Electronic Supplementary Information

Spodium, halogen and hydrogen bonds in the reactivity of *bis*(2,4-*bis*(trichloromethyl)-1,3,5-triazapentadienato)-Zn(II)

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1. Materials and instrumentation

All the chemicals were obtained from commercial sources and used as received. The IR spectra (4000−400 cm^{-1}) were recorded on a Bruker Alpha-P ATR-IR Spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained at room temperature on a Bruker 400.13 MHz spectrometer using $Si(CH_3)_4$ as the internal reference.

2. $^{1}H/^{13}C$ NMR spectroscopy

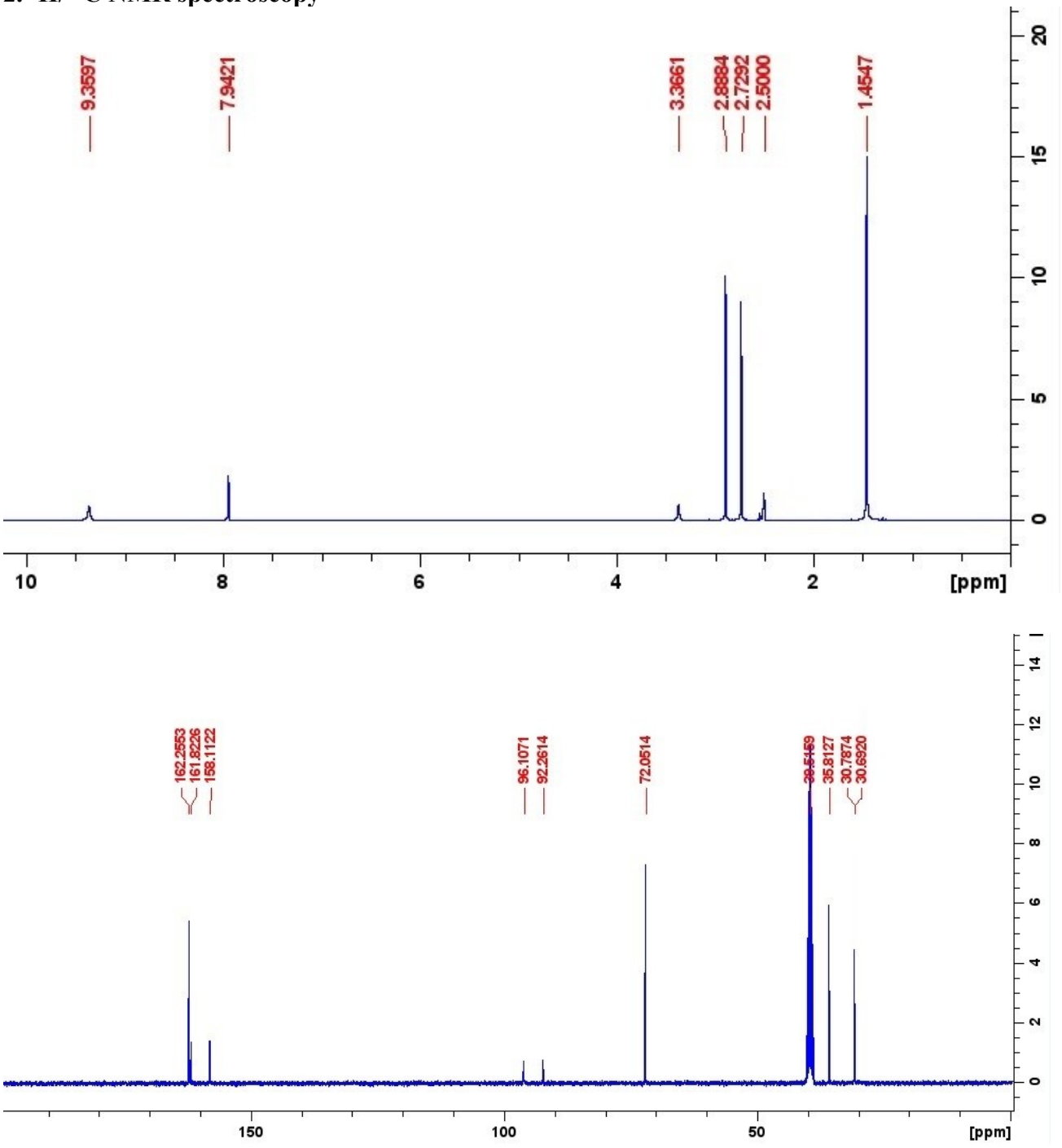

Fig. S1. $^{1}H/^{13}C$ NMR spectra of **4.**

3. IR spectroscopy

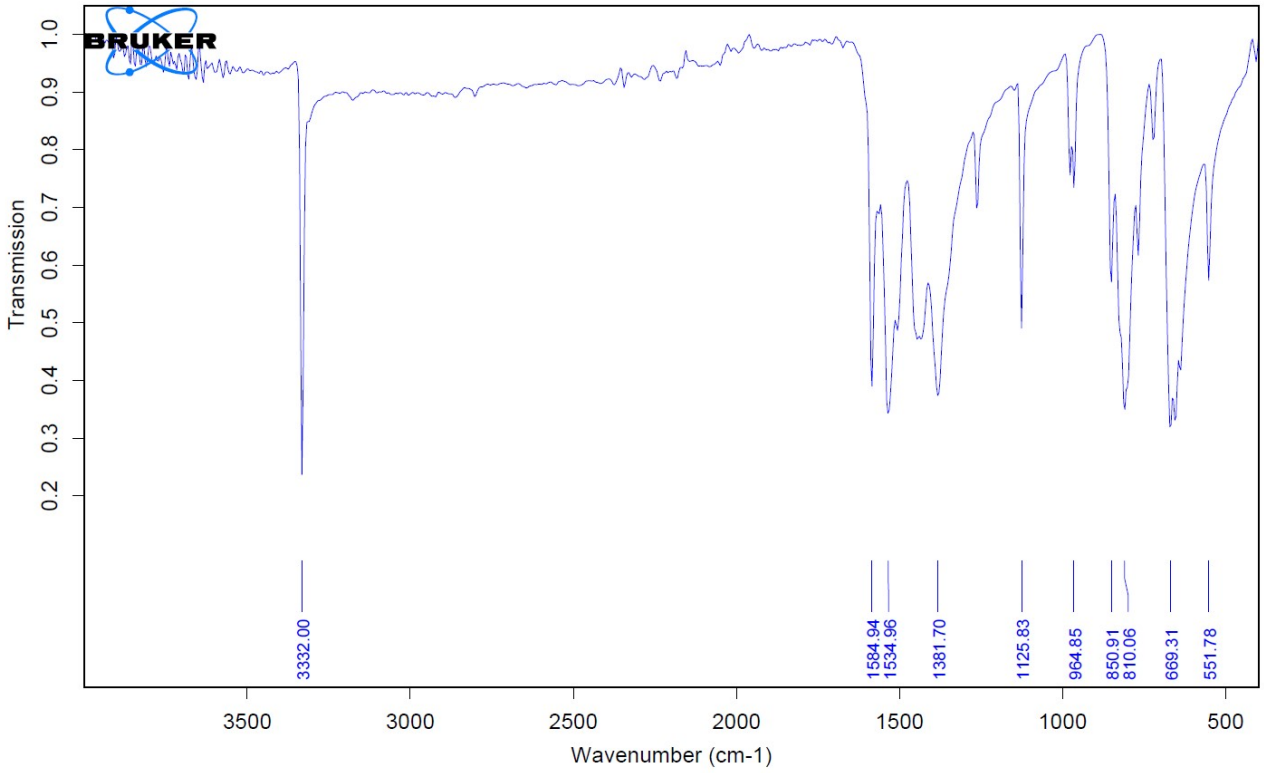

Fig. S2. IR spectrum of **3.**

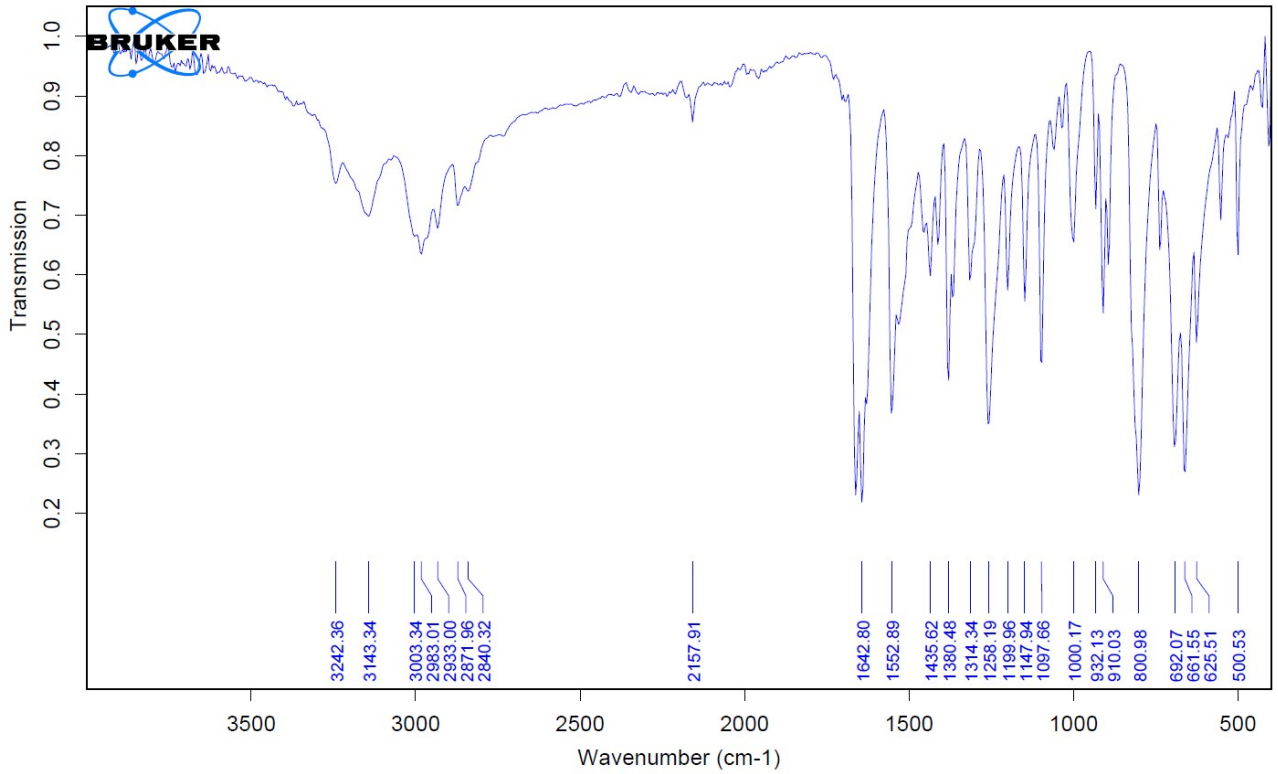

Fig. S3. IR spectrum of **4.**

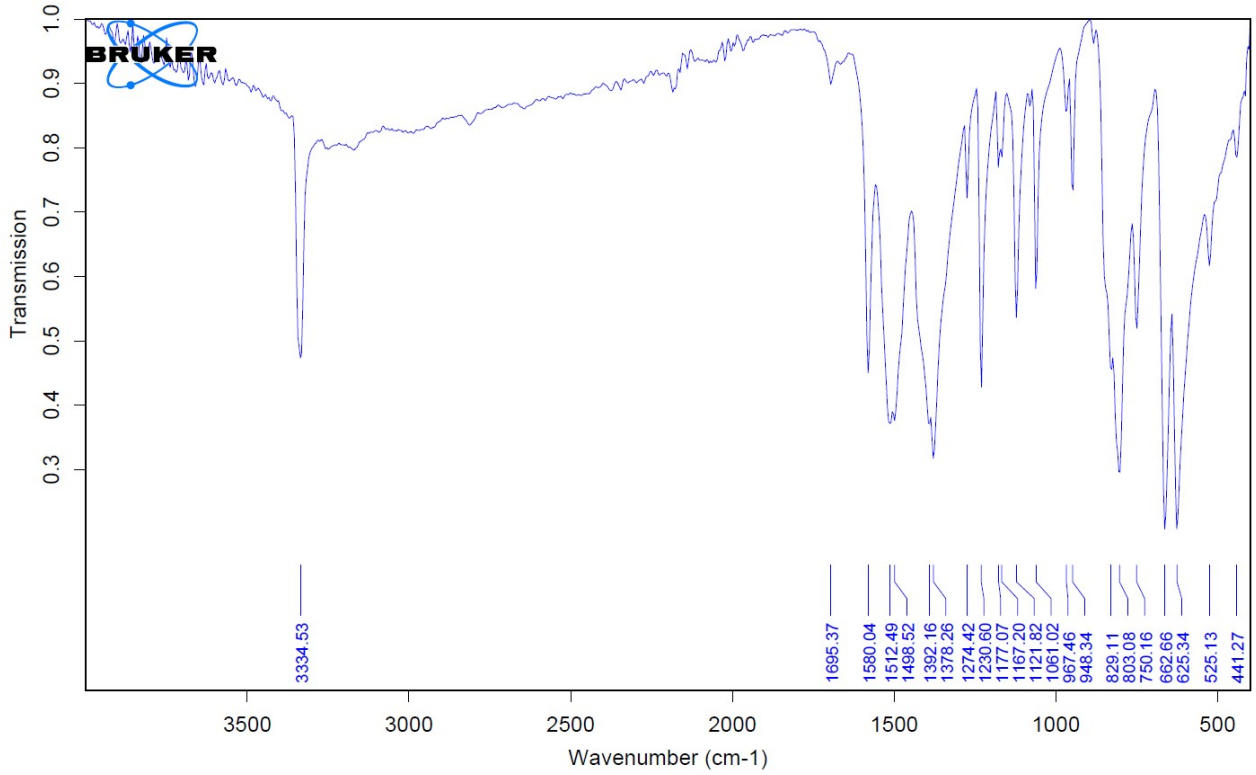

Fig. S4. IR spectrum of **5.**

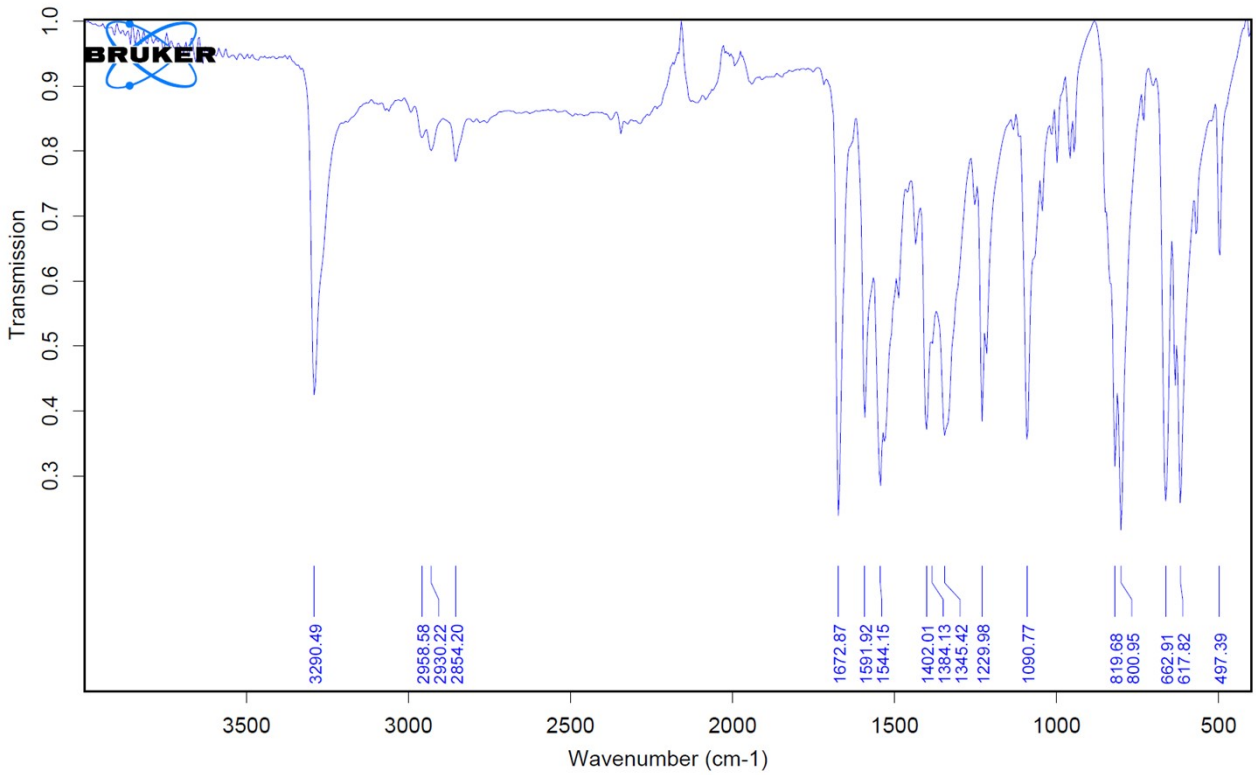

Fig. S5. IR spectrum of **6.**

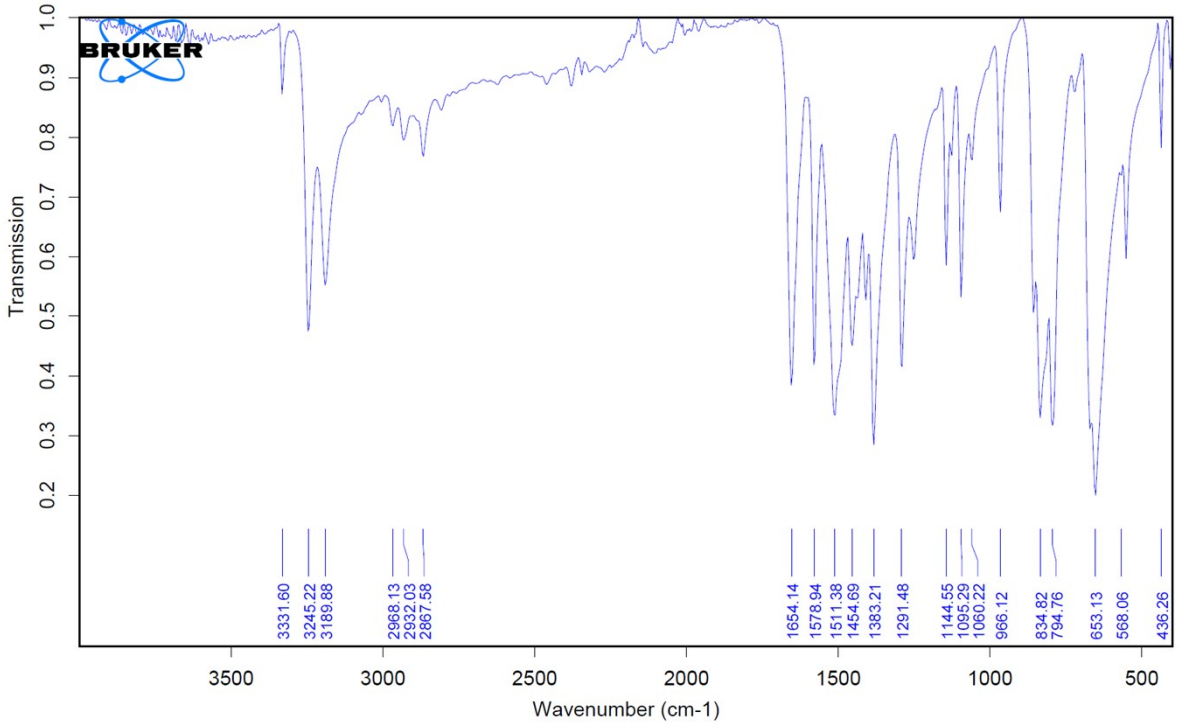

Fig. S6. IR spectrum of **7**.

4. X-ray analysis

X-ray diffraction intensities of **3**−**7** were collected using a Bruker SMART APEX-II CCD area detector equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296 K. Absorption correction was applied by SADABS.[1,2] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using Bruker's SHELXTL-97.[3] All non-hydrogen atoms were refined anisotropically. The details of the crystallographic data for **3**−**7** are summarized in Table S1. Crystallographic data for the structural analysis have been deposited to the Cambridge Crystallographic Data Centre [CCDC 2257225 (for **3**), 2259693 (for **4**), 2252980 (for **5**), 2252981 (for **6**) and 2252982 (for **7**)]. Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif).

Table S1. Crystallographic data and structure refinement details for **3**−**7**.

	3	**4**	**5**	**6**	**7**
Empirical formula	$C_{14}H_{16}Cl_{12}CuN_6O_2$	$C_{10}H_{14}Cl_6N_4O$	$C_{14}H_{10}Cl_{12}N_{10}Zn_2$	$C_{24}H_{26}Cl_{12}N_{10}O_2Zn$	$C_{14}H_{18}Cl_{12}CuN_8O_2$
Formula weight	789.27	418.95	874.46	977.32	819.30
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	C2/m	$Pca2_1$	P-1	C2/c	P-1
a (Å)	12.961(4)	20.3492(17)	8.7888(7)	19.7000(12)	5.8826(7)
b (Å)	9.431(3)	5.7478(5)	12.0326(8)	11.8120(6)	11.8884(14)
c (Å)	13.904(4)	15.0320(15)	15.2596(9)	17.6378(18)	12.3119(14)
α (°)	90	90	79.677(2)	90	112.979(4)
β (°)	119.710(15)	90	82.623(2)	112.803(2)	96.810(4)
γ (°)	90	90	69.903(2)	90	102.216(4)
V (Å^3)	1476.1(8)	1758.2(3)	1487.04(18)	3783.5(5)	755.14(15)
Z	2	4	2	4	1
D_{calc} (g/cm^3)	1.776	1.583	1.953	1.716	1.802
F000	782	848	856	1960	407
μ (mm^{-1})	1.852	0.979	2.719	1.538	1.816
R_{int}	0.0310	0.0444	0.0286	0.0599	0.0705
$R(F)$ ($I \geq 2\sigma$)	0.0232	0.0354	0.0376	0.0339	0.0430
wR (F^2) (all data)	0.0526	0.0730	0.0924	0.0806	0.0737
GOF (F^2)	1.015	1.019	1.067	1.051	0.946

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

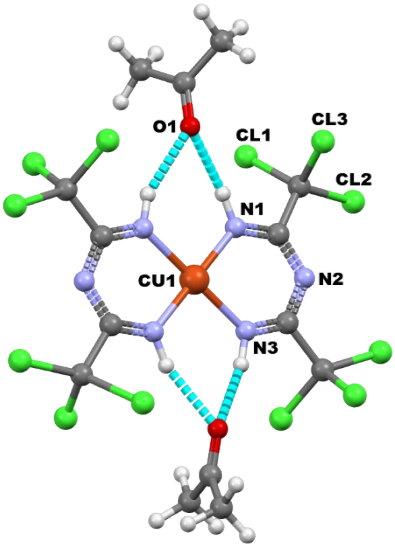

Fig. S7. Molecular structure of **3.**

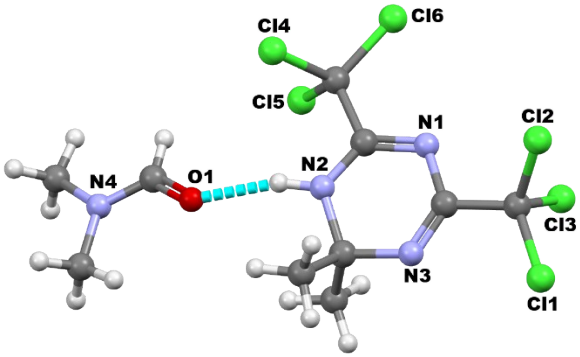

Fig. S8. Molecular structure of **4.**

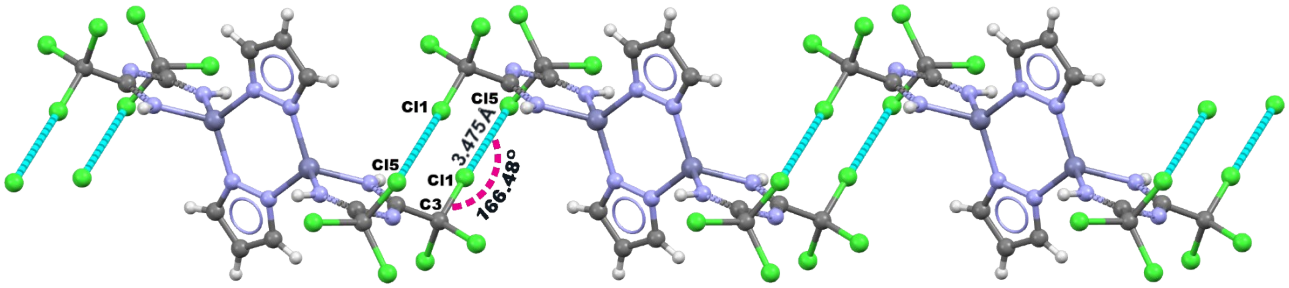

Fig. S9. Halogen bonded 1D supramolecular chain in crystal packing of **5.**

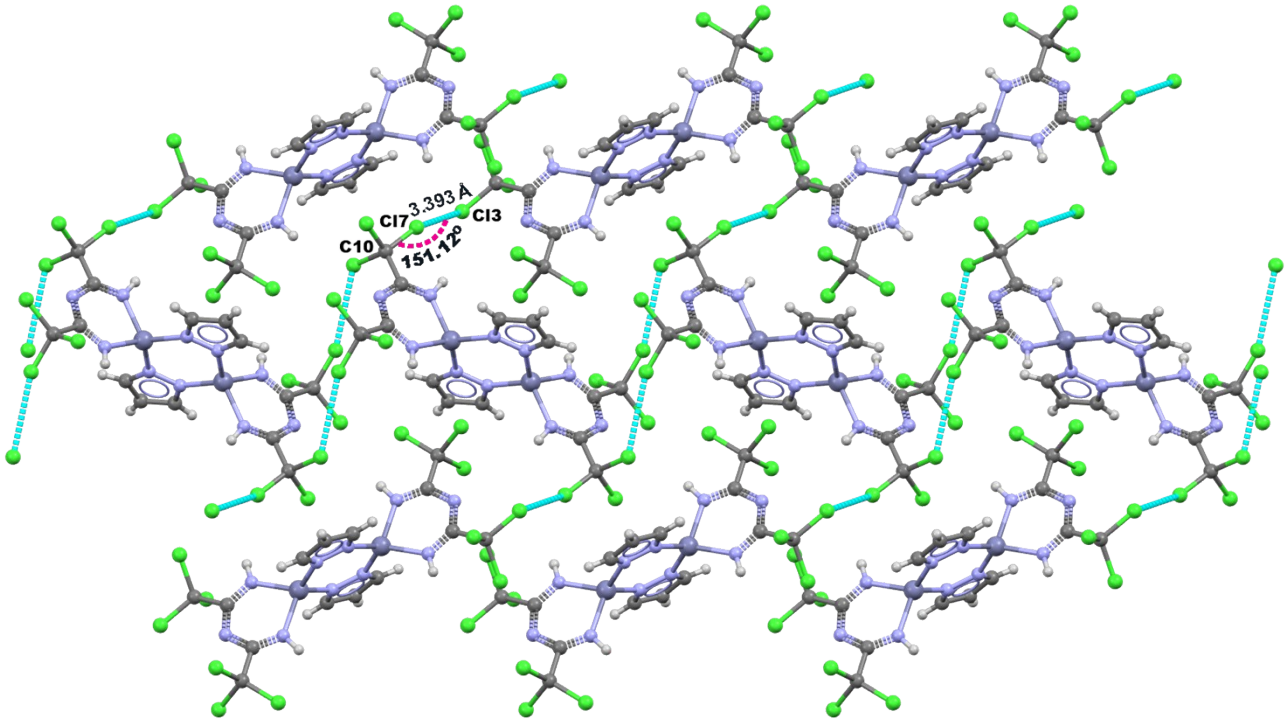

Fig. S10. Halogen bonded 2D network in crystal packing of **5.**

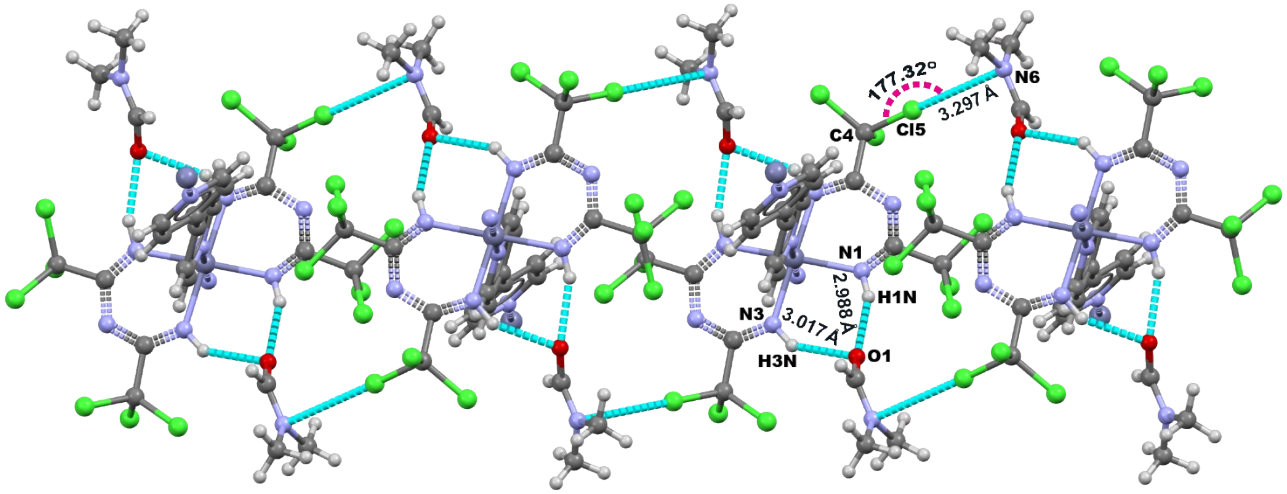

Fig. S11. Halogen bonded 1D supramolecular chain in crystal packing of **6.**

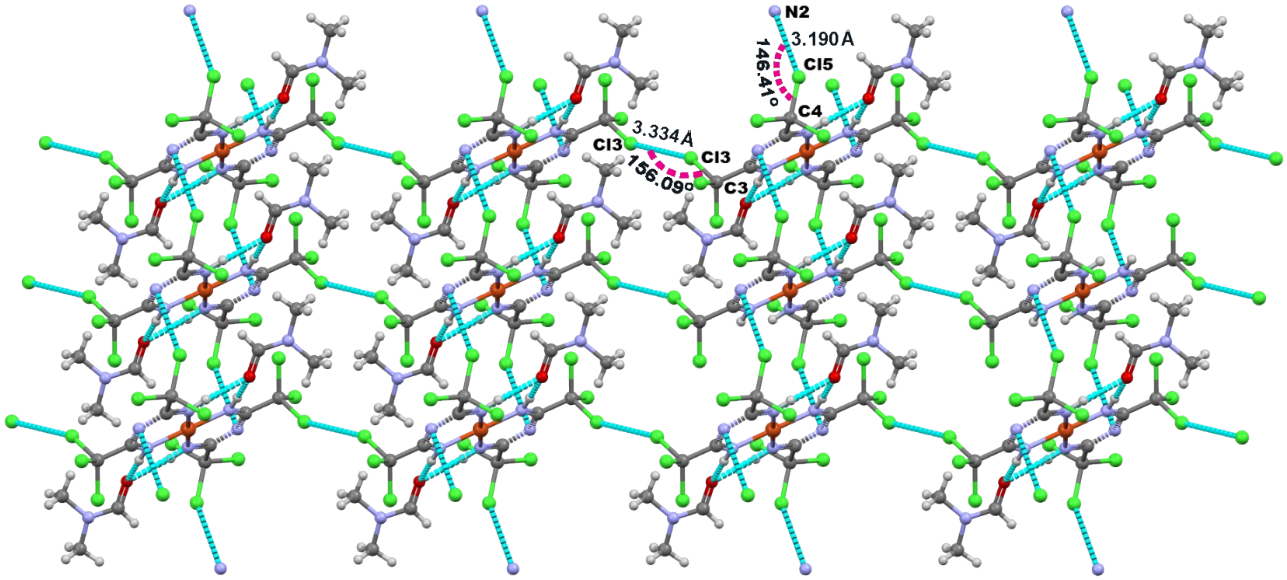

Fig. S12. Halogen bonded 2D network in crystal packing of **7.**

5. DFT calculations

5.1 Theoretical methods

The calculations reported herein were performed using the Turbomole 7.2 program.[4] The crystallographic coordinates were used for the single point calculations of the SpB dimer of Fig. 3c (main text) or as starting point for the optimization of the geometry shown in Fig. 3d (main text). The level of theory used for the calculations was PBE0[5]–D4[6] /def2-TZVP.[7] The MEP surface plots were generated using the wavefunction obtained at the same level of theory and the 0.01 a.u. isosurface to simulate the van der Waals envelope. The topological analysis of the electron density was carried out according to the quantum theory of atoms in molecules (QTAIM) method proposed by Bader[8] and the reduced density gradient (RDG) isosurfaces (NCIplot)[9] and represented using the VMD program.[10] The NBO analysis[11] was performed using the same level of theory and the NBO7.0 program.[12]

5.2 Figure S13

The rotated model used to evaluate the SpB in **6** (energy given at the bottom of Fig. 3c (main text) is shown in Fig. S13.

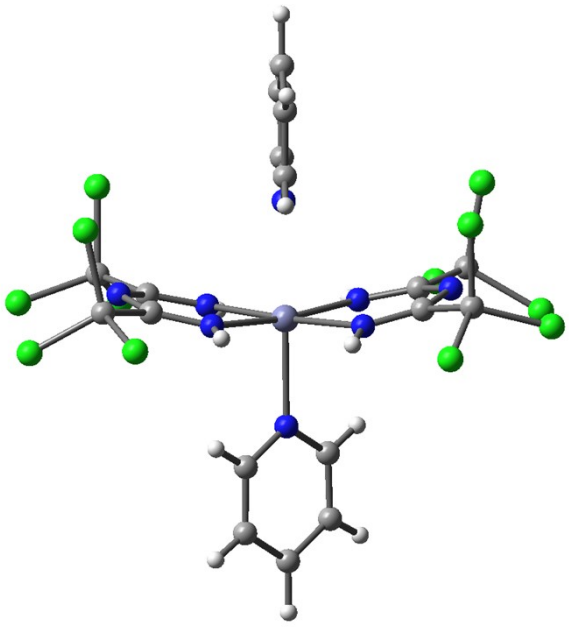

Fig. S13. Rotated model of the SpB complex of compound **6**.

5.3. Cartesian coordinates of the optimized complex (see Fig. 3d, main text)

Zn	0.0000000	0.0000000	-0.0352615
Cl	3.8718361	-3.1350328	0.2453216
Cl	2.2008719	-4.9783718	-1.1855311
Cl	2.0199527	-4.7759535	1.7009037
Cl	-2.1717713	-4.8374552	-1.5399127
Cl	-2.3557262	-4.7967944	1.3531495
Cl	-3.9638580	-3.0201055	-0.2276251
N	1.3928316	-1.5753748	0.0009451
H	2.3889981	-1.3970023	0.0502941
N	-0.0519878	-3.4457357	0.0167064
N	-1.4365617	-1.5319464	-0.0610901
H	-2.4268949	-1.3247714	-0.1136763
N	-0.0000000	-0.0000000	2.2813108
C	1.1235639	-2.8344577	0.0582506
C	-1.2074853	-2.8001844	-0.0529637
C	2.2623882	-3.8811080	0.1959461

C	-2.3811430	-3.8148744	-0.1152367
C	0.1013134	1.1378699	2.9630779
H	0.1824347	2.0470798	2.3781817
C	0.1054387	1.1871040	4.3463117
H	0.1897892	2.1404099	4.8524888
C	0.0000000	-0.0000000	5.0519066
C	-0.1013134	-1.1378699	2.9630779
H	-0.1824347	-2.0470798	2.3781817
C	-0.1054387	-1.1871040	4.3463117
H	-0.1897892	-2.1404099	4.8524888
Cl	-3.8718361	3.1350328	0.2453216
Cl	-2.2008719	4.9783718	-1.1855311
Cl	-2.0199527	4.7759535	1.7009037
Cl	2.1717713	4.8374552	-1.5399127
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C	1.2074853	2.8001844	-0.0529637
C	-2.2623882	3.8811080	0.1959461
C	2.3811430	3.8148744	-0.1152367
N	-0.0000000	-0.0000000	-2.3383143
C	0.0000000	-0.0000000	-5.1079516
C	-0.0664338	1.1900929	-4.4025205
H	-0.1198457	2.1454550	-4.9090602
C	-0.0633803	1.1407843	-3.0192875
H	-0.1138776	2.0512175	-2.4324924
C	0.0664338	-1.1900929	-4.4025205
H	0.1198457	-2.1454550	-4.9090602
C	0.0633803	-1.1407843	-3.0192875
H	0.1138776	-2.0512175	-2.4324924
H	-0.0000000	-0.0000000	-6.1917890
H	-0.0000000	-0.0000000	6.1357372

References

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