

Supporting Information

Halogen Bonded Polypseudorotaxanes Based on Pillar[5]arene Host

Katarzyna Eichstaedt,† Barbara Wicher, ‡ Maria Gdaniec§ and Tadeusz Połoński*†

†Department of Chemistry, Gdańsk University of Technology, 80-233 Gdańsk, Poland,

§Faculty of Chemistry, A. Mickiewicz University, 61-614 Poznań, Poland,

‡Department of Chemical Technology of Drugs, Poznan University of Medical Sciences,
60-780 Poznań, Poland

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Experimental details

All solvents and 1,2,4,5-tetrafluoro-3,6-diiodobenzene (**4**) was purchased from Sigma Aldrich and used without further purification. Permethyated pillar[5]arene (**MeP5A**)¹, 1,4-di(1H-imidazol-1-yl)butane (**1**)², 1,4-bis(iodoethynyl)benzene (**2**)³ and 1,4-diiodobuta-1,3-diyne (**3**)⁴ were obtained according to the reported literatures. ¹H NMR and ¹³C NMR were recorded on Bruker Avance III HD 400 MHz at ambient temperature.

MeP5A·1

40 mg (53,27 μmol; 1 eq.) of **MeP5A** and 20,3 mg (106,54 μmol; 2 eq.) of **1** were dissolved in 5 ml of hot chloroform. After dissolution of all the components 2 ml of toluene was added. The solution was left cool and within 3 days X-ray quality crystals of **MeP5A·1** complex were obtained (mp 229–231°C).

MeP5A·1·2

35 mg of **MeP5A·1** (37,19 μmol; 1 eq.) and 14 mg of **2** (37,19 μmol; 1 eq.) were dissolved in hot dichloromethane (4 ml). After cooling carbon tetrachloride (2 ml) was added. Single, transparent crystals were obtained after 1 week (mp >240°C (dec.))

MeP5A·1·3

33 mg of **MeP5A·1** (35,06 μmol; 1 eq.) 10,6 mg of **3** (35,06 μmol; 1 eq.) were heated in 1:1 (v/v) mixture of toluene and dichloromethane. Upon standing for 4 days single crystals were obtained (mp > 240°C (dec.)).

MeP5A·1·4

27 mg of **MeP5A·1** (28,69 μmol; 1 eq.) and 11,5 mg of **4** (28,69 μmol; 1 eq.) were dissolved in hot dichloromethane (4 ml). After cooling carbon tetrachloride (2 ml) was added. X-ray quality crystals of **MeP5A·1·4** were grown within few days (mp 192–196°C (dec.)).

¹H and ¹³C NMR spectra of **MeP5A·1**, **MeP5A·1·2**, **MeP5A·1·3**, **MeP5A·1·4** (400 MHz, CDCl₃ / CD₃SOCD₃) reflect complex equilibrium between the complexed and uncomplexed components indicating a slow exchange in solution on NMR timescale.⁵

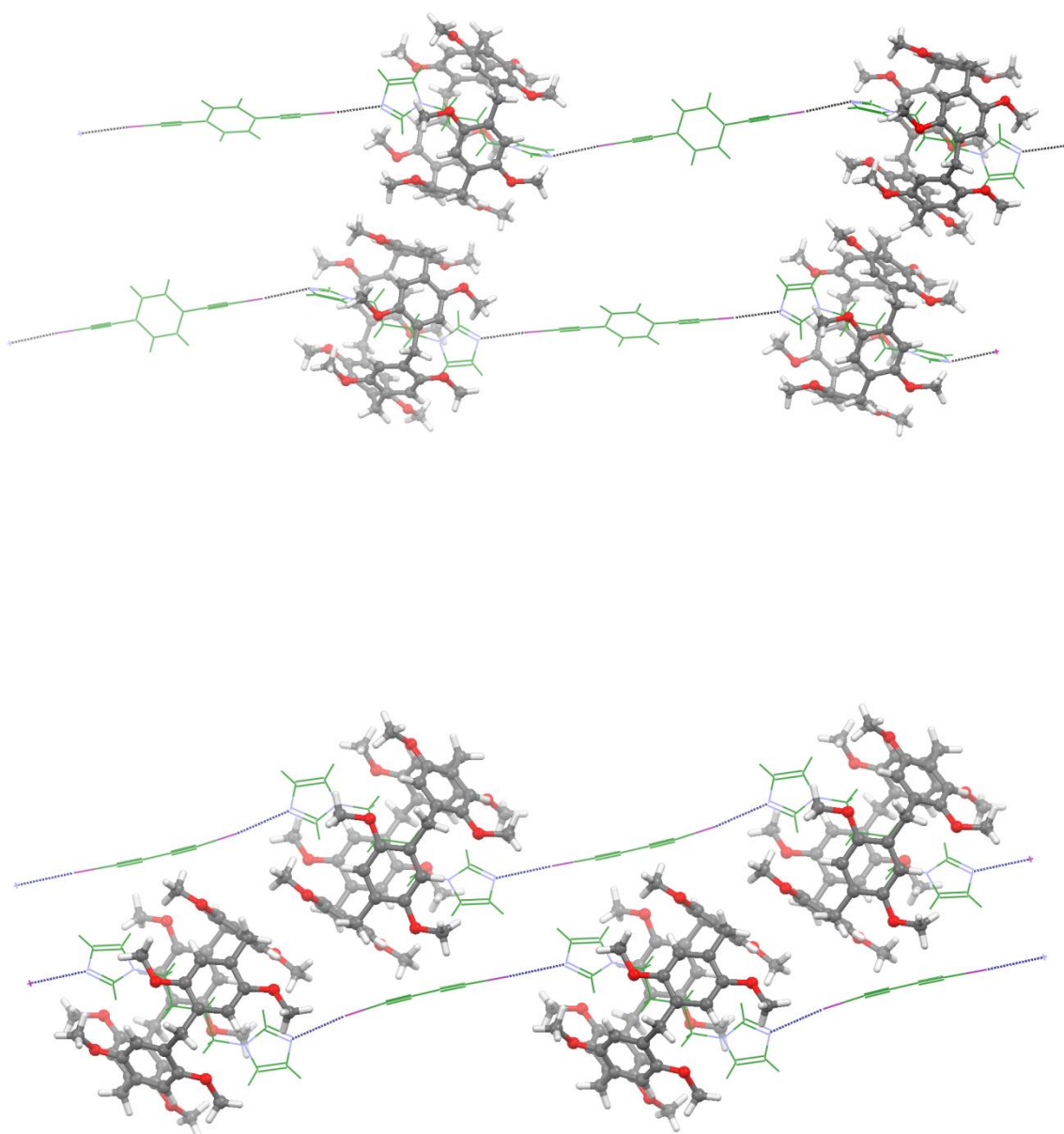


Figure S1. The two symmetry independent molecules of **2** are located around inversion centers making the polypseudorotaxane in **MeP5A-1-2** (top) achiral. In contrary, the polypseudorotaxane in **MeP5A-1-3** (bottom) shows exclusively translational symmetry implying that the **MeP5A** beads are homochiral.

Table S1. Geometry of halogen and hydrogen bonds

	X...Y (Å)	D-X...Y (°)	Symmetry code i
MeP5A·1·2·2(CCl₄)			
C46-I1...N1A ⁱ	2.75(1)	171.5(4)	1-x, -y, 1-z
C46-I1...N1 ⁱ	2.784(7)	175.3(02)	1-x, -y, 1-z
C51-I2 ...N3 ⁱ	2.792(4)	176.3(2)	1-x, 1-y, -z
MeP5A·1·3·1.5(toluene)			
C49-I2...N1	2.753(2)	172.9(1)	
C46-I1...N3 ⁱ	2.734(2)	174.11(8)	-1+x, y, 1+z
MeP5A·1·4₂·2(H₂O)			
O1W-H1W...N3A ⁱ	3.11(5)	156	x, y, 1+z
O1W-H1W...N3B ⁱ	3.32(4)	165	1-x, y, 1.5-z
O2W-H2W...N3B ⁱ	2.82(6)	171(8)	x, y, -1+z
C27-I2...O1W ⁱ	2.89(1)	173.8(2)	1-x, 1-y, 1-z
C27-I2...N12A ⁱ	3.31(6)	158(2)	1-x, 1-y, 1-z
C24-I1...O2W ⁱ	2.978(5)	171.6(2)	0.5-x, 0.5-y, -0.5+z

The crystal structure of MeP5A·1·4₂·2(H₂O)

MeP5A·1·4₂·2(H₂O) crystallizes in the Pbcn space group. The asymmetric part of the unit cell contains one molecule of **4**, one half of **MeP5A** molecule that is situated around twofold symmetry axis, one molecule of **1** having half occupancy due to disorder and two halves of water molecules – one molecule is disordered (O1W) and the other (O2W) is located at the twofold axis. The molecules of **1** and water molecules are accommodated within channels formed by **Me5PA** and **4**. The crystallographic symmetry of the empty channel is higher than the symmetry of the molecular assembly formed by **1** and water molecules enclosed within the channel. As a result there are two possible arrangements of the molecules within the channel that are mutually related by a dyad perpendicular to the channel axis. A closer inspection shows that the molecules within the channel are ordered and the observed disorder arises from a statistical distribution of the two different channels over the crystal. The arrangement of molecules of **1** and water molecules within the ordered channel is shown in Fig. S2. The imidazolyl N3A atom is hydrogen bonded to the water molecule O1w that is also involved in halogen bond with the I2 atom of **4**. The O2W molecule that is situated at the twofold axis forms two halogen bonds with I1 and very weak hydrogen bond with N3B. This N3B atom is additionally involved in halogen bonding with I2. Geometry of intermolecular interactions in **MeP5A·1·4₂·2(H₂O)** is given in Table S1. The halogen and hydrogen bond

interactions of the pseudorotaxane **MeP5A-1** with water molecules and iodine atoms of **4** assemble these entities into a 3D framework. The crystal structure of **MeP5A-1·4₂·2(H₂O)** is formed by a mutual interpenetration of two such 3D frameworks what is schematically shown in Fig. S3 where the two frameworks are presented in different colors and the content of the channel that is oriented perpendicular to the plane of the drawing is represented by a circle. Interestingly, the 3D polypseudorotaxane framework is chiral and the interpenetrating frameworks are of the opposite chirality.

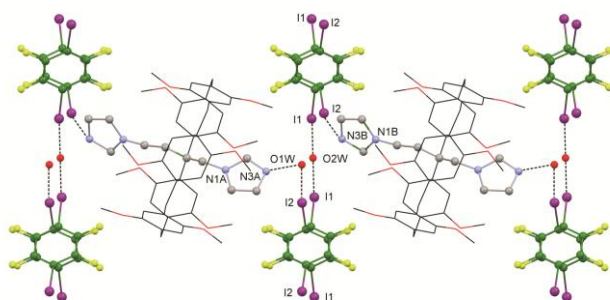


Figure S2. Hydrogen bonds and halogen bonds in **MeP5A-1·4₂·2(H₂O)**. **MeP5A** and **O2W** are located on a twofold symmetry axis, whereas **1** and **O1W** are disordered over two sides related by twofold axis (disorder is not shown).

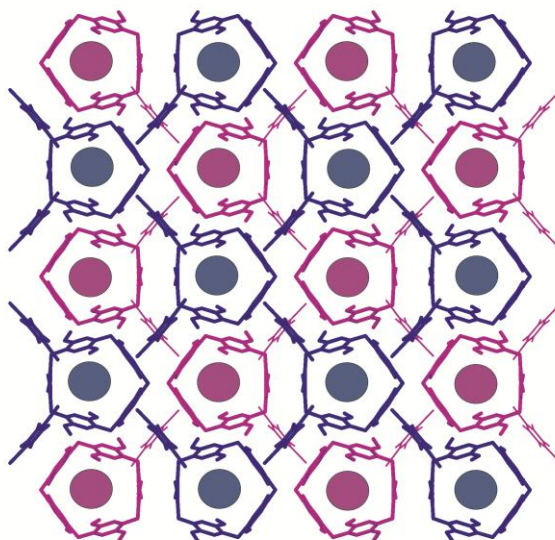
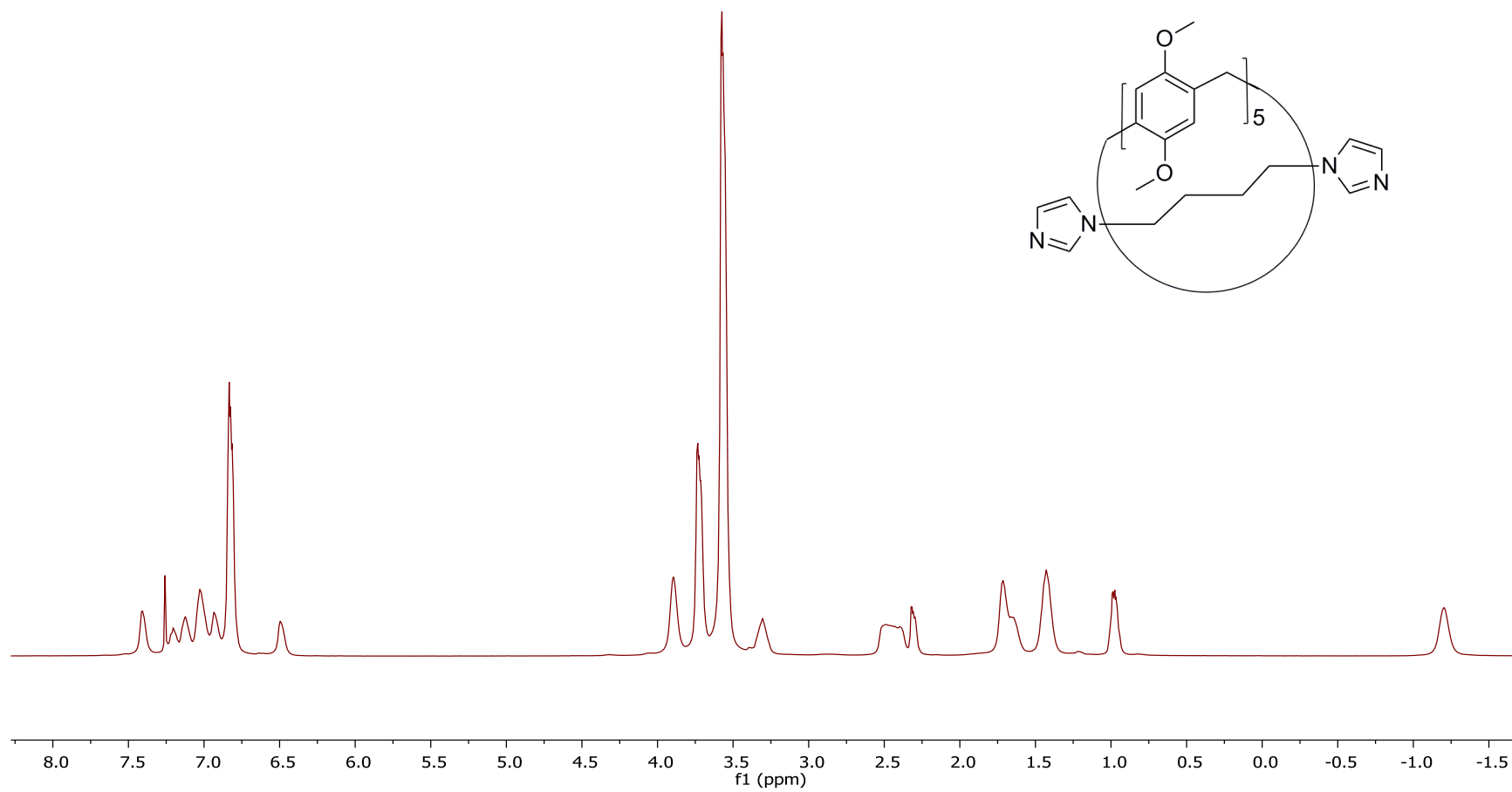


Figure S3. Two interpenetrated chiral 3D frameworks generated via O–H···N hydrogen bonds and C–I···O and C–I···N halogen bonds in **MeP5A-1·4₂·2(H₂O)**. The channels comprising the molecules of **1** and water molecules are represented schematically by circles.

References

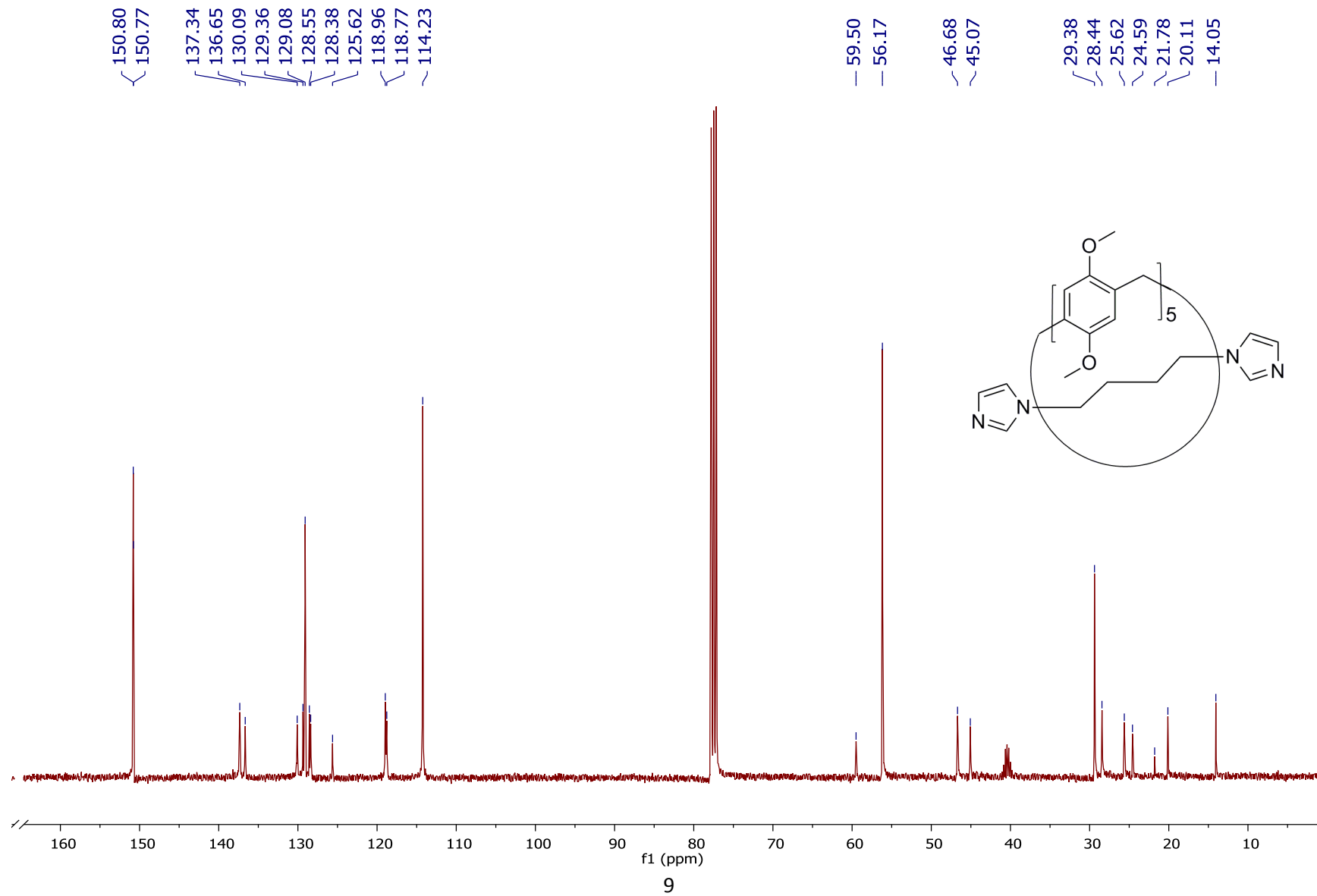
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MeP5A-1

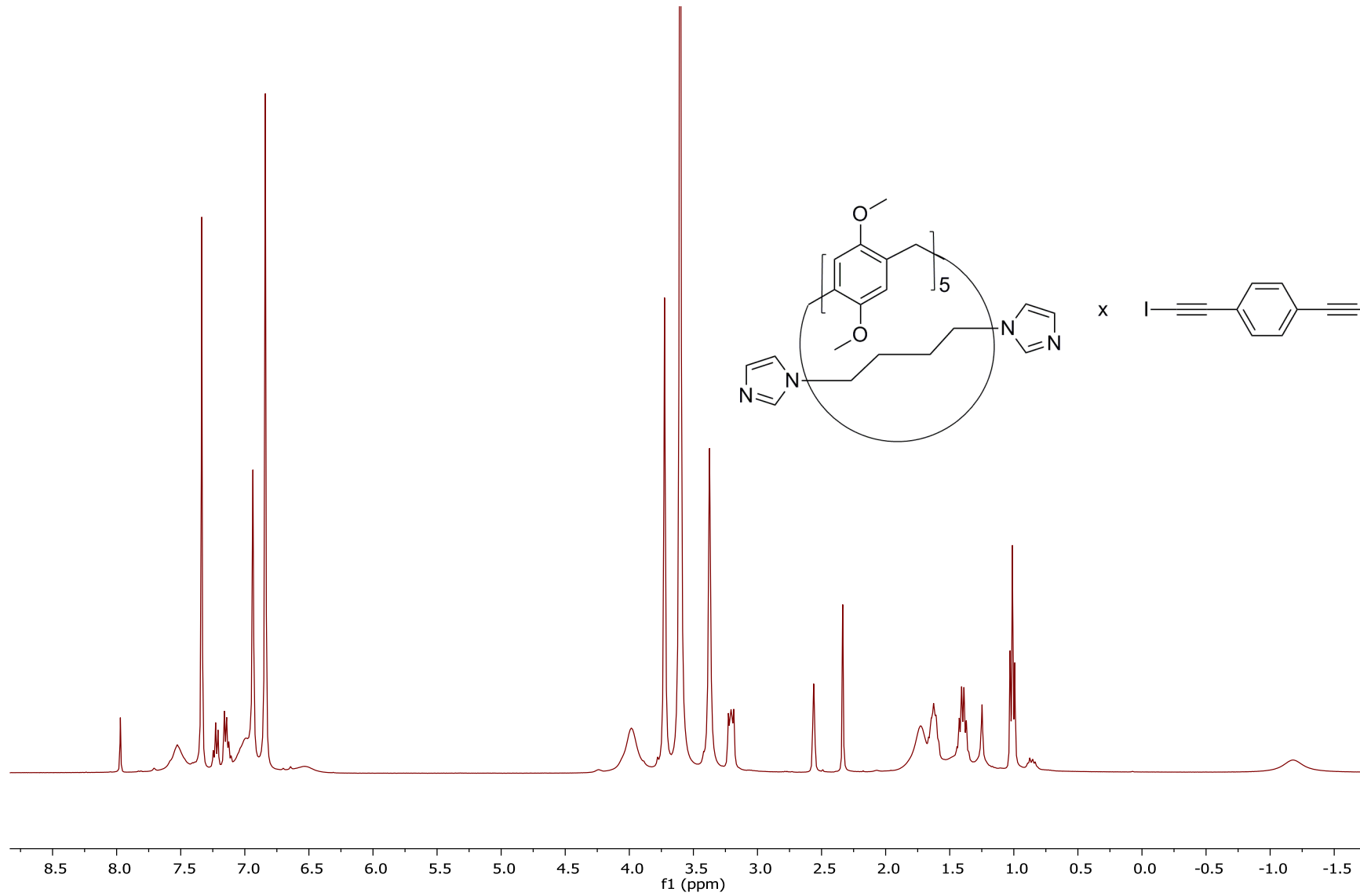


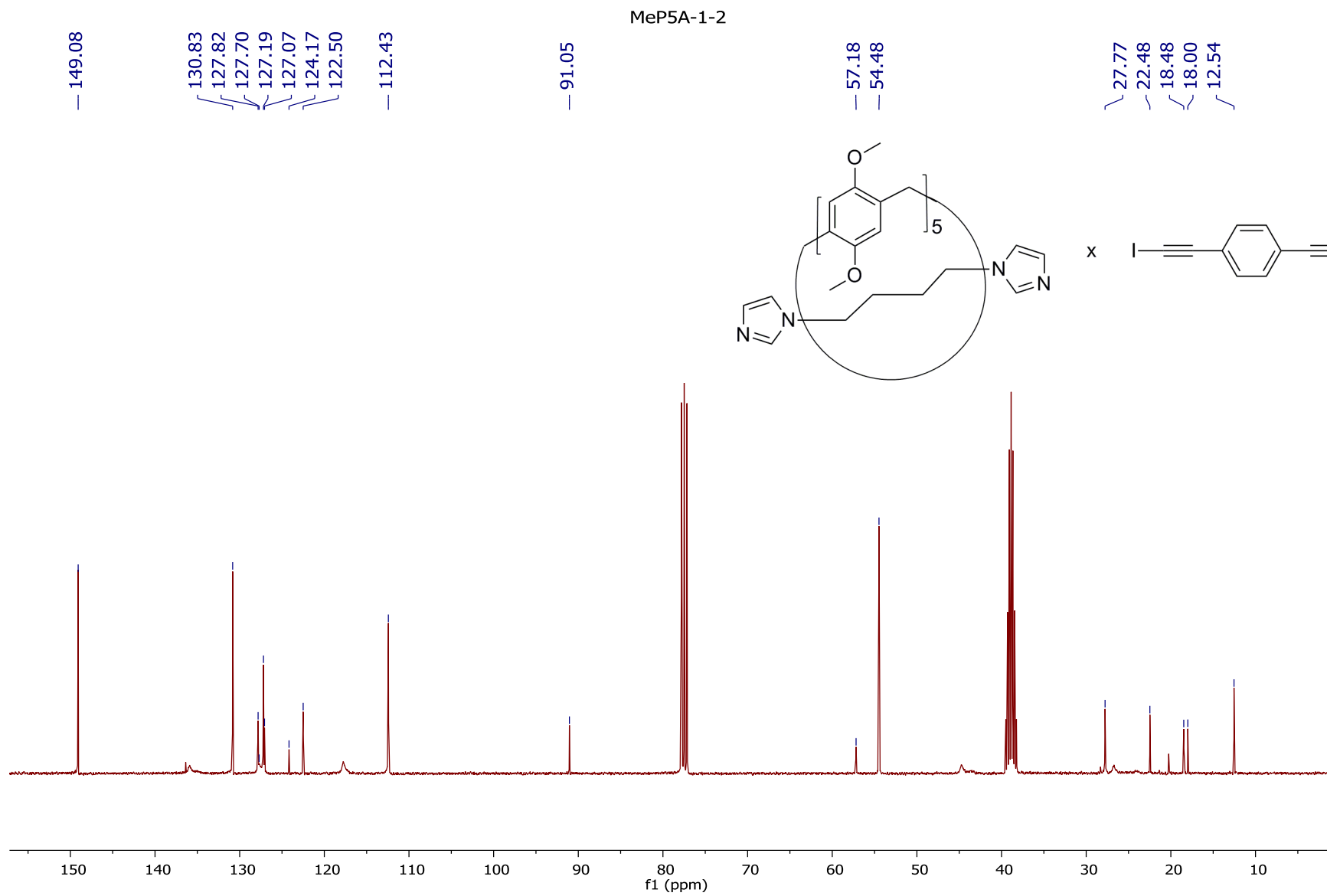
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MeP5A-1

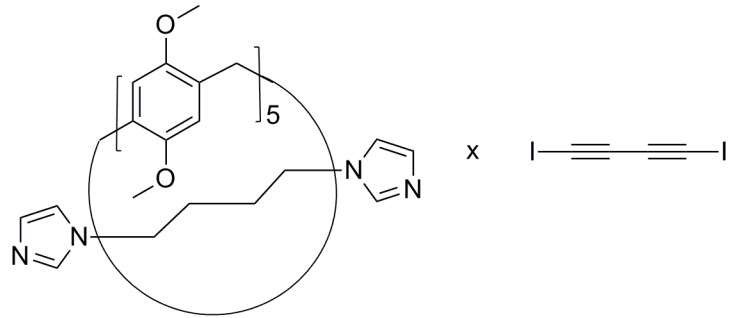
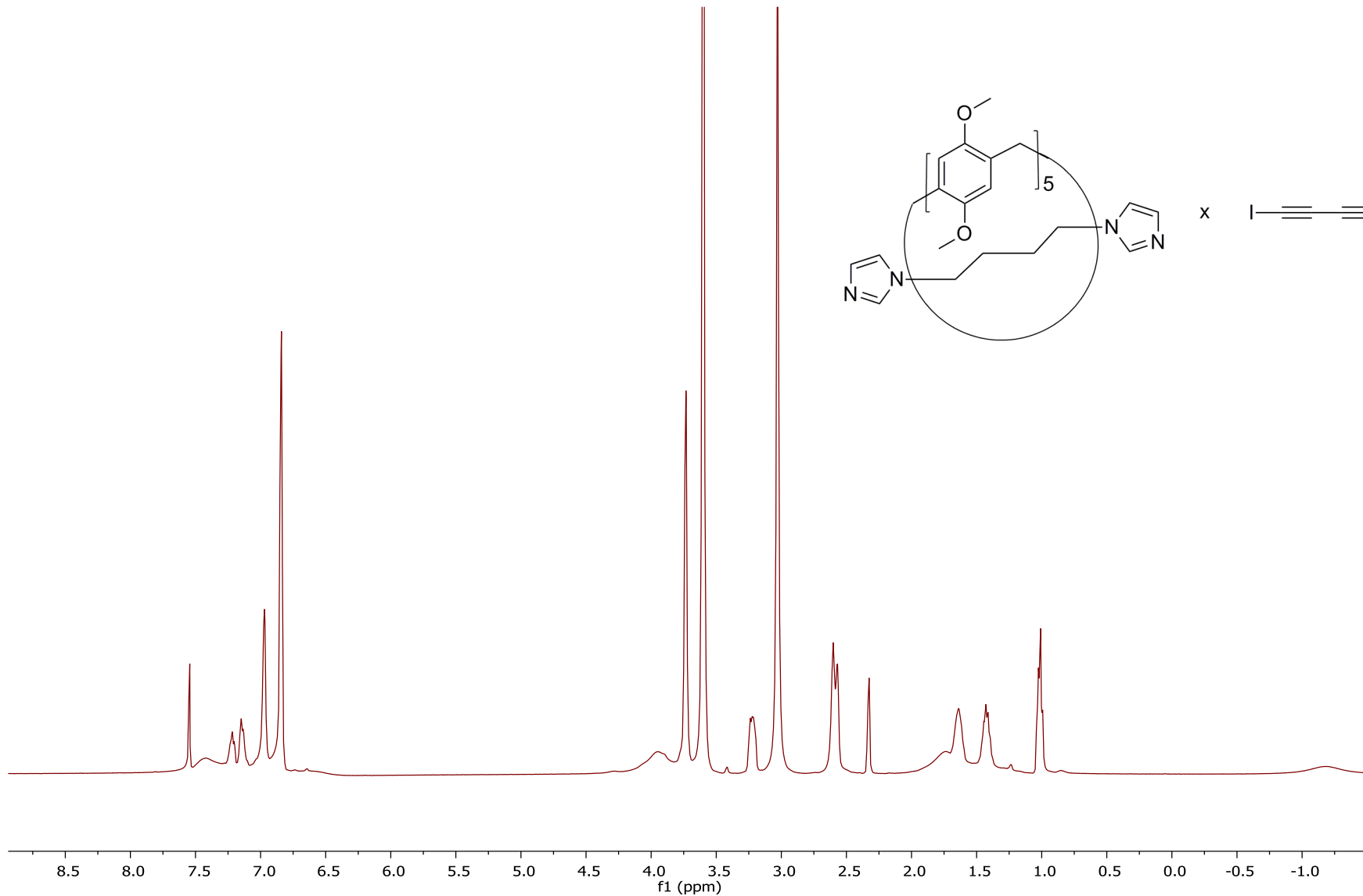


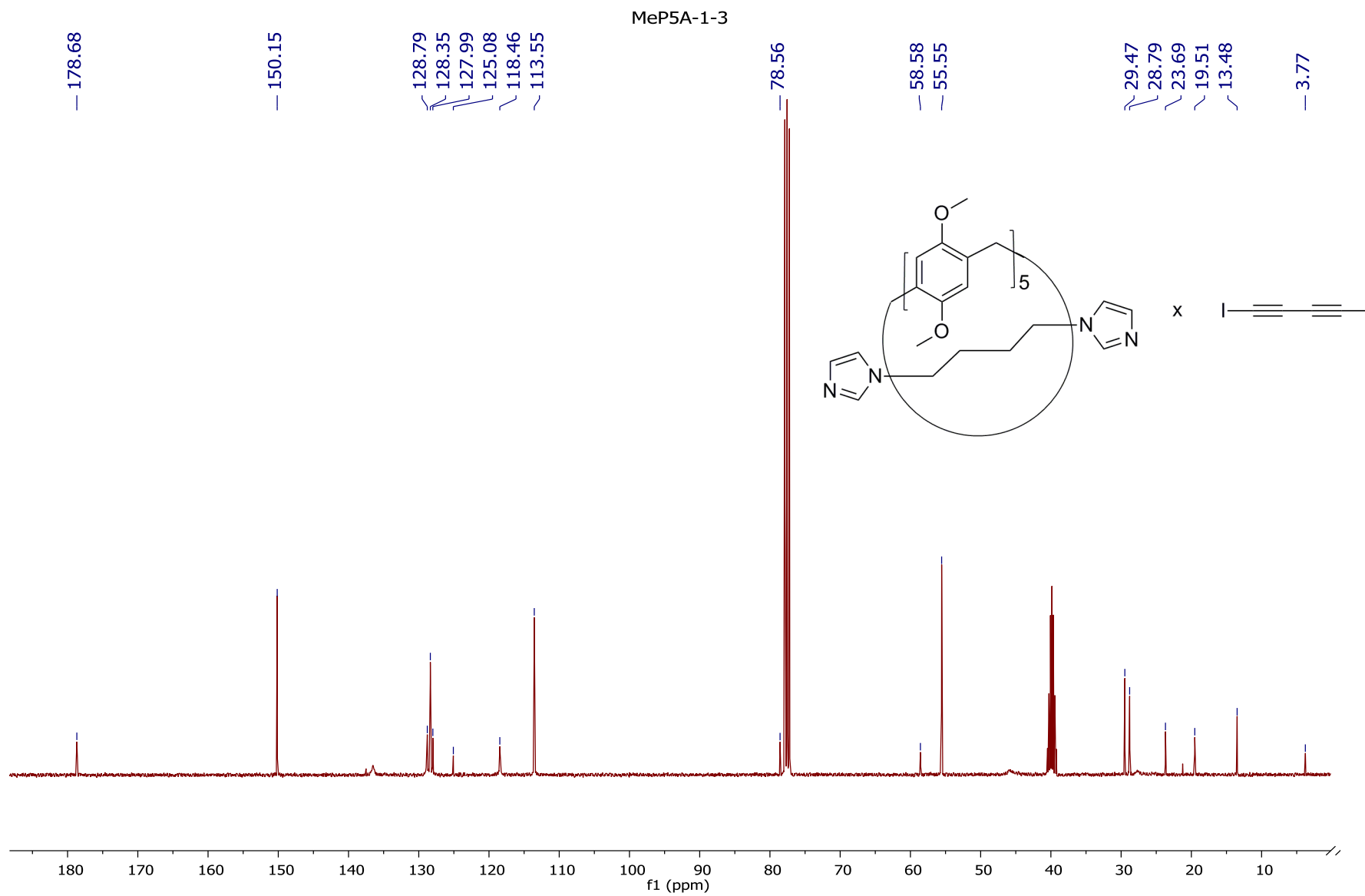
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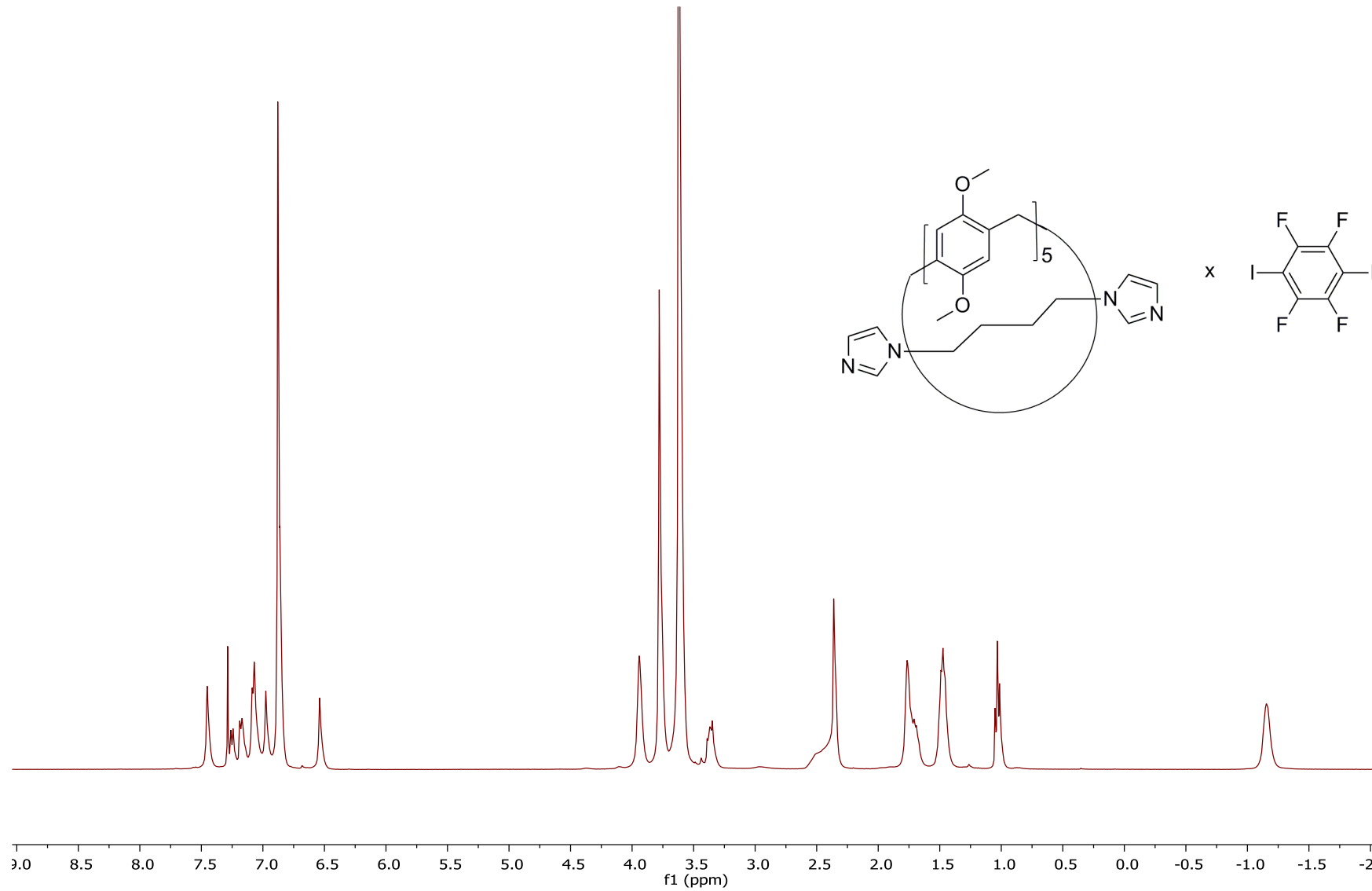


MeP5A-1-3





MeP5A-1-4



MeP5A-1-4

