Electronic Supplementary Material (ESI) for CrystEngComm.

Influence of halogen size on the supramolecular and energetical landscape of the THF solvates of the halogen derivatives of dianthranilide

Bartosz Bieszczad[1], Sylwia Pawlędzio[2], Katarzyna Polak[2], Jerzy Antonowicz[3], Adam Mieczkowski[1], Damian Trzybiński[2,*]

[1]Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Pawińskiego 5a, 02-106 Warsaw, Poland
[2]Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland
[3]Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

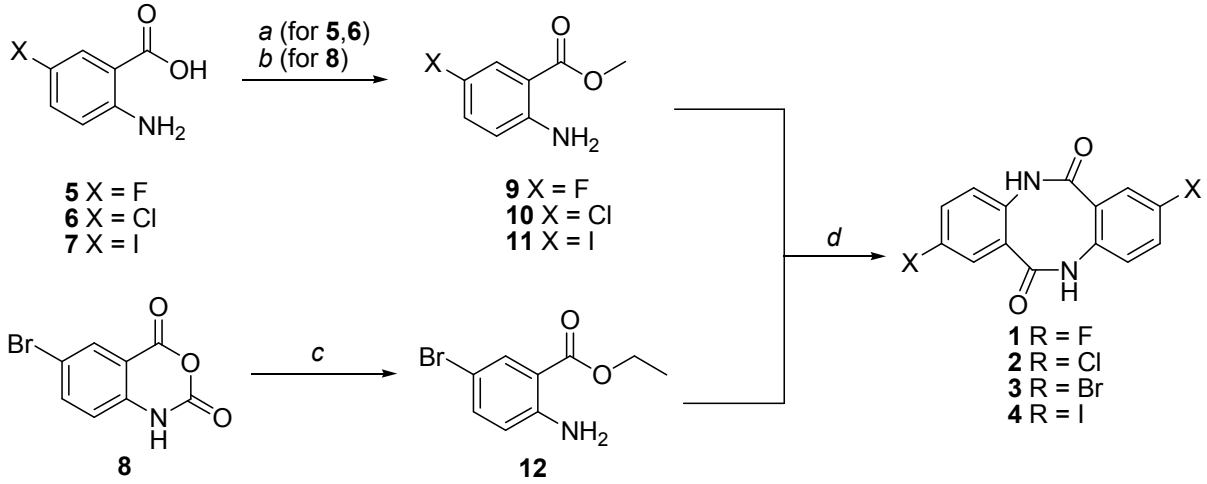
E-mail: dtrzybinski@cnbc.uw.edu.pl

Electronic Supporting Information

EXPERIMENTAL

Commercially available chemicals were of reagent grade and used as received. The reactions were monitored by thin layer chromatography (TLC), using silica gel plates (Kieselgel $60F_{254}$, E. Merck, Darmstadt, Germany). Column chromatography was performed on silica gel 60 M (0.040–0.063 mm, E. Merck, Darmstadt, Germany). Melting points are uncorrected and were measured on a Büchi (New Castle, DE, USA) Melting Point B-540 apparatus. The ^{1}H and ^{13}C-NMR spectra, in $CDCl_3$ and DMSO-d_6, were recorded at the Department of Chemistry, University of Warsaw, using the Bruker AVANCE III (Billerica, MA, USA) 300 MHz spectrometer; shift values in parts per million are relative to the $SiMe_4$ internal reference. The resonance assignments were based on peak integration, peak multiplicity, and 2D correlation experiments. Multiplets were assigned as bs (broad singlet), s (singlet), d, (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), t (triplet), q (quartet) and m (multiplet). High resolution mass spectra were performed by the Laboratory of Mass Spectrometry, Institute of Biochemistry and Biophysics PAS, on a LTQ Orbitrap Velos instrument, Thermo Scientific (Waltham, MA, USA).

1. The synthesis of 5*H*,11*H*-dibenzo[*b,f*][1,5]diazocine-6,12-dione derivatives 1-4.



Scheme S1. The synthesis of 5*H*,11*H*-dibenzo[*b,f*][1,5]diazocine-6,12-diones 1-4: *a*. CH_3OH, H_2SO_4, rfx., 24 h; *b*. CH_3I, K_2CO_3, acetone, rfx., 3 h; *c*. CH_3CH_2ONa, CH_3CH_2OH, rfx., 3 h; *d*. NaH, THF, rfx., 24 h.

1.1. The synthesis of anthranilic esters

The synthesis of methyl 5-fluoroanthranilate (9) and methyl 5-chloroanthranilate (10).

To the stirred suspension of 5-fluoroanthranilic acid (5) (1.55 g, 10.00 mmol, 1 eq.) or 5-chloroanthranilic acid (6) (1.72 g, 10.00 mmol, 1 eq.) in methanol (50 ml), sulphuric acid (4 ml) was added dropwise and obtained solution was refluxed for 24h. The excess of methanol was evaporated, resulting oil was poured into water (100 ml), and solid sodium hydroxide was added until pH reached 8. Obtained solution was extracted with ethyl acetate (3 x 50 ml), combined organic layers were washed with water (100 ml), brine (50 ml) and dried over $MgSO_4$. Evaporation of solvent gave pure products 9 and 10.

Methyl 5-fluoroanthranilate (9) - yellow oil, yield: 0.96 g (57 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, J_{H-H} = 3.2 Hz, J_{H-F} = 9.6 Hz, 1H), 7.03 (ddd, J_{H-F} = 7.6 Hz, J_{H-H} = 3.2, 9.0 Hz, 1H), 6.61 (dd, J_{H-F} = 4.5 Hz, J_{H-H} = 9.0 Hz, 1H), 5.58 (bs, 2H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8 (d, J_{C-F} = 2.9 Hz), 154.0 (d, J_{C-F} = 234.6 Hz), 147.1 (d, J_{C-F} = 1.43 Hz), 122.2 (d, J_{C-F} = 23.5 Hz), 117.9 (d, J_{C-F} = 7.1 Hz), 116.3 (d, J_{C-F} = 23.2 Hz), 110.8 (d, J_{C-F} = 6.7 Hz), 51.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -128.37 (ddd, J_{F-H} = 4.5, 7.6, 9.6 Hz); HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_8H_8FNO_2$: 170.06118, found: 170.06095;

Methyl 5-chloroanthranilate (10) – yellow oil, solidified during storage, m.p.: 70.0-70.5 °C, yield: 1.17 g (63 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.7 Hz, 1H), 7.19 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.59 (d, *J* = 9.0 Hz, 1H), 5.73 (bs, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 149.1, 134.2, 130.5, 120.7, 118.1, 111.6, 51.9; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_8H_8ClNO_2$: 186.03163, 188.02868, found: 186.03171, 188.02870;

Synthesis of methyl 5-iodoanthranilate (11)

To the solution of 5-iodoanthranilic acid (7) (4.00 g, 15.21 mmol, 1 eq.) in acetone (100 ml) potassium carbonate (0.84 g, 6.08 mmol, 0.4 eq.) was added, then methyl iodide (1.94 g, 13.69mmol, 0.9eq) was added dropwise. Resulting mixture was refluxed for 3h, then solvent was evaporated, residue was treated with water (100 ml), and extracted with ethyl acetate (3 x 50 ml). Combined organic layers were washed with water (100 ml), brine (50 ml) and dried with $MgSO_4$. Crude product was purified by column chromatography using cyclohexane : ethyl acetate (9 : 1) as eluent. Yellow oil, solidified during storage, m.p.: 83.5-84.0 °C, yield: 1.73 g (41 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.4 Hz, 1H), 7.47 (dd, *J* = 2,4, 8.7 Hz, 1H), 6.44 (d, *J* = 8.7 Hz, 1H), 5.76 (bs, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 149.8, 142.2, 139.5, 118.8, 112.8, 75.9, 51.8; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_8H_8INO_2$: 277.96725, found: 277.96715;

Synthesis of ethyl 5-bromoanthranilate (12)

To stirred slurry of 5-bromoisatoic anhydride (8) (2.42 g, 10.00 mmol, 1.0 eq.) in absolute ethanol (50 ml), sodium ethoxide (2.04 g, 30.00 mmol, 3.0 eq.) was added, and reaction mixture was refluxed for 3h. Excess of solvent was evaporated, the residue was treated with water (100 ml), and extracted with ethyl acetate (3 x 50 ml). Combined organic layers were washed with water (100 ml), brine (50 ml) and dried over $MgSO_4$. Evaporation of solvent gave pure product as yellow solid. M.p.: 82.0-83.0 °C, yield: 2.34 g (96 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.76 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 2.4, 9.0 Hz, 1H), 6.80 (bs, 1H), 6.76 (d, *J* = 9.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 150.4, 136.4, 132.2, 118.9, 110.3, 104.7, 60.3, 14.1; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_9H_{10}BrNO_2$: 243.99677, 245.99472, found: 243.99676, 245.99463;

1.2. The general procedure for cyclisation of anthranilic esters 9-12

To the solution of appropriate alkyl anthranilate 9-12 (5.00 mmol, 1.0 eq.) in anhydrous THF (50 ml), 60% sodium hydride in mineral oil (10.00 mmol, 2.0 eq) was added. Reaction mixture was refluxed for 24h, then the excess of solvent was evaporated and oily residue was treated with 1M HCl (100ml) followed by extraction with ethyl acetate (3 x 100 ml). Combined organic layers were washed with water (100 ml), brine (50 ml) and dried over $MgSO_4$. Crude products were purified by column chromatography using hexane : ethyl acetate as eluent (1 : 9).

5*H*,11*H*-2,8-difluorodibenzo[*b,f*][1,5]diazocine-6,12-dione (1) – white crystals, m.p.: 70.0-70.5 °C, yield: 0.46 g (67 %).^{1}H NMR (300 MHz, DMSO-d_6) δ 10.26 (s, 1H), 7.29 – 7.07 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.2 (d, $J_{C\text{-}F}$ = 1.2 Hz), 160.9 (d, $J_{C\text{-}F}$ = 245.6 Hz), 135.8 (d, $J_{C\text{-}F}$ = 7.9 Hz), 131.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 128.8 (d, $J_{C\text{-}F}$ = 8.5 Hz), 118.1 (d, $J_{C\text{-}F}$ = 22.6 Hz), 115.1 (d, $J_{C\text{-}F}$ = 24.4 Hz); ^{19}F NMR (282 MHz, DMSO) δ -114.01 – -114.19 (m), main peaks: 114.06, -114.08, -114.09, -114.10, -114.12, -114.13; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_8F_2N_2O_2$: 275.06266, found: 275.06243.

5*H*,11*H*-2,8-dichlorodibenzo[*b,f*][1,5]diazocine-6,12-dione (2) – white crystals, m.p.: 70.0-70.5 °C, yield: 0.55 g (71 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.38 (s, 1H), 7.44 (dd, 1H, J_1=2.4, J_2=8.4 Hz), 7.38 (d, 1H, *J* = 2.4 Hz), 7.13 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.5, 134.9, 133.4, 131.7, 130.6, 127.80, 127.76; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_8Cl_2N_2O_2$: 307.00356, 309.00061, found: 307.00378, 309.00064.

5*H*,11*H*-2,8-dibromodibenzo[*b,f*][1,5]diazocine-6,12-dione (3) – white crystals, m.p.: 70.0-70.5 °C, yield: 0.71 g (72 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.37 (s, 1H), 7.56 (dd, 1H, J_1=2.4, J_2=8.4 Hz), 7.50 (d, 1H, *J* = 2.4 Hz), 7.06 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.3, 135.1, 133.9, 133.5, 130.6, 128.0, 119.9; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_8Br_2N_2O_2$: 394.90253, 396.90048, 398.89844, found: 394.90221, 396.90045, 398.89810;

5*H*,11*H*-2,8-diiododibenzo[*b,f*][1,5]diazocine-6,12-dione (4) – white crystals, m.p.: 70.0-70.5 °C, yield: 0.63 g (53 %). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.32 (s, 1H), 7.71 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.3, 139.3, 136.3, 135.2, 134.3, 127.9, 92.7; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_8I_2N_2O_2$: 490.87479, found: 490.87433;

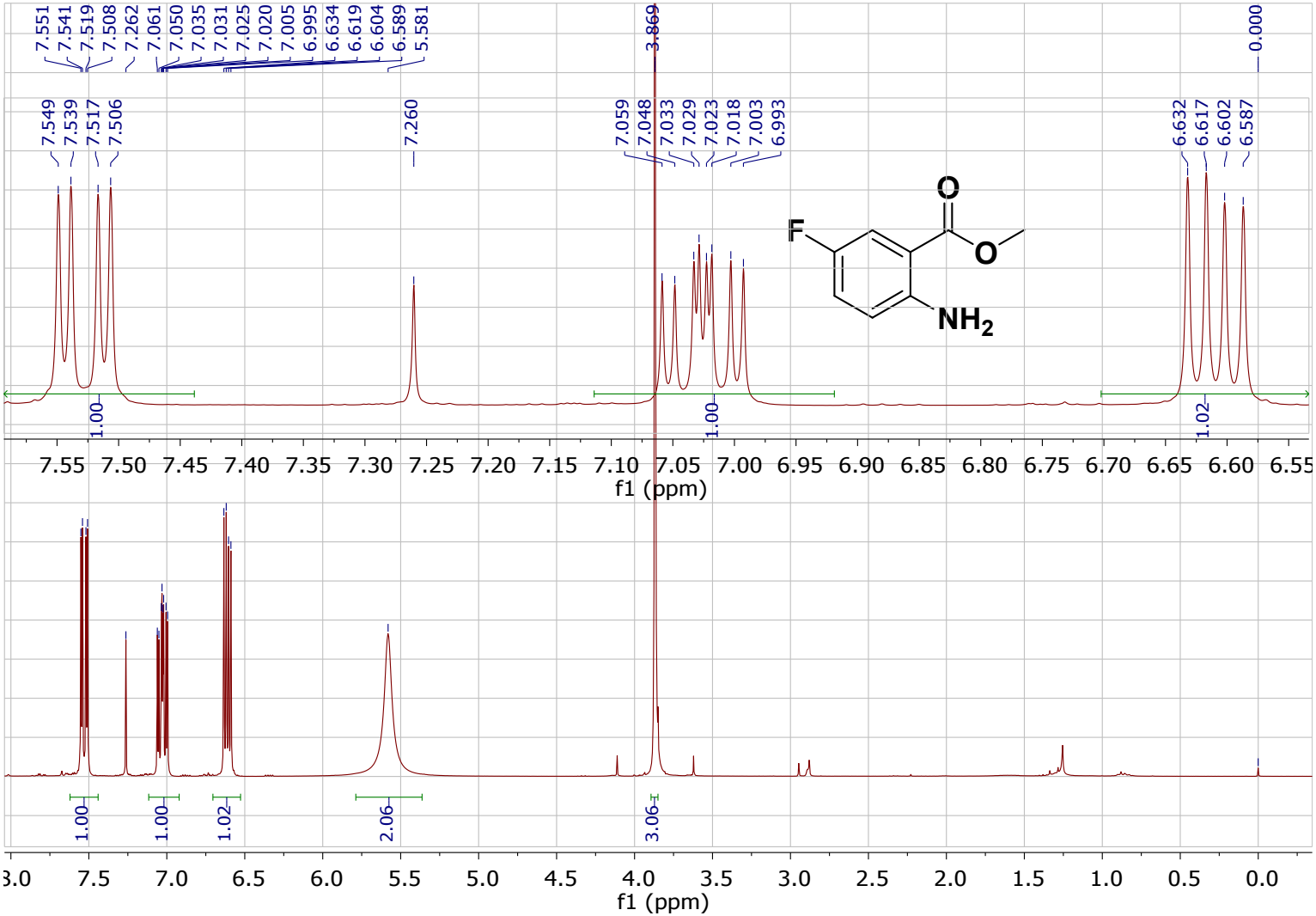


Figure S1. 1H NMR spectrum of methyl 5-fluoroanthranilate (9)

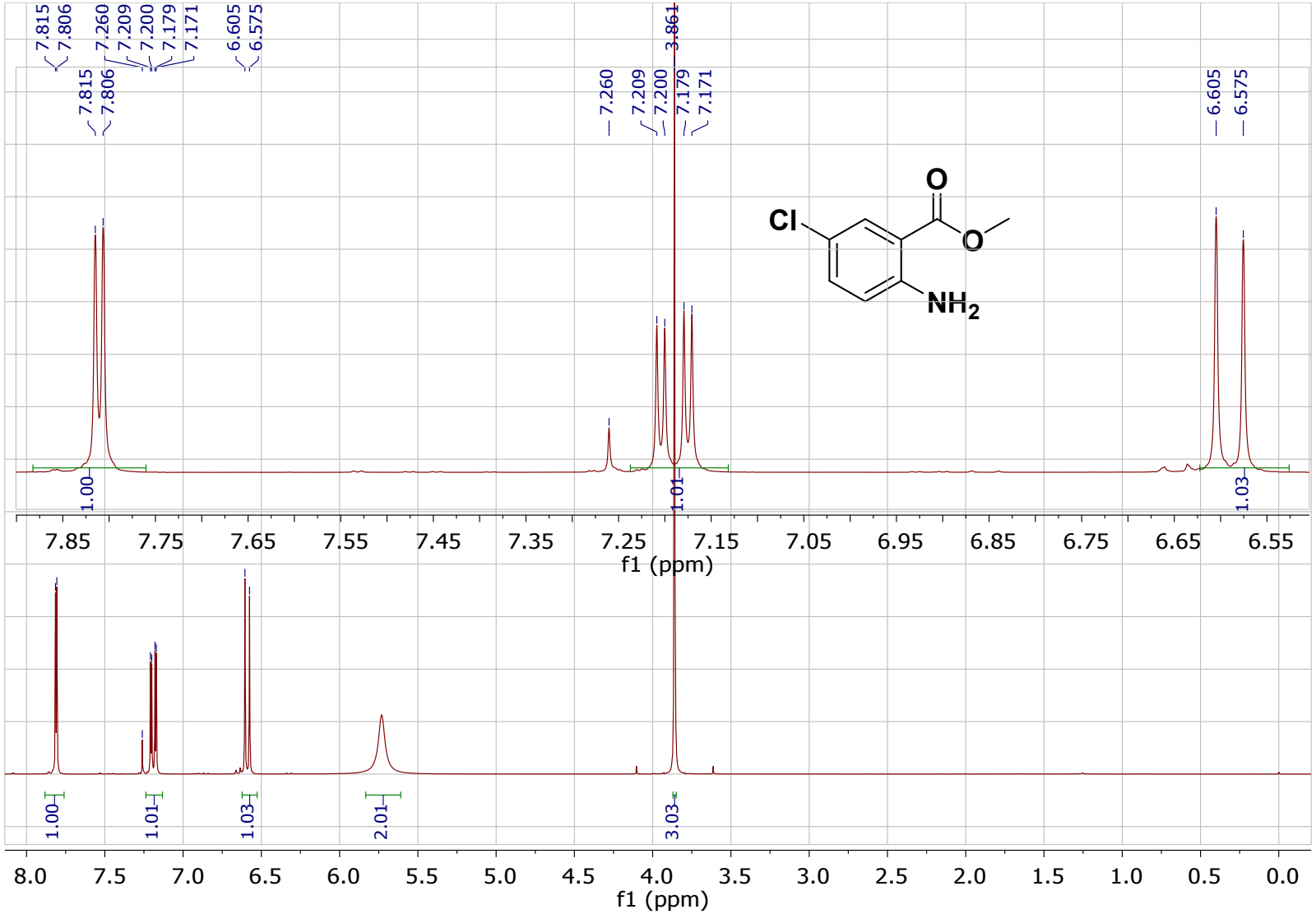


Figure S2. 1H NMR spectrum of methyl 5-chloroanthranilate (10)

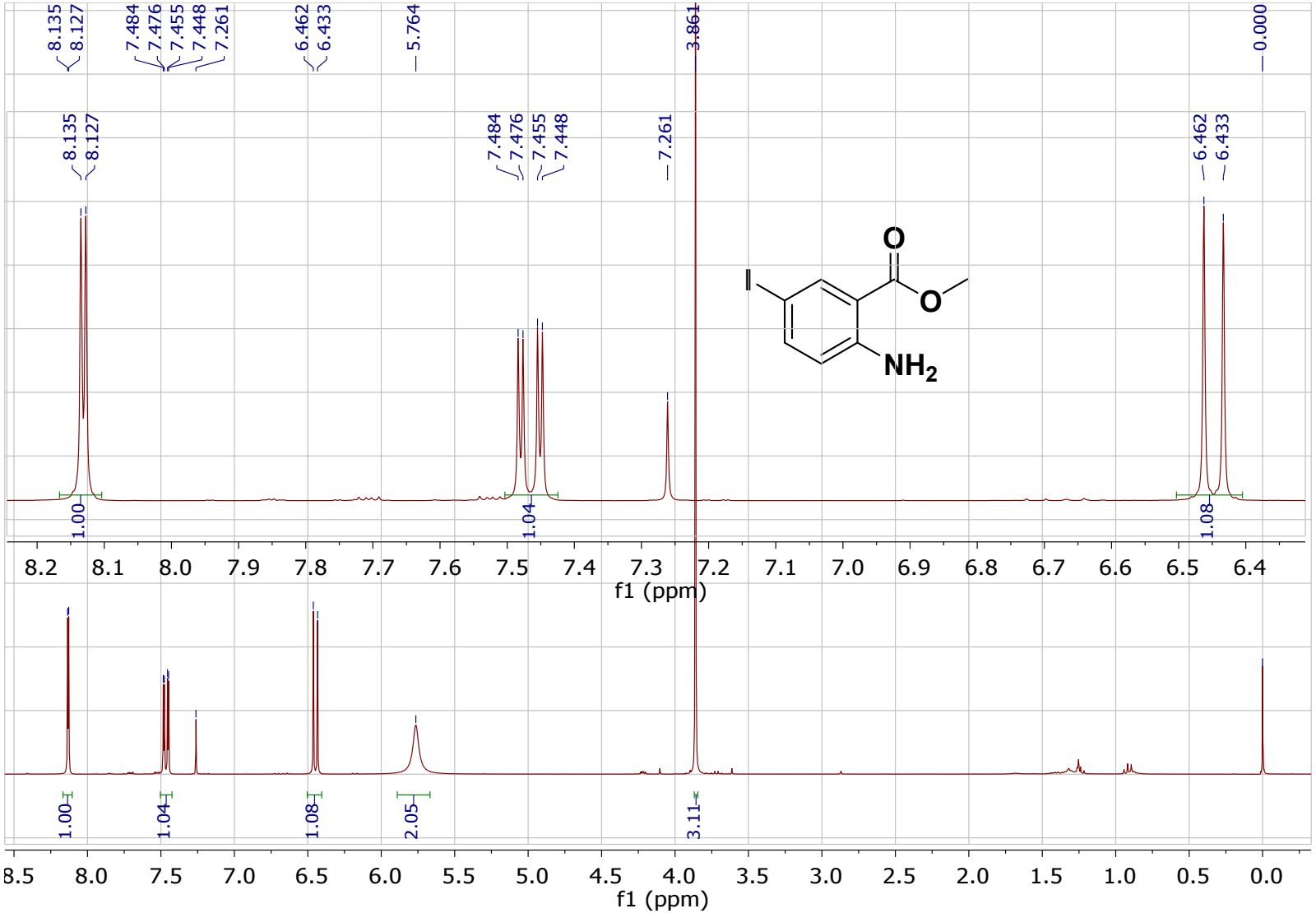


Figure S3. 1H NMR spectrum of methyl 5-iodoanthranilate (11)

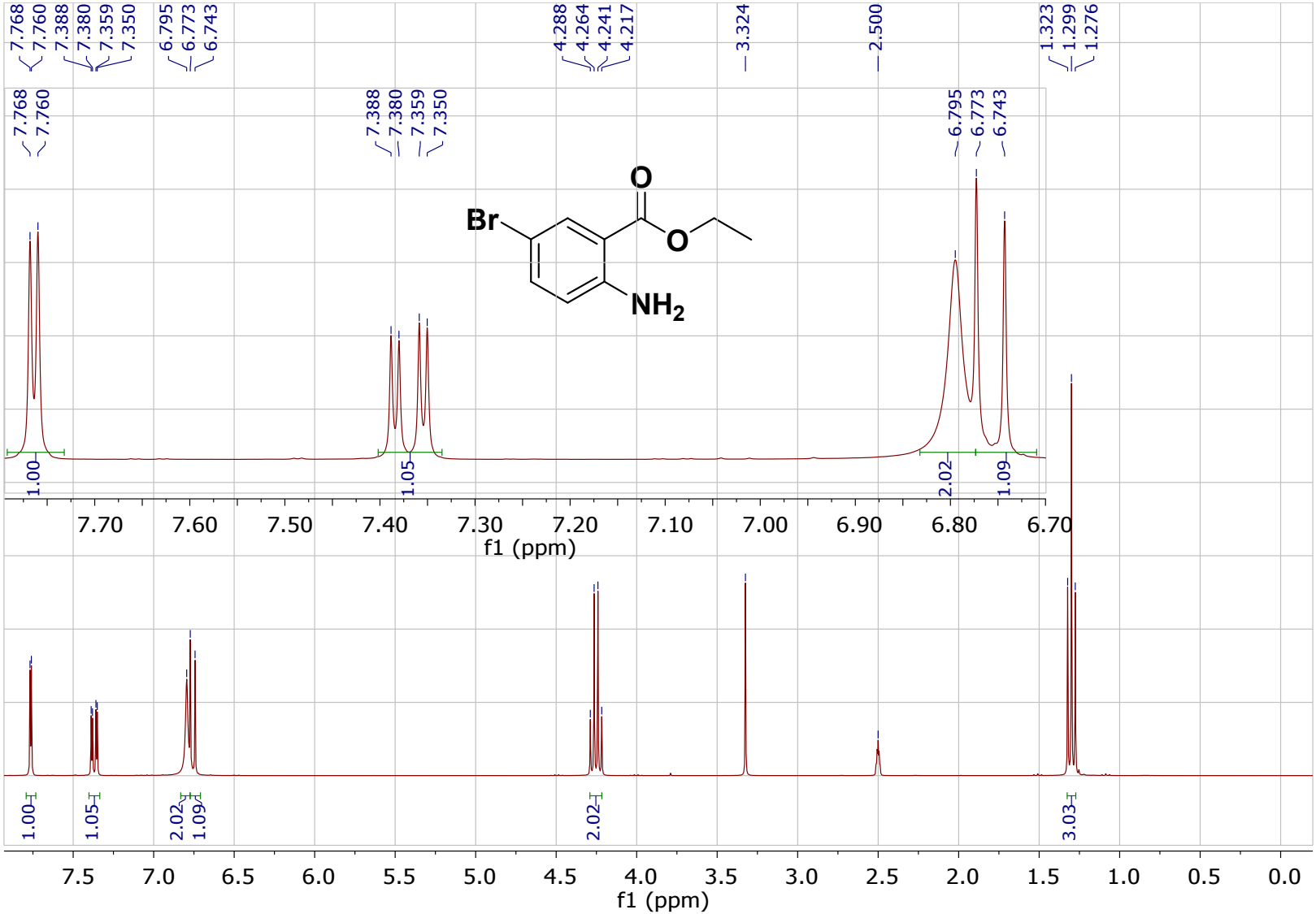


Figure S4. 1H NMR spectrum of ethyl 5-bromoanthranilate (12)

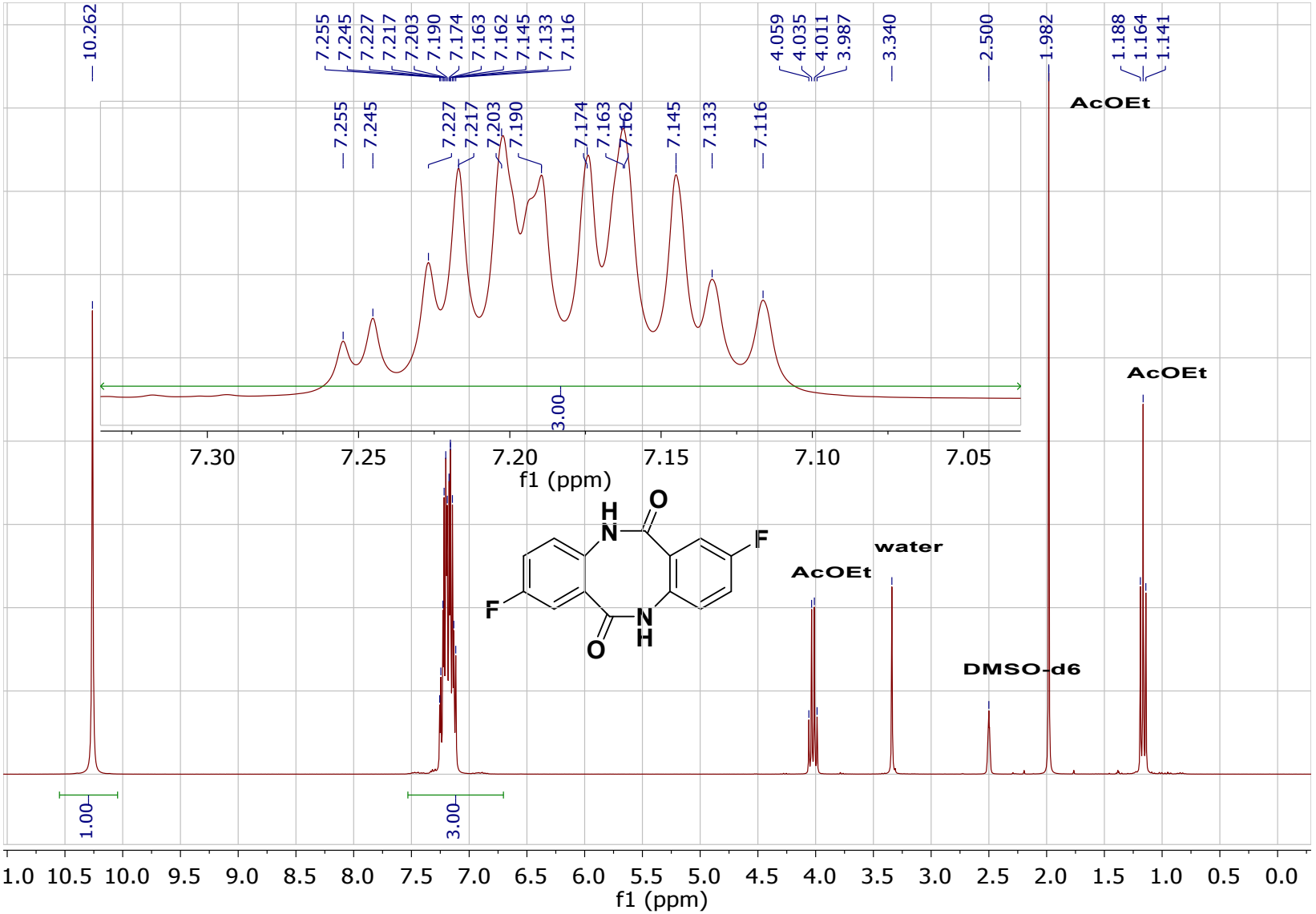


Figure S5. 1H NMR spectrum of 5*H*,11*H*-2,8-difluorodibenzo[*b,f*][1,5]diazocine-6,12-dione (1)

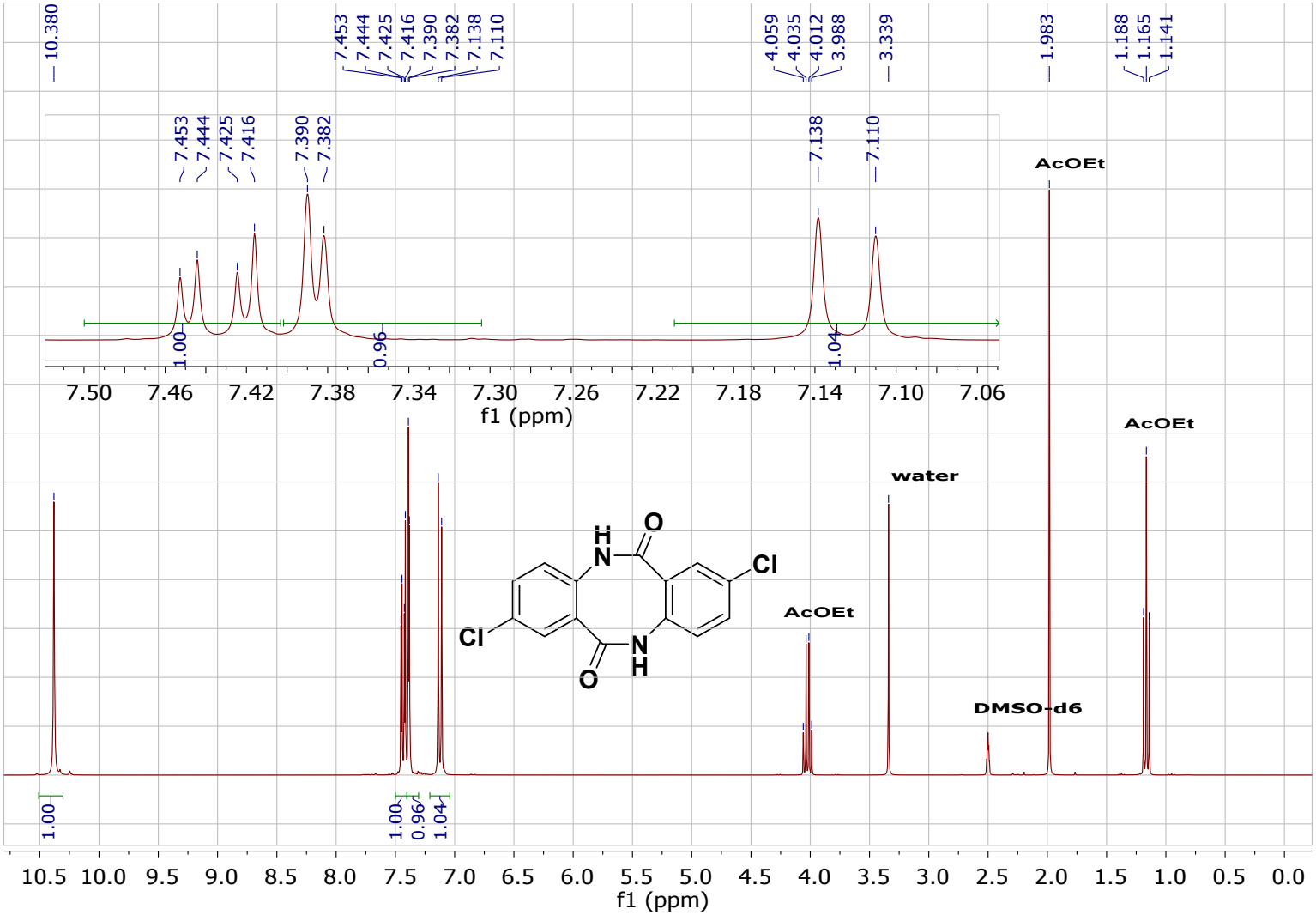


Figure S6. 1H NMR spectrum of 5*H*,11*H*-2,8-dichlorodibenzo[*b,f*][1,5]diazocine-6,12-dione (2)

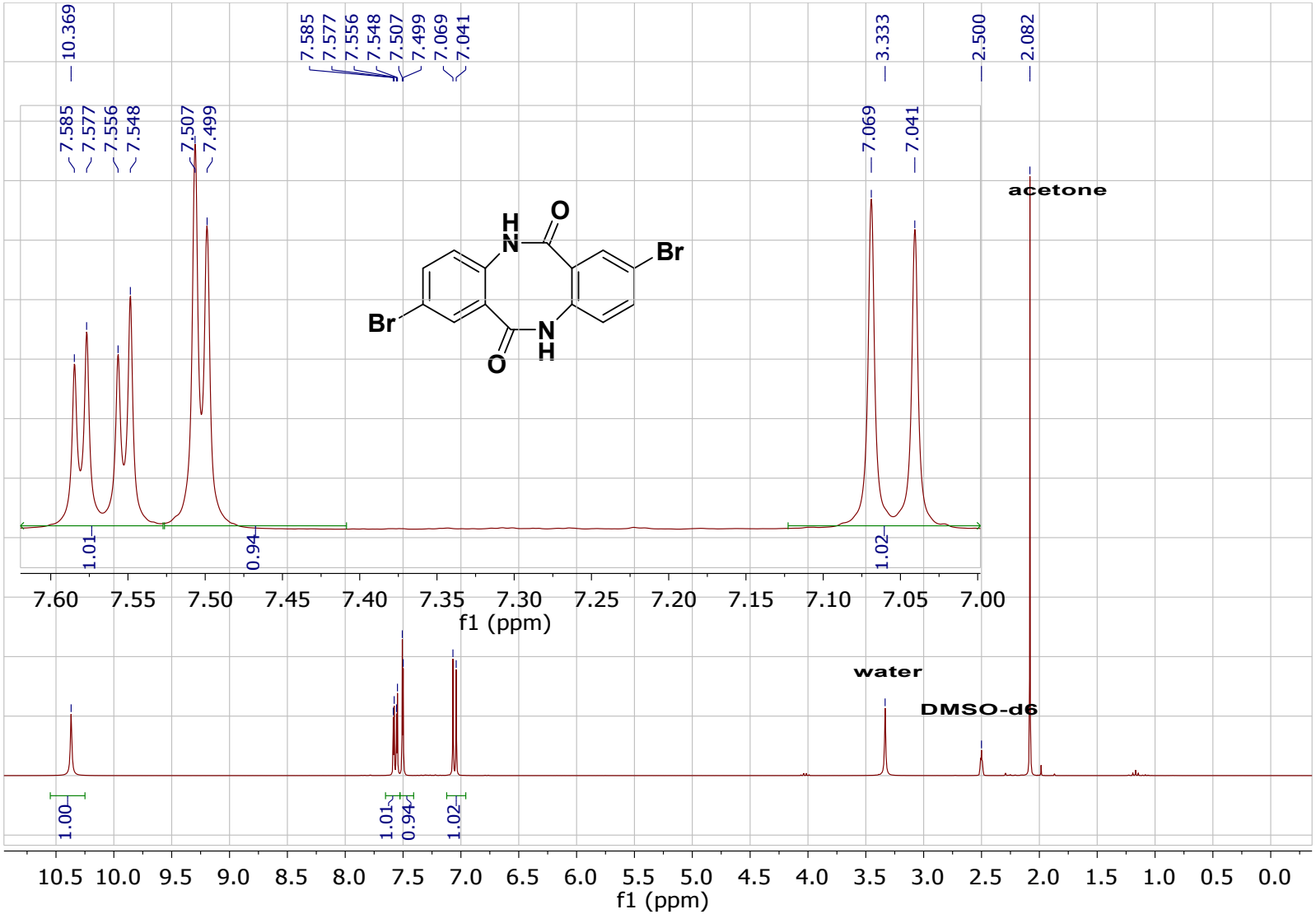


Figure S7. 1H NMR spectrum of 5*H*,11*H*-2,8-dibromodibenzo[*b,f*][1,5]diazocine-6,12-dione (3)

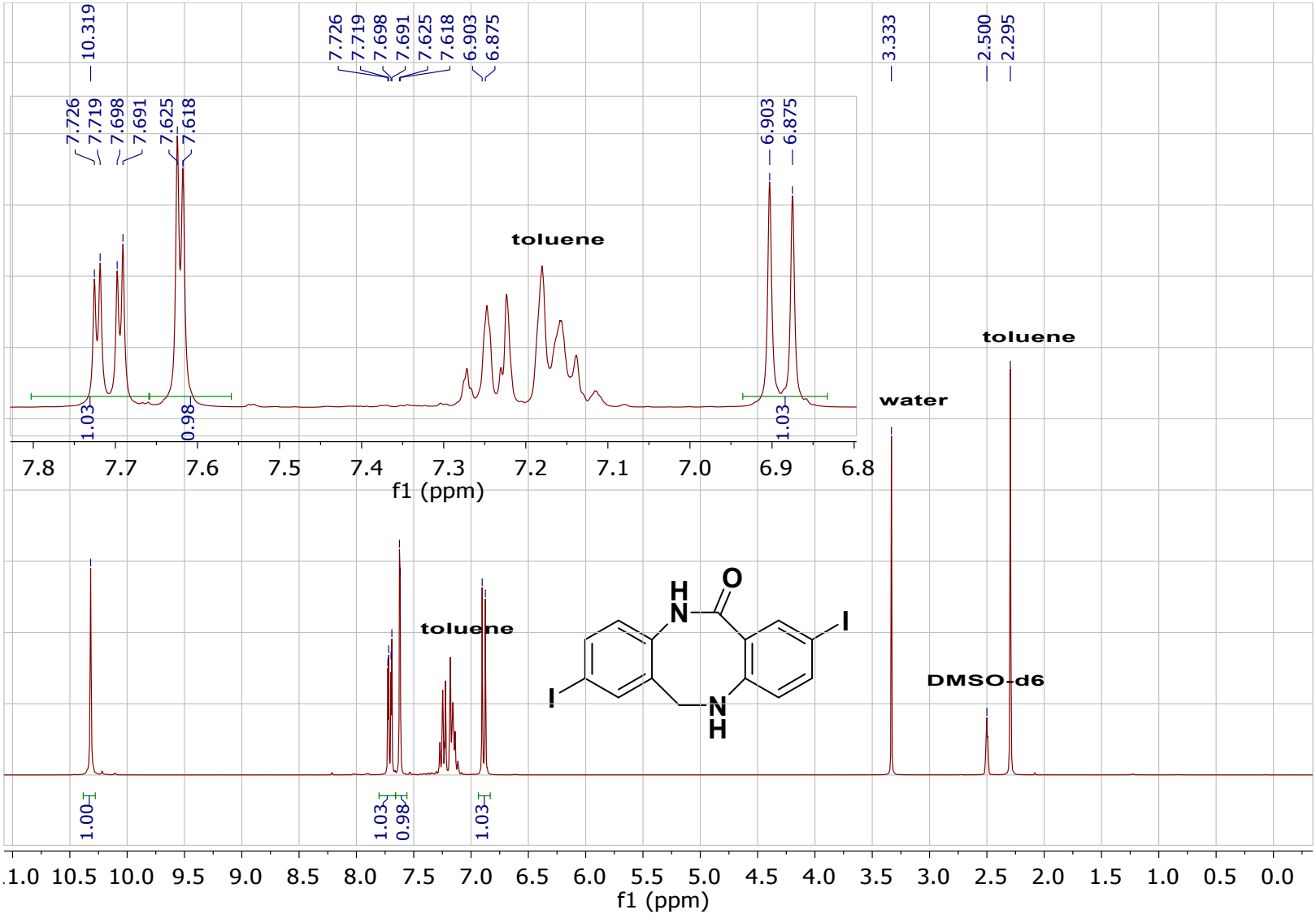


Figure S8. 1H NMR spectrum of 5*H*,11*H*-2,8-diiododibenzo[*b,f*][1,5]diazocine-6,12-dione (4)

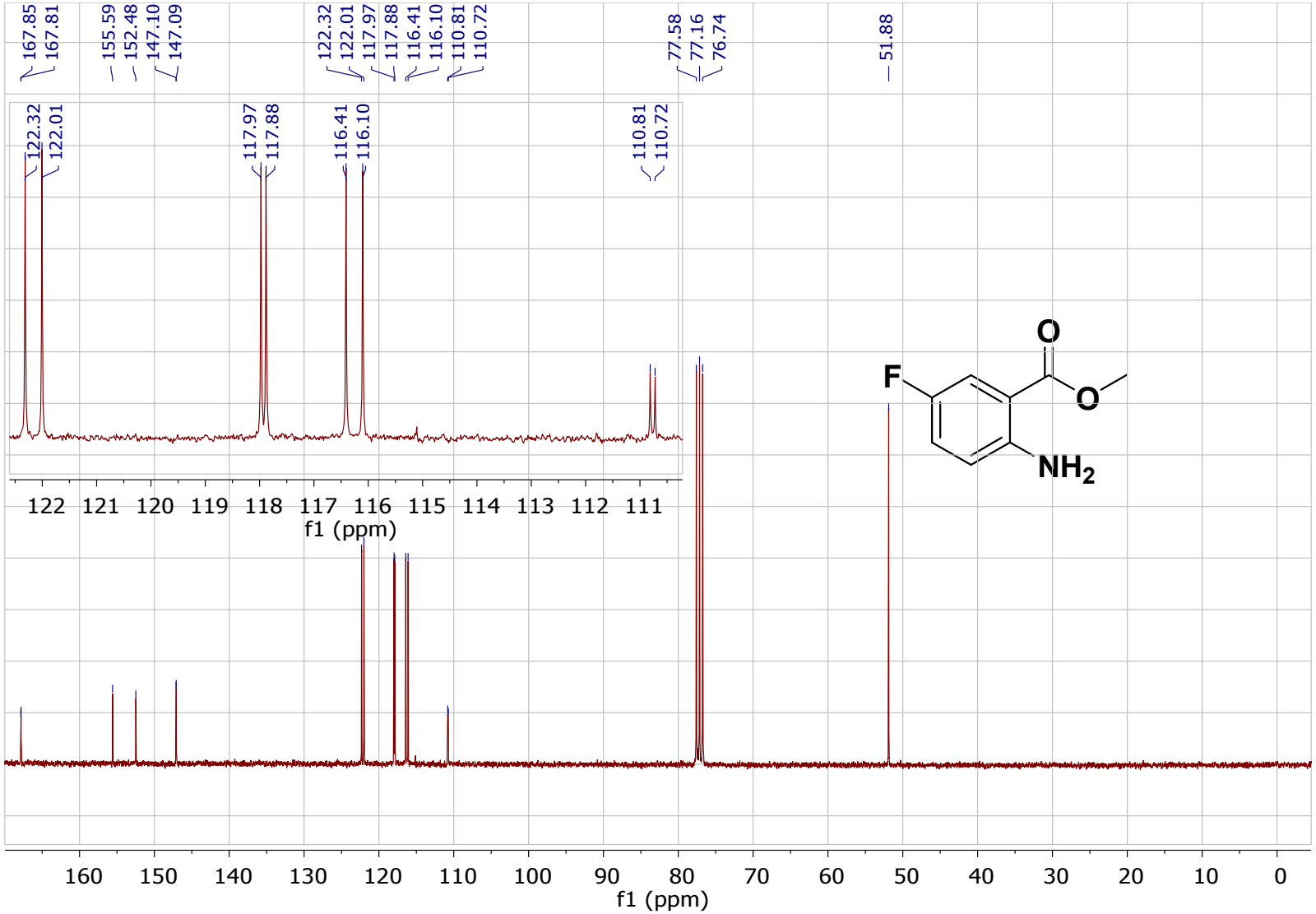


Figure S9. 13C NMR spectrum of methyl 5-fluoroanthranilate (9)

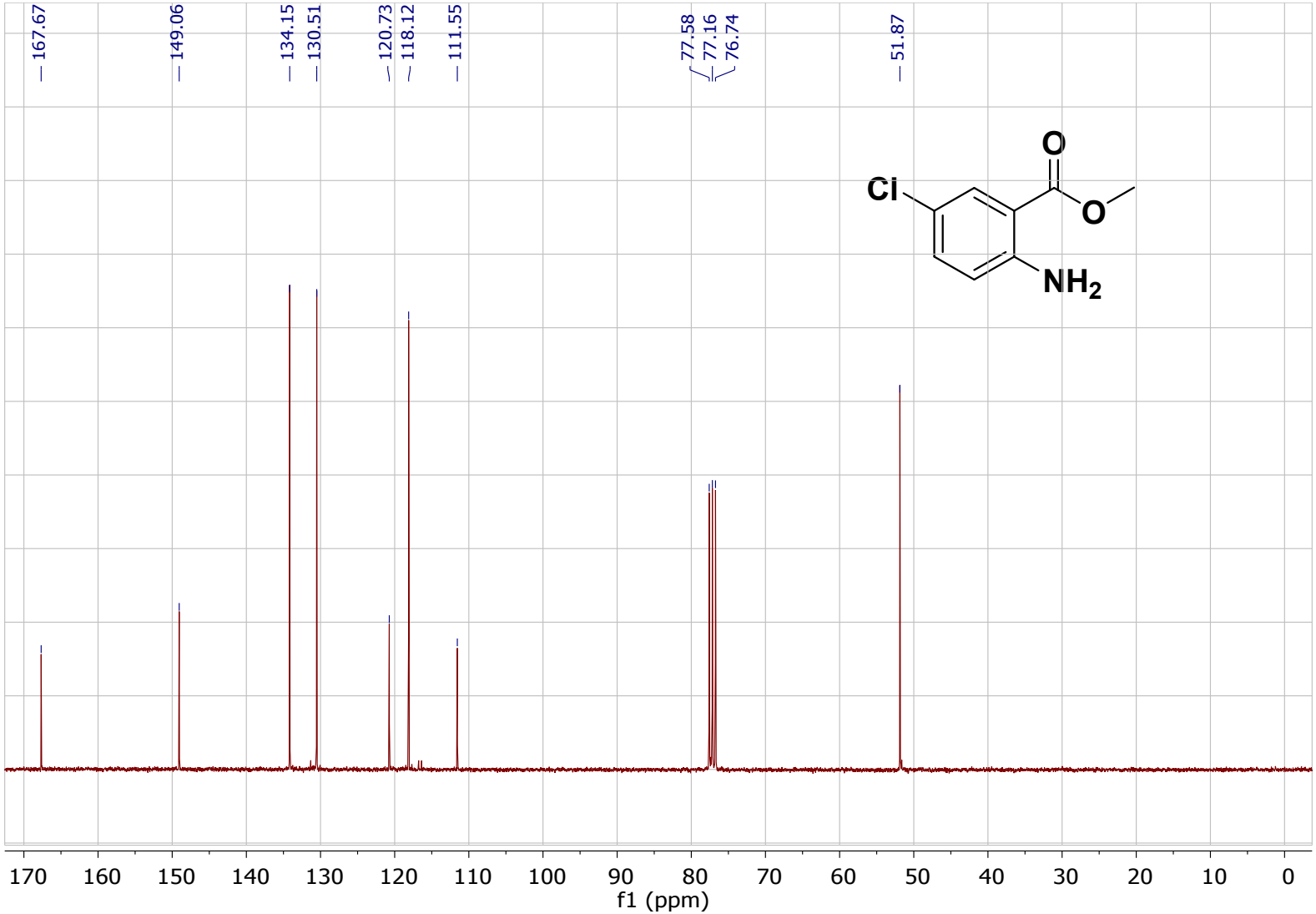


Figure S10. 13C NMR spectrum of methyl 5-chloroanthranilate (10)

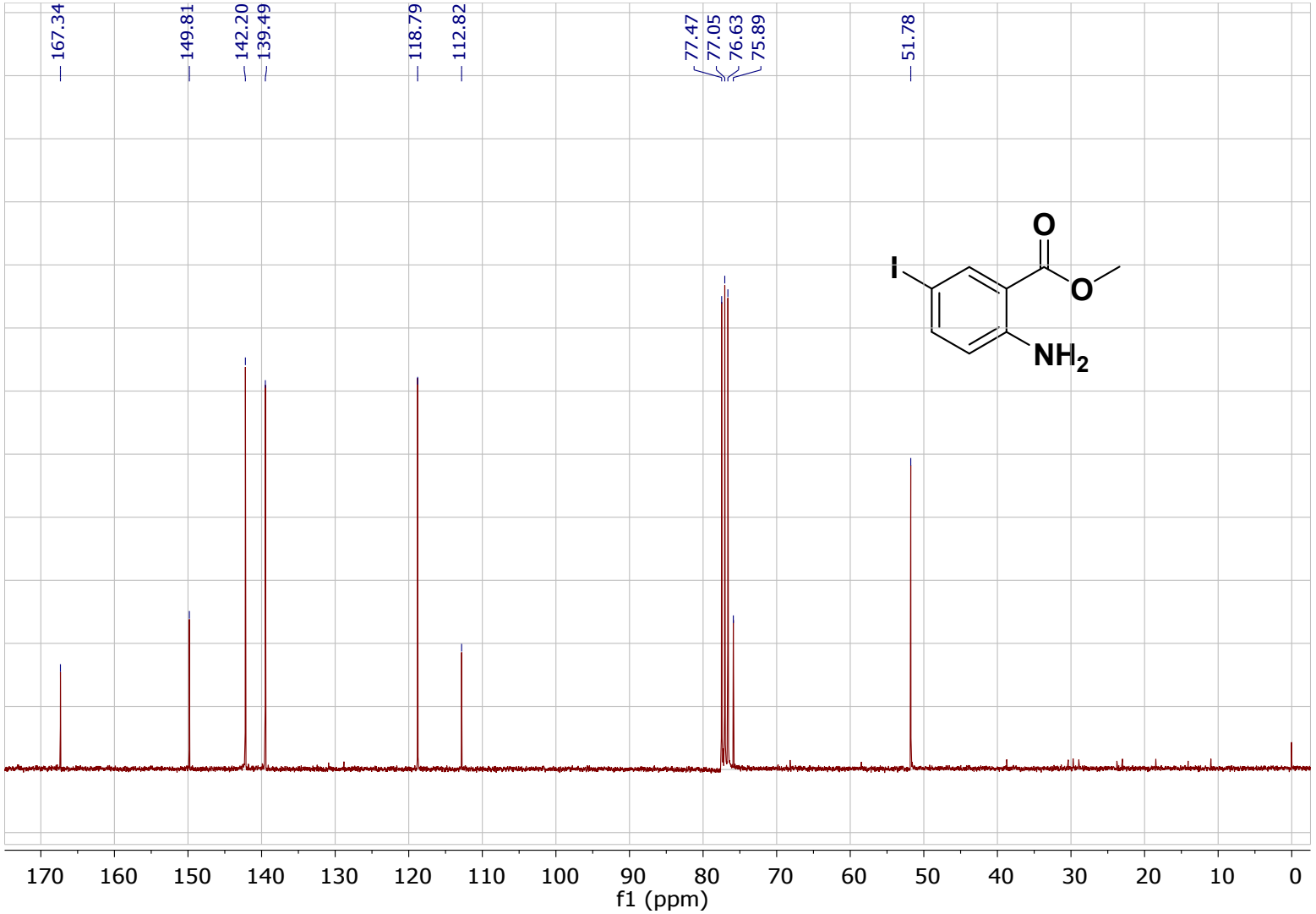


Figure S11. 13C NMR spectrum of methyl 5-iodoanthranilate (11)

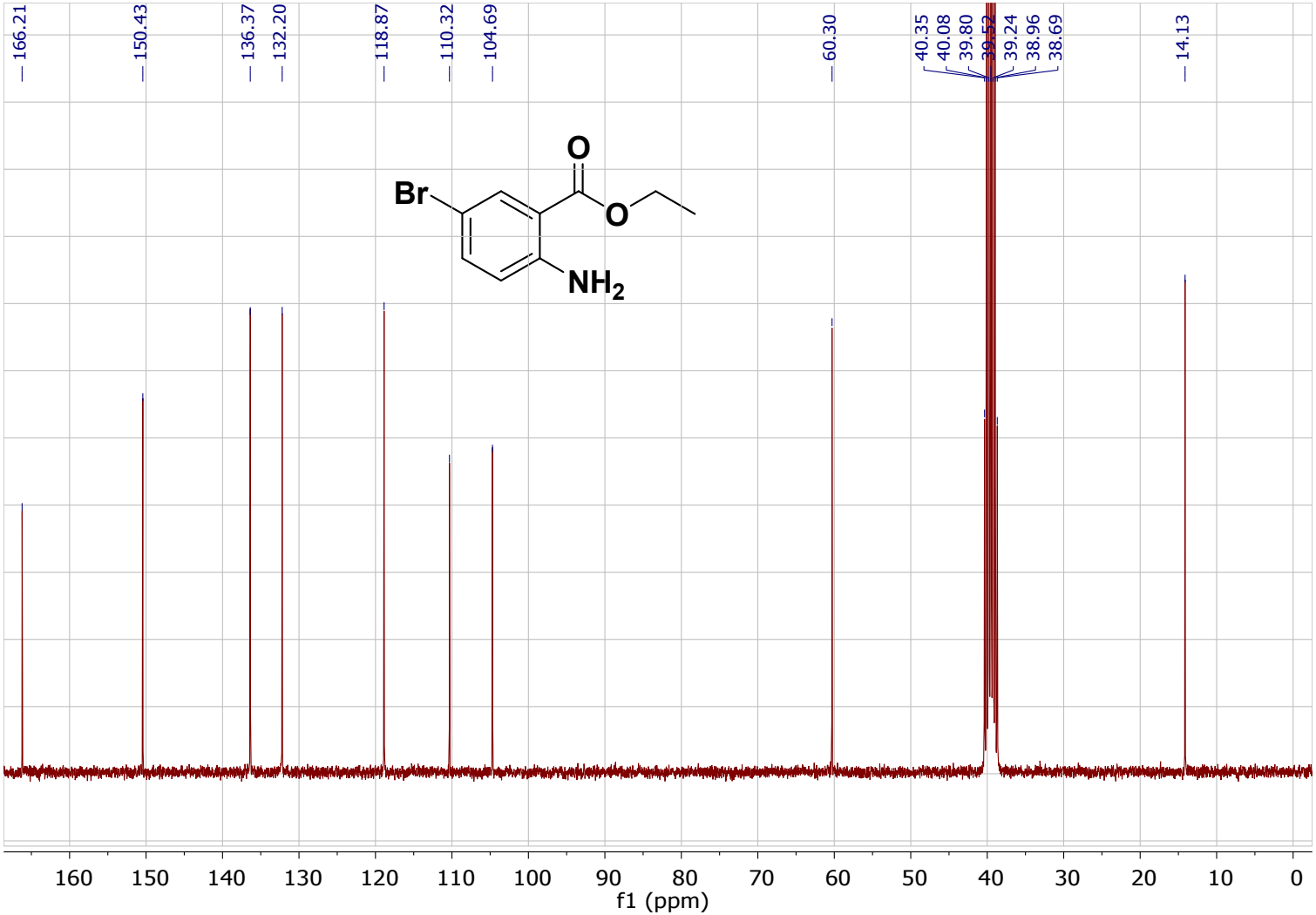


Figure S12. 13C NMR spectrum of ethyl 5-bromoanthranilate (12)

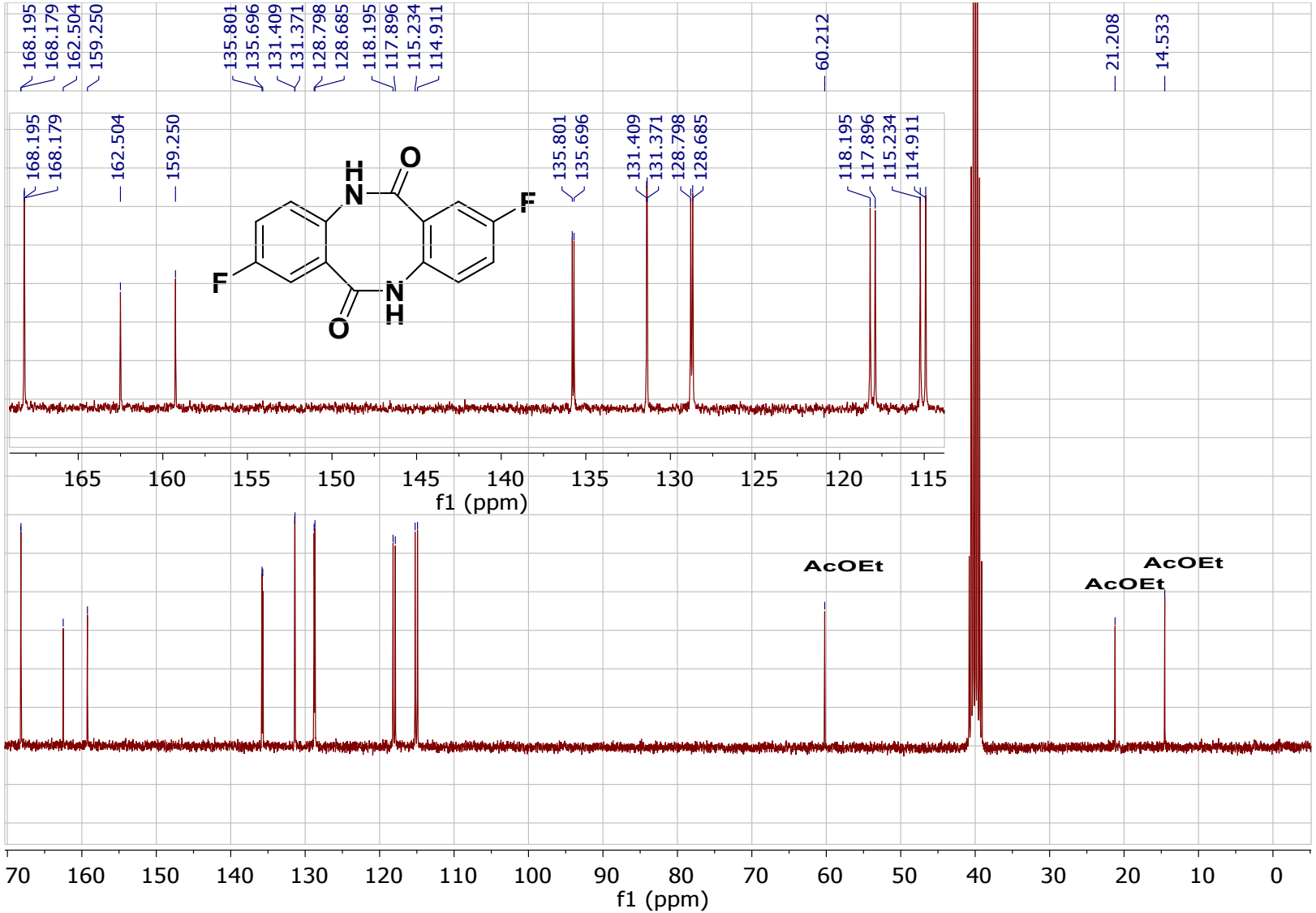


Figure S13. 13C NMR spectrum of 5*H*,11*H*-2,8-difluorodibenzo[*b,f*][1,5]diazocine-6,12-dione (1)

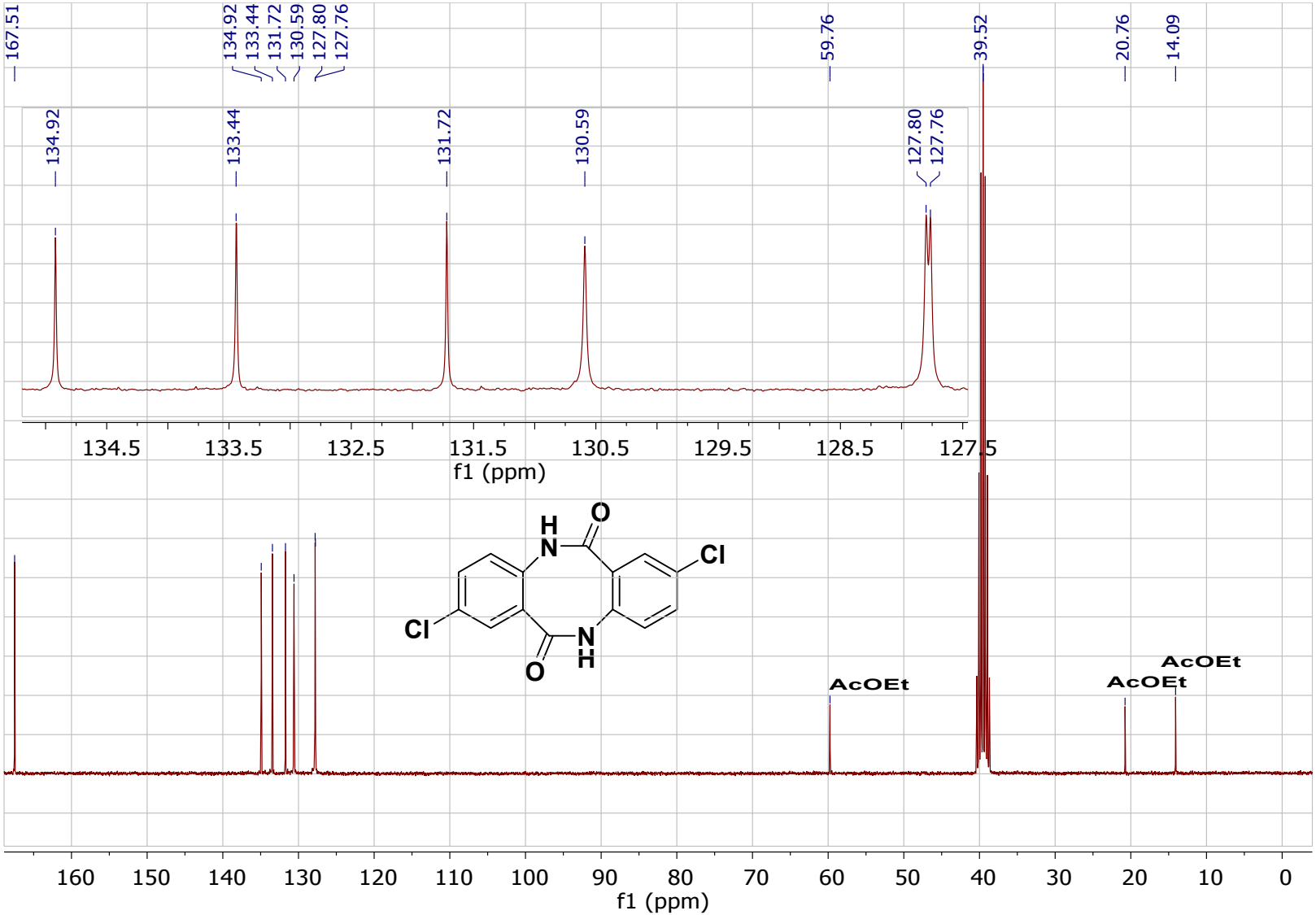


Figure S14. 13C NMR spectrum of 5*H*,11*H*-2,8-dichlorodibenzo[*b,f*][1,5]diazocine-6,12-dione (2)

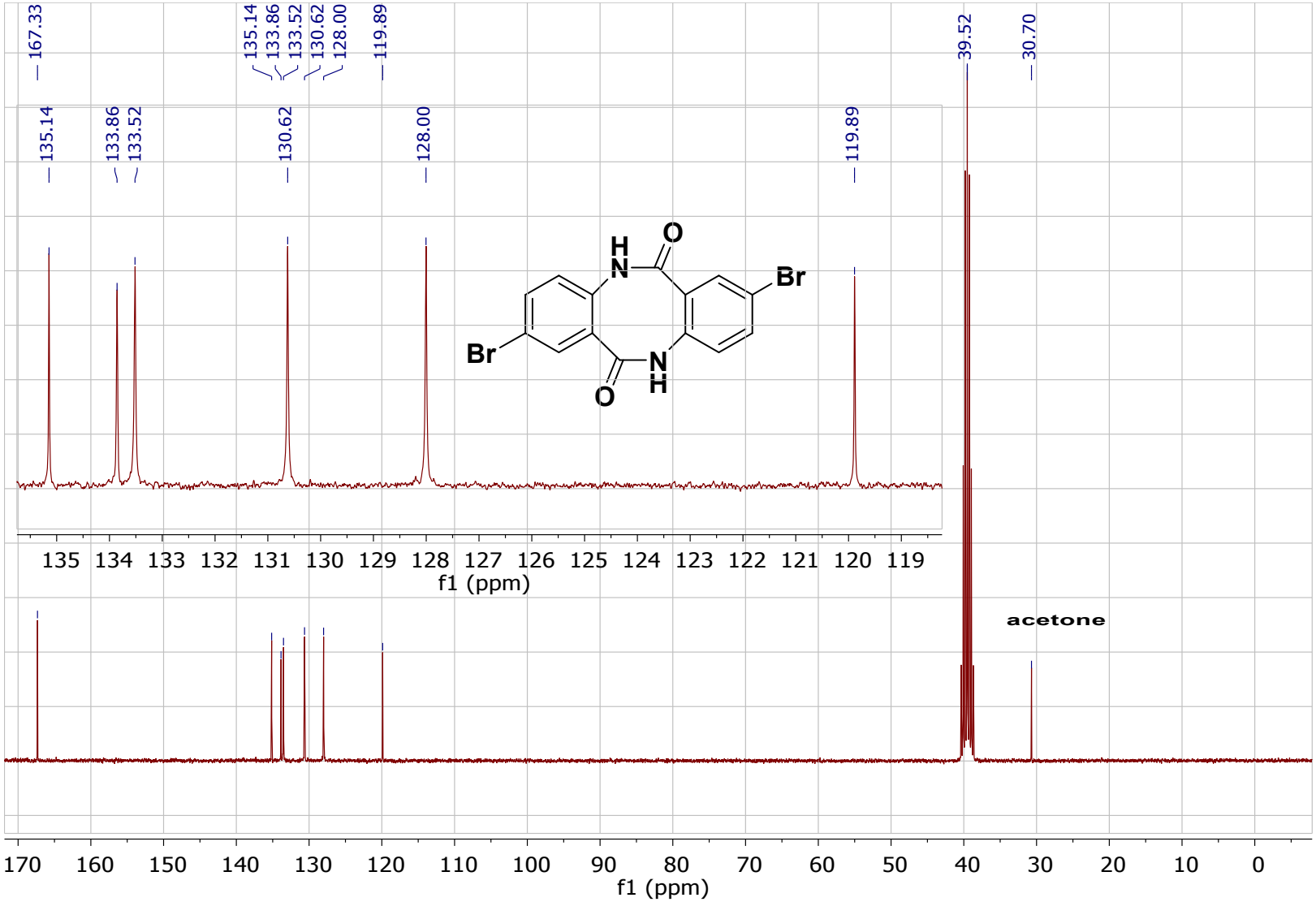


Figure S15. 13C NMR spectrum of 5*H*,11*H*-2,8-dibromodibenzo[*b,f*][1,5]diazocine-6,12-dione (3)

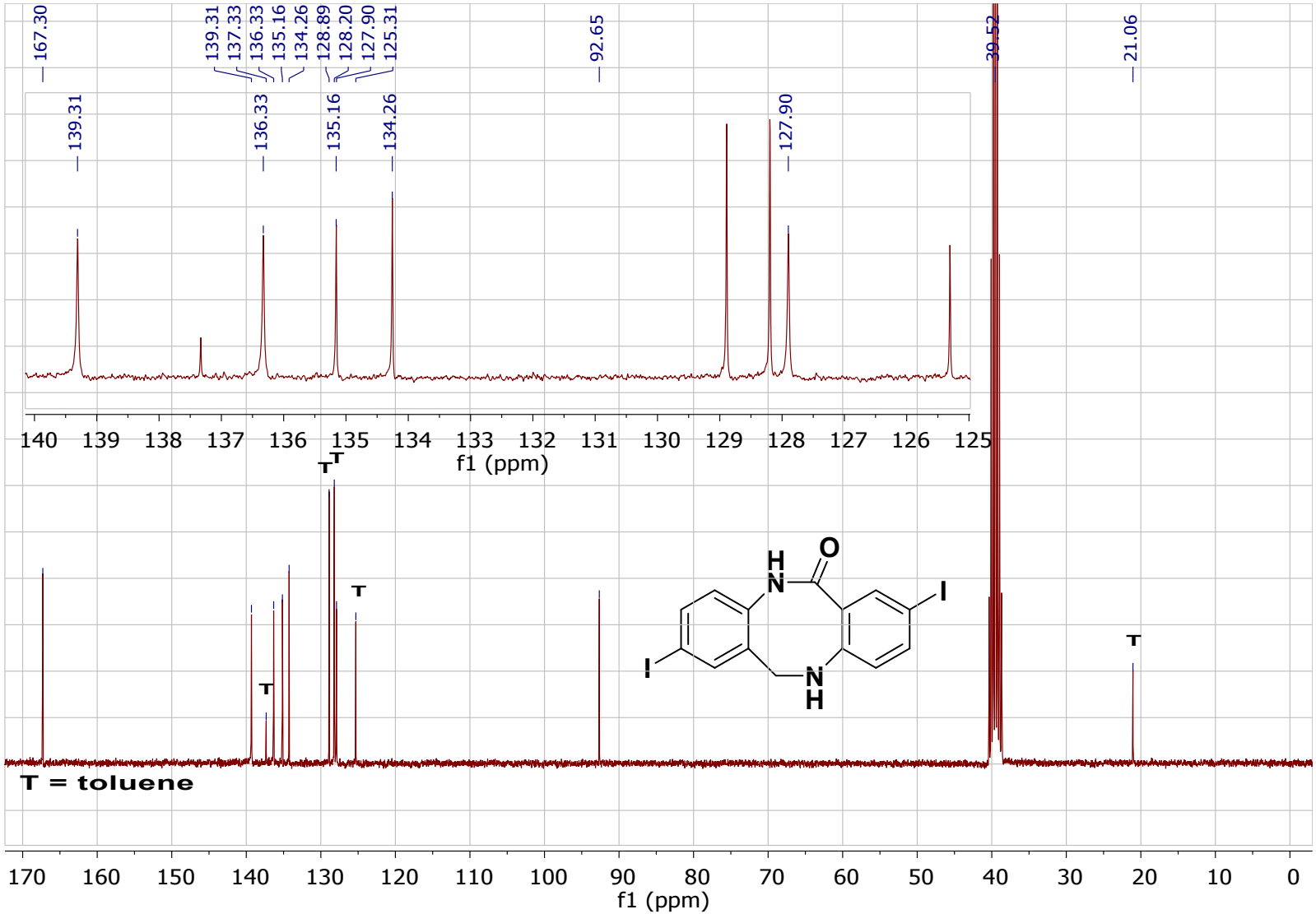


Figure S16. 13C NMR spectrum of 5*H*,11*H*-2,8-diiododibenzo[*b,f*][1,5]diazocine-6,12-dione (4)

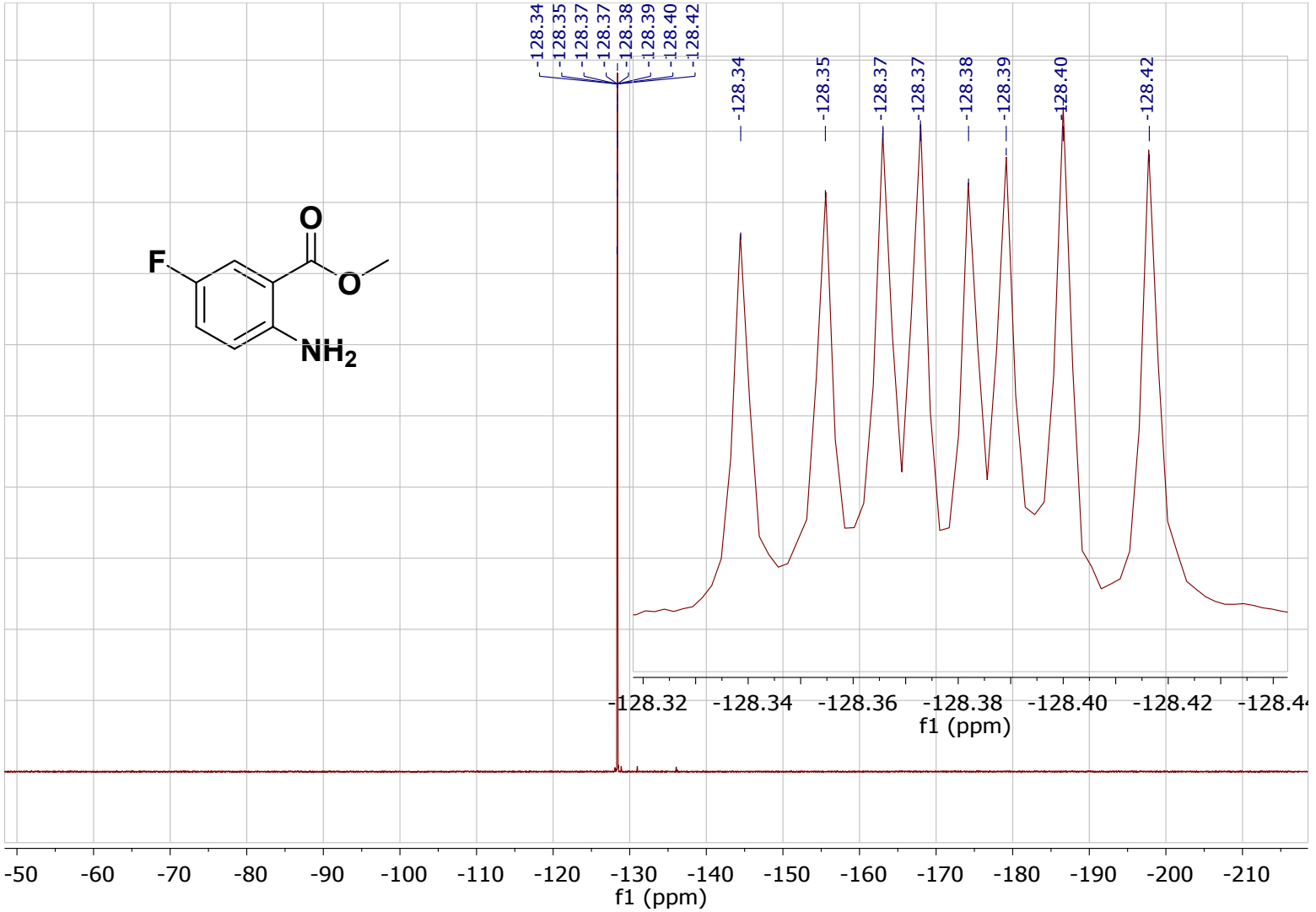


Figure S17. 19F NMR spectrum of methyl 5-fluoroanthranilate (9)

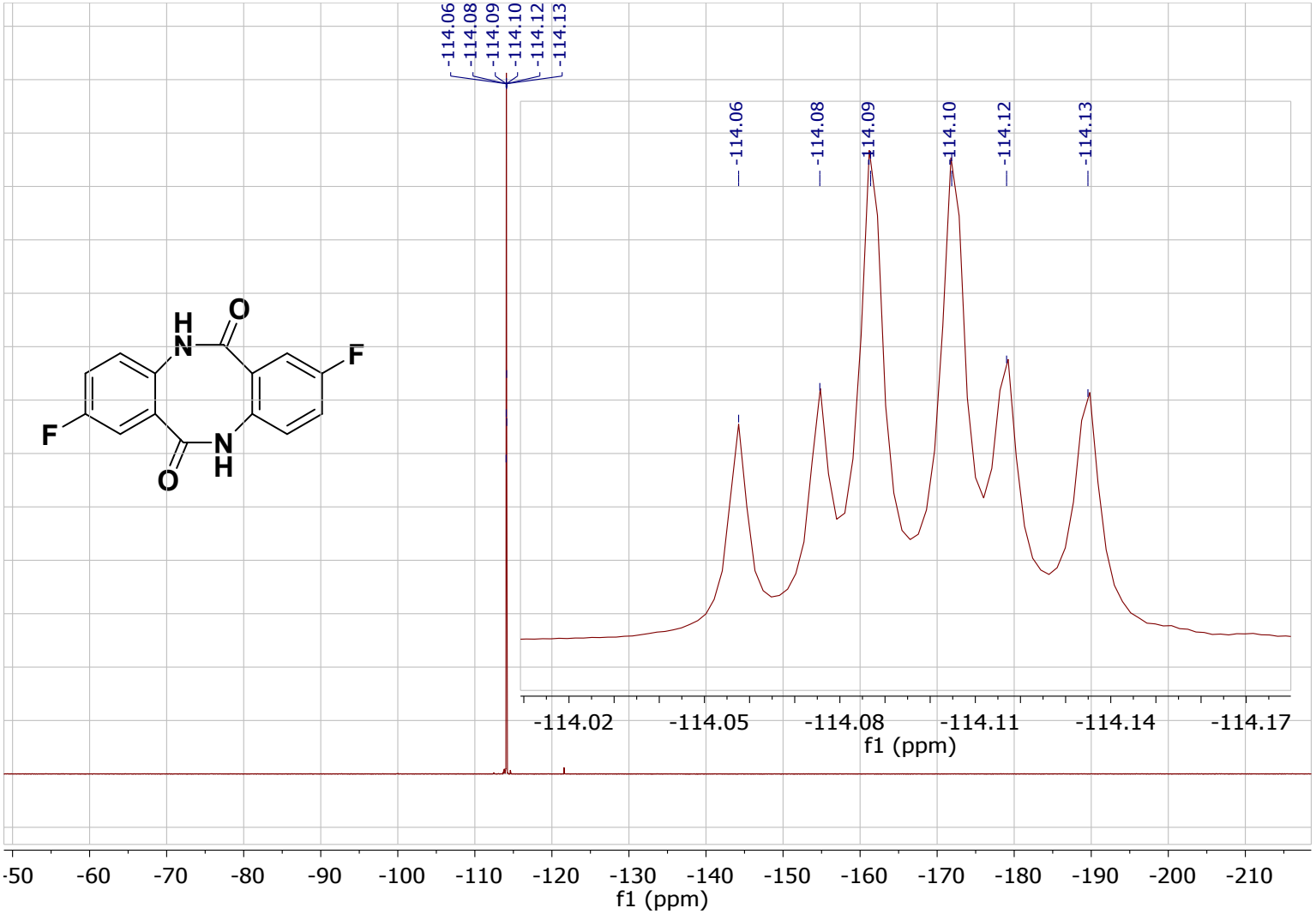


Figure S18. 19F NMR spectrum of 5*H*,11*H*-2,8-difluorodibenzo[*b*,*f*][1,5]diazocine-6,12-dione (1)

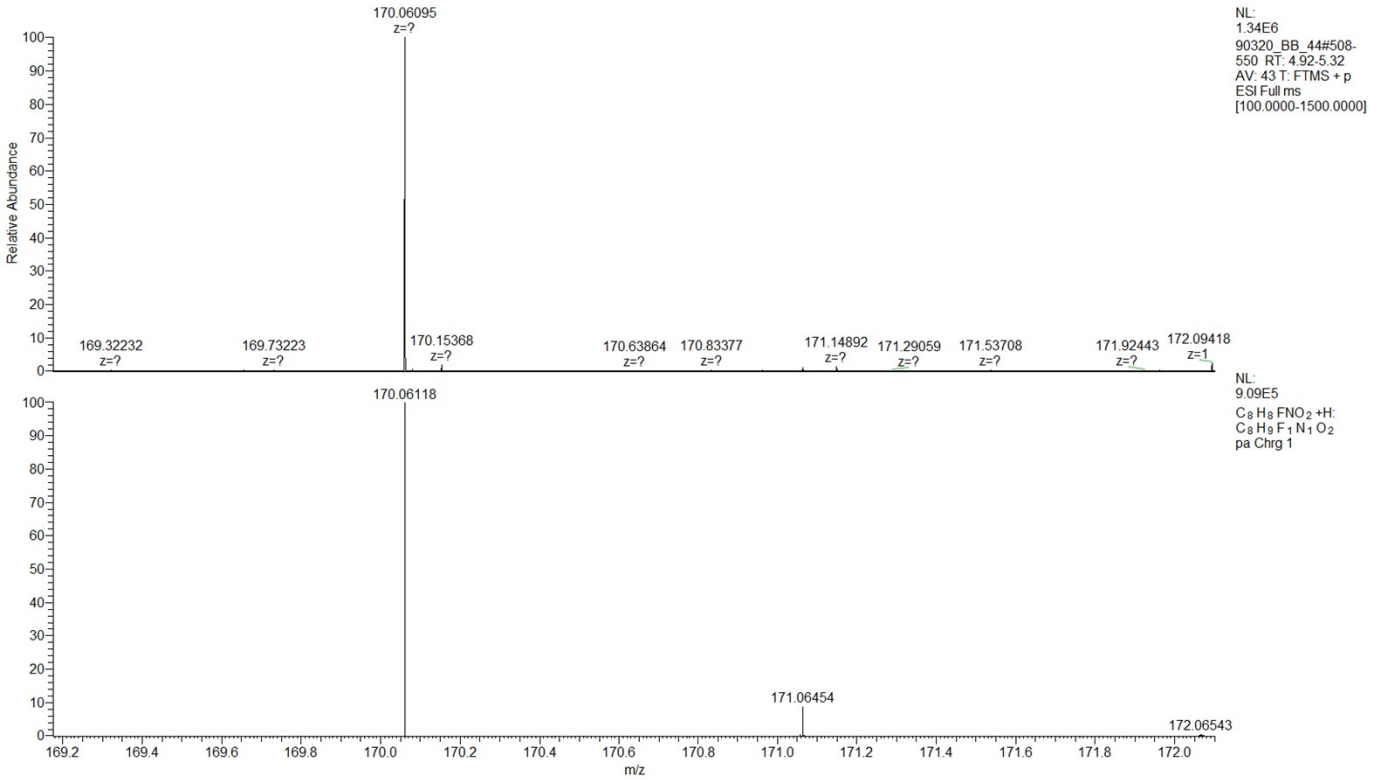


Figure S19. HRMS-ESI spectrum of methyl 5-fluoroanthranilate (9)

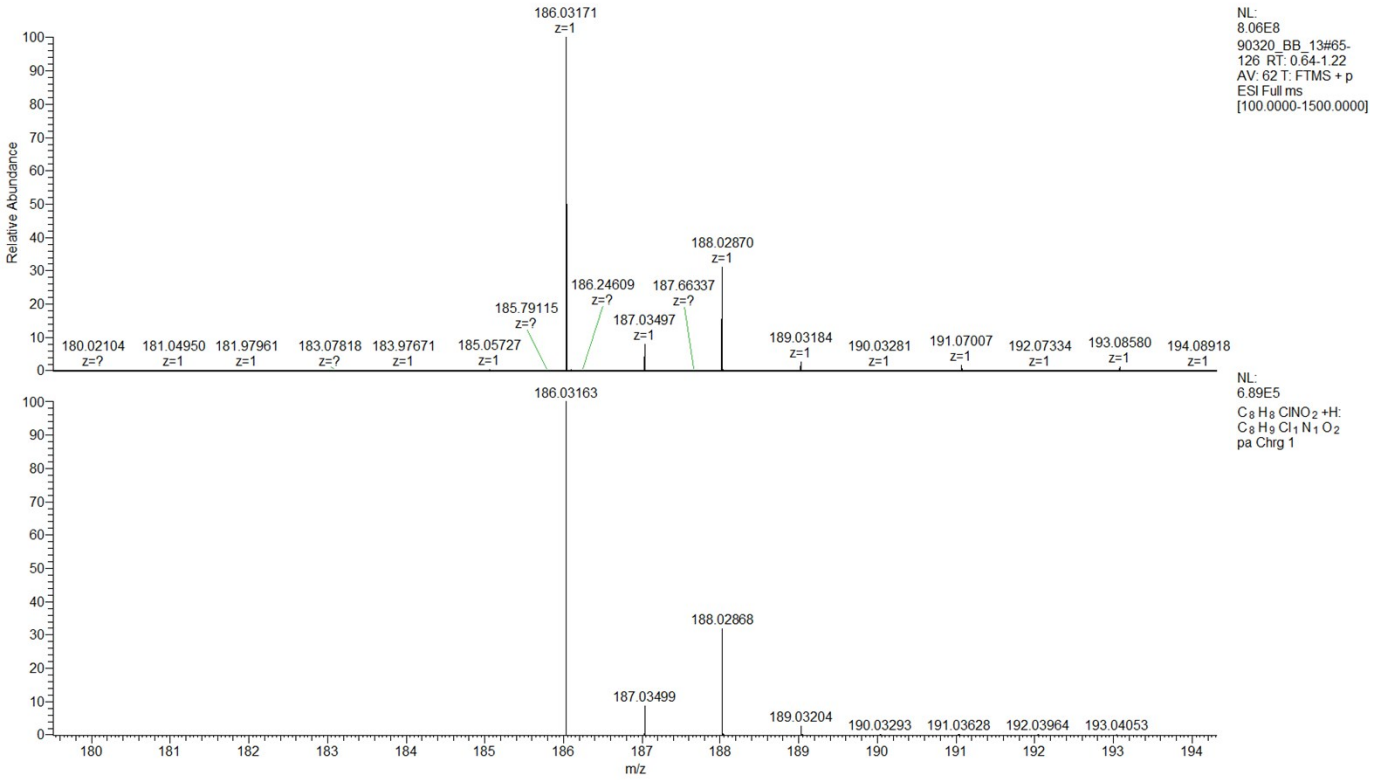


Figure S20. HRMS-ESI spectrum of methyl 5-chloroanthranilate (10)

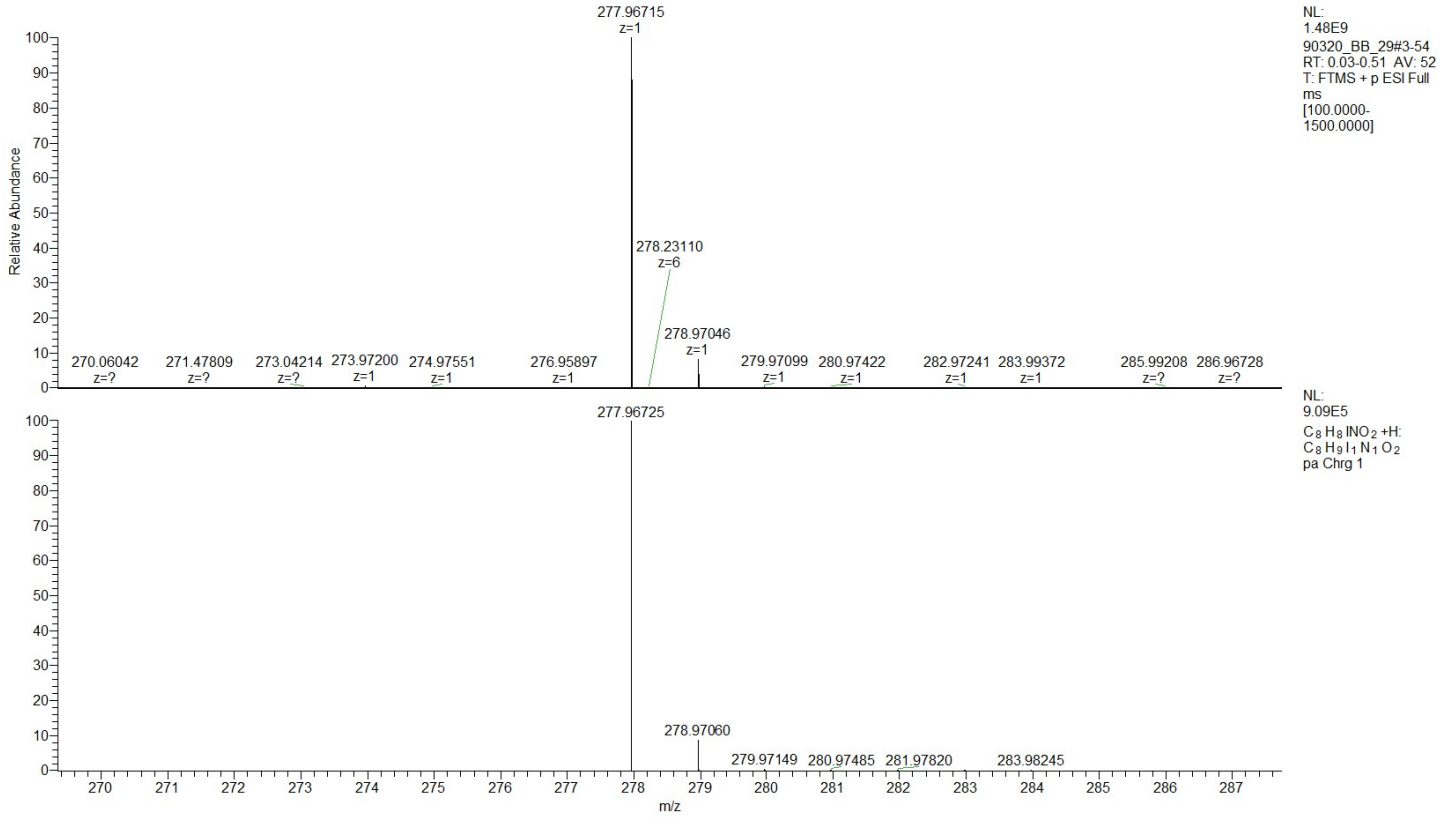


Figure S21. HRMS-ESI spectrum of methyl 5-iodoanthranilate (11)

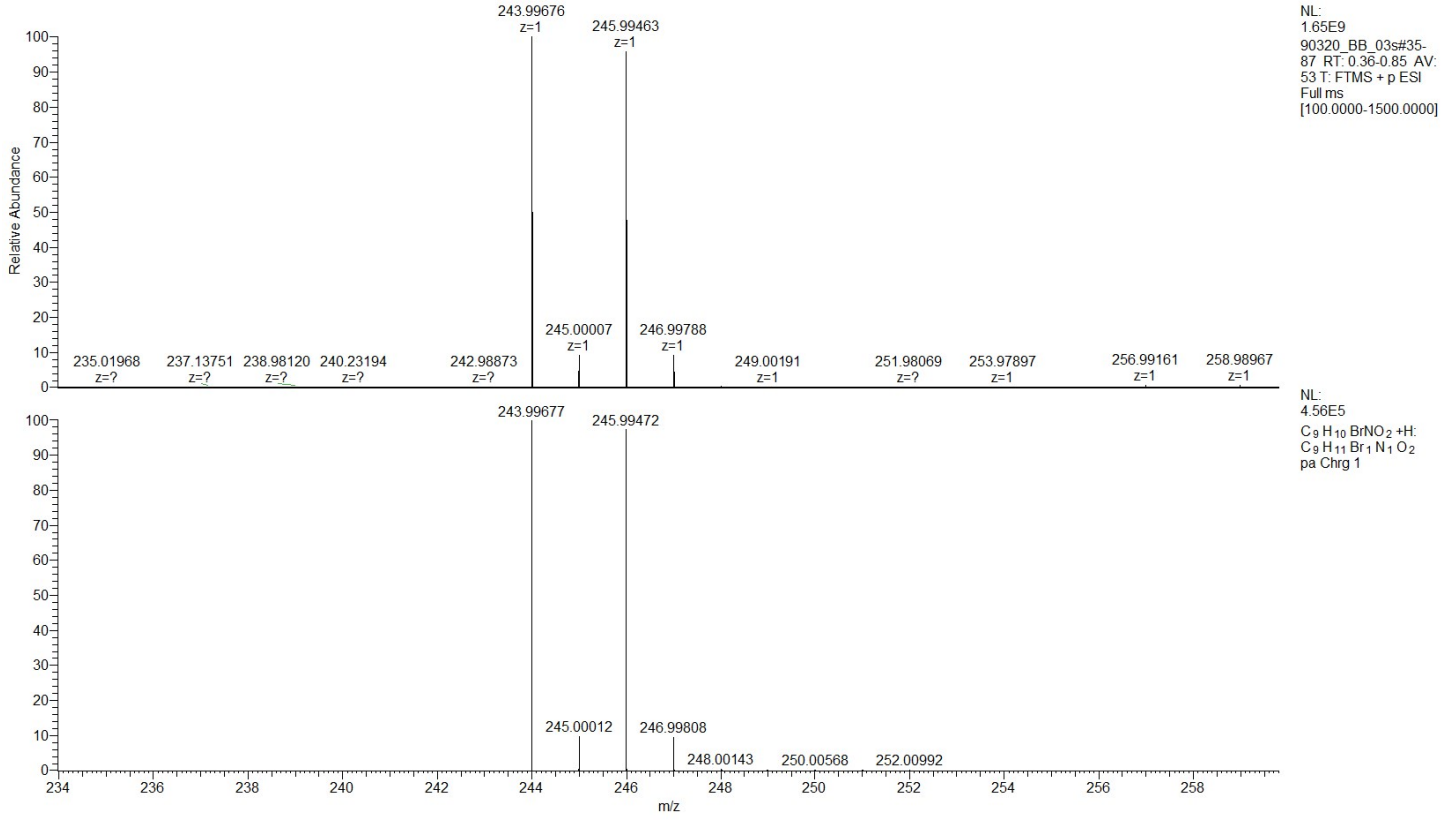


Figure S22. HRMS-ESI spectrum of ethyl 5-bromoanthranilate (12)

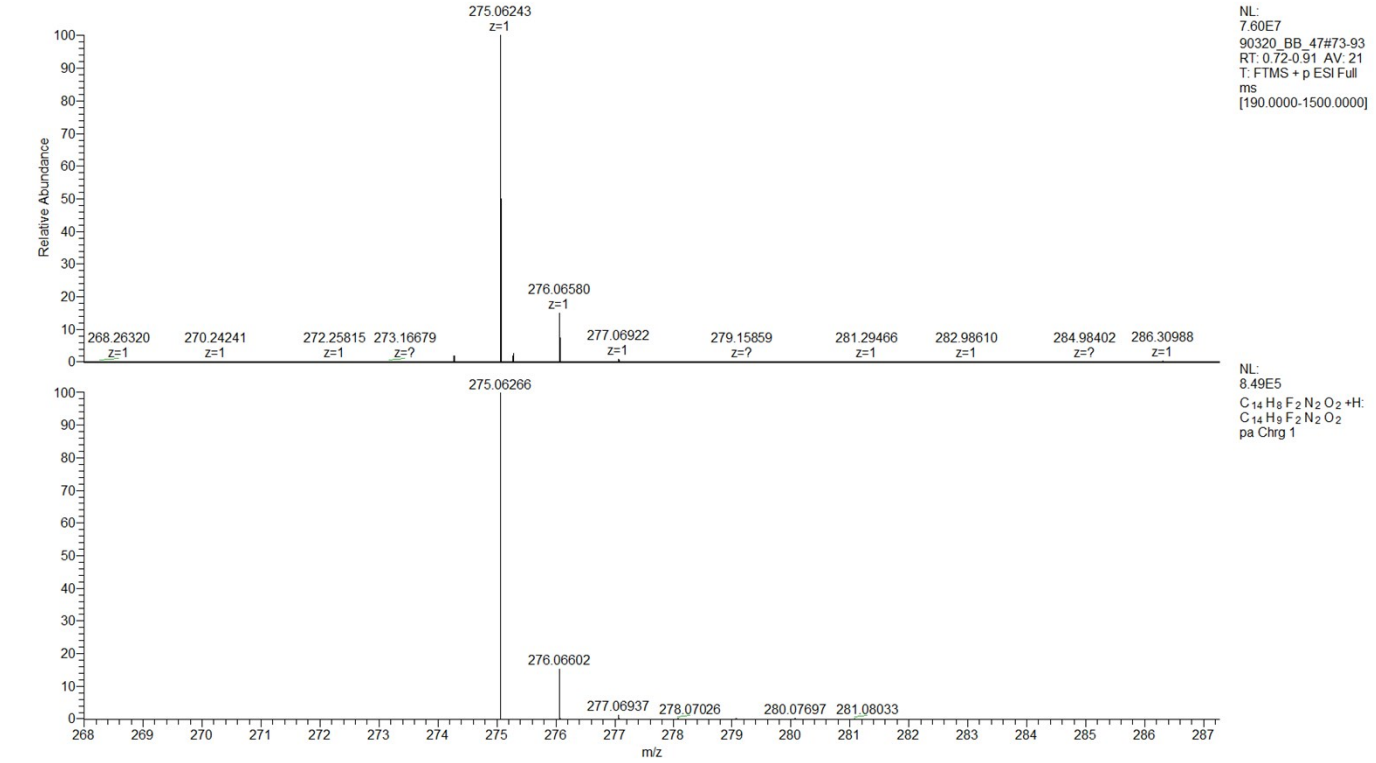


Figure S23. HRMS-ESI spectrum of 5*H*,11*H*-2,8-difluorodibenzo[*b,f*][1,5]diazocine-6,12-dione (1)

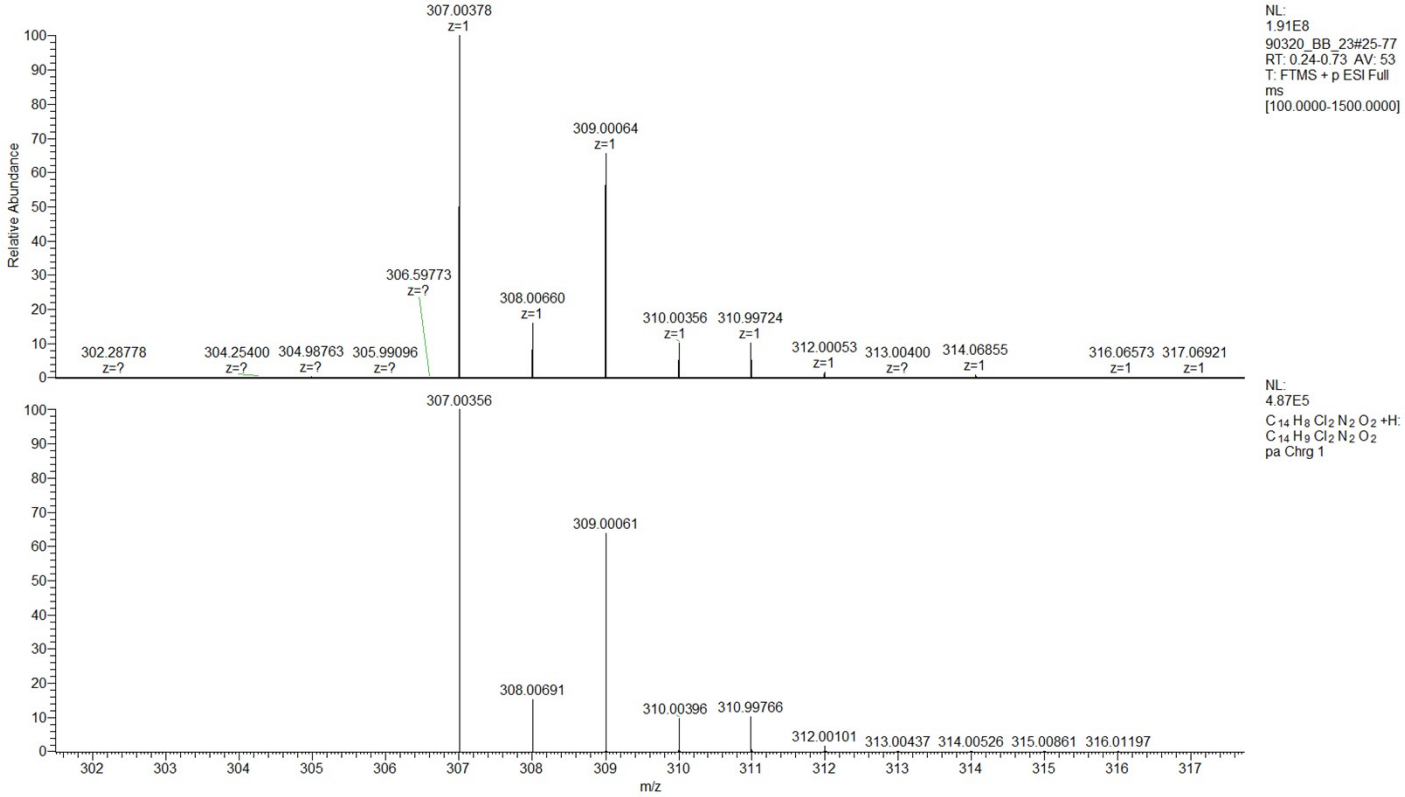


Figure S24. HRMS-ESI spectrum of 5*H*,11*H*-2,8-dichlorodibenzo[*b,f*][1,5]diazocine-6,12-dione (2)

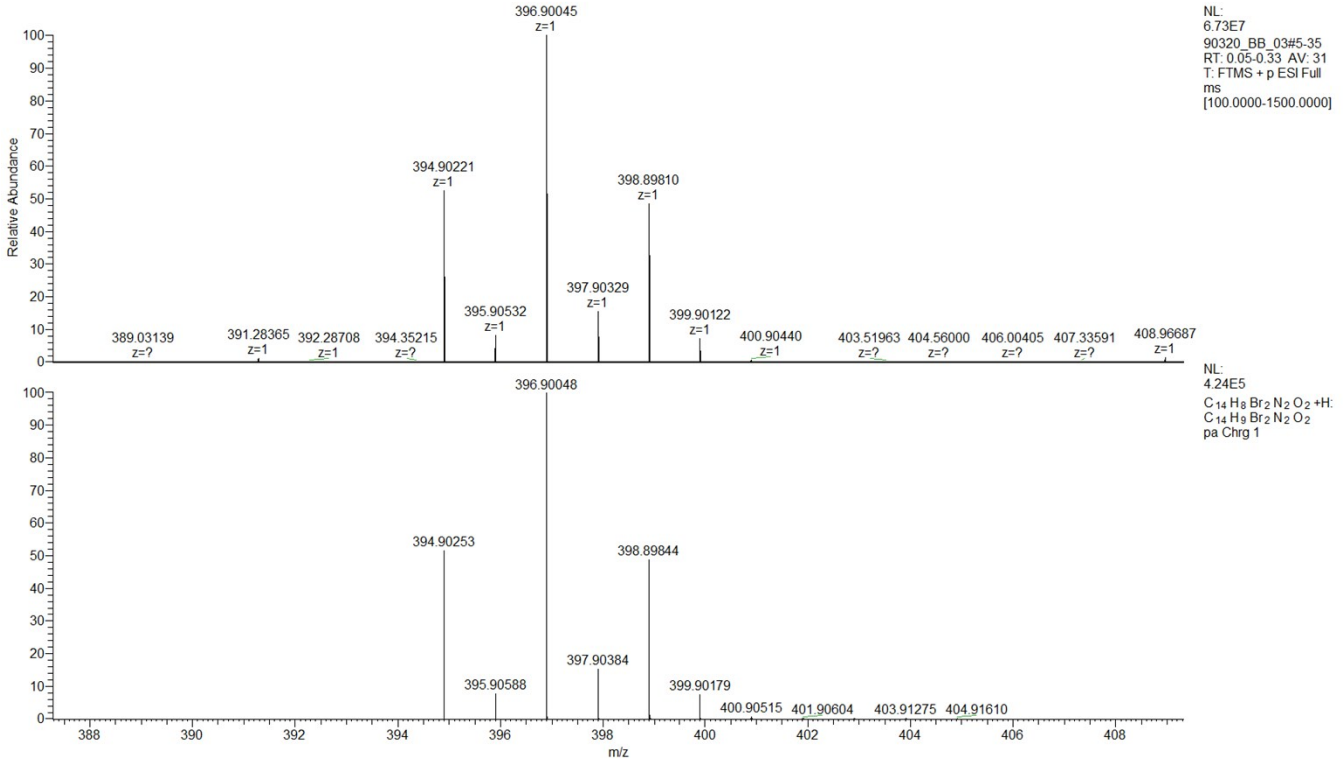


Figure S25. HRMS-ESI spectrum of 5*H*,11*H*-2,8-dibromodibenzo[*b,f*][1,5]diazocine-6,12-dione (3)

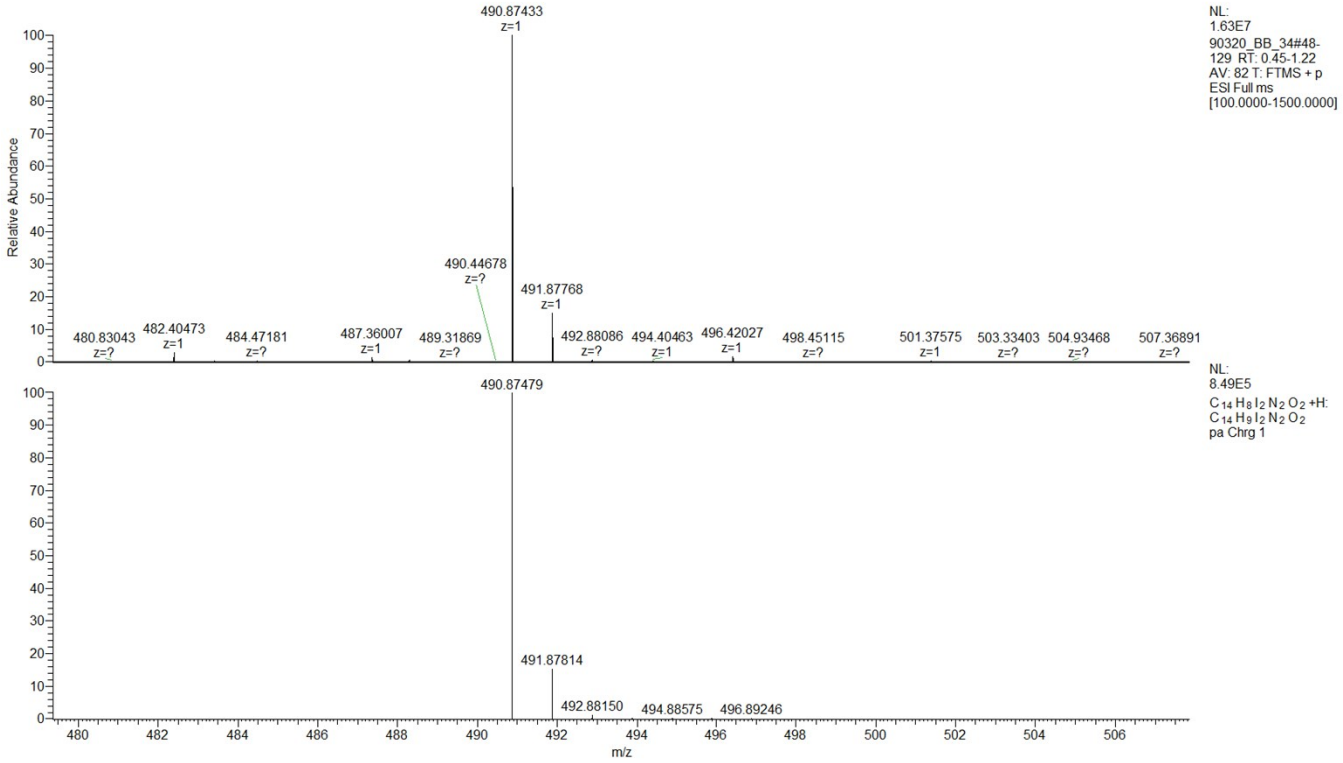


Figure S26. HRMS-ESI spectrum of 5*H*,11*H*-2,8-diiododibenzo[*b,f*][1,5]diazocine-6,12-dione (4)

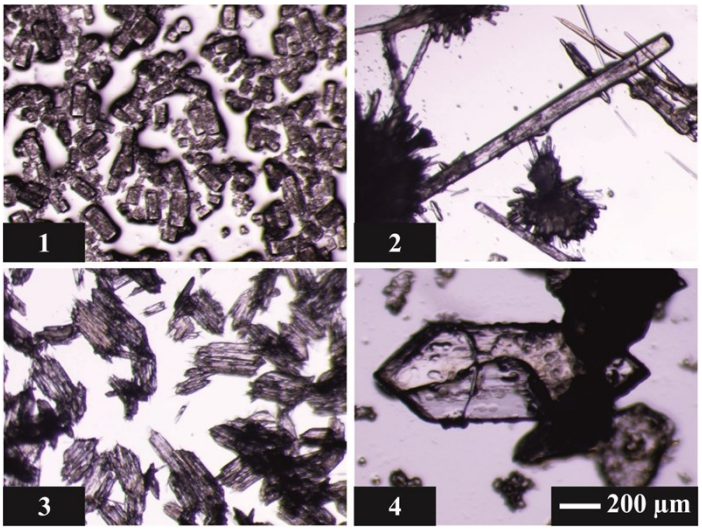


Figure S27. Respective view on the crystals of **1**–**4**.

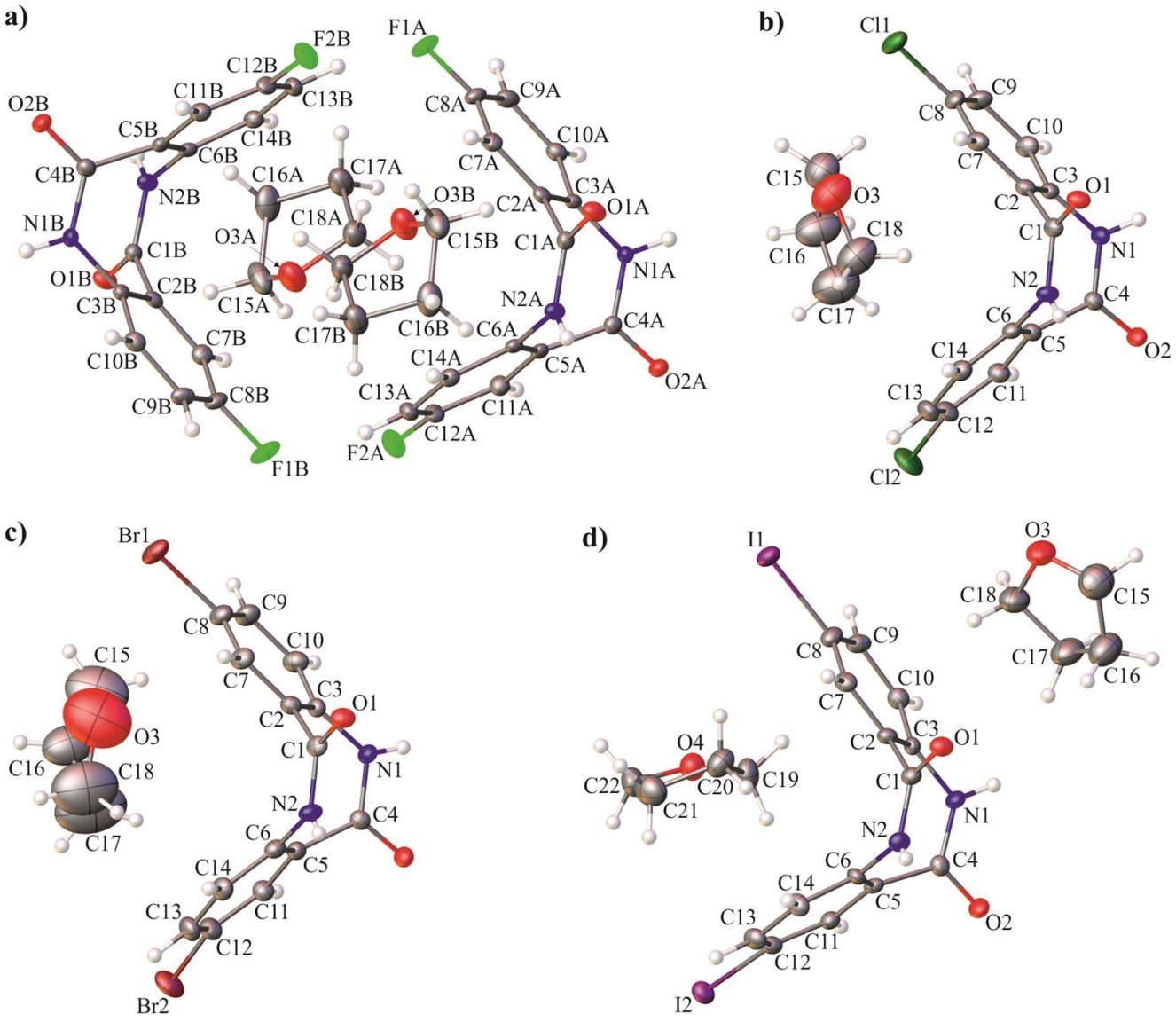


Figure S28. The asymmetric unit of the crystal lattice of **1–4** (a–d) with the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radius

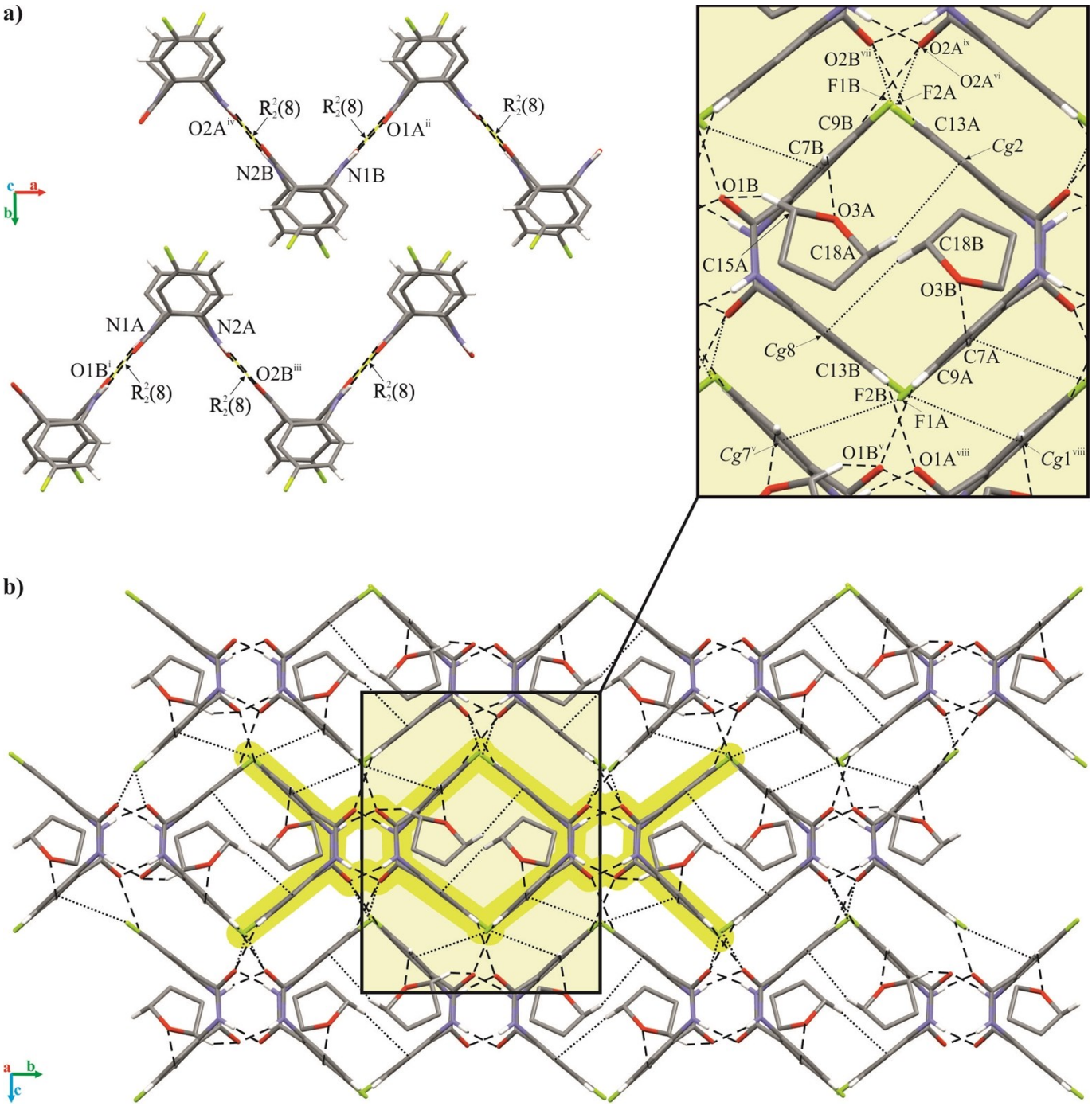


Figure S29. Arrangement of moieties of **1** in the crystal, where: (a) pair of infinite chains of molecules of halogen-derivative running along the [100] direction; (b) 3D-honeycomb framework built of molecules of halogen-derivative and the THF, viewed along the *a*-direction (a pair of chains of molecules of halogen derivative is highlighted in yellowish-green); The N–H···O and C–H···O hydrogen bonds are represented by dashed lines, while the C–H···π, C–F···π and F···O contacts by dotted lines. The H-bonds not involved in the intermolecular interactions have been omitted for clarity. Symmetry codes: Symmetry codes: (i) –*x* + 1/2, *y* + 1/2, –*z* + 1/2; (ii) –*x* + 3/2, *y* – 1/2, –*z* + 1/2; (iii) –*x* + 3/2, *y* + 1/2, –*z* + 1/2; (iv) –*x* + 1/2, *y* – 1/2, –*z* + 1/2; (v) *x* – 1/2, –*y* + 1/2, *z* + 1/2; (vi) –*x* + 1, –*y* + 1, –*z*; (vii) *x* – 1/2, –*y* + 1/2, *z* – 1/2; (viii) –*x* + 1, –*y* + 1, –*z* + 1; (ix) –*x*,–*y* + 1,–*z*.

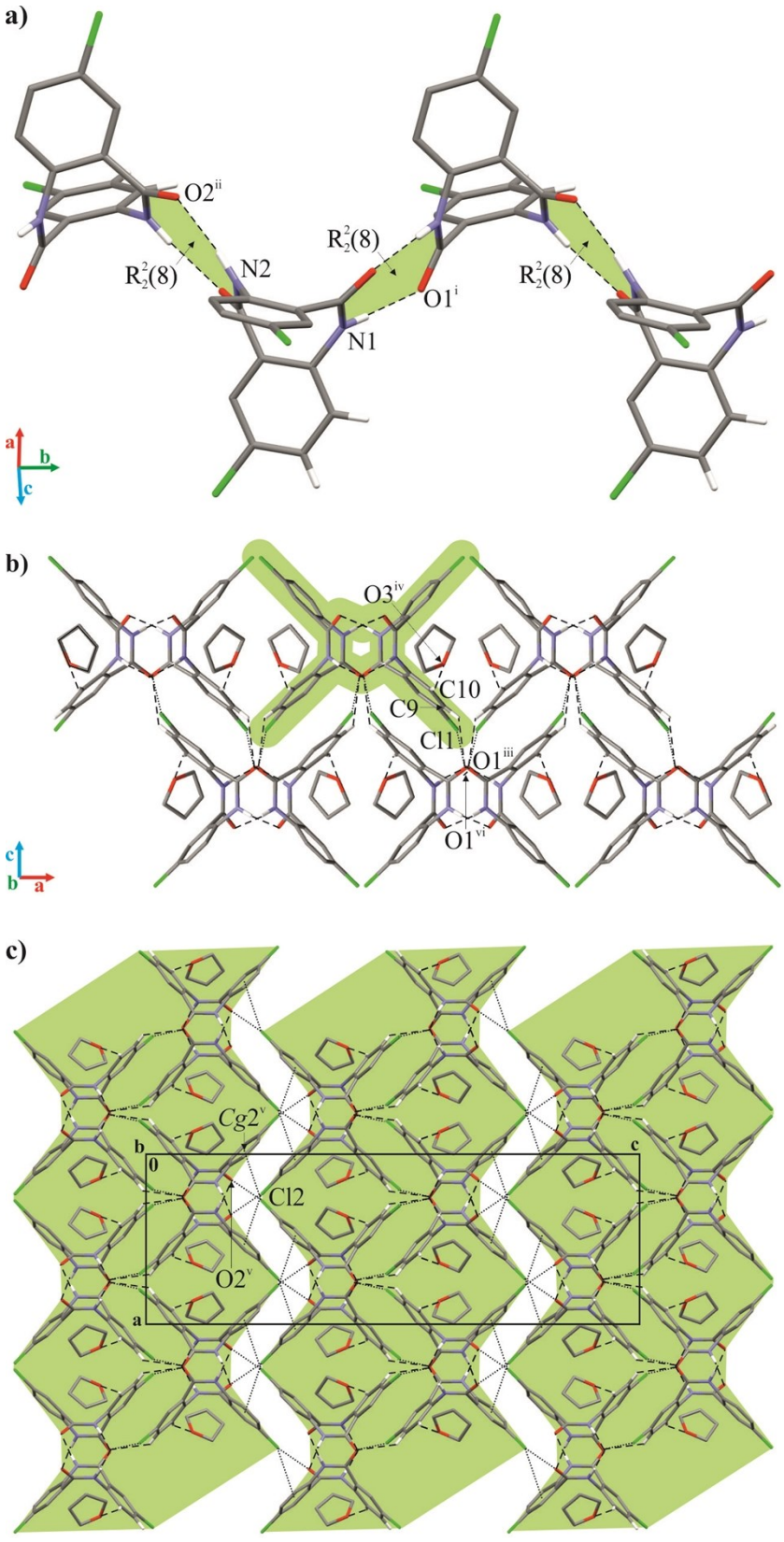


Figure S30. Arrangement of moieties of **2** in the crystal, where: (a) infinite chain of molecules of halogen-derivative runs along the [010] direction; (b) 2D-honeycomb layer built of molecules of halogen-derivative and the THF (view from the side) (single chain of molecules is highlighted in green); (c) general view on complex 3D-supramolecular architecture of **2**, viewed along the *b*-direction. The N–H···O and C–H···O hydrogen bonds are represented by dashed lines, while the C–Cl···π and Cl···O contacts by dotted lines. The H-bonds not involved in the intermolecular interactions have been omitted for clarity. Symmetry codes: (i) –*x* + 3/2, *y* + 1/2, *z*; (ii) –*x* + 3/2, *y* – 1/2, *z*; (iii) *x* – 1/2, –*y* + 1/2, –*z* + 1; (iv) –*x* + 1/2, *y* + 1/2, *z;* (v) *x* – 1/2, *y*, –*z* + 1/2; (vi) –*x* + 1, –*y*, –*z* + 1.

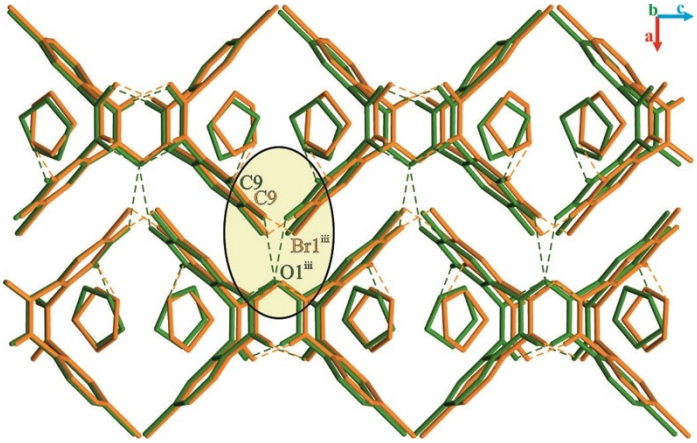


Figure S31. The H-bonding scheme in the superimposed 'honey comb' frameworks of **2** and **3**. The solvates **2** and **3** are coloured in green and orange, respectively. The N−H···O, C−H···O and C−H···Br hydrogen bonds are represented by dashed lines. The H-bonds not involved in the intermolecular interactions have been omitted for clarity. Symmetry codes: (**2**) (iii) $x - 1/2, -y + 1/2, -z + 1$; (**3**) (iii) $-x + 3/2, y + 1/2$, z.

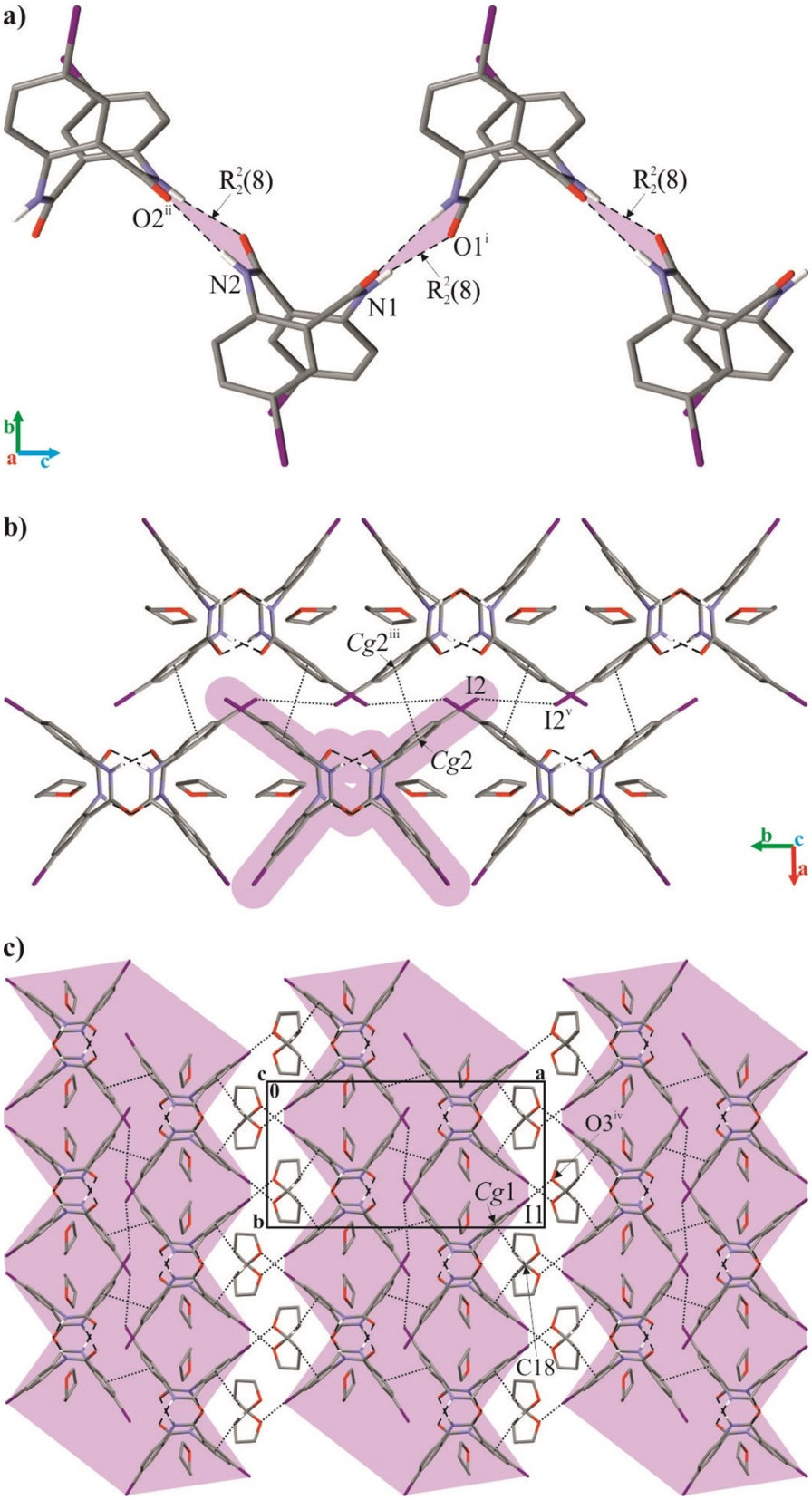


Figure S32. Arrangement of moieties of **4** in the crystal, where: (a) infinite chain of molecules of halogen-derivative that runs along [001] direction; (b) 2D-honeycomb layer built of molecules of halogen-derivative and the THF (view from the side) (single chain of molecules is highlighted in violet); (c) general view on complex 3D-supramolecular architecture of **4**, viewed along the *b*-direction. The N–H···O hydrogen bonds are represented by dashed lines, while the weak C–H···π, π-π, I···O and I···I contacts by dotted lines. The H-bonds not involved in the intermolecular interactions have been omitted for clarity. Symmetry codes: (i) *x*, –*y* + 5/2, *z* + 1/2; (ii) *x*, –*y* + 5/2. *z* –1/2; (iii) –*x* + 1, –*y* + 2, –*z* + 1.; (iv) –*x* + 2, –*y* – 2, –*z* + 1; (v) –*x* + 1, –*y* + 1, –*z* + 1.

Table S1. Crystal data and structure refinement for **1**–**4**.

Identification code	**1**	**2**	**3**	**4**
Empirical formula	$C_{18}H_{16}F_2N_2O_3$	$C_{18}H_{16}Cl_2N_2O_3$	$C_{18}H_{16}Br_2N_2O_3$	$C_{22}H_{24}I_2N_2O_4$
Formula weight	346.33	379.23	468.15	634.23
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/n$	*Pbca*	*Pbca*	$P2_1/c$
a/Å	10.6612(3)	10.6078(5)	10.77295(12)	20.3062(6)
b/Å	20.5090(5)	10.7273(4)	10.79851(9)	10.4583(3)
c/Å	14.3063(3)	31.0150(11)	31.7818(4)	11.1201(4)
α/°	90	90	90	90
β/°	90.046(2)	90	90	102.196(3)
γ/°	90	90	90	90
Volume/Å^3	3128.08(13)	3529.3(2)	3697.23(7)	2308.25(13)
Z	8	8	8	4
ρ_{calc}g/cm^3	1.471	1.427	1.682	1.825
μ/mm^{-1}	0.993	3.483	5.731	21.654
F(000)	1440.0	1568.0	1856.0	1232.0
Crystal size/mm^3	0.19 × 0.11 × 0.10	0.30 × 0.07 × 0.05	0.34 × 0.08 × 0.06	0.32 × 0.13 × 0.07
Radiation	Cu*K*α (*λ* = 1.54184)	Cu*K*α (*λ* = 1.54184)	Cu*K*α (*λ* = 1.54184)	Cu*K*α (*λ* = 1.54184)
2*Θ* range for data collection/°	7.534 to 134.124	5.7 to 134.148	5.562 to 134.074	4.452 to 134.15
Index ranges	-12 ≤ *h* ≤ 12, -24 ≤ *k* ≤ 24, -17 ≤ *l* ≤ 17	-12 ≤ *h* ≤ 12, -12 ≤ *k* ≤ 12, -22 ≤ *l* ≤ 37	-12 ≤ *h* ≤ 12, -12 ≤ *k* ≤ 12, -37 ≤ *l* ≤ 37	-23 ≤ *h* ≤ 24, -8 ≤ *k* ≤ 12, -13 ≤ *l* ≤ 9
Reflections collected	42020	7516	115169	8500
Independent reflections	5600 [R_{int} = 0.0438, R_{sigma} = 0.0228]	3152 [R_{int} = 0.0306, R_{sigma} = 0.0380]	3289 [R_{int} = 0.0731, R_{sigma} = 0.0143]	4122 [R_{int} = 0.0435, R_{sigma} = 0.0456]
Data/restraints/parameters	5600/4/463	3152/39/233	3289/42/217	4122/39/279
Goodness-of-fit on F^2	1.052	1.050	1.079	1.042
Final *R* indexes [*I*>=2σ (*I*)]	R_1 = 0.0518, wR_2 = 0.1452	R_1 = 0.0617, wR_2 = 0.1646	R_1 = 0.0576, wR_2 = 0.1538	R_1 = 0.0480, wR_2 = 0.1271
Final *R* indexes [all data]	R_1 = 0.0700, wR_2 = 0.1642	R_1 = 0.0755, wR_2 = 0.1764	R_1 = 0.0613, wR_2 = 0.1575	R_1 = 0.0557, wR_2 = 0.1362
Largest diff. peak/hole / e Å^{-3}	0.51/-0.24	1.46/-0.95	3.42/-1.31	1.51/-1.73

Table S2. Bond lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(1A)	C(2A)	1.503(2)	C(3B)	C(10B)	1.400(3)
C(1A)	N(2A)	1.347(2)	C(3B)	N(1B)	1.423(2)
C(1A)	O(1A)	1.233(2)	C(4B)	C(5B)	1.503(2)
C(2A)	C(3A)	1.392(3)	C(4B)	N(1B)	1.348(2)
C(2A)	C(7A)	1.393(3)	C(4B)	O(2B)	1.232(2)
C(3A)	C(10A)	1.400(2)	C(5B)	C(6B)	1.396(3)
C(3A)	N(1A)	1.425(2)	C(5B)	C(11B)	1.391(3)
C(4A)	C(5A)	1.501(2)	C(6B)	C(14B)	1.394(3)
C(4A)	N(1A)	1.349(2)	C(6B)	N(2B)	1.427(2)
C(4A)	O(2A)	1.233(2)	C(7B)	C(8B)	1.383(3)
C(5A)	C(6A)	1.396(3)	C(8B)	C(9B)	1.379(3)
C(5A)	C(11A)	1.395(3)	C(8B)	F(1B)	1.354(2)
C(6A)	C(14A)	1.396(2)	C(9B)	C(10B)	1.382(3)
C(6A)	N(2A)	1.428(2)	C(11B)	C(12B)	1.384(3)
C(7A)	C(8A)	1.383(3)	C(12B)	C(13B)	1.379(3)
C(8A)	C(9A)	1.378(3)	C(12B)	F(2B)	1.355(2)
C(8A)	F(1A)	1.358(2)	C(13B)	C(14B)	1.385(3)
C(9A)	C(10A)	1.384(3)	C(15A)	C(16A)	1.503(3)
C(11A)	C(12A)	1.385(3)	C(15A)	O(3A)	1.428(3)
C(12A)	C(13A)	1.380(3)	C(16A)	C(17A)	1.524(3)
C(12A)	F(2A)	1.354(2)	C(17A)	C(18A)	1.534(3)
C(13A)	C(14A)	1.385(3)	C(18A)	O(3A)	1.433(2)
C(1B)	C(2B)	1.501(2)	C(15B)	C(16B)	1.508(3)
C(1B)	N(2B)	1.353(2)	C(15B)	O(3B)	1.423(3)
C(1B)	O(1B)	1.233(2)	C(16B)	C(17B)	1.524(3)
C(2B)	C(3B)	1.394(3)	C(17B)	C(18B)	1.537(3)
C(2B)	C(7B)	1.394(3)	C(18B)	O(3B)	1.431(2)

Table S3. Values for valence angles for **1**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N(2A)	C(1A)	C(2A)	118.52(16)	C(7B)	C(2B)	C(3B)	120.11(17)
O(1A)	C(1A)	C(2A)	118.85(15)	C(2B)	C(3B)	C(10B)	119.85(17)
O(1A)	C(1A)	N(2A)	122.63(16)	C(2B)	C(3B)	N(1B)	121.02(16)
C(3A)	C(2A)	C(1A)	121.58(16)	C(10B)	C(3B)	N(1B)	119.05(17)
C(3A)	C(2A)	C(7A)	120.40(17)	N(1B)	C(4B)	C(5B)	117.94(16)
C(7A)	C(2A)	C(1A)	117.78(17)	O(2B)	C(4B)	C(5B)	119.62(16)
C(2A)	C(3A)	C(10A)	119.74(17)	O(2B)	C(4B)	N(1B)	122.45(16)
C(2A)	C(3A)	N(1A)	120.92(16)	C(6B)	C(5B)	C(4B)	121.38(16)
C(10A)	C(3A)	N(1A)	119.22(17)	C(11B)	C(5B)	C(4B)	118.34(17)
N(1A)	C(4A)	C(5A)	117.95(15)	C(11B)	C(5B)	C(6B)	120.10(17)
O(2A)	C(4A)	C(5A)	119.75(16)	C(5B)	C(6B)	N(2B)	120.55(16)
O(2A)	C(4A)	N(1A)	122.30(16)	C(14B)	C(6B)	C(5B)	119.79(17)
C(6A)	C(5A)	C(4A)	121.23(16)	C(14B)	C(6B)	N(2B)	119.55(17)
C(11A)	C(5A)	C(4A)	118.69(17)	C(8B)	C(7B)	C(2B)	118.10(18)
C(11A)	C(5A)	C(6A)	119.91(17)	C(9B)	C(8B)	C(7B)	123.17(18)
C(5A)	C(6A)	N(2A)	120.53(16)	F(1B)	C(8B)	C(7B)	118.37(18)
C(14A)	C(6A)	C(5A)	120.11(17)	F(1B)	C(8B)	C(9B)	118.46(17)
C(14A)	C(6A)	N(2A)	119.29(17)	C(8B)	C(9B)	C(10B)	118.25(17)
C(8A)	C(7A)	C(2A)	117.87(18)	C(9B)	C(10B)	C(3B)	120.46(18)

C(9A)	C(8A)	C(7A)	123.31(18)	C(12B)	C(11B)	C(5B)	118.14(18)
F(1A)	C(8A)	C(7A)	117.89(17)	C(13B)	C(12B)	C(11B)	123.13(18)
F(1A)	C(8A)	C(9A)	118.80(16)	F(2B)	C(12B)	C(11B)	117.97(17)
C(8A)	C(9A)	C(10A)	118.14(17)	F(2B)	C(12B)	C(13B)	118.89(17)
C(9A)	C(10A)	C(3A)	120.44(18)	C(12B)	C(13B)	C(14B)	118.04(17)
C(12A)	C(11A)	C(5A)	118.16(18)	C(13B)	C(14B)	C(6B)	120.66(17)
C(13A)	C(12A)	C(11A)	122.99(18)	C(4B)	N(1B)	C(3B)	124.92(15)
F(2A)	C(12A)	C(11A)	118.36(17)	C(1B)	N(2B)	C(6B)	124.78(15)
F(2A)	C(12A)	C(13A)	118.65(17)	O(3A)	C(15A)	C(16A)	104.25(17)
C(12A)	C(13A)	C(14A)	118.35(17)	C(15A)	C(16A)	C(17A)	102.66(18)
C(13A)	C(14A)	C(6A)	120.35(18)	C(16A)	C(17A)	C(18A)	103.82(17)
C(4A)	N(1A)	C(3A)	125.27(15)	O(3A)	C(18A)	C(17A)	106.72(17)
C(1A)	N(2A)	C(6A)	124.56(15)	C(15A)	O(3A)	C(18A)	106.17(16)
N(2B)	C(1B)	C(2B)	118.24(16)	O(3B)	C(15B)	C(16B)	104.37(17)
O(1B)	C(1B)	C(2B)	119.52(16)	C(15B)	C(16B)	C(17B)	102.25(18)
O(1B)	C(1B)	N(2B)	122.24(16)	C(16B)	C(17B)	C(18B)	103.84(17)
C(3B)	C(2B)	C(1B)	120.97(16)	O(3B)	C(18B)	C(17B)	106.72(17)
C(7B)	C(2B)	C(1B)	118.68(17)	C(15B)	O(3B)	C(18B)	106.43(16)

Table S4. Values of torsion angles for **1**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C(1A)	C(2A)	C(3A)	C(10A)	-171.56(16)	C(2B)	C(3B)	N(1B)	C(4B)	-71.2(2)
C(1A)	C(2A)	C(3A)	N(1A)	4.4(2)	C(2B)	C(7B)	C(8B)	C(9B)	2.2(3)
C(1A)	C(2A)	C(7A)	C(8A)	174.12(16)	C(2B)	C(7B)	C(8B)	F(1B)	-176.72(15)
C(2A)	C(1A)	N(2A)	C(6A)	-8.7(3)	C(3B)	C(2B)	C(7B)	C(8B)	-0.2(3)
C(2A)	C(3A)	C(10A)	C(9A)	-2.5(3)	C(4B)	C(5B)	C(6B)	C(14B)	171.63(16)
C(2A)	C(3A)	N(1A)	C(4A)	69.7(2)	C(4B)	C(5B)	C(6B)	N(2B)	-4.5(2)
C(2A)	C(7A)	C(8A)	C(9A)	-2.3(3)	C(4B)	C(5B)	C(11B)	C(12B)	-174.73(16)
C(2A)	C(7A)	C(8A)	F(1A)	177.45(15)	C(5B)	C(4B)	N(1B)	C(3B)	7.9(3)
C(3A)	C(2A)	C(7A)	C(8A)	-0.4(3)	C(5B)	C(6B)	C(14B)	C(13B)	3.2(3)
C(4A)	C(5A)	C(6A)	C(14A)	-172.66(16)	C(5B)	C(6B)	N(2B)	C(1B)	-70.9(2)
C(4A)	C(5A)	C(6A)	N(2A)	4.4(2)	C(5B)	C(11B)	C(12B)	C(13B)	2.9(3)
C(4A)	C(5A)	C(11A)	C(12A)	175.88(16)	C(5B)	C(11B)	C(12B)	F(2B)	-178.13(15)
C(5A)	C(4A)	N(1A)	C(3A)	-6.4(3)	C(6B)	C(5B)	C(11B)	C(12B)	0.3(3)
C(5A)	C(6A)	C(14A)	C(13A)	-3.0(3)	C(7B)	C(2B)	C(3B)	C(10B)	-1.8(3)
C(5A)	C(6A)	N(2A)	C(1A)	71.3(2)	C(7B)	C(2B)	C(3B)	N(1B)	-178.38(15)
C(5A)	C(11A)	C(12A)	C(13A)	-3.3(3)	C(7B)	C(8B)	C(9B)	C(10B)	-2.1(3)
C(5A)	C(11A)	C(12A)	F(2A)	176.68(15)	C(8B)	C(9B)	C(10B)	C(3B)	0.0(3)
C(6A)	C(5A)	C(11A)	C(12A)	0.6(3)	C(10B)	C(3B)	N(1B)	C(4B)	112.2(2)
C(7A)	C(2A)	C(3A)	C(10A)	2.7(3)	C(11B)	C(5B)	C(6B)	C(14B)	-3.3(3)
C(7A)	C(2A)	C(3A)	N(1A)	178.63(15)	C(11B)	C(5B)	C(6B)	N(2B)	-179.46(15)
C(7A)	C(8A)	C(9A)	C(10A)	2.5(3)	C(11B)	C(12B)	C(13B)	C(14B)	-3.0(3)
C(8A)	C(9A)	C(10A)	C(3A)	-0.1(3)	C(12B)	C(13B)	C(14B)	C(6B)	-0.1(3)
C(10A)	C(3A)	N(1A)	C(4A)	-114.3(2)	C(14B)	C(6B)	N(2B)	C(1B)	113.0(2)
C(11A)	C(5A)	C(6A)	C(14A)	2.5(3)	F(1B)	C(8B)	C(9B)	C(10B)	176.80(16)
C(11A)	C(5A)	C(6A)	N(2A)	179.53(15)	F(2B)	C(12B)	C(13B)	C(14B)	178.04(15)
C(11A)	C(12A)	C(13A)	C(14A)	2.8(3)	N(1B)	C(3B)	C(10B)	C(9B)	178.54(16)
C(12A)	C(13A)	C(14A)	C(6A)	0.5(3)	N(1B)	C(4B)	C(5B)	C(6B)	66.1(2)
C(14A)	C(6A)	N(2A)	C(1A)	-111.6(2)	N(1B)	C(4B)	C(5B)	C(11B)	-118.92(19)
F(1A)	C(8A)	C(9A)	C(10A)	-177.25(16)	N(2B)	C(1B)	C(2B)	C(3B)	65.7(2)
F(2A)	C(12A)	C(13A)	C(14A)	-177.22(16)	N(2B)	C(1B)	C(2B)	C(7B)	-119.87(19)

N(1A)	C(3A)	C(10A)	C(9A)	-178.50(16)	N(2B)	C(6B)	C(14B)	C(13B)	179.41(16)
N(1A)	C(4A)	C(5A)	C(6A)	-66.9(2)	O(1B)	C(1B)	C(2B)	C(3B)	-114.5(2)
N(1A)	C(4A)	C(5A)	C(11A)	117.96(19)	O(1B)	C(1B)	C(2B)	C(7B)	59.9(2)
N(2A)	C(1A)	C(2A)	C(3A)	-65.3(2)	O(1B)	C(1B)	N(2B)	C(6B)	-171.82(17)
N(2A)	C(1A)	C(2A)	C(7A)	120.32(18)	O(2B)	C(4B)	C(5B)	C(6B)	-114.2(2)
N(2A)	C(6A)	C(14A)	C(13A)	179.86(16)	O(2B)	C(4B)	C(5B)	C(11B)	60.8(2)
O(1A)	C(1A)	C(2A)	C(3A)	114.4(2)	O(2B)	C(4B)	N(1B)	C(3B)	-171.84(17)
O(1A)	C(1A)	C(2A)	C(7A)	-60.0(2)	C(15A)	C(16A)	C(17A)	C(18A)	-21.5(2)
O(1A)	C(1A)	N(2A)	C(6A)	171.64(17)	C(16A)	C(15A)	O(3A)	C(18A)	-40.5(2)
O(2A)	C(4A)	C(5A)	C(6A)	113.8(2)	C(16A)	C(17A)	C(18A)	O(3A)	-1.8(2)
O(2A)	C(4A)	C(5A)	C(11A)	-61.4(2)	C(17A)	C(18A)	O(3A)	C(15A)	26.1(2)
O(2A)	C(4A)	N(1A)	C(3A)	172.86(17)	O(3A)	C(15A)	C(16A)	C(17A)	38.1(2)
C(1B)	C(2B)	C(3B)	C(10B)	172.48(16)	C(15B)	C(16B)	C(17B)	C(18B)	22.3(2)
C(1B)	C(2B)	C(3B)	N(1B)	-4.1(2)	C(16B)	C(15B)	O(3B)	C(18B)	40.3(2)
C(1B)	C(2B)	C(7B)	C(8B)	-174.61(16)	C(16B)	C(17B)	C(18B)	O(3B)	0.7(2)
C(2B)	C(1B)	N(2B)	C(6B)	7.9(3)	C(17B)	C(18B)	O(3B)	C(15B)	-25.3(2)
C(2B)	C(3B)	C(10B)	C(9B)	1.9(3)	O(3B)	C(15B)	C(16B)	C(17B)	-38.4(2)

Table S5. Bond lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(1)	C(2)	1.495(5)	C(7)	C(8)	1.380(5)
C(1)	N(2)	1.357(4)	C(8)	C(9)	1.382(5)
C(1)	O(1)	1.229(4)	C(8)	Cl(1)	1.740(3)
C(2)	C(3)	1.399(5)	C(9)	C(10)	1.394(5)
C(2)	C(7)	1.394(5)	C(11)	C(12)	1.384(5)
C(3)	C(10)	1.394(5)	C(12)	C(13)	1.385(5)
C(3)	N(1)	1.427(4)	C(12)	Cl(2)	1.733(3)
C(4)	C(5)	1.493(4)	C(13)	C(14)	1.387(5)
C(4)	N(1)	1.341(4)	C(15)	C(16)	1.483(7)
C(4)	O(2)	1.239(4)	C(15)	O(3)	1.401(6)
C(5)	C(6)	1.402(5)	C(16)	C(17)	1.453(8)
C(5)	C(11)	1.398(5)	C(17)	C(18)	1.499(9)
C(6)	C(14)	1.387(5)	C(18)	O(3)	1.385(7)
C(6)	N(2)	1.421(4)			

Table S6. Values of valence angles for **2**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N(2)	C(1)	C(2)	118.5(3)	C(7)	C(8)	C(9)	121.9(3)
O(1)	C(1)	C(2)	119.4(3)	C(7)	C(8)	Cl(1)	118.6(3)
O(1)	C(1)	N(2)	122.0(3)	C(9)	C(8)	Cl(1)	119.4(3)
C(3)	C(2)	C(1)	122.6(3)	C(8)	C(9)	C(10)	118.7(3)
C(7)	C(2)	C(1)	117.6(3)	C(9)	C(10)	C(3)	120.4(3)
C(7)	C(2)	C(3)	119.6(3)	C(12)	C(11)	C(5)	119.6(3)
C(2)	C(3)	N(1)	120.6(3)	C(11)	C(12)	C(13)	121.4(3)
C(10)	C(3)	C(2)	119.9(3)	C(11)	C(12)	Cl(2)	117.9(3)
C(10)	C(3)	N(1)	119.4(3)	C(13)	C(12)	Cl(2)	120.7(3)
N(1)	C(4)	C(5)	119.4(3)	C(12)	C(13)	C(14)	118.9(3)
O(2)	C(4)	C(5)	118.1(3)	C(6)	C(14)	C(13)	120.9(3)
O(2)	C(4)	N(1)	122.4(3)	C(4)	N(1)	C(3)	125.2(3)
C(6)	C(5)	C(4)	123.0(3)	C(1)	N(2)	C(6)	126.8(3)
C(11)	C(5)	C(4)	116.9(3)	O(3)	C(15)	C(16)	107.5(5)

C(11)	C(5)	C(6)	119.4(3)	C(17)	C(16)	C(15)	106.0(5)
C(5)	C(6)	N(2)	121.0(3)	C(16)	C(17)	C(18)	105.5(5)
C(14)	C(6)	C(5)	119.8(3)	O(3)	C(18)	C(17)	106.6(5)
C(14)	C(6)	N(2)	118.9(3)	C(18)	O(3)	C(15)	108.8(4)
C(8)	C(7)	C(2)	119.5(3)				

Table S7. Values of torsion angles for **2**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C(1)	C(2)	C(3)	C(10)	-172.1(3)	C(11)	C(5)	C(6)	N(2)	174.9(3)
C(1)	C(2)	C(3)	N(1)	3.3(5)	C(11)	C(12)	C(13)	C(14)	1.0(6)
C(1)	C(2)	C(7)	C(8)	174.5(3)	C(12)	C(13)	C(14)	C(6)	0.5(5)
C(2)	C(1)	N(2)	C(6)	-5.9(5)	C(14)	C(6)	N(2)	C(1)	-119.9(4)
C(2)	C(3)	C(10)	C(9)	-2.0(5)	Cl(1)	C(8)	C(9)	C(10)	-179.7(3)
C(2)	C(3)	N(1)	C(4)	71.2(4)	Cl(2)	C(12)	C(13)	C(14)	179.4(3)
C(2)	C(7)	C(8)	C(9)	-2.3(5)	N(1)	C(3)	C(10)	C(9)	-177.5(3)
C(2)	C(7)	C(8)	Cl(1)	179.8(3)	N(1)	C(4)	C(5)	C(6)	-64.2(5)
C(3)	C(2)	C(7)	C(8)	0.0(5)	N(1)	C(4)	C(5)	C(11)	126.1(3)
C(4)	C(5)	C(6)	C(14)	-167.9(3)	N(2)	C(1)	C(2)	C(3)	-65.2(4)
C(4)	C(5)	C(6)	N(2)	5.4(5)	N(2)	C(1)	C(2)	C(7)	120.5(3)
C(4)	C(5)	C(11)	C(12)	169.9(3)	N(2)	C(6)	C(14)	C(13)	-175.2(3)
C(5)	C(4)	N(1)	C(3)	-9.5(5)	O(1)	C(1)	C(2)	C(3)	117.9(4)
C(5)	C(6)	C(14)	C(13)	-1.7(5)	O(1)	C(1)	C(2)	C(7)	-56.4(4)
C(5)	C(6)	N(2)	C(1)	66.8(5)	O(1)	C(1)	N(2)	C(6)	170.9(3)
C(5)	C(11)	C(12)	C(13)	-1.1(5)	O(2)	C(4)	C(5)	C(6)	116.2(4)
C(5)	C(11)	C(12)	Cl(2)	-179.6(3)	O(2)	C(4)	C(5)	C(11)	-53.5(4)
C(6)	C(5)	C(11)	C(12)	-0.2(5)	O(2)	C(4)	N(1)	C(3)	170.1(3)
C(7)	C(2)	C(3)	C(10)	2.1(5)	C(15)	C(16)	C(17)	C(18)	-5.5(8)
C(7)	C(2)	C(3)	N(1)	177.6(3)	C(16)	C(15)	O(3)	C(18)	21.3(7)
C(7)	C(8)	C(9)	C(10)	2.5(6)	C(16)	C(17)	C(18)	O(3)	18.3(8)
C(8)	C(9)	C(10)	C(3)	-0.3(5)	C(17)	C(18)	O(3)	C(15)	-24.6(7)
C(10)	C(3)	N(1)	C(4)	-113.3(4)	O(3)	C(15)	C(16)	C(17)	-9.0(7)
C(11)	C(5)	C(6)	C(14)	1.6(5)					

Table S8. Bond lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br(1)	C(8)	1.896(5)	C(6)	C(14)	1.395(7)
Br(2)	C(12)	1.896(5)	C(6)	N(2)	1.424(6)
C(1)	C(2)	1.497(7)	C(7)	C(8)	1.375(7)
C(1)	N(2)	1.347(6)	C(8)	C(9)	1.388(7)
C(1)	O(1)	1.236(6)	C(9)	C(10)	1.388(7)
C(2)	C(3)	1.391(7)	C(11)	C(12)	1.377(7)
C(2)	C(7)	1.400(7)	C(12)	C(13)	1.386(8)
C(3)	C(10)	1.394(7)	C(13)	C(14)	1.387(8)
C(3)	N(1)	1.432(6)	O(3)	C(15)	1.4367
C(4)	C(5)	1.501(7)	O(3)	C(18)	1.4352
C(4)	N(1)	1.336(6)	C(15)	C(16)	1.5314
C(4)	O(2)	1.236(6)	C(16)	C(17)	1.5356
C(5)	C(6)	1.399(7)	C(17)	C(18)	1.5322
C(5)	C(11)	1.396(7)			

Table S9. Values of valence angles for **3**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N(2)	C(1)	C(2)	118.9(4)	C(7)	C(8)	Br(1)	118.4(4)
O(1)	C(1)	C(2)	119.1(4)	C(7)	C(8)	C(9)	122.0(5)
O(1)	C(1)	N(2)	122.0(5)	C(9)	C(8)	Br(1)	119.6(4)
C(3)	C(2)	C(1)	123.5(4)	C(8)	C(9)	C(10)	118.8(5)
C(3)	C(2)	C(7)	119.8(5)	C(9)	C(10)	C(3)	120.3(5)
C(7)	C(2)	C(1)	116.4(4)	C(12)	C(11)	C(5)	119.3(5)
C(2)	C(3)	C(10)	120.0(4)	C(11)	C(12)	Br(2)	117.4(4)
C(2)	C(3)	N(1)	120.5(4)	C(11)	C(12)	C(13)	121.8(5)
C(10)	C(3)	N(1)	119.3(4)	C(13)	C(12)	Br(2)	120.8(4)
N(1)	C(4)	C(5)	119.5(4)	C(12)	C(13)	C(14)	119.0(5)
O(2)	C(4)	C(5)	117.9(4)	C(13)	C(14)	C(6)	120.4(5)
O(2)	C(4)	N(1)	122.6(4)	C(4)	N(1)	C(3)	125.5(4)
C(6)	C(5)	C(4)	122.5(4)	C(1)	N(2)	C(6)	126.2(4)
C(11)	C(5)	C(4)	117.0(4)	C(18)	O(3)	C(15)	110.1
C(11)	C(5)	C(6)	119.8(5)	O(3)	C(15)	C(16)	106.3
C(5)	C(6)	N(2)	121.4(4)	C(15)	C(16)	C(17)	101.8
C(14)	C(6)	C(5)	119.7(5)	C(18)	C(17)	C(16)	101.8
C(14)	C(6)	N(2)	118.6(4)	O(3)	C(18)	C(17)	106.3
C(8)	C(7)	C(2)	119.0(5)				

Table S10. Values of torsion angles for **3**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Br(1)	C(8)	C(9)	C(10)	-179.6(4)	C(10)	C(3)	N(1)	C(4)	-115.7(6)
Br(2)	C(12)	C(13)	C(14)	178.5(4)	C(11)	C(5)	C(6)	C(14)	2.0(7)
C(1)	C(2)	C(3)	C(10)	-171.5(5)	C(11)	C(5)	C(6)	N(2)	175.5(4)
C(1)	C(2)	C(3)	N(1)	4.3(7)	C(11)	C(12)	C(13)	C(14)	0.7(8)
C(1)	C(2)	C(7)	C(8)	173.6(5)	C(12)	C(13)	C(14)	C(6)	0.3(8)
C(2)	C(1)	N(2)	C(6)	-6.0(7)	C(14)	C(6)	N(2)	C(1)	-120.1(5)
C(2)	C(3)	C(10)	C(9)	-2.1(8)	N(1)	C(3)	C(10)	C(9)	-178.0(5)
C(2)	C(3)	N(1)	C(4)	68.5(7)	N(1)	C(4)	C(5)	C(6)	-66.0(7)
C(2)	C(7)	C(8)	Br(1)	-179.9(4)	N(1)	C(4)	C(5)	C(11)	123.9(5)
C(2)	C(7)	C(8)	C(9)	-1.3(8)	N(2)	C(1)	C(2)	C(3)	-65.6(7)
C(3)	C(2)	C(7)	C(8)	-0.9(7)	N(2)	C(1)	C(2)	C(7)	120.1(5)
C(4)	C(5)	C(6)	C(14)	-167.8(4)	N(2)	C(6)	C(14)	C(13)	-175.3(5)
C(4)	C(5)	C(6)	N(2)	5.7(7)	O(1)	C(1)	C(2)	C(3)	115.7(5)
C(4)	C(5)	C(11)	C(12)	169.3(5)	O(1)	C(1)	C(2)	C(7)	-58.6(6)
C(5)	C(4)	N(1)	C(3)	-6.8(7)	O(1)	C(1)	N(2)	C(6)	172.6(5)
C(5)	C(6)	C(14)	C(13)	-1.6(8)	O(2)	C(4)	C(5)	C(6)	115.2(5)
C(5)	C(6)	N(2)	C(1)	66.4(7)	O(2)	C(4)	C(5)	C(11)	-54.9(6)
C(5)	C(11)	C(12)	Br(2)	-178.2(4)	O(2)	C(4)	N(1)	C(3)	172.0(4)
C(5)	C(11)	C(12)	C(13)	-0.3(8)	O(3)	C(15)	C(16)	C(17)	-30.6
C(6)	C(5)	C(11)	C(12)	-1.1(7)	C(15)	O(3)	C(18)	C(17)	12.0
C(7)	C(2)	C(3)	C(10)	2.6(7)	C(15)	C(16)	C(17)	C(18)	36.3
C(7)	C(2)	C(3)	N(1)	178.4(4)	C(16)	C(17)	C(18)	O(3)	-30.6
C(7)	C(8)	C(9)	C(10)	1.8(8)	C(18)	O(3)	C(15)	C(16)	12.0
C(8)	C(9)	C(10)	C(3)	-0.1(8)					

Table S11. Bond lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I(2)	C(12)	2.109(6)	C(7)	C(2)	1.393(8)

I(1)	C(8)	2.104(6)	C(7)	C(8)	1.388(8)
O(4)	C(19)	1.423(8)	C(1)	C(2)	1.509(8)
O(4)	C(22)	1.416(8)	C(4)	C(5)	1.488(8)
N(1)	C(4)	1.358(7)	C(3)	C(10)	1.396(8)
N(1)	C(3)	1.418(7)	C(3)	C(2)	1.396(8)
O(1)	C(1)	1.227(7)	C(10)	C(9)	1.388(8)
O(2)	C(4)	1.228(7)	C(20)	C(19)	1.521(11)
O(3)	C(18)	1.429(9)	C(20)	C(21)	1.511(11)
O(3)	C(15)	1.387(11)	C(12)	C(13)	1.386(8)
N(2)	C(1)	1.346(7)	C(6)	C(5)	1.397(8)
N(2)	C(6)	1.428(7)	C(9)	C(8)	1.362(9)
C(14)	C(6)	1.394(8)	C(18)	C(17)	1.507(10)
C(14)	C(13)	1.378(8)	C(22)	C(21)	1.507(11)
C(11)	C(12)	1.369(8)	C(17)	C(16)	1.496(12)
C(11)	C(5)	1.390(8)	C(16)	C(15)	1.447(12)

Table S12. Values of valence angles for **4**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C(22)	O(4)	C(19)	109.5(6)	C(14)	C(6)	N(2)	118.6(5)
C(4)	N(1)	C(3)	126.2(5)	C(14)	C(6)	C(5)	120.0(5)
C(15)	O(3)	C(18)	108.1(6)	C(5)	C(6)	N(2)	121.2(5)
C(1)	N(2)	C(6)	124.2(5)	C(11)	C(5)	C(4)	118.7(5)
C(13)	C(14)	C(6)	120.6(5)	C(11)	C(5)	C(6)	118.8(5)
C(12)	C(11)	C(5)	120.3(5)	C(6)	C(5)	C(4)	122.3(5)
C(8)	C(7)	C(2)	119.6(5)	C(8)	C(9)	C(10)	119.7(5)
O(1)	C(1)	N(2)	122.3(5)	C(7)	C(2)	C(1)	116.8(5)
O(1)	C(1)	C(2)	118.4(5)	C(7)	C(2)	C(3)	119.9(5)
N(2)	C(1)	C(2)	119.4(5)	C(3)	C(2)	C(1)	122.7(5)
N(1)	C(4)	C(5)	118.9(5)	C(14)	C(13)	C(12)	118.6(5)
O(2)	C(4)	N(1)	121.1(5)	C(7)	C(8)	I(1)	117.7(4)
O(2)	C(4)	C(5)	120.0(5)	C(9)	C(8)	I(1)	121.1(4)
C(10)	C(3)	N(1)	119.8(5)	C(9)	C(8)	C(7)	121.1(5)
C(2)	C(3)	N(1)	121.0(5)	O(3)	C(18)	C(17)	106.5(6)
C(2)	C(3)	C(10)	118.9(5)	O(4)	C(19)	C(20)	105.8(6)
C(9)	C(10)	C(3)	120.7(5)	O(4)	C(22)	C(21)	107.4(6)
C(21)	C(20)	C(19)	101.6(6)	C(16)	C(17)	C(18)	102.1(7)
C(11)	C(12)	I(2)	120.3(4)	C(22)	C(21)	C(20)	105.1(6)
C(11)	C(12)	C(13)	121.5(5)	C(15)	C(16)	C(17)	104.2(8)
C(13)	C(12)	I(2)	118.1(4)	O(3)	C(15)	C(16)	110.4(8)

Table S13. Values of torsion angles for **4**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
I(2)	C(12)	C(13)	C(14)	-176.6(4)	C(10)	C(3)	C(2)	C(7)	4.4(8)
O(4)	C(22)	C(21)	C(20)	13.3(8)	C(10)	C(3)	C(2)	C(1)	-166.4(5)
N(1)	C(4)	C(5)	C(11)	119.6(6)	C(10)	C(9)	C(8)	I(1)	-177.9(4)
N(1)	C(4)	C(5)	C(6)	-65.9(7)	C(10)	C(9)	C(8)	C(7)	2.8(9)
N(1)	C(3)	C(10)	C(9)	-176.9(5)	C(12)	C(11)	C(5)	C(4)	173.9(5)
N(1)	C(3)	C(2)	C(7)	178.6(5)	C(12)	C(11)	C(5)	C(6)	-0.8(8)
N(1)	C(3)	C(2)	C(1)	7.9(8)	C(6)	N(2)	C(1)	O(1)	170.3(5)
O(1)	C(1)	C(2)	C(7)	-56.6(7)	C(6)	N(2)	C(1)	C(2)	-9.8(8)
O(1)	C(1)	C(2)	C(3)	114.4(6)	C(6)	C(14)	C(13)	C(12)	0.8(9)

O(2)	C(4)	C(5)	C(11)	-59.8(7)	C(5)	C(11)	C(12)	I(2)	176.6(4)
O(2)	C(4)	C(5)	C(6)	114.7(6)	C(5)	C(11)	C(12)	C(13)	-2.4(8)
O(3)	C(18)	C(17)	C(16)	27.4(9)	C(2)	C(7)	C(8)	I(1)	179.7(4)
N(2)	C(1)	C(2)	C(7)	123.4(6)	C(2)	C(7)	C(8)	C(9)	-1.0(9)
N(2)	C(1)	C(2)	C(3)	-65.6(8)	C(2)	C(3)	C(10)	C(9)	-2.6(8)
N(2)	C(6)	C(5)	C(11)	179.5(5)	C(13)	C(14)	C(6)	N(2)	-179.6(5)
N(2)	C(6)	C(5)	C(4)	5.0(8)	C(13)	C(14)	C(6)	C(5)	-3.9(9)
C(14)	C(6)	C(5)	C(11)	3.9(8)	C(8)	C(7)	C(2)	C(1)	168.6(5)
C(14)	C(6)	C(5)	C(4)	-170.6(5)	C(8)	C(7)	C(2)	C(3)	-2.7(8)
C(11)	C(12)	C(13)	C(14)	2.4(9)	C(18)	O(3)	C(15)	C(16)	-2.8(11)
C(1)	N(2)	C(6)	C(14)	-114.2(6)	C(18)	C(17)	C(16)	C(15)	-28.2(10)
C(1)	N(2)	C(6)	C(5)	70.2(7)	C(19)	O(4)	C(22)	C(21)	7.9(8)
C(4)	N(1)	C(3)	C(10)	-119.5(6)	C(19)	C(20)	C(21)	C(22)	-27.4(8)
C(4)	N(1)	C(3)	C(2)	66.3(8)	C(22)	O(4)	C(19)	C(20)	-25.9(8)
C(3)	N(1)	C(4)	O(2)	172.1(5)	C(17)	C(16)	C(15)	O(3)	20.3(11)
C(3)	N(1)	C(4)	C(5)	-7.3(9)	C(21)	C(20)	C(19)	O(4)	32.7(7)
C(3)	C(10)	C(9)	C(8)	-1.0(9)	C(15)	O(3)	C(18)	C(17)	-15.9(9)

Table S14. Geometrical parameters of hydrogen bonds in the crystal of **1**.

D–H···A	**D–H [Å]**	**d(H···A) [Å]**	**d(D···A) [Å]**	**<(D–H···A) [°]**
N(1A)–H(1A)···O(1B)^{i}	0.87(2)	1.97(2)	2.839(2)	170(2)
N(1B)–H(1B)···O(1A)^{ii}	0.88(2)	1.94(2)	2.815(2)	174(2)
N(2A)–H(2A)···O(2B)^{iii}	0.87(2)	2.03(2)	2.887(2)	169(2)
N(2B)–H(2B)···O(2A)^{iv}	0.87(2)	2.06(2)	2.915(2)	170(2)
C(7A)–H(7A)···O(3B)	0.93	2.55	3.254(3)	133
C(7B)–H(7B)···O(3A)	0.93	2.53	3.239(3)	134
C(9A)–H(9A)···O(1B)^{v}	0.93	2.44	3.256(2)	147
C(9B)–H(9B)···O(2A)^{vi}	0.93	2.40	3.272(2)	156
C(13A)–H(13A)···O(2B)^{vii}	0.93	2.45	3.298(2)	152
C(13B)–H(13B)···O(1A)^{viii}	0.93	2.53	3.304(2)	141
C(15A)–H(15A)···O(1B)	0.97	2.59	3.385(3)	139

Symmetry codes: (i) –*x* + 1/2, *y* + 1/2, –*z* + 1/2; (ii) –*x* + 3/2, *y* – 1/2, –*z* + 1/2; (iii) –*x* + 3/2, *y* + 1/2, –*z* + 1/2; (iv) –*x* + 1/2, *y* – 1/2, –*z* + 1/2; (v) *x* – 1/2, –*y* + 1/2, *z* + 1/2; (vi) –*x* + 1, –*y* + 1, –*z*; (vii) *x* – 1/2, –*y* + 1/2, *z* – 1/2; (viii) –*x* + 1, –*y* + 1, –*z* + 1.

Table S15. Geometrical parameters of the C−H···π contacts in the crystal of **1**.

D–H	***Cg*J**	**d(H···*Cg*J) [Å]**	**d(D···CgJ) [Å]**	**<(C–H···*Cg*J) [°]**
C(18A)–H(18A)	2	2.74	3.600(2)	148
C(18B)–H(18D)	8	2.74	3.598(2)	147

*Cg*2 and *Cg*8 denote the geometric centers of gravity of the aromatic rings delineated by the C(5A)–C(6A)/C(14)A–C11(A) and C(5B)–C(BA)/C(14)A–C11(A) atoms rings, respectively.

Table S16. Geometrical parameters of the C−F···π contacts in the crystal of **1**.

D–X	***Cg*J**	**d(D···*Cg*J) [Å]**	**<(D–X···*Cg*J) [°]**
C(8A)–F(1A)	7^{v}	3.464(2)	137.14(11)
C(12B)–F(2B)	1^{viii}	3.373(2)	142.88(11)

*Cg*1 and *Cg*7 denote the geometric centers of gravity of the aromatic rings delineated by the C(2A)–C(3A)/C(14A)–C(11A) and C(2B)–C(3B)/C(14B)–C(11B) atoms, respectively. Symmetry codes: (v) *x* – 1/2, –*y* + 1/2, *z* + 1/2; (viii) –*x* + 1, –*y* + 1, –*z* + 1.

Table S17. Geometrical parameters of the F···O halogen bonds in the crystal of **1**.

D–X···Y	**d(X···Y) [Å]**	**<(D–X···Y)**

		[°]
C(12A)–F(2A)···O(2A)[ix]	2.972(2)	114.16(11)
C(8B)–F(1B)···O(2B)[vii]	2.878(2)	123.40(11)

Symmetry codes: (vii) *x* – 1/2, –*y* + 1/2, *z* – 1/2; (ix) –*x*,–*y* + 1,–*z*.

Table S18. Geometrical parameters of hydrogen bonds in the crystal of **2**.

D–H···A	D–H [Å]	d(H···A) [Å]	d(D···A) [Å]	<(D–H···A) [°]
N(1)–H(1)···O(1)[i]	0.86(3)	1.99(3)	2.829(4)	166(3)
N(2)–H(2)···O(2)[ii]	0.88(3)	1.95(3)	2.818(4)	172(3)
C(9)–H(9)···O(1)[iii]	0.93	2.58	3.317(4)	137
C(10)–H(10)···O(3)[iv]	0.93	2.40	3.257(5)	153

Symmetry codes: (i) –*x* + 3/2, *y* + 1/2, *z*; (ii) –*x* + 3/2, *y* – 1/2, *z*; (iii) *x* – 1/2, –*y* + 1/2, –*z* + 1; (iv) –*x* + 1/2, *y* + 1/2, *z*.

Table S19. Geometrical parameters of the C–Cl···π contacts in the crystal of **2**.

D–X	*CgJ*	d(X···*CgJ*) [Å]	<(D–X···*CgJ*) [°]
C(12)–Cl(2)	2[v]	3.466(2)	139.96(14)

*Cg*2 denotes the geometric center of gravity of the aromatic ring delineated by the C(5)–C(6)/C(14)–C(11) atoms. Symmetry code: (v) *x* – 1/2, *y*, –*z* + 1/2.

Table S20. Geometrical parameters of the Cl···O halogen bonds in the crystal of **2**.

D–X···*Y*	d(X···Y) [Å]	<(D–X···*Y*) [°]
C(8)–Cl(1)···O(1)[vi]	3.166(2)	155.46(12)
C(12)–Cl(2)···O(2)[v]	3.179(2)	154.28(15)

Symmetry codes: (v) *x* – 1/2, *y*, –*z* + 1/2; (vi) –*x* + 1, –*y*, –*z* + 1.

Table S21. Geometrical parameters of hydrogen bonds in the crystal of **3**.

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(D–H···A) [°}
N(1)–H(1)···O(1)[i]	0.86	1.96	2.816(5)	171
N(2)–H(2)···O(2)[ii]	0.86	2.01	2.823(5)	157
C(9)–H(9)···Br(1)[iii]	0.93	2.90	3.671(5)	141
C(10)–H(10)···O(3)[iii]	0.93	2.58	3.407(10)	147

Symmetry codes: (i) –*x* - 1/2, *y* + 1/2, *z*; (ii) –*x* – 1/2, *y* – 1/2. *z*; (iii) –*x* – 3/2, *y* + 1/2, *z*.

Table S22. Geometrical parameters of the C–Br···π contacts in the crystal of **3**.

D–X	*CgJ*	d(X···CgJ) [Å]	<(D–X···CgJ) [°]
C(12)–Br(2)	2[iv]	3.551(2)	139.56(17)

*Cg*2 denotes the geometric center of gravity of the aromatic rings delineated by the C(5)–C(6)/C(14)–C(11) atoms. Symmetry code: (iv) *x* – 1/2, *y*, –*z* – 3/2.

Table S23. Geometrical parameters of the Br···O halogen bonds in the crystal of **3**.

D–X···*Y*	d(X···Y) [Å]	<(D–X···*Y*) [°]
C(8)–Br(1)···O(1)[v]	3.203(3)	155.98(18)
C(12)–Br(2)···O(2)[iv]	3.140(3)	156.48(18)

Symmetry codes: (iv) *x* – 1/2, *y*, –*z* – 3/2; (v) –*x* – 1, –*y* – 2, –*z* – 1.

Table S24. Geometrical parameters of hydrogen bonds in the crystal of **4**.

D–H···A	d(D–H) [Å]	d(H···A)	d(D···A)	<(D–H···A)

		[Å]	[Å]	[°]
N(1)–H(1)···O(1)[i]	0.87(6)	1.91(6)	2.756(6)	163(7)
N(2)–H(2)···O(2)[ii]	0.87(5)	2.04(7)	2.900(6)	172(4)

Symmetry codes: (i) *x*, –*y* + 5/2, *z* + 1/2; (ii) *x*, –*y* + 5/2. *z* –1/2.

Table S25. Geometrical parameters of the C−H···π contacts in the crystal of **4**.

D–H	*Cg*J	d(H···*Cg*J) [Å]	d(D···*Cg*J) [Å]	C–H···*Cg*J [°]
C(18)–H(18)	1	2.93	3.584(9)	126

*Cg*1 denotes the geometric center of gravity of the aromatic ring delineated by the C(2)–C(3)/C(10)–C(7) atoms.

Table S26. Geometrical parameters of the π-π contacts in the crystal of **4**.

CgI	*Cg*J	d(*Cg*I···C*g*J) [Å]	Dihedral angle [°]	Interplanar distance [Å]	Offset [Å]
2	2[iii]	3.818(3)	0	-3.508(2)	1.507(2)

Cg2 denote the geometric center of gravity of the aromatic ring delineated by the C(5)–C(6)/C(14)–C(11) atoms. Symmetry code: (iii) –*x* + 1, –*y* + 2, –*z* + 1.

Table S27. Geometrical parameters of the I···O and the I···I halogen bonding in the crystal of **4**.

D–X	A	d(D···A) [Å]	<(D–X···A) [°}
C(8)–I(1)	O(3)[iv]	2.933(6)	173.3(2)
C(12)–I(2)	I(2)[v]	3.890(2)	135.99(17)

Symmetry codes: (iv) –*x* + 2, –*y* – 2, –*z* + 1; (v) –*x* + 1, –*y* + 1, –*z* + 1.