

SUPPORTING INFORMATION

Halogen Bond-Involving Self-assembly of Iodonium Carboxylates:

Adding a Dimension to Supramolecular Architecture

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Table S1. Geometrical parameters of C–X···Y (X = Cl, Br) XBs in the structures of **1–3**.

Cation type ^a	XB	<i>d</i> (C–X···Y)	∠(C–X···Y)	Nc ^b	<i>d</i> (C–X···Y)	∠(C–X···Y)	Nc ^b
		1a			1b		
A	C4–X1···X2B	3.5223(17)	171.99(14)	1.01	3.5522(12)	173.00(19)	0.96
B	C10B–X2B···X1B	3.5513(17)	163.54(16)	1.01	3.5578(12)	168.7(2)	0.96
		3a			3b		
A	C4–X1···X2	3.539(3)	176.6(3)	1.01	3.5969(11)	175.8(2)	0.97
B	C4B–X1B···O1A	3.090(6)	154.6(3)	0.94	3.078(5)	155.4(2)	0.91
C	-	-	-	-	-	-	-

Table S2. Parameters in (3, –1) bond critical points (the electron density with sign of λ_2 $\text{sign}(\lambda_2)\rho(r)$ in e/bohr^3 , Laplacian of electron density $\nabla^2\rho(r)$ in e/bohr^5 , the local electronic energy density H_b , local electronic potential energy density $V(r)$, local electronic kinetic energy density $G(r)$ in hartrees/ bohr^3) corresponding to the Cl···Cl (Br···Br), Cl···C (Br···C), Cl···O (Br···O) XBs and HBs in crystal models of all structures.

Structure	Contact	<i>l</i>	$\text{sign}(\lambda_2)\rho(r)$	$\nabla^2\rho(r)$	<i>V</i> (r)	<i>G</i> (r)	<i>H_b</i>
1a	Cl1···Cl2B	3.522	–0.0058	0.0203	–0.0026	0.0038	0.0012
	Cl2B···Cl1B	3.551	–0.0056	0.0192	–0.0025	0.0036	0.0012
1b	Br1···Br2B	3.552	–0.0080	0.0275	–0.0038	0.0054	0.0015
	Br2B···Br1B	3.558	–0.0080	0.0273	–0.0038	0.0053	0.0015
2a	Cl1···C11	3.182	–0.0080	0.0295	–0.0040	0.0057	0.0017
	Cl2···C5	3.355	–0.0067	0.0235	–0.0032	0.0045	0.0014
2b	Br1···C11	3.249	–0.0085	0.0295	–0.0043	0.0058	0.0015
	Br2···C5	3.392	–0.0072	0.0251	–0.0036	0.0049	0.0013
3a	Cl1···Cl2	3.539	–0.0057	0.0198	–0.0026	0.0038	0.0012
	Cl1B···O1A	3.090	–0.0088	0.0365	–0.0049	0.0070	0.0021
	H1SA···O2A	1.769	–0.0378	0.1180	–0.0325	0.0310	–0.0015
	H1SB···O2S	1.781	–0.0368	0.1118	–0.0309	0.0294	–0.0015
	H2SB···O6A	1.767	–0.0369	0.1232	–0.0327	0.0317	–0.0009
	H2SA···O3A	1.930	–0.0259	0.0885	–0.0201	0.0211	0.0010
3b	Br1···Br2	3.597	–0.0074	0.0255	–0.0035	0.0049	0.0014
	Br1B···O1A	3.078	–0.0108	0.0435	–0.0067	0.0088	0.0021
	H1SA···O2A	1.737	–0.0404	0.1217	–0.0353	0.0328	–0.0024
	H1SB···O2S	1.824	–0.0339	0.1032	–0.0275	0.0266	–0.0008
	H2SA···O6A	1.713	–0.0426	0.1296	–0.0385	0.0354	–0.0030
	H2SB···O3A	1.869	–0.0288	0.0956	–0.0229	0.0234	0.0005

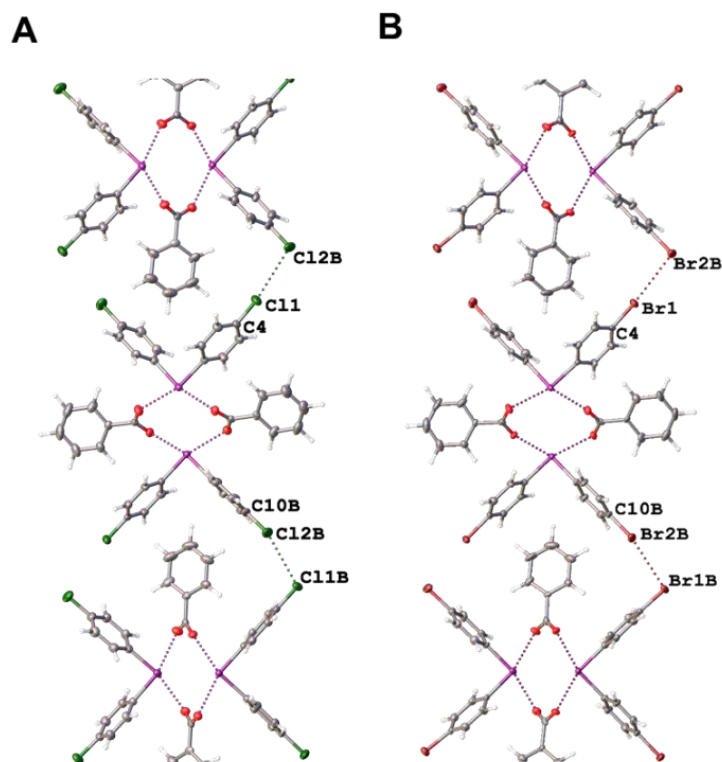


Figure S1. XB C–X...Y in **1a** (A) and **1b** (B).

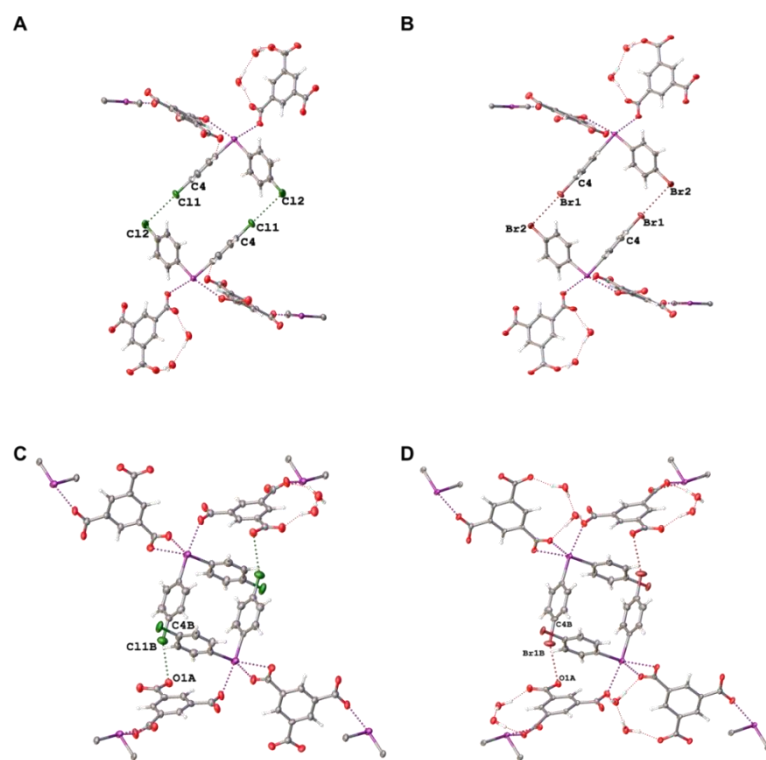


Figure S2. XB C–X...Y in **3a** (A, C) and **3b** (B, D).

Table S3. Crystal structure refinement.

Identification code	1a	1b	2a	2b	3a	3b
CCDC number	2291471	2291472	2291473	2291475	2291476	2291477
Empirical formula	C ₁₉ H ₁₃ Cl ₂ IO ₂	C ₁₉ H ₁₃ Br ₂ IO ₂	C ₃₂ H ₂₀ Cl ₄ I ₂ O ₄	C ₃₂ H ₂₀ Br ₄ I ₂ O ₄	C ₄₅ H ₃₁ Cl ₆ I ₃ O ₈	C ₄₅ H ₃₁ Br ₆ I ₃ O ₈
Formula weight	471.11	1120.03	864.08	1041.92	1293.10	1559.86
Temperature, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic	monoclinic
Space group	Pbca	Pbca	P-1	P-1	P2 ₁ /n	P2 ₁ /n
a, Å	19.8620(6)	20.2173(9)	7.3451(4)	7.5887(5)	11.7190(2)	11.8708(2)
b, Å	9.2439(2)	9.1860(5)	9.6604(5)	9.5201(7)	28.4879(6)	28.5948(4)
c, Å	40.3145(11)	40.790(2)	10.9579(5)	11.0650(7)	14.0194(3)	14.2162(2)
α , °	90	90	104.536(4)	77.605(6)	90	90
β , °	90	90	90.659(4)	88.895(5)	96.078(2)	95.2910(10)
γ , °	90	90	99.660(5)	80.537(6)	90	90
Volume, Å ³	7401.90(3)	7575.3(7)	740.80(7)	770.03(9)	4654.06(16)	4805.03(13)
Z	8	8	1	1	4	4
ρ_{calc} , g/cm ³	1.691	1.964	1.937	2.247	1.845	2.156
μ , mm ⁻¹	2.027	5.918	2.522	7.269	19.427	21.594
F(000)	3680.0	4256.0	418.0	490.0	2504.0	2936.0
Crystal size, mm ³	0.7 × 0.3 × 0.08	1.5 × 1 × 0.5	0.18 × 0.12 × 0.08	0.6 × 0.5 × 0.5	0.18 × 0.15 × 0.13	0.2 × 0.18 × 0.17
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 Θ range for data collection, °	4.532 to 57.538	4.474 to 57.158	5.064 to 58.676	4.44 to 57.27	6.206 to 134.996	6.182 to 129.974
Index ranges	-20 ≤ h ≤ 26, -12 ≤ k ≤ 12, -52 ≤ l ≤ 50	-16 ≤ h ≤ 25, -10 ≤ k ≤ 11, -47 ≤ l ≤ 54	-8 ≤ h ≤ 9, -11 ≤ k ≤ 12, -14 ≤ l ≤ 14	-10 ≤ h ≤ 9, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14	-14 ≤ h ≤ 13, -34 ≤ k ≤ 33, -16 ≤ l ≤ 15	-12 ≤ h ≤ 13, -33 ≤ k ≤ 33, -16 ≤ l ≤ 14
Reflections collected	45164	36807	6076	9155	51478	41302
Independent reflections	8636 [R _{int} = 0.0539, R _{sigma} = 0.0517]	8713 [R _{int} = 0.0869, R _{sigma} = 0.0995]	3384 [R _{int} = 0.0239, R _{sigma} = 0.0447]	3433 [R _{int} = 0.0285, R _{sigma} = 0.0342]	8339 [R _{int} = 0.1651, R _{sigma} = 0.0809]	8172 [R _{int} = 0.0946, R _{sigma} = 0.0508]
Data/restraints/parameters	8636/0/433	8713/0/427	3384/0/190	3433/0/190	8339/2/565	8172/2/565
Goodness-of-fit on F ²	1.037	1.027	1.046	1.057	1.060	1.027
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0428, wR ₂ = 0.0830	R ₁ = 0.0628, wR ₂ = 0.0998	R ₁ = 0.0274, wR ₂ = 0.0558	R ₁ = 0.0254, wR ₂ = 0.0510	R ₁ = 0.0597, wR ₂ = 0.1565	R ₁ = 0.0461, wR ₂ = 0.1171
Final R indexes [all data]	R ₁ = 0.0680, wR ₂ = 0.0910	R ₁ = 0.1098, wR ₂ = 0.1121	R ₁ = 0.0320, wR ₂ = 0.0582	R ₁ = 0.0318, wR ₂ = 0.0526	R ₁ = 0.0735, wR ₂ = 0.1673	R ₁ = 0.0500, wR ₂ = 0.1200
Largest diff. peak/hole, e ⁻ Å ⁻³	0.90/-0.62	0.94/-1.23	1.35/-0.68	1.19/-0.91	2.16/-1.97	2.84/-1.24

Crystal growth

Diaryliodonium benzoates 1.

Crystals of **1** were grown by slow evaporation of methanol solution of **1** at ambient temperature.

Diaryliodonium terephthalates 2.

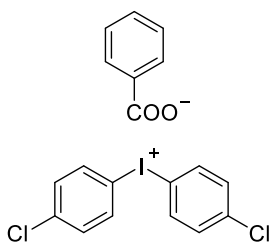
Crystals of **2** were grown by slow diffusion of tetrabutylammonium terephthalate methanol solution to diaryliodonium trifluoromethanesulfonate methanol solution in ampule at ambient temperature. Solution of diaryliodonium salt was carefully added, avoiding significant mixing.

Diaryliodonium trimesates 3.

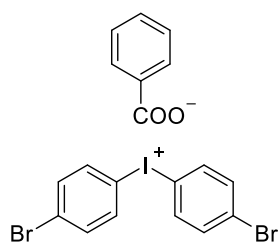
Crystals of **3** suitable for X-Ray diffraction were grown by slow diffusion of tetrabutylammonium terephthalate solution in water/acetonitrile mixture (1:1) to diaryliodonium trifluoromethanesulfonate in acetonitrile at ambient temperature. Solution of diaryliodonium salt was carefully added, avoiding significant mixing.

Synthetic procedures

Synthesis of diaryliodonium benzoates 1. A solution of a diaryliodonium trifluoromethanesulfonate [**1**] (1 mmol) in methanol/water mixture (1 mL) was added dropwise to solution of potassium benzoate (3 mmol, 481 mg) in water (5 mL) at RT, the reaction mixture was stirred for 30 min and the precipitate formed was filtered off and washed with water (3×5 mL). The obtained diaryliodonium benzoates **1** were dried under reduced pressure.

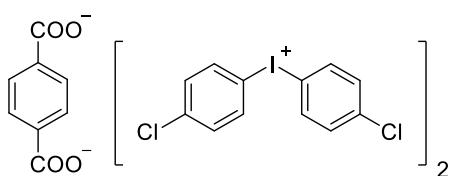


bis(4-chlorophenyl)iodonium benzoate (1a). The reaction of bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (1 mmol, 499 mg) according to described procedure afforded 457 mg (97%) of **1a** isolated as the colorless crystalline solid; mp 152–153 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.18 (d, *J* = 8.8 Hz, 4H), 7.75 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 4H), 7.32–7.23 (m, 3H). ¹³C{¹H} (100 MHz, DMSO-*d*₆) δ 169.7, 138.8, 136.8, 136.2, 131.1, 129.2, 129.0, 127.3, 118.9. HRMS (ESI+) *m/z* calcd. for [M]⁺ C₁₂H₈Cl₂I⁺: 348.9042, found 348.9045.

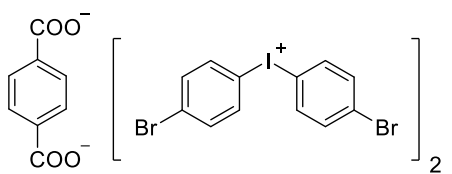


bis(4-bromophenyl)iodonium benzoate (1b). The reaction of bis(4-bromophenyl)iodonium trifluoromethanesulfonate (1 mmol, 588 mg) according to described procedure afforded 527 mg (94%) of **1b** isolated as the colorless crystalline solid; mp 158–159 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 8.09 (d, J = 8.0 Hz, 4H), 7.79 (d, J = 6.8 Hz, 2H), 7.65 (d, J = 8.4 Hz, 4H), 7.37–7.28 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, DMSO- d_6) δ 169.3, 136.9, 134.0, 129.9, 129.8, 129.0, 127.7, 125.1, 119.4. HRMS (ESI+) m/z calcd. for $[\text{M}]^+$ $\text{C}_{12}\text{H}_8\text{Br}_2\text{I}^+$: 436.8032, found 436.8039.

Synthesis of diaryliodonium terephthalates 2. To a solution of a diaryliodonium trifluoromethanesulfonate [1] (2.2 mmol) in methanol/water mixture (5 mL, 1:1) the solution of tetrabutylammonium terephthalate (1 mmol, 649 mg) in methanol (1 mL) was added dropwise at RT. The reaction mixture was stirred for 30 min and the precipitate formed was filtered off and washed with water (3×5 mL). The obtained diaryliodonium terephthalates **2** were dried under reduced pressure.



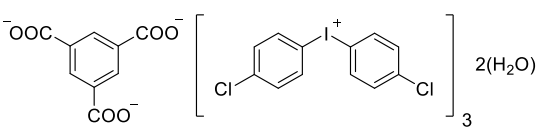
bis(4-chlorophenyl)iodonium terephthalate (2a). The reaction of bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (2.2 mmol, 1.1 g) according to described procedure afforded 682 mg (79%) of **2a** isolated as the colorless crystalline solid; mp 200–202 °C. Elemental analysis (Found; C 43.43%, H 2.49%, Calcd. for $\text{C}_{32}\text{H}_{20}\text{Cl}_4\text{I}_2\text{O}_4$: C 44.48%, H 2.33%). HRMS (ESI+) m/z calcd. for $[\text{M}]^+$ $\text{C}_{12}\text{H}_8\text{Cl}_2\text{I}^+$: 348.9042, found 348.9042.

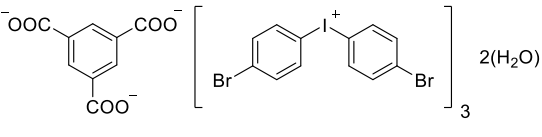


bis(4-bromophenyl)iodonium terephthalate (2b). The reaction of bis(4-bromophenyl)iodonium trifluoromethanesulfonate (2.2 mmol, 1.29 g) according to described procedure afforded 885 mg (85%) of **2b** isolated as the colorless crystalline solid; mp

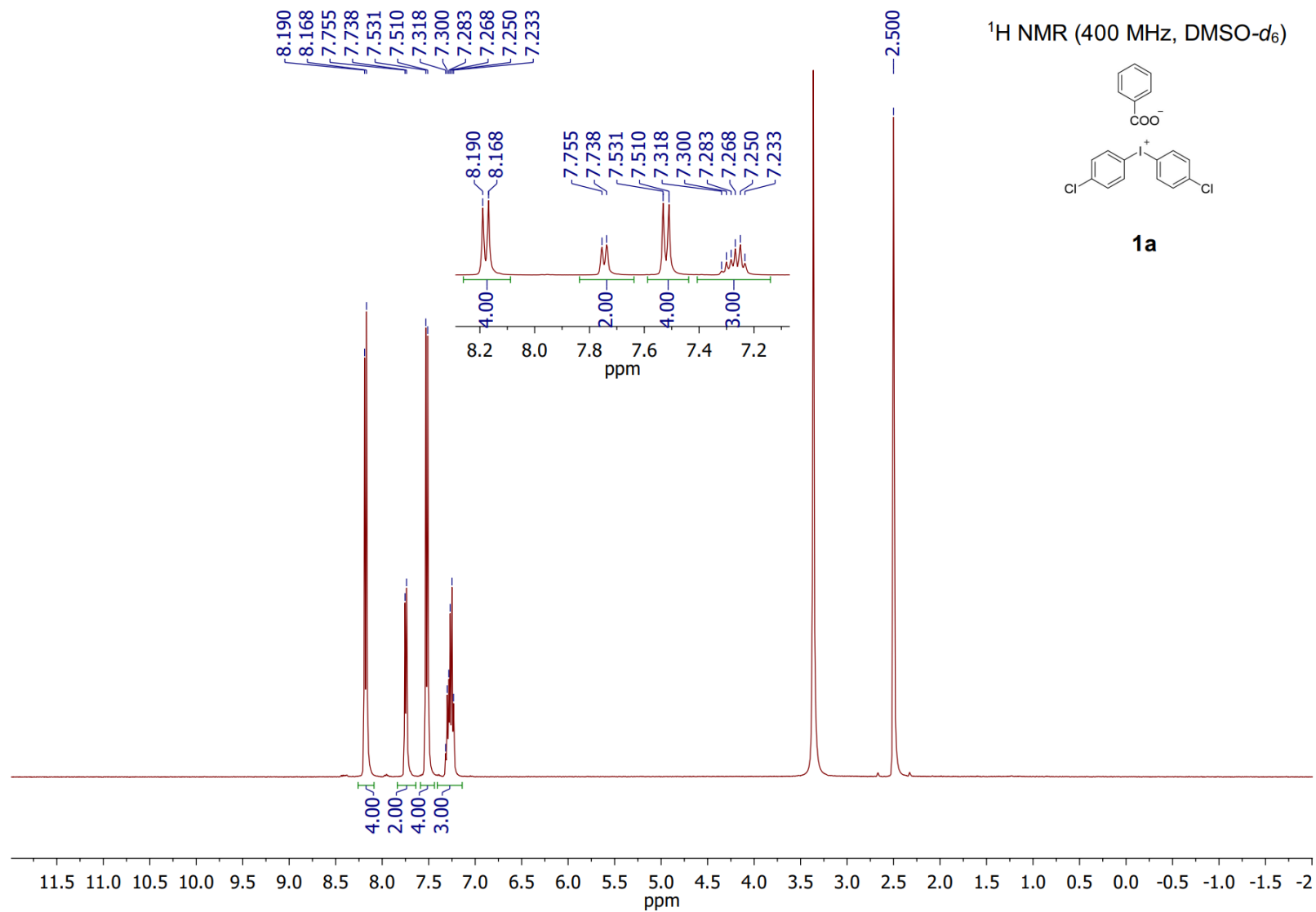
191–193 °C. Elemental analysis (Found; C 36.82%, H 2.24%, Calcd. for C₃₂H₂₀Br₄I₂O₄: C 36.89%, H 1.93%). HRMS (ESI+) *m/z* calcd. for [M]⁺ C₁₂H₈Br₂I⁺: 436.8032, found 436.8043.

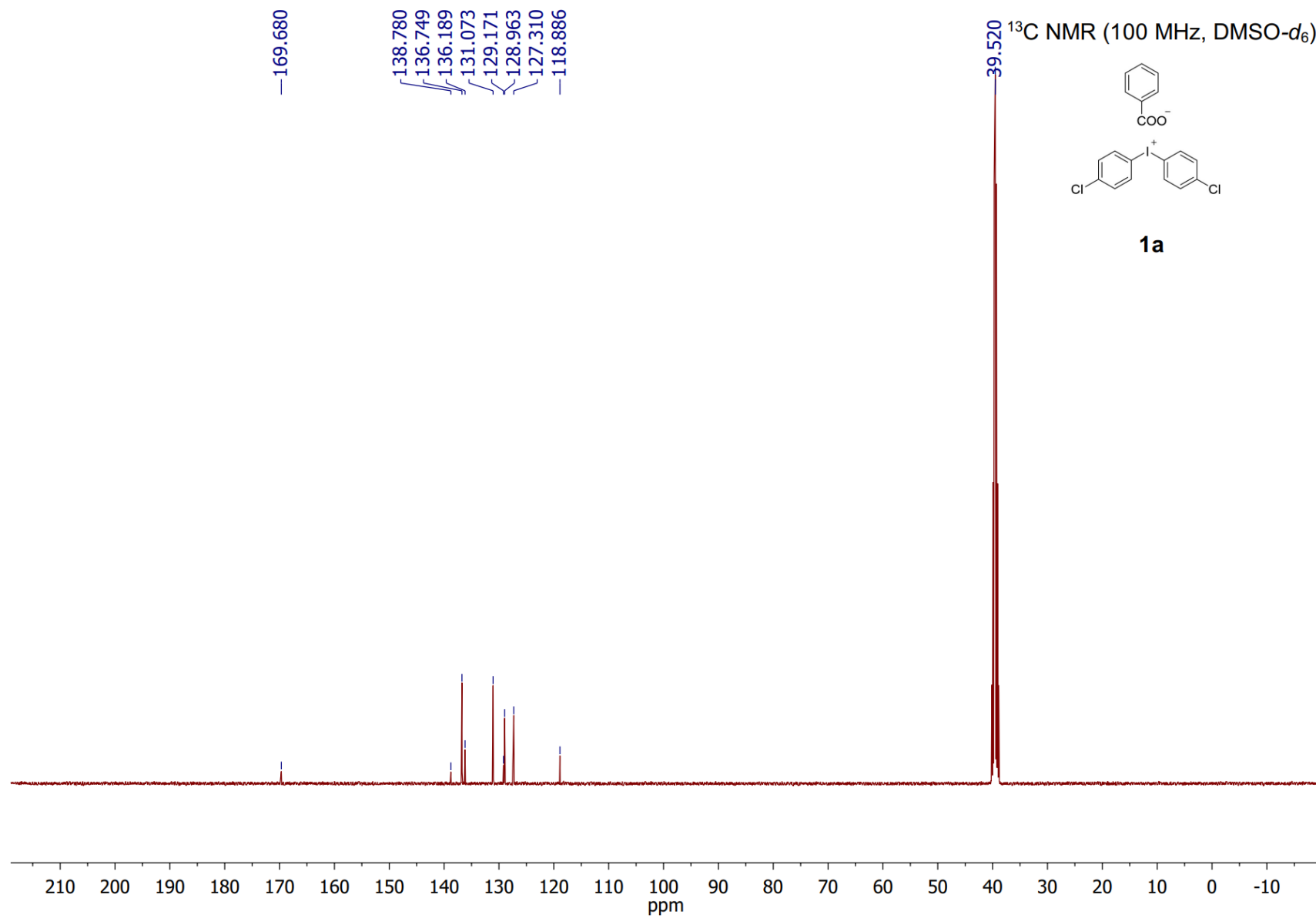
Synthesis of diaryliodonium trimesates 3. To a solution of tetrabutylammonium trimesate (1 mmol, 934 mg) in water/acetonitrile mixture (5 mL, 1:1) a solution of diaryliodonium trifluoromethanesulfonate[1] (3.3 mmol) in acetonitrile (5 mL) was added dropwise at RT. The reaction mixture was stirred for 30 min and the precipitate formed was filtered off and washed with water (3×5 mL). The product **3** was dried in the air.

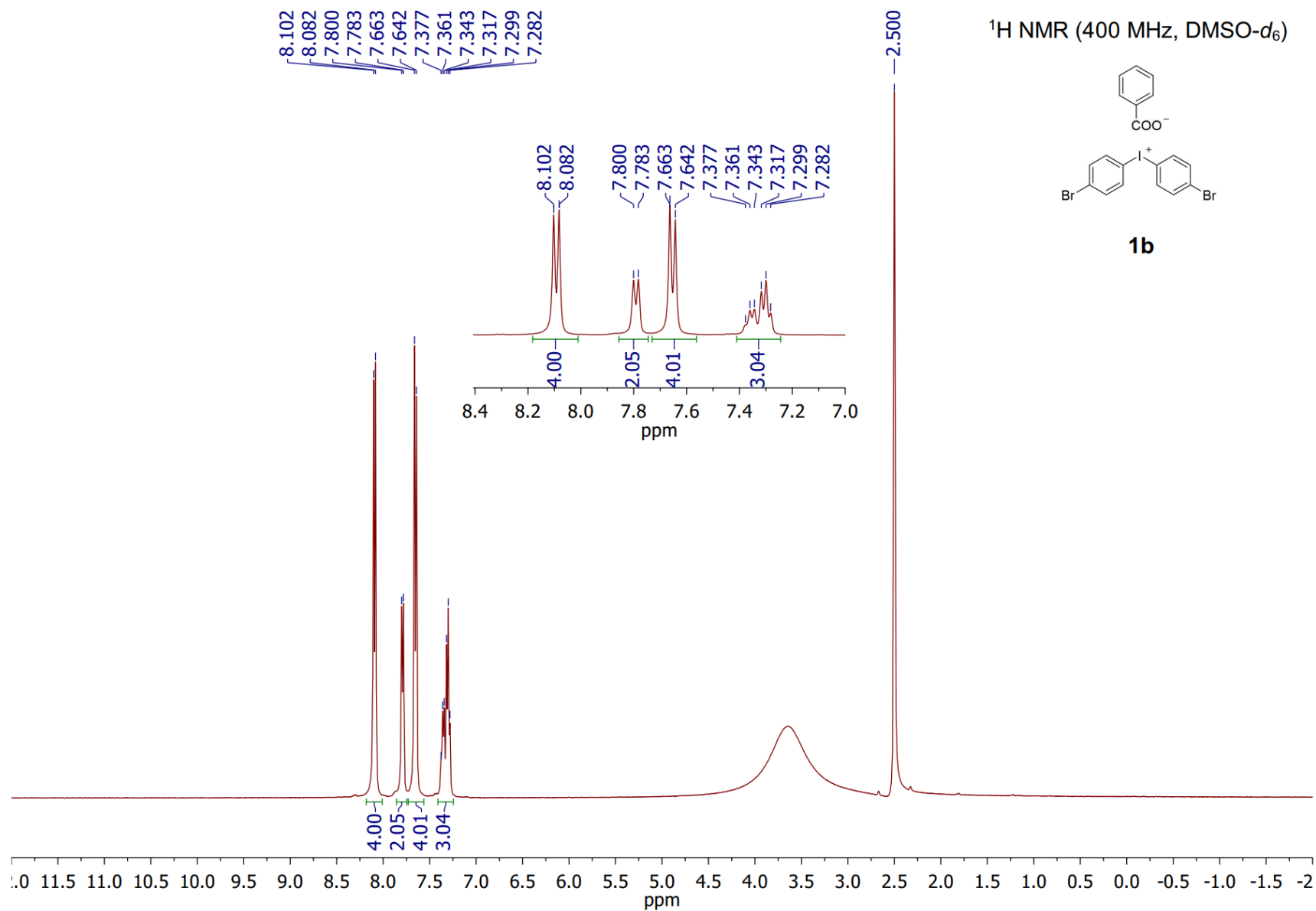
 **bis(4-chlorophenyl)iodonium benzene-1,3,5-tricarboxylate dihydrate (3a).** The reaction of bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (3.3 mmol, 1.65 g) according to described procedure afforded 905 mg (72%) of **3a** isolated as the colorless crystalline solid; mp 152–154 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.23–8.10 (m, 15H), 7.49 (d, *J* = 8.4 Hz, 12H). ¹³C{¹H} (100 MHz, DMSO-*d*₆) δ 170.5, 136.7, 136.6, 135.9, 131.2, 130.9, 119.8. Elemental analysis (Found; C 42.18%, H 2.56%, Calcd. for C₄₅H₃₁Cl₆I₃O₈: C 41.80%, H 2.42%). HRMS (ESI+) *m/z* calcd. for [M]⁺ C₁₂H₈Cl₂I⁺: 348.9042, found 348.9032.

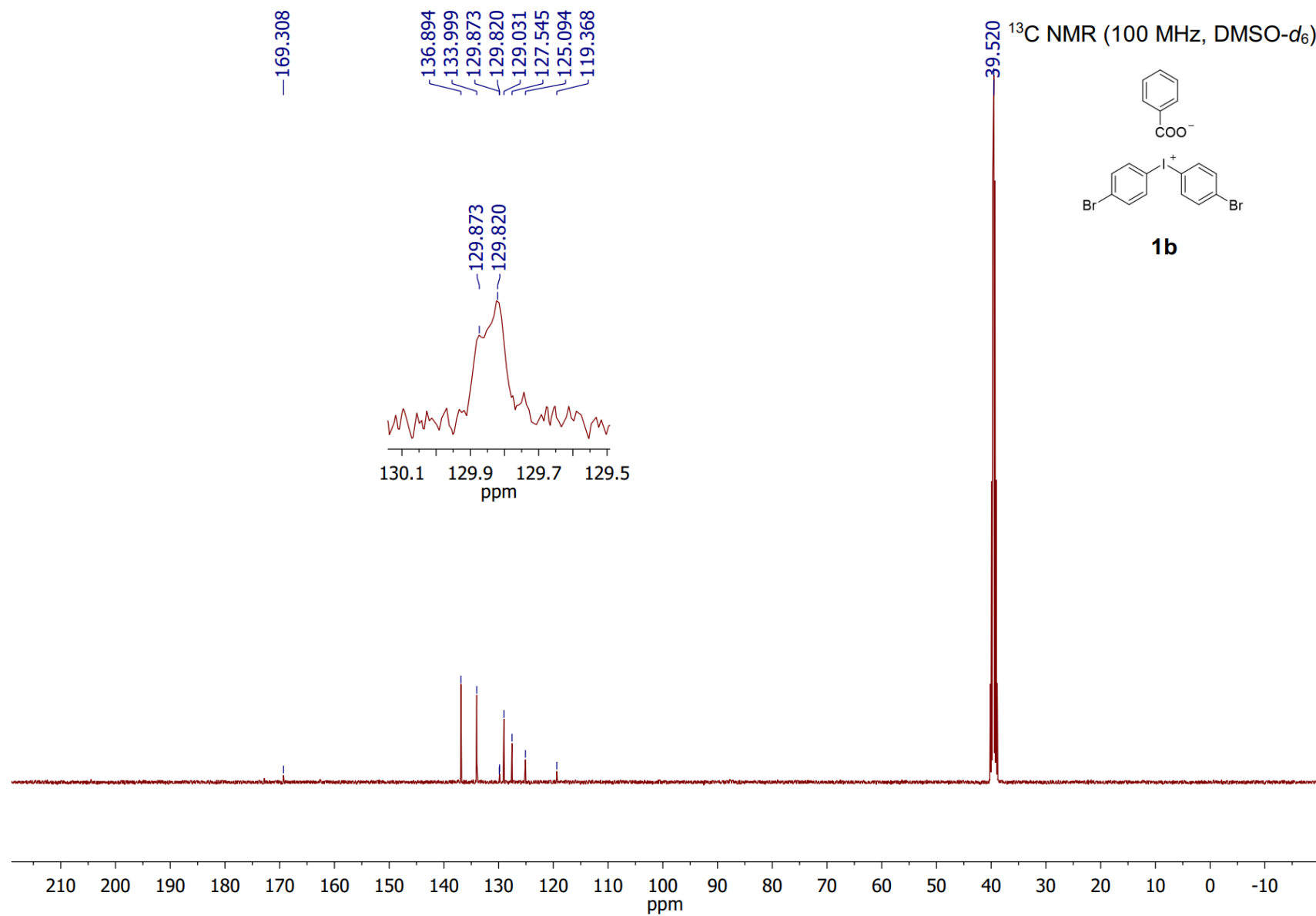
 **bis(4-bromophenyl)iodonium benzene-1,3,5-tricarboxylate dihydrate (3b).** The reaction of bis(4-bromophenyl)iodonium trifluoromethanesulfonate (3.3 mmol, 1.94 g) according to described procedure afforded 1.26 g (83%) of **3b** isolated as the colorless crystalline solid; mp 146–148 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.17 (s, 3H), 8.07 (d, *J* = 8.4 Hz, 12H), 7.62 (d, *J* = 8.4 Hz, 12H). ¹³C{¹H} (100 MHz, DMSO-*d*₆) δ 170.5, 136.8, 136.6, 133.8, 131.2, 124.7, 120.5. Elemental analysis (Found; C 34.73%, H 2.00%, Calcd. for C₄₅H₃₁Br₆I₃O₈: C 34.65%, H 2.00%). HRMS (ESI+) *m/z* calcd. for [M]⁺ C₁₂H₈Br₂I⁺: 436.8032, found 436.8029.

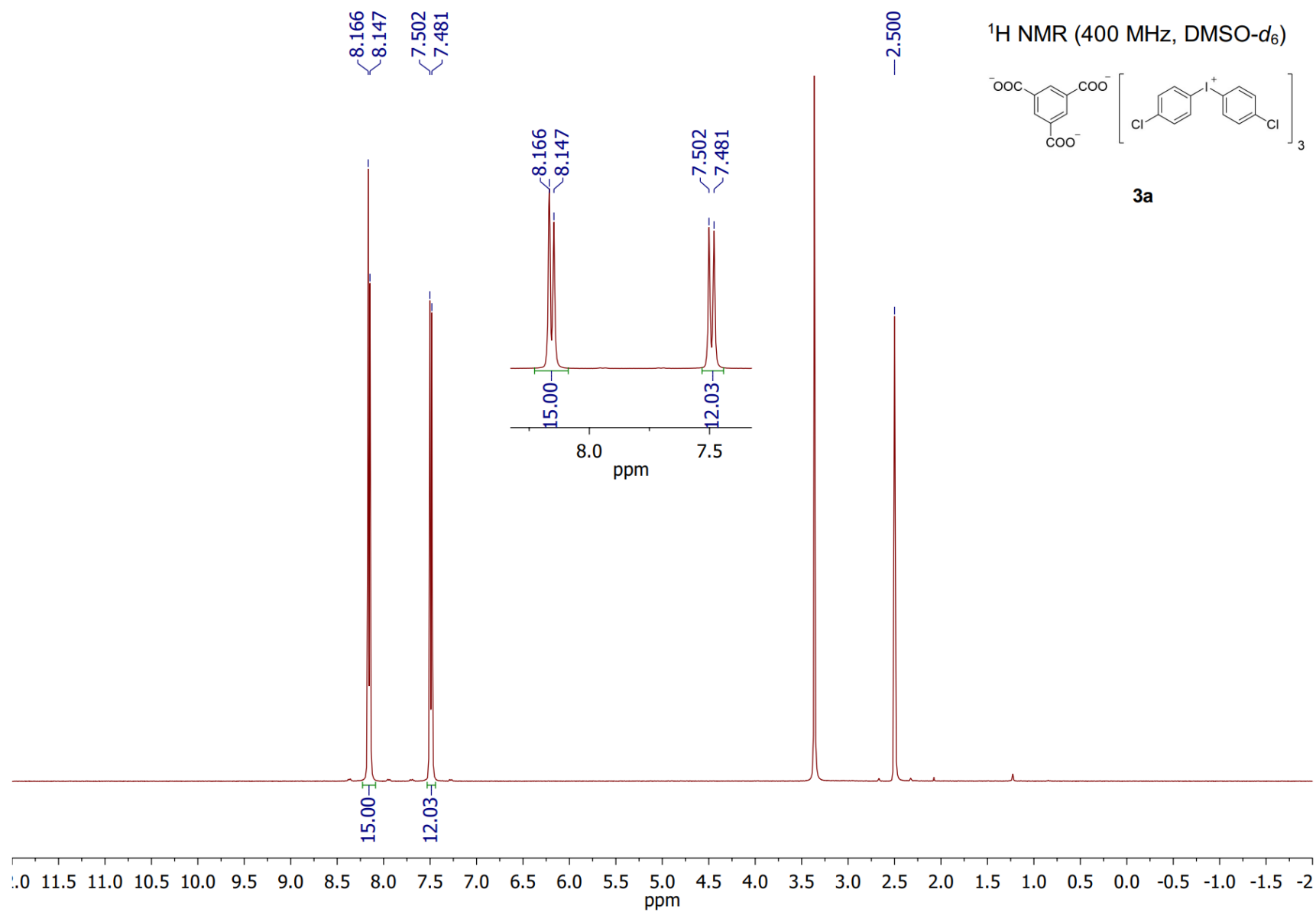
NMR spectra of **1a,b** and **3a,b**

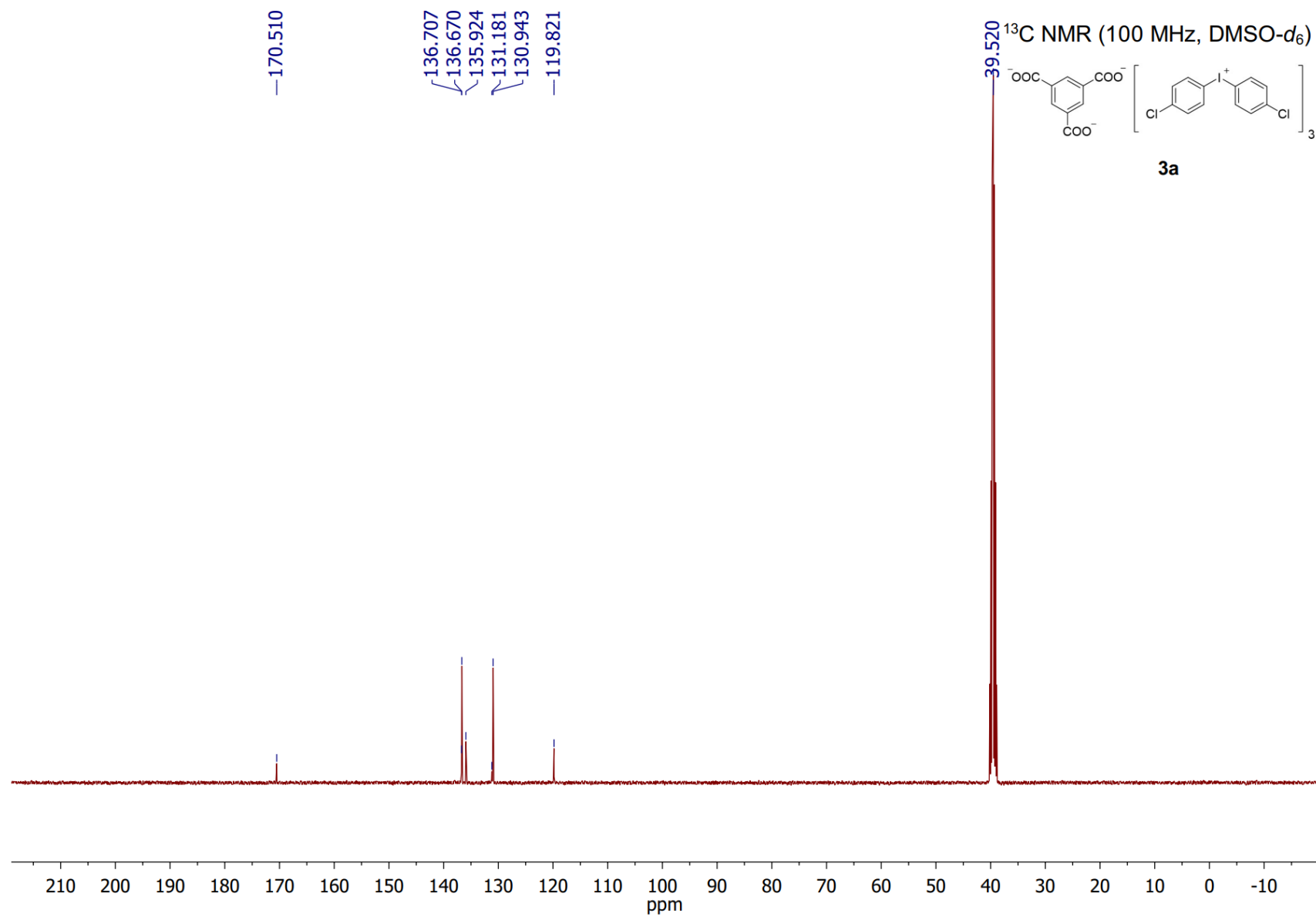


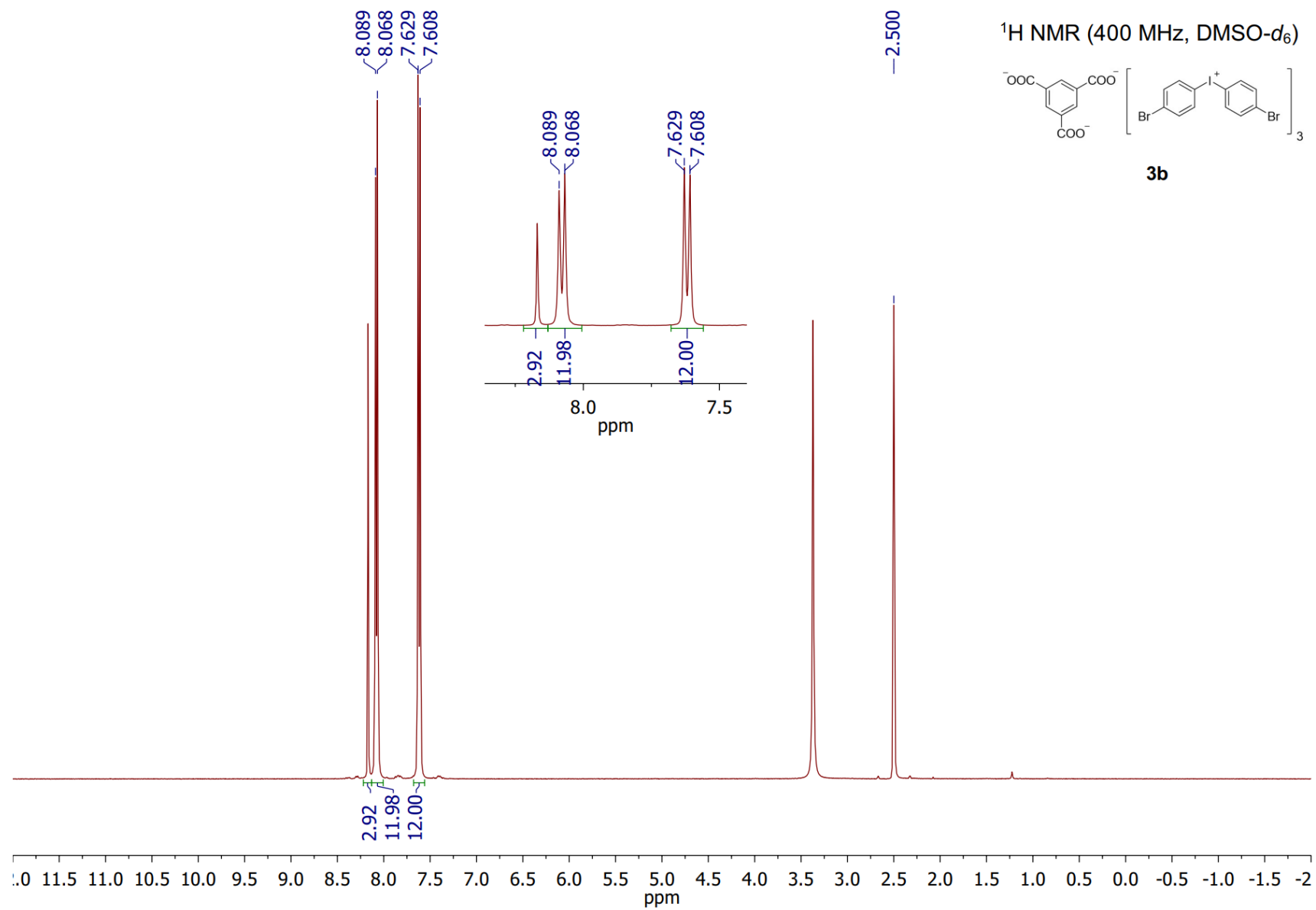


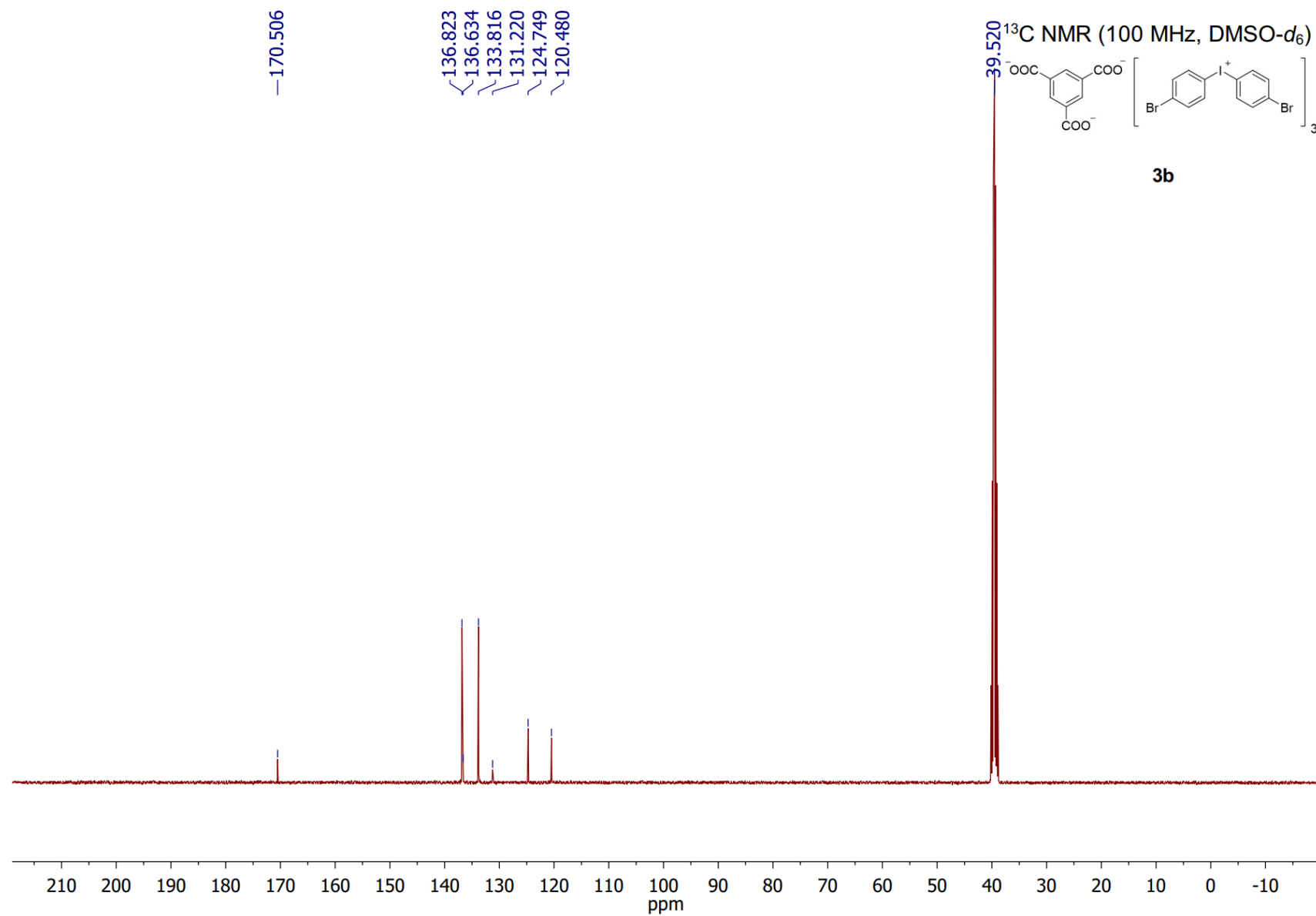












Processing of Cambridge Structure Database

Processing of the Cambridge Structure Database (v 5.44) was performed using the ConQuest module (v 2023.2). To find accessible iodonium species, we analyzed 408 structures obtained by single-crystal XRD, including the C–I⁺–C motif. The type of the supramolecular assembly was determined manually for each structure using Olex2-1.5 software.

References

1. Bielawski, M.; Zhu, M.; Olofsson, B. Efficient and General One-Pot Synthesis of Diaryliodonium Triflates: Optimization, Scope and Limitations. *Adv. Synth. Catal.* **2007**, *349*, 2610–2618, doi:10.1002/adsc.200700373.