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Supporting information for article:

Dibromomethyl- and bromomethyl- or bromo-substituted benzenes and naphthalenes: C—Br···Br interactions

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^{1}H and ^{13}C NMR data for compounds **1** – **9**.

3,5-dibromo-1-(dibromomethyl)benzene **1**.

Synthesized from 3,5-dibromotoluene. M.p. 63-65°C (m.p. lit. 55 °C [Xi *et al.*, 1999])

^{1}H NMR: δ (ppm) = 7.66 (t, 2H, J = 1.6 Hz), 7.64 (t, 1H, J = 1.6 Hz), 6.51 (s, 1H).

^{13}C NMR: δ (ppm) = 144.9, 135.4, 128.6, 122.9, 37.5.

1,4-Dibromo-2,5-bis(dibromomethyl)benzene **2**.

Synthesized from 2,5-dibromo-*para*-xylene' M.p. 167-168 ºC.(m.p. lit. 168-170 ºC[Bodzioch *et al.*, 2016]).

^{1}H NMR: δ (ppm) = 8.15 (s, 2H, Ar*H*), 6.98 (s, 1H, C*H*Br$_2$).

^{13}C NMR: δ (ppm) = 142.9, 134.9, 119.4, 37.1.

2,5-dibromo-1-(dibromomethyl)benzene **3**.

Synthesized from 2,5-dibromotoluene. M.p. 52-53 °C.

^{1}H NMR: δ (ppm) = 8.15 (d, 1H, J = 1.6Hz), 7.39 (d, 1H, J = 8.0Hz), 7.32 (dd, 1H, J_1 = 8 Hz, J_2 = 1.6 Hz), 7.00 (s, 1H).

^{13}C NMR: δ (ppm) = 142.2, 134.2, 134.1, 134.0, 122.3, 118.3, 38.2.

Anal.Calcd. for $C_7H_4Br_4$: C, 20.62; H, 0.99. Found: C, 20.5; H, 0.8.

1,2-bis(dibromomethyl)benzene **4**.

Synthesized from *ortho*-xylene. M.p. 116-118 °C (m.p. lit. 114-116°C [Doe *et al.*, 1978])

^{1}H NMR: δ (ppm) = 7.69 (bs, 2H, Ar*H*), 7.39(AA'XX', 2H, Ar*H*), 7.16 (bs, 2H, C*H*Br$_2$).

^{13}C NMR: δ (ppm) = 137.7, 130.1, 129.6 , 36.5.

1-bromomethyl-2-(dibromomethyl)benzene **5.**

Synthesized from *ortho*-xylene. M.p. 41 °C (DSC) (lit. 40-41 °C [Halford *et al.*, 1953]).

^{1}H NMR: δ (ppm) = 7.98 (d, 1H, Ar*H*), 7.45 (t, 1H, Ar*H*), 7.31 (t, 1H, Ar*H*), 7.28 (d, 1H, Ar*H*), 7.14 (bs, 1H, C*H*Br$_2$), 4.61 (s, 2H, C*H*$_2$Br).

^{13}C NMR: δ (ppm) = 140.4, 132.4, 130.5, 130.2, 130.0, 36.8, 29.2

2-bromomethyl-3-dibromomethylnaphthalene **6**.

Synthesized from 2,3-dimethylnaphthalene. M.p. 113-115 °C.

^{1}H NMR: δ (ppm) = 8.49 (s, 1H, Ar*H*), 7.94-7.89 (m, 1H, Ar*H*), 7.85-7.82 (m, 2H, Ar*H*), 7.60-7.56 (m, 2H, Ar*H*), 7.29(s, 1H, C*H*Br$_2$), 4.84 (s, 2H, C*H*$_2$Br).

^{13}C NMR: δ (ppm) = 137.45, 133.45, 133.32, 130.78, 130.32, 130.17, 128.32, 127.97, 127.62, 127.58, 37.47, 30.40.

Anal.Calcd. for $C_{12}H_9Br_3$: C, 36.68; H, 2.31. Found: C, 36.4; H, 2.35.

2,3-bis(dibromomethyl)naphthalene **7**.

Synthesized from 2,3-dimethylnaphthalene. M.p. 160-162 °C. (lit. 161 °C [Riede *et al.*, 1956]).

^{1}H NMR: δ (ppm) = 8.22 (bs, 2H, Ar*H*), 8.13, 8.06 (AA'BB', 4H, Ar*H*), 7.34 (bs, 2H, C*H*Br_2).

^{13}C NMR: δ (ppm) =133.1 (broad peak), 128.3, 128.1, 37.1.

1-bromomethyl-2-dibromomethylnaphthalene **8.**

Synthesized from 1,2-dimethylnaphthalene. M.p. 132-133 °C. (132-132.5 °C [Gribble *et al.*, 1977])

^{1}H NMR: δ (ppm) = 8.15(d, 1H, J = 8 Hz, Ar*H*), 8.04 (d, 1H, J = 8 Hz, Ar*H*), 7.95 (d, 1H, J = 8 Hz, Ar*H*), 7.89 (d, 1H, J = 8 Hz, Ar*H*), 7.68 (t, 1H, J = 8 Hz, Ar*H*), 7.61 (t, 1H, J = 8 Hz, Ar*H*), 7.32(s, 1H, C*H*Br_2), 5.03(s, 2H, CH_2Br).

^{13}C NMR: δ (ppm) = 137.7, 134.0, 130.7, 130.1, 128.9, 127.9, 127.4, 127.1, 126.5, 124.0, 37.5, 24.0.

1,3-bis(dibromomethyl)benzene **9**.

Synthesized from *meta*-xylene. M.p. 98-100 °C (m.p. lit. 107 °C [Arbuzov *et al.*, 1976])

^{1}H NMR: δ (ppm) = 7.76 (bs, 1H, Ar*H*), 7.58(d, 2H, Ar*H*), 7.42 (t, 1H, Ar*H*), 6.67 (bs, 2H, C*H*Br_2).

^{13}C NMR: δ (ppm) = 142.3, 129.3, 128.1, 124.5, 39.7.

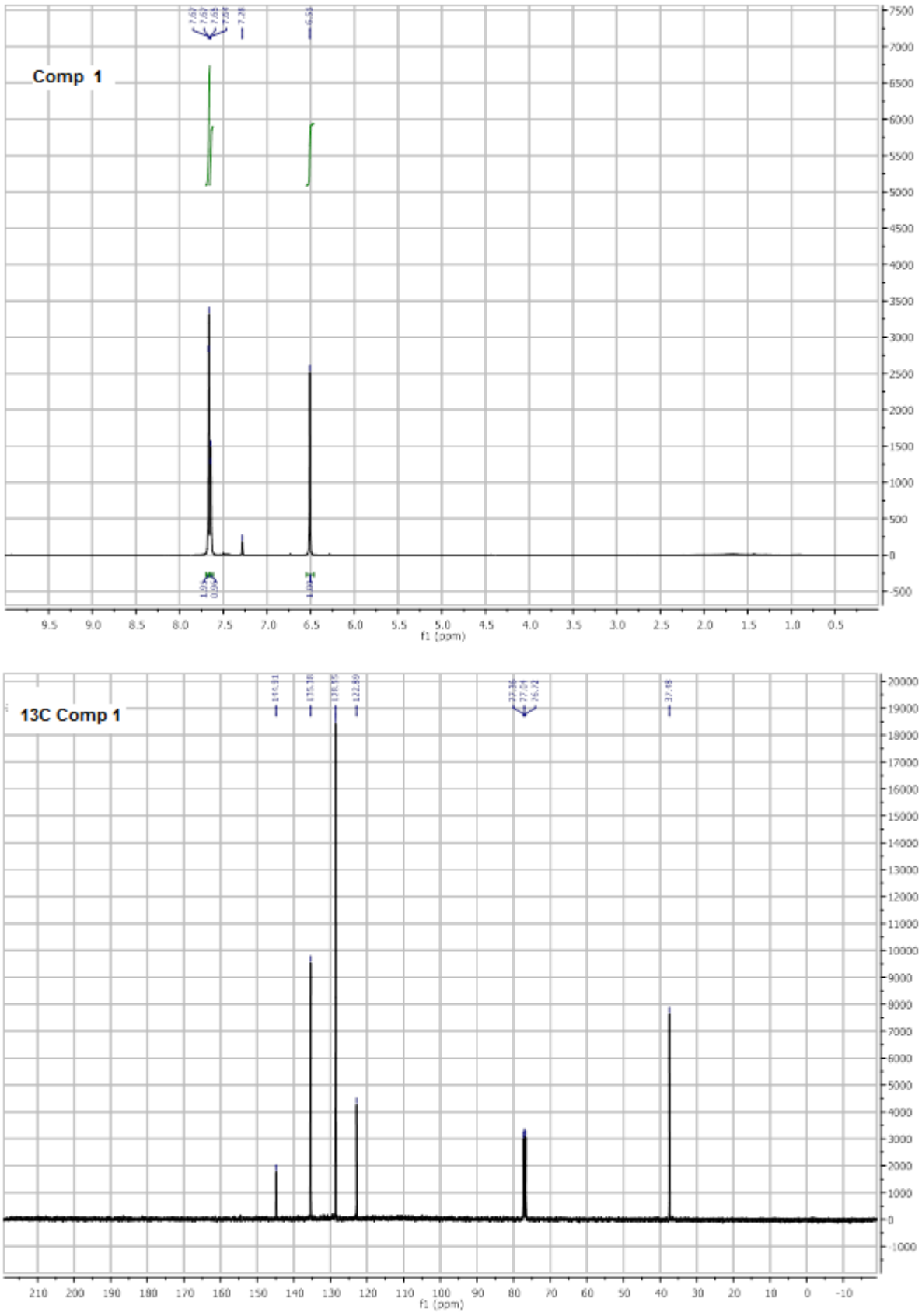


Figure S1. ^{1}H and ^{13} C NMR spectra of compound **1.**

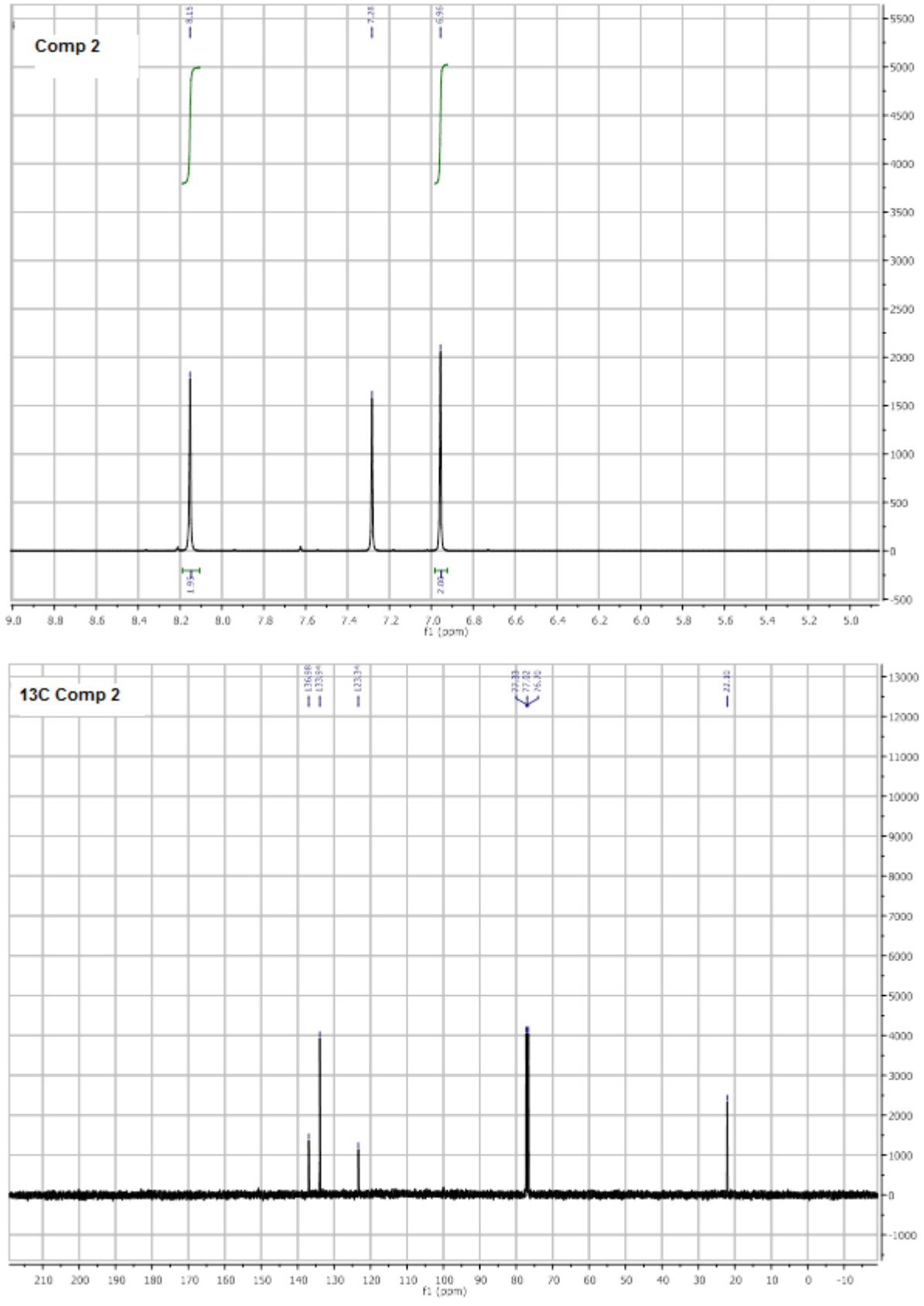


Figure S2. ^{1}H and ^{13}C NMR spectra of compound **2**.

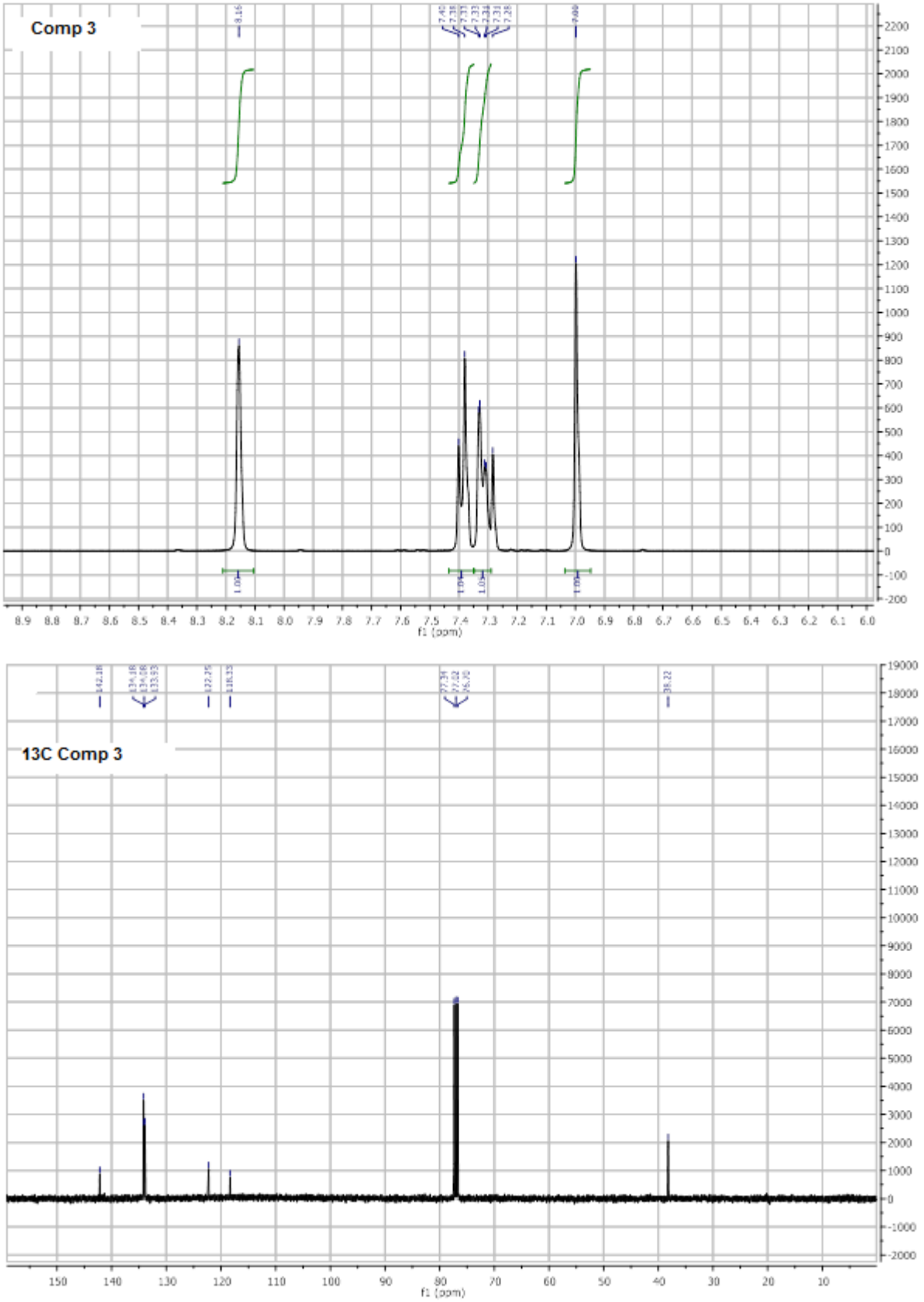


Figure S3. ^{1}H and ^{13}C NMR spectra of compound **3**.

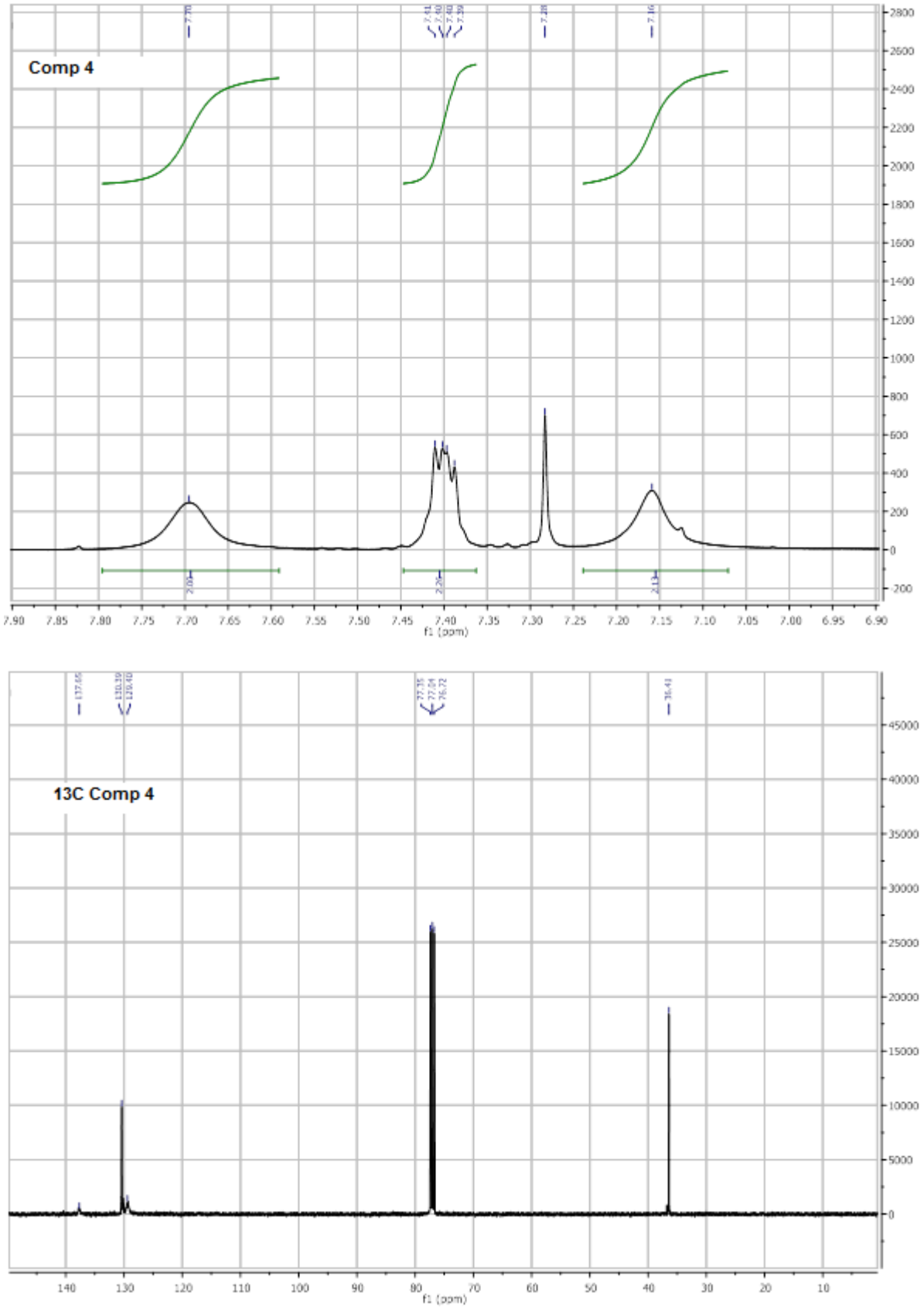


Figure S4. ^{1}H and ^{13}C NMR spectra of compound **4**.

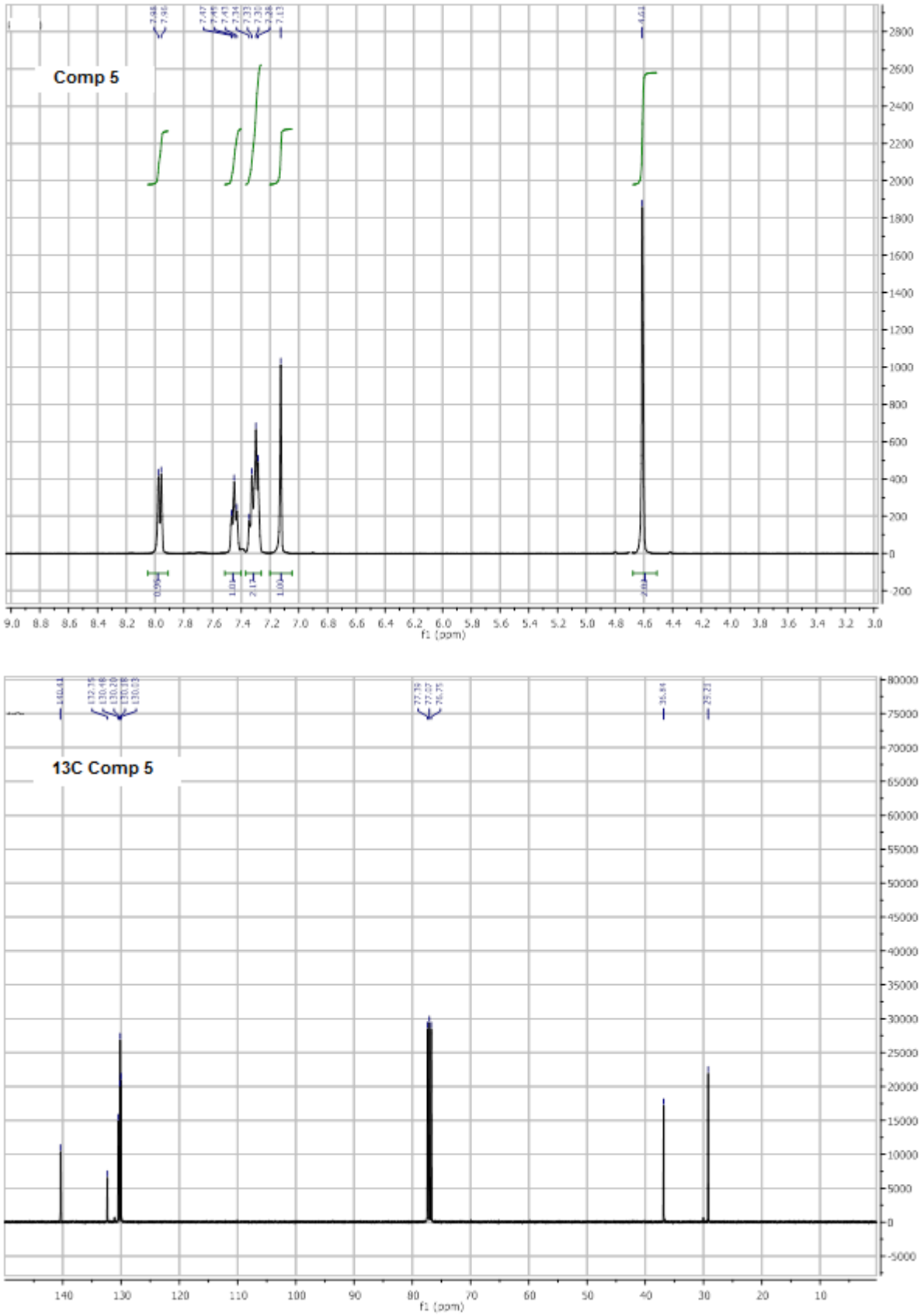


Figure S5. ^{1}H and ^{13}C NMR spectra of compound **5**

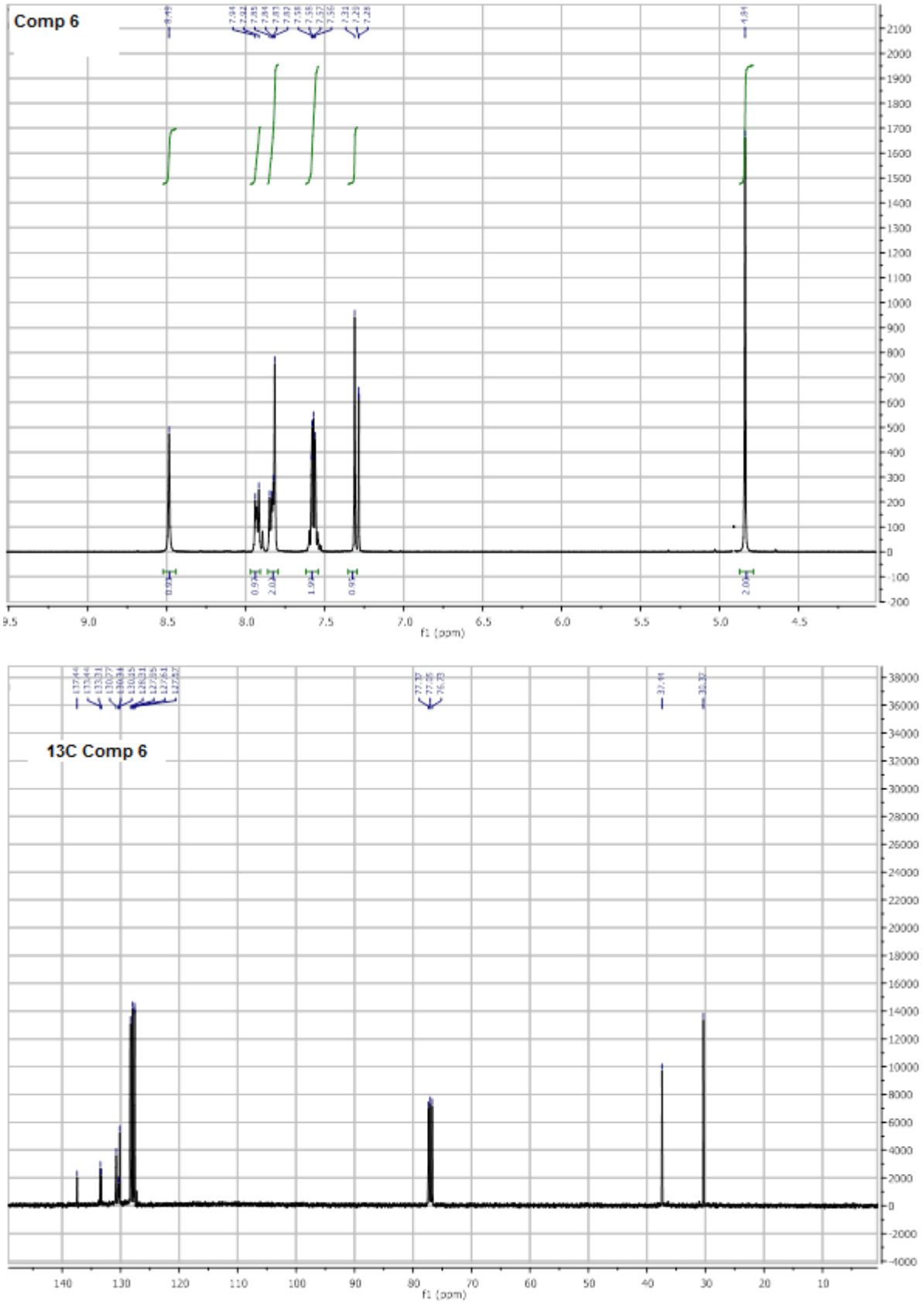


Figure S6. ^{1}H and ^{13}C NMR spectra of compound **6**.

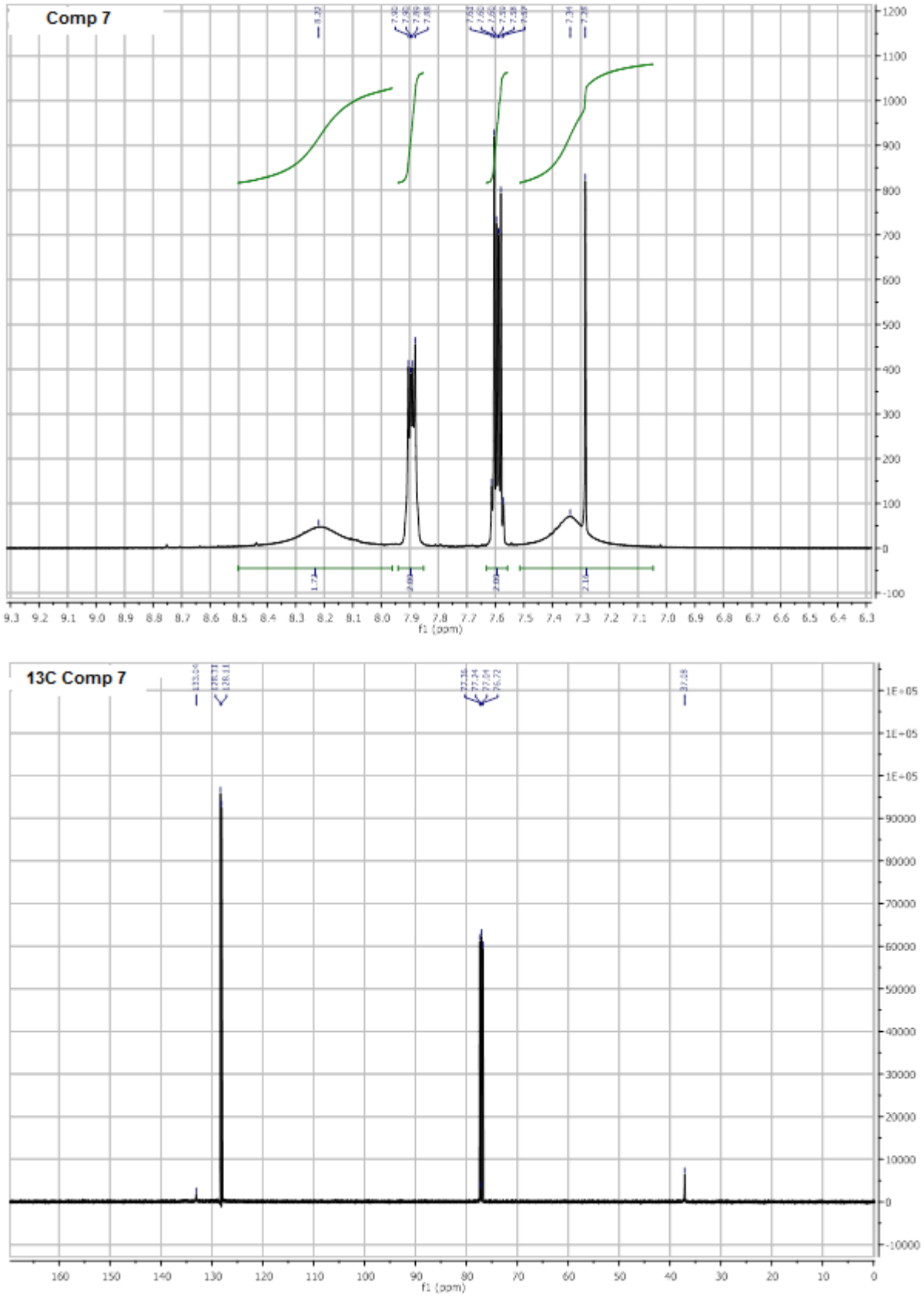


Figure S7. ^{1}H and ^{13}C NMR spectra of compound **7**.

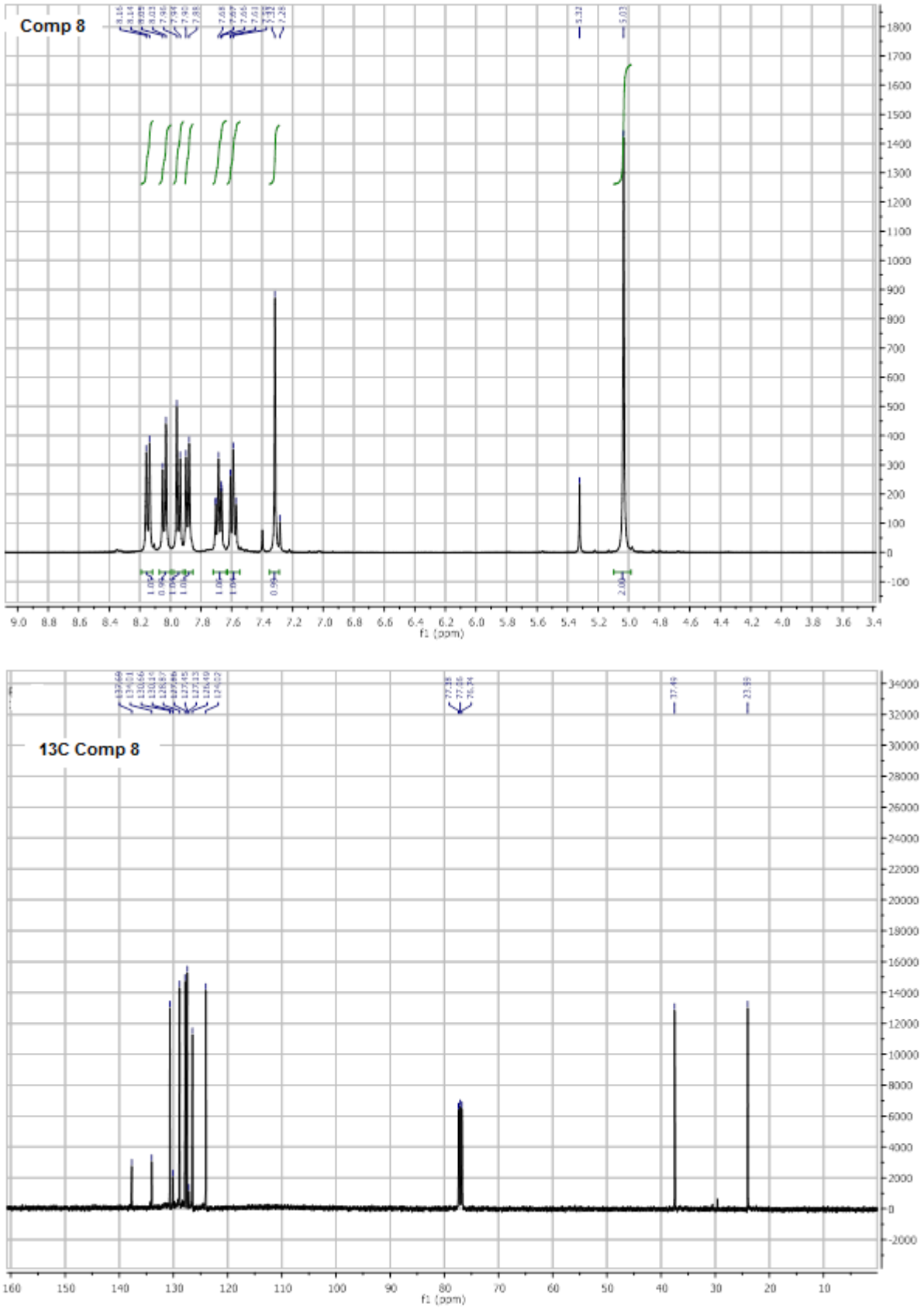


Figure S8. ^{1}H and ^{13}C NMR spectra of compound **8**.

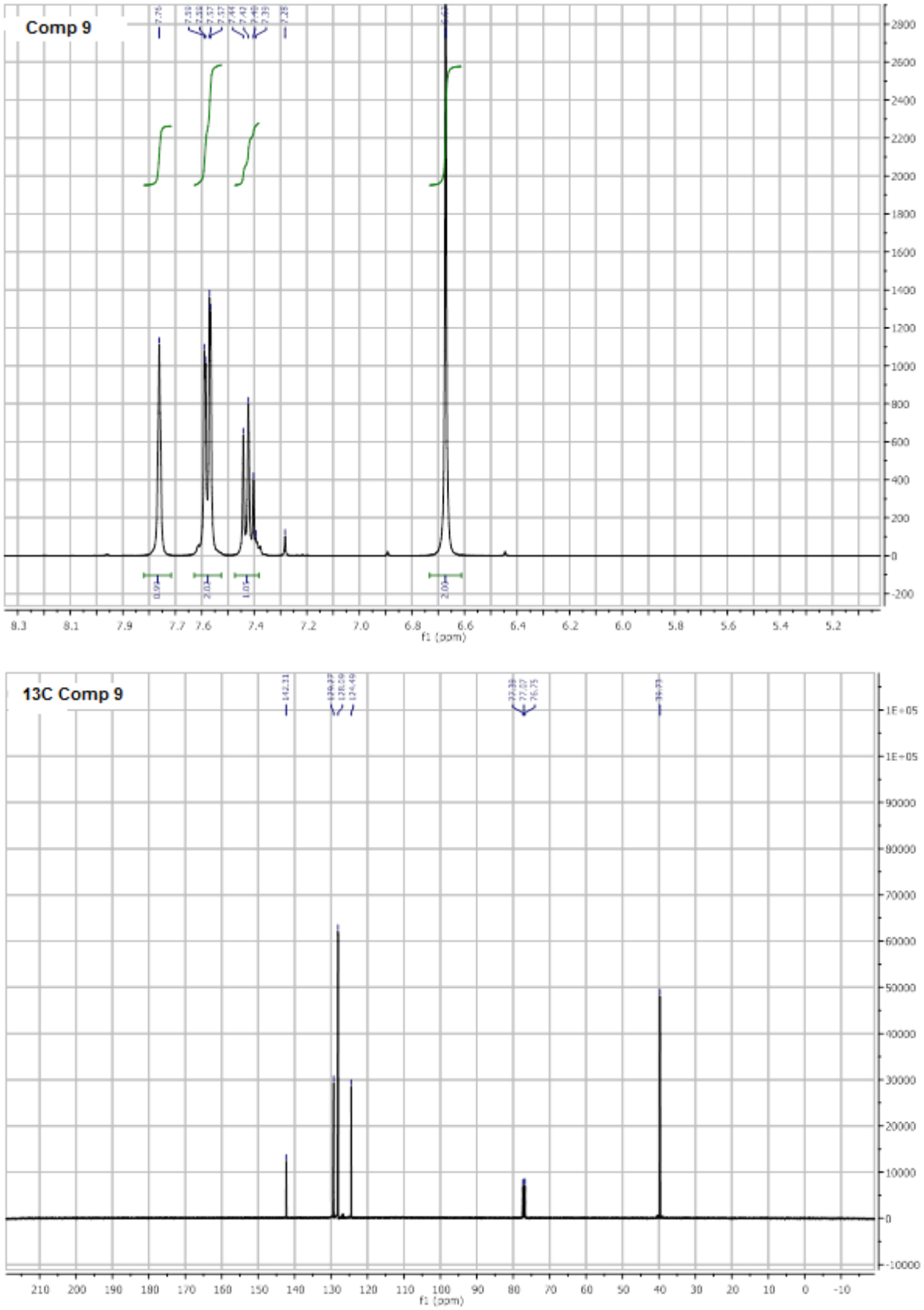
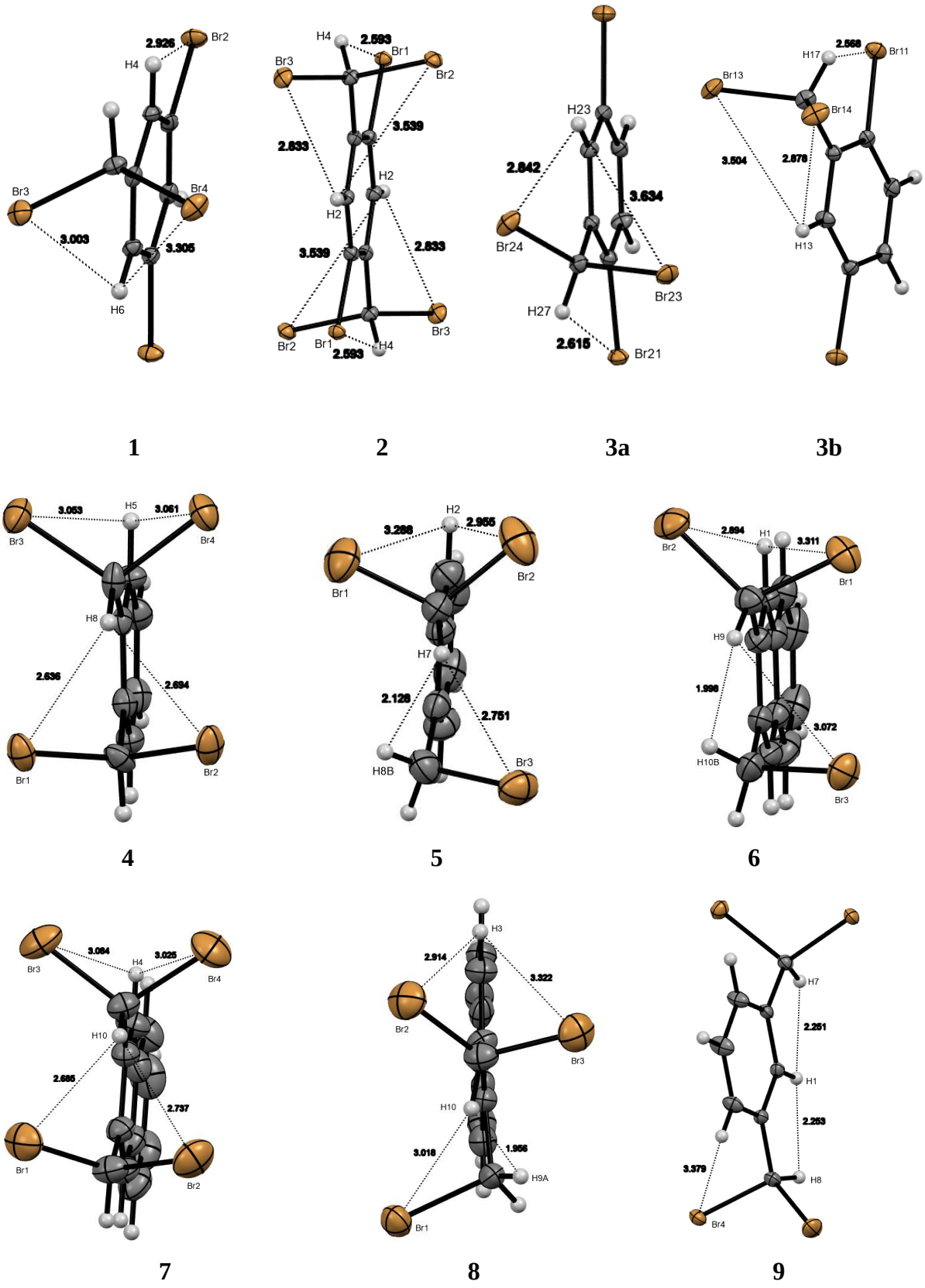


Figure S9. ^{1}H and ^{13}C NMR spectra of compound **9**.



1 **2** **3a** **3b**

4 **5** **6**

7 **8** **9**

Figure S10. Short C-H···H-C and C-H···Br *intra* interactions in the molecule of compounds **1 - 9**. The discussion of individual compounds took place in the main text.

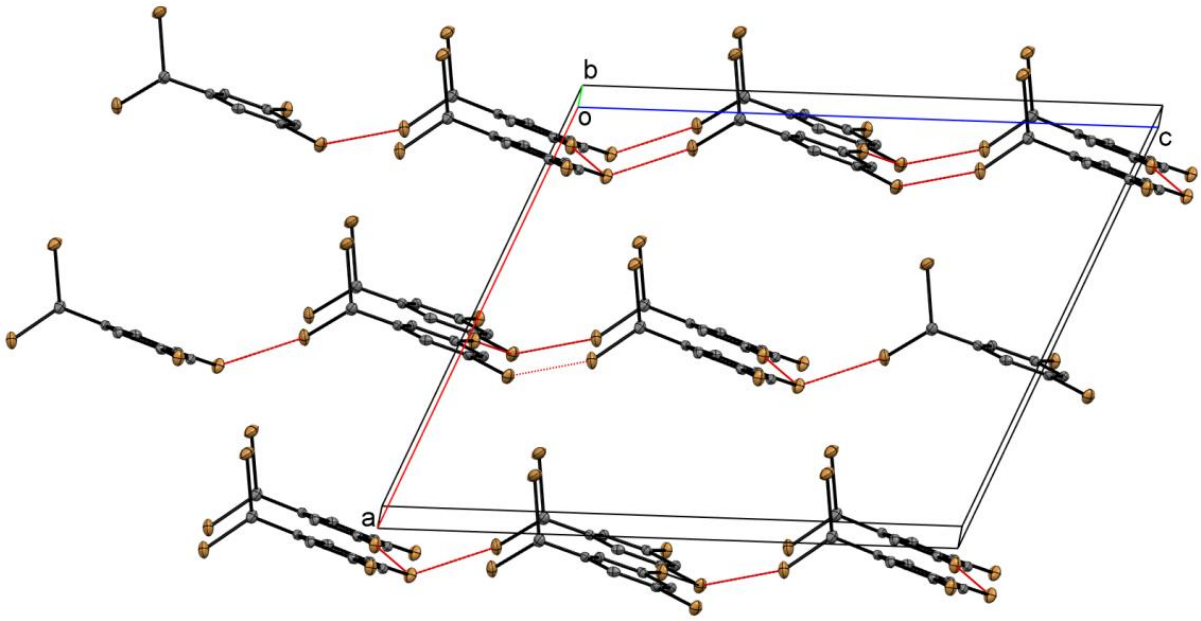


Figure S11.Packing diagram of compound **1**. Thick dashed lines represent Br···Br interactions. Hydrogen atoms omitted for clarity. Displacement ellipsoids for non-H atoms are shown with 50% probability.

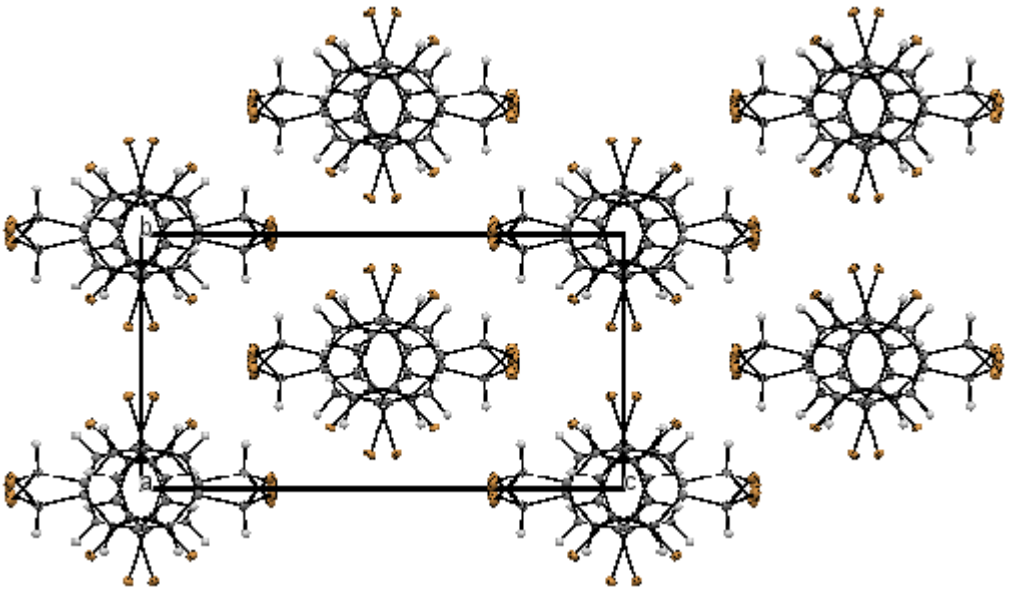


Figure S12. Characteristic column arrangement of molecules of compound **1**.

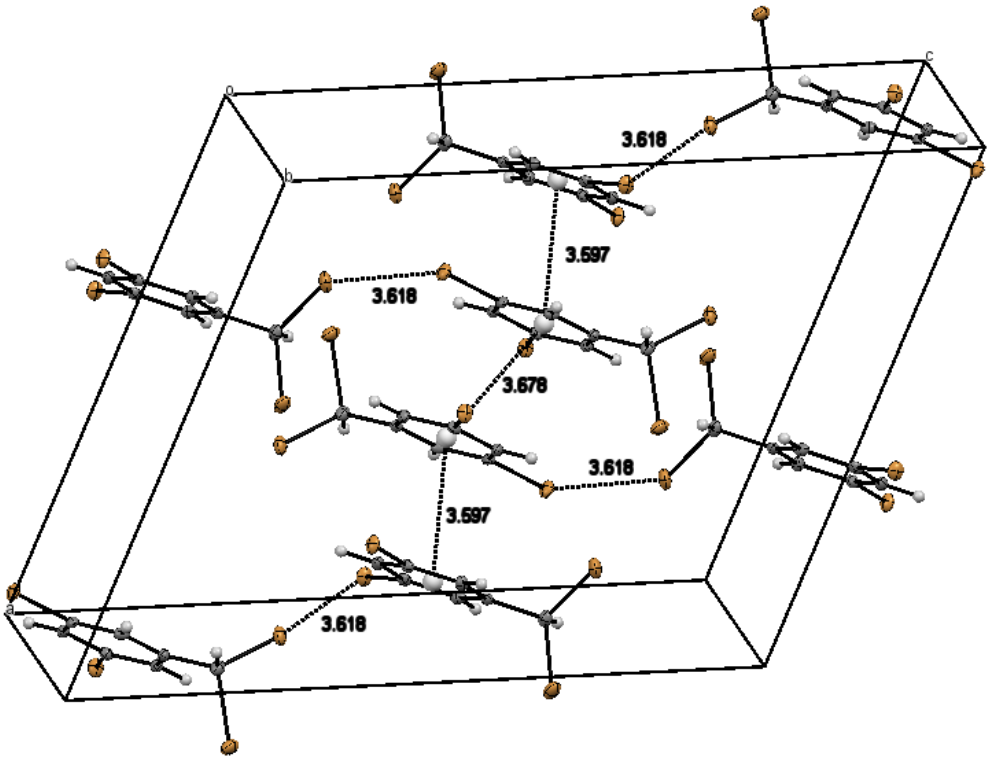


Figure S13. View of the unit cell of compound **1**. Br···Br and π···π contacts between molecules are marked by dotted line.

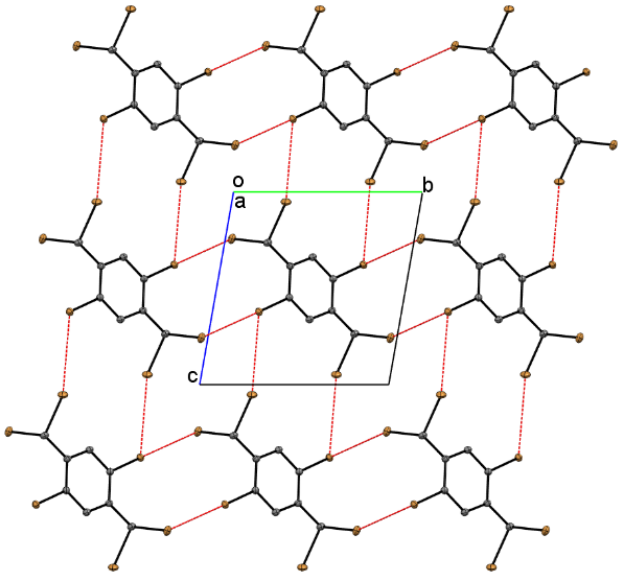


Figure S14. Crystal packing of 1,4-di(bromomethyl)-2,5-dibromobenzene **2** (view parallel to the *a* axis; hydrogen atoms were omitted for clarity). Thick dashed lines represent Br···Br interactions between the central molecule and eight adjacent molecules. Displacement ellipsoids for non-H atoms are shown with 50% probability.

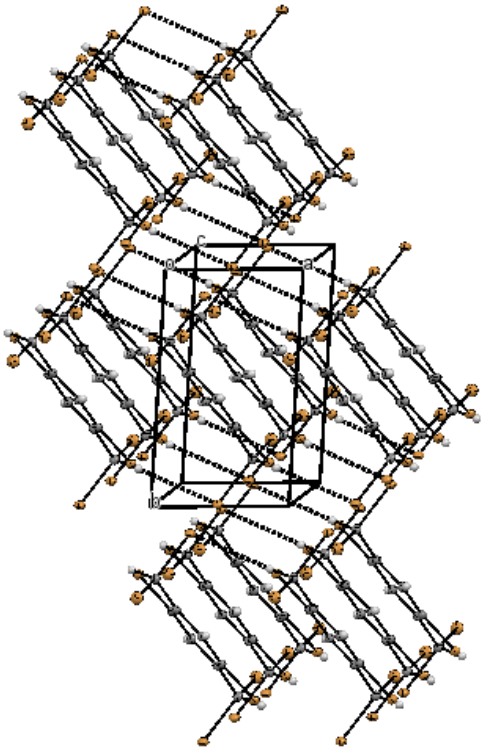


Figure S15. Crystal packing of compound **2**. The dotted lines show the C-H···Br interaction with a length of 2.942 Å.

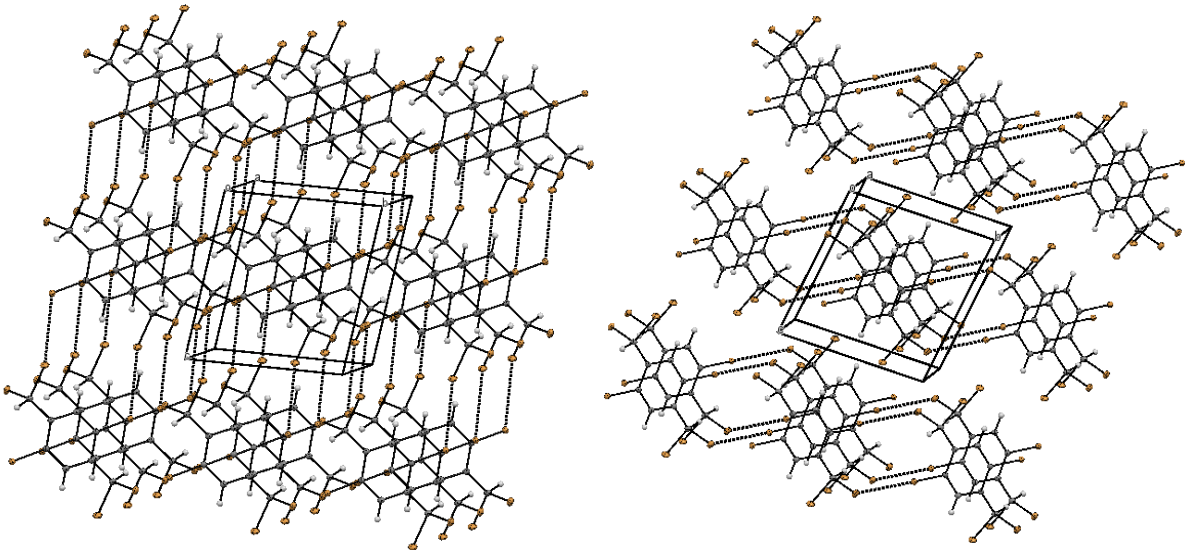


Figure S16. Crystal packing of compound **2** taking into account different Br···Br short contacts. The dotted lines on the left picture correspond to the interaction of Br···Br with a length of 3.577 Å, while on the right picture the interaction of Br···Br with a length of 3.491 Å.

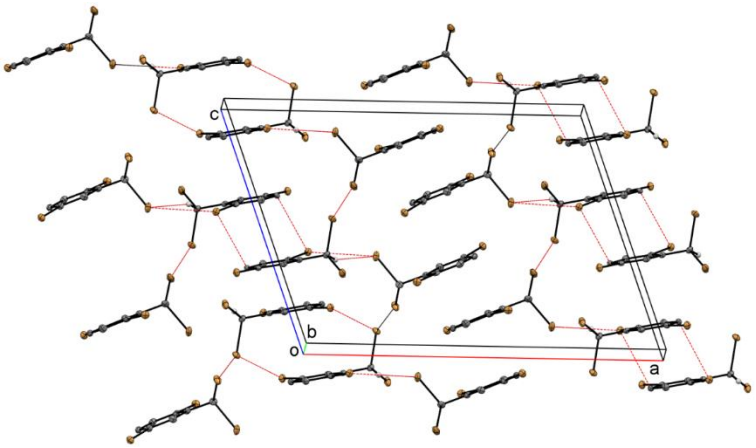


Figure S17. Packing diagram of compound **3**. Hydrogen atoms that not participate in the intermolecular interactions were omitted for clarity. Thick dashed lines represent intermolecular interactions. Displacement ellipsoids for non-H atoms are shown with 50% probability

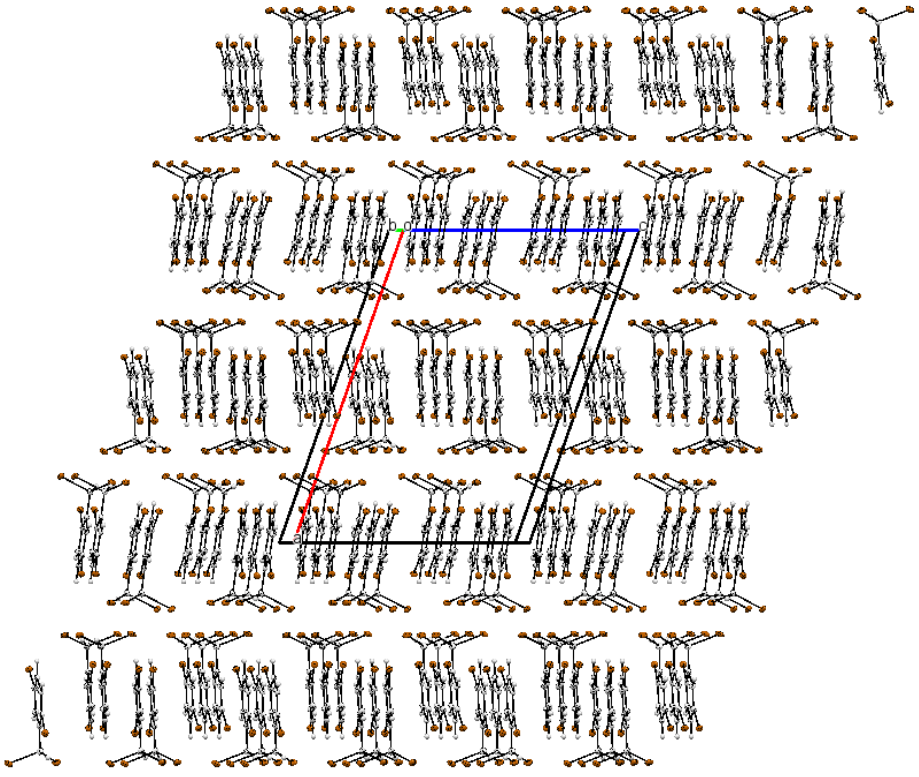


Figure S18. Packing diagram of compound **3**.

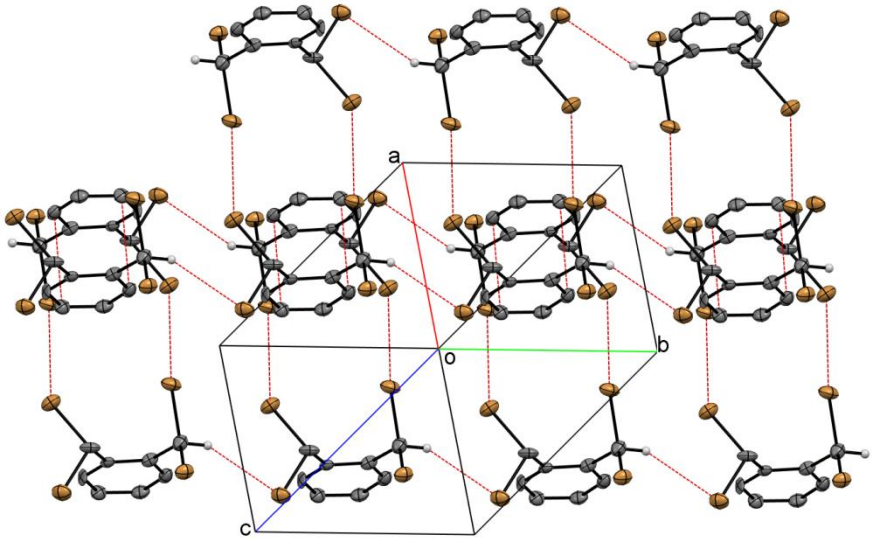


Figure S19. Packing diagram of compound **4** viewed parallel to [111]. Hydrogen atoms that do not participate in the intermolecular interactions were omitted for clarity. Thick dashed lines represent intermolecular interactions. Displacement ellipsoids for non-H atoms are shown with 50% probability.

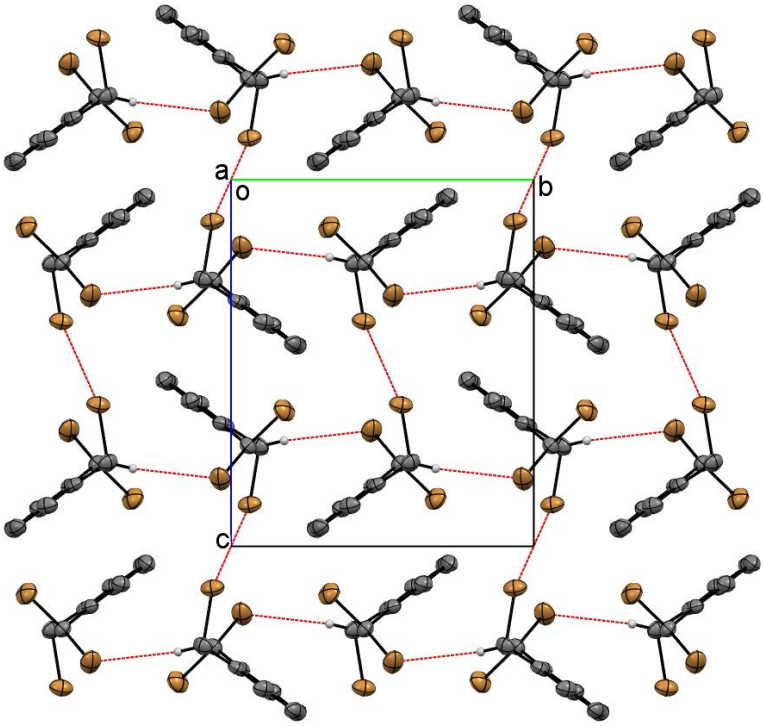


Figure S20. Packing diagram of compound **5** viewed parallel to the *a* axis, showing short Br···π and Br···H-C distances. Hydrogen atoms that do not participate in the intermolecular interactions were omitted for clarity. Thick dashed lines represent intermolecular interactions. Displacement ellipsoids for non-H atoms are shown with 50% probability.

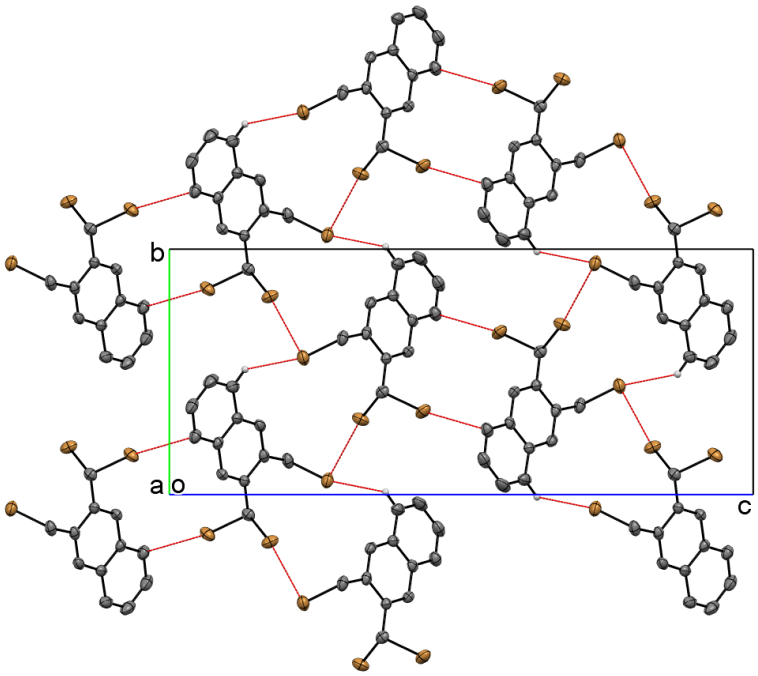


Figure S21. Packing diagram of compound **6** viewed parallel to *a* axis, showing short Br···Br and Br···C_{Ar} distances. Hydrogen atoms that do not participate in the intermolecular interactions were omitted for clarity. Thick dashed lines represent intermolecular interactions. Displacement ellipsoids for non-H atoms are shown with 50% probability.

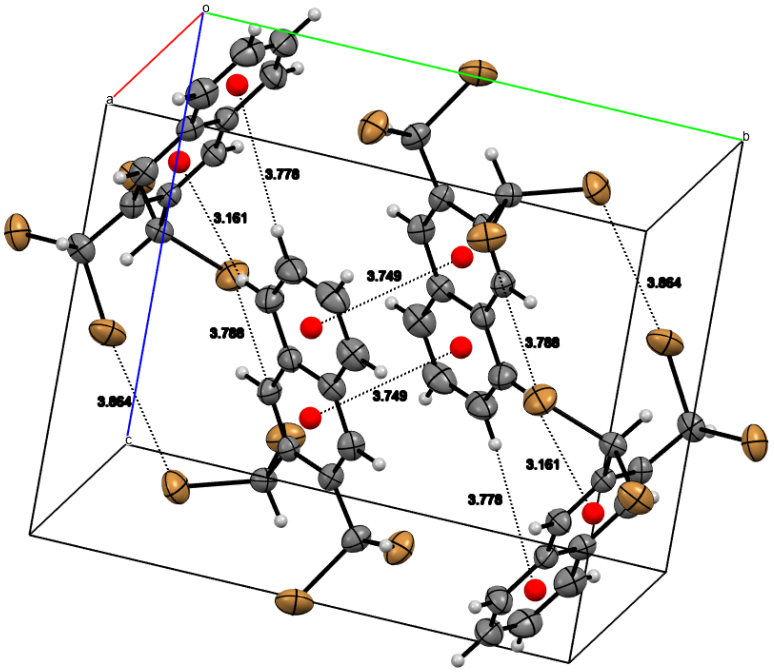


Figure S22. Partial packing diagram of compound **7** showing intermolecular π···π and C-H···π interactions (marked by dashed lines). Displacement ellipsoids for non-H atoms are shown with 50% probability.

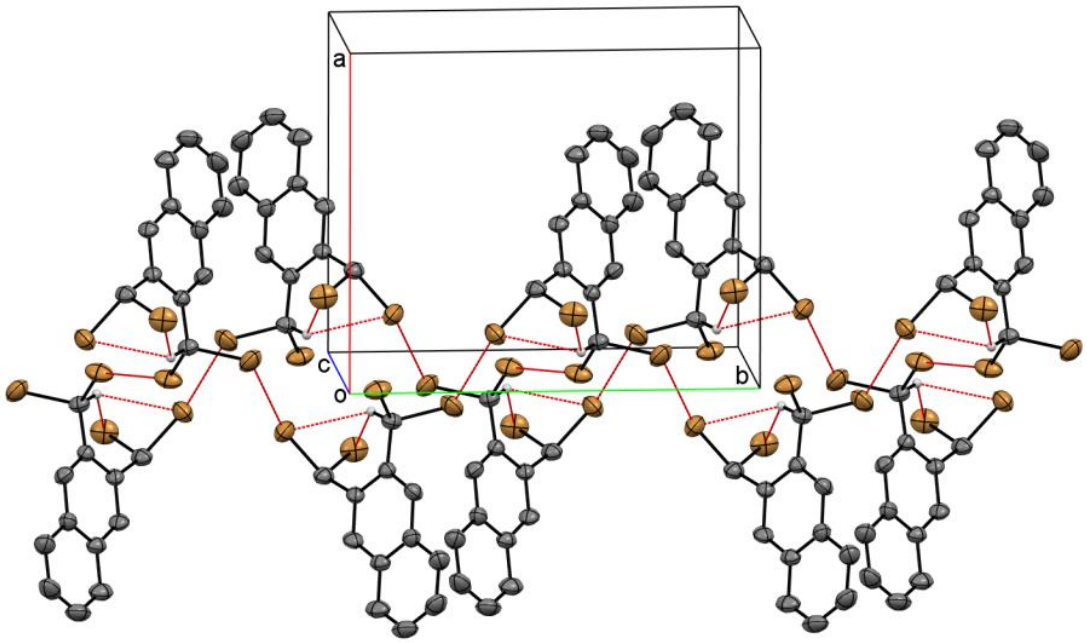


Figure S23. Partial packing diagram of compound **7** showing intermolecular Br···Br interactions (marked by dashed lines). Hydrogen atoms that do not participate in the intermolecular interactions were omitted for clarity. Displacement ellipsoids for non-H atoms are shown with 50% probability.

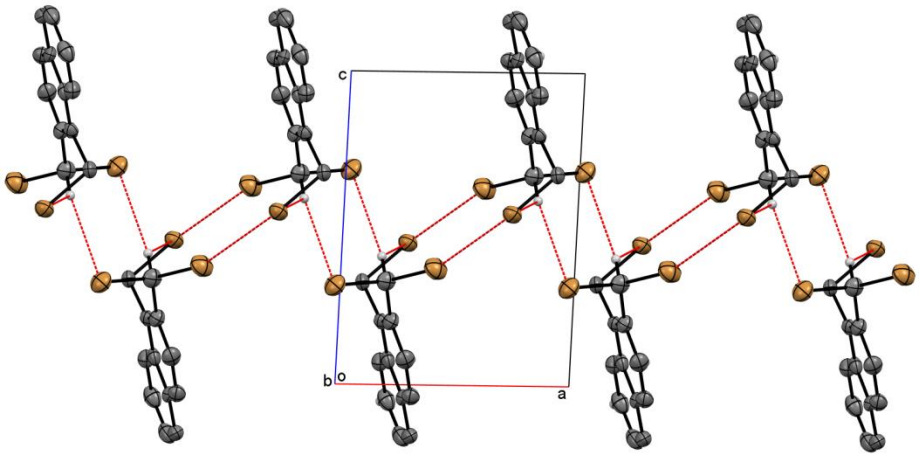


Figure S24. Packing diagram of compound **8** viewed parallel to *b* axis, showing short distances between bromine atoms (marked by thick dashed lines). Hydrogen atoms that do not participate in the intermolecular interactions were omitted for clarity. Displacement ellipsoids for non-H atoms are shown with 50% probability.

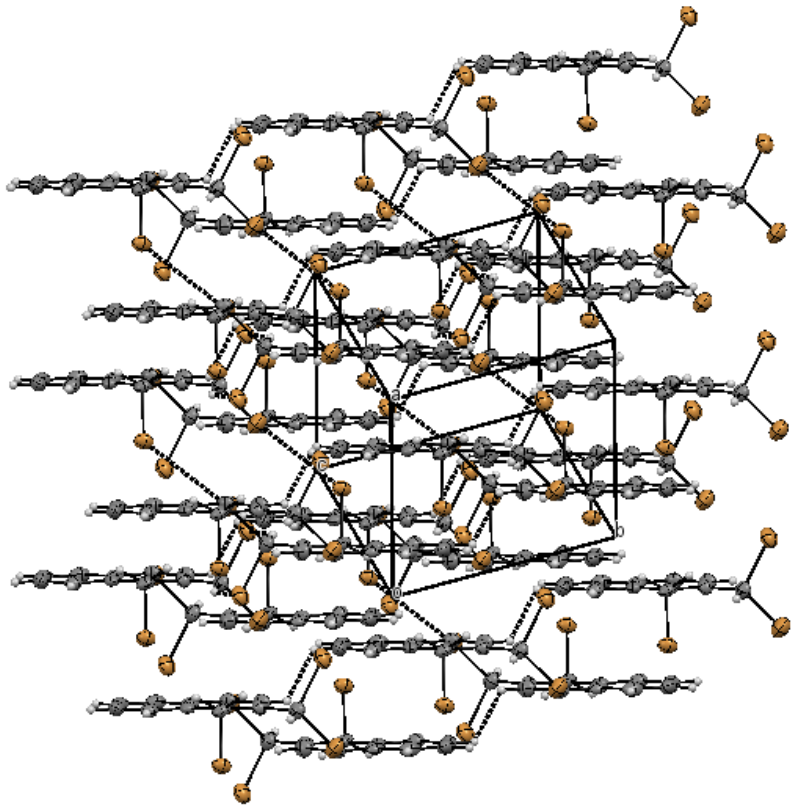


Figure S25. Packing diagram of compound **8**, showing the three-dimensional network of the interactions. Dashed lines represent Br···Br, Br···H-C and C-H···H-C interactions.

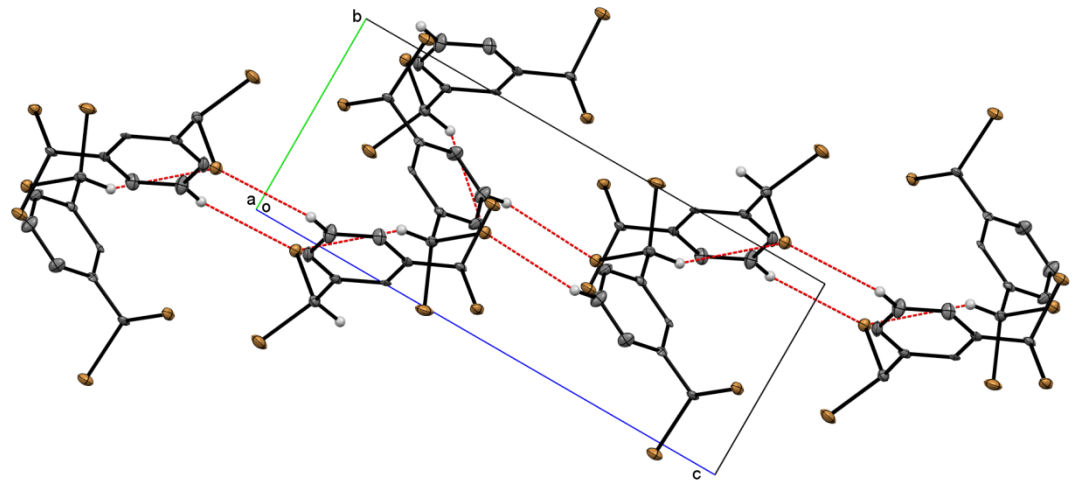


Figure S26. Packing diagram of compound **9** viewed parallel to the *a* axis. Thick dashed lines represent all interactions that occur in the crystal structure. Hydrogen atoms that do not participate in the intermolecular interactions were omitted for clarity. Displacement ellipsoids for non-H atoms are shown with 50% probability.

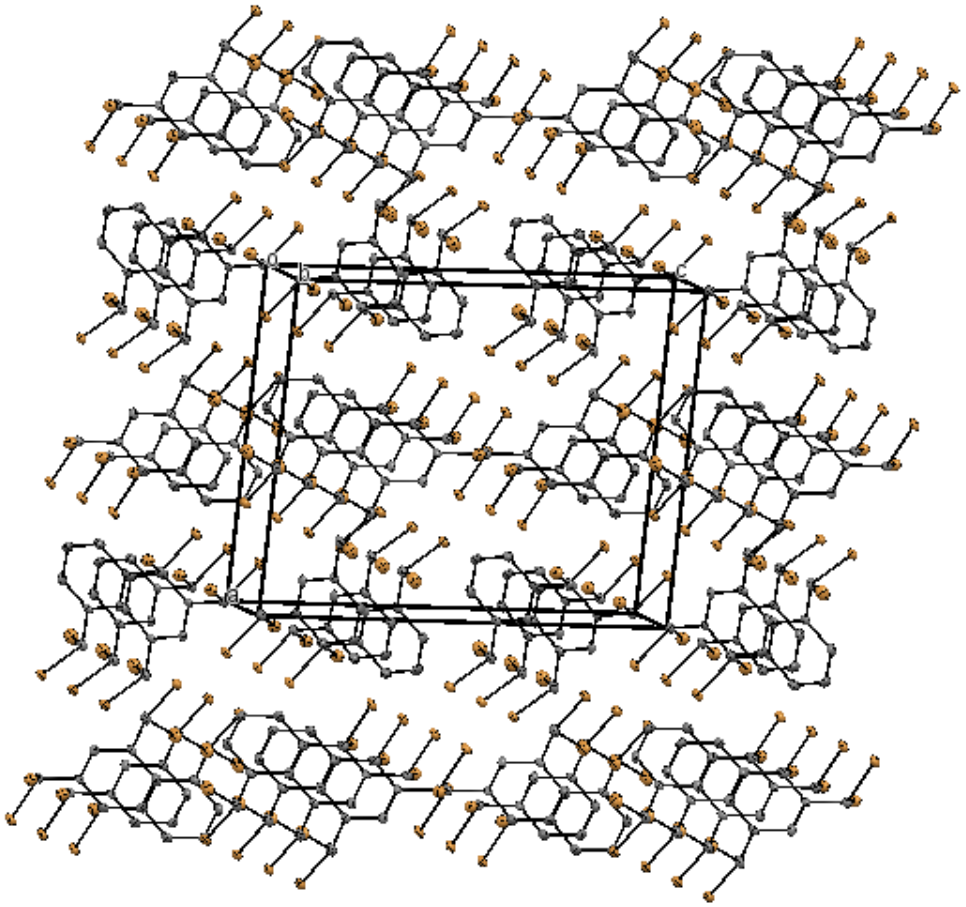
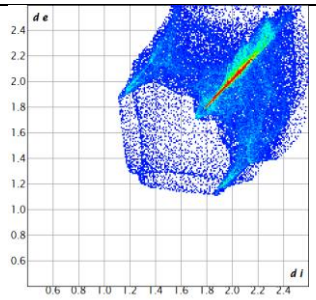
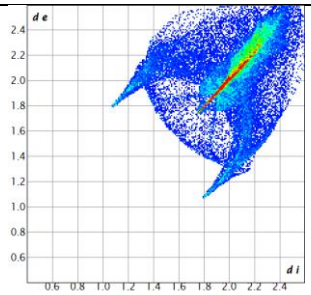
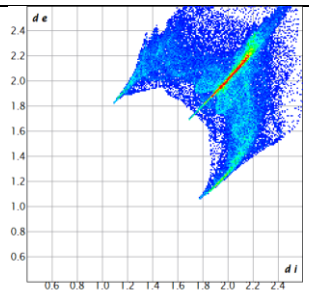
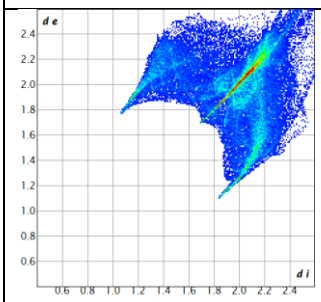
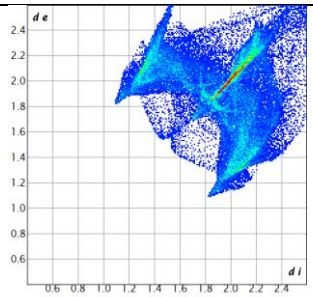
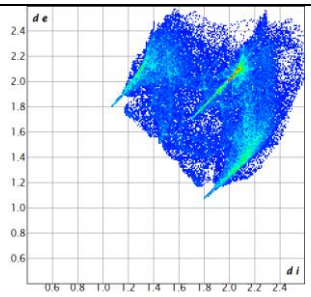
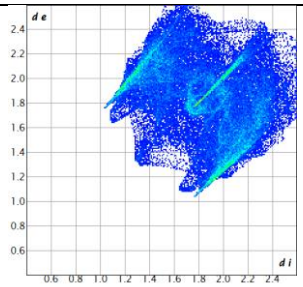
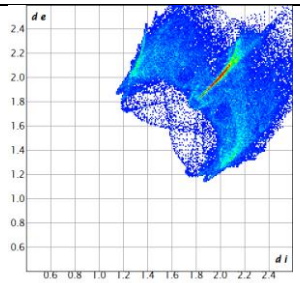
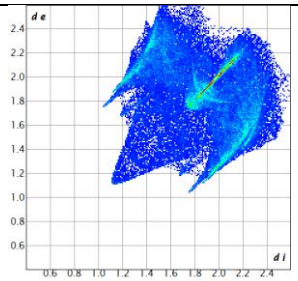
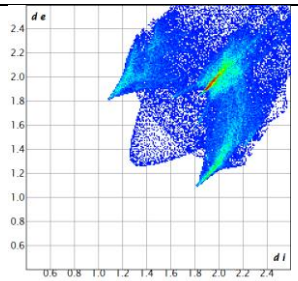


Figure S27. Packing diagram of compound **9**. Hydrogen atoms were omitted for clarity.

Table S1. The contribution of individual interactions to the Hirshfeld surface of compounds **1** – **9**.

		Contribution of the interaction to the surface [%]					
Compounds		**Br···Br**	**Br···C** **C···Br**	**Br···H** **H···Br**	**C···C**	**C···H** **H···C**	**H···H**
1		31.9	1.8	45.8	9.4	4.0	7.1
2		44.1	10.9	34.0	2.2	3.8	5.0
3		24.8	7.4	51.1	3.9	9.3	3.6
		24.0	8.2	50.7	2.9	10.6	3.6
4		21.6	0.0	54.0	6.2	7.9	10.3

		Contribution of the interaction to the surface [%]					
Compounds		**Br···Br**	**Br···C** **C···Br**	**Br···H** **H···Br**	**C···C**	**C···H** **H···C**	**H···H**
5		9.4	5.8	51.8	2.7	9.6	20.7
6		4.9	2.0	50.7	4.4	20.3	17.7
7		16.6	1.1	46.0	4.9	17.8	13.6
8		9.2	0.0	46.2	9.3	12.9	22.3
9		13.5	13.2	56.1	0.0	5.7	11.5