Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Supramolecular patterns in the crystal structures of 1,3,5-trisubstituted 2,4,6-triethylbenzenes bearing halogenophenoxy groups

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1. Crystallographic data (Tables S1 – S3)

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

Geometrical parameters of hydrogen bonds and other interactions in the examined crystal structures (Table S2).

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2. Overlay plots (Figure S1 and S2)

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1. Crystallographic data (Tables S1 – S3)

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

Compound	**1**	**2a**	**3**	**4a**	**5a**	**6**	**7**
Empirical formula	$C_{33}H_{33}Br_3O_3$	$C_{33}H_{33}Br_3O_3 \cdot C_4H_{10}O$	$C_{33}H_{33}I_3O_3$	$C_{33}H_{33}I_3O_3 \cdot C_6H_{14}O$	$C_{33}H_{30}Br_6O_3 \cdot C_4H_{10}O$	$C_{33}H_{27}Br_9O_3$	$C_{33}H_{27}Br_9O_3$
Formula weight	717.32	791.44	858.29	960.46	1028.15	1190.73	1190.73
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	$P2_1/n$	$C2/c$	$P2_1/c$
a (Å)	9.2418(13)	9.543(3)	9.1331(5)	16.379(5)	14.5959(15)	26.4658(18)	17.7349(11)
b (Å)	11.9961(14)	13.487(4)	12.2577(6)	16.507(3)	13.3943(12)	10.9463(5)	23.194(3)
c (Å)	14.3650(19)	14.872(3)	14.8298(7)	16.949(4)	19.924(3)	27.261(2)	8.796(4)
α (°)	87.506(10)	112.213(19)	87.379(4)	72.005(17)	90.0	90.0	90.0
β (°)	79.734(11)	93.826(19)	80.456(4)	70.41(2)	100.189(9)	100.532(6)	97.162(14)
γ (°)	75.312(10)	90.32(2)	74.276(4)	66.18(2)	90.0	90.0	90.0
V (Å^3)	1515.9(4)	1767.1(8)	1575.96(14)	3868.7(18)	3833.8(7)	7764.6(9)	3589.9(16)
Z	2	2	2	4	4	8	4
F(000)	720	804	828	1888	2016	4512	2256
D_c (Mg m^{-3})	1.572	1.487	1.809	1.649	1.781	2.037	2.203
μ (mm^{-1})	4.024	3.461	3.006	2.461	6.321	9.324	10.083
Data collection							
Temperature (K)	203(2)	153(2)	153(2)	153(2)	123(2)	153(2)	123(2)
No. of collected reflections	19493	33718	13070	29109	44493	29182	37376
within the ϑ-limit (°)	1.8 - 26.0	1.5 - 26.0	1.7 - 26.0	1.4 - 25.3	2.6 – 26.5	2.6 - 25.5	2.6 - 26.5
Index ranges ±*h*, ±*k*, ±*l*	-11/11, -14/14, -17/16	-11/11, -15/16, -18/18	-11/11, -15/15, -18/17	-19/19, -19/19, -20/19	-18/18, -16/16, -25/24	-32/32, -13/11, -33/33	-22/22, -29/29, -11/10
No. of unique reflections	5965	6955	6182	13974	7939	7232	7421
R_{int}	0.0703	0.0712	0.0636	0.0504	0.0427	0.0291	0.0680
Refinement							

calculations: full-matrix least-squares on all F^2 values								
No. of refined parameters	365	402	366	907	429	409	409	
No. of F values used [$I>2\sigma(I)$]	4236	5310	4425	10240	6572	5836	5605	
Final *R*-Indices								
$R(=\Sigma\lvert\Delta F\rvert\ /\ \Sigma\lvert F_o\rvert)$	0.0489	0.0475	0.0457	0.0444	0.0359	0.0440	0.0309	
wR on F^2	0.1044	0.1158	0.1087	0.1033	0.0910	0.1149	0.0621	
S (=Goodness of fit on F^2)	1.087	1.069	1.027	1.028	1.057	1.044	1.009	
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.36/-0.65	0.72/-0.80	0.75/-0.97	0.90/-0.87	1.05/-0.70	1.39/-1.06	0.59/-0.52	

Table S2. Geometrical parameters of hydrogen bonds and other interactions in the crystal structures examined.

Atoms	Symmetry	Distance		Angle	Figure
D-H···A X···X (X=Br, I) C-X···□ (X=Br, I) C-X···O (X=Br)		D···A C···X C···*Cg*	H···A X···X X···*Cg* X···O	D-H···A C-X···X C-X···*Cg* C-X···O	
1					
C25-H25B···O2	1-*x*, 1-*y*, 1-*z*	3.512(6)	2.69	142	
C27-H27···O2	1-*x*, 1-*y*, 1-*z*	3.606(5)	2.68	169	
C32-H32B···O2	1-*x*, 1-*y*, 1-*z*	3.673(5)	2.69	176	
C24-H24C···O3	*x*, *y*, *z*	3.218(6)	2.59	123	
C9-H9···*Cg*D[a]	1-*x*, 1-*y*, 1-*z*	3.870(5)	2.94	170	**a** (Fig. 6b)
C25-H25A···*Cg*A[a]	1-*x*, 1-*y*, 1-*z*	3.475(5)	2.73	133	**b** (Fig 6b)
C33-H33C···*Cg*A[a]	-*x*, 1-*y*, 1-*z*	3.516(6)	2.93	120	
C10-Br1···Br3	*x*, 1+*y*, -1+*z*	5.558(1)	3.753(1)	158.9(1)	**c** (Fig. 6a)
C28-Br3···Br1	*x*, -1+*y*, 1+*z*	4.444(1)	3.753(1)	98.1(2)	**c** (Fig. 6a)
C19-Br2A···*Cg*B[a]	1-*x*, 1-*y*, -*z*	5.413(5)	3.850(3)	137.6(2)	
C19-Br2B···*Cg*B[a]	1-*x*, 1-*y*, -*z*	5.413(5)	3.677(13)	162.2(6)	
2a					
C25-H25B···O2	1-*x*, 1-*y*, 1-*z*	3.454(5)	2.62	143	
C27-H27···O2	1-*x*, 1-*y*, 1-*z*	3.551(6)	2.62	167	
C32-H32B···O2	1-*x*, 1-*y*, 1-*z*	3.602(6)	2.61	176	
C14-H14B···O1	*x*, *y*, *z*	3.325(5)	2.64	126	**a** (Fig. 2b)
C14-H14A···O2	*x*, *y*, *z*	3.257(5)	2.57	127	**b** (Fig. 2b)
C21-H21···O1A	*x*, *y*, 1+*z*	3.504(6)	2.63	154	**e** (Fig. 7a)
C24-H24C···O1	1-*x*, 1-*y*, 1-*z*	3.475(6)	2.58	152	**d** (Fig. 7a)
C33-H33A···O3	*x*, *y*, *z*	3.211(5)	2.53	127	**c** (Fig. 2b)
C12-H12···*Cg*A[a]	1+*x*, *y*, *z*	3.577(5)	2.64	167	
C22-H22···*Cg*D[a]	1-*x*, 1-*y*, 1-*z*	3.707(5)	2.92	141	
C11-Br1···Br2	2-*x*, -*y*, 1-*z*	5.407(5)	3.522(1)	170.1(1)	**f** (Fig. 7a)
C20-Br2···Br1	2-*x*, -*y*, 1-*z*	4.122(5)	3.522(1)	94.1(1)	**f** (Fig. 7a)
C20-Br2···Br2	1-*x*, -*y*, 2-*z*	5.396(5)	3.734(1)	144.4(1)	
C29-Br3···*Cg*B[a]	-1+*x*, 1+*y*, *z*	5.426(6)	3.572(2)	163.6(2)	**g** (Fig. 7a)
3					
C25-H25B···O2	1-*x*, 1-*y*, 1-*z*	3.454(7)	2.61	143	**a** (Fig. 9b)
C27-H27···O2	1-*x*, 1-*y*, 1-*z*	3.550(8)	2.62	167	**b** (Fig. 9b)
C32-H32B···O2	1-*x*, 1-*y*, 1-*z*	3.601(8)	2.61	176	**c** (Fig. 9b)
C25-H25A···*Cg*A[a]	1-*x*, 1-*y*, 1-*z*	3.465(8)	2.72	133	
C33-H33A···*Cg*A[a]	-*x*, 1-*y*, 1-*z*	3.475(8)	2.89	119	
C10-I1···I2	1-*x*, 1-*y*, -*z*	3.713(2)	3.844(2)	70.3(1)	**d** (Fig. 9a)
C19-I2···I1	1-*x*, 1-*y*, -*z*	5.824(2)	3.844(2)	172.6(1)	**d** (Fig. 9a)
C10-I1···I3	*x*, 1+*y*, -1+*z*	6.071(2)	4.081(2)	156.8(1)	**e** (Fig. 9a)
C28-I3···I1	*x*, -1+*y*, 1+*z*	4.721(2)	4.081(2)	94.0(1)	**e** (Fig. 9a)
4a					
C25A-H25C···O2	*x*, *y*, *z*	3.556(7)	2.70	151	
C31A-H31B···O2	*x*, *y*, *z*	3.496(7)	2.63	150	
C12-H12···O4E	1+*x*, -1+*y*, *z*	3.487(18)	2.57	163	
C14-H14B···O1	*x*, *y*, *z*	3.265(7)	2.58	126	

C19A-H19A···O4C	*-x*, 1-*y*, 1-*z*	3.468(7)	2.61	150	
C24-H24A···O3	*x*, *y*, *z*	3.182(7)	2.49	128	
C33A-H33E···O3A	*x*, *y*, *z*	3.151(8)	2.46	127	
C10A-H10A···*Cg*A[a]	1-*x*, 1-*y*, *-z*	3.629(7)	2.71	163	
C15-H15C···*Cg*B[a]	1-*x*, *-y*, *-z*	3.481(9)	2.93	117	
C25-H25A···*Cg*A'[a]	*x*, *y*, *z*	3.640(7)	2.83	140	
C25A-H25D···*Cg*A[a]	*x*, *y*, *z*	3.539(7)	2.84	128	
C36E-H36H···*Cg*B'[a]	1-*x*, 1-*y*, *-z*	3.430(18)	2.75	127	
C29-I3···*Cg*C[a]	*x*, 1+*y*, *z*	5.663(7)	3.625(3)	162.6(2)	**a** (Fig. 11)
C29A-I3A···*Cg*B'[a]	*x*, -1+*y*, *z*	5.566(7)	3.646(3)	149.6(2)	**b** (Fig. 11)
C29C-I3C···*Cg*B'[a]	*x*, -1+*y*, *z*	5.566(7)	3.505(3)	170.9(2)	
C11-I1···I1A	*x*, -1+*y*, *z*	4.258(7)	3.771(1)	88.1(2)	**c** (Fig. 11)
C11A-I1A···I1	*x*, 1+*y*, *z*	5.850(7)	3.771(1)	169.7(2)	**c** (Fig. 11)
C20-I2···I2A	*x*, -1+*y*, *z*	5.882(7)	3.803(1)	168.0(2)	**d** (Fig. 11)
C20A-I2A···I2	*x*, 1+*y*, *z*	4.312(7)	3.803(1)	88.8(2)	**d** (Fig. 11)
5a					
C7-H7B···Br2	1.5-*x*, -0.5+*y*, 1.5-*z*	3.777(4)	3.06	130	
C14-H14A···O2	*x*, *y*, *z*	3.344(5)	2.66	126	**a** (Fig. 3a)
C14-H14B···O1	*x*, *y*, *z*	3.330(4)	2.66	125	**b** (Fig. 3a)
C16-H16A···Br1	*x*, 1+*y*, *z*	3.970(4)	3.08	150	
C18-H18···Br1	*x*, 1+*y*, *z*	3.800(4)	3.08	134	
C24-H24B···Br2	*x*, -1+*y*, *z*	3.954(4)	3.00	166	
C24-H24C···O3	*x*, *y*, *z*	3.147(5)	2.43	129	**c** (Fig. 3a)
C11-Br2···Br6	1+*x*, -1+*y*, *z*	4.427(4)	3.443(1)	108.5(1)	**d** (Fig. 12)
C29-Br6···Br2	-1+*x*, 1+*y*, *z*	5.303(4)	3.443(1)	166.1(1)	**d** (Fig. 12)
C28-Br5···Br5	*-x*, 1-*y*, 1-*z*	5.240(4)	3.476(1)	153.2(1)	**e** (Fig. 12)
C9-H9···CgD	1-*x*, 1-*y*, 1-*z*	3.811(4)	2.96	149	
C25-H25A···CgA	1-*x*, 1-*y*, 1-*z*	3.448(4)	2.76	127	
C4A-H4AC···CgB	1-*x*, 1-*y*, 1-*z*	3.759(5)	2.82	162	
6					
C18-H18···C26[b]	0.5-*x*, 1.5-*y*, 1-*z*	3.616(6)	2.81	143	
C32-H32B···O2	0.5-*x*, 1.5-*y*, 1-*z*	3.528(6)	2.57	162	**b** (Fig. 13a,b)
C33-H33C···O3	*x*, *y*, *z*	3.242(7)	2.54	129	**a** (Fig. 3b)
C25-H25B···*Cg*A[a]	0.5-*x*, 1.5-*y*, 1-*z*	3.382(5)	2.71	126	**h** (Fig. 13b)
C19-Br4···Br9	0.5-*x*, 1.5-*y*, 1-*z*	5.075(1)	3.683(1)	127.5(1)	**c** (Fig. 13a,b)
C30-Br9···Br4	0.5-*x*, 1.5-*y*, 1-*z*	3.710(1)	3.683(1)	76.1(1)	**c** (Fig. 13a,b)
C19-Br4···Br9	*x*, 2-*y*, -0.5+*z*	3.609(1)	3.542(1)	76.5(1)	**d** (Fig. 13a)
C30-Br9···Br4	*x*, 2-*y*, 0.5+*z*	5.180(1)	3.542(1)	143.5(1)	**d** (Fig. 13a)
C28-Br7···Br7	*-x*, 2-*y*, 1-*z*	5.247(1)	3.511(1)	150.7(1)	**e** (Fig. 13a)
C10-Br1···*Cg*C[a]	1-*x*, 1-*y*, 1-*z*	5.053(6)	3.417(2)	142.6(1)	**f** (Fig. 13a)
C12-Br3···*Cg*A[a]	*x*, -1+*y*, *z*	5.331(6)	3.466(2)	170.3(1)	
C20-Br5···C13[b]	*x*, 1-*y*, -0.5+*z*	5.180(6)	3.392(2)	156.4(2)	**g** (Fig. 13a)
7					
C23-H23A···O2	*x*, *y*, *z*	3.079(5)	2.35	130	**a** (Fig. 3c)
C23-H23B···O3	*x*, *y*, *z*	3.185(5)	2.45	131	**b** (Fig. 3c)
C28-H28···Br2	*-x*, -0.5+*y*, 0.5-*z*	3.729(4)	2.89	148	
C32-H32B···Br1	*x*, *y*, *z*	3.755(4)	2.89	146	**c** (Fig. 3c)
C32-H32B···O1	*x*, *y*, *z*	3.162(4)	2.43	130	**d** (Fig. 3c)
C13-Br3···Br4	*x*, *y*, *z*	5.228(4)	3.621(2)	141.0(1)	**e** (Fig. 3c)
C18-Br4···Br3	*x*, *y*, *z*	5.210(4)	3.621(2)	139.5(1)	**e** (Fig. 3c)
C20-Br5···Br8	1+*x*, *y*, *z*	5.639(4)	3.784(2)	164.2(1)	**i** (Fig. 14a)
C29-Br8···Br5	-1+*x*, *y*, *z*	4.547(4)	3.784(2)	101.0(1)	**i** (Fig. 14a)
C29-Br8···Br9	*-x*, 1-*y*, *-z*	5.097(4)	3.737(2)	126.3(1)	**g** (Fig. 14a,b)

C31-Br9···Br8	*-x*, 1-*y*, *-z*	3.897(4)	3.737(2)	80.4(1)	**g** (Fig. 14a,b)
C29-Br8···O1	*-x*, 1-*y*, *-z*	5.069(4)	3.266(2)	157.1(1)	**h** (Fig. 14a,b)

[a] Cg means the centroid (centre of gravity) of the aromatic ring. [b] An individual ring atom instead the ring centre was chosen as a acceptor position. **1**, **2a**, **3**, **4a**, **5a**, **7**: Ring A: C1-C6; ring B: C8-C13; ring C: C17-C22; ring D: C26-C31. **6**: Ring A: C1-C6; ring B: C8-C13; ring C: C17-C22; ring A': C1A-C6A; ring B': C8A-C13A.

Table S3. Geometric molecular parameters in the crystal structures examined.

Compound	**1**	**2a**	**3**	**4a-1**	**4a-2**	**5a**	**6**	**7**
Dihedral angle (°)[a]								
mpla(A)-mpla(B)	56.5(2)	88.1(1)	56.1(2)	78.4(1)	89.4(2)	79.1(1)	89.3(2)	33.0(1)
mpla(A)-mpla(C)	83.5(1)	72.0(1)	81.5(5)	86.2(2)	82.5(2)	82.3(1)	84.0(1)	44.2(1)
mpla(A)-mpla(D)	52.4(1)	59.0(1)	53.3(2)	63.7(2)	58.3(2)	62.5(1)	64.6(1)	57.2(1)
mpla(B)-mpla(C)	68.2(1)	73.5(1)	66.7(6)	65.1(2)	70.8(2)	65.3(1)	79.1(2)	21.3(1)
mpla(B)-mpla(D)	83.6(1)	66.0(1)	85.8(2)	57.1(2)	61.7(2)	77.6(1)	46.0(2)	52.2(1)
mpla(C)-mpla(D)	66.0(1)	64.6(1)	61.1(7)	71.0(2)	64.5(2)	46.2(1)	67.7(2)	33.3(1)
Torsion angle (°)								
C1-C7-O1-C8	169.4(4)	174.2(3)	169.2(5)	176.1(4)	174.6(5)	-178.5(3)	175.2(4)	-168.3(3)
C7-O1-C8-C9	-143.7(4)	1.8(6)	-143.3(6)	5.4(8)	179.4(5)	-172.2(3)	-2.9(7)	-82.8(5)
C3-C16-O2-C17	-178.3(3)	-170.3(3)	-173.9(7)	-175.9(4)	-173.5(5)	-168.7(3)	-166.2(4)	136.5(3)
C16-O2-C17-C18	-3.5(6)	-13.9(6)	-8.4(13)	-6.4(8)	167.6(5)	-6.8(5)	168.8(5)	-98.3(4)
C5-C25-O3-C26	175.0(3)	-173.4(3)	177.9(5)	169.2(5)	-178.2(5)	-176.6(3)	167.8(4)	-99.0(4)
C25-O3-C26-C27	17.3(6)	-17.1(6)	16.3(9)	-167.3(5)	167.6(6)	6.7(5)	-2.0(7)	-79.9(4)

[a] mpla means the least-squares-plane through the aromatic ring. **1**, **2a**, **3**, **4a**, **5a**, **7**: Ring A: C1-C6; ring B: C8-C13; ring C: C17-C22; ring D: C26-C31. **6**: Ring A: C1-C6; ring B: C8-C13; ring C: C17-C22; ring D: C26-C31; ring A': C1A-C6A; ring B': C8A-C13A; ring C': C17A-C22A; ring D': C26A-C31A.

2. Overlay plots (Figures S1 and S2)

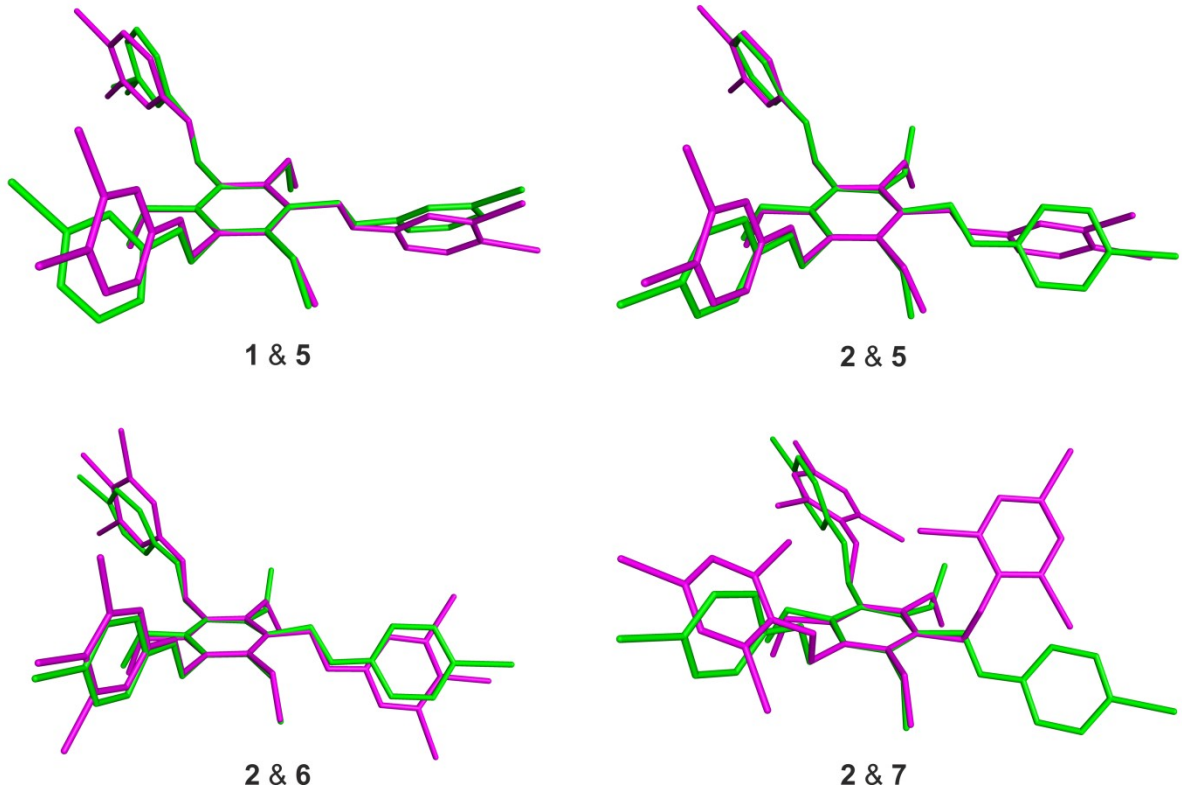

Figure S1. Views of the superpositions of **1** (green) & **5** (purple), **2** (green) & **5** (purple), **2** (green) & **6** (purple) as well as **2** (green) & **7** (purple) fitted on the atoms C1, C3 and C5 of the molecules (H atoms are omitted for clarity).

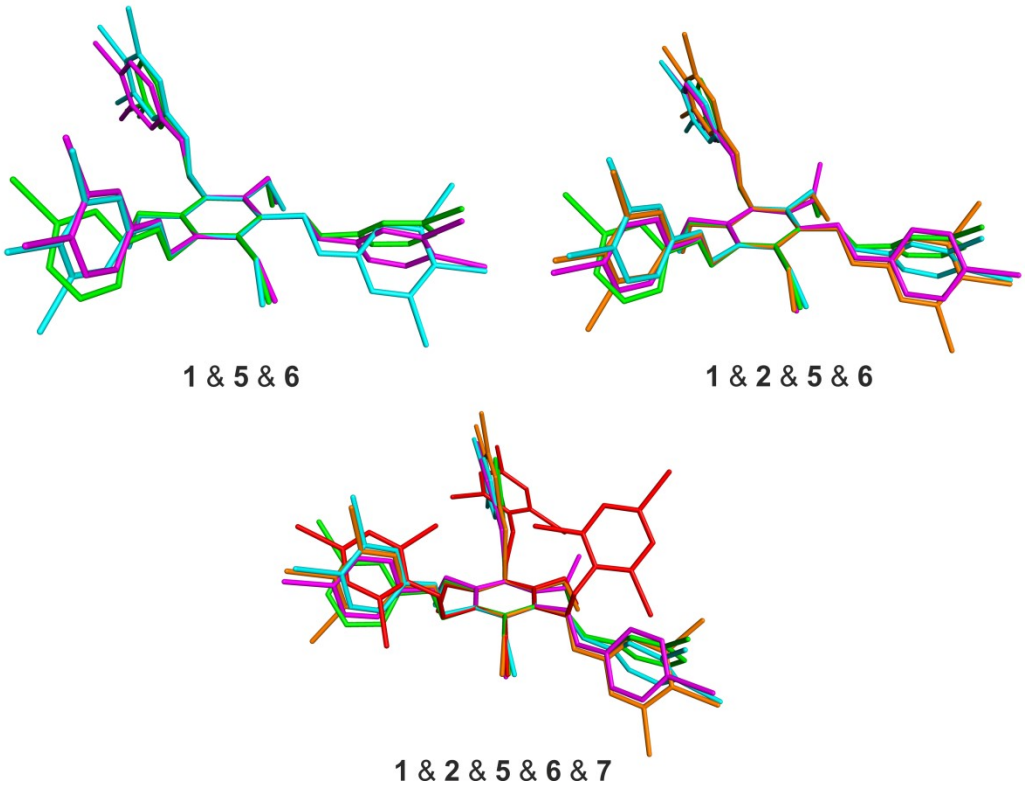

Figure S2. Views of the superpositions of **1** (green) & **5** (purple) & **6** (cyan), **1** (green) & **2** (purple) & **5** (cyan) & **6** (orange) as well as **1** (green) & **2** (purple) & **5** (cyan) & **6** (orange) & **7** (red) fitted on the atoms C1, C3 and C5 of the molecules (H atoms are omitted for clarity).

3. 2D fingerprint plots for overall and individual interactions in crystal packing of 1 – 7 (Figures S3-S10)

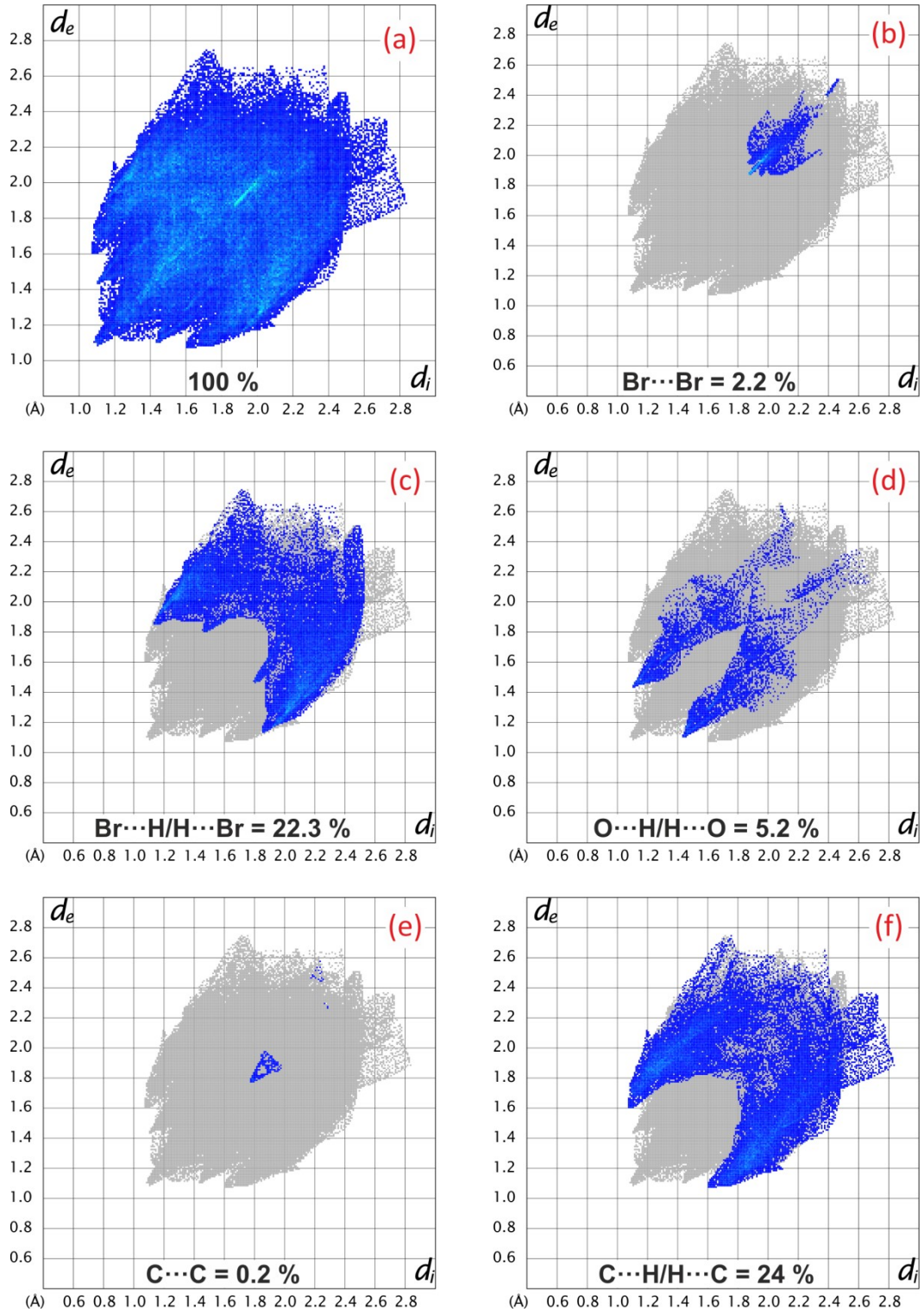

Figure S3 2D fingerprint plots for (a) overall interactions and (b-f) individual interactions in crystal packing of **1**.

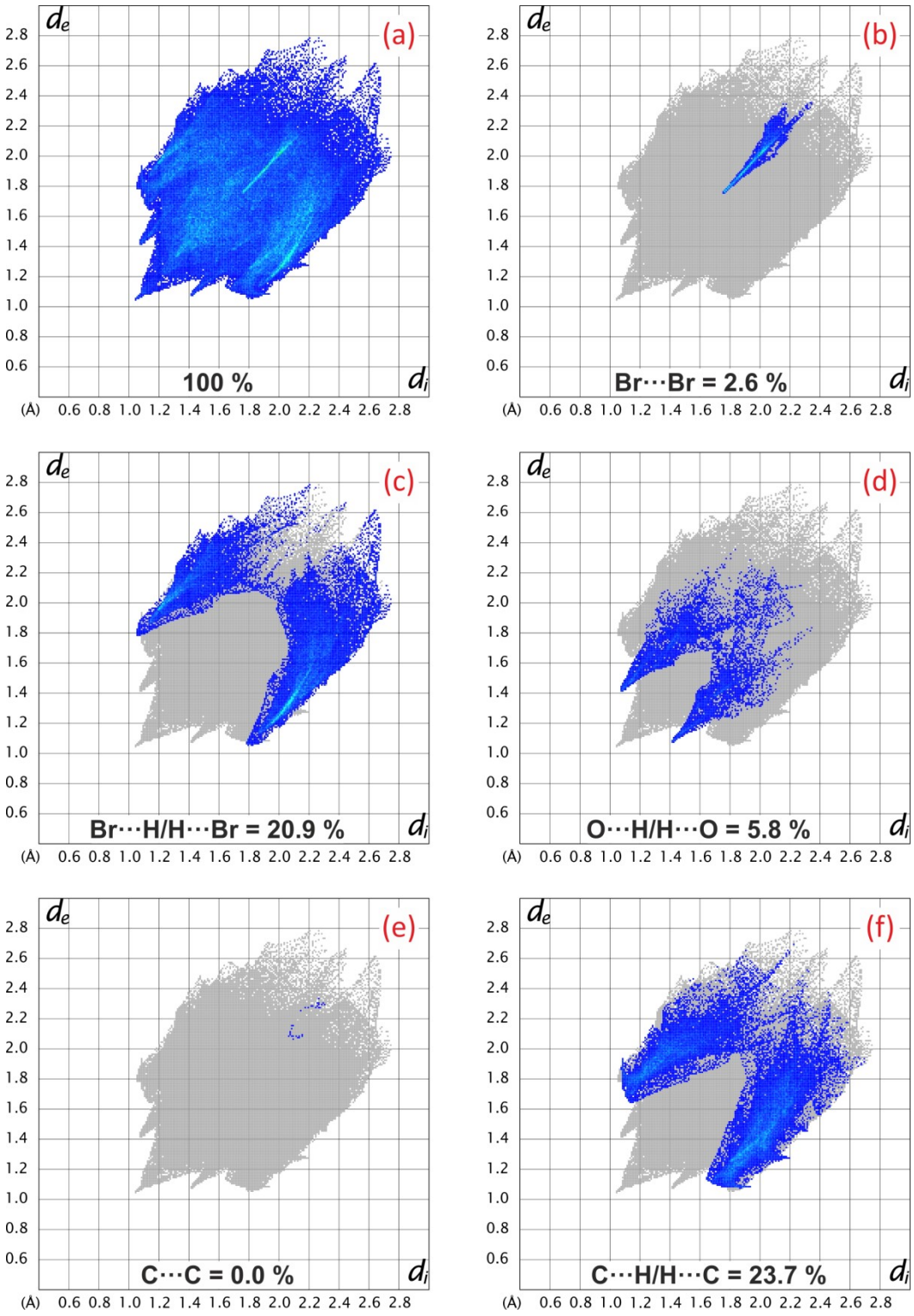

Figure S4 2D fingerprint plots for (a) overall interactions and (b-f) individual interactions in crystal packing of **2**.

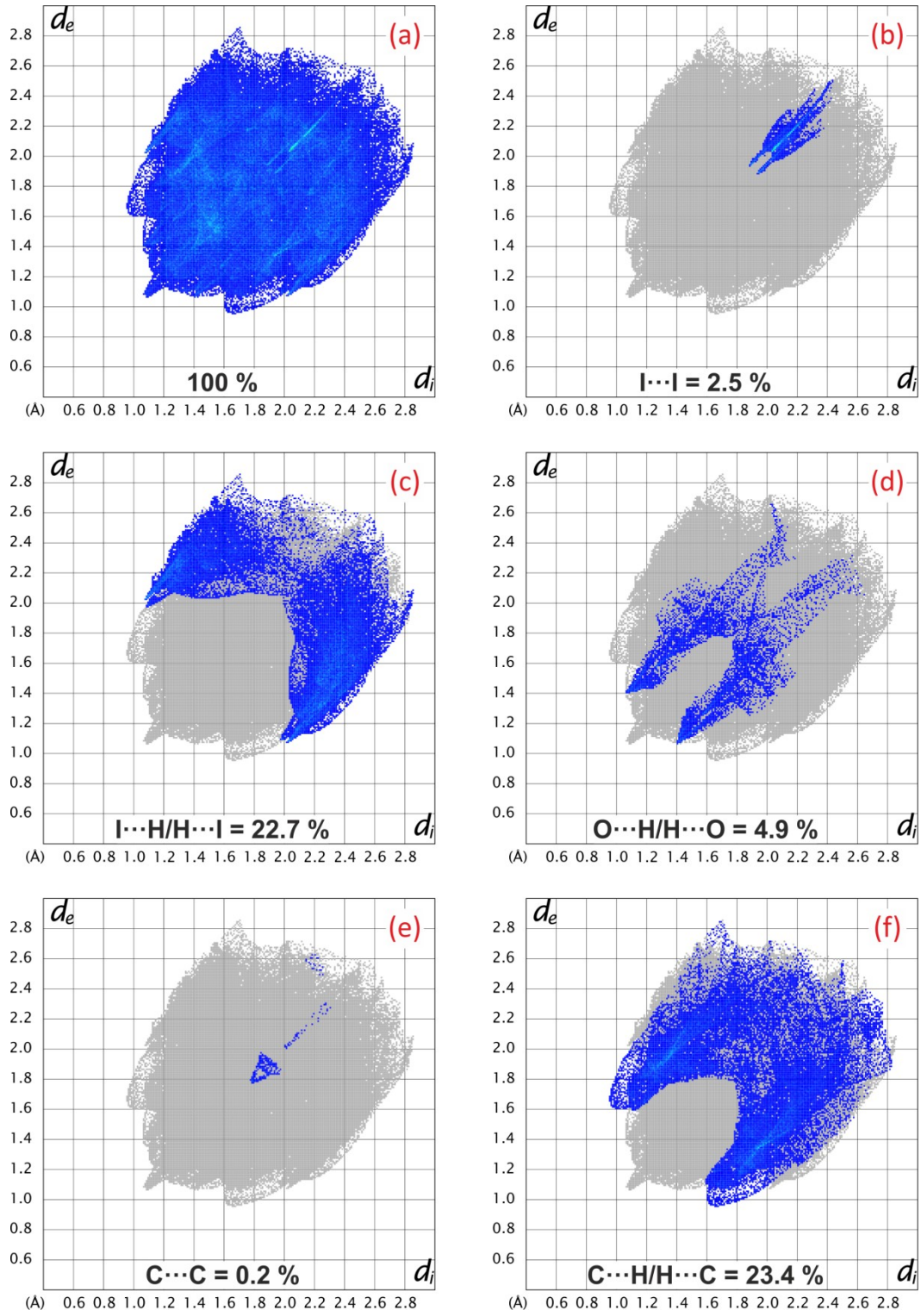

Figure S5 2D fingerprint plots for (a) overall interactions and (b-f) individual interactions in crystal packing of **3**.

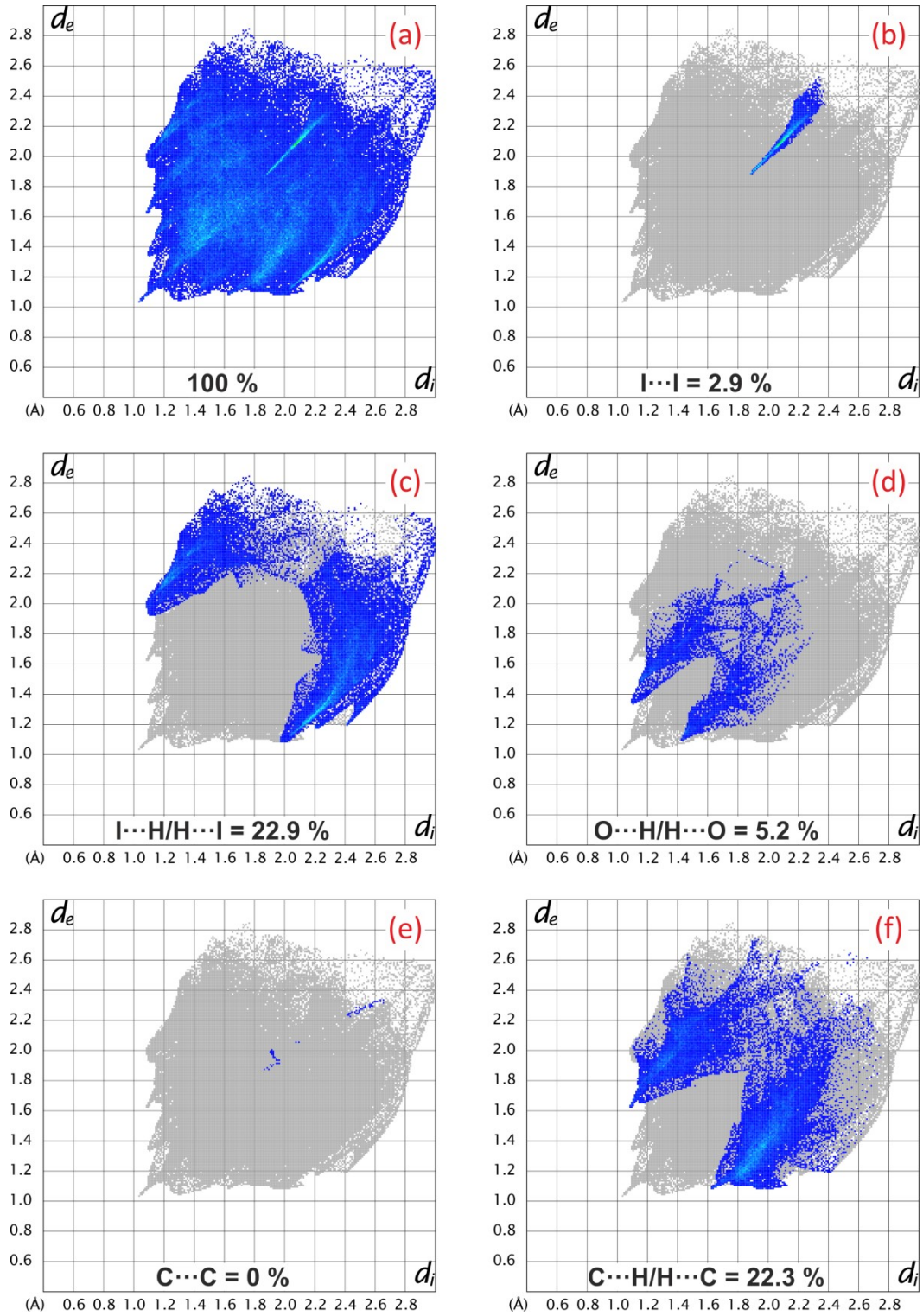

Figure S6 2D fingerprint plots for (a) overall interactions and (b-f) individual interactions in crystal packing of **4-1**.

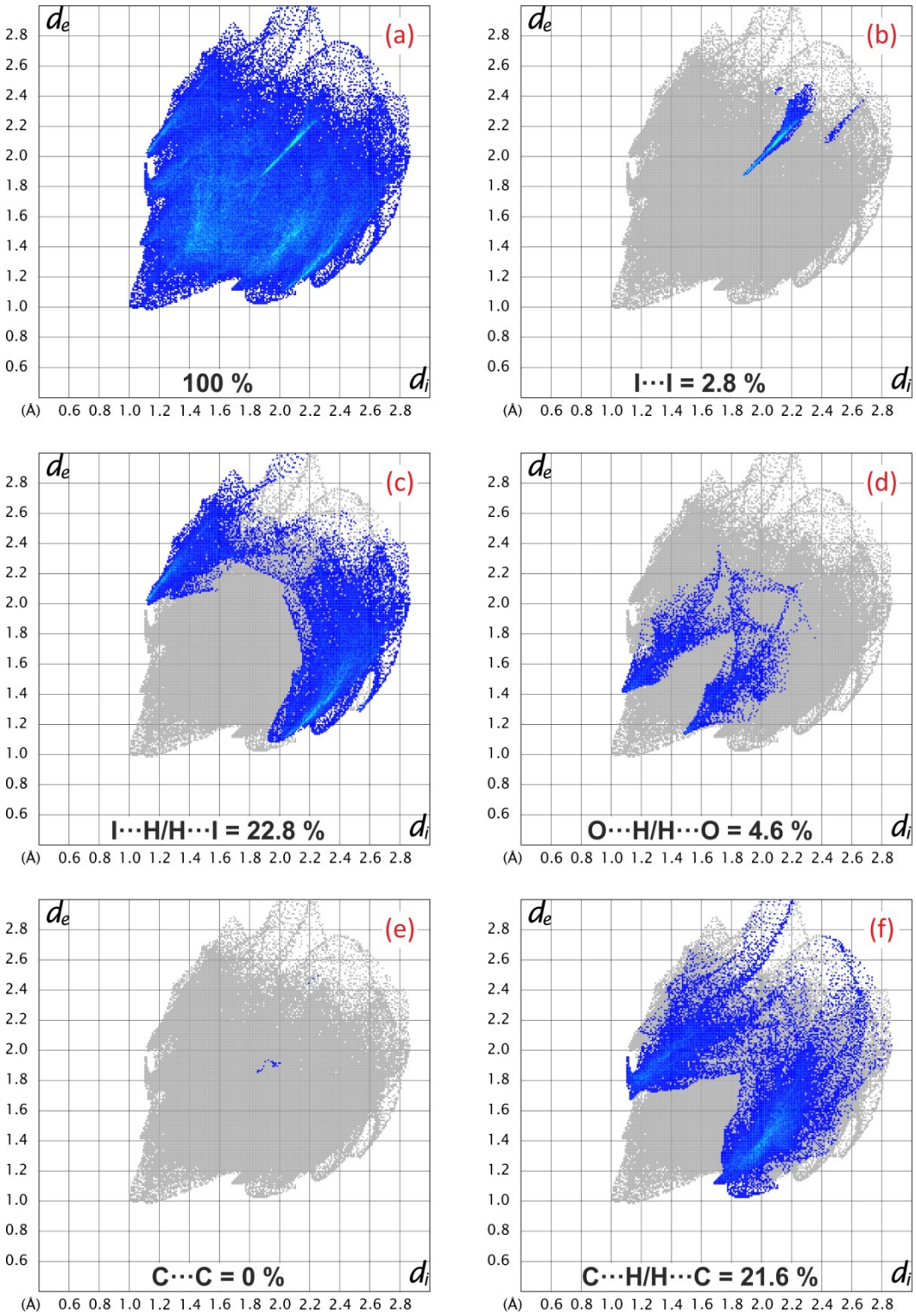

Figure S7 2D fingerprint plots for (a) overall interactions and (b-f) individual interactions in crystal packing of **4-2**.

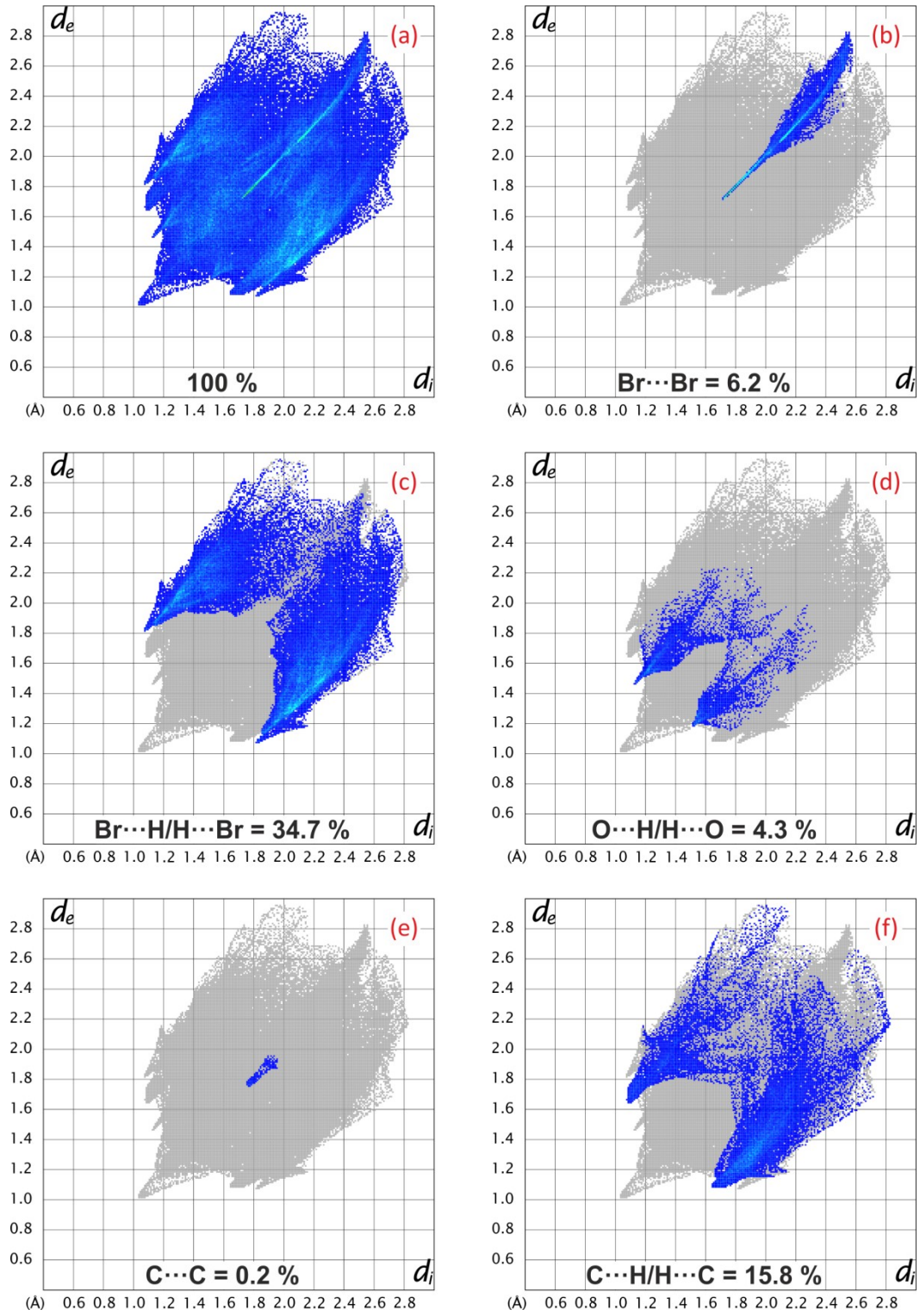

Figure S8 2D fingerprint plots for (a) overall interactions and (b-f) individual interactions in crystal packing of **5**.

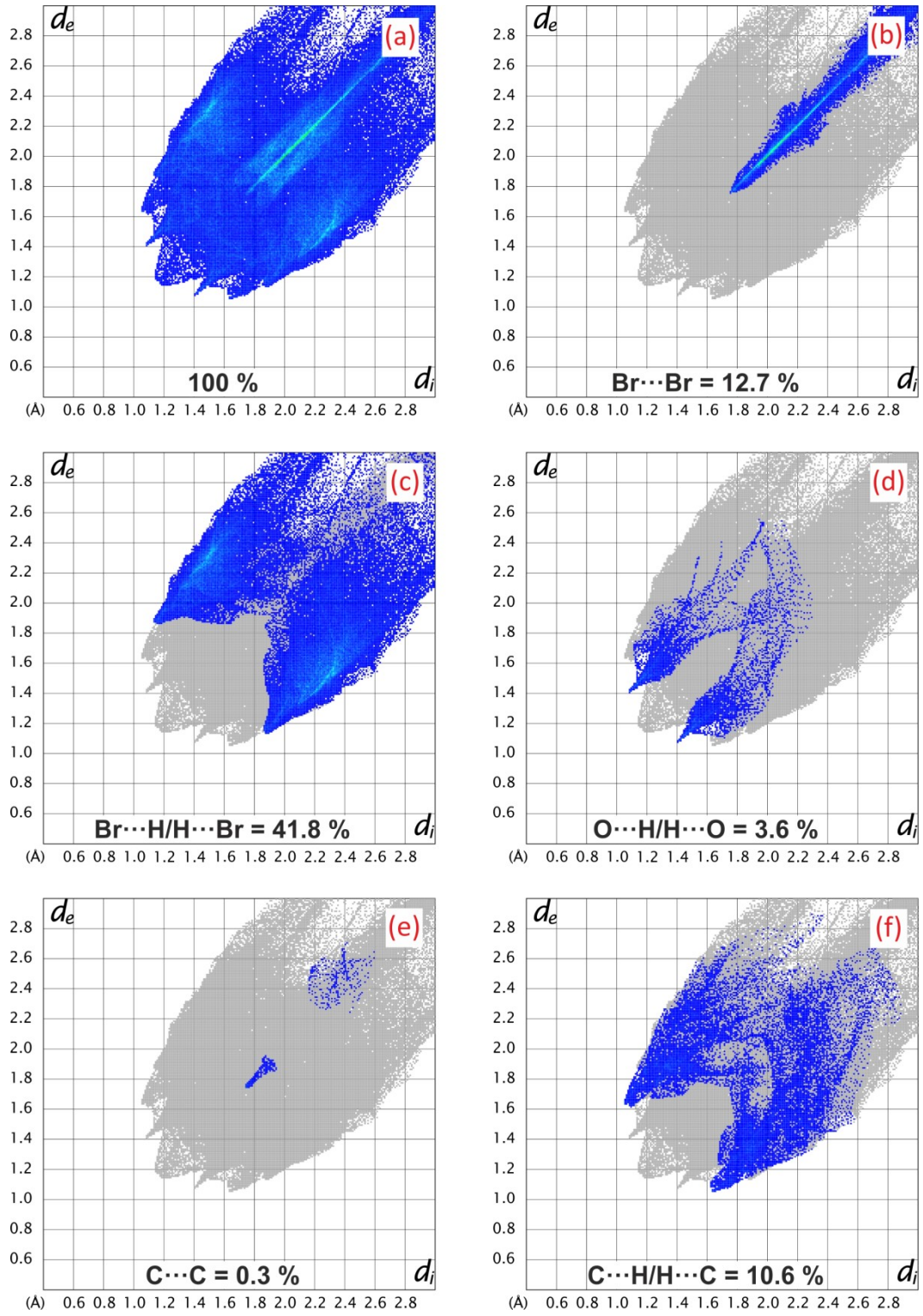

Figure S9 2D fingerprint plots for (a) overall interactions and (b-f) individual interactions in crystal packing of **6**.

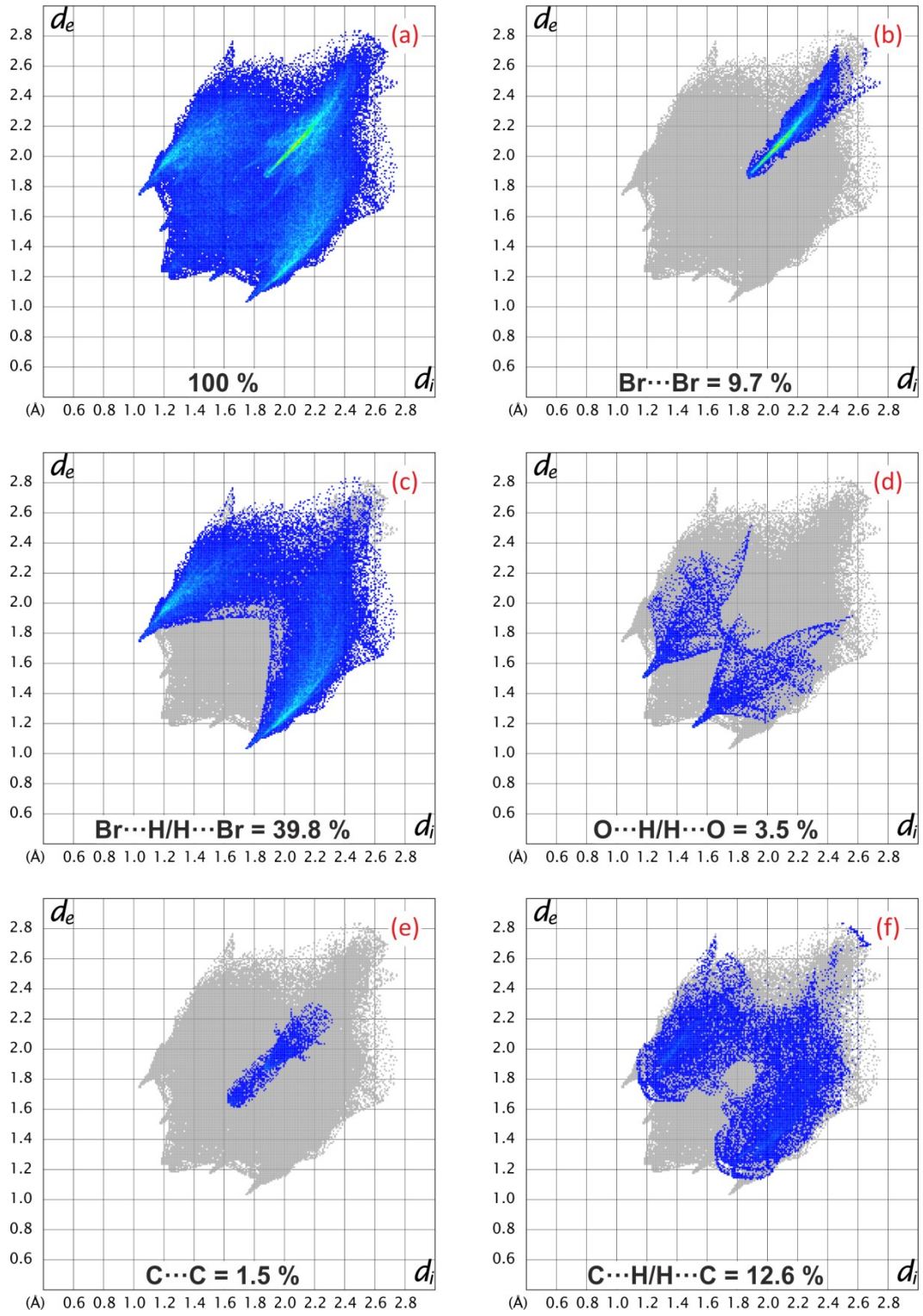

Figure S10 2D fingerprint plots for (a) overall interactions and (b-f) individual interactions in crystal packing of **7**.

4. ^{1}H and ^{13}C NMR spectra of compounds 1 – 7 (Figures S11-S24)

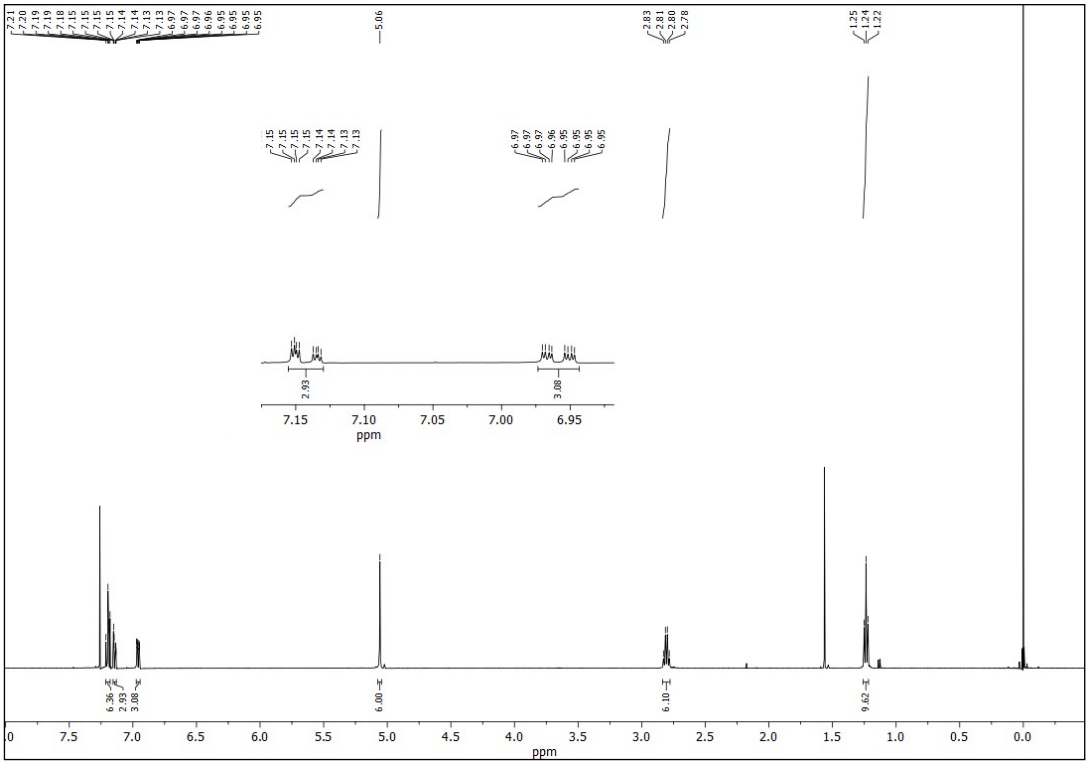

Figure S11 ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

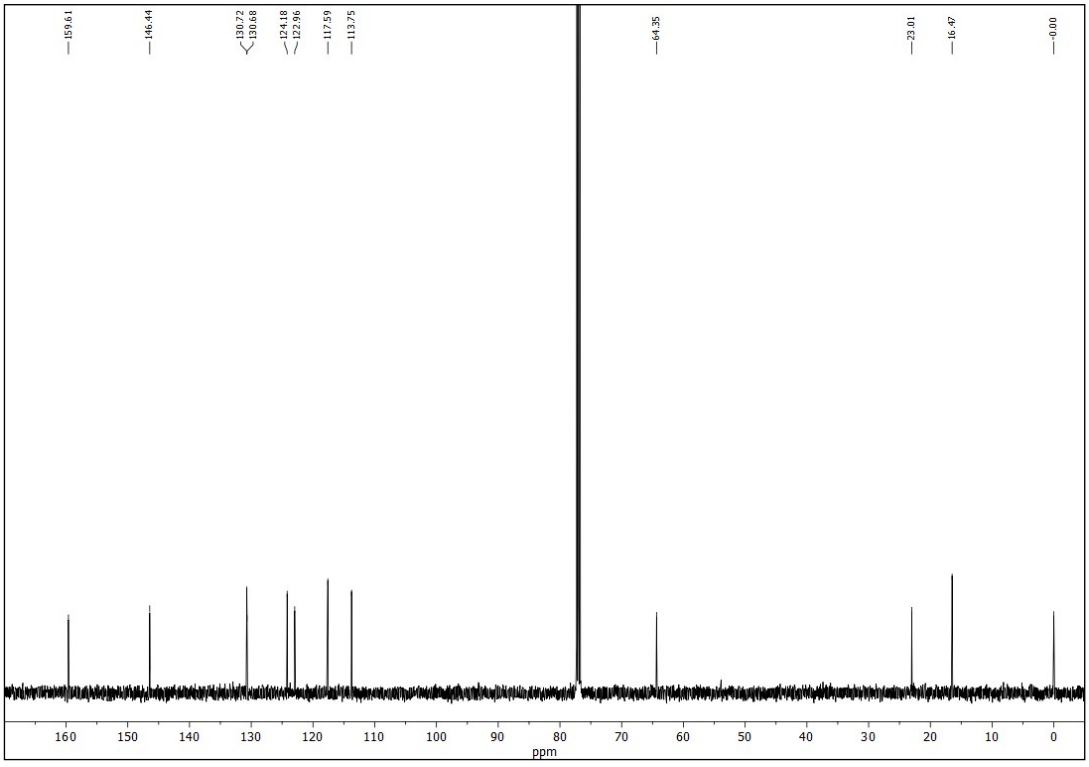

Figure S12 ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

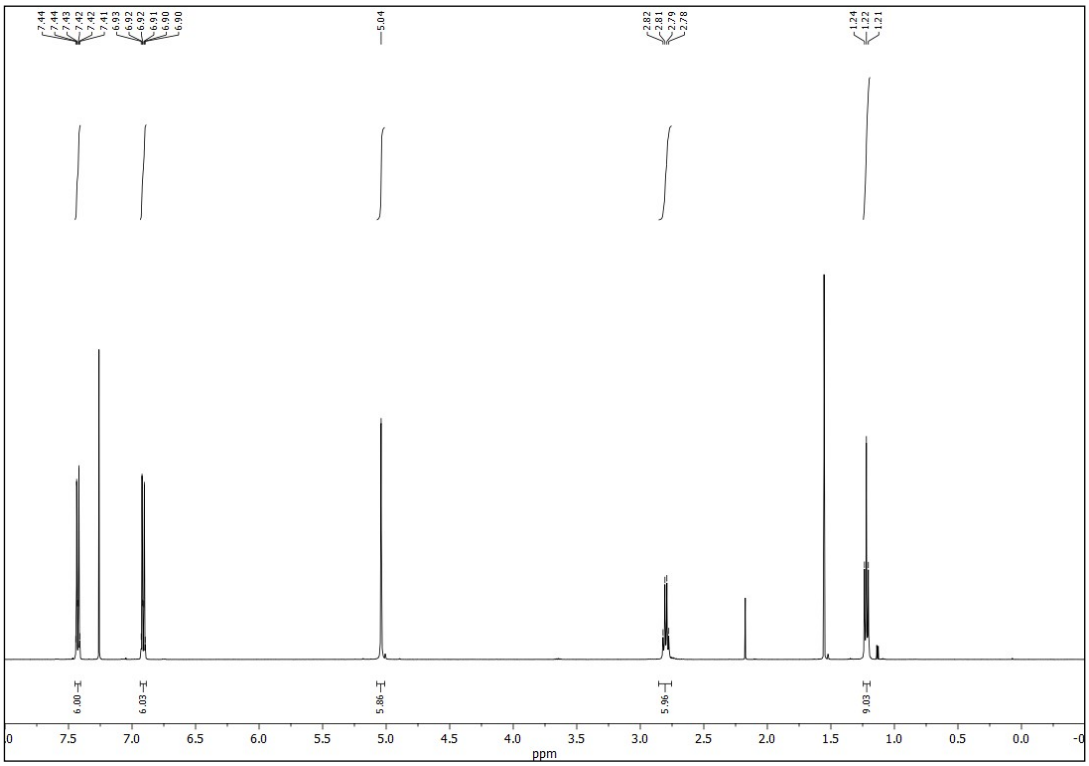

Figure S13 ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

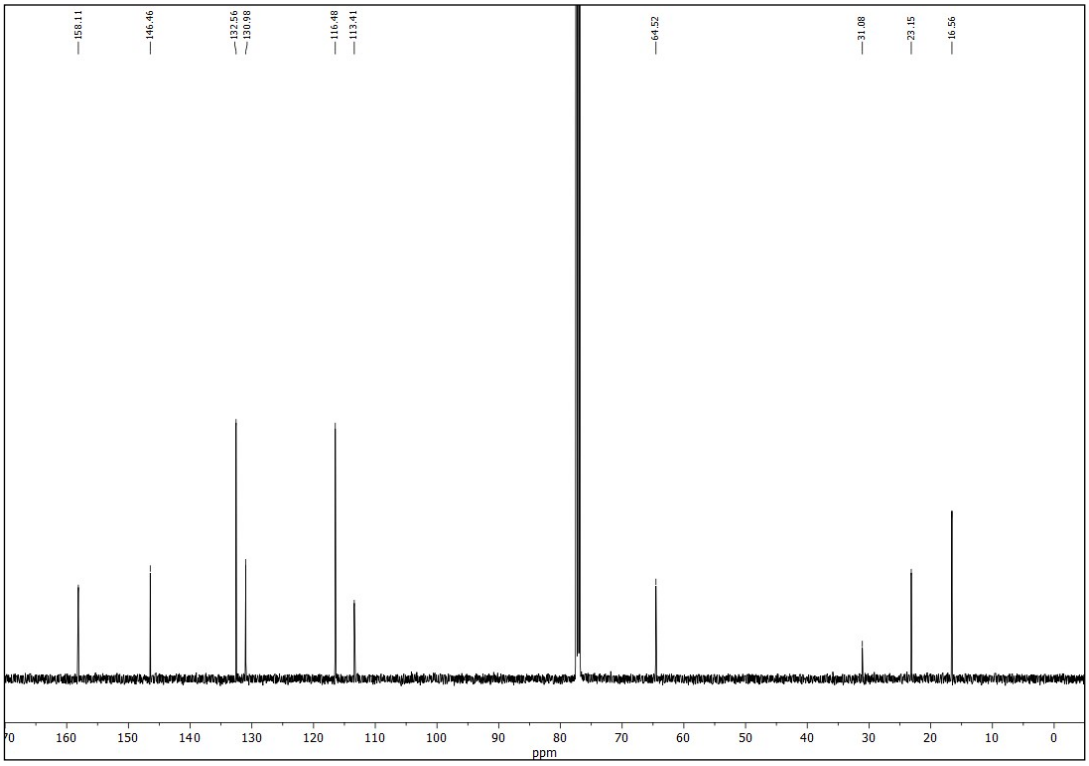

Figure S14 ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

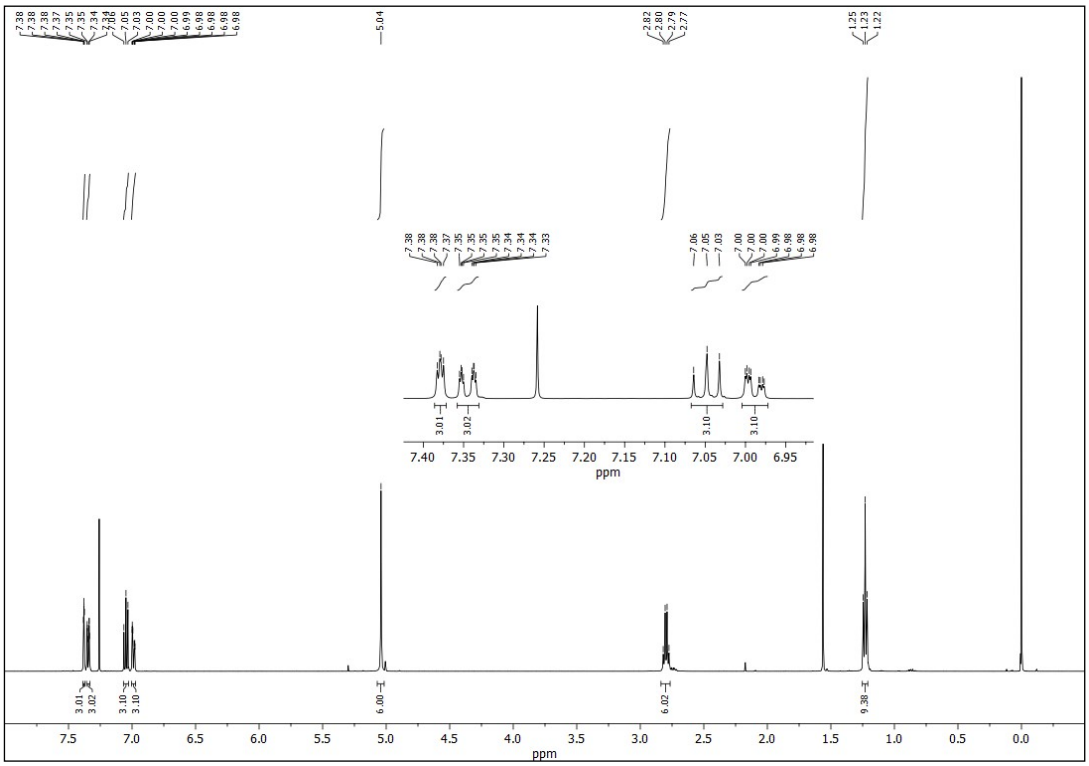

Figure S15 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

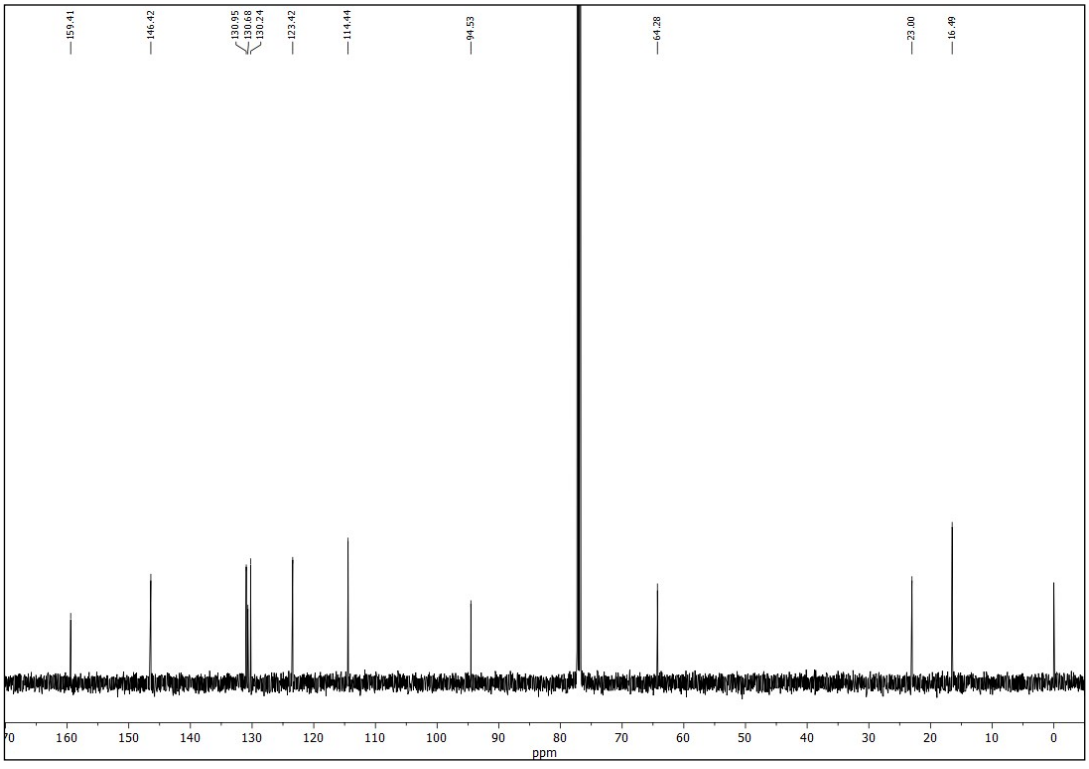

Figure S16 ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

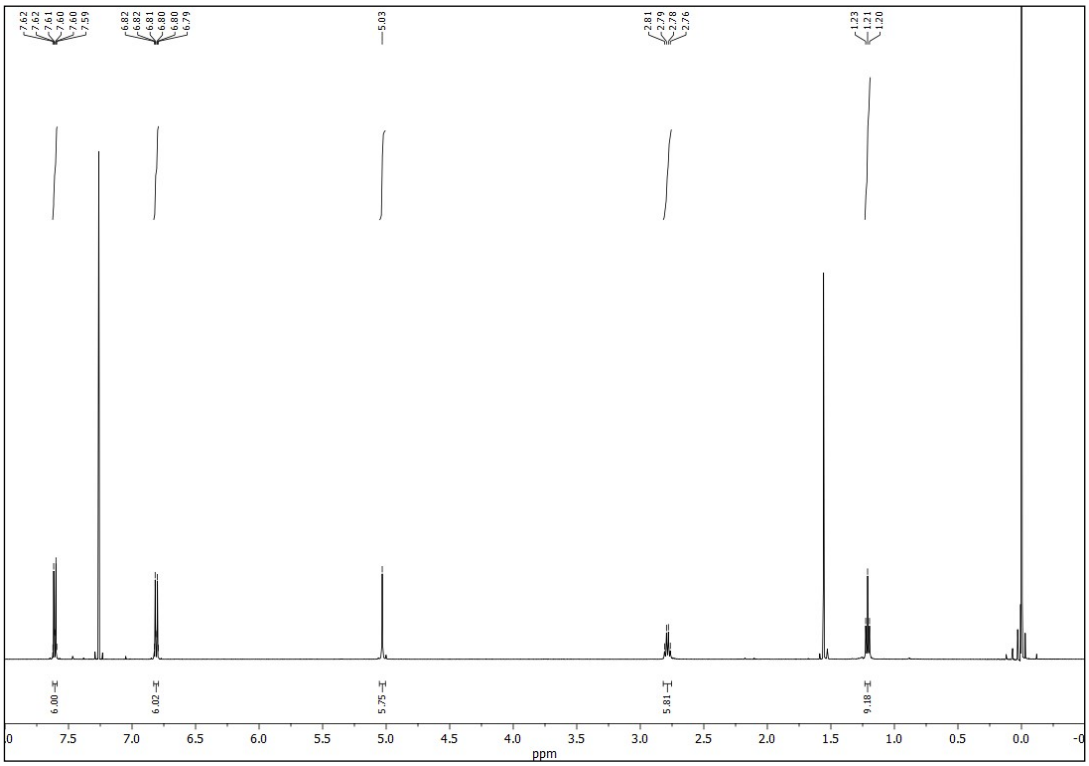

Figure S17 ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

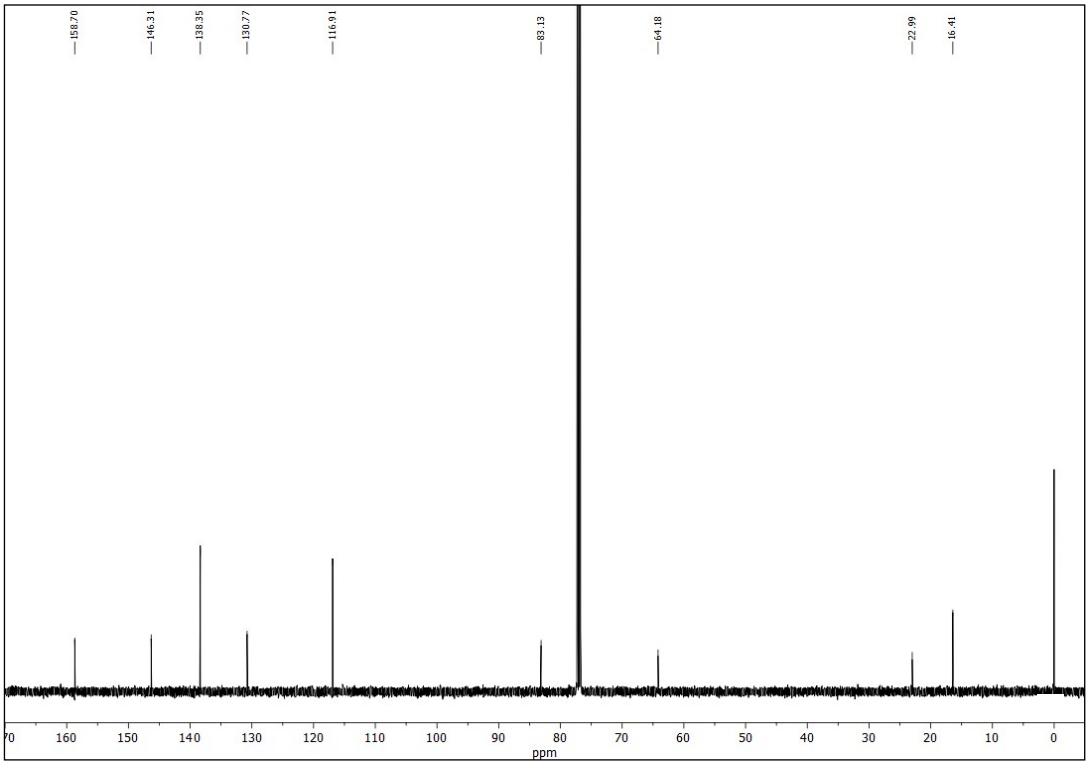

Figure S18 ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

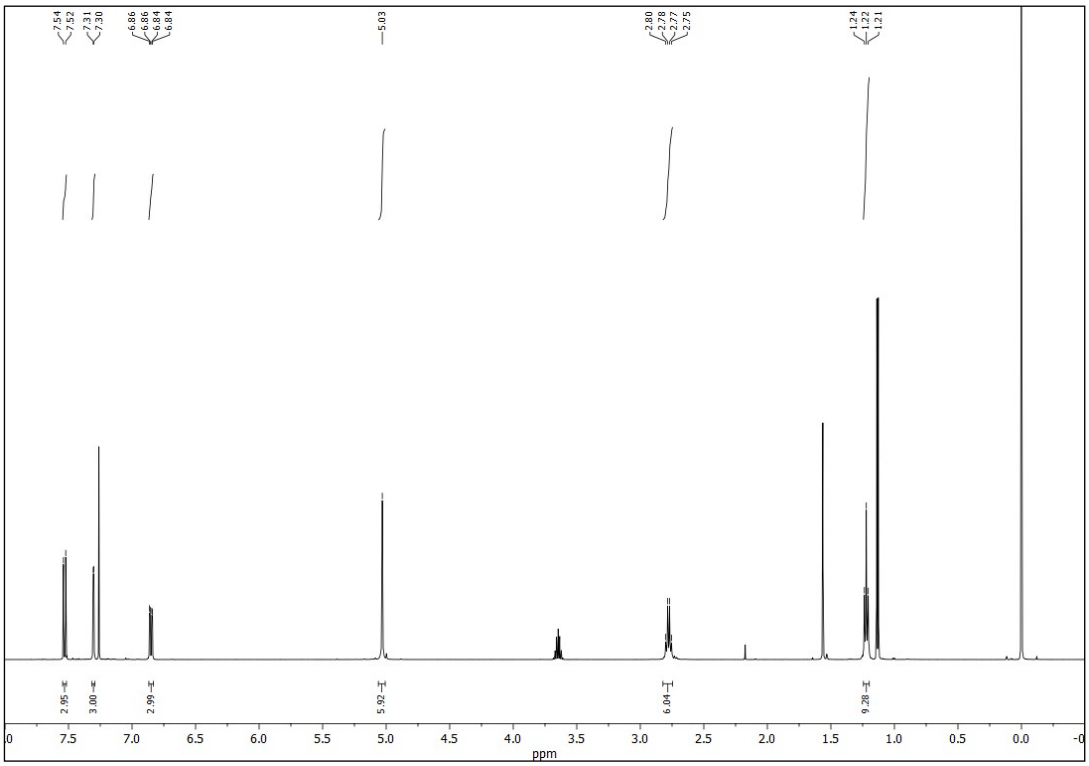

Figure S19 ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

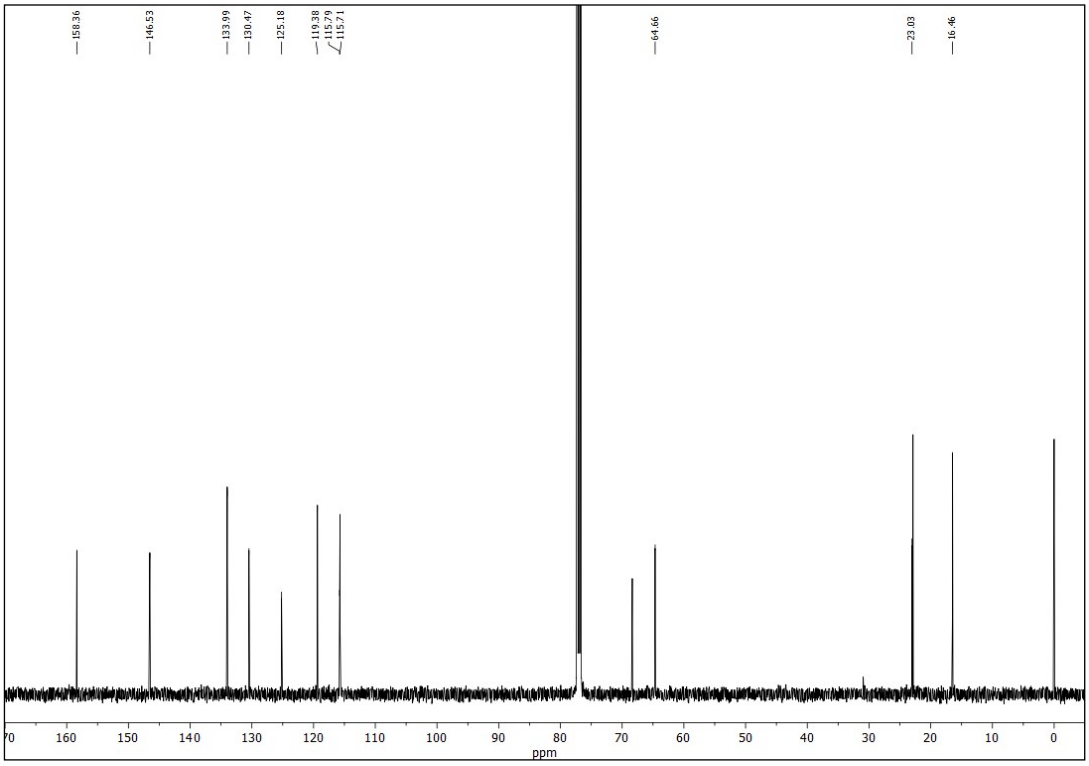

Figure S20 ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

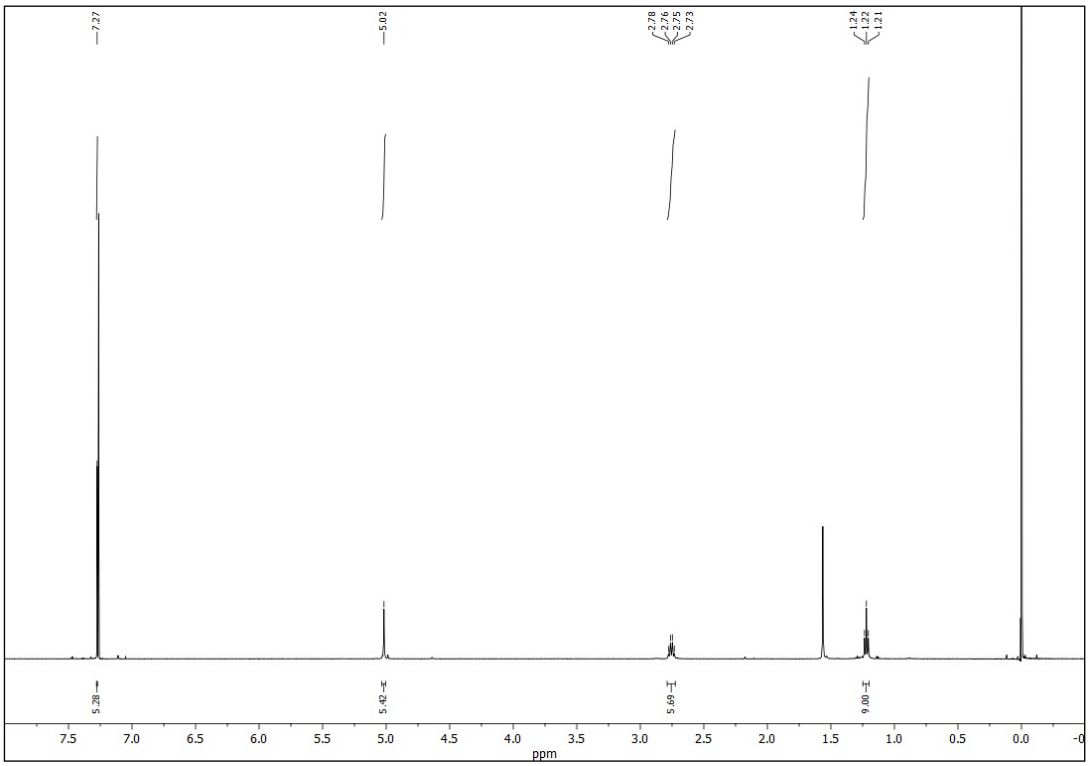

Figure S21 ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

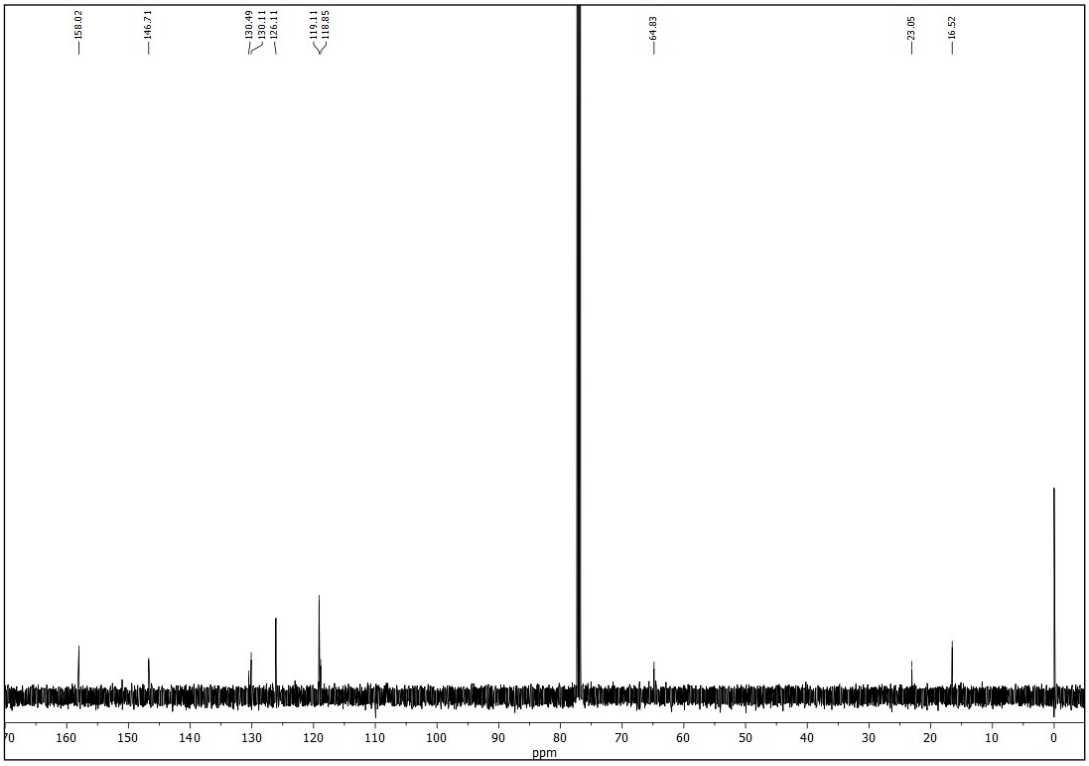

Figure S22 ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

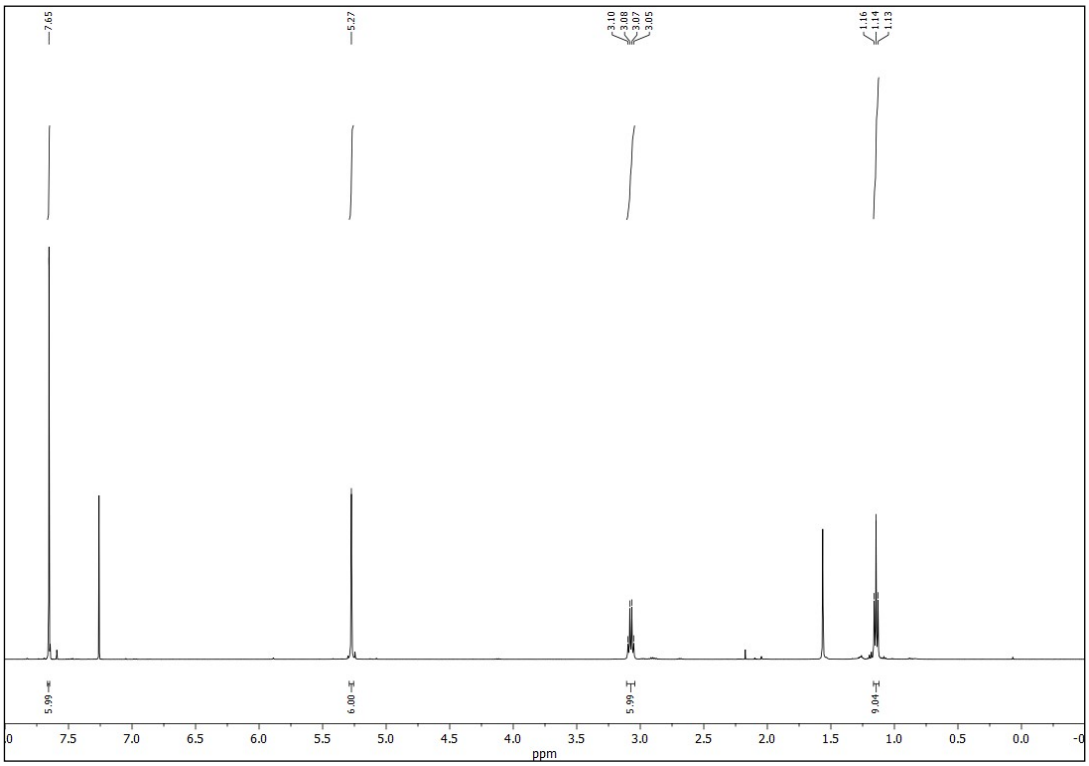

Figure S23 ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

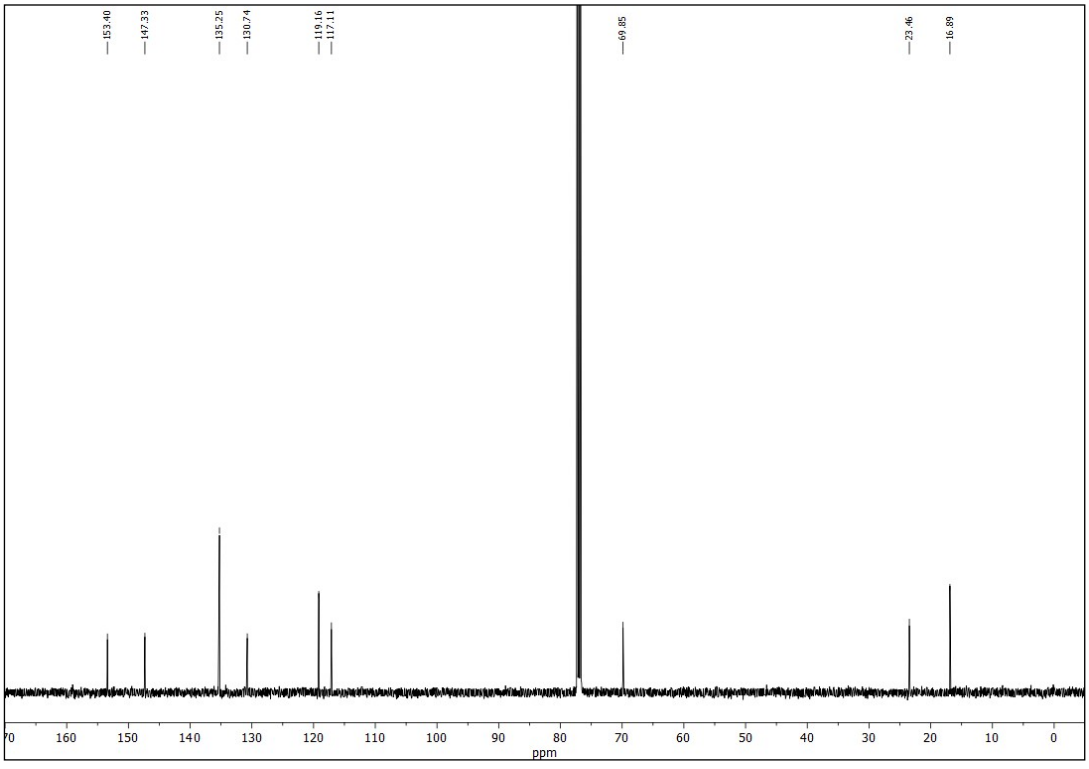

Figure S24 ^{13}C NMR spectrum of compound **7** in $CDCl_3$.