Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis of Rigid Cores Based on 1,1'-Biadamantane

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Experimental Section

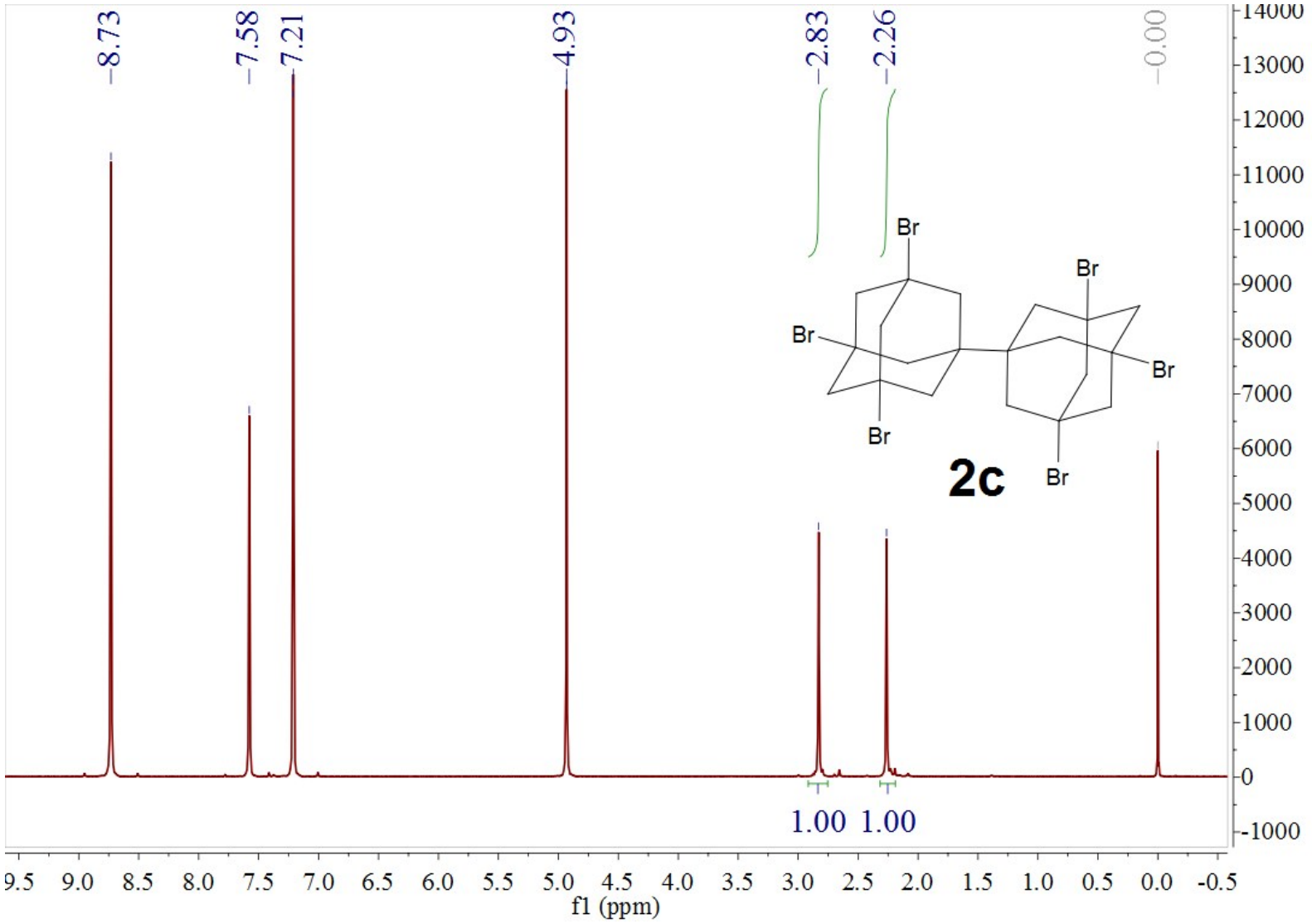
3, 3', 5, 5', 7, 7'-Hexabromo-1, 1'-biadamantane (2c). 1,1'-Biadamantane (2.70g, 9.98mmol) was added portionwise over 30 min to a stirred mixture of Br_2 (50mL) and anhydrous $AlCl_3$ (2.66g, 19.96mmol) at 0℃, and then heated to 85℃ over a period of 1h and kept at that temperature for 48h. Hydrogen bromide was evolved copiously during the addition and heating. The cooled mixture was treated subsequently with saturated aqueous $NaHSO_3$ solution and hydrochloric acid. The solids were removed by filtration, washed and air-dried. The crude product was extracted with $CHCl_3$ for 24h and then recrystallized from N-Methyl-2-pyrrolidinone (NMP), giving 5.20g (70%) of **2d** as white solid. ^{1}H NMR (400 MHz, Pyridine-d_5) δ 2.83 (s, 12H), 2.26 (s, 12H); ^{13}C NMR (101 MHz, Pyridine-d_5) δ 59.44, 55.63, 48.63, 43.49. Anal. Calcd for $C_{20}H_{24}Br_6$: C, 32.29; H, 3.25. Found: C, 32.32; H, 3.33.

General Procedure for the Synthesis of Poly(aryl)-1, 1'-biadamantane (4a-c). To a 100ml flask were successively added bromobenzene (50mL), anhydrous $FeCl_3$ (0.01mol) and **2a-2c** (0.01mol). The mixture was magnetically stirred at room temperature for 30min and then heated to reflux until hydrogen bromide ceased to release. The reaction mixture was cooled to room temperature and then poured into a mixture of 50mL of 0.1M HCl aqueous solution and 100mL of CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×50mL). The combined organic layers were washed successively with saturated $NaHCO_3$ solution, water and brine. The organic layer was transferred to a separatory chamber and added, as a slow stream, to 1L methanol to precipitate a solid during 1h. After the addition was complete, the methanol suspension was stirred vigorously for another 1h. The methanol suspension was filtered and dried in the vacuum-oven.

3, 3'-Bis(4-bromophenyl)-1,1'-biadamantane (4a). The crude product was purified by silica gel chromatography eluted with petroleum ether. The first fraction was concentrated and recrystallized from DMF to afford **4a** as white crystals with the yield of 3.31 g (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.36 (m, 4H), 7.28-7.17 (m, 4H), 2.23-2.12 (m, 4H), 1.87-1.51 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.34, 131.12, 126.86, 119.36, 42.46, 41.70, 37.66, 36.88, 36.39, 34.48, 29.33. Anal. Calcd for $C_{32}H_{36}Br_2$: C, 66.22; H, 6.25. Found: C, 66.13; H, 6.20.

3, 3', 5, 5'-Tetrakis(4-bromophenyl)-1,1'-biadamantane (4b). The crude product was purified by silica gel chromatography eluted with CH_2Cl_2: hexane= 1:50. The fraction with an R_f value of 0.68 was concentrated and recrystallized from DMF to afford **4b** as white crystals with the yield of 4.72 g (53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.13 (m, 16H), 2.27-1.70 (m, 24H), 1.58-1.52 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.34, 131.12, 126.87, 119.36, 42.46, 41.70, 37.66, 36.88, 36.39, 34.47, 29.32. Anal. Calcd for $C_{44}H_{42}Br_4$: C, 59.35; H, 4.75. Found: C, 59.24; H, 4.70.

3, 3', 5, 5', 7, 7'-Hexakis(4-bromophenyl)-1,1'-biadamantane (4c). The crude product was recrystallized from DMF to give 2.64g (44%) of **3d** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dt, J=9.21 ,2.03 Hz, 12H), 7.26 (dt, J=9.21, 2.03 Hz, 12H), 2.06 (d, J=11.97 Hz, 6H), 1.93 (d, J=11.97 Hz, 6H), 1.80(s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.16, 131.52, 126.84, 120.23, 46.65, 40.41, 38.92, 38.58. Anal. Calcd for $C_{56}H_{48}Br_6$: C, 56.03; H, 4.03. Found: C, 56.14; H, 4.12.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Br
Br
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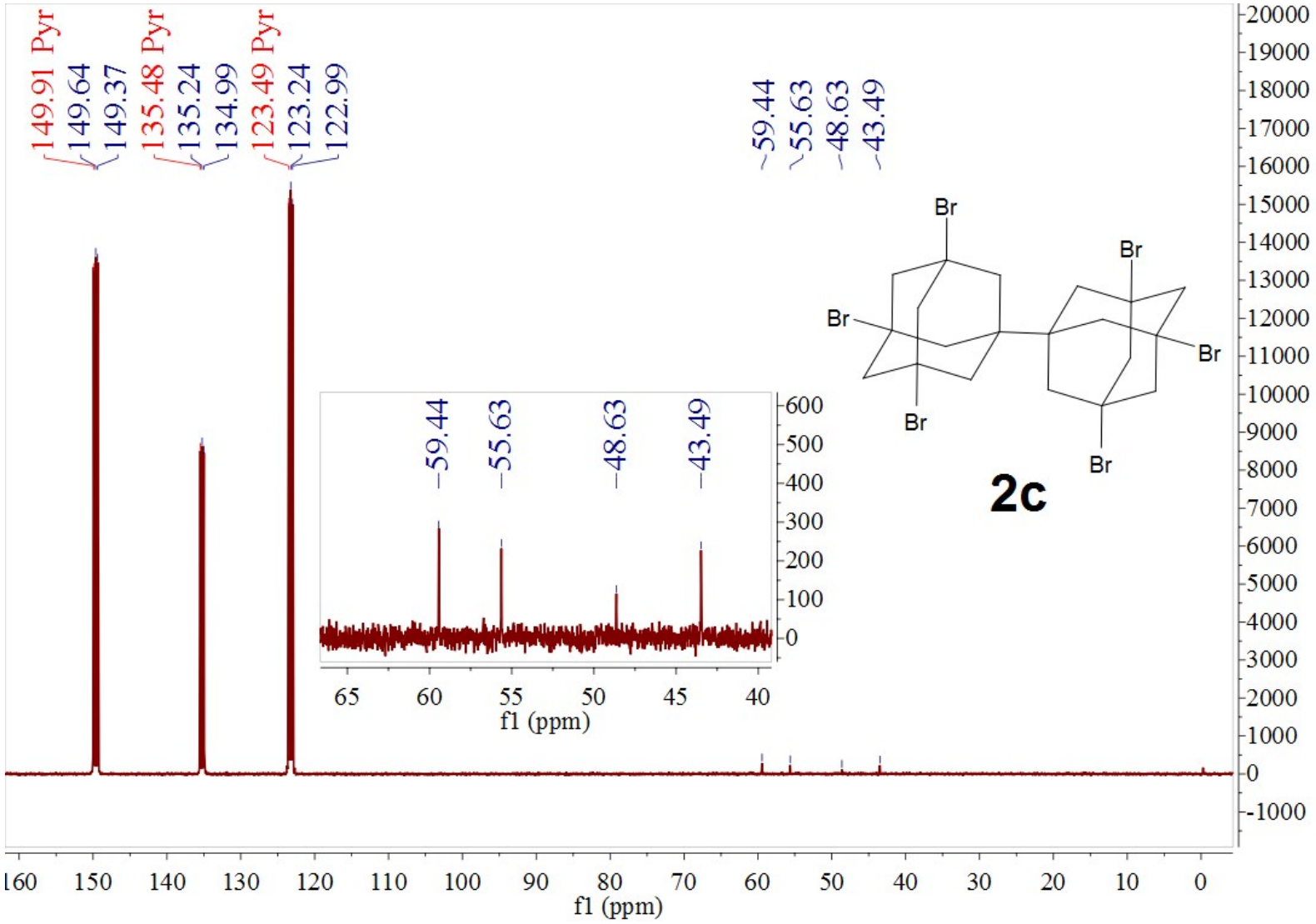
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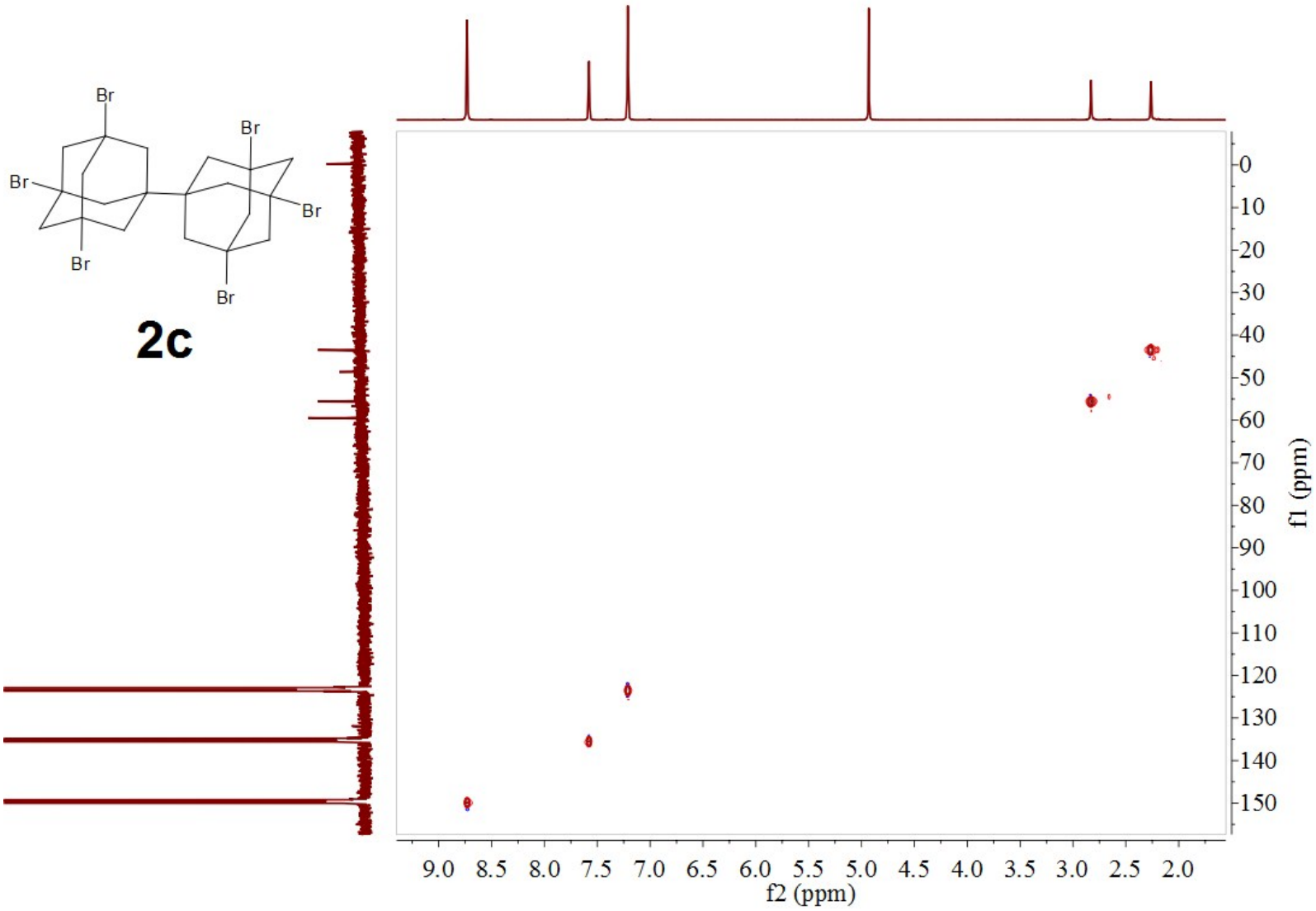
f1 (ppm)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140
150
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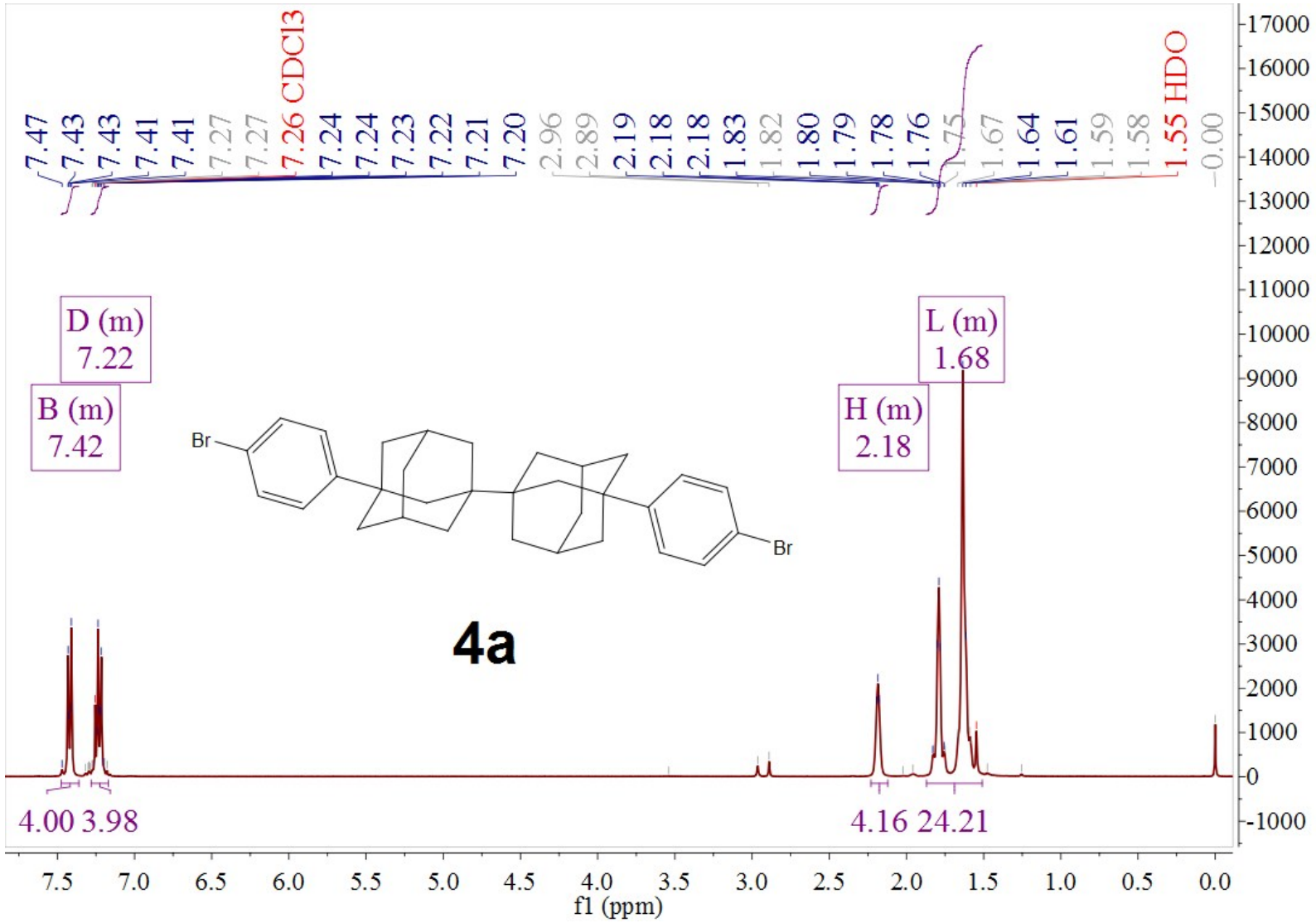
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7.20
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2.18
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1.79
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1.67
1.64
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1.58
1.55 HDO
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D (m)
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B (m)
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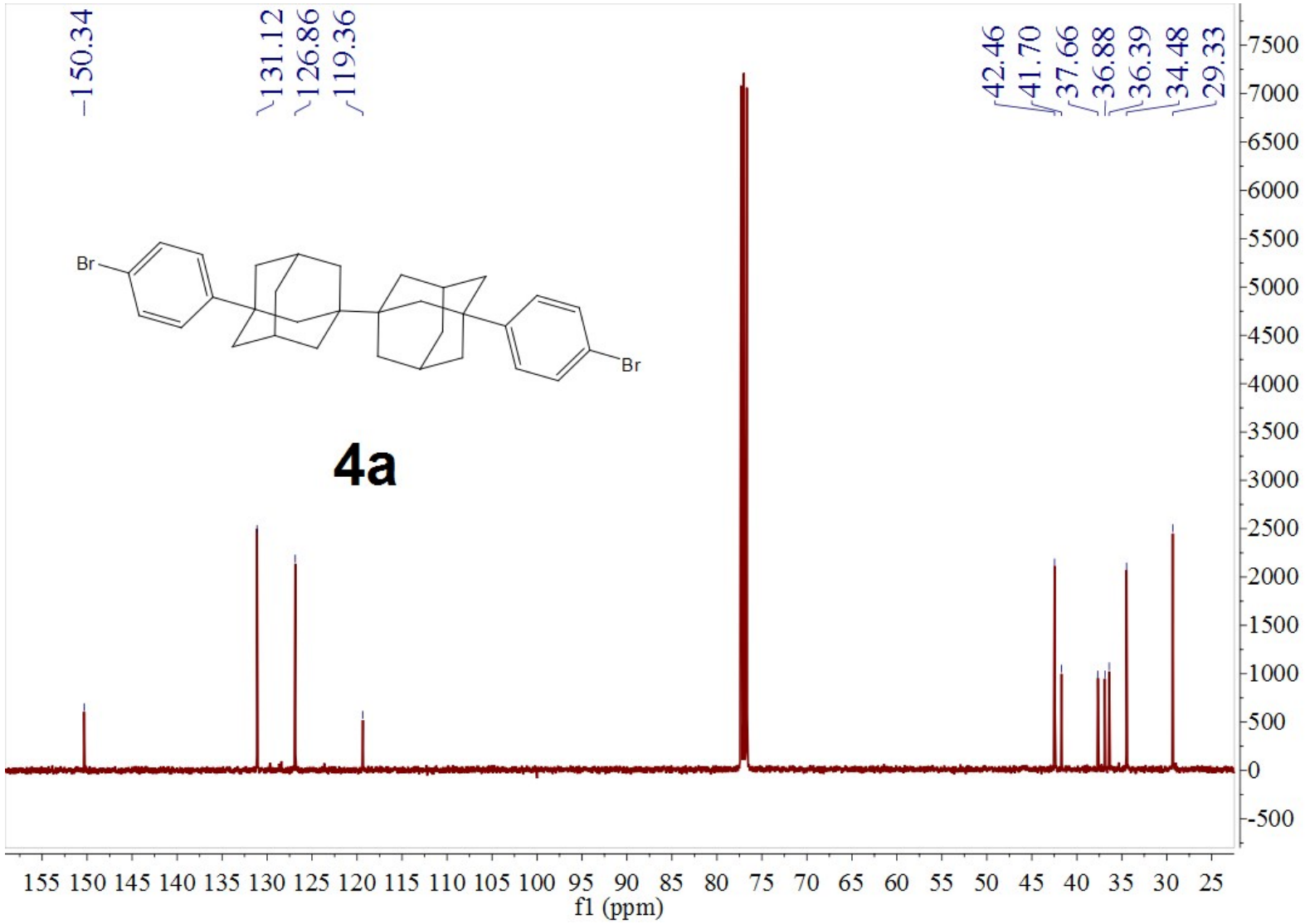
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Br
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7500
7000
6500
6000
5500
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4500
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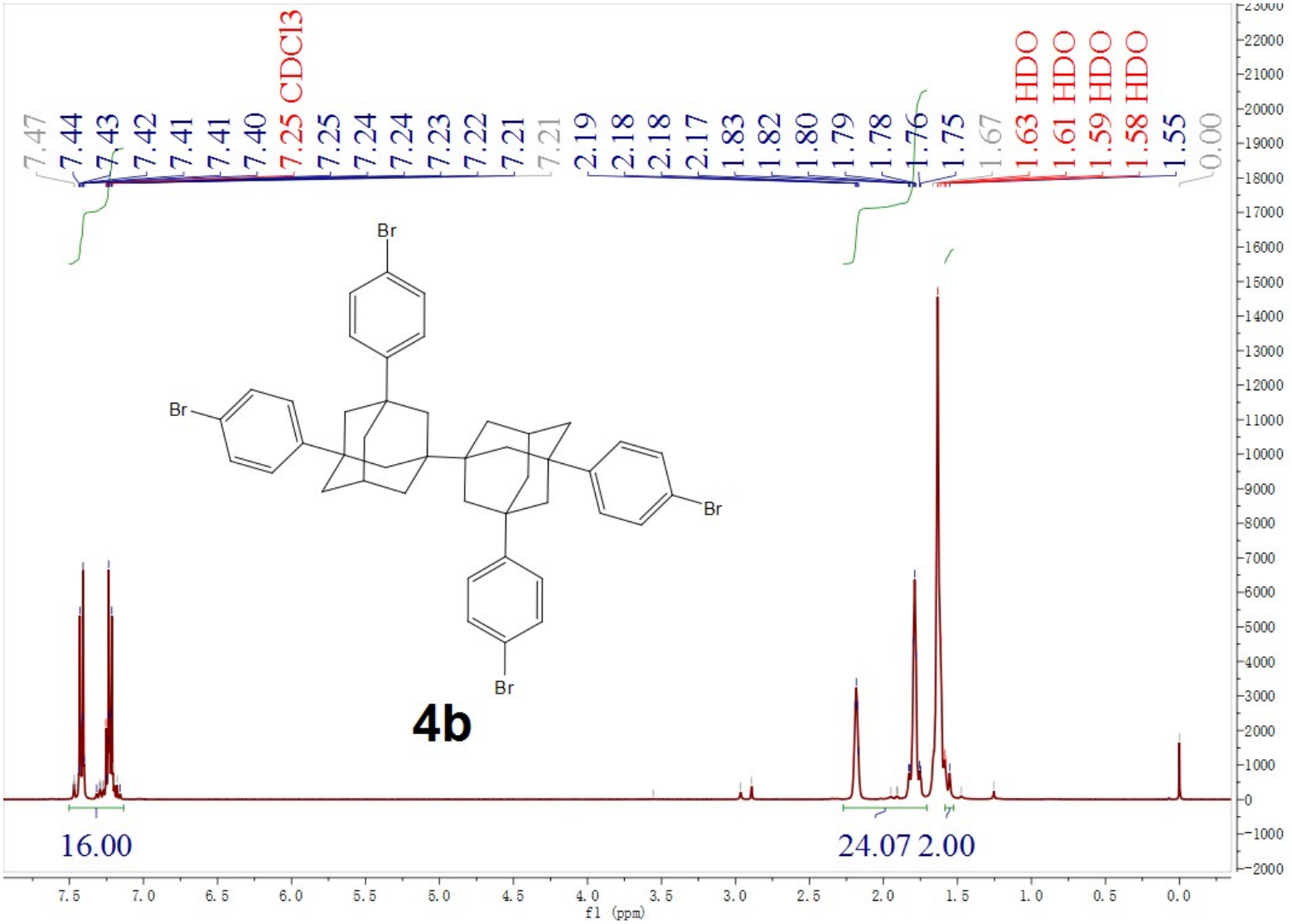
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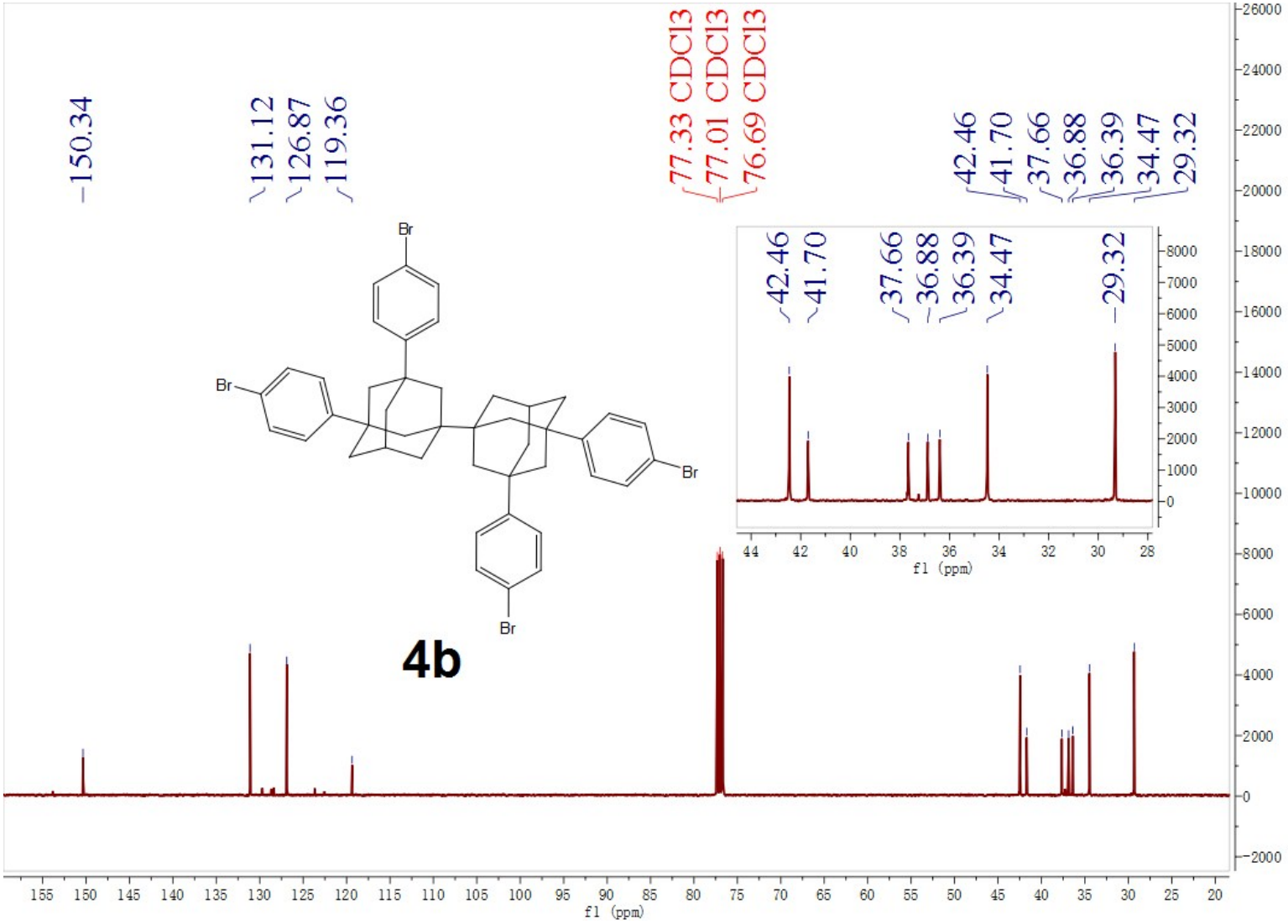
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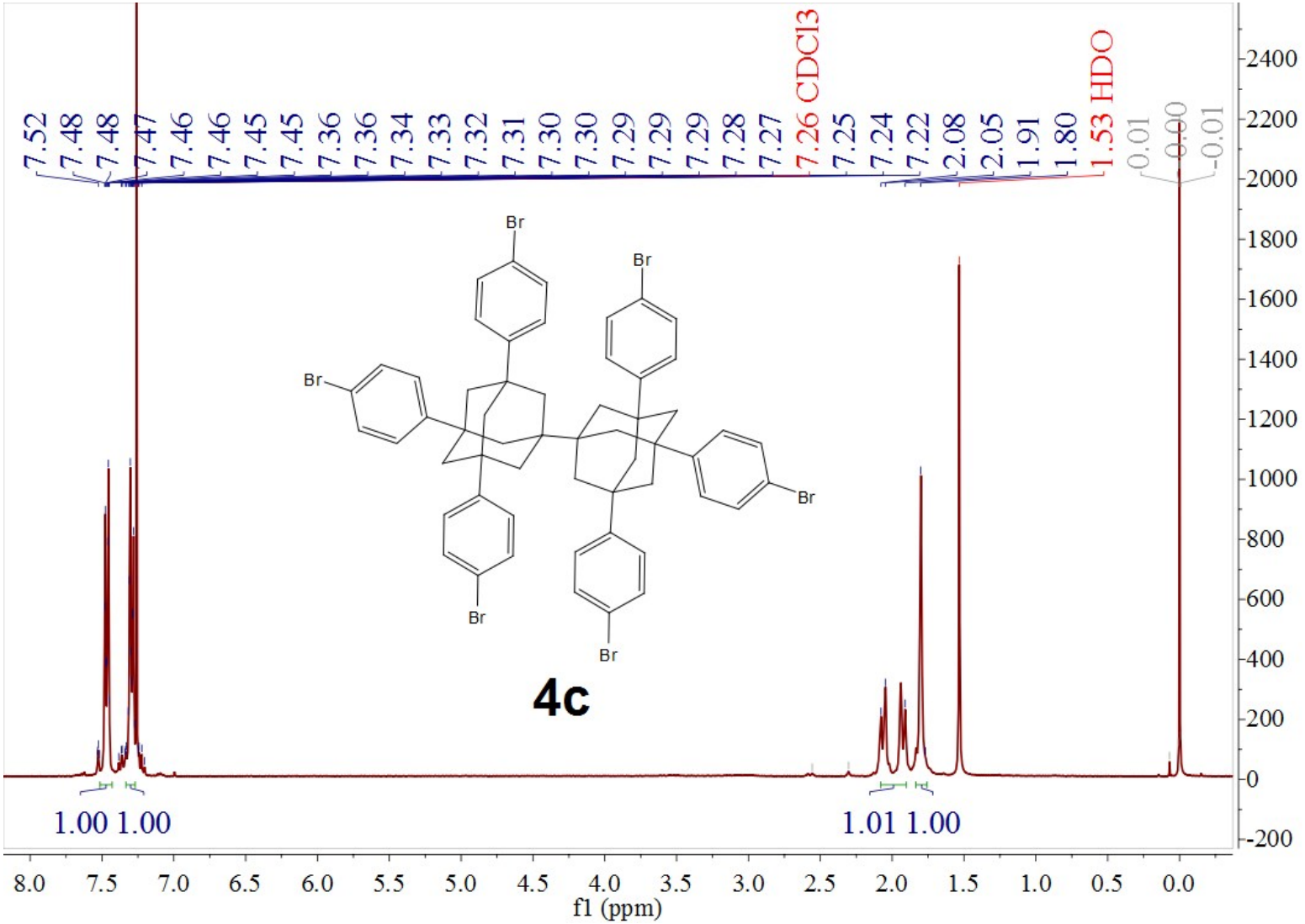
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Br
Br
Br
Br
4c
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1.01 1.00
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2000
1800
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400
200
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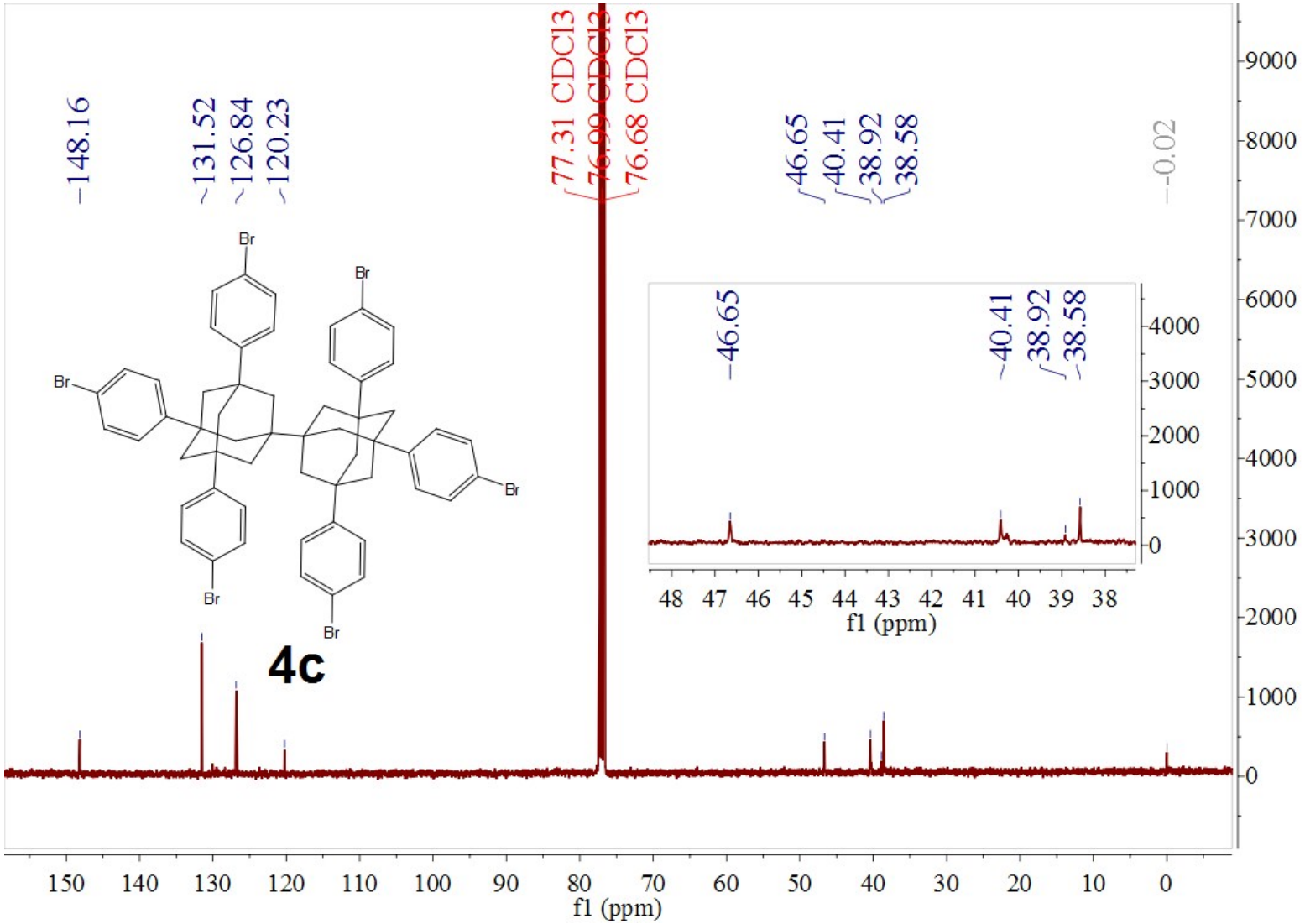
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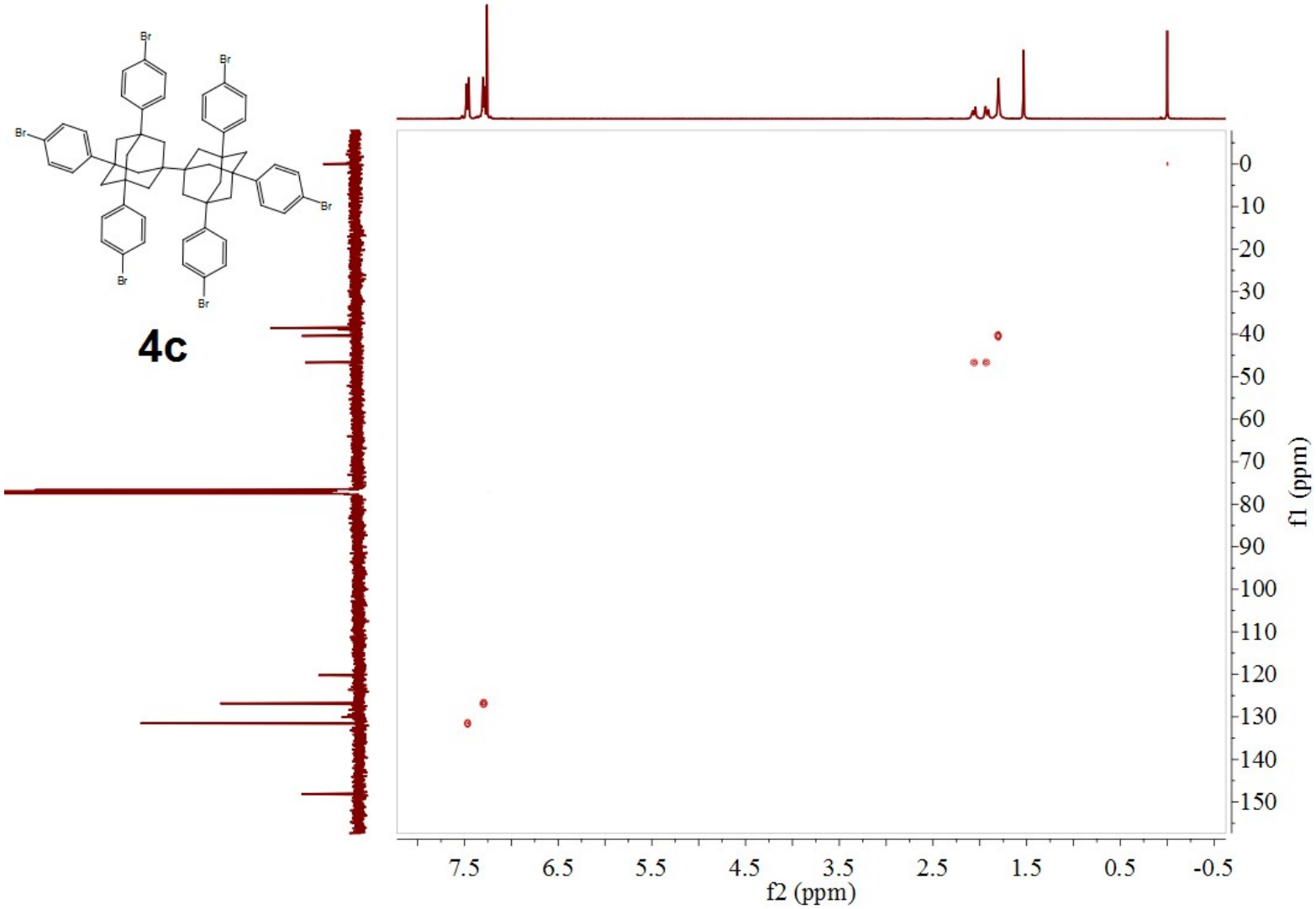
f1 (ppm)
f1 (ppm)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130
140
150
f1 (ppm)
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5.5
4.5
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0.5
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