Supporting Information

Conformations of benzene-based tripodal isatin-bearing compounds in the crystalline state

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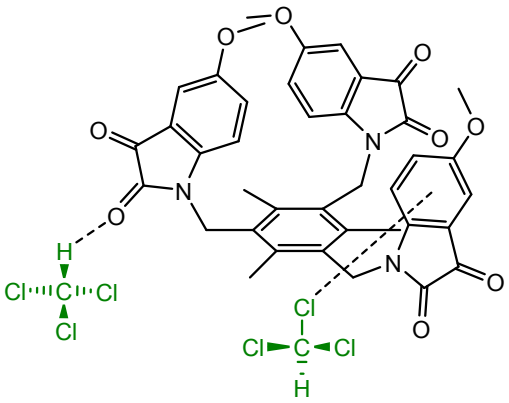
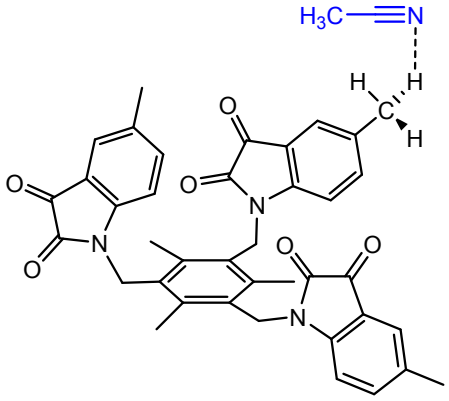
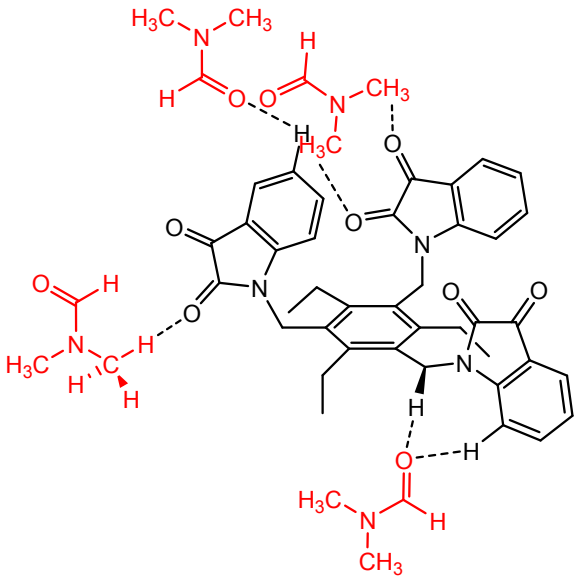


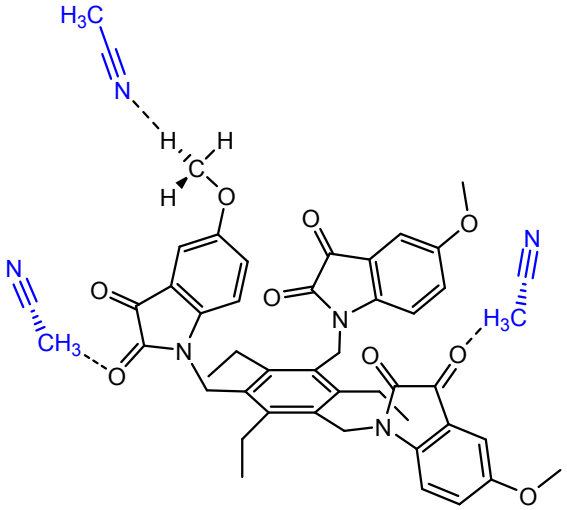
3a (**3**•$CHCl_3$)



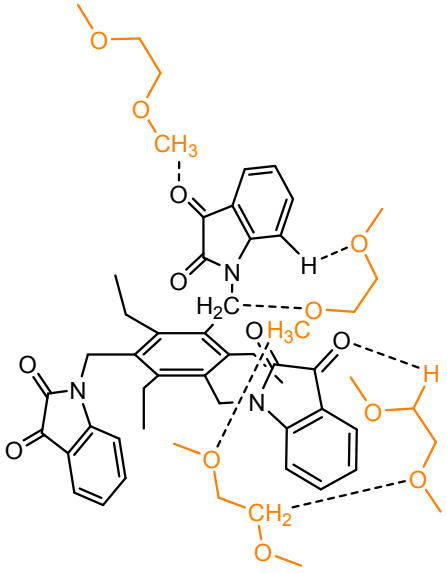
2b (**2**•CH_3CN-II)



4a (**4**•DMF)



6a (**6**•CH_3CN)



4b (**4**•DME)

Figure S1. Schematic representations of the noncovalent interactions of **2**-**4** and **6** with solvent molecules in the solvates **3a** (representative of group 1), **2b**, **4a** and **6a** (representatives of group 4) as well as **4b** (group 3).

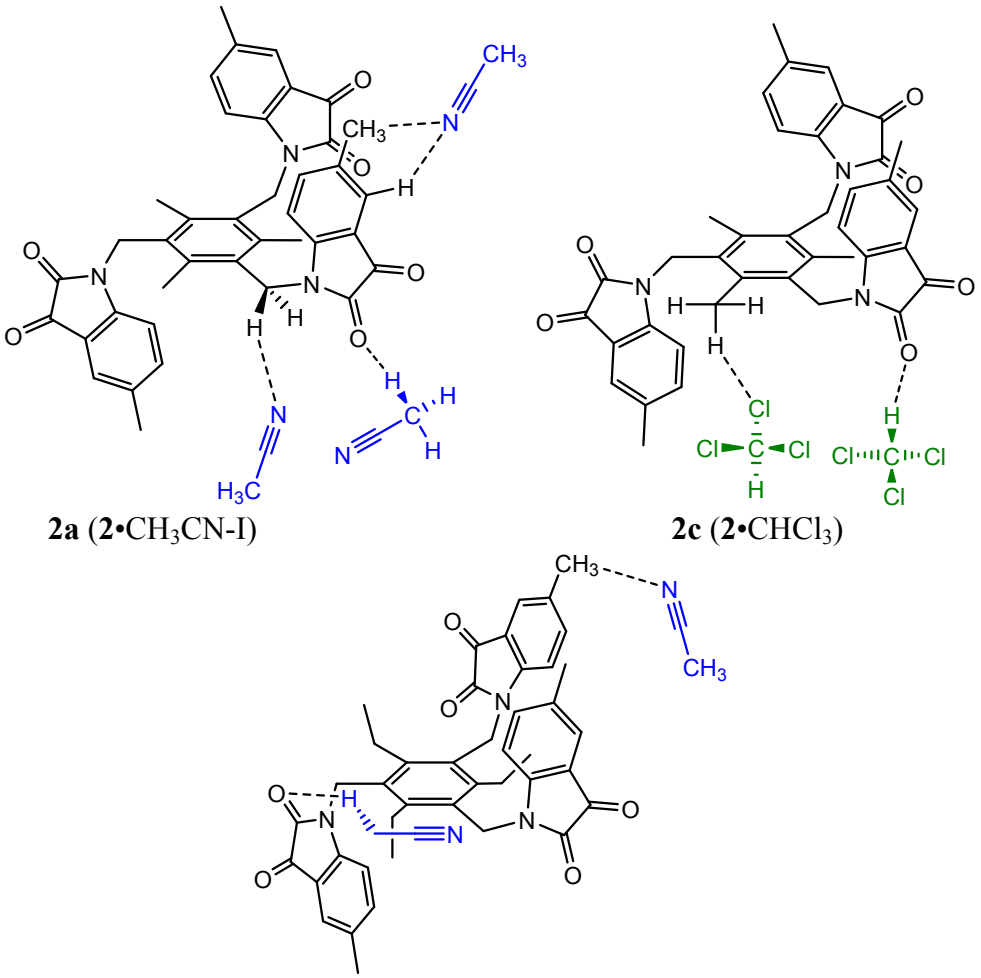


Figure S2. Schematic representations of the noncovalent interactions of **2** and **5** with solvent molecules in the solvates **2a**, **2c** and **5a** (representatives of group 4).

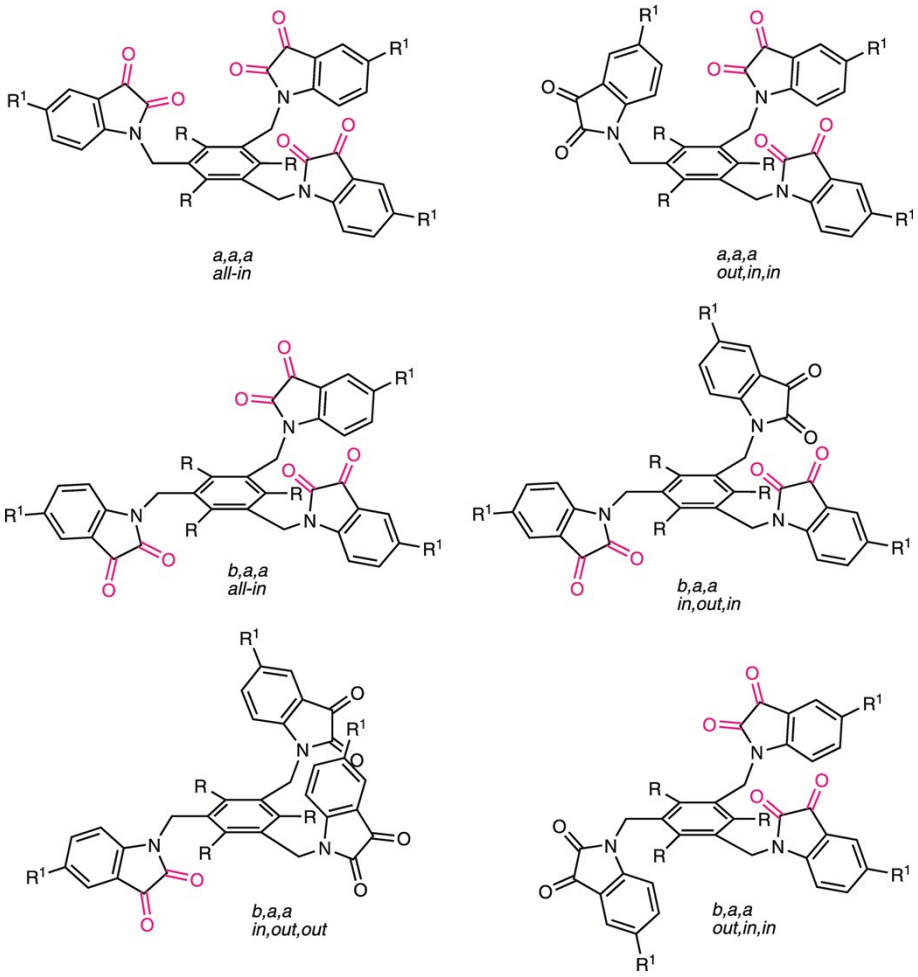


Figure S3. Conformations that are not observed in the crystals obtained for compounds **1**-**6**.

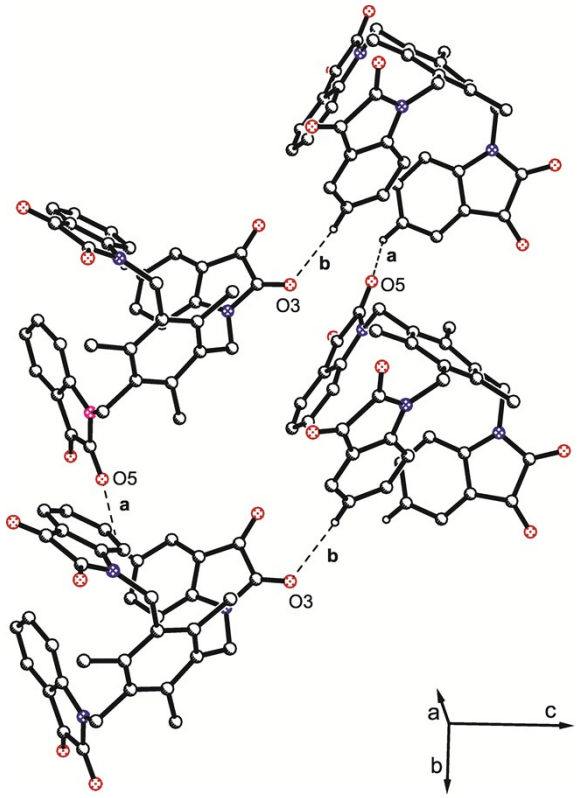


Figure S4. Crystal packing of **1**. The following C-H···O interactions (H···O distance) are shown: C_{aryl}-H···O=C (a = 2.70 Å, b = 2.45 Å).

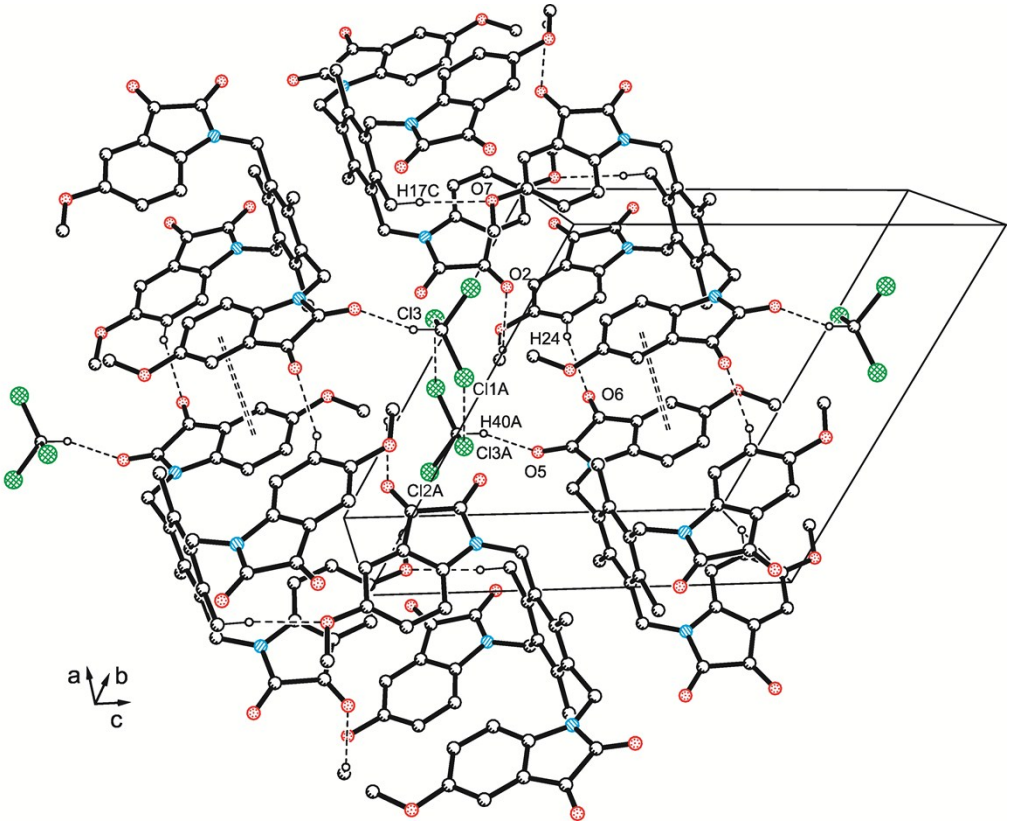


Figure S5. Crystal packing of **3a** (**3**•$CHCl_3$).

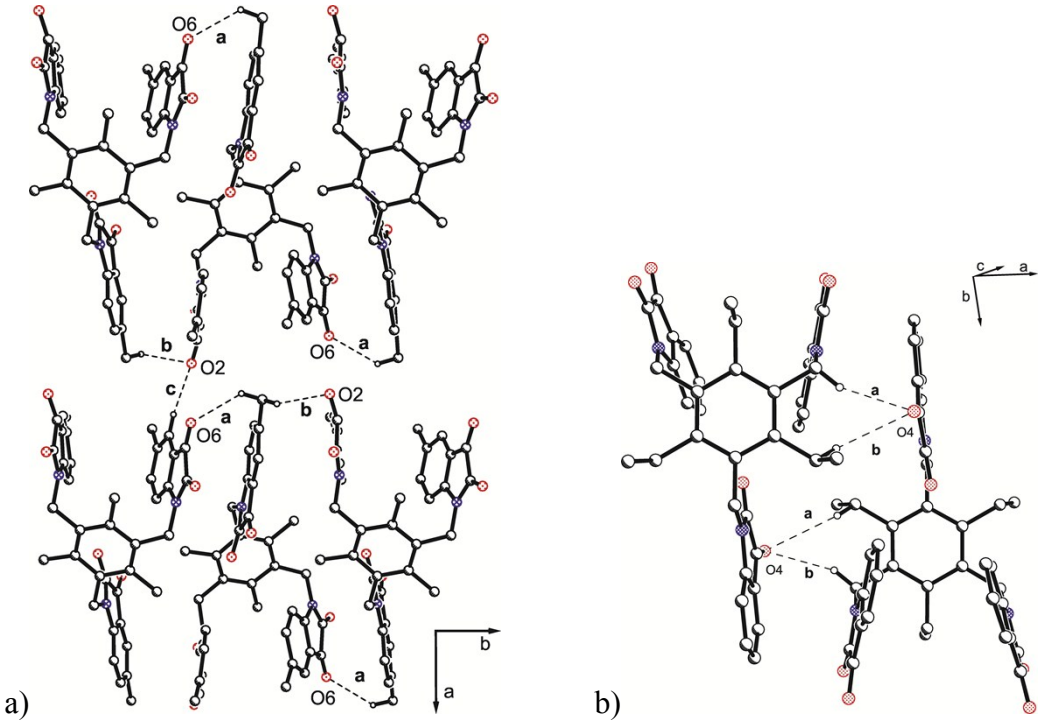


Figure S6. (a) Crystal packing of **2b** (the acetonitrile molecules are omitted for clarity). The following C-H···O interactions are shown: CH_3···O=C (a = 2.48 Å, H···O distance), CH_3···O=C (b = 2.43 Å) and C_{aryl}H···O=C (c = 2.94 Å). (b) Molecular dimer of **4a** (the dimethylformamide molecules are omitted for clarity). The following C-H···O interactions are shown: CH_3CH_2···O=C (a = 2.87 Å) and (bridge)CH_2···O=C (b = 2.70 Å).

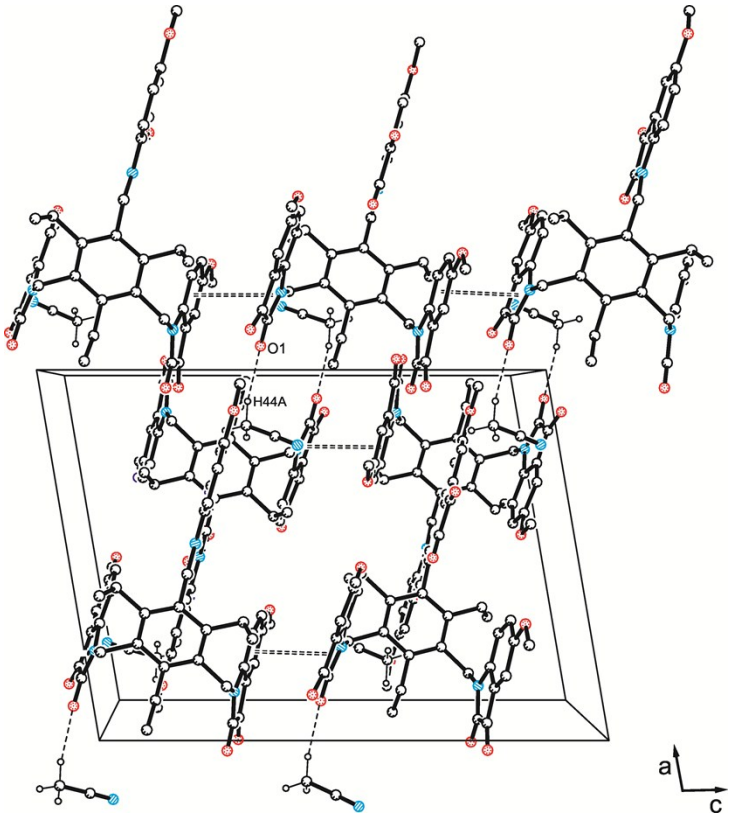
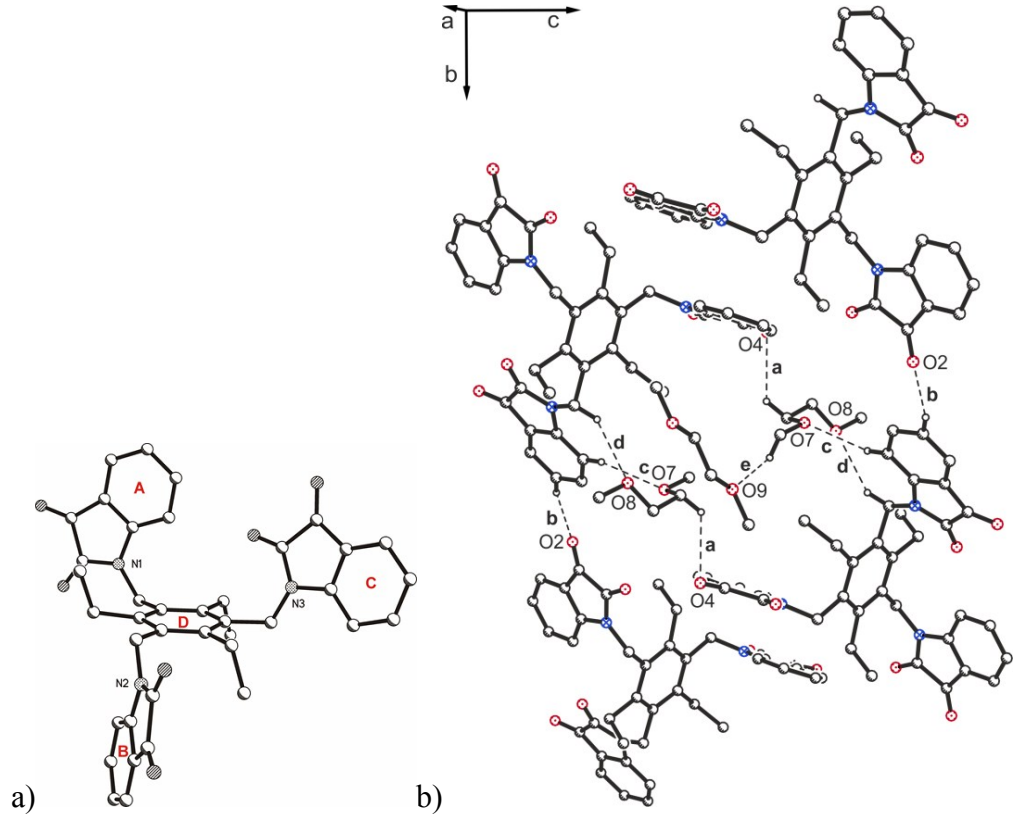


Figure S7. Crystal packing of **6a** (**6**•CH_3CN).



a) b)

Figure S8. (a) Molecular structure including the ring numbering A-D for **4b** (**4**•DME). The isatin units A-C are defined as follows: A contains N1 (B: N2, C: N3); D represents the central benzene ring. (b) Crystal packing of **4b** (**4**•DME). The following C-H···O interactions are shown: $MeOCH_2(MeO)CH_2$···O=C (a = 2.63 Å), $C_{aryl}H$···O=C (b = 2.42 Å), $C_{aryl}H$···$OMe(CH_2)_2OMe$ (c = 2.58 Å), CH_2···$OMe(CH_2)_2OMe$ (d = 2.70 Å), $MeO(CH_2)_2OCH_3$···$OMe(CH_2)_2OMe$ (e = 2.69 Å).

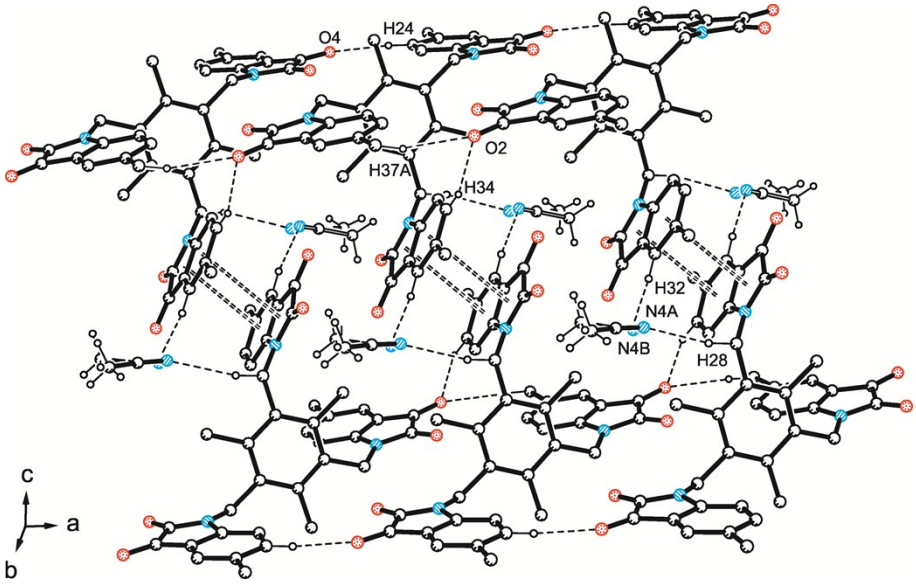


Figure S9. Crystal packing of **2a** (**2**•CH_3CN-I).

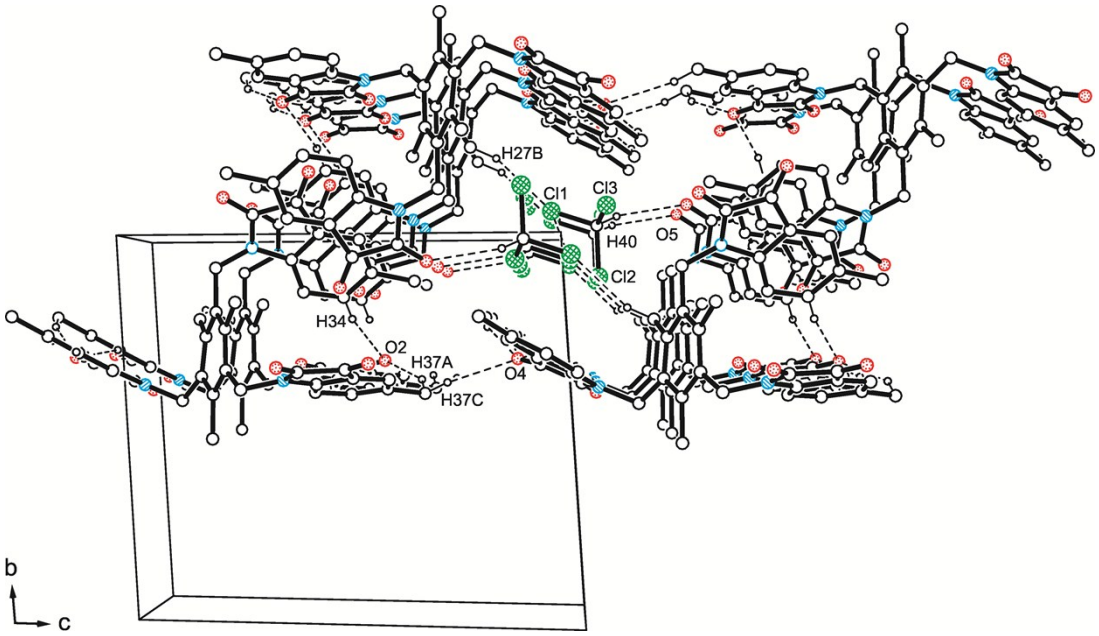


Figure S10. Crystal packingof **2c** (**2**•$CHCl_3$).

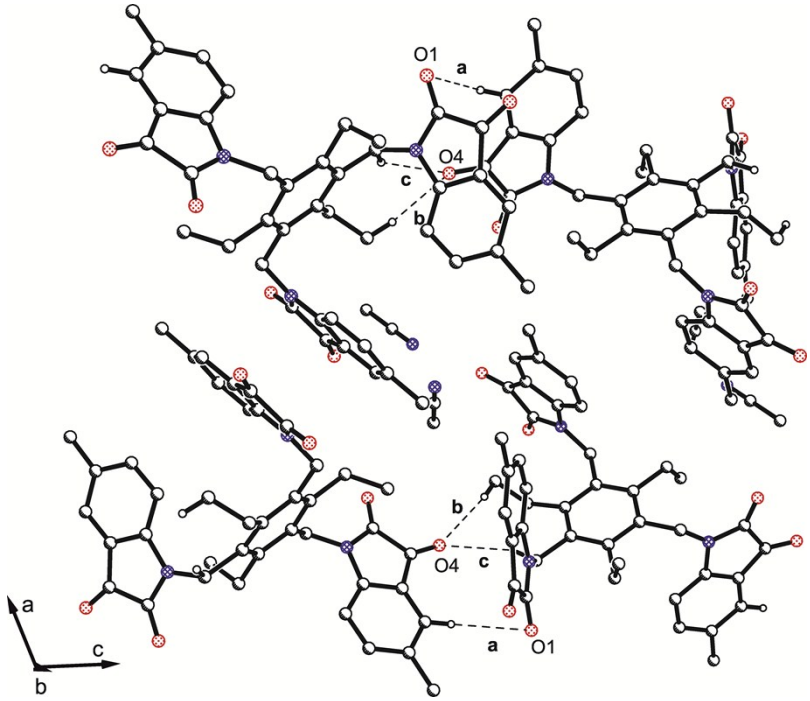


Figure S11. Crystal packing of **5a** (the acetonitrile molecules are omitted for clarity). The following C-H···O interactions: $C_{aryl}H$···O=C (a = 2.71 Å, H···O distance), CH_2CH_3···O=C (b = 2.48 Å) and CH_2···O=C (c = 2.63 Å).

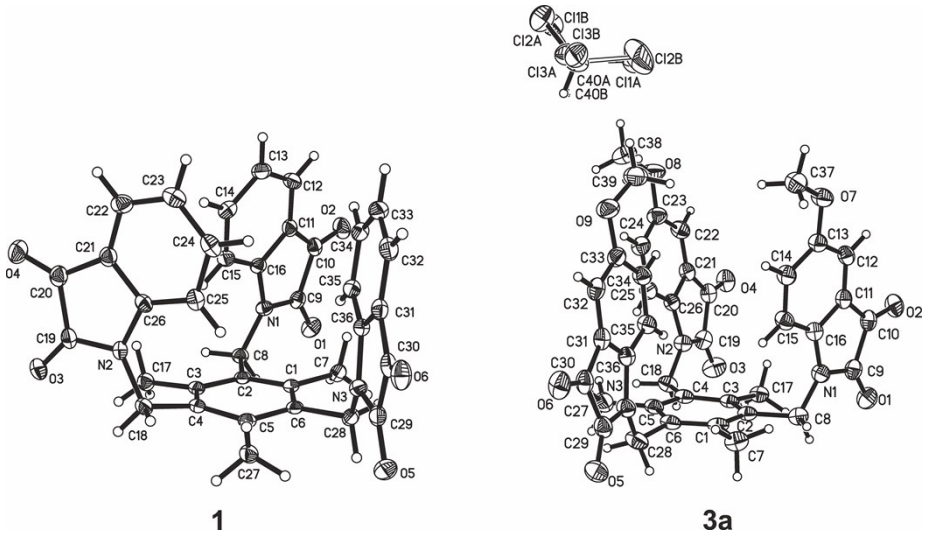


Figure S12. Molecular structure of **1** and **3a** showing the atom labelling scheme and displacement ellipsoids drawn at the probability level of 50%. The chloroform molecule crystallizing with compound **3a** is disordered in two positions (70:18).

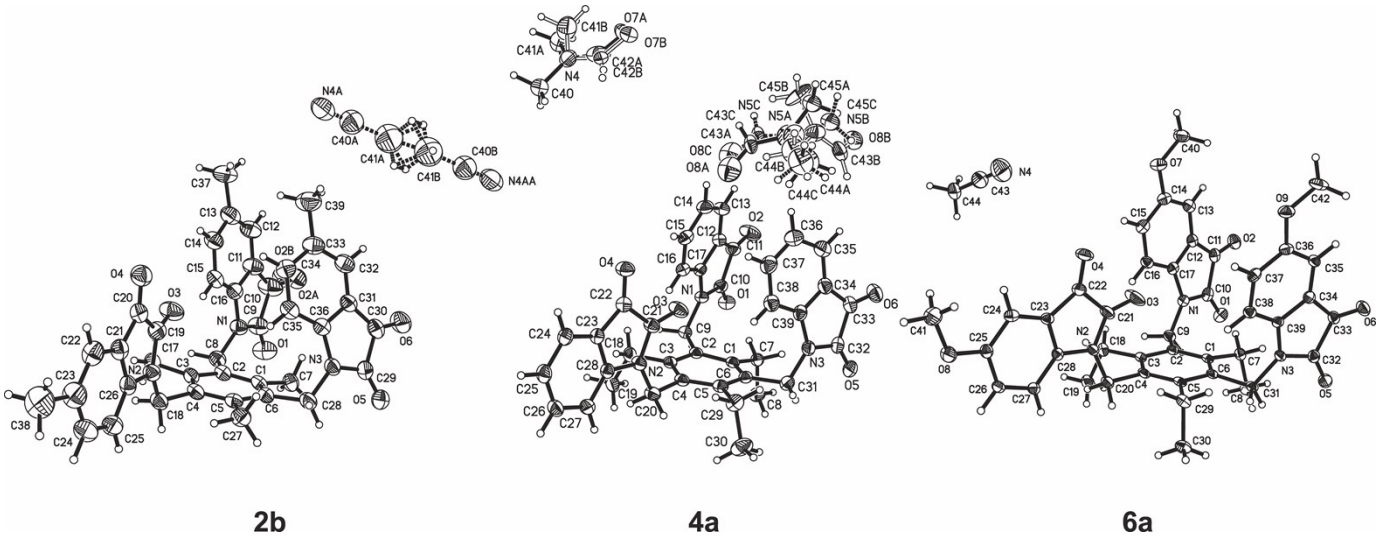


Figure S13. Molecular structure of **2b**, **4a** and **6a** showing the atom labelling scheme and displacement ellipsoids drawn at the probability level of 50%. The acetonitrile molecule crystallizing with compound **2b** is disordered in at least two positions connected via an inversion center. Both dimethylformamide molecules crystallizing with compound **4a** are disordered at least in two positions. The first DMF is disordered in two positions with 42:58. The second DMF is disordered at least in three positions with 42.1:39.8:17.7.

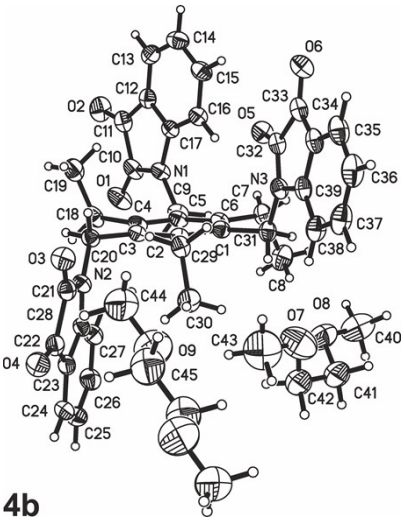


Figure S14. Molecular structure of **4b** showing the atom labelling scheme and displacement ellipsoids drawn at the probability level of 50%.

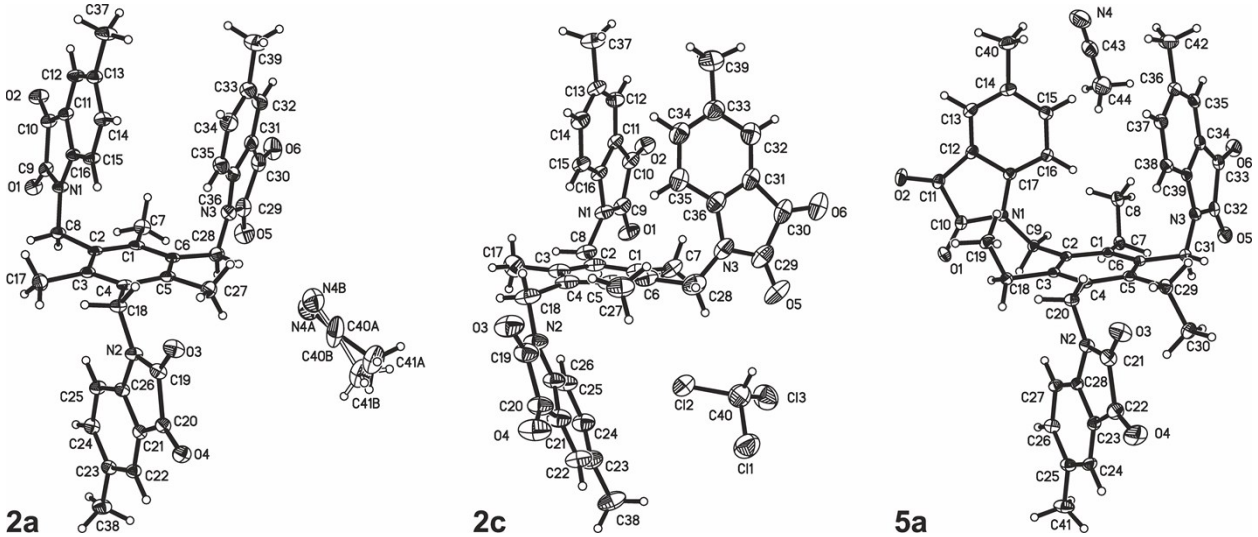


Figure S15. Molecular structure of **2a**, **2c** and **5a** showing the atom labelling scheme and displacement ellipsoids drawn at the probability level of 50%. The acetonitrile molecule crystallizing with compound **2a** is disordered in two positions (51:49).

Table S1. Selected geometric parameters of the host molecules in the crystal structures **1**, **2a-2c**, **3a**, **4a**, **4b**, **5a** and **6a**.

Rings	**1**	**2a**	**2b**	**2c**	**3a**	**4a**	**4b**	**5a**	**6a**
A/B	68.49(3)	8.24(4)	7.64(7)	29.39(7)	22.99(4)	20.01(2)	56.28(5)	60.52(3)	9.63(6)
A/C	52.47(4)	49.42(5)	27.62(6)	44.01(6)	24.33(4)	28.76(2)	19.55(7)	60.83(3)	21.27(4)
B/C	59.29(3)	56.85(5)	35.23(4)	57.65(6)	2.81(6)	9.33(3)	37.61(4)	60.03(4)	11.65(5)
A/D	82.81(4)	80.87(6)	80.50(9)	87.19(10)	87.17(3)	85.24(4)	87.19(5)	89.59(3)	82.69(7)
B/D	87.63(4)	84.69(6)	84.94(9)	68.70(10)	79.60(3)	81.76(4)	81.77(6)	84.40(3)	88.52(7)
C/D	85.86(4)	83.99(5)	67.91(8)	79.35(9)	81.03(3)	79.36(4)	79.86(6)	83.52(4)	84.71(7)

Table S2. Geometric parameters for selected intermolecular interactions in the crystal structures **1**, **2a-2c**, **3a**, **4a**, **4b**, **5a** and **6a**.

No.	Atoms involved		Distance [Å]		Angle [°]	Description in Figures
	D-H···A	Symmetry	H···A	D···A	D-H···A	
	C=O···π		O···π		C=O···π	
1	C7-H7B···O2	2-*x*, -*y*, -*z*	2.59	3.523(3)	159.4	
	C13-H13···O3	*x*, -1/2-*y*, -1/2+*z*	2.45	3.245(3)	141.5	
	C7-H7C···O1	*x*, *y*, *z*	2.67	3.451(3)	136.6	
	C8-H8A···O1	*x*, *y*, *z*	2.52	2.906(3)	103.1	
	C17-H17A···O3	*x*, *y*, *z*	2.57	3.282(3)	130.0	
	C18-H18A···O3	*x*, *y*, *z*	2.56	2.933(3)	102.4	
	C27-H27A···O5	*x*, *y*, *z*	2.55	3.329(3)	136.7	
	C28-H28A···O5	*x*, *y*, *z*	2.52	2.912(2)	103.3	
	C23-H23···O5	*x*, -1+*y*, *z*	2.70	3.049(3)	102.3	
	C28-H28B···O3	*x*, 1/2-*y*, -1/2+*z*	2.64	3.155(2)	112.7	
	C7-H7B···Cg1[a]	*x*, *y*, *z*	2.88	3.419(2)	116	
	C14-H14···Cg6[a]	*x*, *y*, *z*	2.83	3.625(2)	142	
	C24-H24···Cg7[a]	*x*, *y*, *z*	2.99	3.724(2)	136	
	C10-O2···Cg1 [a]	-*x*, 1-*y*, 1-*z*	3.455(2)	4.029(2)	109.9(1)	
	C19-O3···Cg3[a]	*x*, 3/2-*y*, -1/2+*z*	3.155(2)	3.774(2)	111.4(1)	
	C30-O6···Cg2[a]	1-*x*, 1/2+*y*, 1/2-*z*	2.651(2)	3.610(2)	135.1(1)	
2a	C7-H7A···O5	*x*, *y*, *z*	2.69	3.534(3)	143.9	
	C7-H7B···O6	-*x*, 2-*y*, -*z*	2.66	3.316(3)	124.4	
	C8-H8A···O1	*x*, *y*, *z*	2.53	2.873(3)	100	
	C8-H8A···O3	-1+*x*, *y*, *z*	2.62	3.177(3)	115.4	
	C14-H14···O2	1+*x*, *y*, *z*	2.65	3.506(3)	149.9	
	C18-H18A···O3	*x*, *y*, *z*	2.52	2.907(3)	102.9	
	C24-H24···O4	-1+*x*, *y*, *z*	2.33	3.277(3)	175.5	a / Fig. 9
	C28-H28B···O5	*x*, *y*, *z*	2.47	2.881(3)	104.5	
	C28-H28A···N4A	*x*, *y*, *z*	2.65	3.572(5)	155.4	d / Fig. 9
	C32-H32···N4A	1-*x*, 2-*y*, -*z*	2.76	3.595(9)	146.7	
	C32-H32···N4B	1-*x*, 2-*y*, -*z*	2.58	3.461(9)	154.7	e / Fig. 9
	C34-H34···O2	1+*x*, *y*, *z*	2.53	3.454(3)	164.2	c / Fig. 9
	C37-H37A···O2	1+*x*, *y*, *z*	2.57	3.505(3)	160.6	b / Fig. 9
	C39-H39C···N4A	1-*x*, 2-*y*, -*z*	2.64	3.439(10)	139	
	C41B-H41E···O5	1-*x*, 1-*y*, -*z*	2.42	2.991(10)	116.8	
	C41A-H41C···N4B	2-*x*, 1-*y*, -*z*	2.77	3.723(14)	164.5	
	C15-H15···Cg4[a]	*x*, *y*, *z*	2.68	3.452(2)	139	
	C37-H37B···Cg4[a]	*x*, 1+*y*, *z*	2.92	3.550(3)	123	
2b	C7-H7A···O1	*x, y, z*	2.68	3.449(4)	135.4	
	C7-H7B···O5	*x, y, z*	2.70	3.467(4)	135.1	
	C8-H8A···O1	*x, y, z*	2.50	2.902(4)	104.1	
	C12-H12···O6	1-*x*, 1/2+*y*, 1/2-*z*	2.62	3.565(4)	172.2	
	C14-H14···O5	*x*, 1/2-*y*, 1/2+*z*	2.68	3.476(5)	141.9	
	C18-H18B···O1	-*x*, 1-*y*, -*z*	2.68	3.603(4)	155.9	
	C24-H24···N4A	-1+*x*, 1/2-y, -1/2+z	2.78	3.722(10)	172.1	
	C27-H27C···O4	*x*, 1/2-*y*, -1/2+*z*	2.64	3.548(4)	154.7	

	C28-H28B···O4	*x*, 1/2-*y*, -1/2+*z*	2.57	3.171(4)	118.9	
	C28-H28B···O5	*x*, *y*, *z*	2.53	2.916(4)	103.0	
	C32-H32···O2A	1-*x*, -1/2+*y*, 1/2-*z*	2.66	3.545(9)	154.9	
	C32-H32···O2B	1-*x*, -1/2+*y*, 1/2-*z*	2.43	3.357(9)	163.8	
	C38-H38B···O6	-*x*, 1/2+*y*, 1/2-*z*	2.48	3.220(6)	132.5	
	C38-H38C···O2B	-*x*, -1/2+*y*, 1/2-*z*	2.33	2.886(13)	114.8	
	C39-H39A···O5	*x*, 1/2-*y*, 1/2+*z*	2.72	3.594(5)	149.0	
	C39-H39C···N4A	*x*, *y*, *z*	2.78	3.540(10)	134.7	
	C7-H7C···Cg3[a]	*x*, *y*, *z*	2.67	3.227(4)	116	
2c	C7-H7B···O6	1-*x*, -*y*, 1-*z*	2.62	3.558(6)	161.2	
	C8-H8A···O1	*x*, *y*, *z*	2.52	2.895(5)	101.9	
	C18-H18A···O3	*x*, *y*, *z*	2.54	2.907(5)	101.5	
	C24-H24···O4	1+*x*, *y*, *z*	2.49	3.332(5)	147.0	
	C27-H27B···Cl1	1-*x*, -*y*, -*z*	2.88	3.766(5)	151.0	a / Fig. 10
	C28-H28B···O5	*x*, *y*, *z*	2.50	2.896(6)	103.8	
	C28-H28B···Cl2	*x*, *y*, *z*	2.97	3.827(5)	145.7	
	C34-H34···O2	-1+*x*, *y*, *z*	2.52	3.441(5)	163.6	
	C35-H35···O1	-1+*x*, *y*, *z*	2.63	3.292(5)	127.0	
	C37-H37A···O2	-1+*x*, *y*, *z*	2.56	3.465(5)	153.3	
	C37-H37C···O4	*x*, *y*, 1+*z*	2.55	3.398(5)	144.7	
	C38-H38A···O4	1+*x*, *y*, *z*	2.48	3.402(5)	157.1	
	C40-H40···O5	*x*, *y*, *z*	2.55	3.440(8)	147.7	b / Fig. 10
	C7-H7B···Cg3[a]	*x*, *y*, *z*	2.94	3.418(5)	111	
	C17-H17B···Cg6[a]	1-*x*, 1-*y*, -*z*	2.85	3.568(5)	131	
	C25-H25···Cg4[a]	*x*, *y*, *z*	2.88	3.479(3)	122	
	C30-O6···Cg1[a]	1-*x*, -*y*, 1-*z*	3.031(3)	4.120(4)	149.1(3)	
3a	C7-H7A···O3	1+*x*, *y*, *z*	2.43	3.2766(18)	144.8	
	C7-H7C···O3	-*x*, -*y*, 1-*z*	2.68	3.6498(19)	172.1	
	C8-H8B···O1	*x*, *y*, *z*	2.54	2.9318(18)	103.1	
	C14-H14···O4	1+*x*, *y*, *z*	2.49	3.3207(17)	145.9	
	C17-H17B···O1	*x*, *y*, *z*	2.61	3.3893(19)	136.7	
	C17-H17A···O3	*x*, *y*, *z*	2.51	3.2885(18)	136.6	
	C17-H17C···O7	-*x*, -*y*, -*z*	2.47	3.4414(17)	171.3	a / Fig. 3
	C18-H18A···O3	*x*, *y*, *z*	2.52	2.9185(19)	103.9	
	C18-H18B···O6	-1+*x*, *y*, *z*	2.49	3.1650(18)	125.1	b / Fig. 3
	C22-H22···Cl1B	-*x*, 1-*y*, -*z*	2.98	3.779(7)	142.1	
	C24-H24···O6	1-*x*, 1-*y*, 1-*z*	2.35	3.1898(18)	147.3	
	C28-H28B···O5	*x*, *y*, *z*	2.56	2.8259(18)	95.2	
	C37-H37A···Cl3A	1-*x*, 1-*y*, -*z*	2.97	3.543(3)	118.2	
	C38-H38B···O2	-*x*, -*y*, -*z*	2.53	3.366(2)	142.7	
	C39-H39C···O2	-*x*, -*y*, -*z*	2.7	3.192(2)	111.6	
	C39-H39A···Cl3A	*x*, *y*, *z*	2.98	3.889(3)	154.7	
	C39-H39A···Cl3B	*x*, *y* ,*z*	2.84	3.773(13)	158.7	
	C40A-H40A···O5	1-*x*, 1-*y*, 1-*z*	2.03	2.976(2)	157.3	
	C40B-H40B···O5	1-*x*, 1-*y*, 1-*z*	2.05	2.976(2)	153.3	
	C12-H12···Cg6[a]	-x, -y, -z	2.87	3.3600(16)	114	
	C35-H35···Cg4[a]	*x*, *y*, *z*	2.92	3.7594(18)	148	
4a	C7-H7B···O1	*x*, *y*, *z*	2.46	3.439(2)	170.6	
	C7-H7A···O5	*x*, *y*, *z*	2.66	3.585(2)	155.6	

	C7-H7B···O8B	-*x*, -*y*, -*z*+1	2.71	3.196(3)	110.4	
	C8-H8C···O1	-*x*+1, -*y*, -*z*	2.53	3.503(2)	175	
	C8-H8B···O4	*x*, -1+*y*, *z*	2.64	3.500(2)	146	
	C8-H8A···O5	-*x*, -*y*, -*z*	2.63	3.592(2)	167.2	
	C9-H9A···O1	*x*, *y*, *z*	2.56	2.942(2)	102.5	
	C9-H9A···O1	-*x*+1, -*y*, -*z*	2.66	3.440(2)	136.3	
	C9-H9B···O4	-*x*+1, -*y*+1, -*z*	2.7	3.564(2)	146.2	
	C13-H13···O6	-*x*, -*y*, -*z*+1	2.59	3.278(2)	129.2	
	C14-H14···O8A	*x*, *y*, *z*	2.7	3.419(6)	132.8	
	C14-H14···O8C	*x*, *y*, *z*	2.61	3.424(17)	144	
	C16-H16···O3	*x*, *y*, *z*	2.59	3.117(2)	115.1	
	C20-H20A···O7A	*x*, *y*, -1+*z*	2.48	3.206(8)	129.5	b / Fig. 5a
	C20-H20A···O7B	*x*, *y*, -1+*z*	2.63	3.209(6)	117.3	
	C26-H26···O2	*x*, 1+*y*,-1+*z*	2.55	3.330(2)	139.3	a / Fig. 5a
	C27-H27···O7A	*x*, -1+*y*, -1+*z*	2.62	3.517(10)	157.2	
	C27-H27···O7B	*x*, *y*, -1+*z*	2.33	3.266(8)	170.1	
	C31-H31B···O5	*x*, *y*, *z*	2.51	2.900(2)	103.3	
	C38-H38···O3	*x*, *y*, *z*	2.71	3.355(2)	125.9	
	C40-H40C···O1	*x*, 1+*y*, *z*	2.52	3.472(2)	165.2	
	C40-H40B···O5	*x*+1, 1+*y*, *z*	2.55	3.431(2)	149.7	
	C41A-H41B···O6	*x*+1, 1+*y*, *z*	2.6	3.546(10)	161.2	
	C41A-H41C···O7A	-*x*+1, 1-*y*, 1-*z*	2.64	3.262(13)	121.5	
	C41B-H41E···O6	1+*x*, 1+*y*, *z*	2.58	3.557(7)	175.5	
	C42A-H42A···O2	*x*, 1+*y*, *z*	2.81	3.34(2)	116.5	
	C43A-H43A···O6	-*x*, -*y*, 1-*z*	2.87	3.255(6)	105.7	
	C43B-H43B···O2	-*x*, -*y*, 1-*z*	2.13	2.774(5)	124.2	
	C43C-H43C···O6	-*x*, -*y*, 1-*z*	2.56	3.028(13)	110.7	
	C44B-H44D···O7B	-*x*, 1-*y*, 1-*z*	2.6	3.465(14)	147.1	
	C44C-H44G···O8C	-*x*, 1-*y*, 1-*z*	2.6	3.26(5)	124.8	
	C45C-H45H···O2	-*x*, -*y*, 1-z	2.7	3.660(13)	167.3	
	C40-H40A···Cg4[a]	*x*, *y*, 1+*z*	2.94	3.667(2)	132	
	C43B-O8B···Cg3[a]	*x*, 1+*y*, *z*	3.301(4)	4.197(5)	134.5(3)	
4b	C7-H7B···O5	*x*, *y*, *z*	2.55	3.165(3)	119.9	
	C9-H9B···O1	*x*, *y*, *z*	2.50	2.891(3)	102.9	
	C9-H9B···O3	1+*x*, *y*, *z*	2.50	3.367(3)	145.8	
	C16-H16···O5	*x*, *y*, *z*	2.39	3.117(3)	132.7	
	C18-H18A···O4	1-*x*, -*y*, 1-*z*	2.65	3.599(3)	160.4	
	C20-H20A···O3	*x*, *y*, *z*	2.54	2.930(3)	103.4	
	C25-H25···O1	2-*x*, -*y*, 1-*z*	2.59	3.213(3)	123.6	
	C26-H26···O4	1+*x*, *y*, *z*	2.69	3.615(3)	164.5	
	C29-H29A···O3	*x*, *y*, *z*	2.60	3.491(3)	149.7	
	C31-H31A···O8	*x*, *y*, *z*	2.70	3.496(3)	137.5	
	C36-H36···O2	-1+*x*, 1+*y*, *z*	2.42	3.313(3)	156.7	
	C38-H38···O7	*x*, *y*, *z*	2.58	3.267(4)	129.6	a / Fig. 6
	C38-H38···O8	*x*, *y*, *z*	2.62	3.503(4)	154.3	a / Fig. 6
	C40-H40A···O6	1-*x*, 1-*y*, -z	2.71	3.547(5)	143.1	
	C42-H42B···O4	1-*x*, 1-*y*, 1-*z*	2.63	3.324(4)	126.9	
	C43-H43A···O9	*x*, *y*, *z*	2.69	3.164(6)	109.8	
	C45-H45B···O8	-1+*x*, *y*, *z*	2.72	3.586(5)	146.8	

	C8-H8B···Cg7[a]	1+*x*, *y*, *z*	2.74	3.702(3)	169	
	C13-H13···Cg3[a]	1-*x*, -*y*, -*z*	2.91	3.550(3)	125	
	C19-H19C···Cg1[a]	*x*, *y*, *z*	2.81	3.522(3)	130	
	C30-H30A···Cg2[a]	*x*, *y*, *z*	2.65	3.430(3)	137	
5a	C7-H7B···O5	*x*, *y*, *z*	2.68	3.559(2)	147.6	
	C8-H8C···O4	*x*, 3/2-*y*, -1/2+*z*	2.48	3.398(2)	155.7	a / Fig. 11
	C9-H9B···O1	*x*, *y*, *z*	2.52	2.9198(19)	103.9	
	C9-H9B···O1	-*x*, *y*-1/2, -*z*+1/2	2.63	3.2435(19)	120.5	
	C9-H9A···O4	*x*, -*y*+3/2, *z*-1/2	2.63	3.376(2)	132.6	
	C18-H18B···O1	*x*, *y*, *z*	2.47	3.3887(19)	154.0	
	C19-H19A···O1	-*x*, 1/2+*y*, 1/2-*z*	2.31	3.237(2)	157.7	
	C18-H18B···O1	*x*, *y*, *z*	2.47	3.3887(19)	154.0	
	C20-H20A···O3	*x*, *y*, *z*	2.51	2.908(2)	103.8	
	C24-H24···O1	*x*,-*y*+3/2,1/2+*z*	2.71	3.5916(19)	155.5	
	C26-H26···O2	-*x*,-1/2+*y*,1/2-*z*	2.67	3.277(2)	122.0	
	C27-H27···O2	-*x*, *y*-1/2, -*z*+1/2	2.58	3.2138(19)	124.5	b / Fig. 11
	C29-H29A···O3	*x*, *y*, *z*	2.67	3.581(2)	153.1	
	C31-H31B···O5	*x*, *y*, *z*	2.52	2.913(2)	103.5	
	C40-H40C···N4	*x*, *y*, *z*	2.53	3.413(3)	150.4	c / Fig. 11
	C42-H42A···O6	*x*, 1+*y*, *z*	2.57	3.522(2)	164.6	
	C43-H43C···O3	*x*, -*y*+3/2, *z*-1/2	2.55	3.501(3)	162.9	d / Fig. 11
	C43-H43B···N4	-*x*+1, *y*-1/2, -*z*+1/2	2.51	3.454(3)	162.6	e / Fig. 11
	C8-H8B···Cg3[a]	*x*, *y*, *z*	2.50	3.2219(18)	130	
	C19-H19B···Cg1[a]	*x*, *y*, *z*	2.60	3.2504(19)	124	
	C30-H30C···Cg2[a]	*x*, *y*, *z*	2.78	3.558(2)	137	
6a	C7-H7B···O1	*x*, *y*, *z*	2.52	3.398(3)	147.6	
	C7-H7A···O5	*x*, *y*, *z*	2.66	3.485(4)	140.8	
	C8-H8C···O6	2-*x*, 1/2+*y*, 1/2-*z*	2.59	3.541(4)	164.8	
	C9-H9A···O1	*x*, *y*, *z*	2.49	2.901(4)	104.3	
	C27-H27···O3	1-*x*, 1/2+*y*, 1/2-*z*	2.32	3.243(4)	162.9	c / Fig. 5c
	C29-H29A···O7	1-*x*, 1/2+*y*, 1/2-*z*	2.51	3.408(4)	151.4	b / Fig. 5c
	C30-H30C···O4	1-*x*, 1/2+*y*, 1/2-*z*	2.58	3.514(4)	158.7	
	C31-H31B···O5	*x*, *y*, *z*	2.47	2.887(4)	104.7	
	C31-H31B···O6	2-*x*, 1/2+*y*, 1/2-*z*	2.28	3.050(4)	133.9	
	C40-H40C···N4	1-*x*, -*y*, 1-*z*	2.72	3.450(6)	131.6	
	C44-H44A···O1	-1+*x*, *y*, *z*	2.29	3.254(4)	168.7	a / Fig. 5c
	C44-H44C···O4	*x*, 1/2-*y*, 1/2+*z*	2.59	3.194(4)	120.0	
	C44-H44B···Cg4[a]	1-*x*, -1/2+*y*, 1/2-*z*	2.89	3.821(4)	159	
	C10-O1···Cg3[a]	*x*, 1/2-*y*, 1/2+*z*	3.373(2)	3.620(3)	91.8(2)	

[a] Cg is defined as the centroid of the rings (centre of gravity). **1**, **2a-2c**, **3a**: ring 1: N1,C9,C10,C11,C16; ring 2: N2,C19,C20,C21,C26; ring 3: N3,C29,C30,C31,C36; ring 4: C1-C6; ring 6: C21-C26; ring 7: C31-C36. **4a**, **4b**, **5a**, **6a**: ring 1; N1,C10,C11,C12,C17; ring 2: N2,C21,C22,C23,C28; ring 3: N3,C32,C33,C34,C39; ring 4: C1-C6; ring 7: C34-C39.

Table S3. Selected geometric distances of the O···π interactions in the crystal structures **1**, **2c**, **3a**, **4a** and **6a**.

Compound	Involved atoms[a]	Distance [Å] Angle [°]	Symmetry code	Compound	Involved atoms[a]	Distance [Å] Angle [°]	Symmetry code
1	O2···C10	3.194(3)	-*x*,1-*y*,1-*z*	**6a**	O1···C33	3.339(4)	*x*,1/2-*y*,1/2+*z*
	O2···C11	3.208(3)	-*x*,1-*y*,1-*z*		O1···C34	3.109(3)	*x*,1/2-*y*,1/2+*z*
	C10-O2···Cg1	3.455(2) 109.89(13)	-*x*,1-*y*,1-*z*		O1···C35	3.343(4)	*x*,1/2-*y*,1/2+*z*
	O3···N3	2.969(2)	*x*,3/2-*y*,-1/2+*z*		O1···N3	3.180(3)	*x*,1/2-*y*,1/2+*z*
	O3···C28	3.155(3)	*x*,3/2-*y*,-1/2+*z*		O1···C31	3.390(4)	*x*,1/2-*y*,1/2+*z*
	O3···C29	3.167(3)	*x*,3/2-*y*,-1/2+*z*		C10-O1···Cg3	3.373(2) 91.76(18)	*x*,1/2-*y*,1/2+*z*
	C19-O3···Cg3	3.155(2) 111.4(1)	*x*,3/2-*y*,-1/2+*z*		O2···N3	3.180(3)	*x*,1/2-*y*,1/2+*z*
	O6···N2	3.058(2)	1-*x*,1/2+*y*,1/2-*z*		O2···C31	3.390(4)	*x*,1/2-*y*,1/2+*z*
	O6···C19	2.836(3)	1-*x*,1/2+*y*,1/2-*z*		C11-O2···Cg3	3.524(2) 89.31(17)	*x*,1/2-*y*,1/2+*z*
	O6···C20	2.745(3)	1-*x*,1/2+*y*,1/2-*z*	**2c**	O6···C9	3.275(5)	1-*x*,-*y*,1-*z*
	O6···C21	2.907(3)	1-*x*,1/2+*y*,1/2-*z*		O6···C10	2.864(5)	1-*x*,-*y*,1-*z*
	O6···C26	3.045(2)	1-*x*,1/2+*y*,1/2-*z*		O6···C11	3.069(5)	1-*x*,-*y*,1-*z*
	C30-O6···Cg2	2.651(2) 135.1(1)	1-*x*,1/2+*y*,1/2-*z*		O6···C31	3.347(5)	1-*x*,-*y*,1-*z*
3a	O7···C20	3.108(2)	-*x*,-*y*,-*z*		O6···C32	3.371(5)	1-*x*,-*y*,1-*z*
	O7···C21	3.370(2)	-*x*,-*y*,-*z*		C30-O6···Cg1	3.031(3) 149.1(3)	1-*x*,-*y*,1-*z*
	C13-O7···Cg2 C37-O7···Cg2	3.273 108.95 / 107.72	-*x*,-*y*,-*z*				
4a	O8B···C10	2.938(4)	*x*,1+*y*,*z*				
	O8B···C11	2.787(4)	*x*,1+*y*,*z*				
	C43B-O8B···Cg3	3.301(4) 134.5(3)	*x*,1+*y*,*z*				

[a] Cg is defined as the centroid of the rings (centre of gravity). **1**, **2c**, **3a**: ring 1: N1,C9,C10,C11,C16; ring 2: N2,C19,C20,C21,C26; ring 3: N3,C29,C30,C31,C36. **4a**, **5a**, **6a**: Ring 1; N1,C10,C11,C12,C17; ring 2: N2,C21,C22,C23,C28; ring 3: N3,C32,C33,C34,C39.

Table S4. Geometric parameters for selected stacking interactions in the crystal structures **1**, **2a-2c**, **3a**, **4a**, **4b**, **5a** and **6a**.

	CgI[a]	CgJ[a]	Symmetry	CgI···CgJ [Å]	CgI···P(J)[b] [Å]	CgJ···P(I)[c] [Å]	Description in Figure
1	Cg1	Cg4	-*x*, -1/2+*y*, 1/2-*z*	3.466(1)	3.413(1)	-3.358(1)	
2a	Cg2	Cg6	1-*x*, 1-*y*, 1-*z*	3.482(1)	3.463(1)	3.463(1)	
	Cg3	Cg7	-*x*, 2-*y*, -*z*	3.710(2)	3.376(1)	3.390(1)	
	Cg7	Cg7	-*x*, 2-y, -z	3.913(2)	3.373(1)	3.373(1)	f / Fig. 9
2b	Cg2	Cg6	1-*x*, 1-*y*, 1-*z*	3.482(1)		3.464(1)	
	Cg3	Cg7	-*x*, 2-*y*, -*z*	3.710(2)	3.376(1)	3.390(1)	
	Cg2	Cg6	1-*x*, 1-*y*, 1-*z*	3.482(1)		3.464(1)	
2c	Cg1	Cg5	1-*x*, 1-*y*, 1-*z*	3.516(2)	3.513(2)	3.512(2)	
	Cg7	Cg7	-*x*, -*y*, 1-*z*	3.583(2)	-3.546(2)	-3.546(2)	
3a	Cg2	Cg3	-1+*x*, *y*, *z*	3.840(1)	-3.156(1)	3.257(1)	
	Cg7	Cg7	1-*x*, 1-*y*, 1-*z*	3.698(1)	3.280(1)	3.280(1)	
4a	Cg3	Cg6	-*x*, 1-*y*, -*z*	3.566(1)	-3.373(1)	-3.519(1)	
	Cg6	Cg7	-*x*, 1-*y*, -*z*	3.889(1)	-3.506(1)	-3.730(1)	
	Cg1	Cg6	1-*x*, 1-*y*, -*z*	3.928(1)	3.166(1)	3.624(1)	
4b	Cg3	Cg7	1-*x*, 1-*y*, -*z*	3.577(2)	3.397(1)	3.344(1)	
	Cg2	Cg2	1-*x*, -*y*, 1-*z*	3.382(1)	-3.343(1)	-3.343(1)	c / Fig. 6
	Cg1	Cg5	2-*x*, -*y*, -*z*	3.475(2)	3.435(1)	3.444(1)	
5a	Cg3	Cg3	1-*x*, 1-*y*, 1-*z*	3.703(1)	3.353(1)	3.353(1)	f / Fig. 11
	Cg2	Cg6	-*x*, 2-*y*, 1-*z*	3.983(1)	3.705(1)	3.743(1)	f / Fig. 11
6a	Cg1	Cg7	*x*, 1/2-*y*, 1/2+*z*	3.547(2)	-3.331(1)	3.253(1)	
	Cg5	Cg6	1-*x*, -1/2+*y*, 1/2-*z*	3.456(2)	-3.141(1)	-3.338(1)	
	Cg6	Cg7	1-*x*, 1/2+*y*, 1/2-*z*	3.412(2)	3.290(1)	3.160(1)	

[a] Cg is defined as the centroid of the rings (centre of gravity). **1**, **2a-2c**, **3a**: ring 1: N1,C9,C10,C11,C16; ring 2: N2,C19,C20,C21,C26; ring 3: N3,C29,C30,C31,C36; ring 4: C1-C6; ring 5: C11-C16; ring 6: C21-C26; ring 7: C31-C36. **4a**, **4b**, **5a**, **6a**: ring 1: N1,C10,C11,C12,C17; ring 2: N2,C21,C22,C23,C28; ring 3: N3,C32,C33,C34,C39; ring 4: C1-C6; ring 5: C12-C17; ring 6: C23-C28; ring 7: C34-C39.

[b] Perpendicular distance of the centroid CgI on ring plane J; [c] Perpendicular distance of the centroid CgJ on ring plane I.

Table S5. Geometric parameters for O···O and Cl···Cl contacts in the crystal structures **1** and **3a**.

	interaction	symmetry	C-X [Å]	C-Y [Å]	X...Y [Å]	C-X...Y [Å]	C-Y...X [°]
1	C30-O6...O6...C30	1-*x*,1-*y*,-*z*	1.209(2)		2.8088(30)	80.66(0.12)	
3a	C40A-Cl1A...Cl3A-C40A	1-*x*,1-*y*,-*z*	1.790(3)	1.766(3)	3.458(4)	117.7 (1)	125.6(2)
	C40B-Cl1B...Cl3B-C40B	1-*x*,1-*y*,-*z*	1.828(10)	1.810(12)	3.028(17)	122.5(1)	133.8(7)
	C23/C38-O8 - Cl1A-C40A	-*x*,1-*y*,-*z*	1.3649(19) / 1.424(2)	1.766(3)	3.2544(22)	126.9(1)/113.0(1)	131.1(1)

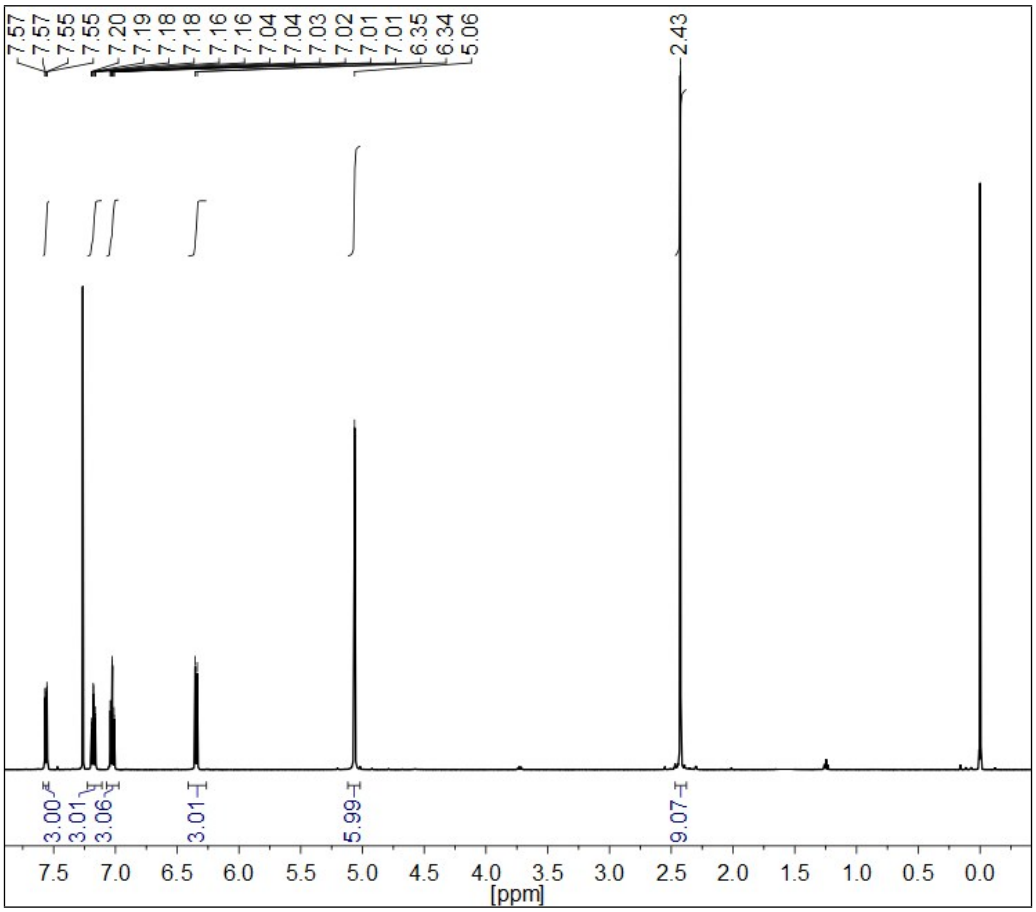


Figure S16a. ^{1}H NMR spectrum of **1** in $CDCl_3$.

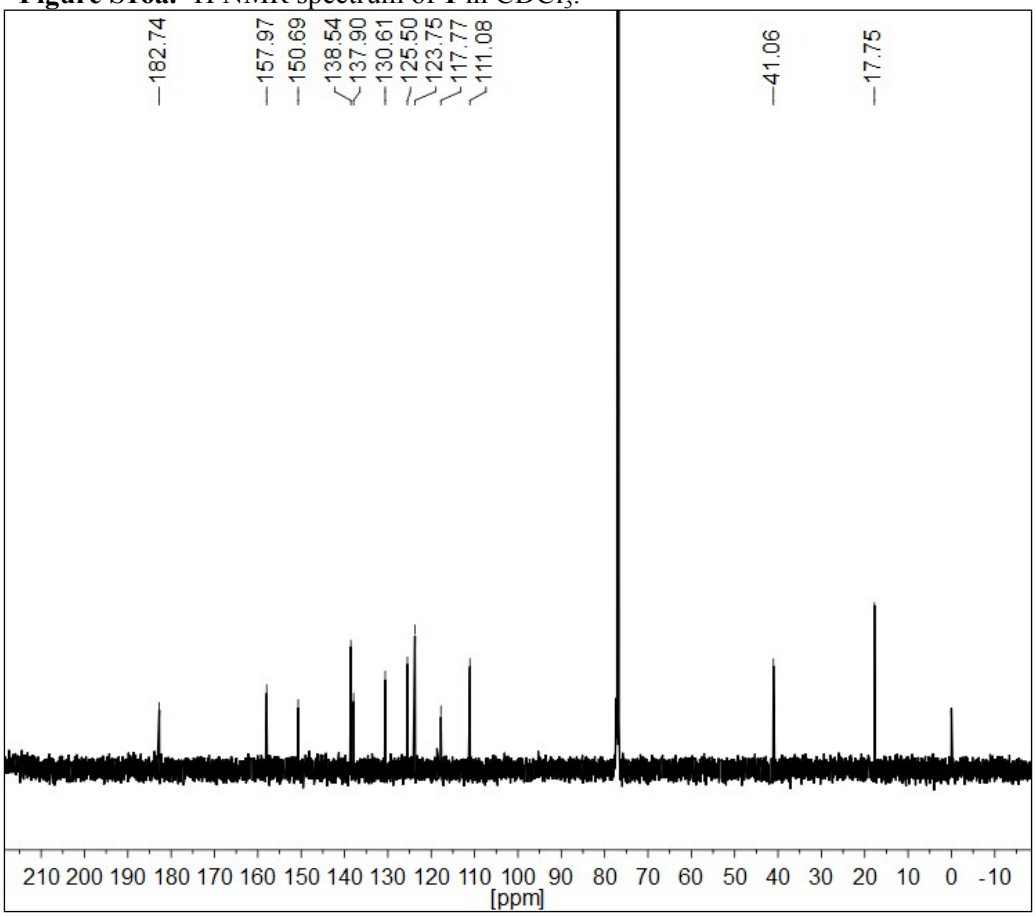


Figure S16b. ^{13}C NMR spectrum of **1** in $CDCl_3$.

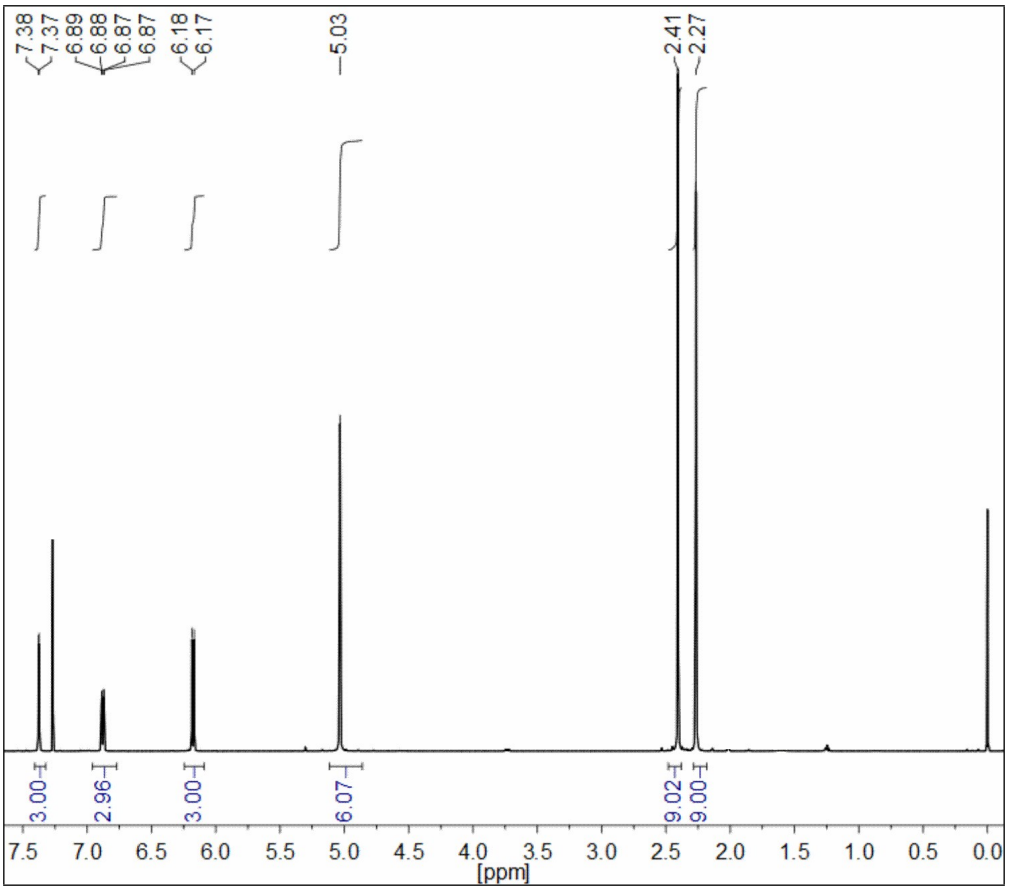


Figure S17a. ^{1}H NMR spectrum of **2** in $CDCl_3$.

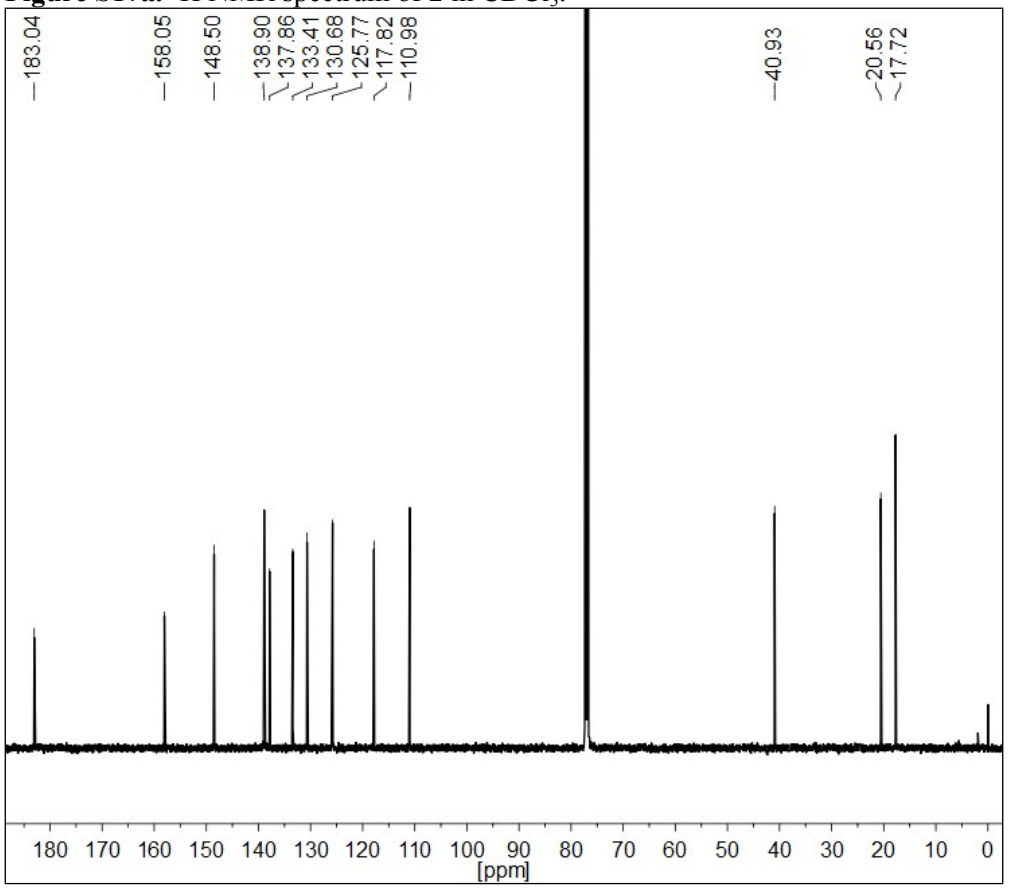


Figure S17b. ^{13}C NMR spectrum of **2** in $CDCl_3$.

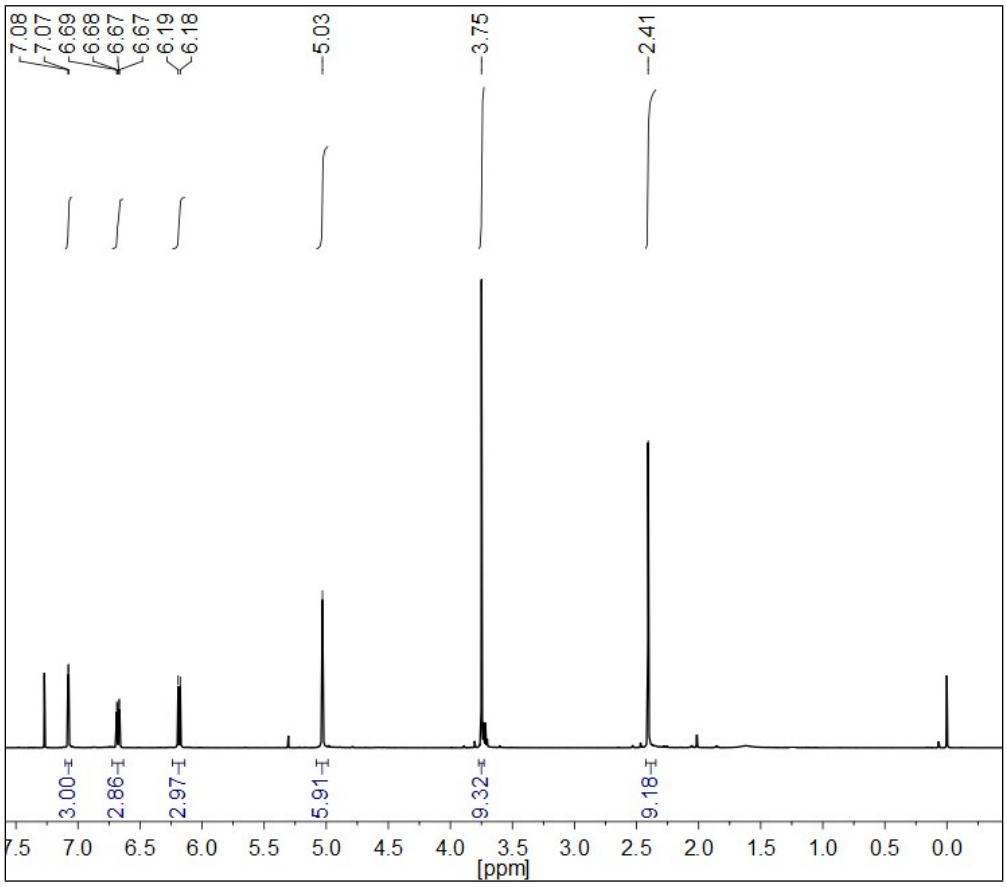


Figure S18a. ^{1}H NMR spectrum of **3** in $CDCl_3$.

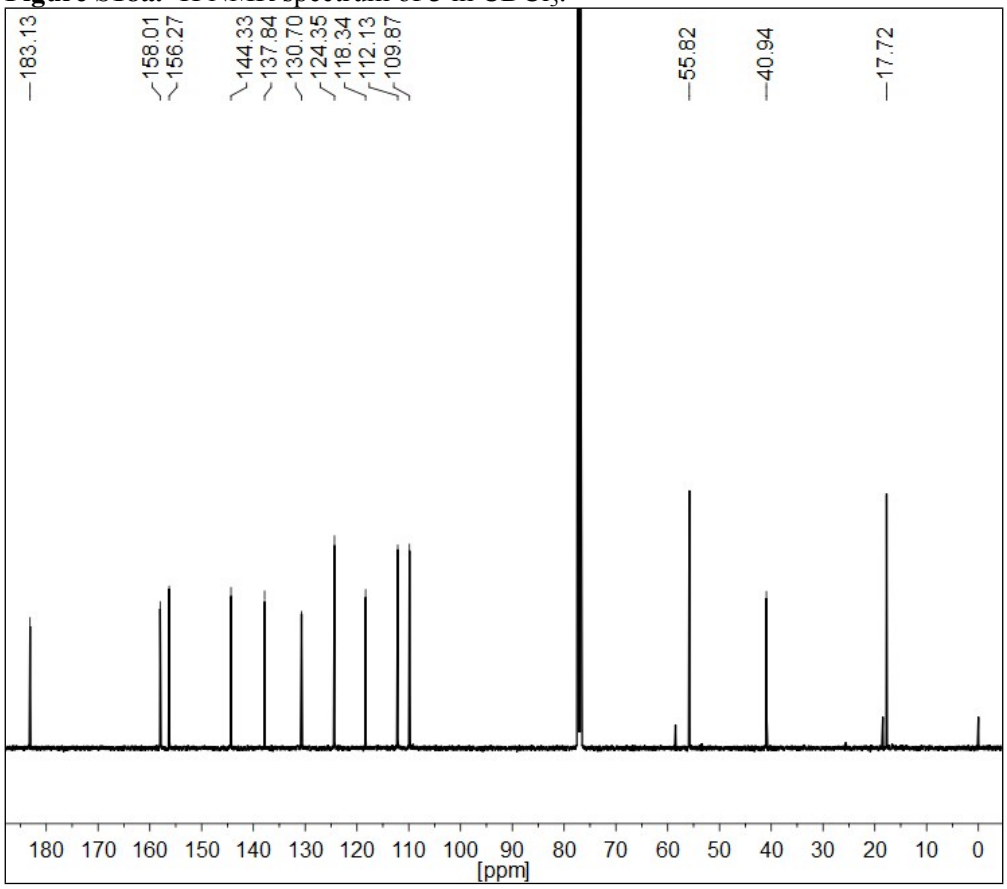


Figure S18b. ^{13}C NMR spectrum of **3** in $CDCl_3$.

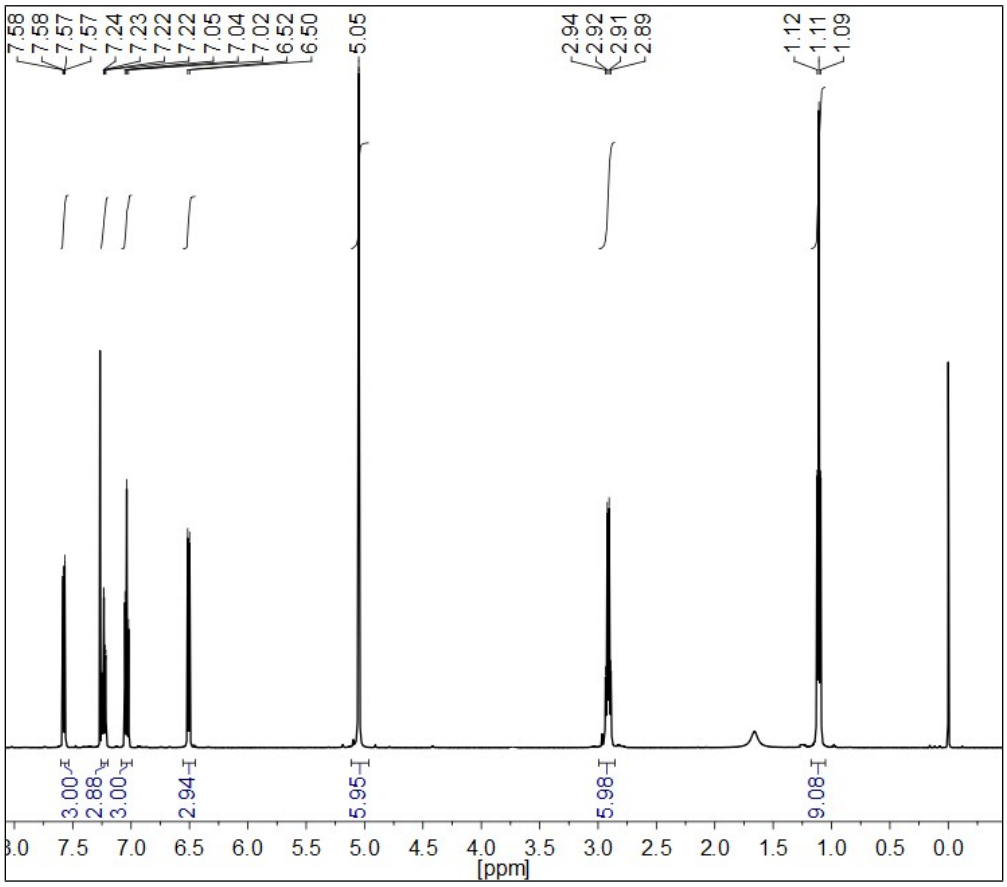


Figure S19a. ^{1}H NMR spectrum of **4** in $CDCl_3$.

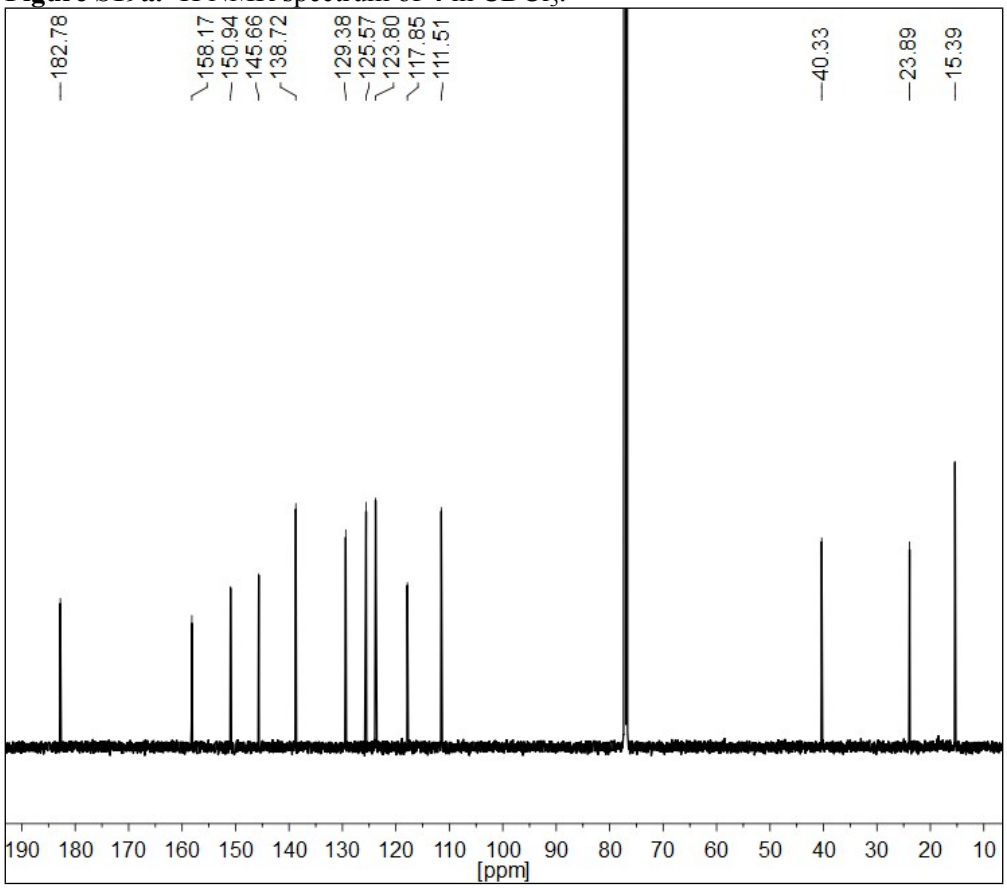


Figure S19b. ^{13}C NMR spectrum of **4** in $CDCl_3$.

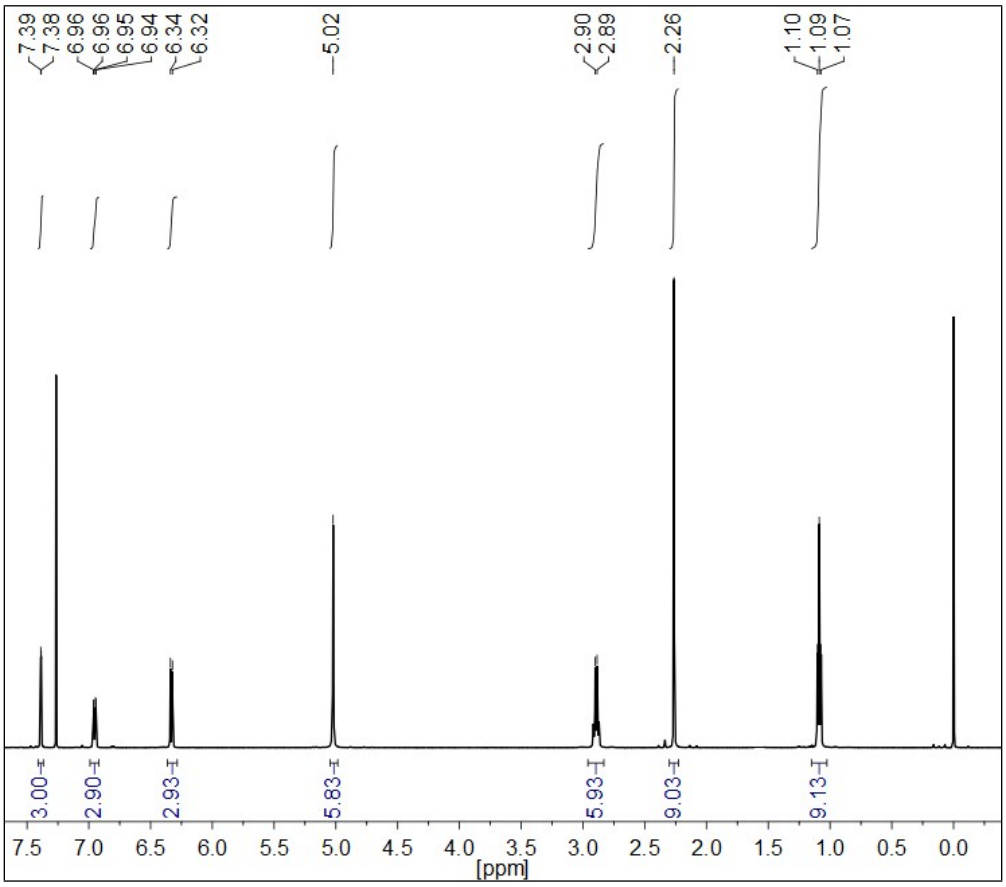


Figure S20a. ^{1}H NMR spectrum of **5** in $CDCl_3$.

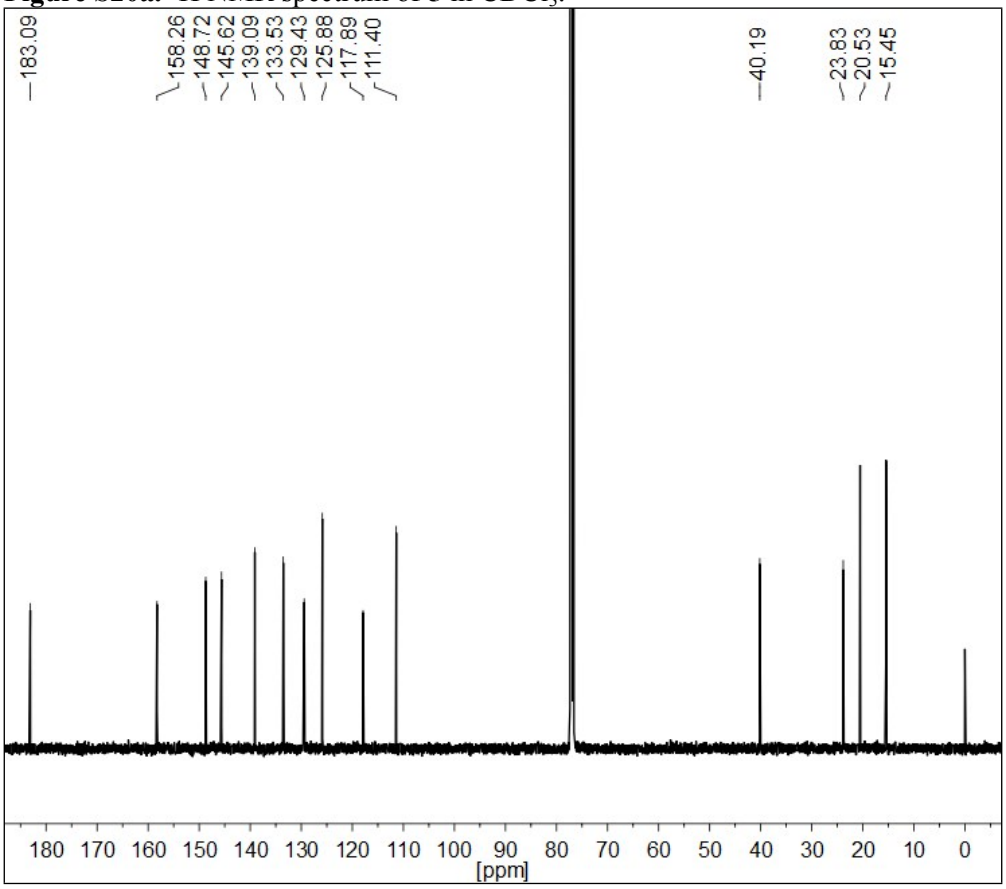


Figure S20b. ^{13}C NMR spectrum of **5** in $CDCl_3$.

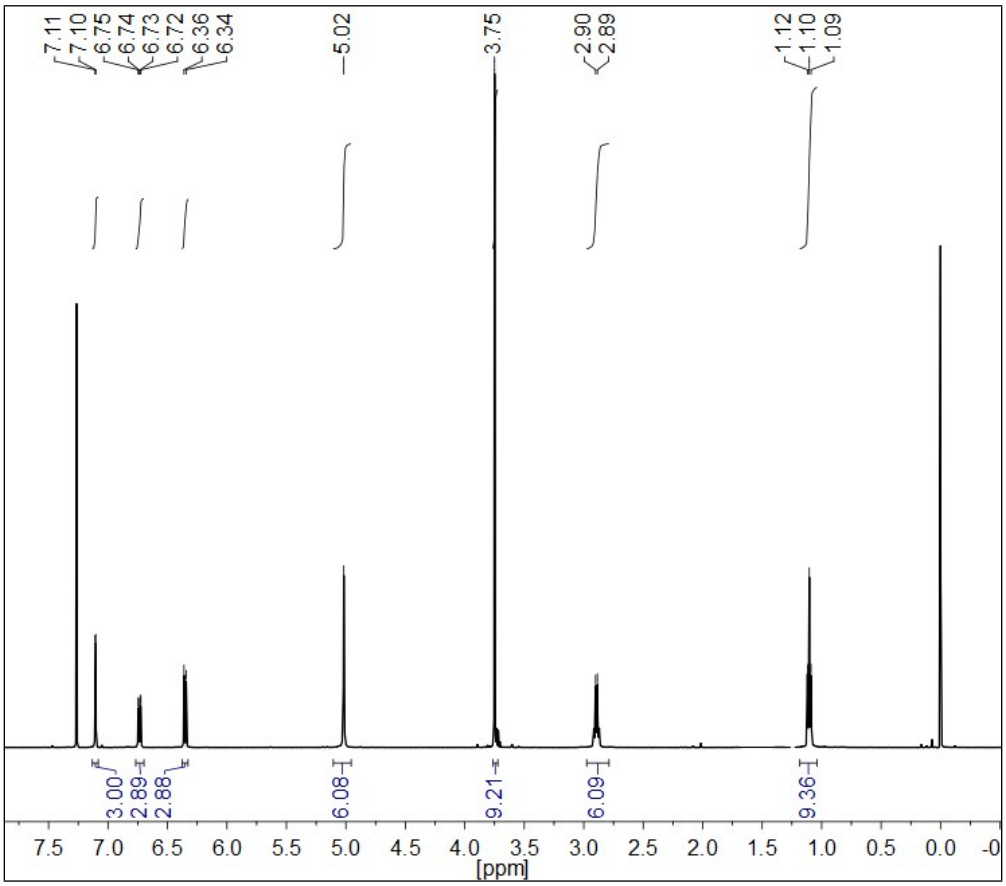


Figure 21a. ^{1}H NMR spectrum of **6** in $CDCl_3$.

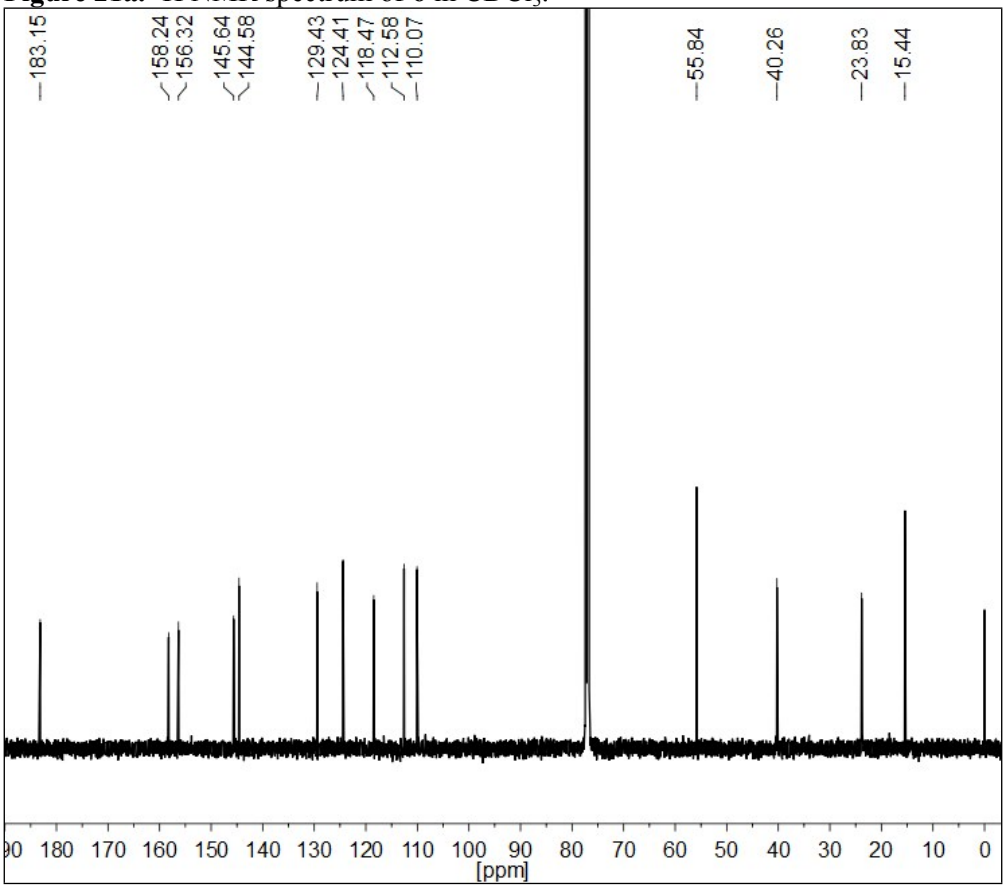
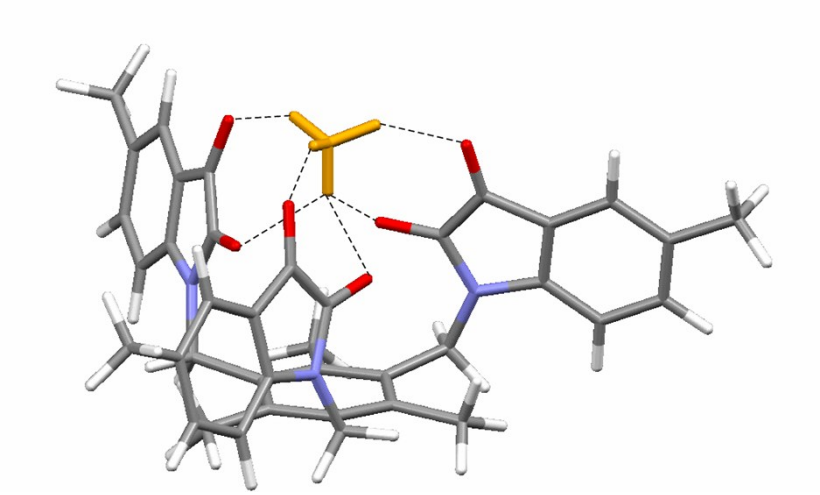


Figure S21b. ^{13}C NMR spectrum of **6** in $CDCl_3$.

a)



b)

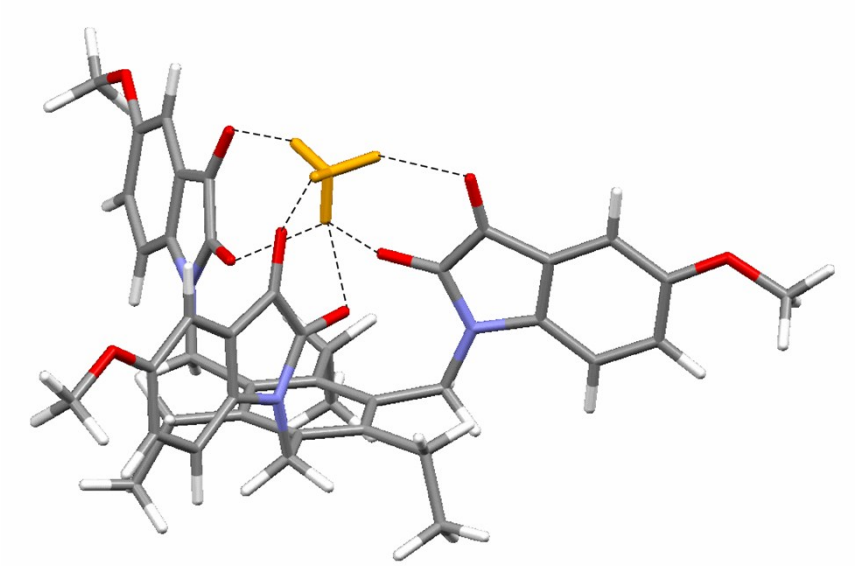


Figure S22. Energy-minimized structure of the 1:1 complex between **2** (a) or **6** (b) and NH_4^+ (MacroModel V.8.5, OPLS 2001 force field, MCMM, 50000 steps). Color code: receptor N, blue; O, red; C, gray; NH_4^+ is highlighted in yellow.