Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Trimethyl-, triethyl- and trimethoxybenzene-based tripodal compounds bearing pyrazole groups: Conformations and halogen-/hydrogen-bond patterns in the crystalline state

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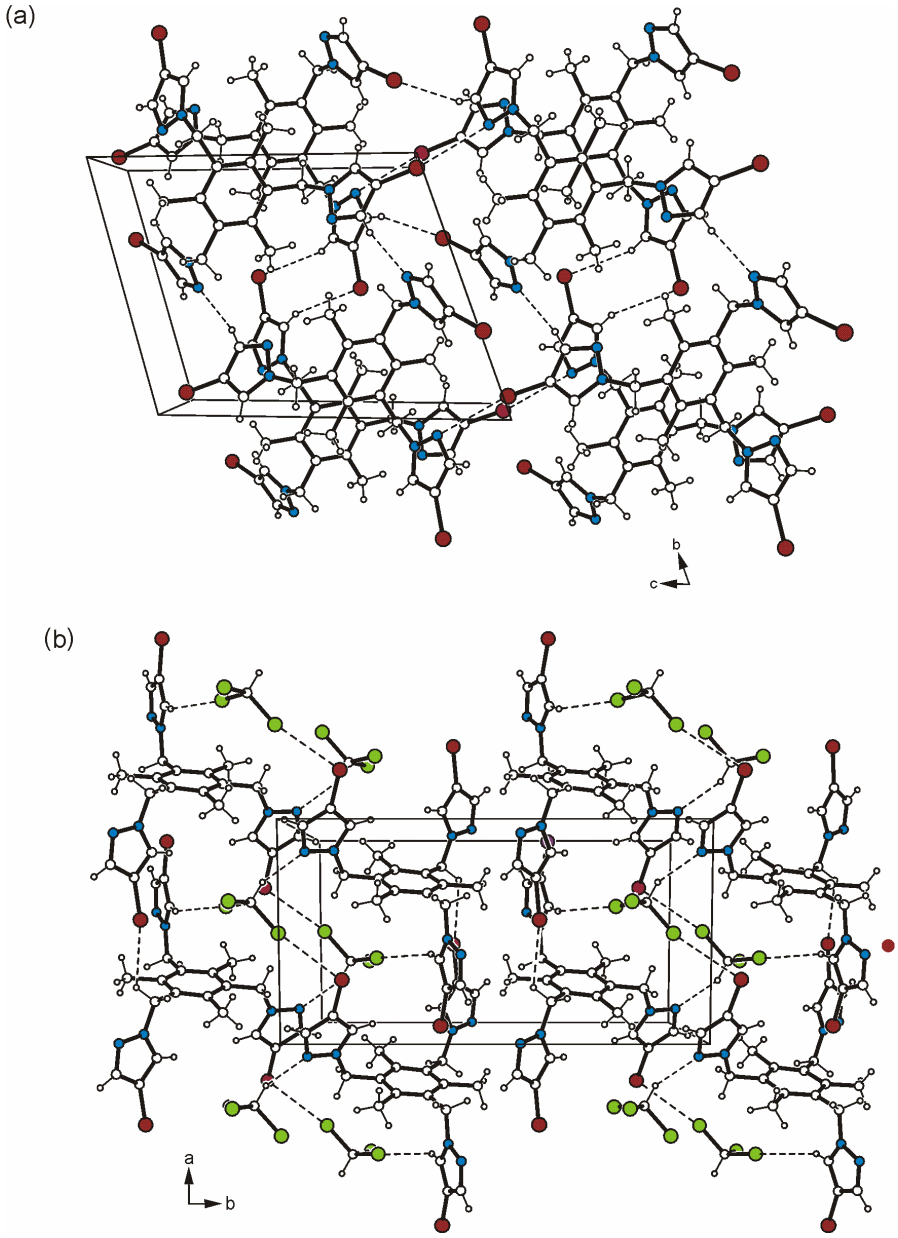

Figure S1. Packing structures of **1** (a) and **1**•$CHCl_3$ (**1a**) (b). Nitrogen atoms are displayed as blue, chlorine as green and bromine atoms as brown circles. Broken lines represent non-covalent intermolecular interactions.

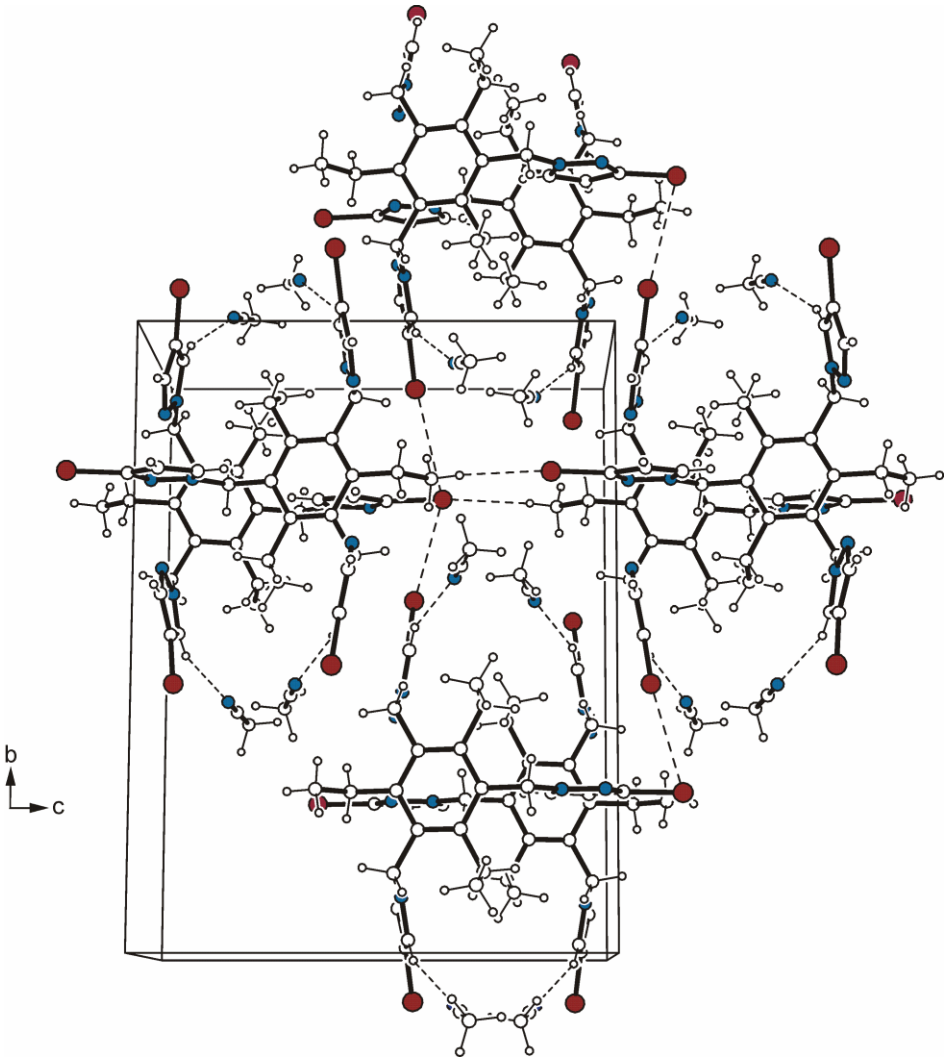

Figure S2. Packing diagrams of **3b** (**3**•CH_3CN, 1:2) viewed down the *a*-axis. Nitrogen atoms are displayed as blue and bromine atoms as brown circles. Broken lines represent hydrogen bond type and Br···Br interactions.

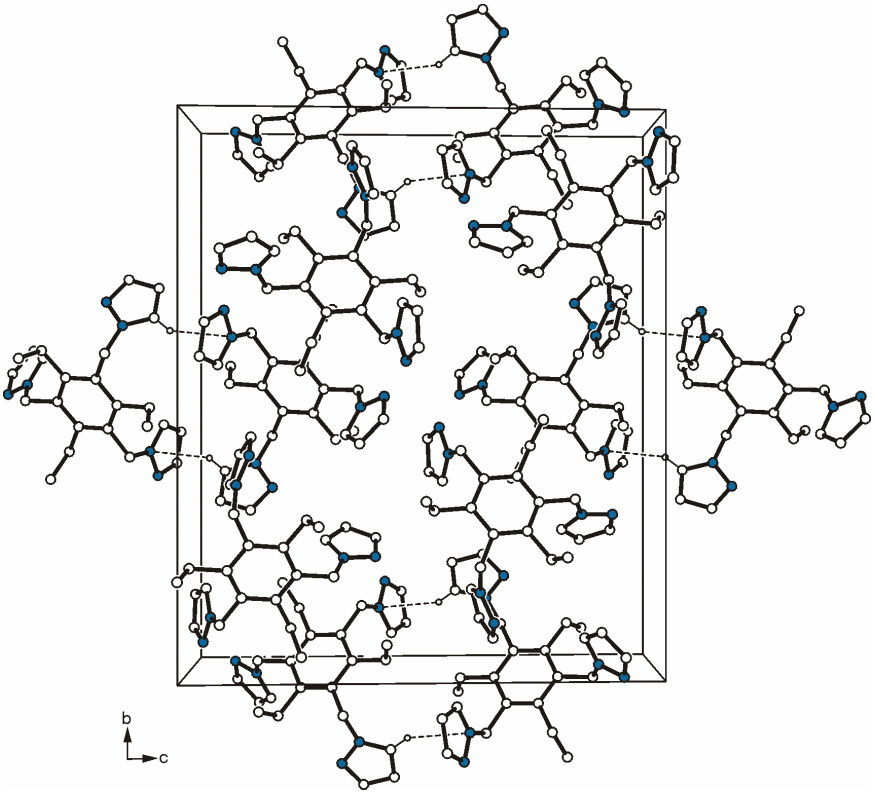

Figure S3. Packing diagram of **5**. Nitrogen atoms are displayed as blue and bromine as brown circles. Broken lines represent hydrogen bond type interactions.

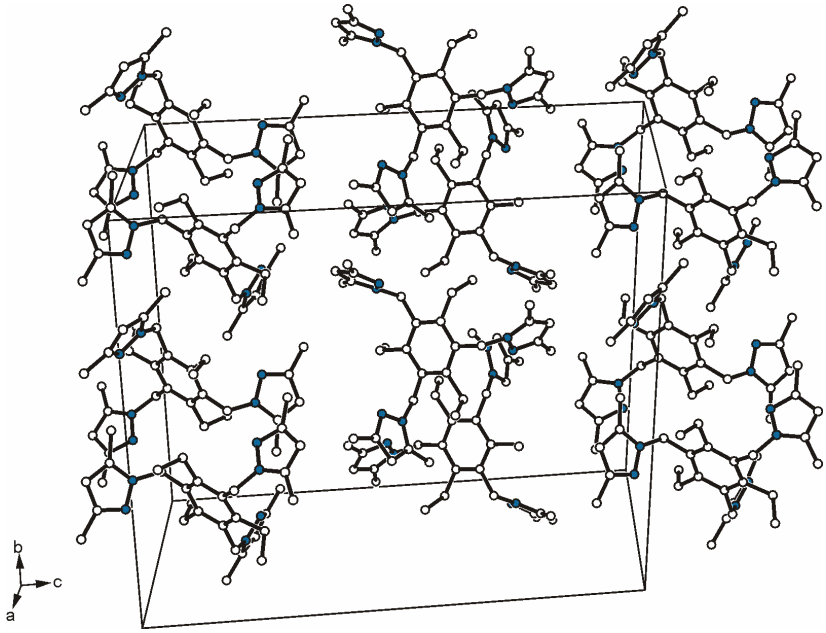

Figure S4. Packing diagram of **6**. Nitrogen atoms are displayed as blue and bromine as brown circles. Broken lines represent hydrogen bond type interactions.

Table S1. Crystallographic and structure refinement data of the compounds studied

Compound	**1**	**1a**	**2**
Empirical formula	$C_{21}H_{21}N_6Br_3$	$C_{21}H_{21}N_6Br_3 \cdot CHCl_3$	$C_{27}H_{33}N_6Br_3$
Formula weight	597.17	716.54	681.32
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1/n$	*P*-1
a (Å)	8.4808(2)	8.8918(4)	13.7217(4)
b (Å)	11.0938(3)	16.9233(8)	14.0379(4)
c (Å)	13.1816(3)	17.9116(8)	16.3771(5)
α (°)	68.194(1)	90.0	75.925(1)
β (°)	79.566(1)	97.758(2)	65.816(1)
γ (°)	69.481(1)	90.0	80.705(1)
V (Å^3)	1076.54(5)	2670.6(2)	2784.52(14)
Z	2	4	4
F(000)	588	1408	1368
D_c (Mg m^{-3})	1.842	1.782	1.625
μ (mm^{-1})	5.643	4.856	4.374
Absorption correction type	multi-scan	multi-scan	multi-scan
Transmission T_{min}, T_{max}	0.161, 0.301	0.1829, 0.5105	0.3959, 0.6688
Data collection			
Temperature (K)	100(2)	100(2)	100(2)
Radiation / wavelength (Å)	MoKα / 0.71073	MoKα / 0.71073	MoKα / 0.71073
Crystal description	irregular	irregular	irregular
Colour	colourless	colourless	colourless
Size (μm^3)	0.51 × 0.41 × 0.28	0.53 × 0.24 × 0.16	0.26 × 0.10 × 0.10
No. of collected reflections	25131	25713	41629
within the θ-limit (°)	2.2 – 29.4	2.4 – 28.1	1.6 – 26.4
Index ranges ±*h*, ±*k*, ±*l*	-11/11, -15/15, -18/18	-11/8, -22/22, -23/23	-16/17, -17/15, -20/20
Measured fraction (max, full)	0.998, 0.998	1.000, 0.999	0.987, 0.990
No. of unique reflections	5944	6514	11325
R_{int}	0.0218	0.0225	0.0313
Refinement calculations: full-matrix least- squares on all F^2 values			
Weighting expression *w* [a]	$[\sigma^2(F_o^2)+(0.0318P)^2 + 1.4580P)^{-1}$	$[\sigma^2(F_o^2)+(0.0283P)^2 + 2.7478P)^{-1}$	$[\sigma^2(F_o^2)+(0.0378P)^2 + 2.0456P)^{-1}$
Flack parameter	-	-	-
Friedel coverage	0	0	0
Friedel fraction (max/full)	-/-	-/-	-/-
No. of restraints	0	0	0
No. of refined parameters	274	310	667
No. of F values used [$I > 2\sigma(I)$]	5298	5312	8933
Final *R*-Indices			
R_1 [$I > 2\sigma(I)$ / all data	0.0246 / 0.0295	0.0292 / 0.0413	0.0338 / 0.0519
$wR(F^2)$ [$I > 2\sigma(I)$ / all data	0.0638 / 0 .0658	0.0646 / 0.0688	0.0731 / 0.0794
S (=Goodness of fit on F^2)	0.985	1.021	1.015
min/max Shift	0.001/ 0	0.001, 0	0.002, 0
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.68/-0.67	0.63/-0.50	0.84/-0.89

[a] $P = (F_o^2 + 2F_c^2)/3$

Table S1. (continued)

Compound	**3a**	**3b**	**4**
Empirical formula	$C_{24}H_{27}N_6Br_3 \cdot C_2H_6O$	$C_{24}H_{27}N_6Br_3 \cdot 2\ C_2H_3N$	$C_{30}H_{39}N_6Br_3$
Formula weight	685.31	721.32	723.40
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1$	*Pnma*	*P*-1
a (Å)	9.0593(3)	10.3117(3)	11.5273(4)
b (Å)	13.4556(5)	19.6259(7)	11.6453(4)
c (Å)	11.5609(4)	14.9856(5)	11.7944(4)
α (°)	90.0	90.0	89.069(2)
β (°)	106.459(2)	90.0	82.606(2)
γ (°)	90.0	90.0	86.469(2)
V (Å^3)	1351.51(8)	3032.73(17)	1567.07(9)
Z	2	4	2
F(000)	688	1448	732
D_c (Mg m^{-3})	1.648	1.580	1.533
μ (mm^{-1})	4.509	4.023	3.891
Absorption correction type	multi-scan	multi-scan	multi-scan
Transmission T_{min}, T_{max}	0.2657, 0.8402	0.2243, 0.3503	0.2918, 0.6970
Data collection			
Temperature (K)	100(2)	100(2)	100(2)
Radiation / wavelength (Å)	MoKα / 0.71073	MoKα / 0.71073	MoKα / 0.71073
Crystal description	irregular	irregular	irregular
Colour	colourless	colourless	colourless
Size (μm^3)	0.40 × 0.12 × 0.04	0.53 × 0.35 × 0.33	0.42 × 0.19 × 0.10
No. of collected reflections	13602	31589	31196
within the θ-limit (°)	2.4 – 28.4	2.4 – 29.4	1.8 – 28.1
Index ranges ±*h*, ±*k*, ±*l*	-12/11, -18/18, -15/15	-14/13, -27/27, -20/20	-9/15, -15/15, -15/15
Measured fraction (max, full)	0.993, 0.995	1.000, 0.999	
No. of unique reflections	6350	4304	7601
R_{int}	0.0280	0.0293	0.0230
Refinement calculations: full-matrix least- squares on all F^2 values			
Weighting expression *w* [a]	$[\sigma^2(F_o^2)+(0.0432P)^2 + 0.0000P)^{-1}$	$[\sigma^2(F_o^2)+(0.0256P)^2 + 2.8501P)^{-1}$	$[\sigma^2(F_o^2)+(0.0279P)^2 + 0.5178P)^{-1}$
Flack parameter	0.026(10)	-	-
Friedel coverage	0.921	0	0
Friedel fraction (max/full)	0.995/0.997	-/-	-/-
No. of restraints	1	0	0
No. of refined parameters	331	196	361
No. of F values used [$I > 2\sigma(I)$]	5770	3785	6632
Final *R*-Indices			
R_1 [$I > 2\sigma(I)$ / all data	0.0326 / 0.0377	0.0245 / 0.0307	0.0221 / 0.0290
$wR(F^2)$ [$I > 2\sigma(I)$ / all data	0.0655 / 0.0666	0.0573 / 0.0603	0.0538 / 0.0560
S (=Goodness of fit on F^2)	1.192	1.033	1.031
min/max Shift	0/ 0	0.001/ 0	0.001/ 0
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.89/-0.57	0.76/-0.70	0.40/-0.37

[a] $P = (F_o^2 + 2F_c^2)/3$

Table S1 (continued)

Compound	**5**	**6**	**7**
Empirical formula	$C_{24}H_{30}N_6$	$C_{30}H_{42}N_6$	$C_{21}H_{21}N_6O_3Br_3$
Formula weight	402.54	486.70	645.17
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	Cc	$P2_1/c$
a (Å)	9.6138(3)	11.1233(4)	9.7139(16)
b (Å)	22.9808(8)	20.7068(7)	9.0347(15)
c (Å)	19.5255(6)	23.8883(8)	26.923(4)
α (°)	90.0	90.0	90.0
β (°)	93.863(1)	97.454(2)	97.855(3)
γ (°)	90.0	90.0	90.0
V (Å^3)	4304.0(2)	5455.6(3)	2340.7(7)
Z	8	8	4
F(000)	1728	2112	1272
D_c (Mg m^{-3})	1.242	1.185	1.831
μ (mm^{-1})	0.077	0.072	5.207
Absorption correction type	none	none	multi-scan
Transmission T_{min}, T_{max}	0.980, 0.995	0.966, 0.986	0.1619, 0.3041
Data collection			
Temperature (K)	100(2)	100(2)	100(2)
Radiation / wavelength (Å)	MoKα / 0.71073	MoKα / 0.71073	MoKα / 0.71073
Crystal description	needle	irregular	prism
Colour	colourless	colourless	colourless
Size (μm^3)	0.42 × 0.10 × 0.10	0.48 × 0.25 × 0.20	0.55 × 0.38 × 0.30
No. of collected reflections	53296	50336	28246
within the θ-limit (°)	2.1 – 26.5	2.3 – 28.5	3.3 – 29.1
Index ranges ±h, ±k, ±l	-12/11, -28/28, -24/24	-14/14, -27/27, -31/32	-13/13, -12/12, -36/36
Measured fraction (max, full)	0.989, 0.999	0.999, 0.999	0.998, 0.997
No. of unique reflections	8859	13476	6282
R_{int}	0.0574	0.0240	0.0296
Refinement calculations: full-matrix least- squares on all F^2 values			
Weighting expression w [a]	$[\sigma^2(F_o^2)+(0.0485P)^2 + 0.9307P)^{-1}$	$[\sigma^2(F_o^2)+(0.0582P)^2 + 1.4003P)^{-1}$	$[\sigma^2(F_o^2)+(0.0265P)^2 + 2.4486P)^{-1}$
Flack parameter	-	-	-
Friedel coverage	0	0.998	0
Friedel fraction (max/full)	-/-	0.999/0.999	-/-
No. of restraints	0	2	0
No. of refined parameters	547	668	301
No. of F values used [$I > 2\sigma(I)$]	6041	12568	5348
Final R-Indices			
R_1 [$I > 2\sigma(I)$ / all data	0.0450, 0.0815	0.0349, 0.0390	0.0253, 0.0342
$wR(F^2)$ [$I > 2\sigma(I)$ / all data	0.0936, 0.1085	0.0885, 0.0913	0.0582, 0.0617
S (=Goodness of fit on F^2)	1.007	0.998	1.022
min/max Shift	0/ 0	0.001/ 0	0/ 0
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.21/-0.23	0.27/-0.26	0.75/-0.74

[a] $P = (F_o^2 + 2F_c^2)/3$

Table S1 (continued)

Compound	**8**	**9**	**9a**
Empirical formula	$C_{27}H_{33}N_6O_3Br_3$	$C_{27}H_{36}N_6O_3$	$2\ (C_{27}H_{36}N_6O_3)\cdot C_2H_6O$
Formula weight	729.32	492.62	1031.30
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*P*-1	*P*-1
a (Å)	20.3559(5)	9.8975(2)	9.9852(2)
b (Å)	23.6203(6)	11.8392(2)	12.5431(3)
c (Å)	12.7536(3)	12.3994(2)	12.9192(3)
α (°)	90.0	113.589(1)	118.483(1)
β (°)	94.697(1)	98.570(1)	93.506(1)
γ (°)	90.0	94.846(1)	102.774(1)
V (Å^3)	6111.5(3)	1299.91(4)	1360.57(5)
Z	8	2	1
F(000)	3032	528	554
D_c (Mg m^{-3})	1.635	1.259	1.259
μ (mm^{-1})	4.002	0.084	0.085
Absorption correction type	multi-scan	none	multi-scan
Transmission T_{min}, T_{max}	0.2169, 0.7146	0.954, 0,981	0.9564, 0.9958
Data collection			
Temperature (K)	100(2)	100(2)	100(2)
Radiation / wavelength (Å)	MoKα / 0.71073	MoKα / 0.71073	MoKα / 0.71073
Crystal description	rod	irregular	irregular
Colour	colourless	colourless	colourless
Size (μm^3)	0.55 × 0.19 × 0.09	0.56 × 0.38 × 0.23	0.53 × 0.38 × 0.05
No. of collected reflections	8195	24608	25181
within the θ-limit (°)	1.3 – 29.1	2.6 – 27.4	2.5 – 28.1
Index ranges ±*h*, ±*k*, ±*l*	-27/27, 0/32, 0/17	-12/12, -15/15, -16/16	-13/13, -16/15, -17/17
No. of unique reflections	8195	5858	6601
R_{int}	0.0315	0.0207	0.0260
Refinement calculations: full-matrix least- squares on all F^2 values			
Weighting expression *w* [a]	$[\sigma^2(F_o^2)+(0.0327P)^2 + 5.4886P)^{-1}$	$[\sigma^2(F_o^2)+(0.0376P)^2 + 0.5761P)^{-1}$	$[\sigma^2(F_o^2)+(0.0486P)^2 + 1.2437P)^{-1}$
Flack parameter	-	-	-
Friedel coverage	0	0	0
Friedel fraction (max/full)	-/-	-/-	-/-
No. of restraints	0	0	1
No. of refined parameters	362	334	353
No. of F values used [$I > 2\sigma(I)$]	7020	5201	5343
Final *R*-Indices			
R_1 [$I > 2\sigma(I)$ / all data	0.0246, 0.0317	0.0355, 0.0406	0.0432, 0.0567
$wR(F^2)$ [$I > 2\sigma(I)$ / all data	0.0608, 0.0627	0.0855, 0.0895	0.1022, 0.1129
S (=Goodness of fit on F^2)	1.035	1.006	0.891
min/max Shift	0.001/ 0	0.001/ 0	0/ 0
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.57/-0.42	0.32/-0.22	0.46/-0.35

[a] $P = (F_o^2 + 2F_c^2)/3$

Table S2. Relevant conformational parameters of the compounds studied

Compound	*1*	1a	*2*	**3a**	**3b**	*4*
Dihedral angles (°)[a]						
mpla(A)-mpla(B)	76.7(1)	79.8(1)	82.8(1)	85.9(1)	90.0(1)	82.0(1)
mpla(A)-mpla(C)	77.2(1)	77.8(1)	68.4(1)	76.6(1)	63.1(1)	76.1(1)
mpla(A)-mpla(D)	68.7(1)	88.6(1)	87.7(1)	80.9(1)		83.9(1)
mpla(B)-mpla(C)	39.5(1)	31.0(1)	57.8(1)	13.0(1)	80.0(1)	22.7(1)
mpla(B)-mpla(D)	24.0(1)	88.5(1)	74.0(1)	67.1(1)		56.1(1)
mpla(C)-mpla(D)	61.6(1)	67.0(1)	32.9(1)	77.9(1)		34.5(1)
mpla(A')-mpla(B')			84.8(1)			
mpla(A')-mpla(C')			70.0(1)			
mpla(A')-mpla(D')			78.8(1)			
mpla(B')-mpla(C')			26.2(1)			
mpla(B')-mpla(D')			72.6(1)			
mpla(C')-mpla(D')			71.8(1)			
Torsion angles						
C1-C10-N1-N2	50.0(2)	154.3(2)	-20.7(3)	157.5(3)		
C1-C13-N1-N2						51.1(2)
C3-C14-N3-N4	124.1(2)	-164.3(2)		148.5(3)		
C3-C19-N3-N4						-52.3(2)
C3-C16-N3-N4			-57.4(3)			
C3-C17-N3-N4						
C5-C18-N5-N6	55.9(2)	173.4(2)		-165.5(3)		
C5-C21-N5-N6						
C5-C25-N5-N6						-49.8(2)
C5-C22-N5-N6			42.4(4)			
C1A-C10A-N1A-N2A			-7.2(3)			
C1A-C13A-N1A-N2A						
C3A-C16A-N3A-N4A			-53.0(3)			
C3A-C17A-N3A-N4A						
C5A-C22A-N5A-N6A			-52.6(3)			
C1A-C13A-N1A-N2A						
C3A-C19A-N3A-N4A						
C5A-C25A-N5A-N6A						
C5A-C21A-N5A-N6A						
C1-C5-N1-N2					180.0	
C3-C11-N3-N4					54.5(2)	
C1-C2-O1-C7						
C3-C4-O2-C8						
C5-C6-O3-C9						

Table S2. (continued)

Compound	**5**	**6**	**7**	**8**	**9**	**9a**
Dihedral angles (°)[a]						
mpla(A)-mpla(B)	71.4(1)	66.8(1)	78.4(1)	81.8(1)	77.0(1)	79.5(1)
mpla(A)-mpla(C)	58.2(1)	85.1(1)	64.8(1)	84.7(1)	84.3(1)	84.3(1)
mpla(A)-mpla(D)	77.6(1)	75.7(1)	84.2(1)	82.7(1)	86.6(1)	79.2(1)
mpla(B)-mpla(C)	40.2(1)	62.8(1)	55.3(1)	63.0(1)	66.2(1)	38.4(1)
mpla(B)-mpla(D)	65.1(1)	52.8(1)	77.2(1)	62.9(1)	26.9(1)	69.7(1)
mpla(C)-mpla(D)	74.9(1)	64.7(1)	28.1(1)	58.4(1)	46.4(1)	32.7(1)
mpla(A')-mpla(B')	83.6(1)	63.5(1)				
mpla(A')-mpla(C')	85.6(1)	72.6(1)				
mpla(A')-mpla(D')	77.7(1)	83.5(1)				
mpla(B')-mpla(C')	73.7(1)	46.9(1)				
mpla(B')-mpla(D')	82.9(1)	70.7(1)				
mpla(C')-mpla(D')	20.1(1)	64.7(1)				
Torsion angles						
C1-C10-N1-N2			56.0(2)	56.6(2)	61.5(1)	-57.8(2)
C1-C13-N1-N2	-148.3(1)	51.9(2)				
C3-C14-N3-N4			109.0(2)			
C3-C19-N3-N4		42.5(2)				
C3-C16-N3-N4				57.1(2)	-51.6(1)	50.6(2)
C3-C17-N3-N4	-78.1(2)					
C5-C18-N5-N6			-35.3(2)			
C5-C21-N5-N6	147.6(1)					
C5-C25-N5-N6		-47.5(2)				
C5-C22-N5-N6				55.3(2)	-41.8(1)	-54.6(2)
C1A-C10A-N1A-N2A						
C1A-C13A-N1A-N2A	178.8(2)					
C3A-C16A-N3A-N4A						
C3A-C17A-N3A-N4A	-130.9(2)					
C5A-C22A-N5A-N6A						
C1A-C13A-N1A-N2A		-58.1(2)				
C3A-C19A-N3A-N4A		46.5(2)				
C5A-C25A-N5A-N6A						
C5A-C21A-N5A-N6A	154.2(1)	-49.1(2)				
C1-C5-N1-N2						
C3-C11-N3-N4						
C1-C2-O1-C7			-90.4(2)	81.3(2)	-100.5(1)	-93.9(2)
C3-C4-O2-C8			-86.5(2)	82.6(2)	101.8(1)	-93.4(2)
C5-C6-O3-C9			-84.9(2)	81.6(2)	-88.4(1)	-79.9(2)

[a] mpla means least-squares plane through the aromatic ring. **1**, **1a**: Ring A: C1…C6, ring B: N1,N2,C11…C13, ring C: N3,N4,C15…C17, ring D: N5,N6,C19…C21. **3a**, **4**: Ring A: C1…C6, ring B: N1,N2,C14…C16, ring C: N3,N4,C18…C20, ring D: N5,N6,C22…C24. **3b**: Ring A: C1…C4,C2',C3', ring B: N1,N2,C6…C8, ring C: N3,N4,C12…C14. **3**: Ring A: C1…C6, ring B: N1,N2,C11…C13, ring C: N3,N4,C15…C17, ring D: N5,N6,C19…C21. **2**, **9**, **9a**: Ring A: C1…C6, ring B: N1,N2,C11…C13, ring C: N3,N4,C17…C19,ring D: N5,N6,C23…C25, Ring A': C1A…C6A, ring B': N1A,N2A,C11A…C13A, ring C': N3A,N4A,C17A…C19A, ring D': N5A,N6A,C23A…C25A. **5**: Ring A: C1…C6, ring B: N1,N2,C14…C16, ring C: N3,N4,C18…C20, ring D: N5,N6,C22…C24, ring A': C1A…C6A, ring B': N1A,N2A,C14A…C16A, ring C': N3A,N4A,C18A…C20A, ring D': N5A,N6A,C22A…C4A. **6**: Ring A: C1…C6, ring B: N1,N2,C14…C16, ring C: N3,N4,C20…C22, ring D: N5,N6,C26…C28, ring A': C1A…C6A, ring B': N1A,N2A,C14A…C16A, ring C': N3A,N4A,C20A…C22A, ring D': N5A,N6A,C26A…C28A. **7**: Ring A: C1…C6, ring B: N1,N2,C8…C10, ring C: N3,N4,C13…C15, ring D: N5,N6,C18…C20. **8**: Ring A: C1…C6, ring B: N1,N2,C11…C13, ring C: N3,N4,C17…C19, ring D: N5,N6,C23…C25.

Table S3. Non-covalent interactions in the crystals **1**, **1a**, **2**, **3a**, **3b**, **4**, **5, 6**, **7, 8, 9** and **9a.**

Atoms involved	Symmetry	Distance		Angle
D-H···A C-Br···N C-Br···X (X = Br, Cl) *Cg*···*Cg*		D···A C···N C···Br(Cl) *Cg*···*Cg*	H···A Br···N Br···Br(Cl)	D-H···A C-Br···N C-Br···Br(Cl)
1				
C(7)-H(7B)···N(2)	*x*, *y*, *z*	3.367(3)	2.61	136
C(11)-H(11)···Br(2)	1-*x*, -*y*, -*z*	3.583(2)	2.80	142
C(19)-H(19)···N(4)	1-*x*, 1-*y*, 1-*z*	3.289(3)	2.40	161
C(10)-H(10A)···*Cg*(D)[a]	2-*x*, -*y*, 1-*z*	3.286(3)	2.56	132
C(18)-H(18A)···*Cg*(B)[a]	1-*x*, -*y*, 1-*z*	3.463(3)	2.66	141
C(20)-Br(3)···N(2)	*x*, *y*, 1+*z*	5.187(3)	3.339(2)	168.4(1)
1a				
C(1A)-H(1A)···N(2)	*x*, *y*, *z*	3.192(3)	2.30	148
C(13)-H(13)···N(6)	1.5-*x*, 0.5+*y*, 0.5-*z*	3.432(3)	2.54	157
C(14)-H(14B)···Br(2)	1+*x*, *y*, *z*	3.568(3)	2.92	124
C(21)-H(21)···Cl(1A)	2-*x*, 1-*y*, -*z*	3.717(3)	2.91	144
C(12)-Br(1)···Cl(2A)	-1+*x*, *y*, *z*	4.248(3)	3.516(1)	99.9(1)
C(1A)-Cl(2A)···Br(1)	1+*x*, *y*, *z*	4.748(3)	3.516(1)	158.7(1)
2				
C(7)-H(7A)···N(6A)	*x*, *y*, *z*	3.373(4)	2.61	136
C(10)-H(10A)···N(4A)	*x*, *y*, *z*	3.319(4)	2.45	149
C(10A)-H(10C)···N(6)	*x*, *y*, *z*	3.454(4)	2.57	151
C(15)-H(15A)···N(6A)	*x*, *y*, *z*	3.476(4)	2.55	161
C(15A)-H(15D)···N(4)	*x*, *y*, *z*	3.484(4)	2.54	166
C(15A)-H(15E)···N(6)	*x*, *y*, *z*	3.352(4)	2.49	150
C(8)-H(8B)···Br(1)	-1+*x*, *y*, *z*	3.590(5)	2.97	123
C(10)-H(10B)···*Cg*(A')[a]	*x*, *y*, *z*	3.552(3)	2.78	137
C(14)-H(14A)···*Cg*(D)[a]	1-*x*, 1-*y*, -*z*	3.716(3)	2.92	141
C(15)-H(15B)···*Cg*(C')[a]	*x*, *y*, *z*	3.771(3)	2.81	177
C(22)-H(22A)···*Cg*(A)[a]	1-*x*, 1-*y*, -*z*	3.750(3)	2.84	157
C(26)-H(26A)···*Cg*(B')[a]	*x*, *y*, *z*	3.631(3)	2.71	161
C(9A)-H(9A2)···*Cg*(C)[a]	*x*, *y*, *z*	3.452(3)	2.82	124
C(10A)-H(10C)···*Cg*(A)[a]	*x*, *y*, *z*	3.391(3)	2.95	109
C(14A)-H(14D)···*Cg*(D')[a]	1-*x*, -*y*, 1-*z*	3.338(3)	2.85	112
C(22A)-H(22D)···*Cg*(A')[a]	1-*x*, -*y*, 1-*z*	3.699(3)	2.84	148
C(24)-Br(3)···Br(2A)	-1+*x*, *y*, *z*	3.836(3)	3.574(1)	83.2(1)
C(18A)-Br(2A)···Br(3)	1+*x*, *y*, *z*	5.445(3)	3.574(1)	173.6(1)
C(12)-Br(1)···Br(3A)	2-*x*, -*y*, -*z*	4.189(3)	3.843(1)	86.9(1)
C(24A)-Br(3A)···Br(1)	2-*x*, -*y*, -*z*	5.624(3)	3.843(1)	157.8(1)
3a				
O(1A)-H(1A)···N(2)	*x*, *y*, *z*	2.853(6)	2.04	174
C(9)-H(9A)···N(5)	*x*, *y*, *z*	3.225(7)	2.51	130
C(9)-H(9B)···N(3)	*x*, *y*, *z*	3.128(7)	2.41	130
C(11)-H(11B)···N(1)	*x*, *y*, *z*	3.305(6)	2.57	133
C(13)-H(13A)···O(1A)	*x*, *y*, *z*	3.369(6)	2.58	138
C(16)-H(16)···Br(2)	-1+*x*, *y*, *z*	3.848(4)	2.92	174
C(21)-H(21B)···N(4)	1-*x*, -*y*, 2-*z*	3.337(7)	2.42	157
C(22)-H(22)···O(1A)	1-*x*, -*y*, 1-*z*	3.316(7)	2.43	159

3b				
C(14)-H(14)···N(1A)	*x*, *y*, *z*	3.305(2)	2.42	159
C(15)-H(15A)···N(4)	*x*, 1.5-*y*, *z*	3.377(2)	2.60	138
C(16)-H(16B)···Br(1)	*x*, *y*, -1+*z*	3.981(2)	3.02	176
C(6)-H(6)···*Cg*(A)[a]	0.5+*x*, 0.5-*y*, 0.5-*z*	3.507(2)	2.71	145
C(7)-Br(1)···Br(2)	1.5-*x*, 1-*y*, 0.5+*z*	3.806(2)	3.697(1)	78.8(1)
C(13)-Br(2)···Br(1)	1.5-*x*, 1-*y*, -0.5+*z*	5.527(2)	3.697(1)	165.2(1)
4				
C(9)-H(9B)···N(3)	*x*, *y*, *z*	3.254(2)	2.52	132
C(10)-H(10A)···N(5)	*x*, *y*, *z*	3.266(2)	2.59	128
C(12)-H(12B)···Br(1)	-*x*, 3-*y*, 2-*z*	3.838(2)	2.92	161
C(18)-H(18A)···N(6)	-*x*, 2-*y*, 2-*z*	3.390(2)	2.53	150
C(30)-H(30C)···N(4)	1-*x*, 2-*y*, 2-*z*	3.408(2)	2.52	154
C(10)-H(10A)···*Cg*(D)[a]	*x*, *y*, *z*	3.382(2)	2.52	149
C(12)-H(12C)···*Cg*(B)[a]	*x*, *y*, *z*	3.496(2)	2.65	143
C(23)-H(23C)···*Cg*(D)[a]	1-*x*, 2-*y*, 2-*z*	3.547(2)	2.91	125
C(29)-H(29A)···*Cg*(B)[a]	-*x*, 2-*y*, 2-*z*	3.588(2)	2.97	124
5				
C(7)-H(7A)···N(4)	*x*, *y*, *z*	3.338(2)	2.45	149
C(7A)-H(7A1)···N(3A)	*x*, *y*, *z*	3.189(2)	2.45	131
C(7A)-H(7A1)···N(4A)	*x*, *y*, *z*	3.441(2)	2.49	162
C(20)-H(20)···N(5)	1-*x*, 1-*y*, -*z*	3.451(2)	2.62	147
C(13A)-H(13C)···N(6)	-1+*x*, *y*, *z*	3.360(2)	2.64	129
C(22A)-H(22A)···N(6A)	1-*x*, 1-*y*, 1-*z*	3.469(2)	2.70	138
C(12A)-H(12F)···*Cg*(B)[a]	-1+*x*, *y*, *z*	3.859(2)	2.91	164
C(17A)-H(17D)···*Cg*(C)[a]	-*x*, -0.5+*y*, 0.5-*z*	3.601(2)	2.85	133
C(19A)-H(19A)···*Cg*(C)[a]	-1+*x*, *y*, *z*	3.859(2)	2.91	164
C(20)-H(20)···*Cg*(D)[a]	1-*x*, -0.5+*y*, 0.5-*z*	3.614(2)	2.97	126
6				
C(7)-H(7A)···N(1)	*x*, *y*, *z*	3.333(2)	2.58	133
C(21)-H(21)···N(2)	-0.5+*x*, 0.5+*y*, *z*	3.514(2)	2.64	153
C(11)-H(11B)···N(2)	*x*, *y*, *z*	3.427(2)	2.64	137
C(10)-H(10C)···N(4)	*x*, *y*, *z*	3.441(3)	2.58	147
C(12)-H(12A)···N(5)	*x*, *y*, *z*	3.333(3)	2.59	132
C(9)-H(9A)···N(6)	*x*, *y*, *z*	3.418(2)	2.62	138
C(11A)-H(11D)···N(1A)	*x*, *y*, *z*	3.380(2)	2.64	131
C(7A)-H(7C)···N(2A)	*x*, *y*, *z*	3.477(2)	2.69	137
C(8A)-H(8F)···N(3A)	*x*, *y*, *z*	3.358(3)	2.59	135
C(9A)-H(9D)···N(4A)	*x*, *y*, *z*	3.387(2)	2.62	134
C(24)-H(24A)···N(4A)	*x*, *y*, *z*	3.504(2)	2.54	168
C(10A)-H(10D)···N(5A)	*x*, *y*, *z*	3.261(2)	2.59	125
C(21)-H(21)···*Cg*(B)[a]	-0.5+*x*, 0.5+*y*, *z*	3.562(2)	2.88	129
C(10)-H(10C)···*Cg*(C)[a]	*x*, *y*, *z*	3.292(2)	2.48	140
C(12)-H(12A)···*Cg*(D)[a]	*x*, *y*, *z*	3.635(2)	2.73	154
C(17)-H(17A)···*Cg*(C')[a]	-0.5+*x*, -0.5+*y*, *z*	3.396(2)	2.50	151
C(29)-H(29A)···*Cg*(D')[a]	*x*, *y*, *z*	3.563(2)	2.92	124
C(8A)-H(8F)···*Cg*(C')[a]	*x*, *y*, *z*	3.717(2)	2.79	159
C(10A)-H(10D)···*Cg*(D')[a]	*x*, *y*, *z*	3.415(2)	2.57	144
C(17A)-H(17F)···*Cg*(D)[a]	0.5+*x*, 0.5+*y*, -*z*	3.446(2)	2.82	123
C(27A)-H(27A)···*Cg*(B')[a]	0.5+*x*, -0.5+*y*, *z*	3.571(2)	2.80	140
C(30A)-H(30F)···*Cg*(A)[a]	*x*, *y*, *z*	3.584(2)	2.94	124

7				
C(7)-H(7C)···O(3)	2-*x*, 0.5+*y*, 0.5-*z*	3.323(2)	2.54	137
C(8)-H(8A)···N(5)	*x*, *y*, *z*	3.299(3)	2.59	129
C(8)-H(8B)···N(4)	2-*x*, 1-*y*, -*z*	3.304(3)	2.48	141
C(9)-H(9A)···N(2)	2-*x*, 0.5+*y*, 0.5-*z*	3.362(3)	2.56	139
C(9)-H(9C)···N(6)	*x*, *y*, *z*	3.347(3)	2.42	157
C(10)-H(10A)···O(1)	*x*, *y*, *z*	2.872(2)	2.43	107
C(11)-H(11)···N(6)	2-*x*, -0.5+*y*, 0.5-*z*	3.413(3)	2.52	156
C(14)-H(14B)···O(1)	*x*, *y*, *z*	2.813(2)	2.47	100
C(18)-H(18B)···O(3)	*x*, *y*, *z*	2.870(2)	2.42	107
C(9)-H(9B)···Br(2)	2-*x*, 0.5+*y*, 0.5-*z*	3.899(3)	2.94	167
C(12)-Br(1)···Br(1)	2-*x*, 1-*y*, 1-*z*	5.179(3)	3.519(1)	146.1(1)
C(8)-H(8A)···*Cg*(D)[a]	*x*, *y*, *z*	3.642(2)	2.76	151
C(11)-H(11)···*Cg*(A)[a]	2-*x*, -0.5+*y*, 0.5-*z*	3.376(2)	2.89	113
C(13)-H(13)···*Cg*(C)[a]	2-*x*, 0.5+*y*, 0.5-*z*	3.564(2)	2.68	155
C(21)-H(21)···*Cg*(C)[a]	-1+*x*, *y*, *z*	3.238(2)	2.81	108
C(16)-Br(2)···N(2)	3-*x*, -0.5+*y*, 0.5-*z*	4.869(4)	3.182(4)	148.0(2)
8				
C(7)-H(7A)···N(2)	*x*, *y*, *z*	3.438(2)	2.54	152
C(8)-H(8A)···N(4)	*x*, *y*, *z*	3.499(2)	2.59	155
C(9)-H(9A)···N(6)	*x*, *y*, *z*	3.497(2)	2.58	156
C(10)-H(10A)···O(1)	*x*, *y*, *z*	2.883(2)	2.41	109
C(10)-H(10B)···O(1)	1-*x*, *y*, 0.5-*z*	2.884(2)	2.61	128
C(16)-H(16A)···O(2)	*x*, *y*, *z*	2.860(2)	2.38	109
C(16)-H(16B)···O(3)	1-*x*, *y*, 0.5-*z*	3.536(2)	2.58	162
C(22)-H(22A)···O(3)	*x*, *y*, *z*	2.876(2)	2.40	109
C(26)-H(26A)···Br(2)	-0.5+*x*, 0.5-*y*, -0.5+*z*	3.834(2)	2.92	155
C(7)-H(7C)···*Cg*(C)[a]	*x*, *y*, *z*	3.332(2)	2.58	133
C(8)-H(8C)···*Cg*(B)[a]	*x*, *y*, *z*	3.330(2)	2.59	132
C(9)-H(9C)···*Cg*(A)[a]	*x*, *y*, *z*	3.404(2)	2.62	138
Cg(A)···*Cg*(A)[a]	1-*x*, *y*, 0.5-*z*	3.644(1)		
Cg(C)···*Cg*(C)[a]	1.5-*x*, 0.5-*y*, 1-*z*	3.766(1)		
C(18)-Br(2)···Br(3)	0.5+*x*, 0.5+*y*, *z*	5.492(2)	3.743(2)	154.5(1)
C(24)-Br(3)···Br(2)	-0.5+*x*, -0.5+*y*, *z*	5.154(2)	3.743(2)	130.2(1)
9				
C(7)-H(7A)···O(2)	1-*x*, -*y*, 1-*z*	3.377(1)	2.43	163
C(7)-H(7C)···N(1)	*x*, *y*, *z*	3.273(1)	2.62	124
C(8)-H(8A)···N(3)	*x*, *y*, *z*	3.228(2)	2.58	124
C(8)-H(8A)···O(3)	2-*x*, -*y*, 1-*z*	3.001(1)	2.59	105
C(9)-H(9A)···N(2)	*x*, *y*, *z*	3.590(2)	2.68	155
C(9)-H(9C)···N(6)	*x*, *y*, *z*	3.633(2)	2.71	156
C(10)-H(10A)···O(3)	*x*, *y*, *z*	2.834(2)	2.35	109
C(16)-H(16B)···O(1)	*x*, *y*, *z*	2.866(1)	2.42	107
C(22)-H(22B)···O(3)	*x*, *y*, *z*	2.821(1)	2.32	110
C(7)-H(7C)···*Cg*(B)[a]	*x*, *y*, *z*	3.465(1)	2.62	144
C(8)-H(8A)···*Cg*(C)[a]	*x*, *y*, *z*	3.498(1)	2.66	143
C(10)-H(10A)···C(13)[b]	2-*x*, 1-*y*, 2-*z*	3.542(3)	2.69	140
C(16)-H(16A)···C(4)[b]	1-*x*, -*y*, 1-*z*	3.638(3)	2.82	140
C(26)-H(26A)···*Cg*(C)[a]	1-*x*, -*y*, 1-*z*	3.511(2)	2.87	124
9a				
O(1A)-H(1A)···N(2)	*x*, *y*, *z*	2.937(3)	2.18	149

C(7)-H(7A)···N(4)	*x*, *y*, *z*	3.539(2)	2.62	157
C(7)-H(7B)···N(2)	*x*, *y*, *z*	3.478(2)	2.56	156
C(8)-H(8A)···N(6)	*x*, *y*, *z*	3.534(2)	2.61	157
C(8)-H(8B)···N(4)	*x*, *y*, *z*	3.504(2)	2.59	155
C(9)-H(9A)···N(1)	*x*, *y*, *z*	3.327(2)	2.68	124
C(9)-H(9B)···N(6)	*x*, *y*, *z*	3.460(2)	2.50	166
C(10)-H(10A)···O(1)	*x*, *y*, *z*	2.850(2)	2.38	109
C(14)-H(14A)···O(1A)	*x*, *y*, *z*	3.134(3)	2.46	125
C(16)-H(16B)···O(1)	*x*, *y*, *z*	2.837(2)	2.35	109
C(16)-H(16A)···O(3)	-*x*, 1-*y*, 1-*z*	3.403(2)	2.46	158
C(22)-H(22B)···O(1)	-*x*, 1-*y*, 1-*z*	3.396(2)	2.46	157
C(22)-H(22A)···O(3)	*x*, *y*, *z*	2.860(2)	2.37	110
C(8)-H(8A)···*Cg*(D)[a]	*x*, *y*, *z*	3.329(2)	2.45	149
C(8)-H(8B)···*Cg*(C)[a]	*x*, *y*, *z*	3.264(2)	2.39	149
C(9)-H(9A)···*Cg*(B)[a]	*x*, *y*, *z*	3.551(2)	2.70	146
C(18)-H(18)···*Cg*(D)[a]	1+*x*, *y*, *z*	3.521(3)	2.87	125
Cg(A)···*Cg*(A)[a]	-*x*, 1-*y*, 1-*z*	3.700(1)		
Cg(B)···*Cg*(B)[a]	-*x*, 1-*y*, 2-*z*	3.649(1)		

[a] means centre of the aromatic ring. **1**: Ring B: N1,N2,C11…C13; ring D: N5,N6,C19…C21. **2**: Ring A: C1…C6; ring C: N3,N4,C17…C19; ring D: N5,N6,C23…C25; ring A': C1A…C6A; ring B': N1A,N2A,C11A…C13A; ring C': N3A,N4A,C17A…C19A; ring D': N5A,N6A,C23A…C25A. **4**: Ring B: N1,N2,C14…C16; ring D: N5,N6,C26…C28. **5**: Ring B: N1,N2,C14…C16; ring C: N3,N4,C18...C20; ring D: N5,N6,C22…C24. **6**: Ring A: C1…C6; ring B: N1,N2,C14…C16; ring C: N3,N4,C20…C22; ring D: N5,N6,C26…C28; ring B': N1A,N2A,C14A…C16A; ring C': N3A,N4A,C20A…C22A; ring D': N5A,N6A,C26A…C28A. **7**: Ring A: C1…C6; ring C: N3,N4,C15…C27; ring D: N5,N6,C19…C21. **8**, **9**, **9a**: Ring A: C1…C6; ring B: N1,N2,C11…C13; ring C: N3,N4, C17…C19; ring D: N5,N6,C23…C25.

[b] to obtain a reasonable hydrogen bond geometry, an individual carbon atom instead of the ring centre was chosen as the acceptor.

Table S4. C-Br···Y (Y = N, Br, Cl or C_{Ph}) distances and angles[a] in the crystal structures **1**, **1a**, **3a**, **3b** and **7**.

Atoms involved	Symmetry	Distance		Angle
C-Br···N C-Br···X (X = Br, Cl) C-Br···π		C···N C···Br(Cl) C···π	Br···N Br···Br(Cl) Br···π	C-Br···N C-Br···Br(Cl) C-Br···π
1				
C(20)-Br(3)···N(2)	*x*, *y*, 1+*z*	5.187(3)	3.339(3)	168.4(1)
1a				
C(12)-Br(1)···Cl(2A)	-1+*x*, *y*, *z*	4.240(3)	3.516(2)	99.3(1)
C(20)-Br(3)···C(4)[a]	1+*x*, *y*, *z*	5.254(3)	3.413(2)	166.7(1)
C(20)-Br(3)···C(5)[a]	1+*x*, *y*, *z*	5.115(3)	3.267(2)	167.9(1)
3a				
C(19)-Br(2)···C(2)[a]	1+*x*, *y*, *z*	5.297(6)	3.475(4)	160.6(1)
C(19)-Br(2)···C(3)[a]	1+*x*, *y*, *z*	5.292(6)	3.418(4)	170.2(1)
3b				
C(7)-Br(1)···Br(2)	1.5-*x*, 1-*y*, 0.5+*z*	3.806(3)	3.697(1)	78.8(1)
C(13)-Br(2)···Br(1)	1.5-*x*, 1-*y*, -0.5+*z*	3.806(3)	3.697(1)	165.2(1)
7				
C(16)-Br(2)···N(2)	3-*x*, -0.5+*y*, 0.5-*z*	4.869(2)	3.182(2)	148.0(1)
C(12)-Br(1)···Br(1)	2-*x*, 1-*y*, 1-*z*	3.519(3)	3.519(1)	146.1(1)

[a] For C-Br···π interaction an individual carbon atom instead of the ring centre was chosen as the acceptor.