H5)2}]Br complex: A theoretical and experimental study of dihalogen bonds and other non-covalent interactions

Juan F. Van der Maelen, Mario Ceroni and Javier Ruiz

S1. Synthesis and crystallization of $[Mn(CO)_4(P(C_6H_5)_2)_2SCBr_2]Br$

To a solution of the complex $[(CO)_4Mn\{(Ph_2P)_2C\text{-}S_2\text{-}C(PPh_2)_2\}Mn(CO)_4]$ (30 mg, 0.026 mmol) in CH_2Cl_2 (5 mL), a solution of Br_2 in CH_2Cl_2 (5.3 mL, 0.1 M, 0.53 mmol) was added under continuous stirring. The resulting mixture was stirred for 0.5 h. The solution was then filtered and the solvent eliminated to dryness under vacuum. The residue was washed with diethyl ether (3 x 5 mL) to yield a yellow solid. Yield: 27 mg (63 %).

Crystals suitable for an X-ray study were obtained by slow diffusion of hexane into a dichloromethane solution of the compound, although most of the crystals obtained were twinned and then discarded for the X-ray study.

S2 Spectroscopic data of $[Mn(CO)_4(P(C_6H_5)_2)_2SCBr_2]Br$

IR (CH_2Cl_2, cm^{-1}, ν(CO)): 2103 (s), 2041 (s), 2029 (vs), 2020 (sh).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 113.2 (br, PSC), 137.1 (br, $PCBr_2$).

S3. X-ray structure determination of $[Mn(CO)_4(P(C_6H_5)_2)_2SCBr_2]Br$

A yellow crystal, 0.264 × 0.231 × 0.099 mm size, was used for collecting data in a Bruker APEX-II CCD single crystal diffractometer provided with a MoK_α radiation graphite crystal monochromator (λ = 0.71073 Å). Measurements were made both at room temperature and at 100 K, but the latter were discarded for this study due to the twinning observed. Unit cell dimensions were determined using Bruker software (Bruker, 2006). Space group C2 was found from systematic absences and structure determination. 3749 reflections were measured, hkl range (-18, 0, -17) to (18, 19, 0), theta limits ($1.42° < \theta < 25.97°$). SAINT v8.34A (Siemens, 1995) integration software was used for cell refinement and SORTAV (Blessing, 1987, 1989) was used for data reduction. A semi-empirical absorption correction was applied using a multi-scan technique (minimum and maximum transmission factors, respectively, 0.528 and 0.996).

The structure was solved by direct methods using the program SIR-97 (Altomare *et al.*, 1999). Isotropic least-squares refinement, using the program SHELXL-2018/3 (Sheldrick, 2015), converged to R = 0.077. A subsequent full matrix anisotropic least-squares refinement over F^2, using the same software, followed by a Difference Fourier synthesis allowed the location of some of the hydrogen atoms. Positional parameters and anisotropic displacement parameters of the non-hydrogen atoms

were then refined. Hydrogen atoms were geometrically fixed to their parent atoms and isotropically refined with their displacement parameters constrained to be $1.2U_{eq}$ of their parent atoms in order to increase the reflexions/parameters ratio. A rather disordered solvent area containing several molecules of CH_2Cl_2 could not be modelled by means of any constrained/restrained method, and thus it was treated by the SQUEEZE procedure included in the PLATON program package (Spek, 2009, 2020) (further details about refinement protocols may be found elsewhere: Van der Maelen & Sheldrick, 1996; Van der Maelen, 1999).

Final conventional agreement factors were R(F) = 0.046 for the 2399 'observed' reflections and 361 variables, and wR(F2) = 0.127 for the whole set of 3603 reflections. The function minimized was $w(|Fo|^2-|Fc|^2)^2$, $w = 1/(\sigma^2(Fo^2) + (0.0823P)^2)$, with $\sigma(Fo)$ obtained from counting statistics and $P = (Fo^2 + 2Fc^2)/3$. The maximum shift over error ratio in the last full matrix least-squares cycle was less than 0.001, while the final Difference Fourier map showed no peaks higher than 0.68 e/Å^3 nor deeper than -0.50 e/Å^3. The residual density map is shown in Fig. S2 (note that the highest residuals are positioned close to Br atoms, where their lone pairs are located). Atomic scattering factors were taken from the International Tables for Crystallography (1995). CIF files and other publication material created with the aid of WinGX (Farrugia, 2012).

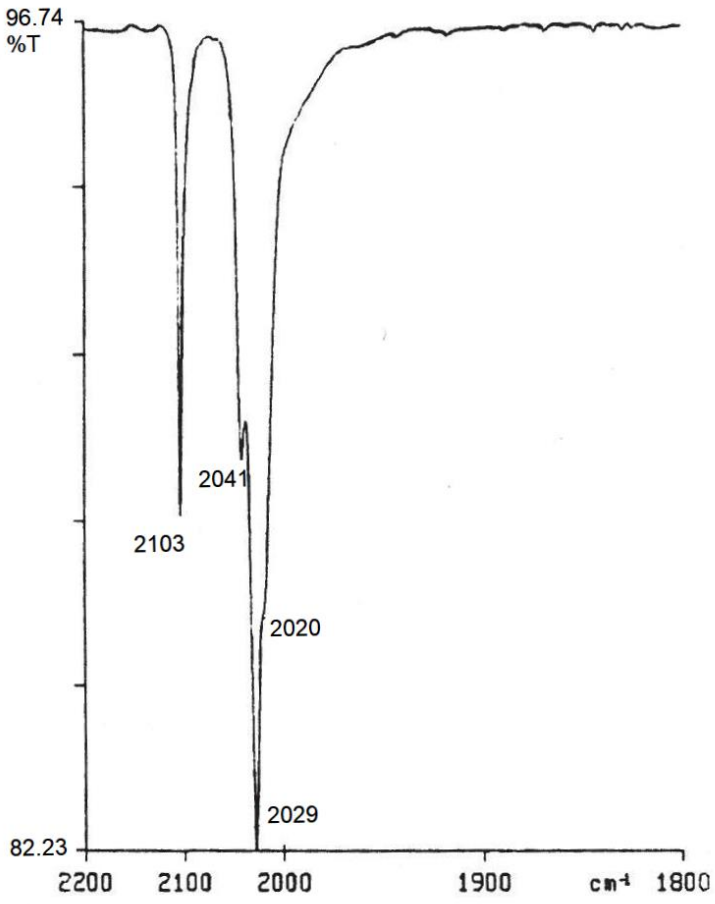


Figure S1 IR spectrum of $[Mn(CO)_4(P(C_6H_5)_2)_2SCBr_2]Br$.

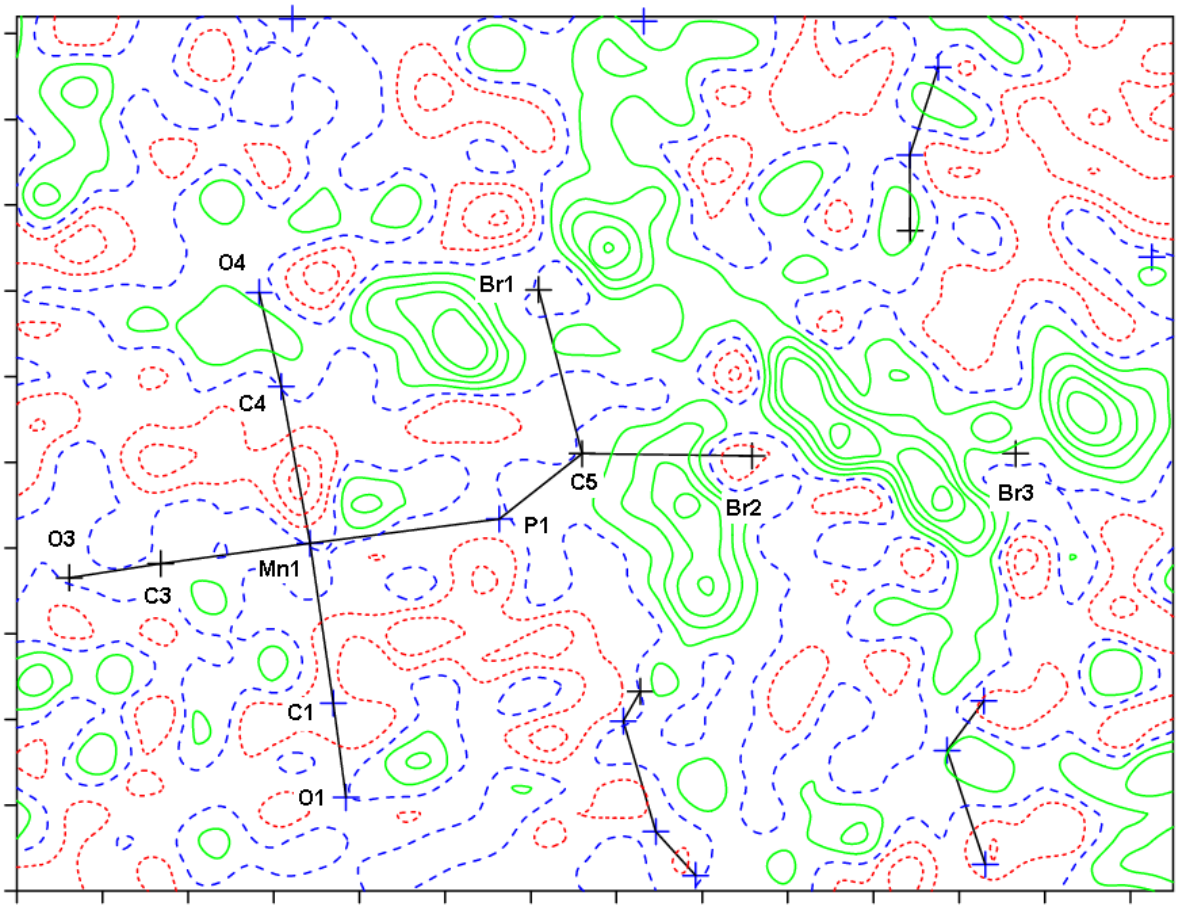
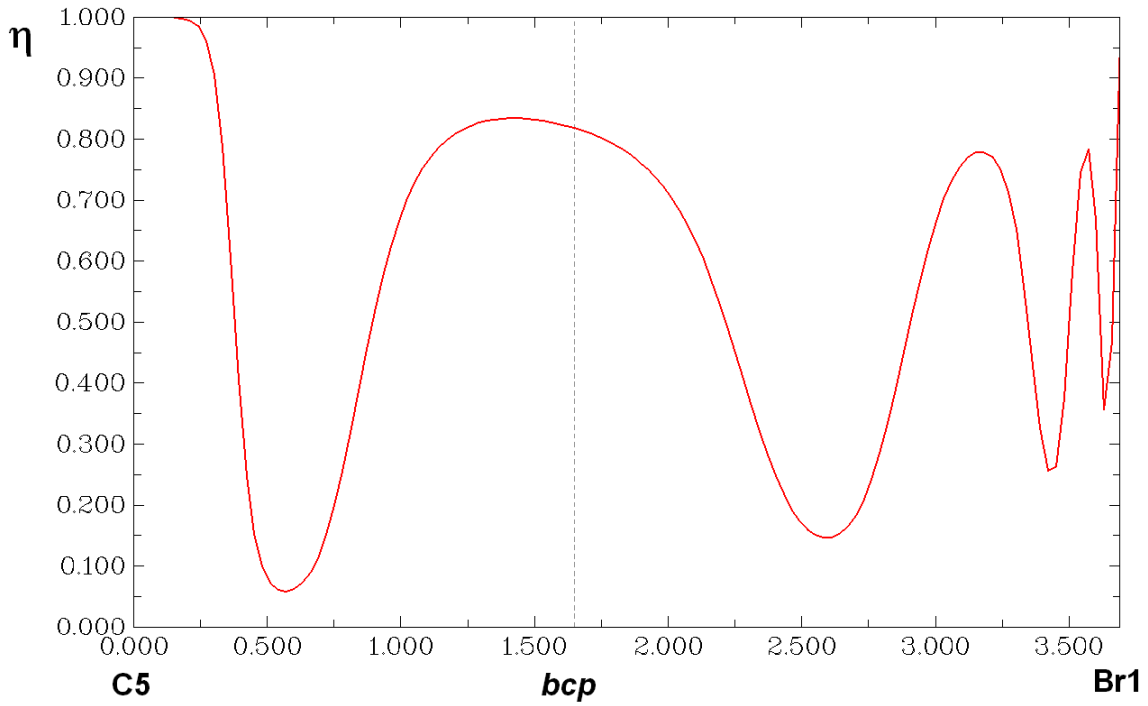


Figure S2. Residual electron density map from the X-ray refinement. The contour intervals are drawn at ±0.10 e Å^{-3} (dotted red lines: negative values, full green lines: positive values, dotted blue lines: zero value).

(a)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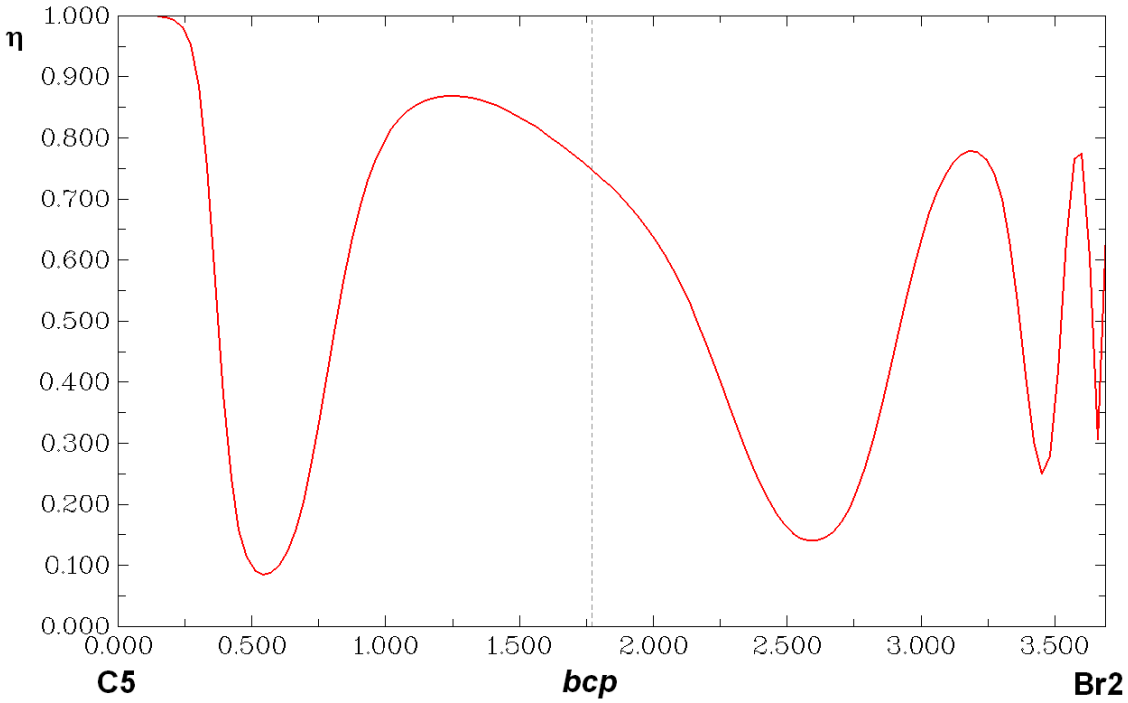
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0.000
0.500
1.000
1.500
2.000
2.500
3.000
3.500
C5
bcp
Br1

(b)


η
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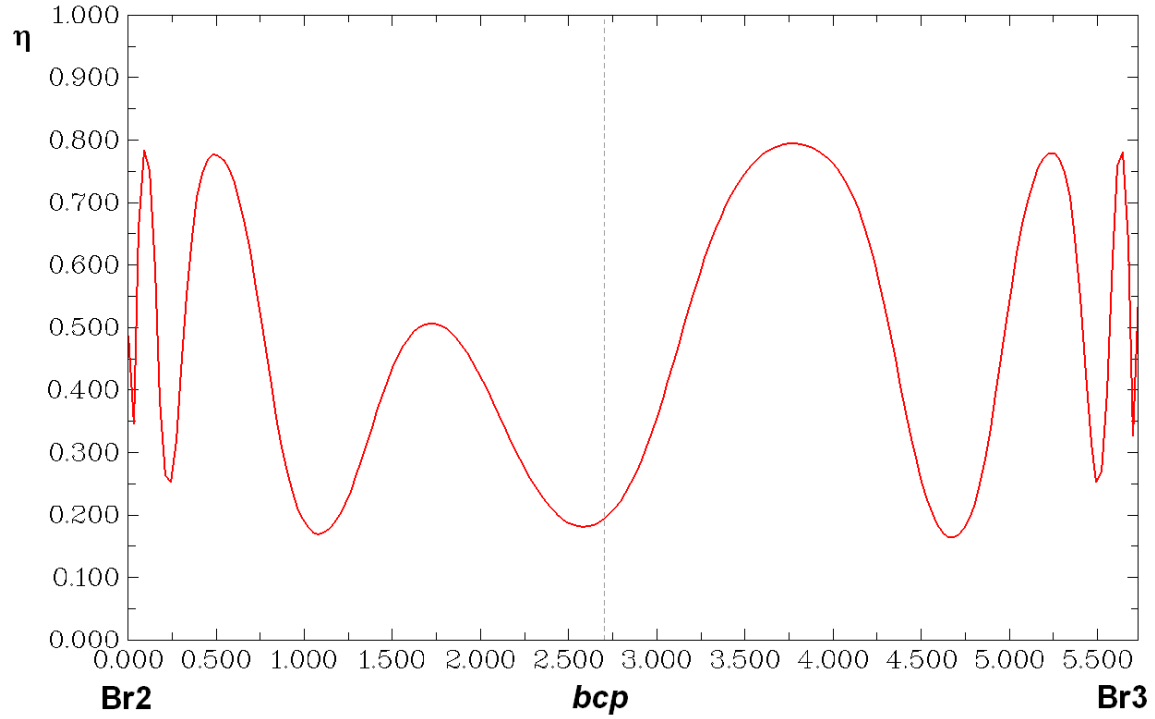
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0.000
0.500
1.000
1.500
2.000
2.500
3.000
3.500
C5
bcp
Br2

(c)


η
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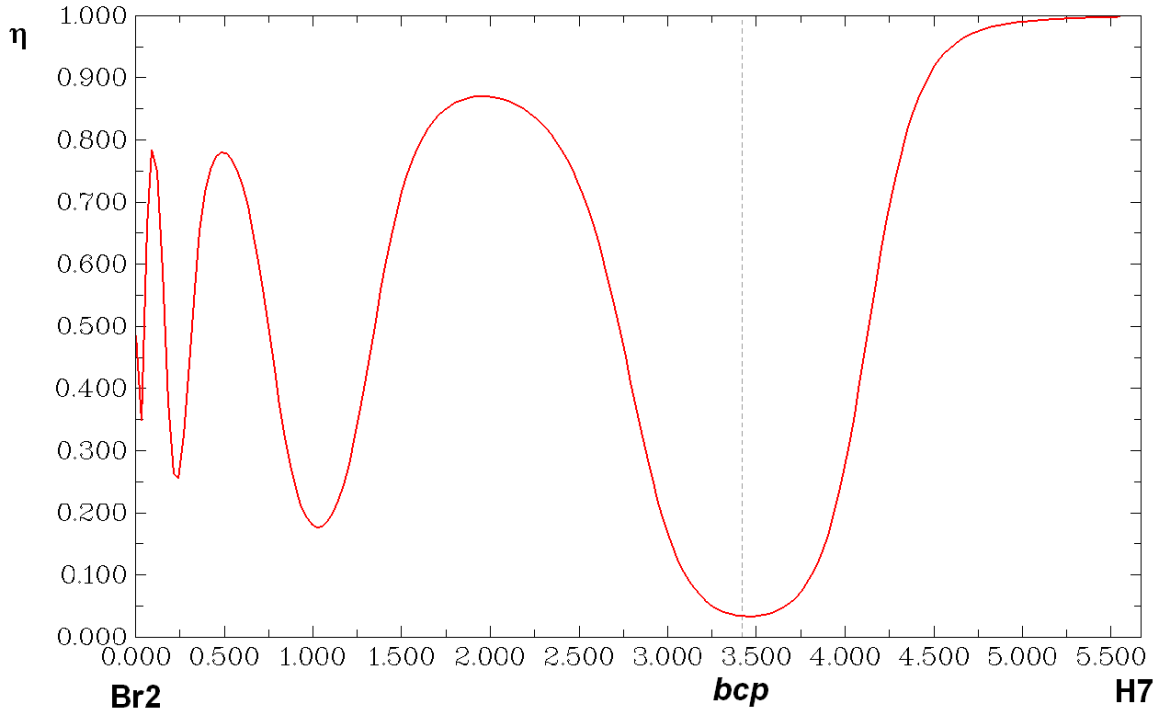
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0.000 0.500 1.000 1.500 2.000 2.500 3.000 3.500 4.000 4.500 5.000 5.500
Br2
bcp
Br3

(d)


η
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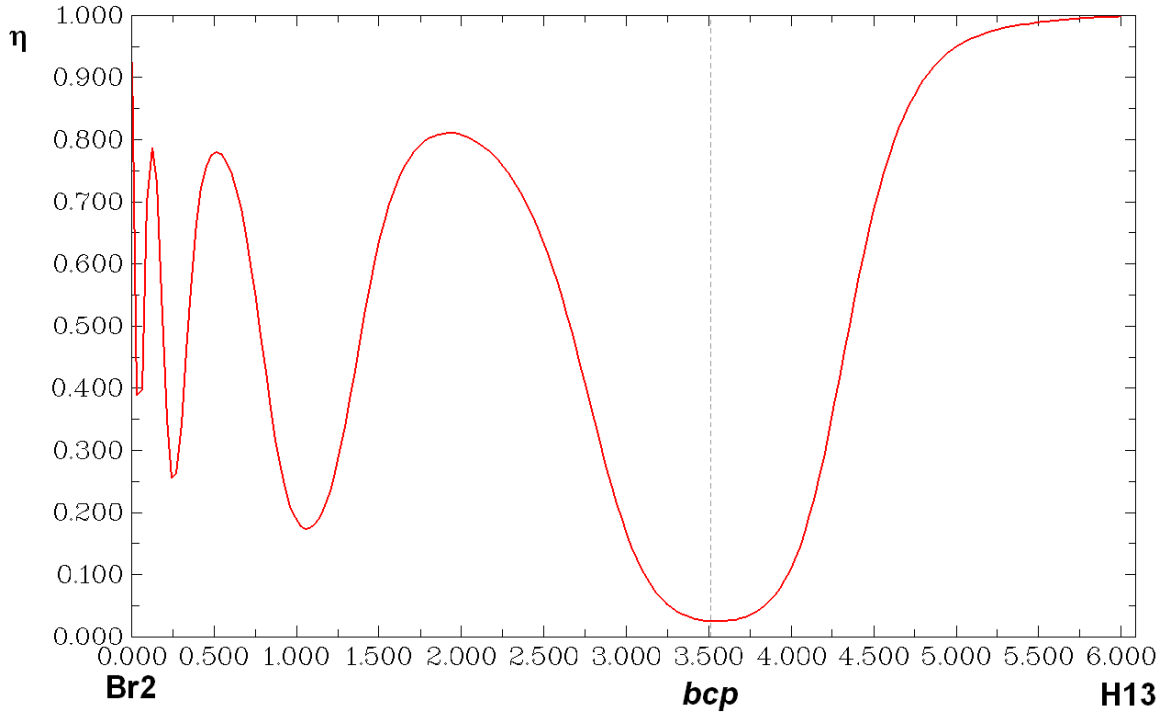
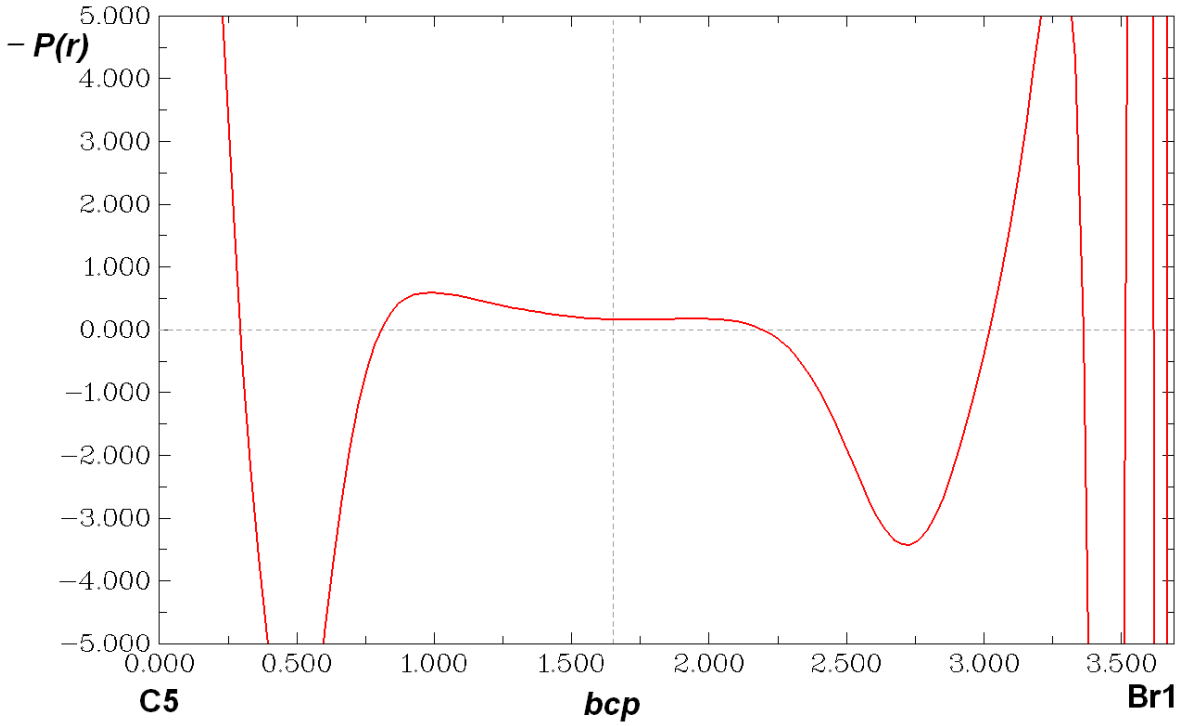
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0.000 0.500 1.000 1.500 2.000 2.500 3.000 3.500 4.000 4.500 5.000 5.500
Br2
bcp
H7

(e)



Figures S3. ELF along several bond paths of complex **1**. The location of bond critical points is shown by a dotted vertical line (distances in bohrs): (a) C5–Br1, (b) C5–Br2, (c) Br2···Br3, (d) Br2···H7, and (e) Br2···H13.

(a)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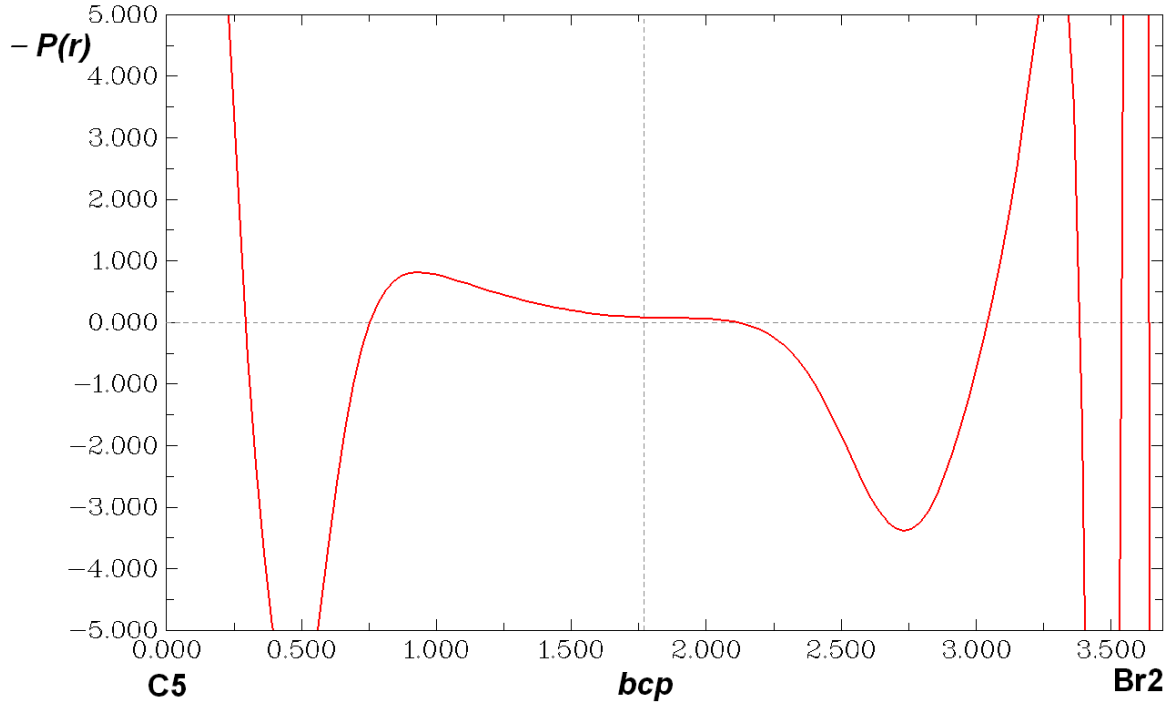
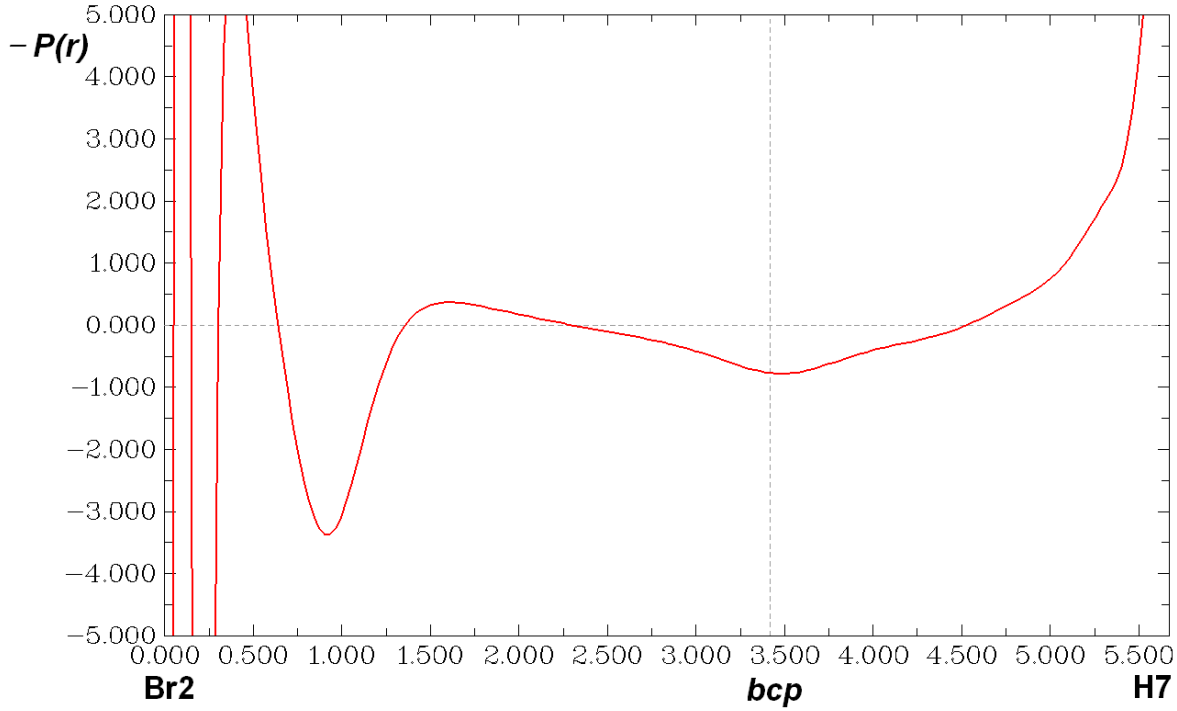
3.000
2.000
1.000
0.000
−1.000
−2.000
−3.000
−4.000
−5.000
0.000
0.500
1.000
1.500
2.000
2.500
3.000
3.500
C5
bcp
Br1

(b)


− P(r)
5.000
4.000
3.000
2.000
1.000
0.000
−1.000
−2.000
−3.000
−4.000
−5.000
0.000
0.500
1.000
1.500
2.000
2.500
3.000
3.500
C5
bcp
Br2

(c)



(d)

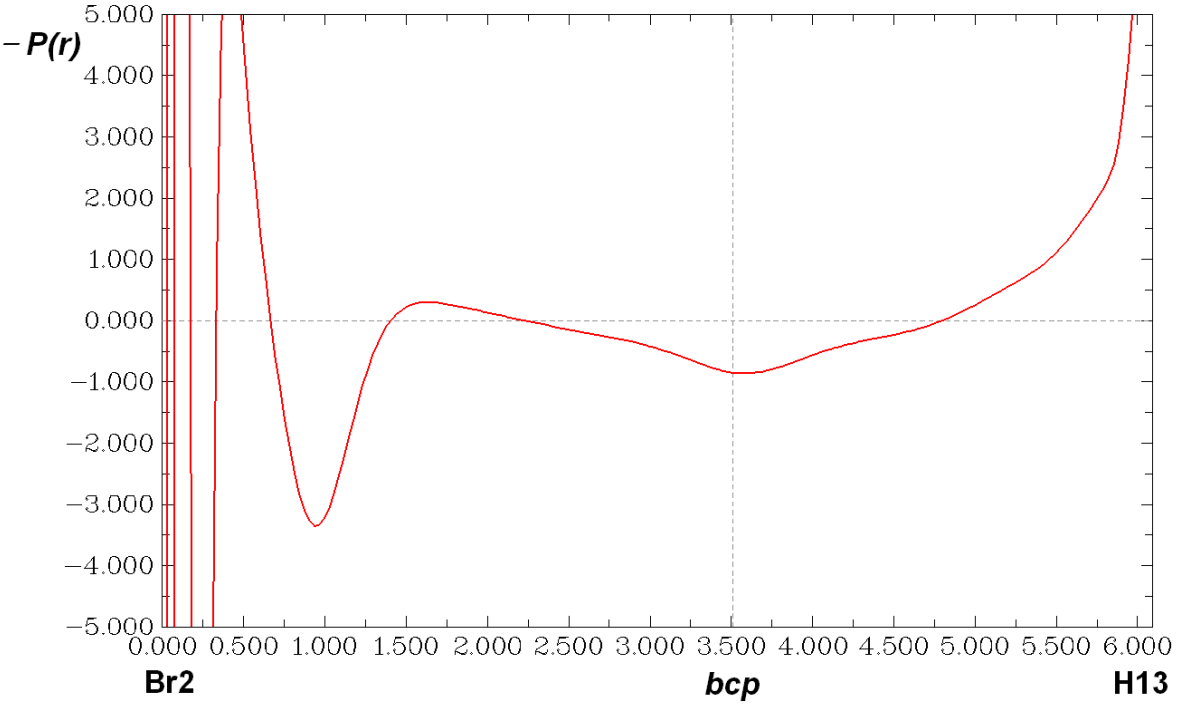
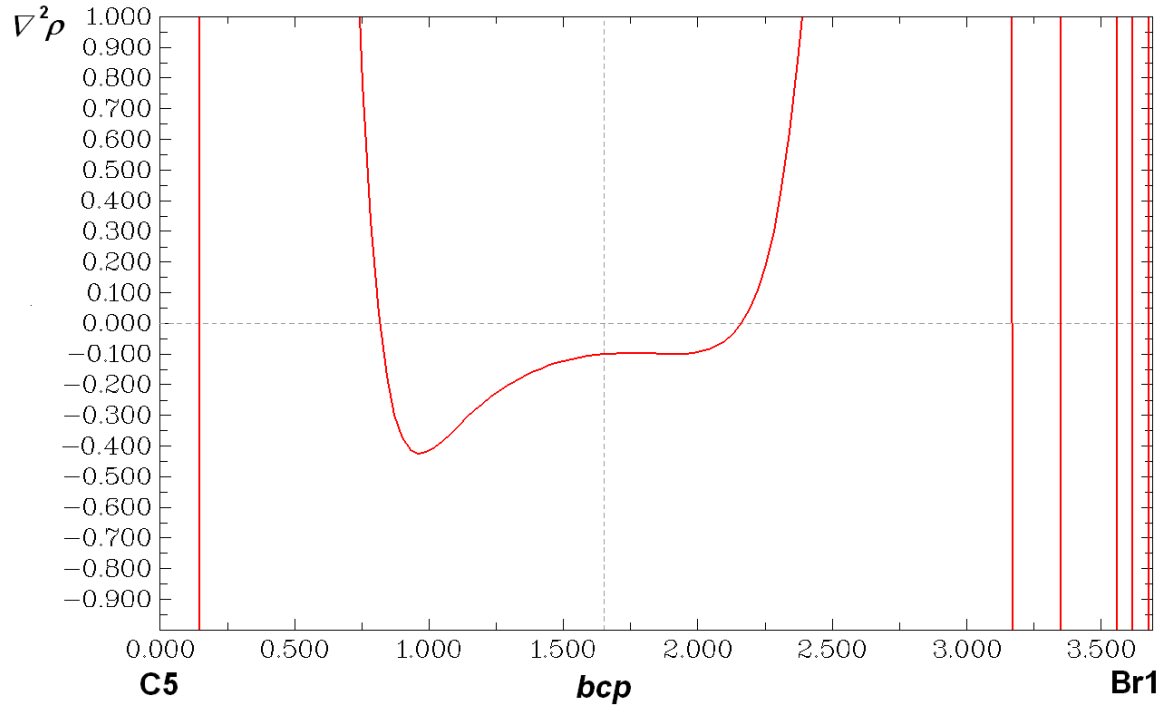


Figure S5. Negative one-electron potential (in a.u.) along several bond paths of complex **1**. The location of bond critical points is shown by a dotted vertical line (distances in bohrs): (a) C5–Br1, (b) C5–Br2, (c) Br2···H7, and (d) Br2···H13.

(a)


$\nabla^2\rho$
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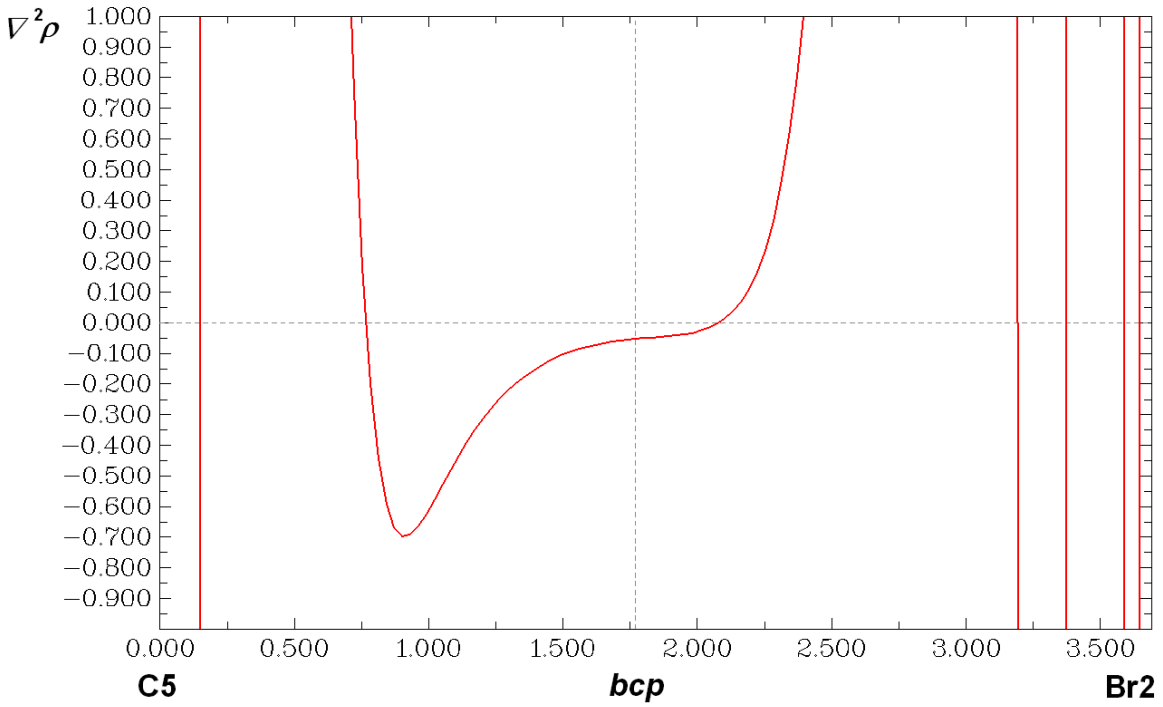
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
−0.100
−0.200
−0.300
−0.400
−0.500
−0.600
−0.700
−0.800
−0.900
0.000
0.500
1.000
1.500
2.000
2.500
3.000
3.500
C5
bcp
Br1

(b)


$\nabla^2\rho$
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
−0.100
−0.200
−0.300
−0.400
−0.500
−0.600
−0.700
−0.800
−0.900
0.000
0.500
1.000
1.500
2.000
2.500
3.000
3.500
C5
bcp
Br2

(c)

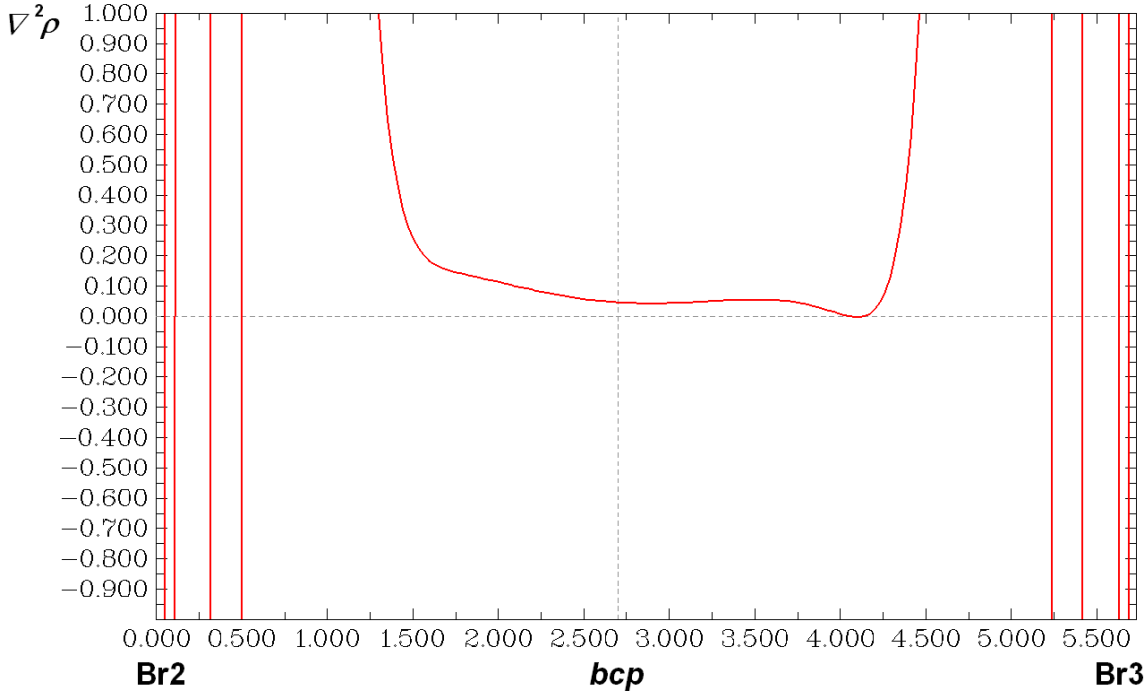


Figure S6. Laplacian of the electron density (in a.u.) along several bond paths of complex **1**, calculated using model 3 (equivalent results for model 4). The location of bond critical points is shown by a dotted vertical line (distances in bohrs): (a) C5–Br1, (b) C5–Br2, and (c) Br2···Br3.

Table S1. Cartesian coordinates of complex **1** (experimental geometry).

Atom	x	y	z
Mn	19.0962	15.2664	10.4983
C	19.7698	13.6179	9.8692
O	20.1994	12.6643	9.5017
C	18.3926	16.9028	11.0378
O	17.949	17.905	11.2993
C	18.995	15.8772	8.7647
O	19.0043	16.2539	7.7227
C	20.8362	15.844	10.5469
O	21.9025	16.1254	10.484
S	16.4857	13.2957	12.1719
C	17.5292	14.1693	13.3279
Br	16.7948	15.9571	13.7487
Br	17.3669	13.1133	15.0058
Br	16.7183	11.4103	17.4927
P	16.979	14.3226	10.386
C	16.8446	13.0012	9.1469
C	16.8324	13.3487	7.7977
H	16.787	14.2485	7.5671
C	16.8842	12.4189	6.8052
H	16.8447	12.6863	5.9153
C	16.9922	11.122	7.109
H	17.0568	10.4912	6.4288
C	17.0077	10.7168	8.4182
H	17.0452	9.8084	8.6143
C	16.9679	11.6576	9.4805
H	17.0223	11.3847	10.368
C	15.5192	15.359	10.0489
C	14.2645	14.9725	10.4651
H	14.1469	14.1902	10.954
C	13.1817	15.7719	10.141
H	12.3472	15.5339	10.4757
C	13.2622	16.8494	9.387
H	12.4959	17.3218	9.1535
C	14.4909	17.2604	8.9541
H	14.5697	18.0373	8.449
C	15.624	16.5181	9.2682
H	16.4566	16.7927	8.9581
P	19.259	14.4883	12.6995
C	20.1692	12.9207	12.7697
C	21.569	13.0098	12.7777
H	21.9913	13.8323	12.878
C	22.3118	11.8452	12.6329
H	23.2405	11.8933	12.6326
C	21.6993	10.6229	12.4899
H	22.2063	9.8527	12.3689
C	20.3475	10.5563	12.5279
H	19.9366	9.7246	12.4631
C	19.555	11.6866	12.6601
H	18.6279	11.6161	12.6746
C	20.0711	15.4932	13.9946

C	20.4071	16.8377	13.7085
H	20.1974	17.2253	12.8894
C	21.0534	17.5452	14.6871
H	21.3278	18.4141	14.501
C	21.3062	17.0409	15.8953
H	21.6942	17.5684	16.5556
C	20.9809	15.7161	16.1521
H	21.1862	15.3418	16.9783
C	20.3537	14.9489	15.1872
H	20.1298	14.0638	15.364

Table S2. Cartesian coordinates of complex **1** (theoretically optimized geometry: B3P86-D3(BJ)/6-31G(d,p) method).

Atom	x	y	z
Mn	19.1043861793	15.2036537807	10.4782038233
C	19.9157417562	13.6477575351	9.9349413709
O	20.4710611652	12.7313598781	9.5301044053
C	18.2759086868	16.7915380364	10.9180964007
O	17.8303932447	17.8383572778	11.0563019262
C	19.1010803147	15.7218960083	8.7609141443
O	19.14921236	16.0610148927	7.6603757654
C	20.7205311876	15.9264444761	10.807391852
O	21.7583928874	16.3800286545	11.0081897433
S	16.5234297154	13.1195269619	12.0403957988
C	17.4210126922	14.052977716	13.2520205782
Br	16.6289063291	15.8257941339	13.5735114249
Br	17.4602094324	12.8938369297	15.1110192073
Br	17.6890074399	11.5521333391	17.2762492747
P	17.0123539458	14.2147471198	10.2759720967
C	16.8733159151	12.9390339344	8.9885834662
C	16.1333323348	13.1454938106	7.8208269991
H	15.573042272	14.064684881	7.6838511233
C	16.1051574665	12.160438928	6.8366968497
H	15.5290658935	12.3244743142	5.9307372473
C	16.8031551453	10.9684839896	7.0162046476
H	16.7763510453	10.2020850778	6.2470798397
C	17.5298460892	10.755480081	8.1871693801
H	18.0676803792	9.8240671078	8.3361656874
C	17.5679063747	11.7356906984	9.1723219051
H	18.1274924009	11.5620746819	10.0879335154
C	15.6706979319	15.4031239348	9.9566444797
C	14.5526211827	15.4949134171	10.7890676226
H	14.4542086462	14.8362360335	11.645217611
C	13.5762817905	16.4544411078	10.5325958366
H	12.7139802953	16.5263836417	11.188647101
C	13.7045409197	17.3179253464	9.4476239105
H	12.9409754989	18.0658375575	9.2545857437
C	14.8177009792	17.226869068	8.6132606386
H	14.9257077831	17.8985693772	7.7668038807
C	15.8021166986	16.2783578786	8.870000806
H	16.6657203982	16.2167387126	8.2149503333
P	19.1303349373	14.3950689659	12.6811556735
C	20.0983559723	12.8590361386	12.7463236911
C	21.4869825651	13.0211203682	12.6459132923
H	21.917927468	14.0195349882	12.6327782977
C	22.3181709936	11.9095242705	12.5753807939
H	23.3933298475	12.04473183	12.503052651
C	21.7696978426	10.6280747131	12.6066871865
H	22.4177736943	9.7579644136	12.5555708608
C	20.3914731569	10.4656398697	12.7180176643
H	19.9612389151	9.4698959951	12.7675838983

C	19.550650367	11.574736142	12.7858476427
H	18.484540093	11.4318291244	12.90559989
C	19.893443592	15.4188394142	13.960931576
C	20.0027077046	16.8037612628	13.8133041892
H	19.672046754	17.2874520488	12.9017406518
C	20.5251071916	17.5759321669	14.8449455394
H	20.6098622964	18.6516038044	14.7227774547
C	20.9298659659	16.9677094153	16.0317531346
H	21.3327259007	17.5717982638	16.8397946357
C	20.8137455152	15.5875167394	16.1864525749
H	21.1151383549	15.1115693518	17.1144221084
C	20.3014926798	14.8081776294	15.1547333395
H	20.1947634145	13.7369127635	15.2857768168

Table S3. Cartesian coordinates of complex **1** (theoretically optimized geometry: ZORA-BLYP-D3(BJ)/TZP method).

Atom	x	y	z
Mn	19.21119	15.5453	11.15428
C	20.25499	14.67259	12.42747
O	20.9922	14.23145	13.19188
C	18.25828	16.454	9.83685
O	17.79991	17.10764	9.00659
C	20.76213	15.95216	10.2896
O	21.75969	16.24835	9.77998
C	19.27783	17.04768	12.1929
O	19.36362	17.99505	12.8503
S	17.28923	12.43987	10.66289
C	16.25016	13.70544	11.33892
Br	15.31712	14.77331	9.9224
Br	14.76807	12.58619	12.58915
Br	13.08313	11.30319	14.14171
P	18.96192	13.57149	9.93959
C	20.26807	12.30953	10.10291
C	21.08202	11.94354	9.02341
H	20.92763	12.3897	8.04749
C	22.08086	10.98613	9.20285
H	22.70704	10.70389	8.36136
C	22.26717	10.38688	10.44905
H	23.0444	9.63917	10.58264
C	21.44629	10.7412	11.52351
H	21.57835	10.27105	12.49357
C	20.45	11.69736	11.35385
H	19.80529	11.95821	12.18717
C	18.74457	13.7941	8.13991
C	17.65064	13.23249	7.4712
H	16.91339	12.6638	8.02722
C	17.50314	13.4232	6.09695
H	16.64632	12.99204	5.5875
C	18.44328	14.16777	5.38393
H	18.32233	14.31749	4.31433
C	19.53755	14.72794	6.04807
H	20.273	15.31006	5.50025
C	19.68689	14.54857	7.42156
H	20.53998	14.98911	7.92522
P	17.24899	14.89674	12.31743
C	17.74102	14.08341	13.87655
C	18.12371	14.94038	14.92317
H	18.00966	16.01509	14.81479
C	18.63362	14.41446	16.10772
H	18.91966	15.08553	16.91244
C	18.76545	13.03235	16.26096
H	19.15736	12.62228	17.18785
C	18.37629	12.17946	15.22754
H	18.4491	11.10269	15.34966

C	17.86903	12.69716	14.03613
H	17.54784	12.02442	13.25152
C	16.09369	16.1859	12.86408
C	16.05324	17.44373	12.24821
H	16.74714	17.68775	11.45274
C	15.10985	18.38734	12.64679
H	15.08684	19.36153	12.16722
C	14.19541	18.07517	13.65557
H	13.45681	18.81068	13.96387
C	14.22709	16.81979	14.26679
H	13.51111	16.56867	15.04351
C	15.17436	15.87397	13.88082
H	15.19191	14.89685	14.35097

Table S4. Bond distances and bond paths lengths for selected interactions of **1**, calculated using the four models[†].

Interaction	D_{A-B}(Å)[a]	d_{A-B}(Å)[b]	d_{A-bcp}(Å)[c]	d_{bcp-B}(Å)[d]
Br2···Br3	2.626	2.627	1.255	1.372
	2.557	2.558	1.220	1.338
	3.083	3.084	1.455	1.629
	3.083	3.084	1.478	1.606
Br2···H7	2.936	3.026	1.837	1.189
	2.867	2.992	1.790	1.202
	2.944	3.045	1.836	1.209
	2.944	2.997	1.844	1.153
Br2···H13	2.912	3.072	1.805	1.267
	2.837	2.953	1.774	1.179
	3.044	3.261	1.871	1.390
	3.044	3.221	1.875	1.346

[†]Models: ZORA-BLYP-D3(BJ)/TZP//ZORA-M06-2X/QZ4P (*model 1*, first row of each entry), B3P86-D3(BJ)/6-31G(d,p)//M06-D3/QZVP (*model 2*, second row of each entry), exp-geom//M06-D3/QZVP (*model 3*, third row of each entry), exp-geom//XCW-B3LYP/6-31G(d,p) (*model 4*, fourth row of each entry). [a]Bond distance. [b]Bond path length. [c]Distance from atom A to the bcp. [d]Distance from atom B to the bcp.