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Structural studies of *N*-(methoxysalicylidene)-fluroaniline, *N*-(methoxysalicylidene)-chloroaniline and *N*-(methoxy-salicylidene)-bromoaniline derivatives

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Table S1 Crystal data and structure refinement for **1-F** to **9-F**.

Identification code	**1-F**	**2-F**	**3-F**	**4-F**	**5-F**	**6-F**	**7-F**	**8-F**	**9-F**

Empirical formula	$C_{14}H_{12}FNO_2$	$C_{14}H_{12}FNO_2$	$C_{14}H_{12}FNO_2$	$C_{14}H_{12}FNO_2$	$C_{14}H_{12}FNO_2$	$C_{14}H_{12}FNO_2$	$C_{14}H_{12}FNO_2$	$C_{14}H_{12}FNO_2$	$C_{14}H_{12}FNO_2$
Formula weight	245.25	245.25	245.25	245.25	245.25	245.25	245.25	245.25	245.25
Temperature/K	120(2)	120(2)	120(2)	120.15	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	*Pbca*	$P2_1/c$	$Pna2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a/Å	5.0834(2)	6.2970(8)	20.3838(10)	19.3411(12)	3.8058(3)	13.1230(9)	11.3352(7)	3.8354(3)	28.1425(12)
b/Å	12.4697(5)	25.465(3)	4.6633(2)	4.9865(3)	10.6818(8)	13.2386(9)	12.0366(7)	10.6493(7)	6.9311(3)
c/Å	18.1059(8)	14.3055(14)	12.6117(6)	12.2219(8)	27.574(2)	6.8116(4)	9.3002(6)	27.9772(19)	12.8535(5)
α/°	90	90	90	90	90	90	90	90	90
β/°	90	90	106.7470(10)	90	91.609(2)	103.690(2)	114.1750(10)	90.8060(10)	113.2170(10)
γ/°	90	90	90	90	90	90	90	90	90
Volume/Å^3	1147.71(8)	2294.0(5)	1147.97(9)	1178.73(13)	1120.53(15)	1149.76(13)	1157.61(12)	1142.60(14)	2304.15(17)
Z	4	8	4	4	4	4	4	4	8
ρ_{calc}g/cm^3	1.419	1.420	1.419	1.382	1.454	1.417	1.407	1.426	1.414
μ/mm^{-1}	0.106	0.106	0.106	0.103	0.109	0.106	0.105	0.107	0.106
F(000)	512.0	1024.0	512.0	512.0	512.0	512.0	512.0	512.0	1024.0
Crystal size/mm^3	0.4 × 0.26 × 0.2	0.41 × 0.28 × 0.03	0.44 × 0.3 × 0.16	0.46 × 0.26 × 0.14	0.2 × 0.16 × 0.06	0.38 × 0.24 × 0.18	0.4 × 0.3 × 0.26	0.46 × 0.14 × 0.12	0.42 × 0.32 × 0.3
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.966 to 56.55	5.696 to 51.364	4.174 to 56.564	4.212 to 56.564	2.956 to 51.362	3.194 to 51.354	3.938 to 56.564	2.912 to 52.744	3.15 to 56.562
Index ranges	-6 ≤ h ≤ 6, -16 ≤ k ≤ 16, -24 ≤ l ≤ 24	-7 ≤ h ≤ 7, -31 ≤ k ≤ 29, -17 ≤ l ≤ 17	-27 ≤ h ≤ 27, -6 ≤ k ≤ 6, -16 ≤ l ≤ 16	-25 ≤ h ≤ 25, -6 ≤ k ≤ 6, -16 ≤ l ≤ 16	-4 ≤ h ≤ 4, -13 ≤ k ≤ 13, -33 ≤ l ≤ 33	-16 ≤ h ≤ 15, -14 ≤ k ≤ 16, -6 ≤ l ≤ 8	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -12 ≤ l ≤ 12	-4 ≤ h ≤ 4, -13 ≤ k ≤ 13, -34 ≤ l ≤ 34	-37 ≤ h ≤ 37, -9 ≤ k ≤ 8, -16 ≤ l ≤ 17
Reflections collected	15619	8769	12140	12283	10327	6467	12782	10926	12612
Independent reflections	2845 [R_{int} = 0.0381, R_{sigma} = 0.0259]	2179 [R_{int} = 0.1099, R_{sigma} = 0.1057]	2834 [R_{int} = 0.0291, R_{sigma} = 0.0238]	2930 [R_{int} = 0.0267, R_{sigma} = 0.0217]	2129 [R_{int} = 0.0653, R_{sigma} = 0.0519]	2183 [R_{int} = 0.0359, R_{sigma} = 0.1086]	2872 [R_{int} = 0.0891, R_{sigma} = 0.0525]	2336 [R_{int} = 0.0443, R_{sigma} = 0.0354]	2865 [R_{int} = 0.0333, R_{sigma} = 0.0259]
Data/restraints/parameters	2845/0/168	2179/0/168	2834/0/168	2930/1/168	2129/0/168	2183/0/174	2872/0/168	2336/0/168	2865/0/168
Goodness-of-fit on F^2	1.036	1.110	1.065	1.044	1.025	1.075	1.043	1.035	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0337, wR_2 = 0.0835	R_1 = 0.0845, wR_2 = 0.1122	R_1 = 0.0383, wR_2 = 0.0985	R_1 = 0.0302, wR_2 = 0.0747	R_1 = 0.0514, wR_2 = 0.1096	R_1 = 0.0472, wR_2 = 0.1310	R_1 = 0.0445, wR_2 = 0.1136	R_1 = 0.0499, wR_2 = 0.1097	R_1 = 0.0408, wR_2 = 0.1044
Final R indexes [all data]	R_1 = 0.0427, wR_2 = 0.0900	R_1 = 0.1369, wR_2 = 0.1289	R_1 = 0.0499, wR_2 = 0.1043	R_1 = 0.0351, wR_2 = 0.0776	R_1 = 0.0916, wR_2 = 0.1262	R_1 = 0.0708, wR_2 = 0.1486	R_1 = 0.0642, wR_2 = 0.1249	R_1 = 0.0723, wR_2 = 0.1182	R_1 = 0.0553, wR_2 = 0.1130
Largest diff. peak/hole / e Å^{-3}	0.20/-0.16	0.27/-0.28	0.25/-0.21	0.18/-0.18	0.23/-0.21	0.15/-0.24	0.40/-0.20	0.18/-0.22	0.26/-0.18

Table S2 Crystal data and structure refinement for **1-Cl** to **9-Cl**.

Identification code	**1-Cl**	**2-Cl**	**3-Cl**	**4-Cl**	**5-Cl**	**6-Cl**	**7-Cl**	**8-Cl**	**9-Cl**
Empirical formula	$C_{14}H_{12}ClNO_2$	$C_{14}H_{12}ClNO_2$	$C_{14}H_{12}ClNO_2$	$C_{14}H_{12}ClNO_2$	$C_{14}H_{12}ClNO_2$	$C_{14}H_{12}ClNO_2$	$C_{14}H_{12}NO_2Cl$	$C_{14}H_{12}NO_2Cl$	$C_{14}H_{12}NO_2Cl$
Formula weight	261.70	261.70	261.70	261.70	261.70	261.70	261.70	261.70	261.70
Temperature/K	120(2)	120(2)	120(2)	100(2)	150(2)	100(2)	120(2)	120(2)	120(2)
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Pna*2_1	*C*2/*c*	*P*2_1/*c*	*P*$2_12_12_1$	*C*2/*c*	*Pc*	*P*2_1/*c*	*P*2_1/*c*	*P*2_1/*c*
a/Å	6.4045(2)	22.2996(14)	13.1915(3)	4.9119(2)	14.1997(4)	12.5233(5)	4.8166(4)	5.5216(11)	21.2023(12)
b/Å	14.5211(4)	7.2002(5)	8.2973(2)	12.4251(5)	6.5840(2)	4.4479(2)	21.3693(16)	8.8865(18)	4.6591(3)
c/Å	12.9892(3)	16.4795(11)	11.9180(2)	19.5142(7)	26.2190(7)	11.8828(6)	23.8639(16)	25.127(5)	12.1240(7)
α/°	90	90	90	90	90	90	90	90	90
β/°	90	113.2315(9)	112.5479(12)	90	102.2648(19)	113.577(3)	92.844(3)	95.001(5)	93.615(2)
γ/°	90	90	90	90	90	90	90	90	90
Volume/Å^3	1208.00(6)	2431.4(3)	1204.76(5)	1190.97(8)	2395.29(12)	606.65(5)	2453.2(3)	1228.2(4)	1195.27(12)
Z	4	8	4	4	8	2	8	4	4
ρ_{calc}g/cm^3	1.439	1.430	1.443	1.460	1.451	1.433	1.417	1.415	1.454
μ/mm^{-1}	0.308	0.306	0.309	0.313	0.311	0.307	0.304	0.303	0.312
F(000)	544.0	1088.0	544.0	544.0	1088.0	272.0	1088.0	544.0	544.0
Crystal size/mm^3	0.44 × 0.28 × 0.19	0.42 × 0.41 × 0.32	0.35 × 0.34 × 0.22	0.25 × 0.2 × 0.15	0.67 × 0.49 × 0.20	0.25 × 0.18 × 0.12	0.48 × 0.28 × 0.08	0.28 × 0.08 × 0.03	0.33 × 0.11 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.208 to 56.08	3.976 to 56.176	3.342 to 56.134	3.886 to 56.376	3.18 to 56.016	6.88 to 56.01	2.56 to 52.74	3.254 to 50.06	3.85 to 52.744
Index ranges	-7 ≤ h ≤ 8, -19 ≤ k ≤ 19, -17 ≤ l ≤ 17	-29 ≤ h ≤ 29, -9 ≤ k ≤ 5, -21 ≤ l ≤ 21	-17 ≤ h ≤ 14, -10 ≤ k ≤ 10, -14 ≤ l ≤ 15	-6 ≤ h ≤ 6, -15 ≤ k ≤ 16, -25 ≤ l ≤ 25	-16 ≤ h ≤ 18, -8 ≤ k ≤ 8, -34 ≤ l ≤ 34	-15 ≤ h ≤ 16, -5 ≤ k ≤ 5, -15 ≤ l ≤ 11	-5 ≤ h ≤ 6, -26 ≤ k ≤ 26, -29 ≤ l ≤ 29	-6 ≤ h ≤ 6, -10 ≤ k ≤ 10, -29 ≤ l ≤ 29	-26 ≤ h ≤ 23, -5 ≤ k ≤ 5, -15 ≤ l ≤ 15
Reflections collected	15606	10887	10548	10919	10346	5290	24571	11727	7498
Independent reflections	2912 [R_{int} = 0.0289, R_{sigma} = 0.0224]	2956 [R_{int} = 0.0174, R_{sigma} = 0.0162]	2920 [R_{int} = 0.0271, R_{sigma} = 0.0272]	2927 [R_{int} = 0.0315, R_{sigma} = 0.0309]	2895 [R_{int} = 0.0256, R_{sigma} = 0.0248]	2268 [R_{int} = 0.0247, R_{sigma} = 0.0325]	4976 [R_{int} = 0.0512, R_{sigma} = 0.0409]	2175 [R_{int} = 0.0686, R_{sigma} = 0.0574]	2429 [R_{int} = 0.0277, R_{sigma} = 0.0299]
Data/restraints/parameters	2912/1/168	2956/0/168	2920/0/168	2927/0/169	2895/0/168	2268/2/168	4976/0/335	2175/0/168	2429/0/168
Goodness-of-fit on F^2	1.053	1.037	1.045	1.046	1.051	1.049	1.067	1.074	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0249, wR_2 = 0.0600	R_1 = 0.0296, wR_2 = 0.0788	R_1 = 0.0292, wR_2 = 0.0754	R_1 = 0.0294, wR_2 = 0.0676	R_1 = 0.0352, wR_2 = 0.0856	R_1 = 0.0298, wR_2 = 0.0680	R_1 = 0.0439, wR_2 = 0.0842	R_1 = 0.0648, wR_2 = 0.1683	R_1 = 0.0379, wR_2 = 0.0985
Final R indexes [all data]	R_1 = 0.0273, wR_2 = 0.0612	R_1 = 0.0343, wR_2 = 0.0823	R_1 = 0.0368, wR_2 = 0.0788	R_1 = 0.0352, wR_2 = 0.0697	R_1 = 0.0477, wR_2 = 0.0916	R_1 = 0.0344, wR_2 = 0.0704	R_1 = 0.0619, wR_2 = 0.0892	R_1 = 0.0872, wR_2 = 0.1846	R_1 = 0.0472, wR_2 = 0.1063
Largest diff. peak/hole / e Å^{-3}	0.21/-0.15	0.31/-0.22	0.32/-0.20	0.22/-0.22	0.32/-0.22	0.23/-0.19	0.25/-0.25	0.56/-0.36	0.33/-0.21
Flack parameter	0.028(17)	-	-	0.26(7)	-	0.13(4)	-	-	-

Table S3 Crystal data and structure refinement for **1-Br** to **9-Br**.

Identification code	**1-Br**	**2-Br**	**3-Br**	**4-Br**	**5-Br**	**6-Br**	**7-Br**	**8-Br**	**9-Br 220 K**	**9-Br 120 K**
Empirical formula	$C_{14}H_{12}NO_2Br$	$C_{14}H_{12}NO_2Br$	$C_{14}H_{12}NO_2Br$	$C_{14}H_{12}NO_2Br$	$C_{14}H_{12}NO_2Br$	$C_{14}H_{12}BrNO_2$	$C_{14}H_{12}BrNO_2$	$C_{14}H_{12}NO_2Br$	$C_{14}H_{12}BrNO_2$	$C_{14}H_{12}NO_2Br$
Formula weight	306.16	306.16	306.16	306.16	306.16	306.16	306.16	306.16	306.16	306.16
Temperature/K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	220(2)	120(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Pna*2_1	*C*2/*c*	*P*2_1/*c*	*P*2_1/*c*	*Pca*2_1	*Pc*	*P*$2_12_12_1$	*Pna*2_1	*Pc*	*Cc*
a/Å	6.2974(11)	22.351(3)	13.290(2)	12.538(2)	13.823(4)	12.547(4)	4.8326(10)	6.1895(12)	14.077(3)	27.874(5)
b/Å	14.718(2)	7.3950(11)	8.5162(13)	4.8315(9)	14.140(4)	4.4109(16)	12.544(3)	7.0146(13)	6.8915(15)	6.8640(12)
c/Å	13.367(2)	16.267(3)	11.9068(18)	21.010(4)	6.3118(18)	11.895(4)	20.346(4)	28.557(5)	6.5365(13)	6.4840(12)
α/°	90	90	90	90	90	90	90	90	90	90
β/°	90	112.973(2)	113.514(3)	103.043(3)	90	113.687(5)	90	90	98.320(4)	95.091(4)
γ/°	90	90	90	90	90	90	90	90	90	90
Volume/Å^3	1239.0(4)	2475.4(6)	1235.7(3)	1239.9(4)	1233.7(6)	602.9(4)	1233.4(4)	1239.9(4)	627.5(2)	1235.7(4)
Z	4	8	4	4	4	2	4	4	2	4
ρ_{calc}g/cm^3	1.641	1.643	1.646	1.640	1.648	1.687	1.649	1.640	1.620	1.646
μ/mm^{-1}	3.310	3.314	3.319	3.308	3.324	3.402	3.325	3.308	3.268	3.319
F(000)	616.0	1232.0	616.0	616.0	616.0	308.0	616.0	616.0	308.0	616.0
Crystal size/mm^3	0.26 × 0.18 × 0.07	0.35 × 0.24 × 0.14	0.3 × 0.2 × 0.06	0.45 × 0.13 × 0.1	0.3 × 0.08 × 0.03	0.22 × 0.09 × 0.04	0.32 × 0.06 × 0.02	0.4 × 0.31 × 0.18	0.16 × 0.1 × 0.08	0.16 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.116 to 56.56	3.958 to 54.192	3.342 to 54.204	3.334 to 54.196	2.88 to 54.166	3.544 to 51.354	3.814 to 51.362	5.706 to 52.734	5.85 to 54.202	2.934 to 52.726
Index ranges	-8 ≤ h ≤ 8, -19 ≤ k ≤ 15, -12 ≤ l ≤ 17	-28 ≤ h ≤ 28, -9 ≤ k ≤ 9, -20 ≤ l ≤ 19	-17 ≤ h ≤ 15, -10 ≤ k ≤ 7, -14 ≤ l ≤ 15	-16 ≤ h ≤ 16, -6 ≤ k ≤ 6, -26 ≤ l ≤ 26	-17 ≤ h ≤ 16, -11 ≤ k ≤ 18, -8 ≤ l ≤ 7	-15 ≤ h ≤ 15, -5 ≤ k ≤ 5, -14 ≤ l ≤ 14	-5 ≤ h ≤ 5, -15 ≤ k ≤ 15, -24 ≤ l ≤ 24	-7 ≤ h ≤ 7, -8 ≤ k ≤ 8, -34 ≤ l ≤ 34	-13 ≤ h ≤ 18, -8 ≤ k ≤ 8, -8 ≤ l ≤ 5	-19 ≤ h ≤ 34, -8 ≤ k ≤ 8, -7 ≤ l ≤ 8
Reflections collected	7921	12177	7467	11740	7073	4965	11274	10666	3788	3511
Independent reflections	2339 [R_{int} = 0.0423, R_{sigma} = 0.0483]	2729 [R_{int} = 0.0349, R_{sigma} = 0.0286]	2717 [R_{int} = 0.0356, R_{sigma} = 0.0418]	2732 [R_{int} = 0.0440, R_{sigma} = 0.0370]	2474 [R_{int} = 0.0567, R_{sigma} = 0.0738]	2292 [R_{int} = 0.0596, R_{sigma} = 0.0872]	2345 [R_{int} = 0.0796, R_{sigma} = 0.0669]	2444 [R_{int} = 0.0283, R_{sigma} = 0.0361]	1818 [R_{int} = 0.0485, R_{sigma} = 0.0791]	1623 [R_{int} = 0.0479, R_{sigma} = 0.0708]
Data/restraints/parameters	2339/1/169	2729/0/168	2717/0/168	2732/0/168	2474/1/166	2292/2/166	2345/0/169	2444/1/169	1818/2/169	1623/2/169
Goodness-of-fit on F^2	1.023	1.030	1.026	1.075	1.008	1.082	1.104	1.089	1.015	1.119
Final R indexes [I>=2σ (I)]	R_1 = 0.0291, wR_2 = 0.0552	R_1 = 0.0250, wR_2 = 0.0543	R_1 = 0.0290, wR_2 = 0.0625	R_1 = 0.0311, wR_2 = 0.0638	R_1 = 0.0382, wR_2 = 0.0720	R_1 = 0.0558, wR_2 = 0.1267	R_1 = 0.0418, wR_2 = 0.0721	R_1 = 0.0188, wR_2 = 0.0422	R_1 = 0.0370, wR_2 = 0.0694	R_1 = 0.0418, wR_2 = 0.0922
Final R indexes [all data]	R_1 = 0.0407, wR_2 = 0.0589	R_1 = 0.0358, wR_2 = 0.0576	R_1 = 0.0412, wR_2 = 0.0669	R_1 = 0.0475, wR_2 = 0.0685	R_1 = 0.0669, wR_2 = 0.0827	R_1 = 0.0670, wR_2 = 0.1327	R_1 = 0.0632, wR_2 = 0.0779	R_1 = 0.0212, wR_2 = 0.0431	R_1 = 0.0642, wR_2 = 0.0781	R_1 = 0.0492, wR_2 = 0.0960
Largest diff. peak/hole / e Å^{-3}	0.35/-0.33	0.36/-0.38	0.36/-0.37	0.45/-0.48	0.52/-0.43	2.10/-1.70	0.48/-0.85	0.31/-0.31	0.43/-0.46	1.00/-0.57

Table S4 C-H···O interactions in **1-F** to **9-F**.

Compound	Interaction	H···O(Å)	C···O (Å)	C-H···O (°)
1-F	C13-H13···O1^{i}	2.494	3.329(3)	147
2-F	C12-H12···O1^{ii}	2.490	3.438(5)	176
	C14-H14···O2^{iii}	2.572	3.405(4)	147
3-F	C1-H1B···O1^{iv}	2.516	3.471(2)	165
	C6-H6···O2^{v}	2.624	3.487(2)	151
4-F	C6-H6···O1^{vi}	2.690	3.470(3)	140
	C8-H8···O1^{vi}	2.665	3.436(2)	139
5-F	C1-H1B···O1^{vii}	2.608	3.490(3)	150
6-F	C1-H1B···O2^{viii}	2.621	3.537(2)	156
	C10-H10···O2^{ix}	2.533	3.383(2)	149
	C12-H12···O1^{x}	2.383	3.310(3)	165
7-F	C13-H13···O1^{xi}	2.486	3.400(2)	161
	C13-H13···O2^{xi}	2.671	3.257(2)	120
	C14-H14···O2^{xi}	2.698	3.282(2)	120
8-F	C1-H1A···O1^{xii}	2.641	3.531(3)	151
9-F	C10-H10···O2^{xiii}	2.605	3.500(2)	157
	C13-H13···O1^{xiv}	2.555	3.432(2)	154

(i) 1-x, -½+y, 3/2-z, (ii) 3/2-x, -½+y, +z, (iii) 1+x, +y, +z, (iv) 1-x, -½+y, 3/2-z, (v) +x, -½-y, ½+z, (vi) 3/2-x, ½+y, ½+z, (vii) –x, -y, 1-z, (viii) –x, 1-y, 1-z, (ix) +x, +y, -1+z, (x) 1+x, +y, +z, (xi) –x, 1-y, -z, (xii) 1-x, 1-y, -z, (xiii) +x, -1+y, +z, (xiv) –½+x, ½-y, -½+z

Table S5 C-H···O interactions in **1-Cl** to **9-Cl**.

Compound	Interaction	H···O(Å)	C···O (Å)	C-H···O (°)
1-Cl	C13-H13···O1^{i}	2.576	3.497 (3)	164
	C13-H13···O2^{i}	2.639	3.379(3)	135
2-Cl	C3-H3···O2^{ii}	2.756	3.705(2)	177
	C5-H5···O1^{iii}	2.710	3.481(2)	139
	C11-H11···O1^{iv}	2.752	3.564(2)	144
3-Cl	C8-H8···O2^{v}	2.520	3.458(1)	169
	C14-H14···O2^{v}	2.628	3.443(1)	144
	C12-H12···O1^{vi}	2.704	3.242(2)	117
4-Cl	C1-H1A···O2^{vii}	2.606	3.445(3)	146
	C13-H13···O1^{viii}	2.596	3.324(3)	135
5-Cl	C1-H1C···O1^{ix}	2.624	3.350(2)	131
6-Cl	C6-H6···O2^{x}	2.712	3.476(3)	138
	C8-H8···O2^{x}	2.476	3.289(3)	144
7-Cl	C6-H6···O3^{xi}	2.718	3.596(3)	154
	C10-H10···O4^{xii}	2.578	3.199(3)	123
	C11-H11···O4^{xii}	2.630	3.220(3)	121
	C25-H25···O1^{xiii}	2.561	3.476(3)	162
8-Cl	C1-H1C···O1^{xiv}	2.653	3.431(5)	137
	C11-H11···O2^{xv}	2.613	3.336(5)	133
9-Cl	C1-H1B···O1^{xvi}	2.485	3.432(2)	162
	C3-H3···O1^{xvii}	2.633	3.449(2)	144
	C6-H6···O2^{xviii}	2.612	3.431(2)	145
	C8-H8···O2^{xviii}	2.567	3.398(2)	146

(i) 2-x, 1-y, -½+z, (ii) 1-x, -y, 1-z, (iii) ½-x, ½+y, ½-z, (iv) ½+x, ½+y, +z, (v) +x, 3/2-y, -½+z, (vi) -1+x, 3/2-y, -½+z, (vii) -1+x, +y, +z, (viii) 1-x, -½+y, ½-z, (ix) ½-x, 3/2-y, 1-z, (x) +x, 1-y, -½+z, (xi) 2-x, 1-y, 1-z, (xii) 1-x, 1-y, 1-z (xiii) 1-x, -½+y, 3/2-z, (xiv) 2-x, 1-y, 1-z, (xv) –x, -½+y, 3/2-z, (xvi) –x, -½+y, ½-z, (xvii) x, -½-y, ½+z, (xviii) x, ½-y, -½+z

Table S6 C-H···O interactions in **1-Br** to **9-Br**.

Compound	Interaction	H···O(Å)	C···O (Å)	C-H···O (°)
1-Br	C13-H13···O1^{i}	2.587	3.498(5)	161
	C13-H13···O2^{i}	2.647	3.413(5)	138
2-Br	C5-H5···O1^{ii}	2.674	3.447(2)	139
3-Br	C8-H8···O2^{iii}	2.517	3.457(3)	170
4-Br	C13-H13···O1^{iv}	2.692	3.219(3)	116
5-Br	C14-H14···O2^{v}	2.611	3.523(7)	161
6-Br	C6-H6···O2^{vi}	2.711	3.326(13)	144
	C8-H8···O2^{vi}	2.508	3.322(13)	144
7-Br	C1-H1A···O2^{vii}	2.654	3.437(9)	137
	C11-H11···O1^{viii}	2.428	3.296(9)	152
8-Br	C1-H1A···O1^{ix}	2.704	3.488(4)	137
9-Br	C10-H10···O2^{x}	2.421	3.247(11)	145

(i) 1-x, 1-y, ½+z, (ii) 3/2-x, -½+y, ½-z, (iii) +x, ½-y, -½+z, (iv) 1-x, 1-y, -z, (v) +x, +y, 1+z, (vi) x, -y, ½+z, (vii) -1+x, +y, +z, (viii) 1-x, ½+y, 3/2-z, (iv) ½+x. ½-y, +z, (x) +x, +y, -1+z

Table S7 C-H···F short contacts in **1-F** to **9-F**.

Compound	Interaction	H···F(Å)	C···F (Å)	C-H···F (°)
1-F	C5-H5···F1^{i}	2.590	3.250(2)	127
2-F	C11-H11···F1^{ii}	2.557	3.500(4)	172
	C5-H5···F1^{iii}	2.583	3.395(4)	144
3-F	C14-H14···F1^{iv}	2.586	3.063(1)	111
4-F	C13-H13···F1^{v}	2.639	3.398(3)	137
5-F	C1-H1C···F1^{vi}	2.460	3.439(3)	177
	C12-H12···F1^{vii}	2.627	3.449(3)	145
6-F	C1-H1C···F1B^{viii}	2.430	3.106(3)	127
Disordered F				
	C14-H14···F1A^{ix}	2.579	3.243(3)	127
7-F	C4-H4···F1^{x}	2.472	3.421(2)	178
8-F	C13-H13···F1^{xi}	2.634	3.310(2)	130
9-F	C4-H4···F1^{xii}	2.612	3.513(2)	159
	C1-H1C···F1B^{xiii}	2.582	3.321(2)	132

(i) 2-x, -½+y, 3/2-z, (ii) 1-x, 1-y, 1-z, (iii) ½+x, 3/2-y, 1-z, (iv) +x, ½-y, ½+z, (v) 1-x, 3-y, ½+z, (vi) –x, ½+y, ½-z, (vii) 1-x, -y, -z, (viii) -1+x, +y, -1+z, (ix) +x, +y, 1+z, (x) 1+x, 3/2-y, 3/2+z , (xi) 2-x, 1-y, 1-z, (xii) ½+x, ½-y, ½+z, (xiii) ½+x, -½-y, ½+z.

Table S8 π-π interactions identified within the 27 compounds studied.

Compound	Plane 1	Plane 2	Centroid-centroid distance (Å)	Shift distance (Å)
5-F	C2-C7	C2-C7^{i}	3.806	1.626
	C9-C14	C9-C14^{i}	3.806	1.699
6-F	C2-C7	C2-C7^{ii}	3.804	1.537
	C9-C14	C9-C14^{iii}	3.957	1.996
8-F	C2-C7	C2-C7^{i}	3.835	1.683
	C9-C14	C9-C14^{i}	3.835	1.658
1-Cl	C2-C7	C9-C14^{iv}	3.641	1.263
3-Cl	C2-C7	C2-C7^{iii}	3.825	1.789
5-Cl	C2-C7	C9-C14^{v}	3.750	1.339
1-Br	C2-C7	C9-C14^{iv}	3.672	1.471
3-Br	C2-C7	C2-C7^{vi}	3.808	1.676
5-Br	C2-C7	C9-C14^{vii}	3.867	1.314

(i) -1+x, +y, +z and 1+x, +y, +z, (ii) –x, 1-y, 1-z, (iii) 1-x, 1-y, 1-z, (iv) -1+x, +y, +z, (v) 1-x, +y, ½-z, (vi) 2-x, -y, 1-z, (vii) 1-x, 1-y, -½+z

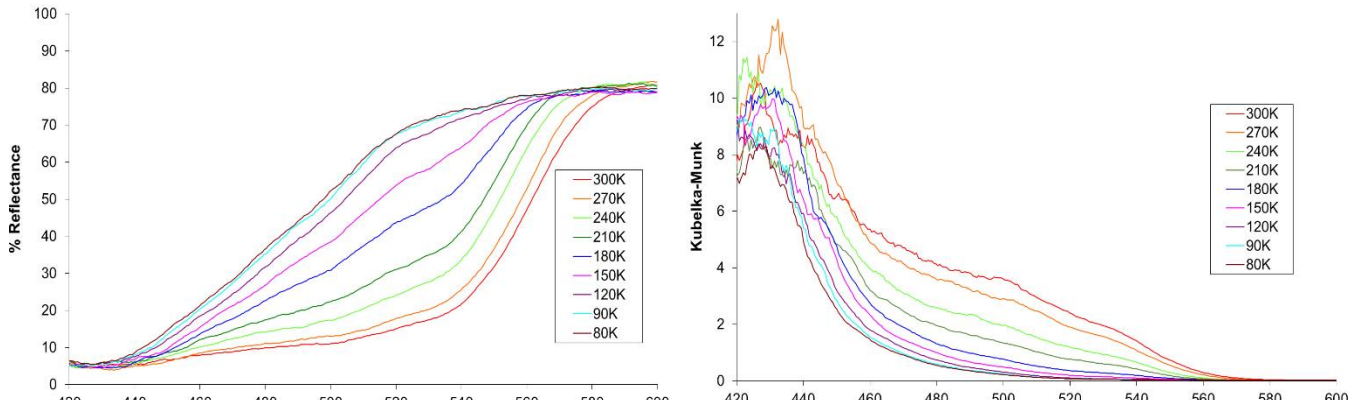


Figure S1 Variable temperature diffuse reflectance spectra between 300 and 80K for **1-Br**, illustrated as wavelength versus (left) % reflectance and (right) the Kubelka-Munk function.

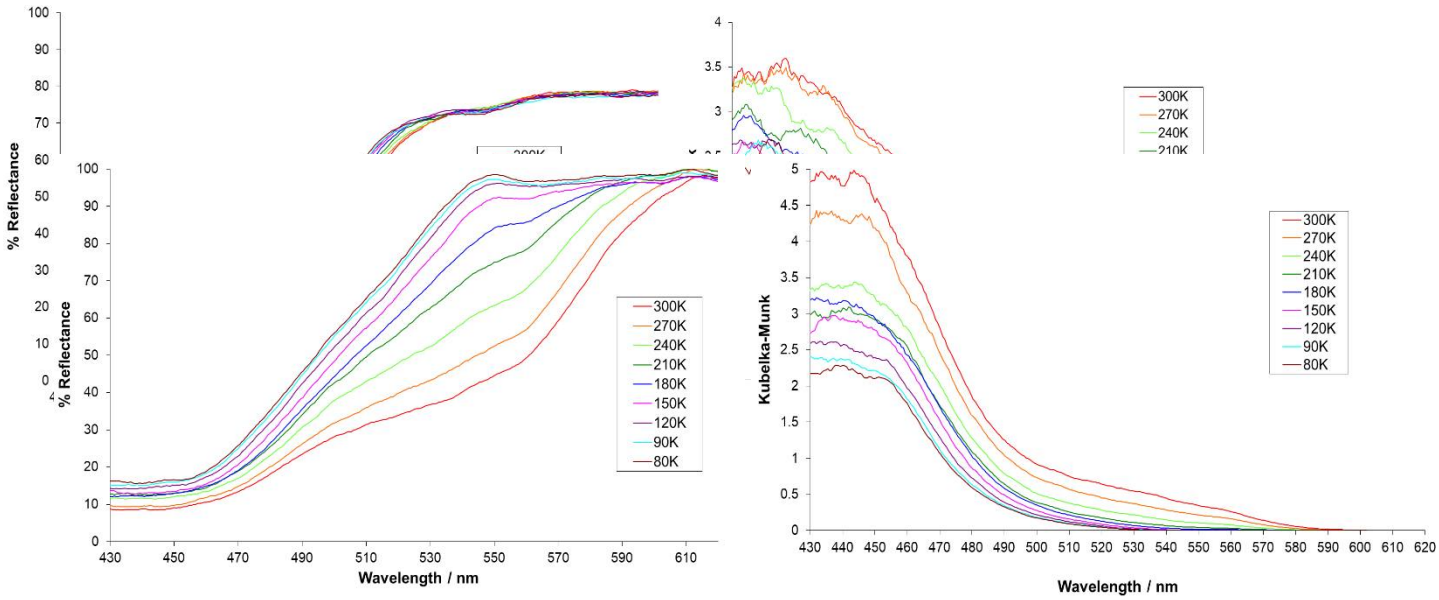


Figure S2 Variable temperature diffuse reflectance spectra between 300 and 80K for **2-Br**, illustrated as wavelength versus (left) % reflectance and (right) the Kubelka-Munk function.

Figure S3 Variable temperature diffuse reflectance spectra between 300 and 80K for **3-Br**, illustrated as wavelength versus (left) % reflectance and (right) the Kubelka-Munk function.

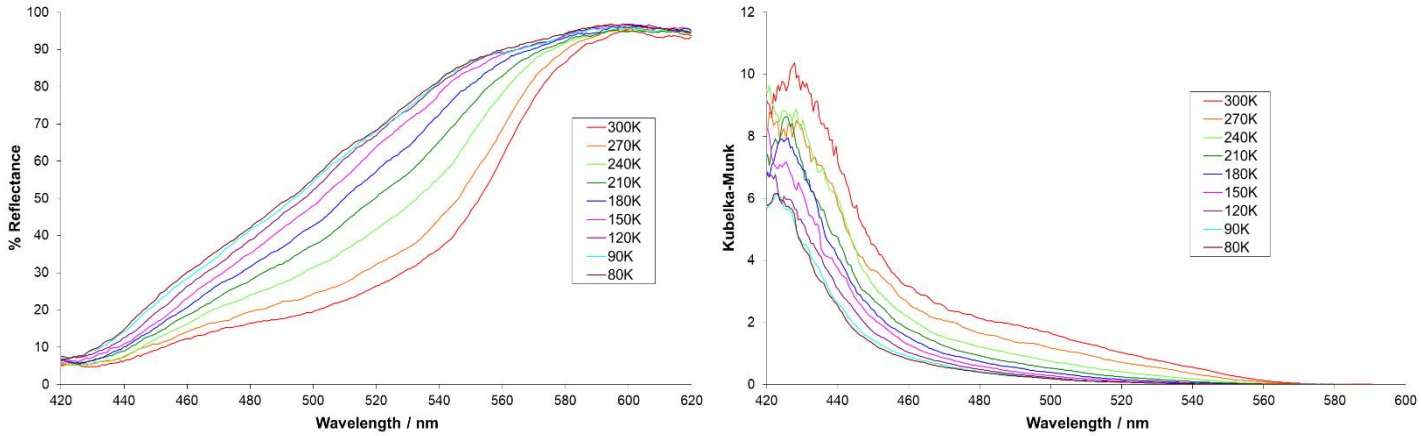


Figure S4 Variable temperature diffuse reflectance spectra between 300 and 80K for **4-Br**, illustrated as wavelength versus (left) % reflectance and (right) the Kubelka-Munk function.

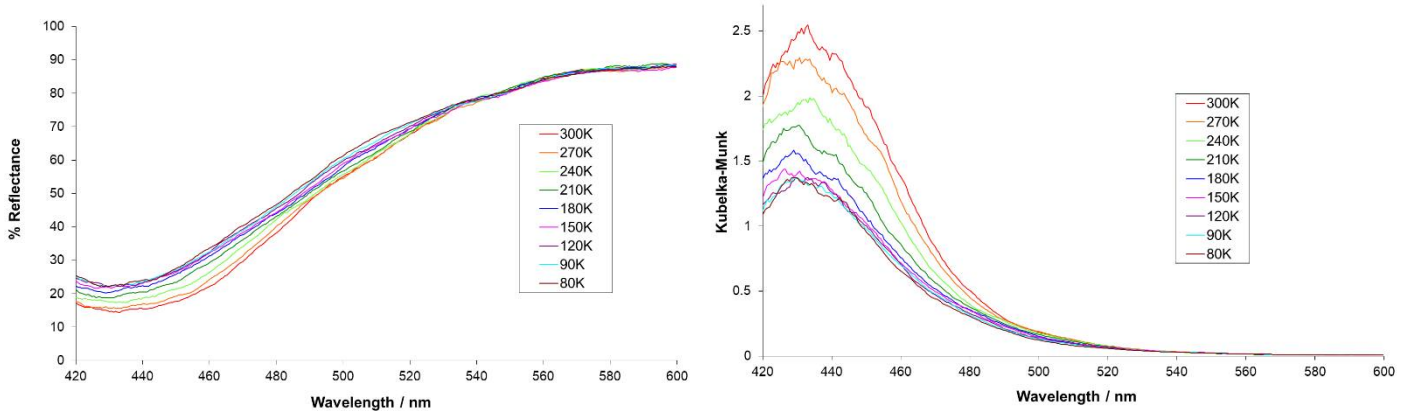


Figure S5 Variable temperature diffuse reflectance spectra between 300 and 80K for **5-Br**, illustrated as wavelength versus (left) % reflectance and (right) the Kubelka-Munk function.

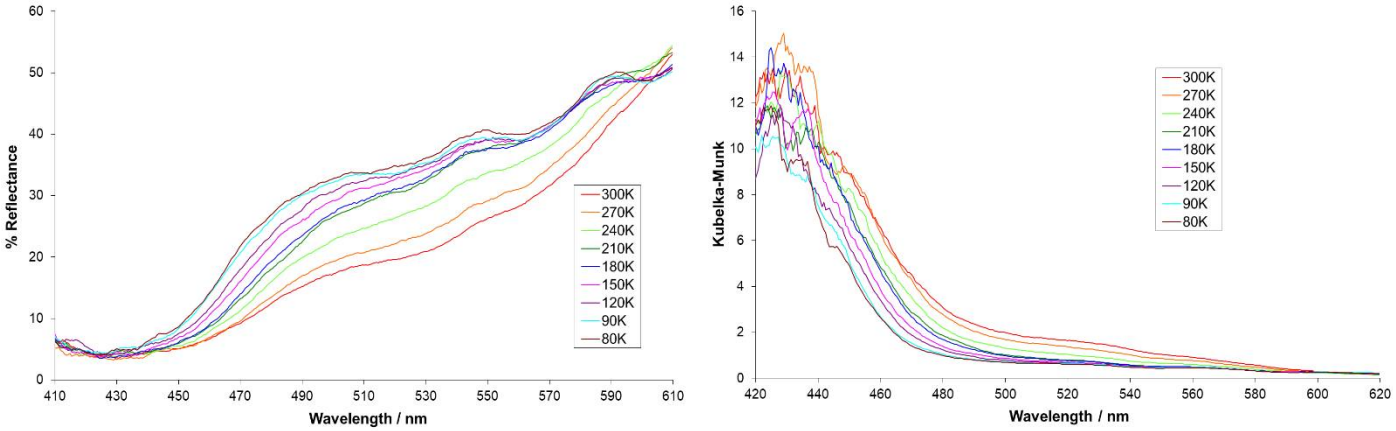


Figure S6 Variable temperature diffuse reflectance spectra between 300 and 80K for **6-Br**, illustrated as wavelength versus (left) % reflectance and (right) the Kubelka-Munk function.

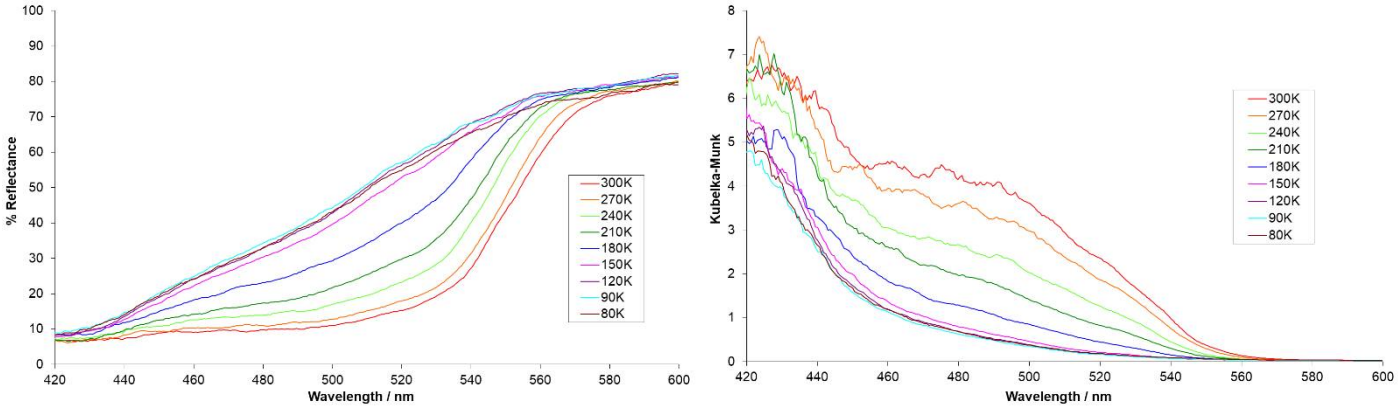


Figure S7 Variable temperature diffuse reflectance spectra between 300 and 80K for **7-Br**, illustrated as wavelength versus (left) % reflectance and (right) the Kubelka-Munk function.

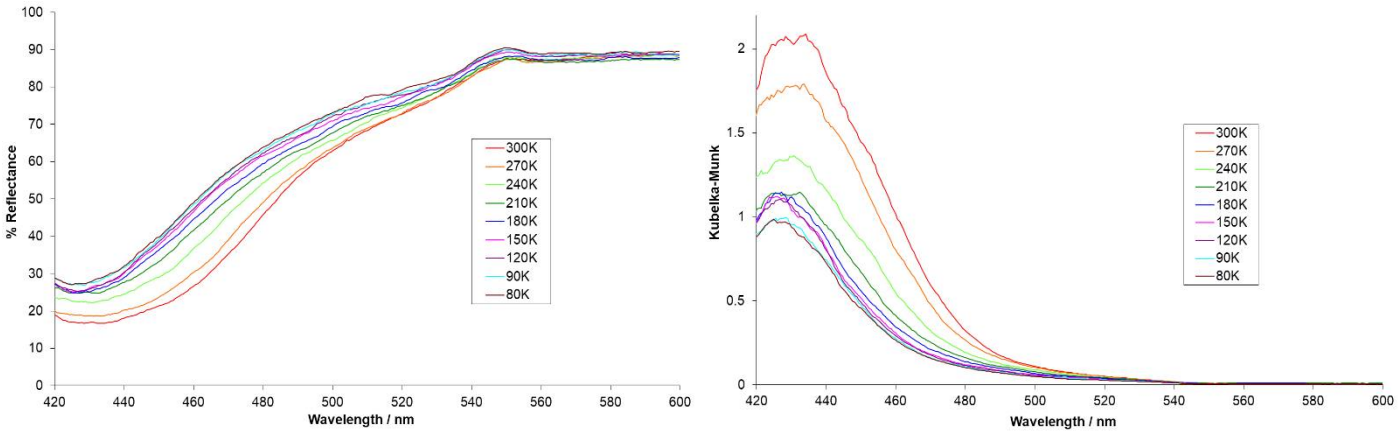
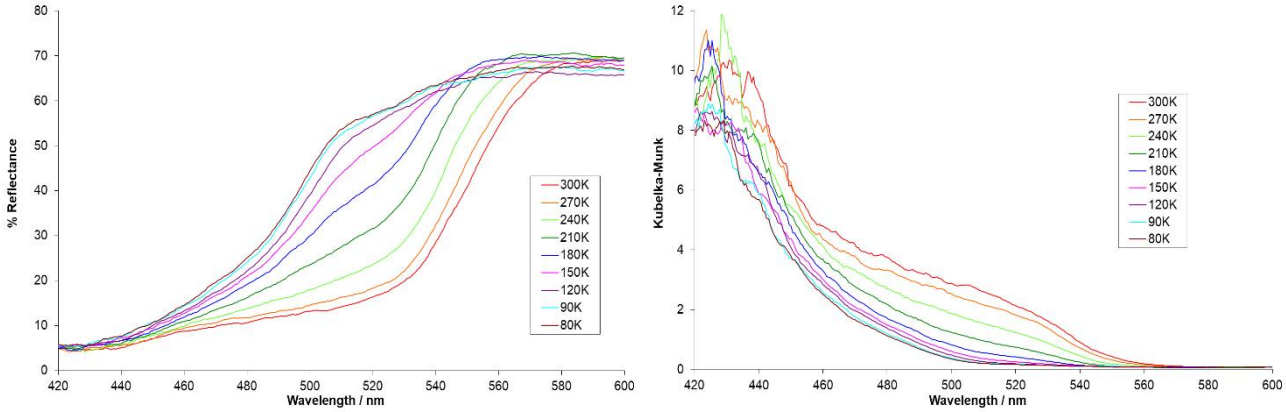


Figure S8 Variable temperature diffuse reflectance spectra between 300 and 80K for **8-Br**, illustrated as wavelength versus (left) % reflectance and (right) the Kubelka-Munk function.

Figure S9 Variable temperature diffuse reflectance spectra between 300 and 80K for **9-Br**, illustrated as wavelength



versus (left) % reflectance and (right) the Kubelka-Munk function.