Electronic Supplementary Information

Unexpected 20-membered macrocycles from the condensation of α,α-dihalo-β-oxoaldehydes with diaminofurazan

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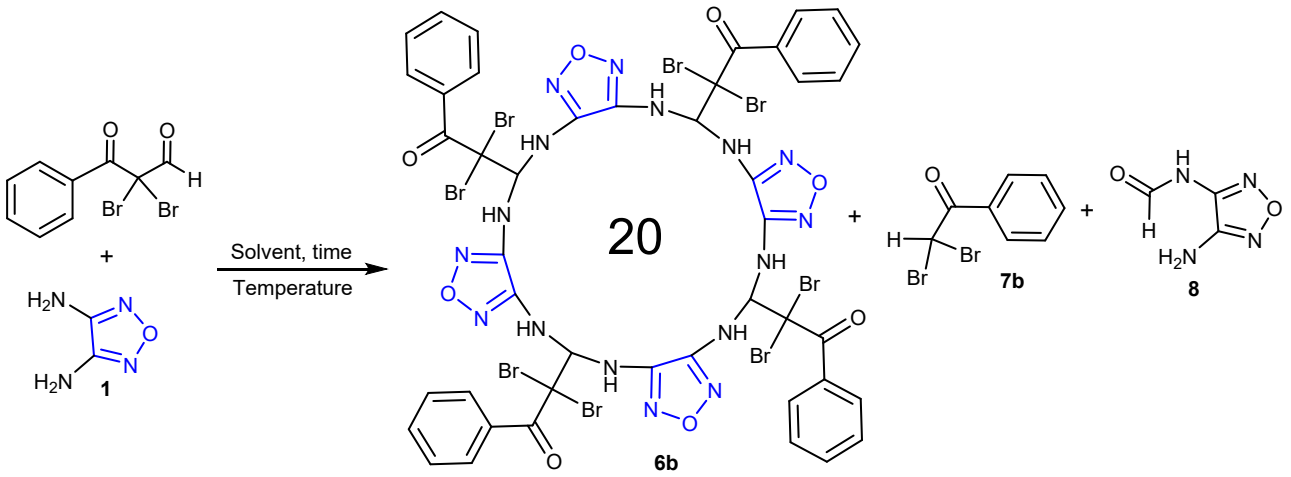
EXPERIMENTAL SECTION

1. Materials and instrumentation

Unless otherwise noted, all standard reagents were purchased from Aldrich or Acros Organics and used without further purification. All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 (300.13 and 75.47 MHz, respectively) spectrometer and referenced to residual solvent peak. ^{14}N NMR spectra were measured on a Bruker AM-300 (21.69 MHz) spectrometer using $MeNO_2$ ($\delta^{14}N$ = 0.0 ppm) as an external standard. The chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, J, are reported in Hertz. Hight-resolution mass spectra were recorded on a Bruker microTOF spectrometer (Münich, Germany) with electrospray ionization (ESI). Measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range m/z: 50–1500 and in a negative (−MS) ion mode (interface capillary voltage: 3200 V) with scan range m/z: 50–1650. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for all analyzed solutions in MeOH (flow rate: 3 μL min^{-1}). Nitrogen was used as a nebulizer gas (0.4 bar in positive mode and 1.0 bar in negative mode) and dry gas (4.0 L min^{-1}); the interface temperature was set at 180 °C in positive mode and 200 °C in negative mode. All spectra were processed using the Bruker DataAnalysis 4.0 software package (Billerica, MA, USA). All solvents were purified and dried using standard methods prior to use.

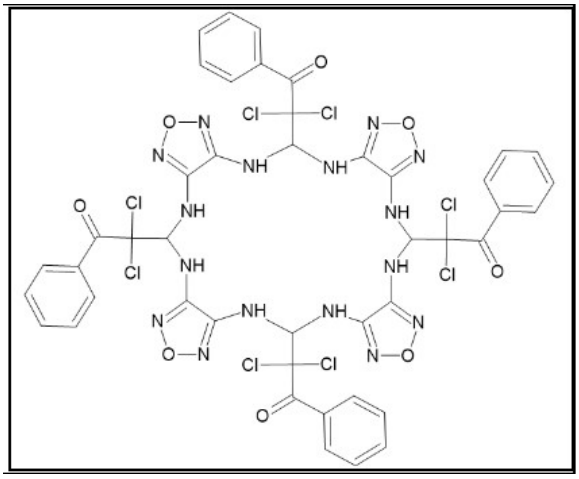
2. Synthetic Procedure

Table S1: Optimization of the reaction condition for synthesis of **6b**.

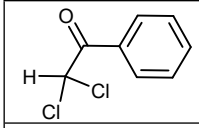
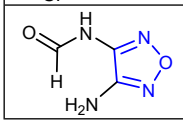


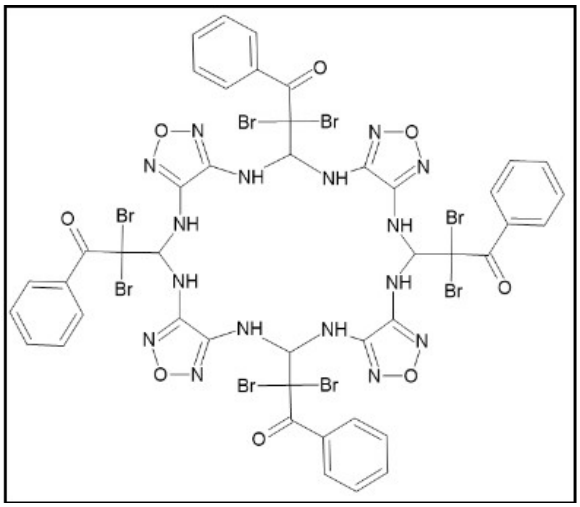
Entry	2,2-dichloro-3-oxo-3-phenylpropanal (eq.)	**1** (eq.)	Solvent	Temp. °C	Time, h	Yield, %		
						6b	**7b**	**8**
1	1	1	MeCN	82	12	15	81	81
2	1	1	EtOH	82	12	-	85	85
3	1	1	MeOH	82	12	-	72	72
4	1	1	THF	82	12	-	77	77
5	1	1	MeCN	25	36	30	10	10
6	1	2	MeCN	25	36	10	10	10
7	2	1	MeCN	25	36	70	10	10
8	2	1	MeCN	25	24	57	7	7
9	2	1	MeCN	-10	72	70	-	-

General procedure for the preparation of compounds 6a-j: To a solution of 2,2-dichloro-3-oxo-3-phenylpropanal (434 mg, 2.0 mmol) in 10 mL of acetonitrile was added diaminofurazan (**1**) (100 mg, 1.0 mmol) and left to stir for 36 hours at room temperature. Upon completion of the reaction, the precipitate was filtered off, washed with 20 mL of diethyl ether, and dried in vacuum to yield **6a** (155 mg, 52 %) as a white crystalline product. By-products, 2,2-dichloro-1-phenylethan-1-one (**7a**) and *N*-(4-amino-1,2,5-oxadiazol-3-yl)formamide (**8**), were isolated from the filtrate by its evoparation under a vacuum, and then column chromatography of the obtained residue using a chloroform/ethyl acetate mixture (3:1 v/v). Following to this general procedure, compounds **6b-6j** were synthesized.

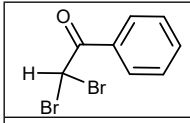
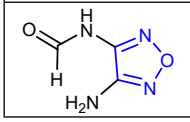


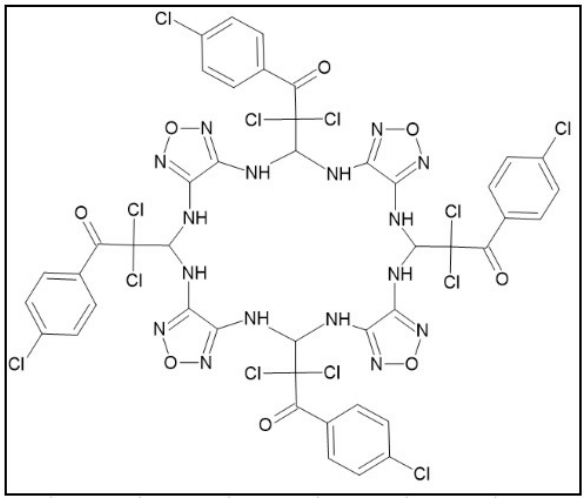
6a (155 mg, 52.0 %): m.p. 496–497 K. Elemental analysis calculated (%) for $C_{44}H_{32}Cl_8N_{16}O_8$: C (44.17), H (2.70) and N (18.73); found (%): C (44.16), H (2.68) and N (18.71). IR (selected bands, cm^{-1}): 3343, 1668, 1581, 1479. ^1H NMR (300 MHz, DMSO-d^6): δ = 8.29 (d, J = 8.1 Hz, 8H); 7.70 (t, J = 7.2 Hz, 4H); 7.59 (t, J = 7.7 Hz, 8H); 6.85 (d, J = 7.6 Hz, 8NH); 5.98 (t, J = 7.4 Hz, 4H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 185.89, 150.21, 132.35, 131.79, 129.75, 129.54, 89.13, 69.41. HRMS (ESI) m/z $(M+H)^+$ calcd. for $C_{44}H_{33}Cl_8N_{16}O_8^+$ 1193.0170, found 1193.0173.

	**7a** (10.0 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 8.21 (d, 2H), 7.97 (s, 1H), 7.65 (t, 1H), 7.49 (t, 2H).[31a]
	**8** (6.8 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

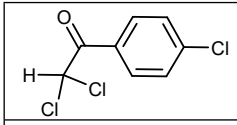
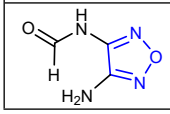


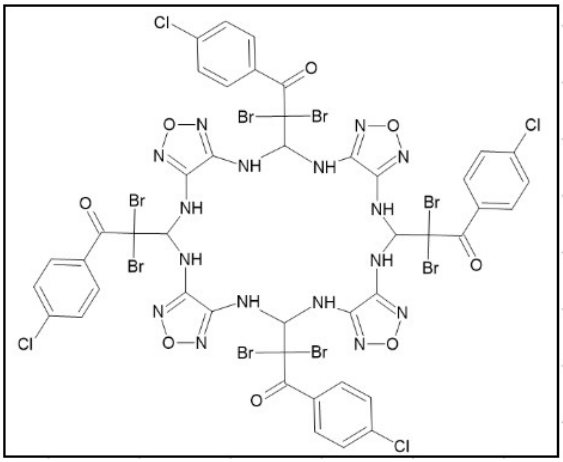
6b: (270 mg, 70.0 %): m.p. 383-384 K with decomposition. Elemental analysis calculated (%) for $C_{44}H_{32}Br_8N_{16}O_8$: C (34.05), H (2.08) and N (14.44); found (%): C (34.04), H (2.06) and N (14.41). IR (selected bands, cm^{-1}): 3331, 1670, 1576, 1486. ^1H NMR (300 MHz, DMSO-d^6) δ = 8.29 (d, J = 8.1 Hz 8H); 7.70 (t, J = 7.2 Hz 4H); 7.59 (t, J = 7.7 Hz, 8H) 6.86 (d, J = 7.6 Hz, 8NH); 5.98 (t, J = 7.4 Hz 4H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 186.38, 148.32, 131.85, 131.71, 129.79, 129.54, 73.22, 65.06. HRMS (ESI) m/z $(M+H)^+$ calcd. for $C_{44}H_{33}Br_8N_{16}O_8^+$ 1544.6128, found 1544.6132.

	**7b** (9.9 %): ^{1}H NMR (300 MHz, DMSO-d^6): δ = 8.19 (d, 2H), 7.70 (s, 1H), 7.61 (t, 1H), 7.43 (t, 2H).[31a]
	**8** (4.8 %): ^{1}H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

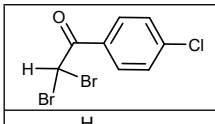
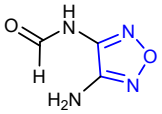


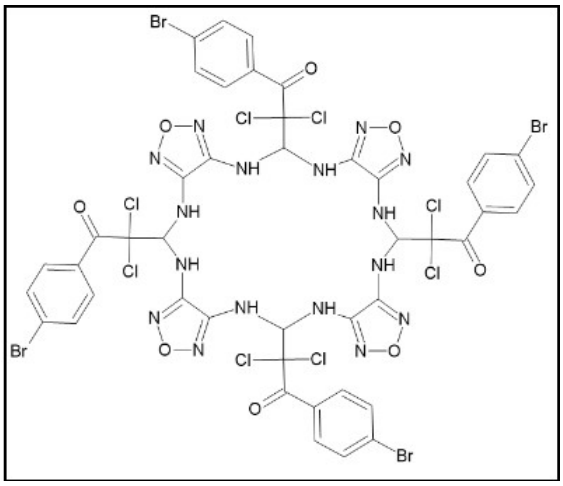
6c: (192.1 mg, 58 %): m.p. 503–504 K. Elemental analysis calculated (%) for $C_{44}H_{28}Cl_{12}N_{16}O_8$: C (39.61), H (2.12) and N (16.80); found (%): C (39.58), H (2.10) and N (16.77). IR (selected bands, cm^{-1}): 3349, 1684, 1586, 1488. ^{1}H NMR (DMSO-d^6, 300 MHz): δ = 8.16 (d, J= 8.3 Hz, 8H); 7.70 (d, J= 8.3 Hz, 8H); 6.92 (d, J= 8.2 Hz, 8NH); 6.01 (t, J= 8.3 Hz, 4H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 185.86, 147.81, 131.82, 131.25, 129.22, 129.01, 88.58, 68.88. HRMS (ESI) m/z $(M+H)^+$ calcd. for $C_{44}H_{29}Cl_{12}N_{16}O_8^+$ 1328.8611, found 1328.8615.

	**7c** (13.0 %): ^{1}H NMR (300 MHz, DMSO-d^6): δ = 8.27 (d, 2H), 7.94 (s, 1H), 7.35 (d, 2H).[31a]
	**8** (6.7 %): ^{1}H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

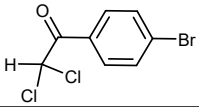
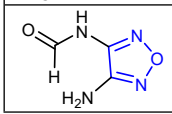


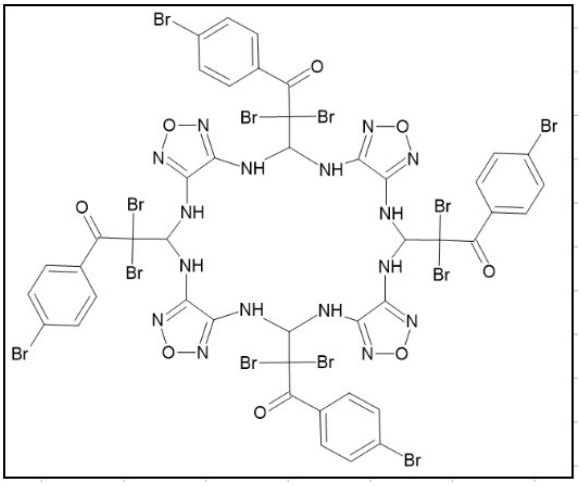
6d: (260 mg, 62.2 %): m.p. 402-403 K with decomposition. Elemental analysis calculated (%) for $C_{44}H_{28}Br_8Cl_4N_{16}O_8$: C (31.27), H (1.67) and N (13.26); found (%): C (31.24), H (1.64) and N (13.22). IR (selected bands, cm^{-1}): 3330, 1669, 1580, 1487. ^{1}H NMR (DMSO-d^6, 300 MHz): δ = 8.29 (d, J= 8.3 Hz 8H); 7.69 (d, J= 8.3 Hz, 8H); 6.87 (d, J= 8.2 Hz, 8NH); 5.95 (t, J= 8.3 Hz, 4H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 186.29, 147.84, 133.04, 132.35, 130.26, 128.83, 73.56, 64.96. HRMS (ESI) m/z $(M+H)^+$ calcd. for $C_{44}H_{29}Br_8Cl_4N_{16}O_8^+$ 1680.4569, found 1680.4568.

	**7d** (15.1 %): ^{1}H NMR (300 MHz, DMSO-d^6): δ = 8.20 (d, 2H), 7.69 (s, 1H), 7.39 (d, 2H).[31a]
	**8** (5.8 %): ^{1}H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

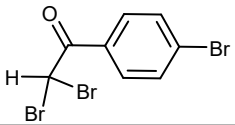
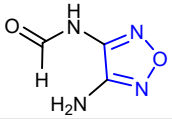


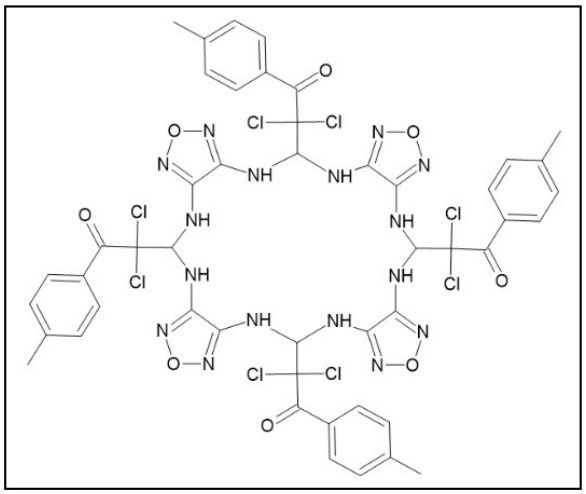
6e: (226 mg, 60.0 %): m.p. 456–457 K. Elemental analysis calculated (%) for $C_{44}H_{28}Br_4Cl_8N_{16}O_8$: C (34.95), H (1.87) and N (14.82); found (%): C (34.92), H (1.83) and N (14.80). IR (selected bands, cm^{-1}): 3359, 1685, 1582, 1484. ^1H NMR (DMSO-d^6, 300 MHz): δ = 8.08 (d, J = 8.3 Hz, 8H) 7.84 (d, J= 8.0 Hz, 8H); 6.93 (d, J = 8.2 Hz, 8NH); 5.99 (t, J = 8.0 Hz, 4H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 185.61, 148.08, 131.96, 131.57, 131.31, 130.67, 88.66, 68.93. HRMS (ESI) m/z $(M+H)^+$ calcd. For $C_{44}H_{29}Br_4Cl_8N_{16}O_8^+$ 1504.6590, found 1504.6592.

	**7e** (12.5 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 8.20 (d, 2H), 7.89 (s, 1H), 7.44 (d, 2H).[31a]
	**8** (6.8 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

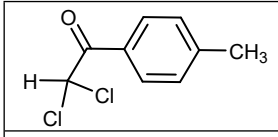
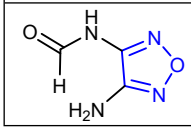


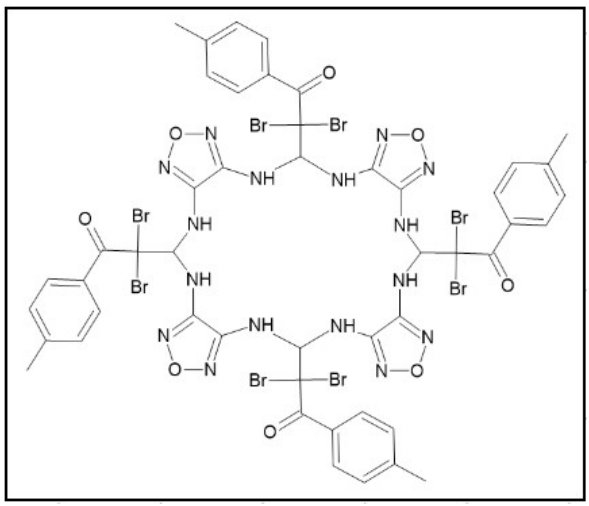
6f: (301 mg, 65.1 %): %): m.p. 385-386 K with decomposition. Elemental analysis calculated (%) for $C_{44}H_{28}Br_{12}N_{16}O_8$: C (28.30), H (1.51) and N (12.00); found (%): C (28.27), H (1.48) and N (11.98). IR (selected bands, cm^{-1}): 3333, 1671, 1574, 1471. ^1H NMR (DMSO-d^6, 300 MHz): δ = 8.18 (d, J = 8.4 Hz, 8H) 7.80 (d, J = 8.4 Hz, 8H); 6.79 (d, J = 7.9 Hz, 8NH); 6.00 (t, J = 7.8 Hz, 4H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 185.85, 146.30, 137.04, 131.60, 130.48, 130.03, 74.34, 62.19. HRMS (ESI) m/z $(M+Na)^+$ calcd. for $C_{44}H_{28}Br_{12}N_{16}O_8Na^+$ 1890.2246, found 1890.2250.

	**7f** (10.9 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 8.15 (d, 2H), 7.73 (s, 1H), 7.41 (d, 2H).[31a]
	**8** (3.4 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

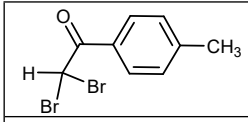
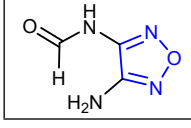


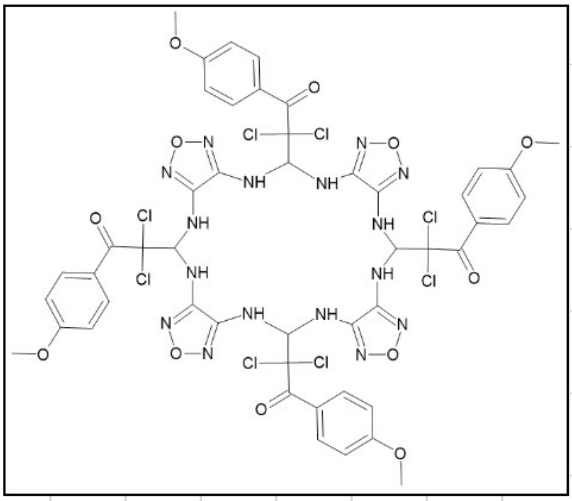
6g: (170 mg, 55.0 %): %): m.p. 521–523 K. Elemental analysis calculated (%) for $C_{48}H_{40}Cl_8N_{16}O_8$: C (46.03), H (3.22) and N (17.89); found (%): C (46.01), H (3.20) and N (17.84). IR (selected bands, cm^{-1}): 3362, 1658, 1591, 1491. ^1H NMR (DMSO-d^6, 300 MHz): δ = 8.09 (d, J= 8.5 Hz, 8H); 7.41 (d, J = 7.8 Hz, 8H); 6.93 (d, J = 8.5 Hz, 8NH); 6.05 (t, J = 7.6 Hz, 4H); 2.40 (s, 12H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 187.97, 149.23, 131.53, 131.26, 129.11, 128.65, 91.43, 70.40, 21.46. HRMS (ESI) m/z $(M+H)^+$ calcd. for $C_{48}H_{41}Cl_8N_{16}O_8^+$ 1249.0796, found 1249.0791.

	**7g** (5.2 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 8.25 (d, 2H), 7.95 (s, 1H), 7.39 (d, 2H), 2.39 (s, 3H).[31b]
	**8** (3.5 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

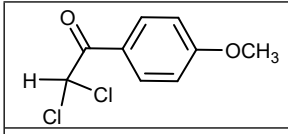
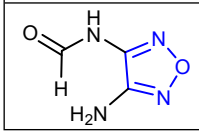


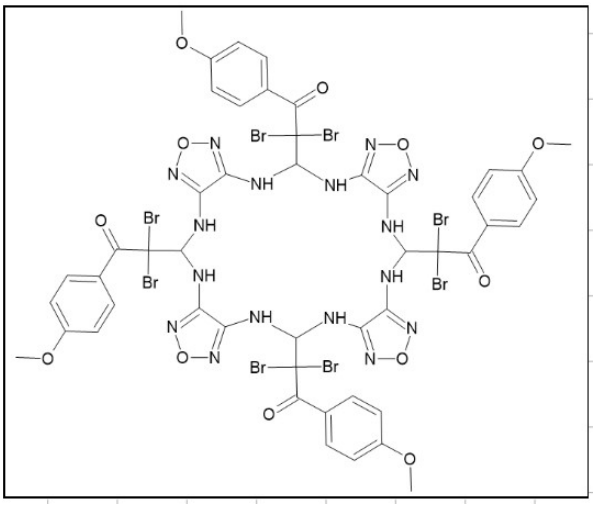
6h: (232 mg, 58.0 %): m.p. 387-388 K with decomposition. Elemental analysis calculated (%) for $C_{48}H_{40}Br_8N_{16}O_8$: C (35.85), H (2.51) and N (13.94); found (%): C (35.82), H (2.48) and N (13.92). IR (selected bands, cm^{-1}): 3359, 1655, 1590, 1494. ^1H NMR (DMSO-d^6, 300 MHz): δ = 8.22 (m, 8H); 7.39 (d, J = 7.8 Hz, 8H); 6.87 (m, 8NH); 6.00 (m, 4H), 2.40 (s, 12H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 187.90, 149.54, 131.52, 129.22, 129.11, 128.67, 75.96, 64.96, 21.27. HRMS (ESI) m/z $(M+H)^+$ calcd. for $C_{48}H_{41}Br_8N_{16}O_8^+$ 1600.6754, found 1600.6755.

	**7h** (7.8 %): ^1H NMR (300 MHz, DMSO-d^6): δ 8.21 (d, 2H), 7.75 (s, 1H), 7.30 (d, 2H), 2.35 (s, 3H).[31b]
	**8** (3.7 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

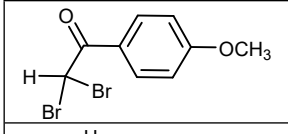
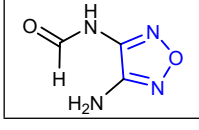


6i: (157 mg, 48.0 %): m.p. 505–506 K. Elemental analysis calculated (%) for $C_{48}H_{40}Cl_8N_{16}O_{12}$: C (43.79), H (3.06) and N (17.02); found (%): C (43.77), H (3.04) and N(17.00). IR (selected bands, cm^{-1}): 3356, 1651, 1594, 1500. ^1H NMR (DMSO-d^6, 300 MHz): δ = 8.37 (m, 8H); 7.13 (d, J = 8.8 Hz, 8H); 6.90 (m, 8NH); 6.00 (m, 4H); 3.88 (s, 12H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 185.45, 163.63, 149.94, 135.98, 132.95, 114.16, 89.20, 69.71, 55,76. HRMS (ESI) m/z $(M+H)^+$ calcd. for $C_{48}H_{41}Cl_8N_{16}O_{12}^+$ 1313.0592, found 1313.0595.

	**7i** (10.4 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 8.11 (d, 2H), 7.81 (s, 1H), 7.11 (d, 2H), 3.91 (s, 3H).[31a]
	**8** (6.9 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]



6j: (254 mg, 61.0 %): m.p. 345-346 K with decomposition. Elemental analysis calculated (%) for $C_{48}H_{40}Br_8N_{16}O_8$: C (34.48), H (2.41) and N (13.40); found (%): C (34.45), H (2.38) and N (13.37). IR (selected bands, cm^{-1}): 3367, 1658, 1593, 1509. ^1H NMR (300 MHz, DMSO-d^6): δ = 8.40 (d, J= 7.0 Hz, 8H); 7.12 (d, J = 8.6 Hz, 8H); 6.88 (m, 8NH); 6.11 (m, 4H), 3.90 (s, 12H). ^{13}C NMR (DMSO-d^6, 125 MHz): δ = 185.41, 163.72, 149.71, 133.13, 129.85, 113.82, 73.17, 64.82, 55,76. HRMS (ESI) m/z $(M+H)^+$ calcd. for $C_{48}H_{41}Br_8N_{16}O_{12}^+$ 1664.6551, found 1664.6551.

	**7j** (10.9 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 8.21 (d, 2H), 7.69 (s, 1H), 7.17 (d, 2H), 3.91 (s, 3H).[31a]
	**8** (5.4 %): ^1H NMR (300 MHz, DMSO-d^6): δ = 10.40 (bd, 1H, NH), 8.75 (bd, 1H, CHO), 6.11 (bs, 2H, NH_2).[32]

4. NMR spectroscopy

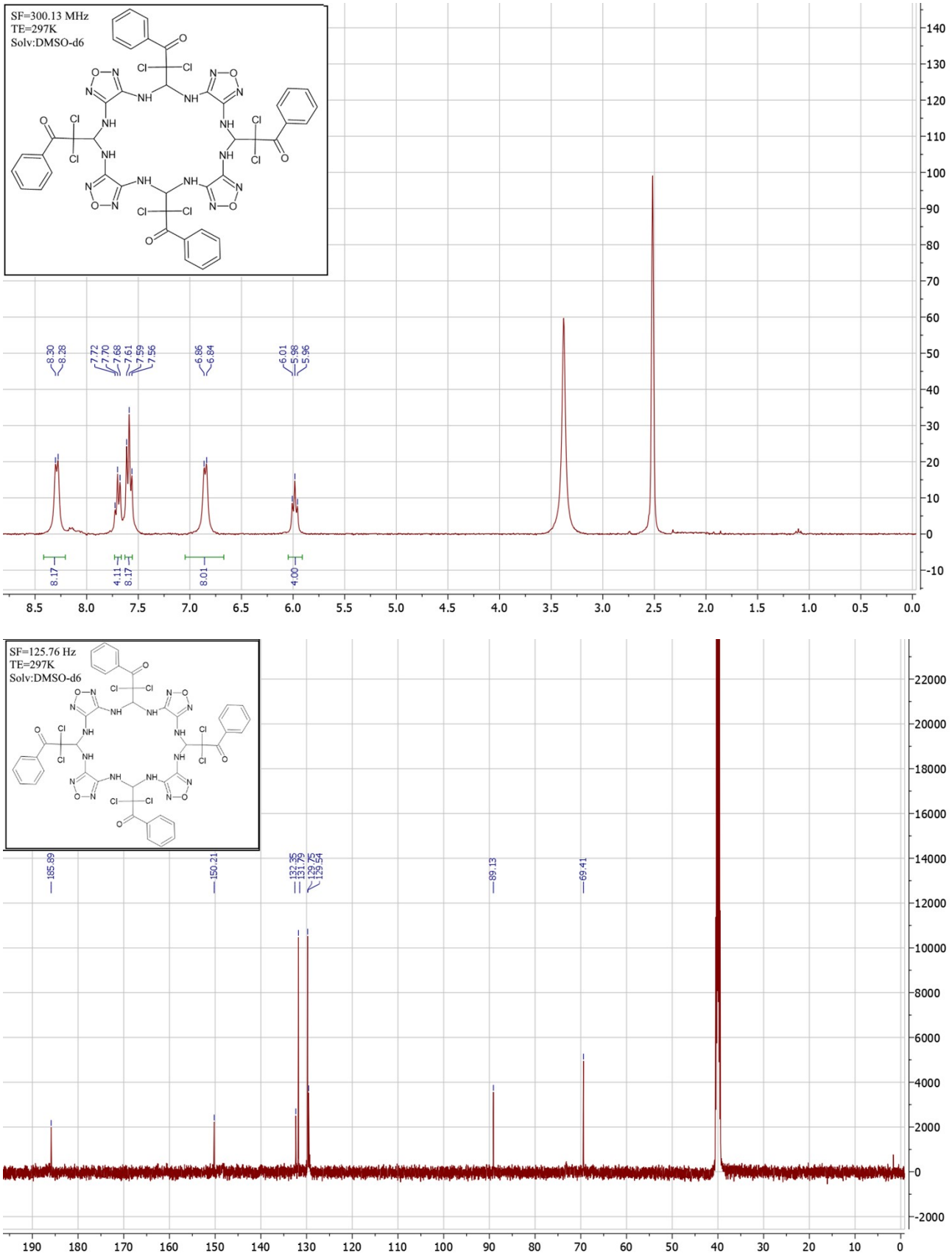


Figure S1. $^{1}H/^{13}C$ NMR spectra of **6a**.

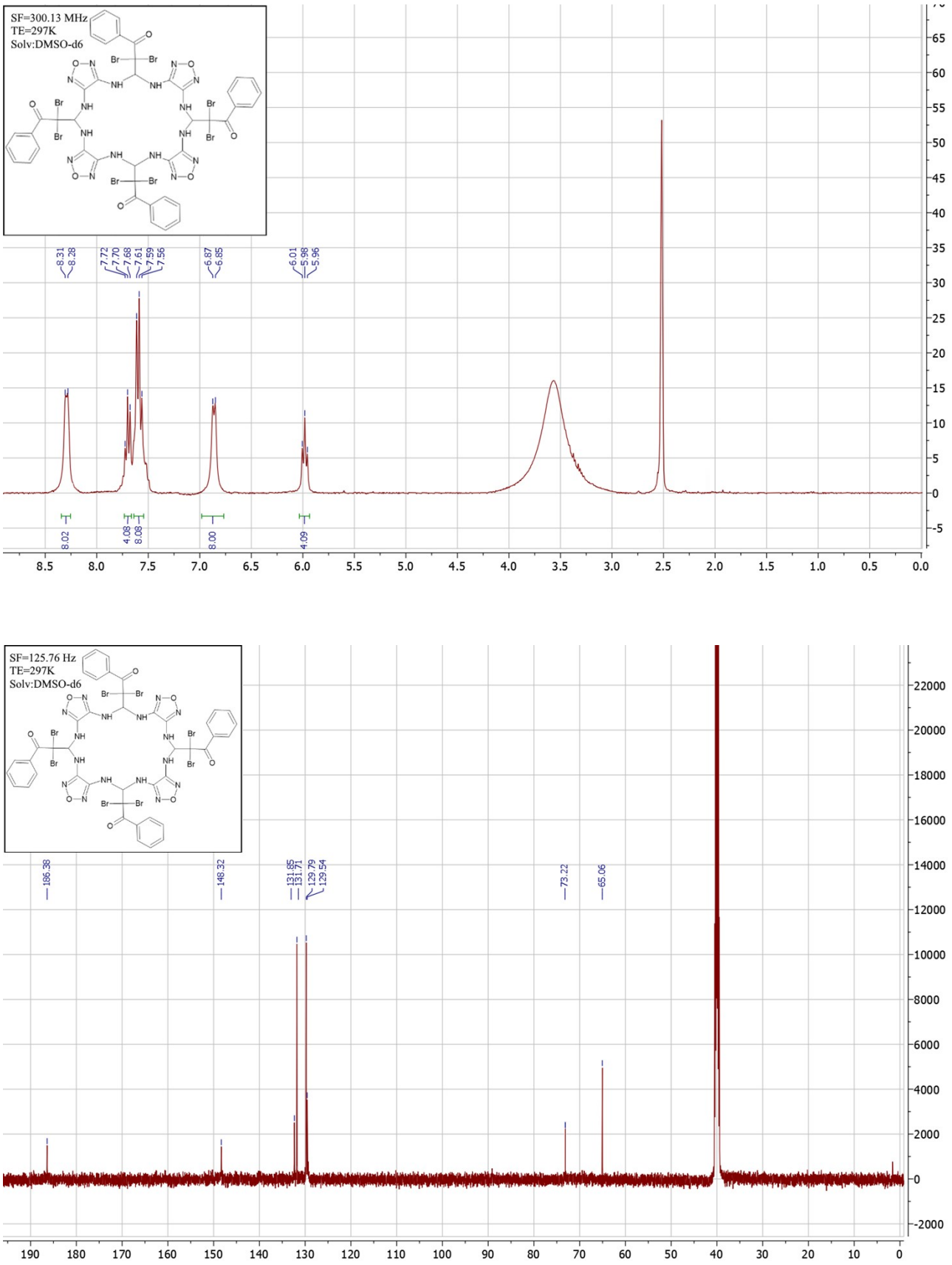
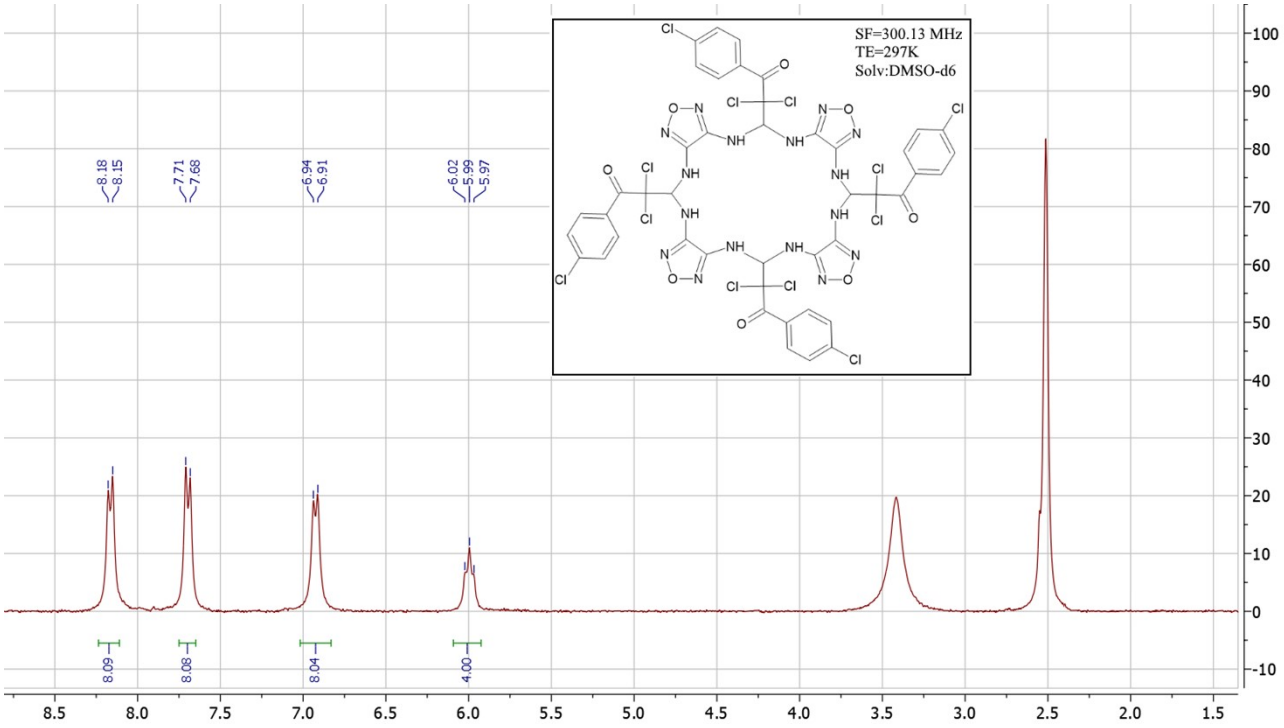


Figure S2. $^{1}H/^{13}C$ NMR spectra of **6b**.



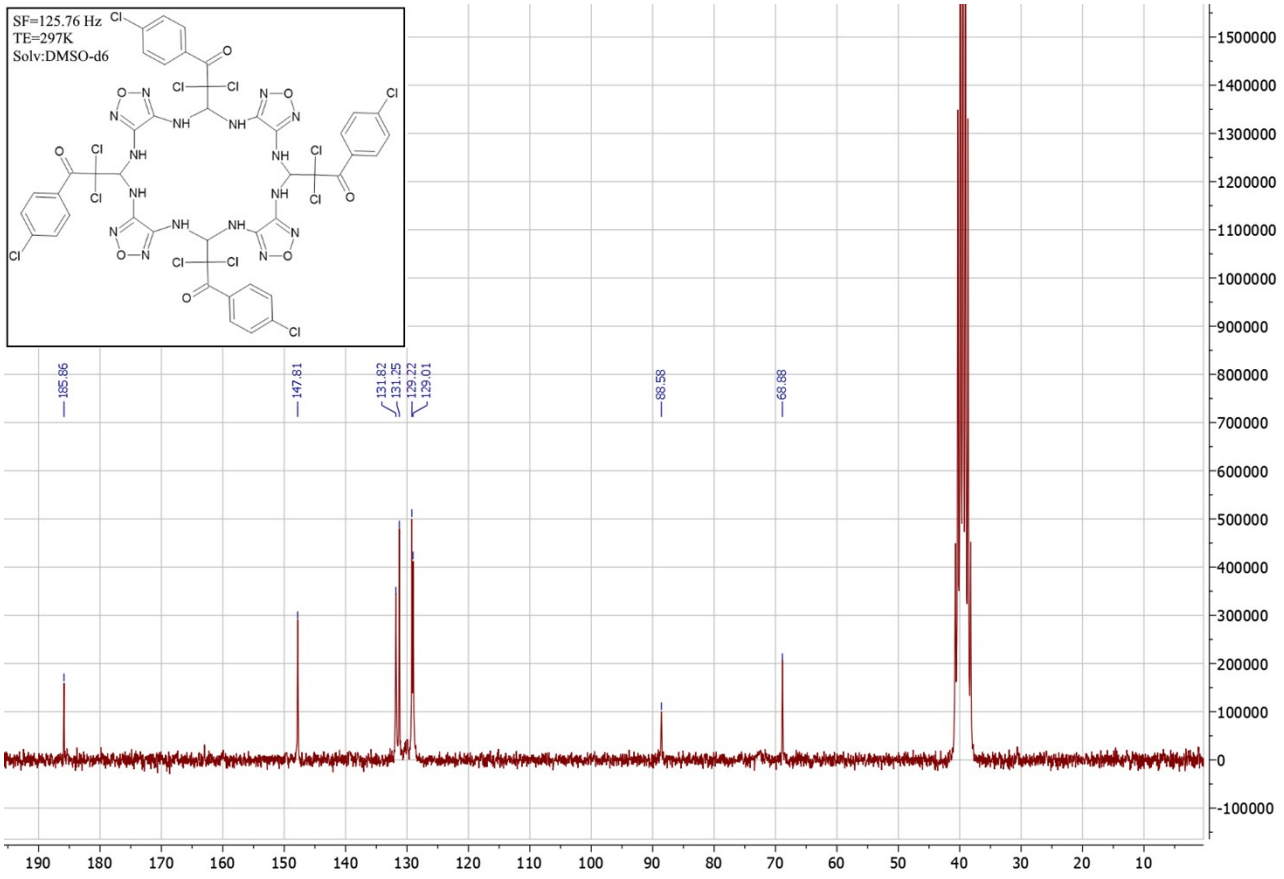


Figure S3. $^{1}H/^{13}C$ NMR spectra of **6c**.

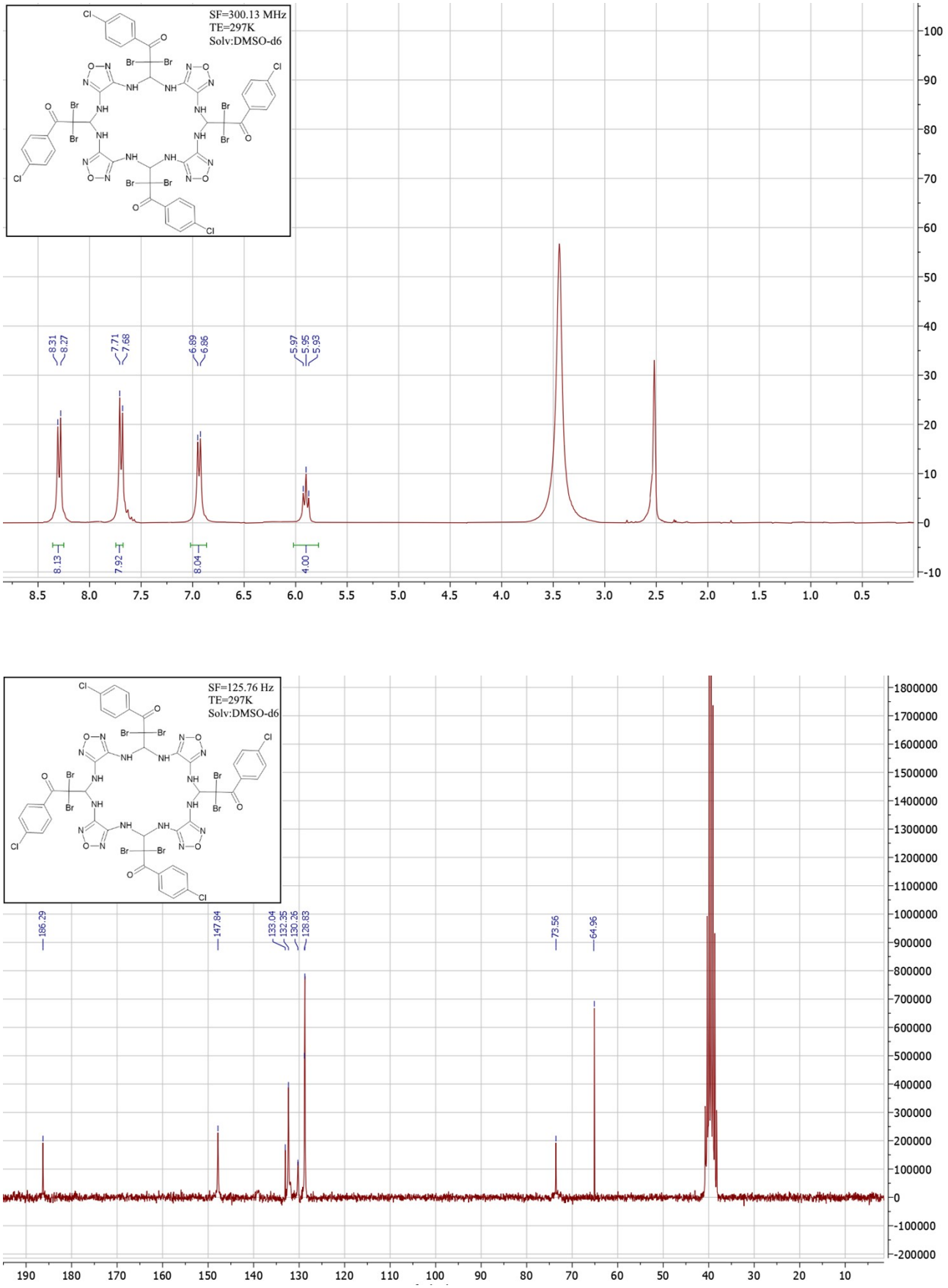


Figure S4. $^{1}H/^{13}C$ NMR spectra of **6d**.

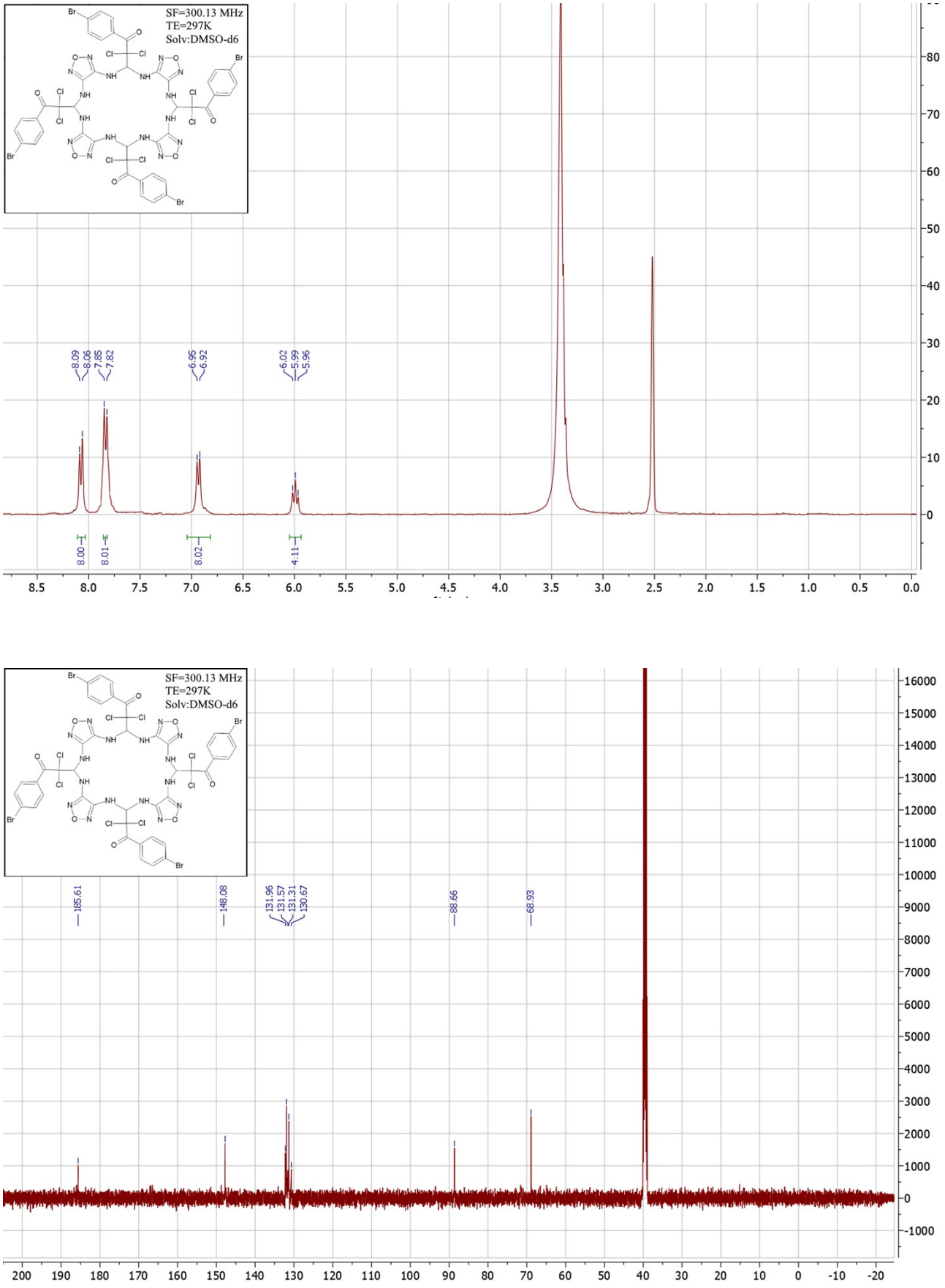


Figure S5. $^{1}H/^{13}C$ NMR spectra of **6e**.

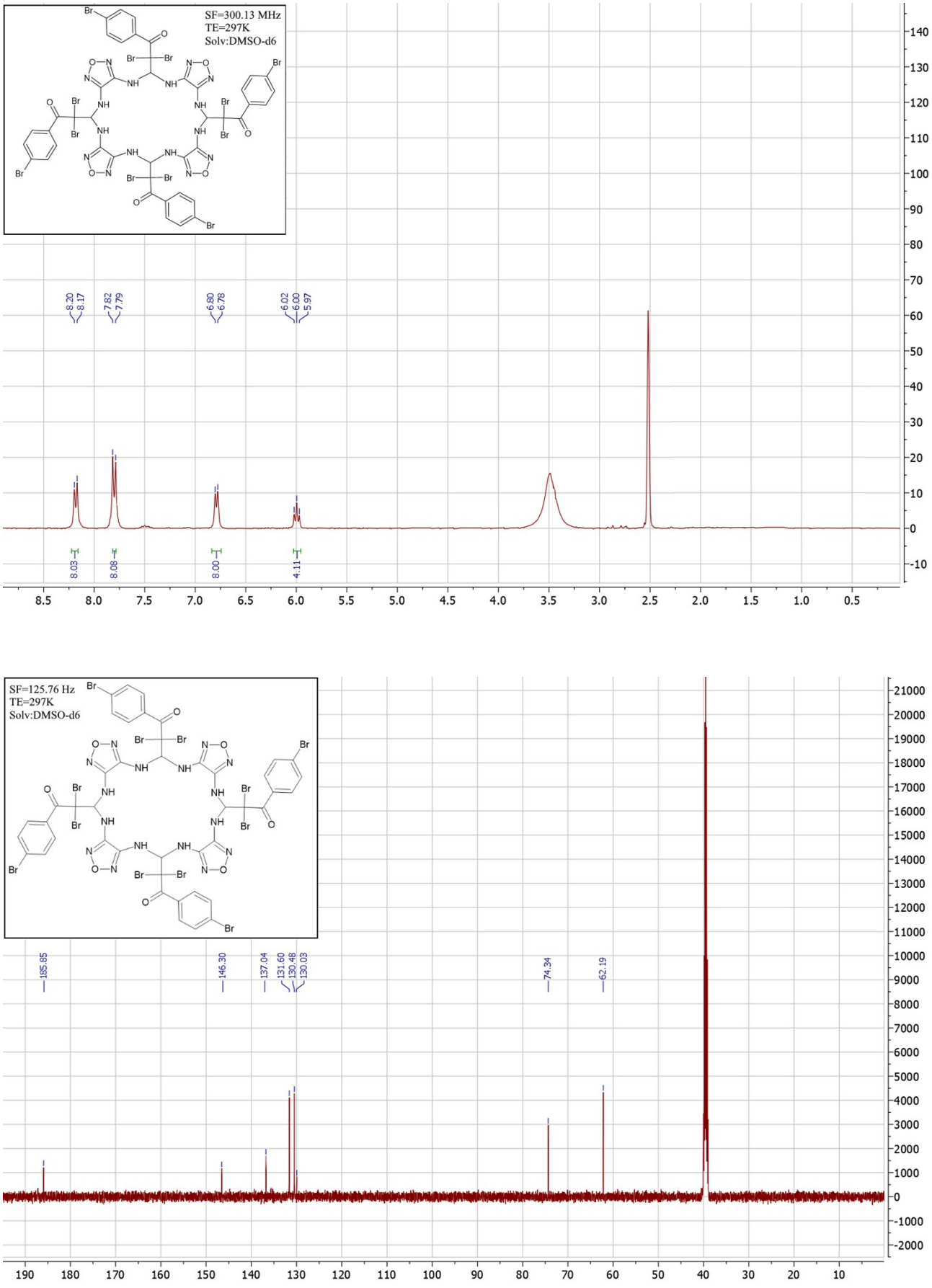
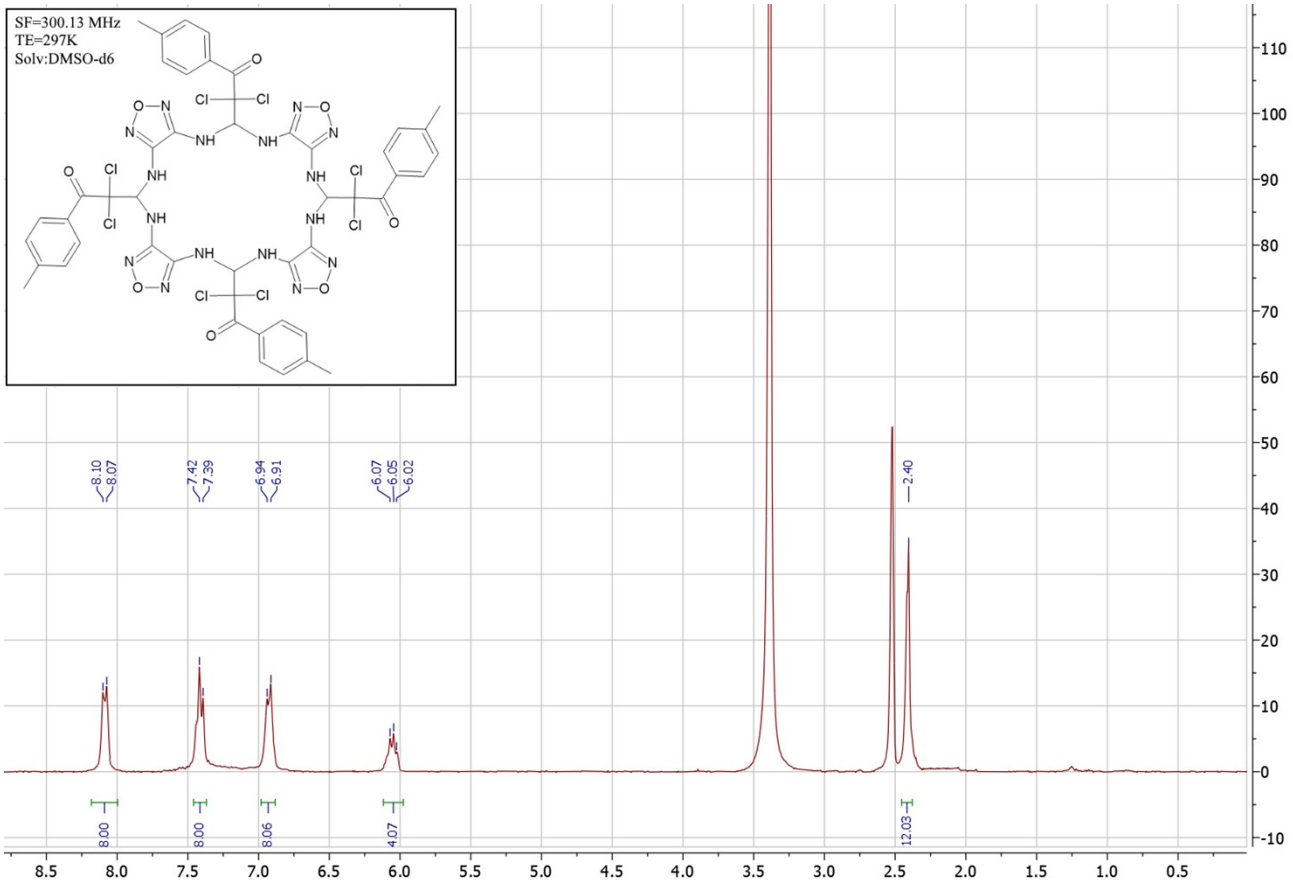


Figure S6. $^{1}H/^{13}C$ NMR spectra of **6f**.



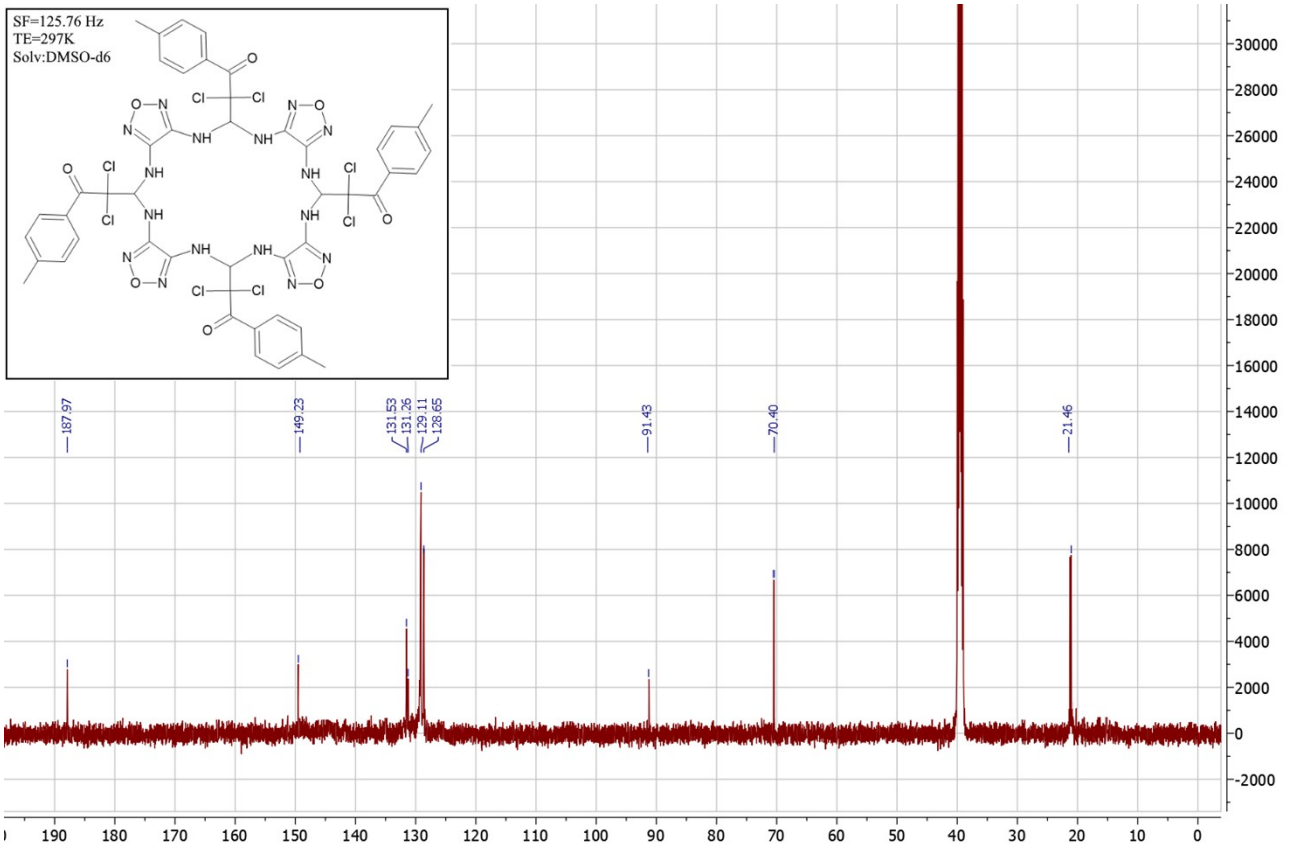


Figure S7. $^{1}H/^{13}C$ NMR spectra of **6g**.

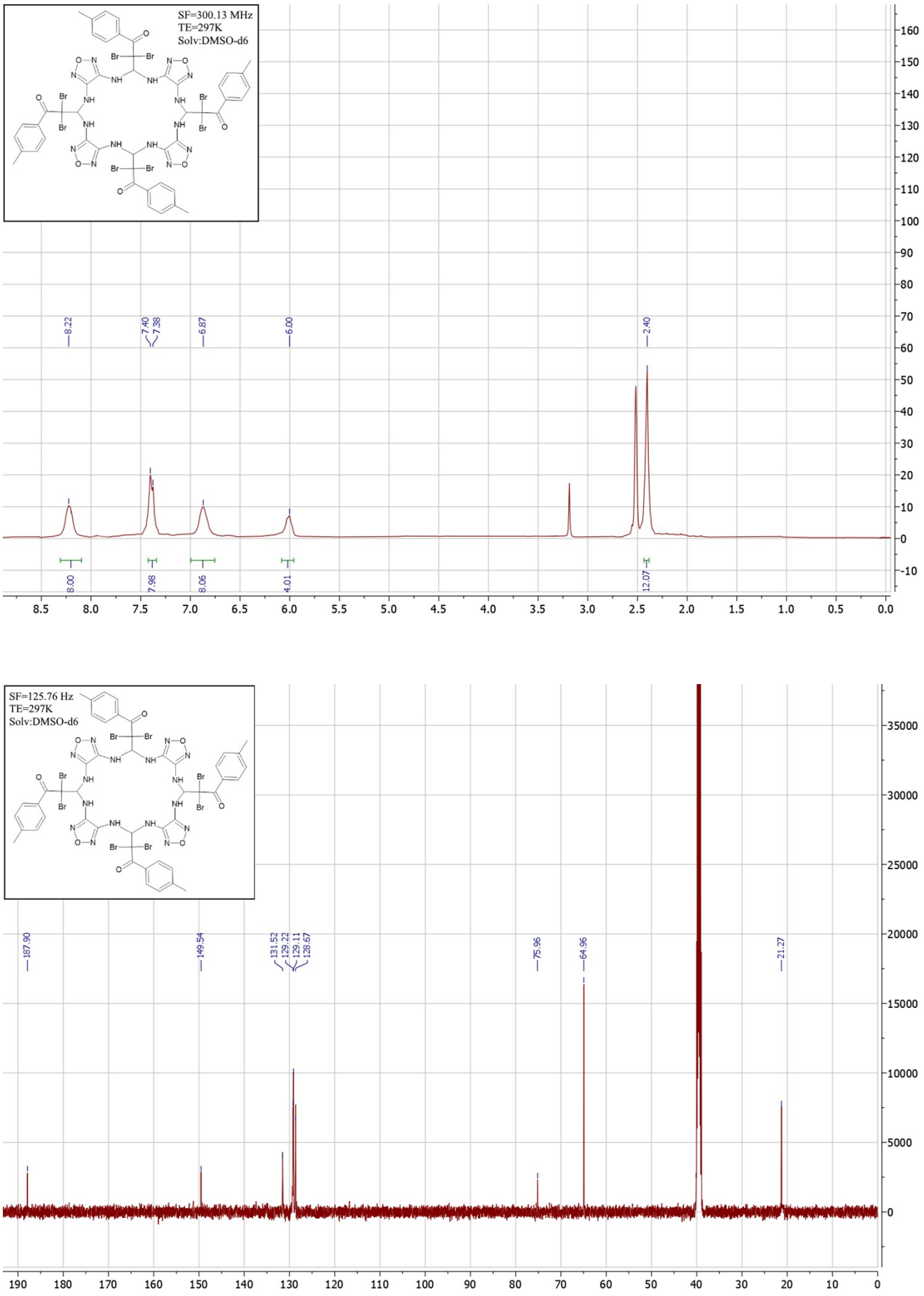


Figure S8. $^{1}H/^{13}C$ NMR spectra of **6h**.

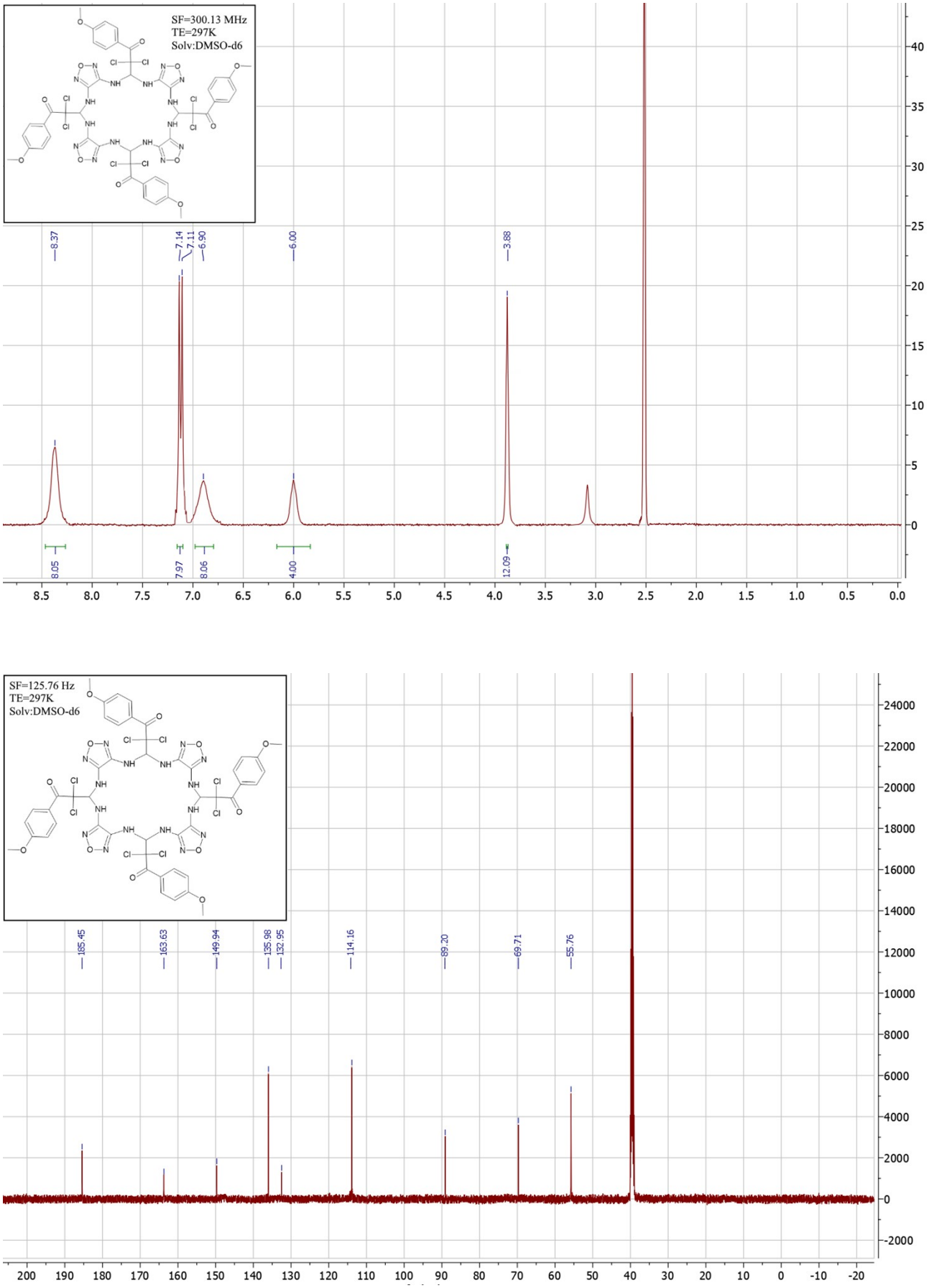


Figure S9. $^{1}H/^{13}C$ NMR spectra of **6i**.

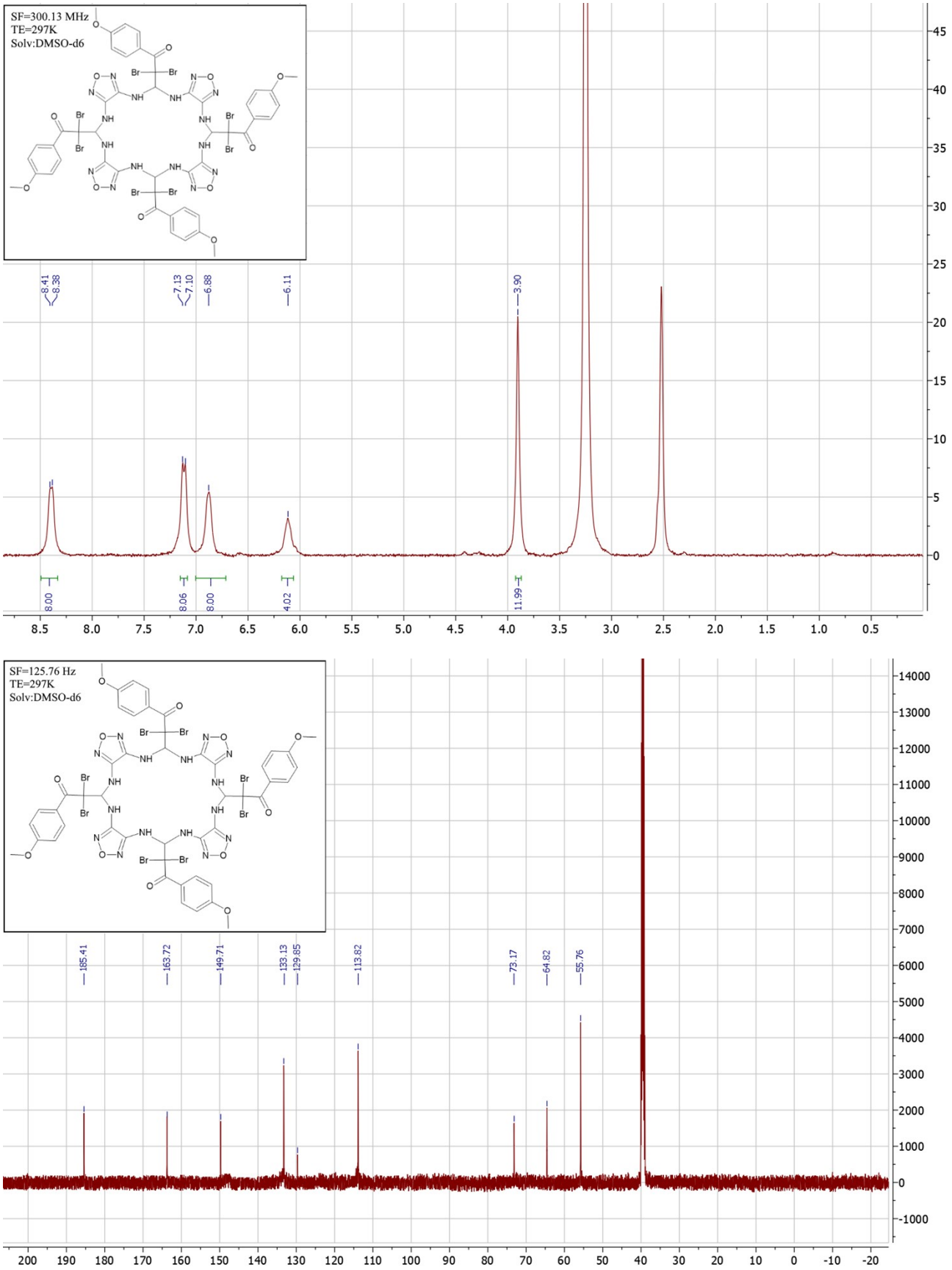


Figure S10. $^{1}H/^{13}C$ NMR spectra of **6j**.

5. X-ray crystallographic analysis

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using graphite monochromatized Cu K_a-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.[s1] The structure was solved by direct methods using SHELXT[s2] and refined on F^2 using SHELXL-2018[s3] in the OLEX2 program.[s4] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite[s5] was used for molecular graphics. A rotating group model was applied for methyl groups. Crystallographic data for the structural analysis have been deposited to the Cambridge Crystallographic Data Center (CCDC 2338046 for **6c**, 2338047 for **6d** and 2338045 for **6j**). 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).

References:

s1. CrysAlisPro. Version 1.171.41.106a. *Rigaku Oxford Diffraction*, 2021.

s2. G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3-8.

s3. G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3-8.

s4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, *J. Appl. Cryst.* 2009, **42**, 339-341.

s5. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, P. A. Wood, *J. Appl. Cryst.* 2020, **53**, 226-235.

Table S2. Crystal data and structure refinement for compounds **6c**, **6d** and **6j.**

Compound	**6c**	**6d**	**6j**
Empirical formula	$2(C_{44}H_{28}Cl_{12}N_{16}O8)$, $5.868(C_2H_6OS)$, $2.132(C_3H_7NO)$, C_2H_3N	$C_{44}H_{27}Br_8Cl_4N_{16}O_8$, $2(C_3H_7NO)$	$C_{48}H_{40}Br_8N_{16}O_{12}$, $3.117(C_3H_7NO)$, $0.883(C_2H_6OS)$
Formula weight	3323.80	1835.09	1969.06
Temperature, K	100	100	100
Wavelength, Å	1.54184	1.54184	1.54184
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*1	$P2_1/c$	$P2_1/n$
a, Å	9.7467(2)	18.1145(6)	13.8694(4)
b, Å	17.9670(4)	23.3689(5)	29.3492(6)
c, Å	21.3451(4)	19.3970(5)	19.4086(5)
α, °	78.320(2)	90	90
β, °	88.543(2)	112.866(3)	109.326(3)
γ, °	81.663(2)	90	90
Volume, $Å^3$	3621.82(13)	7565.8(4)	7455.2(4)
Z, Z′	1, 1	4, 1	4, 1
ρ_{calc}, g/cm^3	1.524	1.611	1.754
μ, mm^{-1}	5.580	6.875	6.026
F(000)	1697.7	3580	3911
Crystal size, mm^3	0.18 x 0.05 x 0.03	0.14 x 0.08 x 0.02	0.25 x 0.06 x 0.03
θ for data collection, °	2.537 – 79.979	2.647 – 82.005	2.844 – 80.331
Index range	-12<=h<=11, -22<=k<=22, -26<=l<=27	-21<=h<=23, -25<=k<=29, -24<=l<=24	-17<=h<=17, -26<=k<=37, -24<=l<=24
Reflections collected	76433	87376	60350
Independent reflections [R(int)]	22939 [0.0605]	16093 [0.0830]	15830 [0.0615]
Reflections with $I > 2\sigma(I)$	20912	9627	14317
T_{max} / T_{min}	1.000 / 0.438	1.000 / 0.535	1.000 / 0.682
Parameters / restraints	1822 / 39	852 / 253	952 / 47
Goodness-of-fit on F^2	1.042	1.116	1.150
R_1 / wR_2 [$I>2\sigma(I)$]	0.0540 / 0.1396	0.0776 / 0.2208	0.1193 / 0.2458
R_1 / wR_2 (all reflections)	0.0592 / 0.1428	0.1219 / 0.2498	0.1258 / 0.2458
ρ_{max}/ρ_{min} ($eÅ^{-3}$)	0.775 / -1.032	1.385 / -1.561	1.594 / -1.937
CCDC number	2338046	2338047	2338045

Compound 6c. Compound crystallize with two molecules in the independent part of unit cell. Each hydrogen atom of amino-group is bonded to a solvent molecule - dimethylforamide or dimethyl sulfoxide. Parameters of intermolecular interactions are presented in the Table S4. Some solvate molecules have partial occupancy in the crystal. The crystal also contains disordered solvent molecules that could not be modeled. Presumably, it includes DMF/DMSO/MeCN/H_2O in the various stochiometric ratio and probably at the same place, which does not allow correct modeling of the solvent molecules in the crystal. A solvent mask SQUEEZE was used by SHELXL[s3] to remove solvent molecules (36 electrons were found in a volume of 169 Å3 in 2 voids per unit cell).

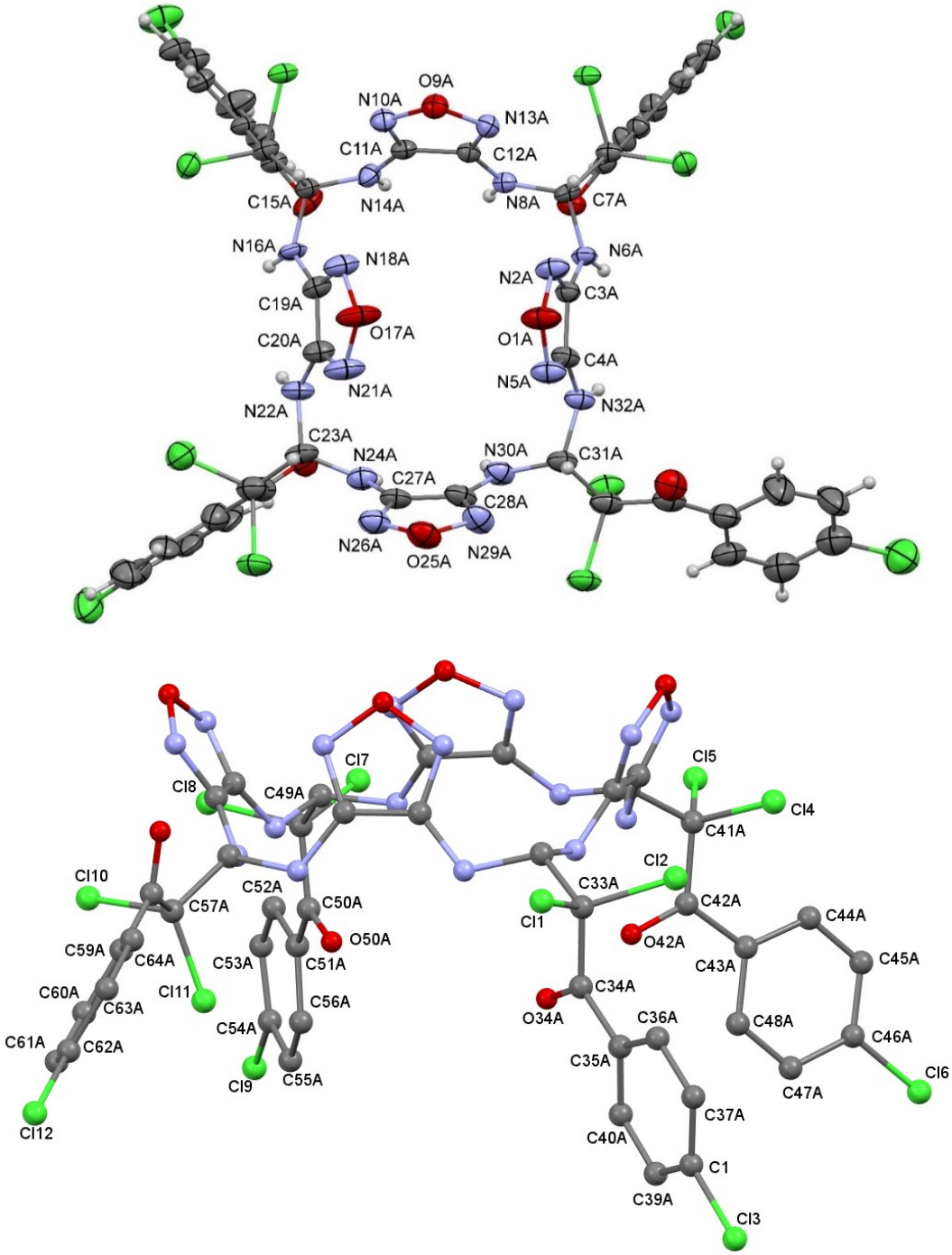


Figure S11. Two projections to the geometry of the independent molecule A in the crystal: (a) ortep-drawing (p=50%) with partial numbering of atoms, (b) ball-sticks representation with partial numbering of atoms.

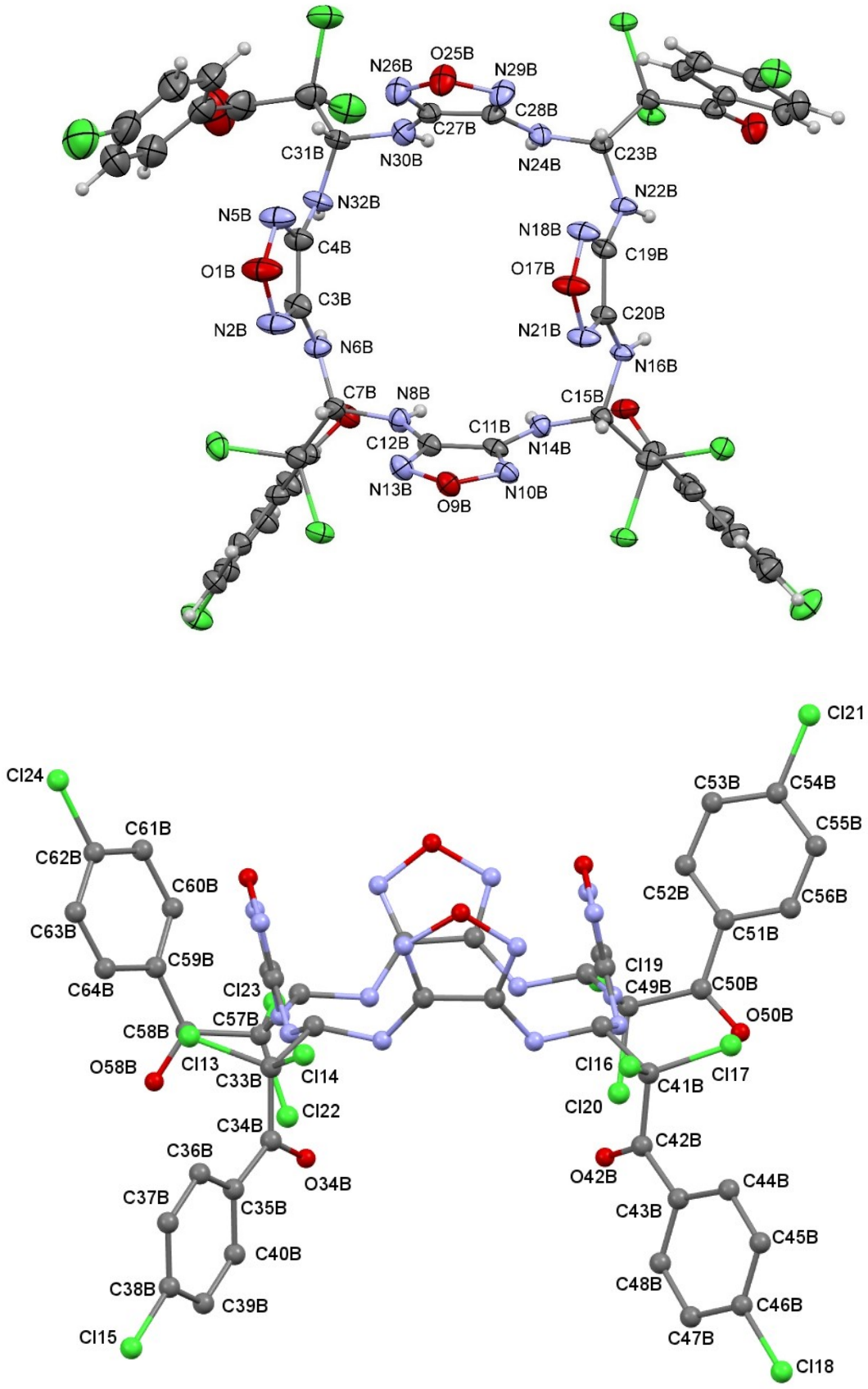
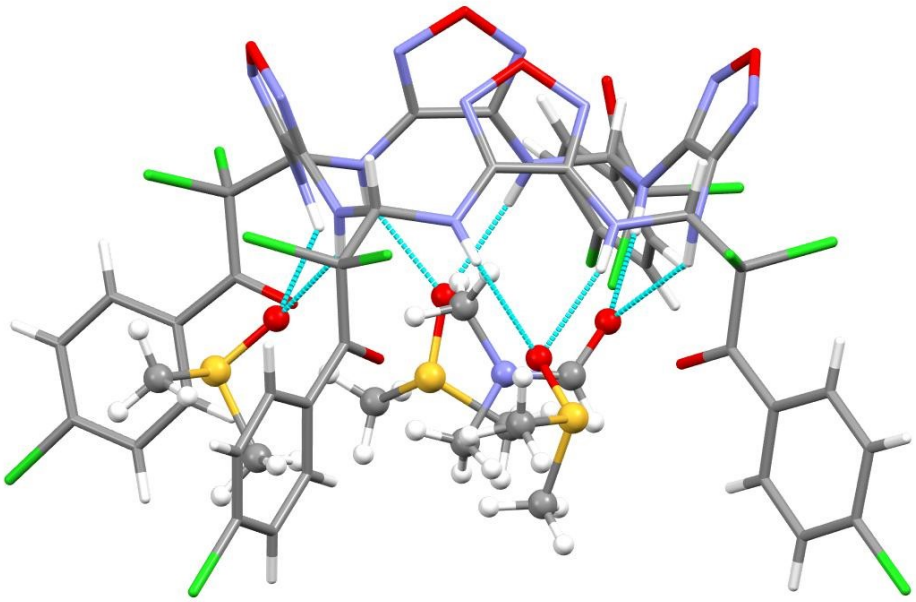
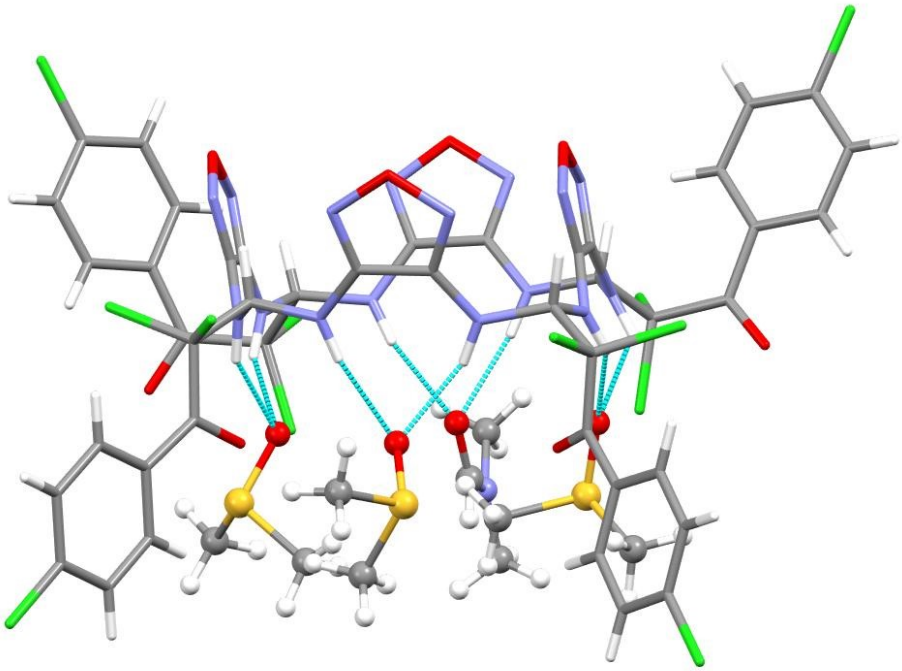


Figure S12. Two projections to the geometry of the independent molecule A in the crystal: (a) ortep-drawing (p=50%) with partial numbering of atoms, (b) ball-sticks representation with partial numbering of atoms.



a)



b)

Figure S13. Intermolecular interactions N-H…O type in the crystal **6c** between compound (capped sticks representation) and solvent molecules (ball-sticks representation): independent molecules A (a) and B (b).

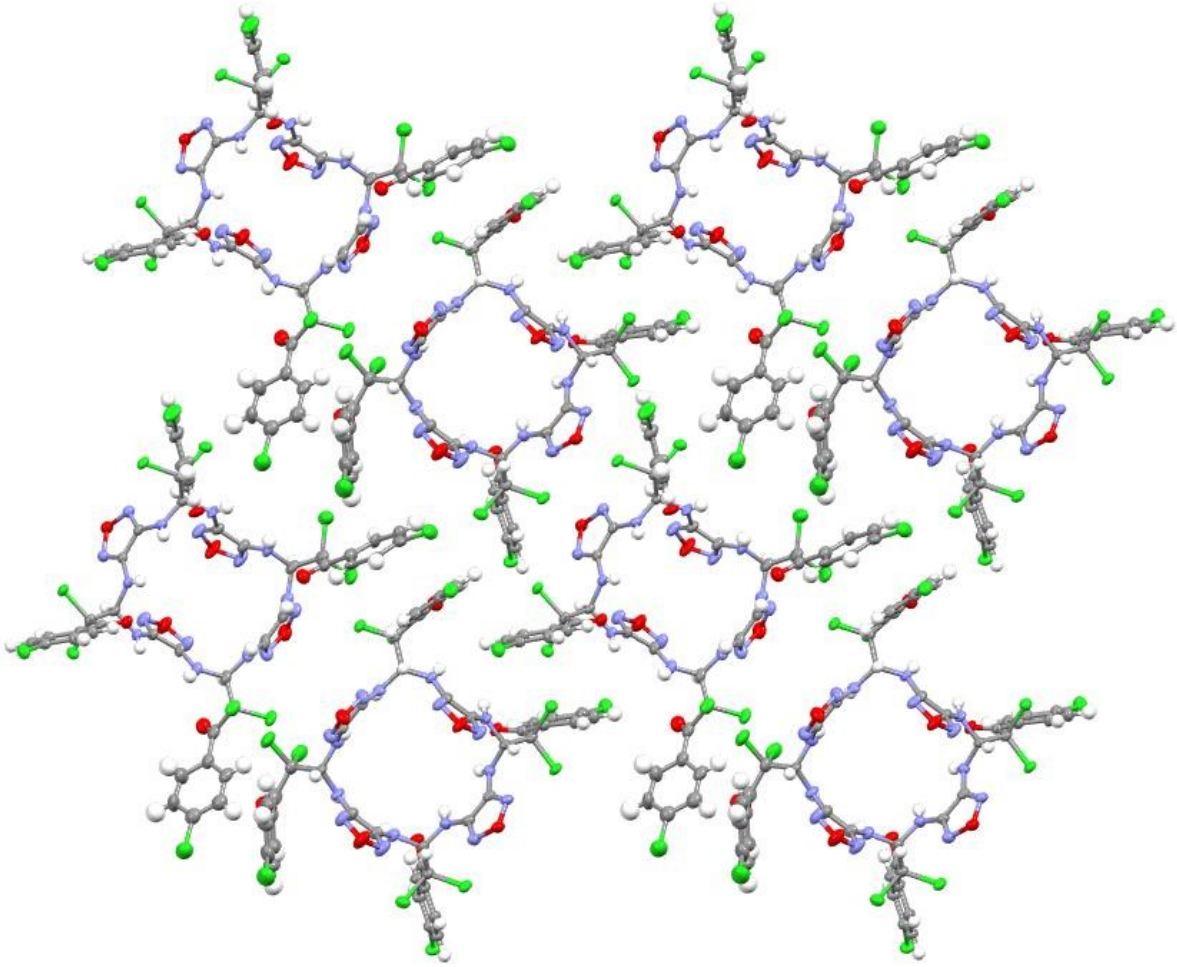


Figure S14. Fragment of the crystal packing for **6c**. Solvent molecules are omitted for clarity. View along the axis 0*a*. The volume occuped by solvent molecules is 1199.6 Å that is 33% from the volume of unit cell (probe radius=1.2Å); calculation is performed using the 'Voids' feature in Mercury[s5].

Table S3. Bond lengths [Å] and angles [°] for independent molecules of **6c**.

Cl(1)-C(33A)	1.777(6)	N(6A)-C(7A)	1.461(7)	N(5A)-O(1A)-N(2A)	110.8(5)
Cl(2)-C(33A)	1.797(5)	N(8A)-C(7A)	1.437(7)	N(13A)-O(9A)-N(10A)	111.4(4)
Cl(3)-C(1)	1.726(6)	N(8A)-C(12A)	1.370(7)	N(18A)-O(17A)-N(21A)	111.1(5)
Cl(4)-C(41A)	1.779(6)	N(10A)-C(11A)	1.312(8)	N(26A)-O(25A)-N(29A)	110.2(5)
Cl(5)-C(41A)	1.791(7)	N(13A)-C(12A)	1.316(8)	C(3A)-N(2A)-O(1A)	105.5(5)
Cl(6)-C(46A)	1.731(7)	N(14A)-C(11A)	1.362(8)	C(4A)-N(5A)-O(1A)	105.6(5)
Cl(7)-C(49A)	1.796(8)	N(14A)-C(15A)	1.431(8)	C(3A)-N(6A)-C(7A)	115.1(5)
Cl(8)-C(49A)	1.785(7)	N(16A)-C(15A)	1.450(7)	C(12A)-N(8A)-C(7A)	120.9(5)
Cl(9)-C(54A)	1.724(12)	N(16A)-C(19A)	1.367(8)	C(11A)-N(10A)-O(9A)	105.2(5)
Cl(10)-C(57A)	1.798(7)	N(18A)-C(19A)	1.314(9)	C(12A)-N(13A)-O(9A)	104.2(4)
Cl(11)-C(57A)	1.767(7)	N(21A)-C(20A)	1.300(9)	C(11A)-N(14A)-C(15A)	120.3(5)
Cl(12)-C(62A)	1.734(14)	N(22A)-C(20A)	1.362(9)	C(19A)-N(16A)-C(15A)	115.7(5)
O(1A)-N(2A)	1.404(7)	N(22A)-C(23A)	1.433(8)	C(19A)-N(18A)-O(17A)	105.0(5)
O(1A)-N(5A)	1.386(7)	N(24A)-C(23A)	1.466(9)	C(20A)-N(21A)-O(17A)	104.6(5)
O(9A)-N(10A)	1.410(7)	N(24A)-C(27A)	1.365(9)	C(20A)-N(22A)-C(23A)	118.3(6)
O(9A)-N(13A)	1.405(7)	O(42B)-C(42B)	1.212(7)	C(27A)-N(24A)-C(23A)	119.9(6)
O(17A)-N(18A)	1.395(7)	O(50B)-C(50B)	1.216(7)	C(27A)-N(26A)-O(25A)	106.2(6)
O(17A)-N(21A)	1.400(8)	O(58B)-C(58B)	1.211(10)	C(28A)-N(29A)-O(25A)	104.7(6)
O(25A)-N(26A)	1.403(8)	N(2B)-C(3B)	1.306(9)	C(28A)-N(30A)-C(31A)	121.9(6)
O(25A)-N(29A)	1.418(8)	N(5B)-C(4B)	1.296(9)	C(4A)-N(32A)-C(31A)	116.5(6)
O(34A)-C(34A)	1.219(7)	N(6B)-C(3B)	1.370(8)	N(8A)-C(7A)-N(6A)	112.9(5)
Cl(13)-C(33B)	1.782(6)	N(6B)-C(7B)	1.441(7)	N(14A)-C(15A)-N(16A)	113.4(5)
Cl(14)-C(33B)	1.796(6)	N(8B)-C(7B)	1.430(7)	N(22A)-C(23A)-N(24A)	113.0(6)
Cl(15)-C(38B)	1.719(6)	N(8B)-C(12B)	1.363(8)	N(30A)-C(31A)-N(32A)	112.8(5)
Cl(16)-C(41B)	1.795(6)	N(10B)-C(11B)	1.317(8)	N(2B)-O(1B)-N(5B)	108.9(5)
Cl(17)-C(41B)	1.789(6)	N(13B)-C(12B)	1.313(8)	N(13B)-O(9B)-N(10B)	110.6(4)
Cl(18)-C(46B)	1.734(7)	N(14B)-C(11B)	1.356(7)	N(18B)-O(17B)-N(21B)	110.5(4)
Cl(19)-C(49B)	1.778(6)	N(14B)-C(15B)	1.437(7)	N(29B)-O(25B)-N(26B)	110.6(5)
Cl(20)-C(49B)	1.784(6)	N(16B)-C(15B)	1.463(6)	C(3B)-N(2B)-O(1B)	106.8(5)
Cl(21)-C(54B)	1.722(7)	N(16B)-C(20B)	1.366(7)	C(4B)-N(5B)-O(1B)	105.9(5)
Cl(22)-C(57B)	1.758(8)	N(18B)-C(19B)	1.310(8)	C(3B)-N(6B)-C(7B)	119.7(5)
Cl(23)-C(57B)	1.809(7)	N(21B)-C(20B)	1.304(8)	C(12B)-N(8B)-C(7B)	120.7(5)
Cl(24)-C(62B)	1.725(11)	N(22B)-C(19B)	1.380(7)	C(11B)-N(10B)-O(9B)	105.3(5)
O(1B)-N(2B)	1.406(7)	N(22B)-C(23B)	1.451(7)	C(12B)-N(13B)-O(9B)	106.2(5)
O(1B)-N(5B)	1.411(7)	N(24B)-C(23B)	1.442(7)	C(11B)-N(14B)-C(15B)	121.2(5)
O(9B)-N(10B)	1.407(6)	N(24B)-C(28B)	1.368(8)	C(20B)-N(16B)-C(15B)	114.9(5)
O(9B)-N(13B)	1.400(7)	N(26A)-C(27A)	1.301(9)	C(19B)-N(18B)-O(17B)	105.8(4)
O(17B)-N(18B)	1.390(6)	N(29A)-C(28A)	1.318(9)	C(20B)-N(21B)-O(17B)	106.1(4)
O(17B)-N(21B)	1.397(6)	N(30A)-C(28A)	1.370(9)	C(19B)-N(22B)-C(23B)	115.6(5)
O(25B)-N(26B)	1.406(7)	N(30A)-C(31A)	1.449(9)	C(28B)-N(24B)-C(23B)	121.6(5)
O(25B)-N(29B)	1.405(7)	N(32A)-C(4A)	1.385(9)	C(27B)-N(26B)-O(25B)	105.3(5)
O(34B)-C(34B)	1.226(7)	N(32A)-C(31A)	1.456(8)	C(28B)-N(29B)-O(25B)	105.0(5)
O(42A)-C(42A)	1.223(7)	N(26B)-C(27B)	1.304(8)	C(27B)-N(30B)-C(31B)	120.7(5)
O(50A)-C(50A)	1.210(9)	N(29B)-C(28B)	1.312(8)	C(4B)-N(32B)-C(31B)	118.9(5)
O(58A)-C(58A)	1.215(9)	N(30B)-C(27B)	1.363(8)	N(8B)-C(7B)-N(6B)	113.6(5)
N(2A)-C(3A)	1.309(9)	N(30B)-C(31B)	1.450(8)	N(14B)-C(15B)-N(16B)	113.1(5)
N(5A)-C(4A)	1.298(9)	N(32B)-C(4B)	1.378(8)	N(24B)-C(23B)-N(22B)	113.2(4)
N(6A)-C(3A)	1.377(8)	N(32B)-C(31B)	1.442(7)	N(32B)-C(31B)-N(30B)	114.3(5)

Table S4. Main geometrical parameters of hydrogen bond in the crystal **6c**.

D–H···A	D–H, Å	H···A, Å	D···A, Å	∠ DHA, °	Symmetry operation
N(6A)-H(6A)...O(70)	0.88	2.25	2.966(8)	138.5	-
N(8A)-H(8A)...O(82)	0.88	2.15	2.828(7)	133.0	-
N(14A)-H(14A)...O(82)	0.88	2.03	2.779(8)	142.1	-
N(16A)-H(16A)...O(95)	0.88	2.21	2.947(11)	141.0	-
N(22A)-H(22A)...O(95)	0.88	2.02	2.860(12)	159.9	-
N(24A)-H(24A)...O(88)	0.88	2.20	2.940(8)	141.9	-
N(30A)-H(30A)...O(88)	0.88	1.99	2.849(7)	164.5	-
N(32A)-H(32A)...O(70)	0.88	2.12	2.876(8)	143.5	-
N(6B)-H(6B)...O(34B)	0.88	2.33	2.809(7)	114.3	-
N(6B)-H(6B)...O(79)	0.88	2.16	2.927(8)	145.1	-
N(8B)-H(8B)...O(76)	0.88	2.07	2.853(7)	148.4	-
N(14B)-H(14B)...O(76)	0.88	2.03	2.833(7)	151.9	-
N(16B)-H(16B)...O(73)	0.88	2.14	2.851(7)	137.2	-
N(22B)-H(22B)...O(73)	0.88	2.06	2.737(6)	132.9	-
N(24B)-H(24B)...O(92)	0.88	2.00	2.865(9)	169.7	-
N(30B)-H(30B)...O(92)	0.88	2.06	2.922(9)	167.5	-
N(32B)-H(32B)...O(79)	0.88	1.99	2.761(8)	145.1	-

Compound 6d. Compound crystallize with one molecule in the independent part of unit cell. Each hydrogen atom of amino-group is bonded to a solvent molecule - dimethylforamide or dimethyl sulfoxide. Parameters of intermolecular interactions are presented in the table S8. The crystal contains disordered solvent molecules in the voids with volume of 221 Åbx^3 per unit cell. A solvent mask was used by OLEX2[4] to remove solvent molecules. Presumably, it includes DMF/DMSO/MeCN/H2O in the various stochiometric ratio and probably at the same place, which does not allow correct modeling of the solvent molecules in the crystal. A solvent mask SQUEEZE was used by SHELXL3 to remove solvent molecules (392 electrons were found in a volume of 1170 Å^3 in 4 voids per unit cell). One of the main reasons for this behavior of a solvent whose molecules cannot be identified is the absence of intermolecular interactions with the molecules of the main compound.

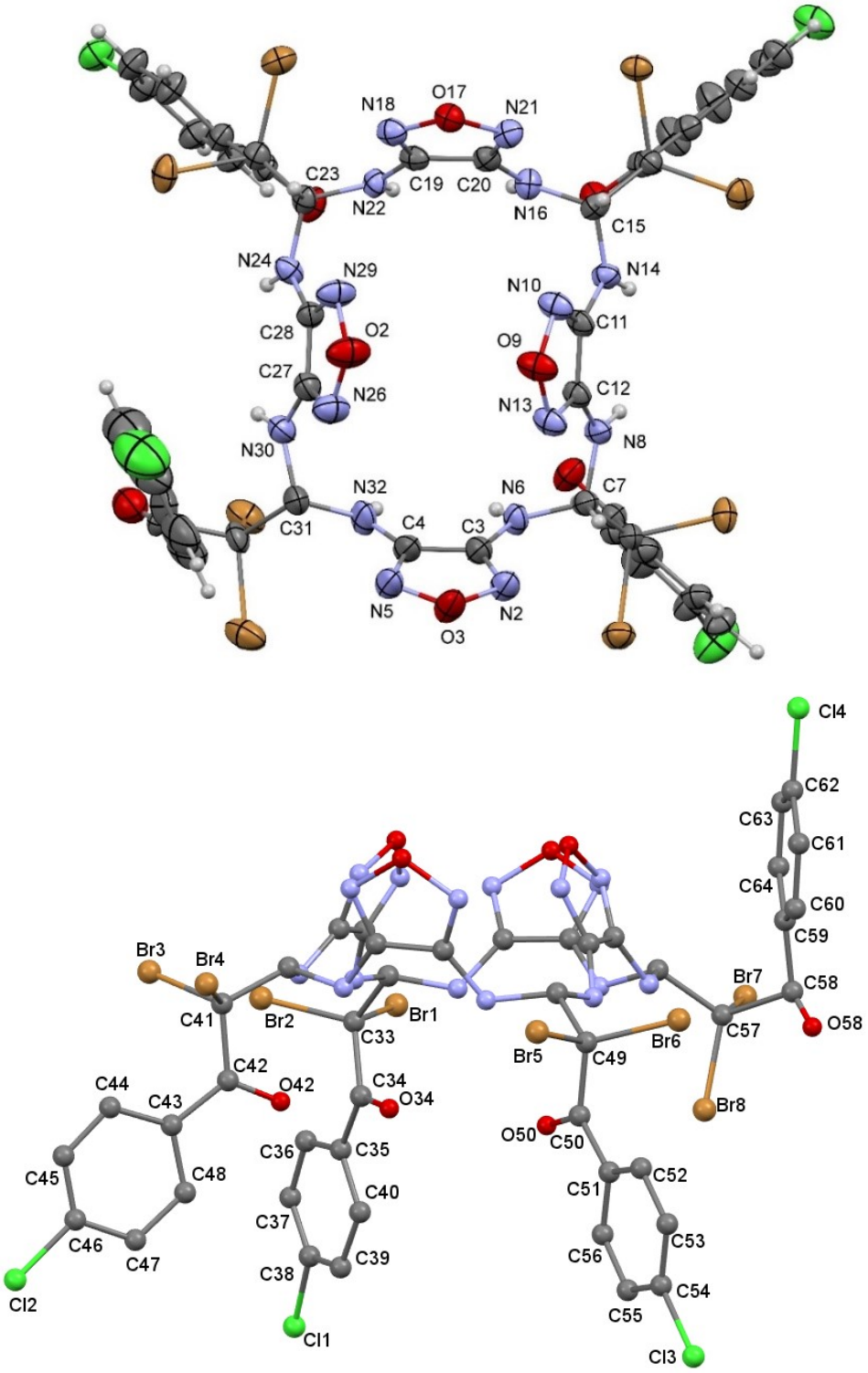


Figure S15. Two projections to the geometry of the molecule in the crystal **6d**: (a) ortep-drawing (p=50%) with partial numbering of atoms, (b) ball-sticks representation with partial numbering of atoms.

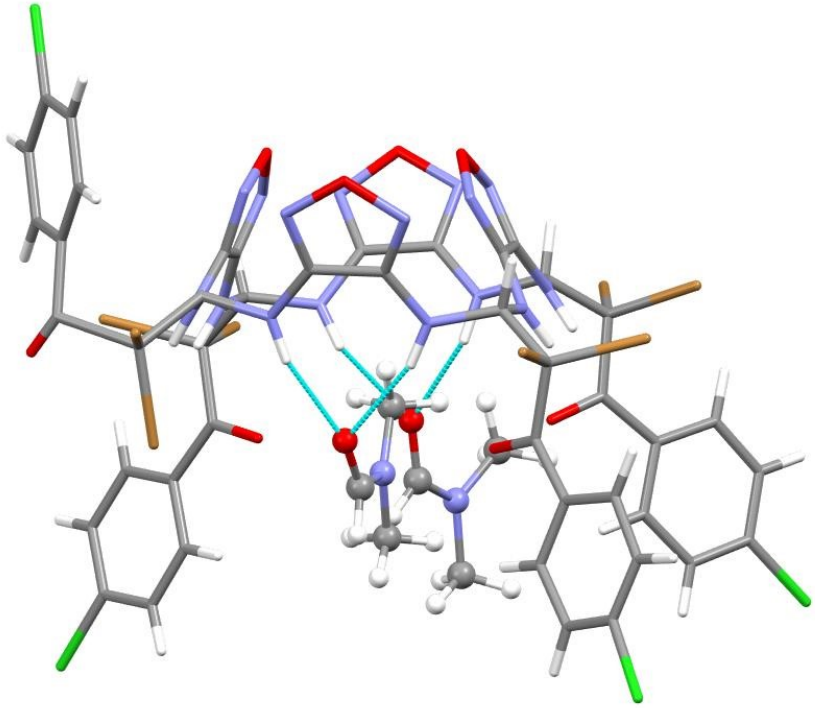


Figure S16. Intermolecular interactions N-H…O type in the crystal **6d** between compound (capped sticks representation) and solvent molecules (ball-sticks representation).

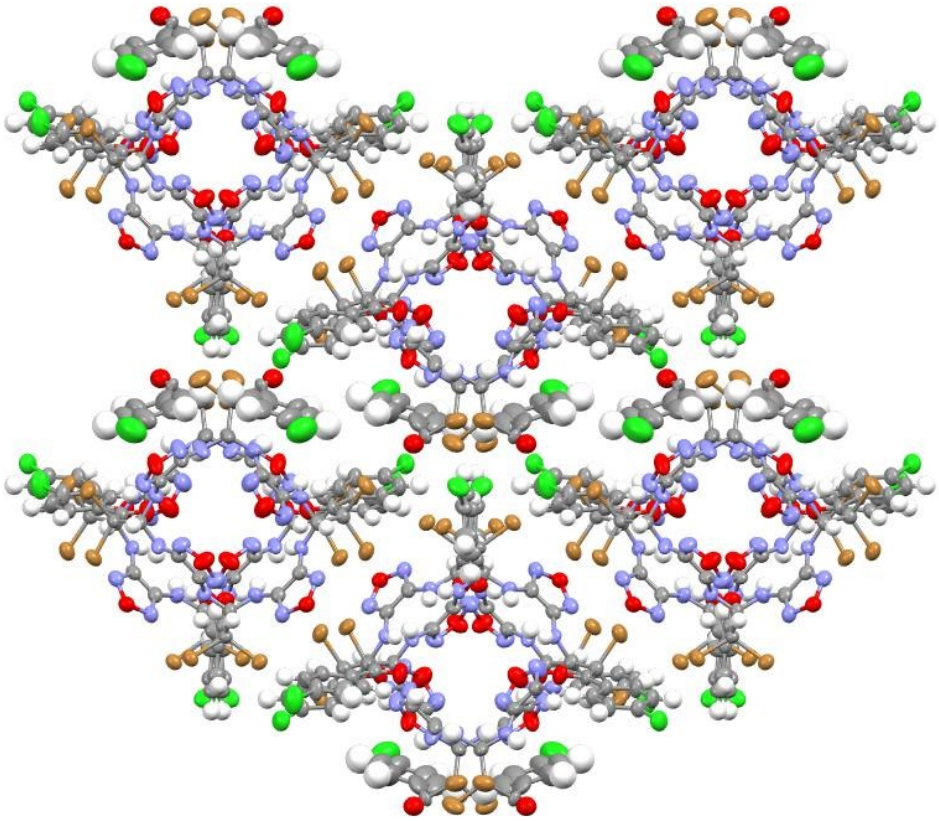


Figure S17. Fragment of the crystal packing for **6d**. Solvent molecules are omitted for clarity. View along the diagonal axis 0*ac*. The volume occuped by solvent molecules is2606.2 Å that is 34.5% from the volume of unit cell (probe radius=1.2Å); calculation is performed using the 'Voids' feature in Mercury[s5].

Table S5. Bond lengths [Å] and angles [°] for independent molecules of **6d**.

Br(1)-C(33)	1.972(7)	N(2)-C(3)	1.309(10)
Br(2)-C(33)	1.936(7)	N(5)-C(4)	1.318(9)
Br(3)-C(41)	1.937(7)	N(6)-C(3)	1.375(9)
Br(4)-C(41)	1.960(7)	N(6)-C(7)	1.424(9)
Br(5)-C(49)	1.960(7)	N(8)-C(7)	1.439(8)
Br(6)-C(49)	1.938(7)	N(8)-C(12)	1.369(9)
Br(7)-C(57)	1.935(18)	N(10)-C(11)	1.315(9)
Br(8)-C(57)	1.939(13)	N(13)-C(12)	1.311(8)
Cl(1)-C(38)	1.753(13)	N(14)-C(11)	1.373(8)
Cl(2)-C(46)	1.741(7)	N(14)-C(15)	1.417(8)
Cl(3)-C(54)	1.740(7)	N(16)-C(15)	1.422(8)
Cl(4)-C(62)	1.758(11)	N(16)-C(20)	1.373(8)
O(2)-N(26)	1.376(9)	N(18)-C(19)	1.295(8)
O(2)-N(29)	1.406(8)	N(21)-C(20)	1.304(9)
O(3)-N(2)	1.392(7)	N(22)-C(19)	1.365(9)
O(3)-N(5)	1.394(9)	N(22)-C(23)	1.443(8)
O(9)-N(10)	1.387(7)	N(24)-C(23)	1.447(9)
O(9)-N(13)	1.409(8)	N(24)-C(28)	1.384(8)
O(17)-N(18)	1.398(8)	N(26)-C(27)	1.291(10)
O(17)-N(21)	1.406(7)	N(29)-C(28)	1.301(10)
O(34)-C(34)	1.208(8)	N(30)-C(27)	1.395(10)
O(42)-C(42)	1.203(8)	N(30)-C(31)	1.435(10)
O(50)-C(50)	1.219(8)	N(32)-C(4)	1.359(11)
O(58)-C(58)	0.914(13)	N(32)-C(31)	1.450(10)
N(26)-O(2)-N(29)	109.9(6)	C(19)-N(22)-C(23)	121.8(5)
N(2)-O(3)-N(5)	110.8(5)	C(28)-N(24)-C(23)	117.2(6)
N(10)-O(9)-N(13)	111.0(5)	C(27)-N(26)-O(2)	106.2(6)
N(18)-O(17)-N(21)	110.1(5)	C(28)-N(29)-O(2)	105.1(6)
C(3)-N(2)-O(3)	104.8(6)	C(27)-N(30)-C(31)	116.5(7)
C(4)-N(5)-O(3)	105.5(6)	C(4)-N(32)-C(31)	119.4(7)
C(3)-N(6)-C(7)	121.1(6)	N(6)-C(7)-N(8)	113.3(6)
C(12)-N(8)-C(7)	119.1(5)	N(14)-C(15)-N(16)	114.1(6)
C(11)-N(10)-O(9)	105.0(6)	N(22)-C(23)-N(24)	113.7(6)
C(12)-N(13)-O(9)	104.7(6)	N(30)-C(31)-N(32)	112.5(6)
C(11)-N(14)-C(15)	118.6(6)	C(20)-N(21)-O(17)	105.0(6)
C(20)-N(16)-C(15)	121.7(6)	C(11)-N(10)-O(9)	105.0(6)
C(19)-N(18)-O(17)	106.0(6)	C(12)-N(13)-O(9)	104.7(6)

Table S6. Main geometrical parameters of hydrogen bond in the crystal **6d**.

D–H···A	D–H, Å	H···A, Å	D···A, Å	∠ DHA, °	Symmetry operation
N(6)-H(6)...O(34)	0.88	2.31	2.789(8)	114.5	-
N(6)-H(6)...O(73)	0.88	2.20	3.039(13)	158.0	-
N(16)-H(16)...O(42)	0.88	2.29	2.770(7)	114.3	-
N(16)-H(16)...O(70)	0.88	2.17	2.923(8)	143.0	-
N(22)-H(22)...O(50)	0.88	2.34	2.808(7)	113.3	-
N(22)-H(22)...O(70)	0.88	2.19	2.907(7)	138.3	-
N(32)-H(32)...O(73)	0.88	2.07	2.908(11)	159.2	-

Compound 6j. Compound crystallize with one molecule in the independent part of unit cell. Each hydrogen atom of amino-group is bonded to a solvent molecule - dimethylforamide or dimethyl sulfoxide. Parameters of intermolecular interactions are presented in the table S6. Some solvate molecules have partial occupancy in the crystal.

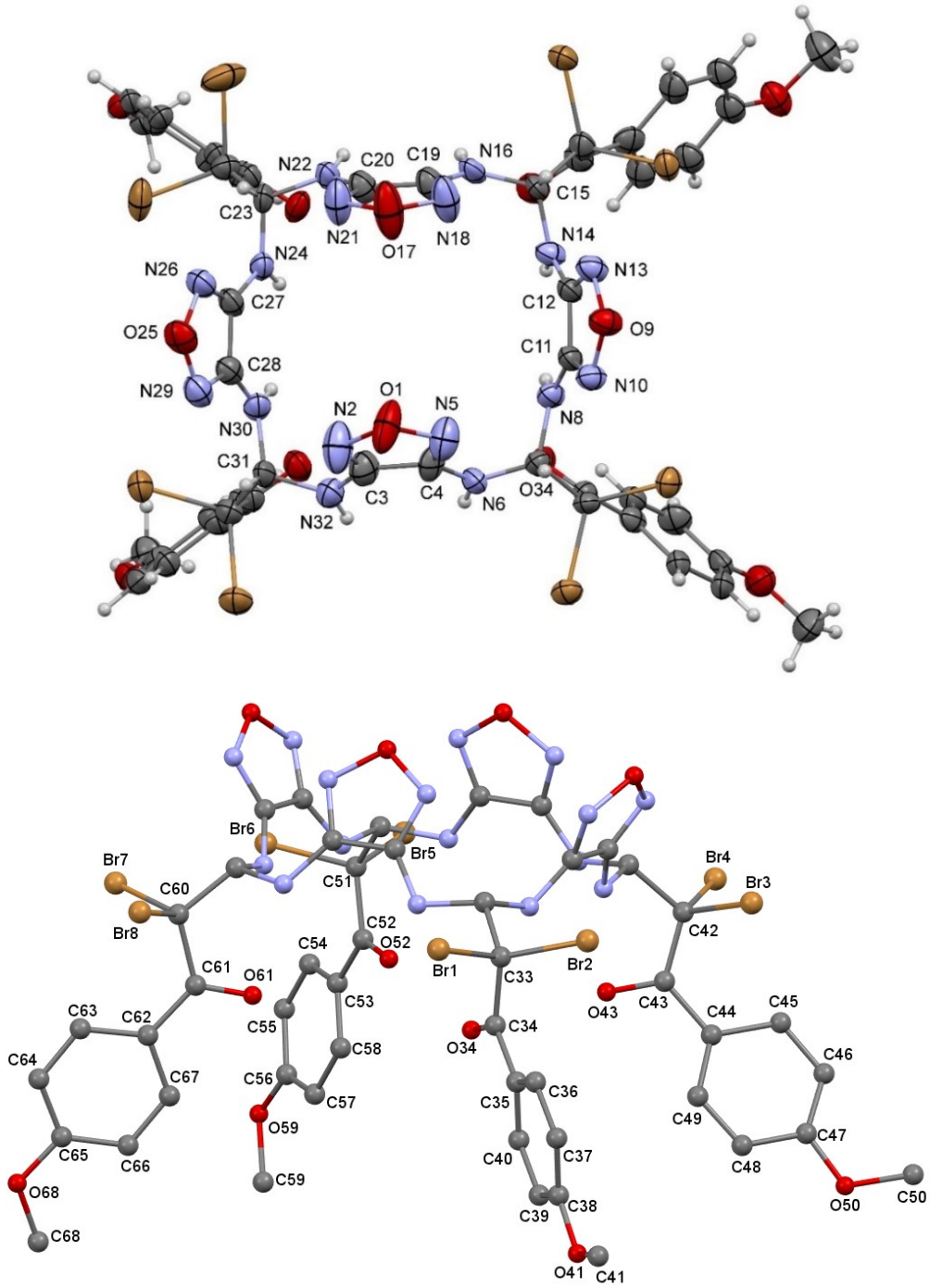


Figure S18. Two projections to the geometry of the molecule in the crystal **6j**: (a) ortep-drawing (p=50%) with partial numbering of atoms, (b) ball-sticks representation with partial numbering of atoms.

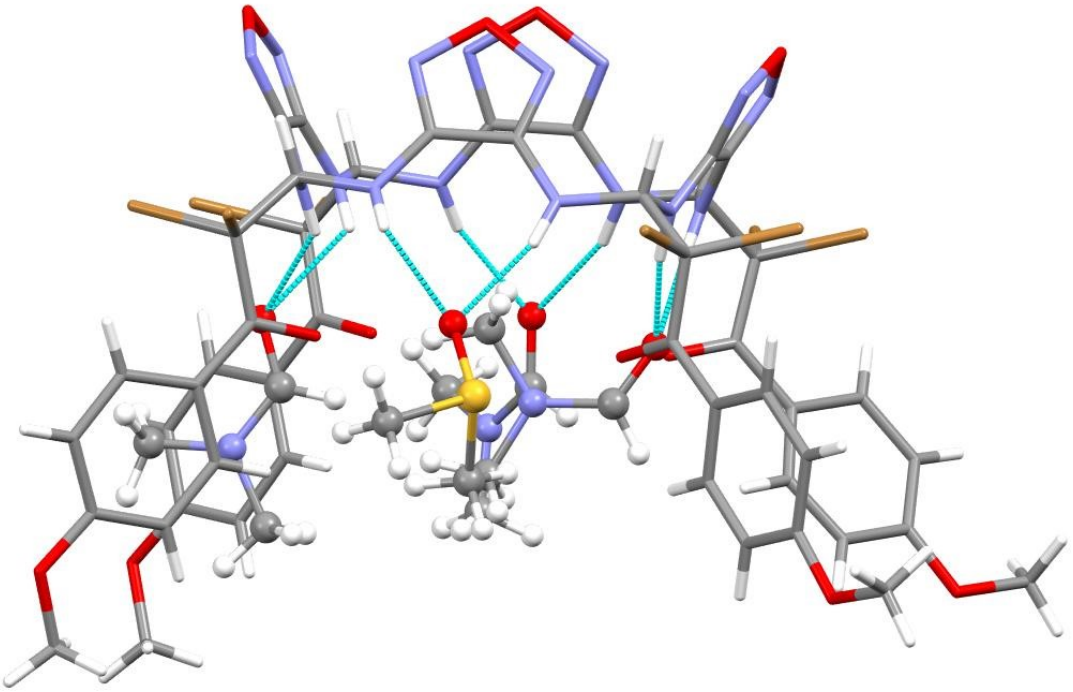


Figure S19. Intermolecular interactions N-H…O type in the crystal **6d** between compound (capped sticks representation) and solvent molecules (ball-sticks representation).

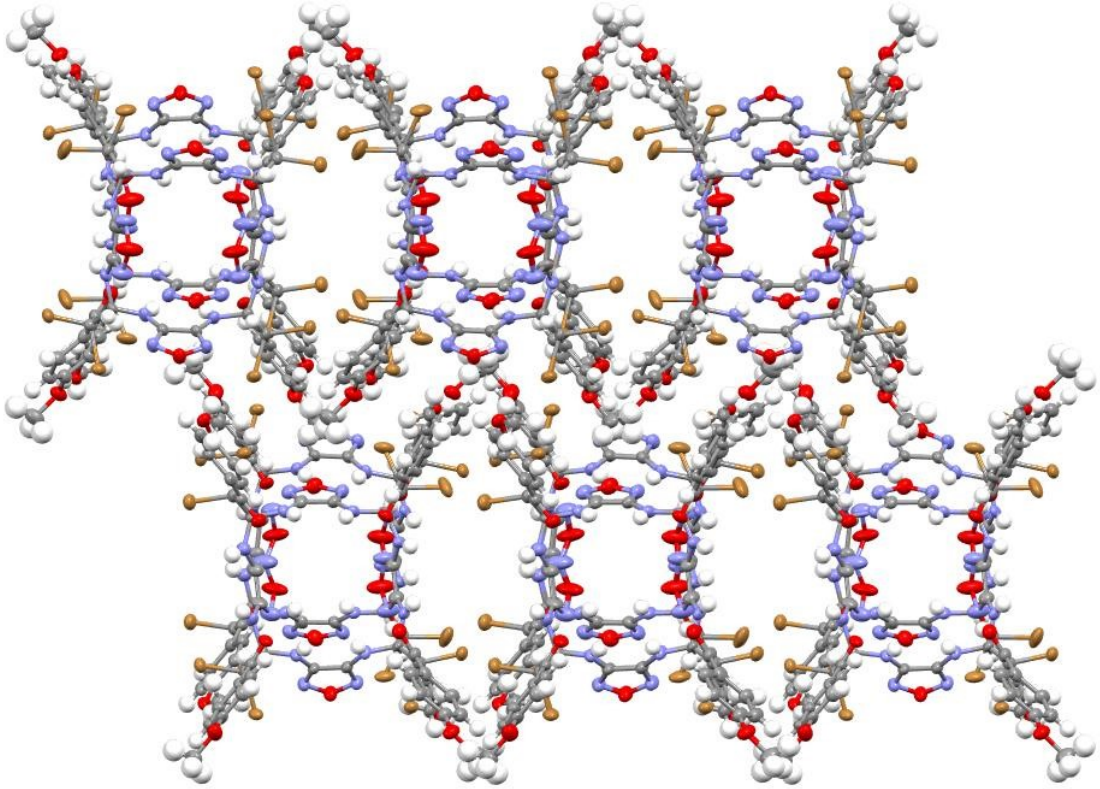


Figure S20. Fragment of the crystal packing for **6j**. Solvent molecules are omitted for clarity. View along the axis 0*c*. The volume occuped by solvent molecules is 2142.6 Å that is 28.7% from the volume of unit cell (probe radius=1.2Å); calculation is performed using the 'Voids' feature in Mercury[s5].

Table S7. Bond lengths [Å] and angles [°] for independent molecules of **6j**.

Br(1)-C(33)	1.975(10)	N(2)-C(3)	1.321(18)
Br(2)-C(33)	1.936(11)	N(5)-C(4)	1.318(17)
Br(3)-C(42)	1.979(11)	N(6)-C(4)	1.351(15)
Br(4)-C(42)	1.958(12)	N(6)-C(7)	1.449(13)
Br(5)-C(51)	1.963(11)	N(8)-C(7)	1.471(13)
Br(6)-C(51)	1.952(12)	N(8)-C(11)	1.349(14)
Br(7)-C(60)	1.973(11)	N(10)-C(11)	1.296(14)
Br(8)-C(60)	1.941(11)	N(13)-C(12)	1.288(14)
O(1)-N(2)	1.414(15)	N(14)-C(12)	1.371(13)
O(1)-N(5)	1.403(14)	N(14)-C(15)	1.474(13)
O(9)-N(10)	1.423(12)	N(16)-C(15)	1.457(13)
O(9)-N(13)	1.402(11)	N(16)-C(19)	1.386(15)
O(17)-N(18)	1.408(14)	N(18)-C(19)	1.291(15)
O(17)-N(21)	1.388(14)	N(21)-C(20)	1.320(16)
O(25)-N(26)	1.398(12)	N(22)-C(20)	1.384(14)
O(25)-N(29)	1.396(14)	N(22)-C(23)	1.452(12)
O(34)-C(34)	1.214(12)	N(24)-C(23)	1.458(14)
O(41)-C(38)	1.361(14)	N(24)-C(27)	1.383(13)
O(41)-C(41)	1.439(15)	N(26)-C(27)	1.290(16)
O(43)-C(43)	1.225(14)	N(29)-C(28)	1.307(14)
O(50)-C(47)	1.36(2)	N(30)-C(28)	1.358(15)
O(50)-C(50)	1.46(3)	N(30)-C(31)	1.455(13)
O(52)-C(52)	1.219(13)	N(32)-C(3)	1.380(16)
O(59)-C(56)	1.357(13)	N(32)-C(31)	1.452(14)
O(59)-C(59)	1.443(15)		
O(61)-C(61)	1.212(13)		
O(68)-C(65)	1.353(14)		
O(68)-C(68)	1.418(13)		
N(5)-O(1)-N(2)	108.6(10)	C(19)-N(18)-O(17)	105.5(10)
N(13)-O(9)-N(10)	110.1(7)	C(20)-N(21)-O(17)	104.9(10)
N(21)-O(17)-N(18)	111.1(9)	C(20)-N(22)-C(23)	116.7(9)
N(29)-O(25)-N(26)	110.6(9)	C(27)-N(24)-C(23)	118.0(10)
C(3)-N(2)-O(1)	107.1(11)	C(27)-N(26)-O(25)	106.4(10)
C(4)-N(5)-O(1)	107.2(10)	C(28)-N(29)-O(25)	105.4(9)
C(4)-N(6)-C(7)	114.3(10)	C(28)-N(30)-C(31)	121.4(9)
C(11)-N(8)-C(7)	120.9(9)	C(3)-N(32)-C(31)	114.9(11)
C(11)-N(10)-O(9)	105.8(8)	N(6)-C(7)-N(8)	113.8(8)
C(12)-N(13)-O(9)	105.2(9)	N(16)-C(15)-N(14)	112.0(8)
C(12)-N(14)-C(15)	118.7(9)	N(22)-C(23)-N(24)	111.2(8)
C(19)-N(16)-C(15)	115.1(10)	N(32)-C(31)-N(30)	112.4(9)

Table S8. Main geometrical parameters of hydrogen bond in the crystal **6j**.

D–H···A	D–H, Å	H···A, Å	D···A, Å	∠ DHA, °	Symmetry operation
N(6)-H(6)...O(79)	0.88	2.01	2.86(3)	163.3	-
N(8)-H(8)...O(34)	0.88	2.44	2.881(13)	111.6	-
N(8)-H(8)...O(76)	0.88	1.92	2.776(13)	164.9	-
N(14)-H(14)...O(43)	0.88	2.47	2.916(12)	111.8	-
N(14)-H(14)...O(76)	0.88	1.92	2.781(14)	164.0	-
N(16)-H(16)...O(73)	0.88	2.06	2.909(15)	161.6	-
N(22)-H(22)...O(73)	0.88	2.07	2.920(14)	161.2	-
N(24)-H(24)...O(52)	0.88	2.45	2.879(12)	110.9	-
N(24)-H(24)...O(70)	0.88	2.32	2.939(15)	127.8	-
N(30)-H(30)...O(61)	0.88	2.41	2.867(13)	112.4	-
N(30)-H(30)...O(70)	0.88	2.18	2.884(13)	136.9	-
N(32)-H(32)...O(79)	0.88	2.11	2.910(16)	150.5	-